Supporting Information

Dynamic Ligand Exchange and Supramolecular Microenvironment Enable Asymmetric C–N Coupling of Electron-Deficient Azaarenes

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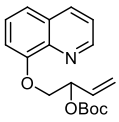
1. General Information

Substrates were obtained from commercial sources or synthesized following literature procedures. All reagents and ligands were purchased from commercial suppliers without further purification unless otherwise noticed. Solvents used in moisture and oxygen sensitive reactions were distilled after dehydration (ether solvents were dried over sodium metal). Reactions involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware dried by heating gun for 5 min prior to use. Column chromatography was carried out using silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 MHz, 500 MHz, or 600 MHz using $CDCl_3$ as solvent with TMS as internal standard. Melting points were measured on a Büchi Melting Point B-545 apparatus. HRMS were recorded on Thermo Scientific LTQ Orbitrap XL or Agilent 6210 TOF LC/MS mass spectrometer, and in the EI mode on Waters GCT Premier TOF MS. Optical rotations were determined using a Rudolph Autopol IV polarimeter. HPLC analyses were performed using Agilent 1260 chromatography. Chiralpak OJ-H, Chiralpak OD-H column were purchased from Daicel Chemical Industries, LTD. Amylose-2, Cellulose-1 and Cellulose-2 columns were purchased from Phenomenex.

2. Substrate Structures



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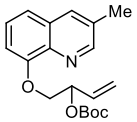

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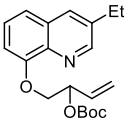

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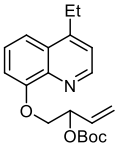

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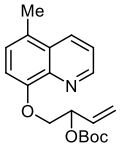

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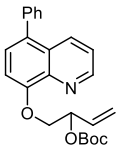

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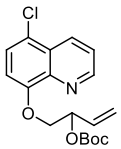

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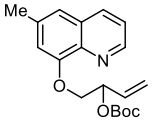

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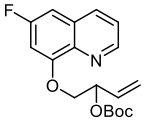

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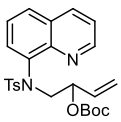

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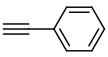

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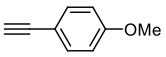

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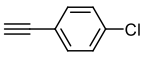

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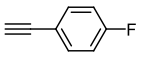

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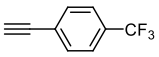

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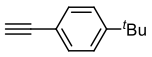

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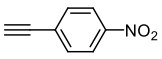

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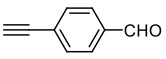

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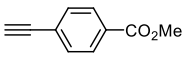

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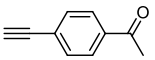

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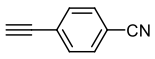

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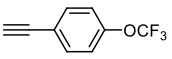

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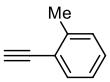

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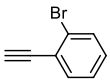

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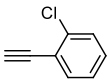

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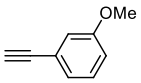

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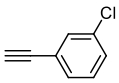

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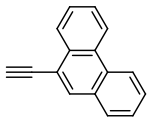

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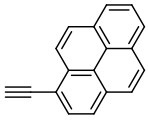

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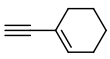

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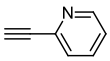

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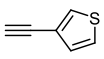

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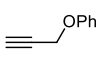

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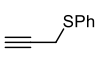
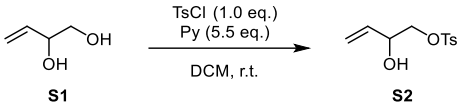


2x

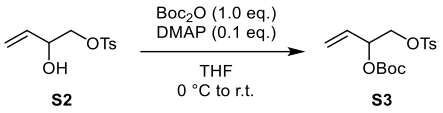
3. Substrate Preparation

3.1 Substrates **2a**-**2x** are commercially available.

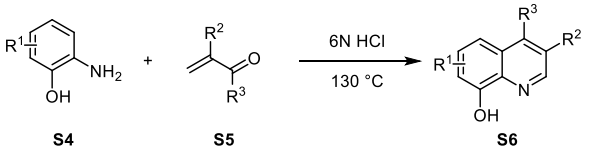
3.2 Substrates **1a**-**1i** and **5a** were synthesized with the following procedure:



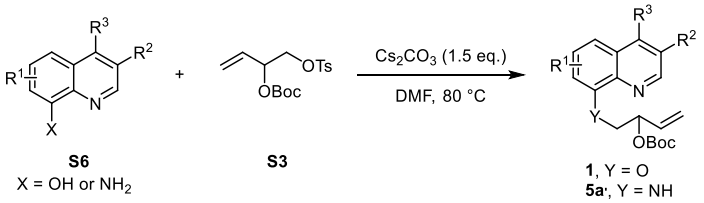
S2 was prepared according to literature method[1] from commercially available diol **S1**.



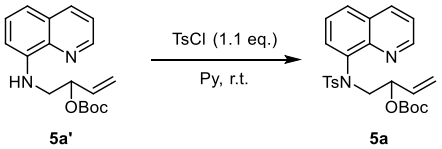
4-dimethylaminopyridine (3.0 mmol, 0.1 eq.) was added to a dry 250 ml three-necked flask, and THF (150 mL) was added as the reaction solvent under nitrogen atmosphere, followed by the addition of **S2** (30 mmol, 1.0 eq.). The three-necked flask was placed in an ice bath, and then Boc_2O (30 mmol, 1.0 eq.) was slowly added and reacted at room temperature for 24 hours. When the reaction was completed (monitored by TLC), the resulting mixture was concentrated under reduced pressure and the crude was purified by chromatography on silica gel to afford **S3**.



S6 was prepared according to literature method[2] from commercially *o*-aminophenol derivative **S4** and acrolein derivative **S5**.



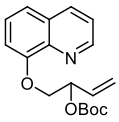
The corresponding **S6** (5 mmol, 1.0 eq.), Cs_2CO_3 (7.5 mmol, 1.5 eq.) and **S3** (7.5 mmol, 1.5 eq.) were added to the dry 100 ml Schlenk flask, and under the nitrogen atmosphere, DMF (25 mL) was added as the reaction solvent, and refluxed at 80 ℃ for 12 hours. After the reaction was completed (monitored by TLC), saturated ammonium chloride aqueous solution was added. The resulting mixture was transferred to a separation funnel and the aqueous layer was extracted with ethyl acetate. The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to afford the crude product. The residue was purified by column chromatography on silica gel to afford **1** or **5a'**.



To a stirred solution of **5a'** (1 mmol, 1.0 eq.) in dry pyridine (2 mL) was added tosylchloride (1.1 mmol, 1.1 eq.). The reaction mixture was stirred for 12 hours. After the reaction was completed (monitored by TLC), saturated $NaHCO_3$ aqueous solution was added. The resulting mixture was transferred to a separation funnel and the aqueous layer was extracted with DCM. The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to afford the

crude product. The residue was purified by column chromatography on silica gel to afford **5a**.

Spectroscopic Characterization



1a

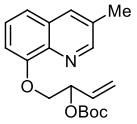
***tert*-butyl (1-(quinolin-8-yloxy)but-3-en-2-yl) carbonate (1a)**

white solid, 44% yield (3 steps). Melting point: 43-44 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49-7.36 (m, 3H), 7.16 (dd, *J* = 6.8, 2.0 Hz, 1H), 6.04 (ddd, *J* = 17.2, 10.8, 6.4 Hz, 1H), 5.67-5.63 (m, 1H), 5.48 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.34 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.42 (ddd, *J* = 40.4, 10.8, 6.8 Hz, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 152.6, 149.3, 140.6, 135.8, 133.0, 129.6, 126.5, 121.5, 120.6, 118.8, 110.5, 82.4, 75.3, 70.5, 27.8.

HRMS (ESI) calcd for $C_{18}H_{22}NO_4^+$ $[M+H]^+$ 316.1543, found 316.1539.



1b

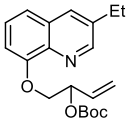
***tert*-butyl (1-((3-methylquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1b)**

white solid, 41% yield (3 steps). Melting point: 88-89 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 1.0 Hz, 1H), 7.40 (t, *J* = 8.5 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.08 (dd, *J* = 6.5, 1.0 Hz, 1H), 6.04 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.66-5.62 (m, 1H), 5.47 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.34 (dt, *J* = 11.0, 1.0 Hz, 1H), 4.41 (ddd, *J* = 53.0, 11.0, 7.0 Hz, 2H), 2.50 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 152.6, 151.2, 138.8, 134.5, 133.0, 131.0, 129.5,126.6, 120.0, 118.8, 109.5, 82.4, 75.3, 70.3, 27.8, 18.6.

HRMS (ESI) calcd for $C_{19}H_{24}NO_4^+$ $[M+H]^+$ 330.1700, found 330.1693.



1c

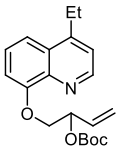
***tert*-butyl (1-((3-ethylquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1c)**

white solid, 38% yield (3 steps). Melting point: 71-73 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, J = 2.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.46-7.35 (m, 2H), 7.09 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.06 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 5.69-5.62 (m, 1H), 5.50 (dt, *J* = 17.5, 1.0 Hz, 1H), 5.36 (dt, *J* = 11.0, 1.0 Hz, 1H), 4.42 (ddd, *J* = 52.5, 11.0, 7.0 Hz, 2H), 2.84 (q, *J* = 7.5 Hz, 2H), 1.48 (s, 9H), 1.35 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 152.6, 150.8, 139.1, 137.1, 133.2, 133.0, 129.6, 126.5, 120.2, 118.8, 109.6, 82.4, 75.2, 70.4, 27.8, 26.2, 15.2.

HRMS (ESI) calcd for $C_{20}H_{26}NO_4^+$ $[M+H]^+$ 344.1856, found 344.1857.



1d

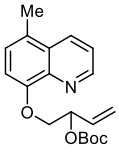
***tert*-butyl (1-((4-ethylquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1d)**

white solid, 28% yield (3 steps). Melting point: 54-56 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.5 Hz, 1H), 7.64 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.04 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 5.66-5.62 (m, 1H), 5.48 (dt, *J* = 17.0, 1.0 Hz, 1H), 5.34 (dt, *J* = 10.5, 1.0 Hz, 1H), 4.41 (ddd, *J* = 51.5, 11.0, 7.0 Hz, 2H), 3.09 (q, *J* = 7.5 Hz, 2H), 1.46 (s, 9H), 1.38 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 152.6, 149.6, 149.2, 140.7, 133.0, 128.8, 126.1, 120.3, 118.7, 116.2, 110.2, 82.3, 75.3, 70.5, 27.8, 25.4, 14.0.

HRMS (ESI) calcd for $C_{20}H_{26}NO_4^+$ $[M+H]^+$ 344.1856, found 344.1848.



1e

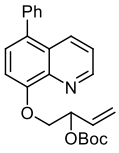
***tert*-butyl (1-((5-methylquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1e)**

white solid, 38% yield (3 steps). Melting point: 107-108 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.5, 2.0 Hz, 1H), 8.28 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.46 (dd, *J* = 8.5, 4.5Hz, 1H), 7.28 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.05 (ddd, *J* = 17.5, 11.0, 6.5 Hz, 1H), 5.67-5.63 (m, 1H), 5.49 (dt, *J* = 17.0, 1.0 Hz, 1H), 5.35 (dt, *J* = 10.5, 1.0 Hz, 1H), 4.41 (ddd, *J* = 49.0, 11.0, 7.5 Hz, 1H), 2.61 (d, *J* = 0.5 Hz, 3H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 152.7, 148.8, 140.9, 133.0, 132.5, 128.6, 126.9, 126.6, 121.1, 118.7, 110.4, 82.3, 75.3, 70.6, 27.8, 18.1.

HRMS (ESI) calcd for $C_{19}H_{24}NO_4^+$ $[M+H]^+$ 330.1700, found 330.1694.



1f

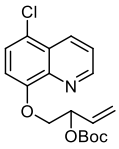
***tert*-butyl (1-((5-phenylquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1f)**

white solid, 27% yield (3 steps). Melting point: 118-119 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.21 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 4H), 7.37 (dd, *J* = 8.5, 4.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.06 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.70-5.66 (m, 1H), 5.51 (dt, *J* = 17.0, 1.0 Hz, 1H), 5.36 (dt, *J* = 11.0, 1.0 Hz, 1H), 4.47 (ddd, *J* = 49.5, 11.0, 7.0 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 152.7, 149.1, 140.6, 139.4, 134.3, 133.3, 133.0, 130.1, 128.4, 127.8, 127.3, 127.1, 121.5, 118.9, 110.0, 82.4, 75.3, 70.5, 27.8.

HRMS (ESI) calcd for $C_{24}H_{26}NO_4^+$ $[M+H]^+$ 392.1856, found 392.1852.



1g

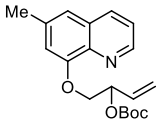
***tert*-butyl (1-((5-chloroquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1g)**

white solid, 33% yield (3 steps). Melting point: 61-63 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.5, 2.0 Hz, 1H), 8.53 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.55-7.52 (m, 2H), 7.09 (d, *J* = 8.5 Hz, 1H), 6.02 (ddd, *J* = 17.5, 11.0, 6.5 Hz, 1H), 5.65-5.61 (m, 1H), 5.48 (dt, *J* = 17.5, 1.0 Hz, 1H), 5.35 (dt, *J* = 11.0, 1.0 Hz, 1H), 4.40 (ddd, *J* = 43.5, 11.0, 7.0 Hz, 2H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 152.6, 149.8, 141.1, 132.9, 132.7, 127.2, 126.3, 123.1, 122.3, 119.0, 110.4, 82.5, 75.1, 70.7, 27.7.

HRMS (ESI) calcd for $C_{18}H_{21}ClNO_4^+$ $[M+H]^+$ 350.1154, found 350.1148.



1h

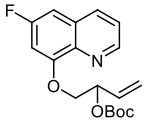
***tert*-butyl (1-((6-methylquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1h)**

white solid, 38% yield (3 steps). Melting point: 63-65 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.35 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.18 (s, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 6.04 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 5.66-5.62 (m, 1H), 5.48 (dt, *J* = 17.0, 1.0 Hz, 1H), 5.34 (dt, *J* = 11.0, 0.5 Hz, 1H), 4.39 (ddd, *J* = 45.5, 11.0, 7.0 Hz, 2H), 2.49 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 152.7, 148.4, 139.1, 136.6, 135.2, 132.9, 129.5, 121.6, 119.4, 118.8, 112.6, 82.5, 75.4, 70.4, 27.7, 22.1.

HRMS (ESI) calcd for $C_{19}H_{24}NO_4^+$ $[M+H]^+$ 330.1700, found 330.1695.



1i

***tert*-butyl (1-((6-fluoroquinolin-8-yl)oxy)but-3-en-2-yl) carbonate (1i)**

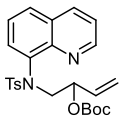
yellow solid, 39% yield (3 steps). Melting point: 52-53℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.03 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.94 (dd, *J* = 10.5, 2.5 Hz, 1H), 6.03 (ddd, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.66-5.62 (m, 1H), 5.50 (dt, *J* = 17.5, 1.0 Hz, 1H), 5.36 (dt, *J* = 10.5, 1.0 Hz, 1H), 4.39 (ddd, *J* = 39.5, 10.5, 7.0 Hz, 2H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4 (d, *J* = 245 Hz), 156.0 (d, *J* = 11.3 Hz), 152.6, 148.4, 148.4, 137.9, 135.3, 135.3, 132.6, 129.5 (d, *J* = 11.3 Hz), 122.4, 119.2, 103.1(d, *J* = 21.3 Hz), 101.32 (d, *J* = 27.5 Hz), 82.6, 75.0, 70.6, 27.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.7.

HRMS (ESI) calcd for $C_{18}H_{21}FNO_4^+$ $[M+H]^+$ 334.1449, found 334.1450.



5a

***tert*-butyl (1-((4-methyl-N-(quinolin-8-yl)phenyl)sulfonamido)but-3-en-2-yl) carbonate (5a)**

yellow solid, 8% yield (3 steps). Melting point: 111-112 ℃

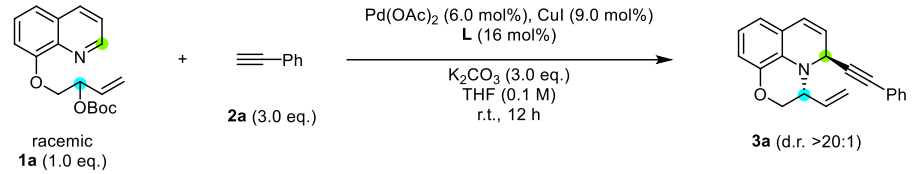
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.81 (s, 2H), 7.61-7.43 (m, 3H), 7.28 (s, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 5.81 (ddd, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.27 (dd, *J* = 31.6, 13.8 Hz, 3H), 4.26 (s, 2H), 2.36 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.4, 144.7, 142.8, 136.8, 136.2, 133.8, 133.7, 129.5, 128.9, 128.8, 127.9, 126.2, 121.0, 118.6, 82.0, 54.0, 27.7, 21.5.

HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S^+$ $[M+H]^+$: 469.1792, found 469.1801.

4. Reaction Conditions Optimization

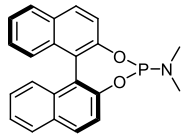
4.1 Ligand Screening



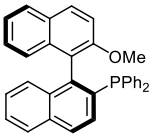
racemic **1a** (1.0 eq.)

2a (3.0 eq.)

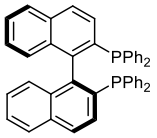
3a (d.r. >20:1)



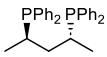
L1
62%, rac.



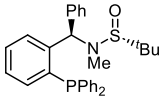
L2
15%, rac.



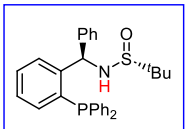
L3
70%, 13% ee



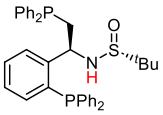
L4
10%, 10% ee



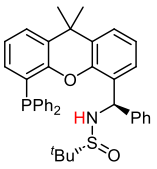
L5
55%, rac.



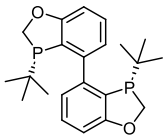
L6
52%, 30% ee



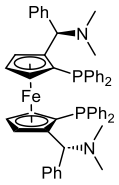
L7
46%, 15% ee



L8
61%, 7% ee



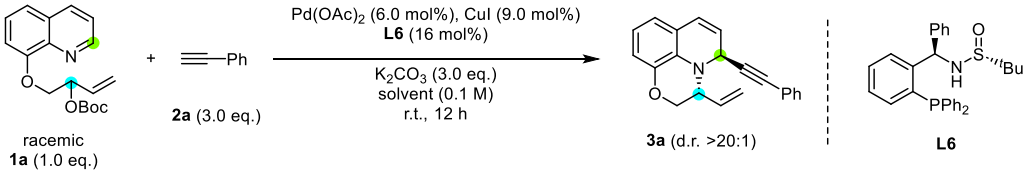
L9
50%, 11% ee



L10
58%, 14% ee

Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (6 mol%), CuI (9 mol%), ligand (16 mol%), phenylacetylene (3.0 eq.), K_2CO_3 (3.0 eq.) in THF (1.0 ml) at r.t. for 12 h under N_2. Isolated yields (%) were given and enantioselectivities (% e.e.) were determined by chiral-phase high-performance liquid chromatography. The diastereomeric ratios (d.r.) were determined by crude ^1H NMR analysis.

4.2 Solvent Screening



racemic **1a** (1.0 eq.)

2a (3.0 eq.)

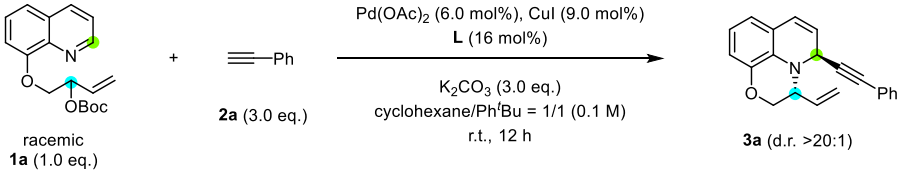
3a (d.r. >20:1)

L6

Entry	solvent	Yield (%)	ee (%)
1	THF	52	30
2	DCM	51	24
3	MeCN	28	26
4	DMF	ND	--
5	DMSO	ND	--
6	MeOH	trace	--
7	nitromethane	ND	--
8	$PhCF_3$	63	30
9	PhCl	27	67
10	toluene	52	75
11	*o*-xylene	42	61
12	mesitylene	61	82
13	Ph^{t}Bu	45	88
14	*n*-hexane	18	95
15	cyclohexane	58	81
16	*n*-hexane/Ph^{t}Bu = 1/1	57	75
17	cyclohexane/Ph^{t}Bu = 1/1	63	89

Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (6 mol%), CuI (9 mol%), **L6** (16 mol%), phenylacetylene (3.0 eq.), K_2CO_3 (3.0 eq.) in solvent (1.0 ml) at r.t. for 12 h under N_2. Isolated yields (%) were given and enantioselectivities (% e.e.) were determined by chiral-phase high-performance liquid chromatography. The diastereomeric ratios (d.r.) were determined by crude ^{1}H NMR analysis. ND, Not Detected.

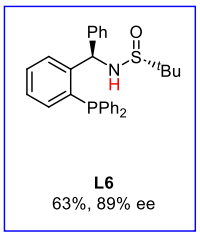
4.3 Further Screening of Ligand Substituents



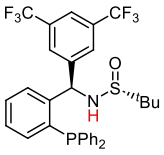
racemic **1a** (1.0 eq.)

2a (3.0 eq.)

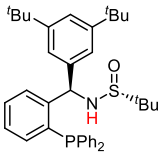
3a (d.r. >20:1)



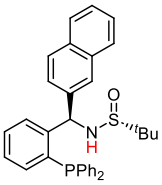
L6
63%, 89% ee



L11
63%, 59% ee



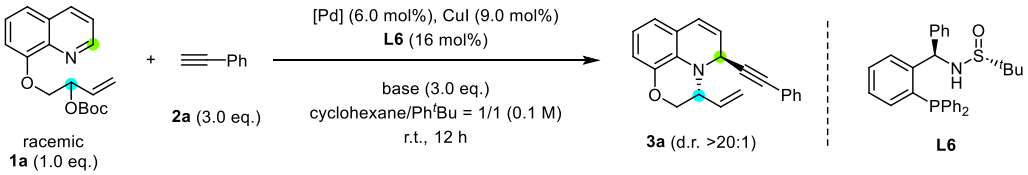
L12
25%, 40% ee



L13
75%, 85% ee

Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (6 mol%), CuI (9 mol%), ligand (16 mol%), phenylacetylene (3.0 eq.), K_2CO_3 (3.0 eq.) in a cosolvent of cyclohexane (0.5 ml) and Ph^{t}Bu (0.5 ml) at r.t. for 12 h under N_2. Isolated yields (%) were given and enantioselectivities (% e.e.) were determined by chiral-phase high-performance liquid chromatography. The diastereomeric ratios (d.r.) were determined by crude ^{1}H NMR analysis.

4.4 Other Parameters Screening



racemic **1a** (1.0 eq.)

2a (3.0 eq.)

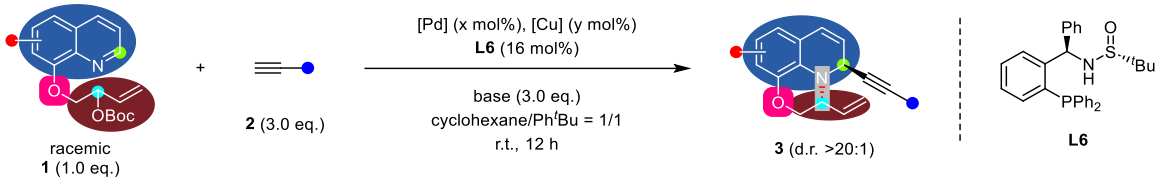
3a (d.r. >20:1)

L6

Entry	[Pd]	base	Yield (%)	ee (%)
1	$Pd(OAc)_2$	K_2CO_3	63	89
2	$Pd(TFA)_2$	K_2CO_3	63	87
3	$Pd(acac)_2$	K_2CO_3	75	81
4	$Pd(dba)_2$	K_2CO_3	74	43
5	PdI_2	K_2CO_3	61	79
6	$PdBr_2$	K_2CO_3	83	85
7	$PdCl_2$	K_2CO_3	32	95
8[a]	$PdCl_2$	K_2CO_3	69	95
9[a]	$PdCl_2$	Na_2CO_3	77	95
10[a]	$PdCl_2$	$NaHCO_3$	60	56
11[a]	$PdCl_2$	K_3PO_4	68	95
12[a]	$PdCl_2$	K_2HPO_4	69	95
13[a]	$PdCl_2$	KH_2PO_4	trace	--
14[a]	$PdCl_2$	KF	71	71
15[a]	$PdCl_2$	TEA	51	54

Reaction conditions: **1a** (0.1 mmol), [Pd] (6 mol%), CuI (9 mol%), **L6** (16 mol%), phenylacetylene (3.0 eq.), base (3.0 eq.) in a cosolvent of cyclohexane (0.5 ml) and Ph^{t}Bu (0.5 ml) at r.t. for 12 h under N_2. Isolated yields (%) were given and enantioselectivities (% e.e.) were determined by chiral-phase high-performance liquid chromatography. The diastereomeric ratios (d.r.) were determined by crude ^{1}H NMR analysis. [a]$PdCl_2$ (9.0 mol%) and CuI (6.0 mol%) were used.

5. General Procedure for Enantioselective C-N Coupling



Condition A

To a dried Schlenk tube were charged with $PdCl_2$ (9.0 mol%, 1.6 mg), CuI (6.0 mol%, 1.1 mg), chiral ligand **L6** (16 mol%, 7.5 mg), Na_2CO_3 (3.0 eq., 31.8 mg), and **1** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL), cyclohexane (0.5 mL) and **2** (0.3 mmol) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature (unless otherwise noticed) until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3**.

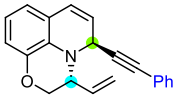
Condition B

To a dried Schlenk tube were charged with $PdBr_2$ (6.0 mol%, 1.6 mg), CuI (9.0 mol%, 1.7 mg), chiral ligand **L6** (16 mol%, 7.5 mg), K_2CO_3 (3.0 eq., 41.4 mg), and **1** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL), cyclohexane (0.5 mL) and **2** (0.3 mmol) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature (unless otherwise noticed) until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3**.

Condition C

To a dried Schlenk tube were charged with $PdBr_2$ (6.0 mol%, 1.6 mg), $Cu(MeCN)_4BF_4$ (9.0 mol%, 2.8 mg), chiral ligand **L6** (16 mol%, 7.5 mg), K_2CO_3 (3.0 eq., 41.4 mg), and **1** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL), cyclohexane (0.5 mL) and **2** (0.3 mmol) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature (unless otherwise noticed) until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3**.

6. Characterization Data of Products



3a

5-(Phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolone (3a)

Condition A, colorless oil, 77% yield, 95% ee.

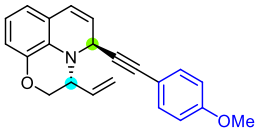
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.30-7.27 (m, 3H), 6.73 (dd, *J* = 6.5, 3.0 Hz, 1H), 6.67-6.65 (m, 2H), 6.51 (dd, *J* = 9.5, 1.0 Hz, 1H), 5.86 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.72 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.61 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.44 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.25-4.21 (m, 2H), 4.11 (dd, *J* = 11.5, 8.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 133.1, 131.9, 129.2, 128.3, 128.2, 126.3, 122.7, 122.4, 121.6, 121.0, 120.2, 118.9, 116.6, 85.6, 84.9, 68.0, 56.6, 46.9.

HRMS (ESI) calcd for $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1391.

Specific rotation $[\alpha]_D^{20}$ = -360.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm) t_R = 25.0 min (major), 22.9 min (minor).



3b

5-((4-methoxyphenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3b)

Condition A, colorless oil, 45% yield, 93% ee.

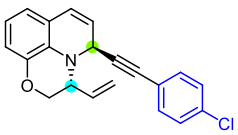
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 6.85-6.78 (m, 2H), 6.76-6.71 (m, 1H), 6.68-6.62 (m, 2H), 6.50 (dd, *J* = 9.6, 0.6 Hz, 1H), 5.86 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.70 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.61 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.43 (dd, *J* = 9.9, 1.5 Hz, 1H), 5.06 (d, *J* = 5.5 Hz, 1H), 4.27-4.20 (m, 2H), 4.19-4.06 (m, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 144.1, 133.3, 133.1, 129.2, 126.2, 122.4, 121.8, 120.9, 120.2, 118.7, 116.5, 114.7, 113.8, 84.7, 84.2, 68.0, 56.5, 55.3, 46.9.

HRMS (ESI) calcd for $C_{22}H_{20}NO_2^+$ $[M+H]^+$ 330.1489, found 330.1497.

Specific rotation $[\alpha]_D^{20}$ = -255.9 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.6 mL/min, λ = 254 nm) t_R = 11.0 min (major), 9.8 min (minor).



3c

5-((4-chlorophenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3c)

Condition C at 15 °C for 24 h, colorless oil, 52% yield, 98% ee.

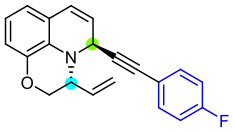
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.3-7.25 (m, 4H), 6.76-6.73 (m, 1H), 6.68-6.65 (m, 2H), 6.51 (d, *J* = 9.5 Hz, 1H), 5.85 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.72 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.60 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.44 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.06 (d, *J* = 5.5 Hz, 1H), 4.24-4.18 (m, 2H), 4.13-4.08 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 134.3, 133.1, 133.1, 129.1, 128.5, 126.5, 122.4, 121.3, 121.1, 121.0, 120.3, 118.9, 116.6, 86.6, 83.8, 68.0, 56.6, 46.8.

HRMS (ESI) calcd for $C_{21}H_{17}ClNO^+$ $[M+H]^+$ 334.0993, found 334.0999.

Specific rotation $[\alpha]_D^{20}$ = -310.8 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm) t_R =17.6 min (major), 25.1min (minor).



3d

5-((4-fluorophenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3d)

Condition C, colorless oil, 41% yield, 96% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 6.98-6.94 (m, 2H), 6.72 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.66-6.63 (m, 2H), 6.50 (dd, *J* = 9.5, 1.0 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.70 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.59 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.42 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.03 (d, *J* = 5.5 Hz, 1H), 4.23-4.18 (m, 2H), 4.09 (td, *J* = 8.5, 2.0 Hz, 1H).

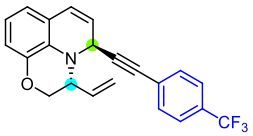
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5(d, *J* = 247.5 Hz), 144.1, 133.7 (d, *J* = 8.8 Hz), 133.1, 129.2, 126.4, 122.4, 121.5, 120.9, 120.2, 118.8, 118.7(d, *J* = 3.8 Hz), 116.6, 115.5 (d, *J* = 21.3 Hz), 85.3, 83.8, 68.0, 56.6, 46.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.9.

HRMS (ESI) calcd for $C_{21}H_{17}FNO^+$ $[M+H]^+$ 318.1289, found 318.1284.

Specific rotation $[\alpha]_D^{20}$ = -309.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm) t_R =13.9 min (major), 11.2min (minor).



3e

5-((4-(trifluoromethyl)phenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3e)

Condition A, colorless oil, 54% yield, 93% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.78-6.70 (m, 1H), 6.69-6.61 (m, 2H), 6.57-6.47 (m, 1H), 5.86-5.78 (m, 1H), 5.77-5.64 (m, 1H), 5.59 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.43 (dd, *J* = 9.9, 1.5 Hz, 1H), 5.06 (d, *J* = 5.7 Hz, 1H), 4.26-4.14 (m, 2H), 4.13-4.05 (m, 1H).

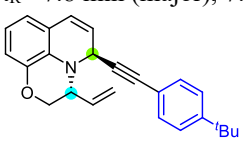
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 133.0, 132.1, 130.2, 129.9, 129.1, 126.7, 126.5, 125.1 (q, *J* = 3.8 Hz), 124.9, 122.8, 122.4, 121.1, 120.3, 119.1, 116.7, 88.2, 83.6, 67.9, 56.7, 46.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.8.

HRMS (ESI) calcd for $C_{22}H_{17}F_3NO^+$ $[M+H]^+$ 368.1257, found 368.1253.

Specific rotation $[\alpha]_D^{20}$ = -263.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.6 mL/min, λ = 254 nm) t_R =7.8 min (major), 7.1 min (minor).



3f

5-((4-(tert-butyl)phenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3f)

Condition C, colorless oil, 65% yield, 92% ee.

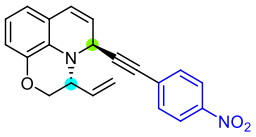
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 4H), 6.71 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.65-6.63 (m, 2H), 6.48 (dd, *J* = 9.5, 1.0 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.71 (ddd, *J* = 17.0, 9.5, 7.5 Hz, 1H), 5.58 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.41 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.05 (d, *J* = 5.5 Hz, 1H), 4.23-4.19 (m, 2H), 4.12-4.08 (m, 1H), 1.29 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 144.1, 133.1, 131.6, 129.2, 126.2, 125.2, 122.4, 121.7, 120.8, 120.2, 119.6, 118.7, 116.5, 85.0, 84.9, 68.0, 56.5, 47.0, 34.7, 31.1.

HRMS (ESI) calcd for $C_{25}H_{25}NONa^+$ $[M+Na]^+$ 378.1834, found 378.1836.

Specific rotation $[\alpha]_D^{20}$ = -345.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.5 mL/min, λ = 254 nm) t_R = 9.7 min (major), 8.5 min (minor).



3g

5-((4-nitrophenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3g)

Condition C, colorless oil, 52% yield, 96% ee.

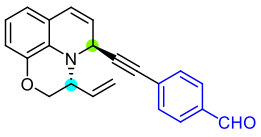
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.49 (dt, *J* = 9.0, 2.0 Hz, 2H), 6.75-6.71 (m, 1H), 6.67-6.66 (m, 2H), 6.53 (dd, *J* = 9.5, 1.0 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.69 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.59 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.44 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.22 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.16 (td, *J* = 8.0, 3.0 Hz, 1H), 4.08 (dd, *J* = 11.0, 8.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 144.3, 132.9, 132.6, 129.5, 129.0, 127.0, 123.5, 122.4, 121.3, 120.7, 120.3, 119.2, 116.8, 91.3, 83.1, 67.9, 56.8, 46.7.

HRMS (ESI) calcd for $C_{21}H_{17}N_2O_3^+$ $[M+H]^+$: 345.1239, found 345.1231.

Specific rotation $[\alpha]_D^{20}$ = -302.1 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.5 mL/min, λ = 254 nm) t_R = 27.5 min (major), 42.5 min (minor).



3h

4-((3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolin-5-yl)ethynyl)benzaldehyde (3h)

Condition C at 15 ℃ for 24 h, colorless oil, 42% yield, 95% ee.

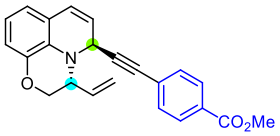
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.78-7.77 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.74-6.71 (m, 1H), 6.67-6.63 (m, 2H), 6.52 (dd, *J* = 9.5, 0.5 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.69 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.59 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.43 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.07 (d, *J* = 5.5 Hz, 1H), 4.23-4.16 (m, 2H), 4.08 (dd, *J* = 10.0, 7.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.4, 144.2, 135.5, 133.0, 132.4, 129.4, 129.1, 128.9, 126.8, 122.4, 121.2, 121.0, 120.3, 119.1, 116.7, 89.9, 84.1, 67.9, 56.7, 46.8.

HRMS (ESI) calcd for $C_{22}H_{18}NO_2^+$ $[M+H]^+$: 328.1338, found 328.1332.

Specific rotation $[\alpha]_D^{20}$ = -315.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 250 nm) t_R = 39.6 min (major), 49.0 min (minor).



3i

methyl 4-((3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolin-5-yl)ethynyl)benzoate (3i)

Condition A, colorless oil, 50% yield, 91% ee.

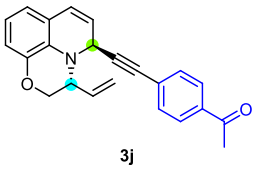
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 6.75-6.70 (m, 1H), 6.68-6.62 (m, 2H), 6.51 (d, *J* = 9.5 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.7 Hz, 1H), 5.76-5.55 (m, 2H), 5.43 (dd, *J* = 9.9, 1.4 Hz, 1H), 5.06 (d, *J* = 5.6 Hz, 1H), 4.27-4.14 (m, 2H), 4.14-4.01 (m, 1H), 3.90 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 144.2, 133.0, 131.8, 129.6, 129.4 129.1, 127.3, 126.7, 122.4, 121.1, 120.3, 118.9, 116.7, 88.7, 84.2, 67.9, 56.7, 52.2, 46.8.

HRMS (ESI) calcd for $C_{23}H_{20}NO_3^+$ $[M+H]^+$: 358.1438, found 358.1431.

Specific rotation $[\alpha]_D^{20}$ = -298.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.6 mL/min, λ = 254 nm), t_R = 21.3 min (major), 18.5 min (minor).



3j

1-(4-((3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolin-5- yl)ethynyl)phenyl)ethan-1-one (3j)

Condition C, colorless oil, 45% yield, 98% ee.

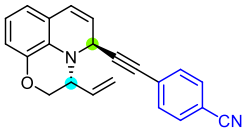
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.77-6.68 (m, 1H), 6.69-6.61 (m, 2H), 6.51 (d, *J* = 9.5 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.7 Hz, 1H), 5.77-5.50 (m, 2H), 5.43 (dd, *J* = 9.8, 1.7 Hz, 1H), 5.06 (d, *J* = 5.7 Hz, 1H), 4.25-4.15 (m, 2H), 4.12-4.02 (m, 1H), 2.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 144.3, 136.4, 133.1, 132.1, 129.2, 128.2, 127.7, 126.8, 122.5, 121.3, 120.4, 119.1, 116.8, 89.2, 84.3, 68.1, 56.8, 46.9, 26.7.

HRMS (ESI) calcd for $C_{23}H_{19}NO_2Na^+$ $[M+Na]^+$: 364.1313, found 364.1308.

Specific rotation $[\alpha]_D^{20}$ = -423.8 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.7 mL/min, λ = 254 nm), t_R = 14.4 min (major), 11.6 min (minor).



3k

4-((3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolin-5-yl)ethynyl)benzonitrile(3k)

Condition C at 15 ℃ for 24 h, colorless oil, 46% yield, 90% ee.

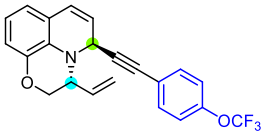
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.70 (dt, *J* = 22.4, 5.0 Hz, 3H), 6.52 (dd, *J* = 9.5, 0.8 Hz, 1H), 5.83 (dd, *J* = 9.5, 5.7 Hz, 1H), 5.69 (ddd, *J* = 17.5, 9.8, 7.8 Hz, 1H), 5.57 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.43 (dd, *J* = 9.8, 1.6 Hz, 1H), 5.05 (d, *J* = 5.7 Hz, 1H), 4.24-4.12 (m, 2H), 4.07 (dd, *J* = 10.4, 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 133.0, 132.5, 132.0, 129.1, 127.7, 127.0, 122.5, 121.4, 121.0, 120.4, 119.2, 118.5, 116.9, 111.8, 90.4, 83.4, 68.0, 56.9, 46.8.

HRMS (ESI) calcd for $C_{22}H_{16}N_2ONa^+$ $[M+Na]^+$: 347.1160, found 347.1160.

Specific rotation $[\alpha]_D^{20}$ = -259.6 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.7 mL/min, λ = 254 nm), t_R = 14.5 min (major), 12.1 min (minor).



3l

5-((4-(trifluoromethoxy)phenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline(3l)

Condition A at 15 ℃ for 24 h, colorless oil, 47% yield, 96% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.29 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.76-6.68 (m, 1H), 6.68-6.61 (m, 2H), 6.50 (dd, *J* = 9.5, 0.9 Hz, 1H), 5.83 (dd, *J* = 9.5, 5.6 Hz, 1H), 5.70 (ddd, *J* = 17.6, 9.8, 7.9 Hz, 1H), 5.58 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.50-5.33 (m, 1H), 5.05 (t, *J* = 9.4 Hz, 1H), 4.26-4.13 (m, 2H), 4.08 (dq, *J* = 4.0, 2.4 Hz, 1H).

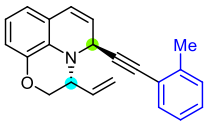
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 144.3, 133.5, 133.2, 129.2, 126.7, 122.6, 121.5 (q, *J* = 13.2 Hz), 121.2, 120.9, 120.4, 119.1, 116.8, 86.7, 83.6, 68.1, 56.8, 46.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8.

HRMS (ESI) calcd for $C_{22}H_{17}F_3NO_2^+$ $[M+H]^+$: 384.1211, found 384.1218.

Specific rotation $[\alpha]_D^{20}$ = -323.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 9.9 min (major), 8.6 min (minor).



3m

5-(o-tolylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3m)

Condition B, colorless oil, 59% yield, 91% ee.

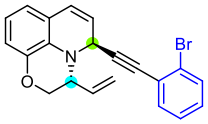
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.18 (dt, *J* = 14.6, 3.9 Hz, 2H), 7.14-7.07 (m, 1H), 6.74 (dd, *J* = 6.5, 2.9 Hz, 1H), 6.70-6.64 (m, 2H), 6.57-6.49 (m, 1H), 5.92 (dd, *J* = 9.5, 5.7 Hz, 1H), 5.80-5.68 (m, 1H), 5.45 (dd, *J* = 9.9, 1.5 Hz, 1H), 5.04 (d, *J* = 5.7 Hz, 1H), 4.33-4.19 (m, 2H), 4.18-4.06 (m, 1H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 140.3, 133.2, 132.0, 129.3, 128.3, 126.4, 125.4, 122.8, 122.5, 122.0, 121.0, 120.1, 119.0, 116.5, 89.6, 83.9, 68.0, 56.7, 46.8, 20.7.

HRMS (ESI) calcd for $C_{22}H_{20}NO^+$ $[M+H]^+$: 314.1539, found 314.1545.

Specific rotation $[\alpha]_D^{20}$ = -289.9 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 92:8, 0.6 mL/min, λ = 254 nm), t_R = 22.4 min (major), 18.0 min (minor).



3n

5-((2-bromophenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3n)

Condition A, colorless soild, Melting point: 51-63 ℃, 63% yield, 92% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.72-6.70 (m, 1H), 6.66-6.62 (m, 2H), 6.51 (d, *J* = 9.5 Hz, 1H), 5.88 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.74-5.63 (m, 2H), 5.43 (dd, *J* = 9.5, 1.5 Hz, 1H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.32 (td,

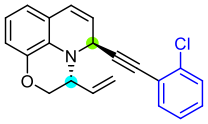
J = 8.0, 3.5 Hz, 1H), 4.24 (dd, *J* = 11.0, 3.0 Hz, 1H), 4.09 (dd, *J* = 11.0, 8.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 133.5, 133.1, 132.3, 129.4, 129.3, 126.9, 126.7, 125.7, 124.9, 122.6, 121.3, 121.2, 120.2, 118.9, 116.6, 90.6, 83.4, 68.0, 56.6, 46.9.

HRMS (ESI) calcd for $C_{21}H_{17}BrNO^+$ $[M+H]^+$: 378.0448, found 378.0500.

Specific rotation $[\alpha]_D^{20}$ = -207.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.5 mL/min, λ = 254 nm), t_R = 12.4 min (major), 11.4 min (minor).



3o

5-((2-chlorophenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3o)

Condition B, colorless oil, 63% yield, 92% ee.

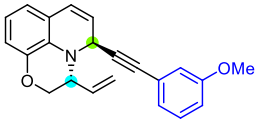
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.35 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.21 (td, *J* = 7.5, 2.0 Hz, 1H), 7.15 (td, *J* = 7.5, 1.5 Hz, 1H), 6.72 (dd, *J* = 6.5, 3.0 Hz, 1H), 6.66-6.63 (m, 2H), 6.52 (dd, *J* = 9.5, 1.5 Hz, 1H), 5.87 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.71 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.64 (dd, *J* = 17.5, 2.5 Hz, 1H), 5.44-5.42 (m, 1H), 5.09 (d, *J* = 5.5 Hz, 1H), 4.30 (td, *J* = 8.0, 3.5 Hz, 1H), 4.23 (dd, *J* = 11.0, 3.0 Hz, 1H), 4.10 (dd, *J* = 11.0, 7.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 136.1, 133.4, 133.0, 129.3, 129.2, 129.2, 126.7, 126.3, 122.7, 122.5, 121.3, 121.2, 120.2, 118.9, 116.6, 91.2, 81.6, 68.0, 56.6, 46.9.

HRMS (ESI) calcd for $C_{21}H_{17}ClNO^+$ $[M+H]^+$: 334.0993, found 334.0992.

Specific rotation $[\alpha]_D^{20}$ = -320.7 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 31.6 min (major), 15.7 min (minor).



3p

5-((3-methoxyphenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3p)

Condition B, colorless oil, 65% yield, 92% ee.

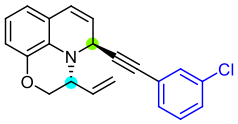
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.0 Hz, 1H), 6.97 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.90 (dd, *J* = 2.5, 1.5 Hz, 1H), 6.85 (ddd, *J* = 8.0, 2.5, 0.5 Hz, 1H), 6.74-6.71 (m, 1H), 6.66-6.63 (m, 2H), 6.50 (dd, *J* = 9.5, 1.0 Hz, 1H), 5.85 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.71 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.60 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.42 (dd, *J* = 9.5, 1.5 Hz, 1H), 5.06 (d, *J* = 6.0 Hz, 1H), 4.24-4.20 (m, 2H), 4.10 (dd, *J* = 11.5, 8.0 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 144.1, 133.1, 129.3, 129.2, 126.4, 124.4, 123.7, 122.4, 121.5, 120.9, 120.2, 118.8, 116.7, 116.6, 114.9, 85.5, 84.8, 68.0, 56.6, 55.3, 46.9.

HRMS (ESI) calcd for $C_{22}H_{20}NO_2^+$ $[M+H]^+$: 330.1489, found 330.1485.

Specific rotation $[\alpha]_D^{20}$ = -362.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 12.2 min (major), 10.6 min (minor).



3q

5-((3-chlorophenyl)ethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3q)

Condition A, colorless oil, 54% yield, 91% ee.

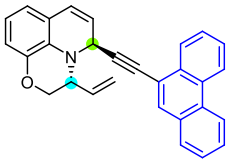
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.27-7.23 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.74-6.71 (m, 1H), 6.66-6.65 (m, 2H), 6.50 (d, *J* = 9.5 Hz, 1H), 5.83 (dd, *J* = 9.5, 6.0 Hz, 1H), 5.70 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.59 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.43 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.04 (d, *J* = 5.5 Hz, 1H), 4.23-4.16 (m, 2H), 4.09 (dd, *J* = 10.5, 7.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 134.0, 133.0, 131.7, 130.0, 129.4, 129.1, 128.6, 126.6, 124.4, 122.4, 121.2, 121.1, 120.3, 118.9, 116.7, 86.9, 83.5, 67.9, 56.7, 46.8.

HRMS (ESI) calcd for $C_{21}H_{17}ClNO^+$ $[M+H]^+$: 334.0993, found 334.0998.

Specific rotation $[\alpha]_D^{20}$ = -247.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 13.8 min (major), 11.8 min (minor).



3r

5-(phenanthren-9-ylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline(3r)

Condition C, yellow solid, Melting point: 95-98 ℃, 57% yield, 97% ee.

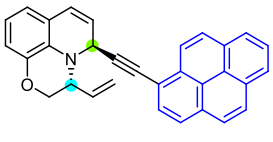
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (t, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.69-7.50 (m, 4H), 6.83-6.69 (m, 3H), 6.60 (d, *J* = 9.5 Hz, 1H), 6.01 (dd, *J* = 9.5, 5.8 Hz, 1H), 5.85-5.59 (m, 2H), 5.48 (dd, *J* = 9.7, 1.5 Hz, 1H), 5.17 (d, *J* = 5.7 Hz, 1H), 4.40-4.21 (m, 2H), 4.14 (dd, *J* = 10.9, 8.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 133.4, 132.0, 131.18, 130.4, 130.1, 129.5, 128.6, 127.6, 127.3, 126.7, 123.0, 122.8, 122.0, 121.3, 120.4, 119.2, 116.7, 90.5, 83.4, 68.2, 57.0, 47.1.

HRMS (ESI) calcd for $C_{29}H_{22}NO^+$ $[M+H]^+$: 400.1696, found 400.1699.

Specific rotation $[\alpha]_D^{20}$ = -353.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel AD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 16.1 min (major), 11.5 min (minor).



3s

5-(pyren-1-ylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline(3s)

Condition A, yellow solid, Melting point: 80-83 ℃, 42% yield, 91% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.1 Hz, 1H), 8.18 (dd, *J* = 7.6, 4.2 Hz, 2H), 8.08-7.97 (m, 6H), 6.80 (dt, *J* = 8.3, 4.1 Hz, 1H), 6.76 (d, *J* = 4.9 Hz, 2H), 6.62 (dd, *J* = 9.5, 0.7 Hz, 1H), 6.05 (dd, *J* = 9.5, 5.8 Hz, 1H), 5.86-5.62 (m, 2H), 5.53-5.40 (m, 1H), 5.22 (d, *J* = 5.8 Hz, 1H), 4.40 (td, *J* = 7.9, 3.3 Hz, 1H), 4.28 (dd, *J* = 10.9, 3.3 Hz, 1H), 4.16 (dd, *J* = 10.9, 8.0 Hz, 1H), 4.16 (dd, *J* = 10.9, 8.0 Hz, 1H).

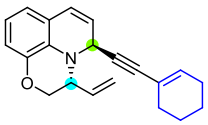
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 133.4, 132.2, 131.3, 131.1, 129.8, 129.6, 128.5, 128.3, 127.3,

126.8, 126.3, 125.7, 124.4, 123.1, 122.1, 121.3, 120.4, 119.3, 117.3, 116.7, 91.6, 84.3, 68.2, 57.0, 47.3.

HRMS (ESI) calcd for $C_{31}H_{22}NO^+$ $[M+H]^+$: 424.1701, found 424.1691.

Specific rotation $[\alpha]_D^{20}$ = -364.2 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 92:8, 0.5 mL/min, λ = 254 nm), t_R = 19.0 min (major), 15.3 min (minor).



3t

5-(cyclohex-1-en-1-ylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3t)

Condition C, colorless oil, 46% yield, 96% ee.

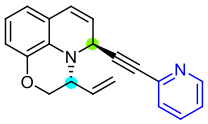
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71-6.67 (m, 1H), 6.63-6.59 (m, 2H), 6.43 (dd, *J* = 9.5, 1.0 Hz, 1H), 6.04-6.02 (m, 1H), 5.77 (dd, *J* = 10.0, 5.5 Hz, 1H), 5.67 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1H), 5.54 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.38 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.93 (d, *J* = 5.5 Hz, 1H), 4.19-4.11 (m, 2H), 4.07 (dd, *J* = 10.0, 7.0 Hz, 1H), 2.06-2.04 (m, 4H), 1.60-1.53 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 135.2, 133.1, 129.2, 125.9, 122.4, 122.0, 120.7, 120.1, 118.6, 116.4, 86.7, 82.7, 67.9, 56.4, 46.9, 29.3, 25.6, 22.2, 21.4.

HRMS (ESI) calcd for $C_{21}H_{22}NO^+$ $[M+H]^+$: 304.1696, found 304.1699.

Specific rotation $[\alpha]_D^{20}$ = -291.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.5 mL/min, λ = 254 nm), t_R = 9.6 min (major), 8.7 min (minor).



3u

5-(pyridin-2-ylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3u)

Condition C at 15 °C for 24 h, colorless oil, 42% yield, 92% ee.

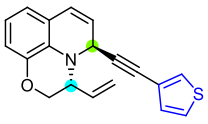
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.59 (td, *J* = 7.8, 1.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.19 (ddd, *J* = 7.6, 4.9, 1.0 Hz, 1H), 6.74-6.68 (m, 1H), 6.66-6.60 (m, 2H), 6.50 (dd, *J* = 9.5, 0.9 Hz, 1H), 5.84 (dd, *J* = 9.5, 5.7 Hz, 1H), 5.75-5.52 (m, 2H), 5.41 (dd, *J* = 9.7, 1.9 Hz, 1H), 5.09 (d, *J* = 5.7 Hz, 1H), 4.22 (ddd, *J* = 11.6, 7.7, 3.3 Hz, 2H), 4.12-4.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 144.2, 142.9, 136.2, 133.0, 129.2, 127.5, 126.9, 123.0, 122.5, 121.3, 121.1, 120.4, 119.0, 116.8, 85.9, 84.3, 68.0, 56.7, 46.9.

HRMS (ESI) calcd for $C_{20}H_{16}N_2ONa^+$ $[M+Na]^+$: 323.1160, found 323.1165.

Specific rotation $[\alpha]_D^{20}$ = -201.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.5 mL/min, λ = 254 nm), t_R = 19.5 min (major), 20.5 min (minor).



3v

5-(thiophen-3-ylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3v)

Condition A, colorless oil, 75% yield, 96% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.22 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.04 (dd, *J*

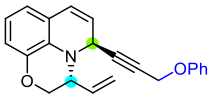
= 5.0, 1.1 Hz, 1H), 6.74-6.68 (m, 1H), 6.66-6.60 (m, 2H), 6.49 (dd, *J* = 9.5, 1.0 Hz, 1H), 5.83 (dd, *J* = 9.5, 5.6 Hz, 1H), 5.76-5.64 (m, 1H), 5.58 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.41 (dd, *J* = 9.8, 1.8 Hz, 1H), 5.03 (d, *J* = 5.6 Hz, 1H), 4.24-4.15 (m, 2H), 4.13-4.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 133.1, 130.2, 129.2, 126.4, 125.3, 122.5, 121.7, 121.1, 120.3, 118.9, 116.7, 85.3, 80.0, 68.1, 56.6, 47.0.

HRMS (ESI) calcd for $C_{19}H_{15}NOSNa^+$ $[M+Na]^+$: 328.0772, found 328.0776.

Specific rotation $[\alpha]_D^{20}$ = -371.8 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 11.6 min (major), 10.3 min (minor).



3w

3-methyl-5-(3-phenoxyprop-1-yn-1-yl)-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3w)

Condition C, colorless oil, 42% yield, 90% ee.

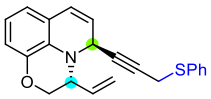
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 6.1 Hz, 1H), 6.98-6.74 (m, 4H), 6.68-6.60 (m, 1H), 6.61-6.50 (m, 2H), 6.38 (d, *J* = 9.5 Hz, 1H), 5.67 (dd, *J* = 9.5, 5.7 Hz, 1H), 5.54-5.40 (m, 1H), 5.27-5.15 (m, 2H), 4.73 (d, *J* = 5.5 Hz, 1H), 4.58 (d, *J* = 1.4 Hz, 2H), 4.02 (dd, *J* = 10.2, 2.7 Hz, 1H), 3.88 (ddd, *J* = 13.1, 10.7, 5.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 144.3, 132.9, 129.6, 129.2, 126.7, 122.5, 121.9, 121.6, 121.3, 120.3, 119.1, 116.7, 115.3, 115.0, 84.0, 80.0, 68.0, 56.5, 56.2, 46.3.

HRMS (ESI) calcd for $C_{22}H_{19}NO_2Na^+$ $[M+Na]^+$: 352.1313, found 352.1313.

Specific rotation $[\alpha]_D^{20}$ = -225.8.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 90:10, 0.7 mL/min, λ = 254 nm), t_R = 18.7 min (major), 15.3 min (minor).



3x

5-(3-(phenylthio)prop-1-yn-1-yl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3x)

Condition C at 15 ℃ for 24 h, yellow oil, 46% yield, 94% ee.

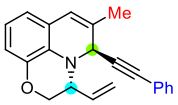
1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.5 Hz, 2H), 7.16 (dt, *J* = 13.9, 7.3 Hz, 3H), 6.63 (dd, *J* = 6.5, 3.0 Hz, 1H), 6.56 (dd, *J* = 8.6, 5.2 Hz, 2H), 6.35 (d, *J* = 9.5 Hz, 1H), 5.63 (dd, *J* = 9.5, 5.6 Hz, 1H), 5.54-5.40 (m, 1H), 5.32-5.15 (m, 2H), 4.67 (d, *J* = 5.5 Hz, 1H), 3.94 (ddd, *J* = 18.5, 10.8, 5.7 Hz, 2H), 3.78 (td, *J* = 7.9, 3.3 Hz, 1H), 3.51 (d, *J* = 4.5 Hz, 2H).

13C NMR (101 MHz, $CDCl_3$) δ 144.2, 135.0, 133.0, 130.3, 129.5, 129.0, 126.9, 126.3, 122.5, 121.7, 121.1, 120.3, 119.0, 116.7, 81.0, 79.9, 67.9, 56.4, 46.3, 23.0.

HRMS (ESI): calcd for $C_{22}H_{19}NOSNa^+$ $[M+Na]^+$: 368.1085, found 368.1089.

Specific rotation $[\alpha]_D^{20}$ = -228.8 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/i-PrOH = 95:5, 0.5 mL/min, λ = 254 nm), tR = 19.4 min (major), 17.5 min (minor).



3ab

6-Methyl-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3ab)

Condition B, colorless oil, 85% yield, 95% ee.

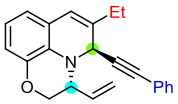
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.30-7.29 (m, 3H), 6.73-6.64 (m, 3H), 6.29 (s, 1H), 5.77-5.61 (m, 2H), 5.46 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.81 (s, 1H), 4.28-4.22 (m, 2H), 4.11 (dd, *J* = 11.2, 8.8 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 133.3, 131.9, 131.0, 128.3, 128.2, 127.6, 123.5, 122.7, 122.0, 121.1, 119.3, 119.0, 115.6, 85.2, 85.1, 68.0, 56.8, 51.6, 20.7.

HRMS (ESI) calcd for $C_{22}H_{20}NO^+$ $[M+H]^+$: 314.1539, found 314.1532.

Specific rotation $[\alpha]_D^{20}$ = -386.83 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 12.4 min (major), 14.7 min (minor).



3ac

6-ethyl-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3ac)

Condition B, colorless oil, 60% yield, 96% ee.

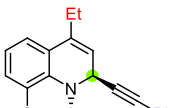
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.29-7.25 (m, 3H), 6.72-6.67 (m, 3H), 6.28 (s, 1H), 5.74-5.61 (m, 2H), 5.45 (dd, *J* = 9.5, 2.0 Hz, 1H), 4.80 (s, 1H), 4.26-4.21 (m, 2H), 4.11-4.07 (m, 1H), 2.46-2.25 (m, 2H), 1.24 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 136.8, 133.3, 131.9, 128.2, 128.2, 127.9, 123.7, 122.8, 121.1, 119.9, 119.6, 119.2, 115.6, 85.4, 85.0, 68.1, 56.8, 50.5, 27.2, 11.7.

HRMS (ESI) calcd for $C_{23}H_{22}NO^+$ $[M+H]^+$: 328.1696, found 328.1698.

Specific rotation $[\alpha]_D^{20}$ = -199.33 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 98:2, 0.5 mL/min, λ = 254 nm), t_R = 12.5 min (major), 13.8 min (minor).



3ad

7-ethyl-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3ad)

Condition B, colorless oil, 63% yield, 95% ee.

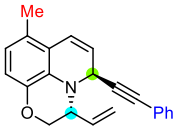
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.27-7.26 (m, 3H), 6.88 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 5.75-5.68 (m, 2H), 5.61 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.43 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.99 (d, *J* = 6.0 Hz, 1H), 4.25-4.20 (m, 2H), 4.10 (td, *J* = 8.5, 2.0 Hz, 1H), 2.53-2.44 (m, 2H), 1.21 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 137.2, 133.3, 131.8, 129.5, 128.2, 123.8, 122.8, 121.0, 118.6, 116.9, 116.8, 116.2, 86.1, 84.5, 67.8, 56.9, 46.8, 24.8, 12.3.

HRMS (ESI) calcd for $C_{23}H_{22}NO^+$ $[M+H]^+$: 328.1696, found 328.1694.

Specific rotation $[\alpha]_D^{20}$ = -317.2 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 19.0 min (major), 13.0 min (minor).



3ae

8-Methyl-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolone (3ae)

Condition A, colorless oil, 63% yield, 94% ee.

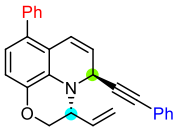
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.31-7.29 (m, 3H), 6.70 (dd, *J* = 21.6, 9.6 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.93 (dd, *J* = 8.8, 6.0 Hz, 1H), 5.78-5.69 (m, 1H), 5.62 (d, *J* = 16.8 Hz, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 5.6 Hz, 1H), 4.27-4.21 (m, 2H), 4.10 (t, *J* = 9.6 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 133.3, 131.9, 129.3, 128.3, 128.2, 127.2, 123.5, 122.7, 121.2, 120.9, 120.6, 120.4, 115.9, 85.8, 84.7, 67.9, 56.9, 46.4, 18.5.

HRMS (ESI) calcd for $C_{22}H_{20}NO^+$ $[M+H]^+$: 314.1539, found 314.1546.

Specific rotation $[\alpha]_D^{20}$ = -389.2 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 27.9 min (major), 21.1 min (minor).



3af

8-phenyl-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3af)

Condition B, colorless oil, 67% yield, 94% ee.

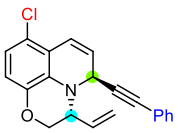
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.28 (m, 10H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 9.5, 0.5 Hz, 1H), 5.83 (dd, *J* = 10.0, 6.0 Hz, 1H), 5.74 (ddd, *J* = 17.5, 10.0, 8.5 Hz, 1H), 5.62 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.44 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.05 (d, *J* = 5.5 Hz, 1H), 4.30-4.24 (m, 2H), 4.16-4.11 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 140.5, 133.6, 133.2, 131.9, 129.9, 129.5, 128.3, 128.2, 128.0, 126.7, 124.9, 122.7, 121.1, 120.9, 120.3, 120.0, 116.1, 85.8, 84.6, 67.9, 56.9, 46.2.

HRMS (ESI) calcd for $C_{27}H_{22}NO^+$ $[M+H]^+$: 376.1696, found 376.1698.

Specific rotation $[\alpha]_D^{20}$ = -20.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 50.4min (major), 26.8 min (minor).



3ag

8-chloro-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3ag)

Condition B, colorless oil, 58% yield, 98% ee.

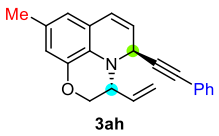
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.30-7.27 (m, 3H), 6.87 (dd, *J* = 10.0, 1.0 Hz, 1H), 6.65 (dd, *J* = 15.5, 8.5 Hz, 2H), 5.94 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.68 (ddd, *J* = 17.5, 10.0, 8.5 Hz, 1H), 5.59 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.43 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.06 (d, *J* = 4.5 Hz, 1H), 4.23-4.18 (m, 2H), 4.07-4.04 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 132.7, 131.9, 130.5, 128.5, 128.3, 124.0, 122.9, 122.6, 122.5, 121.2, 119.6, 119.0, 116.9, 85.1, 67.8, 56.5, 46.5

HRMS (ESI) calcd for $C_{21}H_{17}ClNO^+$ $[M+H]^+$: 334.0993, found 334.0996.

Specific rotation $[\alpha]_D^{20}$ = -196.5 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 17.2 min (major), 13.6 min (minor).



3ah

9-methyl-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3ah)

Condition A, colorless oil, 69% yield, 99% ee.

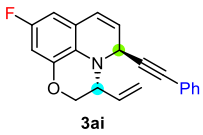
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.3-7.29 (m, 3H), 6.58 (s, 1H), 6.51-6.48 (m, 2H), 5.88 (dd, *J* = 9.6, 5.6 Hz, 1H), 5.77-5.60 (m, 2H), 5.44 (dd, *J* = 9.6, 1.6 Hz, 1H), 5.04 (d, *J* = 5.6 Hz, 1H), 4.25-4.20 (m, 2H), 4.14-4.09 (m, 1H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 133.2, 131.9, 128.5, 128.3, 128.2, 126.7, 126.4, 122.8, 122.5, 121.8, 121.0, 120.7, 117.1, 85.6, 84.9, 68.2, 56.6, 46.9, 20.6.

HRMS (ESI) calcd for $C_{22}H_{20}NO^+$ $[M+H]^+$: 314.1539, found 314.1547.

Specific rotation $[\alpha]_D^{20}$ = -414.0 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6 mL/min, λ = 254 nm), t_R = 18.1 min (major), 16.0 min (minor).



3ai

9-fluoro-5-(phenylethynyl)-3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (3ai)

Condition B, colorless oil, 72% yield, 92% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.29-7.26 (m, 3H), 6.48 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.44-6.40 (m, 2H), 5.93 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.68 (ddd, *J* = 17.0, 9.5, 8.0Hz, 1H), 5.60 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.43 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.98 (d, *J* = 6.0 Hz, 1H), 4.23-4.15 (m, 2H), 4.08 (dd, *J* = 10.0, 7.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2 (d, *J* = 235 Hz), 144.9 (d, *J* = 11.3 Hz), 132.8, 131.9, 128.4, 128.2, 125.8 (d, *J* = 2.5 Hz), 125.4 (d, *J* = 1.3 Hz), 123.4, 123.0 (d, *J* = 10.0 Hz), 122.5, 121.3, 106.2 (d, *J* = 22.5 Hz), 103.9 (d, *J* = 26.3 Hz), 85.2, 85.0, 68.3, 56.4, 46.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -124.5.

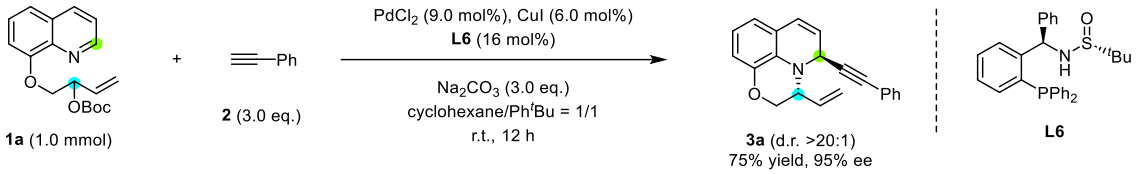
HRMS (ESI) calcd for $C_{21}H_{17}FNO^+$ $[M+H]^+$: 318.1289, found 318.1288.

Specific rotation $[\alpha]_D^{20}$ = -269.7 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 98:2, 0.6 mL/min, λ = 254 nm), t_R = 16.9 min (major), 18.4 min (minor).

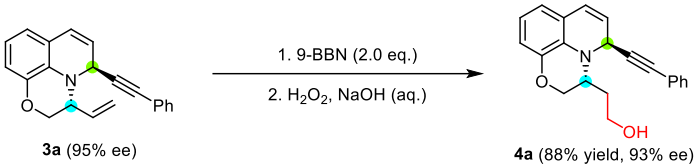
7. Synthetic Applications

7.1 Scale-up Reaction

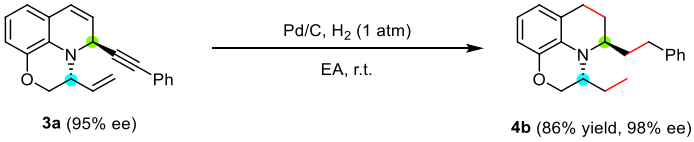


To a dried Schlenk tube was charged with $PdCl_2$ (9.0 mol%, 16.0 mg), CuI (6.0 mol%, 11.4 mg), chiral ligand **L6** (16 mol%, 75.5 mg), Na_2CO_3 (3.0 eq., 318.0 mg), and **1a** (1.0 mmol) under N_2 atmosphere. Ph^{t}Bu (5.0 mL), cyclohexane (5.0 mL) and **2** (3.0 mmol) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature for 12 hours until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3a** (224.5 mg, 75% yield, 95% ee).

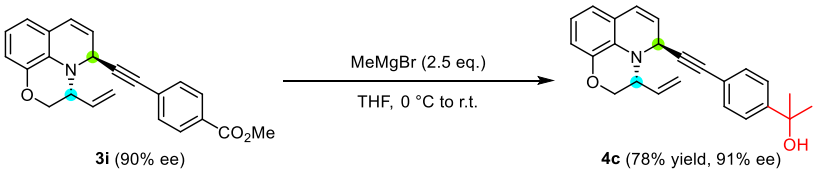
7.2 Synthetic Transformations



To a dried Schlenk tube was added **3a** (0.2 mmol) and 9-BBN (0.5 M in THF, 2 eq., 0.8 mL). The reaction mixture at room temperature for 2 hours until the reaction was completed (monitored by TLC). Then the reaction mixture was cooled to 0 °C, 3 M aqueous NaOH solution (2.0 mL) was added. After 5 min, 30% H_2O_2 (1.5 mL) was added by syringe. After stirring for an additional 2 hours at room temperature, saturated aqueous Na_2SO_3 solution was added, then the reaction mixture was extracted ethyl acetate. The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to afford the crude product. The residue was purified by column chromatography on silica gel to afford **4a**.



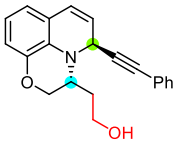
To a dried Schlenk tube was added **3a** (0.2 mmol), ethyl acetate (1.0 mL) and 10% Pd/C (20 mol%) respectively under N_2 atmosphere. The vessel was purged 3 times with hydrogen and stirred at room temperature for 12 hours until the reaction was completed (monitored by TLC). The solvent was removed under reduced pressure was purified and the residue was purified by flash chromatography on silica gel to afford **4b**.



To a dried Schlenk tube was added **3i** (0.2 mmol) and THF (1.0 mL) respectively under N_2 atmosphere. MeMgBr (1.0 M in THF, 2.5 eq., 0.5 mL) was added at 0 °C. The reaction was then gradually warm to

room temperature and stirred for 2 hours. After the reaction was completed (monitored by TLC), saturated $NaHCO_3$ aqueous solution was added. Then the reaction mixture was extracted ethyl acetate. The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to afford the crude product. The residue was purified by column chromatography on silica gel to afford **4c**.

Spectroscopic Characterization



4a

2-(5-(phenylethynyl)-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolin-3-yl)ethan-1-ol (4a)

colorless oil, 88% yield, 93% ee.

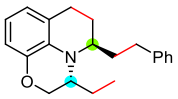
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.21 (m, 2H), 6.84-6.73 (m, 3H), 6.70-6.62 (m, 1H), 6.58-6.44 (m, 2H), 5.84 (dd, *J* = 9.6, 5.7 Hz, 1H), 5.24-5.03 (m, 1H), 4.22 (dt, *J* = 33.2, 16.6 Hz, 1H), 4.02 (dd, *J* = 10.6, 2.6 Hz, 1H), 3.96-3.76 (m, 3H), 2.06 (d, *J* = 11.5 Hz, 1H), 1.93 (ddt, *J* = 13.7, 8.5, 5.1 Hz, 1H), 1.87-1.70 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 131.8, 128.3, 127.9, 126.2, 123.0, 122.5, 121.6, 120.3, 118.1, 116.7, 86.0, 84.8, 66.8, 59.7, 52.4, 50.0, 33.3.

HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1489, found 318.1499.

Specific rotation $[\alpha]_D^{20}$ = -453.7 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 80:20, 0.6 mL/min, λ = 254 nm), t_R = 11.6 min (major), 15.2 min (minor).



4b

3-ethyl-5-phenethyl-2,3,6,7-tetrahydro-5H-[1,4]oxazino[2,3,4-ij]quinoline (4b)

colorless oil, 80% yield, 98% ee.

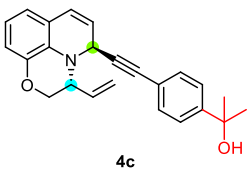
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.25-7.20 (m, 3H), 6.65 (t, *J* = 7.5 Hz, 2H), 6.49 (t, *J* = 7.5 Hz, 1H), 4.21 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.97 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.37 (td, *J* = 8.5, 4.0 Hz, 1H), 3.18-3.15 (m, 1H), 2.88 (ddd, *J* = 16.5, 12.0, 5.5 Hz, 1H), 2.77-2.69 (m, 2H), 2.63-2.57 (m, 1H), 2.04-1.99 (m, 1H), 1.93-1.79 (m, 3H), 1.64-1.57 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 141.9, 130.2, 128.5, 128.3, 126.0, 121.8, 121.3, 114.9, 113.7, 66.0, 55.4, 54.2, 33.4, 32.1, 24.3, 23.3, 22.5, 10.5.

HRMS (ESI) calcd for $C_{21}H_{26}NO^+$ $[M+H]^+$: 308.2009, found 308.2001.

Specific rotation $[\alpha]_D^{20}$ = -330.9 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OJ-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 95:5, 0.6mL/min, λ = 254 nm), t_R = 12.3 min (major), 16.6 min (minor).



4c

2-(4-((3-vinyl-2,3-dihydro-5H-[1,4]oxazino[2,3,4-ij]quinolin-5-yl)ethynyl)phenyl)propan-2-ol (4c)

colorless oil, 78% yield, 91% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 20.6, 8.5 Hz, 4H), 6.73 (dd, *J* = 6.2, 3.3 Hz, 1H), 6.67 (s, 2H), 6.51 (dd, *J* = 9.6, 0.7 Hz, 1H), 5.87 (dd, *J* = 9.5, 5.6 Hz, 1H), 5.70 (dd, *J* = 9.7, 7.7 Hz, 1H), 5.61 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.44 (dd, *J* = 9.8, 1.6 Hz, 1H), 5.06 (t, *J* = 7.3 Hz, 1H), 4.23 (d, *J* = 8.2 Hz, 2H), 4.14-4.08 (m, 1H), 2.11 (d, *J* = 20.2 Hz, 1H), 1.56 (s, 6H).

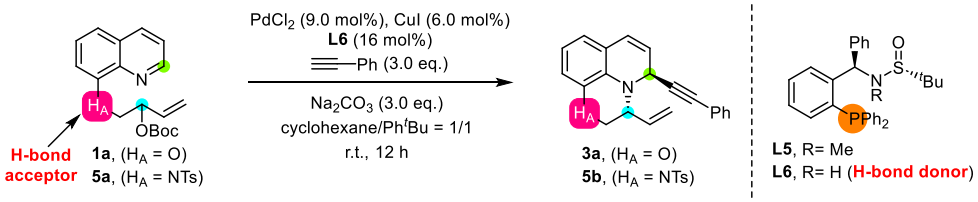
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 144.1, 133.1, 131.7, 129.2, 126.3, 124.4, 122.4, 121.6, 123.0, 120.2, 118.8, 116.6, 85.4, 84.7, 72.4, 67.9, 56.6, 46.9, 31.7.

HRMS (ESI) calcd for $C_{24}H_{24}NO_2^+$ $[M+H]^+$: 358.1802, found 358.1803.

Specific rotation $[\alpha]_D^{20}$ = -388.2 (c = 0.5, CH_2Cl_2).

HPLC (Daicel Chiralcel OD-H (25 cm × 0.46 cm ID), hexane/*i*-PrOH = 80:20, 0.5 mL/min, λ = 254 nm), t_R = 15.4 min (major), 13.6 min (minor).

8. Control Experiments



Entry	Variation of standard conditions	Yield (%)	e.e. (%)
1	None	77	95
2	w/o $PdCl_2$	ND	-
3	w/o CuI	ND	-
4	Cu—≡—Ph (3.0 eq.) instead of CuI and phenylacetylene	trace	95
5	Cu—≡—Ph (1.0 eq.) instead of CuI and phenylacetylene	17	95
6	**5a** instead of **1a**	20	rac.
7	**L5** instead of **L6**	30	15

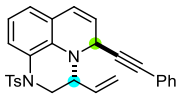
Fig. 5: Control experiments.

Entry 4: To a dried Schlenk tube were charged with $PdCl_2$ (9.0 mol%, 1.6 mg), (phenylethynyl)copper[3] (3.0 eq., 49.4 mg), chiral ligand **L6** (3.1 eq., 146.2 mg), Na_2CO_3 (3.0 eq., 31.8 mg), and **1a** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL) and cyclohexane (0.5 mL) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature for 12 hours until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3a** (trace, 95% ee).

Entry 5: To a dried Schlenk tube were charged with $PdCl_2$ (9.0 mol%, 1.6 mg), (phenylethynyl)copper[3] (1.0 eq., 16.5 mg), chiral ligand **L6** (1.1 eq., 51.9 mg), Na_2CO_3 (3.0 eq., 31.8 mg), and **1a** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL) and cyclohexane (0.5 mL) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature for 12 hours until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3a** (17% yield, 95% ee).

Entry 6: To a dried Schlenk tube were charged with $PdCl_2$ (9.0 mol%, 1.6 mg), CuI (6.0 mol%, 1.1 mg), chiral ligand **L6** (16 mol%, 7.5 mg), Na_2CO_3 (3.0 eq., 31.8 mg), and **5a** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL), cyclohexane (0.5 mL) and **2a** (0.3 mmol) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature for 12 hours until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **5b** (20% yield, racemic).

Entry 7: To a dried Schlenk tube were charged with $PdCl_2$ (9.0 mol%, 1.6 mg), CuI (6.0 mol%, 1.1 mg), chiral ligand **L5** (16 mol%, 7.8 mg), Na_2CO_3 (3.0 eq., 31.8 mg), and **1a** (0.1 mmol) under N_2 atmosphere. Ph^{t}Bu (0.5 mL), cyclohexane (0.5 mL) and **2a** (0.3 mmol) was then introduced respectively via syringe. The resulting mixture was stirred at room temperature for 12 hours until the reaction was completed (monitored by TLC). The solution was washed with water and extracted with ethyl acetate, then removed the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3a** (30% yield, 15% ee).



5b

5-(phenylethynyl)-1-tosyl-3-vinyl-2,3-dihydro-1H,5H-pyrido[1,2,3-de]quinoxaline(5b)

yellow solid, 20% yield, Melting point: 105-108 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 13.1, 4.7 Hz, 3H), 7.31 (ddd, *J* = 12.2, 10.6, 6.4 Hz, 5H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.90-6.83 (m, 1H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 9.5 Hz, 1H), 5.76 (dd, *J* = 9.4, 5.9 Hz, 1H), 5.51 (dd, *J* = 9.4, 8.2 Hz, 1H), 5.42-5.34 (m, 2H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.21 (dd, *J* = 13.6, 2.8 Hz, 1H), 3.39 (ddd, *J* = 23.9, 11.0, 6.6 Hz, 2H), 1.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 135.8, 134.2, 133.5, 132.1, 129.6, 128.4, 127.48, 126.1, 125.2, 124.6, 123.9, 122.8, 122.4, 121.4, 121.2, 118.3, 85.0, 84.4, 55.3, 48.1, 46.4, 21.0.

HRMS (ESI) calcd for $C_{28}H_{25}N_2O_2S^+$ ($[M+H]^+$): 453.1631, found 453.1636.

9. DFT Calculation

Computational Details

In order to understand the origin of enantioselectivity, density functional theory (DFT) calculations were carried out using the Gaussian 09 software package.[4] The stationary structures were optimized using B3LYP-D3 method[5-7] and Def2-SVP basis set.[8] The geometry optimizations were performed without symmetry constraints, and the nature of the extrema was checked by analytical frequency calculations. The intrinsic reaction coordinate (IRC)[9] pathways have been traced to verify two desired minima connected by the transition states. Single-point calculations with the M06L[10-12]/ Def2-TZVP[8] level of theory in cyclohexane medium while using Truhlar's SMD solvation model[13] were performed using the geometries obtained at optimization step. The independent gradient model based on Hirshfeld partition (IGMH) analysis was conducted with Multiwfn and VMD.[14-16] The 3-D images of the calculated structures were prepared using CYLview.[17]

Table S1. Coordination data sets and free energies for DFT optimized structures at M06L/ Def2-TZVP/SMD(cyclohexane)//B3LYP-D3/Def2-SVP level at 298 K.

Ts-R

-2986.048131

C	-0.84231300	0.19623200	-4.22354800
C	-0.48792800	-1.15316800	-4.20417900
C	0.19114400	-1.66972500	-3.09928100
C	0.52710600	-0.86527600	-1.99433200
C	0.17968700	0.51103500	-2.02360700
C	-0.50533600	1.01249600	-3.14312400
P	1.39503600	-1.60332000	-0.52020600
C	0.56761600	1.46185200	-0.89489500
N	-0.42654600	2.55604200	-0.81435100
S	-0.24215600	3.59150800	0.54880400
C	-1.25801200	5.04425500	-0.12318700
O	-1.07230100	3.05770400	1.70042600
C	1.96803400	2.03923300	-1.07525500
C	2.28253400	2.82110400	-2.19656600
C	3.56493000	3.35022800	-2.35019400
C	4.54620800	3.09712300	-1.38321700
C	4.23275700	2.32070600	-0.26572000
C	2.94579900	1.79595500	-0.10356900
C	1.22155200	-3.42257800	-0.82193400
C	-0.06100900	-3.99945800	-0.75293800
C	-0.23892100	-5.37350900	-0.91104300
C	0.86841600	-6.20508600	-1.12057700
C	2.14618700	-5.64524000	-1.18051400
C	2.32358600	-4.26365700	-1.03800500
C	3.17389200	-1.30116100	-0.87802300
C	4.05534800	-1.29585800	0.21678800

C	5.42164400	-1.09156000	0.00375200
C	5.91266600	-0.87523100	-1.28713600
C	5.03289100	-0.86385000	-2.37522300
C	3.66810900	-1.08159700	-2.17402800
C	-2.66584500	4.55307600	-0.45806300
C	-0.52016500	5.61798200	-1.33146200
C	-1.29146300	6.03275100	1.04872600
H	-1.37409600	0.61805100	-5.08057700
H	-0.73276200	-1.80572500	-5.04629100
H	0.46690900	-2.72516000	-3.09782800
H	-0.77423700	2.06962300	-3.16032200
H	0.58368100	0.87054200	0.04046600
H	-1.38358700	2.19223100	-0.82459900
H	1.51902300	3.01293900	-2.95391900
H	2.70883800	1.17654300	0.77187500
H	-0.92981400	-3.35974100	-0.58739700
H	-1.24455500	-5.80057300	-0.86505100
H	0.73294900	-7.28361100	-1.23535100
H	3.01748100	-6.28523900	-1.34292400
H	3.32810200	-3.84066700	-1.09338800
H	3.64680600	-1.35409400	1.23127600
H	6.10123100	-1.07314900	0.86005300
H	6.98009000	-0.69945200	-1.44671700
H	5.40992600	-0.67827000	-3.38440400
H	2.98718400	-1.06493800	-3.02800100
H	-3.06679500	3.95356000	0.37392200
H	-3.33278400	5.41552600	-0.62288300
H	-2.67333100	3.94360700	-1.37473000
H	-0.48181600	4.89210500	-2.15580700
H	0.51506500	5.89584700	-1.07566800
H	-1.03765000	6.52631900	-1.68360200
H	-1.87325800	6.92481900	0.76421100
H	-1.75731100	5.57270500	1.93248600
H	-0.27725000	6.36454100	1.32515200
Pd	0.49446400	-1.11034200	1.62613000
H	4.99336300	2.10735300	0.48904600
H	5.55412400	3.50277600	-1.50671800
H	3.80299600	3.95653400	-3.22861200
C	-6.35449100	0.89285200	-1.59129500
C	-6.89105200	-0.27908400	-1.08828500
C	-6.10585700	-1.09963900	-0.24123800
C	-4.76629000	-0.70168800	0.07363500
C	-4.24963400	0.53529700	-0.42251900
C	-5.04757300	1.30550000	-1.25802100

H	-7.58575800	-2.65092400	0.11402400
H	-6.95475700	1.52751900	-2.24726600
H	-7.91047600	-0.58350100	-1.33372400
C	-6.56586400	-2.32018200	0.32679400
H	-4.63989100	2.24630900	-1.63129300
C	-4.41379500	-2.63415300	1.35443700
C	-5.73727500	-3.07534700	1.13124900
H	-3.69342100	-3.19846600	1.95569200
H	-6.07635600	-4.00862100	1.58366800
N	-3.97262900	-1.50782100	0.83777500
O	-3.01770000	0.97061400	-0.10791900
C	-2.36161400	0.38586900	1.03178900
H	-2.93091100	0.63025000	1.94211700
H	-1.40001700	0.89347500	1.12391100
C	-2.21647900	-1.10787600	0.86312700
H	-2.04918100	-1.39465100	-0.18290700
C	-1.47007900	-1.87210400	1.83713000
H	-1.41878300	-2.95343200	1.66447000
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H	-1.41785500	-0.38054200	3.46878400
H	-0.75613800	-2.03409400	3.89033300
O	2.26534700	-0.22300100	2.31955100
C	2.42135500	0.44497500	3.53537000
C	1.44798800	1.63630700	3.63986300
H	1.57336800	2.20023100	4.58042700
H	1.60395900	2.32880700	2.79837100
H	0.40764800	1.28451900	3.57997900
C	3.87363000	0.97229200	3.57538900
H	4.09946800	1.50036900	4.51747500
H	4.57762800	0.13126400	3.46750200
H	4.04474400	1.66917300	2.74017300
C	2.20725000	-0.51108300	4.72637200
H	2.39133400	-0.01871000	5.69691300
H	1.17550700	-0.89207300	4.71872200
H	2.88679800	-1.37343200	4.63236700

Ts-S

-2986.042570

C	6.26581600	1.09051100	-3.59395900
C	7.23716900	0.99986400	-2.61185400
C	6.92633700	0.37043500	-1.38219500
C	5.61305300	-0.16854800	-1.17990500
C	4.63144100	-0.08172400	-2.21635400
C	4.97610800	0.55718800	-3.40370300

H	8.86031600	0.63967800	-0.42722200
H	6.49778200	1.57938000	-4.54328200
H	8.23745000	1.40962500	-2.76655200
C	7.84913500	0.24252800	-0.30690600
H	4.21492700	0.62378100	-4.18284700
C	6.14822200	-0.84875400	0.99629500
C	7.46903800	-0.36773600	0.87163900
H	5.78738900	-1.31355700	1.91976800
H	8.16409700	-0.48006400	1.70559400
N	5.27870700	-0.74606300	0.00882900
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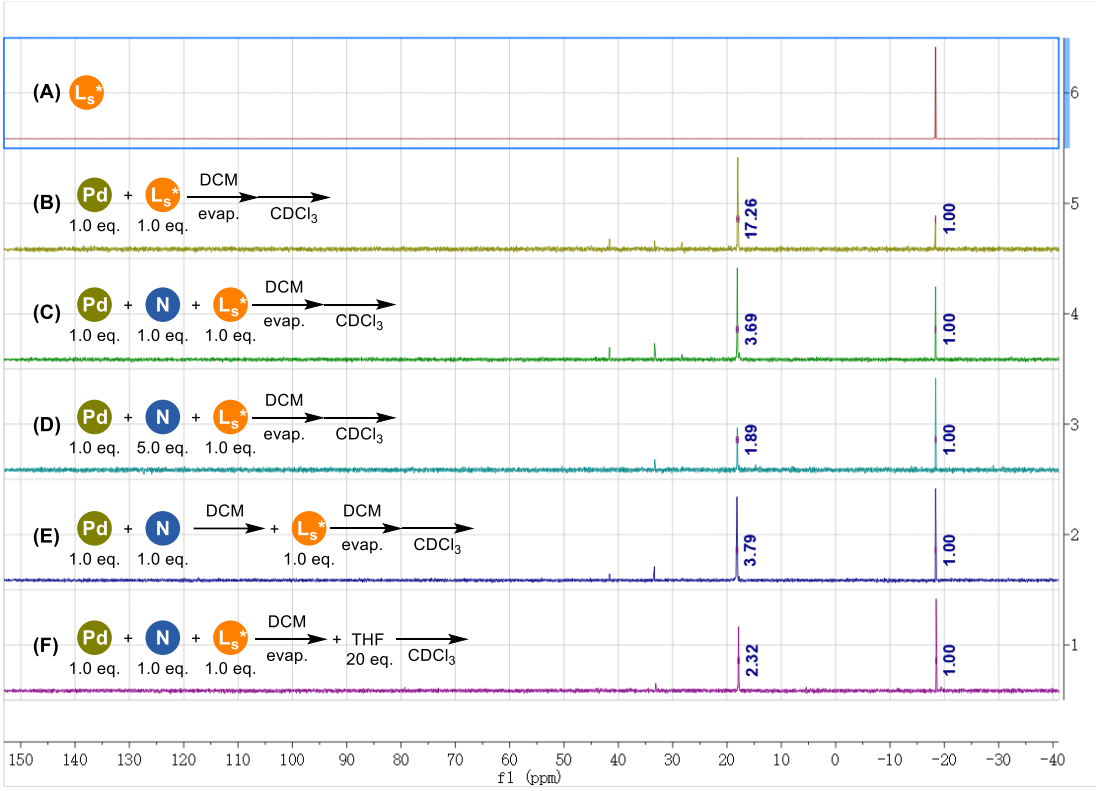
C	3.05942400	-1.43362500	-0.99781400
H	3.56189200	-2.40275200	-1.15918800
H	1.97302200	-1.59070100	-1.07689900
C	3.46605800	-0.87400200	0.34684800
H	3.55545200	-1.65125900	1.11328000
C	3.01997400	0.40289600	0.82652300
H	3.42859400	0.69758000	1.80013200
C	2.27131700	1.37367600	0.07271000
H	2.17252200	1.25274200	-1.01089700
H	2.31996300	2.41979600	0.39861000
C	-1.32309800	1.56513900	-4.07739800
C	-0.46785000	2.38105500	-3.32887500
C	-0.48393600	2.30299700	-1.94031800
C	-1.34944300	1.42405700	-1.25070400
C	-2.19098400	0.57920700	-2.01141800
C	-2.16608000	0.67998700	-3.41466500
P	-1.06876600	1.38154300	0.59157500
C	-3.05475300	-0.53869700	-1.41818300
N	-2.44859600	-1.86842900	-1.59977300
S	-0.94974700	-2.05211600	-0.75023300
C	-1.12758500	-3.84625000	-0.20254900
O	0.15335700	-2.07689500	-1.79615300
C	-4.50059900	-0.51502200	-1.89981500
C	-5.17095600	0.71439500	-2.01568200
C	-6.51802200	0.76402800	-2.37693900
C	-7.22106100	-0.41778600	-2.63623400
C	-6.56322400	-1.64479100	-2.52442500
C	-5.21419800	-1.69378400	-2.15537300
C	-1.00071500	3.17572100	1.04947500
C	-0.24458600	3.51776300	2.18293400
C	-0.20441200	4.83837500	2.63918000
C	-0.91030300	5.83720700	1.96180800
C	-1.65791100	5.50822200	0.82629500

C	-1.70492700	4.18681200	0.37377500
C	-2.65708100	0.88272800	1.39492500
C	-2.63661200	-0.29342800	2.16450600
C	-3.81815000	-0.75071400	2.75870100
C	-5.01348100	-0.04498600	2.59597800
C	-5.02887500	1.13705600	1.84527000
C	-3.85507400	1.60451800	1.25178100
C	-1.42867500	-4.71229200	-1.42163200
C	-2.23459500	-3.87133700	0.85093600
C	0.23873300	-4.17393200	0.41272900
H	-1.32620900	1.61530300	-5.16908700
H	0.21319100	3.07661500	-3.82585100
H	0.19457600	2.93919400	-1.36914600
H	-2.83469500	0.03740000	-3.99448300
H	-3.11450200	-0.40088600	-0.33535000
H	-2.28093600	-2.10194000	-2.58248600
H	-4.62747700	1.64125400	-1.82116500
H	-4.70848900	-2.65449500	-2.05139800
H	0.31689500	2.73830900	2.70533600
H	0.38639800	5.08762400	3.52449600
H	-0.87443800	6.87131300	2.31442800
H	-2.20778500	6.28485700	0.28792300
H	-2.28158900	3.94672000	-0.52231900
H	-1.68936600	-0.84648000	2.26945300
H	-3.79930900	-1.67180400	3.34783500
H	-5.93613500	-0.41166900	3.05384800
H	-5.96117700	1.69262600	1.71567500
H	-3.87945700	2.52721500	0.66851000
H	-0.68872400	-4.52211000	-2.21511100
H	-1.37062400	-5.77750800	-1.14222300
H	-2.43769200	-4.51800200	-1.81588200
H	-3.19497600	-3.53336000	0.43287700
H	-1.96693300	-3.23056000	1.70412400
H	-2.36188200	-4.90239400	1.22139400
H	0.20110100	-5.18049000	0.86171100
H	1.02468200	-4.16612800	-0.35758100
H	0.48328800	-3.43512700	1.19486500
Pd	0.86055100	0.22525300	1.09437800
H	-7.10228000	-2.57517600	-2.72252100
H	-8.27487100	-0.38043000	-2.92423100
H	-7.02150100	1.73101800	-2.45933600
O	0.17706800	-1.46617100	2.26637900
C	0.59210500	-1.65872700	3.58049000
C	-0.24828600	-2.80644200	4.18467600

H	0.02656300	-3.02941200	5.22987200
H	-1.31654600	-2.53720900	4.15841400
H	-0.11778500	-3.72197700	3.58673200
C	0.38456000	-0.38564800	4.43488800
H	0.66301700	-0.53768300	5.49218800
H	0.99544300	0.43945000	4.03119300
H	-0.67008400	-0.07194600	4.39324500
C	2.08819200	-2.05344100	3.63372800
H	2.43360800	-2.27906400	4.65757700
H	2.25811900	-2.94145100	3.00293200
H	2.69877400	-1.22595800	3.23862500

10. Ligand Exchange Experiment



(B): To a dried Schlenk tube was charged with $PdCl_2$ (0.02 mmol, 3.5 mg) and chiral ligand **L6** (0.02 mmol, 9.4 mg) under a nitrogen atmosphere. Anhydrous CH_2Cl_2 (0.5 mL) was then injected via syringe, and the resulting mixture was stirred at room temperature for 30 min. After complete removal of CH_2Cl_2 under reduced pressure, $CDCl_3$ (0.7 mL) was introduced into the reaction system. Subsequently, the ^{31}P NMR spectrum of the solution was recorded.

(C): To a dried Schlenk tube was charged with $PdCl_2$ (0.02 mmol, 3.5 mg), **1a** (0.02 mmol, 6.3 mg) and chiral ligand **L6** (0.02 mmol, 9.4 mg) under a nitrogen atmosphere. Anhydrous CH_2Cl_2 (0.5 mL) was then injected via syringe, and the resulting mixture was stirred at room temperature for 30 min. After complete removal of CH_2Cl_2 under reduced pressure, $CDCl_3$ (0.7 mL) was introduced into the reaction system. Subsequently, the ^{31}P NMR spectrum of the solution was recorded.

(D): To a dried Schlenk tube was charged with $PdCl_2$ (0.02 mmol, 3.5 mg), **1a** (0.1 mmol, 31.5 mg) and chiral ligand **L6** (0.02 mmol, 9.4 mg) under a nitrogen atmosphere. Anhydrous CH_2Cl_2 (0.5 mL) was then injected via syringe, and the resulting mixture was stirred at room temperature for 30 min. After complete removal of CH_2Cl_2 under reduced pressure, $CDCl_3$ (0.7 mL) was introduced into the reaction system. Subsequently, the ^{31}P NMR spectrum of the solution was recorded.

(E): To a dried Schlenk tube was charged with $PdCl_2$ (0.02 mmol, 3.5 mg) and **1a** (0.02 mmol, 6.3 mg) under a nitrogen atmosphere. Anhydrous CH_2Cl_2 (0.5 mL) was then injected via syringe, and the resulting mixture was stirred at room temperature for 30 min. Then chiral ligand **L6** (0.02 mmol, 9.4 mg) was added to the reaction mixture under a nitrogen atmosphere and further stirred at room temperature for 30 min. After complete removal of CH_2Cl_2 under reduced pressure, $CDCl_3$ (0.7 mL) was introduced into the reaction system. Subsequently, the ^{31}P NMR spectrum of the solution was recorded.

(F): To a dried Schlenk tube was charged with $PdCl_2$ (0.02 mmol, 3.5 mg), **1a** (0.02 mmol, 6.3 mg) and chiral ligand **L6** (0.02 mmol, 9.4 mg) under a nitrogen atmosphere. Anhydrous CH_2Cl_2 (0.5 mL) was

then injected via syringe, and the resulting mixture was stirred at room temperature for 30 min. After complete removal of CH_2Cl_2 under reduced pressure, $CDCl_3$ (0.7 mL) and THF (0.4 mmol, 32 μL) was introduced into the reaction system. Subsequently, the ^{31}P NMR spectrum of the solution was recorded.

11. Single crystal X-ray diffraction data of 3s

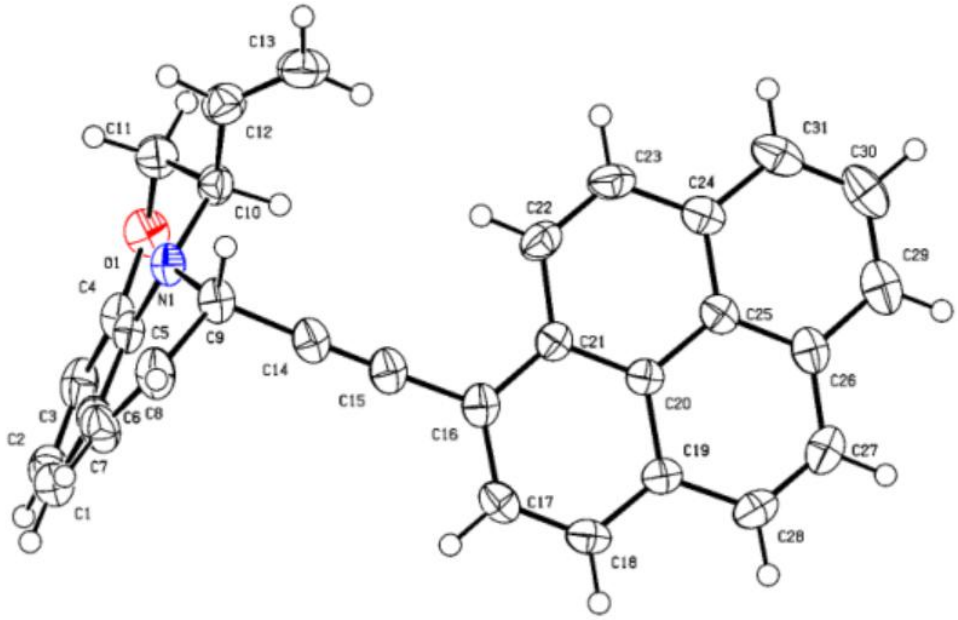


Table 1 Crystal data and structure refinement for 240712_ZL_1131_bi_0m.

Identification code	240712_ZL_1131_bi_0m
Empirical formula	$C_{31}H_{21}NO$
Formula weight	423.49
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.3366(2)
b/Å	14.7782(6)
c/Å	13.3985(6)
α/°	90
β/°	90.342(2)
γ/°	90
Volume/Å^3	1056.66(8)
Z	2
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	0.395
F(000)	444.0
Crystal size/mm^3	0.15 × 0.06 × 0.03
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	5.738 to 121.25
Index ranges	-6 ⩽ h ⩽ 6, -17 ⩽ k ⩽ 19, -17 ⩽ l ⩽ 17
Reflections collected	35644
Independent reflections	4755 [R_{int} = 0.0850, R_{sigma} = 0.0604]
Data/restraints/parameters	4755/1/298

Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1015
Final R indexes [all data]	R_1 = 0.0584, wR_2 = 0.1046
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.22
Flack parameter	-0.03(17)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 240712_ZL_1131_bi_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	8124(3)	6159.9(11)	6867.9(12)	39.0(4)
N1	11190(4)	4861.8(14)	5883.4(14)	29.3(4)
C1	7423(5)	3441.6(19)	7585.8(19)	42.1(7)
C2	5888(5)	4076(2)	8015.0(19)	43.4(7)
C3	6154(5)	4985(2)	7770.6(18)	39.9(6)
C4	7914(5)	5246.4(16)	7081.2(18)	32.2(6)
C5	9403(4)	4609.0(16)	6592.2(17)	28.6(5)
C6	9181(5)	3694.2(16)	6870.0(18)	33.9(6)
C7	10897(5)	3056.5(17)	6402.9(19)	40.2(6)
C8	12158(5)	3284.3(17)	5593.3(19)	39.3(6)
C9	11746(5)	4190.8(17)	5109.6(18)	32.1(5)
C10	11040(5)	5800.0(15)	5521.2(17)	31.0(5)
C11	10446(5)	6398.4(16)	6408(2)	37.5(6)
C12	13469(5)	6074.0(18)	5069(2)	39.2(6)
C13	13769(6)	6298.1(19)	4138(2)	47.6(7)
C14	9737(5)	4137.3(16)	4331.6(18)	32.7(5)
C15	8163(5)	4101.9(17)	3690.0(17)	33.4(5)
C16	6310(4)	4070.7(16)	2911.8(17)	30.8(5)
C17	4658(5)	3340.1(16)	2837.5(17)	33.3(5)
C18	2852(5)	3299.3(15)	2095.9(19)	33.9(6)
C19	2595(4)	3997.4(15)	1401.7(18)	28.3(5)
C20	4246(4)	4753.1(14)	1463.0(17)	26.2(5)
C21	6133(4)	4784.6(15)	2213.5(17)	27.3(5)
C22	7800(5)	5547.7(17)	2225.2(18)	35.4(6)
C23	7554(5)	6228.7(17)	1561.9(19)	38.2(6)
C24	5628(5)	6228.0(16)	813.9(18)	32.9(5)
C25	3988(4)	5476.4(15)	763.6(17)	28.1(5)
C26	2073(5)	5443.4(16)	18.6(17)	32.5(6)
C27	483(5)	4665.8(18)	-28(2)	38.7(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 240712_ZL_1131_bi_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C28	736(5)	3984.2(18)	620(2)	37.5(6)
C29	1814(5)	6176.4(19)	-640(2)	41.9(6)
C30	3424(5)	6902.0(19)	-590(2)	44.8(7)
C31	5322(5)	6932.8(17)	124(2)	42.6(6)

Table 3 Anisotropic Displacement Parameters (Å^2×103) for 240712_ZL_1131_bi_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	45.0(10)	33.7(9)	38.4(10)	-5.0(8)	5.3(8)	10.0(8)
N1	30.7(10)	32.7(10)	24.4(10)	-0.7(8)	-0.7(8)	4.9(8)
C1	44.2(16)	46.5(15)	35.6(15)	5.9(12)	-4.3(12)	-5.5(12)
C2	34.8(14)	63.7(18)	31.6(15)	4.1(13)	1.4(11)	-4.3(13)
C3	32.5(14)	58.9(17)	28.3(13)	-5.1(12)	-1.2(11)	8.0(12)
C4	33.4(13)	37.8(13)	25.3(12)	-3.8(10)	-5.1(10)	7.8(10)
C5	27.0(12)	36.4(12)	22.5(12)	-0.8(9)	-4.7(9)	3.6(9)
C6	37.7(14)	35.8(13)	28.1(13)	0.9(10)	-4.4(10)	2.5(10)
C7	54.0(17)	31.2(13)	35.4(15)	3.2(11)	-4.8(13)	9.9(12)
C8	47.6(16)	35.9(14)	34.3(14)	-2.9(11)	-4.1(12)	16.6(12)
C9	33.6(13)	35.6(13)	27.2(12)	-1.3(10)	2.2(10)	8.7(10)
C10	31.7(13)	31.4(13)	29.9(13)	0.9(10)	-4.7(10)	2.2(9)
C11	42.2(14)	32.9(13)	37.5(14)	-2.7(11)	-0.6(12)	2.8(11)
C12	34.1(13)	40.7(14)	42.8(15)	-0.1(11)	-1.5(11)	-3.2(11)
C13	49.8(17)	43.8(16)	49.2(18)	-2.6(13)	8.9(14)	-13.8(13)
C14	41.1(13)	30.8(12)	26.2(12)	-1.6(10)	2.8(10)	9.1(11)
C15	39.8(14)	35.3(13)	25.2(13)	-4.3(10)	4.0(11)	8.3(11)
C16	34.0(13)	32.8(12)	25.7(12)	-5.3(10)	3.4(10)	7.3(10)
C17	42.2(14)	27.5(12)	30.2(13)	1.8(10)	7.1(10)	5.9(10)
C18	37.6(14)	26.9(12)	37.4(14)	-1.9(10)	8.3(11)	-5.5(10)
C19	27.3(12)	27.4(12)	30.3(13)	-4.9(9)	5.7(9)	-1.1(9)
C20	28.7(12)	24.4(11)	25.4(11)	-5.2(9)	5.6(9)	1.8(9)
C21	28.9(12)	28.6(12)	24.6(11)	-6.1(9)	3.7(9)	3.0(9)
C22	35.1(14)	37.9(14)	33.4(14)	-9.2(11)	-0.5(11)	-6.6(11)
C23	43.0(14)	30.4(13)	41.3(14)	-7.4(11)	7.3(12)	-10.8(11)
C24	39.5(14)	27.7(12)	31.8(13)	-3.4(10)	10.1(11)	0.4(10)
C25	30.9(13)	28.0(11)	25.4(12)	-3.2(9)	8.3(10)	4.2(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×103$) for 240712_ZL_1131_bi_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}
C26	32.5(13)	39.7(13)	25.4(12)	-0.3(10)	7.0(10)	9.3(10)
C27	32.5(14)	50.0(16)	33.6(13)	-7.4(11)	-4.2(11)	2.9(12)
C28	32.6(14)	39.7(14)	40.3(15)	-8.8(12)	0.6(11)	-7.5(11)
C29	40.3(14)	53.0(16)	32.5(14)	4.6(12)	8.3(11)	17.7(13)
C30	55.4(18)	40.4(15)	38.7(15)	10.5(12)	15.3(13)	18.9(14)
C31	53.3(17)	29.0(13)	45.6(16)	1.8(11)	18.9(13)	1.5(12)

Table 4 Bond Lengths for 240712_ZL_1131_bi_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C4	1.385(3)	C16	C17	1.397(3)
O1	C11	1.431(3)	C16	C21	1.413(3)
N1	C5	1.401(3)	C17	C18	1.381(3)
N1	C9	1.466(3)	C18	C19	1.395(3)
N1	C10	1.471(3)	C19	C20	1.425(3)
C1	C2	1.374(4)	C19	C28	1.438(3)
C1	C6	1.396(4)	C20	C21	1.419(3)
C2	C3	1.390(4)	C20	C25	1.428(3)
C3	C4	1.376(4)	C21	C22	1.436(3)
C4	C5	1.398(3)	C22	C23	1.349(4)
C5	C6	1.407(3)	C23	C24	1.431(3)
C6	C7	1.458(4)	C24	C25	1.416(3)
C7	C8	1.324(4)	C24	C31	1.401(3)
C8	C9	1.504(4)	C25	C26	1.425(3)
C9	C14	1.493(3)	C26	C27	1.430(4)
C10	C11	1.517(3)	C26	C29	1.403(4)
C10	C12	1.491(4)	C27	C28	1.336(4)
C12	C13	1.301(4)	C29	C30	1.376(4)
C14	C15	1.199(3)	C30	C31	1.390(4)
C15	C16	1.433(3)			

Table 5 Bond Angles for 240712_ZL_1131_bi_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O1	C11	113.58(18)	C17	C16	C21	119.3(2)

Table 5 Bond Angles for 240712_ZL_1131_bi_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N1	C9	116.14(19)	C21	C16	C15	120.1(2)
C5	N1	C10	116.04(19)	C18	C17	C16	121.5(2)
C9	N1	C10	114.52(18)	C17	C18	C19	120.8(2)
C2	C1	C6	120.6(3)	C18	C19	C20	118.9(2)
C1	C2	C3	119.9(3)	C18	C19	C28	122.7(2)
C4	C3	C2	120.0(3)	C20	C19	C28	118.4(2)
O1	C4	C5	120.9(2)	C19	C20	C25	119.5(2)
C3	C4	O1	117.9(2)	C21	C20	C19	120.16(19)
C3	C4	C5	121.2(2)	C21	C20	C25	120.38(19)
N1	C5	C6	119.6(2)	C16	C21	C20	119.3(2)
C4	C5	N1	122.0(2)	C16	C21	C22	122.7(2)
C4	C5	C6	118.3(2)	C20	C21	C22	118.0(2)
C1	C6	C5	119.8(2)	C23	C22	C21	121.4(2)
C1	C6	C7	123.3(2)	C22	C23	C24	121.8(2)
C5	C6	C7	117.0(2)	C25	C24	C23	118.4(2)
C8	C7	C6	120.7(2)	C31	C24	C23	122.8(2)
C7	C8	C9	120.4(2)	C31	C24	C25	118.8(2)
N1	C9	C8	109.11(19)	C24	C25	C20	119.9(2)
N1	C9	C14	112.45(18)	C24	C25	C26	120.0(2)
C14	C9	C8	110.9(2)	C26	C25	C20	120.0(2)
N1	C10	C11	107.59(19)	C25	C26	C27	118.8(2)
N1	C10	C12	110.1(2)	C29	C26	C25	118.8(2)
C12	C10	C11	110.3(2)	C29	C26	C27	122.4(2)
O1	C11	C10	112.27(19)	C28	C27	C26	121.3(2)
C13	C12	C10	124.8(3)	C27	C28	C19	122.0(2)
C15	C14	C9	178.4(3)	C30	C29	C26	120.8(3)
C14	C15	C16	178.9(3)	C29	C30	C31	120.8(2)
C17	C16	C15	120.6(2)	C30	C31	C24	120.7(2)

Table 6 Torsion Angles for 240712_ZL_1131_bi_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C4	C5	N1	1.1(3)	C16	C21	C22	C23	-178.6(2)
O1	C4	C5	C6	177.4(2)	C17	C16	C21	C20	1.3(3)
N1	C5	C6	C1	179.2(2)	C17	C16	C21	C22	-178.4(2)
N1	C5	C6	C7	1.0(3)	C17	C18	C19	C20	0.6(3)
N1	C10	C11	O1	-59.9(3)	C17	C18	C19	C28	-179.8(2)

Table 6 Torsion Angles for 240712_ZL_1131_bi_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C10	C12	C13	117.2(3)	C18	C19	C20	C21	0.7(3)
C1	C2	C3	C4	1.6(4)	C18	C19	C20	C25	-179.4(2)
C1	C6	C7	C8	166.1(3)	C18	C19	C28	C27	178.8(2)
C2	C1	C6	C5	0.7(4)	C19	C20	C21	C16	-1.6(3)
C2	C1	C6	C7	178.7(2)	C19	C20	C21	C22	178.1(2)
C2	C3	C4	O1	-179.5(2)	C19	C20	C25	C24	-179.6(2)
C2	C3	C4	C5	2.1(4)	C19	C20	C25	C26	0.7(3)
C3	C4	C5	N1	179.5(2)	C20	C19	C28	C27	-1.6(3)
C3	C4	C5	C6	-4.2(3)	C20	C21	C22	C23	1.7(3)
C4	O1	C11	C10	50.4(3)	C20	C25	C26	C27	-1.7(3)
C4	C5	C6	C1	2.8(3)	C20	C25	C26	C29	178.1(2)
C4	C5	C6	C7	-175.3(2)	C21	C16	C17	C18	0.0(3)
C5	N1	C9	C8	-47.3(3)	C21	C20	C25	C24	0.3(3)
C5	N1	C9	C14	76.2(3)	C21	C20	C25	C26	-179.4(2)
C5	N1	C10	C11	40.1(3)	C21	C22	C23	C24	0.0(4)
C5	N1	C10	C12	160.37(19)	C22	C23	C24	C25	-1.5(3)
C5	C6	C7	C8	-15.9(4)	C22	C23	C24	C31	179.3(2)
C6	C1	C2	C3	-2.9(4)	C23	C24	C25	C20	1.3(3)
C6	C7	C8	C9	-3.1(4)	C23	C24	C25	C26	-178.9(2)
C7	C8	C9	N1	33.5(3)	C23	C24	C31	C30	180.0(2)
C7	C8	C9	C14	-90.8(3)	C24	C25	C26	C27	178.5(2)
C9	N1	C5	C4	-151.9(2)	C24	C25	C26	C29	-1.6(3)
C9	N1	C5	C6	31.9(3)	C25	C20	C21	C16	178.5(2)
C9	N1	C10	C11	179.76(19)	C25	C20	C21	C22	-1.8(3)
C9	N1	C10	C12	-60.0(2)	C25	C24	C31	C30	0.8(4)
C10	N1	C5	C4	-12.9(3)	C25	C26	C27	C28	1.2(4)
C10	N1	C5	C6	170.9(2)	C25	C26	C29	C30	2.0(3)
C10	N1	C9	C8	173.2(2)	C26	C27	C28	C19	0.5(4)
C10	N1	C9	C14	-63.4(3)	C26	C29	C30	C31	-1.0(4)
C11	O1	C4	C3	161.2(2)	C27	C26	C29	C30	-178.2(2)
C11	O1	C4	C5	-20.4(3)	C28	C19	C20	C21	-178.9(2)
C11	C10	C12	C13	-124.2(3)	C28	C19	C20	C25	1.0(3)
C12	C10	C11	O1	180.0(2)	C29	C26	C27	C28	-178.7(2)
C15	C16	C17	C18	179.7(2)	C29	C30	C31	C24	-0.5(4)
C15	C16	C21	C20	-178.4(2)	C31	C24	C25	C20	-179.5(2)
C15	C16	C21	C22	1.9(3)	C31	C24	C25	C26	0.3(3)
C16	C17	C18	C19	-0.9(4)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 240712_ZL_1131_bi_0m.

Atom	*x*	*y*	*z*	U(eq)
H1	7288.01	2824.82	7777.97	51
H2	4644.77	3894.36	8478.25	52
H3	5121.77	5426.27	8079.47	48
H7	11112.69	2470.79	6682.87	48
H8	13331.12	2872.61	5316.11	47
H9	13339.01	4373.18	4775.43	39
H10	9670.38	5851.72	5011.63	37
H11A	11814.93	6347.15	6907.31	45
H11B	10365.86	7036.51	6185.71	45
H12	14904.72	6085.84	5491.28	47
H13A	12377.17	6294.35	3693.25	57
H13B	15380.65	6465.54	3904.1	57
H17	4779.94	2860.52	3307.42	40
H18	1771.67	2789.39	2058.21	41
H22	9102.79	5573.16	2710.55	43
H23	8690.96	6722.71	1591.89	46
H27	-777.87	4632.94	-530.43	46
H28	-343.91	3475.64	562.56	45
H29	511	6171.3	-1126.22	50
H30	3235.91	7387.9	-1048.19	54
H31	6424.1	7437.35	145.08	51

Datablock: 240712_zl_1131_bi_0m

Bond precision: C-C = 0.0036 A Wavelength=1.34139

Cell: a=5.3366(2) b=14.7782(6) c=13.3985(6)
alpha=90 beta=90.342(2) gamma=90
Temperature: 170 K

	Calculated	Reported
Volume	1056.66(7)	1056.66(8)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C31 H21 N O	C31 H21 N O
Sum formula	C31 H21 N O	C31 H21 N O
Mr	423.49	423.49
Dx,g cm-3	1.331	1.331
Z	2	2
Mu (mm-1)	0.395	0.395
F000	444.0	444.0
F000'	444.91	
h,k,lmax	6,19,17	6,19,17
Nref	4848[2517]	4755
Tmin,Tmax	0.972,0.988	0.660,0.752
Tmin'	0.942	

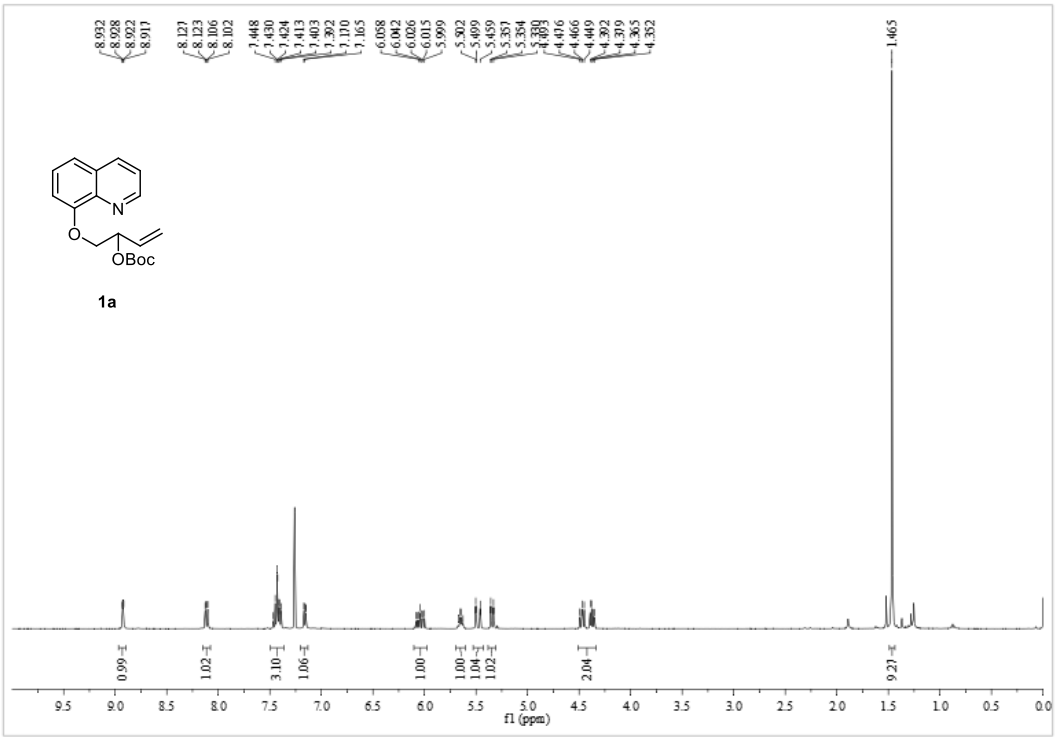
Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.752
AbsCorr = MULTI-SCAN

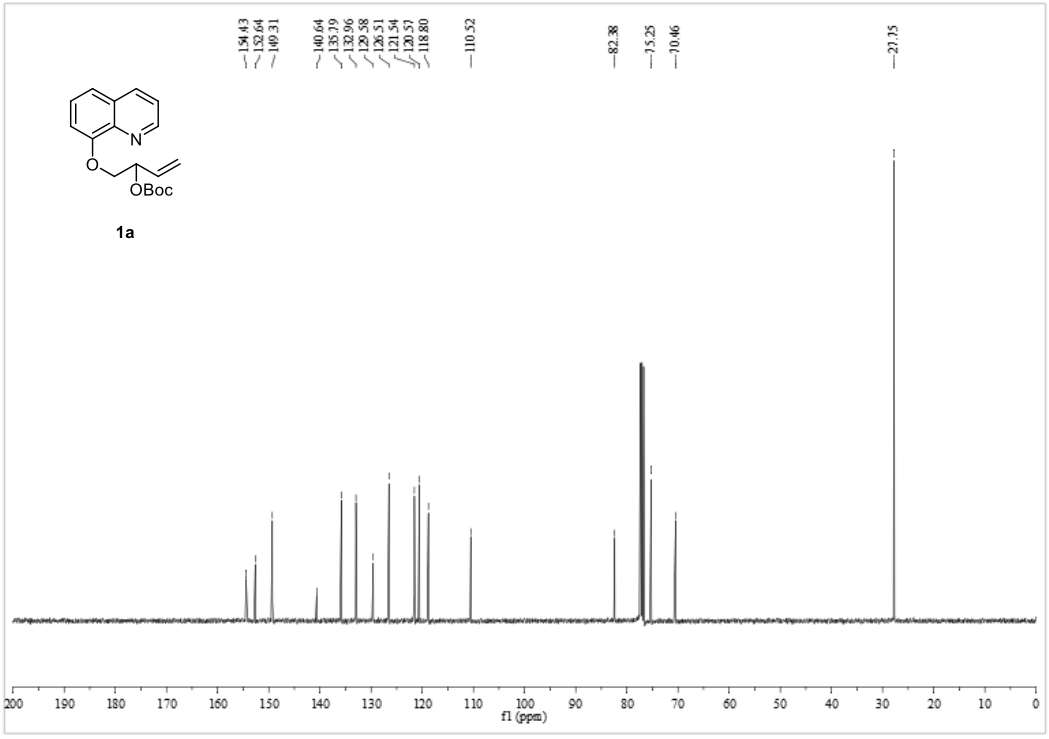
Data completeness= 1.89/0.98 Theta(max)= 60.625

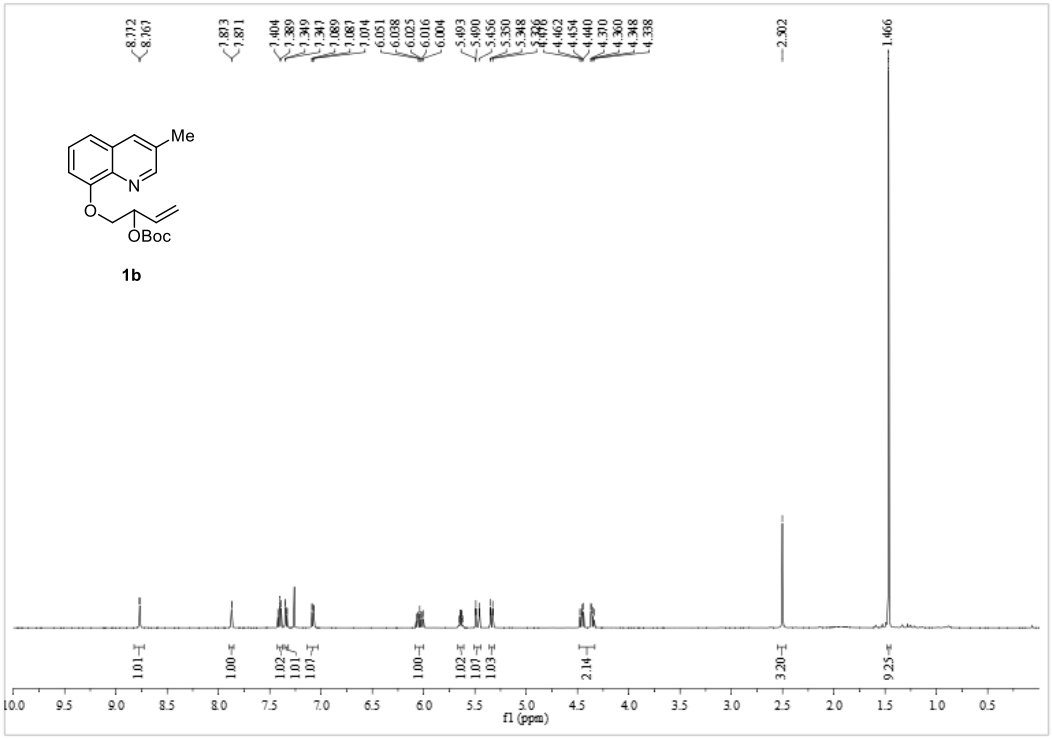
R(reflections)= 0.0481(3958) wR2(reflections)= 0.1046(4755)

S = 1.104 Npar= 298

12. NMR Spectra and HPLC data






8.772
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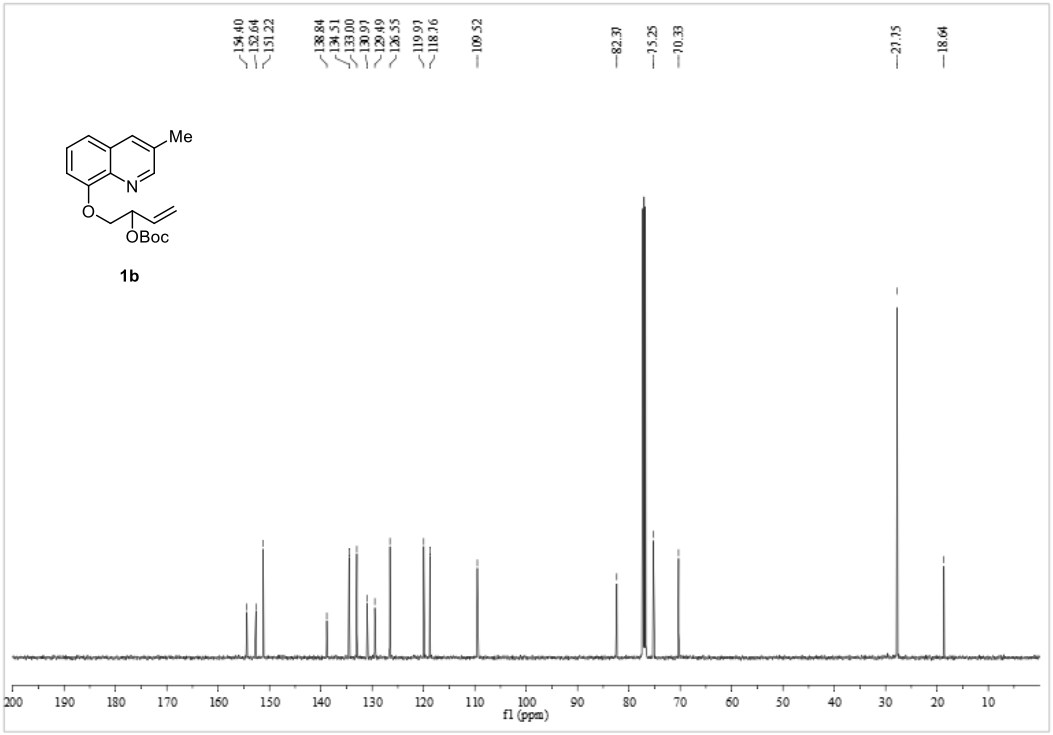
7.807
7.404
7.389
7.349
7.341
7.089
7.087
7.074
6.051
6.038
6.025
6.016
6.004
5.493
5.490
5.456
5.350
5.348
4.462
4.454
4.440
4.370
4.360
4.348
4.338
2.502
1.466
Me
N
O
OBoc
1b
1.01
1.00
1.02
1.01
1.07
1.00
1.02
1.01
1.03
2.14
3.20
9.25
f1 (ppm)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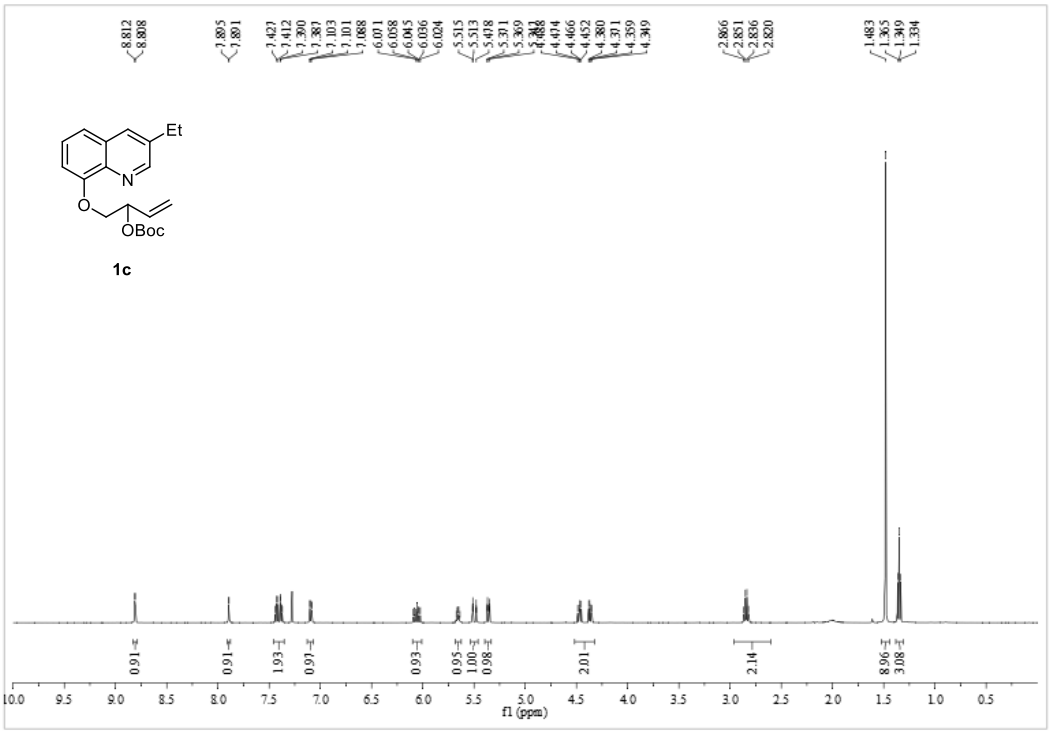
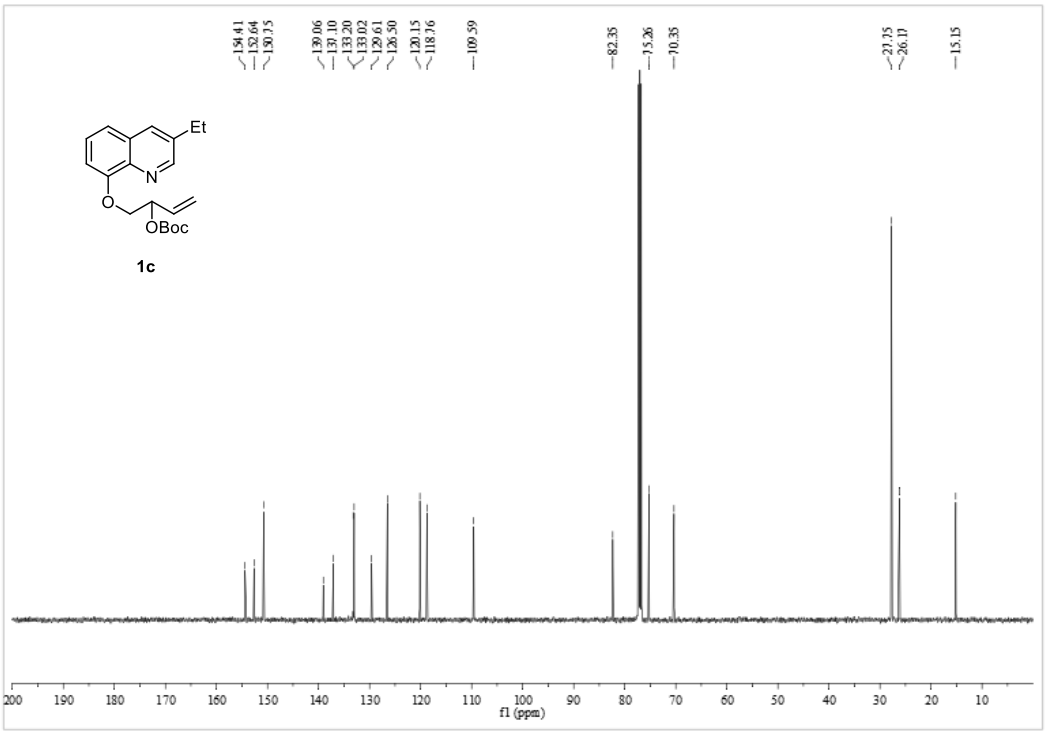
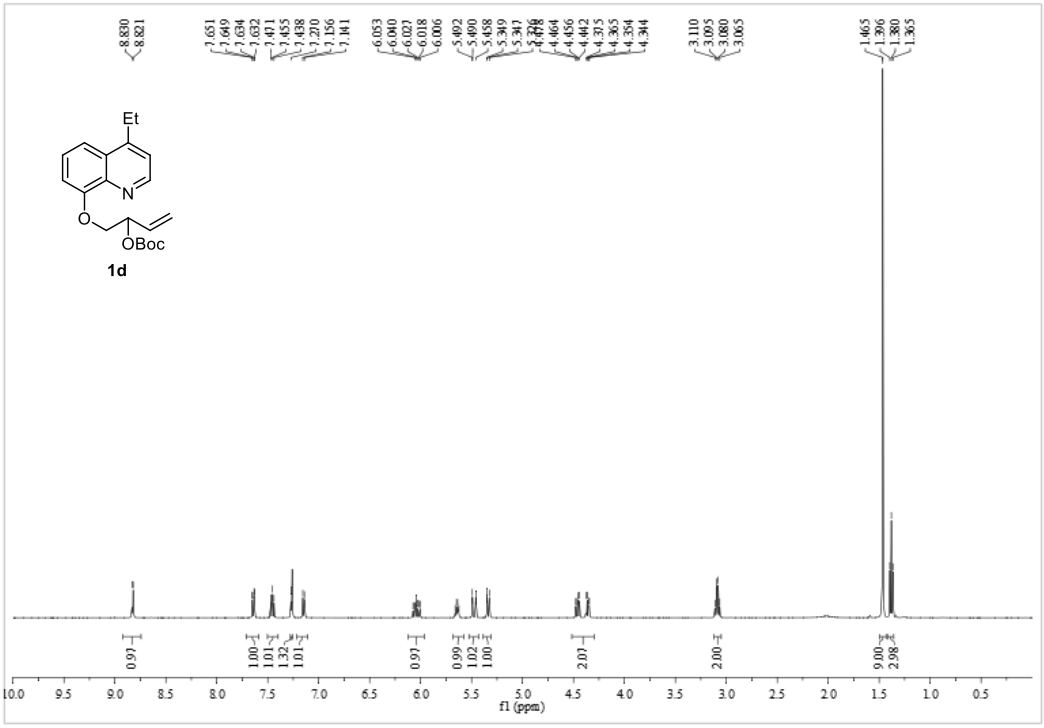
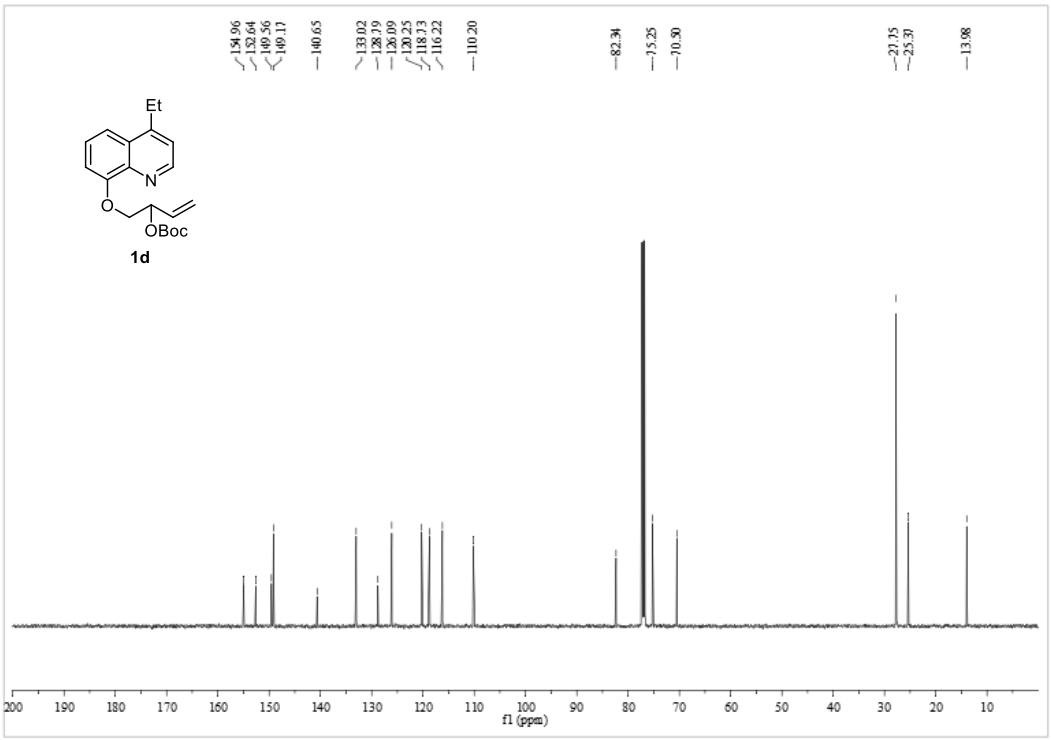
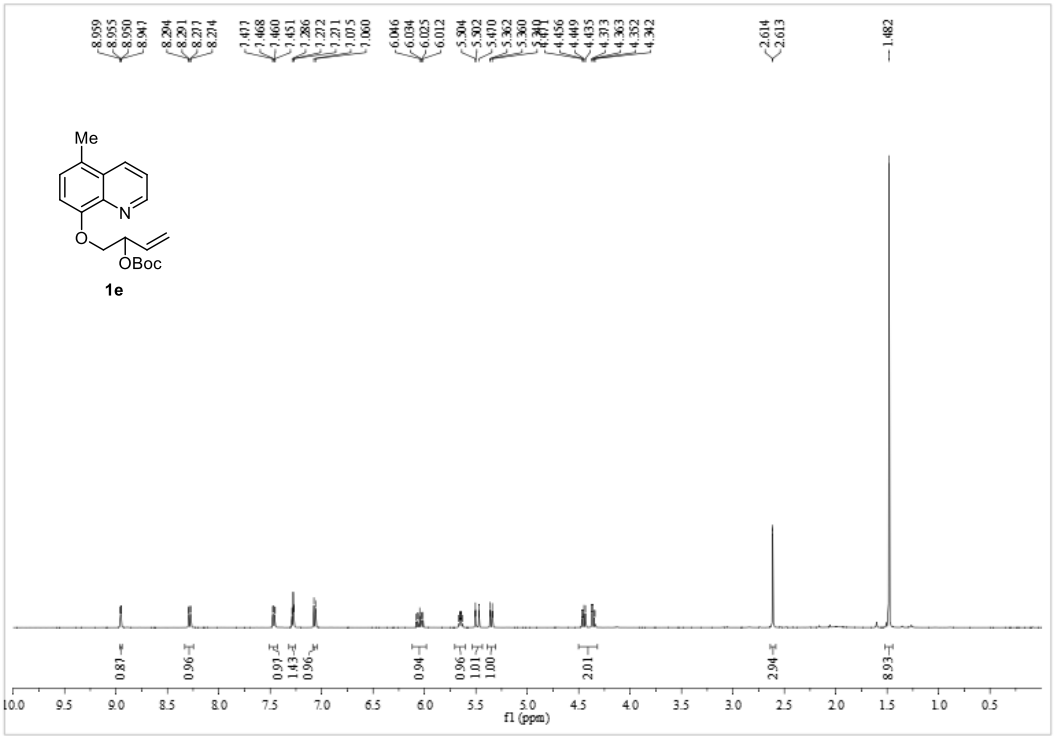
152.64
151.22
138.84
134.51
133.00
130.97
129.49
126.55
119.97
118.76
109.52
82.37
75.25
70.33
27.75
18.64
Me
N
O
OBoc
1b
f1 (ppm)


Et
N
O
OBoc
1c
f1 (ppm)


Et
N
O
OBoc
1c
f1 (ppm)


Et
N
O
OBoc
1d
f1 (ppm)


Et
N
O
OBoc
1d
f1 (ppm)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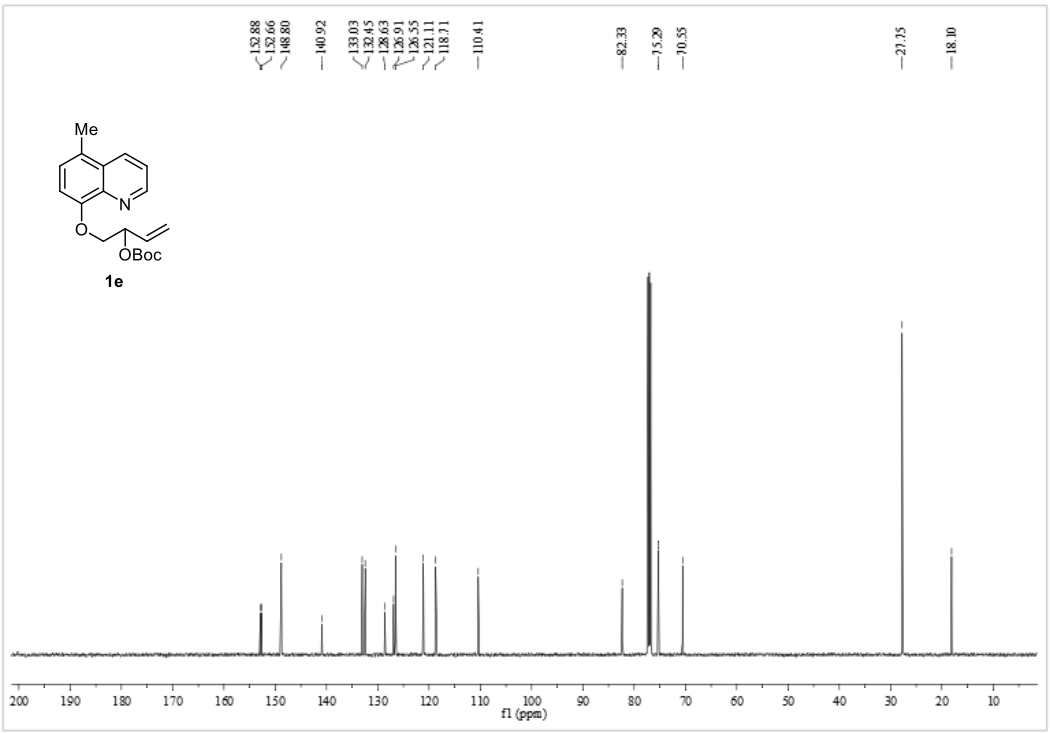
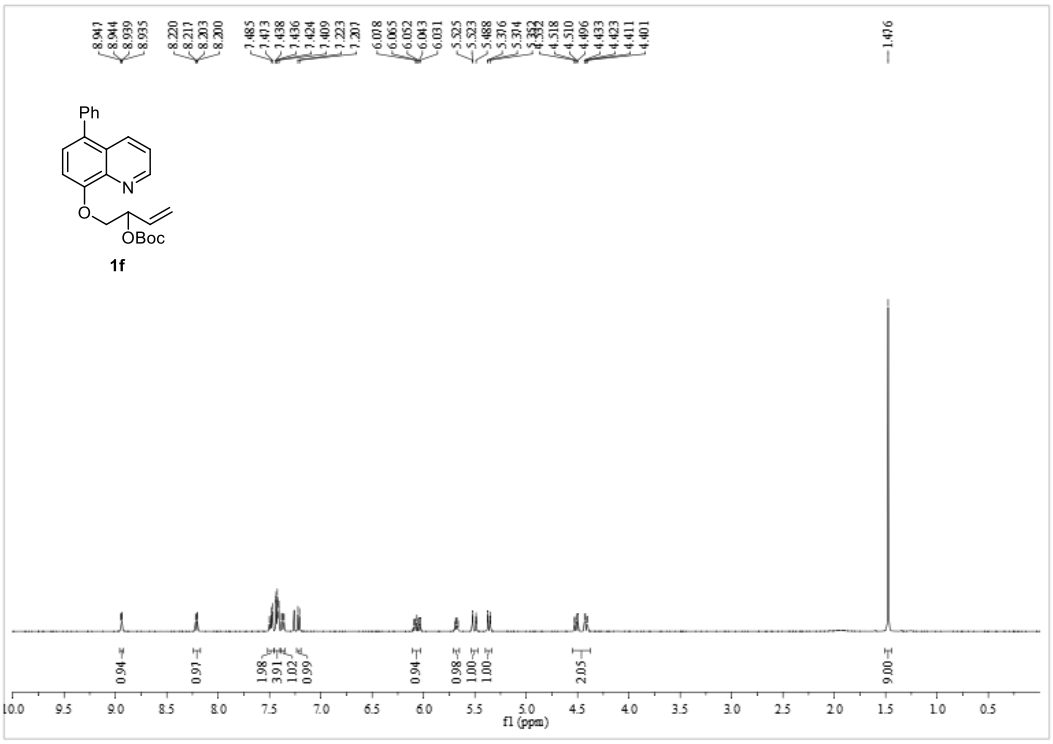
N
O
OBoc
1e
f1 (ppm)


Me
N
O
OBoc
1e
f1 (ppm)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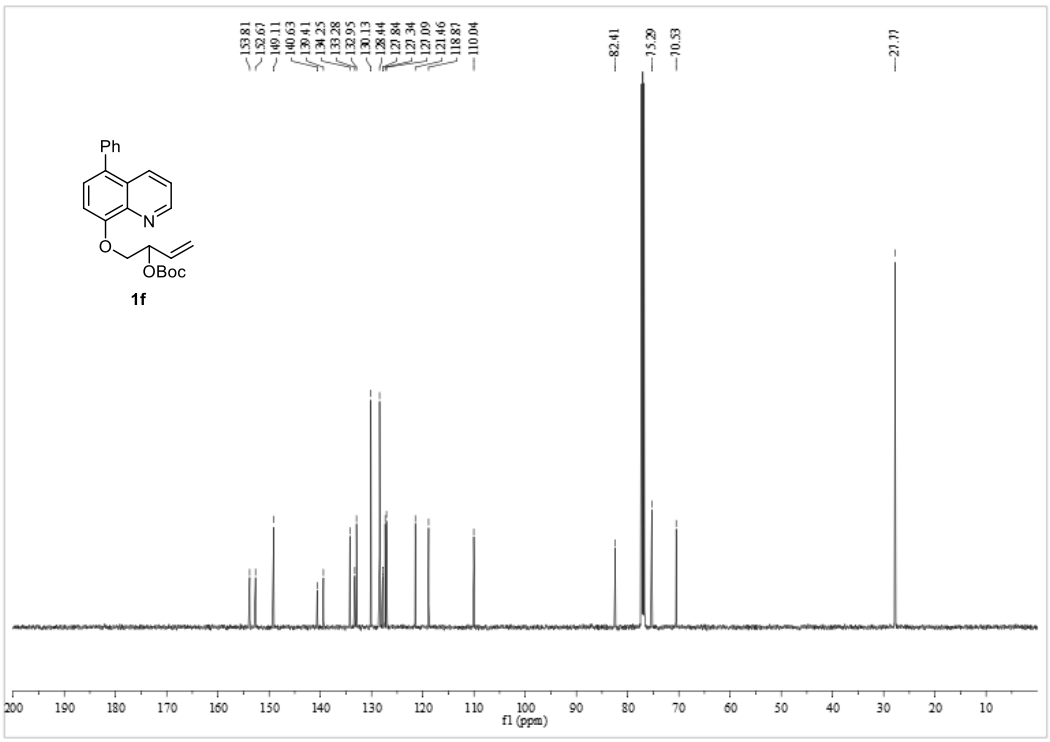
8.935
8.220
8.217
8.203
8.200
7.485
7.473
7.438
7.436
7.424
7.409
7.223
7.207
6.078
6.065
6.052
6.043
6.031
5.525
5.523
5.488
5.316
5.314
4.518
4.510
4.496
4.433
4.423
4.411
4.401
1.476
Ph
N
O
OBoc
1f
0.94
0.93
1.98
3.91
1.02
0.99
0.94
0.98
1.00
1.00
2.05
9.00
f1 (ppm)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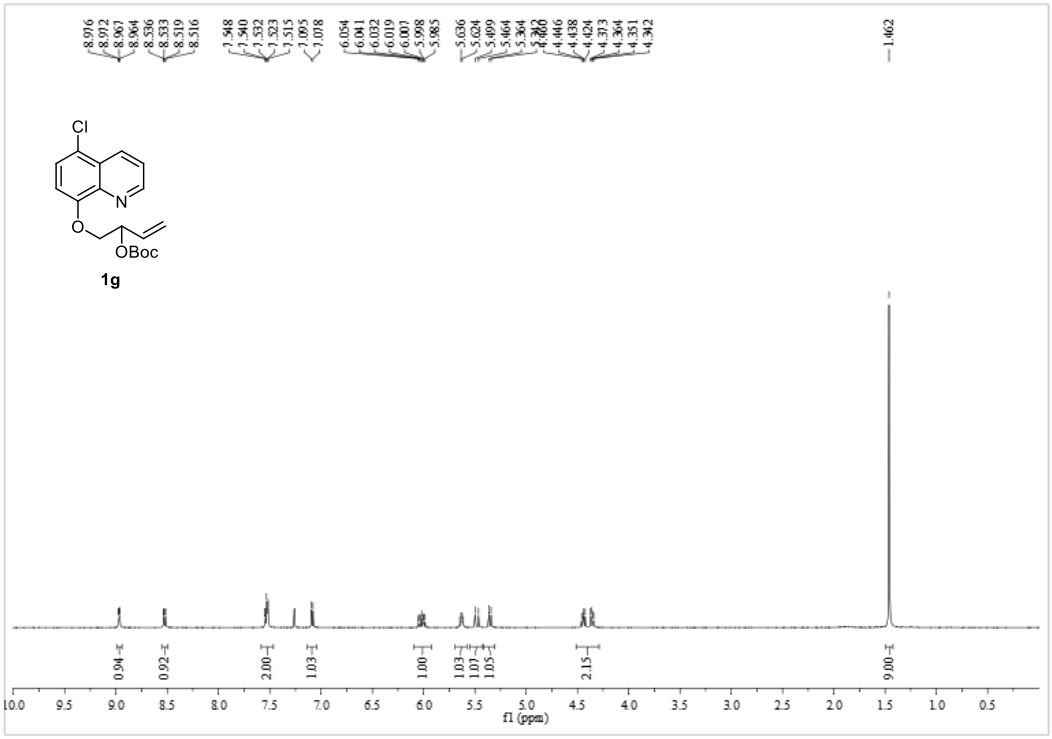
140.63
139.41
134.25
133.28
132.95
130.13
128.44
127.84
127.34
127.09
121.46
118.87
110.04
82.41
75.29
70.53
27.77
Ph
N
O
OBoc
1f
f1 (ppm)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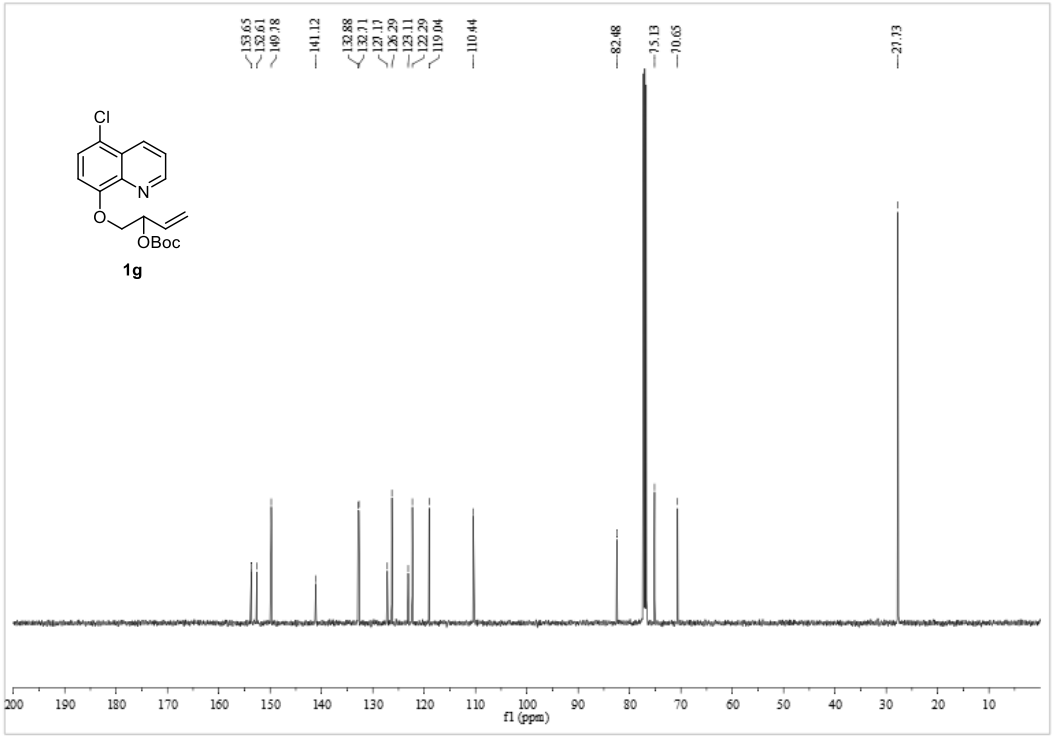
8.967
8.964
8.536
8.533
8.519
8.516
7.548
7.540
7.532
7.523
7.515
7.095
7.078
6.054
6.041
6.032
6.019
6.001
5.998
5.985
5.636
5.624
5.499
5.464
5.364
5.343
5.340
4.446
4.438
4.424
4.373
4.364
4.351
4.342
1.462
Cl
N
O
OBoc
1g
0.94
0.92
2.00
1.03
1.00
1.03
1.01
1.05
2.15
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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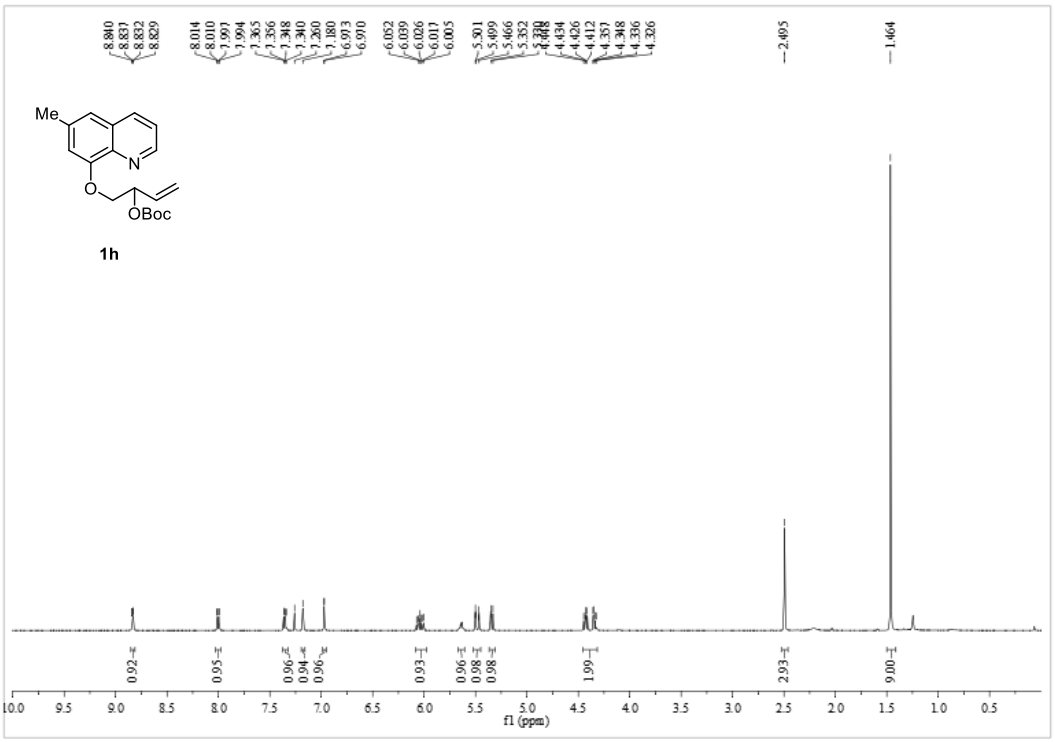
152.61
149.78
141.12
132.88
132.71
127.17
126.29
123.11
122.29
119.04
110.44
82.48
75.13
70.65
27.73
Cl
N
O
OBoc
1g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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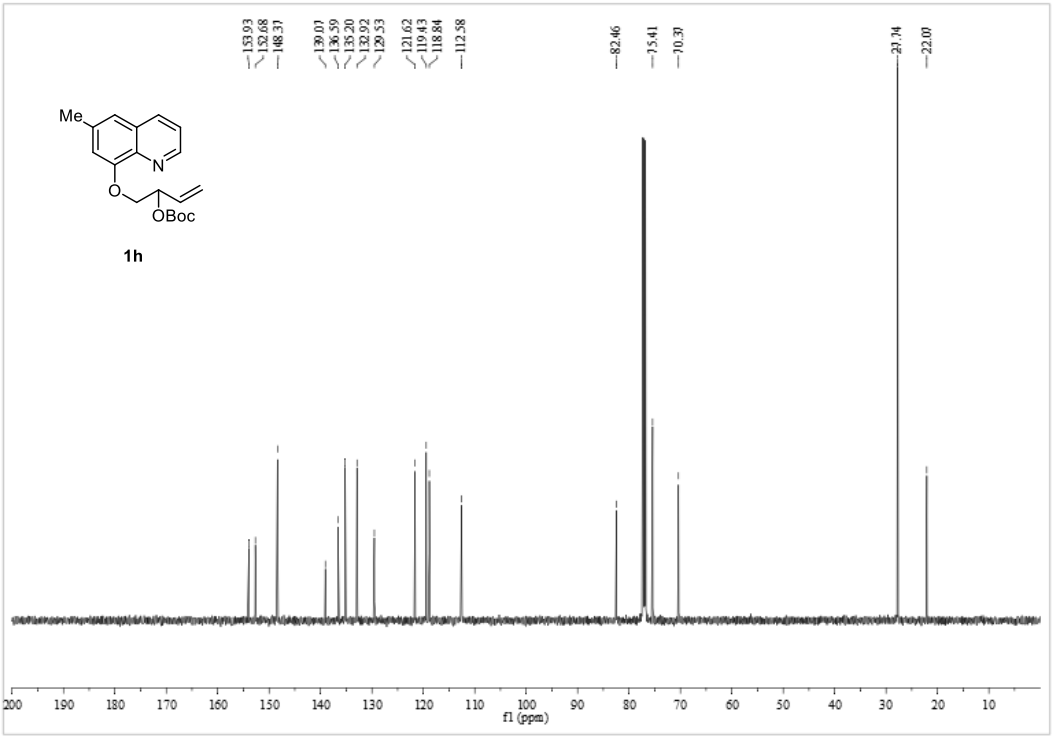
8.832
8.829
8.014
8.010
7.997
7.994
7.365
7.356
7.348
7.340
7.200
7.180
6.913
6.910
6.052
6.039
6.026
6.011
6.005
5.501
5.499
5.466
5.352
4.434
4.426
4.412
4.357
4.348
4.336
4.326
2.495
1.464
Me
N
O
OBoc
1h
0.92
0.95
0.96
0.94
0.96
0.93
0.96
0.98
0.98
1.99
2.93
9.00
f1 (ppm)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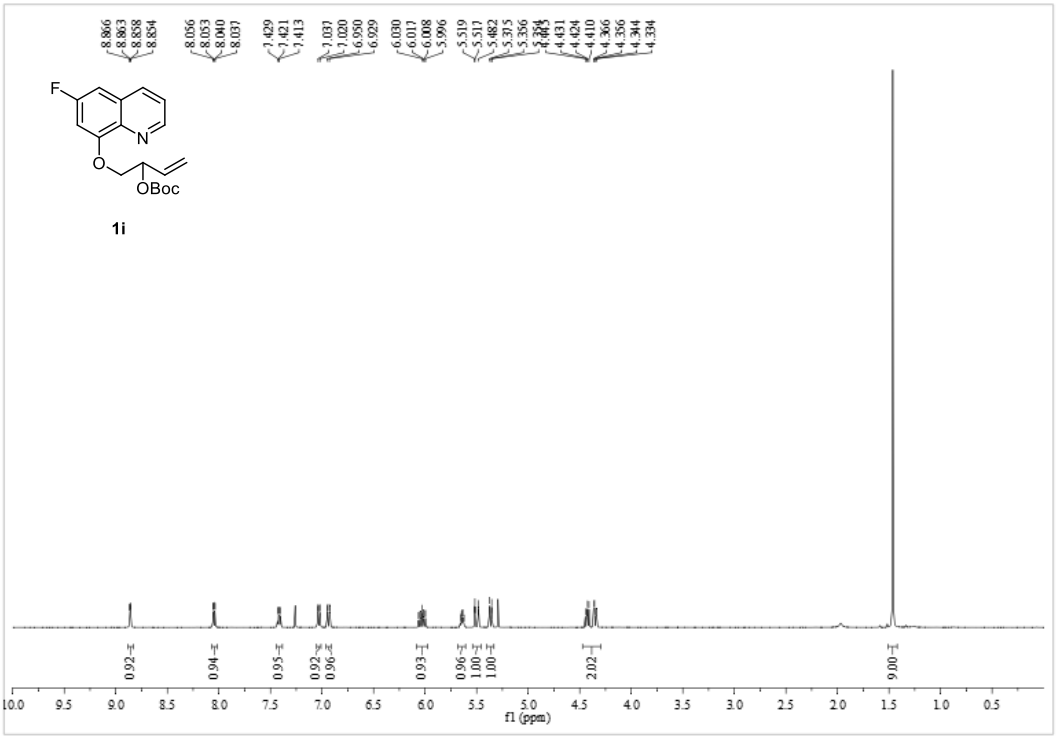
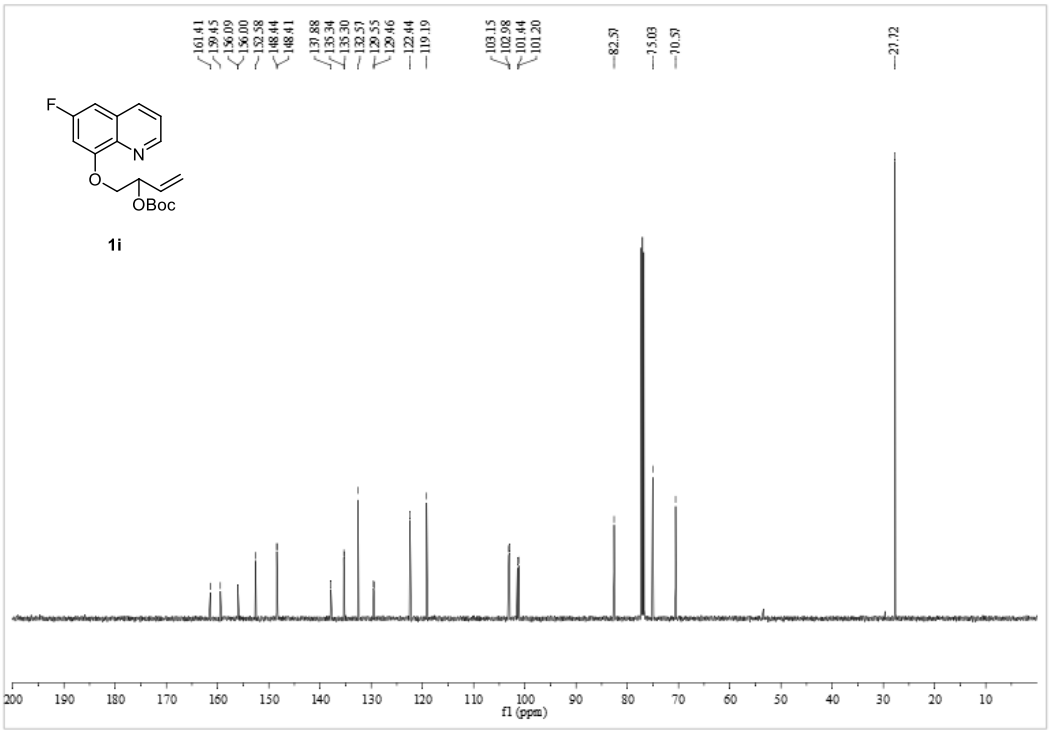
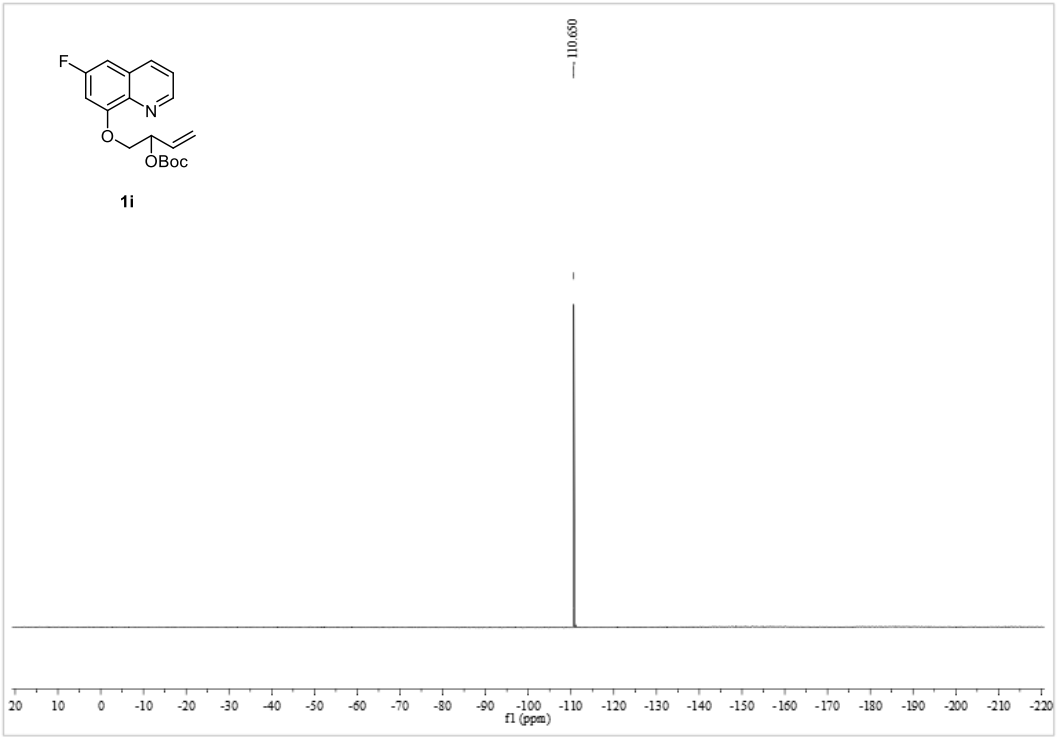
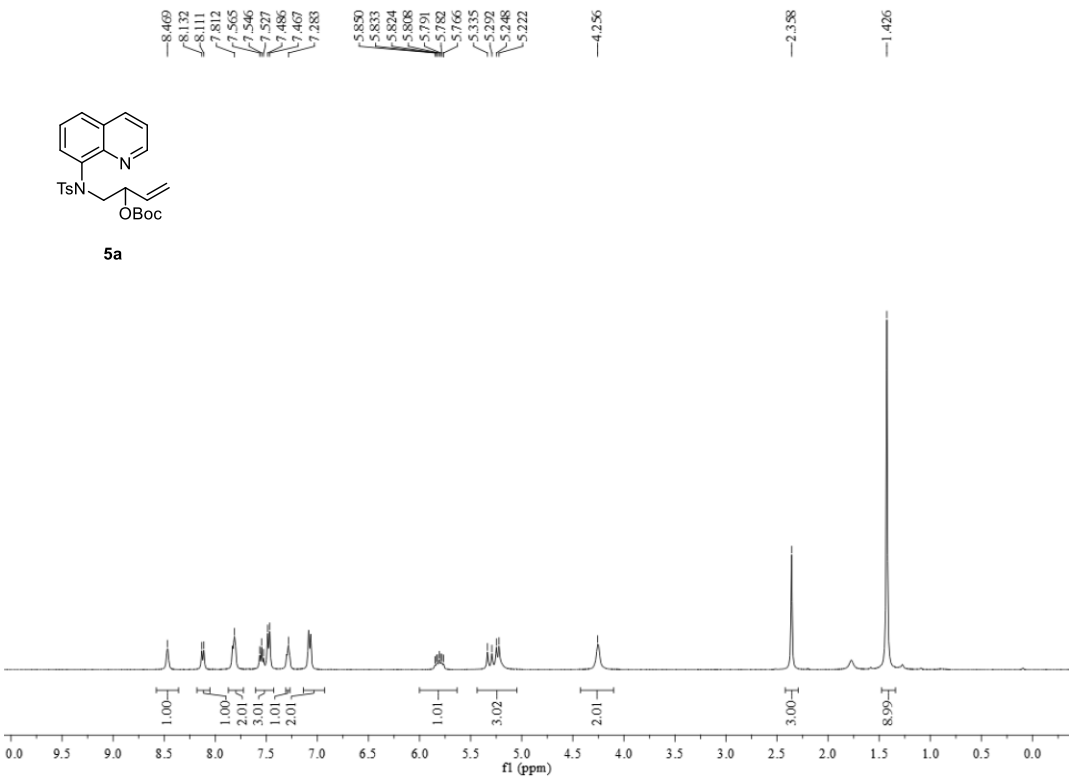
152.68
148.37
139.07
136.59
135.20
132.92
129.53
121.62
119.43
118.84
112.58
82.46
75.41
70.31
27.74
22.07
Me
N
O
OBoc
1h
f1 (ppm)


F
N
O
OBoc
1i
f1 (ppm)


F
N
O
OBoc
1i
f1 (ppm)


F
N
O
OBoc
1i
-110.650
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)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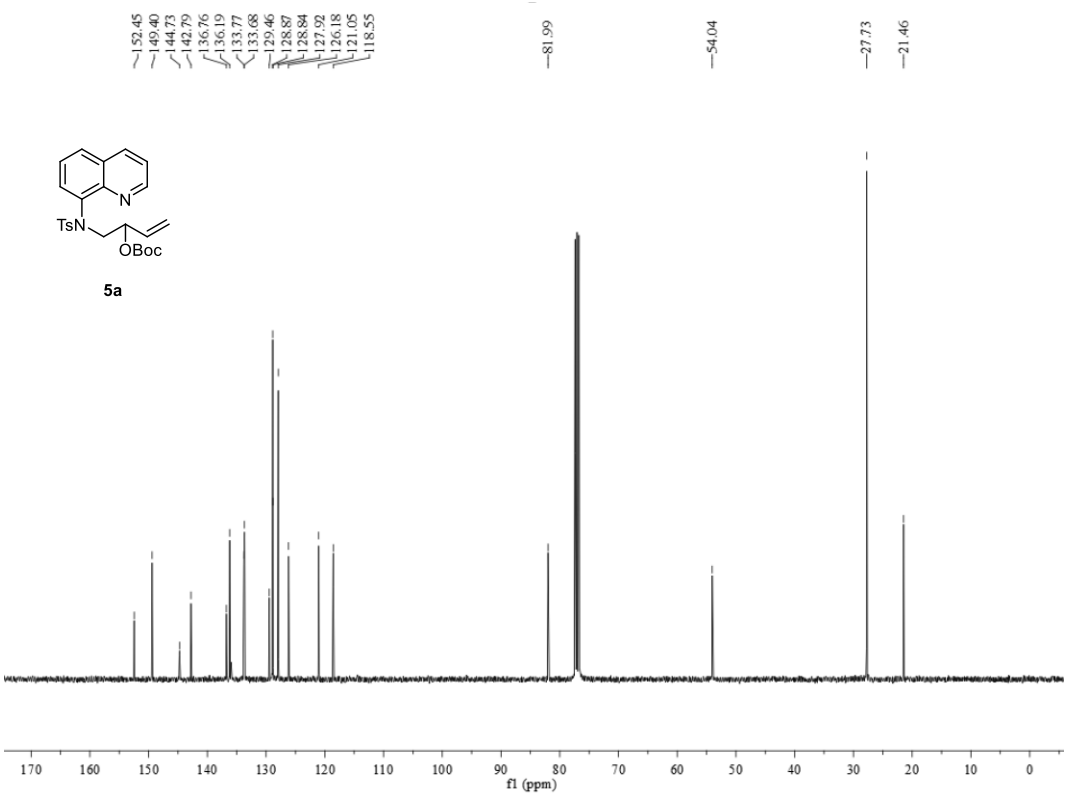
8.111
7.812
7.565
7.546
7.527
7.486
7.467
7.283
5.850
5.833
5.824
5.808
5.791
5.782
5.766
5.335
5.292
5.248
5.222
4.256
2.398
1.426
TsN
OBoc
5a
1.00
1.00
2.01
3.01
1.01
2.01
1.01
3.02
2.01
3.00
8.99
f1 (ppm)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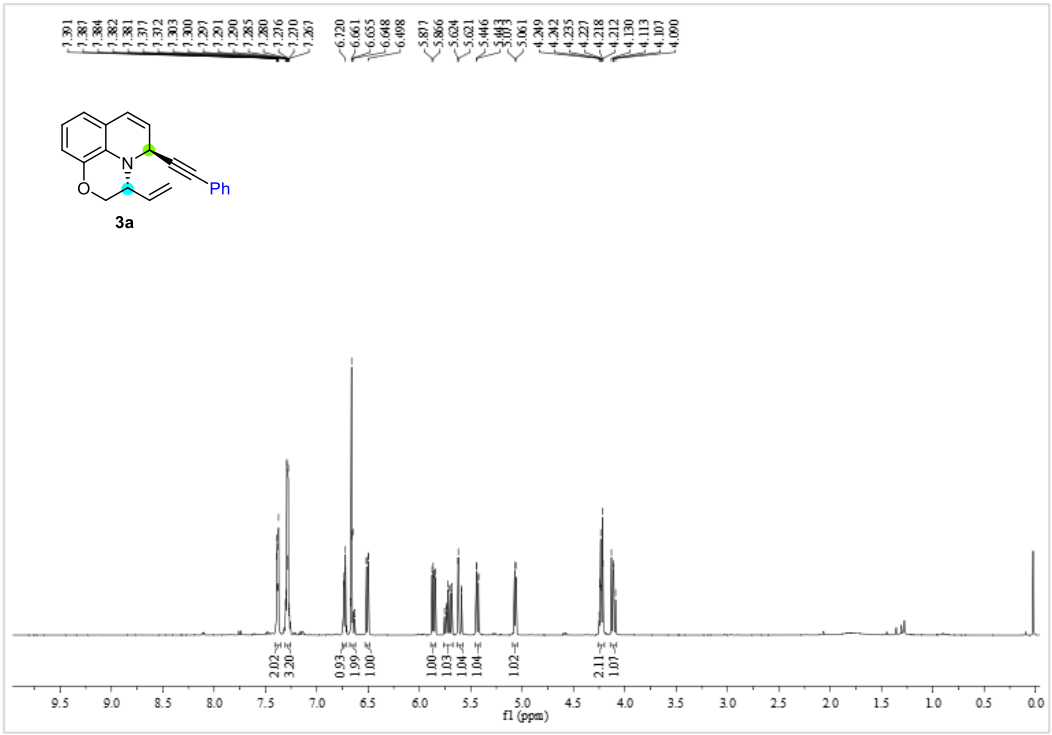
136.19
133.77
133.68
129.46
128.87
128.84
127.92
126.18
121.05
118.55
81.99
54.04
27.73
21.46
TsN
OBoc
5a
f1 (ppm)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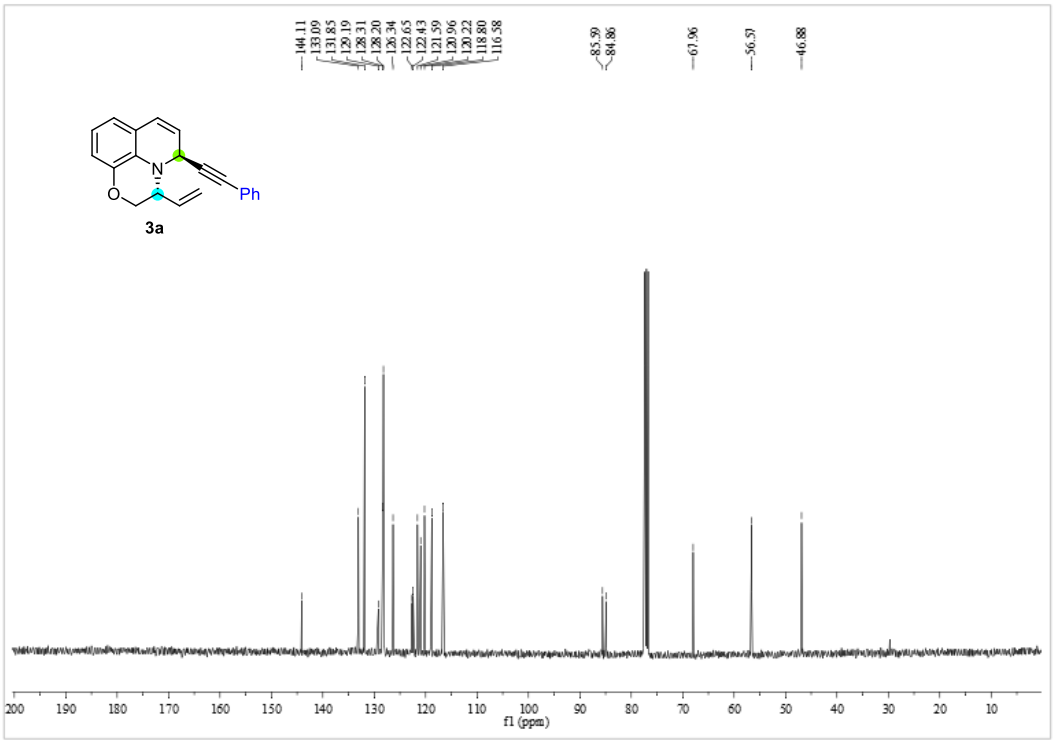
7.381
7.377
7.372
7.303
7.300
7.297
7.291
7.290
7.285
7.280
7.216
7.210
7.203
6.720
6.661
6.655
6.648
6.498
5.887
5.866
5.624
5.621
5.446
5.443
5.061
4.249
4.242
4.235
4.227
4.218
4.212
4.130
4.113
4.107
4.090
N
O
Ph
3a
2.02
3.20
0.93
1.99
1.00
1.00
1.03
1.04
1.04
1.02
2.11
1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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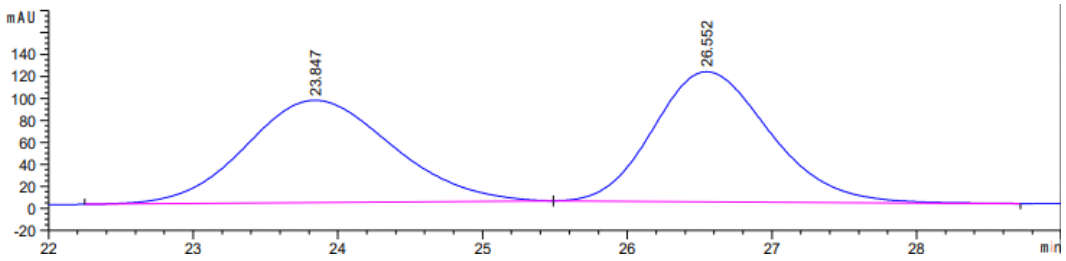
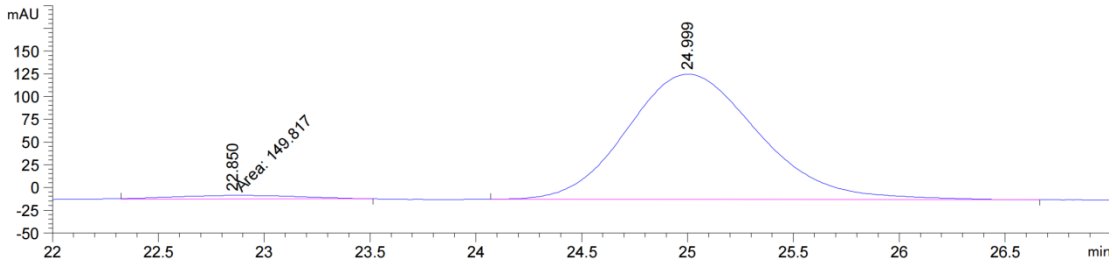
131.85
129.19
128.31
128.20
126.34
122.65
122.43
121.59
120.96
120.22
118.80
116.58
85.59
84.86
67.96
56.53
46.88
N
O
Ph
3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



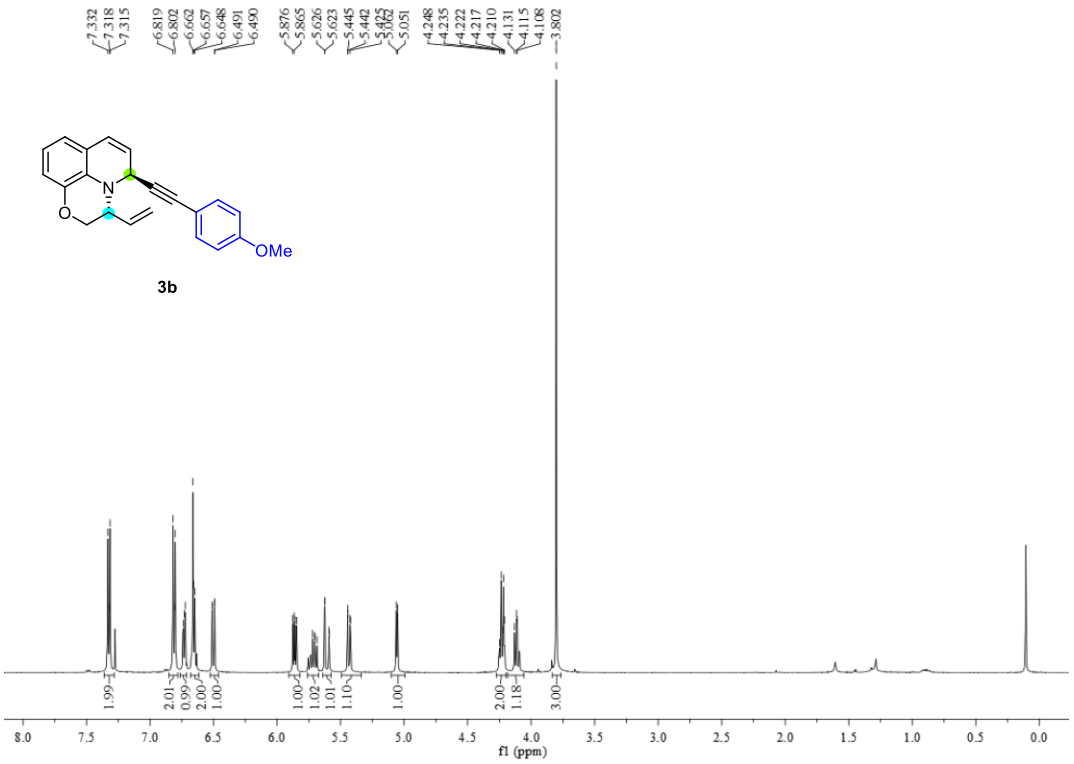
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.847	BB	1.0167	6566.89014	93.12292	49.7684
2	26.552	BB	0.8333	6628.01904	118.36667	50.2316



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.850	MM	0.6571	149.81723	3.79985	2.4452
2	24.999	BB	0.6562	5977.28369	137.75339	97.5548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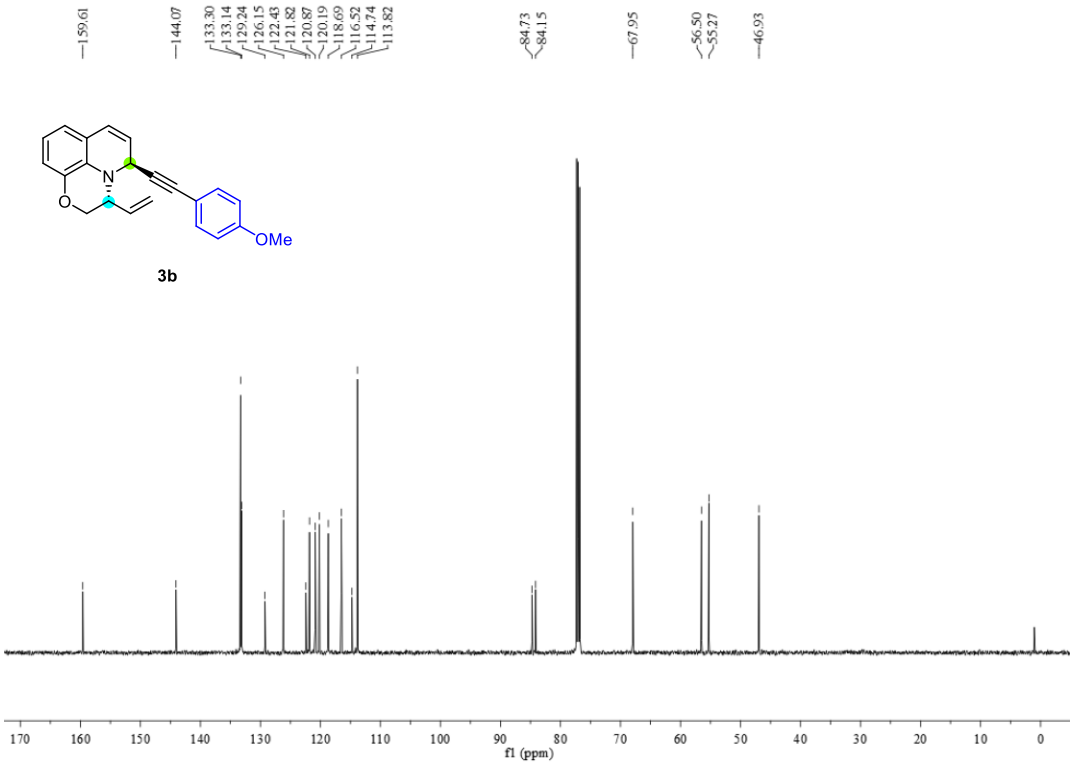
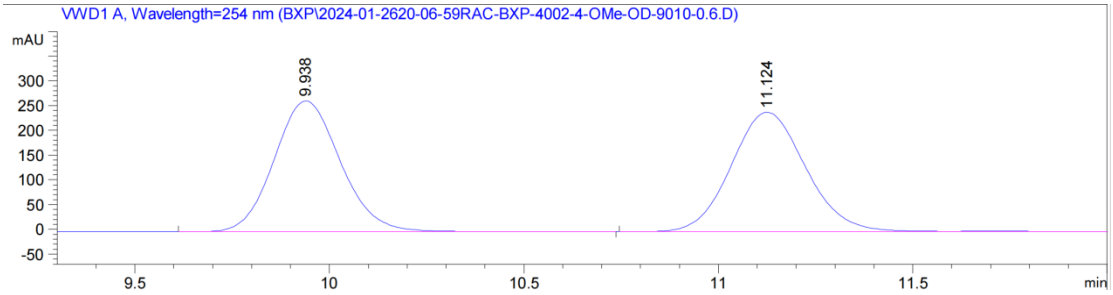
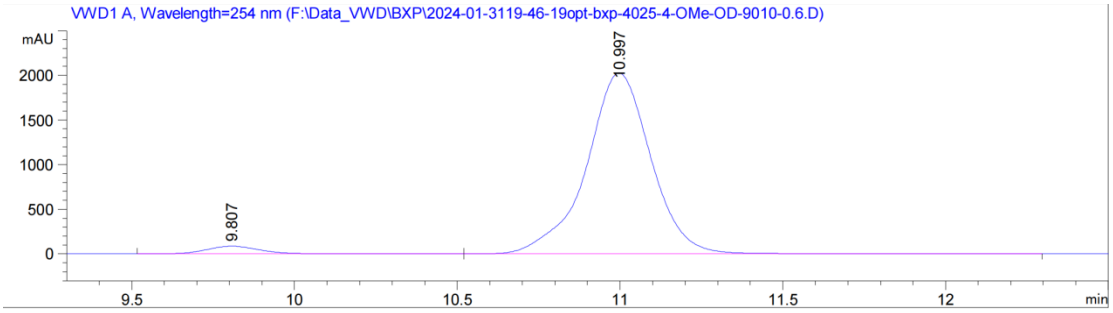
6.802
6.662
6.657
6.648
6.491
6.490
5.876
5.865
5.626
5.623
5.445
5.442
5.425
5.062
5.051
4.248
4.235
4.222
4.217
4.210
4.131
4.115
4.108
3.802
OMe
3b
1.99
2.01
0.99
2.00
1.00
1.00
1.02
1.01
1.10
1.00
2.00
1.18
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.61
144.07
133.30
133.14
129.24
126.15
122.43
121.82
120.87
120.19
118.69
116.52
114.74
113.82
84.73
84.15
67.95
56.50
55.27
46.93
OMe
3b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



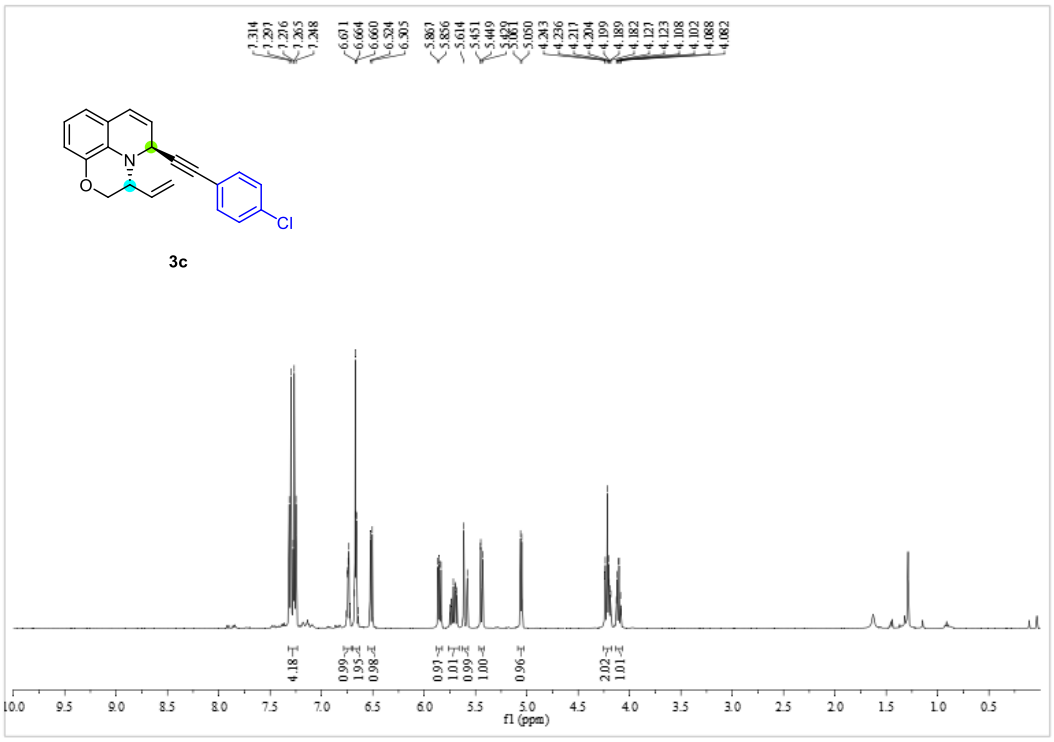
Signal 1: VWD1 A, Wavelength=254 nm

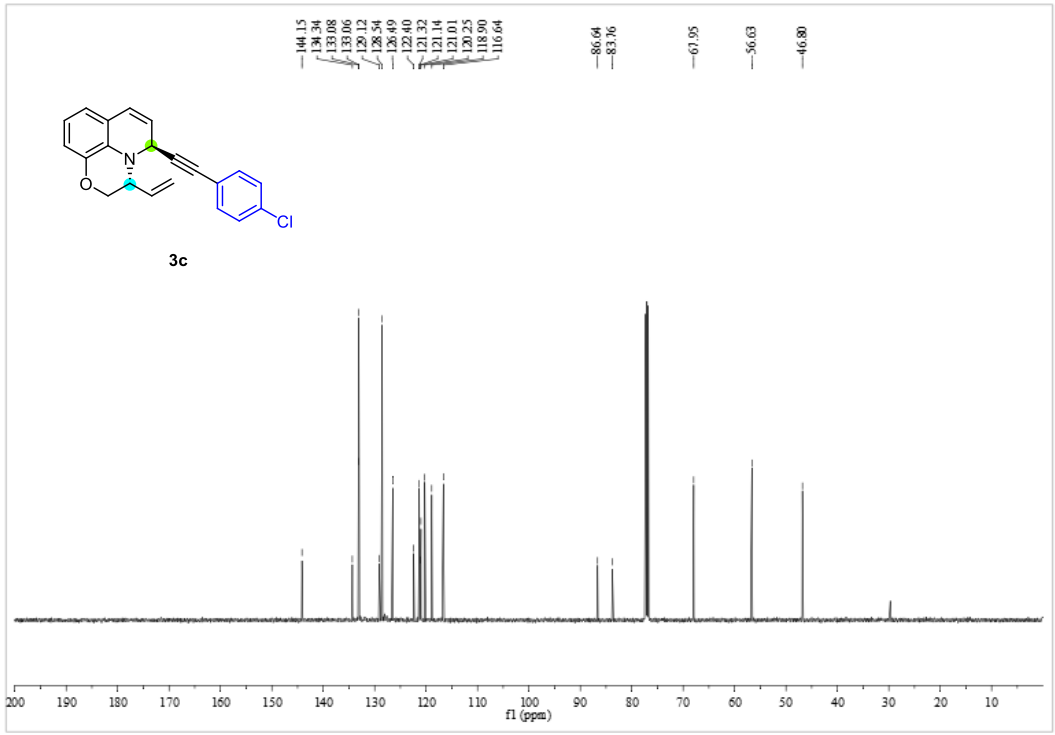
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.938	BB	0.1843	3138.13721	264.65744	49.2776
2	11.124	BV R	0.2081	3230.14502	241.38220	50.7224

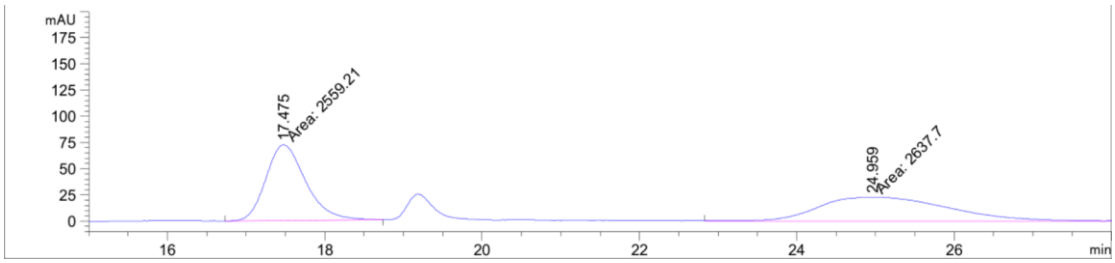


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.807	BV R	0.1724	951.68365	85.16898	3.3018
2	10.997	VB	0.2075	2.78713e4	2026.11084	96.6982

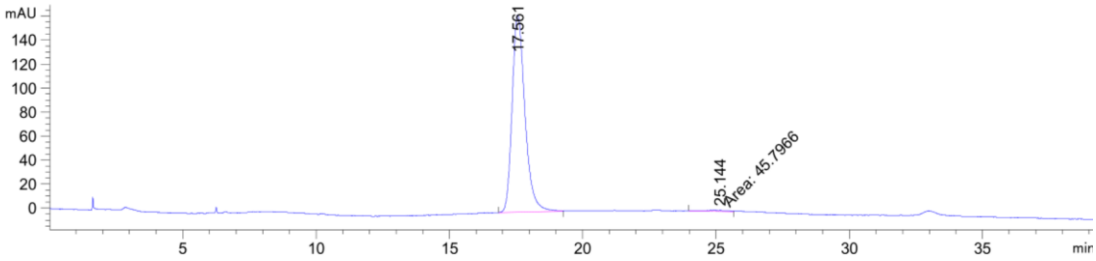

7.314
7.297
7.276
7.265
7.248
6.611
6.664
6.660
6.324
6.305
5.887
5.856
5.614
5.451
5.449
5.063
5.050
4.243
4.236
4.217
4.204
4.199
4.189
4.182
4.127
4.123
4.108
4.102
4.088
4.082
N
O
Cl
3c
4.18
0.99
1.95
0.98
0.97
1.01
0.99
1.00
0.96
2.02
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


144.15
134.34
133.08
133.06
129.12
128.54
126.49
122.40
121.32
121.14
121.01
120.25
118.90
116.64
86.64
83.76
61.95
56.63
46.80
N
O
Cl
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



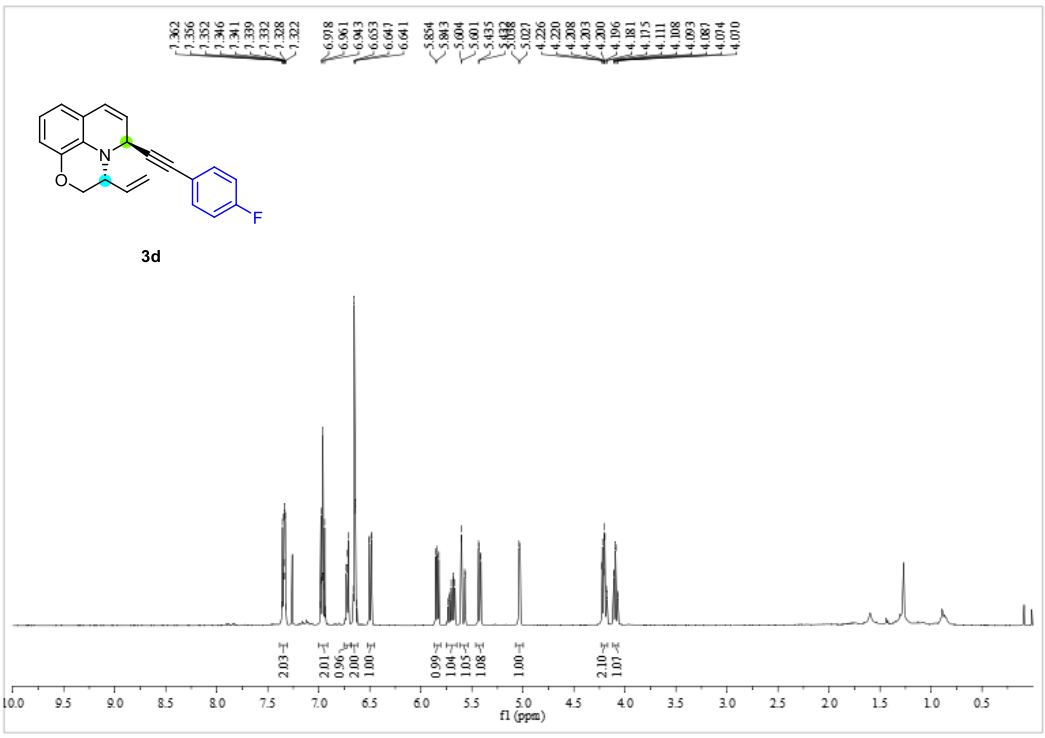
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

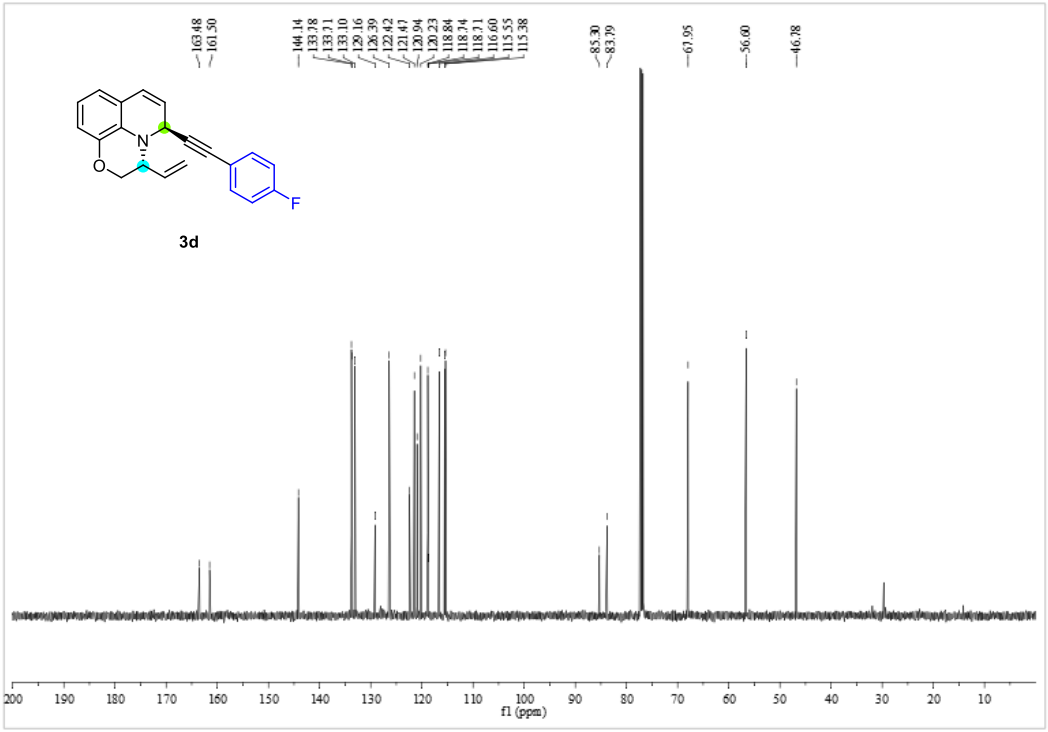
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.475	MM	0.5891	2559.20703	72.39978	49.2449
2	24.959	MM	1.9285	2637.69556	22.79536	50.7551

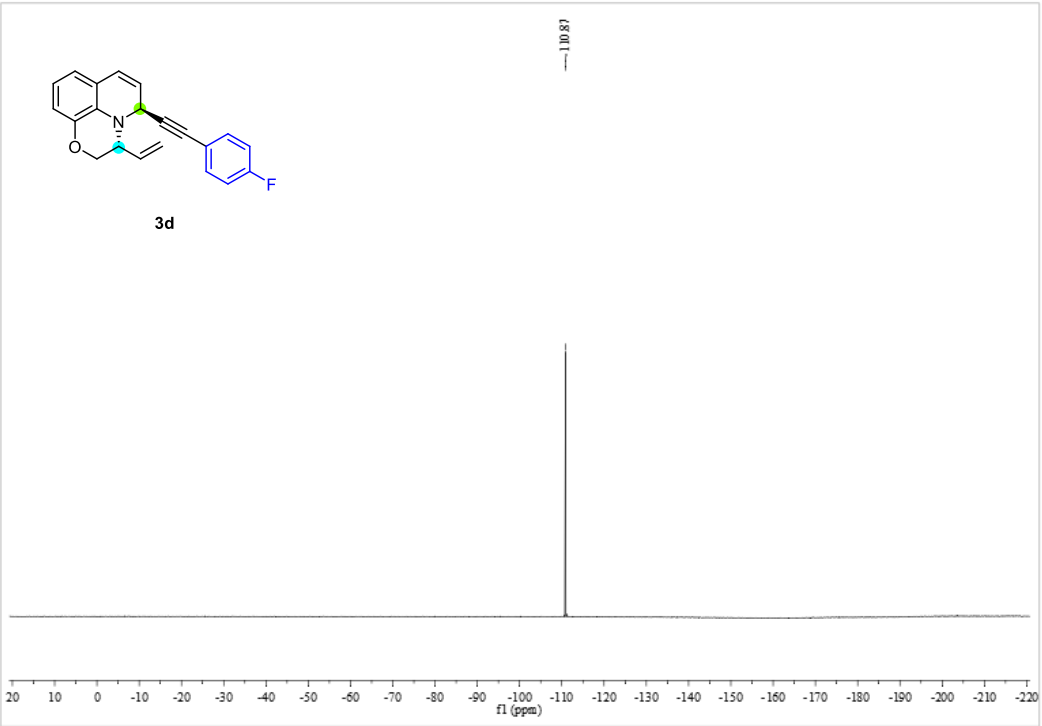


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

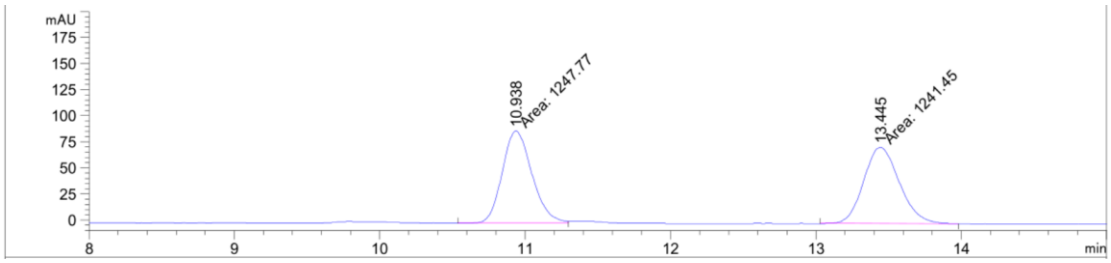
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.561	BB	0.5069	5476.78174	164.29945	99.1707
2	25.144	MM	1.0089	45.79659	7.56524e-1	0.8293


7.362
7.356
7.352
7.346
7.341
7.339
7.332
7.328
7.322
6.918
6.961
6.943
6.653
6.647
6.641
5.854
5.843
5.604
5.601
5.435
5.432
5.038
5.027
4.226
4.220
4.208
4.203
4.200
4.196
4.181
4.175
4.111
4.108
4.093
4.087
4.074
4.070
N
O
F
3d
2.03
2.01
0.96
2.00
1.00
0.99
1.04
1.05
1.08
1.00
2.10
1.07
f1 (ppm)


163.48
161.50
144.14
133.78
133.71
133.10
129.16
126.39
122.42
121.47
120.94
120.23
118.84
118.74
118.71
116.60
115.55
115.38
85.30
83.39
67.95
56.60
46.78
N
O
F
3d
f1 (ppm)

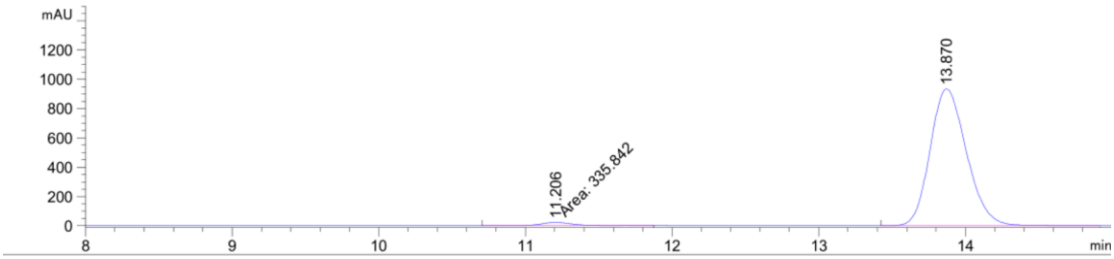

-110.87
N
O
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

3d



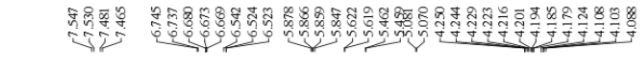
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

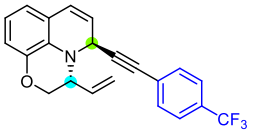
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.938	MM	0.2361	1247.77368	88.08869	50.1270
2	13.445	MM	0.2836	1241.45325	72.96043	49.8730



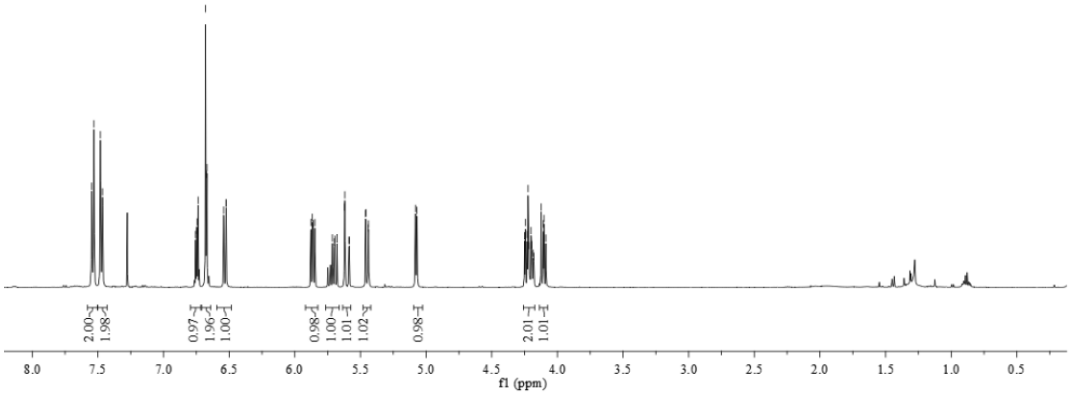
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

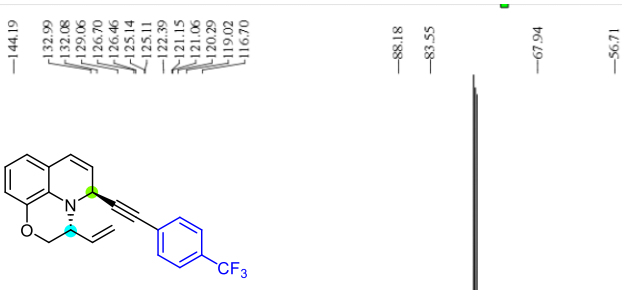
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.206	MM	0.2641	335.84189	21.19779	2.0453
2	13.870	BB	0.2672	1.60841e4	932.45459	97.9547


7.547
7.530
7.481
7.465
6.745
6.737
6.680
6.673
6.669
6.542
6.524
6.523
5.878
5.866
5.859
5.847
5.622
5.619
5.462
5.453
5.081
5.070
4.290
4.244
4.229
4.223
4.216
4.201
4.194
4.185
4.179
4.124
4.108
4.103
4.088


N
O
CF3

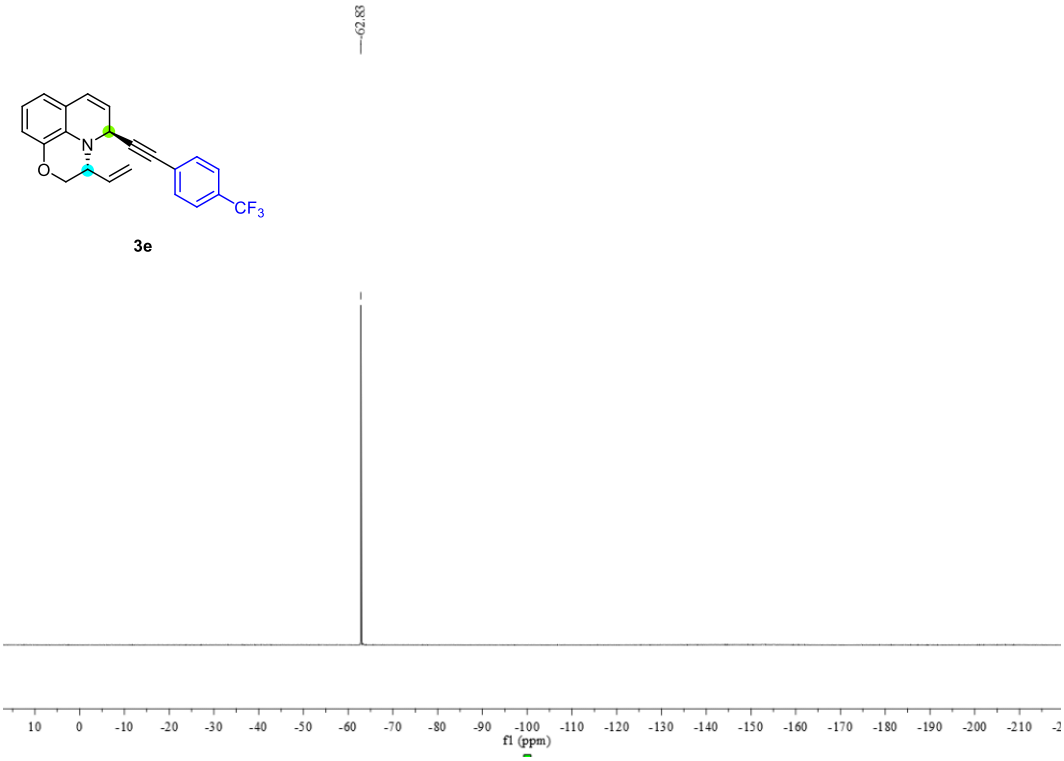
3e


2.00
1.98
0.97
1.96
1.00
0.98
1.00
1.01
1.02
0.98
2.01
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

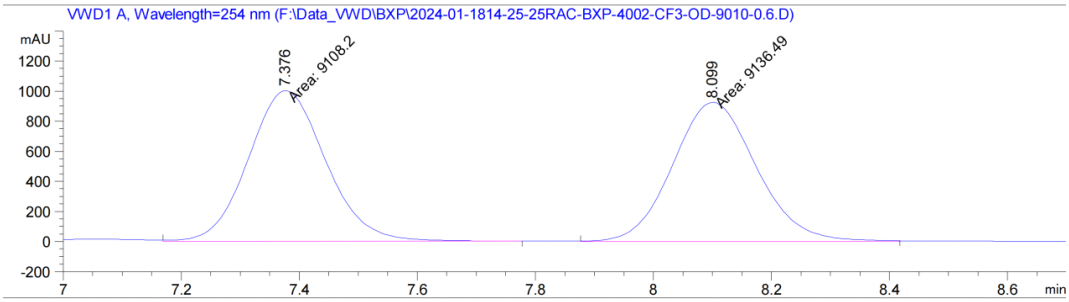

144.19
132.99
132.08
129.06
126.70
126.46
125.14
125.11
122.39
121.15
121.06
120.29
119.02
116.70
88.18
83.55
67.94
56.71
46.72
N
O
CF3

3e

140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

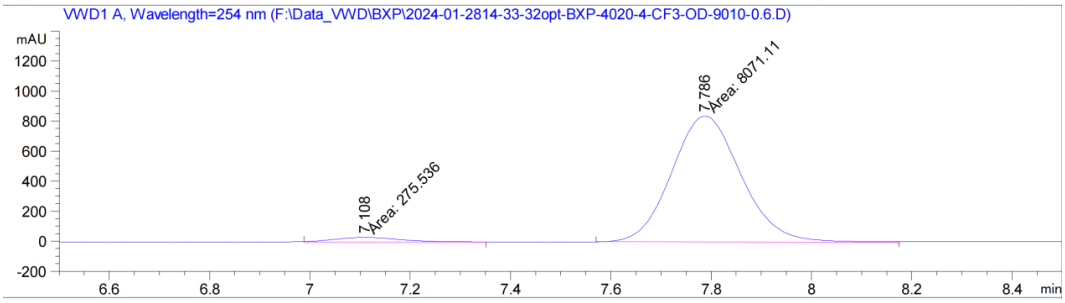

-62.83
N
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3e



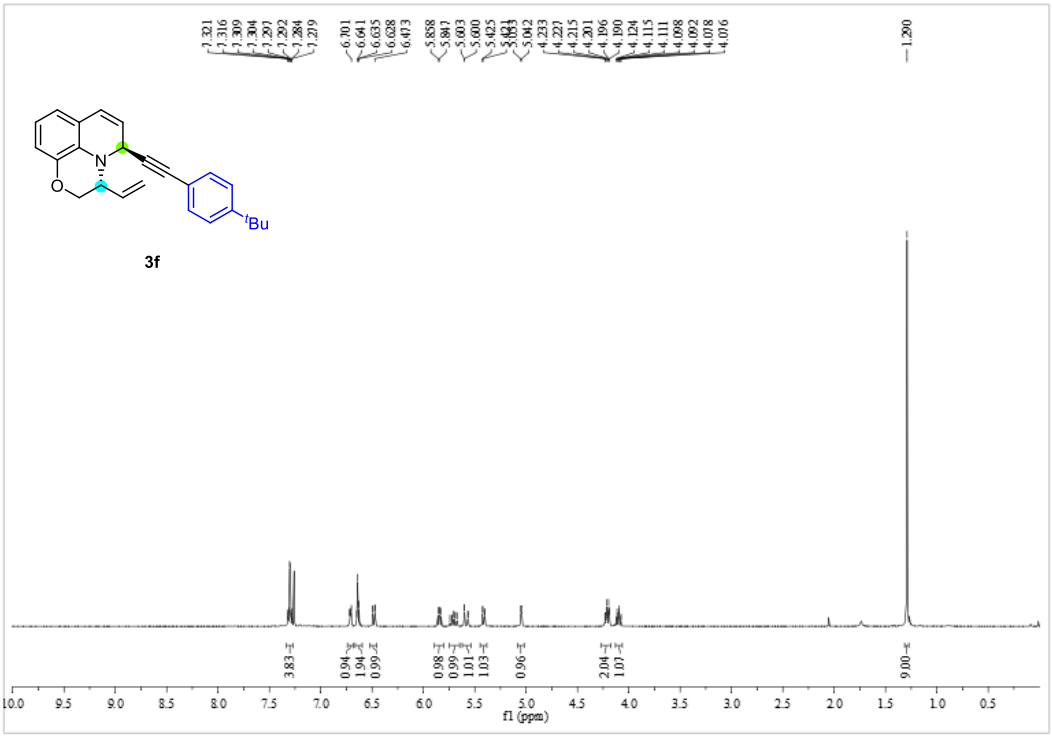
Signal 1: VWD1 A, Wavelength=254 nm

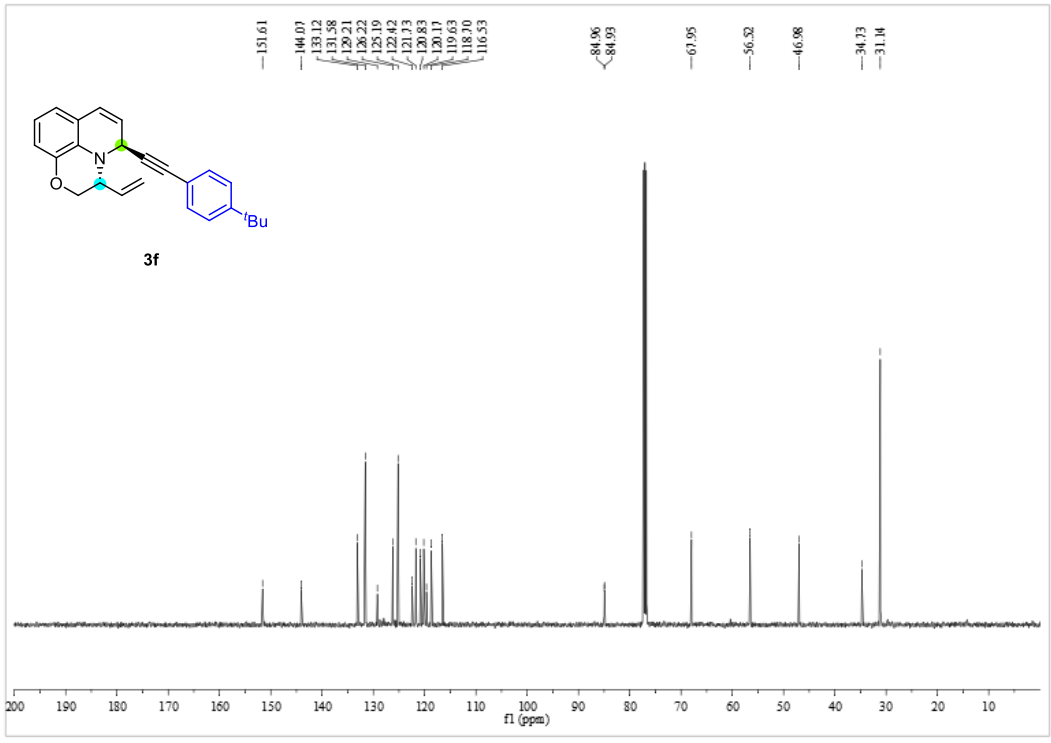
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.376	MM	0.1513	9108.20117	1003.18353	49.9225
2	8.099	MM	0.1644	9136.49023	926.01721	50.0775

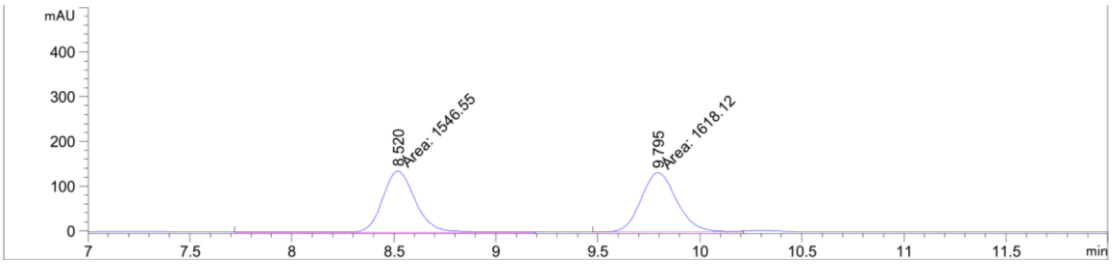


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.108	MM	0.1510	275.53580	30.41716	3.3012
2	7.786	MM	0.1602	8071.11182	839.56122	96.6988

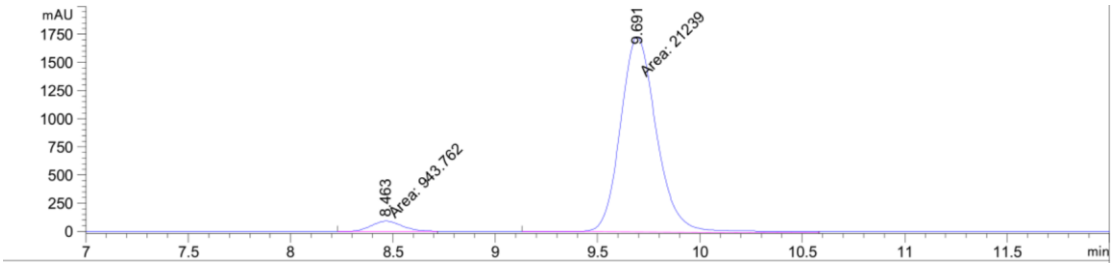

7.321
7.316
7.309
7.304
7.297
7.292
7.284
7.279
6.701
6.641
6.635
6.628
6.473
5.858
5.847
5.603
5.600
5.425
5.423
5.183
5.042
4.233
4.227
4.215
4.201
4.196
4.190
4.124
4.115
4.111
4.098
4.092
4.078
4.076
1.290
3.83
0.94
1.94
0.99
0.98
0.99
1.01
1.03
0.96
2.04
1.07
9.00
f1 (ppm)


151.61
144.07
133.12
131.58
129.21
126.22
125.19
122.42
121.73
120.83
120.17
119.63
118.70
116.53
84.96
84.93
67.95
56.52
46.98
34.73
31.14
f1 (ppm)



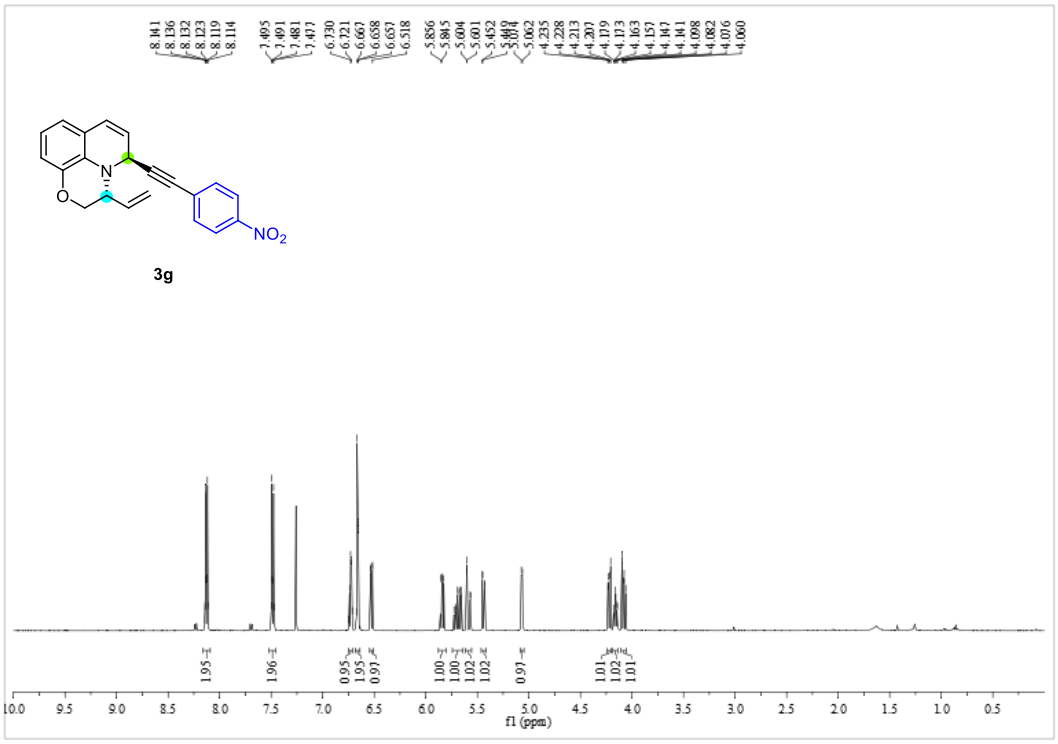
Signal 1: VWD1 A, Wavelength=254 nm

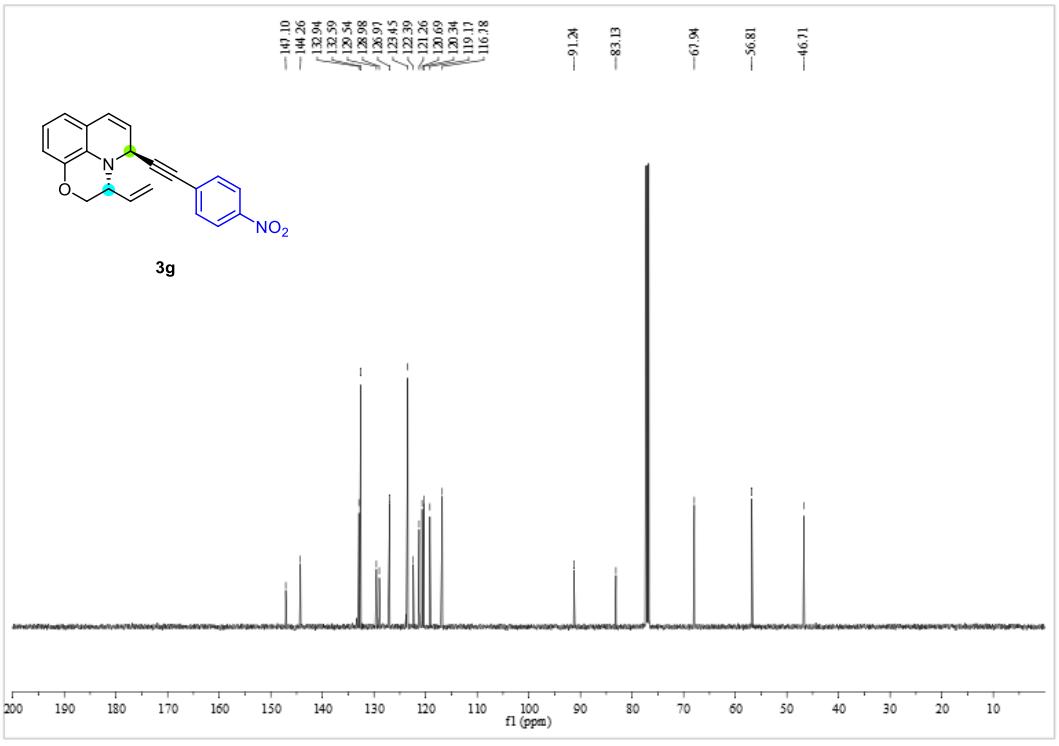
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.520	MM	0.1881	1546.54590	137.02502	48.8691
2	9.795	MM	0.2035	1618.12390	132.51489	51.1309

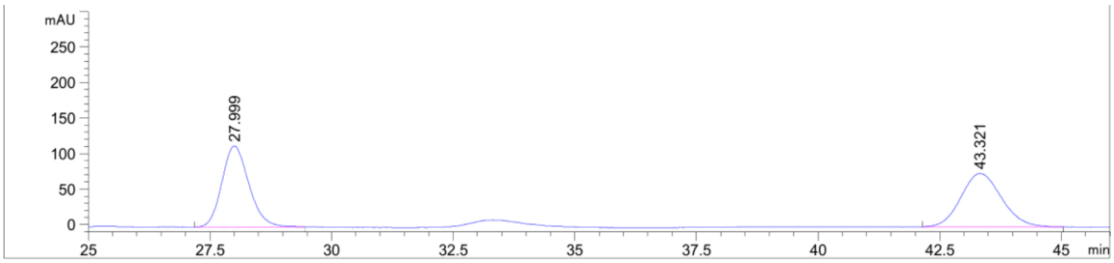


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.463	MM	0.1741	943.76178	90.33245	4.2545
2	9.691	MM	0.2041	2.12390e4	1734.66418	95.7455

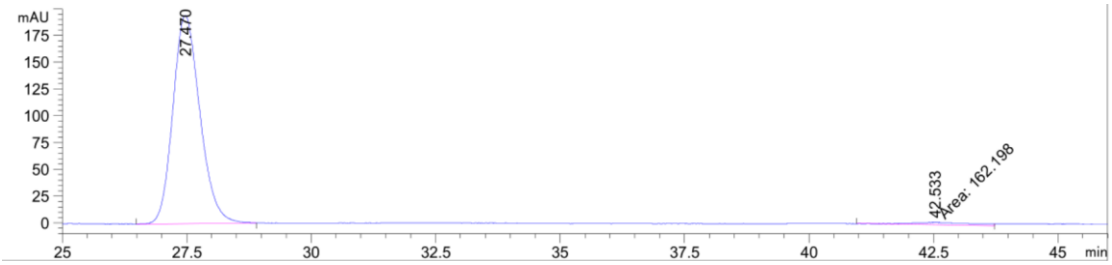

8.141
8.136
8.132
8.123
8.119
8.114
7.495
7.491
7.481
7.477
6.730
6.721
6.667
6.658
6.651
6.518
5.856
5.845
5.604
5.601
5.452
5.062
4.235
4.228
4.213
4.207
4.179
4.173
4.163
4.157
4.147
4.141
4.098
4.082
4.076
4.060
O
N
NO2
3g
1.95
1.96
0.95
1.95
0.91
1.00
1.00
1.02
1.02
0.97
1.01
1.02
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


147.10
144.26
132.94
132.59
129.54
128.98
126.97
123.45
122.39
121.26
120.69
120.34
119.17
116.78
91.24
83.13
67.94
56.81
46.71
O
N
NO2
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



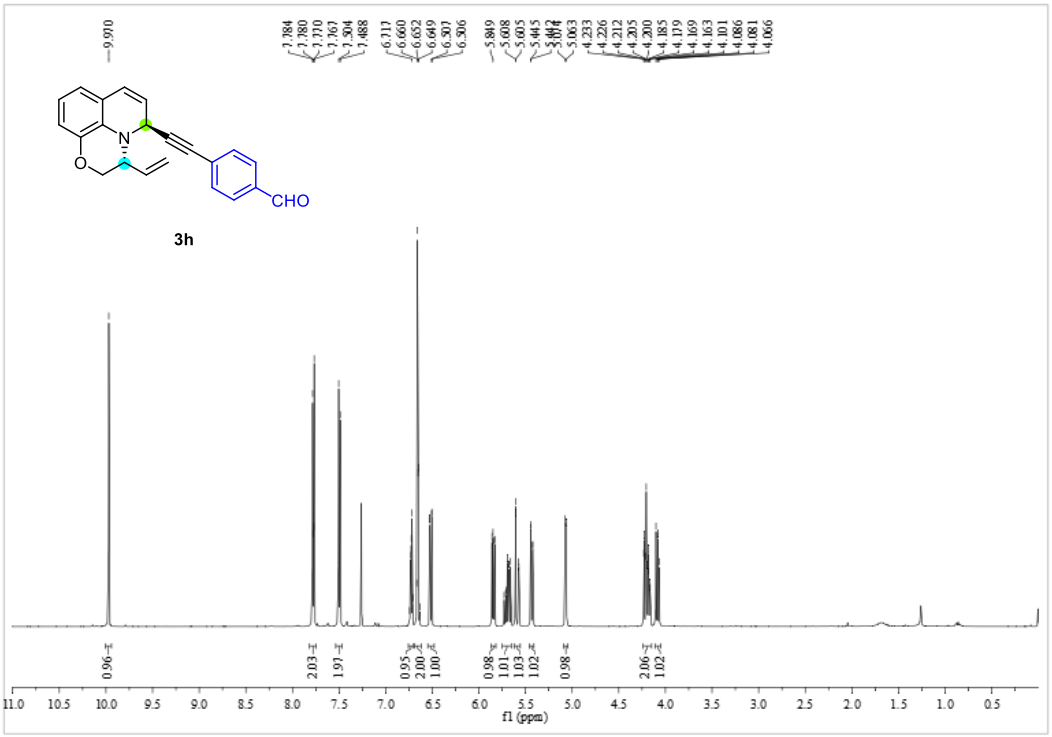
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

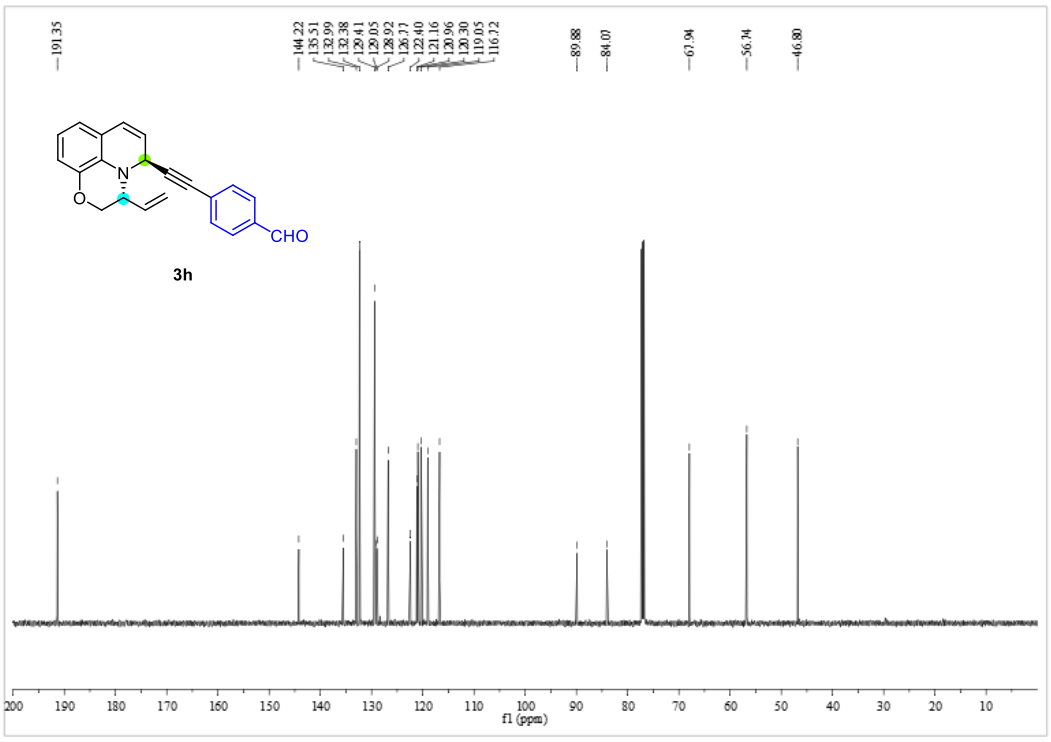
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.999	BB	0.5602	4399.50830	114.00172	50.1984
2	43.321	BB	0.6982	4364.72412	75.08192	49.8016

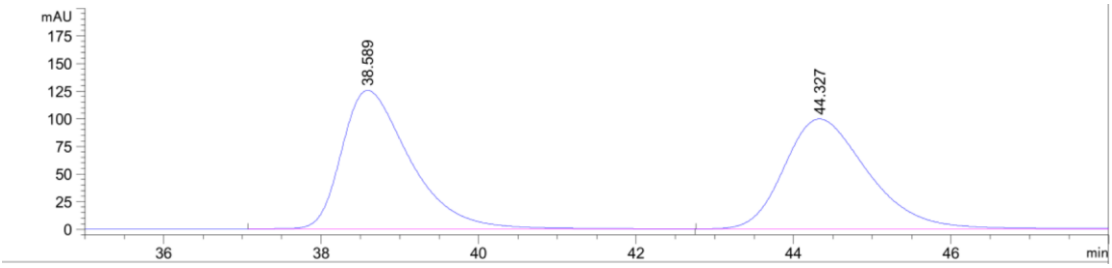


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.470	VB R	0.5790	7343.84473	194.27089	97.8391
2	42.533	MM	1.3991	162.19794	1.93212	2.1609

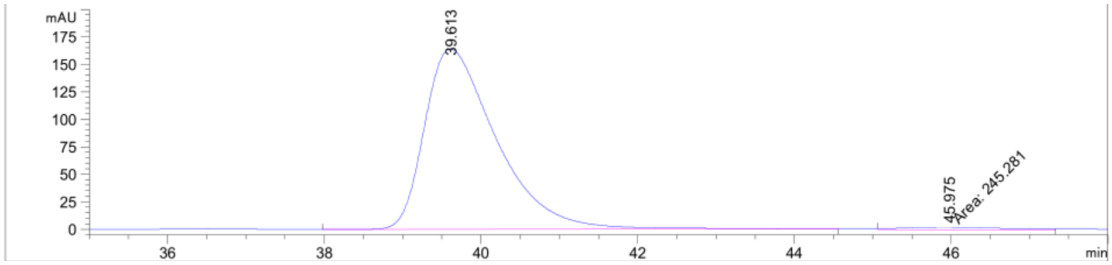

9.910
7.784
7.780
7.710
7.163
7.504
7.488
6.711
6.660
6.652
6.649
6.307
6.306
5.849
5.608
5.605
5.445
5.063
4.233
4.226
4.212
4.205
4.200
4.185
4.179
4.169
4.163
4.101
4.086
4.081
4.066
CHO
3h
0.96
2.03
1.97
0.95
2.00
1.00
0.98
1.01
1.03
1.02
0.98
2.06
1.02
f1 (ppm)


191.35
144.22
135.51
132.99
132.38
129.41
129.05
128.92
126.77
122.40
121.16
120.96
120.30
119.05
116.72
89.88
84.07
67.94
56.74
46.80
CHO
3h
f1 (ppm)



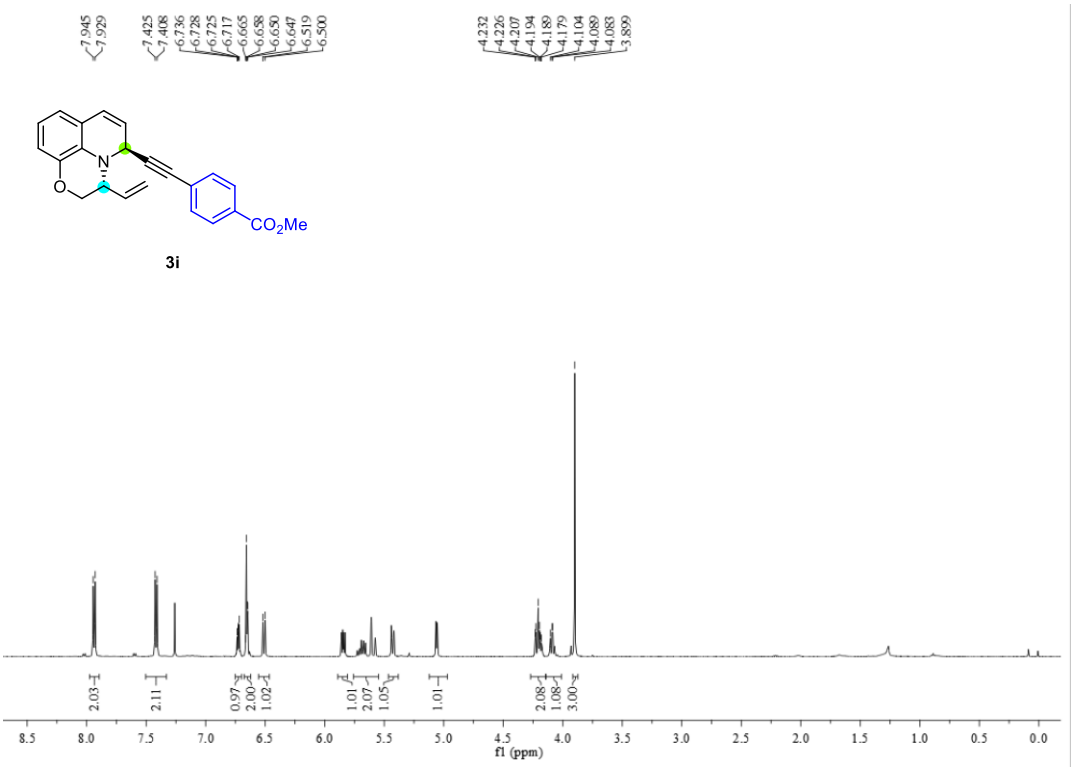
Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.589	BB	0.9137	7538.75684	125.33790	50.5594
2	44.327	BB	1.1372	7371.94629	99.40836	49.4406

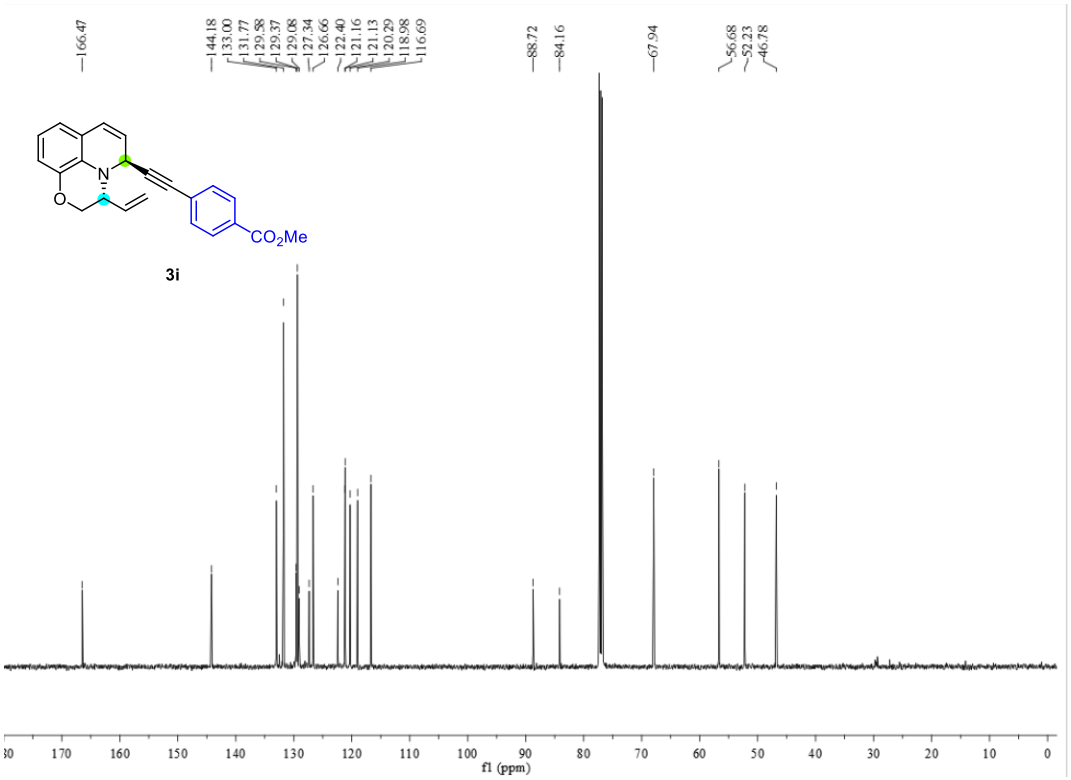


Signal 1: VWD1 A, Wavelength=250 nm

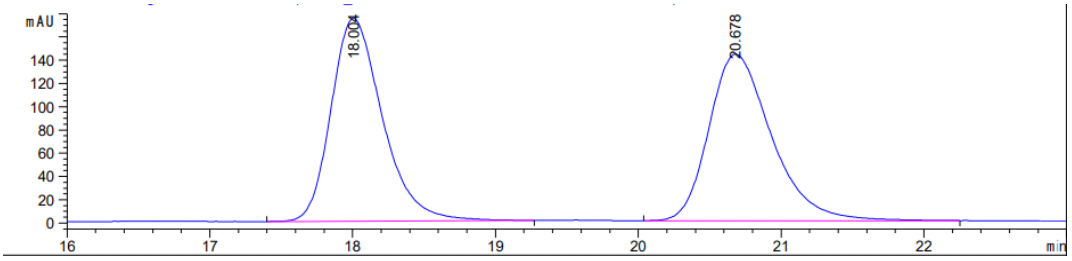
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.613	BB	0.9614	1.04513e4	164.01852	97.7069
2	45.975	MM	1.6894	245.28084	2.41974	2.2931


7.945
7.929
7.425
7.408
6.736
6.728
6.725
6.717
6.665
6.658
6.650
6.647
6.519
6.500
4.232
4.226
4.207
4.194
4.189
4.179
4.104
4.089
4.083
3.899
CO2Me
2.03
2.11
0.97
2.00
1.02
1.01
2.07
1.05
1.01
2.08
1.08
3.00
f1 (ppm)

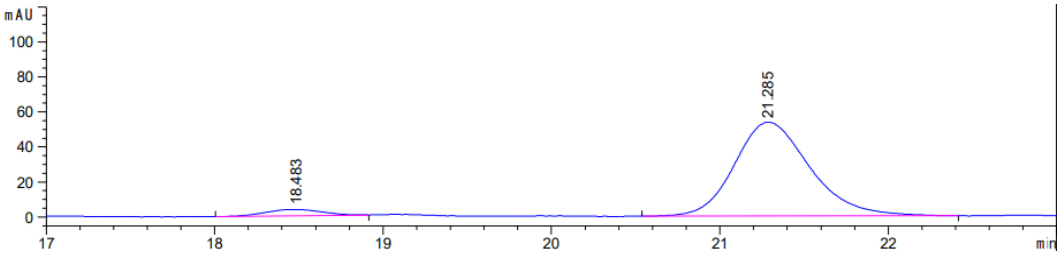
3i


166.47
144.18
133.00
131.77
129.58
129.37
129.08
127.34
126.66
122.40
121.16
121.13
120.29
118.98
116.69
88.72
84.16
67.94
56.68
52.23
46.78
CO2Me
f1 (ppm)

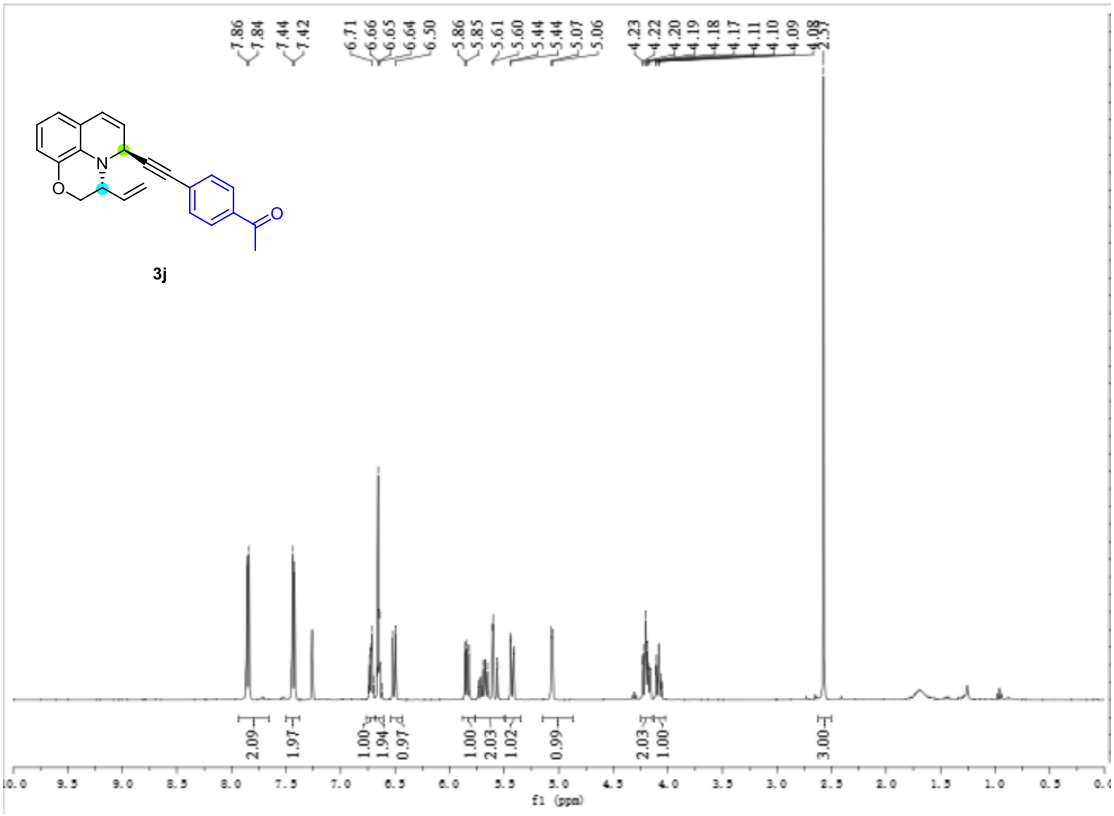
3i



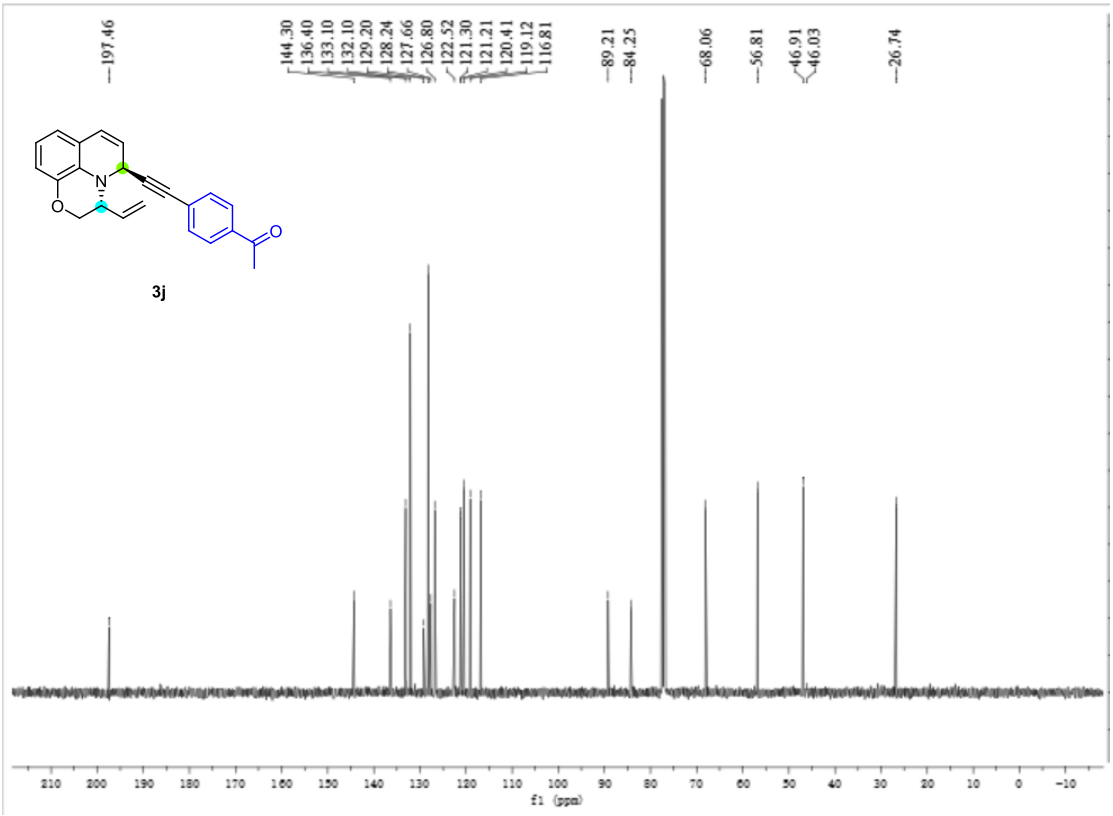
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.004	BB	0.3815	4357.30664	174.38858	49.9639
2	20.678	BB	0.4674	4363.60742	143.22537	50.0361



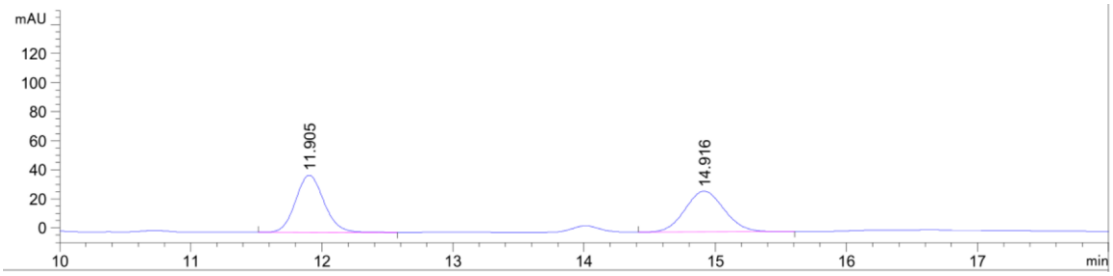
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.483	BB	0.2842	84.47776	3.64812	4.7984
2	21.285	BB	0.4584	1676.07568	53.65416	95.2016


7.86
7.84
7.44
7.42
6.71
6.66
6.65
6.64
6.50
5.86
5.85
5.61
5.60
5.44
5.44
5.07
5.06
4.23
4.22
4.20
4.19
4.18
4.17
4.11
4.10
4.09
2.09
1.97
1.00
1.94
0.97
1.00
2.03
1.02
0.99
2.03
1.00
3.00
f1 (ppm)

3j

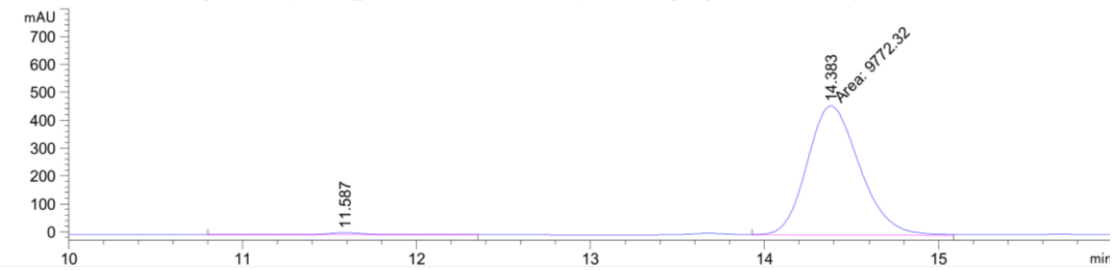

197.46
144.30
136.40
133.10
132.10
129.20
128.24
127.66
126.80
122.52
121.30
121.21
120.41
119.12
116.81
89.21
84.25
68.06
56.81
46.91
46.03
26.74
f1 (ppm)

3j



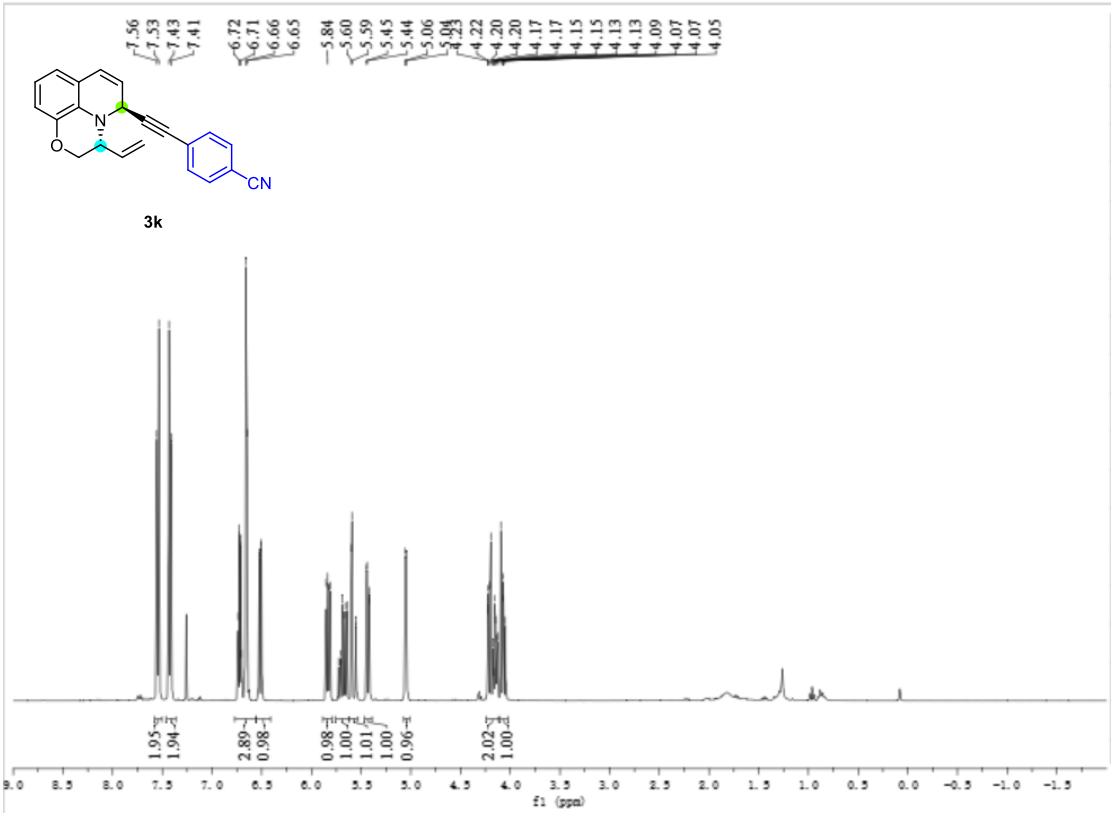
Signal 1: VWD1 A, Wavelength=254 nm

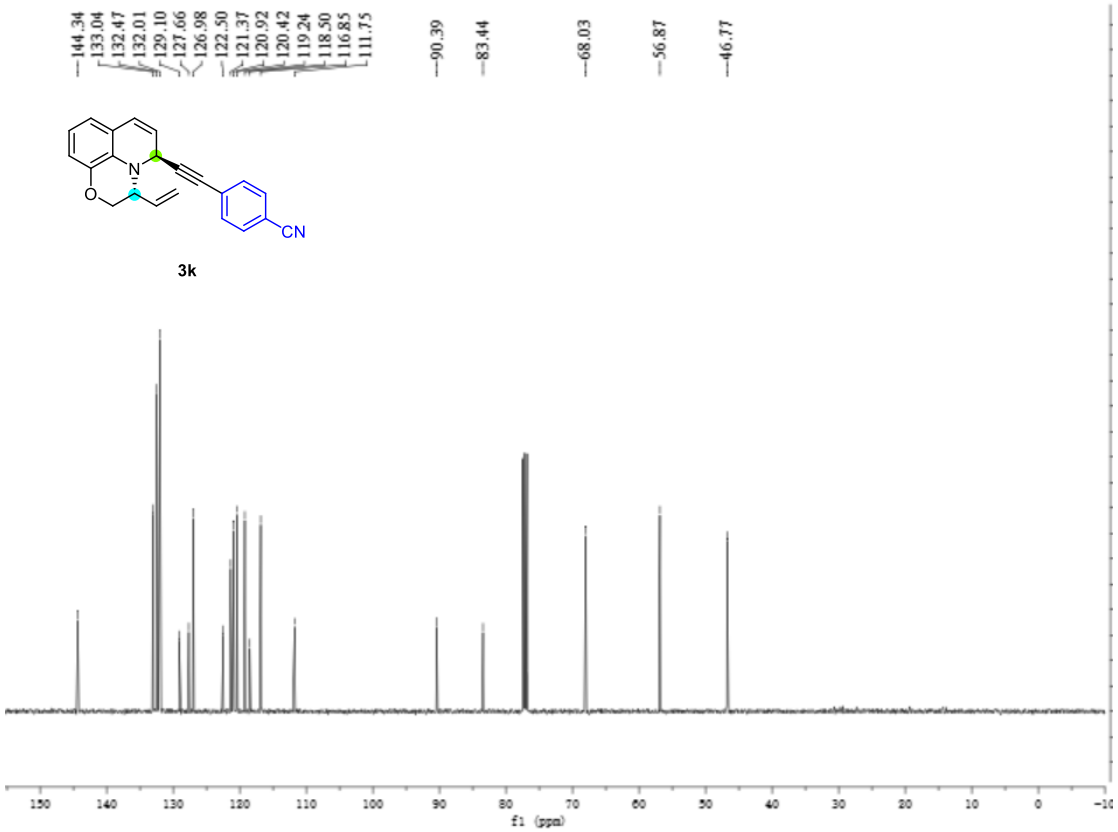
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.905	BB	0.2313	591.01556	39.33305	50.1873
2	14.916	BB	0.3254	586.60376	28.12244	49.8127

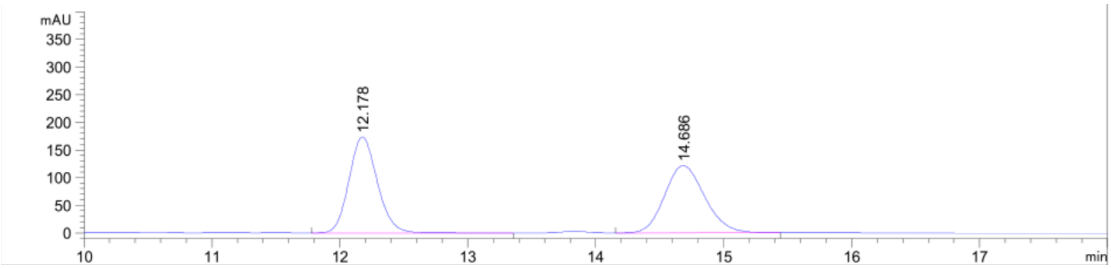


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.587	VB R	0.2358	119.91084	7.78001	1.2122
2	14.383	MM	0.3520	9772.32227	462.75308	98.7878

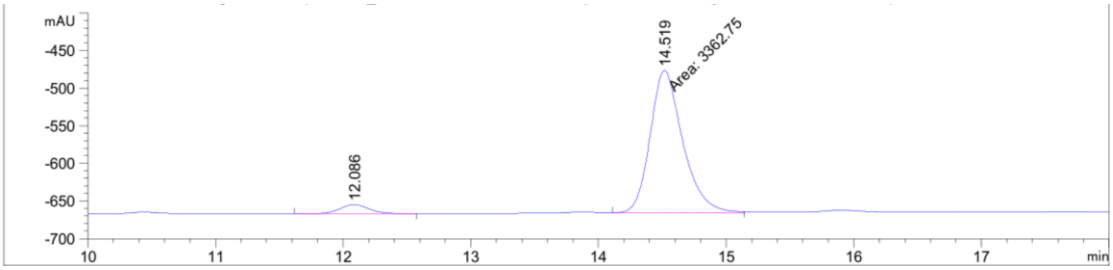

7.56
7.53
7.43
7.41
6.72
6.71
6.66
6.65
5.84
5.60
5.59
5.45
5.44
5.06
4.22
4.20
4.20
4.17
4.17
4.15
4.15
4.13
4.13
4.09
4.07
4.07
4.05
N
O
CN
3k
1.95
1.94
2.89
0.98
0.98
1.00
1.01
1.00
0.96
2.02
1.00
f1 (ppm)


144.34
133.04
132.47
132.01
129.10
127.66
126.98
122.50
121.37
120.92
120.42
119.24
118.50
116.85
111.75
90.39
83.44
68.03
56.87
46.77
N
O
CN
3k
f1 (ppm)



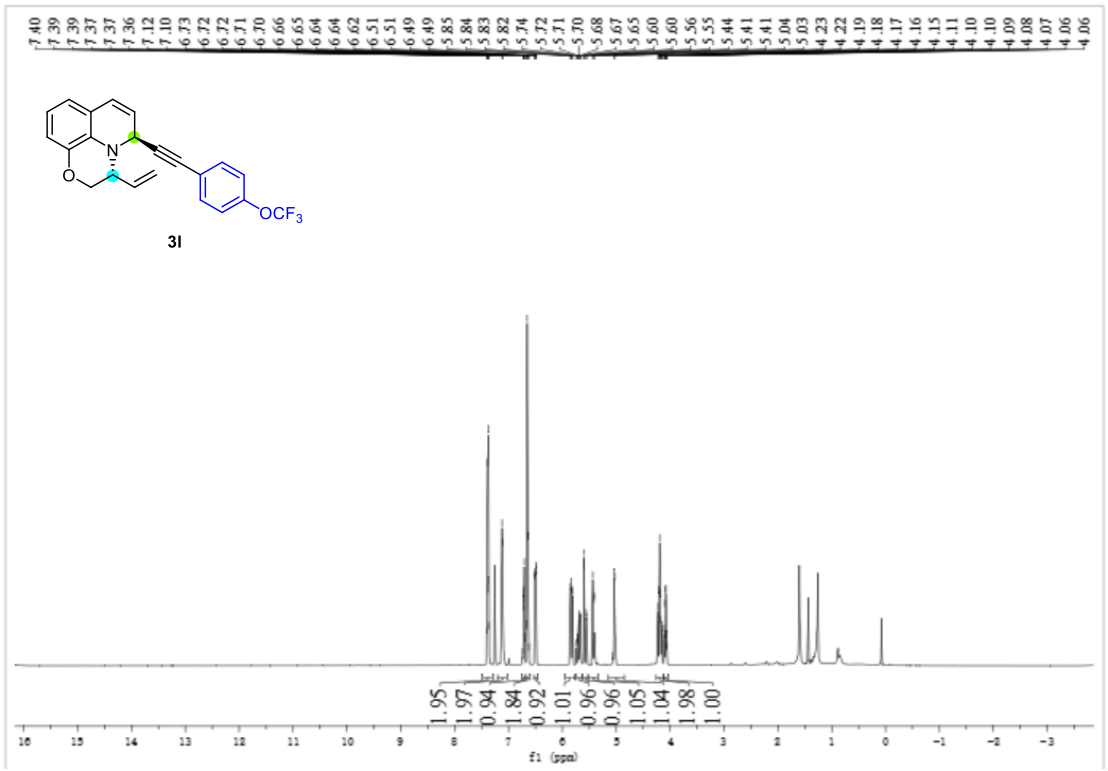
Signal 1: VWD1 A, Wavelength=254 nm

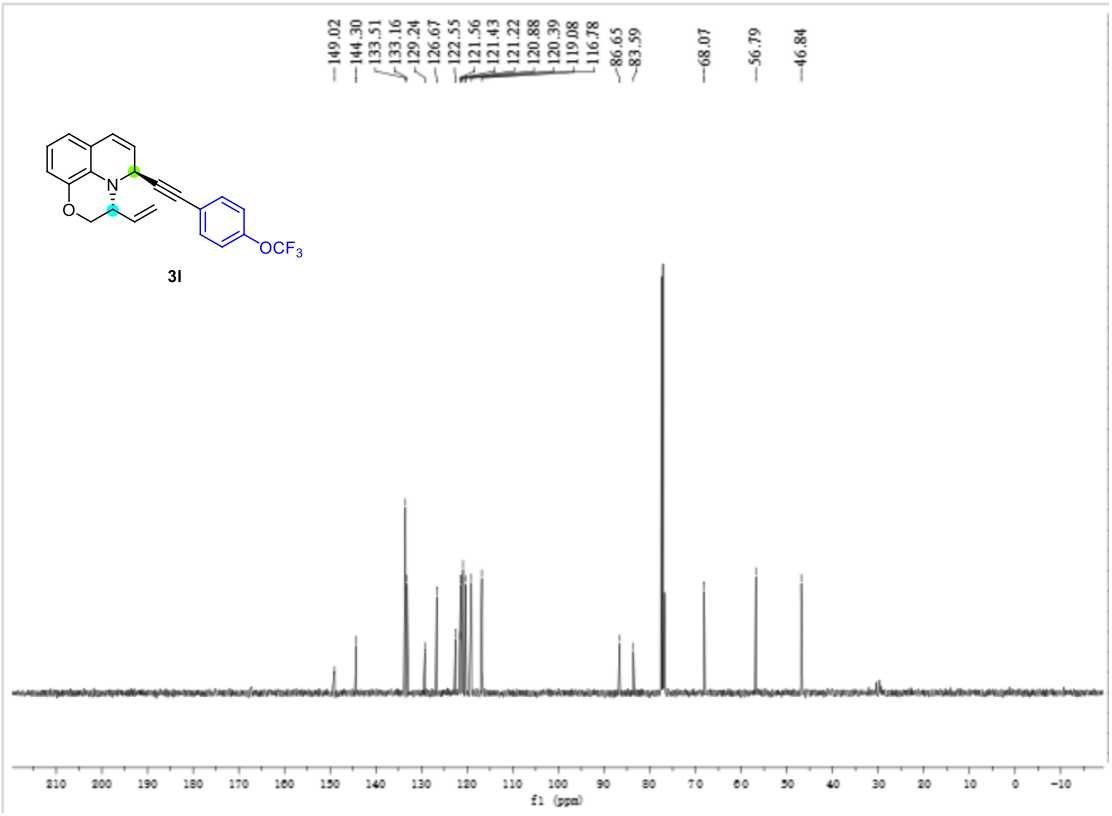
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.178	BB	0.2377	2671.75000	173.45737	50.1531
2	14.686	BB	0.3384	2655.43848	121.79719	49.8469

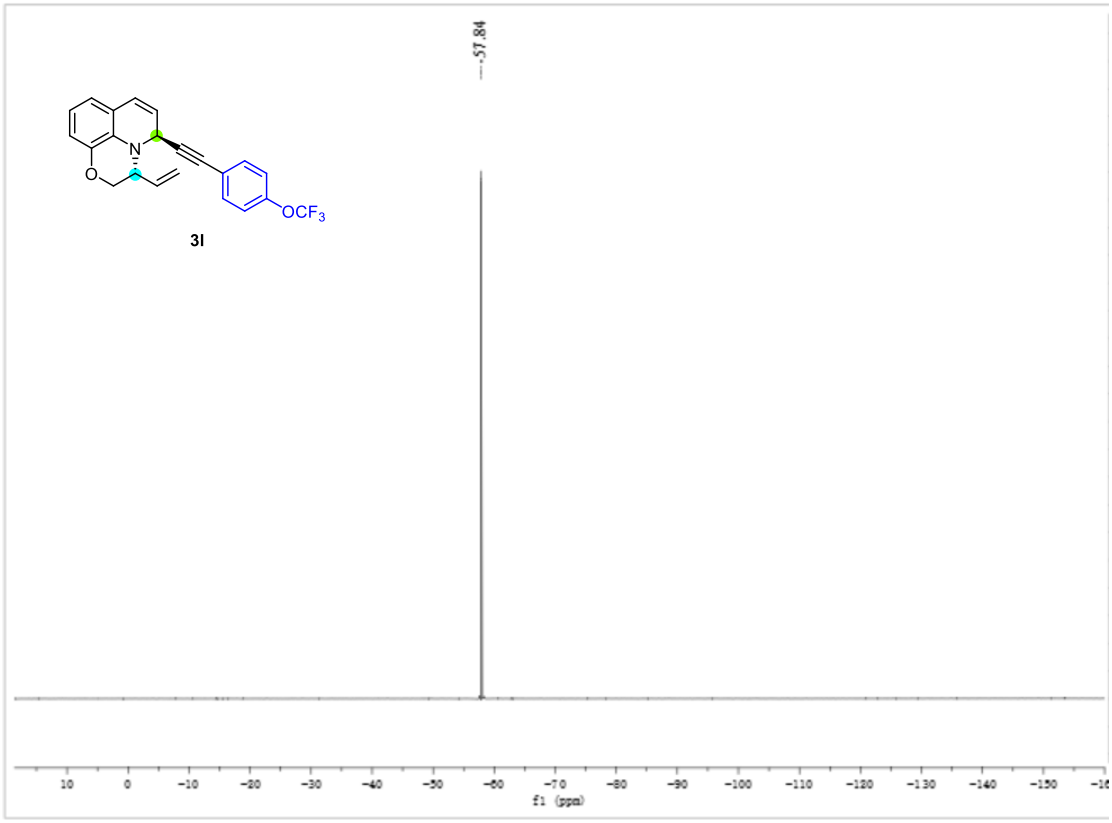


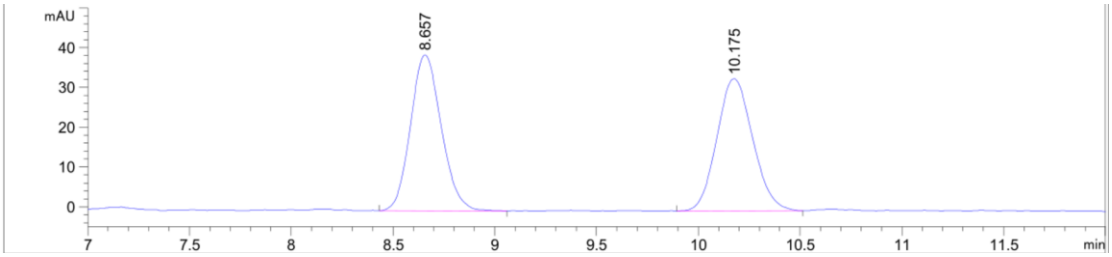
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.086	BB	0.2395	184.70622	12.00586	5.2067
2	14.519	MM	0.2959	3362.74731	189.40312	94.7933


7.40 7.39 7.39 7.37 7.37 7.36 7.12 7.10 6.73 6.72 6.72 6.71 6.70 6.66 6.65 6.64 6.64 6.62 6.51 6.51 6.49 6.49 5.85 5.84 5.83 5.82 5.74 5.72 5.71 5.70 5.68 5.67 5.65 5.60 5.60 5.56 5.55 5.44 5.41 5.41 5.04 5.03 4.23 4.22 4.19 4.18 4.17 4.16 4.15 4.11 4.10 4.10 4.09 4.08 4.07 4.06 4.06
N
O
OCF3
3l
1.95 1.97 0.94 1.84 0.92 1.01 0.96 0.96 1.05 1.04 1.98 1.00
f1 (ppm)

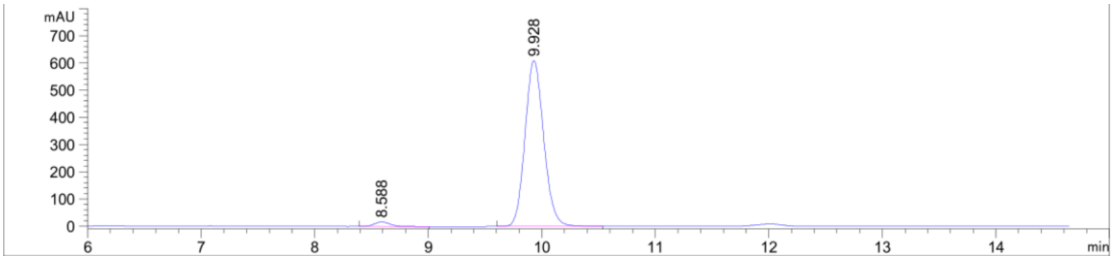

149.02 144.30 133.51 133.16 129.24 126.67 122.55 121.56 121.43 121.22 120.88 120.39 119.08 116.78 86.65 83.59 68.07 56.79 46.84
N
O
OCF3
3l
f1 (ppm)


-57.84
N
O
OCF3
3l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)



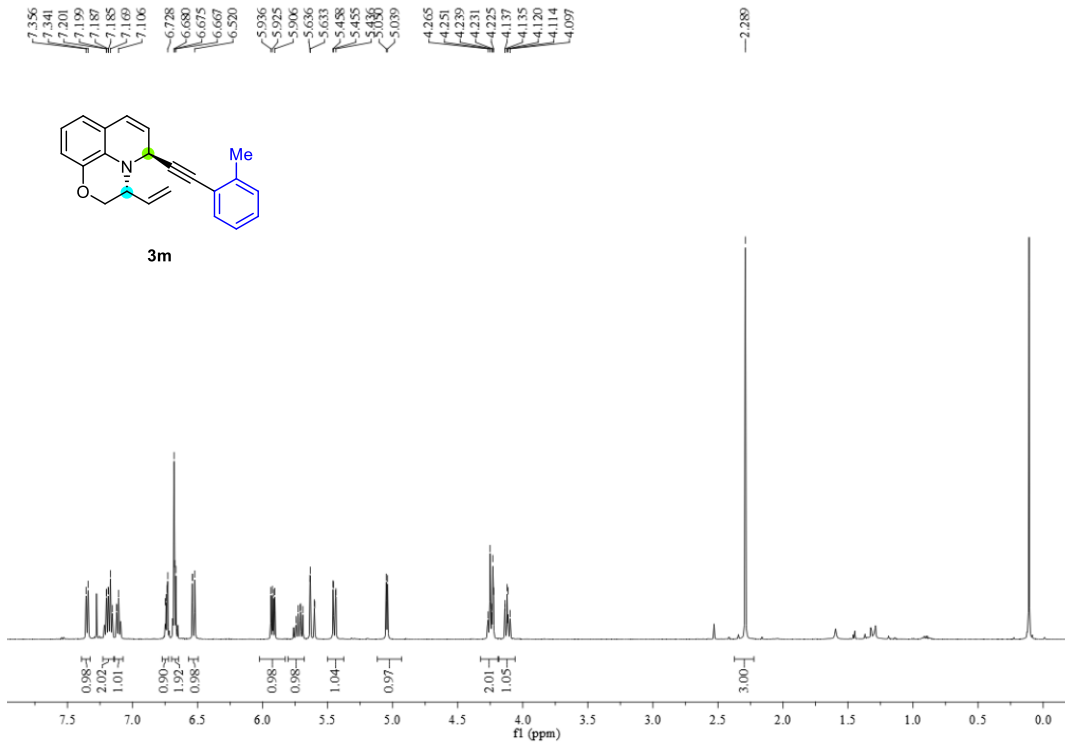
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

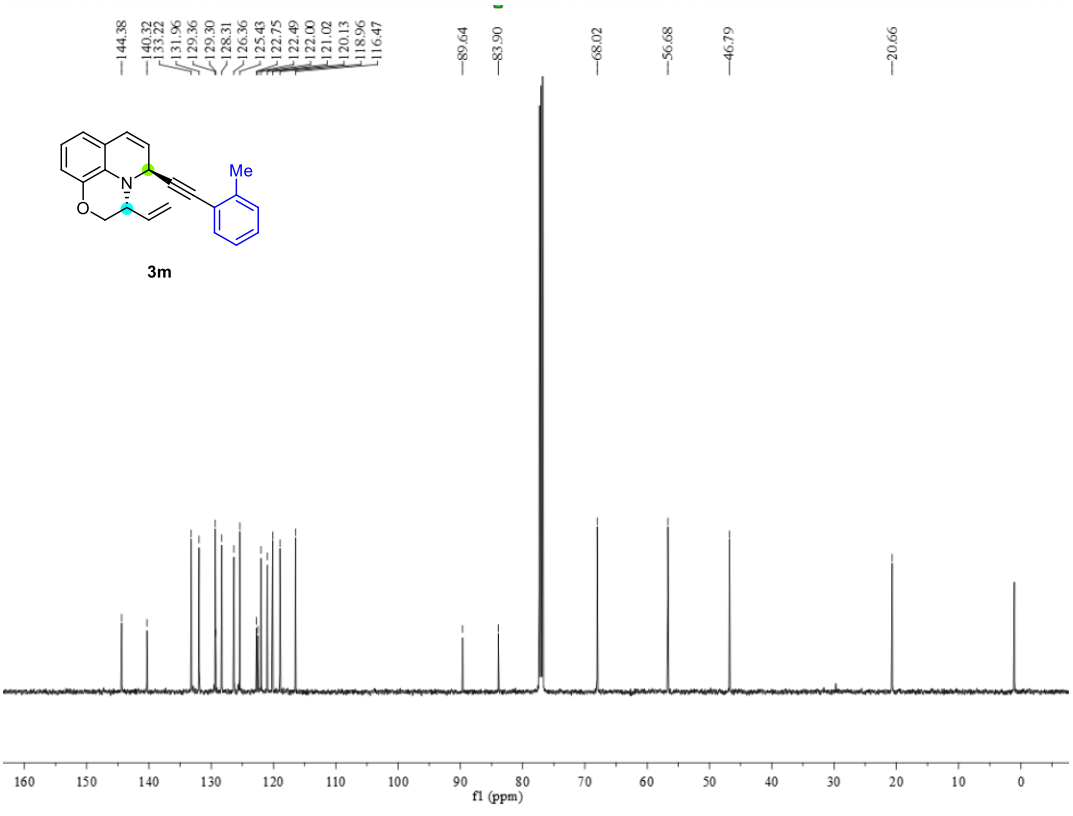
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.657	BB	0.1627	412.54333	39.21161	50.3760
2	10.175	BB	0.1869	406.38443	33.18738	49.6240

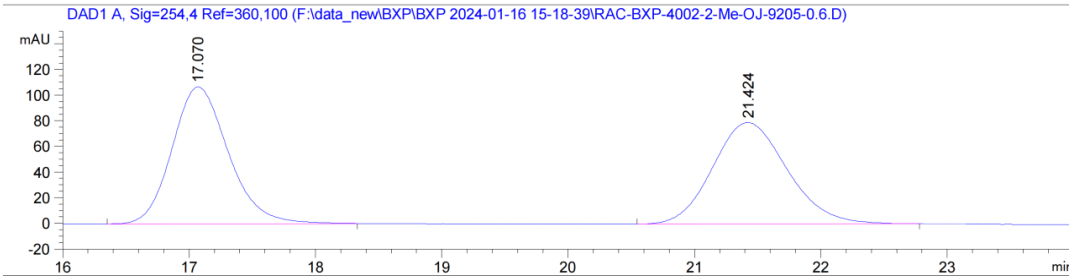


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.588	BB	0.1516	163.79739	16.53376	2.2931
2	9.928	BB	0.1777	6979.19336	609.15680	97.7069

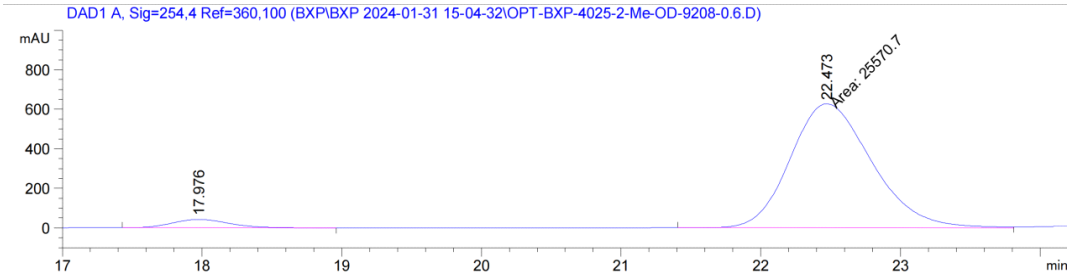

7.356
7.341
7.201
7.199
7.187
7.185
7.169
7.106
6.728
6.680
6.675
6.667
6.520
5.936
5.925
5.906
5.636
5.633
5.458
5.455
5.436
5.039
4.265
4.251
4.239
4.231
4.225
4.137
4.135
4.120
4.114
4.097
2.289
Me
N
O
3m
0.98
2.02
1.01
0.90
1.92
0.98
0.98
0.98
1.04
0.97
2.01
1.05
3.00
f1 (ppm)


144.38
140.32
133.22
131.96
129.36
129.30
128.31
126.36
125.43
122.75
122.49
122.00
121.02
120.13
118.96
116.47
89.64
83.90
68.02
56.68
46.79
20.66
Me
N
O
3m
f1 (ppm)



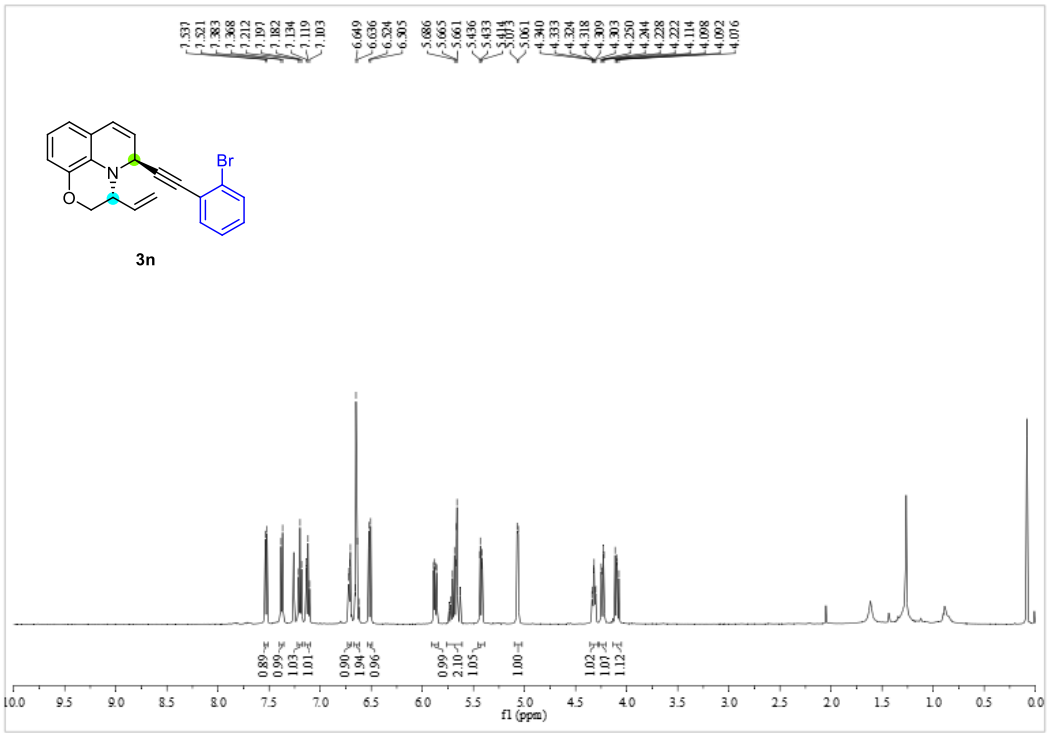
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

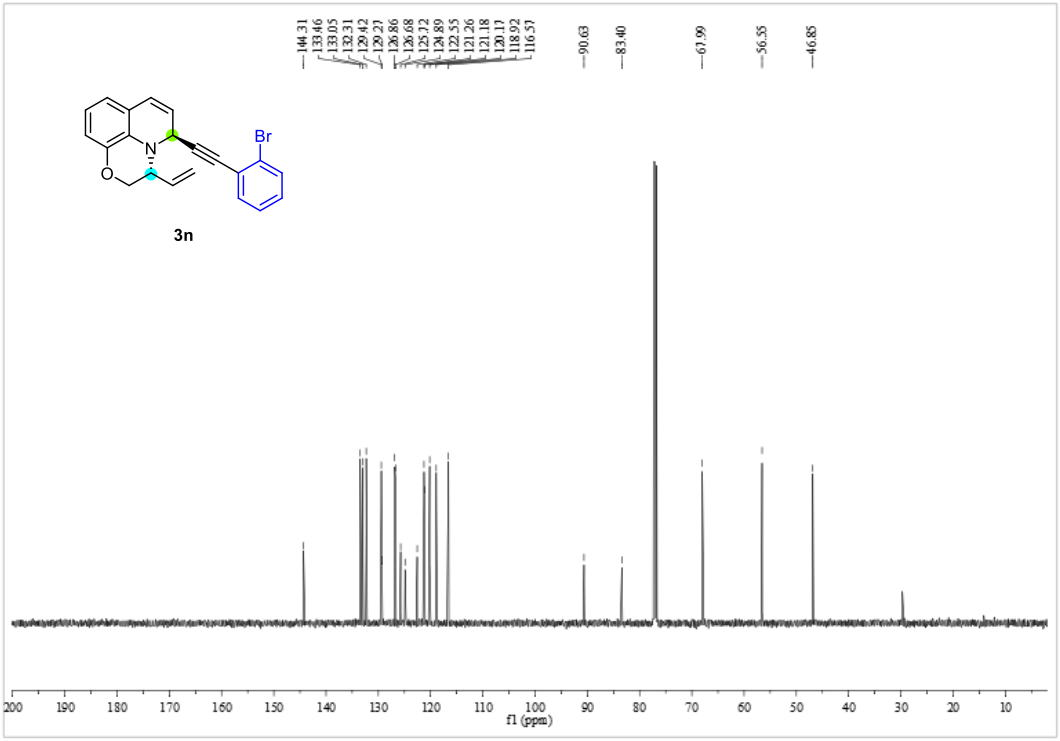
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.070	BB	0.4707	3300.21753	106.73687	50.3969
2	21.424	BB	0.6068	3248.23535	79.15452	49.6031

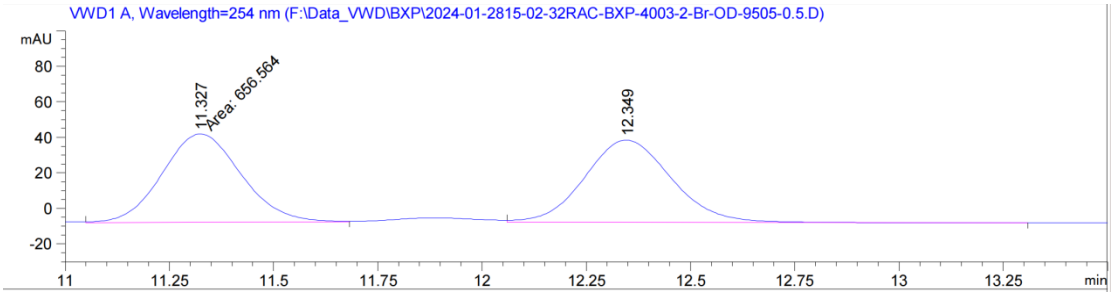


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.976	BB	0.4305	1190.52161	42.27828	4.4487
2	22.473	MM	0.6795	2.55707e4	627.18854	95.5513

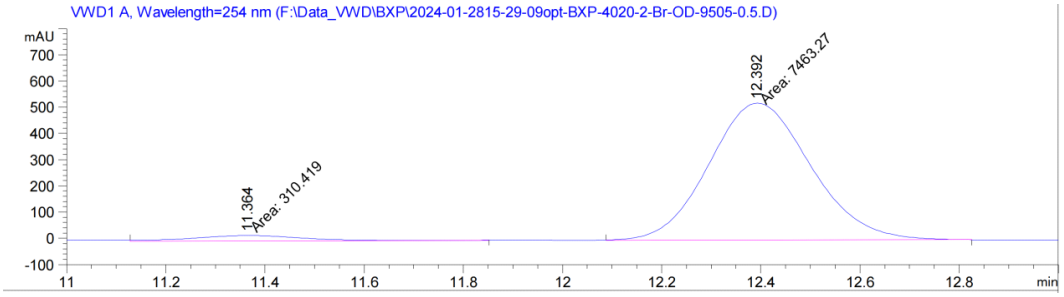

7.537
7.521
7.383
7.368
7.212
7.197
7.182
7.134
7.119
7.103
6.649
6.636
6.524
6.305
5.686
5.665
5.661
5.436
5.433
5.103
5.061
4.340
4.333
4.324
4.318
4.309
4.303
4.250
4.244
4.228
4.222
4.114
4.098
4.092
4.016
Br
N
O
3n
0.89
0.99
1.03
1.01
0.90
1.94
0.96
0.99
2.10
1.05
1.00
1.02
1.07
1.12
f1 (ppm)


144.31
133.46
133.05
132.31
129.42
129.27
126.86
126.68
125.72
124.89
122.55
121.26
121.18
120.17
118.92
116.57
90.63
83.40
61.99
56.55
46.85
Br
N
O
3n
f1 (ppm)



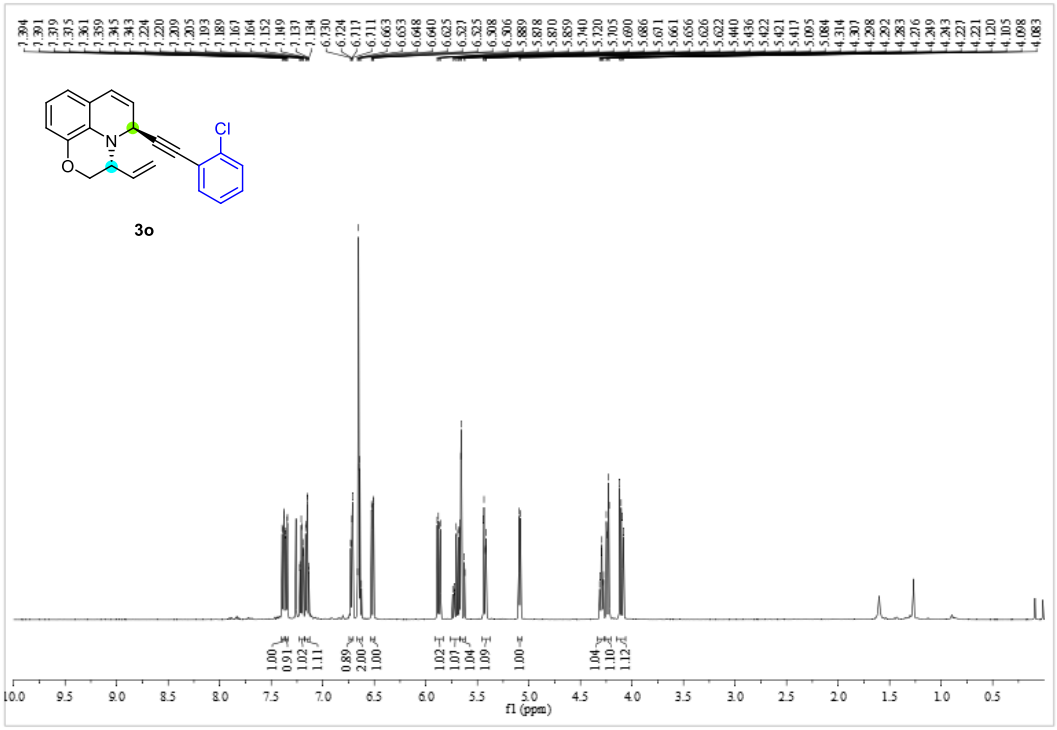
Signal 1: VWD1 A, Wavelength=254 nm

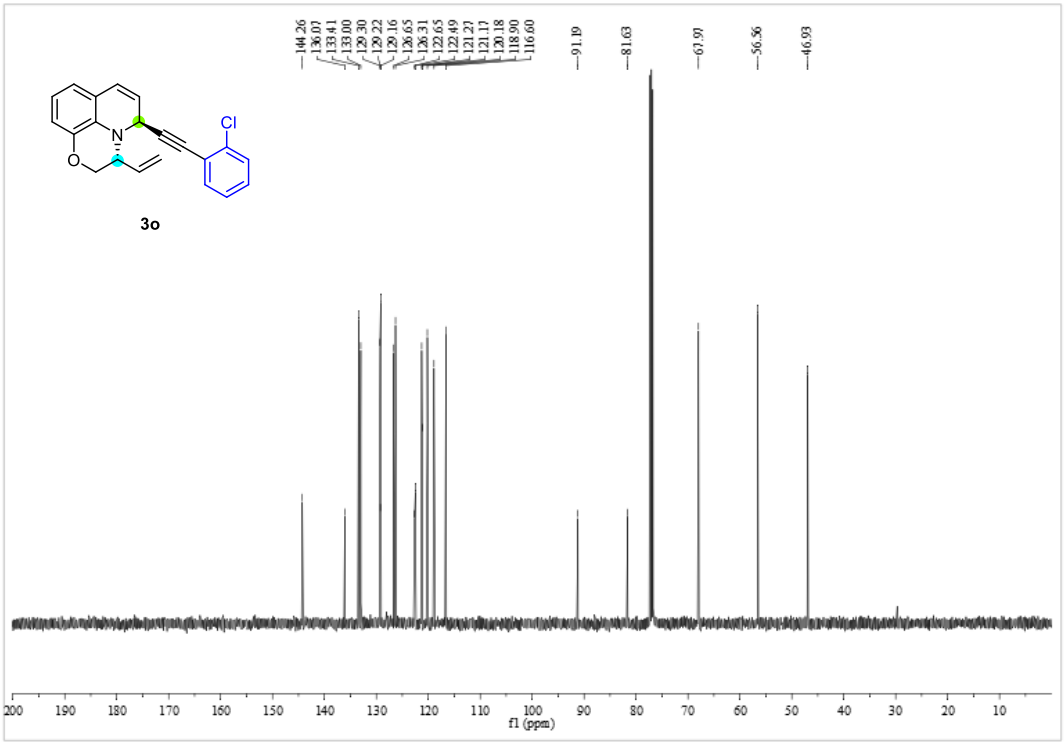
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.327	MM	0.2198	656.56372	49.78597	49.3003
2	12.349	VB	0.2236	675.19910	46.44548	50.6997

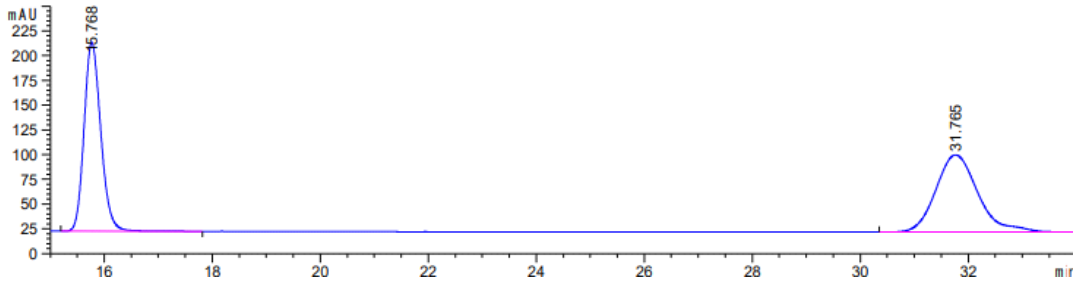


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.364	MM	0.2520	310.41891	20.52813	3.9932
2	12.392	MM	0.2378	7463.27246	523.03015	96.0068

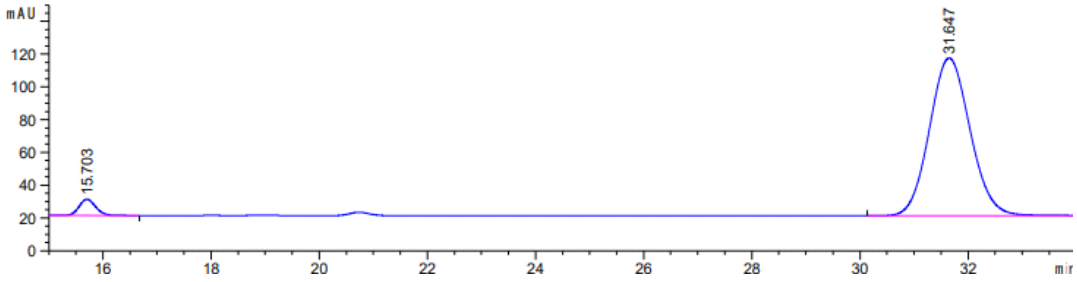

Cl
N
O
3o
f1 (ppm)


Cl
N
O
3o
f1 (ppm)



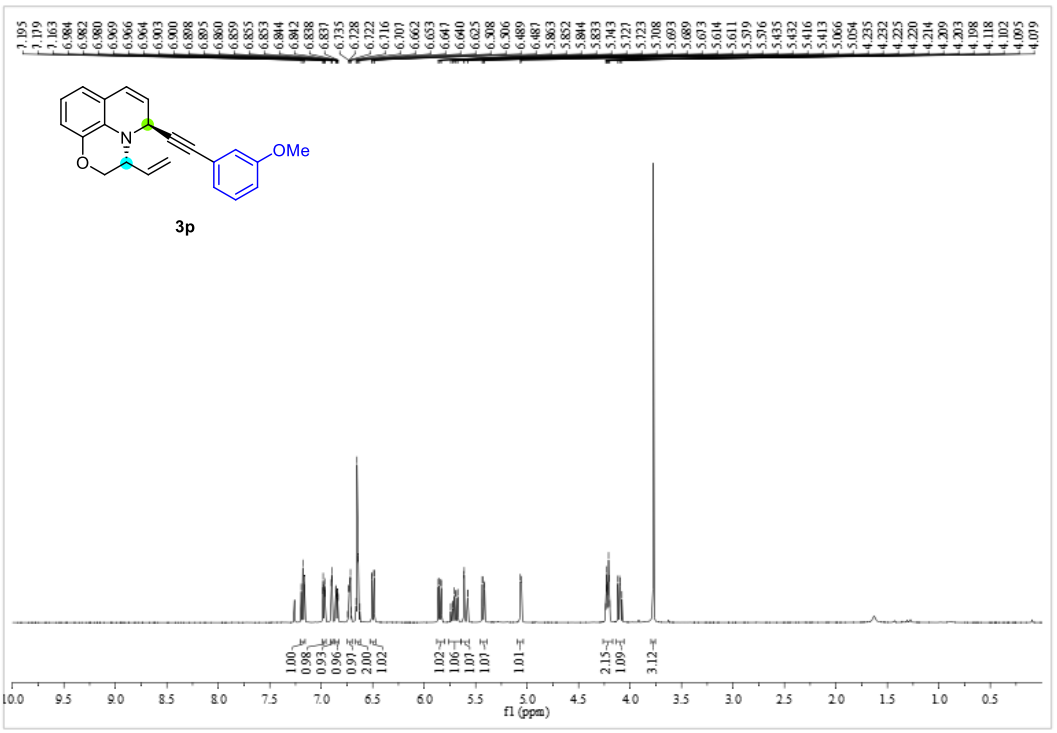
Signal 1: VWD1 A, Wavelength=254 nm

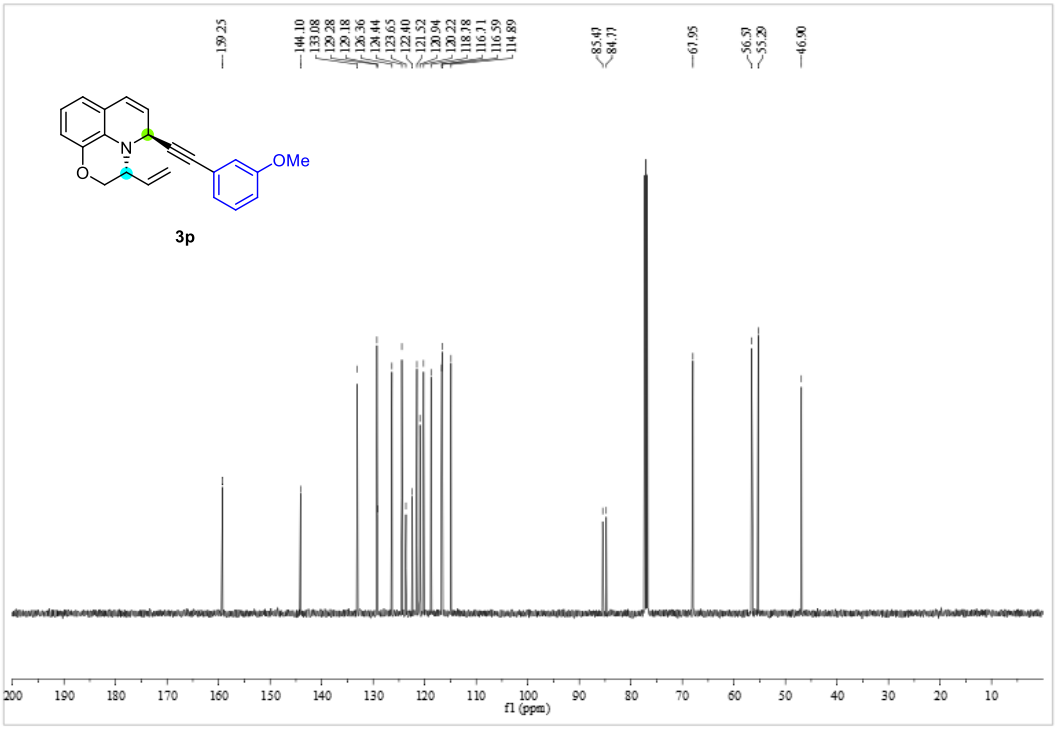
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.768	BB	0.3314	4098.58008	190.96916	49.2843
2	31.765	BB	0.8309	4217.61328	77.99767	50.7157

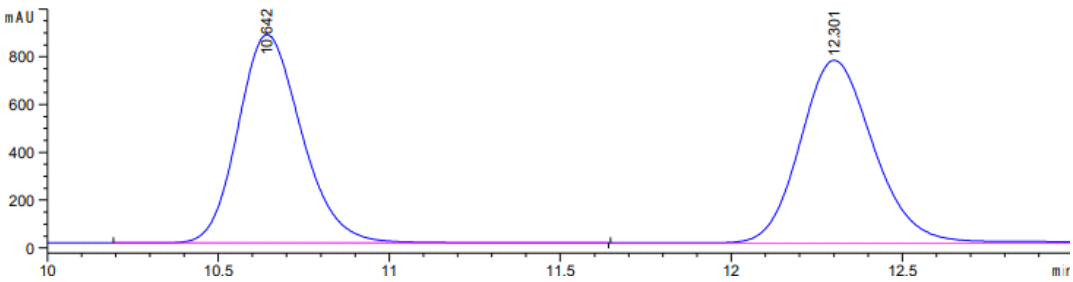


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.703	BB	0.3294	212.40698	9.93695	4.0548
2	31.647	BBA	0.8099	5025.95410	96.29308	95.9452

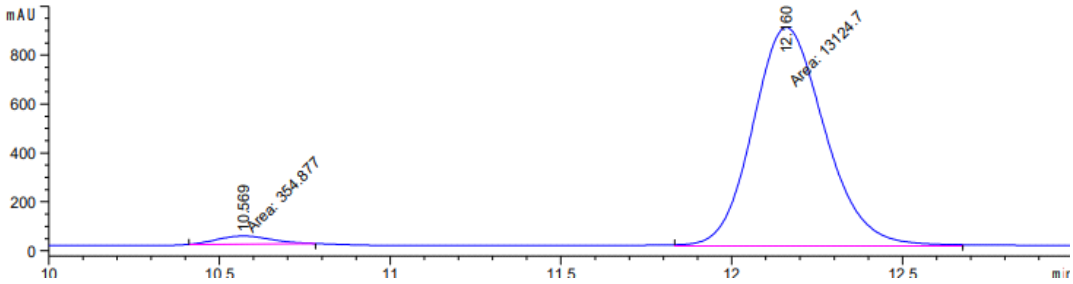

OMe
3p
fl (ppm)


OMe
3p
fl (ppm)



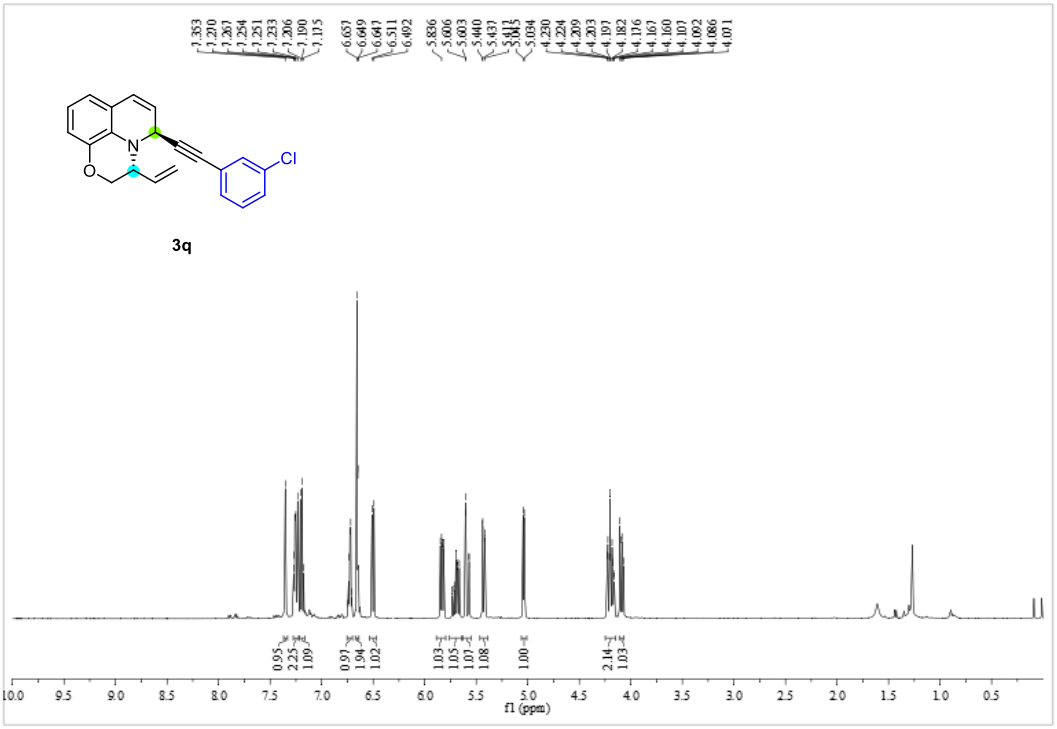
Signal 1: VWD1 A, Wavelength=254 nm

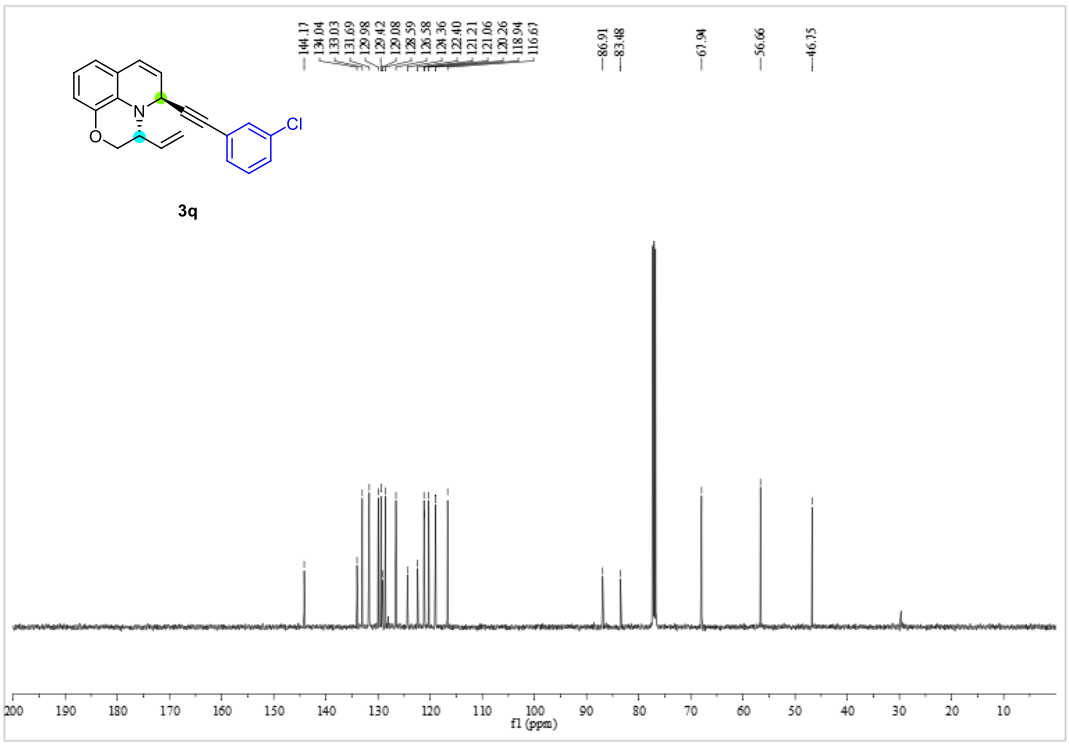
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.642	BB	0.2000	1.12662e4	870.56543	49.4949
2	12.301	BB	0.2316	1.14962e4	763.66144	50.5051

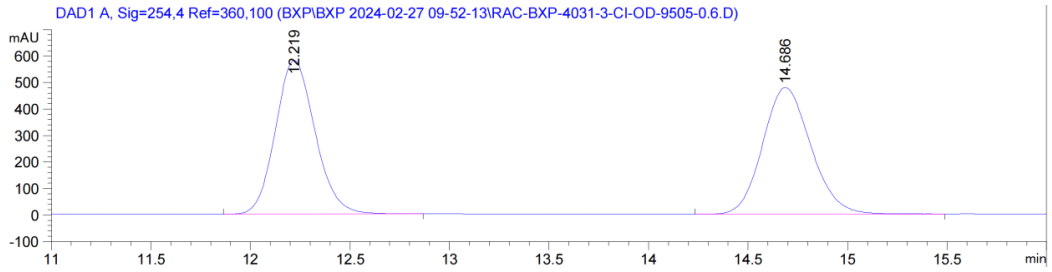


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.569	BB	0.2123	555.55634	38.97804	4.0759
2	12.160	BB	0.2260	1.30749e4	891.91016	95.9241

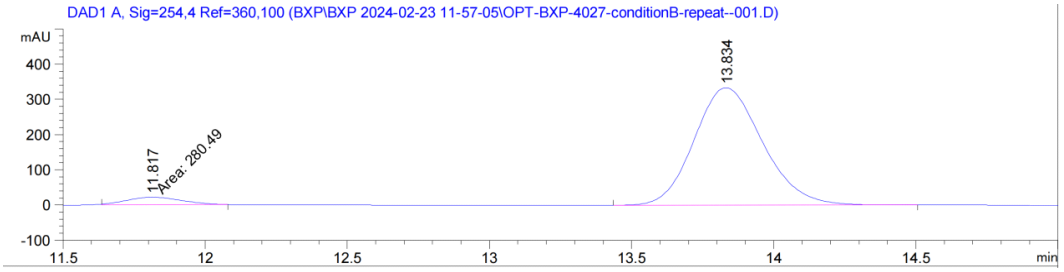

7.353
7.210
7.207
7.254
7.251
7.233
7.206
7.190
7.175
6.657
6.649
6.647
6.511
6.492
5.836
5.606
5.603
5.440
5.437
5.413
5.034
4.230
4.224
4.209
4.203
4.197
4.182
4.176
4.167
4.160
4.107
4.092
4.086
4.071
Cl
3q
0.95
2.25
1.09
0.97
1.94
1.02
1.03
1.05
1.07
1.08
1.00
2.14
1.03
f1 (ppm)


144.17
134.04
133.03
131.69
129.98
129.42
129.08
128.59
126.58
124.36
122.40
121.21
121.06
120.26
118.94
116.67
86.91
83.48
67.94
56.66
46.75
Cl
3q
f1 (ppm)



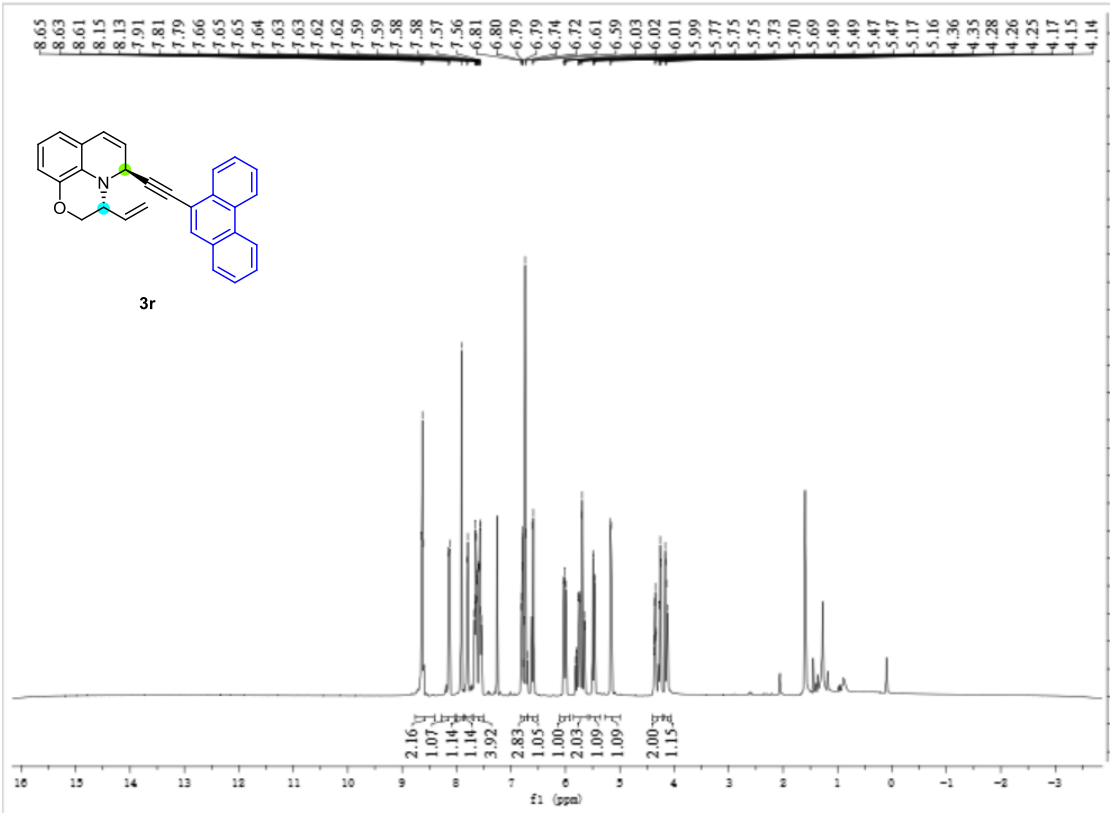
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

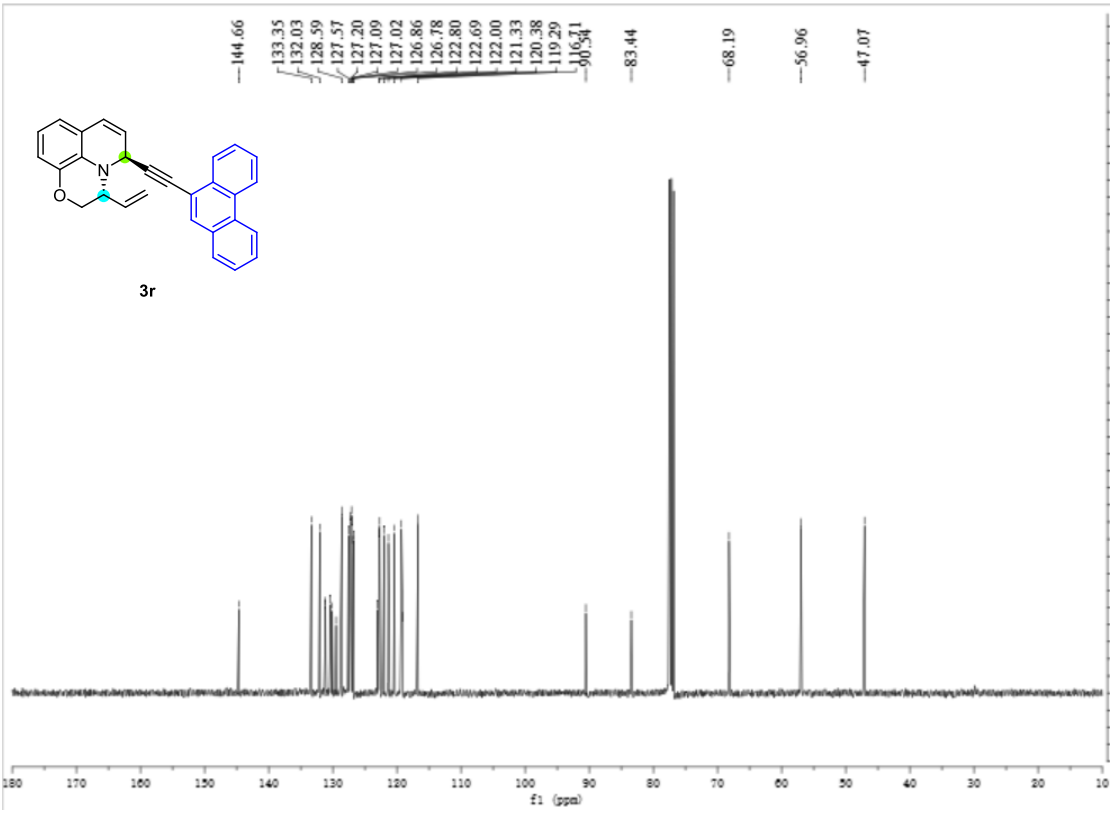
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.219	BB	0.2133	8022.19336	580.35028	49.9657
2	14.686	BB	0.2622	8033.20361	477.64883	50.0343

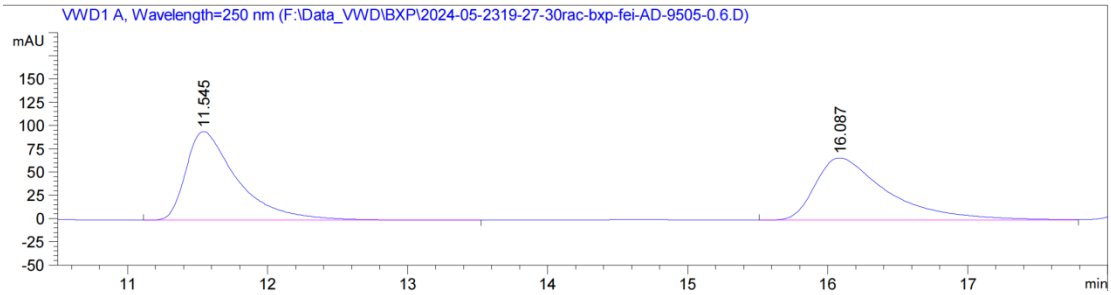


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.817	MM	0.2195	280.48969	21.29956	4.7716
2	13.834	BB	0.2599	5597.86914	333.37787	95.2284

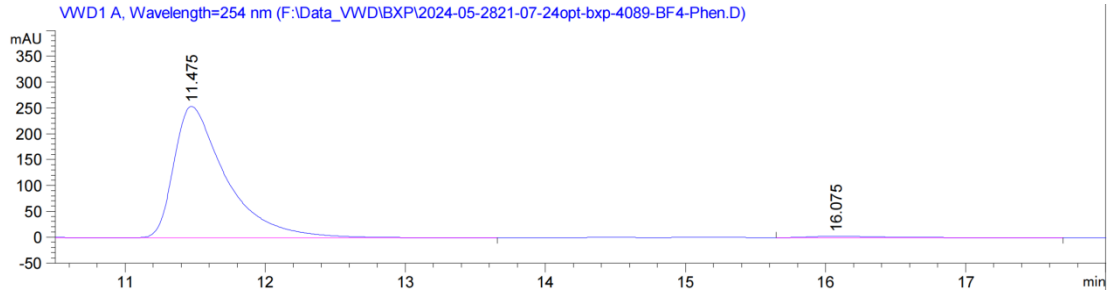

8.65
8.63
8.61
8.15
8.13
7.91
7.81
7.79
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.62
7.59
7.59
7.58
7.58
7.57
7.56
6.81
6.80
6.79
6.79
6.74
6.72
6.61
6.59
6.03
6.02
6.01
5.99
5.77
5.75
5.75
5.73
5.70
5.69
5.49
5.49
5.47
5.47
5.17
5.16
4.36
4.35
4.28
4.26
4.25
4.17
4.15
4.14
3r
2.16
1.07
1.14
1.14
3.92
2.83
1.05
1.00
2.03
1.09
1.09
2.00
1.15
f1 (ppm)


144.66
133.35
132.03
128.59
127.57
127.20
127.09
127.02
126.86
126.78
122.80
122.69
122.00
121.33
120.38
119.29
116.71
90.54
83.44
68.19
56.96
47.07
3r
f1 (ppm)



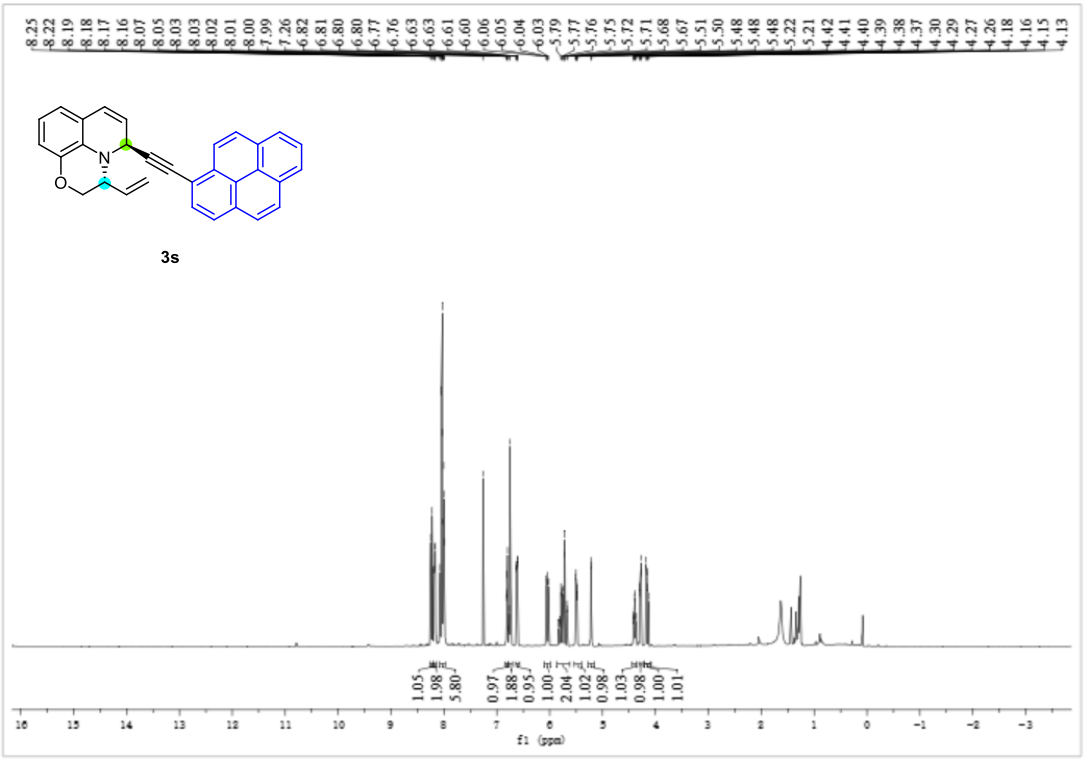
Signal 1: VWD1 A, Wavelength=250 nm

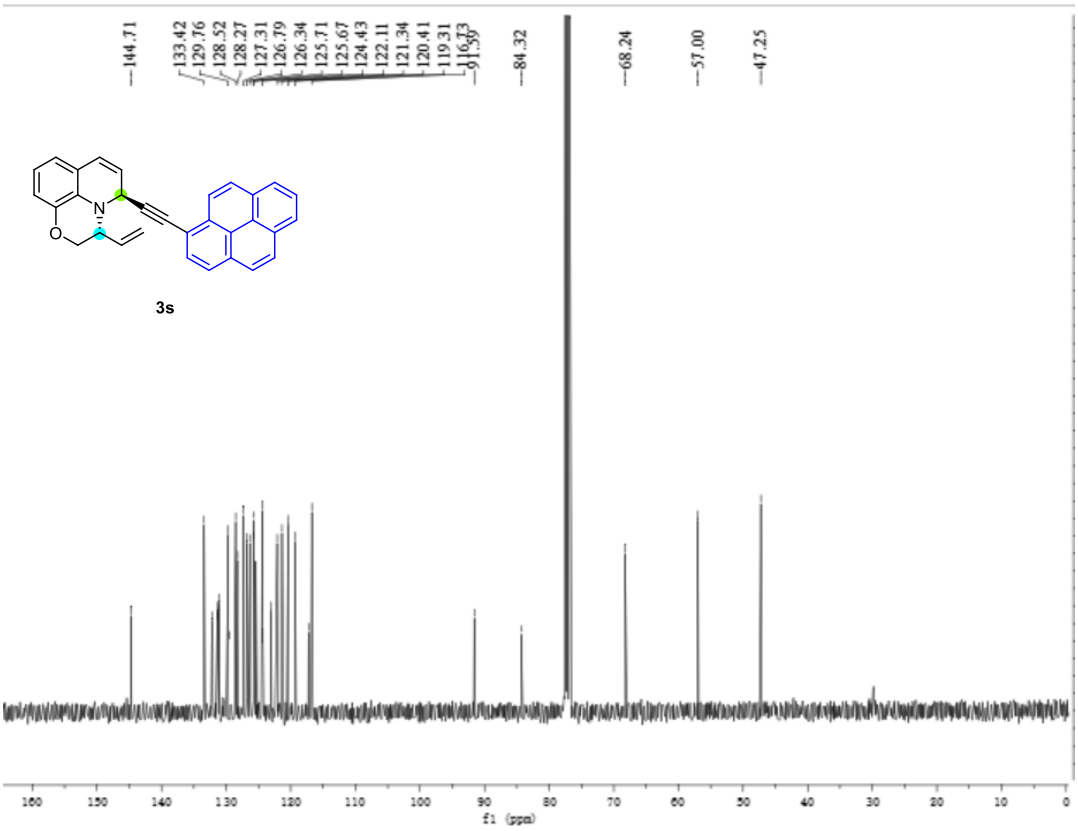
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.545	BB	0.3723	2419.46021	95.25137	50.0633
2	16.087	BV	0.5283	2413.33838	66.99350	49.9367

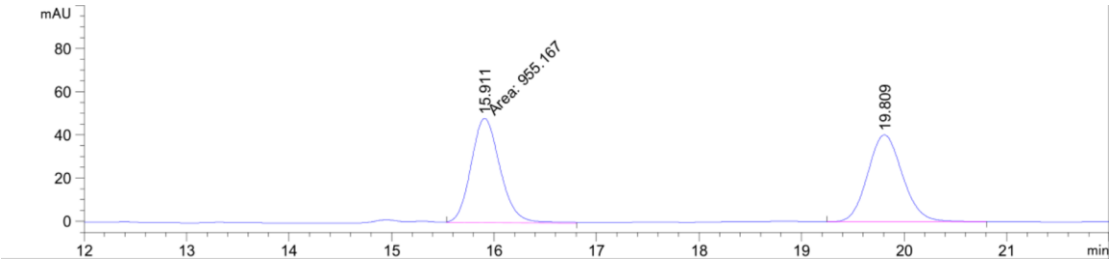


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.475	VB R	0.3795	6560.43799	253.81705	98.5604
2	16.075	BB	0.5051	95.82166	2.80106	1.4396

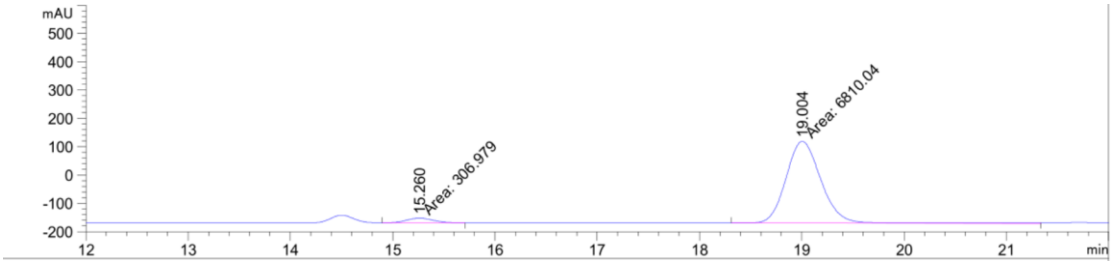

3s
f1 (ppm)


3s
f1 (ppm)



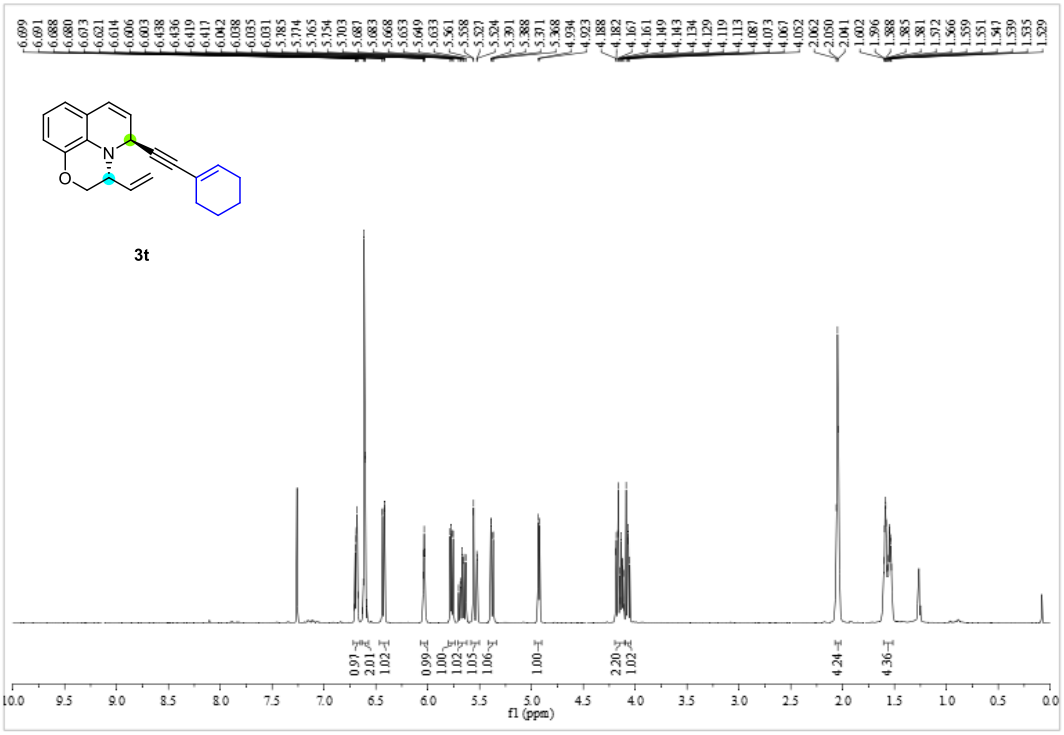
Signal 1: VWD1 A, Wavelength=254 nm

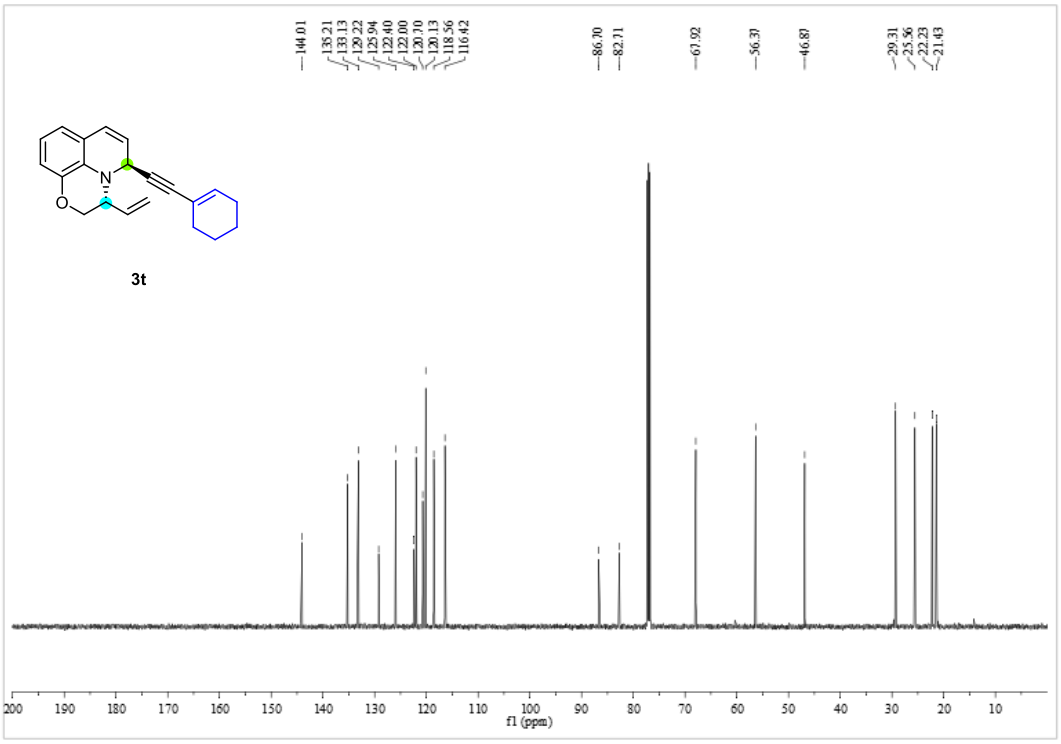
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.911	MM	0.3301	955.16656	48.23220	50.0942
2	19.809	BB	0.3660	951.57458	40.22305	49.9058

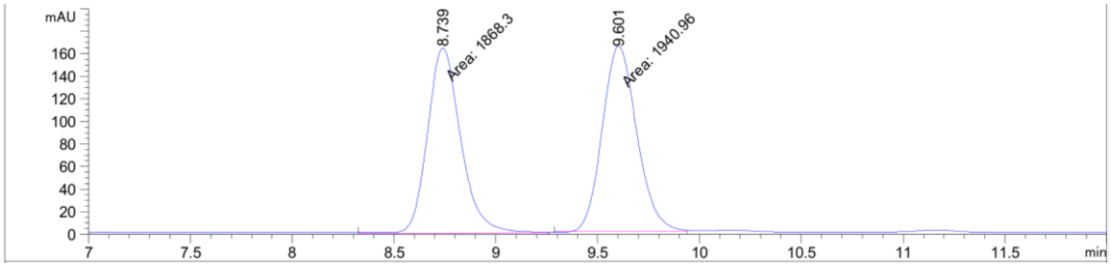


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.260	MM	0.3070	306.97891	16.66780	4.3133
2	19.004	MM	0.3932	6810.03662	288.62546	95.6867

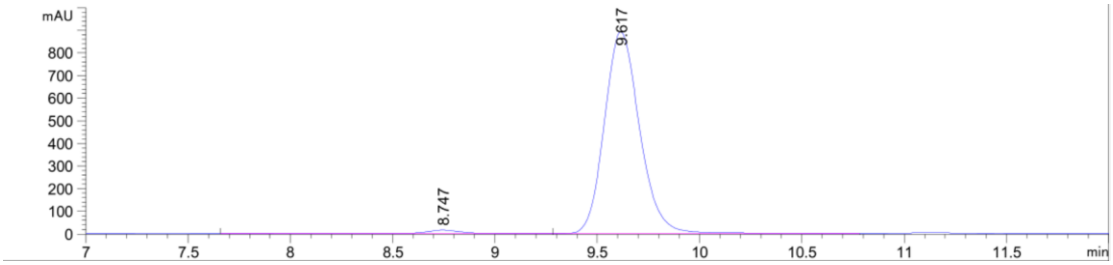

3t
f1 (ppm)


3t
f1 (ppm)



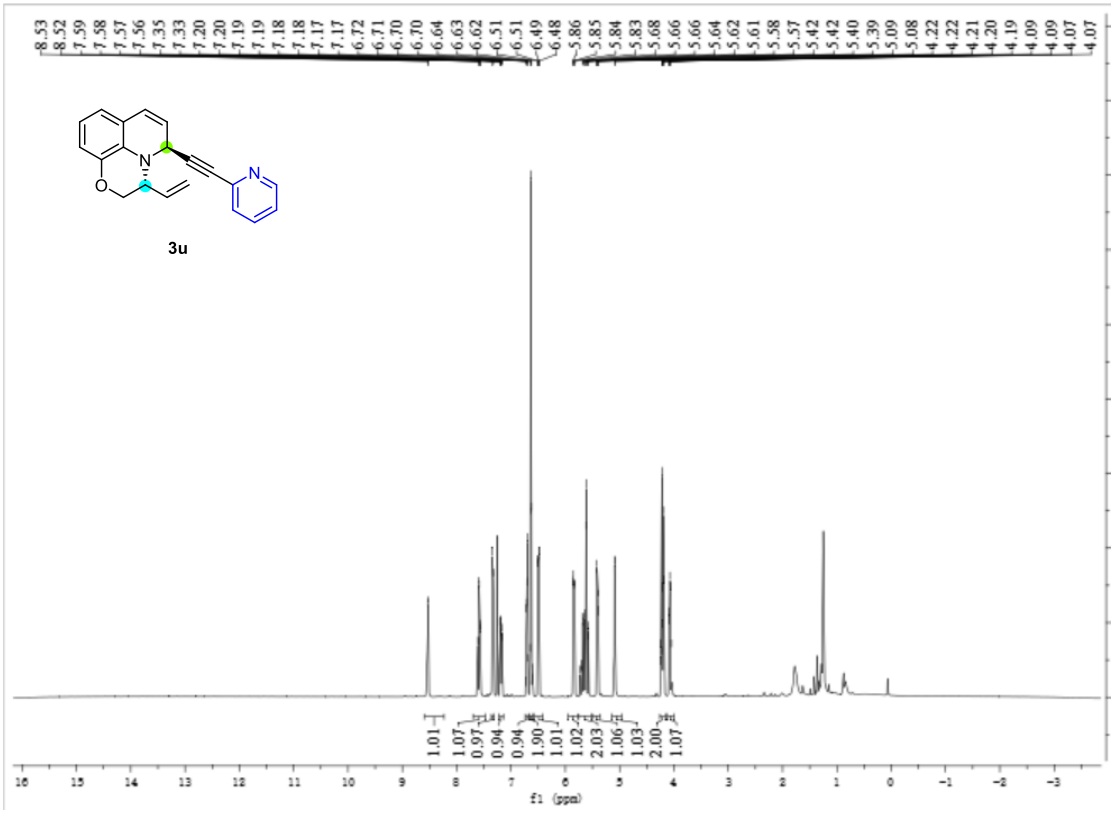
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.739	MM	0.1898	1868.30042	164.08736	49.0463
2	9.601	MM	0.1968	1940.95813	164.41782	50.9537

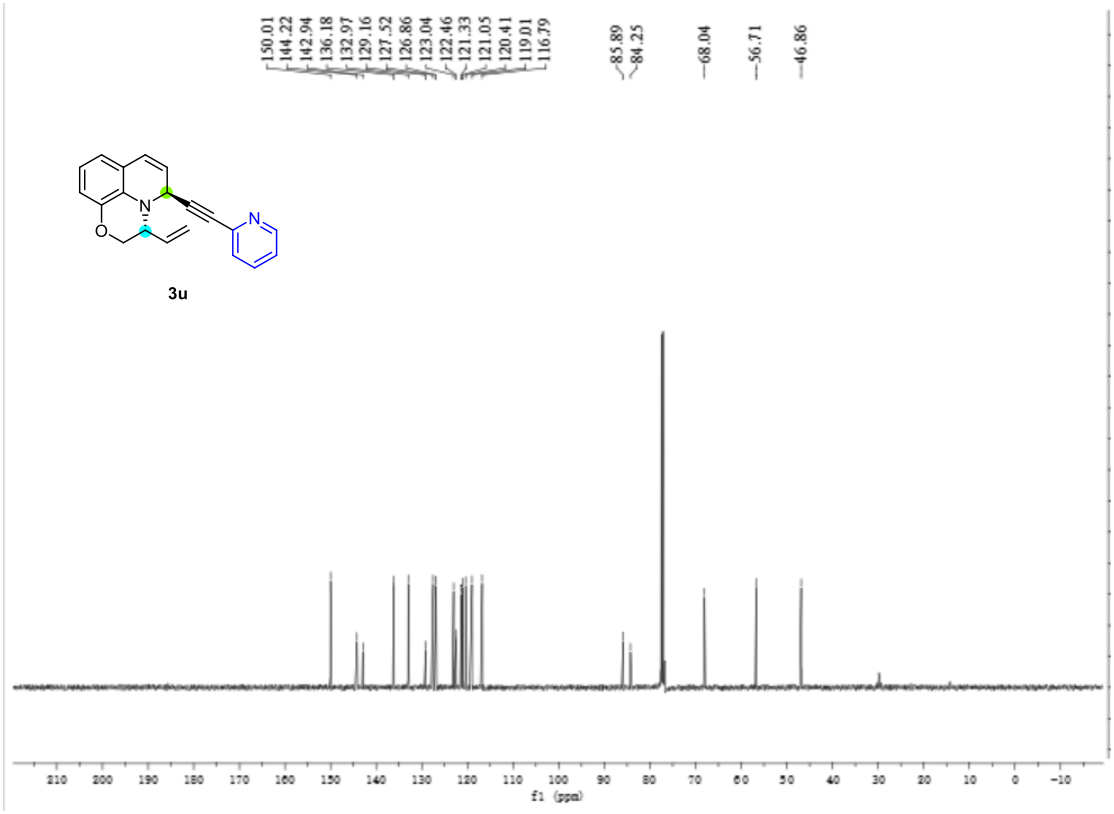


Signal 1: VWD1 A, Wavelength=254 nm

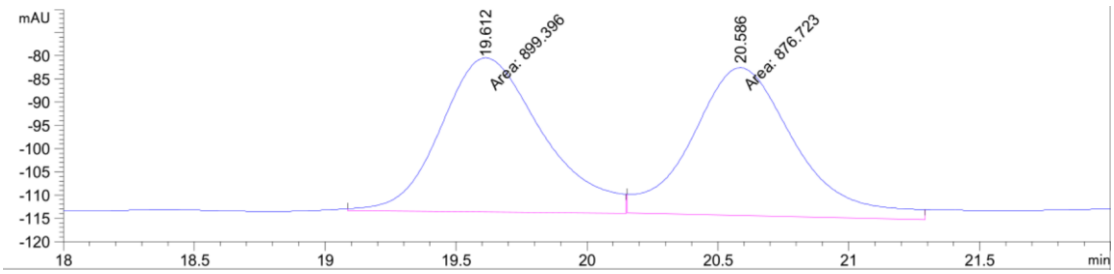
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.747	VB R	0.1736	222.68716	15.11140	2.0401
2	9.617	BB	0.1858	1.06929e4	892.10291	97.9599


8.53
8.52
7.59
7.58
7.57
7.56
7.35
7.33
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
6.72
6.71
6.70
6.70
6.64
6.63
6.62
6.51
6.51
6.49
6.48
5.86
5.85
5.84
5.83
5.68
5.66
5.66
5.64
5.62
5.61
5.58
5.57
5.42
5.42
5.40
5.39
5.09
5.08
4.22
4.22
4.21
4.20
4.19
4.09
4.09
4.07
4.07
1.01
1.07
0.97
0.94
0.94
1.90
1.01
1.02
2.03
1.06
1.03
2.00
1.07
f1 (ppm)

3u

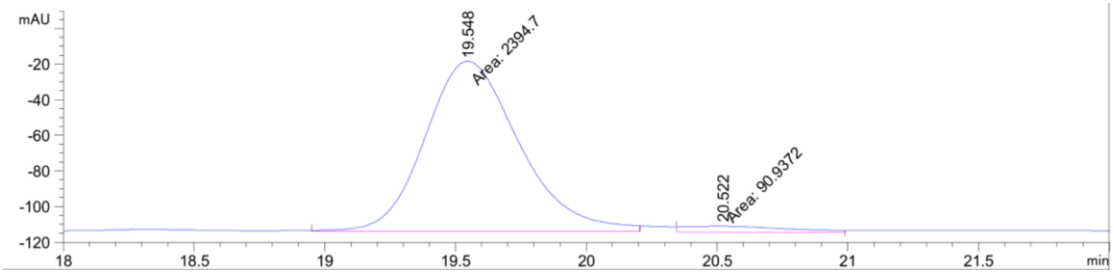

150.01
144.22
142.94
136.18
132.97
129.16
127.52
126.86
123.04
122.46
121.33
121.05
120.41
119.01
116.79
85.89
84.25
68.04
56.71
46.86
f1 (ppm)

3u



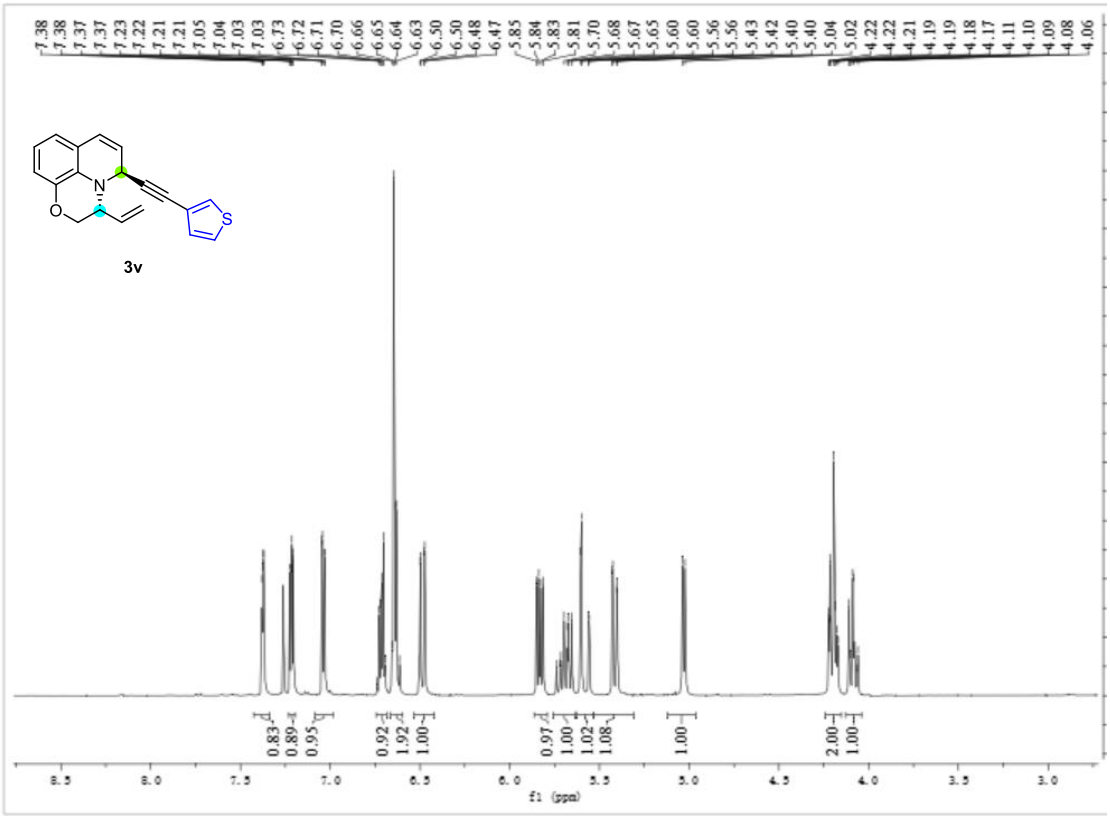
Signal 1: VWD1 A, Wavelength=254 nm

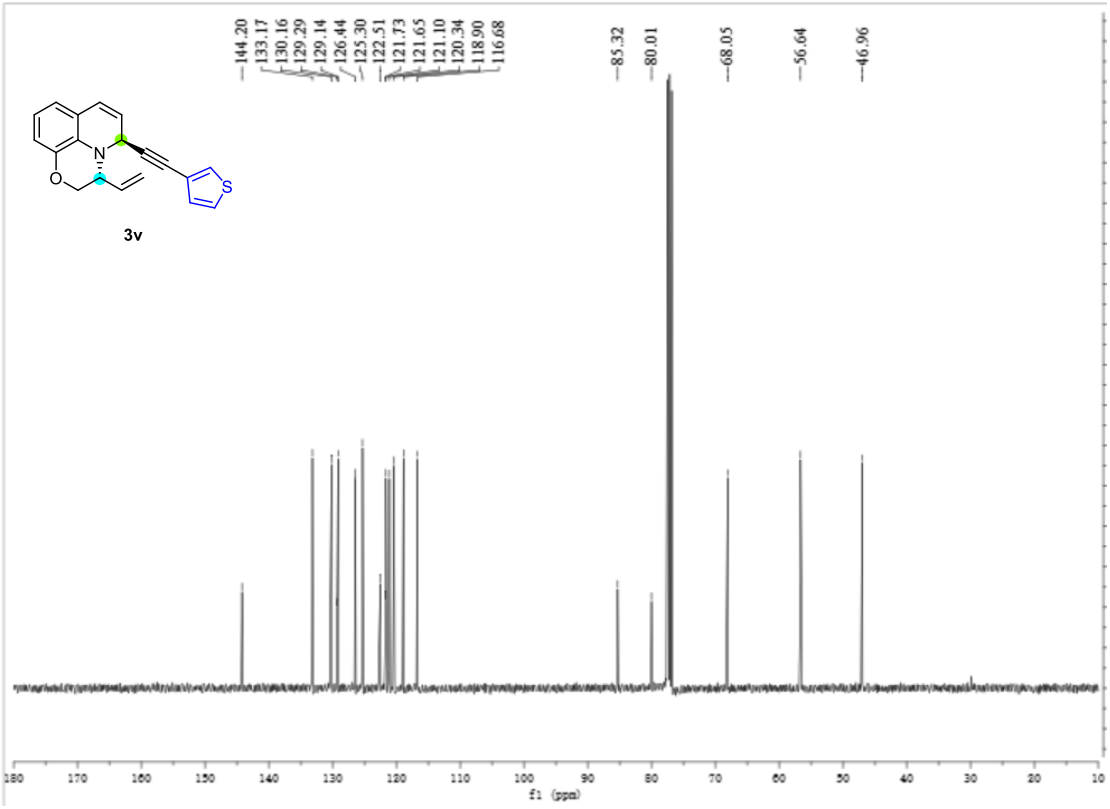
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.612	MM	0.4511	899.39569	33.23215	50.6383
2	20.586	MM	0.4593	876.72278	31.81444	49.3617

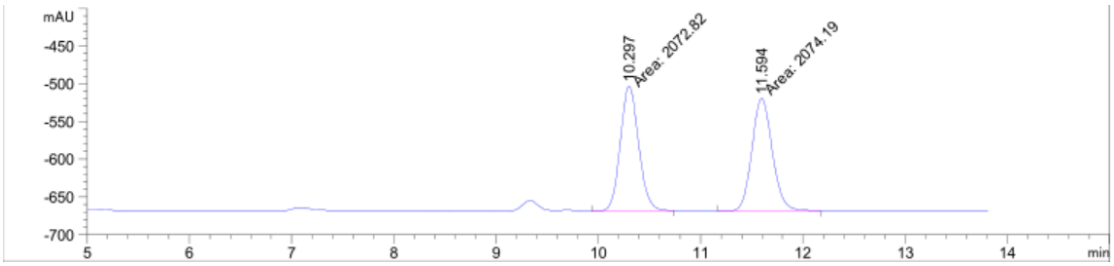


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.548	MM	0.4181	2394.69727	95.46526	96.3415
2	20.522	MM	0.4696	90.93725	3.22721	3.6585

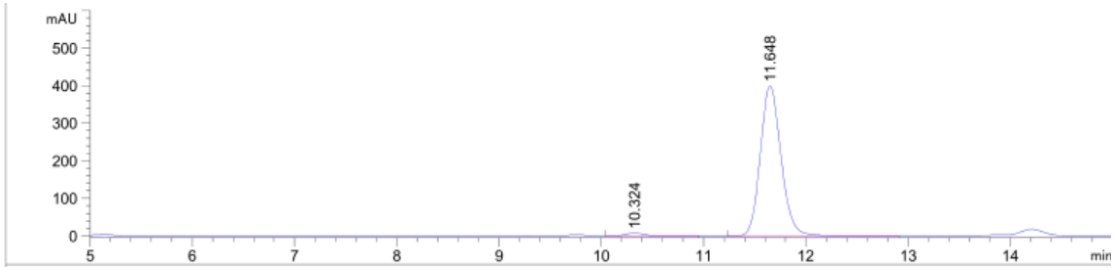

7.38
7.38
7.37
7.37
7.23
7.22
7.21
7.21
7.05
7.04
7.03
7.03
6.73
6.72
6.71
6.70
6.66
6.65
6.64
6.63
6.50
6.50
6.48
6.47
5.85
5.84
5.83
5.81
5.70
5.68
5.67
5.65
5.60
5.60
5.56
5.56
5.43
5.42
5.40
5.40
5.04
5.02
4.22
4.22
4.21
4.19
4.19
4.18
4.17
4.11
4.10
4.09
4.08
4.06
3v
0.83
0.89
0.95
0.92
1.92
1.00
0.97
1.00
1.02
1.08
1.00
2.00
1.00
f1 (ppm)


144.20
133.17
130.16
129.29
129.14
126.44
125.30
122.51
121.73
121.65
121.10
120.34
118.90
116.68
85.32
80.01
68.05
56.64
46.96
3v
f1 (ppm)



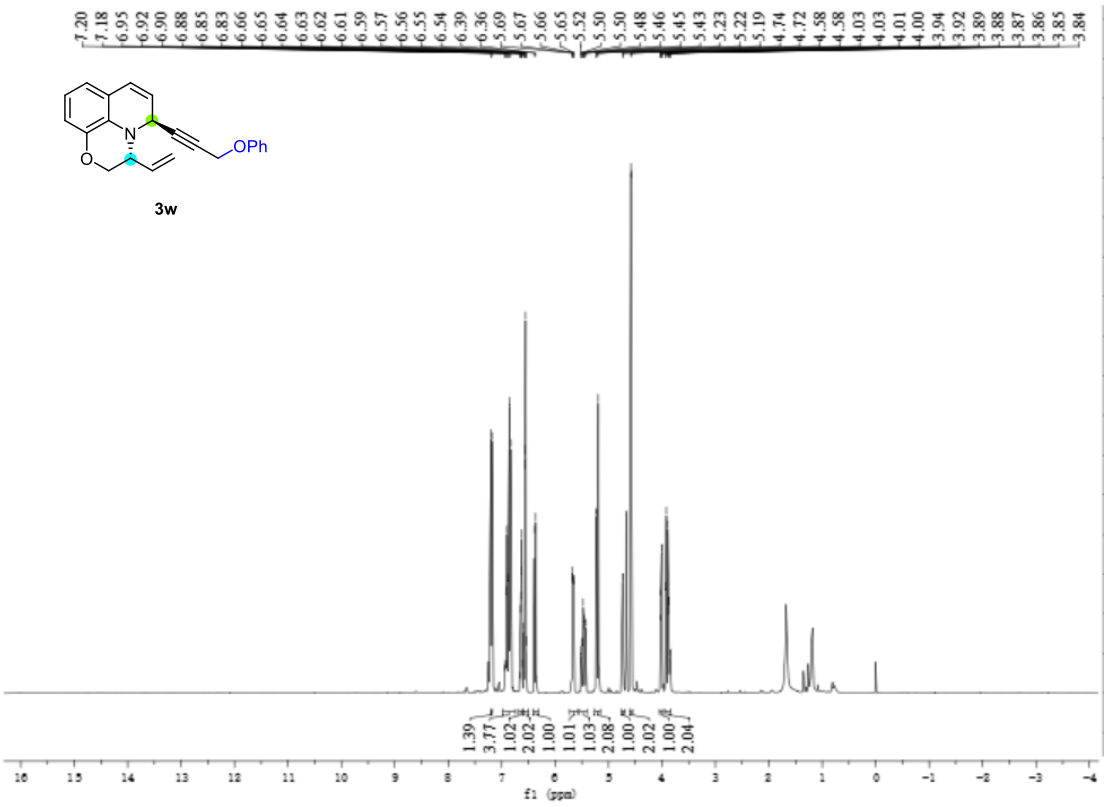
Signal 1: VWD1 A, Wavelength=254 nm

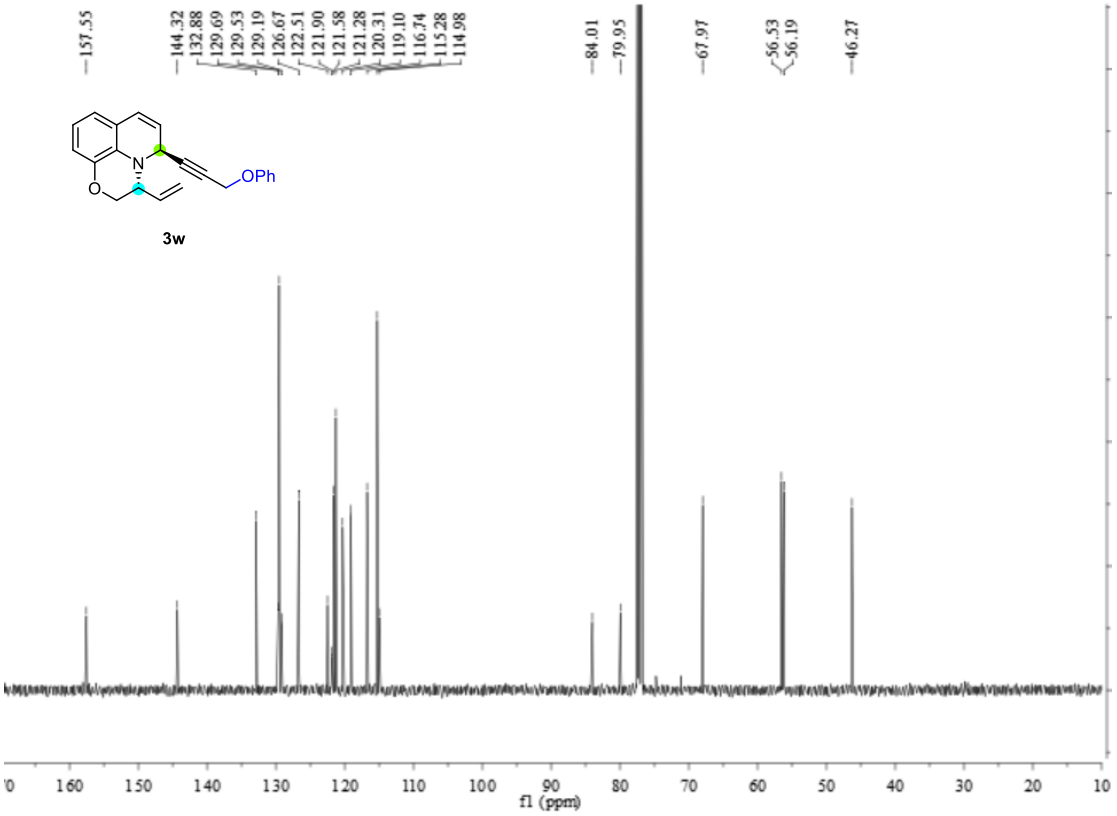
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.297	MM	0.2086	2072.81836	165.63225	49.9834
2	11.594	MM	0.2315	2074.19141	149.32179	50.0166

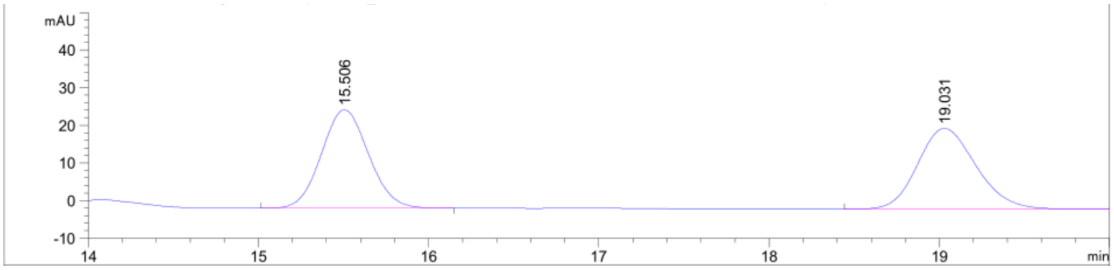


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.324	VB	0.1969	101.09009	7.92004	1.7591
2	11.648	BB	0.2169	5645.66162	399.51547	98.2409

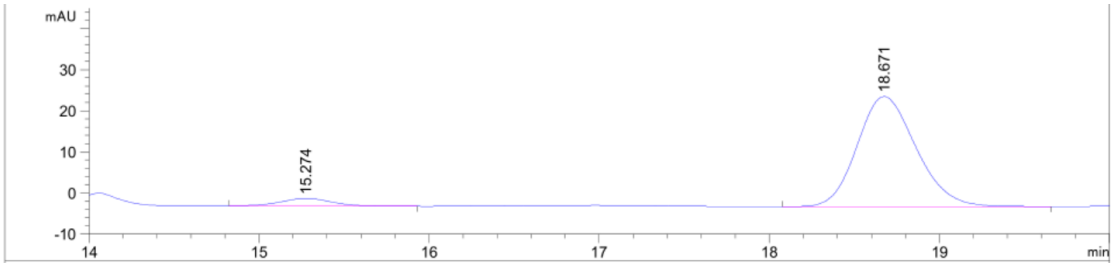

7.20
7.18
6.95
6.92
6.90
6.88
6.85
6.83
6.66
6.65
6.64
6.63
6.62
6.61
6.59
6.57
6.56
6.55
6.54
6.39
6.36
5.69
5.67
5.66
5.65
5.52
5.50
5.50
5.48
5.46
5.45
5.43
5.23
5.22
5.19
4.74
4.72
4.58
4.58
4.03
4.03
4.01
4.00
3.94
3.92
3.89
3.88
3.87
3.86
3.85
3.84
OPh
3w
1.39
3.77
1.02
2.02
1.00
1.01
1.03
2.08
1.00
2.02
1.00
2.04
f1 (ppm)


157.55
144.32
132.88
129.69
129.53
129.19
126.67
122.51
121.90
121.58
121.28
120.31
119.10
116.74
115.28
114.98
84.01
79.95
67.97
56.53
56.19
46.27
OPh
3w
f1 (ppm)



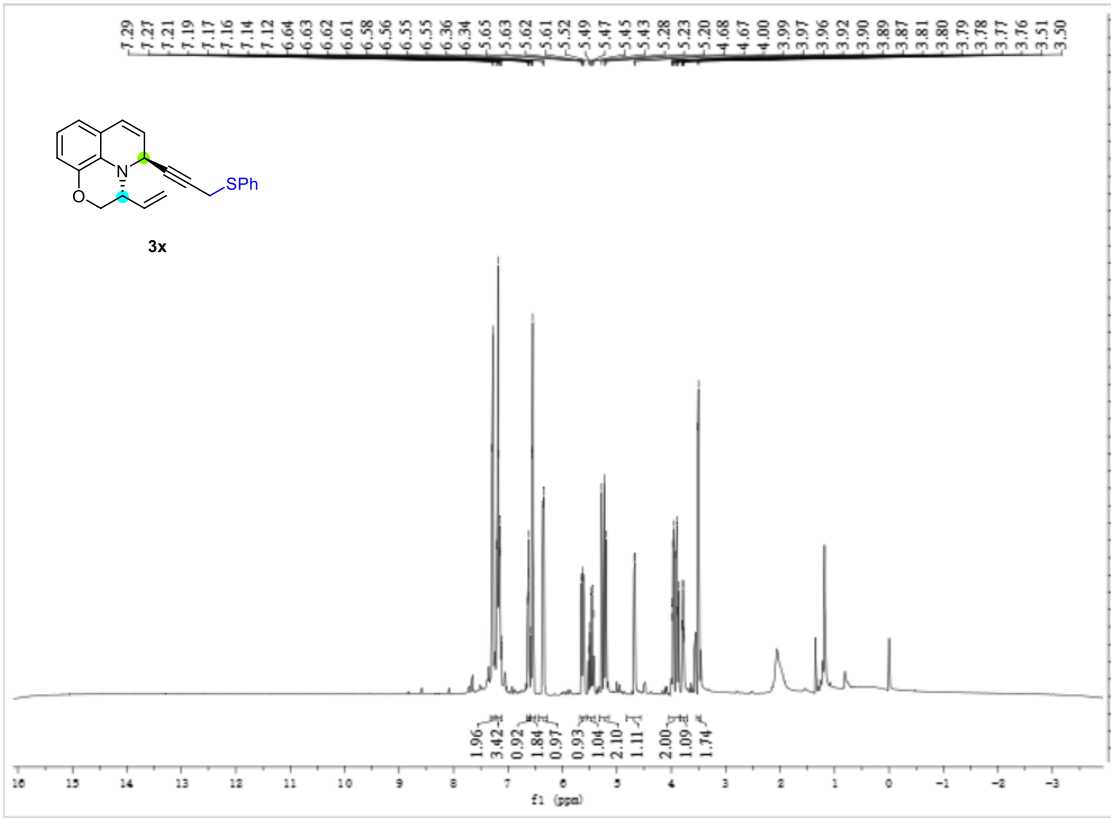
Signal 1: VWD1 A, Wavelength=254 nm

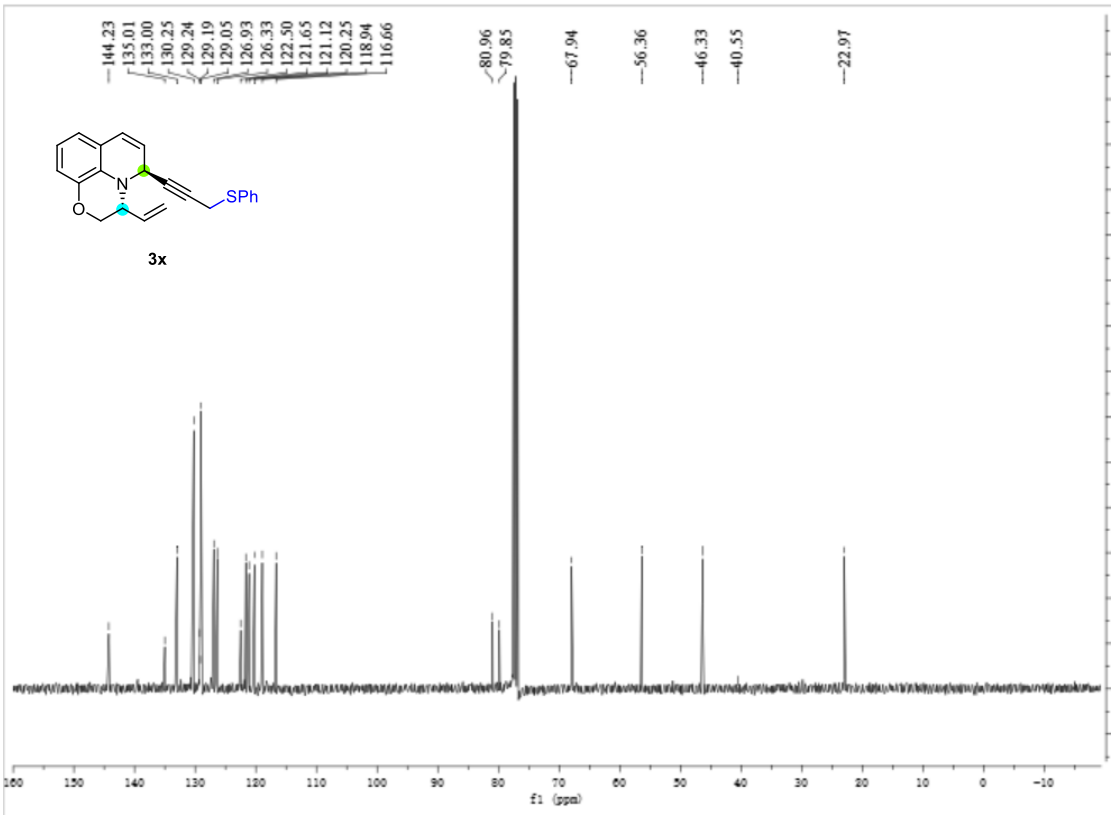
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.506	BB	0.3006	503.89444	26.16869	49.7190
2	19.031	BB	0.3694	509.59012	21.43000	50.2810

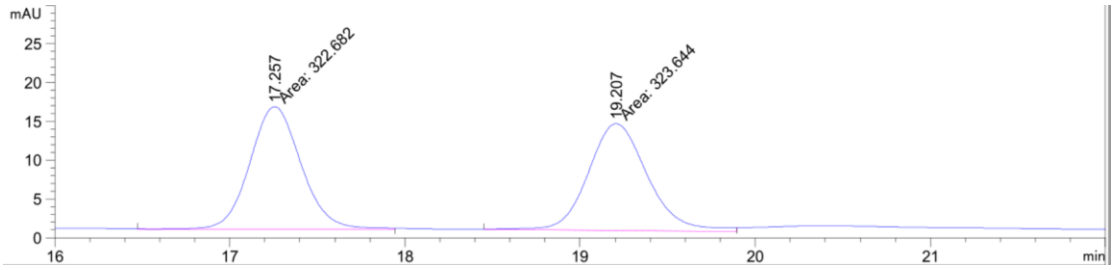


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.274	BB	0.3172	37.09081	1.80936	5.4533
2	18.671	BB	0.3723	643.06769	26.76755	94.5467

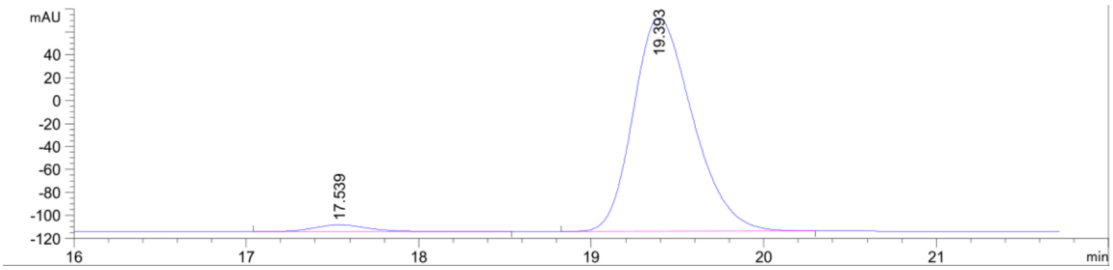

7.29
7.27
7.21
7.19
7.17
7.16
7.14
7.12
6.64
6.63
6.62
6.61
6.58
6.56
6.55
6.55
6.36
6.34
5.65
5.63
5.62
5.61
5.52
5.49
5.47
5.45
5.43
5.28
5.23
5.20
4.68
4.67
4.00
3.99
3.97
3.96
3.92
3.90
3.89
3.87
3.81
3.80
3.79
3.78
3.77
3.76
3.51
3.50
SPh
3x
1.96
3.42
0.92
1.84
0.97
0.93
1.04
2.10
1.11
2.00
1.09
1.74
f1 (ppm)


144.23
135.01
133.00
130.25
129.24
129.19
129.05
126.93
126.33
122.50
121.65
121.12
120.25
118.94
116.66
80.96
79.85
67.94
56.36
46.33
40.55
22.97
SPh
3x
f1 (ppm)



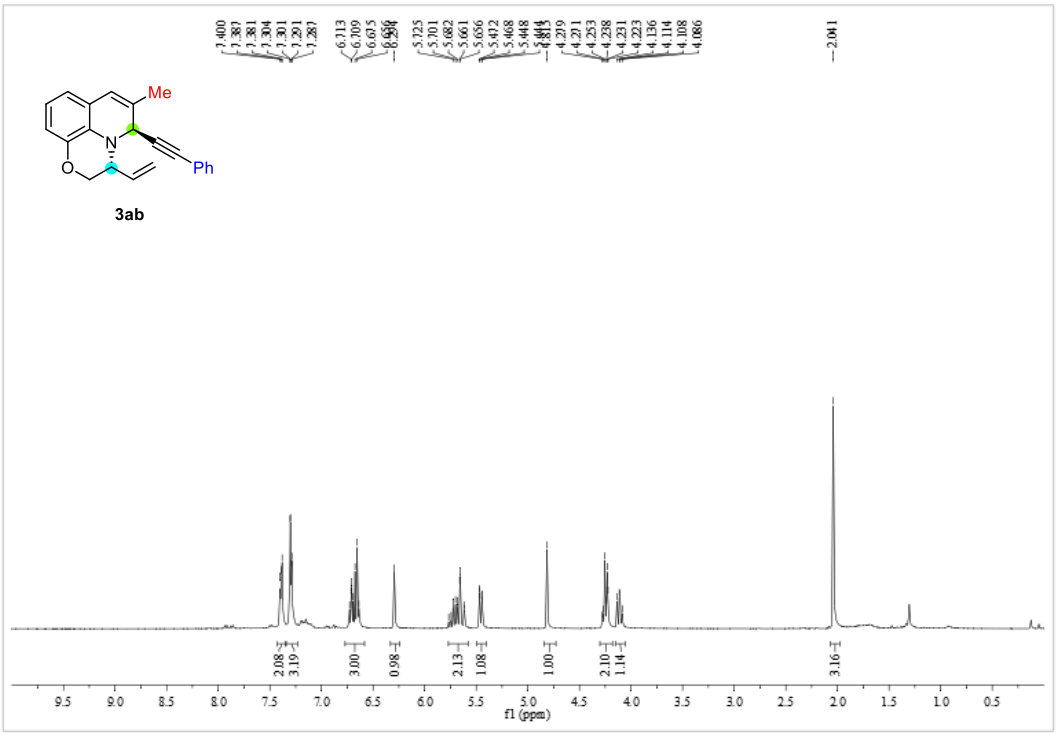
Signal 1: VWD1 A, Wavelength=254 nm

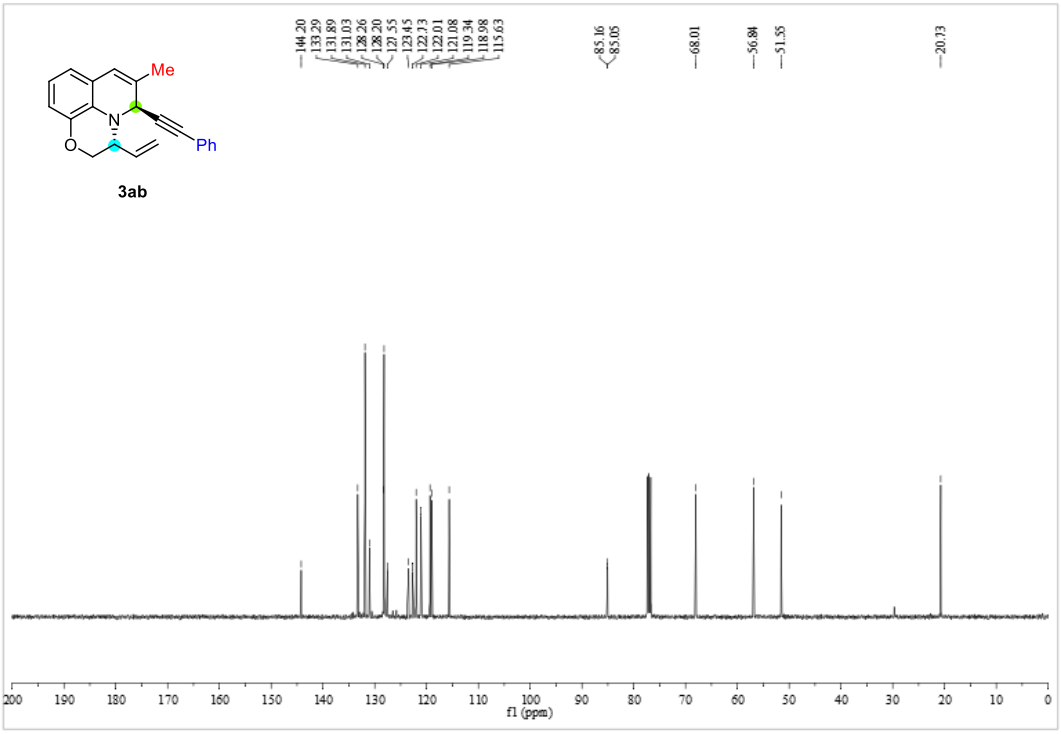
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.257	MM	0.3402	322.68185	15.80914	49.9256
2	19.207	MM	0.3916	323.64392	13.77419	50.0744

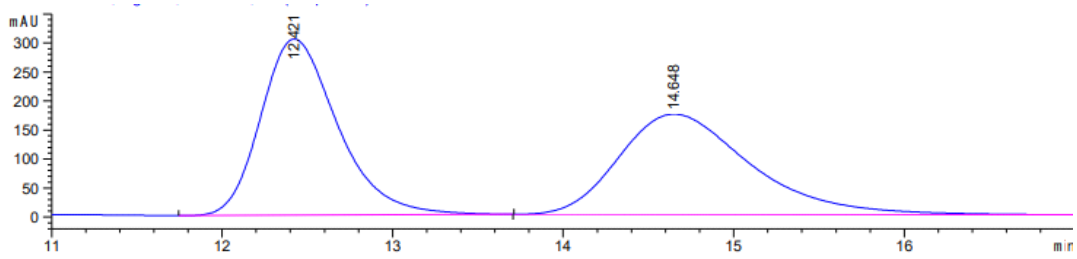


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.539	BB	0.3297	125.33646	5.85717	2.7399
2	19.393	BB	0.3691	4449.14795	185.95331	97.2601

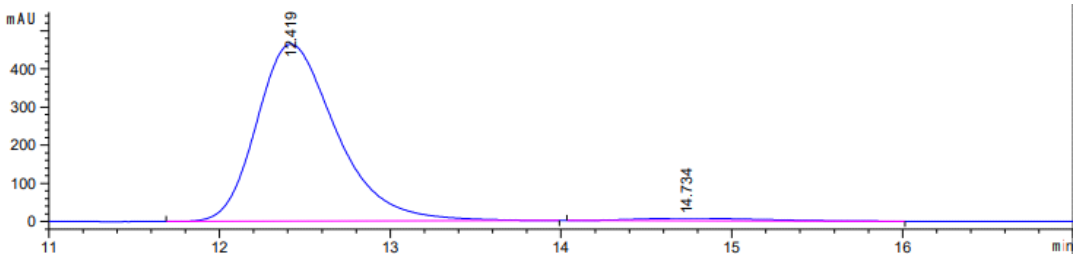

Me
Ph
3ab
f1 (ppm)


Me
Ph
3ab
f1 (ppm)



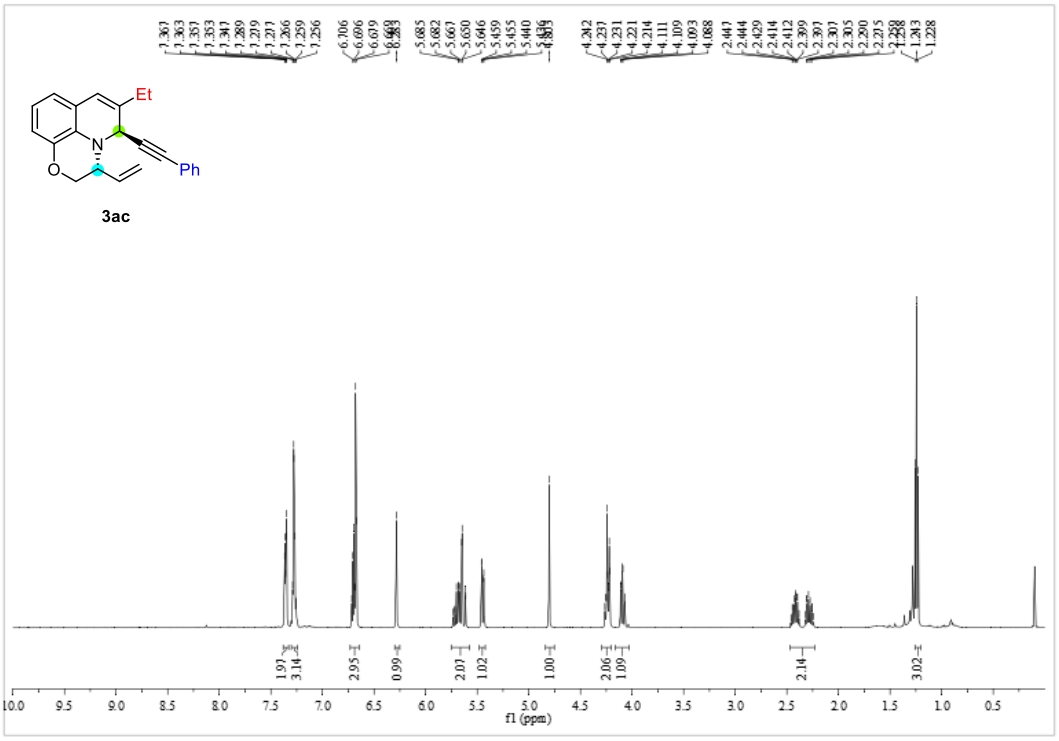
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

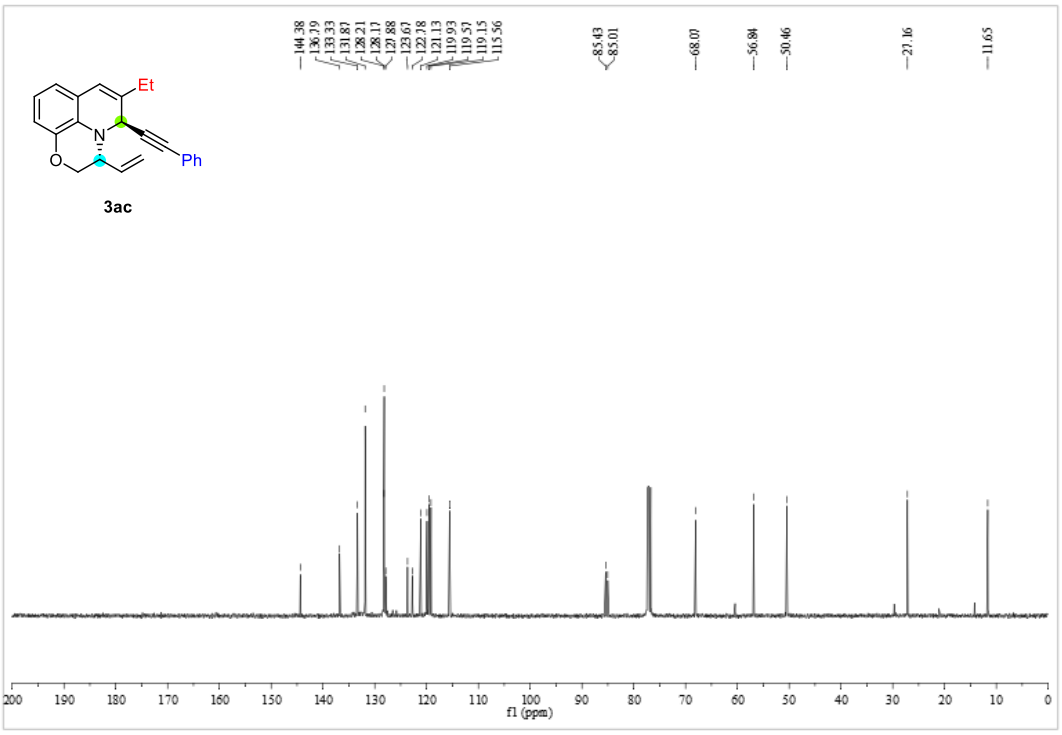
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.421	BB	0.4795	9508.14844	303.53802	50.4432
2	14.648	BBA	0.8219	9341.05078	173.00548	49.5568

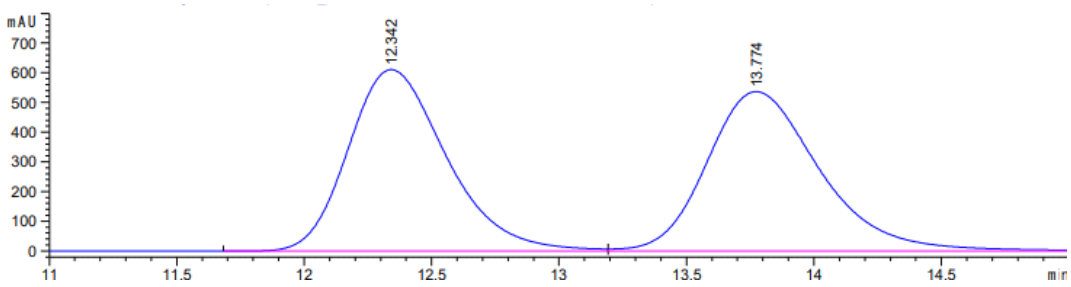


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.419	BB	0.4946	1.50868e4	464.85904	97.7206
2	14.734	BB	0.6097	351.90445	6.84582	2.2794

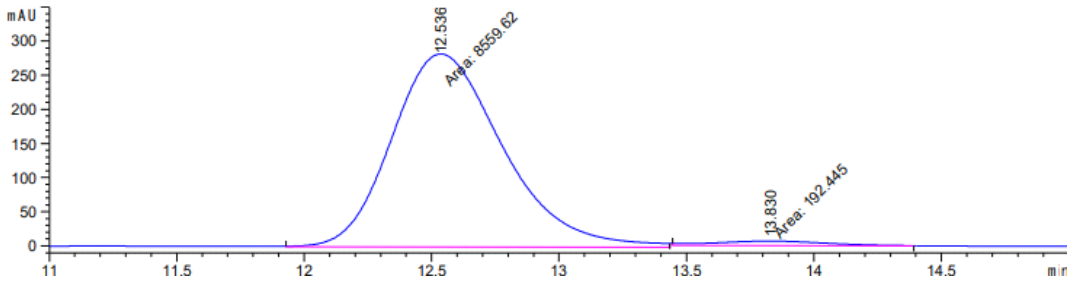

Et
N
O
Ph
3ac
f1 (ppm)


Et
N
O
Ph
3ac
f1 (ppm)



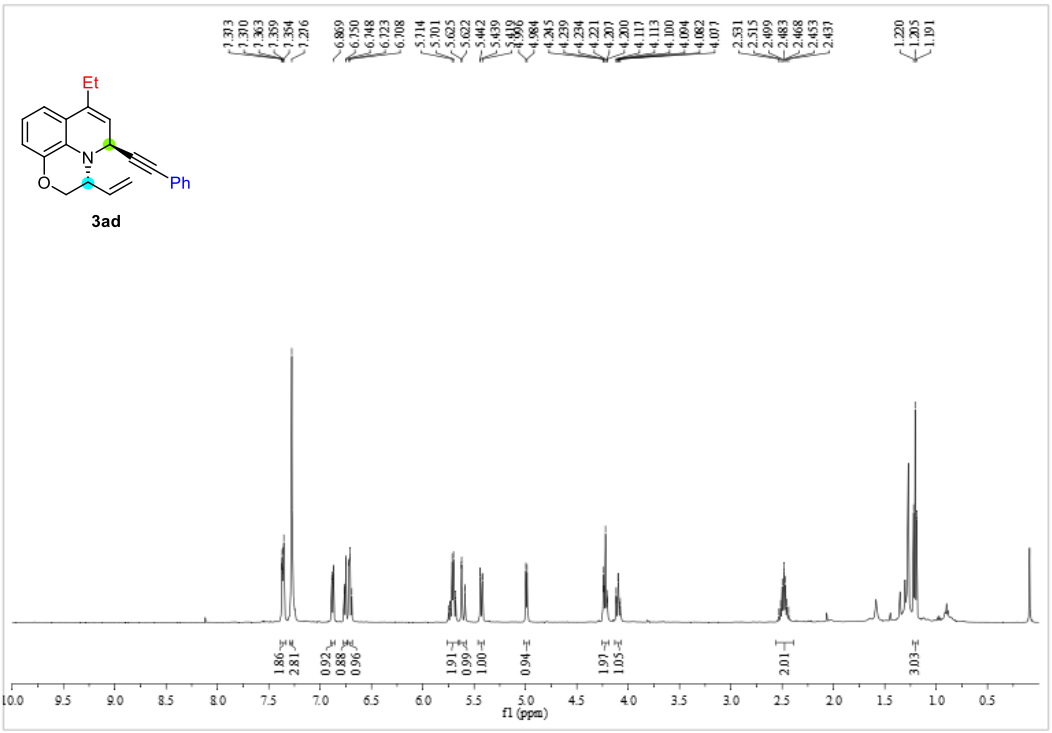
Signal 1: VWD1 A, Wavelength=254 nm

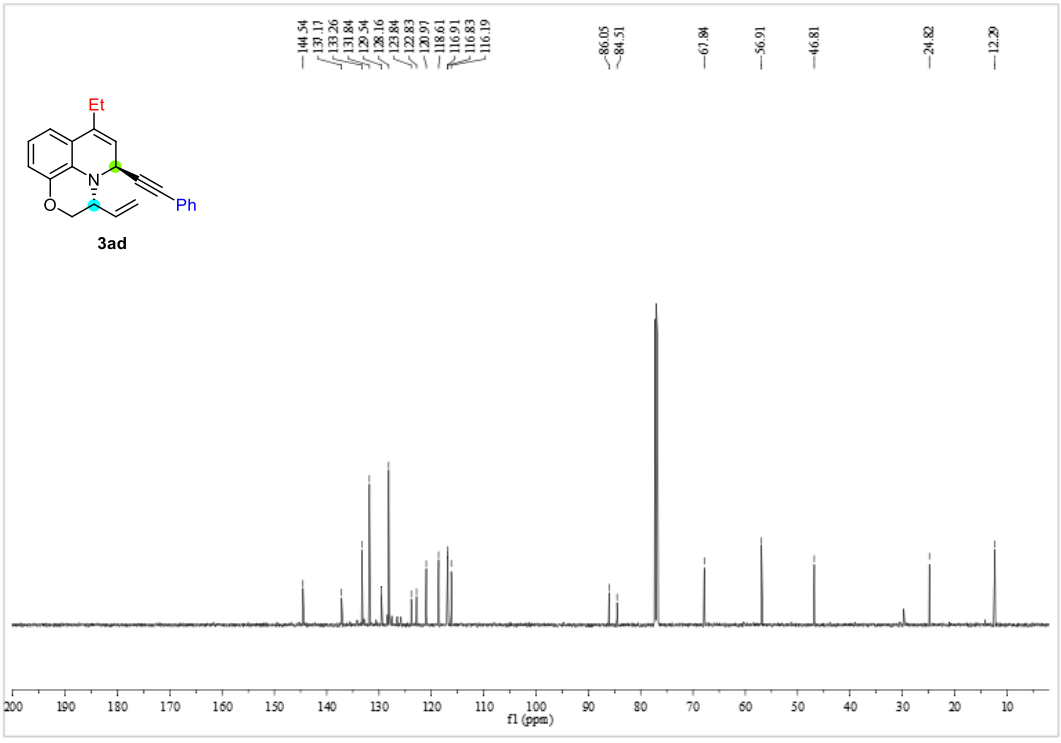
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.342	BV	0.4130	1.64075e4	611.47980	49.7192
2	13.774	VBA	0.4725	1.65929e4	536.91687	50.2808

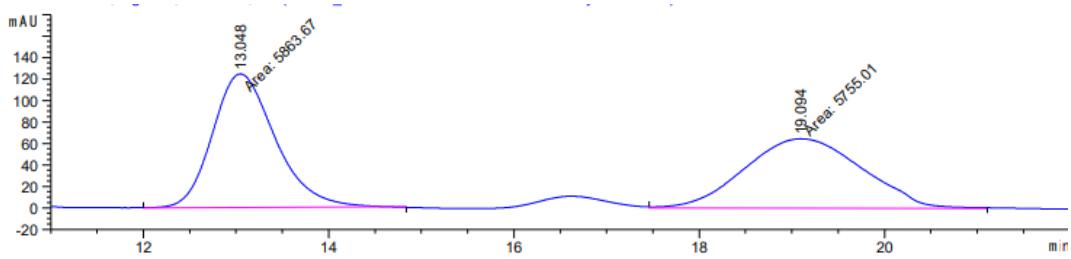


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.536	MM	0.5048	8559.61914	282.59146	97.8011
2	13.830	MM	0.5073	192.44502	6.32280	2.1989

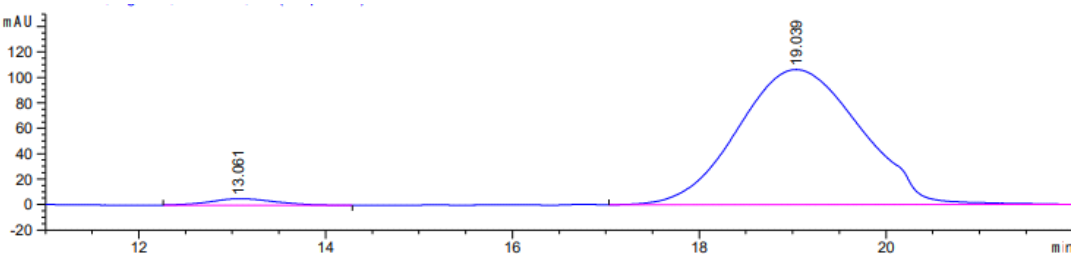

Et
N
O
Ph
3ad
7.373
7.370
7.363
7.359
7.354
7.216
6.869
6.750
6.748
6.723
6.708
5.714
5.701
5.625
5.622
5.442
5.439
4.984
4.245
4.239
4.234
4.221
4.207
4.200
4.117
4.113
4.100
4.094
4.082
4.077
2.531
2.515
2.499
2.483
2.468
2.453
2.437
1.220
1.205
1.191
1.86
2.81
0.92
0.88
0.96
1.91
0.99
1.00
0.94
1.97
1.05
2.01
3.03
f1 (ppm)


Et
N
O
Ph
3ad
144.54
137.17
133.26
131.84
129.54
128.16
123.84
122.83
120.97
118.61
116.91
116.83
116.19
86.05
84.51
67.84
56.91
46.81
24.82
12.29
f1 (ppm)



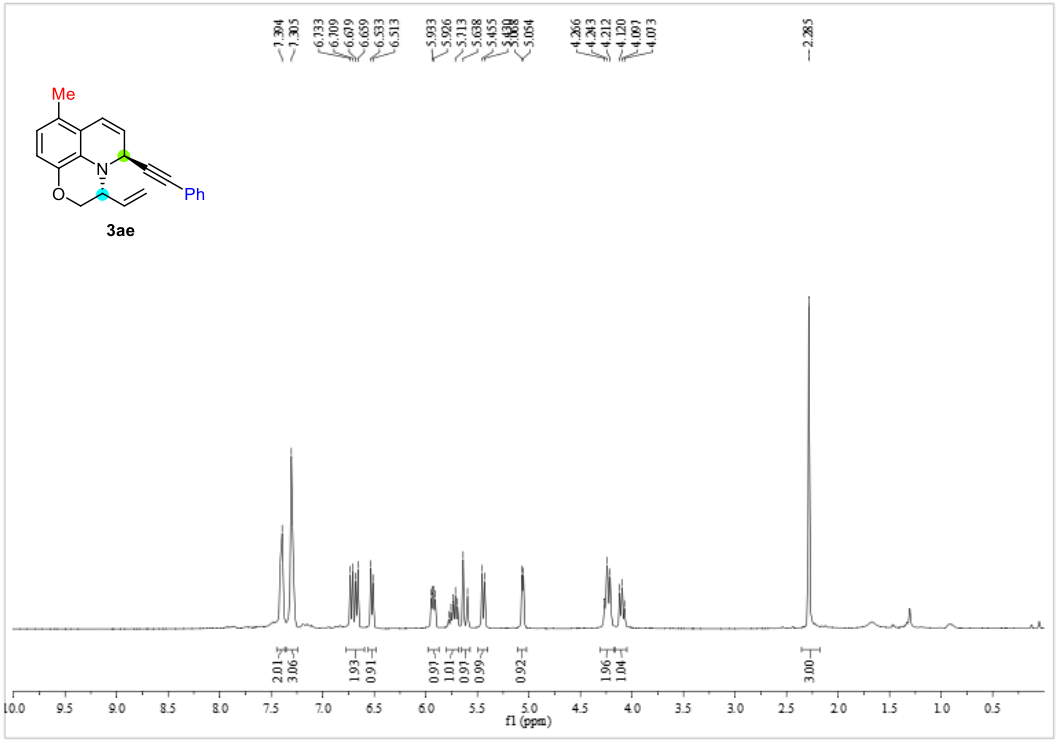
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

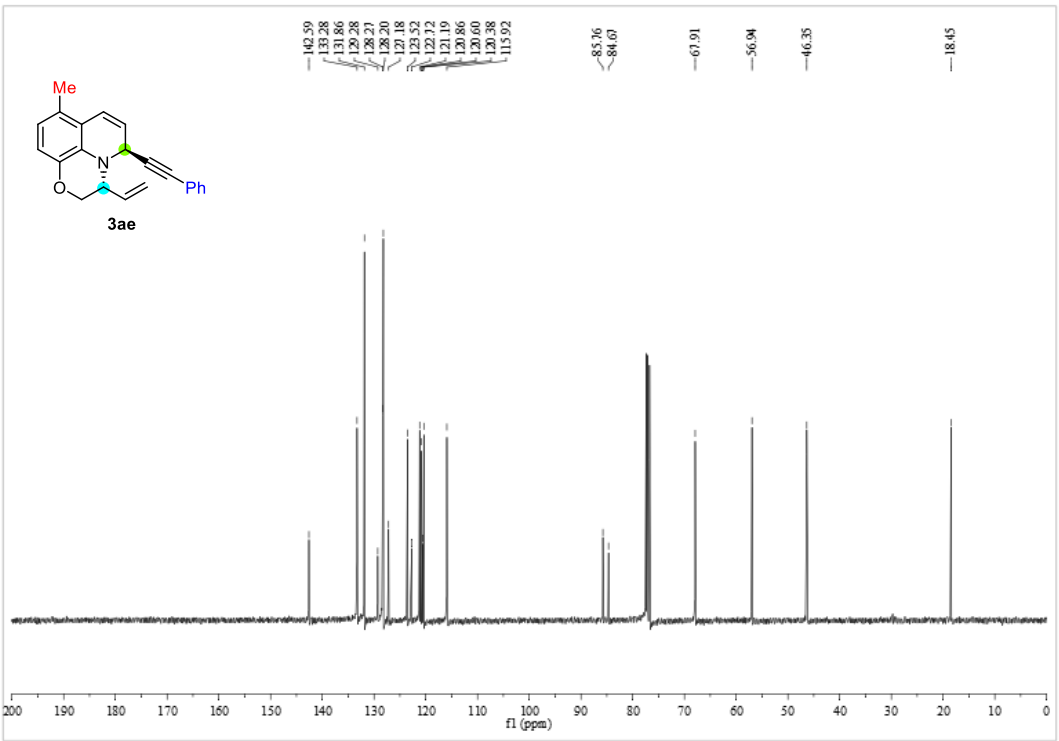
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.048	MM	0.7849	5863.66504	124.51756	50.4676
2	19.094	MM	1.4796	5755.01221	64.82784	49.5324

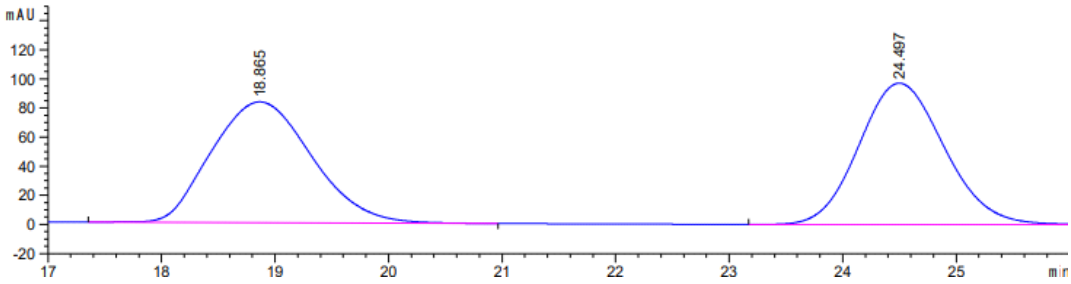


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.061	BB	0.5715	242.02629	5.04690	2.4221
2	19.039	BB	1.2289	9750.32617	106.42563	97.5779

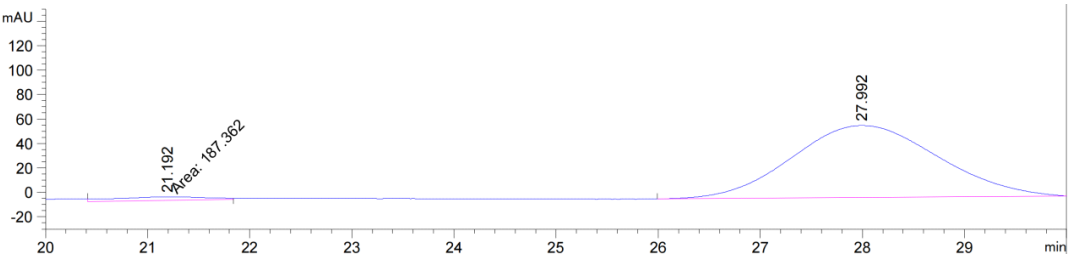

Me
Ph
3ae
7.394
7.305
6.733
6.709
6.689
6.689
6.533
6.513
5.933
5.926
5.713
5.638
5.455
5.054
4.266
4.243
4.212
4.120
4.097
4.073
2.285
2.01
3.06
1.93
0.91
0.91
1.01
0.97
0.99
0.92
1.96
1.04
3.00
f1 (ppm)


Me
Ph
3ae
142.59
133.28
131.86
129.28
128.27
128.20
127.18
123.52
122.72
121.19
120.86
120.60
120.38
115.92
85.76
84.60
67.91
56.94
46.35
18.45
f1 (ppm)



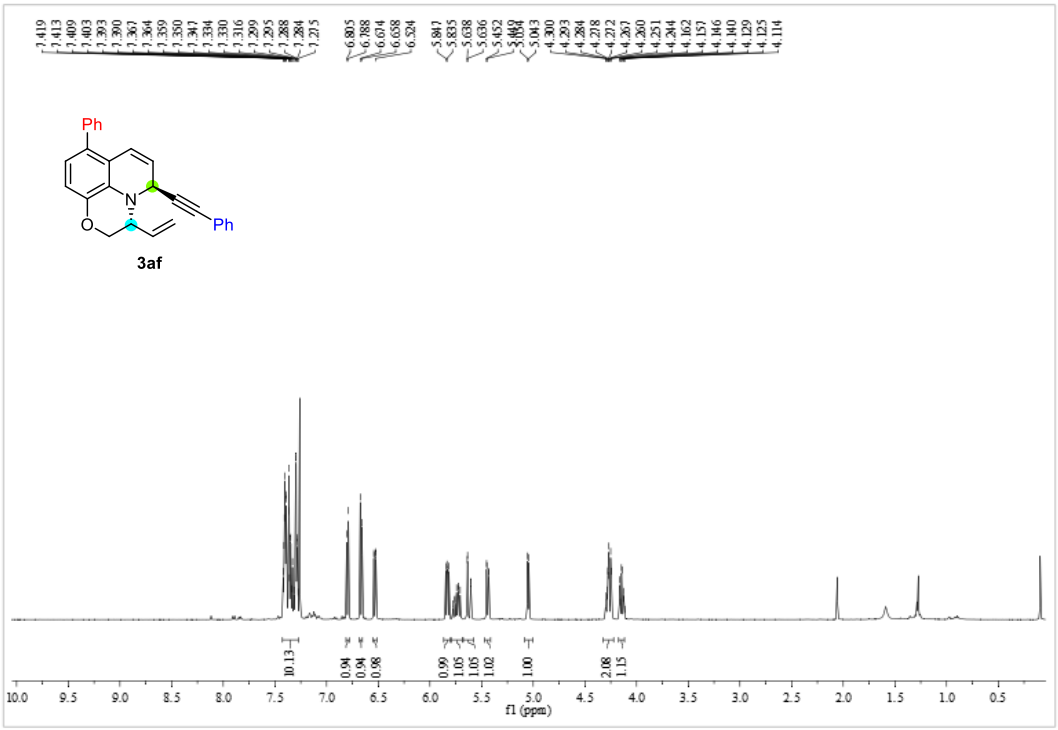
Signal 1: VWD1 A, Wavelength=254 nm

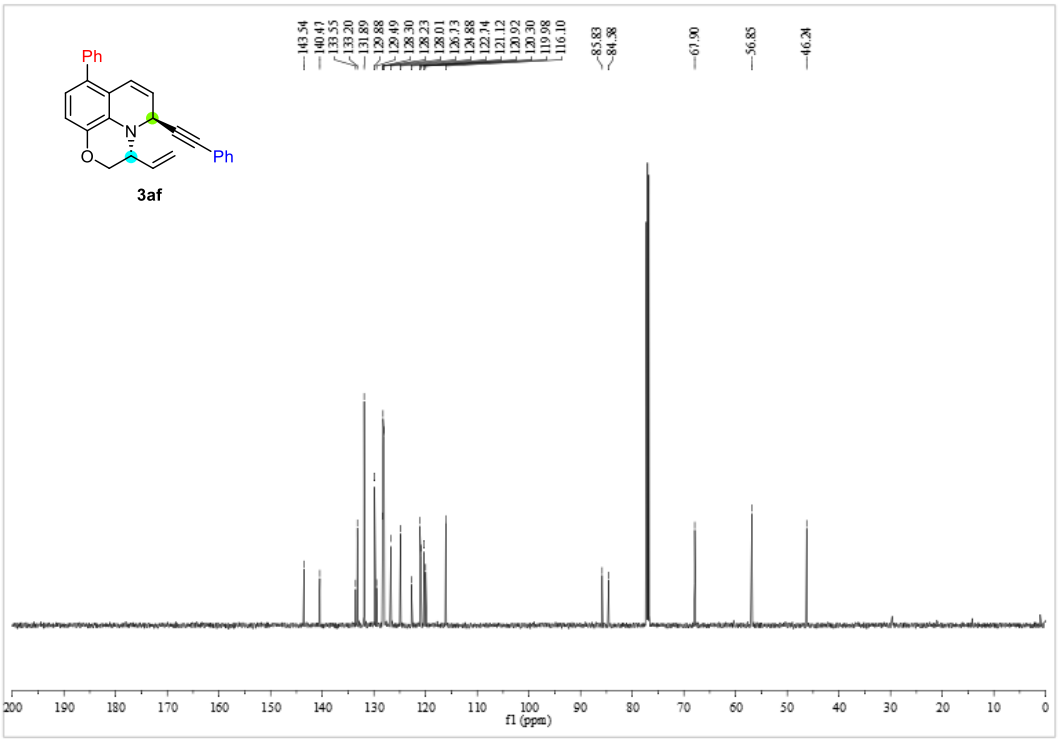
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.865	BB	1.0070	5106.94922	83.09690	50.0793
2	24.497	BBA	0.8157	5090.78564	97.09962	49.9207

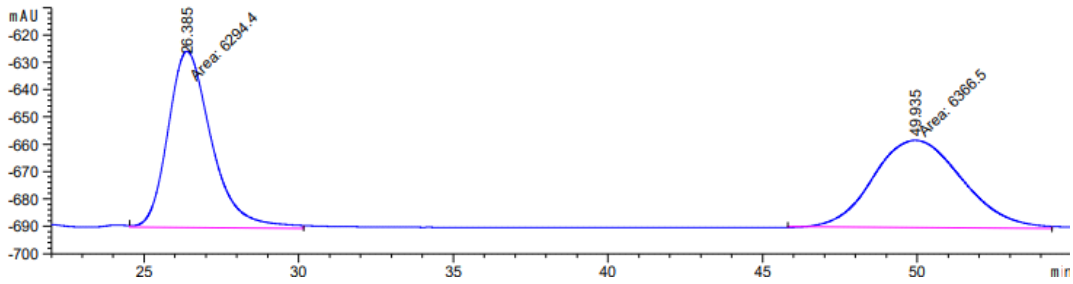


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.192	MM	1.0533	187.36182	2.96464	3.1124
2	27.992	BBA	1.1671	5832.45850	58.90643	96.8876

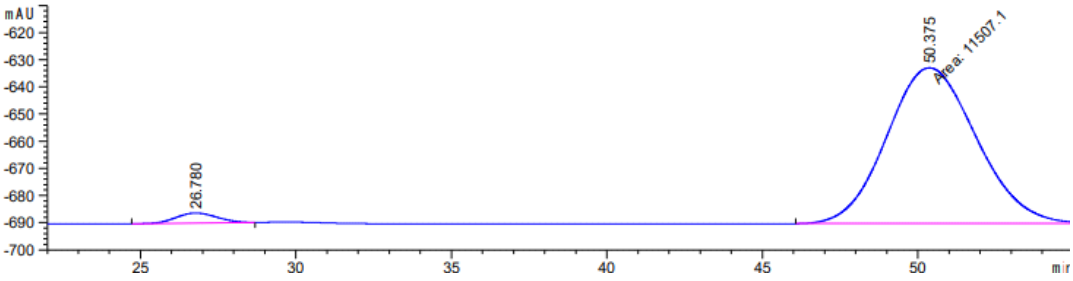

Ph
N
O
Ph
3af
f1 (ppm)


Ph
N
O
Ph
3af
f1 (ppm)



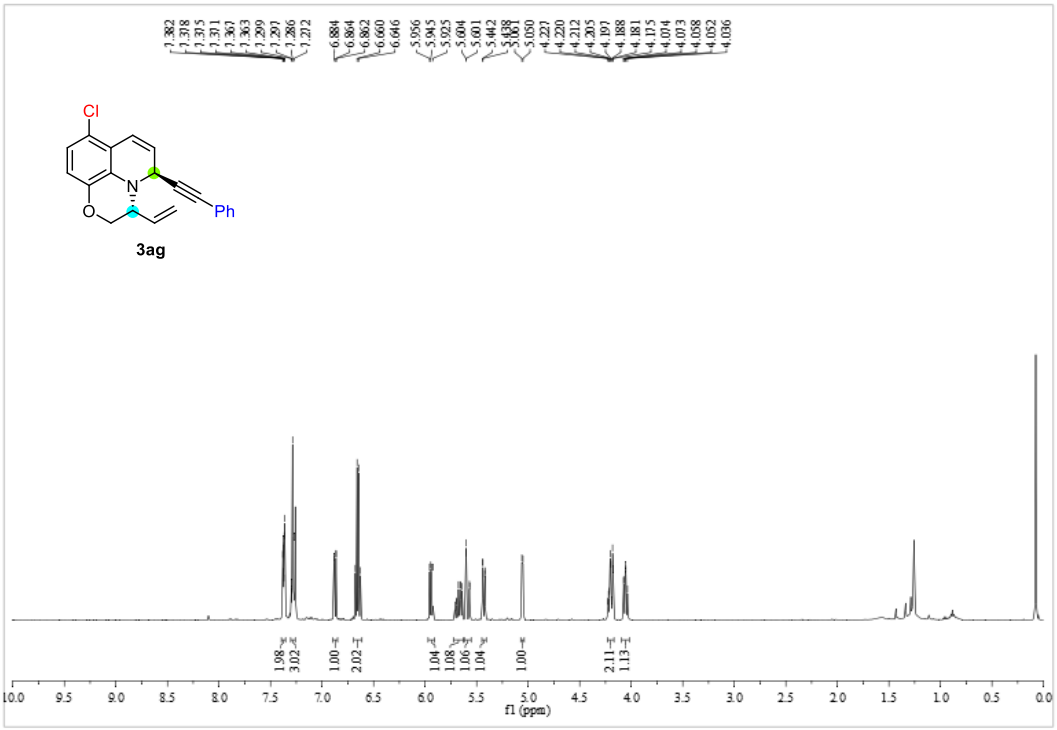
Signal 1: VWD1 A, Wavelength=254 nm

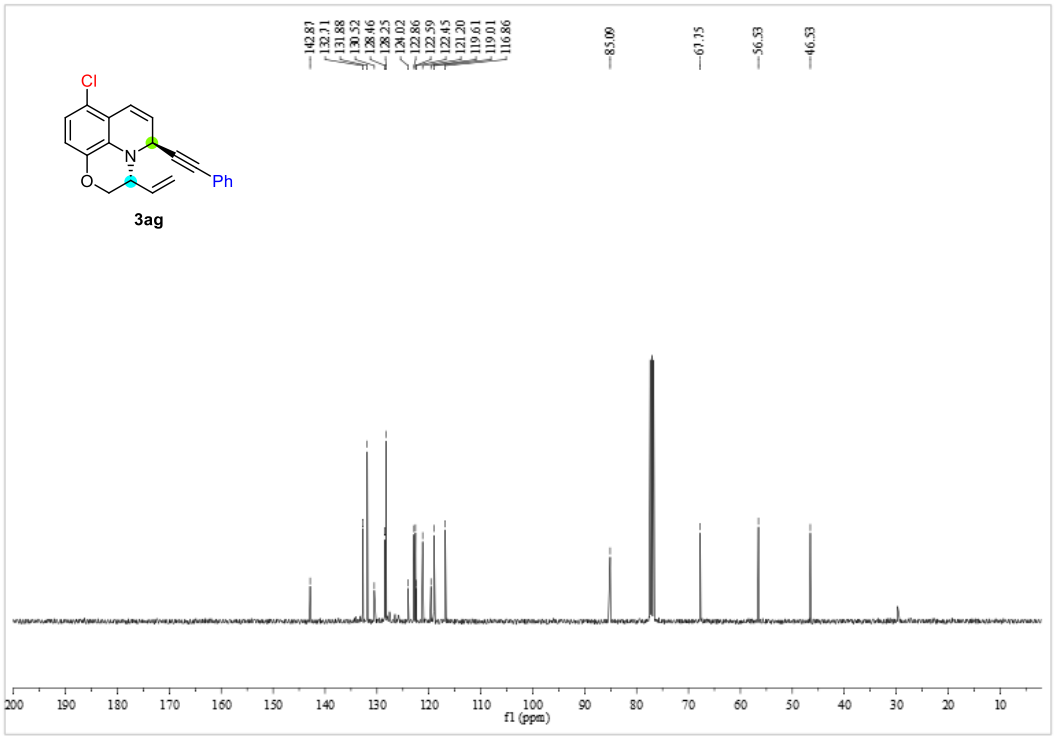
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.386	BB	1.4640	6134.84570	63.90345	49.0956
2	49.930	MM	3.3279	6360.86914	31.85603	50.9044

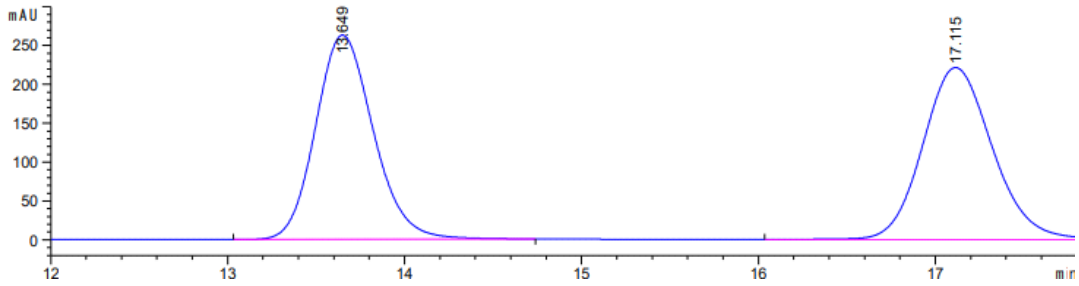


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.780	BB	1.0843	340.49634	3.72561	2.9172
2	50.375	MM	3.3112	1.13313e4	57.03605	97.0828

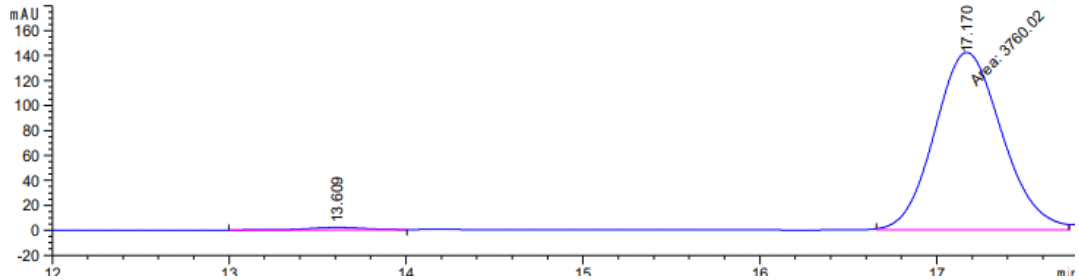

Cl
N
O
Ph
3ag
f1 (ppm)


Cl
N
O
Ph
3ag
f1 (ppm)



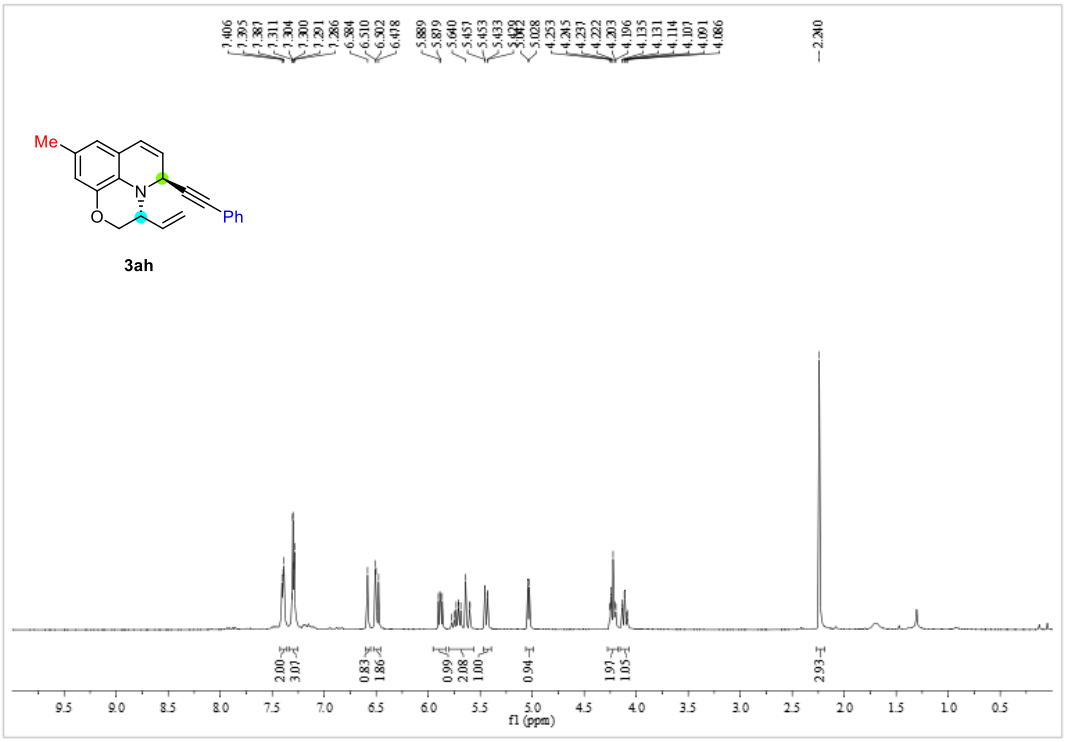
Signal 1: VWD1 A, Wavelength=254 nm

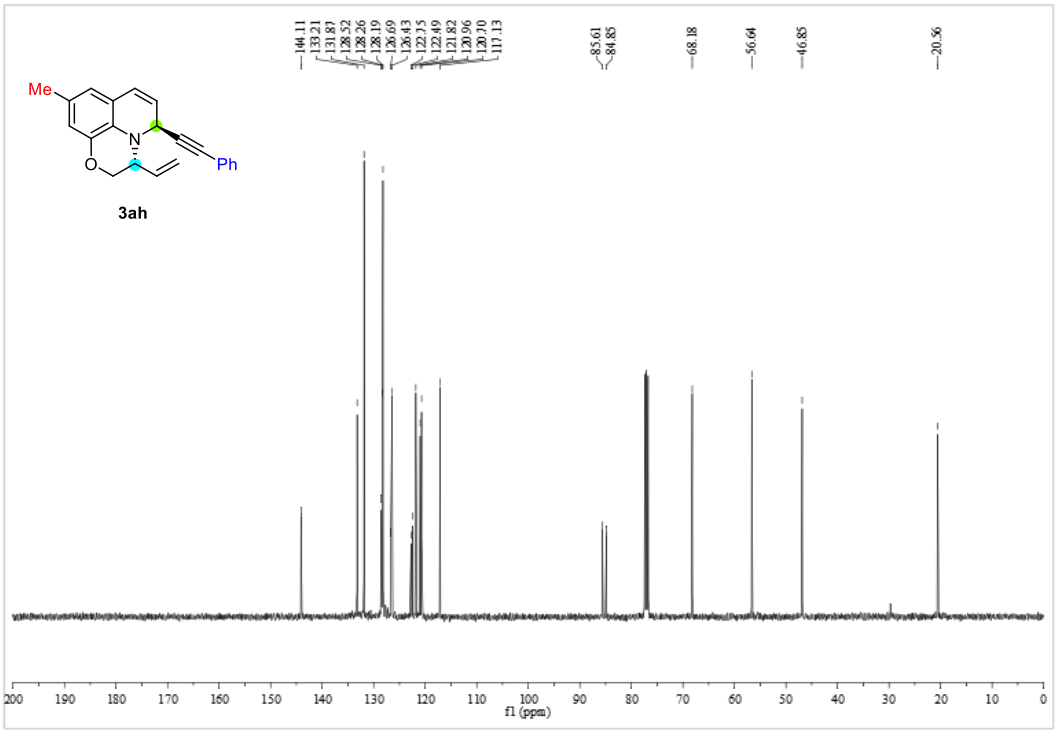
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.649	BB	0.3507	5962.54492	262.80118	49.5323
2	17.115	BB	0.4245	6075.13770	221.14955	50.4677

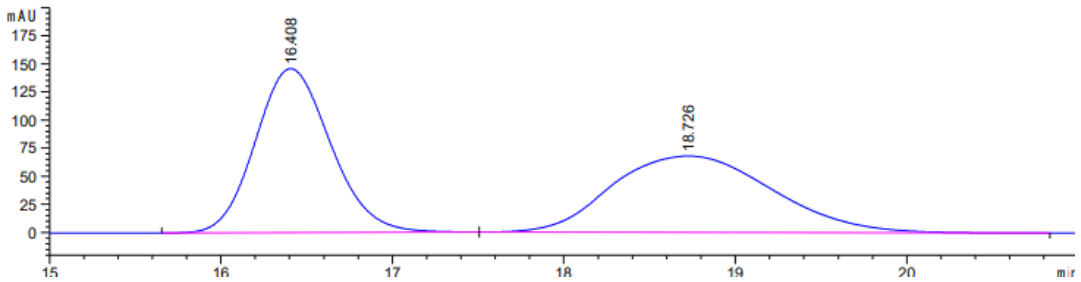


Signal 1: VWD1 A, Wavelength=254 nm

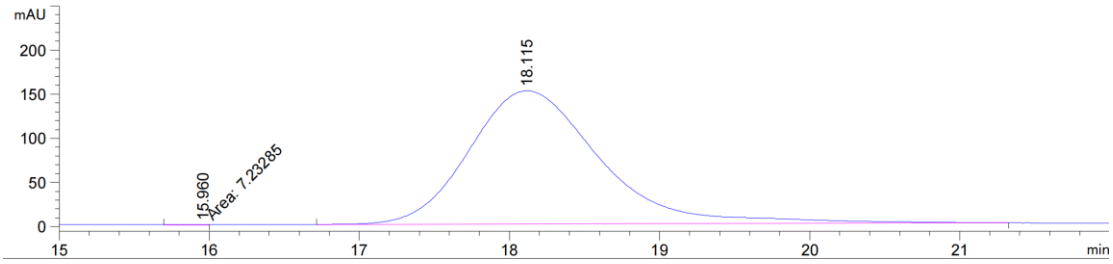
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.609	BB	0.3261	37.87437	1.81045	0.9972
2	17.170	MM	0.4411	3760.01563	142.07867	99.0028


Me
N
O
Ph
3ah
7.406
7.395
7.387
7.311
7.304
7.300
7.291
7.286
6.384
6.510
6.502
6.478
5.889
5.879
5.640
5.457
5.453
5.433
5.028
4.253
4.245
4.237
4.222
4.203
4.196
4.135
4.131
4.114
4.107
4.091
4.086
2.240
2.00
3.07
0.83
1.86
0.99
2.08
1.00
0.94
1.97
1.05
2.93
f1 (ppm)

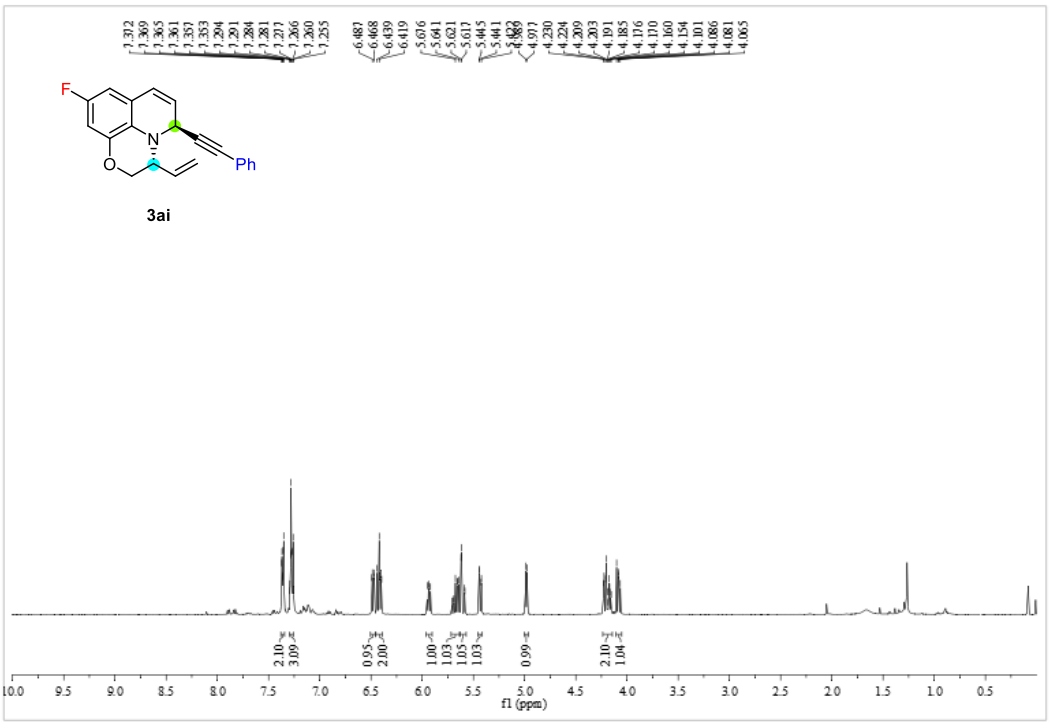

Me
N
O
Ph
3ah
144.11
133.21
131.83
128.52
128.26
128.19
126.69
126.43
122.15
122.49
121.82
120.96
120.30
117.13
85.61
84.85
68.18
56.64
46.85
20.56
f1 (ppm)

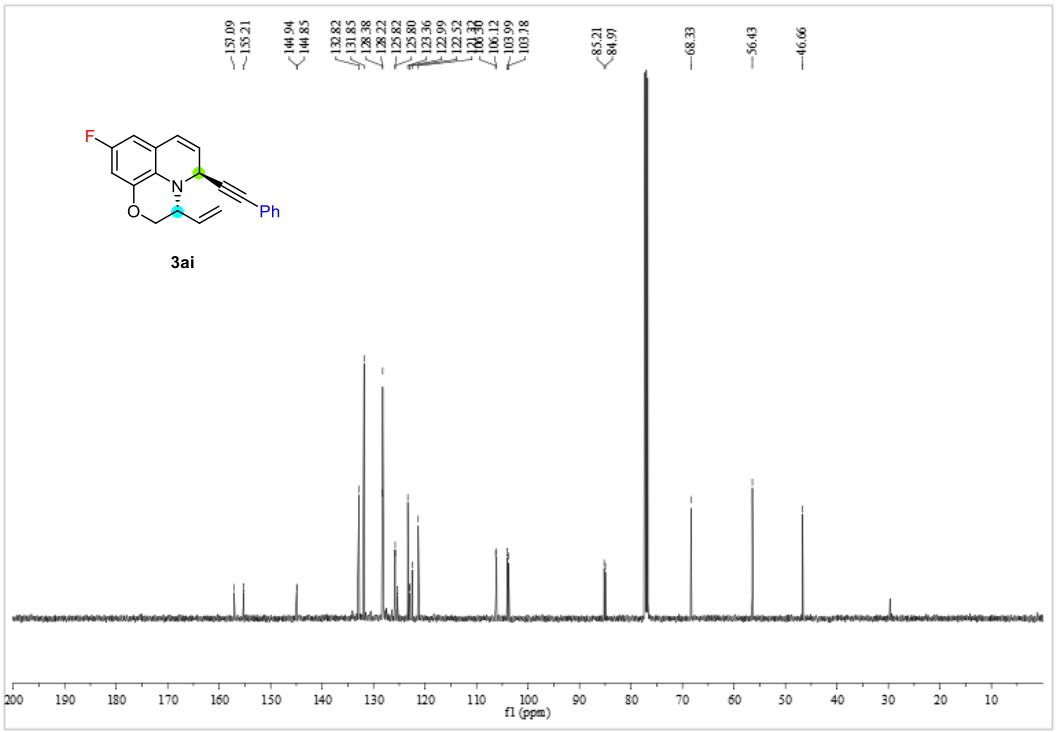


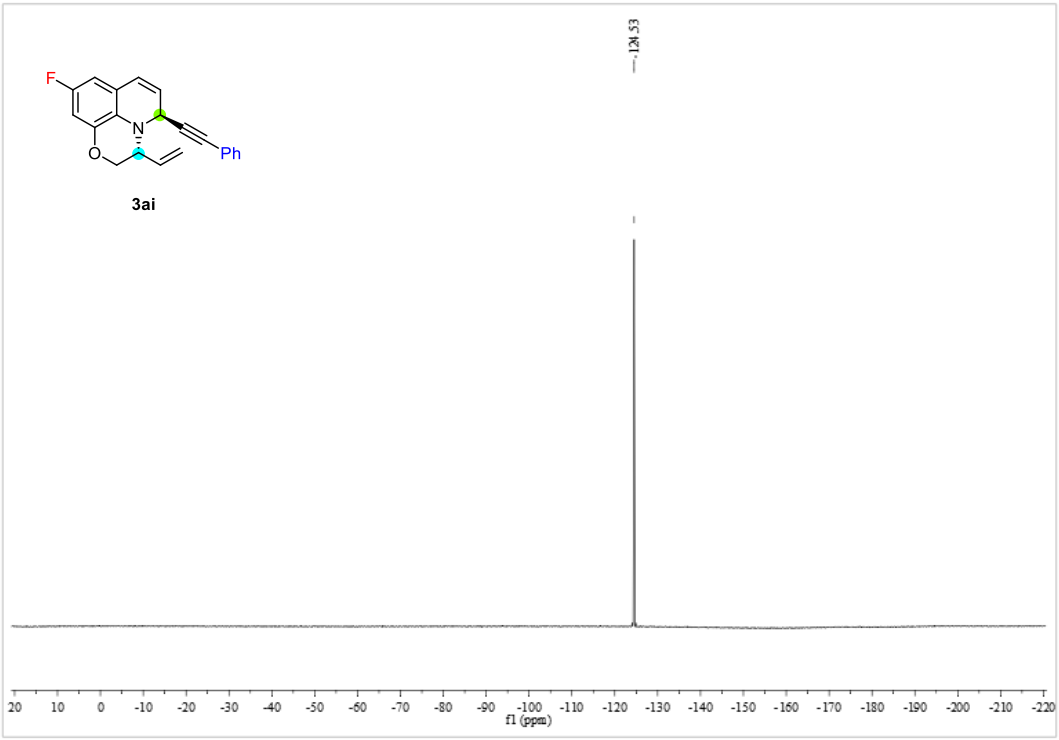
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.408	BB	0.4755	4457.29395	145.88657	50.1065
2	18.726	BBA	1.0497	4438.35107	67.97678	49.8935



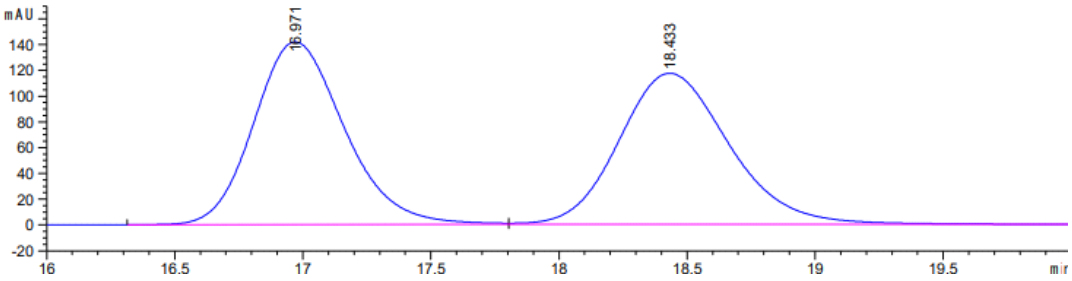
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.960	MM	0.3171	7.23285	3.80171e-1	0.0792
2	18.115	BB	0.9141	9123.85840	150.75311	99.9208


F
N
O
Ph
3ai
fl (ppm)


F
N
O
Ph
3ai
fl (ppm)

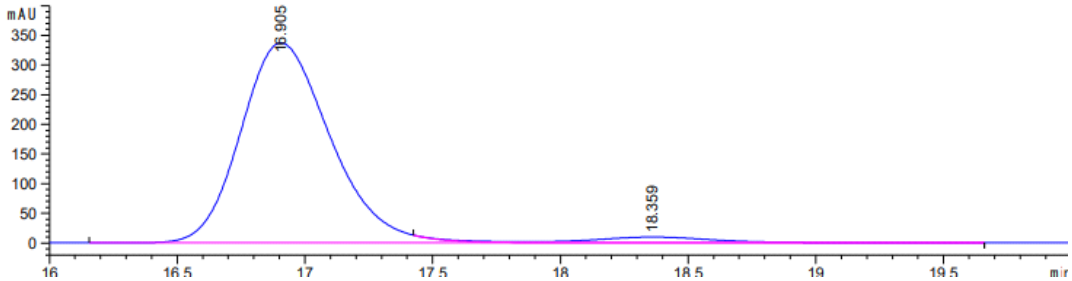

F
N
O
Ph
-124.53
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

3ai



Signal 1: VWD1 A, Wavelength=254 nm

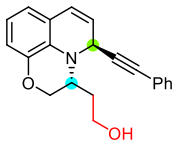
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.971	BV	0.3811	3505.12964	141.93279	49.8251
2	18.433	VBA	0.4638	3529.73193	117.38655	50.1749



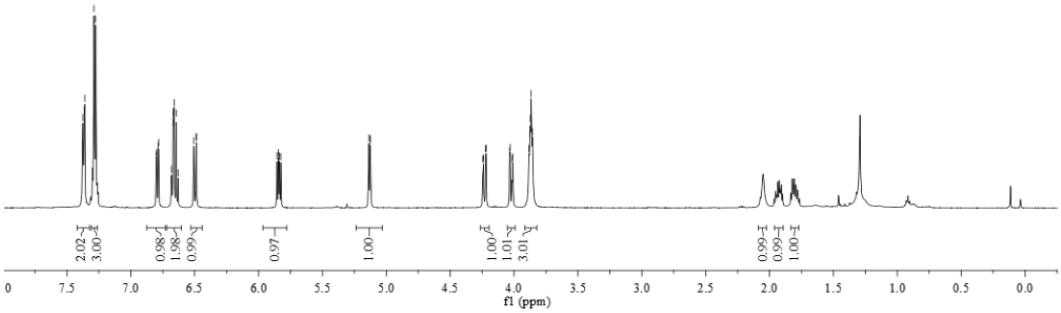
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.905	BV R	0.3764	8213.01465	336.90878	96.1596
2	18.359	VB E	0.5093	328.00882	9.55991	3.8404

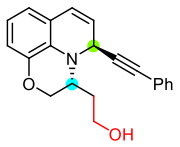

7.376
7.364
7.360
7.289
7.275
6.669
6.666
6.660
6.645
6.507
6.488
6.487
5.856
5.845
5.837
5.826
5.137
5.126
5.125
4.244
4.239
4.223
4.218
4.035
4.030
4.014
4.009
3.888
3.883
3.877
3.872
3.866
3.856


N
O
Ph
OH

4a

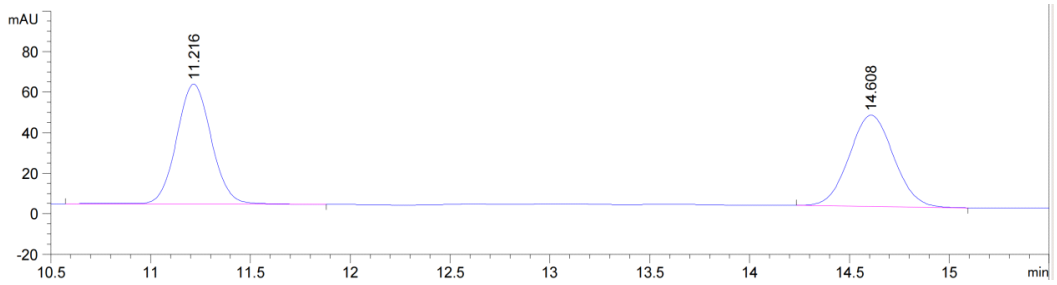

2.02
3.00
0.98
1.98
0.99
0.97
1.00
1.00
1.01
3.01
0.99
0.99
1.00
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.32
131.79
128.41
128.27
127.88
126.22
122.99
122.52
121.57
120.27
118.10
116.74
86.04
84.81
66.80
59.70
52.41
50.00
33.30


N
O
Ph
OH

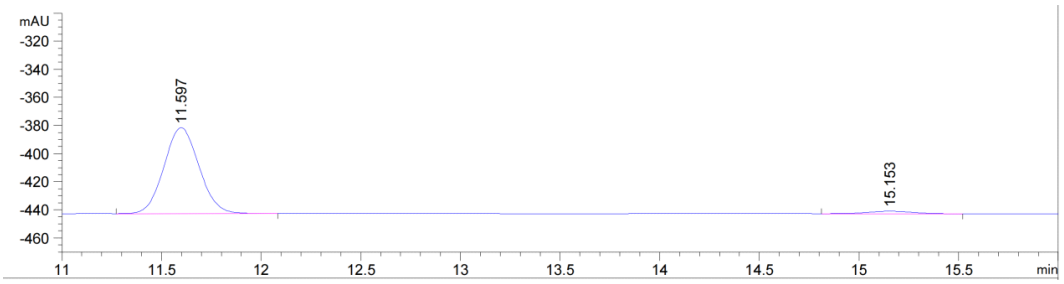
4a

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



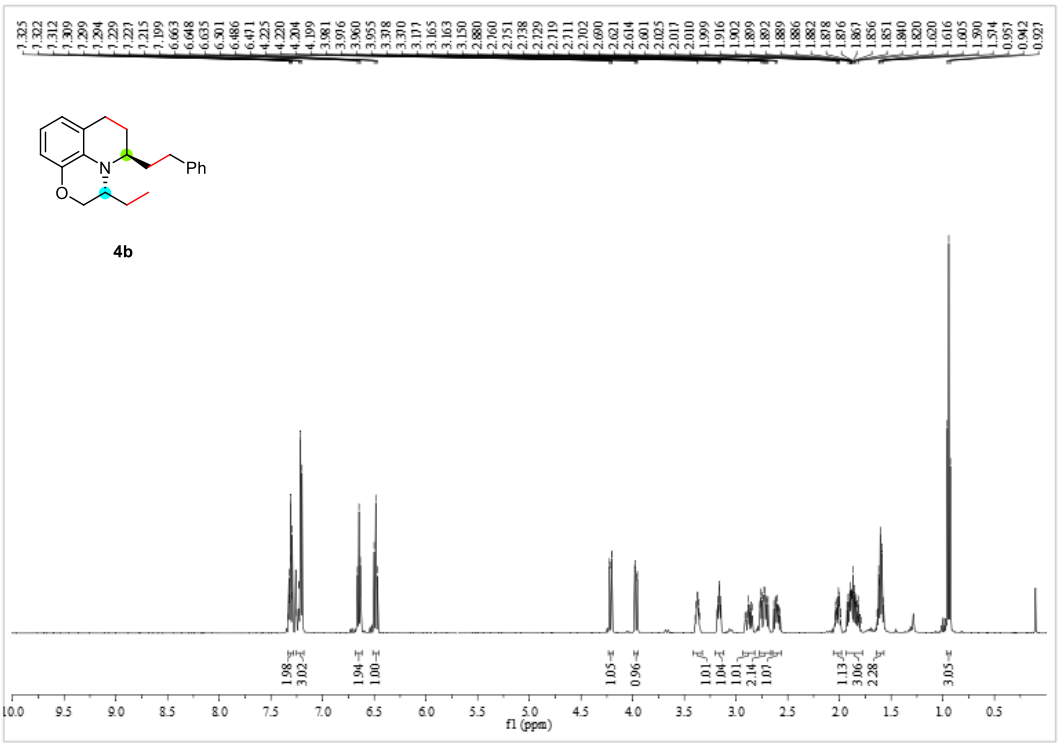
Signal 1: VWD1 A, Wavelength=254 nm

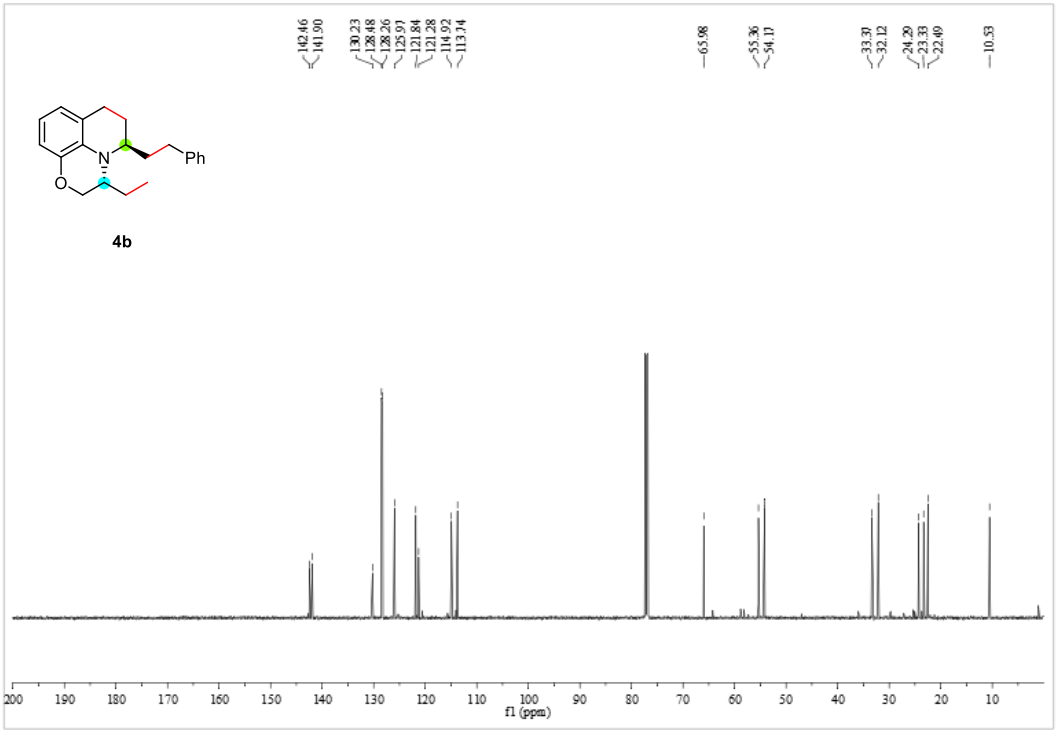
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.216	VB R	0.1873	717.93207	59.27900	50.8216
2	14.608	BB	0.2401	694.72058	44.99556	49.1784

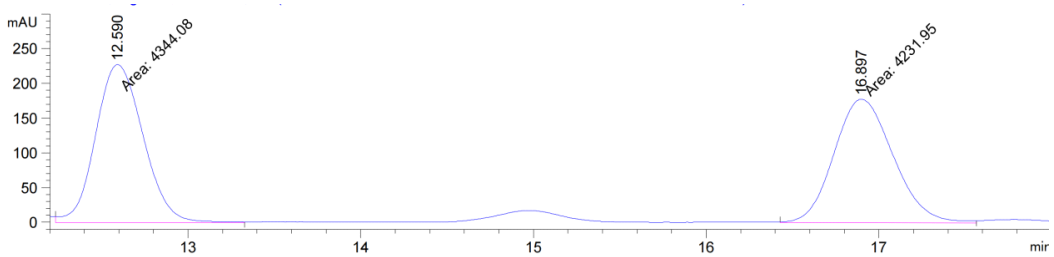


Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.597	BB	0.1907	747.39294	61.08915	96.5273
2	15.153	BB	0.2430	26.88848	1.73327	3.4727

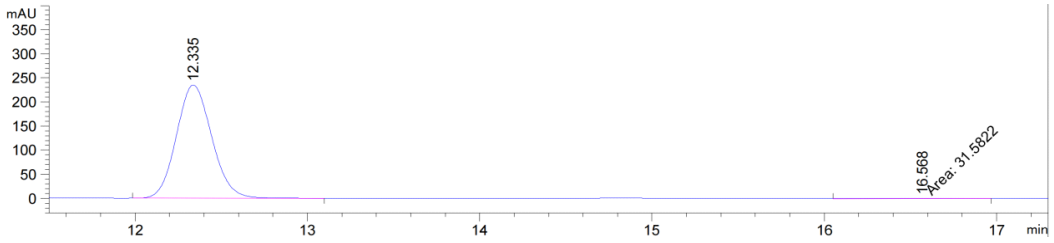

Ph
N
O
4b
fl (ppm)


Ph
N
O
4b
fl (ppm)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.590	MM	0.3185	4344.08496	227.31418	50.6538
2	16.897	MM	0.3966	4231.94678	177.85939	49.3462



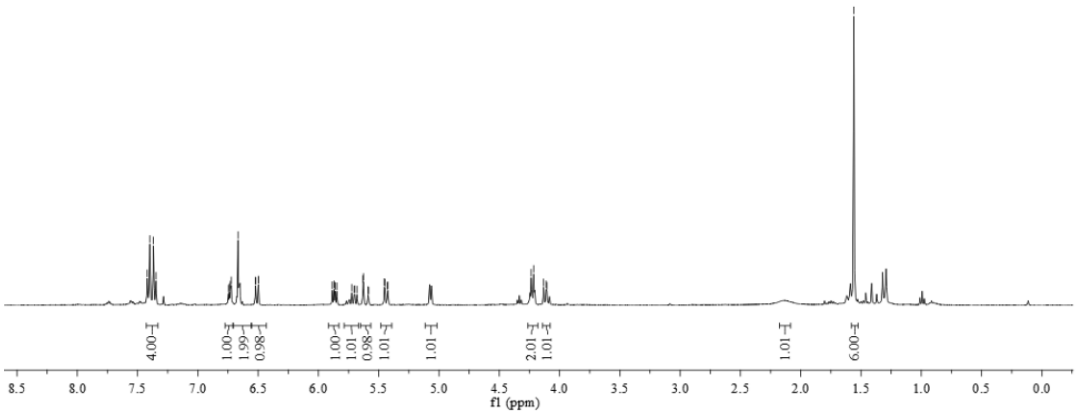
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

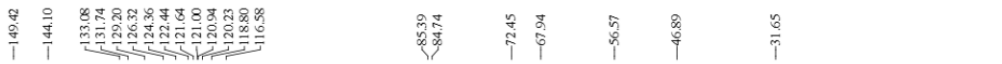
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.335	BB	0.2222	3348.27686	235.00455	99.0656
2	16.568	MM	0.7645	31.58219	6.88510e-1	0.9344

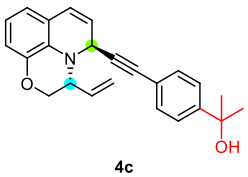

7.420
7.398
7.368
7.347
6.722
6.666
6.522
6.520
6.498
6.496
5.885
5.871
5.861
5.848
5.724
5.699
5.631
5.627
5.453
5.449
5.428
4.215
4.133
4.112
4.104
1.559

O
N
OH

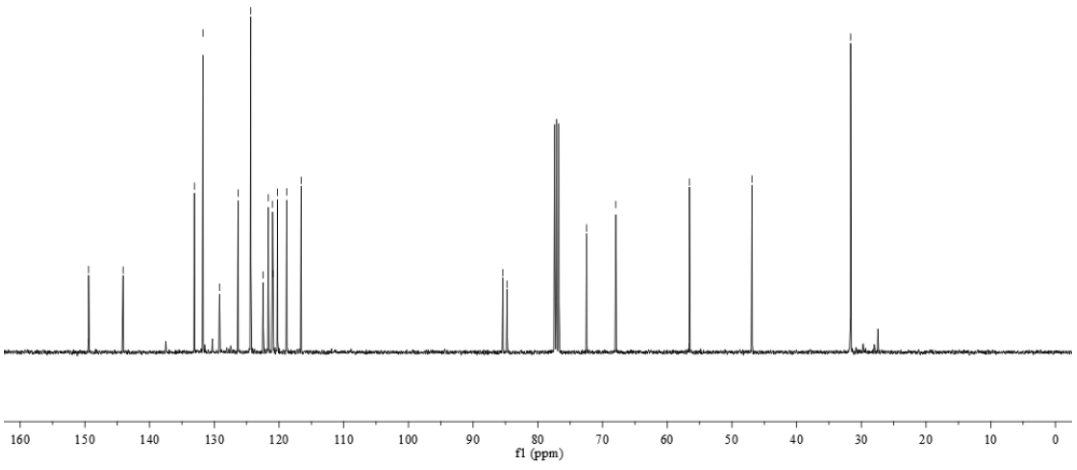
4c

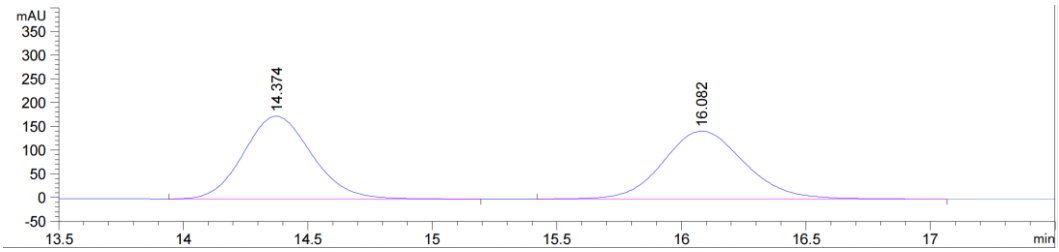

4.00
1.00
1.99
0.98
1.00
1.01
0.98
1.01
1.01
2.01
1.01
1.01
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.42
144.10
133.08
131.74
129.20
126.32
124.36
122.44
121.64
121.00
120.94
120.23
118.80
116.58
85.39
84.74
72.45
67.94
56.57
46.89
31.65


O
N
OH

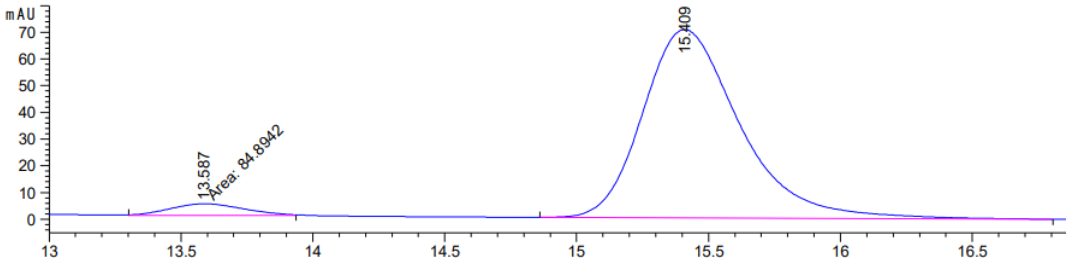
4c


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

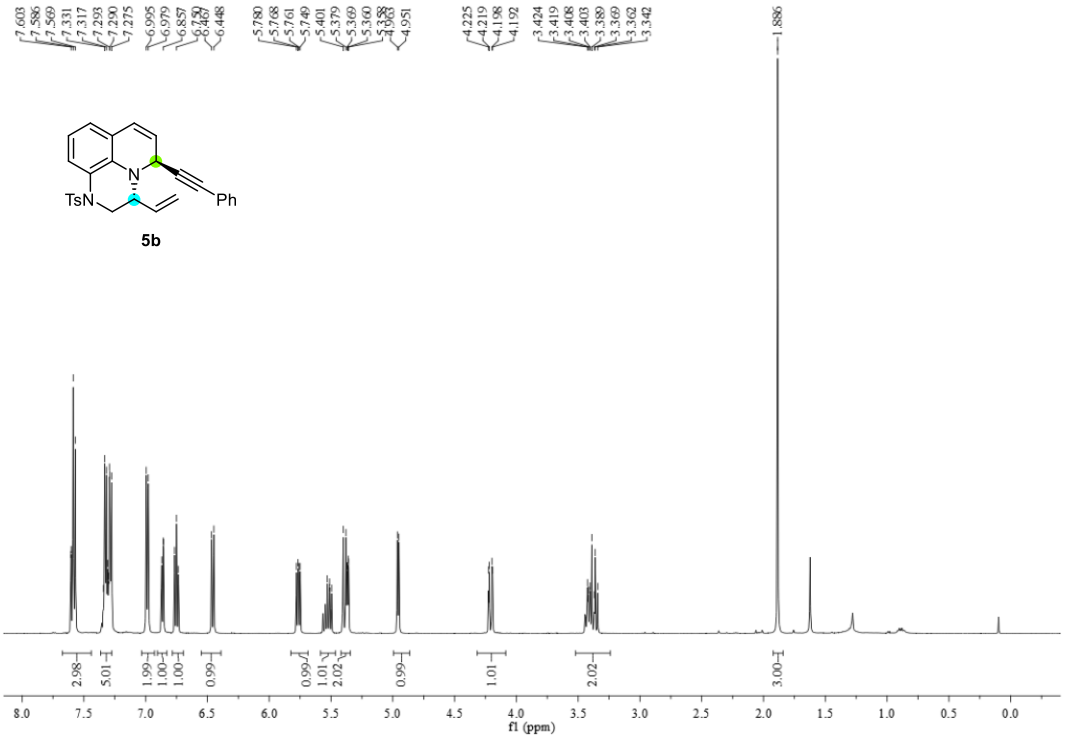


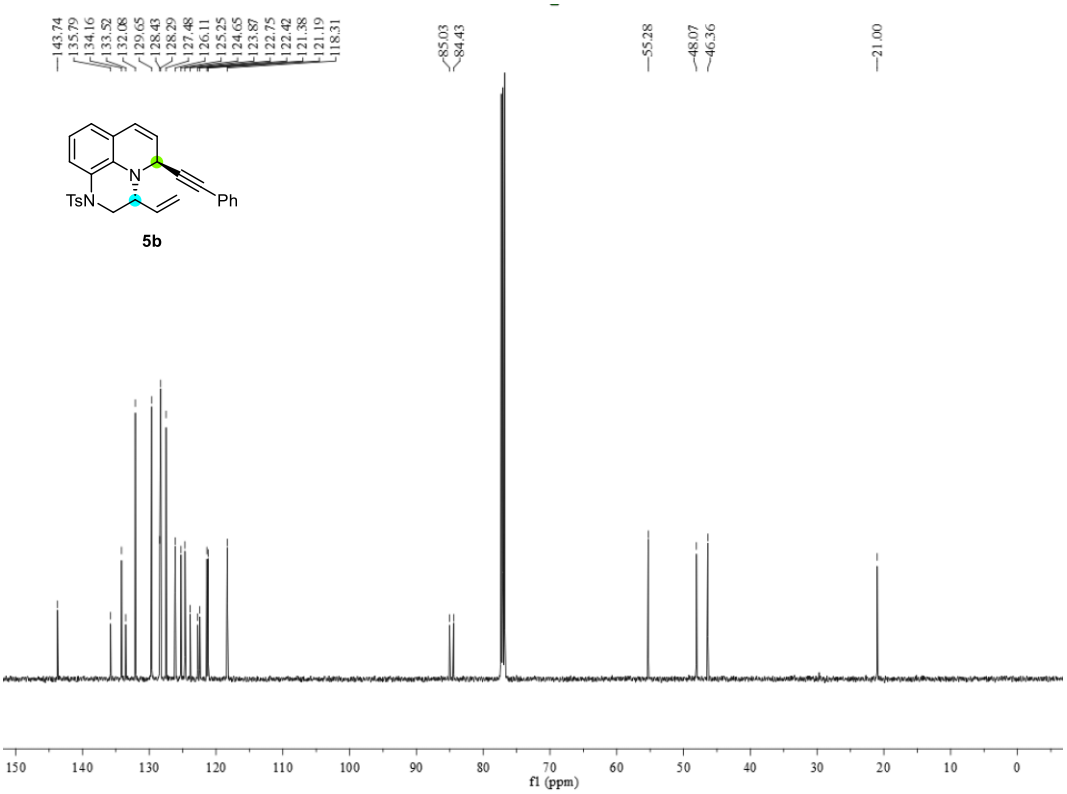
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.374	BV R	0.2950	3340.39111	174.73230	50.4344
2	16.082	BB	0.3510	3282.85132	143.43083	49.5656



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.587	MM	0.3265	84.89421	4.33397	4.4770
2	15.409	BB	0.3915	1811.33716	70.56038	95.5230


7.603
7.586
7.569
7.331
7.317
7.293
7.290
7.275
6.995
6.979
6.857
6.750
6.467
6.448
5.780
5.768
5.761
5.749
5.401
5.379
5.369
5.360
5.338
5.303
4.951
4.225
4.219
4.198
4.192
3.424
3.419
3.408
3.403
3.389
3.369
3.362
3.342
1.886
TsN
Ph
5b
2.98
5.01
1.99
1.00
1.00
0.99
0.99
1.01
2.02
0.99
1.01
2.02
3.00
f1 (ppm)


143.74
135.79
134.16
133.52
132.08
129.65
128.43
128.29
127.48
126.11
125.25
124.65
123.87
122.75
122.42
121.38
121.19
118.31
85.03
84.43
55.28
48.07
46.36
21.00
TsN
Ph
5b
f1 (ppm)

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