Supplementary Information for:

Cyclolignan Synthesis Streamlined by Enantioselective Hydrogenation of Tetrasubstituted Olefins

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1. General Methods

Unless otherwise noted, all reactions were carried out with anhydrous solvents from J&K scientific, under positive pressure of nitrogen atmosphere. Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates. Flash column chromatography was performed over silica gel (200-300 or 300-400 mesh).

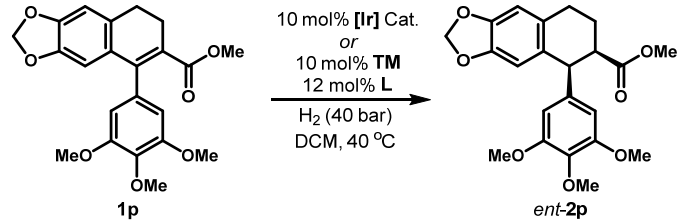
NMR spectra were recorded on Bruker AVANCE NEO (500 and 600MHz) of Bruker AVANCE 400 MHz using residual solvent peaks as an internal standard (e.g. $CDCl_3$ @ 7.26 ppm ^1H NMR, 77.00 ppm ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad. HRMS was recorded on Waters LCT Premier ESI-TOF. The enantiomeric excesses (ee) of the products were determined by chiral stationary phase HPLC with Chiralpak (ADH, ODH, IA-3, IC-3, OJ-3). Optical rotations were measured with Rudolph Autopol IV-T (λ = 589 nm). The single crystal X-ray diffraction studies were carried out on Bruker D8 Venture and APEX-II CCD diffractometers.

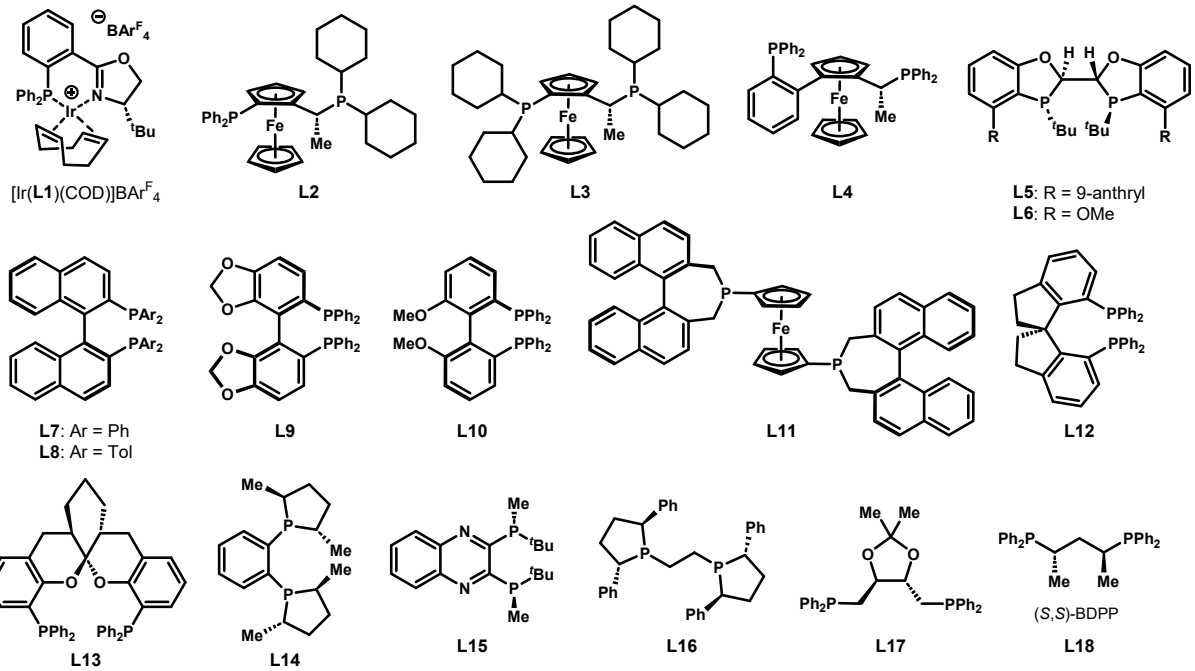
Abbreviations:

DIPEA = *N*,*N*-diisopropylethylamine
DIPA = diisopropylamine
Tf_2O = trifluoromethanesulfonic anhydride
3,5-DMP = 3,5-dimethylpyrazole
NHPI = *N*-hydroxyphthalimide
4CzIPN = 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene
TMEPO = 2,2,6,6-tetramethylpiperidine 1-oxyl
PMHS = polymethylhydrosiloxane
TFE = 2,2,2-trifluoroethanol
LAH = lithium aluminum hydride
EDCI = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
PDC = pyridinium dichromate
NMO = 4-methylmorpholine *N*-oxide
DMAP = 4-(dimethylamino)pyridine
TPAP = tetrapropylammonium perruthenate
NMO = 4-methylmorpholine N-oxide
LHMDS = lithium bis(trimethylsilyl)amide
DIBAL = diisobutylaluminum hydride
p-TSA = *p*-toluenesulfonic acid
DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene
dppf = 1,1′-ferrocenediyl-bis(diphenylphosphine)
TBHP = *tert*-butyl hydroperoxide
NBS = *N*-bromosuccinimide
LTMP = lithium tetramethylpiperidide
TBAB = *tetra*-*n*-butylammonium bromide
LDA = lithium diisopropylamide
NaHMDS = sodium bis(trimethylsilyl)amide
HMPA = hexamethylphosphoramide
RT = room temperature
y = yield
ee = enatiomeric excess
dr = diasteromeric ratio

2. Development of the Enantioselective Hydrogenation

Table S1. The effects of catalyst systems and ligands.[a]





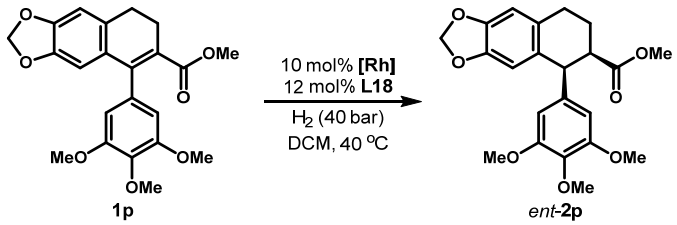
entry	TM	L	additive	yield (%)[b]	ee (%)[c]
1	[Ir(**L1**)(COD)]BAr^F_4		none	trace	NA
2[d]	Ru(Me-allyl)$_2$(COD)	**L2**	$HBF_4 \cdot OEt_2$	trace	NA
3	$Rh(NBD)_2BF_4$	**L2**	none	95	26
4	$Rh(NBD)_2BF_4$	**L3**	none	trace	NA
5	$Rh(NBD)_2BF_4$	**L4**	none	72	77
6	$Rh(NBD)_2BF_4$	**L5**	none	trace	NA
7	$Rh(NBD)_2BF_4$	**L6**	none	99	40
8	$Rh(NBD)_2BF_4$	**L7**	none	trace	NA
9	$Rh(NBD)_2BF_4$	**L8**	none	trace	NA
10	$Rh(NBD)_2BF_4$	**L9**	none	trace	NA
11	$Rh(NBD)_2BF_4$	**L10**	none	trace	NA
12	$Rh(NBD)_2BF_4$	**L11**	none	79	60
13	$Rh(NBD)_2BF_4$	**L12**	none	trace	NA

[a]Reaction conditions: **1p** (0.10 mmol), $Rh(COD)_2BArF_4$ (10 mol %), and **L** (12 mol %) in DCM under H2 (40 bar) at 40 °C for 36 h. [b]Determined by crude NMR. [c]Determined by Chiral HPLC. [d]MeOH was used instead of DCM as the solvent. Ar^F = 3,5-bis(trifluoromethyl)phenyl. NA = Not Available.

Table S1 (*Cont.*). The effects of catalyst systems and ligands.

entry	TM	L	additive	yield (%)	ee (%)
14	$Rh(NBD)_2BF_4$	**L13**	none	trace	NA
15	$Rh(NBD)_2BF_4$	**L14**	none	trace	NA
16	$Rh(NBD)_2BF_4$	**L15**	none	trace	NA
17	$Rh(NBD)_2BF_4$	**L16**	none	trace	NA
18	$Rh(NBD)_2BF_4$	**L17**	none	67	-62
19	$Rh(NBD)_2BF_4$	**L18**	none	50	96

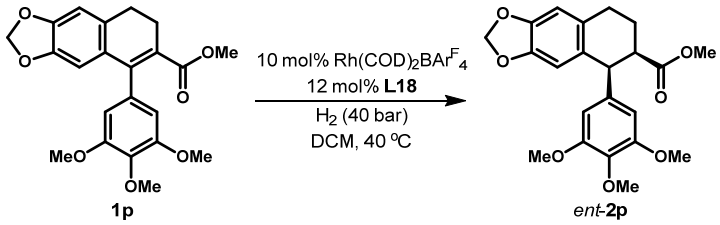
Table S2. The effects of rhodium complexes.



entry	**TM**	yield (%)[b]	ee (%)[c]
1	$Rh(NBD)_2BF_4$	50	96
2	$Rh(COD)_2BF_4$	98	98
3	$Rh(COD)_2OMe$	trace	NA
4	$Rh(COD)_2OTf$	60	98
5	$Rh(COD)_2PF_6$	trace	NA
6	$Rh(COD)_2BAr^F{}_4$	98	97
7	$Rh(acac)(C_2H_4)_2$	trace	NA

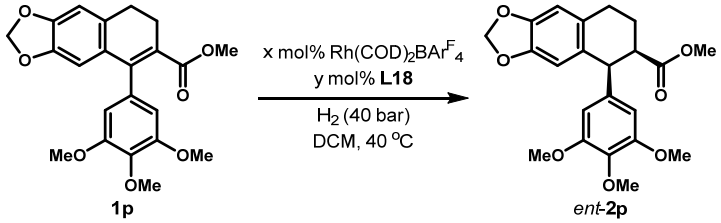
NOTE: results were more consistent and reproducible with $Rh(COD)_2BArF_4$ compared to $Rh(COD)_2BF_4$.

Table S3. Solvent Effects.



entry	**Solvent**	yield (%)[b]	ee (%)[c]
1	DCM	98	97
2	DCE	75	97
3	MeOH	trace	NA
4	TFE	87	95
5	HFIP	94	97
6	dioxane	44	97

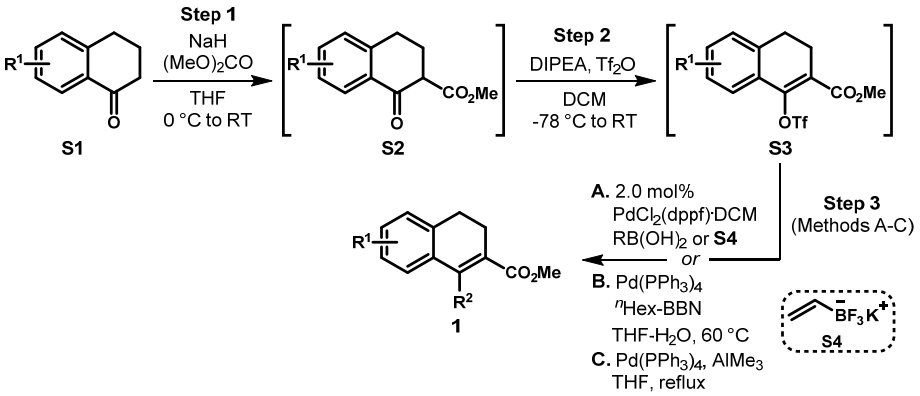
Table S4. The effects of catalyst loading.



entry	x	y	yield (%)[b]	ee (%)[c]
1	10	12	98	97
2	8	9.6	99	97
3	6	7.2	99	96
4	4	4.8	99	96
5	2	2.4	99	97
6	1	1.2	98	> 99

3. Experimental Procedures and Characterizations

3.1 General Procedure for the Preparation of Tetrasubstited Olefins



Step 1[1]: Dimethyl carbonate (0.53 mL, 6.30 mmol, 2.0 equiv.) was added slowly via syringe to a solution of the corresponding 1-tetralone[2] (3.15 mmol, 1.0 equiv.) and NaH (60% dispersion in mineral oil; 378 mg, 9.45 mmol, 3.0 equiv.) in THF (10 mL) at 0 °C. The mixture was allowed to warm to room temperature (RT) and heated at reflux overnight. The reaction was then quenched with 1 N HCl solution (10 mL) at 0 °C and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in *vacuo* to afford the crude α-ketoester intermediate which was used directly for the next step.

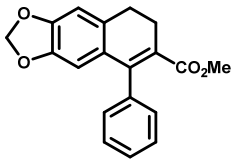
Step 2[3]: DCM (50 mL) and DIPEA (0.82 mL, 4.73 mmol, 1.5 equiv.) were sequentially added to the crude α-ketoester. The mixture was cooled to -78 °C by dry ice-acetone bath. Tf_2O (0.80 mL, 4.73 mmol, 1.5 equiv.) was then added dropwise via syringe. The reaction mixture was allowed to warm slowly to RT. The reaction was then quenched by cautious addition of sat. $NaHCO_3$ (20 mL), extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo* to afford the crude triflate intermediate which was used in the next step

Step 3 (Method A *for* 1a-u & 1x-p')[4]: To a stirred solution of the triflate intermediate and aryl boronic acid or potassium vinyltrifluoroborate (4.73 mmol, 1.5 equiv.) in DMF (10 mL) was added degasedd 2 M Na_2CO_3 (3.8 mL, 7.60 mmol, 2.4 equiv.) via syringe. $PdCl_2(dppf)\cdot DCM$ (51.4 mg, 0.063 mmol, 0.02 equiv.) was added. The mixture was further degassed and heated at 50 °C overnight. The reaction was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was then purified by flash chromatography to afford the desire product.

Step 3 (Method B *for* 1w)[5]: To a solution of 1-hexene (0.58 mL, 4.73 mmol, 1.5 equiv.) in anhydrous THF (20 mL) was added 9-BBN (0.5 M in THF, 18.9 mL, 9.46 mmol, 2.0 equiv.) at 0 °C dropwise. The reaction mixture was allowed to warm to RT and stirred for an additional 2 h. Degassed H_2O (6 mL) was added, and the resulting mixture was sitirred for 30 min. Then, degassed 3 M aq K_3PO_4 (3.15 mL, 9.46 mmol, 3.0 equiv), a solution of the corresponding triflate intermediate in THF (4 mL), and $Pd(PPh_3)_4$ (18.5 mg, 0.16 mmol, 0.05 equiv) were sequentially added. The resulting red reaction mixture was refluxed for 6 h. The reaction mixture was then cooled, diluted water (20 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with sat. $NaHCO_3$ (20 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography to afford the desired olefin **1w**.

Step 3 (Method C *for* 1v)[6]: To a stirred solution of the corresponding triflate intermediate and $Pd(PPh_3)_4$ (37.0 mg, 0.32 mmol, 0.1 equiv.) in THF (30 mL) was added $AlMe_3$ (2 M in PhMe, 2.36 mL, 4.73 mmol, 1.5 equiv.) at RT. The reaction mixture was heated at refulx overnight, then quenched cautiously with sat. NH_4Cl solution (30 mL) at 0 °C and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flushing chromatography to afford the desire olefin.

Methyl 5-phenyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1a). Obtained as white solid (737 mg, 76% y).



1a

R_f 0.50 (Hex/EtOAc = 20:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

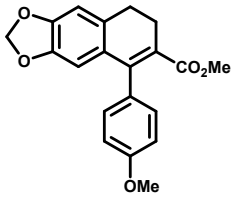
δ 7.40–7.13 (m, 3H), 7.14–7.13 (m, 2H), 6.71 (s, 1H), 6.25 (s, 1H), 5.89 (s, 2H), 3.47 (s, 3H), 2.82 (dd, *J* = 9.7 & 6.5 Hz, 2H), 2.68 (dd *J* = 9.3 & 6.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.3, 147.5, 146.0, 145.5, 139.5, 132.1, 129.3, 128.6, 128.0, 128.0, 127.2, 125.2, 108.6, 108.0, 101.0, 51.2, 28.3, 25.4.

HRMS (ESI) $C_{19}H_{17}O_4$ $[M+H]^+$: calcd 309.1121, found 309.1131.

Methyl 5-(4-methoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1b). Obtained as white solid (596 mg, 56% y).



1b

R_f 0.40 (PE/EtOAc = 3:1, UV/$KMnO_4$)

^{1}H NMR (500 MHz, $CDCl_3$)

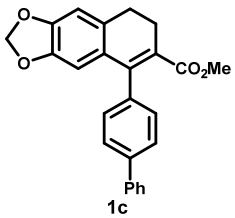
δ 7.05 (d, *J* = 8.5, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.70 (s, 1H), 6.29 (s, 1H), 5.89 (s, 2H), 3.85 (s, 3H), 3.50 (s, 3H), 2.80 (dd, *J* = 9.6 & 6.5 Hz, 2H), 2.65 (dd, *J* = 9.6 & 6.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.6, 158.8, 147.5, 146.0, 145.1, 132.2, 131.6, 129.9, 129.7, 125.2, 113.5, 108.7, 108.0, 101.0, 55.2, 51.3, 28.3, 25.6.

HRMS (ESI) $C_{20}H_{19}O_5$ $[M+H]^+$: calcd 339.1227, found 339.1223.

Methyl 5-([1,1'-biphenyl]-4-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1c). Obtained as white solid (750 mg, 62% y).



1c

R_f 0.21 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

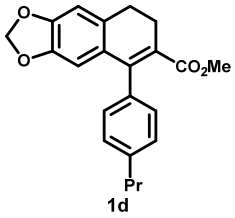
δ 7.65 (dd, *J* = 16.5 & 7.7 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.73 (s, 1H), 6.32 (s, 1H), 5.90 (s, 2H), 3.50 (s, 3H), 2.84 (dd, *J* = 9.6 & 6.5 Hz, 2H), 2.70 (dd, *J* = 9.7 & 6.4 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.4, 147.6, 146.0, 145.3, 140.7, 139.9, 138.5, 132.2, 129.4, 129.1, 128.7, 127.3, 127.0, 126.7, 125.3, 108.7, 108.1, 101.1, 51.3, 28.3, 25.5.

HRMS (ESI) $C_{25}H_{21}O_4$ $[M+H]^+$: calcd 385.1424, found 385.1432.

Methyl 5-(4-propylphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1d). Obtained as white solid (904 mg, 82% y).



1d

$\underline{R_f}$ 0.50 (Hex/EtOAc = 20:1, UV/$KMnO_4$)..

^{1}H NMR (500 MHz, $CDCl_3$)

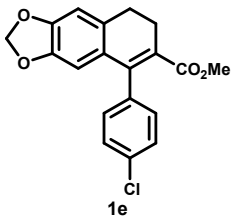
δ 7.18 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.70 (s, 1H), 6.28 (s, 1H), 5.89 (s, 2H), 2.81 (dd, *J* = 9.7 & 6.5 Hz, 2H), 2.67–2.61 (m, 4 H), 1.69 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.6, 147.5, 146.0, 145.5, 141.6, 136.6, 132.2, 129.6, 128.5, 128.1, 125.2, 108.8, 108.0, 101.0, 51.2, 37.8, 28.4, 25.5, 24.4, 13.8.

HRMS (ESI) $C_{22}H_{23}O_4$ $[M+H]^+$: calcd 351.1590, found 351.1597.

Methyl 5-(4-chlorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1e). Obtained as white solid (776 mg, 57% y).



1e

$\underline{R_f}$ 0.60 (PE/EtOAc = 20:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

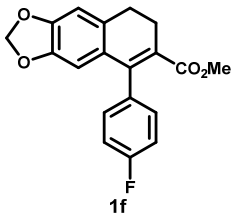
δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.68 (s, 1H), 6.16 (s, 1H), 5.87 (s, 2H), 3.47 (s, 3H), 2.81 (dd, *J* = 9.7 & 6.5 Hz, 2H), 2.64 (dd, *J* = 9.6 & 6.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ166.7, 145.5, 143.9, 142.3, 135.8, 131.0, 129.9, 127.8, 126.7, 126.1, 123.3, 106.2, 105.9, 98.9, 49.1, 26.0, 23.1.

HRMS (ESI) $C_{19}H_{17}ClO_4$ $[M+H]^+$: calcd 434.0732, found 434.0736.

Methyl 5-(4-fluorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1f). Obtained as white solid (432 mg, 42% y).



1f

$\underline{R_f}$ 0.60 (PE/EtOAc = 20:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.11–7.06 (m, 4H), 6.71 (s, 1H), 6.21 (s, 1H), 5.90 (s, 2H), 3.49 (s, 3H), 2.81 (dd, *J* = 9.5 & 6.6 Hz, 2H), 2.67 (dd, *J* = 9.5 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

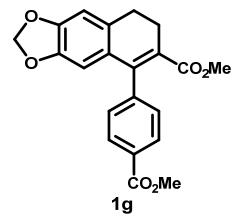
δ 169.2, 162.1 (d, $^1J_{C\text{-}F}$ = 246.0 Hz), 147.8, 145.3 (d, $^2J_{C\text{-}F}$ = 188.3 Hz), 135.3 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 132.2, 130.3 (d, $^1J_{C\text{-}F}$ = 7.9 Hz), 129.3, 125.7, 115.2, 115.1, 108.5, 108.1, 101.2, 51.3, 28.3, 25.4.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -114.8.

HRMS (ESI) $C_{19}H_{16}O_4F$ $[M+H]^+$: calcd 327.1027, found 327.1037.

Methyl 5-(4-(methoxycarbonyl)phenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1g). Obtained as white solid (878 mg, 76% y).



1g

$\underline{R_f}$ 0.40 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.72 (s, 1H), 6.12 (s, 1H), 5.89 (s, 2H), 3.94 (s, 3H), 3.46 (s, 3H), 2.83 (dd, *J* = 9.7 & 6.5 Hz, 2H), 2.69 (dd, *J* = 9.7 & 6.5 Hz, 2H).

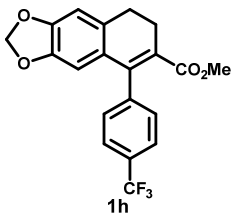
^{13}C NMR (125 MHz, $CDCl_3$)

δ 168.8, 167.0, 147.9, 146.2, 145.0, 144.8, 132.2, 129.5, 129.1,

128.8, 125.5, 108.4, 108.2, 101.2, 52.1, 51.3, 28.2, 25.2.

HRMS (ESI) $C_{21}H_{19}O_6$ $[M+H]^+$: calcd 367.1176, found 367.1173.

Methyl 5-(4-(trifluoromethyl)phenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1h). Obtained as white solid (710 mg, 60% y).



1h

R_f 0.50 (PE/EtOAc = 10:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.65 (d, J = 8.0 Hz, 2H), 7.25 (br, 2H), 6.73 (s, H), 6.10 (s, 1H), 5.90 (s, 2H), 3.48 (s, 3H), 2.83 (dd, J = 9.7 & 6.6 Hz, 2H), 2.77–2.70 (dd, J = 9.7 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

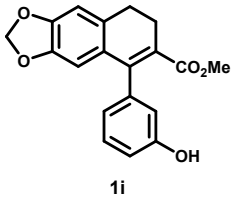
δ 168.6, 147.9, 146.2, 144.7, 143.6, 132.2, 129.4 (q, $J_{C\text{-}F}$ = 32.3 Hz), 129.0, 128.7, 125.7, 125.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $J_{C\text{-}F}$ = 272.0 Hz), 108.3, 108.2, 101.2, 51.3, 28.2, 25.1.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -62.4.

HRMS (ESI) $C_{20}H_{16}O_4F$ $[M+H]^+$: calcd 377.9995, found 377.0998.

Methyl 5-(3-hydroxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1i). Obtained as white solid (480 mg, 75% y).



1i

R_f 0.20 (PE/EtOAc = 10:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

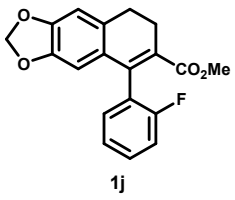
δ 7.23 (t, J = 7.8 Hz, 1H), 6.80 (J = 8.2, 2.4 Hz, 1H), 6.68 (s, 1H), 6.68 (J = 5.2 Hz, 1H), 6.58 (s, 1H), 6.26 (s, 1H), 5.89 (s, 2H), 5.45 (s, 1H), 3.50 (s, 3H), 2.78 (dd, J = 9.6 & 6.5 Hz, 2H), 2.64 (dd, J = 9.6 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 170.0, 155.8, 147.8, 146.2, 145.4, 141.0, 132.2, 129.5, 129.2, 125.1, 121.1, 115.7, 114.6, 108.8, 108.1, 101.3, 51.6, 28.4, 25.6.

HRMS (ESI) $C_{19}H_{17}O_5$[M+H]$^+$: calcd 325.1071, found 325.1075.

Methyl 5-(2-fluorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1j). Obtained as white solid (360 mg, 35% y).



1j

R_f 0.50 (Hex/EtOAc = 20:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.37–7.33 (m, 1H), 7.18–7.07 (m, 3H), 6.72 (s, 1H), 6.23 (s, 1H), 5.89 (s, 2H), 3.52 (s, 3H), 2.83 (dd, J = 6.9 & 5.8 Hz, 2H), 2.72 (dd, J = 8.3 & 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

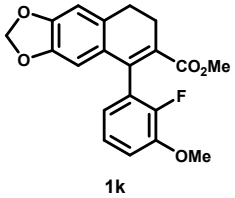
δ 168.3, 159.6 ($^1J_{C\text{-}F}$ = 245.1), 147.0, 140.1, 132.1, 130.6 ($^3J_{C\text{-}F}$ = 3.6 Hz), 129.3 ($^2J_{C\text{-}F}$ = 7.8 Hz), 128.6, 127.0 ($^2J_{C\text{-}F}$ = 17.0 Hz), 126.7, 123.8 ($^3J_{C\text{-}F}$ = 3.6 Hz), 126.7, 115.4, 115.2, 108.2, 107.8, 101.1, 51.4, 28.1, 25.0.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -115.5.

HRMS (ESI) $C_{19}H_{16}O_4F$ $[M+H]^+$: calcd 327.1027, found 327.1029.

Methyl 5-(2-fluoro-3-methoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1k). Obtained as white solid (336 mg, 30% y).



1k

R_f 0.40 (PE/EtOAc = 3:1, UV/$KMnO_4$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.10–7.07 (m, 1H), 6.99–6.96 (m, 1H), 6.71 (s, 1H), 6.67–6.64 (m, 1H), 6.25 (s, 1H), 5.95–5.84 (m, 2H), 3.92 (s, 3H), 3.54 (s, 3H), 2.90–2.78 (m, 2H), 2.77–2.65 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

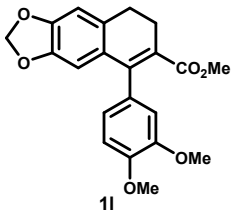
168.2, 149.3 (d, $^1J_{C\text{-}F}$ = 244.9 Hz), 148.3, 147.7 (d, $^3J_{C\text{-}F}$ =11.1 Hz), 147.0 (d, $^2J_{C\text{-}F}$ = 203.1 Hz), 149.8, 132.1, 128.5, 127.8 (d, $^3J_{C\text{-}F}$ = 14.6 Hz), 126.6, 123.6 (d, $^3J_{C\text{-}F}$ = 4.7 Hz), 121.8 (d, $^3J_{C\text{-}F}$ = 2.6 Hz), 112.5, 108.1, 107.9, 101.1, 56.2, 51.4, 28.1, 25.0.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -138.2.

HRMS (ESI) $C_{20}H_{18}O_5F$ $[M+H]^+$: calcd 357.1133, found 357.1128.

Methyl 5-(3,4-dimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1l). Obtained as white solid (754 mg, 65% y).



1l

R_f 0.40 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

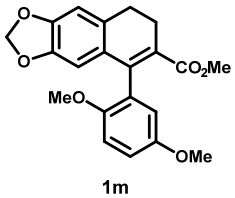
δ 6.88 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 10.1 Hz, 2H), 6.69 (s, 1H), 6.33 (s, 1H), 5.92 (s, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 3.53 (s, 3H), 2.84 (t, J = 8.2 Hz, 2H), 2.68 (t, J = 8.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.7, 148.6, 148.2, 147.5, 146.0, 144.7, 132.0, 131.8, 129.4, 125.3, 121.1, 111.9, 110.7, 108.6, 108.0, 101.0, 55.8, 55.7, 51.3, 28.2, 25.6.

HRMS (ESI) $C_{21}H_{21}O_6$ $[M+H]^+$: calcd 369.1333, found 369.1334.

Methyl 5-(2,5-dimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1m). Obtained as white solid (660 mg,57% y).



1m

R_f 0.45 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.87 (s, 1H), 6.85 (d, J = 2.7 Hz, 2H), 6.70 (s, 1H), 6.56 (d, J = 2.7 Hz, 1H), 6.26 (s, 1H), 5.88 (s, 2H), 3.75 (s, 3H), 3.66 (s, 3H), 3.50 (s, 3H), 2.88–2.77 (m, 2H), 2.73–2.60 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.5, 152.2, 149.6, 146.2, 144.8, 141.1, 130.6, 128.2, 127.7, 124.5, 114.2, 112.0, 110.8, 106.7, 106.6, 99.7, 55.1, 54.3, 49.9, 26.9, 23.8.

HRMS (ESI) $C_{21}H_{21}O_6$ $[M+H]^+$: calcd 369.1333, found 369.1325.

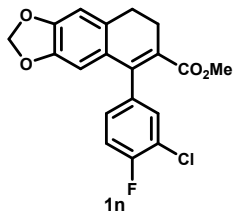
Methyl 5-(3-chloro-4-fluorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1n). Obtained as white solid (170 mg, 15% y).

R_f 0.60 (PE/EtOAc = 20:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.20–7.15 (m, 2H), 7.02–6.99 (m, 1H), 6.71 (s, 1H), 6.18 (s,

1H), 5.90 (s, 2H), 3.53 (s, 3H), 2.80 (dd, J = 9.6 & 6.7 Hz, 2H), 2.67 (dd, J = 9.6 & 6.7 Hz, 2H).



1n

^{13}C NMR (125 MHz, $CDCl_3$)
δ 168.6, 158.3, 156.3, 147.9, 146.1, 143.5, 136.48 (d, $^3J_{C\text{-}F}$ = 4.3 Hz), 132.1, 130.7, 128.6, 128.52 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 125.9, 120.67 (d, $^2J_{C\text{-}F}$ = 18.0 Hz), 116.23 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 108.15 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 101.2, 51.3, 28.1, 25.2.

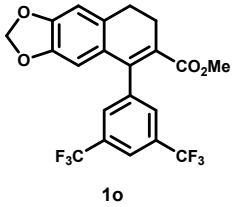
^{19}F NMR (471 MHz, $CDCl_3$)
δ -117.2.

HRMS (ESI) $C_{19}H_{15}O_4ClF$ $[M+H]^+$: calcd 361.0637, found 361.0641.

Methyl 5-(3,5-bis(trifluoromethyl)phenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1o). Obtained as white solid (560 mg, 40% y).

R_f 0.30 (PE/EtOAc = 15:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.88 (s, 1H), 7.61 (s, 2H), 6.75 (s, 1H), 6.03 (s, 1H), 5.92 (s, 2H), 3.48 (s, 3H), 2.85 (dd, J = 9.8 & 6.5 Hz, 2H), 2.73 (dd, J = 9.8 & 6.5 Hz, 2H).



1o

^{13}C NMR (125 MHz, $CDCl_3$)
δ 168.1, 148.3, 146.4, 143.2, 141.9, 132.4, 131.5 (q, $^2J_{C\text{-}F}$ = 33.4 Hz), 129.0 (q, $^3J_{C\text{-}F}$ = 2.7 Hz), 128.1, 126.8, 123.3 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 121.2 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 108.4, 108.0, 101.4, 51.5, 28.1, 25.1.

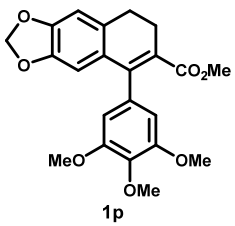
^{19}F NMR (471 MHz, $CDCl_3$)
δ -62.7.

HRMS (ESI) $C_{21}H_{15}O_4F_6$ $[M+H]^+$: calcd 445.0869, found 445.0862.

Methyl 5-(3,4,5-trimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1p). Obtained as white solid (1.1 g, 82% y).

R_f 0.30 (PE/EtOAc = 10:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.71 (s, 1H), 6.35 (s, 2H), 6.34 (s, 1H), 5.91 (s, 2H), 3.90 (s, 3H), 3.81 (s, 6H), 3.50 (s, 3H), 2.81 (dd, J = 9.6 & 6.6 Hz, 2H), 2.65 (dd, J = 9.5 & 6.7 Hz, 2H).



1p

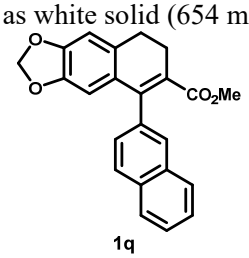
^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.5, 152.9, 147.5, 146.0, 144.6, 137.0, 134.8, 131.9, 128.9, 125.3, 108.4, 107.9, 105.7, 101.0, 60.8, 56.0, 51.2, 28.1, 25.5.

HRMS (ESI) $C_{22}H_{23}O_7$ $[M+H]^+$: calcd 399.1438, found 399.1442.

Methyl 5-(naphthalen-2-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1q). Obtained as white solid (654 mg, 58% y).

R_f 0.50 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.89–7.87 (m, 2H), 7.84–7.79 (m, 1H), 7.62 (s, 1H), 7.53–7.47 (m, 2H), 7.29 (dd, J = 8.4, 1.7 Hz, 1H), 6.74 (s, 1H), 6.23 (s, 1H), 5.87 (s, 2H), 3.41 (s, 3H), 2.87 (t, J = 8.1 Hz, 2H), 2.74 (t, J = 8.1 Hz, 2H).

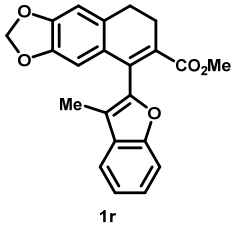


1q

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.4, 147.6, 146.1, 145.4, 137.1, 133.2, 132.6, 132.2, 129.4, 128.0, 127.8, 127.6, 127.2, 127.2, 126.0, 125.9, 125.6, 108.7, 108.0, 101.1, 51.2, 28.3, 25.5.

HRMS (ESI) $C_{23}H_{19}O_4$ $[M+H]^+$: calcd 359.1278, found 359.1280.

Methyl 5-(3-methylbenzofuran-2-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1r). Obtained as white solid (868 mg, 72% y).



1r

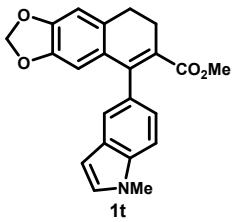
R_f 0.70 (Hex/EtOAc = 5:1, UV/$KMnO_4$).

^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.53 (d, *J* = 7.4, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.28 (m, 2H), 6.73 (s, 1H), 6.36 (s, 1H), 5.90 (s, 2H), 3.55 (s, 3H), 2.86–2.83 (m, 2H), 2.74 (dd, *J* = 9.4 & 6.8 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 168.6, 154.4, 148.2, 148.2, 146.5, 134.1, 131.8, 130.6, 129.8, 127.1, 124.2, 122.4, 119.5, 114.0, 111.2, 108.4, 107.7, 101.2, 51.9, 27.9, 25.6, 8.4.

HRMS (ESI) $C_{22}H_{18}O5Na$ $[M+Na]^+$: calcd 385.1046, found 385.1055.

Methyl 5-(1-methyl-1H-indol-5-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1s). Obtained as white solid (456 mg, 40% y).



1t

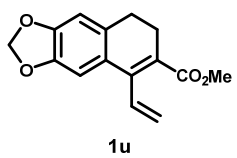
R_f 0.45 (PE/EtOAc = 5:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.38 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 7.00 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.71 (s, 1H), 6.46 (d, *J* = 3.1 Hz, 1H), 6.29 (s, 1H), 5.86 (s, 2H), 3.82 (s, 3H), 3.43 (s, 3H), 2.85–2.82 (m, 2H), 2.68 (dd, *J* = 9.2 & 6.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 170.0, 147.3, 146.2, 145.9, 136.1, 132.1, 130.3, 130.3, 129.0, 128.3, 125.1, 122.8, 120.9, 109.1, 108.8, 107.8, 101.2, 101.0, 51.2, 32.9, 28.5, 25.8.

HRMS (ESI) $C_{22}H_{20}O_4N$ $[M+H]^+$: calcd 362.1387, found 362.1381.

Methyl 5-vinyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1t). Obtained as white solid (308 mg, 38% y).



1u

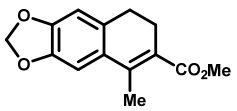
R_f 0.30 (Hex/EtOAc = 80:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.11–6.97 (m, 2H), 6.69 (s, 1H), 5.95 (s, 2H), 5.51 (dt, *J* = 11.5 & 1.9 Hz, 1H), 5.29 (dt, *J* = 17.8 & 2.0 Hz, 1H), 3.77 (s, 3H), 2.67–2.64 (m, 2H), 2.54–2.51 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 168.8, 147.5, 145.8, 143.8, 134.6, 133.2, 127.6, 127.6, 124.0, 120.0, 108.6, 108.0, 101.1, 51.4, 28.3, 25.0.

HRMS (ESI) $C_{15}H_{15}O_4$ $[M+H]^+$: calcd 259.0965, found 259.0572.

Methyl 5-methyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1u). Obtained as white solid (550 mg, 71% y).



1v

R_f 0.30 (Hex/EtOAc = 80:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

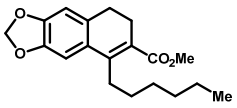
δ 6.98 (s, 1H), 6.66 (s, 1H), 5.95 (s, 2H), 3.78 (s, 3H), 2.65 (dd, *J* = 9.4 & 6.3 Hz, 2H), 2.52–2.49 (m, 2H), 2.40 (t, *J* = 1.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.5, 147.3, 146.4, 141.7, 132.3, 129.9, 124.2, 107.9, 105.8, 101.1, 51.4, 28.4, 24.9, 16.6.

HRMS (ESI) $C_{14}H_{15}O_4$ $[M+H]^+$: calcd 247.0965, found 247.0984.

Methyl 5-hexyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1v). Obtained as white solid (547 mg, 55% y).



1w

R_f 0.35 (PE/EtOAc = 80:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

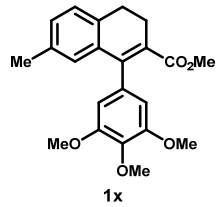
δ 6.98 (s, 1H), 6.67 (s, 1H), 5.96 (s, 2H), 3.77 (s, 3H), 2.84 (t, *J* = 8.1 Hz, 2H), 2.63 (dd, *J* = 9.5 & 6.3 Hz, 2H), 2.48 (dd, *J* = 9.1 & 6.4 Hz, 2H), 1.51–1.45 (m, 2H), 1.42–1.36 (m, 2H), 1.37–1.25 (m, 5H), 0.89 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.4, 147.3, 146.5, 146.3, 132.9, 128.6, 123.8, 108.2, 105.7, 101.1, 51.3, 31.7, 29.8, 29.6, 29.6, 28.6, 25.2, 22.7, 14.1.

HRMS (ESI) $C_{19}H_{25}O_4$ $[M+H]^+$: calcd 317.1747, found 317.1749.

Methyl 7-methyl-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1w). Obtained as white solid (614 mg, 53% y).



1x

R_f 0.50 (PE/EtOAc = 5:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

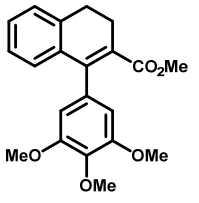
δ 7.11 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.39 (s, 2H), 3.93 (s, 3H), 3.82 (s, 6H), 3.52 (s, 3H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.68–2.65 (m, 2H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.9, 152.9, 144.2, 137.1, 136.0, 134.9, 134.7, 134.0, 129.4, 128.5, 127.8, 127.3, 106.0, 61.0, 56.1, 51.4, 27.5, 25.8, 21.2.

HRMS (ESI) $C_{22}H_{25}O_5$ $[M+H]^+$: calcd 369.1697, found 369.1687.

Methyl 1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1x). Obtained as white solid (791mg, 70% y).



1y

R_f 0.40 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

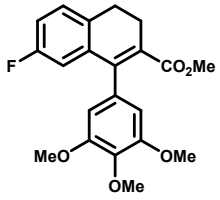
δ 7.23–7.18 (m, 2H), 7.16–7.08 (m, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.39 (s, 2H), 3.91 (s, 3H), 3.81 (s, 6H), 3.53 (s, 3H), 2.92 (dd, *J* = 9.2 & 6.7 Hz, 2H), 2.69 (dd, *J* = 9.2 & 6.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.7, 153.0, 144.1, 137.1, 136.9, 135.0, 134.6, 128.7, 127.9, 127.7, 127.4, 126.5, 106.0, 60.9, 56.1, 51.4, 27.9, 25.6. 30.4, 29.7, 29.6, 25.5.

HRMS (ESI) $C_{21}H_{23}O_5$ $[M+H]^+$: calcd 355.1540, found355.1546.

Methyl 7-fluoro-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1y). Obtained as white solid (552 mg, 47% y).



1z

R_f 0.45 (PE/EtOAc = 8:1, UV/$KMnO_4$).

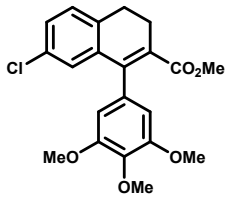
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.16 (dd, *J* = 8.3 & 5.7 Hz, 1H), 6.91 (dt, *J* = 8.3 & 2.7 Hz, 1H), 6.57 (dd, *J* = 10.3 & 2.7 Hz, 1H), 6.37 (s, 2H), 3.91 (s, 3H), 3.82 (s, 3H), 3.52 (s, 3H), 2.88 (dd, *J* = 9.3 & 6.7 Hz, 2H), 2.68 (dd, *J* = 9.3 & 6.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.6, 161.5 (d, $^1J_{C\text{-}F}$ = 243.0 Hz), 153.1, 143.0, 143.0 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 137.4, 136.8 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 133.9, 132.3, 132.3 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.0, 128.5, 128.5 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 114.7 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 105.9, 61.0, 56.1, 51.5, 27.1, 25.7.

^{19}F NMR (471 MHz, $CDCl_3$)
δ -115.8 (q)

HRMS (ESI) $C_{21}H_{22}O_5F$ $[M+H]^+$: calcd 373.1446, found 373.1453.

Methyl 7-chloro-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1z). Obtained as white solid (624 mg, 51% y).



1z

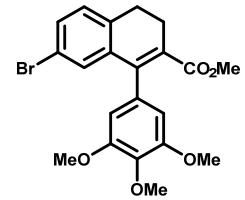
R_f 0.20 (PE/EtOAc = 20:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.19 (dd, *J* = 8.0 & 2.2 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 2.2 Hz, 1H), 6.37 (s, 1H), 3.92 (s, 3H), 3.82 (s, 6H), 3.52 (s, 3H), 2.88 (dd, *J* = 9.3 & 6.7 Hz, 2H), 2.68 (dd, *J* = 9.3 & 6.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.5, 153.1, 142.7, 137.4, 136.7, 135.1, 133.6, 132.2, 129.1, 128.6, 128.4, 127.5, 105.9, 60.9, 56.1, 51.5, 27.3, 25.5.

HRMS (ESI) $C_{21}H_{22}O_5Cl$ $[M+H]^+$: calcd 389.1150, found 389.1159.

Methyl 7-bromo-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1a'). Obtained as white solid (409 mg, 30% y).



1a'

R_f 0.50 (PE/EtOAc = 3:1, UV/$KMnO_4$).

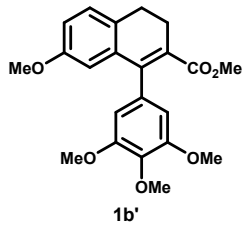
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.34 (dd, *J* = 8.0 & 2.1 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.37 (s, 2H), 3.93 (s, 3H), 3.83 (s, 6H), 3.52 (s, 3H), 2.86 (dd, *J* = 9.3 & 6.7 Hz, 1H), 2.67 (dd, *J* = 9.3 & 6.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.5, 153.1, 142.6, 137.4, 137.0, 135.6, 133.6, 131.4, 130.4, 129.2, 128.9, 120.2, 105.9, 60.9, 56.1, 51.5, 27.4, 25.4.

HRMS (ESI) $C_{21}H_{22}O_5Br$ $[M+H]^+$: calcd 433.0645, found 433.0642.

Methyl 7-methoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1b'). Obtained as white solid (545 mg, 45% y).

R_f 0.35 (PE/EtOAc = 3:1, UV/$KMnO_4$).



1b'

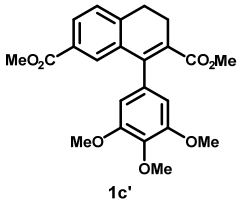
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.13 (d, *J* = 8.2 Hz, 1H), 6.78 (dd, *J* = 8.2 & 2.7 Hz, 1H), 6.44 (d, *J* = 2.7 Hz, 1H), 6.39 (s, 2H), 3.90 (s, 3H), 3.81 (s, 6H), 3.67 (s, 3H), 3.52 (s, 3H), 2.85 (dd, *J* = 9.3 & 6.6 Hz, 2H), 2.67 (dd, *J* = 9.3 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.9, 158.2, 153.0, 143.9, 137.2, 136.1, 134.5, 129.2, 128.5, 128.1, 114.5, 113.2, 106.0, 61.0, 56.2, 55.3, 51.5, 27.1, 26.0.

HRMS (ESI) $C_{22}H_{25}O_6$ $[M+H]^+$: calcd 385.1646, found 385.1661.

Dimethyl 1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2,7-dicarboxylate (1c'). Obtained as white solid (778 mg, 60% y).

R_f 0.25 (PE/EtOAc = 5:1, UV/$KMnO_4$).



1c'

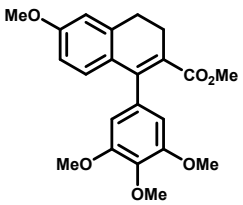
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.90 (dd, *J* = 7.8 & 1.8 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.39 (s, 2H), 3.93 (s, 3H), 3.83 (s, 3H), 3.82 (s, 6H), 3.53 (s, 3H), 2.97 (dd, *J* = 9.2 & 6.8 Hz, 2H), 2.70 (dd, *J* = 9.2 & 6.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.7, 166.8, 153.1, 143.0, 142.1, 137.5, 135.2, 133.7, 129.8, 128.8, 128.8, 128.6, 127.6, 106.0, 61.0, 56.1, 52.1, 51.5, 28.1, 25.3.

HRMS (ESI) $C_{23}H_{25}O_7$ $[M+H]^+$: calcd 413.1495, found 413.1497.

Methyl 6-methoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1d'). Obtained as white solid (582 mg, 48% y).

R_f 0.35 (PE/EtOAc = 3:1, UV/$KMnO_4$).



1d'

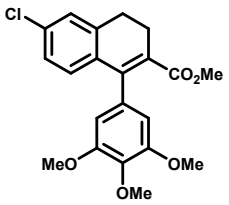
^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.78–6.76 (m, 2H), 6.63 (dd, *J* = 8.6 & 2.7 Hz, 1H), 6.38 (s, 2H), 3.91 (s, 3H), 3.81 (s, 9H), 3.51 (s, 3H), 2.89 (dd, *J* = 9.3 & 6.6 Hz, 2H), 2.69 (dd, *J* = 9.3 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.7, 160.0, 153.0, 144.9, 139.2, 137.1, 135.1, 129.7, 128.2, 124.8, 113.4, 111.3, 105.9, 61.0, 56.1, 55.3, 51.3, 28.5, 25.5.

HRMS (ESI) $C_{22}H_{25}O_6$ $[M+H]^+$: calcd 385.1646, found 385.1647.

Methyl 6-chloro-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1e'). Obtained as white solid (367 mg, 30% y).

R_f 0.20 (PE/EtOAc = 20:1, UV/$KMnO_4$)



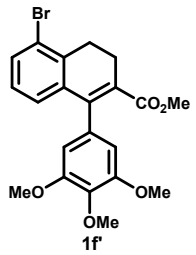
1e'

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.20 (d, *J* = 2.2 Hz, 1H), 7.07 (dd, *J* = 8.4 & 2.2 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.36 (s, 2H), 3.91 (s, 3H), 3.81 (s, 6H), 3.53 (s, 3H), 2.89 (dd, *J* = 9.2 & 6.8 Hz, 2H), 2.68 (dd, *J* = 9.2 & 6.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.5, 153.0, 143.2, 138.7, 137.3, 134.3, 134.1, 133.6, 129.2, 127.8, 127.4, 126.5, 105.9, 60.9, 56.1, 51.5, 27.7, 25.3.

HRMS (ESI) $C_{21}H_{22}O_5Cl$ $[M+H]^+$: calcd 389.1150, found 389.1161.

Methyl 5-bromo-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1f'). Obtained as white solid (353 mg, 26% y).



1f'

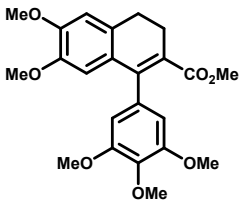
R_f 0.20 (PE/EtOAc = 20:1, UV/$KMnO_4$)

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.47 (dd, *J* = 7.9 & 1.2 Hz, 1H), 6.99–6.96 (m, 1H), 6.81 (dd, *J* = 7.9 & 1.2 Hz, 1H), 6.36 (s, 2H), 3.90 (s, 3H), 3.81 (s, 6H), 3.53 (s, 3H), 3.05 (dd, *J* = 9.3 & 7.0 Hz, 2H), 2.71–2.68 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.3, 153.0, 143.3, 137.3, 137.3, 136.3, 134.2, 132.7, 128.5, 127.4, 127.2, 123.7, 106.0, 60.9, 56.1, 51.5, 27.3, 25.0.

HRMS (ESI) $C_{21}H_{22}O_5Br$ $[M+H]^+$: calcd 433.0645, found 433.0648.

Methyl 6,7-dimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1g'). Obtained as white solid (420 mg, 35% y).



1g'

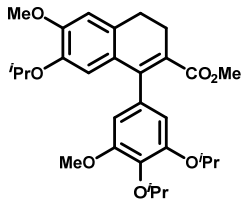
R_f 0.60 (PE/EtOAc = 4:1, UV/$KMnO_4$)

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.74 (s, 1H), 6.40 (s, 3H), 3.91 (s, 6H), 3.81 (s, 6H), 3.62 (s, 3H), 3.52 (s, 3H), 2.84 (dd, *J* = 9.5 & 6.6 Hz, 2H), 2.68 (dd, *J* = 9.5 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.8, 152.9, 149.4, 147.1, 144.6, 137.1, 134.9, 130.6, 127.6, 125.2, 111.9, 110.7, 106.0, 61.0, 56.1, 56.1, 56.0, 51.3, 27.7, 25.7.

HRMS (ESI) $C_{23}H_{28}O_7$ $[M+H]^+$: calcd 415.1751, found 415.1758.

Methyl 1-(3,4-diisopropoxy-5-methoxyphenyl)-7-isopropoxy-6-methoxy-3,4-dihydronaphthalene-2-carboxylate (1h'). Obtained as white solid (1.30 g, 83% y).



1h'

R_f 0.60 (PE/EtOAc = 4:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.73 (s, 1H), 6.39 (s, 1H), 6.37 (d, *J* = 1.8 Hz, 1H), 6.34 (d, *J* = 1.8 Hz, 1H), 4.53–4.41 (m, 2H), 4.17–4.11 (m, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.46 (s, 3H), 2.83 (dd, *J* = 9.3 & 6.8 Hz, 2H), 2.67 (dd, *J* = 9.0 & 7.1 Hz, 2H), 1.31 (dd, *J* = 9.3 & 6.1 Hz, 12H), 1.18 (d, *J* = 6.1 Hz, 6H).

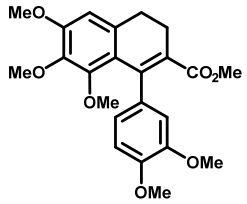
^{13}C NMR (125 MHz, $CDCl_3$)
δ 170.0, 153.9, 151.6, 150.7, 145.2, 144.9, 136.7, 134.5, 130.8, 127.8, 124.7, 116.4, 111.1, 110.4, 105.9, 74.9, 71.5, 71.3, 56.0, 56.0, 51.2, 27.7, 25.7, 22.4, 22.1, 21.9.

HRMS (ESI) $C_{29}H_{38}O_7$ $[M+H]^+$: calcd 499.2690, found 499.2675.

Methyl 1-(3,4-dimethoxyphenyl)-6,7,8-trimethoxy-3,4-dihydronaphthalene-2-carboxylate (1i'). Obtained as white solid (1.10 g, 85% y).

R_f 0.20 (PE/EtOAc = 4:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.83 (d, *J* = 8.0 Hz, 1H), 6.77–6.71 (m, 2H), 6.59 (s, 1H), 3.91 (s, 6H), 3.84 (s, 3H), 3.76 (s, 3H), 3.52 (s, 3H), 3.19 (s, 3H), 2.77



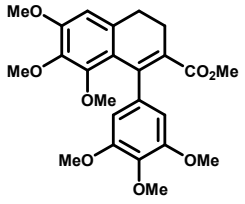
1i'

(dd, J = 9.1 & 5.8 Hz, 2H), 2.58–2.48 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 170.2, 153.5, 152.6, 147.9, 147.5, 141.2, 141.1, 135.2, 134.3, 127.8, 121.6, 119.7, 111.1, 110.0, 106.3, 60.6, 60.5, 55.8, 55.7, 55.6, 51.2, 29.6, 25.9.

HRMS (ESI) $C_{23}H_{27}O_7Na$ $[M+Na]^+$: calcd 437.1571, found 437.1569.

Methyl 6,7,8-trimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate (1j'). Obtained as white solid (1.23 g, 88% y).



1j'

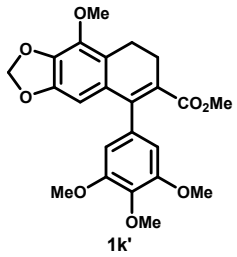
R_f 0.30 (PE /EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.58 (s, 1H), 6.40 (s, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 3.80 (s, 6H), 3.74 (s, 3H), 3.50 (s, 3H), 3.23 (s, 3H), 2.79–2.73 (m, 2H), 2.54–2.47 (m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$)
δ 170.5, 153.7, 152.6, 152.5, 141.3, 140.9, 137.5, 136.6, 135.2, 128.2, 121.4, 106.5, 104.9, 61.0, 60.7, 60.6, 56.1, 55.9, 51.4, 29.7, 26.1.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1869, found 445.1871.

Methyl 9-methoxy-5-(3,4,5-trimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1k'). Obtained as white solid (1.08 g, 80% y).



1k'

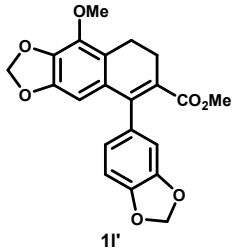
R_f 0.38 (Hex/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.34 (s, 2H), 6.10 (s, 1H), 5.90 (s, 2H), 4.01 (s, 3H), 3.90 (s, 3H), 3.81 (s, 6H), 3.50 (s, 3H), 2.83 (dd, J = 9.5 & 6.8 Hz, 2H), 2.61 (dd, J = 9.3 & 7.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.7, 153.0, 147.1, 144.5, 139.9, 137.2, 137.1, 135.0, 129.7, 126.1, 123.3, 106.0, 104.6, 103.4, 101.1, 61.0, 59.8, 56.1, 51.4, 25.2, 20.4.

HRMS (ESI) $C_{23}H_{25}O_8$ $[M+H]^+$: calcd 429.1544, found 429.1530.

Methyl 5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (1l'). Obtained as white solid (868 mg, 72% y).



1l'

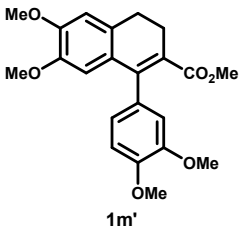
R_f 0.70 (Hex/EtOAc = 1:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.81 (d, J = 7.9 Hz, 1H), 6.61 (s, 1H), 6.58 (d, J = 7.9 Hz, 1H), 6.09 (s, 1H), 5.99 (s, 2H), 5.89 (s, 2H), 4.00 (s, 3H), 3.54 (s, 3H), 2.80 (s, 2H), 2.60 (t, J = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 169.4, 147.3, 147.0, 146.8, 144.6, 139.9, 137.2, 133.1, 130.0, 126.0, 123.4, 122.1, 109.4, 108.1, 103.5, 101.0, 101.0, 59.7, 51.3, 25.0, 20.4.

HRMS (ESI) $C_{21}H_{19}O_7$ $[M+H]^+$: calcd 383.1125, found 383.1120.

Methyl 1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydronaphthalene-2-carboxylate (1m'). Obtained as white solid (680 mg, 83% y).



1m'

R_f 0.30 (PE/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

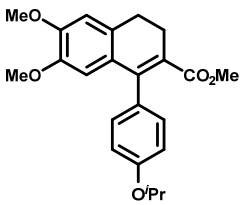
δ 6.90 (d, *J* = 8.1 Hz, 1H), 6.78–6.67 (m, 3H), 6.38 (s, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.84 (s, 3H), 3.60 (s, 3H), 3.52 (s, 3H), 2.84 (dd, *J* = 9.5 & 6.6 Hz, 2H), 2.68 (dd, *J* = 9.4 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.9, 149.3, 148.5, 148.2, 147.1, 144.7, 131.8, 130.7, 128.1, 125.1, 121.3, 112.0, 111.9, 110.7, 110.6, 56.0, 55.9, 55.7, 51.3, 27.8, 25.8.

HRMS (ESI) $C_{22}H_{25}O_6$ $[M+H]^+$: calcd 385.1646, found 385.1231.

Methyl 1-(4-isopropoxyphenyl)-6,7-dimethoxy-3,4-dihydronaphthalene-2-carboxylate (1n'). Obtained as white solid (513 mg, 67% y).



1n'

R_f 0.70 (Hex/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

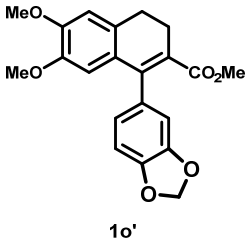
δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 6.36 (s, 1H), 4.66–4.52 (m, 1H), 3.91 (s, 3H), 3.59 (s, 3H), 3.50 (s, 3H), 2.83 (dd, *J* = 9.5 & 6.5 Hz, 2H), 2.68 (dd, *J* = 9.5 & 6.5 Hz, 2H), 1.37 (d, *J* = 6.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 170.0, 157.2, 149.3, 147.0, 145.0, 131.4, 130.8, 130.0, 128.3, 124.9, 115.4, 112.1, 110.7, 69.9, 56.0, 56.0, 51.2, 27.9, 25.8, 22.1.

HRMS (ESI) $C_{23}H_{26}O_5Na$ $[M+Na]^+$: calcd 405.1678, found 383.1680.

Methyl 1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxy-3,4-dihydronaphthalene-2-carboxylate (1o'). Obtained as white solid (710 mg, 90% y).



1o'

R_f 0.60 (Hex/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

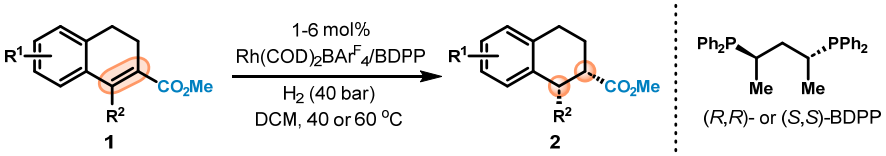
δ 6.84 (d, *J* = 7.9 Hz, 1H), 6.73 (s, 1H), 6.66 (s, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.38 (s, 1H), 6.01 (s, 2H), 3.91 (s, 3H), 3.63 (s, 3H), 3.55 (s, 3H), 2.82 (dd, *J* = 9.6 & 6.6 Hz, 2H), 2.67 (dd, *J* = 9.5 & 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.5, 149.4, 147.4, 147.1, 146.8, 144.9, 133.1, 130.7, 128.0, 125.2, 122.1, 112.0, 110.7, 109.4, 108.1, 101.0, 56.1, 56.0, 51.4, 27.8, 25.6.

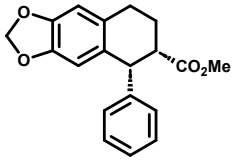
HRMS (ESI) $C_{21}H_{19}O_7$ $[M+H]^+$: calcd 369.1333, found 369.1350.

3.2 General Procedure for the Rhodium-Catalyzed Enantioselective Hydrogenation



A stock solution (0.01 M) was made by stirring $Rh(COD)_2BArF_4$[7] with (*R*,*R*)- or (*S*,*S*)-BDPP[8,9] (1:1.2 molar ratio) in DCM at RT for 20 min in a glovebox. An aliquot of the catalyst solution (0.1-10 mL, 0.001-0.1 mmol; 0.01-0.06 equiv.) was transferred by syringe into the vials charged with **1** (0.1-10.0 mmol, 1.0 equiv.) in anhydrous DCM (0.9-90 mL). The vials were subsequently *quickly* transferred into an autoclave, then charged with hydrogen gas (40 bar) and heated at 40 or 60 °C for 36 h. The reaction was then cooled, and hydrogen gas was released carefully. The mixture was concentrated in *vacuo* and the residue was purified by flash chromatography to afford the desired hydrogenation product **2**. The ee of products were determined by chiral HPLC or SFC analysis.

Methyl (5R,6S)-5-phenyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2a). Obtained as white solid by using 1.0 mol% catalyst at 60 °C (32.1 mg, 99% y, 94% ee).



2a

R_f 0.50 (Hex/EtOAc = 20:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -100.6 (c = 0.91, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.22–7.15 (m, 3H), 6.95 (d, *J* = 7.2, 2H), 6.62 (s, 1H), 6.37 (s, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.85 (d, *J* = 1.4 Hz, 1H), 4.49 (d, *J* = 5.6 Hz, 1H), 3.55 (s, 3H), 3.07–3.00 (m, 1H), 2.96–2.89 (m, 1H), 2.85–2.75 (m, 1H), 2.05–1.83 (m, 2H).

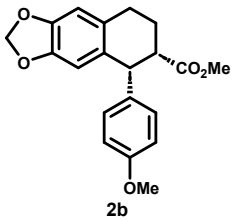
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.8, 146.4, 146.0, 142.3, 130.6, 129.5, 129.2, 127.8, 126.7, 109.6, 108.6, 107.9, 101.0, 100.6, 51.2, 46.4, 45.6, 28.4, 18.9.

HRMS (ESI) $C_{19}H_{19}O_4$ $[M+H]^+$: calcd 311.1278, found 311.1280.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 12.519 min, t_{minor} = 16.365 min.

Methyl (5R,6S)-5-(4-methoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2b). Obtained as white solid by using 1 mol% catalyst at 40 °C (31.3 mg, 92% y, 95% ee).



2b

R_f 0.40 (Hex/EtOAc = 3:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -182.8 (c = 0.77, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.80 (d, *J* = 10.0 Hz, 2H), 6.67 (d, *J* = 10.00 Hz, 2H), 6.54 (s, 1H), 6.29 (s, 1H), 5.79 (d, *J* = 1.4 Hz, 1H), 5.78 (d, *J* = 1.4 Hz, 1H), 4.38 (d, *J* = 5.5 Hz, 1H), 3.68 (s, 3H), 3.50 (s, 3H), 2.97–2.89 (m, 1H), 2.88–2.79 (m, 1H), 2.79–2.66 (m, 1H), 1.96–1.80 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

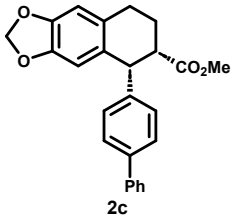
174.0, 158.3, 146.3, 146.0, 134.5, 131.0, 130.4, 129.1, 113.2, 109.7, 107.9, 100.7, 55.1, 51.2, 45.7, 45.7, 28.5, 18.9.

HRMS (ESI) $C_{20}H_{21}O_5$ $[M+H]^+$: calcd 341.1384, found 341.1387.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (90/10), 0.5 mL/min, 210 nm, t_{major} = 13.898 min, t_{minor} = 20.677

min.

Methyl (5R,6S)-5-([1,1'-biphenyl]-4-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2c). Obtained as colorless oil by using 6 mol% catalyst at 40 °C (37.5 mg, 97% y, 92% ee).



2c

R_f 0.50 (Hex/EtOAc = 10:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -129.2 (c = 0.70, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.49–7.36 (m, 4H), 7.33–7.30 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.65 (s, 1H), 6.42 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 5.87 (d, *J* = 1.4 Hz, 1H), 4.55 (d, *J* = 5.5 Hz, 1H), 3.60 (s, 3H), 3.15–3.01 (m, 1H), 3.01–2.90 (m, 1H), 2.91–2.77 (m, 1H), 2.14–1.92 (m, 2H).

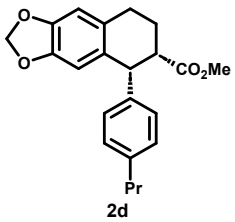
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.9, 146.5, 146.1, 141.4, 140.8, 139.5, 130.6, 129.9, 129.3, 128.7, 127.1, 127.0, 126.6, 109.7, 108.0, 100.7, 51.3, 46.2, 45.7, 28.5, 19.0.

HRMS (ESI) $C_{25}H_{23}O_4$ $[M+H]^+$: calcd 387.1591, found 387.1596.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 14.466 min, t_{minor} =19.525 min.

Methyl (5R,6S)-5-(4-propylphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2d). Obtained as white solid by using 1 mol% catalyst at 60 °C (32.0 mg, 91% y, 95% ee).



2d

R_f 0.50 (Hex/EtOAc = 20:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -161.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.01 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 6.38 (s, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.85 (d, *J* = 1.5 Hz, 1H), 4.47 (d, *J* = 5.5 Hz, 1H), 3.56 (s, 3H), 3.05–2.98 (m, 1H), 2.96–2.88 (m, 1H), 2.85–2.74 (m, 1H), 2.55–2.48 (m, 2H), 1.59 (dd, *J* = 15.4 & 7.9 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H).

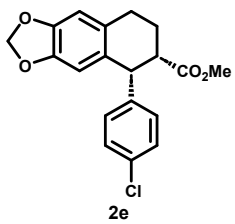
^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.0, 146.3, 146.0, 141.0, 139.5, 130.9, 129.3, 129.2, 127.9, 109.7, 107.9, 100.7, 51.2, 46.1, 45.7, 37.6, 28.5, 24.3, 19.0, 13.8.

HRMS (ESI) $C_{22}H_{25}O_4$ $[M+H]^+$: calcd 353.1747, found 353.1750.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (90/10), 0.5 mL/min, 210 nm, t_{major} = 10.036 min, t_{minor} = 11.346 min.

Methyl (5R,6S)-5-(4-chlorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2e). Obtained as white solid by using 1 mol% catalyst at 60 °C (34.2 mg, 99% y, 96% ee).



2e

R_f 0.60 (PE/EtOAc = 20:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -129.2 (c = 1.00, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

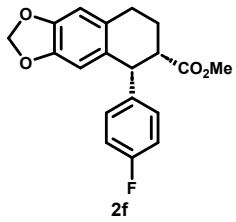
δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.62 (s, 1H), 6.32 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 5.87 (d, *J* = 1.5 Hz, 1H), 4.47 (d, *J* = 5.5 Hz, 1H), 3.57 (s, 3H), 3.07–2.98 (m, 1H), 2.96–2.87 (m, 1H), 2.92 (dt, *J* = 17.0 & 4.0 Hz, 1H), 2.00–1.89 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.7, 146.6, 146.1, 140.9, 132.6, 130.8, 130.1, 129.3, 128.0, 109.5, 108.1, 100.8, 51.4, 45.8, 45.5, 28.4, 18.9.

HRMS (ESI) $C_{19}H_{18}ClO_4$ $[M+H]^+$: calcd 345.0888, found 345.0874.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{minor} = 12.453 min, t_{major} = 13.673 min.

Methyl (5R,6S)-5-(4-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2f). Obtained as white solid by using 1 mol% catalyst at 40 °C (30.6 mg, 99% y, 96% ee).



2f

R_f 0.60 (PE/EtOAc = 20:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -435.7 (c = 1.2, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.96–6.86 (m, 4H), 6.62 (s, 1H), 6.34 (s, 1H), 5.87 (d, *J* = 1.3 Hz, 1H), 5.86 (d, *J* = 1.5 Hz, 1H), 4.48 (d, *J* = 5.5 Hz, 1H), 3.57 (s, 3H), 3.03 (dt, *J* = 10.8 & 5.4 Hz, 1H), 2.96–2.87 (m, 1H), 2.85–2.75 (m, 1H), 1.98–1.89 (m, 2H).

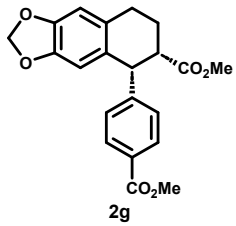
^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.7, 162.5, 160.8, 146.5, 146.1, 138.1, 138.0, 130.9, 130.9, 130.4, 129.2, 114.7, 114.6, 109.5, 108.0, 100.7, 51.2, 45.6, 45.6, 28.4, 18.8.

^{19}F NMR (471 MHz, $CDCl_3$)
δ -116.2.

HRMS (ESI) $C_{19}H_{18}FO_4$ $[M+H]^+$: calcd 329.1184, found 329.1186.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{minor} = 12.578 min, t_{major} = 13.364 min.

Methyl (5R,6S)-5-(4-(methoxycarbonyl)phenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2g). Obtained as white solid by using 1 mol% catalyst at 40 °C (36.5 mg, 99% y, 95% ee).



2g

R_f 0.40 (Hex/EtOAc = 3:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -83.6 (c = 0.50, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.64 (s, 1H), 6.32 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 5.87 (d, *J* = 1.4 Hz, 1H), 4.54 (d, *J* = 5.7 Hz, 1H), 3.88 (s, 3H), 3.55 (s, 3H), 3.11–3.04 (m, 1H), 2.98–2.90 (m, 1H), 2.87–2.77 (m, 1H), 1.99–1.90 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.5, 166.9, 147.6, 146.6, 146.1, 129.8, 129.6, 129.3, 129.2, 128.6, 109.5, 108.1, 100.8, 52.0, 51.3, 46.4, 45.6, 28.4, 19.0.

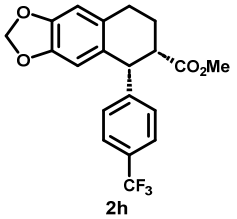
HRMS (ESI) $C_{21}H_{21}O_6$ $[M+H]^+$: calcd 369.1333, found 369.1334.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 20.218 min, t_{minor} = 30.427 min.

Methyl (5R,6S)-5-(4-(trifluoromethyl)phenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2h). Obtained as white solid by using 1 mol% catalyst at 40 °C (35.3 mg, 96% y, 96% ee).

R_f 0.5 (Hex/EtOAc = 10:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -146.8 (c = 0.82, $CHCl_3$).



2h

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.47 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 6.31 (s, 1H), 5.88 (q, J = 1.4 Hz, 1H), 5.87 (d, J = 1.2 Hz, 1H), 4.56 (d, J = 5.6 Hz, 1H), 3.57 (s, 3H), 3.13–3.05 (m, 1H), 2.99–2.91 (m, 1H), 2.88–2.77 (m, 1H), 2.01–1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.5, 146.7, 146.4, 146.2, 129.9, 129.7, 129.4, 129.1, 128.8, 124.81 (q, J = 3.8 Hz), 109.5, 108.2, 100.8, 51.4, 46.2, 45.5, 28.4, 18.9.

^{19}F NMR (471 MHz, $CDCl_3$)
δ -62.4.

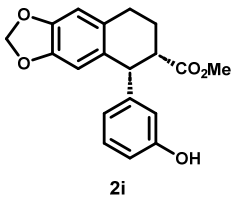
HRMS (ESI) $C_{20}H_{18}F_3O_4$ $[M+H]^+$: calcd 379.1152, found 379.1145.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 13.147 min, t_{minor} = 11.253 min.

Methyl (5R,6S)-5-(3-hydroxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2i). Obtained as white solid by using 1 mol% catalyst at 60 °C (29.3 mg, 96% y, 94% ee).

R_f 0.20 (Hex/EtOAc = 10:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -165.4 (c = 0.70, $CHCl_3$).



2i

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7. 09–7.06 (m, 1H), 6.63–6.61 (m, 2H), 6.56 (d, J = 7.7 Hz, 1H), 6.39–6.38 (m, 1H), 6.37 (s, 1H), 5.87 (d, J = 1.4 Hz, 1H), 5.86 (d, J = 1.4 Hz, 1H), 4.45 (d, J = 5.6 Hz, 1H), 3.58 (s, 3H), 3.05–3.00 (m, 1H), 2.94–2.89 (m, 1H), 2.83–2.76 (m, 1H), 2.05–1.96 (m, 1H), 1.93–1.91 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.3, 155.4, 146.4, 146.0, 144.1, 144.1, 130.4, 129.2, 128.9, 121.8, 121.8, 116.7, 113.8, 109.7, 108.0, 100.7, 51.4, 46.3, 45.7, 28.4, 19.0.

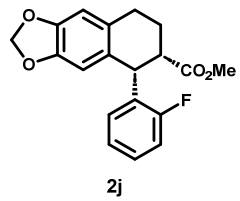
HRMS (ESI) $C_{19}H_{19}O_5$ $[M+H]^+$: calcd 327.1227, found 327.1230.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 14.666 min, t_{minor} = 19.320 min.

Methyl (5S,6S)-5-(2-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2j). Obtained as white solid by using 1 mol% catalyst at 40 °C (31.8 mg, 97% y, 93% ee).

R_f 0.50 (Hex/EtOAc = 20:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -149.5 (c = 1.0, $CHCl_3$).



2j

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.17–7.13 (m, 1H), 7.00–6.95 (m, 2H), 6.78–6.75 (m, 1H), 6.62 (s, 1H), 6.35 (s, 1H), 5.87 (d, J = 1.4 Hz, 1H), 5.86 (d, J = 1.5 Hz, 1H), 4.82 (d, J = 5.5 Hz, 1H), 3.59 (s, 3H), 3.10–3.04 (m, 1H), 2.97–2.90 (m, 1H), 2.86–2.77 (m, 1H), 2.08–1.98 (m, 1H), 1.92–1.84 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.1, 160.48 (d, $^{1}J_{C\text{-}F}$ = 245.7 Hz), 146.5, 146.1, 132.2 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 129.9, 129.4, 129.1 (d, $^{3}J_{C\text{-}F}$ = 14.6 Hz), 129.0, 128.4,

128.3 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 123.6, 123.6 (d, $^{1}J_{C\text{-}F}$ = 3.4 Hz), 114.8 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 109.5, 108.1, 100.8, 51.5, 44.7, 38.8 (fd, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 28.2, 19.8.

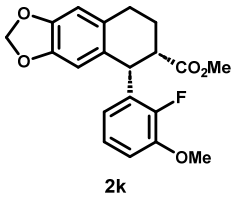
^{19}F NMR (471 MHz, $CDCl_3$)

δ -118.1.

HRMS (ESI) $C_{19}H_{18}FO_4$ $[M+H]^+$: calcd 329.1184, found 329.1185.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 12.030 min, t_{minor} = 15.263 min.

Methyl (5S,6S)-5-(2-fluoro-3-methoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2k). Obtained as white solid by using 2 mol% catalyst at 40 °C (32.3 mg, 90% y, 94% ee).



2k

R_f 0.40 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -212.4 (c = 1.2, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.93–6.83 (m, 1H), 6.84–6.75 (m, 1H), 6.61 (s, 1H), 6.41–6.30 (m, 2H), 5.87 (d, *J* = 1.4 Hz, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 4.83 (d, *J* = 5.4 Hz, 1H), 3.86 (s, 3H), 3.61 (s, 3H), 3.12–3.04 (m, 1H), 2.98–2.90 (m, 1H), 2.86–2.77 (m, 1H), 2.14–1.98 (m, 1H), 1.96–1.82 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.0, 150.4 (d, *J* = 245.0 Hz), 147. 3 (d, *J* = 11.8 Hz), 146.5, 146.0, 130.0, 129.9, 129.4, 123.3 (d, *J* = 3.1 Hz), 123.0 (d, *J* = 4.6 Hz), 111.5 (d, *J* = 1.9 Hz), 109.4, 108.1, 100.7, 56.2, 51.6, 44.7, 38.7 (d, *J* = 2.8 Hz), 28.2, 19.8.

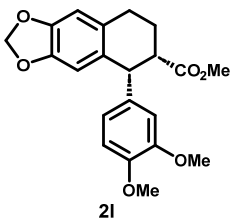
^{19}F NMR (471 MHz, $CDCl_3$)

δ -140.8.

HRMS (ESI) $C_{20}H_{20}FO_5$ $[M+H]^+$: calcd 359.1289, found 359.1287.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 17.422 min, t_{minor} = 16.162 min.

Methyl (5R,6S)-5-(3,4-dimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2l). Obtained as white solid by using 4.0 mol% catalyst at 40 °C (36.7 mg, 99% y, 96% ee).



2l

R_f 0.40 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -154.4 (c = 0.95, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.71 (d, *J* = 8.3 Hz, 1H), 6.61 (s, 1H), 6.54 (d, *J* = 2.1 Hz, 1H), 6.45 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.39 (s, 1H), 5.87 (s, 2H), 4.44 (d, *J* = 5.4 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.58 (s, 3H), 3.05–2.97 (m, 1H), 2.95–2.87 (m, 1H), 2.84–2.74 (m, 1H), 2.05–1.95 (m, 1H), 1.96–1.89 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

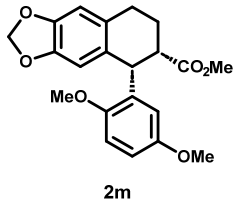
δ 174.0, 148.3, 147.8, 146.4, 146.1, 135.0, 130.9, 129.2, 122.0, 112.9, 110.6, 109.7, 108.0, 100.7, 55.8, 55.7, 51.3, 46.1, 45.8, 28.5, 27.0, 19.1.

HRMS (ESI) $C_{18}H_{16}NaO_3$ $[M+H]^+$: calcd 371.1489, found 371.1491.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH

(80/20), 0.5 mL/min, 210 nm, t_{major} = 20.183 min, t_{minor} = 21.876 min.

Methyl (5S,6S)-5-(2,5-dimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2m). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (33.4 mg, 91% y, 92% ee).



2m

R_f 0.45 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -173.2 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.73 (d, *J* = 8.9 Hz, 1H), 6.67 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.59 (s, 1H), 6.34 (s, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.85 (d, *J* = 1.4 Hfz, 1H), 4.89 (d, *J* = 5.3 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.54 (s, 3H), 3.06–2.97 (m, 1H), 2.96–2.89 (m, 1H), 2.83–2.75 (m, 1H), 2.12–2.02 (m, 1H), 1.83–1.76 (m, 1H).

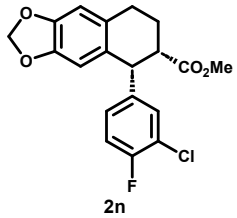
^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.3, 152.7, 151.4, 146.2, 145.9, 131.8, 131.0, 129.2, 119.0, 110.8, 110.0, 109.5, 107.9, 100.6, 55.6, 55.3, 51.0, 44.5, 38.8, 28.1, 20.2.

HRMS (ESI) $C_{21}H_{23}O_6$ $[M+H]^+$: calcd 371.1489, found 371.1489.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 17.193 min, t_{minor} = 28.126 min.

Methyl (5R,6S)-5-(3-chloro-4-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2n). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (35.9 mg, 99% y, 97% ee).



2n

R_f 0.60 (PE/EtOAc = 20:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -171.1 (c = 0.98, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.02–6.94 (m, 2H), 6.85–6.80 (m, 1H), 6.63 (s, 1H), 6.32 (s, 1H), 5.89 (s, 2H), 4.45 (d, *J* = 5.6 Hz, 1H), 3.60 (s, 3H), 3.08–2.97 (m, 1H), 2.99–2.86 (m, 1H), 2.85–2.75 (m, 1H), 1.99–1.83 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.5, 158.0, 156.0, 146.5 (d, *J* = 65.3 Hz), 139.5 (d, *J* = 3.8 Hz), 131.5, 129.5, 129.3, 129.1 (d, *J* = 7.0 Hz), 120.4 (d, *J* = 17.7 Hz), 115.9 (d, *J* = 21.0 Hz), 109.4, 108.2, 100.9, 51.4, 45.5, 45.5, 28.4, 18.8.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -118.2.

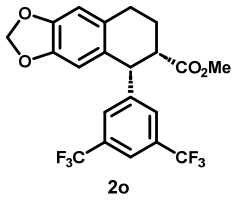
HRMS (ESI) $C_{19}H_{17}ClFO_4$ $[M+H]^+$: calcd 363.0794, found 363.0797 .

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 14.782 min, t_{minor} = 12.776 min.

Methyl (5R,6S)-5-(3,5-bis(trifluoromethyl)phenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2o). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (44.3 mg, 99% y, 97% ee).

R_f 0.30 (Hex/EtOAc = 15:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -344.7 (c = 1.0, $CHCl_3$)



2o

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.72 (s, 1H), 7.41 (s, 2H), 6.67 (s, 1H), 6.30 (s, 1H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 4.64 (d, *J* = 5.6 Hz, 1H), 3.59 (s, 3H), 3.13–3.08 (m, 1H), 3.01–2.94 (m, 1H), 2.88–2.79 (m, 1H), 2.01–1.95 (m, 1H), 1.85–1.75 (m, 1H).

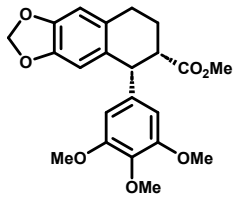
^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.1, 147.1, 146.5, 145.0, 131.1 (q, *J* = 33.2 Hz), 129.6, 128.2, 123.3 (q, *J* = 272.6 Hz), 120.9 (q, *J* = 3.9 Hz), 109.3, 108.4, 101.0, 51.4, 46.1, 45.4, 28.3, 18.8.

^{19}F NMR (471 MHz, $CDCl_3$)
δ -62.7.

HRMS (ESI) $C_{21}H_{17}F6O_4$ $[M+H]^+$: calcd 447.1026, found 447.1036 .

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{minor} = 9.678 min, t_{major} = 10.171 min.

Methyl (5R,6S)-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2p). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (3.92 g from 4.0 g of **1p**, 98% y, >99% ee).



2p

R_f 0.30 (PE/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -232.7 (c = 0.55, $CHCl_3$)

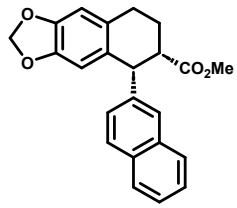
^{1}H NMR (600 MHz, $CDCl_3$)
δ 6.62 (s, 1H), 6.40 (s, 1H), 6.17 (s, 2H), 5.89 (d, *J* = 1.4 Hz, 1H), 5.88 (d, *J* = 1.5 Hz, 1H), 4.43 (d, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 6H), 3.59 (s, 3H), 3.04–2.98 (m, 1H), 2.95–2.89 (m, 1H), 2.85–2.75 (m, 1H), 2.06–1.90 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.7, 152.5, 146.4, 146.0, 137.9, 136.8, 130.4, 129.1, 109.6, 107.9, 106.9, 100.7, 60.7, 56.0, 51.3, 46.6, 45.8, 28.4, 19.2.

HRMS (ESI) $C_{22}H_{24}O_7$ $[M+H]^+$: calcd 401.1595, found 401.1597.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 21.112 min, t_{minor} = 30.285 min.

Methyl (5R,6S)-5-(naphthalen-2-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2q). Obtained as white solid by using 4.0 mol% catalyst at 40 °C (33.1 mg, 92% y, 91% ee).



2q

R_f 0.50 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -135.0 (c = 0.7, $CHCl_3$)

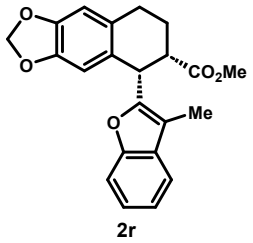
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.76–7.63 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.40–7.29 (m, 3H), 7.04 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.60 (s, 1H), 6.31 (s, 1H), 5.80 (d, *J* = 1.4 Hz, 1H), 5.79 (d, *J* = 1.4 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 3.46 (s, 3H), 3.12–2.98 (m, 1H), 2.97–2.85 (m, 1H), 2.85–2.70 (m, 1H), 2.08–1.94 (m, 1H), 1.93–1.82 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.9, 146.5, 146.1, 140.0, 133.1, 132.3, 130.6, 129.4, 128.5, 127.8, 127.7, 127.5, 127.4, 125.9, 125.6, 109.8, 108.1, 100.7, 51.3, 46.6, 45.9, 28.6, 19.2.

HRMS (ESI) $C_{23}H_{21}O_4$ $[M+H]^+$: calcd 361.1434, found 361.1441.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 17.111 min, t_{minor} = 19.770 min.

Methyl (5S,6S)-5-(3-methylbenzofuran-2-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2r). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (34.6 mg, 94% y, 95% ee).



2r

R_f 0.60 (PE/EtOAc = 7:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -150.4 (c = 0.50, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.44–7.39 (m, 1H), 7.29–7.25 (m, 1H), 7.19–7.14 (m, 2H), 6.63 (s, 1H), 6.43 (s, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.83 (d, *J* = 1.4 Hz, 1H), 4.68 (d, *J* = 5.8 Hz, 1H), 3.55 (s, 3H), 3.07–3.01 (m, 1H), 3.01–2.96 (m, 1H), 2.86–2.79 (m, 1H), 2.46–2.37 (m, 1H), 2.15 (s, 3H), 2.13–2.08 (m, 1H).

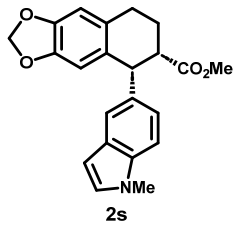
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.7, 154.1, 153.3, 146.7, 146.0, 129.9, 129.8, 127.7, 123.7, 122.0, 119.0, 111.9, 110.9, 109.0, 108.5, 100.8, 51.6, 44.8, 38.8, 28.8, 21.0, 7.9.

HRMS (ESI) $C_{22}H_{21}O_5$ $[M+H]^+$: calcd 365.1384, found 364. 365.1397.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (90/10), 0.5 mL/min, 210 nm, t_{major} = 13.675 min, t_{minor} = 15.082 min.

Methyl (5R,6S)-5-(1-methyl-1H-indol-5-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2s). Obtained as white solid by using 4.0 mol% catalyst at 40 °C (35.3 mg, 97% y, 95% ee).



2s

R_f 0.45 (PE/EtOAc = 5:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -135.4 (c = 0.95, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.16–7.14 (m, 2H), 6.97 (d, *J* = 3.1 Hz, 1H), 6.85 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.64 (s, 1H), 6.40 (s, 1H), 6.35 (d, *J* = 3.1 Hz, 1H), 5.88–5.82 (m, 2H), 4.61 (d, *J* = 5.5 Hz, 1H), 3.73 (s, 3H), 3.55 (s, 3H), 3.09–3.02 (m, 1H), 2.99–2.91 (m, 1H), 2.88–2.76 (m, 1H), 2.16–2.02 (m, 1H), 1.94–1.84 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.2, 146.2, 145.9, 135.7, 133.3, 131.8, 129.2, 128.9, 128.2, 123.3, 121.9, 109.9, 108.4, 107.9, 100.8, 100.6, 51.2, 46.6, 46.1, 32.8, 28.7, 19.0.

HRMS (ESI) $C_{22}H_{22}NO_4$ $[M+H]^+$: calcd 364.1543, found 364.1552.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 17.177 min, t_{minor} = 22.383 min.

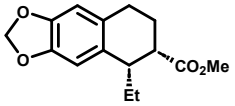
Methyl (5S,6S)-5-ethyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2t). Obtained as white solid by using 2.0 mol% catalyst at 60 °C (26.0 mg, 99% y, 91% ee).

R_f 0.30 (Hex/EtOAc = 80:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -100.9 (c = 0.32, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.50 (d, *J* = 7.1 Hz, 2H), 5.82 (s, 2H), 3.65 (s, 3H), 2.89–2.85



2t

(m, 1H), 2.79–2.62 (m, 3H), 1.99–1.94 (m, 2H), 1.48–1.30 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H).

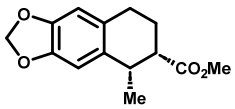
^{13}C NMR (125 MHz, $CDCl_3$)

δ 175.0, 146.0, 145.8, 134.1, 128.1, 108.5, 108.4, 100.7, 51.6, 44.1, 34.9, 28.7, 19.6, 19.2.

HRMS (ESI) $C_{15}H_{19}O_4$ $[M+H]^+$: calcd 263.1278, found 263.1288.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (90/10), 0.5 mL/min, 280 nm, t_{minor} = 9.825 min, t_{major} = 12.151 min.

Methyl (5S,6S)-5-methyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2u). Obtained as white solid by using 4.0 mol% catalyst at 40 °C (24.5 mg, 99% y, 90% ee).



2u

R_f 0.30 (Hex/EtOAc = 80:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -21.0 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.57 (s, 1H), 6.53 (s, 1H), 5.88 (s, 2H), 3.73 (s, 3H), 3.26–3.20 (m, 1H), 2.81–2.66 (m, 3H), 2.04–1.90 (m, 2H), 1.10 (d, J = 7.2 Hz, 3H).

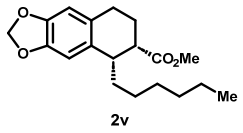
^{13}C NMR (125 MHz, $CDCl_3$)

δ 213.3, 213.3, 159.5, 135.7, 131.7, 130.7, 128.4, 127.0, 126.4, 124.4, 121.6, 111.2, 95.5, 86.4, 38.6, 34.3, 30.6.

HRMS (ESI) $C_{14}H_{17}O_4$ $[M+H]^+$: calcd 249.1121, found 249.1125.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 9.020 min, t_{minor} = 10.373 min.

Methyl (5S,6S)-5-hexyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2v). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (30.2 mg, 95% y, 90% ee).



2v

R_f 0.35 (PE/EtOAc = 80:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -97.0 (c = 0.1, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.55 (d, J = 4.7 Hz, 2H), 5.89 (d, J = 1.5 Hz, 1H), 5.89 (d, J = 1.5 Hz, 1H), 3.72 (s, 3H), 3.05 – 2.98 (m, 1H), 2.86 – 2.69 (m, 3H), 2.08–1.99 (m, 2H), 1.46–1.32 (m, 3H), 1.32–1.17 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.4, 147.3, 146.5, 146.3, 132.9, 128.6, 123.8, 108.2, 105.7, 101.1, 51.3, 31.7, 29.8, 29.6, 29.6, 28.6, 25.2, 22.7, 14.1.

HRMS (ESI) $C_{19}H_{27}O_4$ $[M+H]^+$: calcd 319.1904, found 319.1907.

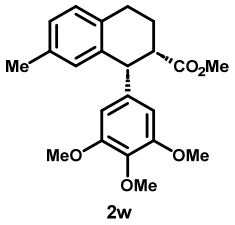
HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 8.204 min, t_{minor} = 9.418 min.

Methyl (1R,2S)-7-methyl-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2w). Obtained as white solid by using 6.0 mol% catalyst at 40 °C (35.2 mg, 95% y, > 99% ee).

R_f 0.50 (Hex/EtOAc = 5:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -83.0 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)



2w

δ 7.07 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.79 (s, 1H), 6.15 (s, 2H), 4.52 (d, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 3.61 (s, 3H), 3.08–2.92 (m, 2H), 2.90–2.78 (m, 1H), 2.11–1.92 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.9, 152.5, 138.2, 137.3, 136.7, 135.5, 132.9, 130.8, 128.6, 127.6, 107.1, 60.8, 56.0, 51.3, 46.6, 45.8, 27.8, 20.9, 19.3.

HRMS (ESI) $C_{22}H_{27}O_5$ $[M+H]^+$: calcd 371.1853, found 371.1856.

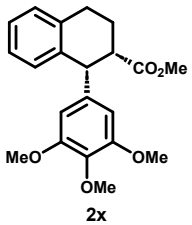
HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 12.393 min, t_{minor} = 17.372 min.

Methyl (1R,2S)-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2x). Obtained as white solid by using 4.0 mol% catalyst at 40 °C (32.0 mg, 90% y, 97% ee).

R_f 0.50 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -158.2 (c = 0.50, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)



2x

δ 7.19–7.15 (m, 2H), 7.10–7.08 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.14 (s, 2H), 4.57 (d, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 6H), 3.61 (s, 3H), 3.09–3.00 (m, 2H), 2.94–2.85 (m, 1H), 2.11–1.96 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.8, 152.5, 138.2, 137.6, 136.7, 136.0, 130.4, 128.8, 126.6, 126.1, 107.1, 60.7, 55.9, 51.3, 46.6, 45.8, 28.2, 19.3.

HRMS (ESI) $C_{21}H_{25}O_5$ $[M+H]^+$: calcd 357.1697, found 357.1701.

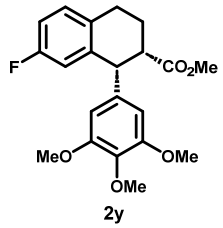
HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 15.141 min, t_{minor} = 18.145 min.

Methyl (1R,2S)-7-fluoro-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2y). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (35.5 mg, 95% y, 97% ee).

R_f 0.45 (Hex/EtOAc = 8:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -254.1 (c = 0.86, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)



2y

δ 7.07 (dd, *J* = 8.6, 5.8 Hz, 1H), 6.87–6.76 (m, 1H), 6.61 (dd, *J* = 9.7, 2.7 Hz, 1H), 6.07 (s, 2H), 4.45 (d, *J* = 5.5 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 6H), 3.53 (s, 3H), 3.01–2.91 (m, 2H), 2.83–2.69 (m, 1H), 2.04–1.88 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.6, 160.1 (d, *J* = 243.9 Hz), 152.7, 139.5 (d, *J* = 6.9 Hz), 137.5, 137.0, 131.6 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 7.8 Hz), 116.4 (d, *J* = 20.7 Hz), 114.1 (d, *J* = 21.4 Hz), 107.1, 60.8, 56.0, 51.4, 46.7 (d, *J* = 1.7 Hz), 45.6, 27.7, 19.5.

^{19}F NMR (471 MHz, $CDCl_3$)

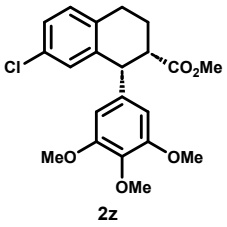
δ -117.1.

HRMS (ESI) $C_{21}H_{24}FO_5$ $[M+H]^+$: calcd 375.1602, found 375.1603.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 13.563 min, t_{minor} = 19.042

min.

Methyl (1R,2S)-7-chloro-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2z). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (37.2 mg, 95% y, 98% ee).



2z

R_f 0.20 (PE/EtOAc = 20:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -88.7 (c = 1.0, $CHCl_3$)

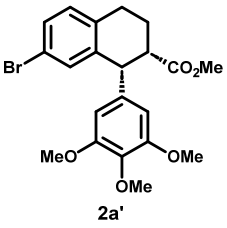
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.15–7.11 (m, 2H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.13 (s, 2H), 4.51 (d, *J* = 5.4 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 6H), 3.60 (s, 3H), 3.08–2.95 (m, 2H), 2.91–2.78 (m, 1H), 2.10–1.96 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.5, 152.6, 139.4, 137.3, 137.0, 134.4, 131.5, 130.2, 130.0, 126.9, 107.1, 60.8, 56.0, 51.4, 46.4, 45.5, 27.7, 19.2.

HRMS (ESI) $C_{21}H_{24}ClO_5$ $[M+H]^+$: calcd 391.1307, found 391.1310 .

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 15.798 min, t_{minor} = 21.278 min.

Methyl (1R,2S)-7-bromo-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2a'). Obtained as white solid by using 6.0 mol% catalyst at 40 °C (41.7 mg, 96% y, 99% ee).



2a'

R_f 0.50 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -36.0 (c = 1.0, $CHCl_3$)

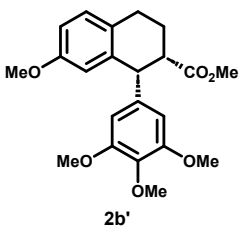
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.28 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.12 (s, 2H), 4.51 (d, *J* = 5.5 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 6H), 3.60 (s, 3H), 3.06–2.94 (m, 2H), 2.87–2.75 (m, 1H), 2.10–1.95 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.4, 152.7, 139.9, 137.3, 137.0, 135.0, 133.0, 130.5, 129.8, 119.6, 107.1, 60.8, 56.0, 51.4, 46.4, 45.5, 27.8, 19.1.

HRMS (ESI) $C_{21}H_{24}BrO_5$ $[M+H]^+$: calcd 435.0802, found 435.0796.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 14.300 min, t_{minor} = 20.413 min.

Methyl (1R,2S)-7-methoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2b'). Obtained as white solid by using 1.0 mol% catalyst at 60 °C (35.5 mg, 91% y, 97% ee).



2b'

R_f 0.30 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -150.1 (c = 1.1, $CHCl_3$)

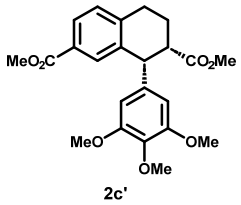
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.09 (d, *J* = 8.5 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.49 (d, *J* = 2.7 Hz, 1H), 6.16 (s, 2H), 4.52 (d, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 3.70 (s, 3H), 3.61 (s, 3H), 3.07–2.94 (m, 2H), 2.86–2.77 (m, 1H), 2.09 – 1.92 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 173.9, 157.7, 152.5, 138.6, 137.9, 136.8, 129.7, 128.2, 114.5, 113.5, 107.1, 60.8, 56.0, 55.2, 51.3, 46.9, 45.8, 27.5, 19.5.

HRMS (ESI) $C_{22}H_{27}O_6$ $[M+H]^+$: calcd 387.1802, found 387.1806.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 16.393 min, t_{minor} = 23.646 min.

Methyl (1R,2S)-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2,7-dicarboxylate (2c'). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (42.0 mg, 97% y, 98% ee).



2c'

R_f 0.25 (PE/EtOAc = 5:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -119.4 (c = 1.1, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.82 (dd, *J* = 7.9 & 1.8 Hz, 1H), 7.69 (s, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.10 (s, 2H), 4.62 (d, *J* = 5.4 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.71 (s, 6H), 3.62 (s, 3H), 3.15–3.01 (m, 2H), 2.97–2.87 (m, 1H), 2.13–1.98 (m, 2H).

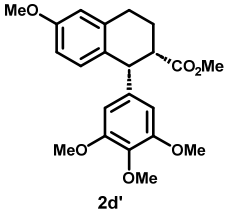
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.5, 167.0, 152.6, 141.5, 138.0, 137.4, 137.0, 131.9, 129.0, 128.2, 127.5, 107.1, 60.8, 56.0, 52.0, 51.4, 46.5, 45.6, 28.5, 19.0.

HRMS (ESI) $C_{23}H_{26}NaO_7$ $[M+Na]^+$: calcd 437.1571, found 437.1572.

HPLC Chiralpak IA-3 column (250*4.6mm/3μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 24.884 min, t_{minor} = 45.628 min.

Methyl (1R,2S)-6-methoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2d'). Obtained as white solid by using 1.0 mol% catalyst at 40 °C (35.9 mg, 99% y, 98% ee).



2d'

R_f 0.35 (Hex/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -218.7 (c = 0.79, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.90 (d, *J* = 8.3 Hz, 1H), 6.68 (d, *J* = 10.3 Hz, 2H), 6.14 (s, 2H), 4.52 (d, *J* = 5.4 Hz, 1H), 3.76 (s, 6H), 3.72 (s, 6H), 3.60 (s, 3H), 3.09–2.95 (m, 2H), 2.93–2.80 (m, 1H), 2.09–1.90 (m, 2H).

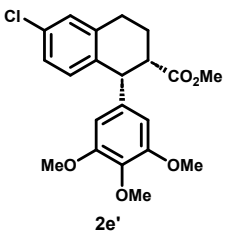
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.9, 158.0, 152.5, 138.4, 137.2, 136.7, 131.4, 129.9, 112.9, 112.8, 107.0, 60.8, 56.0, 55.2, 51.3, 46.0, 45.9, 28.6, 19.2.

HRMS (ESI) $C_{22}H_{27}O_6$ $[M+H]^+$: calcd 387.1802, found 387.1805.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 17.539 min, t_{minor} = 22.739 min.

Methyl (1R,2S)-6-chloro-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2e'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (38.7 mg, 99% y, 97% ee).



2e'

R_f 0.20 (PE/EtOAc = 20:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -122.9 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.18 (d, *J* = 2.2 Hz, 1H), 7.07 (dd, *J* = 8.3 & 2.2 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.12 (s, 2H), 4.53 (d, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 6H), 3.60 (s, 3H), 3.05–2.96 (m, 2H), 2.91–2.81 (m, 1H), 2.09–1.93 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

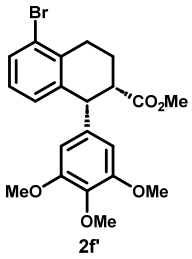
δ 173.5, 152.6, 137.9, 137.6, 136.9, 136.1, 132.1, 131.8, 128.5,

126.4, 107.0, 60.8, 56.0, 51.4, 46.1, 45.7, 28.1, 19.0.

HRMS (ESI) $C_{21}H_{24}ClO_5$ $[M+H]^+$: calcd 391.1307, found 391.1304.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 13.424 min, t_{minor} = 18.843 min.

Methyl (1R,2S)-5-bromo-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2f'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (41.7 mg, 96% y, 98% ee).



2f'

R_f 0.20 (PE/EtOAc = 20:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -150.7 (c = 0.80, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.47 (dd, *J* = 6.2 & 3.0 Hz, 1H), 6.99 (d, *J* = 3.3 Hz, 1H), 6.98 (s, 1H), 6.12 (s, 2H), 4.57 (d, *J* = 5.3 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 6H), 3.62 (s, 3H), 3.18–3.07 (m, 1H), 3.15–3.10 (m, 1H), 3.02–2.98 (m, 1H), 2.76–2.69 (m, 1H), 2.07–2.00 (m, 2H).

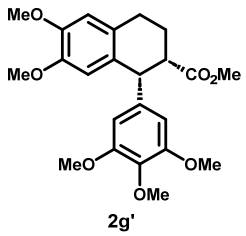
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.5, 152.7, 140.3, 137.5, 137.0, 135.7, 130.9, 129.7, 127.3, 125.5, 107.1, 60.8, 56.1, 51.5, 47.0, 45.2, 29.5, 19.3.

HRMS (ESI) $C_{21}H_{24}BrO_5$ $[M+H]^+$: calcd 435.0802, found 435.0821.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 17.712 min, t_{minor} = 43.482 min.

Methyl (1R,2S)-6,7-dimethoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2g'). Obtained as white solid by using 4.0 mol% catalyst at 40 °C (39.5 mg, 95% y, 97% ee).



2g'

R_f 0.30 (Hex/EtOAc = 2:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = 147.4 (c = 0.6, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.64 (s, 1H), 6.42 (s, 1H), 6.16 (s, 2H), 4.48 (d, *J* = 5.4 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.73 (s, 9H), 3.61 (s, 3H), 3.06–2.99 (m, 1H), 2.96–2.91 (m, 1H), 2.88–2.76 (m, 1H), 2.08–1.90 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.0, 152.5, 147.8, 147.5, 138.0, 136.8, 129.4, 128.1, 112.6, 110.9, 107.0, 60.8, 56.0, 55.9, 55.8, 51.3, 46.3, 46.0, 28.0, 19.2.

HRMS (ESI) $C_{23}H_{29}O_7$ $[M+H]^+$: calcd 417.1908, found 417.1911.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 30.246 min, t_{minor} = 36.850 min.

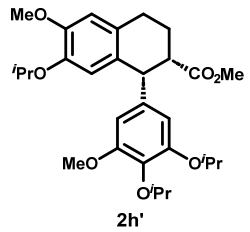
Methyl (1R,2S)-1-(3,4-diisopropoxy-5-methoxyphenyl)-7-isopropoxy-6-methoxy-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2h'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (47.5 mg, 95% y, 97% ee).

R_f 0.60 (PE/EtOAc = 4:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -87.2 (c = 0.2, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.63 (s, 1H), 6.45 (s, 1H), 6.18 (s, 1H), 6.10 (s, 1H), 4.41 (d, *J* = 5.5 Hz, 1H), 4.38–4.27 (m, 3H), 3.84 (s, 3H), 3.70 (s, 3H), 3.56 (s, 3H), 3.04–2.99 (m, 1H), 2.93–2.89 (m, 1H), 2.84–2.75 (m,



2h'

1H), 2.06–1.95 (m, 1H), 1.95–1.89 (m, 1H), 1.26 (t, J = 5.4 Hz, 6H), 1.24 (d, J = 5.3 Hz, 6H), 1.20 (d, J = 2.7 Hz, 3H) 1.19 (d, J = 2.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.1, 153.4, 151.1, 149.3, 145.5, 137.6, 136.6, 129.7, 128.8, 117.8, 112.1, 111.5, 107.3, 75.0, 71.4, 71.3, 56.0, 55.9, 51.3, 46.1, 46.0, 28.1, 22.6, 22.5, 22.2, 22.1, 21.9, 19.4.

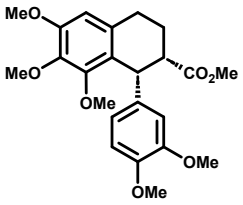
HRMS (ESI) $C_{23}H_{27}O_7$ $[M+H]^+$: calcd 501.2847, found 501.2839.

HPLC Chiralpak IC-3 column (250*4.6mm/3μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 7.953 min, t_{minor} = 10.712 min.

Methyl (1R,2S)-1-(3,4-dimethoxyphenyl)-6,7,8-trimethoxy-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2i'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (39.5 mg, 95% y, 97% ee).

R_f 0.20 (PE/EtOAc = 4:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -125.2 (c = 0.5, $CHCl_3$)



2i'

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.68 (d, J = 8.3 Hz, 1H), 6.60 (s, 1H), 6.48 (s, 1H), 6.44 (dd, J = 8.3 & 2.0 Hz, 1H), 4.73 (d, J = 5.3 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.62 (s, 3H), 3.25 (s, 3H), 2.97–2.89 (m, 2H), 2.86–2.80 (m, 1H), 2.04–1.97 (m, 1H), 1.93–1.90 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.1, 152.3, 151.3, 148.2, 147.5, 140.6, 135.3, 131.4, 124.9, 121.6, 112.7, 110.3, 106.6, 60.6, 60.0, 55.8, 55.8, 55.6, 51.3, 45.5, 40.6, 28.6, 18.8.

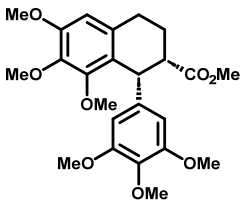
HRMS (ESI) $C_{23}H_{27}O_7$ $[M+H]^+$: calcd 417.1908, found 417.1920.

HPLC Chiralpak IC-3 column (250*4.6mm/3μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{major} = 12.285 min, t_{minor} = 14.525 min.

Methyl (1R,2S)-6,7,8-trimethoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2j'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (5.85 g from 5.94 g of **1j'**, 98% yield, 98% ee; for *ent*-**2j'**: 99% y, 98% ee).

R_f 0.30 (PE/EtOAc = 3:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = 155.20 (c = 1.0, $CHCl_3$); for *ent*-**2k'**: $[\alpha]^{20}_D$ = -150.7 (c = 0.2, $CHCl_3$).



2j'

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.48 (s, 1H), 6.19 (s, 2H), 4.73 (d, J = 5.3 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.78 (s, 3H), 3.73 (s, 6H), 3.63 (s, 3H), 3.30 (s, 3H), 3.04–2.88 (m, 2H), 2.98–2.89 (m, 1H), 2.86–2.79 (m, 1H), 2.06–1.97 (m, 1H), 1.95–1.89 (m, 1H).

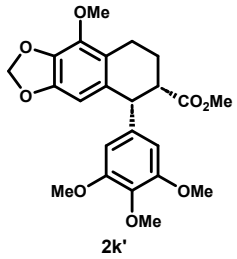
^{13}C NMR (125 MHz, $CDCl_3$)
δ174.0, 152.5, 152.4, 151.3, 140.6, 138.5, 136.8, 131.5, 124.5, 106.8, 106.7, 60.9, 60.6, 60.1, 56.1, 55.8, 51.3, 45.6, 41.1, 28.7, 19.0.

HRMS (ESI) $C_{24}H_{30}O_8$ $[M+H]^+$: calcd 447.201, found 447.2017.

HPLC Chiralpak IC-3 column (250*4.6mm/3μm): *n*-hexane/*i*-PrOH

(80/20), 0.5 mL/min, 210 nm, t_{major} = 16.537 min, t_{minor} = 24.523 min; for *ent*-**2j'**: t_{minor} = 16.860 min, t_{major} = 23.246 min.

Methyl (5R,6S)-9-methoxy-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2k'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (1.88 g from 2.0 g of **1k'**, 94% y, 99% ee).



2k'

R_f 0.38 (PE/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -166.3 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.17 (s, 3H), 5.85 (s, 2H), 4.41 (d, *J* = 5.3 Hz, 1H), 4.04 (s, 3H), 3.79 (s, 3H), 3.74 (s, 6H), 3.59 (s, 3H), 3.02–2.94 (m, 2H), 2.56–2.48 (m, 1H), 2.01–1.88 (m, 2H).

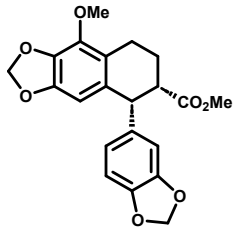
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.9, 152.5, 147.5, 140.4, 137.8, 136.8, 134.4, 131.4, 121.6, 107.0, 103.7, 100.6, 60.7, 59.3, 56.0, 51.3, 46.7, 45.5, 22.6, 18.6.

HRMS (ESI) $C_{23}H_{27}O_8$ $[M+H]^+$: calcd 431.1700, found 431.1721.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 1.0 mL/min, 230 nm, t_{minor} = 18.883 min, t_{major} = 22.289 min.

Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2l'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (1.14 g from 1.2 g of **1l'**, 95% y, 94% ee).



2l'

R_f 0.70 (PE/EtOAc = 1:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -196.2 (c = 0.34, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.58 (dd, *J* = 7.9 & 1.9 Hz, 1H), 6.38 (d, *J* = 8.1 Hz, 1H), 6.33 (s, 1H), 6.06 (s, 1H), 5.81 (s, 2H), 5.77 (d, *J* = 11.0 Hz, 2H), 4.33 (d, *J* = 5.4 Hz, 1H), 3.97 (s, 3H), 3.53 (s, 3H), 2.97–2.84 (m, 2H), 2.50–2.37 (m, 1H), 1.93–1.77 (m, 2H).

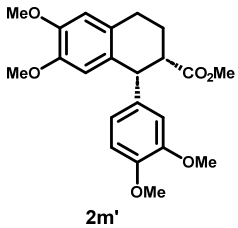
^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.9, 147.5, 147.2, 146.2, 140.4, 136.1, 134.3, 131.6, 122.5, 121.6, 110.0, 107.5, 103.6, 100.8, 100.5, 59.2, 51.2, 46.1, 45.4, 22.6, 18.3.

HRMS (ESI) $C_{21}H_{21}O_7$ $[M+H]^+$: calcd 385.1282, found 385.1290.

HPLC Chiralpak OD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/10), 0.5 mL/min, 230 nm, t_{major} = 12.605 min, t_{minor} = 13.978 min.

Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2m'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (37.1 mg, 96% y, 95% ee).



2m'

R_f 0.30 (PE/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -136.2 (c = 0.22, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.70 (d, *J* = 8.3 Hz, 1H), 6.63 (s, 1H), 6.53 (d, *J* = 2.1 Hz, 1H), 6.43 (dd, *J* = 8.3 & 2.1 Hz, 1H), 6.40 (s, 1H), 4.48 (d, *J* = 5.4 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.59 (s, 3H), 3.07–2.98 (m, 1H), 2.98–2.87 (m, 1H), 2.86–2.74 (m, 1H),

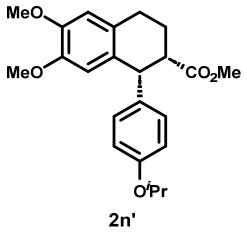
2.0 –1.95 (m, 1H), 1.95–1.89 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.0, 148.2, 147.7, 147.7, 147.4, 135.0, 129.7, 128.1, 121.9, 112.9, 112.5, 110.8, 110.5, 55.8, 55.7, 55.7, 55.7, 51.3, 45.9, 45.7, 28.0, 19.1.

HRMS (ESI) $C_{22}H_{27}O_6$ $[M+H]^+$: calcd 387.1802, found 387.1815

SFC OJ-3 column (250*4.6mm/5μm): MeOH/CO_2 (10/90), 1.0 mL/min, 254 nm, t_{major} = 2.138 min, t_{minor} = 1.238 min.

Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2n'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (36.5 mg, 95% y, 97% ee).



2n'

R_f 0.70 (PE/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -174.5 (c = 0.51, $CHCl_3$)

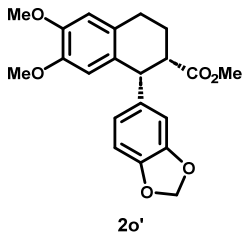
^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.83 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.63 (s, 1H), 6.39 (s, 1H), 4.51–4.41 (m, 2H), 3.87 (s, 3H), 3.71 (s, 3H), 3.58 (s, 3H), 3.05–2.97 (m, 1H), 2.97–2.88 (m, 1H), 2.86–2.75 (m, 1H), 2.06–1.92 (m, 2H), 1.94–1.87 (m, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.0, 147.8, 147.5, 147.3, 146.2, 136.4, 129.6, 128.1, 122.6, 112.5, 110.9, 110.0, 107.6, 100.8, 55.8, 55.8, 51.3, 45.8, 45.8, 28.0, 18.9.

HRMS (ESI) $C_{23}H_{29}O_5$ $[M+H]^+$: calcd 385.2010, found 385.2030.

HPLC Chiralpak AD-H column (250*4.6mm/5μm): *n*-hexane/*i*-PrOH (80/20), 0.5 mL/min, 210 nm, t_{minor} = 10.559 min, t_{minor} = 12.946 min.

Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate (2o'). Obtained as white solid by using 2.0 mol% catalyst at 40 °C (35.2 mg, 96% y, 95% ee).



2o'

R_f 0.60 (PE/EtOAc = 3:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -110.3 (c = 0.25, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.65 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 6.45 (dd, *J* = 8.1 & 1.8 Hz, 1H), 6.39 (d, *J* = 1.7 Hz, 1H), 6.38 (s, 1H), 5.89 (s, 2H), 4.46 (d, *J* = 5.4 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 3.61 (s, 3H), 3.04 – 2.96 (m, 1H), 2.96–2.88 (m, 1H), 2.85–2.76 (m, 1H), 2.05–1.95 (m, 1H), 1.95–1.86 (m, 1H).

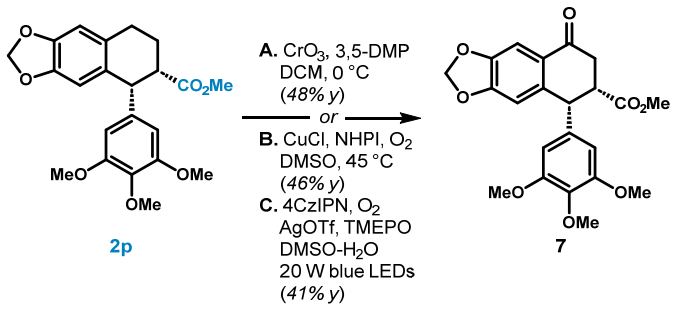
^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.1, 156.6, 147.7, 147.4, 134.2, 130.4, 130.0, 128.1, 115.0, 112.6, 110.8, 69.6, 55.8, 55.7, 51.2, 45.9, 45.3, 28.0, 22.1, 22.0, 18.9.

HRMS (ESI) $C_{21}H_{23}O_6$ $[M+H]^+$: calcd 371.1489, found 371.1472.

SFC OJ-3 column (250*4.6mm/5μm): MeOH/CO_2 (10/90), 1.0 mL/min, 254 nm, t_{minor} = 1.668 min, t_{minor} = 3.455 min.

3.3 Syntheses of Podophyllotoxins and Related Cyclolignans (from 2p, 2k' and 2l')

7: Methyl (5R,6S)-8-oxo-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate



Method A (CrO_3-DMP)[10]: To a solution of CrO_3 (784 mg, 8.0 mmol, 8.0 equiv.) in DCM (10 mL) was added 3,5-dimethylpyrazole (3,5-DMP; 800 mg, 8.0 mmol, 8.0 equiv.) at 0 °C. The reaction mixture was stirred at 0 °C for 20 minutes before a solution of **2p** (800 mg, 2.0 mmol, 1.0 equiv.) in DCM (10 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 50 min and then quenched with sat. aq. $NaHSO_3$ (50 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography to give **7** as white solid (397 mg, 48% y, 73% brsm).

Method B (CuCl-NHPI)[11]: To a solution of **2p** (20 mg, 0.05 mmol, 1.0 equiv.) in dry DMSO (0.5 mL) was added *N*-hydroxyphthalimide (NHPI, 1.6 mg, 0.01 mmol, 0.2 equiv.) and CuCl (1.0 mg, 0.01 mmol, 0.2 equiv.) under O_2 atmosphere (balloon) at RT. The reaction mixture was stirred at 45 ºC for 30 h, then quenched with sat. $NaHSO_3$, diluted with H_2O (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phase was washed with brine (5 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography as white solid (9.6 mg, 46% y, 83% y brsm).

Method C (photoredox)[12]: DMSO (0.25 mL) and H_2O (0.72 μL, 0.8 equiv.) were added to a flask containing **2p** (20 mg, 0.05 mmol, 1.0 equiv.), 4CzIPN (0.8 mg, 2 mol%) and AgOTf (19.3 mg, 0.075 mmol, 1.5 equiv.). The resulting mixture was stirred at RT for 0.5 h, and subjected to three cycles of evacuation and refilling with oxygen (1 atm). Then, TEMPO (1.6 mg, 0.01 mmol, 0.2 equiv.) was added, and the reaction was vigorously stirred for 30 h under irradiation by 20 W blue LEDs cooled by a fan. The reaction mixture was then quenched with sat. $NaHSO_3$ (0.2 mL), diluted with H_2O (2.5 mL) and extracted with EtOAc (3 × 3 mL). The combined organic phase was washed with brine (2 mL), dried over $MgSO_4$, filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography to give **7** as white solid (8.7 mg, 41% y, 49% brsm).

R_f 0.32 (PE/EtOAc = 4:1, UV/$KMnO_4$)

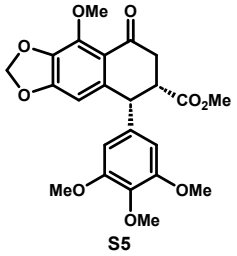
Opt. Rot. $[\alpha]^{20}_D$ = -228.0 (c = 0.27, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.54 (s, 1H), 6.61 (s, 1H), 6.16 (s, 2H), 6.04 (d, *J* = 1.3 Hz, 1H), 6.03 (d, *J* = 1.3 Hz, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 3.68 (s, 3H), 3.53–3.51 (m, 1H), 2.91 (dd, *J* = 18.0 & 13.6 Hz, 1H), 2.74 (dd, *J* = 18.0 & 4.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 194.7, 171.6, 152.9, 152.7, 147.7, 140.7, 137.3, 133.4, 127.2, 108.5, 106.2, 105.6, 101.9, 60.6, 55.9, 51.7, 46.9, 44.9, 34.9.

HRMS (ESI) $C_{22}H_{22}O_8Na$ $[M+Na]^+$: calcd 437.1211, found 437.1243.

S5: Methyl (5R,6S)-9-methoxy-8-oxo-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d]-[1,3]dioxole-6-carboxylate. Obtained as white solid by method A (110 mg from 300 mg of **2k'**, 35% y, 47% brsm).



S5

R_f 0.30 (PE/EtOAc = 3:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -299.3 (c = 1.5, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

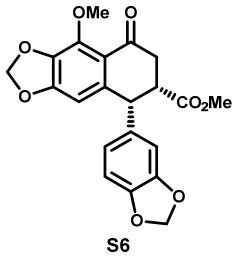
δ 6.34 (s, 1H), 6.10 (s, 2H), 5.96 (d, *J* = 1.4 Hz, 1H), 5.93 (d, *J* = 1.3 Hz, 1H), 4.57 (d, *J* = 4.6 Hz, 1H), 4.03 (s, 3H), 3.73 (s, 3H), 3.66 (s, 6H), 3.61 (s, 3H), 3.39 (dt, *J* = 13.4 & 4.7 Hz, 1H), 2.80 (dd, *J* = 18.4 & 13.3 Hz, 1H), 2.65 (dd, *J* = 18.4 & 3.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 194.6, 171.8, 153.3, 153.1, 144.2, 142.1, 137.3, 137.1, 133.5, 120.8, 106.2, 103.8, 101.9, 60.8, 60.7, 56.1, 51.9, 48.0, 44.5, 36.7.

HRMS (ESI) $C_{23}H_{25}O_9$ $[M+H]^+$: calcd 445.1499, found 445.1497.

S6: Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-8-oxo-5,6,7,8-tetrahydronaphtho[2,3-d]-[1,3]dioxole-6-carboxylate**.** Obtained as white solid by method A (70 mg from 200 mg of **2l'**, 34% y, 55% brsm).



S6

R_f 0.35 (Hex/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -183.4 (c = 0.35, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

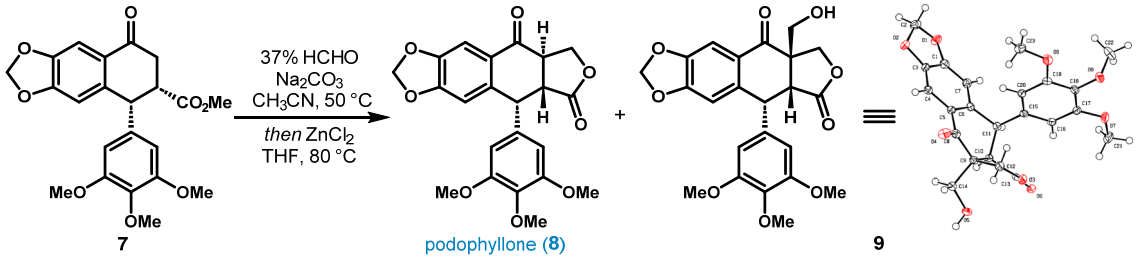
δ 6.67 (d, *J* = 8.5 Hz, 1H), 6.43 (m, 2H), 6.36 (s, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 5.97 (d, *J* = 1.4 Hz, 1H), 5.91 (q, *J* = 1.5 Hz, 2H), 4.62 (d, *J* = 4.6 Hz, 1H), 4.09 (s, 4H), 3.68 (s, 3H), 3.44 (dt, *J* = 13.6 & 4.6 Hz, 1H), 2.85 (dd, *J* = 18.2 & 13.6 Hz, 1H), 2.68 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 194.4, 171.8, 153.2, 147.8, 146.9, 144.3, 142.3, 137.1, 131.8, 122.2, 120.6, 109.2, 108.2, 103.8, 101.8, 101.1, 60.6, 51.8, 47.4, 44.3, 36.4.

HRMS (ESI) $C_{21}H_{19}O_8$ $[M+H]^+$: calcd 399.1080, found 399.1099.

8: Podophyllone



7

podophyllone (**8**)
50% y, 2 steps

9
20% y, 2 steps

By modifying the procedure by Brasili and co-workers:[13] To a solution of **7** (290.8 mg, 0.7 mmol, 1.0 equiv.) and Na_2CO_3 (7.4 mg, 0.07 mmol, 0.1 equiv.) in acetonitrile (12.5 mL) was added 37% aq. formaldehyde solution (1.46 mL, 24.0 equiv.). The mixture was stirred at 40°C overnight. The reaction was diluted with water (20 mL) and then extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was used directly for the next step.

By modifying the procedure reported by Zhang and co-workers:[14] To the residue and molecular severs (4 Å, 840 mg) were sequentially added anhydrous THF (5 mL) and a solution of anhydrous $ZnCl_2$ (285.6 mg, 2.1 mmol, 3.0 equiv.) in THF (5 mL). The resulting mixture was heated at reflux for 12 h. The reaction mixture was then cooled to RT and quenched with saturated $NaHCO_3$ (5 mL). The resulting mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash chromatography on silica gel to afford podophyllone **8** as white solid (145.4 mg, 50% yield over 2 steps) and double aldol product **9** as white solid (61.9 mg, 20% y over 2 steps).

Characterization data of **8**:

R_f 0.35 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -95.2 (c = 2.4, $CHCl_3$) [Lit.[15]: $[\alpha]^{20}_D$ = -106.98 (c = 1.08, $CHCl_3$)].

^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.55 (s, 1H), 6.70 (s, 1H), 6.38 (s, 2H), 6.10 (d, *J* = 1.2 Hz, 1H), 6.08 (d, *J* = 1.2 Hz, 1H), 4.84 (d, *J* = 4.3 Hz, 1H), 4.56 (dd, *J* = 9.3 & 7.6 Hz, 1H), 4.35 (dd, *J* = 10.5 & 9.3 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 6H), 3.56–3.48 (m, 1H), 3.28 (dd, *J* = 15.5 & 4.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 192.3, 173.0, 153.1, 153.0, 148.0, 141.4, 137.6, 132.0, 128.1, 109.6, 107.6, 106.0, 102.3, 66.9, 60.7, 56.2, 46.5, 44.6, 43.4.

HRMS (ESI) $C_{22}H_{21}O_8$ $[M+H]^+$: calcd 413.1237, found 413.1225.

Characterization data of **9**:

R_f 0.35 (PE/EtOAc = 1:1, UV/$KMnO_4$).

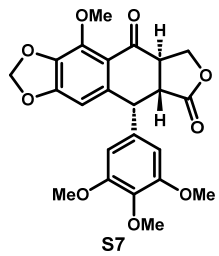
Opt. Rot. $[\alpha]^{20}_D$ = -230.0 (c = 0.32, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.41 (s, 1H), 6.69 (s, 1H), 6.27 (s, 2H), 6.08 (d, *J* = 1.2 Hz, 1H), 6.07 (d, *J* = 1.2 Hz, 1H), 4.62 (d, *J* = 6.4 Hz, 1H), 4.30 (d, *J* = 9.3 Hz, 1H), 3.85 (d, *J* = 11.0 Hz, 2H), 3.83 (d, *J* = 9.6 Hz, 2H), 3.80 (s, 3H), 3.72 (s, 6H), 3.70 (d, *J* = 10.7 Hz, 1H), 3.41 (d, *J* = 6.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 197.3, 175.3, 153.7, 153.2, 148.4, 138.9, 137.5, 133.8, 128.4, 108.5, 106.3, 105.9, 102.3, 71.2, 67.1, 60.8, 56.1, 53.4, 48.1, 43.9.

HRMS (ESI) $C_{23}H_{23}O_9$ $[M+H]^+$: calcd 443.1342, found 443.1354.

S7: (5aR,8aR,9R)-4-Methoxy-9-(3,4,5-trimethoxyphenyl)-5a,6,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxole-5,8-dione. Obtained as white solid by using the same procedure for podophyllone **8**. (320 mg from 400 mg of **S5**, 80% y over 2 steps; no double aldol product was observed in this case).



S7

R_f 0.31 (PE /EtOAc = 3:1, UV/$KMnO_4$).

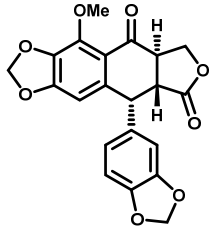
Opt. Rot. $[\alpha]^{20}_D$ = -46.8 (c = 0.22, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)
δ 6.45 (s, 1H), 6.39 (s, 2H), 6.06 (d, *J* = 1.3 Hz, 1H), 6.04 (d, *J* = 1.3 Hz, 1H), 4.81 (d, *J* = 4.6 Hz, 1H), 4.48 (dd, *J* = 9.4 & 7.5 Hz, 1H), 4.39 (dd, *J* = 10.3 & 9.3 Hz, 1H), 4.11 (s, 3H), 3.82 (s, 3H), 3.76 (s, 6H), 3.59–3.48 (m, 1H), 3.23 (dd, *J* = 15.6 & 4.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 192.2, 173.1, 153.6, 153.0, 144.6, 142.6, 137.7, 137.4, 132.7, 121.1, 107.8, 105.2, 102.3, 67.1, 60.8, 60.7, 56.4, 46.5, 45.4, 44.6.

HRMS (ESI) $C_{23}H_{23}O_9$ $[M+H]^+$: calcd 443.1342, found 443.1331.

S8: (5aR,8aR,9R)-9-(Benzo[d][1,3]dioxol-5-yl)-4-methoxy-5a,6,8a,9-tetrahydrofuro[3',4':6,7]naphtho [2,3-d][1,3]dioxole-5,8-dione. Obtained as white solid by using the same procedure for podophyllone **8**. (70 mg from 120 mg of **S6**, 63% y over 2 steps).



S8

R_f 0.38 (PE/EtOAc = 3:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -207.8 (c = 0.18, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

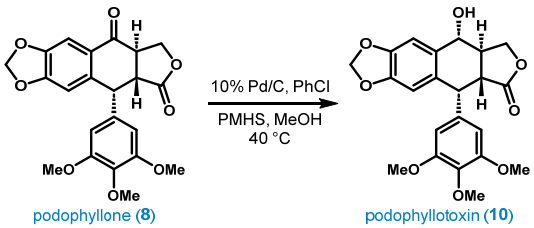
δ 6.65 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 1.8 Hz, 1H), 6.55 (dd, *J* = 8.0 &1.8 Hz, 1H), 6.33 (s, 1H), 5.97 (s, 2H), 5.87 (d, *J* = 1.4 Hz, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 4.71 (d, *J* = 4.6 Hz, 1H), 4.40 (dd, *J* = 9.3 & 7.4 Hz, 1H), 4.34–4.30 (m, 1H), 4.03 (s, 3H), 3.53–3.41 (m, 1H), 3.15 (dd, *J* = 15.6 & 4.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 192.0, 172.8, 153.5, 147.7, 147.1, 144.5, 142.9, 137.3, 130.8, 123.7, 121.1, 110.6, 108.0, 105.0, 102.2, 101.2, 67.0, 60.6, 46.3, 44.8, 44.2.

HRMS (ESI) $C_{21}H_{17}O_8$ $[M+H]^+$: calcd 397.0923, found 397.0928.

10: Podophyllotoxin



podophyllone (**8**) podophyllotoxin (**10**)

By modifying the procedure reported by Verho, Bäckvall, Adolfsson and co-workers:[16] To a solution of podophyllone **8** (100 mg, 0.24 mmol, 1.0 equiv.) in MeOH (5 mL) was added 10% Pd/C (10 mg), PhCl (4.6 μL, 0.046 mmol, 0.19 equiv.), and PMHS (82.8 mg, 0.72 mmol, 3.0 equiv.) at room temperature under N_2 atmosphrere. The reaction mixture was stirred at 40 °C for 2 h before it was filtered through a pad of Celite and the filtration was concentrated under vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product as white solid (93 mg, 93% y).

R_f 0.20 (DCM/Acetone = 10:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -105 (c = 1.0, $CHCl_3$) [Lit.[15]: $[\alpha]^{20}_D$ = -115 (c = 1.0, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

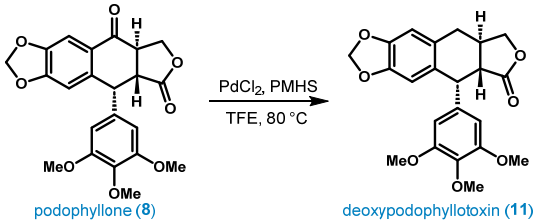
δ 7.11 (s, 1H), 6.51 (s, 1H), 6.37 (s, 2H), 5.99 (d, *J* = 1.4 Hz, 1H), 5.97 (d, *J* = 1.3 Hz, 1H), 4.77 (d, *J* = 9.3 Hz, 1H), 4.63 – 4.57 (m, 2H), 4.08 (t, *J* = 9.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 6H), 2.84 (dd, *J* = 14.2 & 4.7 Hz, 1H), 2.81–2.72 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.3, 152.6, 147.8, 147.7, 137.3, 135.4, 133.1, 131.2, 109.8, 108.4, 106.2, 101.5, 72.9, 71.3, 60.8, 56.3, 45.3, 44.1, 40.8.

HRMS (ESI) $C_{22}H_{22}O_8Na$ $[M+Na]^+$: calcd 437.1212, found 437.1227.

11: Deoxypodophyllotoxin



By modifying the procedure reported by Yang, Xu and co-workers:[17] To a solution of podophyllone **8** (50 mg, 0.12 mmol, 1.0 equiv.) in CF_3CH_2OH (TFE, 1.2 mL) was added $PdCl_2$ (4.2 mg, 0.024 mmol, 0.2 eq) and PMHS (41.4 mg, 0.36 mmol, 3.0 equiv.) at RT. The reaction mixture was stirred at 80 °C for 2 h and then concentrated. The residue was purified by flash chromatography on silica gel to afford deoxypodophyllotoxin **11** as white solid (36.8 mg, 77% y).

R_f 0.38 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -99.0 (c = 1.5, $CHCl_3$) [Lit.[15]: $[\alpha]^{20}_D$ = -94.03 (c = 1.34, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

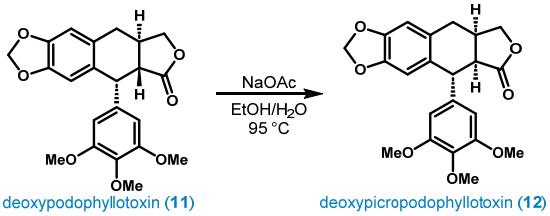
δ 6.67 (s, 1H), 6.52 (s, 1H), 6.35 (s, 2H), 5.95 (d, *J* = 1.5 Hz, 1H), 5.93 (d, *J* = 1.3 Hz, 1H), 4.62–4.59 (m, 1H), 4.48–4.43 (m, 1H), 3.95–3.89 (m, 1H), 3.81 (s, 3H), 3.75 (s, 6H), 3.13–3.03 (m, 1H), 2.81–2.69 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.9, 152.4, 147.0, 146.7, 137.0, 136.2, 130.6, 128.2, 110.4, 108.4, 108.2, 101.1, 72.0, 60.7, 56.1, 47.4, 43.7, 33.0, 32.7.

HRMS (ESI) $C_{22}H_{22}O_7$ $[M+H]^+$: calcd 399.1444, found 399.1412.

12: Deoxypicropodophyllotoxin



By modifying the procedure reported by Xu and coworkers:[18] To a solution of **11** (100 mg, 0.25 mmol, 1.0 equiv.) in EtOH (1.2 mL) was added 10% aq. NaOAc (1 mL) RT. The reaction mixture was stirred at 95 °C for 12 h. Then, H_2O (2 mL) was added and extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (3 mL) and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford deoxypicropodophyllotoxin **12** as white solid (86.1 mg, 86% y).

R_f 0.30 (PE/Acetone = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +15.8 (c = 1.68, $CHCl_3$) [Lit.[15] $[\alpha]^{18}_D$ = +40.39 (c = 0.53, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

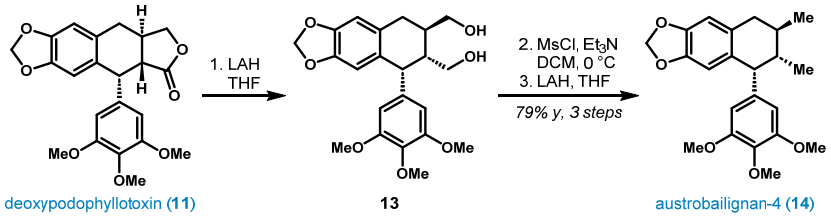
δ 6.66 (s, 1H), 6.58 (s, 1H), 6.33 (s, 2H), 5.94 (d, *J* = 1.5 Hz, 1H), 5.91 (d, *J* = 1.5 Hz, 1H), 4.44 (dd, *J* = 9.2 & 7.4 Hz, 1H), 4.37 (d, *J* = 3.0 Hz, 1H), 3.97 (dd, *J* = 9.2 & 3.2 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 6H), 3.33 (dd, *J* = 9.6 & 3.1 Hz, 1H), 3.06–2.96 (m, 1H), 2.86 (dd, *J* = 15.4 & 6.4 Hz, 1H), 2.49 (dd, *J* = 15.4 & 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 178.4, 153.3, 146.8, 146.7, 138.2, 130.4, 128.3, 109.8, 108.8, 104.9, 101.0, 72.7, 60.8, 56.2, 46.3, 45.3, 33.0, 32.0.

HRMS (ESI) $C_{22}H_{22}O_7Na$ $[M+Na]^+$: calcd 421.1258, found 421.1265.

14: Austrobailignan



To a stirred solution of **11** (17.5 mg, 0.044 mmol, 1.0 equiv.) in THF (1 mL) was added $LiAlH_4$ (3.3 mg, 0.088 mmol, 2.0 equiv.) at 0 °C. The reaction mixture was then stirred at room temperature for 4 h and quenched with H_2O (3.3 μL) at 0 °C followed by 15% NaOH (3.3 μL), and H_2O (10 μL). Thereafter, anhydrous $MgSO_4$ was added. The mixture was stirred at RT for 0.5 h, and then filtrated over Celite, and the filtrate was concentrated to give the crude diol which used directly for the next step.

To the solution of crude diol in DCM (1 mL) was added dropwise with stirring MsCl (13.2 mg, 0.176 mmol, 4.0 equiv.) followed by Et_3N (18 mg, 0.176 mmol, 4.0 equiv.) at 0 °C. The reaction mixture was allowed to warm gradually to ambient temperature, and quenched by addition of cold 2 N aq. HCl (1 mL). The resulting suspension was extracted with DCM (1 mL × 3). The combined organic layers were washed sequentially with sat. $NaHCO_3$ (2 mL), brine (1 mL), dried over $MgSO_4$ and filtered. The filtrate was concentrated in *vacuo* to give the crude dimesylate which used directly in the next step.

The crude dimesylate in THF (0.5 mL) was added to a suspension of $LiAlH_4$ (8.4 mg, 0.22 mmol, 5.0 equiv.) in dry THF (1 mL) at 0 °C. After the addition process had been completed, the reaction mixture was allowed to warm gradually to ambient temperature and stirred overnight. The reaction was cautiously quenched by successive addition of H_2O (8.4 μL), aqueous 15% NaOH solution (8.4 μL), and H_2O (25 μL). Thereafter, anhydrous $MgSO_4$ was added. The mixture was stirred at RT for 0.5 h, and then filtrated over Celite. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography to give the desired product **14** as white solid (13 mg, 79% y over 3 steps).

R_f 0.60 (toluene/EtOAc = 5:1, UV/$KMnO_4$).

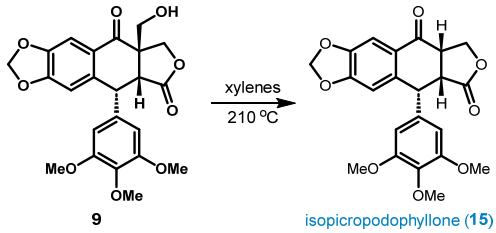
Opt. Rot. $[\alpha]^{20}_D$ = -111.6 (c = 0.58, $CHCl_3$) [Lit.[19]: $[\alpha]^{20}_D$ = -124.0 (c = 2.4, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.58 (s, 1H), 6.39 (s, 1H), 6.20 (s, 2H), 5.86 (d, *J* = 1.5 Hz, 1H), 5.85 (d, *J* = 1.5 Hz, 1H), 3.89 (d, *J* = 5.1 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 6H), 2.90 (dd, *J* = 16.9 & 5.2 Hz, 1H), 2.43 (dd, *J* = 16.9 & 10.0 Hz, 1H), 1.91–1.75 (m, 2H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 152.3, 145.9, 145.7, 139.2, 132.4, 129.6, 109.6, 107.8, 107.8, 100.5, 60.8, 56.1, 51.3, 39.2, 38.3, 29.0, 19.5, 17.2.

HRMS (ESI) $C_{22}H_{27}O_5$ $[M+H]^+$: calcd 371.1853, found 371.1845.

15: Isopicropodophyllone



By modifying the procedure reported by Meyers and coworkers:[20] A degassed solution of **9** (60 mg, 0.14 mmol) in anhydrous xylene (3 mL) was heated at 210 °C for 6 h. Thereafter, the reaction mixture was concentrated, purified by flash chromatography on silica gel to afford isopicropodophyllone **15** (40.4 mg, 70% y).

R_f 0.30 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -270.4 (c = 2.2, $CHCl_3$) [Lit.[21]: $[\alpha]_D$ = -288 (c = 1.106, $CHCl_3$)].

^{1}H NMR (600 MHz, $CDCl_3$)

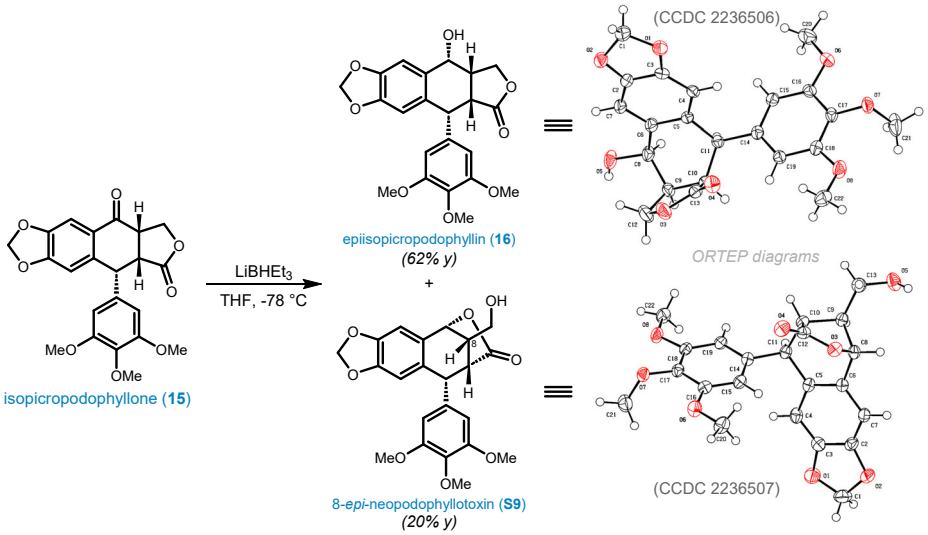
δ 7.43 (s, 1H), 6.68 (s, 1H), 6.28 (s, 2H), 6.08 (d, *J* = 1.2 Hz, 1H), 6.06 (d, *J* = 1.2 Hz, 1H), 4.57 (d, *J* = 5.8 Hz, 1H), 4.54–4.51 (m, 1H), 3.86–3.83 (m, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 3.64–3.53 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 222.2, 194.2, 175.3, 153.4, 153.3, 148.3, 138.9, 137.6, 133.8, 128.7, 108.5, 106.4, 106.1, 102.2, 69.4, 60.9, 56.1, 45.0, 44.6, 44.2.

HRMS (ESI) $C_{22}H_{20}O_8Na$ $[M+Na]^+$: calcd 435.1056, found 435.1053.

16: Epiisopicropodophyllin (first successful synthesis)[22]



To a solution of **15** (20 mg, 0.049 mmol, 1.0 equiv.) in THF (1.0 mL) cooled by dry ice-acetone bath was added Super-Hydride® (0.6 mL, 0.06 mmol, 1.2 equiv., 0.1 M in THF) dropwise via syringe to at -78 °C. The reaction mixture was stirred at -78 °C for 30 min before it was cautiously quenched with sat. aq. NH_4Cl (2 mL) and extracted with cold ethyl acetate (2 mL × 3). The combined organic phase was washed with cold brine, dried over anhydrous Na_2SO_4 under N_2, filtered and concentrated under vacuum (ice bath) under N_2. The residue was purified by flash chromatographed on silica gel to afford **16** (12.6 mg, 62% y) and **S9** (4.1 mg, 20% y) as white solids.

Characterization data of epiisopicropodophyllin **16**:

R_f 0.20 (Hex/EtOAc = 1:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +6.7 (c = 0.30, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.09 (s, 1H), 6.89 (s, 2H), 6.55 (s, 1H), 5.93 (d, *J* = 1.5 Hz, 1H), 5.92 (d, *J* = 1.5 Hz, 1H), 4.98 (d, *J* = 6.9 Hz, 1H), 4.35 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.24 (dd, *J* = 9.8 & 8.1 Hz, 1H), 4.08 (d, *J* = 4.3 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 6H), 3.49 (dd, *J* = 10.1 & 4.3 Hz, 1H), 3.47 – 3.39 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 176.6, 152.9, 147.0, 146.9, 137.2, 132.8, 130.9, 130.7, 107.9, 107.6, 105.1, 101.0, 67.0, 66.4, 60.9, 56.2, 44.6, 44.1, 40.6.

HRMS (ESI) $C_{22}H_{22}O_8Na$ $[M+Na]^+$: calcd 437.1207, found 437.1230.

Characterization data of 8-*epi*-neopodophyllotoxin **S9**:

R_f 0.25 (PE/Acetone = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -10.9 (c = 0.33, $CHCl_3$).

^{1}H NMR (600 MHz, DMSO-d_6)

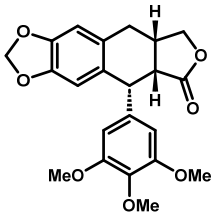
δ 7.04 (s, 1H), 6.42 (s, 1H), 6.34 (s, 2H), 6.02 (d, *J* = 1.1 Hz, 1H), 5.99 (d, *J* = 1.1 Hz, 1H), 5.26 (s, 1H), 5.07 (t, *J* = 5.2 Hz, 1H), 4.58 (d, *J* = 4.7 Hz, 1H), 3.67 (s, 6H), 3.66 (s, 3H), 3.54 – 3.48 (m, 1H), 3.48 – 3.43 (m, 1H), 2.85 – 2.81 (m, 1H), 2.57 (dd, *J* = 8.2, 6.6 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-d_6)

δ 176.0, 152.9, 148.3, 146.1, 138.4, 136.9, 131.8, 130.9, 110.2, 108.0, 107.1, 101.7, 79.1, 60.4, 60.4, 56.3, 50.8, 48.3, 48.1.

HRMS (ESI) $C_{22}H_{23}O_8$ $[M+H]^+$: calcd 415.1387, found 415.1382.

17: Deoxyisopicropodophyllin. Obtained as white solid from **15** by using the same procedure as for deoxypodophyllotoxin **11** (16.4 mg from 20 mg of **15**, 84% y).



deoxyisopicropodophyllin (**17**)

R_f 0.6 (Hex/EtOAc = 1:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -103.3 (c = 0.43, $CHCl_3$) [Lit.[23]: $[\alpha]^{20}_D$ = -114 (c = 0.51, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.74 (s, 1H), 6.64 (s, 1H), 6.50 (s, 2H), 5.95 (s, 2H), 4.43–4.37 (m, 2H), 3.83 (s, 3H), 3.76 (s, 6H), 3.49 (t, *J* = 8.2 Hz, 1H), 3.19–3.11 (m, 2H), 2.97 (dd, *J* = 15.6 & 8.1 Hz, 1H), 2.70 (dd, *J* = 15.6 & 5.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 177.8, 153.1, 146.9, 146.7, 137.0, 133.8, 132.0, 128.9, 108.8, 108.6, 106.4, 101.1, 74.1, 60.9, 56.1, 46.4, 45.5, 34.8, 31.0.

HRMS (ESI) $C_{22}H_{22}O_7Na$ $[M+Na]^+$: calcd 421.1263, found 421.1255.

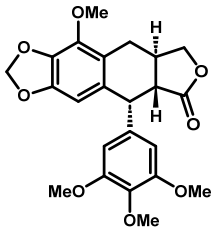
18: β-Peltatin-A-methylether. Obtained as white solid from **19** by using the same procedure as for picrobursenin **22** (21 mg from 30 mg of **19**; white solid; 72% y).

R_f 0.6 (Hex/EtOAc = 1:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -103.3 (c = 0.43, $CHCl_3$) [Lit.[24]: $[\alpha]^{21}_D$ = −120.6 (c = 1.02, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.36 (s, 2H), 6.28 (s, 1H), 5.92 (d, *J* = 1.5 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 4.58 (d, *J* = 4.2 Hz, 1H), 4.48 (dd, *J* = 8.5 & 6.4



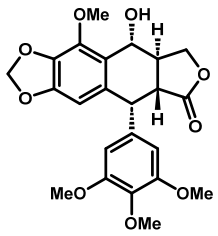
β-peltatin-A-methylether (**18**)

Hz, 1H), 4.07 (s, 3H), 3.94 (t, *J* = 9.4 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 6H), 3.18 (dd, *J* = 16.6 & 4.9 Hz, 1H), 2.72–2.59 (m, 2H), 2.45 (dd, *J* = 16.6 & 10.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 175.2, 152.6, 148.4, 140.8, 137.2, 136.3, 134.9, 131.7, 121.0, 108.4, 104.5, 101.1, 72.5, 60.9, 59.5, 56.4, 47.4, 43.9, 32.5, 27.6.

HRMS (ESI) $C_{22}H_{22}O_7Na$ $[M+Na]^+$: calcd 421.1263, found 421.1255.

19: 6-Methoxypodophyllotoxin. Obtained as white solid from **S7** by using the same procedure as for **16** (25.3 mg from 30 mg of **S7**, 84% y).



6-methoxypodophyllotoxin (**19**)

R_f 0.40 (DCM/Acetone = 10:1, $KMnO_4$).

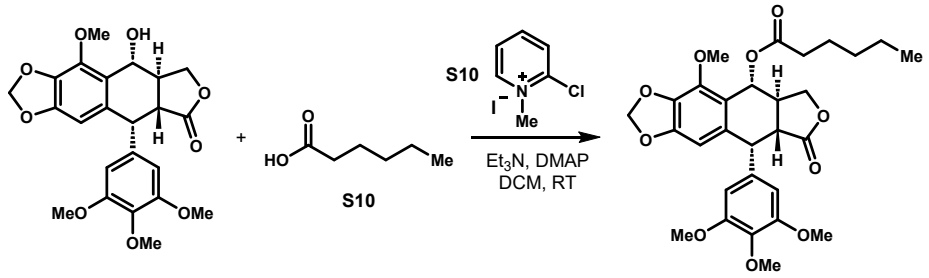
Opt. Rot. $[\alpha]^{20}_D$ = -95.7 (c = 1.1, $CHCl_3$) [Lit.[25]: $[\alpha]^{24}_D$ = -124.2 (c = 0.86, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.44 (s, 2H), 6.29 (s, 1H), 5.94 (s, 2H), 5.02 (dd, *J* = 9.2 &1.6 Hz, 1H), 4.63 (dd, *J* = 8.6 & 7.3 Hz, 1H), 4.53 (d, *J* = 4.5 Hz, 1H), 4.15 (s, 3H), 4.06 (dd, *J* = 10.5 & 8.6 Hz, 1H), 4.02 (d, *J* = 1.7 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 6H), 2.95–2.81 (m, 1H), 2.74 (dd, *J* = 14.8 & 4.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 174.4, 152.6, 149.4, 141.5, 137.0, 134.9, 134.7, 132.8, 124.9, 108.0, 104.3, 101.4, 71.9, 70.5, 60.7, 59.9, 56.1, 45.1, 44.5, 39.0.

HRMS (ESI) $C_{23}H_{24}O_9Na$ $[M+Na]^+$: calcd 467.1318, found 467.1325.

20: 6-Methoxypodophyllotoxin-7-*O*-n-hexanoate



6-methoxy podophyllotoxin (**19**) 6-methoxypodophyllotoxin-7-*O*-n-hexanoate (**20**)

To a solution of 6-methoxyl podophyllotoxin (**19**), Mukaiyama reagent[26] (**S10**, 69.4 mg, 0.272 mmol, 4.0 equiv.), Et_3N (95 μL, 0.68 mmol, 10 equiv.) and DMAP (8.3 mg, 0.068 mmol) in DCM (1.5 mL) was added hexanoic acid (31.5 mg, 0.272 mmol, 4.0 equiv.) at room temperature. The reaction mixture was stirred for 2 h at room temperature. Then diluted with 1 N HCl (2 mL), extracted with DCM (2 ml × 3). The organic phases were combined and washed with sat. $NaHCO_3$ (2 mL), sat. NaCl (2 mL) and dried over Na_2SO_4, filtered, concentrated under vacuum and purified by flushing chromatographed on silica gel to afford the desired product (23 mg, 62% y).

R_f 0.30 (Pentane/Acetone = 5:1, $KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -126.5 (c = 0.20, MeOH) [Lit.[27]: $[\alpha]^{20}_D$ = −122 (c = 0.5, MeOH)].

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.47 (s, 2H), 6.32 (s, 1H), 6.11 (d, *J* = 7.9 Hz, 1H), 5.96 (d, *J* = 1.4 Hz, 1H), 5.95 (d, *J* =

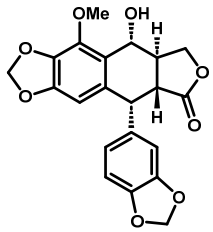
1.5 Hz, 1H), 4.57 (d, *J* = 3.8 Hz, 1H), 4.42 (dd, *J* = 9.2 & 6.8 Hz, 1H), 4.20 (t, *J* = 9.8 Hz, 1H), 4.00 (s, 3H), 3.82 (s, 3H), 3.77 (s, 6H), 2.81 (dd, *J* = 15.0 & 3.9 Hz, 1H), 2.78–2.69 (m, 1H), 2.31 (q, *J* = 7.3 Hz, 2H), 1.69–1.61 (m, 2H), 1.38–1.26 (m, 4H), 0.93–0.85 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.8, 173.7, 152.7, 150.1, 142.3, 137.0, 135.5, 134.4, 134.2, 120.6, 107.8, 103.9, 101.4, 71.8, 69.9, 60.8, 59.5, 56.1, 46.0, 44.2, 39.4, 34.2, 31.3, 24.6, 22.3, 13.9.

HRMS (ESI) $C_{29}H_{35}O_{10}[M+H]^+$: calcd 543.2231, found 543.2233.

21: Cleistantoxin. Obtained as white solid from **S8** by using the same procedure as for **16**. (23 mg from 35 mg of **S8**, 65% y).



cleistantoxin (**21**)

R_f 0.31 (DCM/Acetone = 10:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D = -140.0$ (c = 0.5, $CHCl_3$) [Lit.[28]: $[\alpha]^{30}_D = -148.0$ (c = 0.5, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

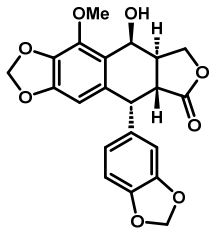
δ 6.73 (d, *J* = 1.7 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 8.1 & 1.8 Hz, 1H), 6.25 (s, 1H), 5.94 (d, *J* = 1.4 Hz, 1H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 5.90 (d, *J* = 1.5 Hz, 1H), 5.02 (d, *J* = 9.3 Hz, 1H), 4.63 (dd, *J* = 8.6 & 7.3 Hz, 1H), 4.50 (d, *J* = 4.6 Hz, 1H), 4.15 (s, 3H), 4.06 (dd, *J* = 10.5 & 8.6 Hz, 1H), 2.94 – 2.81 (m, 1H), 2.73 (dd, *J* = 14.8 & 4.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.2, 149.5, 147.3, 146.7, 141.6, 134.9, 133.1, 133.0, 124.7, 124.2, 111.2, 107.7, 104.3, 101.3, 101.0, 71.9, 70.6, 59.9, 44.7, 44.0, 38.7.

HRMS (ESI) $C_{21}H_{18}O_8Na\,[M+Na]^+$: calcd 421.0899, found 421.0890.

S11: 7-*epi*-Cleistantoxin. Obtained as white solid (7 mg from 35 mg of **S8**, 20% y).



7-*epi*-cleistantoxin (**S11**)

R_f 0.31 (DCM/Acetone = 10:1, $KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D = -36.1$ (c = 0.18, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

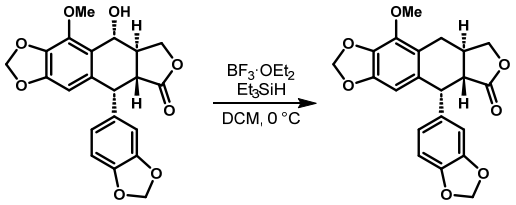
δ 6.67 (d, *J* = 8.0 Hz, 1H), 6.57 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.54 (d, *J* = 1.8 Hz, 1H), 6.24 (s, 1H), 5.93 (d, *J* = 1.4 Hz, 1H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.90 (d, *J* = 1.5 Hz, 1H), 5.89 (d, *J* = 1.4 Hz, 1H), 5.15 (d, *J* = 3.9 Hz, 1H), 4.55 (d, *J* = 5.1 Hz, 1H), 4.46 (dd, *J* = 10.8 & 8.4 Hz, 1H), 4.32 (t, *J* = 8.1 Hz, 1H), 4.15 (s, 3H), 3.24 (dd, *J* = 14.1 & 5.2 Hz, 1H), 2.79-2.72 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 174.2, 149.5, 147.3, 146.7, 141.6, 134.9, 133.1, 133.0, 124.7, 124.2, 111.2, 107.7, 104.3, 101.3, 101.0, 71.9, 70.7, 59.9, 44.8, 44.0, 38.7.

HRMS (ESI) $C_{21}H_{18}O_8Na\,[M+Na]^+$: calcd 421.0899, found 421.0909 .

22: Picrobursenin



cleistantoxin (**21**) picrobursenin (**22**)

By modifying the procedure reported by Fry and co-workers:[29] To a solution of **21** (30 mg, 0.083 mmol, 1.0 equiv.) in DCM (0.8 mL) was added $HSiEt_3$ (56.0 mg, 0.50 mmol, 6.0 equiv.) at room temperature under N_2. The reaction mixture was cooled to 0 °C and $BF_3{\cdot}OEt_2$ (35.2 mg, 0.25 mmol, 3.0 equiv.) was added slowly. After addition, the reaction mixture was stirred at 0 °C for 10 min before it was quenched with H_2O (2 mL). The reaction mixture was extracted with cold DCM (3 × 3 mL) under N_2 protection. The combined organic phase was washed with cold brine, dried over anhydrous Na_2SO_4 under N_2, filtered and concentrated under vacuum (ice bath) under N_2 protection. The residue was purified by flash chromatographed on silica gel to provide picrobursenin **22** as white solid (21 mg, 67% y).

R_f 0.38 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -140.9 (c = 0.45, $CHCl_3$) [Lit.[30]: $[\alpha]^{30}_D = -100.5$ (c = 0.55, $CHCl_3$)].

^{1}H NMR (500 MHz, acetone-d_6)

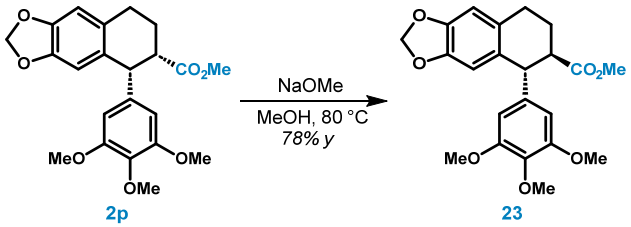
δ 6.68 (d, J = 8.1 Hz, 1H), 6.65 (d, J = 1.8 Hz, 1H), 6.24 (s, 1H), 5.95 (d, J = 1.1 Hz, 1H), 5.93 (d, J = 1.1 Hz, 1H), 5.93 (d, J = 1.1 Hz, 1H), 5.92 (d, J = 1.1 Hz, 1H), 4.45 (dd, J = 8.4 & 7.1 Hz, 1H), 3.99 (dd, J = 10.6 & 8.4 Hz, 1H), 4.03 (s, 3H), 3.18 (dd, J = 16.4 & 5.2 Hz, 1H), 2.81–2.77 (m, 1H), 2.68–2.57 (m, 1H), 2.49 (dd, J = 16.4 & 11.5 Hz, 1H).

^{13}C NMR (125 MHz, acetone-d_6)

δ 175.3, 149.1, 148.0, 147.2, 141.7, 136.1, 135.8, 133.2, 124.9, 122.5, 112.0, 108.0, 105.0, 101.9, 101.9, 72.7, 47.2, 44.2, 33.1, 27.7.

HRMS (ESI) $C_{21}H_{18}O_7Na$ $[M+Na]^+$: calcd 405.0950, found 405.0957.

23: Methyl (5S,6S)-5-(2-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate



2p **23**

By modifying the procedure reported by Lu and co-workers:[31] Sodium methoxide (135 mg, 0.5 mmol) was added to a solution of **2p** (200 mg, 0.5 mmol) in 5 mL anhydrous MeOH. The mixture was heated under reflux for 12 h. The reaction mixture was then cooled to RT, acidified with acetic acid (1 mL). Solvent was removed in *vacuo*, and sat. $NaHCO_3$ (15 mL) was added. The resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford the desired product as white solid (156 mg, 78% y).

R_f 0.30 (toluene/EtOAc = 15:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -50.4 (c = 0.23, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

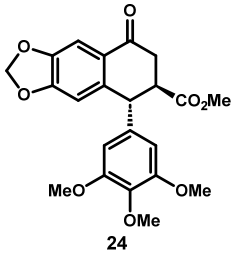
δ 6.57 (s, 1H), 6.30 (s, 3H), 5.86 (d, J = 9.7 Hz, 2H), 4.25 (d, J = 9.1 Hz, 1H), 3.84 (s,

3H), 3.79 (s, 6H), 3.58 (s, 3H), 2.97–2.75 (m, 3H), 2.18–2.07 (m, 1H), 2.05–1.91 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 175.2, 153.1, 146.0, 145.9, 140.4, 136.6, 130.8, 129.0, 109.5, 108.0, 106.0, 100.7, 60.8, 56.1, 51.7, 49.1, 48.0, 28.6, 25.7.

HRMS (ESI) $C_{22}H_{25}O_7$ $[M+H]^+$: calcd 401.1600, found 401.1581.

24: Methyl (5R,6R)-8-oxo-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate. Prepared from **23** by using the method A for **7** (232 mg, 45% y).



24

R_f 0.30 (PE/EtOAc = 2:1, $KMnO_4$).

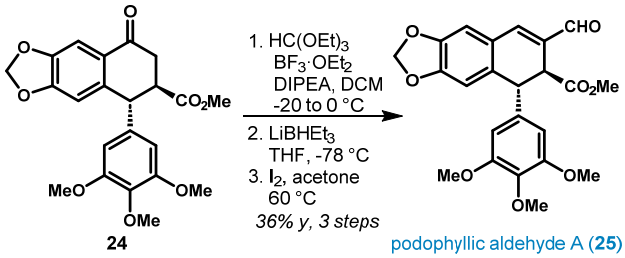
Opt. Rot. $[\alpha]^{20}_D$ = +0.62 (c = 0.27, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.52 (s, 1H), 6.43 (s, 1H), 6.30 (s, 2H), 6.02 (d, *J* = 1.3 Hz, 1H), 6.01 (d, *J* = 1.3 Hz, 1H), 4.52 (d, *J* = 7.0 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 6H), 3.59 (s, 3H), 3.35–3.28 (m, 1H), 2.89 (dd, *J* = 17.0 & 8.2 Hz, 1H), 2.79 (dd, *J* = 17.1 & 4.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 193.5, 173.1, 153.4, 152.7, 147.6, 140.3, 137.2, 137.0, 127.1, 109.0, 105.8, 101.9, 60.8, 56.2, 52.2, 48.3, 47.8, 37.9.

HRMS (ESI) $C_{22}H_{22}O_8Na$ $[M+Na]^+$: calcd 437.1207, found 437.1214.

25: Podophyllic Aldehyde A



By modifying literature procedures:[32] A solution of triethyl orthoformate (0.75 g, 5 mmol, 20 equiv.) in CH_2Cl_2 (3 mL) was cooled to -30 °C. $BF_3{\cdot}Et_2O$ (0.8 mL, 6.25 mmol, 25 equiv.) was then added dropwise. The resulting slurry was stirred at -30 °C for an additional 30 min then warmed to 0 °C for 30 min. The solution was thereafter cooled to -78 °C and **23** (100 mg, 0.25 mmol, 1.0 equiv.) in CH_2Cl_2 (3 mL) was added dropwise followed by dropwise addition of diisopropylethylamine (1.6 mL, 7.5 mmol, 30 equiv.). The reaction was then warmed to -20 °C and stirred for 30 min and slowly warmed to 0 °C over 90 min. The reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and diluted with CH_2Cl_2 (5 mL). The layers were separated, and the organic layer was washed with 0.5 M H_2SO_4 (2 × 10 mL), H_2O (2 × 10 mL), brine (1 × 10 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography to give the desired adduct as yellow oil.

The above aducct was dissolved in THF (3 mL) and cooled to -78 °C. Super-Hydride® (1 M in THF,0.5 mL, 0.5 mmol, 2.0 equiv.) was added dropwise. The reaction mixture was stirred at -78 °C for 4 h. Thereafter, the mixture was quenched with NH_4Cl (3 mL), and extracted with EtOAc (3 × 3 mL). The organic combined phase was washed with brine (1 × 3 mL), dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo* to afford the crude hydroxy acetal as orange oil which was used directly for the next step without further purification.

A solution of iodine (4.8 mg, 0.0183 mmol) in dry acetone (0.3 mL) was added to a solution of the above crude hydroxy acetal in dry acetone (4.7 mL) at 60 °C. After stired for 5 min, the reaction mixture

was concentrated and purified by flash chromatography on silica gel to give podophyllic aldehyde A **25** as white solid (77 mg, 36% y in 3 steps).

R_f 0.20 (PE/Acetone = 3:1, $KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -135.9 (c = 0.94, $CHCl_3$) [Lit.[33]: $[\alpha]^{22}_D$ = -160.9 (c = 0.45, $CHCl_3$)].

^{1}H NMR (500 MHz, $CDCl_3$)

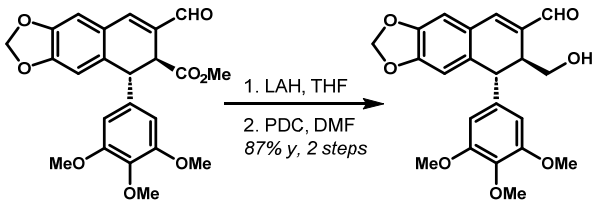
δ 9.61 (s, 1H), 7.35 (s, 1H), 6.89 (s, 1H), 6.68 (s, 1H), 6.21 (s, 2H), 6.02 (d, *J* = 1.3 Hz, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 4.62 (d, *J* = 3.3 Hz, 1H), 4.01 (d, *J* = 3.3 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 6H), 3.63 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.3, 172.1, 153.2, 150.5, 147.4, 145.6, 137.3, 137.1, 133.7, 133.0, 125.1, 110.1, 108.9, 104.7, 101.8, 60.8, 56.1, 52.6, 46.2, 44.4.

HRMS (ESI) $C_{23}H_{22}O_8Na$ $[M+H]^+$: calcd 449.1207, found 449.1220.

26: Podophyllic Aldehyde C



podophyllic aldehyde A (**25**) podophyllic aldehyde C (**26**)

To a suspension of $LiAlH_4$ (5.7 mg, 0.15 mmol, 1.5 equiv.) in THF (1 mL) at 0 °C was added a solution of **25** (42.6 mg, 0.10 mmol, 1.0 equiv.) in THF (1 mL) dropwise at RT. The reaction mixture was stirred at RT for 5 h and quenched with cautious addition of H_2O (6 μL), aqueous 15% NaOH (6 μL), and H_2O (18 μL). The mixture was stirred for 30 min and anhydrous $MgSO_4$ was added. After stirred for another 30 min, the suspension was filtered and washed with THF. The combined filtrate was concentrated in *vacuo* to afford crude diol which was used inmediately without further purification.

The crude diol was dissolved in anhydrous DMF (2 mL) and PDC (56.4 mg, 0.15 mmol, 1.5 equiv) was added at RT. The reaction mixture was efficiently stirred at RT for 1 h and then diluted with EtOAc. The resulting suspension was filtered through a short Celite pad and washed with EtOAc. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography on silica gel to give podophyllic aldehyde C **26** as white solid (34.8 mg, 87% y over 2 steps).

R_f 0.30 (PE/EtOAc = 2:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -125.8 (c = 0.5, $CHCl_3$) [Lit.[33]: $[\alpha]^{22}_D$ = -85.1 (c = 0.22, $CHCl_3$)].

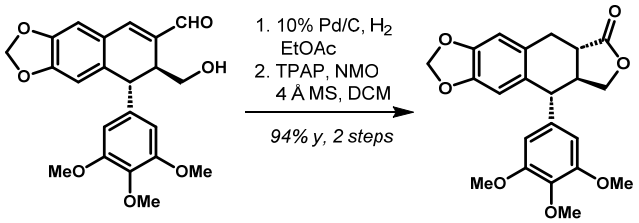
^{1}H NMR δ 9.56 (s, 1H), 7.28 (s, 1H), 6.87 (s, 1H), 6.71 (s, 1H), 6.18 (s, 2H), 6.02 (s, 2H), 4.29 (s, 1H), 3.80 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 6H), 3.65 (dd, *J* = 10.6 & 5.7 Hz, 1H), 3.42 (t, *J* = 9.5 Hz, 1H), 3.26 (t, *J* = 7.1 Hz, 1H), 1.87 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.8, 153.1, 150.5, 147.2, 146.5, 139.2, 136.8, 135.6, 134.0, 125.0, 110.9, 108.7, 104.6, 101.7, 63.4, 60.8, 56.1, 44.9, 42.4.

HRMS (ESI) $C_{22}H_{23}O_7$ $[M+H]^+$: calcd 399.1444, found 399.1431.

27: α-Conidendrin analogue



podophyllic aldehyde C (**26**) α-conidendrin analogue (**27**)

A suspention of **26** (10 mg, 0.025 mmol) and 10% Pd/C (1 mg) in ethyl acetate (1 mL) was vigorously stirred under hydrogen atmosphere (1 atm) at RT for 24 h. The reaction was filtered through a pad of Celite. The filtrate was concentrated and the residue was used directly for the next step.

To the residue obtained above were sequentially added DCM (1 mL), TPAP (1.75 mg, 0.005 mmol, 0.2 equiv.), NMO (8.8 mg, 0.075 mmol, 3.0 equiv.) and 4 Å molecular sieves (24 mg). The reaction mixture was stired at room temperature for 12 h. After completion, the mixture was concentrated and purified by flash chromatography to afford the desired product **27** as white solid (9.4 mg, 94% y over 2 steps).

R_f 0.40 (PE/Acetone = 2:1, UV/$KMnO_4$).

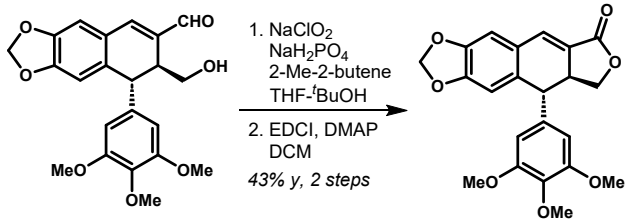
Opt. Rot. $[\alpha]^{20}_D$ = +83.1 (c = 0.26, $CHCl_3$) [Lit. (*ent*-**27**: 95% ee)[34]: $[\alpha]^{25}_D$ = -71 (c = 1.0, $CHCl_3$)].

^{1}H NMR (600 MHz, $CDCl_3$)
δ 6.67 (s, 1H), 6.31 (s, 3H), 5.91 (d, *J* = 1.4 Hz, 1H), 5.89 (d, *J* = 1.4 Hz, 1H), 4.25 (dd, *J* = 8.9 & 5.9 Hz, 1H), 4.02 (dd, *J* = 10.5 & 8.7 Hz, 1H), 3.86 (s, 3H), 3.85 (br, 1H), 3.82 (s, 6H), 3.20 (dd, *J* = 16.0 & 4.2 Hz, 1H), 3.01–2.94 (m, 1H), 2.59–2.54 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 176.7, 153.2, 146.7, 146.6, 137.9, 137.2, 131.6, 128.1, 109.1, 109.0, 101.1, 71.7, 60.9, 56.2, 51.0, 47.4, 41.8, 29.6.

HRMS (ESI) $C_{22}H_{23}O_7$ $[M+H]^+$: calcd 398.1366, found 398.1362.

28: Oleralignan A analogue



podophyllic aldehyde C (**26**) oleralignan A analogue (**28**)

To a stirred solution of **26** (90 mg, 0.225 mmol, 1.0 equiv.) and 2-methyl-2-butene (0.30 mL, 2.25 mmol, 13 equiv.) in THF (4.5 mL) and *t*-BuOH (4.5 mL) was added the mixture of $NaClO_2$ (180 mg, 2.02 mmol, 9 equiv.) and NaH_2PO_4 (216 mg, 1.58 mmol, 7 equiv.) in H_2O (5.4 mL) dropwise at room temperature. The reaction mixture was stirred at room temperature for 12 h before it was quenched with 1M aq. HCl (5 mL), and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (2 mL), dried over sodium sulfate, and concentrated under reduced pressure to yield crude product as a dark brown sticky liquid used in subsequent reaction without further purification.

To a stirred solution of crude product in DCM (4 mL) was added EDCI (54 mg, 0.27 mmol, 1.2 equiv.) and DMAP (2 mg, 0.016 mmol, 7 mol%) at 0 °C. The mixture was stirred at room temperature for 12 h, and then quenched with 2 M aq. HCl (3 mL), and extracted with DCM (3 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to yield the desired product **28** as white solid (38.7 mg, 43% y).

R_f 0.3 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -161.4 (c = 0.29, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.38 (d, *J* = 3.2 Hz, 1H), 6.85 (s, 1H), 6.48 (d, *J* = 5.4 Hz, 2H), 6.29 (s, 1H), 5.96 (d, *J* = 7.8 Hz, 2H), 4.44 (t, *J* = 8.8 Hz, 1H), 3.97 (t, *J* = 8.9 Hz, 1H), 3.88 (s, 6H), 3.81 (s, 3H), 3.78 (s, 1H), 3.54–3.44 (m, 1H).

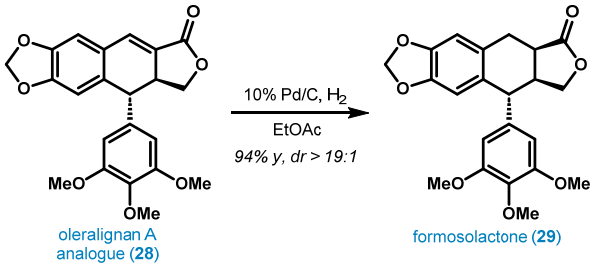
^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.6, 154.3, 153.4, 149.5, 146.8, 137.5, 135.0, 134.3, 132.4, 127.0, 125.7, 109.2, 108.7, 107.9, 103.1, 101.7, 71.9, 60.9, 56.2, 51.3, 40.8.

HRMS (ESI) $C_{22}H_{21}O_7$ $[M+H]^+$: calcd 397.1287, found 397.1280.

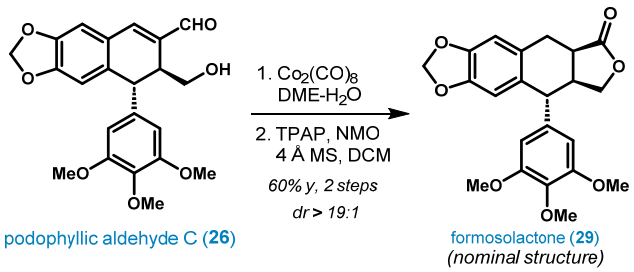
29: Formosolactone (nominal; its originally reported spectra data were found to match with deoxypodophyllotoxin **11**)[35]

*A. Through hydrogenation of **28***



A suspension of **28** (20 mg, 0.05 mmol) and 10% Pd/C (1.0 mg) in MeOH (2 mL) was vigorously stirred under hydrogen atmosphere (1 atm) at RT for 12 h. The reaction was filtered through a pad of Celite. The filtrate was concentrated in *vacuo* and the residue was purified by flash chromatography to yield **29** as white solid (18.7 mg, 94% y).

*B. By means of **26***



By modifying the procedure reported by Lee and An:[36] In a test tube charged with N_2 atmosphere and DME (0.5 mL), $Co_2(CO)_8$ (4.3 mg, 0.0126 mmol, 1.0 equiv.), H_2O (0.005 mL, 0.0252 mmol, 20.0 equiv.) and **26** (5.0 mg, 0.0125, 1.0 equiv.) were added. And the mixture was refluxed for 2 h. Upon completion of the reaction, the mixture was cooled to room temperature and filtrated through a thin pad of silica gel. After concentration, the residue was used directly in next step.

To the residue obtained above in DCM (1 mL) was added TPAP (0.9 mg, 0.0026 mmol, 0.2 equiv.), NMO (3.0 mg, 0.026 mmol, 2.0 equiv.) and 4 Å molecular sieve (5 mg). The reaction mixture was stired at room temperature for 12 h.[32] After reaction completion, the mixture was concentrated and purified by flash chromatography to give **29** as white solid (3.2 mg, 65% y).

R_f 0.3 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_{D}$ = +1.90 (c = 0.42, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

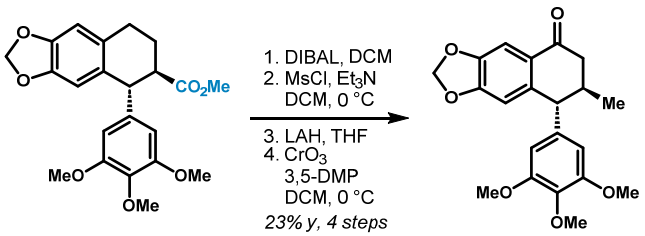
δ 6.74 (s, 1H), 6.39 (s, 2H), 6.28 (s, 1H), 5.91 (s, 1H), 5.89 (s, 1H), 4.38 (t, *J* = 8.5 Hz, 1H), 4.05 (dd, *J* = 9.6 & 3.3 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 6H), 3.59 (d, *J* = 9.7 Hz, 1H), 3.17 (dd, *J* = 15.2 & 8.5 Hz, 1H), 3.14–3.06 (m, 1H), 3.05–2.96 (m, 1H), 2.88 (dd, *J* = 15.1 & 6.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 179.3, 153.7, 146.4, 146.4, 137.3, 135.4, 132.8, 128.7, 108.4, 108.3, 105.9, 100.9, 71.4, 60.9, 56.2, 48.0, 41.1, 38.8, 28.7.

HRMS (ESI) $C_{22}H_{22}O_7Na$ $[M+ Na]^+$: calcd 421.1258, found 421.1245.

32: (7R,8R)-7-Methyl-8-(3,4,5-trimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxol-5(6H)-one)



23 32

To a stirred solution of **23** (300 mg, 0.75 mmol, 1.0 equiv.) in DCM (10 mL) was added Dibal-H (1.0 M in toluene, 1.1 mL, 1.1 mmol, 1.5 equiv.) at -78 °C. The reaction mixture was stirred at room temperature for 4 h, and quenched cautiously with 10% aq. sodium potassium tartrate (10 mL). The resulting mixture was stirred at RT for 2 h, and extracted with DCM (5 mL × 3). The combined organic phase was washed with brine (5 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo* to provide the desired crude alcohol which was used without further purification.

To the solution of crude alcohol obtained above and Et_3N (375 mg, 3.75 mmol, 5.0 equiv.) in DCM (10 mL) was added dropwise addition of MsCl (427 mg, 3.75 mmol, 5.0 equiv.) at 0 °C. The resulting mixture was allowed to warm slowly to RT. The reaction then quenched by with aq. 2 N HCl (10 mL) at 0 °C, and extracted with DCM (6 mL × 3). The combined organic phase was washed sequentially with sat. aq. $NaHCO_3$ (6 mL), brine (5 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo* to give crude mesylate which was used directly in the next step.

A solution of the crude mesylate in THF (2 mL) was added dropwise to a suspension of $LiAlH_4$ (85 mg, 2.25 mmol 3.0 equiv.) in THF (5 mL) at 0 °C. The reaction mixture was allowed to warm gradually to RT and stirred overnight. The reaction mixture was quenched by careful addition of H_2O (85 μL), aq. 15% NaOH solution (85 μL) and H_2O (0.26 mL) at 0 °C. Thereafter, anhydrous $MgSO_4$ was added. After stired for 30 min, the suspension was filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash column chromatography to afford the desired intermediate.

To a solution of CrO_3 (400 mg, 4.08 mmol, 8.0 equiv.) in DCM (6 mL) was added 3,5-dimethylpyrazole (400 mg, 4.08 mmol, 8.0 equiv.) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min before a solution of the above intermediate (181mg, 0.51 mmol, 1.0 equiv.) in DCM (3 mL) was added. The reaction mixture was stirred at 0 °C for 50 min before it was filtered through a pad of silica gel, eluted with PE/EA = 2/1. The filtration was concentrated then diluted with ethyl acetate, washed with 1 N HCl (5 mL 0.085 mL × 3), sat. aq. $NaHSO_3$ (5 mL), and brine (5 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by flash chromatography to give **32** as white solid (64.0 mg, 23% over 4 steps).

R_f 0.30 (PE/EtOAc = 5:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +5.0 (c = 0.14, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

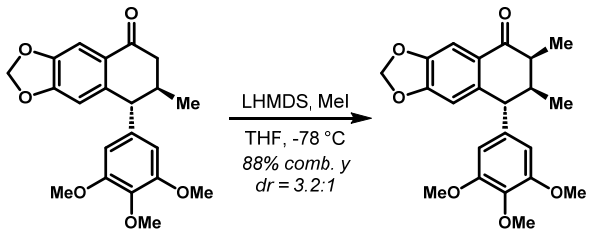
δ 7.50 (s, 1H), 6.32 (s, 2H), 6.30 (s, 1H), 5.98 (s, 2H), 5.97 (s, 1H), 3.87 (s, 3H), 3.81 (s, 6H), 3.64 (d, *J* = 8.6 Hz, 1H), 2.82–2.74 (m, 1H), 2.46–2.34 (m, 2H), 0.97 (d, *J* = 5.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 196.2, 153.4, 152.3, 147.0, 143.4, 138.6, 136.9, 127.4, 109.1, 106.0, 105.5, 101.7, 60.9, 56.2, 54.2, 45.7, 37.5, 20.3.

HRMS (ESI) $C_{21}H_{23}O_6$ $[M+H]^+$: calcd 371.1494, found 371.1484.

33: 8'-*epi*-aristoligone analogue



A solution of **32** (35 mg, 0.094 mmol, 1.0 equiv.) in THF (0.5 mL) was added dropwise to a stirred solution of LiHMDS (1 M in THF, 0.94 mL, 0.94 mmol, 10 equiv.) in THF (1 mL) at -78 °C and slowly warmed to -10 °C during 4 h. The reaction mixture was again cooled to -78 °C and MeI (534 mg, 3.76 mmol, 40 equiv.) was added via syringe. After stirred for 1 h, the reaction was quenched with sat. aq. NH_4Cl (2 ml) and extracted with EtOAc (2 mL × 3). The combined organic layers were washed with brine (2 mL), dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford the title compound **32** as a 3.2:1 mixture of diastereomers (32 mg, 88% y).

R_f 0.30 (PE/EtOAc = 4:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -0.91 (c = 1.7, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

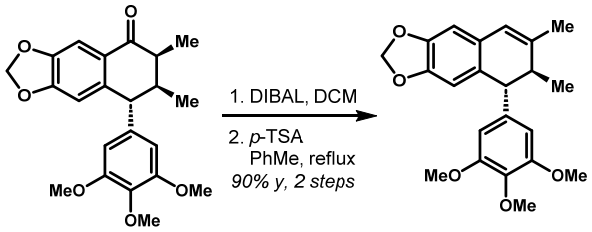
δ 7.49 (s, 1H), 6.41 (s, 1H), 6.25 (s, 2H), 5.98 (d, *J* = 9.5 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 6H), 2.77 (m, 1H), 2.41 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 199.5, 153.3, 152.2, 147.2, 140.8, 139.2, 136.8, 126.9, 109.5, 106.0, 105.8, 101.7, 60.9, 56.2, 51.1, 43.2, 41.9, 16.0, 11.7.

HRMS (ESI) $C_{22}H_{25}O_6$ $[M+H]^+$: calcd 385.1652, found 385.1657.

34: Cyclogalgravin analogue



8'-*epi*-aristoligone analogue (**33**) — cyclogalgravin analogue (**34**)

To a stirred solution of **33** (32 mg, 0.083 mmol, *d.r.* = 3.2:1, 1.0 equiv.) in DCM (2 mL) was added DIBAL (1.0 M in hexane, 0.17 mL, 0.166 mmol, 2.0 equiv.) at -78 °C. The reaction mixture was then stirred at RT for 4 h, and quenched cautiously with 10% aq. sodium potassium tartrate (5 mL). The resulting mixture was stirred at RT for 2 h, and extracted with DCM (5 mL × 3). The combined organic phase was washed with brine (2 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo* to provide the desired crude alcohol which was used without further purification.

To a solution of the crude alcohol obtained above in toluene (2 mL) was added *p*-TsOH (21 mg, 0.12 mmol, 1.5 equiv.) at RT. The reaction mixture was then heated at 80 °C for 10 min, quenched with aqeous sat. Na_2CO_3 (2 mL), and extracted with EtOAc (1 mL × 3). The combined organic layers were washed with brine (1 mL), dried over Na_2SO_4 and filtrated. The filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford **34** as white solid (27.5 mg, 90% y over 2 steps).

R_f 0.30 (PE/EtOAc = 8:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -20.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

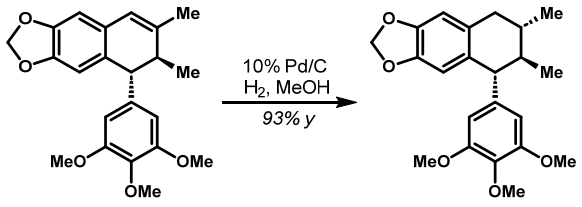
δ 6.57 (s, 1H), 6.51 (s, 1H), 6.33 (s, 2H), 6.10 (d, *J* = 1.7 Hz, 1H), 5.89 (q, *J* = 1.5 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 6H), 3.61 (d, *J* = 3.8 Hz, 1H), 2.41 (m, 1H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.08 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 152.9, 146.2, 145.9, 141.0, 139.0, 136.3, 128.6, 128.1, 121.4, 109.8, 106.0, 104.5, 100.7, 60.8, 56.0, 52.0, 41.4, 22.0, 18.6.

HRMS (ESI) $C_{22}H_{25}O_5$ $[M+H]^+$: calcd 369.1703, found 369.1720.

35: Isoaustrobailignan-4



cyclogalgravin analogue (**34**) — isoaustrobailignan-4 (**35**)

A mixture of **34** (27.5 mg, 0.075 mmol), 10% Pd/C (2.7 mg) and MeOH (2 mL) was vigorously stirred under hydrogen atmosphere (balloon) at RT for 12 h. The reaction mixture was filtrated through a pad of Celie and washed with EtOAc. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to give the desired product **35** (25.8 mg, 93% y).

R_f 0.30 (PE/EtOAc = 8:1, UV/$KMnO_4$).

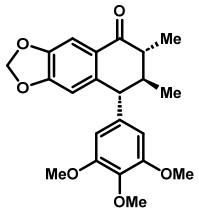
Opt. Rot. $[\alpha]^{20}_D$ = -12.3 (c = 0.9, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.53 (s, 1H), 6.31 (s, 2H), 6.18 (s, 1H), 5.83 (d, *J* = 1.5 Hz, 1H), 5.82 (d, *J* = 1.4 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 6H), 3.37 (d, *J* = 9.7 Hz, 1H), 2.73 (dd, *J* = 16.3 & 4.5 Hz, 1H), 2.64–2.54 (m, 1H), 1.66–1.57 (m, 1H), 1.57–1.48 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 153.0, 145.5, 145.4, 142.1, 136.3, 133.2, 129.9, 109.5, 107.6, 106.3, 100.5, 60.9, 56.1, 55.4, 43.5, 39.4, 35.5, 19.9, 17.3.

HRMS (ESI) $C_{22}H_{27}O_5$ $[M+H]^+$: calcd 371.1888, found 371.1883.

36: 8,8'-*epi*-Aristoligone analogue. Obtained as white solid from **35** by using the method A for **7** (7.1 mg from 42.0 mg of **35**, 34% y).



8,8'-*epi*-aristoligone analogue (**36**)

R_f 0.20 (PE/EtOAc = 8:1, $KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -25.6 (c = 0.10, $CHCl_3$)

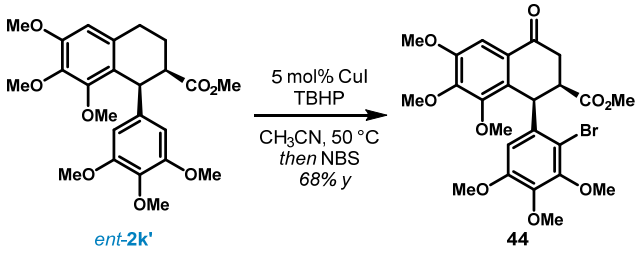
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.48 (s, 1H), 6.33 (s, 2H), 6.21 (d, *J* = 1.0 Hz, 1H), 5.96 (d, *J* = 1.3 Hz, 1H), 5.95 (d, *J* = 1.3 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 6H), 3.63 (d, *J* = 10.7 Hz, 1H), 2.39–2.32 (m, 1H), 2.11–2.03 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 198.3, 153.4, 151.9, 146.9, 143.3, 139.3, 136.8, 127.2, 108.8, 106.2, 105.7, 101.6, 60.9, 56.2, 54.4, 48.5, 43.3, 18.1, 12.5.

HRMS (ESI) $C_{22}H_{24}O_6Na$ $[M+Na]^+$: calcd 407.1465, found 407.1470.

3.4 Syntheses of (+)-Lirionol and Alleged Aglacins D, G, and H (from ent-2j')

44: Methyl (1R,2S)-1-(2-bromo-3,4,5-trimethoxyphenyl)-6,7,8-trimethoxy-4-oxo-1,2,3,4-tetrahydro-naphthalene-2-carboxylate



ent-**2k'** **44**

By modifying the procedure reported by Einhorn and co-workers:[11] To a solution of *ent*-**2j'** (2.5 g, 5.6 mmol, 1.0 equiv.) and CuI (5 mol%) in acetonitrile (0.17 M, 33 mL) was added a solution of TBHP in hexane solution (5.5 M, 7.1 mL, 39.2 mmol, 7.0 equiv.). The mixture was then stirred at 50°C and the reaction was monitored by TLC. After complete disappearance of the starting material, the reaction mixture was cooled to RT and NBS (1.01 g, 5.7 mmol, 1.02 equiv.) was added. The mixture was stirred at RT for another 3 h and quenched with saturated $NaHSO_3$ (15 mL). The resulting mixture was concentrated in *vacuo*, and the residue was extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with washed with H_2O (10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography to give **44** as white solid (2.0 g, 68% y).

R_f 0.45 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +277.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

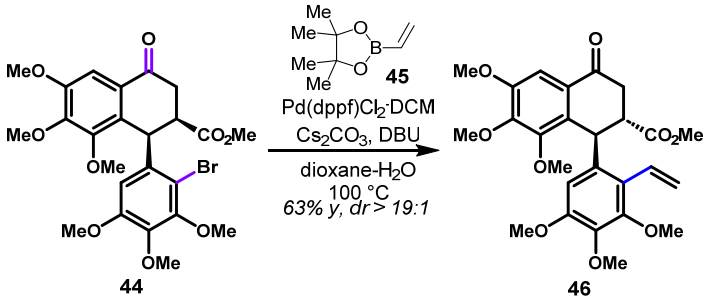
δ7.45 (s, 1H), 6.10 (s, 1H), 5.56 (d, *J* = 5.2 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 3.65 (s, 3H), 3.57 (s, 3H), 3.52 (dt, *J* = 14.1 & 4.7 Hz, 1H), 3.47 (s, 3H), 3.14 (dd, *J* = 18.3 & 14.2 Hz, 1H), 2.67 (dd, *J* = 18.3 & 4.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ195.8, 171.7, 153.2, 152.1, 151.1, 150.3, 148.1, 142.4, 133.2, 132.5, 127.4, 112.5, 109.8, 104.6, 61.1, 61.0, 60.9, 60.3, 56.1, 56.1, 52.1, 43.5, 38.7, 35.6.

HRMS (ESI) $C_{24}H_{28}BrO_9$ $[M+H]^+$: calcd 539.0917/541.0900, found 539.1032/541.1003.

46: Methyl (1S,2S)-6,7,8-trimethoxy-4-oxo-1-(3,4,5-trimethoxy-2-vinylphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate



To a flask containing **44** (644 mg, 1.2 mmol, 1.0 equiv.), Cs_2CO_3 (1.2 g, 3.6 mmol, 3.0 equiv.) and $PdCl_2$(dppf)·DCM (87 mg, 0.12 mmol, 10 mol%) was added dioxane/H_2O (10 mL /1 mL), vinylboronic acid pinacol ester **45** (3.2 mmol, 0.55 mL, 2.7 equiv.) and DBU (53 μL, 0.36 mmol, 0.3 equiv.) under nitrogen atmosphere at RT. The reaction was stirred at 100 °C overnight. The reaction misture was cooled to RT, quenched with water (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with water (10 mL), brine (10 mL), dried over Na_2SO_4, filtered and the filtrated was concentrated in *vacuo*. The residue was purified by flash chromatography to afford the desired product **46** as white solid (367 mg, 63% y).

R_f 0.30 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +154.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

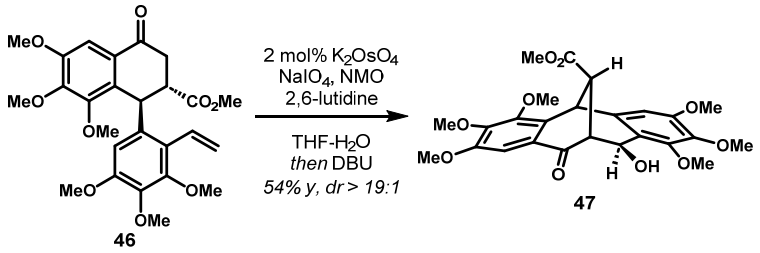
δ7.46 (s, 1H), 6.90 (dd, *J* = 17.8 & 11.6 Hz, 1H), 5.89 (s, 1H), 5.81 (dd, *J* = 17.8 & 2.1 Hz, 1H), 5.65 (dd, *J* = 11.6 & 2.1 Hz, 1H), 5.39–5.36 (m, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 3.83 (s, 3H), 3.62 (s, 3H), 3.53 (s, 3H), 3.50 (s, 3H), 3.20 (dt, *J* = 5.0 & 2.4 Hz, 1H), 2.90–2.81 (m, 1H), 2.65 (dd, *J* = 17.5 & 5.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ195.0, 173.6, 153.0, 152.5, 152.0, 150.6, 147.9, 141.4, 135.3, 130.3, 129.8, 128.2, 124.5, 120.5, 107.8, 104.7, 60.9, 60.9, 60.6, 60.5, 56.0, 56.0, 52.4, 44.7, 36.9, 35.0.

HRMS (ESI) $C_{26}H_{31}O_9$ $[M+H]^+$: calcd 487.1968, found 487.1963.

47: Methyl (7S,12S)-7-hydroxy-1,2,3,8,9,10-hexamethoxy-5-oxo-5,6,7,12-tetrahydro-6,12-methanodibenzo[a,d][8]annulene-13-carboxylate



By modifying the procedure reported by Jin and co-workers:[37] To a flask containing alkene **46** (1.2 g, 2.56 mmol, 1.0 equiv.) was added NMO (450 mg, 3.8 mmol, 1.5 equiv.), $NaIO_4$ (1.2 g, 5.8 mmol, 2.3 equiv.), THF/H_2O (25 mL/0.5 mL), 2,6-lutidine (6.4 mmol, 0.74 mL, 2.5 equiv.) and 0.1 N aq. K_2OsO_4 (0.5 mL, 0.05 mmol, 2 mol%) at RT. The reaction was stirred at room temperature for 2 h. DBU (3.9 mL, 25.6 mmol, 10.0 equiv.) was then added and the reaction was stirred at RT for another 1 h. The reaction was then quenched with saturated $NaHSO_3$ (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with water (10 mL), brine (10 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography to afford the desired product **47** as white solid (674 mg, 54% y).

R_f 0.25 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +48.3 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

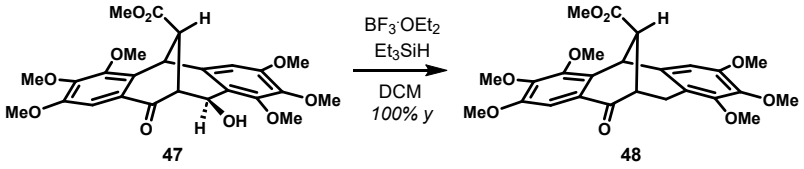
δ7.21 (s, 1H), 6.82 (s, 1H), 5.08 (s, 1H), 4.83 (dd, *J* = 3.5 & 1.5 Hz, 1H), 4.03 (s, 2H), 3.93 (s, 2H), 3.91 (s, 2H), 3.81 (s, 7H), 3.79 (s, 2H), 3.61 (d, *J* = 2.1 Hz, 1H), 3.59 (s, 3H), 2.80–2.77 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ195.3, 173.1, 154.0, 152.5, 152.2, 149.1, 147.6, 140.8, 136.0, 133.3, 125.4, 120.4, 106.7, 106.0, 65.8, 61.3, 61.2, 60.9, 60.7, 56.0, 55.9, 52.1, 50.4, 42.5, 34.8.

HRMS (ESI) $C_{25}H_{29}O_{10}$ $[M+H]^+$: calcd 489.1761, found 489.1760.

48: Methyl (12S)-1,2,3,8,9,10-hexamethoxy-5-oxo-5,6,7,12-tetrahydro-6,12-methanodibenzo [a,d][8]-annulene-13-carboxylate



By modifying the procedure reported by Fry and co-workers:[29] To a solution of **47** (200 mg, 0.4 mmol, 1.0 equiv.) in DCM (2 mL) was added triethylsilane (0.48 mmol, 76 µL, 1.2 equiv.) at 0 °C. Boron trifluoride diethyl etherate in DCM (0.1 M, 0.4 mmol, 4.0 mL, 1.0 equiv.) was then added dropwise. The mixture was stirred at 0 °C for another 15 min and quenched with sat. aq. NH_4Cl (2 mL). The mixture was extracted with DCM (3 × 10 mL). The combined organic layer was washed with water (10 mL), brine (10 mL), dried over Na_2SO_4, filtered and the filtrate eas concentrated in *vacuo*. The residue was purified by flash chromatography to afford the desired product **48** as colorless oil (188 mg, *quant.*).

R_f 0.55 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +51.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

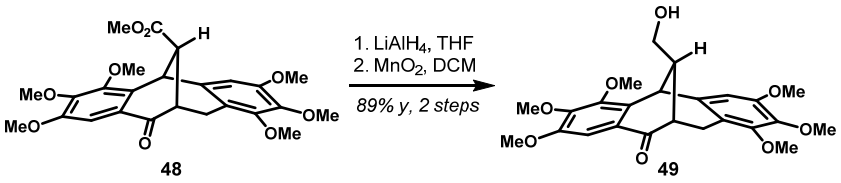
δ7.29 (s, 1H), 6.85 (s, 1H), 4.84 (dd, *J* = 3.5 & 1.7 Hz, 1H), 4.03 (s, 3H), 3.93 (s, 3H), 3.83 (s, 3H), 3.81 (d, *J* = 2.8 Hz, 7H), 3.79 (s, 3H), 3.59 (s, 3H), 3.56–3.53 (m, 1H), 3.31

(t, J = 2.7 Hz, 1H), 3.09–3.05 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ198.4, 173.0, 152.2, 152.1, 151.5, 149.3, 147.5, 140.9, 134.8, 134.1, 126.0, 118.3, 107.1, 105.8, 61.2, 60.9, 60.7, 60.3, 56.0, 55.9, 52.2, 46.2, 41.6, 34.7, 27.7.

HRMS (ESI) $C_{25}H_{29}O_9$ $[M+H]^+$: calcd 473.1812, found 473.1814.

49: (12S)-13-(Hydroxymethyl)-1,2,3,8,9,10-hexamethoxy-7,12-dihydro-6,12-methanodibenzo[a,d] [8]-annulen-5(6H)-one



A solution of ester **48** (526 mg, 1.1 mmol, 1.0 equiv.) in THF (1.8 mL) added dropwise to a suspension of $LiAlH_4$ (2.5 mmol, 97 mg, 2.3 equiv.) in THF (2.5 mL) at 0 °C. The mixture was then stirred at RT. After completion as observed by TLC analysis, the reaction was quenched by careful addition of H_2O (97 µL), 15% aq. NaOH (97 µL) and H_2O (291 µL) at 0 °C. The mixture was then stirred at room temperature for 15 min and Na_2SO_4 was added. After filtration, the solvents were removed and the residue was dried in *vacuo*.

To the crude diol (1.0 equiv.) was added CH_2Cl_2 (11.0 mL) and activated MnO_2 (16.5 mmol, 1.4 g, 15 equiv.). The reaction was vigorously stirred at RT for 2 h. The mixture was filtered through Celite and washed with EtOAc. The filtrated was concentrated in *vacuo* and the residue was purified by flash chromatography to afford the desired product **49** colorless oil (488 mg, 89% y over 2 steps).

R_f 0.60 (PE/EtOAc = 1:3, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +74.20 (c = 1.0, $CHCl_3$).

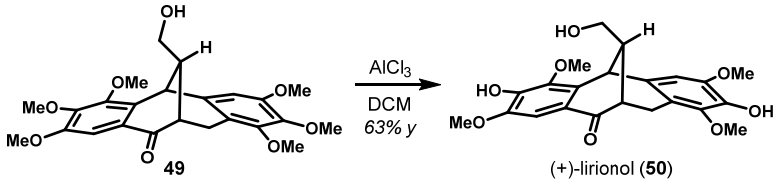
^{1}H NMR (500 MHz, $CDCl_3$)
δ7.29 (s, 1H), 6.83 (s, 1H), 4.51 (dd, J = 3.2 & 1.6 Hz, 1H), 4.02 (s, 3H), 3.93 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.67 (dd, J = 10.7 & 6.6 Hz, 1H), 3.56 (dd, J = 10.6 & 8.8 Hz, 1H), 3.12–2.92 (m, 3H), 2.59 (dt, J = 8.3 & 1.8 Hz, 1H), 1.66 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ198.8, 151.0, 150.8, 150.5, 149.0, 146.6, 139.7, 135.2, 133.1, 125.2, 117.8, 106.3, 104.6, 62.8, 60.4, 59.8, 59.7, 59.2, 55.0, 55.0, 42.3, 41.5, 32.8, 27.2.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1872.

50: (+)-Lirionol

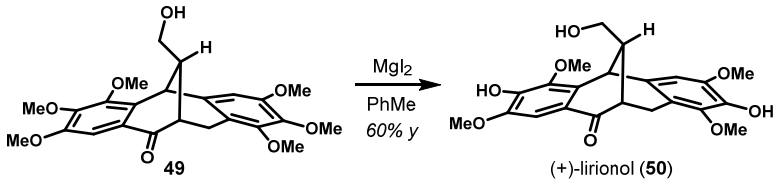
A. By means of $AlCl_3$



Prepared by modifying the procedure reported by Rodrigo and co-workers:[38a] To a solution of **49** (44.4 mg, 0.1 mmol, 1.0 equiv.) in dry CH_2Cl_2 (1.0 mL) was added anhydrous $AlCl_3$ (80 mg, 0.6 mmol, 6.0 equiv.). The reaction was stirred at RT for 8 h and then quenched by sat. aq. NH_4Cl. The mixture was

extracted with CH_2Cl_2 (3 × 2 mL). The combined organic extracts were washed with brine (3 mL), dried over $MgSO_4$, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography (eluent with PE/TBME/acetone =2:2:1) to provide lirionol **50** as white solid (26 mg, 63% y).

B. By means of MgI_2



By modifying the procedure reported by Yao and co-workers:[39] To a solution of **49** (48 mg, 0.11 mmol, 1.0 equiv.) in toluene (1.1 mL) was added a solution of MgI_2 in diethyl ether solution (0.4 M, 1.4 mL, 0.55 mmol, 5.0 equiv.) dropwisely. The resulting reaction miture was stirred at 80°C for 12 h. After cooling, the reaction was quenched with sat. aq. NH_4Cl (1.0 mL) and extracted by EA (3 × 2 mL). The combined organic layers were washed with brine (3 mL), dried over Na_2SO_4 and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography (petroleum ether/TBME/acetone =2:2:1) to afford the desired lirionol **50** as white solid (27 mg, 60%).

R_f 0.30 (PE/EtOAc = 1:3, UV/$KMnO_4$).

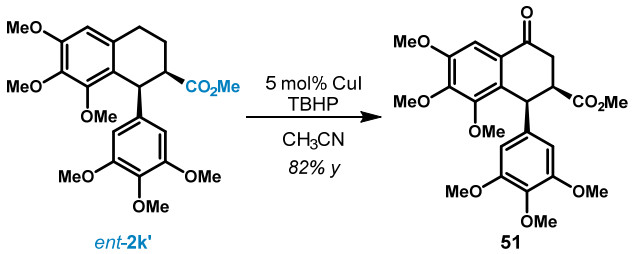
Opt. Rot. $[\alpha]^{20}_D$ = +124.40 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, DMSO-*d*$_6$)
δ 9.80 (s, 1H), 8.42 (s, 1H), 7.12 (s, 1H), 6.74 (s, 1H), 4.70 (t, *J* = 4.8 Hz, 1H), 4.36 (s, 0H), 3.90 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.30–3.25 (m, 1H), 3.00 (dd, *J* = 17.7 & 7.5 Hz, 1H), 2.86 (d, *J* = 7.3 Hz, 1H), 2.73 (d, *J* = 17.5 Hz, 0H), 2.44–2.38 (m, 1H).

^{13}C NMR (125 MHz, DMSO-*d*$_6$)
δ 198.9, 147.4, 147.4, 146.3, 146.1, 144.5, 138.3, 135.7, 131.8, 121.8, 119.0, 107.6, 105.0, 62.5, 60.9, 59.5, 56.3, 56.3, 43.5, 42.3, 33.7, 28.3.

HRMS (ESI) $C_{22}H_{25}O_8$ $[M+H]^+$: calcd 417.1549, found 417.1550.

51: Methyl (1S,2R)-6,7,8-trimethoxy-4-oxo-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydro-naphthalene-2-carboxylate



Prepared by modifying the procedure reported by Einhorn and co-workers:[11] To a solution of *ent*-**2k'** (2.5 g, 5.6 mmol, 1.0 equiv.) and CuI (5 mol%) in acetonitrile (0.17 M, 33 mL) was added a solution of TBHP in hexane solution (5.5 M, 7.1 mL, 39.2 mmol, 7.0 equiv.). The reaction was stirred at 50°C for 4 h. After cooled, the reaction was quenched with sat. aq. $NaHSO_3$. The resulting mixture was concentrated in *vacuo*, and extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with H_2O (10 mL), brine (30 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography (petroleum ether/EA=5:1) to give the desired ketone **51** as white solid (2.1 g, 82%).

R_f 0.30 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +188.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

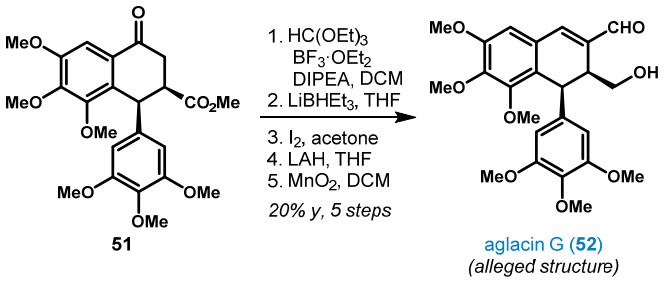
δ 7.46 (s, 1H), 6.19 (s, 2H), 5.01 (d, *J* = 4.8 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.79 (s, 3H), 3.71 (s, 7H), 3.70 (s, 3H), 3.50–3.45 (m, 1H), 3.44 (s, 4H), 2.95 (dd, *J* = 18.1 & 14.1 Hz, 1H), 2.73 (dd, *J* = 18.2 & 4.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ196.1, 171.9, 153.1, 153.1, 150.3, 148.0, 137.4, 134.0, 132.1, 127.7, 106.4, 104.7, 60.9, 60.8, 60.7, 56.2, 56.1, 51.9, 44.8, 40.7, 35.1.

HRMS (ESI) $C_{24}H_{28}O_9Na$ $[M+Na]^+$: calcd 483.1631, found 483.1632.

52: originally assigned structure of aglacin G[40]



To a 25-mL round flask that had been flame-dried under high vacuum and purged with N_2 was added distilled triethyl orthoformate (1.7 mL, 13.40 mmol, 20 equiv.) and CH_2Cl_2 (6 mL), which was then cooled to –30 °C. Subsequently, $BF_3{\cdot}Et_2O$ (1.8 mL, 16.75 mmol, 25 equiv.) was added dropwise. The resulting slurry was stirred at –30 °C for an additional 30 min then warmed to 0 °C for 30 min. The solution was thereafter cooled to –78 °C and **50** (310 mg, 0.67 mmol, 1.0 equiv.) in CH_2Cl_2 (3 mL) was added dropwise followed by dropwise addition of diisopropylethylamine (3.6 mL, 20.1 mmol, 30 equiv.). The reaction was then warmed to –20 °C and stirred for 30 min and slowly warmed to 0 °C over 90 min. Thereafter, the reaction was added saturated aqueous $NaHCO_3$ (10 mL) followed by vigorous stirring for 10 min. The resulting layers were separated, and the organic layer was washed with 0.5 M H_2SO_4 (3 × 10 mL), H_2O (2 × 5 mL), brine (1 × 5 mL) and dried over Na_2SO_4.[17] The organic layer was filtered, and concentrated in vacuo. The residue was purified by flash chromatography to yield the desired the product as a yellow oil.

A dry 25 mL round bottomed flask was charged with starting materail obtained above and THF (6 mL). The mixture was cooled to -78 °C, then $LiBHEt_3$ (1 M in THF, 0.8 mL, 0.8 mmol, 1.2 equiv.) was added dropwise. After addition, the reaction was stirred at -78 °C for 4 h. Thereafter, the mixture was quenched with NH_4Cl (5 mL), Subsequently, the reaction mixture was extracted with EtOAc (3 × 5 mL), and the organic layer was combined and washed with brine (1 × 6 mL), dried over Na_2SO_4, filtered, and the volatiles were removed in vacuo to afford a crude acetal orange oil used directly without further purification.

To a round-bottom flask containing the acetal in 20 mL of chloroform was added 50% trifluoroacetic acid aqueous solution at ambient temperature.[34] The resulting solution was stirred at room temperature for 2 h, then the mixture was poured in sat. $NaHCO_3$ (20 mL) and stirred for 20 min. The aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. After concentration, the residue was purified by flash chromatography to afford unsaturated aldehyde as light yellow solid (142 mg, 45% yield, 3 steps)

To a suspension of $LiAlH_4$ (17.1 mg, 0.45 mmol, 1.5 equiv.) in THF (5 mL) at 0 °C was added a solution of unsaturated aldehyde (142 mg, 0.30 mmol, 1.0 equiv.) in THF (1 mL) dropwise. The reaction mixture was stirred at room temperature for 2 h before it was quenched with H_2O (0.017 mL), aqueous 15% NaOH (0.017 mL), and H_2O (0.051 mL). After addition, the mixture was stirred for 30 min before anhydrous $MgSO_4$ was added and stirred for another 30 min. After filteration, the volatiles were removed in vacuo to afford crude diol used immediately without further purification.

The crude diol was dissolved in anhydrous DCM (10 mL) and MnO_2 (391.5 mg, 4.5 mmol, 10.0 equiv) was added at room temperature. The reaction mixture was efficiently stirred at room temperature for 4 h. And the crude mixture was diluted with EtOAc (10 mL), filtered through a short Celite pad. The organic solvent was removed in vacuo, purified by column chromatography to give **51** as white solid (59.5 mg, 20% yield over 5 steps).

R_f 0.2 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +58.6 (c = 0.5, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

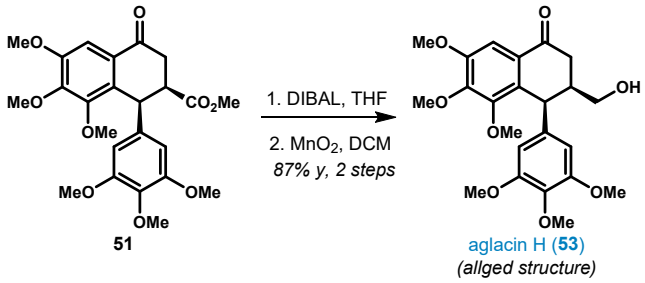
δ 9.57 (s, 1H), 7.50 (s, 1H), 6.77 (s, 1H), 6.31 (s, 2H), 4.47 (d, *J* = 7.4 Hz, 1H), 4.35 (d, *J* = 10.7 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.83 (t, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 3.73 (s, 6H), 3.52 (s, 3H), 3.23–3.15 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 195.0, 152.8, 152.7, 152.4, 150.7, 145.8, 138.6, 137.2, 134.9, 128.3, 126.4, 108.4, 105.9, 62.7, 60.8, 60.8, 60.7, 56.1, 56.1, 43.2, 41.2.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1857, found 445.1860

53: originally assigned structure of aglacin H[40]



DIBAL (1.0 M, 4.0 mL, 4.0 mmol, 4.0 equiv.) was added dropwisely to a solution of **51** (460 mg, 1.0 mmol, 1.0 equiv.) in THF (10.0 mL) at -78 °C. The resulting mixture was stirred at this temperature for 1 h and at RT for 1h. The reaction was then recooled to 0 °C, quenched with sat. aq. potassium sodium tartrate (10.0 mL), and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (3 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*.

The above dried residue was dissolved in CH_2Cl_2 (5.0 mL) and activated MnO_2 (870 mg, 10.0 mmol, 10 equiv.) was added. The suspension was vigorously stirred at RT for 4 h, then filtered through celite and washed with EtOAc. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford the alleged aglacin H **53** as white solid (375 mg, 87% over 2 steps).

R_f 0.30 (PE/EtOAc = 1:2, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +239.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

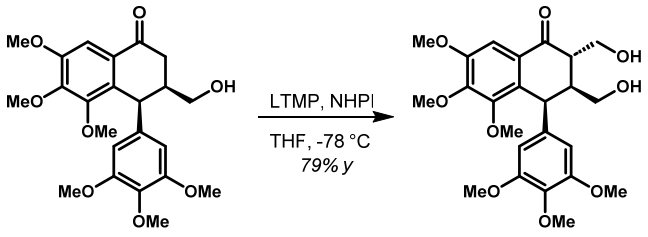
δ 7.43 (s, 1H), 6.29 (s, 2H), 4.73 (d, *J* = 4.7 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.77 (s, 3H), 3.70 (s, 6H), 3.43 (d, *J* = 6.0 Hz, 2H), 3.38 (s, 3H), 2.60 (dt, *J* = 13.0 & 5.6 Hz, 1H), 2.42 (d, *J* = 9.1 Hz, 2H), 1.85 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 196.4, 152.1, 151.9, 149.6, 147.0, 136.1, 133.4, 133.2, 127.1, 106.0, 103.9, 63.3, 60.0, 59.9, 59.7, 55.3, 55.1, 39.9, 39.0, 35.3.

HRMS (ESI) $C_{23}H_{29}O_8$ $[M+H]^+$: calcd 433.1862, found 433.1867.

54: (2S,3S,4S)-2,3-Bis(hydroxymethyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxyphenyl)-3,4-dihydro-naphthalen-1(2H)-one



By modifying the procedure reported by Bischoff and co-workers:[41] A solution of 1.6 M n-BuLi in hexanes (1.0 mL, 4.5 equiv., 1.6 mmol) was added to 2,2,6,6-tetramethylpiperidine (0.27 mL, 4.5 equiv., 1.6 mmol) in THF (2.2 mL) at -10 °C. The mixture was stirred for 30 min at 0 °C and then cooled to -78 °C. A solution of **53** (151 mg, 0.35 mmol, 1.0 equiv.) in THF (1.2 mL, 0.3 M) was added dropwise and stirred for 30 min at -78°C. A solution of N-(hydroxymethyl)phthalimide (NHPI, 124 mg, 0.70 mmol, 2.0 equiv.) in THF (3.5 mL) was then added dropwise. The mixture was stirred for another 2 h at -78°C, quenched with sat. aq. NH_4Cl (2 mL) and extracted with EtOAc (3 × 8 mL). The combined organic phase was washed with brine (3 mL), dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography to afford the desired adduct **54** as white solid (127 mg, 79% y).

R_f 0.25 (PE/EtOAc = 1:3, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +198.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

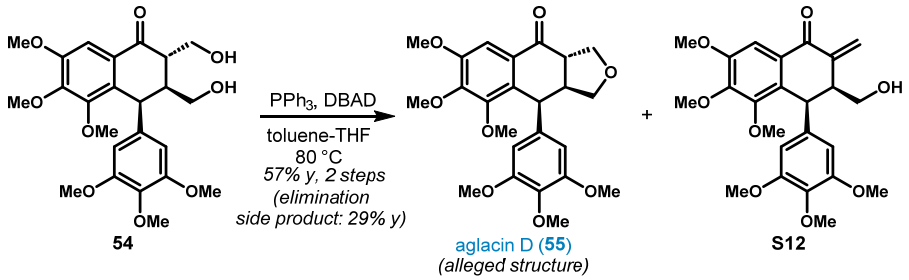
δ 7.44 (s, 1H), 6.35 (s, 2H), 4.75 (d, *J* = 4.6 Hz, 1H), 4.26 (dd, *J* = 11.6 & 3.1 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.87–3.76 (m, 5H), 3.74–3.68 (m, 7H), 3.39 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 199.3, 153.1, 152.9, 150.2, 148.1, 137.1, 134.9, 133.7, 127.4, 106.8, 104.9, 63.2, 60.9, 60.8, 60.6, 59.7, 56.2, 56.0, 46.9, 41.8, 40.5.

HRMS (ESI) $C_{24}H_{31}O_9$ $[M+H]^+$: calcd 463.1968, found 463.1962.

55: originally assigned structure of aglacin D[42]



To a solution of diol **54** (20 mg, 0.04 mmol, 1.0 equiv.) in THF/toluene (0.4 mL/0.4 mL) under were added dibenzyl azodicarboxylate (DBAD, 26 mg, 0.08 mmol, 2.0 equiv.) and triphenylphosphine (23 mg, 0.08 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 9 hours. After cooled to RT, the reaction was quenched with H_2O (1.0 mL) and extracted with EtOAc (3 × 2 mL). The combined organic

phase was washed with brine (3 mL), dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography to afford the alleged aglacin D **55** (11 mg, 57% y) as white solid and elimination side product **S12** as colorless oil (6 mg, 29% y).

Characterization data of **55**:

R_f 0.80 (PE/EtOAc = 1:2, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +53.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.46 (s, 1H), 6.17 (s, 2H), 4.73 (d, *J* = 5.2 Hz, 1H), 4.11 (t, *J* = 8.4 Hz, 1H), 4.08 (t, *J* = 7.3 Hz, 1H), 3.94 (s, 4H), 3.89 (s, 3H), 3.82 (s, 3H), 3.74 (s, 3H), 3.39 (s, 3H), 3.30 (dd, *J* = 10.9 & 7.7 Hz, 1H), 3.21 (dt, *J* = 17.5 & 9.5 Hz, 1H), 2.83 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 194.7, 152.2, 152.0, 150.1, 146.7, 136.3, 132.9, 132.6, 127.9, 105.7, 103.8, 68.8, 65.6, 59.9, 59.7, 59.5, 55.3, 55.1, 45.8, 44.6, 39.6.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1860.

Characterization data of **S12**:

R_f 0.50 (PE/EtOAc = 1:2, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +79.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

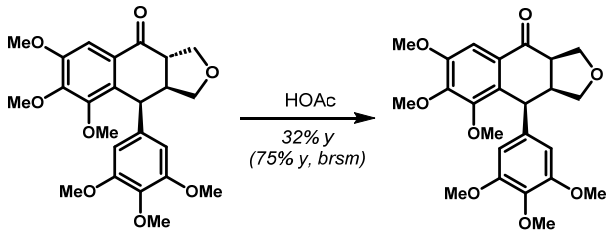
δ 7.52 (s, 1H), 6.37–6.30 (m, 1H), 6.28 (s, 2H), 5.14 (d, *J* = 2.5 Hz, 1H), 4.82 (d, *J* = 5.2 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.87 (dd, *J* = 10.4 & 5.1 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 6H), 3.58–3.50 (m, 1H), 3.46 (s, 3H), 3.21 (m, 1H), 1.77 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 187.4, 153.0, 152.7, 150.4, 147.8, 142.3, 136.8, 134.3, 134.0, 127.5, 121.5, 106.7, 105.8, 61.6, 60.9, 60.8, 60.8, 56.1, 56.1, 46.0, 40.8.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1860.

56: (3aS,9S,9aS)-6,7,8-Trimethoxy-9-(3,4,5-trimethoxyphenyl)-3,3a,9,9a-tetrahydronaphtho[2,3-c]-furan-4(1H)-one



Prepared by modifying the procedure reported by López-Pérez and co-workers:[43] To **55** (28 mg, 0.06 mmol, 1.0 equiv.) was added HOAc (1.8 mL). The reaction mixture was refluxed for 5 h. After cooled to RT, the reaction was quenched by careful addition of sat. aq. $NaHCO_3$ (3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (3 mL) and dried over Na_2SO_4, filtered and the filtrated was concentrated in *vacuo*. Purification by flash chromatography (petroleum ether/EA=5:1) afforded alcohol **56** as colorless oil (9 mg, 32% y) and recovered **55** (16 mg).

R_f 0.25 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = +111.0 (c = 0.58, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.34 (s, 1H), 6.18 (s, 2H), 4.64–4.60 (m, 1H), 4.10 (dd, *J* = 8.4 & 5.3 Hz, 1H), 4.03 (t, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.79 (s, 3H), 3.78–3.74 (m, 1H), 3.73 (s, 6H),

3.70–3.63 (m, 1H), 3.42 (s, 3H), 3.24–3.15 (m, 2H).

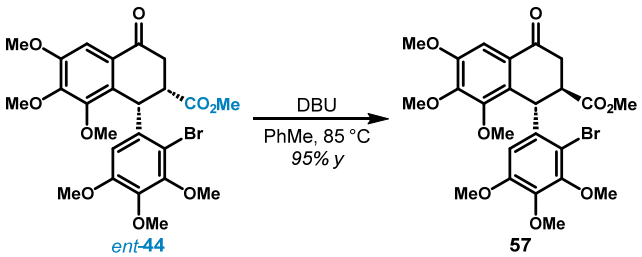
^{13}C NMR (125 MHz, $CDCl_3$)

δ 197.7, 153.0, 150.7, 147.8, 137.9, 136.8, 131.7, 128.9, 105.8, 104.6, 70.4, 69.7, 60.9, 60.8, 60.7, 56.1, 56.1, 48.8, 42.1, 39.3.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1860.

3.5 Synthesis of Authentic Aglacins, Lyoniresinol Dimethyl Ether, Lyoniresinol and Ovafolinin D (from 2j')

57: Methyl (1S,2R)-1-(2-Bromo-3,4,5-trimethoxyphenyl)-6,7,8-trimethoxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate



To a solution of *ent*-**44** (2.0 g, 3.7 mmol, 1.0 equiv.) in toluene (18.5 mL) was added DBU (2.4 mL, 18.6 mmol, 5.0 equiv.) at RT. The mixture was then stirred at 85°C for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford the desired product **57** as white solid (1.9 g, 95%).

R_f 0.45 (PE/EtOAc = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -97.67 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

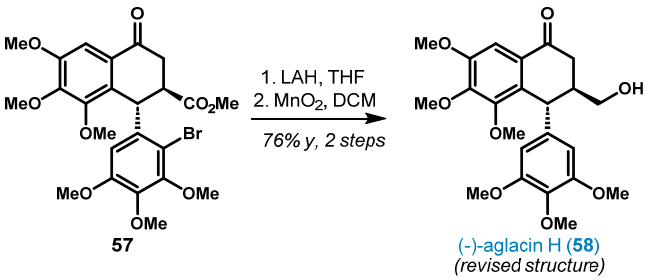
δ 7.47 (s, 1H), 5.94 (s, 1H), 5.43 (s, 1H), 3.94 (s, 6H), 3.91 (s, 3H), 3.85 (s, 3H), 3.66 (s, 3H), 3.60 (s, 3H), 3.51 (s, 3H), 3.39 (dt, *J* = 5.0 & 2.4 Hz, 1H), 2.93–2.89 (m, 1H), 2.61 (dd, *J* = 17.5 & 5.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 194.8, 173.4, 153.2, 152.4, 151.5, 150.6, 148.0, 142.3, 136.1, 129.5, 128.1, 111.0, 108.7, 104.8, 61.1, 61.0, 60.9, 60.7, 56.2, 56.0, 52.5, 43.8, 40.2, 35.2.

HRMS (ESI) $C_{24}H_{28}BrO_9$ $[M+H]^+$: calcd 539.0917/541.0900, found 539.1032/541.1003.

58: (-)-Aglacin H (revised structure).



A solution of **57** (538 mg, 1.0 mmol, 1.0 equiv.) in THF (10.0 mL) was added dropwise to a suspension of $LiAlH_4$ (228 mg, 6.0 mmol, 6.0 equiv.) in THF (2.5 mL) at 0 °C. The mixture was allowed to stir at RT for 1 h and then cooled to 0 °C. The reaction was quenched by careful addition of H_2O (0.25 mL), 15% aq.

NaOH (0.25 mL) and H_2O (0.7 mL). Some Na_2SO_4 was added, and the mixture was filtered. The filtrate was concentrated in *vacuo*.

To the above dried residue were added CH_2Cl_2 (5.0 mL) and activated MnO_2 (1.3 g, 15.0 mmol, 15 equiv.). The suspension was vigorously stirred at RT for 4 h, filtered through celite and washed with EtOAc. The filtrate was concentrated and the residue was purified by flash chromatography to afford the desired aglacin H as colorless oil (328 mg, 76% y over 2 steps).

R_f 0.30 (PE /EtOAc = 1:2, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -82.05 (c = 1.0, $CHCl_3$); Lit.[40] $[\alpha]^{20}_D$ = -40 (c = 0.57, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

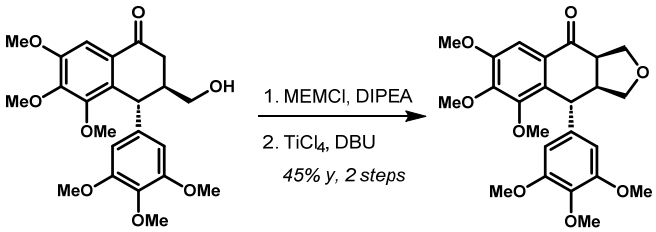
δ 7.44 (s, 1H), 6.25 (s, 2H), 4.63 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 3.74 (s, 6H), 3.71–3.60 (m, 2H), 3.49 (s, 3H), 2.77 (dd, *J* = 17.4 & 5.2 Hz, 1H), 2.57–2.50 (m, 1H), 2.46 (dd, *J* = 17.5 & 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 196.4, 153.0, 152.6, 151.3, 147.8, 139.4, 136.5, 130.1, 127.8, 105.1, 104.3, 64.7, 60.7, 60.6, 60.6, 56.0, 55.8, 44.4, 39.5, 36.1.

HRMS (ESI) $C_{23}H_{29}O_8$ $[M+H]^+$: calcd 433.1862, found 433.1862.

59: (-)-Aglacin D (revised structure).



(-)-aglacin H (**58**) (-)-aglacin D (**59**) *(revised structure)*

By modifying literature procedures:[44] To a stirred solution of **58** (216 mg, 0.5 mmol, 1.0 equiv.) in $CHCl_3$ (5 mL) were added 2-methoxyethoxymethyl chloride (MEMCl, 0.28 mL, 2.5 mmol, 5.0 equiv.) and DIPEA (0.87 mL, 5.0 mmol, 10.0 equiv.) sequentially at 0 °C. The reaction mixture was stirred at RT for 8 h, quenched by addition of sat. aq. $NaHCO_3$ (3 mL), and extracted with EtOAc (3 × 3 mL). The combined organic extracts were washed with brine (3 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*.

To a stirred solution of the above dried residue in DCM (0.2 mL) at -78 °C was added DBU (9.1μL, 0.12 mmol, 6.0 equiv.). A solution of $TiCl_4$ in THF (1.0 M, 0.12 mL, 0.12 mmol, 6.0 equiv.) was added dropwise, and the reaction was then stirred at -20 °C for 3.5 hours. The reaction was quenched by addition of sat. aq. $NaHCO_3$ (0.3 mL) and extracted with DCM (3 × 0.5 mL). The combined organic extracts were washed with brine (3 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. Purification by flash chromatography of the residue afforded the authentic algacin D **59** as colorless oil (4.3 mg, 45% y over 2 steps).

R_f 0.55 (PE/EtOAc = 1:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -120.48 (c = 0.58, $CHCl_3$); Lit.[42] $[\alpha]^{20}_D$ = -87.2 (c = 0.58, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

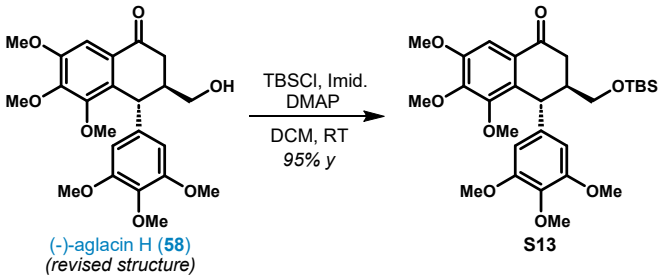
δ7.43 (s, 1H), 6.24 (s, 2H), 4.52 (s, 1H), 4.28 (d, *J* = 8.7 Hz, 1H), 4.19 (t, *J* = 8.2 Hz, 1H), 3.97 (m, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.79 (s, 3H), 3.74 (s, 6H), 3.52 (s, 3H), 3.44 (t, *J* = 8.6 Hz, 1H), 3.07–2.97 (m, 2H).

^{13}C NMR (125 MHz, CDCl3)

δ197.7, 153.4, 153.1, 151.2, 148.2, 140.2, 136.8, 130.1, 127.6, 105.1, 104.7, 73.1, 71.9, 60.9, 60.9, 60.9, 56.2, 56.1, 47.0, 46.0, 37.4.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1866.

S13: (3R,4R)-3-(((*tert*-Butyldimethylsilyl)oxy)methyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxy-phenyl)-3,4-dihydronaphthalen-1(2H)-one



(-)-aglacin H (**58**)
(revised structure)

S13

To a solution of **58** (110 mg, 0.25 mmol, 1.0 equiv.) and imidazole (52 mg, 0.76 mmol, 3.0 equiv.) in DCM (5 mL) was added TBSCl (57 mg, 0.38 mmol, 1.5 equiv.) at 0 °C. The reaction mixture was allowed to warm to RT and stirred overnight. The mixture was concentrated, and the residue was purified by flash chromatography to give **S13** as colorless oil (130 mg, 95% yield).

R_f 0.40 (PE/EtOAc = 3:1, UV/phosphomolybdic acid stain)

Opt. Rot. $[\alpha]^{20}_D$ = -86.60 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, MeOH-d_4)

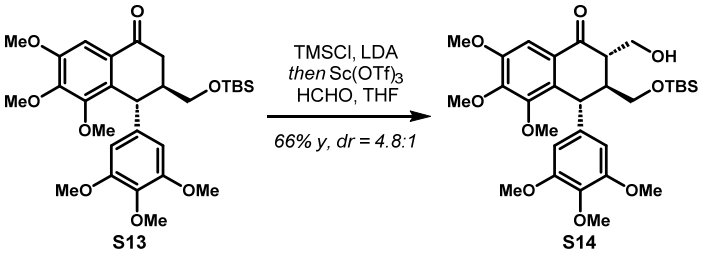
δ 7.47 (s, 1H), 6.35 (s, 2H), 4.66 (s, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.75–3.72 (m, 10H), 3.64 (dd, *J* = 10.2 & 7.3 Hz, 1H), 3.50 (s, 3H), 2.74 (dd, *J* = 17.3 & 5.4 Hz, 1H), 2.51–2.45 (m, 1H), 2.43 (dd, *J* = 17.4 & 2.8 Hz, 1H), 0.86 (s, 9H), -0.01 (d, *J* = 4.4 Hz, 6H).

^{13}C NMR (125 MHz, MeOH-d_4)

δ 198.5, 198.5, 154.6, 154.3, 152.7, 149.4, 142.0, 137.8, 132.3, 129.6, 106.5, 105.4, 67.0, 61.2, 61.2, 61.1, 56.6, 56.4, 46.0, 41.6, 37.3, 26.3, 19.1, -5.5, -5.5.

HRMS (ESI) $C_{29}H_{43}O_8Si$ $[M+H]^+$: calcd 547.2727, found 547.2731.

S14: (2S,3S,4R)-3-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-(hydroxymethyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one



S13 **S14**

Prepared according to the method developed by Kobayashi and Hachiya:[45] To a solution of LDA in THF (5 mL, 1.38 mmol, 2.0 equiv.) was added a solution of **S13** (300 mg, 0.55 mmol, 1.0 equiv.) in THF (2.7 mL) dropwise via syringe at -78 °C. The resulting mixture was stirred for 30 min, and TMSCl (0.27 mL, 2.08 mmol, 3.0 equiv.) was added dropwise via syringe. After further stirred at -78 °C for 20 min, the reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with TBME (3 × 10 mL). The combined organic phase was washed with water (5 × 5 mL), brine (5 mL) and concentrated in *vacuo*.

To a stirred solution of crude silyl enol ether obtained above in THF (6 mL) at -20 °C were added aq. 37% formaldehyde (1.2 mL, 13.8 mmol, 25 equiv.) and $Sc(OTf)_3$ (34 mg, 0.07 mmol, 0.12 equiv.). The reaction mixture was stirred at -20 °C overnight, then quenched with saturated aqueous $NaHCO_3$ (10 mL). and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL),

dried over Na_2SO_4, filtered. The filtrate was concentrated and the residue was purified by flash chromatography to give adduct **S14** as white solid (209 mg, 66% y, 4.8:1 dr).

R_f 0.20 (PE/EtOAc = 2:1, UV/phosphomolybdic acid stain)

Opt. Rot. $[\alpha]^{20}_D$ = -77.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, CD_3OD)

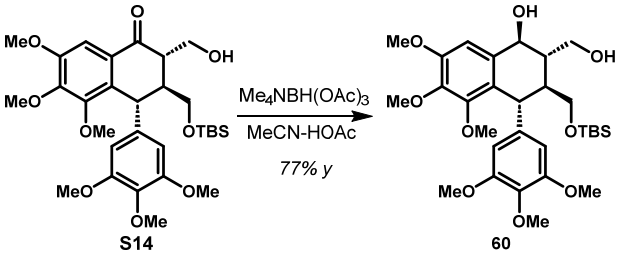
δ 7.40 (s, 1H), 6.31 (s, 2H), 4.58 (d, *J* = 4.9 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.72 (s, 9H), 3.71–3.58 (m, 5H), 3.38 (s, 3H), 2.58 (m, 2H), 0.90 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD)

δ 198.2, 153.0, 153.0, 151.5, 147.8, 142.4, 136.3, 131.2, 128.5, 105.5, 104.2, 63.6, 60.1, 59.8, 59.7, 59.3, 55.2, 55.0, 49.8, 44.8, 40.3, 24.9, 17.7, -6.7, -6.9.

HRMS (ESI) $C_{30}H_{44}O_9SiNa$ $[M+Na]^+$: calcd 599.2652, found 599.2664.

60: (1S,2S,3S,4R)-3-(((tert-butyldimethylsilyl)oxy)methyl)-2-(hydroxymethyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol



Prepared according to the method developed by Evans and co-workers:[46] To a solution of **S14** (200 mg, 0.35 mmol) in MeCN (2.2 mL) at -10 °C was added a solution of $Me_4NBH(OAc)_3$ (727 mg, 2.78 mmol, 8 equiv.) in MeCN/HOAc (7 mL /2.2 mL). The resulting mixture was stirred at -10 °C for 12 h, then quenched with aq. ammonia solution (ca. 28%, 10 mL) and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered. The filtrate was concentrated and the residue was purified by flash chromatography to afford the desired diol **60** as colorless oil (184 mg, 77% yield).

R_f 0.5 (PE/Acetone = 2:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = -22.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

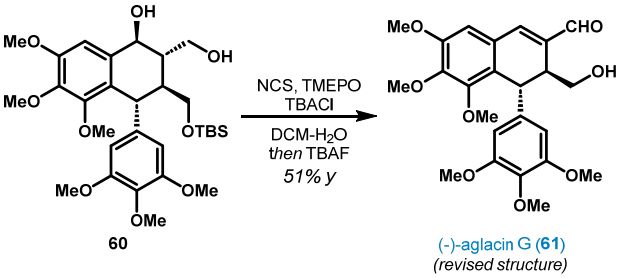
δ 7.04 (s, 1H), 6.25 (s, 2H), 4.77 (dd, *J* = 10.3 & 3.9 Hz, 1H), 4.14 (d, *J* = 6.7 Hz, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.73 (s, 6H), 3.62–3.55 (m, 2H), 3.54–3.51 (m, 1H), 3.32 (s, 3H), 3.01 (s, 1H), 1.97–1.89 (m, 1H), 1.59–1.49 (m, 1H), 0.86 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 152.9, 152.4, 151.5, 142.4, 141.1, 136.6, 136.2, 123.4, 105.4, 103.2, 70.7, 64.2, 63.9, 60.8, 60.5, 59.9, 56.1, 55.8, 46.9, 45.6, 41.6, 25.8, 25.7, 18.1, -5.5, -5.6.

HRMS (ESI) $C_{30}H_{46}O_9SiNa$ $[M+Na]^+$: calcd 601.2809, found 601.2809.

61: (-)-Aglacin G (revised structure)[40]



A solution of **60** (15 mg, 0.026 mmol, 1.0 equiv.), TEMPO (4.7 mg, 0.026 mmol, 1.0 equiv.), TBACl (0.0026 mmol, 1.0 mg, 0.1 equiv.) in 1.0 mL of dichloromethane and 1.0 mL of an aqueous solution containing $NaHCO_3$ (0.5 M) and K_2CO_3 (0.05 M) were vigorously stirred at room temperature. NCS (23 mg, 0.172 mmol, 2.0 equiv.) was then added. Stirring was maintained for 12 h. Then the organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 3 mL). The CH_2Cl_2 extracts were washed with brine (5 mL), dried over Na_2SO_4, and evaporated. The residue was concentrated and used directly without further purification.

To the residue obtained above in THF (1.0 mL) at room temperature was added TBAF (1M in THF, 0.081 mL, 0.081 mmol, 3.1 equiv.). The mixture was stirred at room temperature for 4 h. Then the reaction mixture was quenched with water (2 mL), and extracted with EtOAc (3 × 3 mL). The organic extracts were washed with brine (3 mL), dried over Na_2SO_4, evaporated, and purified by column chromatography eluted with PE/EA=2/1 to yield **61** as white solid (5.9 mg, 51% yield).

R_f 0.5 (PE/Acetone = 2:1, $KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -30.0 (c = 2.1, $CHCl_3$); Lit.[40]: $[\alpha]^{20}_D$ = -42 (c = 0.78, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

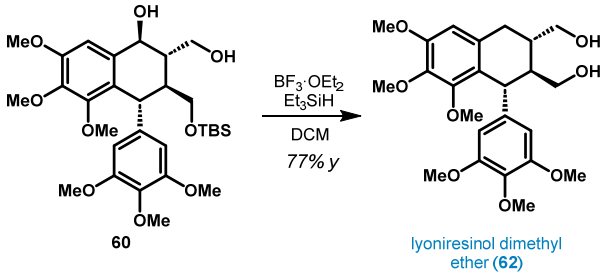
δ 9.58 (s, 1H), 7.30 (s, 1H), 6.76 (s, 1H), 6.20 (s, 2H), 4.66 (s, 1H), 3.92 (s, 6H), 3.91 (s, 6H), 3.76 (s, 3H), 3.71 (s, 6H), 3.64–3.60 (m, 1H), 3.59 (s, 4H), 3.43–3.36 (m, 1H), 3.30 (dd, J = 8.6, 5.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.9, 153.0, 152.8, 152.2, 146.1, 145.3, 139.4, 137.2, 136.6, 126.7, 125.1, 108.4, 104.6, 68.0, 63.8, 60.9, 60.8, 56.1, 56.1, 42.1, 38.0, 25.6.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1863, found 445.1872.

62: (-)-Lyoniresinol dimethyl ether



To a solution of the diol **60** (80 mg, 0.16 mmol, 1.0 equiv.) in DCM (3.0 mL) was added triethylsilane (0.12 mL, 0.96 mmol, 6.0 eq) at room temperature. The reaction mixture was cooled to 0 °C and boron trifluoride etherate (0.04 mL, 0.48 mmol, 3.0 eq) was added dropwise via syringe. After that, the reaction mixture was stirred at 0 °C for an additional 10 min and quenched with H_2O (3 mL). The resulting mixture was extracted with DCM (3 mL × 3). The combined organic phase was washed with brine (4 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford (-)-lyoniresinol dimethyl ether **62** as white solid (79.7 mg, 77% yield).

R_f 0.5 (PE/Acetone = 2:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = -47.0 (c = 0.67, $CHCl_3$); Lit.[47]: $[\alpha]^{28}_D$ = -20.7 (c = 0.58, EtOH).

^{1}H NMR (600 MHz, $CDCl_3$)

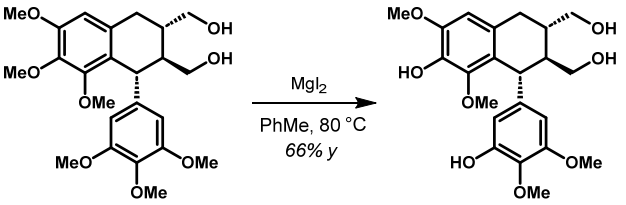
δ 6.46 (s, 1H), 6.34 (s, 2H), 3.97 (d, J = 8.2 Hz, 1H), 3.87 (d, J = 3.5 Hz, 1H), 3.86 (s, 3H), 3.84 – 3.81 (m, 1H), 3.80 (s, 3H), 3.77 (s, 6H), 3.76 (s, 3H), 3.67 (dd, J = 10.9, 6.7 Hz, 1H), 3.63 (dd, J = 11.0, 6.0 Hz, 1H), 3.22 (d, J = 0.8 Hz, 3H), 2.73 (dd, J = 15.4, 12.0 Hz, 1H), 2.63 (dd, J = 15.5, 3.9 Hz, 1H), 1.92–1.86 (m, 1H), 1.79 (tdd, J = 13.6, 7.0, 3.9 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 152.8, 152.1, 152.0, 143.3, 140.7, 136.1, 133.1, 125.0, 106.6, 105.8, 66.6, 63.7, 60.9, 60.5, 59.5, 56.2, 55.8, 49.4, 43.7, 40.2, 34.0.

HRMS (ESI) $C_{24}H_{33}O_8$ $[M+H]^+$: calcd 449.2175, found 449.2187.

63: (-)-Lyoniresinol



To a solution of **62** (14 mg, 0.03 mmol, 1.0 equiv.) in toluene (0.3 mL, 0.1 M) was added a solution of MgI_2 in diethyl ether (0.4 M, 0.75 mL, 0.3 mmol, 10.0 equiv.) at RT. The resulting mixture was then stirred at 80°C for another 13 h, then quenched with sat. NH_4Cl (1.0 mL) and extracted with EtOAc (3 × 8.0 mL). The combined organic layers were washed with brine (1 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ DCM/MeOH =5:5:1) to afford lyoniresinol **63** as colorless oil (8 mg, 66% y).

R_f 0.65 (DCM/MeOH = 10:1, UV/phosphomolybdic acid stain)

Opt. Rot. $[\alpha]^{20}_D$ = -34.2 (c = 2.0, MeOH); Lit.[48]: $[\alpha]^{28}_D$ = -56.3 (c = 0.28, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$)

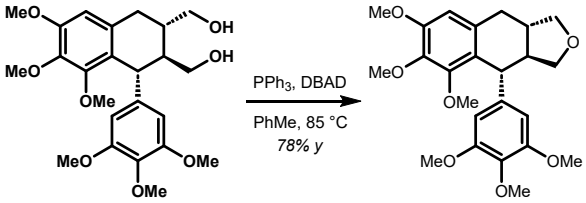
δ 6.45 (s, 1H), 6.35 (s, 2H), 5.34 (s, 2H), 4.02 (d, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 3.85–3.74 (m, 9H), 3.64 (dd, *J* = 10.8 & 6.7 Hz, 1H), 3.58 (dd, *J* = 11.0 & 6.0 Hz, 1H), 3.30 (s, 3H), 2.68 (dd, *J* = 15.3 & 11.8 Hz, 1H), 2.59 (dd, *J* = 15.2 & 4.3 Hz, 1H), 1.94–1.89 (m, 1H), 1.80–1.72 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 146.8, 146.2, 145.6, 138.4, 137.1, 132.9, 128.7, 125.3, 105.9, 105.4, 66.8, 64.0, 59.5, 56.5, 56.1, 49.6, 43.2, 40.4, 33.6.

HRMS (ESI) $C_{22}H_{28}O_8Na$ $[M+ Na]^+$: calcd 443.1682, found 443.1676.

64: (+)-Aglacin B



Iyoniresinol dimethyl ether (**62**) — (+)-aglacin B (**64**)

To a solution of **62** (294 mg, 0.656 mmol, 1.0 equiv.) and PPh_3 (343.0 mg, 1.31 mmol, 2.0 equiv.) in toluene (16.0 mL) was added DBAD (391.0 mg, 1.31 mmol, 2.0 equiv.). The mixture was stirred at 85 °C for 4 hours. Then the mixture was concentrated under reduced pressure. The residue was purified by flushinging chromatography to afford aglacin B **64** as white solid (240.0 mg, 85% y).

R_f 0.5 (PE/Acetone = 2:1, UV/$KMnO_4$)

Opt. Rot. $[\alpha]^{20}_D$ = +60.5 (c = 0.38, $CHCl_3$); Lit.[42]: $[\alpha]^{20}_D$ = +45.0 (c = 0.38, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

δ 6.48 (s, 1H), 6.27 (s, 2H), 4.16 (t, *J* = 9.0 Hz, 1H), 3.91 (t, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.83 (d, *J* = 12.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 6H), 374 (s, 3H), 3.60 (dd, *J* = 12.0 & 7.2 Hz, 1H), 3.49 (dd, *J* = 12.6 & 9.6 Hz, 1H), 3.15 (s, 3H), 2.92 (dd, *J* = 18.0 & 4.8 Hz, 1H), 2.73 (dd, *J* = 19.6 & 13.2 Hz, 1H), 2.11–2.00 (m, 1H), 2.00–1.88 (m, 1H).

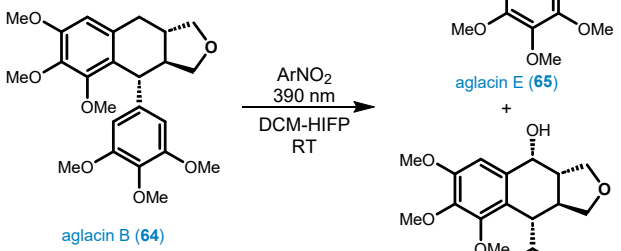
^{13}C NMR (150 MHz, $CDCl_3$)

δ 153.1, 152.5, 152.2, 144.0, 140.7, 136.0, 133.0, 125.5, 107.4, 103.7, 77.2, 72.7, 72.5, 60.8, 60.3, 59.3, 56.1, 55.7, 52.7, 46.8, 41.6, 33.4.

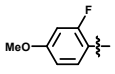
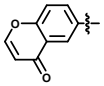
HRMS (ESI) $C_{24}H_{30}O_7Na$ $[M+Na]^+$: calcd 453.1884, found 453.1862.

65 & 66: (+)-Aglacins E & F

*A. By direct hydroxylation of aglacin B (**64**)*



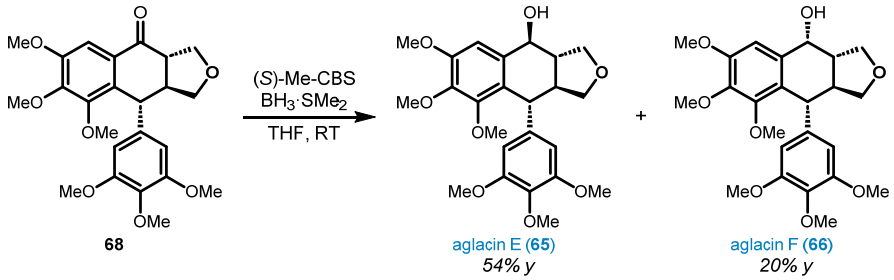
aglacin B (**64**) — aglacin E (**65**) + aglacin F (**66**)

Ar	y of **65** (%)	y of **66** (%)
	10	12
	10	12
	4	3
	10	13
	7	9
	8	12
	12	17
	8	12

Prepared by modifying the procedure reported by Parasram and co-workers:[49] A solution of $ArNO_2$ (0.02 mmol, 1.0 equiv.) and aglacin B **64** (8.6 mg, 0.02 mmol, 1.0 equiv.) in a mixture of DCM/HFIP

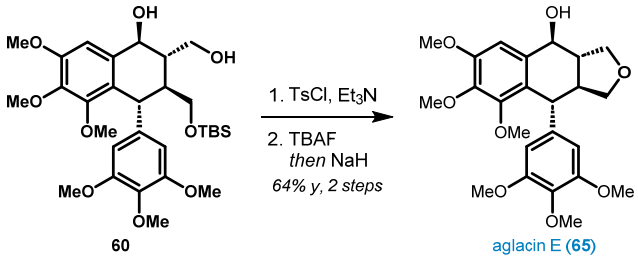
(180 μL, V/V 8:2, 0.1 M) was degassed, and placed on a stir plate in front of a 390 nm lamp with a cooling fan. After irradiated for 24 h, the reaction mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography to give **65** and **66** as colorless oil.

*B. By reduction of ketone **68***



Prepared by modifying literature procedures:[50] To a solution of (*S*)-(-)-2-methyl-CBS-oxazaborolidine in THF (60 μL, 20 mol%, 0.1 M) were sequentially added a solution of **68** (15 mg, 0.03 mmol, 1.0 equiv.) in THF (0.3 mL) and $BH_3 \cdot SMe_2$ (2.0 M in THF, 15 μL, 0.03 mmol, 1.0 equiv.) in THF (2.5 mL) dropwise. After stirred for 40 min, the reaction mixture was quenched by the addition of MeOH (0.3 mL), H_2O (1 mL), and extracted with EtOAc (3 × 2 mL). The combined organic extracts were washed with brine (2 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated and the residue was purified by flash chromatography to afford (+)-aglacin E (**65**) (8 mg, 54% y) and (+)-aglacin F (**66**) (3 mg, 20% y) as colorless oil.

*C. Aglacin E from diol **60***



To a solution of diol **60** (408 mg, 0.7 mmol, 1.0 equiv.) and *p*-TsCl (199.0 mg, 1.05 mmol, 1.5 equiv.) in DCM (7.0 mL) was added Et_3N (0.58 mL, 4.2 mmol, 6.0 equiv.) at 0 °C. After that, the reaction was stirred at RT for 2 h, then quenched by addition of sat. $NaHCO_3$ (5 mL) and extracted with DCM (3 × 5 mL). The combined organic extracts were washed with brine (7 mL), dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*.

To a solution of the the above dried crude mono tosylate (115 mg, 0.157 mmol, 1.0 equiv.) in THF (1.5 mL) was added a solution of TBAF in THF (1.0 M, 0.23 mL, 0.23 mmol, 1.5 equiv.) at 30 °C. After 10 minutes, the mixture was cooled to 0 °C, then NaH (60% dispersion in mineral oil; 168 mg, 4.2 mmol, 6.0 equiv.) was added. The resulting reaction mixture was then allowed to stirr at RT for another 30 minutes, then quenched by carefully addition of sat. $NaHCO_3$ (1 mL) and extracted with EtOAc (3 × 3 mL). The combined organic extracts were washed with brine (3 mL), dried over Na_2SO_4, filtered. The filtrate was concentrated and purification by flash chromatography of the residue afforded (+)-aglacin E (**65**) as colorless oil (52 mg, 64% y over 2 steps).

Characterization data of aglacin E (**65**):

R_f	0.30 (PE/DCM/EtOAc = 1:1:4, phosphomolybdic acid stain).
Opt. Rot.	$[\alpha]^{20}_D$ = +16.0 (c = 0.69, $CHCl_3$); Lit.[40]: $[\alpha]^{20}_D$ = +17 (c = 0.69, $CHCl_3$).
^{1}H NMR	(500 MHz, $CDCl_3$)

δ 7.05 (s, 1H), 6.24 (s, 2H), 4.75 (t, *J* = 8.9 Hz, 1H), 4.31 (t, *J* = 7.5 Hz, 1H), 3.92–3.89 (m, 1H), 3.91 (s, 3H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 6H), 3.76-3.72 (m, 1H), 3.75 (s, 3H), 3.67–3.64 (m, 1H), 3.14 (s, 3H), 2.21–2.09 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 153.2, 152.9, 151.8, 143.5, 141.7, 137.4, 136.3, 125.8, 104.0, 103.7, 73.2, 72.5, 72.1, 60.9, 60.4, 59.5, 56.2, 55.9, 50.1, 49.8, 47.1.

HRMS (ESI) $C_{24}H_{30}O_8Na$ $[M+Na]^+$: calcd 469.1838, found 469.1833

Characterization data of aglacin F (**66**):

R_f 0.25 (PE/THF = 1:1, phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = +4.4 (c = 0.41, $CHCl_3$); Lit.[40]: Aglacin F: $[\alpha]^{20}_D$ = -1 (c = 0.41, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

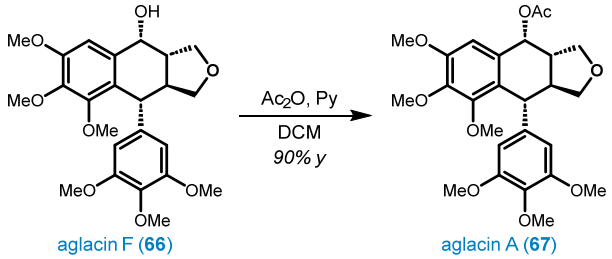
δ 6.71 (s, 1H), 6.30 (s, 2H), 4.83 (s, 1H), 4.10 (t, *J* = 7.8 Hz, 1H), 3.94 (t, *J* = 7.5 Hz, 1H), 3.91 (s, 3H), 3.87 (dd, *J* = 10.6 & 7.7 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 6H), 3.76 (s, 3H), 3.74 (d, *J* = 4.8 Hz, 1H), 3.61 (dd, *J* = 10.4 & 7.7 Hz, 1H), 3.15 (s, 3H), 2.64–2.57 (m, 1H), 2.20–2.15 (m, 1H), 1.85 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 153.2, 152.8, 152.7, 143.5, 142.7, 136.2, 135.1, 126.1, 108.3, 103.9, 72.5, 68.2, 67.3, 60.9, 60.4, 59.5, 56.2, 55.9, 46.9, 46.1, 43.7.

HRMS (ESI) $C_{24}H_{31}O_8$ $[M+H]^+$: calcd 447.2019, found 447.2011.

67: (+)-Aglacin A



A solution of (+)-aglacin F (**65**) (4.5 mg, 0.01 mmol, 1.0 equiv.), DMAP (1.2 mg, 0.01 mmol, 1.0 equiv.) in DCM (0.1 mL, 0.1 M) was added pyridine (15 μL, 0.2 mmol, 20 equiv.) and acetic anhydride (10 μL, 0.1 mmol, 10 equiv.) at 0 °C. The reaction was stirred at 0 °C for 1 h and then quenched by addition of saturated $NaHCO_3$ solution (0.1 mL). The mixture was then extracted with DCM (3 × 0.5 mL). The combined organic extracts were washed with brine (1 mL) and dried over Na_2SO_4, filtered and concentrated in *vacuo*. Purification by flash chromatography afforded alcohol (+)-aglacin A **(67)** as white solid (4.4 mg, 90% y).

R_f 0.20 (PE/THF = 4:1, phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = +20.0 (c = 0.52, $CHCl_3$); Lit.[42]: $[\alpha]^{20}_D$ = +55.6 (c = 0.52, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

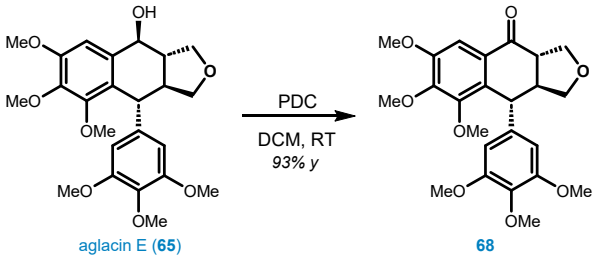
δ 6.77 (s, 1H), 6.31 (s, 2H), 6.11 (d, *J* = 2.7 Hz, 1H), 4.06 (t, *J* = 7.9 Hz, 1H), 3.94 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.79 (s, 6H), 3.77 (s, 1H), 3.76 (s, 3H), 3.59 (dd, *J* = 10.5 & 7.7 Hz, 1H), 3.48 (dd, *J* = 10.2 & 7.8 Hz, 1H), 3.14 (s, 3H), 2.63–2.56 (m, 1H), 2.30–2.24 (m, 1H), 2.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 170.8, 153.2, 152.6, 152.5, 143.5, 143.1, 136.3, 131.3, 126.8, 109.1, 104.0, 72.2, 68.3, 68.1, 61.0, 60.4, 59.5, 56.3, 55.9, 46.5, 44.8, 44.7, 21.3.

HRMS (ESI) $C_{26}H_{32}O_9Na$ $[M+Na]^+$: calcd 511.1944, found 511.1942.

68: (3aS,9R,9aS)-6,7,8-Trimethoxy-9-(3,4,5-trimethoxyphenyl)-3,3a,9,9a-tetrahydronaphtho[2,3-c]-furan-4(1H)-one



By modifying the procedure reported by López-Pérez and co-workers:[43] Aglacin E **65** (49 mg, 0.11 mmol, 1.0 equiv.) was dissolved in DCM (1.1 mL, 0.1 M) and PDC (62 mg, 0.165 mmol, 1.5 equiv.) was added at RT. The reaction suspension was vigorously stirred at RT for 2 h, then diluted with EtOAc, filtered through a short Celite pad and washed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel to give ketone **68** as yellow oil (45.8 mg, 93% y).

R_f 0.65 (PE/EtOAc = 1:3, phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = -35.4 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

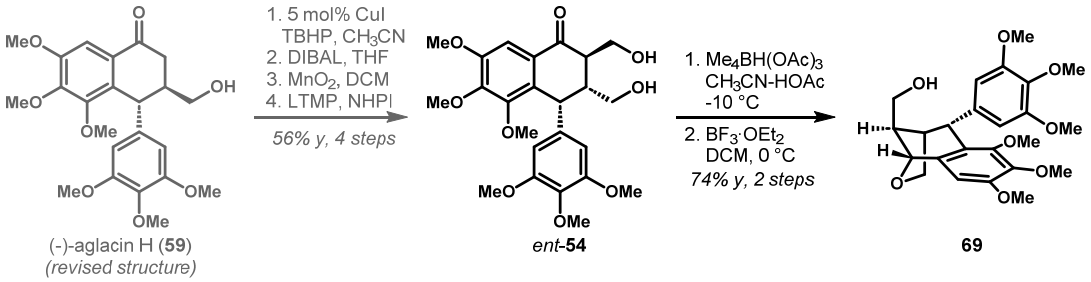
δ7.35 (s, 1H), 6.26 (s, 2H), 4.19 (t, *J* = 8.3 Hz, 1H), 4.07 (t, *J* = 9.2 Hz, 1H), 4.04 (d, *J* = 10.7 Hz, 1H), 3.93 (s, 3H), 3.85 (t, *J* = 7.4 Hz, 1H), 3.81 (d, *J* = 5.0 Hz, 6H), 3.77 – 3.69 (m, 7H), 3.14 (s, 3H), 3.00 (m, 1H), 2.59 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ195.7, 153.4, 153.2, 152.0, 147.3, 141.8, 136.6, 132.9, 130.2, 104.4, 103.7, 71.7, 66.9, 61.0, 60.6, 59.7, 56.3, 56.1, 52.2, 51.4, 47.4.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1845.

69: ((1R,4R,5S,10R)-6,7,8-Trimethoxy-5-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydro-1,4-methano-benzo[c]oxepin-10-yl)methanol



To a solution of *ent*-**54** (809 mg, 1.75 mmol, 1.0 equiv.) in CH_3CN (0.2 M, 8.7 mL) at -10 °C was added a solution of $Me_4BH(OAc)_3$ (3.67 g, 14.0 mmol, 8.0 equiv.) in CH_3CN/AcOH (26.2mL /8.7 mL) dropwise and stirred for another 12 h at -10 °C. The reaction was then quenched with aq. ammonia solution (ca. 28%, 5.0 mL) at -10 °C, extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (8 mL), dried with Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*.

To a solution of the above dried crude triol in DCM (0.1 M, 17 mL) was added a freshly prepared solution of $BF_3{\cdot}OEt_2$ in DCM (0.7 N, 11.9 mmol, 7.0 equiv.) at 0 °C and stirred for another 2 h at 0°C. Then, the reaction was quenched with sat. $NaHCO_3$ (5.0 mL) and extracted by DCM (4 × 20 mL). The combined organic layers were washed with brine (17 mL), dried with Na_2SO_4, filtered and the filtrate was concentrated. The residue was purified by flash chromatography to afford the desired product **69** as white solid (790 mg, *quant.*).

R_f 0.45 (EtOAc, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = -30.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

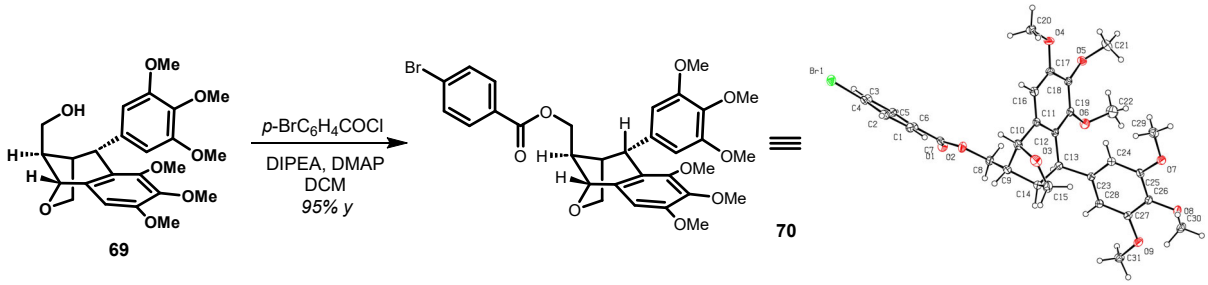
δ j6.52 (s, 1H), 6.30 (s, 2H), 4.71 (d, *J* = 4.9 Hz, 1H), 4.38 (d, *J* = 5.1 Hz, 1H), 3.91 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.78 (s, 8H), 3.73–3.64 (m, 3H), 3.59 (dd, *J* = 10.8 & 7.5 Hz, 1H), 3.40 (s, 3H), 2.77 (ddd, *J* = 12.0, 7.6 & 4.4 Hz, 1H), 2.64 (q, *J* = 4.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 153.1, 152.8, 152.3, 142.6, 140.0, 136.9, 134.5, 122.1, 106.7, 105.9, 77.7, 69.7, 60.8, 60.5, 60.2, 59.8, 56.3, 56.3, 56.0, 48.4, 43.9, 42.4.

HRMS (ESI) $C_{24}H_{29}O_7$ $[M+H–H_2O]^+$: calcd 429.1913, found 429.1942.

70: ((1R,4R,5R,10R)-6,7,8-Trimethoxy-5-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydro-1,4-methanobenzo[c]oxepin-10-yl)methyl 4-bromobenzoate



To a solution of **69** (60 mg, 0.13 mmol, 1.0 equiv.) in DCM (1.3 mL, 0.1 M) were sequentially added DIPEA (0.53 mmol, 4.0 equiv.), DMAP (0.04 mmol, 0.3 equiv.) and 4-bromobenzoyl chloride (0.33 mmol, 2.5 equiv.) at 0 °C. The reaction was allowed to stir at RT for another 3 h, then quenched with sat. $NaHCO_3$. (1.0 mL) and extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (1 mL), dried with Na_2SO_4, filtered and the filtrate was concentrated. The residue was purified by flash chromatography to afford the desired ester **70** as white solid (80 mg, 95% y).

R_f 0.30 (PE/EtOAc = 2:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = -36.4 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

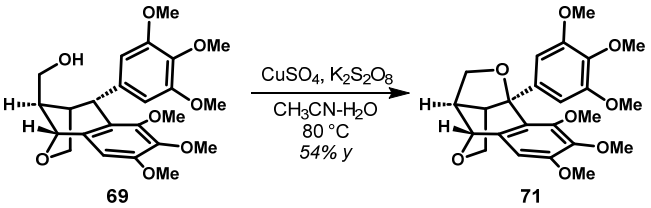
δ 7.96–7.82 (m, 2H), 7.74–7.57 (m, 2H), 6.53 (s, 1H), 4.78 (d, *J* = 4.9 Hz, 1H), 4.49–4.37 (m, 2H), 4.16 (dd, *J* = 11.4 & 7.6 Hz, 1H), 3.85 (m, 17H), 3.39 (s, 1H), 2.98 (dt, *J* = 7.2 & 3.6 Hz, 1H), 2.70 (q, *J* = 4.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.7, 152.9, 152.4, 142.5, 139.8, 136.4, 133.9, 131.9, 131.1, 128.9, 128.3, 121.6, 106.4, 105.2, 77.8, 69.6, 62.8, 60.9, 60.6, 60.0, 56.2, 55.9, 44.8, 43.9, 42.6.

HRMS (ESI) $C_{24}H_{29}O_7$ $[M+H]^+$: calcd 629.1386, found 629.1382.

71: (1S,4R,5R)-7,8,9-Trimethoxy-1-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydro-5,1,4-(epoxyethane-[1,2,2]triyl)benzo[c]oxepine



Prepared by modifying the procedure reported by LaLonde and co-workers:[51] To a flask containing **69** (75 mg, 0.16 mmol, 1.0 equiv.), $K_2S_2O_8$ (91 mg, 2.0 equiv.) and $CuSO_4{\cdot}5H_2O$ (42 mg, 1.0 equiv.) were added CH_3CN (0.05 M, 3.3 mL) and H_2O (0.05 M, 3.3 mL). The mixture was stirred at 80 °C for 1 h, then quenched with sat. $NaHCO_3$. (2.0 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (1 mL), dried with Na_2SO_4 and filtered. The filtrate was concentrated and the residue was purified by flash chromatography to afford the desired product **71** as white solid (40 mg, 54% y).

R_f 0.65 (PE/EtOAc = 1:2, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = -134.5 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)

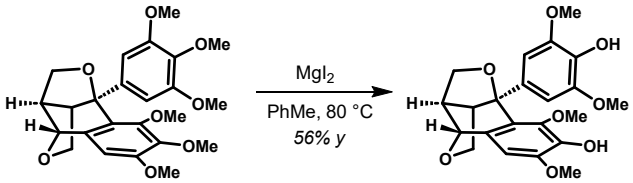
δ 7.07 (s, 1H), 6.61 (s, 1H), 6.39 (s, 1H), 4.82 (d, *J* = 5.3 Hz, 1H), 4.25 (dd, *J* = 9.5 & 6.4 Hz, 1H), 4.04 (dd, *J* = 9.8 & 6.2 Hz, 1H), 3.94 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.46 (d, *J* = 9.5 Hz, 1H), 3.32 (s, 3H), 3.12 (q, *J* = 6.1 Hz, 1H), 2.72 (t, *J* = 6.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 154.0, 153.2, 152.5, 152.4, 143.4, 139.7, 136.3, 131.1, 121.1, 106.7, 101.2, 100.1, 85.9, 81.0, 64.3, 64.1, 60.9, 60.6, 57.9, 56.1, 56.0, 55.9, 49.0.

HRMS (ESI) $C_{24}H_{29}O_8$ $[M+H]^+$: calcd 445.1862, found 445.1900.

72: (-)-Ovafolinin D



To a solution of **71** (44 mg, 0.1 mmol, 1.0 equiv.) in toluene (1.0 mL, 0.1 M) was added a solution of MgI_2 in diethyl ether (0.4 N, 0.5 mmol, 5.0 equiv., 1.25 mL) dropwise at RT. The reaction was then stirred at 80 °C for 1.5 h. After cooled, it was quenched with sat. NH_4Cl (1.0 mL) and extracted with EtOAc (4 × 3 mL). The combined organic layers were dried over Na_2SO_4, filtered and the filtrate was concentrated. The residue was purified by flash chromatography to furnish ovafolinin D (**72**) as white solid (23 mg, 56% y).

R_f 0.45 (PE/EtOAc = 1:2, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = -26.4 (c = 0.09, MeOH); Lit.[52]: $[\alpha]^{20}_D$ = -33.0 (c = 0.09, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.11 (s, 1H), 6.63 (s, 1H), 6.44 (s, 1H), 5.60 (s, 1H), 5.46 (s, 1H), 4.83 (d, *J* = 5.4 Hz, 1H), 4.26 (dd, *J* = 9.4, 6.4 Hz, 1H), 4.01 (dd, *J* = 9.7, 6.3 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.87 (d, *J* = 9.8 Hz, 1H), 3.77 (s, 3H), 3.49 (d, *J* = 9.5 Hz, 1H), 3.33 (s, 3H), 3.12 (q, *J* = 6.4 Hz, 1H), 2.72 (t, *J* = 6.4 Hz, 1H).

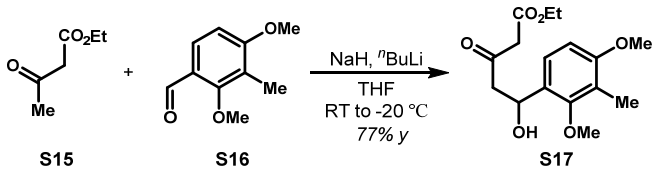
^{13}C NMR (125 MHz, $CDCl_3$)

δ 147.7, 146.7, 146.5, 145.4, 139.9, 134.3, 133.3, 126.7, 121.1, 106.6, 101.7, 100.1, 86.0, 81.2, 64.1, 64.0, 61.0, 58.4, 56.3, 56.3, 56.1, 48.9.

HRMS (ESI) $C_{22}H_{25}O_8$ $[M+H]^+$: calcd 417.1549, found 417.1559.

3.6 Synthesis and Structure Revision of (+)-Fimbricalyxoid A

S17: Ethyl 5-(2,4-dimethoxy-3-methylphenyl)-5-hydroxy-3-oxopentanoate



S15 S16 S17

To a solution of NaH (60% in oil, 3.80 g, 95.39 mmol, 1.2 equiv.) in THF (50 mL) was added **S15** (10.00 mL, 79.49 mmol, 1.0 equiv.) slowly at 0 ℃ and stirred at RT for 30 min. Then, ^{n}BuLi (2.4 M in hexane, 39.58 mL, 95.39 mmol, 1.2 equiv.) was added dropwise via syringe at -20 ℃ and stirred at -20 ℃ for 1 h. Finally, **S16** (15.47 g, 85.85 mmol, 1.08 equiv.) in THF (50 mL) was added dropwise to this mixture at -20 ℃. After completion as indicated by TLC (*ca.* 2h), the reaction was quenched with sat. aq. NH_4Cl (50 mL) and extracted by DCM (50 mL×3). The combined organic layers were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **S17** as yellow oil (19.08 g, 77% y).

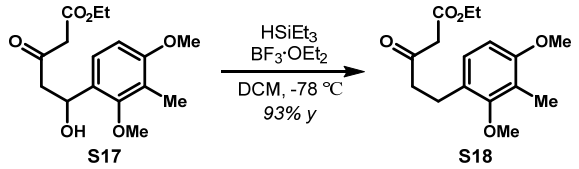
R_f 0.20 (Hex/EtOAc = 3:1, UV/phosphomolybdic acid stain).

^{1}H NMR (600 MHz, $CDCl_3$)
δ 7.24 (d, *J* = 6.0 Hz, 1H), 6.66 (d, *J* = 6.0 Hz, 1H), 5.39–5.37 (m, 1H), 4.20 (q, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 3.49 (s, 2H), 3.49 (br, 1H), 2.98 (s, 1H), 2.97 (d, *J* = 6.0 Hz, 1H), 2.14 (s, 3H), 1.28 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 203.5, 166.9, 158.4, 156.0, 127.4, 123.9, 119.6, 106.2, 65.1, 61.5, 61.1, 55.6, 50.6, 49.8, 14.1, 9.1.

HRMS (ESI) $C_{16}H_{21}O_5$ $[M\text{-}OH]^+$: calcd 293.1389, found 293.1384

S18: Ethyl 5-(2,4-dimethoxy-3-methylphenyl)-3-oxopentanoate



S17 S18

To a solution of **S17** (9.85 g, 31.75 mmol, 1.0 equiv.) in DCM (60 mL) were sequentially added Et_3SiH (30.40 mL, 190.5 mmol, 6.0 equiv.) and a solution of $BF_3{\cdot}OEt_2$ (12.06 mL, 95.25 mmol, 3.0 equiv.) in DCM (30 mL) at -78 ℃. The reaction mixture was stirred at the same temperature. After completion as indicated by TLC (*ca.* 10 min), the reaction was quenched with sat. aq. NH_4Cl (20 mL) and extracted by DCM (20 mL×3). The combined organic layers were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **S18** as yellow oil (8.66 g, 93% y).

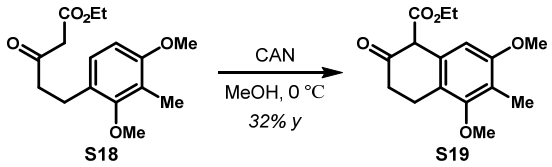
R_f 0.40 (Hex/EtOAc = 3:1, phosphomolybdic acid stain).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 6.95 (d, *J* = 10.0 Hz, 1H), 6.57 (d, *J* = 5.0 Hz, 1H), 4.18 (q, *J* = 10.0 Hz, 2H), 3.80 (s, 3H), 3.70 (s, 3H), 3.42 (s, 2H), 2.88–2.82 (m, 4H), 2.14 (s, 3H), 1.27 (t, *J* = 10.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 202.5, 167.2, 157.5, 157.3, 126.9, 125.4, 119.8, 106.0, 61.3, 60.5, 55.6, 49.3, 44.0, 24.1, 14.1, 9.1.

HRMS (ESI) $C_{16}H_{23}O_5$ $[M+H]^+$: calcd 295.1545, found 295.1547.

S19: Ethyl 5,7-dimethoxy-6-methyl-2-oxo-1,2,3,4-tetrahydronaphthalene-1-carboxylate



Prepared by modifying the procedure reported by Flowers and co-workers:[53] To a solution of **S18** (400 mg, 1.36 mmol, 1.0 equiv.) in MeOH (40 mL) was added a solution of CAN (148.99 mg, 1.63 mmol, 2.0 equiv.) in MeOH (14.0 mL) at 0 ℃. The resulting mixture was stirred at the same temperature. After completion as indicated by TLC (*ca.* 30 min), the reaction was quenched with sat. aq. NH_4Cl (5 mL) and extracted by DCM (5 mL×3). The combined organic layer was washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **S19** as white oil (125.9 mg, 32% y).

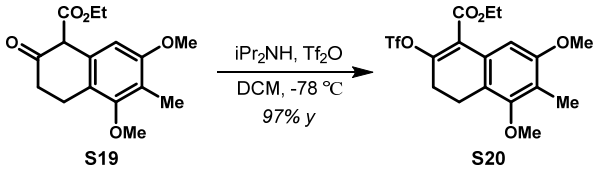
R_f 0.70 (Hex/EtOAc = 9:1, phosphomolybdic acid stain).

^{1}H NMR (500 MHz, $CDCl_3$)
δ 13.40 (s, 1H), 7.17 (s, 1H), 4.39 (q, *J* = 5.0 Hz, 2H), 3.82 (s, 3H), 3.67 (s, 3H), 2.82 (t, *J* = 5.0 Hz, 2H), 2.49 (t, *J* = 5.0 Hz, 2H), 2.15 (s, 3H), 1.43 (t, *J* = 5.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)
δ 178.7, 171.9, 156.5, 155.4, 130.2, 118.2, 116.4, 105.1, 99.8, 60.9, 60.4, 55.5, 29.5, 19.9, 14.2, 8.8.

HRMS (ESI) $C_{16}H_{21}O_5$ $[M+H]^+$: calcd 293.1389, found 293.1392.

(S20): Ethyl 5,7-dimethoxy-6-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4-dihydronaphthalene-1-carboxylate



To a solution of **S19** (5.26 g, 17.99 mmol, 1.0 equiv.) in DCM (285 mL) were sequentially added ^{i}Pr$_2$NH (10.20 mL, 71.97 mmol, 4.0 equiv.) and Tf_2O (6.30 mL, 35.99 mmol, 2.0 equiv.) at -78 ℃. The resulting mixture was stirred at the same temperature. After completion as indicated by TLC (*ca.* 50 min), the reaction was quenched with sat. aq. NH_4Cl (10 mL) and extracted by DCM (10 mL×3). The combined organic layers were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **S20** as white solid (7.41 g, 97% y).

R_f 0.60 (Hex/EtOAc = 9:1, phosphomolybdic acid stain).

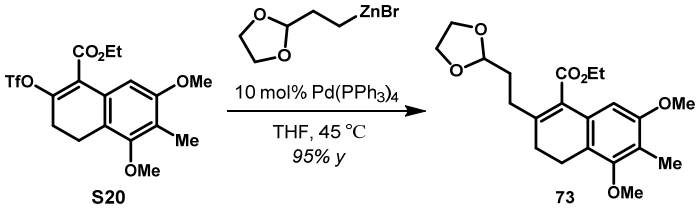
^{1}H NMR (600 MHz, $CDCl_3$)
δ 6.65 (s, 1H), 4.42 (q, *J* = 6.0 Hz, 2H), 3.79 (s, 3H), 3.67 (s, 3H), 3.02 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 3H), 1.41 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 164.3, 157.3, 156.0, 148.7, 129.1, 127.6, 126.3, 124.8, 121.2, 118.3, 118.2 (q, $^1J_{C\text{-}F}$ = 320.0 Hz), 104.4, 62.1, 60.4, 55.7, 26.4, 21.2, 14.0, 9.1.

^{19}F NMR (565 MHz, $CDCl_3$)
δ -74.35.

HRMS (ESI) $C_{17}H_{20}F_3O_7S$ $[M+H]^+$: calcd 425.0882, found 425.0888.

73: Ethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-5,7-dimethoxy-6-methyl-3,4-dihydronaphthalene-1-carboxylate



Prepared by modifying the procedure reported by Fu and coworkers:[54] A flask charged with Zn-powder (0.98 g, 15.0 mmol, 1.5 equiv.) was heated to 70 °C under high vacuum for 1 h. After cooled to RT, the flask was flushed with argon, DMA (10 mL, abs., degassed) was added followed by I_2 (127 mg, 0.5 mmol, 0.05 equiv.). The resulting mixture was heated at 70 °C and stirred until discoloration was observed. Then, 2-(2-bromoethyl)-1,3-dioxolane (1.20 mL, 10.0 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 70 °C for another 16 h. After cooled to RT, the suspension was filtered in glove box to afford (1,3-dioxolan-2-ylethyl)zinc bromide. Its concentration was determined to be 0.52 M by titration.

To a flame-dried round bottom flask charged with **S20** (500 mg, 1.17 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (136 mg, 0.12 mmo, 0.1 equiv.l) was added THF (10 mL, degassed) and a solution of (2-(1,3-dioxolan-2-yl)ethyl)zinc(II) bromide in DMA (7 mL, 0.52 M, 3.5 mmol, 3.0 equiv.). The reaction mixture was heated at 45 °C for 5 h, then quenched with sat. aq. NH_4Cl (10 mL) and extracted with DCM (3×20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and filtered. The filtrated was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired coupling product **73** as yellow oil (424 mg, 95 % y).

R_f 0.30 (Hex/EtOAc = 3:1, UV/$KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$)

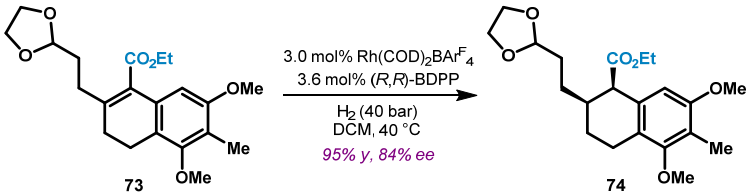
δ 6.49 (s, 1H), 4.91 (t, *J* = 5.0 Hz, 1H), 4.37 (q, *J* = 10.0 Hz, 2H), 3.98–3.93 (m, 2H), 3.87–3.84 (m, 2H), 3.77 (s, 3H), 3.66 (s, 3H), 2.76 (t, *J* = 5.0 Hz, 2H), 2.44–2.40 (m, 2H), 2.28 (t, *J* = 5.0 Hz, 2H), 2.14 (s, 3H), 1.90–1.86 (m, 2H), 1.38 (t, *J* = 10.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.0, 157.0, 156.3, 132.2, 122.8, 118.3, 106.1, 104.4, 64.7 (2C), 60.2, 59.5, 55.3, 48.5, 36.7, 31.4, 27.7, 24.0, 22.9, 14.2, 8.8.

HRMS (ESI) $C_{21}H_{29}O_6$ $[M+H]^+$: calcd 377.1964, found 377.1959.

74: Ethyl (1S,2R)-2-(2-(1,3-dioxolan-2-yl)ethyl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate



A stock solution (0.1 M, 5 mL) was made by stirring $Rh(COD)_2BArF_4$ (47 mg, 0.04 mmol) with (*R*,*R*)-BDPP (32 mg, 0.048 mmol) in anhydrous DCM (5 mL) at RT for 20 min in glove box. Then the catalyst solution was transferred into the vial charged with **73** (500 mg, 1.33 mmol) in anhydrous DCM (8 mL). The vial was quickly transferred into an autoclave, then charged with hydrogen gas (40 bar) and heated at 40 °C for 36 h. The reaction was then cooled, and hydrogen gas was released carefully. The mixture was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **74** as a yellow oil (467 mg, 95% y, 84% *ee*).

R_f 0.40 (Hex/EtOAc = 5:1, UV/$KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D$ = 82.60 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 6.45 (s, 1H), 4.88 (t, *J* = 5.0 Hz, 1H), 4.19–4.09 (m, 2H), 4.00–3.94 (m, 2H), 3.90–3.84 (m, 2H), 3.80 (d, *J* = 5.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 2.97 (dd, *J* = 15.0 & 5.0 Hz, 1H), 2.60–2.53 (m, 2H), 2.12 (s, 3H), 2.09–2.01 (m, 1H), 1.90–1.76 (m, 4H), 1.61–1.57 (m, 1H), 1.55–1.46 (m, 1H), 1.25 (t, *J* = 10.0 Hz, 3H).

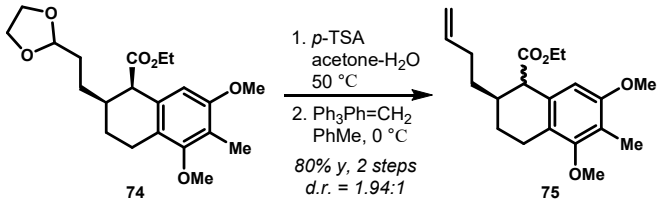
^{13}C NMR (125 MHz, $CDCl_3$)

δ 168.8, 156.6, 155.6, 142.3, 130.3, 128.3, 119.3, 118.5, 103.6, 102.7, 64.7, 60.5, 60.0, 55.4, 32.1, 29.5, 27.6, 20.3, 14.2, 8.8.

HPLC Chiralpak IG-3 column (250 × 4.6 mm/3μm), *n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 210 nm, t_{major} = 28.28 min, t_{minor} = 30.72 min.

HRMS (ESI) $C_{21}H_{31}O_6$ $[M+H]^+$: calcd 379.2121, found 379.2121.

75: Ethyl (1S,2S)-2-(but-3-en-1-yl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate



To a solution of **74** (2.24 g, 5.92 mmol, 1.0 equiv.) in H_2O (60 mL) and acetone (60 mL) was added *p*-TSA (1.01 g, 5.86 mmol, 1.0 equiv.) in one portion. The reaction mixture was stirred at 50 °C for 6 h. The reaction was quenched with sat. $NaHCO_3$ (25 mL) and extracted with DCM (3 × 25 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in *vacuo*.

To the crude aldehyde in PhMe (33 mL) was added a freshly prepared solution of salt-free $Ph_3P{=}CH_2$ PhMe (0.39 M, 61 mL, 23.79 mmol, 4.0 equiv.) at 0 °C. The reaction mixture was stirred at the same temperature. After completion as indicated by TLC (*ca.* 0.5 h), the reaction was quenched with H_2O (25 mL) and extracted by DCM (25 mL×3). The combined organic layers were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **75** as white oil (1.56 g, 80% y, d.r. = 1.94:1).

R_f 0.70 (Hex/EtOAc = 5:1, phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = 23.20 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

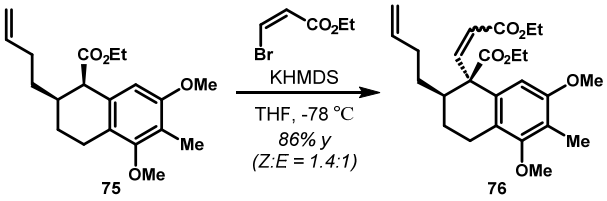
δ 6.46 (s, 1H), 5.85–5.79 (m, 1H), 5.06–5.02 (m, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.28–4.09 (m, 2H), 3.79 (d, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 2.99–2.95 (m, 1H), 2.59–2.53 (m, 1H), 2.24–2.14 (m, 2H), 2.12 (s, 3H), 2.09–2.02 (m, 1H), 1.89–1.76 (m, 1H), 1.58–1.45 (m, 3H), 1.25 (t, *J* = 6.0 Hz, 3H); δ 6.46 (s, 1H), 5.85–5.79 (m, 1H), 5.06–5.02 (m, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.28–4.09 (m, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.51 (d, *J* = 6.0 Hz, 1H), 2.85–2.80 (m, 1H), 2.64–2.60 (m, 1H), 2.24–2.14 (m, 2H), 2.12 (s, 3H), 2.09–2.02 (m, 1H), 1.89–1.76 (m, 1H), 1.44–1.34 (m, 3H), 1.29 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 174.9, 173.3, 157.2, 156.8, 156.6, 156.4, 138.5, 132.4, 131.6, 123.0, 122.6 118.5, 118.2, 114.7, 114.6, 106.3, 105.8, 60.7, 60.3, 59.8, 59.7, 55.5, 55.5, 52.0, 48.7, 36.2, 36.1, 33.3, 32.8, 31.3, 31.0, 25.6, 24.0, 23.0, 21.6, 14.4, 14.3, 8.9, 8.9.

HRMS (ESI) $C_{20}H_{29}O_4$ $[M+H]^+$: calcd 333.2066, found 333.2062.

76: Ethyl (1R,2S)-2-(but-3-en-1-yl)-1-(-3-ethoxy-3-oxoprop-1-en-1-yl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate



Prepared by modifying the procedure reported by Crich and coworkers:[55] To a solution of **75** (1.93 g, 5.84 mmol, 1.0 equiv.) in THF (30 mL) was added KHMDS (1M in THF, 7.6 mL, 7.60 mmol, 1.3 equiv.) slowly via syringde at -78 °C. The reaction solution was stirred at the same temperature for 0.5 h. Then a solution of ethyl (*Z*)-3-bromoacrylate (0.90 mL, 7.0 mmol, 1.2 equiv.) in THF (6.0 mL) was added, and stirred at -78 °C for another 1.5 h. After consumption of **75**, the reaction was quenched with sat. aq. NH_4Cl (20 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give (Z) and (E)-**76**) as colorless oil (2.15 g, 86% y, *Z*:*E* = 1.4:1).

Characterization data of (*Z*)-**76**:

R_f 0.70 (Hex/EtOAc = 9:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D = 20.60$ (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

δ 6.95 (d, *J* = 12.0 Hz, 1H), 6.41 (s, 1H), 5.89 (d, *J* = 12.0 Hz, 1H), 5.82–5.74 (m, 1H), 5.01 (d, *J* = 24.0 Hz, 1H), 4.94 (d, *J* = 12.0 Hz, 1H), 4.16–4.02 (m, 2H), 3.81–3.71 (m, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.00–2.95 (m, 1H), 2.70–2.63 (m, 1H), 2.33–2.20 (m, 2H), 2.09 (s, 3H), 2.05–1.93 (m, 2H), 1.90–1.84 (m, 1H), 1.69–1.64 (m, 1H), 1.30–1.23 (m, 1H), 1.15 (t, *J* = 6.0 Hz, 3H), 1.17 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 173.2, 165.7, 156.0, 155.9, 148.3, 138.5, 135.0, 124.3, 121.0, 117.9, 114.7, 106.9, 61.0, 59.9, 59.6, 56.6, 55.5, 44.0, 32.1, 30.9, 23.7, 22.8, 14.1, 13.8, 8.8.

HRMS (ESI) $C_{25}H_{35}O_6$ $[M+H]^+$: calcd 431.2434, found 431.2437.

Characterization data of (*E*)-**76**:

R_f 0.60 (Hex/EtOAc = 9:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D = 20.80$ (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

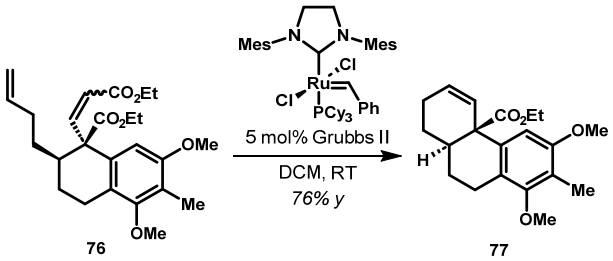
δ 7.61 (d, *J* = 12.0 Hz, 1H), 6.27 (s, 1H), 5.79 – 5.73 (m, 1H), 5.46 (d, *J* = 18.0 Hz, 1H), 5.02 (d, *J* = 18.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 4.20–4.16 (m, 4H), 3.71 (s, 3H), 3.70 (s, 3H), 2.88–2.84 (m, 1H), 2.57–2.52 (m, 1H), 2.26–2.21 (m, 1H), 2.13 (s, 3H), 2.04–1.99 (m, 1H), 1.89–1.83 (m, 3H), 1.59–1.54 (m, 1H), 1.39–1.33 (m, 1H), 1.27 (t, *J* = 6.0 Hz, 3H), 1.23 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 172.7, 166.7, 156.5, 156.3, 153.2, 138.1, 133.3, 123.4, 122.4, 118.8, 115.0, 107.8, 61.2, 60.4, 59.9, 57.5, 55.6, 43.3, 31.7, 29.1, 22.4, 21.5, 14.2, 14.2, 9.0.

HRMS (ESI) $C_{25}H_{35}O_6$ $[M+H]^+$: calcd 431.2434, found 431.2437.

77: Ethyl (4aR,10aS)-6,8-dimethoxy-7-methyl-1,9,10,10a-tetrahydrophenanthrene-4a(2H)-carboxylate



To a solution of **76** (992.0 mg, 2.30 mmol, 1.0 equiv.) in DCM (461 mL) was added Grubbs-II (99 mg, 0.12 mmol, 0.05 equiv.) in one protion. Then the reaction mixture was stirred at RT for 12 h. After consumption of **76**, the reaction mixture was concentrated in *vacuo*, and the residue was purified by flash chromatography to give the desired product **77** as colorless oil (580.1 mg, 76% y).

R_f 0.80 (Hex/EtOAc = 9:1, phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = -10.40 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

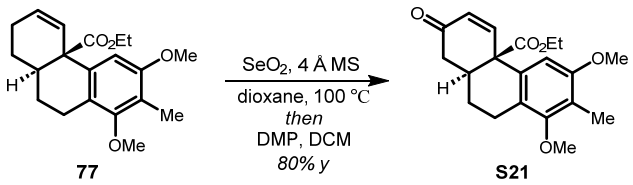
δ 6.82 (s, 1H), 6.33 (d, *J* = 10.0 Hz, 1H), 5.93–5.90 (m, 1H), 4.09–4.02 (m, 1H), 3.83 (s, 1H), 3.69 (s, 1H), 2.85–2.81 (m, 2H), 2.25–2.17 (m, 2H), 2.14 (s, 3H), 2.01–1.92 (m, 1H), 1.84–1.66 (m, 3H), 1.17 (t, *J* = 10.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 173.2, 157.0, 156.2, 137.4, 130.0, 129.7, 123.4, 118.2, 104.2, 60.6, 59.7, 55.6, 50.1, 40.7, 25.8 (2C), 25.0, 22.7, 14.1, 8.9.

HRMS (ESI) $C_{20}H_{27}O_4$ $[M+H]^+$: calcd 331.1909, found 331.1907.

S21: Ethyl (4aR,10aR)-6,8-dimethoxy-7-methyl-2-oxo-1,9,10,10a-tetrahydrophenanthrene-4a(2H) carboxylate



To a solution of **77** (25 mg, 0.075 mmol, 1.0 equiv.) in dioxane (0.75 mL) was added SeO_2 (17 mg, 0.15 mmol, 2.0 equiv.) and 4 Å MS (50 mg) in one protion. The reaction solution was heated at 100 °C for 7 h. After consumption of **77**, the mixture was concentrated and completely dried in *vacuo* to remove any residual dioxane. To the residue was added DCM (0.75 mL) and DMP (48 mg, 0.11 mmol, 1.5 equiv.) at RT. After completion of the reaction as indicated by TLC, the reaction was filtered over Celite. To the filtrate was added sat. $NaHCO_3$ (1 mL) and extracted by DCM (2 mL×3). The combined organic layers were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to afford the desired product **S21** as yellow oil (20 mg, 80% y).

R_f 0.70 (Hex/EtOAc = 2:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = +76.60 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

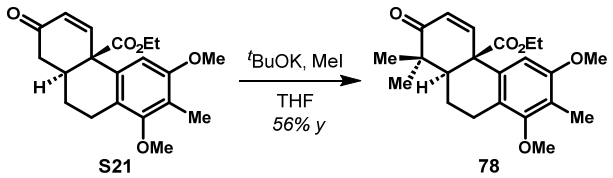
δ 7.49 (d, *J* = 10.0 Hz, 1H), 6.84 (s, 1H), 6.13 (d, *J* = 5.0 Hz, 1H), 4.15–4.05 (m, 2H), 3.84 (s, 1H), 3.70 (s, 1H), 2.97 (dd, *J* = 20.0 & 5.0 Hz, 1H), 2.79–2.72 (m, 2H), 2.52–2.32 (m, 3H), 2.15 (s, 3H), 1.78–1.74 (m, 1H), 1.18 (t, *J* = 10.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 199.3, 170.6, 157.4, 156.6, 151.8, 133.7, 129.9, 123.4, 119.4, 104.0, 61.5, 59.7, 55.6, 51.1, 41.8, 41.5, 24.2, 22.9, 14.0, 9.0.

HRMS (ESI) $C_{20}H_{25}O_5$ $[M+H]^+$: calcd 345.1702, found 345.1695.

78: Ethyl (4aS,10aR)-6,8-dimethoxy-1,1,7-trimethyl-2-oxo-1,9,10,10a-tetrahydrophenanthrene-4a(2H-)-carboxylate



Prepared by modifying the procedure reported by Carter and co-workers:[56] To a solution of **S21** (360 mg, 1.05 mmol, 1.0 equiv.) in THF (4.2 mL) at -78 °C was added a solution of ^{t}BuOK in THF (1.0 M, 6.3 mL, 6.3 mmol, 6.0 equiv.) dropwise. Iodomethane (0.39 mL, 6.3 mmol, 6.0 equiv.) was added 5 min later. The reaction mixture was moved to -40 °C. After 30 min, the reaction was quenched by sat. NH_4Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to afford **78** as colorless oil (217 mg, 56% y).

R_f 0.60 (PE/EtOAc = 5:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = 143.60 (c = 0.5, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

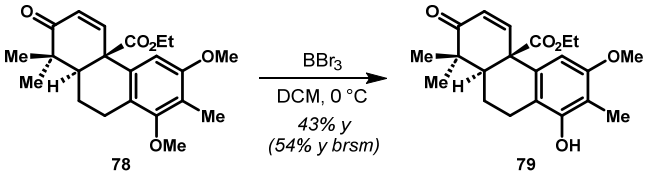
δ 7.48 (d, *J* = 10.8 Hz, 1H), 6.71 (s, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.16–4.10 (m, 1H), 4.04–3.99 (m, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 3.13–3.09 (m, 1H), 2.76–2.70 (m, 1H), 2.63–2.55 (m, 1H), 2.26 (dd, *J* = 12.6 & 2.4 Hz, 1H), 2.14 (s, 3H), 1.91–1.88 (m, 1H), 1.24 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.01 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 204.0, 172.7, 157.7, 156.8, 150.9, 135.3, 128.0, 123.5, 119.4, 103.0, 61.6, 59.8, 55.7, 50.1, 49.3, 45.2, 24.7, 23.8, 19.5, 18.0, 13.9, 9.0.

HRMS (ESI) $C_{22}H_{29}O_5$ $[M+H]^+$: calcd 373.2015, found 373.2012.

79: Ethyl (4aS,10aR)-8-hydroxy-6-methoxy-1,1,7-trimethyl-2-oxo-1,9,10,10a-tetrahydrophenanthrene-4a(2H)-carboxylate



A solution of BBr_3 in DCM solution (1.0 M, 1.46 mL, 1.46 mmol, 2.0 equiv.) was added dropwise to a solution of **78** (274 mg, 0.73 mmol) in DCM (8.6 mL) at 0 °C. The resulting mixture was stirred at 0°C for 1.5 h, and then quenched by careful addition of sat. $NaHCO_3$ solution (2 mL). The mixture was extracted with DCM (3 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to afford the desired phenol **79** as colorless oil (113 mg, 42% y, 54% y brsm) and recovered **78** (55 mg).

R_f 0.50 (PE/EtOAc = 5:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = 139.80 (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

δ 7.49 (d, *J* = 10.2 Hz, 1H), 6.56 (s, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.93 (s, 1H), 4.17–4.12 (m, 1H), 4.05–3.99 (m, 1H), 3.81 (s, 3H), 2.98–2.92 (m, 1H), 2.69–2.61 (m, 2H), 2.27–2.24 (m, 1H), 2.09 (s, 3H), 1.98–1.91 (m, 1H), 1.24 (s, 3H), 1.19 (t, *J* = 6.6 Hz, 3H),

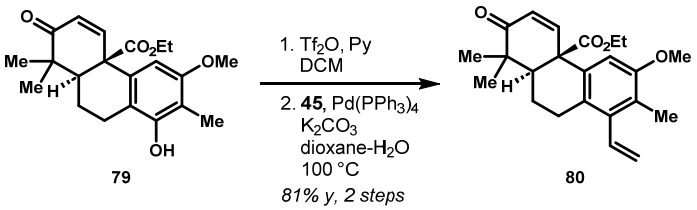
1.01 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 204.0, 172.7, 156.4, 152.9, 150.9, 135.0, 127.9, 116.4, 111.1, 99.7, 61.7, 55.8, 49.8, 49.1, 45.2, 24.6, 23.4, 19.5, 17.8, 13.9, 8.1.

HRMS (ESI) $C_{21}H_{27}O_5$ $[M+H]^+$: calcd 359.1859, found 359.1859.

80: Ethyl (4aS,10aR)-6-methoxy-1,1,7-trimethyl-2-oxo-8-vinyl-1,9,10,10a-tetrahydrophenanthrene-4a-(2H)-carboxylate



Prepared by modifying the procedure reported by Xie and co-workers:[57] A solution of Tf_2O in DCM (0.3 M, 5.1 mL, 1.55 mmol, 5.0 equiv.) was added dropwise to a solution of **79** (113 mg, 0.31 mmol, 1.0 equiv.) and pyridine (250 μL, 3.1 mmol, 10.0 equiv.) in DCM (5.2 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for another 1 h. The reaction was then quenched with 2 M HCl (2 mL) at 0°C and extracted with DCM (3 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo*, and the residue was used directly for the next step.

To the crude triflate were sequentially added K_2CO_3 (169 mg, 1.23 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (56.8 mg, 0.05 mmol, 12 mol%), a mixture of 1,4-dioxane and water (v/v = 4/1, 10 mL) and vinylboronic acid pinacol ester **45** (90 μL, 0.53 mmol, 1.3 equiv.). The reaction mixture was then heated at 100 °C for 12 h. After cooled to RT, the resulting suspension was filtered over Celite, and the filtrate was concentrated in *vacuo*. The residue was purified by a flash chromatography to give **80** (135 mg, 81% y over 2 steps) as colorless oil.

R_f 0.65 (PE/EtOAc = 9:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D$ = 124.40 (c = 0.5, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

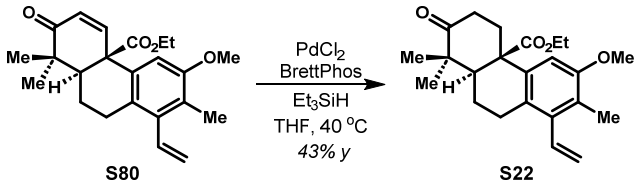
δ 7.51 (d, *J* = 10.5 Hz, 1H), 6.86 (s, 1H), 6.61 (dd, *J* = 18.0 & 11.5 Hz, 1H), 6.12 (d, *J* = 10.5 Hz, 1H), 5.57 (dd, *J* = 11.5 & 2.0 Hz, 1H), 5.19 (dd, *J* = 18.0 & 2.0 Hz, 1H), 4.19–4.13 (m, 1H), 4.06–4.00 (m, 1H), 3.83 (s, 3H), 2.95–2.90 (m, 1H), 2.73–2.58 (m, 2H), 2.25 (dd, *J* = 13.0 & 3.0 Hz, 1H), 2.17 (s, 3H), 1.89–1.86 (m, 1H), 1.23 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 204.0, 172.8, 156.0, 151.3, 140.4, 135.0, 134.3, 127.9, 127.4, 124.5, 120.1, 105.8, 61.6, 55.6, 49.8, 49.5, 45.1, 28.4, 24.7, 19.5, 18.5, 13.9, 13.2.

HRMS (ESI) $C_{23}H_{29}O_4$ $[M+H]^+$: calcd 369.2218, found 369.2215.

S22: Ethyl (4aS,10aR)-6-methoxy-1,1,7-trimethyl-2-oxo-8-vinyl-1,3,4,9,10,10a-hexahydrophenanthrene-4a(2H)-carboxylate



Prepared by modifying literature procedures:[58] To **80** (36 mg, 0.1 mmol, 1.0 equiv.) were sequentially added $PdCl_2$ (3.5 mg, 0.02 mmol, 20 mol%), BrettPhos (21.4 mg, 0.04 mmol, 40 mol%), THF (1.0 mL) and Et_3SiH (24 μL, 0.15 mmol, 1.5 equiv) at RT. The reaction mixture was then moved to an oil bath, which had been pre-heated to 40 ºC. After stirring at 40 ºC for 10 h, the reaction was cooled to room temperature and filtered over Celite. The filtrate was concentrated in *vacuo*, and the residue was purified by a flash chromatography to give **S22** (16 mg, 43% y) as colorless oil.

R_f 0.55 (Toluene/EtOAc = 15:1, phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D = 41.80$ (c = 1.0, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$)

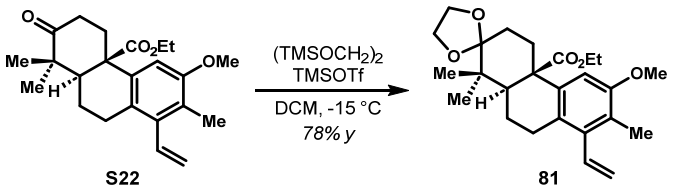
δ 6.65 (s, 1H), 6.61 (dd, *J* = 18.0 & 11.4 Hz, 1H), 5.56 (dd, *J* = 11.4 & 1.8 Hz, 1H), 5.19 (dd, *J* = 18.0 & 1.8 Hz, 1H), 4.17–4.12 (m, 1H), 4.08–4.02 (m, 1H), 3.77 (s, 3H), 3.13–3.09 (m, 1H), 3.05–3.00 (m, 1H), 2.91 (dd, *J* = 16.8 & 4.8 Hz, 1H), 2.65–2.59 (m, 1H), 2.55–2.51 (m, 1H), 2.49–2.43 (m, 1H), 2.16 (s, 3H), 1.96 (dd, *J* = 12.6 & 2.4 Hz, 1H), 1.85–1.82 (m, 1H), 1.77–1.71 (m, 1H), 1.20–1.18 (m, 6H), 1.00 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)

δ 215.3, 175.0, 156.0, 139.6, 137.1, 135.2, 126.3, 123.8, 119.9, 106.2, 61.1, 55.6, 51.0, 47.8, 47.7, 35.8, 35.7, 28.8, 25.2, 19.8, 19.5, 13.9, 13.1.

HRMS (ESI) $C_{23}H_{31}O_4$ $[M+H]^+$: calcd 371.2222, found 371.2220.

81: Ethyl (4aS,10aR)-6-methoxy-1,1,7-trimethyl-8-vinyl-1,3,4,9,10,10a-hexahydro-4aH-spiro[phenanthrene-2,2'-[1,3]dioxolane]-4a-carboxylate



S22 **81**

A solution of TMSOTf solution in DCM (0.2 M, 0.11 mL, 0.022 mmol, 0.2 equiv.) was added to a solution of **S22** (42.0 mg, 0.11 mmol, 1.0 equiv.) and 2,2,7,7-tetramethyl-3,6-dioxa-2,7-disilaoctane (80 μL, 0.33 mmol, 3.0 equiv.) in DCM (2.8 mL) at -15 °C. The resulting mixture was stirred at the same temperature for 12 h. The reaction was then quenched by sat. $NaHCO_3$ solution (3 mL) and extracted with DCM (3 mL × 3). The combined organic extracts were washed with brine (5 mL) and dried over Na_2SO_4, filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to give product **81** (36 mg, 78% y) as colorless oil.

R_f 0.50 (PE/EtOAc = 10:1, $KMnO_4$).

Opt. Rot. $[\alpha]^{20}_D = 80.40$ (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$)

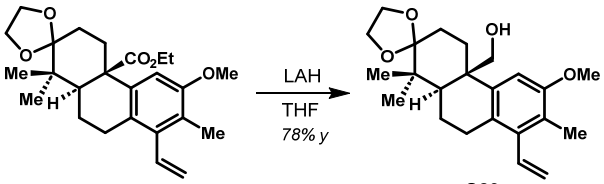
δ 6.72 (s, 1H), 6.59 (dd, *J* = 18.0 & 11.5 Hz, 1H), 5.52 (dd, *J* = 11.0 & 2.0 Hz, 1H), 5.15 (dd, *J* = 18.0 & 2.5 Hz, 1H), 4.14–4.07 (m, 1H), 4.02–3.86 (m, 5H), 3.76 (s, 3H), 2.88 – 2.80 (m, 2H), 2.67–2.60 (m, 1H), 2.55–2.47 (m, 1H), 2.20 (dt, *J* = 14.0 & 4.0 Hz, 1H), 2.14 (s, 3H), 2.00 (dd, *J* = 13.0 & 3.0 Hz, 1H), 1.85–1.81 (m, 1H), 1.69 (dt, *J* = 14.0 & 3.5 Hz, 2H), 1.60–1.54 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.93 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 175.5, 155.6, 139.5, 138.0, 135.5, 126.9, 123.2, 119.5, 112.6, 106.2, 65.2, 64.8, 60.6, 55.6, 48.5, 47.6, 42.7, 33.8, 29.1, 28.7, 21.8, 18.8, 18.4, 13.9, 13.1.

HRMS (ESI) $C_{25}H_{35}O_5$ $[M+H]^+$: calcd 415.2484, found 415.2484.

S23: ((4aS,10aS)-6-Methoxy-1,1,7-trimethyl-8-vinyl-1,3,4,9,10,10a-hexahydro-4aH-spiro[phenanthrene-2,2'-[1,3]dioxolan]-4a-yl)methanol



81 **S23**

To a sealed tube were added **81** (58 mg, 0.14 mmol, 1.0 equiv.) and anhydrous THF (2.8 mL, 0.05 M). $LiAlH_4$ (26.6 mg, 0.7 mmol, 5.0 equiv.) at room temperature. The resulting mixture was heated at 80 °C for 12 h under argon atmosphere. The reaction was then cooled by an ice-water bath and quenched by careful addition of water (27 μL), 15% aq. NaOH (27 μL) and water (81 μL). The mixture was then stirred at room temperature for 15 min, dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash chromatography to afford alcohol **S23** (41 mg, 78% y) as white solid.

R_f 0.40 (PE/EtOAc = 3:1, $KMnO_4$).

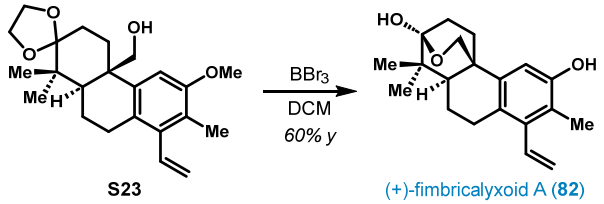
Opt. Rot. $[\alpha]^{20}_D = 17.0$ (c = 1.0, MeOH).

^{1}H NMR (600 MHz, CD_3OD)
δ 6.75 (s, 1H), 6.57 (dd, *J* = 18.0 & 11.4 Hz, 1H), 5.46 (dd, *J* = 11.4 & 1.8 Hz, 1H), 5.04 (dd, *J* = 18.0 & 2.4 Hz, 1H), 3.98 (d, *J* = 11.4 Hz, 1H), 3.94–3.87 (m, 3H), 3.82–3.79 (m, 1H), 3.75 (s, 3H), 3.56 (d, *J* = 11.4 Hz, 1H), 3.27 (s, 1H), 2.77–2.73 (m, 1H), 2.63–2.58 (m, 1H), 2.53 (dt, *J* = 12.6 & 3.6 Hz, 1H), 2.08 (s, 3H), 1.89 (dt, *J* = 13.8 & 3.6 Hz, 1H), 1.79–1.72 (m, 3H), 1.61 (dt, *J* = 11.5 & 3.0 Hz, 1H), 1.55 (dt, *J* = 13.8 & 3.6 Hz, 1H), 1.00 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (150 MHz, CD_3OD)
δ 156.3, 143.8, 140.0, 137.2, 126.4, 122.7, 119.7, 113.9, 109.4, 65.9, 65.8, 64.4, 55.9, 49.4, 43.3, 43.2, 30.6, 29.4, 28.1, 23.6, 21.1, 19.3, 13.3.

HRMS (ESI) $C_{23}H_{31}O_3$ $[M\text{-}OH]^+$: calcd 355.2273, found 355.2267.

82: (+)-Fimbricalyxoid A



S23 (+)-fimbricalyxoid A (**82**)

A solution of BBr_3 in DCM (1.0 M, 0.21 mL, 0.21 mmol, 3.0 equiv.) was added dropwise to a solution of **S23** (26.0 mg, 0.07 mmol, 1.0 equiv.) in DCM (1.7 mL, 0.04 M) at 0 °C. The resulting mixture was stirred at the same temperature for 1 h, then diluted with water (2 mL) and extracted with diethyl ether (3 mL × 3). The combined organic layers were washed with sat. aq. $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by preparative chromatography to provide (+)-fimbricalyxoid A (**82**) (13 mg, 60% y) as off-white solid.

R_f 0.20 (PE/EtOAc = 1:1, UV/phosphomolybdic acid stain).

Opt. Rot. $[\alpha]^{20}_D = +43.4$ (c = 1.37, $CHCl_3$); Lit.[59]: $[\alpha]^{24}_D = -153$ (c = 1.37, $CHCl_3$).
$[\alpha]^{20}_D = +60.0$ (c = 0.02, MeOH); Lit.[60]: $[\alpha]^{25}_D = +13$ (c = 0.02, MeOH).

^{1}H NMR (600 MHz, $CDCl_3$)
δ 6.71 (s, 1H), 6.60 (dd, *J* = 18.0, 11.4 Hz, 1H), 5.88 (s, 1H), 5.55 (dd, *J* = 12.0 & 1.2 Hz, 1H), 5.17 (dd, *J* = 18.0 & 1.2 Hz, 1H), 4.15 (dd, *J* = 9.6 & 2.4 Hz, 1H), 4.07 (d, *J* = 9.0 Hz, 1H), 2.85 (d, *J* = 16.2 Hz, 1H), 2.66 (s, 1H), 2.45–2.40 (m, 2H), 2.32–2.27 (m, 1H), 2.17 (s, 3H), 1.97–1.92 (m, 1H), 1.87–1.84 (m, 1H), 1.73-1.67 (m, 1H), 1.65–1.61 (m,

1H), 1.60-1.56 (m, 1H), 1.11 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$)
δ 152.3, 139.4, 136.5, 135.2, 127.3, 120.8, 120.0, 111.6, 99.6, 72.5, 47.8, 40.3, 36.2, 35.2, 29.4, 28.8, 26.9, 20.7, 17.9, 12.9.

HRMS (ESI) $C_{20}H_{27}O_3$ $[M+H]^+$: calcd 315.1960, found 315.1962.

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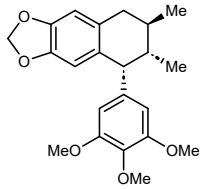
5. Comparison of Spectroscopic Data of Cyclolignans

Table S5. Austrobilignan-4 (**13**).



austrobailignan-4 (**13**)

^{1}H NMR ($CDCl_3$)			^{13}C NMR ($CDCl_3$)		
Natural[a] (100 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural** δ (NA)	**Synthetic** (125 MHz) δ	**Deviation** Δδ (NA)
6.57 (s,1H)	6.58 (s,1 H)	0.01		152.3	
6.38 (s,1H)	6.39 (s, 1H)	0.01		145.9	
6.20 (s, 2H)	6.20 (s, 2H)	0.00		145.7	
5.82 (q, 2H)	5.85 (q, 2H)	0.03		139.2	
3.89 (d, 1H)	3.89 (d, 5.1 Hz, 1H)	0.00		132.4	
3.81 (s, 3H)	3.82 (s, 3H)	0.01		129.6	
3.75 (s, 6H)	3.77 (s, 6H)	0.02		109.6	
2.90 (dd, 5.2 Hz, 1H)	2.90 (dd, 16.9 & 5.2 Hz, 1H)	0.00		107.8	
2.41 (dd, 1H)	2.43 (dd, 16.9 & 10.0 Hz, 1H)	0.02		107.8	
2.06-1.58 (m, 2H)	1.91-1.75 (m, 2H)	0.00		100.5	
0.96 (d, 3H)	0.96 (d, 6.3 Hz, 3H)	0.00		60.8	
0.82 (d, 3H)	0.81 (d, 6.6 Hz, 3H)	0.01		56.1	
				51.3	
				39.2	
				38.3	
				29.0	
				19.5	
				17.2	

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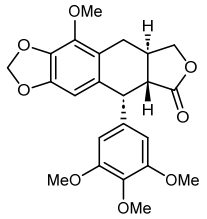
Table S6. β-Peltatin-A-methylether (**18**).

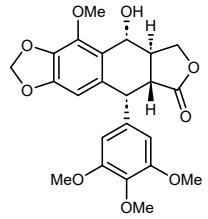


ß-peltatin-A-methylether (**18**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (NA MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[b] (150 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.36 (s, 2H)	6.36 (s, 2H)	0.00	175.2	175.2	0.0
6.28 (s, 1H)	6.28 (s, 1H)	0.00	152.8	152.6	0.2
5.93 (d, 1H)	5.92 (d, 1.5 Hz, 1H)	0.01	148.4	148.4	0.0
5.91 (d, 1H)	5.91 (d, 1.4 Hz, 1H)	0.00	140.9	140.8	0.1
4.59 (d, 1H)	4.58 (d, 4.2 Hz, 1H)	0.01	137.3	137.2	0.2
4.48 (dd, 1H)	4.48 (dd, 8.5 & 6.4 Hz, 1H)	0.00	136.4	136.3	0.1
4.04 (s, 3H)	4.07 (s, 3H)	0.03	134.9	134.9	0.0
NA	3.94 (t, 9.4 Hz, 1H)	NA	131.8	131.7	0.1
3.81 (s, 3H)	3.81 (s, 3H)	0.00	121.1	121.0	0.1
3.76 (s, 6H)	3.76 (s, 6H)	0.00	108.6	108.4	0.2
3.30-2.40 (m, 4H)	3.18 (dd, 16.6 & 4.9 Hz, 1H)	NA	104.6	104.5	0.1
	2.72–2.59 (m, 2H)	NA	101.2	101.1	0.1
	2.45 (dd, 16.6 & 10.4 Hz, 1H)	NA	72.5	72.5	0.0
			60.9	60.9	0.0
			59.5	59.5	0.0
			56.5	56.4	0.1
			47.5	47.4	0.1
			44.1	43.9	0.2
			32.6	32.5	0.1
			27.7	27.6	0.1

[a]Arimoto, M.; Yamaguchi H. & Nishibe, S. Structure elucidation and synthesis of the lignans from the seeds of *Hernandia ovigera* L. *Studies in Natural Products Chemistry* (Ed. Atta-ur-Rahman) **18**, 551–606 (1995). [b]Zeng, D.-L.; Wang, C.-Y.; Gao, H.-Q.; Chen, D.-F.; Lu, Y. A new abietane diterpene and anti-complementary constituents from Juniperus tibetica. *Nat. Prod. Res.* **35**, 3452–3459 (2021). NA = Not Available.

Table S7. 6-Methoxypodophyllotoxin (**19**).

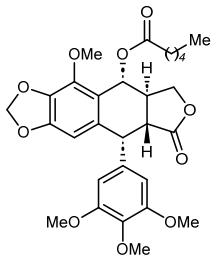


6-methoxypodophyllotoxin (**19**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (200 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (50 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.44 (s, 2H)	6.44 (s, 2H)	0.00	174.3	174.4	0.1
6.29 (s, 1H)	6.29 (s, 1H)	0.00	152.7	152.6	0.1
5.94 (s, 2H)	5.94 (s, 2H)	0.00	149.5	149.4	0.1
5.03 (d, 8.5 Hz, 1H)	5.02 (dd, 9.2 & 1.6 Hz, 1H)	0.01	141.7	141.5	0.2
4.62 (dd, 8.7 & 6.9 Hz, 1H)	4.63 (dd, 8.6 & 7.3 Hz, 1H)	0.01	137.5	137.0	0.5
4.52 (d, 4.1 Hz, 1H)	4.53 (d, 4.5 Hz, 1H)	0.01	135.0	134.9	0.1
4.15 (s, 3H)	4.15 (s, 3H)	0.00	134.7	134.7	0.0
4.06 (dd, 9.7 & 4.8, 1H)	4.06 (dd, 10.5 & 8.6 Hz, 1H)	0.00	132.9	132.8	0.1
NA	4.02 (d, 1.7 Hz, 1H)	NA	125.1	124.9	0.2
3.80 (s, 3H)	3.80 (s, 3H)	0.00	108.5	108.0	0.5
3.76 (s, 6H)	3.76 (s, 6H)	0.00	104.3	104.3	0.0
2.90 (m, 1H)	2.95–2.81 (m, 1H)	0.00	101.3	101.4	0.1
2.73 (dd, 14.8 & 4.3 Hz, 1H)	2.74 (dd, 14.8 & 4.5 Hz, 1H)	0.01	71.8	71.9	0.1
			70.5	70.5	0.0
			60.6	60.7	0.1
			59.8	59.9	0.1
			56.2	56.1	0.1
			45.1	45.1	0.0
			44.6	44.5	0.1
			39.1	39.0	0.1

[a]Feliciano, A. S.; del Corral, J. M. M.; Gordaliza, M. & Castro, A. Lignans from *Juniperus sabina*. *Phytochemistry* **29**, 1335–1338 (1990). NA = Not Available.

Table S8. 6-Methoxypodophyllotoxin-7-*O*-n-hexanoate (**20**).

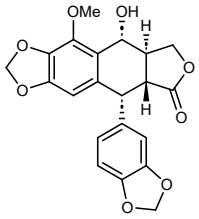


6-methoxypodophyllotoxin-7-*O*-n-hexanoate (**20**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (400 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (100 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.46 (s, 2H)	6.47 (s, 2H)	0.01	173.79	173.82	0.03
6.32 (s, 1H)	6.32 (s, 1H)	0.00	173.68	173.70	0.02
6.10 (d, 8.0 Hz, 1H)	6.11 (d, 7.9 Hz, 1H)	0.01	152.64	152.67	0.03
5.96 (d, 1.0 Hz, 1H)	5.96 (d, 1.4 Hz, 1H)	0.00	150.03	150.06	0.03
5.95 (d, 1.5 Hz, 1H)	5.95 (d, 1.5 Hz, 1H)	0.00	142.25	142.29	0.04
NA	4.57 (d, 3.8 Hz, 1H)	NA	136.94	136.99	0.05
4.41 (dd, 9.0 & 7.0 Hz, 1H)	4.42 (dd, 9.2 & 6.8 Hz, 1H)	0.01	135.52	135.54	0.02
4.19 (dd, 9.0, 10 Hz, 1H)	4.20 (t, 9.8 Hz, 1H)	0.01	134.36	134.39	0.03
4.00 (s, 3H)	4.00 (s, 3H)	0.00	134.22	134.23	0.01
3.81 (s, 3H)	3.82 (s, 3H)	0.01	120.53	120.56	0.03
3.77 (s, 6H)	3.77 (s, 6H)	0.00	107.72	107.77	0.05
2.76 (dd, 15.0, 4.0 Hz, 1H)	2.81 (dd, 15.0 & 3.9 Hz, 1H)	0.05	103.82	103.86	0.04
2.76 (m, 1H)	2.78–2.69 (m, 1H)	NA	101.37	101.39	0.02
2.31 (m, 2H)	2.31 (q, 7.3 Hz, 2H)	0.00	71.74	71.76	0.02
1.63 (m, 2H)	1.69 – 1.61 (m, 2H)	NA	69.84	69.86	0.02
1.31(m, 2H) 1.32 (m, 2H)	1.38 – 1.26 (m, 4H)	NA	60.73	60.75	0.02
0.89 (t, 3H)	0.93 – 0.85 (m, 3H)	NA	59.49	59.51	0.02
			56.04	56.06	0.02
			45.93	45.96	0.03
			44.13	44.15	0.02
			39.34	39.35	0.02
			34.18	34.20	0.02
			31.27	31.29	0.02
			24.63	24.64	0.01
			22.28	22.29	0.01
			13.87	13.87	0

[a]Klaes, M.; Ellendorff, T. & Schmidt, T. J. 6-Methoxypodophyllotoxin-7-O-n-hexanoate, a new aryltetralin lignan ester from seeds of *Linum flavum*. *Planta Med.* **76**, 719–721 (2010). NA = Not Available.

Table S9. Cleistantoxin (**21**).

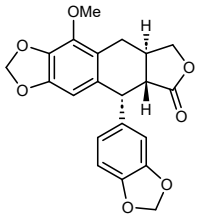


cleistantoxin (**21**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.72 (d, 1.5 Hz, 1H)	6.71 (d, 1.7 Hz, 1H)	0.01	174.2	174.2	0.0
6.66 (d, 8.0 Hz, 1H)	6.66 (d, 8.0 Hz, 1H)	0.00	149.4	148.5	0.1
6.64 (dd, 8.0, 1.5 Hz, 1H)	6.64 (dd, 8.1 & 1.8 Hz, 1H)	0.00	147.2	147.3	0.1
6.22 (s, 1H)	6.22 (s, 1H)	0.00	146.5	146.7	0.2
5.91 (d, 1.5 Hz, 1H)	5.91 (d, 1.4 Hz, 1H)	0.00	141.5	141.6	0.1
5.88 (d, 1.5 Hz, 1H)	5.88 (d, 1.4 Hz, 1H)	0.00	134.9	134.9	0.0
5.87 (d, 1.3 Hz, 1H)	5.87 (d, 1.4 Hz, 1H)	0.00	133.0	133.1	0.1
5.86 (d, 1.3 Hz, 1H)	5.86 (d, 1.5 Hz, 1H)	0.00	132.9	133.0	0.1
4.99 (d, 9.0 Hz, 1H)	4.99 (d, 9.3 Hz, 1H)	0.00	124.7	124.7	0.0
4.59 (dd, 9.0, 9.0 Hz, 1H)	4.60 (dd, 8.6 & 7.3 Hz, 1H)	0.00	124.1	124.2	0.1
4.47 (d, 4.5 Hz, 1H)	4.47 (d, 4.6 Hz, 1H)	0.00	111.1	111.2	0.1
4.12 (s, 3H)	4.12 (s, 3H)	0.00	107.6	107.7	0.1
4.02 (dd, 10.5 & 9.0 Hz, 1H)	4.02 (dd, 10.5 & 8.6 Hz, 1H)	0.00	104.1	104.3	0.2
2.89-2.80 (m, 1H)	2.89–2.80 (m, 1H)	NA	101.2	101.3	0.1
2.71 (dd, 15.0 & 4.5 Hz, 1H)	2.70 (dd, 14.8 & 4.6 Hz, 1H)	0.01	100.9	101.0	0.1
			71.8	71.9	0.1
			70.4	70.6	0.2
			59.8	59.9	0.1
			44.6	44.7	0.1
			43.9	44.0	0.1
			38.7	38.7	0.0

[a]Thanh, V. T. T. et al. Cytotoxic lignans from fruits of cleistanthus indochinensis: synthesis of cleistantoxin derivatives. *J. Nat. Prod.* **75**, 1578–1583 (2012). NA = Not Available.

Table S10. Picrobursenin (**22**).

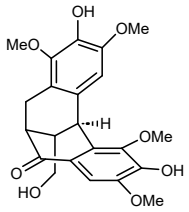


picrobursenin (**22**)

^{1}H NMR (Acetone-d_6)			**^{13}C NMR (Acetone-d_6)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.68 (d, 8.5 Hz, 1H)	6.68 (d, 8.1 Hz, 1H)	0.00	175.3	175.3	0.0
6.65 (d, 1.5 Hz, 1H)	6.65 (d, 1.8 Hz, 1H)	0.00	149.1	149.1	0.0
6.24 (s, 1H)	6.24 (s, 1H)	0.00	148.0	148.0	0.0
5.95 (d, 1.0 Hz, 1H)	5.95 (d, 1.1 Hz, 1H)	0.00	147.2	147.2	0.0
5.94 (d, 1.0 Hz, 1H)	5.93 (d, 1.1 Hz, 1H)	0.01	141.8	141.7	0.1
5.93 (d, 1.0 Hz, 1H)	5.93 (d, 1.1 Hz, 1H)	0.00	136.1	136.1	0.0
5.92 (d, 1.0 Hz, 1H)	5.92 (d, 1.1 Hz, 1H)	0.00	135.9	135.8	0.1
4.46 (dd, 8.5 & 7.5 Hz, 1H)	4.45 (dd, 8.4 &7.1 Hz, 1H)	0.01	133.2	133.2	0.0
4.03 (s, 3H)	4.03 (s, 3H)	0	124.9	124.9	0.0
4.00 (dd, 10.0 & 8.5 Hz, 1H)	3.99 (dd, 10.6 & 8.4 Hz, 1H)	0.01	122.5	122.5	0.0
3.19 (dd, 16.2 & 5.5 Hz, 1H)	3.18 (dd, 16.4 & 5.2 Hz, 1H)	0.01	111.9	112.0	0.1
2.82 (dd, 14.0 & 4.5 Hz, 1H)	2.81–2.77 (m, 1H)	0.00	108.0	108.0	0.0
2.63 (m, 1H)	2.68–2.57 (m, 1H)	NA	105.0	105.0	0.0
2.49 (dd, 16.2 & 11.0 Hz, 1H)	2.49 (dd, 16.4 &11.5 Hz, 1H)	0.00	101.8	101.9	0.1
			101.9	101.9	0.0
			72.8	72.7	0.1
			47.3	47.2	0.1
			44.2	44.2	0.0
			33.1	33.1	0.0
			27.7	27.7	0.0

[a]Thanh, V. T. T. et al. Cytotoxic aryltetralin lignans from fruits of cleistanthus indochinensis. *Planta Med.* **80**, 695–702 (2014). NA = Not Available.

Table S11. (+)-Lirionol (**50**).

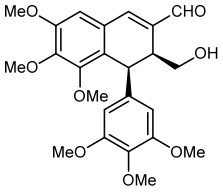


(+)-lirionol (**50**)

^{1}H NMR (CDCl$_3$)			**^{13}C NMR (CDCl$_3$)**		
Rodrigo's Work[a] (250 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (NA) δ (NA)	**Synthetic** (125 MHz) δ	**Deviation** (NA)
NA	9.80 (s, 1H)	NA		198.9	
NA	8.42 (s, 1H)	BA		147.4	
7.11 (1H)	7.12 (s, 1H)	0.01		147.4	
6.74 (1H)	6.74 (s, 1H)	0.00		146.3	
NA	4.70 (t, 4.8 Hz, 1H)	NA		146.1	
4.35 (1H, 2,6 Hz)	4.36 (s, 1H)	0.01		144.5	
3.89 (3H)	3.90 (s, 3H)	0.01		138.3	
3.75 (3H)	3.77 (s, 3H)	0.02		135.7	
3.72 (3H)	3.72 (s, 3H)	0.00		131.8	
3.63 (3H)	3.63 (s, 3H)	0.00		121.8	
3.38 (8.7 Hz, 1H)	NA	NA		119.0	
3.28 (8.7 Hz, 1H)	3.27 (m, 2H)	0.01		107.6	
3.00 (7.3 Hz, 1H)	3.00 (dd, 17.7, 7.5 Hz, 1H)	0.00		105.0	
2.86 (7.3 Hz, 1H)	2.86 (d, 7.3 Hz, 1H)	0.00		62.5	
2.73 (17.3 Hz, 1H)	2.73 (d, 17.5 Hz, 1H)	0.00		60.9	
2.42 (2.6 Hz 1H)	2.41 (m, 1H)	0.01		59.5	
				56.3	
				43.5	
				42.3	
				33.7	
				28.3	

[a]Gamini Weeratunga, Dayananda Rajapaksa, and Russell Rodrigo, The synthesis and relative configuration of (±)-lirionol. *J. Org. Chem.* **50**, 5902–5905 (1985). NA = Not Available.[b]No data nor spectra of it could be obtained.

Table S12. The alleged structure of aglacin G (**52**).

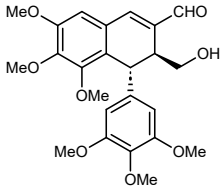


aglacin G (**52**)
(alleged structure)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
9.59 (s, 1H)	9.56 (s, 1H)	0.03	193.0	195.0	2.0
7.30 (s, 2H)	7.49 (s, 2H)	0.19	153.0	152.8	0.2
6.76 (s, 1H)	6.76 (s, 1H)	0.00	152.8	152.7	0.1
6.20 (s, 2H)	6.30 (s, 2H)	0.10	152.2	152.4	0.2
4.66 (br, 1H)	4.47 (d, 7.4 Hz, 1H)	0.19	146.1	150.7	4.6
3.92 (s, 3H)	4.35 (d, 10.7 Hz, 1H)	0.43	145.3	145.8	0.5
3.91 (s, 3H)	3.90 (s, 3H)	0.01	139.4	138.6	0.8
3.76 (s, 3H)	3.89 (s, 3H)	0.13	137.2	137.2	0.0
3.71 (s, 6H)	3.84 (t, 6.6 Hz, 2H)	0.13	136.6	134.9	1.7
3.60 (s, 3H)	3.76 (s, 3H)	0.16	127.0	128.3	1.3
3.60 (dd, 8.8 & 6.7, 1H)	3.72 (s, 6H)	0.12	125.1	126.4	1.3
3.39 (dd, 10.4 & 8.6, 1H)	3.51 (s, 3H)	0.12	108.3	108.4	0.1
3.30 (m, 1H)	3.18–3.16 (m, 1H)	NA	104.6	105.9	1.3
			63.9	62.7	1.2
			60.9	60.8	0.1
			60.9	60.8	0.1
			60.8	60.7	0.1
			56.1	56.1	0.0
			56.0	56.1	0.1
			42.0	43.2	1.2
			38.0	41.2	3.2

[a]Wang, B.-G.; Ebel, R.; Wang, C.-Y.; Wray, V.; Proksch, P. New methoxylated aryltetrahydronaphthalene lignans and a norlignan from *Aglaia cordata*. *Tetrahedron Lett.* **43**, 5783–5787 (2002). NA = Not Available.

Table S13. (-)-Aglacin G (**61**).

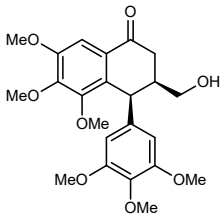


(-)-aglacin G (**61**)
(revised structure)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
9.59 (s, 1H)	9.58 (s, 1H)	0.01	193.0	192.9	0.1
7.30 (s,2H)	7.30 (s, 1H)	0.00	153.0	153.0	0.0
6.76 (s, 1H)	6.76 (s, 1H)	0.00	152.8	152.8	0.0
6.20 (s, 2H)	6.20 (s, 2H)	0.00	152.2	152.2	0.0
4.66 (br, 1H)	4.66 (s, 1H),	0.00	146.1	146.1	0.0
3.92 (s, 3H)	3.92 (s, 6H)	0.00	145.3	145.3	0.0
3.91 (s, 3H)	3.91 (s, 6H)	0.00	139.4	139.4	0.0
3.76 (s, 3H)	3.76 (s, 3H)	0.00	137.2	137.2	0.0
3.71 (s, 6H)	3.71 (s, 6H)	0.00	136.6	136.6	0.0
3.60 (s, 3H)	3.59 (s, 3H)	0.01	127.0	126.7	0.3
3.60 (dd, 8.8 & 6.7, 1H)	3.64–3.60 (m, 1H)	NA	125.1	125.1	0.0
3.39 (dd, 10.4 & 8.6, 1H)	3.43–3.36 (m, 1H)	NA	108.3	108.4	0.1
3.30 (m, 1H)	3.30 (dd, 8.6 & 5.7 Hz, 1H)	0.00	104.6	104.6	0.0
			63.9	63.8	0.1
			60.9	60.9	0.0
			60.9	60.8	0.1
			60.8	60.8	0.0
			56.1	56.1	0.0
			56.0	56.1	0.1
			42.0	42.1	0.1
			38.0	38.0	0.0

[a]Wang, B.-G.; Ebel, R.; Wang, C.-Y.; Wray, V.; Proksch, P. New methoxylated aryltetrahydronaphthalene lignans and a norlignan from *Aglaia cordata*. *Tetrahedron Lett.* **43**, 5783–5787 (2002). NA = Not Available.

Table S14. The alleged structure of aglacin H (**53**).

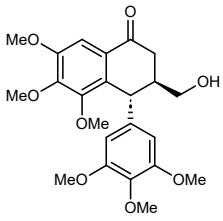


aglacin H (**53**)
(allged structure)

^{1}H NMR (CDCl$_3$)			**^{13}C NMR (CDCl$_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
7.44 (s, 1H)	7.44 (s, 1H)	0.00	196.4	196.4	0.0
6.25 (s, 2H)	6.30 (s, 2H)	0.05	153.2	152.1	1.1
4.63 (d, 2.6 Hz, 1H)	4.73 (d, 4.7 Hz, 1H)	0.10	152.8	151.9	0.9
3.94 (s, 3H)	3.92 (s, 3H)	0.02	151.5	149.6	0.9
3.92 (s, 3H)	3.89 (s, 3H)	0.03	147.9	147.0	0.9
3.81 (s, 3H)	3.78 (s, 3H)	0.03	139.5	136.1	3.4
3.74 (s, 6H)	3.71 (s, 6H)	0.03	136.7	133.4	3.3
3.66 (d, 6.3 Hz, 2H)	3.44 (d, 6.0 Hz, 2H)	0.22	130.2	133.2	3.0
3.49 (s, 3H)	3.39 (s, 3H)	0.10	128.0	127.1	0.9
2.77 (dd, 17.6 & 5.7 Hz, 1H)	2.61 (m, 1H)	0.16	105.3	106.0	0.7
2.53 (m, 1H)	2.44 (s, 1H)	0.09	104.5	103.9	0.6
2.46 (dd, 17.6 & 1.9 Hz, 1H)	2.42 (s, 1H)	0.04	65.0	63.3	1.7
			60.9	60.0	0.9
			60.8	59.9	0.9
			60.7	59.7	1.0
			56.2	55.3	0.9
			56.0	55.1	0.9
			44.6	39.9	4.7
			39.7	39.0	0.7
			36.3	35.3	1.0

[a]Wang, B.-G.; Ebel, R.; Wang, C.-Y.; Wray, V.; Proksch, P. New methoxylated aryltetrahydronaphthalene lignans and a norlignan from *Aglaia cordata*. *Tetrahedron Lett.* **43**, 5783–5787 (2002). NA = Not Available.

Table S15. (-)-Aglacin H (**58**).

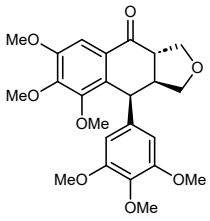


(-)-aglacin H (**58**)
(revised structure)

^{1}H NMR (CDCl$_3$)			**^{13}C NMR (CDCl$_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
7.44 (s, 1H)	7.44 (s, 1H)	0.00	196.4	196.4	0.0
6.25 (s, 2H)	6.25 (s, 2H)	0.00	153.2	153.0	0.2
4.63 (d, 2.6 Hz, 1H)	4.63 (d, 1H, d, (2.5)	0.00	152.8	152.6	0.2
3.94 (s, 3H)	3.94 (s, 3H)	0.00	151.5	151.3	0.2
3.92 (s, 3H)	3.92 (s, 3H)	0.00	147.9	147.8	0.1
3.81 (s, 3H)	3.81 (s, 3H)	0.00	139.5	139.4	0.1
3.74 (s, 6H)	3.74 (s, 6H)	0.00	136.7	136.5	0.2
3.66 (d, 6.3 Hz, 2H)	3.65 (m, 2H)	0.01	130.2	130.1	0.1
3.49 (s, 3H)	3.49 (s, 3H)	0.00	128.0	127.8	0.2
2.77 (dd, 17.6 & 5.7 Hz, 1H)	2.77 (dd, 17.4 & 5.2 Hz, 1H)	0.00	105.3	105.1	0.2
2.53 (m, 1H)	2.54 (m, 1H)	0.01	104.5	104.3	0.2
2.46 (dd, 17.6 & 1.9 Hz, 1H)	2.46 (dd, 17.5 & 2.5 Hz, 1H)	0.00	65.0	64.7	0.3
			60.9	60.7	0.2
			60.8	60.6	0.2
			60.7	60.6	0.1
			56.2	56.0	0.2
			56.0	55.8	0.2
			44.6	44.4	0.2
			39.7	39.5	0.2
			36.3	36.1	0.2

[a]Wang, B.-G.; Ebel, R.; Wang, C.-Y.; Wray, V.; Proksch, P. New methoxylated aryltetrahydronaphthalene lignans and a norlignan from *Aglaia cordata*. *Tetrahedron Lett.* **43**, 5783–5787 (2002). NA = Not Available.

Table S16. The alleged structure of aglacin D (**55**).

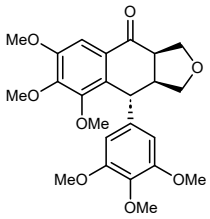


aglacin D (**55**)
(alleged structure)

^{1}H NMR (CDCl$_3$)			**^{13}C NMR (CDCl$_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
7.43 (s, 1H)	7.43 (s, 1H)	0.00	197.7	197.7	0.0
6.24 (s, 2H)	6.14 (s, 2H)	0.10	153.4	155.2	1.8
6.24 (s, 2H)	6.14 (s, 2H)	0.10	151.5	155.1	3.6
4.52 (br, 1H)	4.70 (d, 5.2 Hz, 1H)	0.18	151.2	153.1	1.9
4.29 (d, 8.8 Hz, 1H)	4.08 (t, 8.4 Hz, 1H)	0.21	148.1	149.7	1.6
4.19 (t, 8.8 Hz, 1H)	4.05 (t, 7.3 Hz, 1H)	0.14	140.2	139.4	0.8
3.98 (dd, 8.8 & 6.3 Hz, 1H)	3.91 (m, 1H)	0.07	136.7	136.0	0.7
3.94 (s, 3H)	3.91 (s, 3H)	0.03	130.3	135.6	5.3
3.93 (s, 3H)	3.86 (s, 3H)	0.07	127.5	131.0	3.5
3.80 (s, 3H)	3.79 (s, 3H)	0.01	105.1	108.7	3.6
3.75 (s, 6H)	3.71 (s, 6H)	0.04	104.7	106.8	2.1
3.75 (s, 6H)	3.71 (s, 6H)	0.04	73.1	71.9	1.2
3.53 (s, 3H)	3.36 (s, 3H)	0.17	71.9	68.6	3.3
3.45 (t, 9.5 Hz, 1H)	3.27 (dd, 10.9 &7.7 Hz, 1H)	0.18	60.9	63.0	2.1
2.02 (m, 1H)	3.18 (m, 1H)	1.16	60.8	62.8	2.0
2.02 (m, 1H)	2.80 (m, 1H)	0.78	60.8	62.6	1.8
			56.2	58.4	2.2
			56.0	58.1	2.1
			46.9	48.9	2.0
			45.9	47.6	1.7
			37.3	42.6	5.3

[a]Wang, B.-G.; Ebel, R.; Nugroho, B. W.; Prijono, D.; Frank, W.; Steube, K. G.; Hao, X.-J.; Proksch, P. Aglacins A-D, first representatives of a new class of aryltetralin cyclic ether lignans from *Aglaia cordata*. *J. Nat. Prod.* **64**, 1521–1526 (2001). NA = Not Available.

Table S17. (-)-Aglacin D (**59**).

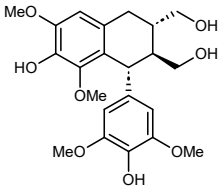


(-)-aglacin D (**59**)
(revised structure)

^{1}H NMR (CDCl$_3$)			**^{13}C NMR (CDCl$_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
7.43 (s, 1H)	7.43 (s, 1H)	0.00	197.7	197.7	0.0
6.24 (s, 2H)	6.24 (s, 2H)	0.00	153.4	153.4	0.0
6.24 (s, 2H)	6.24 (s, 2H)	0.00	NA	153.1	NA
4.52 (br, 1H)	4.52 (br, 1H)	0.00	151.2	151.2	0.0
4.29 (d, 8.8 Hz, 1H)	4.29 (d, 8.7 Hz, 1H)	0.00	148.1	148.2	0.1
4.19 (t, 8.8 Hz, 1H)	4.19 (t, 8.2 Hz, 1H)	0.00	140.2	140.2	0.0
3.98 (dd, 8.8 & 6.3 Hz, 1H)	3.97 (dd, 8.6 & 5.7 Hz, 1H)	-0.01	136.7	136.8	0.1
3.94 (s, 3H)	3.94 (s, 3H)	0.00	130.0	130.1	0.1
3.93 (s, 3H)	3.93 (s, 3H)	0.00	127.5	127.6	0.1
3.80 (s, 3H)	3.79 (s, 3H)	-0.01	105.1	105.1	0.0
3.75 (s, 6H)	3.74 (s, 6H)	-0.01	104.7	104.7	0.0
3.75 (s, 6H)	3.74 (s, 6H)	-0.01	104.7	104.7	0.0
3.53 (s, 3H)	3.52 (s, 3H)	-0.01	73.1	73.1	0.0
3.45 (t, 9.5 Hz, 1H)	3.44 (t, 8.6 Hz, 1H)	-0.01	71.9	71.9	0.0
2.02 (m, 1H)	NA	NA	60.9	60.9	0.0
2.02 (m, 1H)	NA	NA	60.8	60.9	0.1
NA	3.02 (m, 1H)	NA	60.8	60.9	0.1
NA	3.02 (m, 1H)	NA	56.2	56.2	0.0
			56.2	56.2	0.0
			56.0	56.1	0.1
			46.9	47.0	0.1
			45.9	46.0	0.1
			37.3	37.4	0.1

[a]Wang, B.-G.; Ebel, R.; Nugroho, B. W.; Prijono, D.; Frank, W.; Steube, K. G.; Hao, X.-J.; Proksch, P. Aglacins A-D, first representatives of a new class of aryltetralin cyclic ether lignans from *Aglaia cordata*. *J. Nat. Prod.* **64**, 1521–1526 (2001). NA = Not Available.

Table S18. (-)-Lyoniresinol (**63**).

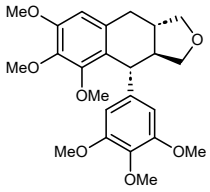


(-)-Lyoniresinol (**63**)

^{1}H NMR (CDCl$_3$)			**^{13}C NMR (CDCl$_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.45 (s, 1H)	6.45 (s, 1H)	0.00	183.4	NA	1.0
6.34 (s, 2H)	6.35 (s, 2H)	0.01	146.8	146.8	0.0
5.37 (br, 1H)	NA	NA	146.2	146.2	0.0
5.33 (br, 1H)	5.34 (br, 2H)	0.01	145.6	145.6	0.0
4.01 (d, 7.6 Hz, 1H)	4.02 (d, 7.9 Hz, 1H)	0.01	NA	138.4	NA
3.88 (s, 3H)	3.88 (s, 3H)	0.00	137.1	137.1	0.0
3.80 (s, 6H)	3.80 (s, 6H)	0.00	132.9	132.9	0.0
3.77 (dd, 10.7, 4.6 Hz, 1H)	3.85-3.74 (m, 3H)	0.02	128.7	128.7	0.0
3.64 (dd, 10.7, 6.9 Hz, 1H)	3.64 (dd, 10.8, 6.7 Hz, 1H)	0.00	125.3	125.3	0.0
NA	3.58 (dd, 11.0, 6.0 Hz, 1H)	NA	106.0	105.9	-0.1
3.29 (s, 3H)	3.30 (s, 3H)	0.01	105.4	105.4	0.0
2.68 (dd, 15.3, 11.5 Hz, 1H)	2.68 (dd, 15.3, 11.8 Hz, 1H)	0.00	66.9	66.8	-0.1
2.59 (dd, 15.3, 3.8 Hz, 1H)	2.59 (dd, 15.2, 4.3 Hz, 1H)	0.00	64.0	64.0	0.0
1.91 (m, 1H)	1.92 (m, 1H)	0.01	59.6	59.5	0.0
1.77 (m, 1H)	1.77 (m, 1H)	0.00	56.5	56.5	0.0
			56.2	56.1	-0.1
			49.6	49.6	0.0
			43.3	43.3	0.0
			40.5	40.4	-0.1
			33.7	33.6	-0.1

[a]Luong, T. M.; Pilkington, L. I.; Barker, D. Total Asymmetric Synthesis and Stereochemical Confirmation of (+)- and (−)-Lyoniresinol and Its Deuterated Analogues. *J. Org. Chem.* **87**, 4254–4262 (2022). NA = Not Available.

Table S19. (+)-Aglacin B (**64**).

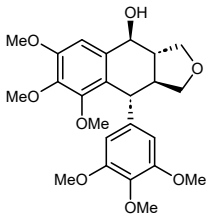


(+)-aglacin B (**64**)

^{1}H NMR ($CDCl_3$)			^{13}C NMR ($CDCl_3$)		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (600 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (150 MHz) δ	**Deviation** Δδ
6.48 (s, 1H)	6.48 (s, 1H)	0.00	153.1	153.1	0.0
6.27 (s, 2H)	6.27 (s, 2H)	0.00	152.6	152.5	0.1
4.16 (t, 7.6 Hz, 1H)	4.16 (t, 9.0 Hz, 1H)	0.00	152.3	152.2	0.1
3.91 (t, 7.6 Hz, 1H)	3.91 (t, 9.0 Hz, 1H)	0.00	144.1	144.0	0.1
3.86 s	3.87 (s, 3H)	0.01	140.8	140.7	0.1
3.82 d (7.7)	3.83 (d, 12.6 Hz, 1H)	0.01	136.1	136.0	0.1
3.81 s	3.81 (s, 3H)	0.00	133.0	133.0	0.0
3.77 s	3.78 (s, 6H)	0.01	125.5	125.5	0.0
3.73 s	3.74 (s, 3H)	0.01	107.5	107.4	0.1
3.60 dd (10.1, 7.6)	3.60 (dd, 12.0 & 7.2 Hz, 1H)	0.00	103.8	103.7	0.1
3.49 dd (10.1, 7.9)	3.49 (dd, 12.6 & 9.6 Hz, 1H)	0.00	72.7	72.7	0.0
3.15 s	3.15 (s, 3H)	0.00	72.6	72.5	0.0
2.91 dd (15.5, 4.1)	2.92 (dd, 18.0 & 4.8 Hz, 1H)	0.01	60.9	60.8	0.1
2.73 dd (15.1, 11.7)	2.73 (dd, 19.6 & 13.2 Hz, 1H)	0.00	60.4	60.3	0.1
2.11 m	2.16-1.98 (m, 2H)	NA	59.4	59.3	0.1
			56.2	56.1	0.1
			55.8	55.7	0.1
			52.8	52.7	0.1
			46.9	46.8	0.1
			41.7	41.6	0.1
			33.5	33.4	0.1

[a]Wang, B.-G.; Ebel, R.; Nugroho, B. W.; Prijono, D.; Frank, W.; Steube, K. G.; Hao, X.-J.; Proksch, P. Aglacins A-D, first representatives of a new class of aryltetralin cyclic ether lignans from *Aglaia cordata*. *J. Nat. Prod.* **64**, 1521–1526 (2001). NA = Not Available.

Table S20. (-)-Aglacin E (**65**).

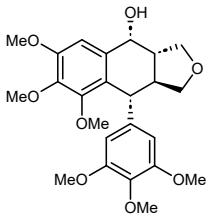


(+)-aglacin E (**65**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
7.05 (s, 1H)	7.05 (s, 1H)	0.00	153.2	153.2	0.0
6.23 (s, 2H)	6.24 (s, 2H)	0.01	152.9	152.9	0.0
4.76 (t, 9.0 Hz, 1H)	4.75 (t, 9.0 Hz, 1H)	0.01	151.8	151.8	0.0
4.32 (t, 7.4 Hz, 1H)	4.31 (t, 7.4 Hz, 1H)	0.01	143.4	143.5	0.1
3.92 (t, 7.1 Hz, 1H)	3.92-3.89 (m, 1H)	NA	141.7	141.7	0.0
3.91 (s, 3H)	3.91 (s, 3H)	0.00	137.4	137.4	0.0
3.86 (d, 9.2 Hz, 1H)	3.86 (d, 9.2 Hz, 1H)	0.00	136.3	136.3	0.0
3.81 (s, 3H)	3.81 (s, 3H)	0.00	125.9	125.8	0.1
3.77 (s, 6H)	3.77 (s, 6H)	0.00	104.0	104.0	0.0
3.75 (s, 3H)	3.75 (s, 3H)	0.00	103.7	103.7	0.0
3.74 (t, 7.9 Hz, 1H)	3.76-3.72 (m, 1H)	NA	73.3	73.2	0.1
3.66 (dd, 9.8 & 7.9 Hz, 1H)	3.67-3.64 (m, 1H)	NA	72.4	72.4	0.0
3.15 (s, 3H)	3.14 (s, 3H)	0.01	72.1	72.1	0.0
2.16 (m, 2H)	2.21-2.09 (m, 2H)	NA	60.9	60.9	0.0
			60.4	60.4	0.0
			59.5	59.5	0.0
			56.2	56.2	0.0
			55.9	55.9	0.0
			50.1	50.1	0.0
			49.8	49.8	0.0
			47.1	47.1	0.0

[a]Wang, B.-G.; Ebel, R.; Wang, C.-Y.; Wray, V.; Proksch, P. New methoxylated aryltetrahydronaphthalene lignans and a norlignan from *Aglaia cordata*. *Tetrahedron Lett.* **43**, 5783–5787 (2002). NA = Not Available.

Table S21. (-)-Aglacin F (**66**).

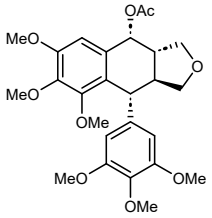


(-)-aglacin F (**66**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
6.71 (s, 1H)	6.71 (s, 1H)	0.00	153.2	153.2	0.0
6.30 (s, 2H)	6.30 (s, 2H)	0.00	152.8	152.8	0.0
4.83 (d, 3.2 Hz, 1H)	4.83 (s, 1H)	0.00	152.7	152.7	0.0
4.09 (t, 7.7 Hz, 1H)	4.10 (t, 7.8 Hz, 1H)	0.01	143.5	143.5	0.0
3.94 (t, 7.6 Hz, 1H)	3.94 (t, 7.6 Hz,1H)	0.00	142.7	142.7	0.0
3.91 (s, 3H)	3.91 (s, 3H)	0.00	136.2	136.2	0.0
3.87 (dd, 10.5 & 7.7 Hz, 1H)	3.87 (dd, 10.6 & 7.7 Hz, 1H)	0.00	135.1	135.1	0.0
3.82 (s, 3H)	3.82 (s, 3H)	0.00	126.1	126.1	0.0
3.78 (s, 6H)	3.78 (s, 6H)	0.00	108.3	108.3	0.0
3.76 (s, 3H)	3.76 (s, 3H)	0.00	103.9	103.9	0.0
3.74 (d, 9.5 Hz, 1H)	3.74 (d, 4.8 Hz, 1H)	0.00	72.5	72.5	0.0
3.61 (dd, 10.4 & 7.6 Hz, 1H)	3.61 (dd, 10.4 & 7.7 Hz, 1H)	0.00	68.2	68.2	0.0
3.15 (s, 3H)	3.15 (s, 3H)	0.00	67.3	67.3	0.0
2.61 (m, 1H)	2.67-2.53 (m, 1H)	NA	60.9	60.9	0.0
2.18 (m, 1H)	2.20-2.15 (m, 1H)	NA	60.4	60.4	0.0
NA	1.85 (s, 1H)	NA	59.5	59.5	0.0
			56.2	56.2	0.0
			55.9	55.9	0.0
			46.9	46.9	0.0
			46.1	46.1	0.0
			43.8	43.7	0.1

[a]Wang, B.-G.; Ebel, R.; Wang, C.-Y.; Wray, V.; Proksch, P. New methoxylated aryltetrahydronaphthalene lignans and a norlignan from *Aglaia cordata*. *Tetrahedron Lett.* **43**, 5783–5787 (2002). NA = Not Available.

Table S22. (+)-Aglacin A (**67**).

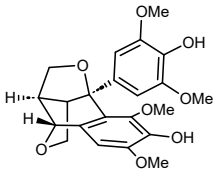


(-)-aglacin A (**67**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (600 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (150 MHz) δ	**Deviation** Δδ
6.77 (s, 1H)	6.77 (s, 1H)	0.00	170.8	170.9	0.1
6.32 (s, 2H)	6.31 (s, 2H)	0.01	153.2	153.2	0.0
6.11 (d, 2.5 Hz, 2H)	6.11 (d, 2.7 Hz, 2H)	0.00	152.6	152.7	0.1
4.06 (br, 7.9 Hz, 1H)	4.06 (t, 7.9 Hz, 1H)	0.00	152.5	152.5	0.0
3.94 (t, 7.6 Hz, 1H)	3.94 (t, 7.5 Hz, 1H)	0.00	143.5	143.5	0.0
3.86 (s, 3H)	3.87 (s, 3H)	0.01	143.1	143.1	0.0
3.81 (s, 3H)	3.81 (s, 3H)	0.00	136.3	136.3	0.0
3.79 (s, 6H)	3.79 (s, 6H)	0.00	131.2	131.3	0.1
3.77 (d, 8.0 Hz, 1H)	3.77 (s, 1H)	0.00	126.8	126.9	0.1
3.76 (s, 3H)	3.76 (s, 3H)	0.00	109.1	109.1	0.0
3.59 (dd, 10.4, 7.6 Hz, 1H)	3.59 (dd, 10.5, 7.7 Hz, 1H)	0.00	104.0	104.0	0.0
3.48 (dd, 10.7, 7.9 Hz, 1H)	3.48 (dd, 10.2, 7.8 Hz, 1H)	0.00	72.2	72.3	0.1
3.15 (s, 3H)	3.14 (s, 3H)	-0.01	68.3	68.3	0.0
2.60 (m, 1H)	2.59 (m, 1H)	-0.01	68.1	68.1	0.0
2.25 (m, 1H)	2.27 (m, 1H)	0.02	60.9	61.0	0.1
2.12 (s, 3H)	2.12 (s, 3H)	0.00	60.4	60.4	0.0
			59.5	59.5	0.0
			56.2	56.3	0.1
			55.9	55.9	0.0
			46.4	46.5	0.1
			44.8	44.8	0.0
			44.6	44.7	0.1
			21.2	21.3	0.1

[a]Wang, B.-G.; Ebel, R.; Nugroho, B. W.; Prijono, D.; Frank, W.; Steube, K. G.; Hao, X.-J.; Proksch, P. Aglacins A-D, first representatives of a new class of aryltetralin cyclic ether lignans from *Aglaia cordata*. *J. Nat. Prod.* **64**, 1521–1526 (2001). NA = Not Available.

Table S23. (-)-Ovafolinin D (**72**).

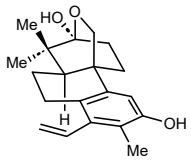


ovafolinin D (**72**)

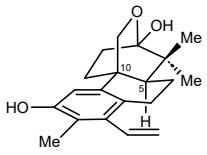
^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (500 MHz) δ (mult, *J*, n)	**Synthetic** (500 MHz) δ (mult, *J*, n)	**Deviation** Δδ	**Natural**[a] (125 MHz) δ	**Synthetic** (125 MHz) δ	**Deviation** Δδ
7.51 (s, 1H)	NA	NA	146.7	147.7	1.0
7.10 (d, 1.4 Hz, 1H)	7.11 (s, 1H)	0.01	146.5	146.7	0.2
6.63 (s, 1H)	6.63 (s, 1H)	0.00	145.4	146.5	0.1
6.43 (d, 1.4 Hz, 1H)	6.44 (s, 1H)	0.01	145.4	145.4	0.0
NA	5.60 (s, 1H)	NA	139.9	139.9	0.0
NA	5.46 (s, 1H)	NA	134.3	134.3	0.0
NA	4.83 (d, 5.4 Hz, 1H)	NA	133.3	133.3	0.0
4.24 (dd, 9.3, 6.4 Hz, 1H)	4.26 (dd, 9.4, 6.4 Hz, 1H)	0.02	126.7	126.7	0.0
3.99 (dd, 9.8, 6.2 Hz, 1H)	4.01 (dd, 9.7, 6.3 Hz, 1H)	0.02	121.1	121.1	0.0
3.95 (s, 3H)	3.95 (s, 3H)	0.00	106.6	106.6	0.0
3.93 (s, 3H)	3.93 (s, 3H)	0.00	101.7	101.7	0.0
3.86 (brd, 9.8 Hz, 1H)	3.87 (d, 9.8 Hz, 1H)	0.01	100.2	100.1	-0.1
3.76 (s, 3H)	3.77 (s, 3H)	0.01	86.0	86.0	0.0
3.48 (brd, 9.3 Hz, 1H)	3.49 (d, 9.5 Hz, 1H)	0.01	81.2	81.2	0.0
3.33 (s, 3H)	3.33 (s, 3H)	0.00	64.1	64.1	0.0
3.10 (*, 1H)	3.12 (q, 6.4 Hz, 1H)	0.02	64.0	64.0	0.0
2.70 (brt, 6.2 Hz, 1H)	2.72 (t, 6.4 Hz, 1H)	0.02	61.0	NA	NA
			61.0	58.4	-2.6
			58.4	56.3	-2.1
			56.3	56.3	0.0
			56.3	56.1	-0.2
			48.9	48.9	0.0

[a]Kashima, K.; Sano, K.; Yun, Y. S.; Ina, H.; Kunugi, A.; Inoue, H. Ovafolinins A—E, five new lignans from *Lyonia ovalifolia*. *Chem. Pharm. Bull.* **58**, 191–194 (2010). NA = Not Available.

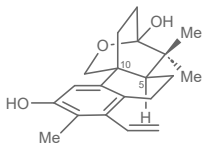
Table S24. Fimbricalyxoid A (**82**).



(+)-fimbricalyxoid A (**82**)
(**synthetic**)



(-)-fimbricalyxoid A
(**natural**)



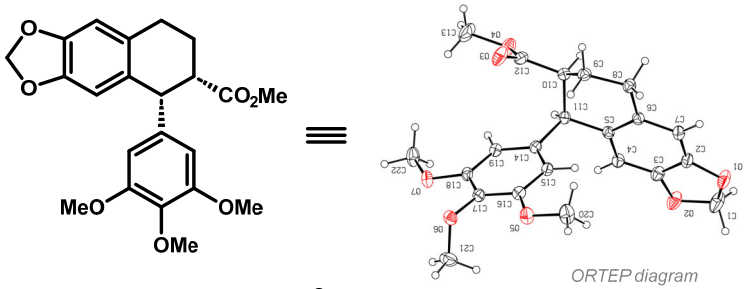
fimbricalyxoid A
(**alleged**)

^{1}H NMR ($CDCl_3$)			**^{13}C NMR ($CDCl_3$)**		
Natural[a] (400 MHz) δ (mult, *J*, n)	**Synthetic** (600 MHz) δ (mult, *J*, n)	**The Alleged**[b] (600 MHz) δ (mult, *J*, n)	**Natural**[a] (100 MHz) δ	**Synthetic** (150 MHz) δ	**The Alleged**[b] (150 MHz) δ
6.68 (s, 1H)	6.71 (s, 1H)	6.68 (s, 1H)	152.0	152.3	152.3
6.60 (dd, 18.0, 11.4 Hz, 1H)	6.60 (dd, 18.0, 11.4 Hz, 1H)	6.60 (dd, 17.9, 11.5 Hz, 1H)	139.3	139.4	139.5
NA	5.88 (brs, 1H)	NA	136.8	136.5	137.0
5.55 (dd, 11.4, 2.0 Hz, 1H)	5.55 (dd, 12.0, 1.2 Hz, 1H)	5.55 (dd, 11.5, 1.6 Hz, 1H)	135.2	135.2	135.4
5.17 (dd, 18.0, 2.0 Hz, 1H)	5.17 (dd, 18.0, 1.2 Hz, 1H)	5.16 (dd, 17.9, 1.6 Hz, 1H)	127.6	127.3	127.7
4.12 (dd, 9.0, 2.2 Hz, 1H)	4.15 (dd, 9.6, 2.4 Hz, 1H)	4.12 (d, 9.2 Hz, 1H)	120.4	120.8	120.8
4.01 (d, 9.0 Hz, 1H)	4.07 (d, 9.0 Hz, 1H)	4.01 (d, 9.2 Hz, 1H)	120.0	120.0	120.2
2.85 (m, 1H)	2.85 (d, 16.2 Hz, 1H)	2.84 (d, 17.0 Hz, 1H)	111.8	111.6	112.0
NA	2.66 (brs, 1H)	NA	99.2	99.6	99.5
2.41 (m, 1H)	2.45-2.40 (m, 2H)	2.41 (m, 2H)	72.5	72.5	72.7
2.28 (m, 1H)	2.32-2.27 (m, 1H)	2.29 (m, 1H)	47.8	47.8	48.1
2.17 (s, 3H)	2.17 (s, 3H)	2.17 (s, 3H)	40.2	40.3	40.5
1.91 (m, 1H)	1.97-1.92 (m, 1H)	1.91 (m, 1H)	36.3	36.2	36.5
1.85 (m, 1H)	1.87-1.84 (m, 1H)	1.85 (m, 1H)	35.1	35.2	35.3
1.66 (m, 1H)	1..73-1.67 (m, 1H)	1.66 (m, 2H)	29.4	29.4	29.6
1.63 (m, 1H)	1.65-1.61 (m, 1H)	1.63 (m, 1H)	28.8	28.8	29.1
1.58 (m, 1H)	1.60-1.56 (m, 1H)	1.58 (m, 1H)	26.9	26.9	27.2
1.11 (s, 3H)	1.11 (s, 3H)	1.11 (s, 3H)	20.7	20.7	20.9
1.04 (s, 3zH)	1.04 (s, 3H)	1.04 (s, 3H)	17.9	17.9	18.1
			12.8	12.9	13.1

[a]Chao, C.-H. et al. Terpenoids from *Flueggea virosa* and their anti-hepatitis C virus activity. *Phytochemistry* **128**, 60–70 (2016). [b]Cheng, L. et al. Diterpenoids and phenanthrenones from the leaves and stems of *Strophioblachia fimbricalyx*. *Tetrahedron Lett.* **57**, 2262–2265 (2016). NA = Not Available.

6. Single X-ray Crystal Diffraction data for 2p, 9, 16, S9, 47 and 70.

2p: (CCDC 2261541)



2p

Table 1 Crystal data and structure refinement for 230504_pz_podo_0m.

Identification code	230504_pz_podo_0m
Empirical formula	$C_{22}H_{24}O_7$
Formula weight	400.41
Temperature/K	170.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.9777(6)
b/Å	12.0839(6)
c/Å	13.9093(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2013.19(17)
Z	4
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	0.521
F(000)	848.0
Crystal size/mm^3	0.06 × 0.04 × 0.03
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.432 to 121.526
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	30726
Independent reflections	4625 [R_{int} = 0.0577, R_{sigma} = 0.0394]
Data/restraints/parameters	4625/0/266
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.0926

Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.0972
Largest diff. peak/hole / e Å^{-3}	0.16/-0.21
Flack parameter	0.04(10)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 230504_pz_podo_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7784.0(14)	7396.2(15)	2518.9(14)	50.6(5)
O2	7232.4(14)	5734.8(15)	3208.1(14)	50.3(5)
O3	891.0(15)	6375.1(15)	834.5(15)	52.1(5)
O4	1819.6(15)	4803.9(13)	531.3(14)	49.3(4)
O5	1741.0(15)	8386.5(12)	4418.1(12)	41.7(4)
O6	206.2(13)	6867.9(12)	4815.0(11)	35.5(4)
O7	207.1(13)	4888.5(12)	3979.2(12)	38.3(4)
C1	8154(2)	6465(2)	3050(3)	62.5(8)
C2	6690.8(18)	7165.8(18)	2266.2(17)	35.2(5)
C3	6361.6(19)	6185.5(19)	2690.9(17)	36.2(5)
C4	5301.5(18)	5789.2(18)	2584.1(15)	32.7(5)
C5	4550.9(17)	6405.3(16)	2016.9(14)	27.5(4)
C6	4886.2(17)	7386.2(17)	1573.3(14)	29.0(4)
C7	5987.2(18)	7780.0(18)	1706.0(16)	33.0(5)
C8	4128.0(19)	8018.7(17)	891.4(16)	34.2(5)
C9	2926.5(19)	7603.9(17)	851.9(15)	32.4(5)
C10	2908.7(18)	6345.6(17)	910.1(15)	29.6(4)
C11	3382.8(17)	5944.6(15)	1889.1(14)	26.5(4)
C12	1759(2)	5877.2(18)	751.7(15)	34.7(5)
C13	771(3)	4237(2)	392(2)	64.6(9)
C14	2595.0(16)	6186.4(16)	2722.1(14)	26.3(4)
C15	2605.3(17)	7203.2(17)	3202.1(15)	29.8(4)
C16	1814.0(18)	7425.0(17)	3905.3(15)	30.8(4)
C17	1017.0(17)	6630.2(17)	4140.5(15)	29.4(4)
C18	1018.5(17)	5607.5(17)	3678.8(15)	29.2(4)
C19	1810.1(17)	5384.8(16)	2971.6(14)	28.8(4)
C20	2507(2)	9247(2)	4204(2)	54.8(7)
C21	525(2)	6624(3)	5769.4(17)	52.5(7)
C22	136(2)	3845(2)	3508(2)	50.9(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230504_pz_podo_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	27.0(8)	53.8(10)	71.0(13)	7.7(9)	-11.0(8)	-7.0(8)
O2	32.5(8)	49.9(10)	68.4(12)	11.1(9)	-17.7(8)	-0.3(8)
O3	33.8(10)	46.5(9)	76.1(13)	3.1(9)	-19.4(9)	-0.3(8)
O4	46.7(10)	37.0(9)	64.1(11)	-12.5(8)	-5.0(9)	-12.0(8)
O5	40.9(9)	32.9(8)	51.4(9)	-12.0(7)	11.2(8)	-3.6(7)
O6	26.6(8)	43.7(8)	36.3(8)	2.6(6)	5.7(6)	8.5(7)
O7	31.0(8)	33.4(8)	50.5(9)	4.2(7)	8.8(7)	-5.9(7)
C1	36.8(15)	60.6(17)	90(2)	11.1(16)	-23.1(15)	-7.4(13)
C2	24.1(11)	39.5(11)	42.0(11)	-3.4(9)	0.3(9)	-3.9(9)
C3	29.5(11)	36.6(12)	42.6(12)	2.2(10)	-5.6(9)	4.1(9)
C4	29.0(11)	31.4(10)	37.6(11)	3.3(9)	-0.9(9)	-2.2(9)
C5	26.1(10)	28.4(10)	27.9(9)	-2.4(8)	2.9(8)	-0.4(8)
C6	28.0(10)	29.6(10)	29.4(10)	-1.6(8)	1.6(8)	-1.1(8)
C7	29.9(11)	31.6(11)	37.5(11)	0.3(9)	2.7(9)	-4.5(9)
C8	34.2(12)	30.6(10)	37.9(11)	5.0(9)	-3.0(9)	-4.1(9)
C9	33.0(11)	32.6(10)	31.5(10)	2.7(8)	-4.7(9)	-0.4(9)
C10	30.2(11)	30.8(10)	28.0(10)	-1.6(8)	-0.6(8)	-1.4(9)
C11	24.7(10)	23.0(9)	31.9(9)	-0.9(7)	1.1(8)	-0.8(8)
C12	38.4(12)	32.9(11)	32.7(10)	1.4(9)	-8.6(9)	-4.3(10)
C13	66(2)	53.6(16)	73.7(19)	-0.2(15)	-22.4(16)	-30.8(15)
C14	23.5(10)	26.5(9)	28.8(9)	0.2(7)	-2.0(8)	2.3(8)
C15	26.2(10)	30.1(10)	33.0(10)	-1.0(8)	-0.1(8)	-3.6(8)
C16	29.7(11)	28.8(10)	34.0(10)	-3.7(8)	-0.7(9)	2.8(9)
C17	23.2(10)	33.8(10)	31.2(10)	2.2(8)	-0.1(8)	3.6(8)
C18	21.7(9)	30.5(10)	35.3(10)	5.9(8)	-0.5(8)	-0.3(8)
C19	26.8(10)	26.6(9)	32.9(10)	0.9(8)	-1.6(8)	-0.3(8)
C20	56.8(17)	35.4(13)	72.2(18)	-15.5(12)	17.6(14)	-9.3(12)
C21	41.5(15)	83.7(19)	32.4(12)	2.3(12)	3.4(11)	16.3(14)
C22	45.9(15)	36.0(12)	70.8(17)	-2.8(12)	12.1(13)	-14.7(11)

Table 4 Bond Lengths for 230504_pz_podo_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.417(3)	C4	C5	1.409(3)
O1	C2	1.384(3)	C5	C6	1.395(3)
O2	C1	1.430(3)	C5	C11	1.516(3)
O2	C3	1.379(3)	C6	C7	1.414(3)
O3	C12	1.207(3)	C6	C8	1.519(3)
O4	C12	1.335(3)	C8	C9	1.525(3)

Table 4 Bond Lengths for 230504_pz_podo_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C13	1.443(3)	C9	C10	1.523(3)
O5	C16	1.366(2)	C10	C11	1.553(3)
O5	C20	1.418(3)	C10	C12	1.505(3)
O6	C17	1.380(3)	C11	C14	1.523(3)
O6	C21	1.412(3)	C14	C15	1.398(3)
O7	C18	1.369(2)	C14	C19	1.394(3)
O7	C22	1.423(3)	C15	C16	1.388(3)
C2	C3	1.381(3)	C16	C17	1.393(3)
C2	C7	1.367(3)	C17	C18	1.393(3)
C3	C4	1.365(3)	C18	C19	1.392(3)

Table 5 Bond Angles for 230504_pz_podo_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	105.59(19)	C9	C10	C11	110.67(16)
C3	O2	C1	105.08(18)	C12	C10	C9	112.37(18)
C12	O4	C13	116.4(2)	C12	C10	C11	110.22(17)
C16	O5	C20	118.19(18)	C5	C11	C10	109.01(16)
C17	O6	C21	113.91(17)	C5	C11	C14	114.34(16)
C18	O7	C22	117.66(18)	C14	C11	C10	112.38(16)
O1	C1	O2	109.2(2)	O3	C12	O4	123.6(2)
C3	C2	O1	109.5(2)	O3	C12	C10	125.9(2)
C7	C2	O1	128.2(2)	O4	C12	C10	110.5(2)
C7	C2	C3	122.2(2)	C15	C14	C11	121.77(18)
O2	C3	C2	110.23(19)	C19	C14	C11	118.31(17)
C4	C3	O2	128.4(2)	C19	C14	C15	119.84(18)
C4	C3	C2	121.3(2)	C16	C15	C14	120.01(19)
C3	C4	C5	117.98(19)	O5	C16	C15	125.16(19)
C4	C5	C11	117.42(17)	O5	C16	C17	114.82(18)
C6	C5	C4	120.85(19)	C15	C16	C17	120.01(19)
C6	C5	C11	121.71(18)	O6	C17	C16	119.88(18)
C5	C6	C7	119.78(19)	O6	C17	C18	119.93(18)
C5	C6	C8	122.10(19)	C18	C17	C16	120.17(19)
C7	C6	C8	118.00(18)	O7	C18	C17	114.93(18)
C2	C7	C6	117.8(2)	O7	C18	C19	125.19(19)
C6	C8	C9	114.91(17)	C19	C18	C17	119.87(18)
C10	C9	C8	109.85(18)	C18	C19	C14	120.06(18)

Table 6 Torsion Angles for 230504_pz_podo_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C2	C3	O2	-1.6(3)	C8	C9	C10	C11	63.4(2)
O1	C2	C3	C4	177.6(2)	C8	C9	C10	C12	−172.90(17)
O1	C2	C7	C6	-178.1(2)	C9	C10	C11	C5	-56.5(2)
O2	C3	C4	C5	179.8(2)	C9	C10	C11	C14	71.3(2)
O5	C16	C17	O6	2.8(3)	C9	C10	C12	O3	-19.9(3)
O5	C16	C17	C18	−178.84(19)	C9	C10	C12	O4	162.06(18)
O6	C17	C18	O7	-2.6(3)	C10	C11	C14	C15	-86.2(2)
O6	C17	C18	C19	177.49(18)	C10	C11	C14	C19	90.6(2)
O7	C18	C19	C14	179.70(19)	C11	C5	C6	C7	−179.45(18)
C1	O1	C2	C3	5.1(3)	C11	C5	C6	C8	-3.5(3)
C1	O1	C2	C7	-176.2(3)	C11	C10	C12	O3	104.0(3)
C1	O2	C3	C2	-2.6(3)	C11	C10	C12	O4	-74.0(2)
C1	O2	C3	C4	178.3(3)	C11	C14	C15	C16	174.74(19)
C2	O1	C1	O2	-6.7(3)	C11	C14	C19	C18	−175.01(18)
C2	C3	C4	C5	0.7(3)	C12	C10	C11	C5	178.57(16)
C3	O2	C1	O1	5.7(3)	C12	C10	C11	C14	-53.6(2)
C3	C2	C7	C6	0.5(3)	C13	O4	C12	O3	-0.1(3)
C3	C4	C5	C6	0.4(3)	C13	O4	C12	C10	177.9(2)
C3	C4	C5	C11	178.88(19)	C14	C15	C16	O5	-179.8(2)
C4	C5	C6	C7	-1.1(3)	C14	C15	C16	C17	0.7(3)
C4	C5	C6	C8	174.82(19)	C15	C14	C19	C18	1.8(3)
C4	C5	C11	C10	−151.75(17)	C15	C16	C17	O6	−177.64(19)
C4	C5	C11	C14	81.5(2)	C15	C16	C17	C18	0.7(3)
C5	C6	C7	C2	0.6(3)	C16	C17	C18	O7	179.08(18)
C5	C6	C8	C9	9.1(3)	C16	C17	C18	C19	-0.8(3)
C5	C11	C14	C15	38.8(3)	C17	C18	C19	C14	-0.4(3)
C5	C11	C14	C19	−144.48(18)	C19	C14	C15	C16	-1.9(3)
C6	C5	C11	C10	26.7(2)	C20	O5	C16	C15	2.0(3)
C6	C5	C11	C14	-100.0(2)	C20	O5	C16	C17	-178.5(2)
C6	C8	C9	C10	-38.2(2)	C21	O6	C17	C16	-88.4(3)
C7	C2	C3	O2	179.6(2)	C21	O6	C17	C18	93.3(3)
C7	C2	C3	C4	-1.2(4)	C22	O7	C18	C17	177.6(2)
C7	C6	C8	C9	−174.96(19)	C22	O7	C18	C19	-2.5(3)
C8	C6	C7	C2	−175.47(19)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230504_pz_podo_0m.

Atom	*x*	*y*	*z*	U(eq)
H1A	8465.59	6708.7	3674.79	75
H1B	8749.21	6075.27	2690.7	75
H4	5076.73	5118.46	2883.17	39
H7	6229.8	8449.54	1415.35	40
H8A	4449.27	7979.53	236.48	41
H8B	4120.98	8806.67	1086.26	41
H9A	2496.35	7919.62	1394.31	39
H9B	2572.35	7848.14	244.84	39
H10	3405.34	6053.54	390.88	36
H11	3456.5	5121.76	1846.48	32
H13A	353.43	4595.05	-127.28	97
H13B	334.4	4267.63	987.43	97
H13C	914.45	3462.56	222.53	97
H15	3153.86	7742.13	3046.94	36
H19	1815.17	4685.89	2658.95	35
H20A	2436.69	9453.31	3525.46	82
H20B	3269.13	8990.49	4330.6	82
H20C	2344.2	9891.12	4608.4	82
H21A	445.33	5827.68	5885.25	79
H21B	45.52	7032.34	6216.79	79
H21C	1304.34	6841.86	5868.51	79
H22A	-38.42	3958.93	2827.26	76
H22B	-453.5	3400.67	3807.46	76
H22C	851.71	3457.58	3566.52	76

Experimental

A suitable crystal was selected and analysed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{22}H_{24}O_7$ (M =400.41 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.9777(6) Å, b = 12.0839(6) Å, c = 13.9093(7) Å, V = 2013.19(17) Å^3, Z = 4, T = 170.00 K, μ(GaKα) = 0.521 mm^{-1}, *Dcalc* = 1.321 g/cm^3, 30726 reflections measured (8.432° ≤ 2Θ ≤ 121.526°), 4625 unique (R_{int} = 0.0577, R_{sigma} = 0.0394) which were used in all calculations. The final R_1 was 0.0391 (I > 2σ(I)) and wR_2 was 0.0972 (all data).

Refinement model description

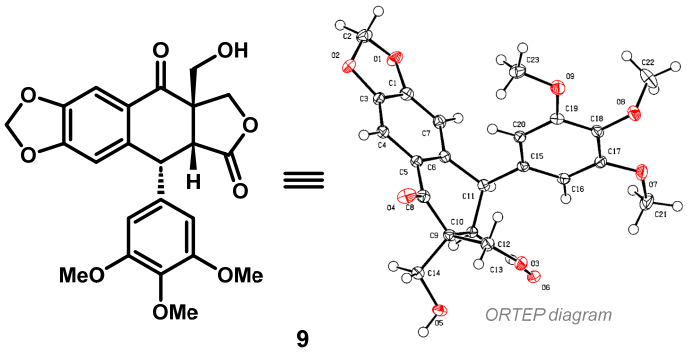
Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C10(H10), C11(H11)
2.b Secondary CH2 refined with riding coordinates:
 C1(H1A,H1B), C8(H8A,H8B), C9(H9A,H9B)
2.c Aromatic/amide H refined with riding coordinates:
 C4(H4), C7(H7), C15(H15), C19(H19)
2.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C20(H20A,H20B,H20C), C21(H21A,H21B,H21C), C22(H22A,H22B,
 H22C)
```

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

9: (CCDC 2232313)



9

Table 1. Crystal data and structure refinement for cu_PZ_829C_1123_0m_a-finalcif.

Identification code	cu_PZ_829C_1123_0m_a	
Empirical formula	C23 H22 O9	
Formula weight	442.40	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.8725(3) Å	α= 90°.
	b = 11.7428(4) Å	β= 90°.
	c = 25.1570(9) Å	γ = 90°.
Volume	2030.23(13) $Å^3$	
Z	4	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	0.949 mm^{-1}	

F(000)	928
Crystal size	0.2 x 0.1 x 0.05 mm^3
Theta range for data collection	4.155 to 74.438°.
Index ranges	-8<=h<=7, -14<=k<=14, -31<=l<=31
Reflections collected	26875
Independent reflections	4067 [R(int) = 0.0296]
Completeness to theta = 67.679°	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.6524
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4067 / 1 / 295
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0666
R indices (all data)	R1 = 0.0259, wR2 = 0.0668
Absolute structure parameter	0.09(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.196 and -0.139 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cu_PZ_829C_1123_0m_a-finalcif. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2360(2)	9714(1)	4171(1)	23(1)
O(2)	5501(2)	9614(1)	4496(1)	21(1)
O(3)	3236(2)	2864(1)	3846(1)	20(1)
O(4)	7406(2)	5337(1)	4443(1)	25(1)
O(5)	3476(2)	2896(1)	5032(1)	24(1)
O(6)	70(2)	2960(1)	4021(1)	21(1)
O(7)	-244(2)	3909(1)	2204(1)	23(1)
O(8)	2801(2)	4834(1)	1713(1)	21(1)
O(9)	5445(2)	6058(1)	2236(1)	22(1)
C(1)	2925(3)	8602(1)	4195(1)	18(1)
C(2)	4110(3)	10364(2)	4252(1)	22(1)
C(3)	4829(2)	8534(1)	4393(1)	16(1)
C(4)	5734(2)	7521(1)	4472(1)	17(1)

C(5)	4661(2)	6529(1)	4338(1)	15(1)
C(6)	2762(2)	6593(1)	4135(1)	15(1)
C(7)	1869(2)	7659(1)	4063(1)	17(1)
C(8)	5643(2)	5420(1)	4390(1)	16(1)
C(9)	4405(2)	4348(1)	4409(1)	15(1)
C(10)	2225(2)	4511(1)	4301(1)	14(1)
C(11)	1737(2)	5536(1)	3935(1)	14(1)
C(12)	5002(2)	3472(1)	3982(1)	19(1)
C(13)	1668(3)	3383(1)	4052(1)	16(1)
C(14)	4694(2)	3868(1)	4971(1)	18(1)
C(15)	2127(2)	5333(1)	3342(1)	14(1)
C(16)	742(2)	4711(1)	3058(1)	15(1)
C(17)	1000(2)	4518(1)	2518(1)	16(1)
C(18)	2607(2)	4979(1)	2253(1)	16(1)
C(19)	3979(2)	5611(1)	2536(1)	16(1)
C(20)	3761(2)	5770(1)	3084(1)	15(1)
C(21)	-1948(3)	3457(2)	2448(1)	27(1)
C(22)	1635(3)	5664(2)	1433(1)	31(1)
C(23)	6836(3)	6775(2)	2493(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for cu_PZ_829C_1123_0m_a-finalcif.

O(1)-C(1)	1.364(2)
O(1)-C(2)	1.439(2)
O(2)-C(3)	1.3748(19)
O(2)-C(2)	1.438(2)
O(3)-C(13)	1.341(2)
O(3)-C(12)	1.449(2)
O(4)-C(8)	1.223(2)
O(5)-C(14)	1.4239(19)
O(6)-C(13)	1.208(2)
O(7)-C(17)	1.366(2)
O(7)-C(21)	1.425(2)
O(8)-C(18)	1.3754(19)
O(8)-C(22)	1.445(2)

O(9)-C(19)	1.364(2)
O(9)-C(23)	1.429(2)
C(1)-C(7)	1.366(2)
C(1)-C(3)	1.402(2)
C(3)-C(4)	1.357(2)
C(4)-C(5)	1.419(2)
C(5)-C(6)	1.403(2)
C(5)-C(8)	1.472(2)
C(6)-C(7)	1.406(2)
C(6)-C(11)	1.514(2)
C(8)-C(9)	1.521(2)
C(9)-C(14)	1.534(2)
C(9)-C(10)	1.534(2)
C(9)-C(12)	1.543(2)
C(10)-C(13)	1.515(2)
C(10)-C(11)	1.553(2)
C(11)-C(15)	1.532(2)
C(15)-C(20)	1.395(2)
C(15)-C(16)	1.396(2)
C(16)-C(17)	1.390(2)
C(17)-C(18)	1.399(2)
C(18)-C(19)	1.396(2)
C(19)-C(20)	1.401(2)

C(1)-O(1)-C(2)	105.27(13)
C(3)-O(2)-C(2)	105.06(13)
C(13)-O(3)-C(12)	110.96(11)
C(17)-O(7)-C(21)	117.41(13)
C(18)-O(8)-C(22)	110.12(13)
C(19)-O(9)-C(23)	118.08(13)
O(1)-C(1)-C(7)	127.92(15)
O(1)-C(1)-C(3)	109.62(14)
C(7)-C(1)-C(3)	122.46(15)
O(2)-C(2)-O(1)	106.97(13)
C(4)-C(3)-O(2)	128.76(15)
C(4)-C(3)-C(1)	122.00(15)

O(2)-C(3)-C(1)	109.21(14)
C(3)-C(4)-C(5)	116.49(14)
C(6)-C(5)-C(4)	121.74(15)
C(6)-C(5)-C(8)	120.36(14)
C(4)-C(5)-C(8)	117.81(14)
C(5)-C(6)-C(7)	120.03(15)
C(5)-C(6)-C(11)	120.70(14)
C(7)-C(6)-C(11)	118.92(14)
C(1)-C(7)-C(6)	117.28(15)
O(4)-C(8)-C(5)	122.28(15)
O(4)-C(8)-C(9)	119.02(15)
C(5)-C(8)-C(9)	118.61(13)
C(8)-C(9)-C(14)	105.11(12)
C(8)-C(9)-C(10)	115.92(13)
C(14)-C(9)-C(10)	109.61(13)
C(8)-C(9)-C(12)	112.42(13)
C(14)-C(9)-C(12)	111.23(12)
C(10)-C(9)-C(12)	102.69(13)
C(13)-C(10)-C(9)	102.18(13)
C(13)-C(10)-C(11)	112.10(12)
C(9)-C(10)-C(11)	114.41(12)
C(6)-C(11)-C(15)	111.72(13)
C(6)-C(11)-C(10)	109.67(12)
C(15)-C(11)-C(10)	114.82(12)
O(3)-C(12)-C(9)	105.67(13)
O(6)-C(13)-O(3)	121.24(14)
O(6)-C(13)-C(10)	128.01(15)
O(3)-C(13)-C(10)	110.75(14)
O(5)-C(14)-C(9)	108.49(13)
C(20)-C(15)-C(16)	120.20(14)
C(20)-C(15)-C(11)	122.39(14)
C(16)-C(15)-C(11)	117.39(13)
C(17)-C(16)-C(15)	119.98(15)
O(7)-C(17)-C(16)	124.84(15)
O(7)-C(17)-C(18)	114.93(14)
C(16)-C(17)-C(18)	120.22(14)

O(8)-C(18)-C(19)	120.32(15)
O(8)-C(18)-C(17)	119.93(14)
C(19)-C(18)-C(17)	119.72(14)
O(9)-C(19)-C(18)	114.91(14)
O(9)-C(19)-C(20)	124.93(15)
C(18)-C(19)-C(20)	120.14(15)
C(15)-C(20)-C(19)	119.67(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cu_PZ_829C_1123_0m_a-finalcif. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	12(1)	31(1)	-3(1)	-1(1)	3(1)
O(2)	26(1)	13(1)	23(1)	-3(1)	-2(1)	-3(1)
O(3)	26(1)	15(1)	19(1)	-2(1)	-2(1)	1(1)
O(4)	15(1)	21(1)	38(1)	4(1)	2(1)	1(1)
O(5)	30(1)	21(1)	21(1)	9(1)	-6(1)	-8(1)
O(6)	26(1)	18(1)	18(1)	3(1)	-2(1)	-9(1)
O(7)	25(1)	26(1)	18(1)	-3(1)	-2(1)	-10(1)
O(8)	26(1)	24(1)	13(1)	-1(1)	0(1)	0(1)
O(9)	21(1)	28(1)	17(1)	2(1)	4(1)	-7(1)
C(1)	24(1)	14(1)	16(1)	-1(1)	3(1)	6(1)
C(2)	26(1)	14(1)	26(1)	-2(1)	3(1)	2(1)
C(3)	21(1)	14(1)	14(1)	-2(1)	2(1)	-4(1)
C(4)	18(1)	18(1)	14(1)	0(1)	1(1)	-2(1)
C(5)	18(1)	14(1)	13(1)	0(1)	1(1)	-1(1)
C(6)	17(1)	15(1)	12(1)	-1(1)	2(1)	-1(1)
C(7)	18(1)	18(1)	16(1)	-1(1)	0(1)	2(1)
C(8)	16(1)	18(1)	15(1)	0(1)	3(1)	1(1)
C(9)	17(1)	14(1)	15(1)	1(1)	1(1)	2(1)
C(10)	17(1)	13(1)	12(1)	0(1)	1(1)	-2(1)
C(11)	14(1)	14(1)	14(1)	0(1)	0(1)	1(1)
C(12)	21(1)	17(1)	19(1)	-2(1)	0(1)	2(1)

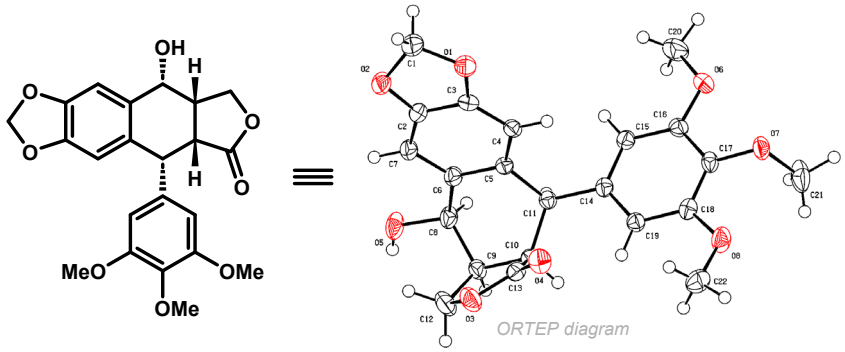
C(13)	24(1)	14(1)	12(1)	4(1)	-1(1)	-1(1)
C(14)	20(1)	17(1)	16(1)	1(1)	-3(1)	-1(1)
C(15)	15(1)	11(1)	14(1)	1(1)	-1(1)	3(1)
C(16)	15(1)	14(1)	16(1)	3(1)	-1(1)	0(1)
C(17)	17(1)	13(1)	18(1)	0(1)	-4(1)	0(1)
C(18)	20(1)	16(1)	12(1)	0(1)	1(1)	2(1)
C(19)	16(1)	15(1)	17(1)	3(1)	2(1)	1(1)
C(20)	15(1)	13(1)	16(1)	1(1)	-2(1)	1(1)
C(21)	26(1)	27(1)	28(1)	-4(1)	-2(1)	-12(1)
C(22)	28(1)	48(1)	16(1)	6(1)	-2(1)	7(1)
C(23)	18(1)	24(1)	28(1)	2(1)	3(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cu_PZ_829C_1123_0m_a-finalcif.

	x	y	z	U(eq)
H(1)	3820(40)	2560(20)	5319(7)	36
H(2A)	4614	10648	3908	26
H(2B)	3847	11025	4486	26
H(4)	7019	7479	4610	20
H(7)	582	7720	3927	20
H(10)	1523	4601	4647	17
H(11)	309	5679	3971	17
H(12A)	5542	3861	3666	23
H(12B)	5994	2942	4124	23
H(14A)	6072	3652	5024	21
H(14B)	4349	4452	5239	21
H(16)	-375	4420	3234	18
H(20)	4721	6174	3280	18
H(21A)	-2725	3052	2181	40
H(21B)	-2719	4080	2599	40
H(21C)	-1574	2928	2731	40
H(22A)	1741	5534	1049	46

H(22B)	2102	6432	1518	46
H(22C)	272	5590	1542	46
H(23A)	7753	7073	2229	35
H(23B)	7548	6333	2761	35
H(23C)	6163	7410	2666	35

16: (CCDC 2236506)



epiisopicropodophyllin (**16**)

Table 1 Crystal data and structure refinement for cu_230112_pz_1444a_0m.

Identification code	cu_230112_pz_1444a_0m
Empirical formula	$C_{22}H_{22}O_8$
Formula weight	414.39
Temperature/K	170.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.4236(2)
b/Å	11.1986(2)
c/Å	16.7198(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1951.70(6)
Z	4
ρ_{calc}g/cm^3	1.410
μ/mm^{-1}	0.907
F(000)	872.0
Crystal size/mm^3	0.42 × 0.35 × 0.23
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.506 to 136.764

Index ranges	$-11 \le h \le 12$, $-13 \le k \le 13$, $-20 \le l \le 20$
Reflections collected	16940
Independent reflections	3582 [R_{int} = 0.0332, R_{sigma} = 0.0219]
Data/restraints/parameters	3582/0/275
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0257, wR_2 = 0.0648
Final R indexes [all data]	R_1 = 0.0269, wR_2 = 0.0658
Largest diff. peak/hole / e Å^{-3}	0.15/-0.19
Flack parameter	-0.01(5)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for cu_230112_pz_1444a_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	5998.0(13)	3756.7(12)	7124.5(8)	32.3(3)
O2	6201.9(13)	1733.8(12)	7360.3(8)	36.0(3)
O3	3755.9(14)	1446.2(13)	4156.3(9)	37.9(3)
O4	3922.9(13)	3408.9(12)	4243.5(8)	34.5(3)
O5	2458.3(15)	-409.6(12)	6033.4(10)	42.0(4)
O6	446.3(14)	7040.6(12)	6630.9(8)	33.7(3)
O7	750.5(13)	8110.4(11)	5230.8(8)	31.4(3)
O8	1596.9(15)	6905.2(12)	3937.7(8)	36.8(3)
C1	6601(2)	2888.5(18)	7632.0(13)	39.7(5)
C2	5075.9(17)	1954.5(16)	6949.3(10)	25.8(3)
C3	4957.5(16)	3166.5(15)	6807.3(9)	23.6(3)
C4	3951.2(16)	3635.4(15)	6374.3(9)	22.4(3)
C5	3043.4(16)	2828.3(14)	6084.2(9)	21.3(3)
C6	3175.2(17)	1595.5(15)	6224.4(10)	24.8(3)
C7	4210.2(18)	1137.2(15)	6661.0(10)	27.5(3)
C8	2145.3(18)	800.5(15)	5885.4(11)	28.8(4)
C9	1924.2(17)	1052.9(14)	4983.8(11)	27.3(4)
C10	2019.0(17)	2401.6(14)	4797.1(10)	23.8(3)
C11	1908.1(16)	3171.0(14)	5562.7(9)	21.2(3)
C12	2948(2)	492.0(17)	4443.0(13)	39.4(5)
C13	3312.9(17)	2521.7(16)	4381.5(10)	27.7(4)
C14	1663.6(16)	4496.3(14)	5444.5(10)	22.3(3)
C15	1236.7(16)	5143.3(15)	6106.3(10)	24.2(3)
C16	905.3(16)	6338.1(15)	6029.5(10)	24.6(3)
C17	1026.3(16)	6908.4(15)	5287.8(11)	24.1(3)
C18	1469.1(17)	6267.3(15)	4631.4(10)	25.8(3)
C19	1764.7(16)	5057.5(15)	4704.7(10)	23.7(3)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_230112_pz_1444a_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C20	166(3)	6474(2)	7371.5(12)	48.2(6)
C21	-410(2)	8377(2)	4833.1(18)	51.4(6)
C22	2311(2)	6371(2)	3306.6(11)	39.4(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_230112_pz_1444a_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	31.4(7)	27.3(6)	38.2(7)	-4.2(5)	-10.9(5)	-3.5(5)
O2	35.1(7)	29.0(6)	43.8(7)	-3.4(6)	-19.2(6)	4.2(5)
O3	36.1(7)	33.5(7)	44.1(7)	-8.8(6)	3.5(6)	10.0(6)
O4	32.5(7)	34.5(7)	36.6(7)	3.0(6)	7.6(5)	1.3(6)
O5	46.7(8)	18.0(6)	61.4(9)	6.9(6)	-27.0(7)	-5.0(6)
O6	44.3(8)	27.6(6)	29.3(6)	-6.0(5)	-0.2(5)	7.7(6)
O7	34.0(7)	17.6(5)	42.7(7)	-0.2(5)	-9.8(6)	2.6(5)
O8	47.5(8)	30.3(7)	32.6(6)	12.1(5)	7.1(6)	8.3(6)
C1	41.4(11)	33.1(10)	44.6(10)	-5.6(8)	-21.3(9)	1.2(8)
C2	24.8(8)	26.6(8)	25.8(7)	-0.7(7)	-4.5(7)	3.9(7)
C3	25.2(8)	25.1(8)	20.4(7)	-4.5(6)	-0.1(6)	-2.9(6)
C4	27.3(8)	19.1(7)	20.8(7)	-0.8(6)	2.1(6)	-0.8(6)
C5	23.4(8)	20.9(7)	19.7(7)	0.1(6)	0.5(6)	0.5(6)
C6	27.1(8)	21.2(8)	26.1(8)	1.5(6)	-2.0(7)	-0.5(7)
C7	32.5(9)	19.9(7)	30.2(8)	1.1(7)	-6.1(7)	1.2(7)
C8	30.9(9)	18.4(8)	37.1(9)	4.6(7)	-8.5(7)	-2.2(7)
C9	27.8(8)	19.2(8)	34.9(9)	-4.9(7)	-8.9(7)	1.8(7)
C10	24.7(8)	21.4(8)	25.4(8)	-2.2(6)	-6.4(6)	2.8(7)
C11	21.2(8)	19.7(7)	22.6(7)	0.0(6)	0.0(6)	-0.6(6)
C12	44.0(11)	25.5(9)	48.7(11)	-9.9(8)	-0.8(9)	5.8(8)
C13	29.1(9)	31.1(9)	22.9(8)	-2.2(7)	-3.9(7)	7.3(8)
C14	19.3(8)	20.7(8)	26.9(8)	0.6(6)	-2.6(6)	-0.6(6)
C15	25.5(8)	23.1(8)	23.9(7)	1.7(6)	-1.1(6)	0.4(7)
C16	22.4(8)	23.6(8)	27.7(8)	-4.3(7)	-3.6(6)	-0.2(7)
C17	21.8(8)	17.3(7)	33.3(8)	0.5(7)	-4.8(7)	-0.9(6)
C18	24.3(8)	24.1(8)	28.9(8)	4.7(7)	-1.9(6)	-0.2(7)
C19	24.2(8)	22.9(8)	24.0(7)	0.3(6)	1.0(6)	1.7(6)
C20	71.4(16)	43.7(12)	29.5(10)	-5.7(9)	9.8(10)	9.7(11)
C21	36.7(11)	31.5(10)	85.9(17)	-1.5(11)	-18.4(11)	11.9(9)
C22	47.6(12)	43.0(11)	27.6(9)	8.4(8)	3.6(8)	0.7(9)

Table 4 Bond Lengths for cu_230112_pz_1444a_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.435(2)	C4	C5	1.396(2)
O1	C3	1.376(2)	C5	C6	1.407(2)
O2	C1	1.432(2)	C5	C11	1.519(2)
O2	C2	1.382(2)	C6	C7	1.400(2)
O3	C12	1.443(3)	C6	C8	1.505(2)
O3	C13	1.344(2)	C8	C9	1.551(2)
O4	C13	1.202(2)	C9	C10	1.545(2)
O5	C8	1.416(2)	C9	C12	1.533(3)
O6	C16	1.364(2)	C10	C11	1.547(2)
O6	C20	1.422(3)	C10	C13	1.523(3)
O7	C17	1.380(2)	C11	C14	1.519(2)
O7	C21	1.413(3)	C14	C15	1.395(2)
O8	C18	1.369(2)	C14	C19	1.392(2)
O8	C22	1.423(3)	C15	C16	1.388(2)
C2	C3	1.383(2)	C16	C17	1.401(2)
C2	C7	1.373(3)	C17	C18	1.390(3)
C3	C4	1.378(2)	C18	C19	1.395(2)

Table 5 Bond Angles for cu_230112_pz_1444a_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O1	C1	104.33(14)	C12	C9	C10	103.70(15)
C2	O2	C1	104.05(13)	C9	C10	C11	111.85(13)
C13	O3	C12	111.72(15)	C13	C10	C9	103.60(14)
C16	O6	C20	117.21(15)	C13	C10	C11	113.23(14)
C17	O7	C21	114.68(15)	C5	C11	C10	106.02(13)
C18	O8	C22	117.37(15)	C14	C11	C5	116.88(13)
O2	C1	O1	107.28(14)	C14	C11	C10	116.68(13)
O2	C2	C3	109.66(15)	O3	C12	C9	107.39(14)
C7	C2	O2	127.84(16)	O3	C13	C10	110.67(15)
C7	C2	C3	122.36(16)	O4	C13	O3	120.35(17)
O1	C3	C2	109.55(15)	O4	C13	C10	128.98(16)
O1	C3	C4	128.25(16)	C15	C14	C11	117.24(14)
C4	C3	C2	122.13(15)	C19	C14	C11	122.98(15)
C3	C4	C5	116.86(15)	C19	C14	C15	119.64(15)
C4	C5	C6	120.76(15)	C16	C15	C14	120.44(15)
C4	C5	C11	124.34(14)	O6	C16	C15	125.12(16)
C6	C5	C11	114.80(14)	O6	C16	C17	114.93(15)

Table 5 Bond Angles for cu_230112_pz_1444a_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	C6	C8	116.61(15)	C15	C16	C17	119.95(15)
C7	C6	C5	121.45(15)	O7	C17	C16	119.17(16)
C7	C6	C8	121.94(15)	O7	C17	C18	121.22(15)
C2	C7	C6	116.44(15)	C18	C17	C16	119.56(15)
O5	C8	C6	109.63(14)	O8	C18	C17	115.58(15)
O5	C8	C9	112.24(15)	O8	C18	C19	124.05(16)
C6	C8	C9	111.35(14)	C17	C18	C19	120.37(15)
C10	C9	C8	111.41(13)	C14	C19	C18	120.00(15)
C12	C9	C8	113.28(15)				

Table 6 Torsion Angles for cu_230112_pz_1444a_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C4	C5	176.81(15)	C8	C9	C10	C11	-16.8(2)
O2	C2	C3	O1	-0.21(19)	C8	C9	C10	C13	105.52(16)
O2	C2	C3	C4	176.93(15)	C8	C9	C12	O3	−106.78(17)
O2	C2	C7	C6	−176.59(17)	C9	C10	C11	C5	62.22(17)
O5	C8	C9	C10	−161.65(15)	C9	C10	C11	C14	−165.65(14)
O5	C8	C9	C12	-45.2(2)	C9	C10	C13	O3	14.52(18)
O6	C16	C17	O7	3.4(2)	C9	C10	C13	O4	−165.82(18)
O6	C16	C17	C18	−179.11(15)	C10	C9	C12	O3	14.1(2)
O7	C17	C18	O8	-0.5(2)	C10	C11	C14	C15	163.92(15)
O7	C17	C18	C19	178.84(16)	C10	C11	C14	C19	-11.7(2)
O8	C18	C19	C14	176.86(16)	C11	C5	C6	C7	176.82(15)
C1	O1	C3	C2	-13.46(19)	C11	C5	C6	C8	-3.5(2)
C1	O1	C3	C4	169.62(17)	C11	C10	C13	O3	135.89(15)
C1	O2	C2	C3	13.8(2)	C11	C10	C13	O4	-44.4(2)
C1	O2	C2	C7	−170.36(19)	C11	C14	C15	C16	−175.35(15)
C2	O2	C1	O1	-22.0(2)	C11	C14	C19	C18	177.03(16)
C2	C3	C4	C5	0.2(2)	C12	O3	C13	O4	174.48(17)
C3	O1	C1	O2	22.0(2)	C12	O3	C13	C10	-5.8(2)
C3	C2	C7	C6	-1.2(3)	C12	C9	C10	C11	−138.94(15)
C3	C4	C5	C6	-0.8(2)	C12	C9	C10	C13	-16.65(17)
C3	C4	C5	C11	−176.90(15)	C13	O3	C12	C9	-5.6(2)

Table 6 Torsion Angles for cu_230112_pz_1444a_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C5	C6	C7	0.4(2)	C13	C10	C11	C5	-54.37(17)
C4	C5	C6	C8	−179.93(15)	C13	C10	C11	C14	77.75(18)
C4	C5	C11	C10	123.83(16)	C14	C15	C16	O6	178.15(16)
C4	C5	C11	C14	-8.2(2)	C14	C15	C16	C17	-1.4(2)
C5	C6	C7	C2	0.6(3)	C15	C14	C19	C18	1.5(3)
C5	C6	C8	O5	176.32(16)	C15	C16	C17	O7	−176.96(15)
C5	C6	C8	C9	51.5(2)	C15	C16	C17	C18	0.5(2)
C5	C11	C14	C15	-69.1(2)	C16	C17	C18	O8	−177.94(15)
C5	C11	C14	C19	115.25(17)	C16	C17	C18	C19	1.4(3)
C6	C5	C11	C10	-52.47(18)	C17	C18	C19	C14	-2.4(3)
C6	C5	C11	C14	175.52(14)	C19	C14	C15	C16	0.4(3)
C6	C8	C9	C10	-38.3(2)	C20	O6	C16	C15	-6.6(3)
C6	C8	C9	C12	78.15(19)	C20	O6	C16	C17	172.97(18)
C7	C2	C3	O1	−176.32(16)	C21	O7	C17	C16	-107.1(2)
C7	C2	C3	C4	0.8(3)	C21	O7	C17	C18	75.5(2)
C7	C6	C8	O5	-4.0(2)	C22	O8	C18	C17	166.09(17)
C7	C6	C8	C9	−128.82(17)	C22	O8	C18	C19	-13.2(3)
C8	C6	C7	C2	−179.03(16)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for cu_230112_pz_1444a_0m.

Atom	*x*	*y*	*z*	U(eq)
H5	1896.82	-852.42	5828.71	63
H1A	7545.76	2962.03	7599.06	48
H1B	6336.95	3011.28	8194.86	48
H4	3879.06	4468.71	6277.87	27
H7	4308.12	305.01	6752.75	33
H8	1328.01	981.4	6174.28	35
H9	1057.98	752.33	4823.91	33
H10	1321.09	2628.93	4416	29
H11	1134.7	2862.27	5849.93	25
H12A	3462.84	-94.82	4747.86	47
H12B	2537.11	75.41	3987.77	47
H15	1172.4	4763.36	6612.72	29

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for cu_230112_pz_1444a_0m.

Atom	*x*	*y*	*z*	U(eq)
H19	2035.08	4616.58	4249.44	28
H20A	-491.86	5861.24	7288.63	72
H20B	-150.43	7069.46	7753.35	72
H20C	945.97	6102	7582.96	72
H21A	-286.04	8301.35	4254.33	77
H21B	-671.28	9196.15	4960.92	77
H21C	-1078.35	7820.05	5008.14	77
H22A	2415.44	6946.85	2870.18	59
H22B	1852.23	5666.14	3109	59
H22C	3156.81	6131.37	3505.94	59

Experimental

A suitable crystal was selected and analyzed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 16

Crystal Data for $C_{22}H_{22}O_8$ (M =414.39 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.4236(2) Å, b = 11.1986(2) Å, c = 16.7198(3) Å, V = 1951.70(6) Å^3, Z = 4, T = 170.00 K, μ(CuKα) = 0.907 mm^{-1}, *Dcalc* = 1.410 g/cm^3, 16940 reflections measured (9.506° ≤ 2Θ ≤ 136.764°), 3582 unique (R_{int} = 0.0332, R_{sigma} = 0.0219) which were used in all calculations. The final R_1 was 0.0257 (I > 2σ(I)) and wR_2 was 0.0658 (all data).

Refinement model description

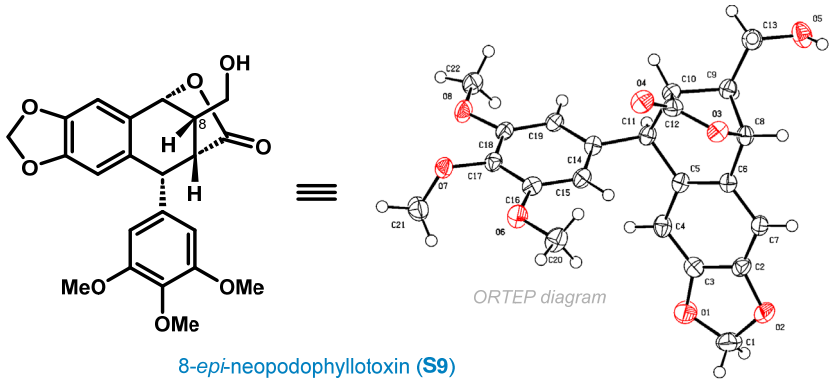
Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2.a Ternary CH refined with riding coordinates:
 C8(H8), C9(H9), C10(H10), C11(H11)
2.b Secondary CH2 refined with riding coordinates:
 C1(H1A,H1B), C12(H12A,H12B)
2.c Aromatic/amide H refined with riding coordinates:
 C4(H4), C7(H7), C15(H15), C19(H19)
2.d Idealised Me refined as rotating group:
 C20(H20A,H20B,H20C), C21(H21A,H21B,H21C), C22(H22A,H22B,H22C)
2.e Idealised tetrahedral OH refined as rotating group:
 O5(H5)
```

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

S9: 8-*epi*-neopodophyllotoxin (CCDC 2236507)



8-*epi*-neopodophyllotoxin (**S9**)

Table 1 Crystal data and structure refinement for 230111_pz_1444b_0m.

Identification code	230111_pz_1444b_0m
Empirical formula	$C_{22}H_{22}O_8$
Formula weight	414.39
Temperature/K	170.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.9062(18)
b/Å	13.207(2)
c/Å	14.739(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1928.4(6)
Z	4
ρ_{calc}g/cm^3	1.427
μ/mm^{-1}	0.584
F(000)	872.0
Crystal size/mm^3	0.18 × 0.16 × 0.12
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	9.358 to 107.784
Index ranges	$-11 \le h \le 11$, $-15 \le k \le 15$, $-16 \le l \le 17$
Reflections collected	20574
Independent reflections	3486 [R_{int} = 0.0484, R_{sigma} = 0.0489]
Data/restraints/parameters	3486/0/275
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0949
Final R indexes [all data]	R_1 = 0.0383, wR_2 = 0.0954
Largest diff. peak/hole / e Å^{-3}	0.26/-0.28
Flack parameter	0.04(7)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 230111_pz_1444b_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3761(2)	2259.6(16)	7340.3(13)	43.5(5)
O2	5087.9(19)	2854.5(15)	8528.3(12)	40.3(5)
O3	8079.9(17)	5428.0(12)	6086.8(11)	28.6(4)
O4	7429.2(19)	6089.9(13)	4753.2(12)	34.8(4)
O5	11520.5(19)	3859.7(15)	6000.2(13)	38.8(5)
O6	2929.2(17)	5903.8(13)	4271.3(11)	32.3(4)
O7	2695.0(17)	5134.7(12)	2587.3(11)	28.8(4)
O8	4201.3(18)	3562.7(14)	2045.2(11)	31.7(4)
C1	3876(3)	2327(2)	8302.5(19)	41.2(7)
C2	5658(2)	3127.1(18)	7709.8(16)	27.9(5)
C3	4848(3)	2786.4(17)	7004.3(17)	28.0(5)
C4	5170(3)	2957.1(17)	6110.2(16)	28.0(5)
C5	6382(2)	3479.1(17)	5926.6(15)	23.6(5)
C6	7187(2)	3828.8(16)	6641.7(15)	23.1(5)
C7	6827(2)	3659.4(17)	7556.4(15)	26.4(5)
C8	8461(2)	4403.0(17)	6408.4(15)	24.3(5)
C9	9142(2)	3932.6(18)	5575.0(15)	25.6(5)
C10	8113(2)	4288.8(17)	4859.2(15)	24.6(5)
C11	6810(2)	3621.9(17)	4932.8(14)	24.1(5)
C12	7827(2)	5372.4(18)	5170.7(16)	26.9(5)
C13	10579(2)	4311(2)	5398.0(17)	32.2(5)
C14	5675(2)	4002.0(17)	4321.8(15)	24.3(5)
C15	4812(2)	4773.8(17)	4622.4(15)	26.1(5)
C16	3805(2)	5146.4(17)	4047.4(16)	25.2(5)
C17	3653(2)	4732.7(17)	3177.6(15)	24.2(5)
C18	4484(2)	3936.9(17)	2895.2(15)	24.2(5)
C19	5512(2)	3575.9(17)	3460.8(15)	23.9(5)
C20	3095(3)	6372(2)	5139.9(17)	37.0(6)
C21	1402(3)	4659(2)	2638(2)	39.2(6)
C22	4935(3)	2683.8(19)	1757.7(17)	32.6(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 230111_pz_1444b_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	39.8(10)	51.9(12)	38.8(10)	10.5(9)	-1.4(8)	-19.7(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230111_pz_1444b_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	37.1(10)	56.8(12)	26.9(9)	12.9(8)	0.6(8)	-8.7(9)
O3	35.6(9)	21.8(8)	28.4(8)	-2.4(6)	0.9(7)	-1.8(7)
O4	43.3(10)	25.2(8)	35.9(9)	7.1(7)	1.2(8)	0.2(8)
O5	33.4(9)	40.4(10)	42.7(10)	-11.6(8)	-10.6(8)	3.3(8)
O6	37.7(9)	28.3(9)	30.8(9)	-5.2(7)	-3.0(7)	9.5(7)
O7	30.5(9)	30.3(8)	25.6(8)	5.9(6)	-3.9(6)	1.0(7)
O8	35.8(9)	37.9(9)	21.4(8)	-7.9(7)	-5.2(7)	7.1(8)
C1	37.0(14)	48.0(17)	38.5(14)	0.7(12)	11.9(12)	-7.1(12)
C2	32.8(12)	27.7(11)	23.2(11)	5.3(9)	1.7(10)	3.8(10)
C3	27.7(11)	22.3(10)	34.1(12)	4.6(9)	-1.1(10)	-0.6(9)
C4	31.8(12)	23.8(11)	28.4(12)	-1.6(9)	-6.9(10)	-4.9(10)
C5	29.2(11)	19.5(10)	22.1(10)	-1.6(8)	-2.4(9)	1.1(8)
C6	25.0(11)	20.4(10)	23.8(11)	-1.1(8)	-2.1(9)	1.8(8)
C7	27.3(11)	28.7(12)	23.3(11)	-0.6(9)	-3.5(9)	2.4(9)
C8	26.7(11)	22.4(11)	23.7(11)	-2.6(8)	-3.6(9)	0.1(9)
C9	29.0(12)	25.5(11)	22.4(11)	-1.6(9)	-2.0(9)	0.8(9)
C10	27.1(11)	24.9(11)	21.7(10)	-1.6(8)	1.0(9)	0.2(9)
C11	29.3(12)	22.3(10)	20.7(10)	-3.5(8)	-2.3(9)	0.9(10)
C12	26.6(11)	27.1(12)	26.9(12)	-0.8(9)	3.3(9)	-2.8(9)
C13	31.3(12)	35.4(13)	29.8(12)	-2.9(10)	-0.4(10)	-2.2(10)
C14	27.1(11)	22.9(10)	23.0(11)	0.4(9)	-2.7(8)	-0.7(9)
C15	32.4(12)	24.5(11)	21.4(10)	-4.3(8)	-0.9(9)	-1.3(9)
C16	29.5(11)	20.4(10)	25.6(11)	0.2(9)	2.0(9)	-1.1(9)
C17	27.7(12)	22.0(11)	22.8(11)	4.4(8)	-1.6(9)	-2.4(9)
C18	28.2(11)	25.3(11)	19.1(11)	-0.6(9)	0.1(9)	-4.2(9)
C19	27.4(11)	22.4(10)	21.8(11)	-1.0(8)	0.2(9)	0.1(9)
C20	48.9(16)	31.2(13)	31.0(13)	-6.5(10)	-0.7(11)	9.2(12)
C21	35.0(14)	41.4(15)	41.4(14)	6.5(12)	-6.7(11)	-0.2(12)
C22	37.2(13)	34.2(13)	26.3(12)	-9.5(10)	-1.3(10)	1.2(11)

Table 4 Bond Lengths for 230111_pz_1444b_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.426(3)	C4	C5	1.410(3)
O1	C3	1.374(3)	C5	C6	1.400(3)
O2	C1	1.427(4)	C5	C11	1.537(3)
O2	C2	1.380(3)	C6	C7	1.412(3)
O3	C8	1.483(3)	C6	C8	1.512(3)
O3	C12	1.375(3)	C8	C9	1.533(3)

Table 4 Bond Lengths for 230111_pz_1444b_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C12	1.197(3)	C9	C10	1.541(3)
O5	C13	1.419(3)	C9	C13	1.531(3)
O6	C16	1.364(3)	C10	C11	1.566(3)
O6	C20	1.431(3)	C10	C12	1.529(3)
O7	C17	1.393(3)	C11	C14	1.526(3)
O7	C21	1.429(3)	C14	C15	1.402(3)
O8	C18	1.375(3)	C14	C19	1.398(3)
O8	C22	1.434(3)	C15	C16	1.398(3)
C2	C3	1.388(3)	C16	C17	1.402(3)
C2	C7	1.373(4)	C17	C18	1.398(3)
C3	C4	1.374(4)	C18	C19	1.400(3)

Table 5 Bond Angles for 230111_pz_1444b_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O1	C1	105.3(2)	C13	C9	C10	113.51(19)
C2	O2	C1	105.52(19)	C9	C10	C11	109.02(17)
C12	O3	C8	108.14(17)	C12	C10	C9	101.68(18)
C16	O6	C20	117.38(19)	C12	C10	C11	110.68(19)
C17	O7	C21	114.22(18)	C5	C11	C10	111.27(17)
C18	O8	C22	117.19(18)	C14	C11	C5	113.54(19)
O1	C1	O2	109.3(2)	C14	C11	C10	112.42(17)
O2	C2	C3	109.5(2)	O3	C12	C10	108.13(19)
C7	C2	O2	128.5(2)	O4	C12	O3	121.5(2)
C7	C2	C3	122.0(2)	O4	C12	C10	130.4(2)
O1	C3	C2	110.3(2)	O5	C13	C9	111.6(2)
O1	C3	C4	127.6(2)	C15	C14	C11	120.1(2)
C4	C3	C2	122.1(2)	C19	C14	C11	119.24(19)
C3	C4	C5	117.5(2)	C19	C14	C15	120.6(2)
C4	C5	C11	118.6(2)	C16	C15	C14	120.0(2)
C6	C5	C4	120.1(2)	O6	C16	C15	124.4(2)
C6	C5	C11	121.3(2)	O6	C16	C17	116.0(2)
C5	C6	C7	121.5(2)	C15	C16	C17	119.6(2)
C5	C6	C8	118.02(19)	O7	C17	C16	119.7(2)
C7	C6	C8	120.5(2)	O7	C17	C18	120.1(2)
C2	C7	C6	116.8(2)	C18	C17	C16	120.1(2)
O3	C8	C6	108.57(18)	O8	C18	C17	114.9(2)
O3	C8	C9	103.05(17)	O8	C18	C19	124.6(2)
C6	C8	C9	110.26(18)	C17	C18	C19	120.5(2)
C8	C9	C10	97.68(18)	C14	C19	C18	119.2(2)

Table 5 Bond Angles for 230111_pz_1444b_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	C9	C8	114.42(19)				

Table 6 Torsion Angles for 230111_pz_1444b_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C4	C5	-176.9(2)	C8	O3	C12	C10	-2.8(2)
O2	C2	C3	O1	-1.9(3)	C8	C6	C7	C2	-179.7(2)
O2	C2	C3	C4	179.7(2)	C8	C9	C10	C11	-75.5(2)
O2	C2	C7	C6	179.5(2)	C8	C9	C10	C12	41.4(2)
O3	C8	C9	C10	-43.9(2)	C8	C9	C13	O5	76.8(2)
O3	C8	C9	C13	76.4(2)	C9	C10	C11	C5	44.8(2)
O6	C16	C17	O7	3.1(3)	C9	C10	C11	C14	173.38(18)
O6	C16	C17	C18	-178.5(2)	C9	C10	C12	O3	-25.6(2)
O7	C17	C18	O8	-4.5(3)	C9	C10	C12	O4	155.8(3)
O7	C17	C18	C19	175.5(2)	C10	C9	C13	O5	−172.26(19)
O8	C18	C19	C14	-178.3(2)	C10	C11	C14	C15	-84.5(3)
C1	O1	C3	C2	3.1(3)	C10	C11	C14	C19	95.1(2)
C1	O1	C3	C4	-178.6(3)	C11	C5	C6	C7	-177.1(2)
C1	O2	C2	C3	-0.2(3)	C11	C5	C6	C8	3.2(3)
C1	O2	C2	C7	179.1(3)	C11	C10	C12	O3	90.1(2)
C2	O2	C1	O1	2.1(3)	C11	C10	C12	O4	-88.5(3)
C2	C3	C4	C5	1.3(3)	C11	C14	C15	C16	177.6(2)
C3	O1	C1	O2	-3.2(3)	C11	C14	C19	C18	-179.0(2)
C3	C2	C7	C6	-1.3(3)	C12	O3	C8	C6	-86.5(2)
C3	C4	C5	C6	-1.9(3)	C12	O3	C8	C9	30.4(2)
C3	C4	C5	C11	176.3(2)	C12	C10	C11	C5	-66.3(2)
C4	C5	C6	C7	0.9(3)	C12	C10	C11	C14	62.3(2)
C4	C5	C6	C8	−178.74(19)	C13	C9	C10	C11	163.54(18)
C4	C5	C11	C10	175.51(19)	C13	C9	C10	C12	-79.5(2)
C4	C5	C11	C14	47.5(3)	C14	C15	C16	O6	-179.0(2)
C5	C6	C7	C2	0.7(3)	C14	C15	C16	C17	1.0(3)
C5	C6	C8	O3	73.8(2)	C15	C14	C19	C18	0.7(3)
C5	C6	C8	C9	-38.4(3)	C15	C16	C17	O7	-176.9(2)
C5	C11	C14	C15	42.9(3)	C15	C16	C17	C18	1.5(3)
C5	C11	C14	C19	-137.4(2)	C16	C17	C18	O8	177.2(2)
C6	C5	C11	C10	-6.4(3)	C16	C17	C18	C19	-2.9(3)
C6	C5	C11	C14	-134.4(2)	C17	C18	C19	C14	1.8(3)
C6	C8	C9	C10	71.9(2)	C19	C14	C15	C16	-2.1(3)

Table 6 Torsion Angles for 230111_pz_1444b_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C8	C9	C13	167.92(18)	C20	O6	C16	C15	2.7(3)
C7	C2	C3	O1	178.7(2)	C20	O6	C16	C17	-177.4(2)
C7	C2	C3	C4	0.3(4)	C21	O7	C17	C16	-91.2(3)
C7	C6	C8	O3	-105.9(2)	C21	O7	C17	C18	90.5(3)
C7	C6	C8	C9	141.9(2)	C22	O8	C18	C17	-174.1(2)
C8	O3	C12	O4	176.0(2)	C22	O8	C18	C19	5.9(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230111_pz_1444b_0m.

Atom	*x*	*y*	*z*	U(eq)
H5	11668	4253.46	6436.65	58
H1A	3894.72	1639.78	8569.45	49
H1B	3087.26	2692.77	8553.4	49
H4	4598.25	2731.94	5633.84	34
H7	7367.02	3902.17	8042.4	32
H8	9091.9	4436.9	6936.93	29
H9	9132.72	3177.23	5621.36	31
H10	8502.12	4271.84	4233.43	30
H11	7061.58	2935.23	4702.29	29
H13A	10836.71	4151.4	4764.96	39
H13B	10606.17	5055.77	5471.97	39
H15	4910.9	5043.33	5216.25	31
H19	6092.58	3048.06	3261.7	29
H20A	4007.59	6653.8	5186.83	56
H20B	2961.42	5865.76	5617.98	56
H20C	2430.64	6915.65	5209.82	56
H21A	842.67	4883.08	2127.94	59
H21B	962.42	4844.34	3210.18	59
H21C	1513.78	3921.98	2611.44	59
H22A	4526.9	2412.27	1203.11	49
H22B	4904.75	2168.93	2236.02	49
H22C	5876.35	2869.43	1637.29	49

Experimental

A suitable crystal was selected and analyzed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of S9

Crystal Data for $C_{22}H_{22}O_8$ (M =414.39 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.9062(18) Å, b = 13.207(2) Å, c = 14.739(3) Å, V = 1928.4(6) Å^3, Z = 4, T = 170.00 K, μ(GaKα) = 0.584 mm^{-1}, *Dcalc* = 1.427 g/cm^3, 20574 reflections measured (9.358° ≤ 2Θ ≤ 107.784°), 3486 unique (R_{int} = 0.0484, R_{sigma} = 0.0489) which were used in all calculations. The final R_1 was 0.0374 (I > 2σ(I)) and wR_2 was 0.0954 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2.a Ternary CH refined with riding coordinates:
 C8(H8), C9(H9), C10(H10), C11(H11)
2.b Secondary CH2 refined with riding coordinates:
 C1(H1A,H1B), C13(H13A,H13B)
2.c Aromatic/amide H refined with riding coordinates:
 C4(H4), C7(H7), C15(H15), C19(H19)
2.d Idealised Me refined as rotating group:
 C20(H20A,H20B,H20C), C21(H21A,H21B,H21C), C22(H22A,H22B,H22C)
2.e Idealised tetrahedral OH refined as rotating group:
 O5(H5)
```

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

47: (CCDC 2236638)

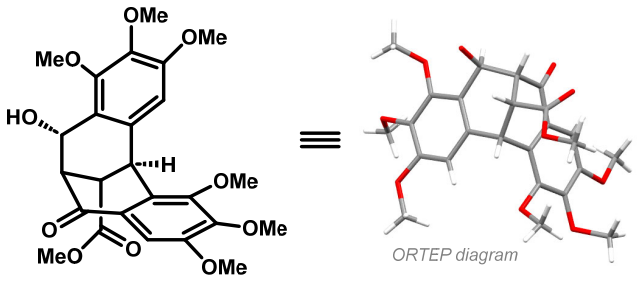


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Table 1. Crystal data and structure refinement for CU-PARTIAL3_a-finalcif.

Identification code	CU-PARTIAL3_a
Empirical formula	C25 H27 O10
Formula weight	487.46
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	a = 11.5700(7) Å	α= 63.948(4)°.
	b = 15.5982(10) Å	β= 68.541(4)°.
	c = 15.6112(10) Å	γ = 84.548(5)°.
Volume	2348.4(3) $Å^3$	
Z	4	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.904 mm^{-1}	
F(000)	1028	
Crystal size	0.2 x 0.15 x 0.12 mm^3	
Theta range for data collection	3.163 to 55.386°.	
Index ranges	-12<=h<=12, -16<=k<=16, -15<=l<=16	
Reflections collected	28995	
Independent reflections	5930 [R(int) = 0.1835]	
Completeness to theta = 55.386°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.897 and 0.850	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5930 / 0 / 646	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0752, wR2 = 0.1745	
R indices (all data)	R1 = 0.1753, wR2 = 0.2335	
Extinction coefficient	0.0053(5)	
Largest diff. peak and hole	0.357 and -0.399 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CU-PARTIAL3_a-finalcif. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7677(4)	9253(3)	10240(3)	52(1)
O(2)	9202(4)	10698(3)	8649(3)	49(1)
O(3)	10058(4)	10738(3)	6677(3)	43(1)
O(4)	10572(4)	9048(3)	6073(3)	45(1)
O(5)	7763(4)	6084(3)	7641(3)	53(1)
O(6)	7275(4)	9724(3)	5337(4)	50(1)
O(7)	2750(4)	8872(3)	7871(3)	45(1)

O(8)	2929(4)	7596(3)	9654(3)	46(1)
O(9)	5200(4)	7059(3)	9797(3)	45(1)
O(10)	7756(5)	7122(3)	6105(4)	58(1)
O(11)	3047(5)	7258(3)	3084(4)	57(1)
O(12)	3832(4)	8495(3)	3562(4)	54(1)
O(13)	5995(4)	8198(3)	4025(3)	50(1)
O(14)	9822(5)	6966(3)	2337(3)	51(1)
O(15)	7552(4)	3467(3)	4175(3)	52(1)
O(16)	9590(4)	6729(3)	-759(3)	48(1)
O(17)	7590(4)	5466(3)	42(3)	45(1)
O(18)	6051(4)	4831(3)	2053(3)	46(1)
O(19)	6868(4)	6159(3)	5287(3)	53(1)
O(20)	9349(6)	4244(4)	3767(4)	71(2)
C(1)	8021(6)	8535(5)	8192(5)	40(2)
C(2)	7591(6)	8515(5)	9176(5)	42(2)
C(3)	8013(6)	9233(5)	9316(5)	42(2)
C(4)	8828(6)	9989(5)	8492(5)	40(2)
C(5)	9225(6)	10019(5)	7521(5)	41(2)
C(6)	8832(6)	9295(5)	7364(5)	37(2)
C(7)	9316(6)	9351(5)	6296(5)	42(2)
C(8)	8540(6)	8691(4)	6192(5)	42(2)
C(9)	8379(6)	7698(4)	7088(5)	39(2)
C(10)	7505(6)	7760(4)	8066(5)	38(2)
C(11)	6861(7)	8473(5)	11106(5)	60(2)
C(12)	10472(7)	10684(5)	8583(6)	63(2)
C(13)	9639(7)	11696(5)	6410(5)	53(2)
C(14)	7290(7)	9079(5)	6145(5)	42(2)
C(15)	6150(6)	8662(5)	7064(5)	41(2)
C(16)	4996(7)	8971(5)	6986(5)	40(2)
C(17)	3935(6)	8622(5)	7839(5)	39(2)
C(18)	3997(7)	7964(5)	8786(5)	40(2)
C(19)	5139(7)	7676(5)	8857(5)	41(2)
C(20)	6234(6)	8010(5)	7992(5)	37(2)
C(21)	7925(6)	6952(5)	6885(6)	46(2)
C(22)	7528(7)	5310(5)	7445(5)	59(2)
C(23)	2647(6)	9524(5)	6923(5)	50(2)

C(24)	2468(7)	8230(5)	10137(5)	54(2)
C(25)	4915(7)	6071(5)	10056(5)	54(2)
C(26)	5829(7)	6122(5)	3564(5)	44(2)
C(27)	4778(7)	6282(5)	3291(5)	46(2)
C(28)	4121(7)	7057(5)	3299(5)	47(2)
C(29)	4487(7)	7715(5)	3538(5)	45(2)
C(30)	5531(7)	7554(5)	3811(5)	46(2)
C(31)	6231(7)	6758(5)	3826(5)	46(2)
C(32)	6590(6)	5280(5)	3480(5)	42(2)
C(33)	7432(6)	5619(5)	2357(5)	39(2)
C(34)	8525(7)	6188(5)	1968(5)	45(2)
C(35)	9278(6)	6584(5)	930(5)	42(2)
C(36)	8955(7)	6367(5)	283(5)	43(2)
C(37)	7904(7)	5723(5)	667(5)	44(2)
C(38)	7142(7)	5383(5)	1691(5)	42(2)
C(39)	2603(7)	6617(5)	2827(6)	66(2)
C(40)	3988(7)	9239(6)	2562(6)	64(2)
C(41)	5234(7)	8224(5)	4985(5)	61(2)
C(42)	7330(7)	6589(5)	4172(5)	49(2)
C(43)	8204(6)	5895(5)	3821(5)	46(2)
C(44)	8940(7)	6405(5)	2666(5)	48(2)
C(45)	7426(6)	5008(5)	4118(5)	43(2)
C(46)	8224(8)	4215(6)	4003(5)	51(2)
C(47)	8250(7)	2662(5)	4094(5)	56(2)
C(48)	10549(6)	7475(5)	-1191(5)	48(2)
C(49)	8538(6)	4958(5)	-430(5)	48(2)
C(50)	6209(7)	3857(5)	2196(5)	57(2)

Table 3. Bond lengths [Å] and angles [°] for CU-PARTIAL3_a-finalcif.

O(1)-C(3)	1.365(7)
O(1)-C(11)	1.428(7)
O(2)-C(4)	1.369(7)
O(2)-C(12)	1.433(8)
O(3)-C(5)	1.379(7)

O(3)-C(13)	1.450(7)
O(4)-C(7)	1.449(7)
O(5)-C(21)	1.321(8)
O(5)-C(22)	1.439(7)
O(6)-C(14)	1.226(7)
O(7)-C(17)	1.378(7)
O(7)-C(23)	1.423(7)
O(8)-C(18)	1.385(7)
O(8)-C(24)	1.446(7)
O(9)-C(19)	1.380(7)
O(9)-C(25)	1.449(8)
O(10)-C(21)	1.213(8)
O(11)-C(28)	1.376(8)
O(11)-C(39)	1.423(8)
O(12)-C(29)	1.378(8)
O(12)-C(40)	1.434(8)
O(13)-C(30)	1.392(7)
O(13)-C(41)	1.450(7)
O(14)-C(44)	1.209(8)
O(15)-C(46)	1.335(8)
O(15)-C(47)	1.455(7)
O(16)-C(36)	1.380(7)
O(16)-C(48)	1.432(7)
O(17)-C(37)	1.370(8)
O(17)-C(49)	1.460(7)
O(18)-C(38)	1.383(7)
O(18)-C(50)	1.439(7)
O(19)-C(42)	1.458(7)
O(20)-C(46)	1.215(8)
C(1)-C(6)	1.391(8)
C(1)-C(2)	1.418(8)
C(1)-C(10)	1.512(8)
C(2)-C(3)	1.391(9)
C(3)-C(4)	1.387(9)
C(4)-C(5)	1.396(9)
C(5)-C(6)	1.400(8)

C(6)-C(7)	1.516(9)
C(7)-C(8)	1.523(9)
C(8)-C(14)	1.527(9)
C(8)-C(9)	1.534(8)
C(9)-C(21)	1.514(9)
C(9)-C(10)	1.531(8)
C(10)-C(20)	1.518(9)
C(14)-C(15)	1.476(9)
C(15)-C(20)	1.390(8)
C(15)-C(16)	1.405(9)
C(16)-C(17)	1.368(8)
C(17)-C(18)	1.405(8)
C(18)-C(19)	1.383(9)
C(19)-C(20)	1.399(9)
C(26)-C(31)	1.397(9)
C(26)-C(27)	1.397(9)
C(26)-C(32)	1.538(9)
C(27)-C(28)	1.368(9)
C(28)-C(29)	1.381(9)
C(29)-C(30)	1.389(9)
C(30)-C(31)	1.412(9)
C(31)-C(42)	1.514(9)
C(32)-C(33)	1.528(9)
C(32)-C(45)	1.537(9)
C(33)-C(34)	1.391(9)
C(33)-C(38)	1.394(9)
C(34)-C(35)	1.398(9)
C(34)-C(44)	1.507(10)
C(35)-C(36)	1.369(9)
C(36)-C(37)	1.419(9)
C(37)-C(38)	1.388(9)
C(42)-C(43)	1.549(9)
C(43)-C(45)	1.519(9)
C(43)-C(44)	1.535(9)
C(45)-C(46)	1.508(10)

C(3)-O(1)-C(11)	116.8(5)
C(4)-O(2)-C(12)	114.2(5)
C(5)-O(3)-C(13)	115.5(5)
C(21)-O(5)-C(22)	116.2(5)
C(17)-O(7)-C(23)	116.0(5)
C(18)-O(8)-C(24)	114.2(5)
C(19)-O(9)-C(25)	111.8(5)
C(28)-O(11)-C(39)	117.3(5)
C(29)-O(12)-C(40)	113.1(5)
C(30)-O(13)-C(41)	114.6(5)
C(46)-O(15)-C(47)	115.5(6)
C(36)-O(16)-C(48)	116.1(5)
C(37)-O(17)-C(49)	113.6(5)
C(38)-O(18)-C(50)	115.1(5)
C(6)-C(1)-C(2)	119.4(6)
C(6)-C(1)-C(10)	122.0(5)
C(2)-C(1)-C(10)	118.4(6)
C(3)-C(2)-C(1)	120.1(6)
O(1)-C(3)-C(4)	115.5(6)
O(1)-C(3)-C(2)	123.9(6)
C(4)-C(3)-C(2)	120.6(6)
O(2)-C(4)-C(3)	119.3(6)
O(2)-C(4)-C(5)	121.6(6)
C(3)-C(4)-C(5)	119.1(6)
O(3)-C(5)-C(4)	121.9(6)
O(3)-C(5)-C(6)	116.7(6)
C(4)-C(5)-C(6)	121.4(6)
C(1)-C(6)-C(5)	119.4(6)
C(1)-C(6)-C(7)	121.4(6)
C(5)-C(6)-C(7)	119.2(6)
O(4)-C(7)-C(6)	109.0(5)
O(4)-C(7)-C(8)	107.0(5)
C(6)-C(7)-C(8)	112.4(5)
C(7)-C(8)-C(14)	112.2(5)
C(7)-C(8)-C(9)	107.8(6)
C(14)-C(8)-C(9)	112.1(6)

C(21)-C(9)-C(10)	113.6(5)
C(21)-C(9)-C(8)	110.4(6)
C(10)-C(9)-C(8)	107.9(5)
C(1)-C(10)-C(20)	108.7(5)
C(1)-C(10)-C(9)	109.7(5)
C(20)-C(10)-C(9)	109.4(5)
O(6)-C(14)-C(15)	122.5(7)
O(6)-C(14)-C(8)	118.3(6)
C(15)-C(14)-C(8)	119.3(6)
C(20)-C(15)-C(16)	121.3(6)
C(20)-C(15)-C(14)	120.1(6)
C(16)-C(15)-C(14)	118.6(6)
C(17)-C(16)-C(15)	119.4(6)
C(16)-C(17)-O(7)	125.2(6)
C(16)-C(17)-C(18)	120.4(6)
O(7)-C(17)-C(18)	114.4(6)
C(19)-C(18)-O(8)	119.2(6)
C(19)-C(18)-C(17)	119.8(6)
O(8)-C(18)-C(17)	121.0(6)
O(9)-C(19)-C(18)	119.5(6)
O(9)-C(19)-C(20)	119.6(6)
C(18)-C(19)-C(20)	120.9(6)
C(15)-C(20)-C(19)	118.3(6)
C(15)-C(20)-C(10)	119.7(6)
C(19)-C(20)-C(10)	121.6(6)
O(10)-C(21)-O(5)	123.2(7)
O(10)-C(21)-C(9)	124.1(7)
O(5)-C(21)-C(9)	112.6(7)
C(31)-C(26)-C(27)	120.6(7)
C(31)-C(26)-C(32)	121.0(7)
C(27)-C(26)-C(32)	118.3(6)
C(28)-C(27)-C(26)	119.8(7)
C(27)-C(28)-O(11)	124.4(7)
C(27)-C(28)-C(29)	122.0(7)
O(11)-C(28)-C(29)	113.6(6)
O(12)-C(29)-C(28)	123.0(7)

O(12)-C(29)-C(30)	118.9(6)
C(28)-C(29)-C(30)	118.0(7)
C(29)-C(30)-O(13)	122.0(6)
C(29)-C(30)-C(31)	122.0(6)
O(13)-C(30)-C(31)	115.9(7)
C(26)-C(31)-C(30)	117.5(7)
C(26)-C(31)-C(42)	122.2(6)
C(30)-C(31)-C(42)	120.2(6)
C(33)-C(32)-C(45)	108.0(6)
C(33)-C(32)-C(26)	107.0(5)
C(45)-C(32)-C(26)	111.0(6)
C(34)-C(33)-C(38)	117.8(6)
C(34)-C(33)-C(32)	119.9(6)
C(38)-C(33)-C(32)	122.3(6)
C(33)-C(34)-C(35)	122.4(6)
C(33)-C(34)-C(44)	120.3(6)
C(35)-C(34)-C(44)	117.2(7)
C(36)-C(35)-C(34)	118.6(6)
C(35)-C(36)-O(16)	124.7(6)
C(35)-C(36)-C(37)	120.5(6)
O(16)-C(36)-C(37)	114.8(6)
O(17)-C(37)-C(38)	119.2(6)
O(17)-C(37)-C(36)	121.6(6)
C(38)-C(37)-C(36)	119.1(7)
O(18)-C(38)-C(37)	119.7(6)
O(18)-C(38)-C(33)	119.1(6)
C(37)-C(38)-C(33)	121.1(7)
O(19)-C(42)-C(31)	108.8(5)
O(19)-C(42)-C(43)	107.9(5)
C(31)-C(42)-C(43)	111.8(6)
C(45)-C(43)-C(44)	112.4(6)
C(45)-C(43)-C(42)	108.7(6)
C(44)-C(43)-C(42)	109.7(5)
O(14)-C(44)-C(34)	121.7(6)
O(14)-C(44)-C(43)	120.2(6)
C(34)-C(44)-C(43)	118.1(7)

C(46)-C(45)-C(43)	111.9(6)
C(46)-C(45)-C(32)	111.6(6)
C(43)-C(45)-C(32)	109.2(6)
O(20)-C(46)-O(15)	123.1(7)
O(20)-C(46)-C(45)	124.9(7)
O(15)-C(46)-C(45)	112.0(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for CU-PARTIAL3_a-finalcif. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	59(3)	60(3)	38(3)	-31(3)	-7(3)	2(3)
O(2)	53(3)	45(3)	52(3)	-30(3)	-14(3)	7(2)
O(3)	46(3)	39(3)	45(3)	-25(2)	-9(2)	9(2)
O(4)	49(3)	48(3)	47(3)	-30(2)	-18(2)	13(2)
O(5)	74(4)	44(3)	44(3)	-24(3)	-17(3)	0(3)
O(6)	49(3)	53(3)	39(3)	-16(3)	-11(2)	3(2)
O(7)	44(3)	48(3)	42(3)	-21(2)	-15(2)	9(2)
O(8)	46(3)	44(3)	38(3)	-18(2)	-4(2)	4(2)
O(9)	50(3)	47(3)	39(3)	-21(2)	-13(2)	4(2)
O(10)	81(4)	49(3)	45(3)	-20(3)	-23(3)	0(3)
O(11)	55(3)	55(3)	76(4)	-44(3)	-24(3)	15(3)
O(12)	61(3)	55(3)	52(3)	-35(3)	-15(3)	17(3)
O(13)	59(3)	47(3)	46(3)	-32(3)	-5(3)	2(2)
O(14)	55(3)	49(3)	47(3)	-23(3)	-11(3)	-4(3)
O(15)	53(3)	49(3)	56(3)	-32(3)	-12(3)	8(3)
O(16)	48(3)	46(3)	42(3)	-20(2)	-8(3)	3(3)
O(17)	48(3)	46(3)	41(3)	-25(2)	-12(2)	6(2)
O(18)	51(3)	42(3)	47(3)	-27(2)	-10(2)	4(3)
O(19)	61(3)	54(3)	37(3)	-20(3)	-8(2)	-3(3)
O(20)	59(4)	60(4)	91(4)	-37(3)	-20(3)	14(3)
C(1)	46(5)	43(4)	34(4)	-23(4)	-12(4)	17(4)
C(2)	50(5)	38(4)	41(5)	-24(4)	-12(4)	9(3)

C(3)	49(5)	38(4)	40(5)	-22(4)	-13(4)	11(4)
C(4)	46(5)	36(4)	46(5)	-26(4)	-19(4)	12(4)
C(5)	39(4)	37(4)	42(5)	-18(4)	-8(4)	6(4)
C(6)	38(4)	37(4)	35(4)	-18(3)	-11(3)	10(3)
C(7)	48(5)	38(4)	39(4)	-22(3)	-7(4)	4(4)
C(8)	47(5)	39(4)	38(4)	-22(4)	-5(4)	5(4)
C(9)	40(4)	39(4)	36(4)	-22(3)	-6(3)	7(3)
C(10)	46(5)	31(4)	33(4)	-17(3)	-7(3)	6(3)
C(11)	70(6)	55(5)	44(5)	-24(4)	-4(4)	1(4)
C(12)	66(6)	57(5)	79(6)	-36(5)	-35(5)	9(4)
C(13)	61(5)	41(5)	57(5)	-24(4)	-19(4)	13(4)
C(14)	57(5)	43(5)	34(5)	-28(4)	-10(4)	6(4)
C(15)	44(5)	41(4)	36(4)	-21(4)	-10(4)	10(4)
C(16)	53(5)	38(4)	31(4)	-19(3)	-15(4)	10(4)
C(17)	41(5)	35(4)	40(5)	-21(4)	-12(4)	15(4)
C(18)	43(5)	40(4)	34(4)	-19(4)	-9(4)	9(4)
C(19)	53(5)	41(4)	34(5)	-22(4)	-15(4)	11(4)
C(20)	35(4)	44(4)	33(4)	-21(4)	-7(4)	7(3)
C(21)	44(5)	46(5)	37(5)	-18(4)	-3(4)	6(4)
C(22)	85(6)	42(4)	52(5)	-23(4)	-24(4)	-1(4)
C(23)	50(5)	50(5)	41(5)	-16(4)	-14(4)	12(4)
C(24)	58(5)	53(5)	53(5)	-36(4)	-9(4)	8(4)
C(25)	59(5)	48(5)	50(5)	-18(4)	-20(4)	3(4)
C(26)	45(5)	44(4)	33(4)	-18(3)	-3(4)	9(4)
C(27)	46(5)	48(5)	44(5)	-30(4)	-4(4)	5(4)
C(28)	48(5)	56(5)	43(5)	-31(4)	-11(4)	6(4)
C(29)	42(5)	51(5)	43(5)	-30(4)	-4(4)	5(4)
C(30)	57(5)	43(5)	34(4)	-26(4)	2(4)	-6(4)
C(31)	52(5)	46(5)	42(4)	-25(4)	-9(4)	4(4)
C(32)	50(5)	39(4)	32(4)	-17(3)	-6(4)	4(4)
C(33)	46(5)	35(4)	40(4)	-24(4)	-10(4)	2(4)
C(34)	56(5)	39(4)	42(5)	-20(4)	-17(4)	11(4)
C(35)	44(5)	45(4)	39(5)	-22(4)	-11(4)	-1(3)
C(36)	47(5)	32(4)	37(5)	-10(4)	-8(4)	8(4)
C(37)	49(5)	41(4)	43(5)	-24(4)	-12(4)	9(4)
C(38)	46(5)	31(4)	40(5)	-12(3)	-9(4)	1(4)

C(39)	62(5)	64(5)	101(7)	-58(5)	-36(5)	24(4)
C(40)	71(6)	65(6)	68(6)	-42(5)	-27(5)	18(5)
C(41)	73(6)	57(5)	50(5)	-32(4)	-10(4)	4(4)
C(42)	58(5)	51(5)	37(5)	-21(4)	-12(4)	3(4)
C(43)	55(5)	43(4)	41(5)	-18(4)	-21(4)	7(4)
C(44)	52(5)	42(5)	47(5)	-22(4)	-15(4)	13(4)
C(45)	48(5)	48(4)	37(4)	-22(4)	-14(4)	2(4)
C(46)	53(6)	57(5)	34(5)	-22(4)	-5(4)	10(5)
C(47)	54(5)	52(5)	67(5)	-41(4)	-13(4)	22(4)
C(48)	46(5)	46(4)	45(5)	-19(4)	-11(4)	3(4)
C(49)	54(5)	48(4)	45(5)	-26(4)	-16(4)	13(4)
C(50)	69(6)	53(5)	55(5)	-27(4)	-24(4)	5(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for CU-PARTIAL3_a-finalcif.

	x	y	z	U(eq)
H(2)	7014	8011	9741	51
H(7)	9323	10026	5788	50
H(8)	9017	8636	5542	51
H(9)	9209	7533	7151	47
H(10)	7423	7131	8670	46
H(11A)	6784	8514	11733	90
H(11B)	7201	7867	11126	90
H(11C)	6039	8502	11053	90
H(12A)	10640	11155	8788	94
H(12B)	11028	10843	7877	94
H(12C)	10616	10045	9038	94
H(13A)	10205	12133	5730	80
H(13B)	9634	11909	6915	80
H(13C)	8796	11691	6403	80
H(16)	4953	9417	6347	48
H(22A)	7544	4698	8011	88
H(22B)	8171	5354	6806	88
H(22C)	6708	5353	7385	88
H(23A)	1768	9630	7023	75
H(23B)	2989	9257	6425	75
H(23C)	3112	10134	6667	75
H(24A)	1704	7929	10733	81
H(24B)	2291	8834	9649	81
H(24C)	3099	8354	10359	81
H(25A)	4975	5655	10723	81
H(25B)	5508	5897	9533	81
H(25C)	4067	5993	10088	81
H(27)	4520	5854	3099	55
H(32)	6022	4716	3705	51
H(35)	9998	6996	679	51

H(39A)	1805	6809	2743	99
H(39B)	2488	5966	3375	99
H(39C)	3210	6634	2186	99
H(40A)	3401	9723	2623	95
H(40B)	3828	8965	2155	95
H(40C)	4842	9536	2226	95
H(41A)	5701	8583	5150	91
H(41B)	5011	7569	5530	91
H(41C)	4474	8536	4922	91
H(42)	7811	7213	3891	59
H(43)	8806	5700	4186	55
H(45)	6874	4773	4854	52
H(47A)	7670	2125	4308	84
H(47B)	8740	2467	4537	84
H(47C)	8810	2851	3384	84
H(48A)	10884	7721	-1938	72
H(48B)	11218	7221	-926	72
H(48C)	10202	7995	-1006	72
H(49A)	8141	4534	-573	72
H(49B)	8968	4577	37	72
H(49C)	9142	5421	-1070	72
H(50A)	5390	3506	2511	86
H(50B)	6688	3553	2642	86
H(50C)	6656	3850	1531	86

70: (CCDC 2236477)

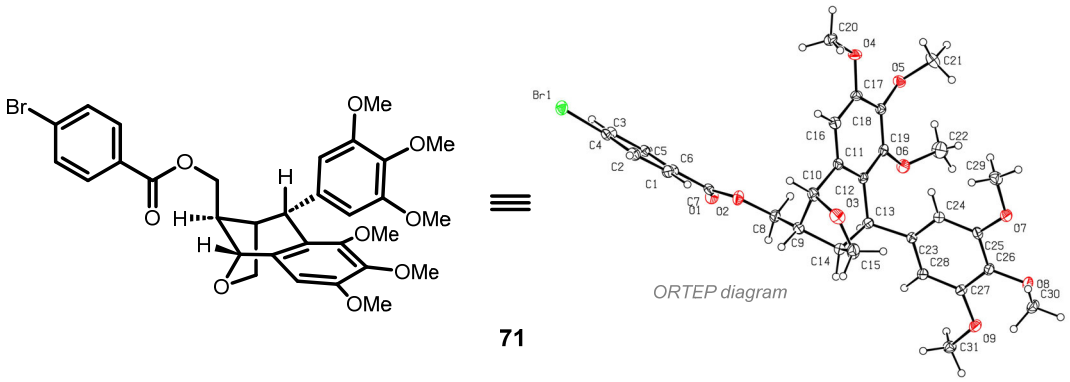

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Table 1 Crystal data and structure refinement for mo_220625_XWX_742_2_0m.

Identification code	mo_220625_XWX_742_2_0m
Empirical formula	$C_{31}H_{33}BrO_9$
Formula weight	629.48
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.6753(14)
b/Å	6.1512(7)
c/Å	18.2258(17)
α/°	90
β/°	101.938(3)
γ/°	90
Volume/Å^3	1390.3(3)
Z	2
ρ_{calc}g/cm^3	1.504
μ/mm^{-1}	1.535
F(000)	652.0
Crystal size/mm^3	0.23 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.568 to 54.33
Index ranges	-16 ≤ h ≤ 16, -7 ≤ k ≤ 7, -22 ≤ l ≤ 23
Reflections collected	28144
Independent reflections	6121 [R_{int} = 0.0650, R_{sigma} = 0.0640]
Data/restraints/parameters	6121/1/376
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0647
Final R indexes [all data]	R_1 = 0.0581, wR_2 = 0.0721
Largest diff. peak/hole / e Å^{-3}	0.44/-0.53
Flack parameter	0.013(5)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for mo_220625_XWX_742_2_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	10376.9(3)	9855.5(8)	3216.4(2)	33.30(12)
O1	7927(2)	2335(5)	5121.2(17)	31.3(7)
O2	7132(2)	5447(4)	5346.3(17)	30.3(8)
O3	5160(3)	8949(5)	6519.3(18)	40.3(8)
O4	9379(2)	8640(5)	8468.9(17)	30.8(7)
O5	8880(2)	4991(7)	9109.0(14)	27.9(6)
O6	6963(2)	2682(5)	8438.6(17)	33.4(8)
O7	3965(2)	7213(5)	9302.5(17)	31.0(7)
O8	2465(2)	4094(5)	9125.2(16)	30.3(7)
O9	2311(2)	1148(5)	8038.2(18)	33.4(8)
C1	8077(3)	7740(7)	4368(2)	27.6(10)
C2	8642(3)	8967(7)	3938(2)	28.9(10)
C3	9560(3)	8094(7)	3751(2)	25.9(10)
C4	9915(3)	6018(7)	3970(2)	25.3(10)
C5	9338(3)	4780(9)	4387.2(19)	23.5(8)
C6	8418(3)	5644(7)	4591(2)	24.9(10)
C7	7818(3)	4266(7)	5040(2)	25.5(11)
C8	6519(3)	4262(6)	5810(2)	27.8(11)
C9	5707(3)	5874(7)	5967(2)	28.1(10)
C10	6140(3)	7877(7)	6425(2)	28.8(10)
C11	6836(3)	7215(7)	7166(2)	22.6(9)
C12	6547(3)	5382(6)	7527(2)	21.4(10)
C13	5508(3)	4175(7)	7215(2)	25.0(10)
C14	4914(3)	5106(10)	6447(2)	32.3(11)
C15	4365(4)	7275(9)	6514(3)	43.3(13)
C16	7776(3)	8349(7)	7469(2)	24.9(9)
C17	8433(3)	7663(7)	8129(2)	23.5(9)
C18	8174(3)	5781(6)	8487(2)	21.7(9)
C19	7240(3)	4629(8)	8177(2)	21.6(9)
C20	9682(4)	10551(7)	8128(3)	34.9(12)
C21	8936(4)	6224(9)	9783(3)	42.2(13)
C22	7151(5)	2210(11)	9212(3)	65.6(19)
C23	4733(3)	4126(7)	7761(2)	24.3(10)
C24	4775(3)	5694(7)	8309(2)	25.2(9)
C25	4001(3)	5709(7)	8757(2)	24.7(9)
C26	3195(3)	4155(6)	8659(2)	24.7(10)
C27	3151(3)	2585(7)	8098(2)	26.2(9)
C28	3929(3)	2554(7)	7655(2)	25.7(10)

C29	4761(4)	8893(8)	9415(3)	35.6(11)
C30	1566(3)	5537(7)	8889(3)	33.7(12)
C31	2267(3)	-580(7)	7516(2)	29.1(11)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for mo_220625_XWX_742_2_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	40.0(2)	31.5(2)	30.3(2)	3.8(3)	11.71(17)	-3.2(3)
O1	37.8(19)	22.0(17)	36(2)	-1.2(14)	11.7(15)	-0.6(14)
O2	34.6(17)	29(2)	32.1(18)	-3.3(12)	17.6(14)	-0.5(13)
O3	36.3(18)	44(2)	39(2)	-4.5(15)	2.1(15)	18.5(16)
O4	27.5(17)	32.2(18)	30.3(18)	0.0(14)	0.3(13)	-11.6(14)
O5	25.5(13)	32.1(15)	24.2(14)	1.6(17)	0.8(11)	3.0(17)
O6	39.3(19)	29.7(18)	31.3(19)	8.2(14)	7.5(15)	-7.0(15)
O7	31.8(17)	33.6(18)	29.2(18)	-8.5(14)	10.3(14)	-4.5(14)
O8	29.2(17)	37.3(19)	27.9(17)	3.8(12)	14.1(13)	3.9(13)
O9	31.2(18)	35.6(19)	37(2)	-9.3(15)	15.0(15)	-10.3(15)
C1	28(2)	28(2)	28(3)	-5.8(19)	7.6(19)	0.7(19)
C2	36(3)	24(2)	26(2)	-2.2(18)	4(2)	-0.9(19)
C3	30(2)	30(2)	17(2)	-4.6(18)	4.2(18)	-4.9(19)
C4	27(2)	29(2)	20(2)	-1.6(18)	4.0(18)	-0.7(19)
C5	26.4(19)	22.5(18)	21.0(19)	-3(2)	3.6(14)	-1(2)
C6	26(2)	29(2)	19(2)	-5.4(16)	4.3(17)	-2.0(18)
C7	26(2)	32(3)	19(2)	-6.9(17)	3.6(17)	-0.6(17)
C8	32(2)	28(3)	26(2)	-2.1(16)	11.6(19)	-5.9(18)
C9	26(2)	35(2)	22(2)	-3.0(19)	4.0(18)	1.2(19)
C10	32(3)	30(3)	25(3)	-2.0(19)	7(2)	5(2)
C11	22(2)	26(2)	21(2)	-2.9(17)	7.2(17)	2.7(18)
C12	20(2)	23(3)	22(2)	-3.6(16)	8.8(16)	0.8(16)
C13	22(2)	28(2)	26(2)	-3.9(16)	6.8(17)	-3.0(17)
C14	25(2)	48(3)	24(2)	-4(2)	6.3(16)	-6(3)
C15	30(3)	69(4)	32(3)	8(3)	9(2)	16(3)
C16	31(2)	18(2)	26(2)	-1.0(17)	6.3(19)	-1.7(18)
C17	21(2)	23(2)	27(2)	-5.7(18)	5.3(18)	-3.6(18)
C18	22(2)	23(2)	21(2)	-1.0(16)	5.5(17)	1.6(17)
C19	23.5(19)	20(2)	24(2)	-1(2)	11.3(15)	2(2)
C20	34(3)	34(3)	39(3)	-4(2)	13(2)	-14(2)
C21	51(3)	49(3)	24(3)	-1(2)	0(2)	2(3)
C22	72(4)	82(5)	40(4)	27(3)	6(3)	-33(4)
C23	20(2)	32(2)	21(2)	-1.0(17)	5.3(17)	0.2(17)
C24	24(2)	29(2)	23(2)	-1.0(17)	5.3(18)	-2.4(17)

C25	28(2)	28(2)	19(2)	-2.2(17)	5.6(18)	1.9(18)
C26	22(2)	30(2)	23(2)	3.2(16)	8.0(17)	0.6(17)
C27	22(2)	30(2)	26(2)	0.6(18)	5.6(18)	-4.4(19)
C28	23(2)	29(2)	25(2)	-4.5(18)	6.7(18)	-0.8(19)
C29	42(3)	31(2)	33(3)	-7(2)	8(2)	-6(2)
C30	24(2)	42(3)	37(3)	2(2)	13(2)	3.0(19)
C31	30(2)	25(3)	33(3)	-2.0(18)	6.1(18)	-4.6(19)

Table 4 Bond Lengths for mo_220625_XWX_742_2_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C3	1.901(4)	C5	C6	1.400(5)
O1	C7	1.201(5)	C6	C7	1.491(6)
O2	C7	1.340(5)	C8	C9	1.498(6)
O2	C8	1.456(5)	C9	C10	1.525(6)
O3	C10	1.448(5)	C9	C14	1.539(6)
O3	C15	1.439(6)	C10	C11	1.508(6)
O4	C17	1.369(5)	C11	C12	1.392(6)
O4	C20	1.419(5)	C11	C16	1.393(6)
O5	C18	1.380(5)	C12	C13	1.516(5)
O5	C21	1.434(6)	C12	C19	1.400(5)
O6	C19	1.361(6)	C13	C14	1.555(6)
O6	C22	1.410(6)	C13	C23	1.536(6)
O7	C25	1.366(5)	C14	C15	1.521(8)
O7	C29	1.429(5)	C16	C17	1.379(6)
O8	C26	1.380(5)	C17	C18	1.400(6)
O8	C30	1.438(5)	C18	C19	1.395(6)
O9	C27	1.371(5)	C23	C24	1.382(6)
O9	C31	1.420(5)	C23	C28	1.389(6)
C1	C2	1.389(6)	C24	C25	1.400(6)
C1	C6	1.394(6)	C25	C26	1.383(5)
C2	C3	1.386(6)	C26	C27	1.399(6)
C3	C4	1.385(6)	C27	C28	1.398(5)
C4	C5	1.387(6)			

Table 5 Bond Angles for mo_220625_XWX_742_2_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O2	C8	116.1(3)	C19	C12	C13	119.9(4)
C15	O3	C10	106.8(3)	C12	C13	C14	112.2(4)
C17	O4	C20	117.2(4)	C12	C13	C23	113.0(3)

C18	O5	C21	115.3(4)	C23	C13	C14	109.5(3)
C19	O6	C22	121.9(4)	C9	C14	C13	111.9(3)
C25	O7	C29	117.8(3)	C15	C14	C9	98.0(4)
C26	O8	C30	112.9(3)	C15	C14	C13	113.3(4)
C27	O9	C31	117.3(3)	O3	C15	C14	107.3(4)
C2	C1	C6	120.1(4)	C17	C16	C11	120.4(4)
C3	C2	C1	119.0(4)	O4	C17	C16	125.1(4)
C2	C3	Br1	118.6(3)	O4	C17	C18	114.8(4)
C4	C3	Br1	119.6(3)	C16	C17	C18	120.1(4)
C4	C3	C2	121.7(4)	O5	C18	C17	120.0(4)
C3	C4	C5	119.1(4)	O5	C18	C19	120.3(4)
C4	C5	C6	120.0(5)	C19	C18	C17	119.5(4)
C1	C6	C5	119.9(4)	O6	C19	C12	115.2(4)
C1	C6	C7	121.5(4)	O6	C19	C18	124.3(4)
C5	C6	C7	118.5(4)	C18	C19	C12	120.3(4)
O1	C7	O2	123.6(4)	C24	C23	C13	121.3(4)
O1	C7	C6	124.8(4)	C24	C23	C28	120.2(4)
O2	C7	C6	111.6(3)	C28	C23	C13	118.3(4)
O2	C8	C9	104.5(3)	C23	C24	C25	119.9(4)
C8	C9	C10	117.1(4)	O7	C25	C24	124.2(4)
C8	C9	C14	117.5(4)	O7	C25	C26	115.3(4)
C10	C9	C14	98.0(4)	C26	C25	C24	120.6(4)
O3	C10	C9	102.3(3)	O8	C26	C25	120.7(4)
O3	C10	C11	111.9(3)	O8	C26	C27	120.0(4)
C11	C10	C9	110.5(4)	C25	C26	C27	119.2(4)
C12	C11	C10	118.7(4)	O9	C27	C26	114.6(4)
C12	C11	C16	120.3(4)	O9	C27	C28	125.0(4)
C16	C11	C10	121.0(4)	C28	C27	C26	120.3(4)
C11	C12	C13	120.8(4)	C23	C28	C27	119.7(4)
C11	C12	C19	119.2(4)				

Table 6 Torsion Angles for mo_220625_XWX_742_2_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C3	C4	C5	177.3(3)	C11	C16	C17	C18	1.9(6)
O2	C8	C9	C10	-64.2(5)	C12	C11	C16	C17	0.2(6)
O2	C8	C9	C14	179.5(4)	C12	C13	C14	C9	35.6(5)
O3	C10	C11	C12	77.1(5)	C12	C13	C14	C15	-74.1(4)
O3	C10	C11	C16	-105.8(4)	C12	C13	C23	C24	24.4(5)
O4	C17	C18	O5	-3.2(5)	C12	C13	C23	C28	-160.3(4)
O4	C17	C18	C19	-178.5(4)	C13	C12	C19	O6	6.7(5)
O5	C18	C19	O6	-1.5(6)	C13	C12	C19	C18	-177.2(4)

O5 C18 C19 C12	-177.3(3)	C13 C14 C15 O3	85.5(4)
O7 C25 C26 O8	-4.1(6)	C13 C23 C24 C25	174.7(4)
O7 C25 C26 C27	178.3(4)	C13 C23 C28 C27	-174.2(4)
O8 C26 C27 O9	3.6(6)	C14 C9 C10 O3	-48.9(4)
O8 C26 C27 C28	-176.0(4)	C14 C9 C10 C11	70.4(4)
O9 C27 C28 C23	178.8(4)	C14 C13 C23 C24	-101.4(5)
C1 C2 C3 Br1	-176.1(3)	C14 C13 C23 C28	73.8(5)
C1 C2 C3 C4	1.2(6)	C15 O3 C10 C9	29.3(4)
C1 C6 C7 O1	164.0(4)	C15 O3 C10 C11	-89.0(4)
C1 C6 C7 O2	-15.9(6)	C16 C11 C12 C13	178.1(3)
C2 C1 C6 C5	0.5(6)	C16 C11 C12 C19	-3.2(6)
C2 C1 C6 C7	-178.8(4)	C16 C17 C18 O5	174.2(4)
C2 C3 C4 C5	0.0(6)	C16 C17 C18 C19	-1.0(6)
C3 C4 C5 C6	-1.0(6)	C17 C18 C19 O6	173.8(4)
C4 C5 C6 C1	0.7(6)	C17 C18 C19 C12	-2.0(6)
C4 C5 C6 C7	180.0(4)	C19 C12 C13 C14	-173.7(4)
C5 C6 C7 O1	-15.2(6)	C19 C12 C13 C23	61.9(5)
C5 C6 C7 O2	164.8(3)	C20 O4 C17 C16	2.5(6)
C6 C1 C2 C3	-1.5(6)	C20 O4 C17 C18	179.8(3)
C7 O2 C8 C9	-170.9(3)	C21 O5 C18 C17	73.2(5)
C8 O2 C7 O1	1.2(6)	C21 O5 C18 C19	-111.5(5)
C8 O2 C7 C6	-178.8(3)	C22 O6 C19 C12	-145.9(5)
C8 C9 C10 O3	-175.5(3)	C22 O6 C19 C18	38.1(6)
C8 C9 C10 C11	-56.1(5)	C23 C13 C14 C9	161.9(4)
C8 C9 C14 C13	55.3(6)	C23 C13 C14 C15	52.2(5)
C8 C9 C14 C15	174.5(4)	C23 C24 C25 O7	-178.8(4)
C9 C10 C11 C12	-36.2(5)	C23 C24 C25 C26	0.5(6)
C9 C10 C11 C16	140.8(4)	C24 C23 C28 C27	1.1(6)
C9 C14 C15 O3	-32.6(4)	C24 C25 C26 O8	176.6(4)
C10 O3 C15 C14	2.6(4)	C24 C25 C26 C27	-1.1(6)
C10 C9 C14 C13	-70.9(5)	C25 C26 C27 O9	-178.8(4)
C10 C9 C14 C15	48.2(4)	C25 C26 C27 C28	1.7(6)
C10 C11 C12 C13	-4.8(5)	C26 C27 C28 C23	-1.7(7)
C10 C11 C12 C19	173.9(3)	C28 C23 C24 C25	-0.5(6)
C10 C11 C16 C17	-176.8(4)	C29 O7 C25 C24	0.9(6)
C11 C12 C13 C14	5.0(5)	C29 O7 C25 C26	-178.4(4)
C11 C12 C13 C23	-119.4(4)	C30 O8 C26 C25	85.0(5)
C11 C12 C19 O6	-172.1(3)	C30 O8 C26 C27	-97.4(4)
C11 C12 C19 C18	4.1(6)	C31 O9 C27 C26	-175.6(4)
C11 C16 C17 O4	179.1(4)	C31 O9 C27 C28	4.0(6)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_220625_XWX_742_2_0m.

Atom	*x*	*y*	*z*	U(eq)
H1	7455.87	8330.95	4509.54	33
H2	8403.51	10383.26	3773.81	35
H4	10546.25	5449.37	3835.9	30
H5	9566.48	3345.71	4534.44	28
H8A	6993.83	3767.21	6281.43	33
H8B	6157.48	2982.48	5538.76	33
H9	5275.32	6383.11	5474.17	34
H10	6553.21	8823.33	6138.14	35
H13	5704.98	2635.57	7129.08	30
H14	4390.95	4023.56	6169.22	39
H15A	3753.24	7481.6	6083.67	52
H15B	4086.03	7324.13	6982.11	52
H16	7965.79	9601.2	7220.26	30
H20A	9776.87	10210.88	7620.73	52
H20B	10361.4	11107.49	8426.79	52
H20C	9117.94	11654.32	8102.69	52
H21A	9276.11	7631.62	9734.03	63
H21B	9362.77	5425.51	10208.17	63
H21C	8205.66	6457.07	9868.74	63
H22A	6761.34	883.35	9291.19	98
H22B	6897.56	3422.56	9478.05	98
H22C	7925.32	1994.52	9403.04	98
H24	5328.92	6761.11	8382.04	30
H28	3907.98	1462.28	7284.03	31
H29A	4729.11	9683.98	8944.33	53
H29B	5477.93	8248.39	9578.02	53
H29C	4620.51	9900.66	9800.59	53
H30A	1199.54	5169.19	8376.28	51
H30B	1825.97	7039.77	8903.15	51
H30C	1060.66	5384.26	9226.24	51
H31A	2298.18	14.37	7021.9	44
H31B	1592.13	-1387.31	7482.82	44
H31C	2879.64	-1558.43	7682.34	44

Experimental

A suitable crystal was selected and analyzed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 71

Crystal Data for $C_{31}H_{33}BrO_9$ (M =629.48 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 12.6753(14) Å, b = 6.1512(7) Å, c = 18.2258(17) Å, β = 101.938(3)°, V = 1390.3(3) Å^3, Z = 2, T = 170.0 K, μ(MoKα) = 1.535 mm^{-1}, *Dcalc* = 1.504 g/cm^3, 28144 reflections measured (4.568° ≤ 2Θ ≤ 54.33°), 6121 unique (R_{int} = 0.0650, R_{sigma} = 0.0640) which were used in all calculations. The final R_1 was 0.0374 (I > 2σ(I)) and wR_2 was 0.0721 (all data).

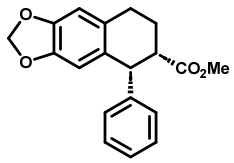
Refinement model description

Number of restraints - 1, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C9(H9), C10(H10), C13(H13), C14(H14)
2.b Secondary CH2 refined with riding coordinates:
 C8(H8A,H8B), C15(H15A,H15B)
2.c Aromatic/amide H refined with riding coordinates:
 C1(H1), C2(H2), C4(H4), C5(H5), C16(H16), C24(H24), C28(H28)
2.d Idealised Me refined as rotating group:
 C20(H20A,H20B,H20C), C21(H21A,H21B,H21C), C22(H22A,H22B,H22C), C29(H29A,H29B,
 H29C), C30(H30A,H30B,H30C), C31(H31A,H31B,H31C)
```

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

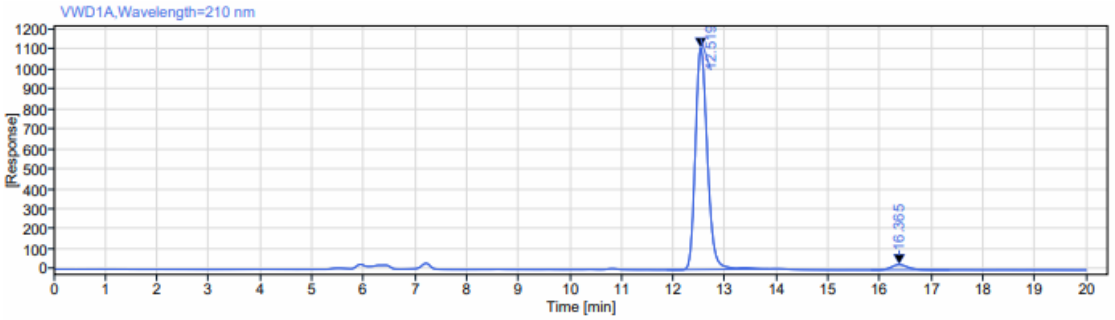
7. HPLC Spectra



2a

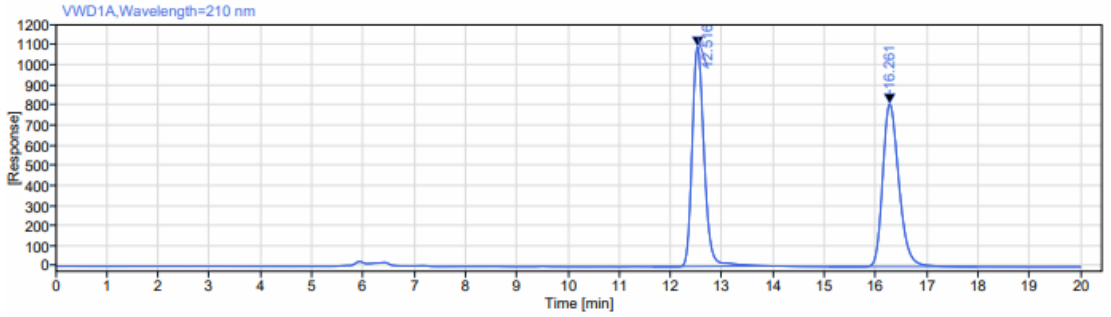
(94% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.519 min (major enantiomer), 16.365 min (minor enantiomer).



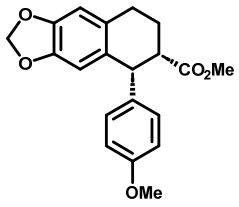
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.519	MM m	1.97	17902.73	1110.51	96.83
16.365	MM m	1.51	586.77	26.33	3.17
		Sum	18489.51		



Signal: VWD1A,Wavelength=210 nm

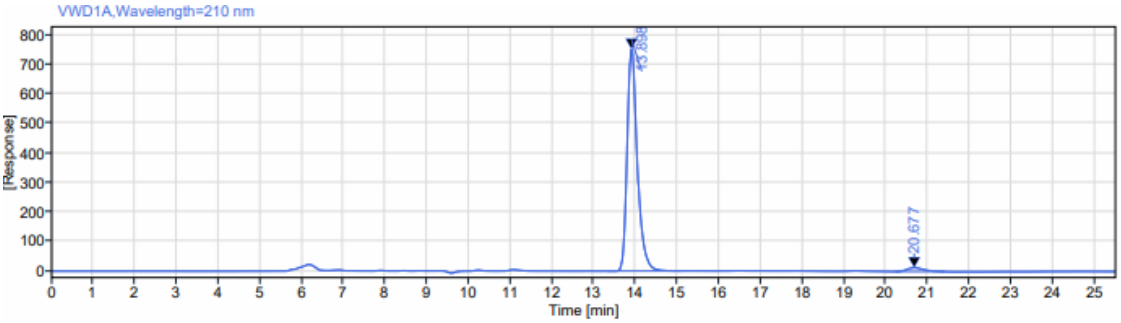
RT [min]	Type	Width [min]	Area	Height	Area%
12.516	MM m	2.25	17723.93	1093.07	49.90
16.261	MM m	2.89	17792.68	809.87	50.10
		Sum	35516.61		



2b

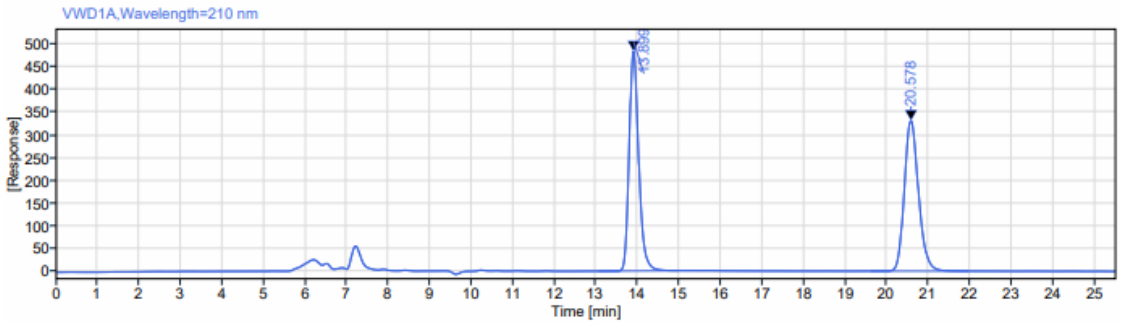
(95% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (90/10), 0.5 mL/min, 210 nm, 13.898 min (major enantiomer), 20.677 min (minor enantiomer).



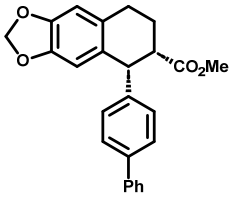
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
13.898	MM m	1.78	12779.53	752.02	97.32
20.677	MM m	1.19	351.53	12.63	2.68
		Sum	13131.05		



Signal: VWD1A,Wavelength=210 nm

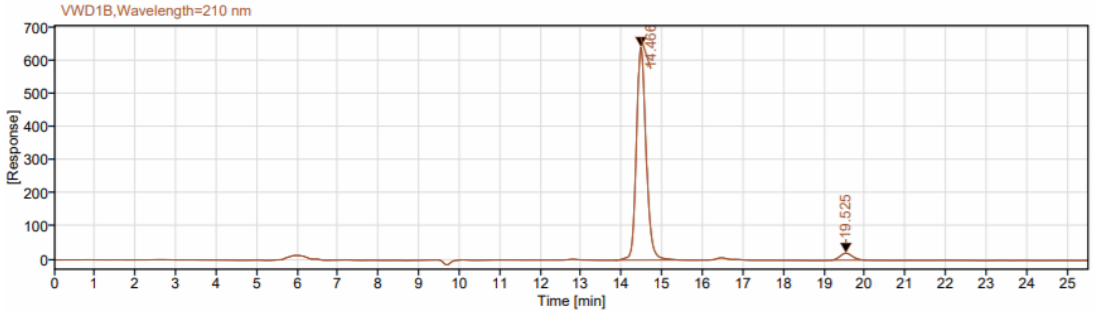
RT [min]	Type	Width [min]	Area	Height	Area%
13.899	MM m	1.93	7727.56	481.31	49.70
20.578	MM m	2.35	7820.16	329.73	50.30
		Sum	15547.72		



2c

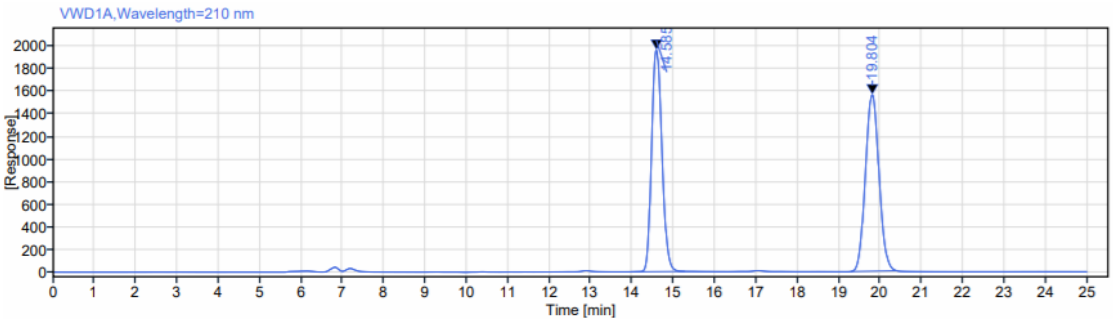
(92% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 14.466 min (major enantiomer), 19.525 min (minor enantiomer).



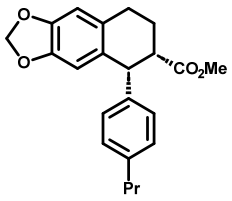
Signal: VWD1B,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
14.466	MM m	1.64	10737.25	640.24	95.97
19.525	MM m	0.87	450.73	21.04	4.03
		Sum	11187.98		



Signal: VWD1A,Wavelength=210 nm

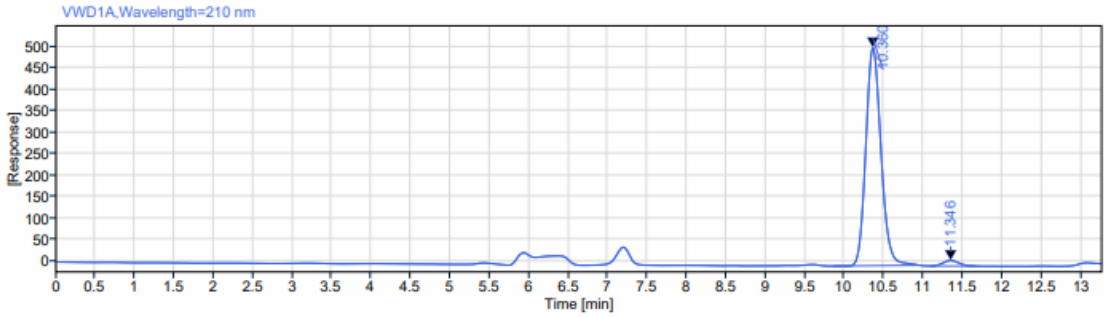
RT [min]	Type	Width [min]	Area	Height	Area%
14.585	MM m	1.31	34281.43	1967.70	48.87
19.804	MM m	1.10	35863.28	1566.54	51.13
		Sum	70144.71		



2d

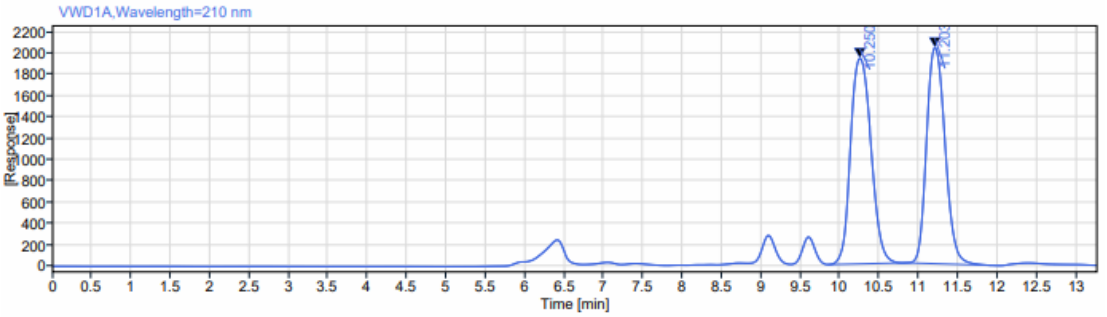
(95% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (90/10), 0.5 mL/min, 210 nm, 10.360 min (major enantiomer), 11.346 min (minor enantiomer).



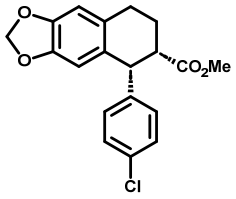
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
10.360	MM m	1.10	6762.18	509.25	97.40
11.346	MM m	0.58	180.45	12.94	2.60
		Sum	6942.63		



Signal: VWD1A,Wavelength=210 nm

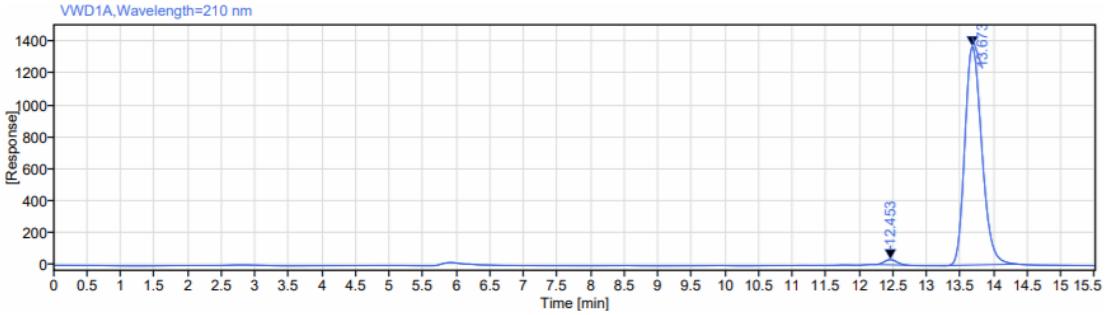
RT [min]	Type	Width [min]	Area	Height	Area%
10.250	MM m	0.99	34997.23	1931.37	51.45
11.203	MM m	1.08	33029.95	2029.19	48.55
		Sum	68027.17		



2e

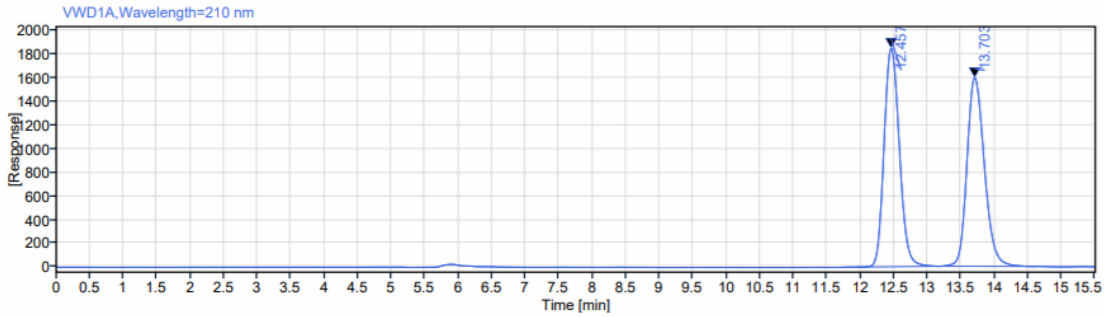
(96% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.453 min (minor enantiomer), 13.673 min (major enantiomer).



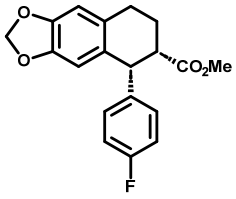
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.453	MM m	0.49	434.58	32.72	1.77
13.673	MM m	1.11	24115.51	1367.15	98.23
		Sum	24550.08		



Signal: VWD1A,Wavelength=210 nm

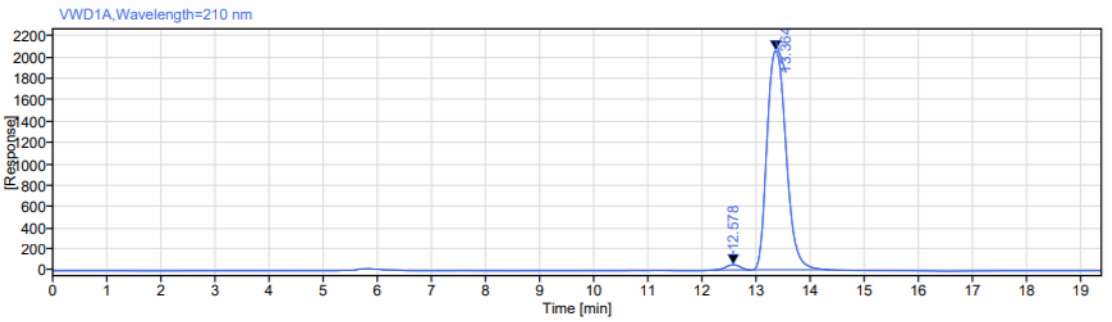
RT [min]	Type	Width [min]	Area	Height	Area%
12.457	MM m	1.22	29311.44	1844.99	50.41
13.703	MM m	1.47	28836.91	1593.10	49.59
		Sum	58148.35		



2f

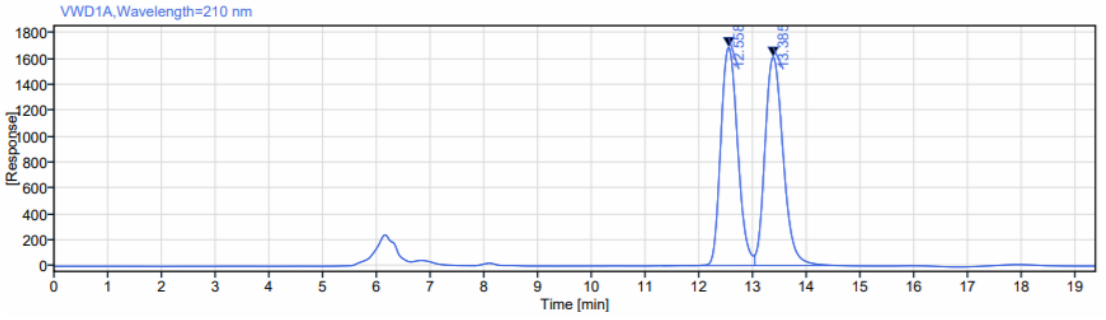
(96% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.578 min (minor enantiomer), 13.364 min (major enantiomer).



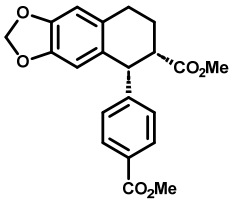
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.578	MM m	0.68	926.41	49.53	1.80
13.364	MM m	1.42	50588.38	2057.95	98.20
		Sum	51514.78		



Signal: VWD1A,Wavelength=210 nm

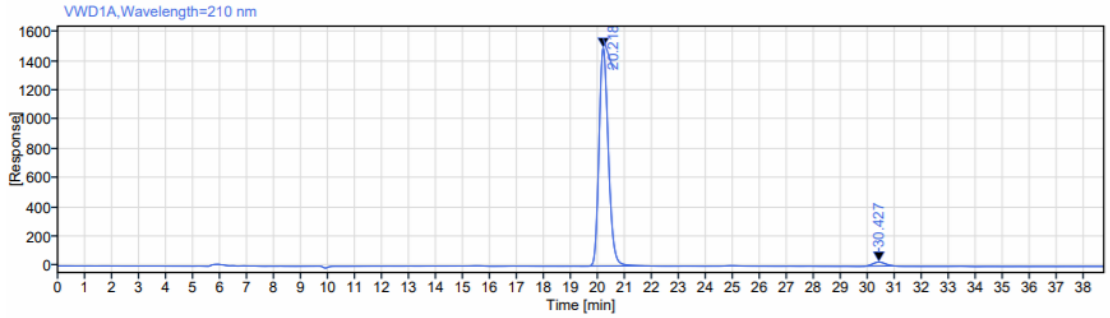
RT [min]	Type	Width [min]	Area	Height	Area%
12.558	MM m	1.72	36853.84	1682.67	49.27
13.385	MM m	1.55	37946.96	1608.56	50.73
		Sum	74800.80		



2g

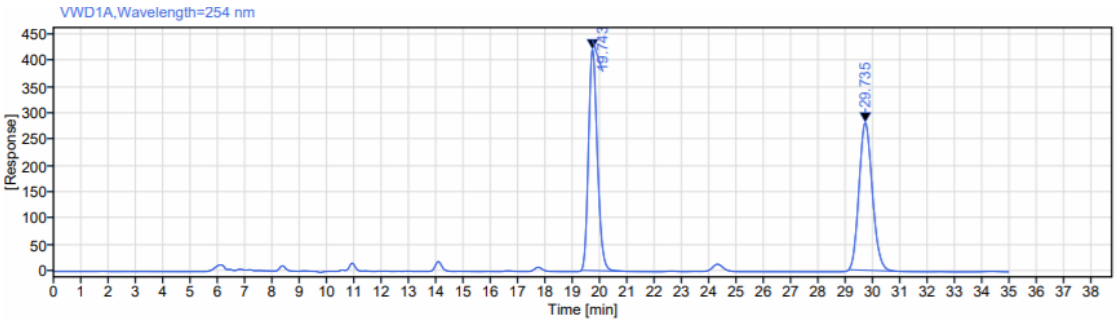
(95% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 20.218 min (major enantiomer), 30.427 min (minor enantiomer).



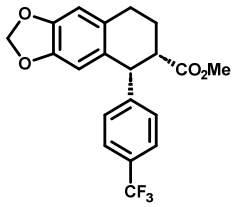
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
20.218	BM m	0.37	35825.43	1491.00	97.57
30.427	MM m	0.50	891.73	27.89	2.43
		Sum	36717.16		



Signal: VWD1A,Wavelength=254 nm

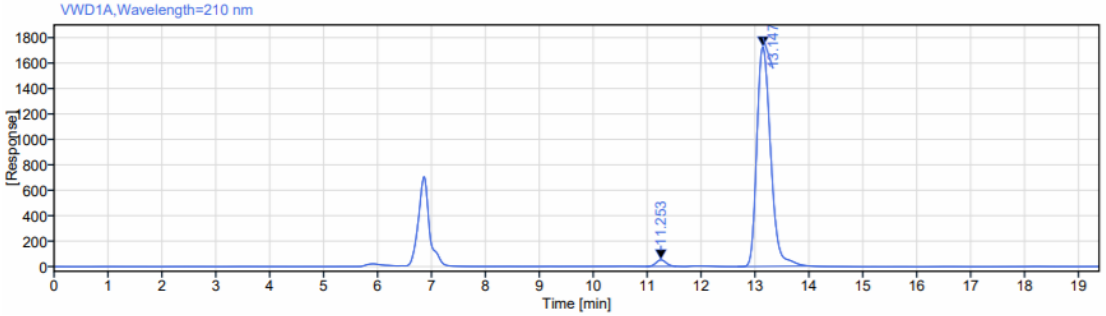
RT [min]	Type	Width [min]	Area	Height	Area%
19.743	BB	1.76	9448.60	419.13	49.92
29.735	BB	1.89	9480.11	279.63	50.08
		Sum	18928.70		



2h

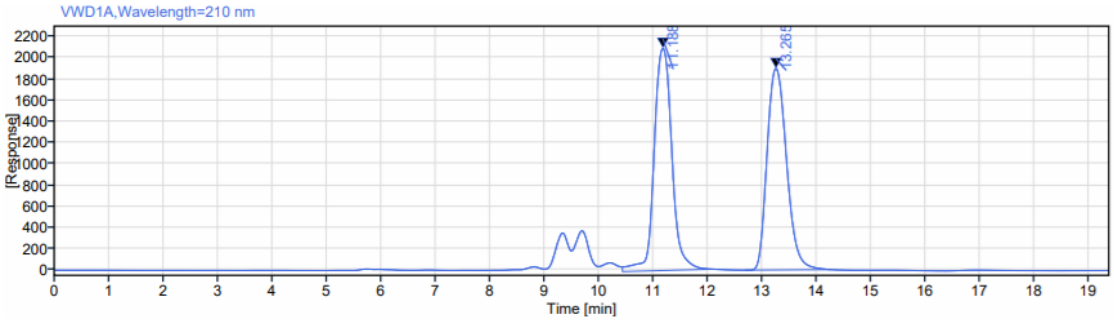
(96% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 13.147 min (major enantiomer), 11.253 min (minor enantiomer).



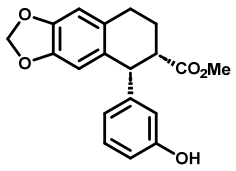
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
11.253	MM m	0.56	657.66	51.14	2.09
13.147	MM m	1.34	30865.16	1735.97	97.91
		Sum	31522.82		



Signal: VWD1A,Wavelength=210 nm

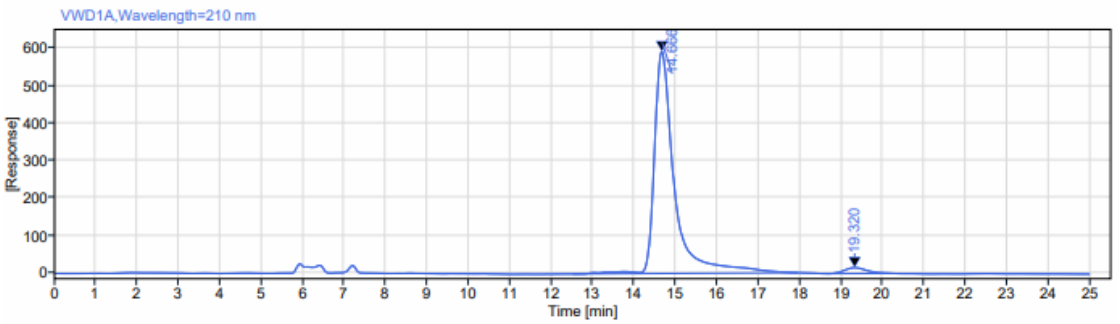
RT [min]	Type	Width [min]	Area	Height	Area%
11.188	MM m	0.36	47598.08	2096.84	50.13
13.265	MM m	0.39	47342.15	1902.07	49.87
		Sum	94940.23		



2i

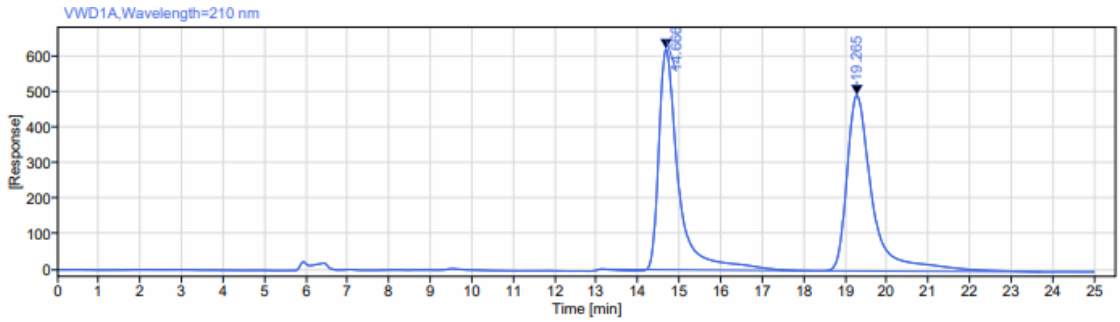
(94% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 11.666 min (major enantiomer), 19.320 min (minor enantiomer).



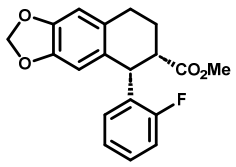
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
14.666	MM m	5.43	20066.60	592.38	97.15
19.320	MM m	1.63	588.96	15.62	2.85
		Sum	20655.56		



Signal: VWD1A,Wavelength=210 nm

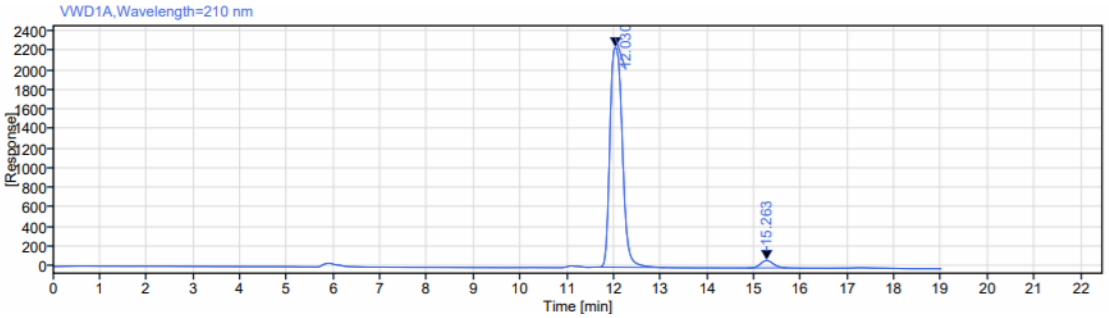
RT [min]	Type	Width [min]	Area	Height	Area%
14.666	MM m	4.70	20382.95	620.69	49.05
19.265	MM m	5.81	21171.47	494.41	50.95
		Sum	41554.43		



2j

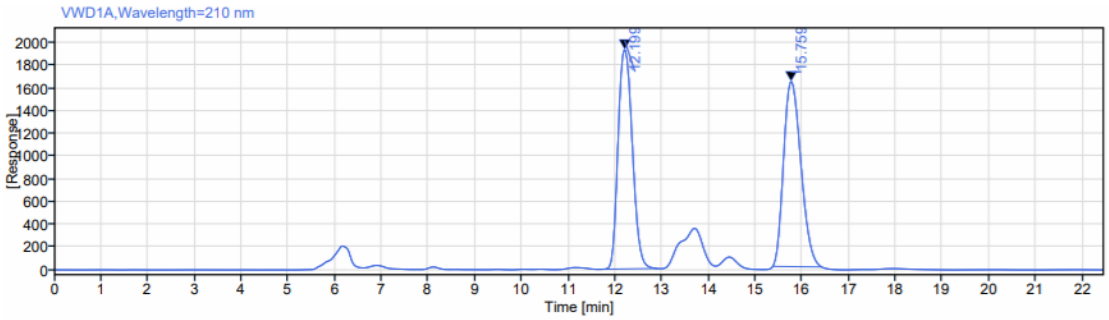
(93% ee)

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.030 min (major enantiomer), 15.263 min (minor enantiomer).



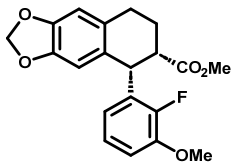
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.030	MM m	0.30	41388.85	2242.20	96.65
15.263	BM m	0.29	1435.87	76.10	3.35
		Sum	42824.72		



Signal: VWD1A,Wavelength=210 nm

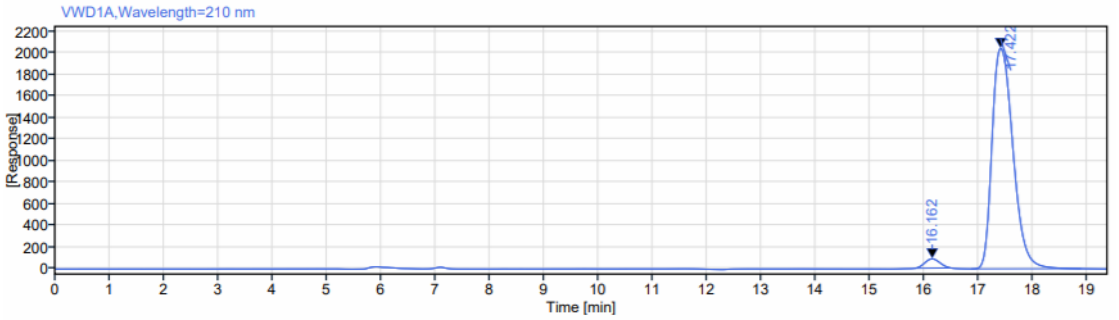
RT [min]	Type	Width [min]	Area	Height	Area%
12.199	MM m	1.28	41061.16	1931.57	49.32
15.759	MM m	1.05	42194.70	1630.51	50.68
		Sum	83255.87		



2k

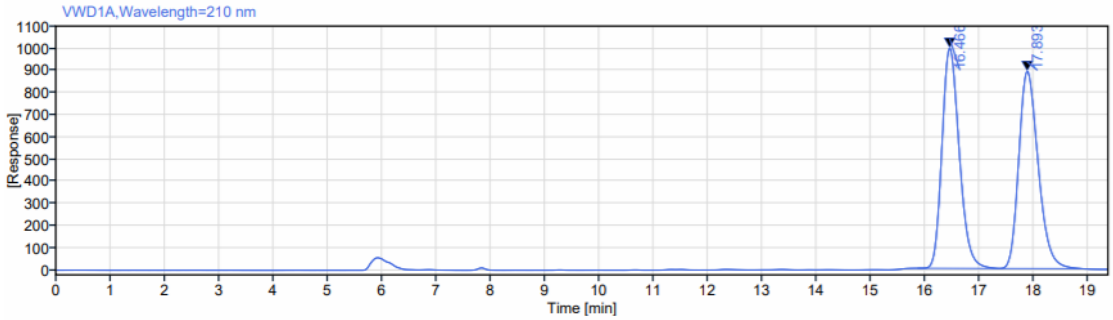
(94% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 17.422 min (major enantiomer), 16.162 min (minor enantiomer).



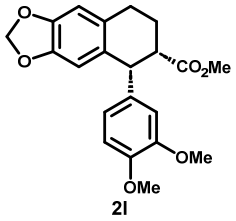
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
16.162	MM m	0.67	1651.45	85.80	2.92
17.422	BB	2.02	54923.60	2042.13	97.08
		Sum	56575.05		



Signal: VWD1A,Wavelength=210 nm

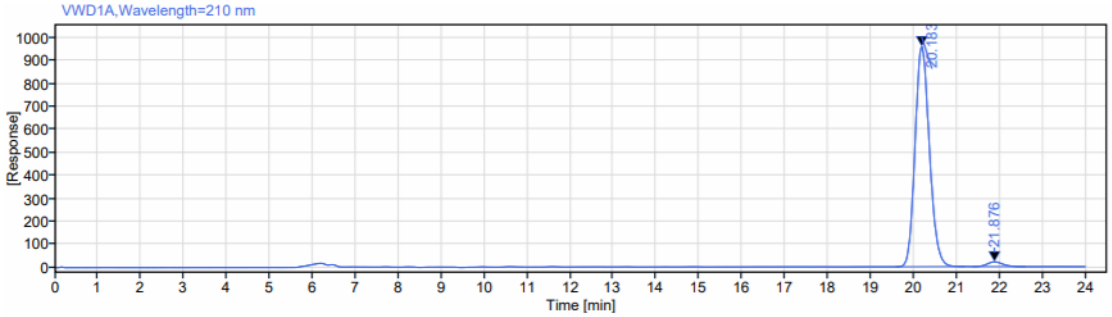
RT [min]	Type	Width [min]	Area	Height	Area%
16.466	MM m	1.51	22013.16	994.08	49.87
17.893	MM m	1.51	22130.64	890.15	50.13
		Sum	44143.80		



2l

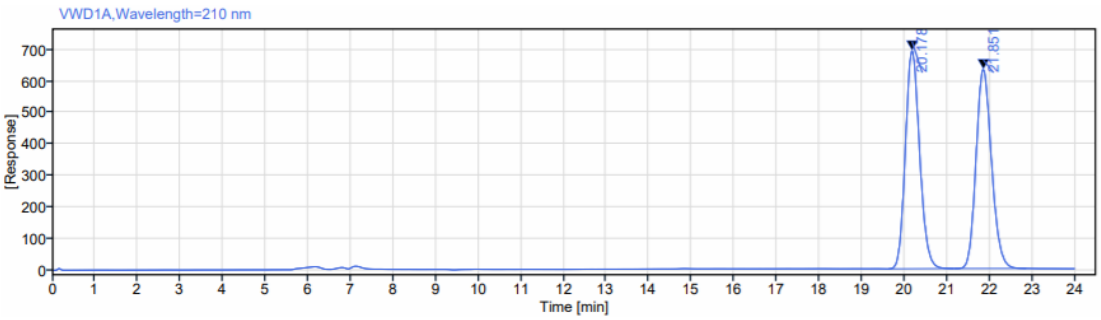
(96% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 20.183 min (major enantiomer), 21.876 min (minor enantiomer).



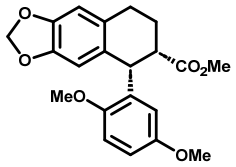
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
20.183	MM m	1.60	22323.77	958.24	97.76
21.876	MM m	1.24	512.34	20.68	2.24
		Sum	22836.11		



Signal: VWD1A,Wavelength=210 nm

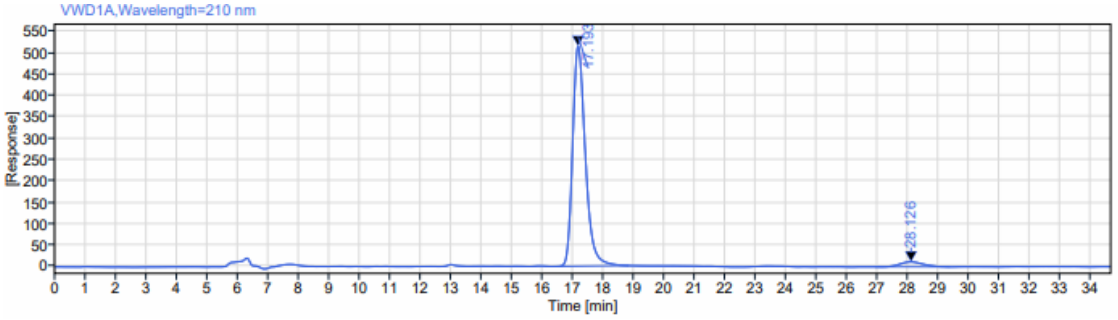
RT [min]	Type	Width [min]	Area	Height	Area%
20.178	MM m	1.53	16091.68	691.71	50.14
21.851	BB	1.68	16002.94	631.88	49.86
		Sum	32094.62		



2m

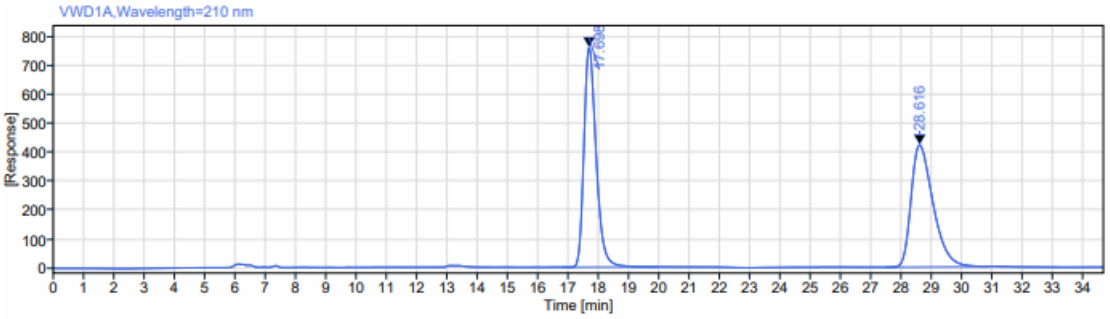
(92% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 17.193 min (major enantiomer), 28.126 min (minor enantiomer).



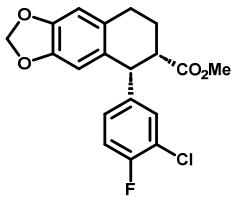
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
17.193	MM m	2.46	14914.56	514.12	96.02
28.126	MM m	2.46	617.72	11.62	3.98
		Sum	15532.28		



Signal: VWD1A,Wavelength=210 nm

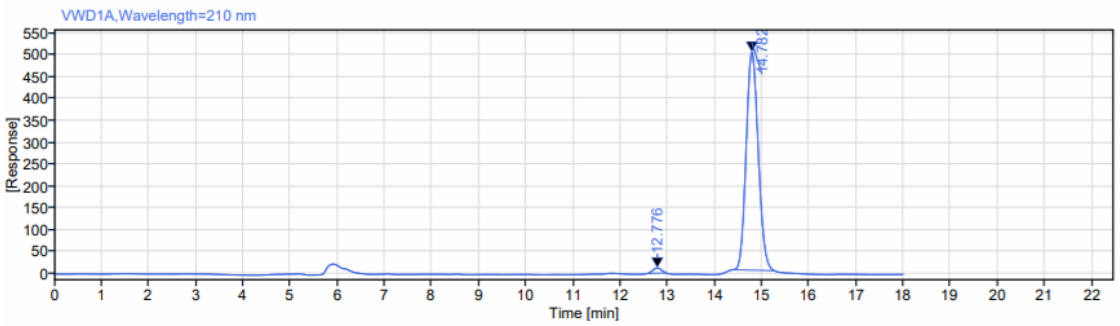
RT [min]	Type	Width [min]	Area	Height	Area%
17.698	MM m	3.19	21273.57	761.27	49.79
28.616	MM m	4.02	21448.74	423.30	50.21
		Sum	42722.31		



2n

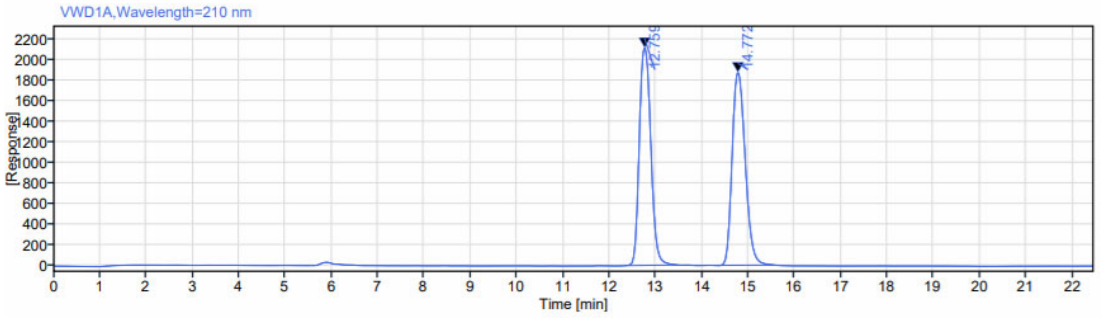
(97% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 14.782 min (major enantiomer), 12.776 min (minor enantiomer).



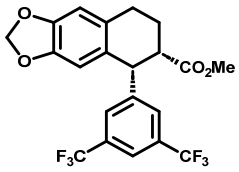
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.776	MM m	0.39	148.62	11.79	1.65
14.782	MM m	0.88	8880.85	498.74	98.35
		Sum	9029.46		



Signal: VWD1A,Wavelength=210 nm

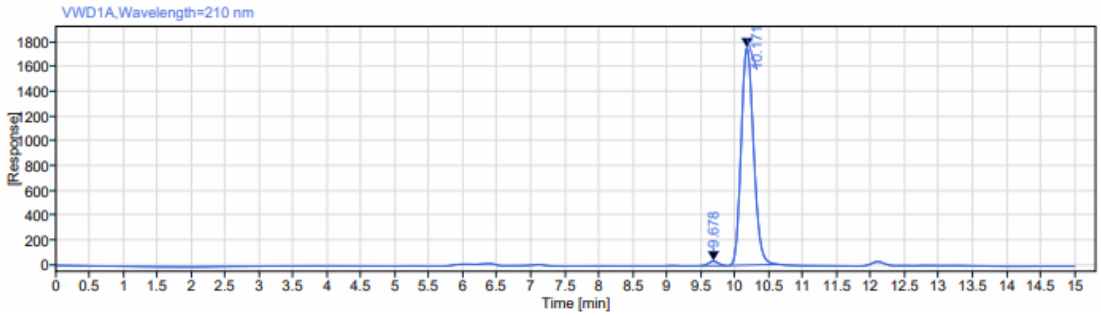
RT [min]	Type	Width [min]	Area	Height	Area%
12.759	MM m	1.13	36660.69	2118.01	49.85
14.772	MM m	1.29	36875.03	1876.88	50.15
		Sum	73535.72		



2o

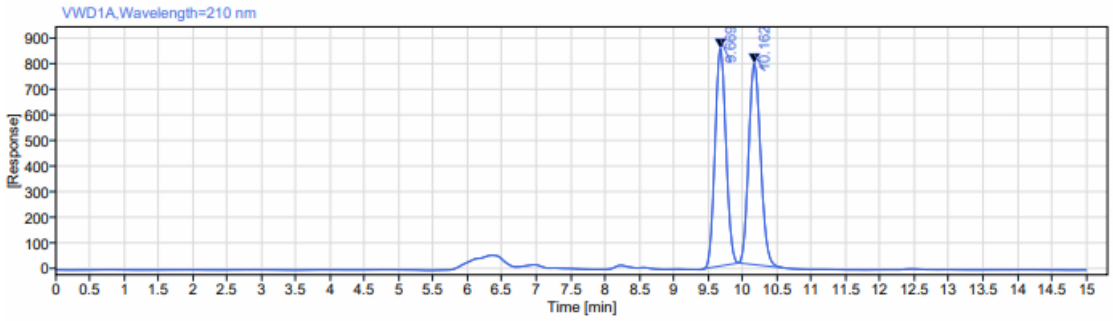
(97% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 9.678 min (minor enantiomer), 10.171 min (major enantiomer).



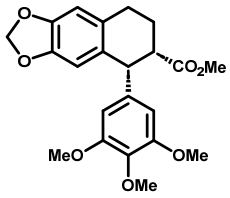
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
9.678	MM m	0.39	376.87	35.86	1.66
10.171	MM m	0.71	22283.49	1750.28	98.34
		Sum	22660.36		



Signal: VWD1A,Wavelength=210 nm

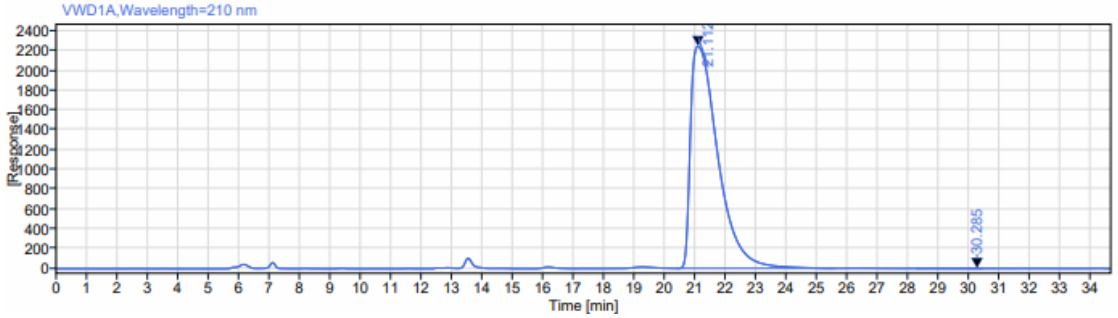
RT [min]	Type	Width [min]	Area	Height	Area%
9.669	MM m	0.58	9381.95	846.47	49.76
10.162	MM m	0.68	9472.71	783.56	50.24
		Sum	18854.67		



2p

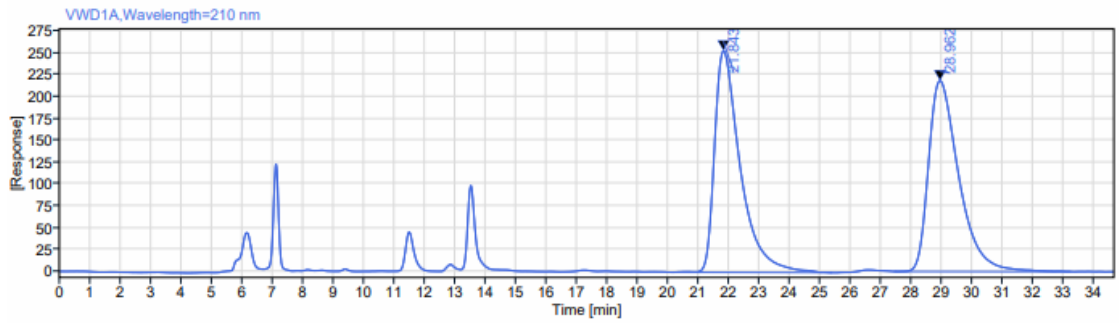
(> 99% ee)

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 21.112 min (major enantiomer), 30.285 min (minor enantiomer).



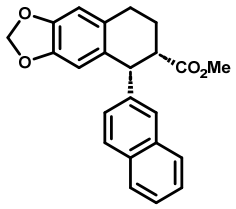
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
21.112	MM m	5.22	140198.61	2244.58	99.97
30.285	MM n	2.20	41.94	0.14	0.03
		Sum	140240.55		



Signal: VWD1A,Wavelength=210 nm

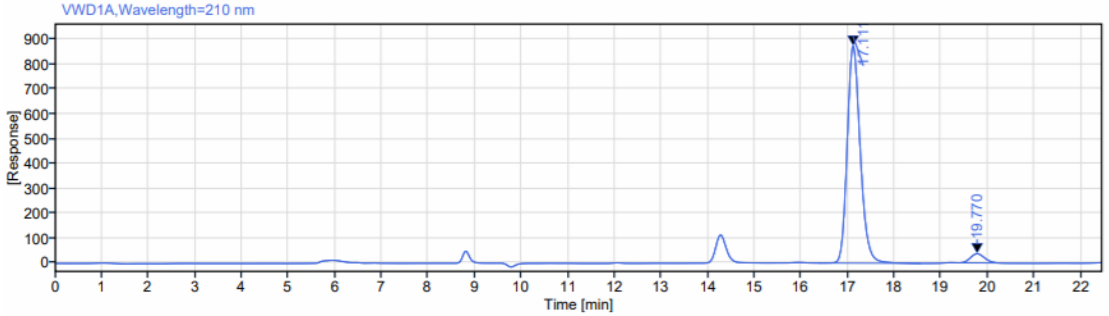
RT [min]	Type	Width [min]	Area	Height	Area%
21.843	MM m	5.22	14961.81	253.66	49.74
28.962	MM m	5.81	15121.09	218.57	50.26
		Sum	30082.90		



2q

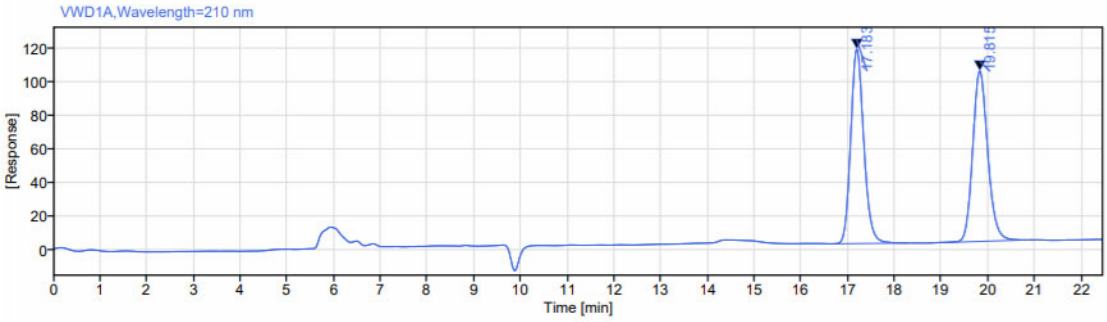
(91% ee)

Daicel Chiralpak AD-H column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 17.111 min (major enantiomer), 19.770 min (minor enantiomer).



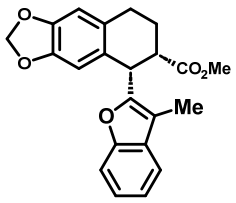
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
17.111	BB	2.19	16945.23	871.96	95.66
19.770	MM m	0.33	768.15	36.77	4.34
		Sum	17713.38		



Signal: VWD1A,Wavelength=210 nm

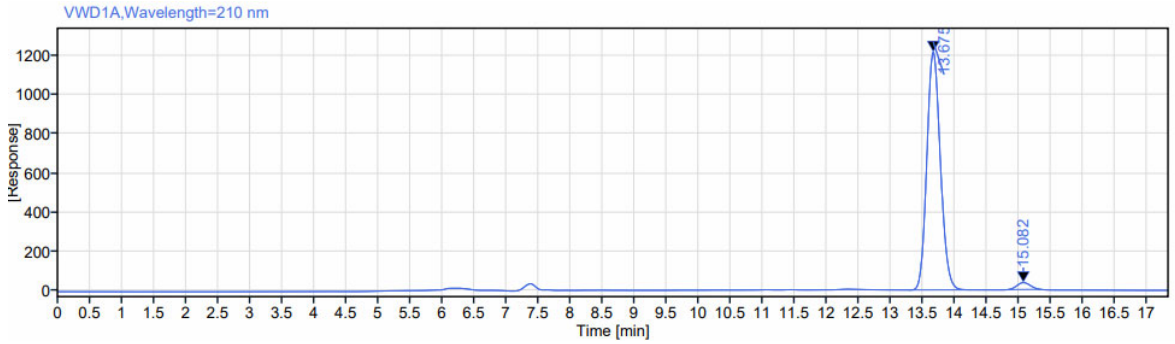
RT [min]	Type	Width [min]	Area	Height	Area%
17.183	BB	1.58	2249.48	115.64	49.74
19.815	BB	2.09	2272.59	101.48	50.26
		Sum	4522.06		



2r

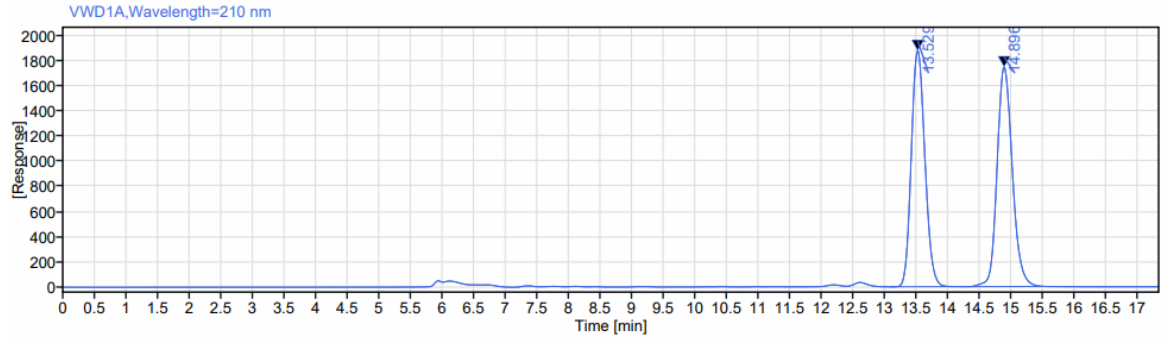
(95% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (90/10), 0.5 mL/min, 210 nm, 13.675 min (major enantiomer), 15.082 min (minor enantiomer).



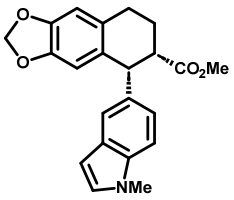
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
13.675	MM m	0.99	17802.02	1209.97	97.26
15.082	MM m	0.50	501.72	34.84	2.74
		Sum	18303.75		



Signal: VWD1A,Wavelength=210 nm

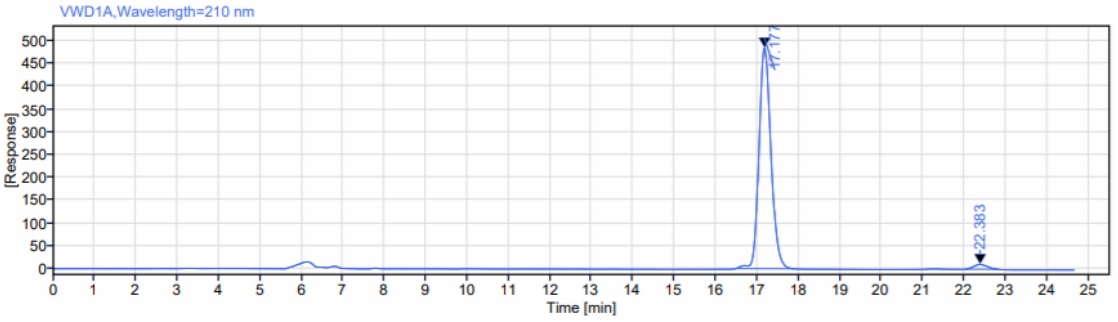
RT [min]	Type	Width [min]	Area	Height	Area%
13.529	MM m	1.01	28168.11	1882.55	48.94
14.896	MM m	1.21	29386.02	1751.45	51.06
		Sum	57554.13		



2s

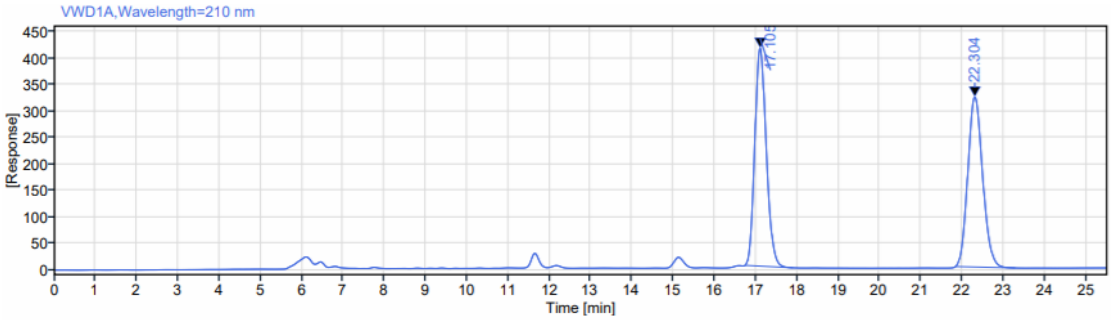
(95% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 17.177 min (major enantiomer), 22.383 min (minor enantiomer).



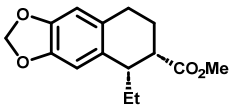
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
17.177	MM m	1.42	9760.07	483.88	97.64
22.383	MM m	0.78	236.22	10.36	2.36
		Sum	9996.29		



Signal: VWD1A,Wavelength=210 nm

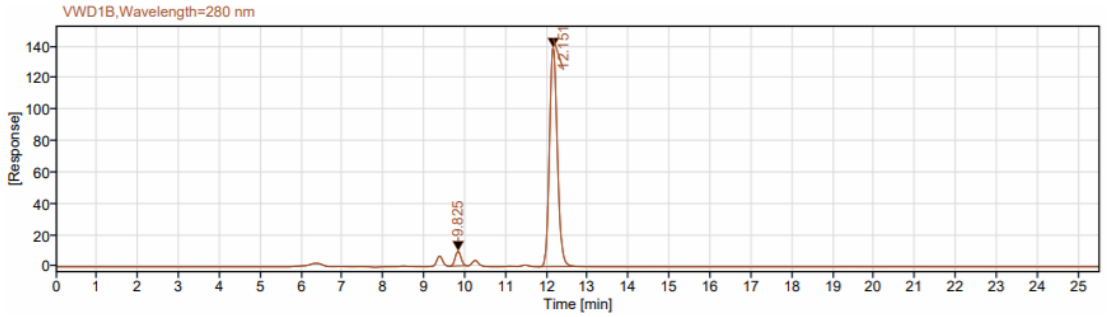
RT [min]	Type	Width [min]	Area	Height	Area%
17.105	BB	1.16	8009.81	412.47	49.85
22.304	BB	1.45	8058.47	321.75	50.15
		Sum	16068.29		



2t

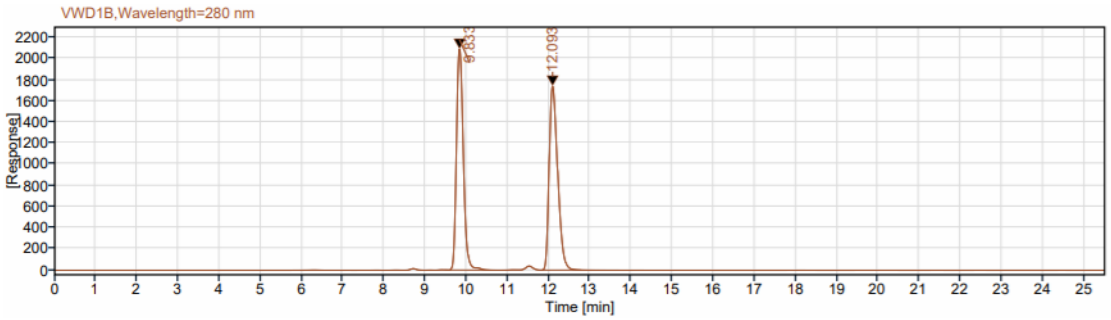
(91% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (90/10), 0.5 mL/min, 280 nm, 9.825 min (minor enantiomer), 12.151 min (major enantiomer).



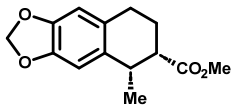
Signal: VWD1B,Wavelength=280 nm

RT [min]	Type	Width [min]	Area	Height	Area%
9.825	MM m	0.40	91.87	9.25	4.69
12.151	MM m	0.95	1865.01	139.08	95.31
		Sum	1956.88		



Signal: VWD1B,Wavelength=280 nm

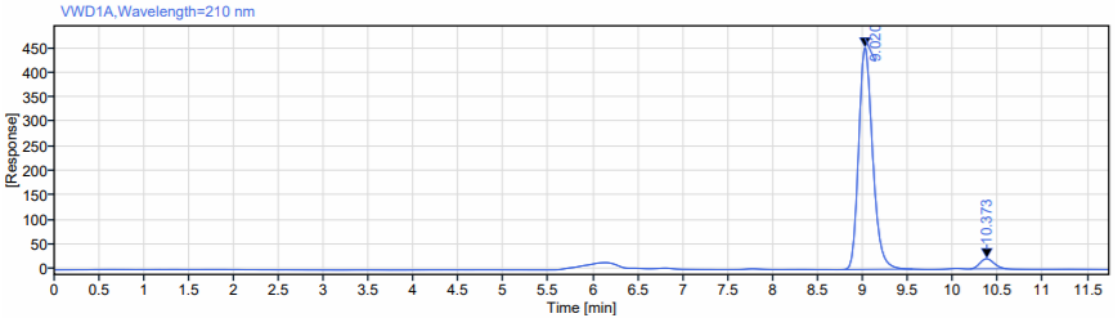
RT [min]	Type	Width [min]	Area	Height	Area%
9.833	MM m	1.08	24223.26	2087.60	49.22
12.093	MM m	0.96	24987.65	1738.67	50.78
		Sum	49210.91		



2u

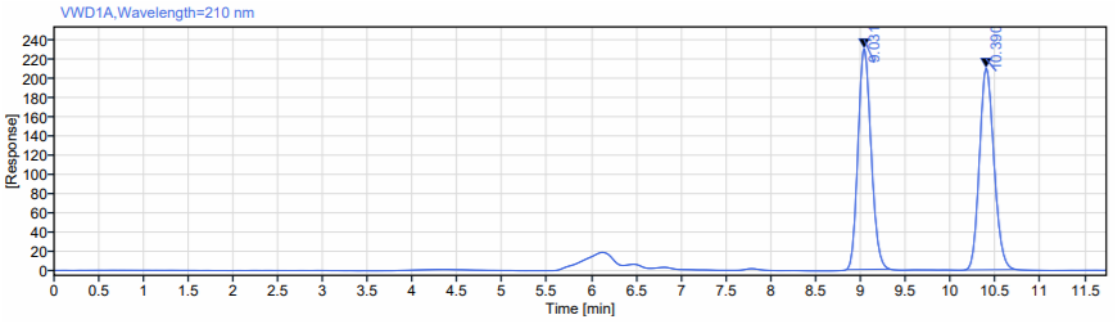
(91% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 9.020 min (major enantiomer), 10.373 min (minor enantiomer).



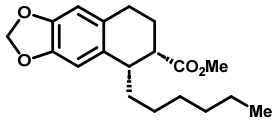
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
9.020	MM m	0.83	4909.17	450.40	95.64
10.373	MM m	0.41	223.96	20.66	4.36
		Sum	5133.13		



Signal: VWD1A,Wavelength=210 nm

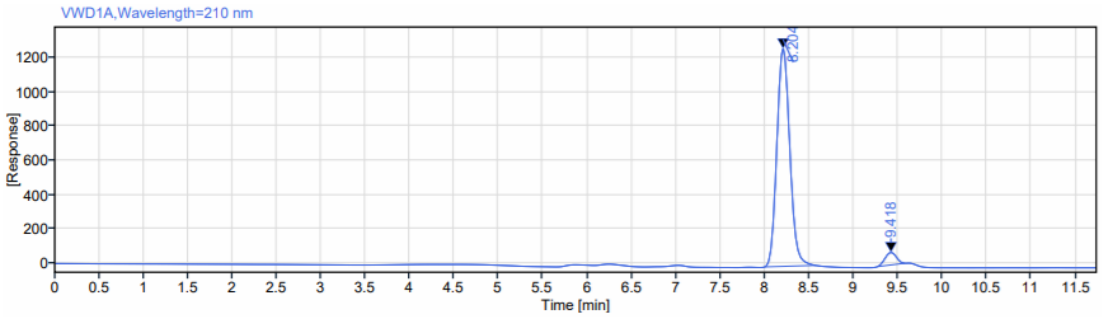
RT [min]	Type	Width [min]	Area	Height	Area%
9.031	MM m	0.49	2338.04	229.94	49.58
10.390	MM m	0.57	2377.59	209.91	50.42
		Sum	4715.63		



2v

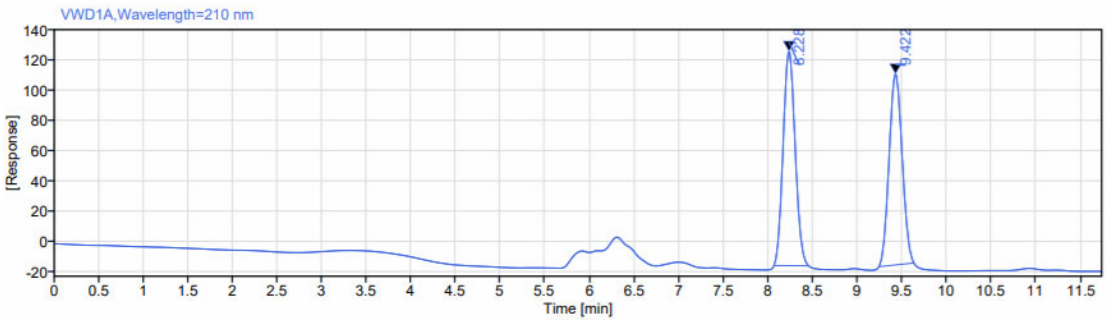
(90% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 8.204 min (major enantiomer), 9.418 min (minor enantiomer).



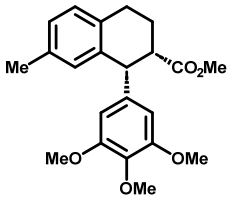
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
8.204	MM m	0.16	12871.55	1270.00	95.25
9.418	MM m	0.14	641.60	72.46	4.75
		Sum	13513.15		



Signal: VWD1A,Wavelength=210 nm

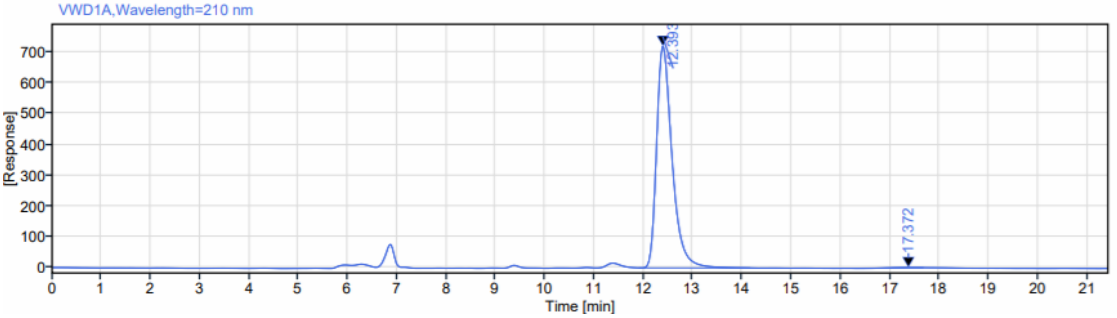
RT [min]	Type	Width [min]	Area	Height	Area%
8.228	MM m	0.15	1322.88	141.37	50.84
9.422	MM m	0.16	1279.29	125.94	49.16
		Sum	2602.17		



2w

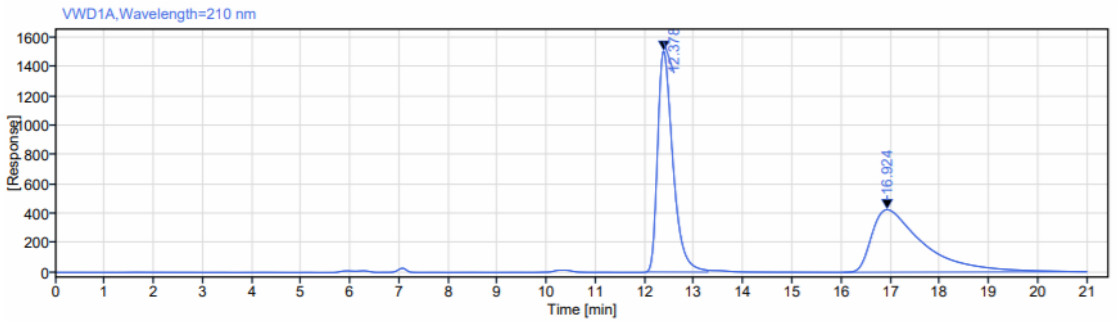
(> 99% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.393 min (major enantiomer), 17.372 min (minor enantiomer).



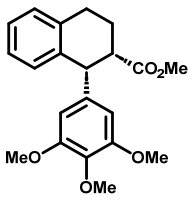
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.393	MM m	2.26	15809.90	722.95	99.96
17.372	MM m	1.44	6.84	0.75	0.04
		Sum	15816.74		



Signal: VWD1A,Wavelength=210 nm

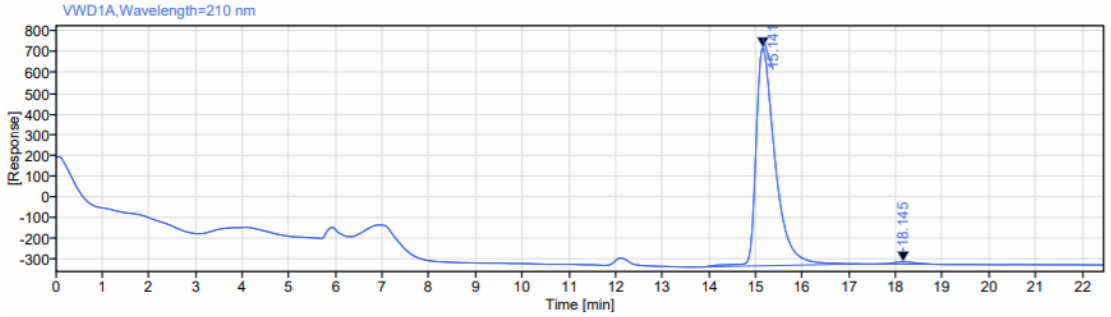
RT [min]	Type	Width [min]	Area	Height	Area%
12.378	MM m	1.25	32505.28	1503.72	51.12
16.924	MM m	4.95	31079.87	425.99	48.88
		Sum	63585.15		



2x

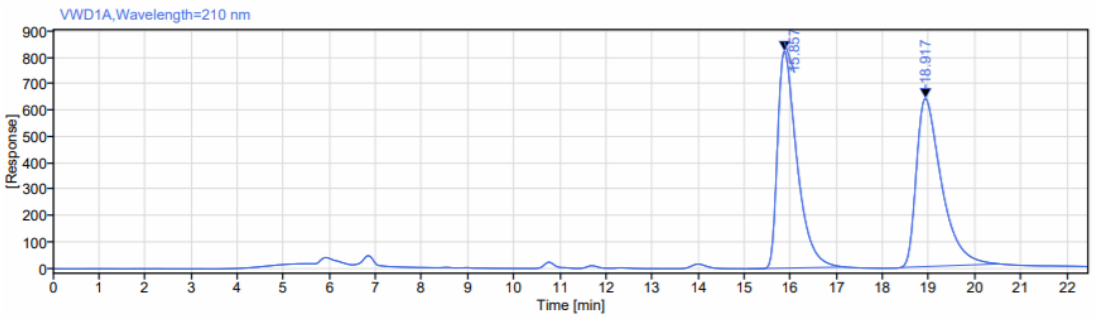
(98% ee)

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 15.141 min (major enantiomer), 18.145 min (minor enantiomer).



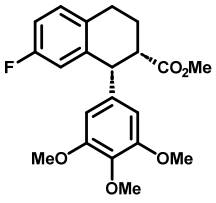
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
15.141	BB	3.38	29875.30	1053.20	98.76
18.145	MM m	0.54	375.45	10.58	1.24
		Sum	30250.75		



Signal: VWD1A,Wavelength=210 nm

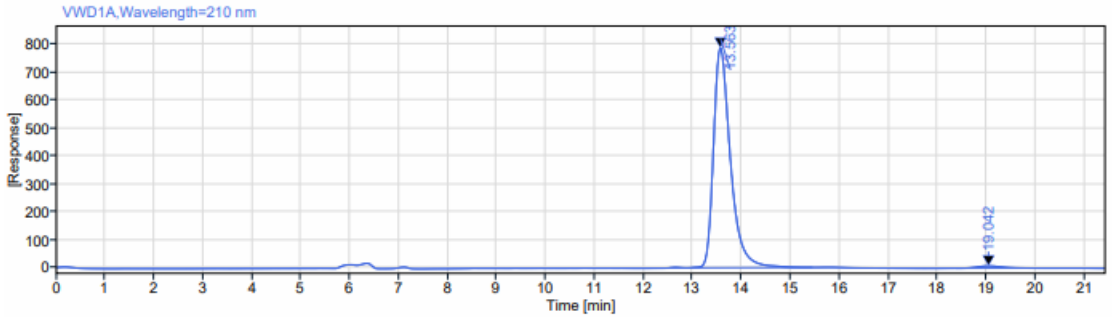
RT [min]	Type	Width [min]	Area	Height	Area%
15.857	MM m	2.11	24049.24	823.31	49.86
18.917	BB	2.14	24185.12	637.75	50.14
		Sum	48234.36		



2y

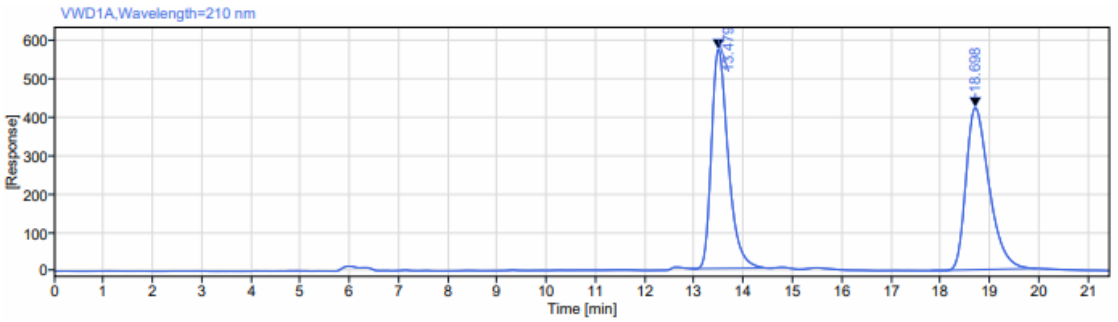
(97% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 13.563 min (major enantiomer), 19.042 min (minor enantiomer).



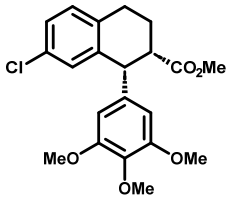
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
13.563	MM m	2.92	18952.66	785.04	98.63
19.042	MM m	1.52	262.57	7.89	1.37
		Sum	19215.23		



Signal: VWD1A,Wavelength=210 nm

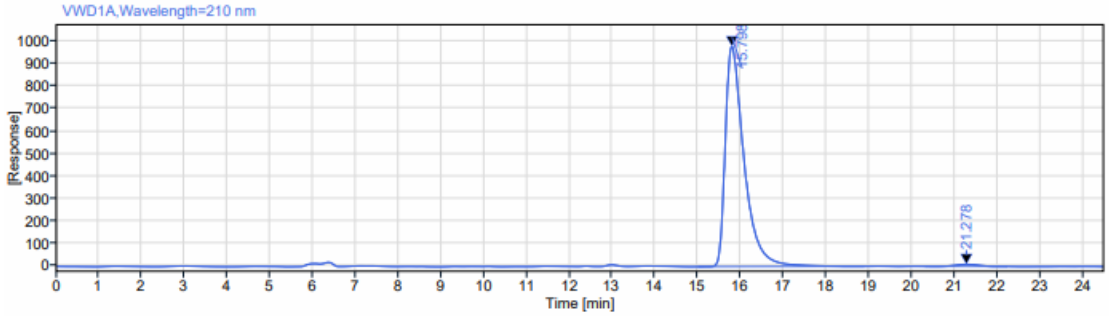
RT [min]	Type	Width [min]	Area	Height	Area%
13.479	MM m	1.72	13451.44	569.53	49.40
18.698	MM m	2.14	13776.18	421.78	50.60
		Sum	27227.62		



2z

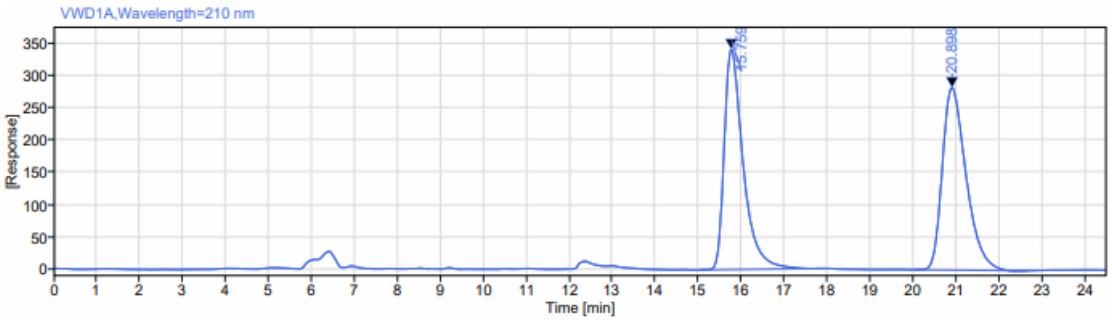
(98% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 15.798 min (major enantiomer), 21.278 min (minor enantiomer).



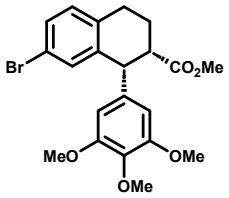
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
15.798	MM m	3.89	29932.79	978.07	98.92
21.278	MM m	1.92	326.30	9.06	1.08
		Sum	30259.09		



Signal: VWD1A,Wavelength=210 nm

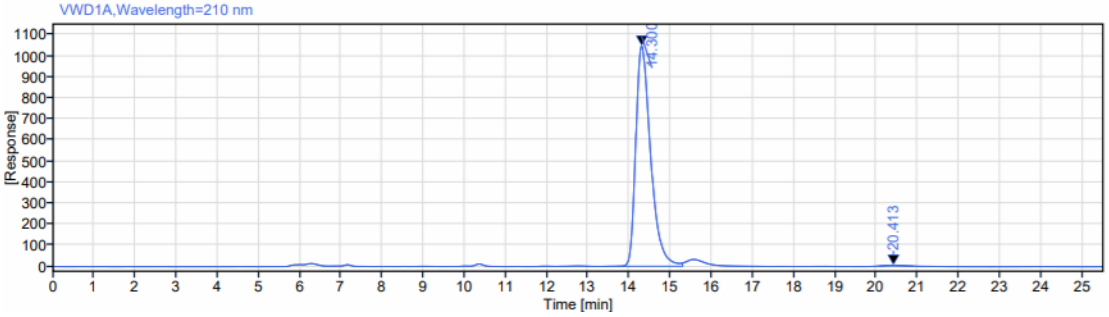
RT [min]	Type	Width [min]	Area	Height	Area%
15.759	MM m	2.83	10498.31	342.22	49.11
20.898	MM m	2.63	10879.62	283.41	50.89
		Sum	21377.93		



2a'

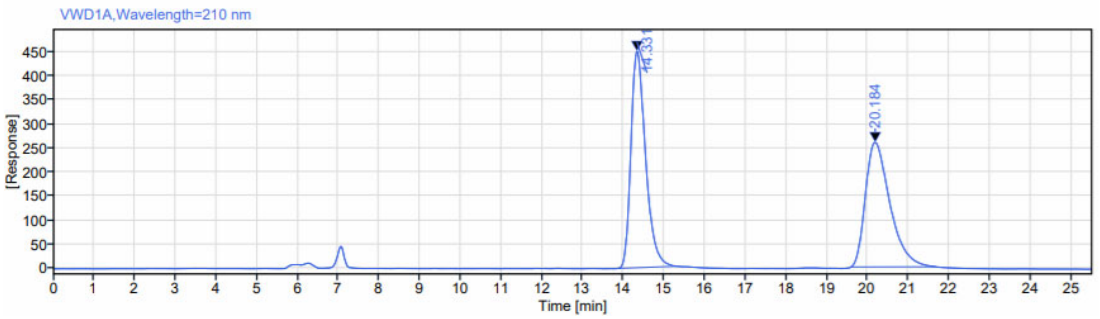
(99% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 14.300 min (major enantiomer), 20.413 min (minor enantiomer).



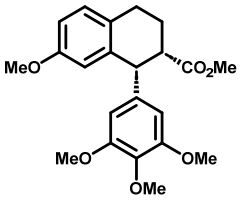
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
14.300	MM m	1.60	26320.66	1046.61	99.56
20.413	MM m	0.82	116.10	4.03	0.44
		Sum	26436.76		



Signal: VWD1A,Wavelength=210 nm

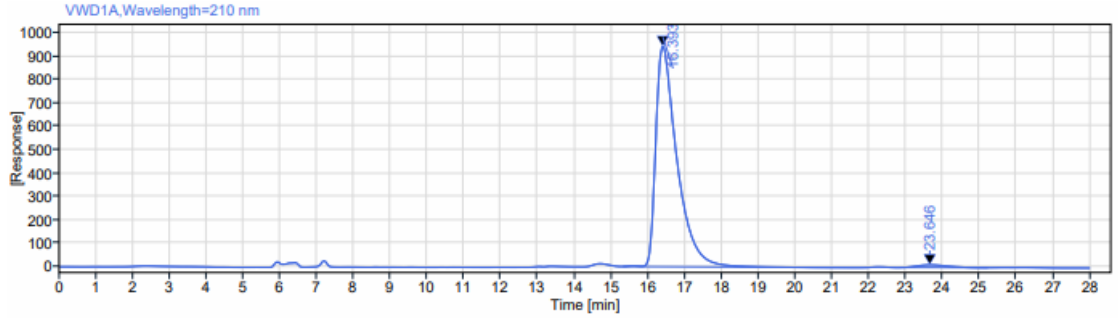
RT [min]	Type	Width [min]	Area	Height	Area%
14.331	MM m	1.57	11227.67	449.29	50.98
20.184	BB	2.07	10797.16	258.41	49.02
		Sum	22024.83		



2b'

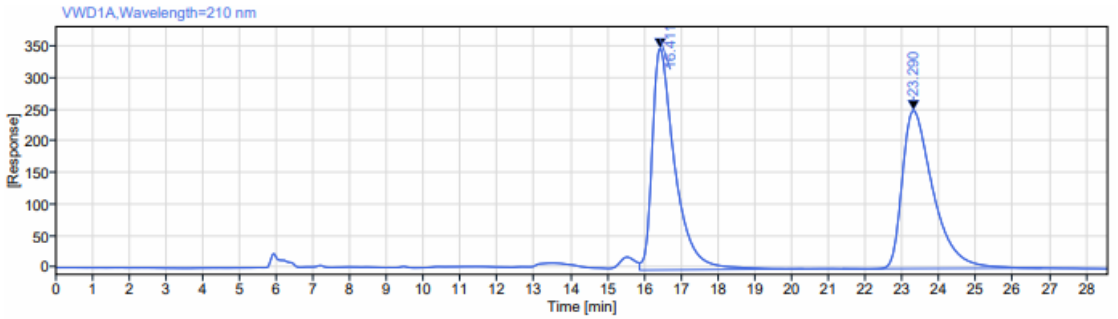
(97% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 16.393 min (major enantiomer), 23.646 min (minor enantiomer).



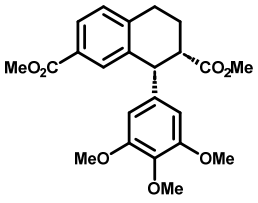
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
16.393	MM m	4.61	37797.87	941.98	98.35
23.646	MM m	2.30	632.52	11.36	1.65
		Sum	38430.39		



Signal: VWD1A,Wavelength=210 nm

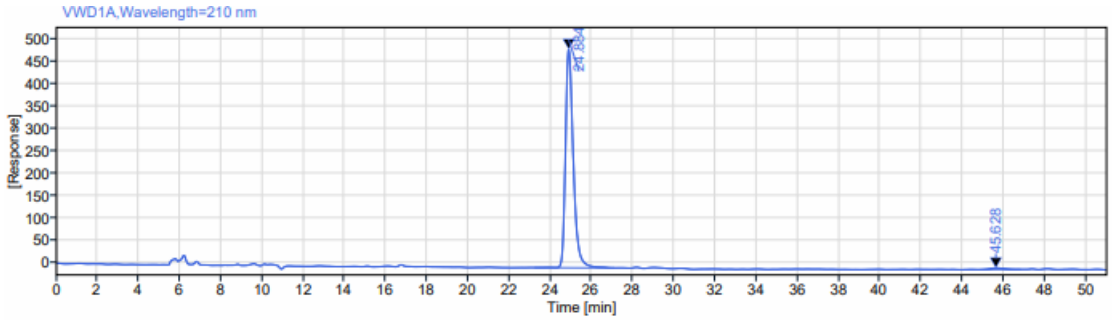
RT [min]	Type	Width [min]	Area	Height	Area%
16.411	MM m	4.45	14947.08	350.37	50.72
23.290	MM m	5.42	14522.96	250.06	49.28
		Sum	29470.04		



2c'

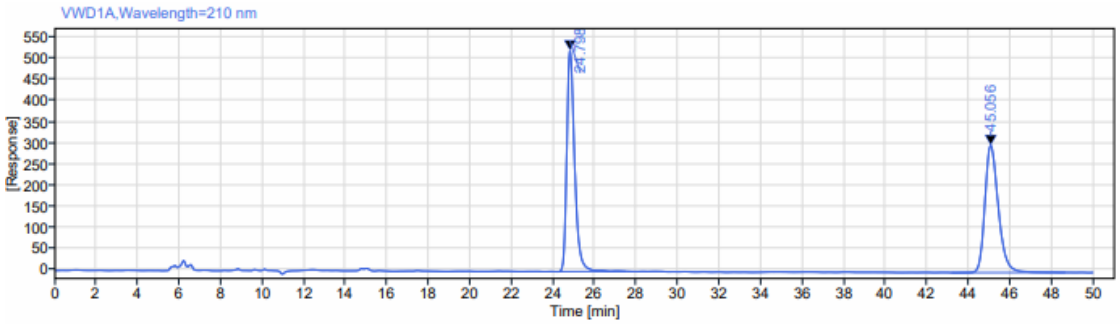
(98% ee)

Daicel Chiralpak IA-3 column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 24.884 min (major enantiomer), 45.628 min (minor enantiomer).



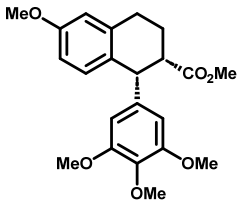
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
24.884	MM m	3.87	12836.44	486.26	98.80
45.628	MM m	2.78	156.41	3.39	1.20
		Sum	12992.85		



Signal: VWD1A,Wavelength=210 nm

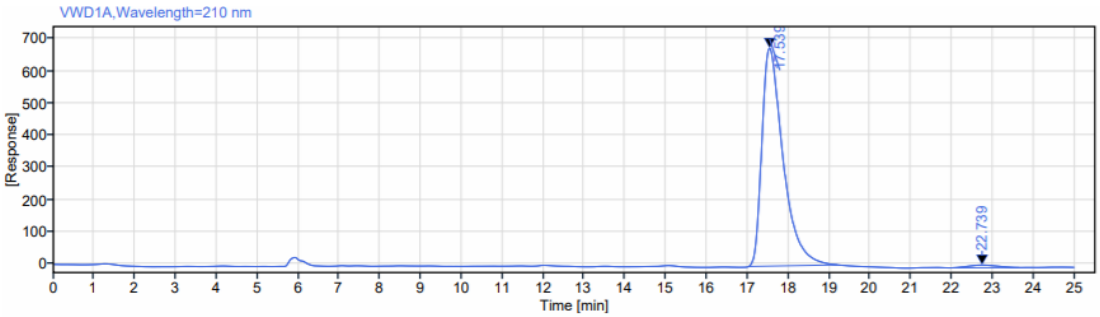
RT [min]	Type	Width [min]	Area	Height	Area%
24.798	MM m	3.96	13678.09	521.32	50.31
45.056	MM m	5.47	13512.09	300.14	49.69
		Sum	27190.18		



2d'

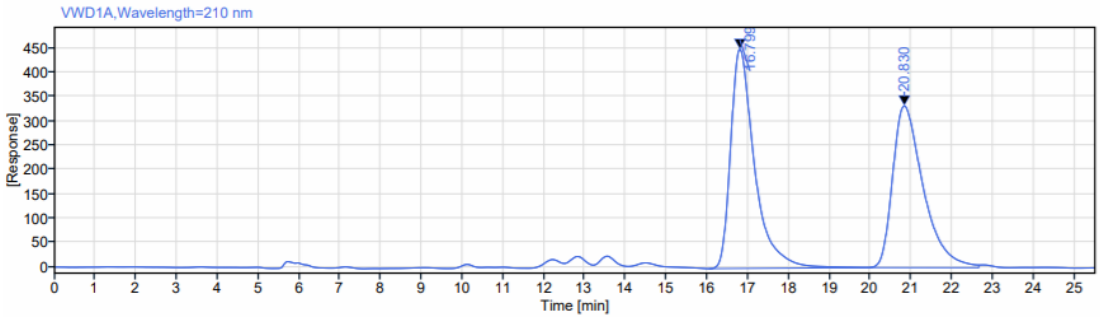
(98% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 17.539 min (major enantiomer), 22.739 min (minor enantiomer).



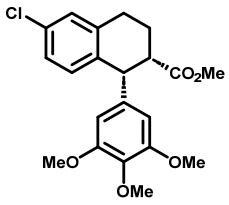
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
17.539	BB	2.17	24465.48	676.57	98.43
22.739	MM m	1.60	389.39	8.04	1.57
		Sum	24854.87		



Signal: VWD1A,Wavelength=210 nm

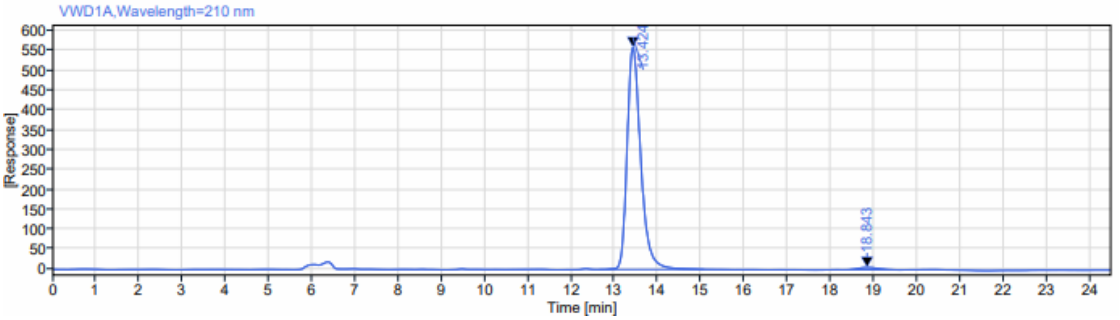
RT [min]	Type	Width [min]	Area	Height	Area%
16.799	BB	3.86	18386.70	450.20	51.53
20.830	BV	2.76	17294.41	332.14	48.47
		Sum	35681.11		



2e'

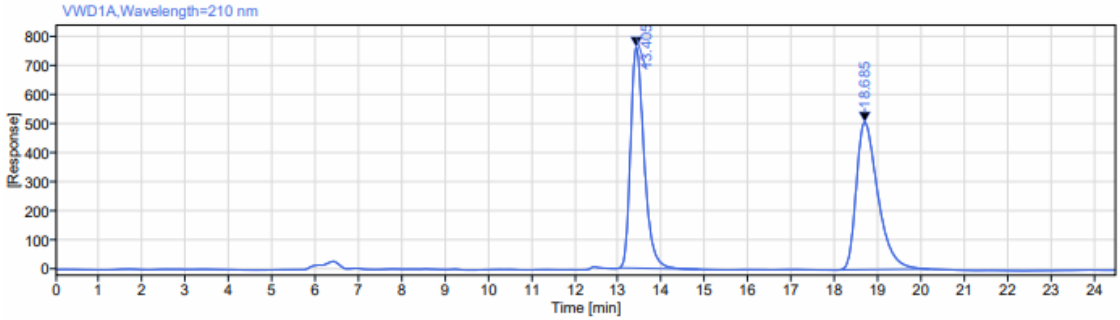
(97% ee)

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 13.424 min (major enantiomer), 18.843 min (minor enantiomer).



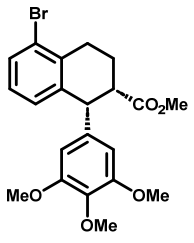
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
13.424	MM m	2.43	12303.03	559.79	98.47
18.843	MM m	1.51	190.96	5.88	1.53
		Sum	12493.99		



Signal: VWD1A,Wavelength=210 nm

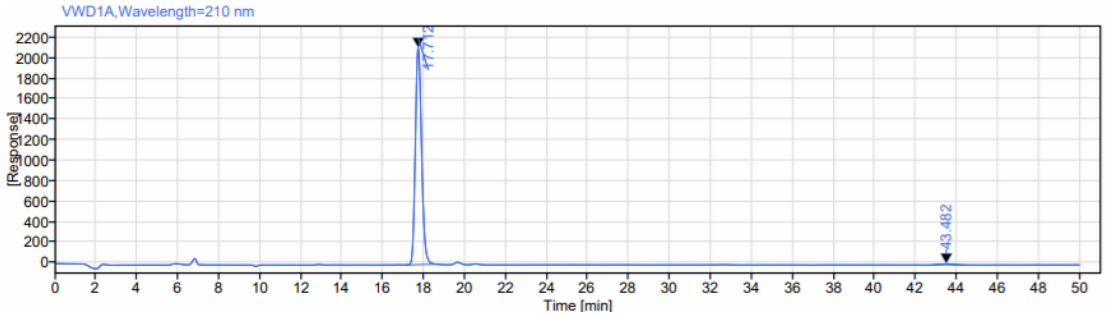
RT [min]	Type	Width [min]	Area	Height	Area%
13.405	MM m	1.82	16551.62	761.69	48.38
18.685	MM m	2.18	17663.11	508.46	51.62
		Sum	34214.73		



2f'

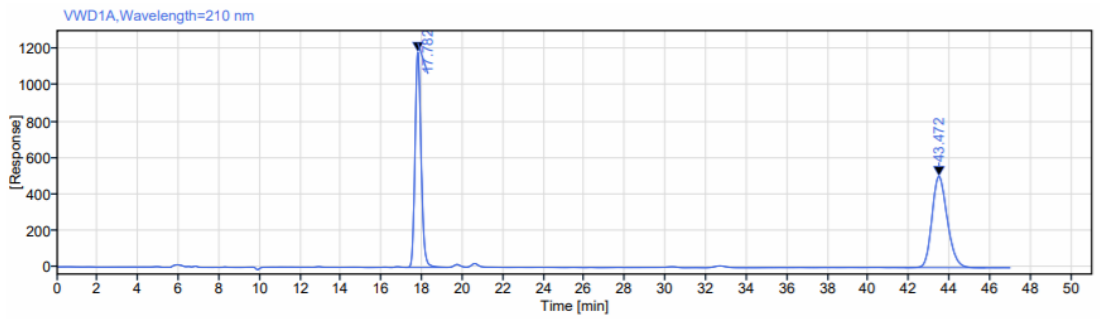
(98% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 17.712 min (major enantiomer), 43.482 min (minor enantiomer).



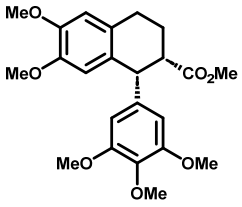
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
17.712	VM m	0.33	44832.48	2115.66	99.11
43.482	MM m	0.65	402.69	9.25	0.89
		Sum	45235.18		



Signal: VWD1A,Wavelength=210 nm

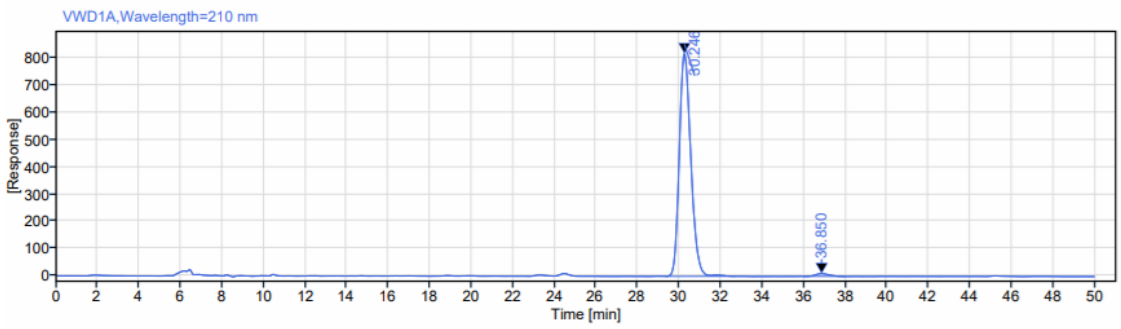
RT [min]	Type	Width [min]	Area	Height	Area%
17.782	VV	2.10	24788.39	1185.55	48.46
43.472	BB	3.97	26360.70	502.06	51.54
		Sum	51149.10		



2g'

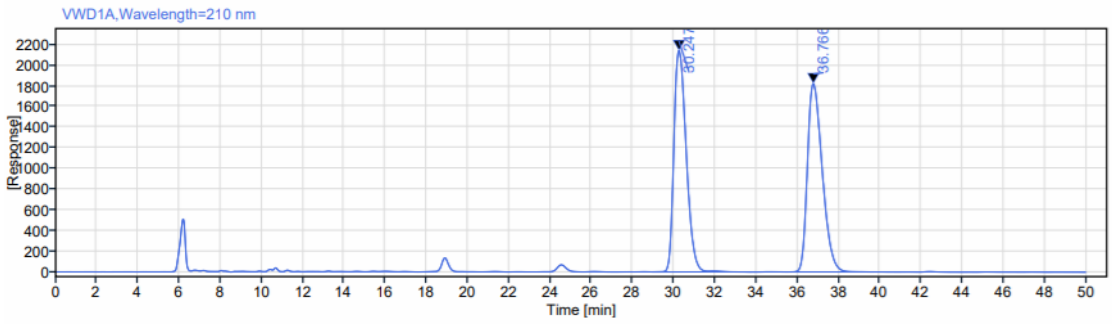
(97% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 30.246 min (major enantiomer), 36.850 min (minor enantiomer).



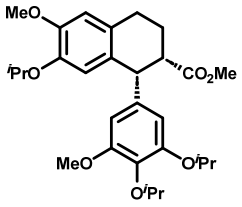
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
30.246	VM m	0.60	31625.20	819.14	98.57
36.850	MM m	0.69	457.63	10.16	1.43
		Sum	32082.83		



Signal: VWD1A,Wavelength=210 nm

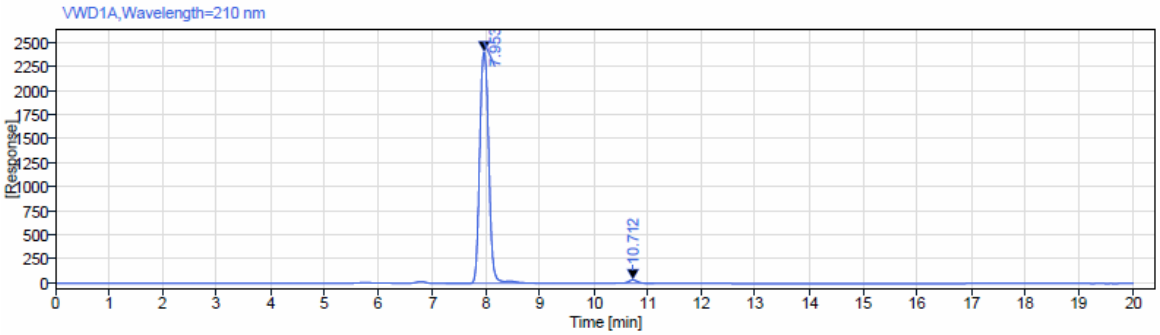
RT [min]	Type	Width [min]	Area	Height	Area%
30.247	VM m	0.65	89542.08	2146.04	49.50
36.766	BB	4.23	91334.59	1826.38	50.50
		Sum	180876.67		



2h'

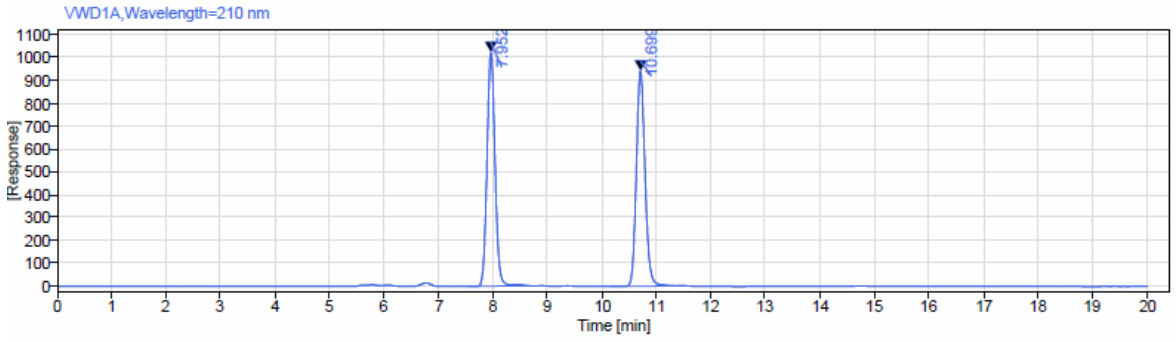
(97% ee)

Daicel Chiralpak IC-3 column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 7.953 min (major enantiomer), 10.712 min (minor enantiomer).



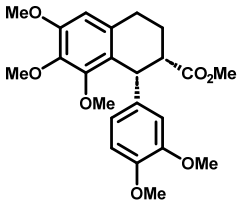
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
7.953	MM m	1.67	28115.90	2403.90	98.65
10.712	MM m	0.72	385.96	34.06	1.35
		Sum	28501.87		



Signal: VWD1A,Wavelength=210 nm

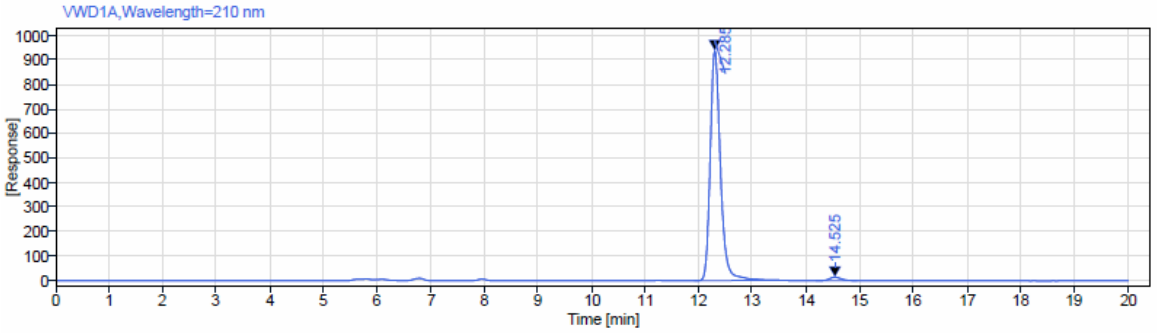
RT [min]	Type	Width [min]	Area	Height	Area%
7.952	MM m	1.15	10428.85	1022.52	50.03
10.699	MM m	1.45	10416.57	941.24	49.97
		Sum	20845.41		



2i'

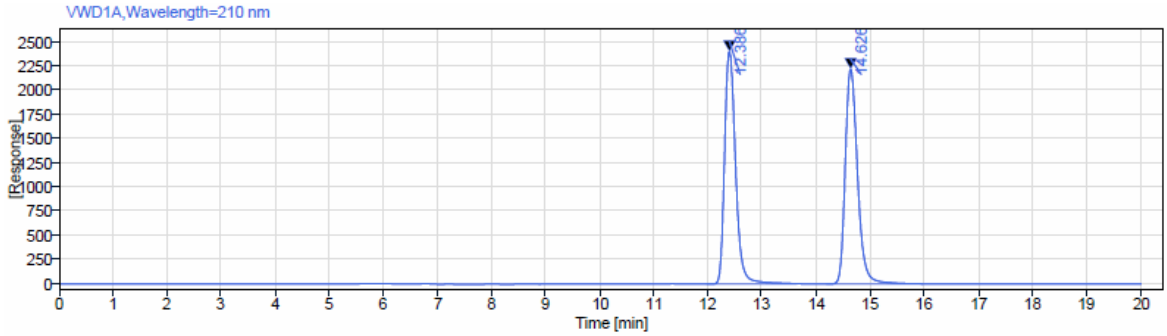
(97% ee)

Daicel Chiralpak IC-3 column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.285 min (major enantiomer), 14.525 min (minor enantiomer).



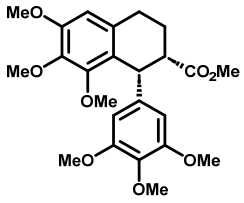
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.285	MM m	1.62	12491.37	940.25	98.34
14.525	MM m	0.77	210.96	14.34	1.66
		Sum	12702.32		



Signal: VWD1A,Wavelength=210 nm

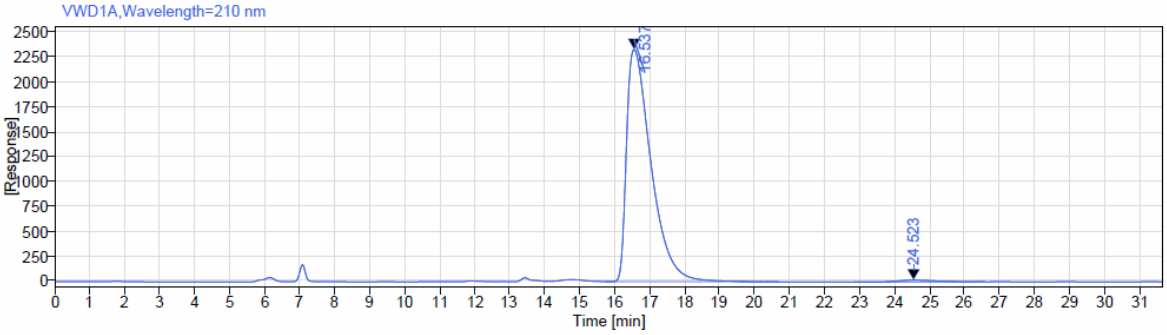
RT [min]	Type	Width [min]	Area	Height	Area%
12.386	MM m	1.74	34042.88	2401.54	49.23
14.626	MM m	1.78	35109.19	2220.51	50.77
		Sum	69152.07		



2j'

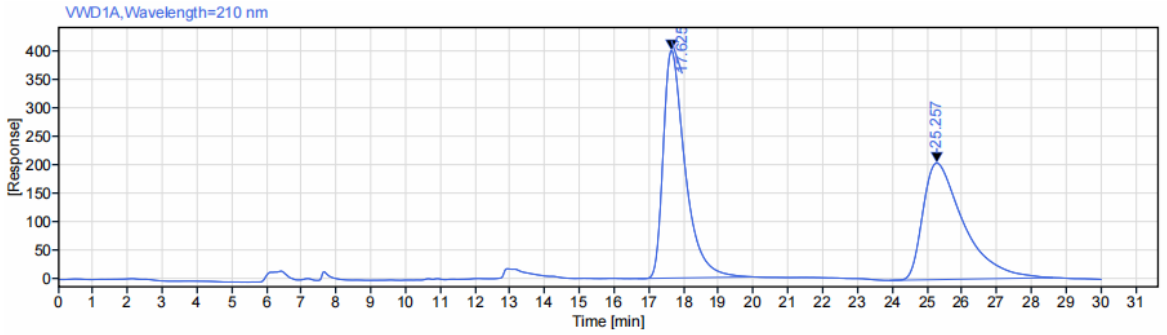
(98% ee)

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 16.537 min (major enantiomer), 24.523 min (minor enantiomer).



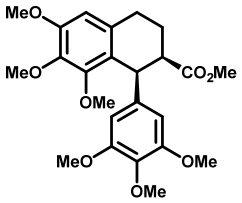
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
16.537	MM m	4.98	113630.51	2331.95	98.82
24.523	MM m	3.74	1360.24	17.32	1.18
		Sum	114990.75		



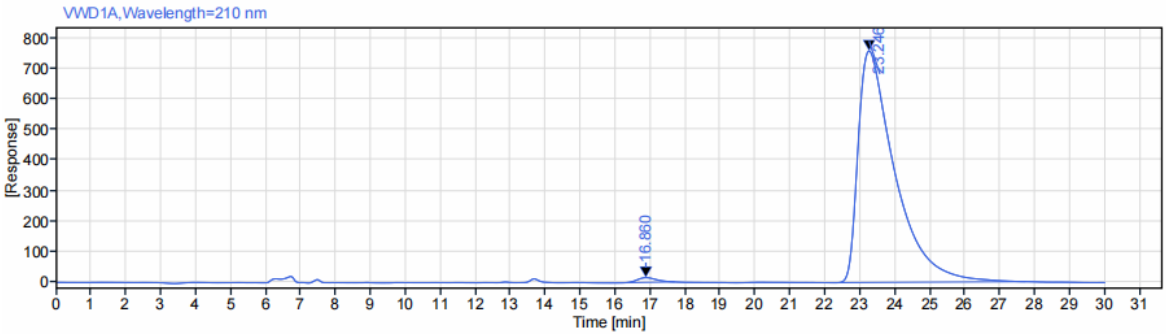
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
17.625	MM m	3.32	17505.49	400.28	51.25
25.257	MM m	4.70	16648.99	205.11	48.75
		Sum	34154.48		



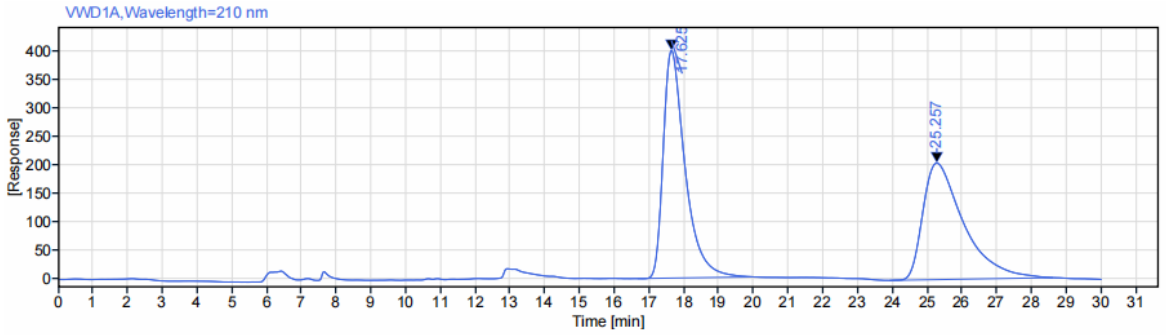
ent-**2j'**
(98% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 23.246 min (major enantiomer), 16.860 min (minor enantiomer).



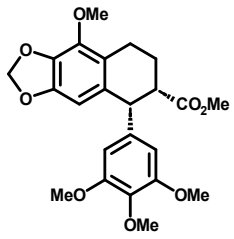
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
16.860	MM m	1.45	591.69	15.52	1.06
23.246	MM m	5.38	55258.87	757.19	98.94
		Sum	55850.56		



Signal: VWD1A,Wavelength=210 nm

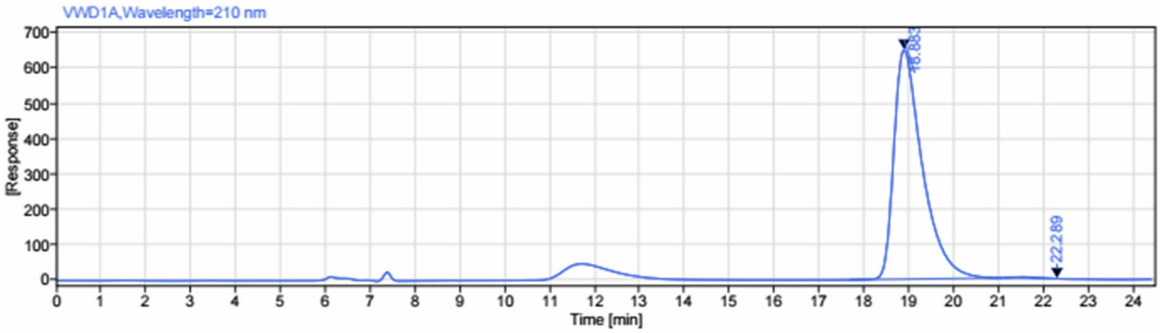
RT [min]	Type	Width [min]	Area	Height	Area%
17.625	MM m	3.32	17505.49	400.28	51.25
25.257	MM m	4.70	16648.99	205.11	48.75
		Sum	34154.48		



2k'

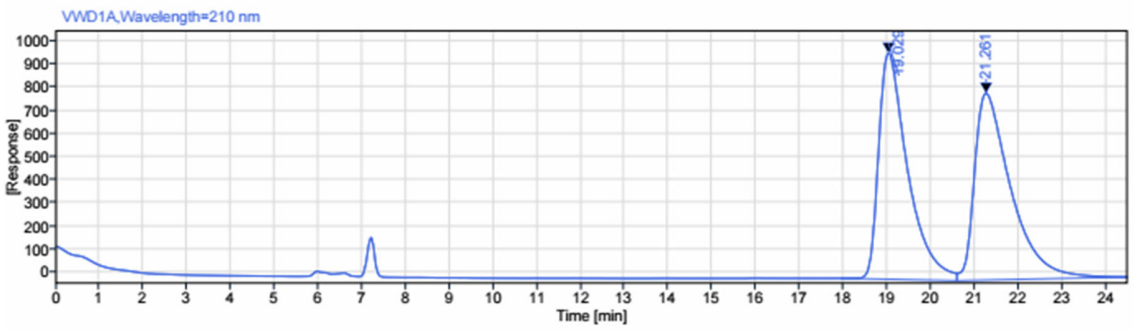
(99% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 18.883 min (major enantiomer), 22.289 min (minor enantiomer).



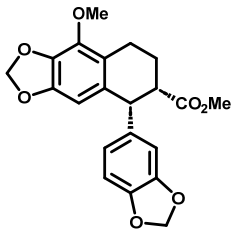
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
18.883	MM m	3.39	28619.76	649.67	99.57
22.289	MM n	1.18	123.80	0.01	0.43
		Sum	28743.56		



Signal: VWD1A,Wavelength=210 nm

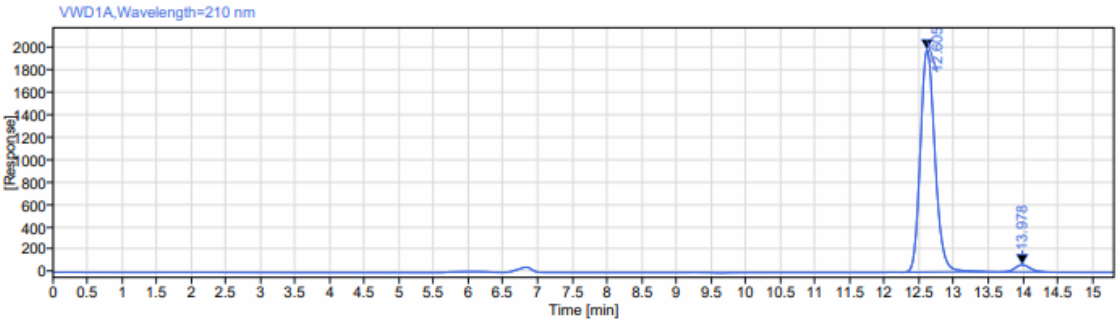
RT [min]	Type	Width [min]	Area	Height	Area%
19.029	MM m	2.66	45082.25	975.38	49.16
21.261	MM m	3.98	46619.25	805.77	50.84
		Sum	91701.50		



2l'

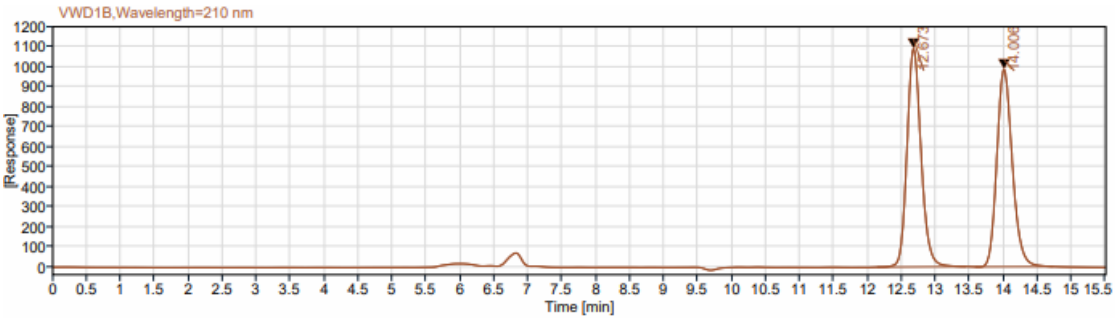
(94% ee)

Daicel Chiralpak OD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 12.605 min (major enantiomer), 13.978 min (minor enantiomer).



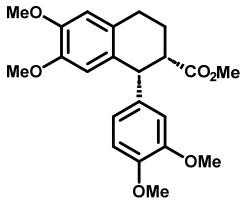
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.605	MM m	1.18	28924.19	1979.99	96.80
13.978	MM m	0.63	954.70	63.78	3.20
		Sum	29878.89		



Signal: VWD1B,Wavelength=210 nm

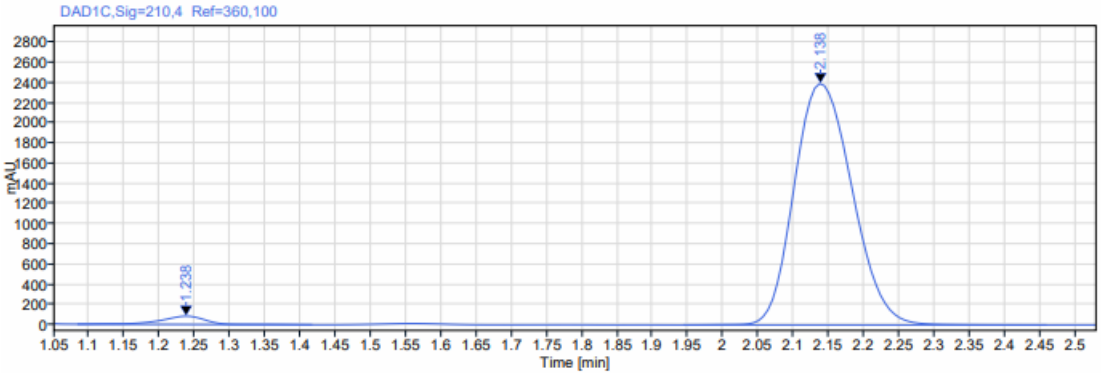
RT [min]	Type	Width [min]	Area	Height	Area%
12.673	MM m	1.31	15754.91	1092.30	50.14
14.006	MM m	1.15	15668.90	987.88	49.86
		Sum	31423.81		



2m'

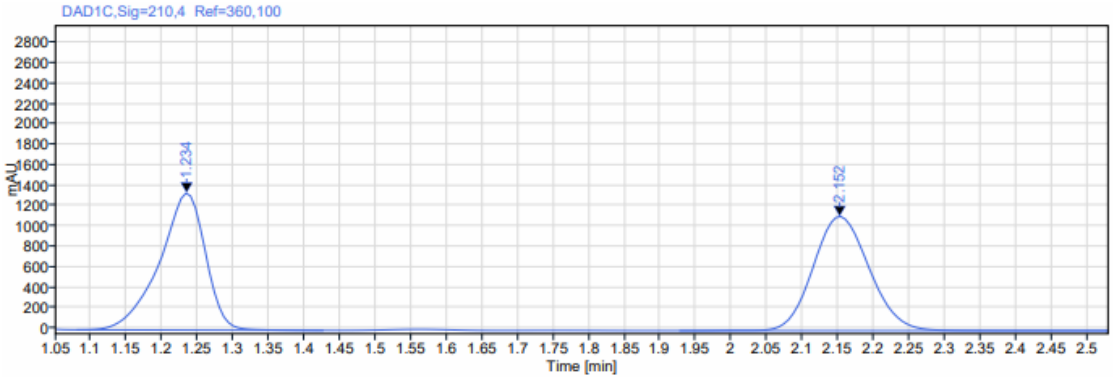
(95% ee)

The enantiomeric excess was determined by SFC analysis by means of OJ-3 column: MeOH/CO_2 (10/90), 1.0 mL/min, 254 nm, 2.138 min (major enantiomer), 1.238 min (minor enantiomer).



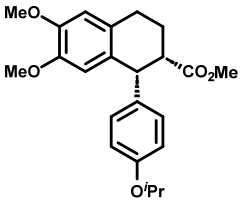
Signal: DAD1C,Sig=210,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
1.238	BB	0.33	365.42	82.61	2.60
2.138	BV	0.52	13696.54	2395.63	97.40
		Sum	14061.96		



Signal: DAD1C,Sig=210,4 Ref=360,100

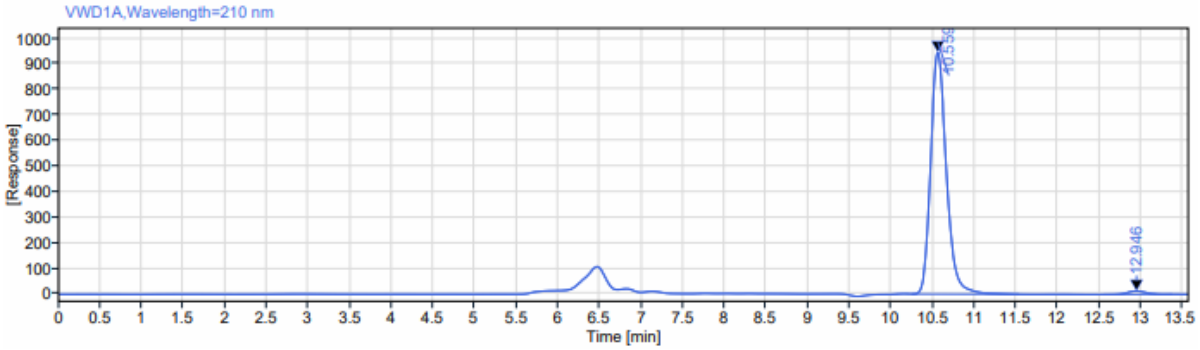
RT [min]	Type	Width [min]	Area	Height	Area%
1.234	BB	0.35	6039.42	1345.97	49.55
2.152	BB	0.74	6148.98	1122.43	50.45
		Sum	12188.40		



2n'

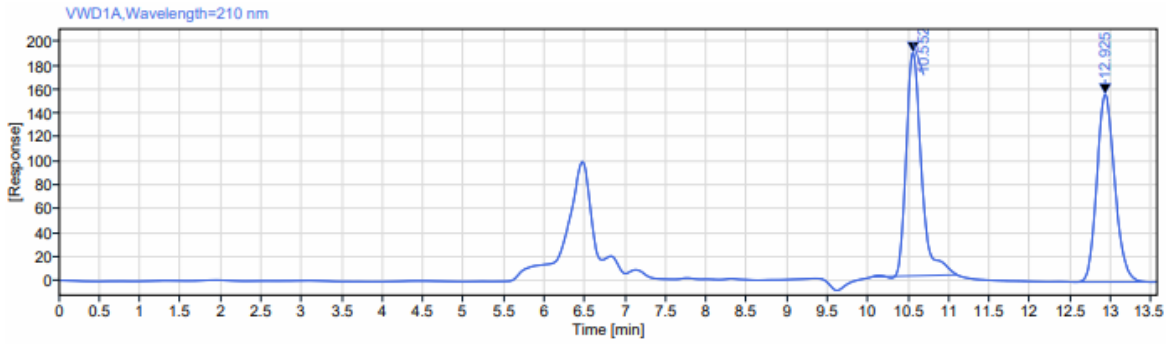
(97% ee)

Daicel Chiralpak AD-H column: n-hexane/i-PrOH (80/20), 0.5 mL/min, 210 nm, 10.559 min (major enantiomer), 12.946 min (minor enantiomer).



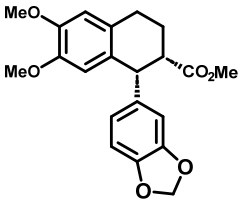
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
10.559	MM m	1.29	12433.02	944.67	98.48
12.946	MM m	0.82	192.18	13.14	1.52
		Sum	12625.20		



Signal: VWD1A,Wavelength=210 nm

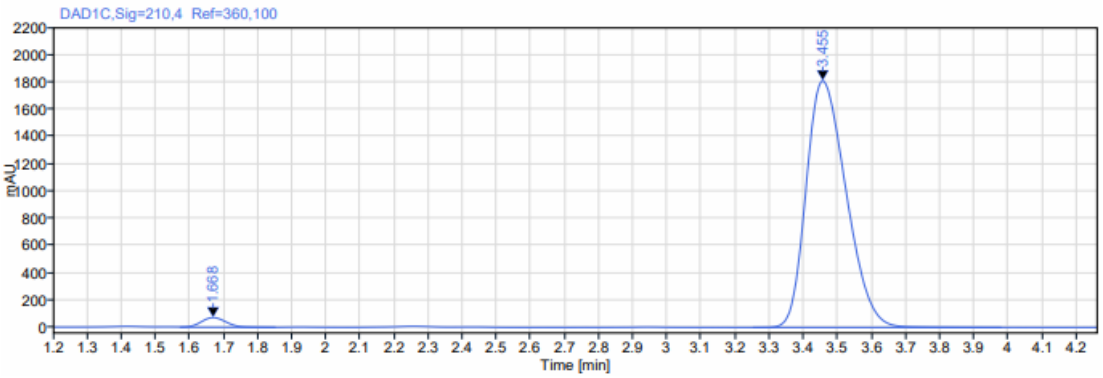
RT [min]	Type	Width [min]	Area	Height	Area%
10.552	MM m	1.05	2455.52	186.65	50.41
12.925	MM m	0.91	2415.63	156.87	49.59
		Sum	4871.15		



2o'

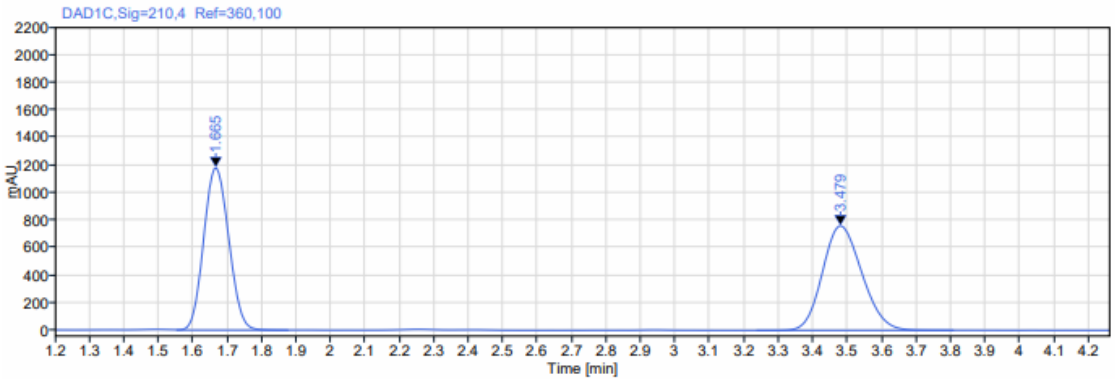
(95% ee)

The enantiomeric excess was determined by SFC analysis by means of OJ-3 column: MeOH/CO_2 = 10:90, 1.0 mL/min, 254 nm, 3.455 min (major enantiomer), 1.668 min (minor enantiomer).



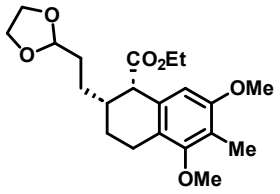
Signal: DAD1C,Sig=210,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
1.668	VB	0.28	357.66	71.08	2.37
3.455	BV	0.73	14752.28	1812.02	97.63
		Sum	15109.93		



Signal: DAD1C,Sig=210,4 Ref=360,100

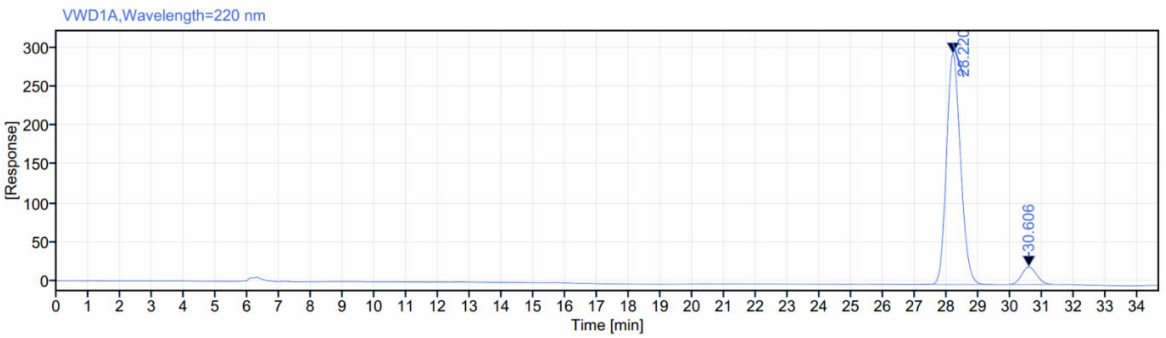
RT [min]	Type	Width [min]	Area	Height	Area%
1.665	VV	0.32	5950.60	1180.38	49.66
3.479	BV	0.57	6032.05	759.55	50.34
		Sum	11982.65		



74

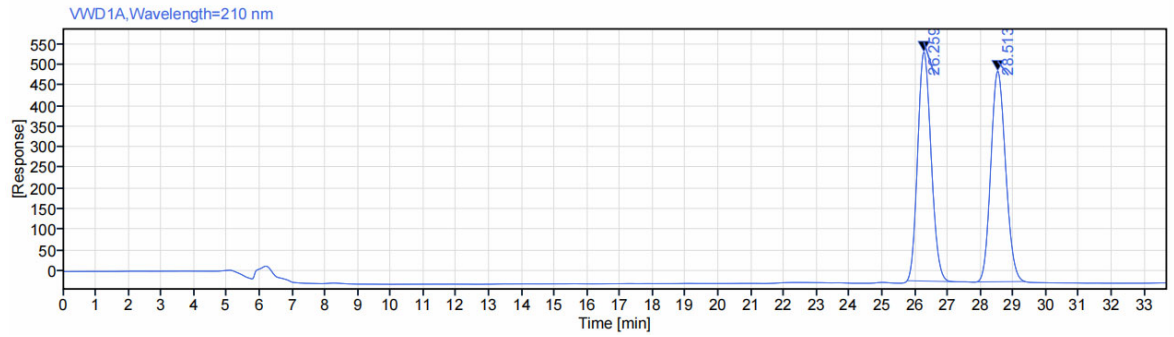
(85% ee)

Chiralpak IG-3 column (250*4.6 mm/3μm): *n*-hexane/*i*-PrOH (90/10), 0.5 mL/min, 210 nm, 28.220 min (major enantiomer), 30.606 min (minor enantiomer).



Signal: VWD1A,Wavelength=220 nm

RT [min]	Type	Width [min]	Area	Height	Area%
28.220	MM m	2.31	9149.20	297.79	92.52
30.606	MM m	1.43	739.25	22.59	7.48
		Sum	9888.46		



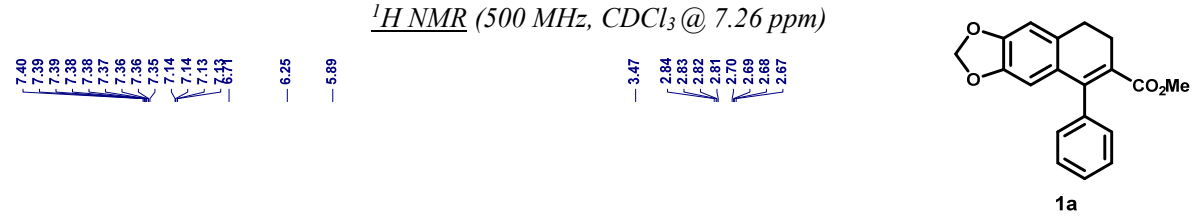
Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%
26.259	MM m	1.95	15807.57	553.54	49.78
28.513	MM m	1.64	15950.28	509.05	50.22
		Sum	31757.85		

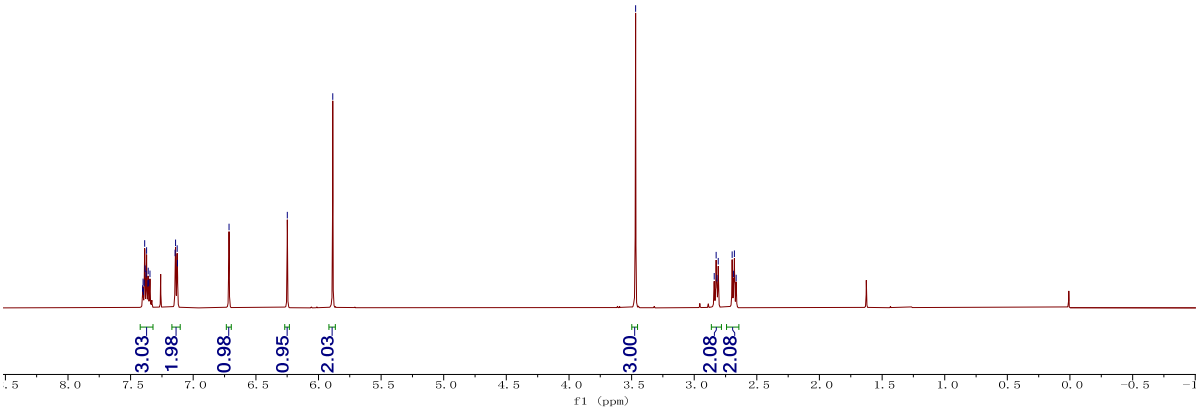
8. NMR Spectra

1a: Methyl 5-phenyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

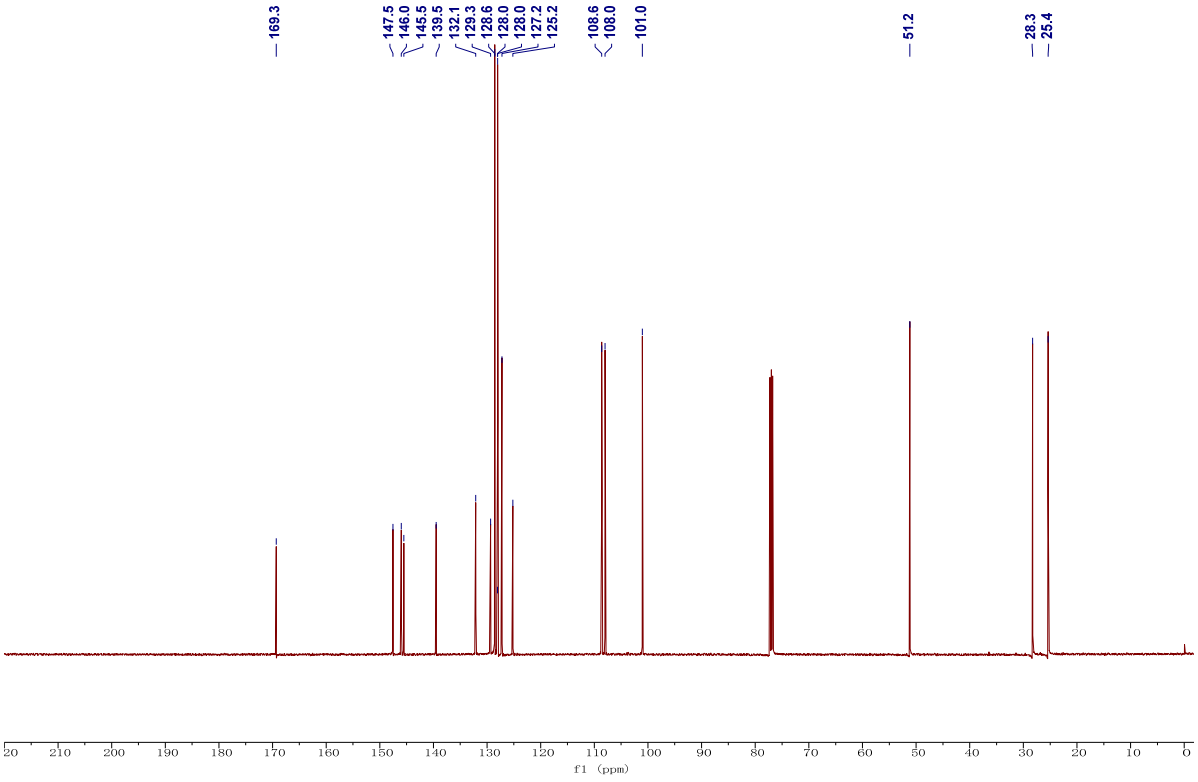
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



1a

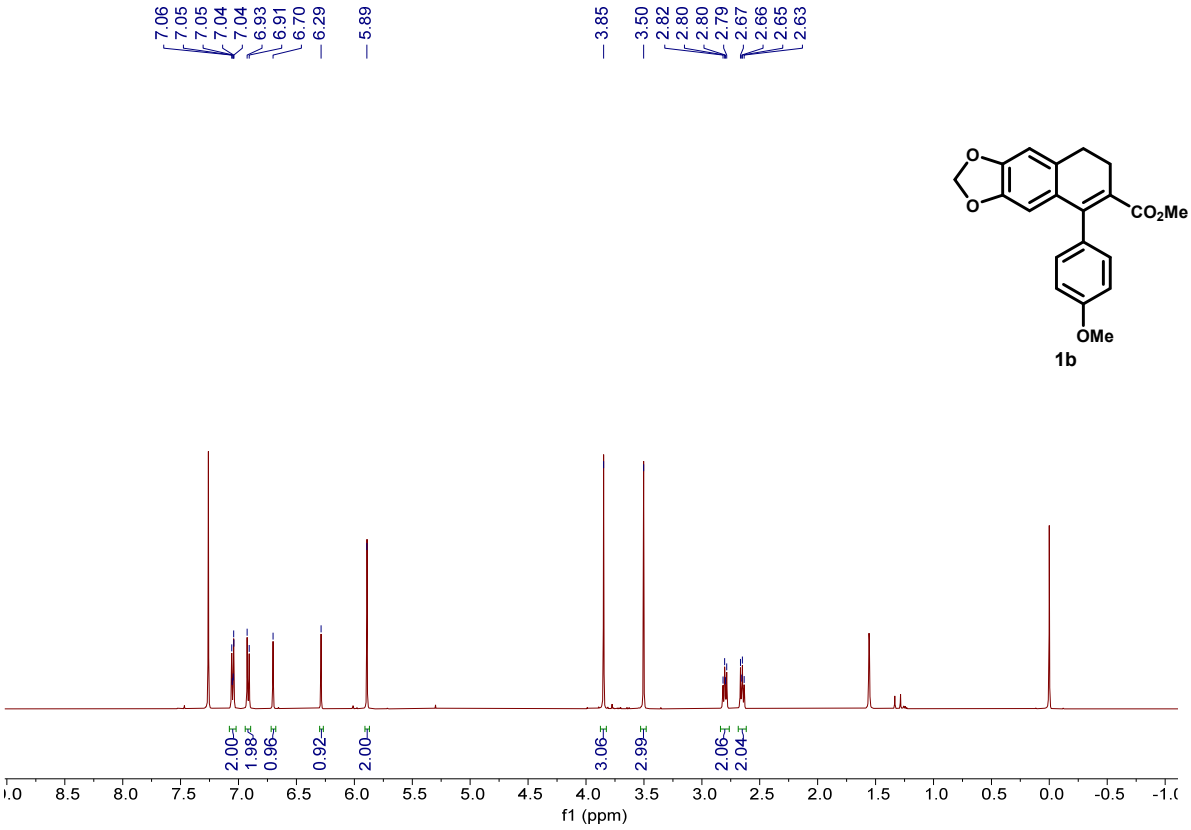


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

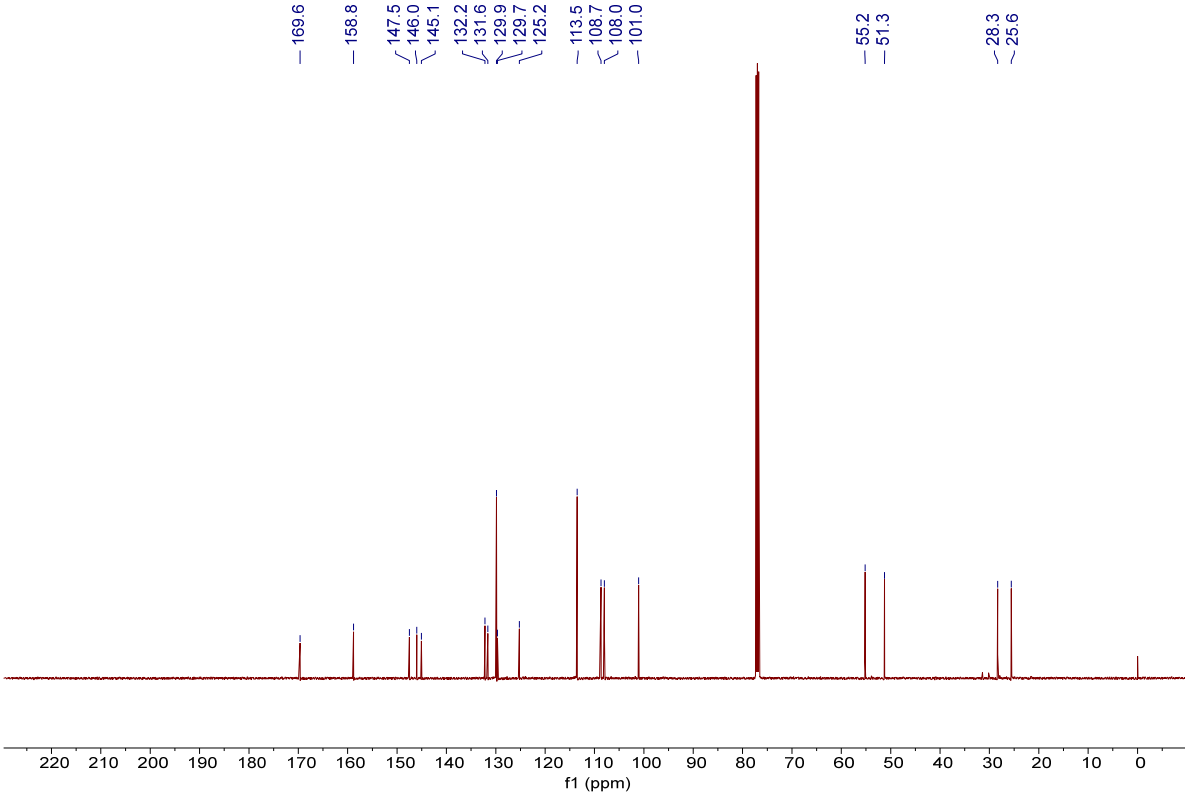


1b: Methyl 5-(4-methoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

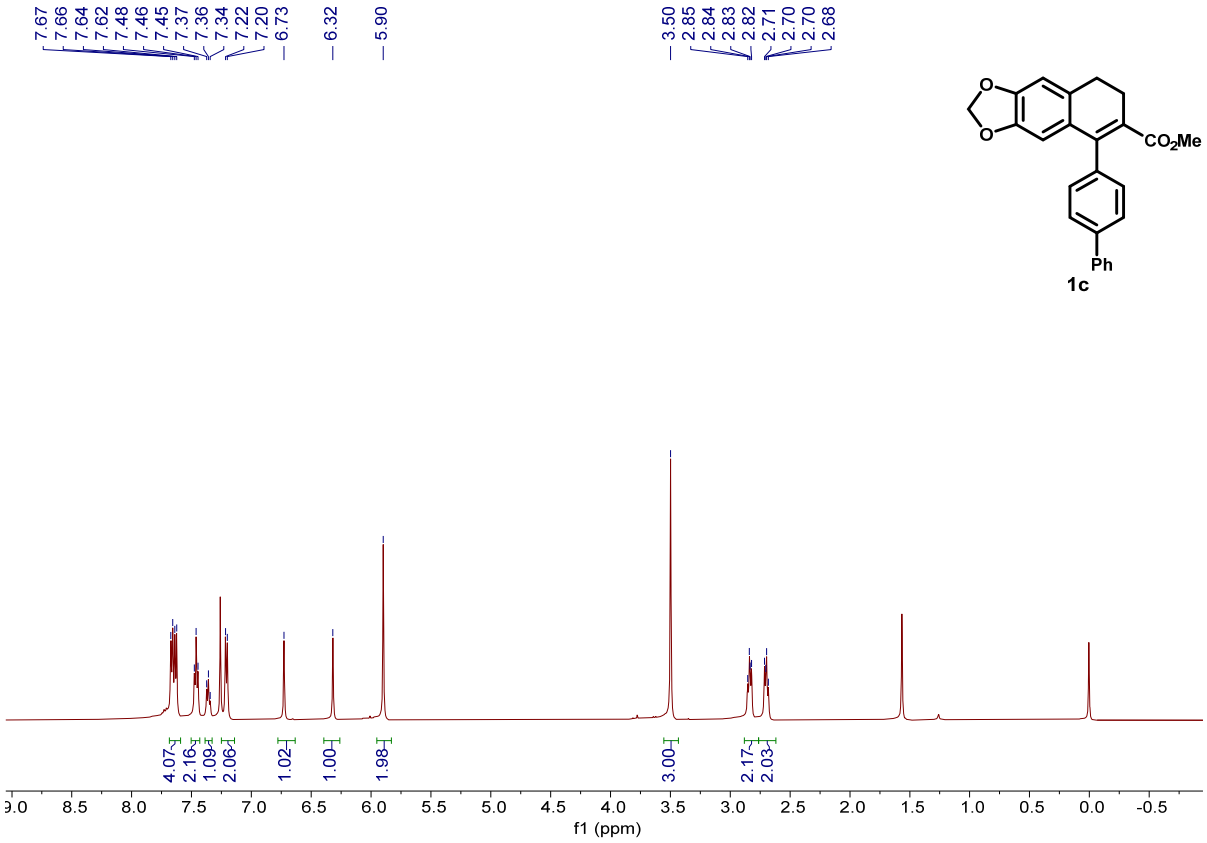


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

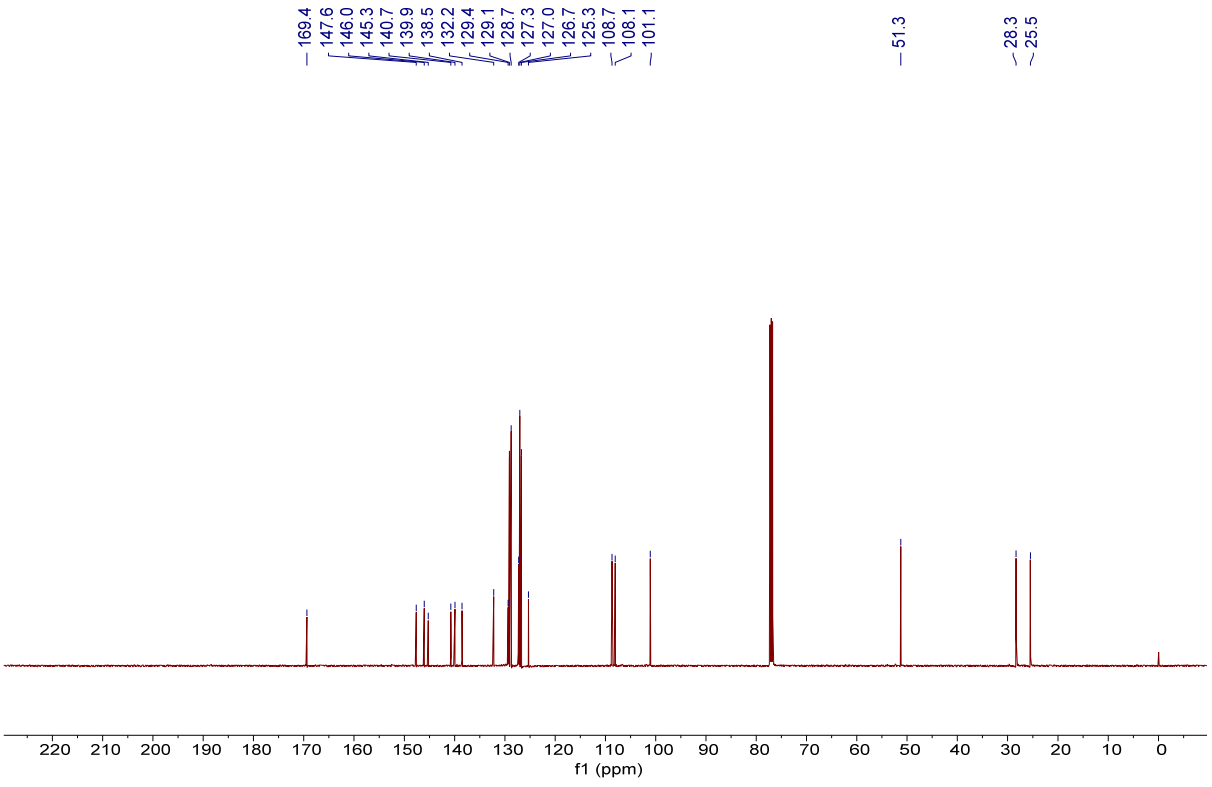


1c: methyl 5-([1,1'-biphenyl]-4-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

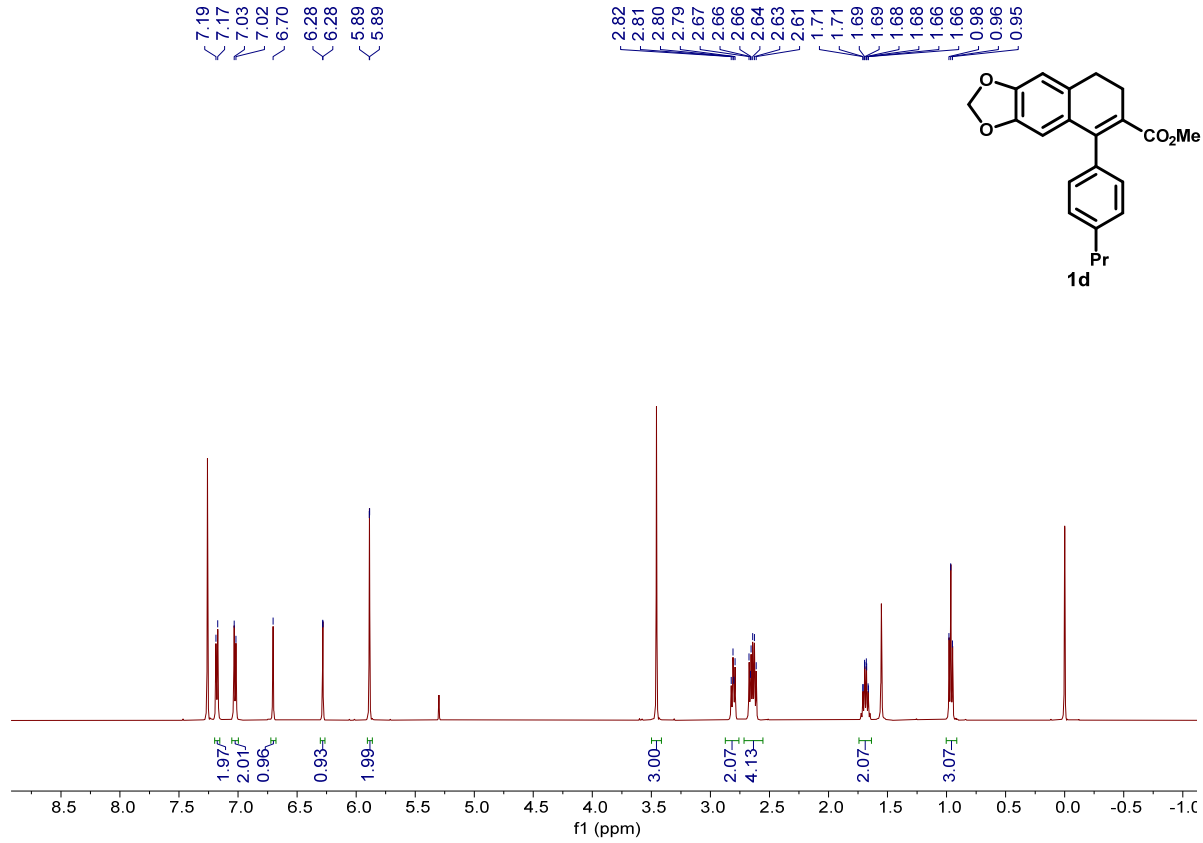


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

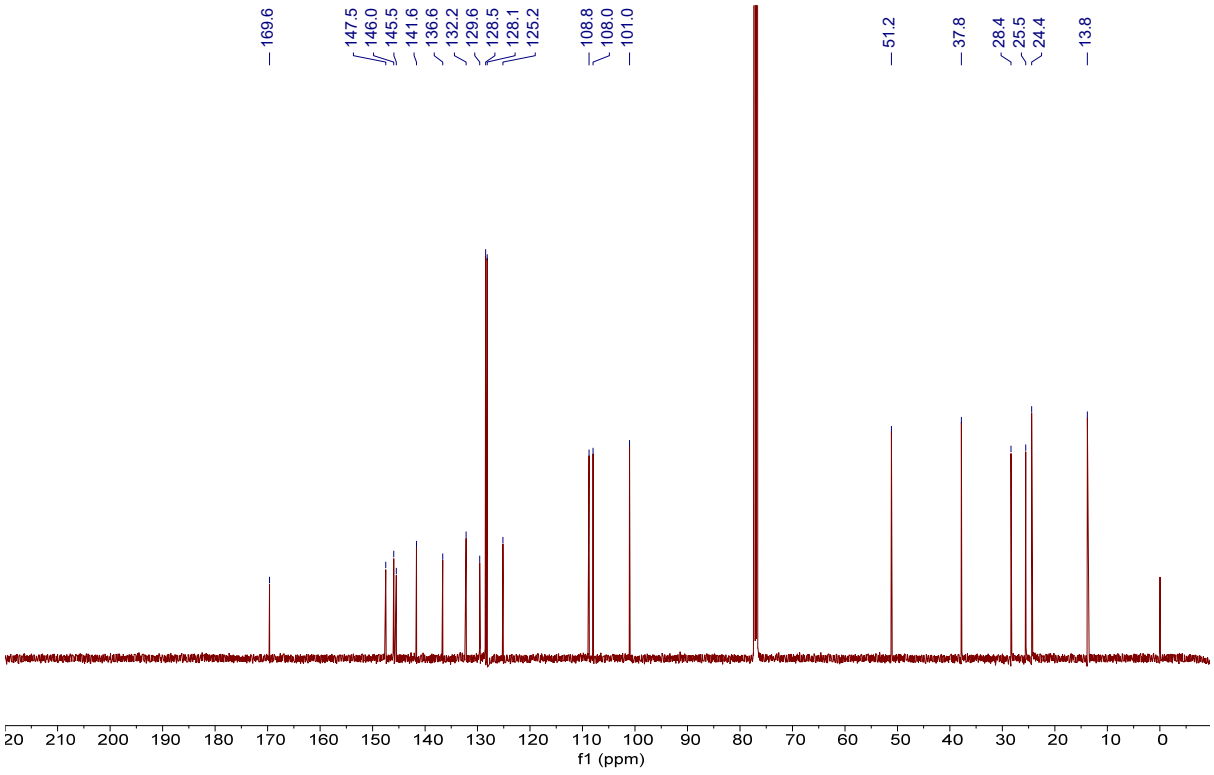


1d: Methyl 5-(4-propylphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

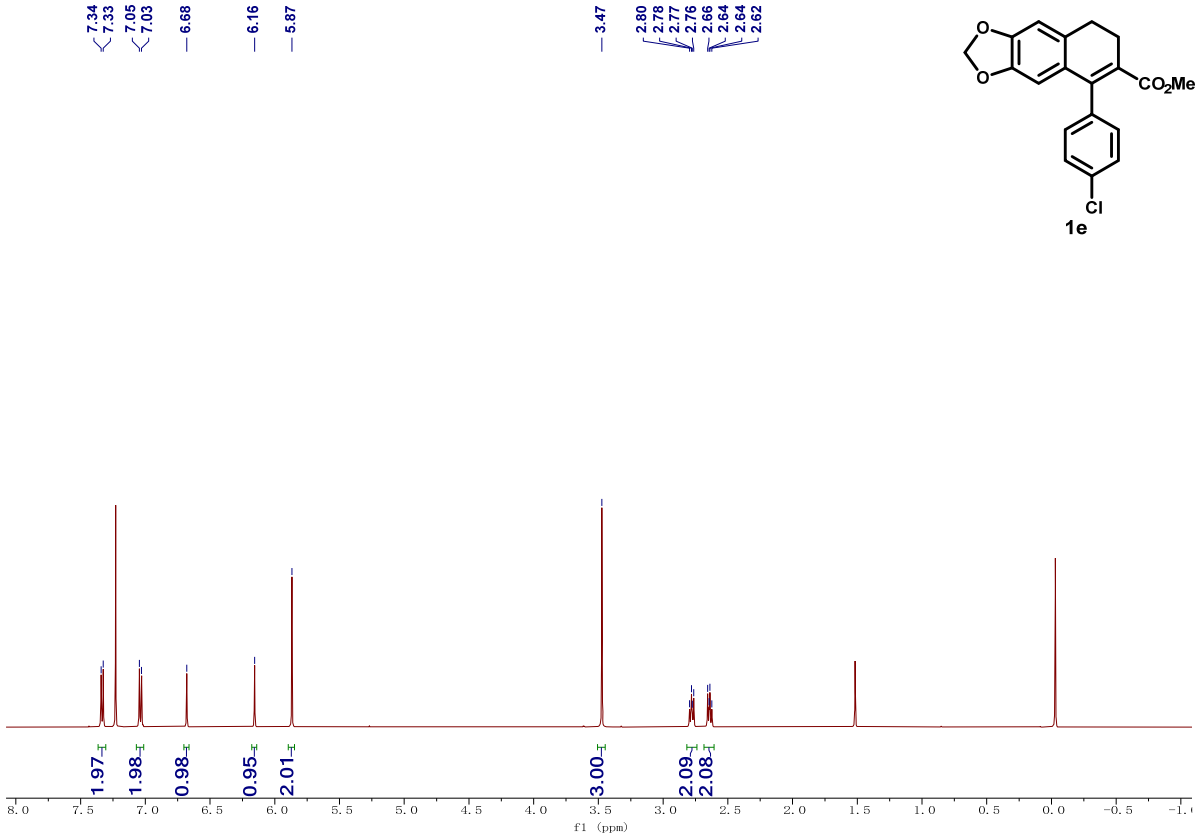


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

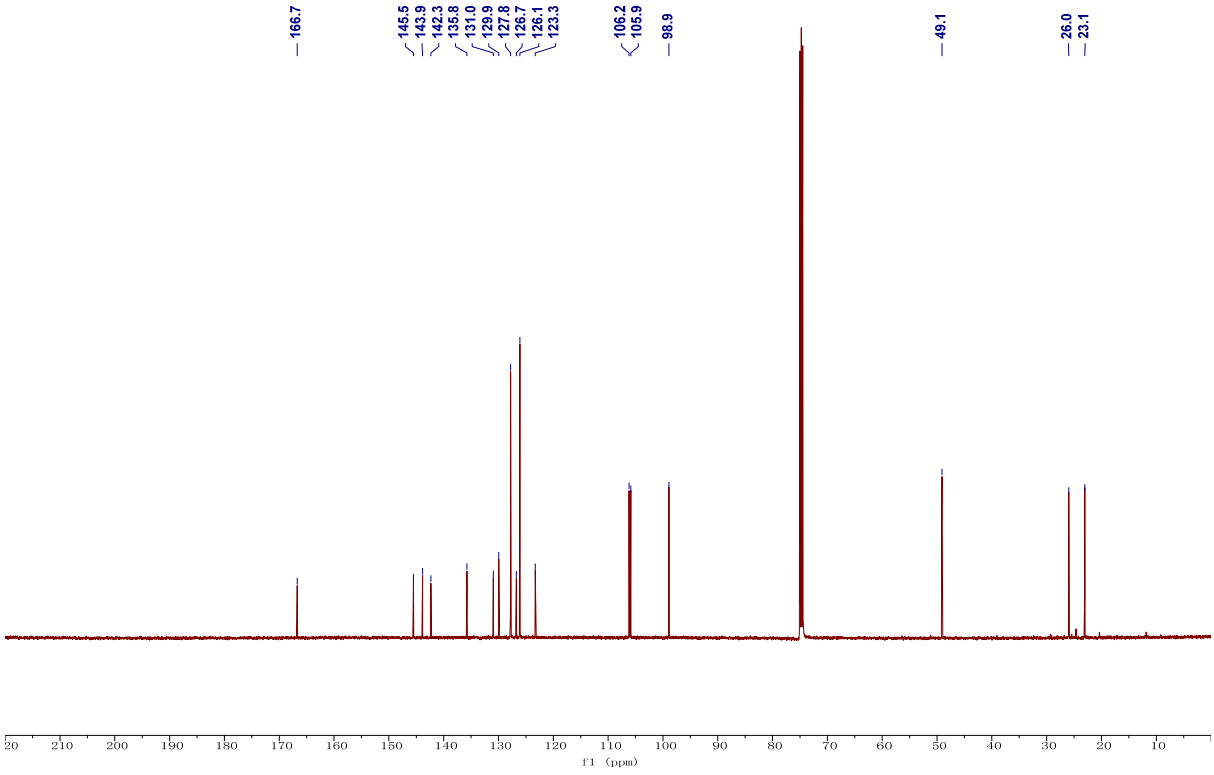


1e: Methyl 5-(4-chlorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

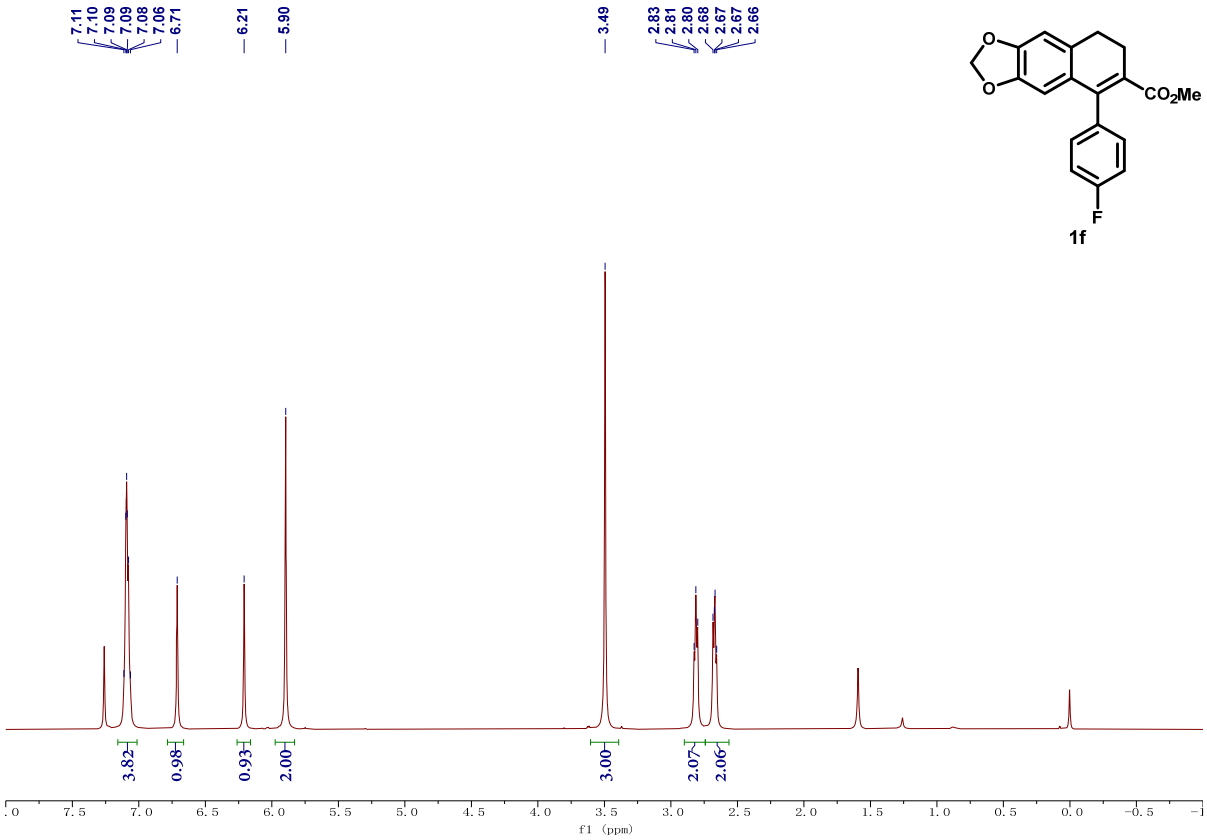


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

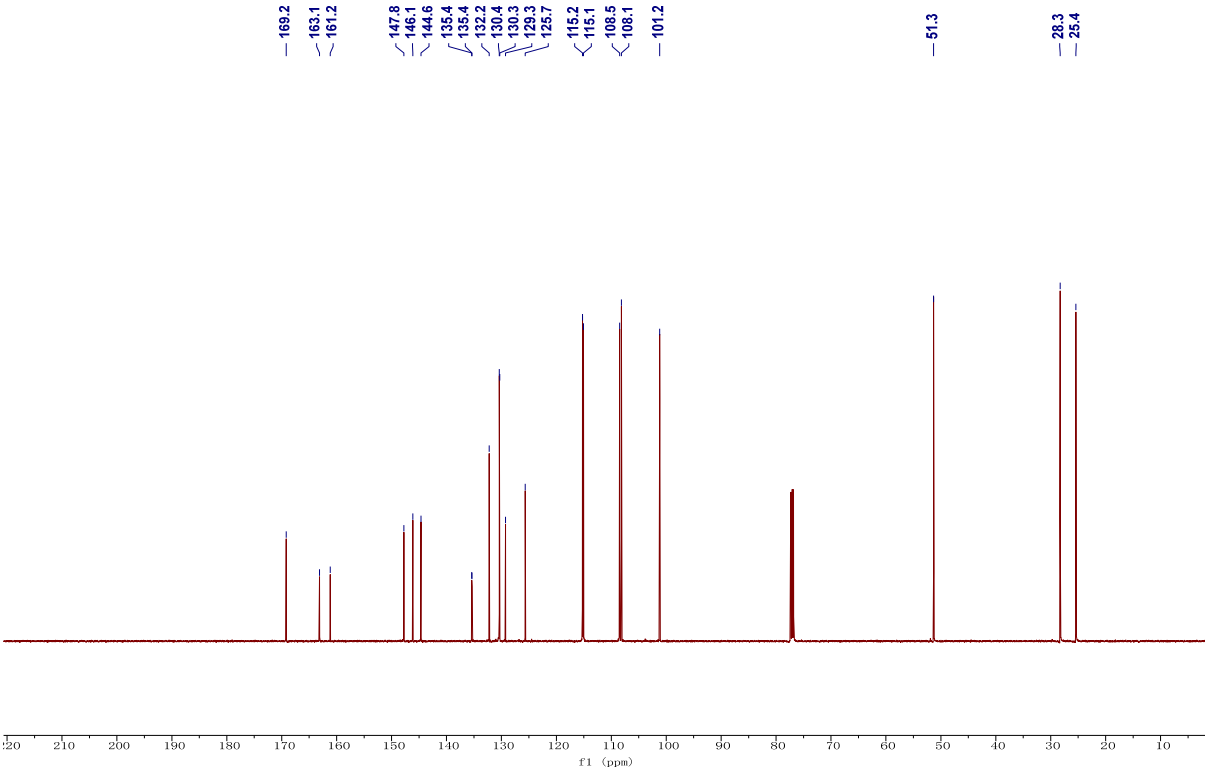


1f: Methyl 5-(4-fluorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

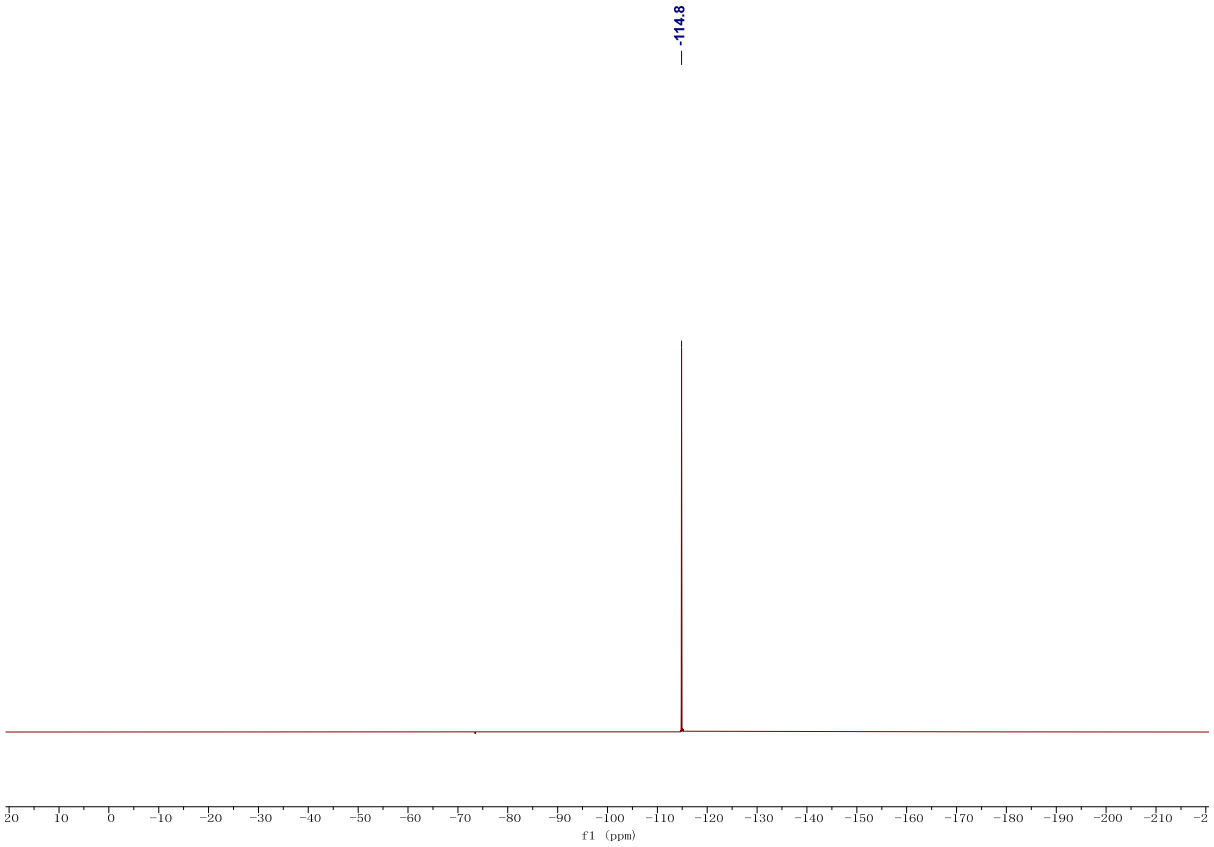
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

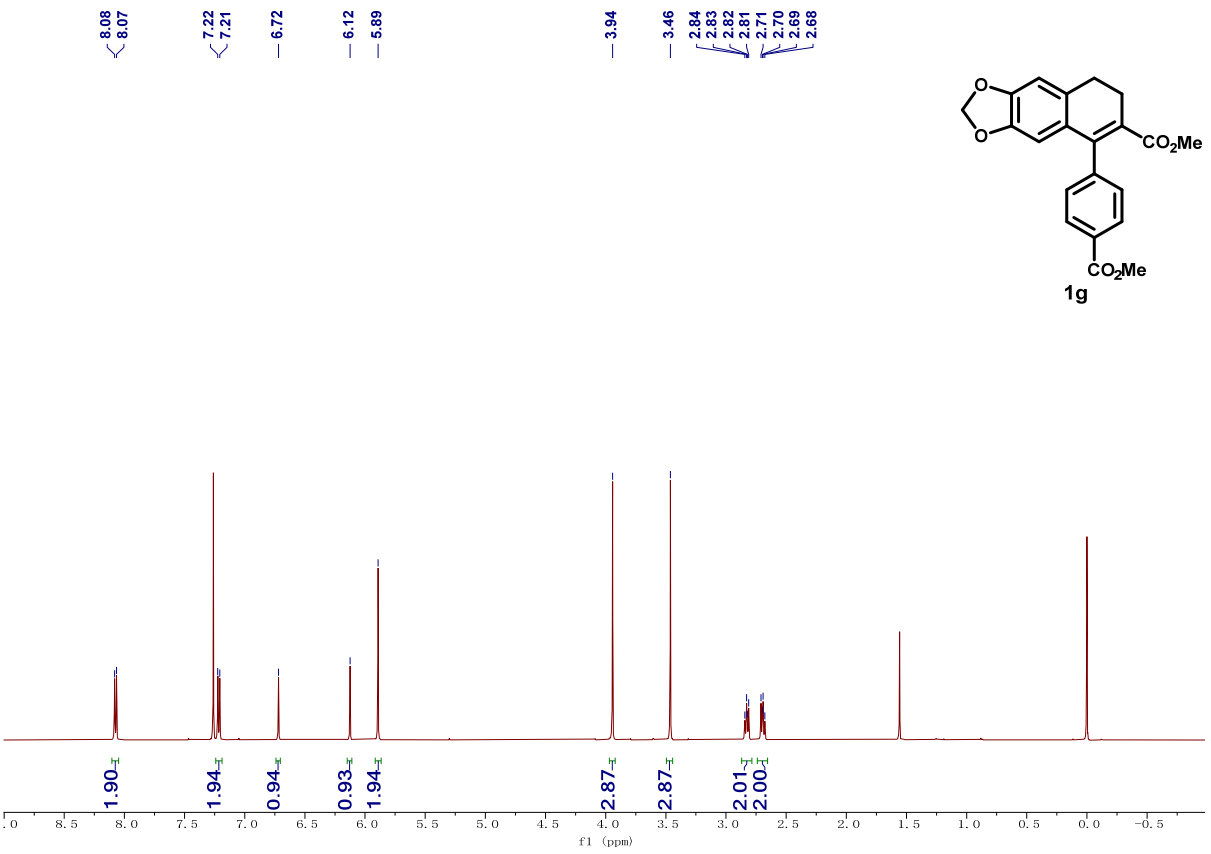


^{19}F NMR (471 MHz, $CDCl_3$)

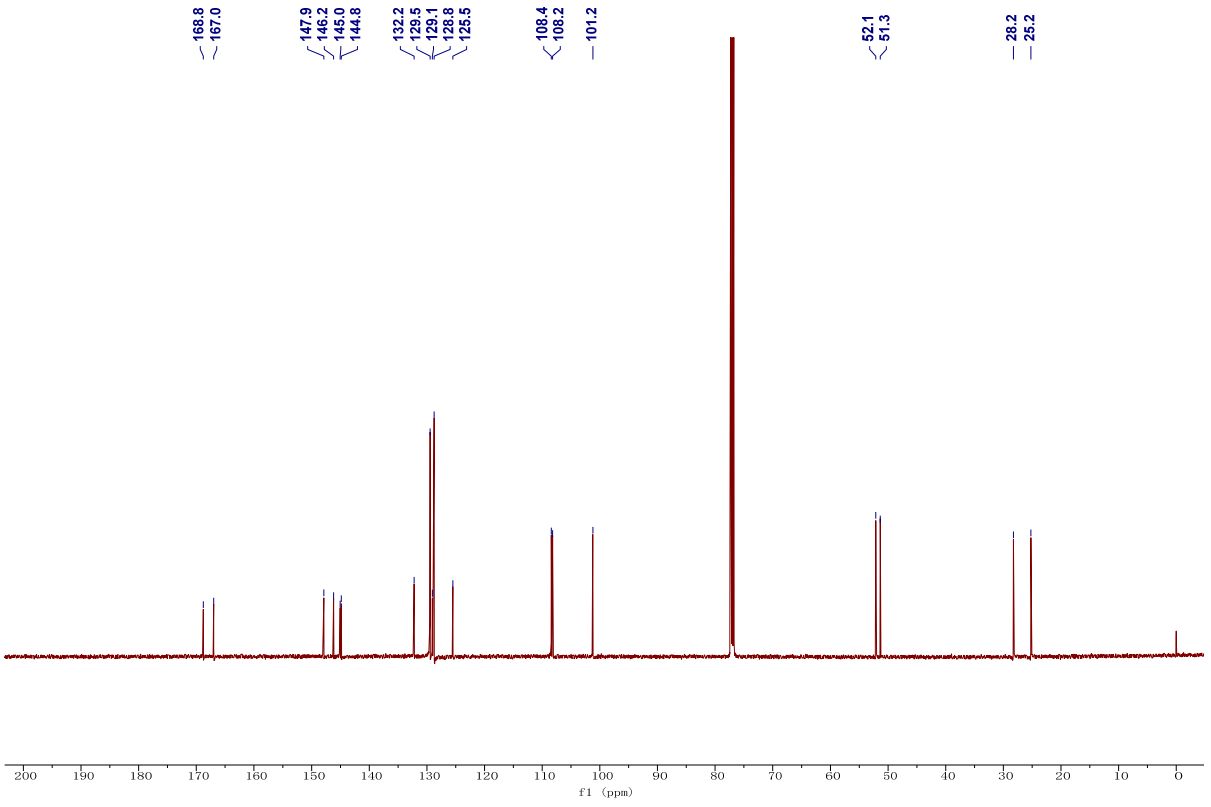


1g: Methyl5-(4-(methoxycarbonyl)phenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

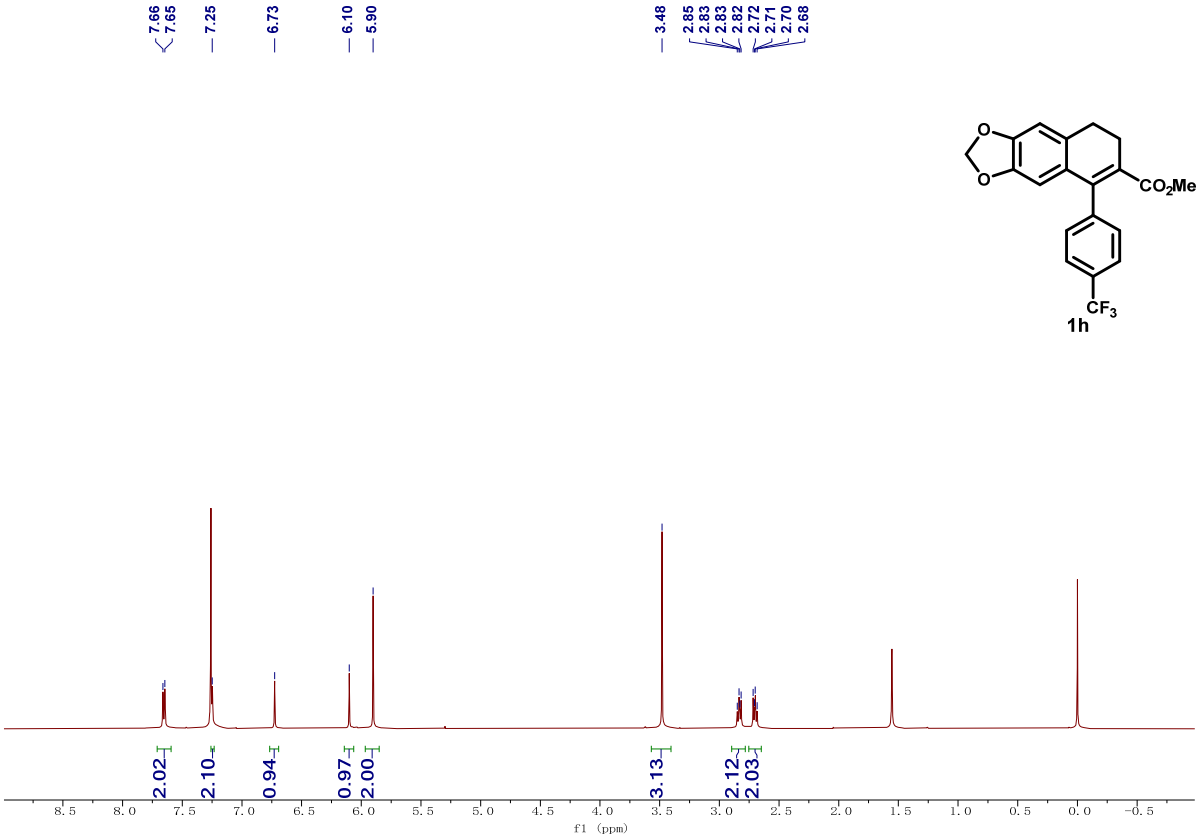


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

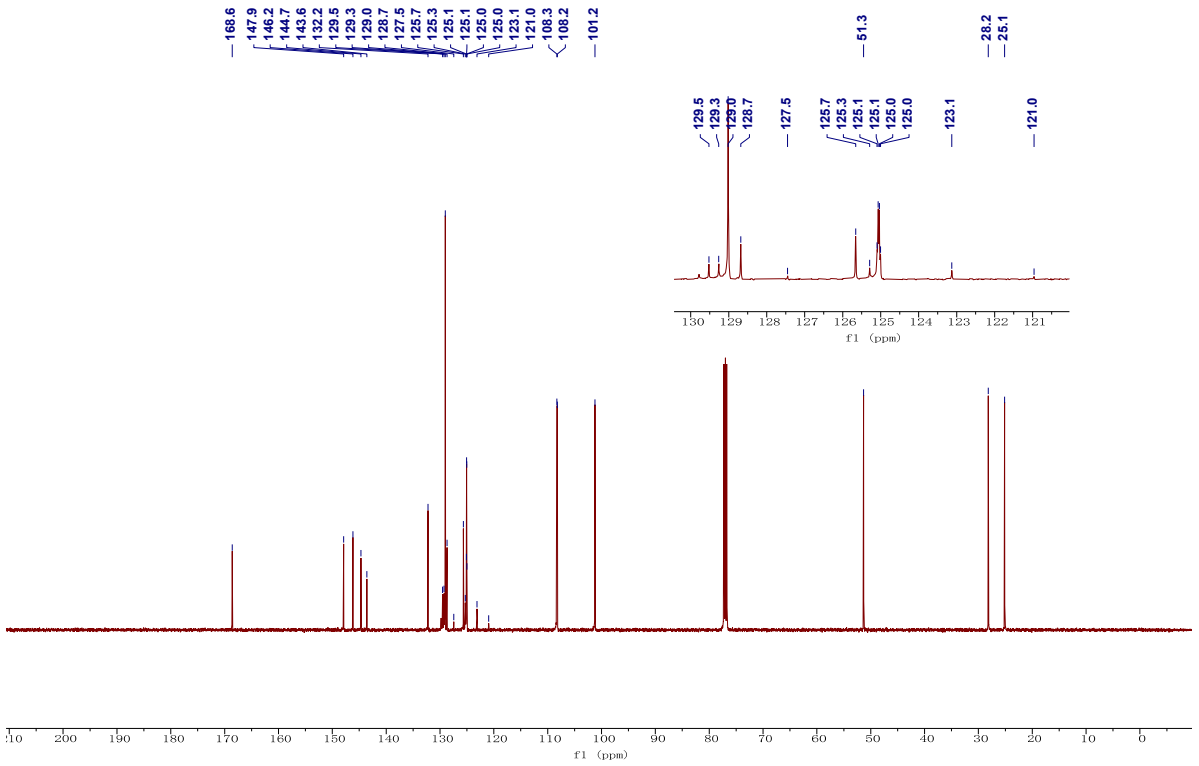


1h: Methyl 5-(4-(trifluoromethyl)phenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

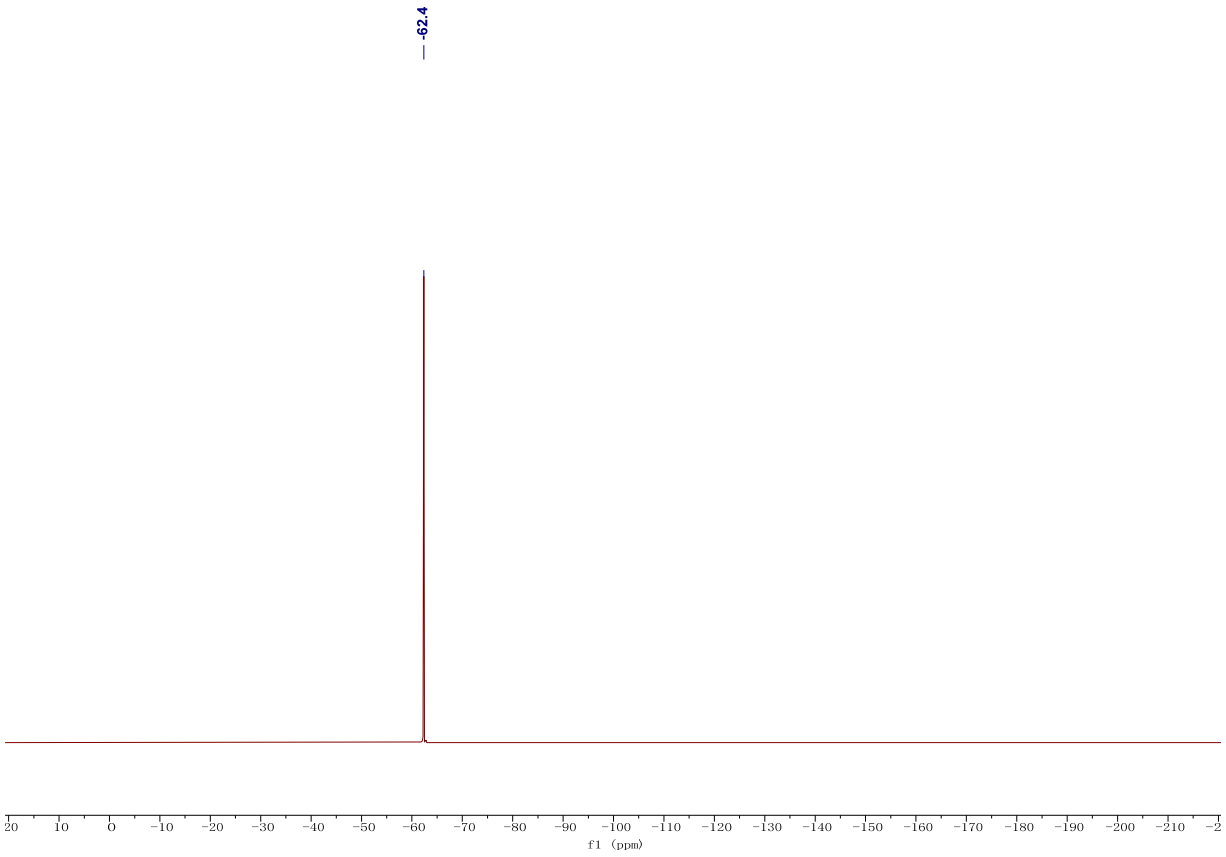
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

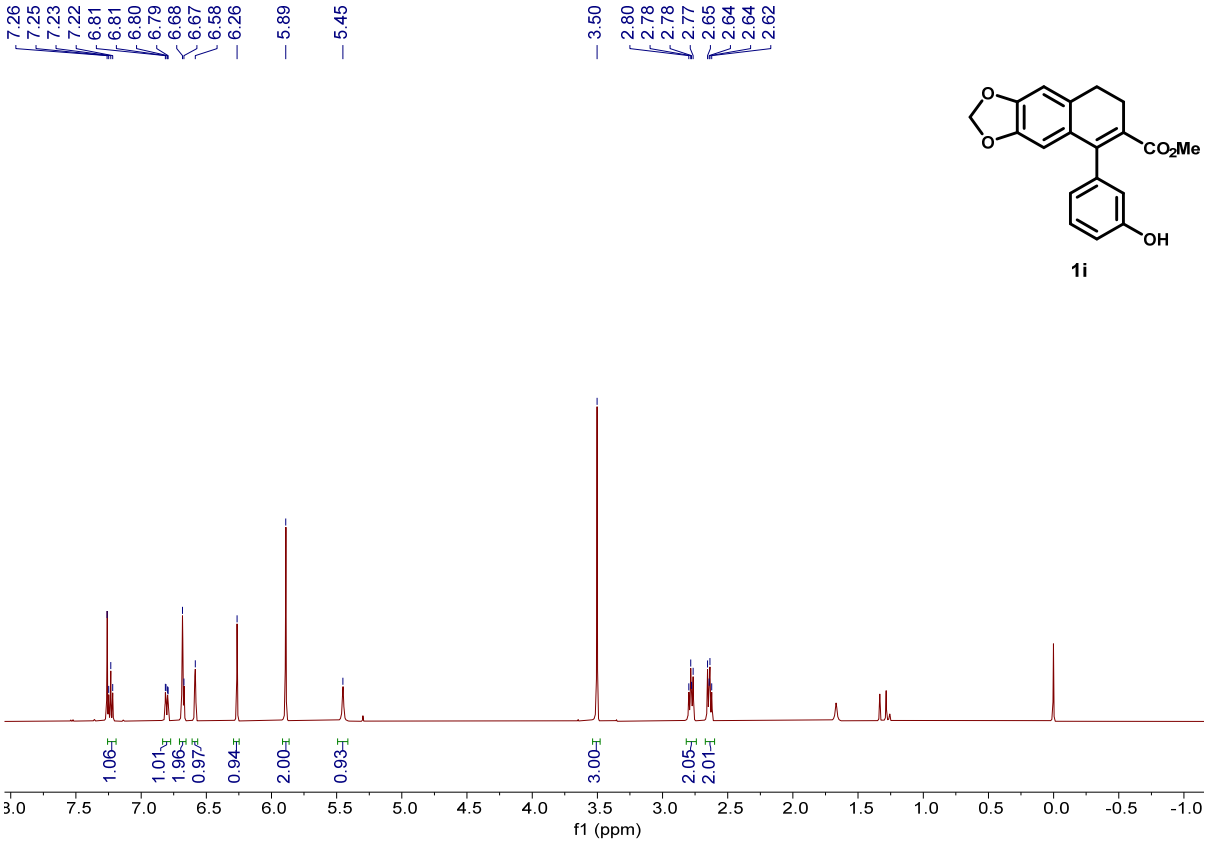


^{19}F NMR (471 MHz, $CDCl_3$)



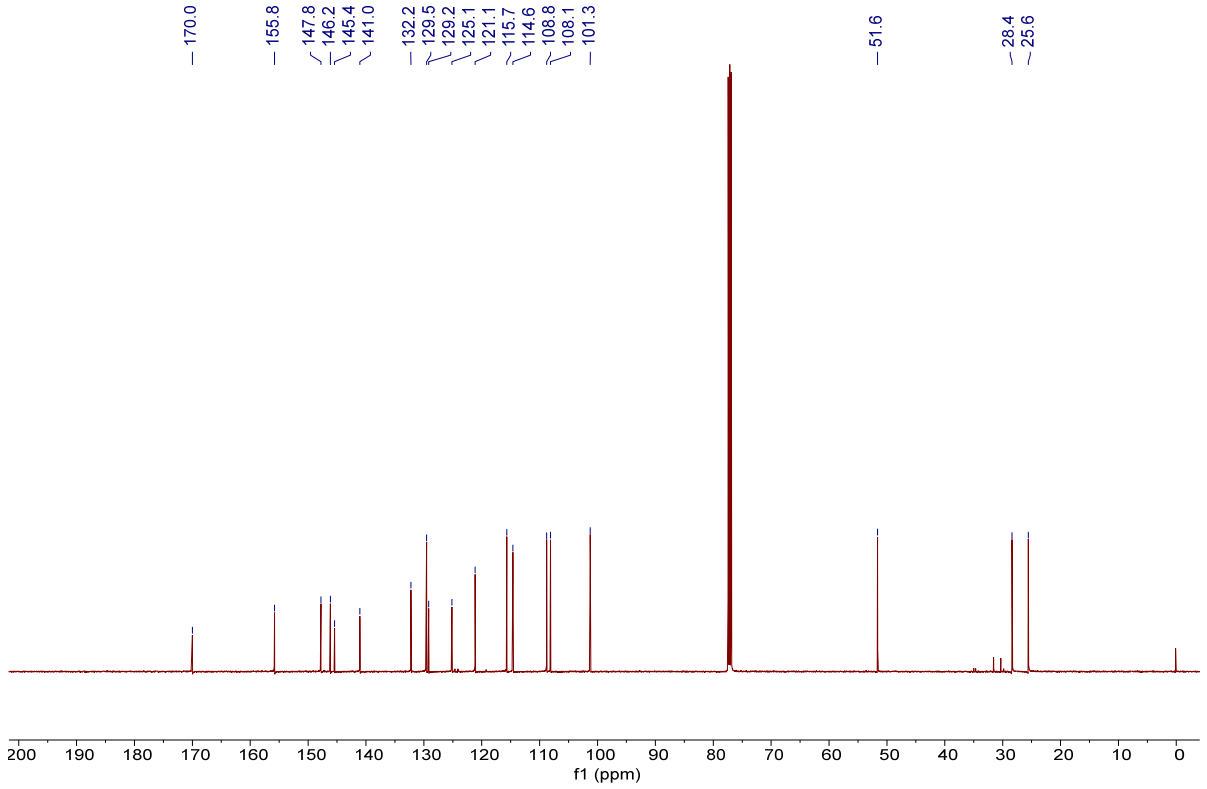
1i: Methyl 5-(3-hydroxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



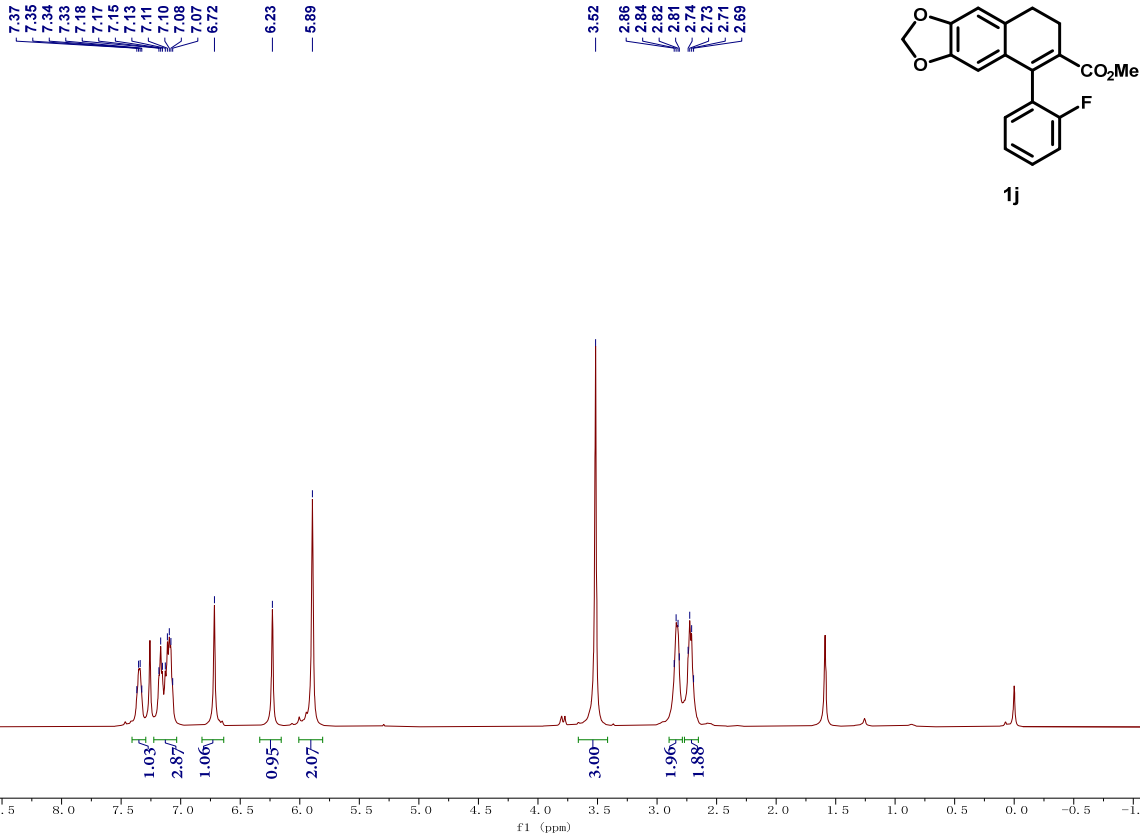
1i

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



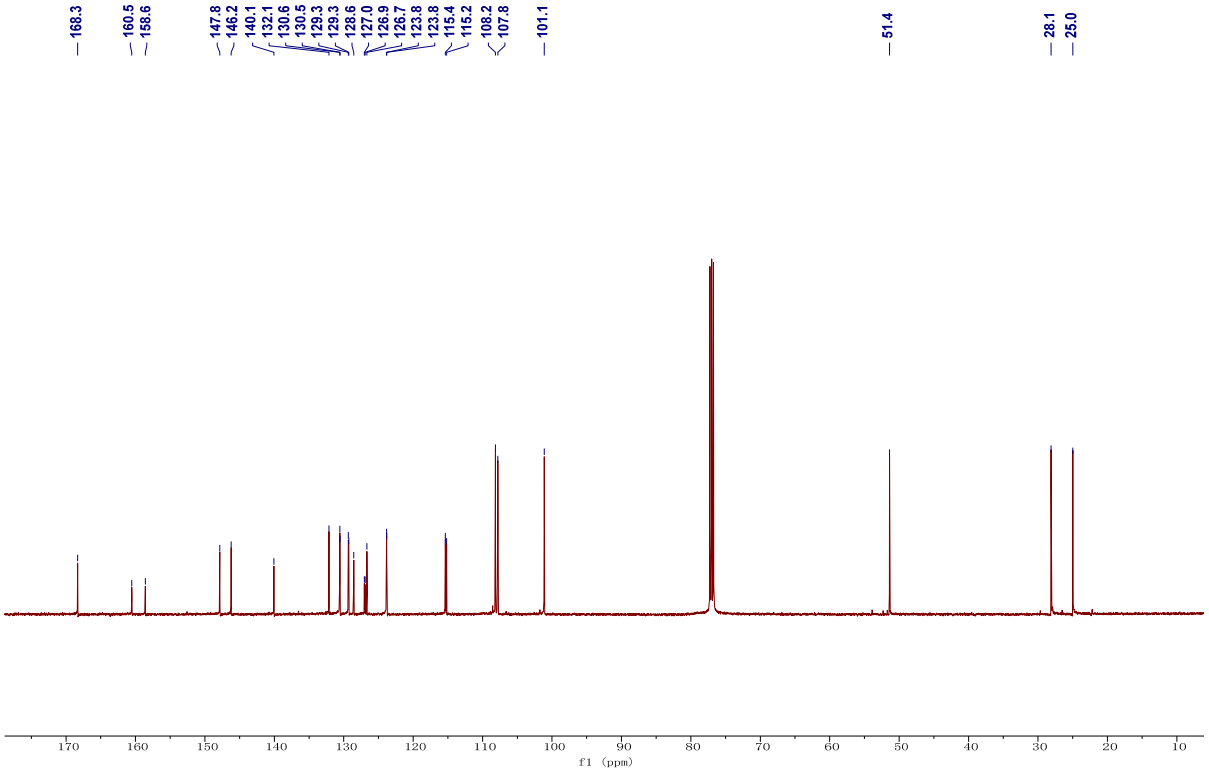
1j: Methyl 5-(2-fluorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

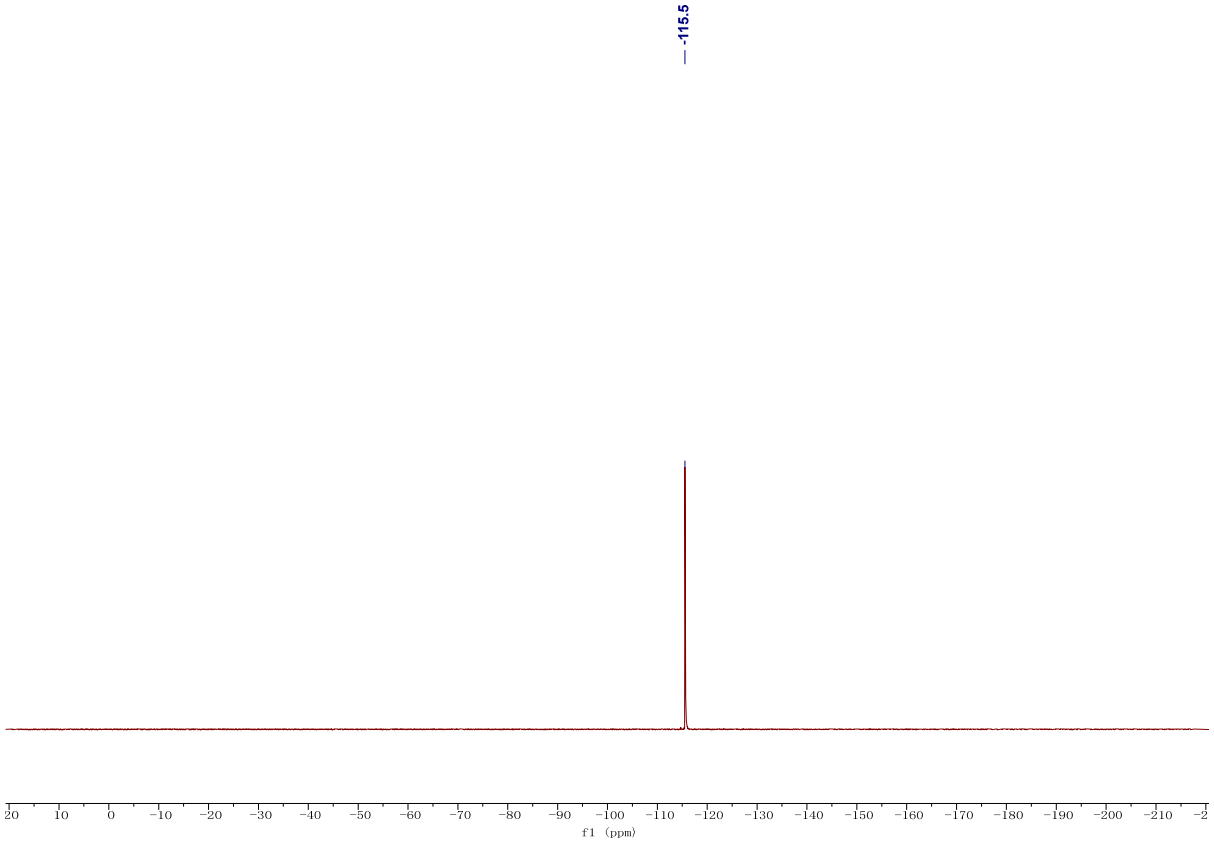


1j

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

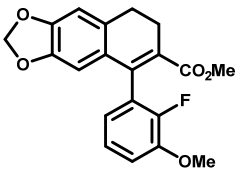


^{19}F NMR (471 MHz, $CDCl_3$)

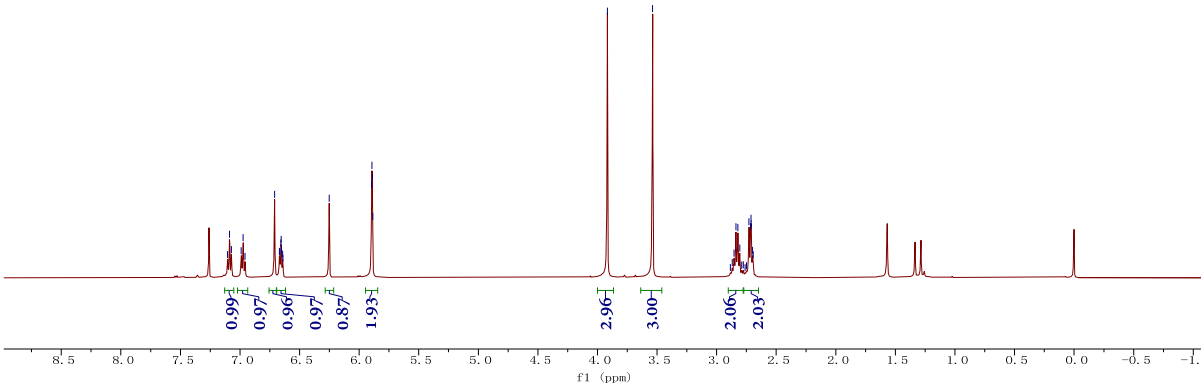


1k: Methyl 5-(2-fluoro-3-methoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

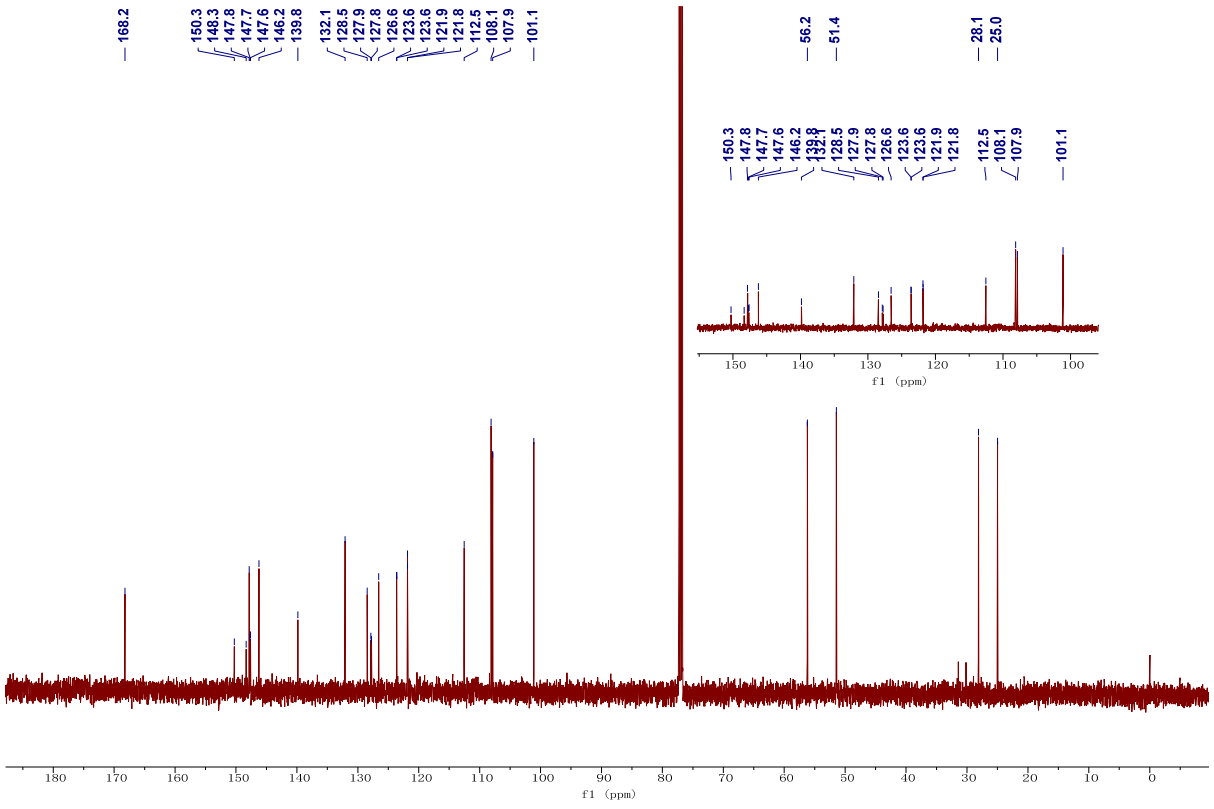
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



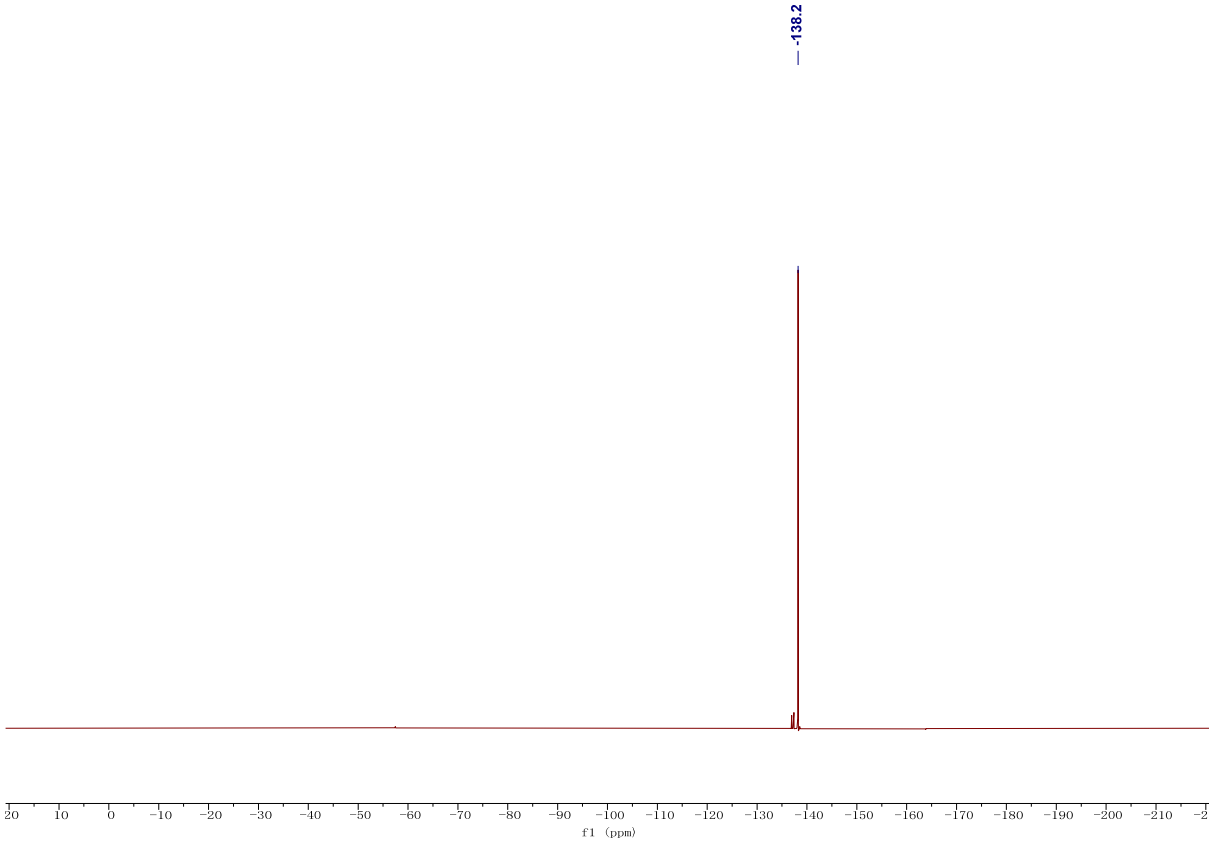
1k



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

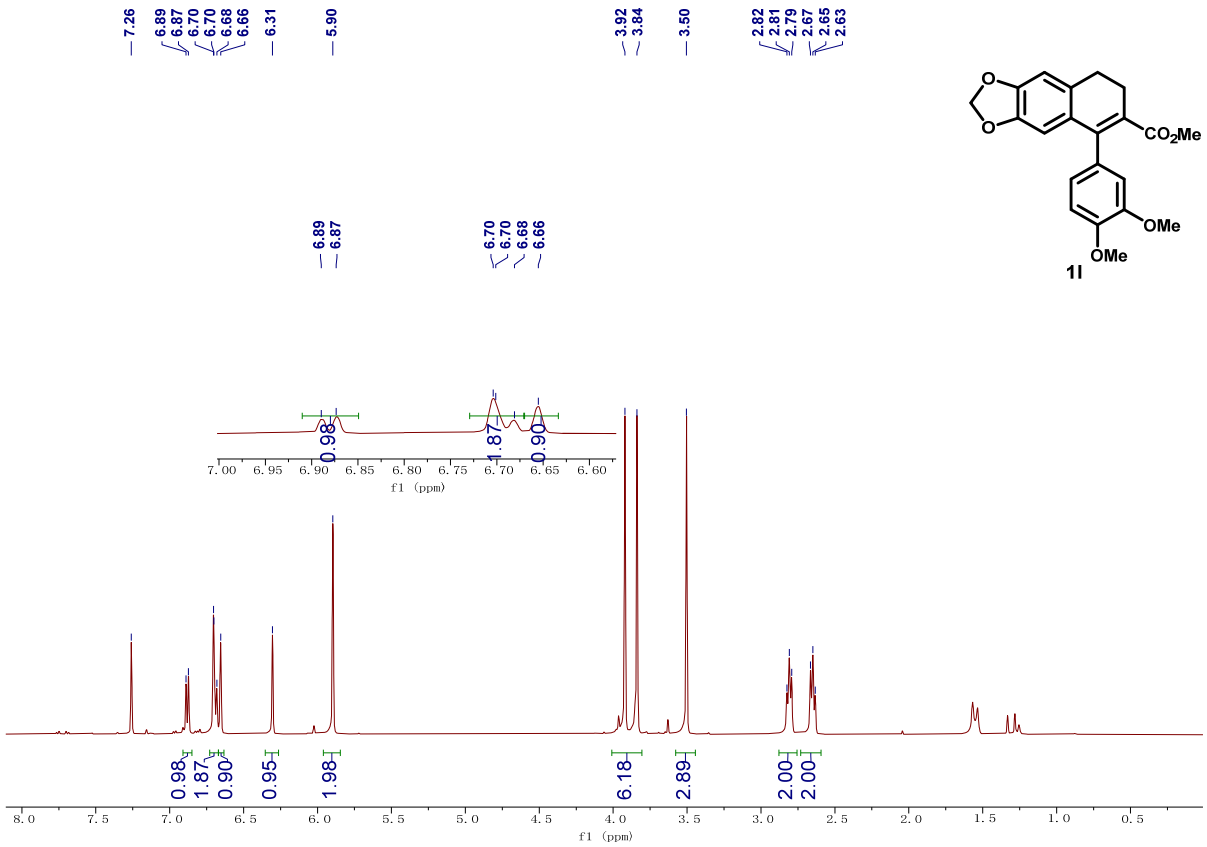


^{19}F NMR (471 MHz, $CDCl_3$)

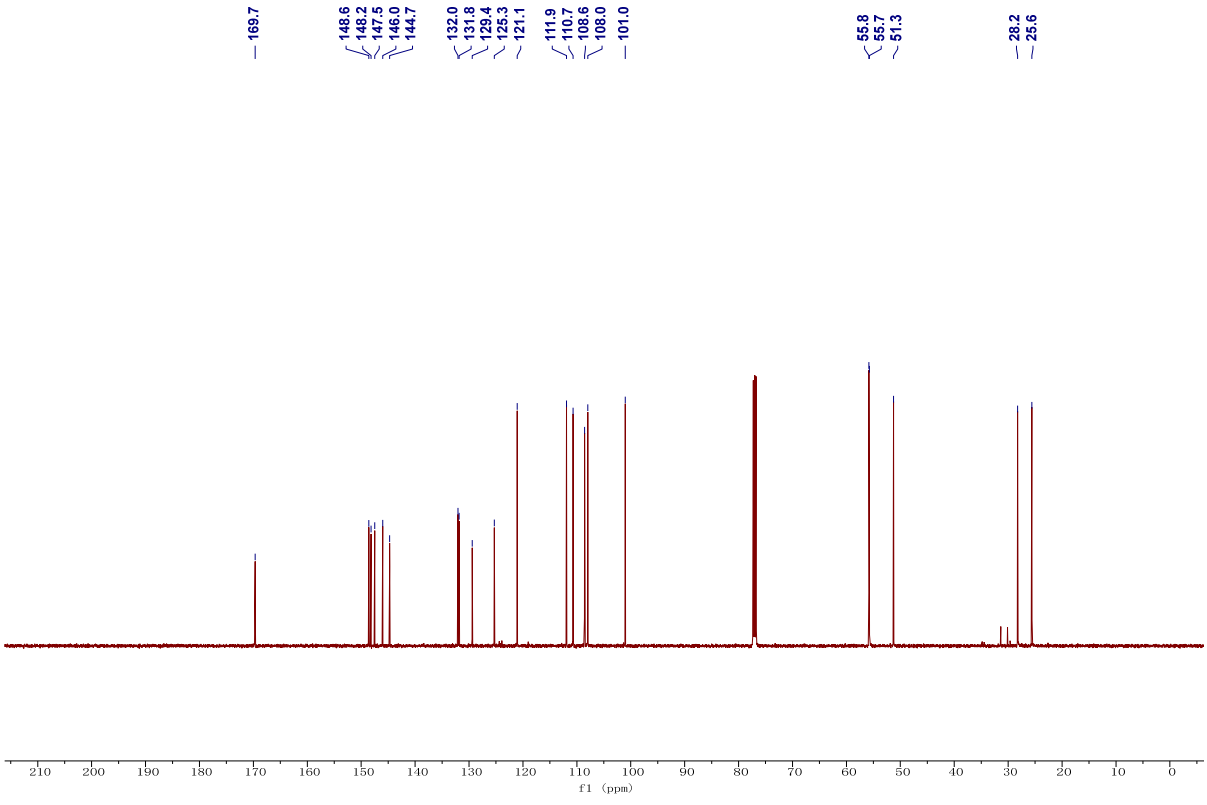


1l: Methyl 5-(3,4-dimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

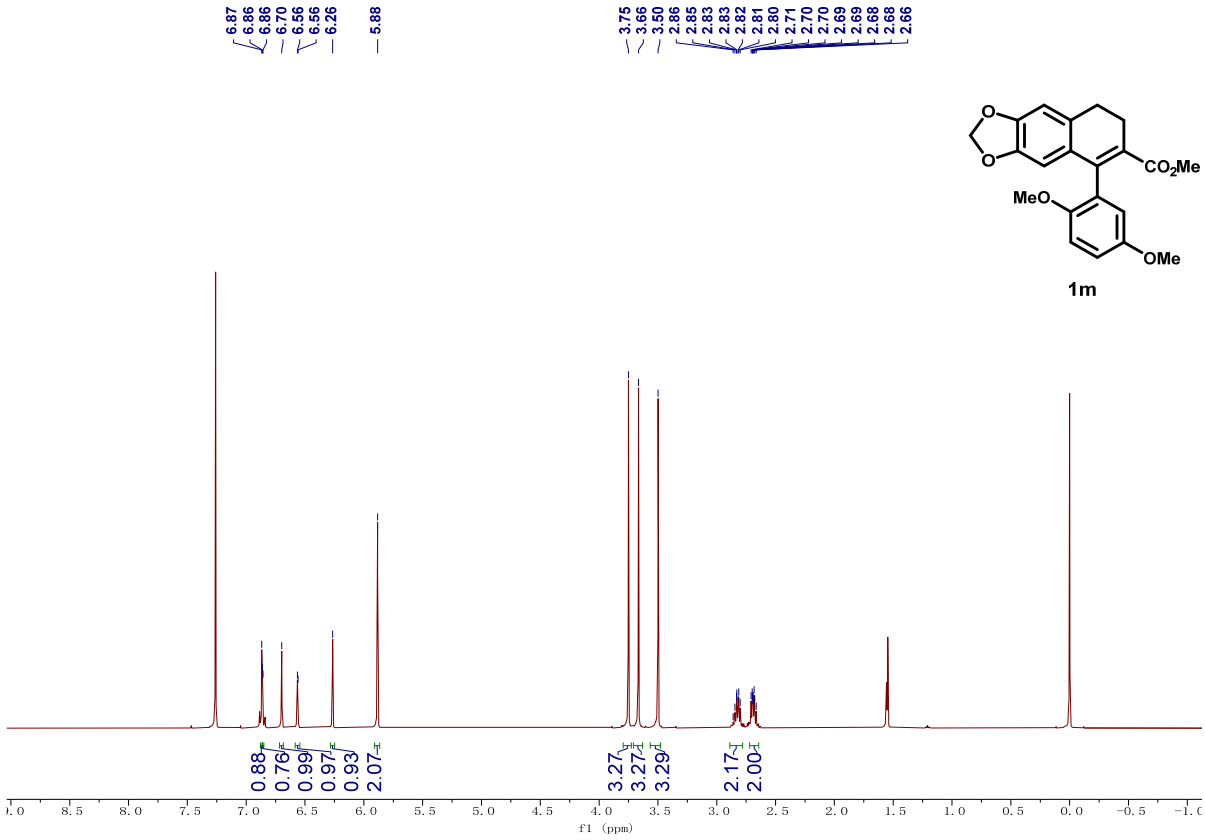


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

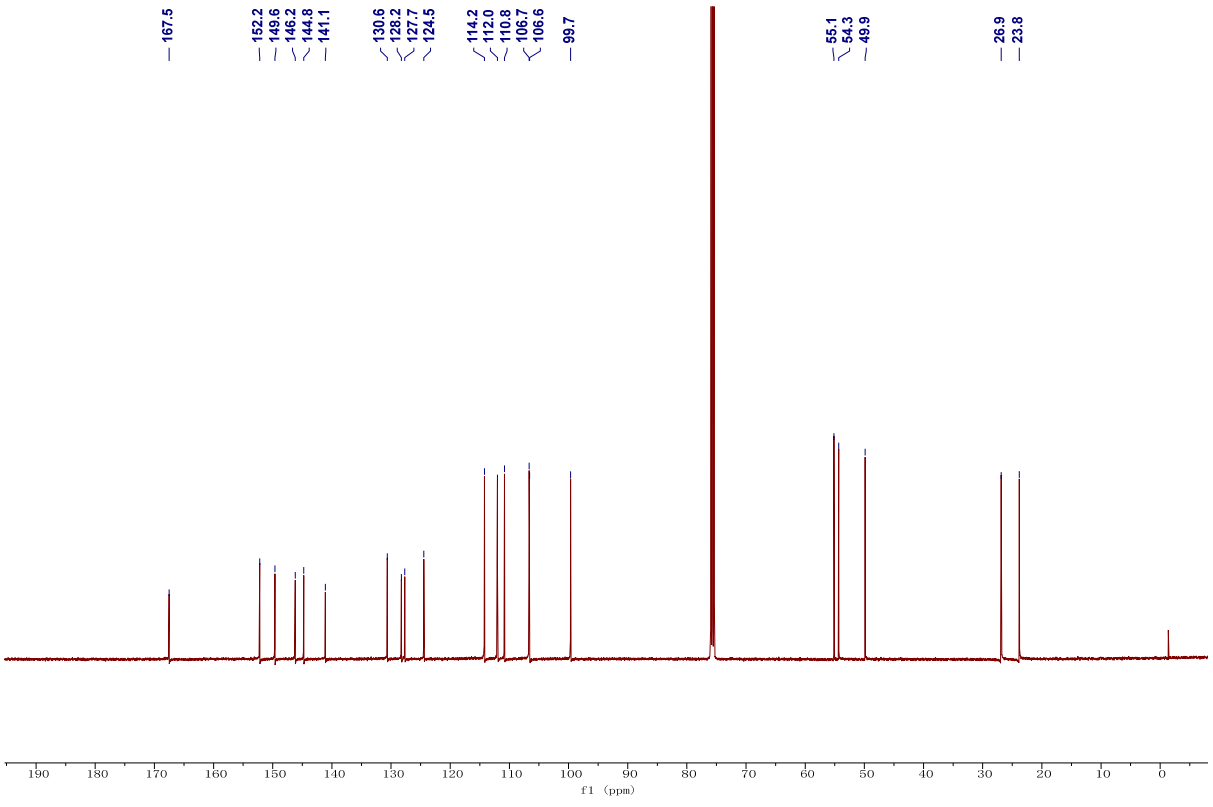


1m: Methyl 5-(2,5-dimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

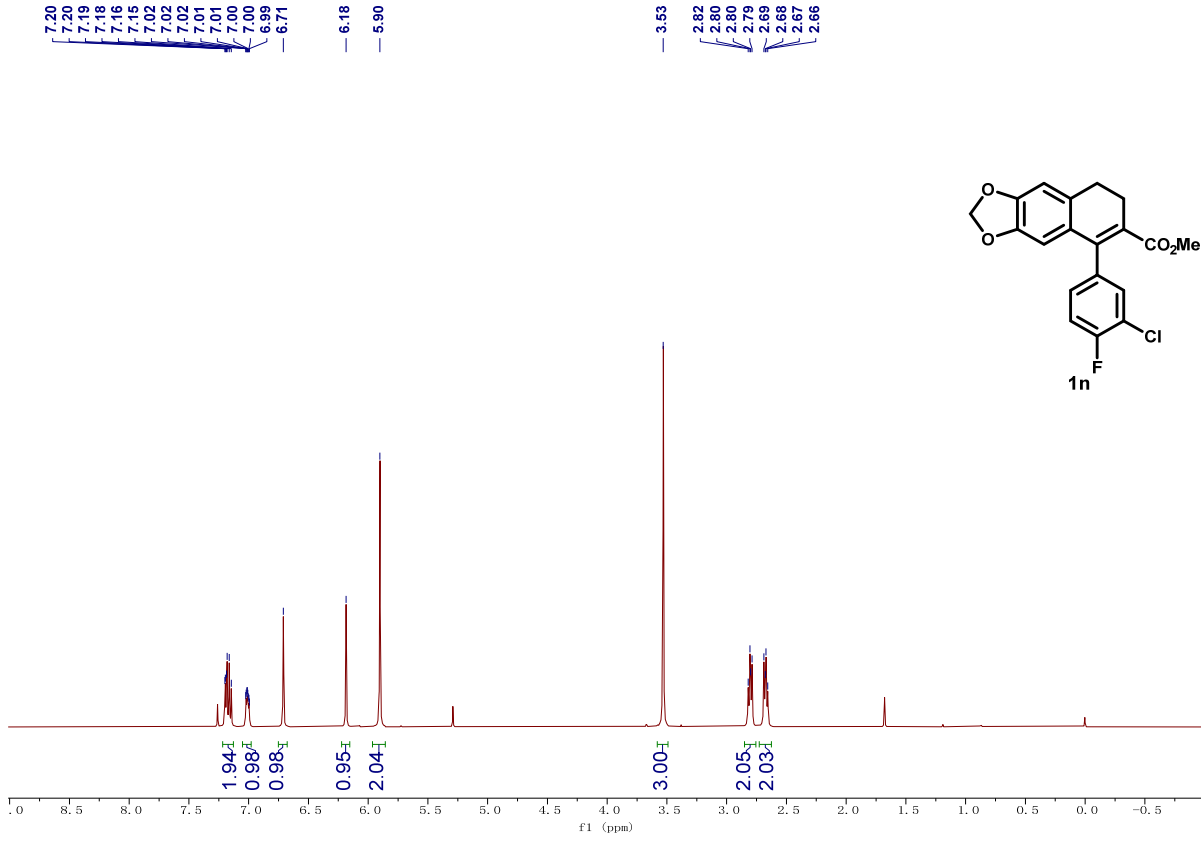


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

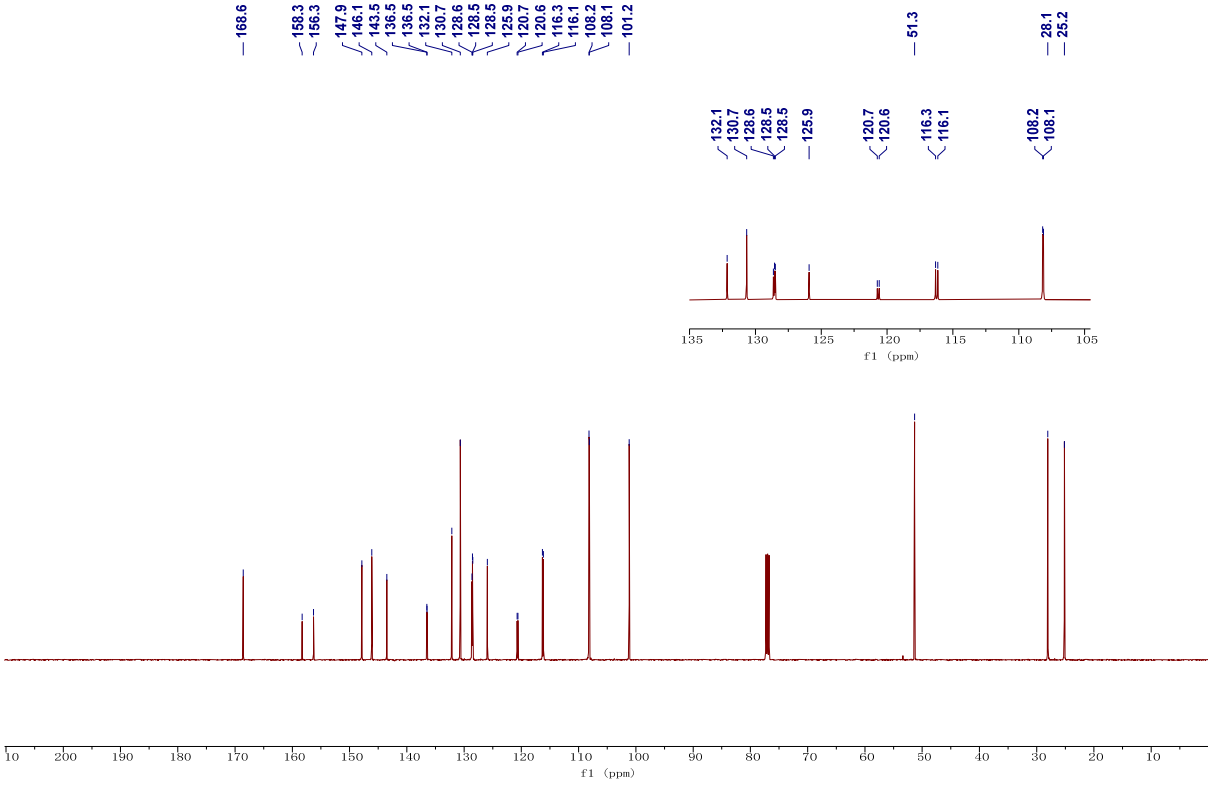


1n: Methyl 5-(3-chloro-4-fluorophenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

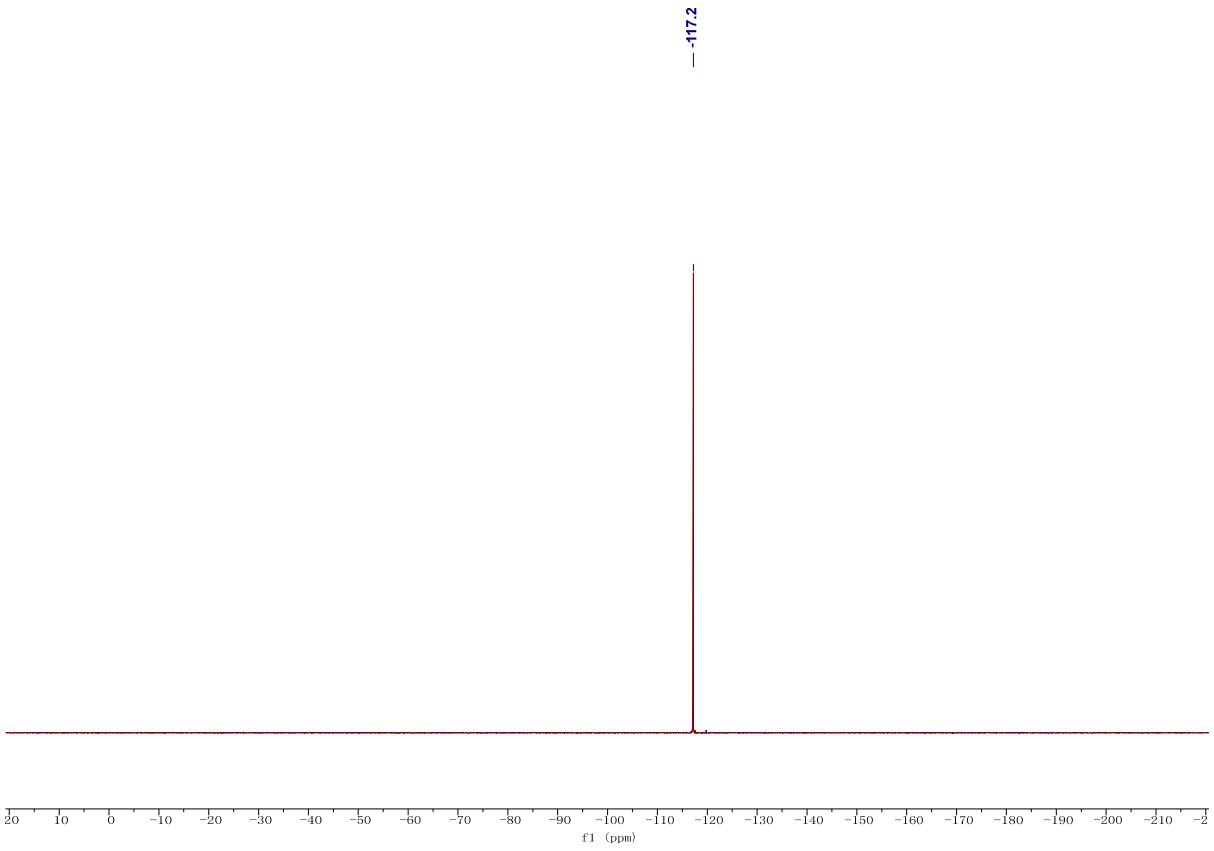
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

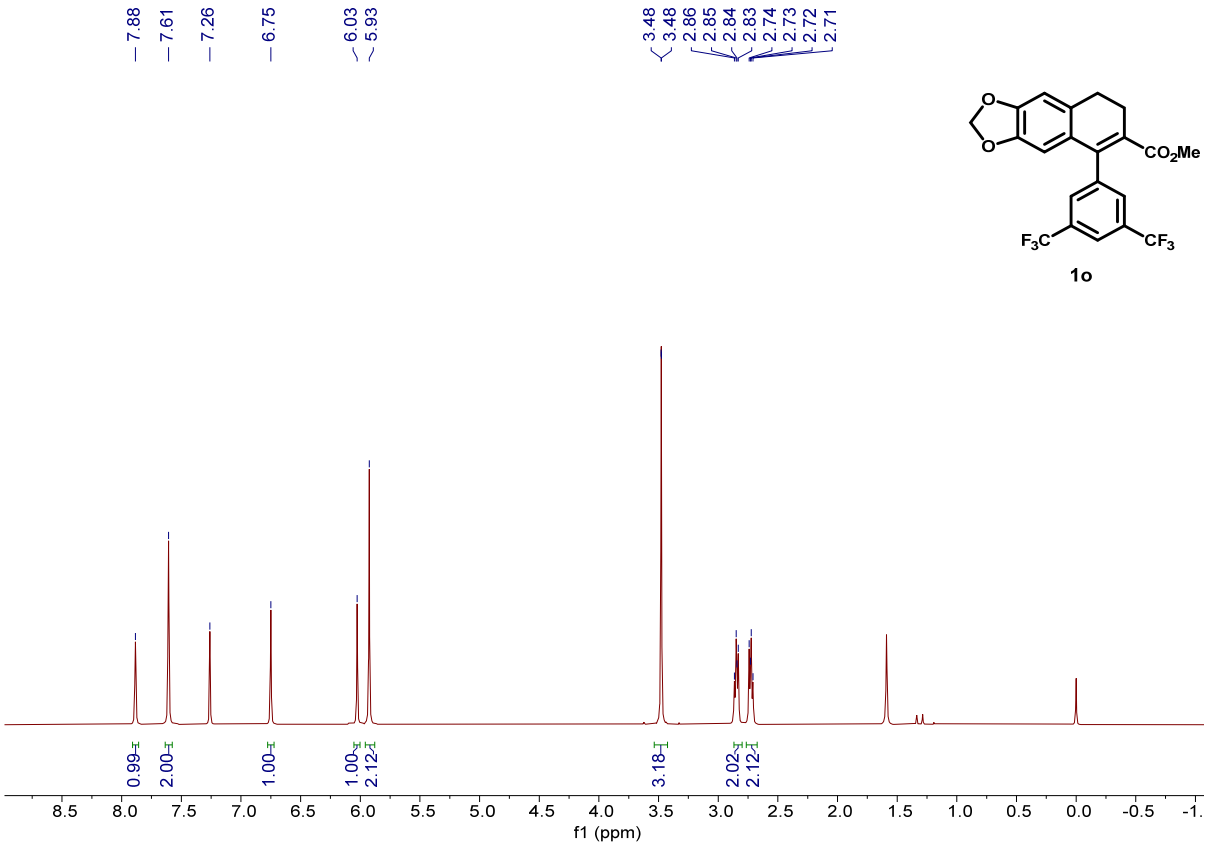


^{19}F NMR (471 MHz, $CDCl_3$)

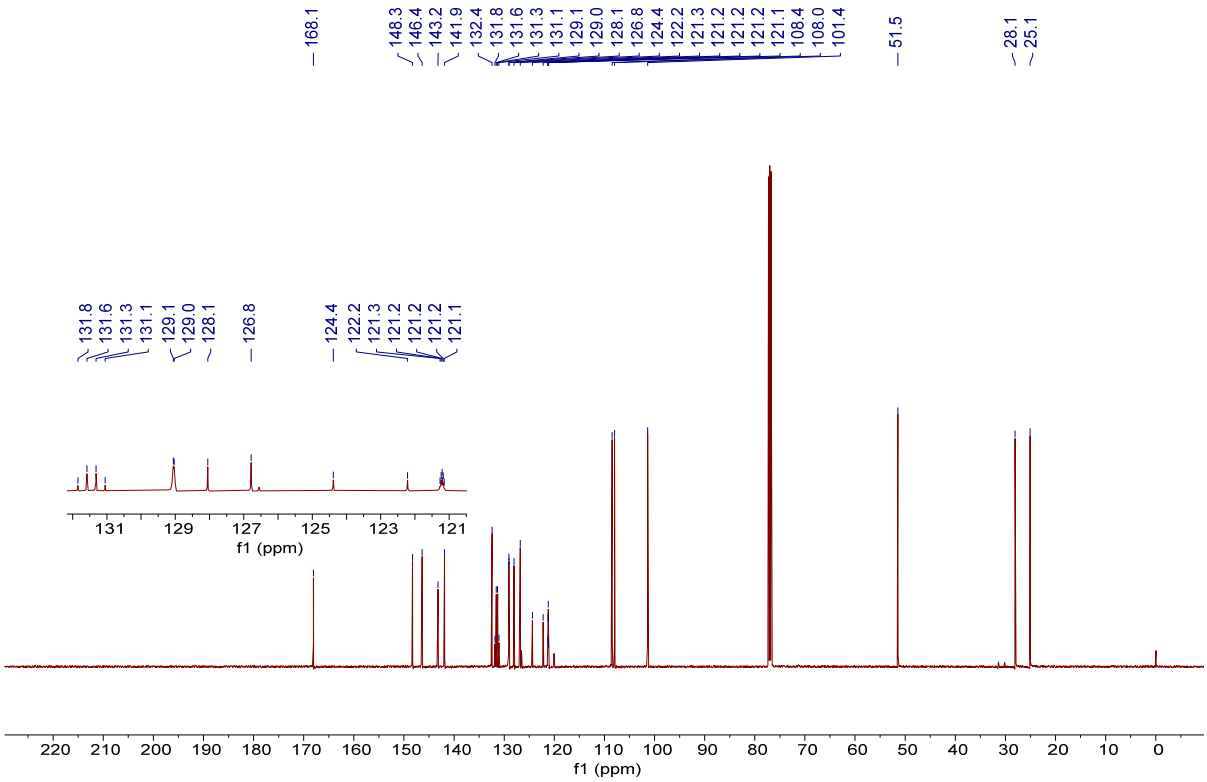


1o: Methyl-5-(3,5-bis(trifluoromethyl)phenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

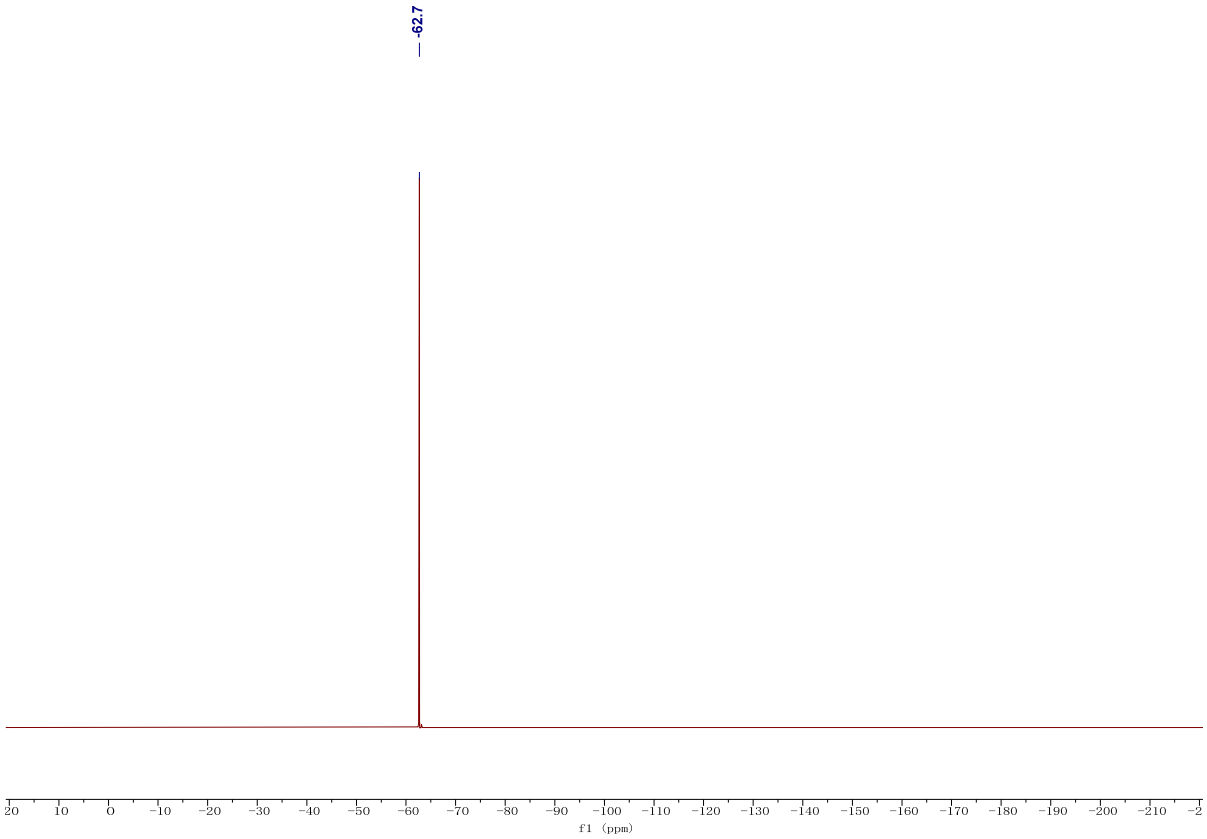
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

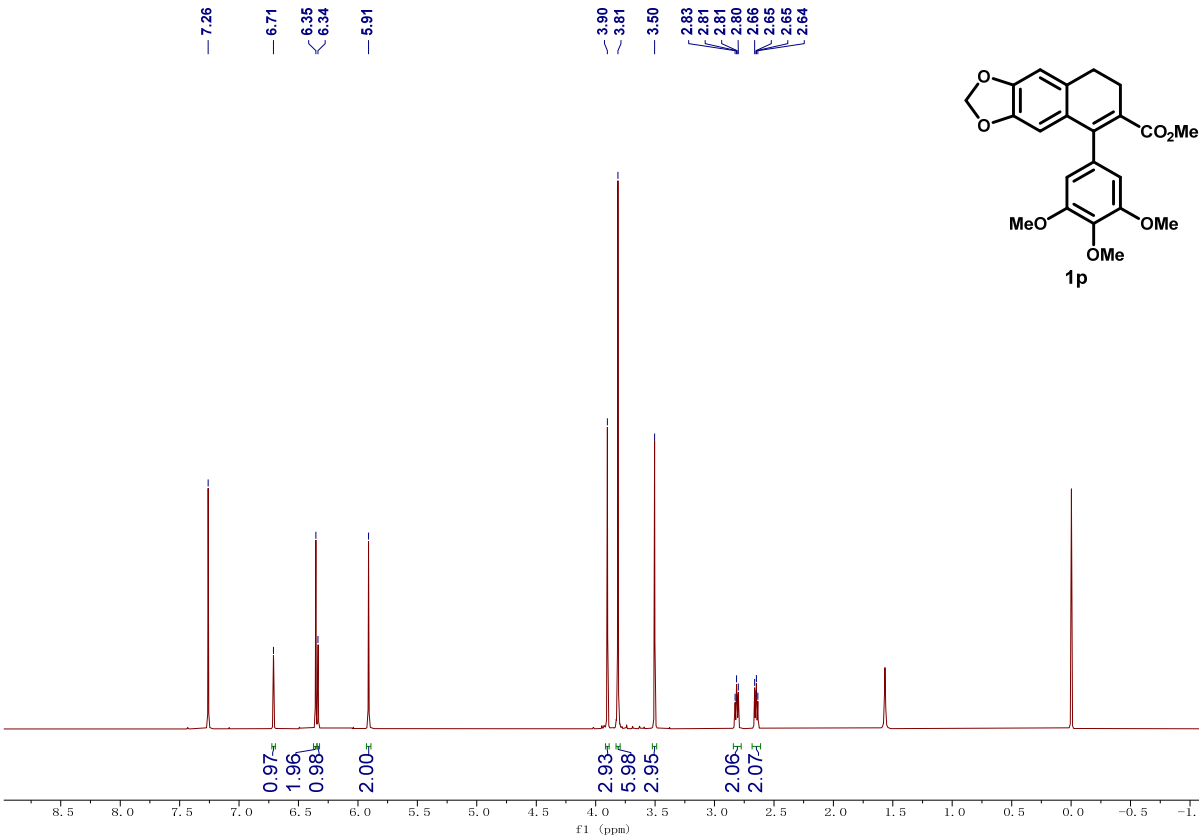


^{19}F NMR (471 MHz, $CDCl_3$)

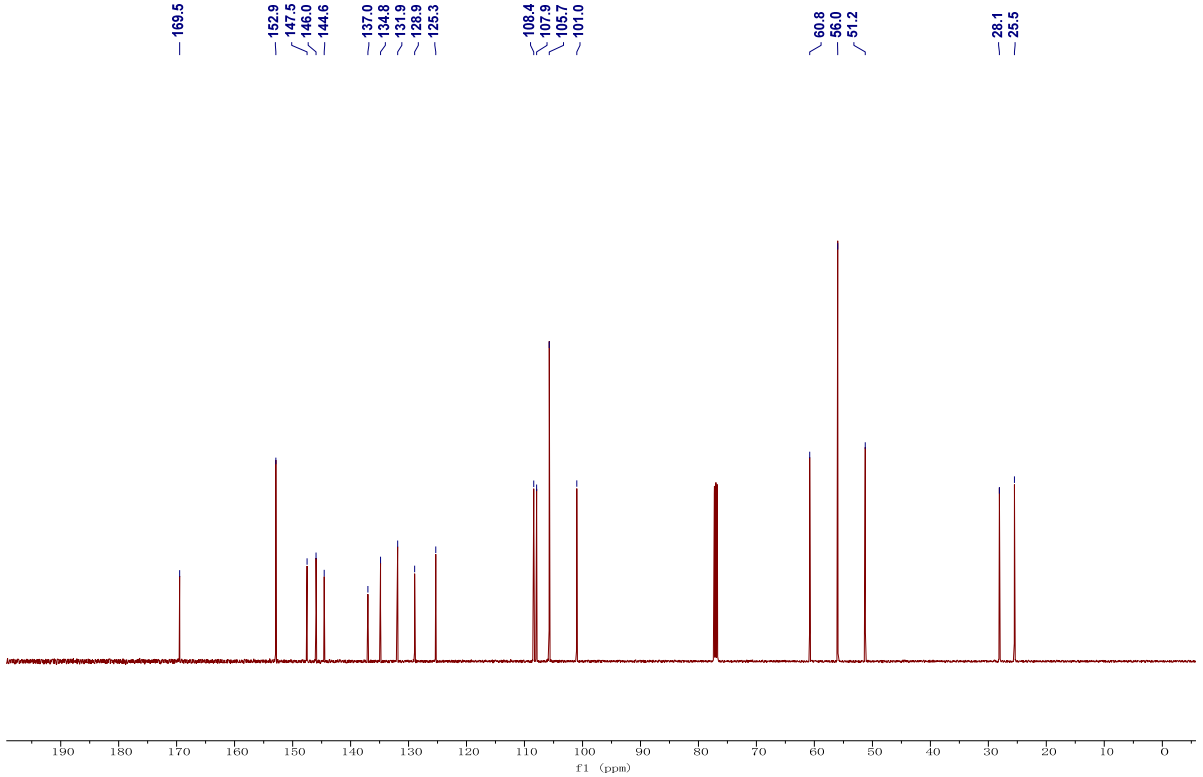


1p: Methyl 5-(3,4,5-trimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

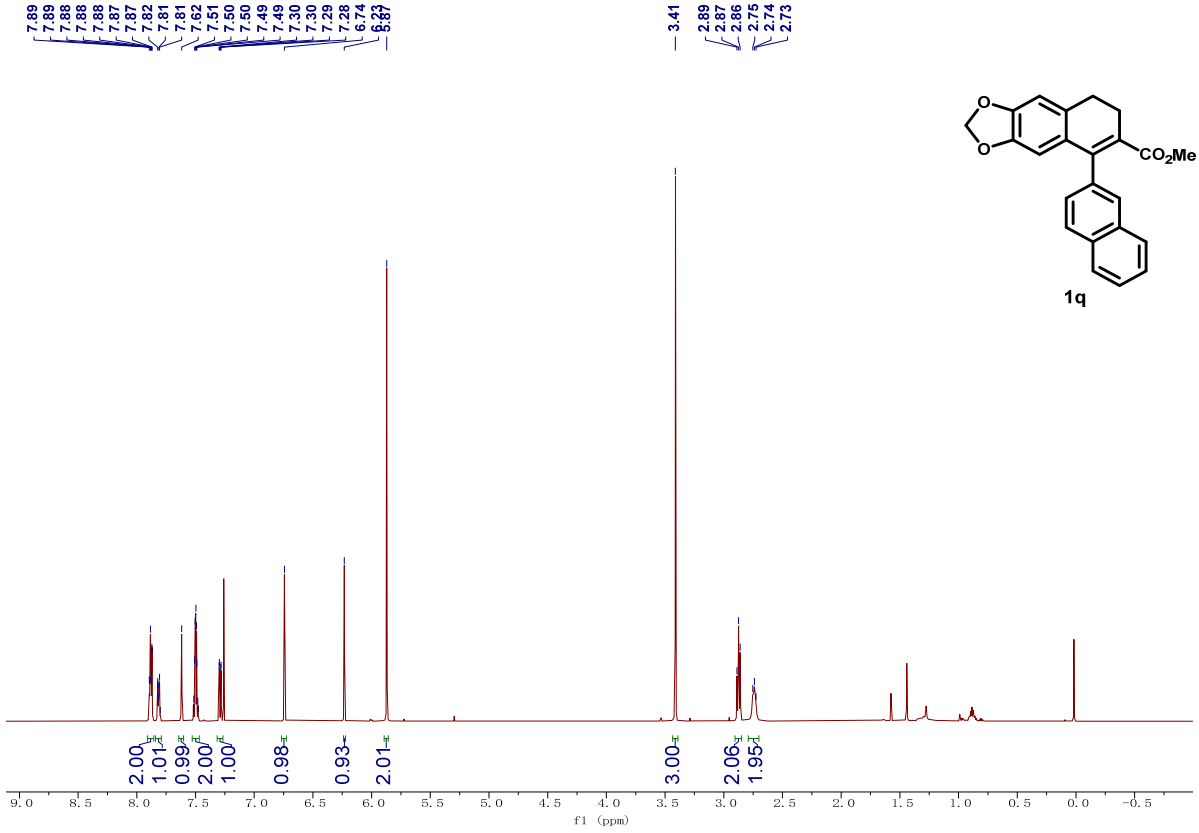


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

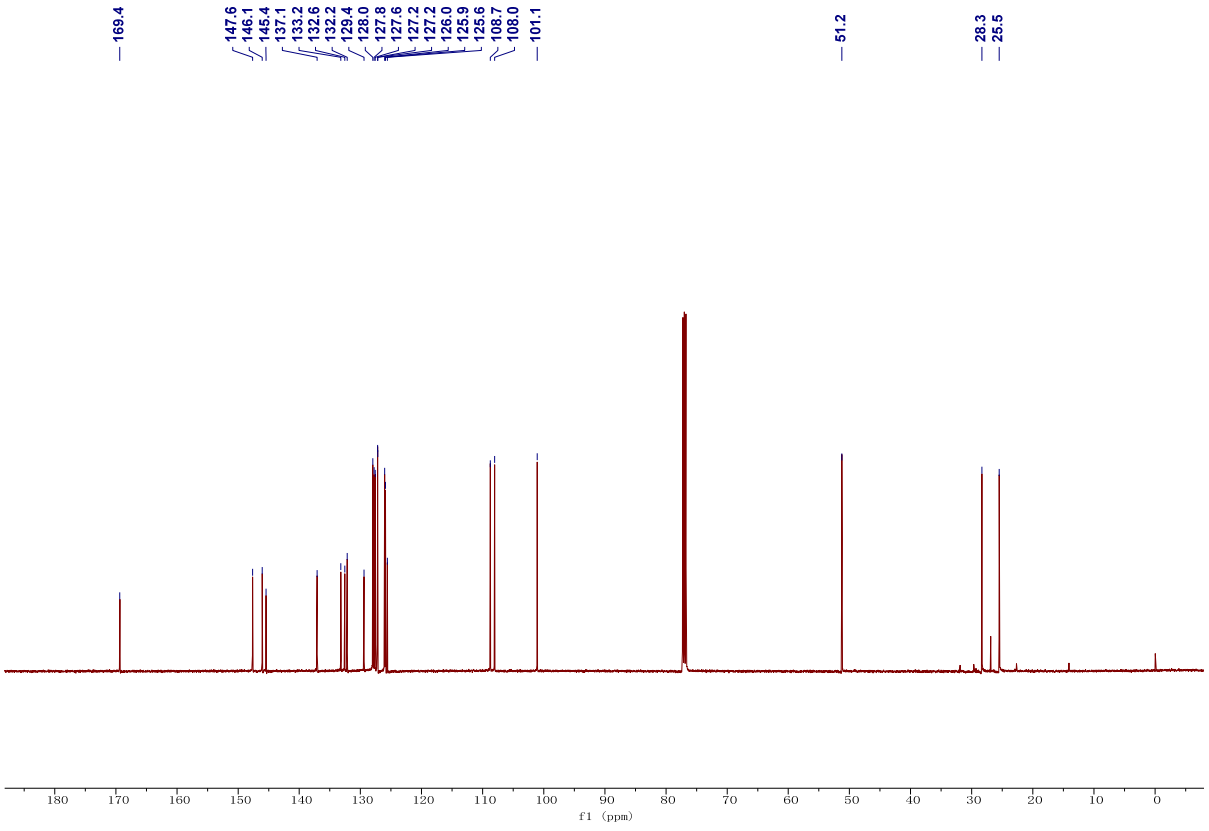


1q: Methyl 5-(naphthalen-2-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

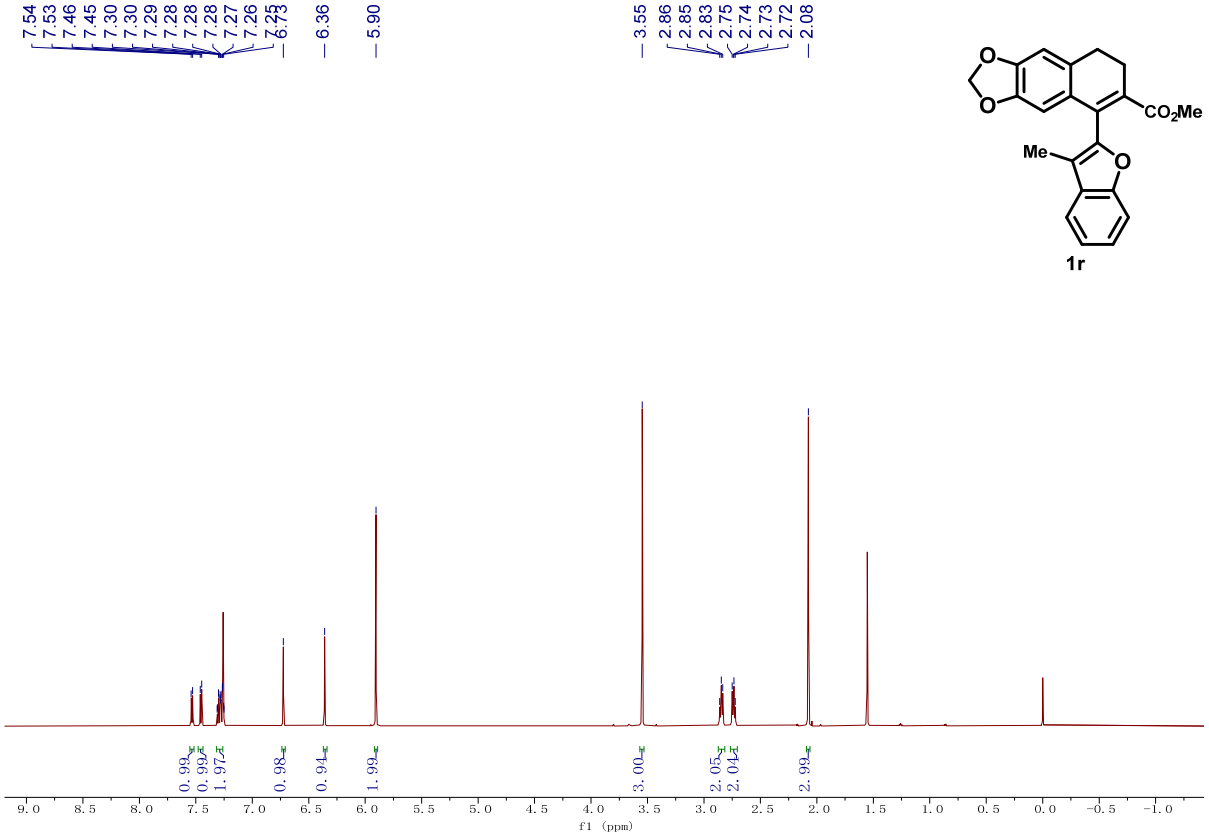


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

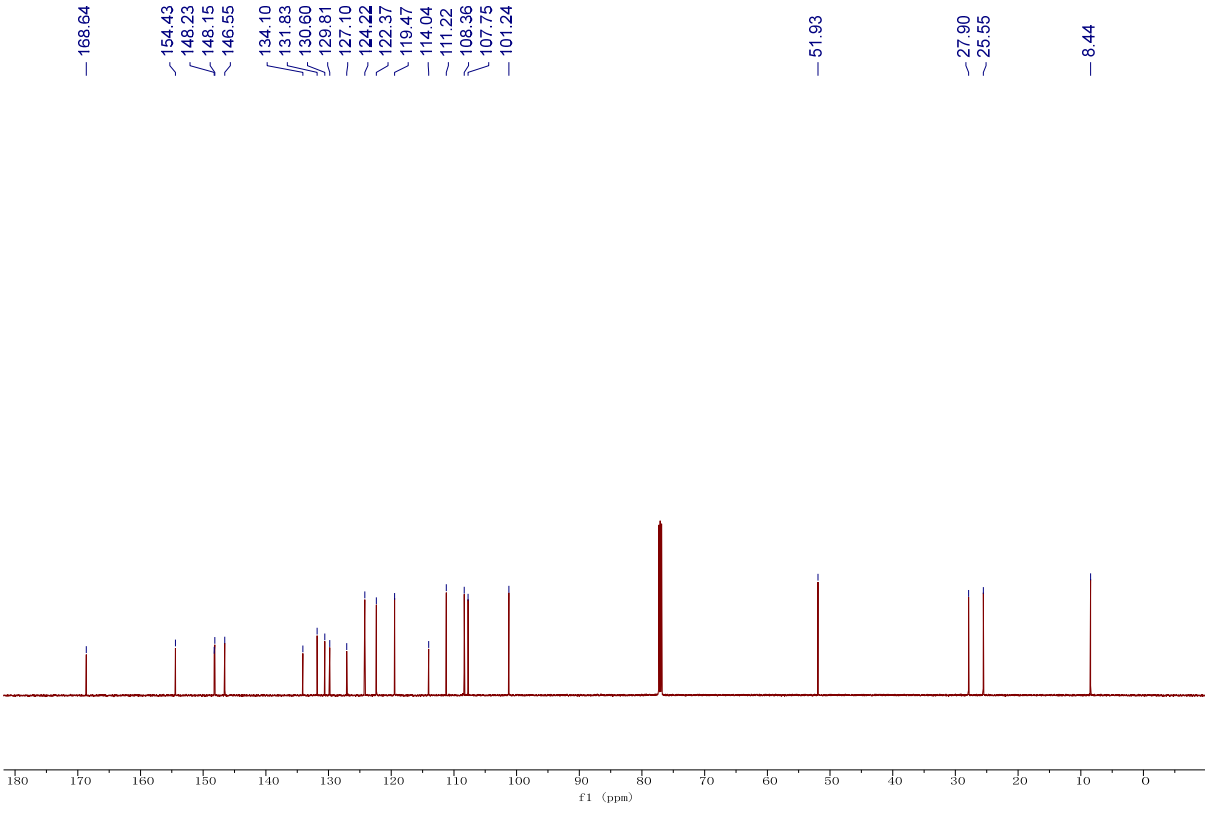


1r: Methyl 5-(3-methylbenzofuran-2-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

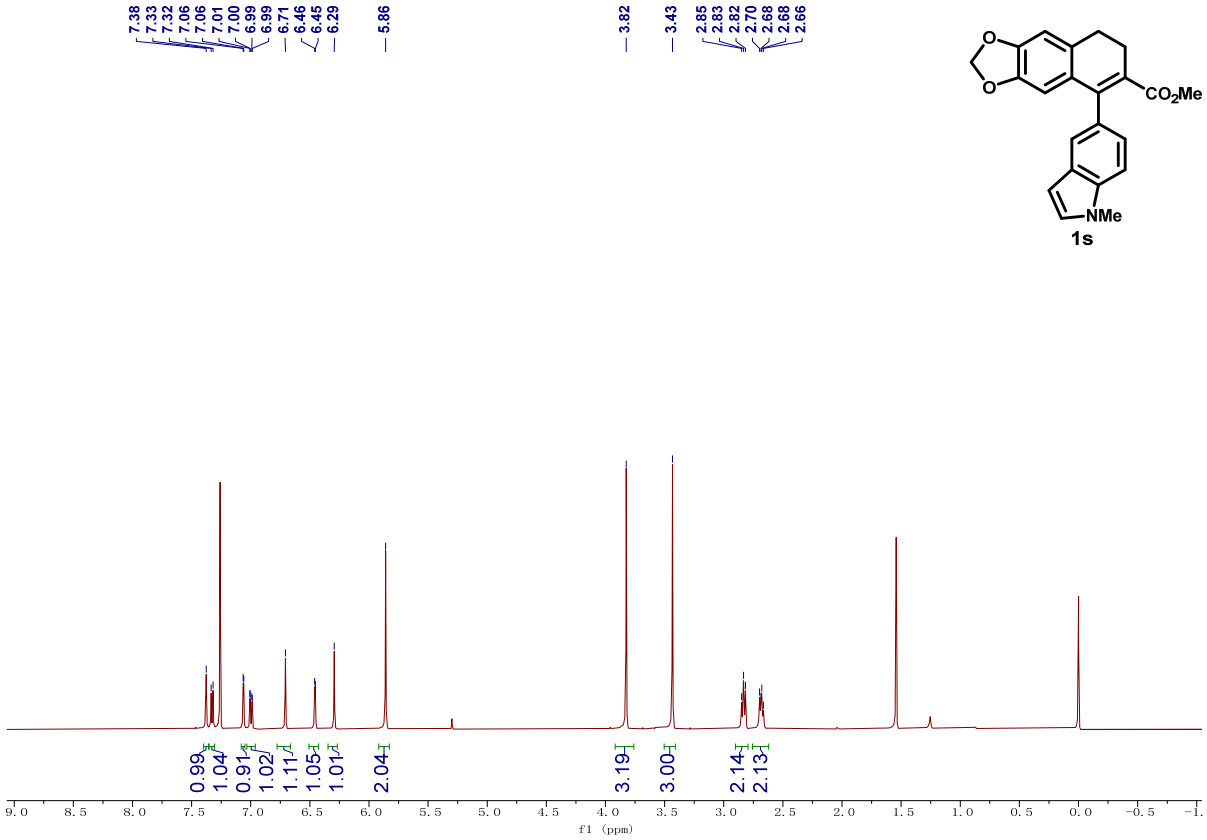


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

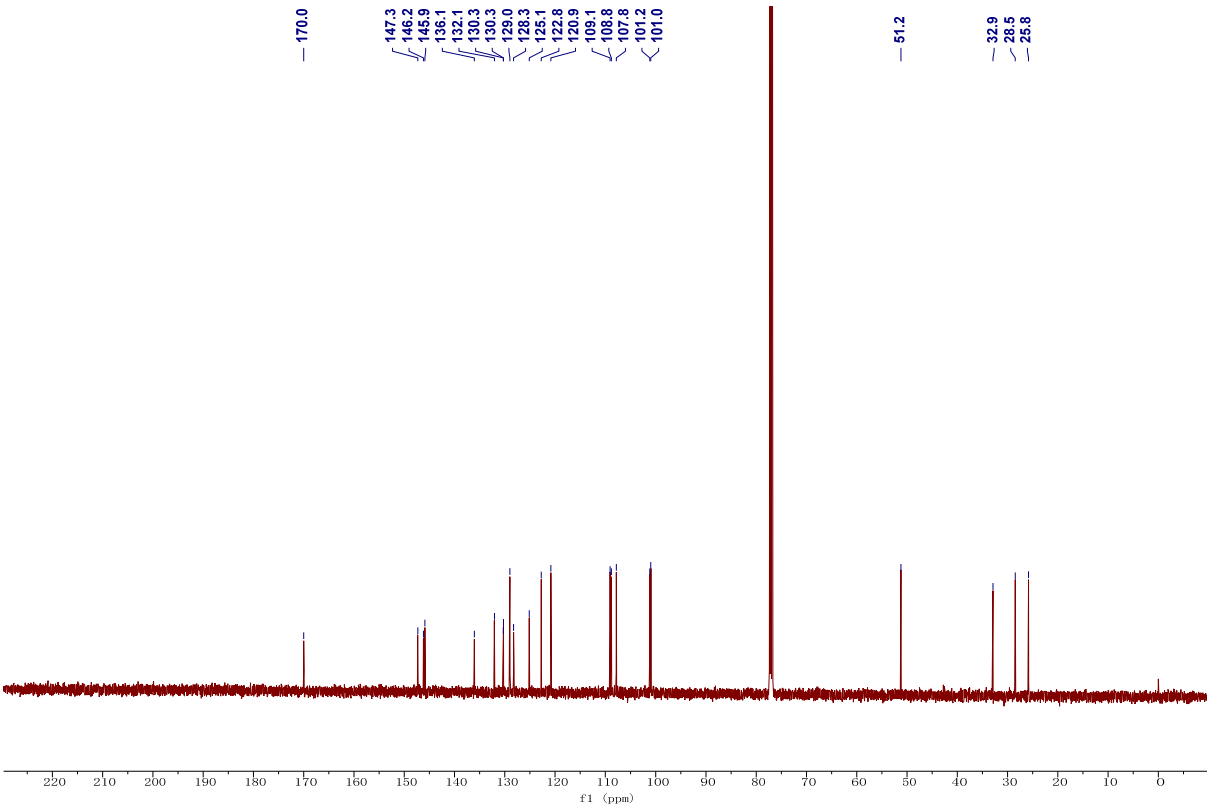


1s: Methyl 5-(1-methyl-1H-indol-5-yl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

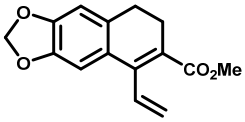


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

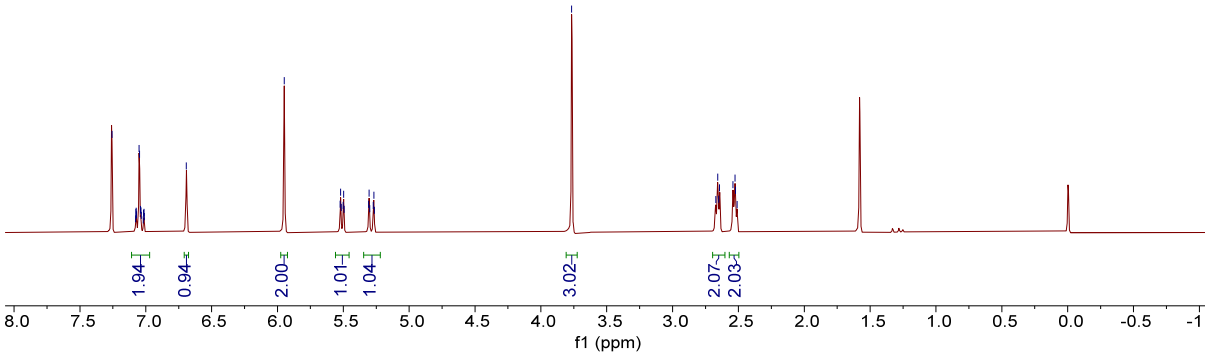


1t: Methyl 5-vinyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

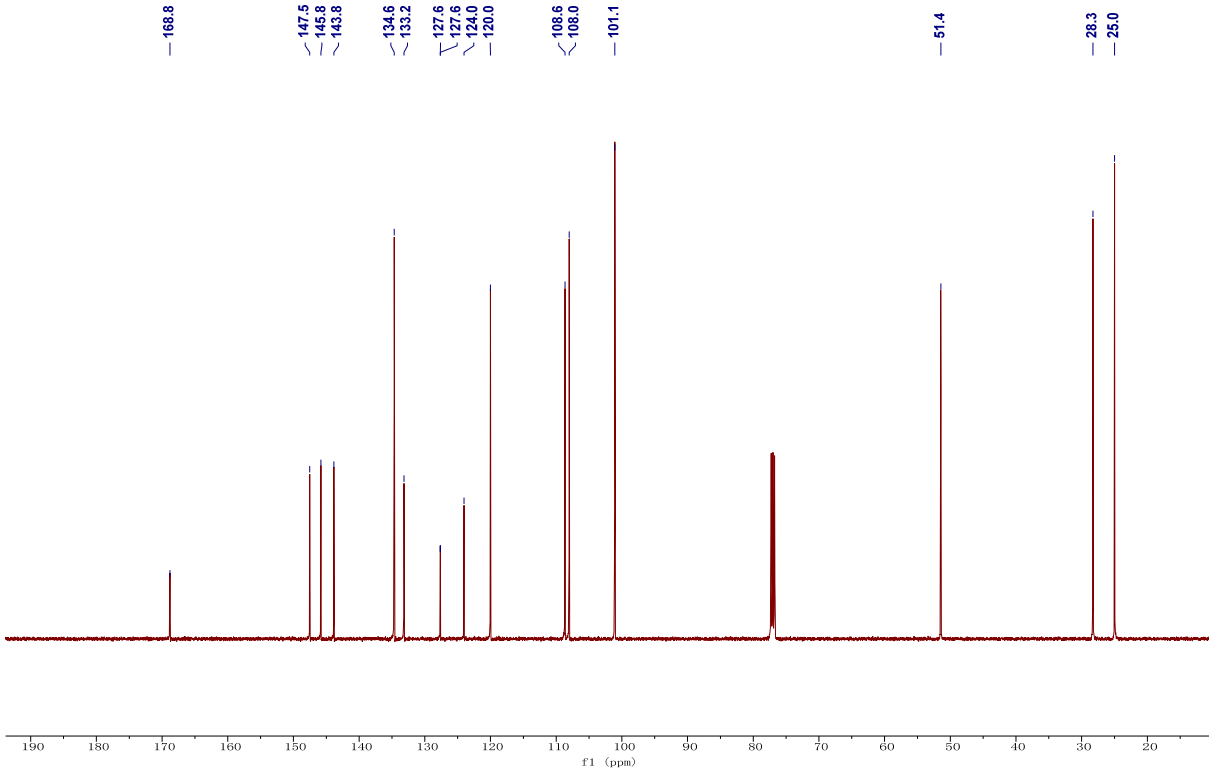
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



1t

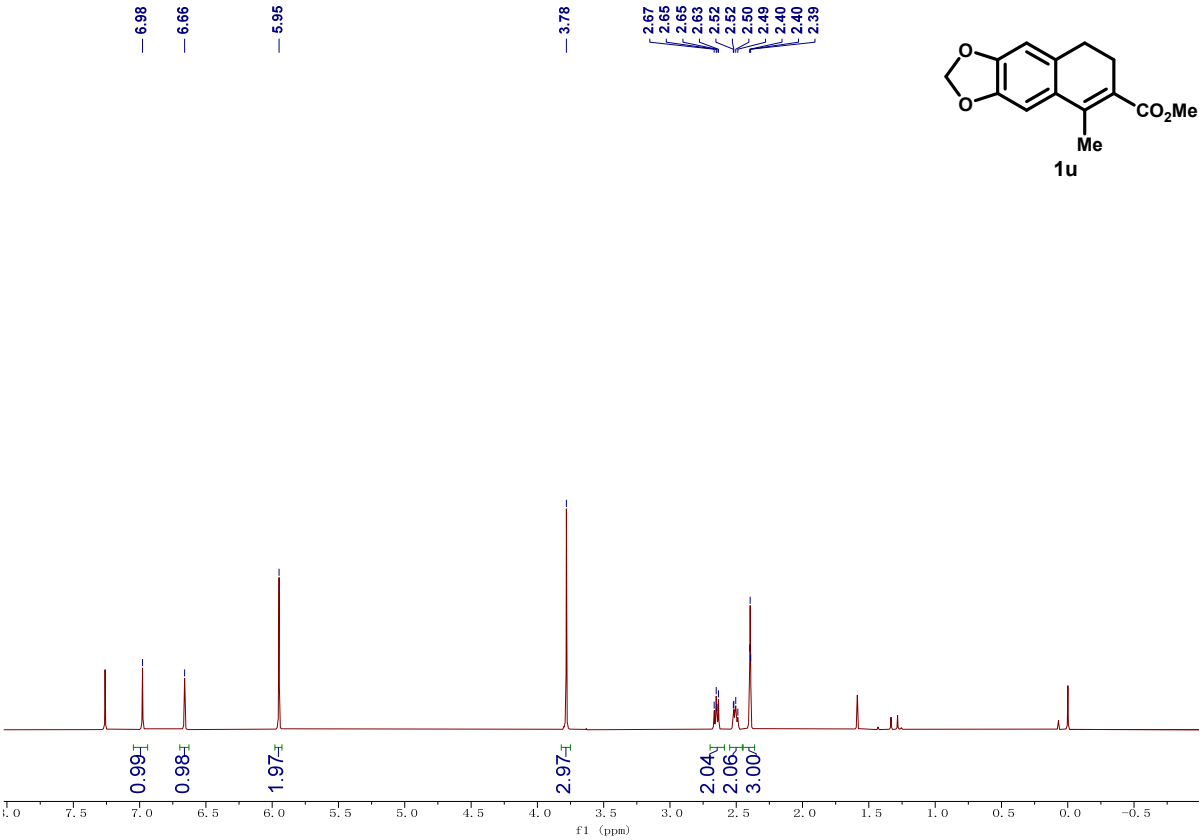


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

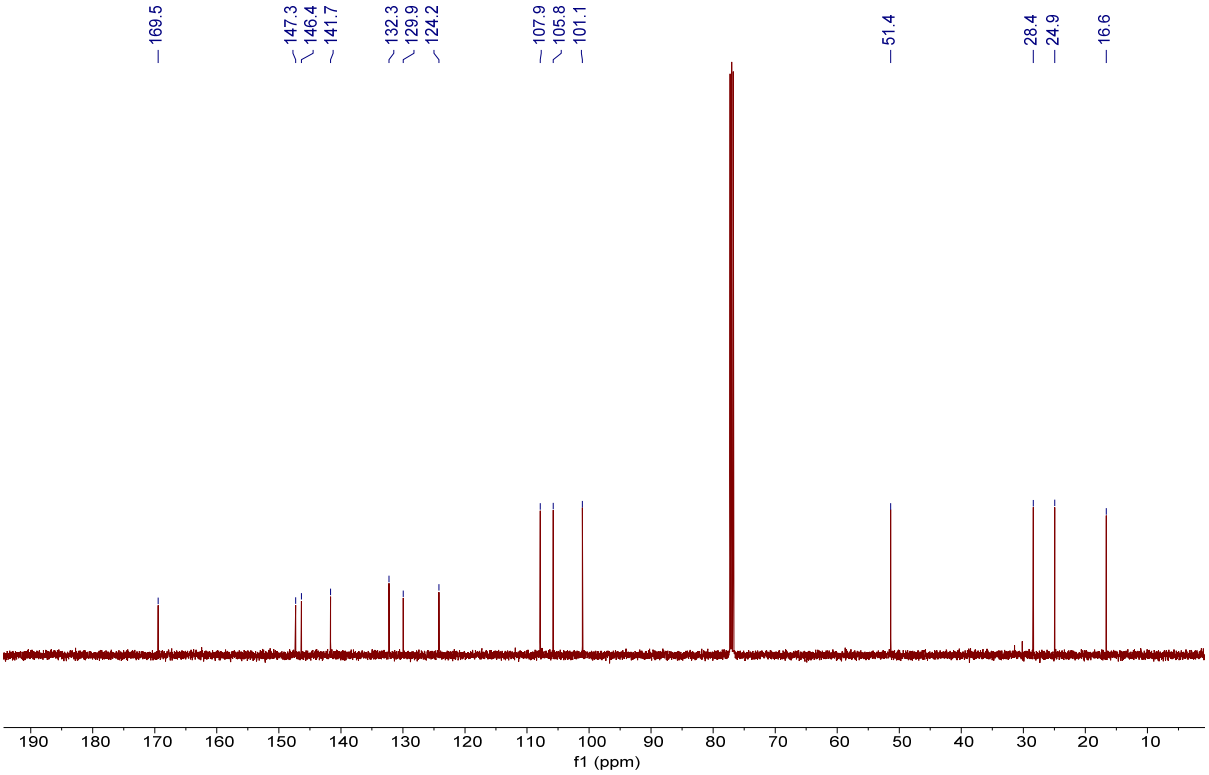


1u: Methyl 5-methyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

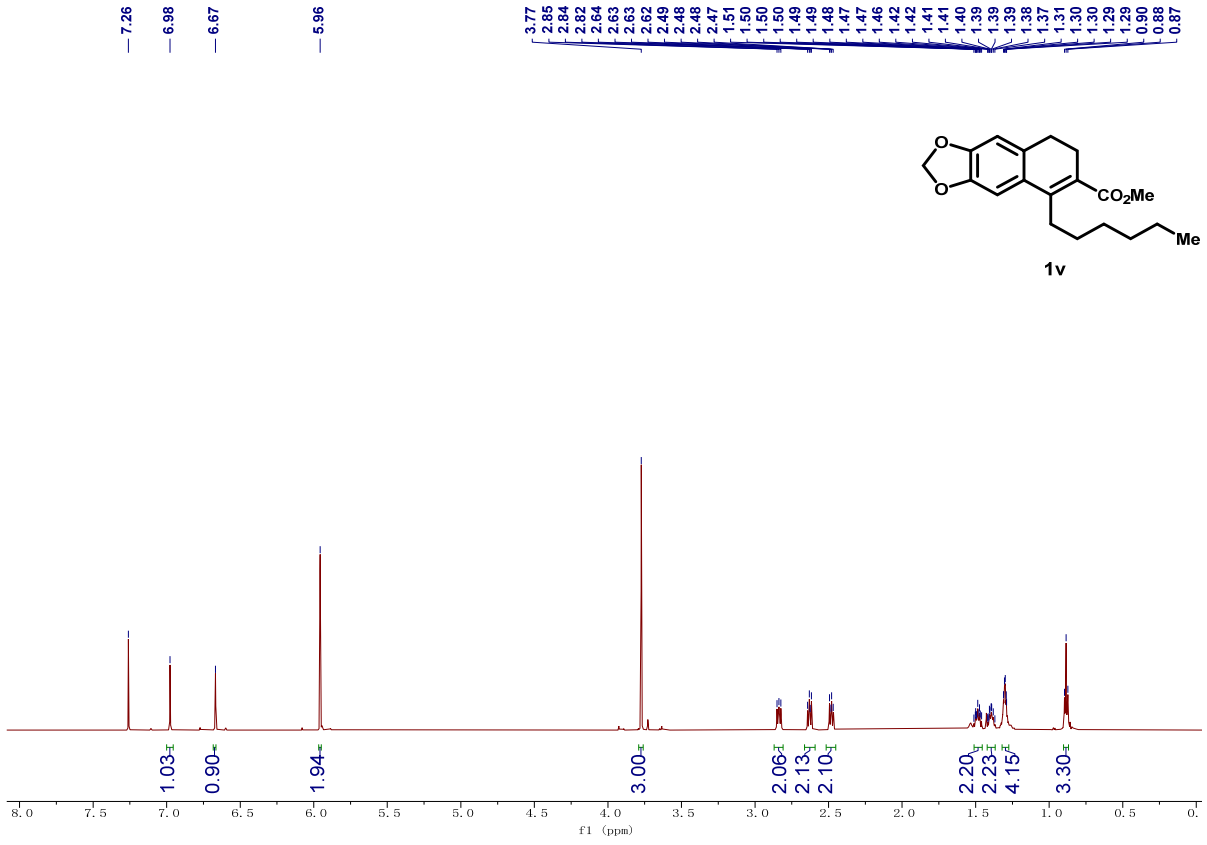


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

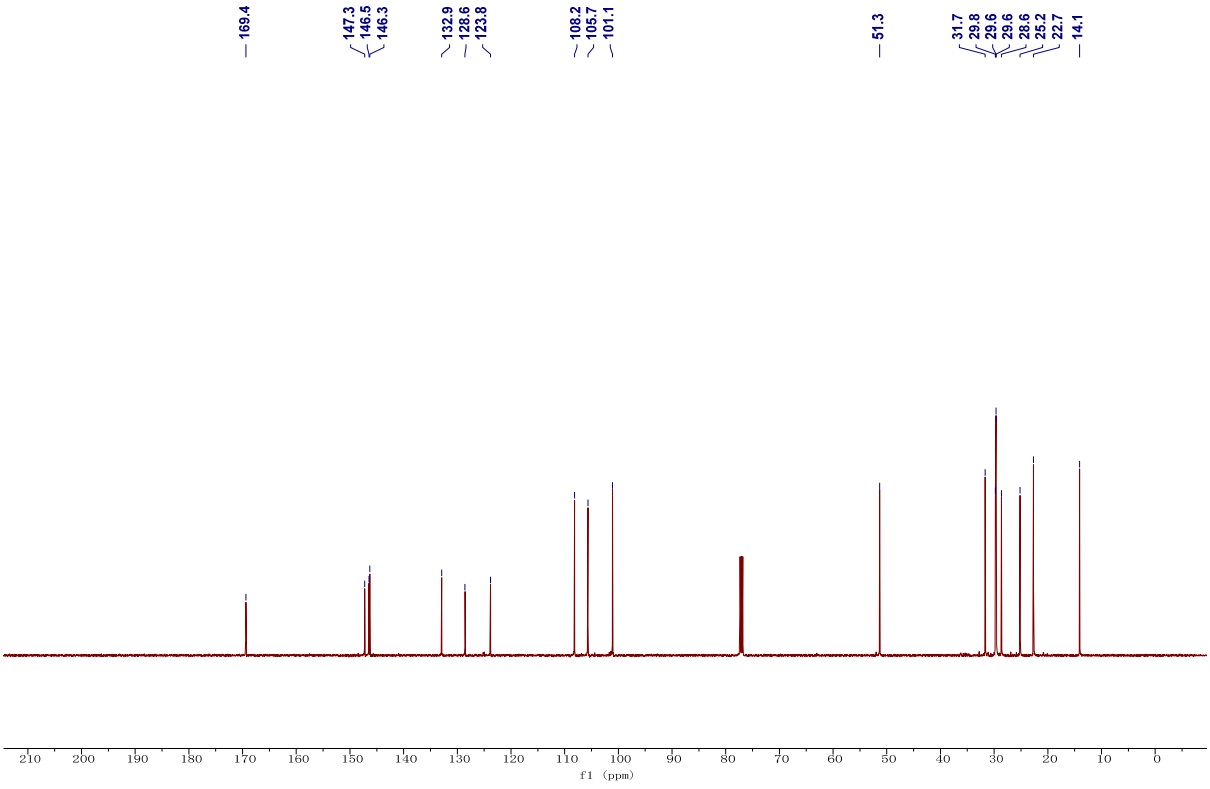


1v: Methyl 5-hexyl-7,8-dihydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

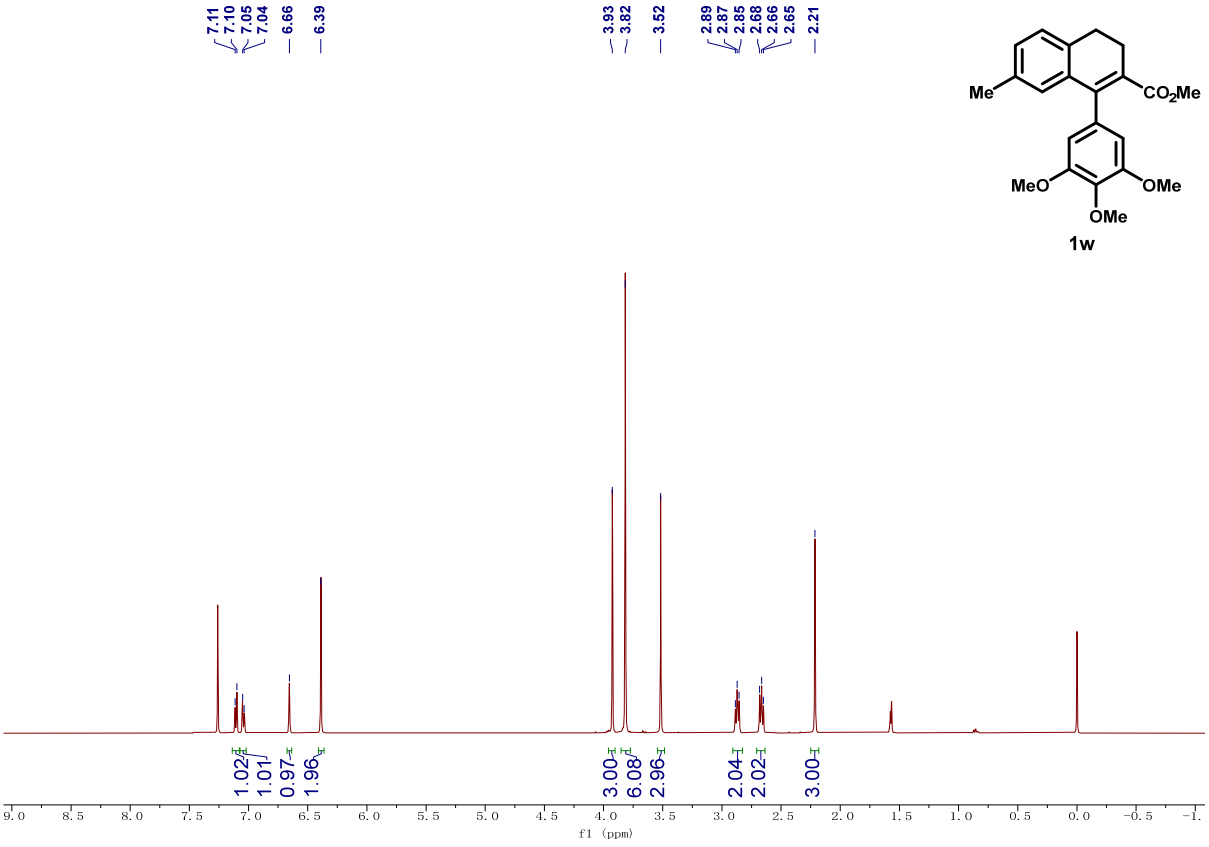


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

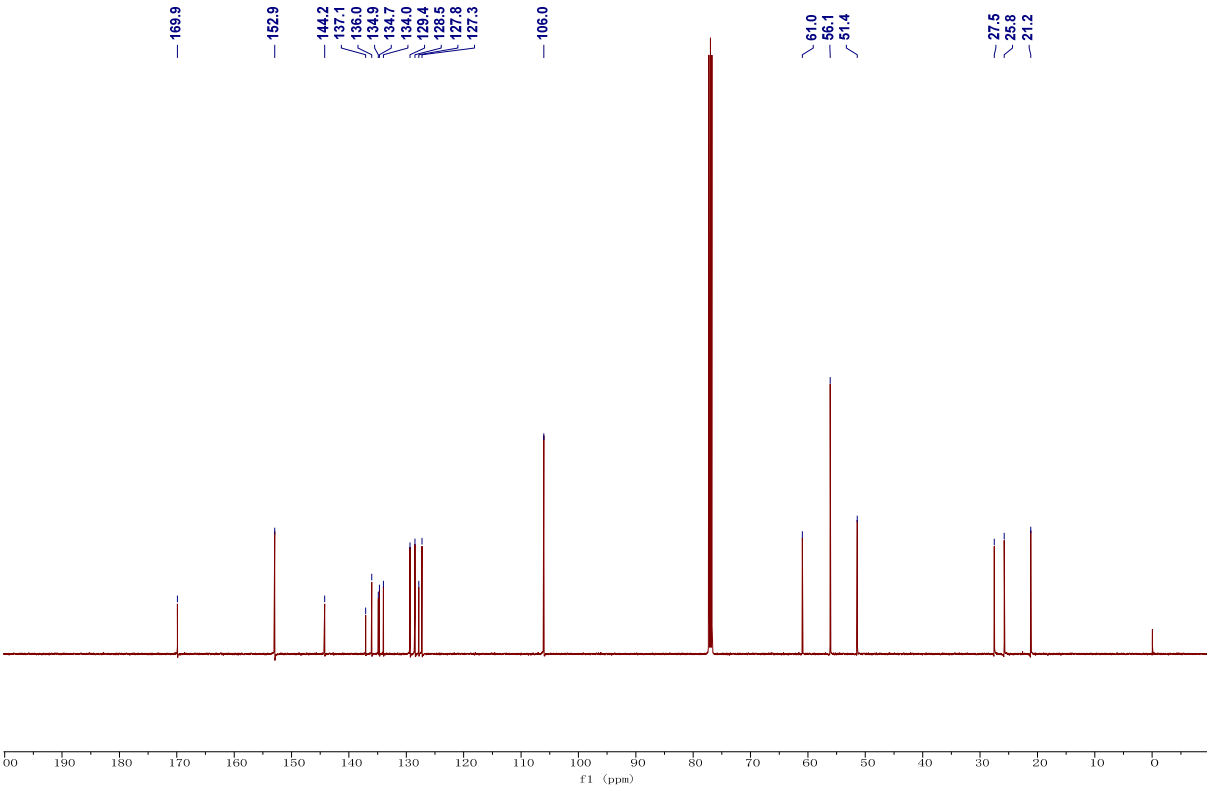


1w: Methyl 7-methyl-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

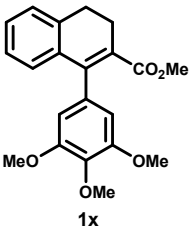


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

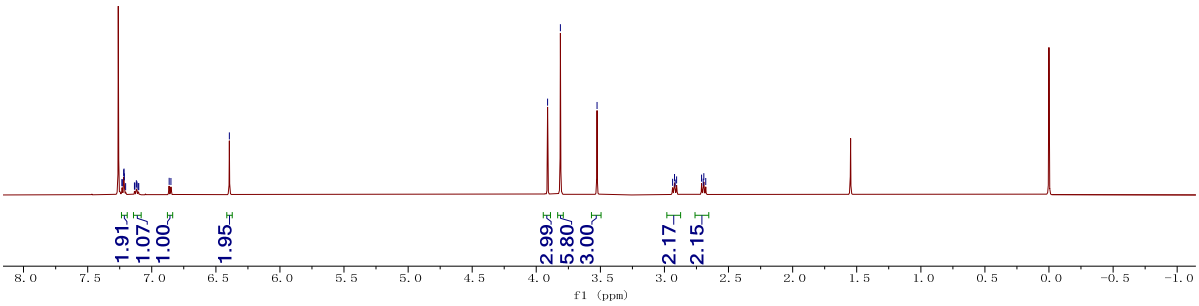


1x: Methyl 1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

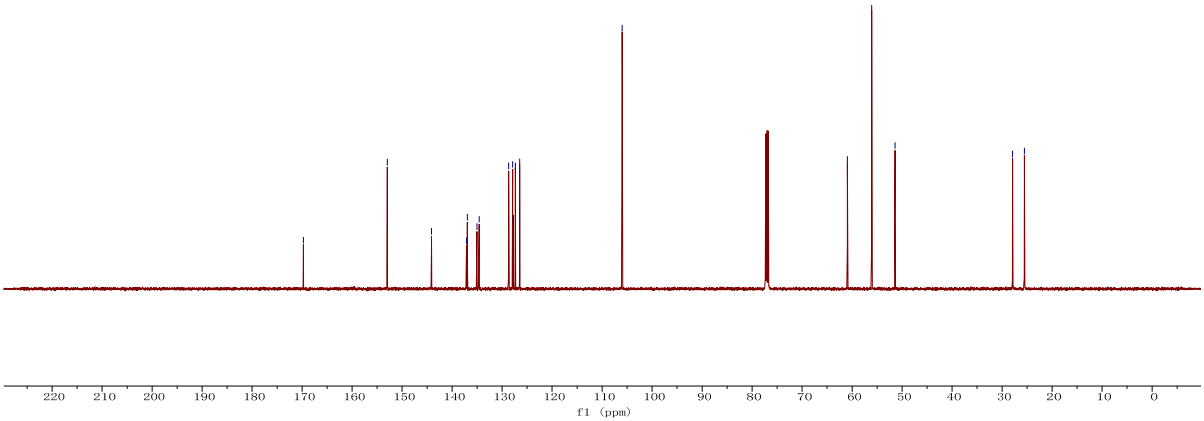
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



1x

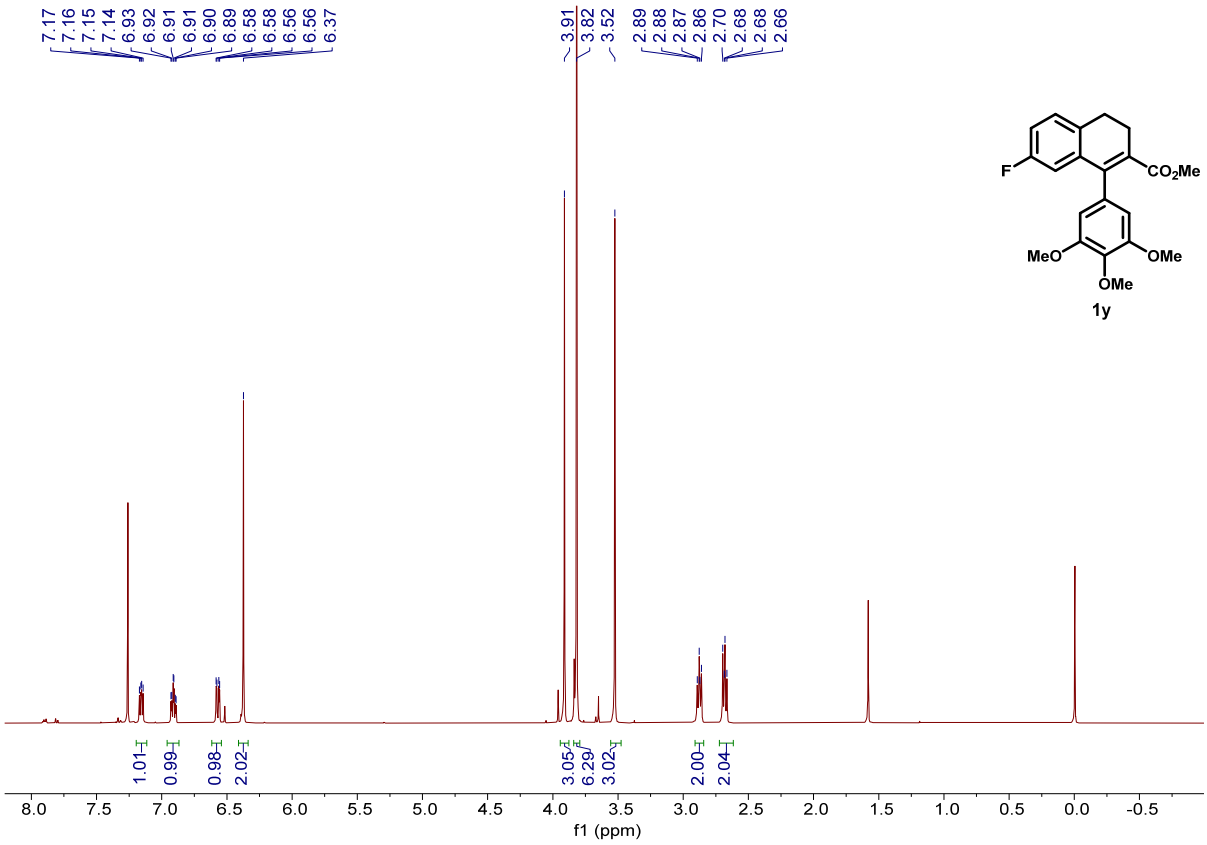


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

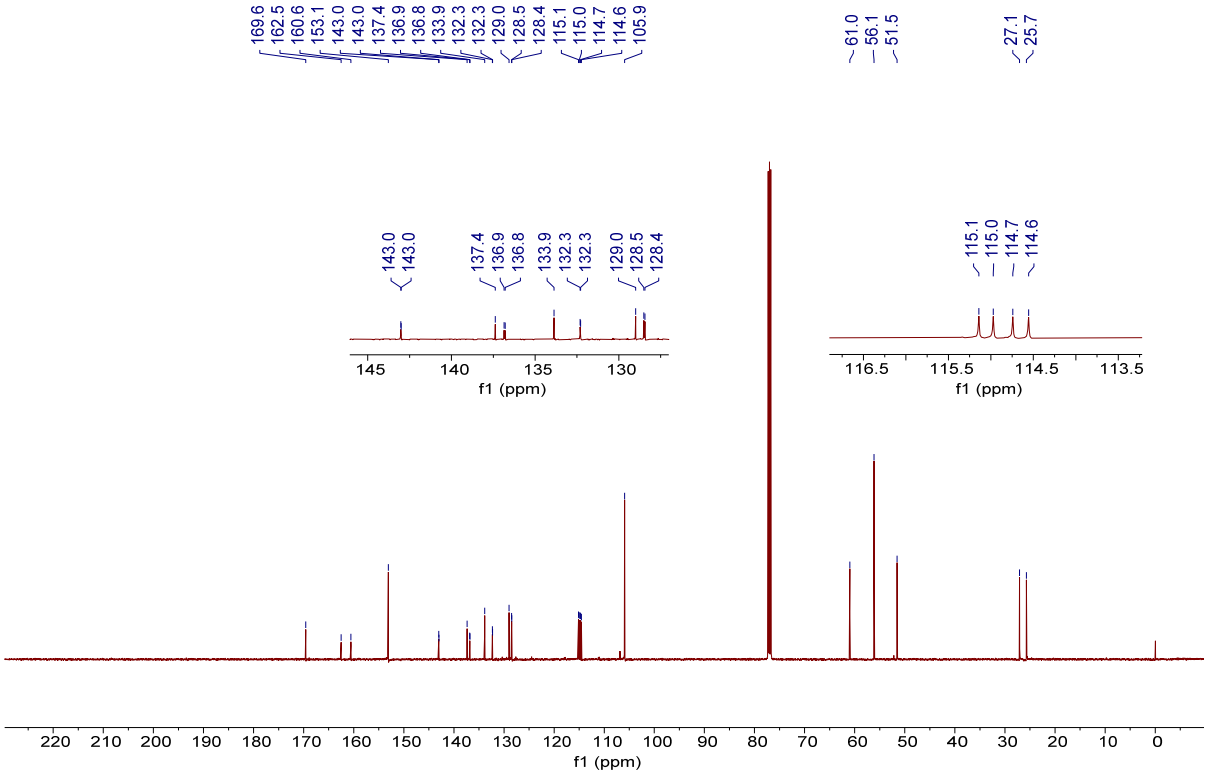


1y: Methyl 7-fluoro-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

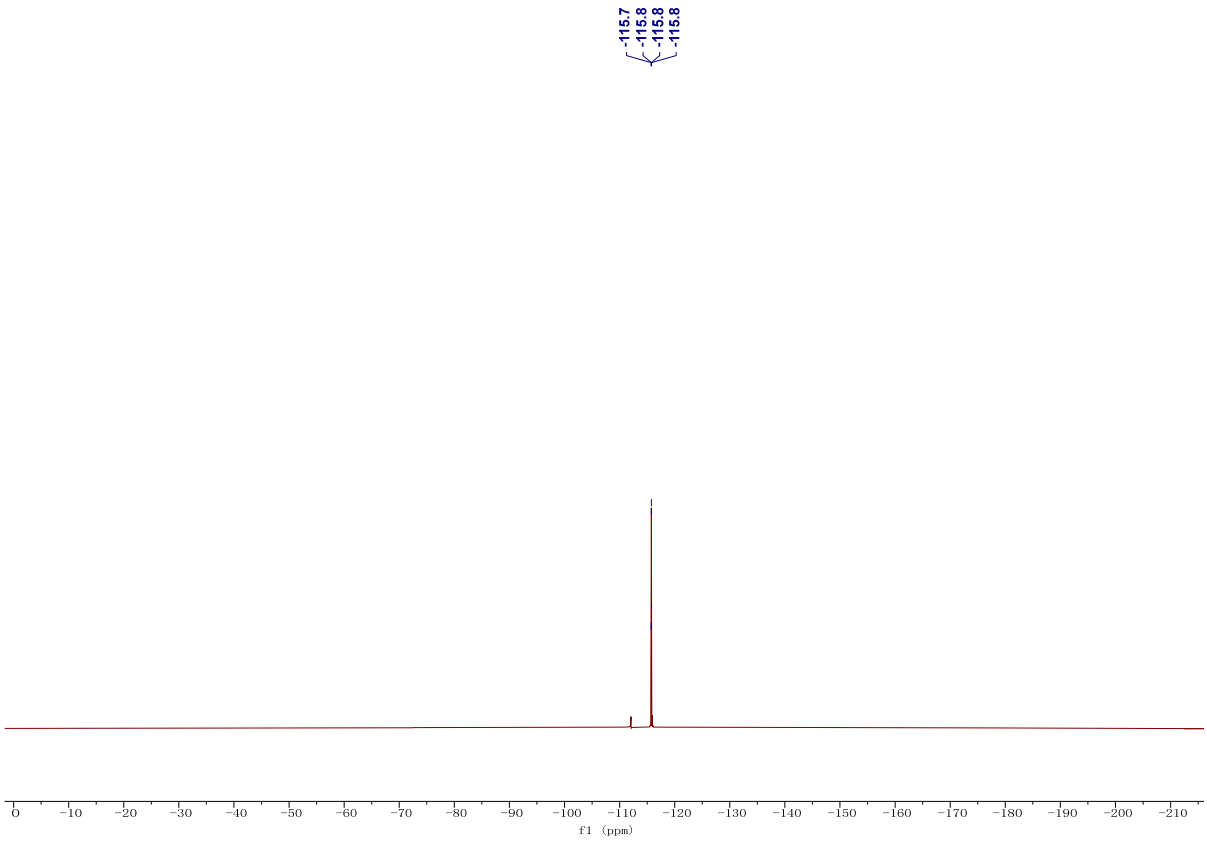
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

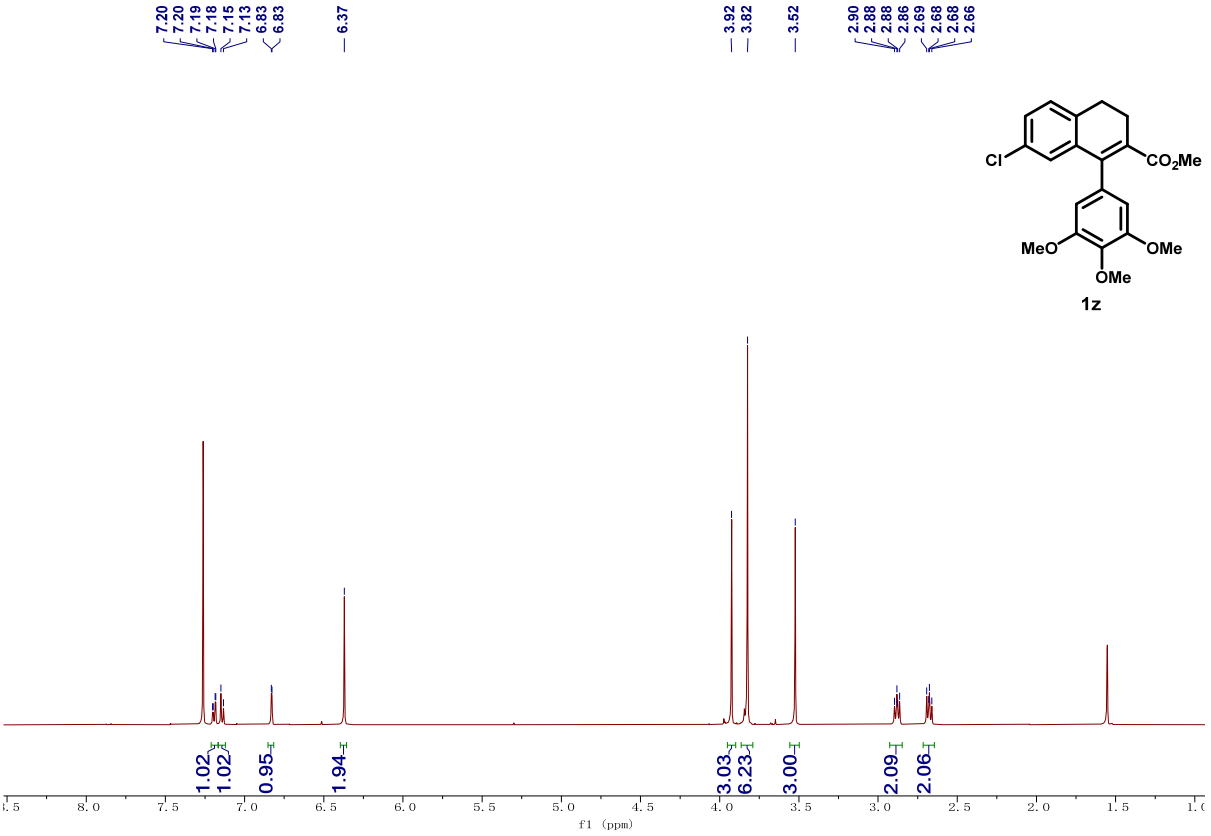


^{19}F NMR (471 MHz, $CDCl_3$)

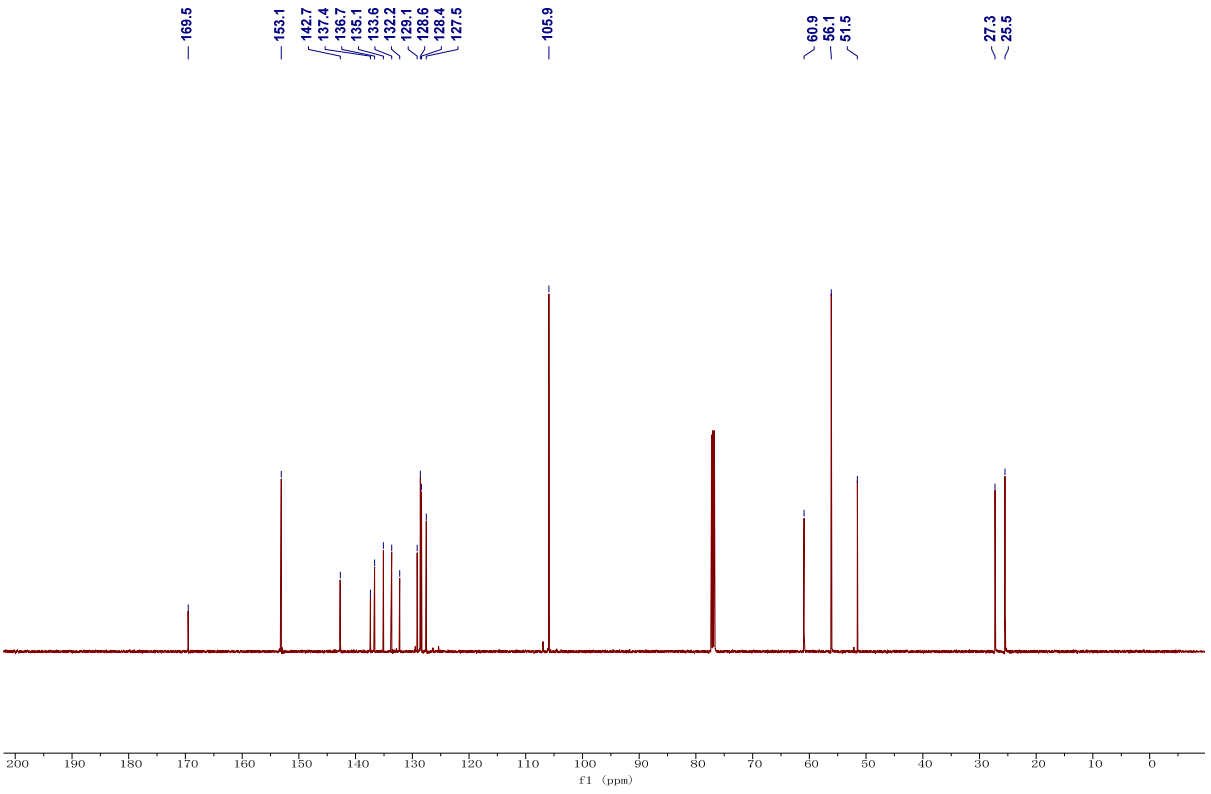


1z: Methyl 7-chloro-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

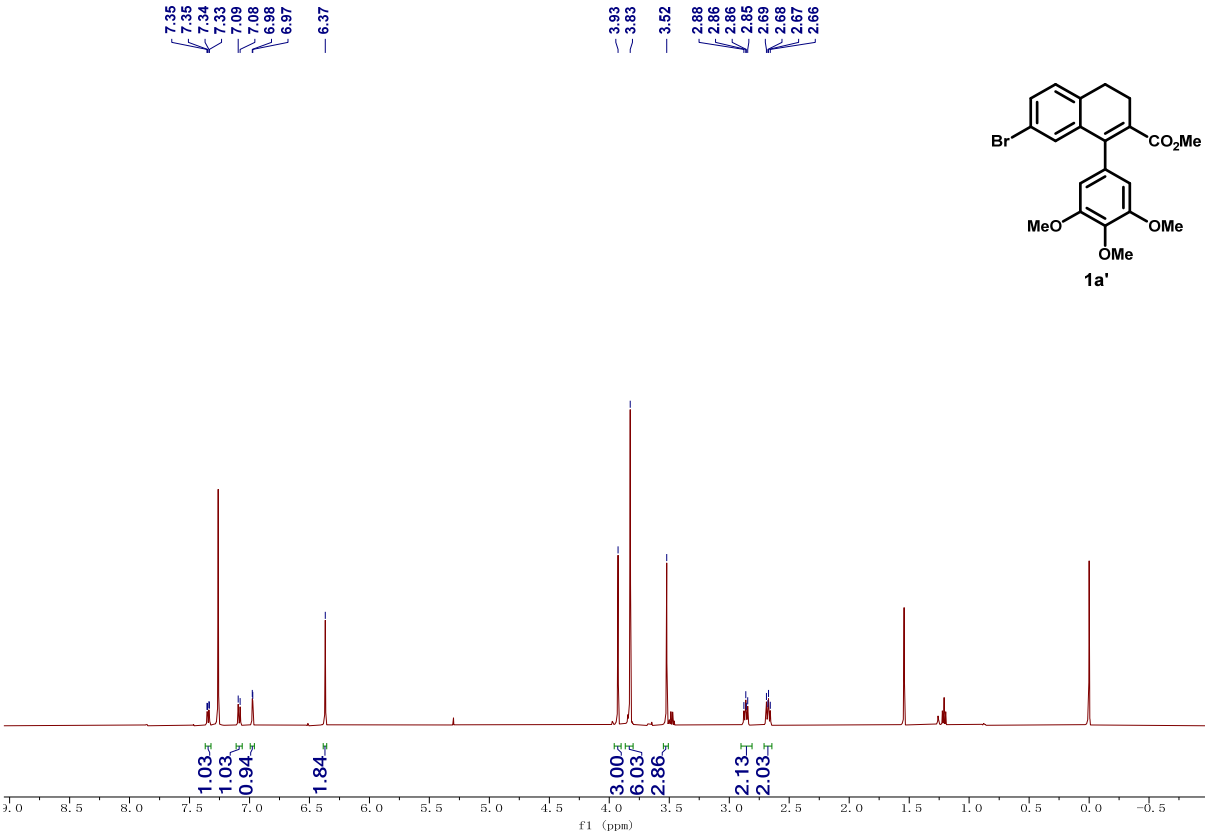


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

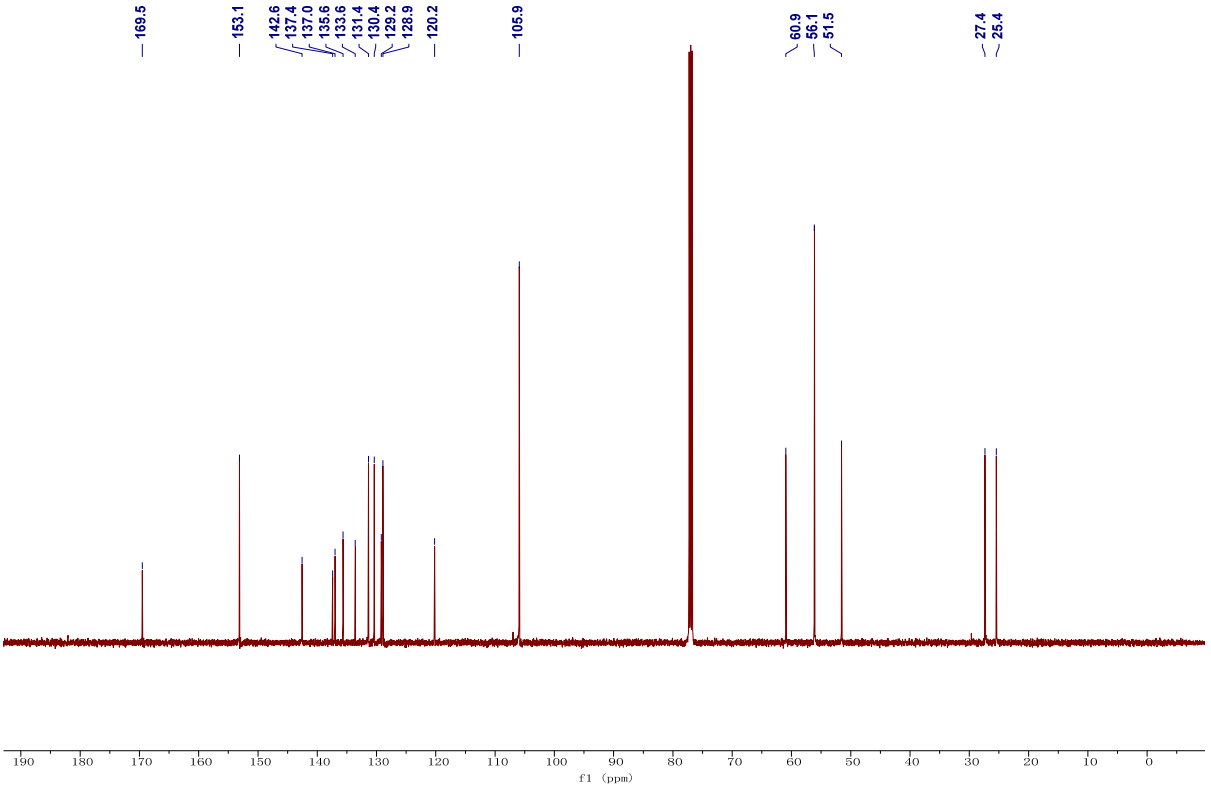


1a': Methyl 7-bromo-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

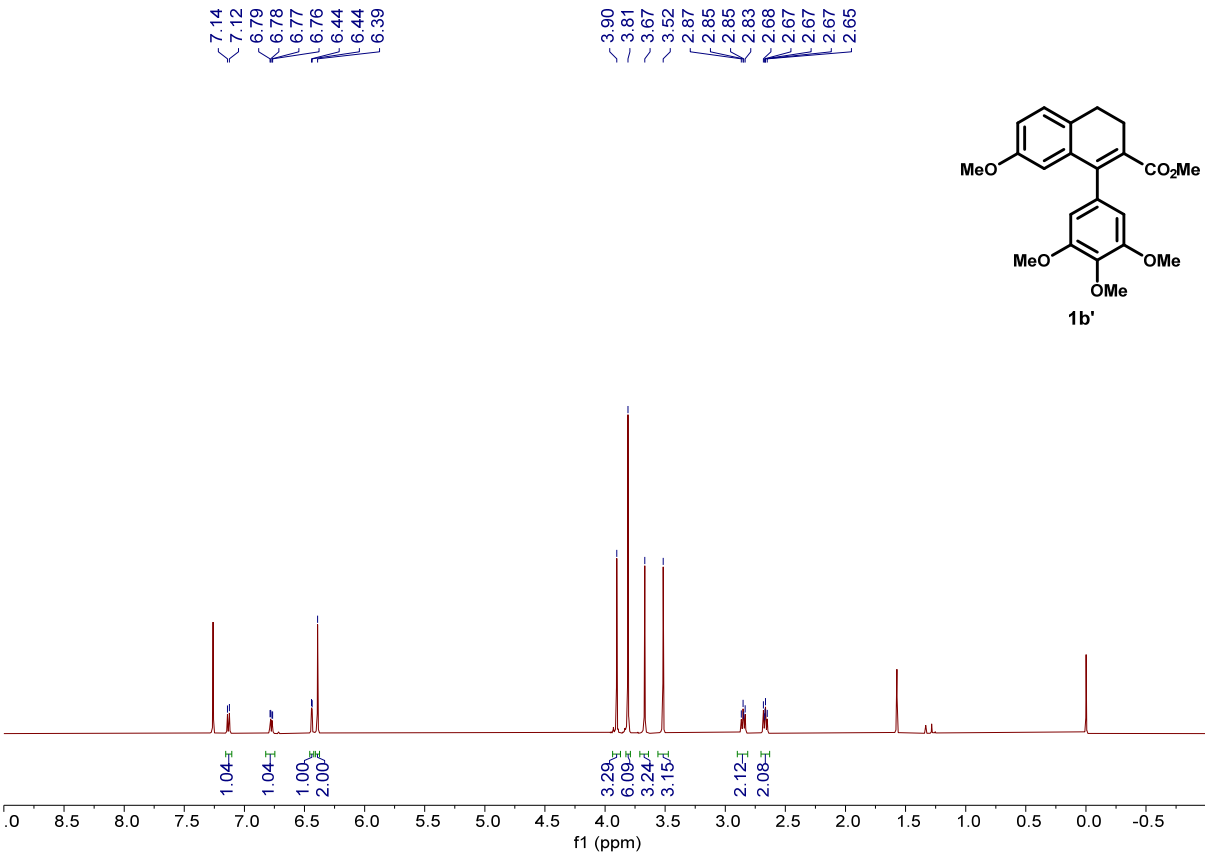


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

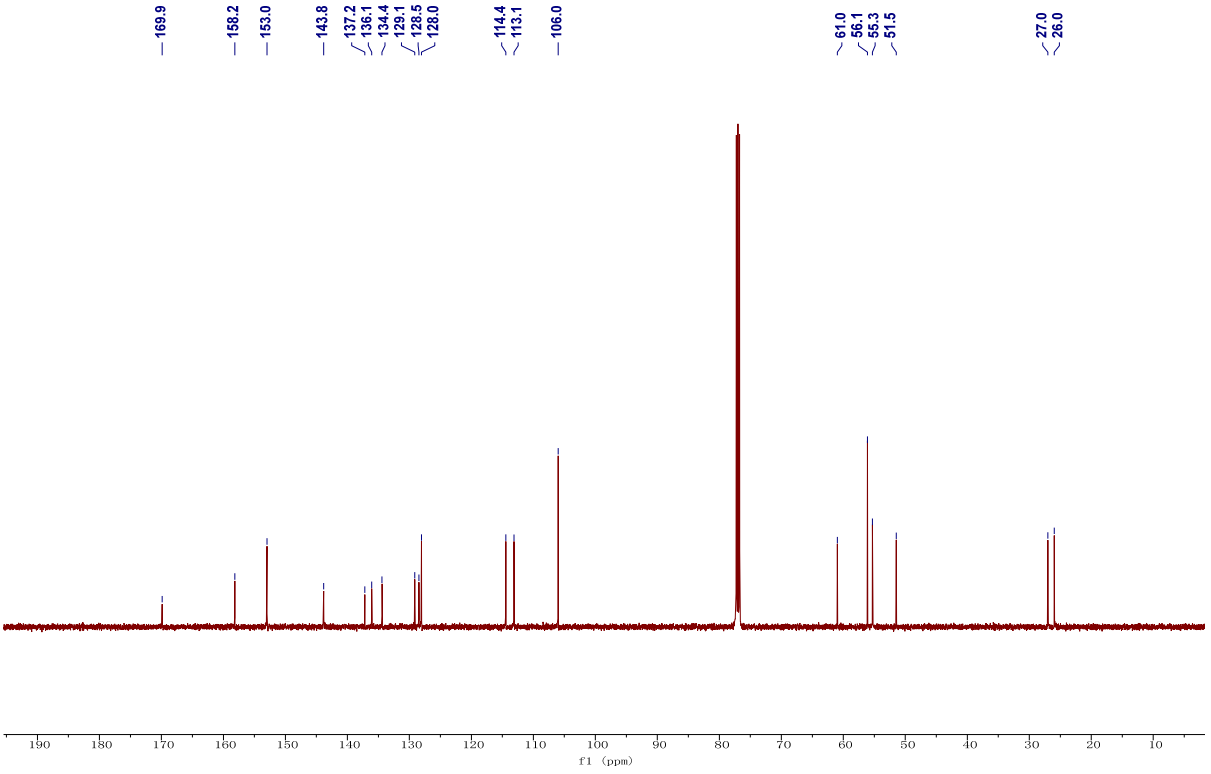


1b': Methyl 7-methoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

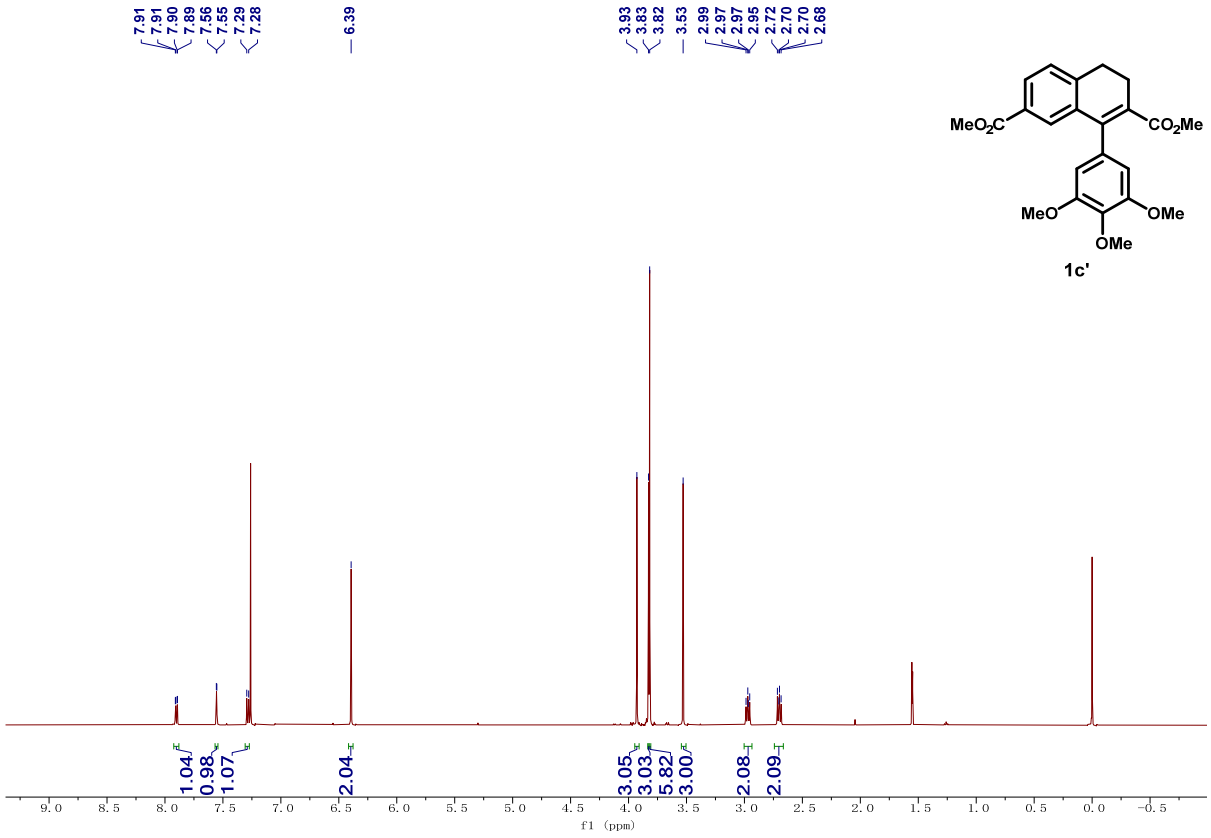


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

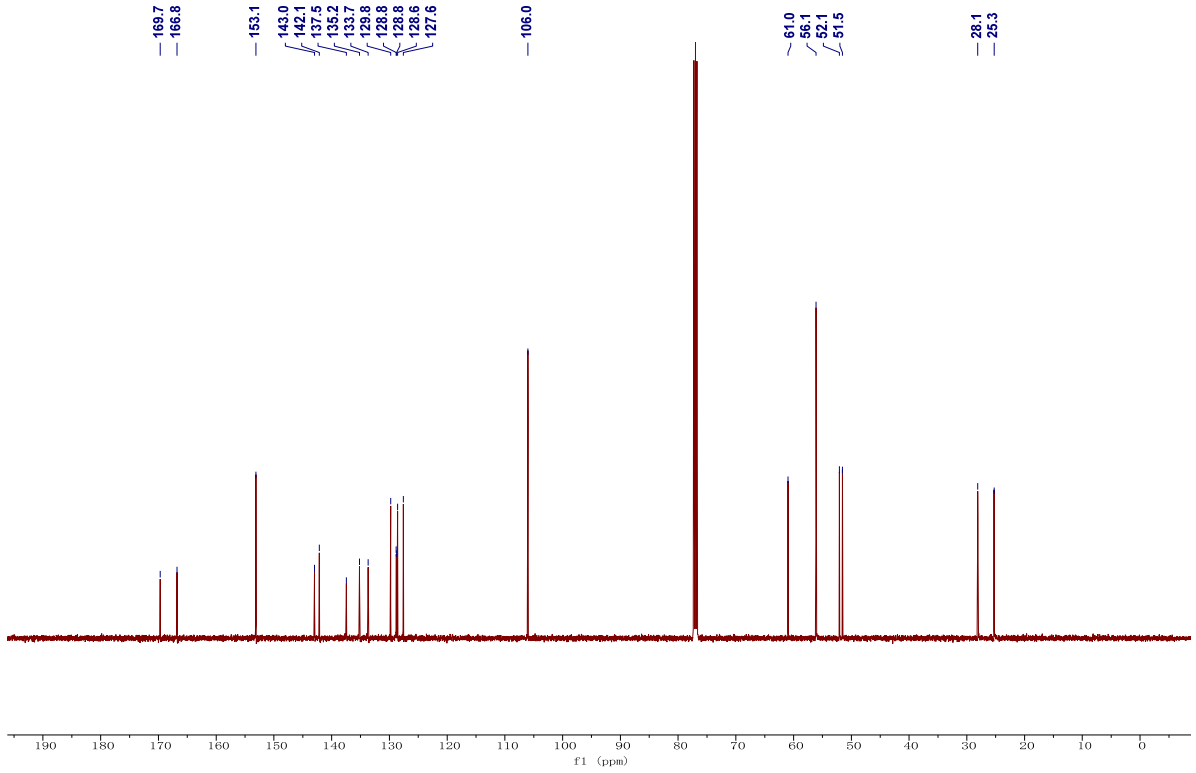


1c': Dimethyl 1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2,7-dicarboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

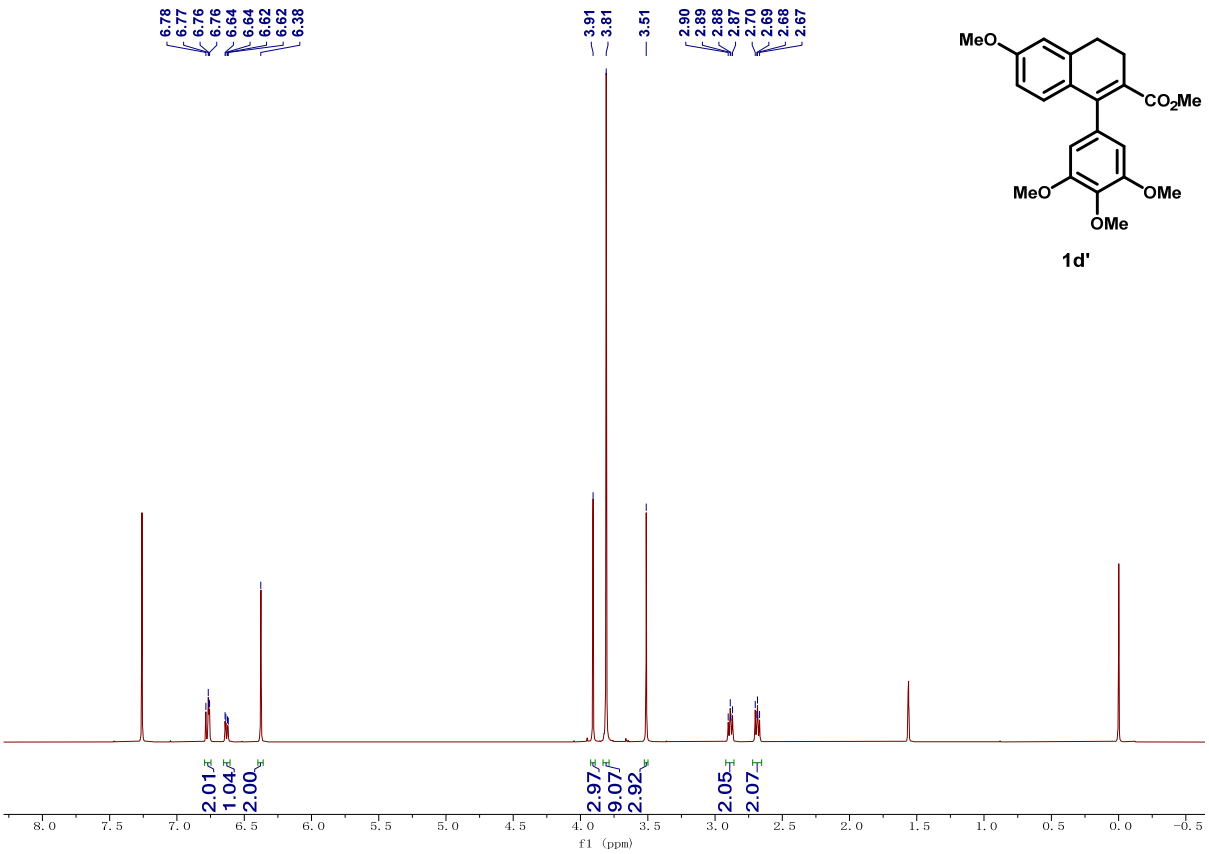


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

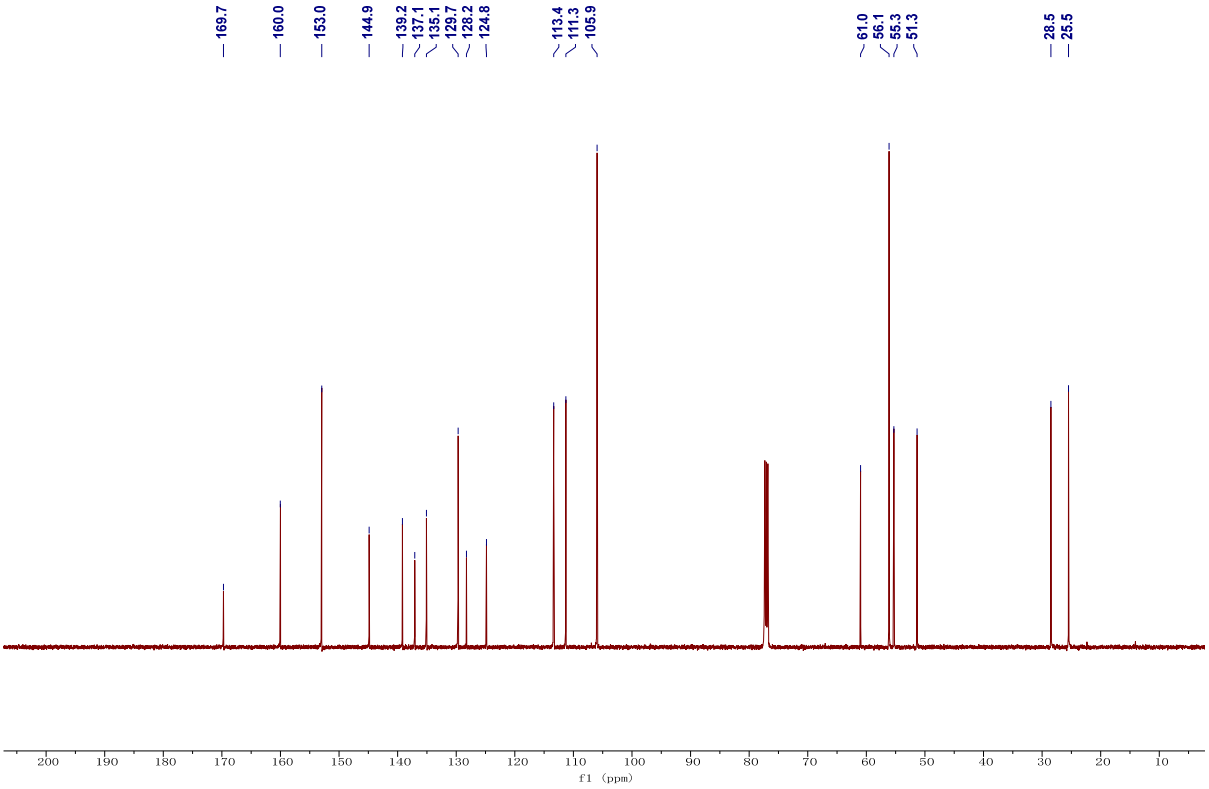


1d': Methyl 6-methoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

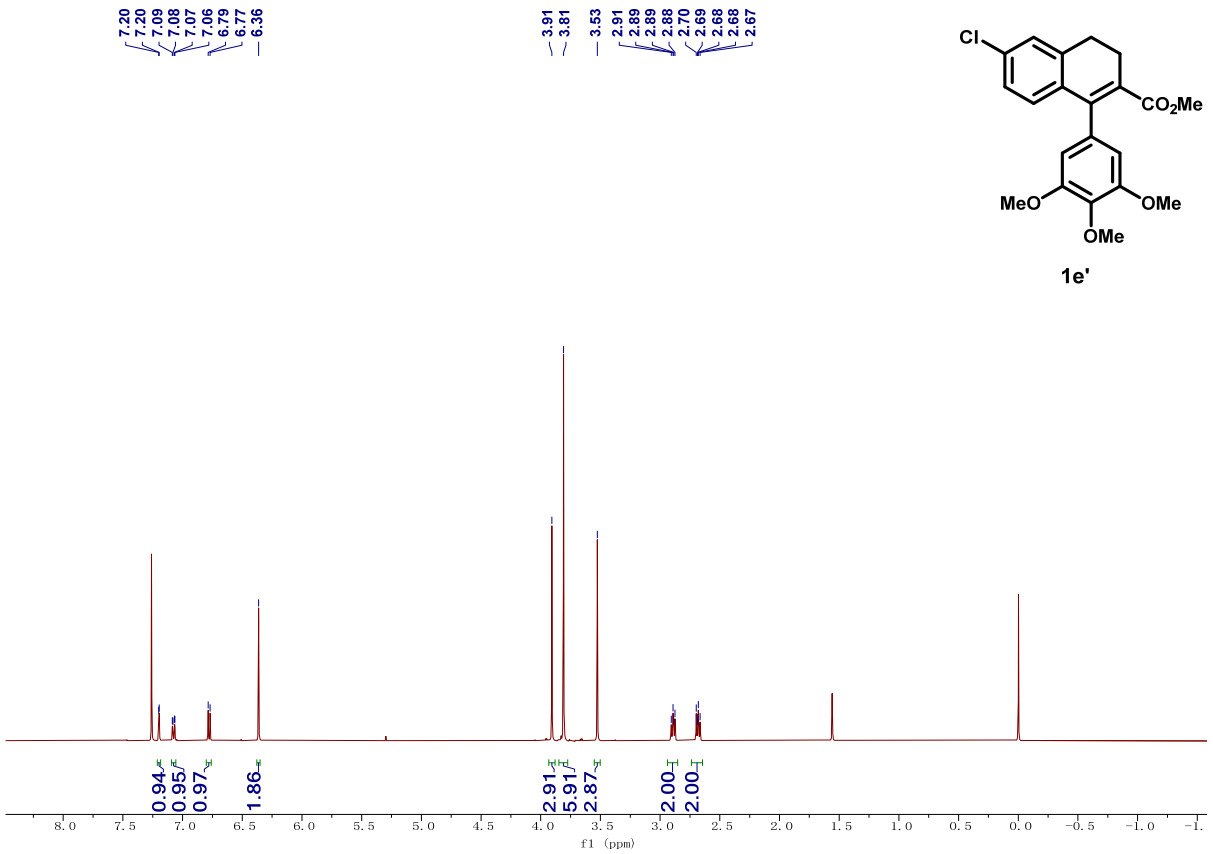


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



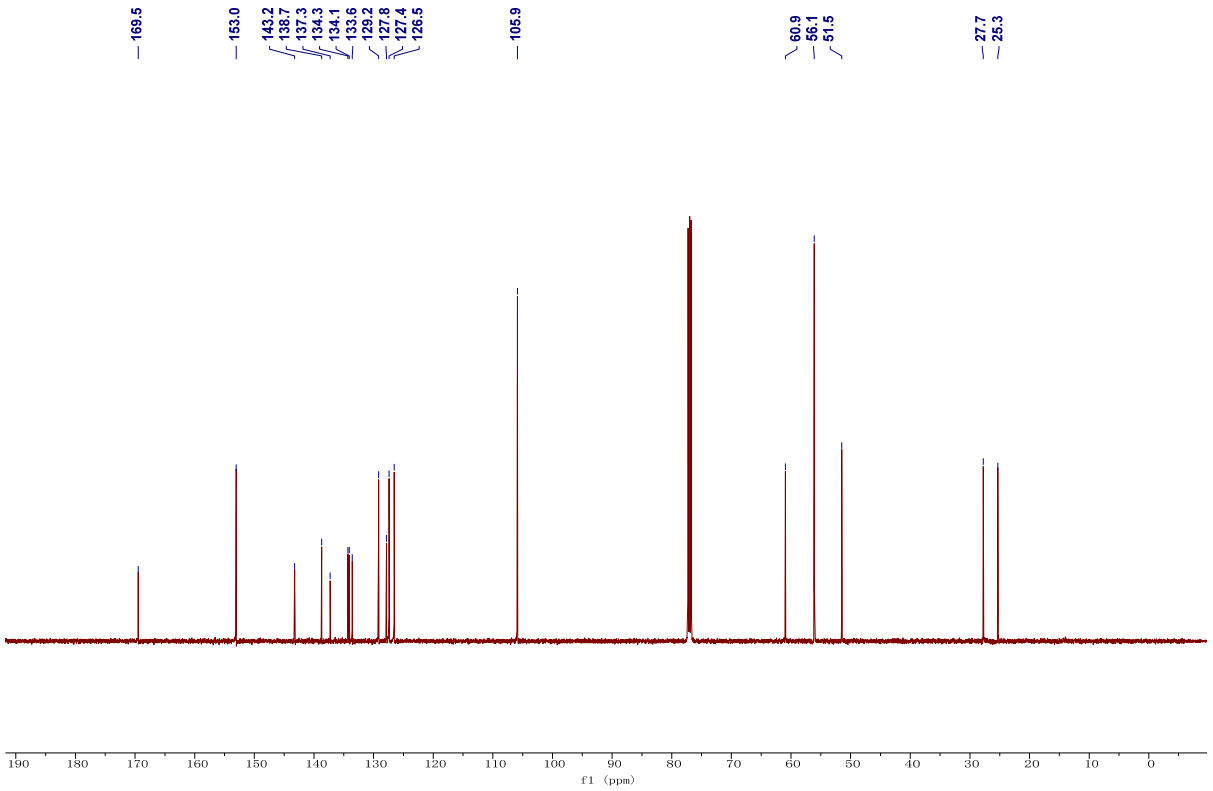
1e': Methyl 6-chloro-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



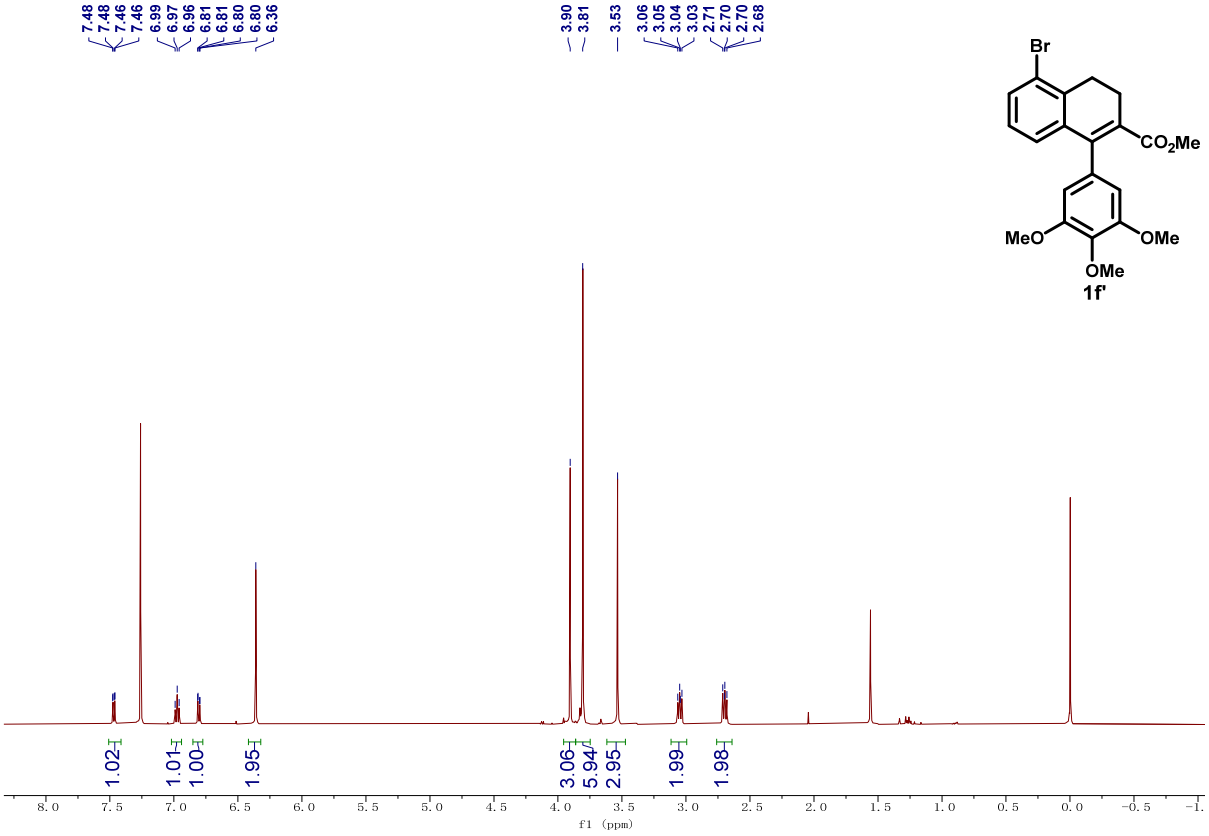
1e'

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

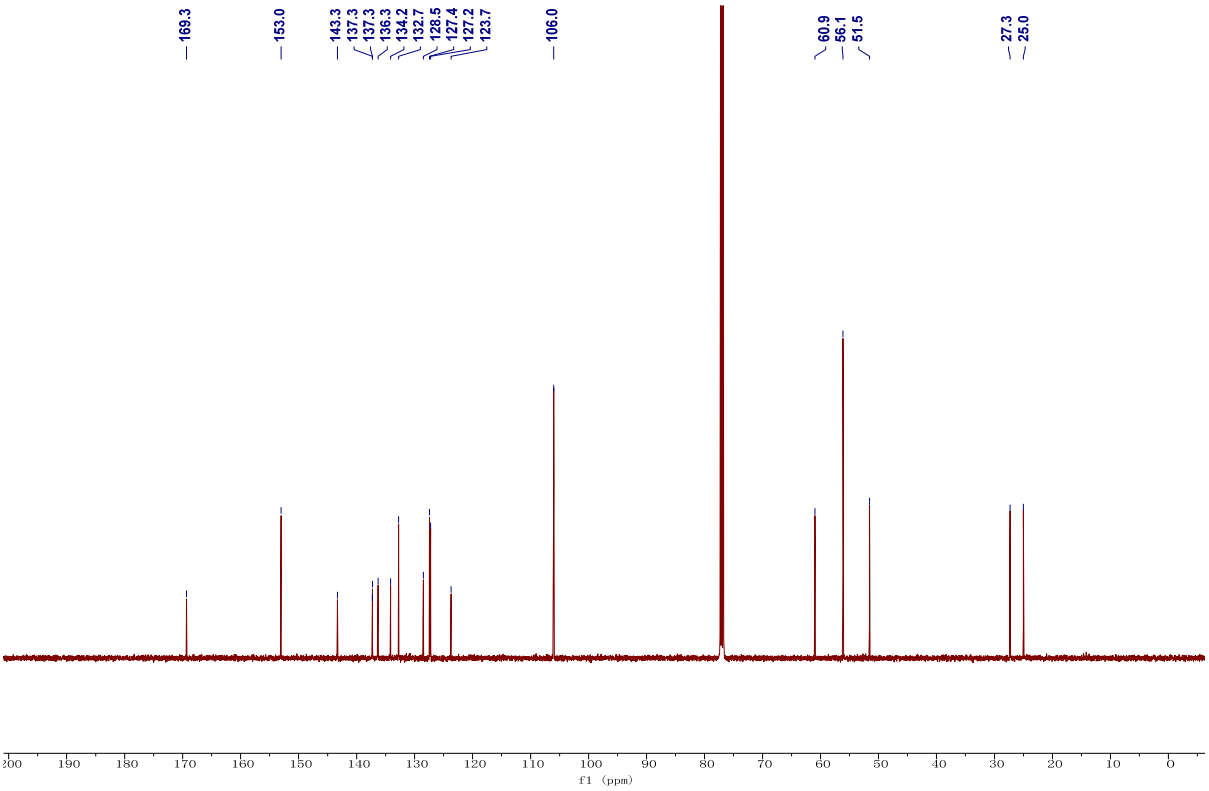


1f': Methyl 5-bromo-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

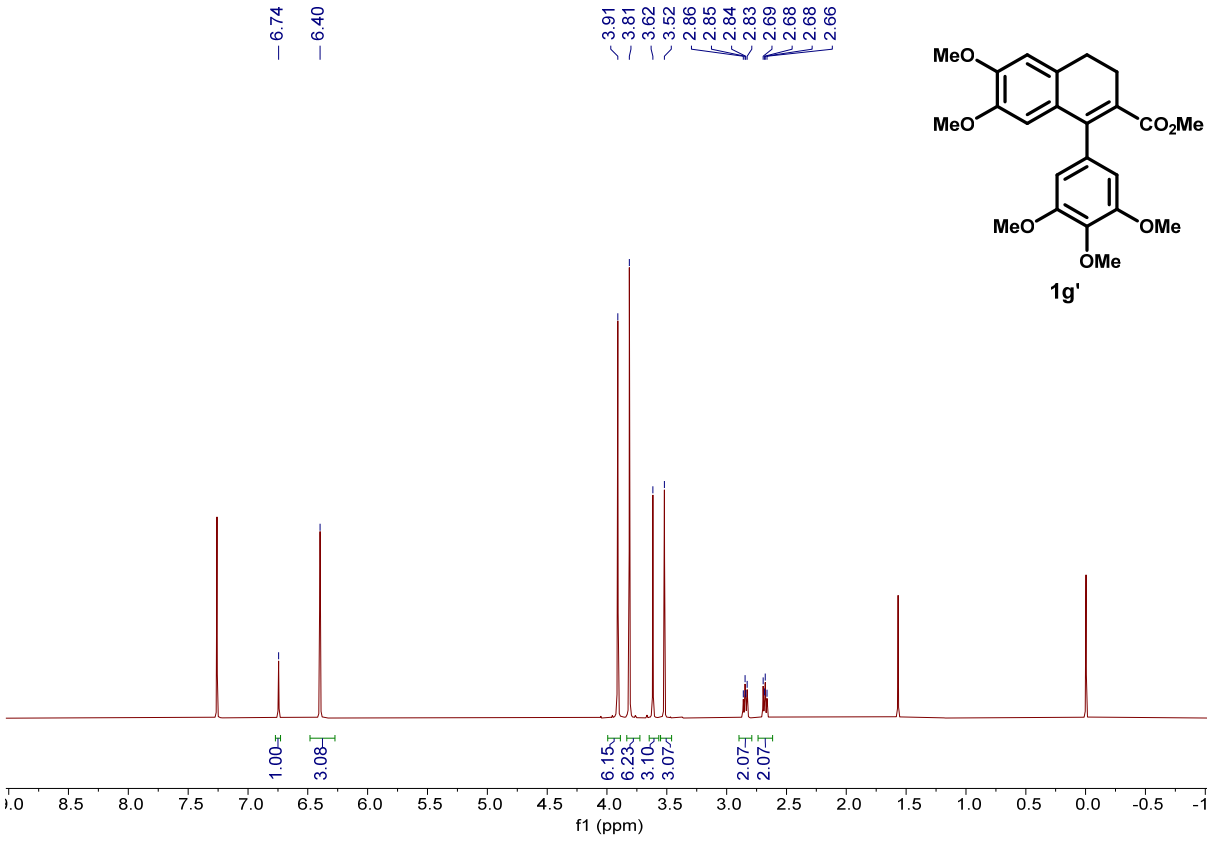


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

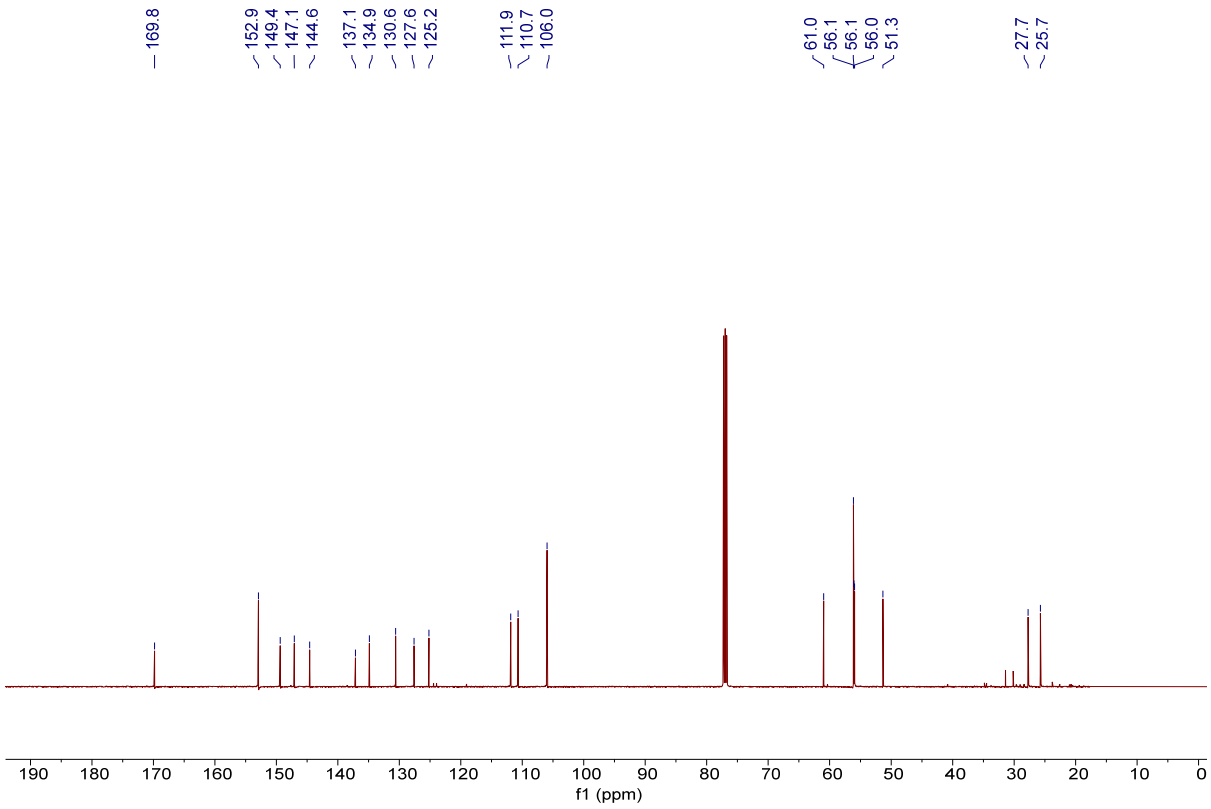


1g': Methyl 6,7-dimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

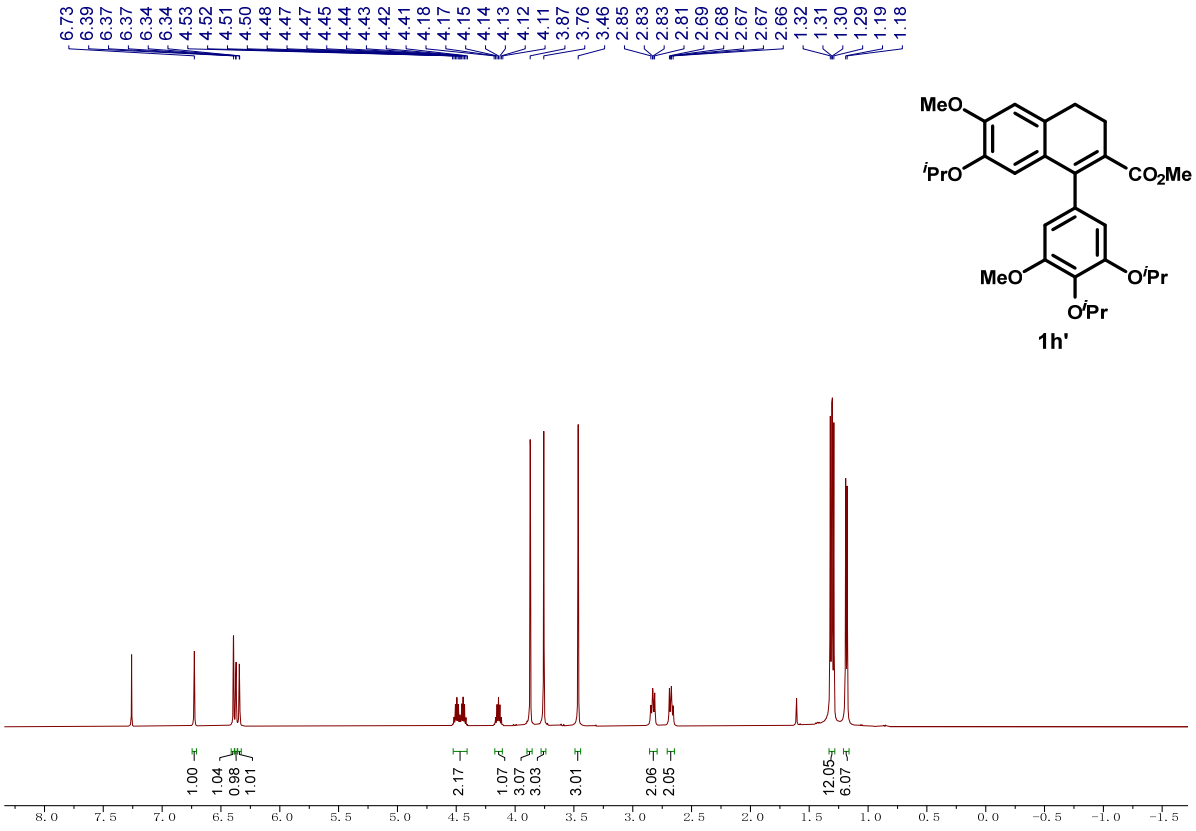


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

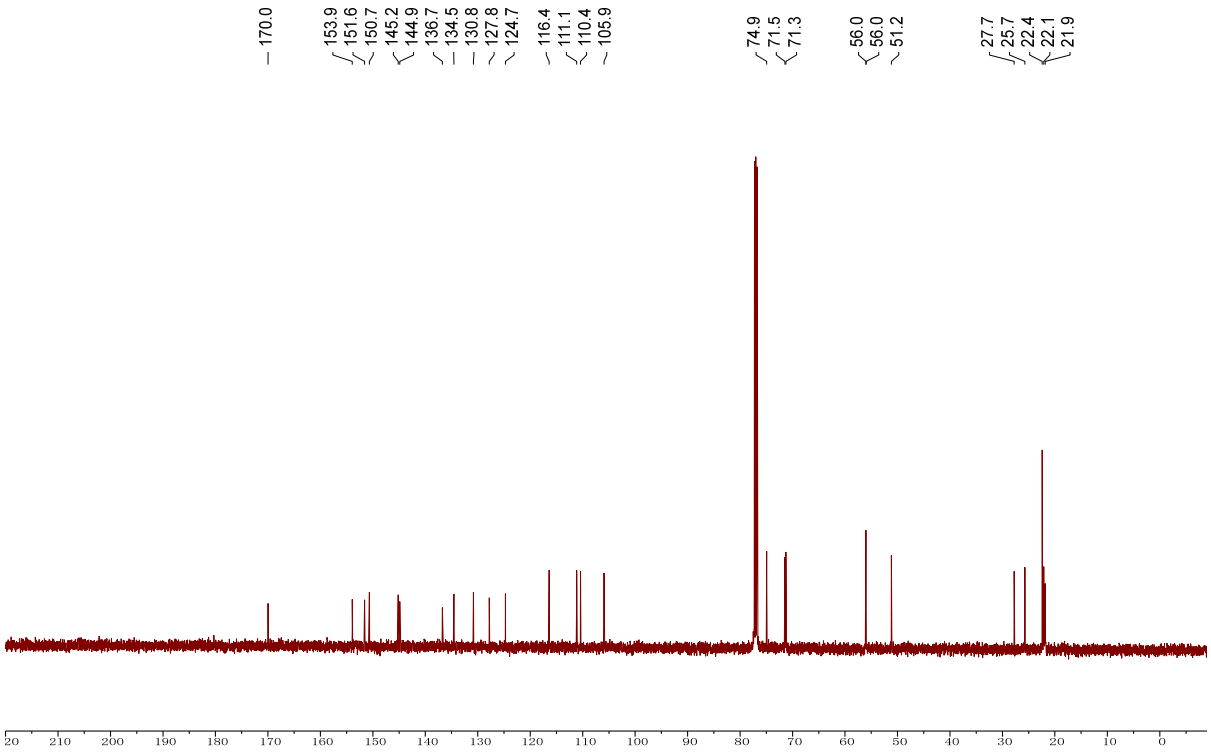


1h': Methyl1-(3,4-diisopropoxy-5-methoxyphenyl)-7-isopropoxy-6-methoxy-3,4-dihydro-naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

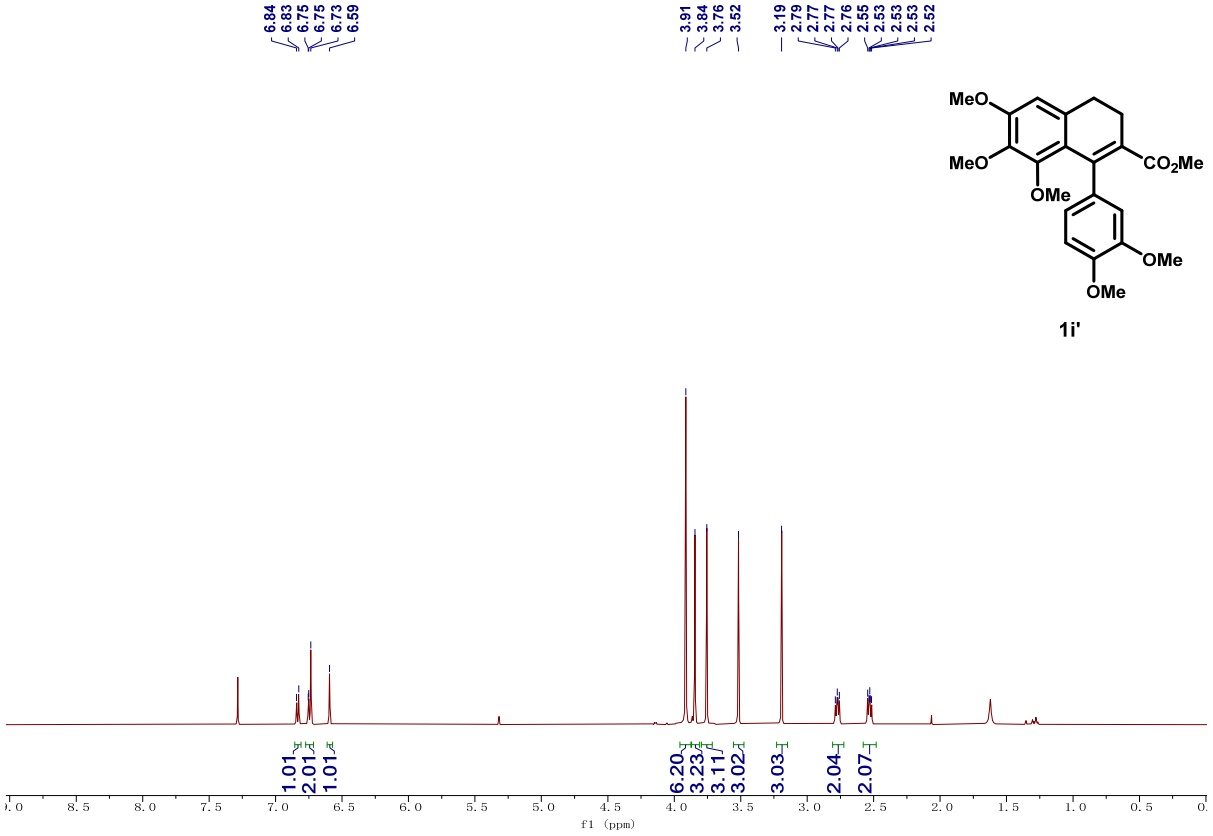


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

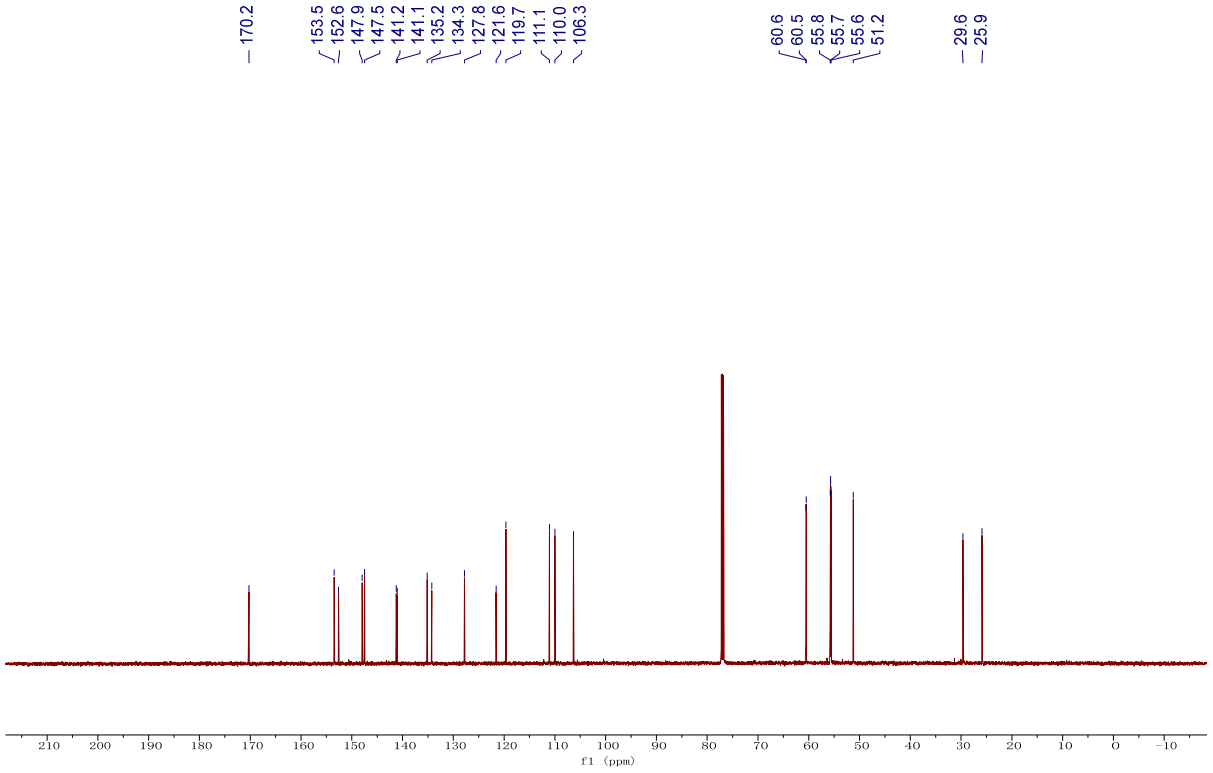


1i': Methyl 1-(3,4-dimethoxyphenyl)-6,7,8-trimethoxy-3,4-dihydronaphthalene-2- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

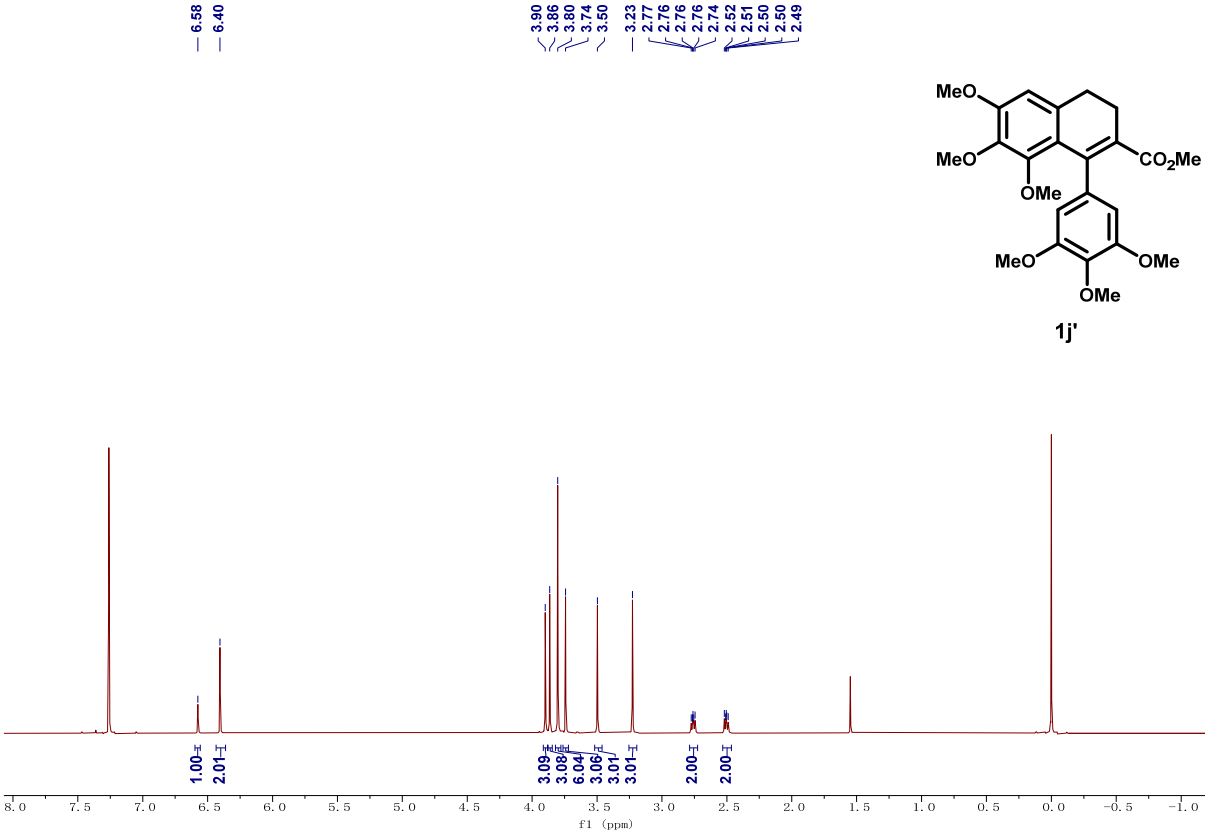


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



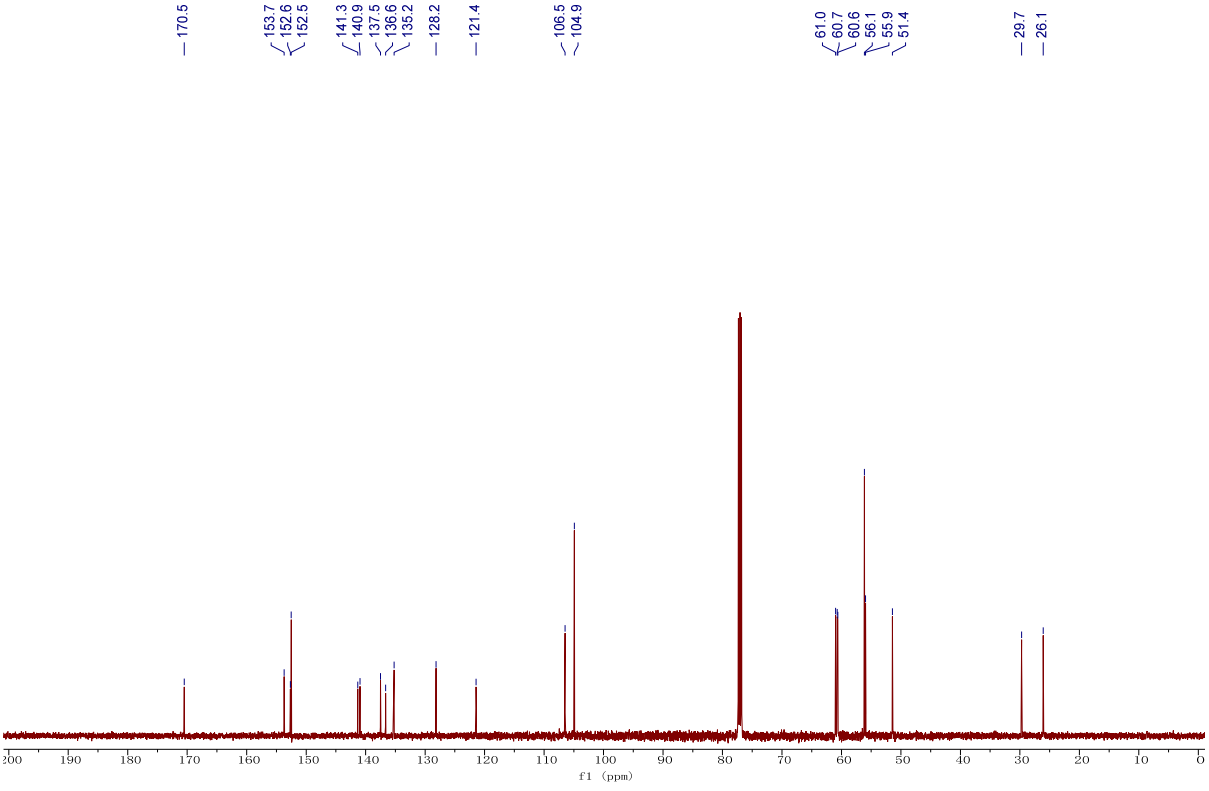
1j': Methyl6,7,8-trimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



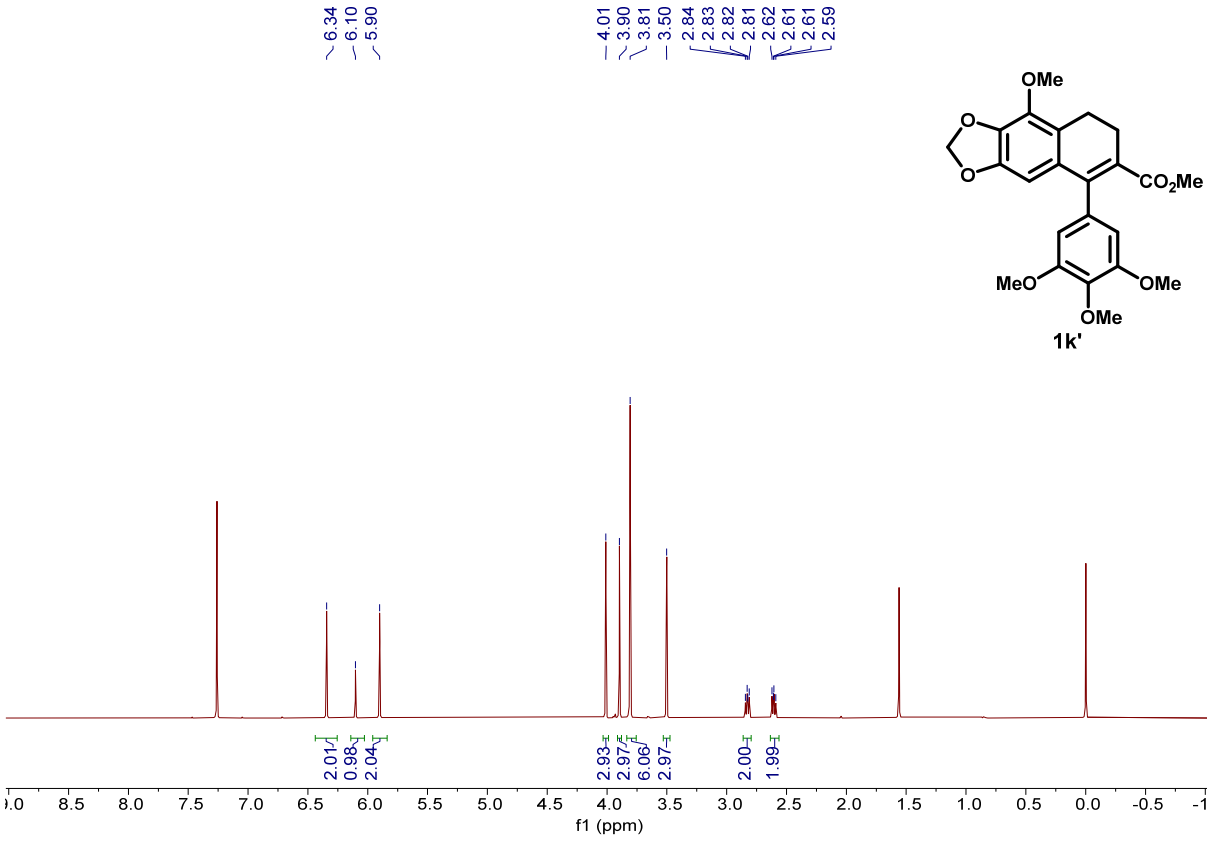
1j'

[13]C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

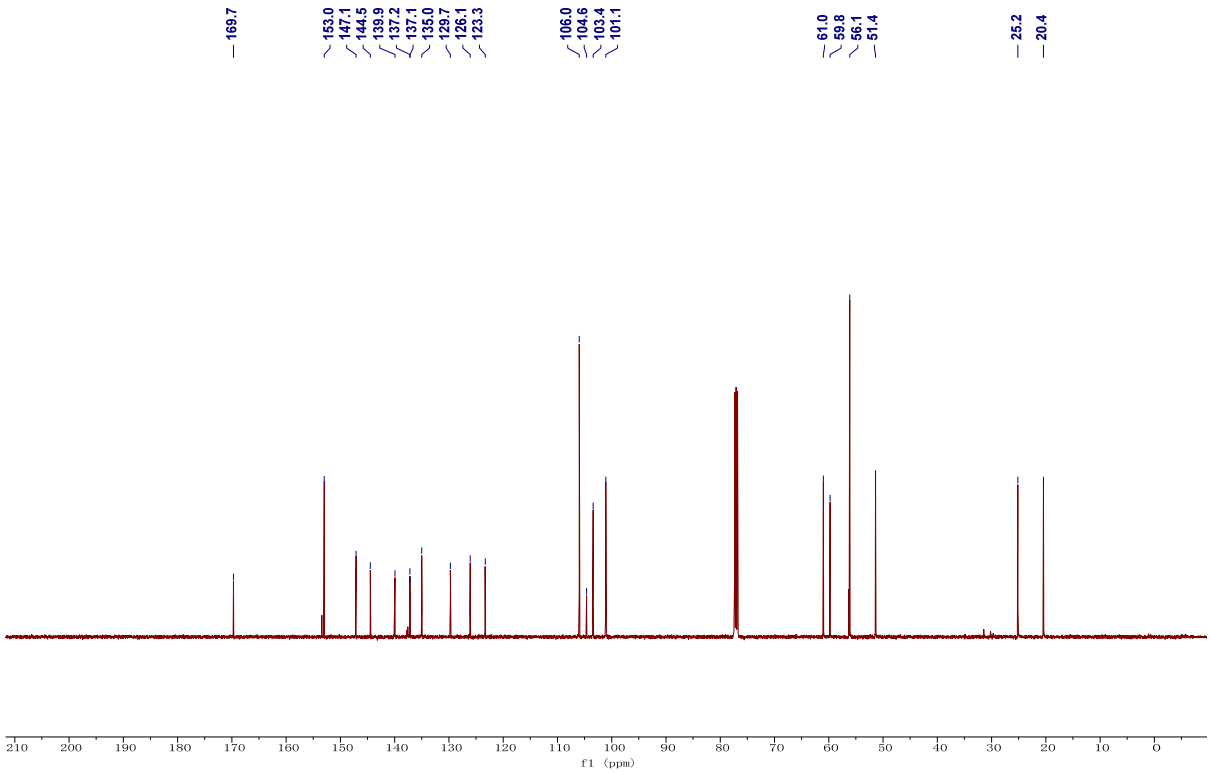


1k': Methyl 9-methoxy-5-(3,4,5-trimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxole 6-carboxylate

[1]H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

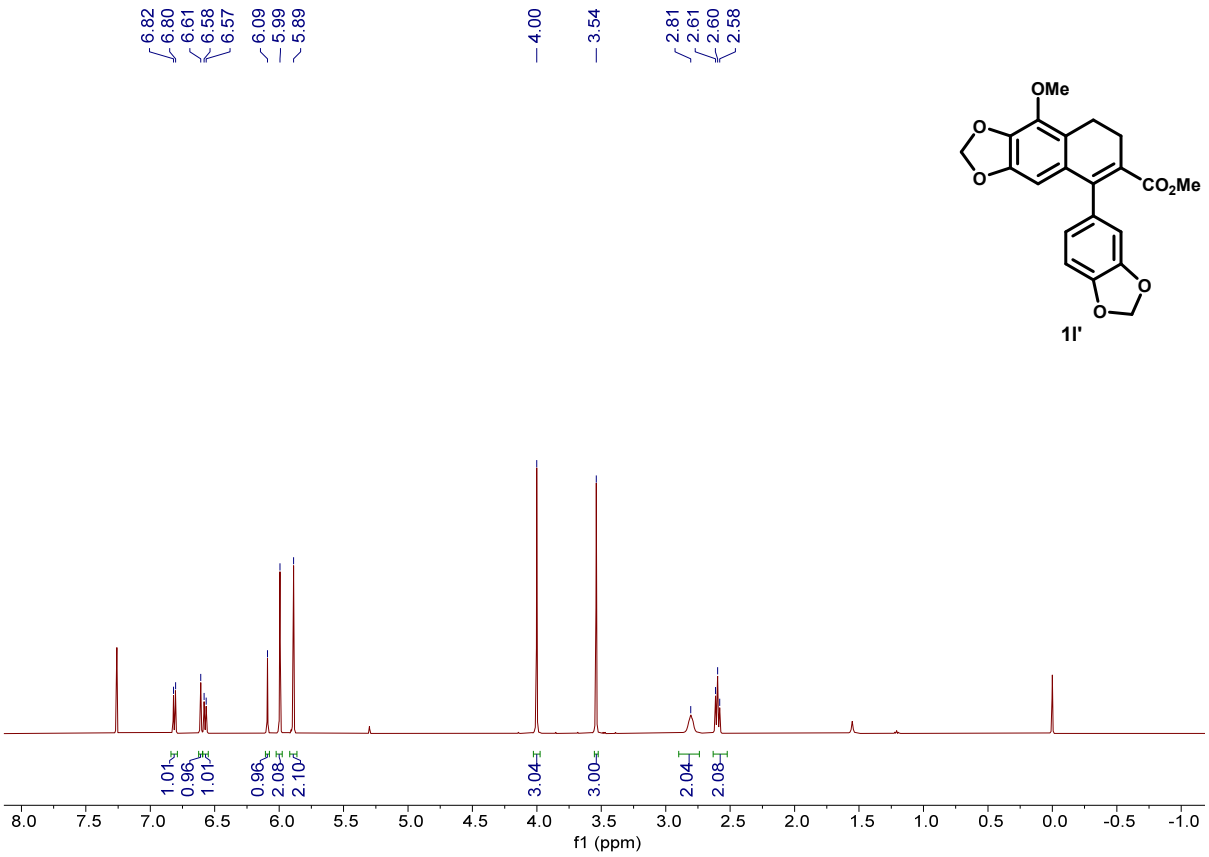


[13]C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

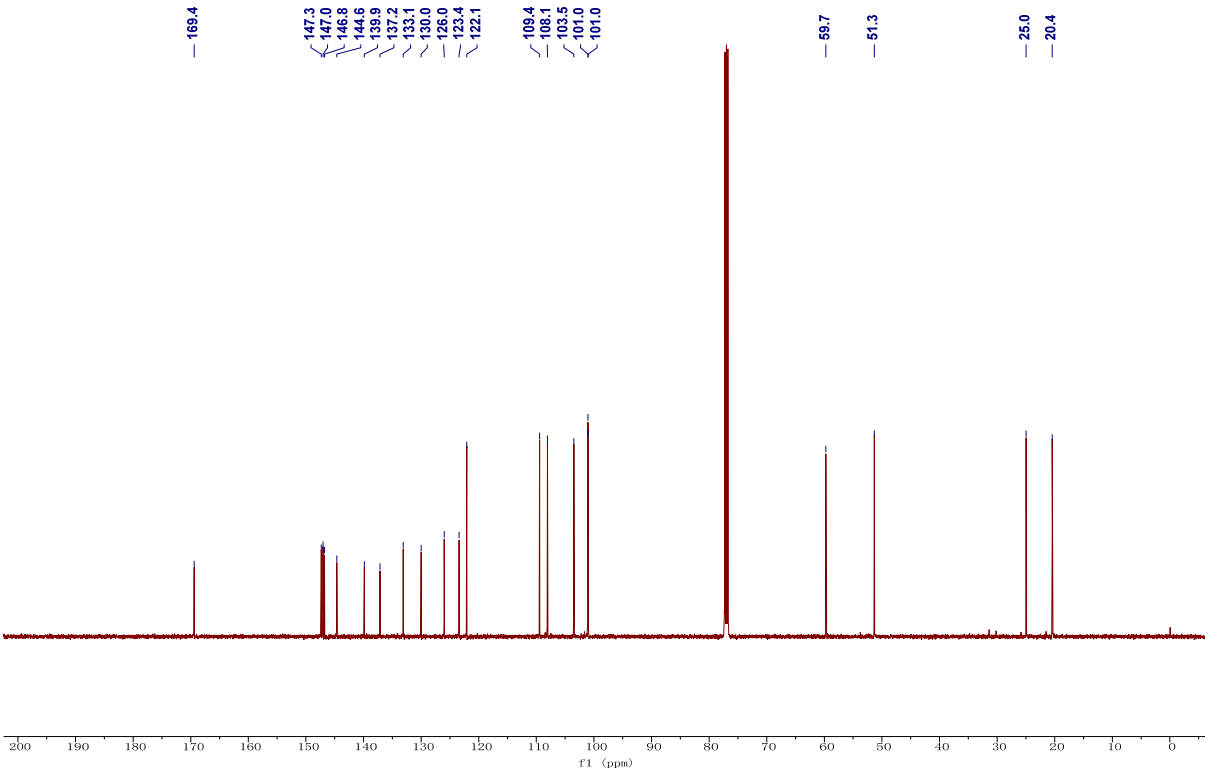


1l': Methyl 5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-7,8-dihydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

[1]H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

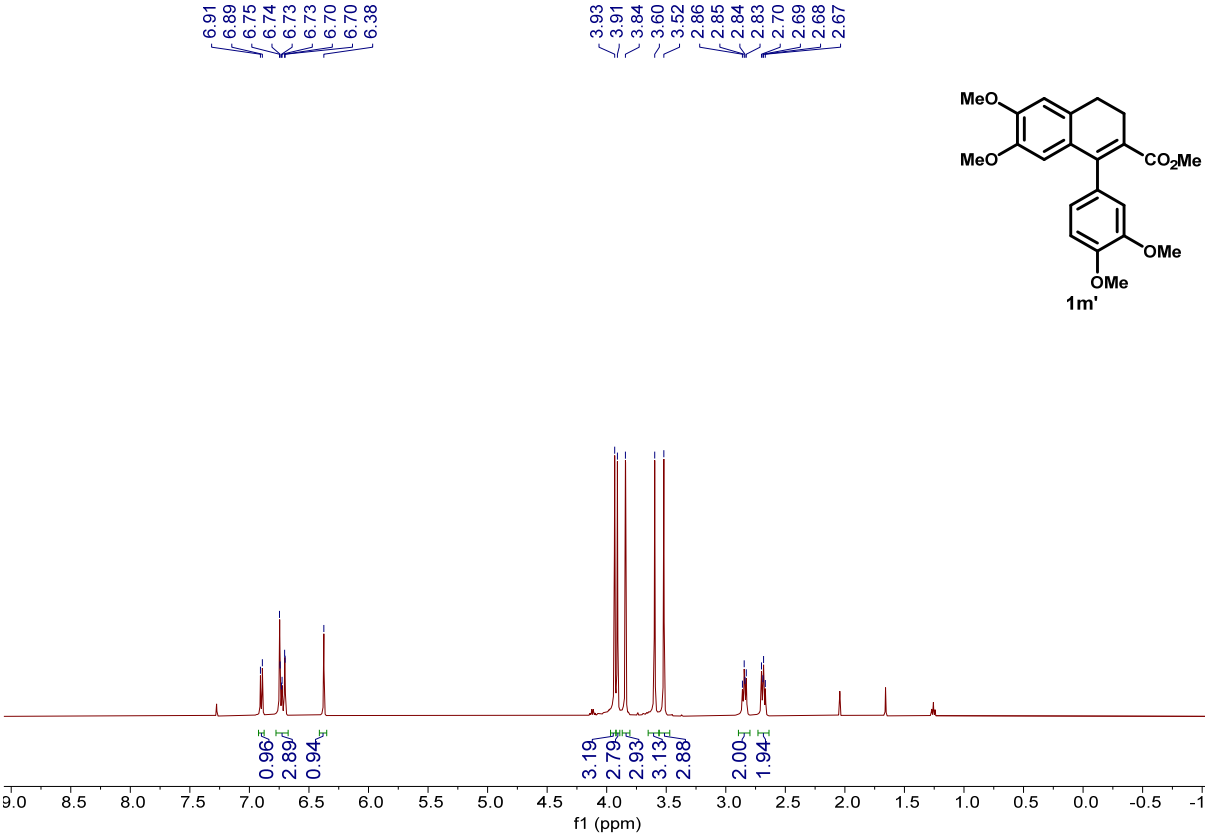


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

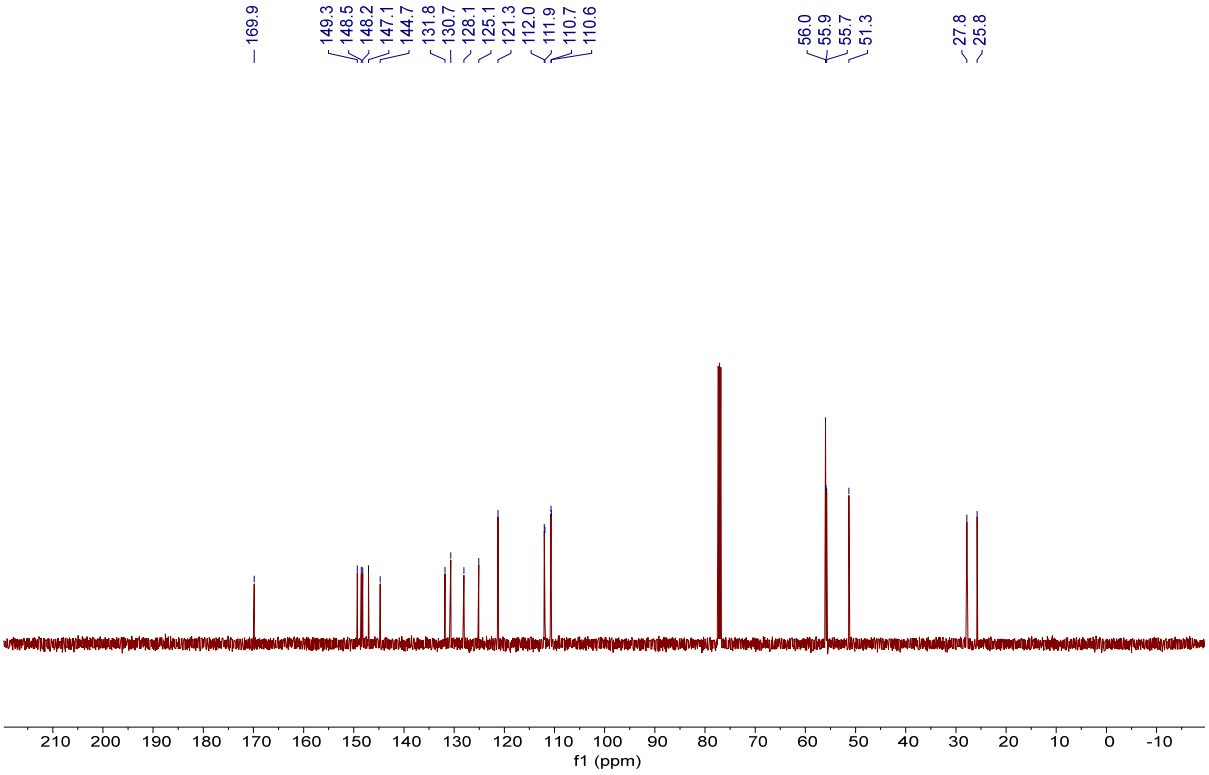


1m': Methyl 1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydronaphthalene-2- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

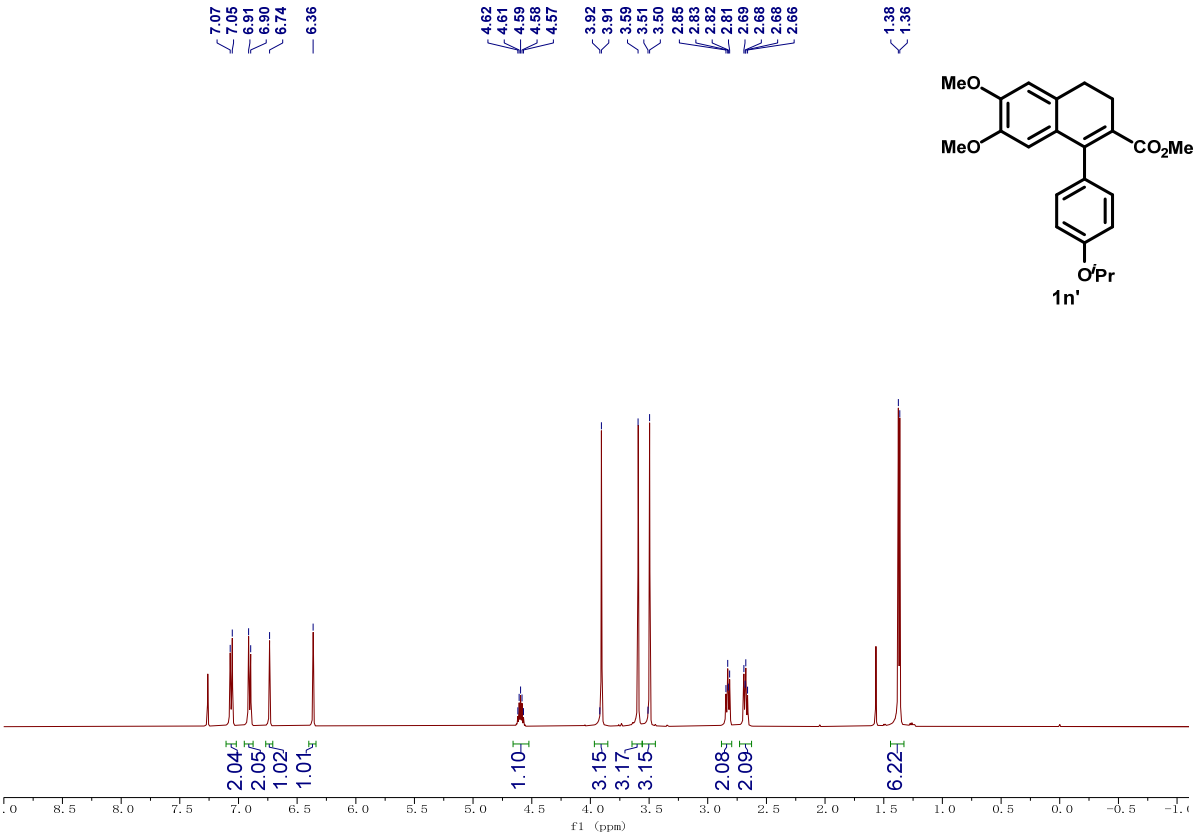


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

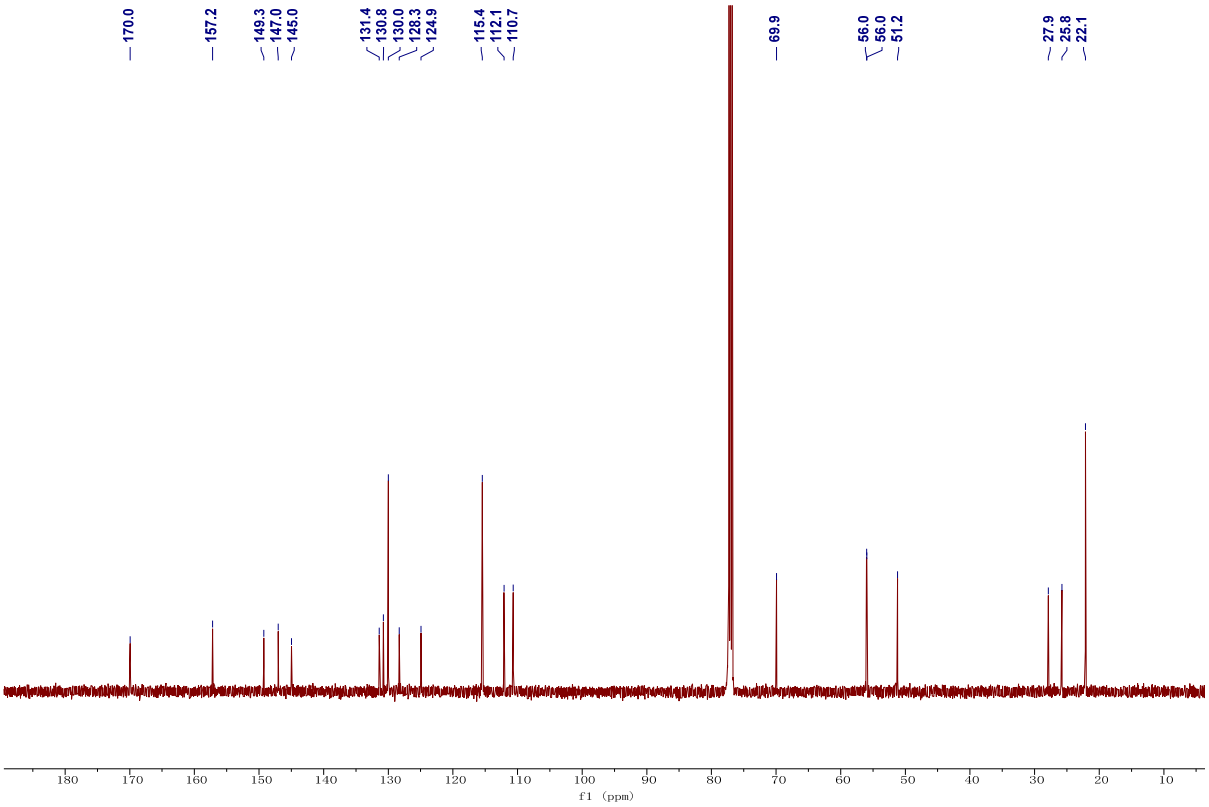


1n': Methyl 1-(4-isopropoxyphenyl)-6,7-dimethoxy-3,4-dihydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

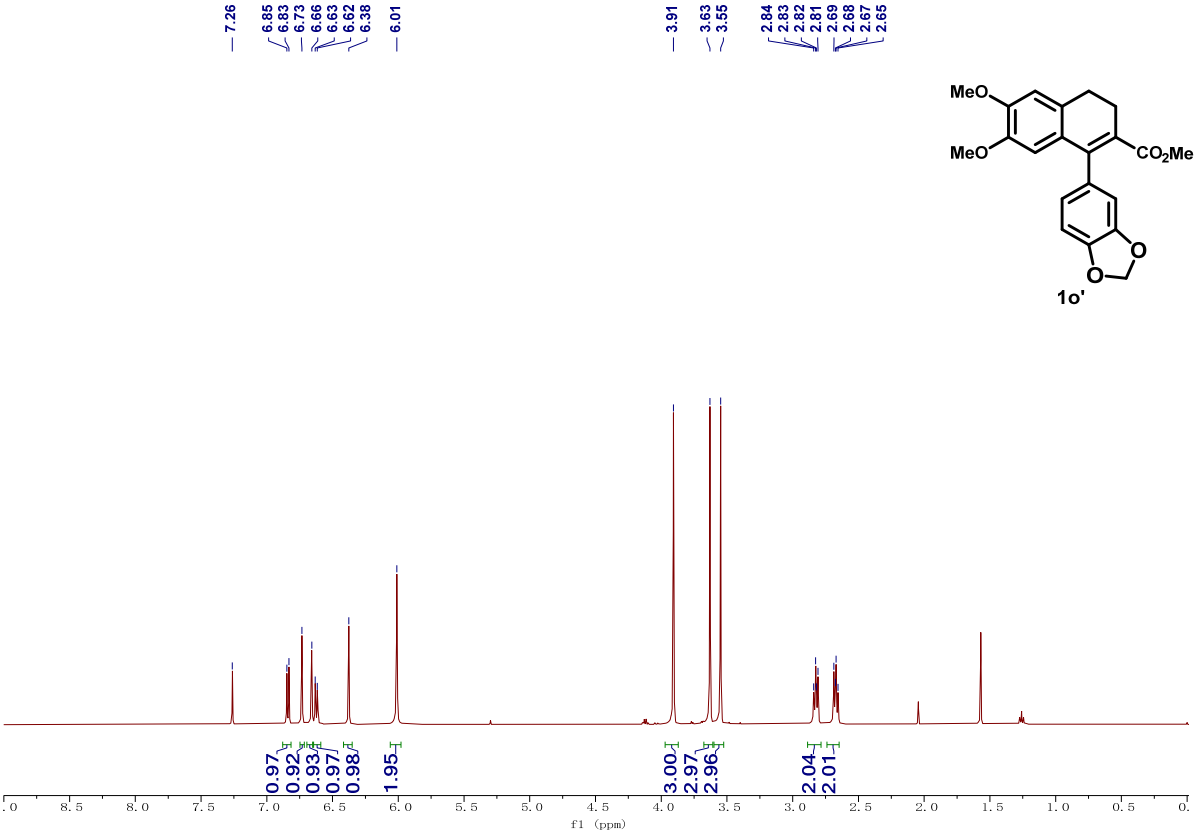


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

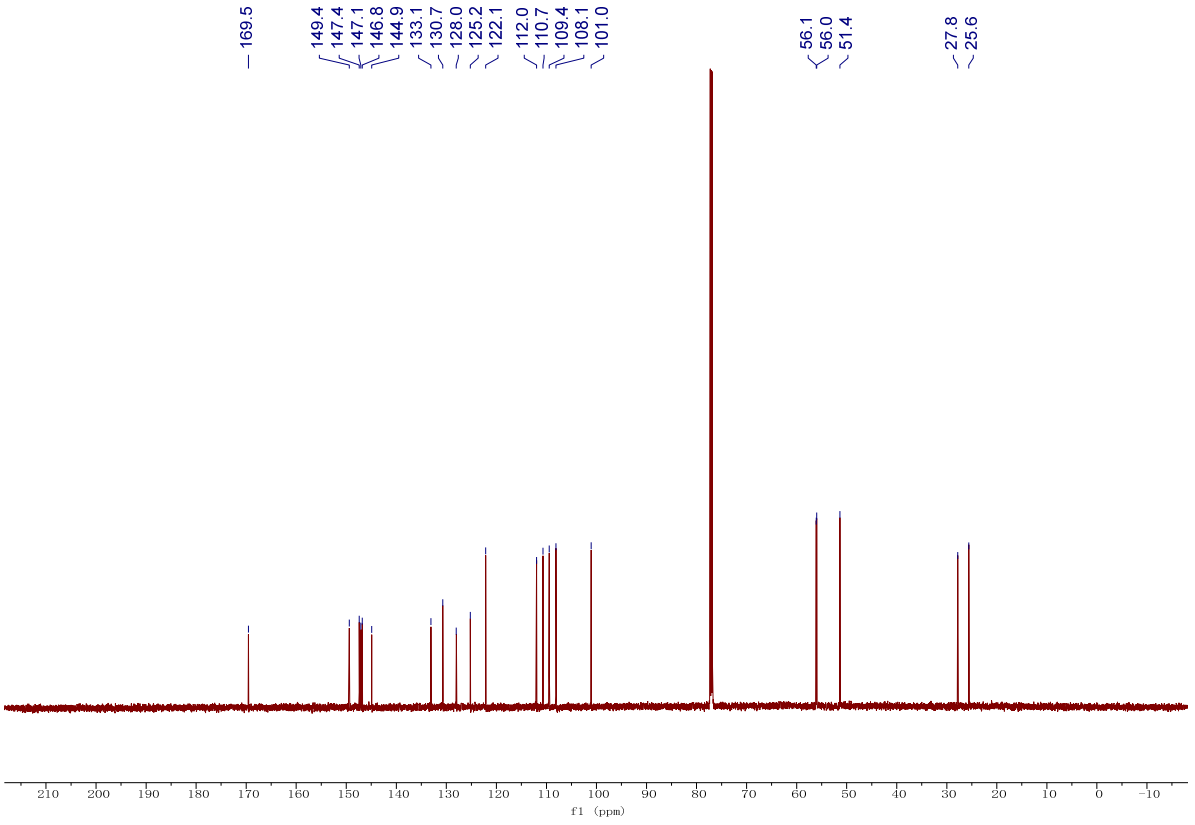


1o': Methyl 1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxy-3,4-dihydronaphthalene-2- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

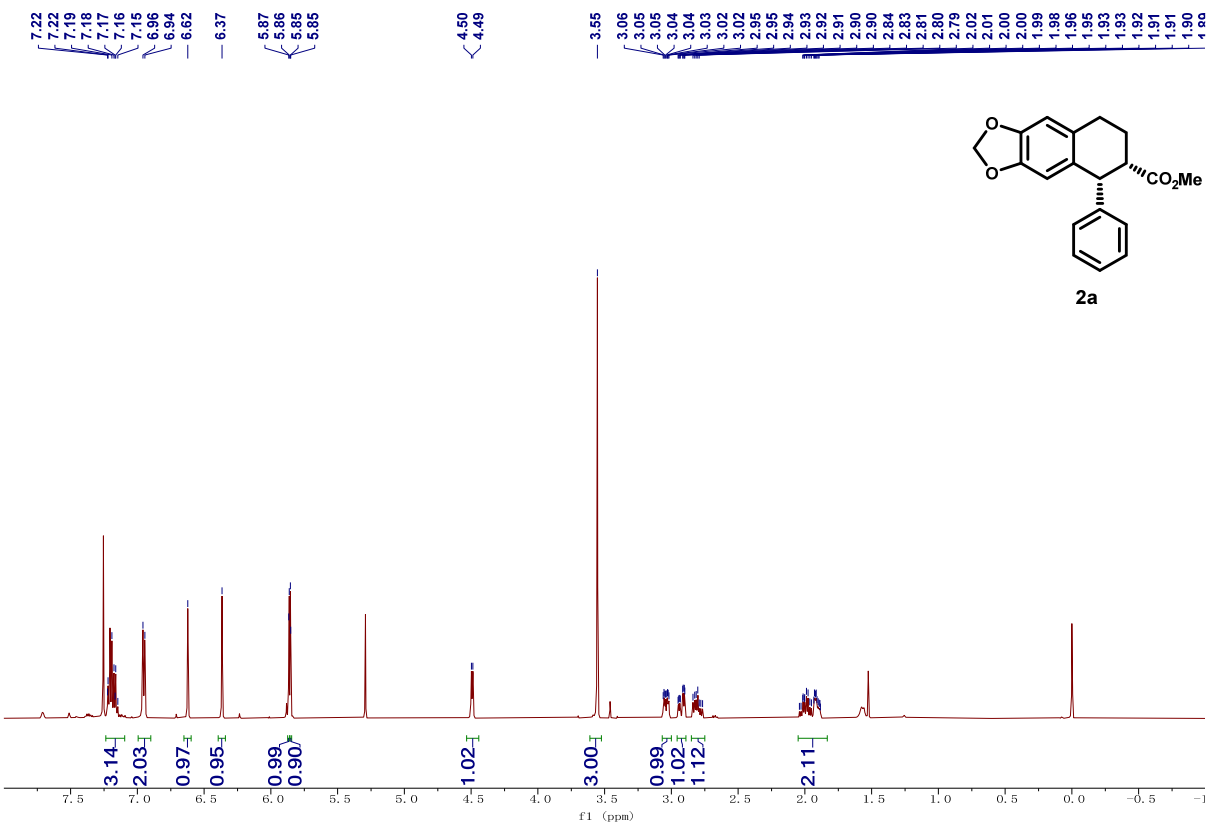


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

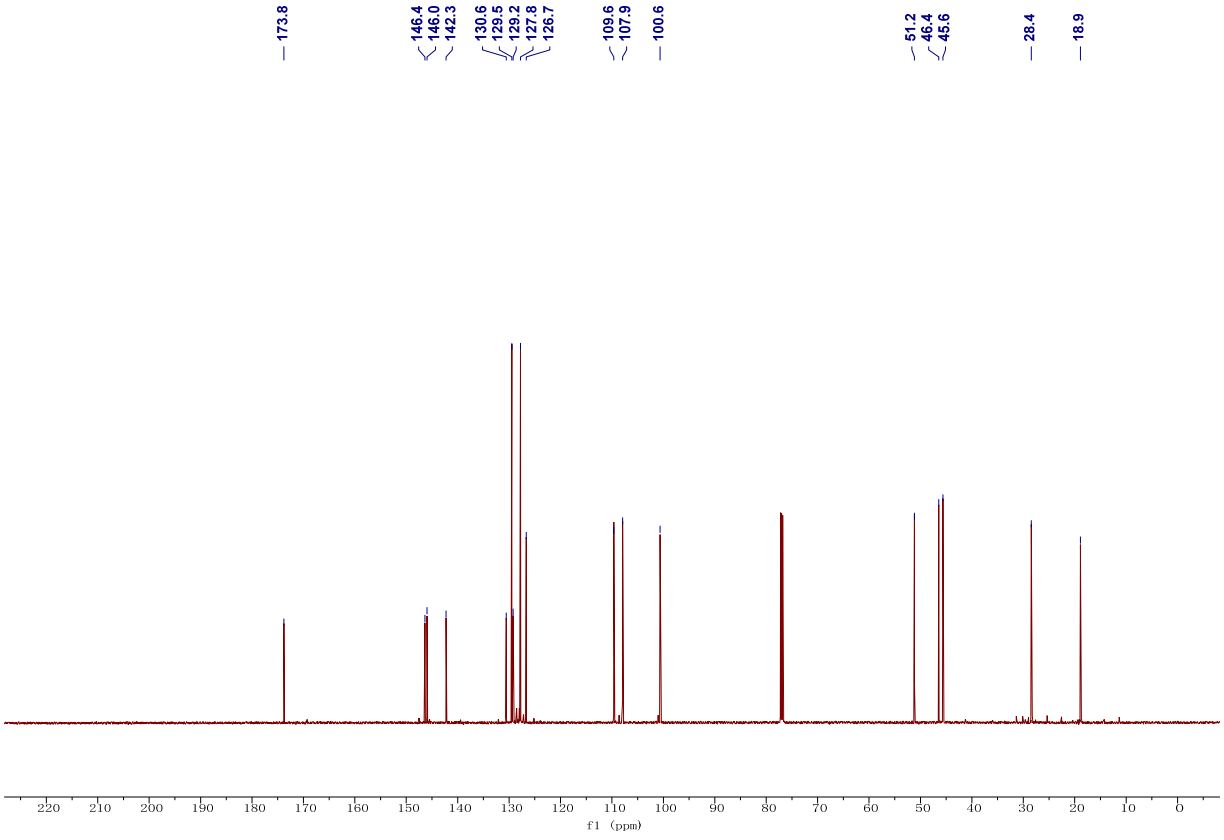


2a: Methyl (5R,6S)-5-phenyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

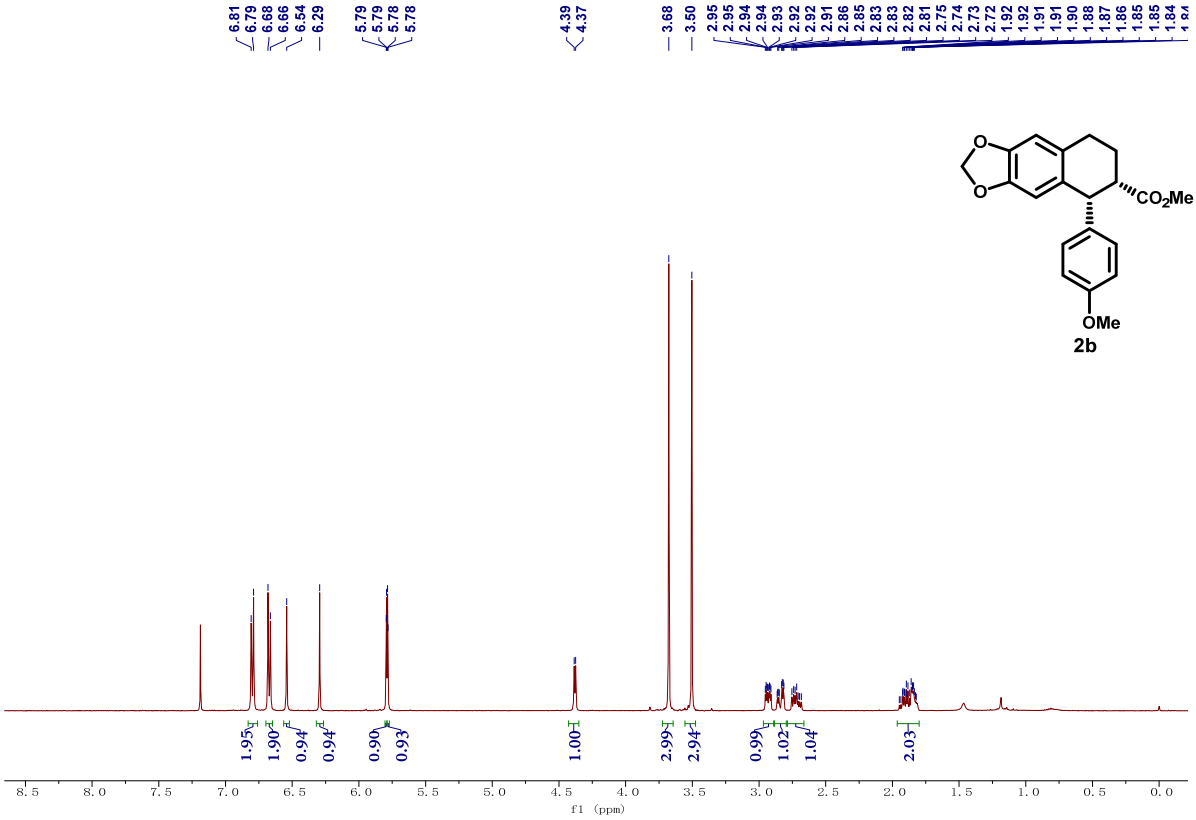


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

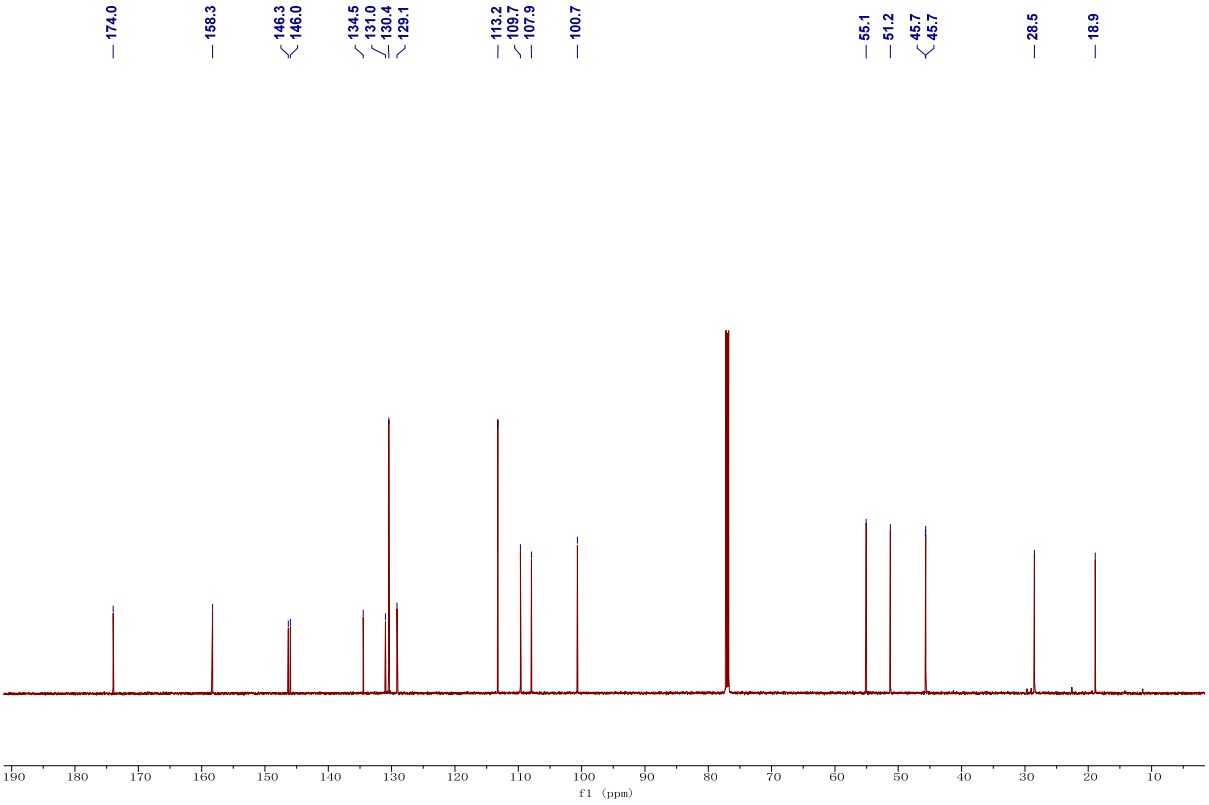


2b: Methyl (5R,6S)-5-(4-methoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



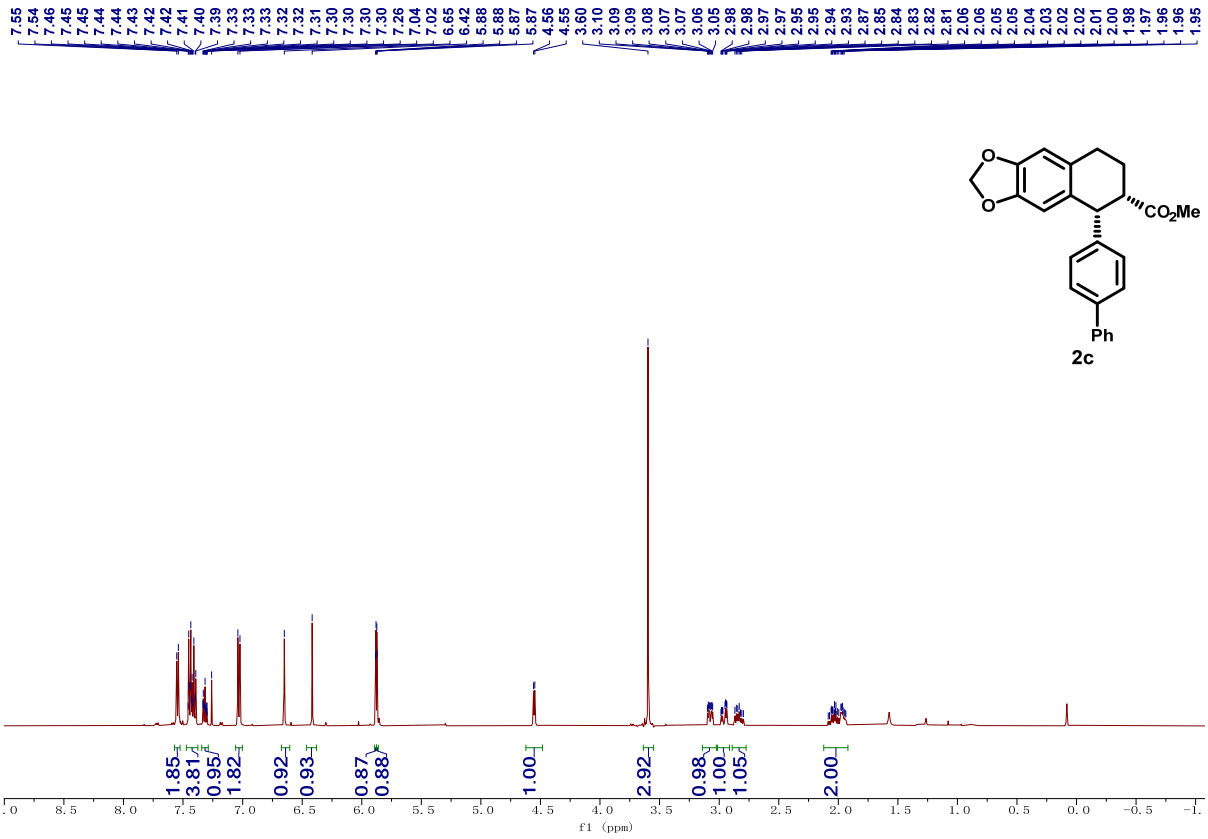
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



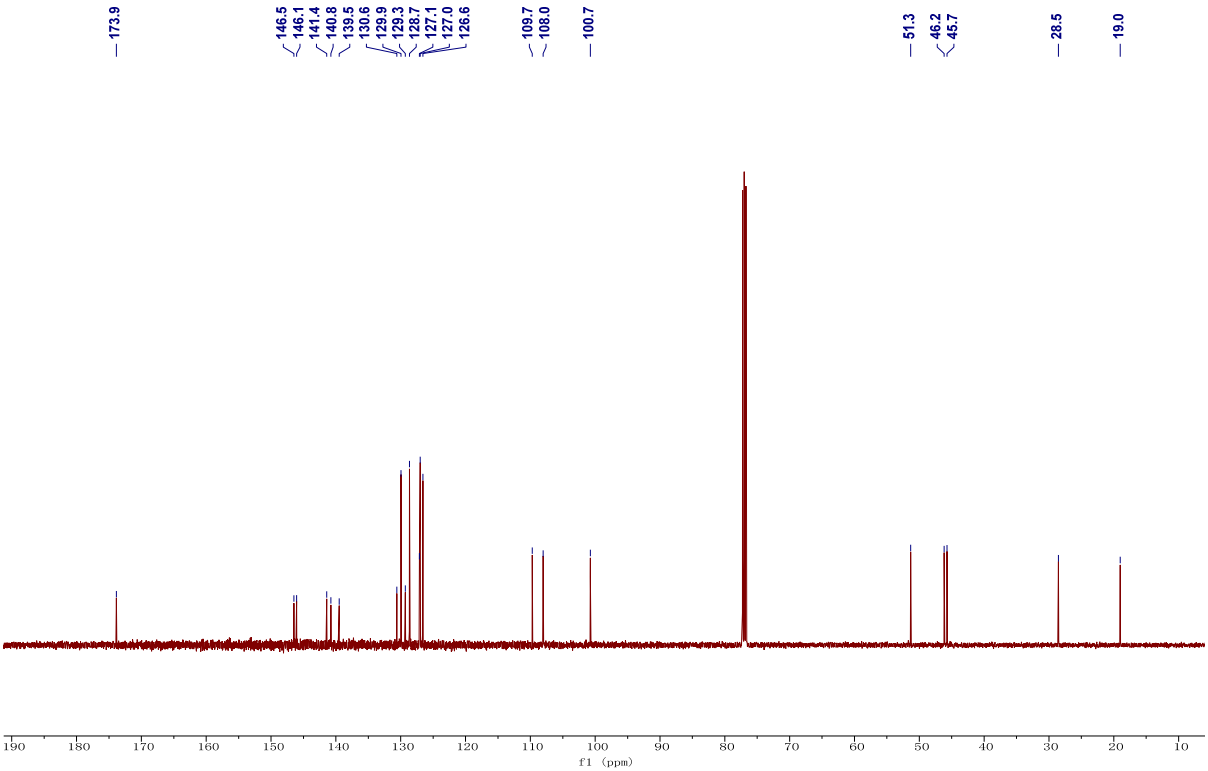
2c: Methyl (5R,6S)-5-([1,1'-biphenyl]-4-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole- 6-

carboxylate

[1]H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

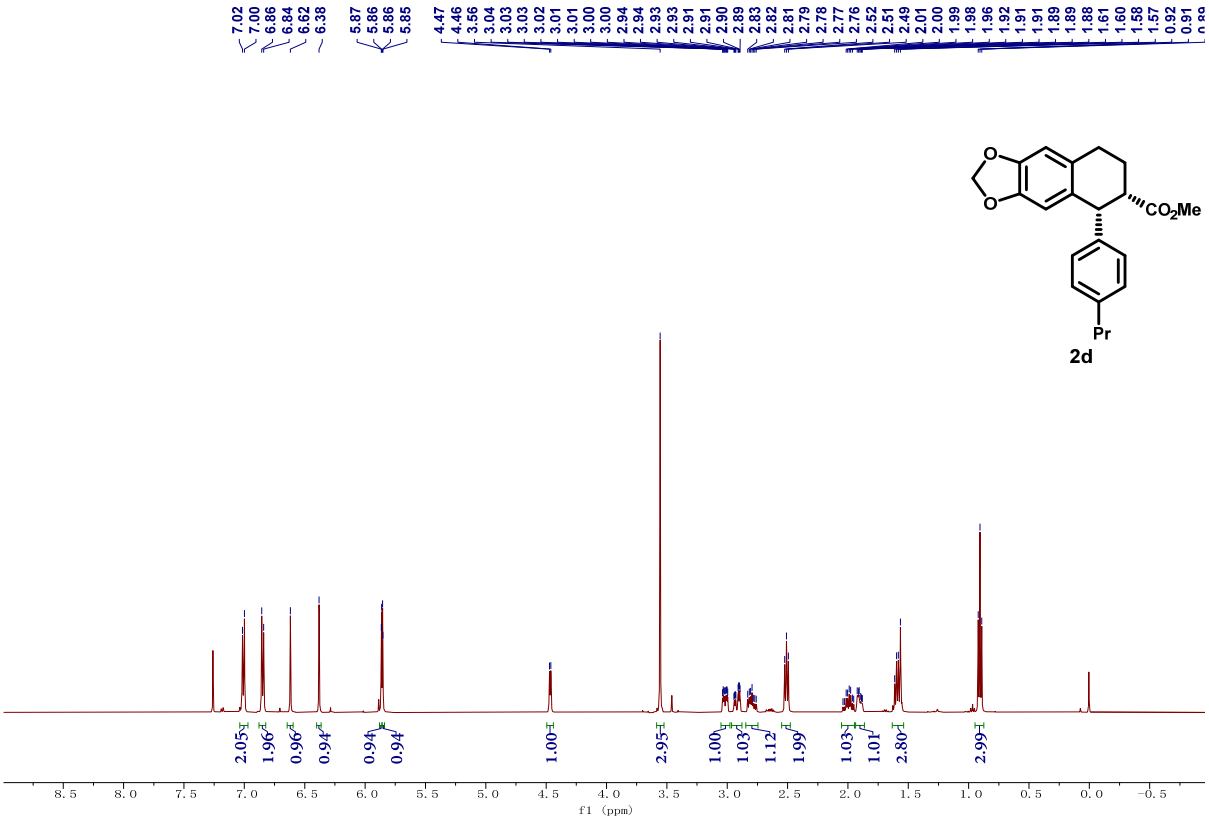


[13]C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

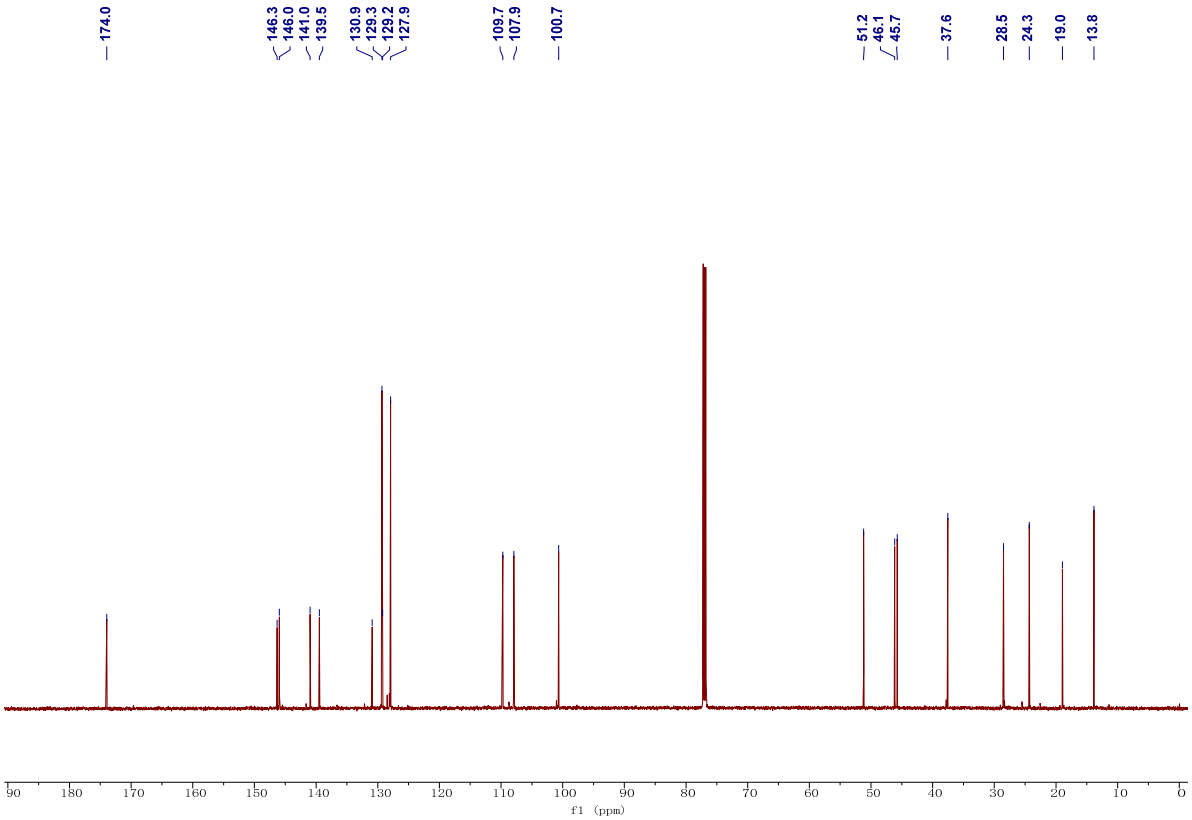


2d: Methyl (5R,6S)-5-(4-propylphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole 6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

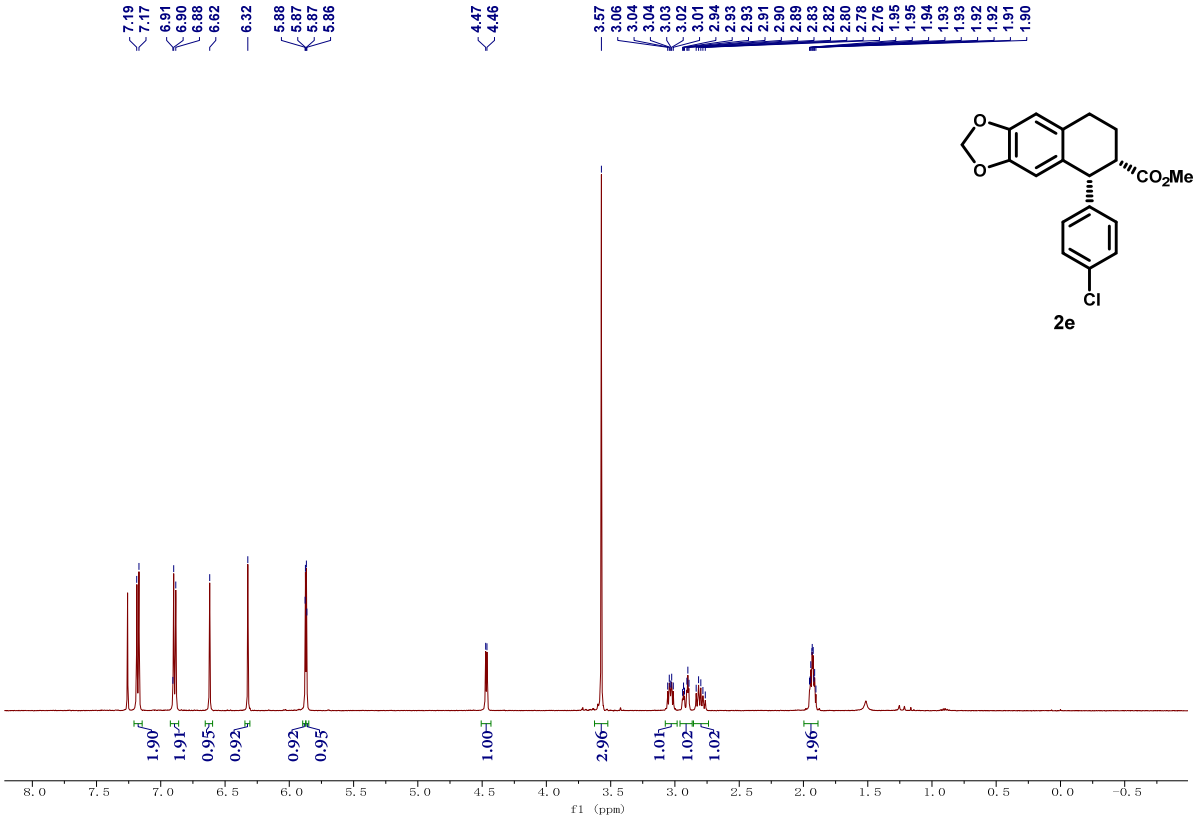


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

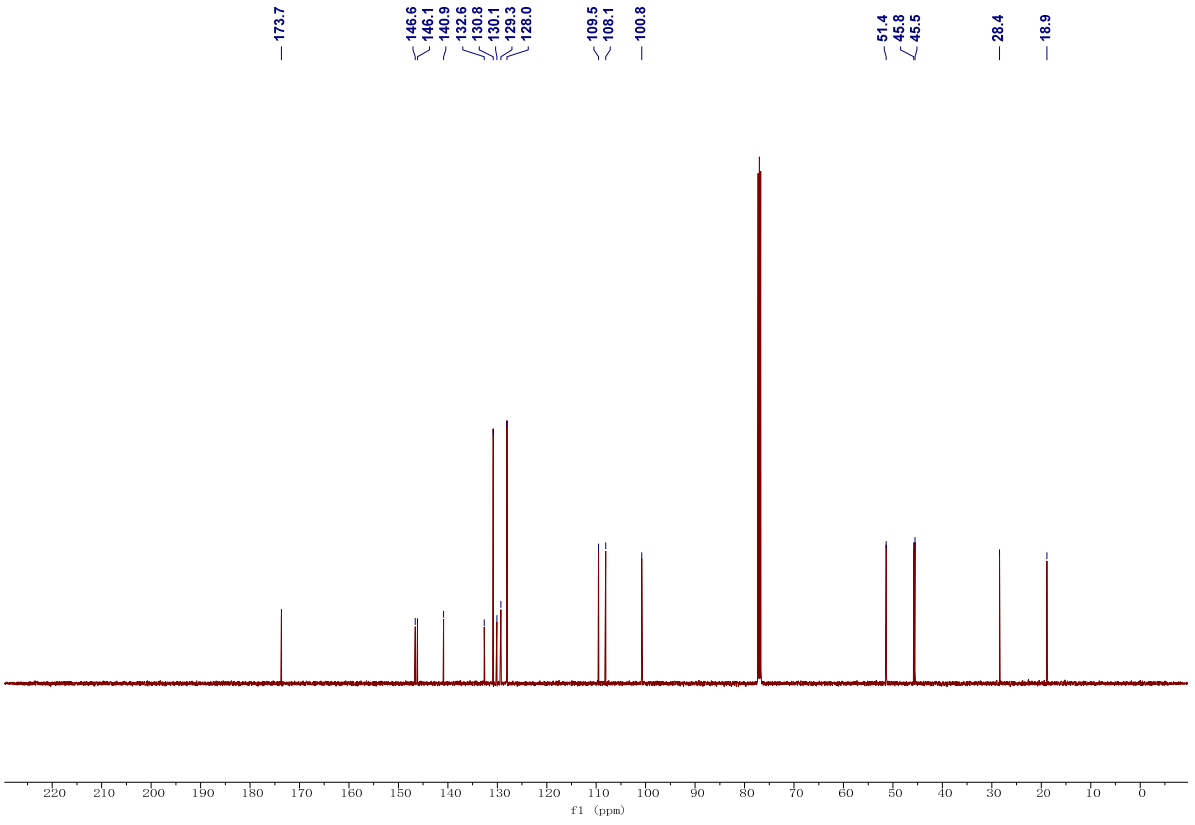


2e: Methyl (5R,6S)-5-(4-chlorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

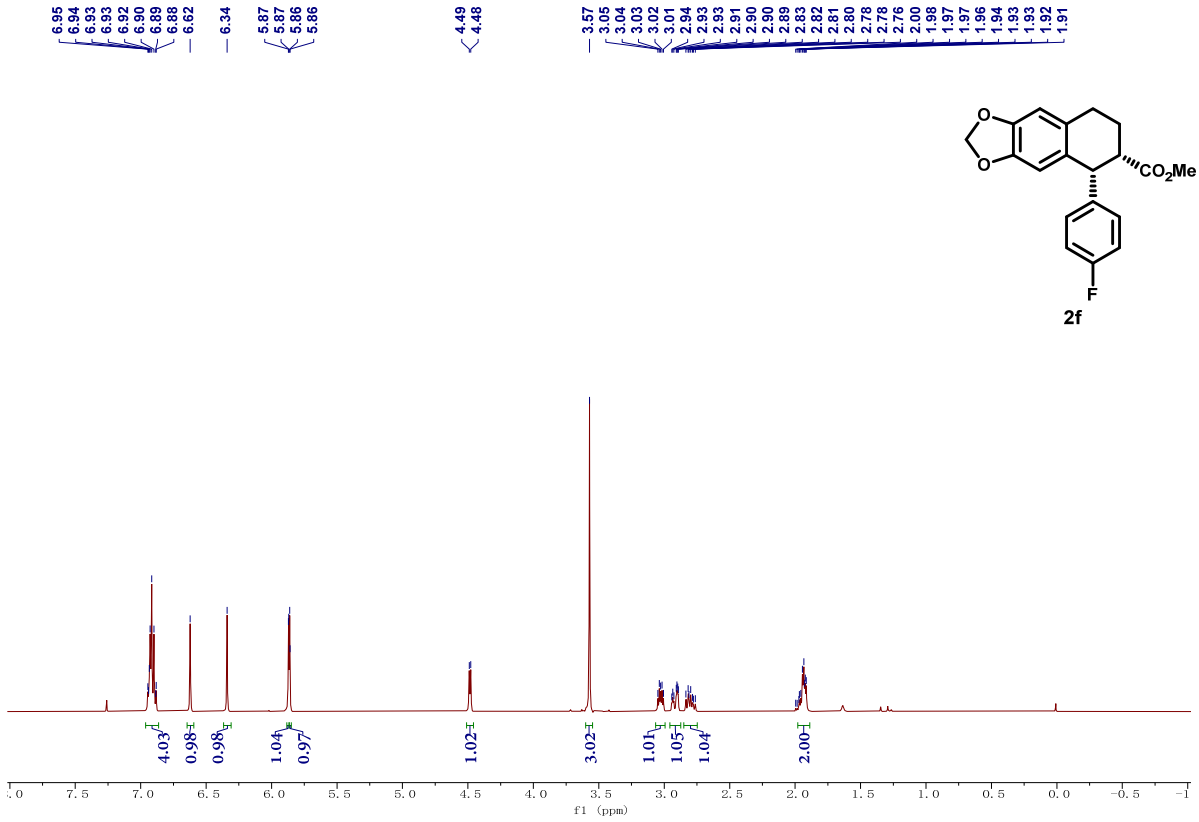


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

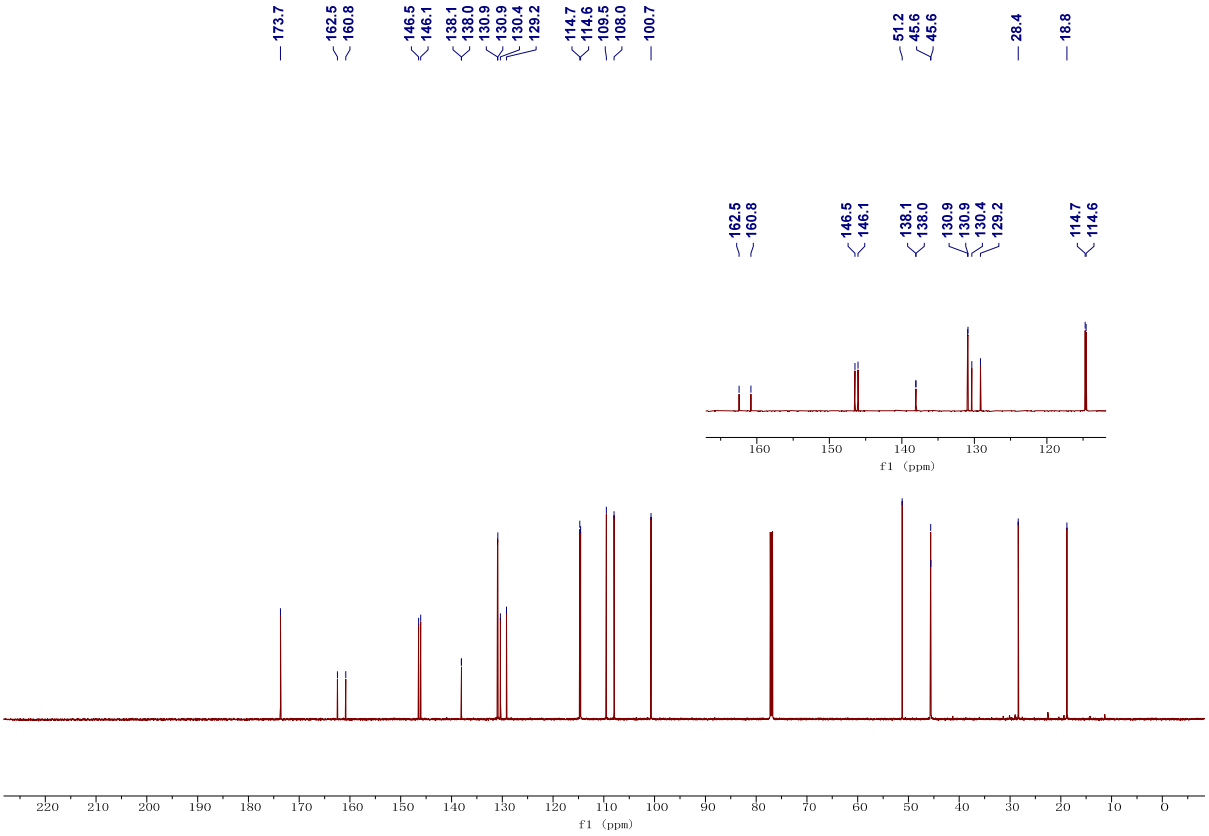


2f: Methyl (5R,6S)-5-(4-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

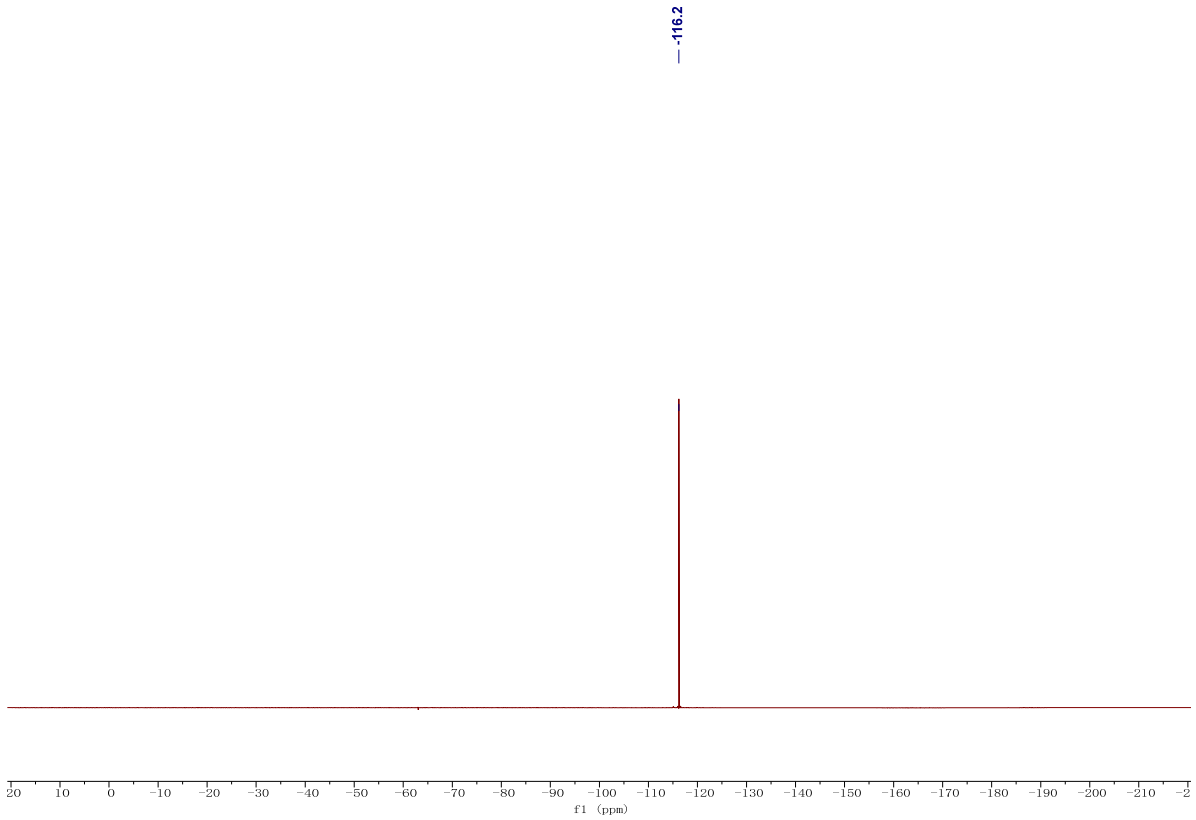
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

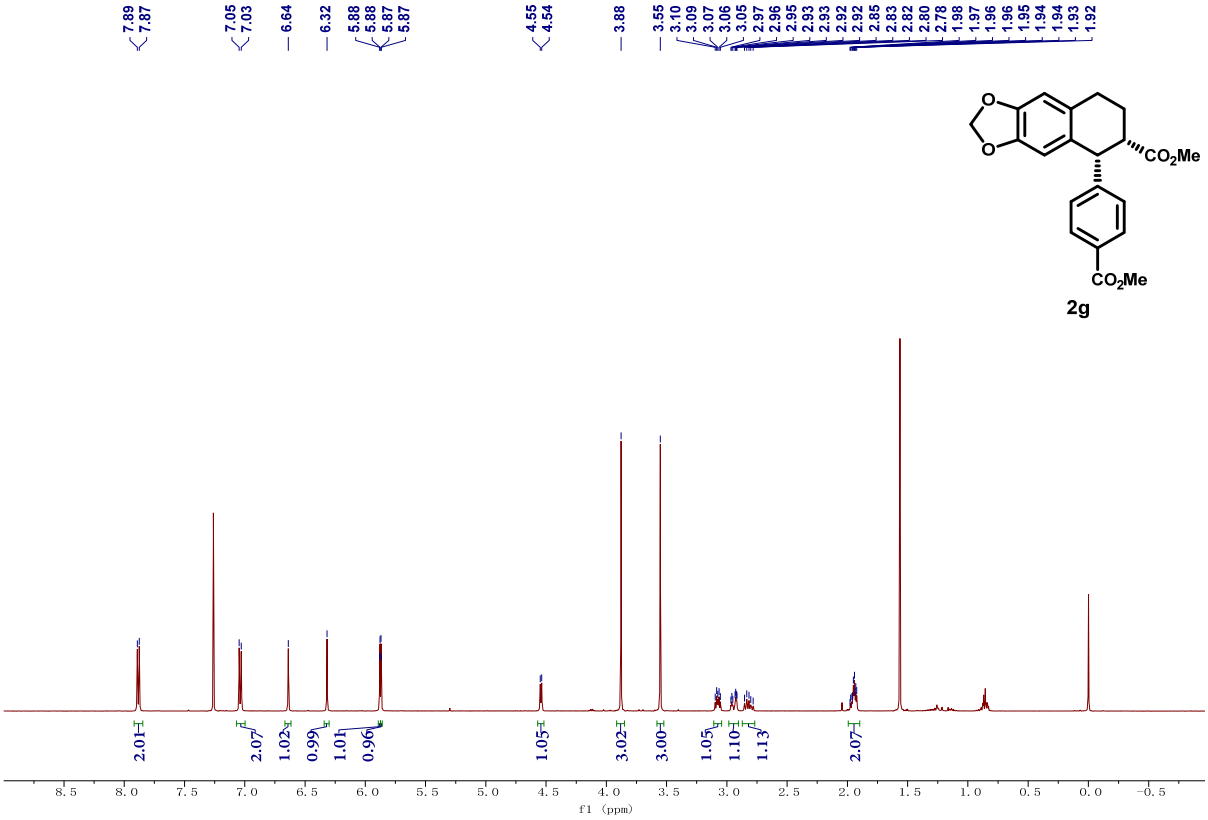


^{19}F NMR (471 MHz, $CDCl_3$)

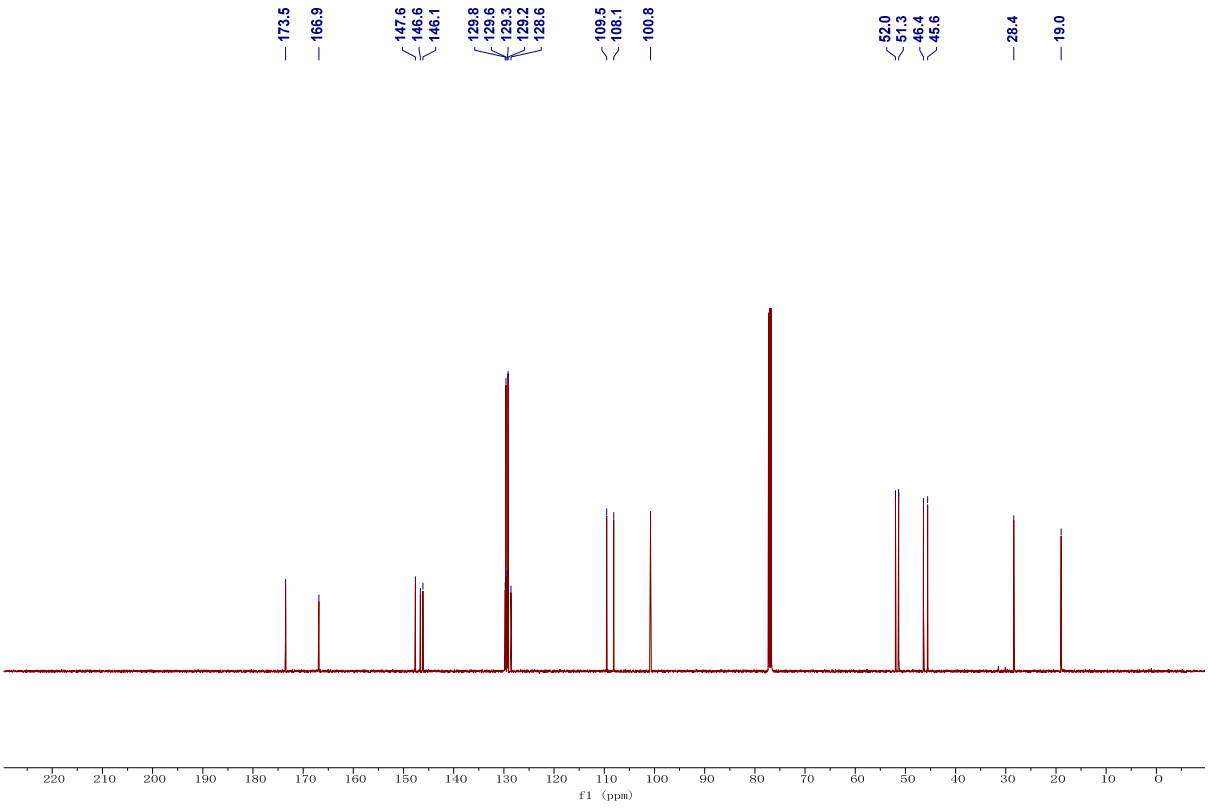


2g: Methyl (5R,6S)-5-(4-(methoxycarbonyl)phenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



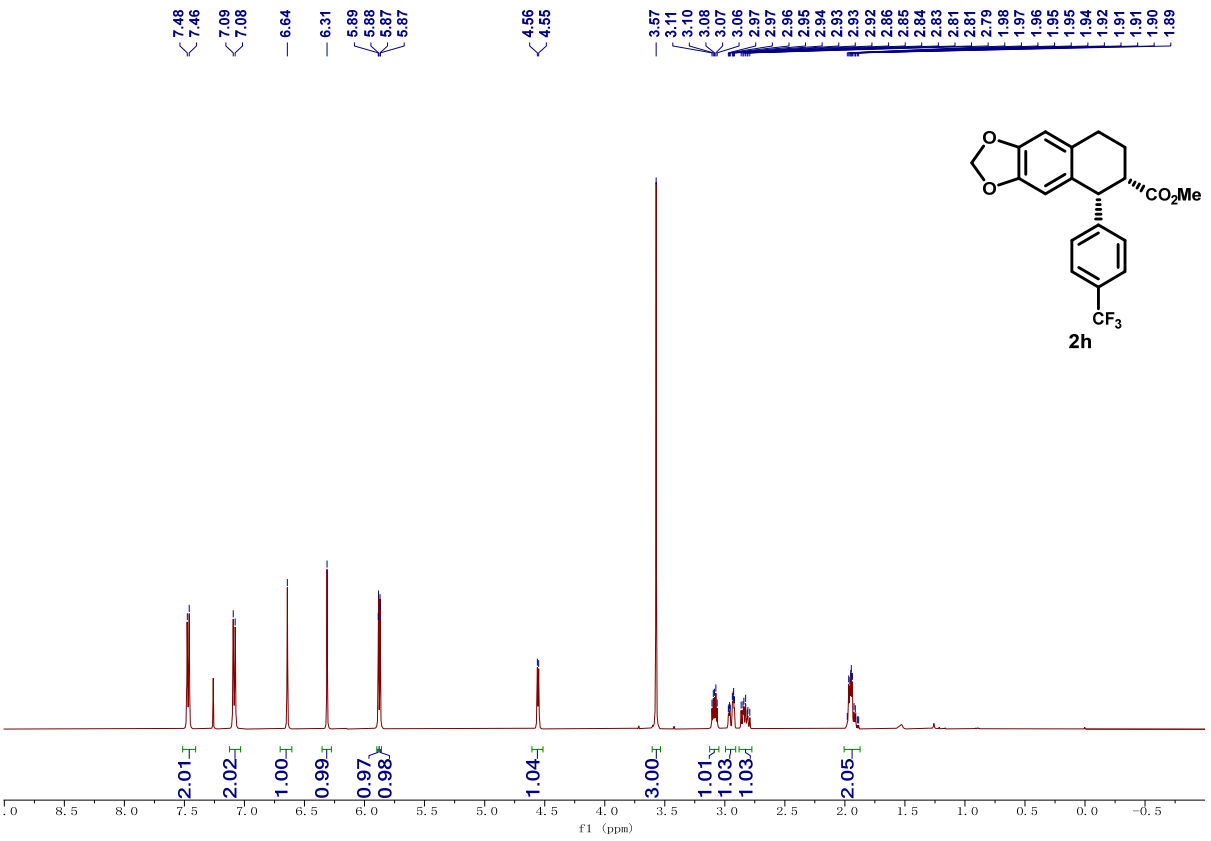
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



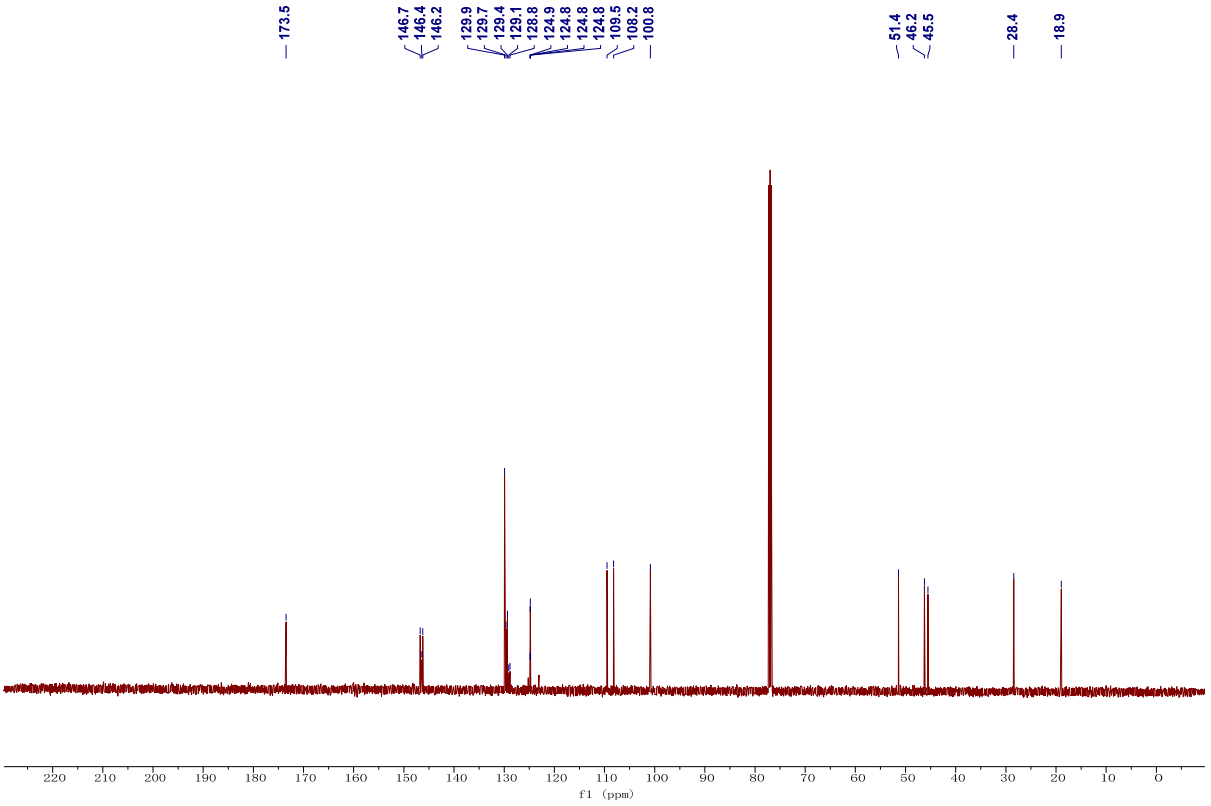
2h: Methyl (5R,6S)-5-(4-(trifluoroMethyl)phenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-

6-carboxylate

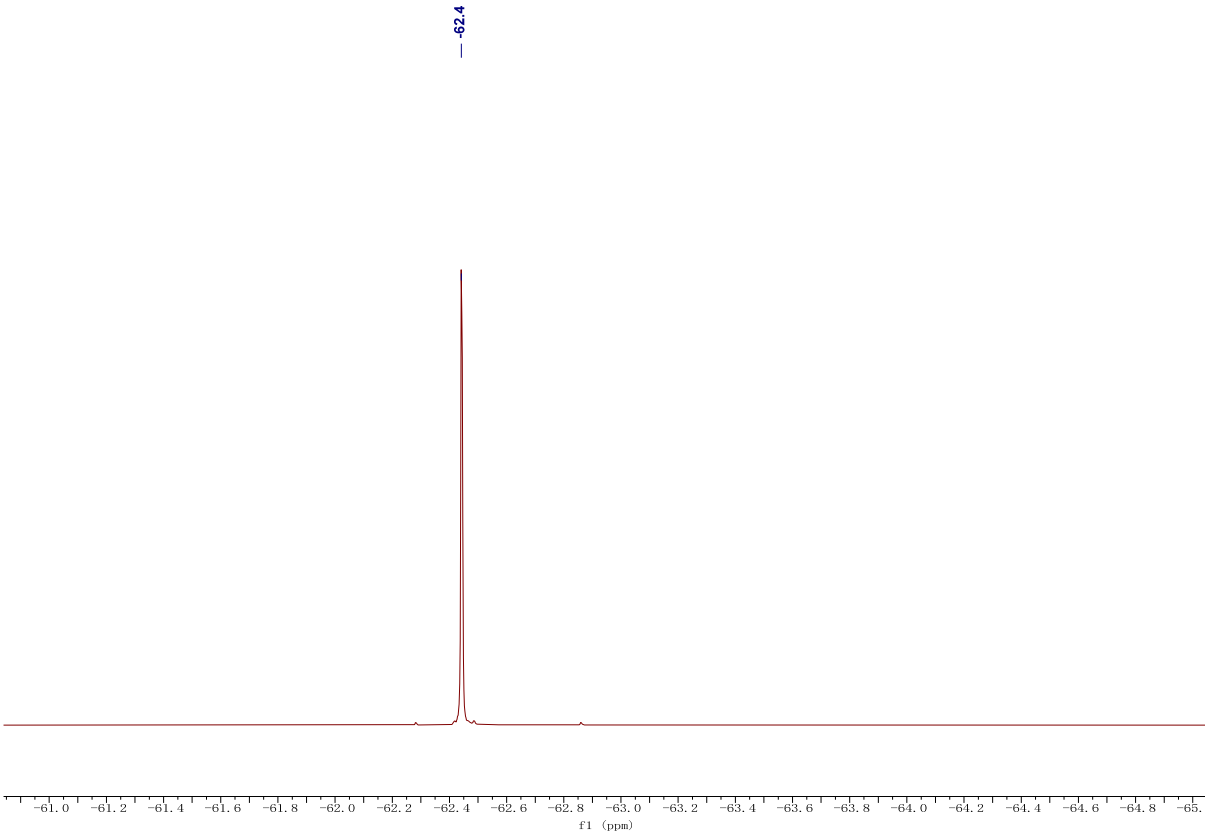
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

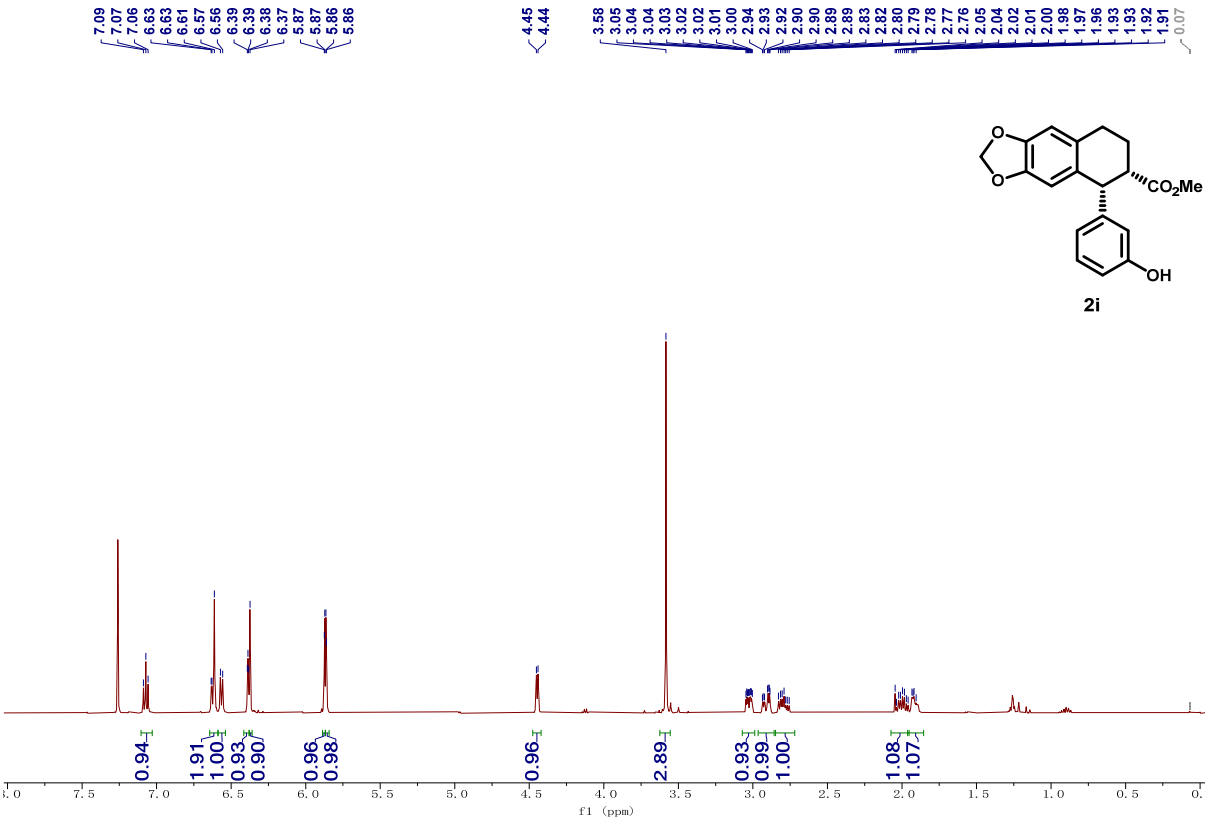


^{19}F NMR (471 MHz, $CDCl_3$)

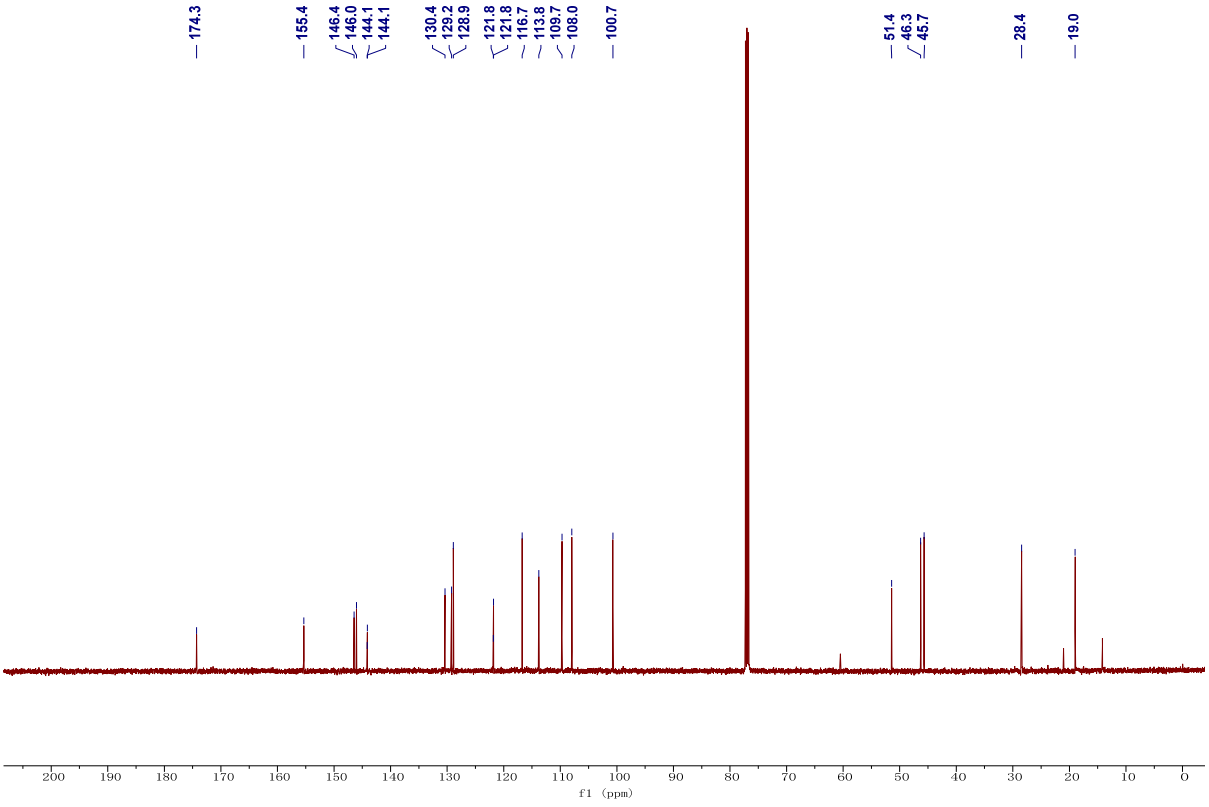


2i: Methyl (5R,6S)-5-(3-hydroxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

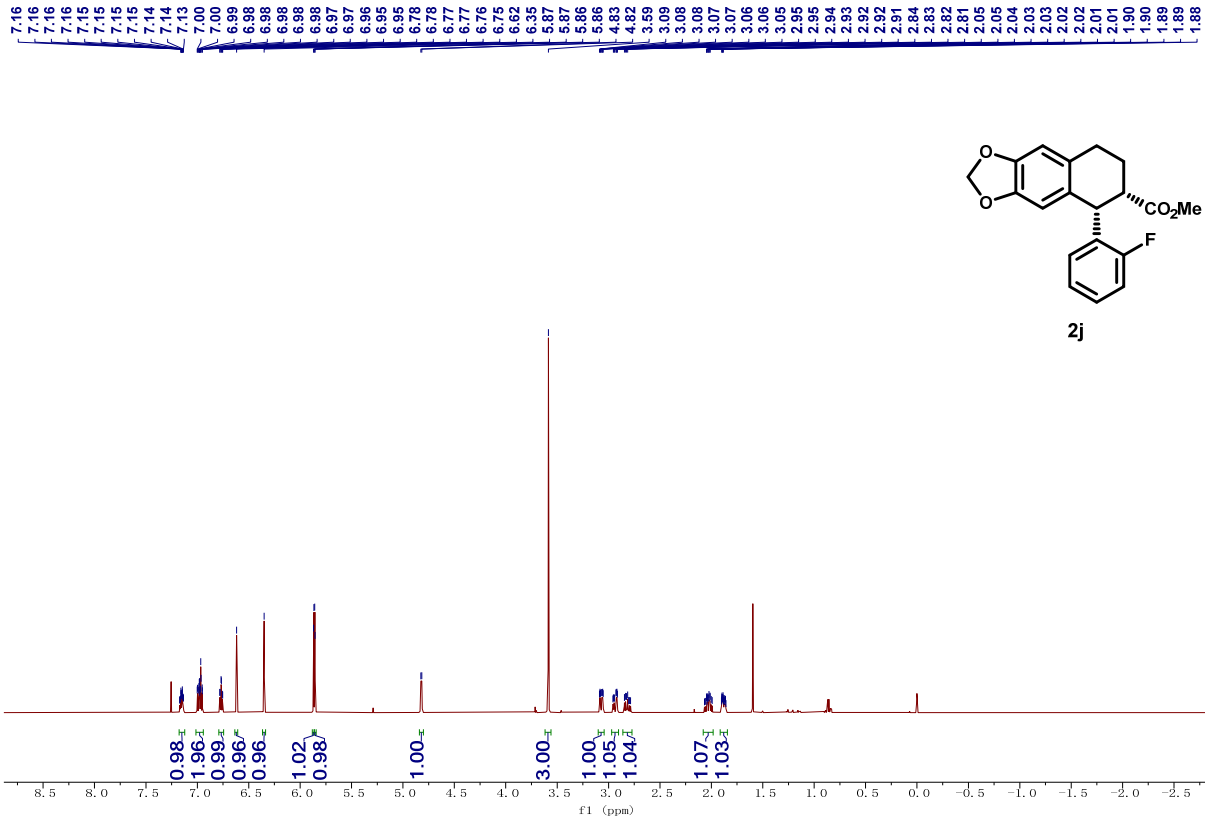


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



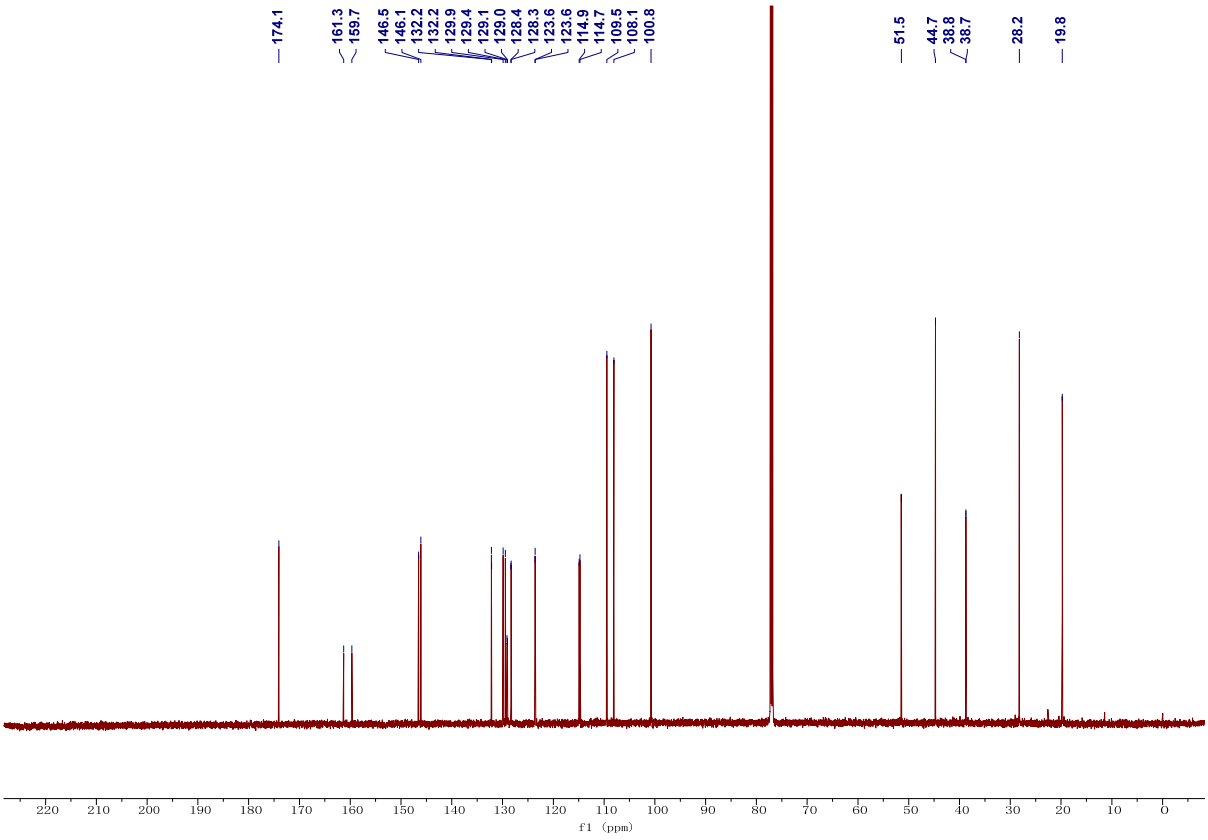
2j: Methyl (5S,6S)-5-(2-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

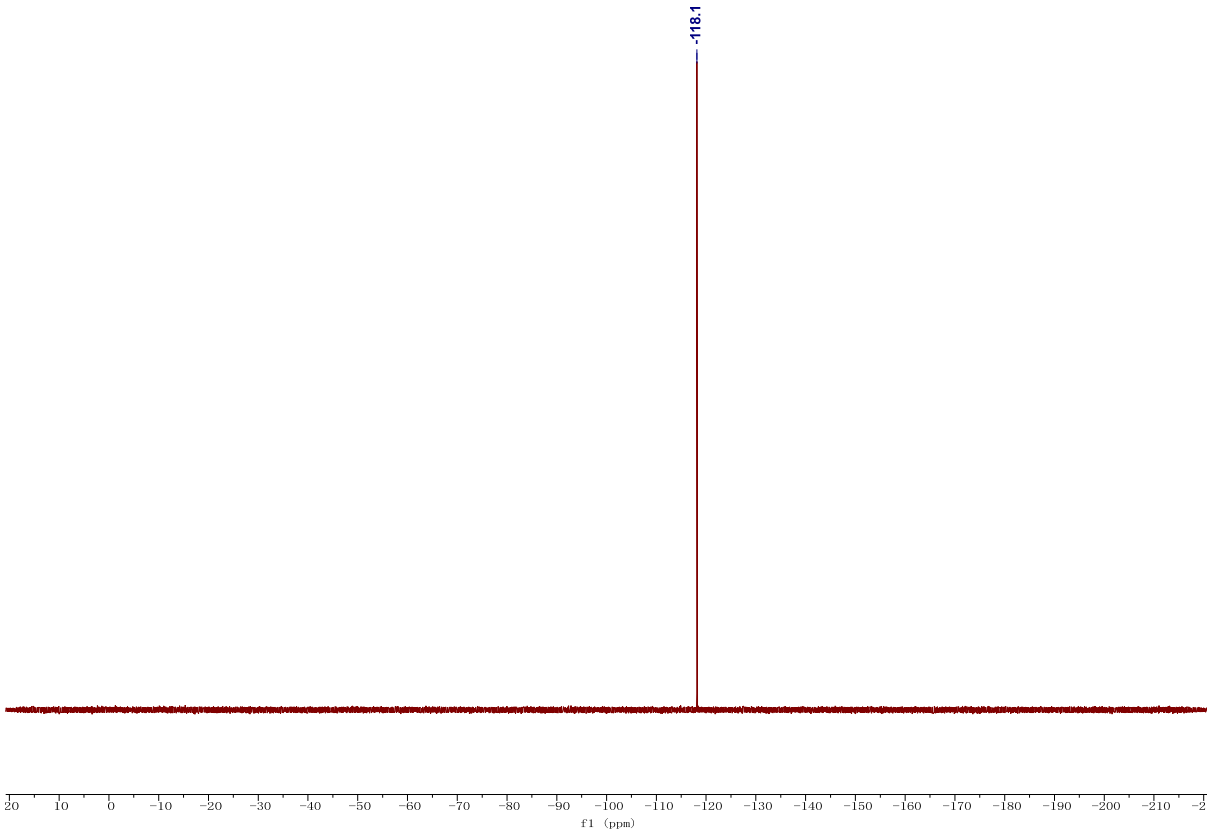


2j

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

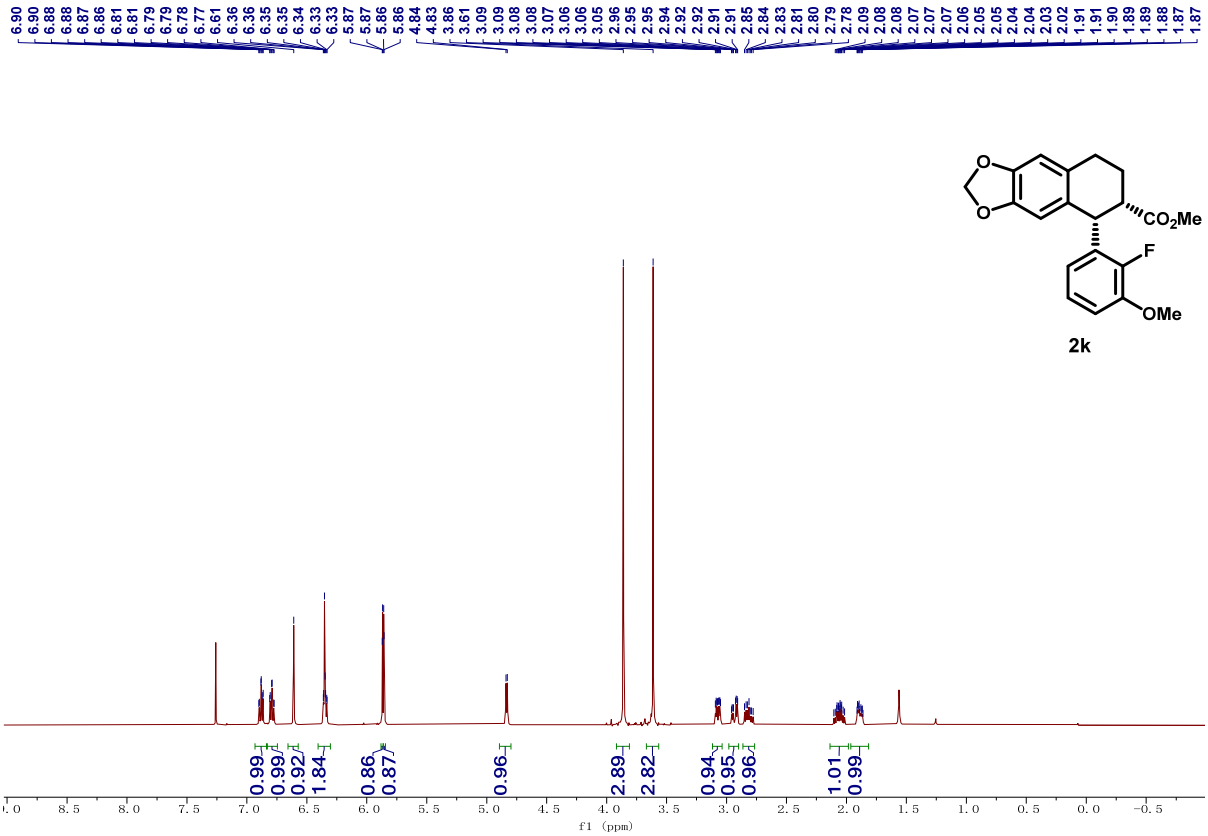


^{19}F NMR (471 MHz, $CDCl_3$)

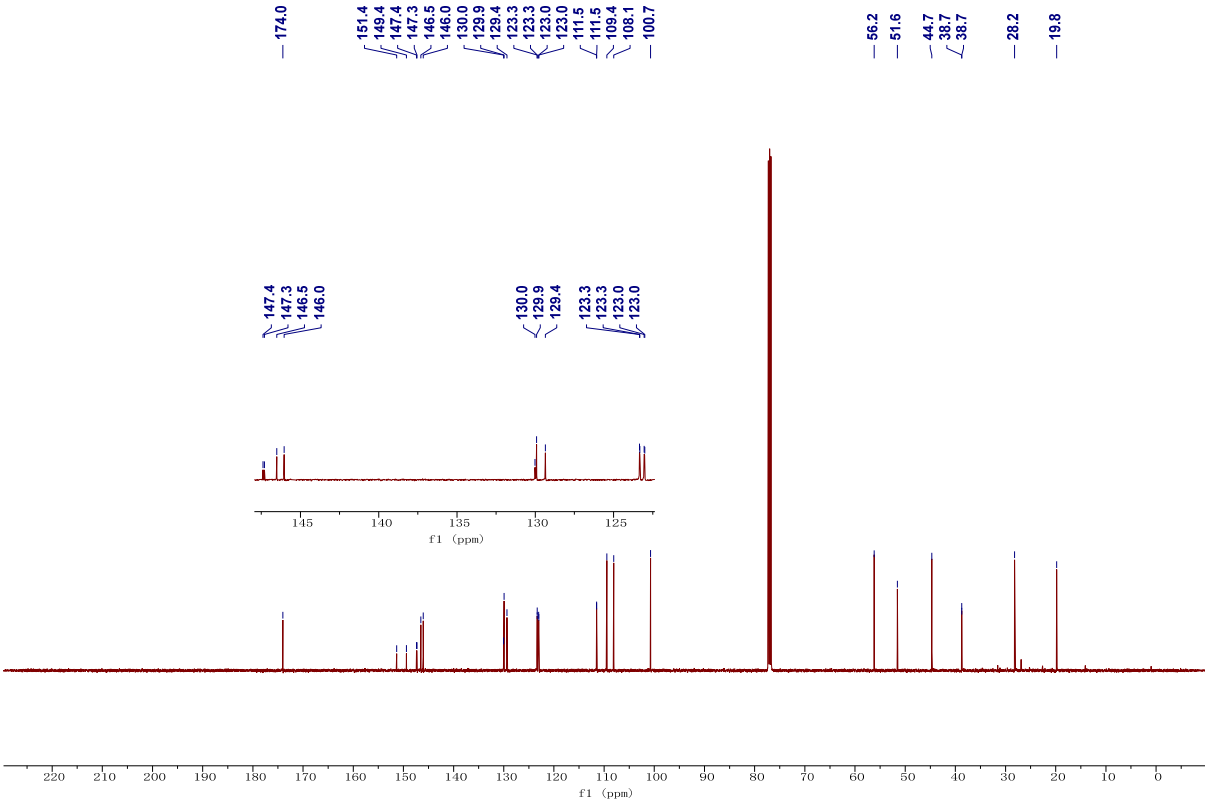


2k: Methyl (5S,6S)-5-(2-fluoro-3-methoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

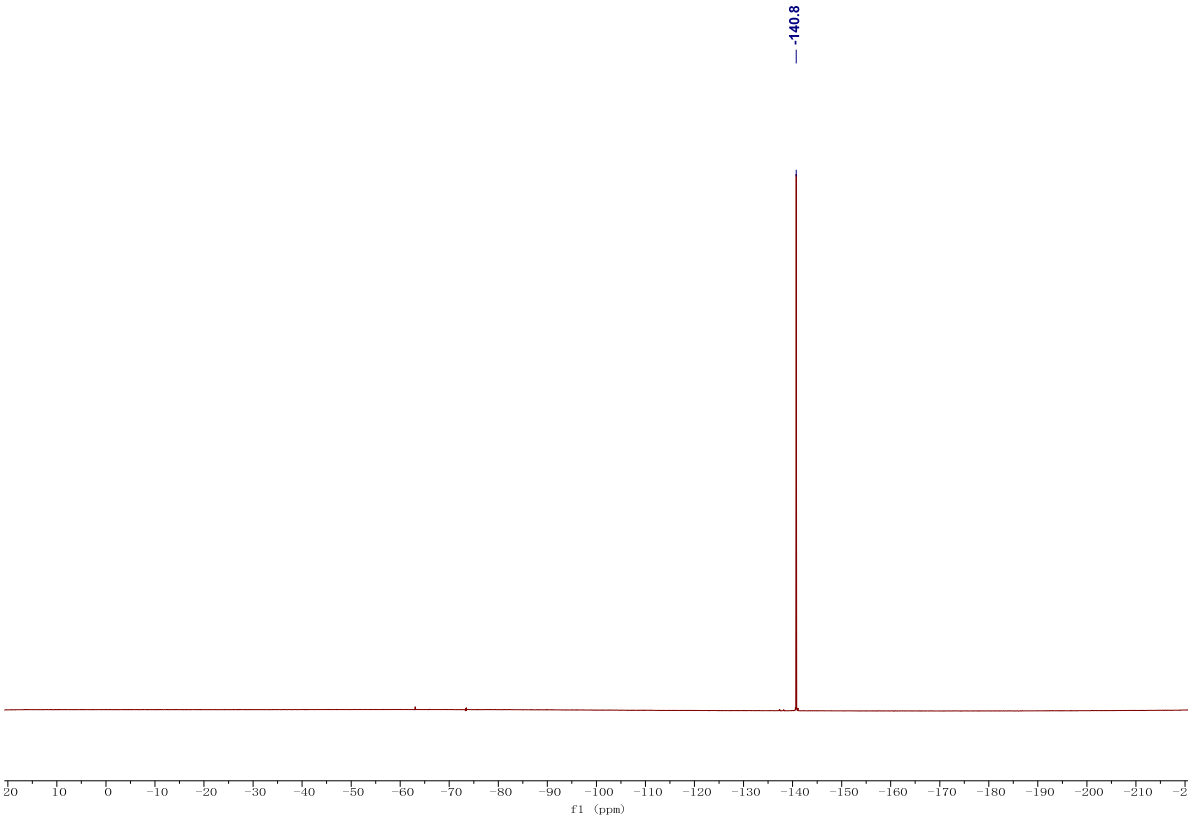
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

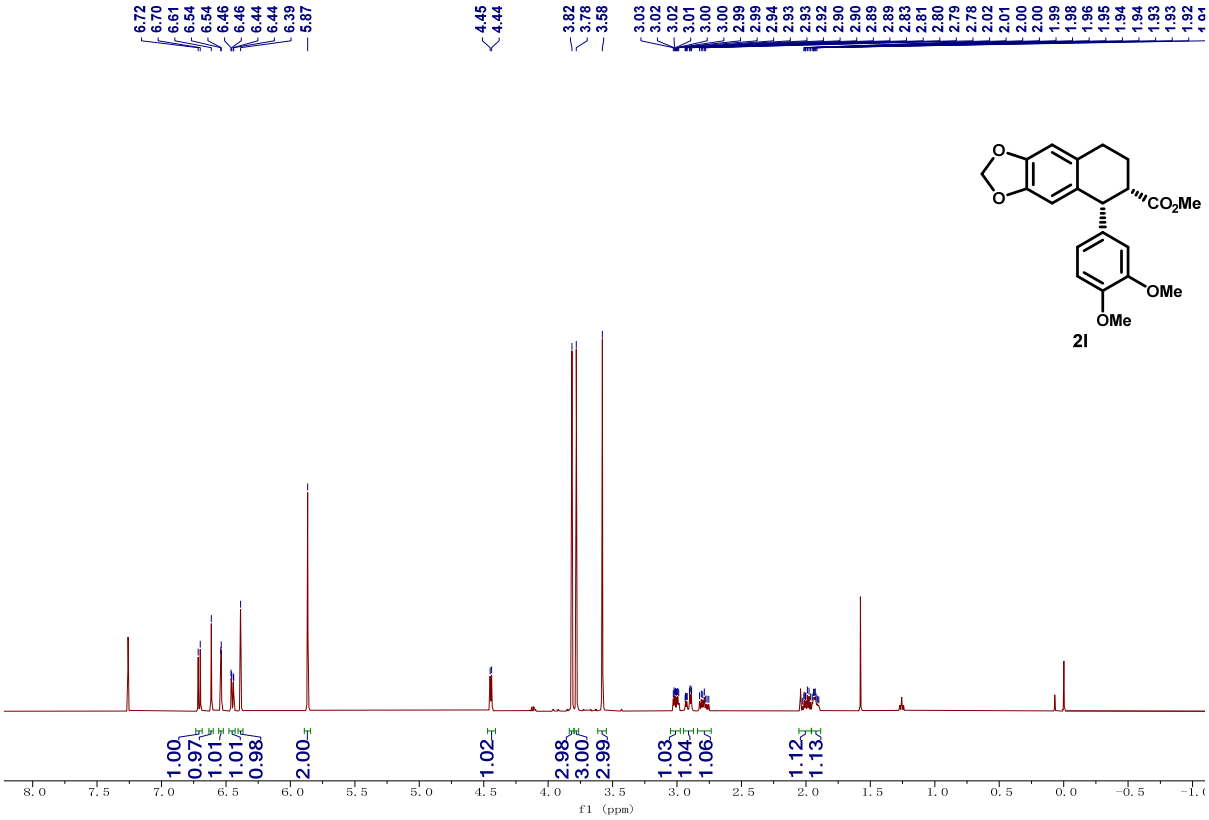


^{19}F NMR (471 MHz, $CDCl_3$)

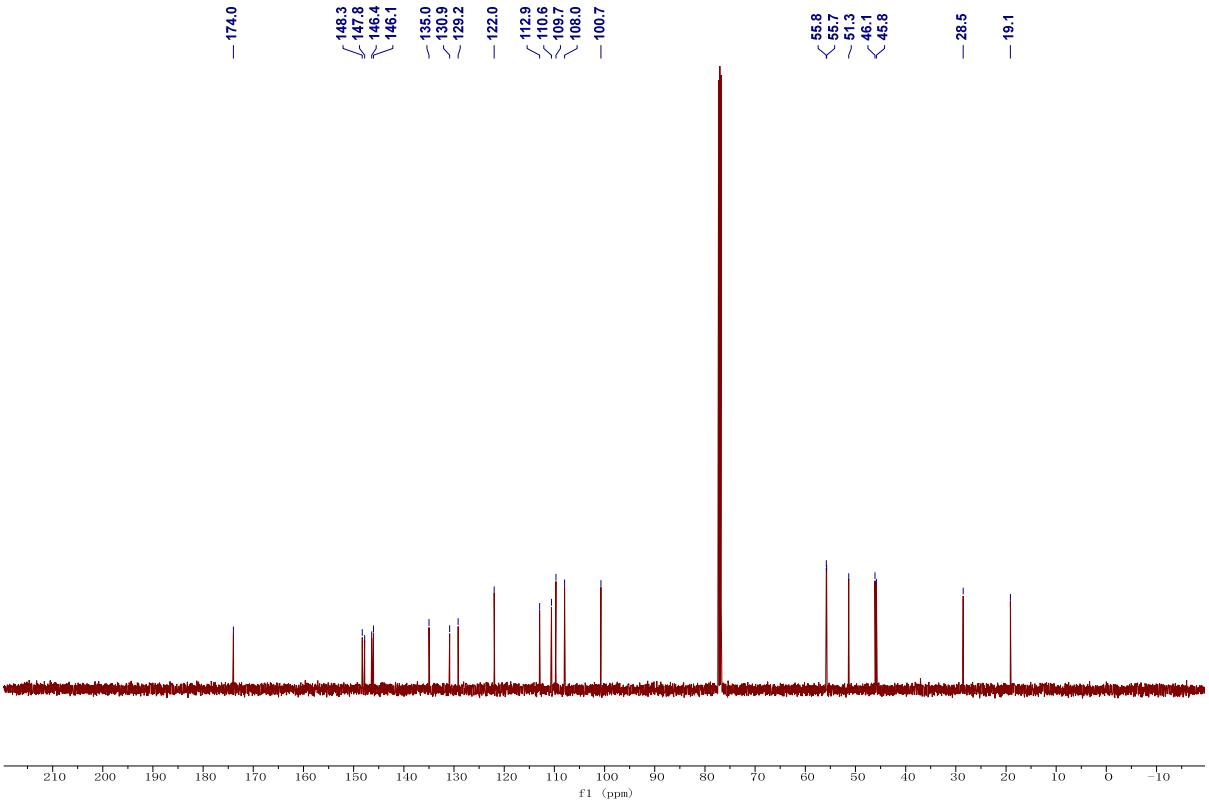


2l: Methyl (5R,6S)-5-(3,4-dimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole- 6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

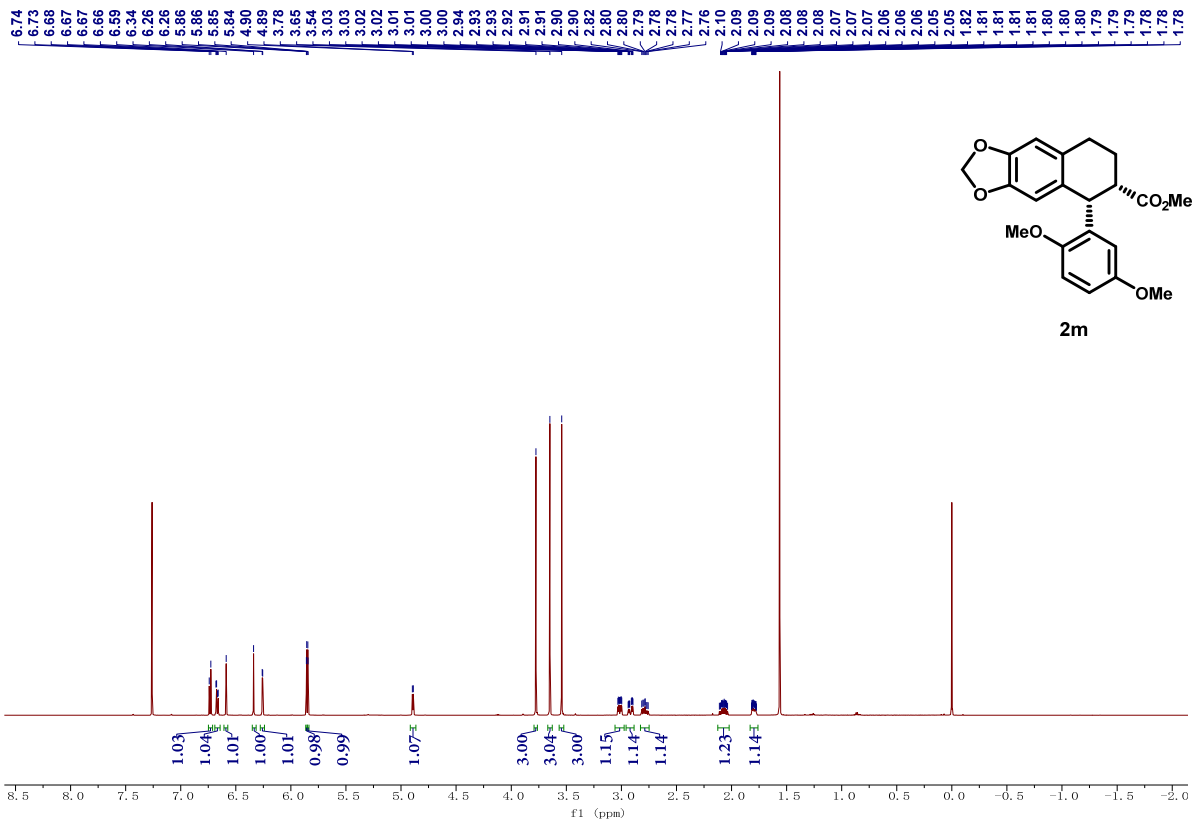


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

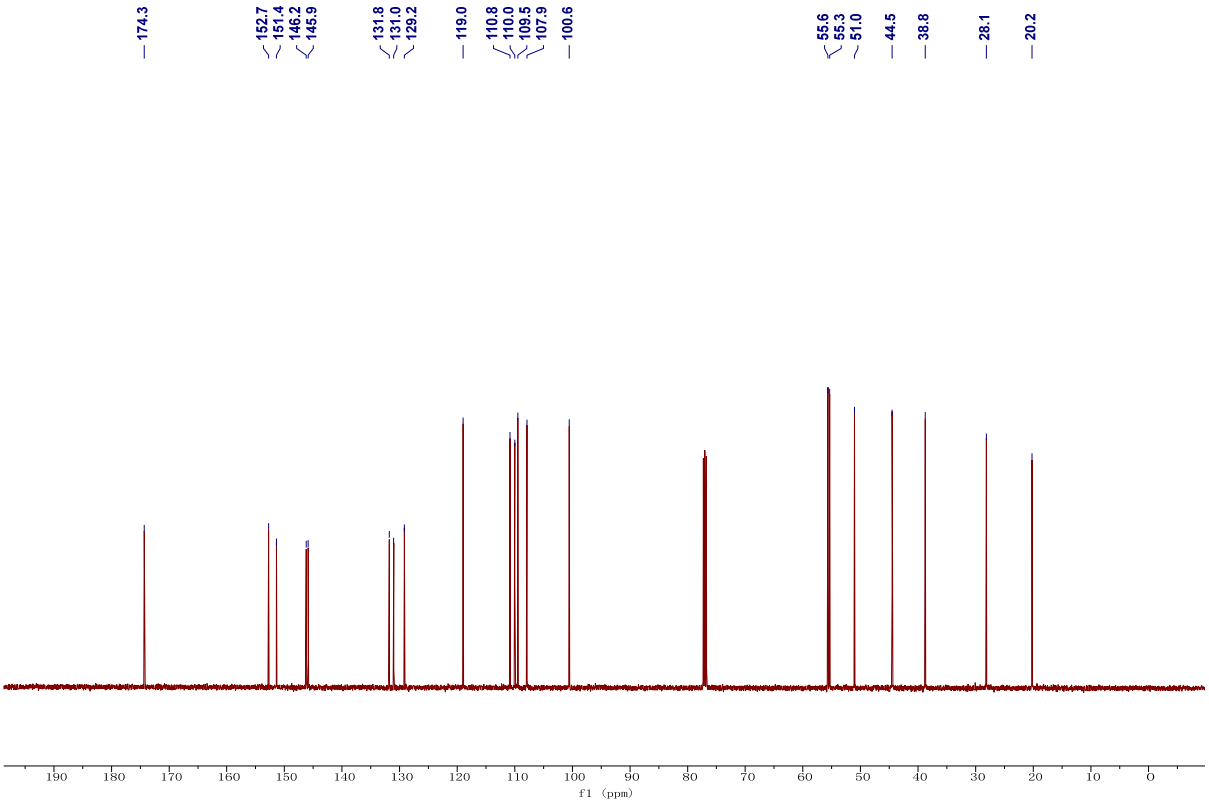


2m: Methyl (5S,6S)-5-(2,5-dimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

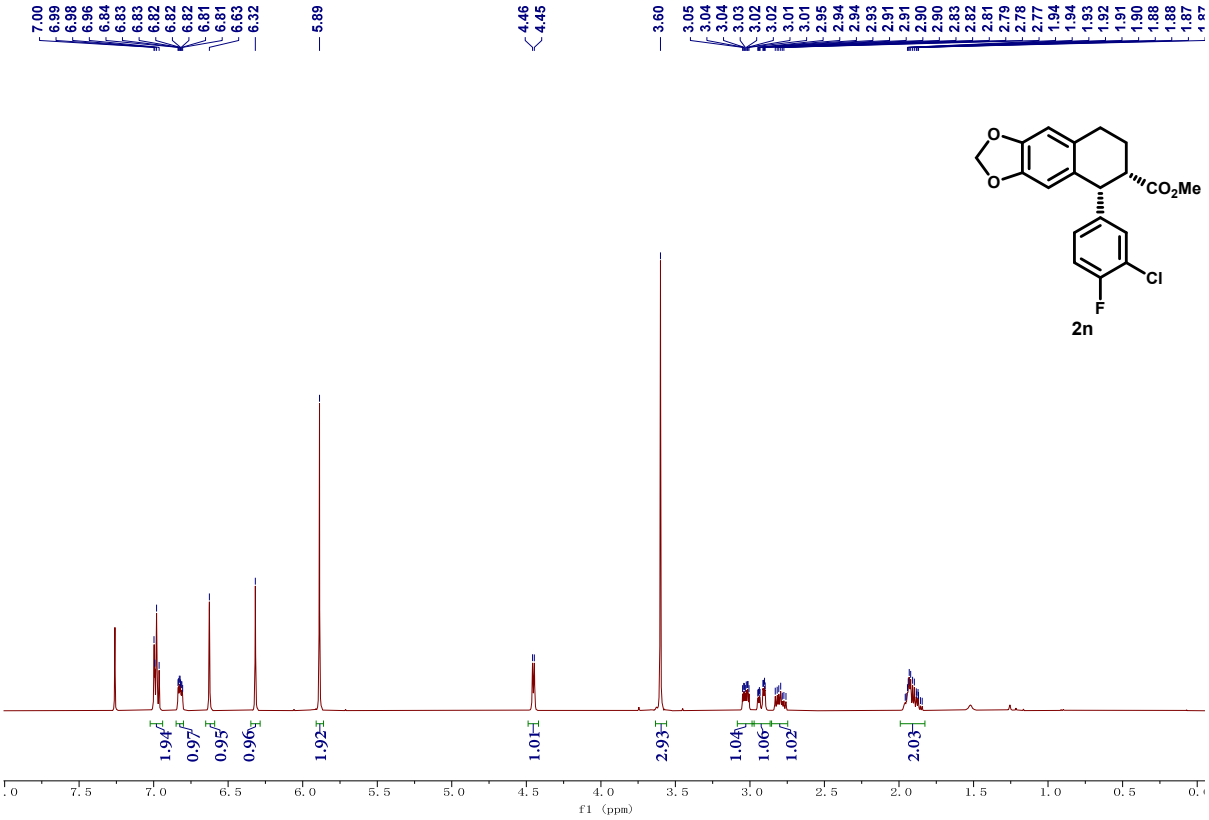


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

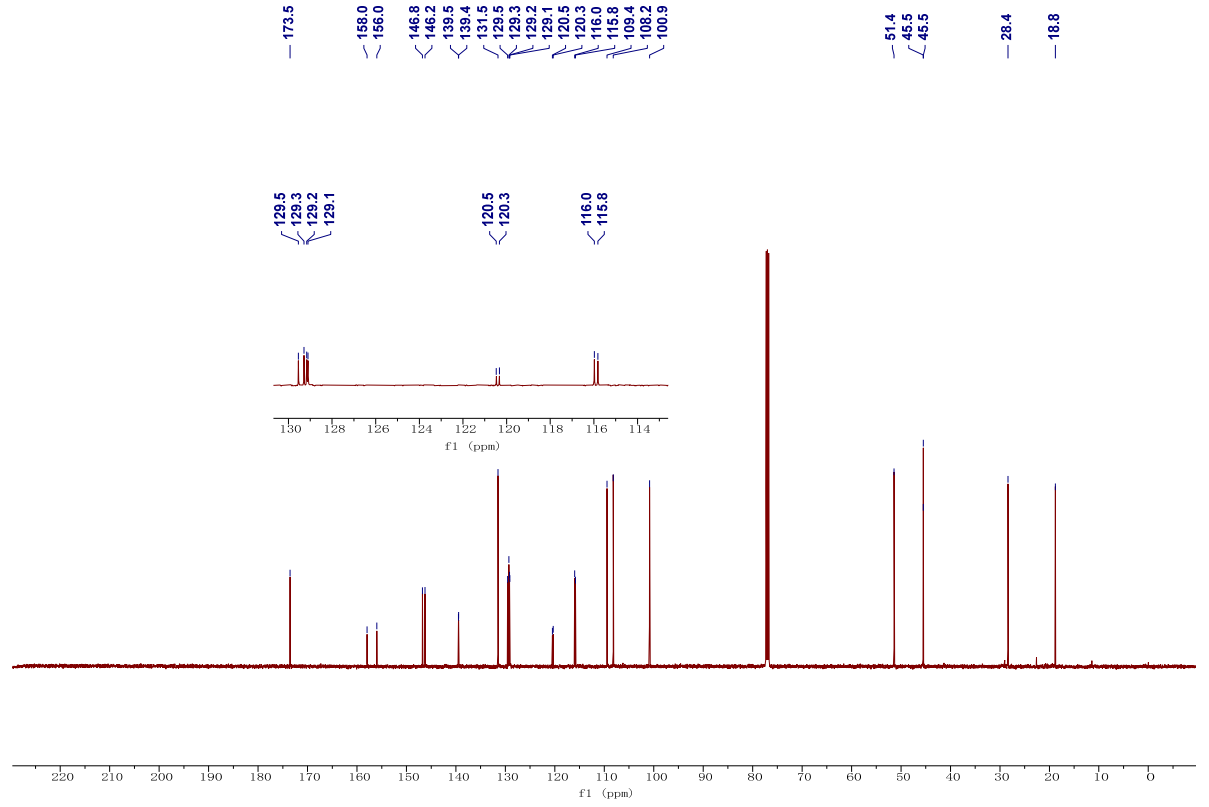


2n: Methyl (5R,6S)-5-(3-chloro-4-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

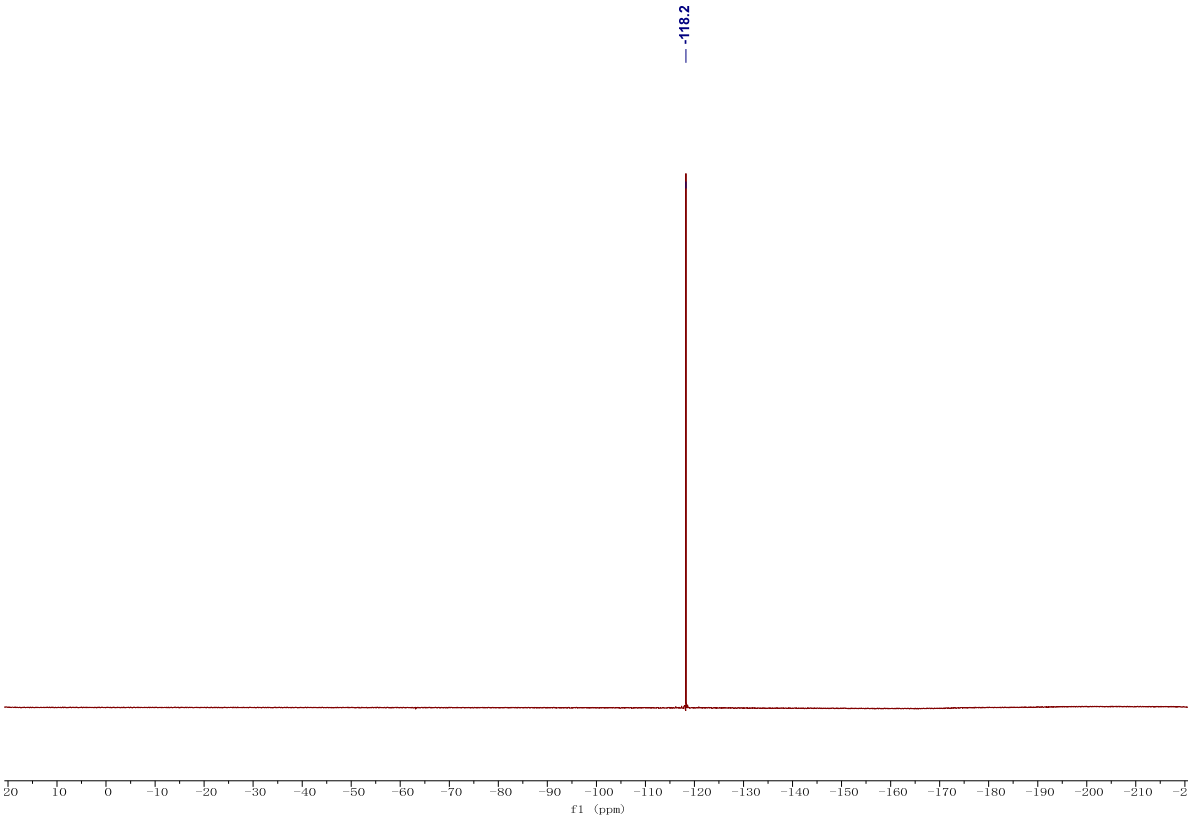
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

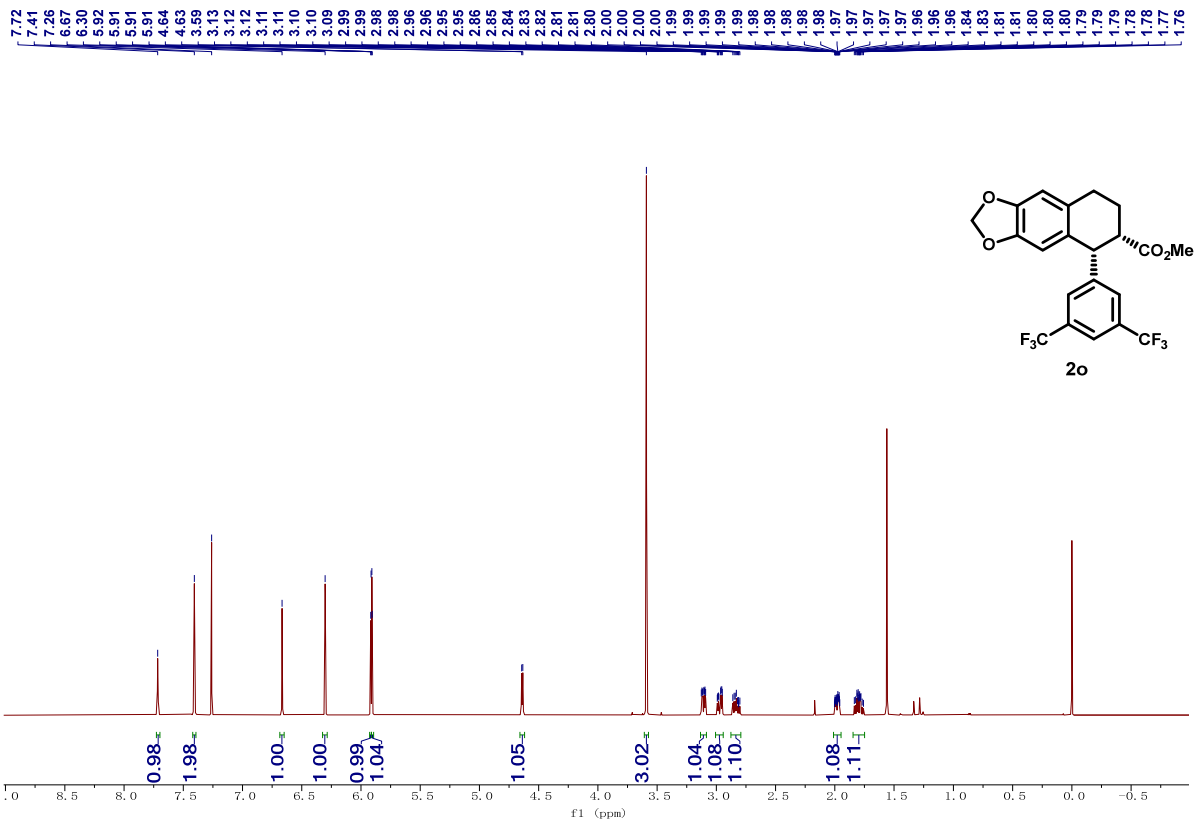


^{19}F NMR (471 MHz, $CDCl_3$)

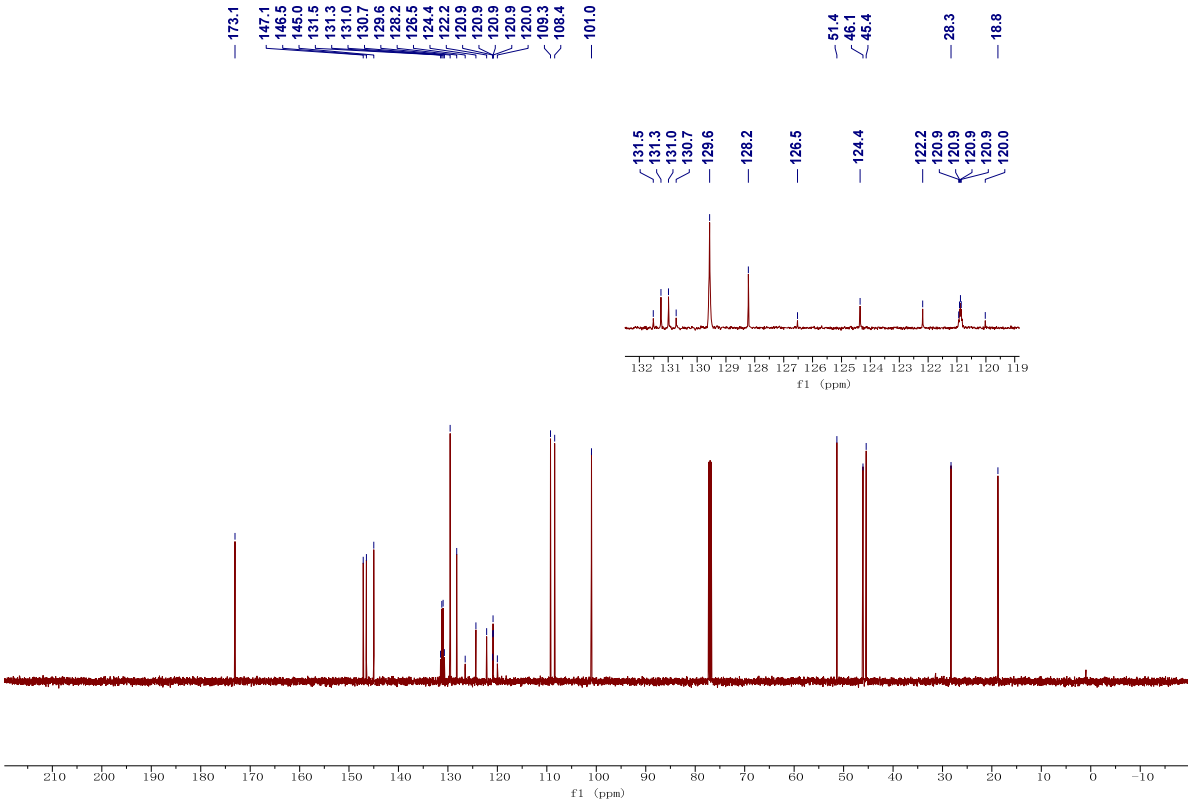


2o: Methyl (5R,6S)-5-(3,5-bis(trifluoroMethyl)phenyl)-5,6,7,8-tetrahydronaphtho[2,3-d]- [1,3]-dioxole-6-carboxylate

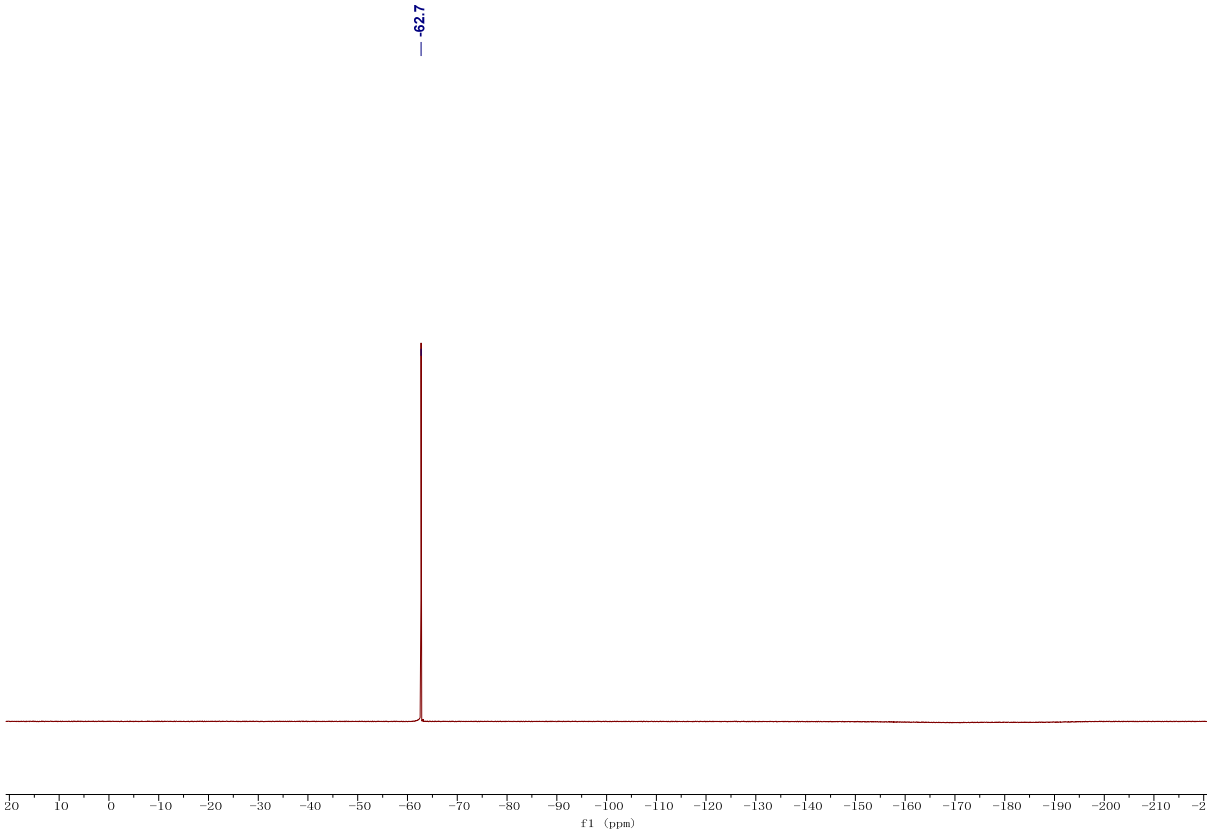
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

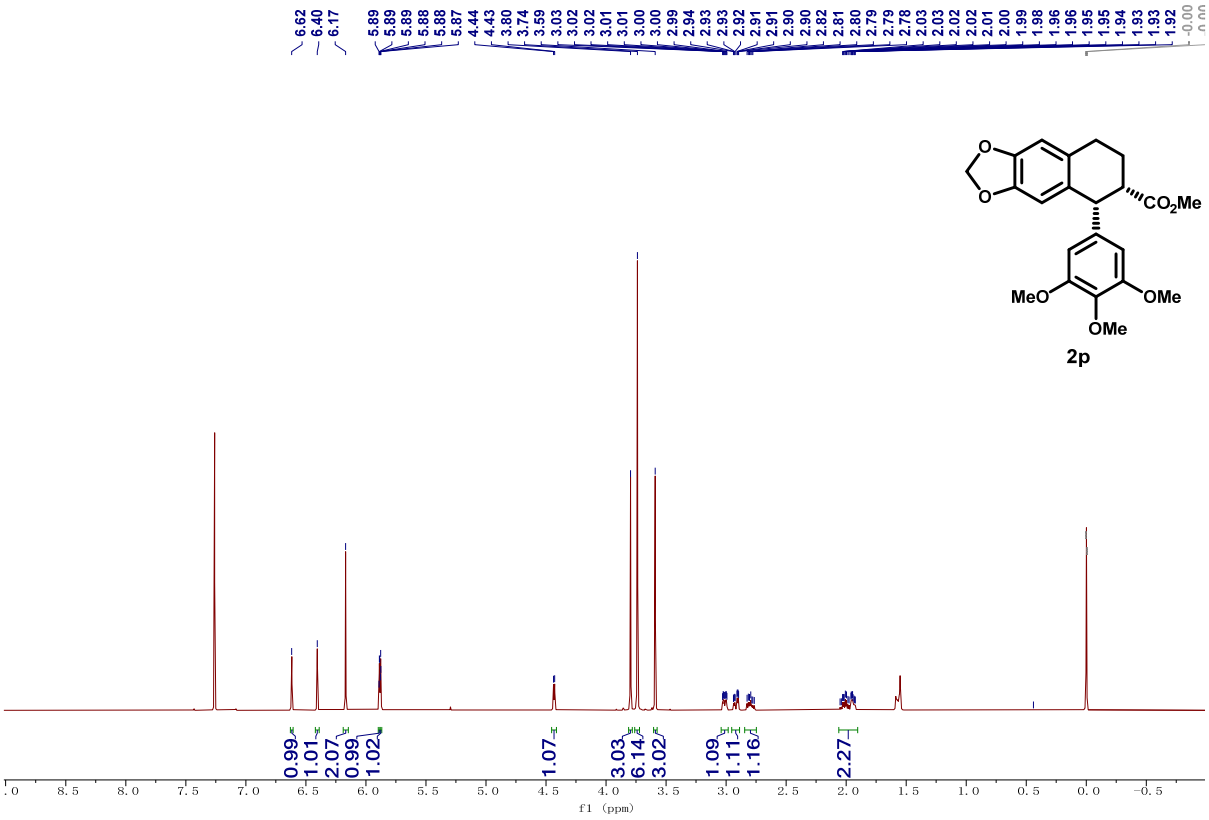


^{19}F NMR (471 MHz, $CDCl_3$)

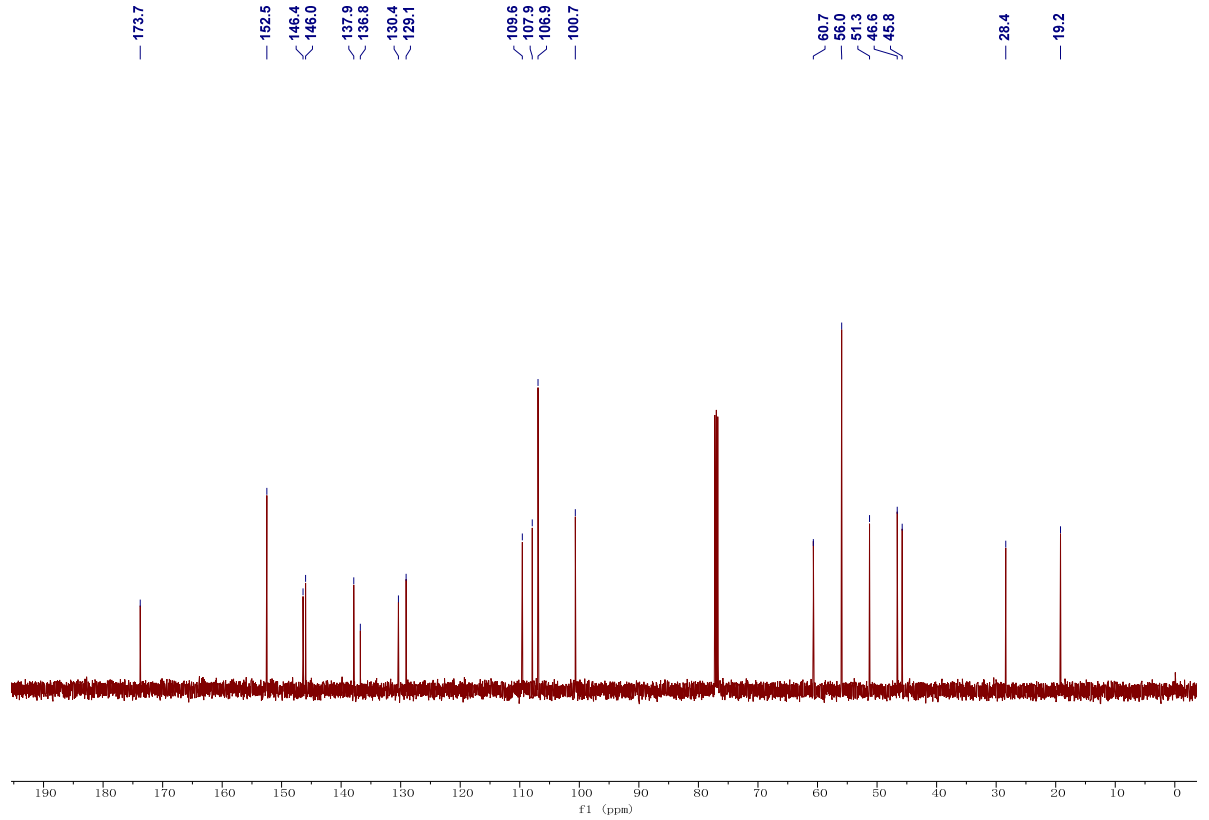


2p: Methyl (5R,6S)-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

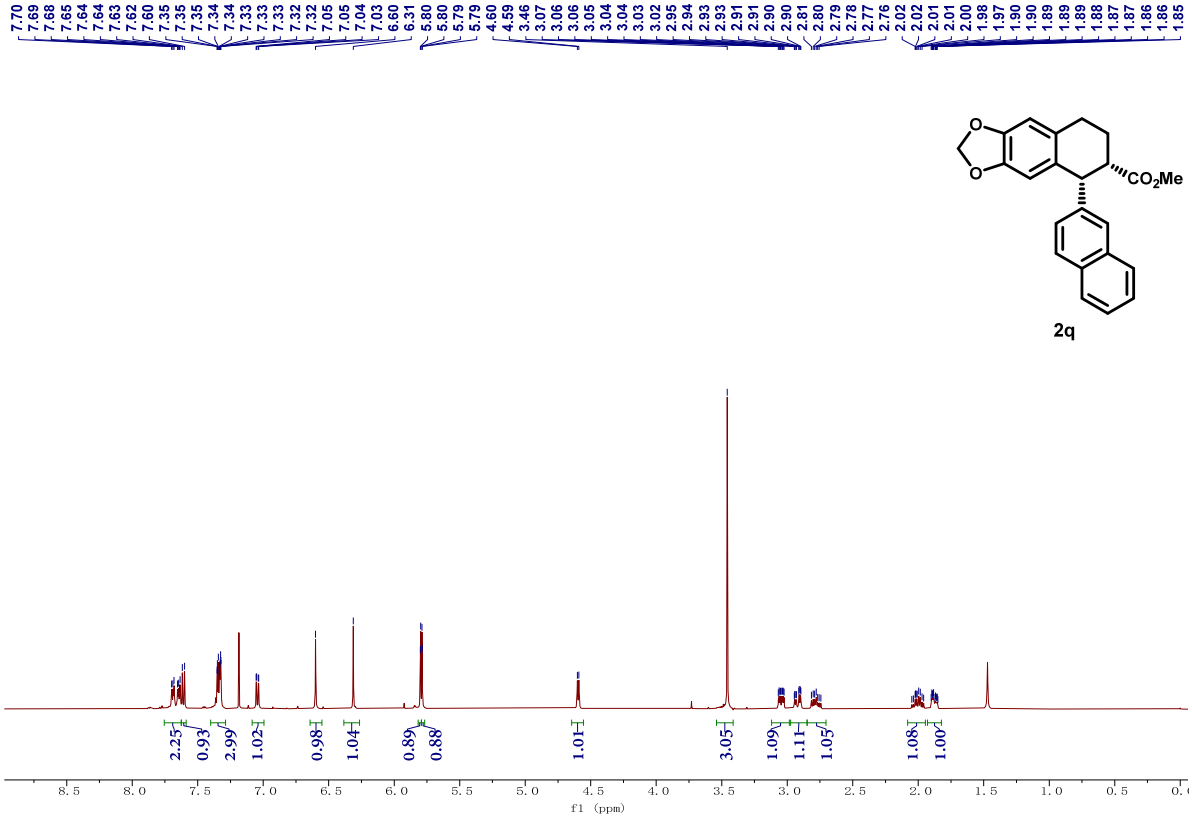


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

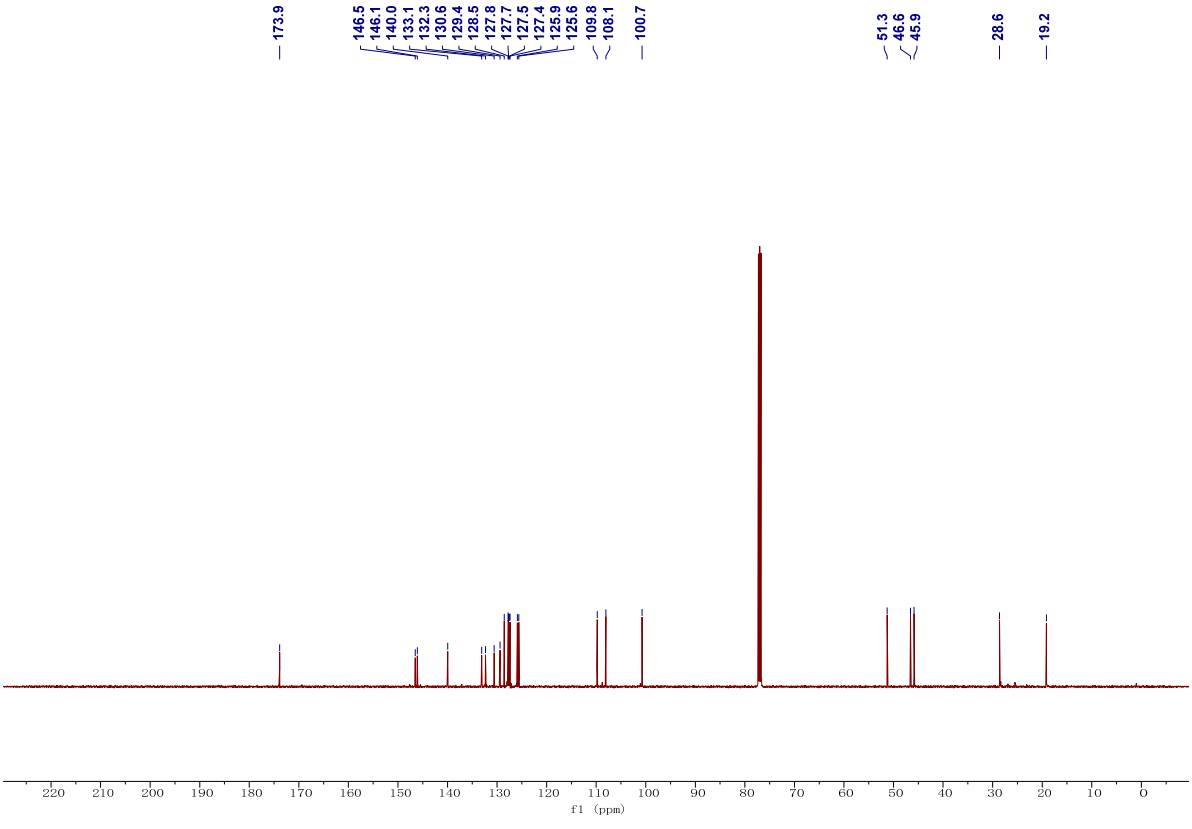


2q: Methyl (5R,6S)-5-(naphthalen-2-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

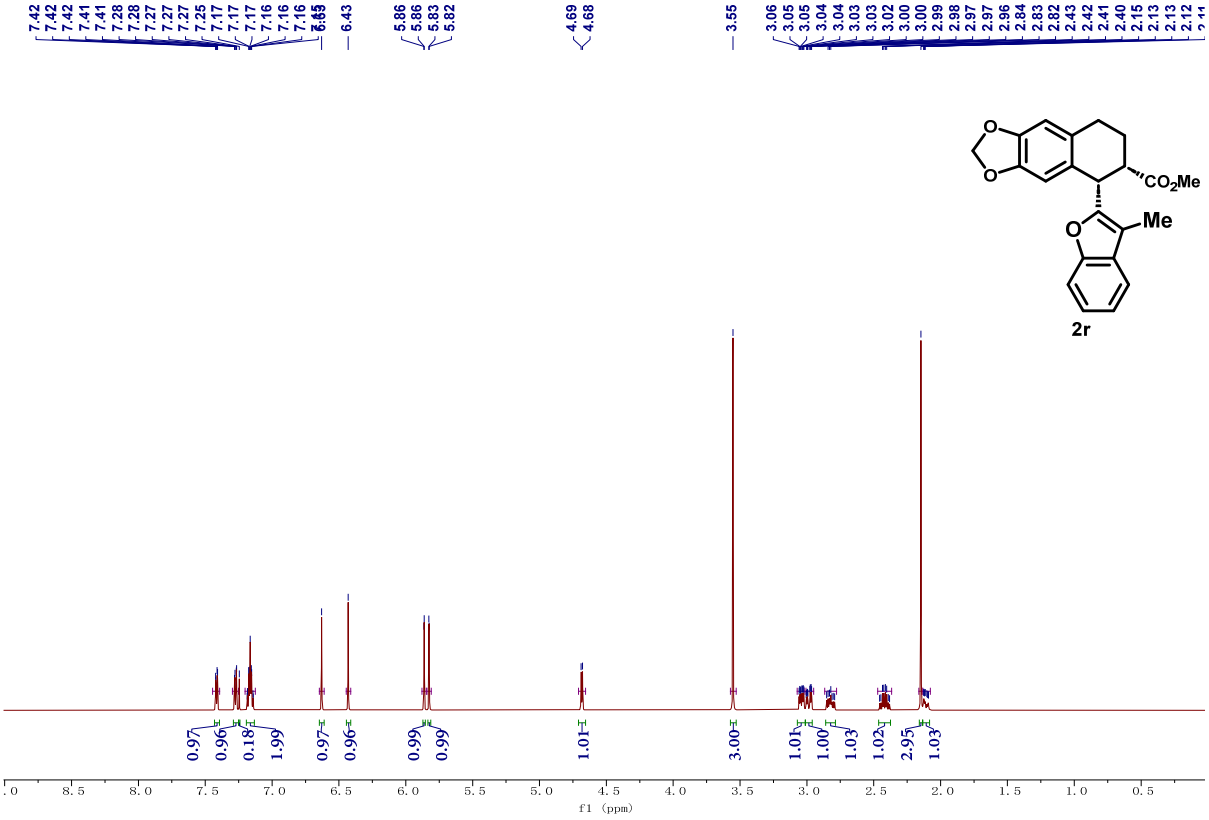


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

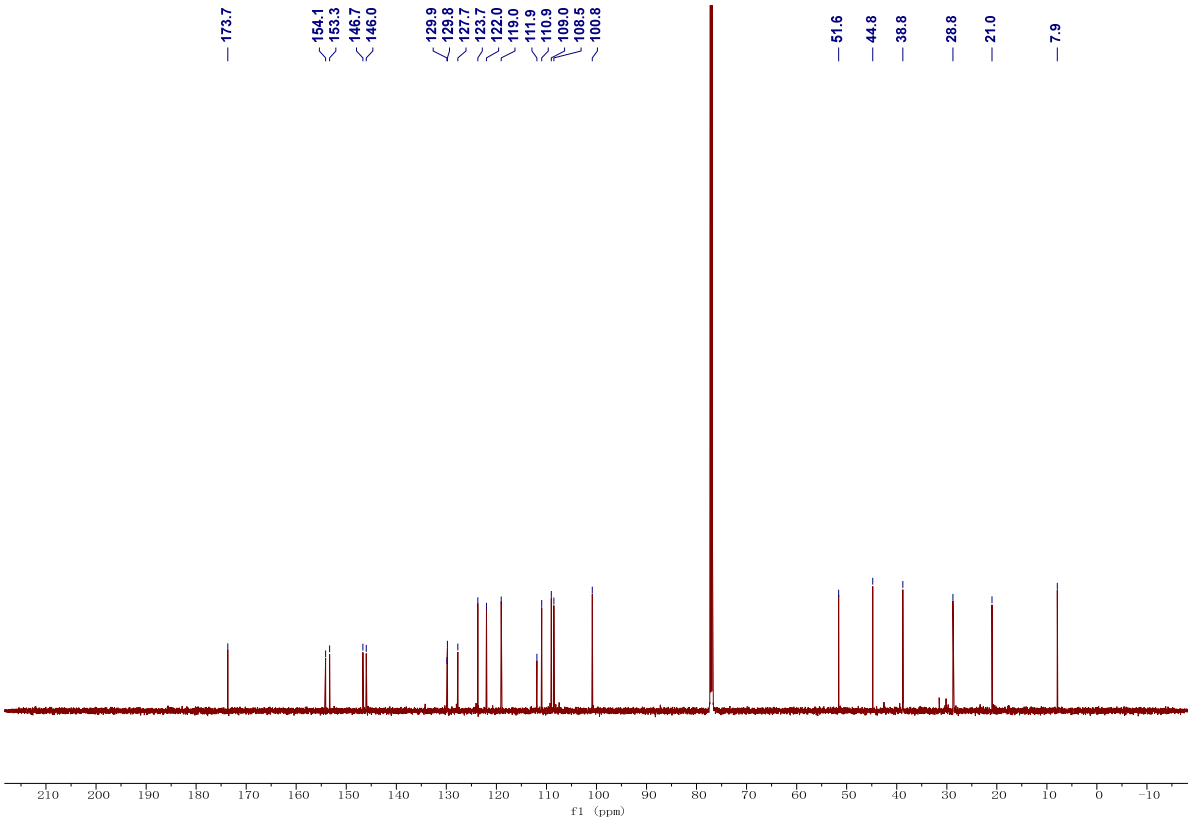


2r: Methyl (5S,6S)-5-(3-Methylbenzofuran-2-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

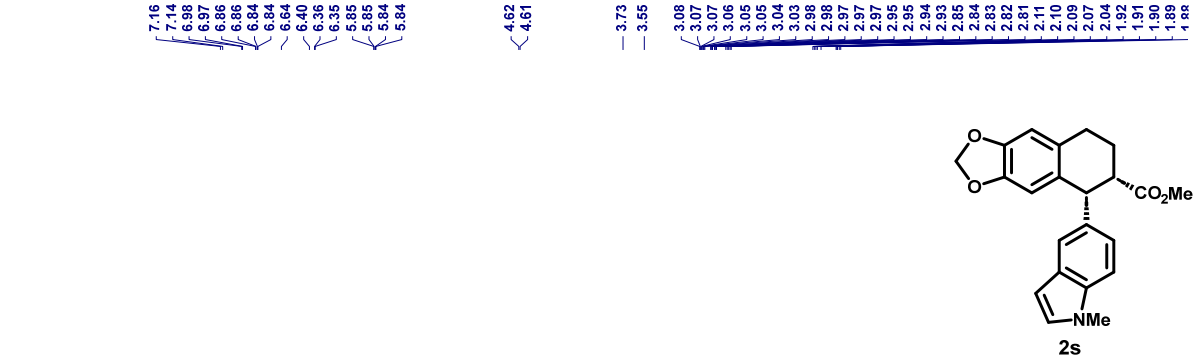


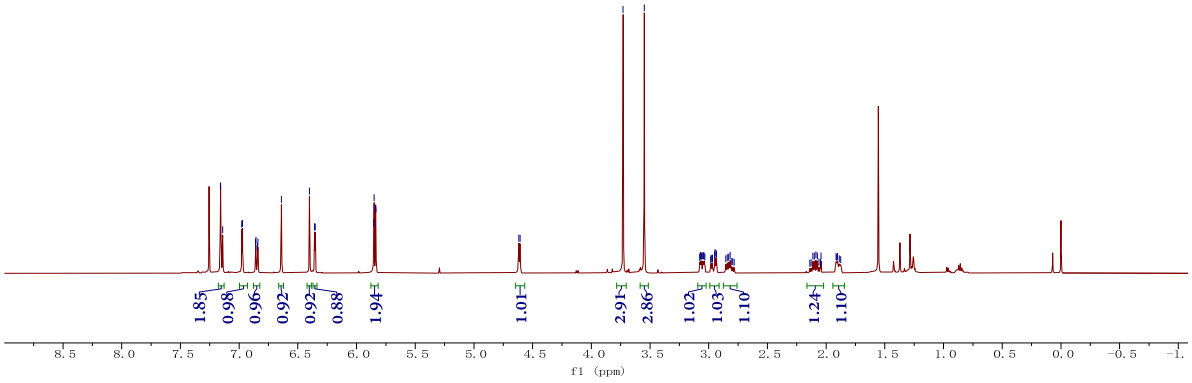
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



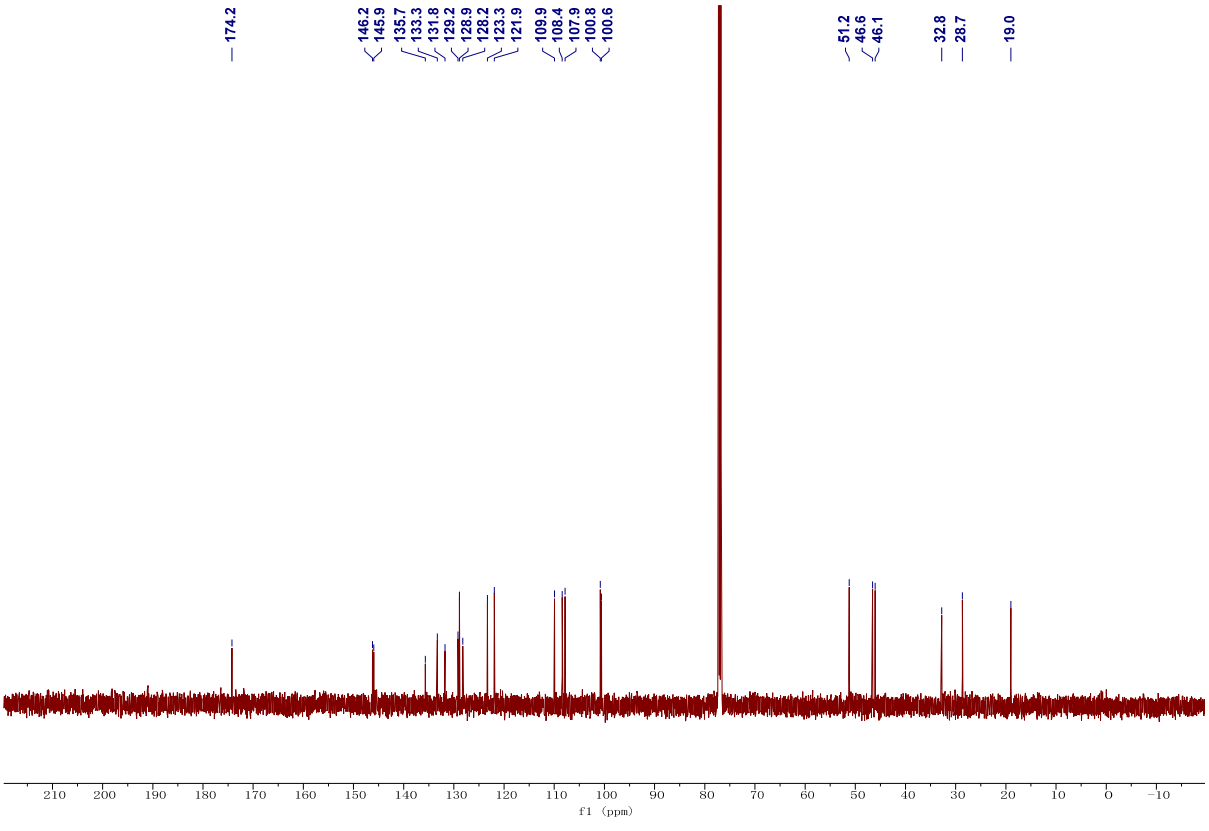
2s: Methyl (5R,6S)-5-(1-Methyl-1H-indol-5-yl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]- dioxole-6 carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



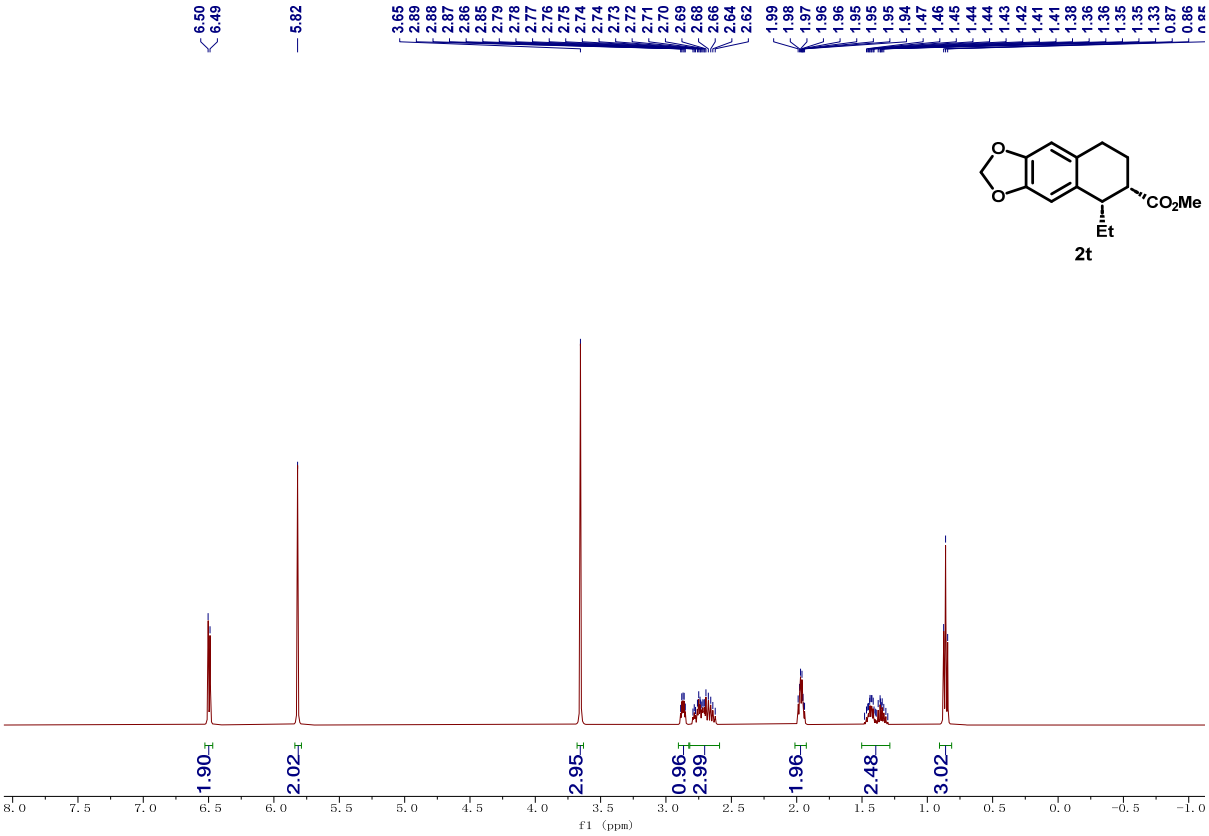


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

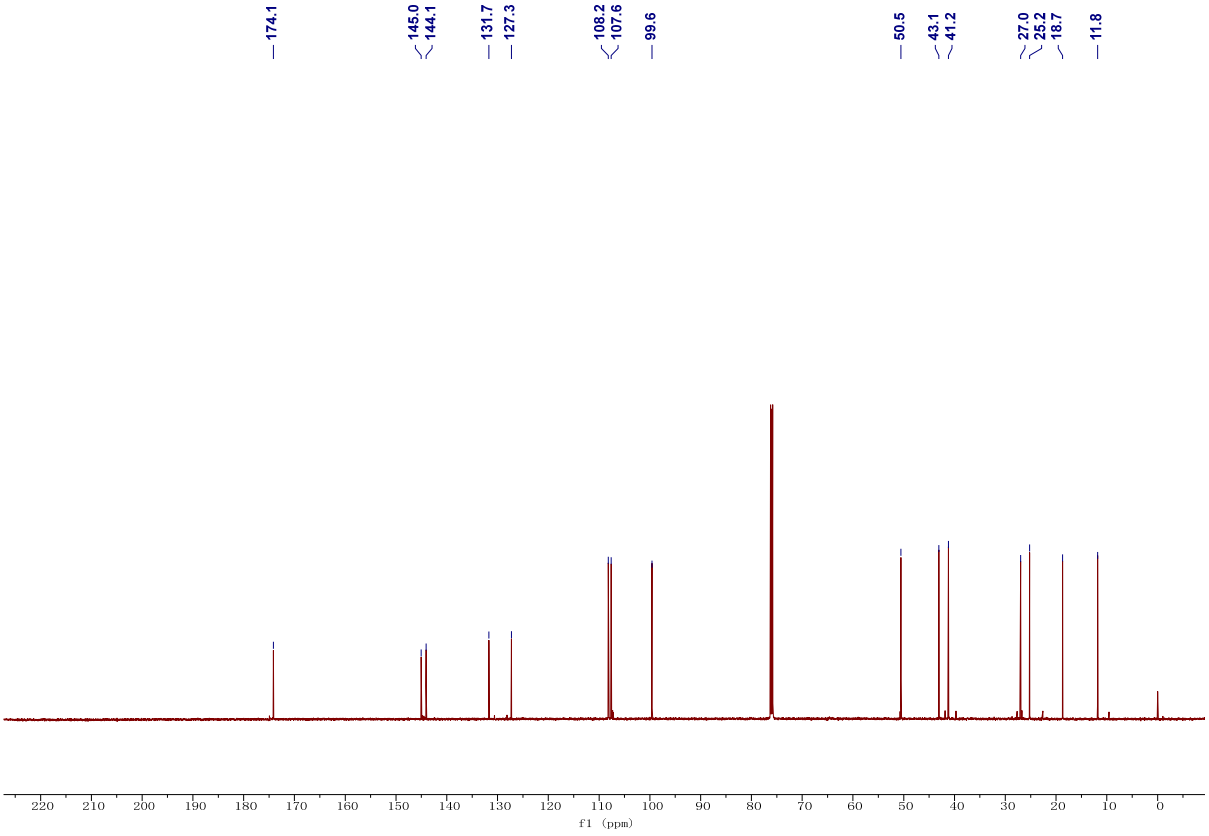


2t: Methyl (5S,6S)-5-ethyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

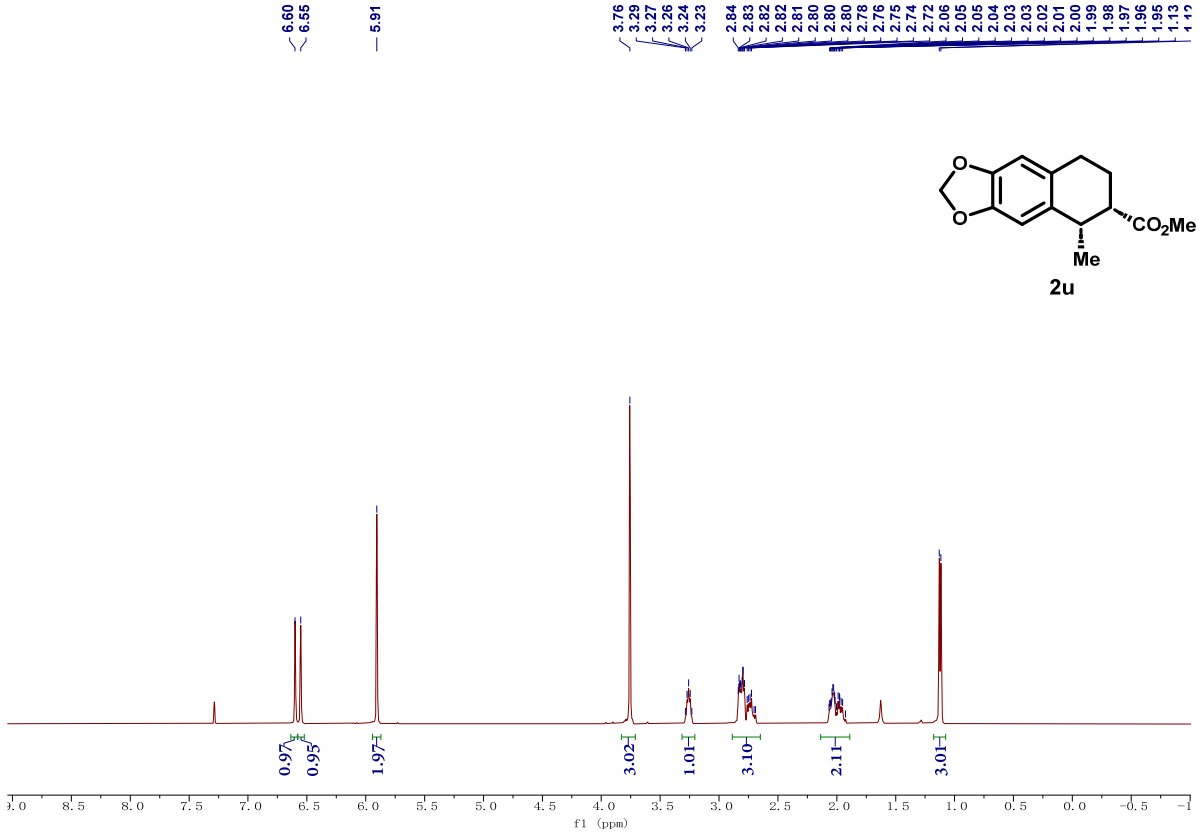


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

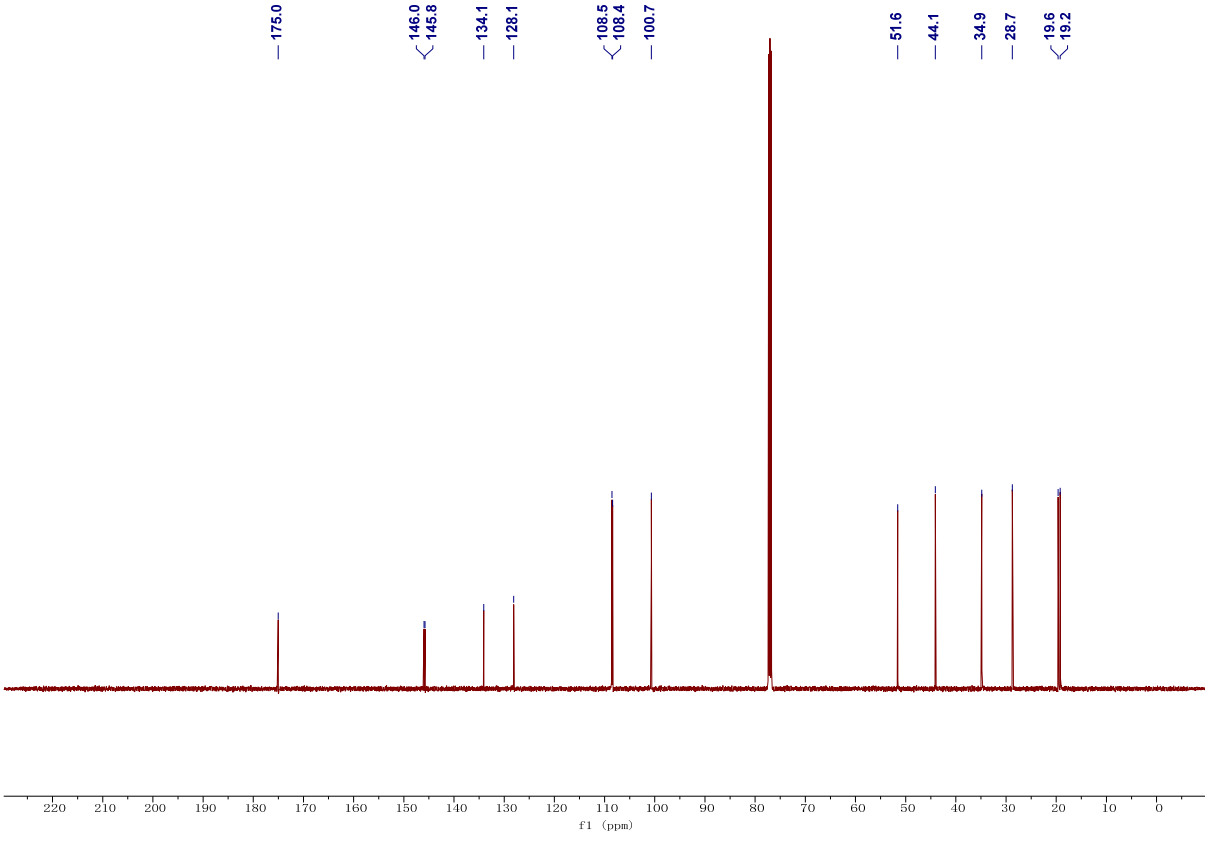


2u: Methyl (5S,6S)-5-ethyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

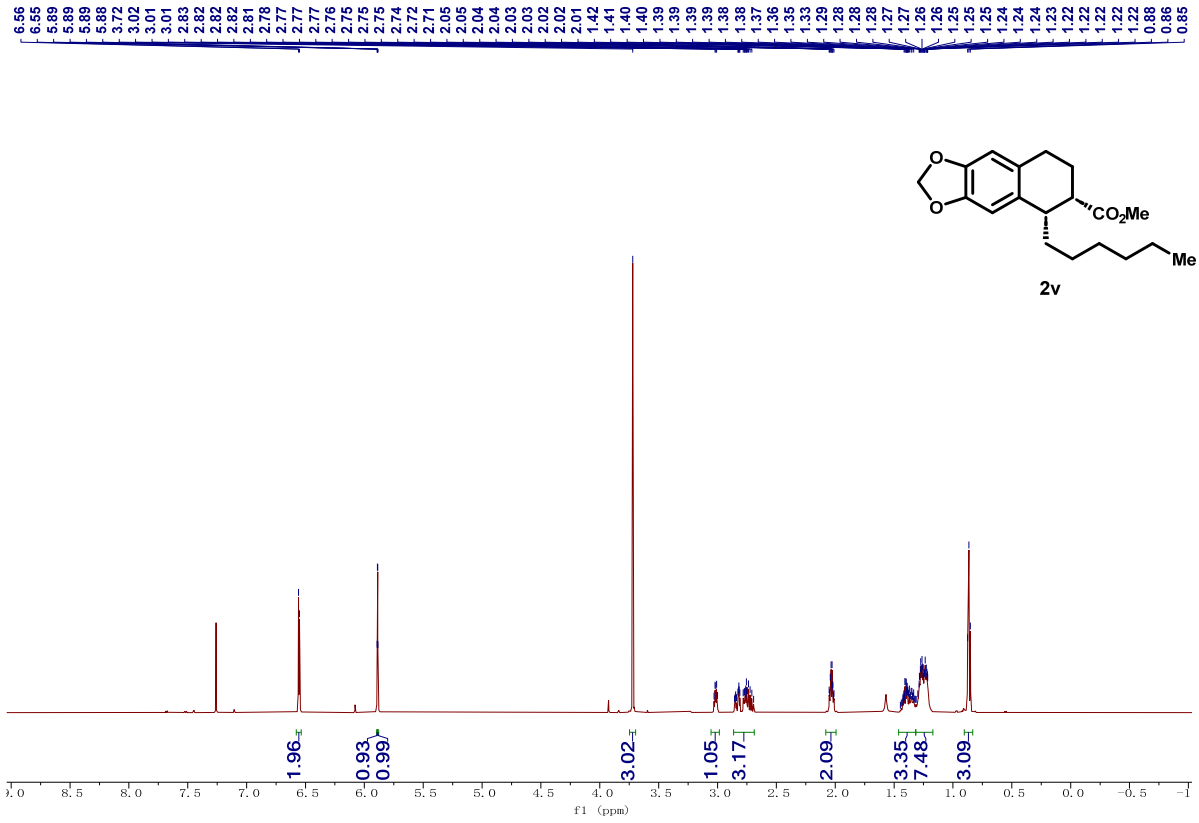


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

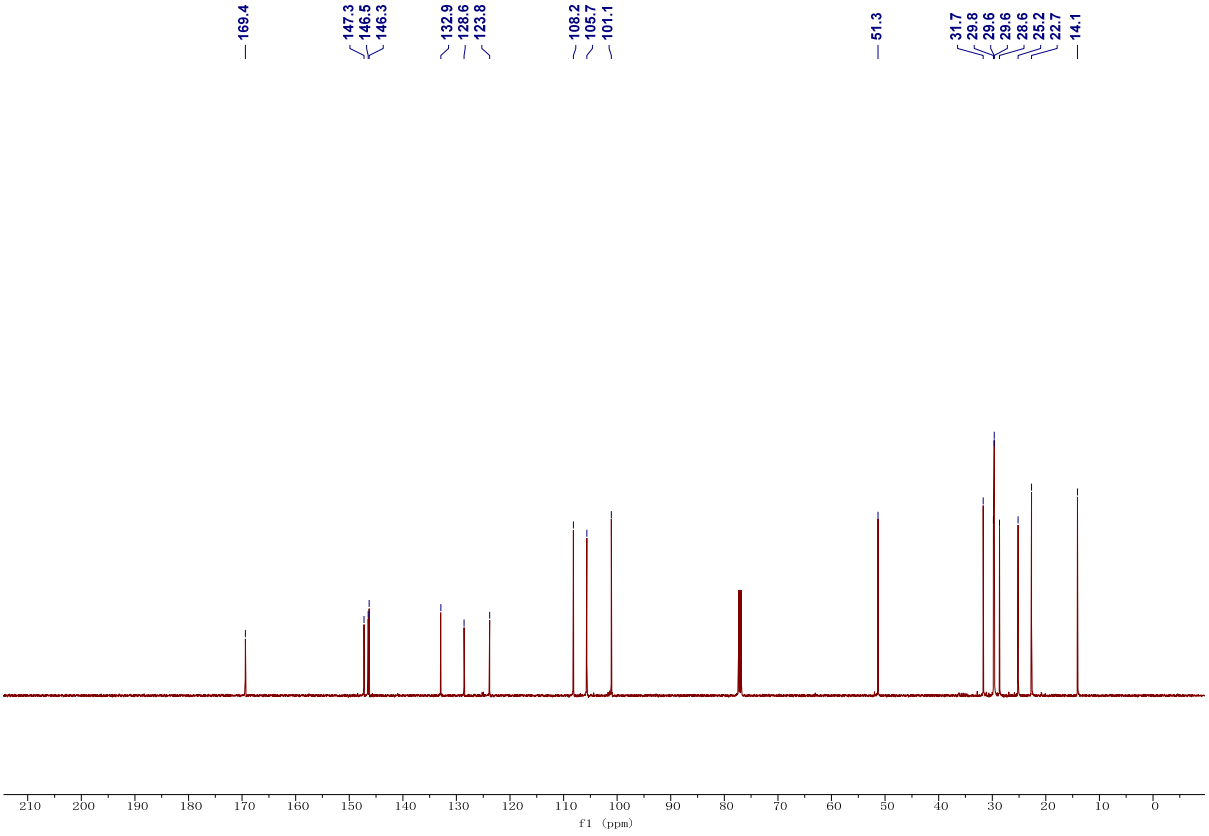


2v: Methyl (5S,6S)-5-hexyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

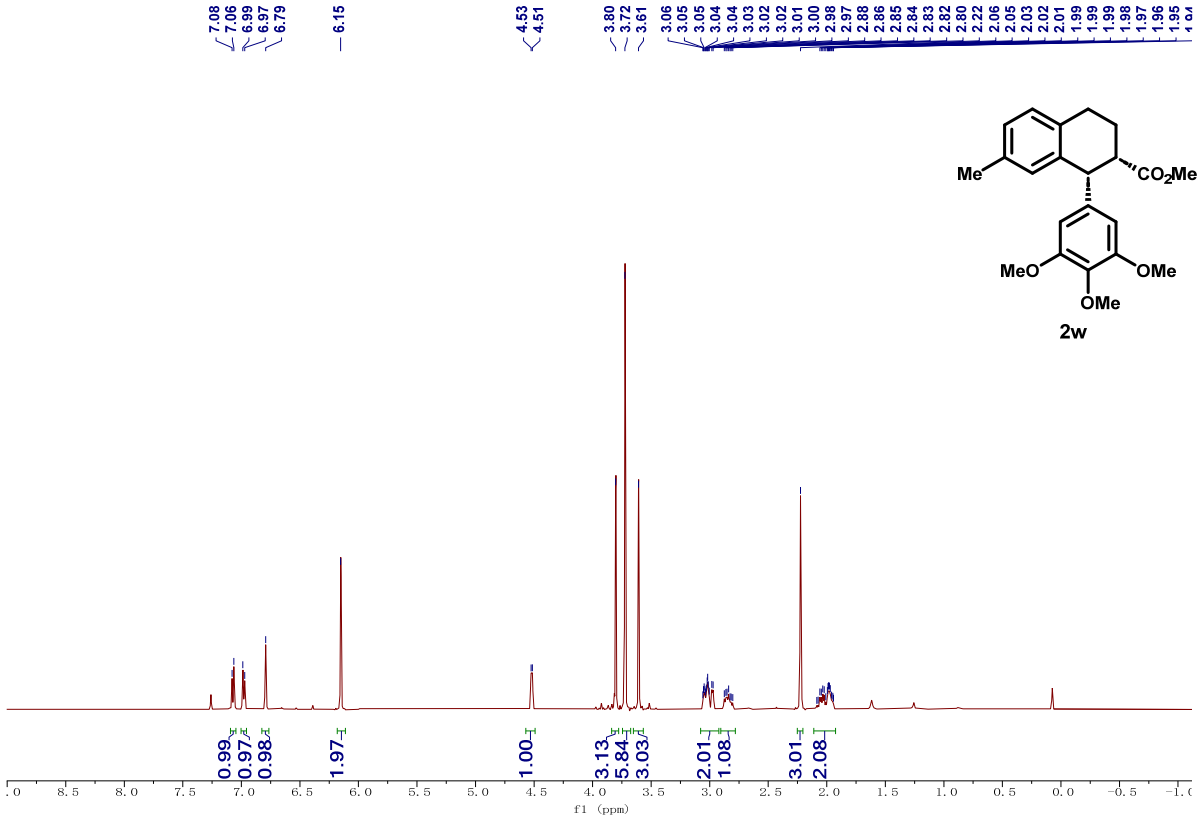


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

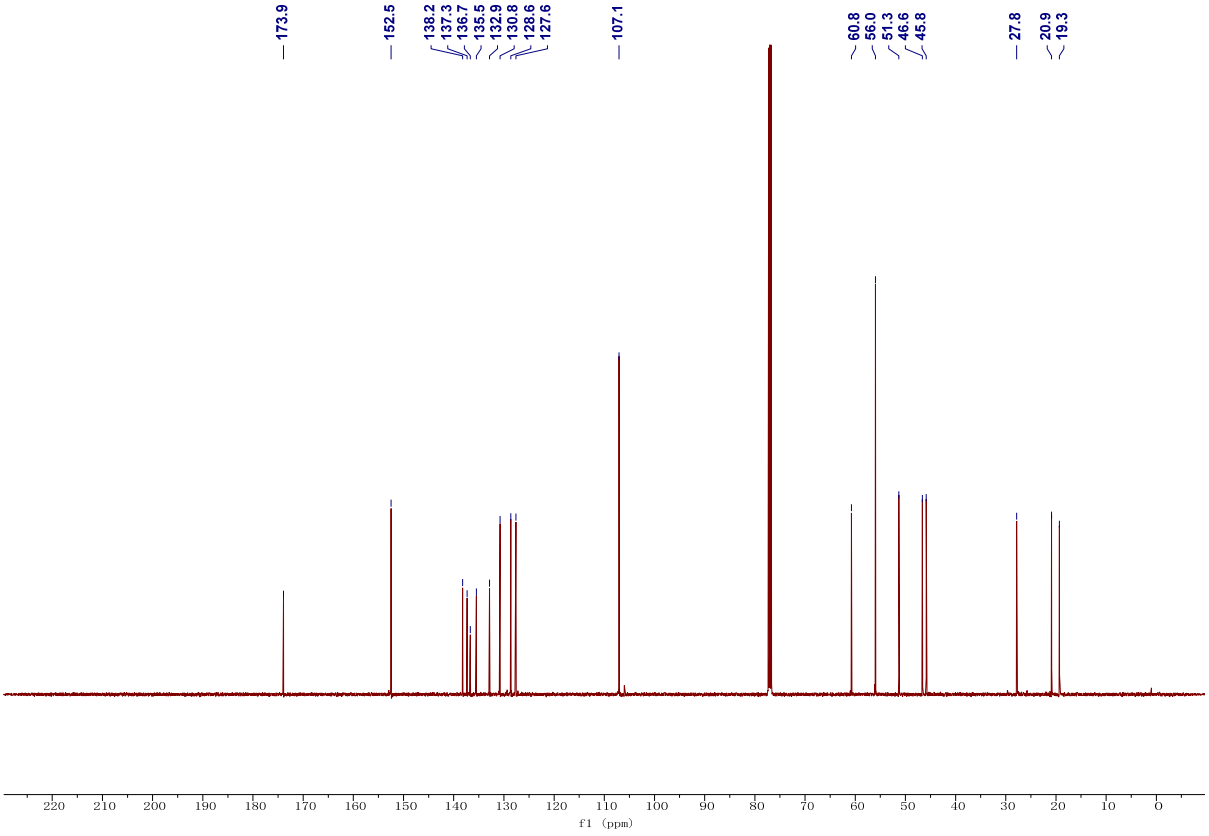


2w: Methyl (1R,2S)-7-Methyl-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

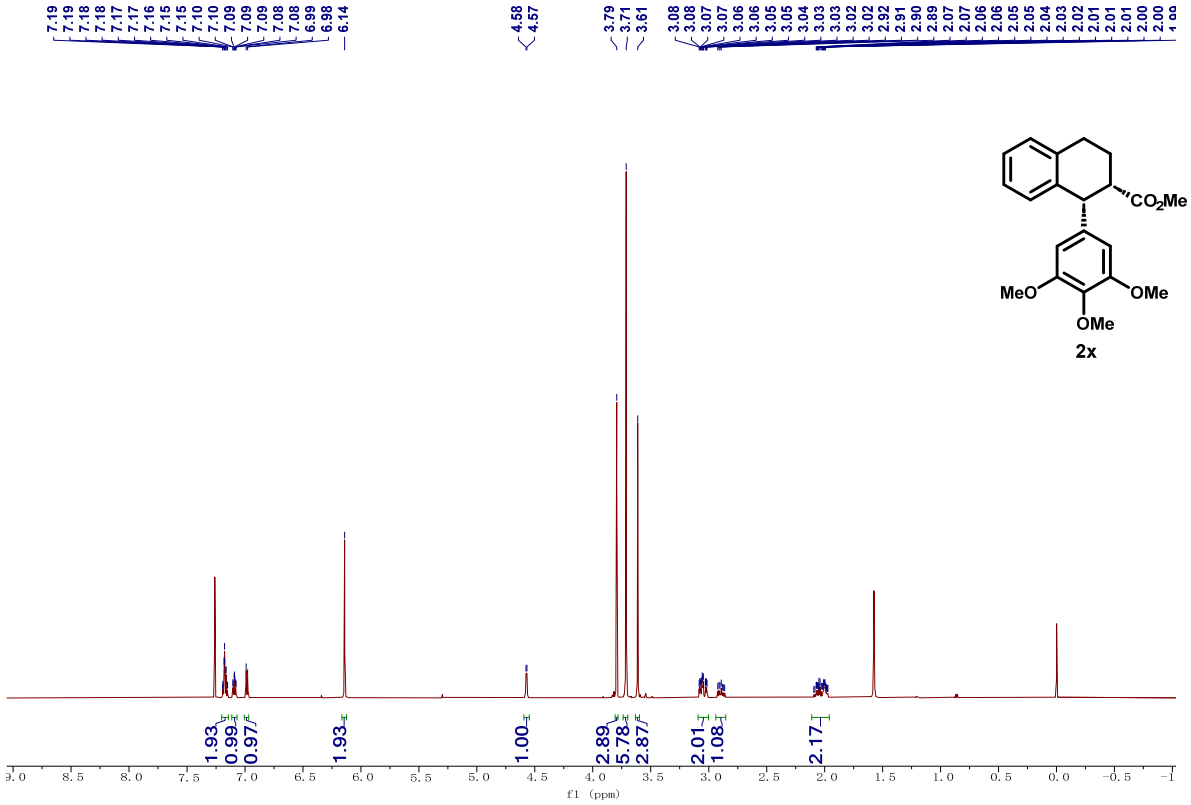


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

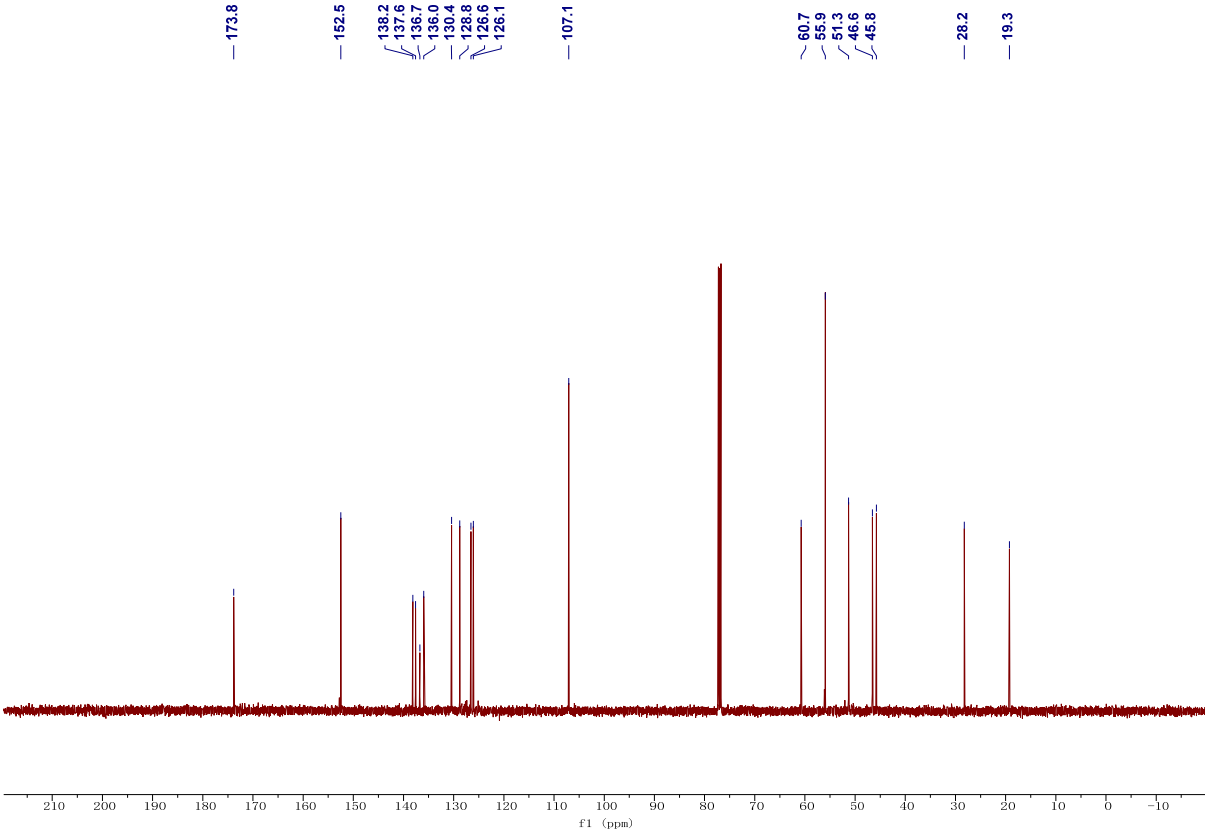


2x: Methyl (1R,2S)-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2- carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

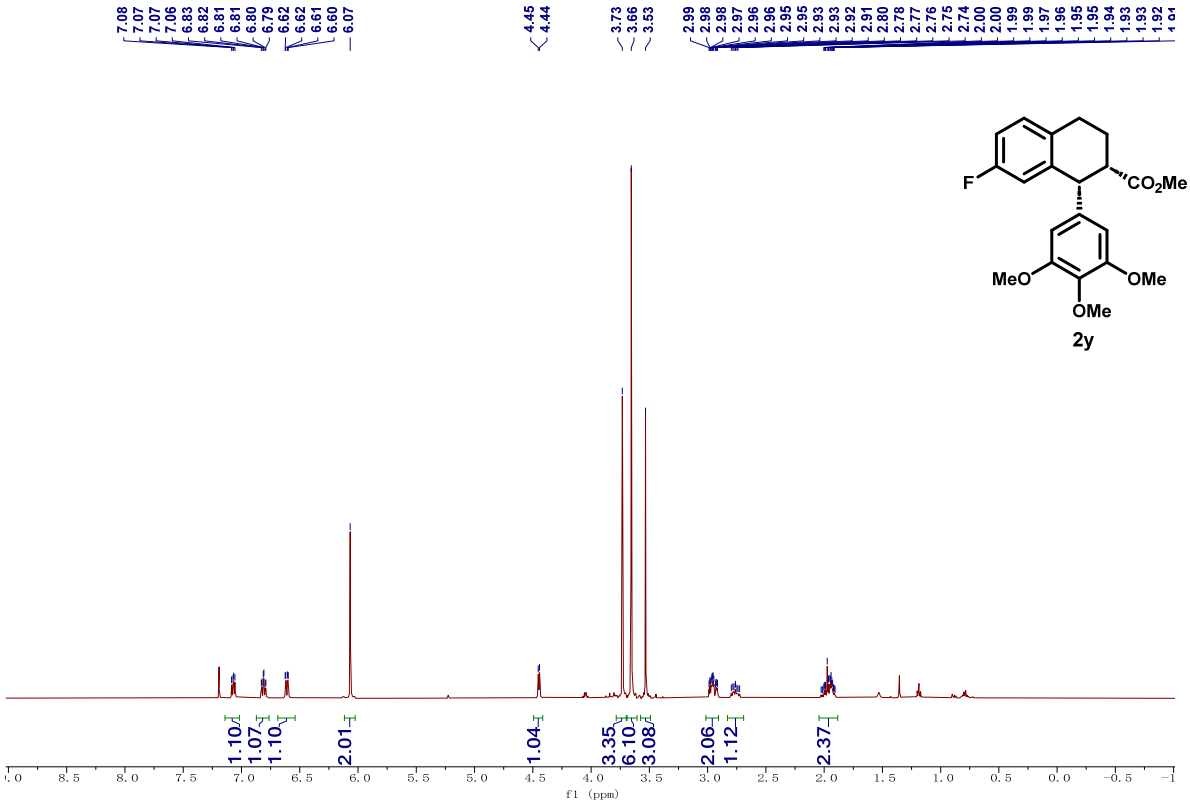


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

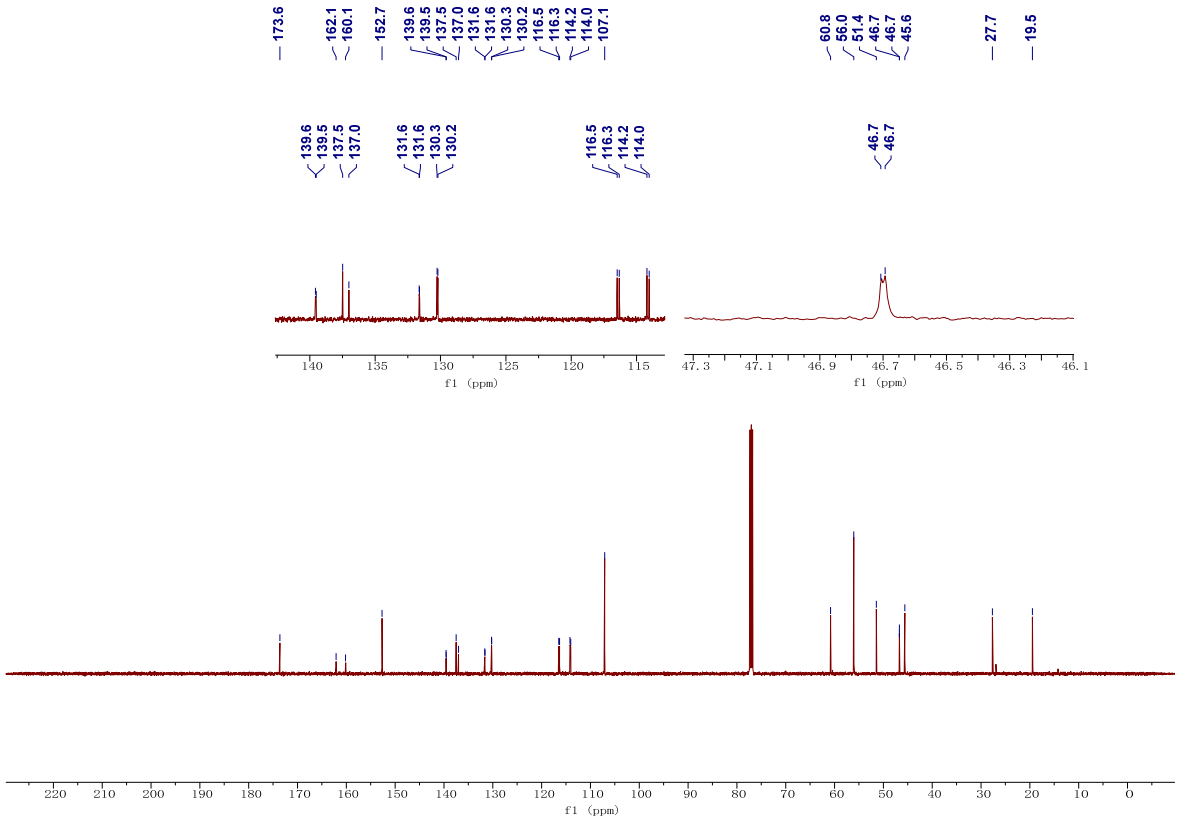


2y: Methyl (1R,2S)-7-fluoro-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

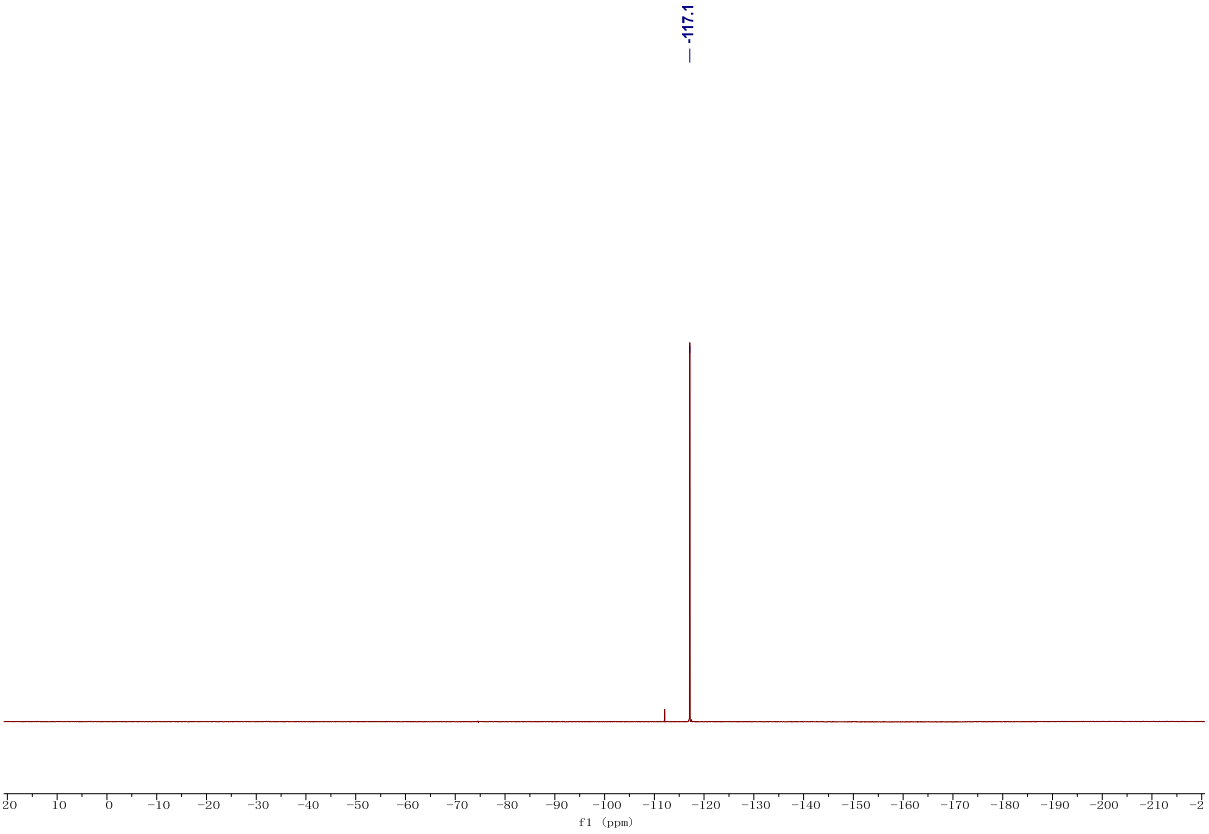
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

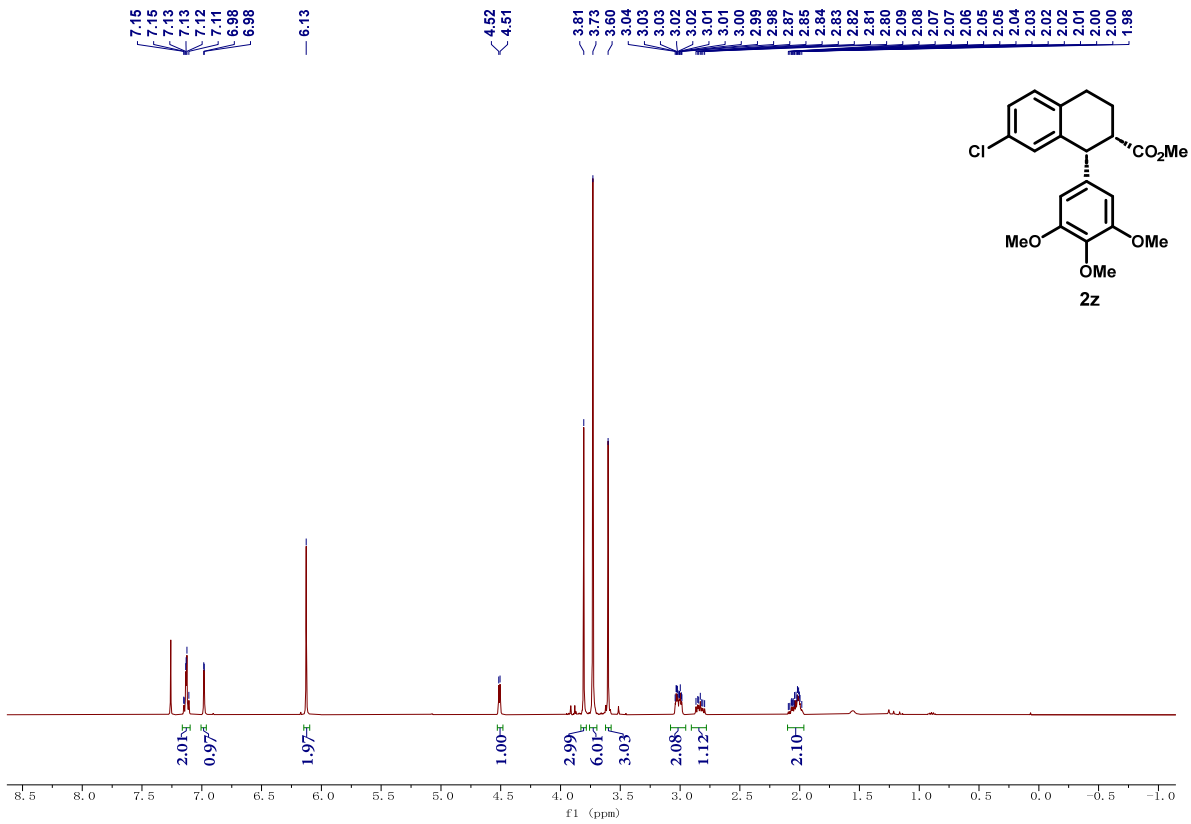


^{19}F NMR (471 MHz, $CDCl_3$)

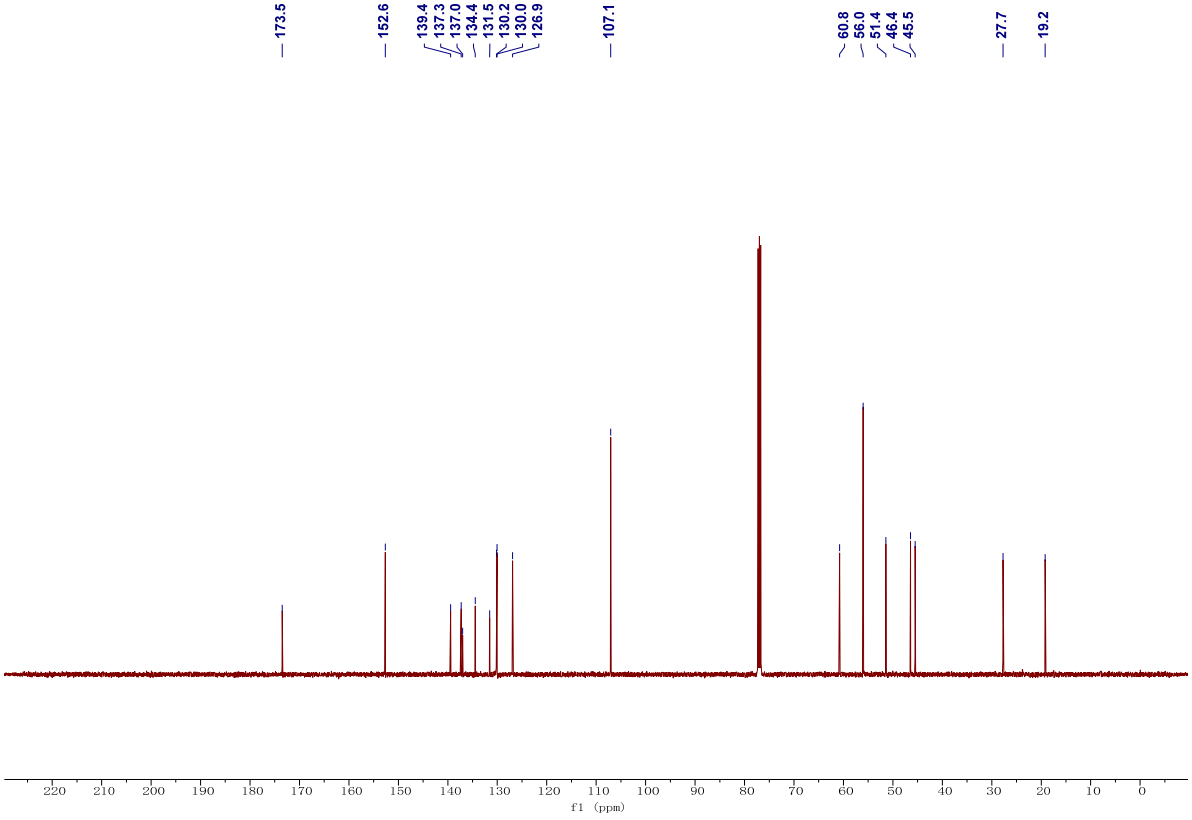


2z: Methyl (1R,2S)-7-chloro-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

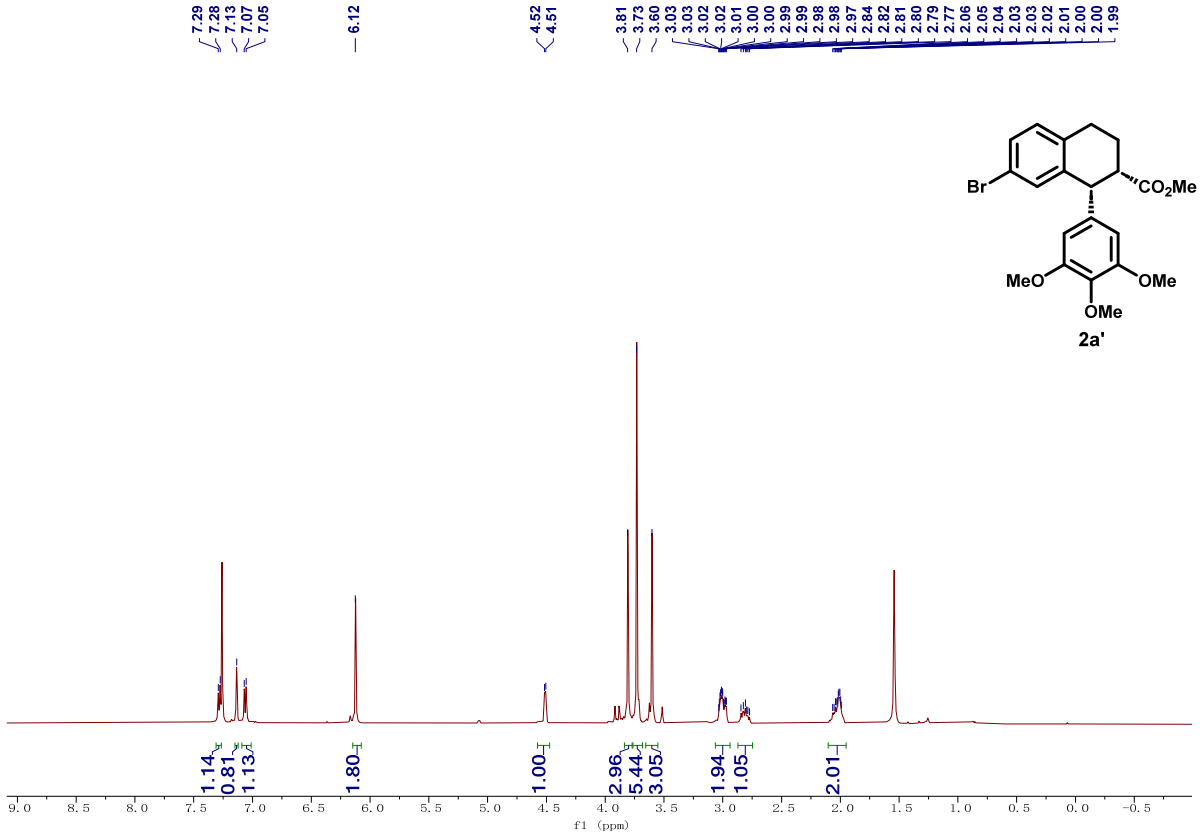


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

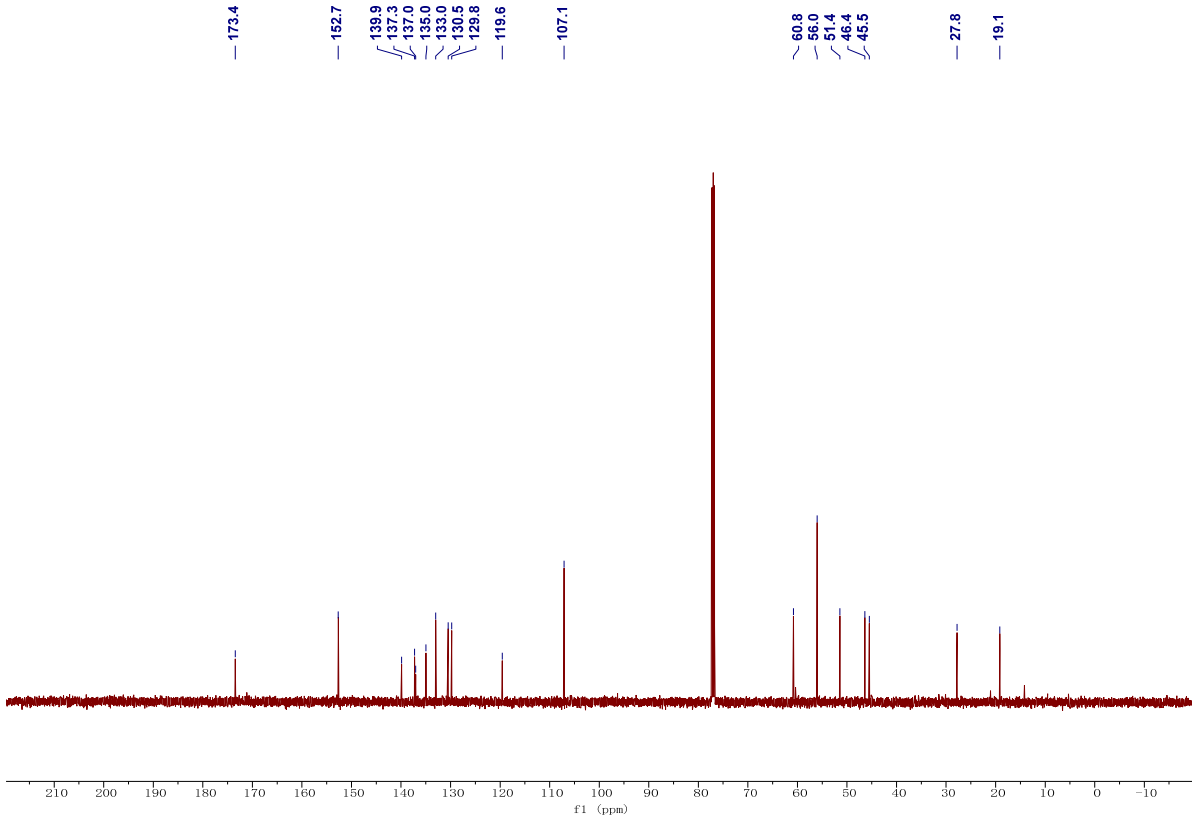


2a': Methyl (1R,2S)-7-bromo-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

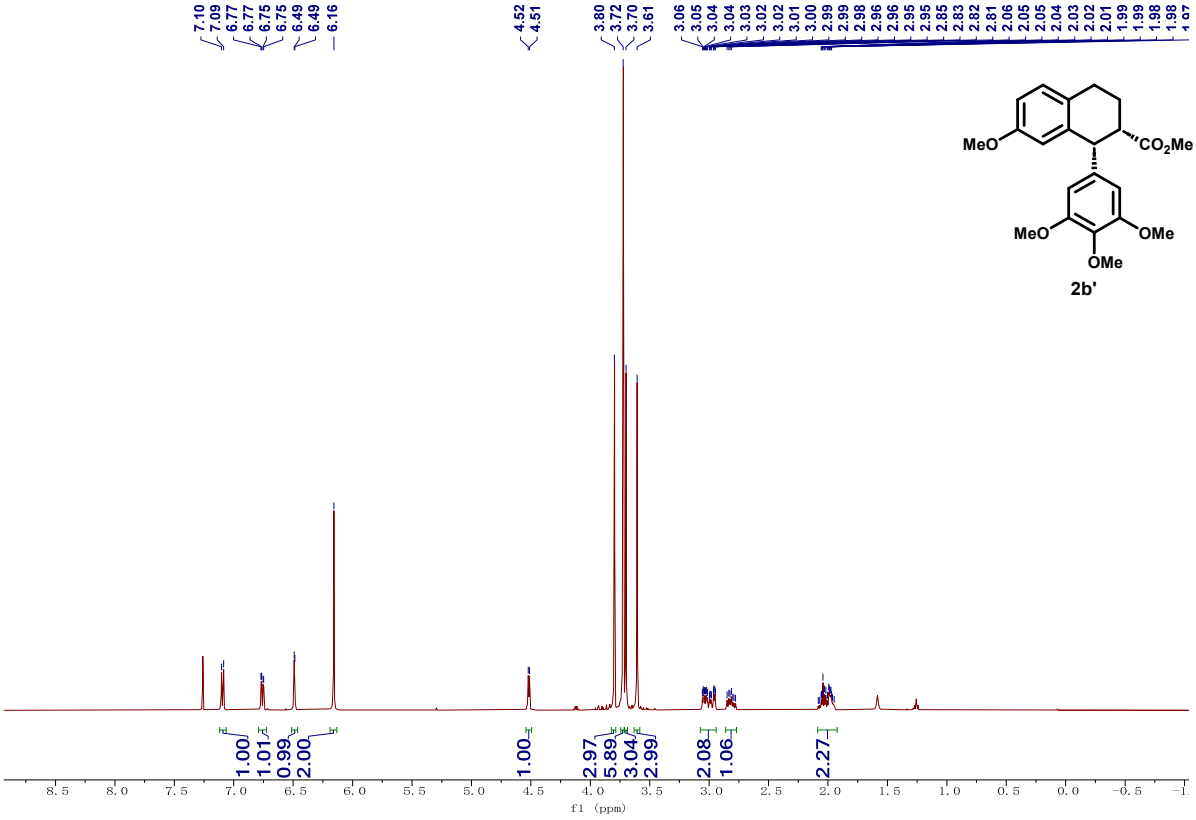


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

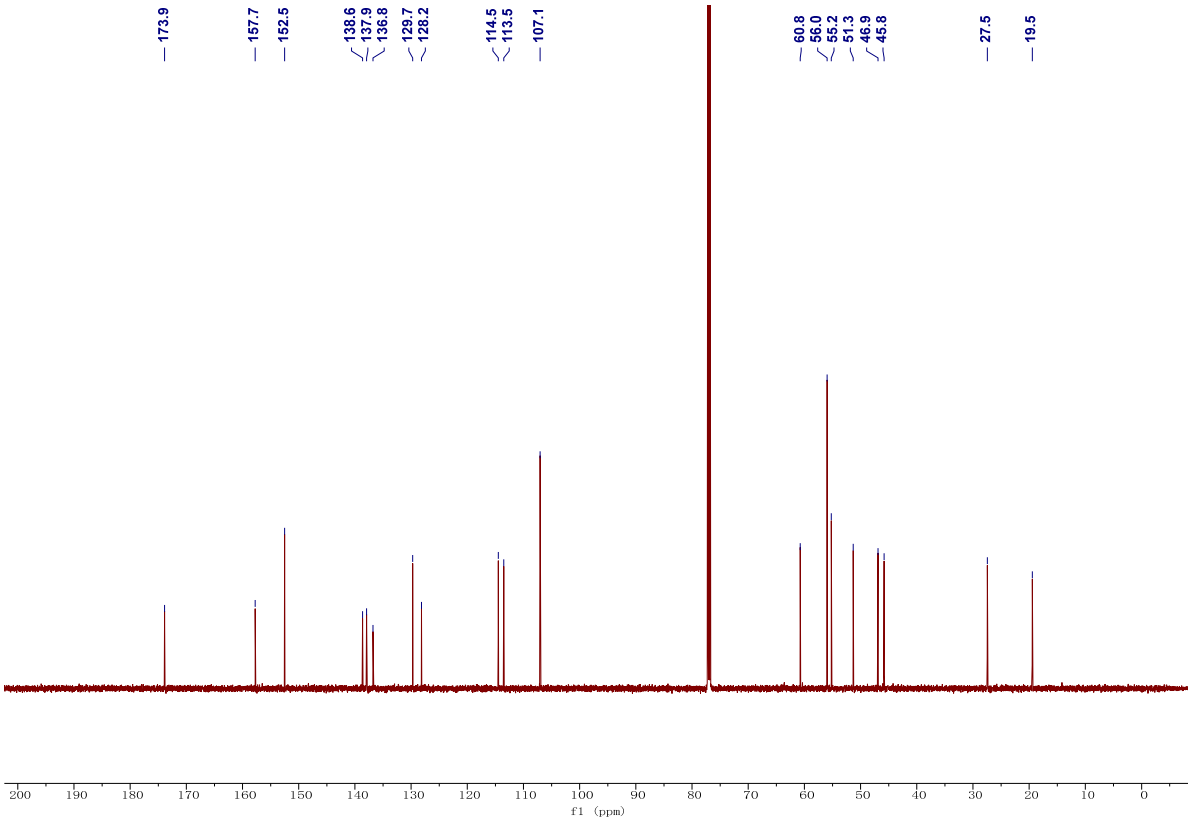


2b': Methyl (1R,2S)-7-methoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydro- naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

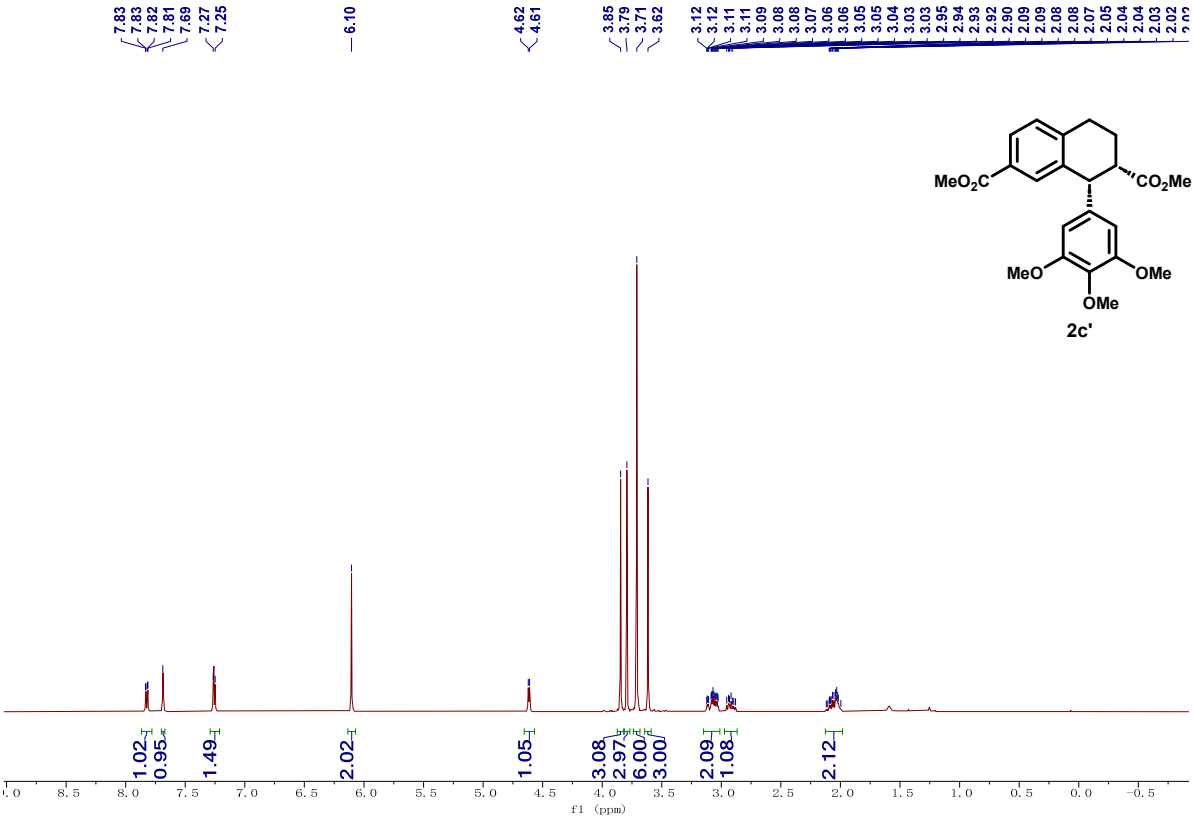


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

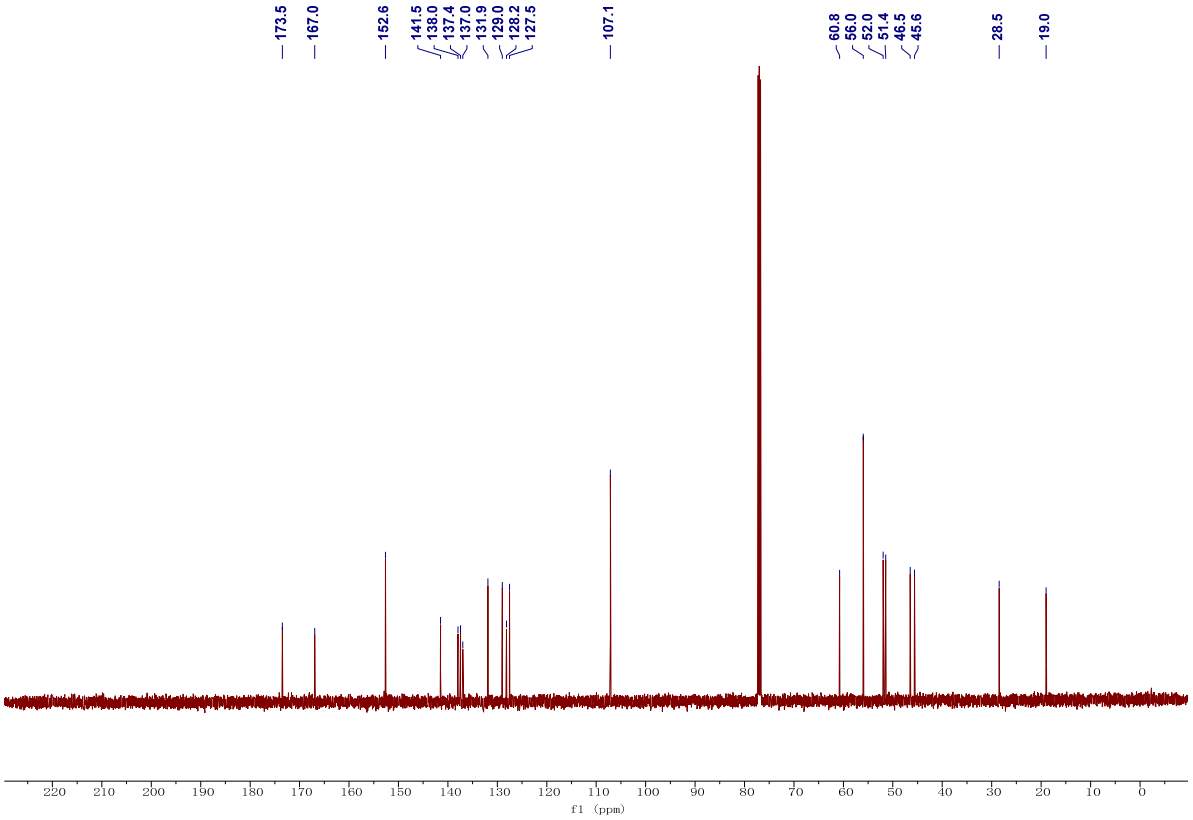


2c': Methyl (1R,2S)-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2,7- dicarboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

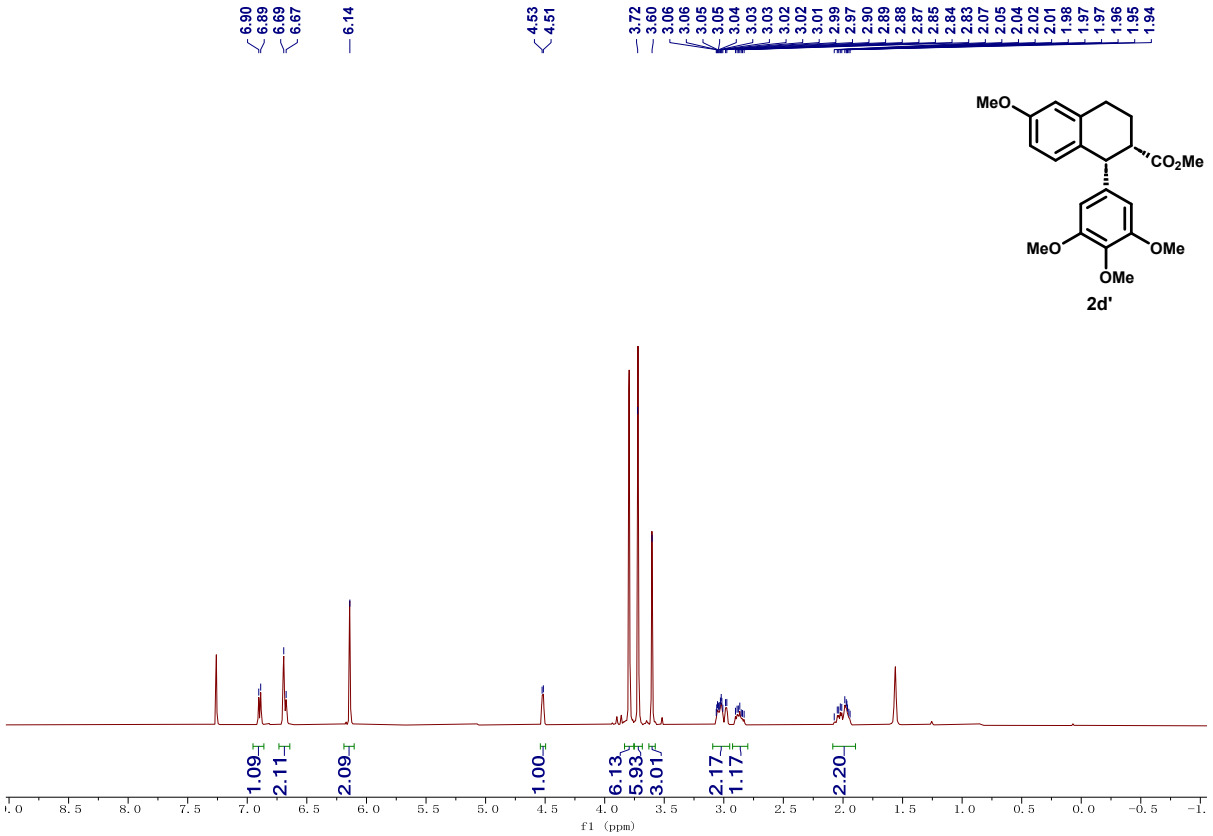


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

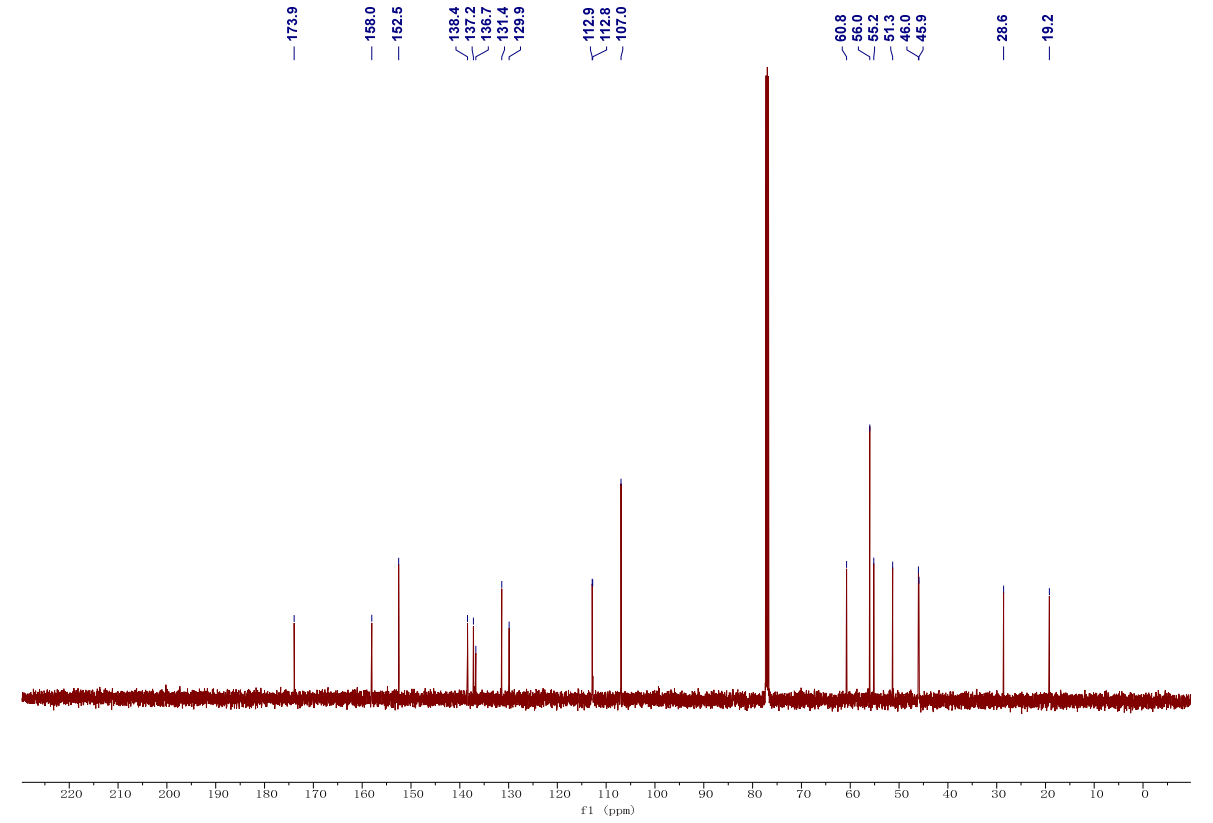


2d': Methyl (1R,2S)-6-methoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

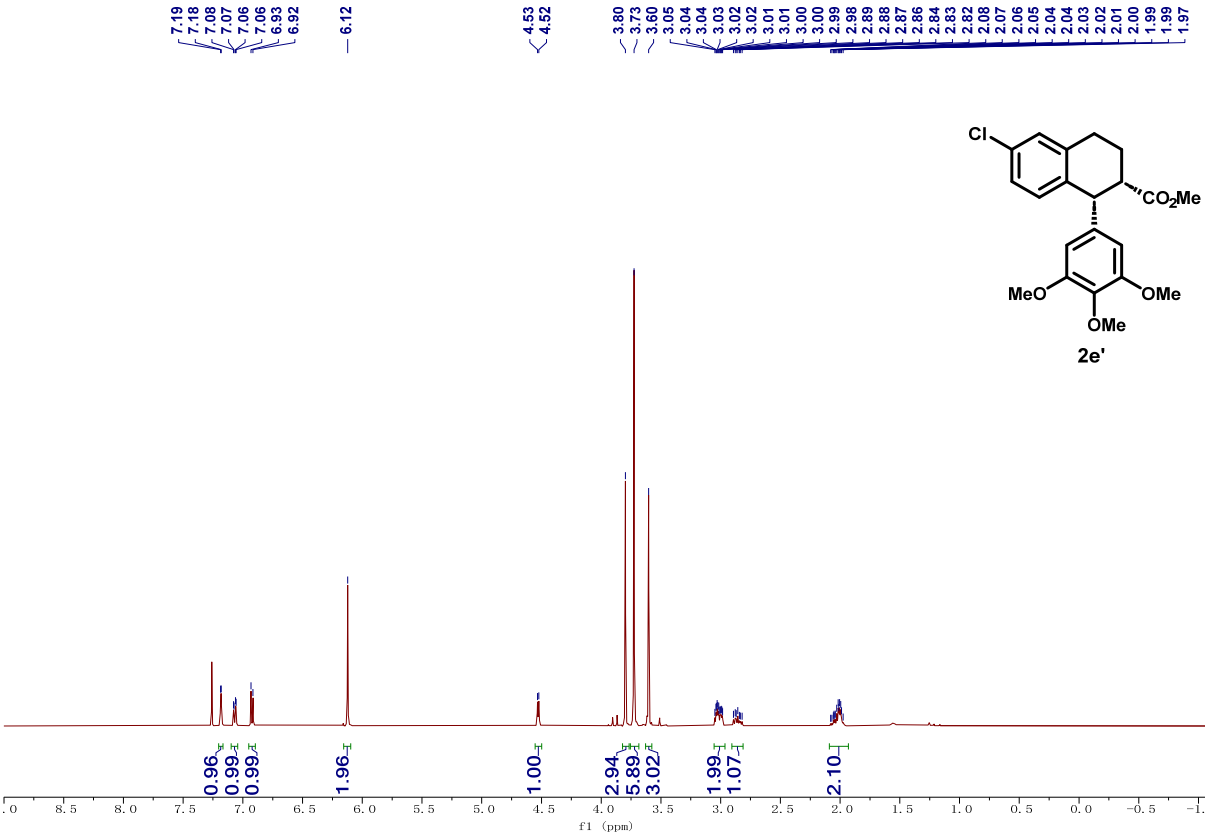


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

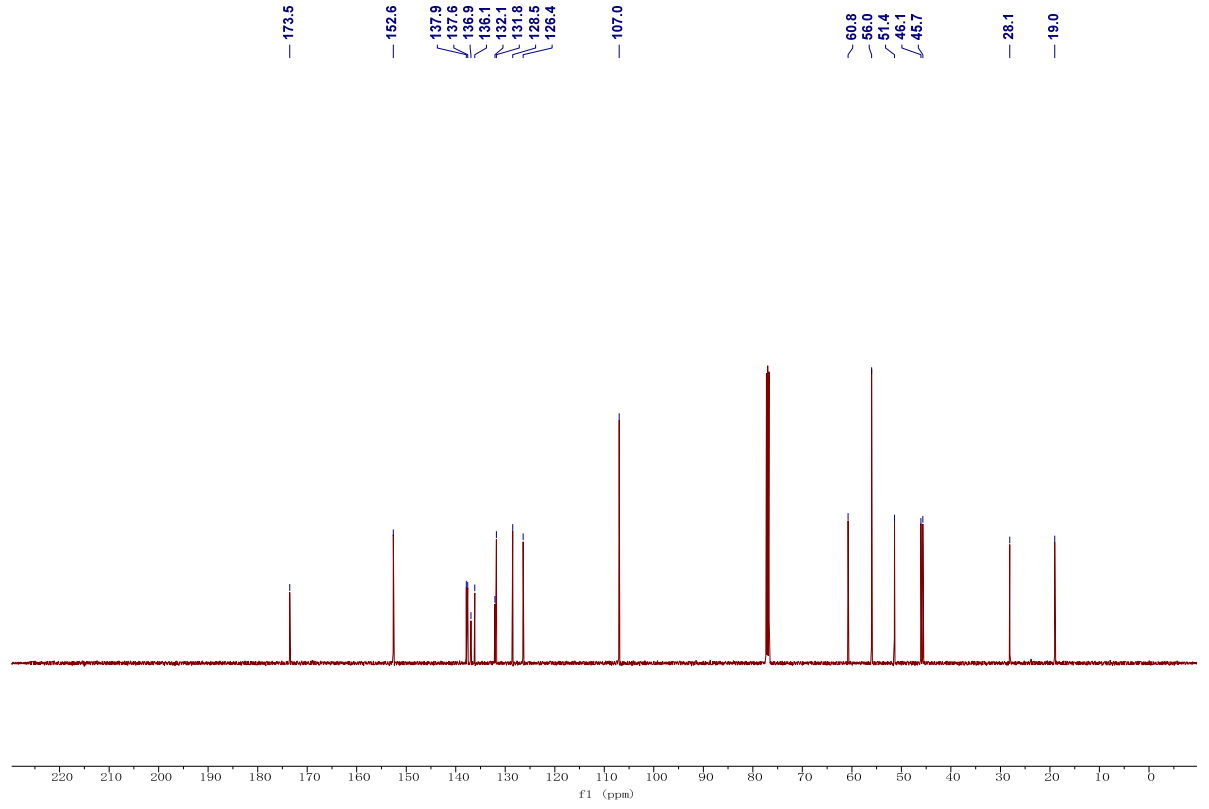


2e': Methyl (1R,2S)-6-chloro-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

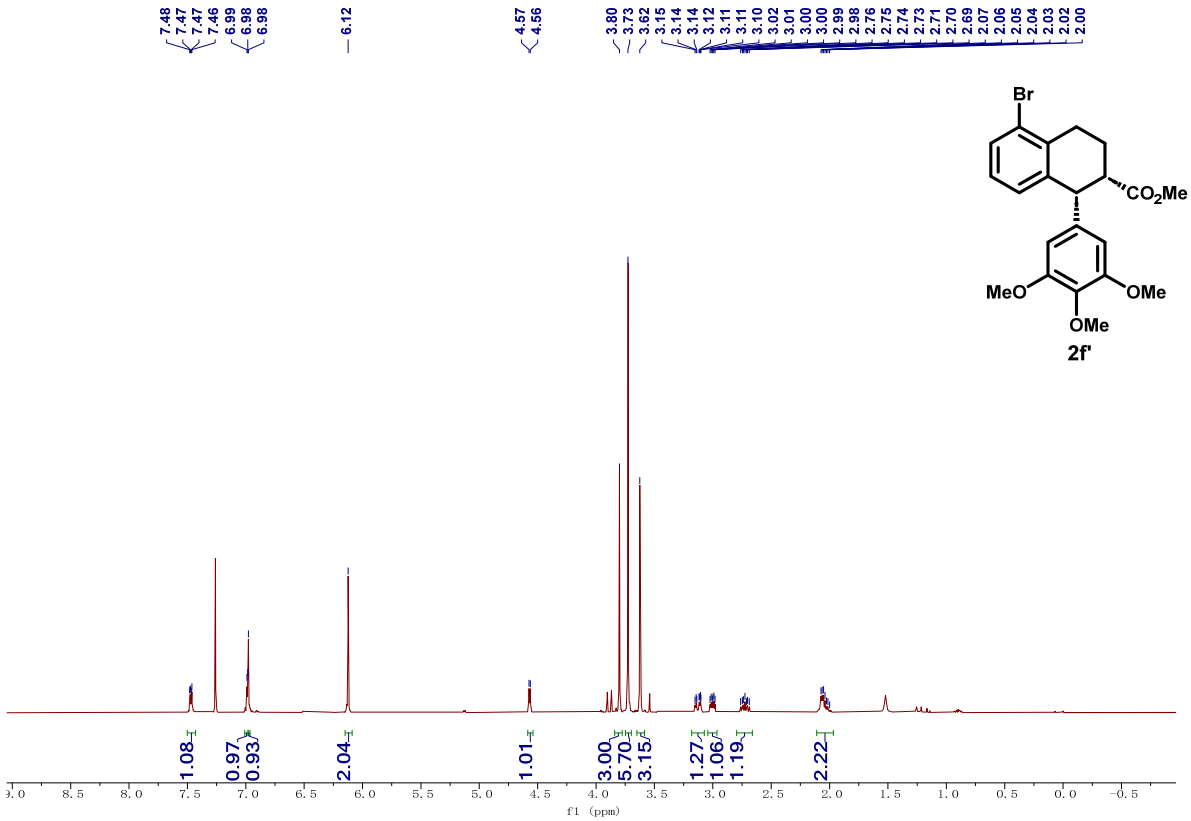


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

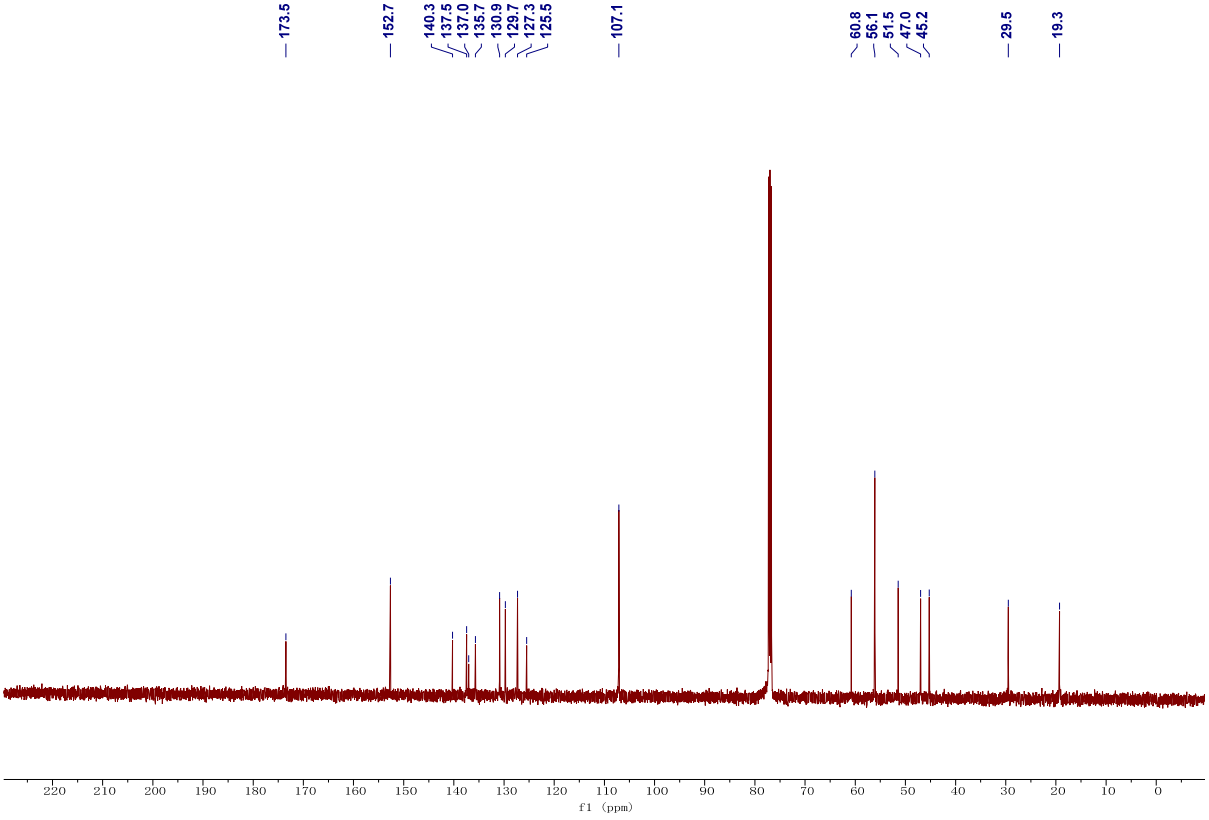


2f': Methyl (1R,2S)-5-bromo-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

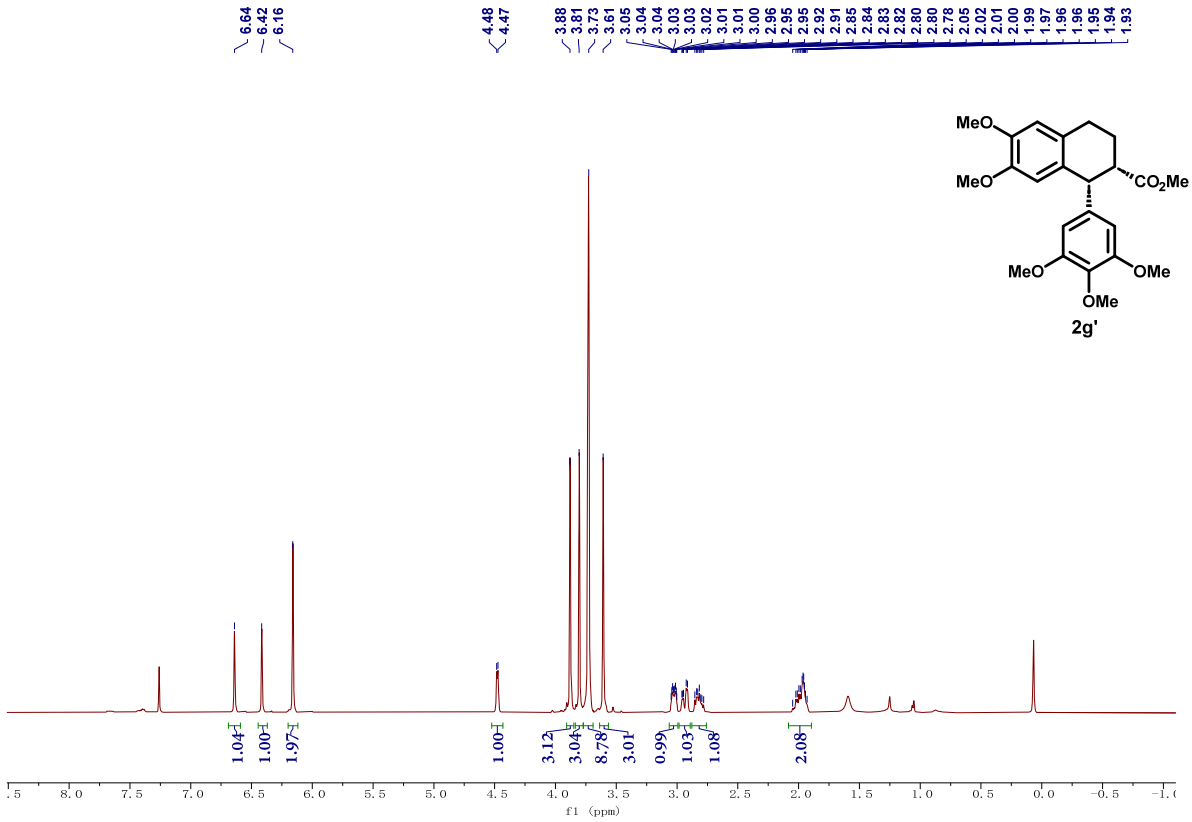


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

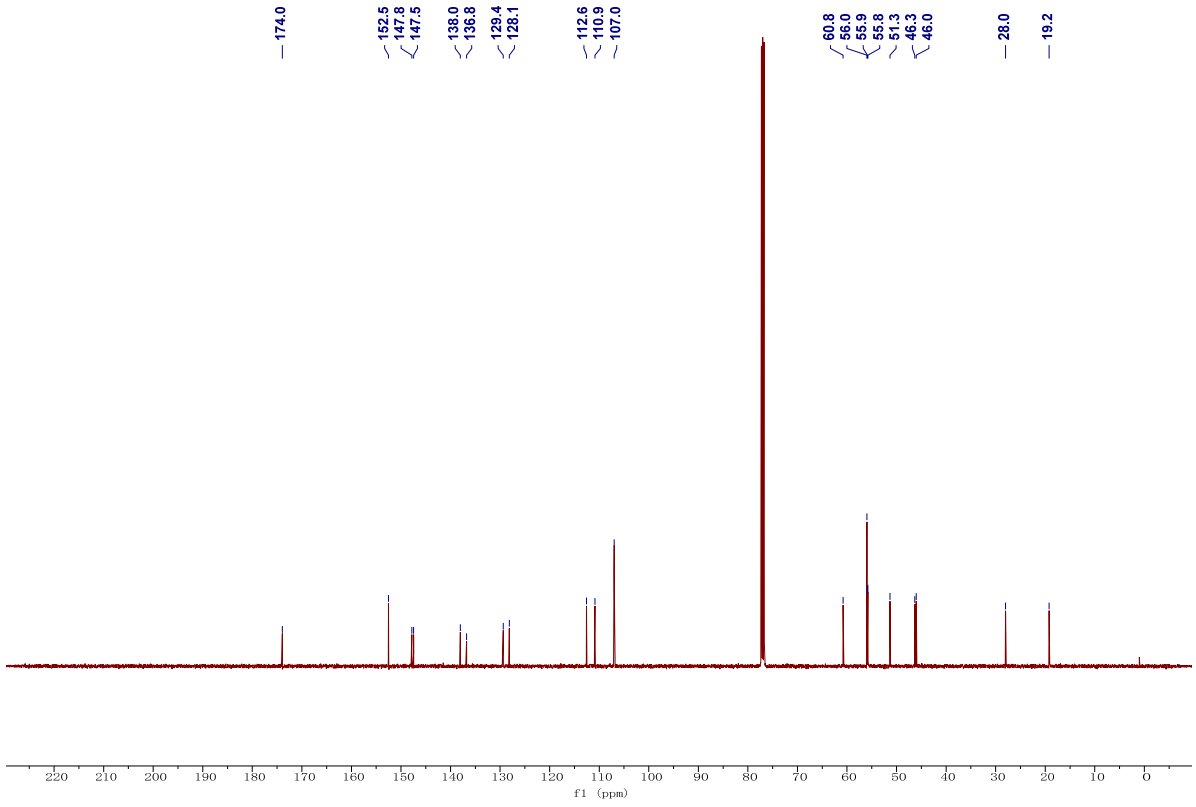


2g': Methyl (1R,2S)-6,7-dimethoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydro- naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

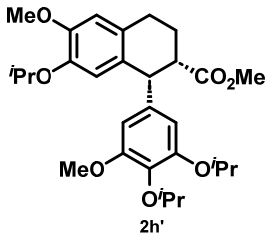


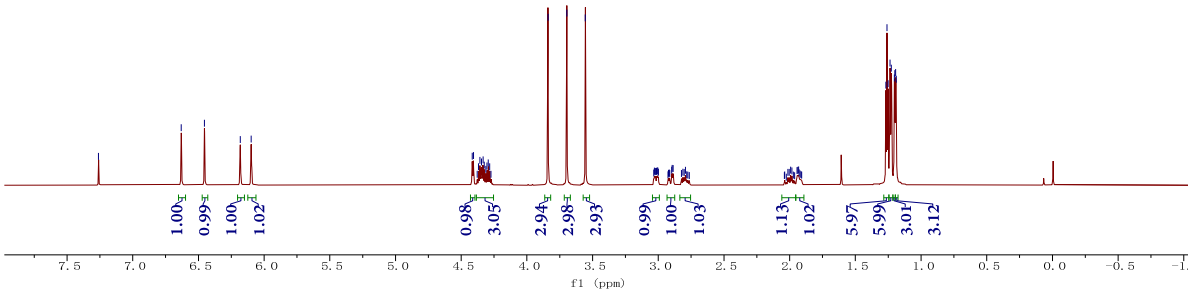
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



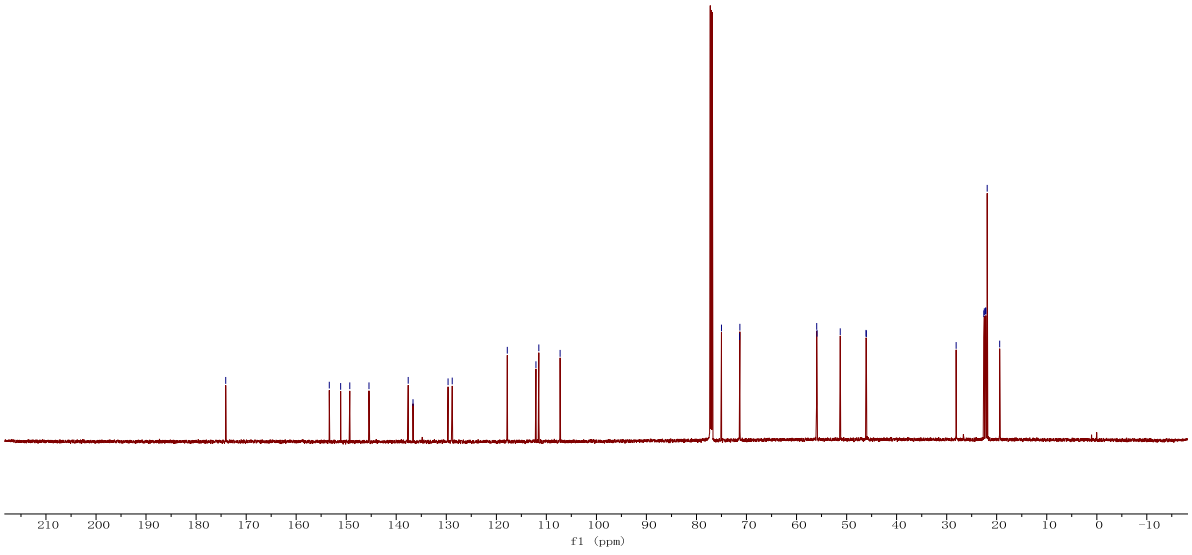
2h': Methyl (1R,2S)-1-(3,4-diisopropoxy-5-methoxyphenyl)-7-isopropoxy-6-methoxy- 1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



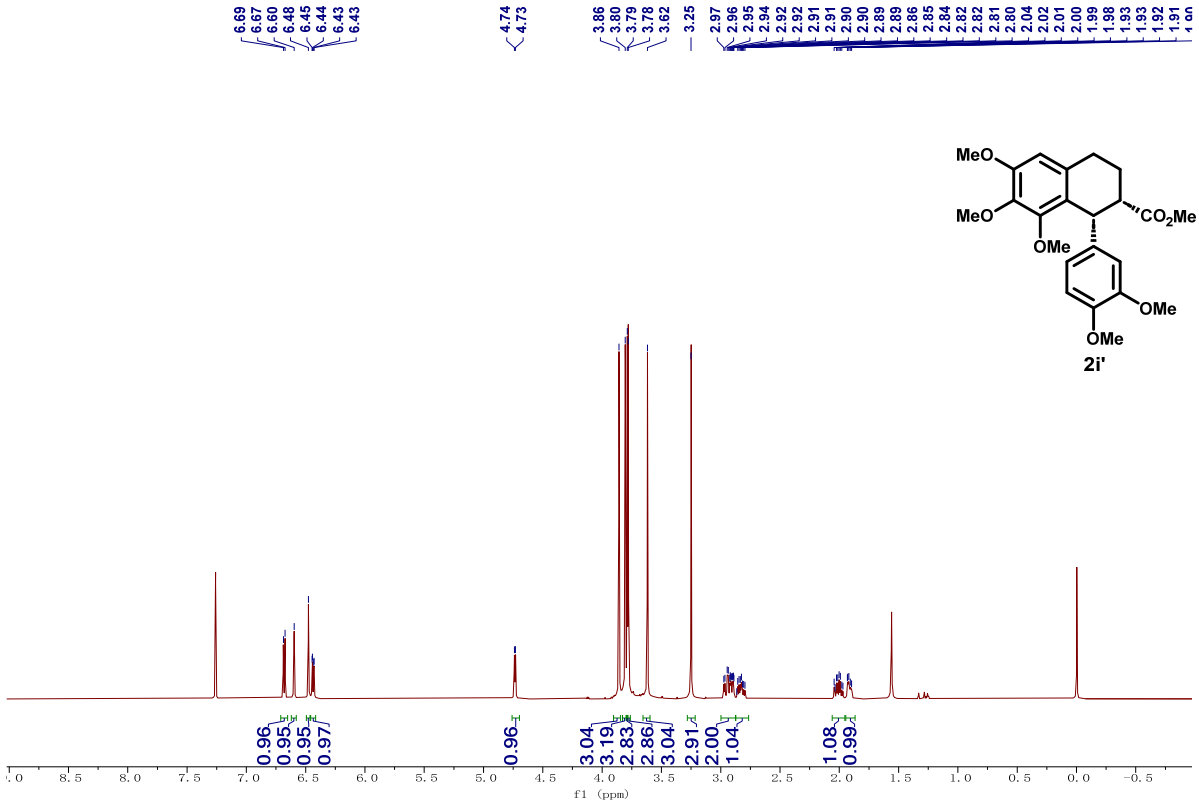


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

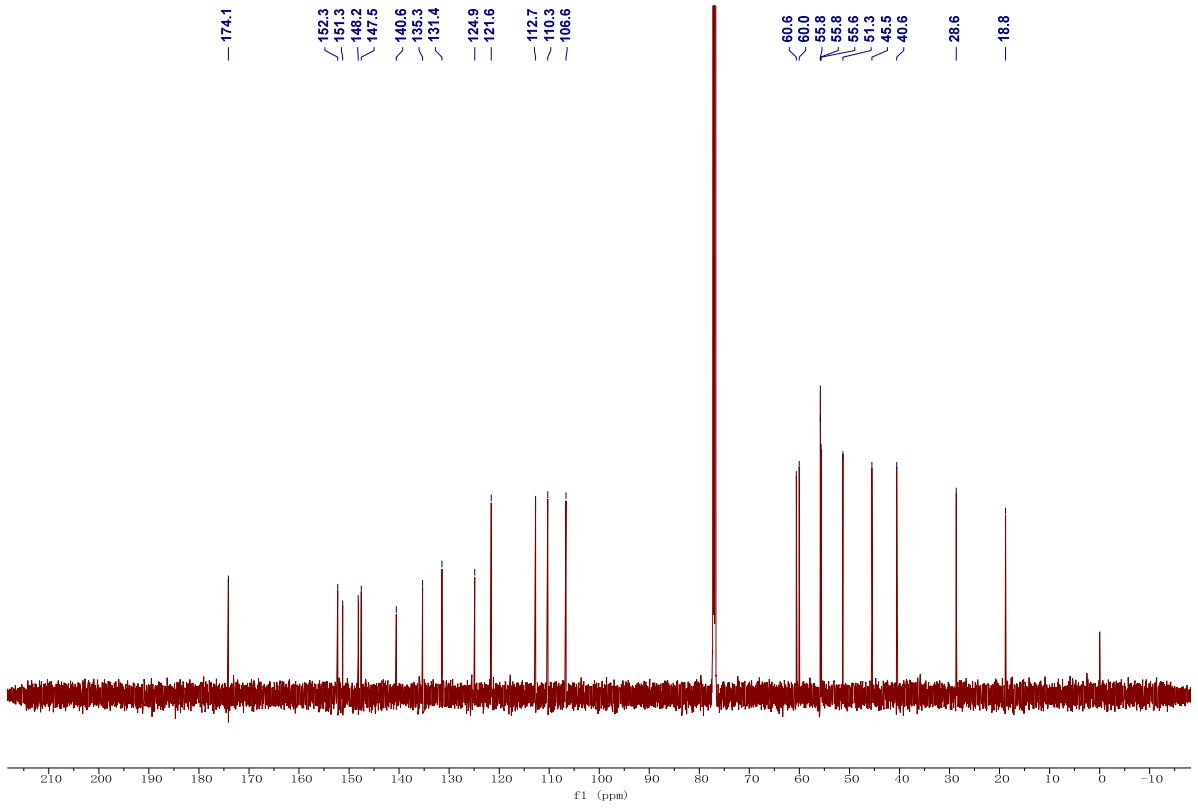


2i': Methyl (1R,2S)-1-(3,4-dimethoxyphenyl)-6,7,8-trimethoxy-1,2,3,4-tetrahydro- naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

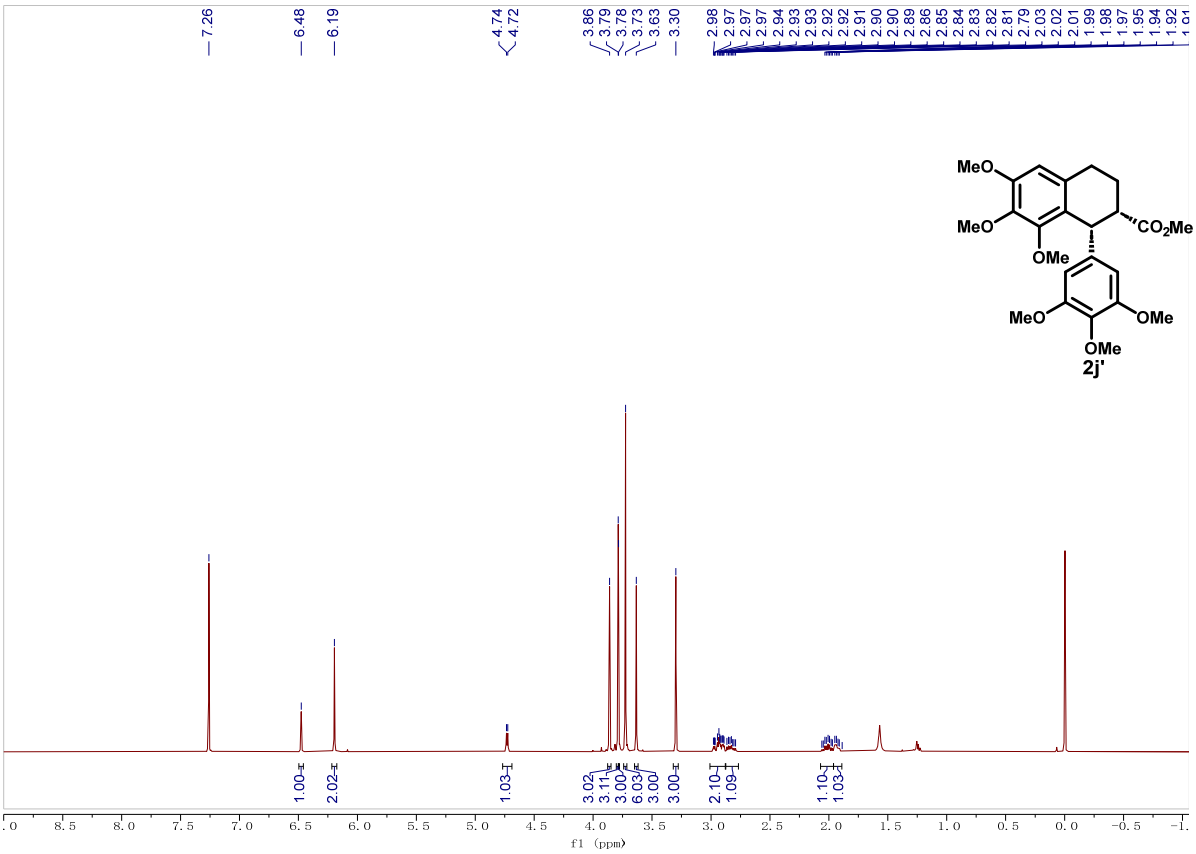


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

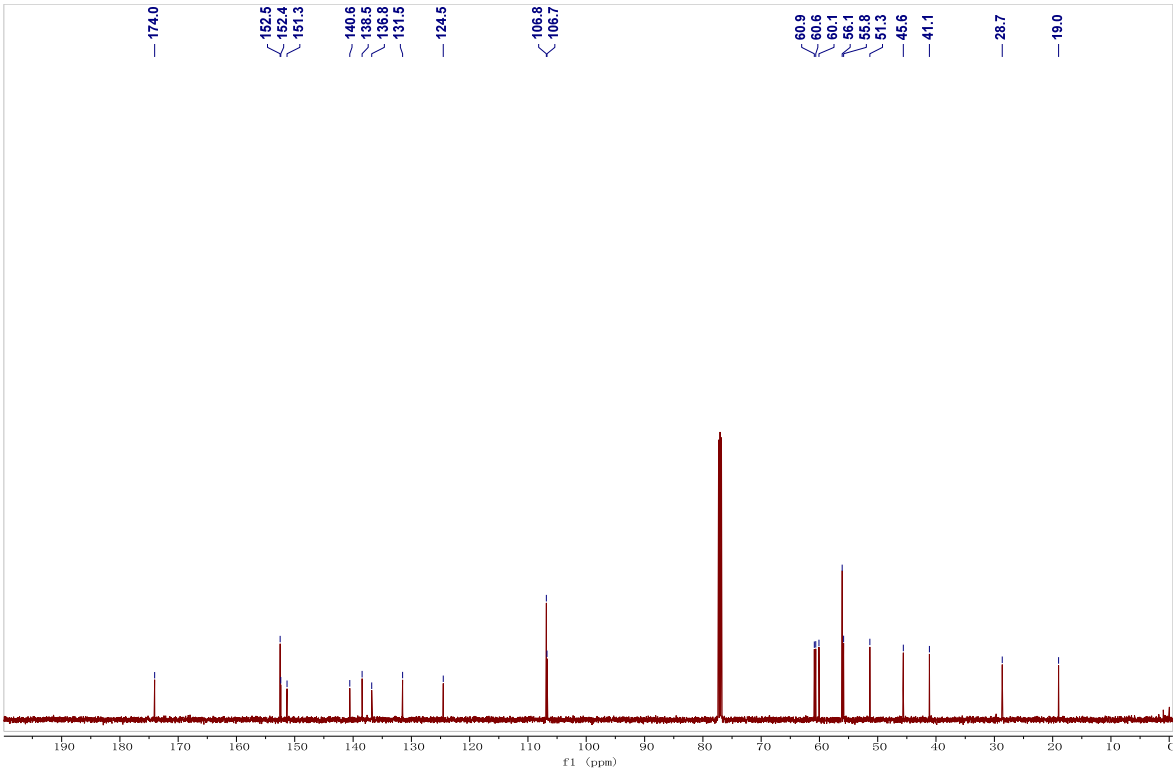


2j': Methyl (1R,2S)-6,7,8-trimethoxy-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydro- naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

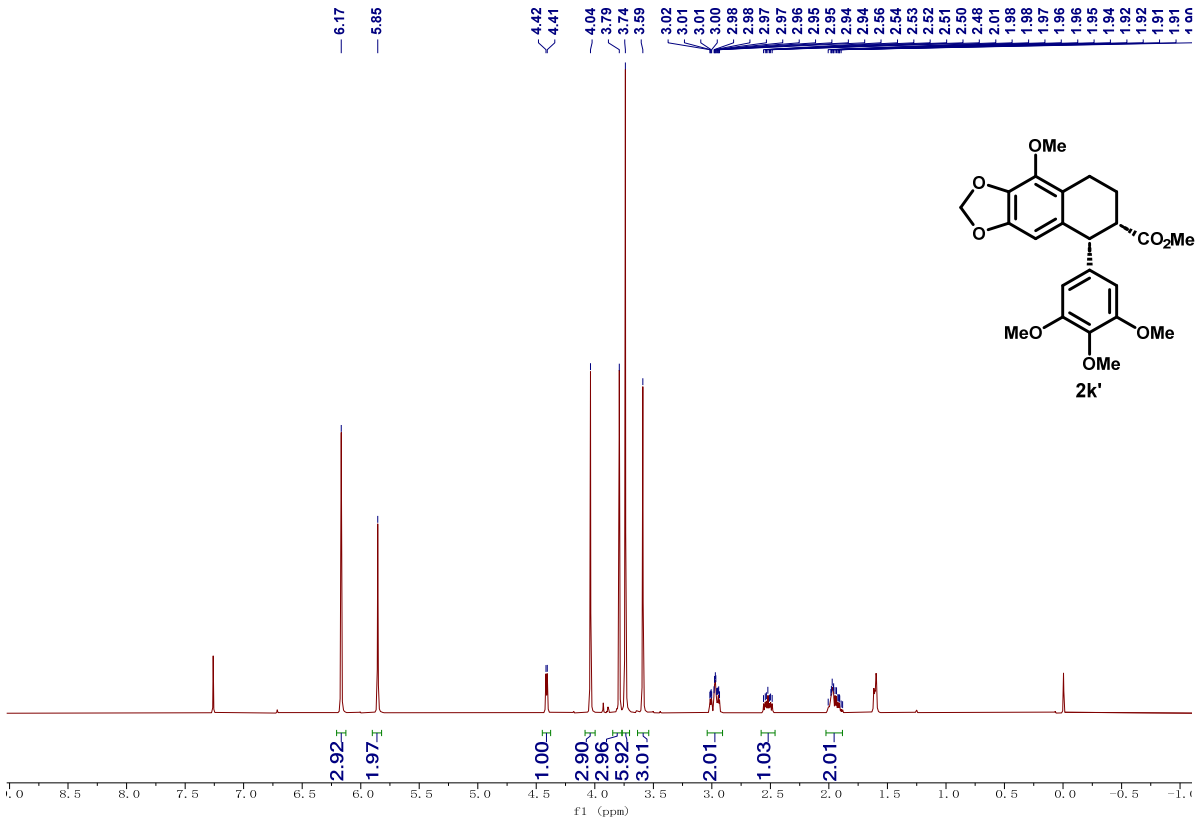


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

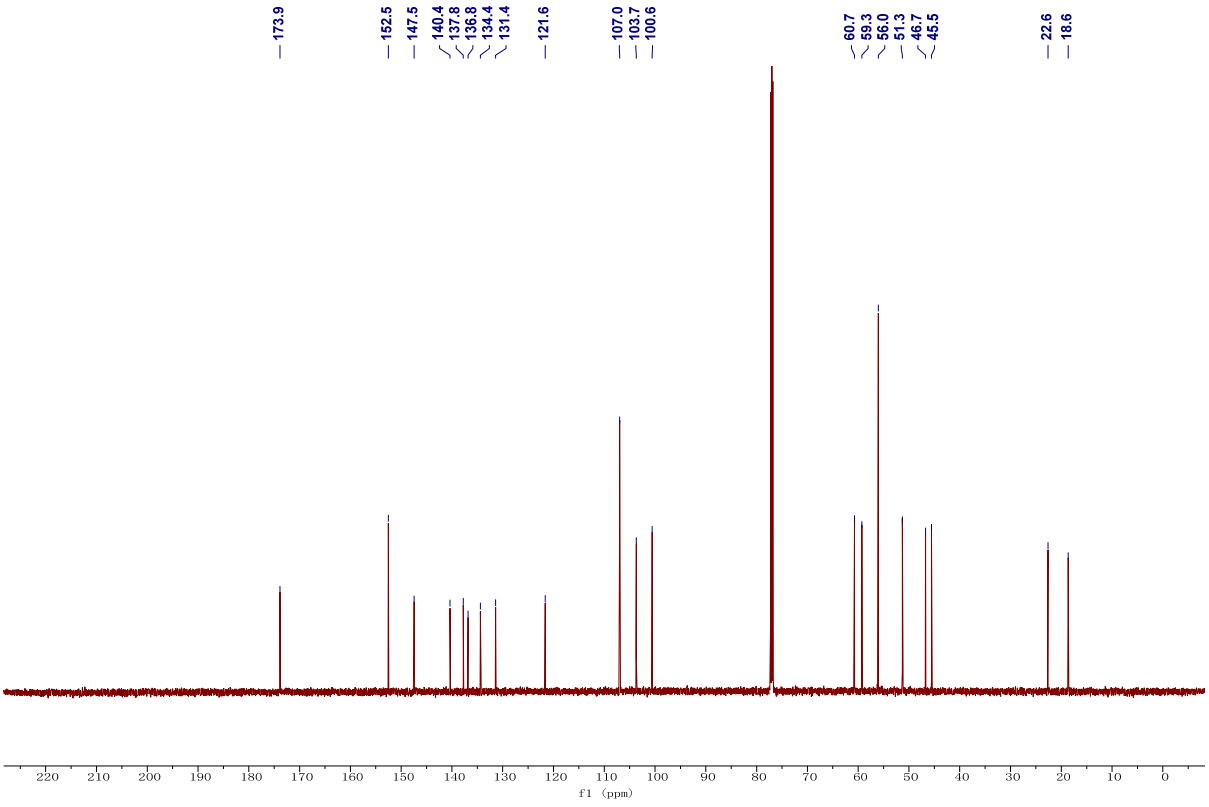


2k': Methyl (5R,6S)-9-methoxy-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho- [2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

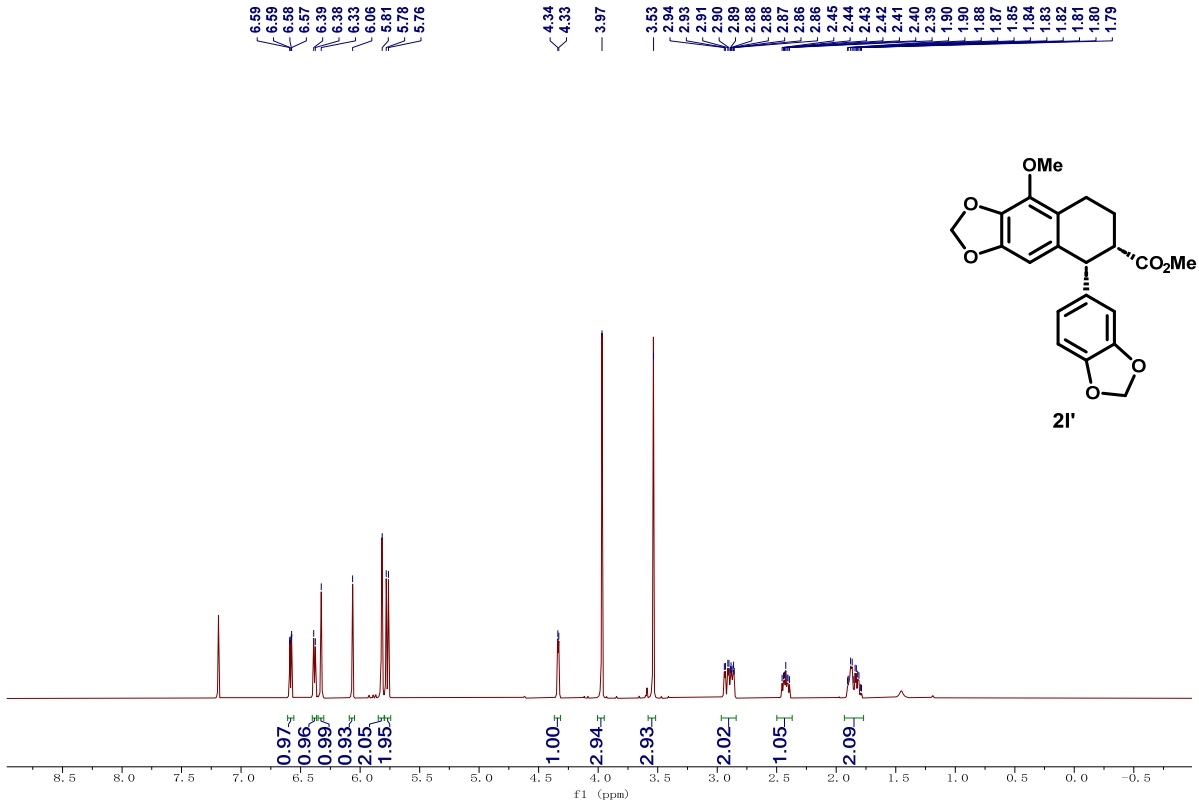


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

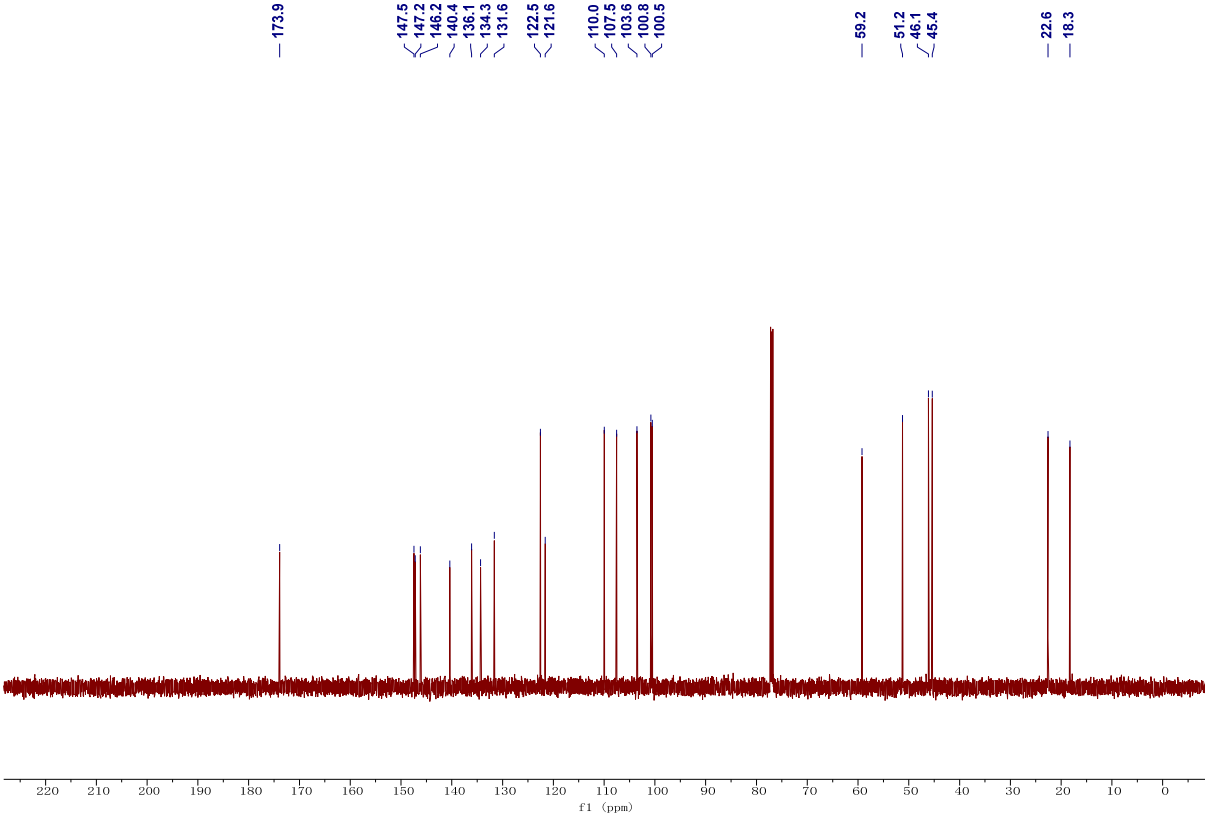


2l': Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-5,6,7,8-tetrahydronaphtho- [2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

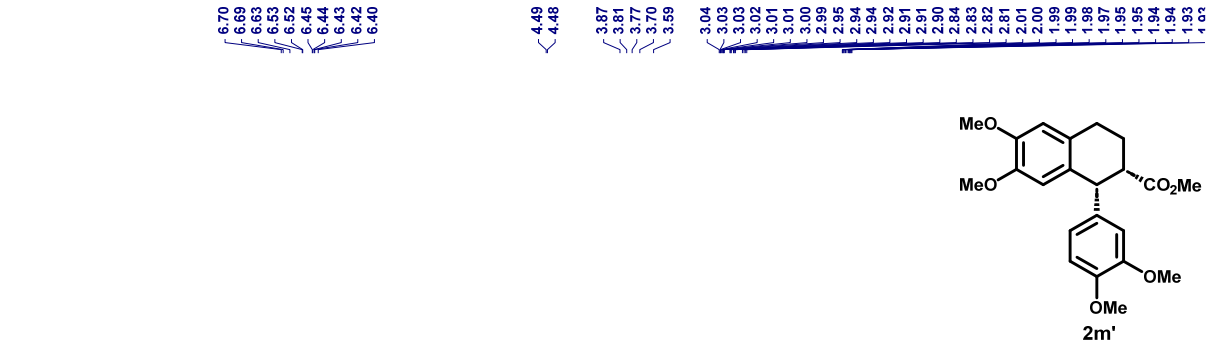


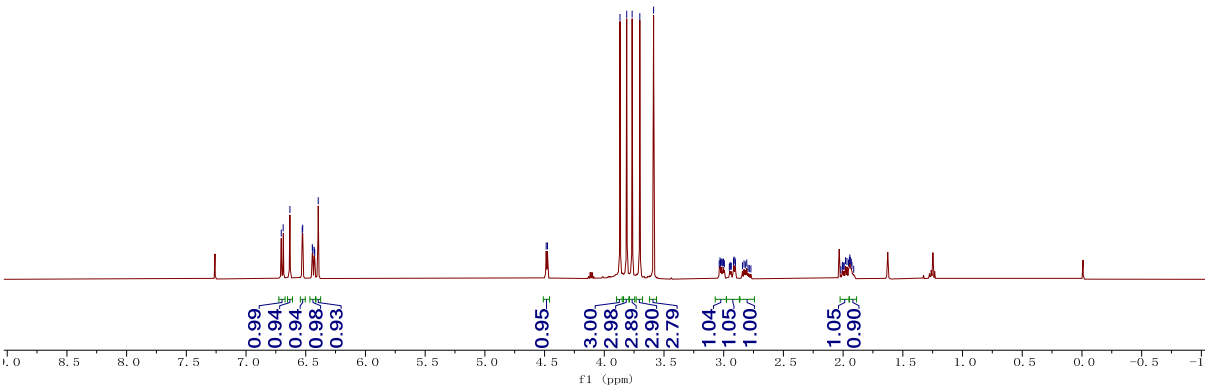
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



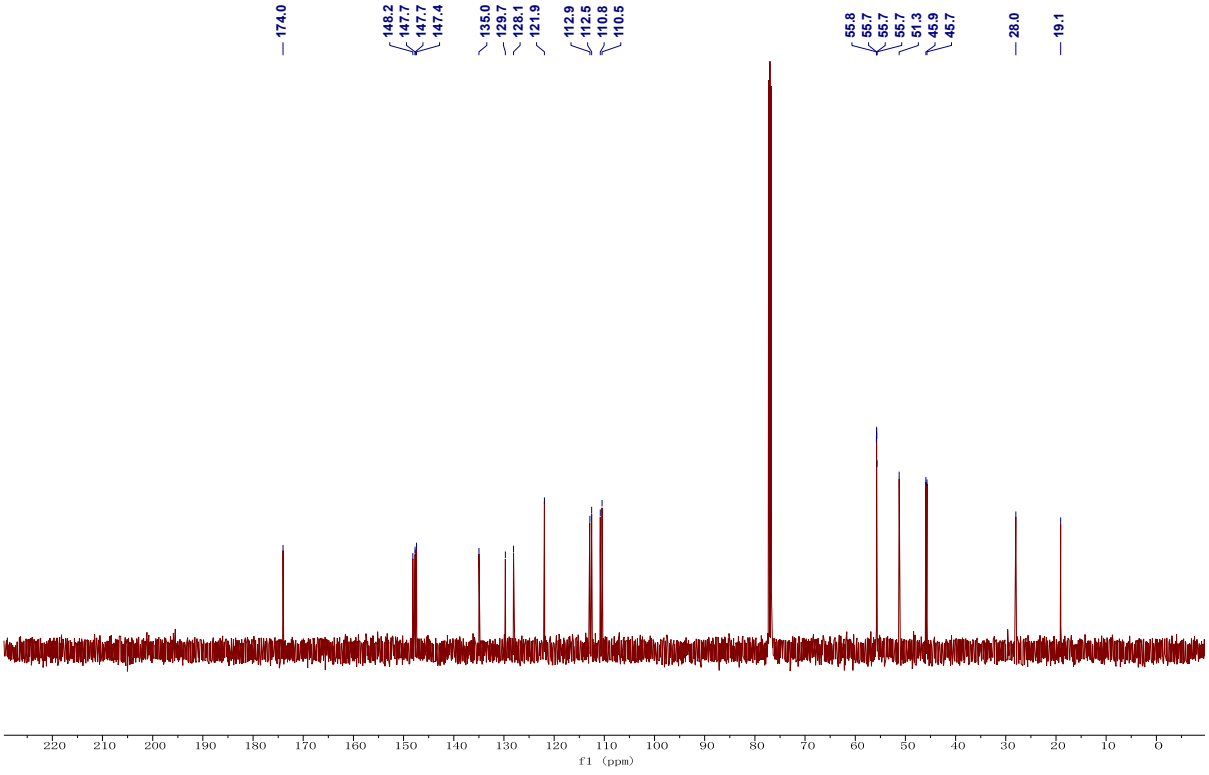
2m': Methyl (5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-5,6,7,8-tetrahydronaphtho- [2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



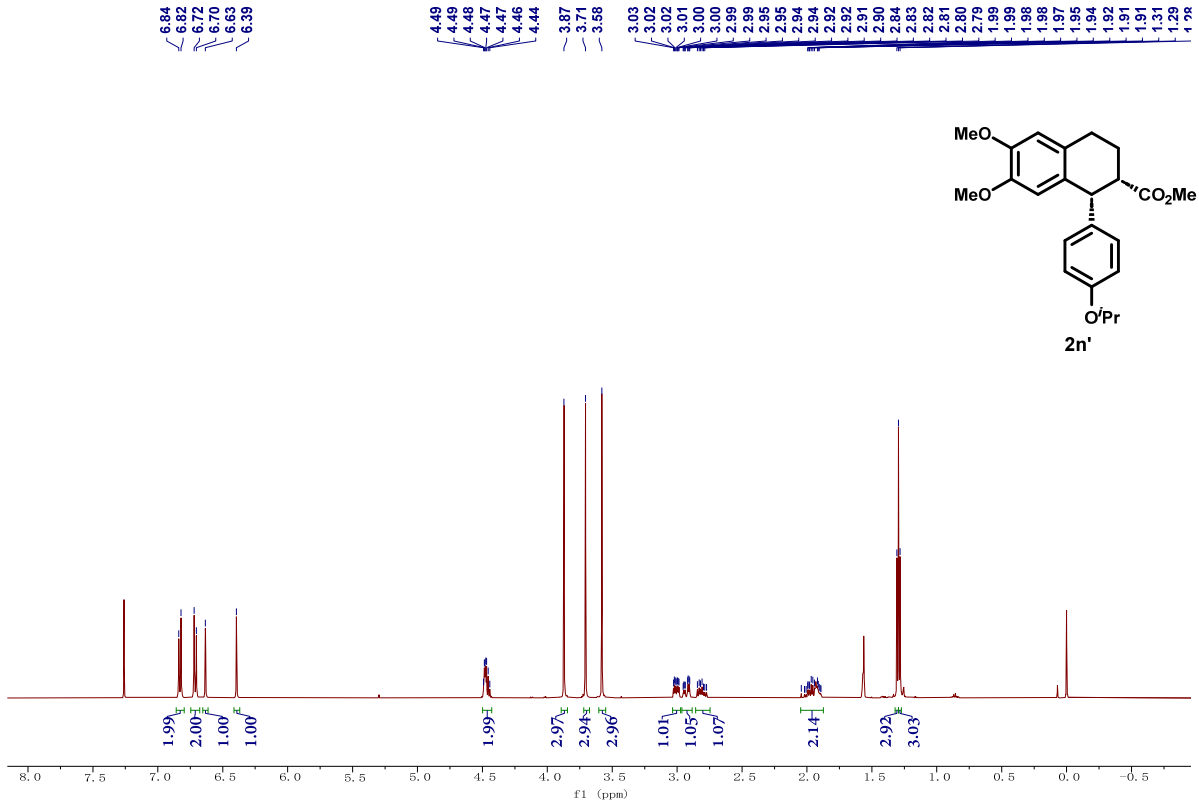


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

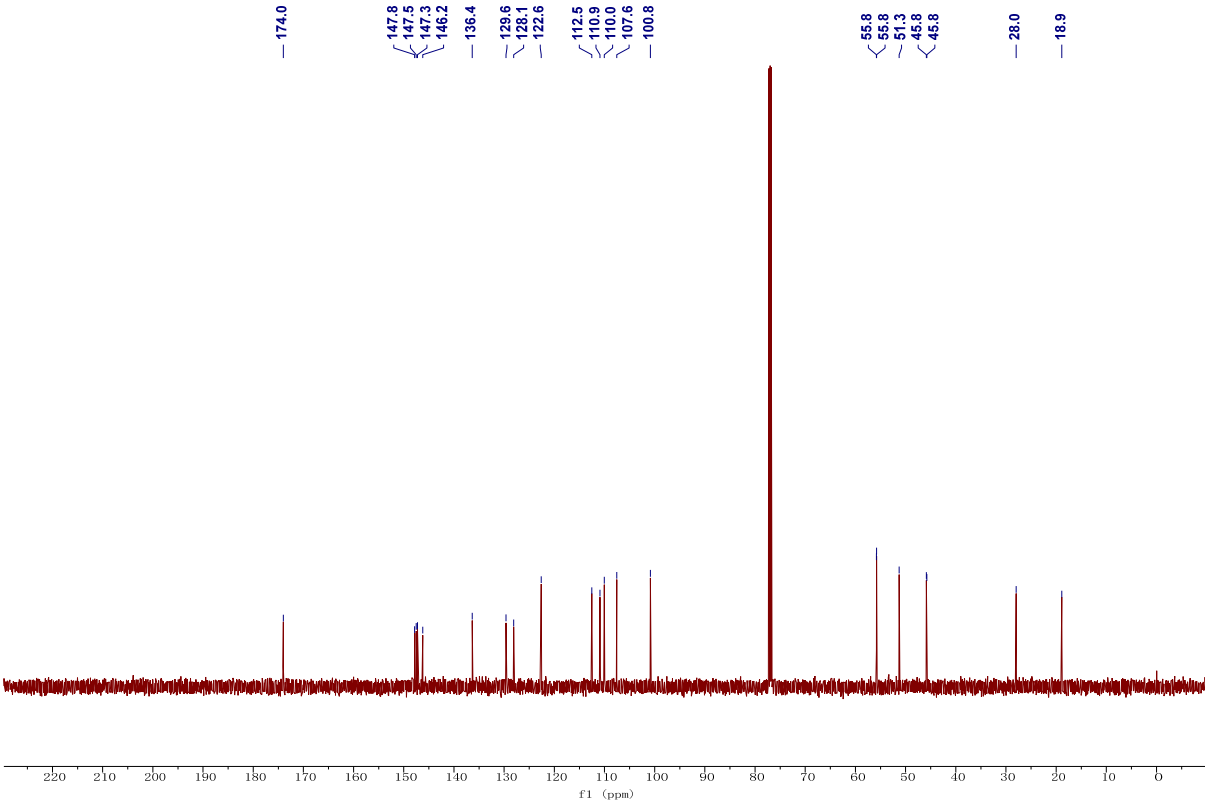


2n': Methyl (1R,2S)-1-(4-isopropoxyphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydro- naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

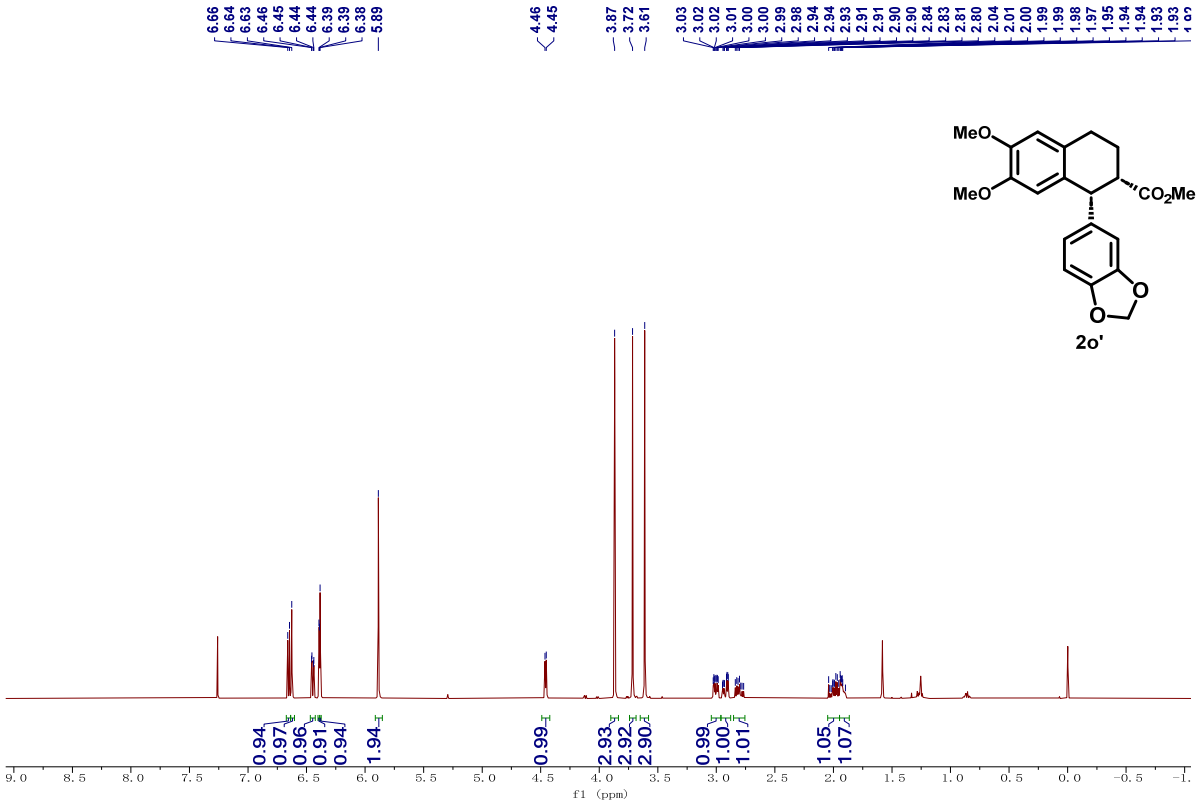


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

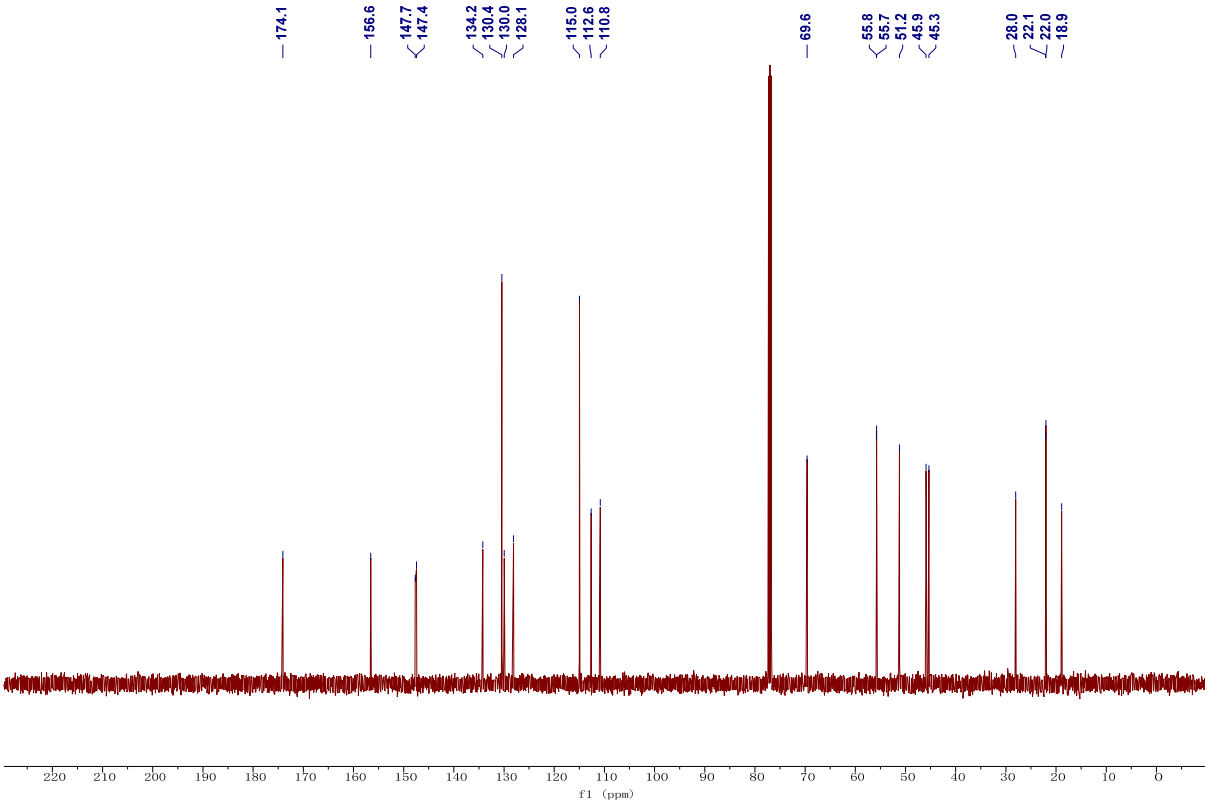


2o': Methyl (1R,2S)-1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxy-1,2,3,4-tetrahydro- naphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

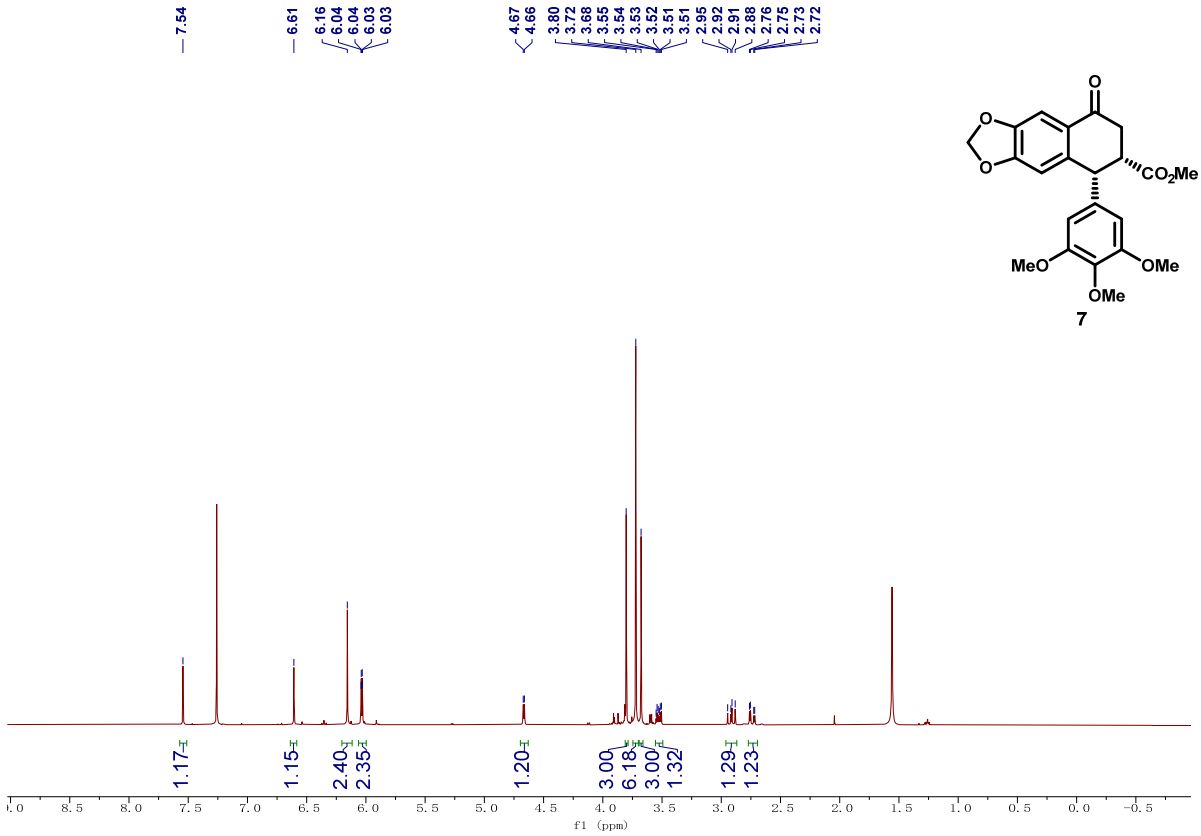


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

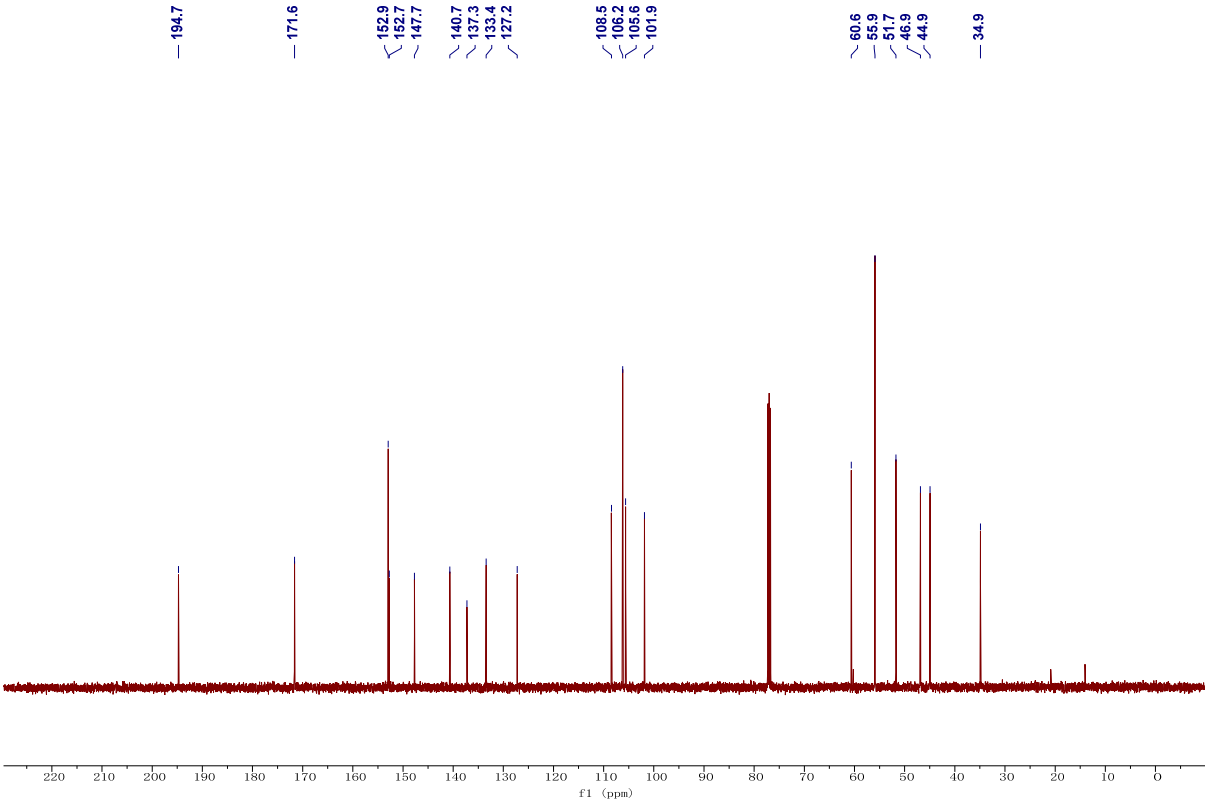


7: Methyl (5R,6S)-8-oxo-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3] dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

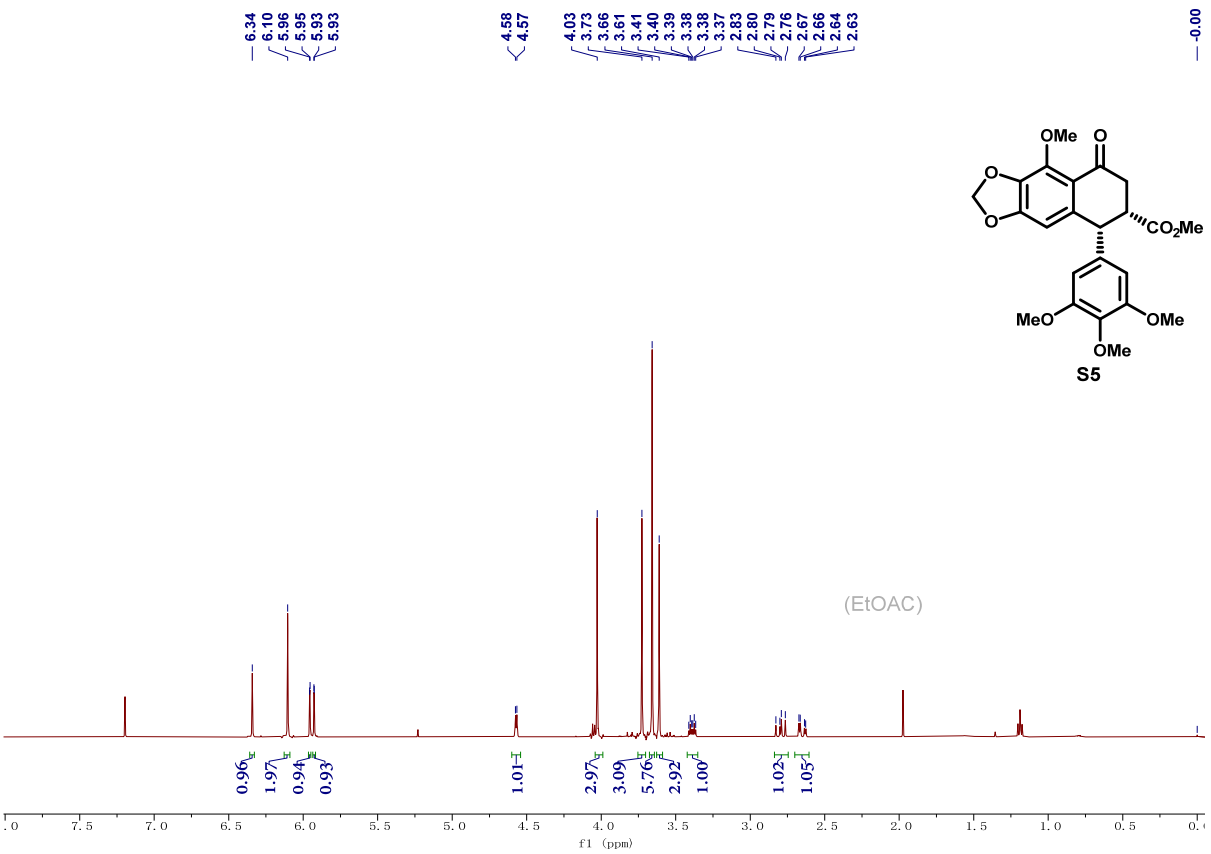


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

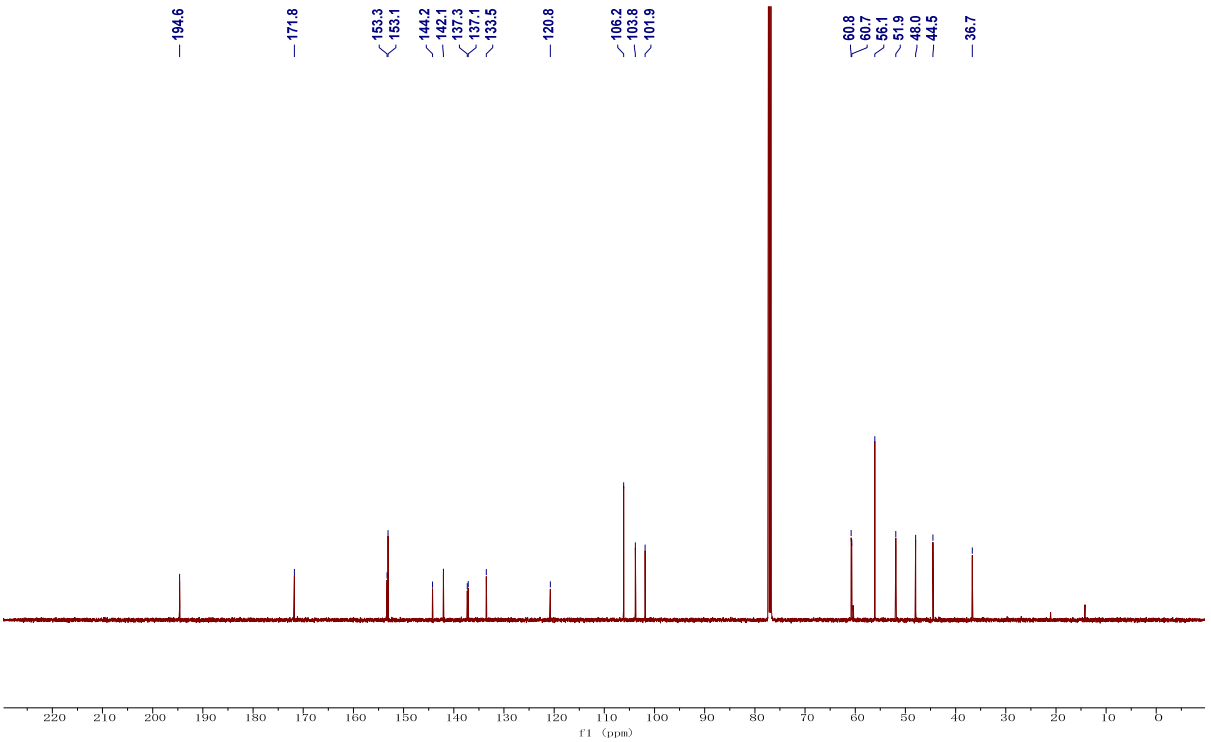


S5: Methyl(5R,6S)-9-methoxy-8-oxo-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydro-naphtho[2,3-d]-[1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

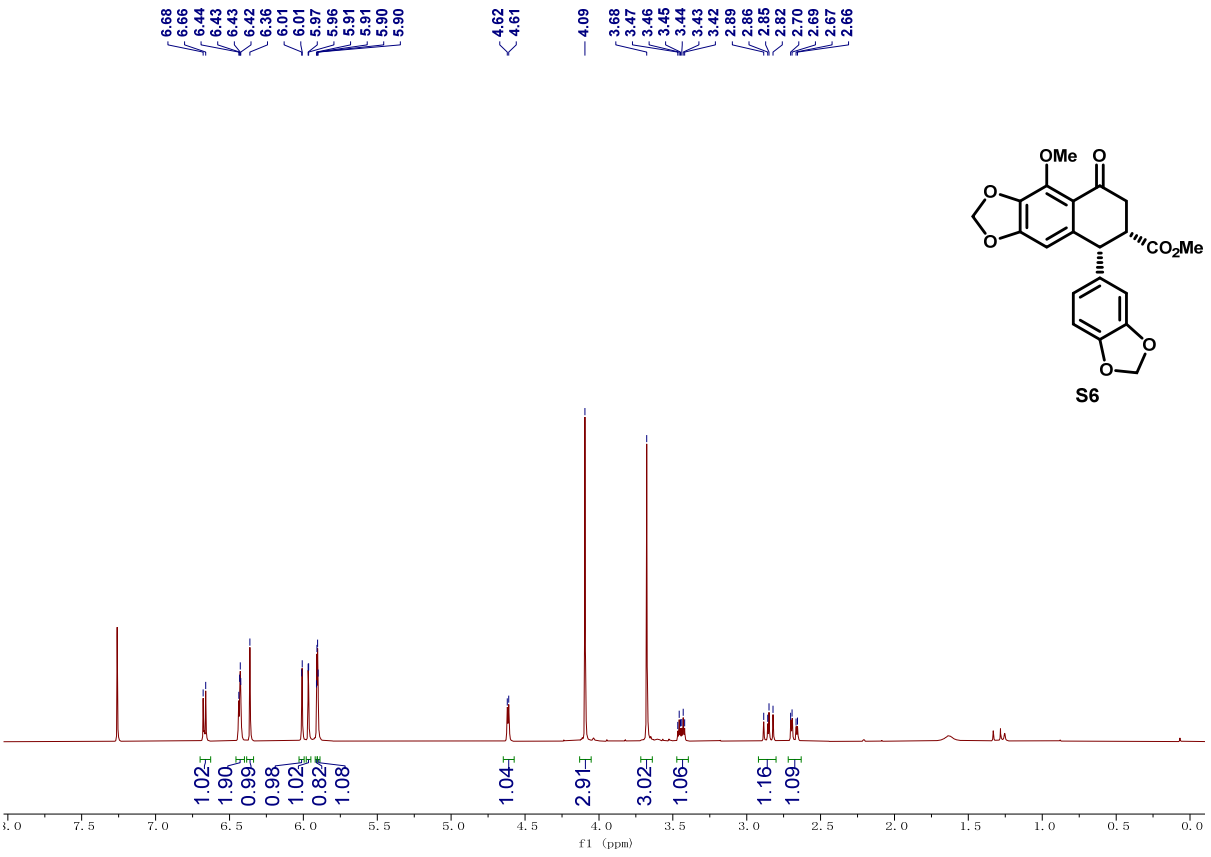


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

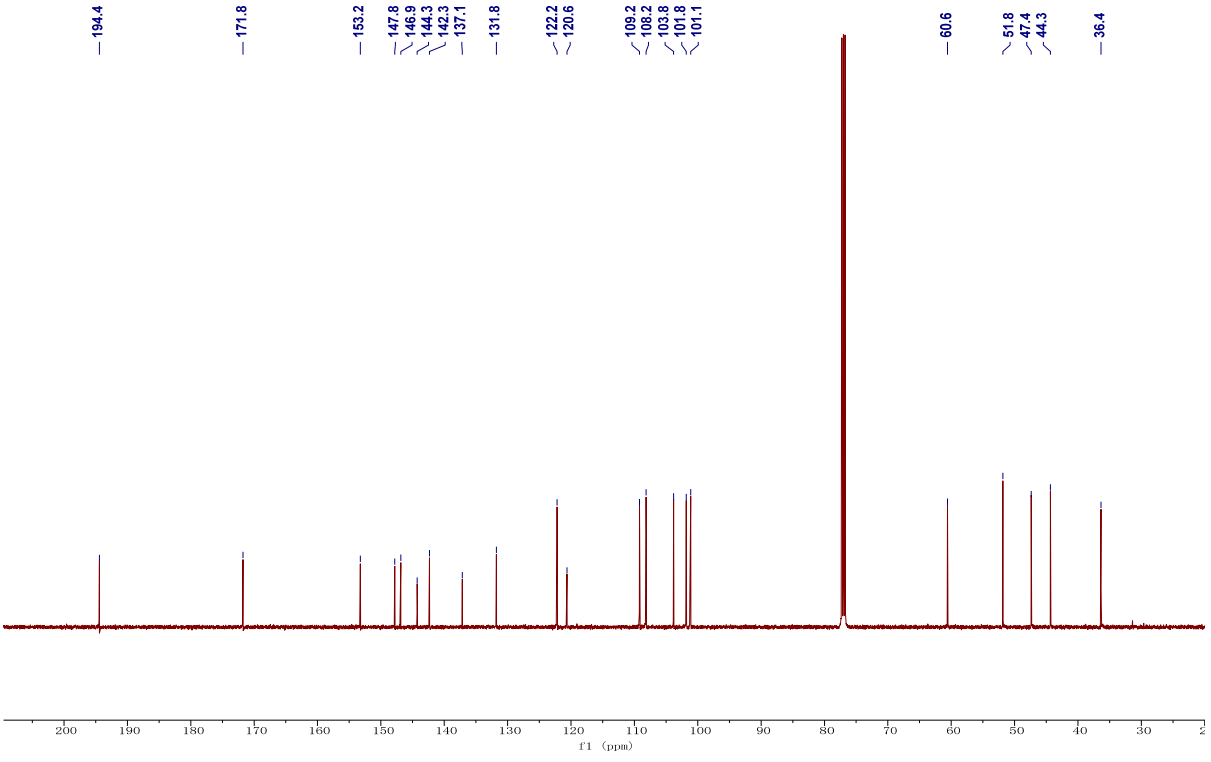


S6: Methyl(5R,6S)-5-(benzo[d][1,3]dioxol-5-yl)-9-methoxy-8-oxo-5,6,7,8-tetrahydro-naphtho[2,3-d][1,3]dioxole-6-carboxylate.

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

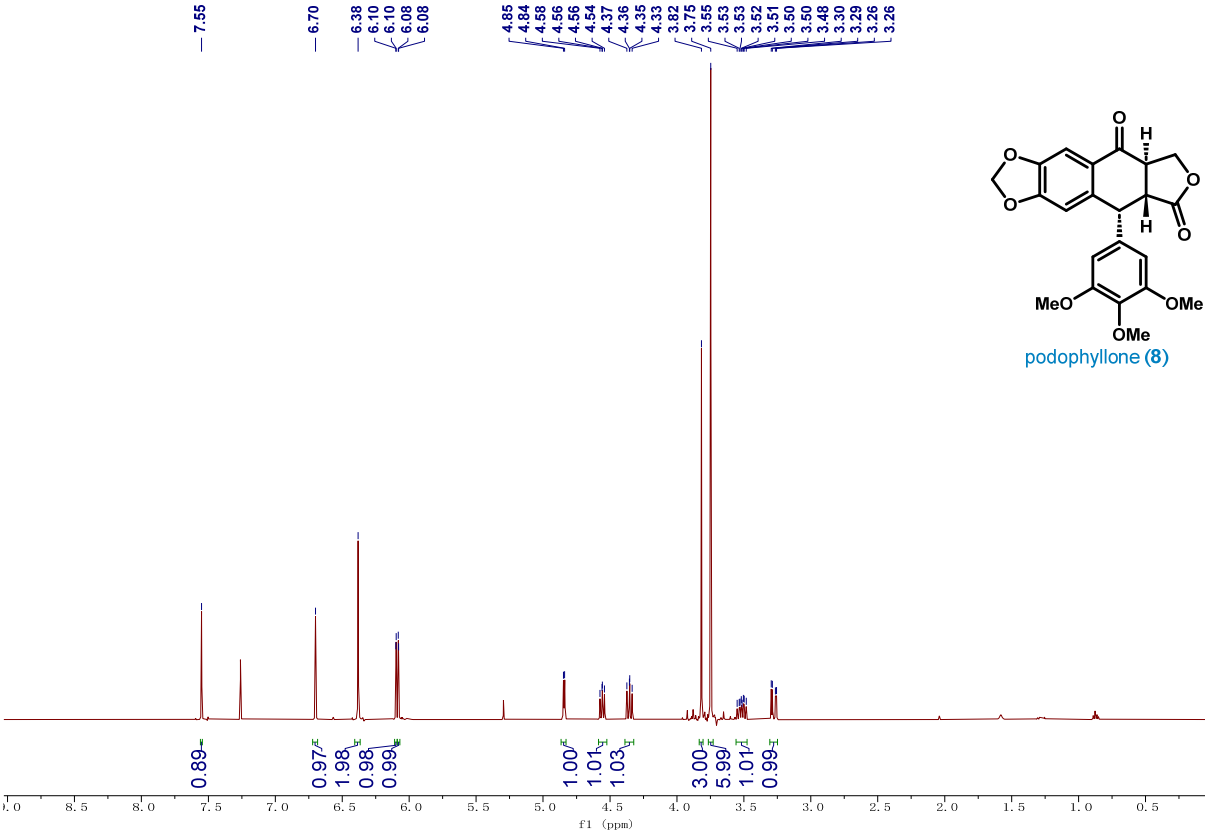


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



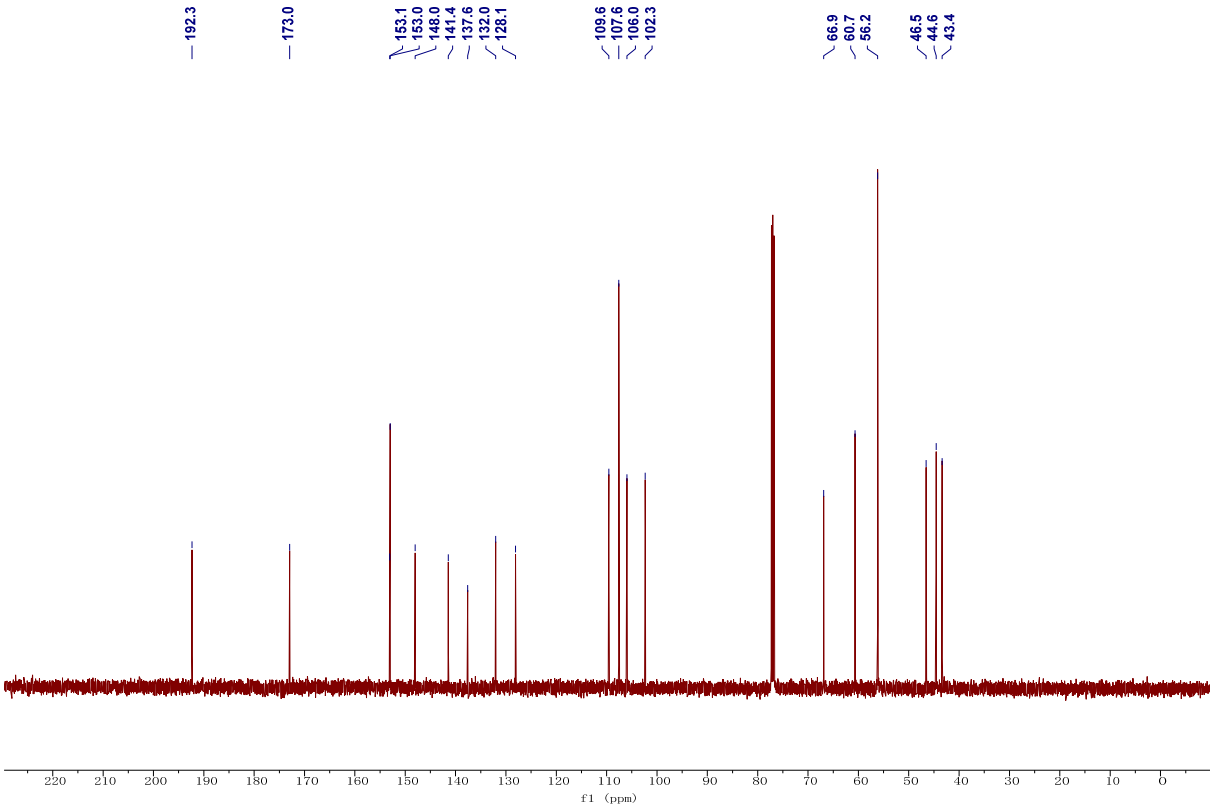
8: Podophyllone

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

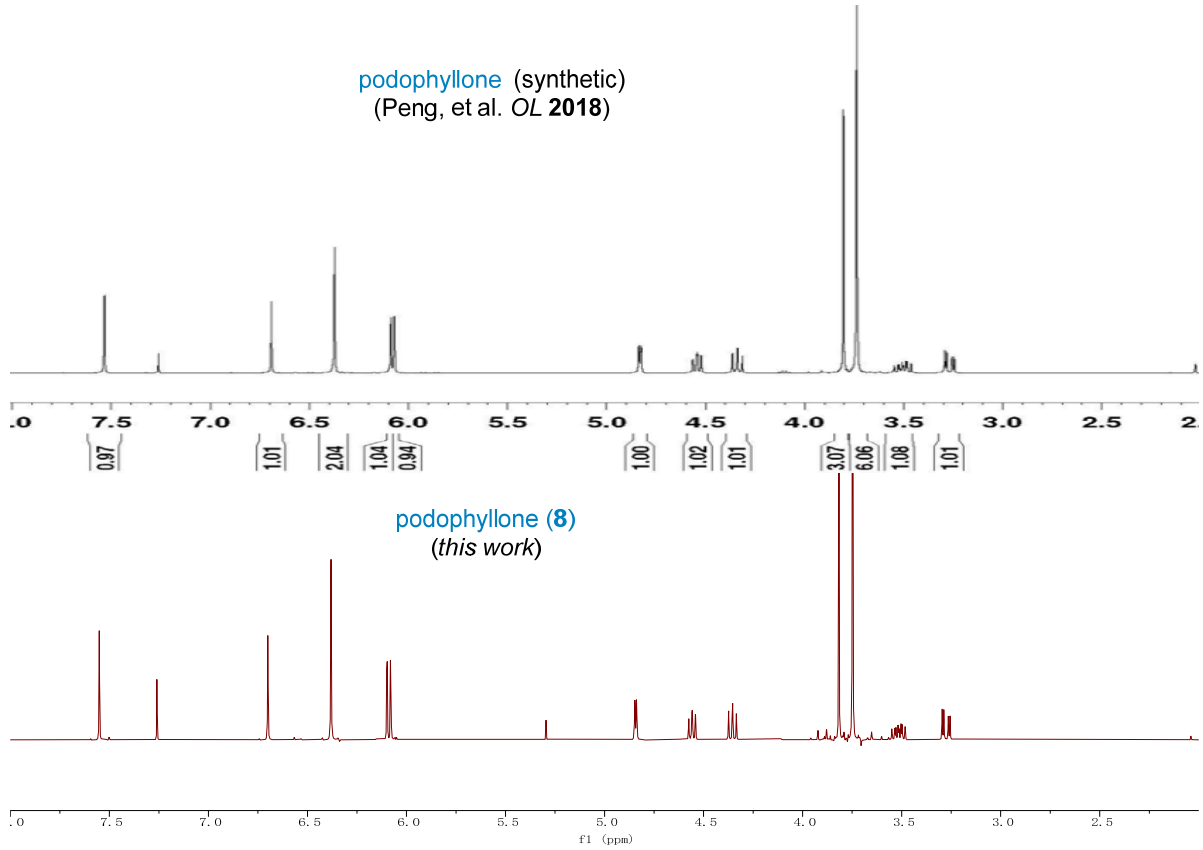


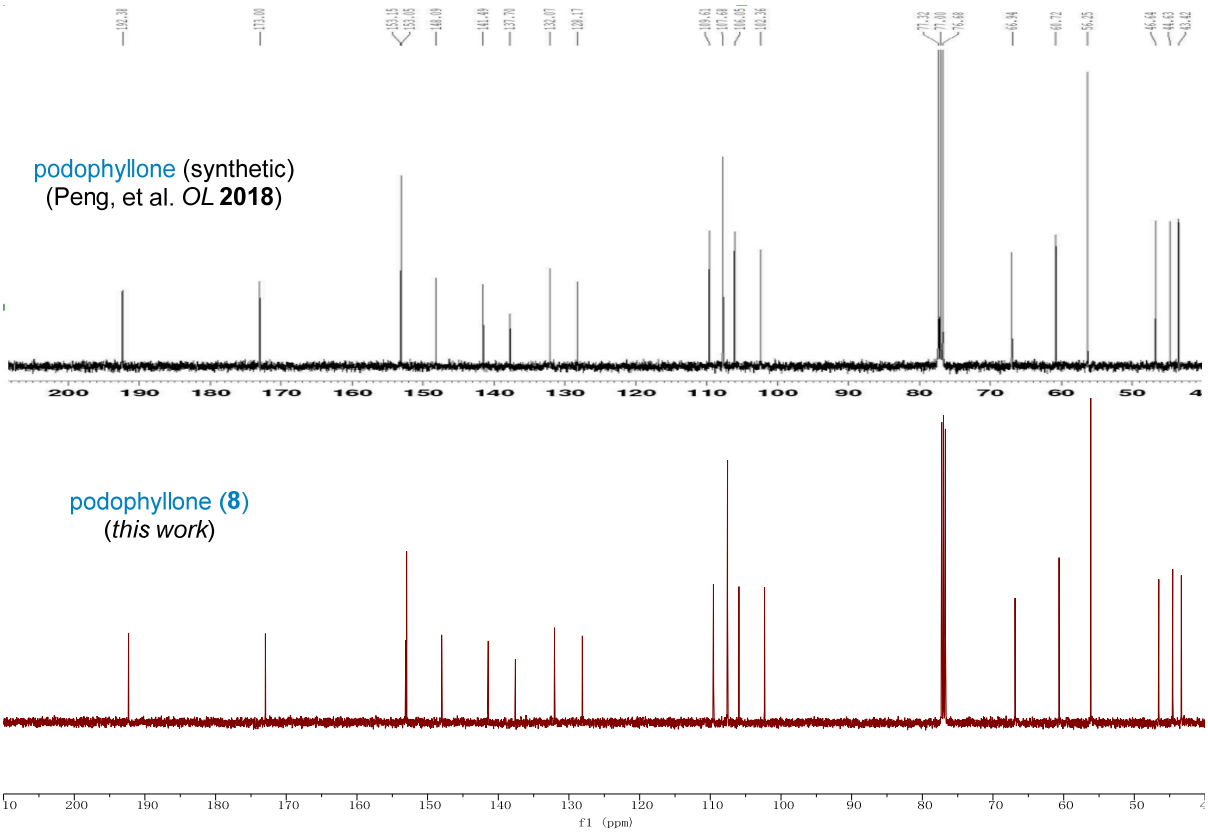
podophyllone (**8**)

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



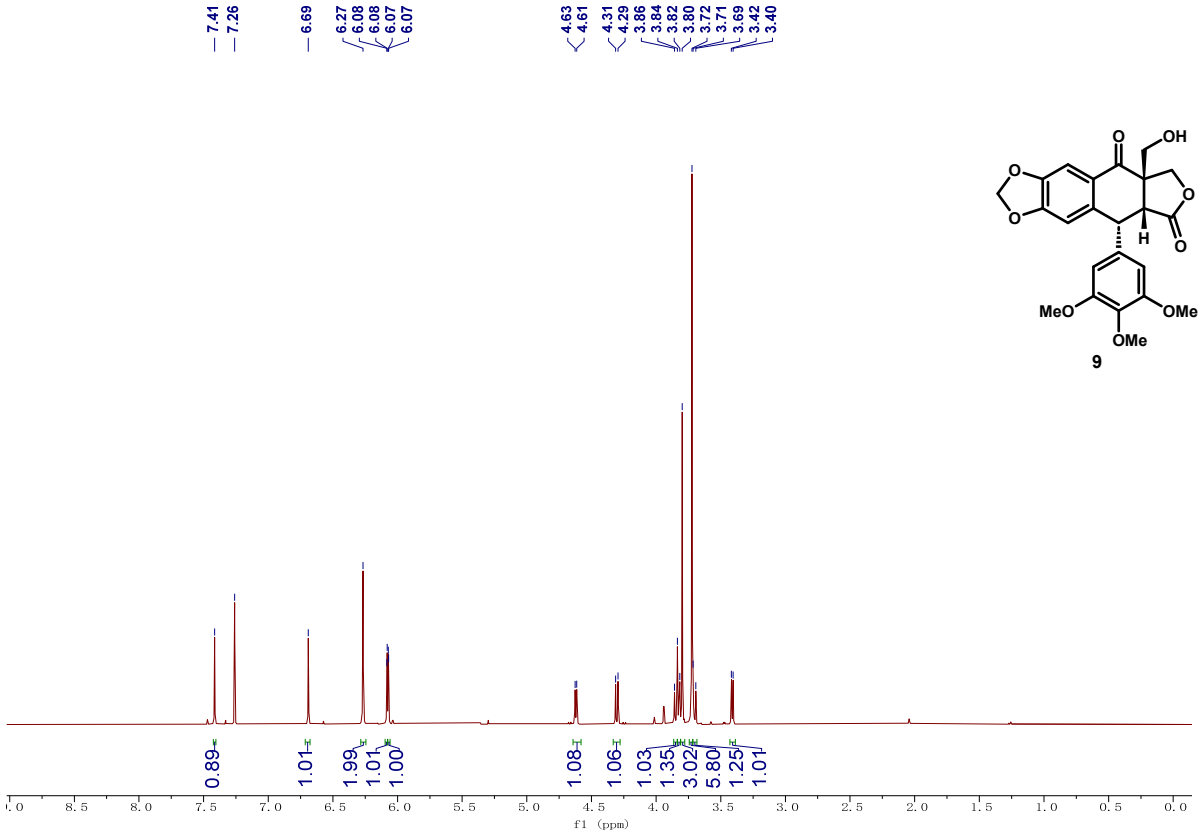
NMR spectra comparison of podophyllone





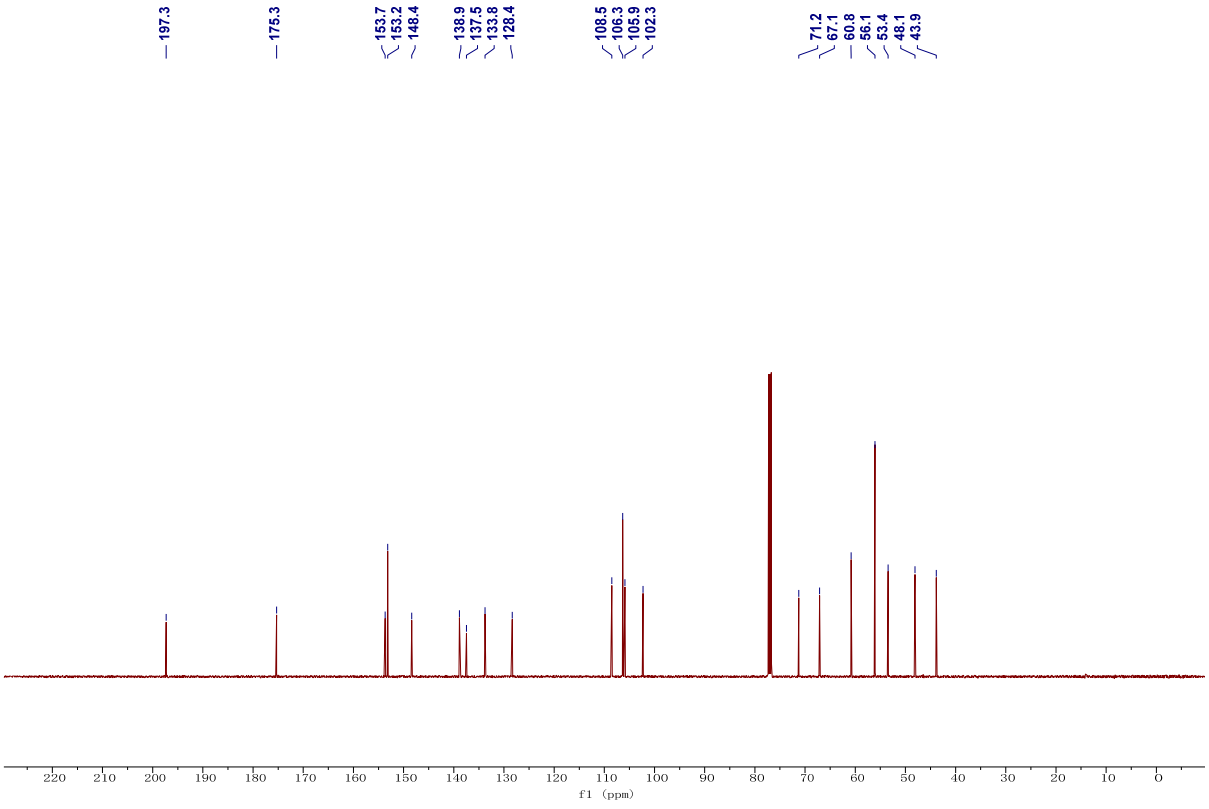
Intermediate 9

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



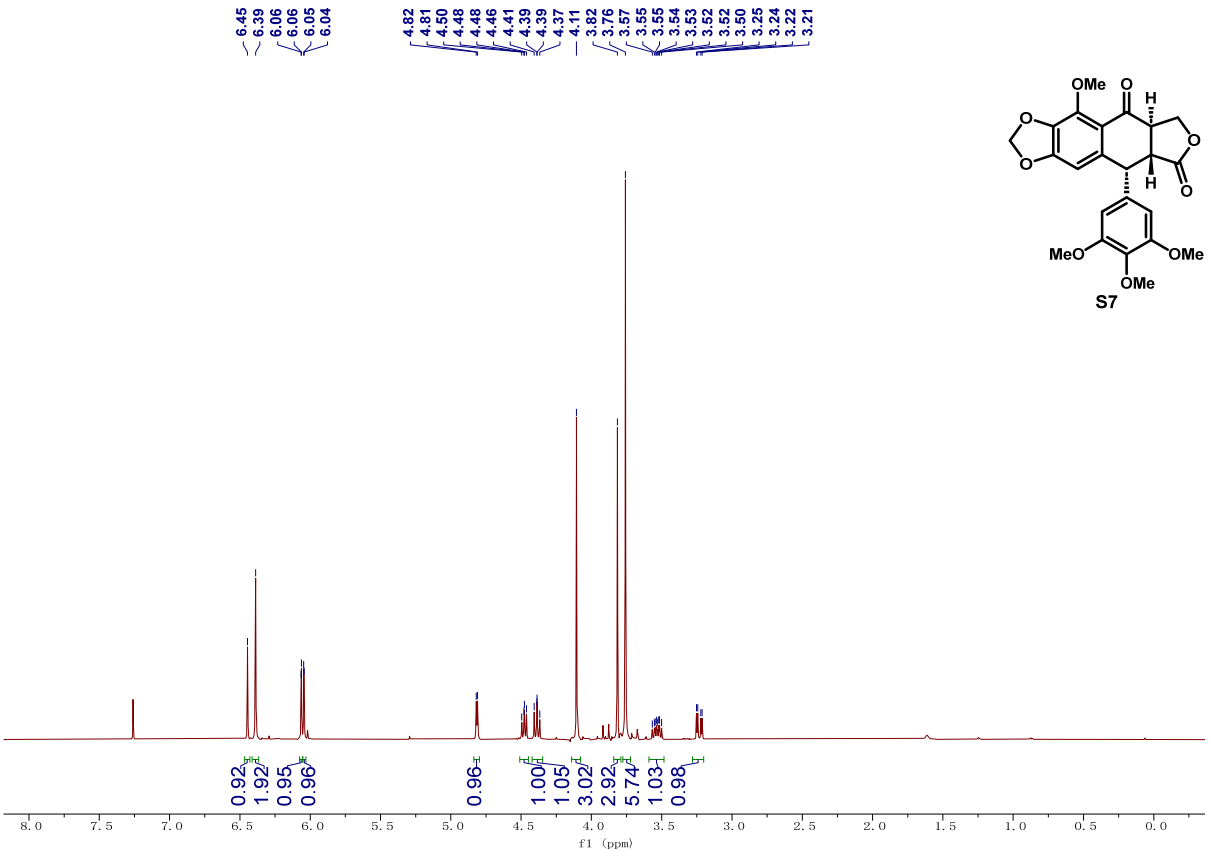
9

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



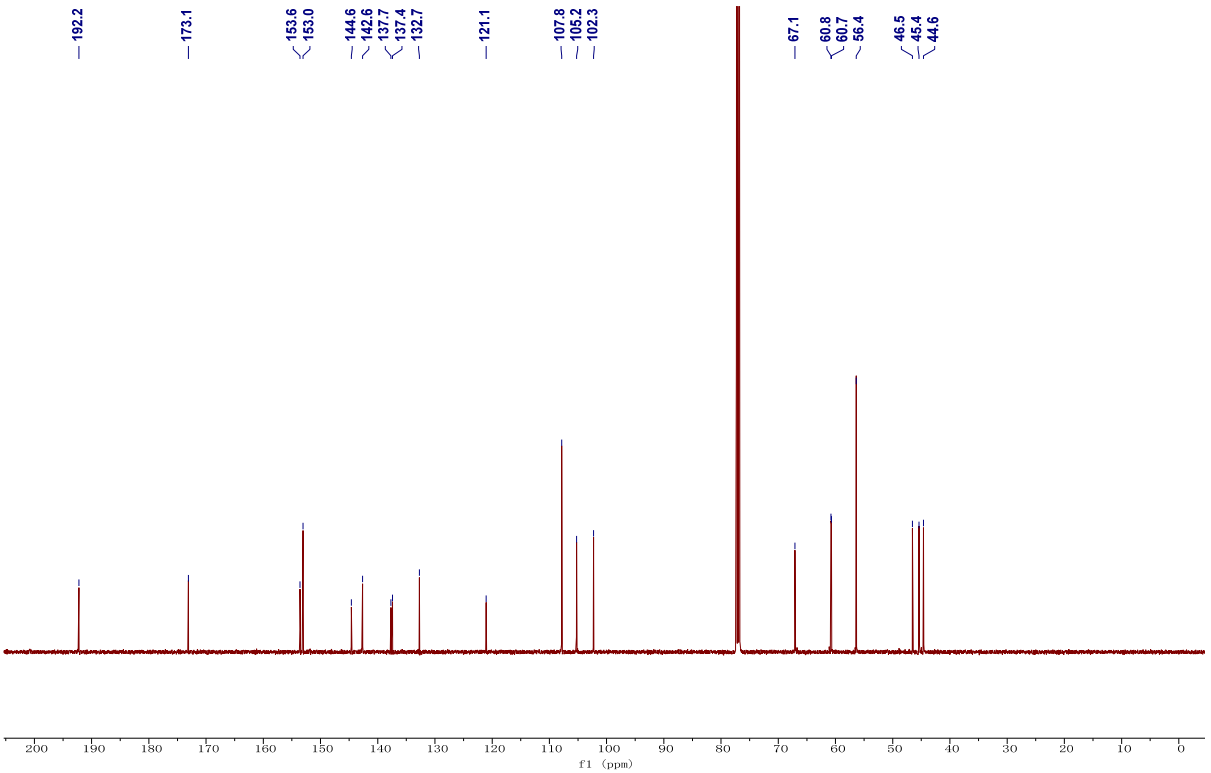
S7: (5aR,8aR,9R)-4-Methoxy-9-(3,4,5-trimethoxyphenyl)-5a,6,8a,9-tetrahydrofuro[3',4':6,7] naphtho[2,3-d][1,3]dioxole-5,8-dione

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



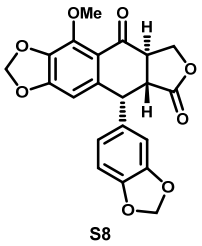
S7

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

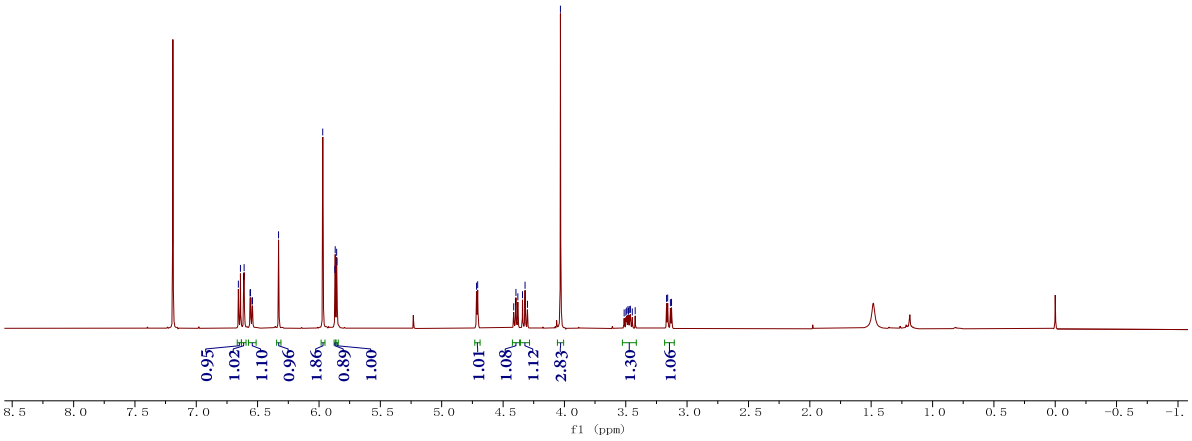


S8: (5aR,8aR,9R)-9-(Benzo[d][1,3]dioxol-5-yl)-4-methoxy-5a,6,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxole-5,8-dione

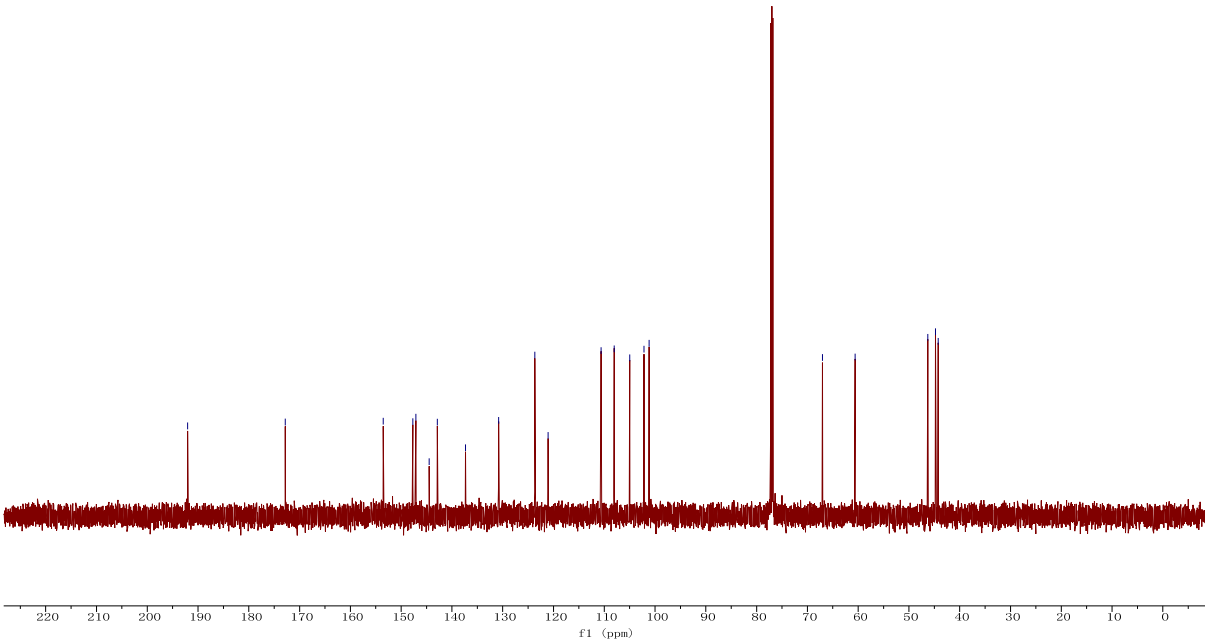
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



S8

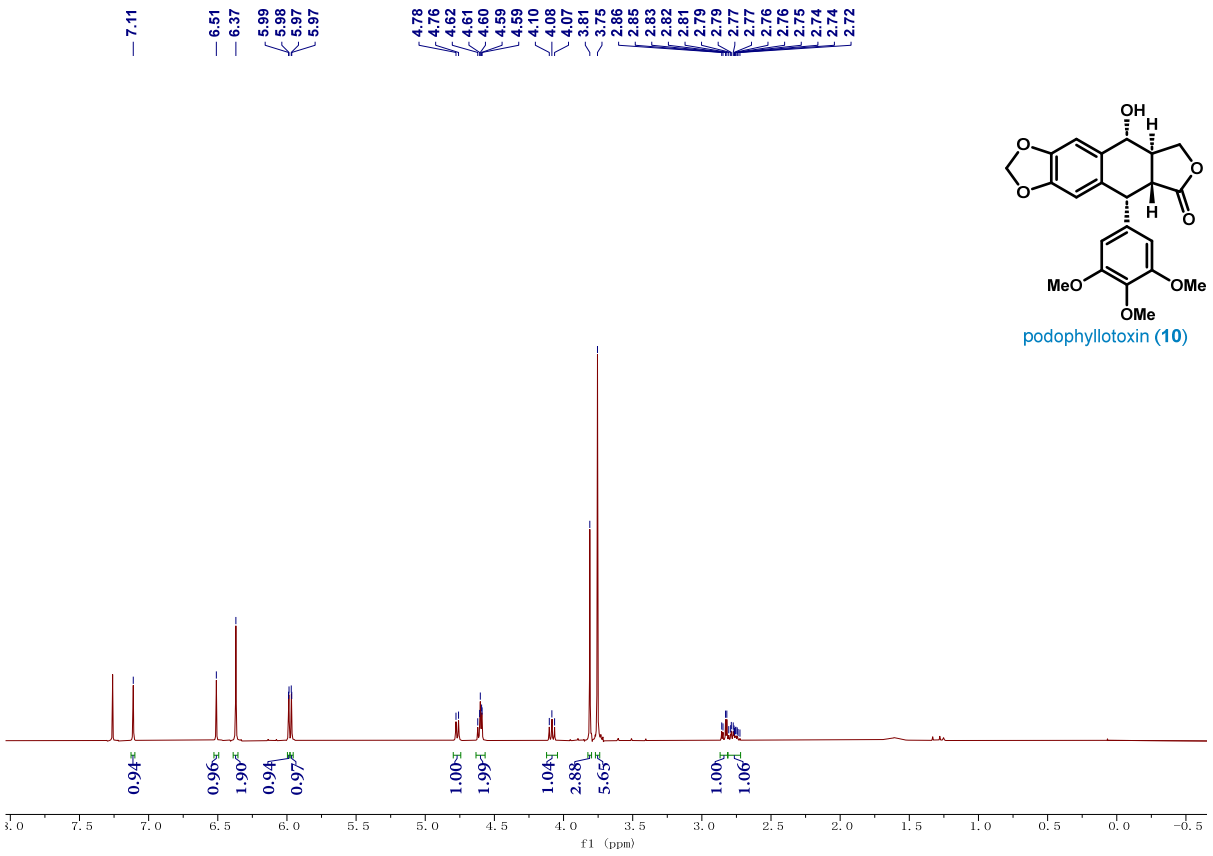


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



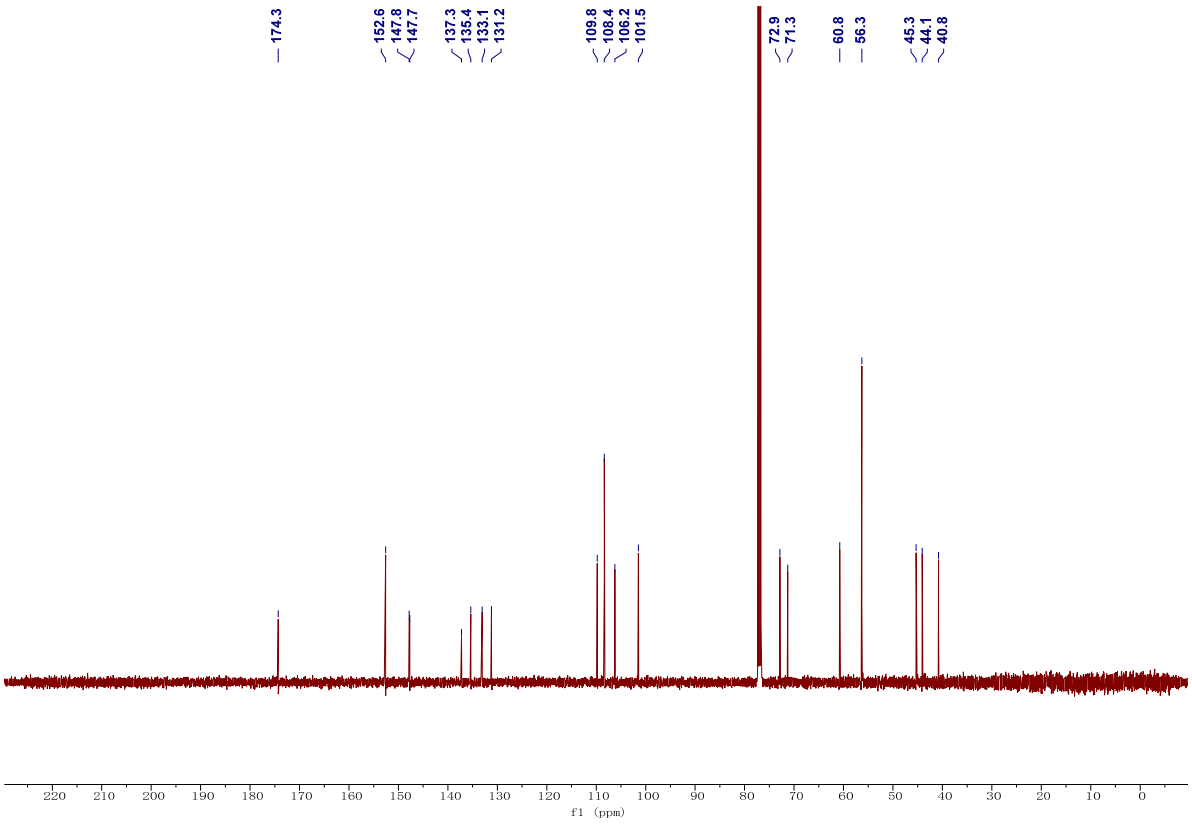
10: Podophyllotoxin

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

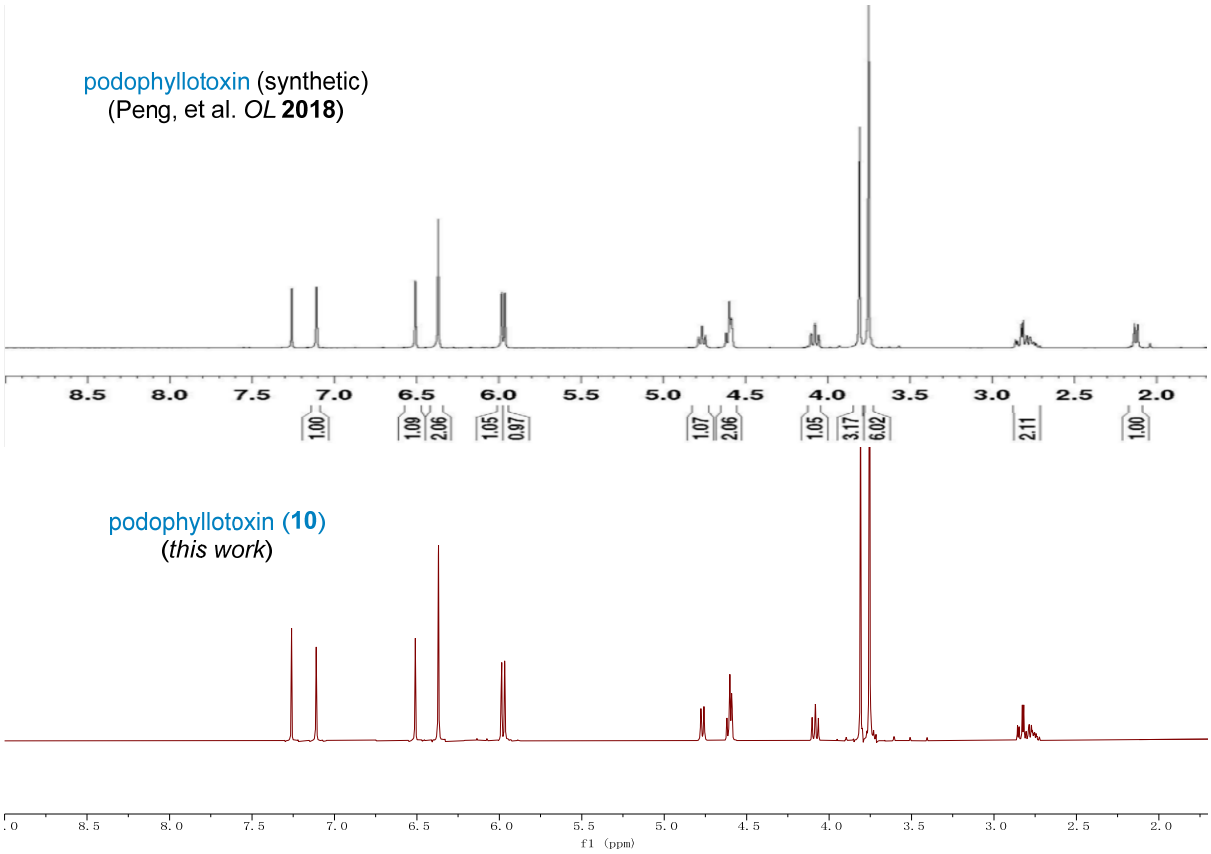


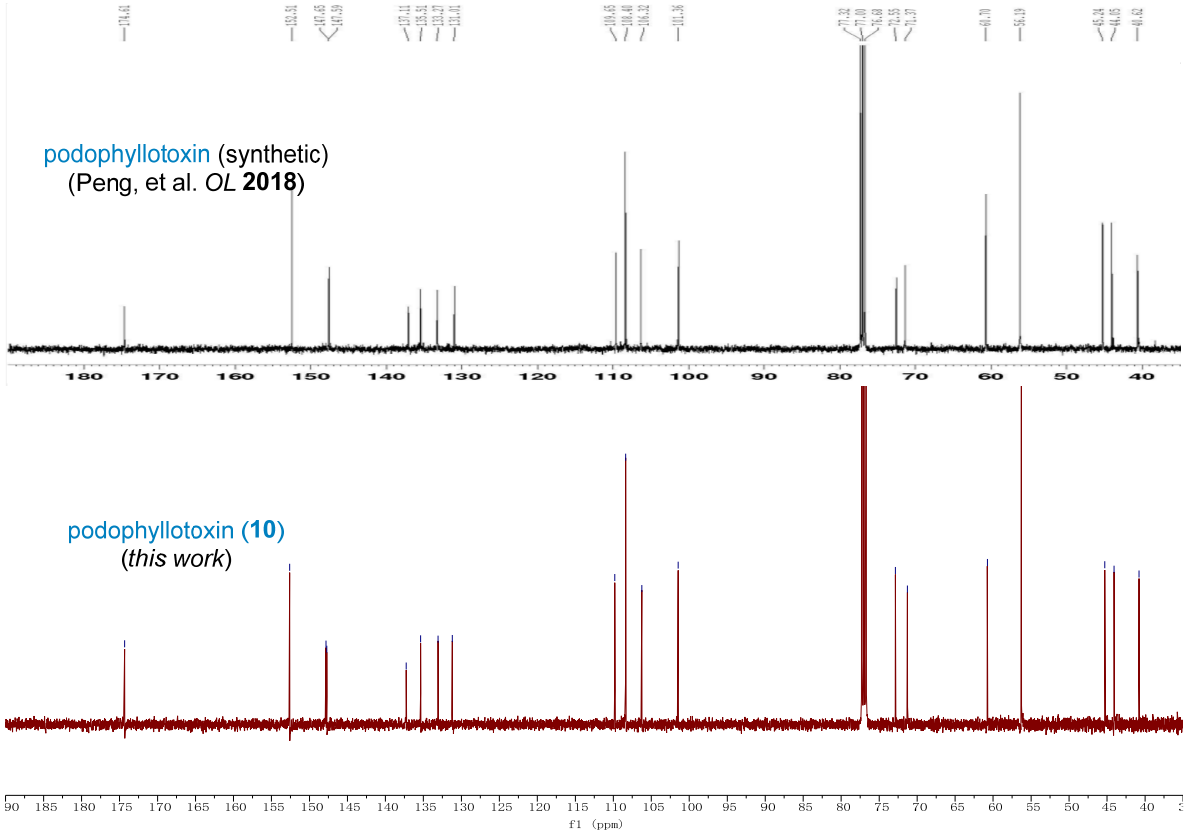
podophyllotoxin (**10**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



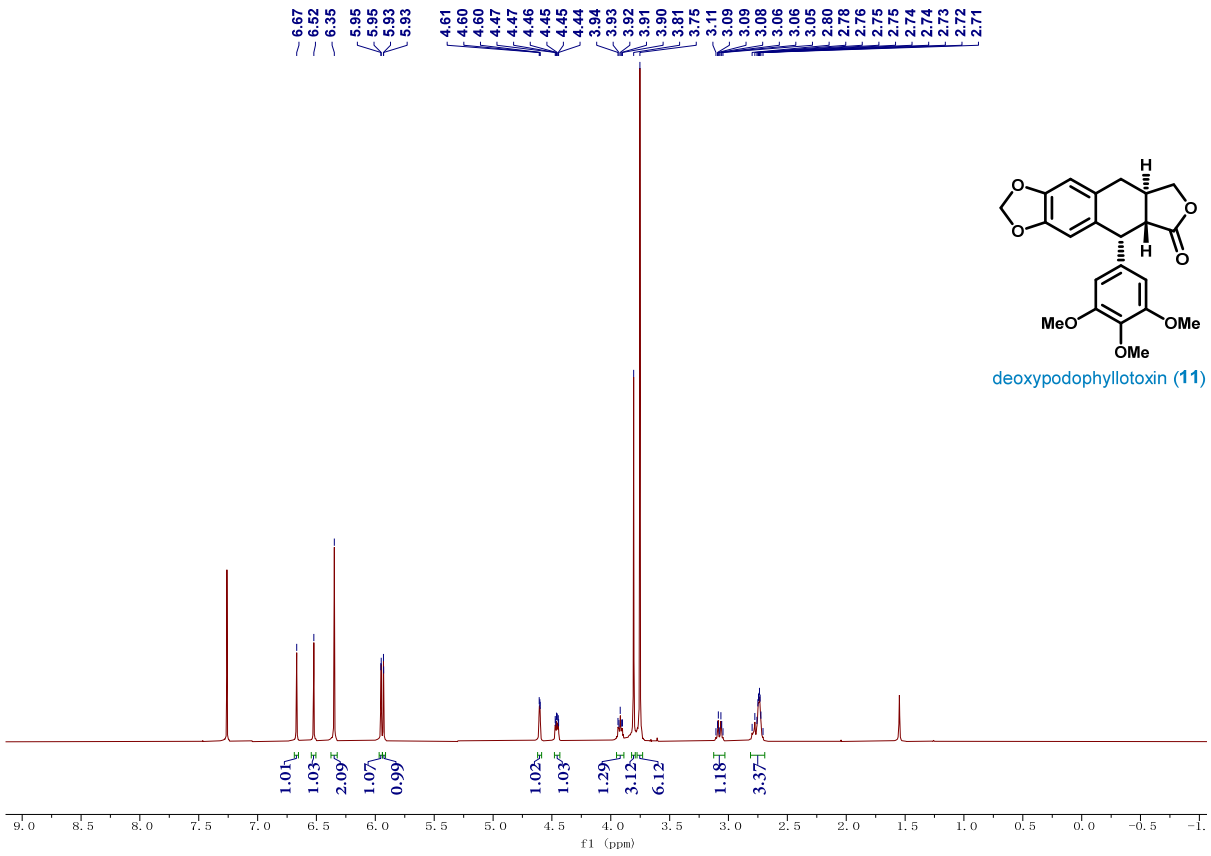
NMR spectra comparison of podophyllotoxin





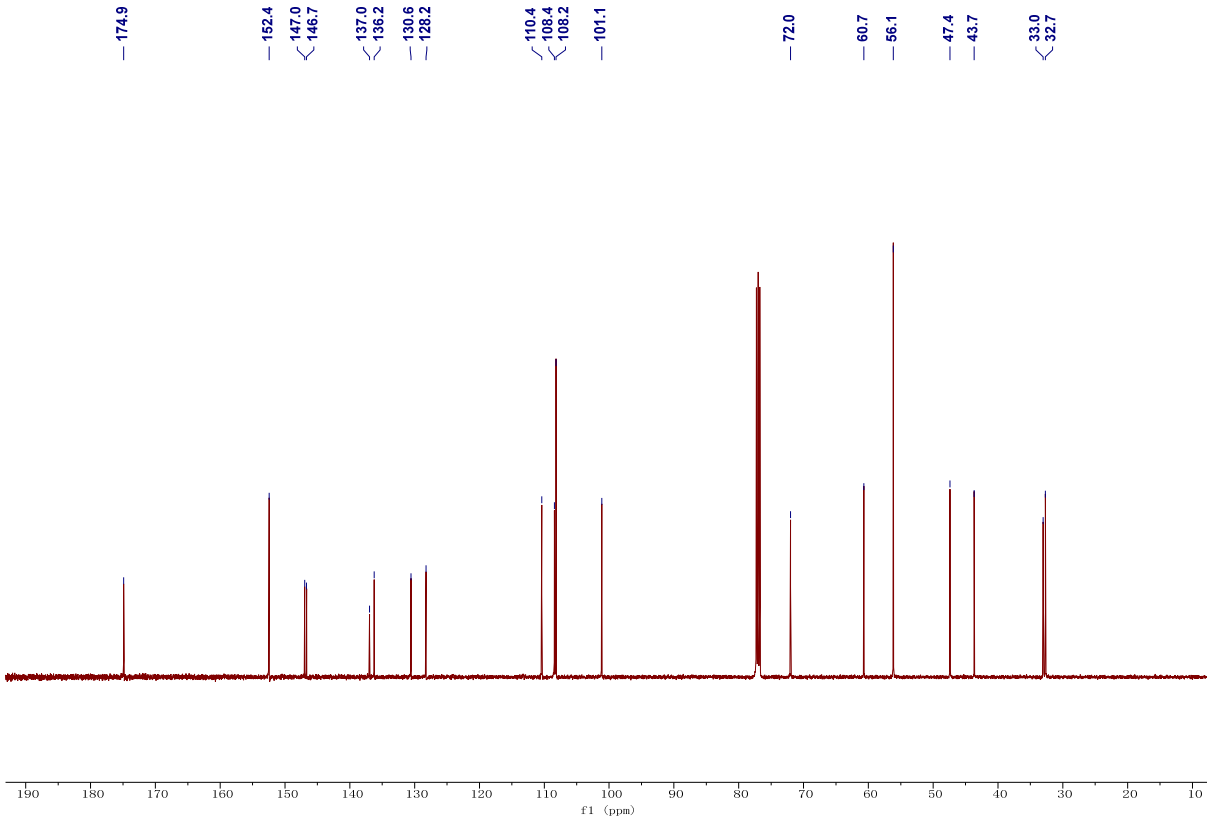
11: Deoxypodophyllotoxin

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

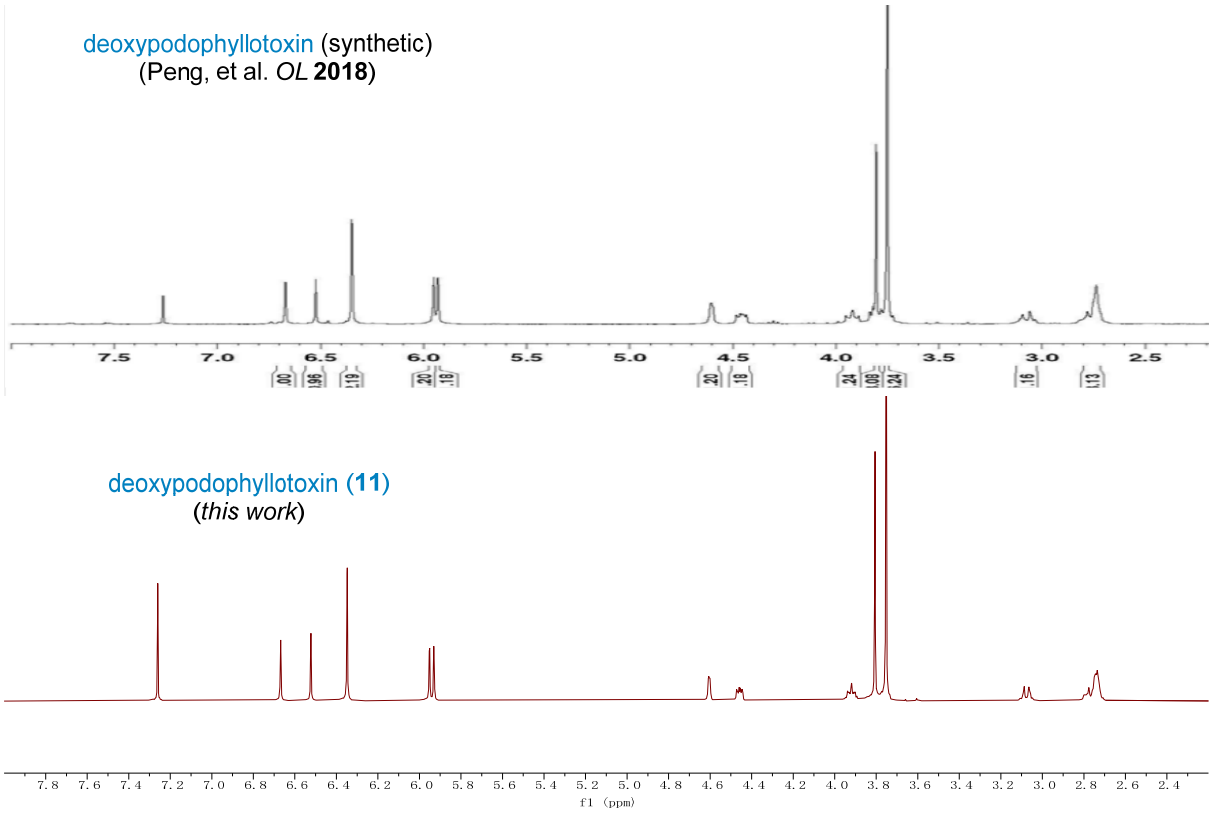


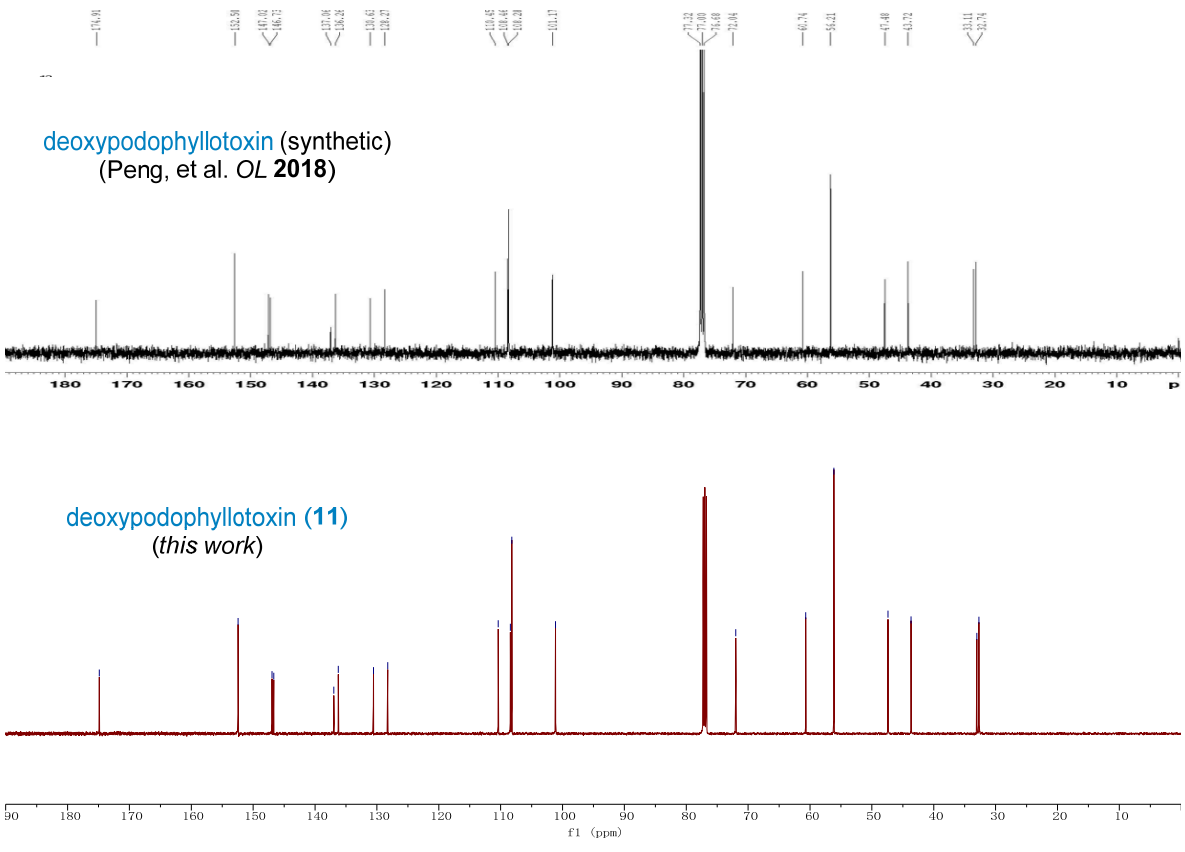
deoxypodophyllotoxin (**11**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



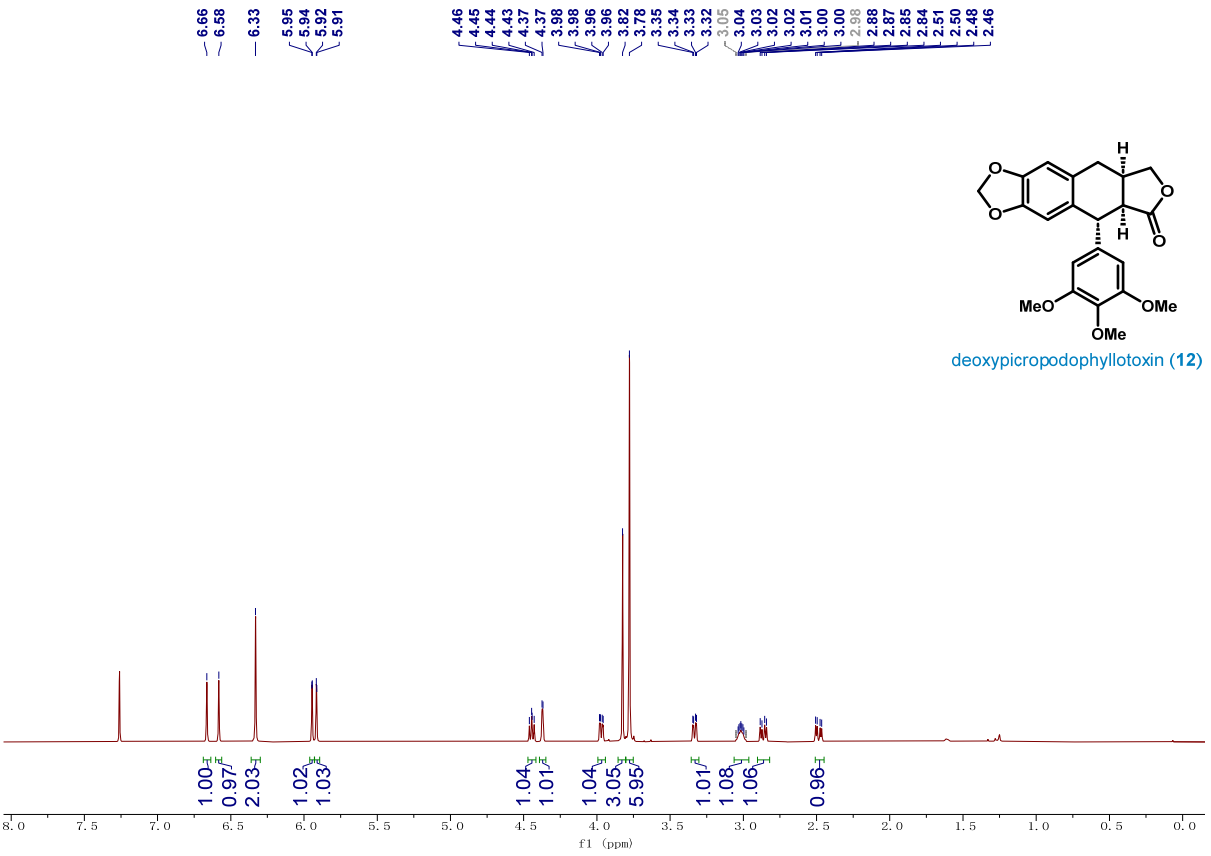
NMR spectra comparison of deoxypodophyllotoxin





12: Deoxypicropodophyllotoxin

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

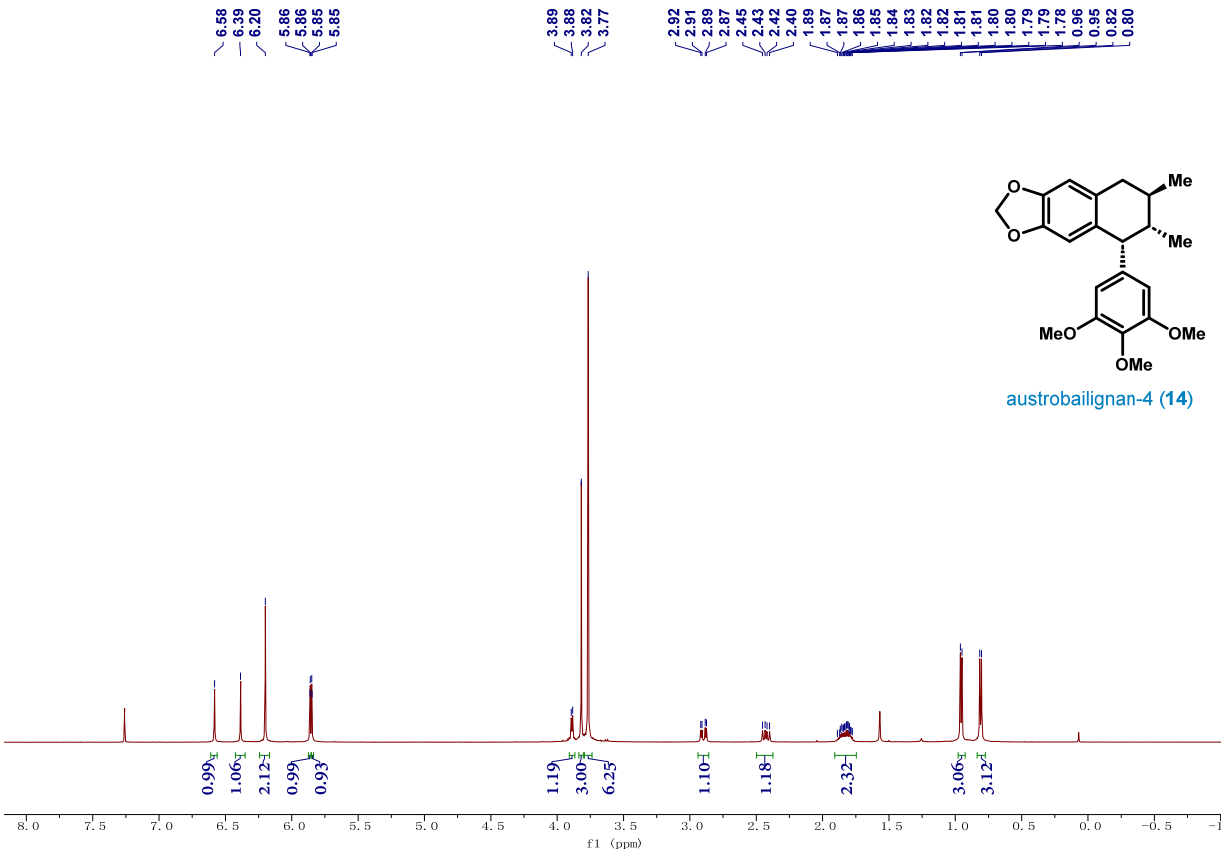


deoxypicropodophyllotoxin (**12**)

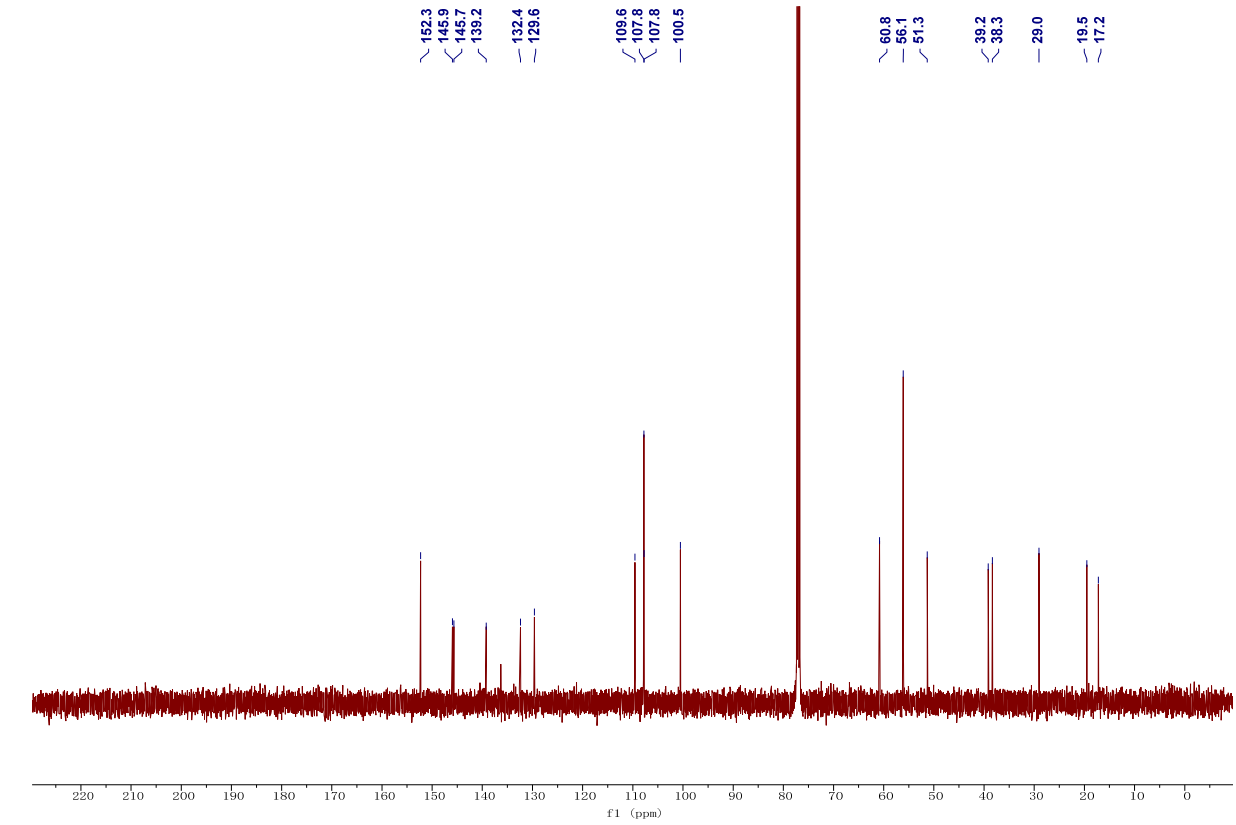
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

14: Austrobailignan

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

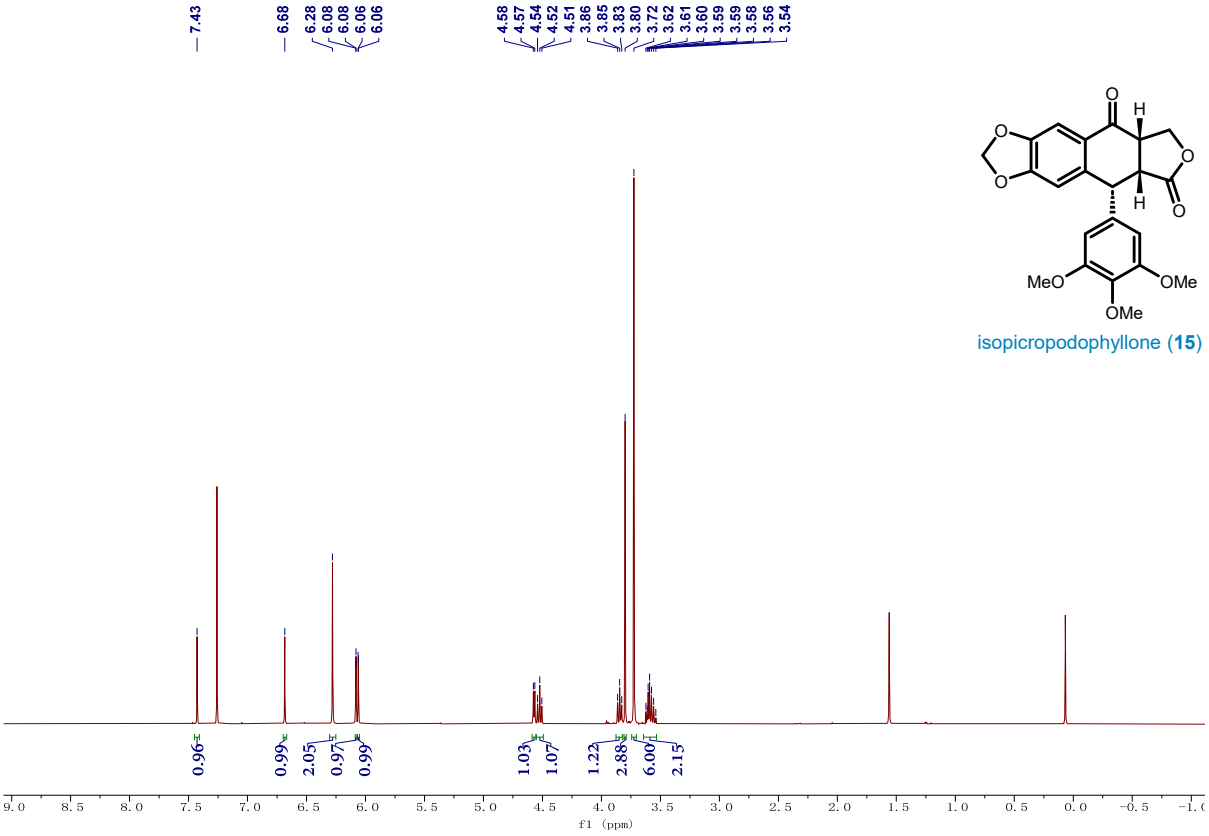


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



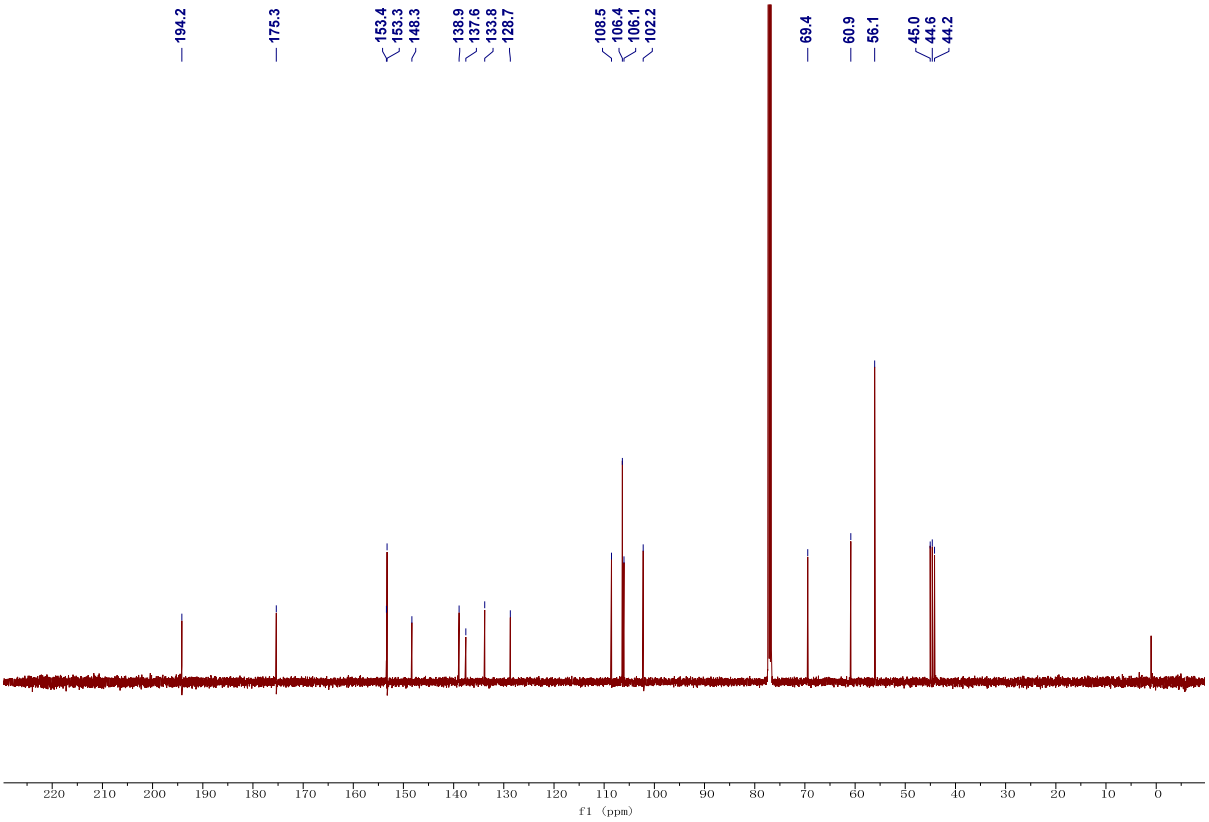
15: Isopicropodophyllone

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

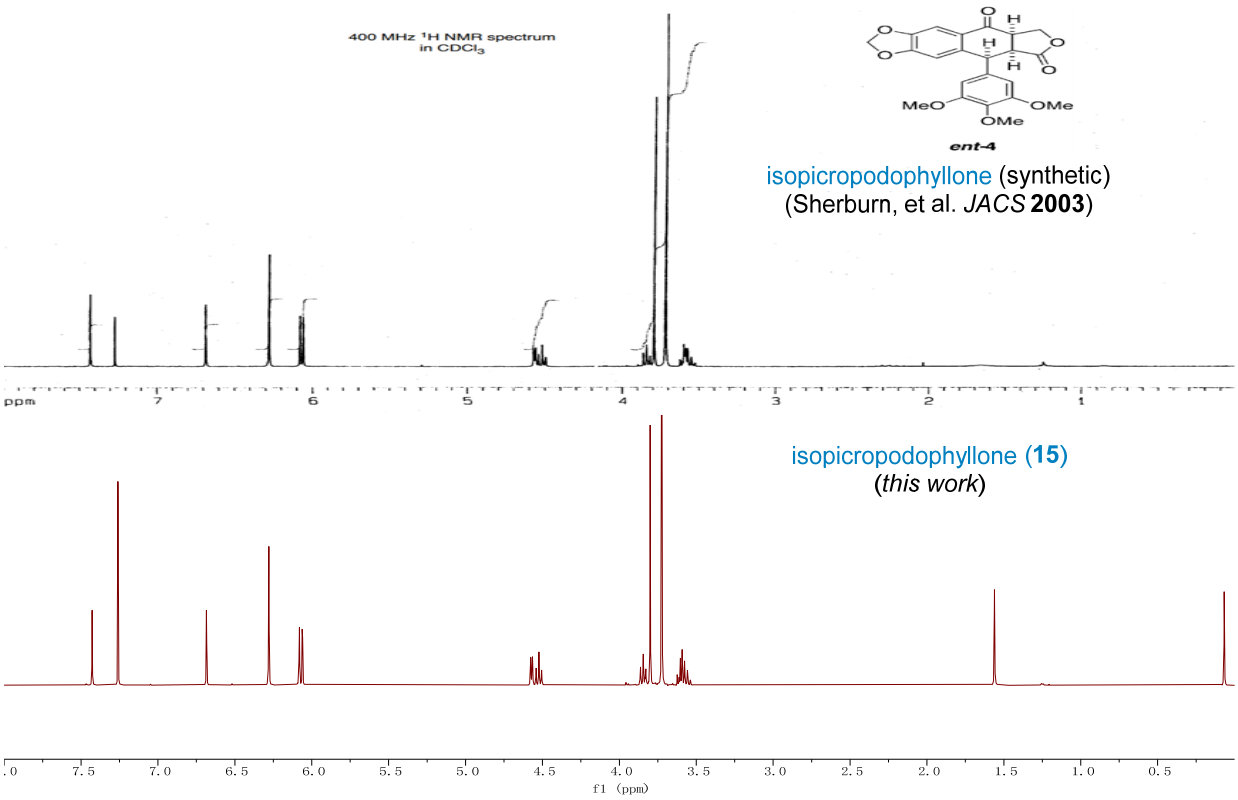


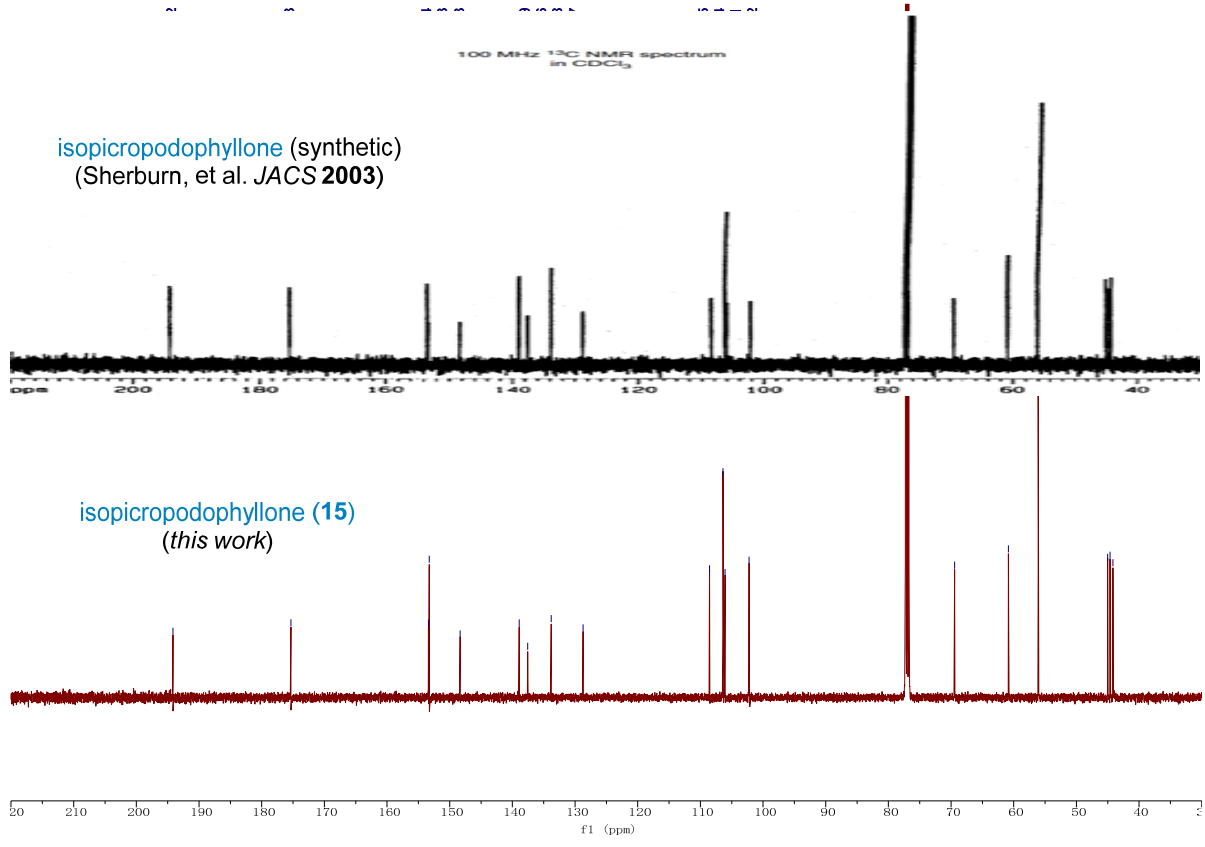
isopicropodophyllone (**15**)

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



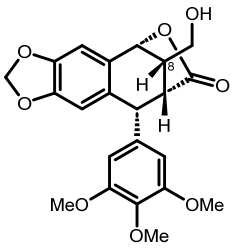
NMR spectra comparison of isopicropodophyllone



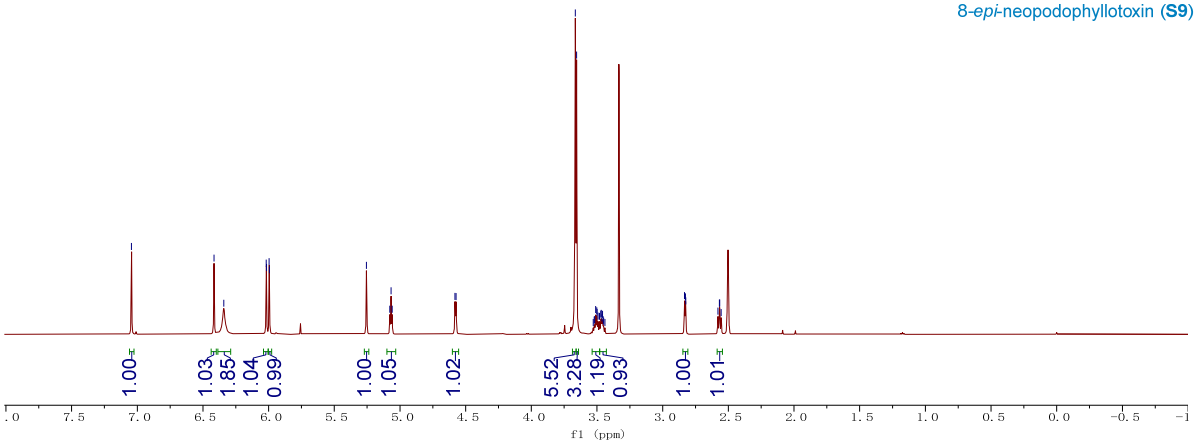


S9: 8-*epi*-Neopodophyllotoxin

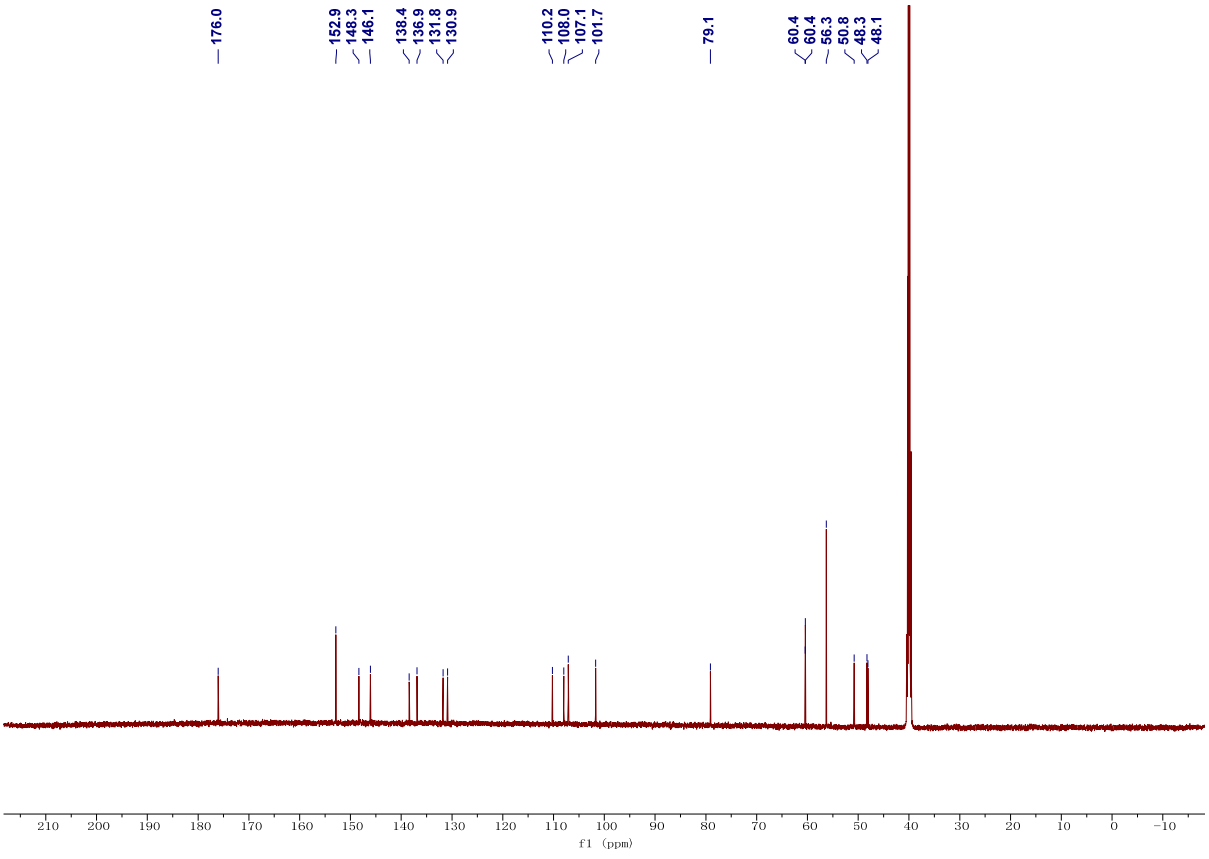
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



8-*epi*-neopodophyllotoxin (**S9**)

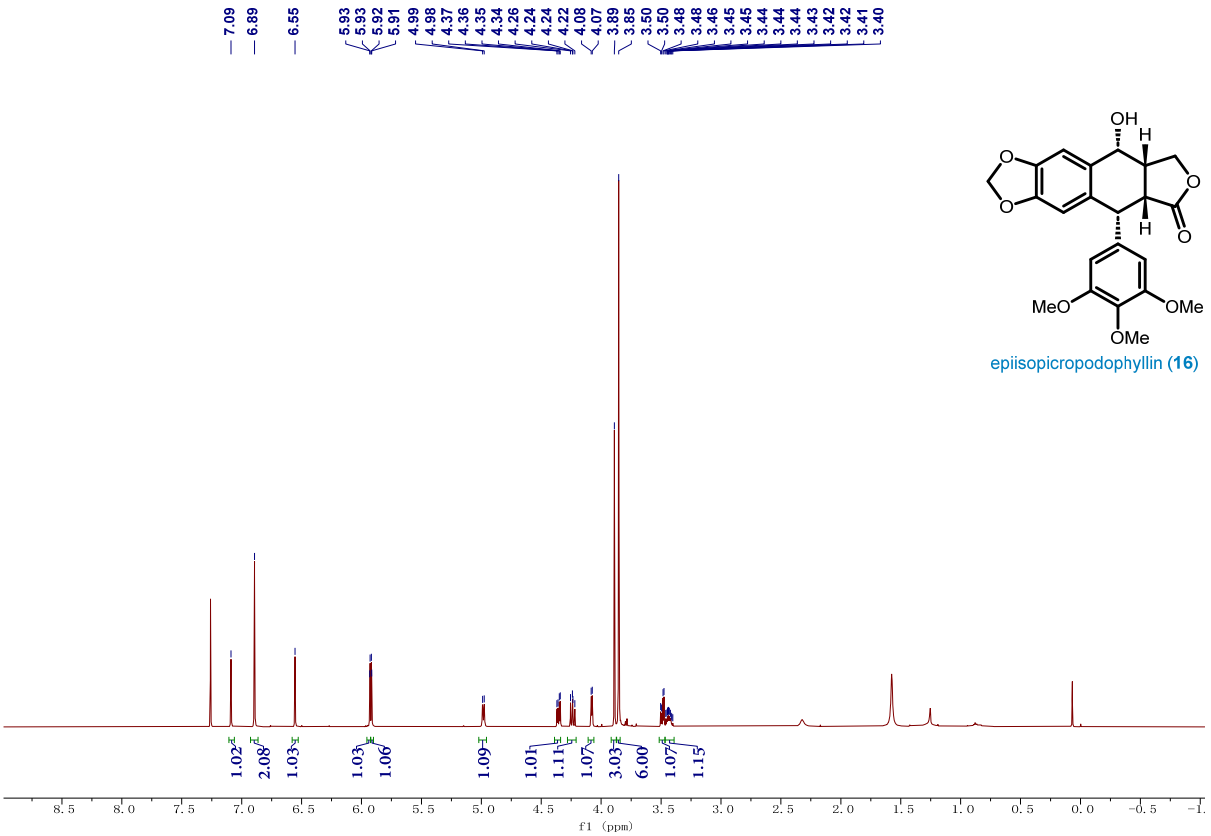


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



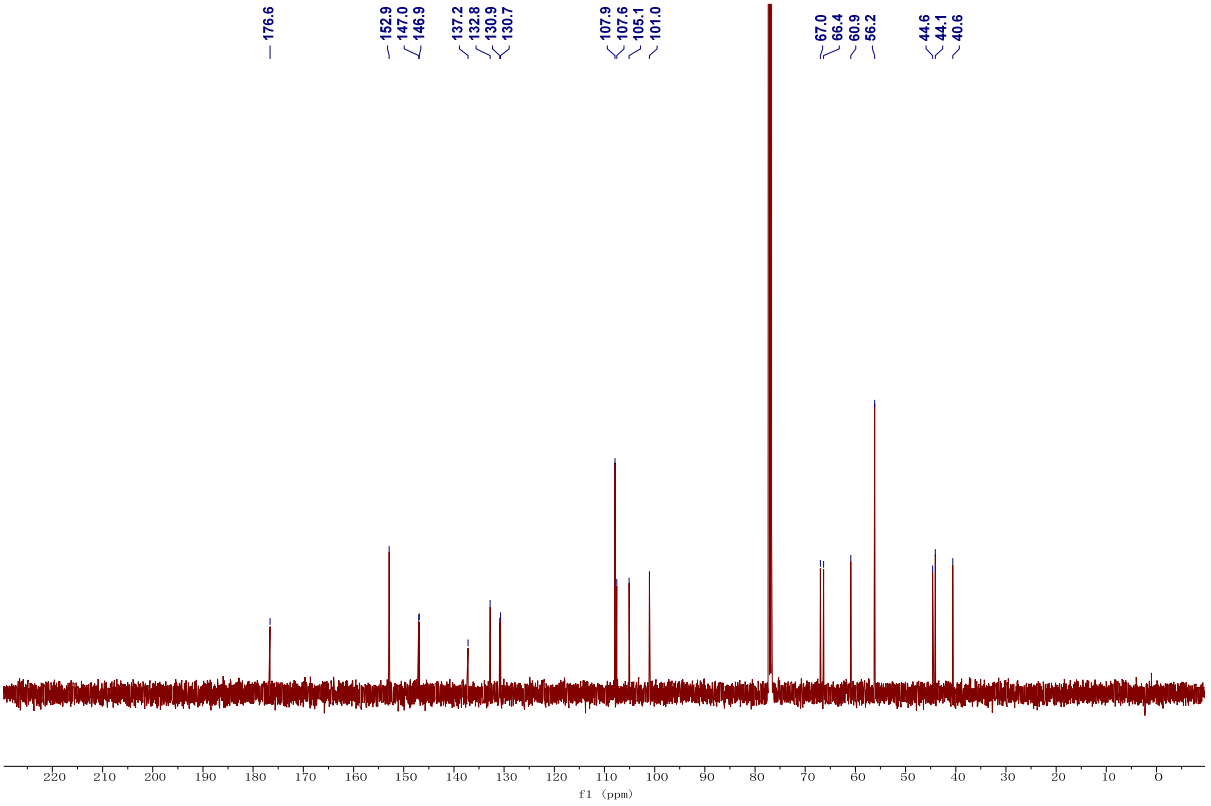
16: Epiisopicropodophyllin

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



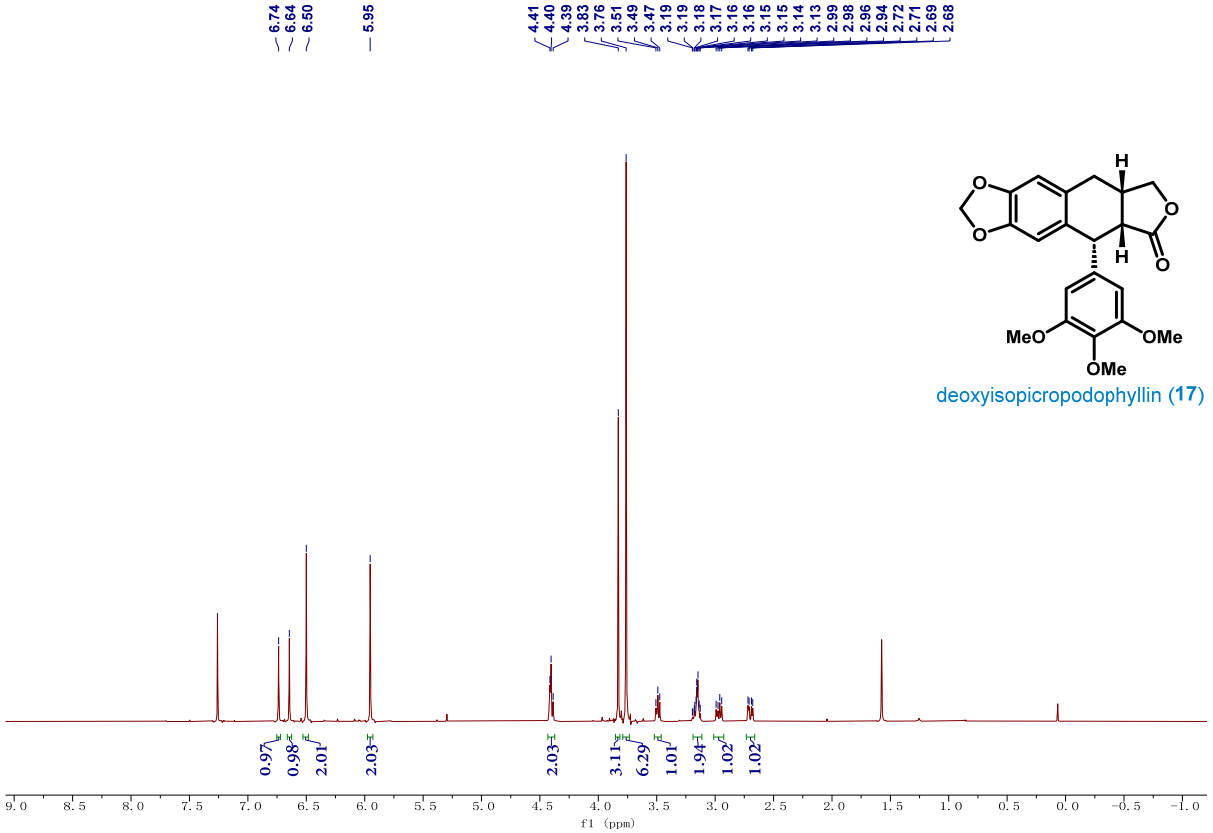
epiisopicropodophyllin (**16**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



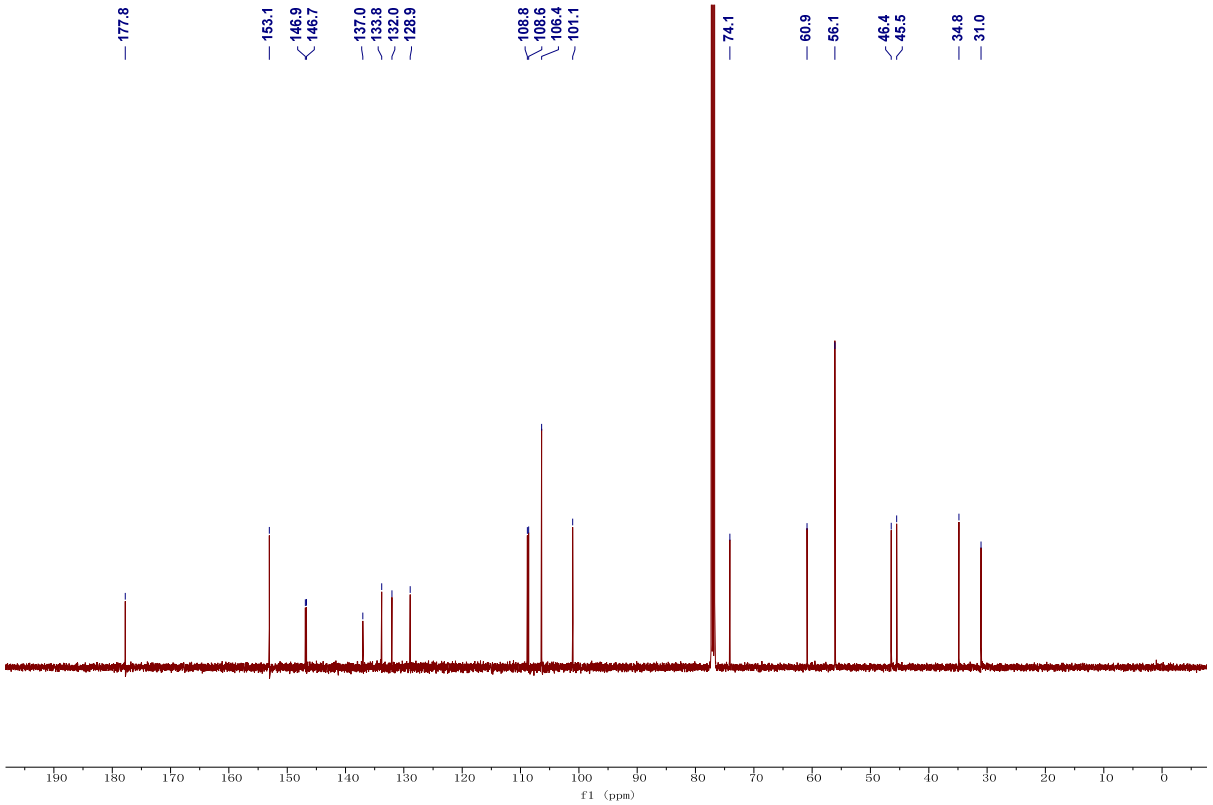
17: Deoxyisopicropodophyllin

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



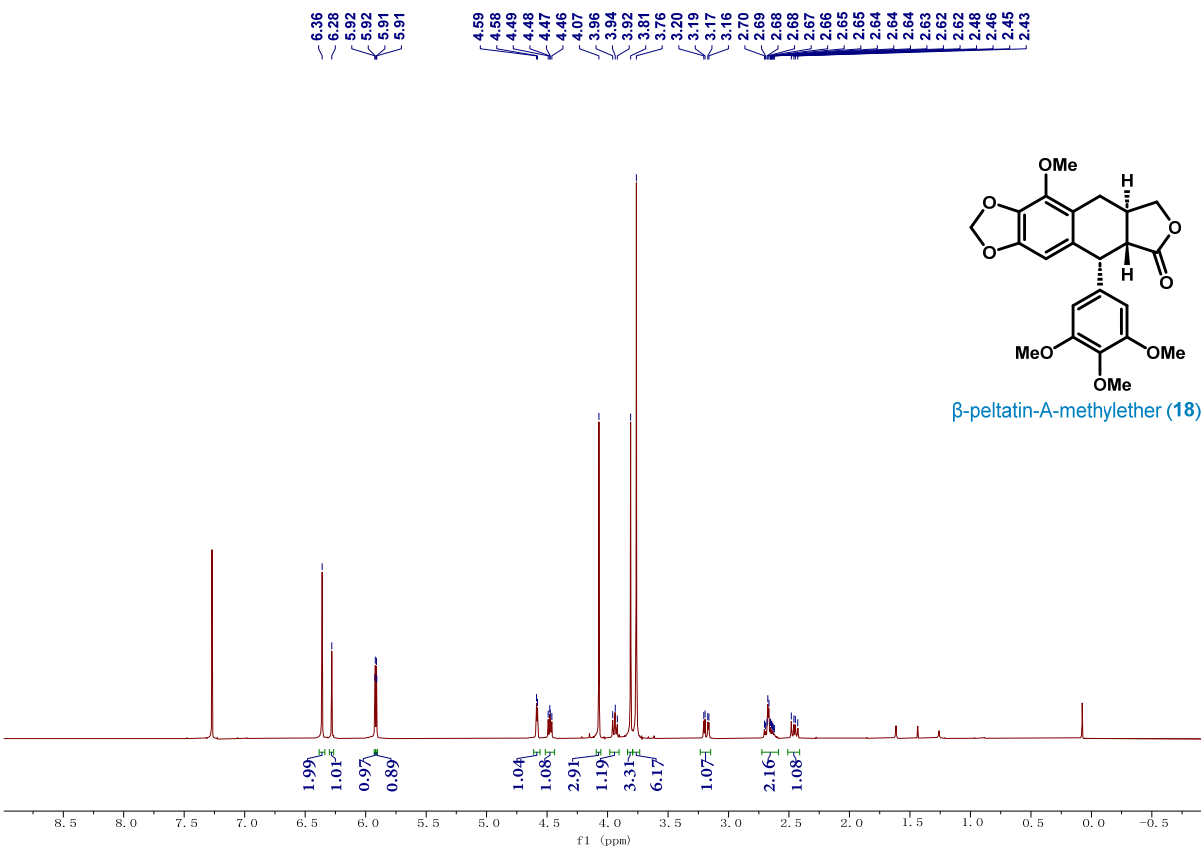
deoxyisopicropodophyllin (**17**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

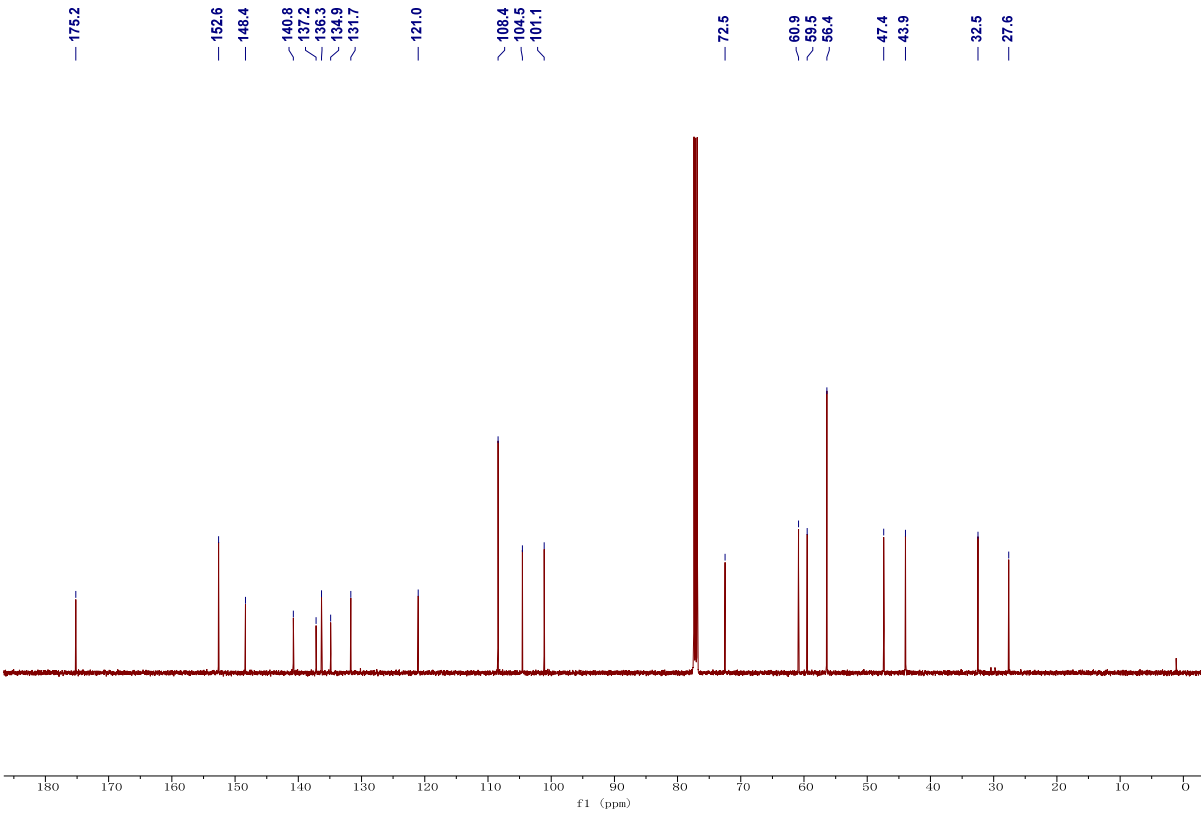


18: β-Peltatin-A-methylether

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

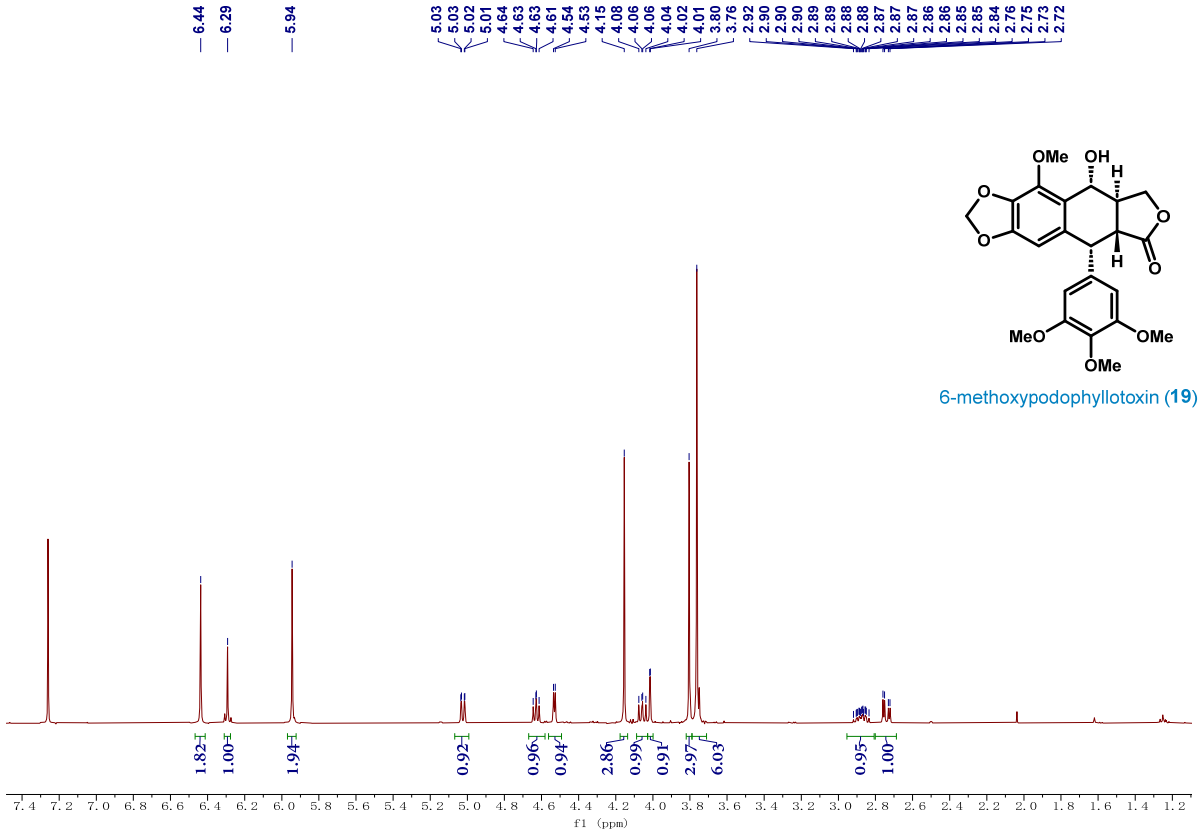


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



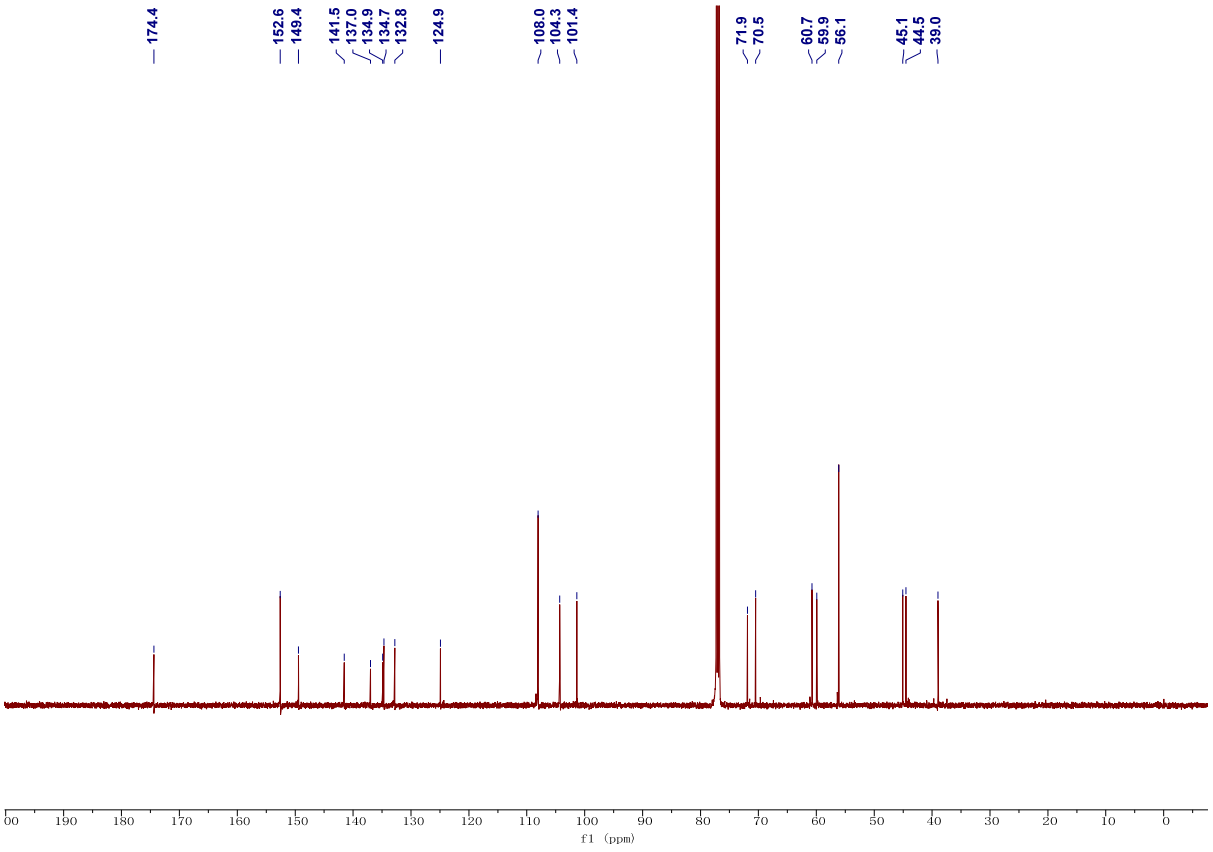
19: 6-Methoxypodophyllotoxin

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



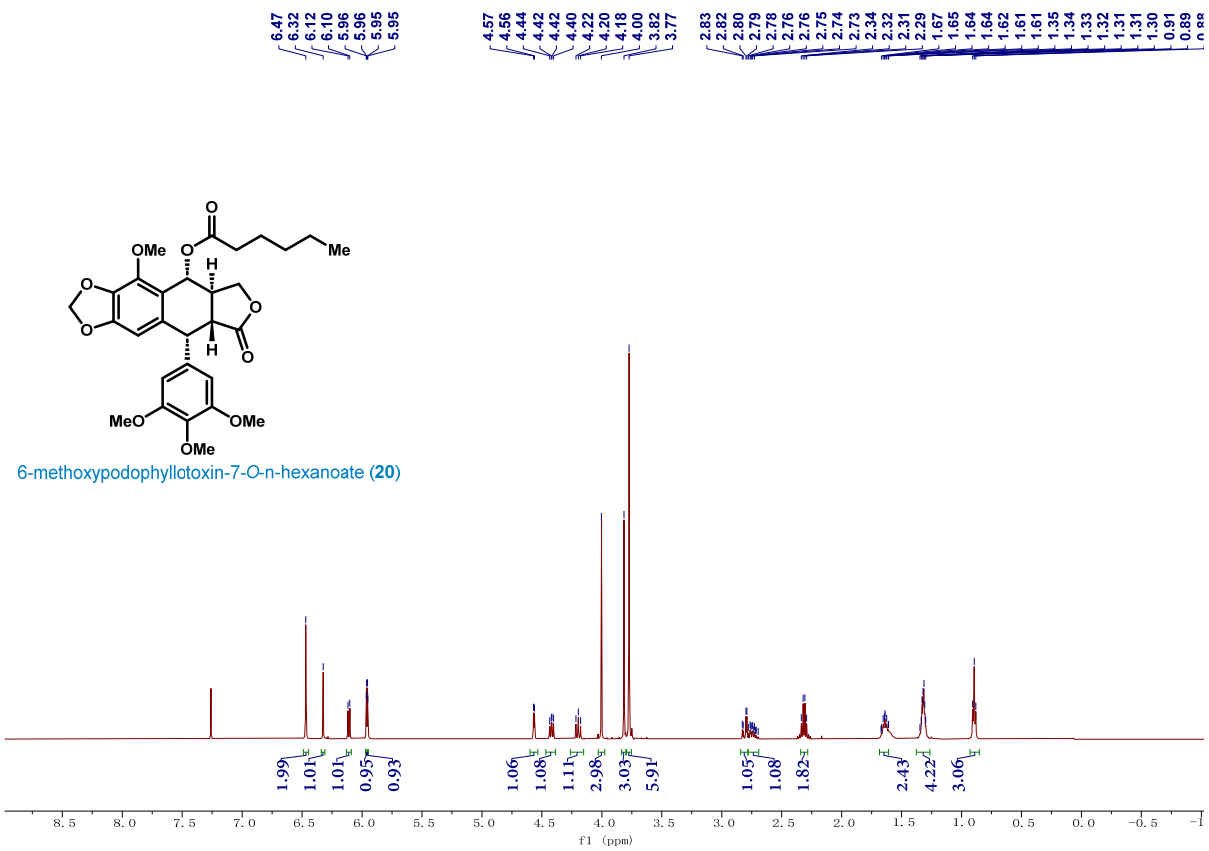
6-methoxypodophyllotoxin (**19**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

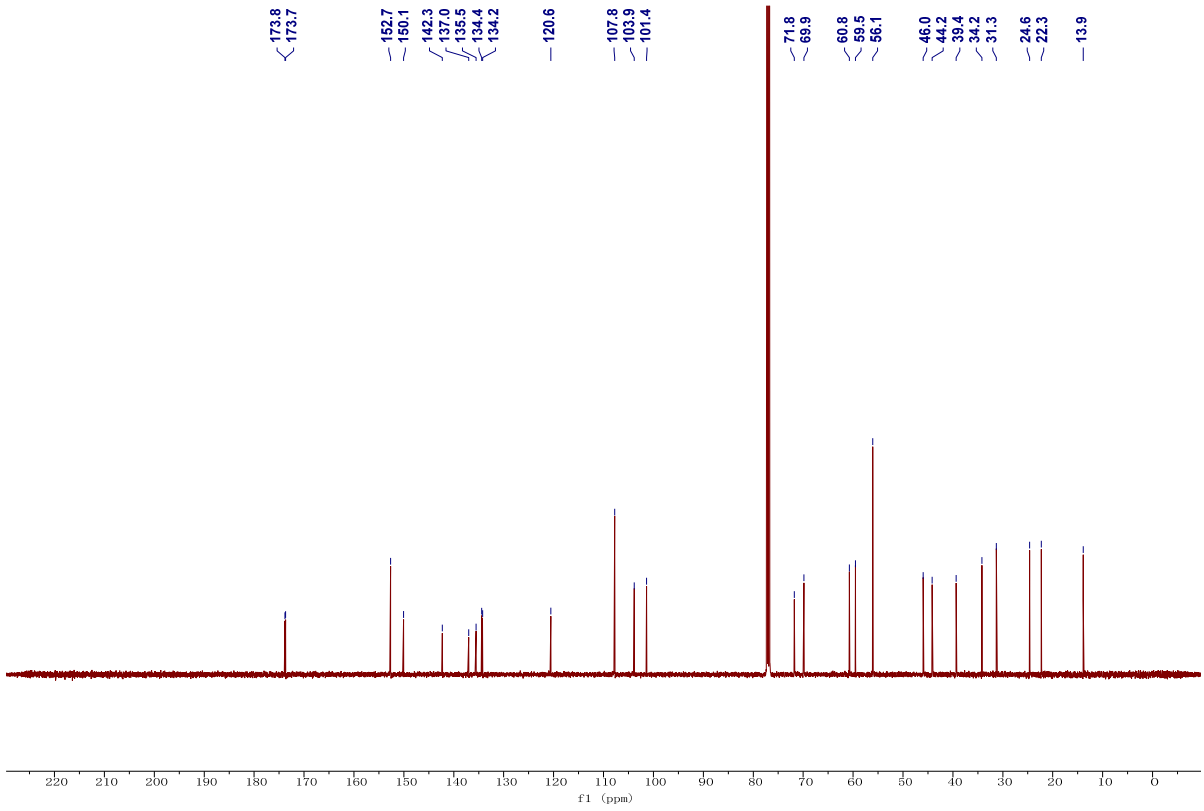


20: 6-Methoxypodophyllotoxin-7-*O*-n-hexanoate

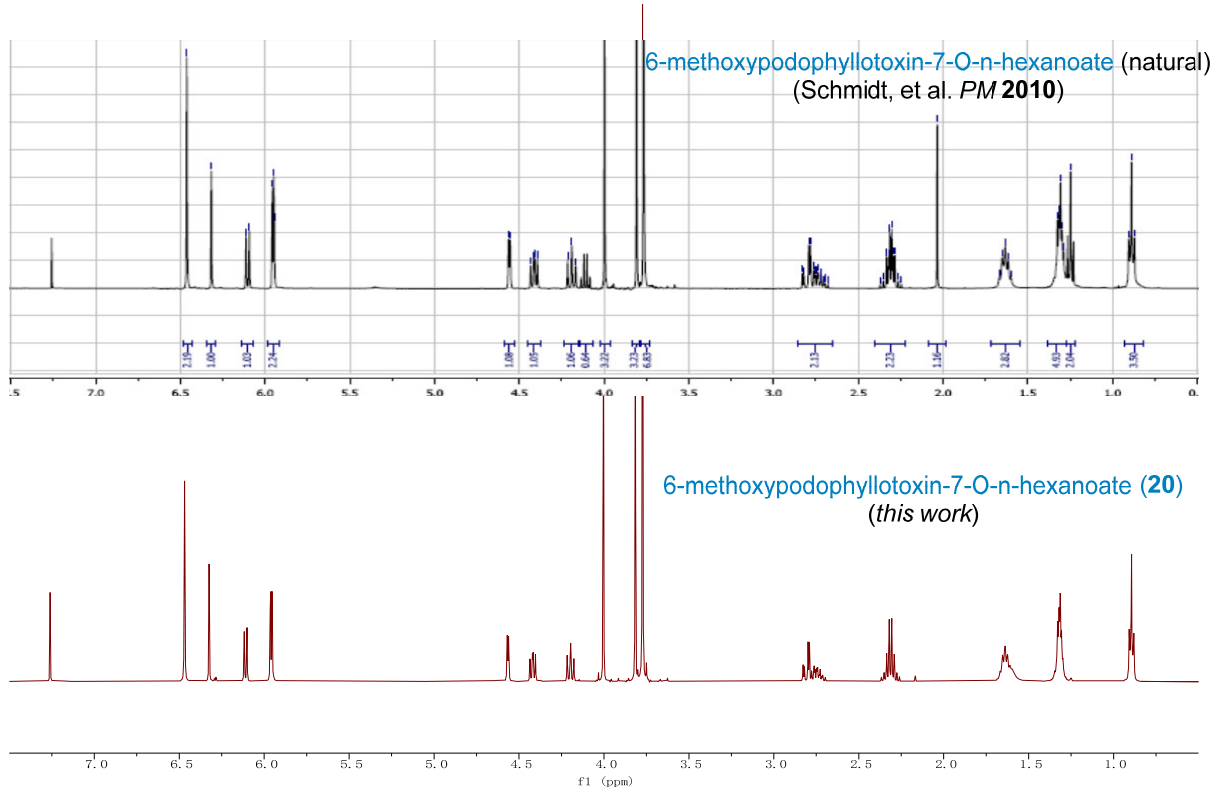
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

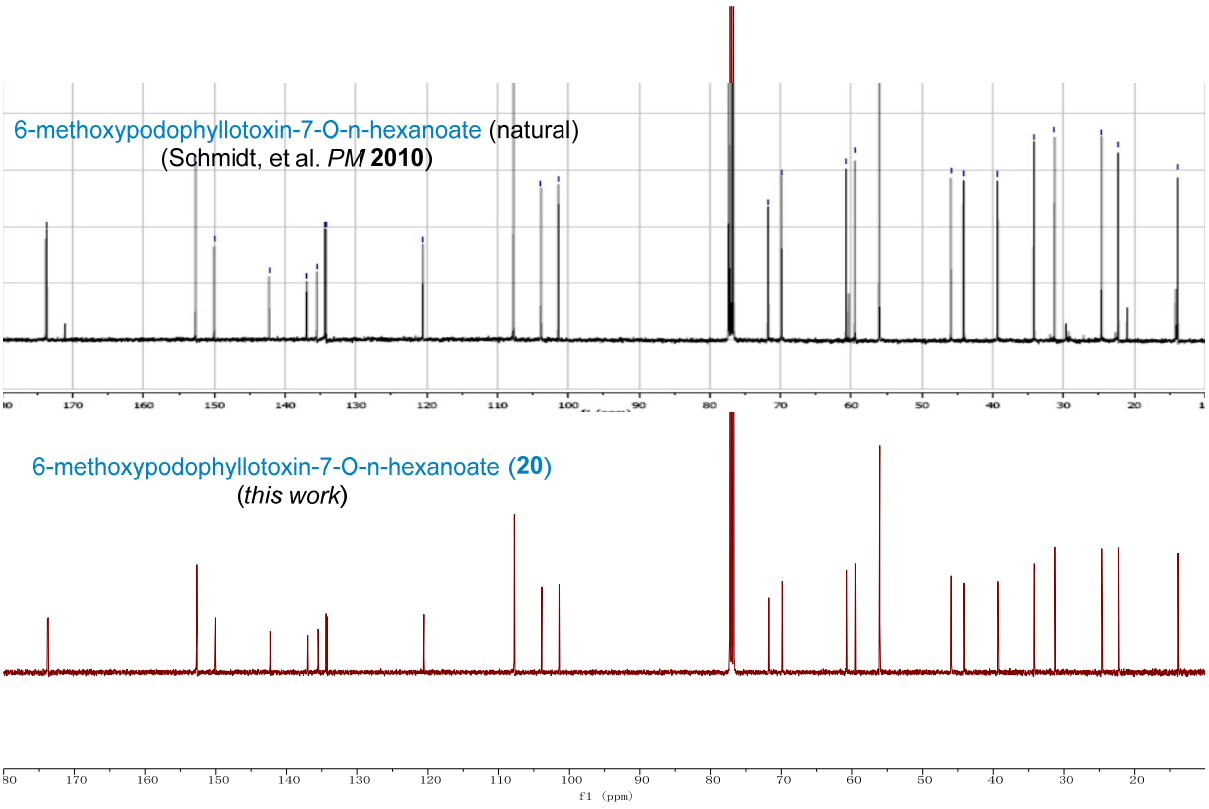


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



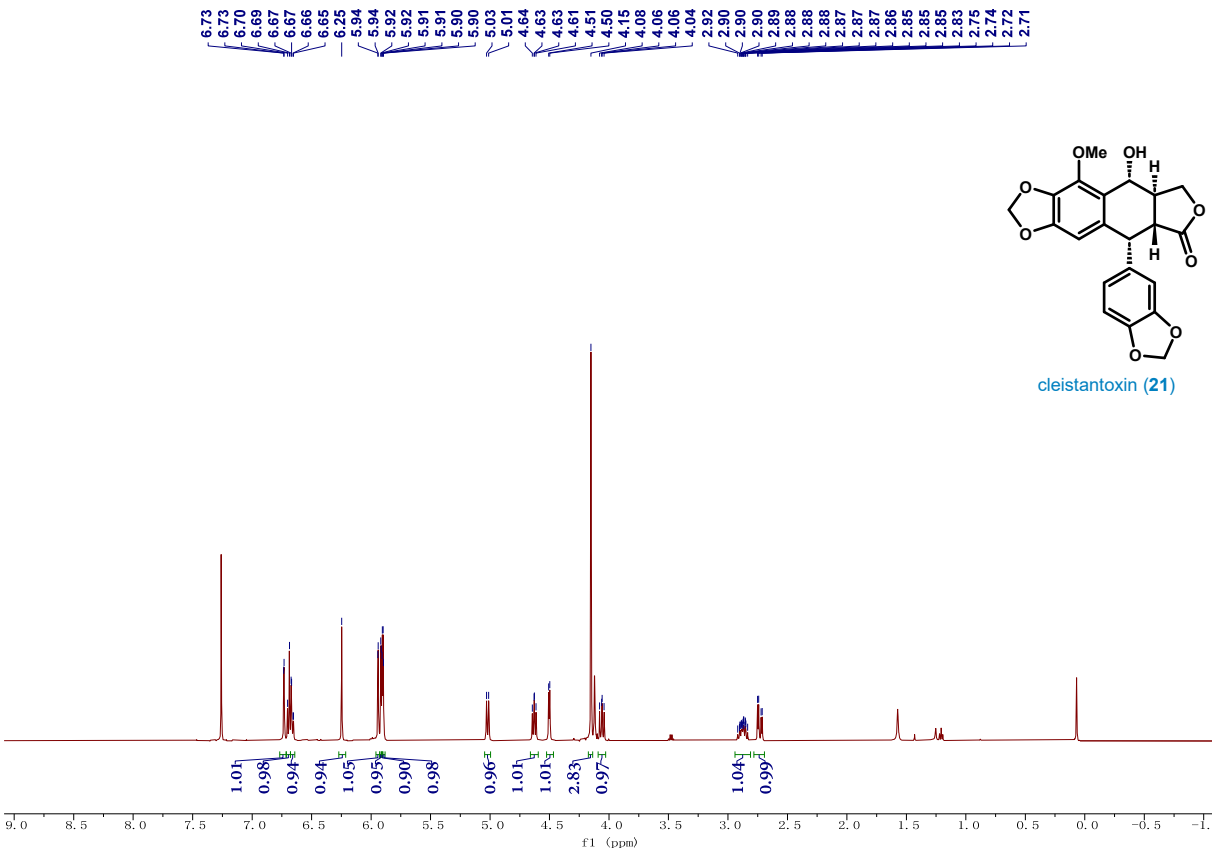
NMR spectra comparison of 6-methoxypodophyllotoxin-7-O-n-hexanoate



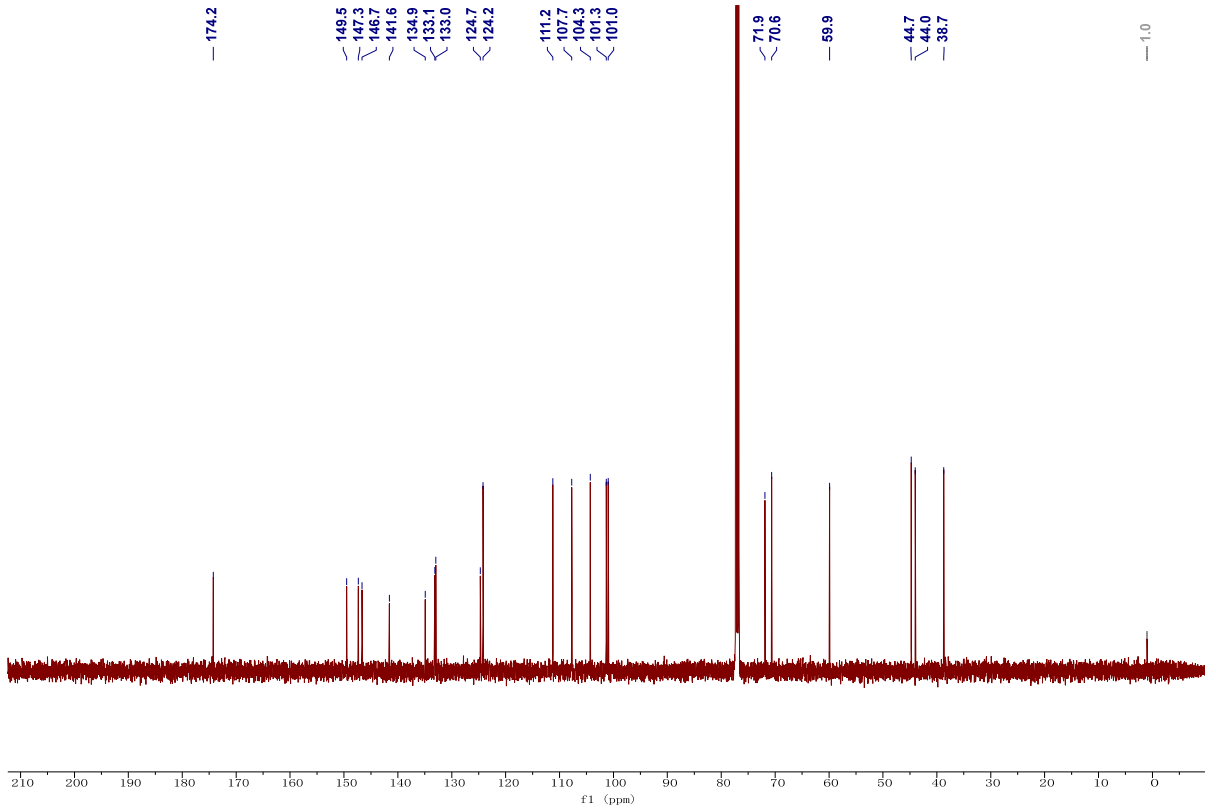


21: Cleistantoxin

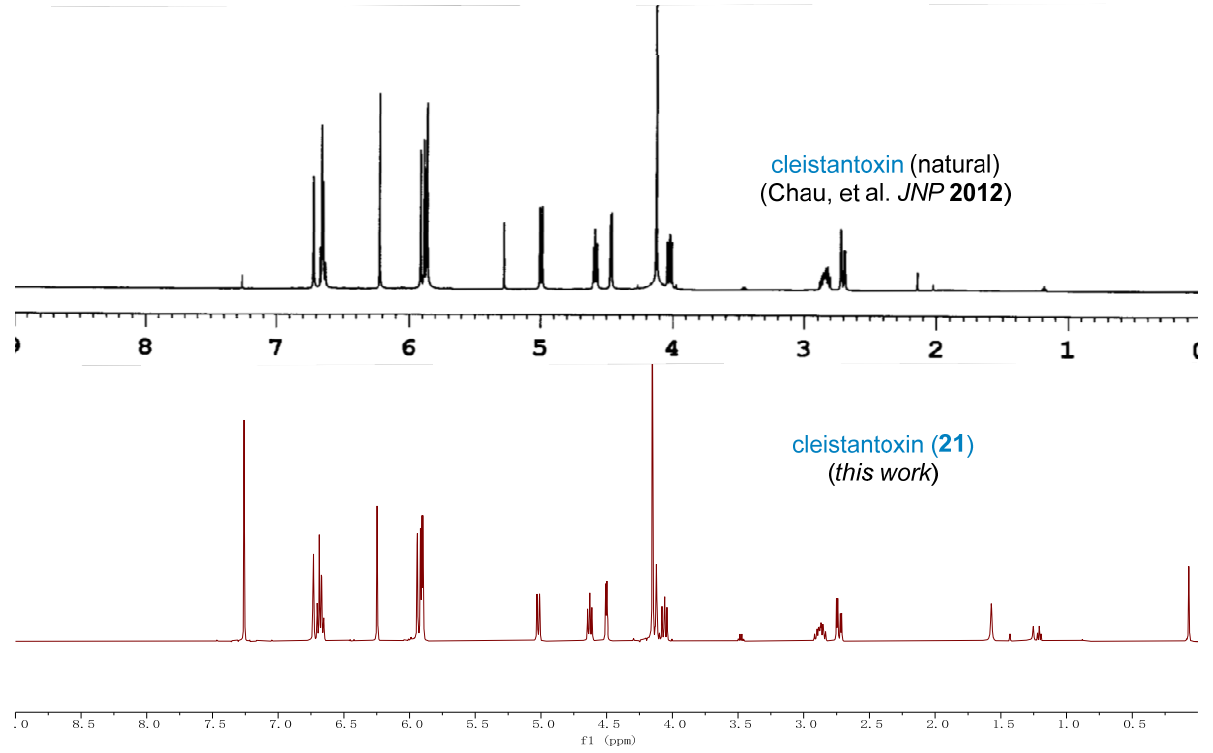
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

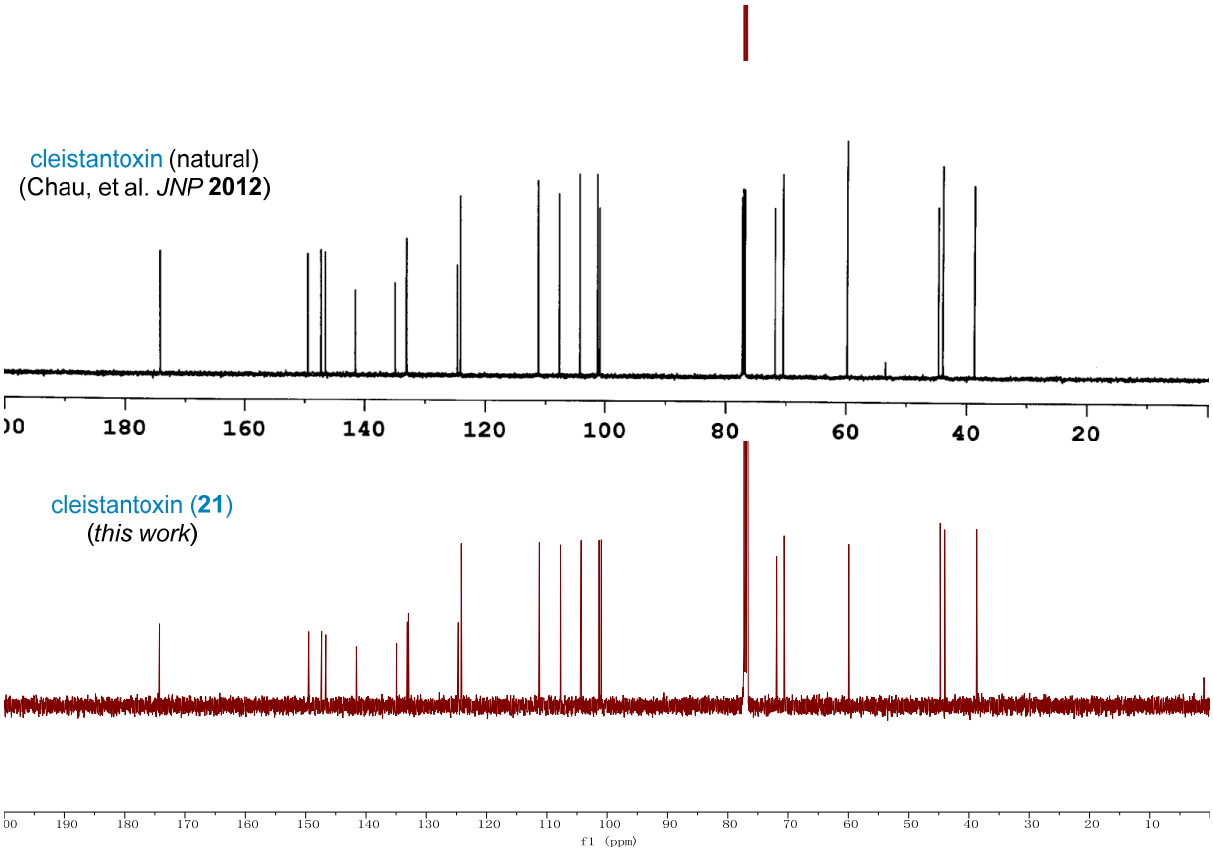


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



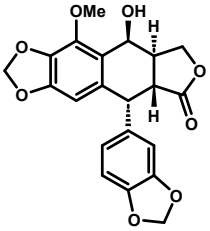
NMR spectra comparison of cleistantoxin



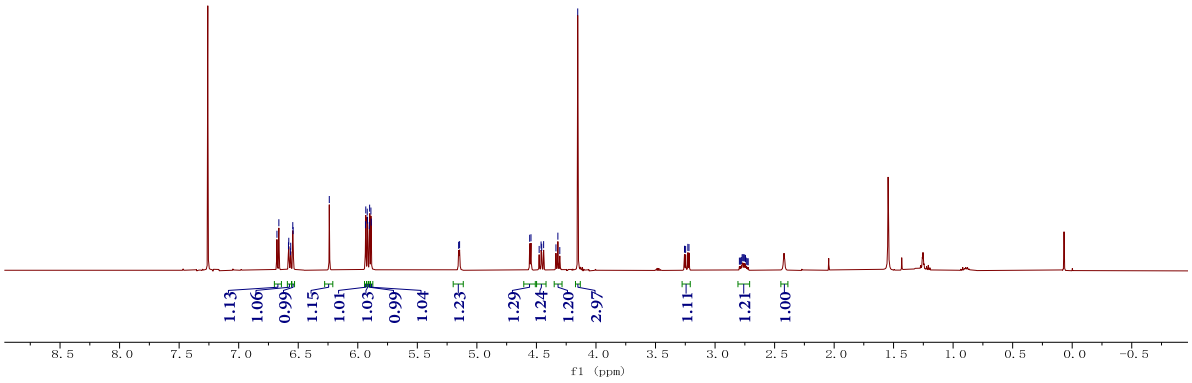


S10: 7-*epi*-Cleistantoxin

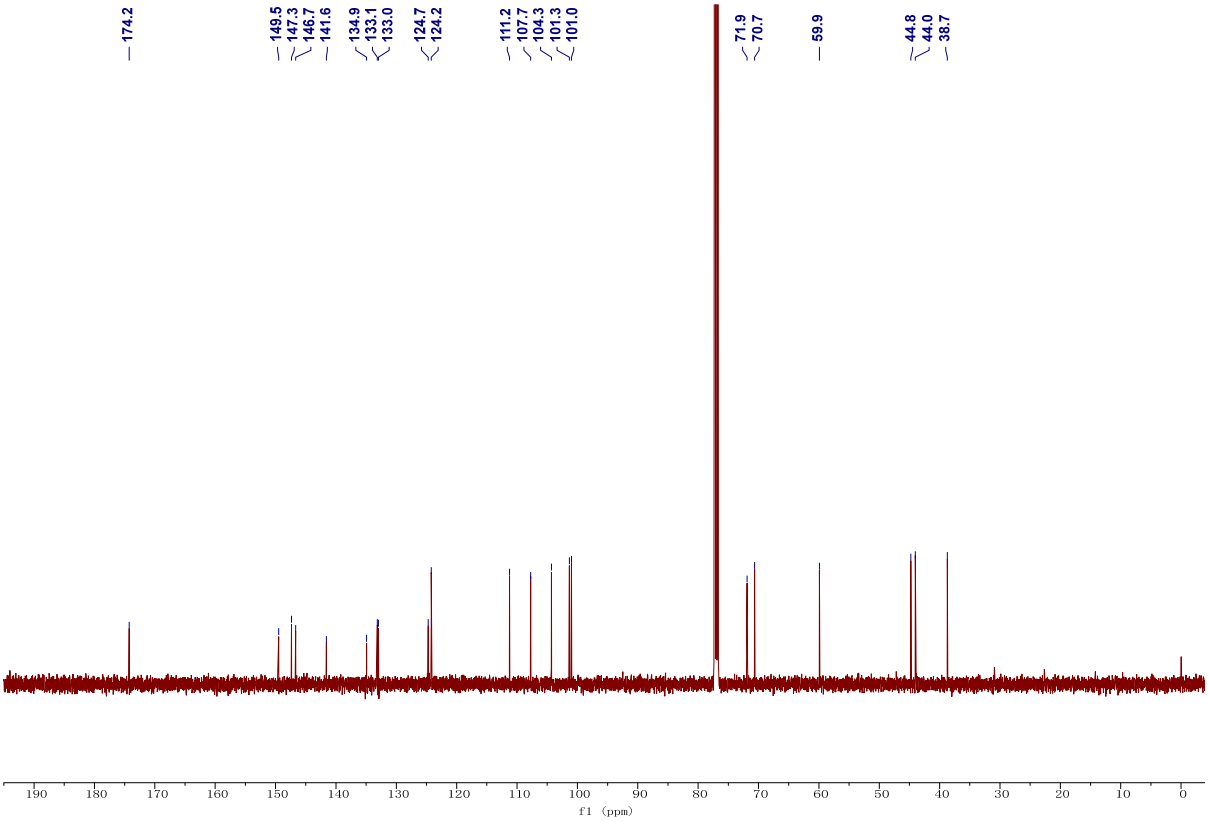
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



7-*epi*-cleistantoxin (**S10**)

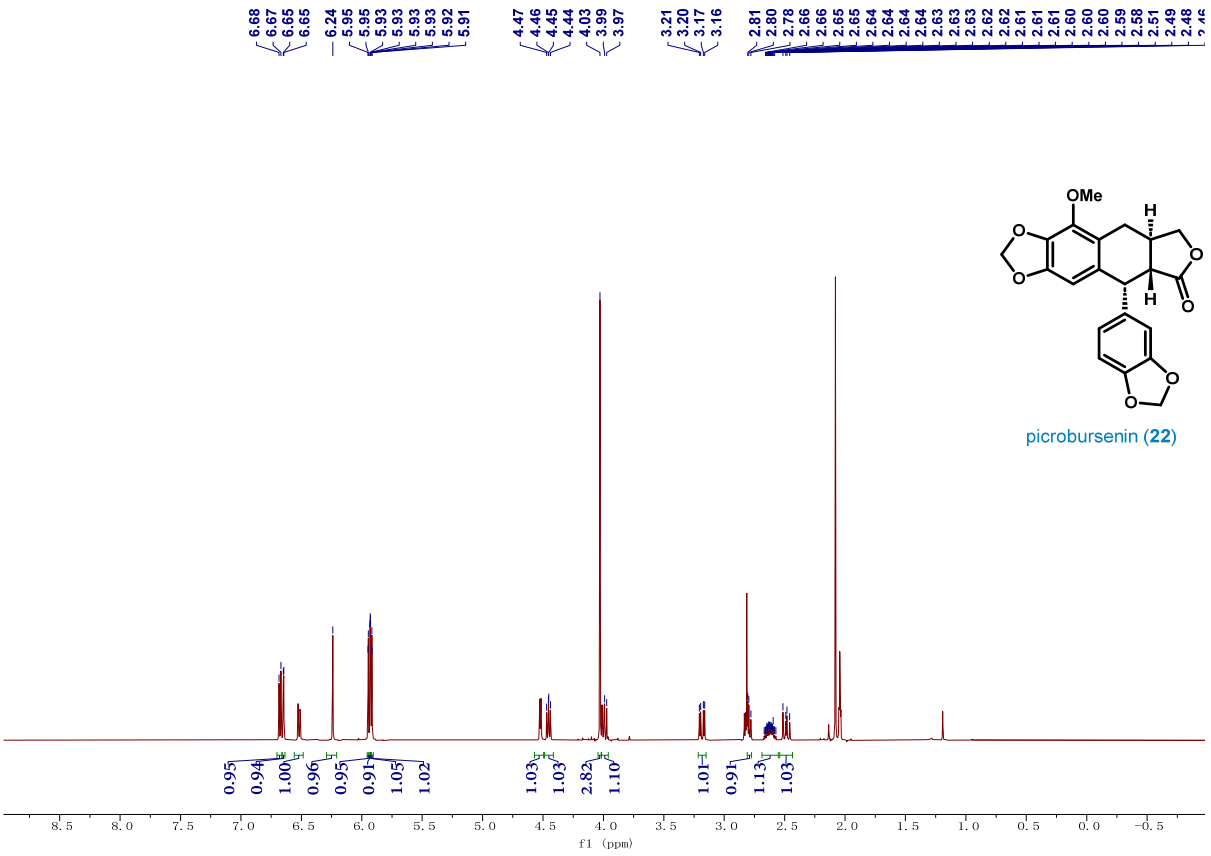


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

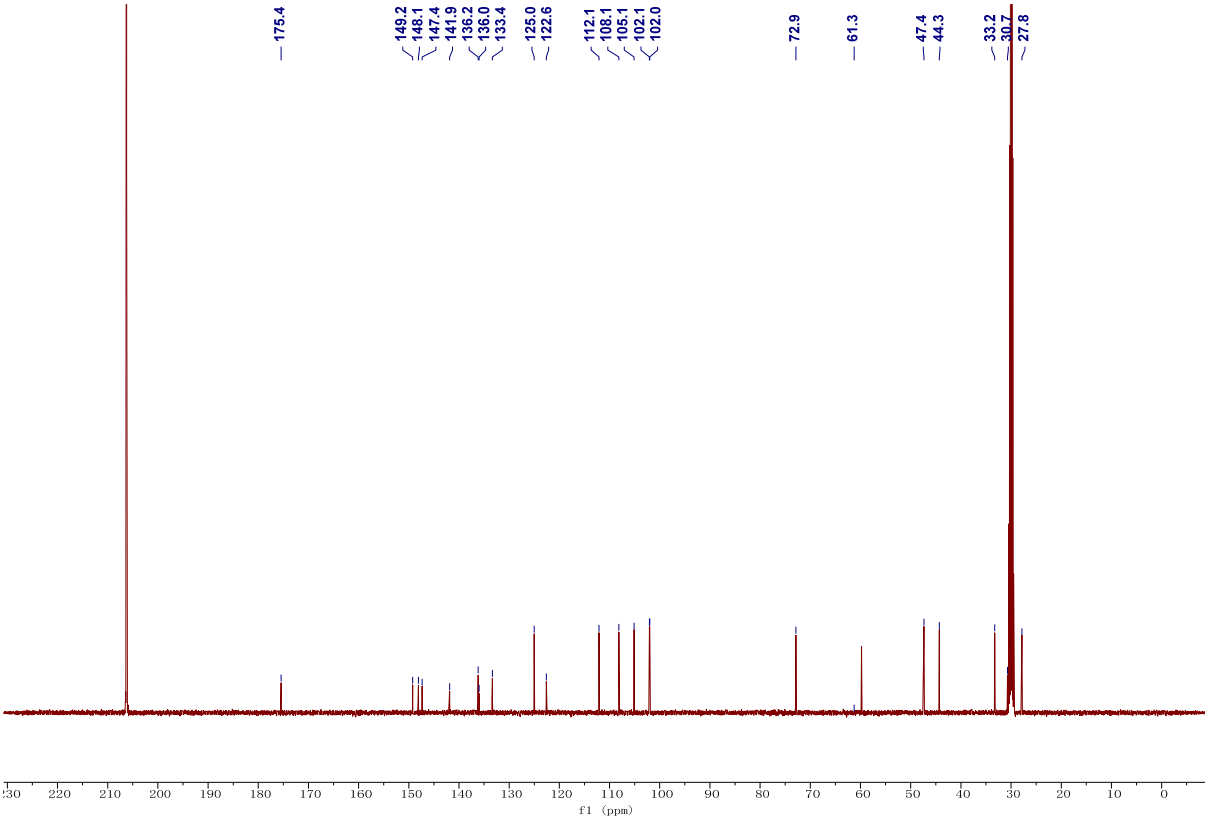


22: Picrobursenin

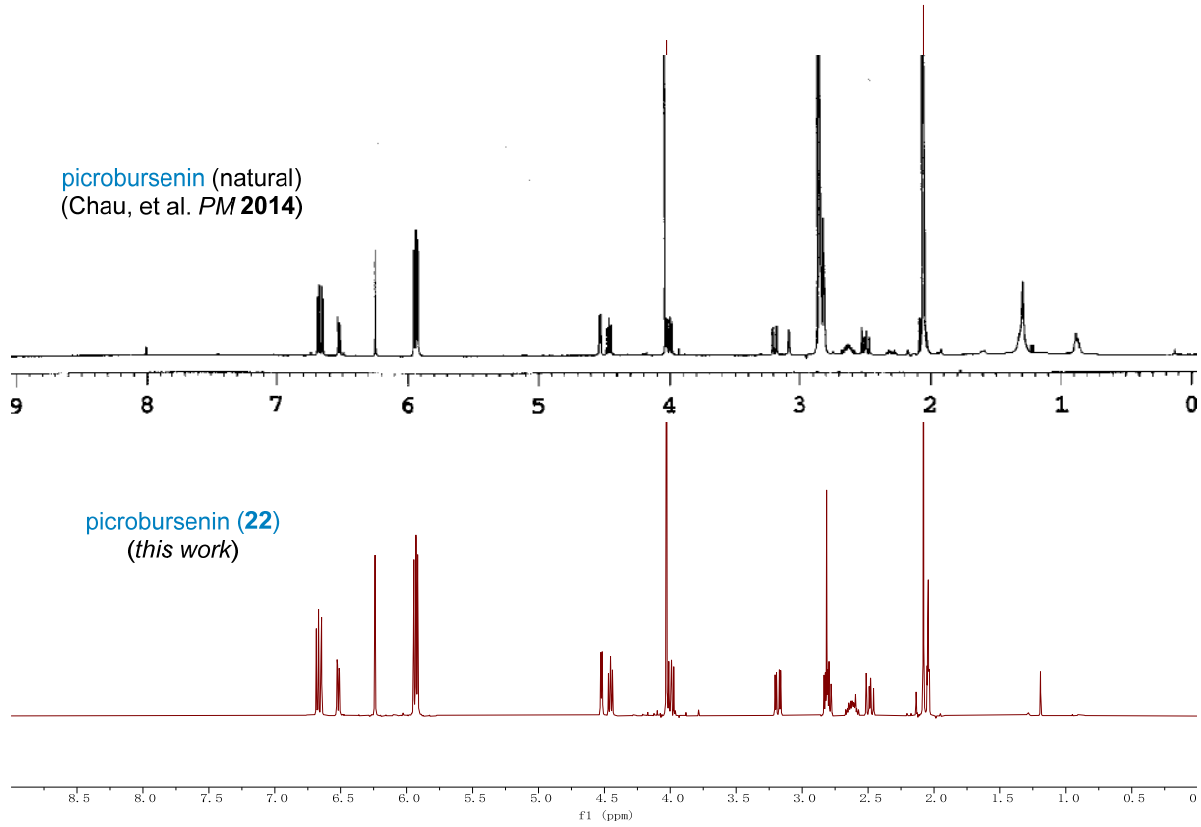
^{1}H NMR (500 MHz, acetone-d_6 @ 2.05 ppm)

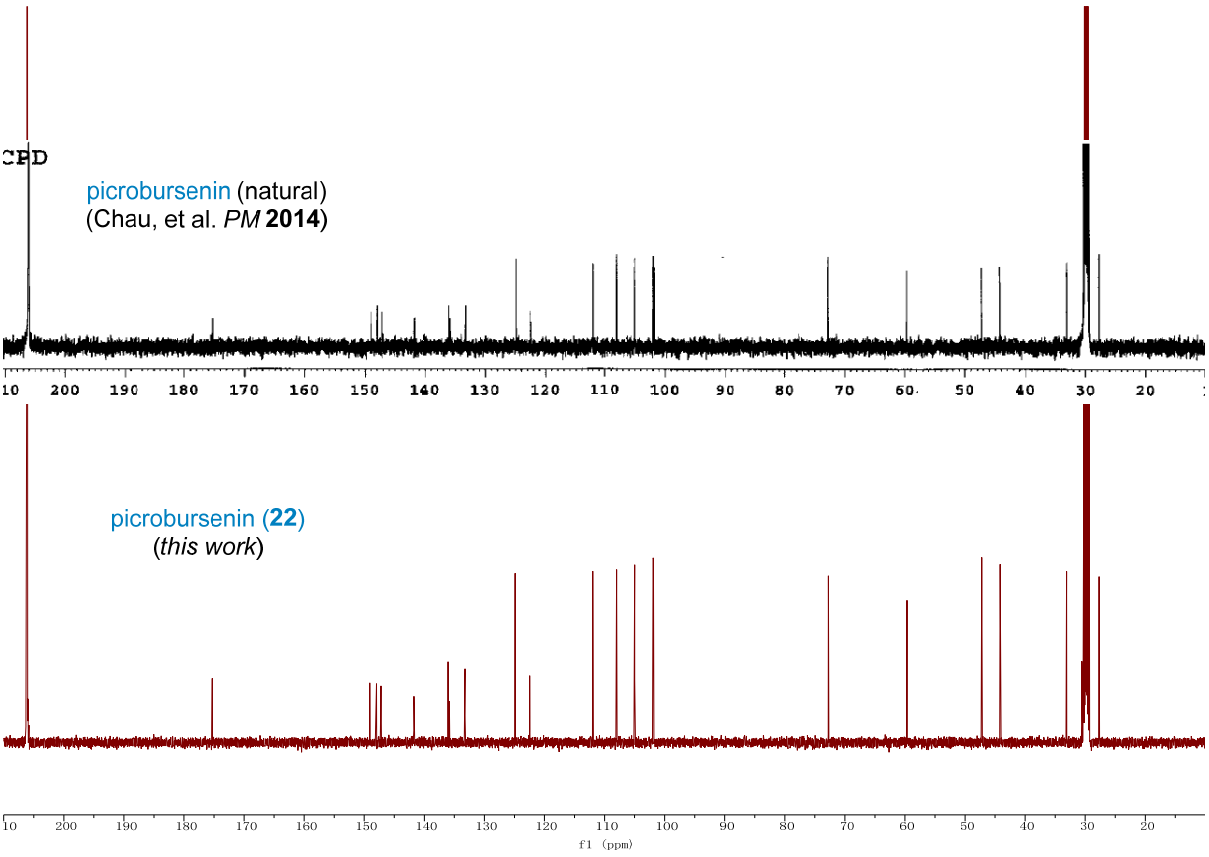


^{13}C NMR (125 MHz, acetone-d_6 @ 29.84 & 206.26 ppm)



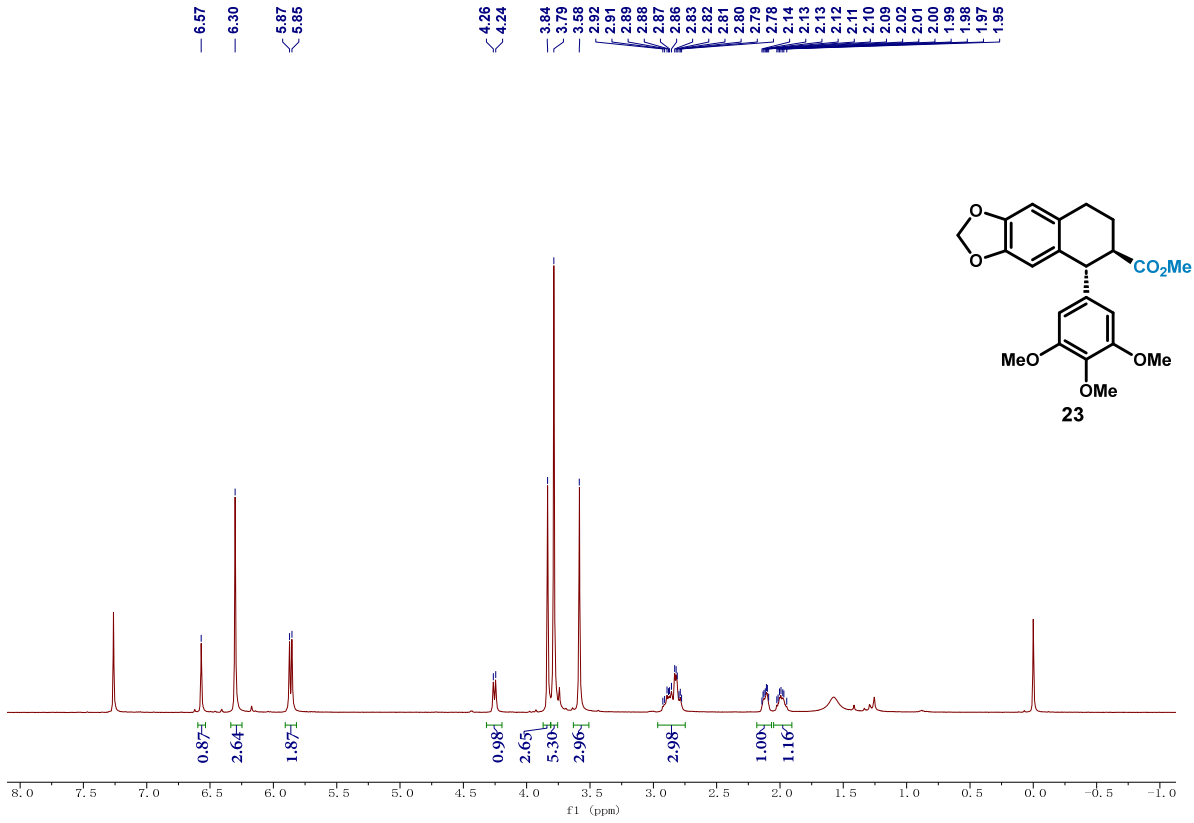
NMR spectra comparison of picrobursenin



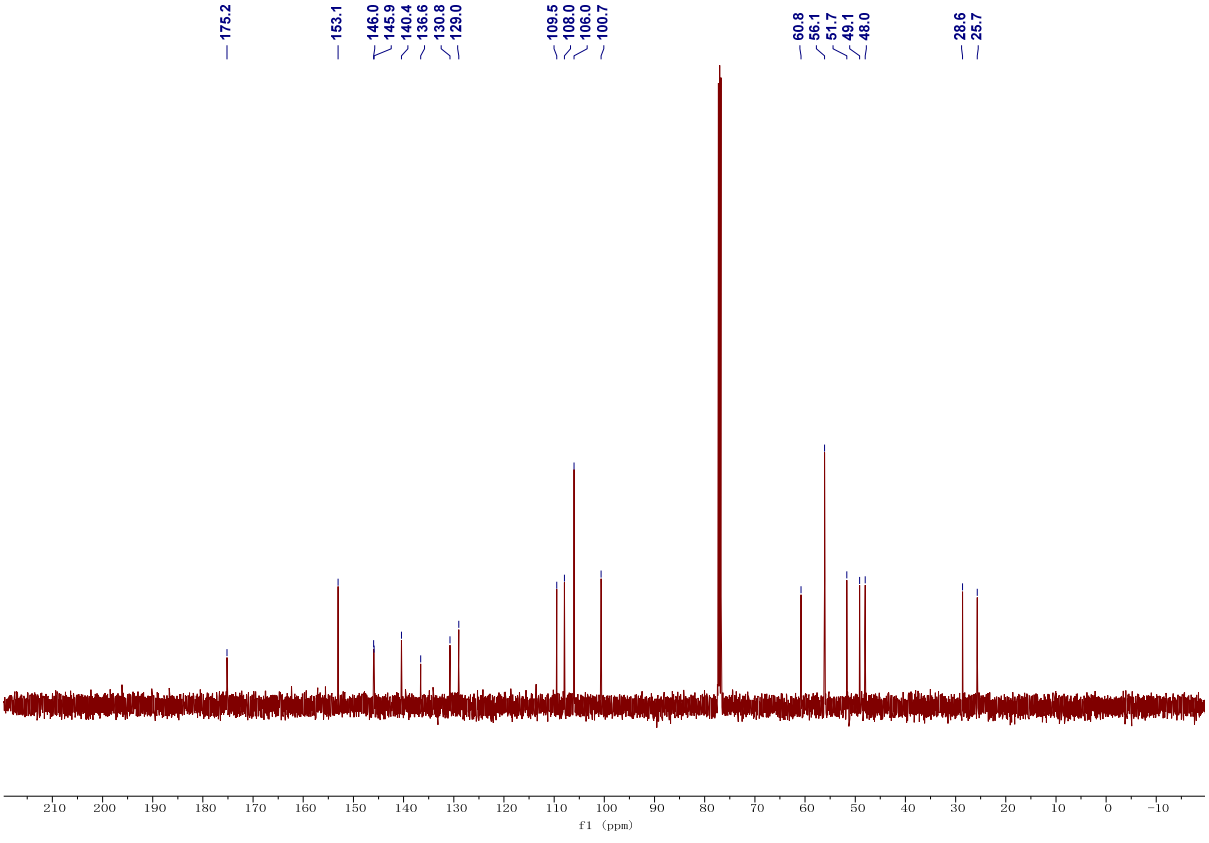


23: Methyl(5S,6S)-5-(2-fluorophenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

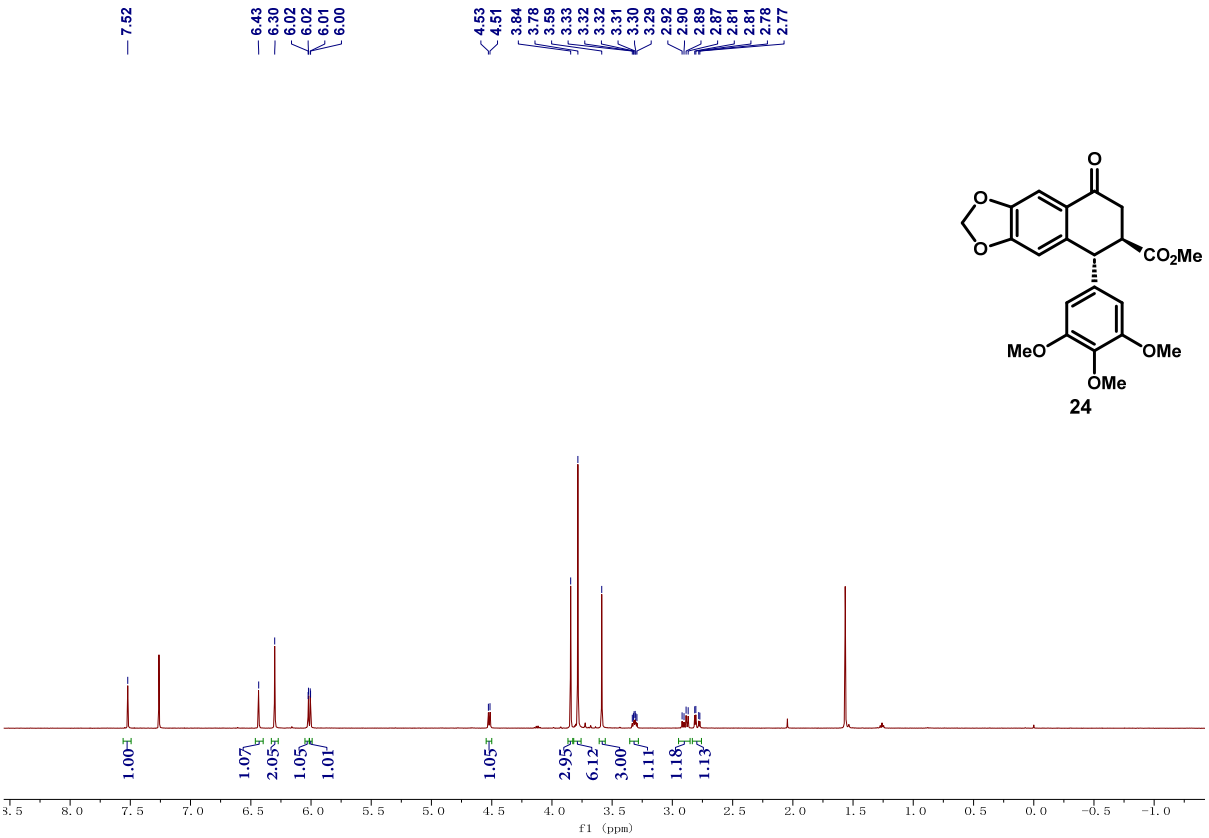


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



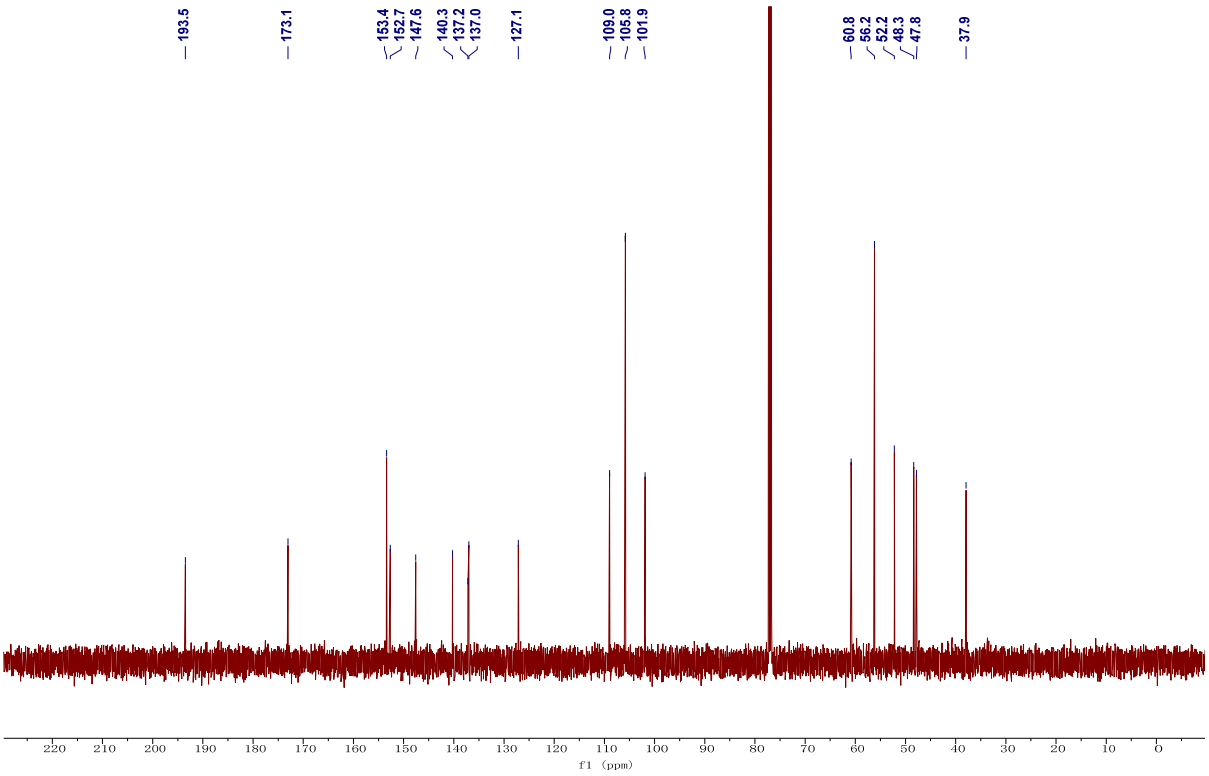
24: Methyl(5R,6R)-8-oxo-5-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3] dioxole-6-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



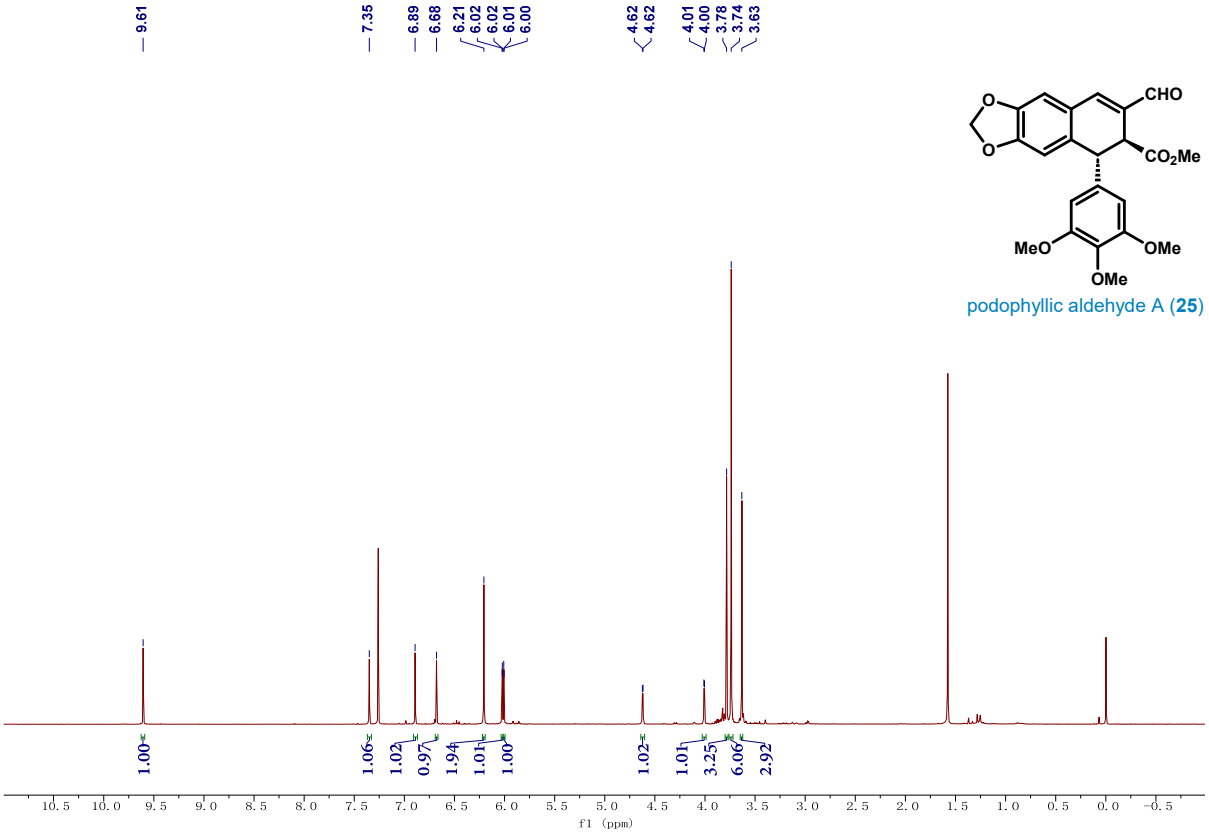
24

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



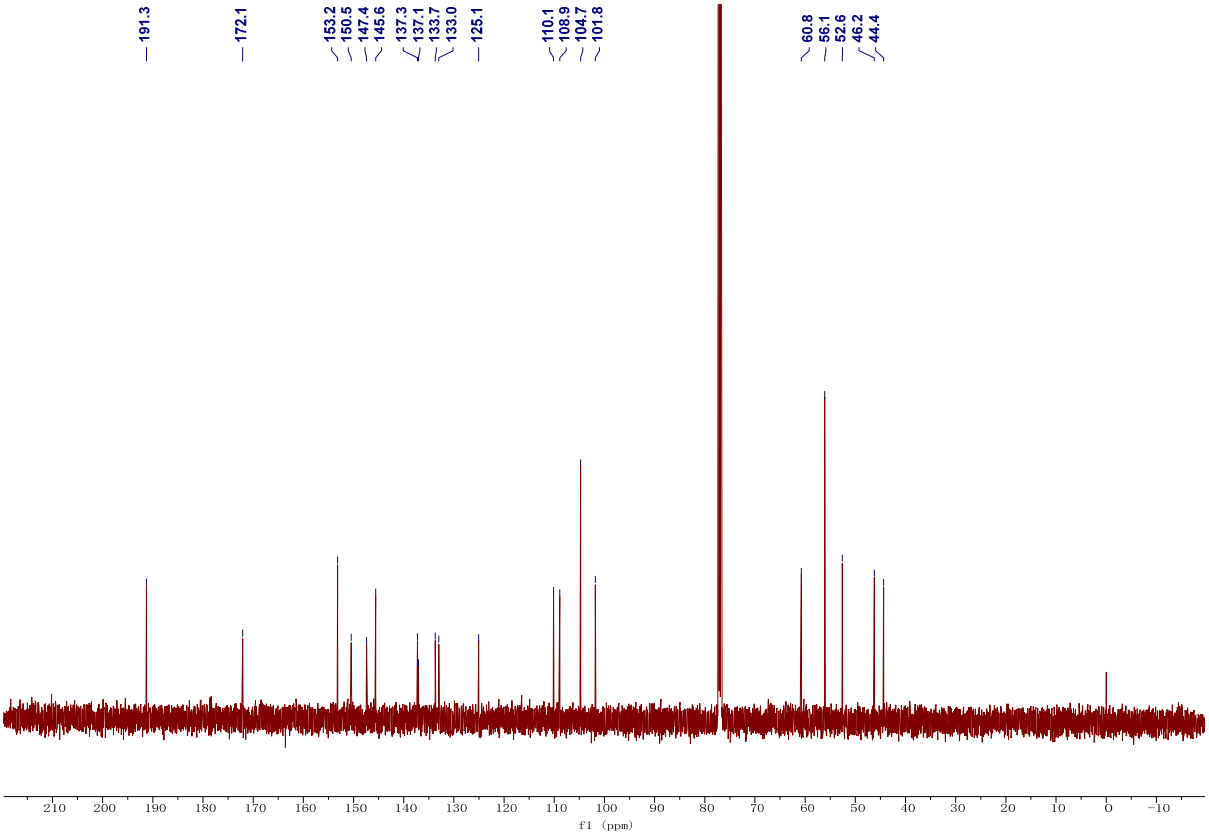
25: Podophyllic aldehyde A

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



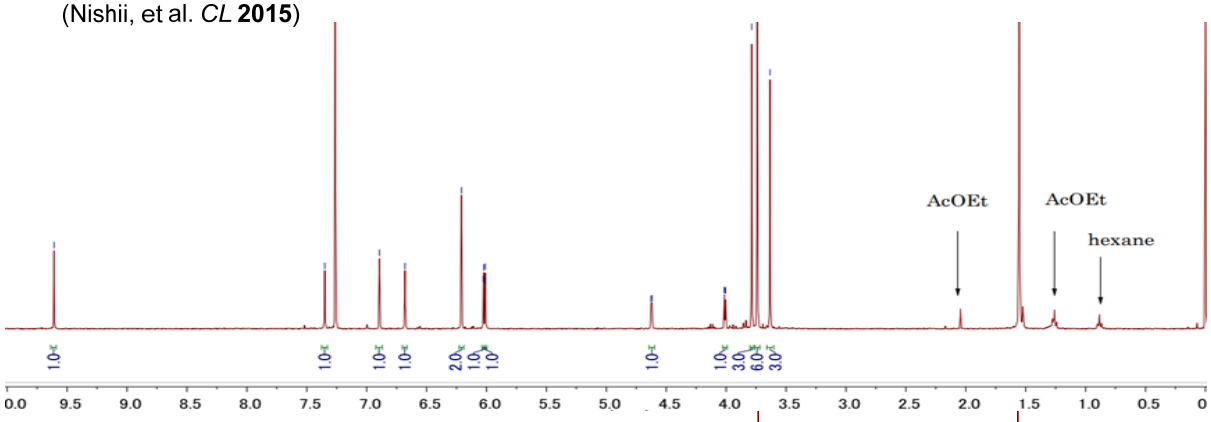
podophyllic aldehyde A (**25**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

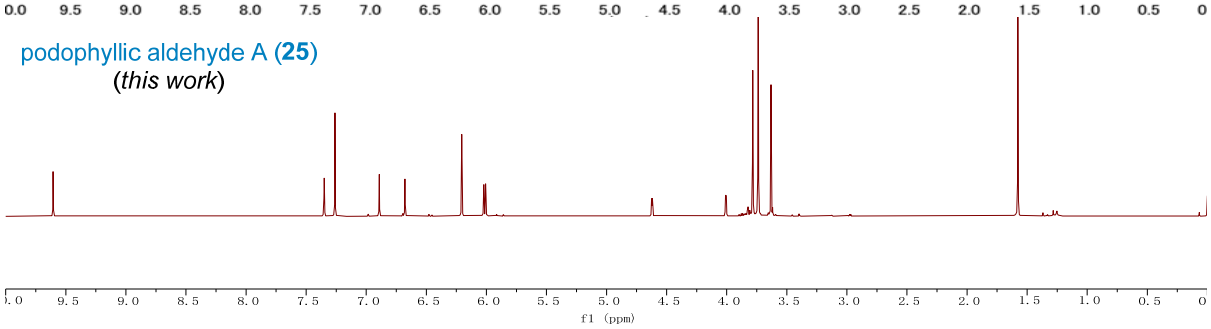


NMR spectra comparison of podophyllic aldehyde A

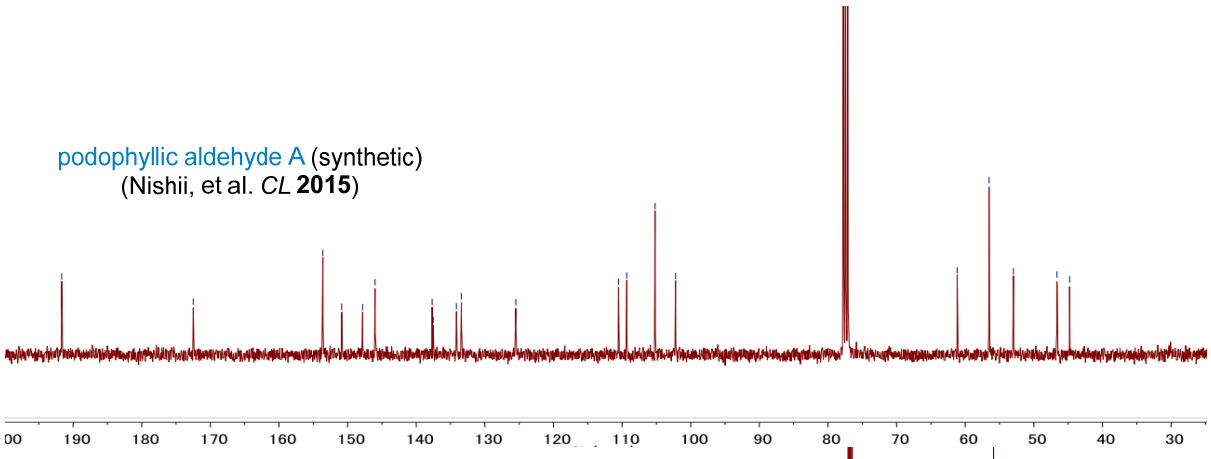
podophyllic aldehyde A (synthetic)
(Nishii, et al. *CL* **2015**)



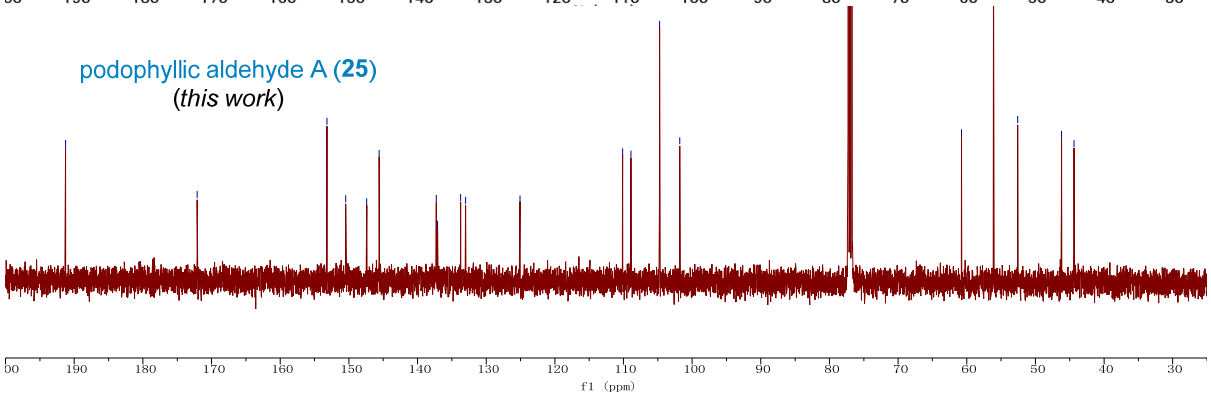
podophyllic aldehyde A (**25**)
(*this work*)



podophyllic aldehyde A (synthetic)
(Nishii, et al. *CL* **2015**)

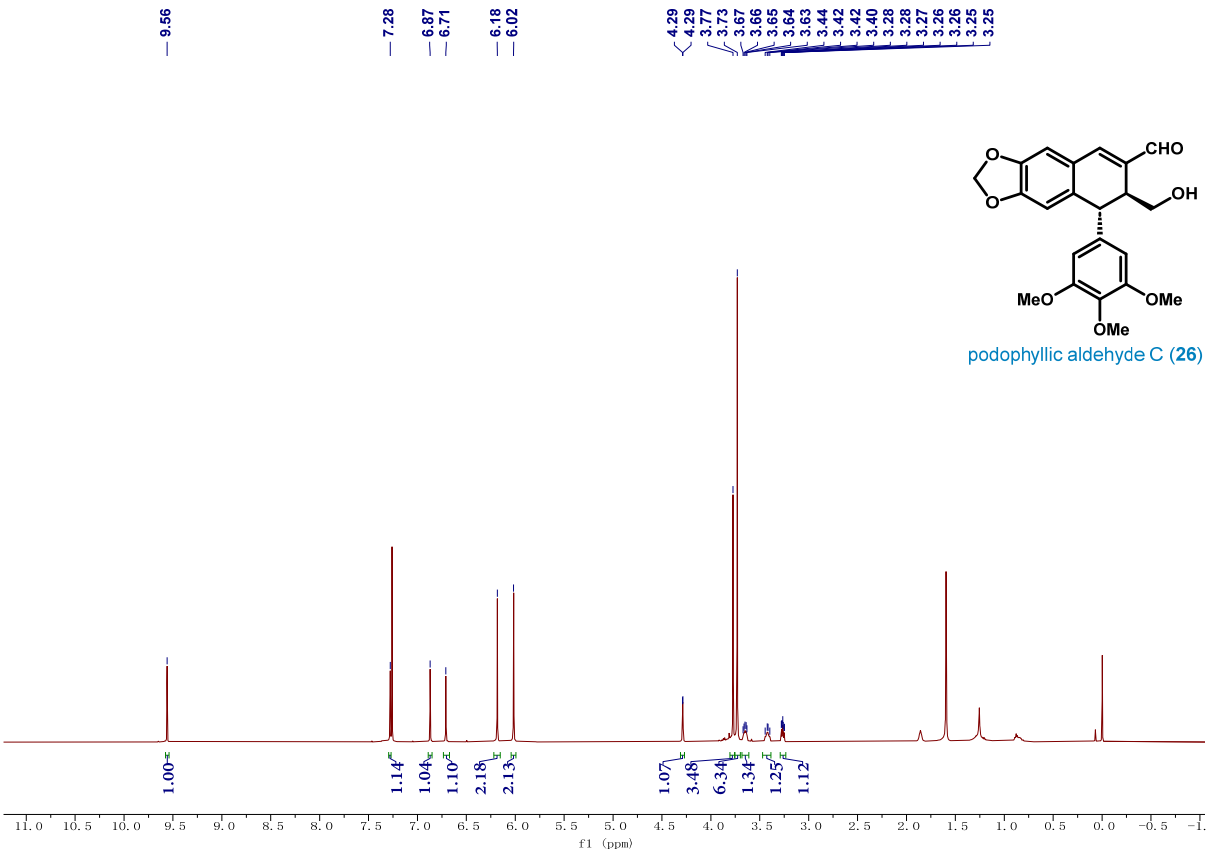


podophyllic aldehyde A (**25**)
(*this work*)



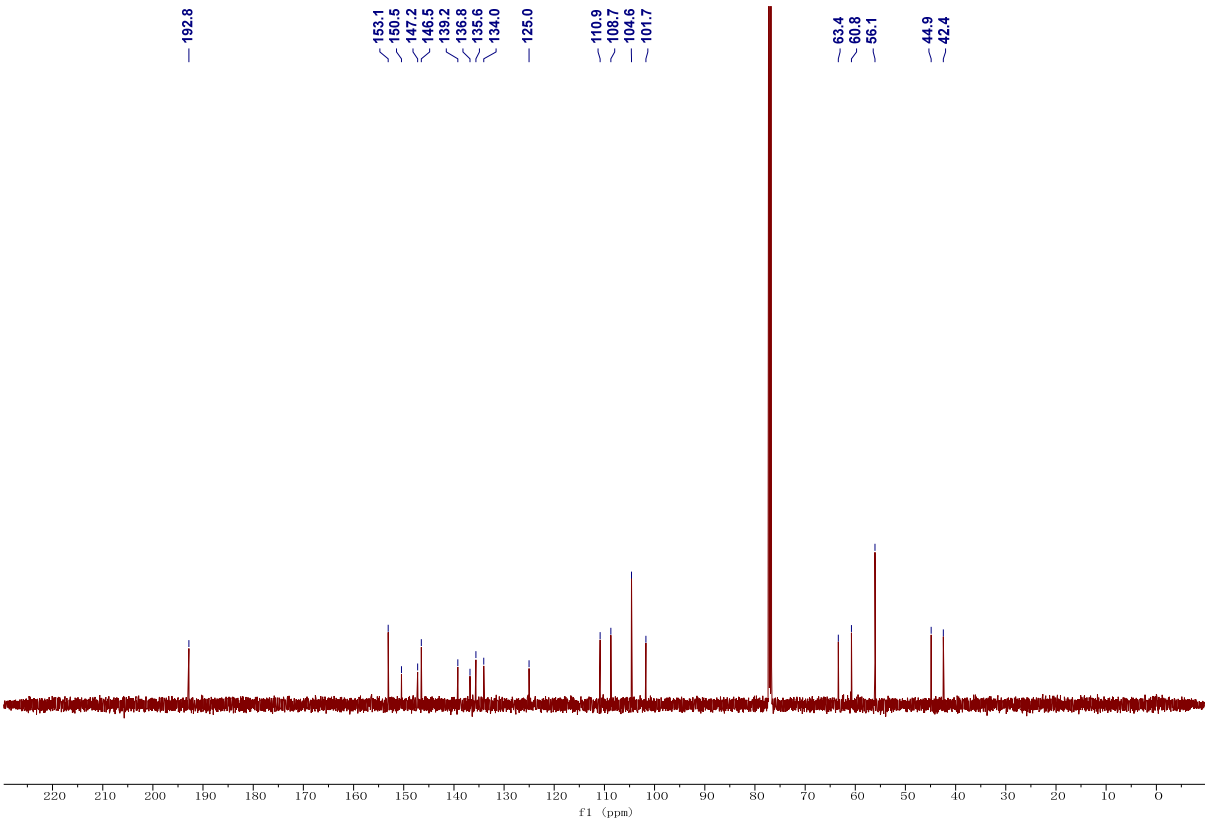
26: Podophyllic aldehyde C

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

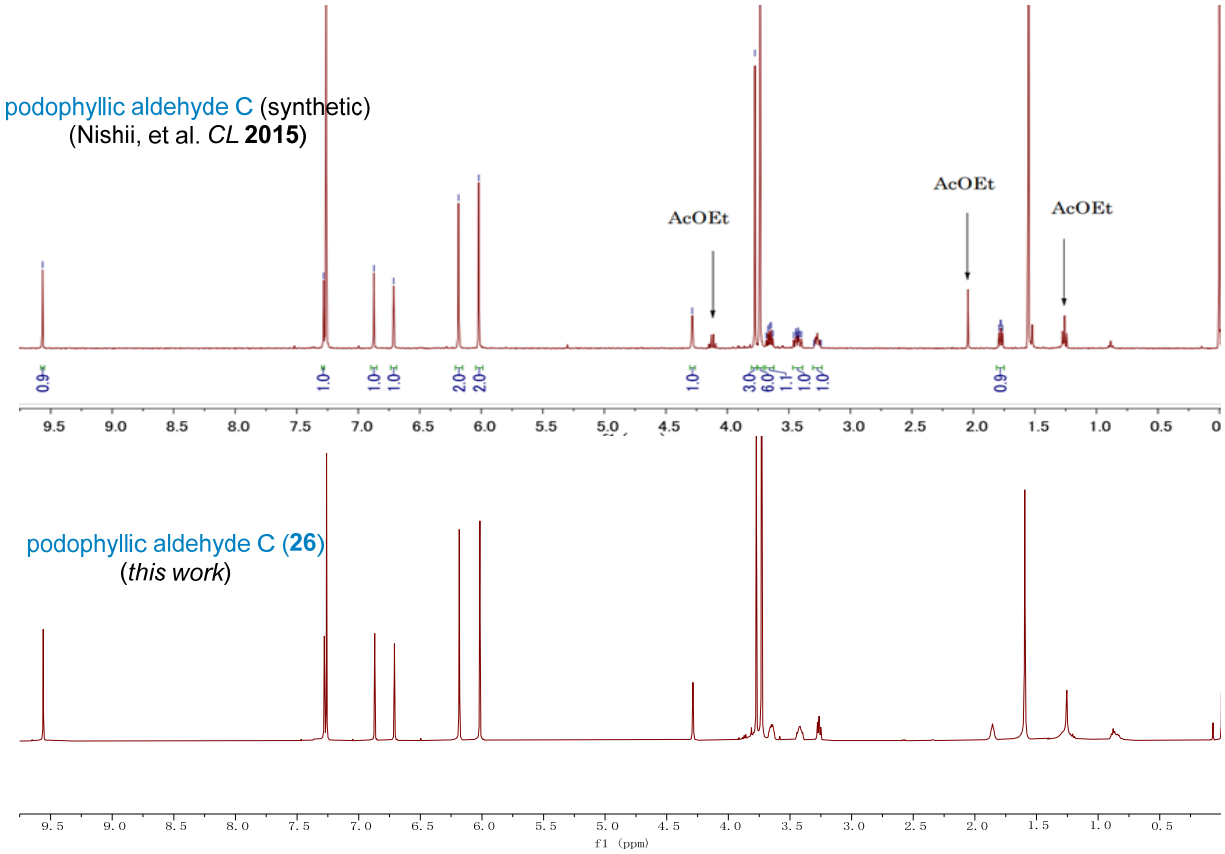


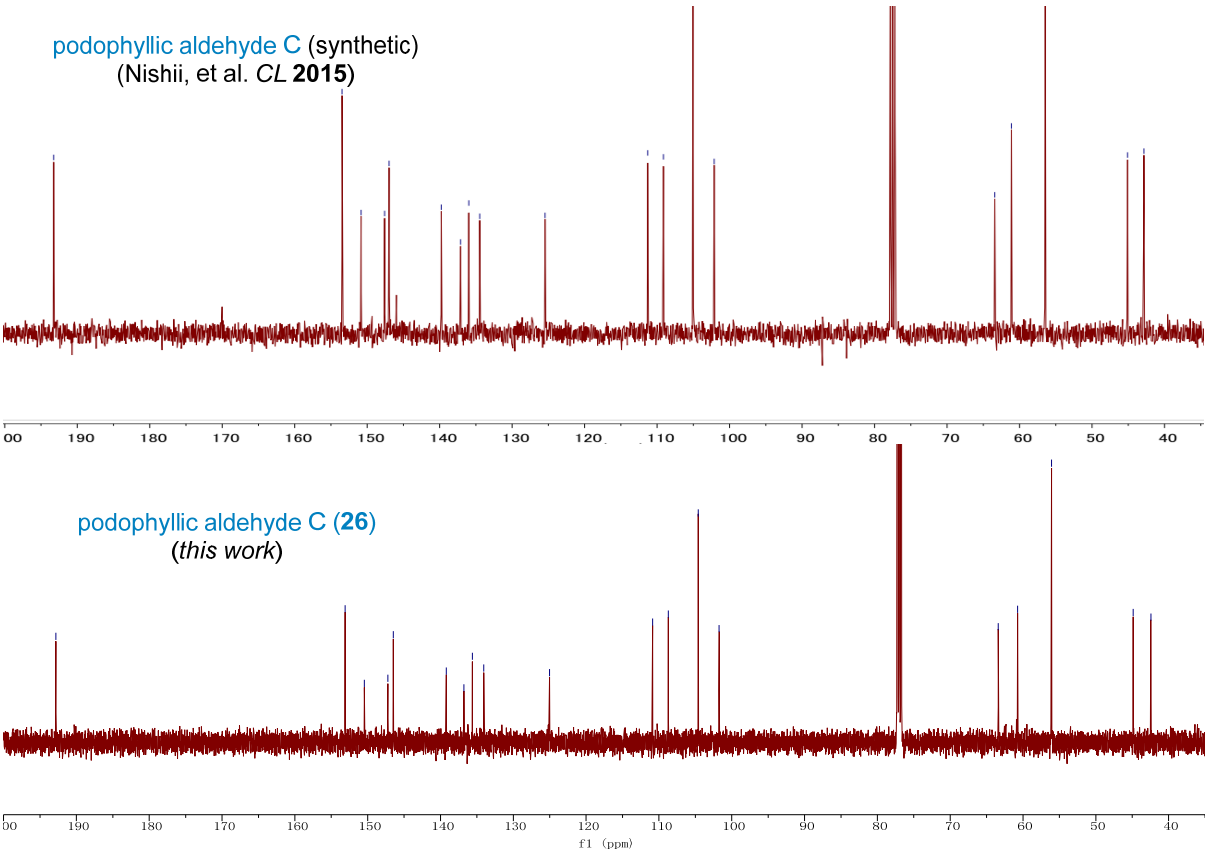
podophyllic aldehyde C (**26**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



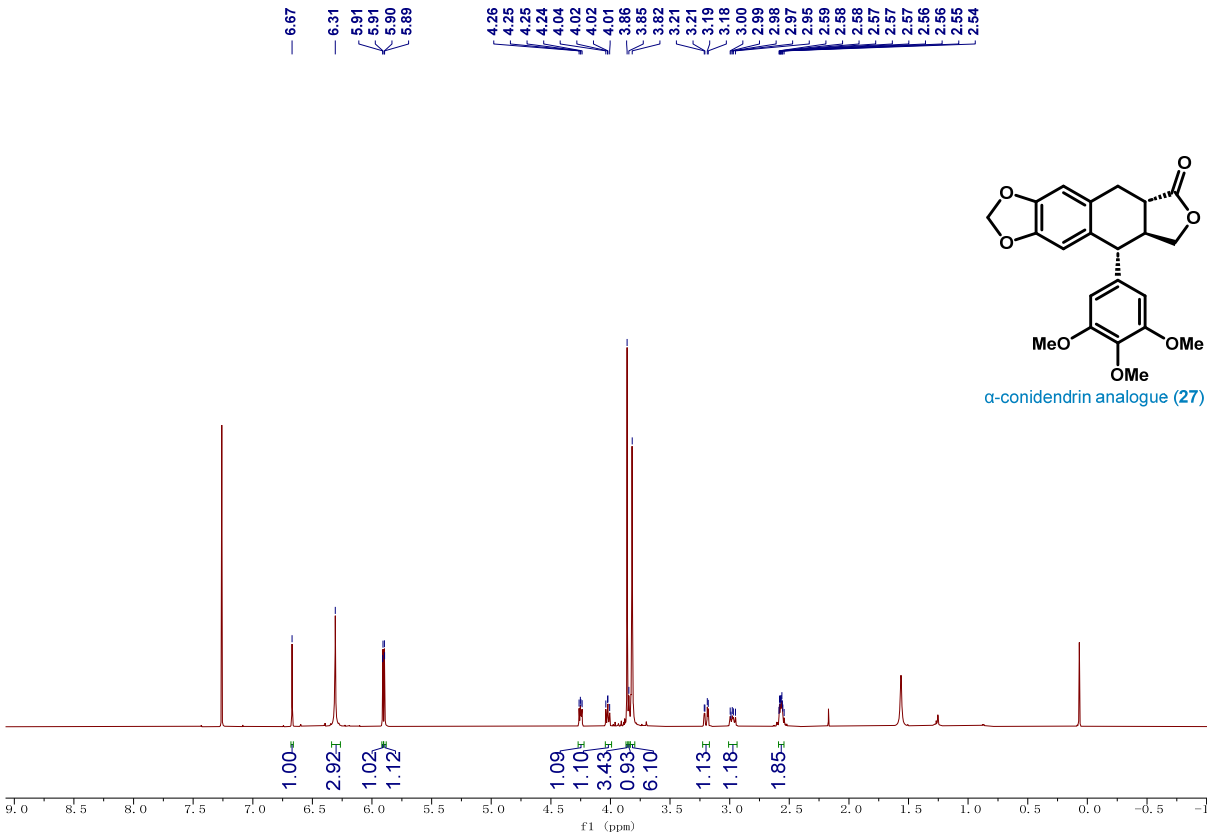
NMR spectra comparison of podophyllic aldehyde C



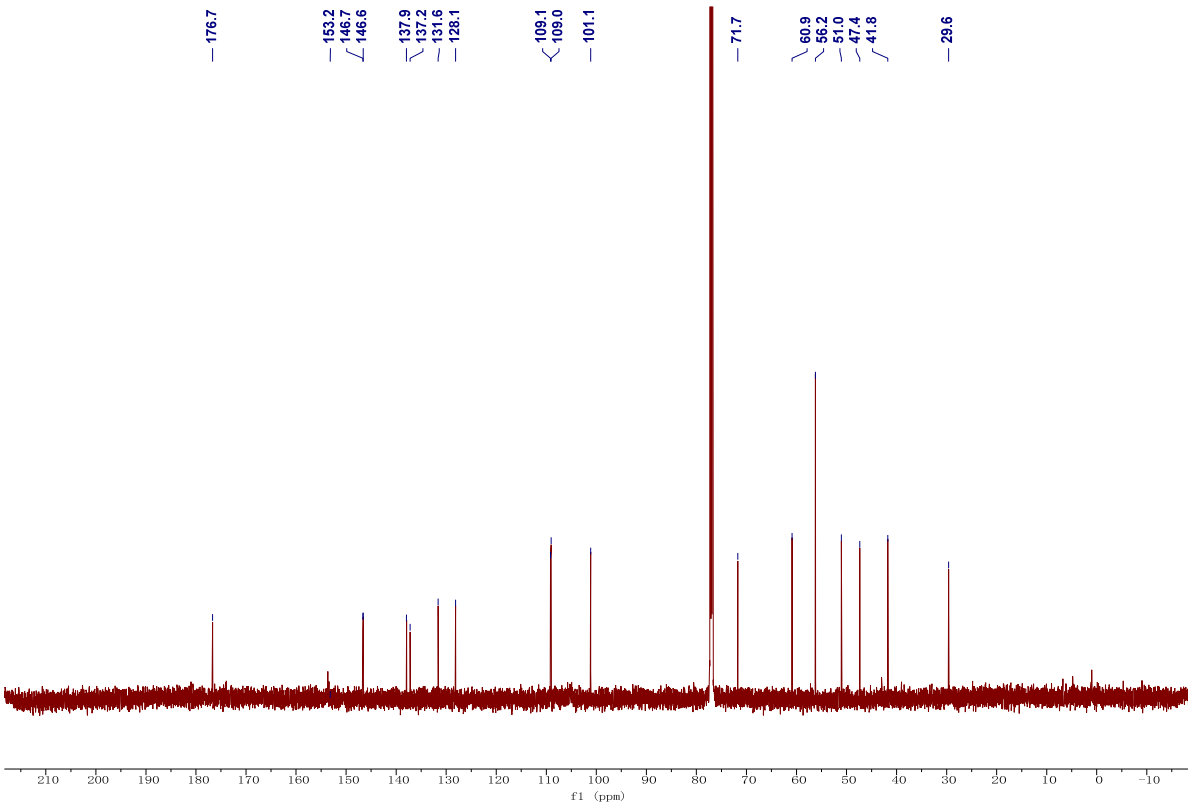


27: α-Conidendrin analogue

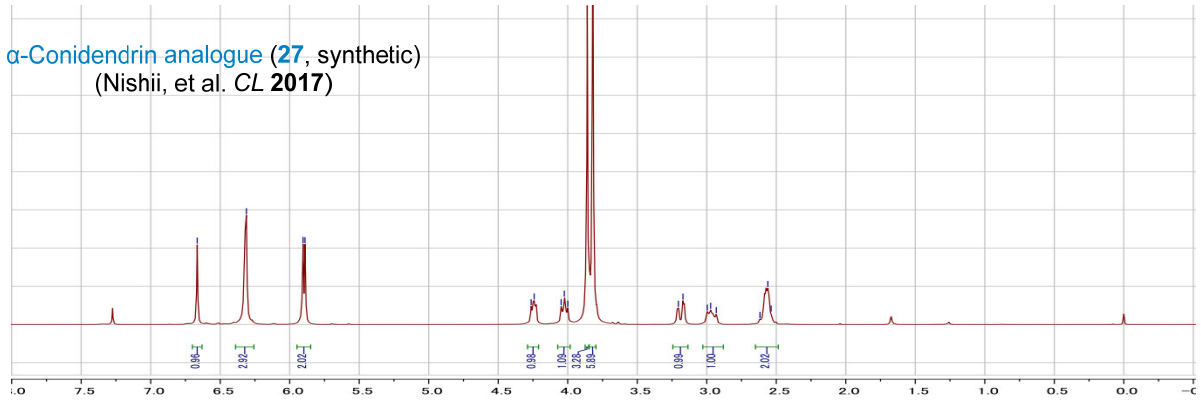
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

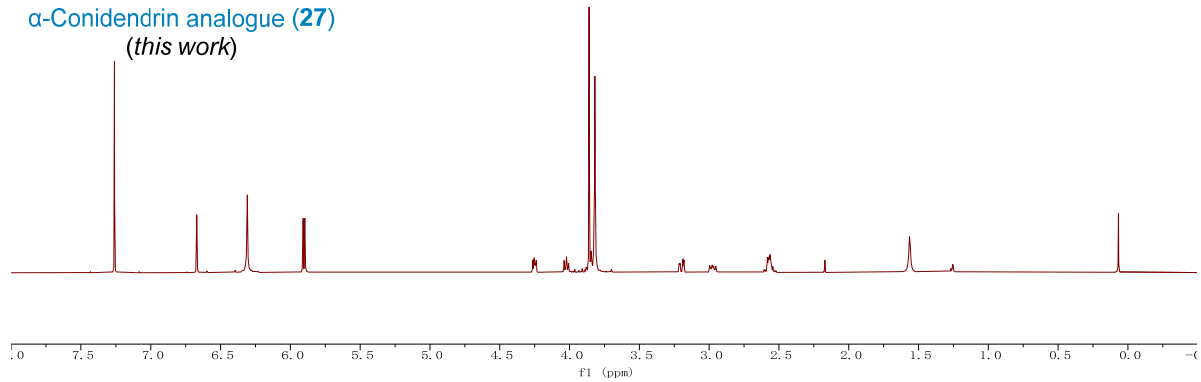


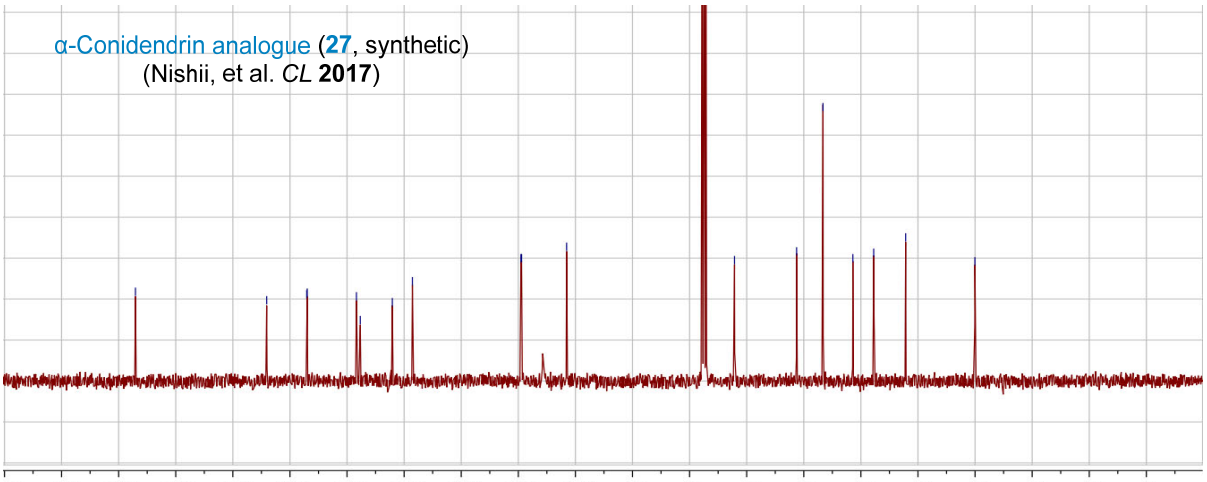
^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

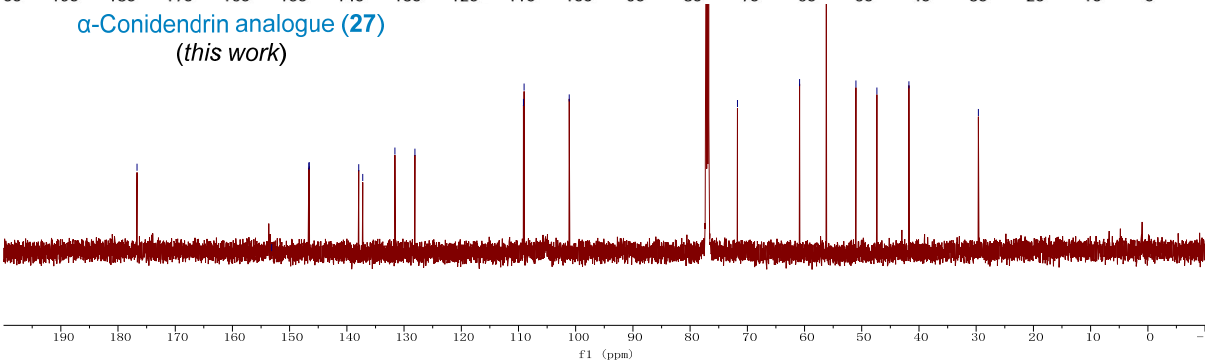


NMR spectra comparison of α-Conidendrin analogue



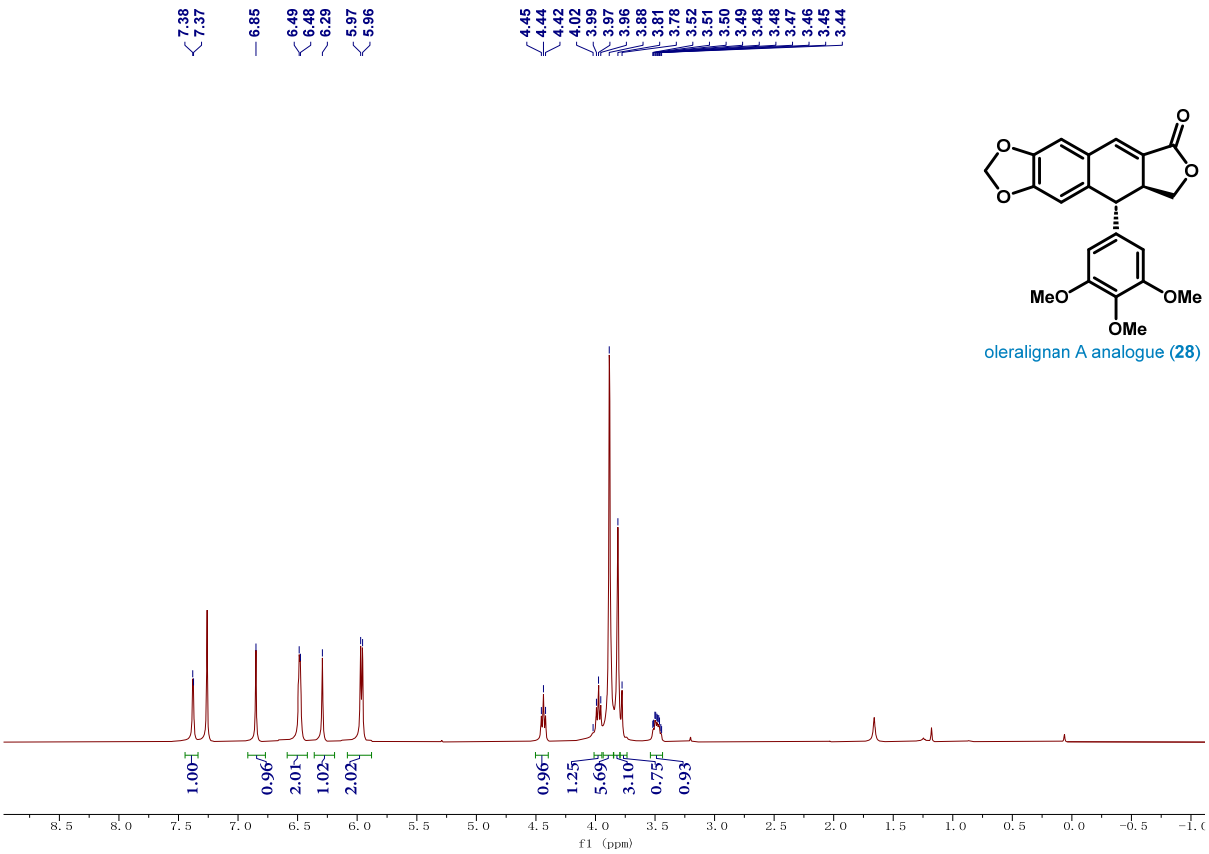






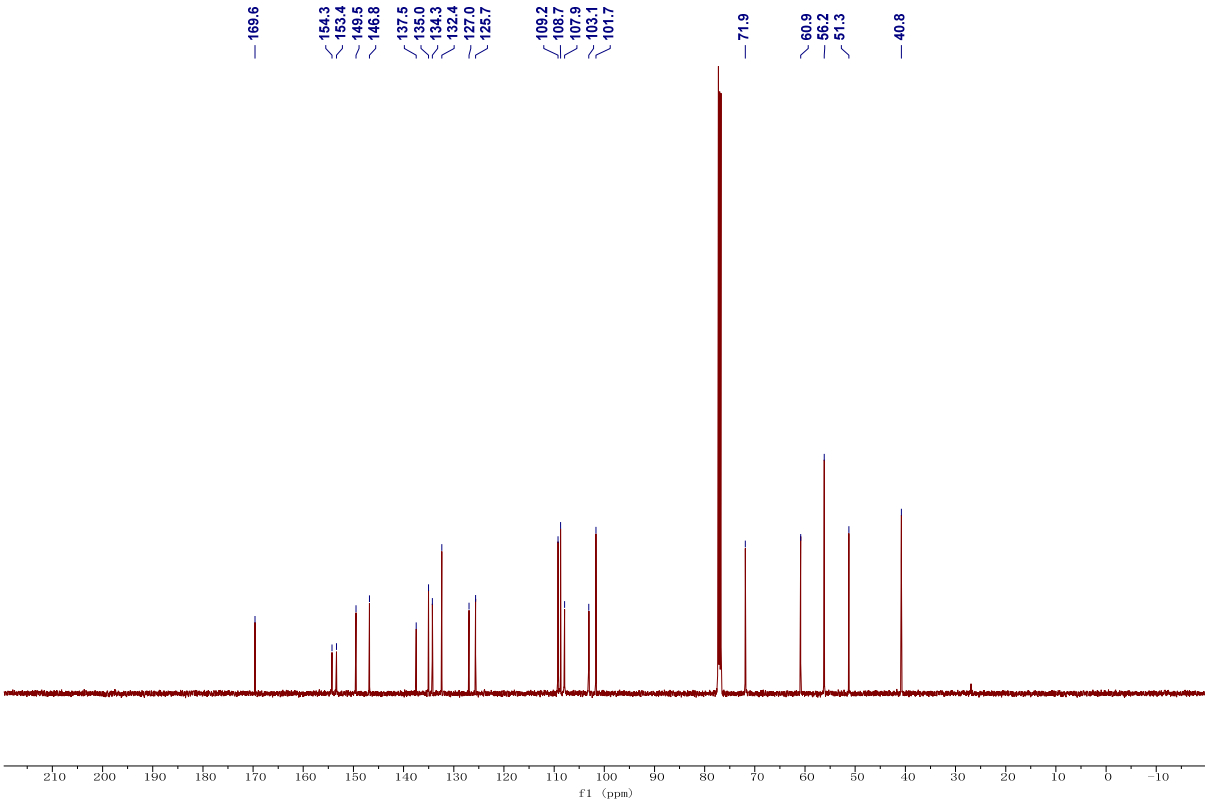
28: Oleralignan A analogue

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



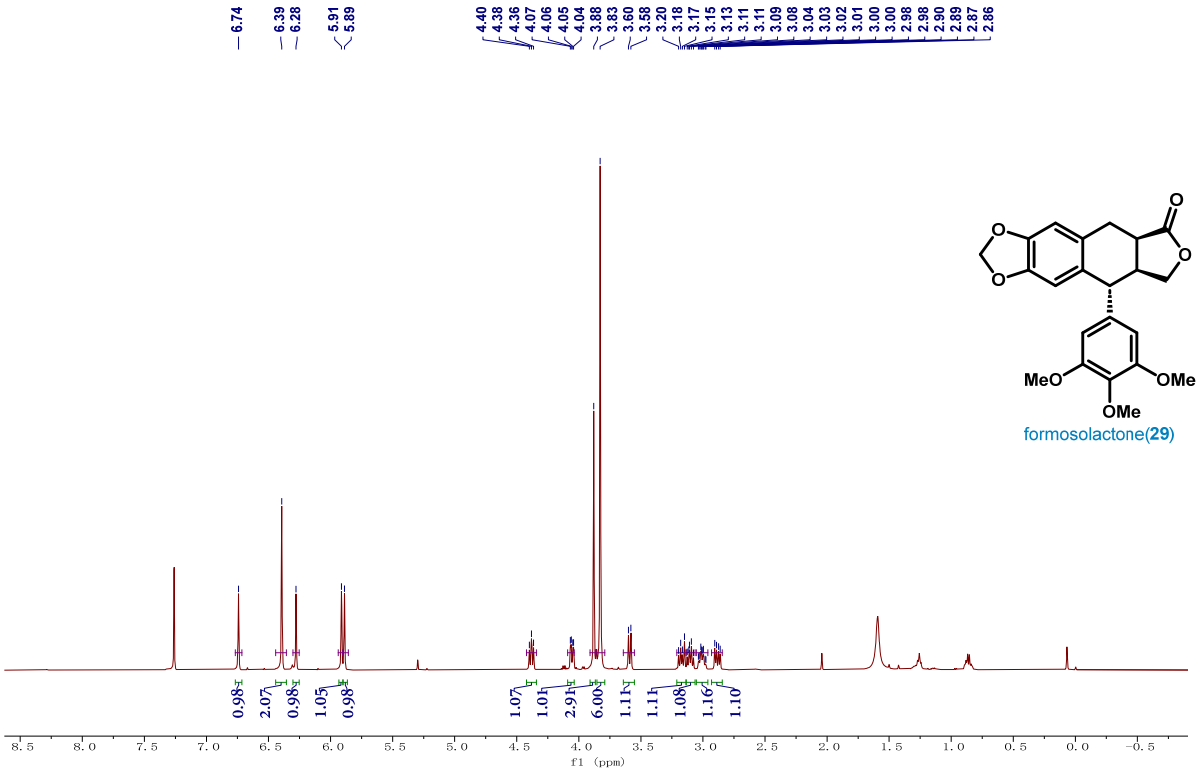
oleralignan A analogue (**28**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

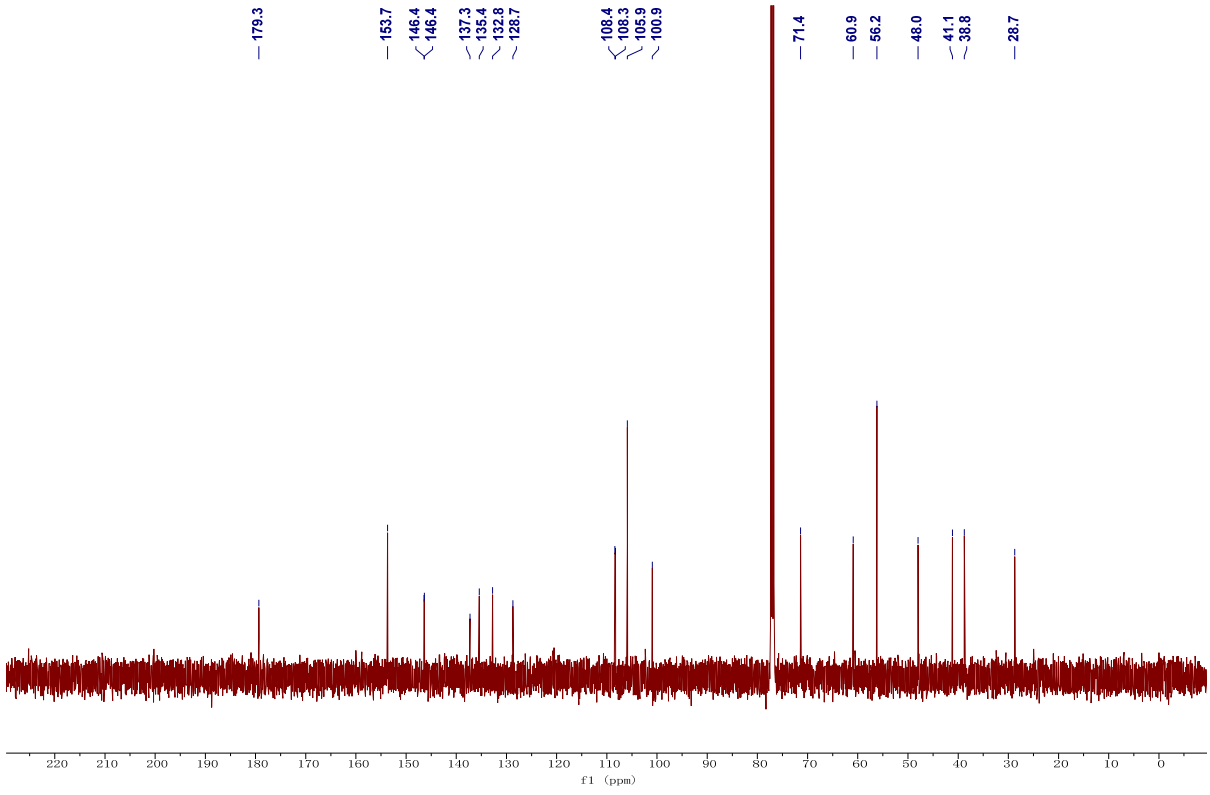


29: Formosolactone (alleged structure; but its originally reported spectra data actually matched well with deoxypodophyllotoxin **11**)

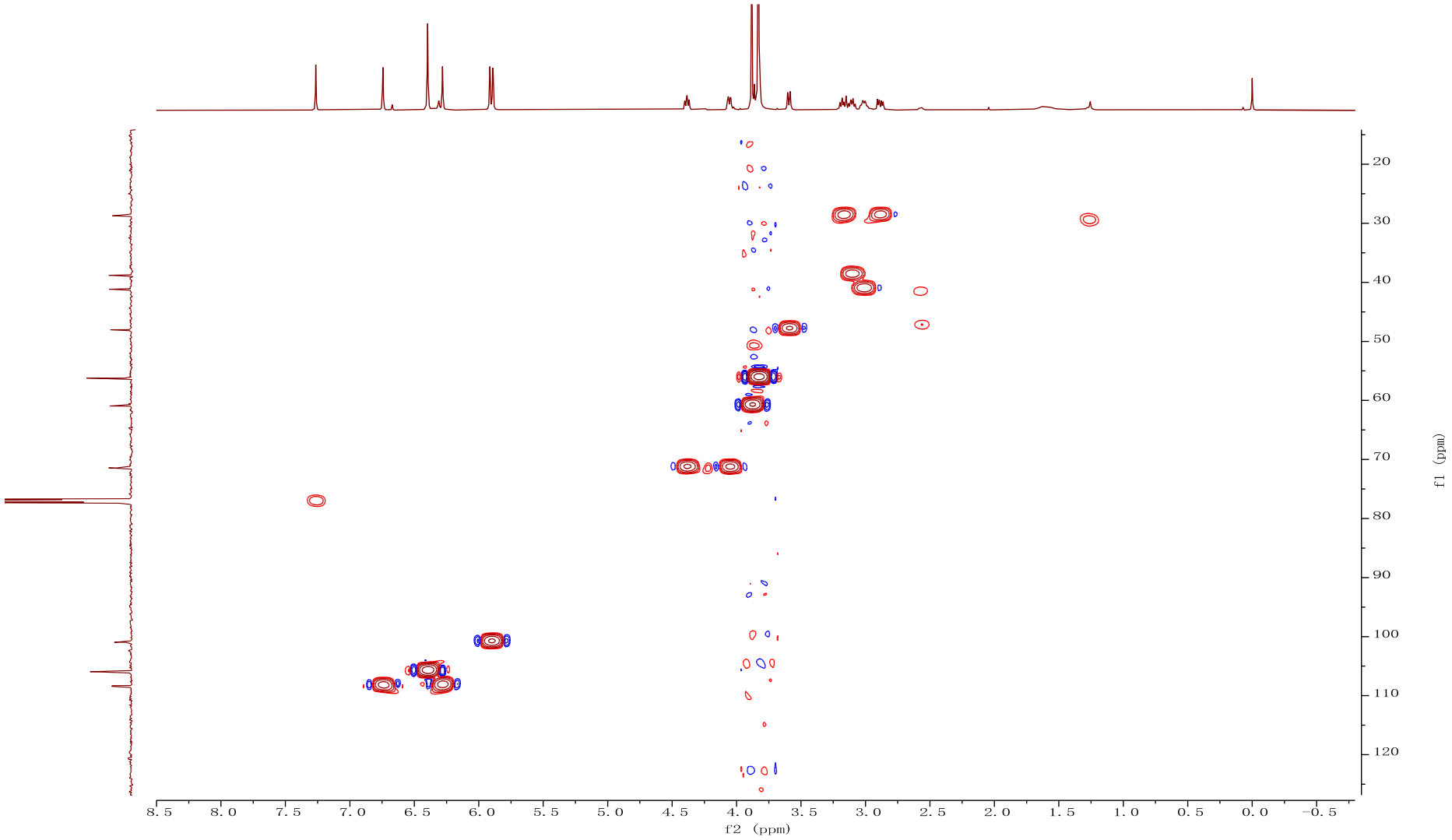
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



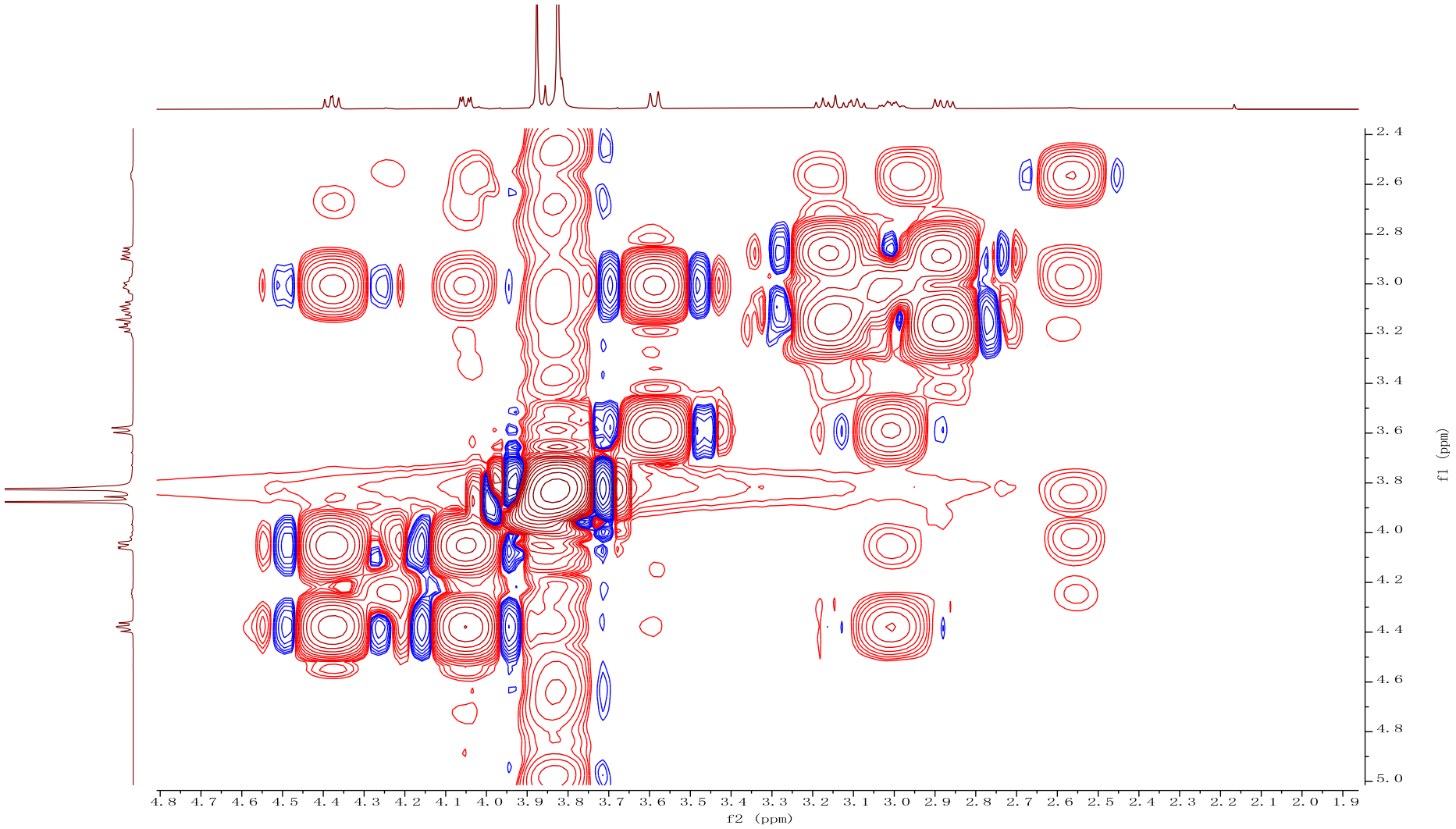
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



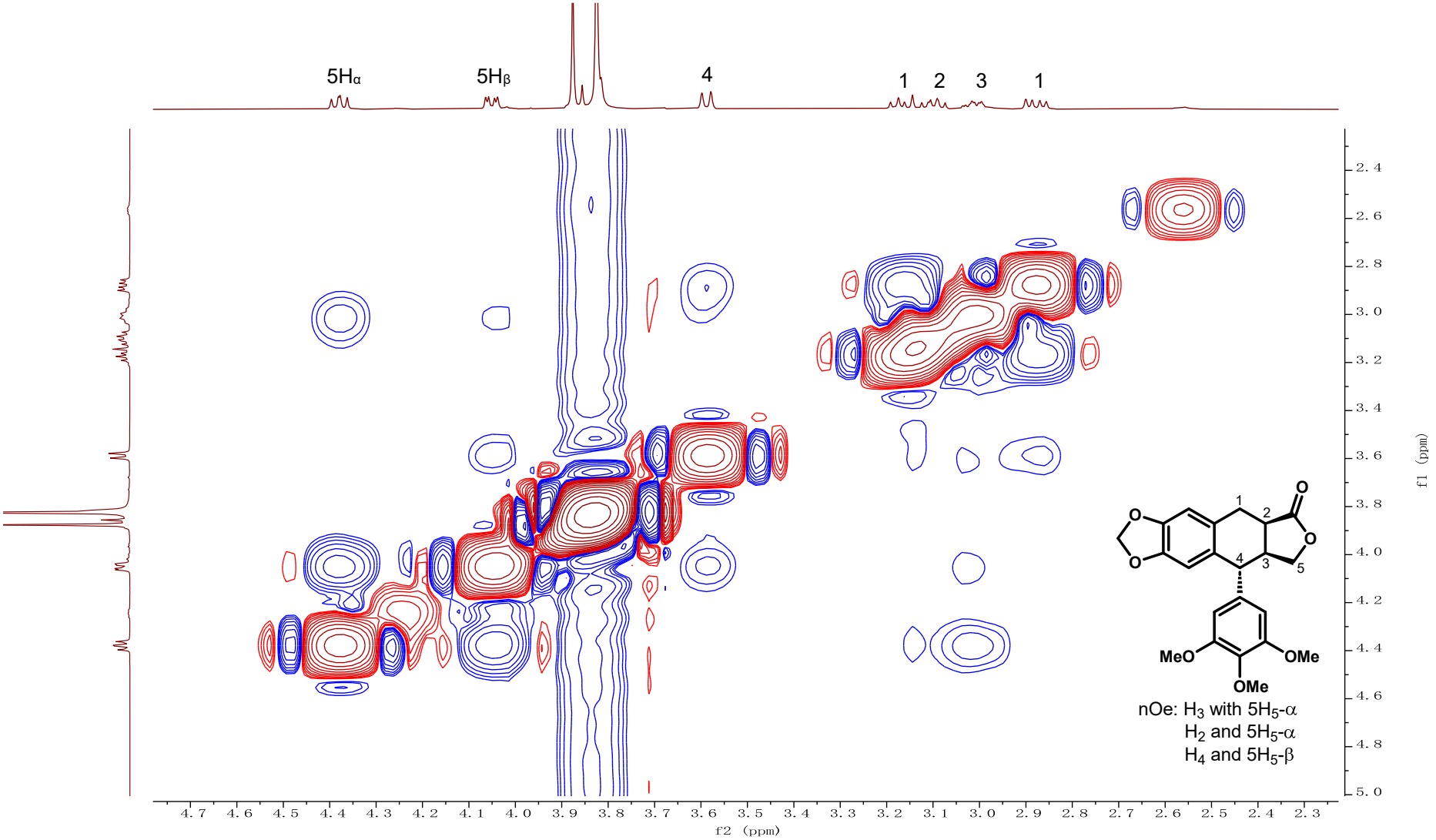
HSQC (500 MHz, $CDCl_3$)



<u>COSY</u> (500 MHz, $CDCl_3$)

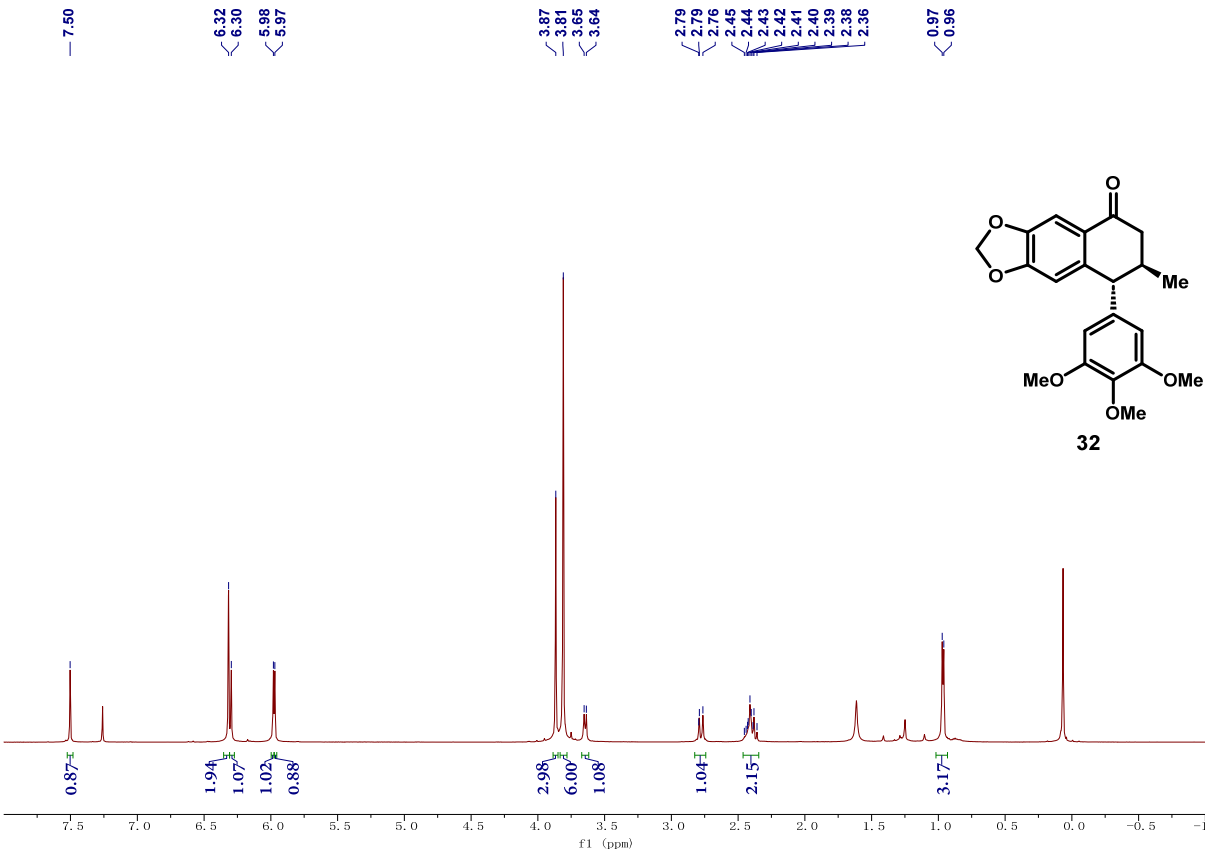


NOESY (500 MHz, $CDCl_3$)



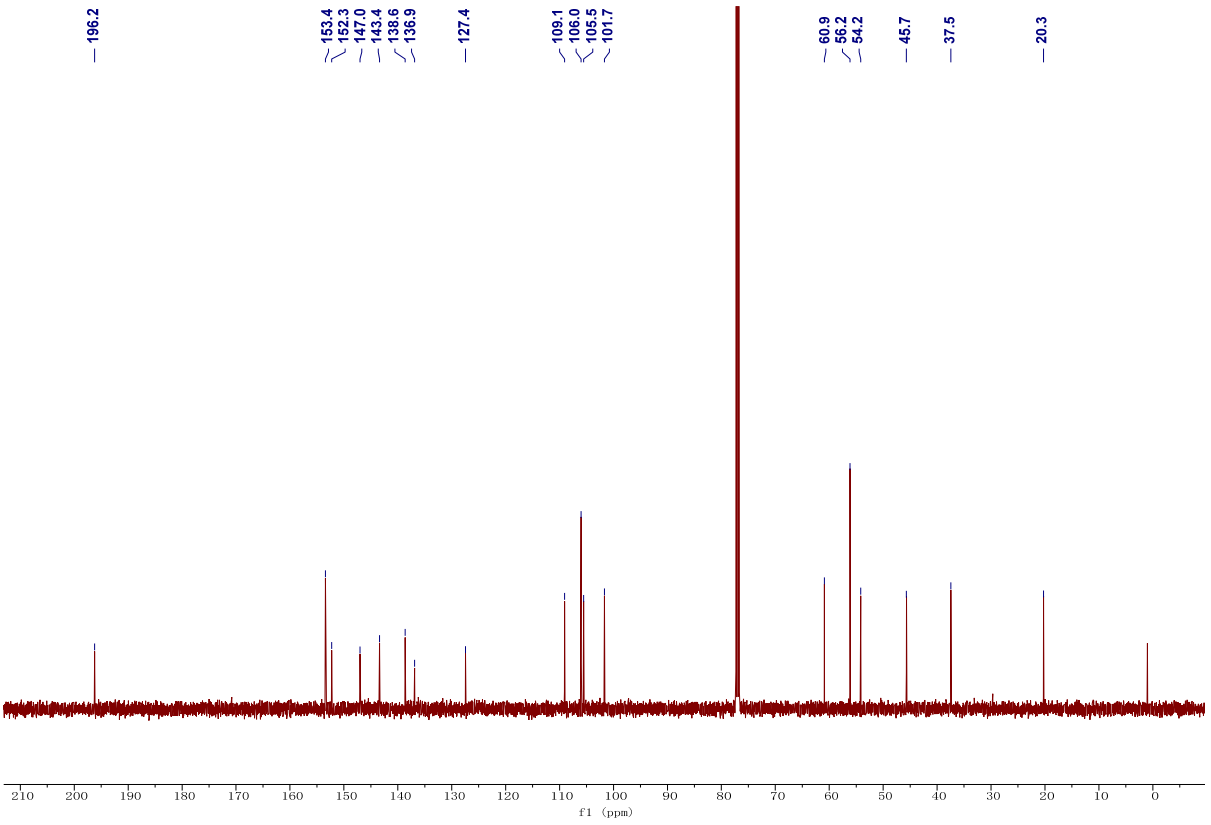
32: (7R,8R)-7-methyl-8-(3,4,5-trimethoxyphenyl)-7,8-dihydronaphtho[2,3-d][1,3]dioxol-5(6H)-one

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



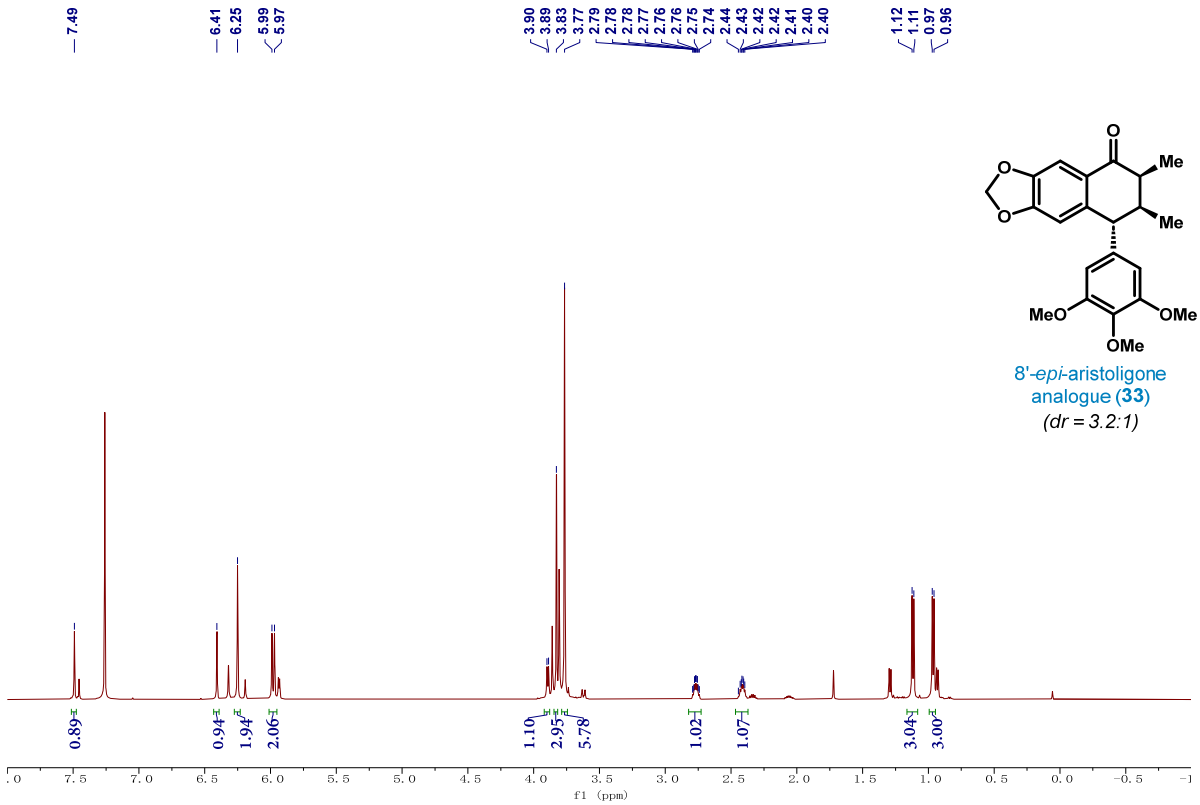
32

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



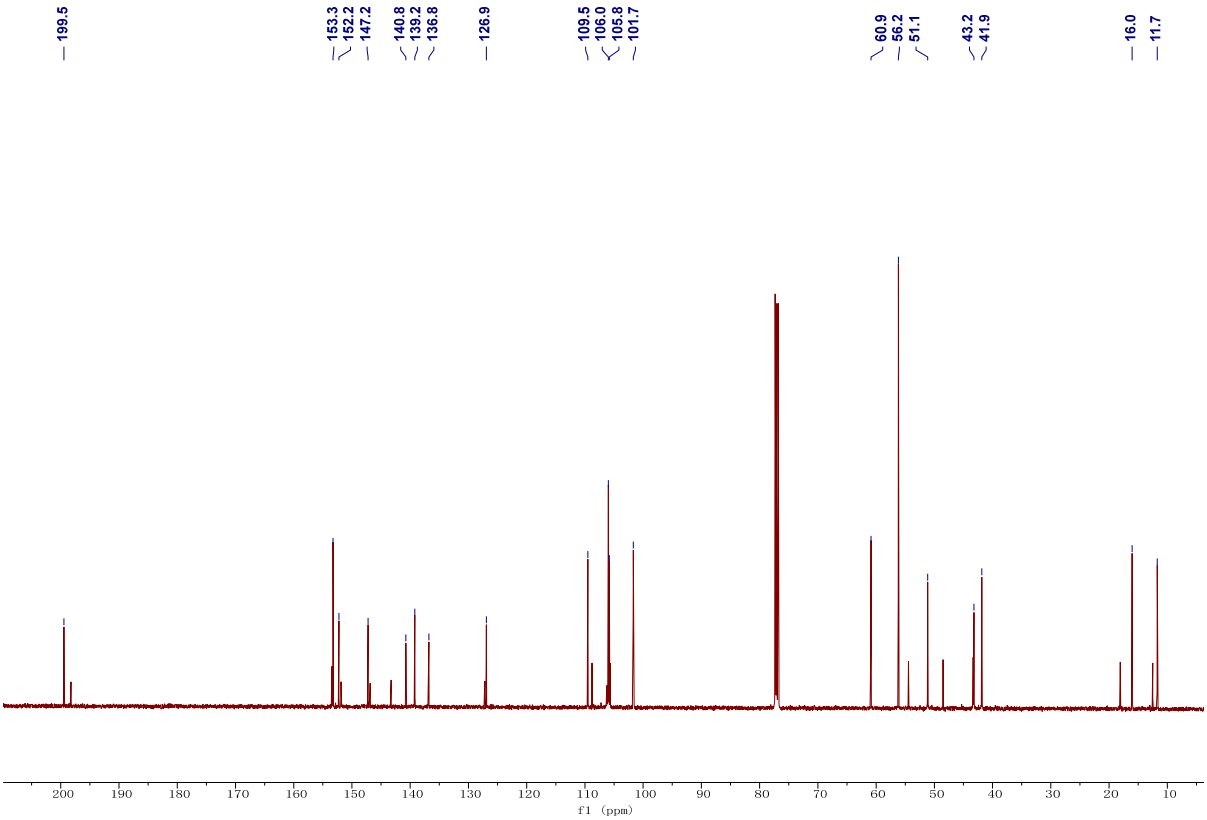
33: 8'-*epi*-aristoligone analogue

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

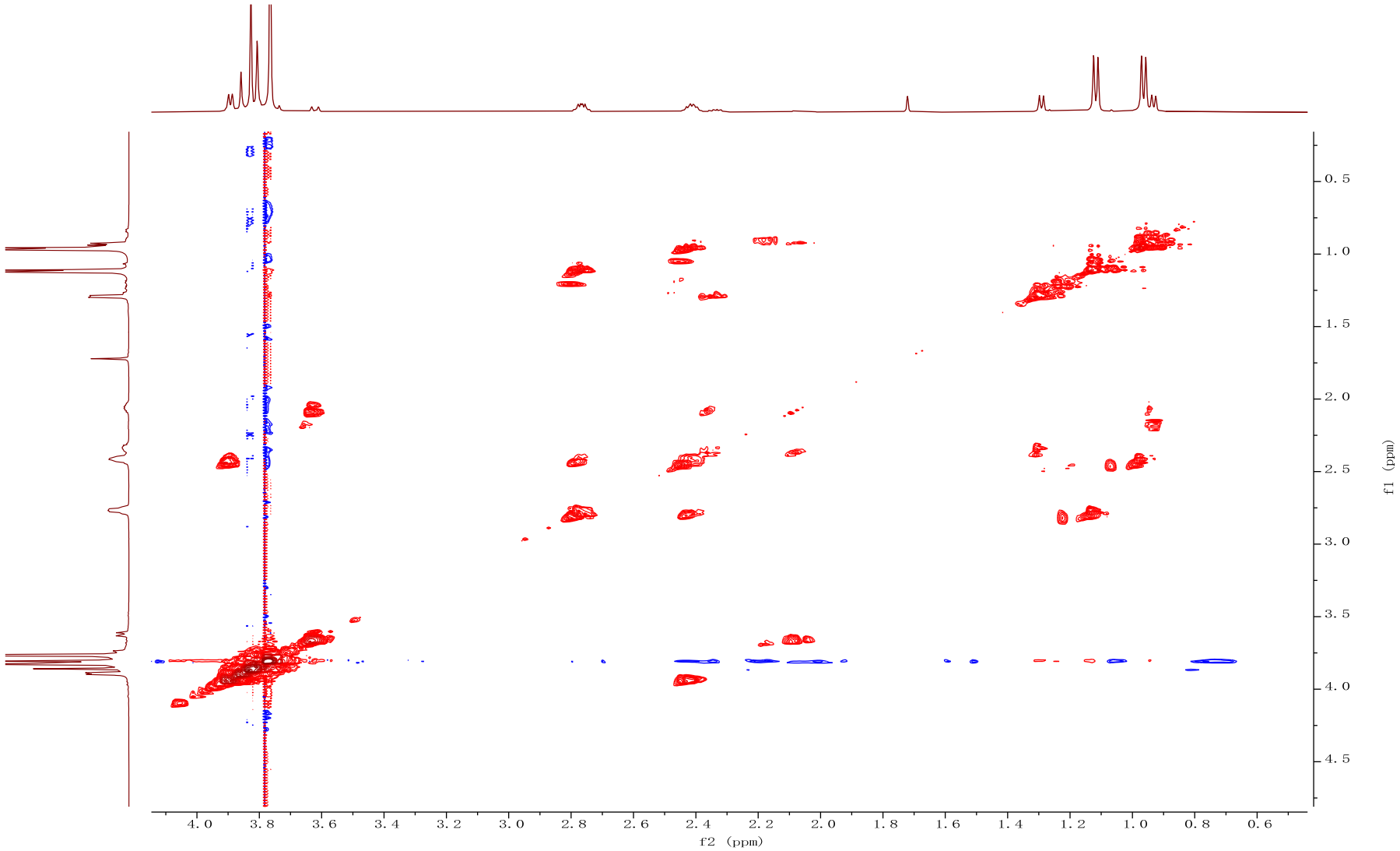


8'-*epi*-aristoligone analogue (**33**)
(dr = 3.2:1)

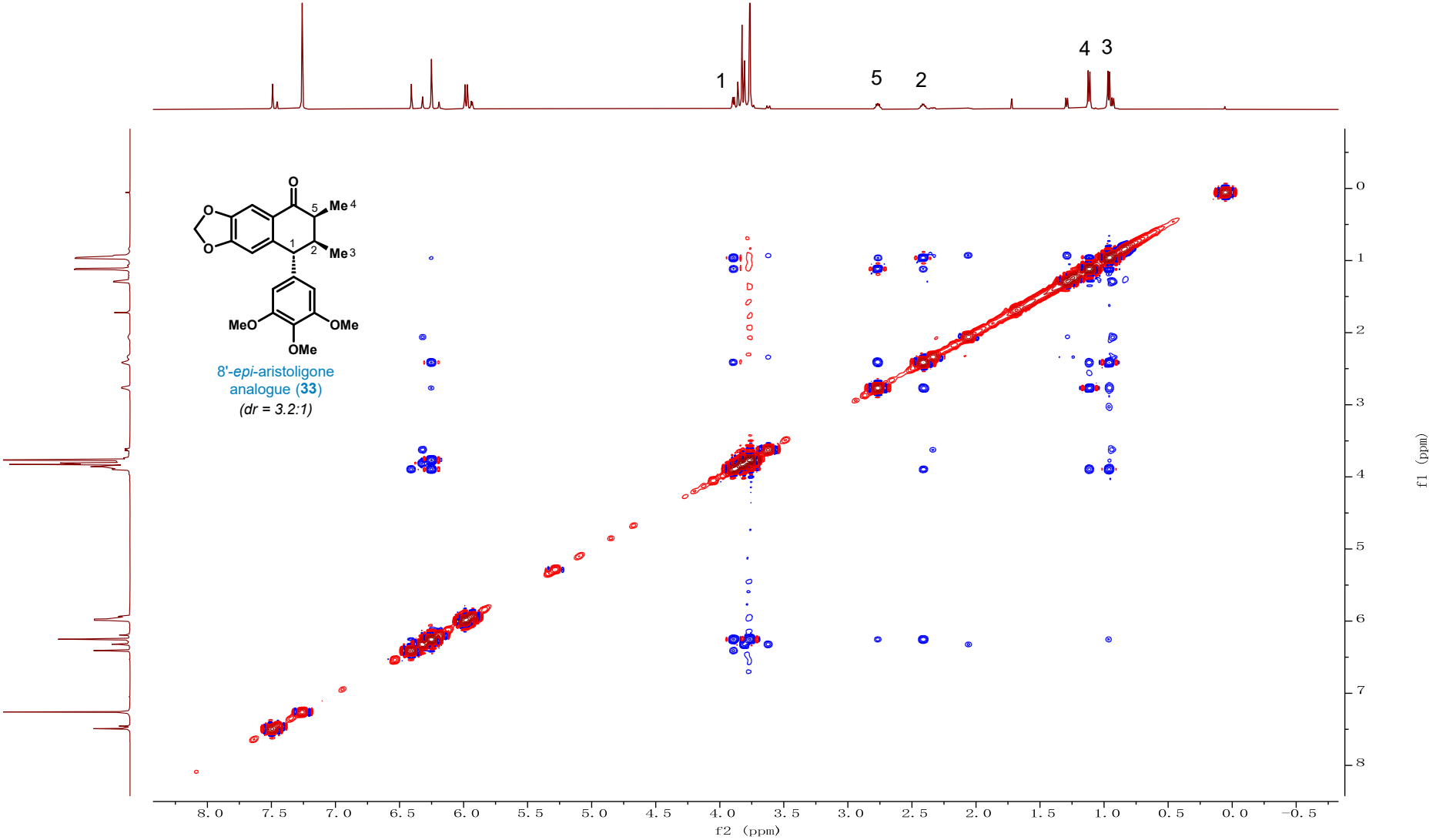
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



<u>COSY</u> (500 MHz, $CDCl_3$)

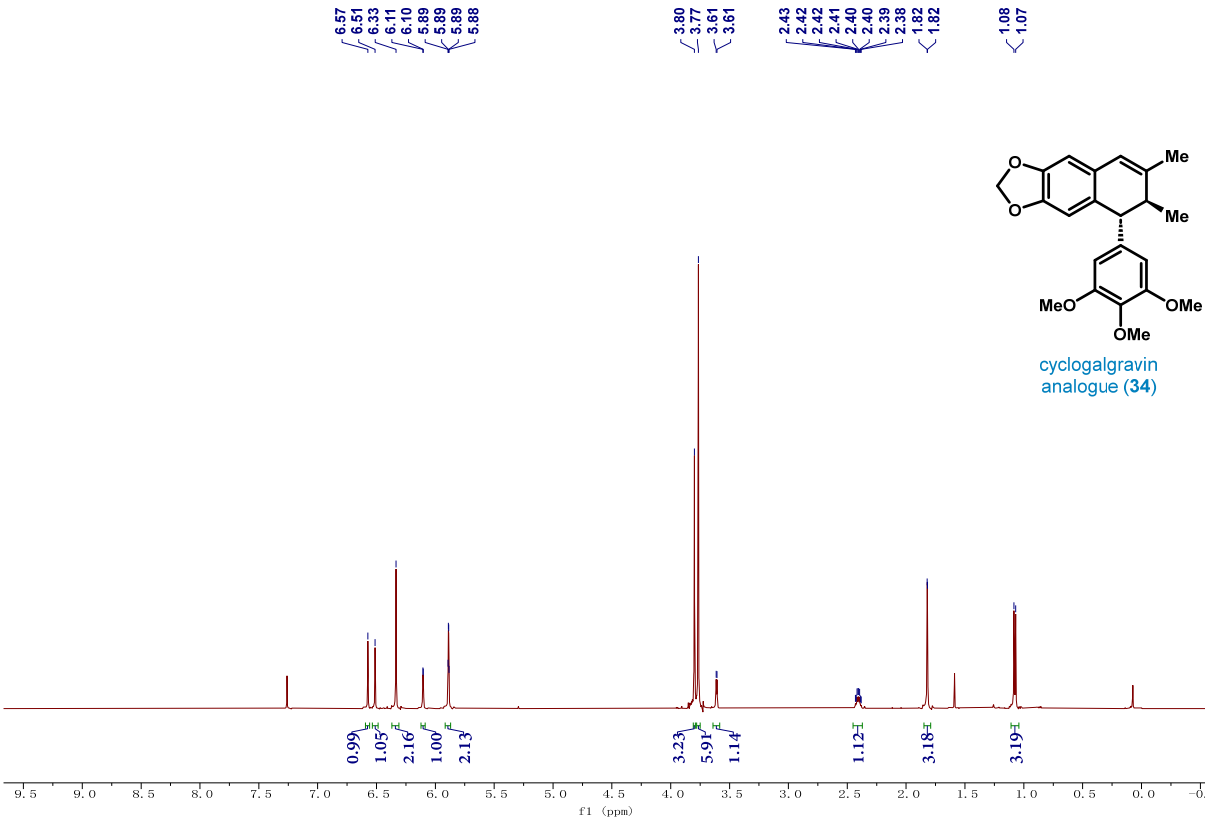


NOESY (500 MHz, $CDCl_3$)

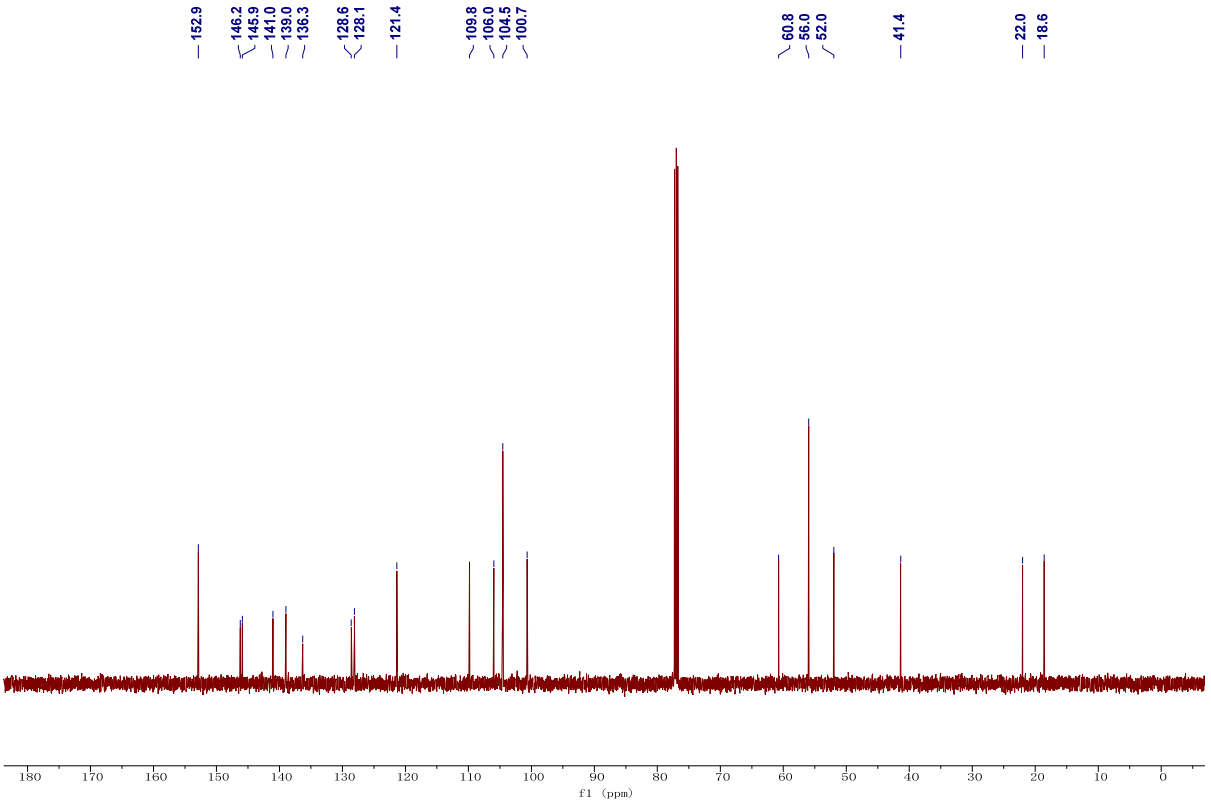


34: Cyclogalgravin analogue

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

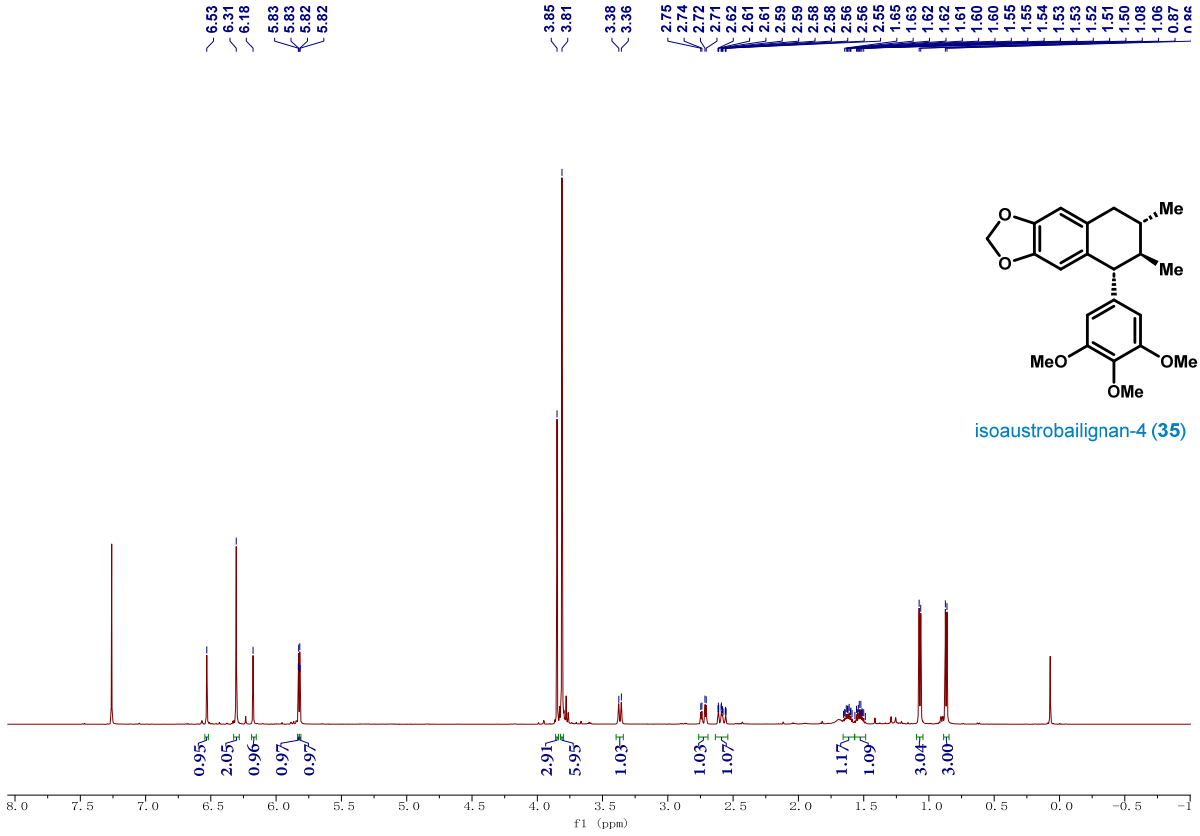


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



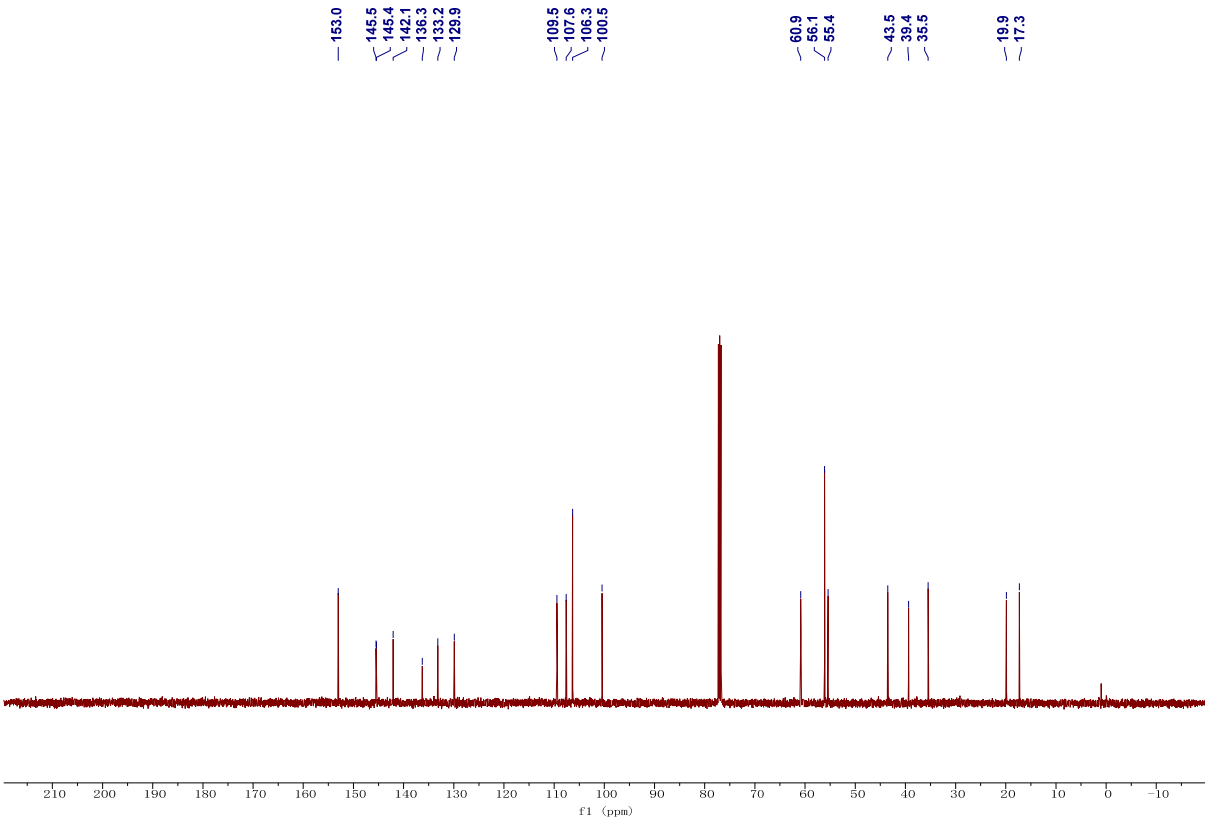
35: Isoaustrobailignan-4

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

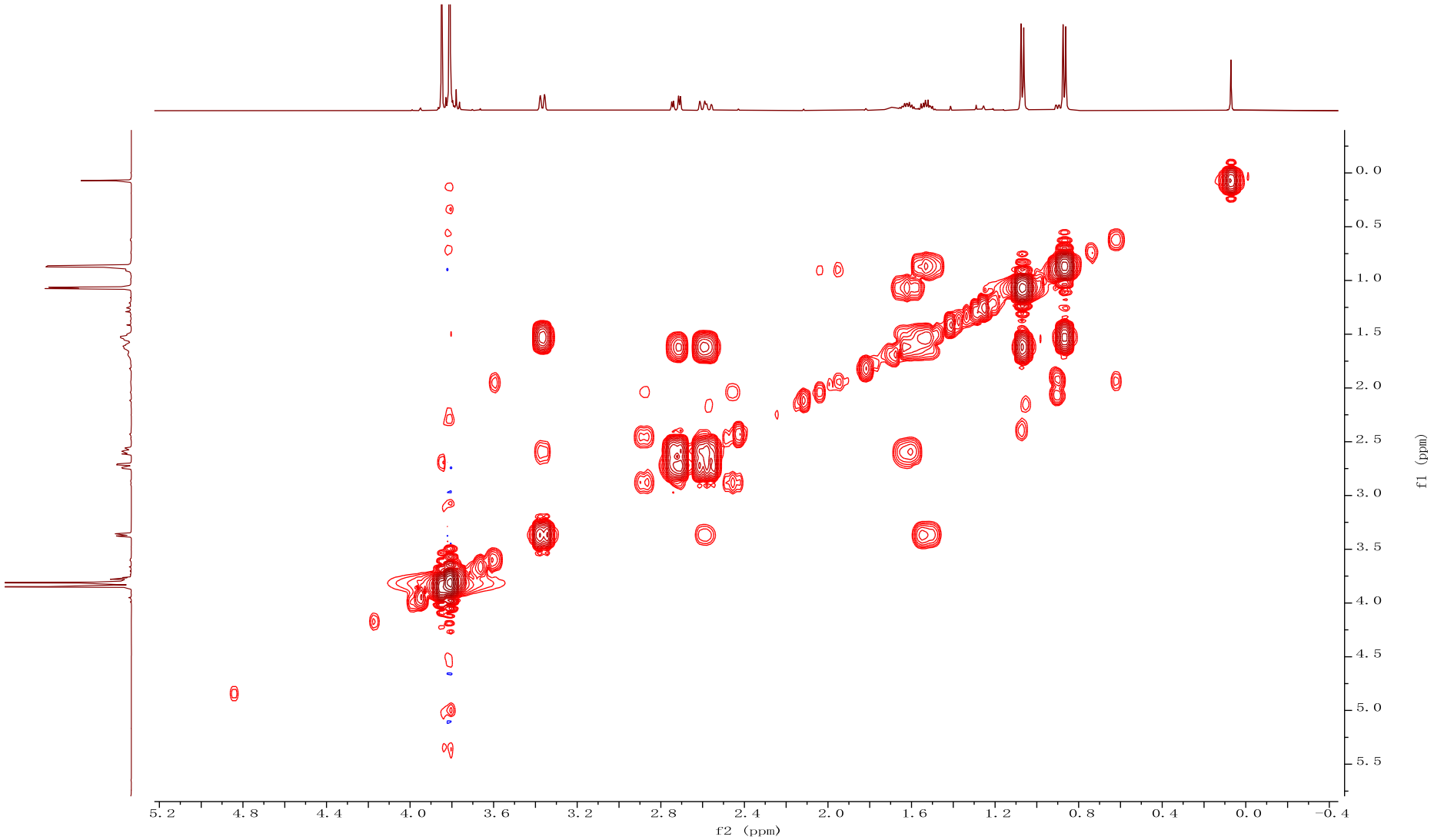


isoaustrobailignan-4 (**35**)

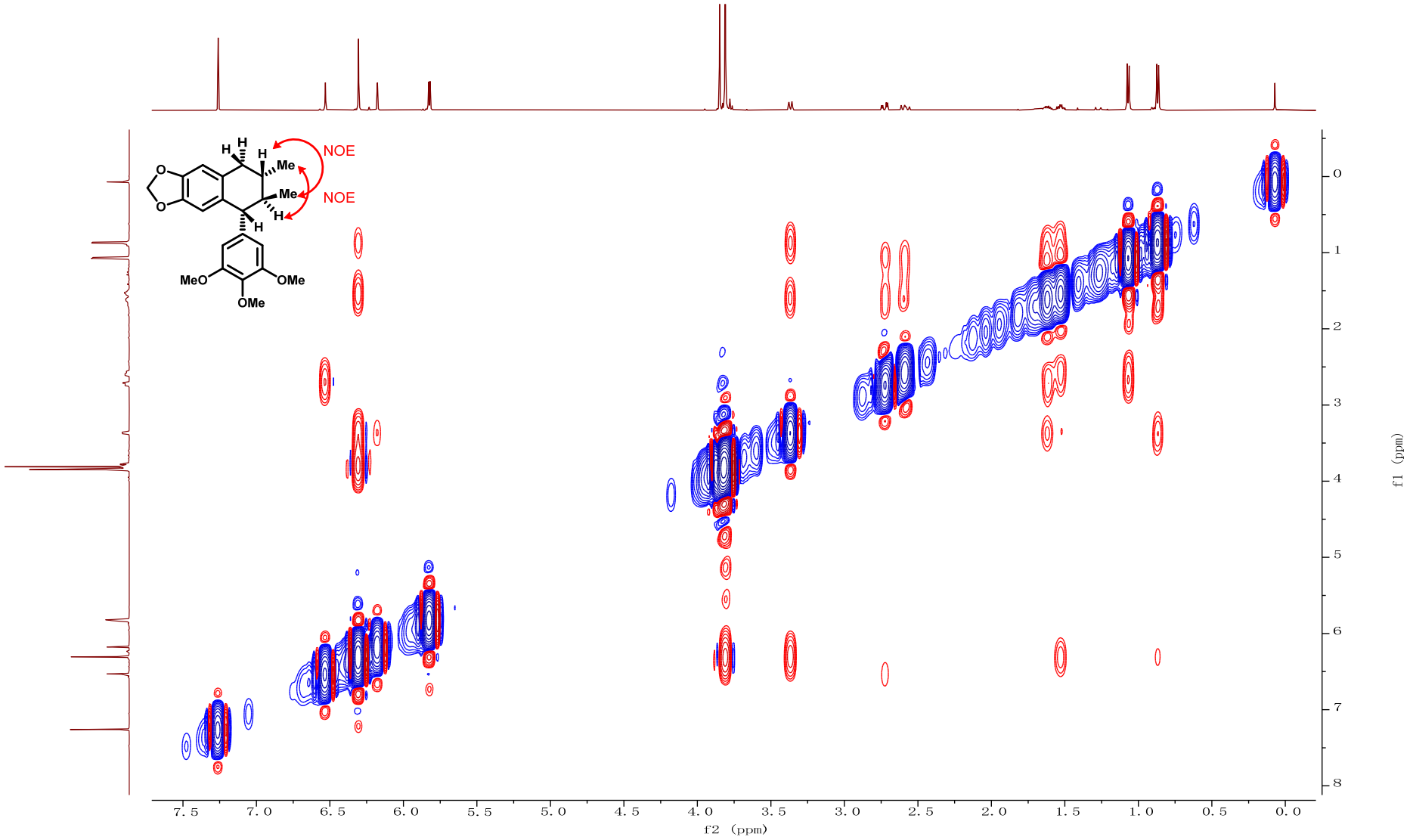
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



COSY (500 MHz, $CDCl_3$)

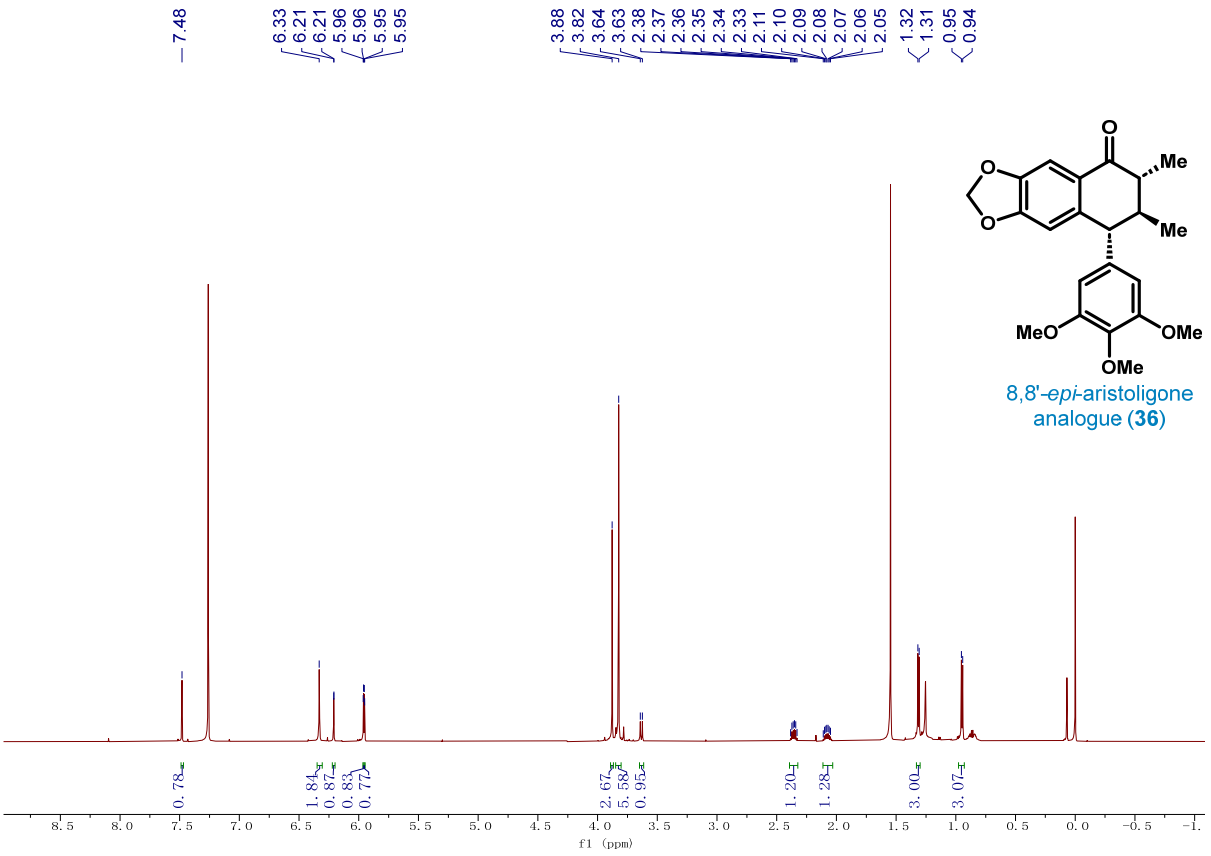


NOESY (500 MHz, $CDCl_3$)

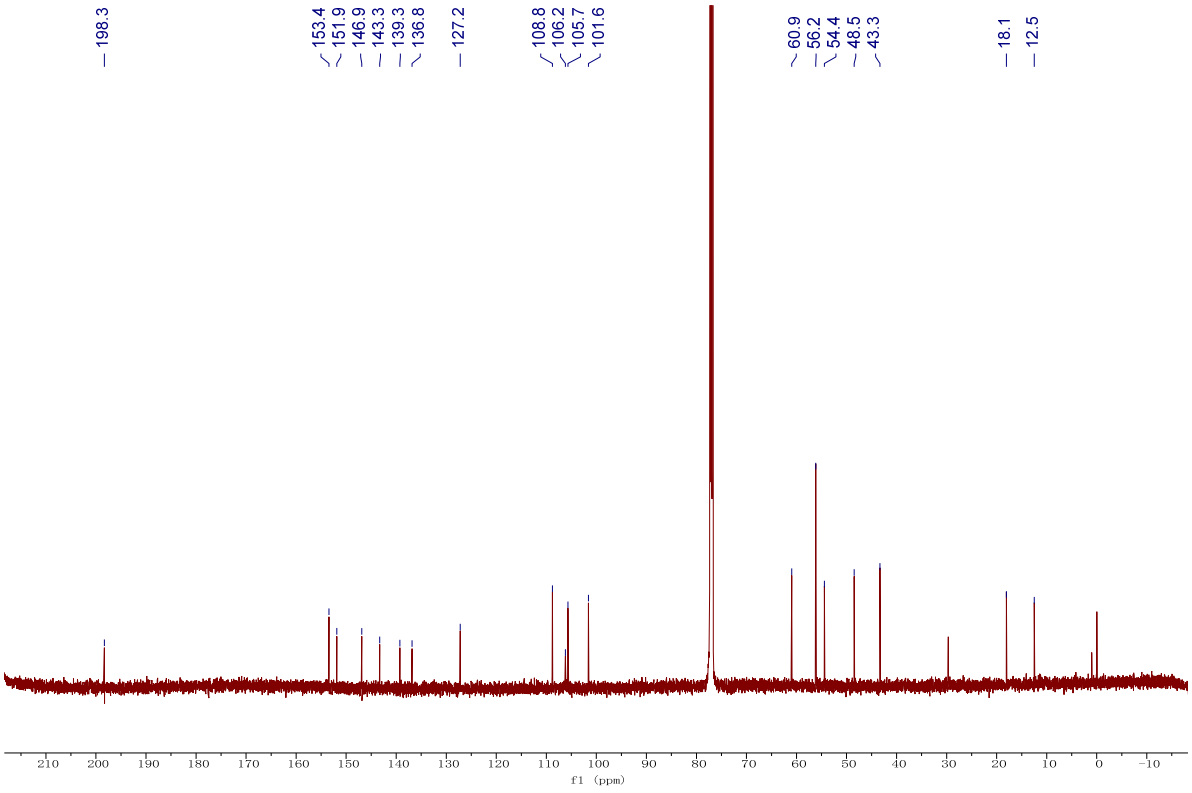


36: 8, 8'-*epi*-Aristoligone analogue

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

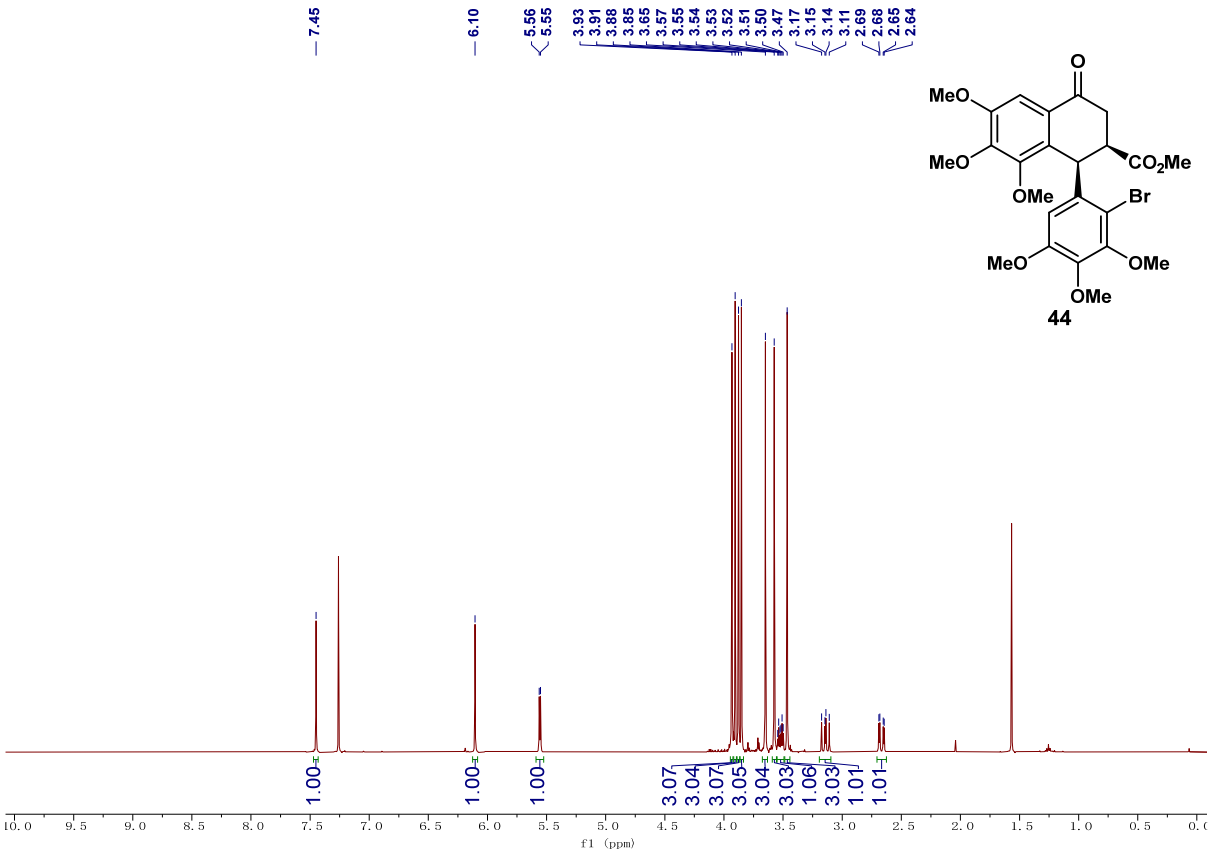


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

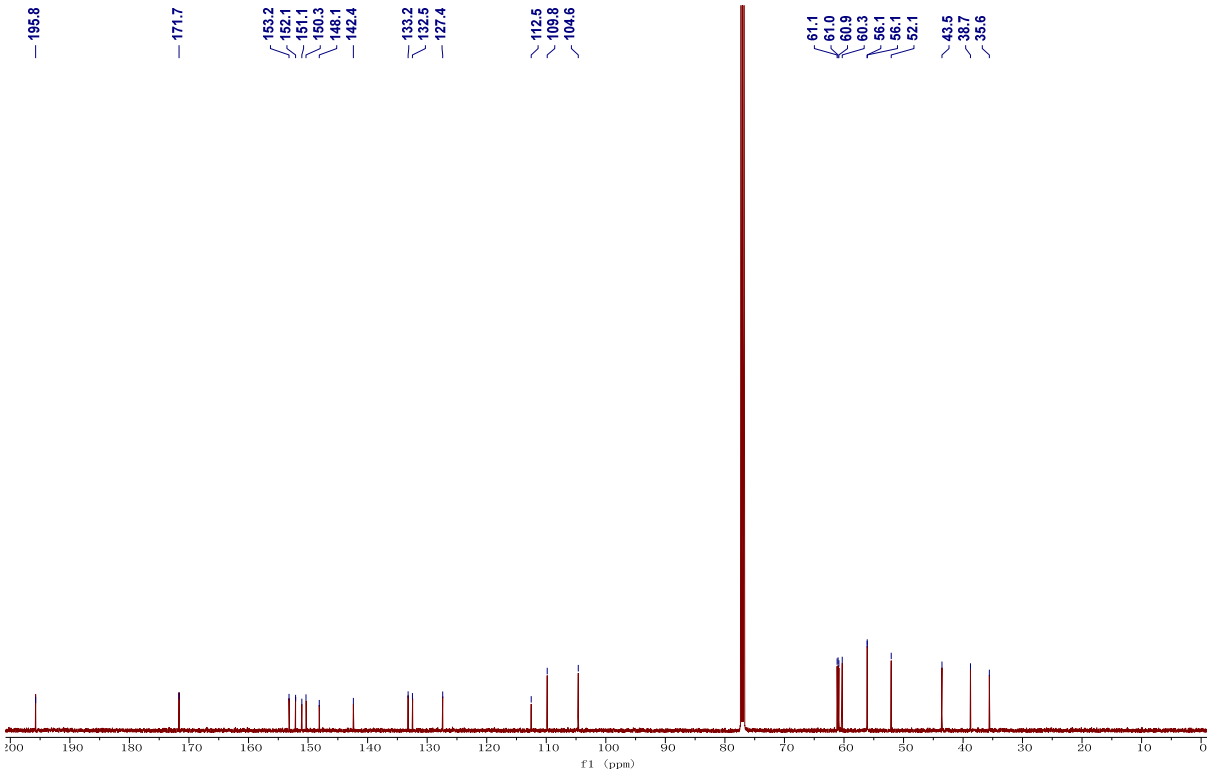


44: Methyl (1R,2R)-1-(2-bromo-3,4,5-trimethoxyphenyl)-6,7,8-trimethoxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

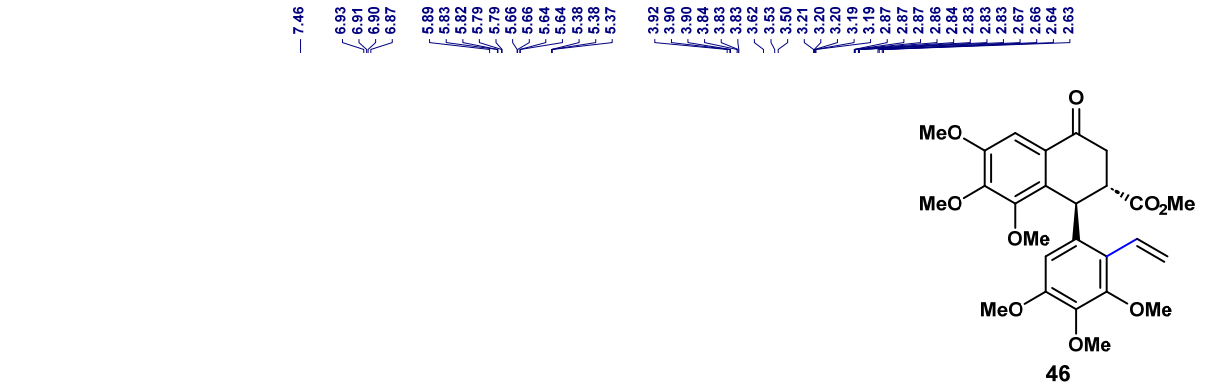


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

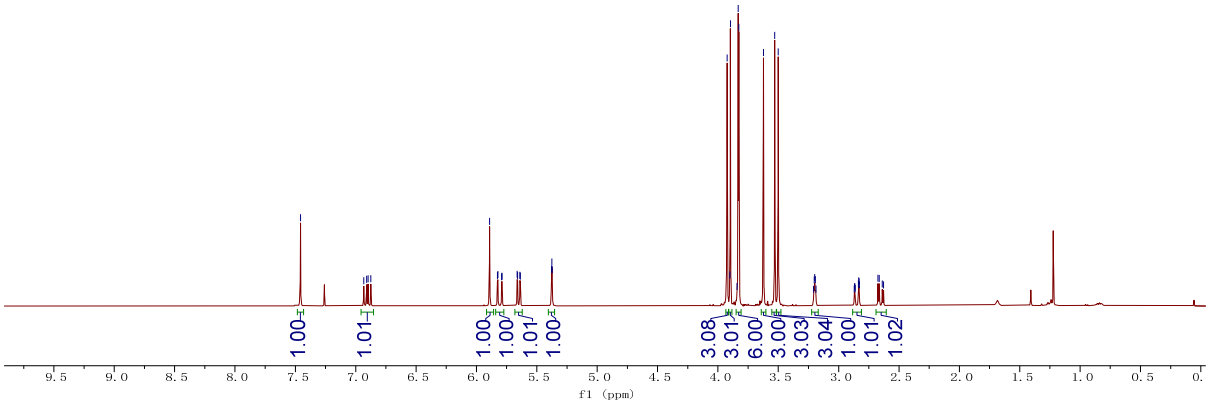


46: Methyl (1S,2S)-6,7,8-trimethoxy-4-oxo-1-(3,4,5-trimethoxy-2-vinylphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

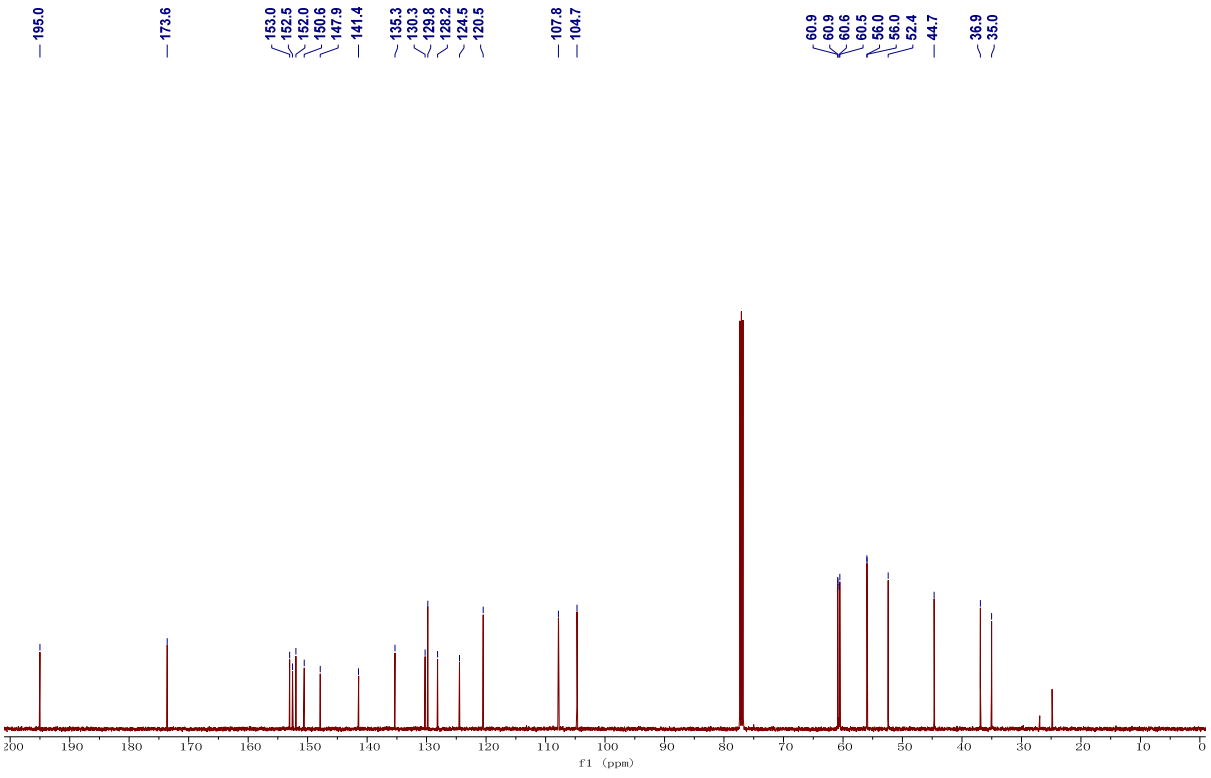
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



46

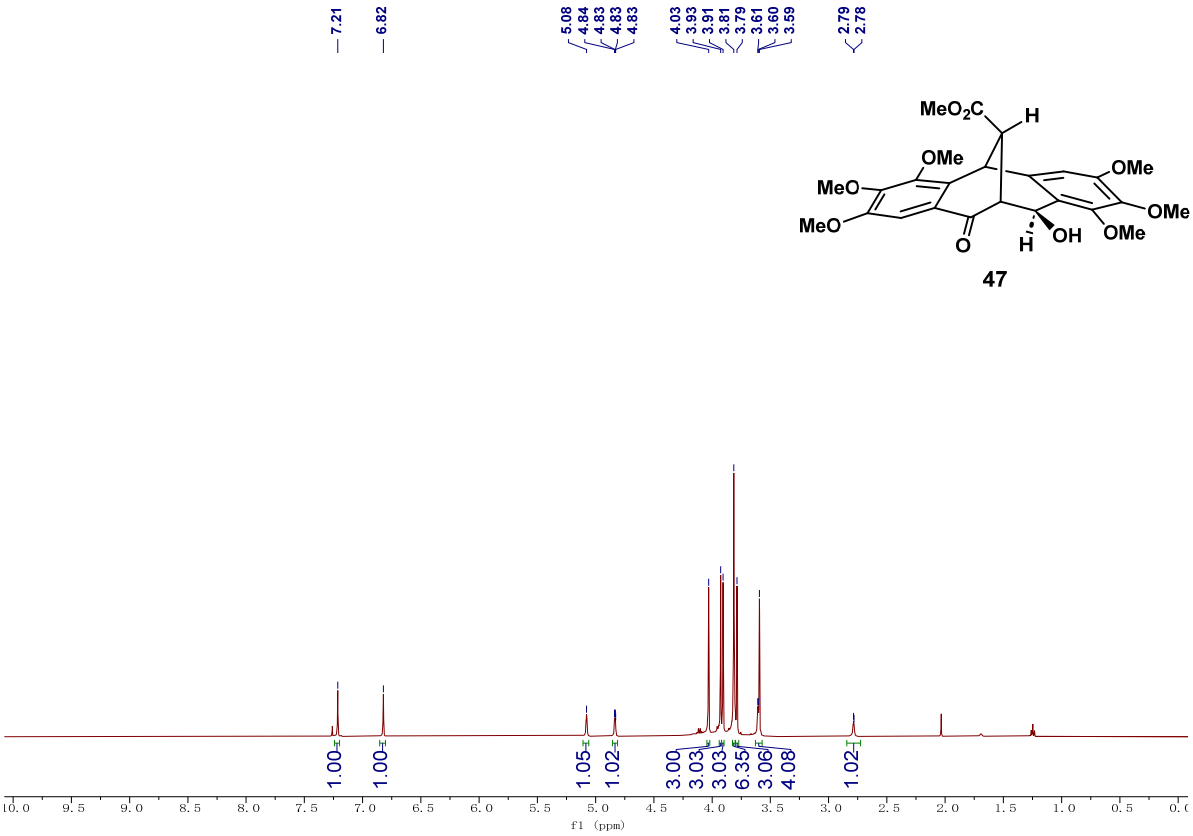


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



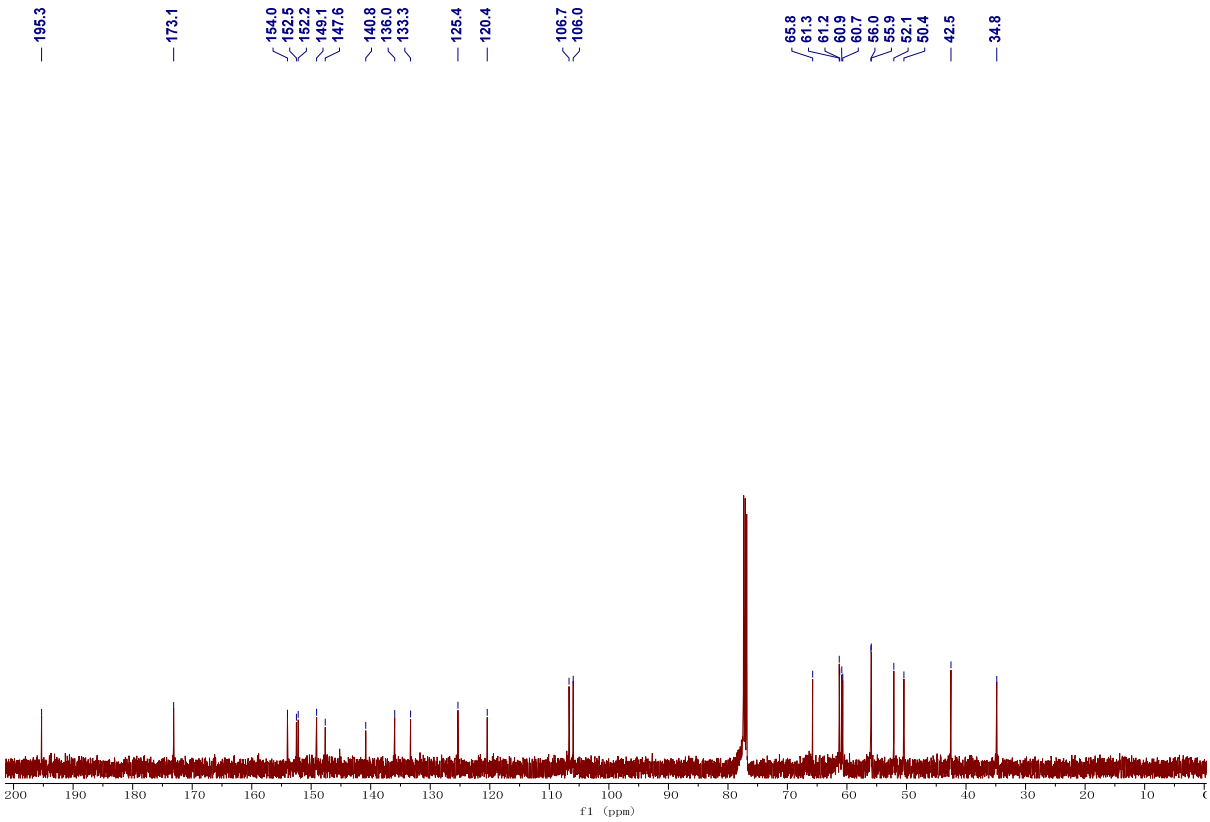
47: Methyl (7S,12S)-7-hydroxy-1,2,3,8,9,10-hexamethoxy-5-oxo-5,6,7,12-tetrahydro-6,12-methanodibenzo[a,d][8]annulene-13-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



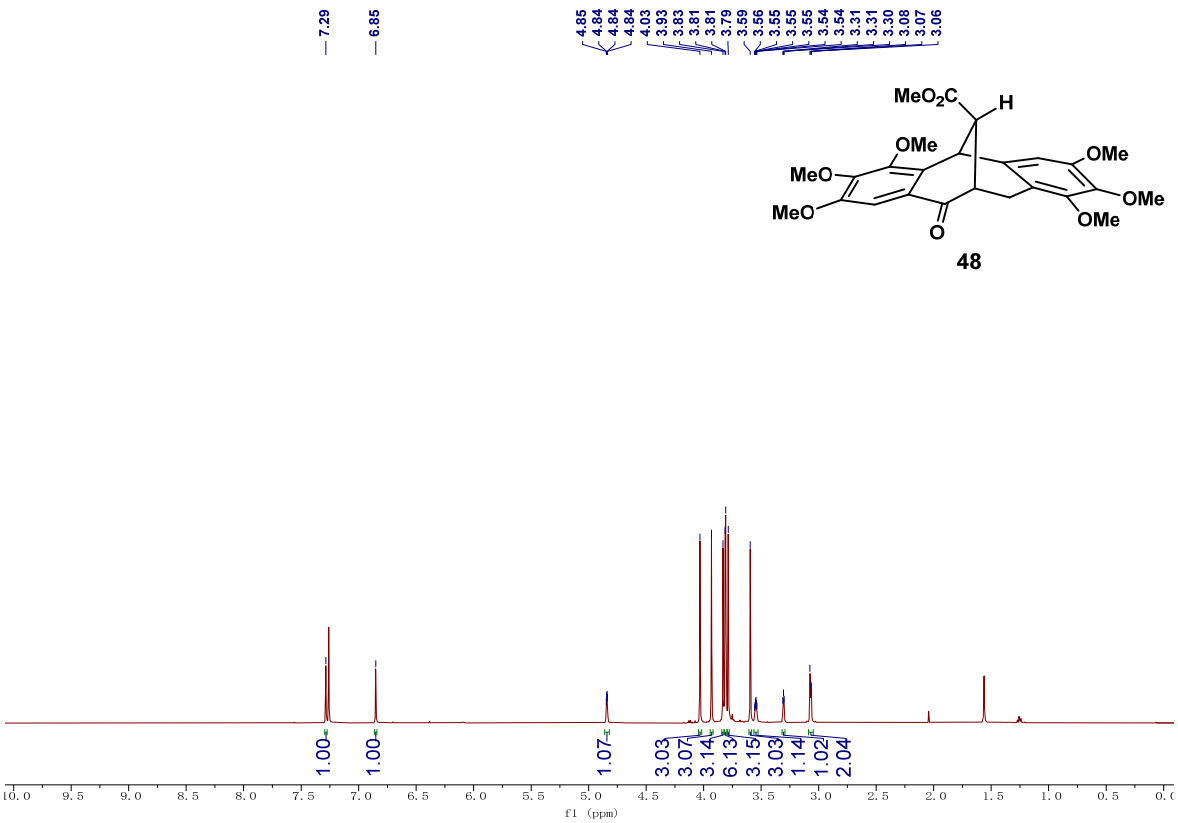
47

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

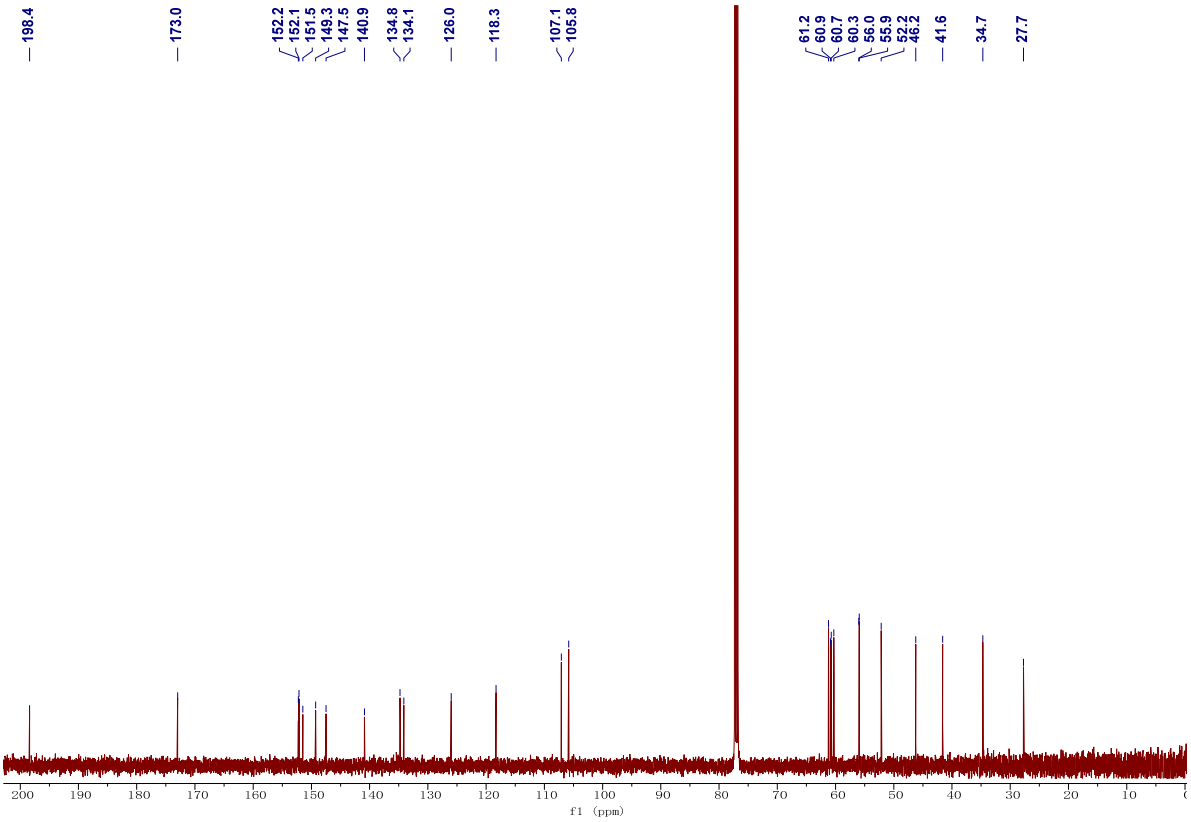


48: Methyl (12S)-1,2,3,8,9,10-hexamethoxy-5-oxo-5,6,7,12-tetrahydro-6,12-methanodibenzo[a,d][8]annulene-13-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

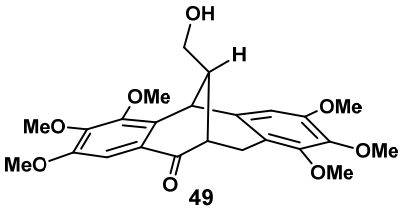


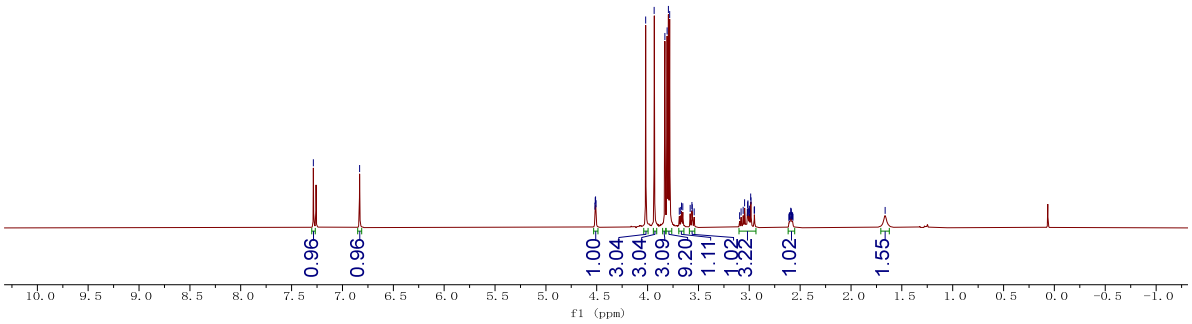
^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



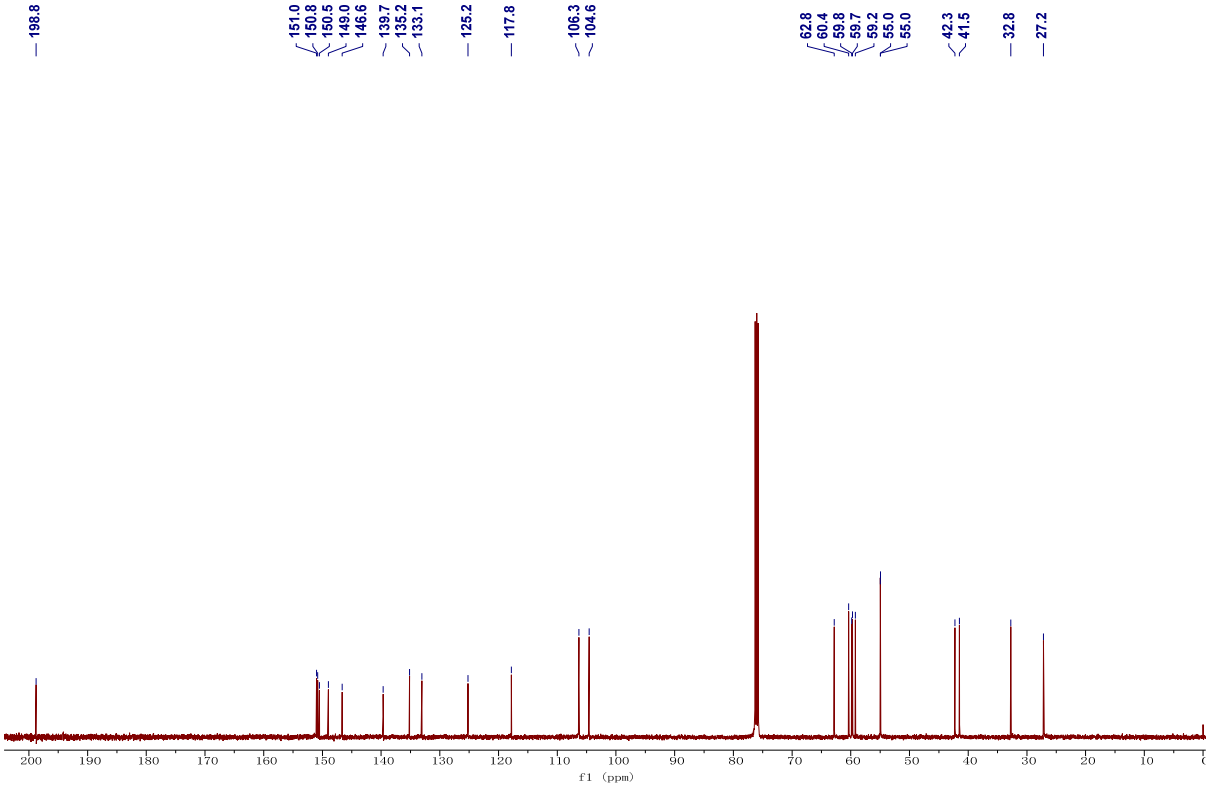
49: (12S)-13-(Hydroxymethyl)-1,2,3,8,9,10-hexamethoxy-7,12-dihydro-6,12-methanodibenz-o[a,d][8]annulen-5(6H)-one

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



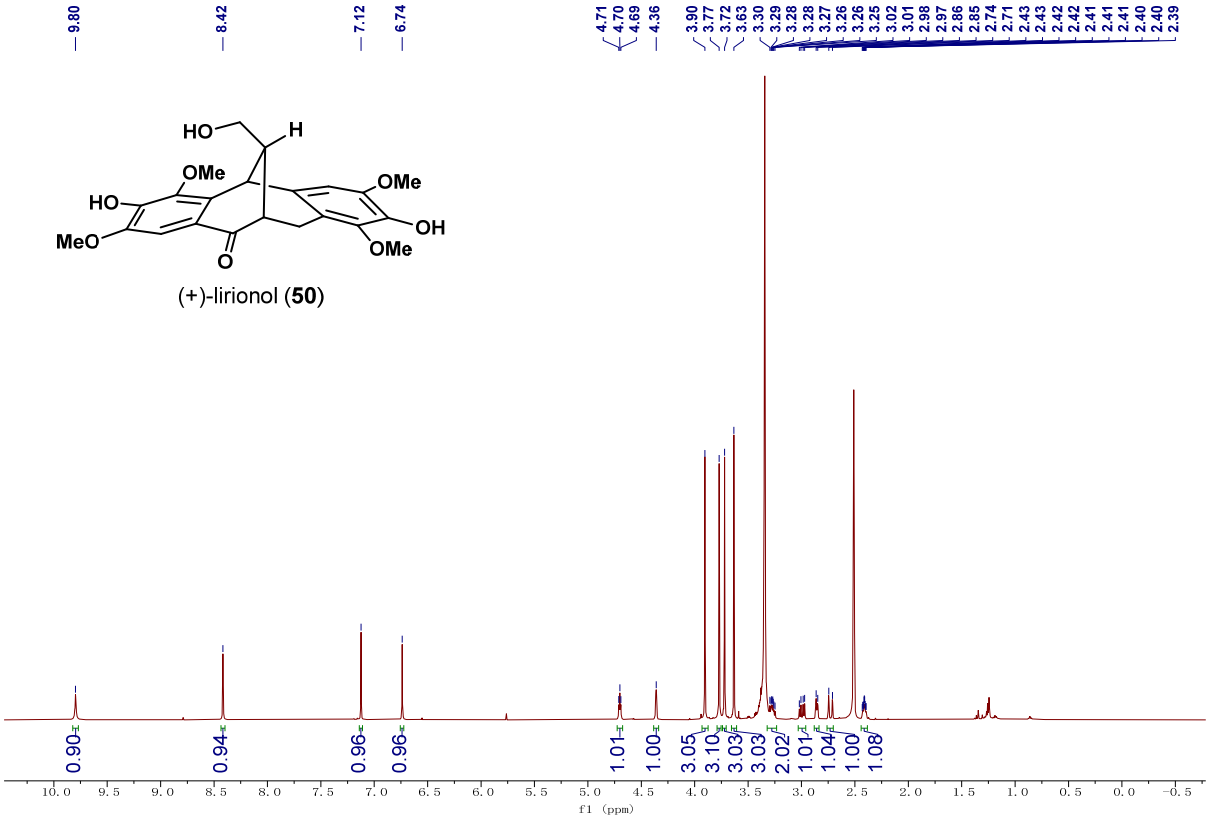


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



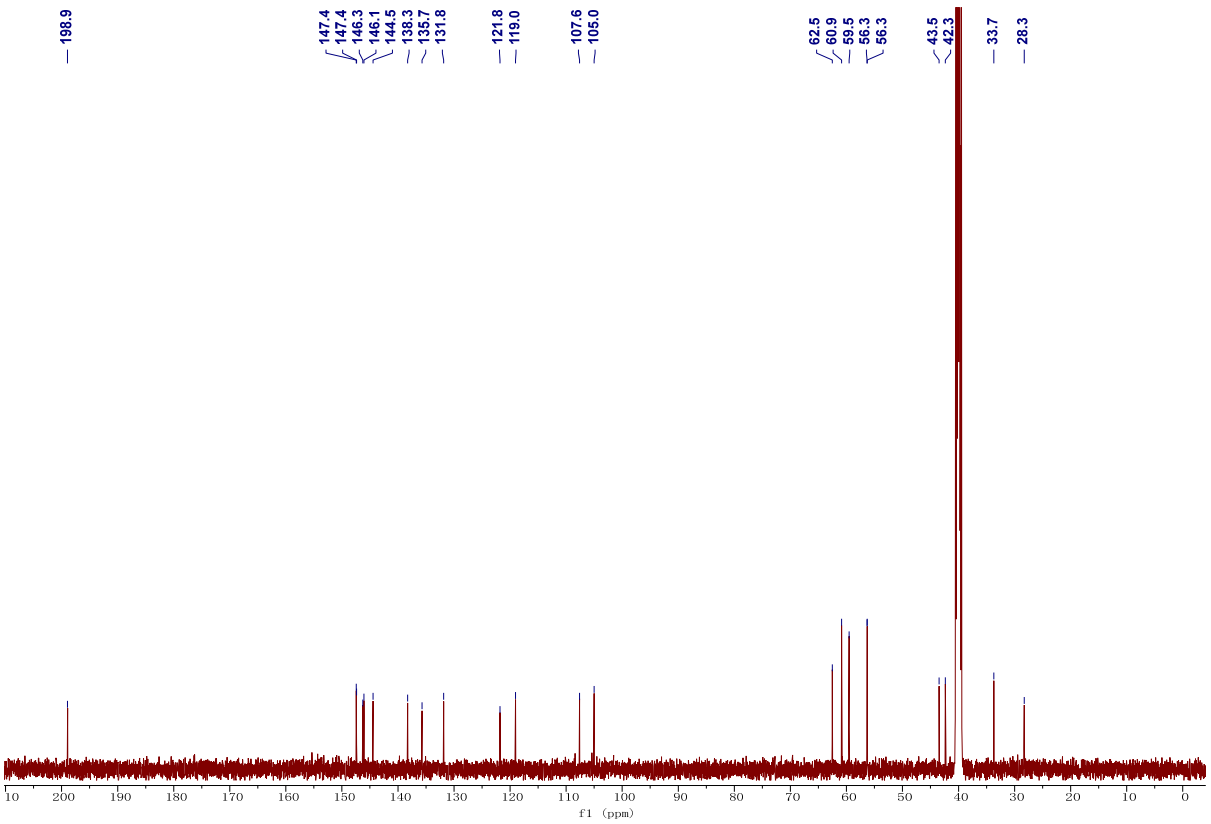
50: (+)-Lirionol

[1]H NMR (500 MHz, DMSO-d6 @ 2.50 ppm)



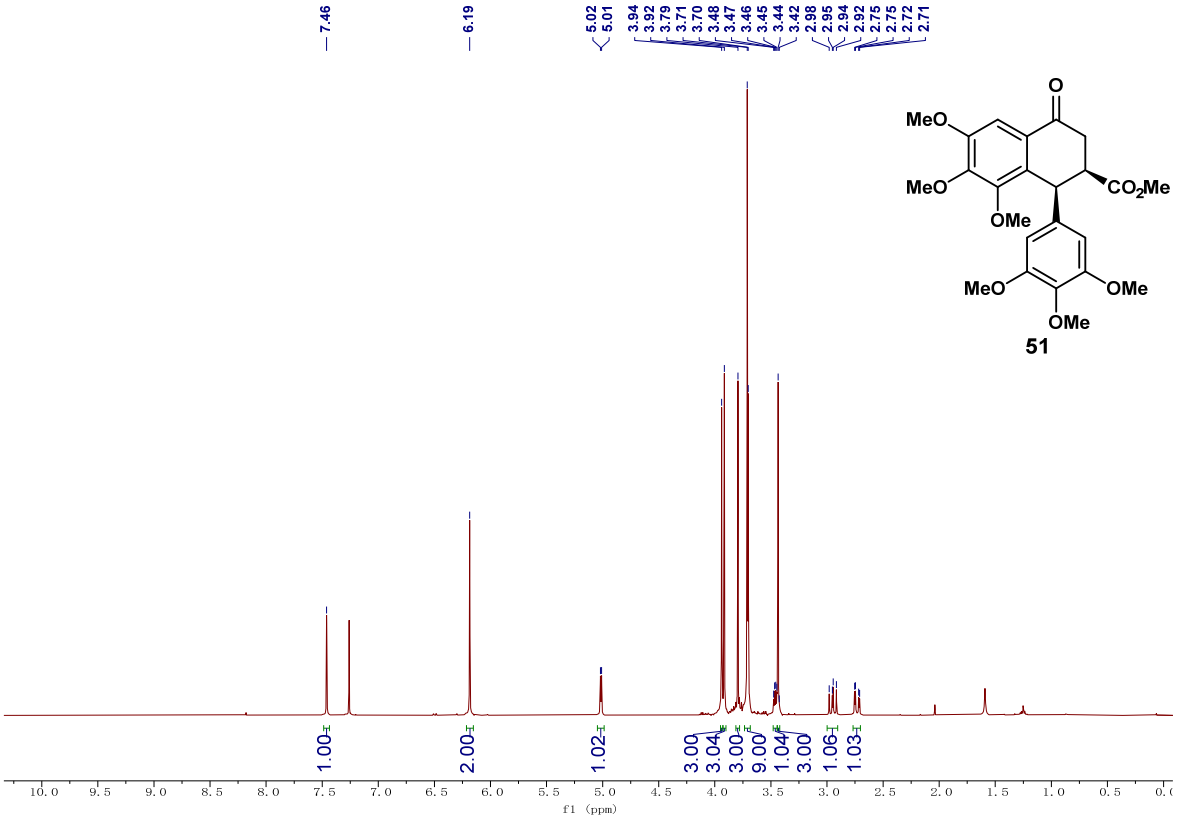
(+)-lirionol (**50**)

[13]C NMR (125 MHz, DMSO-d6 @ 39.51 ppm)

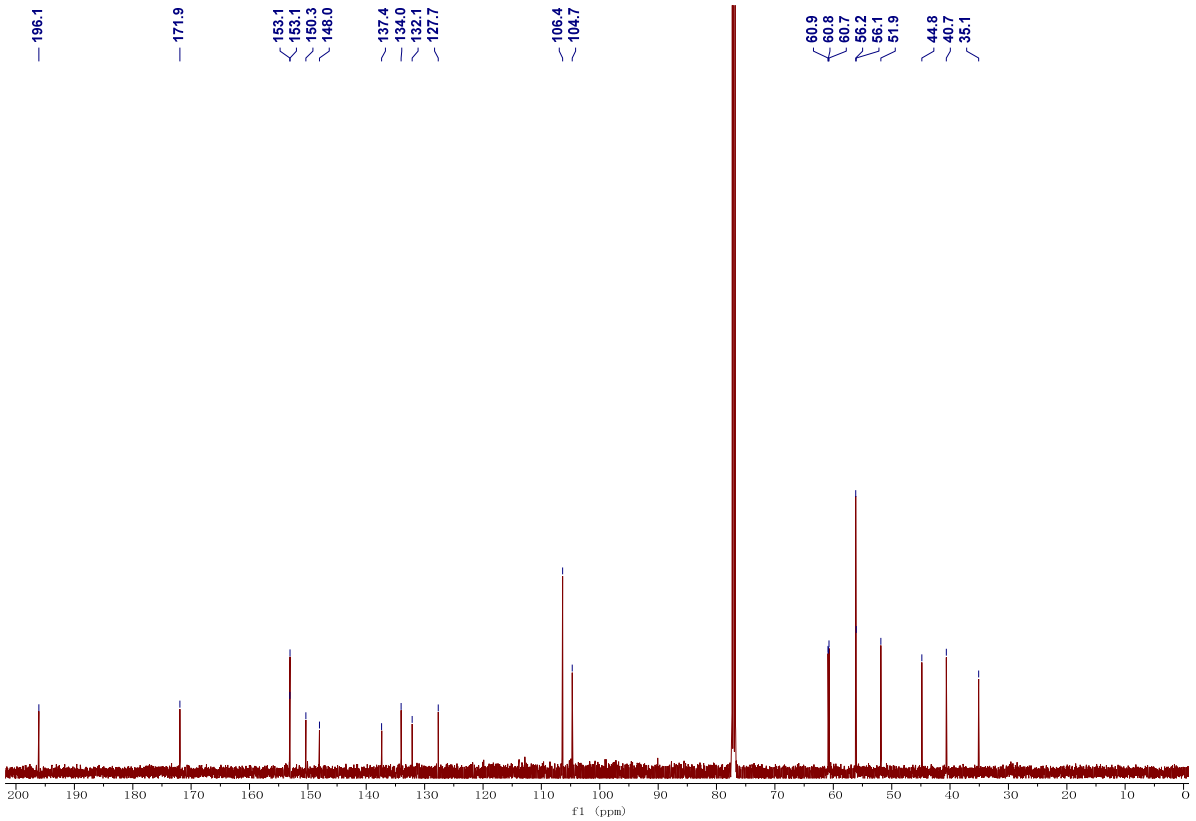


51: Methyl (1S,2R)-6,7,8-trimethoxy-4-oxo-1-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

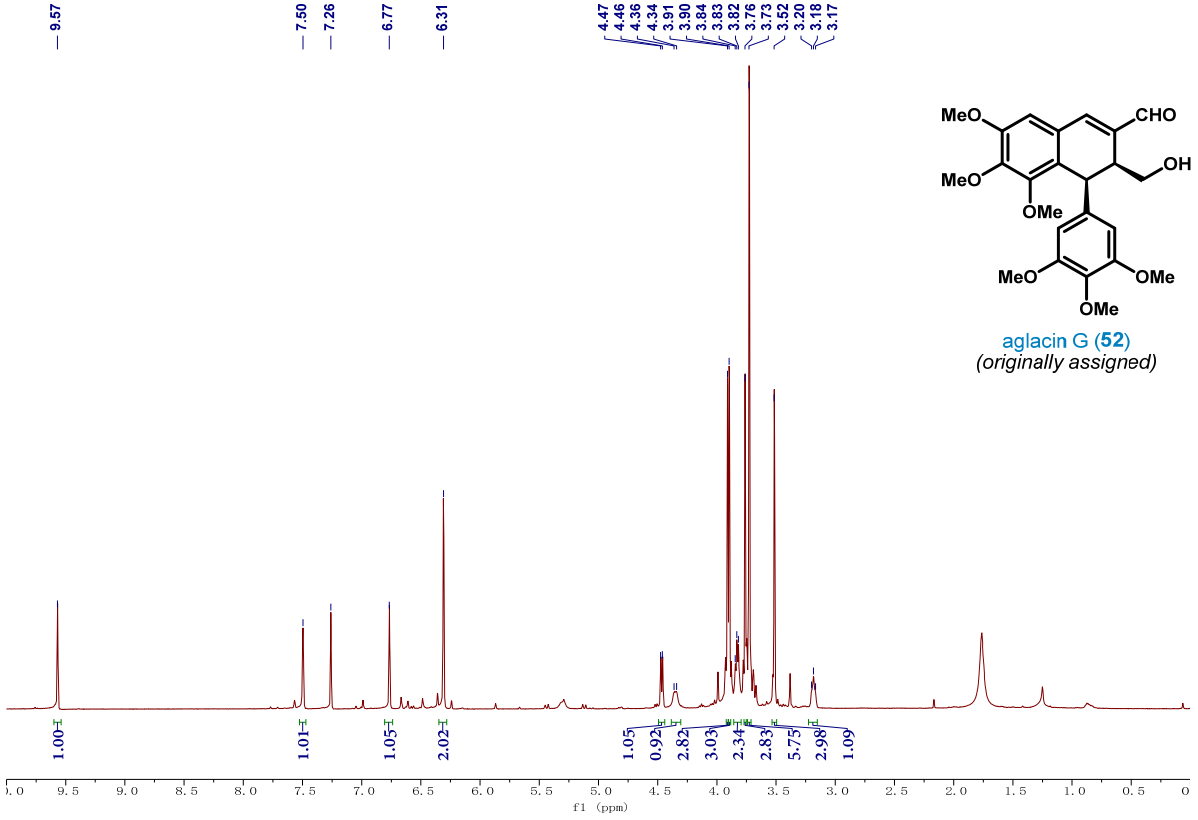


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



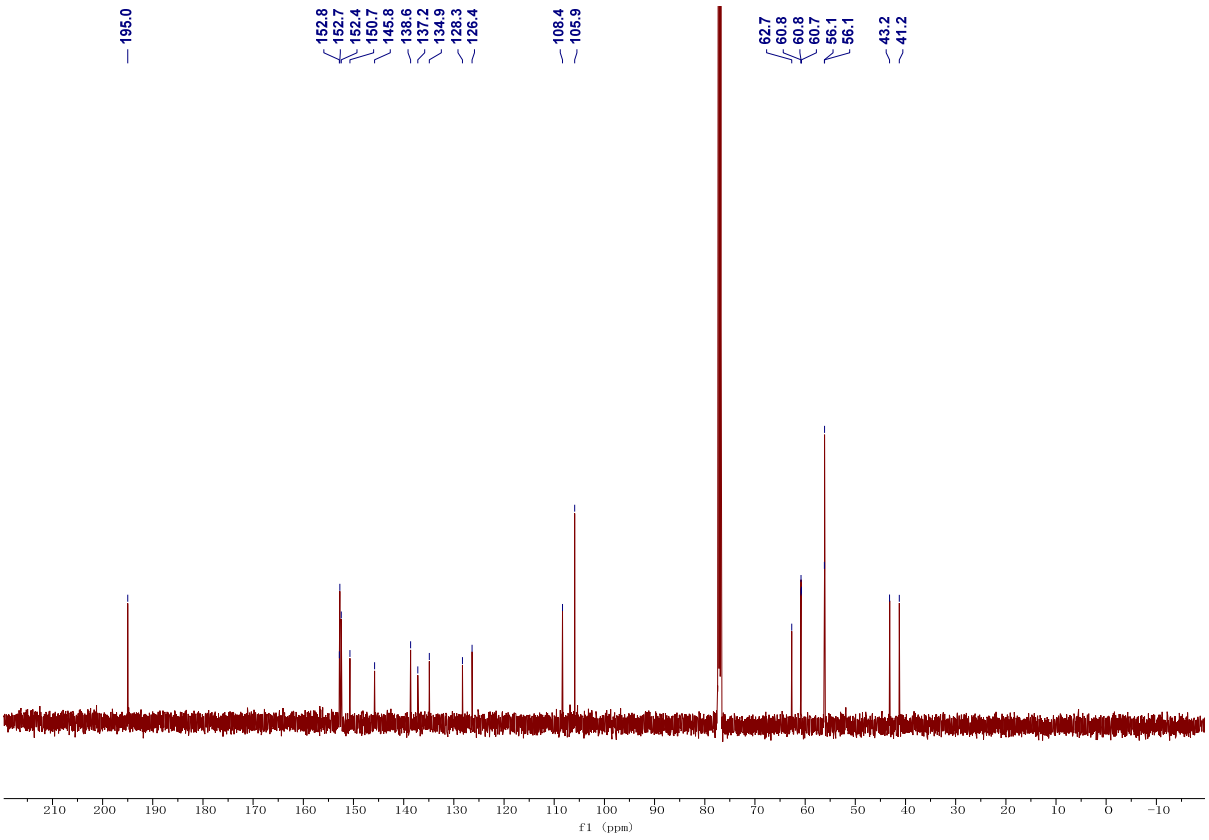
52: Originally assigned structure of aglacin G

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



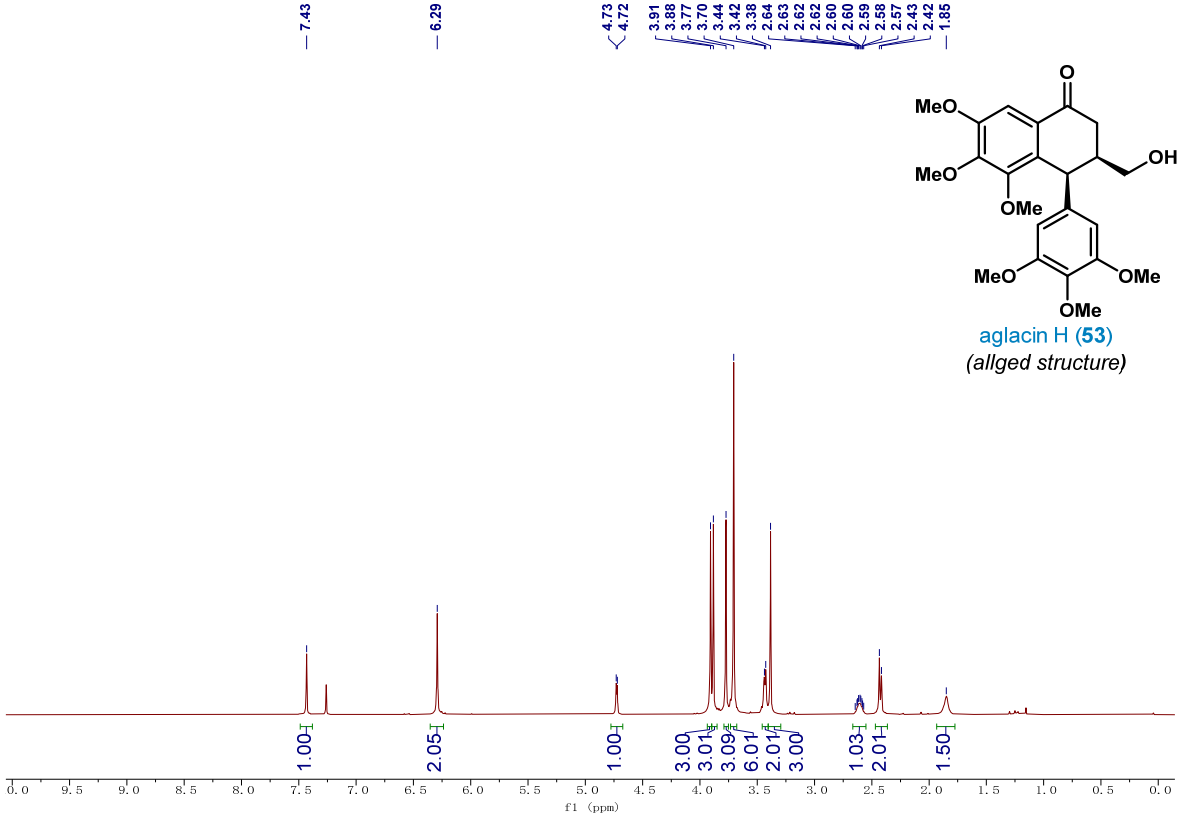
aglacin G (**52**)
(originally assigned)

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



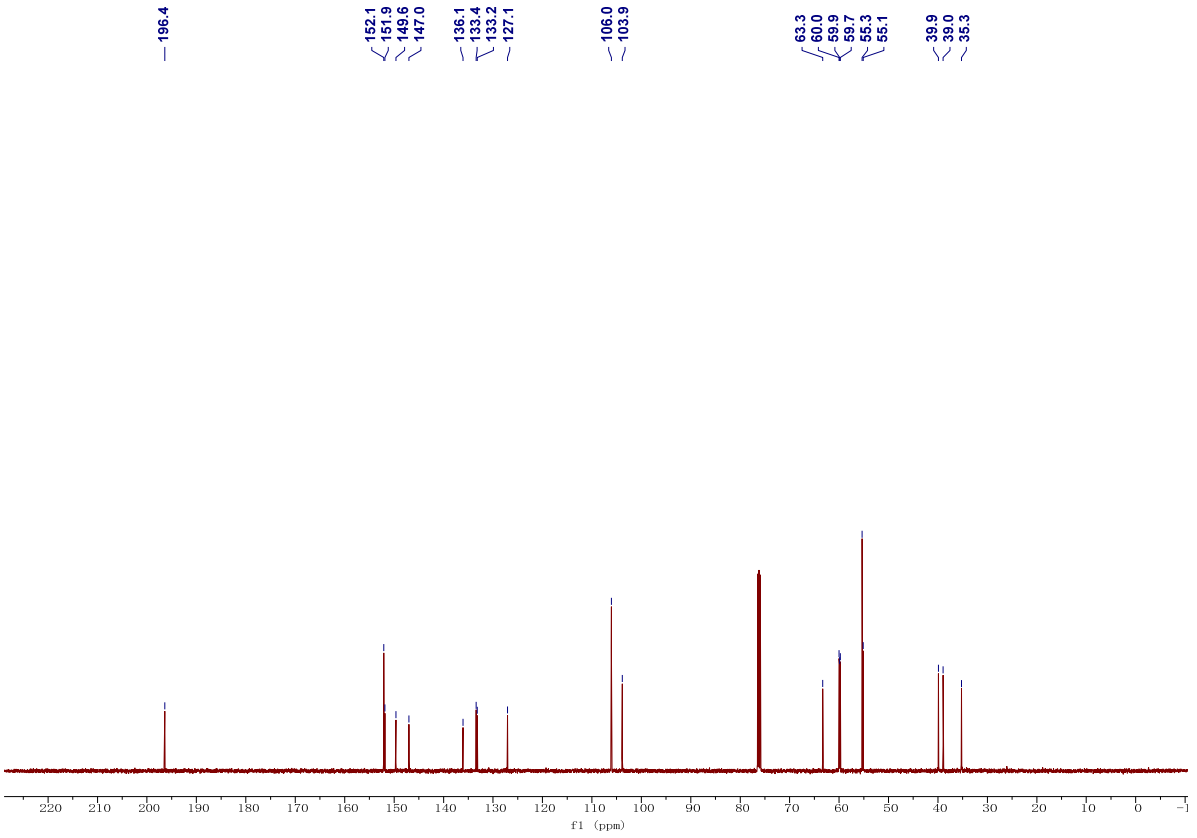
53: Originally assigned structure of aglacin H

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



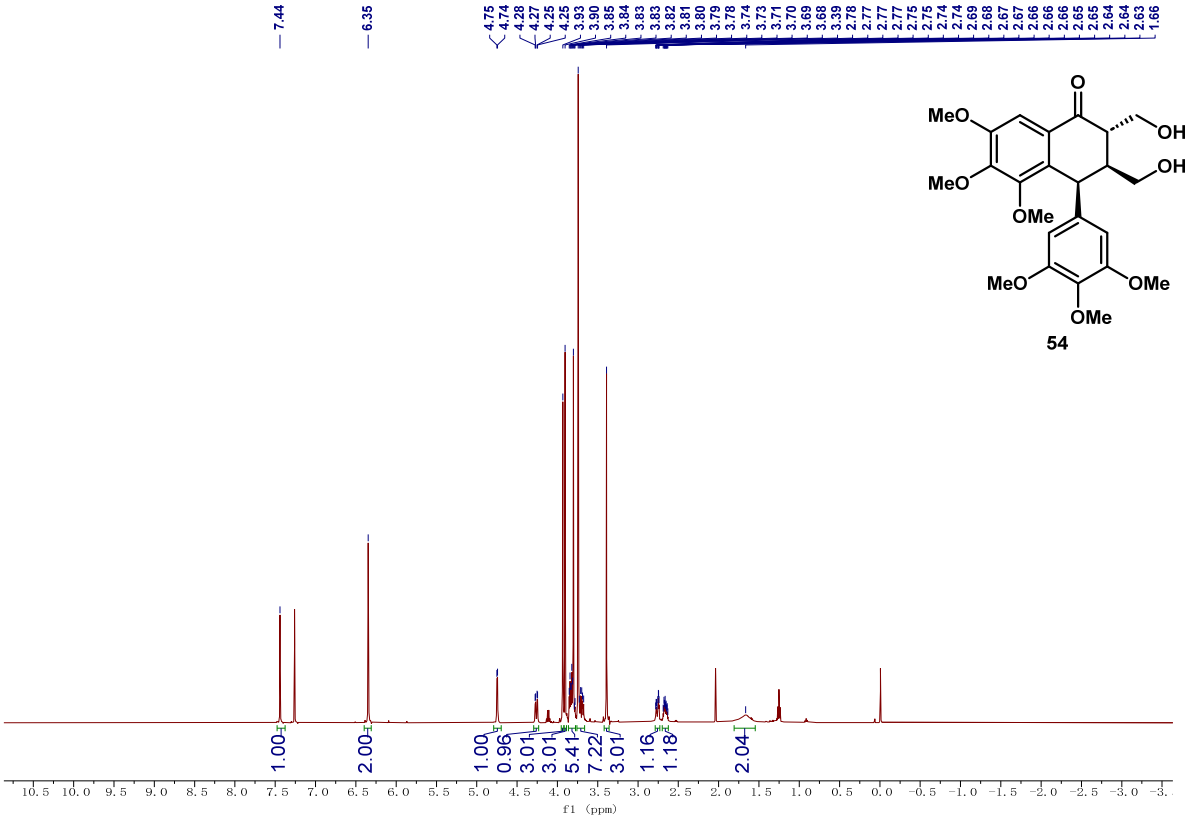
aglacin H (**53**)
(allged structure)

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



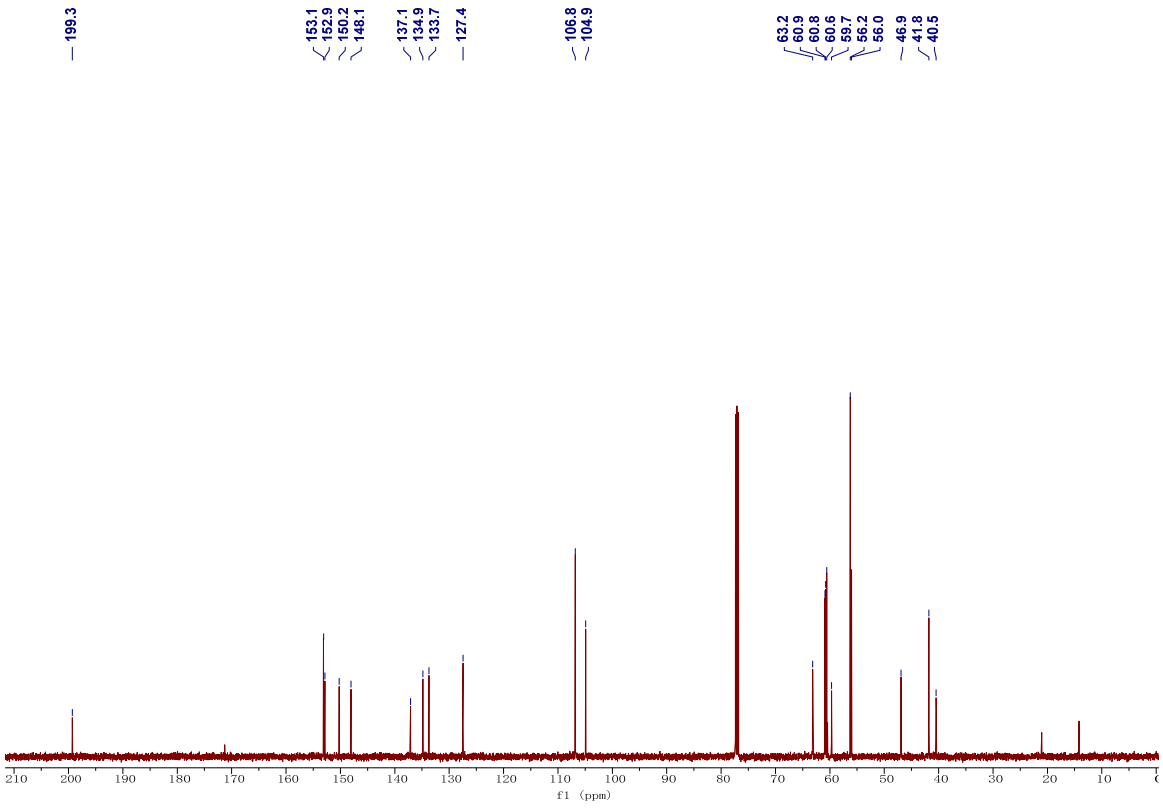
54: (2S,3S,4S)-2,3-Bis(hydroxymethyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



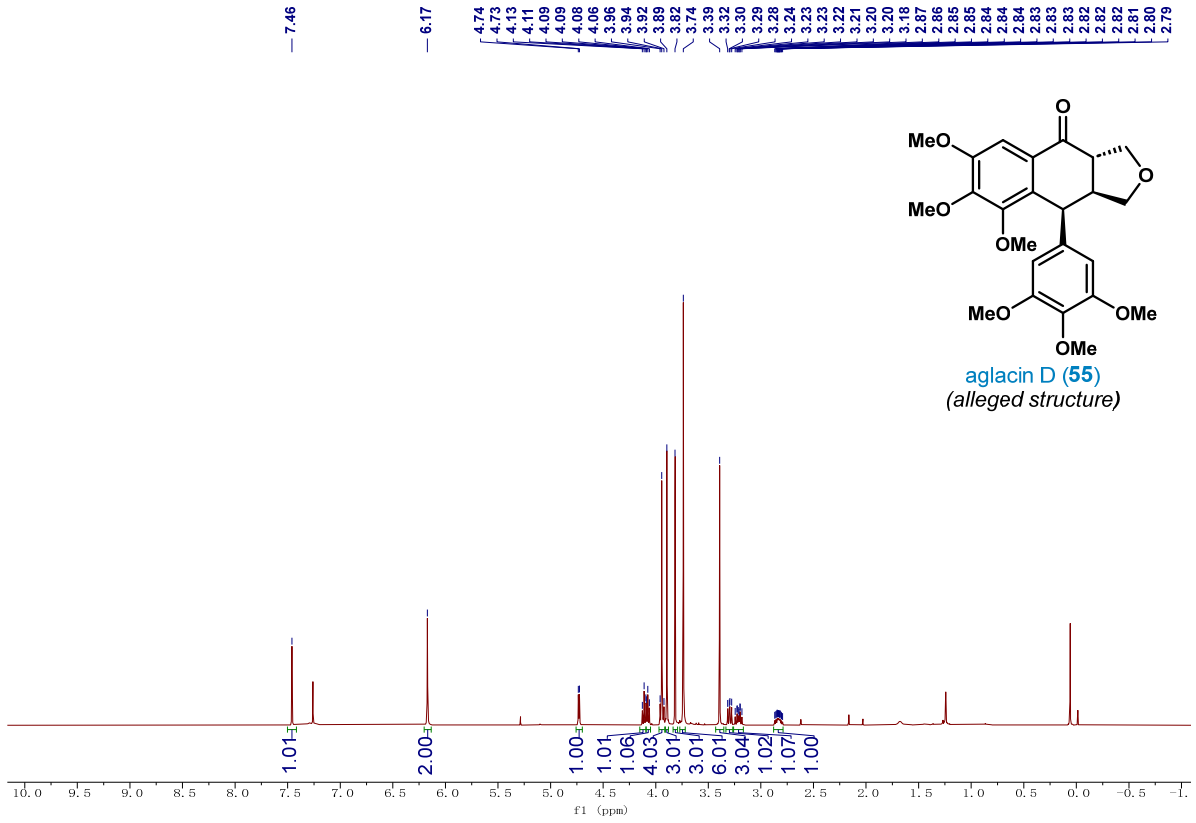
54

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



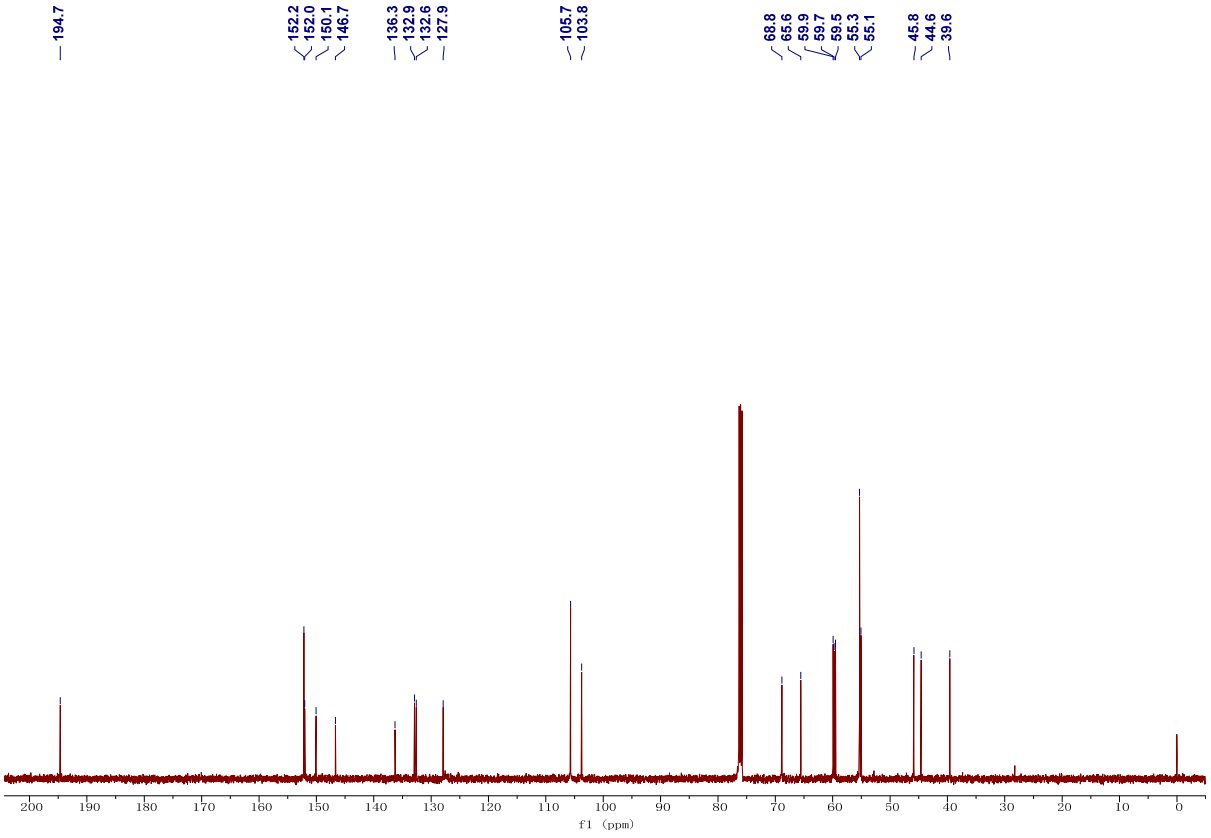
55: Originally assigned structure of aglacin D

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



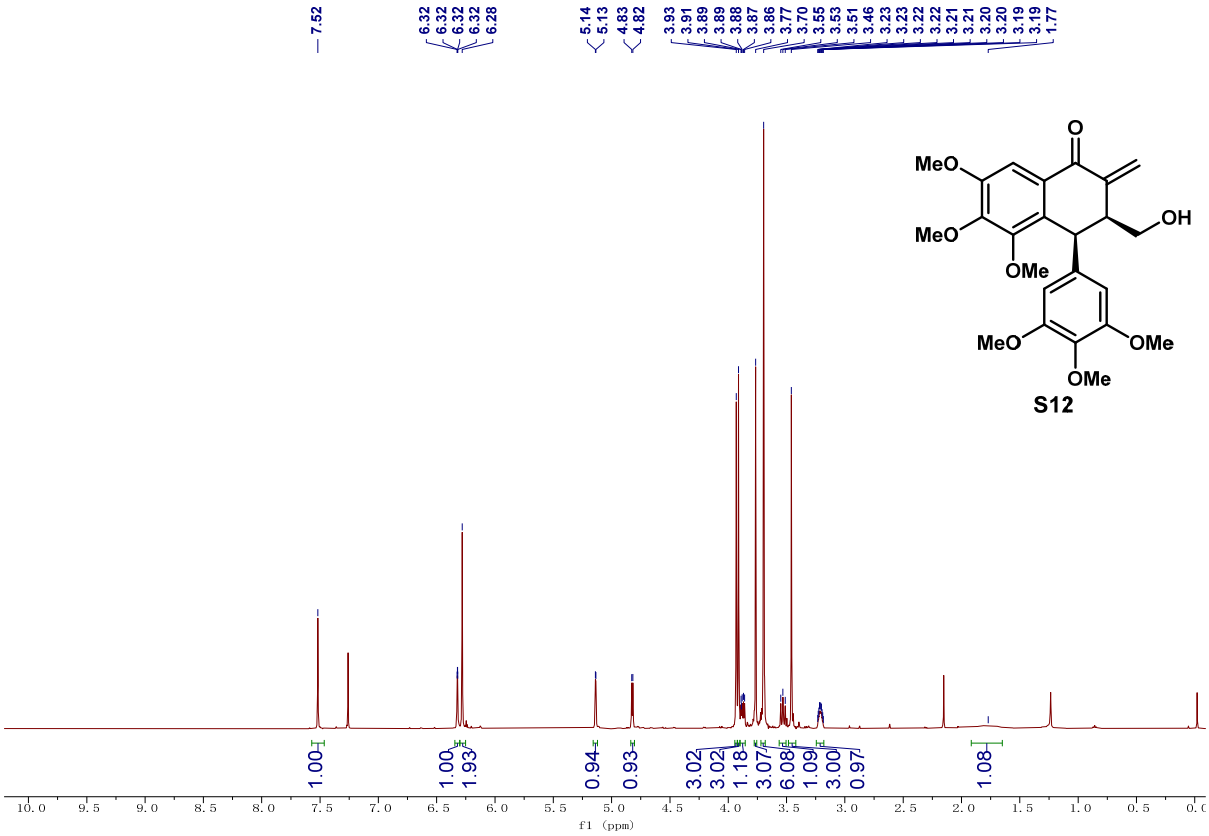
aglacin D (**55**)
(alleged structure)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

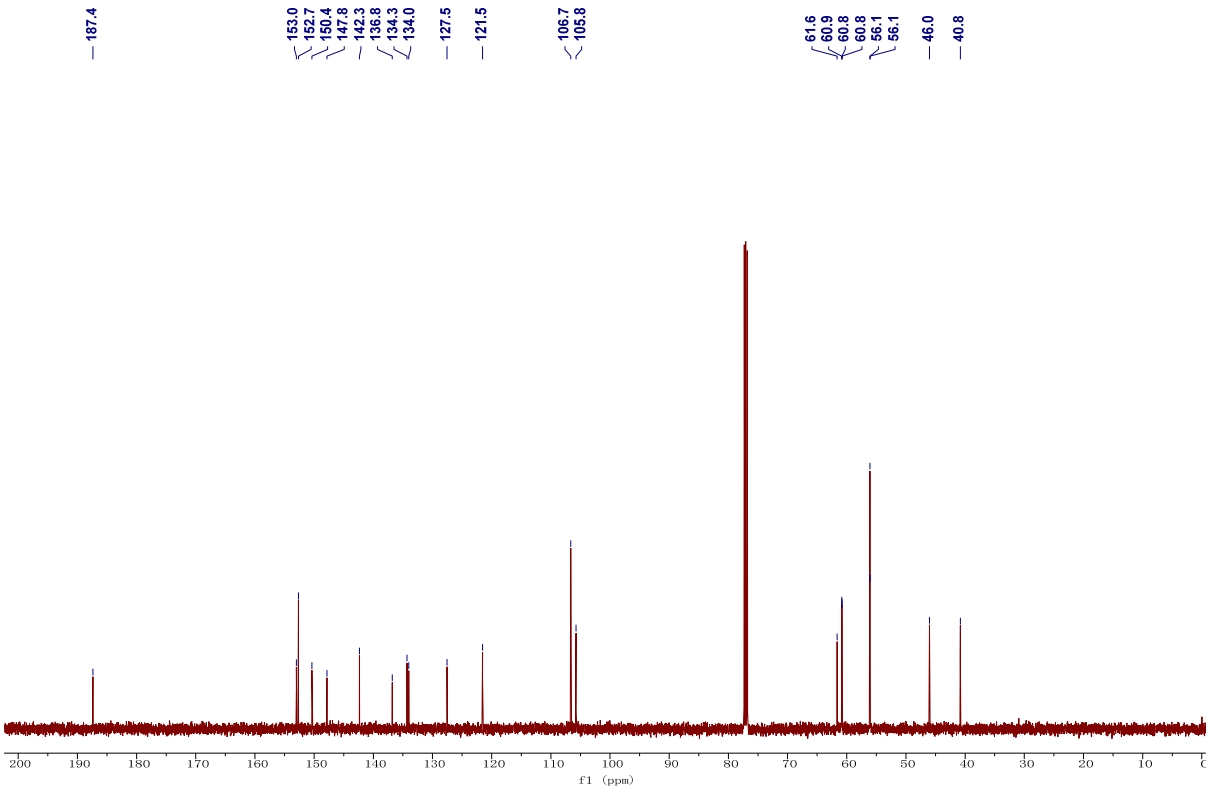


S12: (3S,4S)-3-(Hydroxymethyl)-5,6,7-trimethoxy-2-methylene-4-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

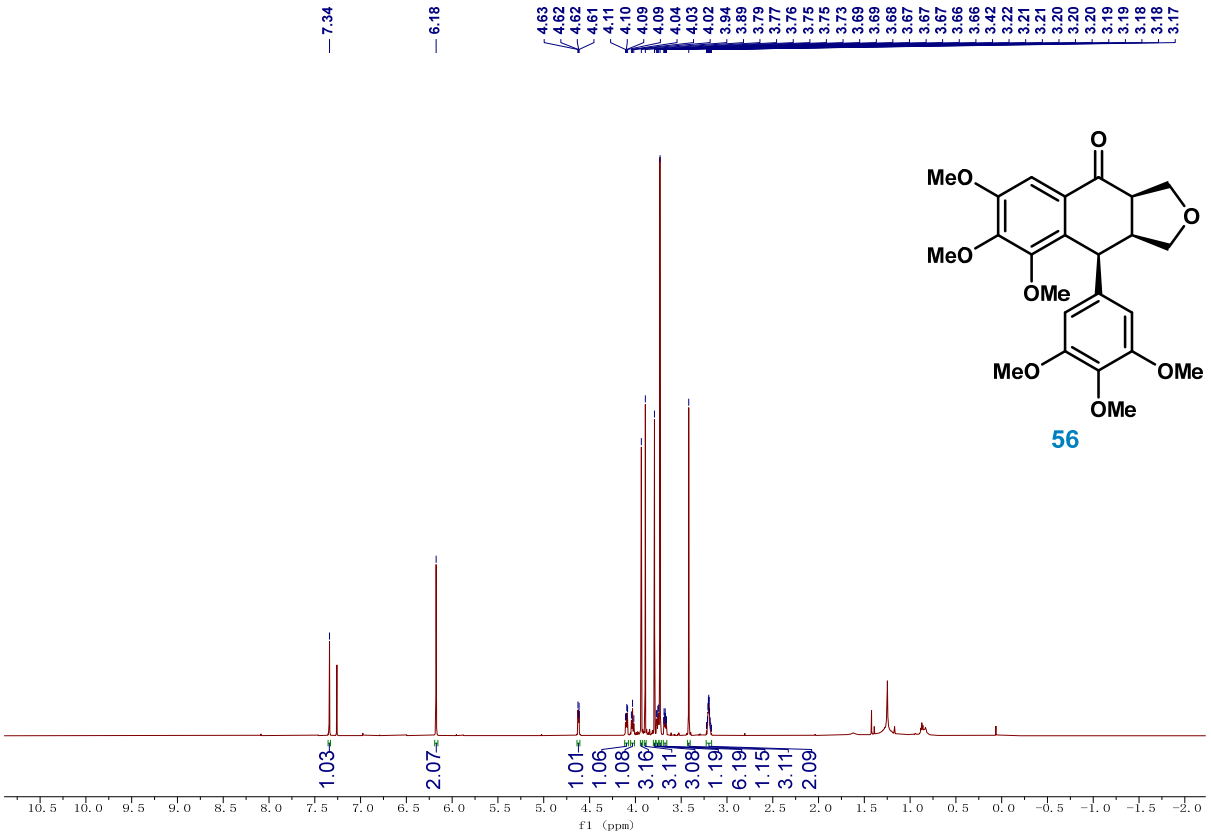


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



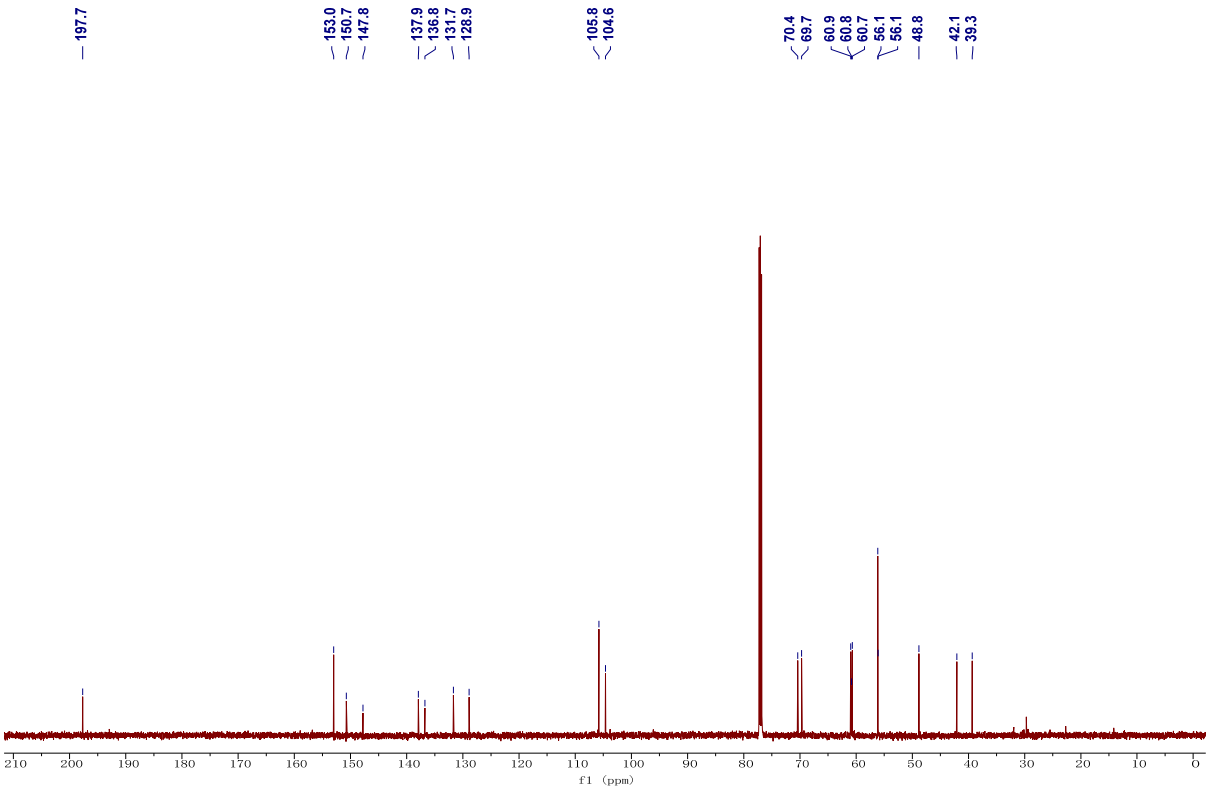
56: (3aS,9S,9aS)-6,7,8-Trimethoxy-9-(3,4,5-trimethoxyphenyl)-3,3a,9,9a-tetrahydronaphtho-[2,3-c]furan-4(1H)-one

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



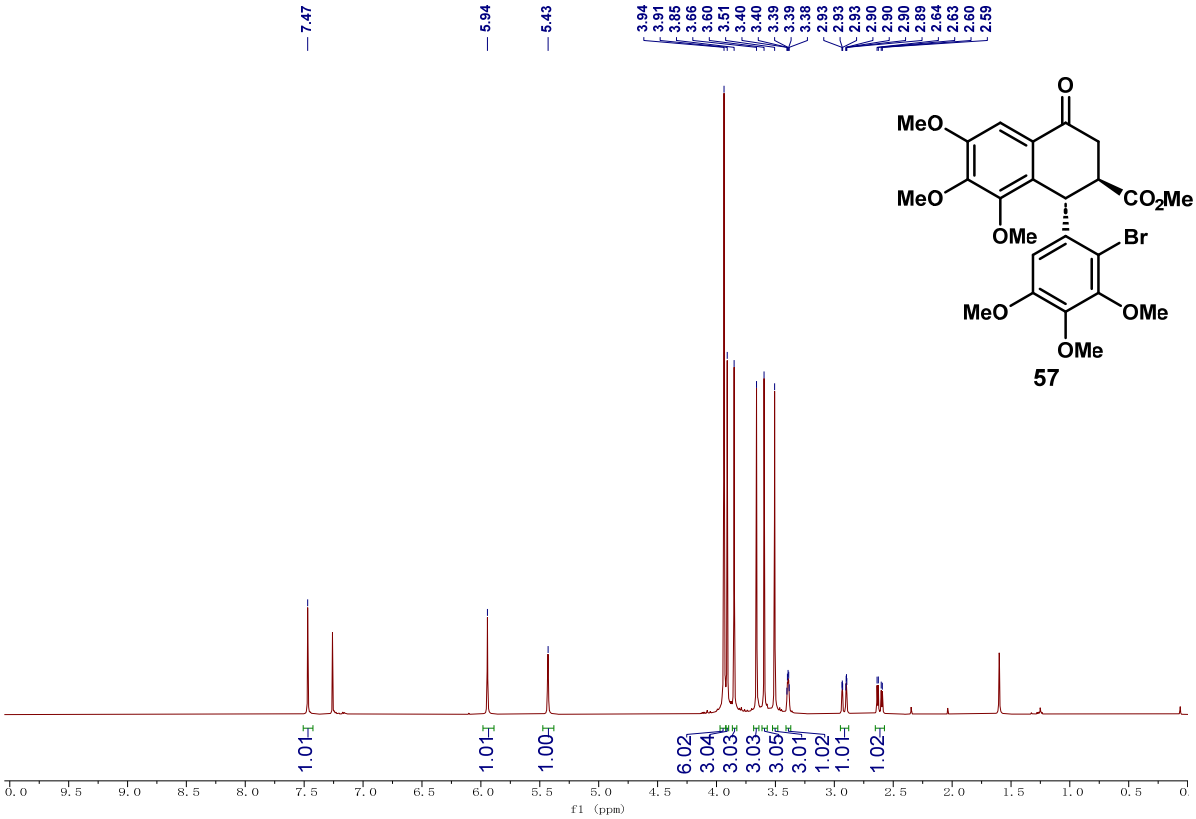
56

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



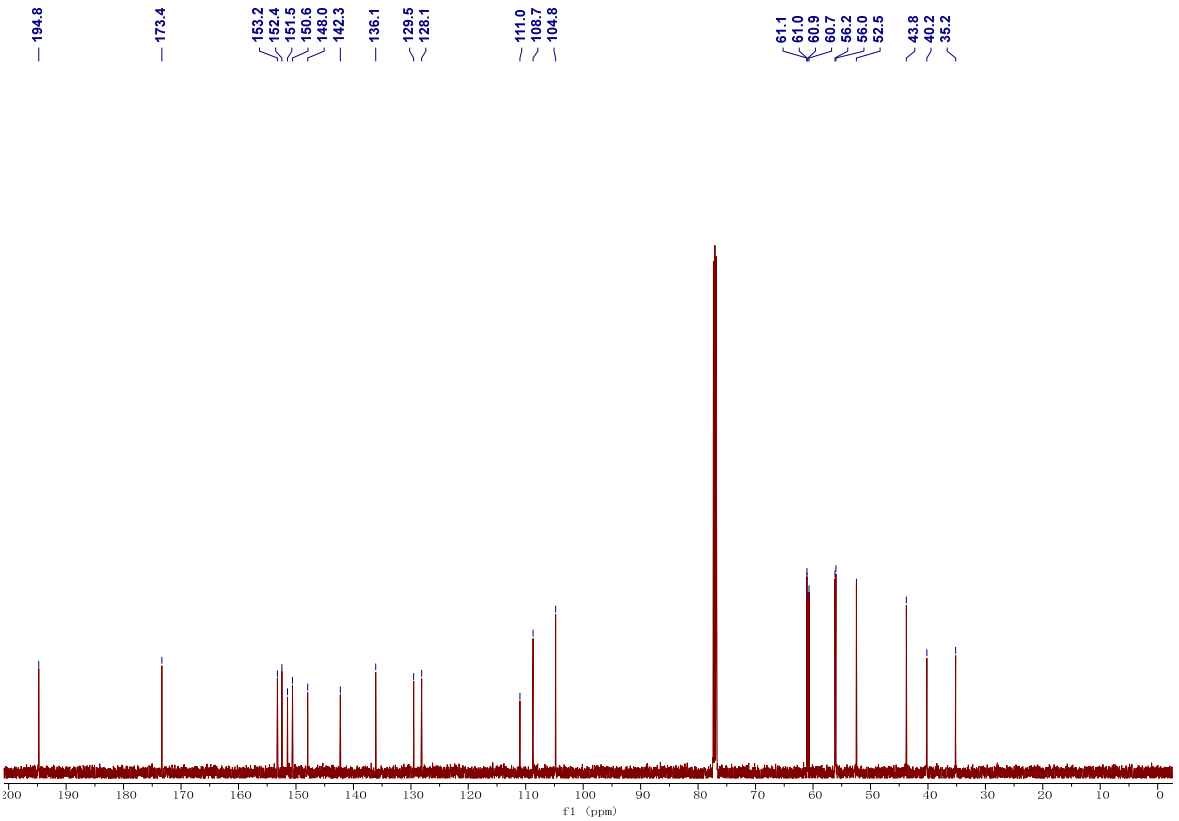
57: Methyl (1S,2R)-1-(2-bromo-3,4,5-trimethoxyphenyl)-6,7,8-trimethoxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



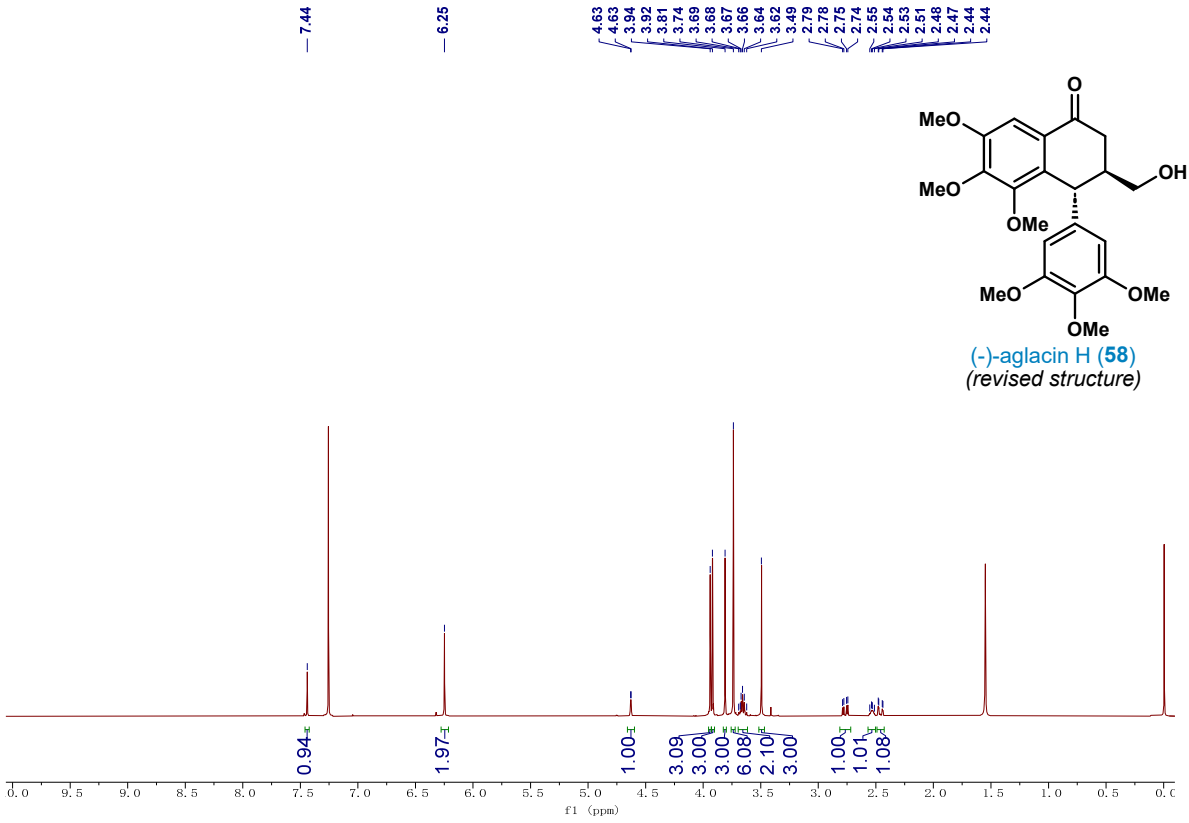
57

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



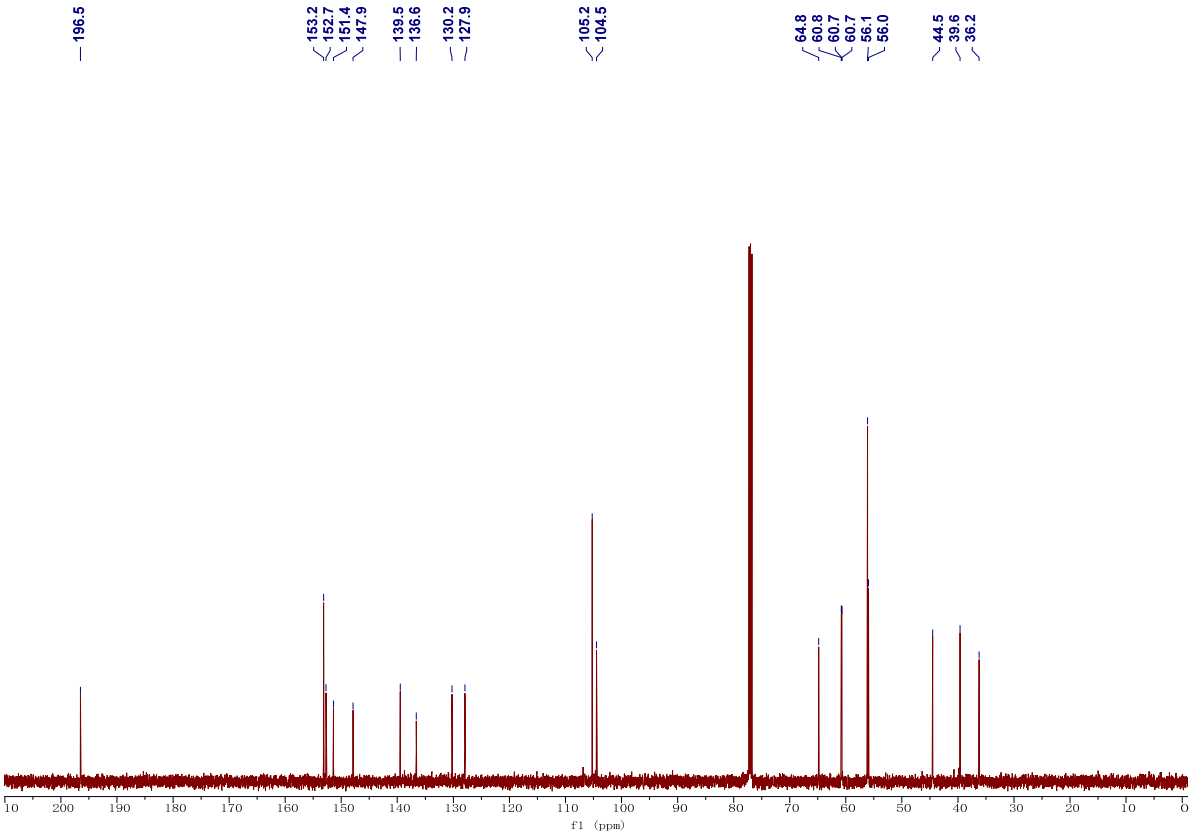
58: (-)-Aglacin H (revised structure)

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



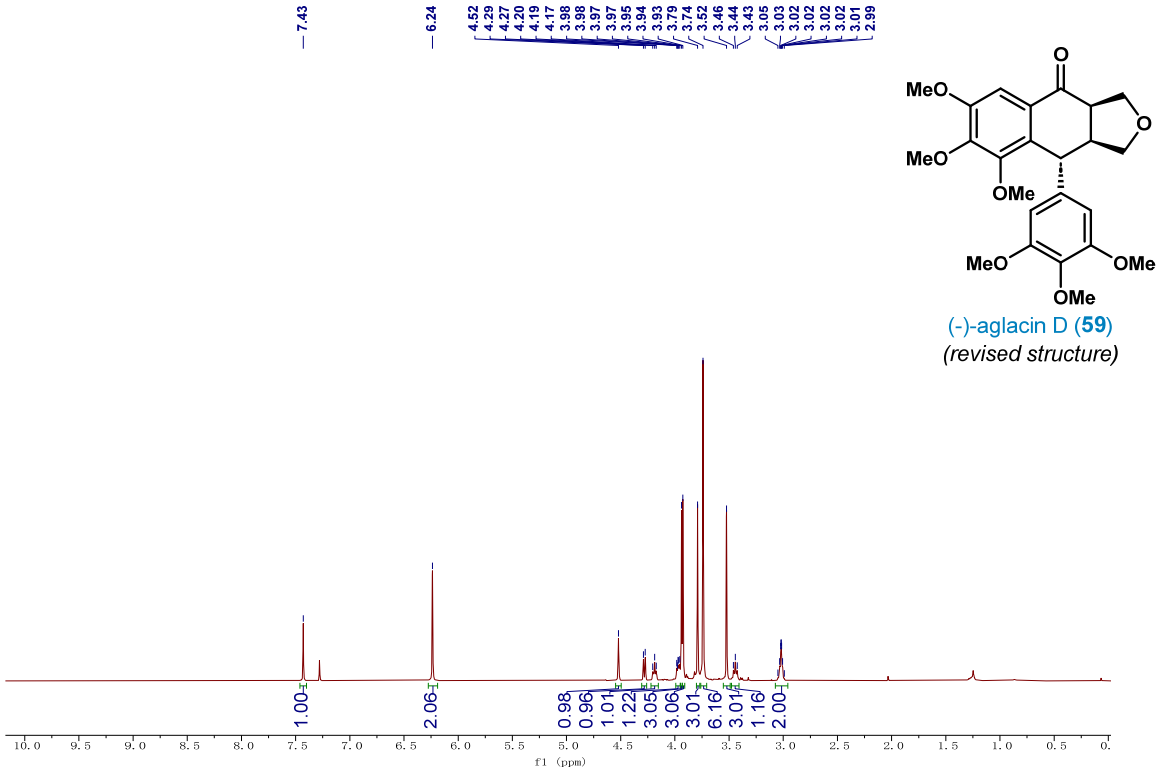
(-)-aglacin H (**58**)
(revised structure)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



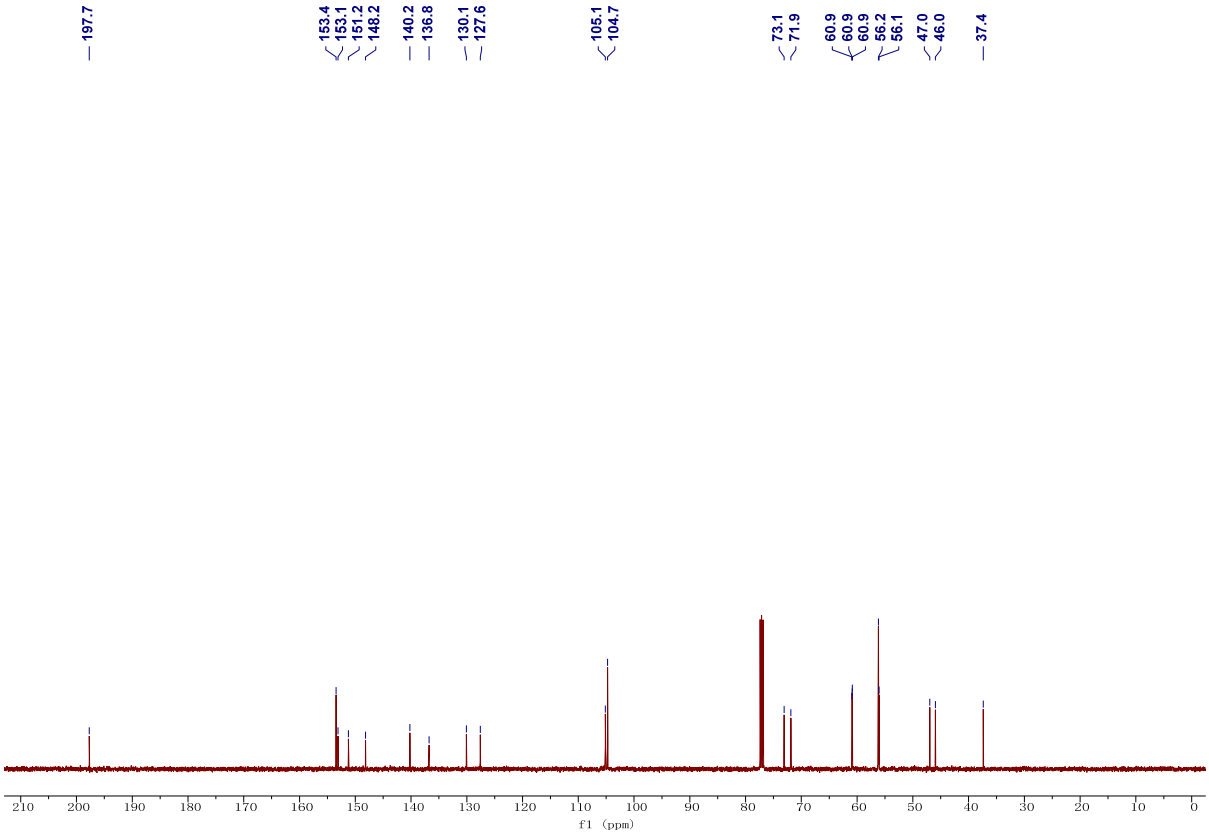
59: (-)-Aglacin D (revised structure)

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



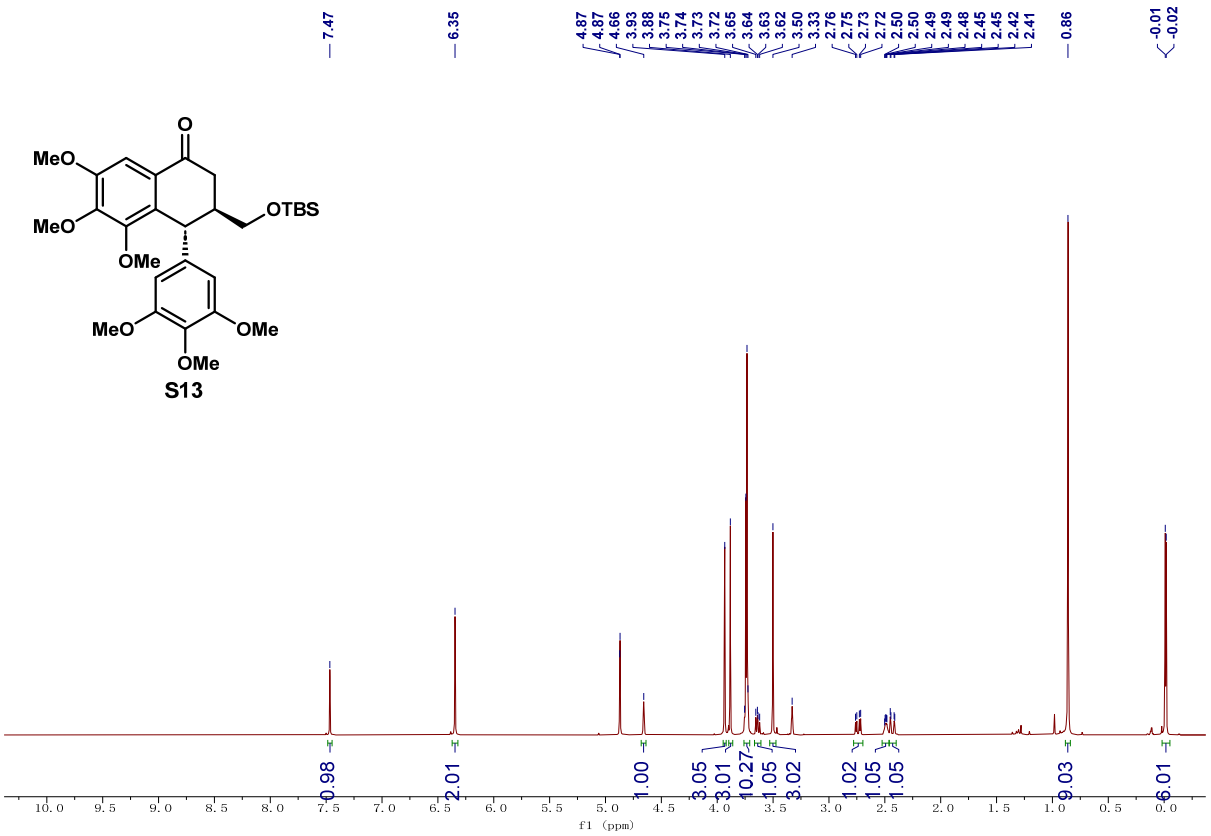
(-)-aglacin D (**59**)
(revised structure)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

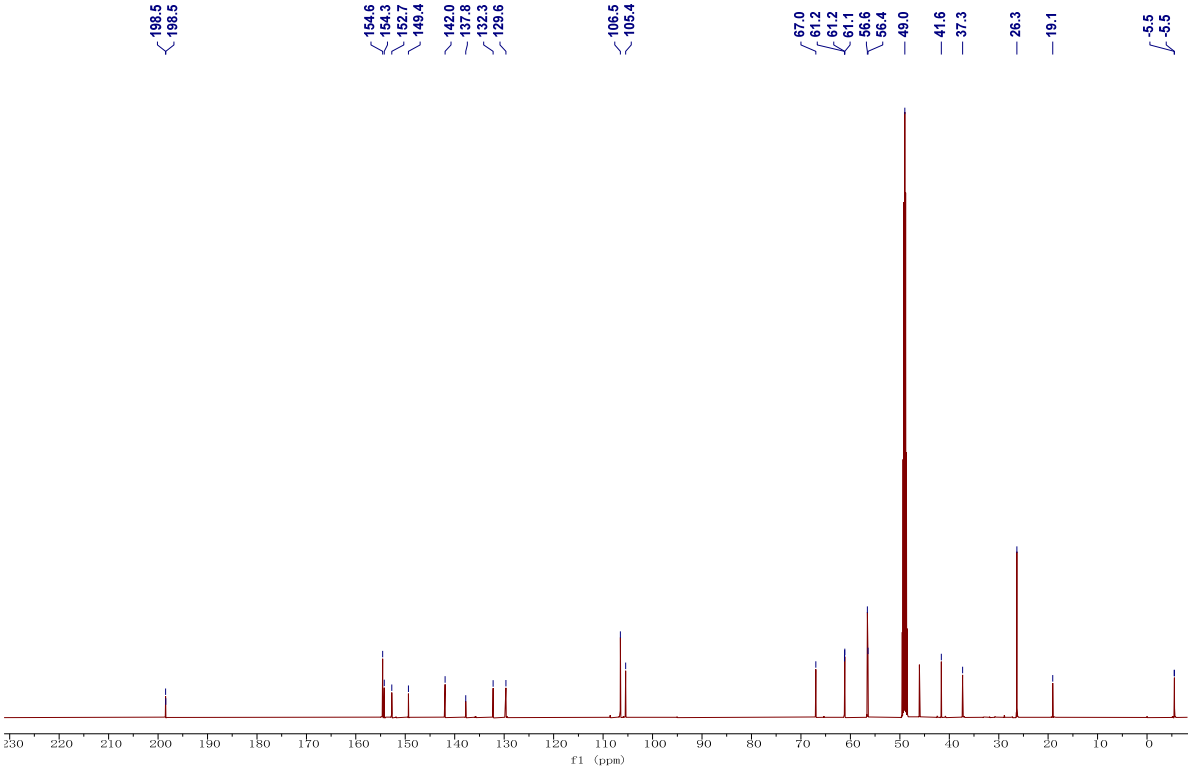


S13: (3R,4R)-3-(((Tert-butyldimethylsilyl)oxy)methyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one

^{1}H NMR (500 MHz, MeOH-d_4 @ 4.87 ppm)

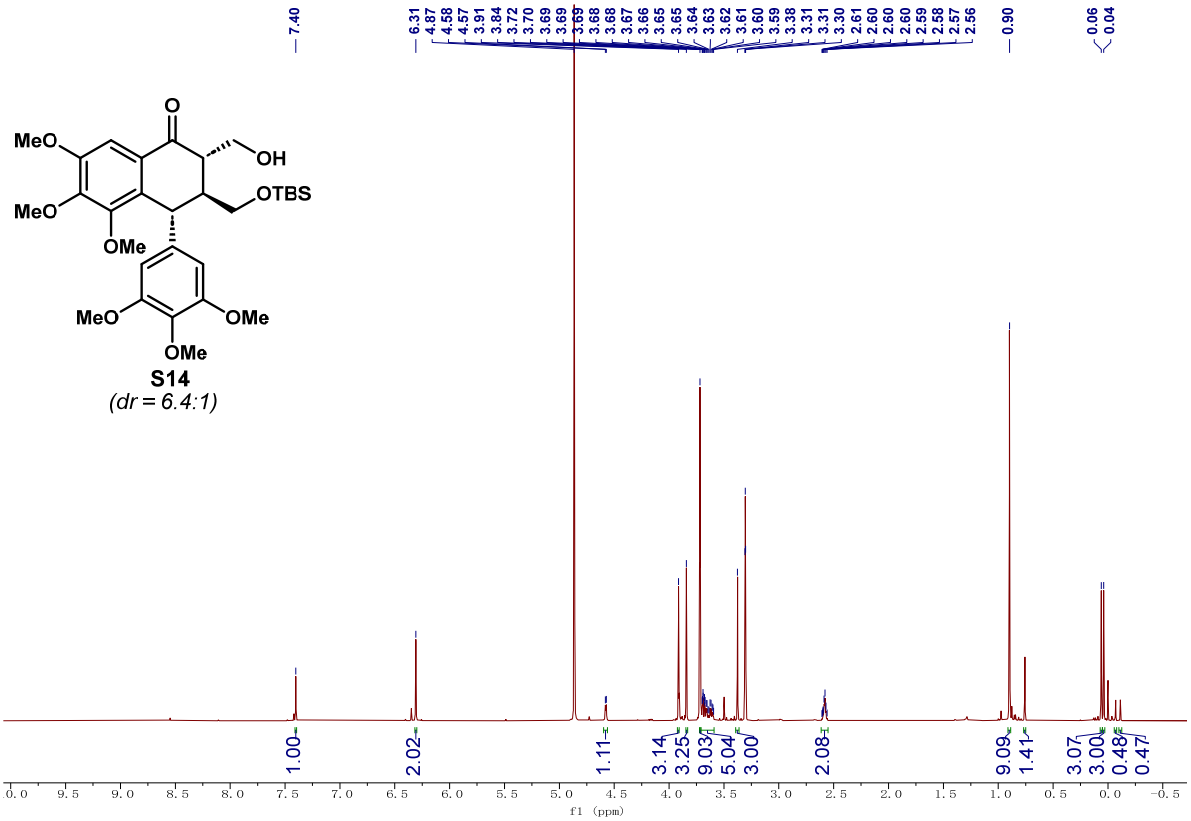


^{13}C NMR (125 MHz, MeOH-d_4 @ 49 ppm)



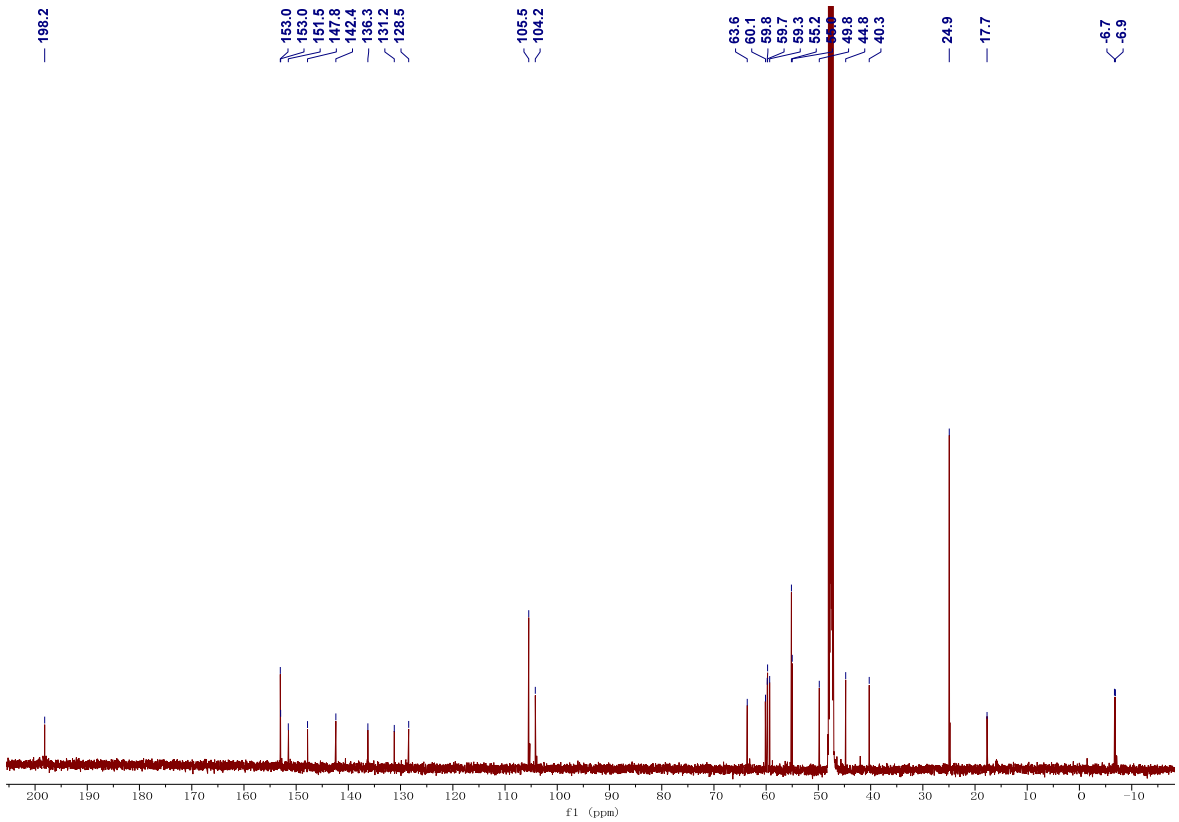
S14: (2S,3S,4R)-3-(((Tert-butyldimethylsilyl)oxy)methyl)-2-(hydroxymethyl)-5,6,7-trimetho-xy-4-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one

^{1}H NMR (500 MHz, MeOH-d_4 @ 4.87 ppm)



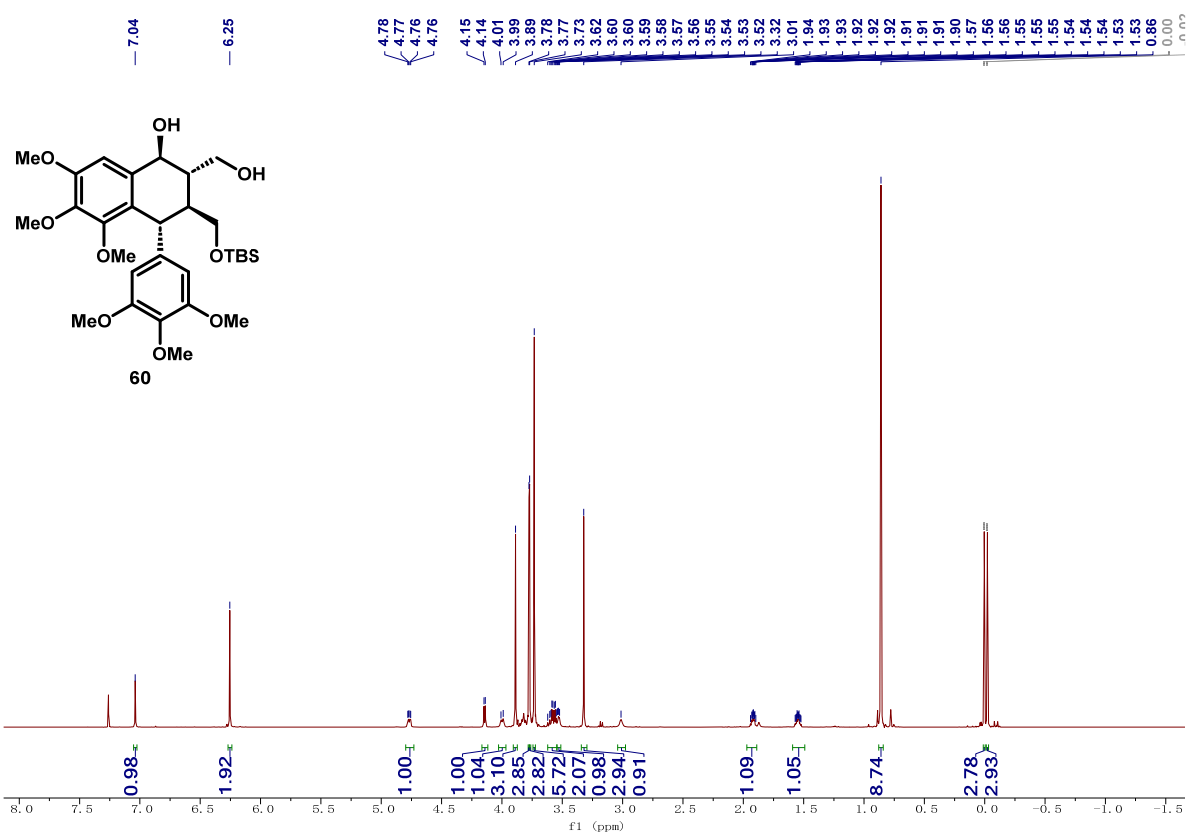
S14
(dr = 6.4:1)

^{13}C NMR (125 MHz, MeOH-d_4 @ 49 ppm)

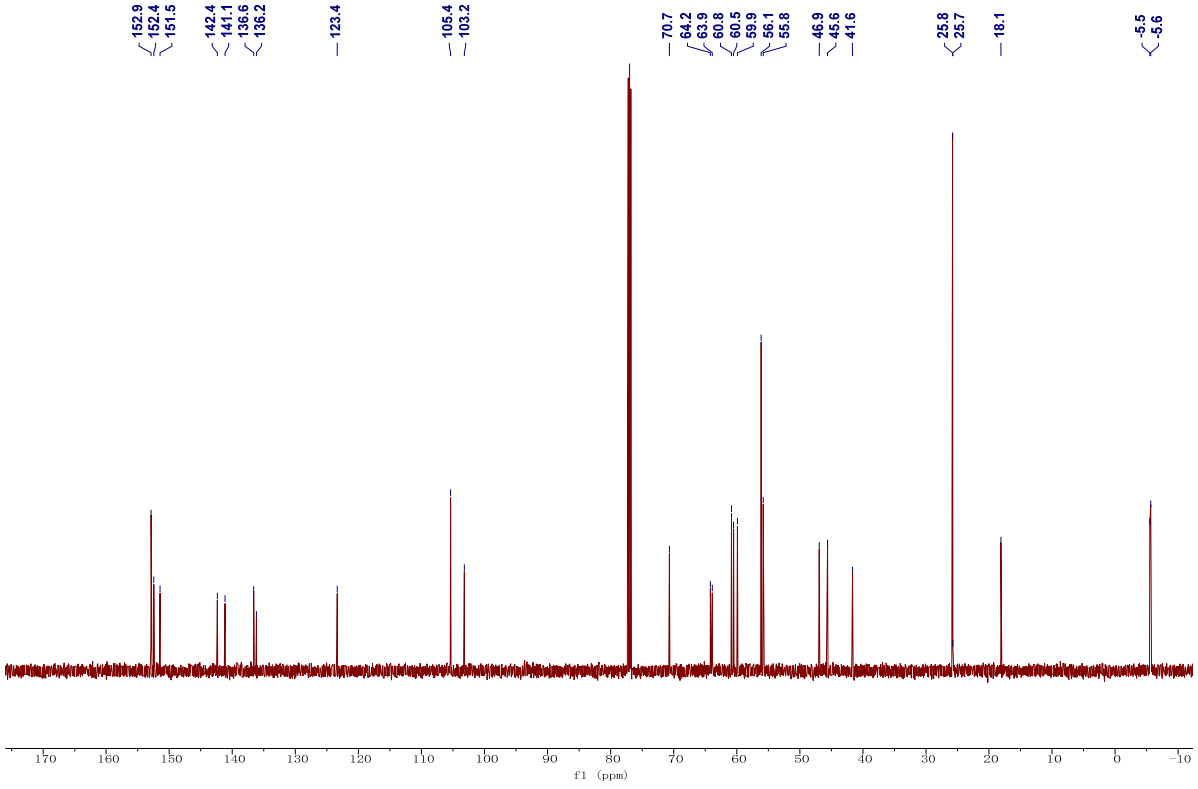


60: (1S,2S,3S,4R)-3-(((tert-butyldimethylsilyl)oxy)methyl)-2-(hydroxymethyl)-5,6,7-trimethoxy-4-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

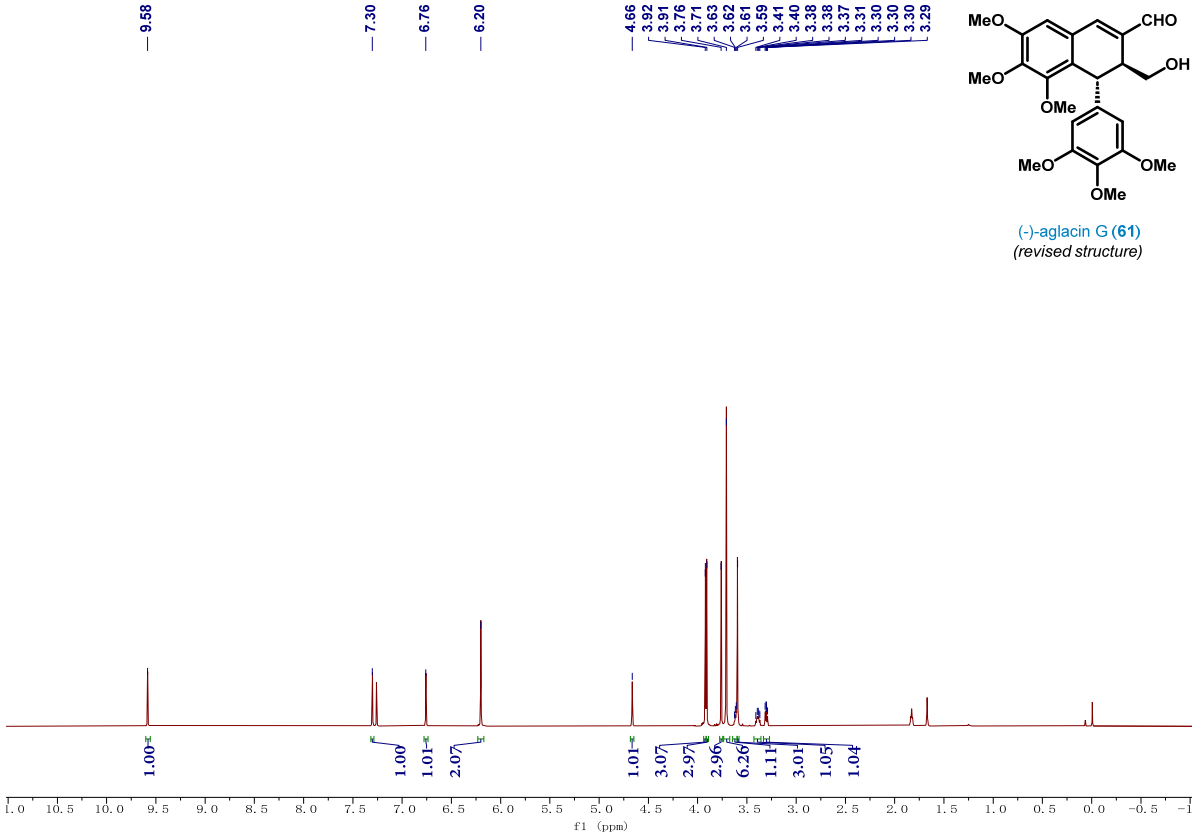


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



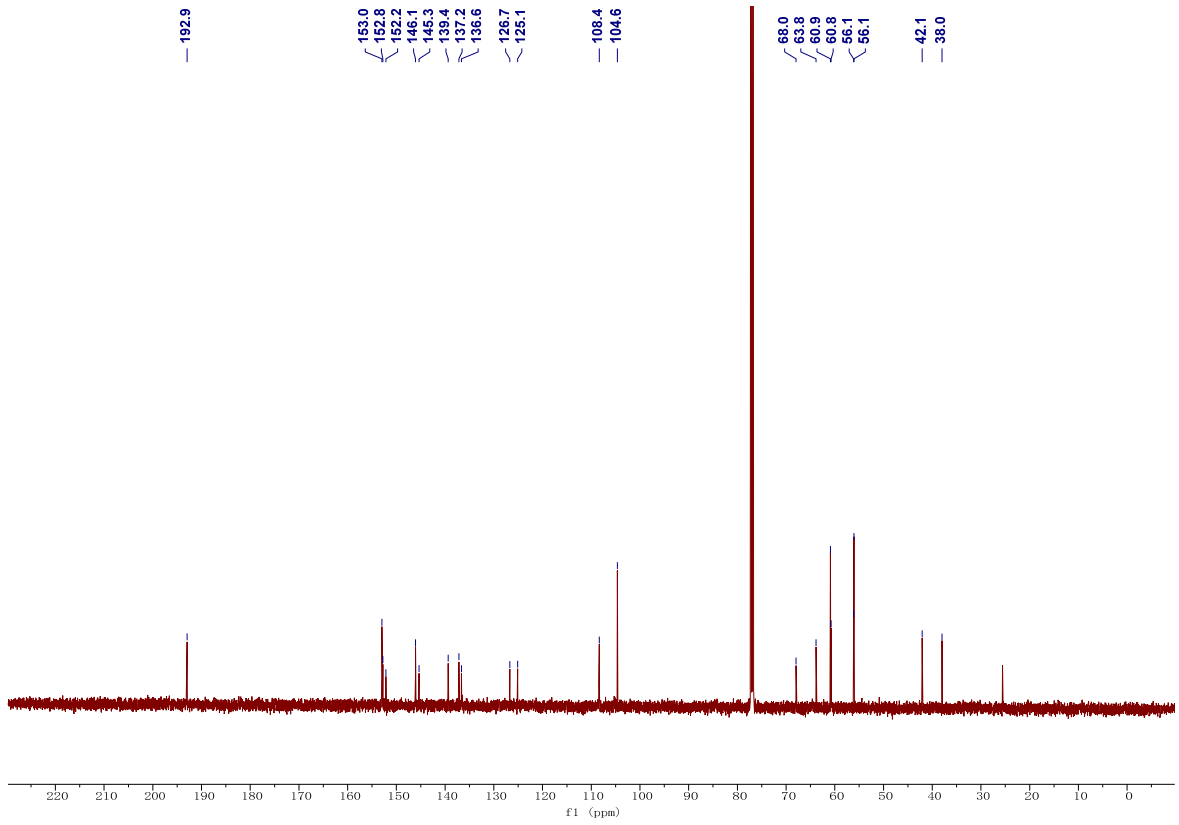
61: (-)-Aglacin G (revised structure)

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



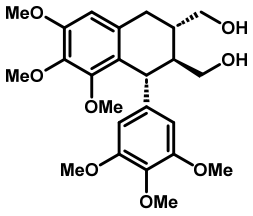
(-)-aglacin G (**61**)
(revised structure)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

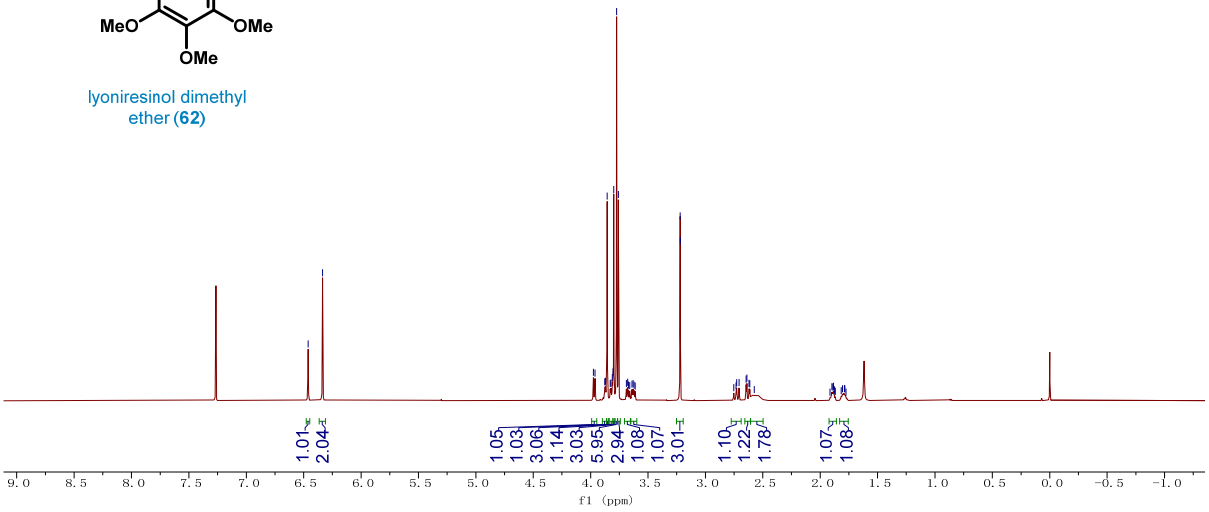


62: (-)-Lyoniresinol dimethyl ether

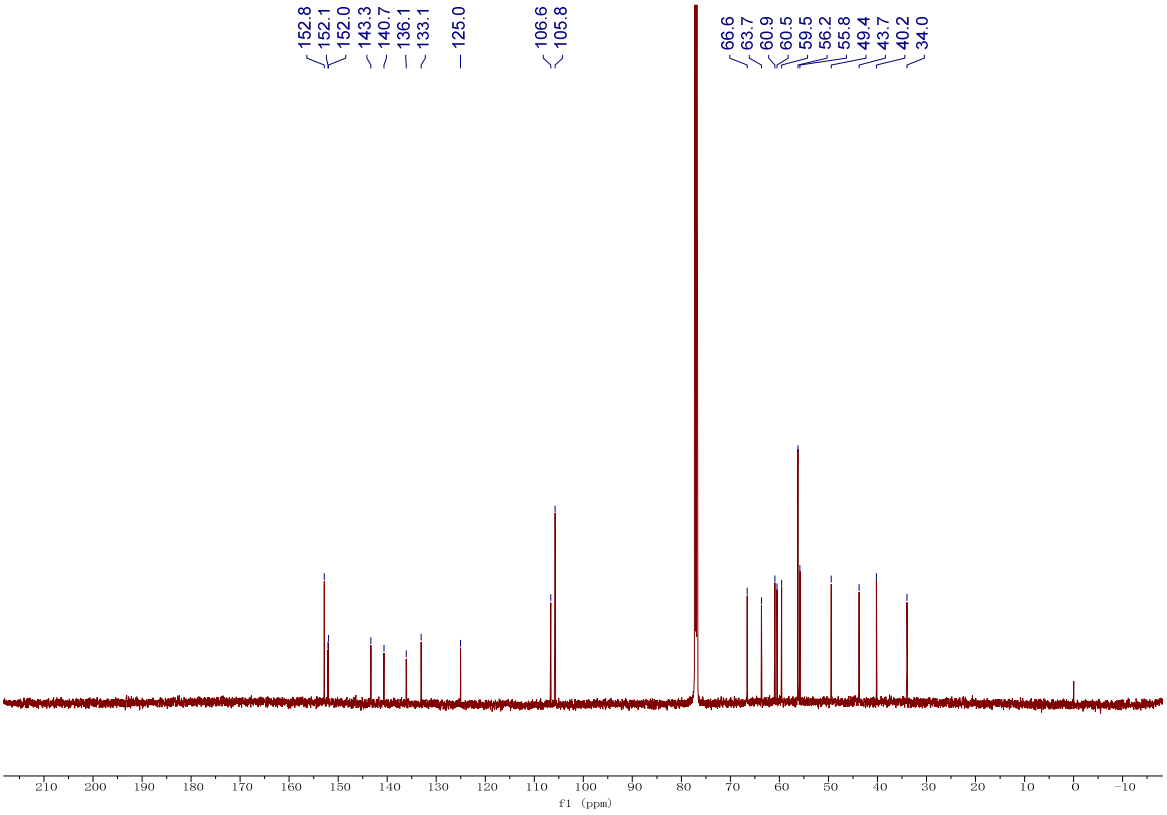
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



lyoniresinol dimethyl ether (**62**)

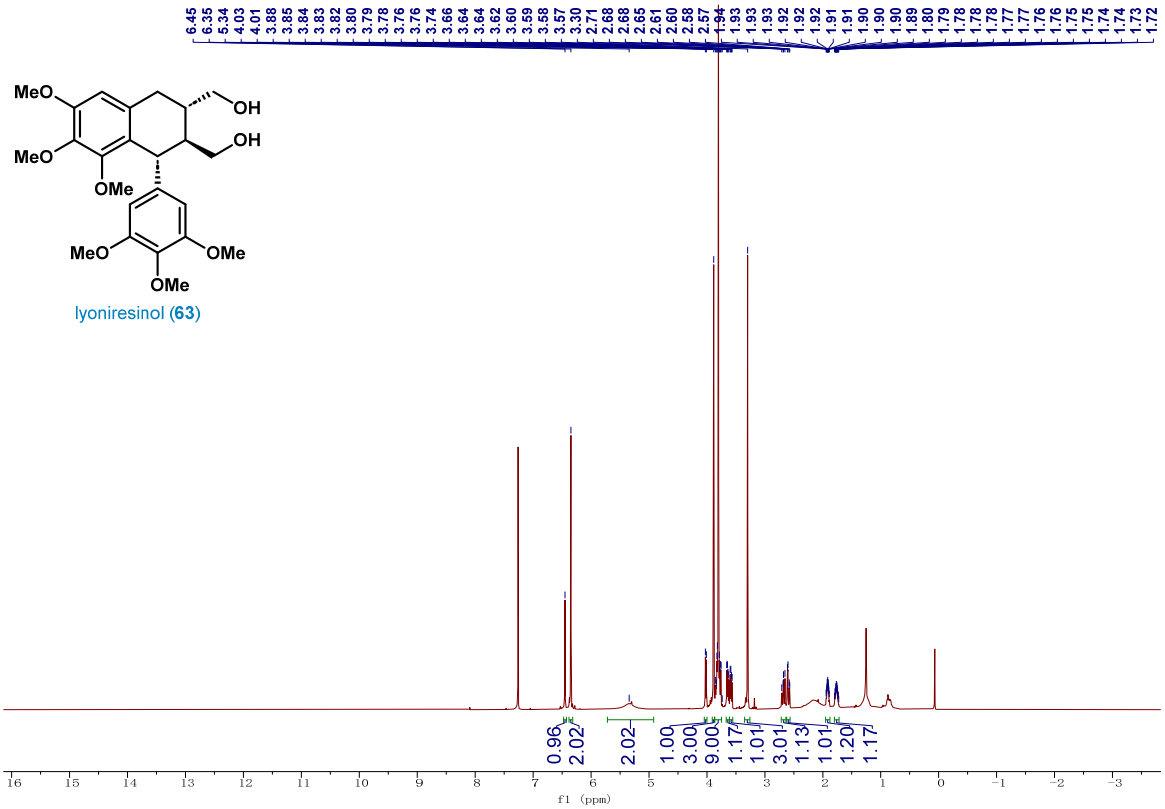


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

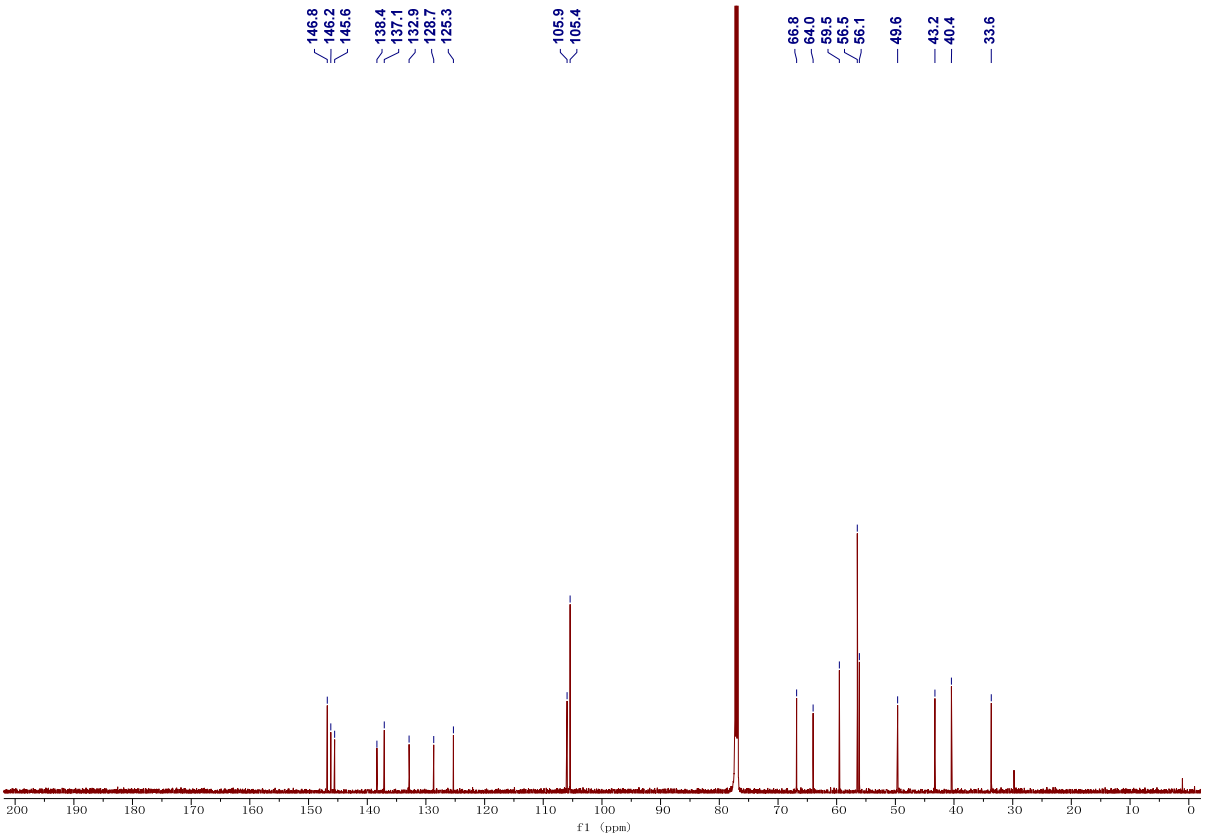


63: (-)-Lyoniresinol

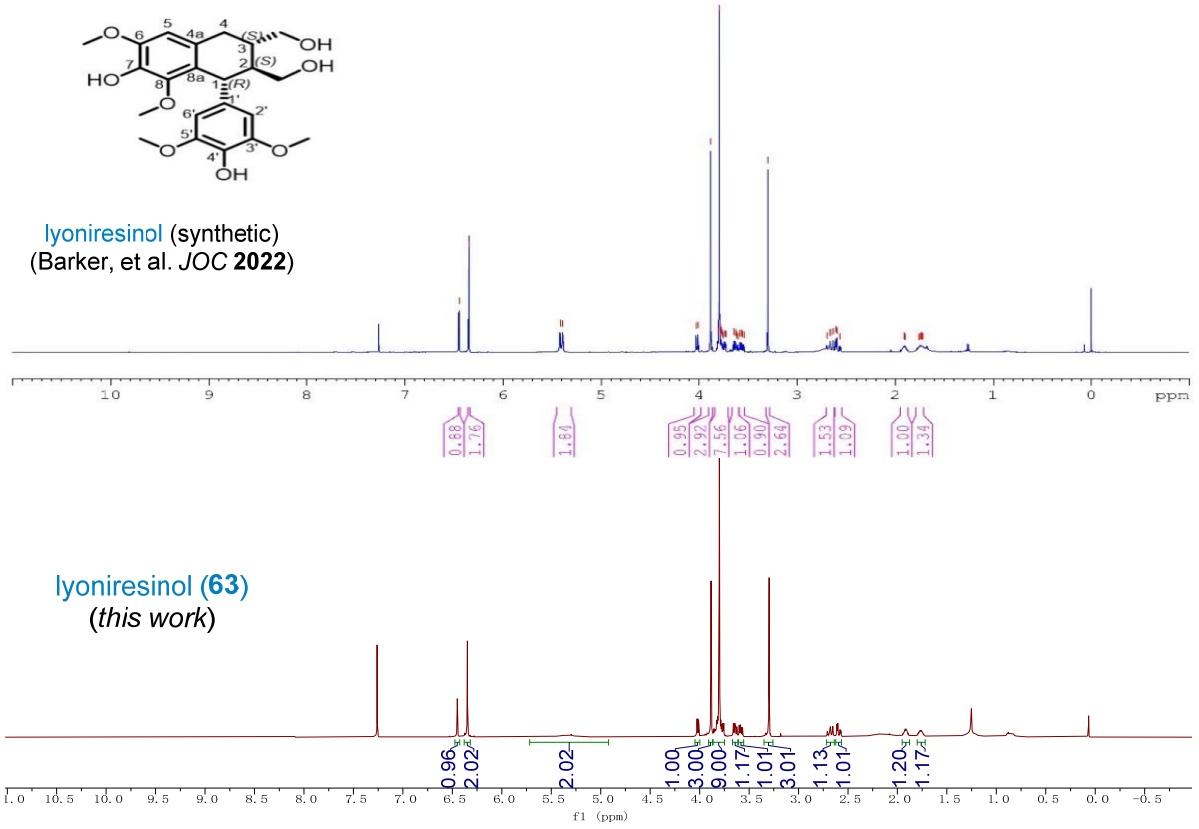
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

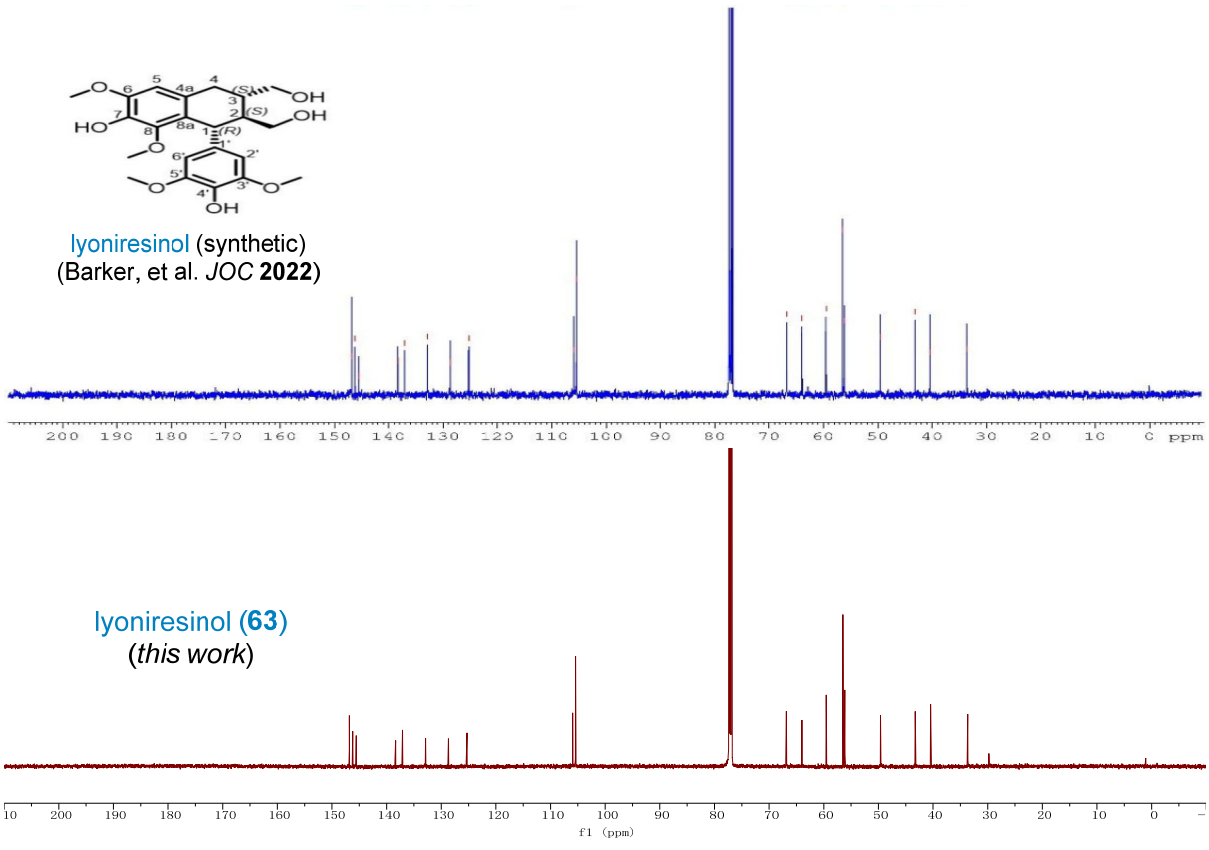


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



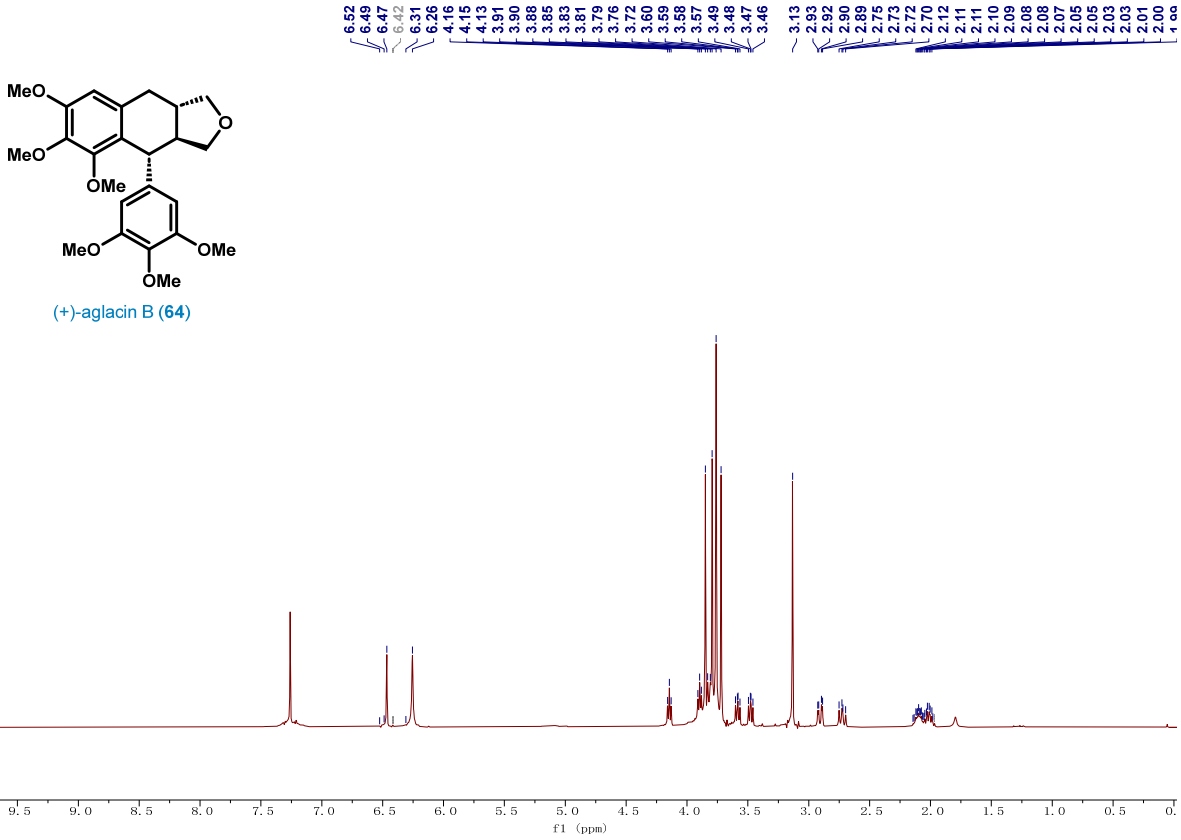
NMR spectra comparison of lyoniresinol



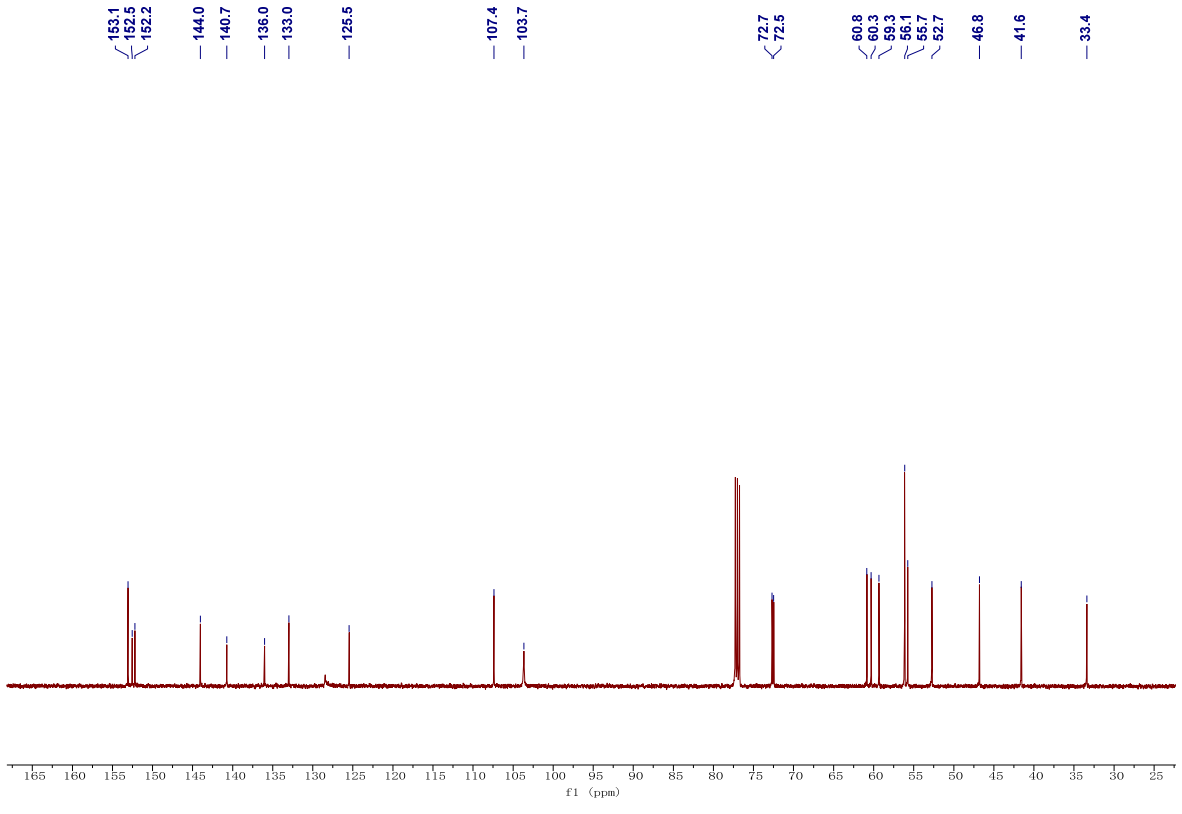


64: (+)-Aglacin B

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

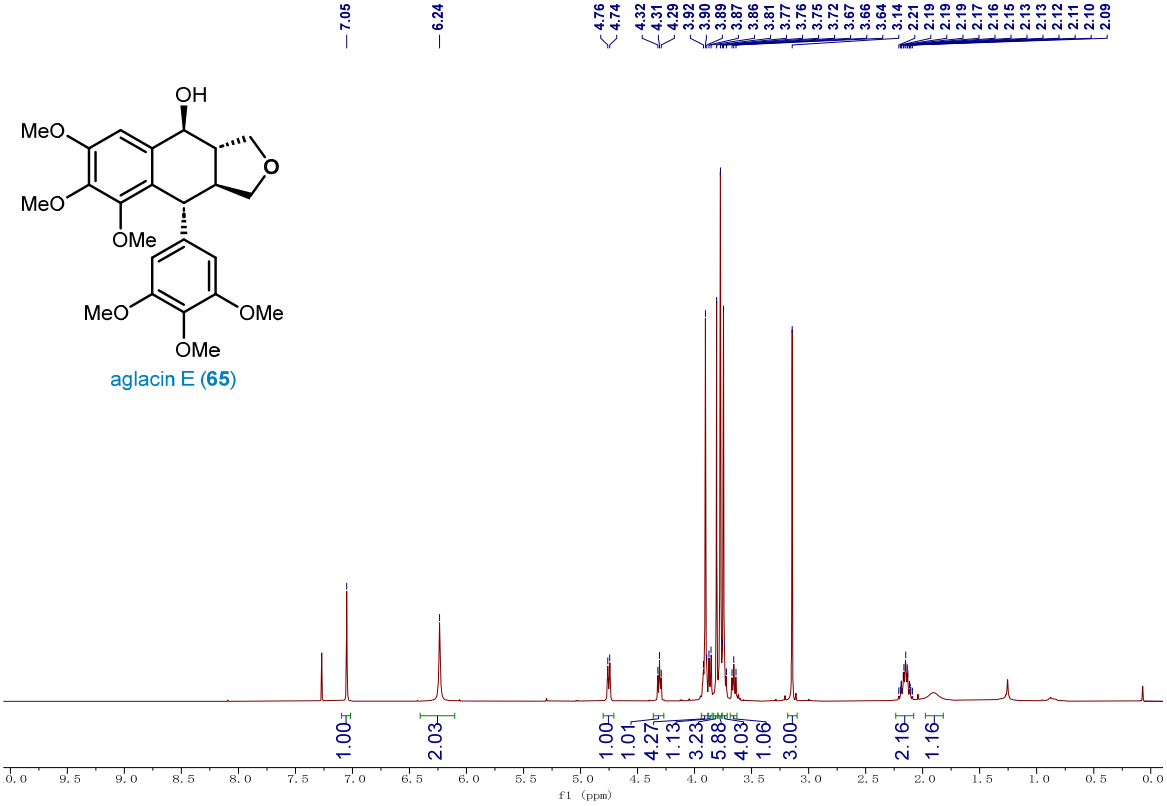


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



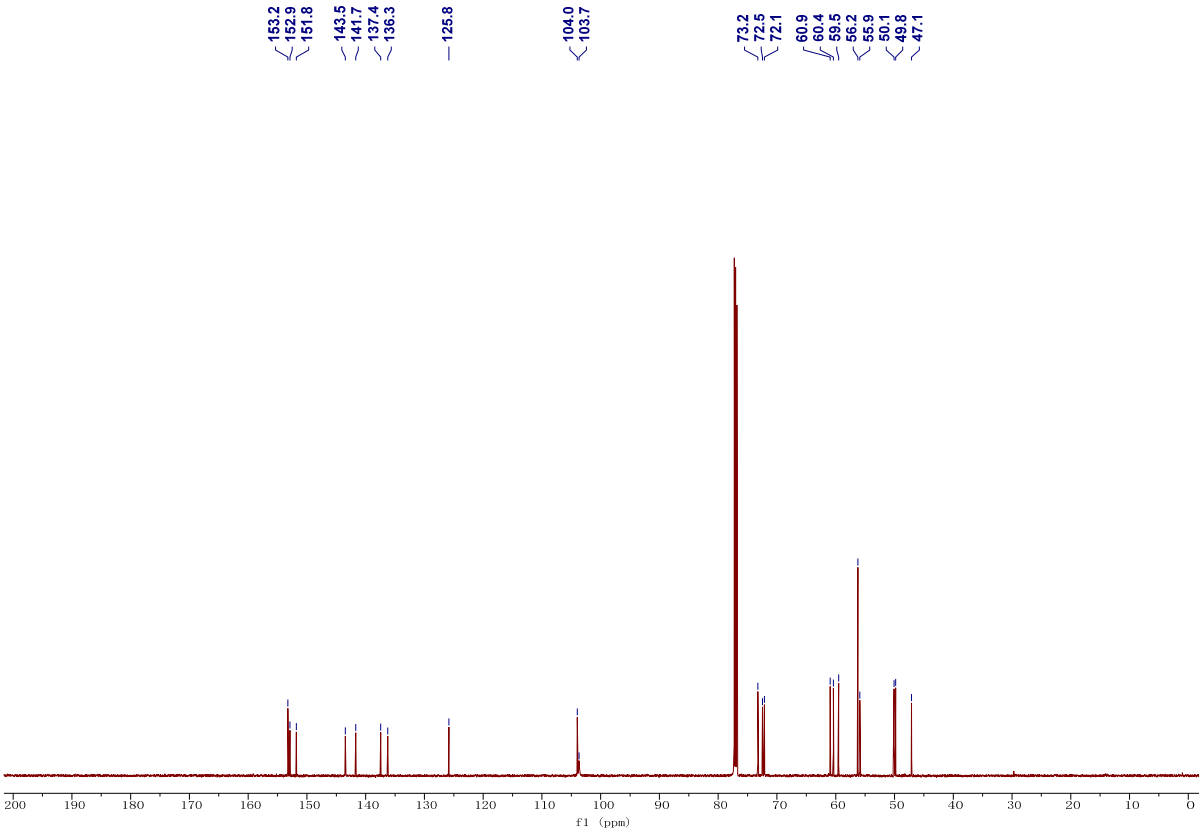
65: (+)-Aglacin E

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

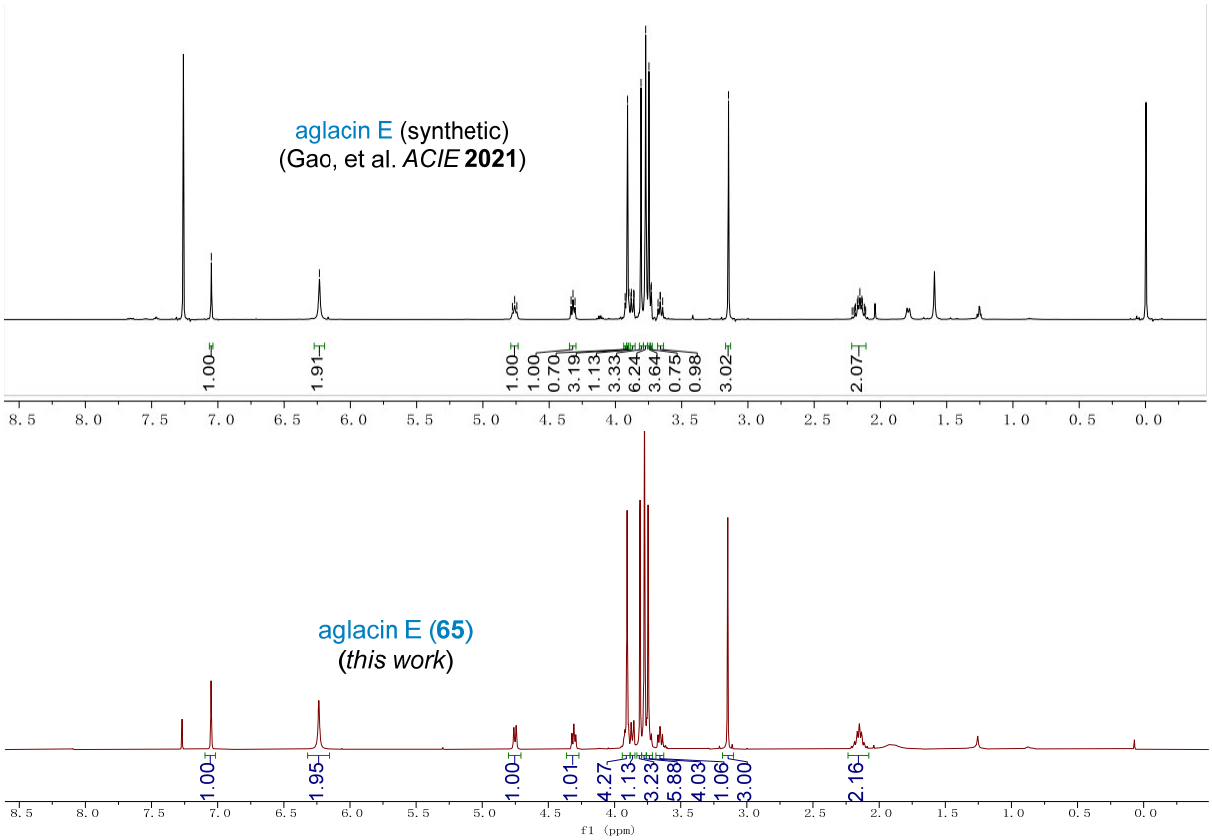


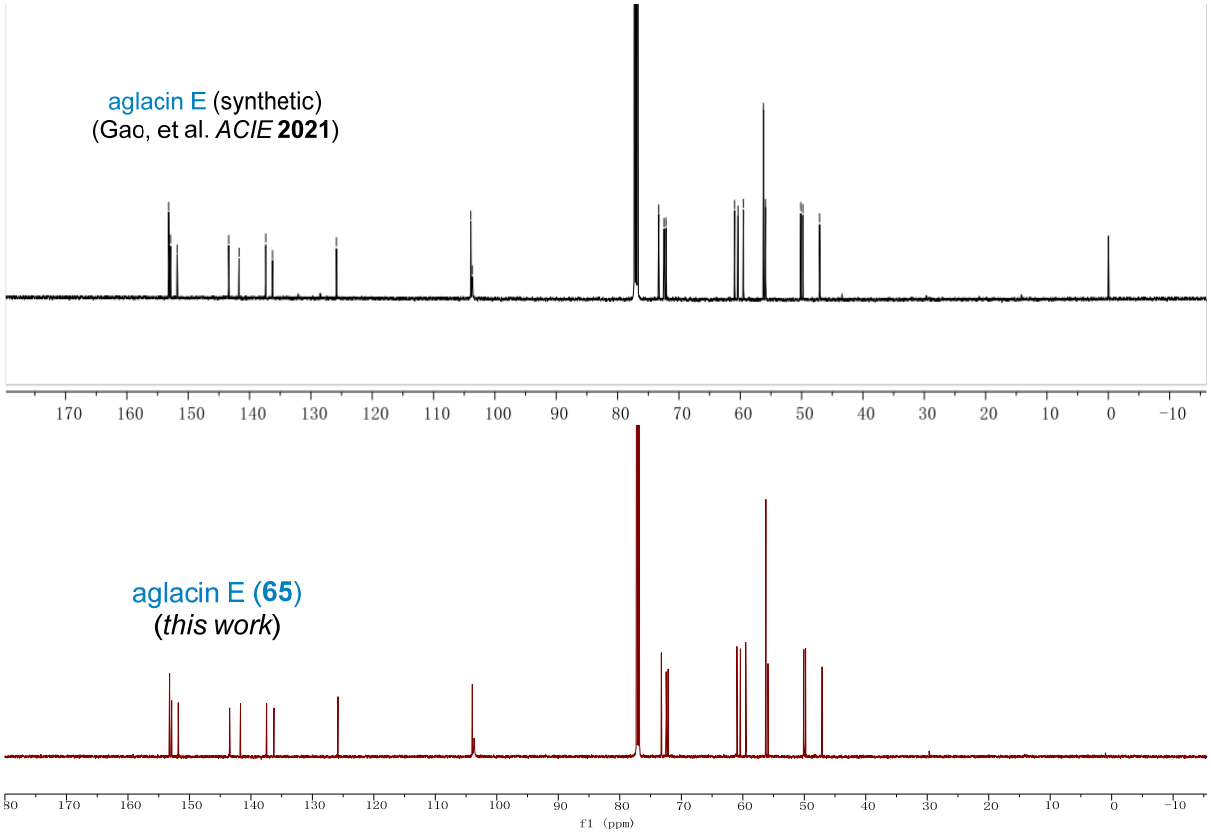
aglacin E (**65**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



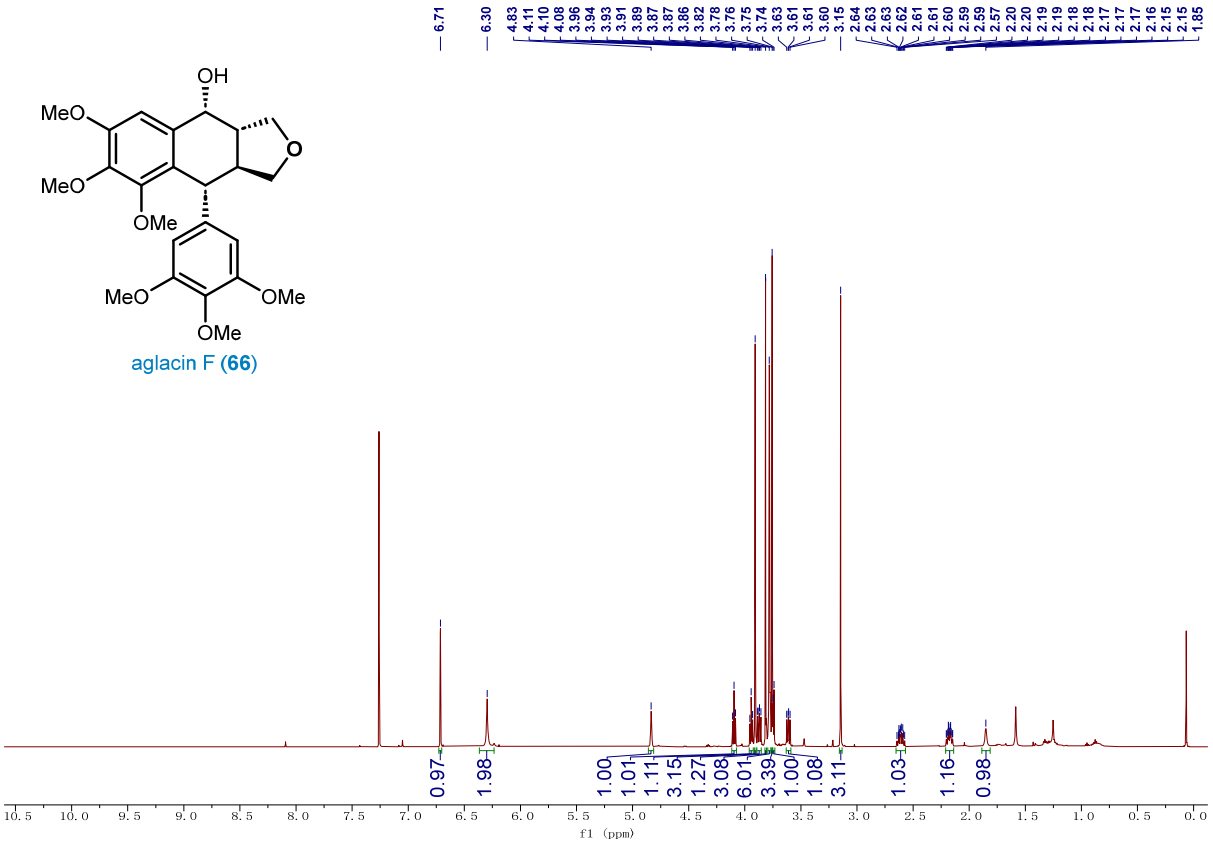
NMR spectra comparison of aglacin E



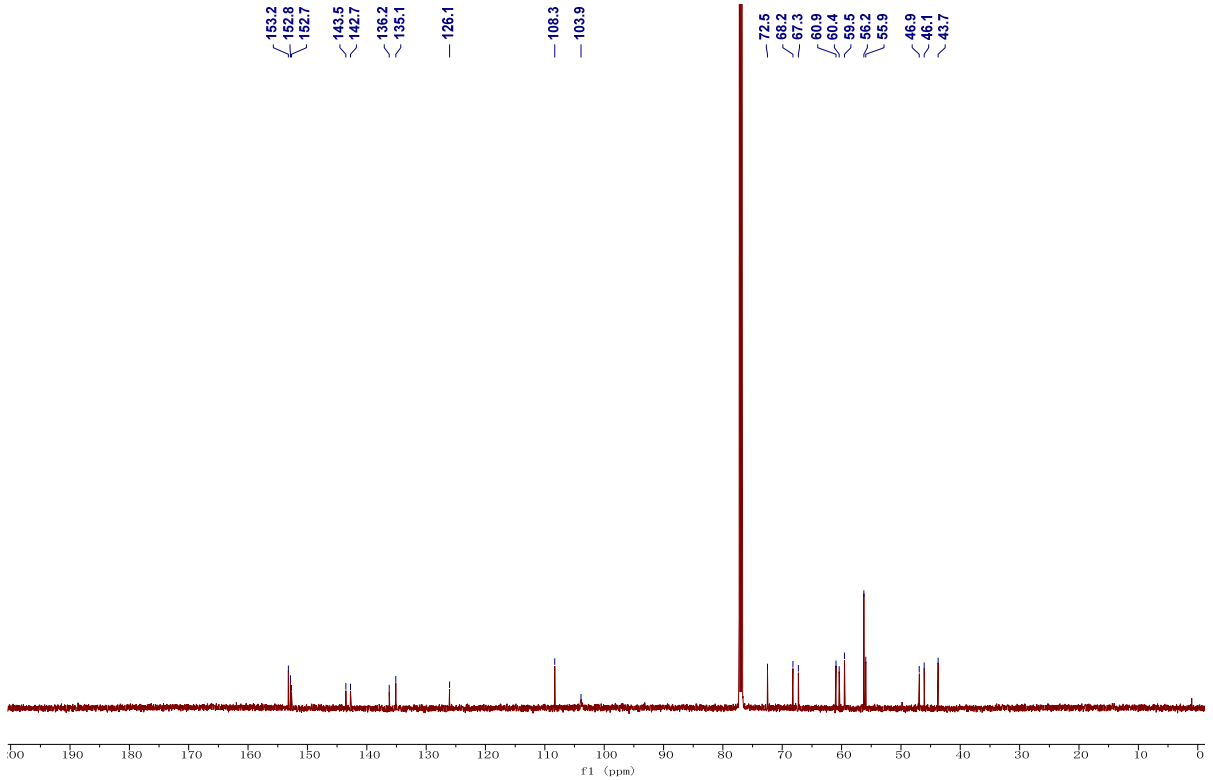


66: (+)-Aglacin F

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

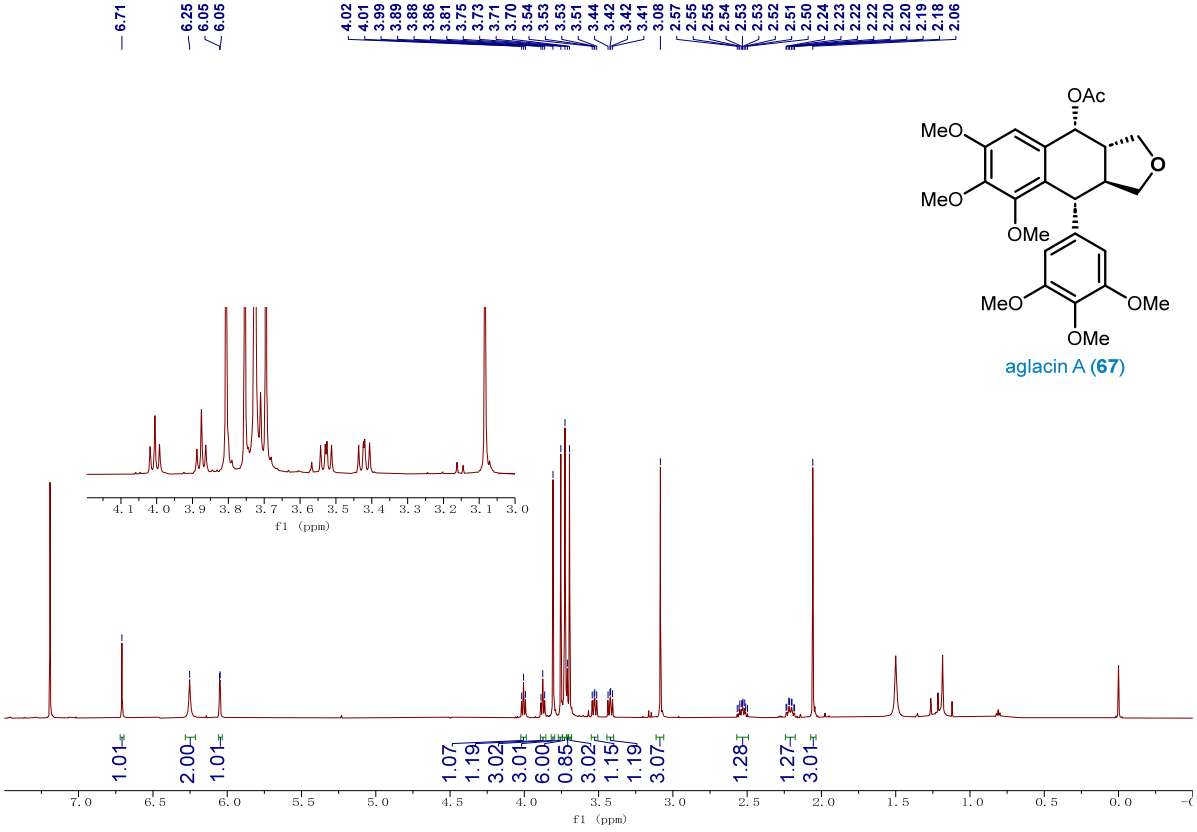


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



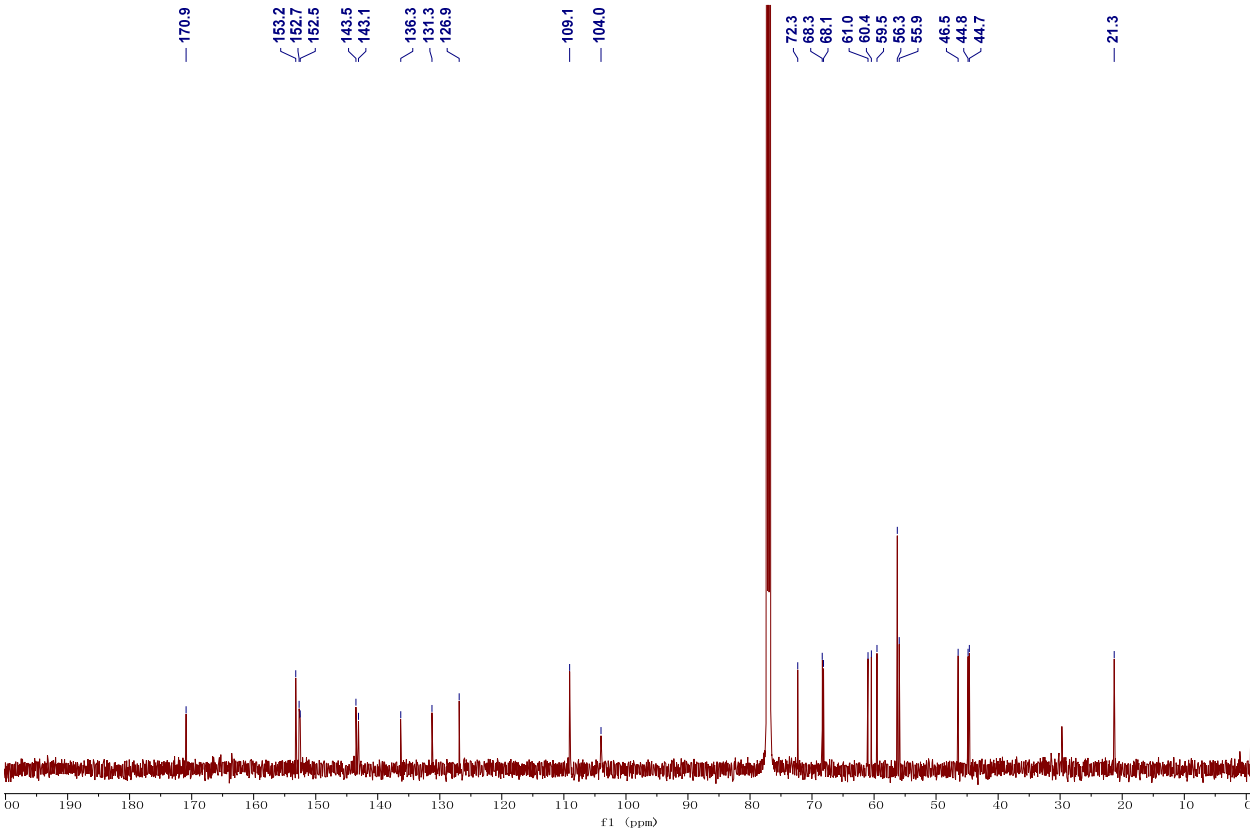
67: (+)-Aglacin A

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

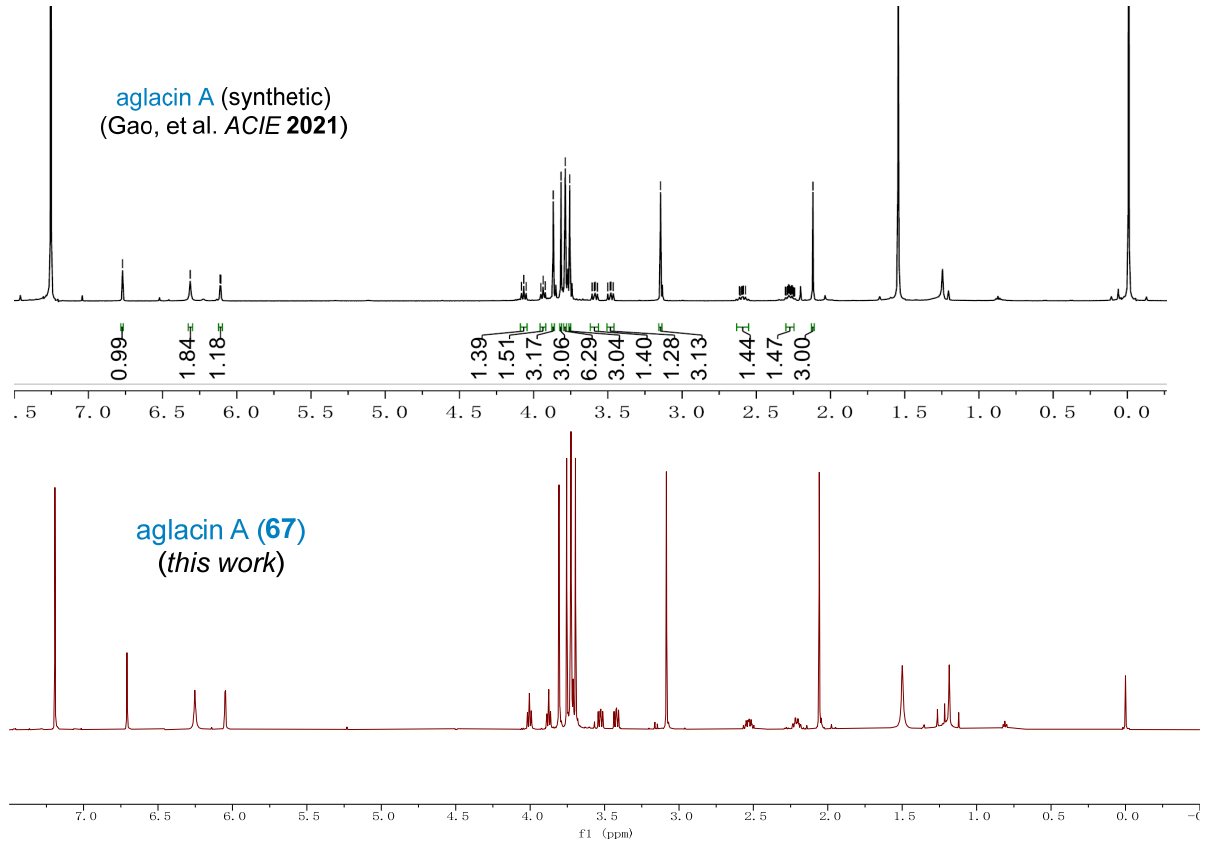


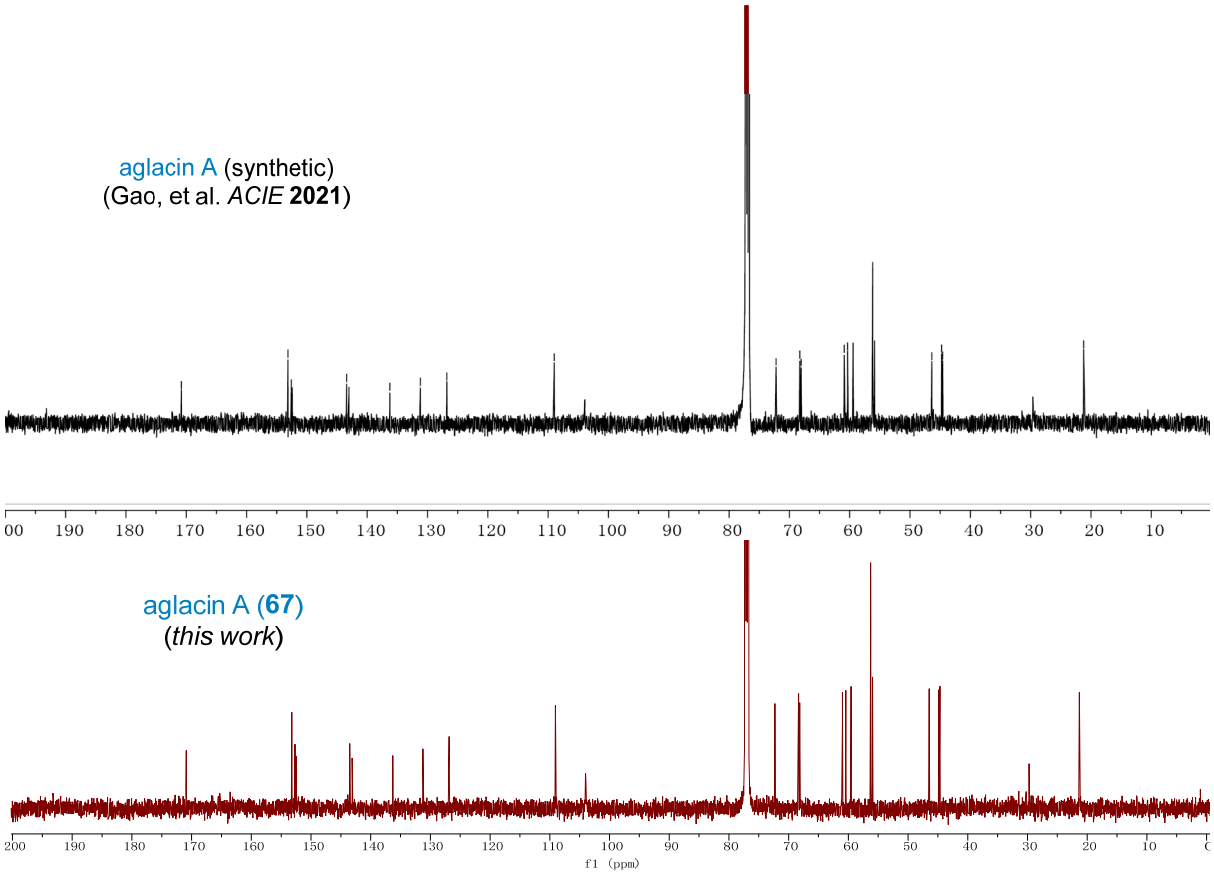
aglacin A (**67**)

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



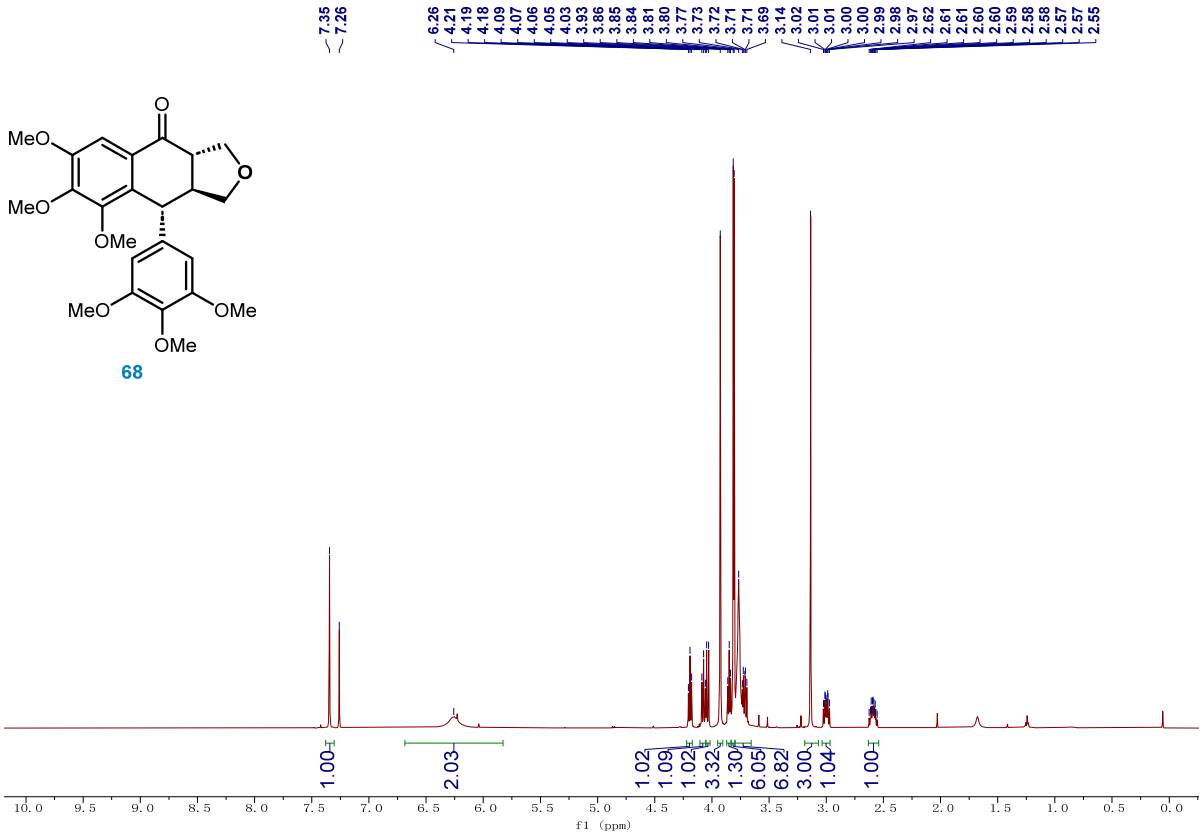
NMR spectra comparison of aglacin A



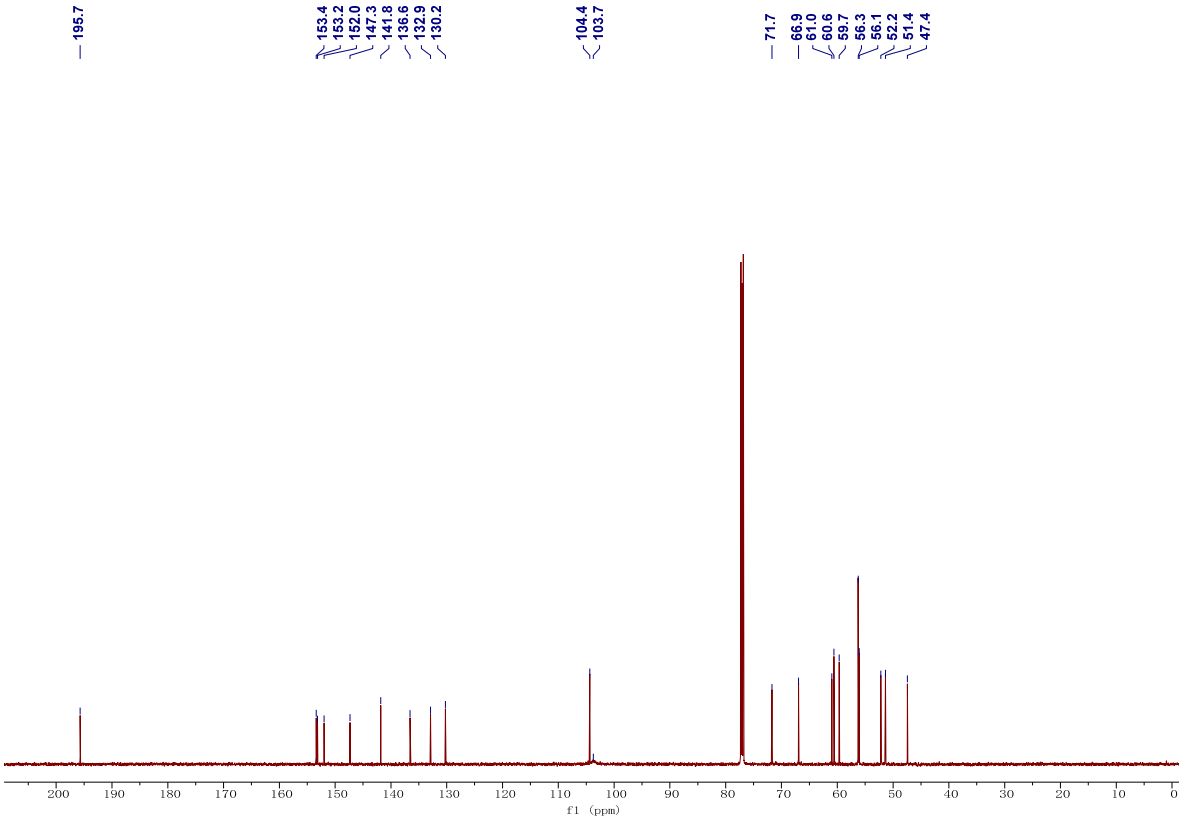


68: (3aS,9R,9aS)-6,7,8-Trimethoxy-9-(3,4,5-trimethoxyphenyl)-3,3a,9,9a-tetrahydronaphtho-[2,3-c]furan-4(1H)-one

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

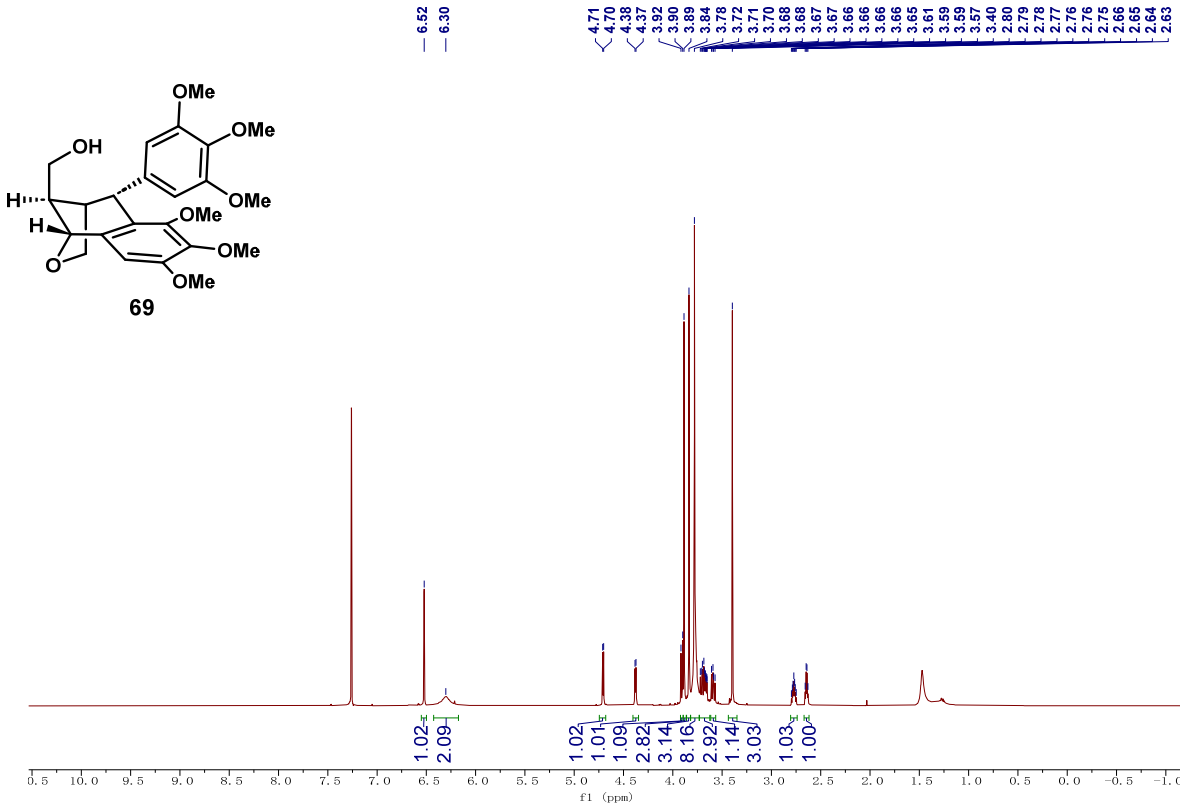


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

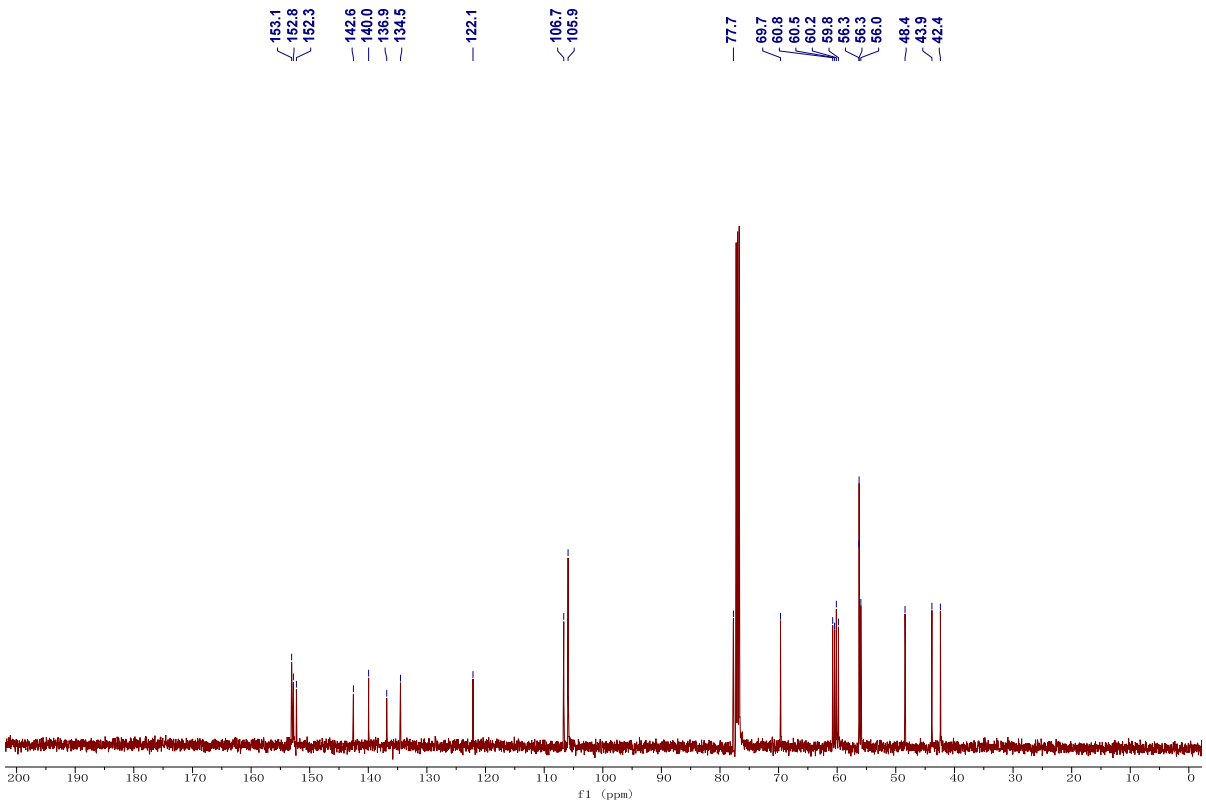


69: ((1R,4R,5S,10R)-6,7,8-Trimethoxy-5-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydro-1,4-methanobenzo[c]oxepin-10-yl)methanol

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm; 55 °C)

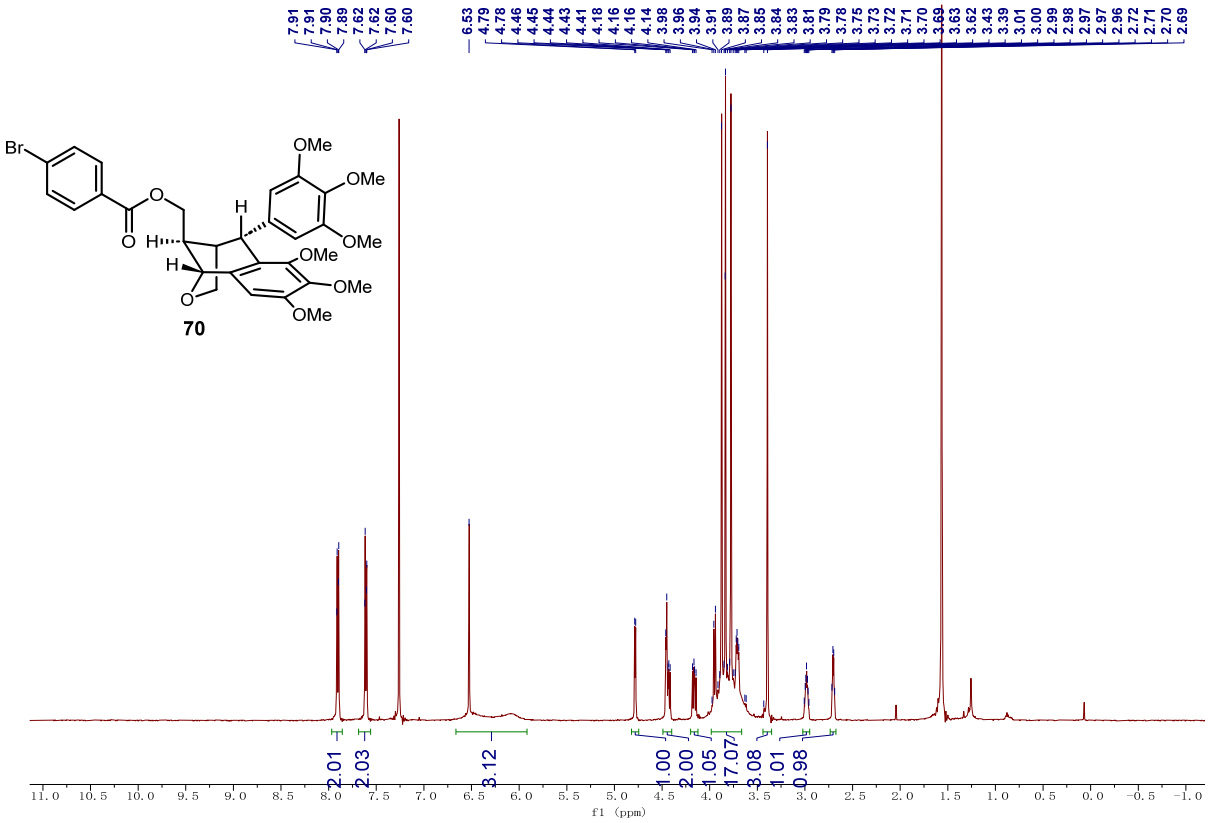


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm; 55 °C)

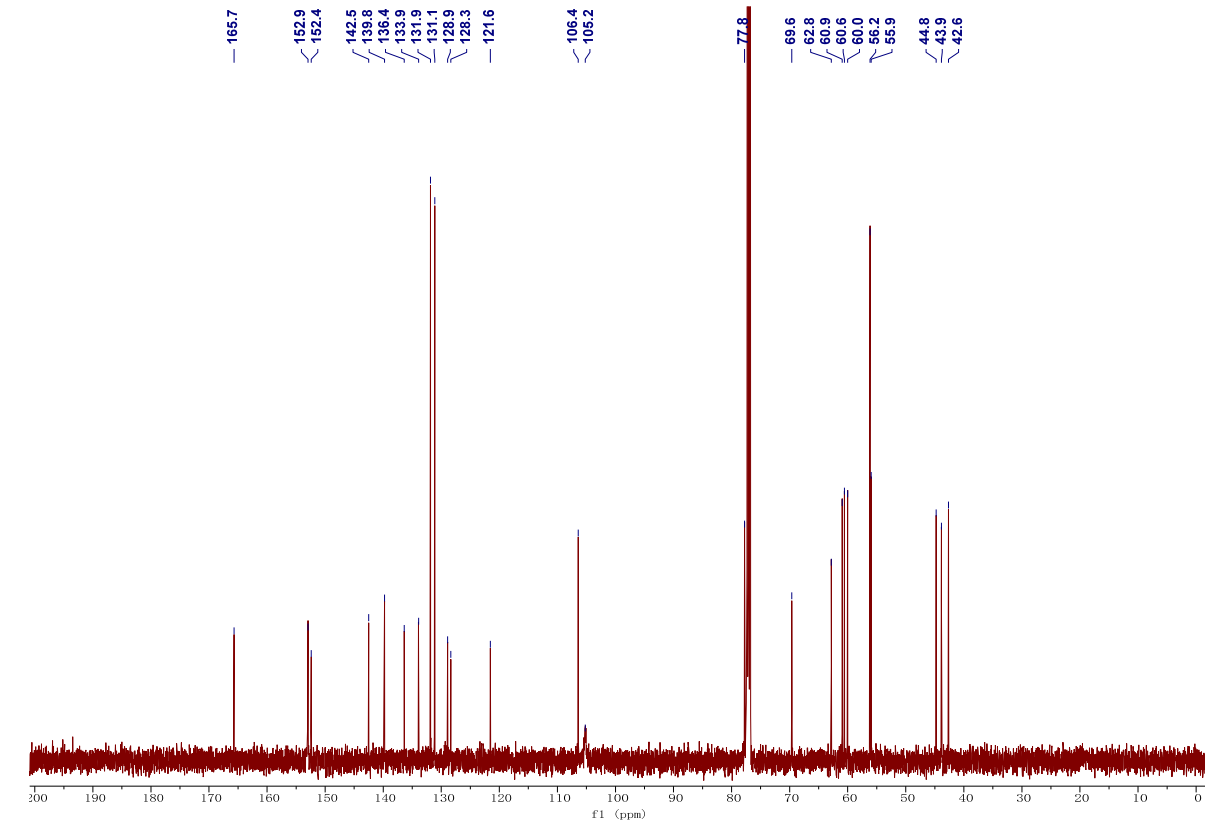


70: ((1R,4R,5R,10R)-6,7,8-Trimethoxy-5-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydro-1,4-methanobenzo[c]oxepin-10-yl)methyl 4-bromobenzoate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

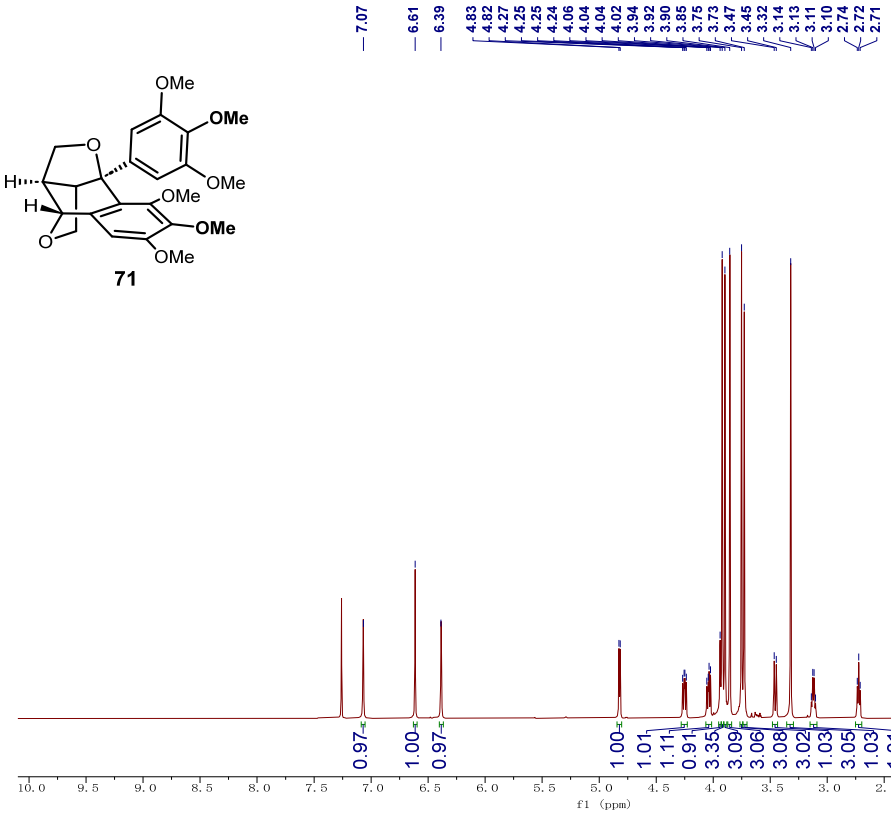


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

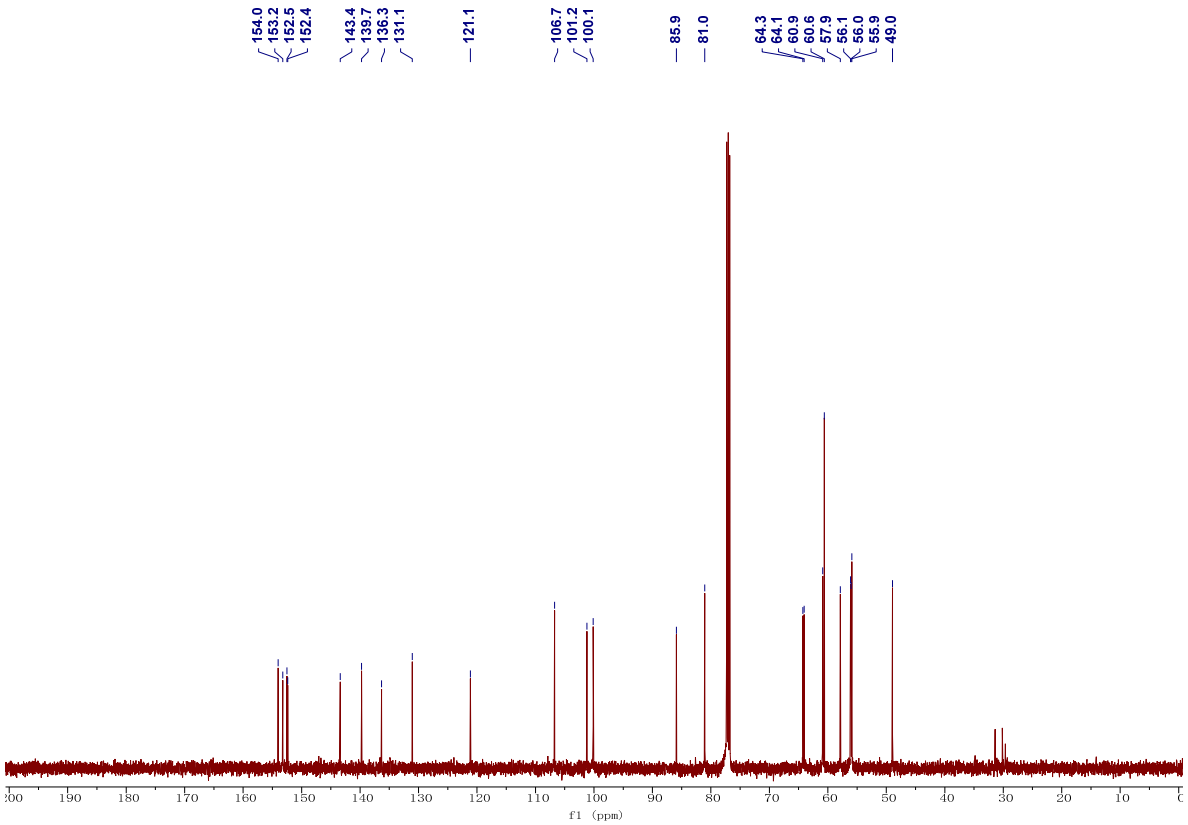


71: (1S,4R,5R)-7,8,9-Trimethoxy-1-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydro-5,1,4-(epoxyethane[1,2,2]triyl)benzo[c]oxepine

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

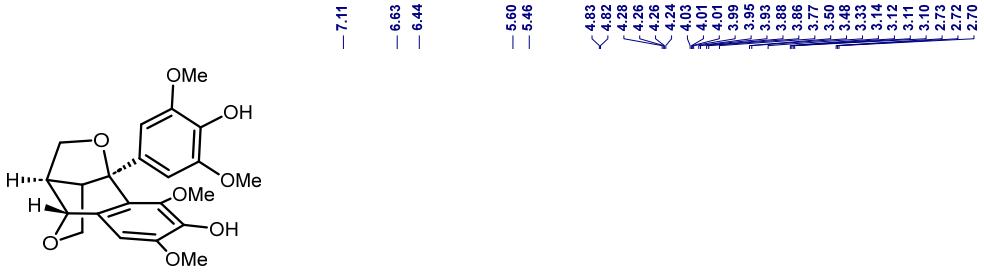


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

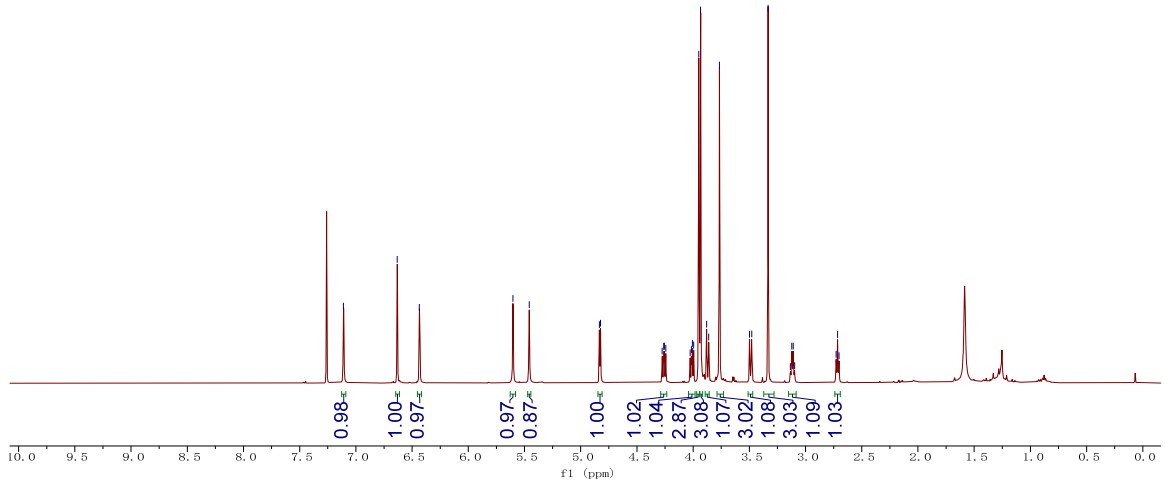


72: (-)-Ovafonin D

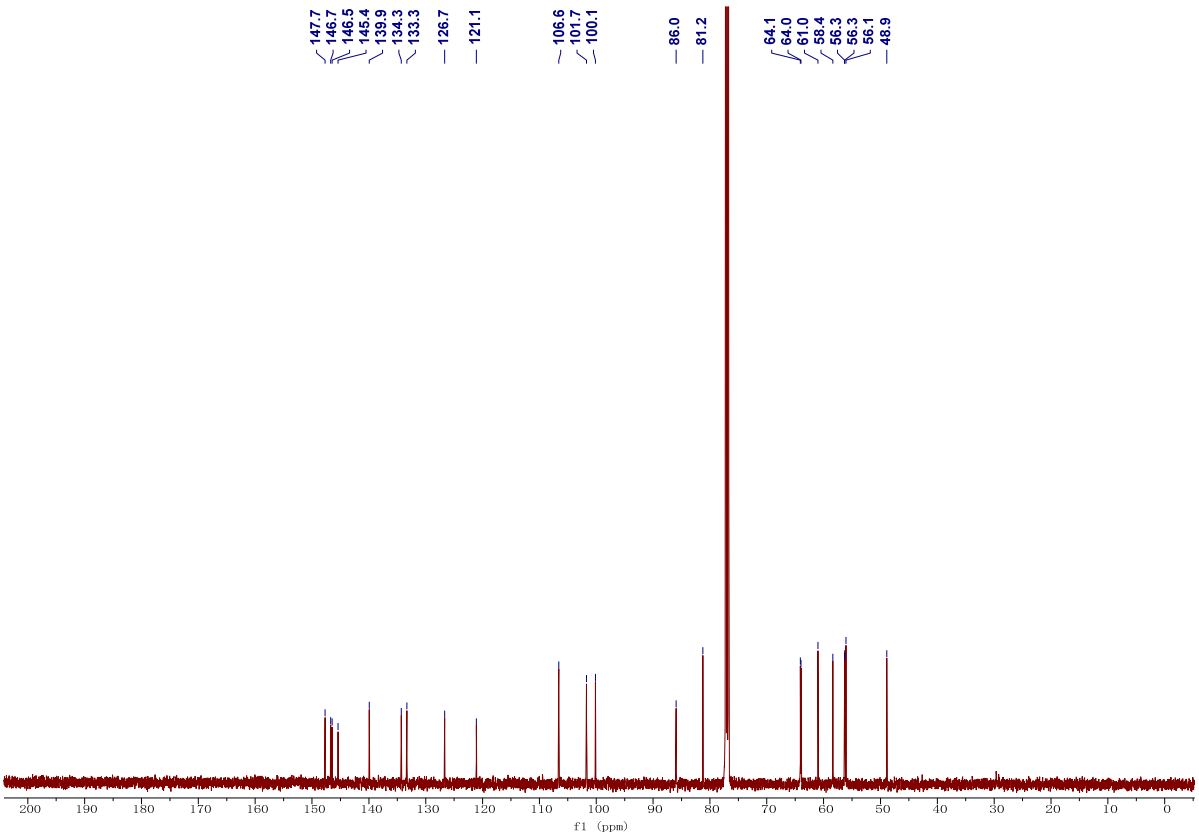
^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



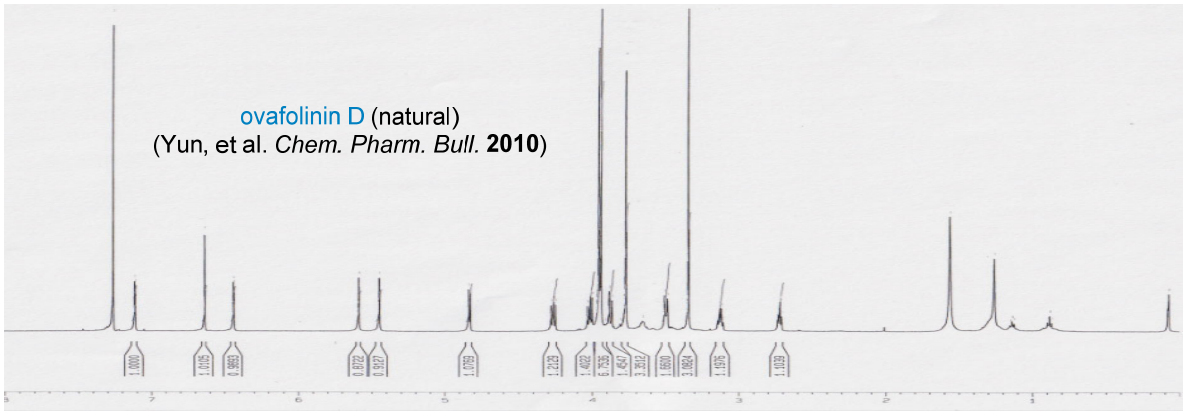
ovafolinin D (**72**)

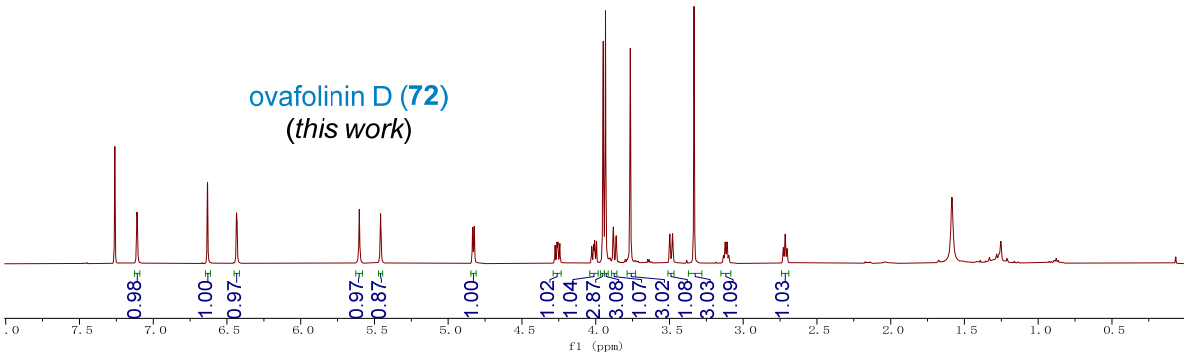


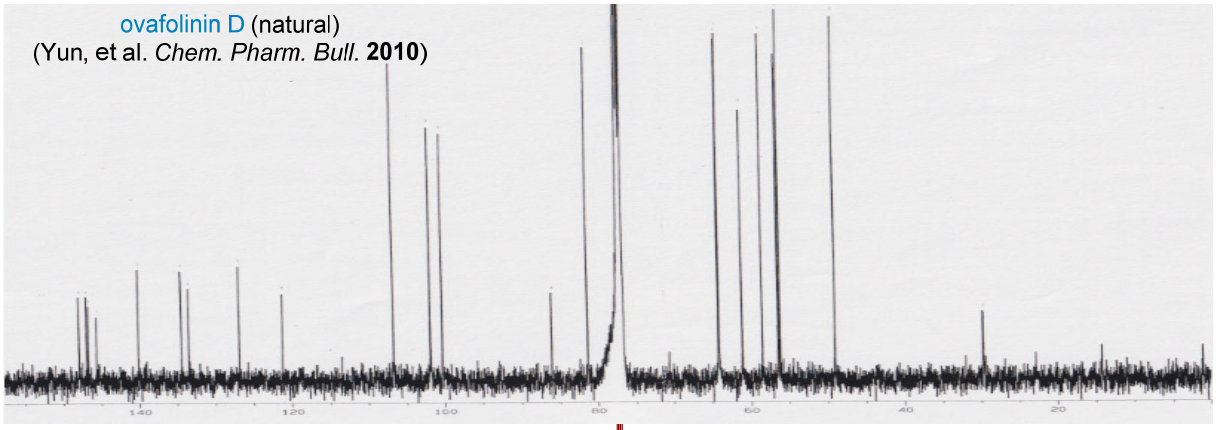
^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

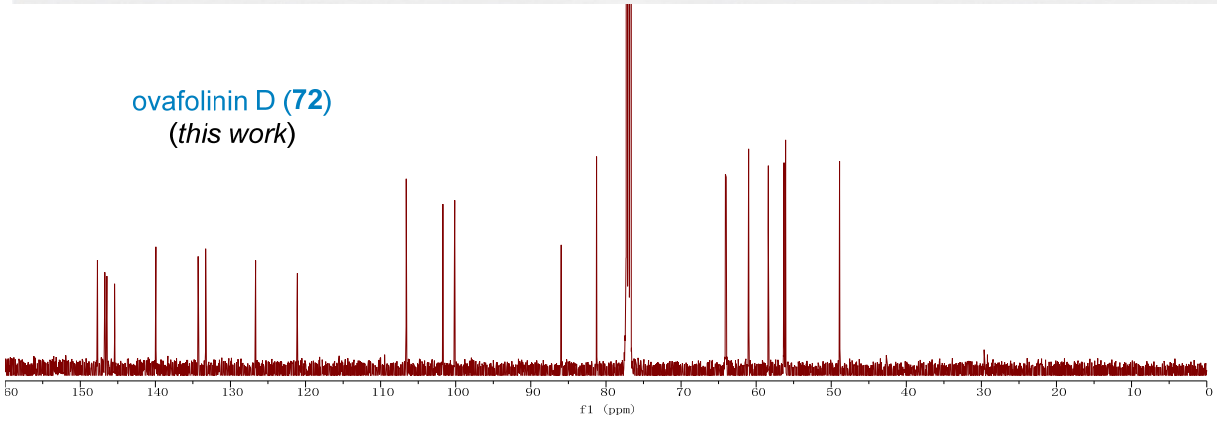


NMR spectra comparison of ovafolinin D



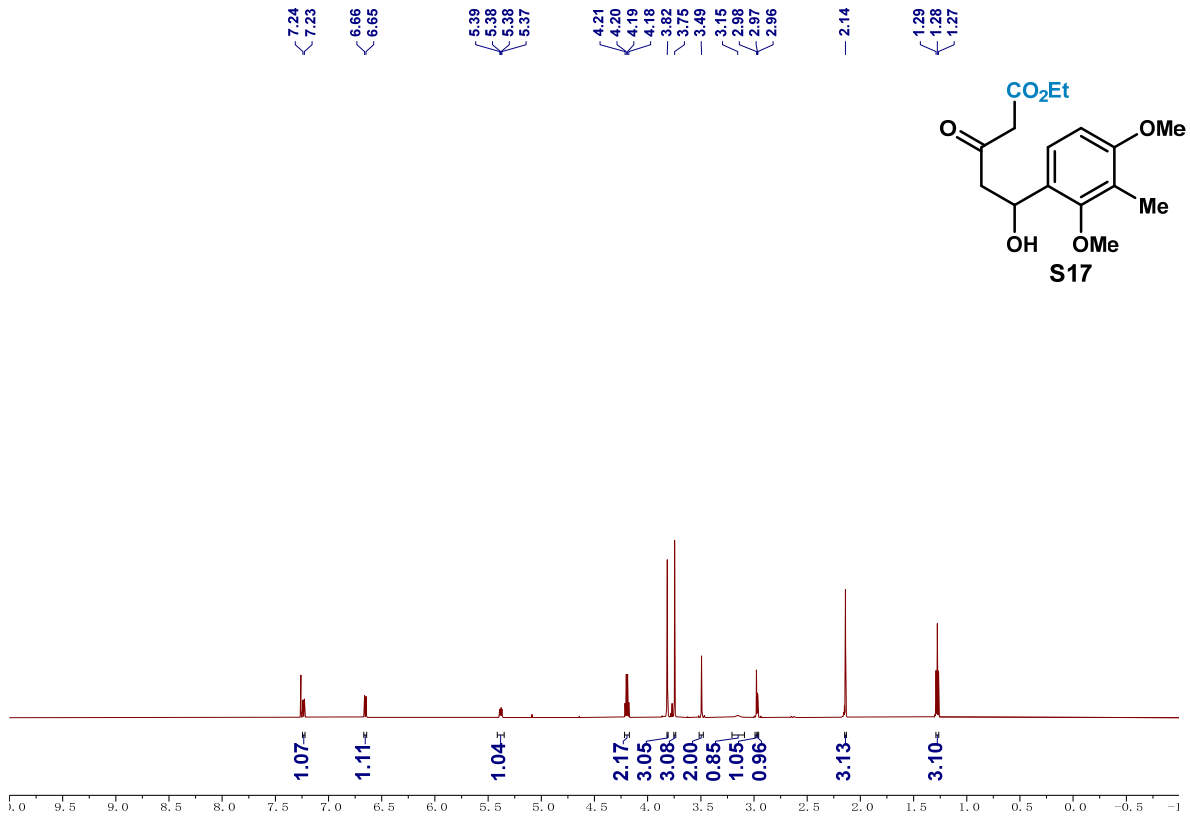




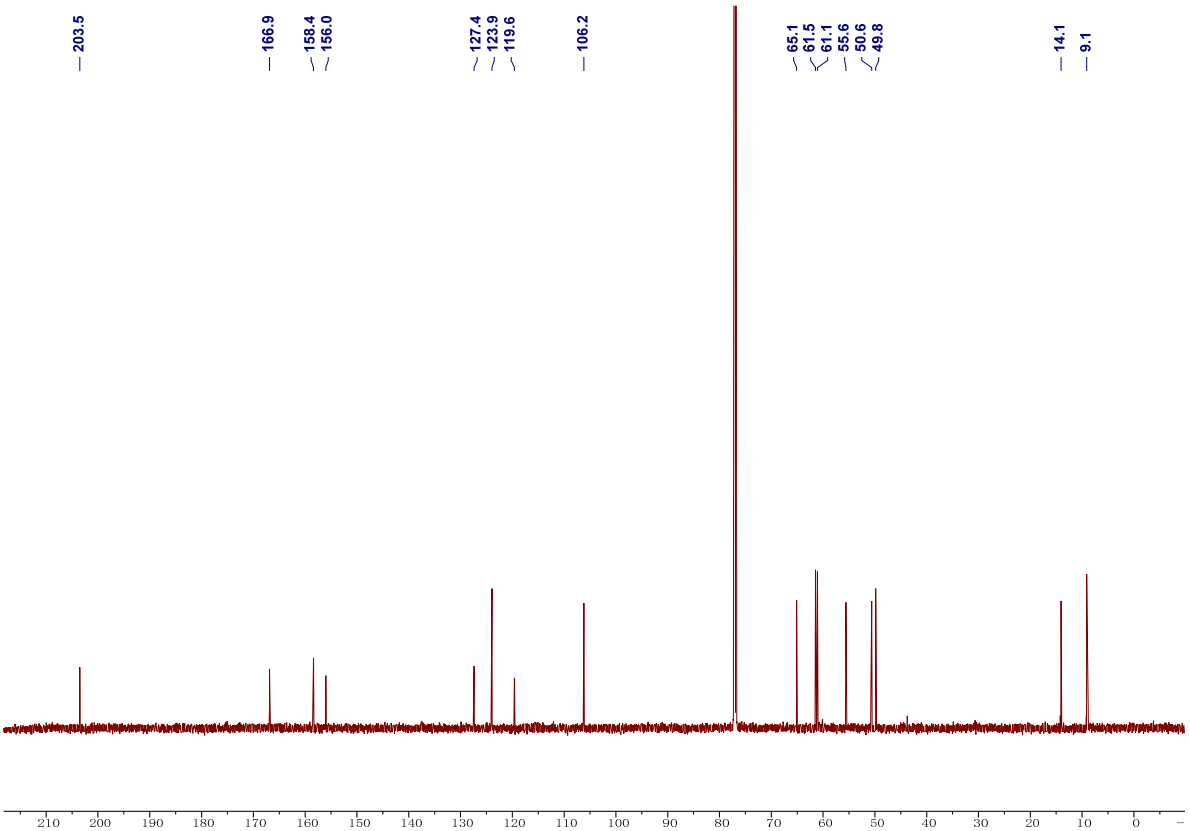


S17: Ethyl 5-(2,4-dimethoxy-3-methylphenyl)-5-hydroxy-3-oxopentanoate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

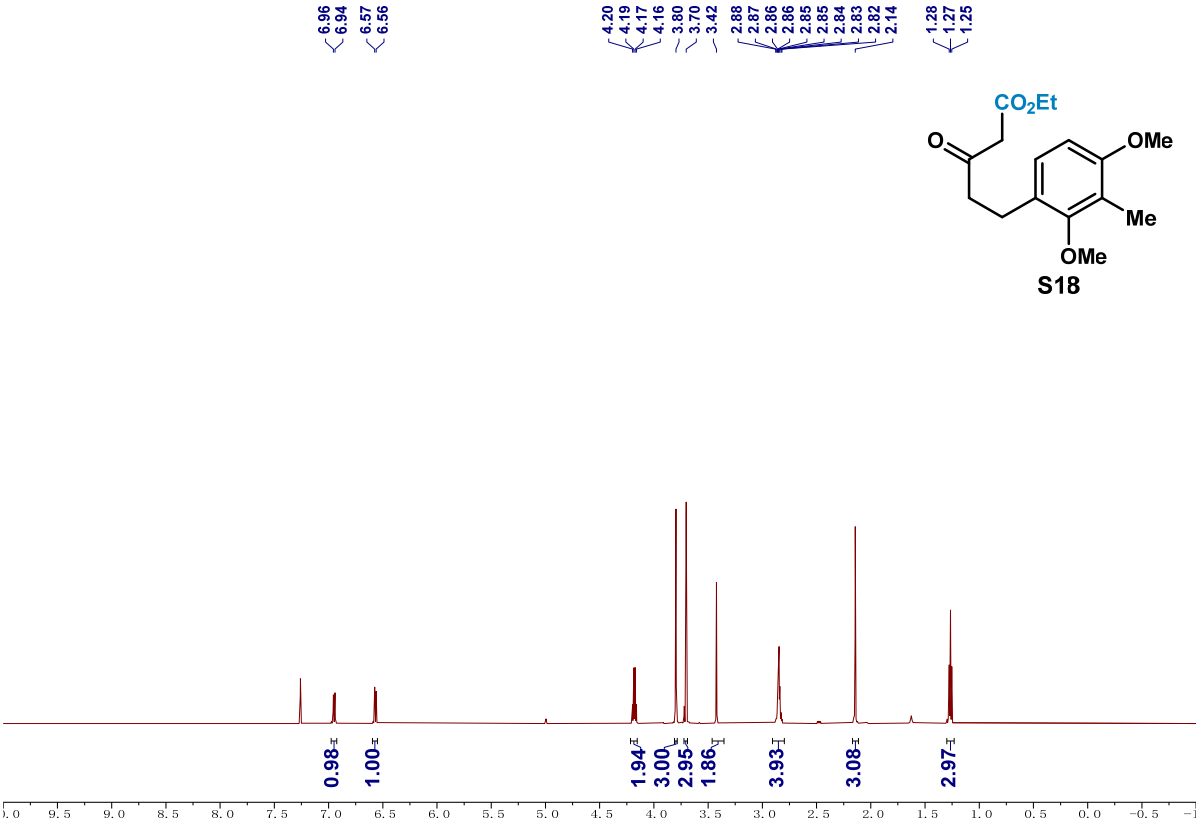


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)



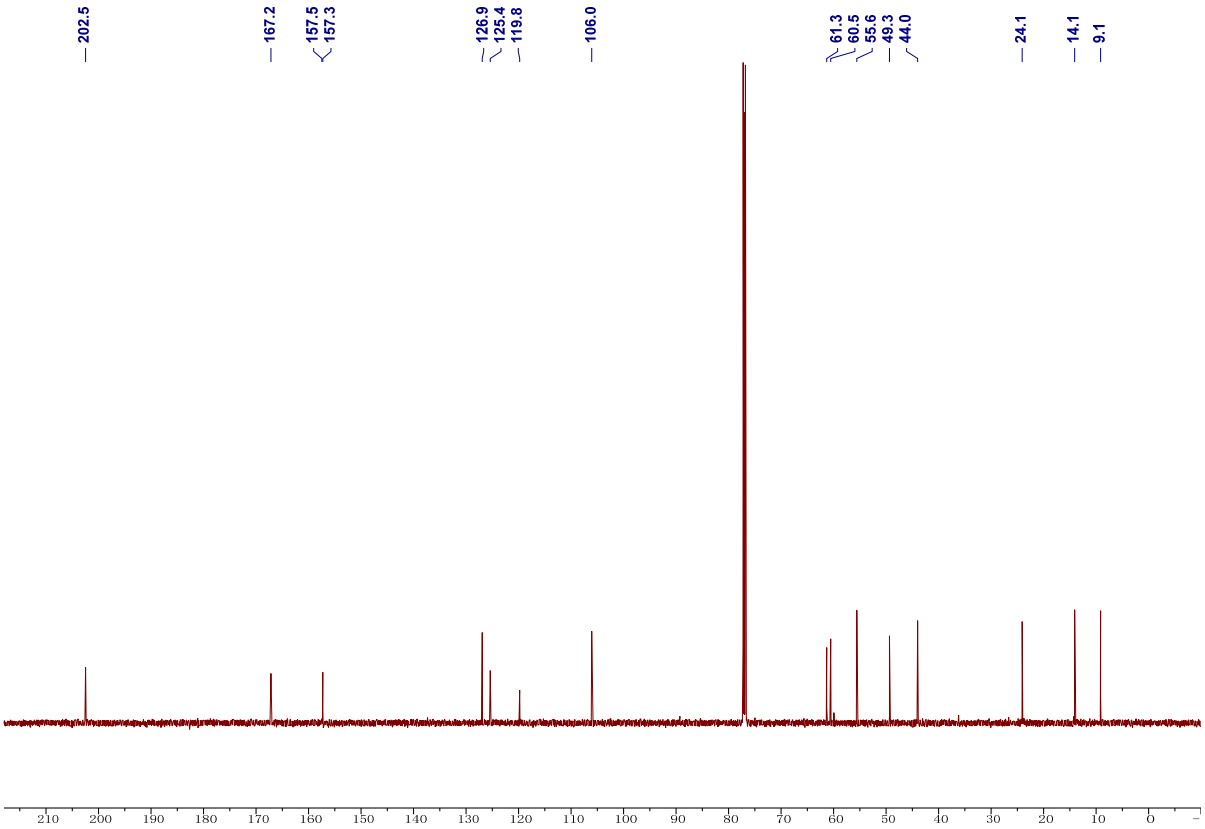
S18: Ethyl 5-(2,4-dimethoxy-3-methylphenyl)-3-oxopentanoate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)



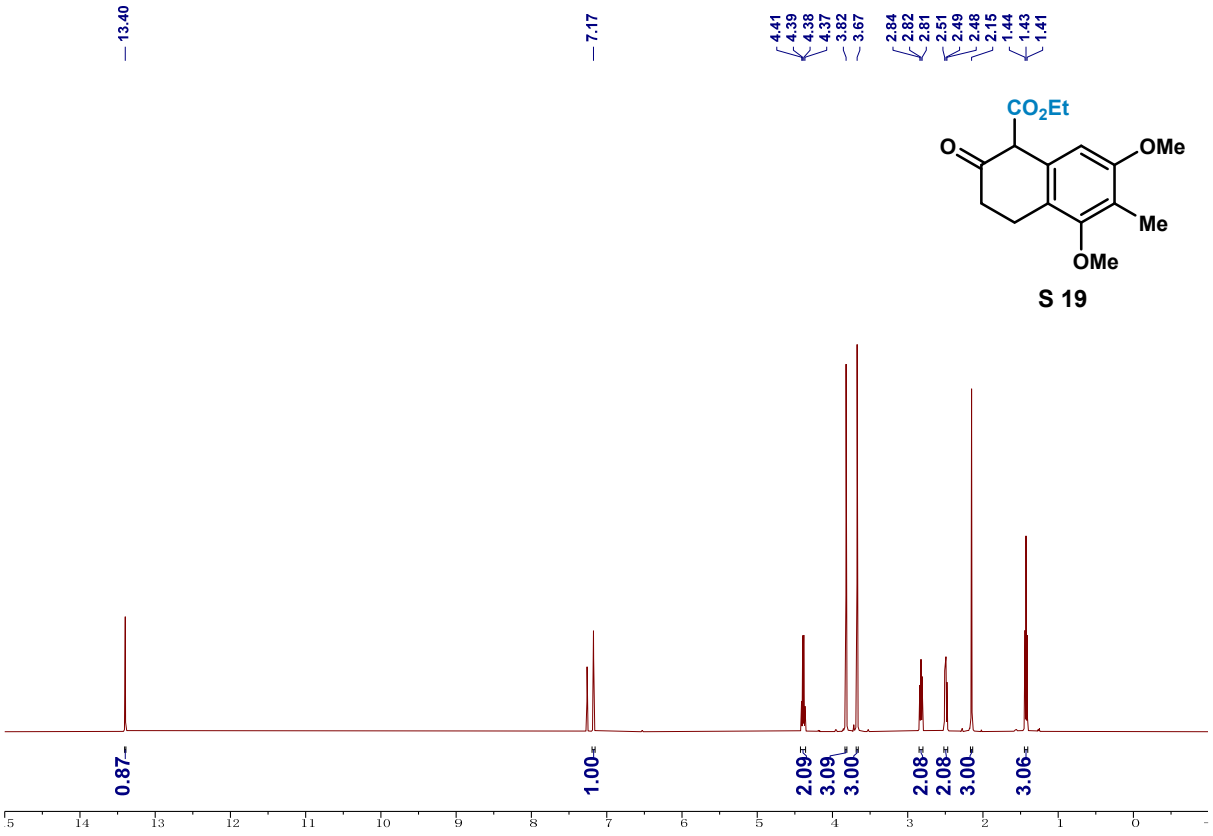
S18

^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

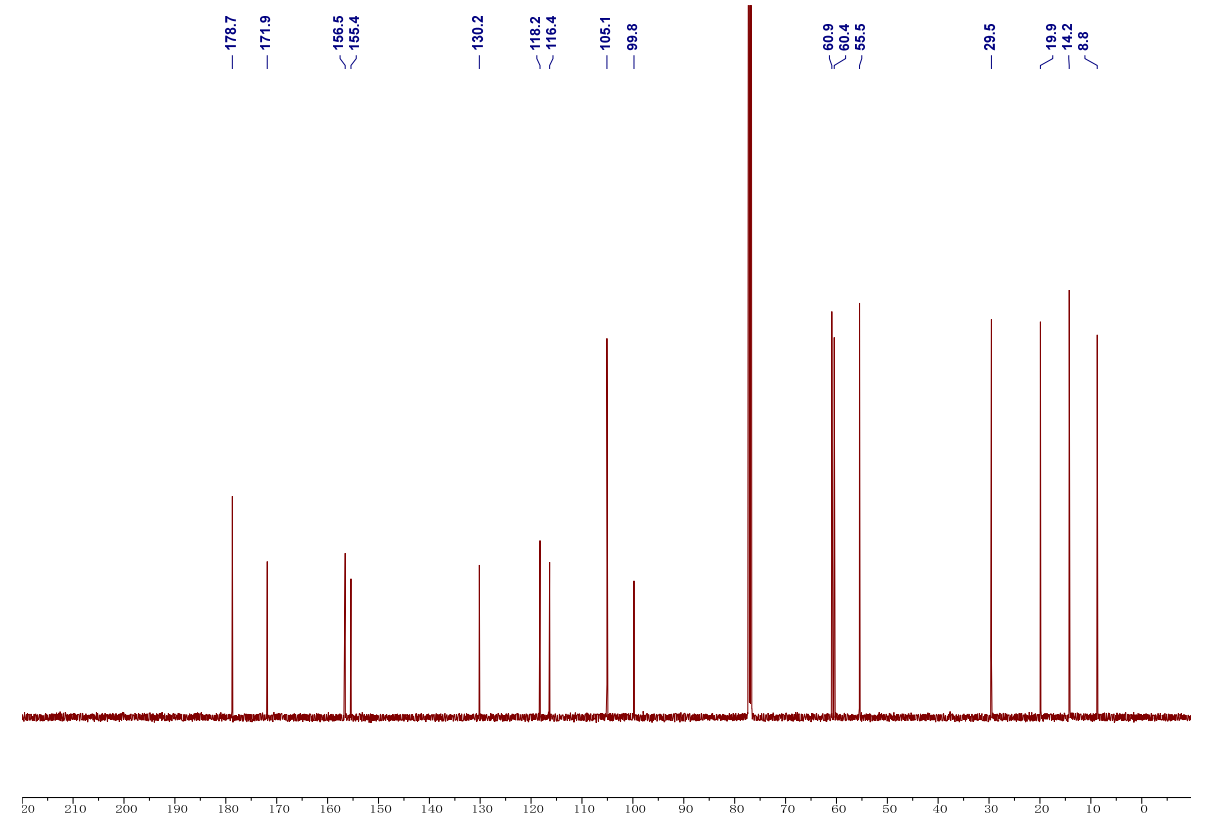


S19: Ethyl 5,7-dimethoxy-6-methyl-2-oxo-1,2,3,4-tetrahydronaphthalene-1-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

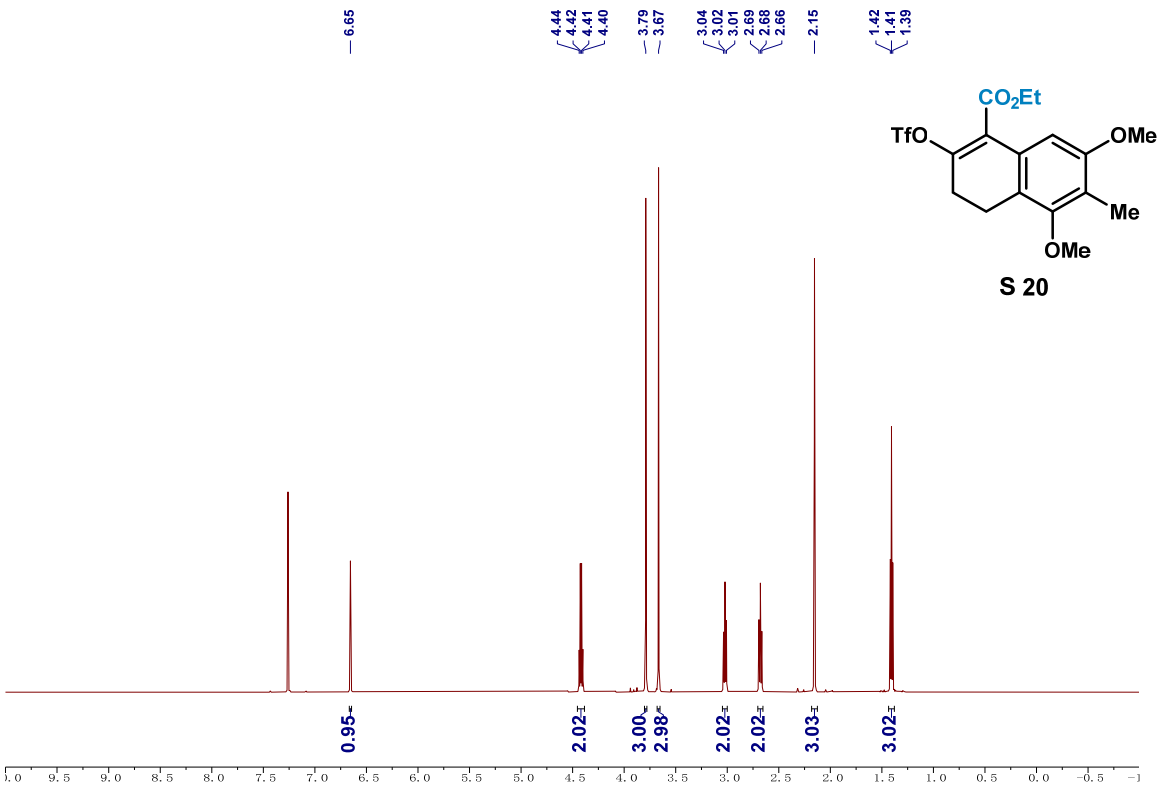


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

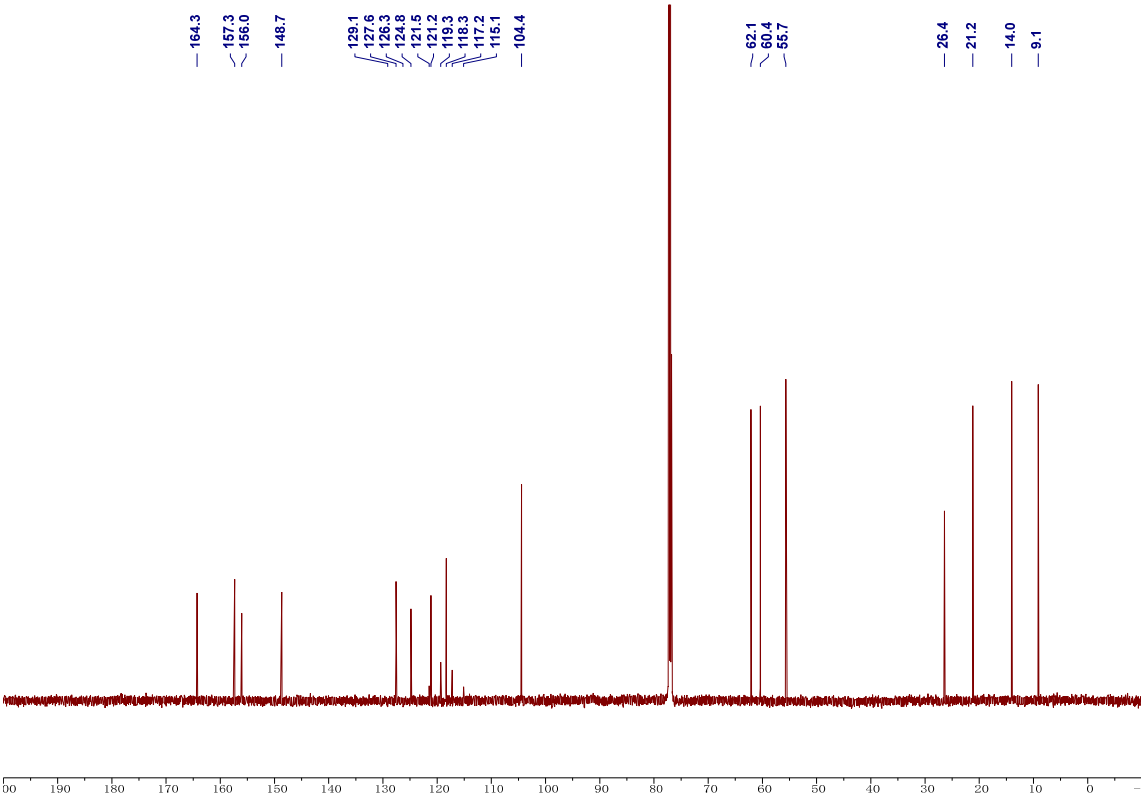


S20: Ethyl 5,7-dimethoxy-6-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4-dihydronaphthalene-1-carboxylate

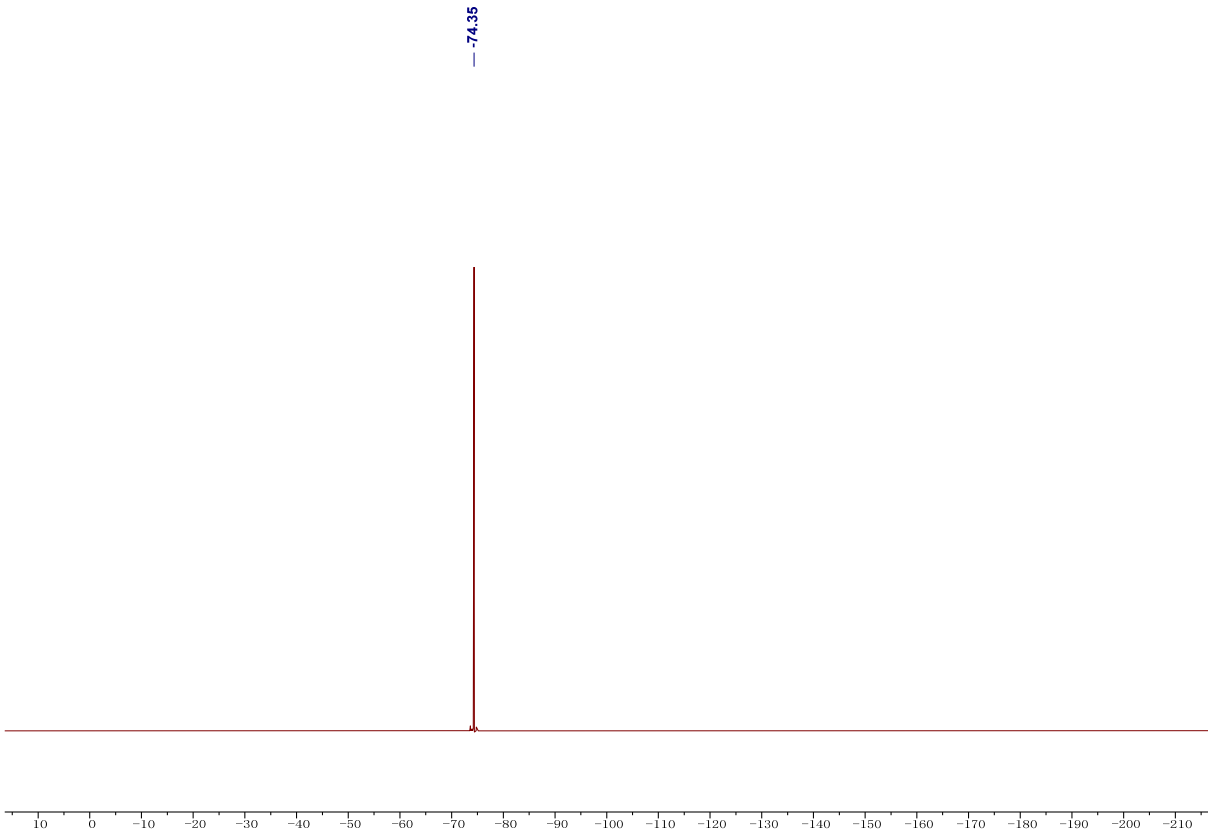
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

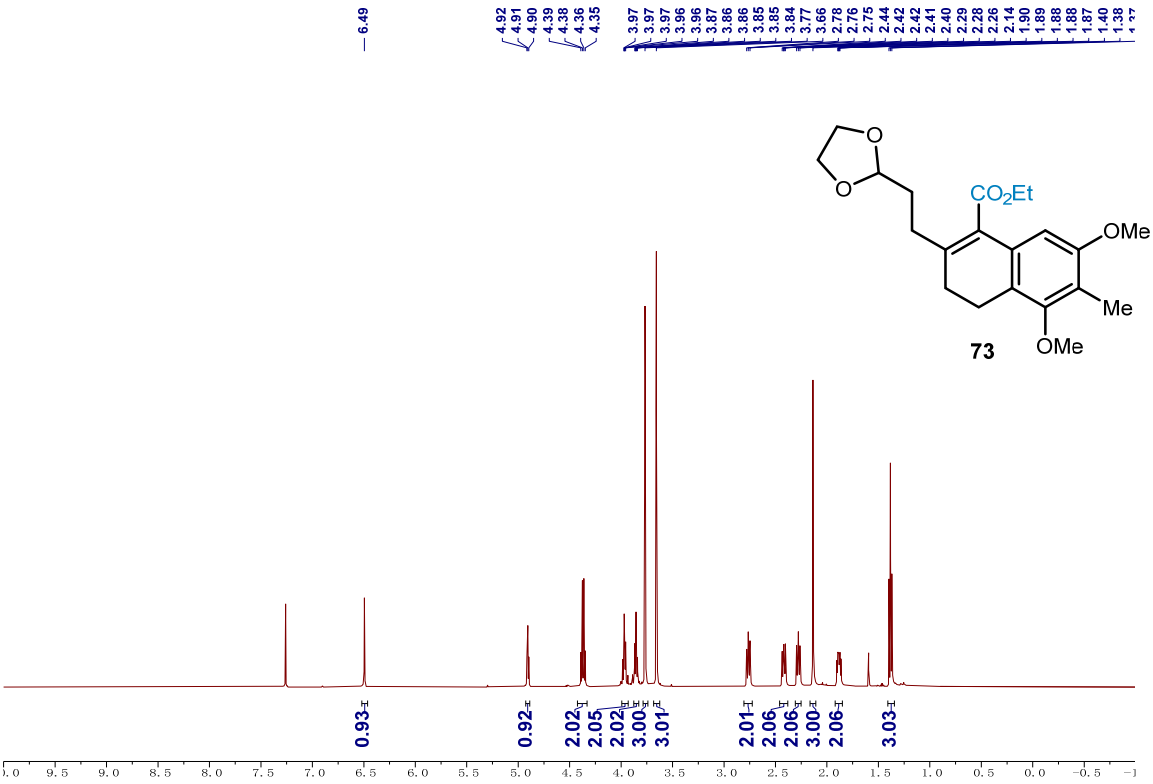


^{19}F NMR (565 MHz, $CDCl_3$)

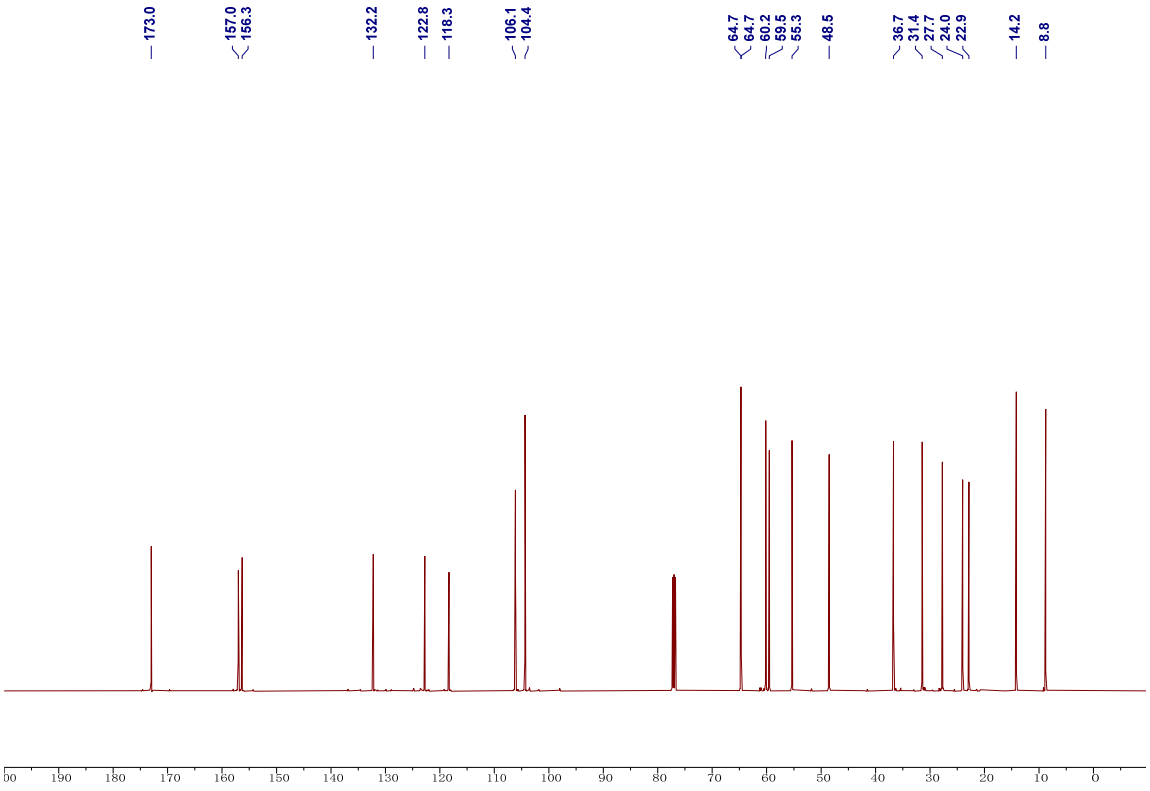


73: Ethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-5,7-dimethoxy-6-methyl-3,4-dihydronaphthalene-1-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

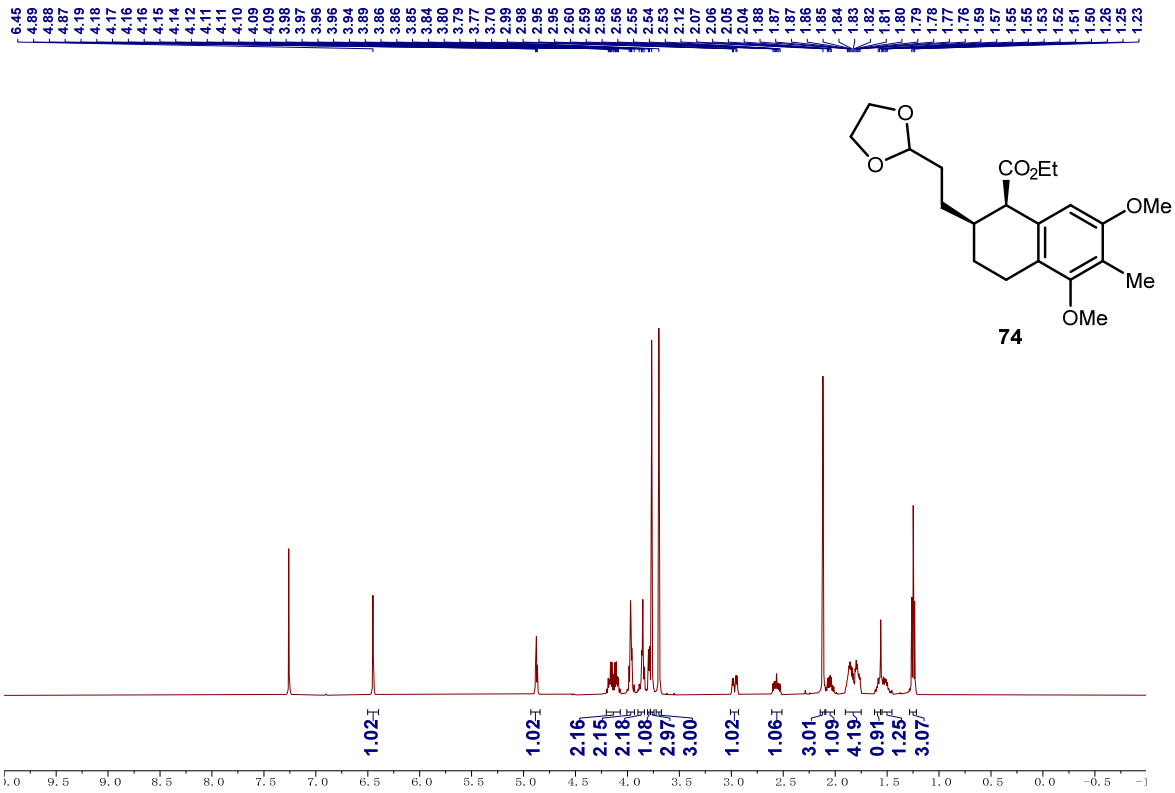


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

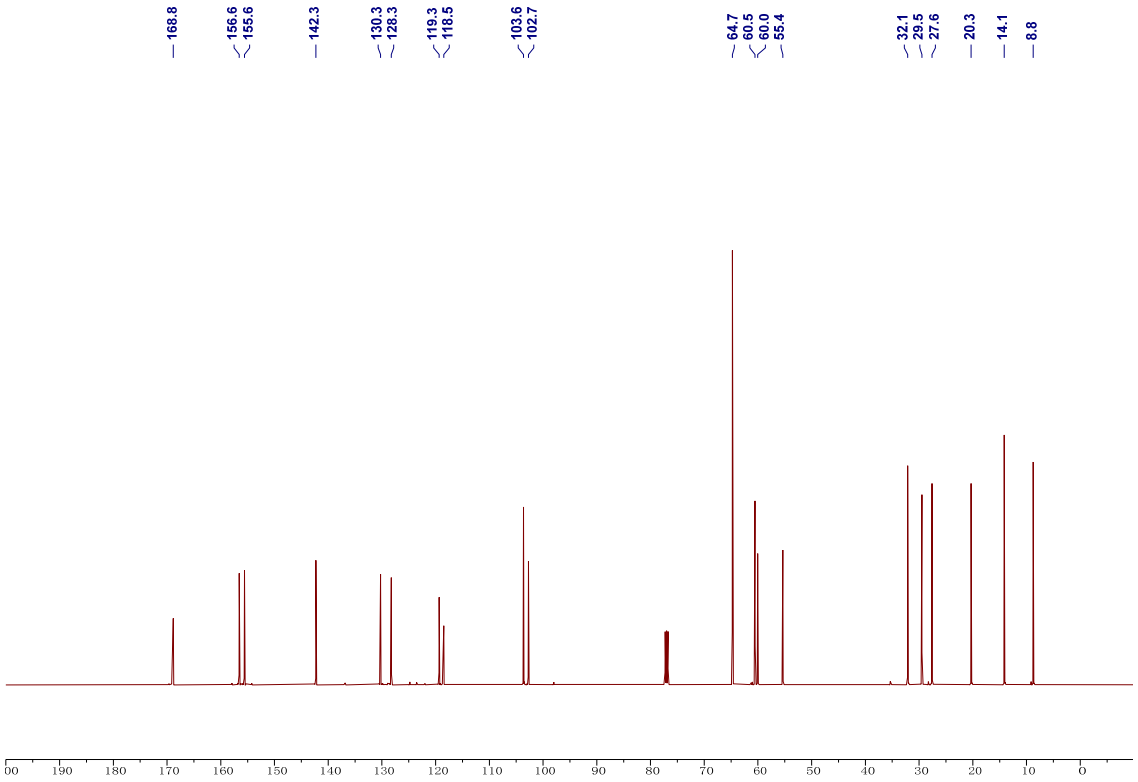


74: Ethyl (1S,2R)-2-(2-(1,3-dioxolan-2-yl)ethyl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydro-naphthalene-1-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

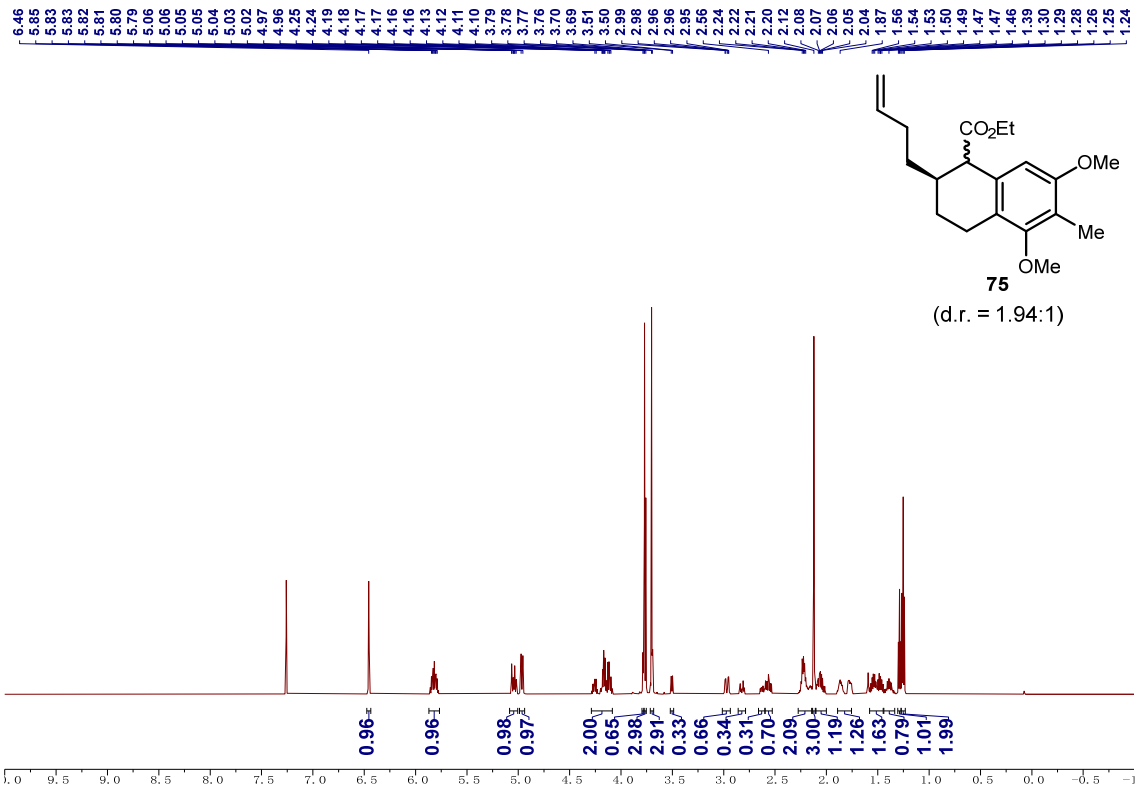


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

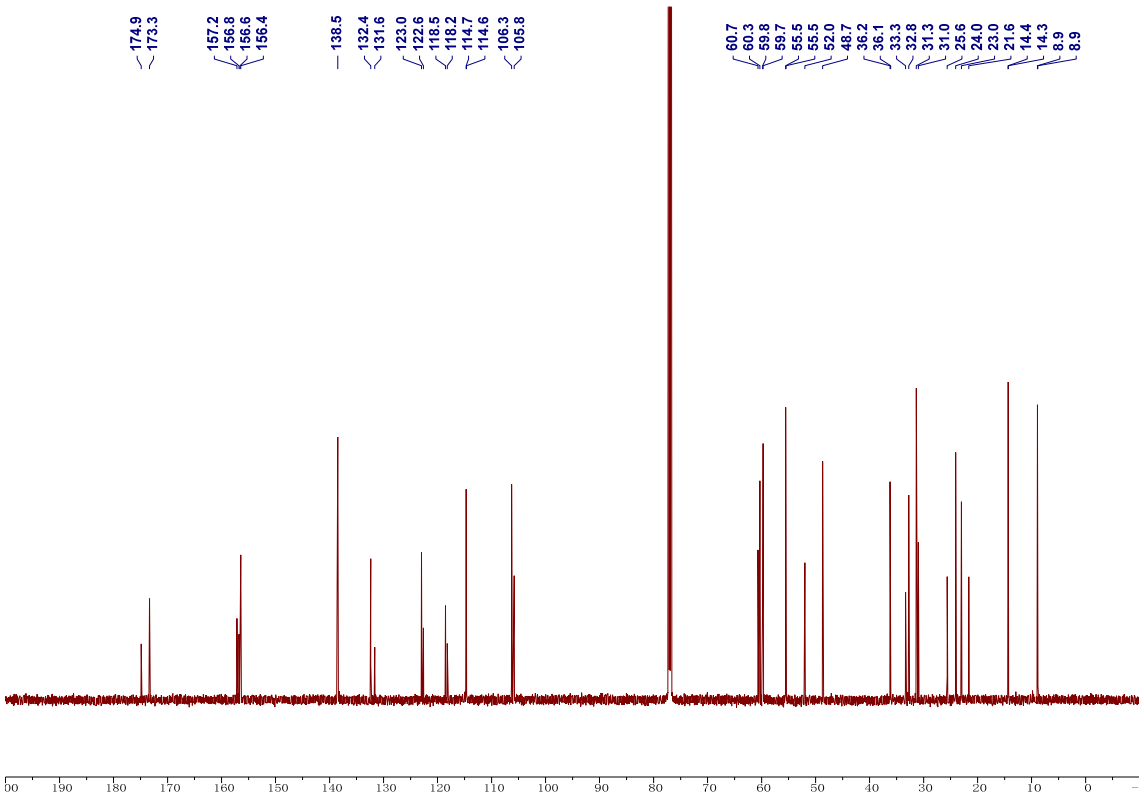


75: Ethyl (1S,2S)-2-(but-3-en-1-yl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

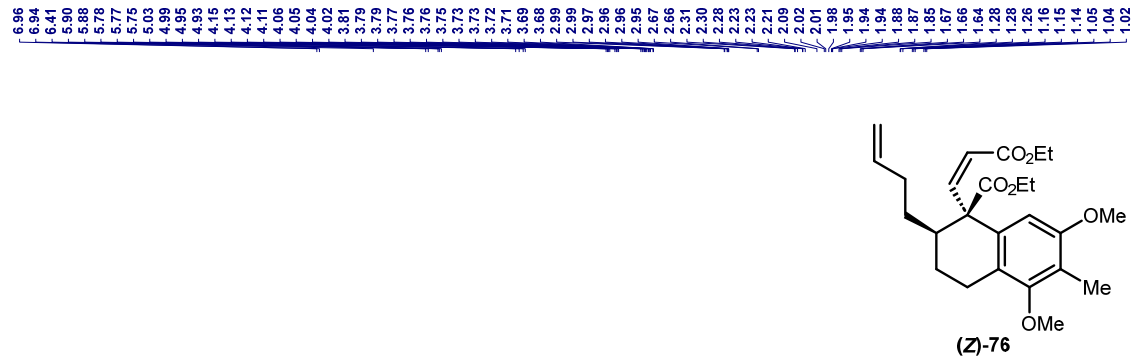


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

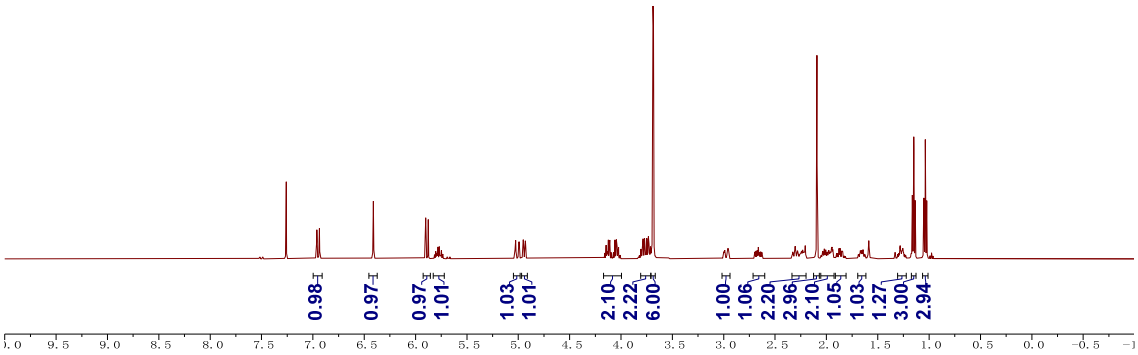


(Z)-76: Ethyl (1R,2S)-2-(but-3-en-1-yl)-1-((Z)-3-ethoxy-3-oxoprop-1-en-1-yl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate

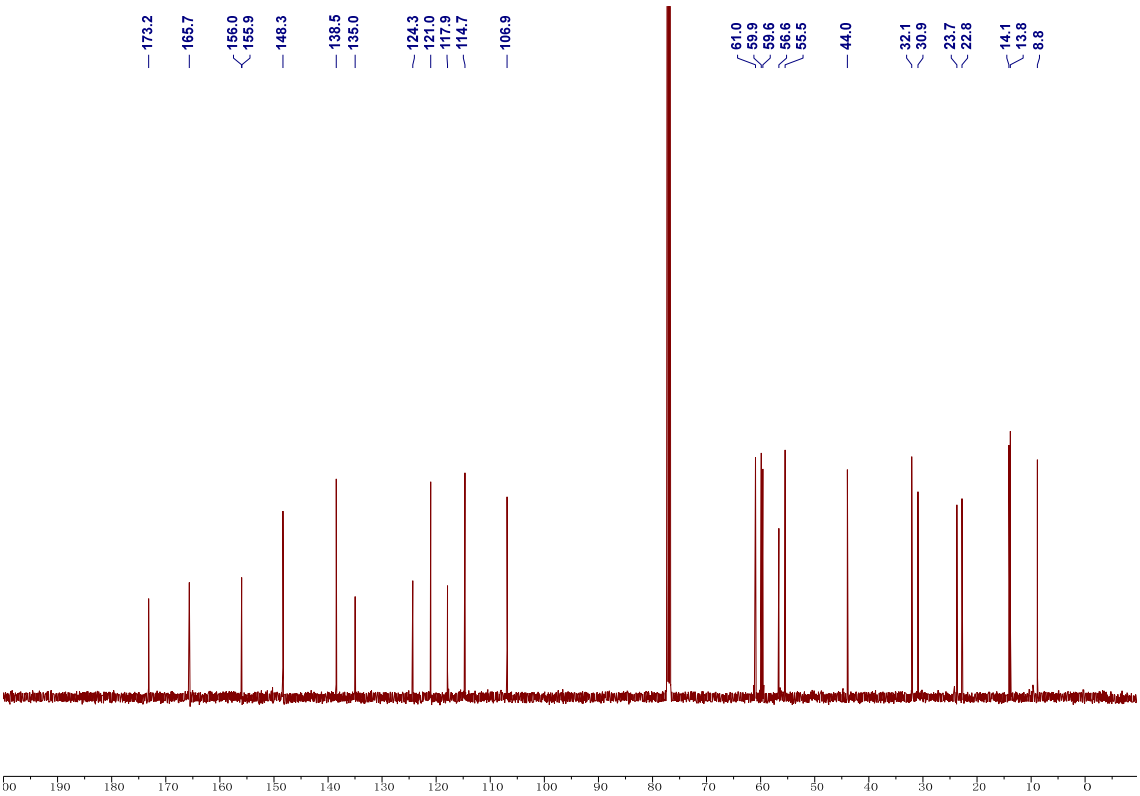
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



(Z)-76

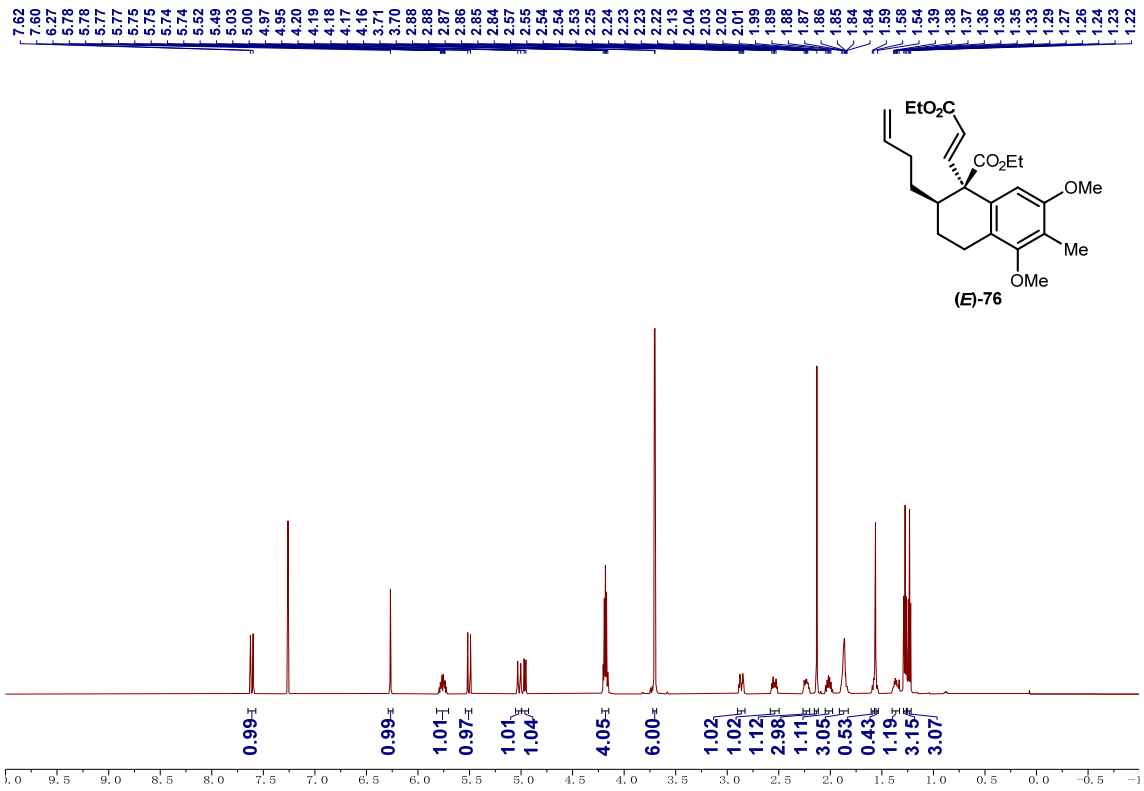


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

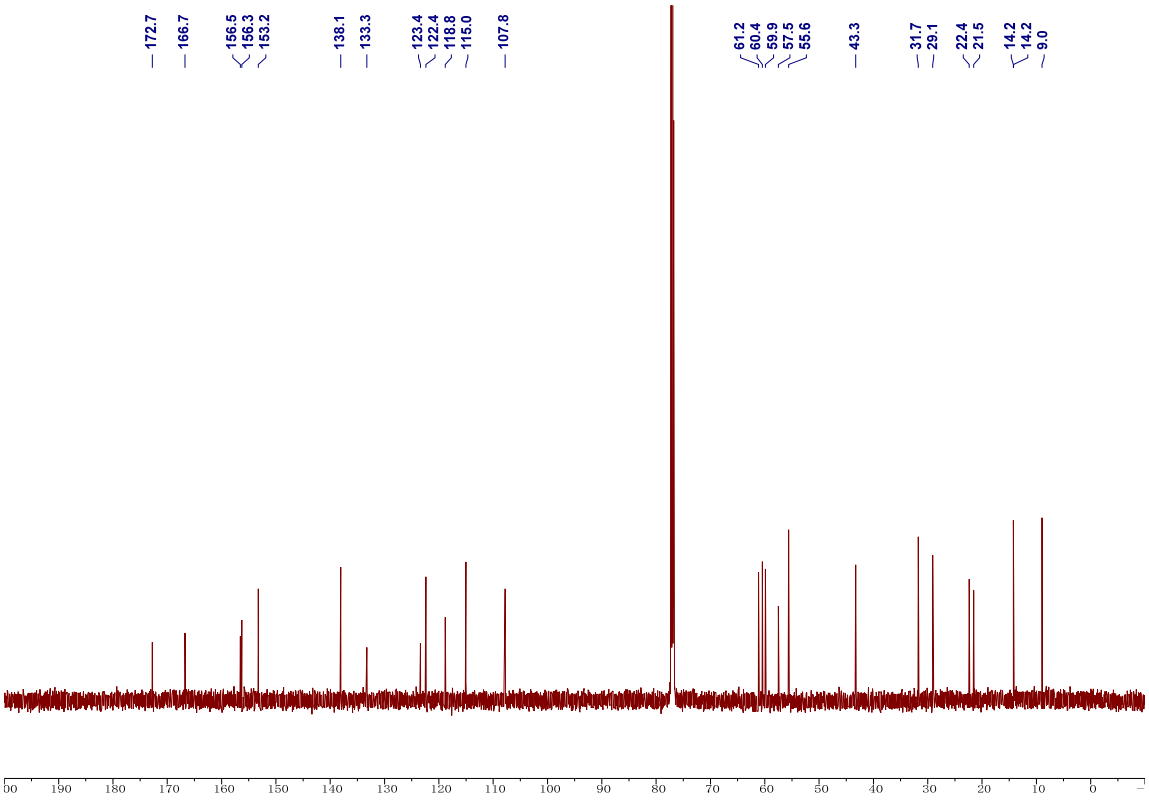


(*E*)-76: Ethyl (1R,2S)-2-(but-3-en-1-yl)-1-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-5,7-dimethoxy-6-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

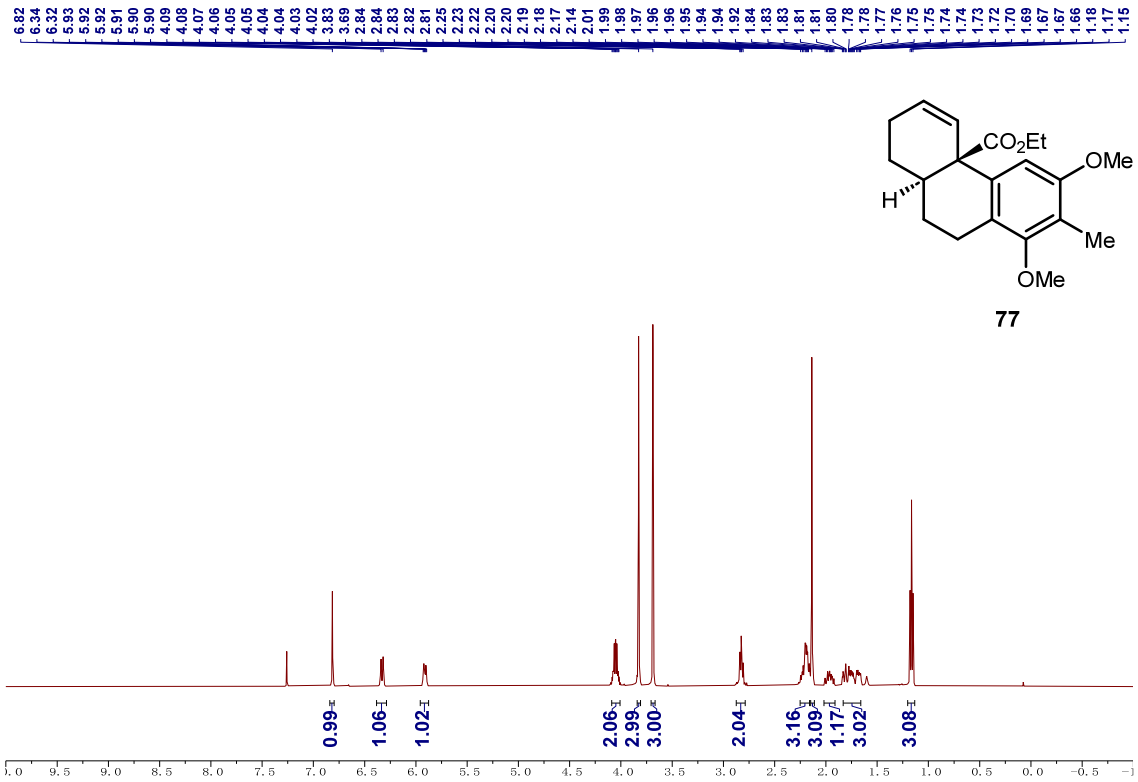


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

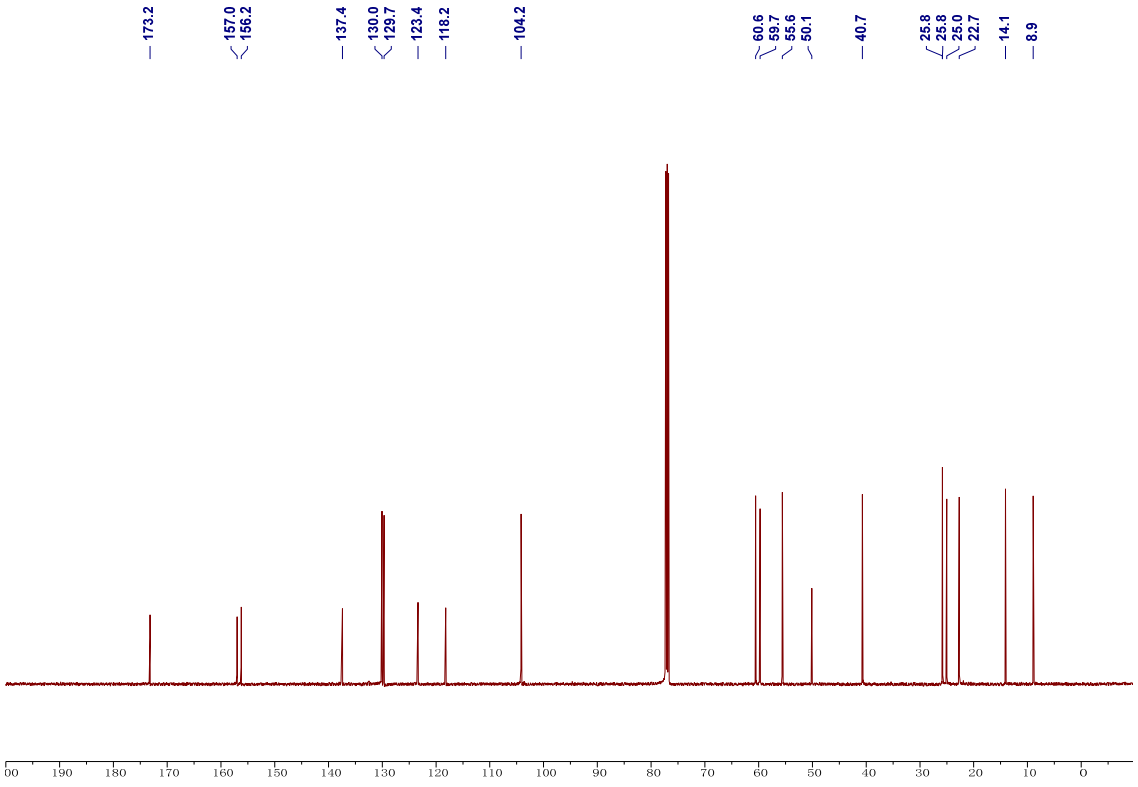


77: Ethyl (4aR,10aS)-6,8-dimethoxy-7-methyl-1,9,10,10a-tetrahydrophenanthrene-4a(2H)-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

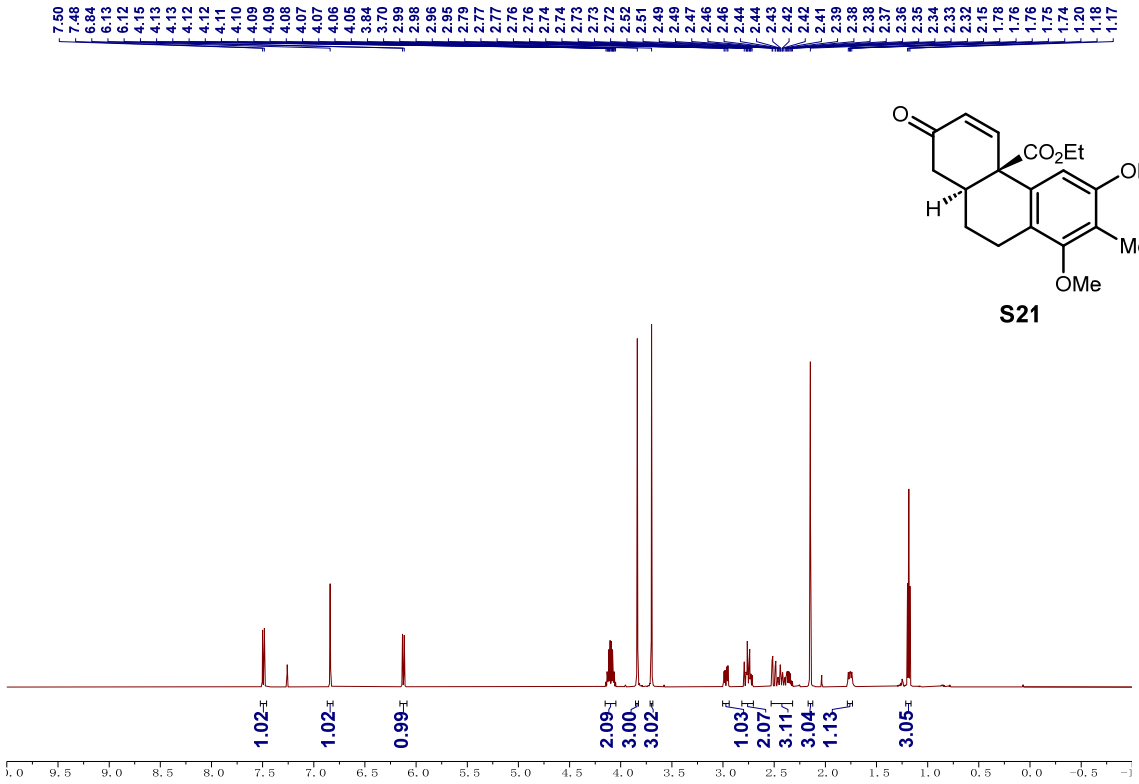


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

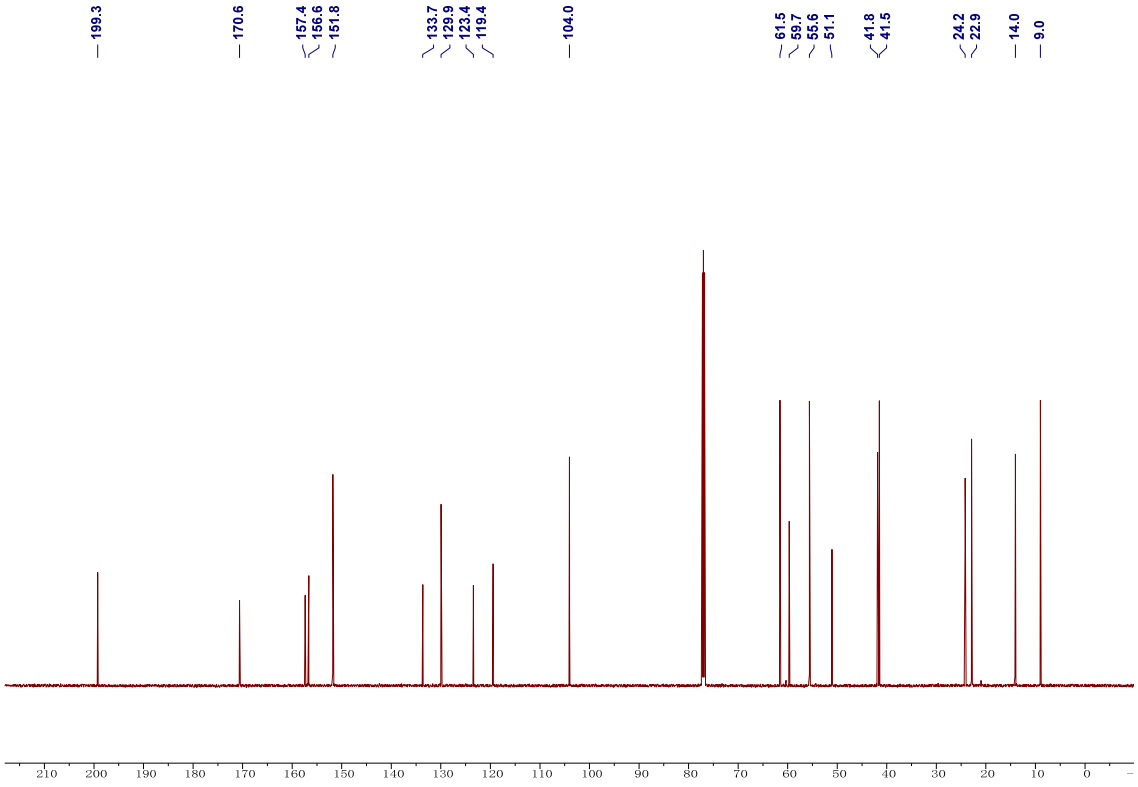


S21: Ethyl (4aR,10aR)-6,8-dimethoxy-7-methyl-2-oxo-1,9,10,10a-tetrahydrophenanthrene-4a(2H) carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

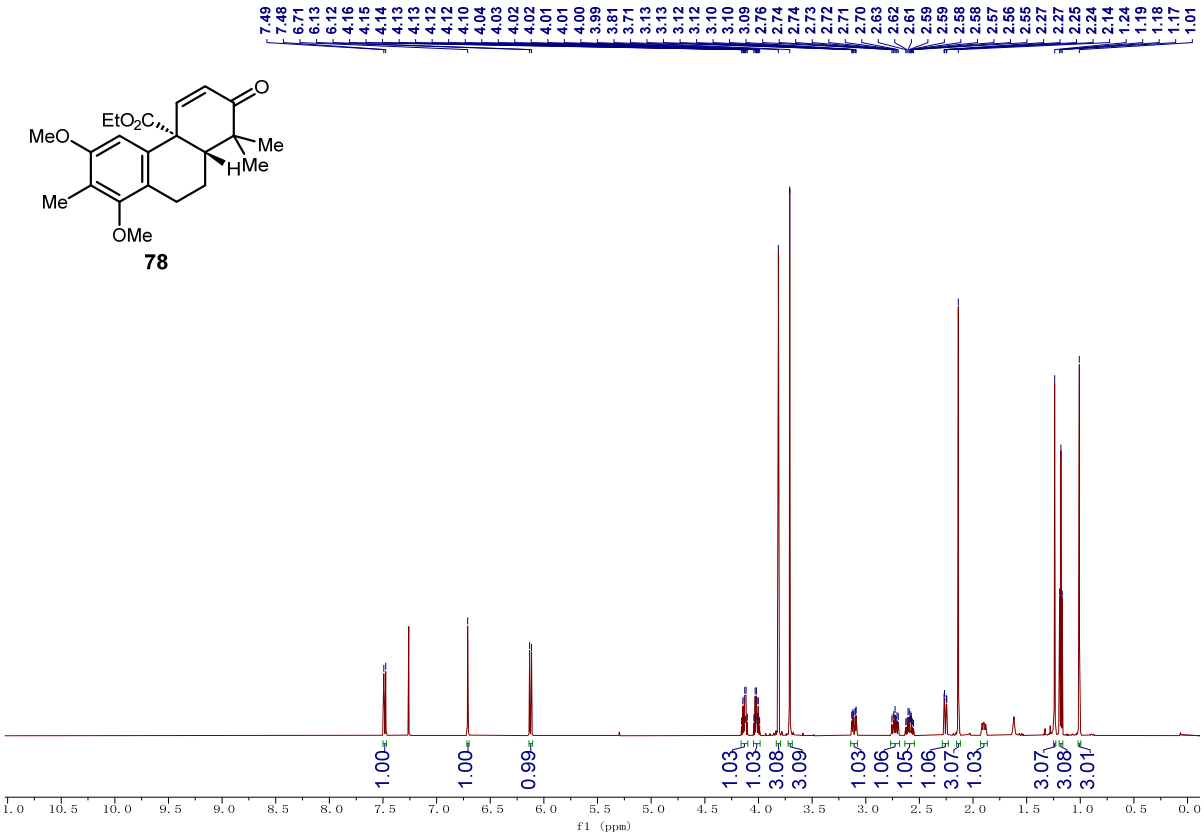


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

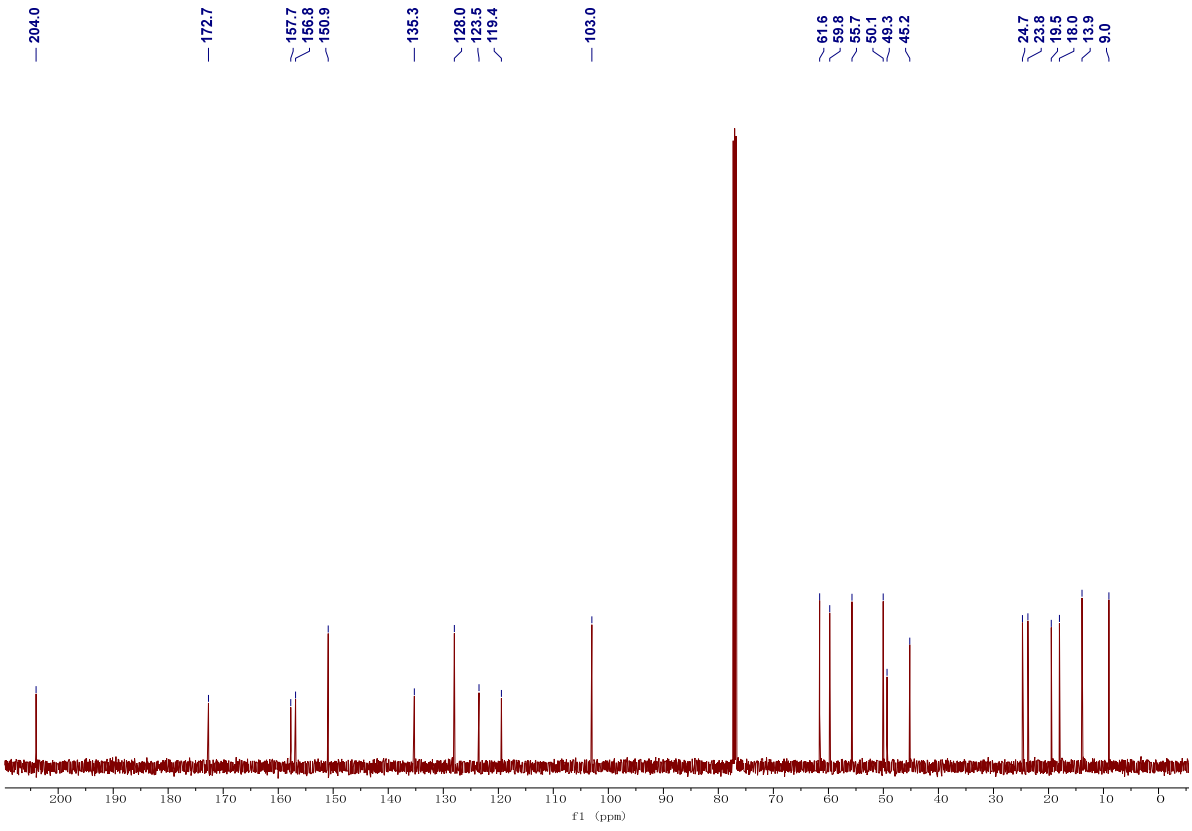


78: Ethyl (4aS,10aR)-6,8-dimethoxy-1,1,7-trimethyl-2-oxo-1,9,10,10a-tetrahydrophenan-threne-4a(2H-)-carboxylate

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

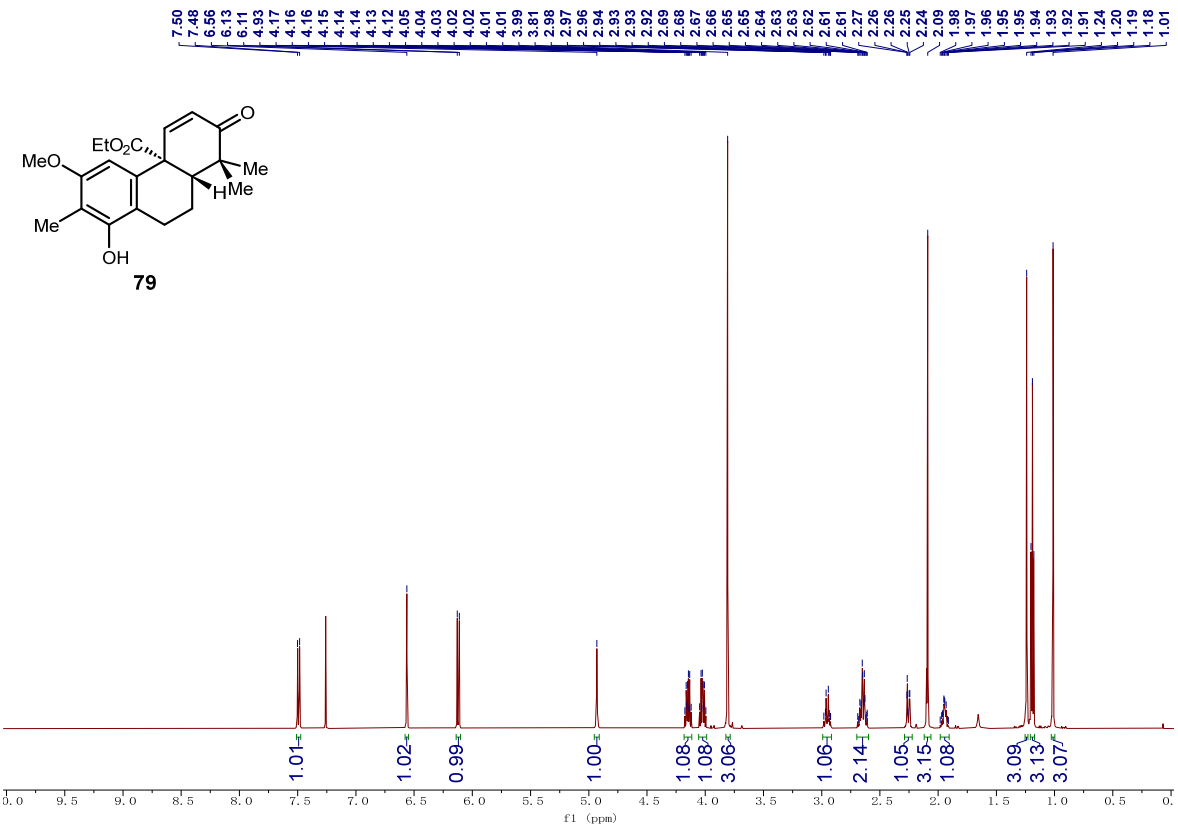


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

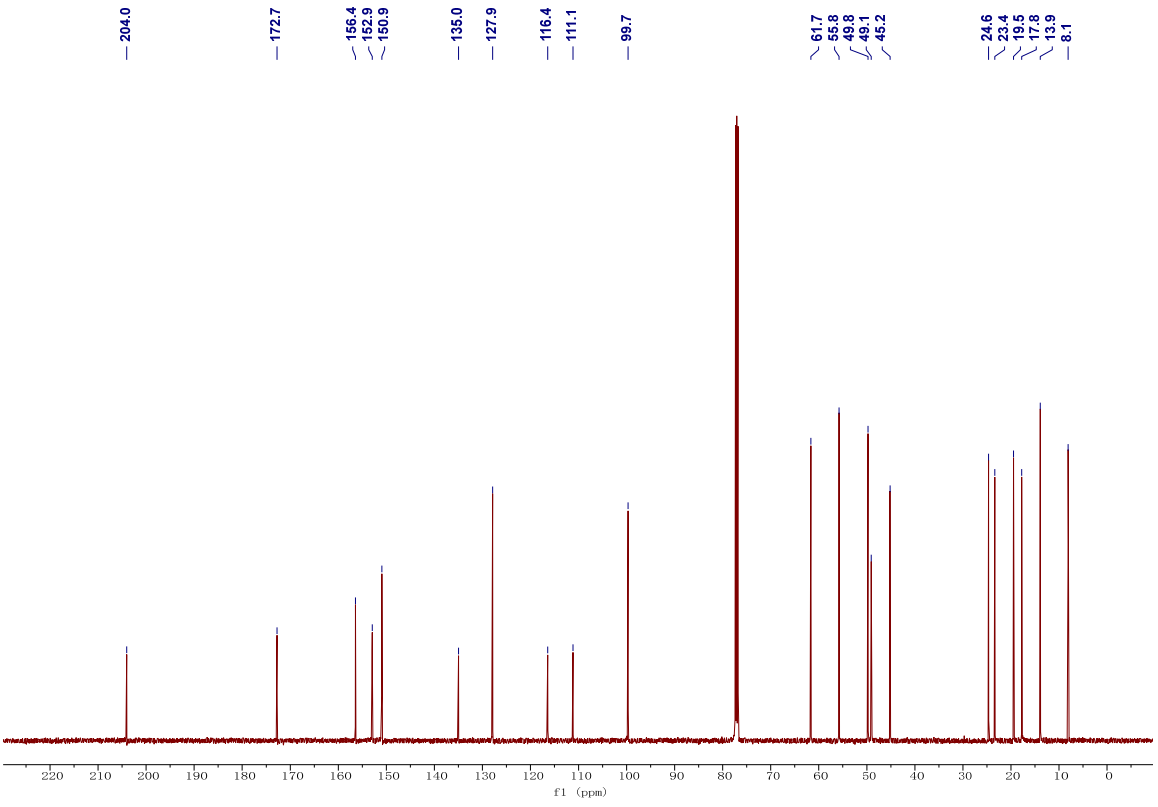


79: Ethyl (4aS,10aR)-8-hydroxy-6-methoxy-1,1,7-trimethyl-2-oxo-1,9,10,10a-tetrahydro-phenanthrene-4a(2H)-carboxylate

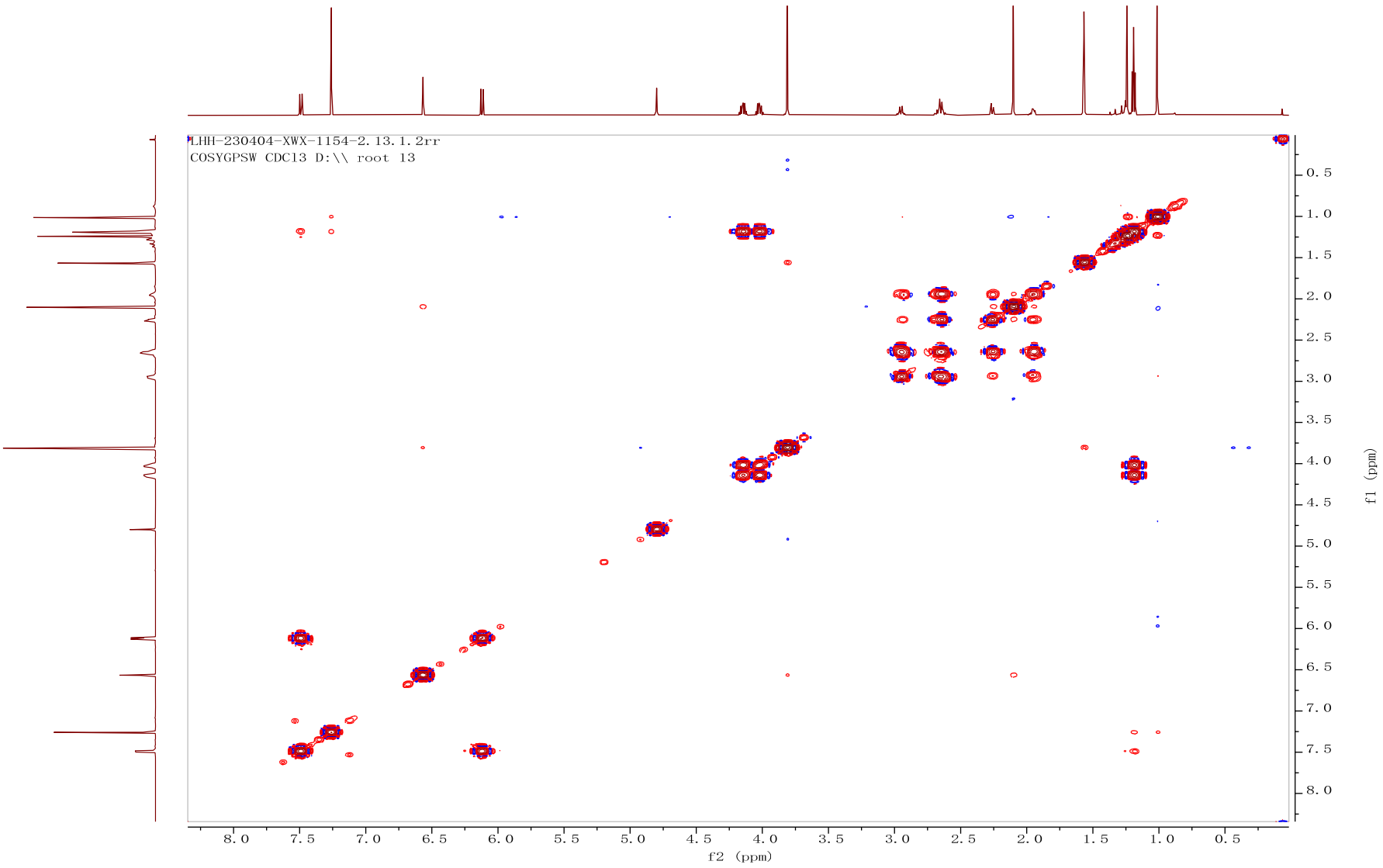
^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



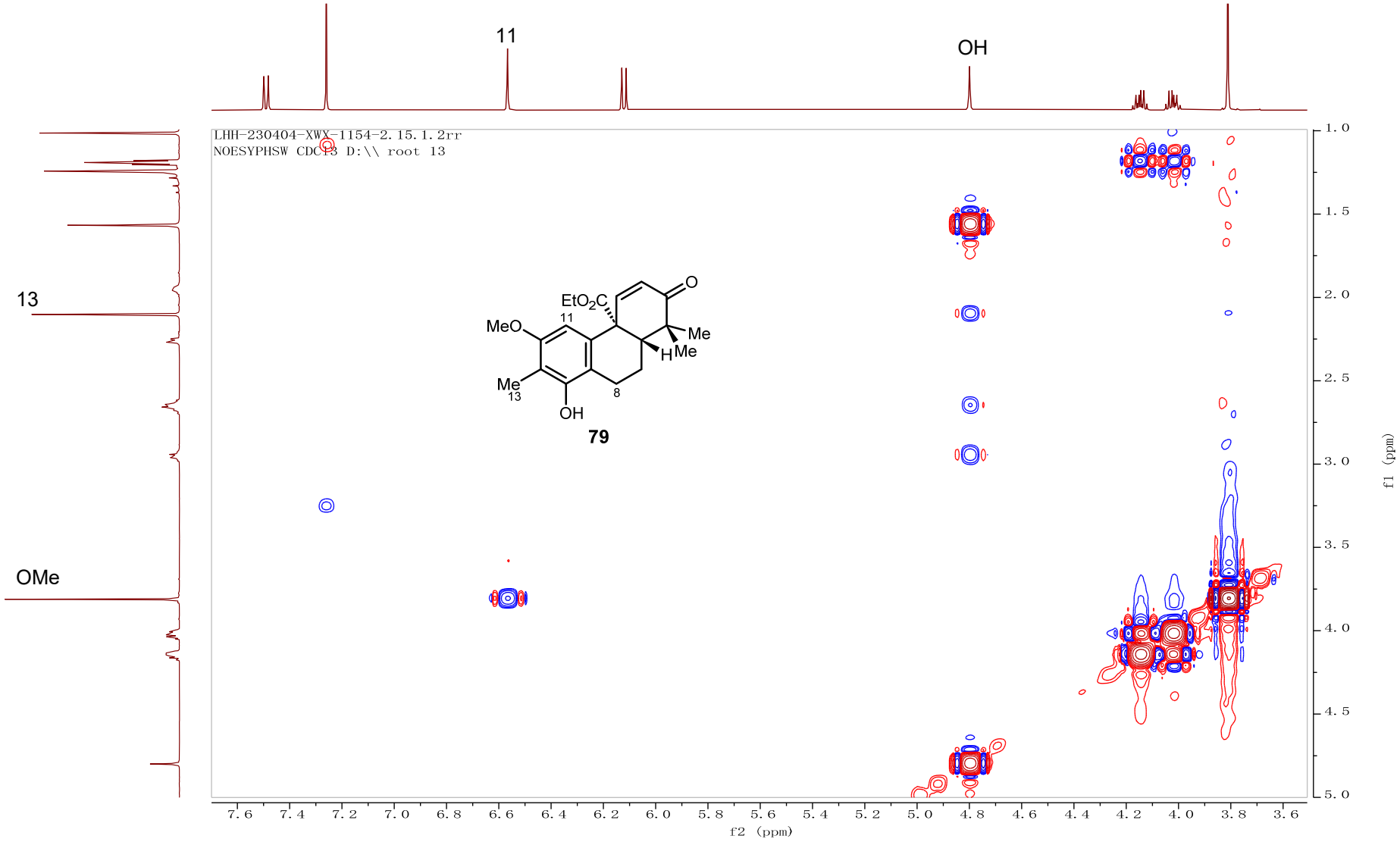
^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



COSY (600 MHz, $CDCl_3$)

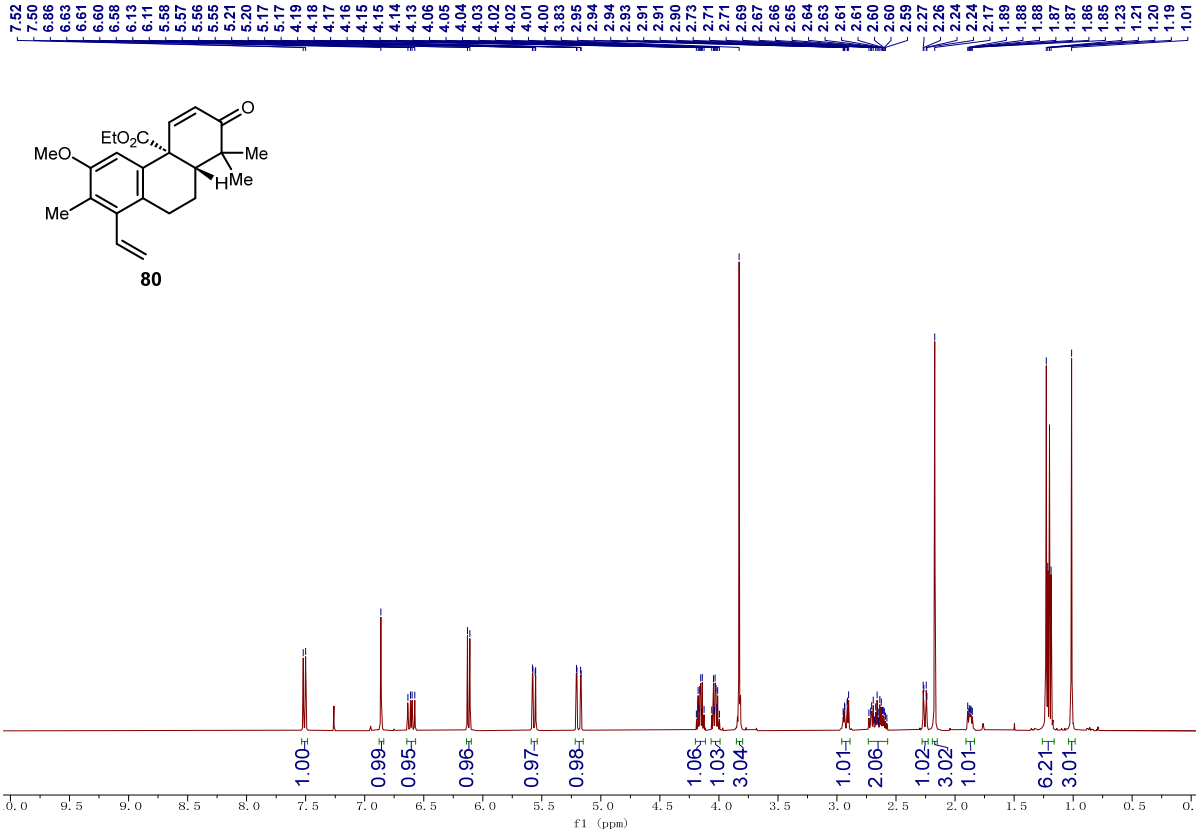


NOESY (600 MHz, $CDCl_3$)

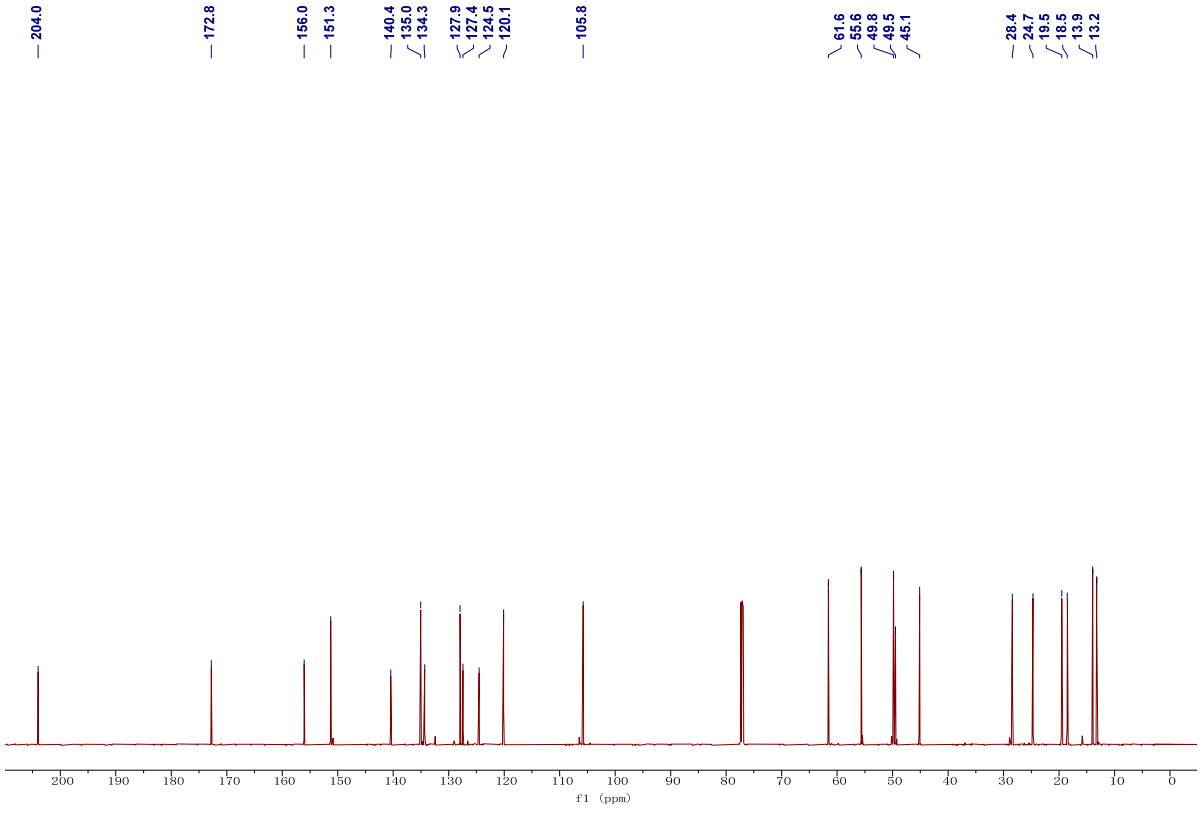


80: Ethyl (4aS,10aR)-6-methoxy-1,1,7-trimethyl-2-oxo-8-vinyl-1,9,10,10a-tetrahydrophenanthrene-4a-(2H)-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

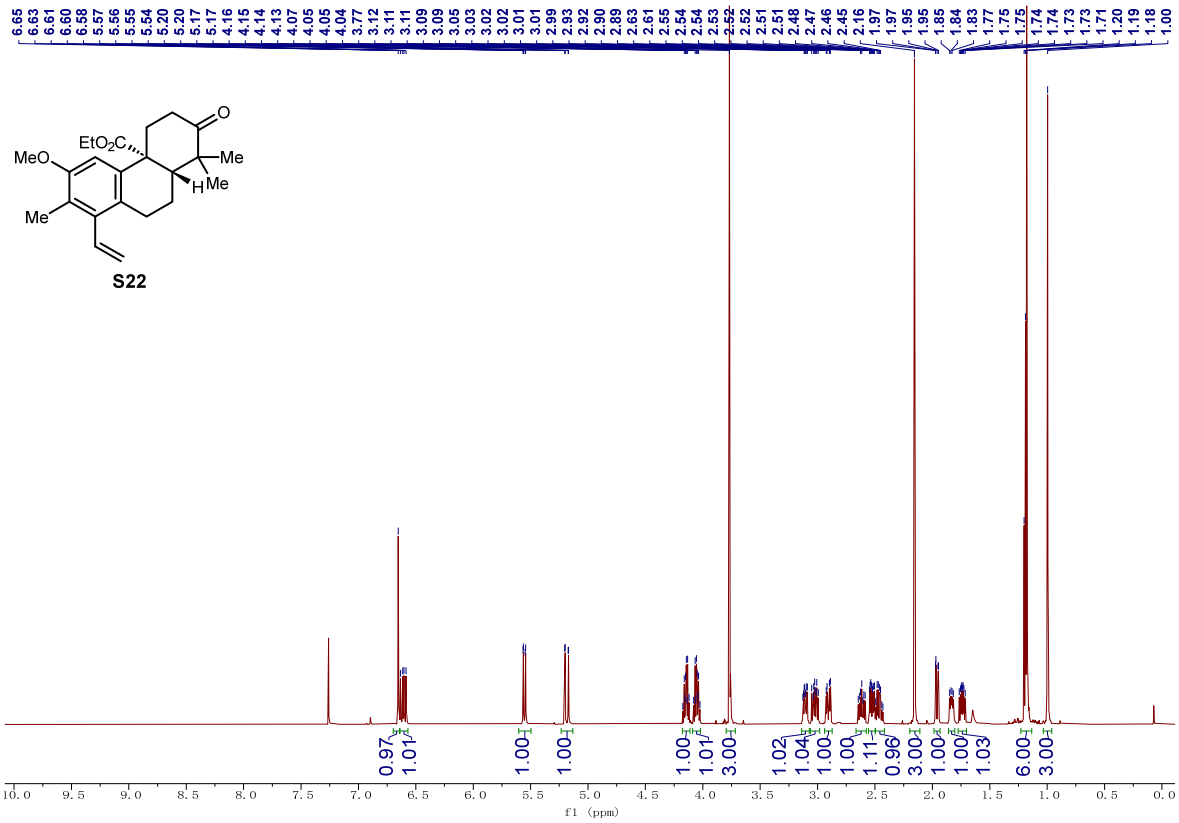


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

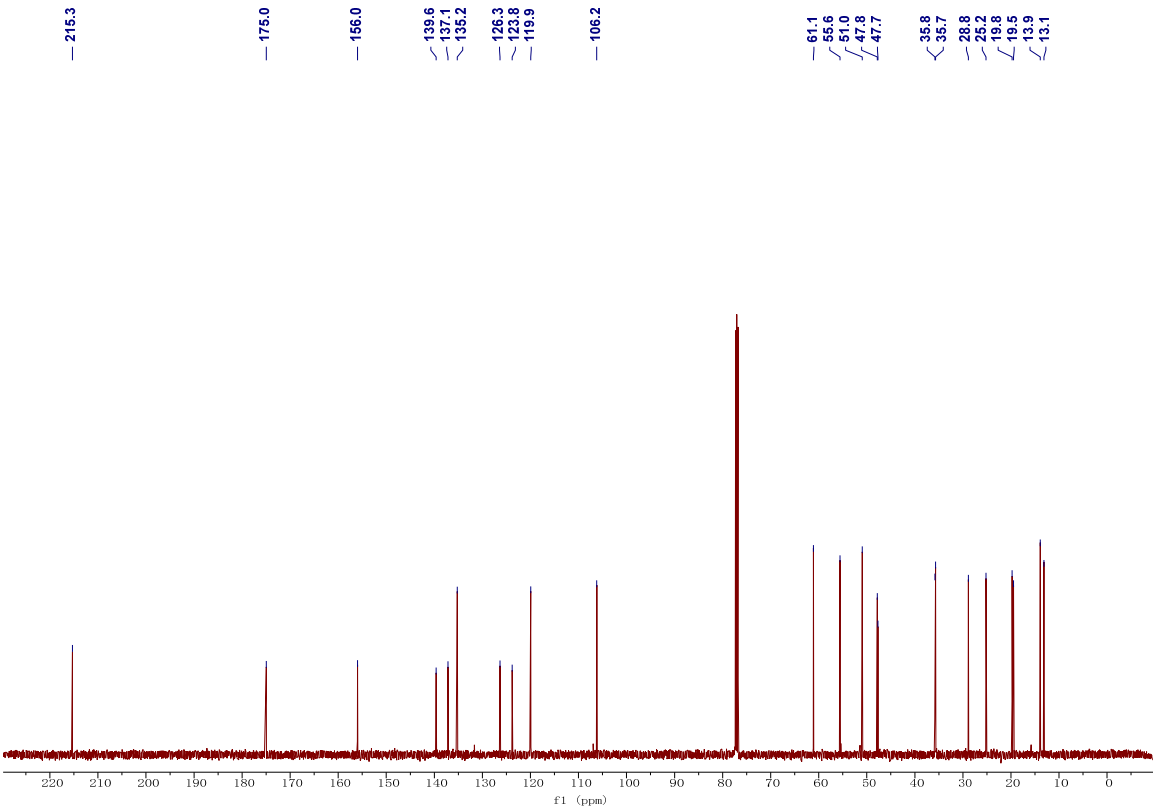


S22: Ethyl (4aS,10aR)-6-methoxy-1,1,7-trimethyl-2-oxo-8-vinyl-1,3,4,9,10,10a-hexahydro-phenanth-rene-4a(2H)-carboxylate

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)

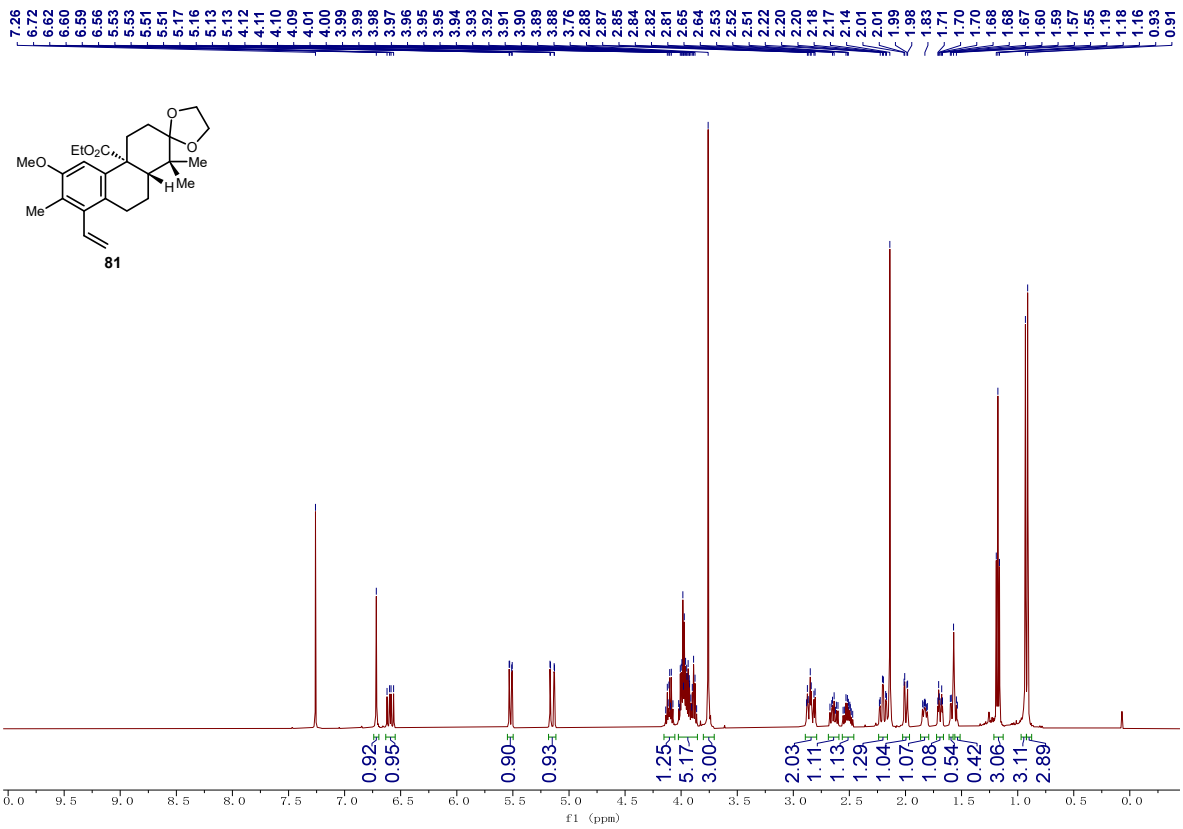


^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)

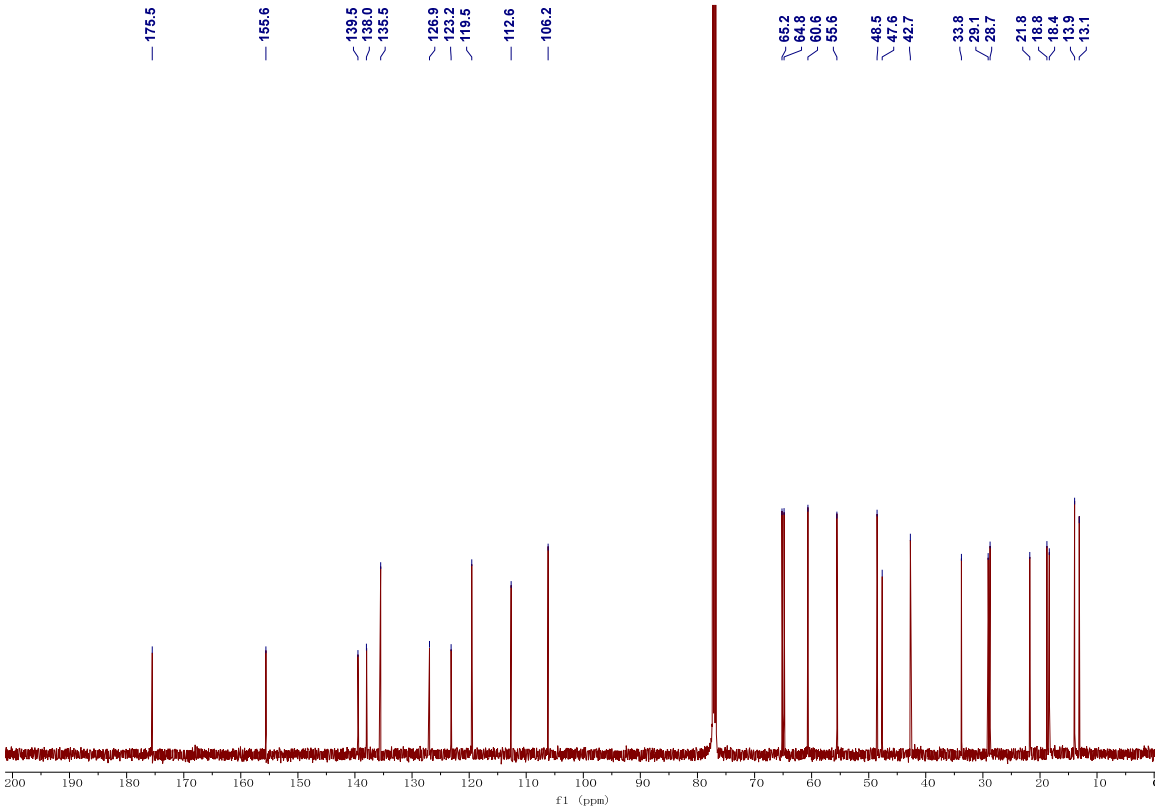


81: Ethyl (4aS,10aR)-6-methoxy-1,1,7-trimethyl-8-vinyl-1,3,4,9,10,10a-hexahydro-4aH-spiro[phenant-hrene-2,2'-[1,3]dioxolane]-4a-carboxylate

^{1}H NMR (500 MHz, $CDCl_3$ @ 7.26 ppm)

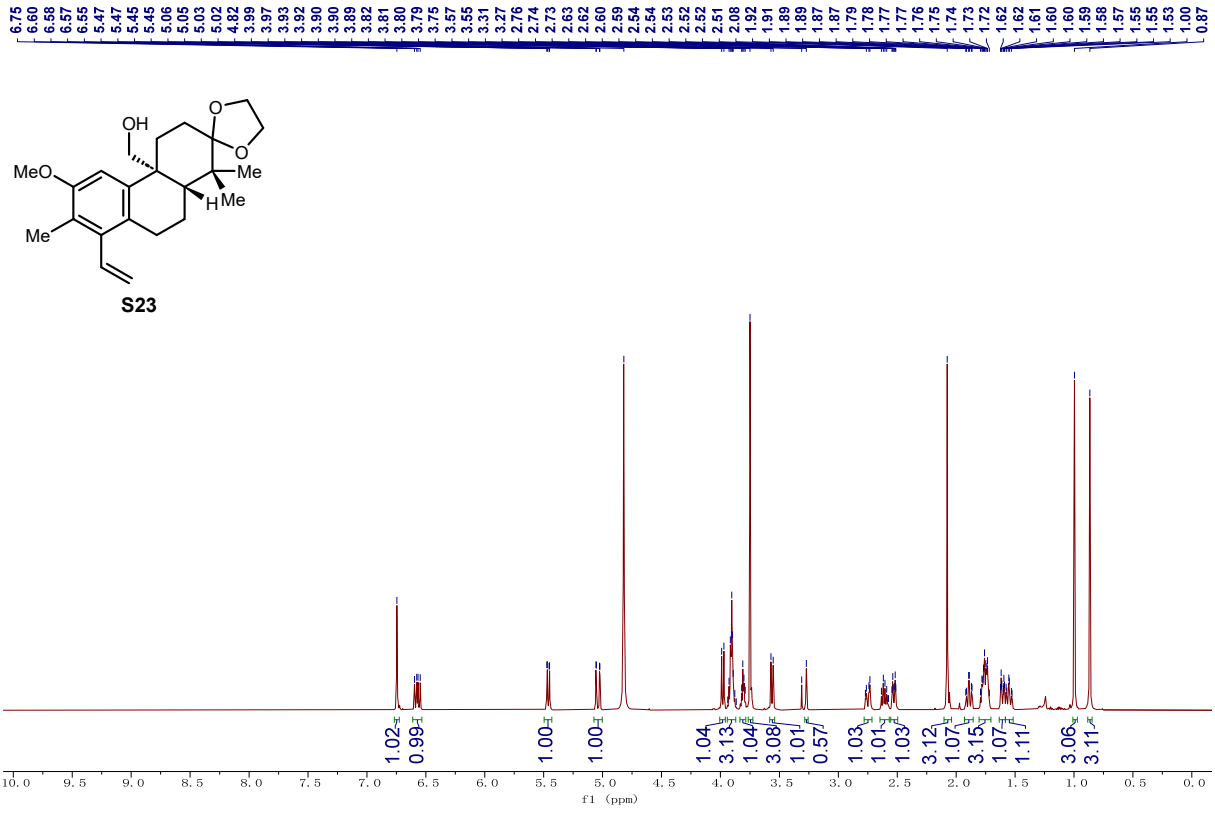


^{13}C NMR (125 MHz, $CDCl_3$ @ 77 ppm)

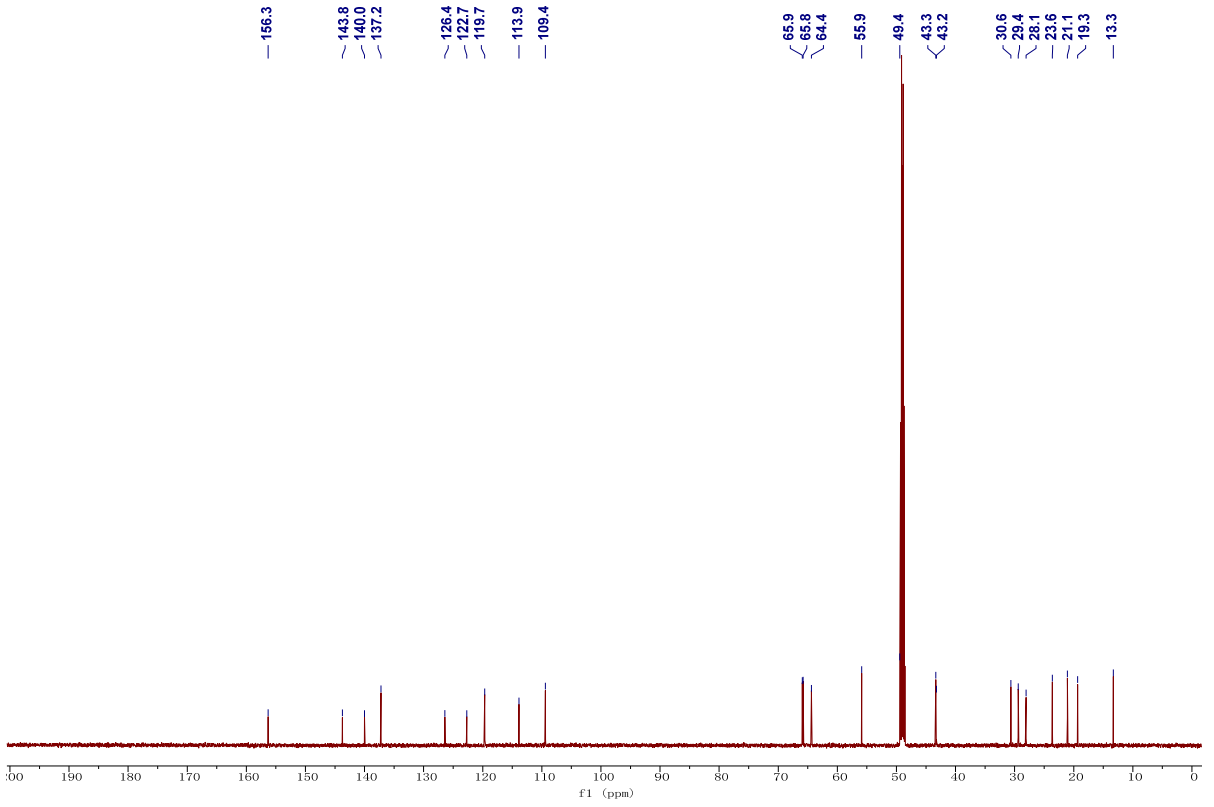


S23: ((4aS,10aS)-6-Methoxy-1,1,7-trimethyl-8-vinyl-1,3,4,9,10,10a-hexahydro-4aH-spiro-[phenanth-rene-2,2'-[1,3]dioxolan]-4a-yl)methanol

^{1}H NMR (600 MHz, CD_3OD @ 3.31 ppm)

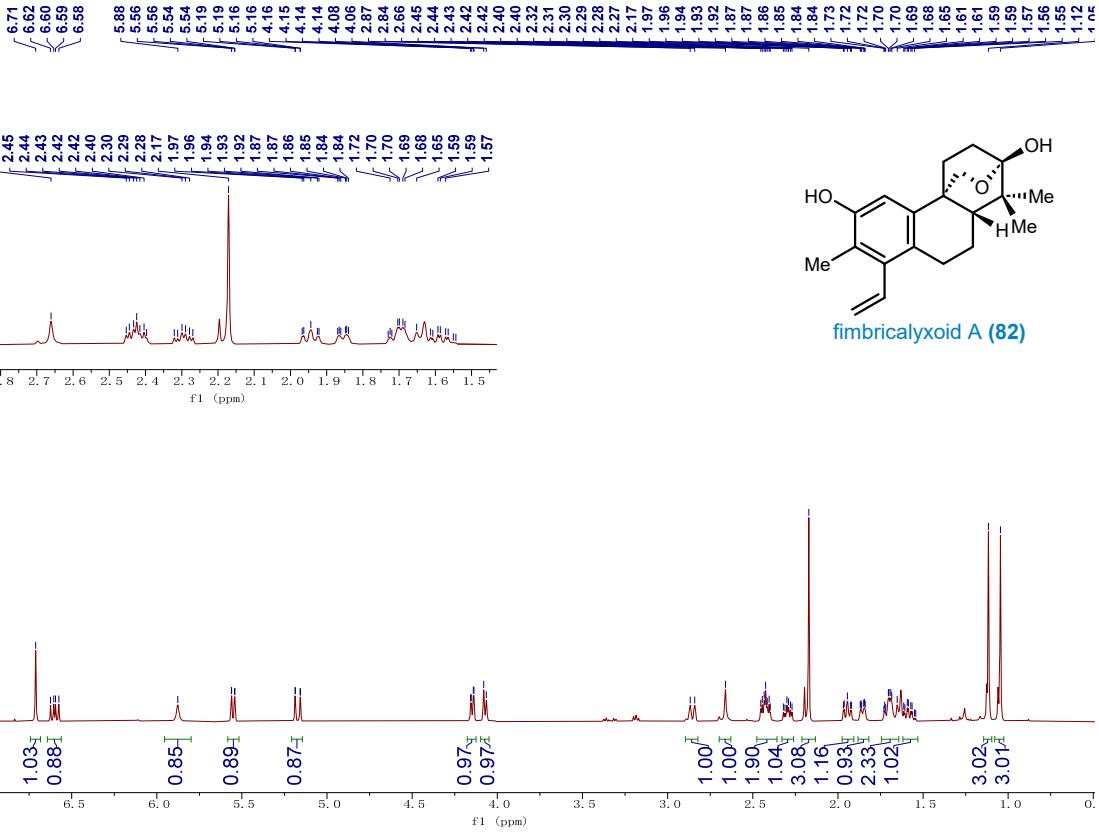


^{13}C NMR (150 MHz, CD_3OD @ 49.0 ppm)



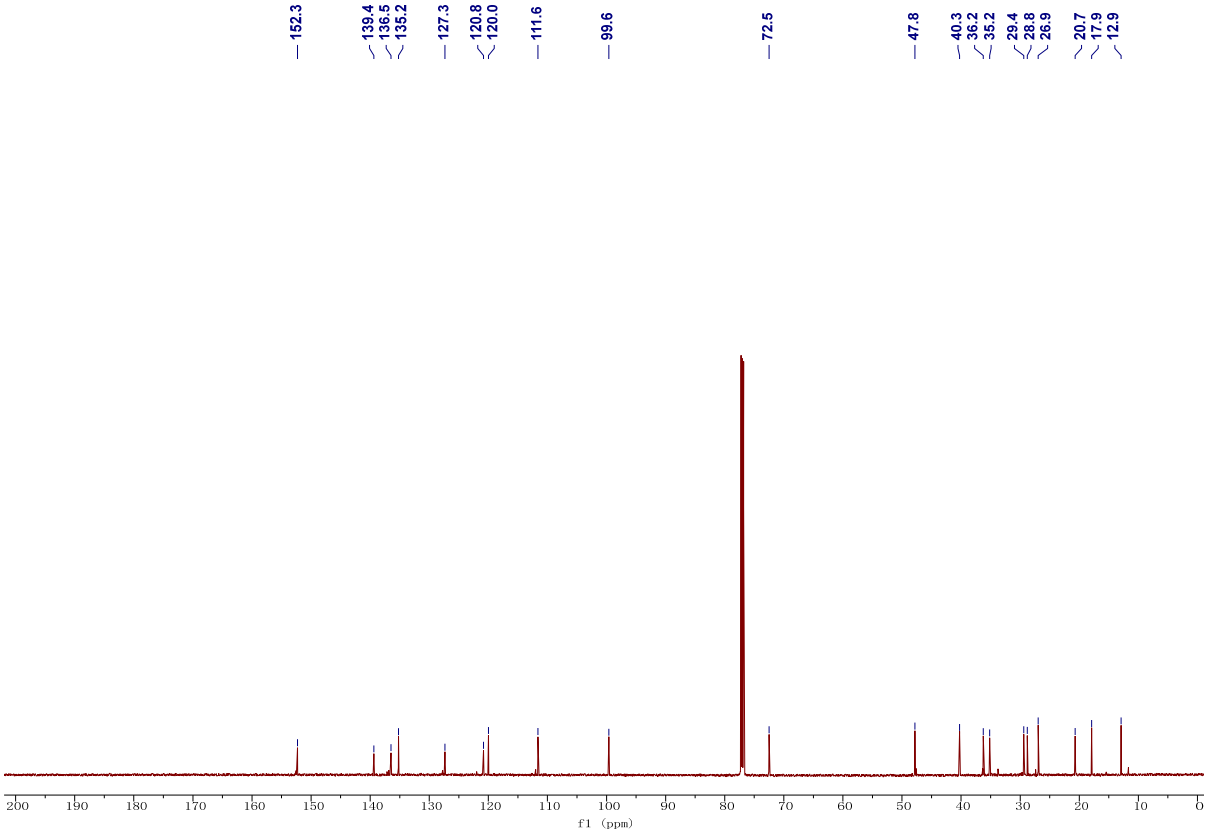
82: (+)-Fimbricalyxoid A

^{1}H NMR (600 MHz, $CDCl_3$ @ 7.26 ppm)



fimbricalyxoid A **(82)**

^{13}C NMR (150 MHz, $CDCl_3$ @ 77 ppm)



NMR spectra comparison of fimbricalyxoid A