Supplementary Information

Enantioselective Carbonylative Coupling Reactions: Merging Nickel-Based Selectivity and Photoredox Reactivity

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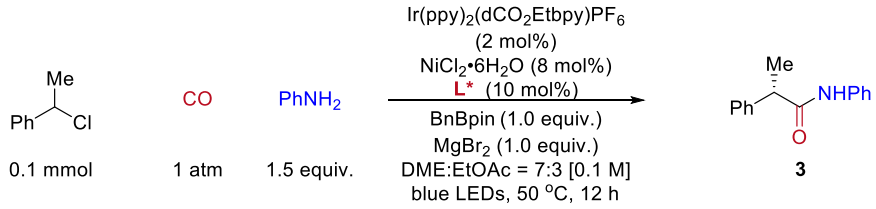
1. Materials and Methods

Commercial reagents were purchased from Adamas, Aldrich, TCI, Energy Chemical, Bide, Leyan.com, Aladdin, Merck, Alfer and J&K chemical, and were used as received.

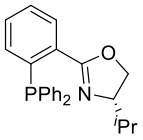
All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen or CO unless otherwise noted. Research grade carbon monoxide (99.99%) was used as received. Warning: CO is a poisonous gas that requires all the experiments to be conducted in well-ventilated fume hoods. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. **^{1}H**, **^{13}C**, **^{19}F** and **^{31}P NMR** spectra were recorded on Bruker 400 (400, 101 and 377 MHz) and are internally referenced to residual solvent signals (for $CDCl_3$, 7.26 and 77.16 ppm, and for Acetone-d_6, 2.05, and 29.84, 206.26 ppm). Data for **^{1}H NMR**, **^{19}F NMR** and **^{31}P NMR** are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. EPR spectra for radicals were obtained at East China Normal University on BrukerEMX instrument EMXPLUS-10/12. EPR spectra simulation was conducted on the Bruker SpinFit software. Optical rotations were measured on an automatic polarimeter. $[\alpha]_D^T$ values reported in 10^{-1} deg cm^2 g^{-1}; concentrations (c) are quoted in g/100 mL. D refers to the D-line of sodium (589 nm); temperatures (T) are given in degrees Celsius (^{o}C). High performance liquid chromatography (HPLC) analysis on chiral stationary phase was performed on a Shimadzu 20-series instrument. Chiralpak IA-H or AD-H columns with hexane: ^{i}PrOH as the eluents were used. Photochemical experiments have been performed using a blue LED light (λ_{max} = 467 nm, 393 mW/cm^2, Kessil A360W E-SERIES TUNA Blue LED). Benzyl chlorides,[1] anilines, [2-4] and chiral ligands [5] prepared according to the previously reported procedures.

2. Supplementary Tables and Figures

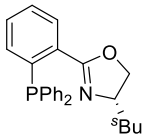
Supplementary Table S1: Effect of chiral ligands



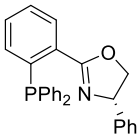
0.1 mmol | 1 atm | 1.5 equiv. | **3**



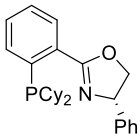
(*S*)-**L1** 13%, 14% ee



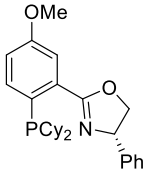
(*S*)-**L2** 19%, 11% ee



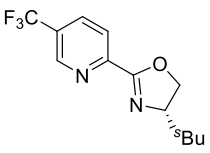
(*S*)-**L3** 47%, 43% ee



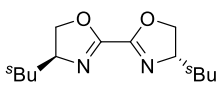
(*S*)-**L4** 70%, 90% ee



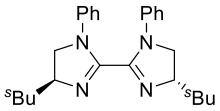
(*S*)-**L5** 75%, 92% ee



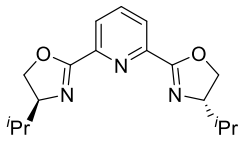
(*S*)-**L6** 7%, 0% ee



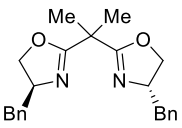
(*S*,*S*)-**L7** 0%



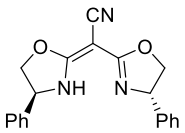
(*S*,*S*)-**L8** 10%, 9% ee



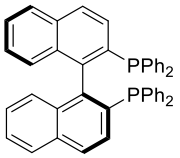
(*S*,*S*)-**L9** 0%



(*S*,*S*)-**L10** 6%, 14% ee



(*S*,*S*)-**L11** 0%

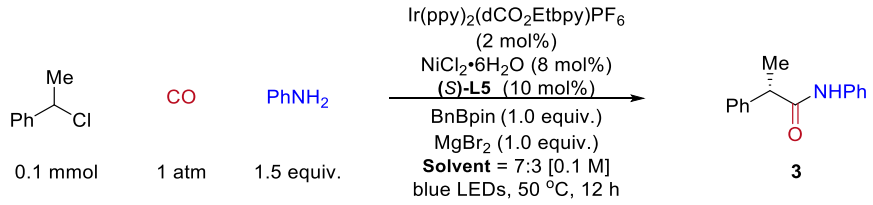


(*S*)-**L12** 10%, 7% ee

Reaction conditions: (1-chloroethyl)benzene (0.1 mmol), $PhNH_2$ (0.15 mmol), CO (1 atm), $Ir(ppy)_2(dCO_2Etbpy)PF_6$ (2 mol%), $NiCl_2 \cdot 6H_2O$ (8 mol%), **chiral ligand** (10 mol%), BnBpin (1.0 equiv.), $MgBr_2$ (1.0 equiv.), DME/EtOAc (0.1 M, v/v = 7:3), ~50 ^oC, 12 hours, blue LED.

Comment: The chiral PHOX ligand (*S*)-**L5** was selected as the optimal ligand.

Supplementary Table S2: Effect of solvents

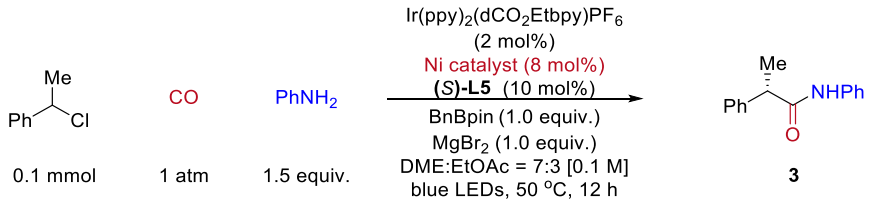


0.1 mmol | 1 atm | 1.5 equiv. | **3**

Entry	solvents	yield of 3 (%)	ee of 3 (%)
1	THF	65	88
2	DME	72	89
3	Dioxane	46	81
4	DMA	53	88
5	EtOAc	68	90
6	PhCl	45	86
7	DME/DMA = 7:3	60	83
8	**DME/EtOAc = 7:3**	**75**	**92**

Reaction conditions: (1-chloroethyl)benzene (0.1 mmol), $PhNH_2$ (0.15 mmol), CO (1 atm), $Ir(ppy)_2(dCO_2Etbpy)PF_6$ (2 mol%), $NiCl_2 \cdot 6H_2O$ (8 mol%), (*S*)-**L5** (10 mol%), BnBpin (1.0 equiv.), $MgBr_2$ (1.0 equiv.), **solvent** (0.1 M), ~50 °C, 12 hours, blue LED.

Supplementary Table S3: Effect of catalysts

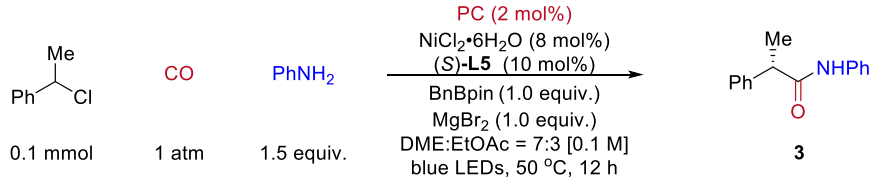


0.1 mmol | 1 atm | 1.5 equiv. | **3**

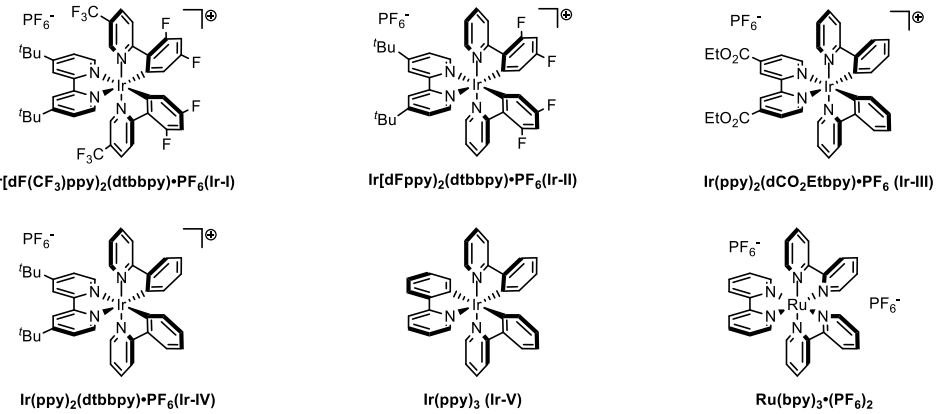
Entry	conditions	yield of 3 (%)	ee of 3 (%)
1	$NiBr_2 \cdot DME$	67	92
2	**$NiCl_2 \cdot 6H_2O$**	**75**	**92**
3	$NiCl_2 \cdot DME$	72	91
4	$Ni(COD)_2$	66	90

Reaction conditions: (1-chloroethyl)benzene (0.1 mmol), $PhNH_2$ (0.15 mmol), CO (1 atm), $Ir(ppy)_2(dCO_2Etbpy)PF_6$ (2 mol%), **Ni catalyst** (8 mol%), (*S*)-**L5** (10 mol%), BnBpin (1.0 equiv.), $MgBr_2$ (1.0 equiv.), DME/EtOAc (0.1 M, v/v = 7:3), ~50 °C, 12 hours, blue LED.

Supplementary Table S4: Effect of photocatalysts



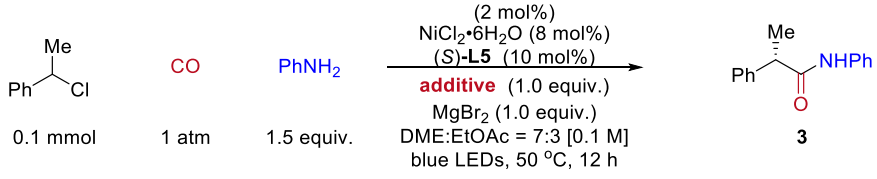
0.1 mmol | 1 atm | 1.5 equiv. | **3**



Entry	Photocatalyst	yield of 3 (%)	ee of 3 (%)
1	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy) PF$_6$	67	91
2	Ir[dFppy]$_2$(dtbbpy)·PF$_6$	64	90
3	**Ir(ppy)$_2$(dCO$_2$Etbpy)·PF$_6$**	**75**	**92**
4	Ir(ppy)$_2$(dtbbpy)·PF$_6$	55	90
5	Ir(ppy)$_3$	29	82
6	Ru(bpy)$_3$·PF$_6$	0	-

Reaction conditions: (1-chloroethyl)benzene (0.1 mmol), PhNH$_2$ (0.15 mmol), CO (1 atm), **Photocatalyst** (2 mol%), NiCl$_2$·6H$_2$O (8 mol%), (*S*)-**L5** (10 mol%), BnBpin (1.0 equiv.), MgBr$_2$ (1.0 equiv.), DME/EtOAc (0.1 M, v/v = 7:3), ~50 °C, 12 hours, blue LED.

Supplementary Table S5: Effect of additives



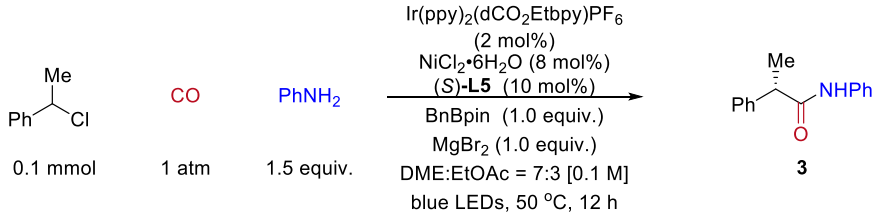
0.1 mmol | 1 atm | 1.5 equiv. | **3**

Entry	additives	yield of 3 (%)	ee of 3 (%)
1	**BnBpin**	**75**	**92**
2	CyBpin	52	84
3	allylBpin	45	78
4	$CyB(OH)_2$	64	92
5	$PhB(OH)_2$	61	77

Reaction conditions: (1-chloroethyl)benzene (0.1 mmol), $PhNH_2$ (0.15 mmol), CO (1 atm), $Ir(ppy)_2(dCO_2Etbpy)PF_6$ (2 mol%), $NiCl_2 \cdot 6H_2O$ (8 mol%), (*S*)-**L5** (10 mol%), **additive** (1.0 equiv.), $MgBr_2$ (1.0 equiv.), DME/EtOAc (0.1 M, v/v = 7:3), ~50 °C, 12 hours, blue LED.

Comment: The BnBpin was selected as the optimal additive.

Supplementary Table S6: Control experiments

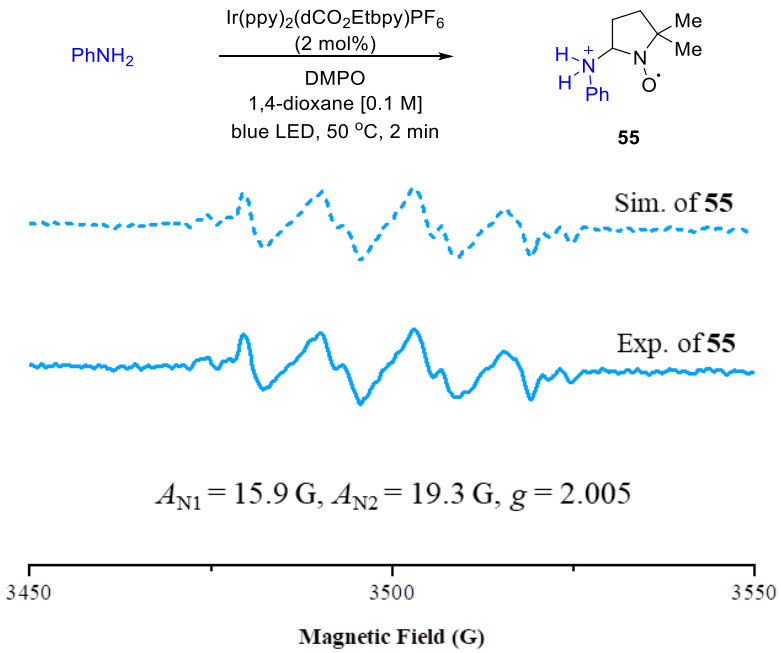


Entry	Reaction conditions	yield of 3 (%)	ee of 3 (%)
1	w/o $Ir(ppy)_2(dCO_2Etbpy)PF_6$	**0**	-
2	w/o $NiCl_2 \cdot 6H_2O$	0	-
3	w/o (*S*)-**L5**	0	-
4	w/o light	0	-
5	w/o BnBpin	65	71
6	w/o $MgBr_2$	68	86

Reaction conditions: (1-chloroethyl)benzene (0.1 mmol), $PhNH_2$ (0.15 mmol), CO (1 atm), $Ir(ppy)_2(dCO_2Etbpy)PF_6$ (2 mol%), $NiCl_2 \cdot 6H_2O$ (8 mol%), (*S*)-**L5** (10 mol%), BnBpin (1.0 equiv.), $MgBr_2$ (1.0 equiv.), DME/EtOAc (0.1 M, v/v = 7:3), ~50 °C, 12 hours, blue LED.

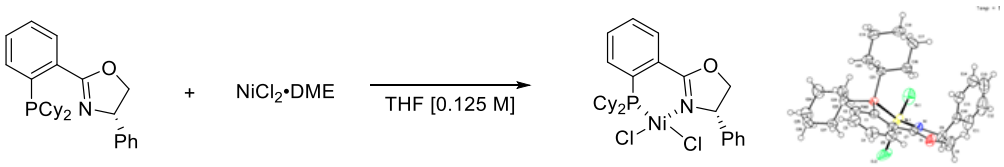
Supplementary Figure S1: Electron paramagnetic resonance (EPR) study

We carried out paramagnetic resonance (EPR) studies by using 5,5-dimethyl-pyrroline N-oxide (DMPO) as free radical spin-trapping agent. Operando spin trapping experiments were carried out using the aniline solution (0.1 M) and DMPO (0.1 M) in anhydrous 1,4-dioxane in a capillary tube under light irradiation (blue LEDs). the radical species was dissolved into solvent to a certain concentration, then solution was drawn into the capillary tube, and the capillary tube was sealed. After that, the capillary tube was loaded into EPR tube to be measured. Such spectra were in good agreement with the simulated EPR spectroscopy of amido radical adduct **55**.



Supplementary Figure S2: Reaction with (L4)$NiCl_2$ (A)

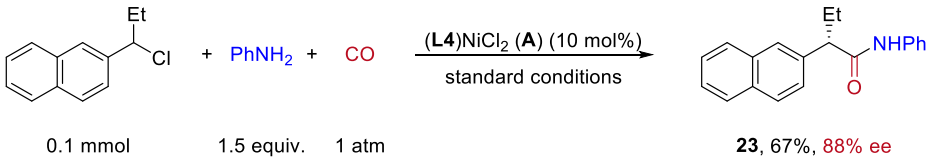
Synthesis of (L4)$NiCl_2$ (A)



An oven-dried 8 mL vial equipped with a PTFE-coated stir bar was charged with (*S*)-**L4** (54.5 mg, 0.25 mmol, 1 equiv), $NiCl_2$·DME (121.2 mg, 1.1 equiv) and anhydrous THF (2 mL). This reaction mixture was stirred at room temperature for 2.5 hours in an argon-filled glovebox. Dry pentane (3 mL) was added to the deep purple colored mixture and filtered. The resulting precipitate was washed with pentane and dried to afford (**L4**)$NiCl_2$ (**A**) as a purple solid (116 mg, 85% yield). The product was used without further purification. The complex was stored in a nitrogen filled glove box at -30 ºC.

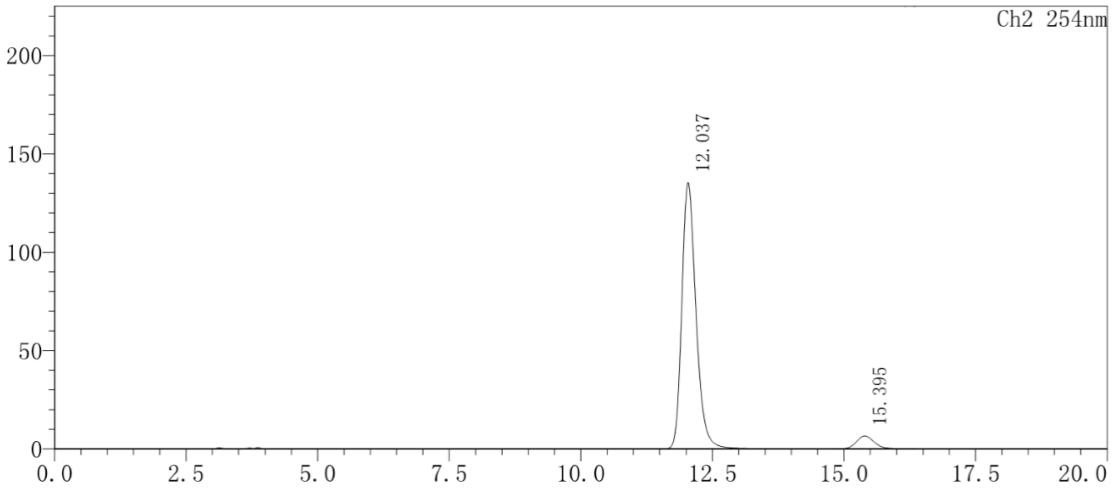
Note: The (**L4**)$NiCl_2$ (**A**) is paramagnetic. ^{1}**H** and ^{13}**C** NMR showed signal broadening, therefore no complete analytical characterization was possible.

Catalytic reaction with (L4)$NiCl_2$ (A)



To a flame-dried 20 mL test tube was charged with 2-(1-chloropropyl)naphthalene (0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dCO_2Etbpy)]PF_6$ (2.0 mg, 0.002 mmol, 2 mol%), (**L4**)$NiCl_2$ **(A)** (5.5 mg, 0.01 mmol, 10 mol%), and $MgBr_2$ (18.4 mg, 0.1 mmol, 1.0 equiv.). Then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO balloon three times, DME /EtOAc (1 mL, v/v = 7:3) was added via a syringe, followed by the addition of with aniline (0.15 mmol), BnBPin (22.3 μL, 0.1 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 hours at 50 °C by 90 W blue LEDs, and then quenched with water and extracted with EtOAc. The combined organic layers were washed by brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatograph to afford the product **23** (67% yield, 88% ee).

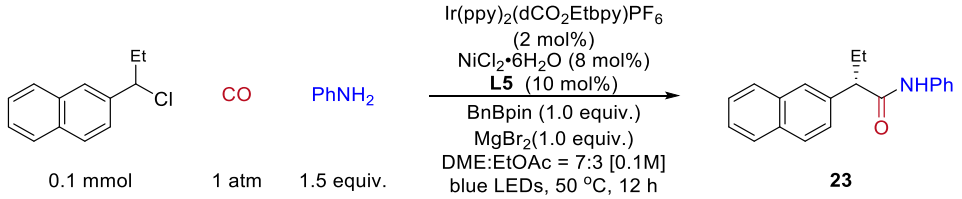
HPLC: The ee was determined to be 88% ee on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.0 min, t_R (minor) = 15.4 min.



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.037	2520625	135324	94.121
2	15.395	157442	6627	5.879

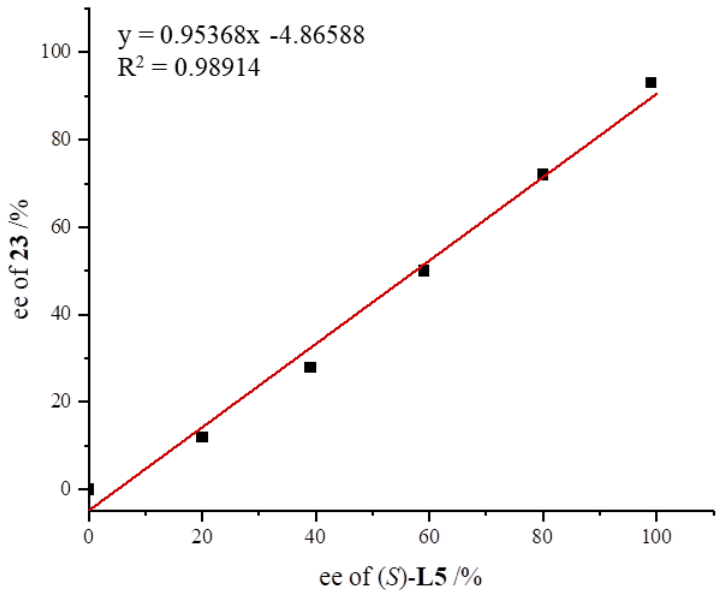
Supplementary Figure S3: Study of nonlinear effect

To a flame-dried 10 mL test tube was charged with 2-(1-chloropropyl)naphthalene (0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dCO_2Etbpy)]PF_6$ (2.0 mg, 0.002 mmol, 2 mol%), (*S*, *S*)-**L5** + (*R, R*)-**L5** (5.5 mg, 0.01 mmol, 10 mol%), and $MgBr_2$ (18.4 mg, 0.1 mmol, 1.0 equiv.). Then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO balloon three times, DME /EtOAc (7:3) (1 mL) was added via a syringe, followed by the addition of with aniline (0.15 mmol), BnBPin (22.3 μL, 0.1 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 hours at 50 °C by 90 W blue LEDs. The ee. values of product **23** was determined by HPLC analysis.



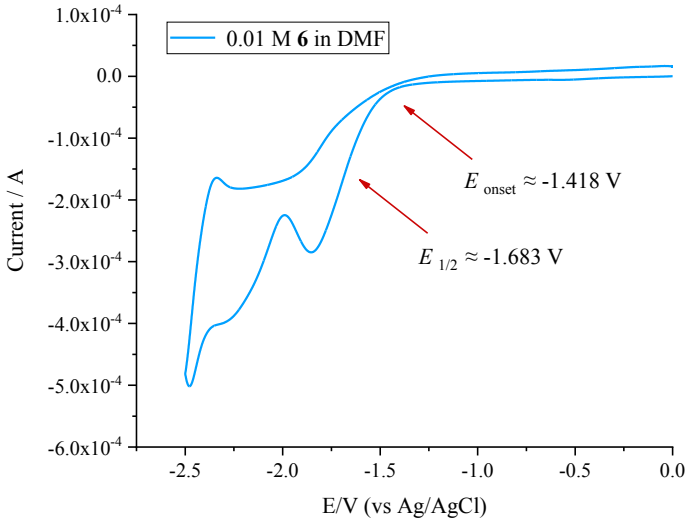
Entry	ee of L5	ee of 23
1	0%	0%

2	20%	12%
3	39%	28%
4	59%	50%
5	80%	72%
6	99%	93%



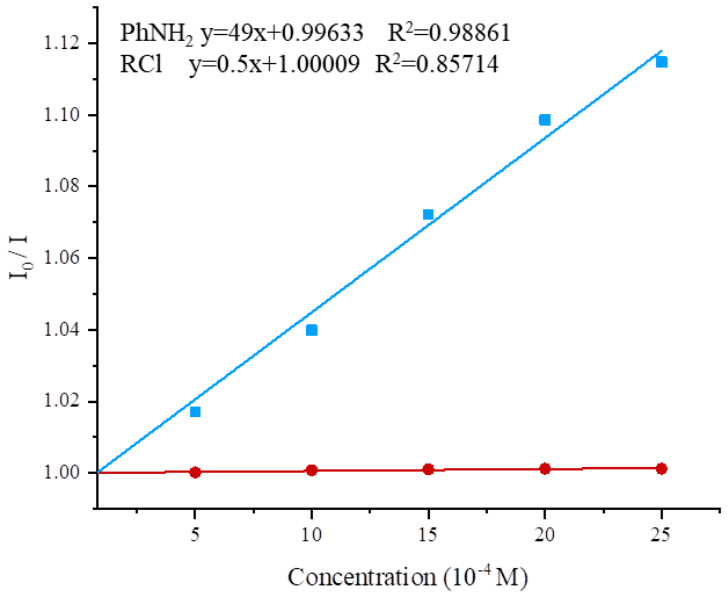
Supplementary Figure S4: Cyclic Voltammetry Data of 6

Cyclic voltammetry was conducted on an Electrochemical Workstation (CHI730E) using a 3-electrode cell configuration. A glassy carbon working electrode was employed alongside a platinum wire counter electrode and an Ag/AgCl reference electrode. DMF was degassed by bubbling N_2 prior to measurements. 0.01 M solutions of **6** (2-(1-chloropropyl)naphthalene) were freshly prepared along with 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte and were examined at a scan rate of 0.05 V. s^{-1}.



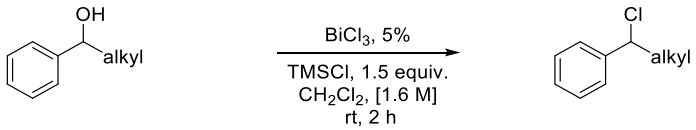
Supplementary Figure S5: Stern-Volmer quenching experiments

Stern-Volmer quenching experiments were carried by Edinburgh Fluorescence Spectrometer FS5, using a 0.1 mM solution of photocatalyst $Ir(ppy)_2(dCO_2Etbpy)PF_6$ and variable concentrations (0.5, 1.0, 1.5, 2.0, 2.5 mM) of aniline, using a 0.01 mM solution of photocatalyst $Ir(ppy)_2(dCO_2Etbpy)PF_6$ and variable concentrations (0.5, 1.0, 1.5, 2.0, 2.5 mM) of 2-(1-chloropropyl)naphthalene (RCl) and $PhNH_2$ in mixed solvent EtOAc/DME (7:3). The samples were prepared in 4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box. The intensity of the emission peak at 637 nm (λ_{ex} = 532 nm) expressed as the ratio I_0/I, where I_0 is the emission intensity of photocatalyst at 637 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Stern-Volmer plots for each component are given below.

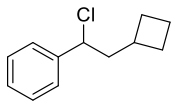

PhNH2 y=49x+0.99633 R2=0.98861
RCl y=0.5x+1.00009 R2=0.85714
I0 / I
1.12
1.10
1.08
1.06
1.04
1.02
1.00
5
10
15
20
25
Concentration (10-4 M)

3. Substrate Synthesis

1) Synthesis of benzyl chlorides



To a stirred solution of $BiCl_3$ (5 mol%) and the benzyl alcohol (8 mmol, 1.0 equiv.) in dichloromethane (5 mL) was slowly added trimethylsilyl chloride (12 mmol, 1.5 equiv.) at room temperature. The mixture was stirred for 2 hours, and then quenched by saturated NH_4Cl solution (3 mL). The mixture was extracted with CH_2Cl_2 (2*10 mL). The collected organic layer was washed with brine (20 mL) and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, pentane with 3% Et_3N) to give the product.[1]



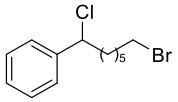
(1-chloro-2-cyclobutylethyl)benzene (1a)

The title compound was obtained as a colorless oil, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 4.78 – 4.75 (m, 1H), 2.42 – 2.30 (m, 1H), 2.29 – 2.22 (m, 1H), 2.15 – 2.09 (m, 1H), 2.08 – 2.03 (m, 1H), 2.00 – 1.92 (m, 1H), 1.90 – 1.77 (m, 2H), 1.74 – 1.65 (m, 1H), 1.62 – 1.58 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.10, 128.71, 128.33, 127.08, 62.13, 47.26, 33.81, 28.31, 28.25, 18.79.

HRMS (FI): $C_{12}H_{15}Cl$: 194.0862, found: 194.0860.



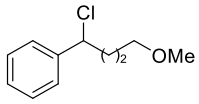
(7-bromo-1-chloroheptyl)benzene (1b)

The title compound was obtained as a colorless oil, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 4.87 – 4.83 (m, 1H), 3.39 (t, J = 8.0 Hz, 2H), 2.18 – 2.09 (m, 1H), 2.08 – 1.99 (m, 1H), 1.88 – 1.81 (m, 2H), 1.53 – 1.49 (m, 1H), 1.47 – 1.42 (m, 2H), 1.39 – 1.31 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.00, 128.76, 128.37, 127.04, 63.85, 40.00, 33.94, 32.73, 28.27, 28.05, 27.01.

HRMS (FI): $C_{13}H_{18}BrCl$: 288.0280, found: 288.0268.



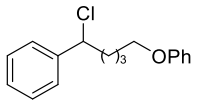
(1-chloro-4-methoxybutyl)benzene (1c)

The title compound was obtained as a colorless oil, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 4.91 – 4.87 (m, 1H), 3.44 – 3.36 (m, 2H), 3.32 (s, 3H), 2.24 – 2.09 (m, 2H), 1.84 – 1.73 (m, 1H), 1.66 – 1.56 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.90, 128.75, 128.38, 127.07, 72.04, 63.80, 58.72, 36.96, 27.40.

HRMS (EI): $C_{11}H_{15}ClO$: 198.0811, found: 198.0803.



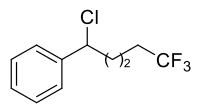
(1-chloro-5-phenoxypentyl)benzene (1d)

The title compound was obtained as a colorless oil, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.25 – 7.22 (m, 1H), 7.22 – 7.20 (m, 1H), 7.19 – 7.18 (m, 1H), 6.88 – 6.84 (m, 1H), 6.82 – 6.79 (m, 2H), 4.83 – 4.80 (m, 1H), 3.88 (t, J = 8.0 Hz, 2H), 2.19 – 2.09 (m, 1H), 2.07 – 1.98 (m, 1H), 1.79 – 1.72 (m, 2H), 1.67 – 1.56 (m, 1H), 1.47 – 1.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.08, 141.90, 129.58, 128.80, 128.43, 127.08, 120.77, 114.63, 67.56, 63.75, 39.87, 28.83, 23.95.

HRMS (FI): $C_{17}H_{19}ClO$: 274.1124, found: 274.1121.



(1-chloro-5,5,5-trifluoropentyl)benzene (1e)

The title compound was obtained as a colorless oil, 73% yield.

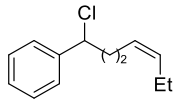
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 4.87 – 4.84 (m, 1H), 2.25 – 2.06 (m,

4H), 1.88 – 1.77 (m, 1H), 1.69 – 1.57 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.33, 128.91, 128.65, 127.05 (q, J = 277.8 Hz), 126.95, 63.05, 39.01, 33.24 (q, J = 29.3 Hz), 19.88.

^{19}F NMR (377 MHz, $CDCl_3$) δ -66.22 (t, J = 12 Hz).

HRMS (FI): $C_{11}H_{12}ClF_3$ (M): 236.0580, found: 236.0578.



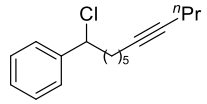
(Z)-(1-chlorohept-4-en-1-yl)benzene (1f)

The title compound was obtained as a colorless oil, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.33 – 7.28 (m, 1H), 5.48 – 5.42 (m, 1H), 5.34 – 5.28 (m, 1H), 4.89 – 4.85 (m, 1H), 2.25 – 2.16 (m, 3H), 2.10 – 1.98 (m, 3H), 0.96 (t, J = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.94, 133.51, 128.75, 128.38, 127.11, 127.06, 63.26, 39.96, 24.81, 20.71, 14.43.

HRMS (EI): $C_{13}H_{17}Cl$: 208.1019, found: 208.1011.



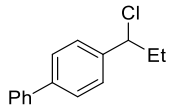
(1-chloroundec-7-yn-1-yl)benzene (1g)

The title compound was obtained as a colorless oil, 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 4.89 – 4.86 (m, 1H), 2.21 – 2.12 (m, 5H), 2.10 – 2.01 (m, 1H), 1.57 – 1.47 (m, 6H), 1.44 – 1.30 (m, 2H), 1.00 (t, J = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.02, 128.67, 128.26, 127.00, 80.35, 80.09, 63.80, 40.01, 28.95, 28.24, 26.72, 22.63, 20.85, 18.73, 13.58.

HRMS (FI): $C_{17}H_{23}Cl$: 262.1488, found: 262.1481.



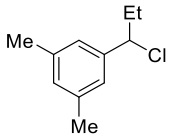
4-(1-chloropropyl)-1,1'-biphenyl (1h)

The title compound was obtained as a white solid, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 4H), 7.46 – 7.43(m, 4H), 7.38 – 7.34 (m, 1H), 4.86 – 4.83 (m, 1H), 2.23 – 2.09 (m, 2H), 1.04 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.30, 140.91, 140.74, 128.95, 128.92, 127.58, 127.48, 127.26, 65.41, 33.30, 11.92.

HRMS (FI): $C_{15}H_{15}Cl$: 230.0862, found: 230.0857.



1-(1-chloropropyl)-3,5-dimethylbenzene (1i)

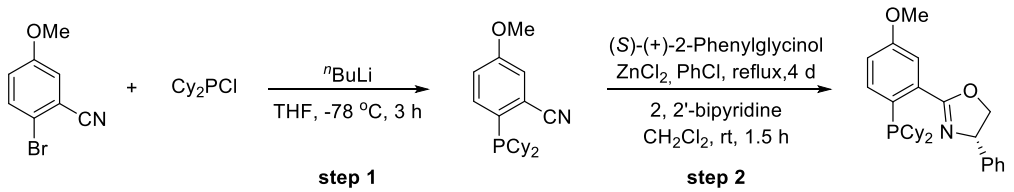
The title compound was obtained as a white solid, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 2H), 6.93 (s, 1H), 4.73 – 4.69 (m, 1H), 2.32 (s, 6H), 2.18 – 2.09 (m, 1H), 2.09 – 2.00 (m, 1H), 0.99 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.80, 138.29, 130.03, 124.89, 65.94, 33.24, 21.43, 11.98.

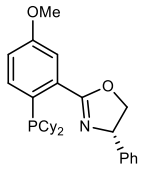
HRMS (EI): $C_{11}H_{15}Cl$: 182.0862, found: 182.0852.

2) Synthesis of chiral ligand



Step 1: To a solution of 2-bromo-5-methoxybenzonitrile (1.09 g, 6 mmol, 1.0 equiv) in anhydrous THF (11 mL), kept in an oven-dried 50 mL Schlenk, was added dropwise a solution of ^{n}BuLi in hexane (3.94 mL, 1.6 M in hexanes, 6.3 mmol, 1.05 eq) at -78 °C. After stirring at -78 °C for 1 hour, Cy_2PCl (6 mmol, 1.0 equiv) in anhydrous THF (4 mL) was added dropwise. The solution was stirred for 1 hour at -78 °C, then allowed to warm to room temperature. Next, the solvent was evaporated under reduced pressure, and the resulting residue purified by flash column chromatography (silica gel, pentane with 3% EtOAc) to afford the product.

Step 2: To a solution of (*S*)-(+)-2-phenylglycinol (148 mg, 1.08 mmol, 1.20 equiv) and the product obtained in the step 1 (0.90 mmol, 1.00 equiv) in chlorobenzene (7.0 mL) was added $ZnCl_2$ (1.15 equiv) in Et_2O (1.2 mL). The reaction was refluxed for 4 days at 135 ^oC. After cooling to room temperature, the reaction mixture was added CH_2Cl_2 (6.0 mL) and 2,2'- bipyridine (0.9 mmol, 1.0 equiv.). The solution was stirred for 1.5 hours at room temperature, then concentrated and the residue was purified by flash column chromatography (silica gel, pentane with 6% EtOAc) to afford the chiral ligand [5].



(*S*)-2-(2-(dicyclohexylphosphanyl)-5-methoxyphenyl)-4-phenyl-4,5-dihydrooxazole (*S*)-L5

The title compound was obtained as a white solid, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 3H), 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.21 (t, *J* = 4.0 Hz, 1H), 7.01 – 6.98 (m, 1H), 5.43 – 5.38 (m, 1H), 4.83 – 4.79 (m, 1H), 4.29 (t, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 1.88 – 1.87 (m, 4H), 1.76 – 1.75 (m, 2H), 1.66 – 1.65 (m, 3H), 1.58 – 1.49 (m, 2H), 1.35 – 1.03 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 159.67, 142.68, 138.18 (d, *J* = 31.3 Hz), 134.33, 128.69, 127.55, 127.50 (d, *J* = 25.3 Hz), 127.24, 116.51, 114.25, 74.92, 70.55, 55.49, 34.93 (d, *J* = 14 Hz), 34.67 (d, *J* = 14.1 Hz), 30.64 (d, *J* = 19.2 Hz), 30.45 (d, *J* = 16.2 Hz), 29.80, 29.70, 27.47, 27.36, 27.34, 27.23, 26.61, 26.55.

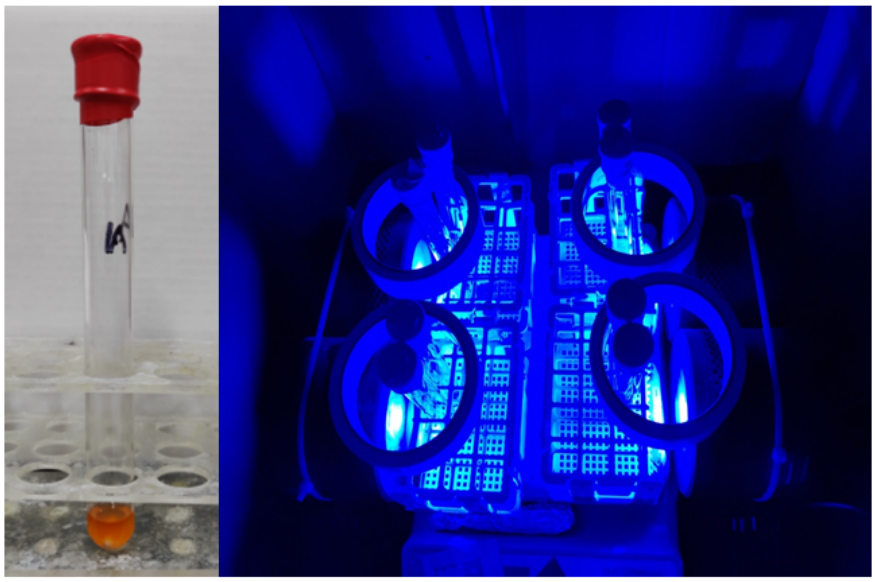
^{31}P NMR (162 MHz, $CDCl_3$) δ -7.76.

HRMS (ESI): $C_{28}H_{37}NO_2P^+$ ($M+H^+$): 450.2556, found: 450.2561.

$[\alpha]_D^{25}$ = -32.1 (c = 0.9, $CHCl_3$).

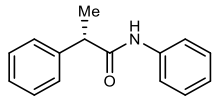
4. General Procedure for Enantioselective Carbonylative Couplings

To a flame-dried 20 mL test tube was charged with benzyl chloride (0.1 mmol, 1.0 equiv., if solid), aniline (0.15 mmol, if solid), $Ir(ppy)_2(dCO_2Etbpy)PF_6$ (2.0 mg, 0.002 mmol, 2 mol%), (*S*)-**L5** (4.5 mg, 0.01 mmol, 10 mol%), $NiCl_2•6H_2O$ (1.9 mg, 0.008 mmol, 8 mol%), and $MgBr_2$ (18.4 mg, 0.1 mmol, 1.0 equiv.). Then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO balloon three times, DME /EtOAc (1 mL, v/v = 7:3) was added via a syringe, followed by the addition of with benzyl chloride (0.1 mmol, 1.0 equiv., if liquid), aniline (0.15 mmol, if liquid), BnBpin (22.3 μL, 0.1 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 hours at 50 ^oC by 90 W blue LEDs. Upon completion, the reaction mixture was diluted with EtOAc (10 mL) and transferred to a separatory funnel. The organic layer was washed with brine (2×10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resultant crude residue was purified by flash column chromatography to give the products.



Supplementary Figure S6 Reaction Setup for the enantioselective carbonylative coupling

5. Characterization of Products



(*S*)-*N*,2-diphenylpropanamide (3) [6]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (16.9 mg, 75%, 92% ee).

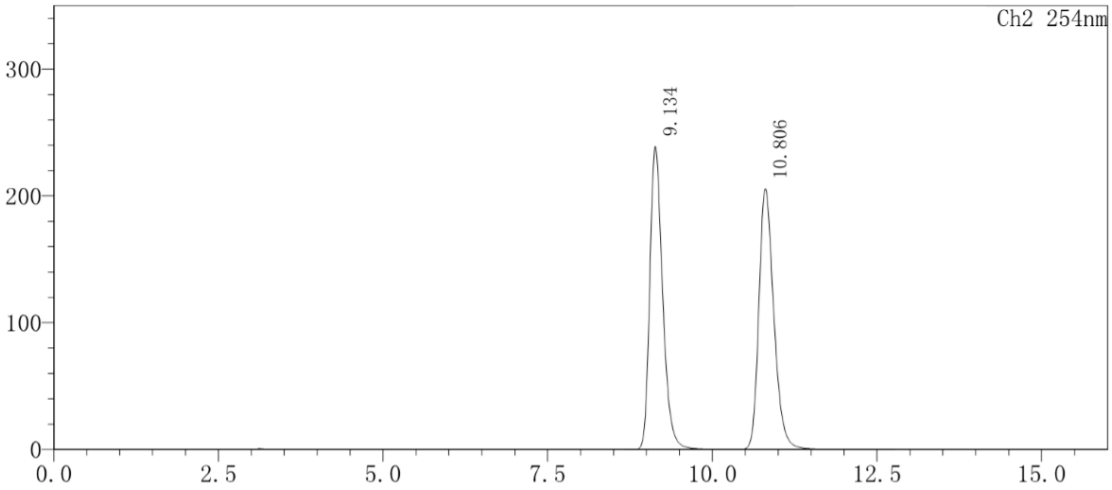
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 -7.27(m 3H), 7.24 – 7.15 (m, 4H), 6.97 (t, *J* = 8.0 Hz, 1H), 3.63 (q, *J* = 8.0 Hz, 1H), 1.50 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.54, 141.03, 137.97, 129.20, 128.99, 127.78, 127.63, 124.33, 119.86, 48.10, 18.68.

$[\alpha]_D^{25}$ = 41.3 (c = 0.71, $CHCl_3$).

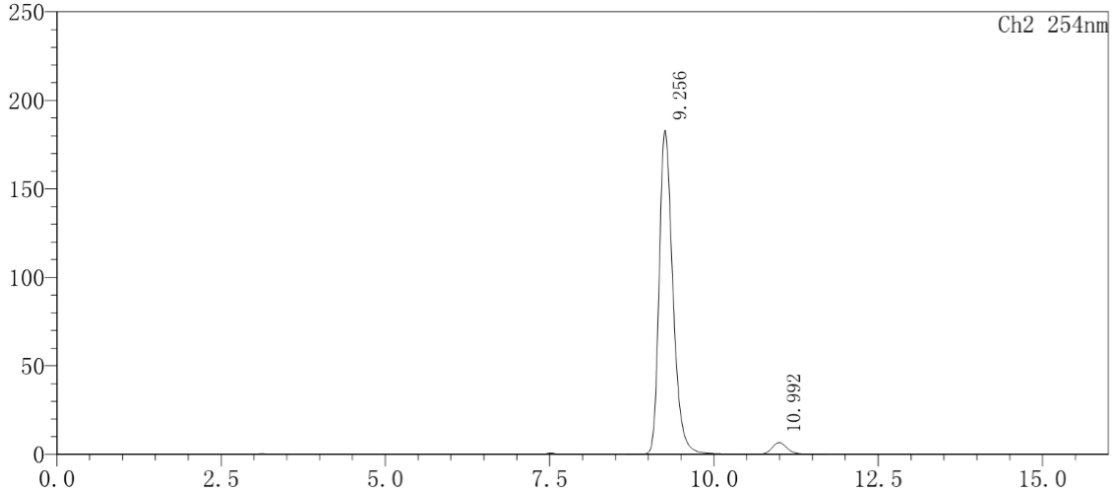
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^oC, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.3 min, t_R (minor) = 11.0 min.

3 racemic

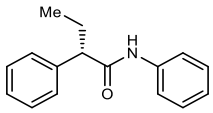


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.134	3259914	239322	49.989
2	10.806	3261314	205730	50.011

3 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.256	2660415	183337	96.020
2	10.992	110262	6663	3.980



(*S*)-*N*,2-diphenylbutanamide (8) [7]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (17.4 mg, 73%, 93% ee).

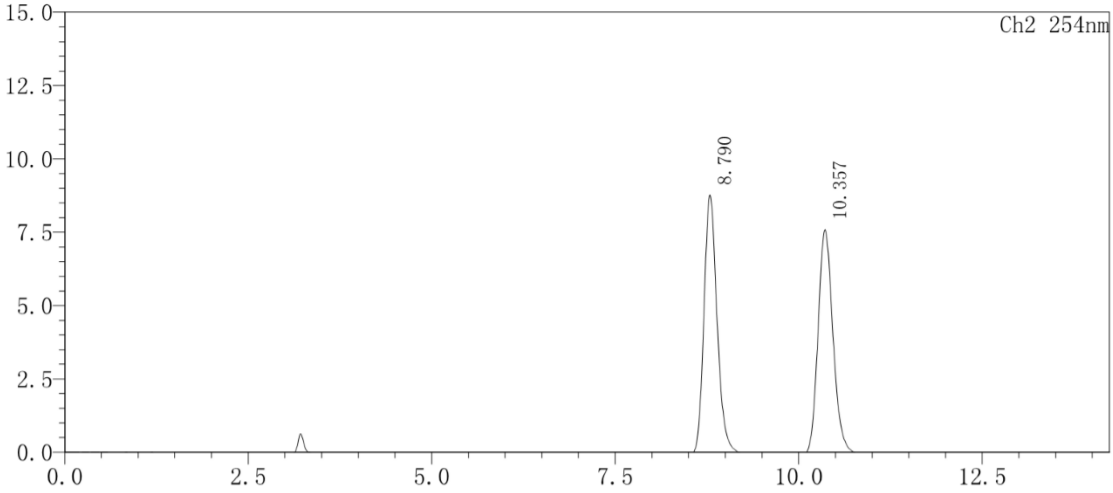
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 –7.46 (m, 2H), 7.39 – 7.35 (m, 4H), 7.35 –7.28 (m, 3H), 7.08 (t, *J* = 8.0 Hz, 1H), 3.43 (t, *J* = 8.0 Hz, 1H), 2.35 – 2.24 (m, 1H), 1.95 – 1.84 (m, 1H), 0.95 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.90, 139.65, 138.01, 129.09, 129.01, 128.17, 127.59, 124.35, 119.91, 56.23, 26.54, 12.46.

$[\alpha]_D^{25}$ = 51.5 (c = 1.01, $CHCl_3$).

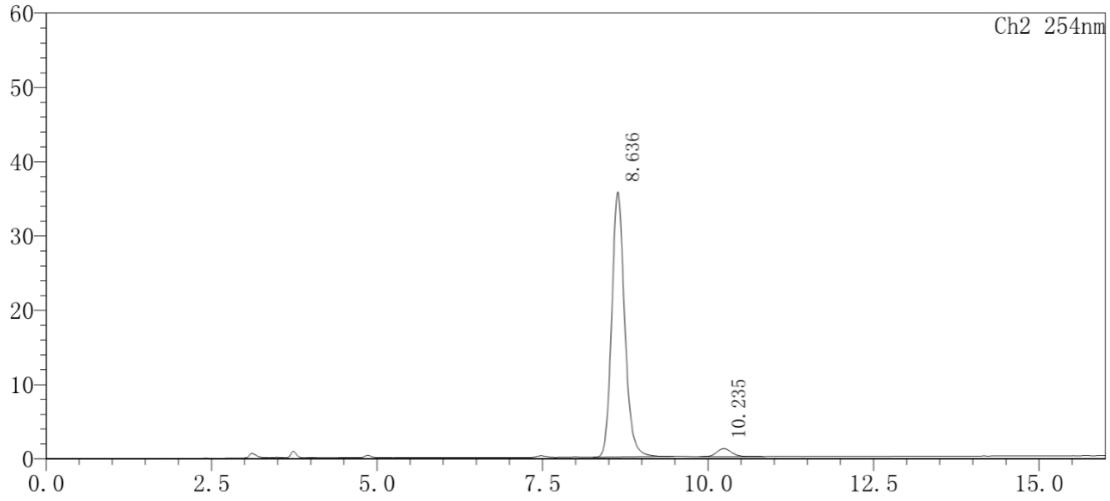
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.6 min, t_R (minor) = 10.2 min.

8 racemic

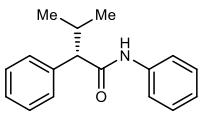


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	8.790	113165	8887	50.338
2	10.357	111647	7712	49.662

8 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	8.636	488083	35728	96.638
2	10.235	16978	1076	3.362



(*S*)-3-methyl-*N*,2-diphenylbutanamide (9) [8]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (18.2 mg, 72%, 93% ee).

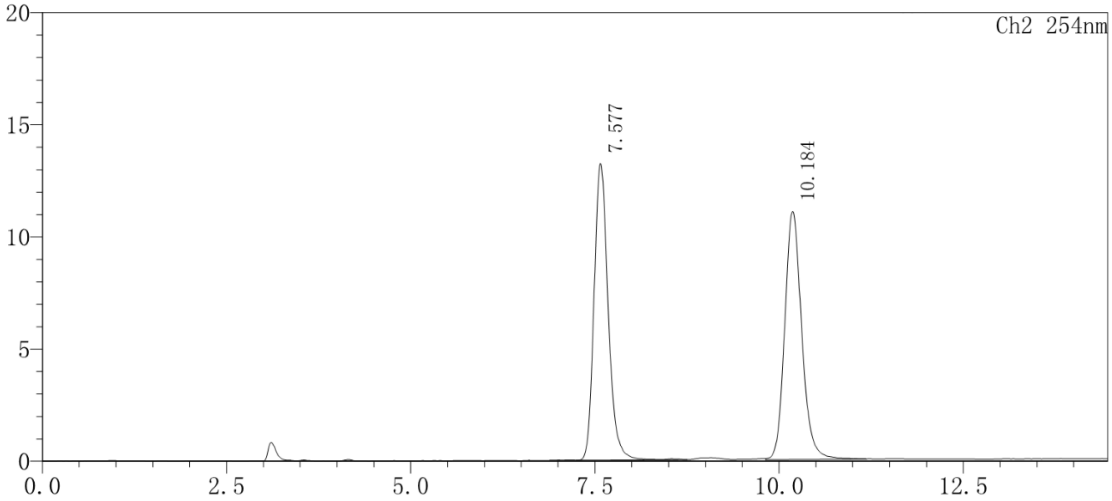
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.38 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 3H), 7.22 (s,1H), 7.07 (t, *J* = 8.0 Hz, 1H), 2.99 (d, *J* = 12.0 Hz, 1H), 2.58 – 2.47 (m, 1H), 1.12 (d, *J* = 4.0 Hz, 3H), 0.75 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 139.05, 138.02, 129.05, 128.80, 128.45, 127.47, 124.39, 119.97, 63.08, 31.75, 21.86, 20.50.

$[\alpha]_D^{25}$ = 38.2 (c = 0.92, $CHCl_3$).

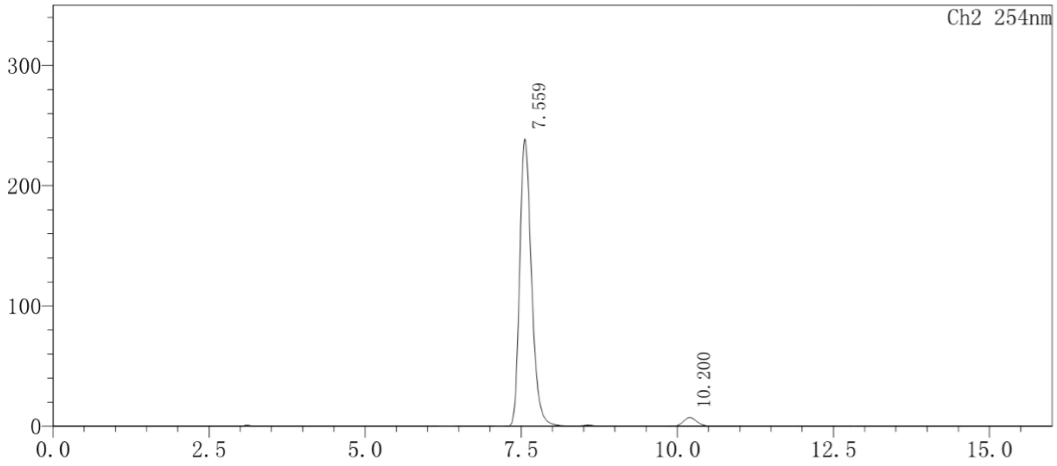
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.6 min, t_R (minor) = 10.2 min.

9 racemic

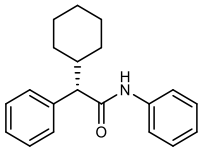


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	7.577	176315	13242	49.796
2	10.184	177761	11069	50.204

9 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	7.559	3148734	239282	96.355
2	10.200	119110	7442	3.645



(*S*)-2-cyclohexyl-*N*,2-diphenylacetamide (10) [9]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 5% EtOAc) as a white solid (13.8 mg, 47%, 90% ee).

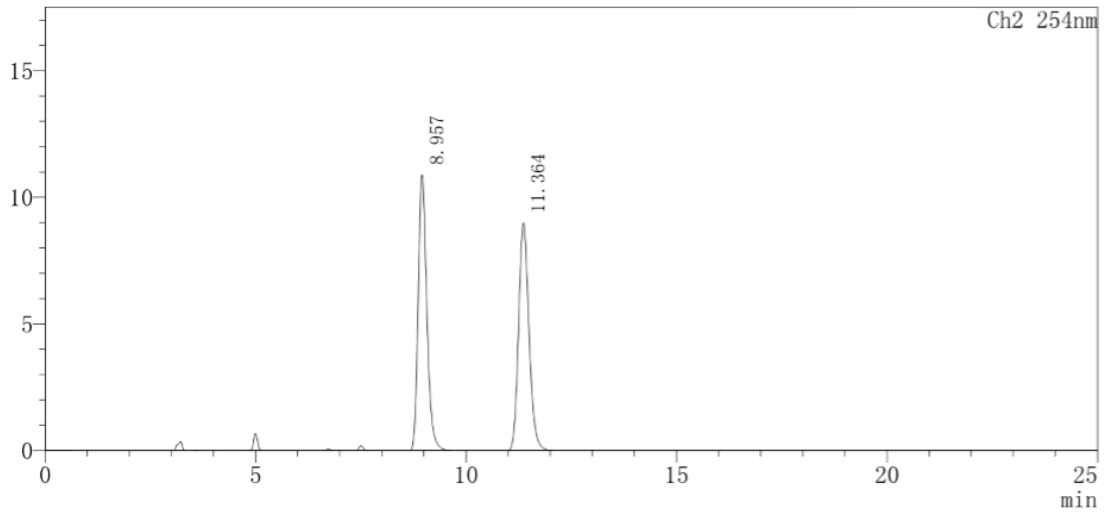
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.38 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.06 (t, *J* = 8.0 Hz, 1H), 3.08 (d, *J* = 8.0 Hz, 1H), 2.24 – 2.14 (m, 1H), 2.01 (d, *J* = 12 Hz, 1H), 1.74 – 1.71 (m, 1H), 1.66 – 1.62 (m, 2H), 1.38 – 1.33 (m, 2H), 1.20 – 1.01 (m, 3H), 0.81 – 0.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.72, 138.61, 138.02, 129.02, 128.74, 128.53, 127.37, 124.36, 119.98, 61.95, 40.94, 32.41, 30.79, 26.52, 26.22.

$[\alpha]_D^{25}$ = 42.1 (c = 0.83, $CHCl_3$).

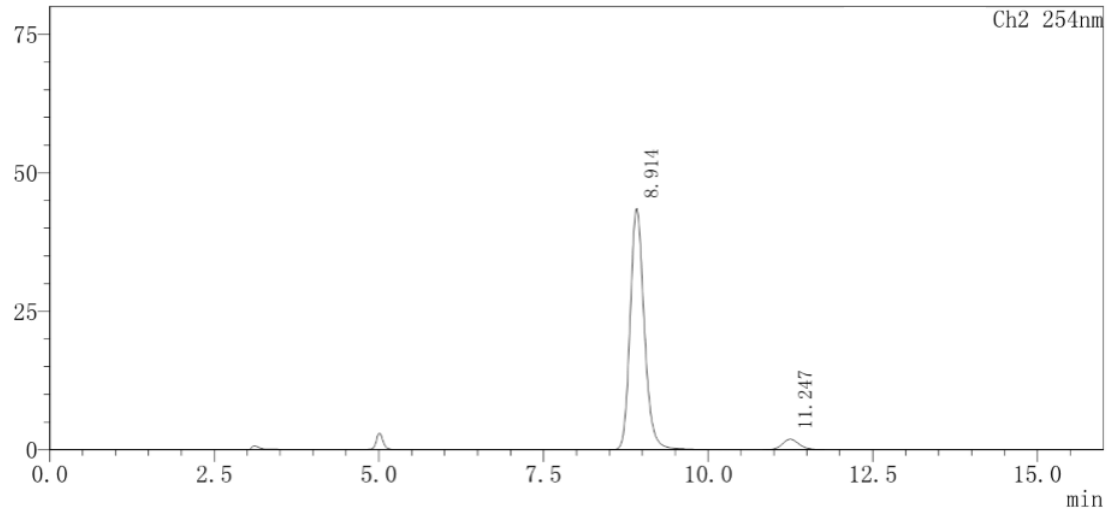
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.9 min, t_R (minor) = 11.2 min.

10 racemic

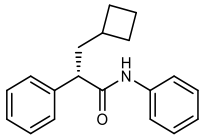


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	8.957	158473	10958	49.980
2	11.364	158599	9041	50.020

10 enantioenriched, 90% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	8.914	648130	43549	95.160
2	11.247	32962	1883	4.840



(*S*)-3-cyclobutyl-*N*,2-diphenylpropanamide (11) [10]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (19.0 mg, 68%, 92% ee).

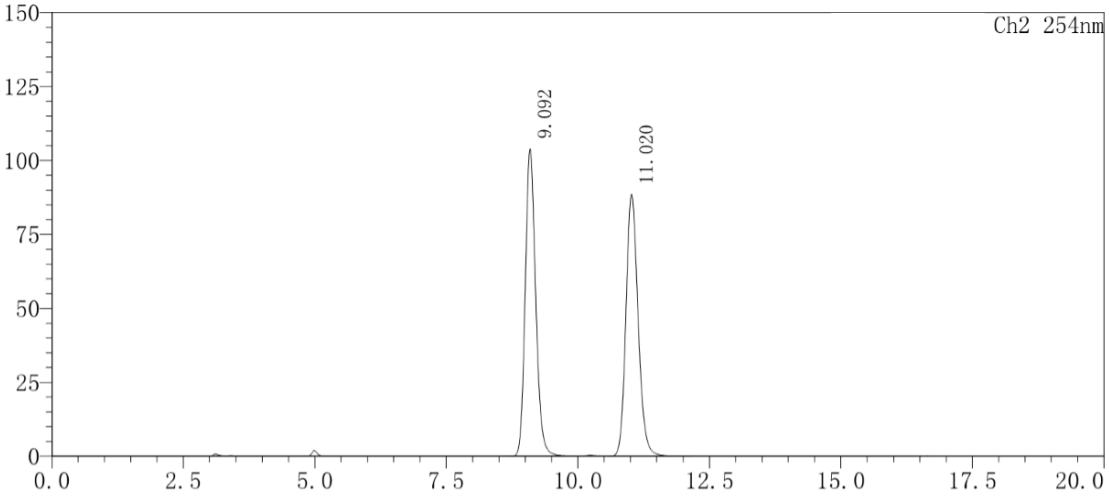
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.32 (m, 4H), 7.28 – 7.26 (m, 1H), 7.24 – 7.22 (m, 2H), 7.13 (s, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 3.40 (t, *J* = 8.0 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.23 –2.15 (m, 1H), 2.03 – 1.87 (m, 3H), 1.81 – 1.71 (m, 2H), 1.69 – 1.62 (m, 1H), 1.60 –1.53 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.86, 139.79, 138.01, 129.10, 129.03, 128.16, 127.59, 124.34, 119.85 , 52.47, 40.40, 34.17, 28.43, 28.13, 18.53.

$[\alpha]_D^{25}$ = 33.7 (c = 0.62, $CHCl_3$).

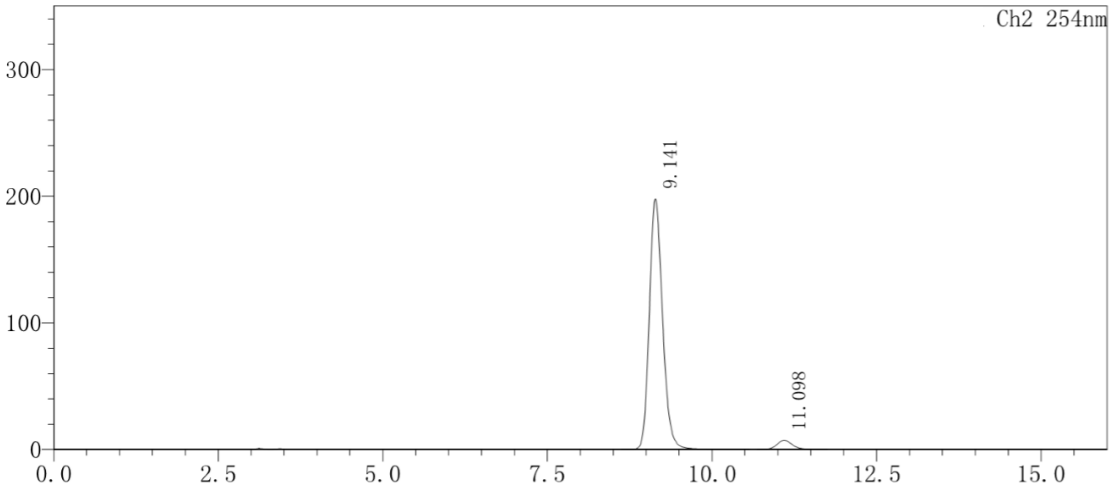
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.1 min, t_R (minor) = 11.1 min.

11 racemic

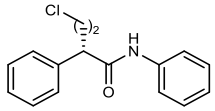


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.092	1438151	104029	50.106
2	11.020	1432049	88619	49.894

11 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.141	2772493	197999	95.951
2	11.098	116995	7202	4.049



(*S*)-4-chloro-*N*,2-diphenylbutanamide (12) [11]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (21.3 mg, 78%, 93% ee).

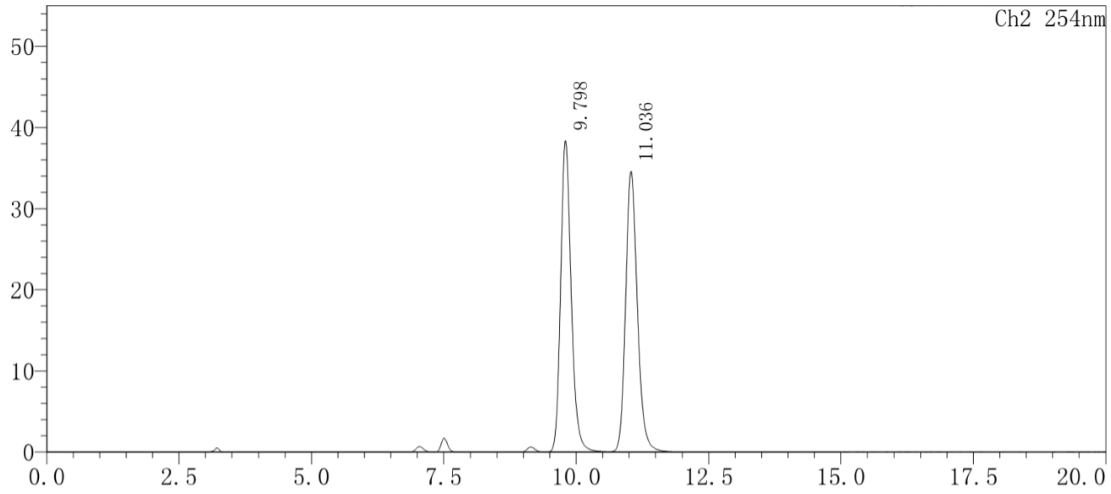
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34(m, 5H), 7.32 – 7.22 (m, 4H), 7.14 (s, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 3.83 (t, *J* = 8.0 Hz, 1H), 3.63 – 3.57 (m, 1H), 3.42 – 3.36 (m, 1H), 2.69 – 2.60 (m, 1H), 2.25 – 2.17 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.79, 138.40, 137.79, 129.41, 129.09, 128.26, 128.10, 124.59, 119.95, 50.63, 43.23, 35.86.

$[\alpha]_D^{25}$ = 47.2 (c = 1.07, $CHCl_3$).

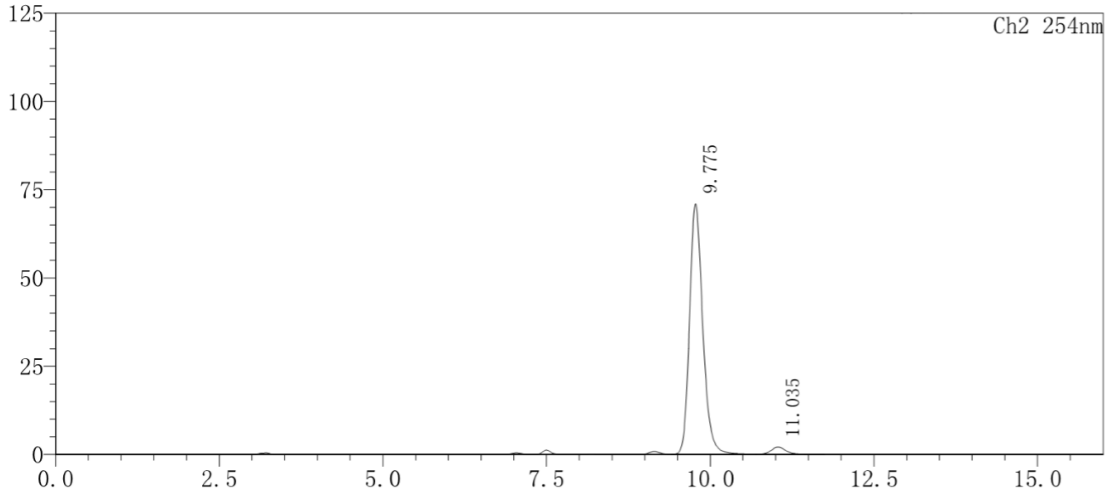
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.8 min, t_R (minor) = 11.0 min.

12 racemic

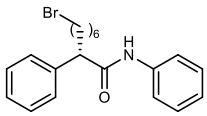


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.798	532852	38400	49.901
2	11.036	534960	34580	50.099

12 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.775	1002305	71035	96.669
2	11.035	34534	2093	3.331



(*S*)-8-bromo-*N*,2-diphenyloctanamide (13)

According to **General Procedure**, the title compound was isolated by flash column

chromatography (silica gel, pentane with 8% EtOAc) as a white solid (23.9 mg, 64%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.31 – 7.25 (m, 4H), 7.24 – 7.17 (m, 3H), 7.10 (s, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 3.40 (t, *J* = 8.0 Hz, 1H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.20 – 2.12 (m, 1H), 1.80 – 1.70 (m, 3H), 1.32 – 1.15 (m, 6H).

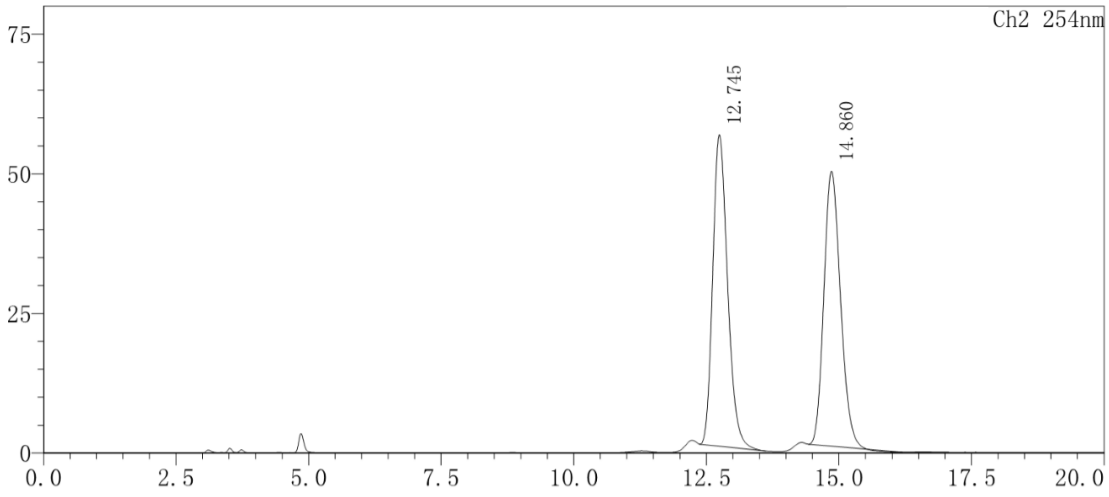
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.68, 139.62, 137.85, 129.09, 128.94, 128.00, 127.58, 124.29, 119.75, 54.40, 33.94, 33.11, 32.69, 28.61, 27.95, 27.56.

HRMS (ESI): $C_{20}H_{25}BrNO^+$ ($M+H^+$): 374.1114, found: 374.1110.

$[\alpha]_D^{25}$ = 52.1 (c = 1.02, $CHCl_3$).

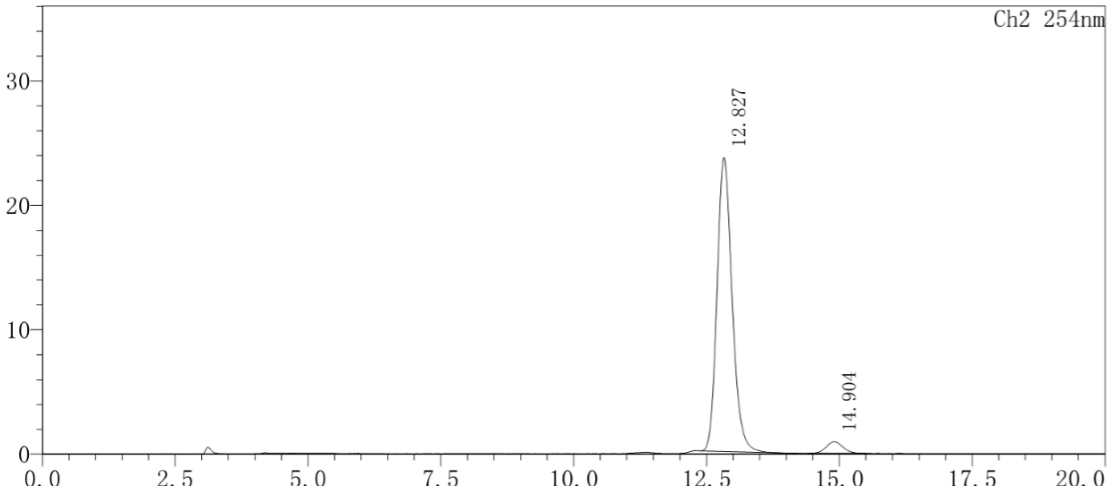
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.8 min, t_R (minor) = 14.9 min.

13 racemic

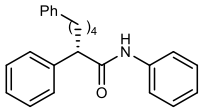


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.745	1087552	55748	50.367
2	14.860	1071715	49242	49.633

13 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.827	467011	23616	95.857
2	14.904	20186	920	4.143



(*S*)-*N*,2,6-triphenylhexanamide (14)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (26.1 mg, 76%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.24 (m, 3H), 7.23 – 7.15 (m, 5H), 7.09 – 7.04 (m, 4H), 6.98 (t, *J* = 8.0 Hz, 1H), 3.37 (t, *J* = 8.0 Hz, 1H), 2.49 (t, *J* = 8.0 Hz, 2H), 2.24 – 2.15 (m, 1H), 1.83 – 1.73 (m, 1H), 1.62 – 1.57 (m, 1H), 1.55 – 1.48 (m, 1H), 1.36 – 1.26 (m, 1H), 1.25 – 1.19 (m, 1H).

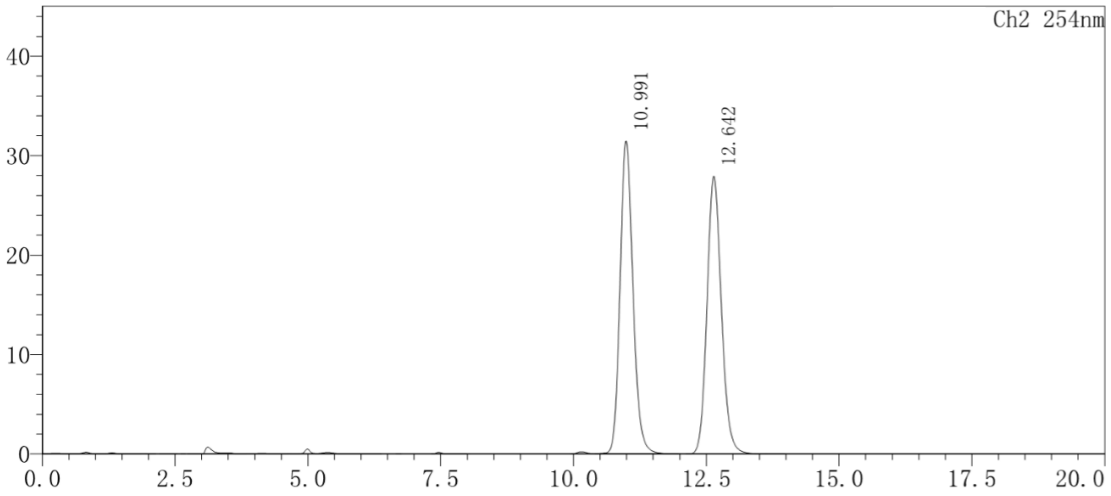
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.84, 142.62, 139.77, 137.97, 129.16, 129.03, 128.49, 128.38, 128.11, 127.64, 125.77, 124.39, 119.89, 54.45, 35.78, 33.21, 31.41, 27.48.

HRMS (ESI): $C_{24}H_{26}NO^+$ ($M+H^+$): 344.2009, found: 344.2004.

$[\alpha]_D^{25}$ = 29.3 (c = 0.51, $CHCl_3$).

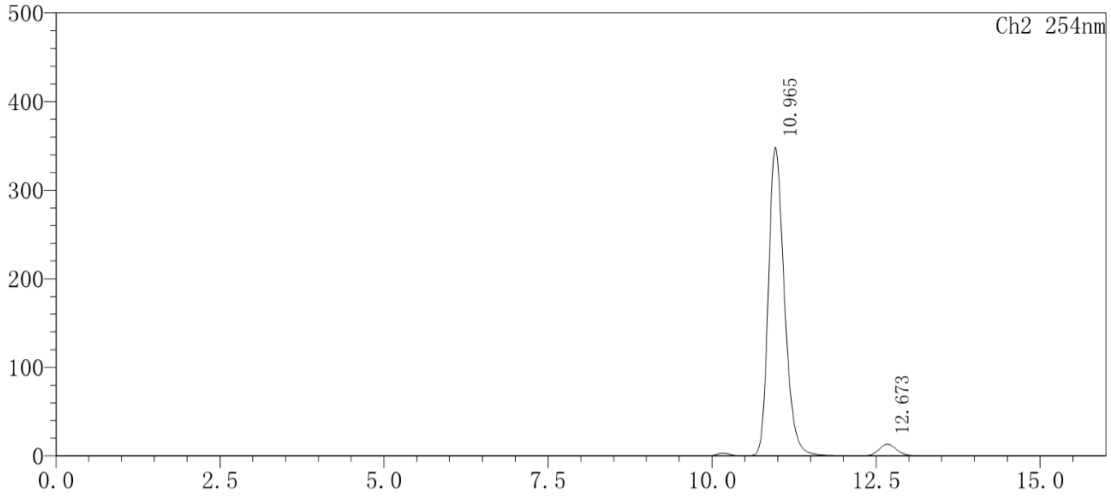
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.0 min, t_R (minor) = 12.7 min.

14 racemic

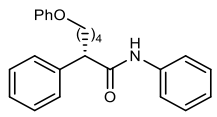


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.991	536114	31491	50.246
2	12.642	530873	27972	49.754

14 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.965	5908150	348749	95.873
2	12.673	254316	13218	4.127



(*S*)-6-phenoxy-*N*,2-diphenylhexanamide (15)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (25.1 mg, 70%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.27 – 7.26 (m, 4H), 7.22 – 7.14 (m, 5H), 7.08 (s, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.82 (t, *J* = 8.0 Hz, 2H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.26 – 2.17 (m, 1H), 1.86 – 1.78 (m, 1H), 1.76 – 1.65 (m, 2H), 1.46 – 1.33 (m, 2H).

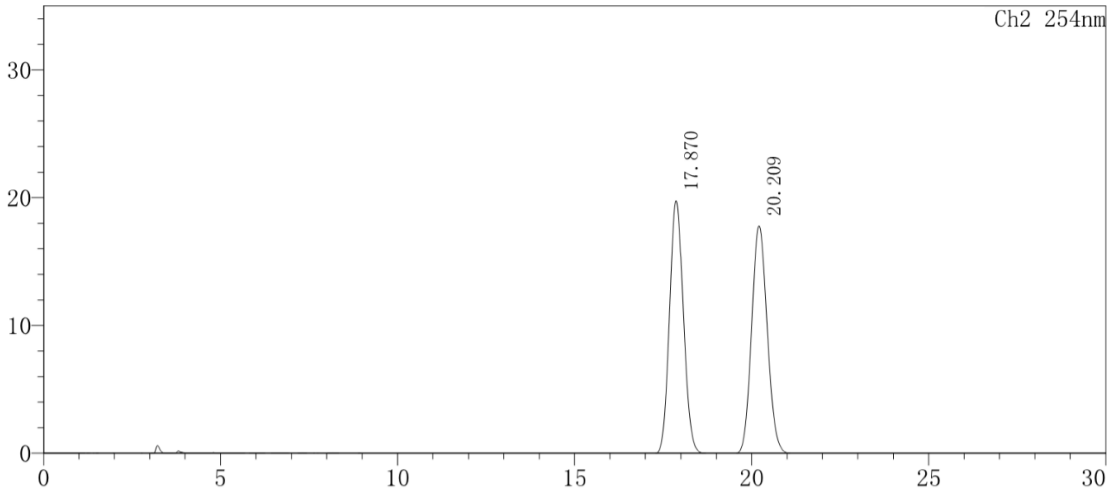
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.71, 159.08, 139.61, 137.94, 129.54, 129.22, 129.05, 128.13, 127.72, 124.42, 120.67, 119.90, 114.61, 67.59, 54.45, 33.07, 29.24, 24.43.

HRMS (ESI): $C_{24}H_{26}NO_2^+$ ($M+H^+$): 360.1958, found: 360.1956.

$[\alpha]_D^{25}$ = 43.7 (c = 0.80, $CHCl_3$).

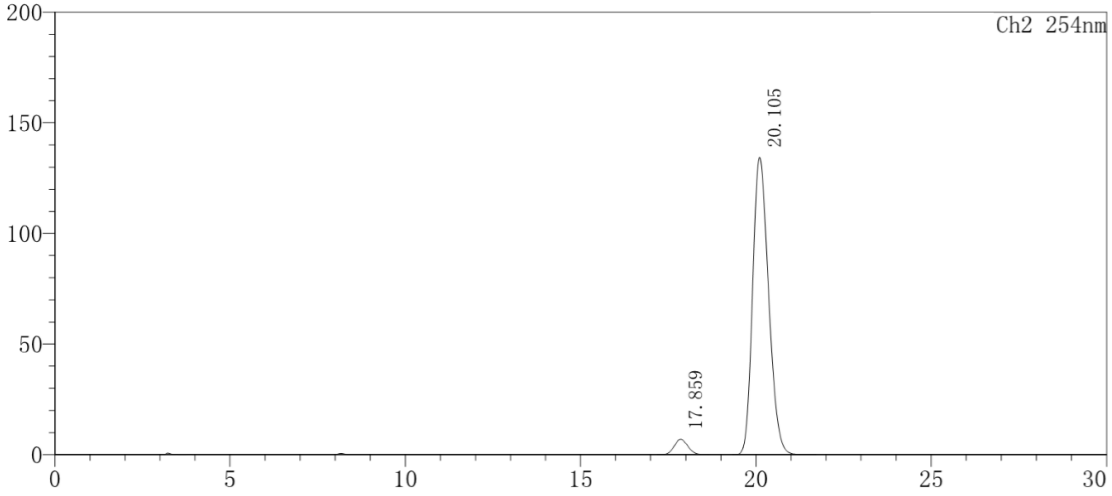
HPLC: The ee was determined to be 92% on a CHIRALPAK ADH column at 254 nm, 25 ^oC, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 20.1 min, t_R (minor) = 17.9 min.

15 racemic

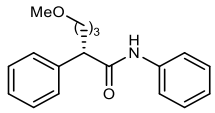


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	17.870	538440	19834	49.409
2	20.209	551329	17872	50.591

15 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	17.859	188553	6983	4.241
2	20.105	4257339	134374	95.759



(*S*)-5-methoxy-*N*,2-diphenylpentanamide (16)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (19.5 mg, 69%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.27 – 7.23 (m, 4H), 7.20 – 7.14 (m, 3H), 6.96 (t, *J* = 8.0 Hz, 1H), 3.44 (t, *J* = 8.0 Hz, 1H), 3.35 – 3.25 (m, 2H), 3.22 (s, 3H), 2.24 – 2.15 (m, 1H), 1.85 – 1.76 (m, 1H), 1.57 – 1.40 (m, 2H).

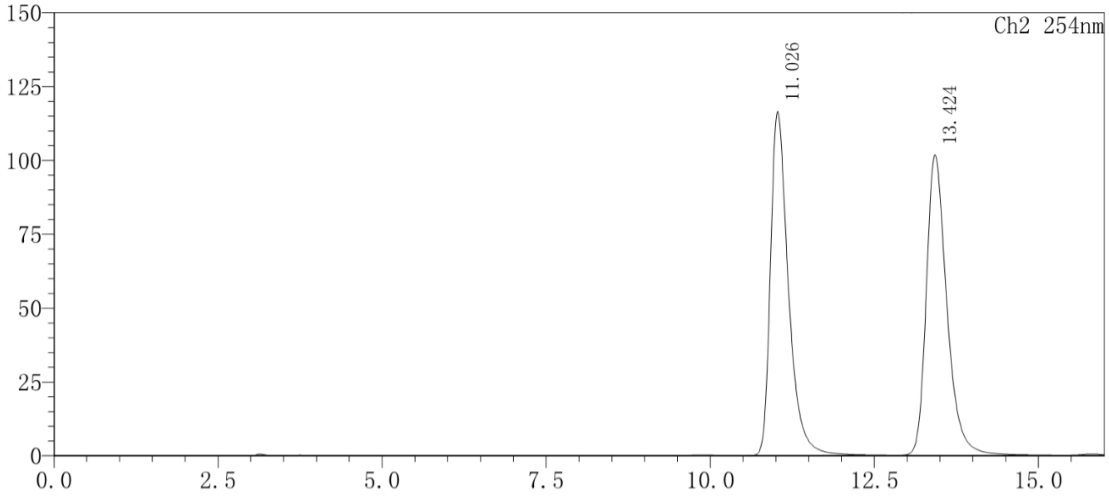
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 139.71, 138.03, 129.12, 129.02, 128.16, 127.64, 124.33, 119.86, 72.81, 58.73, 54.10, 30.46, 27.82.

HRMS (ESI): $C_{18}H_{22}NO_2^+$ ($M+H^+$): 284.1645, found: 284.1642.

$[\alpha]_D^{25}$ = 39.1 (c = 1.69, $CHCl_3$).

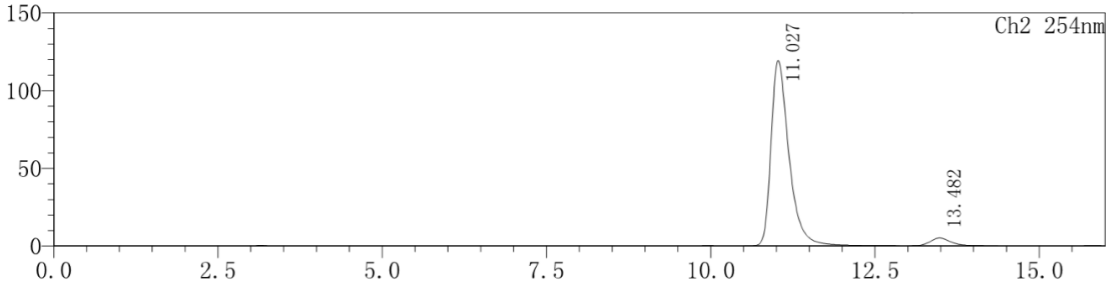
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.0 min, t_R (minor) = 13.5 min.

16 racemic

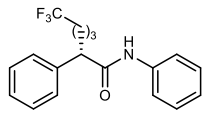


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	11.026	2224030	116682	50.050
2	13.424	2219553	101761	49.950

16 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	11.027	2274645	119458	95.402
2	13.482	109625	4969	4.598



(*S*)-6,6,6-trifluoro-*N*,2-diphenylhexanamide (17)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (24.7 mg, 77%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 3H), 7.28 – 7.19 (m, 4H), 7.08 (s, 1H), 7.02 (t, J = 8.0 Hz, 1H), 3.42 (t, J = 8.0 Hz, 1H), 2.29 – 2.20 (m, 1H),

2.13 – 1.94 (m, 2H), 1.88 – 1.79 (m, 1H), 1.56 – 1.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.16, 139.04, 137.78, 129.42, 129.09, 128.06, 128.02, 127.10 (q, J = 277.8 Hz), 124.59, 119.96, 54.12, 33.77 (q, J = 28.3 Hz), 32.32, 20.43.

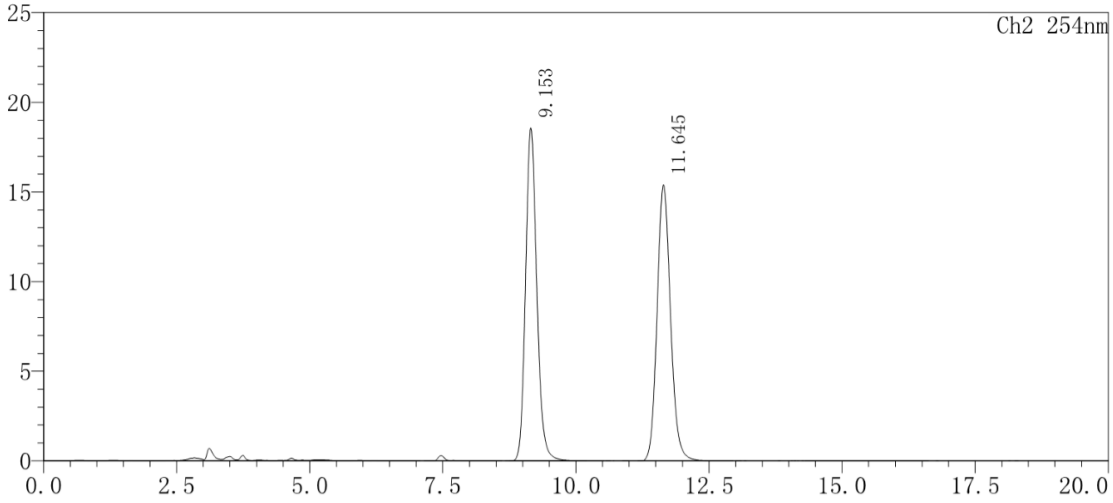
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.26 (t, J = 11.3 Hz, 3F).

HRMS (ESI): $C_{18}H_{19}F_3NO^+$ ($M+H^+$): 322.1413, found: 322.1409.

$[\alpha]_D^{25}$ = 98.2 (c = 1.02, $CHCl_3$).

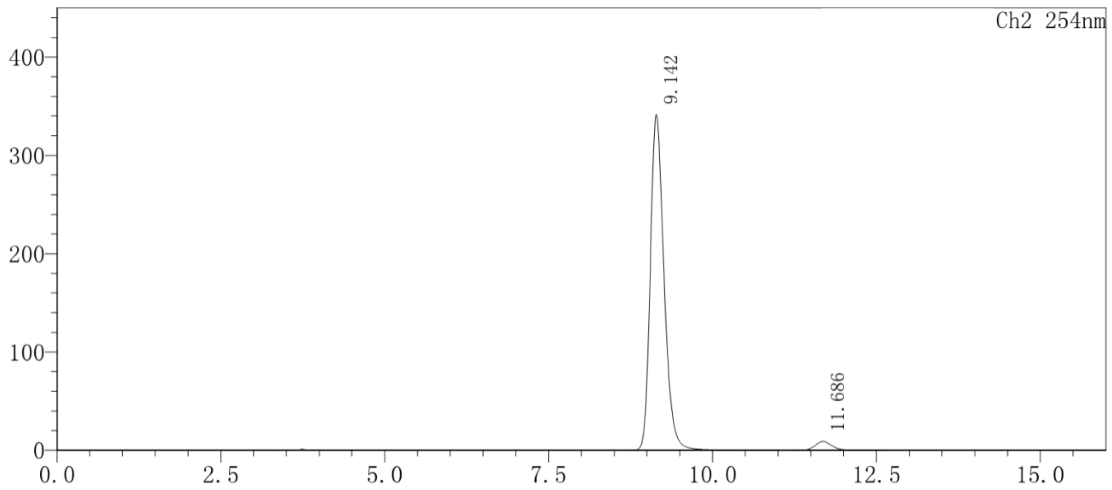
HPLC: The ee was determined to be 94% on a CHIRALPAK IA column at 254 nm, 25 ^oC, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.1 min, t_R (minor) = 11.7 min.

17 racemic

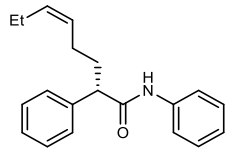


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.153	274785	18582	50.293
2	11.645	271587	15414	49.707

17 enantioenriched, 94% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.142	4980014	341692	96.856
2	11.686	161642	8990	3.144



(*S*,*Z*)-*N*,2-diphenyloct-5-enamide (18)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 5% EtOAc) as a white solid (17.9 mg, 61%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.27 – 7.26 (m, 3H), 7.22 – 7.14 (m, 4H), 6.96 (t, *J* = 8.0 Hz, 1H), 5.34 – 5.20 (m, 2H), 3.43 (t, *J* = 8.0 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.97 – 1.92 (m, 2H), 1.88 – 1.76 (m, 3H), 0.82 (t, *J* = 8.0 Hz, 3H).

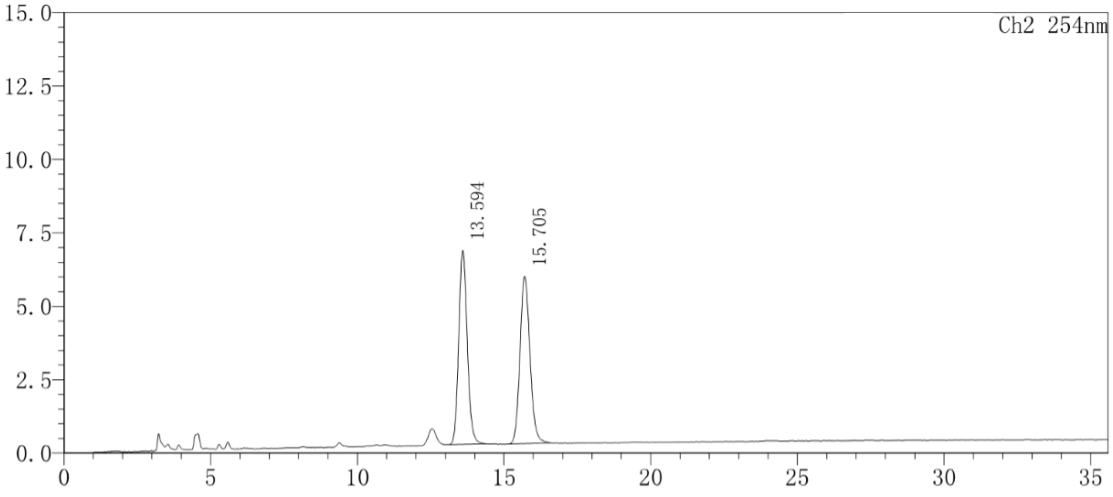
^{13}C NMR (101 MHz, $CDCl_3$) 171.79, 139.59, 137.97, 132.97, 129.12, 129.00, 128.18, 127.97, 127.64, 124.36, 119.91, 53.56, 33.21, 25.11, 20.67, 14.42.

HRMS (ESI): $C_{20}H_{24}NO^+$ ($M+H^+$): 294.1852, found: 294.1848.

$[\alpha]_D^{25}$ = 51.2 (c = 0.87, $CHCl_3$).

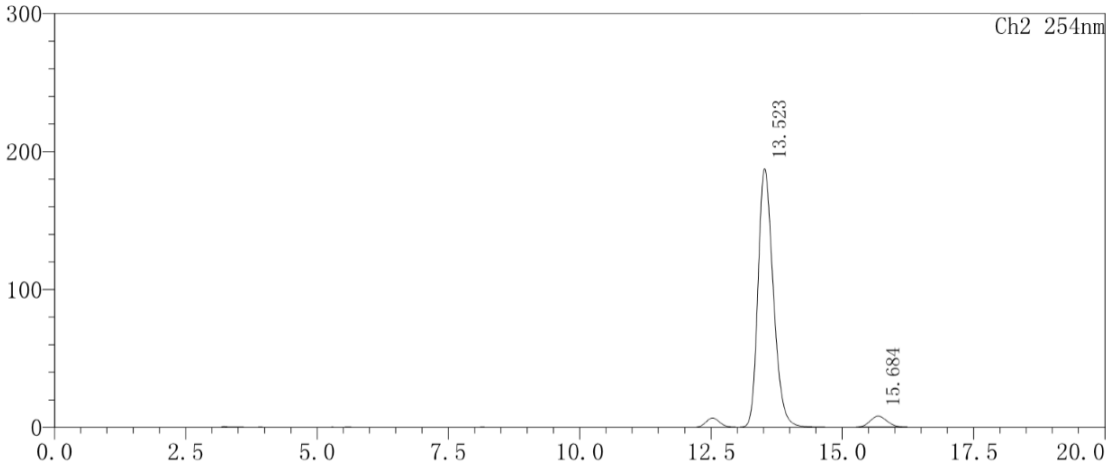
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 13.5 min, t_R (minor) = 15.7 min.

18 racemic

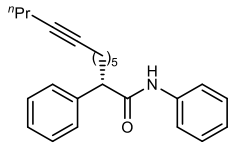


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13.594	133421	6604	49.685
2	15.705	135112	5692	50.315

18 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13.523	3799596	187486	95.505
2	15.684	178832	7947	4.495



(*S*)-*N*,2-diphenyldodec-8-ynamide (19)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (23.6 mg, 68%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.25 (s, 1H), 7.08 – 7.01 (m, 2H), 3.47 (t, *J* = 8.0 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.12 – 2.09 (m, 3H), 1.89 – 1.80 (m, 1H), 1.51 – 1.44 (m, 5H), 1.40 – 1.26 (m, 4H), 0.96 (t, *J* = 8.0 Hz, 3H).

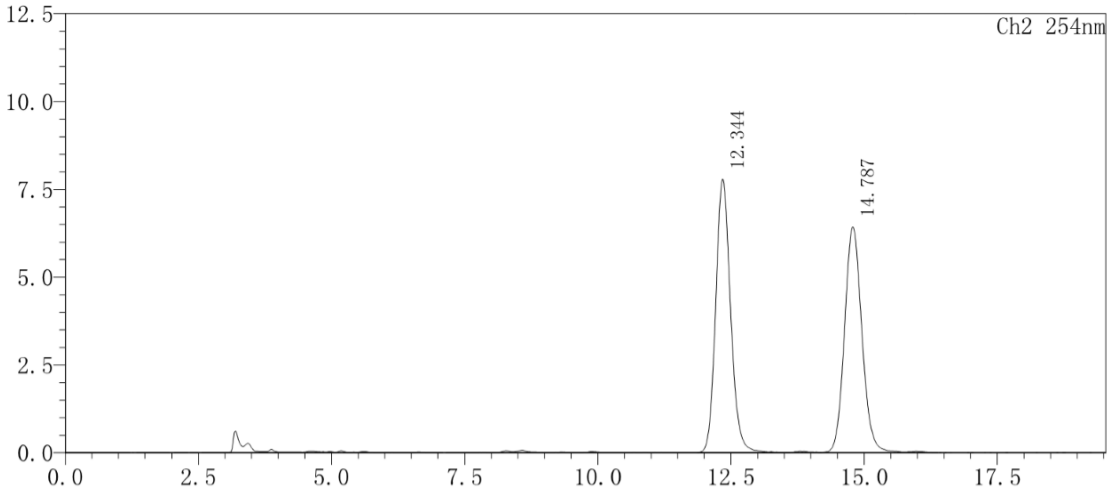
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.81, 139.79, 137.99, 129.19, 129.06, 128.15, 127.67, 124.39, 119.84, 80.37, 80.30, 54.54, 33.26, 29.02, 28.73, 27.38, 22.68, 20.90, 18.80, 13.63.

HRMS (ESI): $C_{24}H_{30}NO^+$ ($M+H^+$): 348.2322, found: 348.2318.

$[\alpha]_D^{25}$ = 39.3 (c = 0.91, $CHCl_3$).

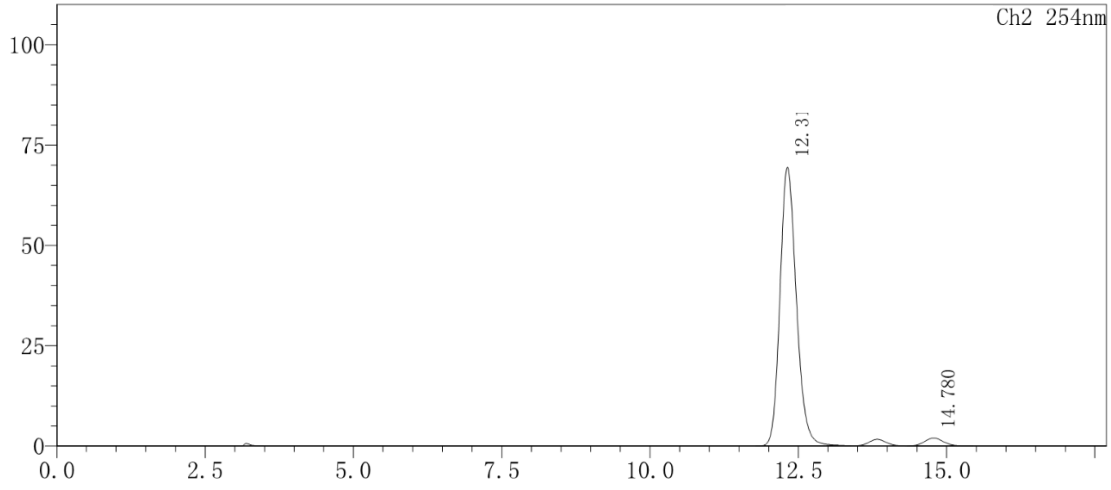
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^oC, with hexane: ^iPrOH = 94:6 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.3 min, t_R (minor) = 14.8 min.

19 racemic

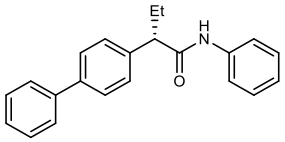


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.344	151526	7791	50.679
2	14.787	147466	6437	49.321

19 enantioenriched, 94% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.316	1330666	69538	96.837
2	14.780	43461	1970	3.163



(*S*)-2-([1,1'-biphenyl]-4-yl)-*N*-phenylbutanamide (20)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (23.0 mg, 73%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 4H), 7.48 – 7.43 (m, 6H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.20 (s, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 3.44 (t, *J* = 8.0 Hz, 1H), 2.37 – 2.26 (m, 1H), 1.97 – 1.86 (m, 1H), 0.97 (t, *J* = 8.0 Hz, 3H).

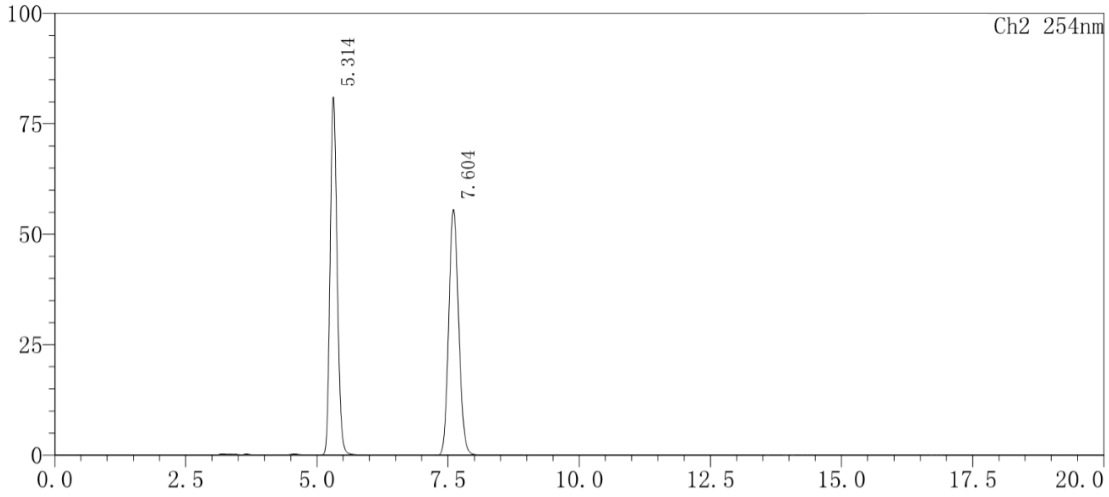
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 140.72, 140.58, 138.65, 137.99, 129.09, 128.95, 128.61, 127.85, 127.53, 127.18, 124.43, 119.90, 56.03, 26.63, 12.54..

HRMS (ESI): $C_{22}H_{22}NO^+$ ($M+H^+$): 316.1696, found: 316.1692.

$[\alpha]_D^{25}$ = 47.6 (c = 1.02, $CHCl_3$).

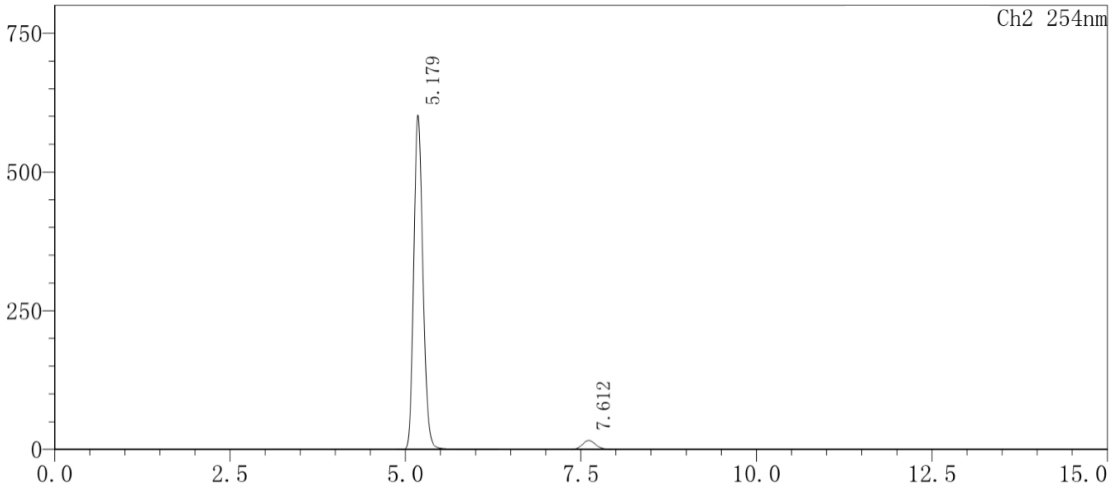
HPLC: The ee was determined to be 93% on a CHIRALPAK ADH column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 75:25 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.2 min, t_R (minor) = 7.6 min.

20 racemic

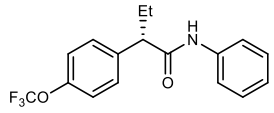


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.314	756716	81066	50.728
2	7.604	735001	55623	49.272

20 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.179	5491037	602023	96.347
2	7.612	208170	15890	3.653



(*S*)-*N*-phenyl-2-(4-(trifluoromethoxy)phenyl)butanamide (21)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 8% EtOAc) as a white solid (20.3 mg, 63%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.34 – 7.31 (m, 2H), 7.23 – 7.17 (m, 3H), 7.13 – 7.11 (m, 2H), 7.03 – 6.99 (m, 1H), 3.30 (t, *J* = 7.5 Hz, 1H), 2.25 – 2.08 (m, 1H), 1.82 – 1.71 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.34, 148.66, 138.40, 137.80, 129.44, 129.12, 124.65, 120.59 (q, *J* = 258.6 Hz), 121.47, 120.01, 55.65, 27.05, 12.39.

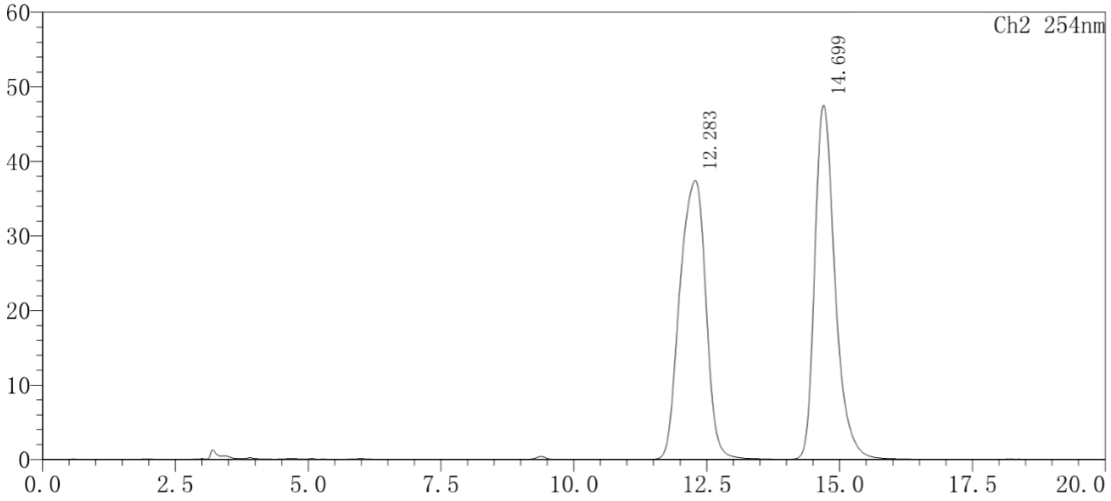
^{19}F NMR (377 MHz, $CDCl_3$) δ -57.85 (s, 3F).

HRMS (ESI): $C_{17}H_{17}F_3NO_2^+$ ($M+H^+$): 324.1206, found: 324.1203.

$[\alpha]_D^{25}$ = 31.5 (c = 1.12, $CHCl_3$).

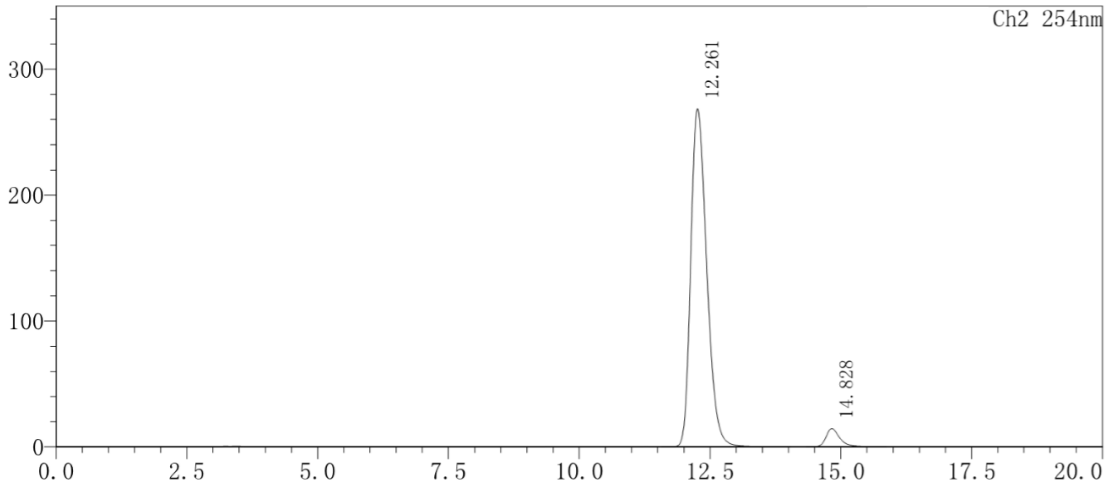
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.3 min, t_R (minor) = 14.8 min.

21 racemic

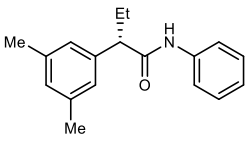


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.283	1272790	37395	50.229
2	14.699	1261197	47479	49.771

21 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.261	5723388	268654	95.433
2	14.828	273908	14681	4.567



(*S*)-2-(3,5-dimethylphenyl)-*N*-phenylbutanamide (22)

According to **General Procedure**, the title compound was isolated by flash column

chromatography (silica gel, pentane with 5% EtOAc) as a white solid (19.2 mg, 72%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.25 (s, 1H), 7.18 – 7.15 (m, 2H), 6.96 (t, J = 8.0 Hz, 1H), 6.87 (s, 2H), 6.83 (s, 1H), 3.25 (t, J = 8.0 Hz, 1H), 2.21 (s, 6H), 2.19 – 2.13 (m, 1H), 1.81 – 1.70 (m, 1H), 0.84 (t, J = 8.0 Hz, 3H).

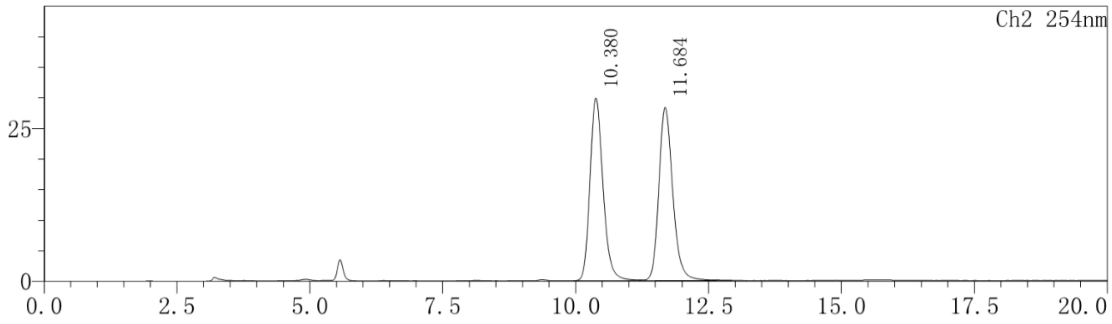
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.14, 139.52, 138.59, 138.12, 129.25, 128.96, 125.91, 124.22, 119.87, 56.08, 26.41, 21.43, 12.54.

HRMS (EI): $C_{18}H_{21}NO$: 267.1623, found: 267.1617.

$[\alpha]_D^{25}$ = 29.8 (c = 0.61, $CHCl_3$).

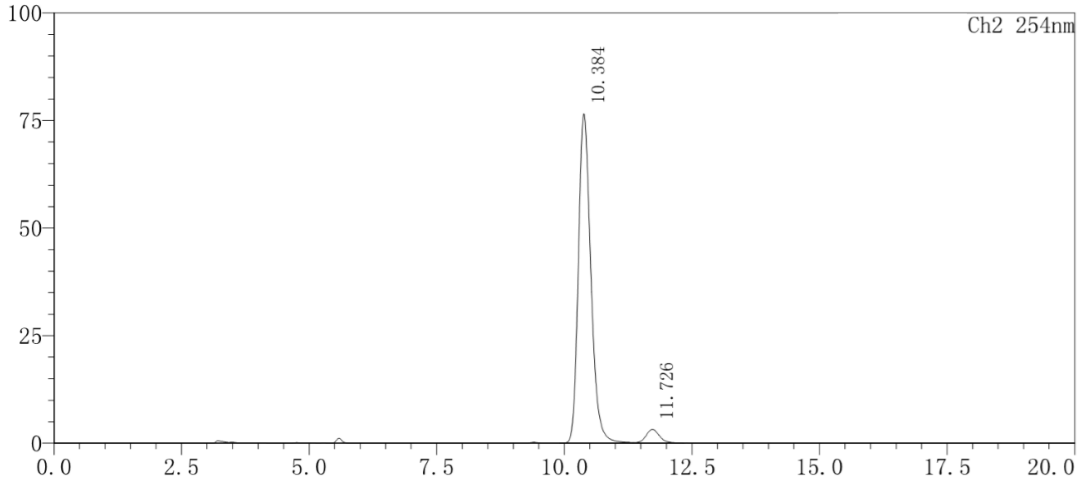
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.4 min, t_R (minor) = 11.7 min.

22 racemic

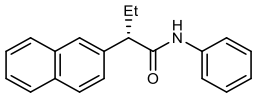


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.380	512750	29863	49.794
2	11.684	517000	28369	50.206

22 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.384	1308894	76628	95.590
2	11.726	60385	3204	4.410



(*S*)-2-(naphthalen-2-yl)-*N*-phenylbutanamide (23)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (21.7 mg, 75%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 4H), 7.52 – 7.44 (m, 5H), 7.36 (s, 1H), 7.27 – 7.23 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 3.59 (t, *J* = 8.0 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.04 – 1.93 (m, 1H), 0.96 (t, *J* = 8.0 Hz, 3H).

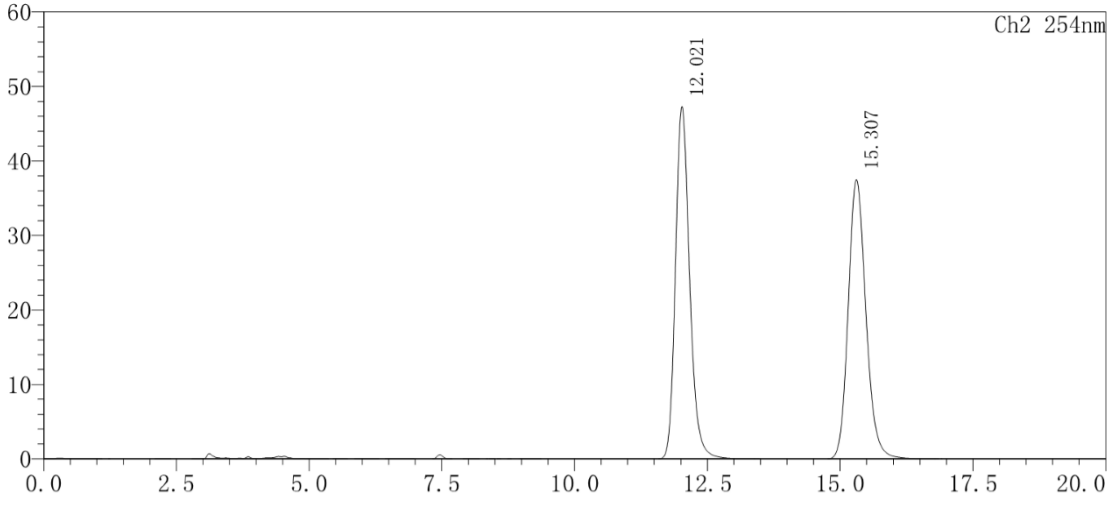
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.90, 137.97, 137.10, 133.63, 132.86, 128.99, 128.95, 127.88, 127.82, 127.18, 126.47, 126.12, 125.92, 124.38, 119.97, 56.24, 26.42, 12.47.

HRMS (ESI): $C_{20}H_{20}NO^+$ ($M+H^+$): 290.1539, found: 290.1536.

$[\alpha]_D^{25}$ = 68.1 (c = 1.01, $CHCl_3$).

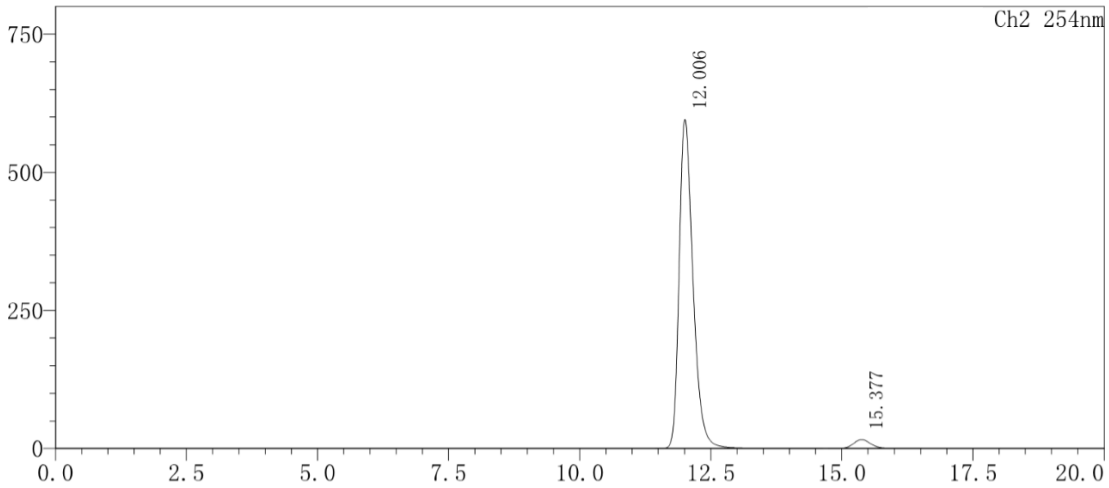
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.0 min, t_R (minor) = 15.4 min.

23 racemic

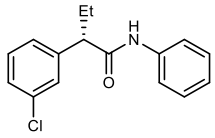


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.021	877547	47387	49.980
2	15.307	878237	37580	50.020

23 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.006	10907664	596047	96.657
2	15.377	377301	16137	3.343



(*S*)-2-(3-chlorophenyl)-*N*-phenylbutanamide (24)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (21.8 mg, 80%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.37 (s, 1H), 7.30 – 7.27 (m, 4H), 7.22 (s, 1H), 7.08 (t, J = 8.0 Hz, 1H), 3.34 (t, J = 8.0 Hz, 1H), 2.29 – 2.18 (m, 1H), 1.90 – 1.79 (m, 1H), 0.93 (t, J = 8.0 Hz, 3H).

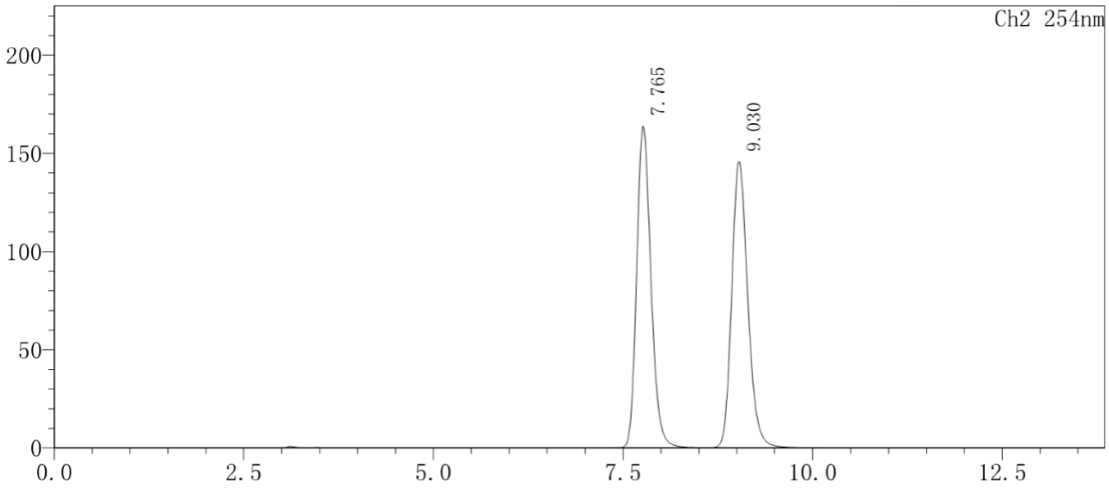
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.09, 141.70, 137.80, 134.84, 130.30, 129.10, 128.32, 127.82, 126.23, 124.60, 120.01, 55.97, 26.82, 12.39.

HRMS (EI): $C_{16}H_{16}ClNO$ (M): 273.0920, found: 273.0921.

$[\alpha]_D^{25}$ = 43.1 (c = 0.97, $CHCl_3$).

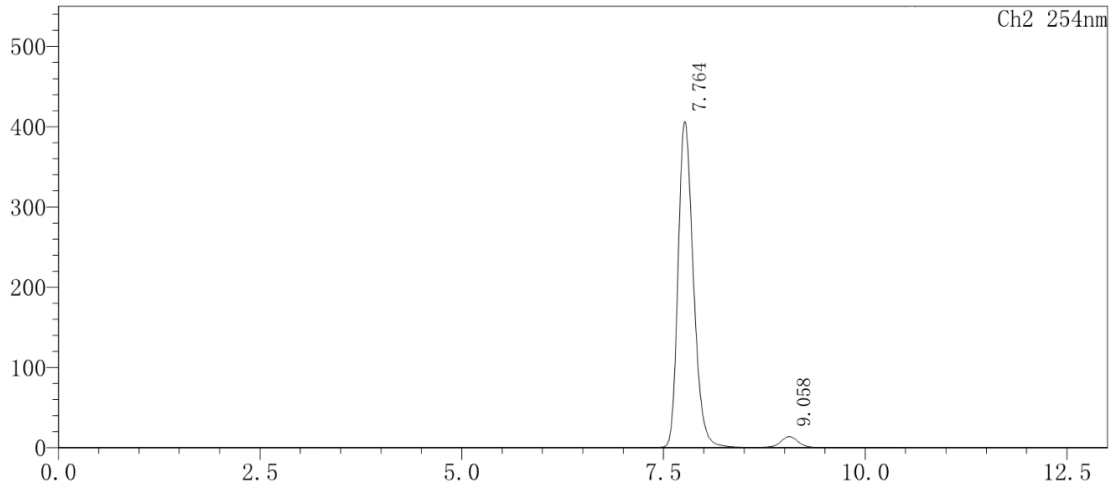
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.8 min, t_R (minor) = 9.1 min.

24 racemic

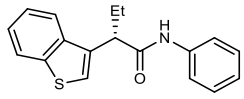


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	7.765	2155781	163845	50.005
2	9.030	2155341	145720	49.995

24 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	7.764	5378796	406618	95.998
2	9.058	224216	13994	4.002



(*S*)-2-(benzo[b]thiophen-3-yl)-*N*-phenylbutanamide (25)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a yellow oil (19.2 mg, 65%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.20 – 7.15 (m, 5H), 7.07 – 7.04 (m, 2H), 6.87 (t, *J* = 8.0 Hz, 1H), 3.70 (t, *J* = 8.0 Hz, 1H), 2.19 – 2.12 (m, 1H), 1.93 – 1.86 (m, 1H), 0.85 (t, *J* = 8.09 Hz, 3H).

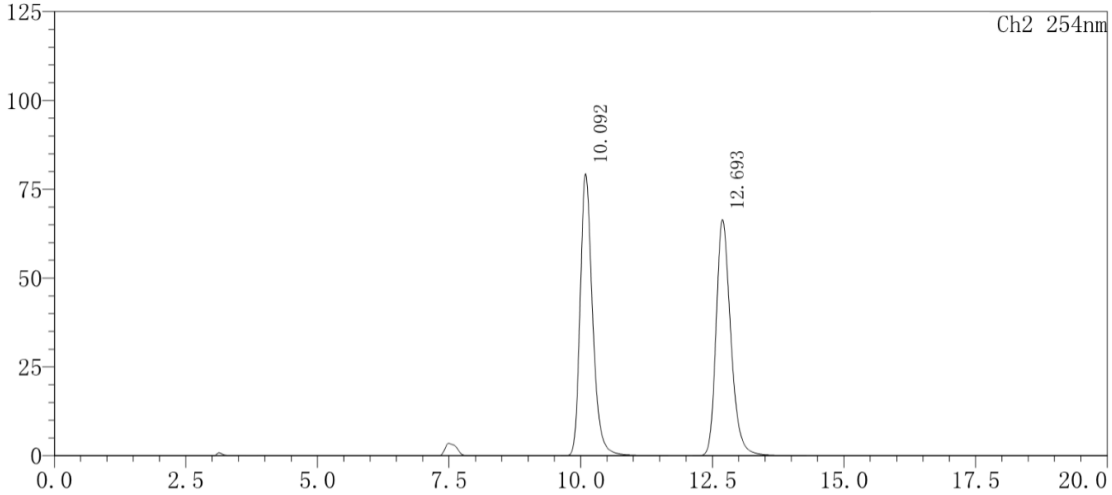
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 140.82, 138.18, 137.77, 134.12, 129.00, 124.89, 124.57, 124.50, 123.70, 123.19, 121.89, 120.12, 50.02, 25.64, 12.67.

HRMS (ESI): $C_{18}H_{18}NOS^+$ ($M+H^+$): 296.1104, found: 296.1099.

$[\alpha]_D^{25}$ = 42.6 (c = 1.29, $CHCl_3$).

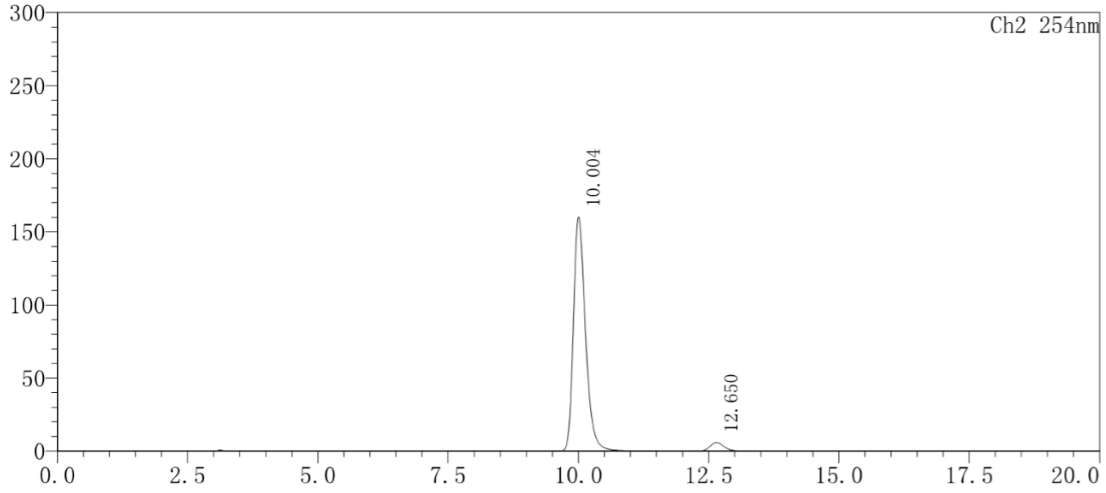
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.0 min, t_R (minor) = 12.7 min.

25 racemic

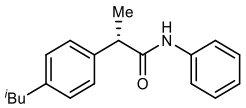


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.092	1293736	79411	50.027
2	12.693	1292345	66476	49.973

25 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.004	2573043	160243	95.794
2	12.650	112961	5922	4.206



(*S*)-2-(4-isobutylphenyl)-*N*-phenylpropanamide (26) [6]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (23.0 mg, 82%, 93% ee).

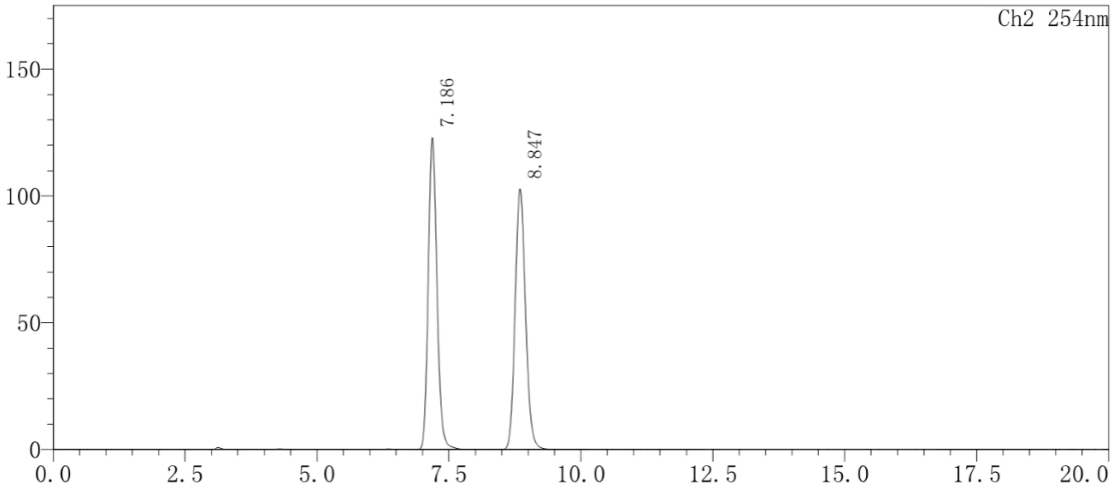
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.29 – 7.27 (m, 2H), 7.26 – 7.25 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 3.69 (q, *J* = 8.0 Hz, 1H), 2.48 (d, *J* = 4.0 Hz, 2H), 1.92 – 1.82 (m, 1H), 1.60 (d, *J* = 4.0 Hz, 3H), 0.91 (d, *J* = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.71, 141.26, 138.19, 138.05, 130.02, 129.04, 127.58, 124.30, 119.74, 47.91, 45.15, 30.32, 22.52, 18.62.

$[\alpha]_D^{25}$ = 37.8 (c = 1.13, $CHCl_3$).

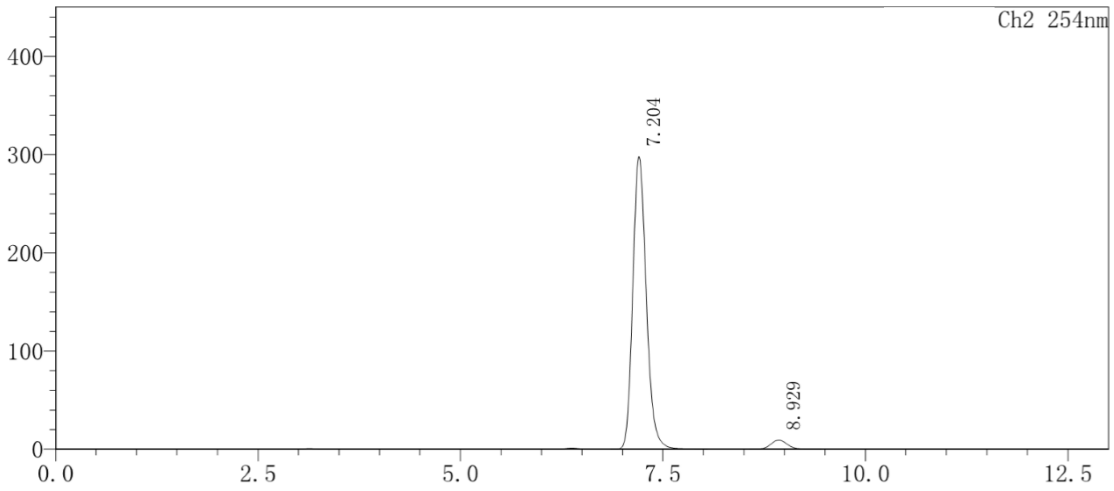
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.2 min, t_R (minor) = 8.9 min.

26 racemic

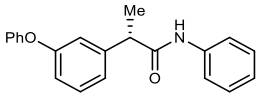


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	7.186	1422581	123146	50.025
2	8.847	1421179	102903	49.975

26 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	7.204	3461110	297626	96.264
2	8.929	134309	9381	3.736



(*S*)-2-(3-phenoxyphenyl)-*N*-phenylpropanamide (27) [6]

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 8% EtOAc) as a white solid (25.0 mg, 79%,

90% ee).

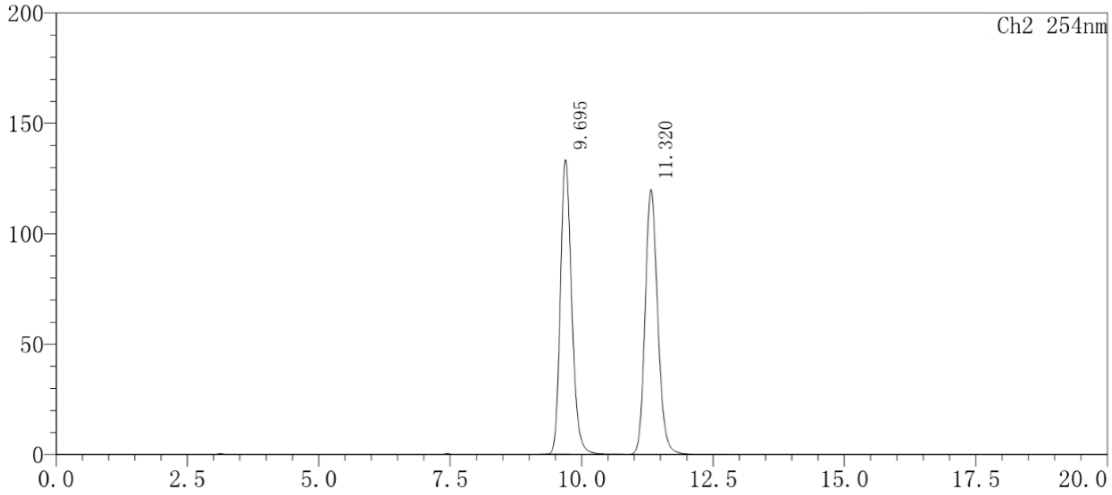
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.11 (s, 1H), 7.05 – 6.97 (m, 3H), 6.95 – 6.92 (m, 3H), 6.83 (dd, *J* = 8.1, 1.8 Hz, 1H), 3.59 (q, *J* = 8.0 Hz, 1H), 1.49 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ172.01, 158.05, 156.90, 143.06, 137.90, 130.52, 129.96, 129.05, 124.45, 123.70, 122.40, 119.92, 119.20, 118.20, 117.64, 48.06, 18.59.

$[\alpha]_D^{25}$ = 32.7 (c = 0.71, $CHCl_3$).

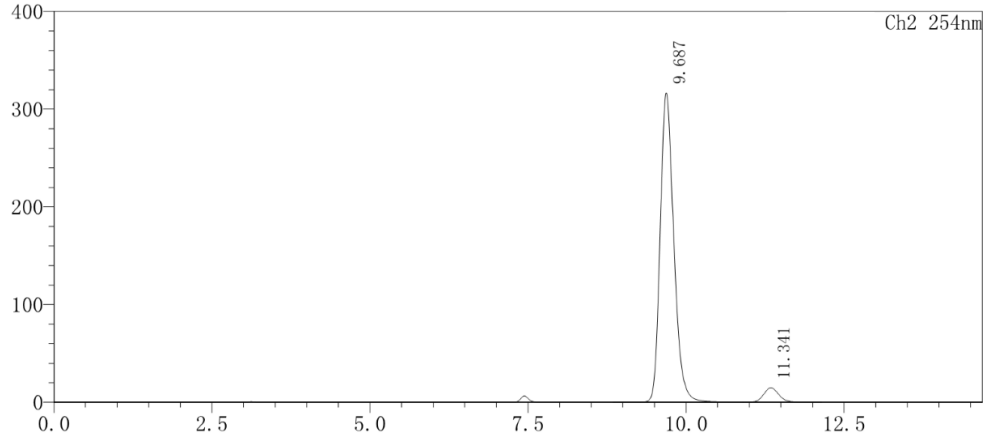
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.7 min, t_R (minor) = 11.3 min.

27 racemic

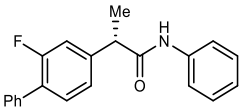


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.695	2000239	133355	49.908
2	11.320	2007639	120030	50.092

27 enantioenriched, 90% ee



Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	9.687	4775495	316893	94.950
2	11.341	253992	14985	5.050



(*S*)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)-*N*-phenylpropanamide (28) [6]

According to **General Procedure A**, the title compound was isolated by flash column chromatography (silica gel, pentane with 8% EtOAc) as a white solid (16.3 mg, 51%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H), 7.49 – 7.43 (m, 5H), 7.40 – 7.36 (m, 1H), 7.30 – 7.19 (m, 5H), 7.12 – 7.10 (m, 1H), 3.74 (q, *J* = 8.0 Hz, 1H), 1.63 (d, *J* = 8.0 Hz, 3H).

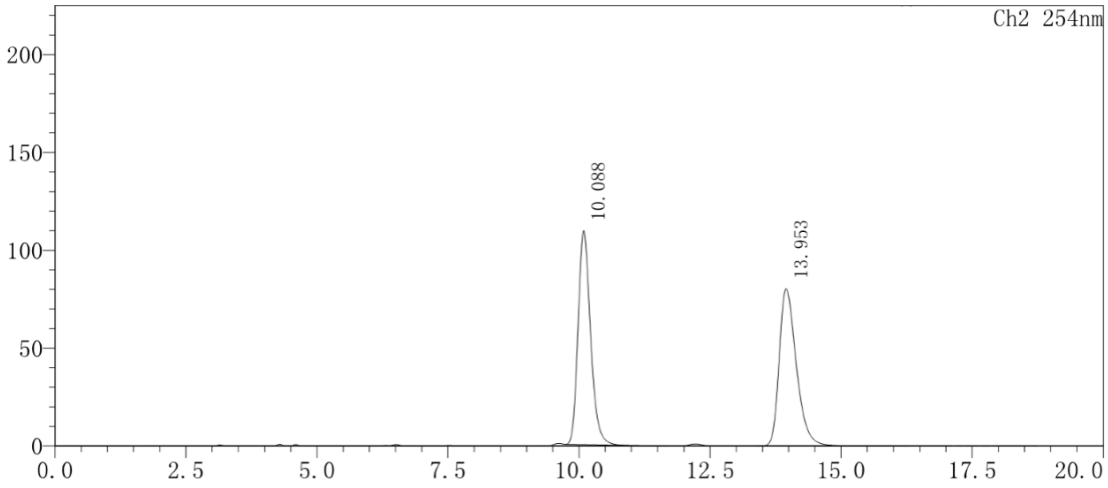
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.76, 160.03 (d, *J* = 249 Hz,), 142.41, 137.83, 135.40, 131.42, 129.12, 129.07, 128.63, 128.34 (d, *J* = 14 Hz,), 127.93, 124.63, 123.74, 120.02, 115.50 (d, *J* = 23 Hz), 47.73, 18.76.

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.73 (t, *J* = 9.3 Hz).

$[\alpha]_D^{25}$ = 33.4 (c = 1.07, $CHCl_3$).

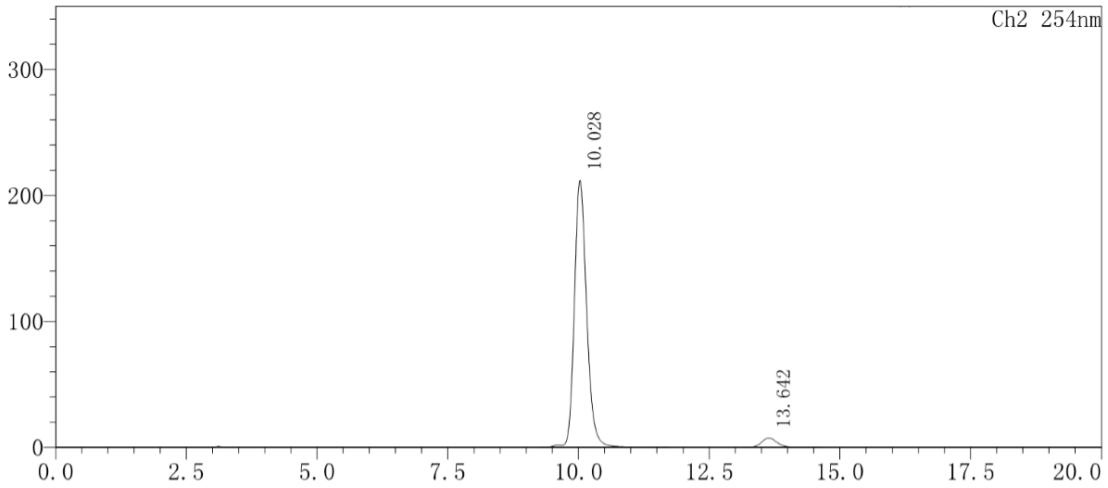
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.0 min, t_R (minor) = 13.6 min.

28 racemic

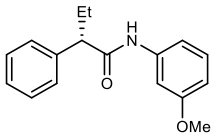


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.088	1798764	109213	49.394
2	13.953	1842931	80568	50.606

28 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.028	3450426	212142	95.601
2	13.642	158761	7521	4.399



(*S*)-*N*-(3-methoxyphenyl)-2-phenylbutanamide (29)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (21.0 mg, 78%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 3H), 7.23 – 7.17 (m, 3H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.67 (s, 3H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.23 – 2.12 (m, 1H), 1.83 – 1.72 (m, 1H), 0.84 (t, *J* = 8.0 Hz, 3H).

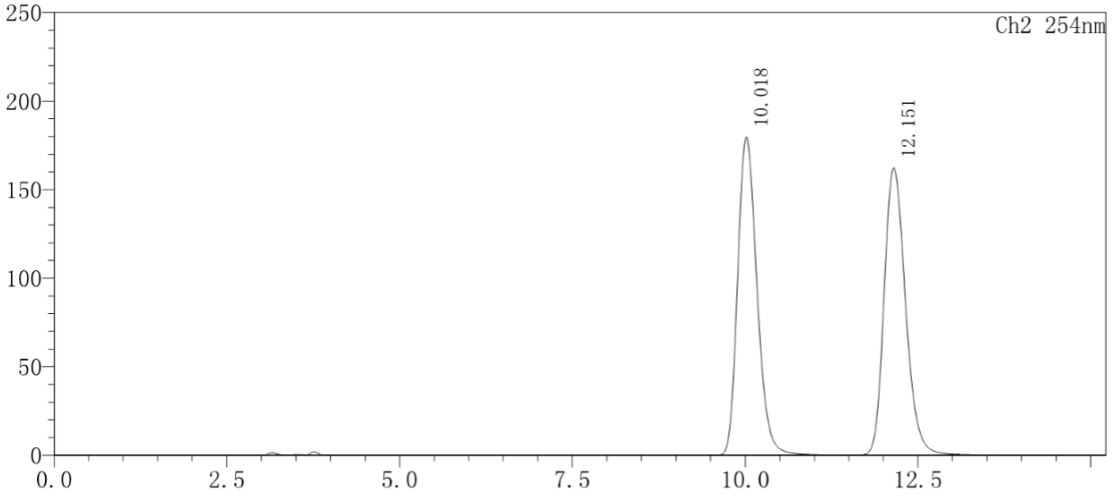
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.87, 160.26, 139.58, 139.27, 129.67, 129.15, 128.18, 127.65, 111.84, 110.40, 105.40, 56.38, 55.42, 26.53, 12.47.

HRMS (ESI): $C_{17}H_{20}NO_2^+$ ($M+H^+$): 270.1489, found: 270.1486.

$[\alpha]_D^{25}$ = 65.3 (c = 0.75, $CHCl_3$).

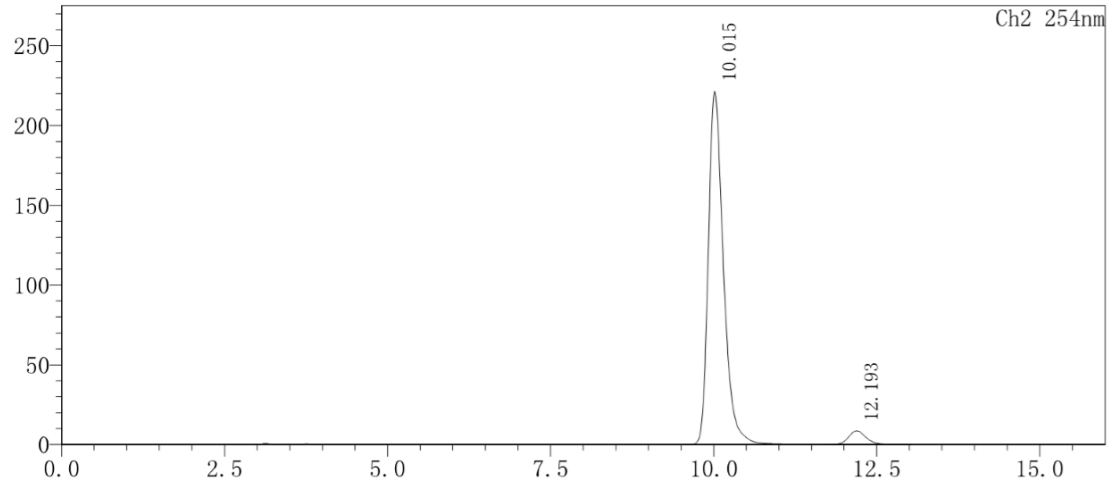
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.0 min, t_R (minor) = 12.2 min.

29 racemic

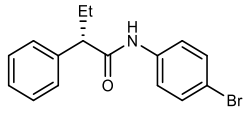


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.018	3510643	179878	49.987
2	12.151	3512531	162320	50.013

29 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.015	3579766	221524	95.700
2	12.193	160856	8603	4.300



(*S*)-*N*-(4-bromophenyl)-2-phenylbutanamide (30)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 7% EtOAc) as a white solid (16.5 mg, 52%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 7H), 7.33 – 7.28 (m, 2H), 7.12 (s, 1H), 3.38 (t, *J* = 8.0 Hz, 1H), 2.33 – 2.21 (m, 1H), 1.92 – 1.81 (m, 1H), 0.92 (t, *J* = 8.0 Hz, 3H).

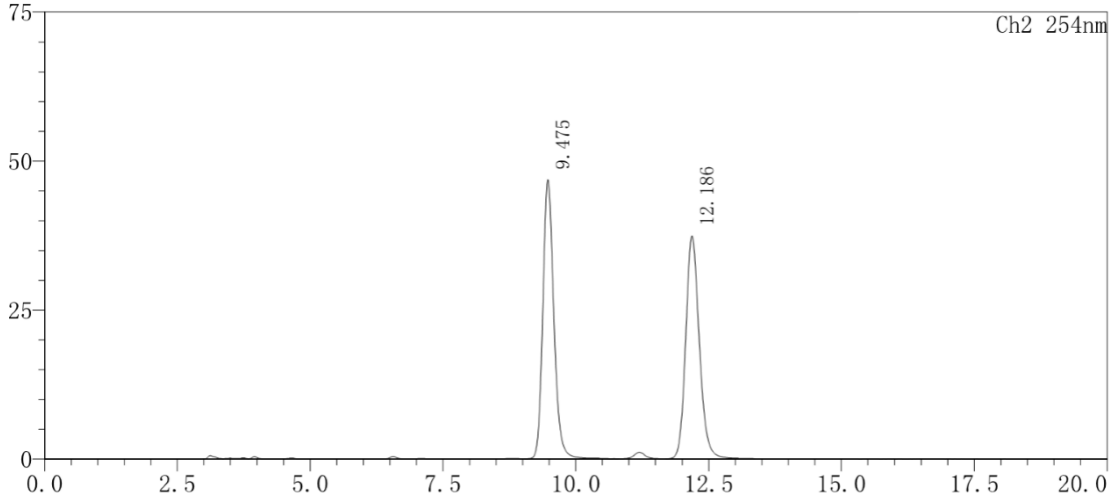
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.89, 139.37, 137.05, 131.99, 129.23, 128.19, 127.79, 121.44, 116.92, 56.28, 26.50, 12.45.

HRMS (ESI): $C_{16}H_{16}BrNNaO^+$ ($M+Na^+$): 340.0307, found: 340.0306.

$[\alpha]_D^{25}$ = 43.0 (c = 0.92, $CHCl_3$).

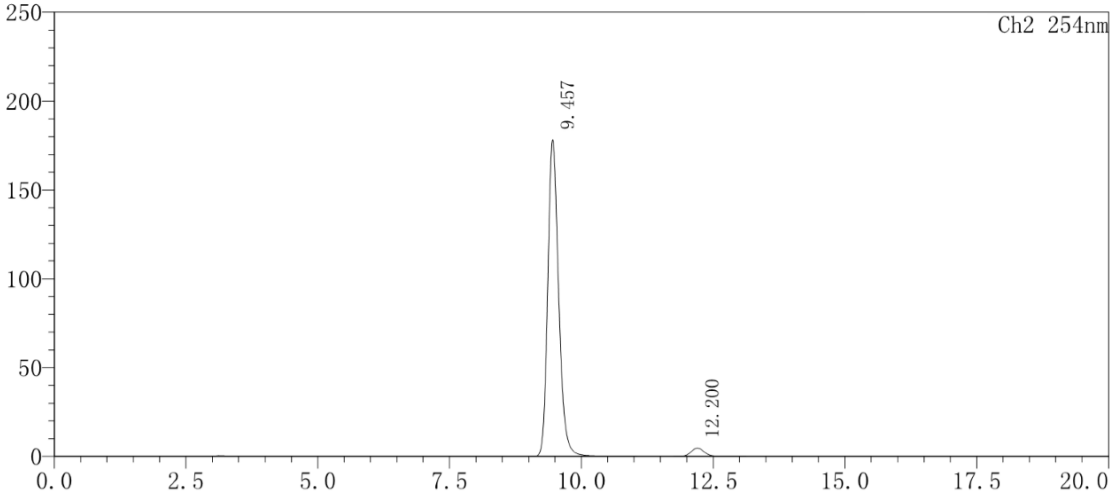
HPLC: The ee was determined to be 94% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.5 min, t_R (minor) = 12.2 min.

30 racemic

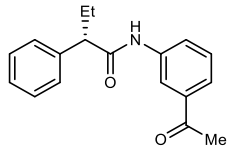


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.475	676851	46865	50.380
2	12.186	666634	37406	49.620

30 enantioenriched, 94% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	9.457	2568744	178382	96.826
2	12.200	84207	4720	3.174



(*S*)-*N*-(3-acetylphenyl)-2-phenylbutanamide (31)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 10% EtOAc) as a white solid (17.7 mg, 63%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.35 (m, 5H), 7.33 – 7.29 (m, 1H), 3.42 (t, *J* = 8.0 Hz, 1H), 2.58 (s, 3H), 2.32 – 2.23 (m, 1H), 1.94 – 1.83 (m, 1H), 0.93 (t, *J* = 8.0 Hz, 3H).

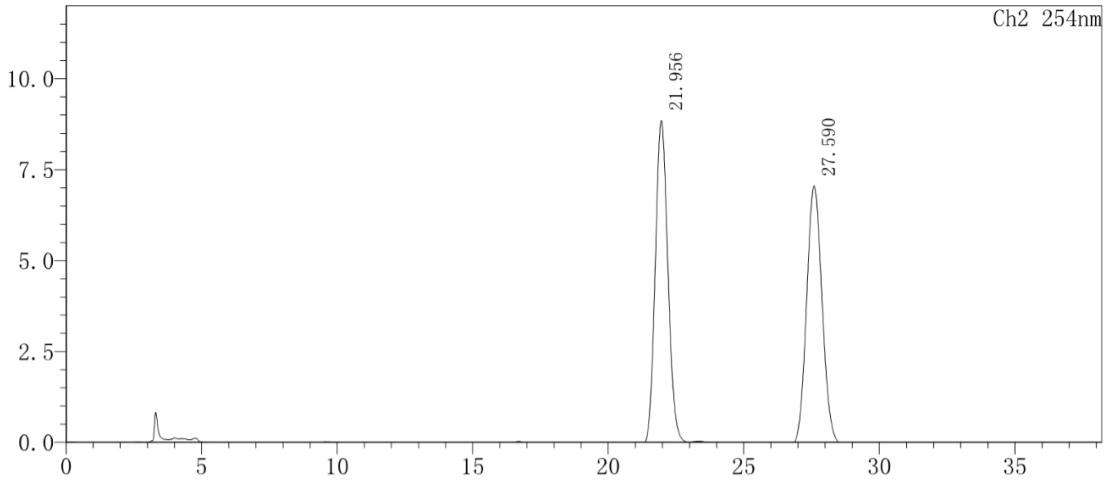
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.05, 172.14, 139.33, 138.53, 137.87, 129.41, 129.29, 128.20, 127.84, 124.44, 124.24, 119.23, 56.33, 26.84, 26.46, 12.47.

HRMS (ESI): $C_{18}H_{20}NO_2^+$ ($M+H^+$): 282.1489, found: 282.1490.

$[\alpha]_D^{25}$ = 46.1 (c = 1.15, $CHCl_3$).

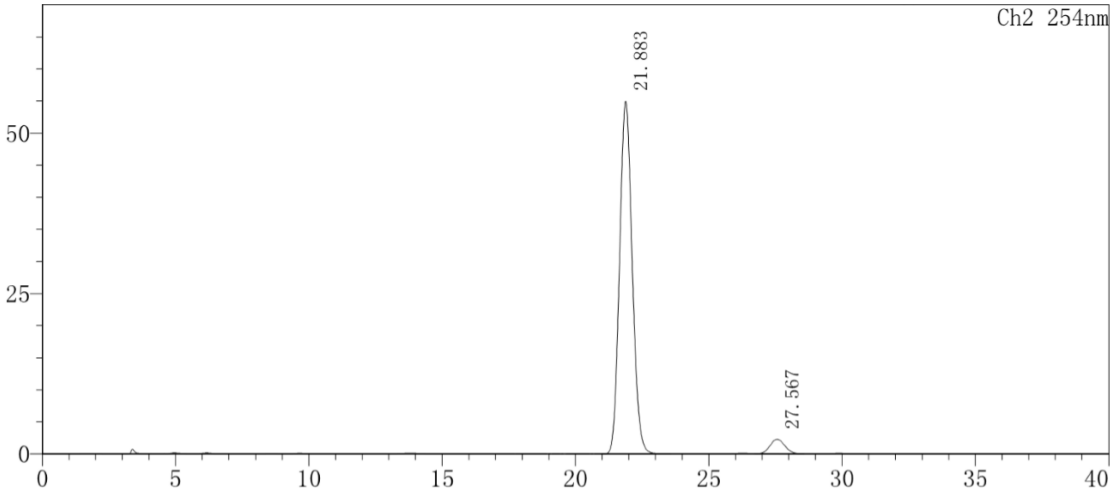
HPLC: The ee was determined to be 91% on a CHIRALPAK ADH column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 21.9 min, t_R (minor) = 27.6 min.

31 racemic

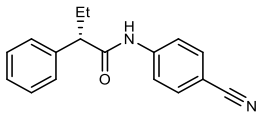


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	21.956	290316	8914	50.116
2	27.590	288973	7161	49.884

31 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	21.883	1815478	55051	95.359
2	27.567	88366	2275	4.641



(*S*)-*N*-(4-cyanophenyl)-2-phenylbutanamide (32)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a yellow oil (10.8 mg, 41%, 92%

ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.40 – 7.38 (m, 1H), 7.37 – 7.36 (m, 1H), 7.35 – 7.34 (m, 1H), 7.33 – 7.29 (m, 2H), 3.42 (t, *J* = 8.0 Hz 1H), 2.31 – 2.21 (m, 1H), 1.92 – 1.81 (m, 1H), 0.92 (t, *J* = 8.0 Hz, 3H).

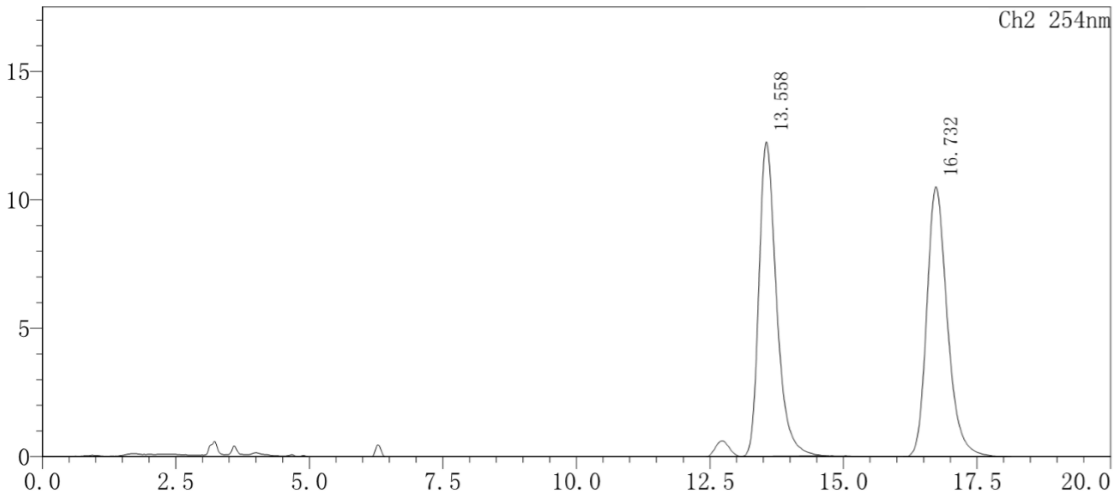
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.26, 142.06, 138.97, 133.32, 129.34, 128.15, 127.97, 119.60, 118.96, 107.13, 56.35, 26.45, 12.38.

HRMS (ESI): $C_{17}H_{17}N_2O^+$ ($M+H^+$): 265.1335, found: 265.1334.

$[\alpha]_D^{25}$ = 51.2 (c = 0.93, $CHCl_3$).

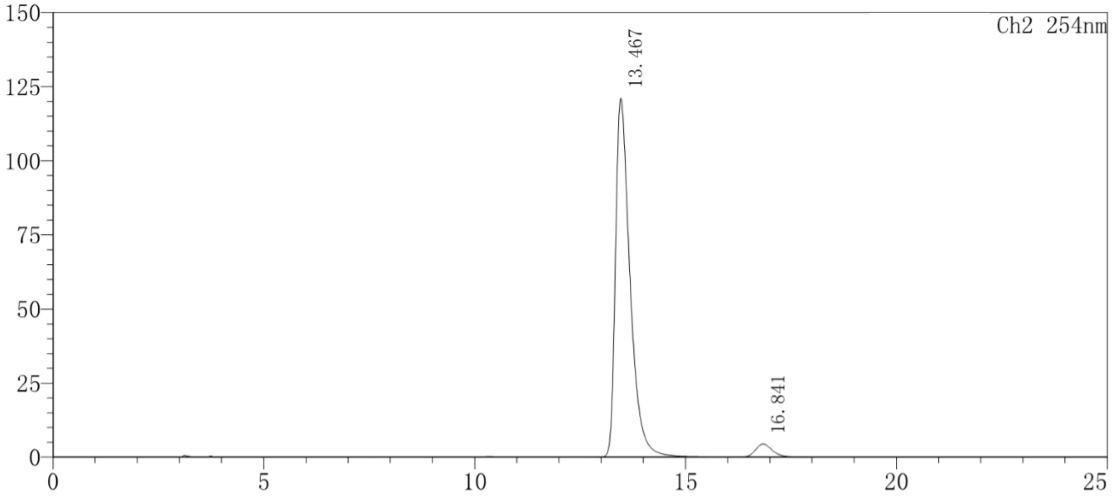
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 13.5 min, t_R (minor) = 16.8 min.

32 racemic

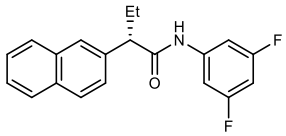


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13.558	279824	12237	49.800
2	16.732	282074	10510	50.200

32 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13.467	2909119	121093	95.943
2	16.841	123008	4399	4.057



(*S*)-*N*-(3,5-difluorophenyl)-2-(naphthalen-2-yl)butanamide (33)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a yellow oil (17.6 mg, 54%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 3H), 7.78 (s, 1H), 7.54 – 7.48 (m, 2H), 7.46 – 7.43 (m, 1H), 7.20 (s, 1H), 7.06 – 7.04 (m, 2H), 6.52 – 6.47 (m, 1H), 3.55 (t, *J* = 8.0 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.02 – 1.91 (m, 1H), 0.94 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.02, 163.21 (dd, *J* = 247.5, 15.2 Hz), 140.03 (t, *J* = 13 Hz), 139.90, 136.40, 133.64, 132.97, 129.29, 127.89, 127.34, 126.71, 126.38, 125.64, 102.79 (d, *J* = 29.3 Hz) 99.57 (t, *J* = 25.3 Hz), 56.37, 26.26, 12.41.

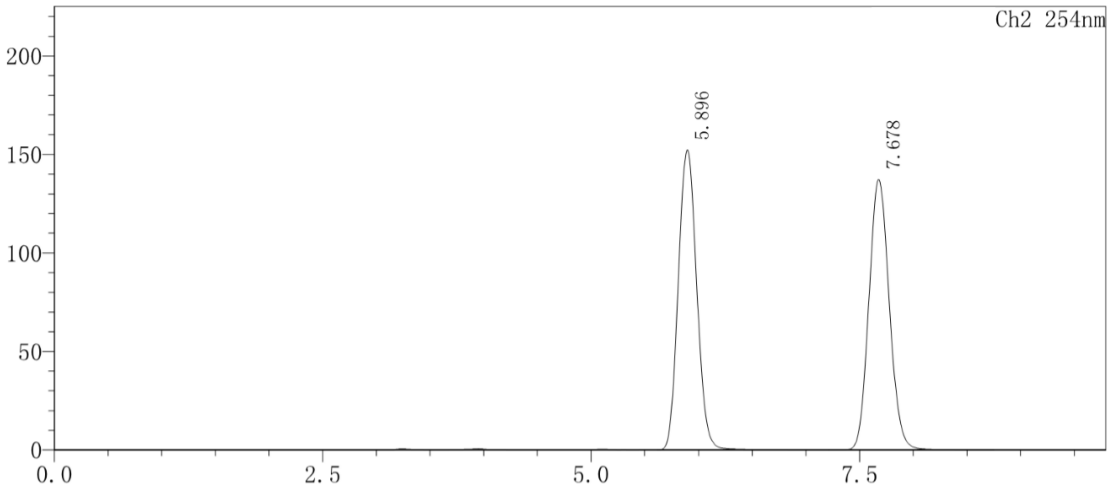
^{19}F NMR (377 MHz, $CDCl_3$) δ -108.90 (s).

HRMS (ESI): $C_{20}H_{17}F_2NNaO^+$ ($M+Na^+$): 348.1170, found: 348.1168.

$[\alpha]_D^{25}$ =46.9 (c = 1.27, $CHCl_3$).

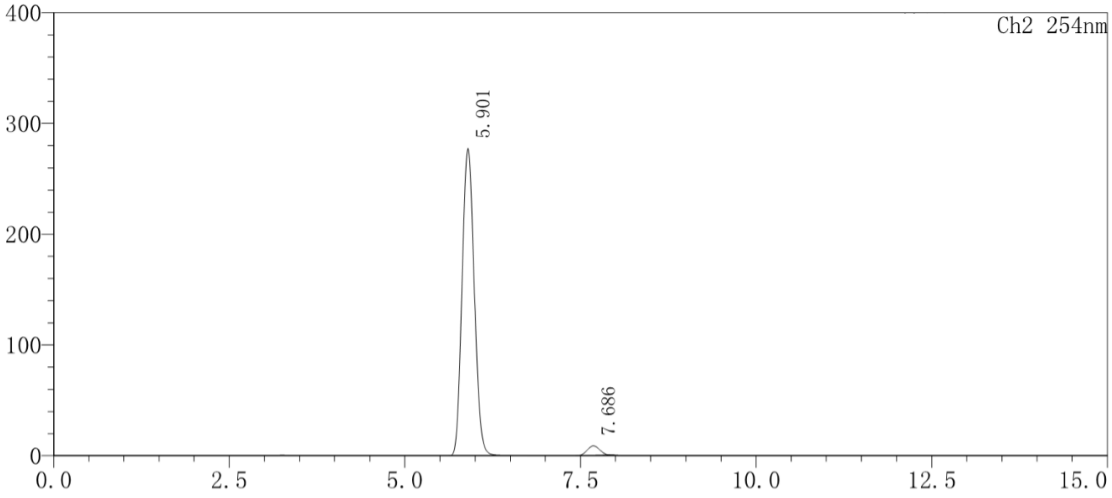
HPLC: The ee was determined to be 94% on a CHIRALPAK ADH column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.9 min, t_R (minor) = 7.7 min.

33 racemic

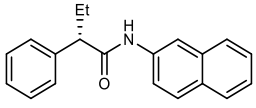


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.896	1815094	152048	50.050
2	7.678	1811449	137308	49.950

33 enantioenriched, 94% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.901	3309594	277317	96.996
2	7.686	102512	8442	3.004



(*S*)-*N*-(naphthalen-2-yl)-2-phenylbutanamide (34)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (19.7 mg, 68%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.75 – 7.70 (m, 3H), 7.45 – 7.39 (m, 4H), 7.38 – 7.29 (m, 4H), 3.46 (t, *J* = 8.0 Hz, 1H), 2.37 – 2.27 (m, 1H), 1.97 – 1.86 (m, 1H), 0.96 (t, *J* = 8.0 Hz, 3H).

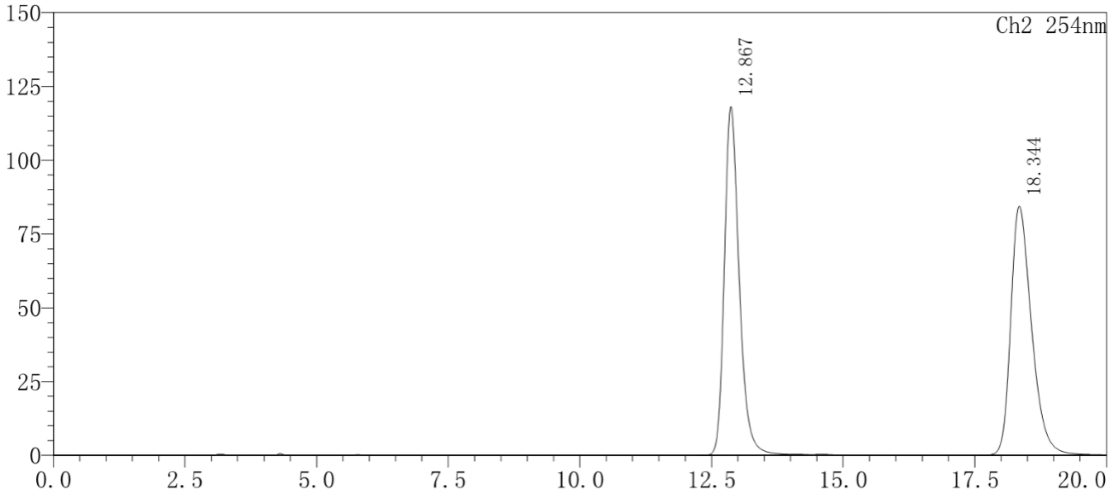
^{13}C NMR (101 MHz, $CDCl_3$)) δ 172.16, 139.63, 135.41, 133.90, 130.71, 129.16, 128.73, 128.22, 127.74, 127.66, 127.61, 126.58, 125.08, 119.94, 116.70, 56.31, 26.62, 12.49.

HRMS (ESI): $C_{20}H_{20}NO^+$ ($M+H^+$): 290.1539, found: 290.1537.

$[\alpha]_D^{25}$ = 79.2 (c = 1.04, $CHCl_3$).

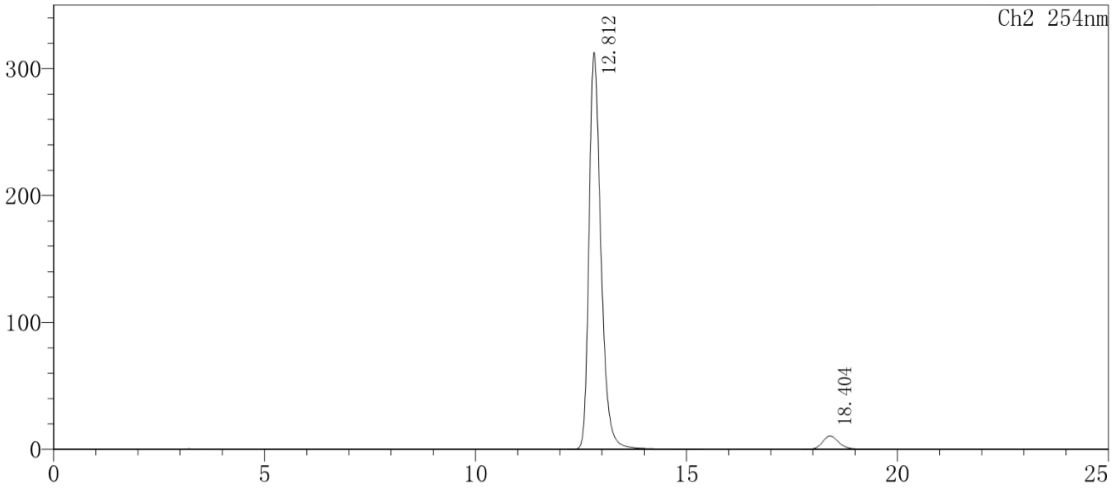
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.8 min, t_R (minor) = 18.4 min.

34 racemic

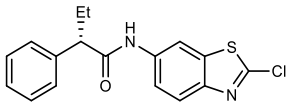


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.867	2322790	118192	49.960
2	18.344	2326474	84436	50.040

34 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12.812	6162824	312899	95.565
2	18.404	285996	10547	4.435



(*S*)-*N*-(2-chlorobenzo[d]thiazol-6-yl)-2-phenylbutanamide (35)

According to **General Procedure A**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (18.2 mg, 55%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.62 – 7.60(m, 2H), 7.47 (s, 1H), 7.37 – 7.36 (m, 3H), 7.32 – 7.28 (m, 1H), 3.44 (t, J = 8.0 Hz, 1H), 2.37 – 2.23 (m, 1H), 1.94 – 1.83 (m, 1H), 0.93 (t, J = 8.0 Hz, 3H).

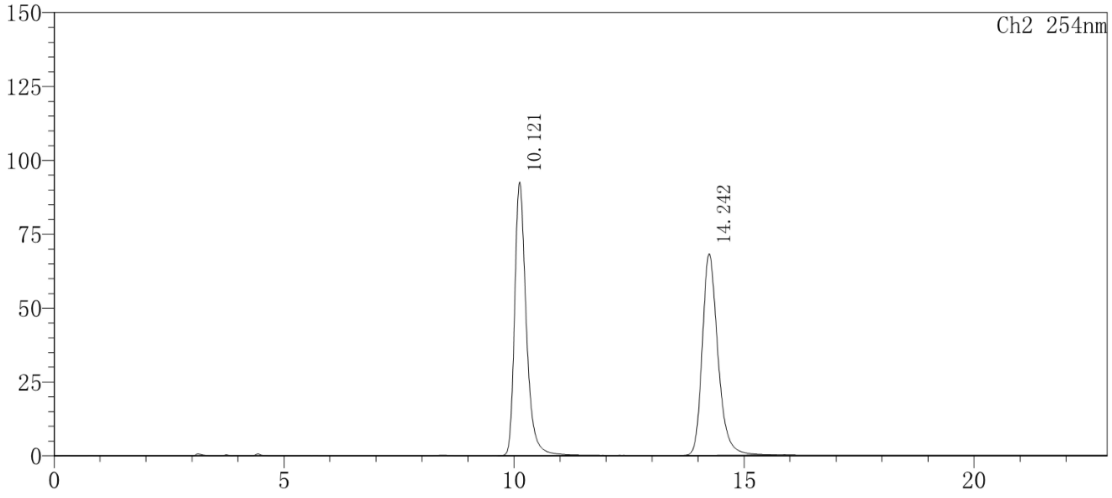
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.19, 154.34, 151.48, 139.45, 137.19, 131.48, 129.17, 128.18, 127.72, 121.25, 119.04, 113.86, 56.19, 26.61, 12.45.

HRMS (ESI): $C_{17}H_{16}ClN_2OS^+$ ($M+H^+$): 331.0666, found: 331.0661.

$[\alpha]_D^{25}$ = 17.2 (c = 0.77, $CHCl_3$).

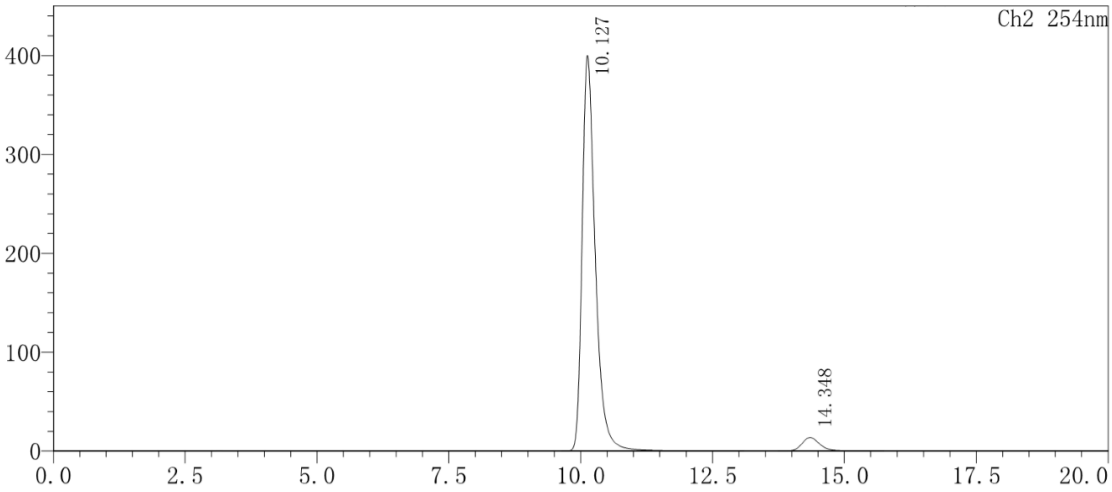
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.1 min, t_R (minor) = 14.4 min.

35 racemic

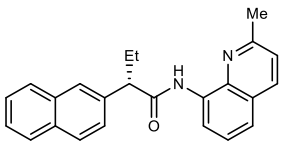


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.121	1629442	92616	50.213
2	14.242	1615616	68185	49.787

35 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	10.127	6930657	400143	95.432
2	14.348	331752	13736	4.568



(*S*)-*N*-(2-methylquinolin-8-yl)-2-(naphthalen-2-yl)butanamide (36)

According to **General Procedure**, the title compound was isolated by flash column

chromatography (silica gel, pentane with 6% EtOAc) as a white solid (14.9 mg, 42%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.72 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.96 – 7.83 (m, 5H), 7.60 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.43 – 7.36 (m, 2H), 7.17 (d, *J* = 12 Hz, 1H), 3.84 – 3.80 (m, 1H), 2.56 – 2.45 (m, 1H), 2.34 (s, 3H), 2.18 – 2.05 (m, 1H), 1.04 (t, *J* = 8.0 Hz, 3H).

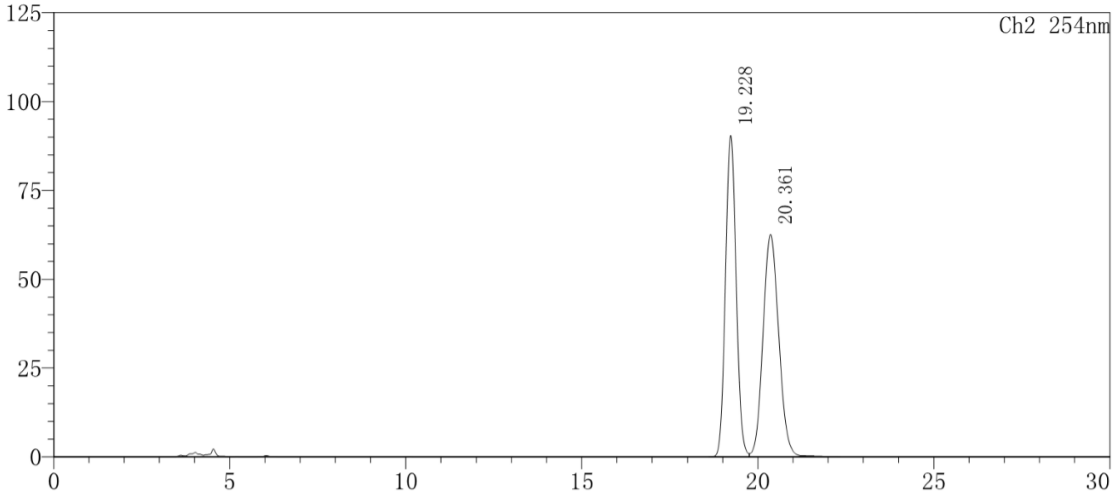
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.17, 157.11, 137.88, 137.17, 136.28, 133.94, 133.84, 132.97, 128.91, 127.99, 127.80, 127.57, 126.35, 126.33, 125.99, 122.35, 121.27, 116.15, 56.89, 25.93, 24.85, 12.67.

HRMS (ESI): $C_{24}H_{23}N_2O^+$ ($M+H^+$): 355.1805, found: 355.1800.

$[\alpha]_D^{25}$ = 78.1 (c = 0.92, $CHCl_3$).

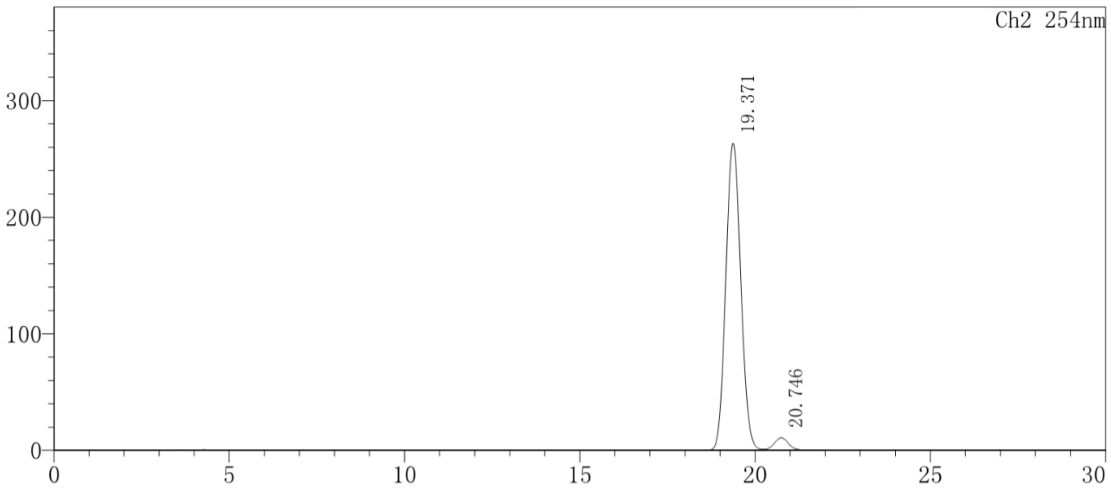
HPLC: The ee was determined to be 92% on a CHIRALPAK ADH column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 97:3 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 19.4 min, t_R (minor) = 20.8 min.

36 racemic

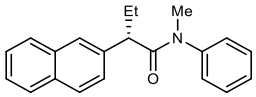


Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	19.228	1911191	90455	49.438
2	20.361	1954607	62617	50.562

36 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	19.371	7844601	263369	96.134
2	20.746	315432	10889	3.866



(*S*)-*N*-methyl-2-(naphthalen-2-yl)-*N*-phenylbutanamide (37)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 3% EtOAc) as a colorless oil (20.0 mg, 66%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.37 – 7.36 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 2H), 3.53 (t, *J* = 8.0 Hz, 1H), 3.26 (s, 3H), 2.24 – 2.13 (m, 1H), 1.82 – 1.72 (m, 1H), 0.84 (t, *J* = 8.0 Hz, 3H).

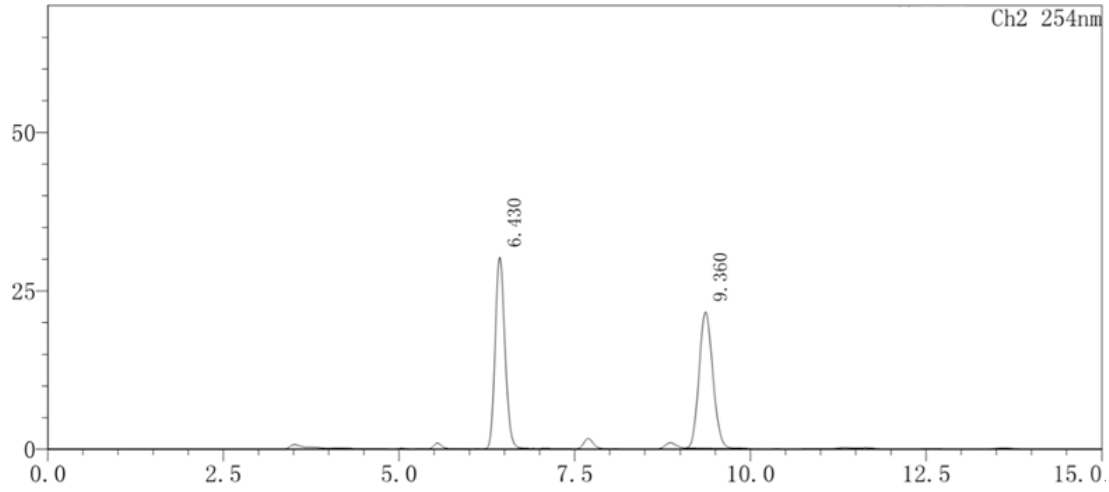
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.37, 143.91, 137.99, 133.48, 132.56, 129.65, 128.21, 128.02, 127.99, 127.89, 127.64, 126.85, 126.52, 125.92, 125.59, 51.06, 37.75, 28.43, 12.51.

HRMS (ESI): $C_{21}H_{22}NO^+$ ($M+H^+$): 304.1696, found: 304.1692.

$[\alpha]_D^{25}$ = -90.4 (c = 1.02, $CHCl_3$).

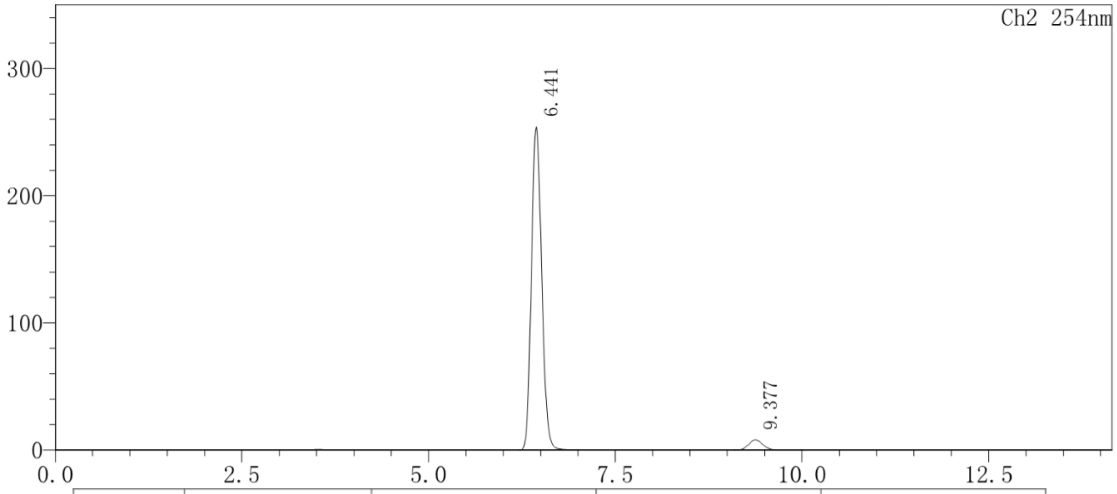
HPLC: The ee was determined to be 92% on a CHIRALPAK ADH column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.4 min, t_R (minor) = 9.4 min.

37 racemic

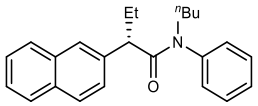


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	6.430	293527	30209	49.857
2	9.360	295215	21547	50.143

37 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	6.441	2433998	254211	95.761
2	9.377	107744	8080	4.239



(*S*)-*N*-butyl-2-(naphthalen-2-yl)-*N*-phenylbutanamide (38)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 2.5% EtOAc) as a a yellow oil (14.8 mg, 43%,

92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 1H), 7.63 –7.61 (m, 2H), 7.37 – 7.28 (m, 6H), 7.17 – 6.86 (m, 3H), 3.68 – 3.52 (m, 2H), 3.35 (t, *J* = 8.0 Hz, 1H), 2.14 – 2.04 (m, 1H), 1.70 – 1.59 (m, 1H), 1.40 – 1.33 (m, 2H), 1.24 – 1.15 (m, 2H), 0.80 – 0.73 (m, 6H).

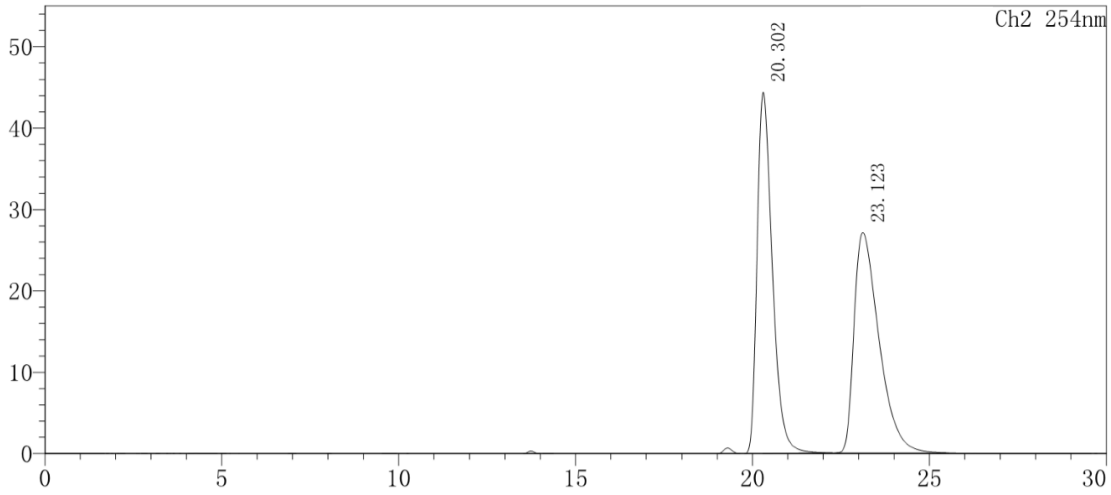
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.84, 142.51, 138.22, 133.49, 132.55, 129.49, 129.24, 128.03, 127.95, 127.90, 127.64, 126.84, 126.58, 125.89, 125.56, 51.45, 49.43, 29.94, 28.53, 20.14, 13.92, 12.57.

HRMS (ESI): $C_{24}H_{28}NO^+$ ($M+H^+$): 346.2165, found: 346.2160.

$[\alpha]_D^{25}$ = -23.5 (c = 0.78, $CHCl_3$).

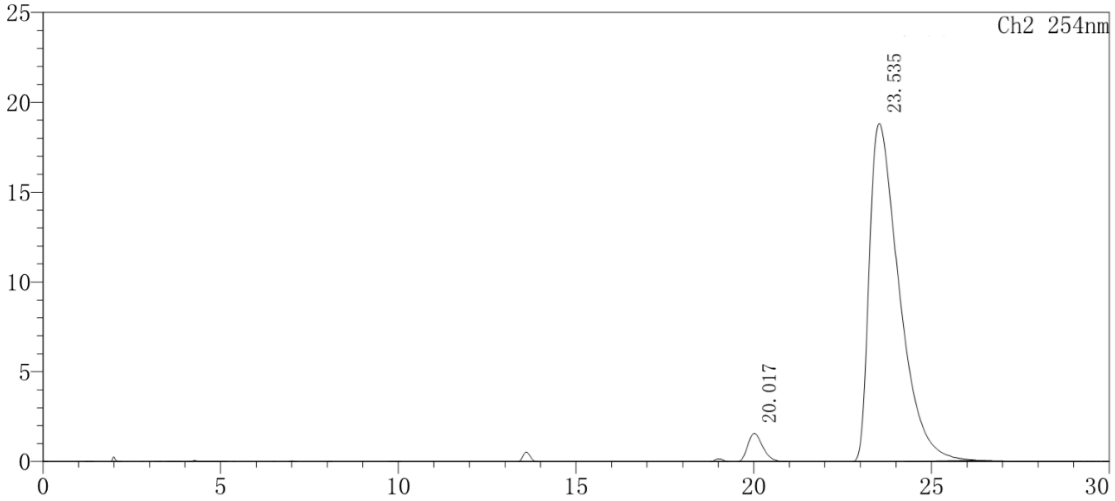
HPLC: The ee was determined to be 92% on a CHIRALPAK ADH column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 99.8:0.2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 23.5 min, t_R (minor) = 20.0 min.

38 racemic

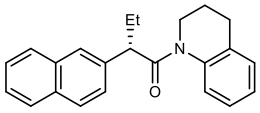


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	20.302	1330480	44414	50.054
2	23.123	1327625	27070	49.946

38 enantioenriched, 92% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	20.017	48615	1612	4.240
2	23.535	1097918	18860	95.760



(*S*)-1-(3,4-dihydroquinolin-1(2H)-yl)-2-(naphthalen-2-yl)butan-1-one (39)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 4% EtOAc) as a colorless oil (21.7 mg, 66%, 88% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 3H), 7.57 (s, 1H), 7.46 – 7.42 (m, 2H), 7.35 (s, 1H), 7.23 – 7.08 (m, 4H), 4.09 (s, 1H), 3.84 – 3.77 (m, 2H), 2.54 – 2.47 (m, 1H), 2.34 – 2.16 (m, 2H), 1.89 – 1.73 (m, 3H), 0.89 (t, J = 8.0 Hz, 3H).

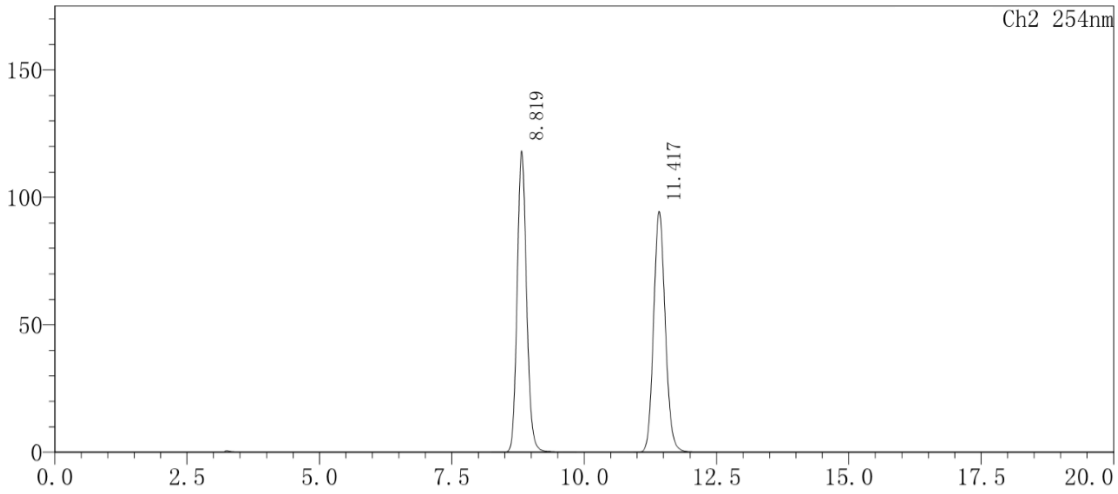
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.56, 139.63, 137.94, 133.56, 132.52, 128.44, 128.25, 127.94, 127.66, 126.67, 126.30, 126.13, 126.03, 125.69, 125.43, 50.97, 42.73, 28.82, 26.38, 24.17, 12.58.

HRMS (ESI): $C_{23}H_{23}NNaO^+$ ($M+Na^+$): 352.1672, found: 352.1668.

$[\alpha]_D^{25}$ = 52.6 (c = 1.36, $CHCl_3$).

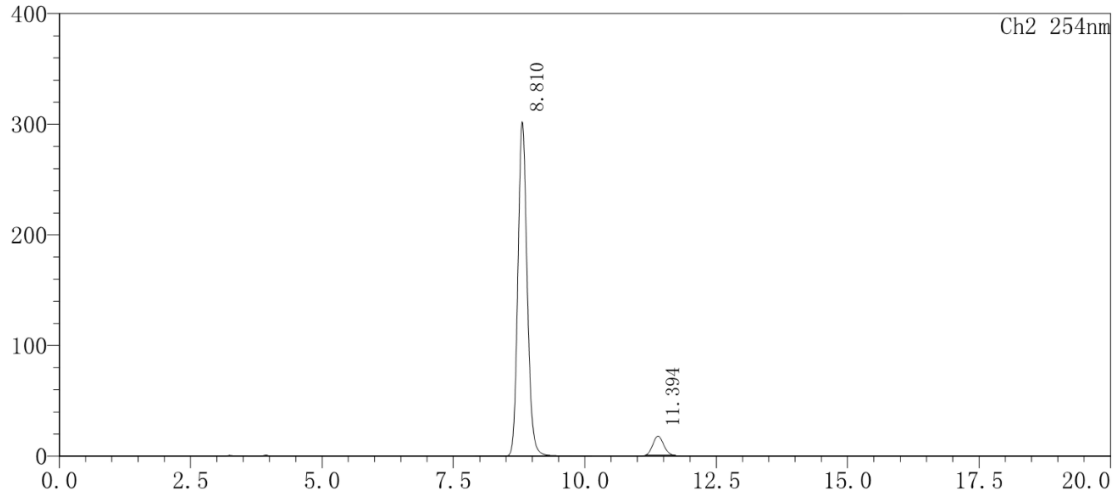
HPLC: The ee was determined to be 88% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.8 min, t_R (minor) = 11.4 min.

39 racemic

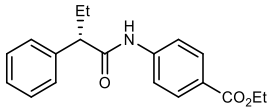


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	8.819	1468341	118292	50.195
2	11.417	1456923	94538	49.805

39 enantioenriched, 88% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	8.810	3739819	302493	93.947
2	11.394	240940	17233	6.053



Ethyl (*S*)-4-(2-phenylbutanamido)benzoate (40)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 7% EtOAc) as a white solid (19.6 mg, 63%,

95% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.54 – 7.51 (m, 2H), 7.43 (s, 1H), 7.39 – 7.28 (m, 5H), 4.33 (q, *J* = 8.0 Hz, 2H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.34 – 2.20 (m, 1H), 1.92 – 1.81 (m, 1H), 1.37 (t, *J* = 8.0 Hz, 3H), 0.92 (t, *J* = 8.0 Hz, 3H).

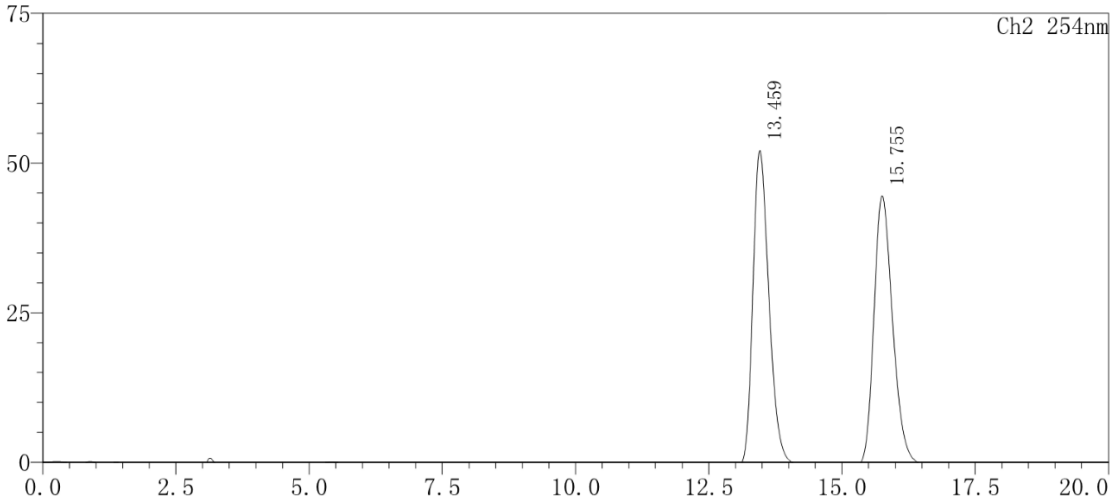
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.15, 166.30, 142.14, 139.25, 130.80, 129.22, 128.16, 127.79, 125.97, 118.87, 61.00, 56.34, 26.53, 14.44, 12.41.

HRMS (ESI): $C_{19}H_{22}NO_3^+$ ($M+H^+$): 312.1594, found: 312.1591.

$[\alpha]_D^{25}$ = 32.1 (c = 0.57, $CHCl_3$).

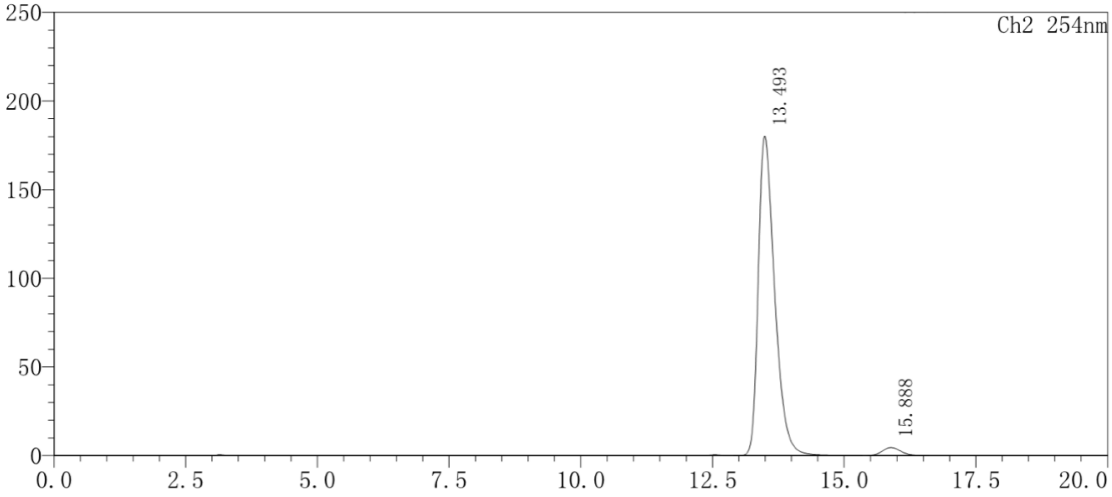
HPLC: The ee was determined to be 95% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 13.5 min, t_R (minor) = 15.9 min.

40 racemic

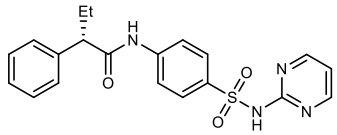


Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	13.459	1140476	53005	50.049
2	15.755	1138249	45412	49.951

40 enantioenriched, 95% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13.493	3921284	180429	97.386
2	15.888	105272	4471	2.614



(*S*)-2-phenyl-*N*-(4-(*N*-(pyrimidin-2-yl)sulfamoyl)phenyl)butanamide (41)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 33% EtOAc) as a white solid (17.0 mg, 43%, 95% ee).

^{1}H NMR (400 MHz, Acetone-d_6) δ 10.26 (s, 1H), 9.69 (s, 1H), 8.47 (d, J = 8.0 Hz, 2H), 8.035 – 7.99 (m, 2H), 7.83 – 7.80 (m, 2H), 7.40 – 7.38 (m, 2H), 7.31 – 7.27 (m, 2H), 7.254 – 7.19 (m, 1H), 7.01 (t, J = 8.0 Hz, 1H), 3.59 (d, J = 8.0 Hz, 1H), 2.20 – 2.11 (m, 1H), 1.80 – 1.70 (m, 1H), 0.89 (t, J = 8.0 Hz, 3H).

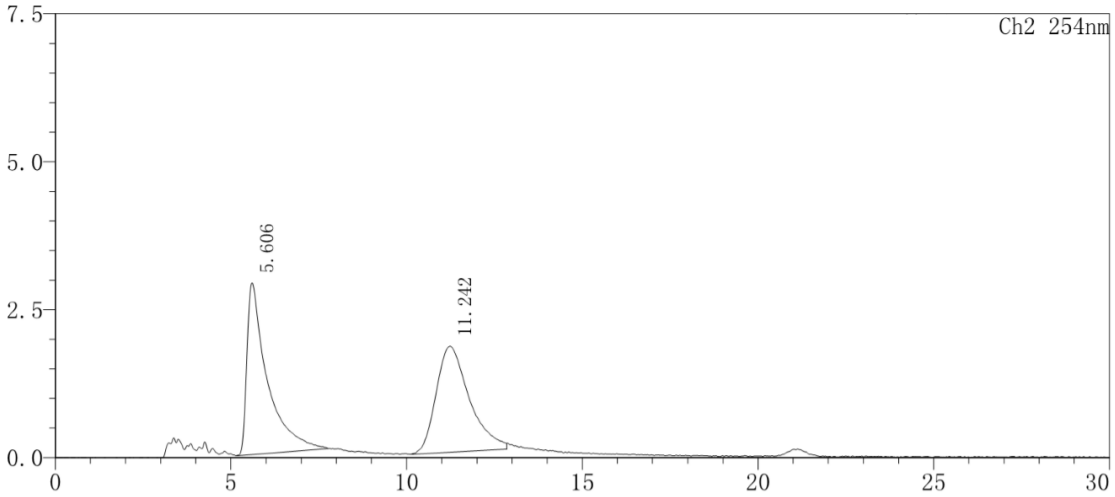
^{13}C NMR (101 MHz, Acetone-d_6) δ 172.27, 158.29, 157.31, 143.55, 140.30, 134.39, 129.52, 128.43, 127.82, 126.97, 118.30, 115.97, 55.21, 26.89, 11.66.

HRMS (ESI): $C_{20}H_{20}N_4NaO_3S^+$ ($M+Na^+$): 419.1148, found: 419.1150.

$[\alpha]_D^{25}$ = 33.1 (c = 0.72, $CHCl_3$).

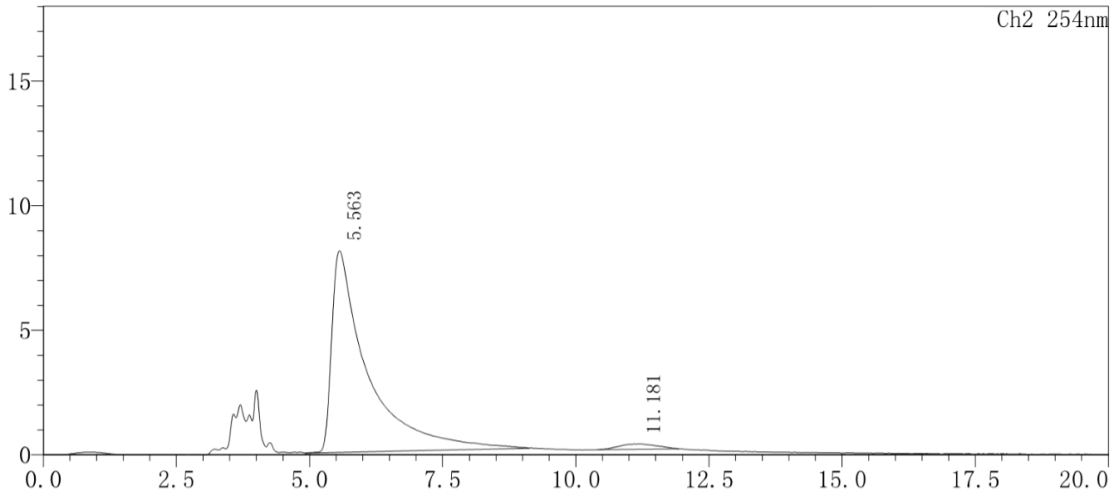
HPLC: The ee was determined to be 95% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.6 min, t_R (minor) = 11.2 min.

41 racemic

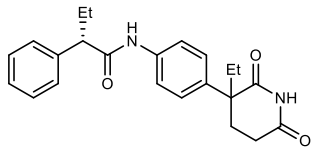


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.606	116711	2898	49.794
2	11.242	117675	1788	50.206

41 enantioenriched, 95% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.563	381074	8096	97.383
2	11.181	10240	205	2.617



(2*S*)-*N*-(4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl)-2-phenylbutanamide (42)

According to **General Procedure A**, the title compound was isolated by flash column chromatography (silica gel, pentane with 9% EtOAc) as a white solid (16.3 mg, 43%, dr = 1:1, 93% ee, 96% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.22 (m, 1H), 7.46 – 7.44 (m, 3H), 7.34 – 7.27 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.58 – 2.52 (m, 1H), 2.39 – 2.28 (m, 2H), 2.26 – 2.21 (m, 1H), 2.20 – 2.13 (m, 1H), 2.01 – 1.93 (m, 1H), 1.89 – 1.82 (m, 2H), 0.91 (t, *J* = 8.0 Hz, 3H), 0.83 (td, *J* = 7.4, 2.5 Hz, 3H).

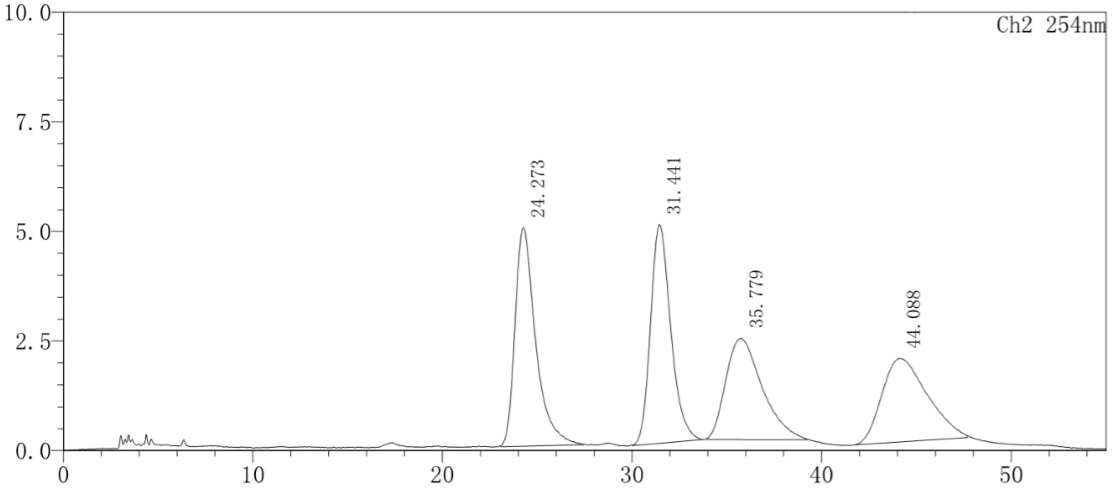
^{13}C NMR (101 MHz, $CDCl_3$) δ175.34, 172.56, 172.09, 139.55, 137.50, 134.35, 129.07, 128.09, 127.61, 126.83, 120.23, 56.11, 50.74, 32.91, 29.32, 27.04, 26.56, 12.42, 9.07.

HRMS (ESI): $C_{23}H_{27}N_2O_3^+$ ($M+H^+$): 379.2016, found: 379.2017.

$[\alpha]_D^{25}$ = 43.5 (c = 0.97, $CHCl_3$).

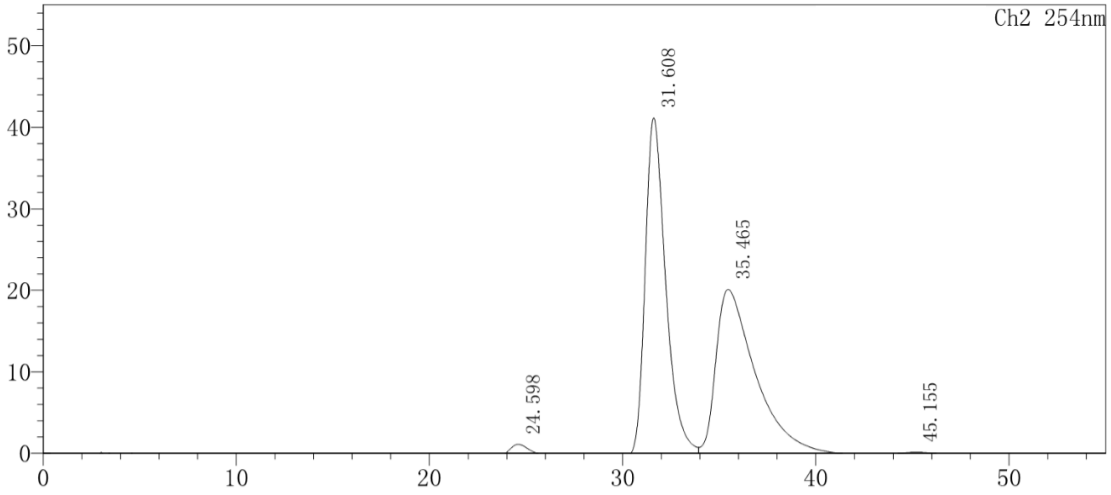
HPLC: The ee was determined to be 93%, 96% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 75:25 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 31.6, 35.5 min, t_R (minor) = 24.6 min, 45.2 min (93% ee, 96% ee)

42 racemic

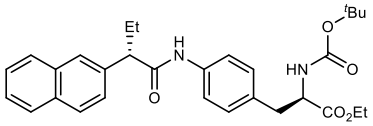


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	24.273	377628	4981	27.517
2	31.441	370417	4991	26.992
3	35.779	308843	2316	22.505
4	44.088	315438	1903	22.986

42 enantioenriched, 93% ee, 96% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	24.598	113710	1502	1.807
2	31.608	3115659	41566	49.519
3	35.465	2995333	20455	47.606
4	45.155	67196	452	1.068



Ethyl (*R*)-2-((tert-butoxycarbonyl)amino)-3-(4-((*S*)-2-(naphthalen-2-yl)butanamido)phenyl)propanoate (43)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (39.8 mg, 79%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 4H), 7.49 – 7.47 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.50 – 4.46 (m, 1H), 4.13 – 4.08 (m, 2H), 3.56 (t, *J* = 8.0 Hz, 1H), 3.04 – 2.95 (m, 2H), 2.37 – 2.30 (m, 1H), 1.99 – 1.92 (m, 1H), 1.41 (s, 9H), 1.20 (t, *J* = 4.0 Hz, 3H), 0.94 (t, *J* = 4.0 Hz, 3H).

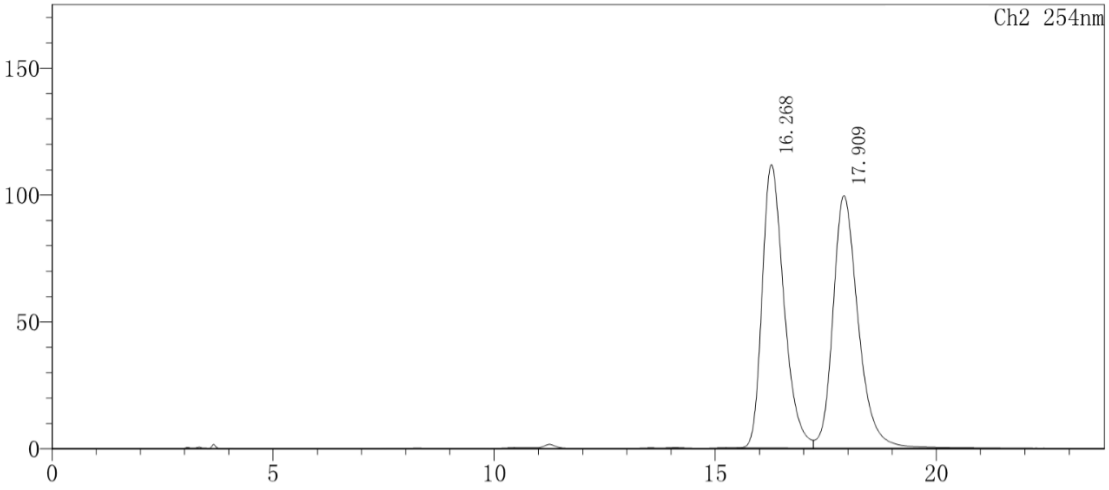
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.83, 155.23, 137.09, 136.98, 133.59, 132.82, 131.92, 129.86, 128.90, 127.85, 127.79, 127.12, 126.43, 126.08, 125.88, 119.91, 79.98, 61.45, 56.16, 54.53, 37.64, 28.39, 26.43, 14.22, 12.46.

HRMS (ESI): $C_{30}H_{37}N_2O_5^+$ ($M+H^+$): 505.2697, found: 505.2693.

$[\alpha]_D^{25}$ = 49.3 (c = 1.05, $CHCl_3$).

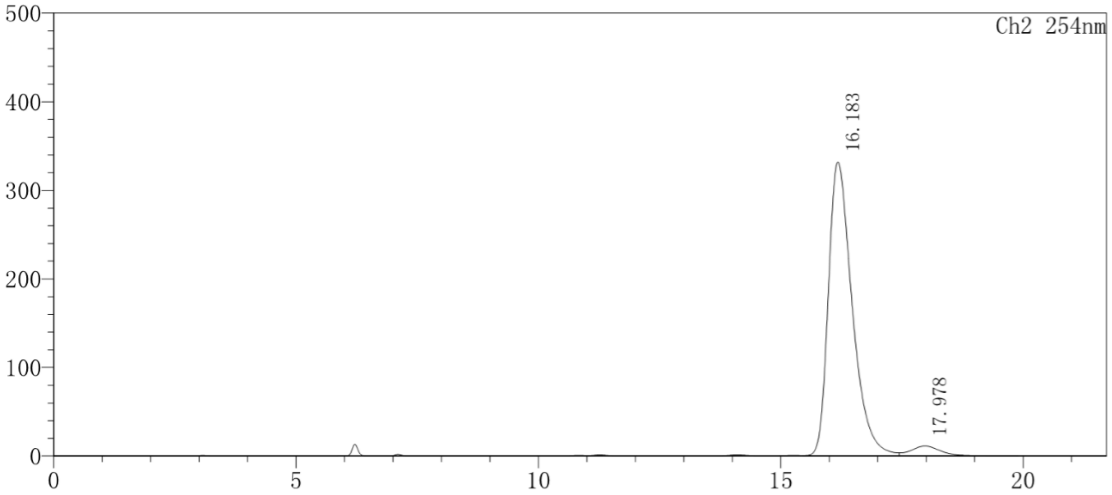
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 85:15 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 16.2 min, t_R (minor) = 18.0 min.

43 racemic

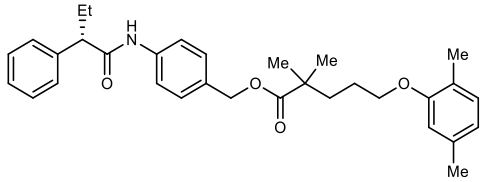


Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	16.268	3827327	111719	49.253
2	17.909	3943410	99531	50.747

43 enantioenriched, 92% ee



Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	16.183	11335251	331716	96.022
2	17.978	469613	11052	3.978



(*S*)-4-(2-phenylbutanamido)benzyl

5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (44)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 8% EtOAc) as a white solid (25.6 mg, 51%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.37 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 7.26 – 7.24 (m, 2H), 7.11 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 5.03 (s, 2H), 3.86 (t, *J* = 4.0 Hz, 2H), 3.38 (t, *J* = 8.0 Hz, 1H), 2.30 – 2.22 (m, 4H), 2.14 (s, 3H), 1.90 – 1.83 (m, 1H), 1.72 – 1.68 (m, 4H), 1.21 (s, 6H), 0.93 (t, *J* = 8.0 Hz, 3H).

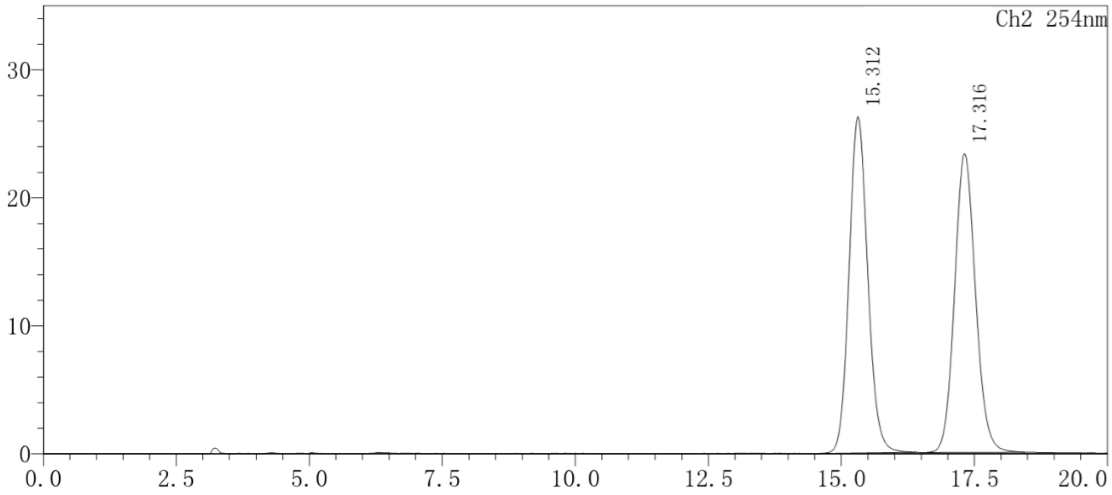
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.71, 171.81, 157.07, 139.55, 137.86, 136.58, 132.26, 130.39, 129.17, 128.99, 128.18, 127.69, 123.71, 120.78, 119.82, 112.08, 68.02, 65.88, 56.29, 42.25, 37.18, 29.84, 26.53, 25.25, 21.54, 15.88, 12.47.

HRMS (ESI): $C_{32}H_{40}NO_4^+$ ($M+H^+$): 502.2952, found: 502.2943.

$[\alpha]_D^{25}$ = 41.5 (c = 0.79, $CHCl_3$).

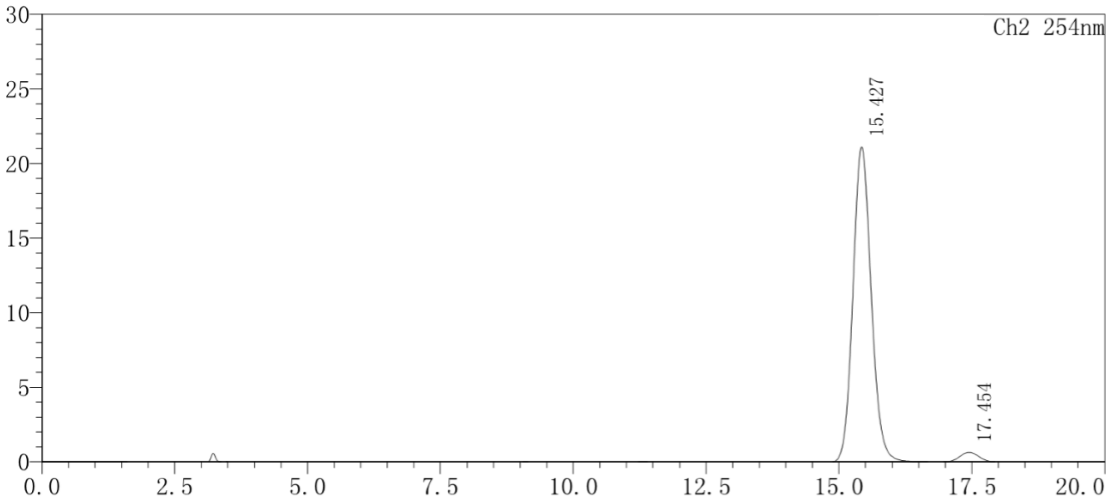
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 92:8 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 15.4 min, t_R (minor) = 17.5 min.

44 racemic

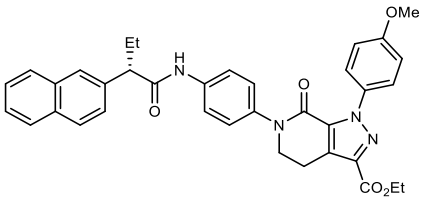


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	15.312	643628	26281	50.118
2	17.316	640601	23364	49.882

44 enantioenriched, 93% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	15.427	511695	21180	96.575
2	17.454	18149	691	3.425



Ethyl (*S*)-1-(4-methoxyphenyl)-6-(4-(2-(naphthalen-2-yl)butanamido)phenyl)-

7-oxo- 4,5,6,7-tetrahydro-1H-pyrazolo[3,4-c]pyridine-3-carboxylate (45)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 33% EtOAc) as a white solid (37.9 mg, 63%, 88% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.72 (m, 3H), 7.58 – 7.55 (m, 1H), 7.51 (s, 1H), 7.48 – 7.43 (m, 2H), 7.39 – 7.30 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.84 – 6.79 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 8.0 Hz, 2H), 3.85 – 3.76 (m, 1H), 3.74 – 3.68 (m, 4H), 3.20 (t, *J* = 8.0 Hz, 1H), 3.16 – 3.11 (m, 2H), 2.15 – 2.08 (m, 1H), 1.74 – 1.67 (m, 1H), 1.36 (t, *J* = 8.0 Hz, 3H), 0.76 (t, *J* = 8.0 Hz, 3H).

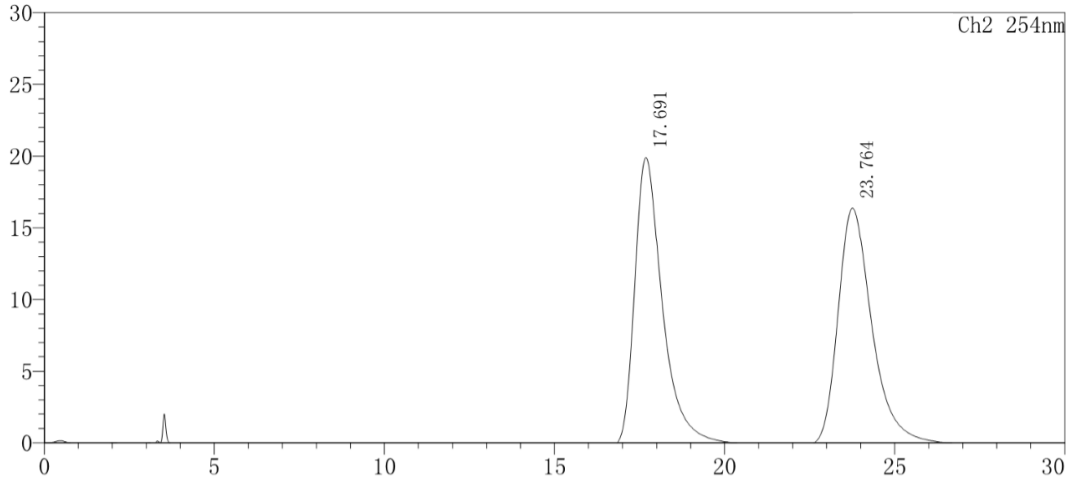
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.67, 162.24, 160.05, 157.46, 139.23, 137.49, 133.46, 133.21, 132.74, 132.69, 128.73, 127.86, 127.69, 127.26, 127.12, 127.10, 126.38, 126.02, 125.98, 125.80, 120.56, 120.53, 113.68, 63.01, 61.40, 55.58, 51.37, 26.62, 21.51, 14.54, 12.34.

HRMS (ESI): $C_{36}H_{35}N_4O_5^+$ ($M+H^+$): 603.2602, found: 603.2607.

$[\alpha]_D^{25}$ = 26.9 (c = 0.83, $CHCl_3$).

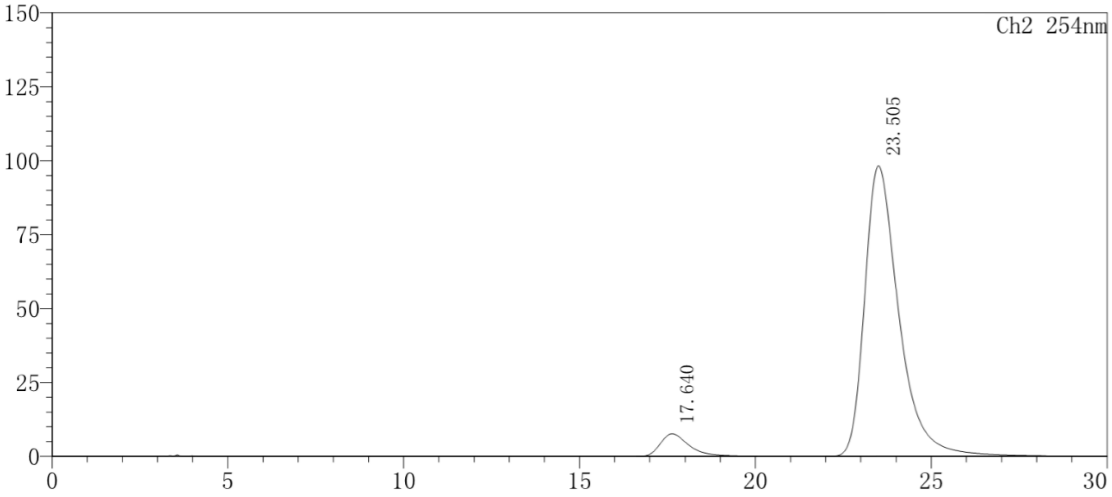
HPLC: The ee was determined to be 88% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 60:40 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 23.5 min, t_R (minor) = 17.6 min.

45 racemic

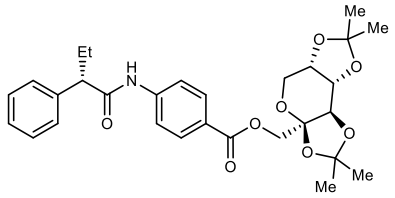


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	17.691	1145692	20096	49.835
2	23.764	1153256	16517	50.165

45 enantioenriched, 88% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	17.640	440163	7702	6.229
2	23.505	6626150	98284	93.771



((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 4-((*S*)-2-phenylbutanamido)benzoate (46)

According to **General Procedure**, the title compound was isolated by flash column chromatography (silica gel, pentane with 6% EtOAc) as a white solid (24.2 mg, 46%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.98 (d, *J* = 12.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.38 – 7.30 (m, 5H), 4.67 – 4.62 (m, 2H), 4.44 (d, *J* = 1.9 Hz, 1H), 4.31 – 4.24 (m, 2H), 3.94 (d, *J* = 12.0 Hz, 1H), 3.78 (d, *J* = 12.0 Hz, 1H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.32 – 2.23 (m, 1H), 1.90 – 1.83 (m, 1H), 1.53 (s, 3H), 1.45 (s, 3H), 1.33 (d, *J* = 8.0 Hz, 6H), 0.92 (t, *J* = 8.0 Hz, 3H).

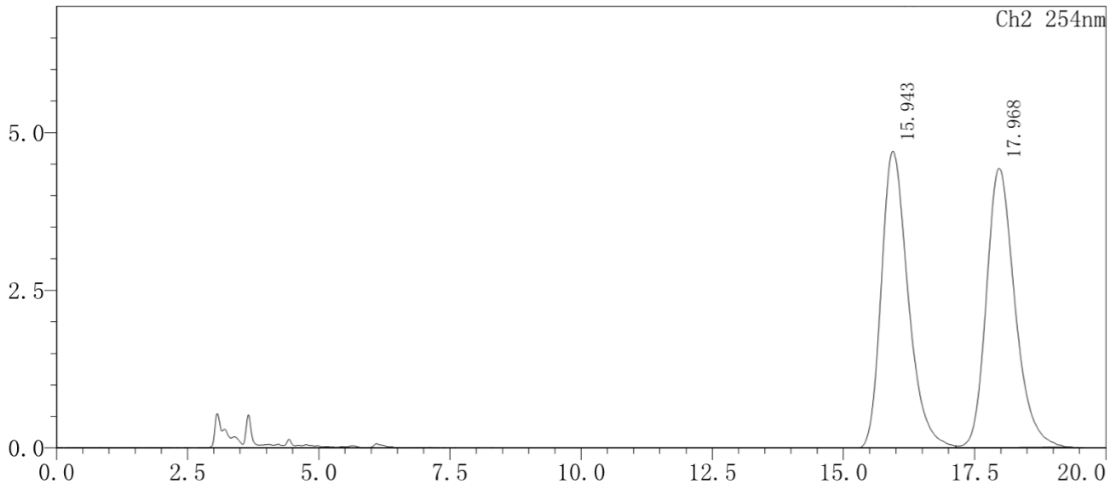
^{13}C NMR (101 MHz, $CDCl_3$) δ172.16, 165.52, 142.40, 139.19, 131.07, 129.25, 128.16, 127.83, 125.29, 118.86, 109.29, 108.96, 101.81, 70.93, 70.61, 70.23, 65.17, 61.47, 56.35, 26.64, 26.50, 26.02, 25.63, 24.14, 12.41.

HRMS (ESI): $C_{29}H_{35}NNaO_8^+$ ($M+Na^+$): 548.2255, found: 548.2245.

$[\alpha]_D^{25}$ = 31.2 (c = 0.97, $CHCl_3$).

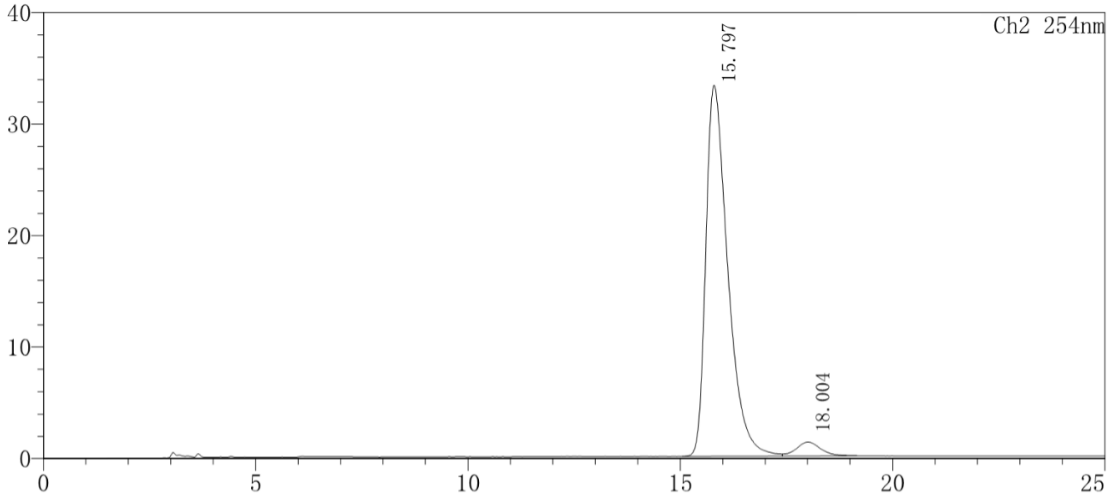
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 85:15 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 15.8 min, t_R (minor) = 18.0 min.

46 racemic



Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	15.943	167657	4717	50.068
2	17.968	167201	4428	49.932

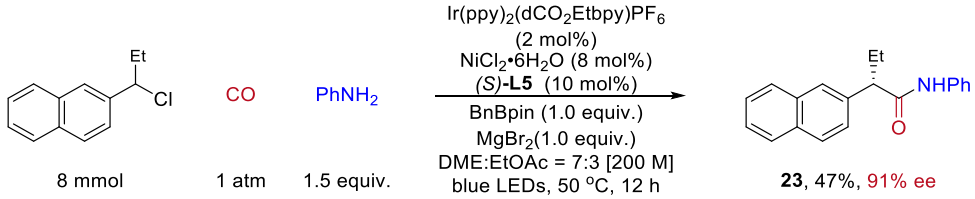
46 enantioenriched, 92% ee



Peak	Ret Time	Area	Height	Area
#	[min]	[mAU*s]	[mAU]	[%]
1	15.797	1196514	33297	95.959
2	18.004	50382	1250	4.041

6. Gram-Scale Reaction

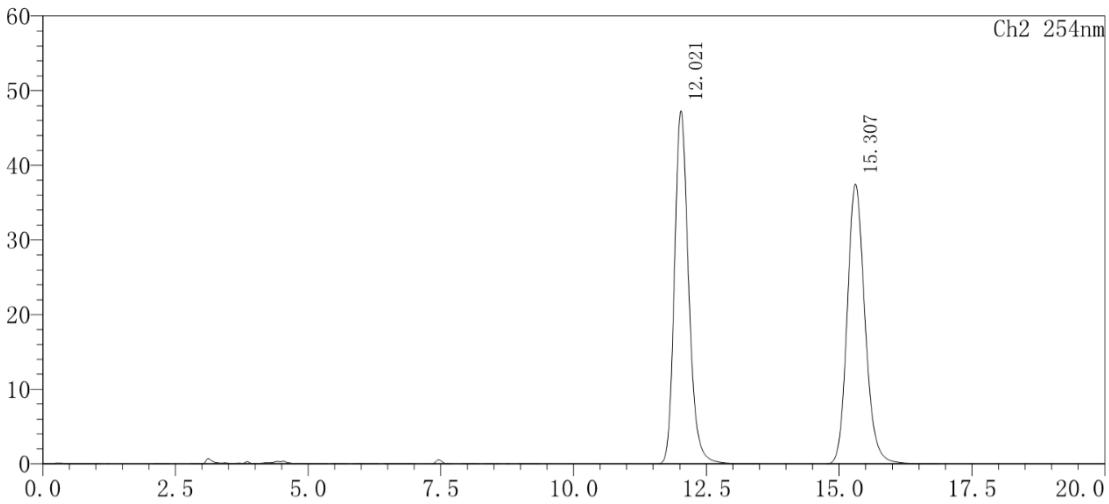
Gram-Scale Synthesis of (*S*)-23:



To a flame-dried 100 mL round bottom flask was charged with 2-(1-chloropropyl)naphthalene (8 mmol, 1.0 equiv.) $Ir(ppy)_2(dCO_2Etbpy)]PF_6$ (0.16 mmol, 2 mol%), (*S*)-**L5** (0.8 mmol, 10 mol%), $NiCl_2$•$6H_2O$ (0.64 mmol, 8 mol%), and $MgBr_2$ (8 mmol, 1.0 equiv.). Then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO balloon three times, DME /EtOAc (40 mL, v/v = 7:3) was added via a syringe, followed by the addition of with aniline (12 mmol), BnBpin (8 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 hours at 50 °C by 90 W blue LEDs, and then quenched with water and extracted with EtOAc (3*20 mL). The combined organic layers were washed by brine, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel, pentane with 6% EtOAc) to afford the product **23** (1.09 g, 47% yield, 91% ee).

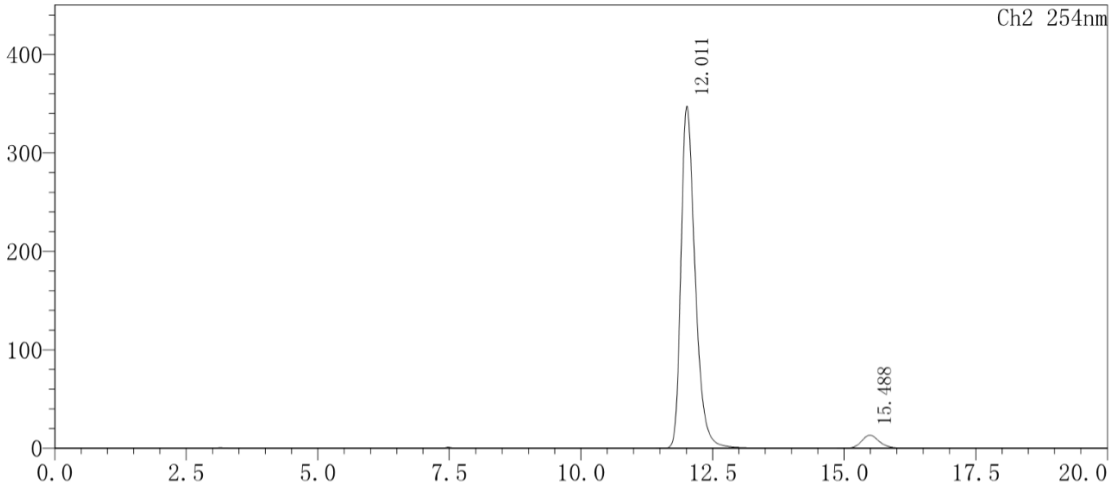
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.0 min, t_R (minor) = 15.5 min.

23 racemic

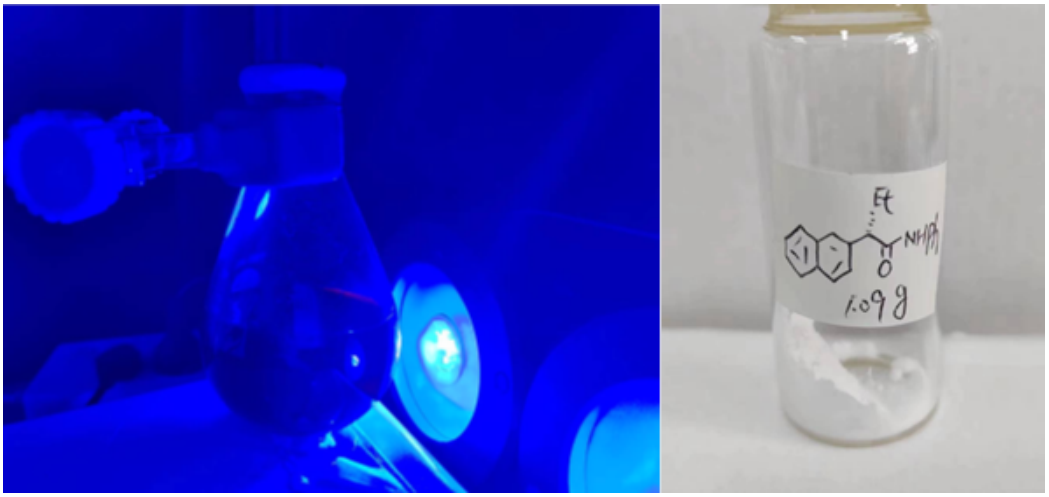


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12. 021	877547	47387	49. 980
2	15. 307	878237	37580	50. 020

23 enantioenriched, 91% ee



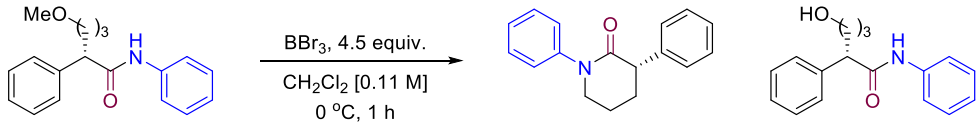
Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	12. 011	6481819	347811	95. 338
2	15. 488	316991	13348	4. 662



Supplementary Figure S7 Gram-Scale Reaction experimental setup

7. Synthetic Transformations

7.1 Synthesis of chiral amides and amines

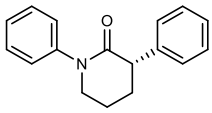


16, 0.1 mmol 91% ee

47, 35%, 91% ee

48, 43%, 91% ee

BBr_3 (1 M in CH_2Cl_2, 0.45 mL, 0.45 mmol) was slowly added to a suspension of **16** (0.1 mmol) in anhydrous CH_2Cl_2 (1 mL) at 0 °C and the solution was stirred for 1 hour at 0 °C. Next, water was added for quenching and the formed precipitate was filtered, washed with CH_2Cl_2 (2 × 5 mL) and water (2 × 5 mL) and dried in vacuo, the residue was purified by flash column chromatography (silica gel, pentane with 7% EtOAc) to obtain **47** (8.8 mg, 35%, 91% ee) and **48** [12] (10.4 mg, 43%, 91% ee).



(*S*)-1,3-diphenylpiperidin-2-one (47)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.28 – 7.26 (m, 3H), 7.21 – 7.16 (m, 3H), 7.01– 6.95 (m, 2H), 3.41 (t, J = 8.0 Hz, 1H), 3.35 – 3.25 (m, 2H), 2.34 – 2.20 (m, 1H), 1.96 – 1.78 (m, 2H), 1.75 – 1.64 (m, 1H).

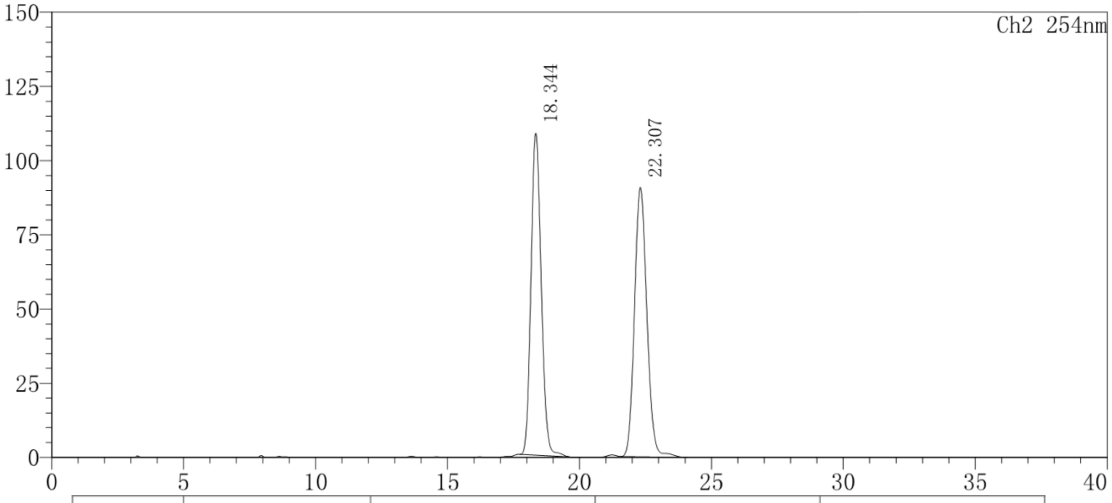
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 139.11, 137.81, 129.39, 129.09, 128.11, 127.97, 124.54, 119.88, 53.61, 33.41, 31.91, 30.96.

HRMS (ESI): $C_{17}H_{18}NO^+$ ($M+H^+$): 252.1383, found: 252.1380.

$[\alpha]_D^{25}$ = 37.9 (c = 1.03, $CHCl_3$).

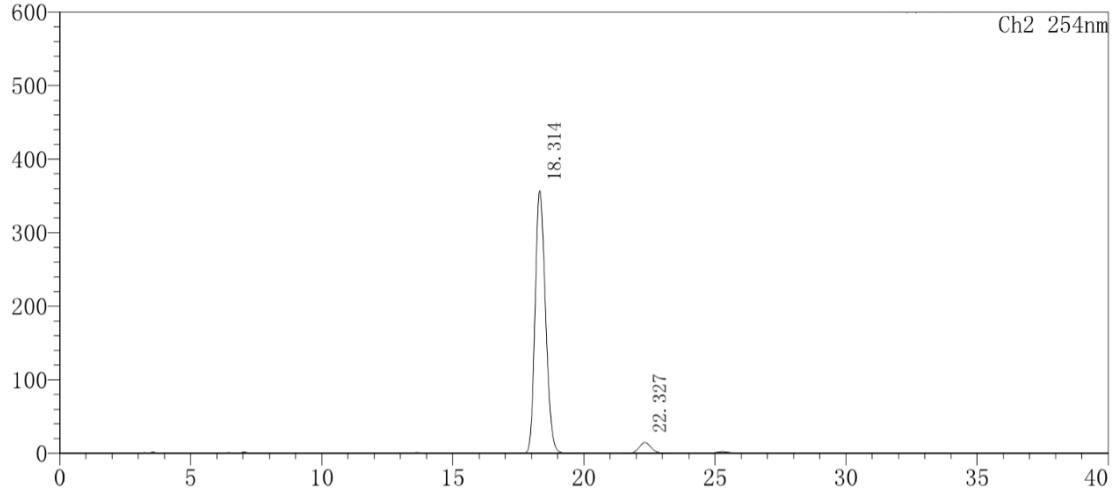
HPLC: The ee was determined to be 91% on a CHIRALPAK ADH column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 92:8 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 18.3 min, t_R (minor) = 22.3 min.

47 racemic

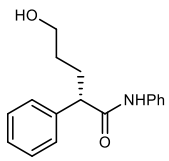


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	18.344	2931285	108555	49.692
2	22.307	2967624	90741	50.308

47 enantioenriched, 91% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	18.314	9900120	357270	95.479
2	22.327	468768	14592	4.521



(*S*)-5-hydroxy-*N*,2-diphenylpentanamide (48)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H), 7.36 – 7.35 (m, 4H), 7.28 – 7.24 (m, 3H), 7.06 (t, *J* = 8.0 Hz, 1H), 3.67 – 3.66 (m, 2H), 3.56 (t, *J* = 8.0 Hz, 1H), 2.38 – 2.29 (m, 1H), 1.95 – 1.86 (m, 2H), 1.59 (m, 1H).

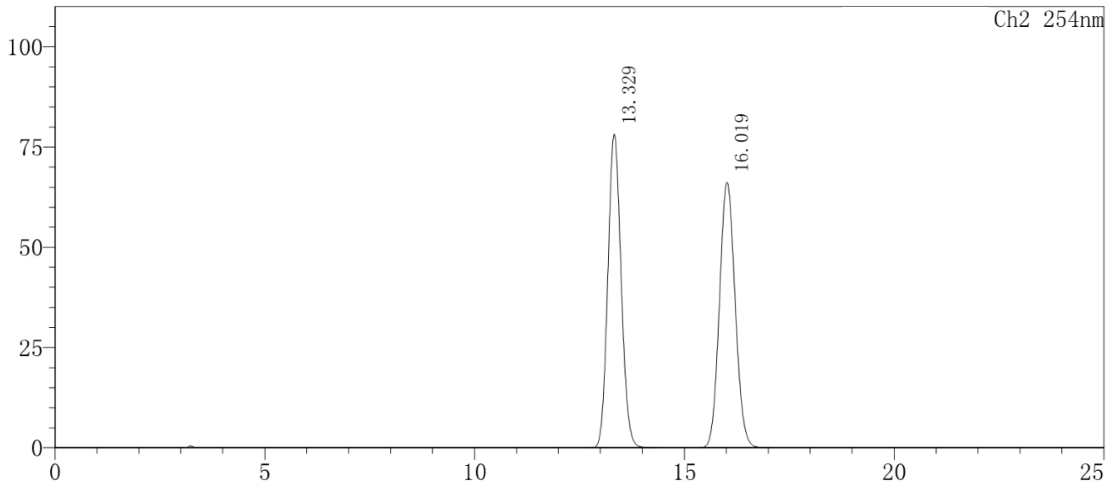
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.92, 139.67, 137.93, 129.21, 129.05, 128.12, 127.73, 124.45, 119.93, 62.60, 53.98, 30.79, 29.79.

HRMS (ESI): $C_{17}H_{20}NO_2^+$ ($M+H^+$): 270.1489, found: 270.1483.

$[\alpha]_D^{25}$ = 29.2 (c = 0.65, $CHCl_3$).

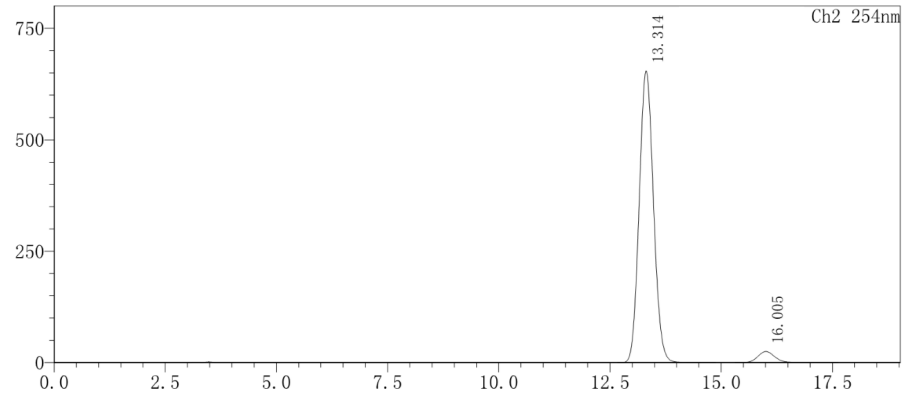
HPLC: The ee was determined to be 91% on a CHIRALPAK ADH column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 13.3 min, t_R (minor) = 16.0 min.

48 racemic

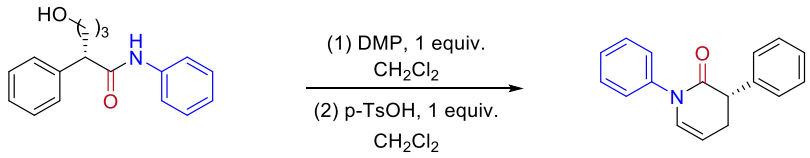


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13.329	1726422	78193	50.005
2	16.019	1726046	66186	49.995

48 nantioenriched, 91% ee



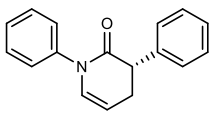
Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	13. 314	14641669	654701	95. 650
2	16. 005	665883	24883	4. 350



48, 0.1 mmol

49, 75%, 91% ee

To a solution of **48** (0.1 mmol) in CH_2Cl_2 (2.00 mL) was added Dess-Martin periodinane (42.4 mg, 0.1 mmol), and the reaction mixture was stirred for 2 hours. After the reaction was quenched with sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$, the whole mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed in vacuo to give a pale yellow oil, which was dissolved in CH_2Cl_2 (2.00 mL). The mixture was treated with p-toluene sulfonic acid monohydrate (19 mg, 0.1 mmol), and the reaction mixture was stirred for 2 hrs. After the reaction was quenched by the addition of H_2O (1 mL), and the mixture was extracted with EtOAc, washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo and the crude product was purified by flash column chromatography (silica gel, pentane with 9% EtOAc) to afford the desired product **49** [13] (18.7 mg, 75% yield, 91% ee).



(*S*)-1,3-diphenyl-3,4-dihydropyridin-2(1H)-one (49)

^{1}H NMR (400 MHz, $CDCl_3$) δ7.33 – 7.25 (m, 6H), 7.22 – 7.18 (m, 4H), 6.27 (d, J = 8.0 Hz, 1H), 5.29 – 5.25 (m, 1H), 3.86 (t, J = 8.0 Hz, 1H), 2.77 – 2.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ169.80, 140.86, 139.10, 131.04, 129.10, 128.67, 128.17, 127.30, 127.06, 126.09, 106.17, 47.65, 28.38.

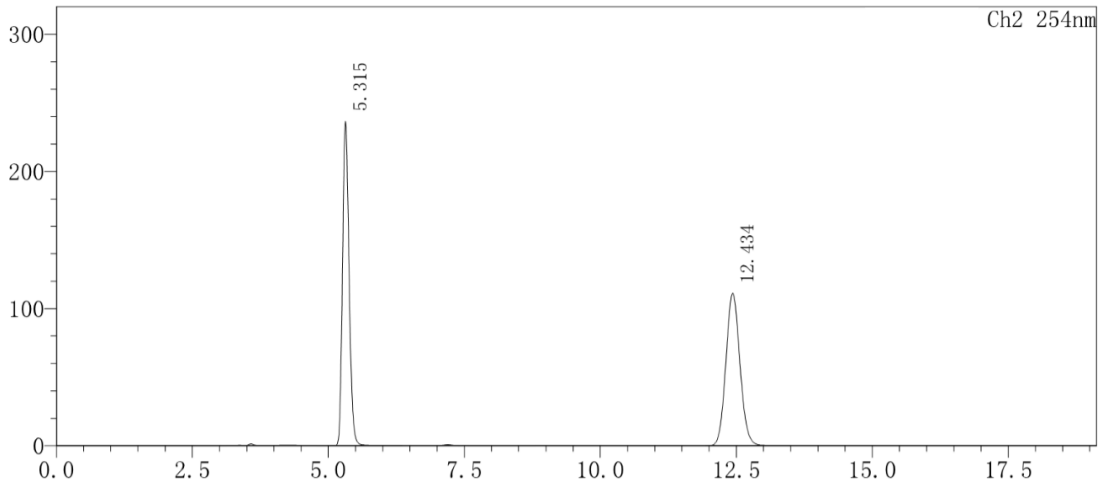
HRMS (ESI): $C_{17}H_{16}NO^+$ ($M+H^+$): 250.1226, found: 250.1223.

$[\alpha]_D^{25}$ = 43.1 (c = 0.76, $CHCl_3$).

HPLC: The ee was determined to be 91% on a CHIRALPAK ADH column at 254 nm,

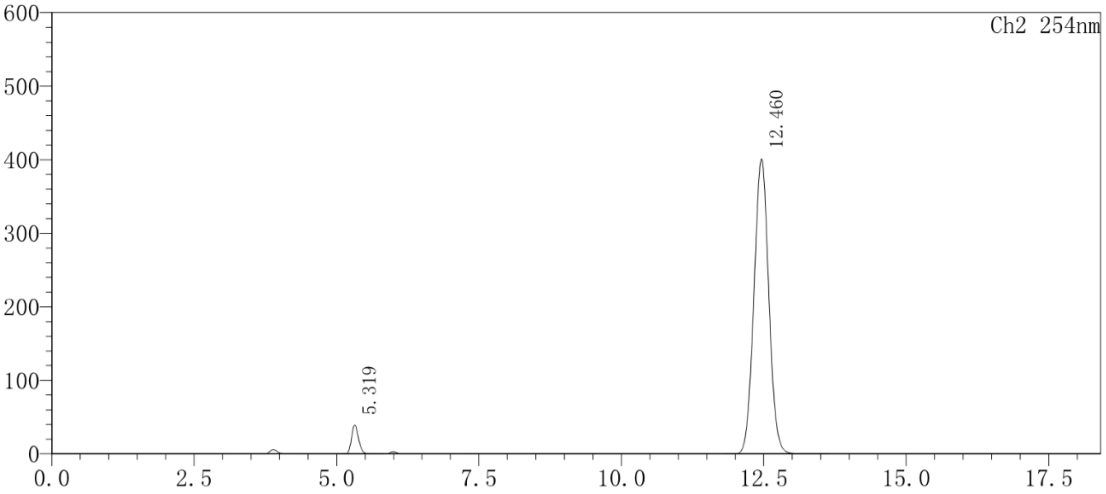
25 °C, with hexane: ^{i}PrOH = 60:40 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.5 min, t_R (minor) = 5.3 min.

49 racemic

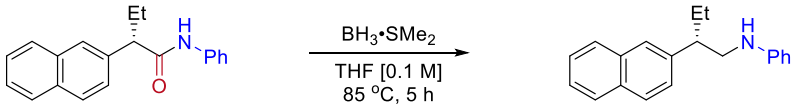


Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.315	1978593	236636	49.829
2	12.434	1992210	111229	50.171

49 enantioenriched, 91% ee



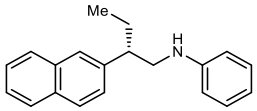
Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	5.319	338209	39254	4.447
2	12.460	7267080	401505	95.553



23, 0.2 mmol 93% ee

50, 92%, 96% ee

Borane-SMe_2 (120 μL, 2.0 M in THF, 0.24 mmol, 1.2 equiv) was added dropwise to a solution of (S)-2-(naphthalen-2-yl)-N-phenylbutanamide (**23**, 0.20 mmol, 1.0 equiv) in THF (2.0 mL) at 0 ℃ in a 10-mL Schlenk tube. Next, the reaction mixture was allowed to warm to room temperature, and then it was heated to 85 °C. After being stirred at 85 °C in the sealed Schlenk tube for 8 hours, the reaction was quenched with aqueous NaOH (1.0 M, 0.5 mL), and the reaction mixture was extracted with Et_2O (3 ×10.0 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, pentane with 2.5% EtOAc) to provide the title compound **50** [14] as a colorless oil (26.4 mg, 92% yield, 96% ee).



(*S*)-N-(2-(naphthalen-2-yl)butyl)aniline (50)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 3H), 7.65 (s, 1H), 7.51 – 7.44 (m, 2H), 7.35 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.71 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 3.57 – 3.52 (m, 1H), 3.35 – 3.30 (m, 1H), 3.02 – 2.95 (m, 1H), 2.63 (s, 1H), 1.95 – 1.84 (m, 1H), 1.82 – 1.71 (m, 1H), 0.88 (t, *J* = 8.0 Hz, 3H).

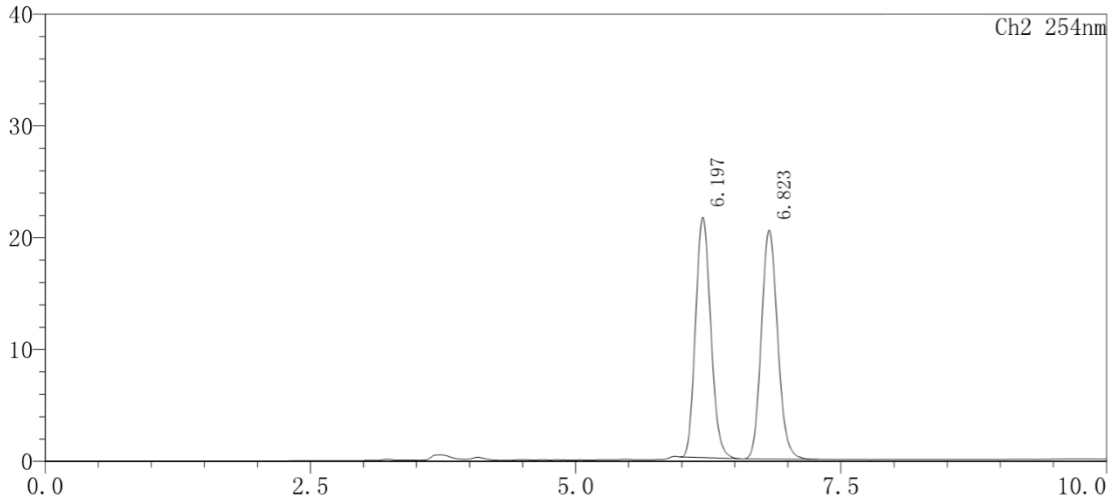
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.02, 140.43, 133.67, 132.70, 129.36, 128.61, 127.79, 127.74, 127.15, 126.22, 125.76, 125.65, 117.71, 113.35, 49.60, 47.41, 27.28, 12.22.

HRMS (ESI): $C_{20}H_{22}N^+$ ($M+H^+$): 276.1747, found: 276.1748.

$[\alpha]_D^{25}$ = 29.3 (c = 0.56, $CHCl_3$).

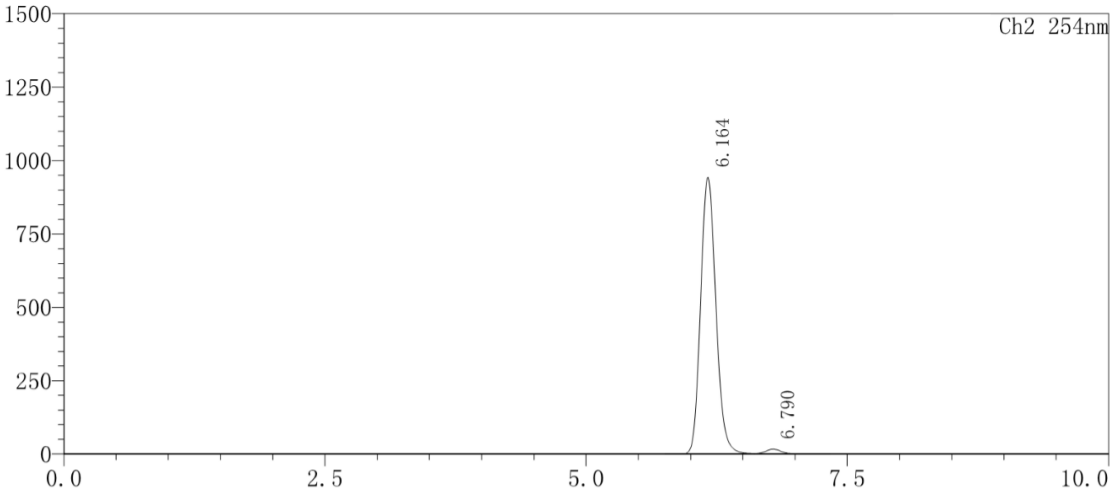
HPLC: The ee was determined to be 96% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 98:2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.2 min, t_R (minor) = 6.8 min.

50 racemic



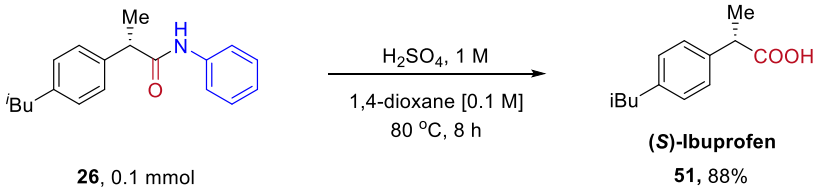
Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	6.197	215555	21520	49.585
2	6.823	219162	20501	50.415

50 enantioenriched, 96% ee



Peak #	Ret Time [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	6.164	9633577	943604	98.100
2	6.790	186629	16866	1.900

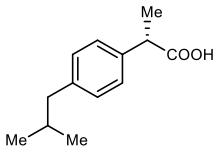
7.2 Synthesis of non-steroidal anti-inflammatory drugs



26, 0.1 mmol

(*S*)-Ibuprofen
51, 88%

A solution of compounds **26**, 0.1 mmol in 1 M H_2SO_4 (aq, 1.0 mL) and 1,4-dioxane (1.0 mL) was stirred at 80 °C for 8 hours. After the reaction completed, the reaction was cooled down to room temperature. The mixture was extracted with CH_2Cl_2 (20 mL × 3). The organic layers were dried over sodium sulfate and concentrated. The residue was then purified by flash column chromatography (silica gel, pentane with 12% EtOAc) to give the corresponding (*S*)-ibuprofen **51**[6] (18.1 mg, 88% yield).

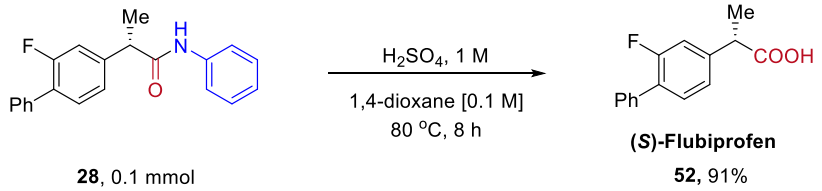


(*S*)-2-(4-isobutylphenyl)propanoic acid (51)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.71 (q, *J* = 8.0 Hz, 1H), 2.45 (d, *J* = 8.0 Hz, 2H), 1.90 – 1.80 (m, 1H), 1.50 (d, *J* = 8.0 Hz, 3H), 0.90 (d, *J* = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ180.79, 141.00, 137.14, 129.54, 127.42, 45.19, 45.08, 30.31, 22.54, 18.25.

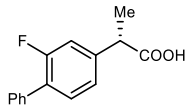
$[\alpha]_D^{25}$ = 42.0 (c = 0.78, $CHCl_3$).



28, 0.1 mmol

(*S*)-Flubiprofen
52, 91%

A solution of compounds **28**, 0.1 mmol in 1 M H_2SO_4 (aq, 1.0 mL) and 1,4-dioxane (1.0 mL) was stirred at 80 °C for 8 hours. After the reaction was complete, the mixture was cooled down to room temperature. The mixture was extracted with CH_2Cl_2 (20 mL × 3). The organic layers were dried over sodium sulfate and concentrated. The residue was then purified by flash column chromatography (silica gel, pentane with 10% EtOAc) to give the corresponding (*S*)-flubiprofen **52** [6] (22.3 mg, 91% yield).



(*S*)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (52)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.45 – 7.34 (m, 4H), 7.19 – 7.13 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H).

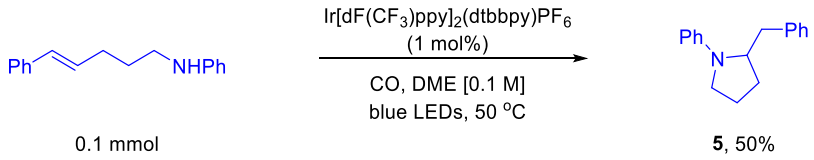
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.15, 159.85 (d, *J* = 249.5 Hz), 141.09, 135.56, 131.03, 129.11, 128.60, 128.31(d, *J* = 13 Hz), 127.86, 123.83, 115.53 (d, *J* = 23 Hz), 44.97, 18.15.

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.41 (t, *J* = 8.0 Hz).

$[\alpha]_D^{25}$ = 37.0 (c = 0.9, $CHCl_3$).

8. Mechanistic Studies

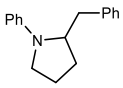
8.1 Aminium radical cation trap (Figure 2B)



0.1 mmol

5, 50%

To a flame-dried 20 mL test tube was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (1.1 mg, 0.001 mmol, 1 mol%), then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO three times, DME (1 mL) was added via a syringe, followed by the addition of with aniline **4** (0.1 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 hours at 50 °C by 90 W blue LEDs, and then quenched with water and extracted with EtOAc. The combined organic layers were washed by brine, dried over MgSO$_4$, and concentrated. The residue was purified by flash column chromatography (silica gel, pentane with 3% EtOAc) to afford the product **5**.

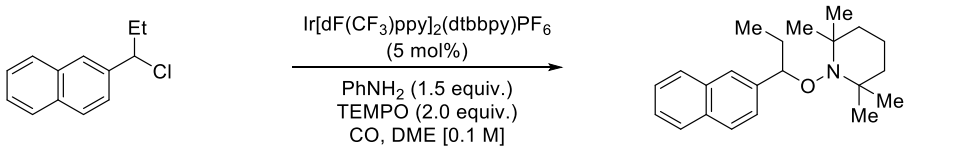


2-benzyl-1-phenylpyrrolidine (5)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 7H), 6.74 – 6.70 (m, 3H), 4.00 (ddd, *J* = 9.2, 6.3, 2.8 Hz, 1H), 3.48 – 3.43 (m, 1H), 3.24 – 3.18 (m, 1H), 3.10 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.59 (dd, *J* = 13.6, 9.6 Hz, 1H), 1.97 – 1.85 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.08, 139.66, 129.51, 129.47, 128.55, 126.31, 115.60, 111.95, 59.89, 48.48, 38.69, 29.60, 23.14.

8.2 Benzyl radical trap (Figure 2c)

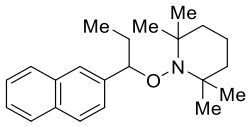


0.1 mmol

no (**L5**)Ni(CO)$_2$, 5% **PC**: **7,** 34%

no **PC**, 10% (**L5**)Ni(CO)$_2$: **7,** 0%

To a flame-dried 20 mL test tube was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.5 mg, 0.005 mmol, 5 mol%), 2-(1-chloropropyl)naphthalene (20.4 mg, 0.1 mmol, 1.0 equiv.), TEMPO (31.2 mg, 0.2 mmol, 2.0 equiv.), then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO three times, DME (1 mL) was added via a syringe, followed by the addition of with $PhNH_2$ (13.7 uL, 0.15 mmol, 1.5 equiv.). The reaction mixture was allowed to stir for 1 hour at 50 ^oC by 90 W blue LEDs, and then quenched with water and extracted with EtOAc (10 mL). The combined organic layers were washed by brine (2×5 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel, pentane) to afford product **7**.



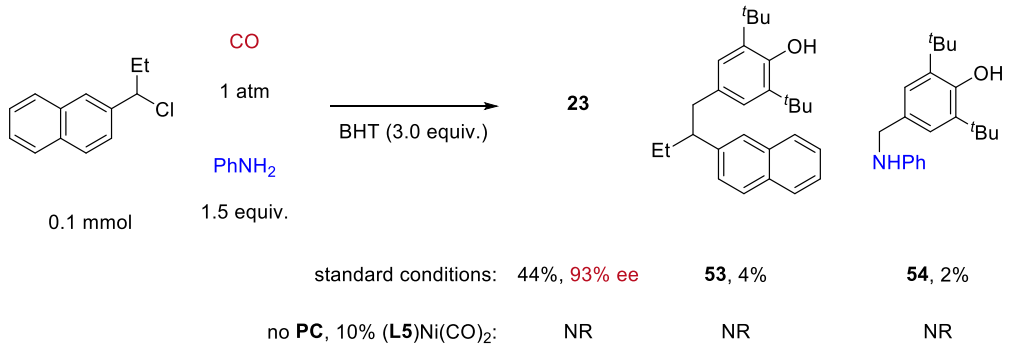
2,2,6,6-tetramethyl-1-(1-(naphthalen-2-yl)propoxy)piperidine (7)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 3H), 7.69 (s, 1H), 7.50 – 7.43 (m, 3H), 4.71 (dd, J = 9.7, 3.7 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.96 – 1.85 (m, 1H), 1.52 (s, 3H), 1.37 – 1.20 (m, 9H), 1.04 (s, 3H), 0.69 (t, J = 7.5 Hz, 3H), 0.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.11, 133.21, 132.91, 128.08, 127.77, 127.72, 126.74, 125.94, 125.86, 125.51, 89.07, 60.12, 59.74, 40.60, 34.41, 29.86, 28.85, 20.52, 17.35, 9.89.

HRMS (ESI): $C_{22}H_{32}NO^+$ ($M+H^+$): 326.2478, found: 326.2480.

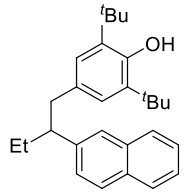
8.3 Radical trap with BHT (Figure 4D)



According to General Procedure with the addition of BHT (72.0 mg, 0.30 mmol, 3.0 equiv.). The reaction mixture was irradiated with blue LED light for 12 hours. The

reaction was quenched with saturated sodium chloride aqueous solution, extracted with EtOAc. The combined organic layers were dried with Mg_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel, pentane with 2% EtOAc) to afford **23** (12.7 mg, 44% yield, 93% ee), benzyl-adduct **53** (1.6 mg, 4% yield) and amino-adduct **54** (0.6 mg, 2% yield).

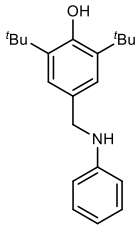
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.0 min, t_R (minor) = 15.4 min.



2,6-di-tert-butyl-4-(2-(naphthalen-2-yl)butyl)phenol (53)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 3H), 7.53 (s, 1H), 7.48 – 7.42 (m, 2H), 7.21 – 7.19 (m, 1H), 6.62 (d, *J* = 4.0 Hz, 1H), 6.48 (d, *J* = 4.0 Hz, 1H), 2.77 (dd, *J* = 12.0, 4.0 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.70 – 1.62 (m, 1H), 1.27 (s, 9H), 1.14 (s, 2H), 1.08 (s, 9H), 0.69 (t, *J* = 8.0 Hz, 3H).

HRMS (FI): $C_{28}H_{36}O$ (M): 388.2766, found: 388.2862.



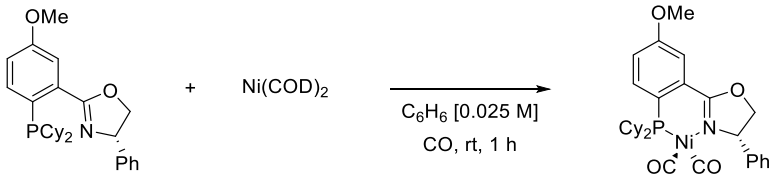
2,6-di-tert-butyl-4-((phenylamino)methyl)phenol (54) [15]

The title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 30:1) as a white solid (0.6 mg, 2%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 4H), 6.75 – 6.68 (m, 3H), 5.20 (s, 1H), 4.19 (s, 2H), 1.45 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.29, 148.51, 136.24, 129.75, 129.39, 125.16, 117.66, 113.02, 49.18, 34.50, 30.42.

8.4 Synthesis of (L5)Ni(CO)$_2$ B (Figure 4F)



1.05 equiv. 0.1 mmol 71%, (**L5**)$Ni(CO)_2$

In the glovebox under nitrogen atmosphere, to an oven-dried 25 mL Schlenk flask equipped with Teflon cap and stir bar was charged $Ni(COD)_2$ (0.1 mmol) and (*S*)-**L5** (0.105 mmol) in C_6H_6 (4 mL). The flask was sealed, brought out of the glovebox and connected to the Schlenk line. The Schlenk flask was evacuated by freeze-pump-thaw cycle followed by loading of 4 atmospheric pressure of carbon monoxide. The reaction was allowed to stir at room temperature for 1 hour. Excess carbon monoxide was evacuated by freeze-pump-thaw cycle on the Schlenk line. The reaction was brought into the glovebox and solvent was removed under reduced pressure. The remaining solid was dissolved in pentane (3 mL) and extracted with acetonitrile (3 mL). the acetonitrile layer was collected, and solvent was removed by high vacuum.

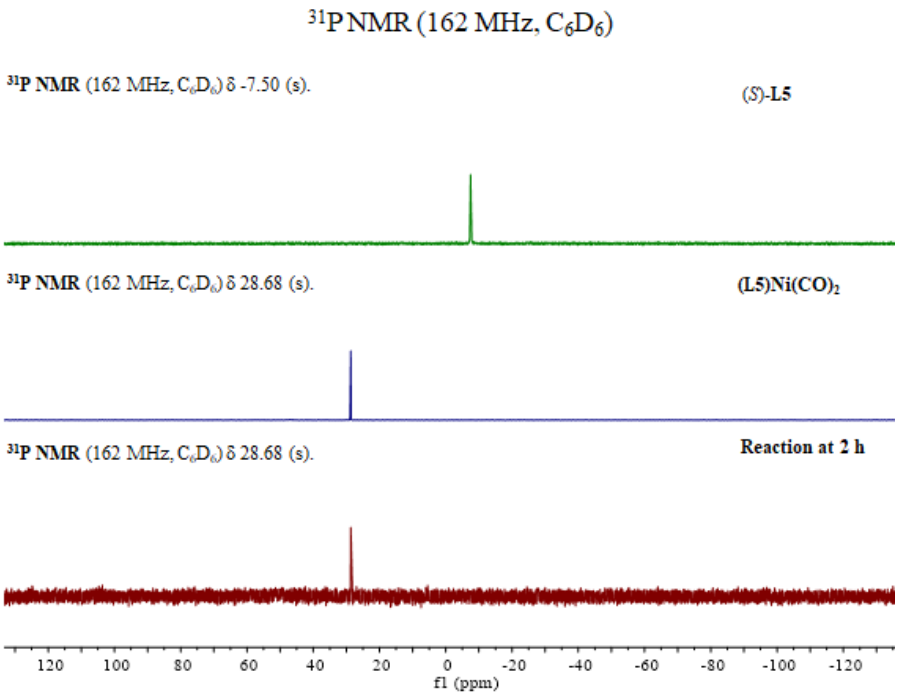
The title compound was obtained as an orange solid, 71% yield.

^{1}H NMR (500 MHz, C_6D_6) δ 7.87 – 7.75 (m, 1H), 7.38 – 7.35 (m, 1H), 7.22 – 7.19 (m, 2H), 7.15 – 7.13 (m, 3H), 6.79 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.02 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.86 – 3.77 (m, 2H), 3.29 (s, 3H), 2.10 – 1.96 (m, 3H), 1.84 – 1.72 (m, 2H), 1.65 – 1.47 (m, 8H), 1.39 – 1.31 (m, 2H), 1.27 – 1.05 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.03, 200.05, 162.45, 160.45, 141.32, 134.16, 133.29 (d, *J* = 15.1 Hz), 129.00, 128.82, 128.64, 123.77 (d, *J* = 10.1 Hz), 117.18, 116.76, 77.39, 72.63, 54.92, 36.35 (d, *J* = 13.9 Hz), 36.05 (d, *J* = 13.9 Hz), 28.71, 28.63, 27.58, 27.47, 27.36, 27.27, 27.21, 26.68, 26.63.

^{31}P NMR (162 MHz, C_6D_6) δ 28.68.

HRMS (ESI): $[C_{30}H_{35}NO_4PNi]^+$: 562.1652, found: 562.1629.



^{31}P NMR analysis of the reaction mixture

8.5 Determination of quantum yield

We utilized protocol reported by Chiba and co-workers to determine the photon flux of blue LED.[16] All solutions were stored in the black vial and stored in the dark when not in use. Measurements were performed with the lights off to protect the samples from ambient light as much as possible.

a) Preparation of stock solutions

A 0.15 M solution of ferrioxalate was obtained by dissolving potassium ferrioxalate trihydrate ($[K_3Fe^{III}(C_2O_4)_3] \cdot 3H_2O$; 1.11 g, 2.26 mmol) in 0.05 M H_2SO_4 (prepared by fresh deionized water) (15 mL total volume).

A buffered phenanthroline solution was obtained by dissolving 1,10-phenanthroline (10.0 mg) and sodium acetate (2.25 g) in 0.5 M H_2SO_4 (prepared by fresh deionized water) (10 mL total volume).[16]

b) Determination of background Fe^{2+} concentration

2 mL of the ferrioxalate solution was added to a 8 mL vial. Next, 0.35 mL of the phenanthroline solution was added and the mixture was stored in the dark for 1 hour. Then the solution was transferred to a cuvette and a UV–vis spectrum was measured using UV–vis absorption spectrometer (lambda 950). The absorbance value at 510 nm was recorded. This process was repeated twice. Average value: 1.653546.

c) Determination of photon flux

2 mL of the ferrioxalate solution was added to a 8 mL vial. The vial was immediately irradiated with blue LED light (λmax = 467 nm) for 20 seconds and removed from the blue LED. Then, 0.35 mL of the phenanthroline solution was added to the ferrioxalate solution, and the resulting mixture was stored in the dark for 1 hour. Then the solution was transferred to a cuvette and the UV–vis spectrum was measured. The absorbance value at 510 nm was recorded. This process was repeated twice. Average value: 3.793243.

d) Calculations

The amount of Fe^{2+} formed was calculated according to the following equation:

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

where V is the volume of the sample analyzed (2.35 mL), ΔA is the difference in average absorbances (between irradiated and unirradiated ferrioxalate solutions) at 510 nm, l is the path length, and ε is the molar absorptivity at 510 nm.[17]

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{(0.00235\ L)(2.139697)}{(1\ cm)(11100\ {}^{L}/_{mol \cdot cm})} = 45.299 \cdot 10^{-8}\ mol$$

The fraction of light absorbed by the ferrioxalate actinometer was calculated by the following equation:

$$f = 1 - 10^{-A}$$

where A is the absorbance at 468 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline (**Figure S8**).

$$f = 1 - 10^{-A} = 1\text{-}10^{-0.520746} = 0.698523$$

The photon flux was calculated using the following equation:

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot \mathrm{t} \cdot f}$$

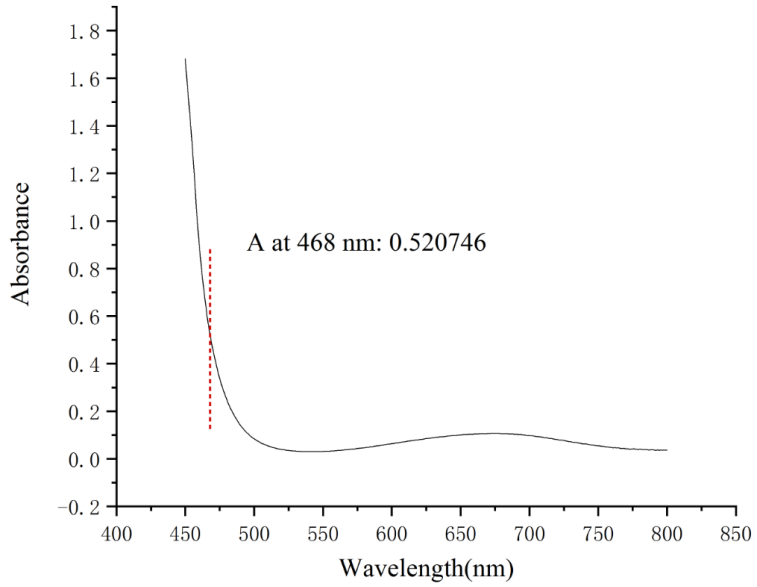
Where Φ is the quantum yield for the ferrioxalate actinometer at 468 nm,[17] t is the time and f is the fraction of light absorbed by the ferrioxalate actinometer solution.

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot \mathrm{t} \cdot f} = \frac{45.299 \cdot 10^{-8}\ mol}{(0.92) \cdot (10\mathrm{s}) \cdot (0.698523)}$$

$$= 7.048879 \cdot 10^{-8}\ einsterin/_{s}$$

e) Determination of fraction of light absorbed at 468 nm for the ferrioxalate solution

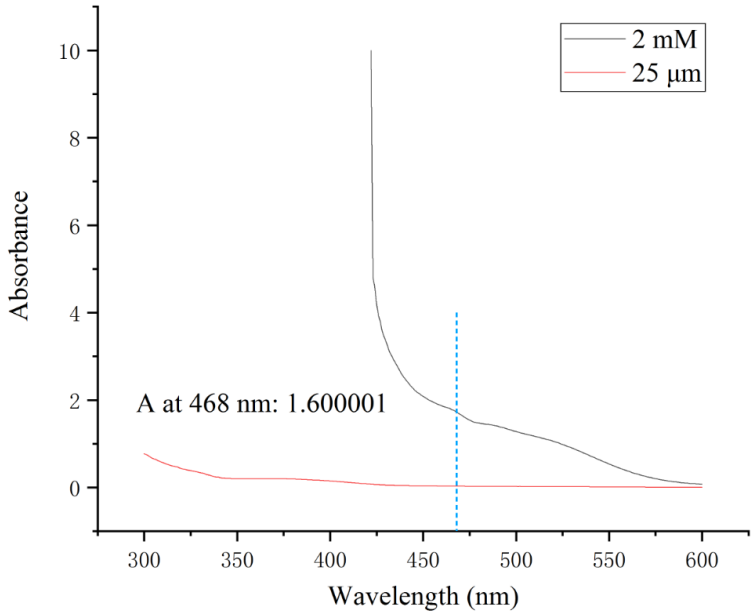
The absorbance at 468 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline was measured to be 0.520746.



Supplementary Figure S8 UV-vis absorbance spectra of ferrioxalate solution

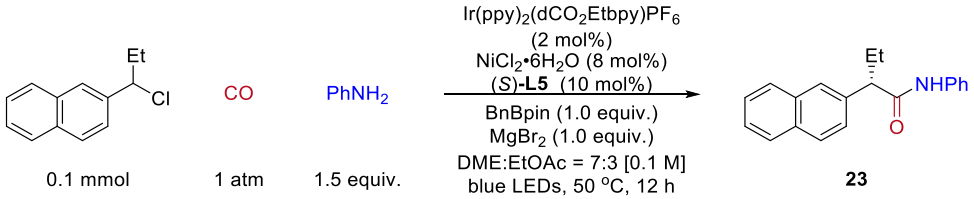
f) Absorbance of photocatalyst Ir(ppy)$_2$(dCO$_2$Etbpy)·(PF$_6$)

The absorbance of Ir(ppy)$_2$(dCO$_2$Etbpy)·(PF$_6$) in DME and EtOAc was measured at the reaction concentration of 2 mM or a dilute concentration of 25 μM (**Figure S10**). The absorbance at 468 nm for 2 mM is 1.600001.



Supplementary Figure S9 UV-vis absorbance spectra of $Ir(ppy)_2(dCO_2Etbpy)\cdot(PF_6)$ black line: 2 mM in DME and EtOAc, red line: 25 μM in DME and EtOAc.

g) Determination of quantum yield



To a flame-dried 20 mL test tube was charged with 2-(1-chloropropyl)naphthalene (20.4 mg, 0.1 mmol, 1.0 equiv.), $Ir(ppy)_2(dCO_2Etbpy)]PF_6$ (2.0 mg, 0.002 mmol, 2 mol%), (*S*)-**L5** (4.5 mg, 0.01 mmol, 10 mol%), $NiCl_2\bullet6H_2O$ (1.9 mg, 0.008 mmol, 8 mol%) and $MgBr_2$ (18.4 mg, 0.1 mmol, 1.0 equiv.). Then the test tube was capped by rubber plug with 3M tape. After it was evacuated and backfilled with a CO balloon three times, DME /EtOAc (7:3) (1 mL) was added via a syringe, followed by the addition of with aniline (13.7 μL, 0.15 mmol, 1.5 equiv.), BnBPin (22.3 μL, 0.1 mmol, 1.0 equiv.). Once added, the reaction mixture was then irradiated with a blue LED light (λ_{max} = 467 nm, 393 mW/cm^2, Kessil A360W E-SERIES TUNA Blue LED, at approximately 3 cm away from the light source) for 1800 seconds. After irradiation, the reaction mixtures were analyzed by GC with an internal standard. Provide the

desired product (19 % GC yield). The quantum yield (Φ) was calculated using the following equation:

The quantum yield (Φ) was calculated using the following equation:

$$\Phi = \frac{mol\ \text{product}}{\text{photon flux} \cdot \text{t} \cdot f}$$

Where t is the reaction time and f is the fraction of light absorbed by photocatalyst that was calculated using the following equation:

$$\text{f} = 1-10^{-A} = 1\text{-}10^{\text{-}1.600001} = 0.97488$$

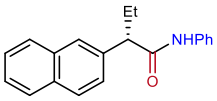
Where A is the absorbance at 468 nm of the photocatalyst solution (2 mM in DME and EtOAc) (**Figure S10**).

$$\Phi = \frac{mol\ \text{product}}{\text{photon flux} \cdot \text{t} \cdot f} = \frac{0.000019\ mol}{\left(7.048879 \cdot 10^{-8}\ einsterin/_{s}\right) \cdot (1800s) \cdot (0.97488)}$$

$$= 0.154$$

9. X-Ray Crystallographic Data

9.1 X-Ray Crystallographic Analysis of 23



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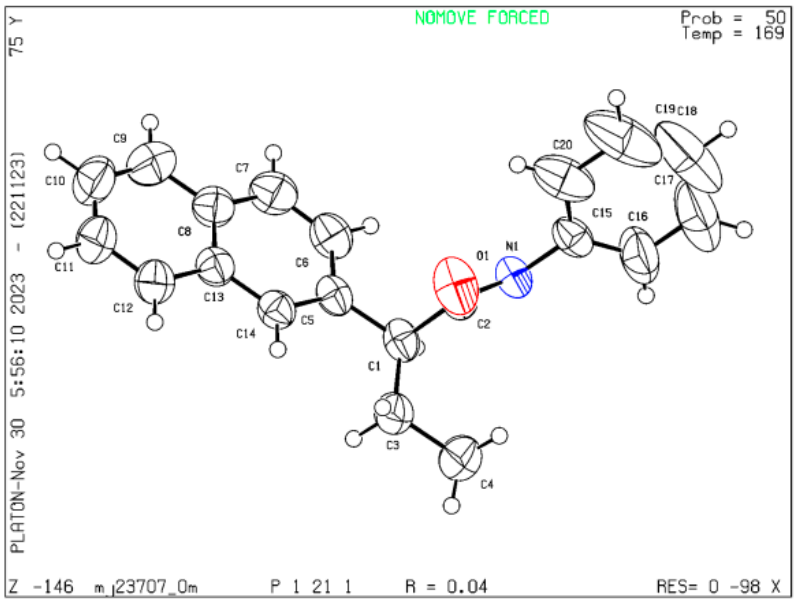


Supplementary Figure S10 X-ray structure of **23**

Supplementary Table S7 Crystal data and structure refinement for mj23707_0m.

Identification code	mj23707_0m
Empirical formula	$C_{20}H_{19}NO$
Formula weight	289.36
Temperature/K	169.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.87580(10)
b/Å	10.6693(3)
c/Å	15.5772(4)
α/°	90
β/°	98.1810(10)
γ/°	90

Volume/Å^3	802.10(3)
Z	2
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	0.363
F(000)	308.0
Crystal size/mm^3	0.17 × 0.17 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.986 to 109.86
Index ranges	-5 ≤ h ≤ 5, -12 ≤ k ≤ 13, -18 ≤ l ≤ 18
Reflections collected	13354
Independent reflections	3007 [R_{int} = 0.0420, R_{sigma} = 0.0351]
Data/restraints/parameters	3007/37/200
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.1040
Largest diff. peak/hole / e Å^{-3}	0.15/-0.19
Flack parameter	-0.09(13)

Supplementary Table S8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mj23707_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4348(3)	6894(2)	2669.9(14)	78.8(7)
N1	217(3)	7230.9(18)	3128.2(12)	50.6(5)
C1	333(4)	5988(2)	1825.3(15)	53.6(6)
C2	1828(4)	6745(2)	2579.6(15)	52.2(5)
C3	852(6)	6572(3)	970.3(18)	66.5(7)
C4	-308(7)	7889(3)	846(2)	83.6(9)
C5	1216(4)	4625(2)	1951.4(15)	51.4(5)
C6	198(6)	3925(3)	2606.6(19)	69.5(7)
C7	932(6)	2710(3)	2764(2)	76.1(8)

Supplementary Table S8 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for mj23707_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C8	2722(5)	2089(3)	2268.2(17)	63.6(6)
C9	3542(7)	815(3)	2402(2)	84.0(9)
C10	5196(8)	251(3)	1888(3)	87.5(9)
C11	6188(8)	925(3)	1231(2)	84.4(9)
C12	5479(6)	2147(3)	1086.1(19)	73.0(8)
C13	3724(5)	2768(2)	1601.9(15)	56.0(6)
C14	2960(5)	4039(2)	1464.3(15)	53.8(5)
C15	1160(5)	7948(3)	3879.1(15)	57.6(6)
C16	-208(10)	9005(4)	4047(3)	102.2(12)
C17	704(17)	9710(6)	4790(4)	147(2)
C18	2878(16)	9324(8)	5360(4)	160(3)
C19	4226(13)	8278(8)	5196(3)	158(2)
C20	3386(8)	7568(5)	4451(2)	109.3(14)

Supplementary Table S9 Anisotropic Displacement Parameters ($Å^2\times10^3$) for mj23707_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	32.4(7)	104.5(16)	99.7(14)	-34.5(13)	10.3(8)	-3.8(9)
N1	35.3(8)	64.1(12)	52.3(10)	-13.9(9)	6.0(7)	-1.2(8)
C1	37.8(10)	65.2(14)	58.2(13)	-15.4(11)	7.7(9)	4.3(10)
C2	33.7(10)	61.1(14)	61.8(13)	-10.1(11)	6.7(9)	2.5(9)
C3	68.7(15)	68.2(16)	62.5(14)	-5.1(12)	8.8(12)	14.4(13)
C4	92(2)	75.2(19)	81.0(18)	-2.5(17)	3.3(16)	21.0(17)
C5	40.9(11)	62.3(14)	50.7(12)	-13.0(10)	5.5(9)	-1.4(10)
C6	66.4(16)	82(2)	64.8(15)	-7.9(14)	25.2(13)	-0.1(14)

Supplementary Table S9 Anisotropic Displacement Parameters ($Å^2×10^3$) for mj23707_0m. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	78.8(19)	86(2)	67.1(16)	7.5(15)	23.6(14)	-6.4(16)
C8	59.8(13)	66.9(16)	62.3(15)	-1.2(13)	2.9(11)	-0.2(12)
C9	89(2)	76(2)	86.6(19)	15.0(17)	9.4(17)	0.7(17)
C10	94(2)	65.1(17)	101(2)	0.0(18)	5.9(19)	19.3(17)
C11	92(2)	72.7(19)	88(2)	-6.2(17)	12.2(17)	27.4(17)
C12	76.8(17)	74.1(18)	70.0(16)	-4.2(15)	16.9(13)	19.8(15)
C13	49.7(12)	62.7(14)	54.4(12)	-5.4(11)	2.9(10)	4.0(11)
C14	49.0(12)	61.6(14)	51.3(12)	-4.0(11)	9.0(9)	2.5(10)
C15	61.1(13)	67.2(14)	47.1(11)	-7.1(11)	16.3(10)	-18.5(11)
C16	131(3)	93(2)	90(2)	-33(2)	41(2)	7(2)
C17	214(6)	122(4)	124(4)	-60(3)	93(4)	-46(4)
C18	197(6)	210(6)	87(3)	-66(4)	68(3)	-129(5)
C19	147(4)	245(7)	72(3)	-18(3)	-20(3)	-75(5)
C20	98(2)	155(4)	65.6(18)	-8(2)	-22.6(17)	-17(2)

Supplementary Table S10 Bond Lengths for mj23707_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.227(3)	C8	C13	1.409(4)
N1	C2	1.344(3)	C9	C10	1.356(5)
N1	C15	1.418(3)	C10	C11	1.393(5)
C1	C2	1.523(3)	C11	C12	1.360(5)
C1	C3	1.524(4)	C12	C13	1.419(4)
C1	C5	1.522(3)	C13	C14	1.415(4)
C3	C4	1.517(4)	C15	C16	1.355(5)
C5	C6	1.411(4)	C15	C20	1.365(5)

Supplementary Table S10 Bond Lengths for mj23707_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C14	1.368(3)	C16	C17	1.399(7)
C6	C7	1.358(5)	C17	C18	1.346(11)
C7	C8	1.410(4)	C18	C19	1.338(11)
C8	C9	1.424(5)	C19	C20	1.398(7)

Supplementary Table S11 Bond Angles for mj23707_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N1	C15	125.61(19)	C10	C9	C8	121.0(3)
C2	C1	C3	109.7(2)	C9	C10	C11	120.2(3)
C5	C1	C2	108.16(18)	C12	C11	C10	120.7(3)
C5	C1	C3	115.14(19)	C11	C12	C13	120.9(3)
O1	C2	N1	122.9(2)	C8	C13	C12	118.5(2)
O1	C2	C1	121.3(2)	C8	C13	C14	119.5(2)
N1	C2	C1	115.85(17)	C14	C13	C12	121.9(2)
C4	C3	C1	112.7(2)	C5	C14	C13	121.6(2)
C6	C5	C1	118.5(2)	C16	C15	N1	119.9(3)
C14	C5	C1	123.5(2)	C16	C15	C20	119.3(3)
C14	C5	C6	118.1(2)	C20	C15	N1	120.8(3)
C7	C6	C5	121.7(3)	C15	C16	C17	120.0(5)
C6	C7	C8	121.1(3)	C18	C17	C16	120.6(6)
C7	C8	C9	123.4(3)	C19	C18	C17	119.5(5)
C13	C8	C7	118.0(3)	C18	C19	C20	121.1(6)
C13	C8	C9	118.6(3)	C15	C20	C19	119.5(5)

Supplementary Table S12 Torsion Angles for mj23707_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°

Supplementary Table S12 Torsion Angles for mj23707_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C15	C16	C17	179.6(3)	C7	C8	C13	C12	-178.7(3)
N1	C15	C20	C19	-178.4(4)	C7	C8	C13	C14	1.2(3)
C1	C5	C6	C7	-179.0(3)	C8	C9	C10	C11	1.8(5)
C1	C5	C14	C13	-179.9(2)	C8	C13	C14	C5	-1.4(3)
C2	N1	C15	C16	135.4(3)	C9	C8	C13	C12	0.8(4)
C2	N1	C15	C20	-46.5(4)	C9	C8	C13	C14	-179.3(3)
C2	C1	C3	C4	-63.1(3)	C9	C10	C11	C12	-1.1(5)
C2	C1	C5	C6	72.8(3)	C10	C11	C12	C13	0.2(5)
C2	C1	C5	C14	-106.9(2)	C11	C12	C13	C8	-0.1(4)
C3	C1	C2	O1	-58.9(3)	C11	C12	C13	C14	180.0(3)
C3	C1	C2	N1	120.9(2)	C12	C13	C14	C5	178.5(2)
C3	C1	C5	C6	-164.2(2)	C13	C8	C9	C10	-1.7(5)
C3	C1	C5	C14	16.1(3)	C14	C5	C6	C7	0.8(4)
C5	C1	C2	O1	67.4(3)	C15	N1	C2	O1	-1.2(4)
C5	C1	C2	N1	-112.8(2)	C15	N1	C2	C1	179.0(2)
C5	C1	C3	C4	174.7(2)	C15	C16	C17	C18	-2.4(7)
C5	C6	C7	C8	-0.9(5)	C16	C15	C20	C19	-0.4(6)
C6	C5	C14	C13	0.4(3)	C16	C17	C18	C19	2.2(8)
C6	C7	C8	C9	-179.6(3)	C17	C18	C19	C20	-1.1(9)
C6	C7	C8	C13	-0.1(4)	C18	C19	C20	C15	0.2(8)
C7	C8	C9	C10	177.8(3)	C20	C15	C16	C17	1.5(6)

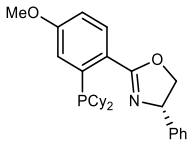
Supplementary Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mj23707_0m.

Atom	*x*	*y*	*z*	U(eq)
H1	-1576.36	7092.41	3011.28	61
H1A	-1699.82	6035.54	1854.03	64

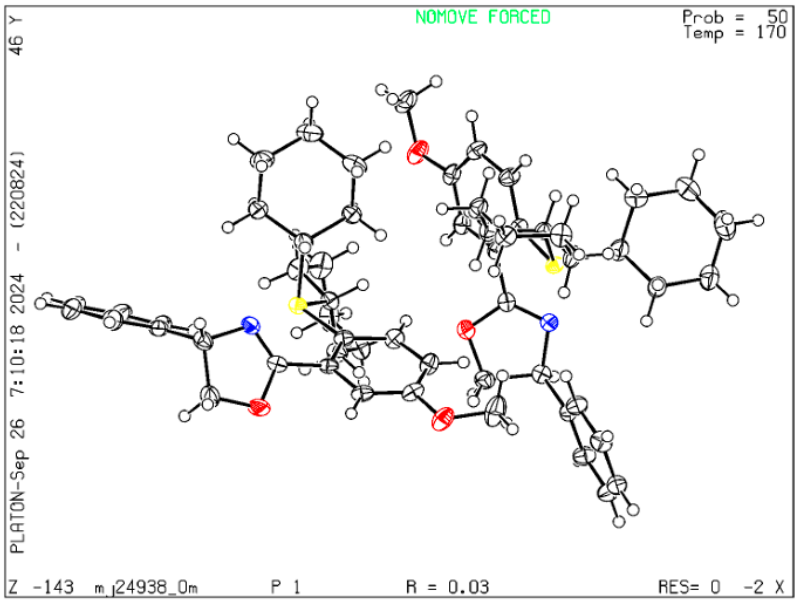
Supplementary Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mj23707_0m.

Atom	*x*	*y*	*z*	U(eq)
H3A	2871.96	6596.21	951.18	80
H3B	-5.59	6037.76	485.57	80
H4A	-49.56	8196.63	269.77	125
H4B	664.76	8442.29	1290.62	125
H4C	-2288.68	7878.94	895.88	125
H6	-1033.11	4313.78	2946.31	83
H7	228.67	2270.15	3216.34	91
H9	2920.88	353.67	2859.27	101
H10	5680.26	-606.69	1976.76	105
H11	7370.55	525.96	879.48	101
H12	6169.11	2591.61	633.58	88
H14	3674.84	4497.94	1022.76	65
H16	-1786.39	9268.12	3660.3	123
H17	-217.79	10467.89	4893.77	176
H18	3449.21	9790.2	5873.76	192
H19	5778.89	8013.28	5593.5	190
H20	4359.32	6825.7	4343.81	131

9.2 X-Ray Crystallographic Analysis of (*S*)-L5



CCDC: 2324906



Supplementary Figure S11 X-ray structure of (*S*)-**L5**

Supplementary Table S14 Crystal data and structure refinement for mj24938_0m.

Identification code	mj24938_0m
Empirical formula	$C_{28}H_{36}NO_2P$
Formula weight	449.55
Temperature/K	170.00
Crystal system	triclinic
Space group	P1
a/Å	9.8924(2)
b/Å	10.4608(2)
c/Å	12.6166(2)
α/°	76.9300(10)
β/°	76.7930(10)
γ/°	89.0140(10)
Volume/Å^3	1237.32(4)
Z	2
ρ_{calc}g/cm^3	1.207
μ/mm^{-1}	0.756
F(000)	484.0
Crystal size/mm^3	0.17 × 0.17 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.552 to 109.796
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	19858

Independent reflections	8447 [R_{int} = 0.0352, R_{sigma} = 0.0451]
Data/restraints/parameters	8447/3/579
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0831
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0845
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.18
Flack parameter	0.044(8)

Supplementary Table S15 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for mj24938_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P1	3202.4(6)	2065.4(6)	6850.4(5)	22.22(15)
O1	2229.4(19)	5333.4(19)	4505.7(16)	29.2(4)
O2	5379(2)	3069(2)	1862.9(16)	35.5(5)
N1	966(2)	3601(2)	5729.8(18)	25.1(5)
C1	3748(3)	2218(3)	5327(2)	23.4(6)
C2	4781(3)	1443(3)	4849(2)	28.3(6)
C3	5328(3)	1672(3)	3702(2)	28.1(6)
C4	4871(3)	2718(3)	2995(2)	26.5(6)
C5	3810(3)	3478(3)	3433(2)	25.8(6)
C6	3238(2)	3217(3)	4581(2)	22.2(5)
C7	2077(3)	4019(3)	4994(2)	21.8(5)
C8	1068(3)	5931(3)	5123(2)	28.5(6)
C9	96(3)	4758(3)	5829(2)	24.6(6)
C10	-499(3)	4844(3)	7022(2)	23.8(5)
C11	-1766(3)	5426(3)	7290(2)	31.4(6)
C12	-2330(3)	5537(3)	8377(3)	34.5(7)
C13	-1638(3)	5063(3)	9211(2)	32.9(6)
C14	-376(3)	4471(3)	8955(2)	32.8(7)
C15	194(3)	4369(3)	7868(2)	29.9(6)
C16	6497(3)	2319(4)	1404(3)	40.1(8)
C17	4797(3)	1427(3)	7309(2)	22.3(5)
C18	4507(3)	1208(3)	8587(2)	28.6(6)
C19	5802(3)	834(3)	9043(2)	33.0(6)
C20	6979(3)	1851(3)	8492(2)	31.4(6)
C21	7304(3)	2000(3)	7228(2)	31.4(6)

C22	6025(3)	2426(3)	6768(2)	28.3(6)
C23	1920(3)	657(3)	7248(2)	32.5(7)
C24	978(3)	550(3)	8409(3)	33.2(7)
C25	-163(4)	-523(4)	8690(3)	47.5(8)
C26	424(4)	-1810(4)	8544(4)	56.4(10)
C27	1296(4)	-1697(4)	7351(3)	51.7(9)
C28	2476(3)	-657(3)	7092(3)	41.9(8)
P1A	6808.1(6)	7779.0(6)	3185.6(5)	21.76(15)
O1A	7804(2)	9946(2)	5458.2(18)	34.9(5)
O2A	4360(2)	6669(2)	8167.1(16)	35.8(5)
N1A	8949(2)	8646(2)	4364.8(19)	26.5(5)
C1A	6055(3)	7373(3)	4706(2)	23.1(6)
C2A	4942(3)	6470(3)	5216(2)	27.5(6)
C3A	4354(3)	6177(3)	6363(2)	29.7(6)
C4A	4853(3)	6849(3)	7034(2)	28.2(6)
C5A	5941(3)	7777(3)	6559(2)	26.2(6)
C6A	6562(3)	8007(3)	5422(2)	21.8(5)
C7A	7843(3)	8864(3)	5021(2)	22.5(5)
C8A	9160(3)	10594(3)	5002(3)	35.2(7)
C9A	9964(3)	9727(3)	4248(2)	28.0(6)
C10A	10506(3)	10456(3)	3044(2)	26.6(6)
C11A	11813(3)	11085(3)	2710(3)	33.1(7)
C12A	12319(3)	11759(3)	1617(3)	38.1(7)
C13A	11524(3)	11820(3)	833(3)	36.9(7)
C14A	10219(3)	11202(3)	1157(3)	35.0(7)
C15A	9712(3)	10521(3)	2249(2)	29.5(6)
C16A	3434(4)	5553(4)	8723(3)	50.3(9)
C17A	5363(3)	7320(3)	2607(2)	23.8(5)
C18A	5896(3)	7458(3)	1335(2)	31.8(6)
C19A	4740(3)	7165(4)	786(3)	40.7(8)
C20A	3510(3)	8028(4)	1026(3)	39.4(8)
C21A	2975(3)	7896(3)	2276(3)	30.8(6)
C22A	4132(3)	8212(3)	2822(3)	29.5(6)
C23A	8039(3)	6400(3)	3111(2)	24.5(5)
C24A	9228(3)	6697(3)	2060(3)	32.8(6)
C25A	10278(3)	5603(3)	2086(3)	41.3(8)
C26A	9589(3)	4260(3)	2253(3)	40.3(7)
C27A	8435(3)	3971(3)	3309(3)	34.3(7)
C28A	7357(3)	5038(3)	3287(2)	27.3(6)

Supplementary Table S16 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mj24938_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}
P1	23.2(3)	25.8(4)	17.1(3)	-5.3(3)	-3.2(2)	2.9(3)
O1	30.0(10)	22.5(10)	29.8(10)	-0.5(8)	-1.8(8)	1.3(8)
O2	34.5(11)	50.3(14)	18.5(10)	-7.8(9)	0.4(8)	-3.1(10)
N1	26.3(11)	22.4(12)	24.3(11)	-4.9(9)	-1.9(9)	1.1(9)
C1	22.7(13)	26.7(15)	19.4(13)	-4.7(11)	-2.7(10)	0.9(10)
C2	29.6(14)	33.2(16)	21.8(13)	-6.4(11)	-5.5(11)	7.5(12)
C3	24.7(13)	36.8(16)	24.0(14)	-12.3(12)	-2.8(10)	2.1(11)
C4	25.0(13)	37.1(16)	18.0(13)	-9.7(12)	-2.4(10)	-7.7(12)
C5	26.3(13)	29.3(15)	21.0(13)	-3.0(11)	-6.3(10)	-3.7(11)
C6	19.9(12)	25.9(14)	20.6(12)	-4.6(10)	-4.7(10)	-2.4(10)
C7	23.3(12)	23.7(14)	19.1(12)	-1.4(10)	-9.3(10)	-0.7(10)
C8	32.2(14)	24.9(15)	27.3(14)	-3.7(11)	-7.0(11)	5.1(11)
C9	24.9(13)	25.9(15)	24.8(13)	-5.6(11)	-9.5(10)	2.4(11)
C10	22.6(12)	21.9(14)	25.6(14)	-4.4(11)	-4.3(10)	-0.3(10)
C11	30.6(15)	32.8(16)	32.6(15)	-8.1(12)	-10.4(12)	8.9(12)
C12	28.0(14)	35.9(17)	39.0(17)	-12.6(13)	-3.0(12)	6.3(12)
C13	37.7(16)	29.7(16)	29.1(15)	-9.4(12)	-0.7(12)	-2.1(12)
C14	37.6(16)	31.7(17)	30.4(15)	-5.8(12)	-12.2(12)	3.9(13)
C15	26.3(14)	33.1(16)	31.5(15)	-8.2(12)	-8.5(12)	5.4(12)
C16	38.3(16)	54(2)	26.1(15)	-18.0(14)	6.0(12)	-6.4(14)
C17	23.7(12)	22.8(14)	19.5(12)	-4.1(10)	-3.8(10)	2.1(10)
C18	25.8(13)	35.6(17)	20.2(13)	0.3(11)	-3.6(10)	-1.1(11)
C19	33.9(15)	38.9(17)	27.3(15)	-2.7(13)	-14.4(12)	0.3(13)
C20	29.7(14)	39.4(17)	29.1(15)	-13.3(13)	-9.3(12)	-1.2(12)
C21	25.1(13)	39.4(17)	30.2(15)	-13.3(13)	-1.4(11)	-6.3(12)
C22	30.5(14)	28.4(15)	23.1(14)	-4.1(12)	-1.5(11)	-5.6(12)
C23	32.0(15)	38.2(18)	27.6(15)	-11.6(13)	-2.7(12)	-7.0(12)
C24	30.6(15)	34.3(17)	32.4(16)	-10.0(13)	0.3(12)	-5.7(12)
C25	38.5(17)	46(2)	52(2)	-12.3(16)	4.4(15)	-13.2(15)
C26	55(2)	41(2)	66(3)	-2.3(18)	-8.5(19)	-13.4(17)
C27	61(2)	33.1(19)	62(2)	-17.0(17)	-8.8(19)	-4.1(16)
C28	42.6(18)	37.3(19)	43.8(18)	-11.9(15)	-3.4(14)	3.1(14)
P1A	22.8(3)	22.3(3)	22.3(3)	-7.6(3)	-7.2(2)	0.2(2)
O1A	31.5(10)	31.4(12)	47.3(13)	-25.0(10)	-3.9(9)	-1.9(8)

Supplementary Table S16 Anisotropic Displacement Parameters ($Å^2×10^3$) for mj24938_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}
O2A	30.6(10)	52.9(14)	23.1(11)	-10.8(10)	-2.1(8)	-2.8(9)
N1A	26.4(12)	20.9(12)	32.6(13)	-8.2(10)	-5.9(9)	0.3(9)
C1A	21.7(12)	26.2(14)	24.2(13)	-8.9(11)	-8.2(10)	6.1(10)
C2A	26.0(13)	33.1(16)	26.7(14)	-10.5(12)	-8.8(11)	-1.3(11)
C3A	23.6(13)	36.4(17)	28.0(14)	-6.2(12)	-4.2(11)	-3.4(11)
C4A	24.0(13)	38.9(17)	22.5(14)	-9.8(12)	-5.1(11)	7.9(12)
C5A	24.5(13)	32.1(16)	27.8(14)	-15.0(12)	-10.1(11)	7.5(11)
C6A	20.3(12)	23.1(14)	25.9(13)	-10.0(11)	-8.9(10)	6.3(10)
C7A	26.4(13)	21.8(14)	24.2(13)	-8.8(11)	-12.6(10)	5.7(10)
C8A	40.9(16)	31.0(17)	33.9(16)	-11.1(13)	-4.8(13)	-9.6(13)
C9A	26.8(14)	24.5(15)	36.1(15)	-9.1(12)	-11.7(12)	-1.2(11)
C10A	22.0(13)	24.3(14)	35.4(15)	-13.1(12)	-4.5(11)	2.5(10)
C11A	22.9(13)	33.8(17)	45.5(18)	-13.9(14)	-8.4(12)	-0.7(12)
C12A	22.1(14)	38.8(18)	50.7(19)	-14.0(15)	0.5(13)	-1.4(12)
C13A	31.7(15)	37.5(18)	36.2(16)	-13.2(14)	7.9(12)	-1.3(13)
C14A	32.1(16)	42.7(19)	31.7(16)	-15.4(14)	-3.3(12)	1.2(13)
C15A	23.8(13)	33.0(16)	33.6(15)	-14.6(13)	-3.1(11)	-2.8(11)
C16A	48(2)	69(3)	27.4(16)	-3.6(16)	-1.9(14)	-18.3(18)
C17A	26.9(13)	22.9(14)	23.4(13)	-5.7(11)	-8.7(10)	-0.5(10)
C18A	32.0(15)	42.2(18)	21.9(14)	-6.4(12)	-8.4(11)	0.2(12)
C19A	45.0(18)	55(2)	25.1(15)	-8.6(14)	-15.0(13)	-5.6(15)
C20A	37.5(16)	46.2(19)	32.0(16)	7.6(14)	-18.3(13)	-10.6(14)
C21A	27.2(14)	28.0(15)	37.7(17)	-2.4(13)	-13.5(12)	-0.8(11)
C22A	28.5(14)	28.3(15)	34.9(15)	-10.6(12)	-10.2(12)	1.0(11)
C23A	24.3(13)	25.2(14)	26.8(13)	-9.5(11)	-8.1(10)	0.3(10)
C24A	27.7(14)	31.4(16)	38.6(16)	-13.9(13)	-0.1(12)	-2.2(12)
C25A	26.8(15)	43(2)	57(2)	-24.0(16)	-3.1(14)	3.6(13)
C26A	35.9(16)	38.0(18)	56(2)	-25.8(16)	-13.8(14)	10.4(13)
C27A	41.6(16)	27.1(16)	42.0(17)	-14.8(13)	-19.0(14)	5.6(12)
C28A	28.5(14)	26.4(15)	28.7(14)	-9.4(11)	-6.8(11)	-0.6(11)

Supplementary Table S17 Bond Lengths for mj24938_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.845(3)	P1A	C1A	1.846(3)

Supplementary Table S17 Bond Lengths for mj24938_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C17	1.864(3)	P1A	C17A	1.862(3)
P1	C23	1.863(3)	P1A	C23A	1.877(3)
O1	C7	1.369(3)	O1A	C7A	1.363(3)
O1	C8	1.450(3)	O1A	C8A	1.447(3)
O2	C4	1.367(3)	O2A	C4A	1.372(3)
O2	C16	1.435(4)	O2A	C16A	1.438(4)
N1	C7	1.276(3)	N1A	C7A	1.264(4)
N1	C9	1.485(3)	N1A	C9A	1.485(3)
C1	C2	1.405(4)	C1A	C2A	1.399(4)
C1	C6	1.410(4)	C1A	C6A	1.413(4)
C2	C3	1.391(4)	C2A	C3A	1.395(4)
C3	C4	1.387(4)	C3A	C4A	1.388(4)
C4	C5	1.394(4)	C4A	C5A	1.392(4)
C5	C6	1.394(4)	C5A	C6A	1.392(4)
C6	C7	1.478(4)	C6A	C7A	1.485(4)
C8	C9	1.542(4)	C8A	C9A	1.543(4)
C9	C10	1.508(4)	C9A	C10A	1.515(4)
C10	C11	1.389(4)	C10A	C11A	1.392(4)
C10	C15	1.393(4)	C10A	C15A	1.397(4)
C11	C12	1.387(4)	C11A	C12A	1.381(5)
C12	C13	1.380(4)	C12A	C13A	1.387(5)
C13	C14	1.387(4)	C13A	C14A	1.386(4)
C14	C15	1.386(4)	C14A	C15A	1.382(4)
C17	C18	1.536(3)	C17A	C18A	1.546(4)
C17	C22	1.541(3)	C17A	C22A	1.533(4)
C18	C19	1.530(4)	C18A	C19A	1.533(4)
C19	C20	1.520(4)	C19A	C20A	1.519(5)
C20	C21	1.525(4)	C20A	C21A	1.520(4)
C21	C22	1.528(4)	C21A	C22A	1.540(4)
C23	C24	1.527(4)	C23A	C24A	1.533(4)
C23	C28	1.509(5)	C23A	C28A	1.535(4)
C24	C25	1.530(4)	C24A	C25A	1.533(4)
C25	C26	1.491(6)	C25A	C26A	1.522(5)
C26	C27	1.534(5)	C26A	C27A	1.518(5)
C27	C28	1.536(5)	C27A	C28A	1.530(4)

Supplementary Table S18 Bond Angles for mj24938_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C17	101.40(12)	C1A	P1A	C17A	102.69(12)
C1	P1	C23	100.47(12)	C1A	P1A	C23A	98.83(12)
C23	P1	C17	106.88(13)	C17A	P1A	C23A	104.57(12)
C7	O1	C8	105.3(2)	C7A	O1A	C8A	105.8(2)
C4	O2	C16	116.4(2)	C4A	O2A	C16A	117.1(2)
C7	N1	C9	106.7(2)	C7A	N1A	C9A	107.0(2)
C2	C1	P1	122.3(2)	C2A	C1A	P1A	123.2(2)
C2	C1	C6	116.7(2)	C2A	C1A	C6A	116.1(2)
C6	C1	P1	120.7(2)	C6A	C1A	P1A	120.7(2)
C3	C2	C1	122.4(3)	C3A	C2A	C1A	123.4(2)
C4	C3	C2	119.5(3)	C4A	C3A	C2A	118.8(3)
O2	C4	C3	124.5(3)	O2A	C4A	C3A	124.8(3)
O2	C4	C5	115.8(3)	O2A	C4A	C5A	115.4(2)
C3	C4	C5	119.7(2)	C3A	C4A	C5A	119.8(2)
C4	C5	C6	120.4(2)	C4A	C5A	C6A	120.5(2)
C1	C6	C7	120.9(2)	C1A	C6A	C7A	121.8(2)
C5	C6	C1	121.1(2)	C5A	C6A	C1A	121.3(2)
C5	C6	C7	118.0(2)	C5A	C6A	C7A	116.7(2)
O1	C7	C6	115.2(2)	O1A	C7A	C6A	115.0(2)
N1	C7	O1	118.3(2)	N1A	C7A	O1A	118.8(2)
N1	C7	C6	126.5(2)	N1A	C7A	C6A	126.1(2)
O1	C8	C9	104.2(2)	O1A	C8A	C9A	104.6(2)
N1	C9	C8	103.7(2)	N1A	C9A	C8A	103.7(2)
N1	C9	C10	113.4(2)	N1A	C9A	C10A	112.7(2)
C10	C9	C8	114.3(2)	C10A	C9A	C8A	113.7(2)
C11	C10	C9	119.5(2)	C11A	C10A	C9A	120.1(2)
C11	C10	C15	118.6(3)	C11A	C10A	C15A	118.6(3)
C15	C10	C9	121.9(2)	C15A	C10A	C9A	121.3(2)
C12	C11	C10	120.9(3)	C12A	C11A	C10A	120.8(3)
C13	C12	C11	120.2(3)	C11A	C12A	C13A	120.2(3)
C12	C13	C14	119.6(3)	C14A	C13A	C12A	119.5(3)
C15	C14	C13	120.3(3)	C15A	C14A	C13A	120.4(3)
C14	C15	C10	120.5(3)	C14A	C15A	C10A	120.4(3)
C18	C17	P1	108.35(17)	C18A	C17A	P1A	108.77(17)
C18	C17	C22	109.5(2)	C22A	C17A	P1A	110.79(18)
C22	C17	P1	110.23(18)	C22A	C17A	C18A	109.4(2)
C19	C18	C17	112.8(2)	C19A	C18A	C17A	111.8(2)
C20	C19	C18	111.2(2)	C20A	C19A	C18A	111.3(3)

Supplementary Table S18 Bond Angles for mj24938_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	C20	C21	109.5(2)	C19A	C20A	C21A	111.0(2)
C20	C21	C22	110.8(2)	C20A	C21A	C22A	111.4(2)
C21	C22	C17	111.4(2)	C17A	C22A	C21A	110.9(2)
C24	C23	P1	112.2(2)	C24A	C23A	P1A	112.8(2)
C28	C23	P1	116.9(2)	C24A	C23A	C28A	111.3(2)
C28	C23	C24	111.7(3)	C28A	C23A	P1A	115.34(18)
C23	C24	C25	112.2(3)	C25A	C24A	C23A	111.1(3)
C26	C25	C24	111.6(3)	C26A	C25A	C24A	112.0(2)
C25	C26	C27	110.9(3)	C27A	C26A	C25A	110.7(3)
C26	C27	C28	109.9(3)	C26A	C27A	C28A	111.4(3)
C23	C28	C27	111.4(3)	C27A	C28A	C23A	111.2(2)

Supplementary Table S19 Torsion Angles for mj24938_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P1	C1	C2	C3	-171.1(2)	P1A	C1A	C2A	C3A	-178.9(2)
P1	C1	C6	C5	169.3(2)	P1A	C1A	C6A	C5A	175.5(2)
P1	C1	C6	C7	-10.7(3)	P1A	C1A	C6A	C7A	-9.5(3)
P1	C17	C18	C19	-173.4(2)	P1A	C17A	C18A	C19A	-177.0(2)
P1	C17	C22	C21	173.67(19)	P1A	C17A	C22A	C21A	176.2(2)
P1	C23	C24	C25	174.5(2)	P1A	C23A	C24A	C25A	174.77(19)
P1	C23	C28	C27	-174.9(2)	P1A	C23A	C28A	C27A	-175.22(19)
O1	C8	C9	N1	12.5(3)	O1A	C8A	C9A	N1A	-0.2(3)
O1	C8	C9	C10	136.6(2)	O1A	C8A	C9A	C10A	122.5(2)
O2	C4	C5	C6	-178.8(2)	O2A	C4A	C5A	C6A	177.5(2)
N1	C9	C10	C11	-150.0(2)	N1A	C9A	C10A	C11A	-153.1(3)
N1	C9	C10	C15	30.9(3)	N1A	C9A	C10A	C15A	27.3(4)
C1	P1	C17	C18	-178.67(19)	C1A	P1A	C17A	C18A	-173.63(19)
C1	P1	C17	C22	61.6(2)	C1A	P1A	C17A	C22A	66.1(2)
C1	P1	C23	C24	-163.2(2)	C1A	P1A	C23A	C24A	-158.2(2)
C1	P1	C23	C28	65.8(3)	C1A	P1A	C23A	C28A	72.3(2)
C1	C2	C3	C4	1.4(4)	C1A	C2A	C3A	C4A	2.8(4)
C1	C6	C7	O1	137.8(2)	C1A	C6A	C7A	O1A	142.6(2)
C1	C6	C7	N1	-43.6(4)	C1A	C6A	C7A	N1A	-40.5(4)
C2	C1	C6	C5	-4.7(4)	C2A	C1A	C6A	C5A	-2.6(4)
C2	C1	C6	C7	175.3(2)	C2A	C1A	C6A	C7A	172.5(2)
C2	C3	C4	O2	177.0(3)	C2A	C3A	C4A	O2A	179.2(3)

Supplementary Table S19 Torsion Angles for mj24938_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C3	C4	C5	-3.9(4)	C2A	C3A	C4A	C5A	-1.3(4)
C3	C4	C5	C6	2.0(4)	C3A	C4A	C5A	C6A	-2.0(4)
C4	C5	C6	C1	2.4(4)	C4A	C5A	C6A	C1A	4.1(4)
C4	C5	C6	C7	-177.6(2)	C4A	C5A	C6A	C7A	-171.2(2)
C5	C6	C7	O1	-42.2(3)	C5A	C6A	C7A	O1A	-42.1(3)
C5	C6	C7	N1	136.4(3)	C5A	C6A	C7A	N1A	134.8(3)
C6	C1	C2	C3	2.8(4)	C6A	C1A	C2A	C3A	-0.8(4)
C7	O1	C8	C9	-12.1(3)	C7A	O1A	C8A	C9A	0.1(3)
C7	N1	C9	C8	-8.5(3)	C7A	N1A	C9A	C8A	0.3(3)
C7	N1	C9	C10	-133.1(2)	C7A	N1A	C9A	C10A	-123.0(3)
C8	O1	C7	N1	7.7(3)	C8A	O1A	C7A	N1A	0.2(3)
C8	O1	C7	C6	-173.6(2)	C8A	O1A	C7A	C6A	177.3(2)
C8	C9	C10	C11	91.3(3)	C8A	C9A	C10A	C11A	89.2(3)
C8	C9	C10	C15	-87.8(3)	C8A	C9A	C10A	C15A	-90.4(3)
C9	N1	C7	O1	0.9(3)	C9A	N1A	C7A	O1A	-0.3(3)
C9	N1	C7	C6	-177.7(2)	C9A	N1A	C7A	C6A	-177.1(2)
C9	C10	C11	C12	-179.0(3)	C9A	C10A	C11A	C12A	-179.7(3)
C9	C10	C15	C14	179.5(3)	C9A	C10A	C15A	C14A	179.4(3)
C10	C11	C12	C13	-0.2(5)	C10A	C11A	C12A	C13A	0.1(5)
C11	C10	C15	C14	0.4(4)	C11A	C10A	C15A	C14A	-0.3(4)
C11	C12	C13	C14	-0.2(5)	C11A	C12A	C13A	C14A	0.1(5)
C12	C13	C14	C15	0.7(5)	C12A	C13A	C14A	C15A	-0.4(5)
C13	C14	C15	C10	-0.8(4)	C13A	C14A	C15A	C10A	0.5(5)
C15	C10	C11	C12	0.1(4)	C15A	C10A	C11A	C12A	0.0(4)
C16	O2	C4	C3	-2.5(4)	C16A	O2A	C4A	C3A	11.3(4)
C16	O2	C4	C5	178.4(2)	C16A	O2A	C4A	C5A	-168.2(3)
C17	P1	C1	C2	26.2(3)	C17A	P1A	C1A	C2A	22.5(3)
C17	P1	C1	C6	-147.5(2)	C17A	P1A	C1A	C6A	-155.4(2)
C17	P1	C23	C24	91.3(2)	C17A	P1A	C23A	C24A	96.1(2)
C17	P1	C23	C28	-39.6(3)	C17A	P1A	C23A	C28A	-33.4(2)
C17	C18	C19	C20	55.6(3)	C17A	C18A	C19A	C20A	55.7(3)
C18	C17	C22	C21	54.6(3)	C18A	C17A	C22A	C21A	56.3(3)
C18	C19	C20	C21	-57.2(3)	C18A	C19A	C20A	C21A	-55.2(3)
C19	C20	C21	C22	59.2(3)	C19A	C20A	C21A	C22A	56.2(3)
C20	C21	C22	C17	-58.8(3)	C20A	C21A	C22A	C17A	-57.4(3)
C22	C17	C18	C19	-53.2(3)	C22A	C17A	C18A	C19A	-55.9(3)
C23	P1	C1	C2	-83.6(2)	C23A	P1A	C1A	C2A	-84.7(2)
C23	P1	C1	C6	102.8(2)	C23A	P1A	C1A	C6A	97.4(2)

Supplementary Table S19 Torsion Angles for mj24938_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C23	P1	C17	C18	-73.9(2)	C23A	P1A	C17A	C18A	-70.8(2)
C23	P1	C17	C22	166.32(18)	C23A	P1A	C17A	C22A	168.87(19)
C23	C24	C25	C26	53.6(4)	C23A	C24A	C25A	C26A	54.8(4)
C24	C23	C28	C27	53.9(4)	C24A	C23A	C28A	C27A	54.5(3)
C24	C25	C26	C27	-56.7(4)	C24A	C25A	C26A	C27A	-56.1(4)
C25	C26	C27	C28	58.2(4)	C25A	C26A	C27A	C28A	56.5(3)
C26	C27	C28	C23	-56.7(4)	C26A	C27A	C28A	C23A	-56.1(3)
C28	C23	C24	C25	-51.9(4)	C28A	C23A	C24A	C25A	-53.7(3)

Supplementary Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mj24938_0m.

Atom	*x*	*y*	*z*	U(eq)
H2	5117.33	736.51	5327.02	34
H3	6010.57	1116.85	3405.19	34
H5	3474.43	4176.62	2947.07	31
H8A	594.58	6530.38	4607.19	34
H8B	1381.44	6430.11	5607.59	34
H9	-691.1	4703.04	5463.48	30
H11	-2251.68	5753.48	6721.96	38
H12	-3196.33	5940.54	8547.21	41
H13	-2022.02	5140.84	9954.34	39
H14	99.52	4133.59	9528.24	39
H15	1064.46	3972.21	7699.32	36
H16A	6773.46	2649.88	590.96	60
H16B	6191.26	1393.6	1574.79	60
H16C	7290.25	2400.12	1731.31	60
H17	5029.44	575.74	7088.33	27
H18A	4143.79	2021.92	8805.88	34
H18B	3781.54	502.6	8930.87	34
H19A	5571.95	759.33	9861.11	40
H19B	6105.6	-32.34	8904.74	40
H20A	7815.95	1571.51	8777.9	38
H20B	6708.01	2704.62	8676.03	38
H21A	7610.68	1153.39	7046.9	38
H21B	8071.14	2662.51	6869.54	38
H22A	6258.3	2512.72	5948.56	34

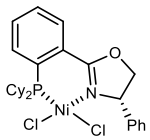
Supplementary Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mj24938_0m.

Atom	*x*	*y*	*z*	U(eq)
H22B	5750.91	3295.59	6914.45	34
H23	1290.09	889.25	6721.28	39
H24A	544	1403.75	8446.58	40
H24B	1546.21	356.03	8974.66	40
H25A	-689.25	-614.21	9472.74	57
H25B	-818.12	-262.59	8197.5	57
H26A	-342.89	-2471.21	8700.22	68
H26B	1011.39	-2111.76	9084.28	68
H27A	699.11	-1446.79	6810.6	62
H27B	1691.81	-2556.23	7275.71	62
H28A	3115.86	-949.69	7590.98	50
H28B	3009.38	-564.69	6310.48	50
H2A	4566.34	6034.38	4758.4	33
H3A	3624.36	5528.69	6679.64	36
H5A	6262.17	8257.14	7013.96	31
H8AA	9628.21	10645.82	5606.55	42
H8AB	9083.42	11493.2	4561.44	42
H9A	10766.22	9351.79	4559.33	34
H11A	12364.47	11049.7	3240.81	40
H12A	13213.76	12182.31	1400.74	46
H13A	11872.35	12281.46	80.8	44
H14A	9668.43	11245.98	624.16	42
H15A	8819.2	10094.76	2460.99	35
H16D	2557.07	5676.92	8482.1	75
H16E	3251.71	5462.67	9534.13	75
H16F	3861.09	4757.21	8533.2	75
H17A	5051.57	6386.93	2969.9	29
H18C	6278.65	8362.73	985.07	38
H18D	6657.26	6845.7	1199.64	38
H19C	5108.76	7315.54	-31.96	49
H19D	4430.05	6230.66	1073.25	49
H20C	2756.4	7774.29	707.17	47
H20D	3793.09	8955.86	661.27	47
H21C	2603.36	6988.5	2628.8	37
H21D	2205.75	8501.13	2407.27	37
H22D	4452.81	9141.23	2513.07	35
H22C	3759.25	8090.38	3637.46	35

Supplementary Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mj24938_0m.

Atom	*x*	*y*	*z*	U(eq)
H23A	8491.34	6339.88	3752.64	29
H24C	8843.03	6786.07	1389.12	39
H24D	9703.82	7541.1	2008.82	39
H25C	10994.04	5788.94	1374.59	50
H25D	10749.14	5592.9	2701.08	50
H26D	9201.6	4236.12	1600.06	48
H26C	10291.3	3577.07	2307	48
H27C	8837.62	3912.32	3967.03	41
H27D	7973.37	3112.1	3383.24	41
H28D	6647.15	4845.62	4001.9	33
H28C	6883.83	5034.6	2675.74	33

9.3 X-Ray Crystallographic Analysis of (L4)$NiCl_2$ (A)



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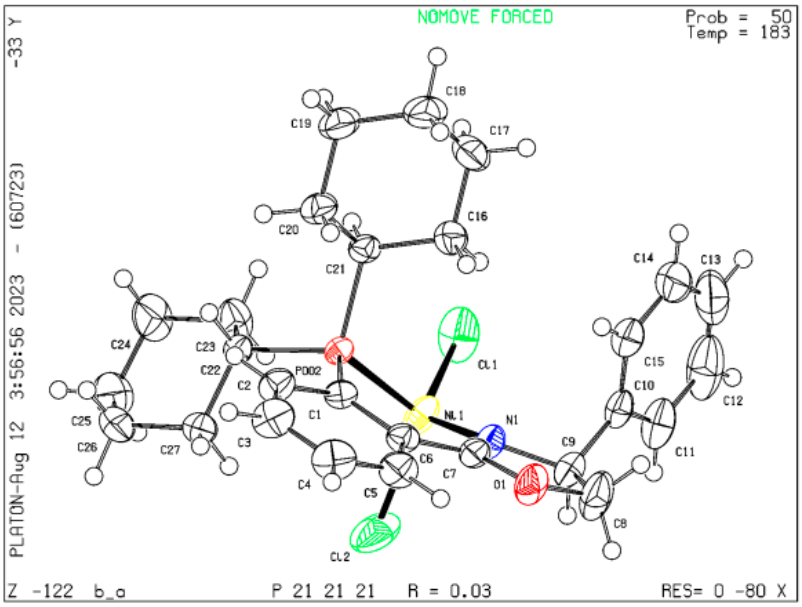


Supplementary Figure S12 X-ray structure of (**L4**)$NiCl_2$ (A)

Supplementary Table S21 Crystal data and structure refinement for B_a.

Identification code	B_a
Empirical formula	$C_{27}H_{34}Cl_2NNiOP$
Formula weight	549.13
Temperature/K	183.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.8147(5)
b/Å	15.3503(9)
c/Å	19.9299(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2696.7(3)
Z	4
ρ_{calc}g/cm^3	1.353
μ/mm^{-1}	3.567
F(000)	1152.0
Crystal size/mm^3	0.12 × 0.08 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.268 to 136.522
Index ranges	$-10 \leq h \leq 10$, $-18 \leq k \leq 14$, $-23 \leq l \leq 24$
Reflections collected	17441
Independent reflections	4818 [R_{int} = 0.0273, R_{sigma} = 0.0318]
Data/restraints/parameters	4818/0/299
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0284, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.0285, wR_2 = 0.0732
Largest diff. peak/hole / e Å^{-3}	0.55/-0.48
Flack parameter	0.042(19)

Supplementary Table S22 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for B_a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ni1	3859.0(6)	4593.0(3)	3233.6(3)	37.84(15)
P002	4664.0(7)	5982.7(4)	3103.7(3)	24.69(14)
Cl1	5626.4(11)	3896.7(6)	3795.1(5)	63.5(3)
Cl2	2839.7(12)	4135.6(8)	2273.9(6)	75.2(3)
O1	-224(2)	5660.4(16)	3887.4(12)	46.2(5)
N1	1949(3)	4968.4(16)	3680.5(12)	33.8(5)
C21	5733(3)	6405.1(18)	3831.4(14)	29.2(5)
C6	1556(3)	6475.6(18)	3246.6(14)	30.1(5)
C27	5063(3)	6103(2)	1706.8(15)	42.5(7)
C1	3013(3)	6694.9(17)	3011.8(13)	28.2(5)
C9	1024(4)	4323(2)	4060.5(16)	40.5(7)
C7	1172(3)	5663.6(19)	3605.5(14)	32.2(6)
C22	5904(3)	6184.0(18)	2376.2(13)	29.6(5)
C5	360(3)	7060(2)	3144.8(16)	41.7(7)
C16	4998(3)	6144(2)	4496.2(14)	38.6(7)
C23	7220(4)	5538(3)	2397.8(16)	47.7(8)
C10	1835(3)	3990(2)	4672.7(15)	37.1(6)
C11	2003(4)	3105(2)	4779(2)	54.0(9)
C20	6030(4)	7386(2)	3810.5(16)	41.0(7)
C4	579(4)	7838(2)	2812.2(18)	48.0(8)
C3	1993(4)	8047(2)	2576.3(19)	46.9(8)
C26	6151(5)	6253(3)	1121.2(16)	57.1(9)
C15	2395(4)	4566(3)	5149.6(17)	49.1(8)
C2	3201(3)	7484.9(19)	2679.8(16)	37.4(6)
C8	-427(4)	4832(3)	4212(2)	61.3(11)
C13	3292(5)	3382(5)	5808(3)	83.7(17)
C24	8304(4)	5680(3)	1807.1(19)	62.6(10)

Supplementary Table S22 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for B_a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C19	7011(4)	7665(3)	4401.1(18)	54.3(9)
C17	5964(4)	6442(3)	5088.3(16)	55.4(9)
C25	7475(5)	5629(3)	1142.1(19)	66.5(11)
C18	6295(5)	7403(3)	5064.0(18)	61.0(11)
C14	3130(5)	4255(4)	5713(2)	72.0(14)
C12	2735(6)	2806(4)	5354(3)	81.3(16)

Supplementary Table S23 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for B_a. 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}
Ni1	30.9(2)	24.7(2)	57.9(3)	-2.2(2)	11.2(2)	-1.52(19)
P002	20.2(3)	24.8(3)	29.1(3)	-0.8(2)	0.7(2)	0.1(2)
Cl1	57.0(5)	53.7(5)	79.7(6)	23.9(5)	13.9(5)	21.1(4)
Cl2	66.4(6)	79.3(7)	79.9(7)	-42.9(6)	16.7(5)	-36.7(5)
O1	21.7(9)	63.9(14)	52.9(13)	12.6(11)	8.8(9)	4.1(9)
N1	27.4(11)	36.0(12)	38.1(13)	3.7(10)	5.2(10)	-2.7(10)
C21	20.3(12)	36.2(14)	31.0(13)	-3.2(11)	-0.9(10)	2.0(10)
C6	25.1(12)	35.1(13)	30.1(13)	-3.4(11)	-1.7(10)	3.3(10)
C27	36.3(15)	58.7(19)	32.4(14)	-3.6(14)	-1.5(12)	-7.4(14)
C1	25.6(12)	26.6(12)	32.4(13)	-3.1(10)	-2.6(10)	1.7(10)
C9	33.2(14)	44.1(16)	44.1(16)	5.5(13)	4.7(13)	-11.1(13)
C7	20.3(12)	45.0(15)	31.2(13)	-0.5(11)	1.0(10)	-0.8(11)
C22	26.4(13)	34.1(13)	28.4(13)	-0.6(10)	1.2(10)	-2.8(11)
C5	27.8(13)	51.5(17)	45.8(16)	-1.4(14)	-0.4(14)	10.9(13)
C16	35.1(15)	46.7(17)	33.9(14)	-0.9(12)	1.1(11)	-1.7(13)

Supplementary Table S23 Anisotropic Displacement Parameters ($Å^2×10^3$) for B_a. 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}
C23	39.7(17)	63(2)	40.8(16)	5.6(15)	11.2(14)	14.8(16)
C10	28.2(13)	40.1(16)	43.1(15)	6.8(13)	11.7(12)	-2.1(12)
C11	49.3(19)	46.2(19)	66(2)	11.1(17)	23.0(18)	3.9(16)
C20	41.8(16)	38.7(15)	42.7(16)	-6.9(13)	-1.4(14)	-11.8(14)
C4	37.3(16)	44.4(17)	62(2)	1.7(15)	-5.7(15)	18.7(14)
C3	44.6(18)	32.5(15)	64(2)	8.0(14)	-8.5(16)	6.2(13)
C26	52.2(19)	90(3)	29.5(15)	-1.2(16)	-0.9(14)	-16(2)
C15	41.5(17)	61(2)	44.7(17)	3.2(16)	8.4(14)	-12.3(16)
C2	31.6(14)	33.4(14)	47.3(17)	2.6(12)	-2.5(13)	0.8(12)
C8	30.8(15)	78(3)	76(3)	34(2)	10.5(17)	-0.1(17)
C13	49(2)	139(5)	63(3)	49(3)	9(2)	3(3)
C24	39.5(17)	101(3)	47.3(19)	-2(2)	16.7(16)	13.7(18)
C19	43.8(18)	69(2)	49.5(19)	-21.0(17)	3.9(15)	-21.8(18)
C17	48.1(19)	89(3)	29.2(15)	-3.1(16)	-2.2(14)	-5.7(19)
C25	60(2)	97(3)	42.0(19)	-17(2)	17.7(17)	-5(2)
C18	44.8(18)	95(3)	43.8(18)	-29.5(19)	5.2(15)	-21(2)
C14	46(2)	125(4)	45(2)	8(2)	5.6(17)	-23(2)
C12	63(3)	80(3)	101(4)	52(3)	28(3)	23(2)

Supplementary Table S24 Bond Lengths for B_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	P002	2.2629(8)	C9	C10	1.503(4)
Ni1	Cl1	2.1957(11)	C9	C8	1.530(5)
Ni1	Cl2	2.2269(12)	C22	C23	1.526(4)
Ni1	N1	1.990(2)	C5	C4	1.380(5)

Supplementary Table S24 Bond Lengths for B_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P002	C21	1.847(3)	C16	C17	1.526(4)
P002	C1	1.829(3)	C23	C24	1.532(4)
P002	C22	1.842(3)	C10	C11	1.383(5)
O1	C7	1.353(3)	C10	C15	1.388(5)
O1	C8	1.438(4)	C11	C12	1.392(7)
N1	C9	1.490(4)	C20	C19	1.522(5)
N1	C7	1.276(4)	C4	C3	1.370(5)
C21	C16	1.528(4)	C3	C2	1.386(4)
C21	C20	1.529(4)	C26	C25	1.510(6)
C6	C1	1.408(4)	C15	C14	1.382(6)
C6	C7	1.476(4)	C13	C14	1.361(8)
C6	C5	1.399(4)	C13	C12	1.358(8)
C27	C22	1.531(4)	C24	C25	1.515(6)
C27	C26	1.528(4)	C19	C18	1.518(5)
C1	C2	1.391(4)	C17	C18	1.504(6)

Supplementary Table S25 Bond Angles for B_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Ni1	P002	107.14(4)	O1	C7	C6	114.4(2)
Cl1	Ni1	Cl2	124.78(5)	N1	C7	O1	115.9(3)
Cl2	Ni1	P002	108.99(4)	N1	C7	C6	129.8(2)
N1	Ni1	P002	92.50(7)	C27	C22	P002	112.61(19)
N1	Ni1	Cl1	120.88(8)	C23	C22	P002	108.65(19)
N1	Ni1	Cl2	97.72(8)	C23	C22	C27	109.9(2)
C21	P002	Ni1	113.64(9)	C4	C5	C6	121.3(3)
C1	P002	Ni1	108.99(9)	C17	C16	C21	110.8(3)
C1	P002	C21	105.94(12)	C22	C23	C24	111.1(3)

Supplementary Table S25 Bond Angles for B_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P002	C22	107.04(12)	C11	C10	C9	120.5(3)
C22	P002	Ni1	115.74(9)	C11	C10	C15	118.9(3)
C22	P002	C21	104.85(12)	C15	C10	C9	120.6(3)
C7	O1	C8	107.7(2)	C10	C11	C12	119.9(4)
C9	N1	Ni1	119.83(19)	C19	C20	C21	110.7(3)
C7	N1	Ni1	130.0(2)	C3	C4	C5	119.6(3)
C7	N1	C9	108.8(2)	C4	C3	C2	120.1(3)
C16	C21	P002	111.86(19)	C25	C26	C27	111.6(3)
C16	C21	C20	110.7(2)	C14	C15	C10	120.2(4)
C20	C21	P002	114.3(2)	C3	C2	C1	121.5(3)
C1	C6	C7	124.9(2)	O1	C8	C9	105.0(3)
C5	C6	C1	119.1(3)	C12	C13	C14	120.6(4)
C5	C6	C7	116.0(3)	C25	C24	C23	111.3(3)
C26	C27	C22	110.4(2)	C18	C19	C20	111.3(3)
C6	C1	P002	123.3(2)	C18	C17	C16	112.2(3)
C2	C1	P002	118.3(2)	C26	C25	C24	111.3(3)
C2	C1	C6	118.4(2)	C17	C18	C19	111.6(3)
N1	C9	C10	112.2(2)	C13	C14	C15	120.2(5)
N1	C9	C8	102.6(2)	C13	C12	C11	120.2(4)
C10	C9	C8	114.2(3)				

Supplementary Table S26 Torsion Angles for B_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ni1	P002	C21	C16	-42.3(2)	C9	C10	C15	C14	179.5(3)
Ni1	P002	C21	C20	-169.22(18)	C7	O1	C8	C9	-2.3(4)
Ni1	P002	C1	C6	22.8(2)	C7	N1	C9	C10	-125.7(3)
Ni1	P002	C1	C2	-155.7(2)	C7	N1	C9	C8	-2.7(3)

Supplementary Table S26 Torsion Angles for B_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ni1	P002	C22	C27	69.1(2)	C7	C6	C1	P002	1.3(4)
Ni1	P002	C22	C23	-52.8(2)	C7	C6	C1	C2	179.9(3)
Ni1	N1	C9	C10	66.1(3)	C7	C6	C5	C4	-179.6(3)
Ni1	N1	C9	C8	-170.9(2)	C22	P002	C21	C16	-169.7(2)
Ni1	N1	C7	O1	168.0(2)	C22	P002	C21	C20	63.4(2)
Ni1	N1	C7	C6	-11.0(5)	C22	P002	C1	C6	148.7(2)
P002	C21	C16	C17	175.8(2)	C22	P002	C1	C2	-29.9(3)
P002	C21	C20	C19	-175.9(2)	C22	C27	C26	C25	57.0(4)
P002	C1	C2	C3	178.3(3)	C22	C23	C24	C25	-55.8(5)
P002	C22	C23	C24	-179.4(3)	C5	C6	C1	P002	-179.2(2)
N1	C9	C10	C11	-127.1(3)	C5	C6	C1	C2	-0.7(4)
N1	C9	C10	C15	54.6(4)	C5	C6	C7	O1	-10.7(4)
N1	C9	C8	O1	2.9(4)	C5	C6	C7	N1	168.3(3)
C21	P002	C1	C6	-99.8(2)	C5	C4	C3	C2	-0.9(5)
C21	P002	C1	C2	81.6(2)	C16	C21	C20	C19	56.6(3)
C21	P002	C22	C27	-164.8(2)	C16	C17	C18	C19	-54.4(4)
C21	P002	C22	C23	73.3(2)	C23	C24	C25	C26	54.5(5)
C21	C16	C17	C18	54.6(4)	C10	C9	C8	O1	124.6(3)
C21	C20	C19	C18	-56.3(4)	C10	C11	C12	C13	-0.4(6)
C6	C1	C2	C3	-0.3(4)	C10	C15	C14	C13	-0.8(6)
C6	C5	C4	C3	-0.1(5)	C11	C10	C15	C14	1.2(5)
C27	C22	C23	C24	57.0(4)	C20	C21	C16	C17	-55.4(3)
C27	C26	C25	C24	-55.4(4)	C20	C19	C18	C17	55.2(5)
C1	P002	C21	C16	77.3(2)	C4	C3	C2	C1	1.1(5)
C1	P002	C21	C20	-49.6(2)	C26	C27	C22	P002	-178.6(3)
C1	P002	C22	C27	-52.6(2)	C26	C27	C22	C23	-57.3(4)
C1	P002	C22	C23	-174.5(2)	C15	C10	C11	C12	-0.6(5)
C1	C6	C7	O1	168.7(3)	C8	O1	C7	N1	0.6(4)

Supplementary Table S26 Torsion Angles for B_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C6	C7	N1	-12.2(5)	C8	O1	C7	C6	179.8(3)
C1	C6	C5	C4	0.9(5)	C8	C9	C10	C11	116.7(3)
C9	N1	C7	O1	1.4(3)	C8	C9	C10	C15	-61.6(4)
C9	N1	C7	C6	-177.6(3)	C14	C13	C12	C11	0.7(7)
C9	C10	C11	C12	-178.9(3)	C12	C13	C14	C15	-0.1(7)

Supplementary Table S27 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for B_a.

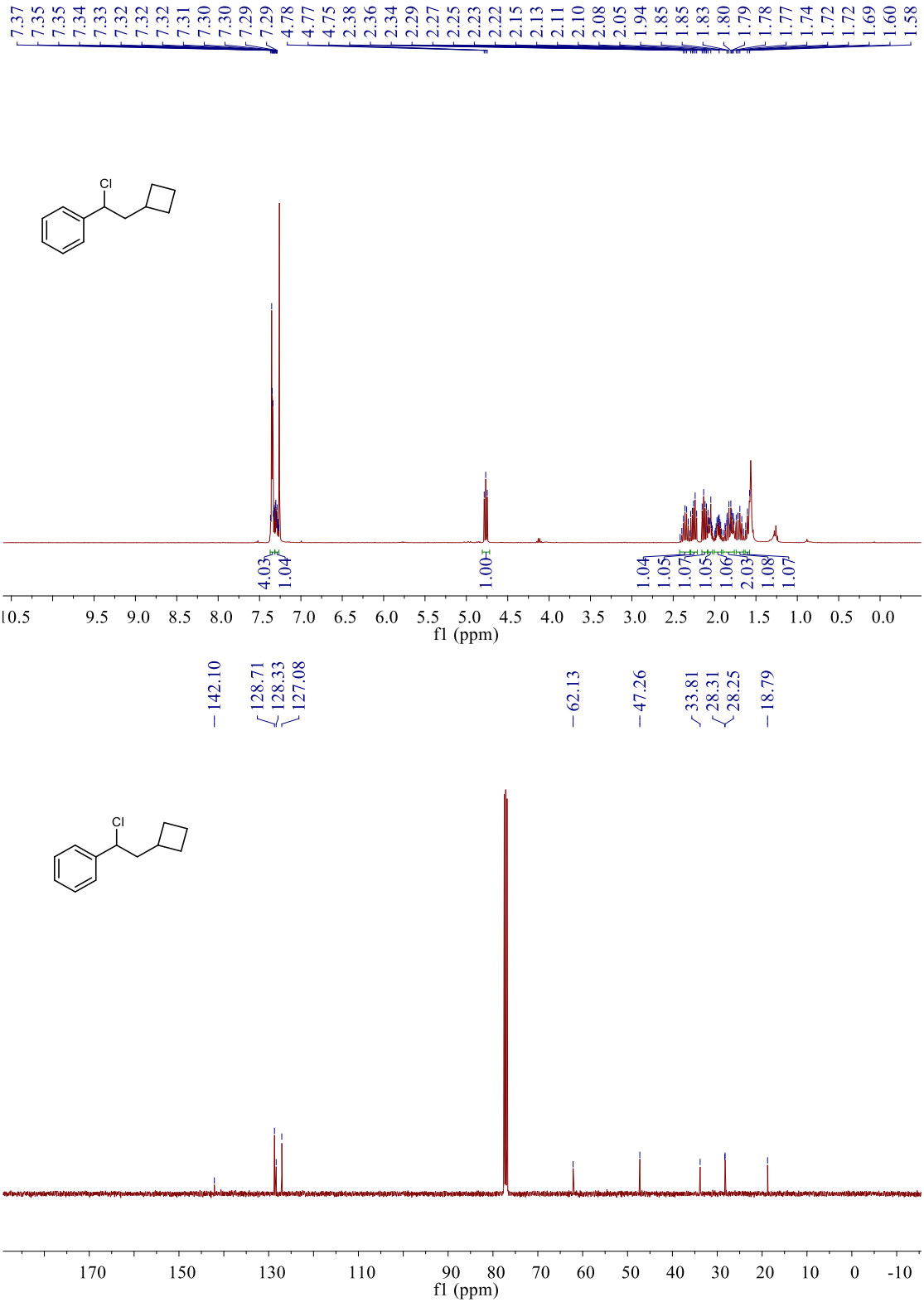
Atom	*x*	*y*	*z*	U(eq)
H21	6748.99	6115.8	3819.98	35
H27A	4608.12	5514.97	1669.99	51
H27B	4232.62	6536.45	1688.73	51
H9	774.88	3820.57	3760.28	49
H22	6324.42	6787.33	2412.59	36
H5	-621.68	6918.18	3308.01	50
H16A	3976.89	6410.05	4528.34	46
H16B	4877	5503.3	4511.98	46
H23A	6816.97	4936.65	2382.39	57
H23B	7781.69	5609.71	2824.39	57
H11	1619.21	2701.25	4459.89	65
H20A	6547.63	7537.91	3385.46	49
H20B	5052.5	7703.05	3824.97	49
H4	-246.83	8227.31	2747.15	58
H3	2145.68	8578.51	2341.24	56
H26A	5597.05	6176.93	693.13	69
H26B	6535.41	6858.48	1137.91	69
H15	2272.54	5175.37	5088.13	59

Supplementary Table S27 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for B_a.

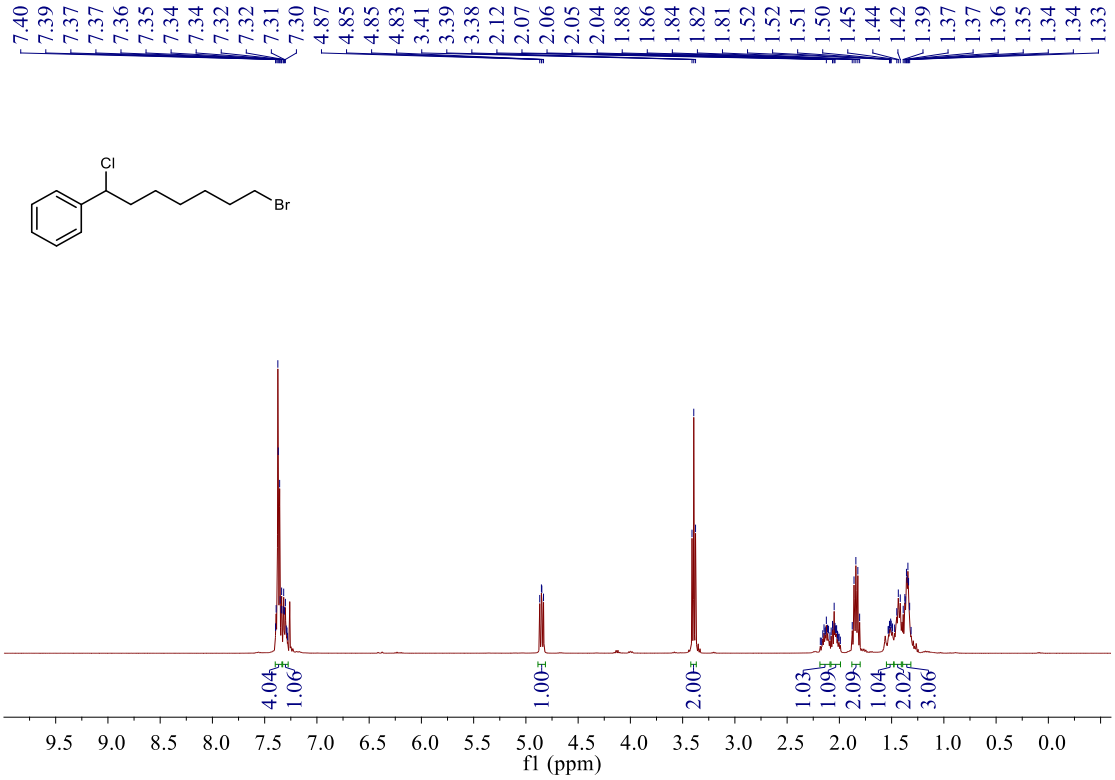
Atom	*x*	*y*	*z*	U(eq)
H2	4179.03	7642.52	2520.55	45
H8A	-1326.49	4526.35	4030.57	74
H8B	-559.83	4908.64	4702.25	74
H13	3799.73	3173.52	6197.01	100
H24A	8792	6257.92	1850.19	75
H24B	9111.24	5231.48	1819.03	75
H19A	8024.02	7391.22	4361.63	65
H19B	7148.12	8304.78	4390.44	65
H17A	5426.5	6305.64	5511.62	66
H17B	6932.74	6116.3	5087.41	66
H25A	8187.85	5769.26	773.7	80
H25B	7102.9	5027.13	1071.94	80
H18A	6990.26	7557.57	5435.66	73
H18B	5339.76	7732.09	5127.91	73
H14	3522.72	4651.74	6035.13	86
H12	2844.74	2198.21	5427.7	98

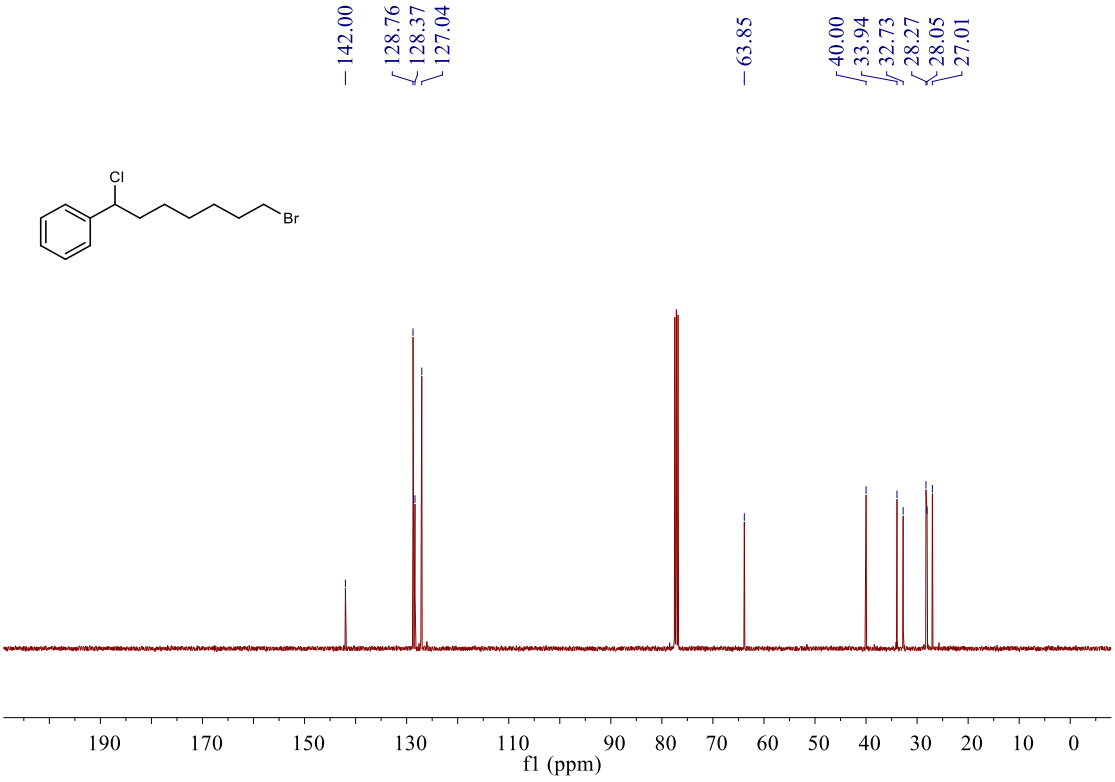
10. NMR Spectral Data

Compound 1a (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

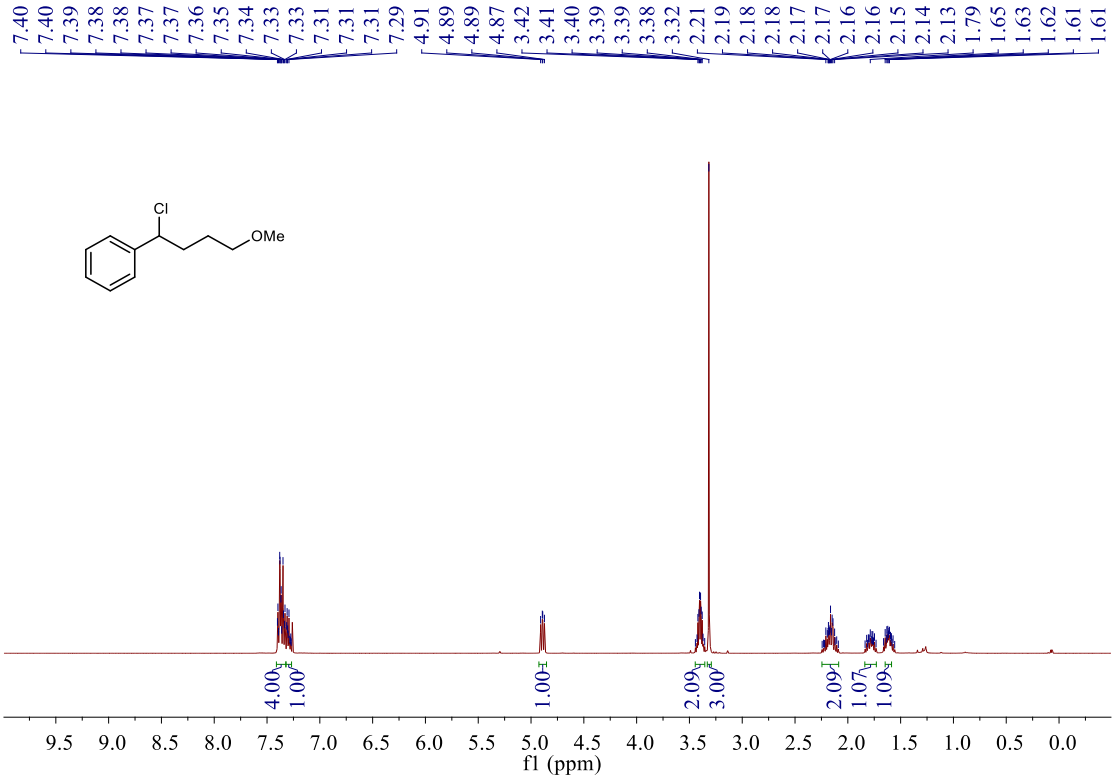


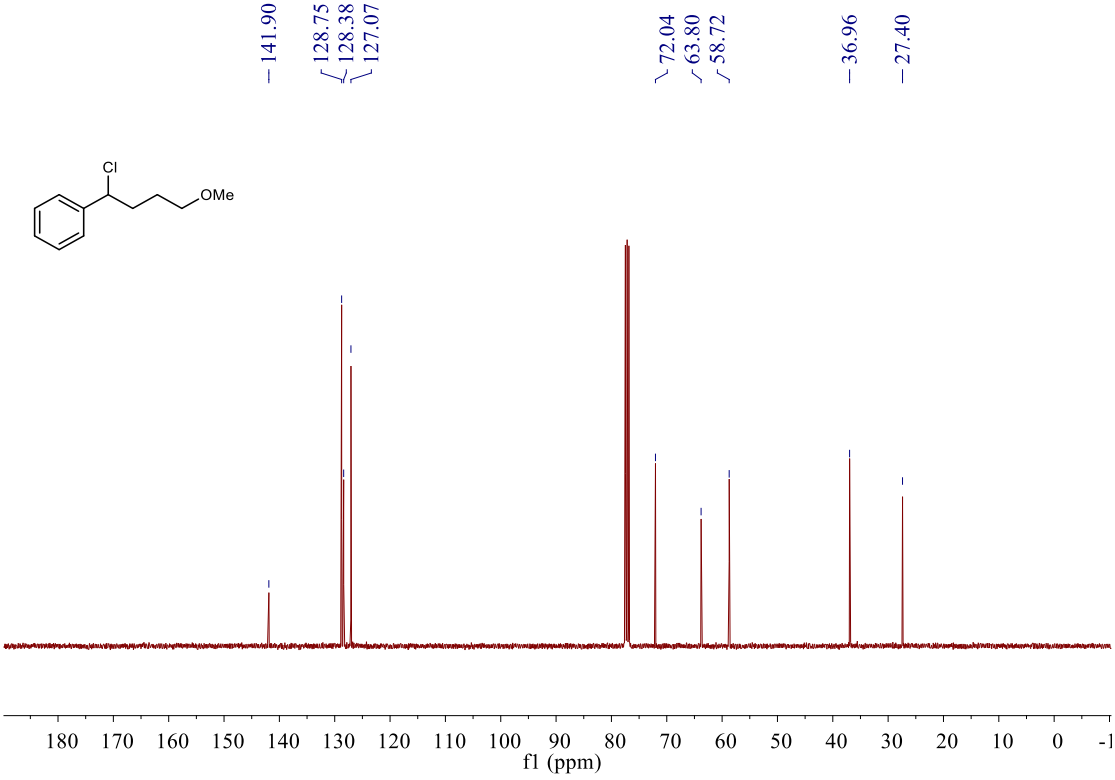
Compound 1b (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



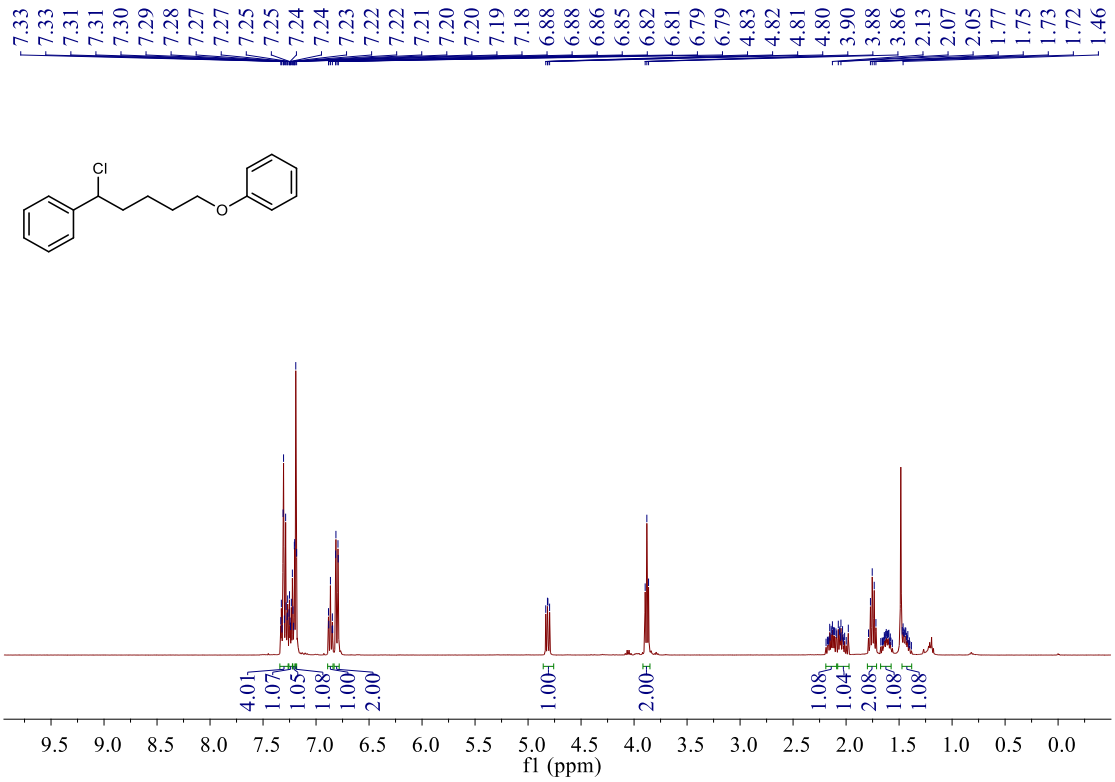


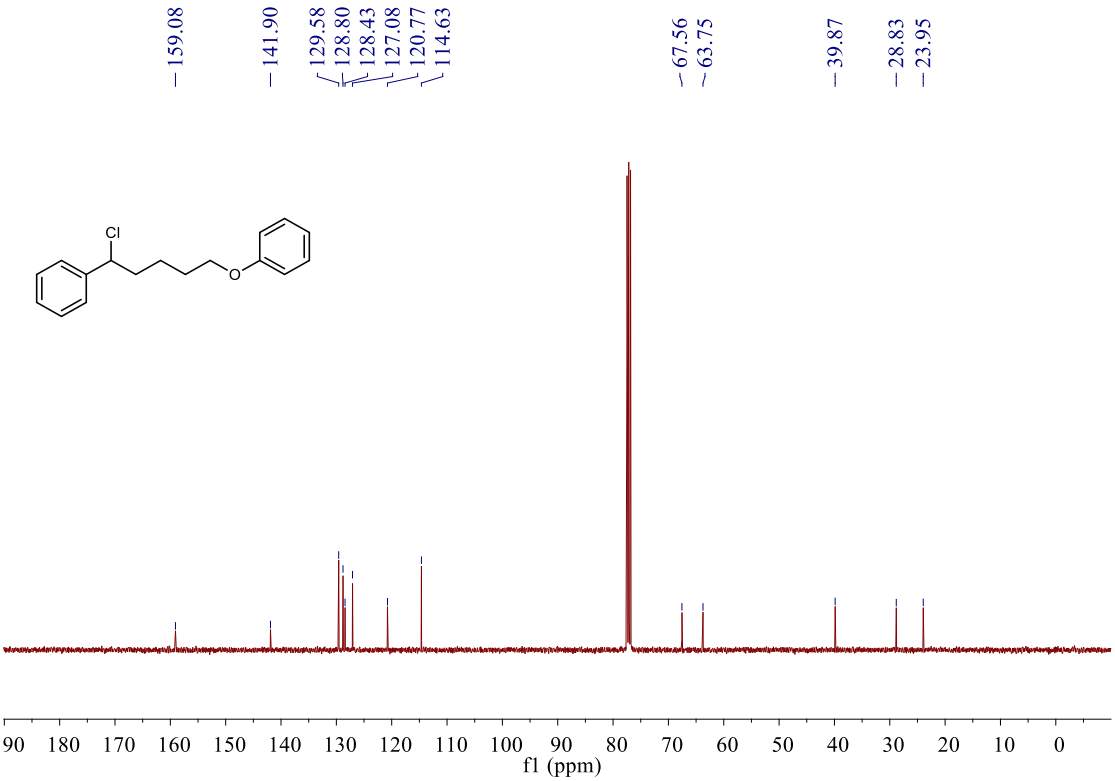
Compound 1c (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



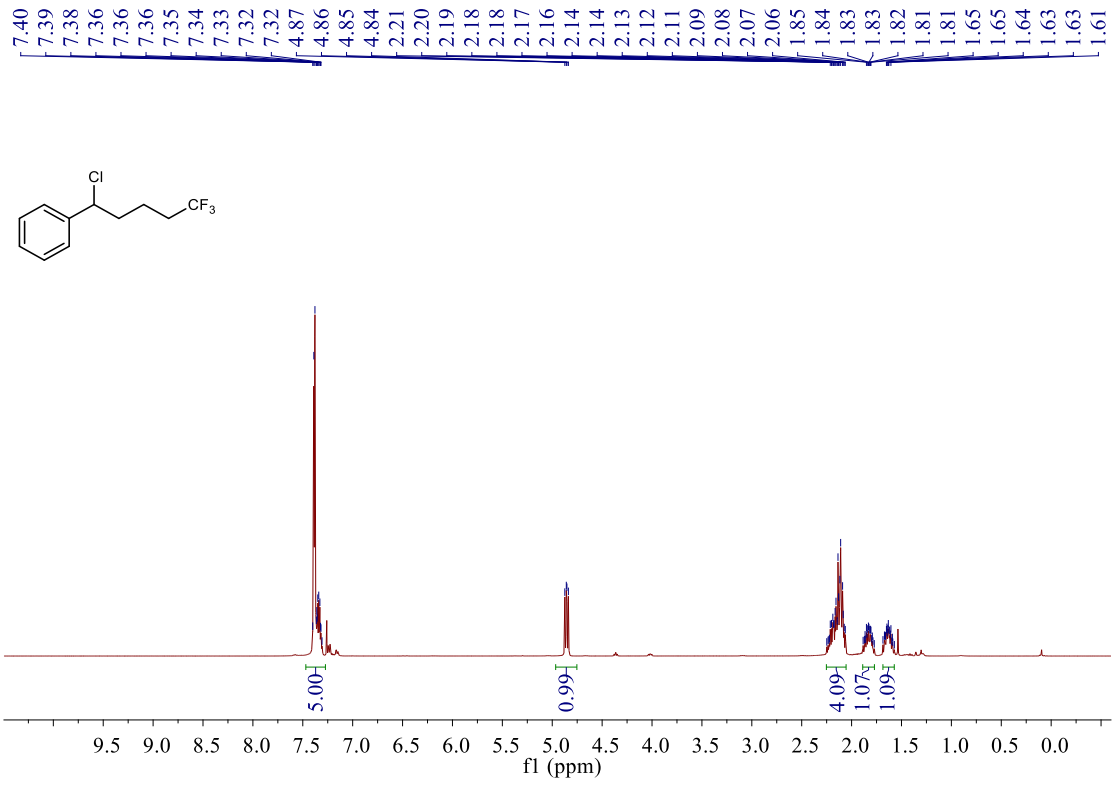


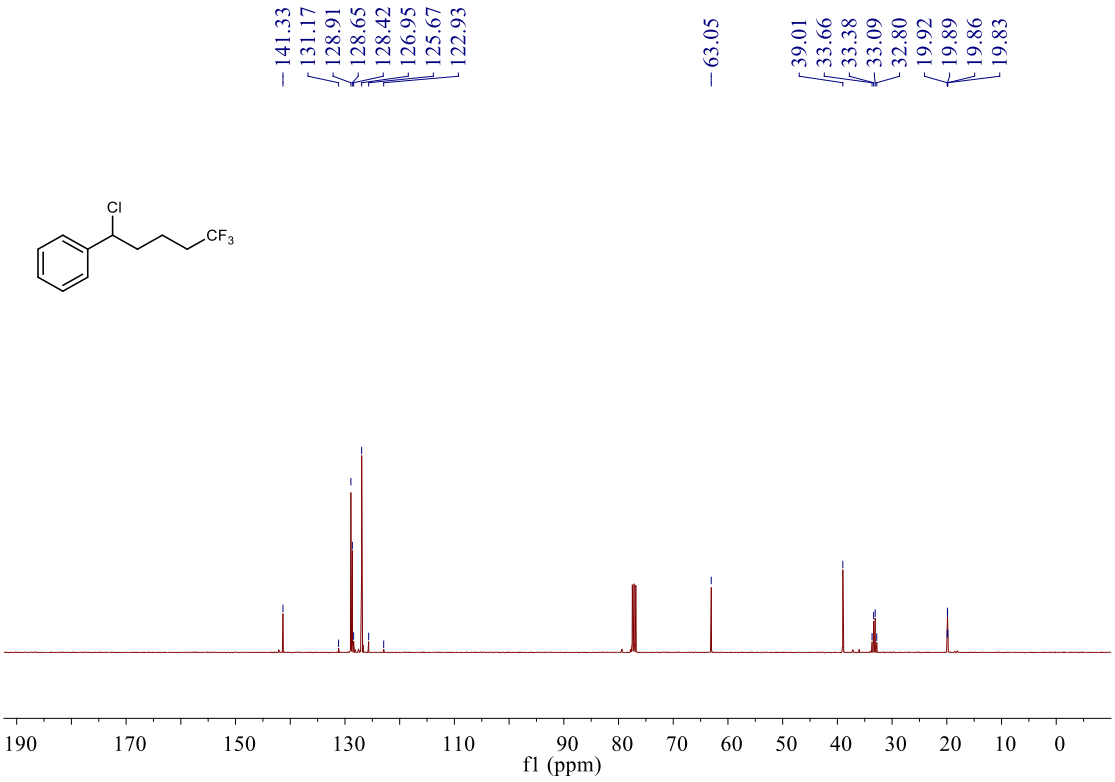
Compound 1d (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

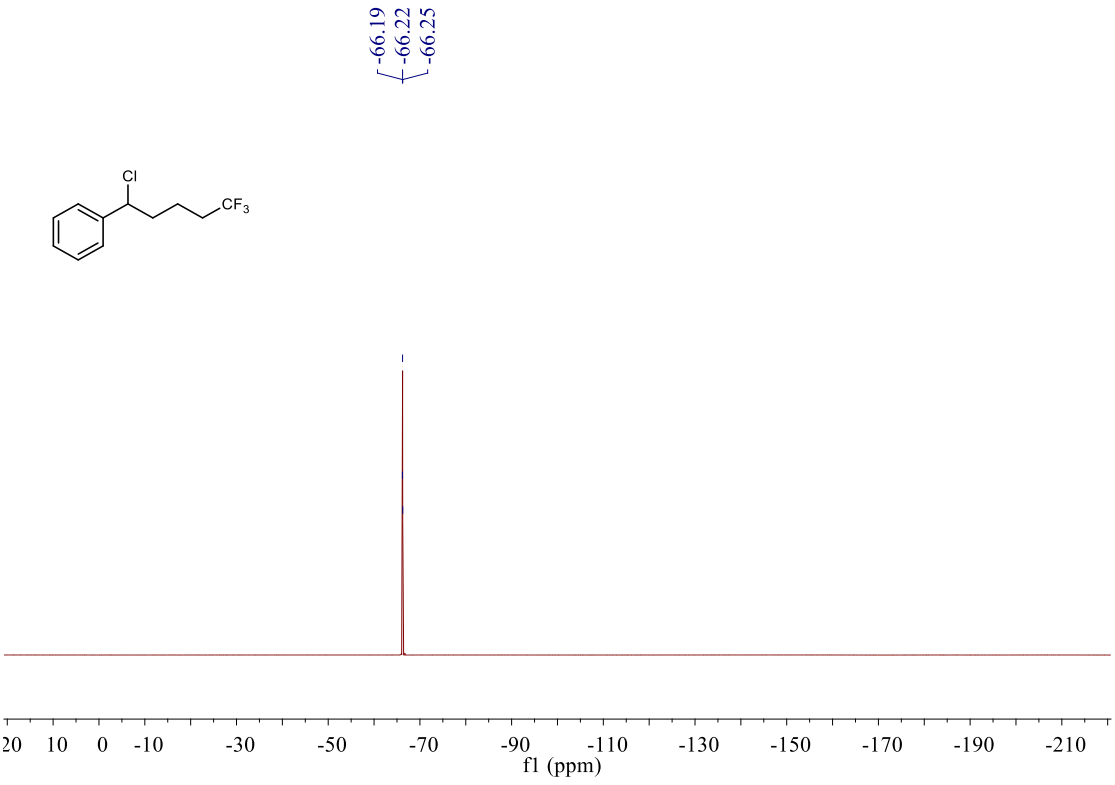




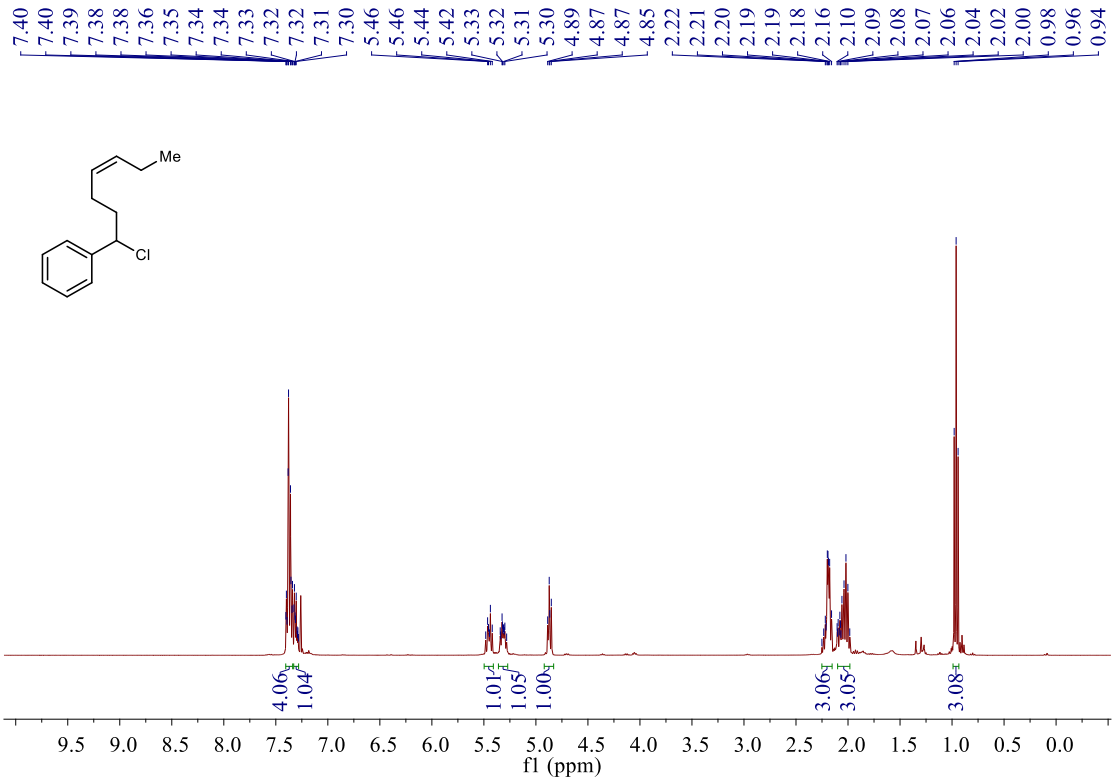
Compound 1e (^{1}H NMR, ^{13}C NMR and ^{19}F NMR, $CDCl_3$, 400 MHz, 101 MHz and 377 MHz respectively)

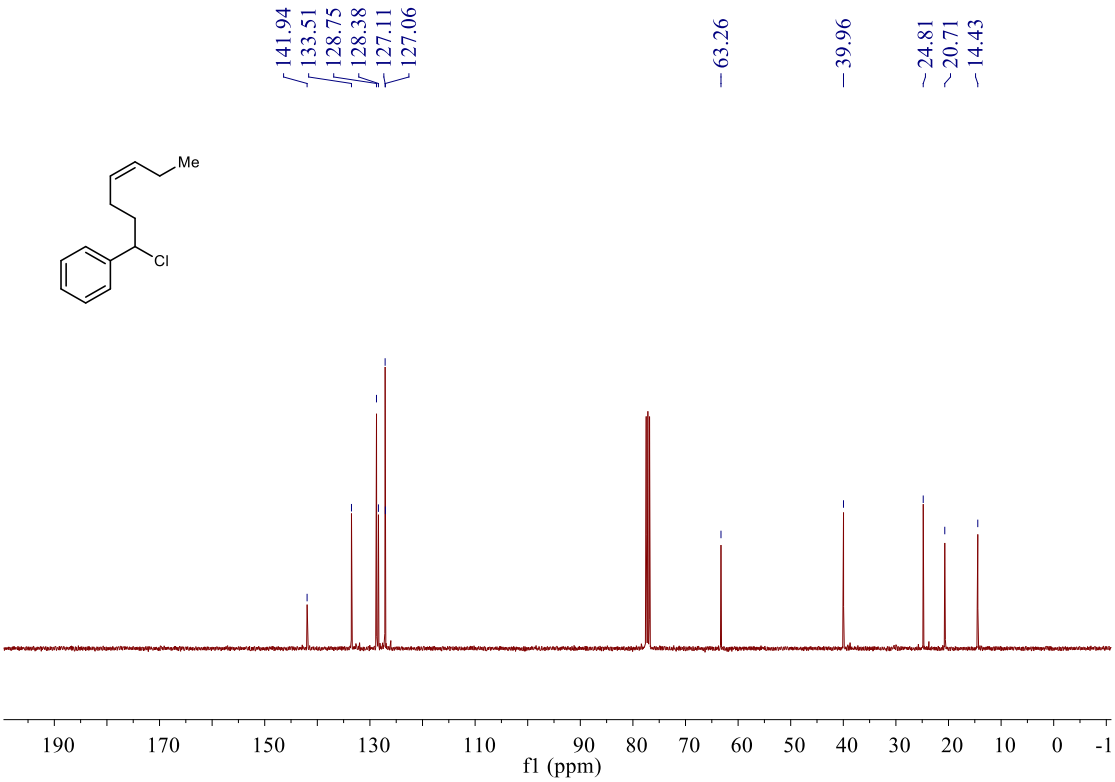



141.33
131.17
128.91
128.65
128.42
126.95
125.67
122.93
63.05
39.01
33.66
33.38
33.09
32.80
19.92
19.89
19.86
19.83
Cl
CF3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

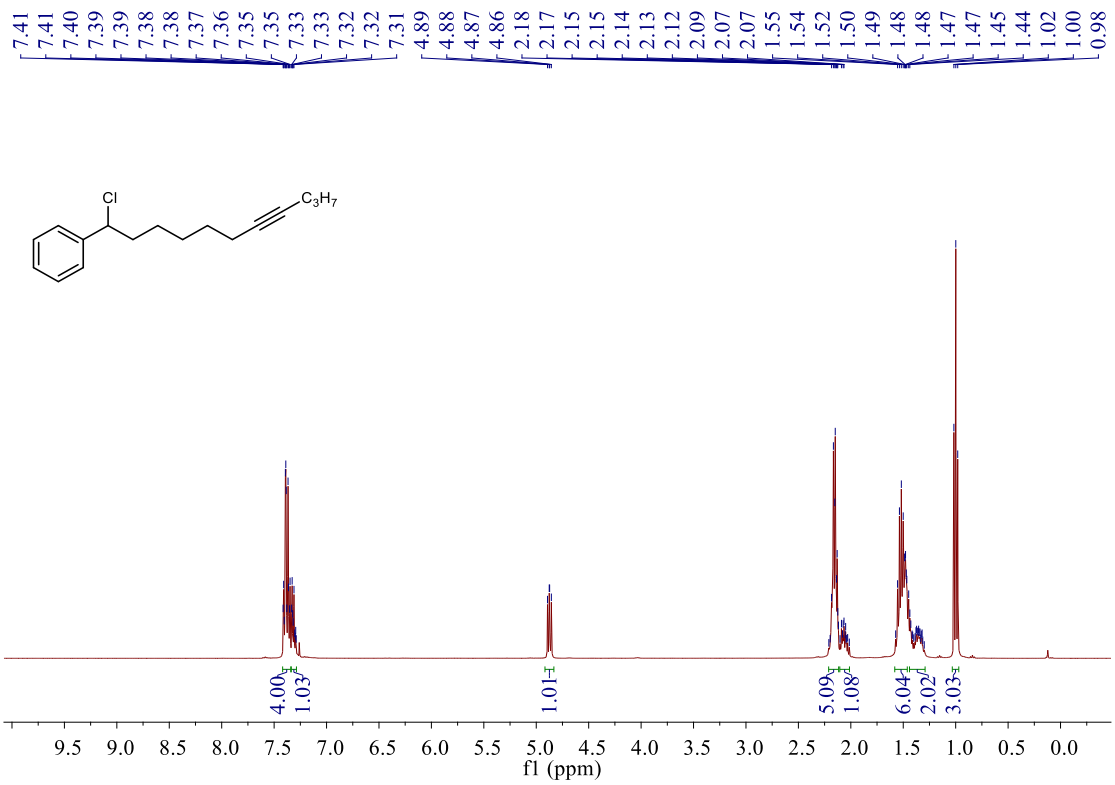

-66.19
-66.22
-66.25
Cl
CF3
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

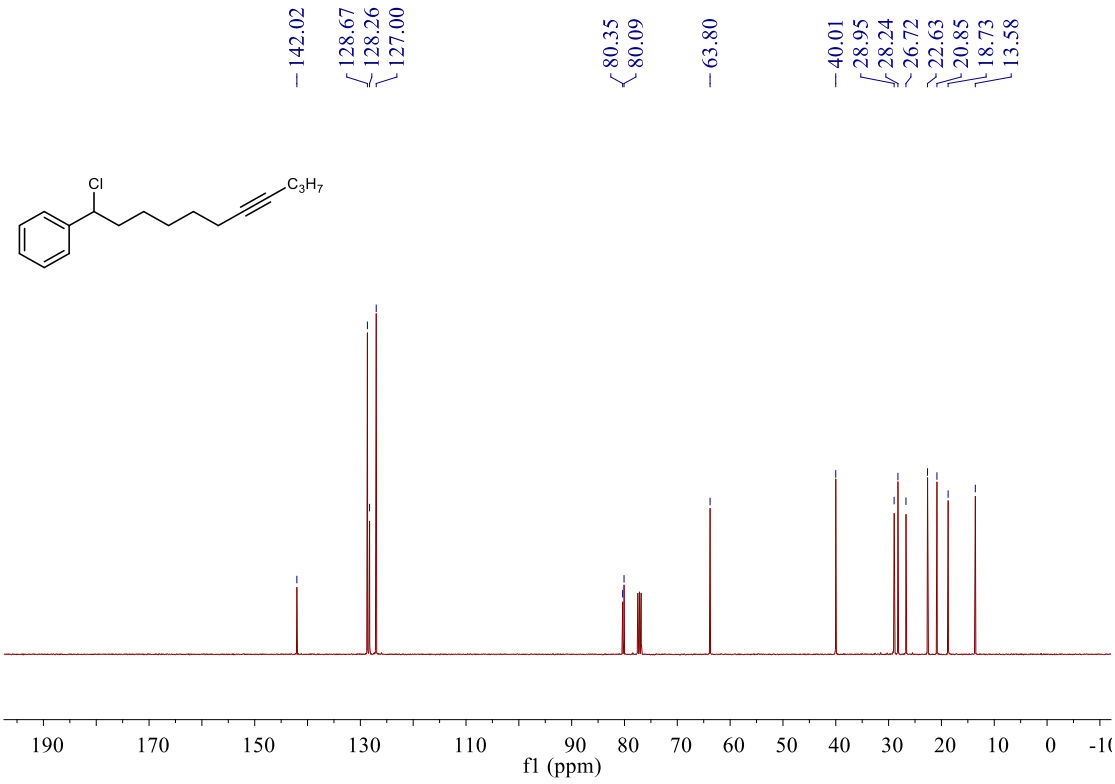
Compound 1f (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



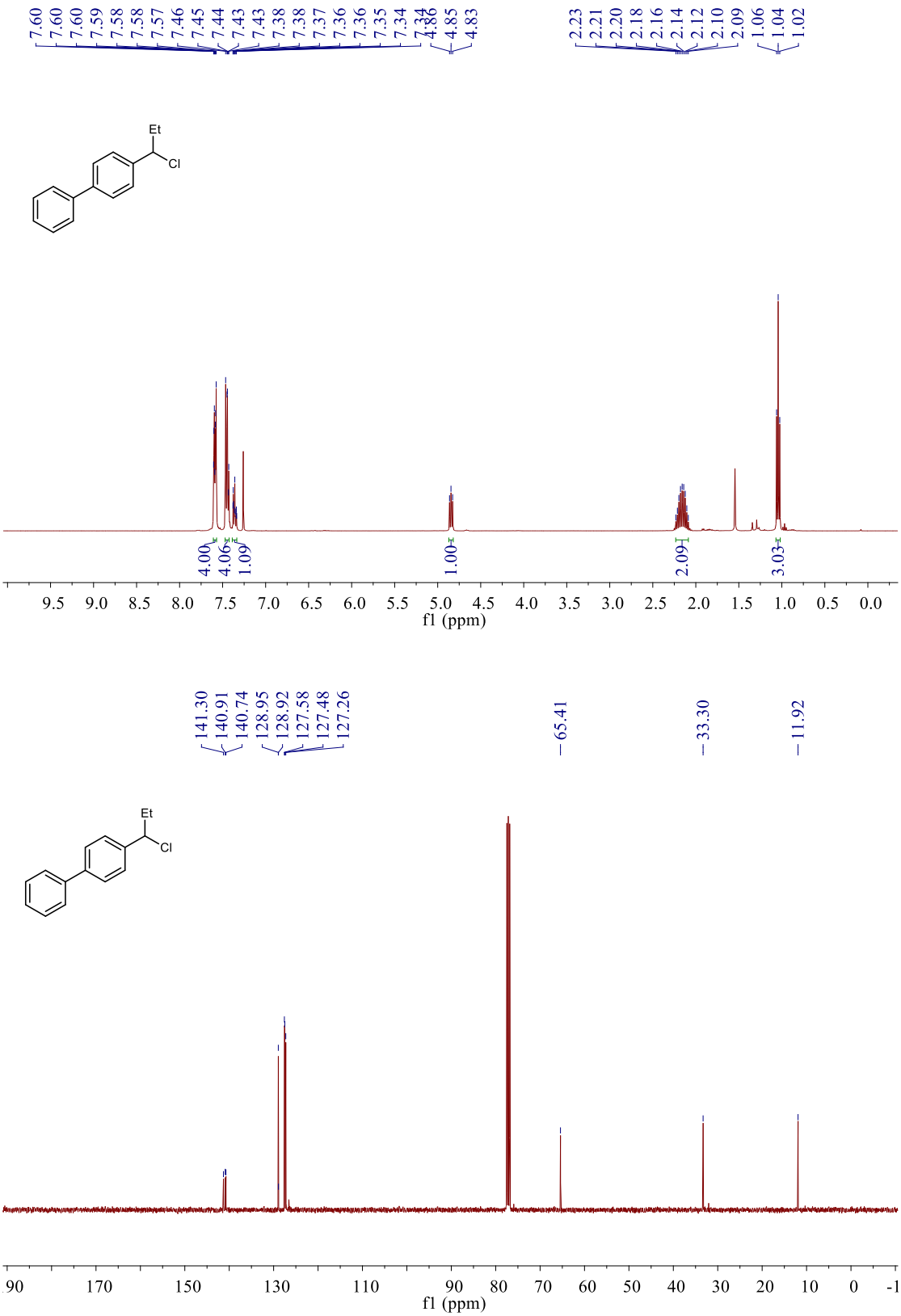


Compound 1g (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

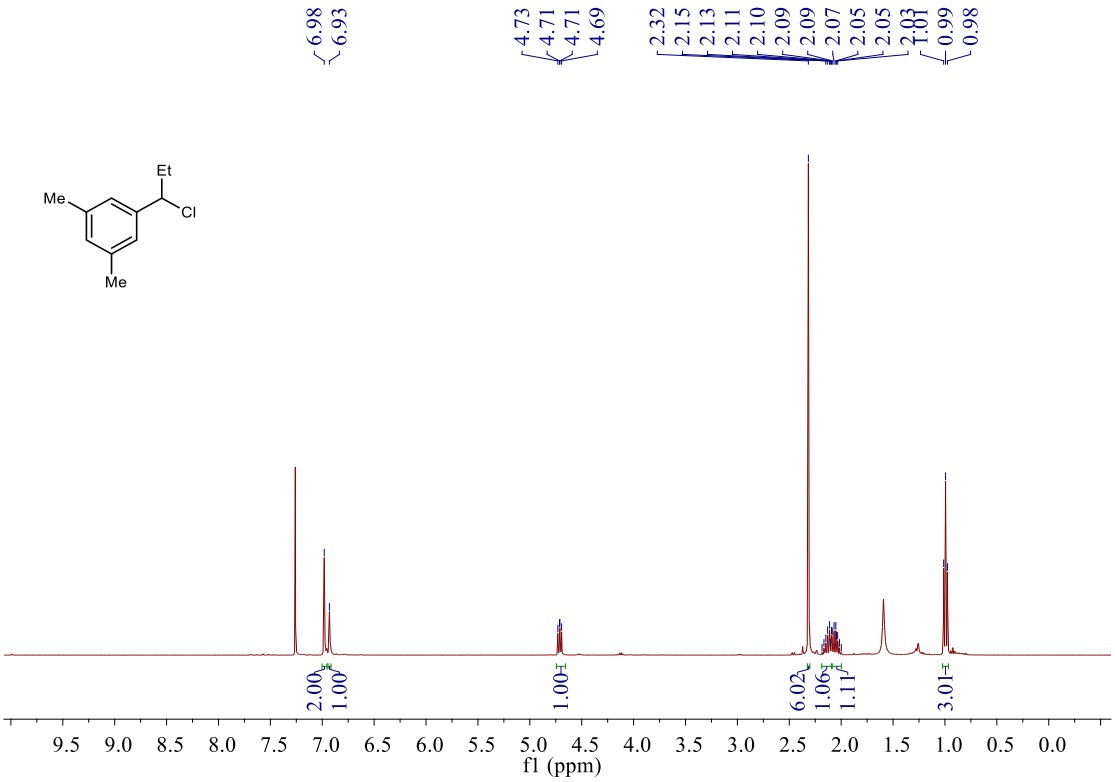


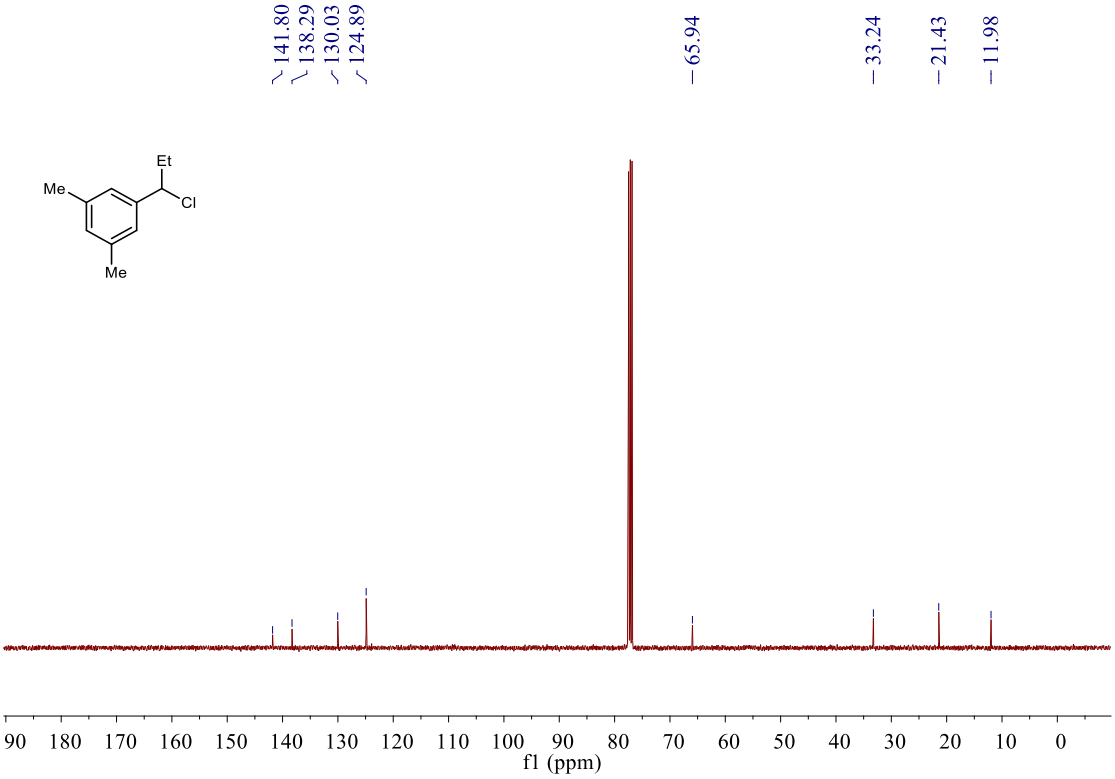


Compound 1h (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

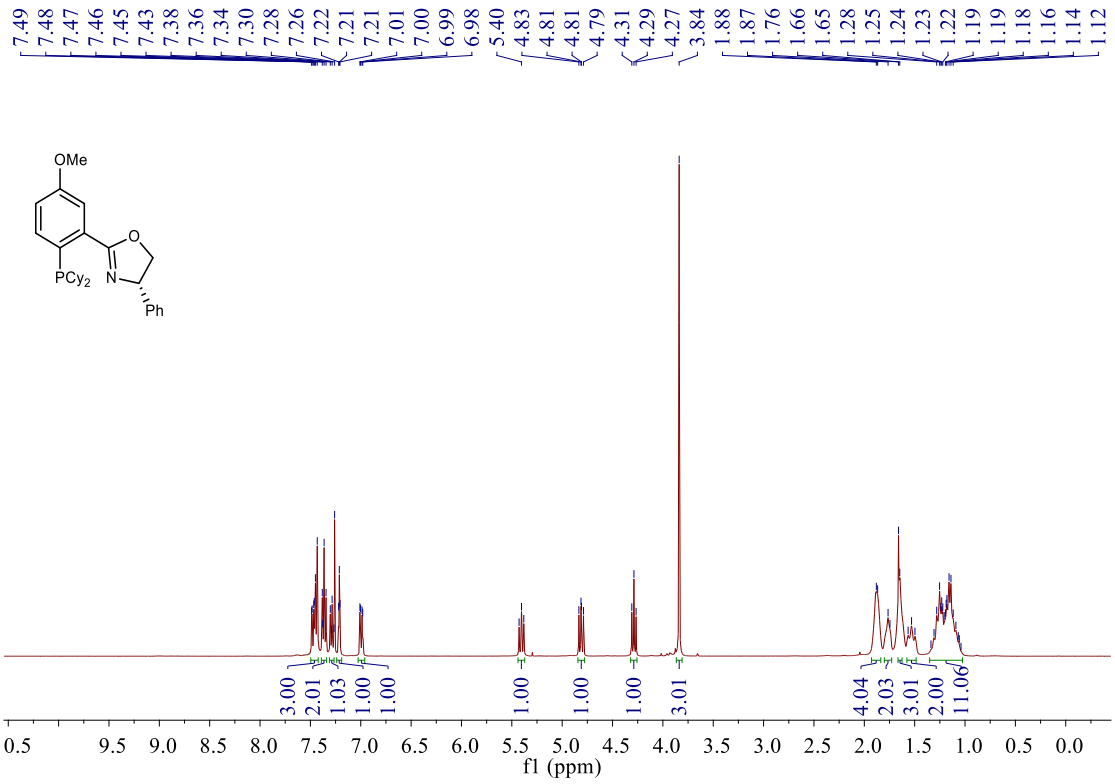


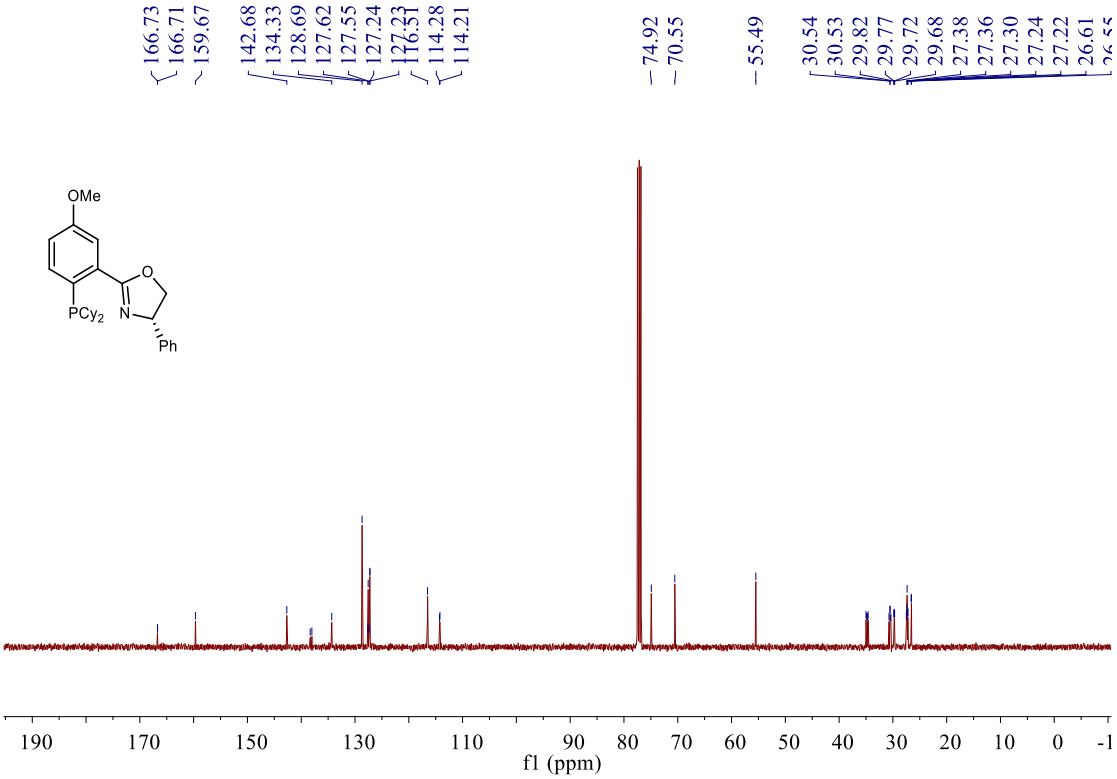
Compound 1i (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

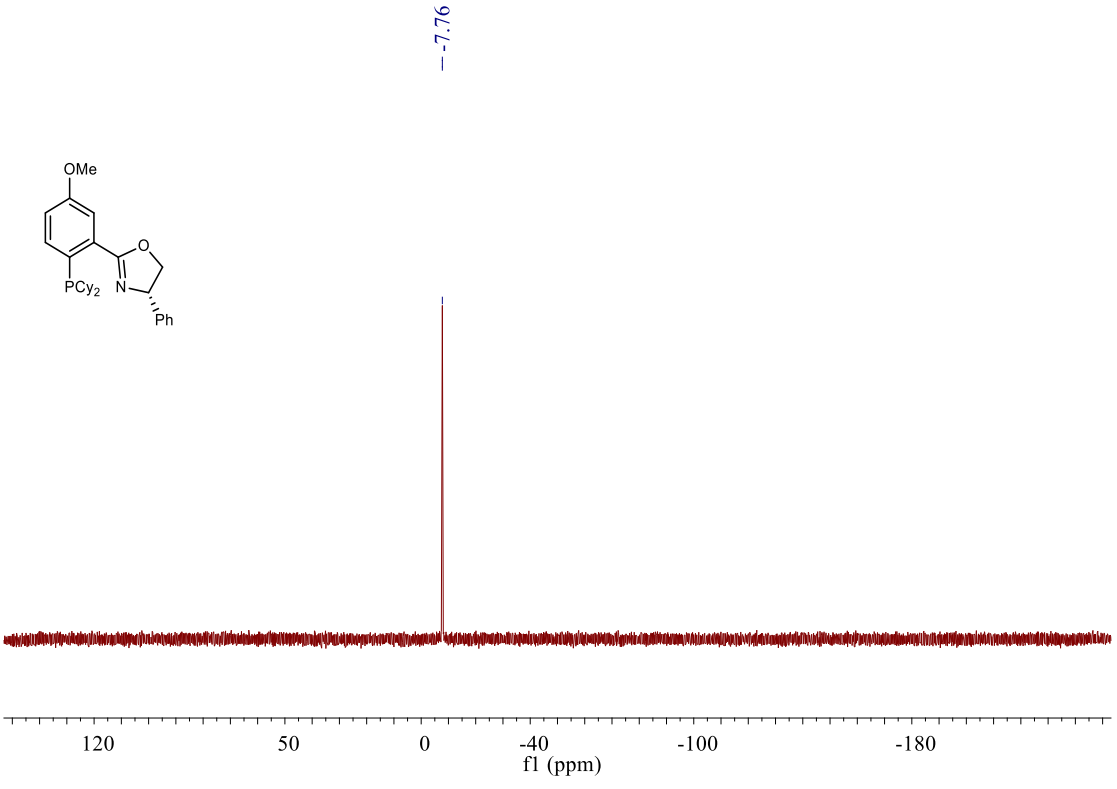




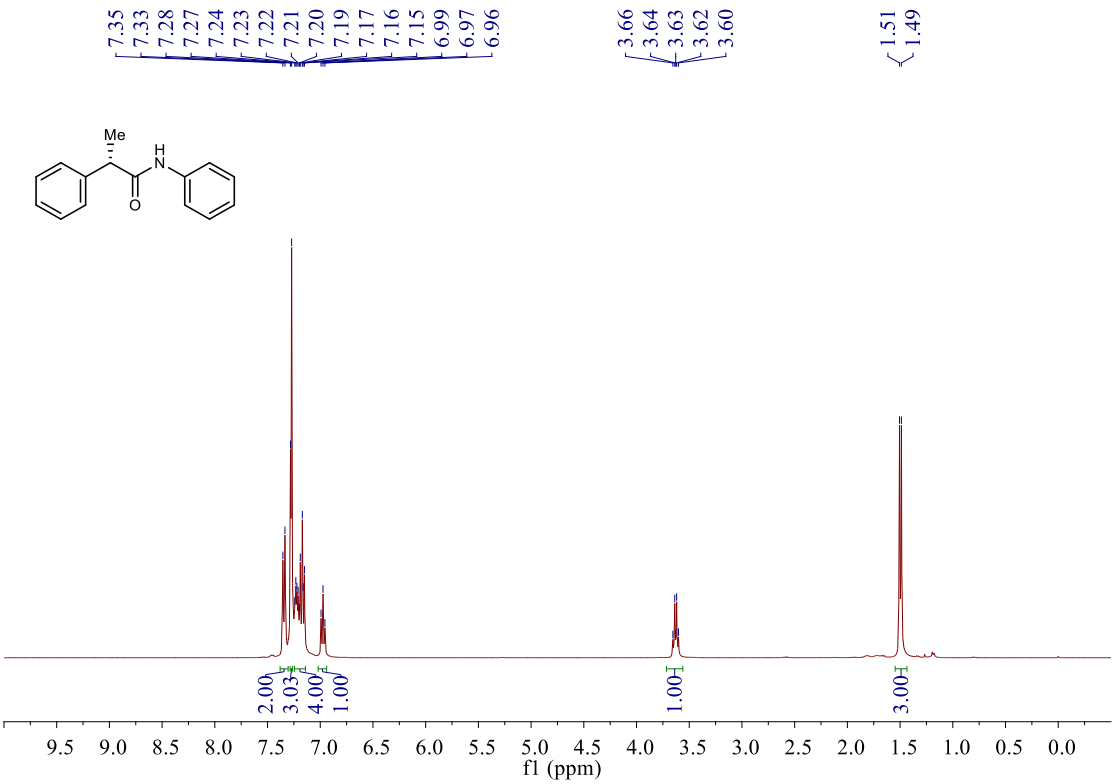
Compound (*S*)-L5 (^{1}H NMR, ^{13}C NMR and ^{31}P NMR, $CDCl_3$, 400 MHz, 101 MHz and 162 MHz respectively)

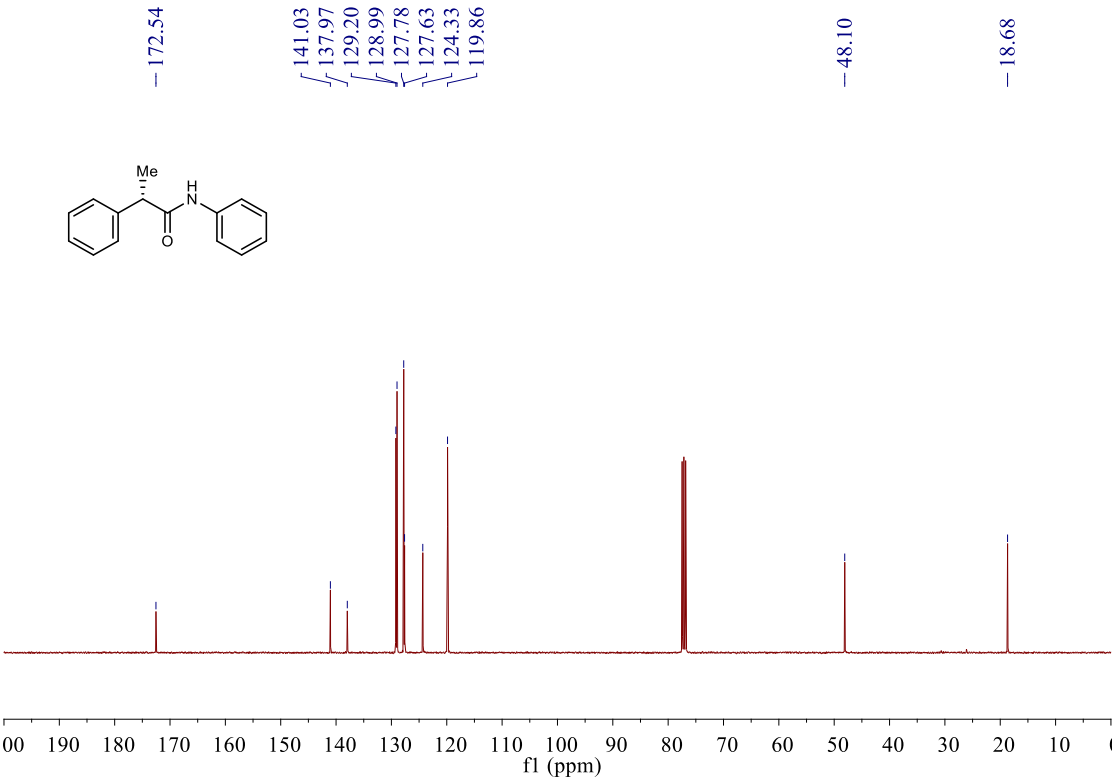



166.73
166.71
159.67
142.68
134.33
128.69
127.62
127.55
127.24
127.23
116.51
114.28
114.21
74.92
70.55
55.49
30.54
30.53
29.82
29.77
29.72
29.68
27.38
27.36
27.30
27.24
27.22
26.61
OMe
O
N
PCy2
Ph
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

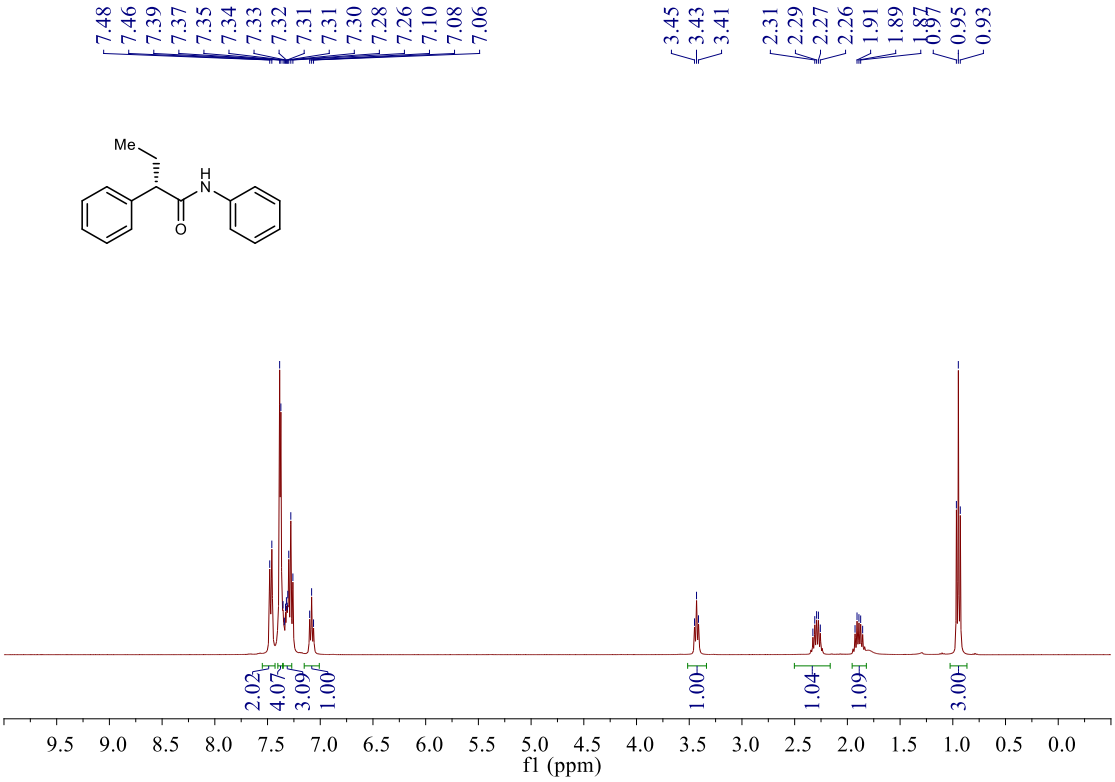

-7.76
OMe
O
N
PCy2
Ph
120
50
0
-40
-100
-180
f1 (ppm)

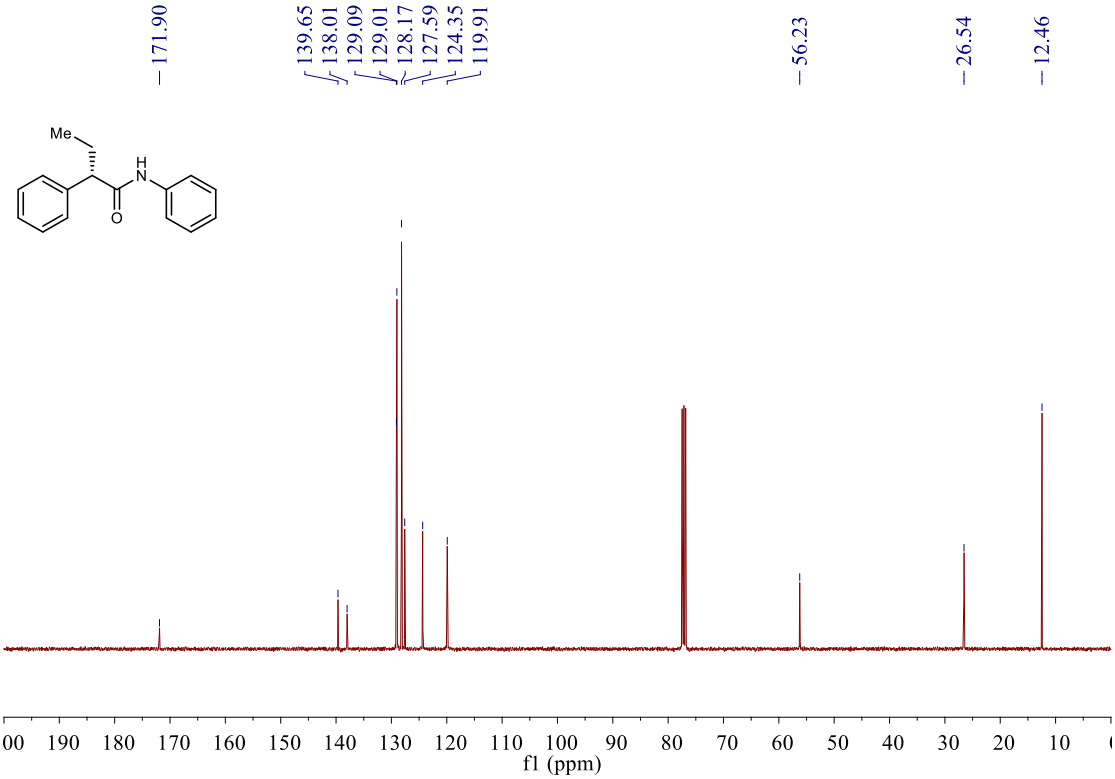
Compound 3 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



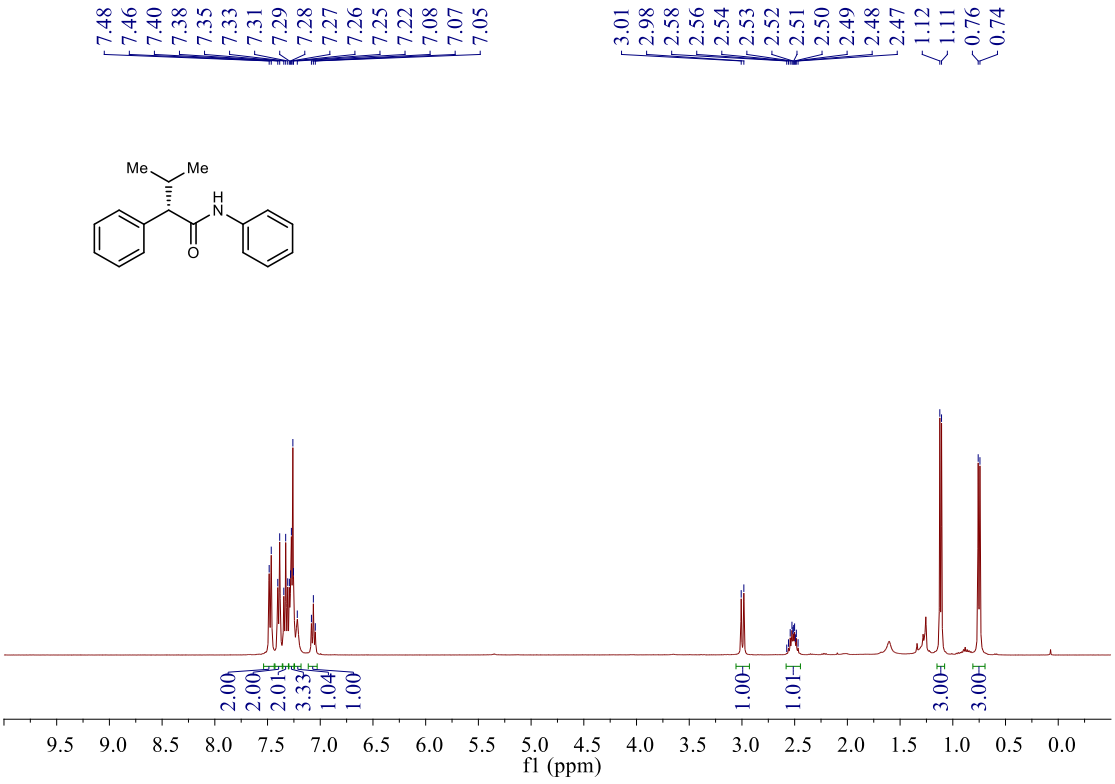


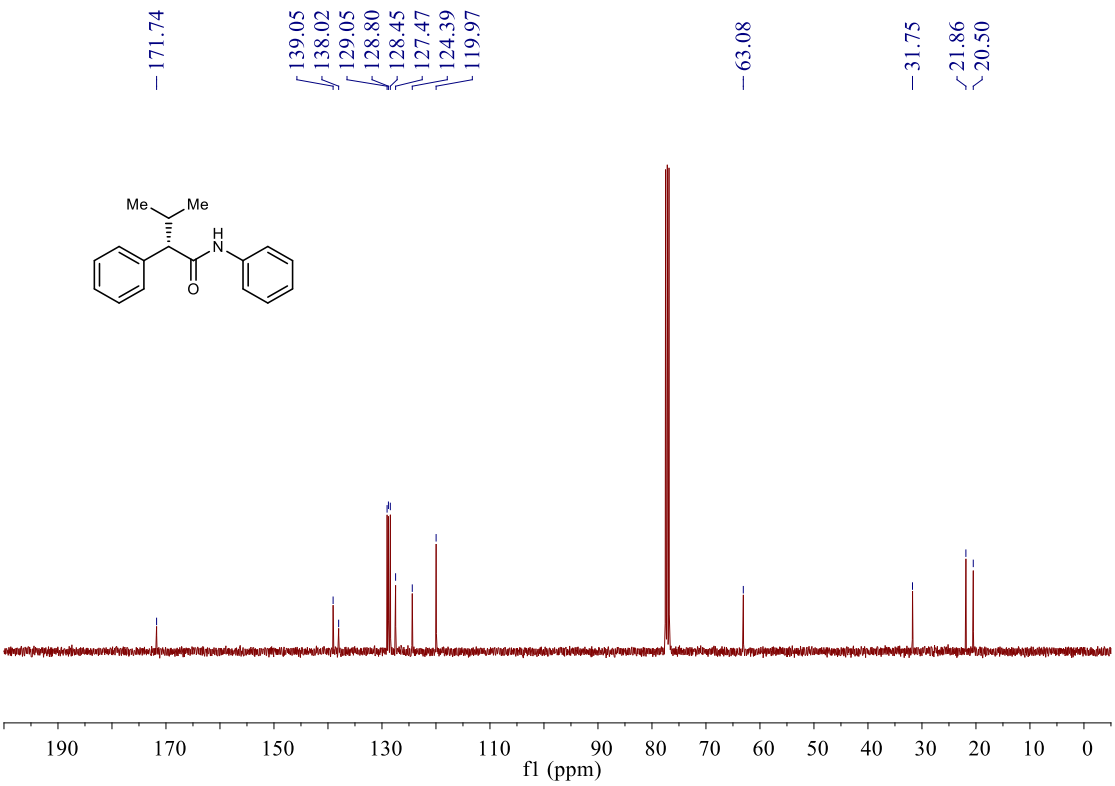
Compound 8 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



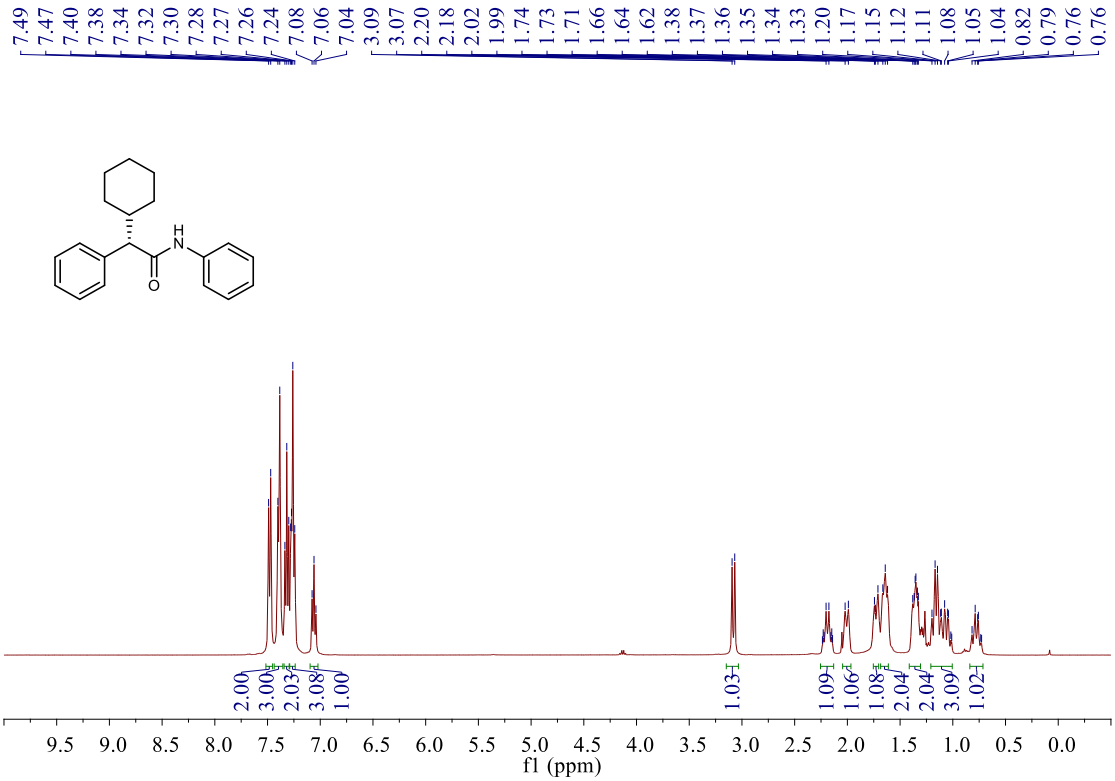


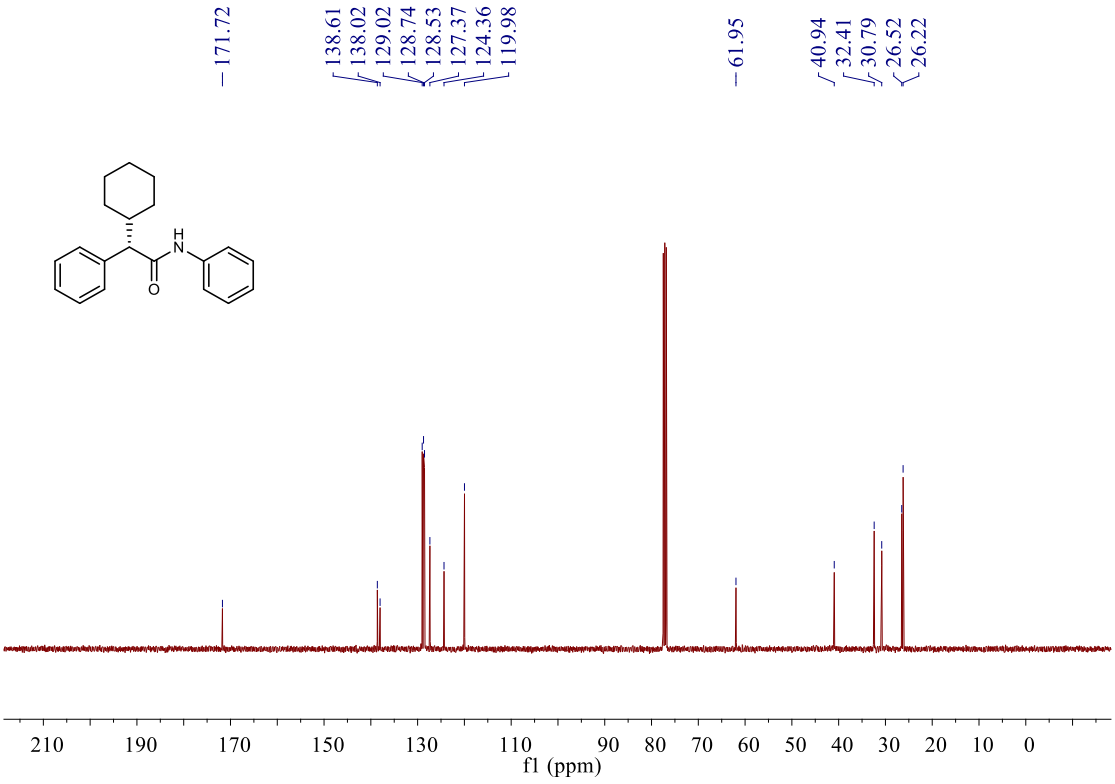
Compound 9 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



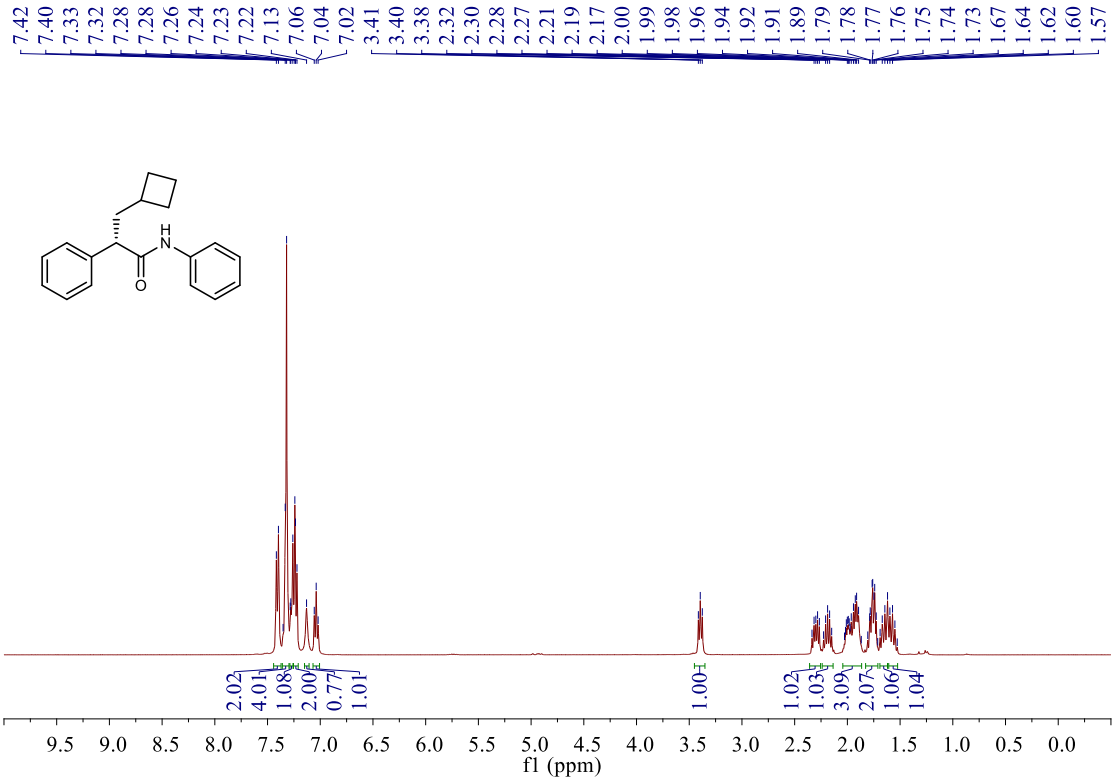


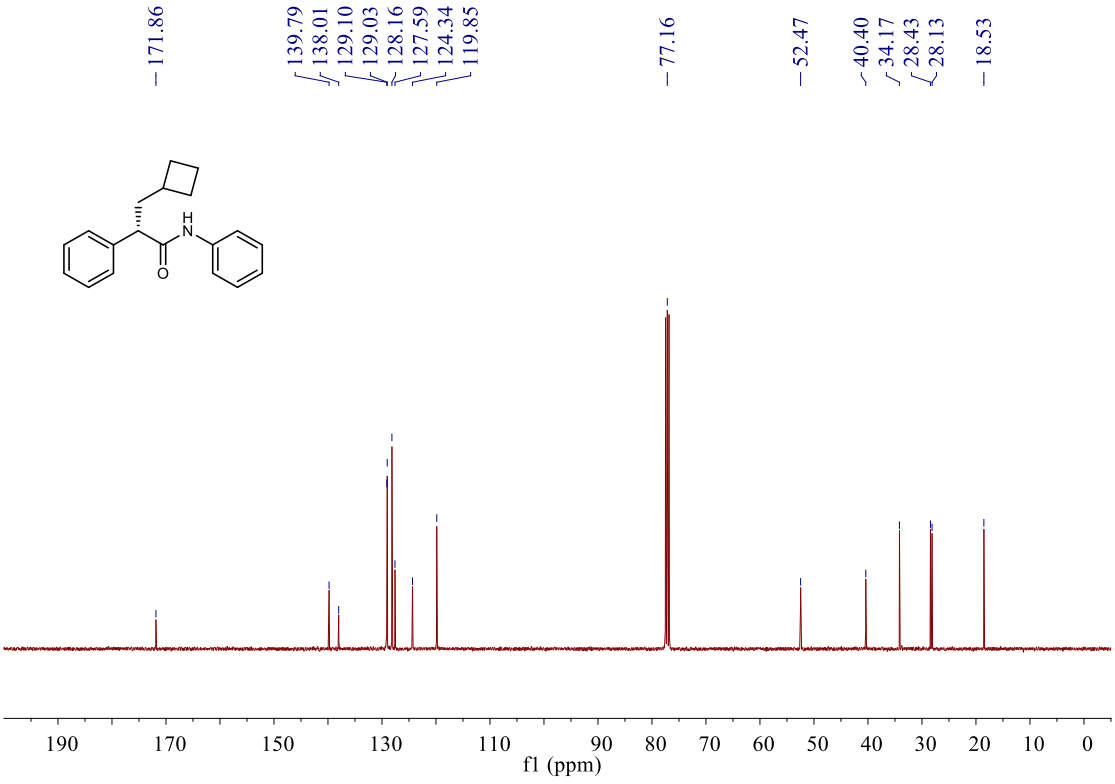
Compound 10 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



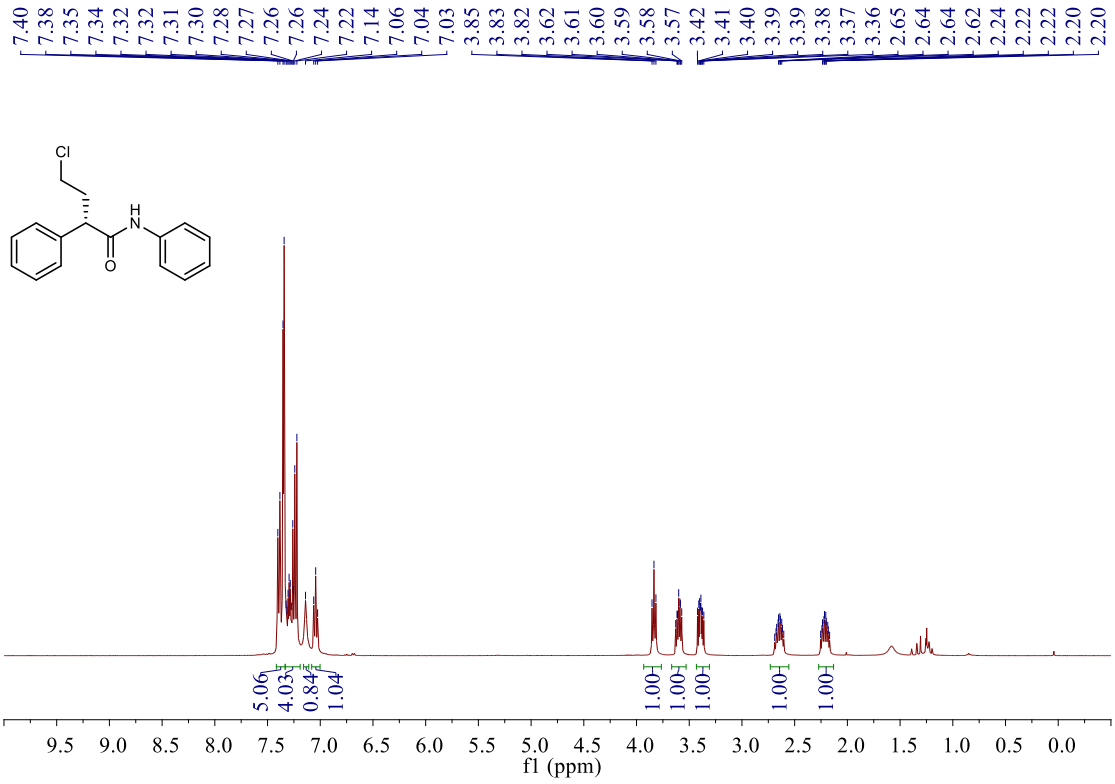


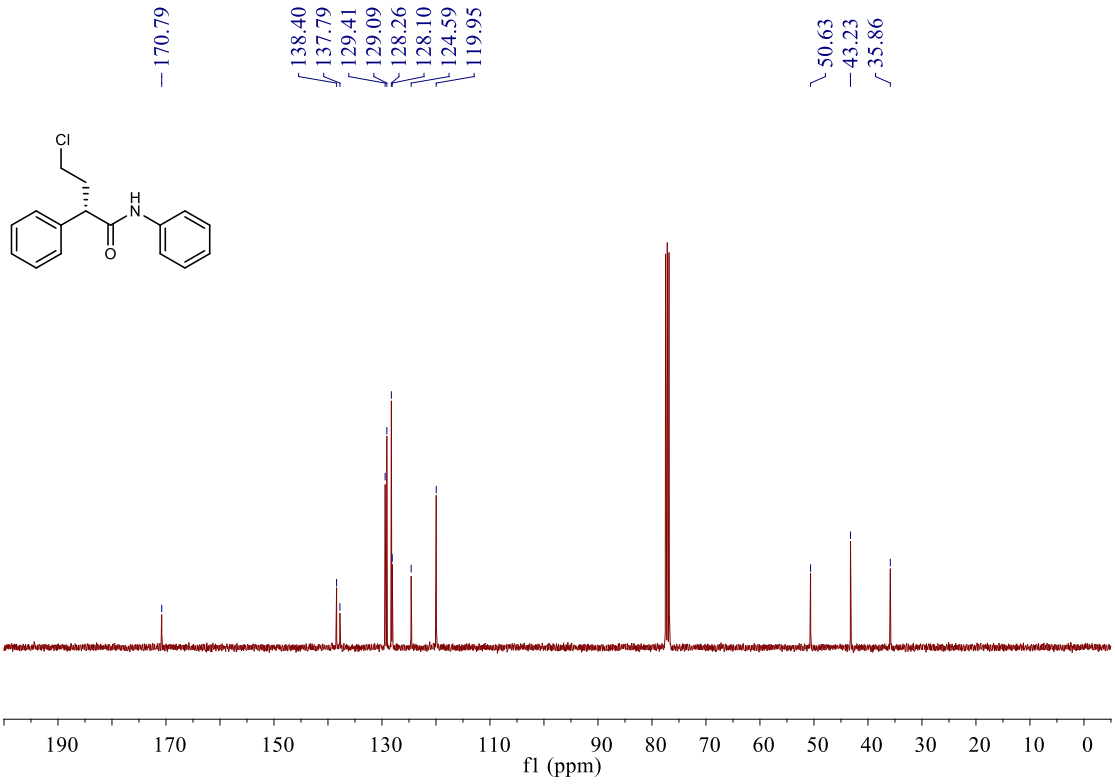
Compound 11 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)


7.42
7.40
7.33
7.32
7.28
7.28
7.26
7.24
7.23
7.22
7.13
7.06
7.04
7.02
3.41
3.40
3.38
2.32
2.30
2.28
2.27
2.21
2.19
2.17
2.00
1.99
1.98
1.96
1.94
1.92
1.91
1.89
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.67
1.64
1.62
1.60
1.57
H
N
O
2.02
4.01
1.08
2.00
0.77
1.01
1.00
1.02
1.03
3.09
2.07
1.06
1.04
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)

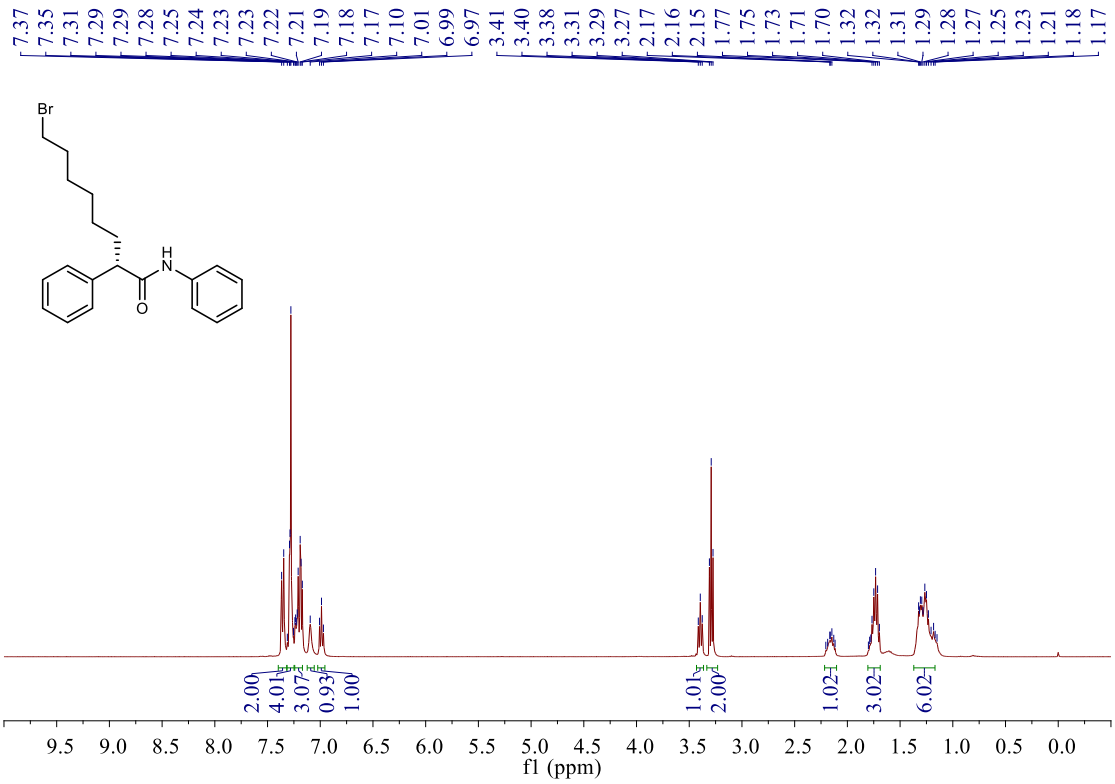

171.86
139.79
138.01
129.10
129.03
128.16
127.59
124.34
119.85
77.16
52.47
40.40
34.17
28.43
28.13
18.53
H
N
O
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

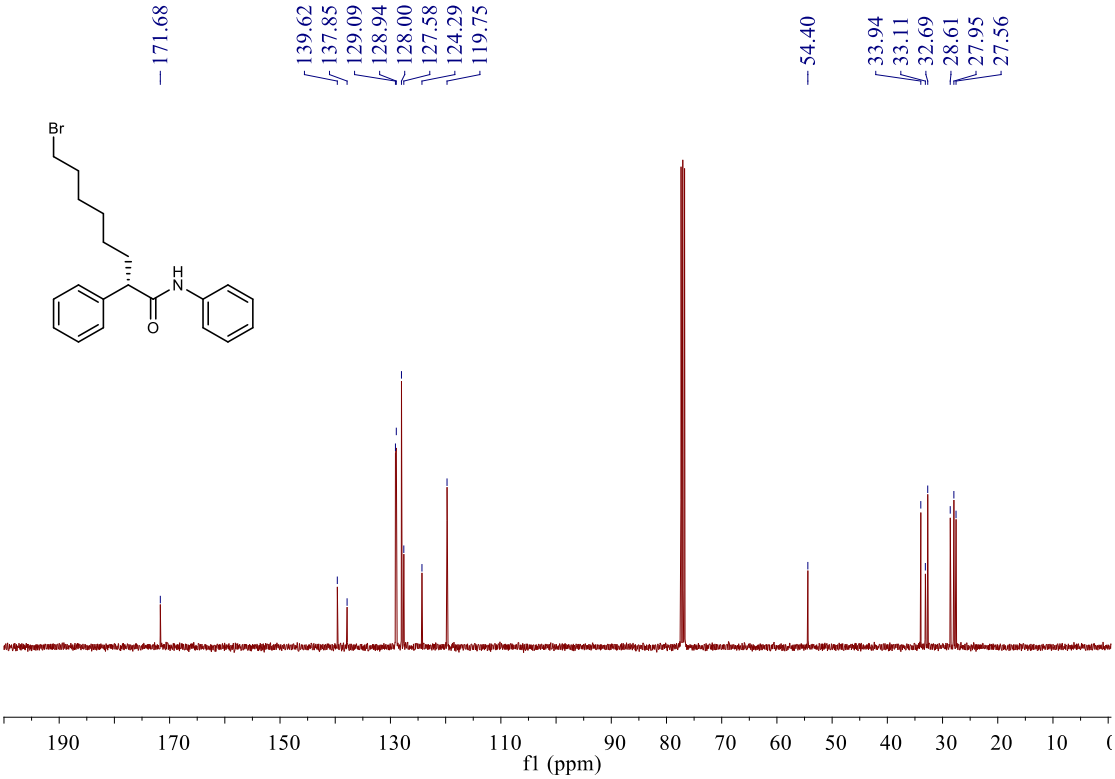
Compound 12 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



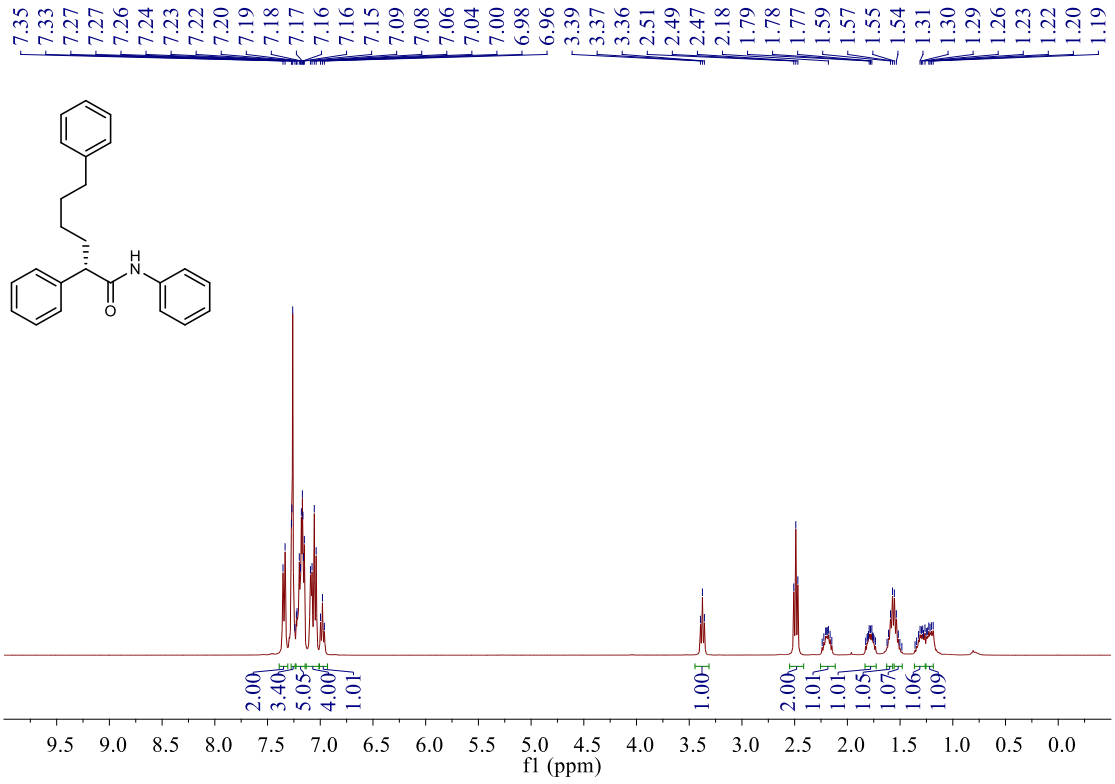


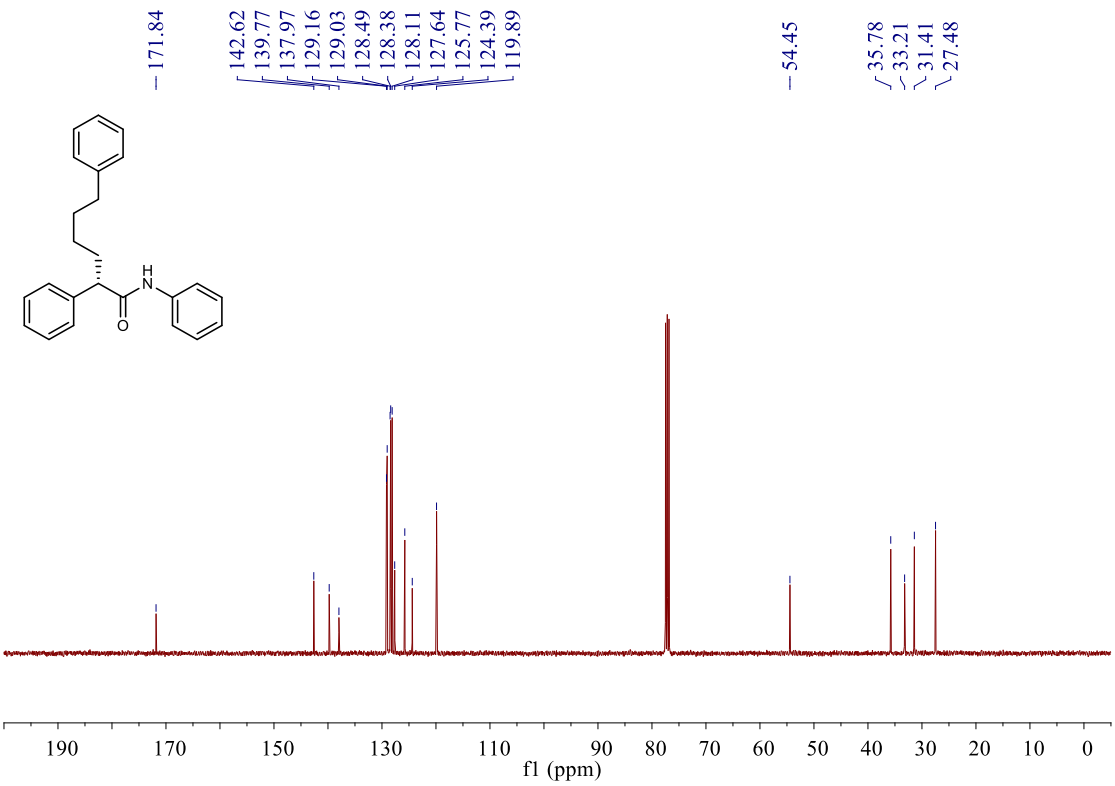
Compound 13 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



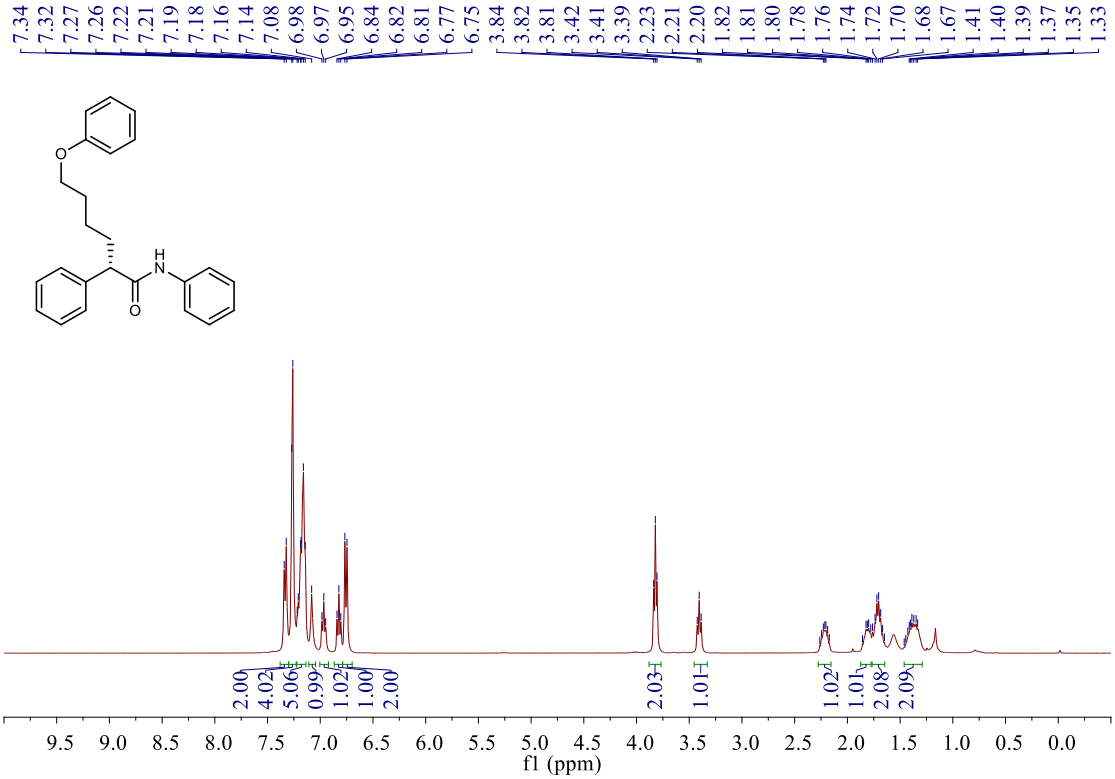


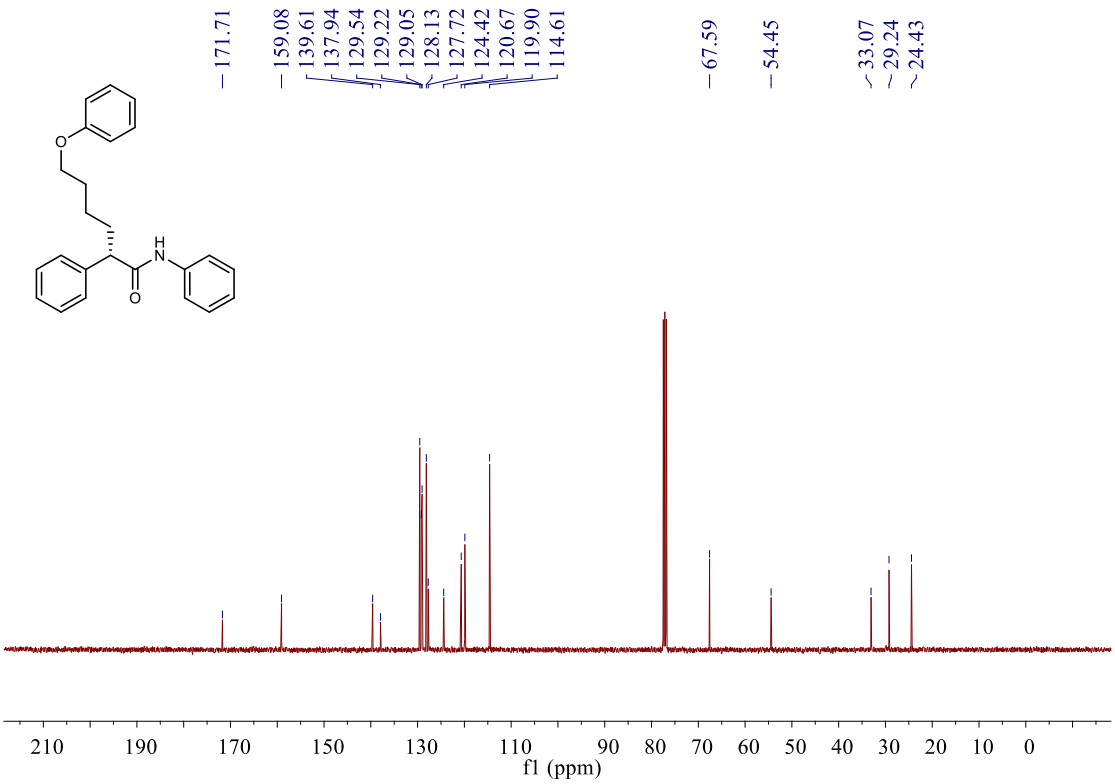
Compound 14 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



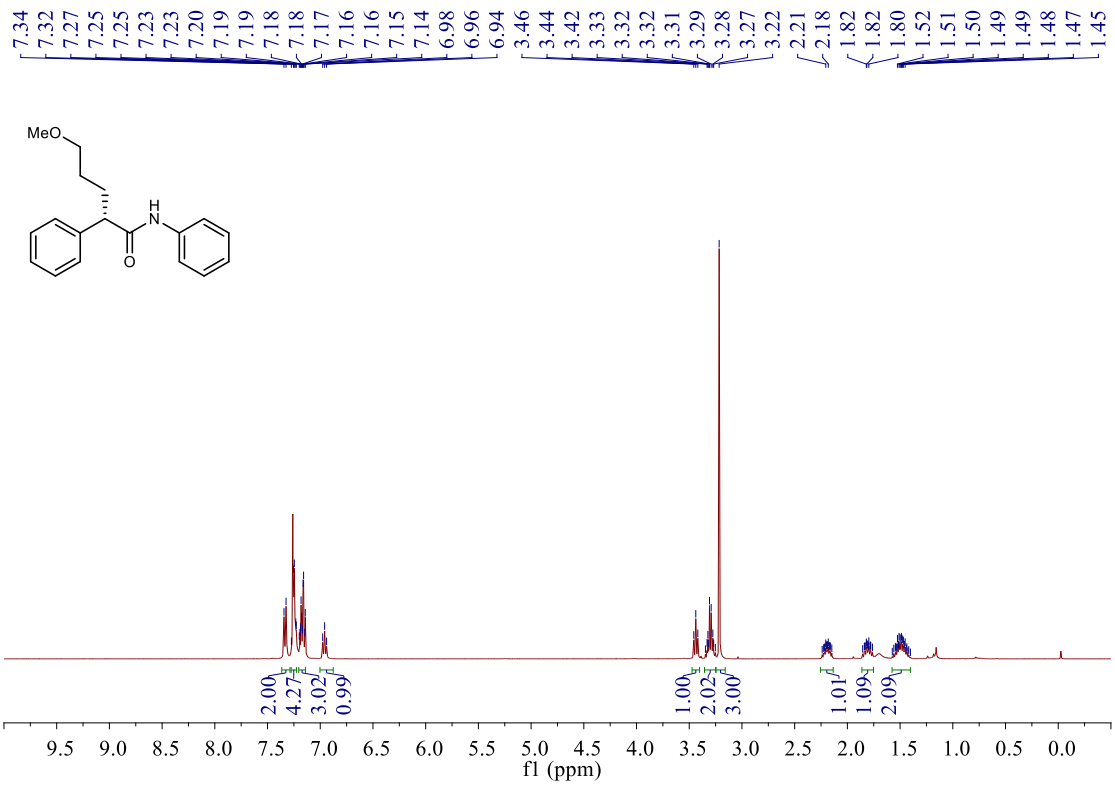


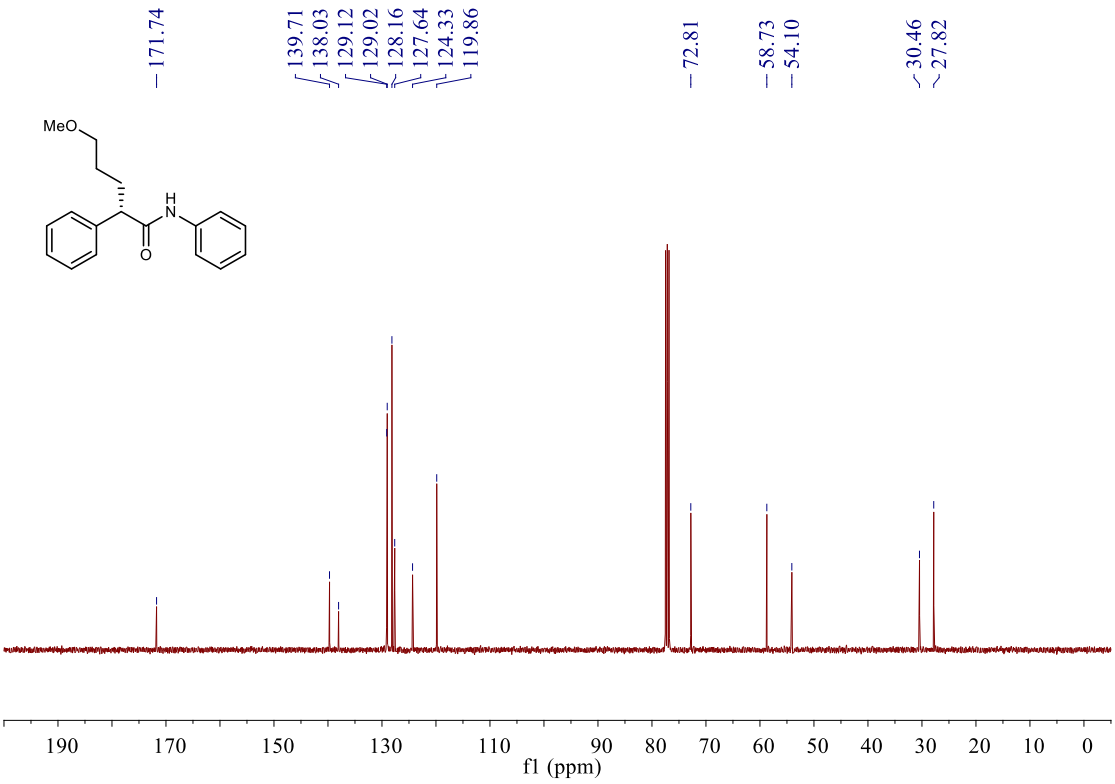
Compound 15 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



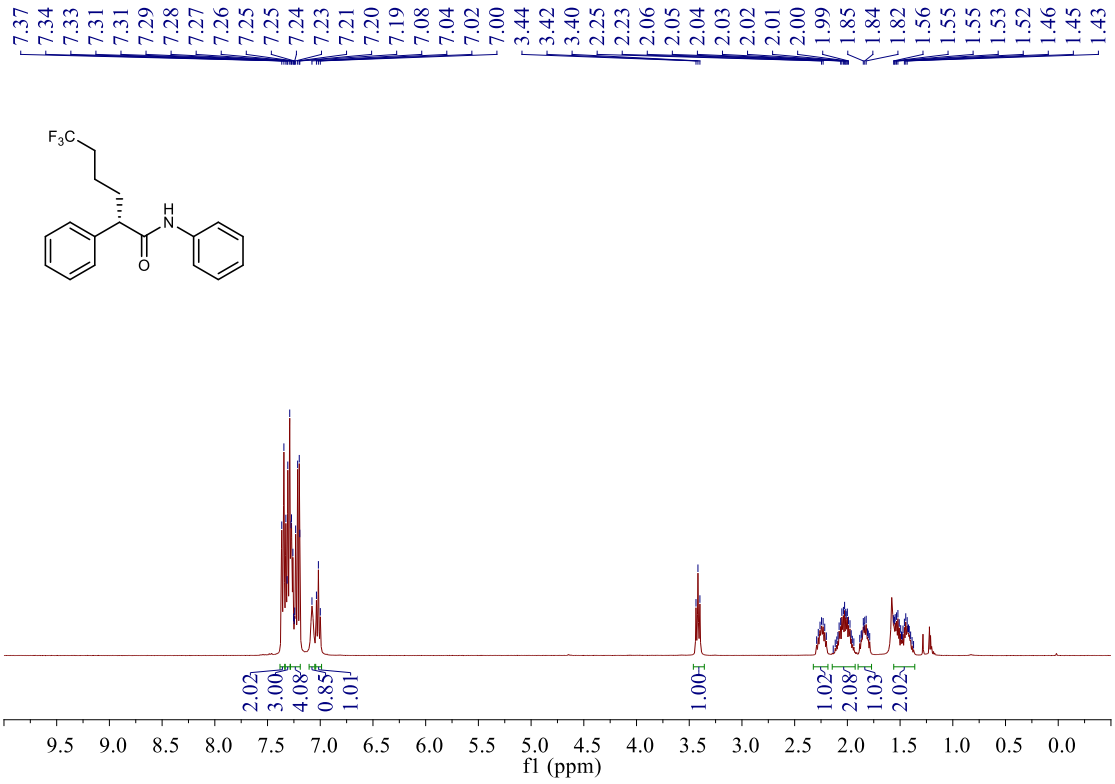


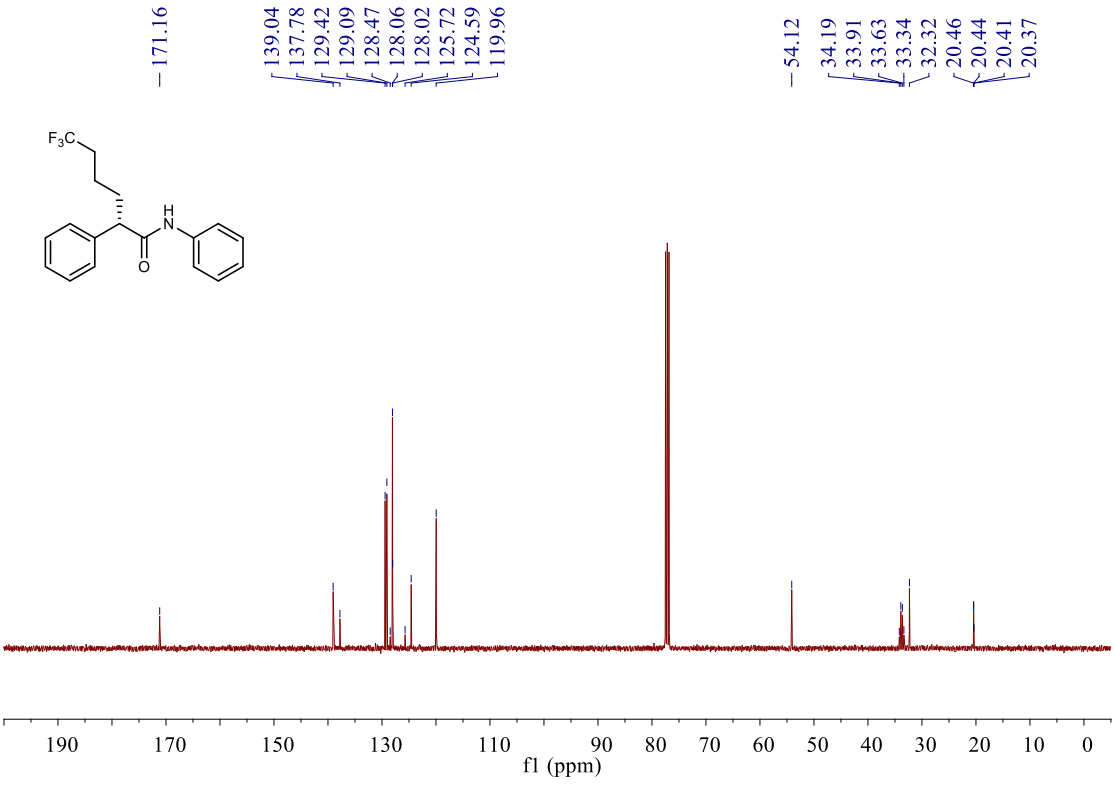
Compound 16 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

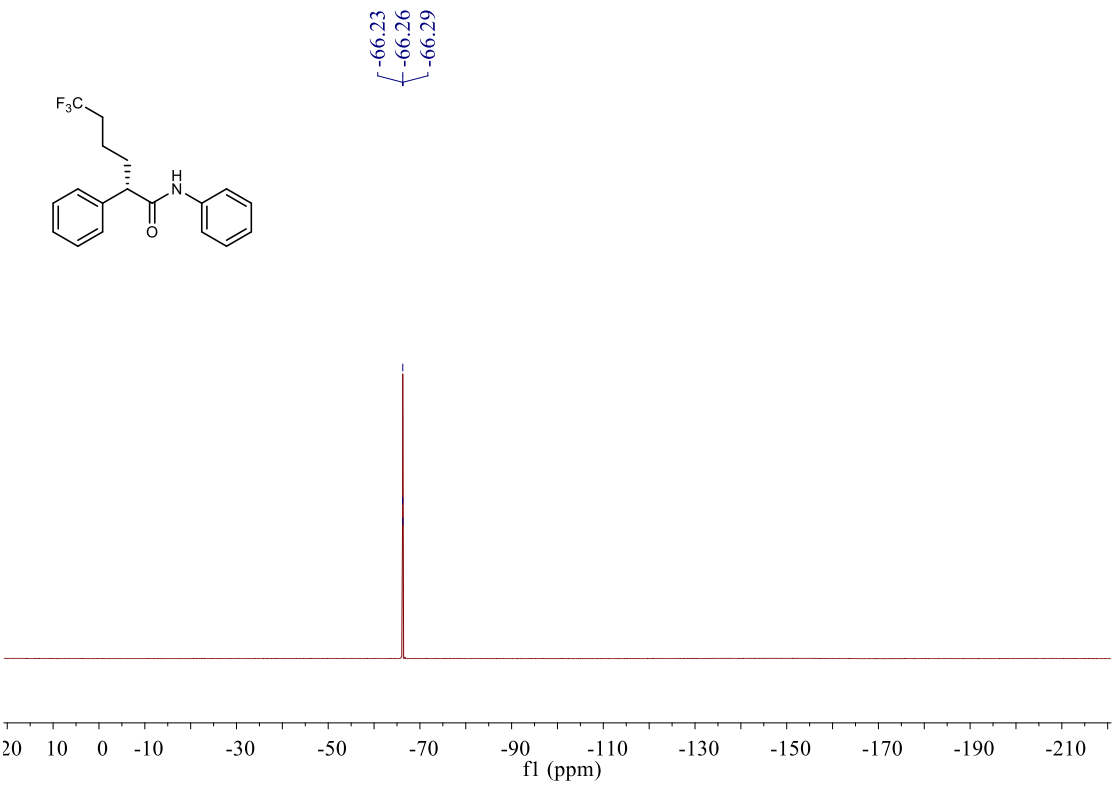

7.34
7.32
7.27
7.25
7.25
7.23
7.23
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.14
6.98
6.96
6.94
3.46
3.44
3.42
3.33
3.32
3.32
3.31
3.29
3.28
3.27
3.22
2.21
2.18
1.82
1.82
1.80
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.45
MeO
H
N
O
2.00
4.27
3.02
0.99
1.00
2.02
3.00
1.01
1.09
2.09
9.5 9.0 8.5 8.0 7.5 7.0 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)


171.74
139.71
138.03
129.12
129.02
128.16
127.64
124.33
119.86
72.81
58.73
54.10
30.46
27.82
MeO
H
N
O
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

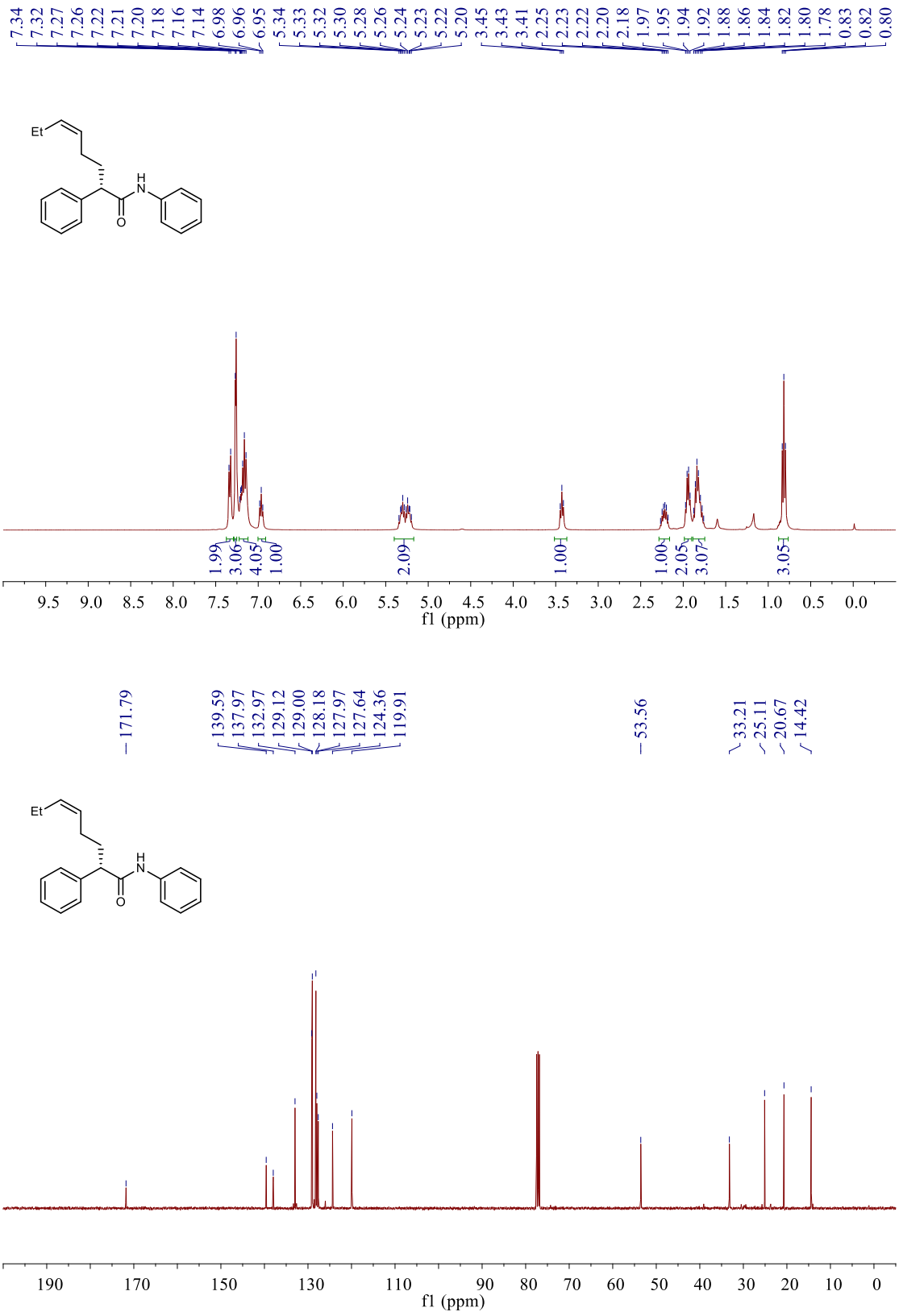
Compound 17 (^{1}H NMR, ^{13}C NMR and ^{19}F NMR, $CDCl_3$, 400 MHz, 101 MHz and 377 MHz respectively)



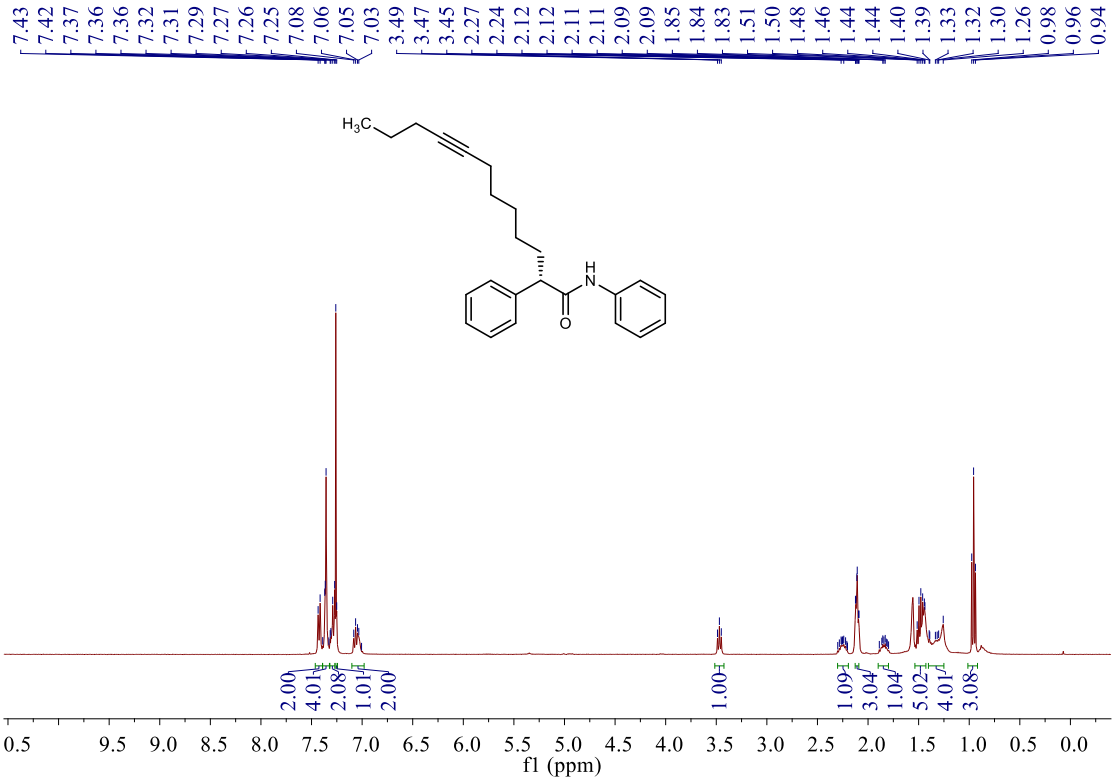


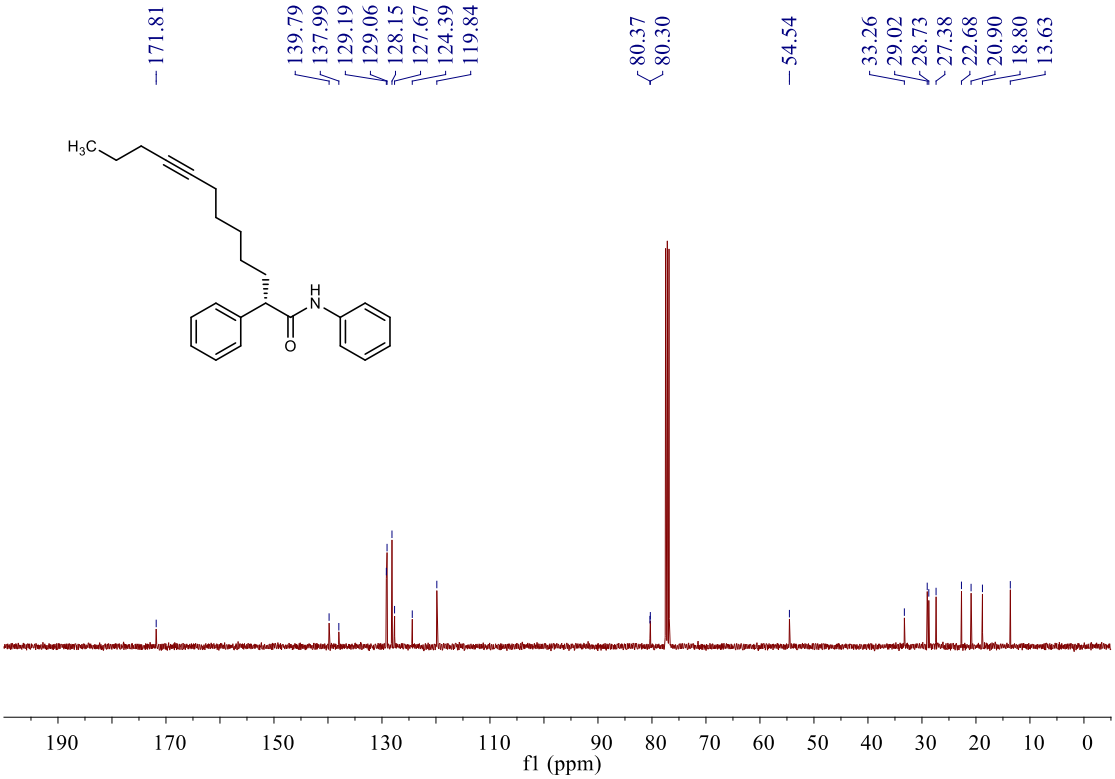

-66.23
-66.26
-66.29
F3C
H
N
O
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

Compound 18 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

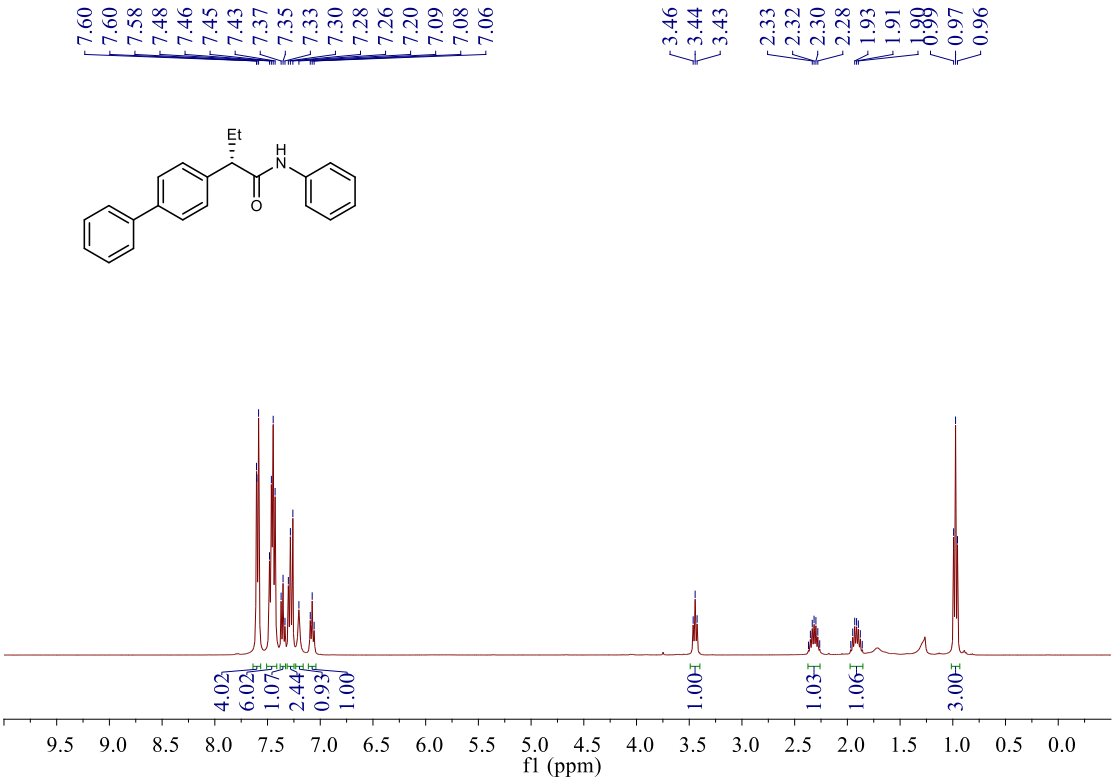


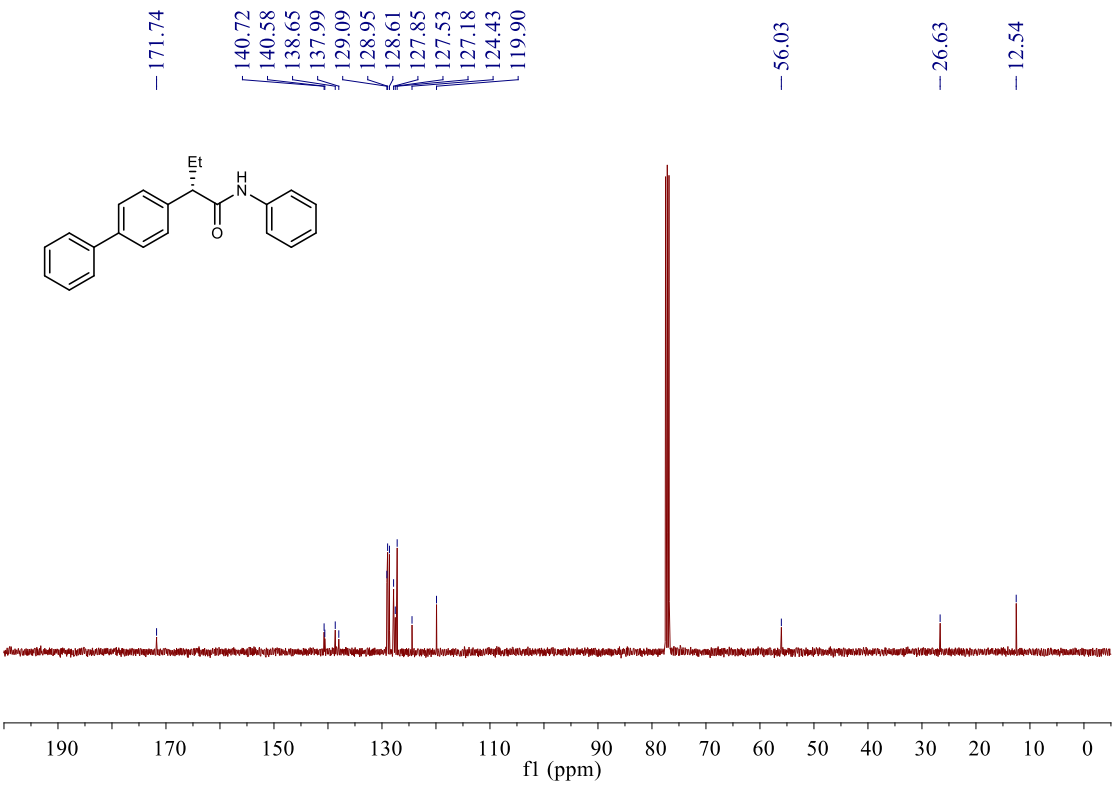
Compound 19 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



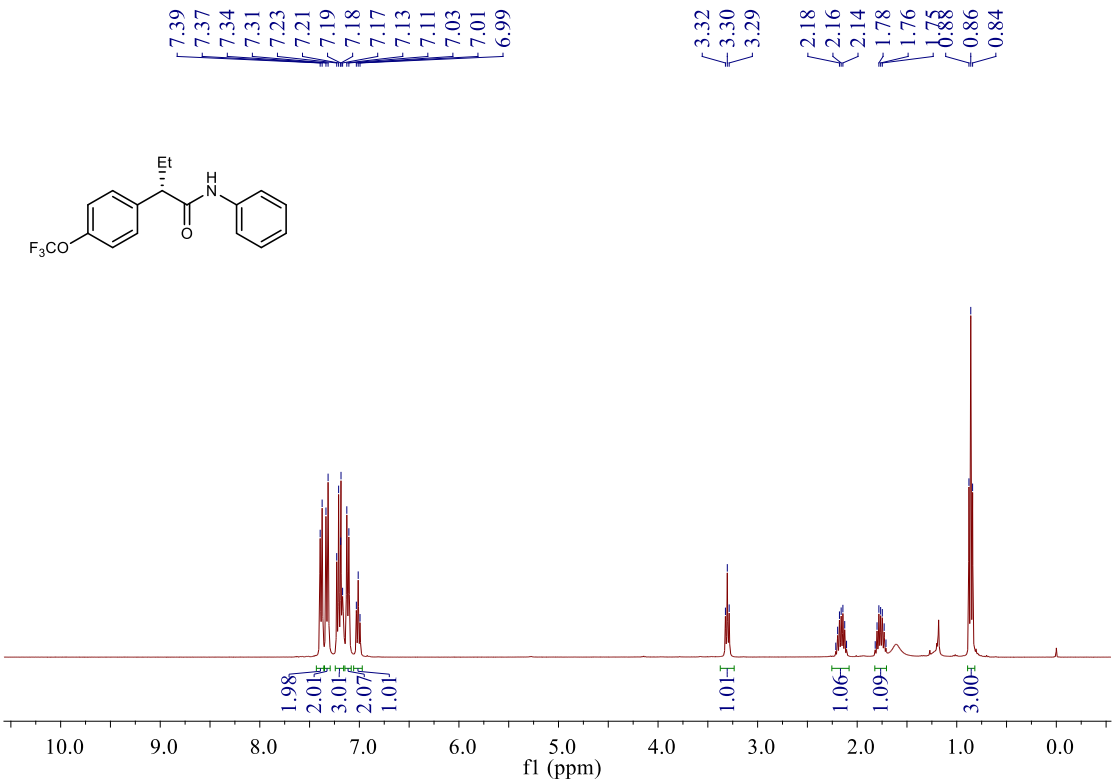


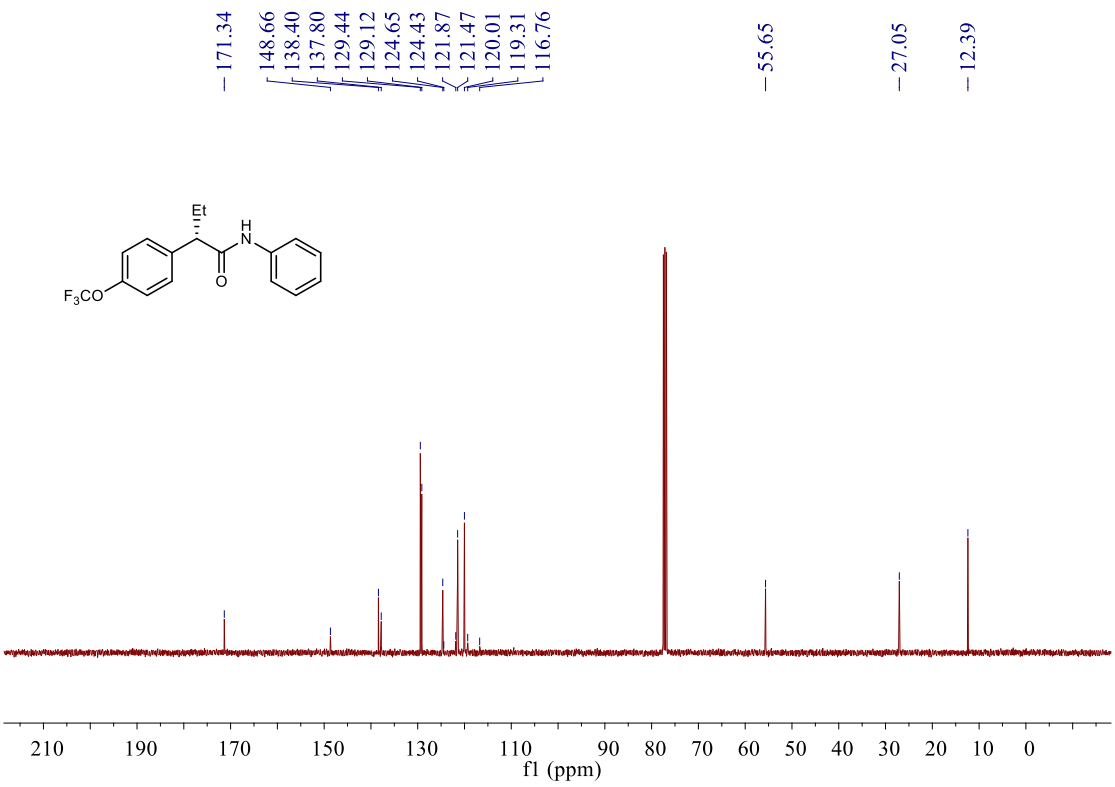
Compound 20 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

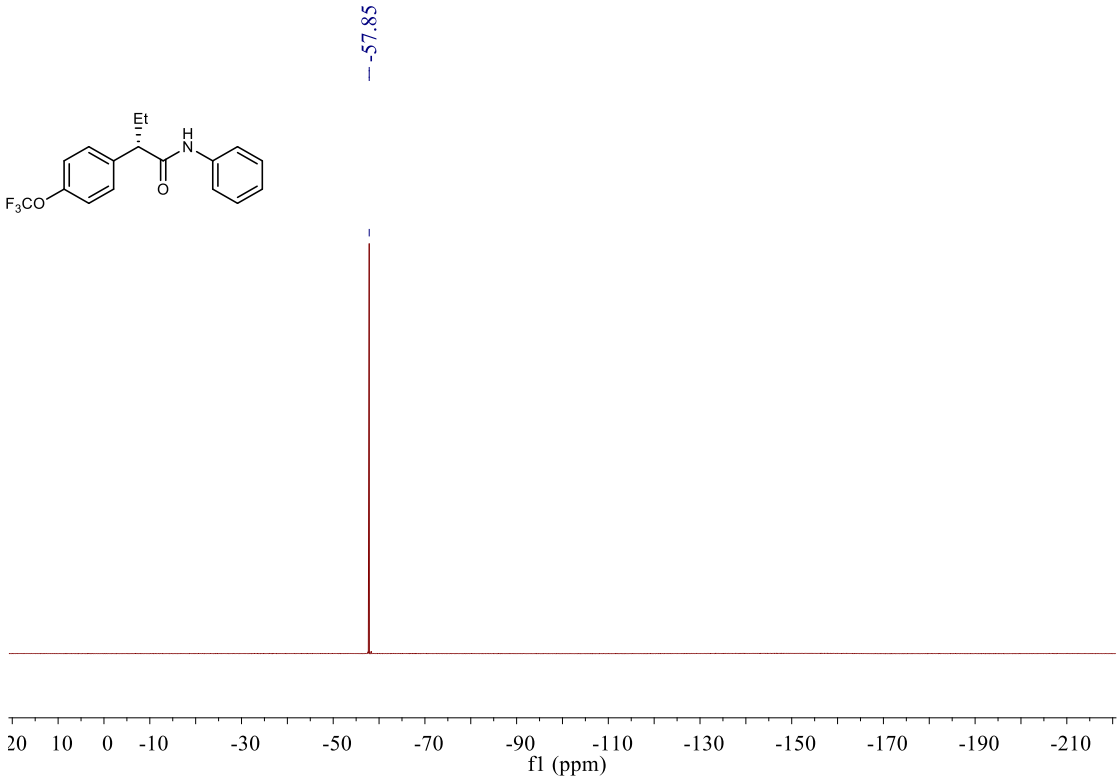




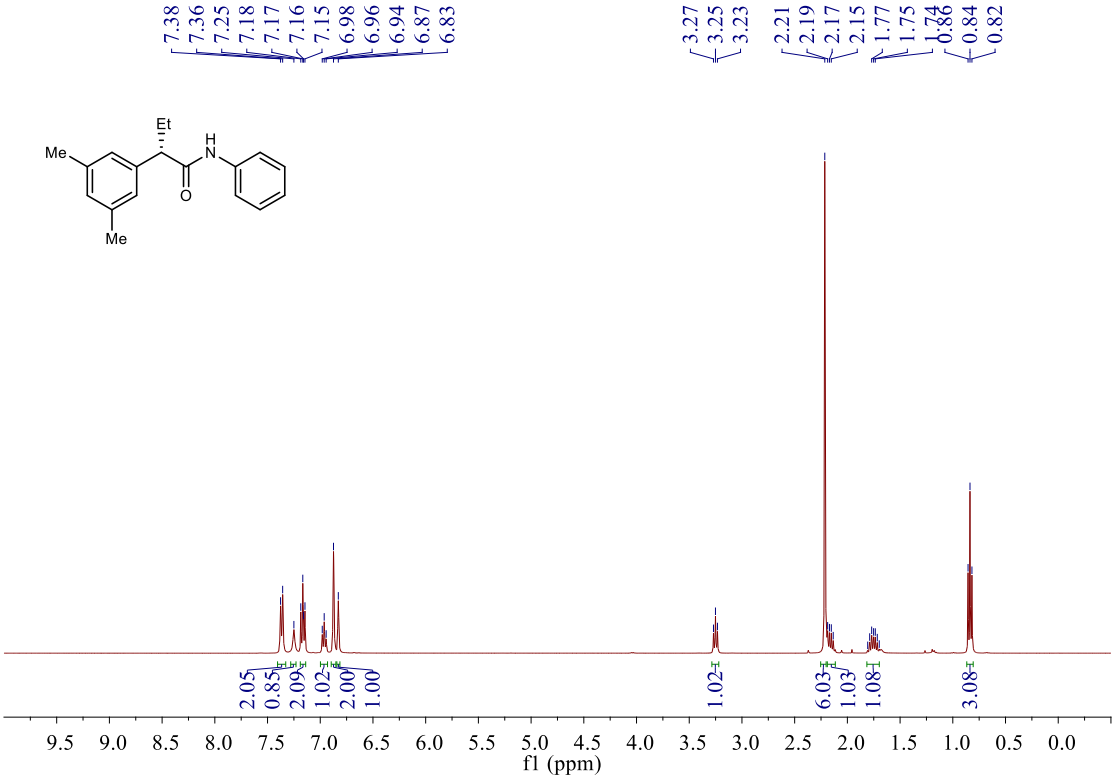
Compound 21 (^{1}H NMR, ^{13}C NMR and ^{19}F NMR, $CDCl_3$, 400 MHz, 101 MHz and 377 MHz respectively)

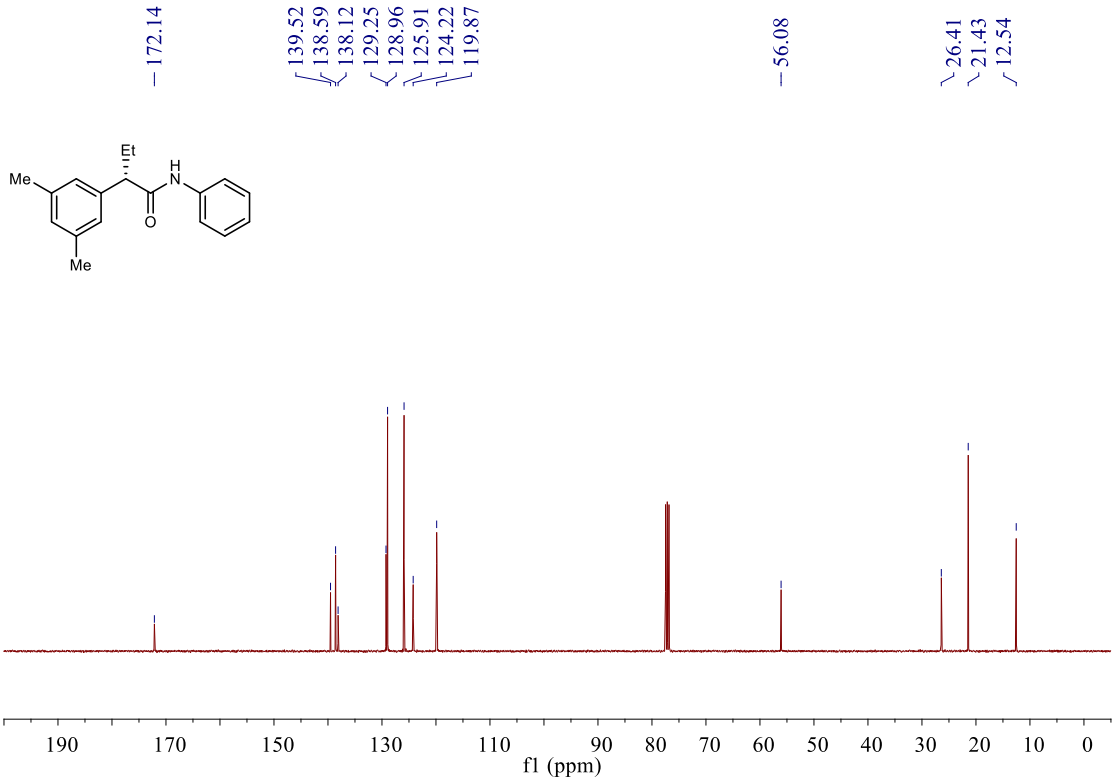

7.39
7.37
7.34
7.31
7.23
7.21
7.19
7.18
7.17
7.13
7.11
7.03
7.01
6.99
3.32
3.30
3.29
2.18
2.16
2.14
1.78
1.76
1.75
1.88
0.86
0.84
Et
H
N
O
F3CO
1.98
2.01
3.01
2.07
1.01
1.01
1.06
1.09
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.34
148.66
138.40
137.80
129.44
129.12
124.65
124.43
121.87
121.47
120.01
119.31
116.76
55.65
27.05
12.39
Et
H
N
O
F3CO
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

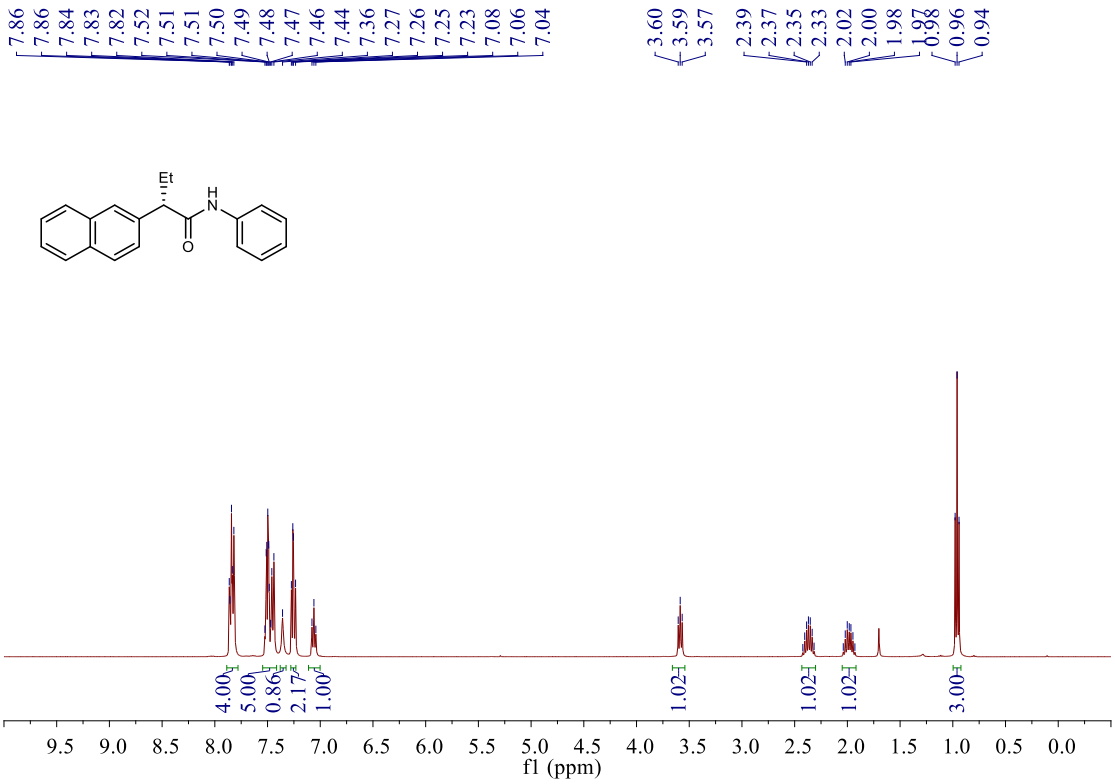

-57.85
Et
H
N
O
F3CO
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

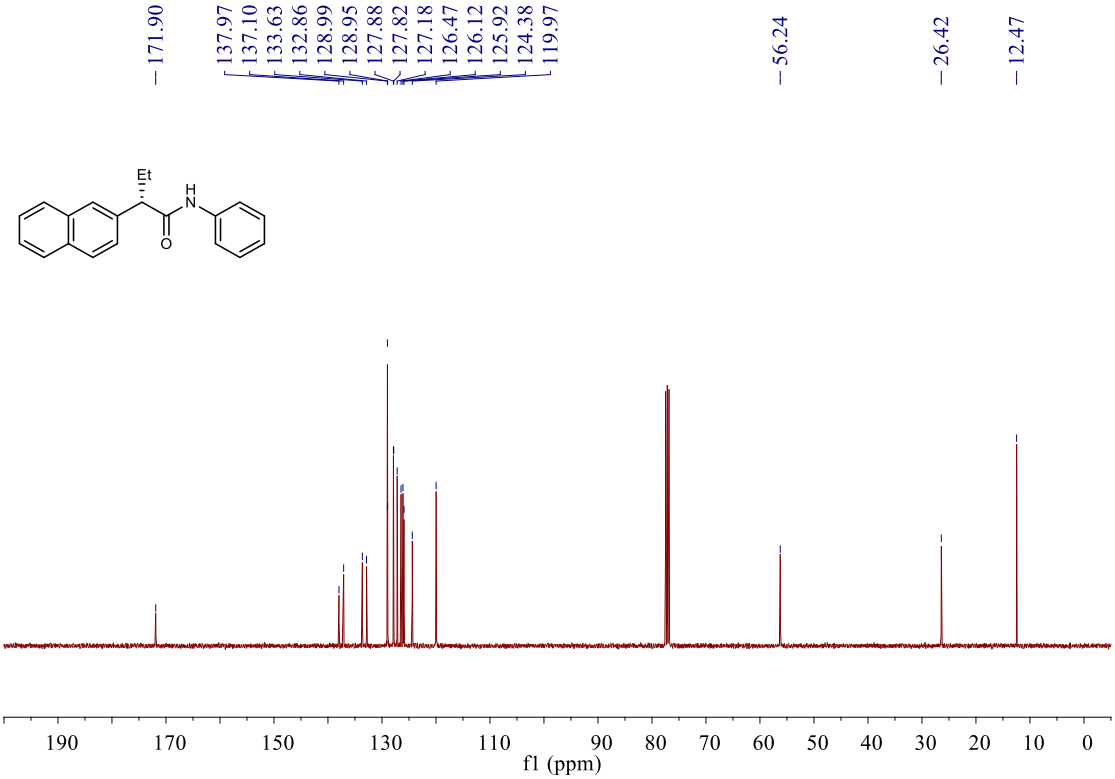
Compound 22 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



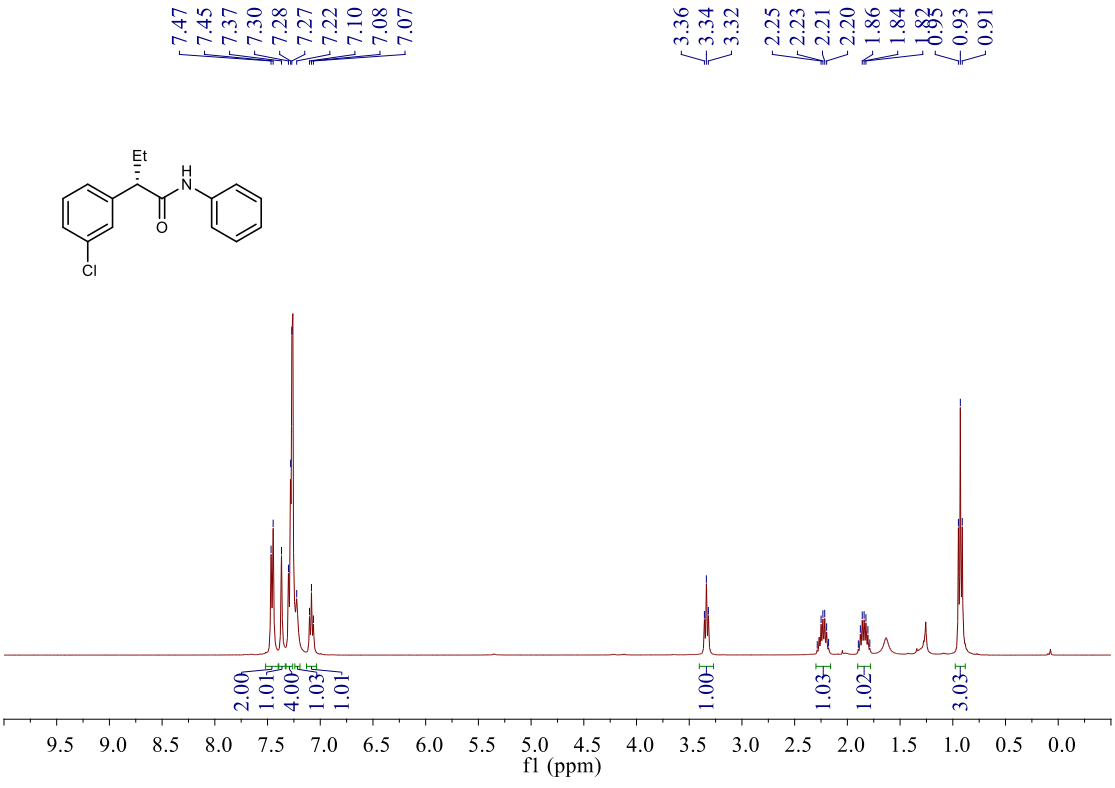


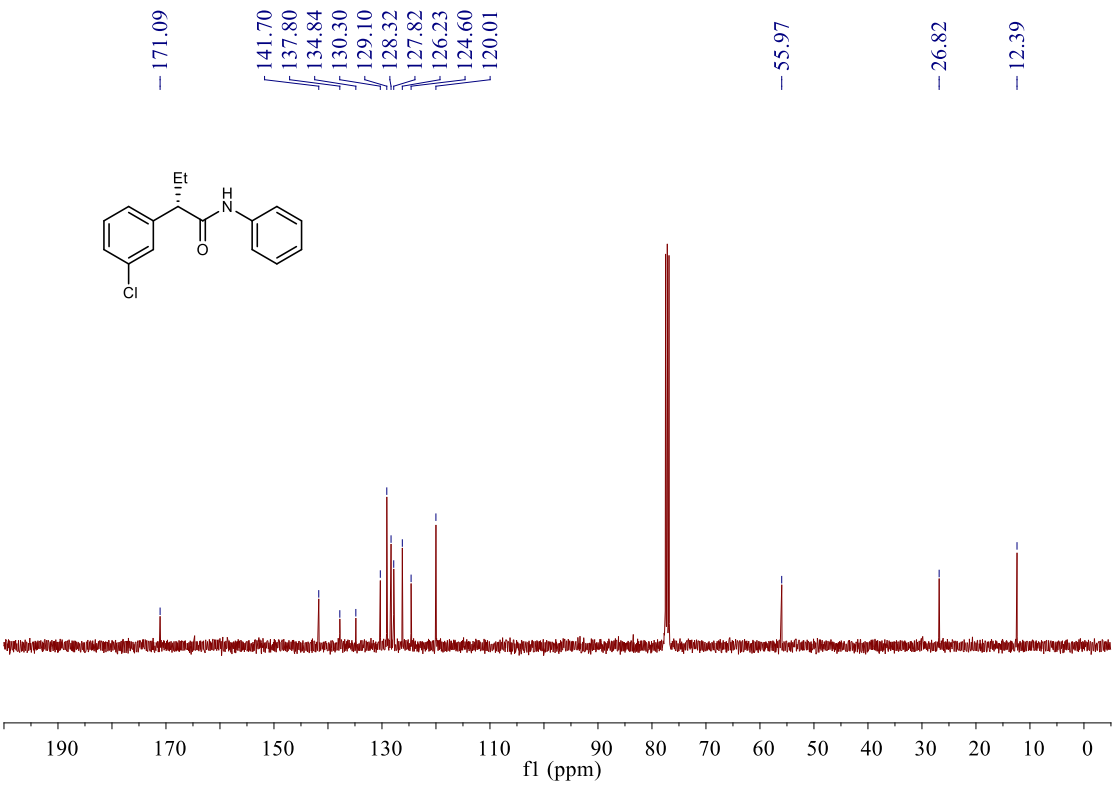
Compound 23 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



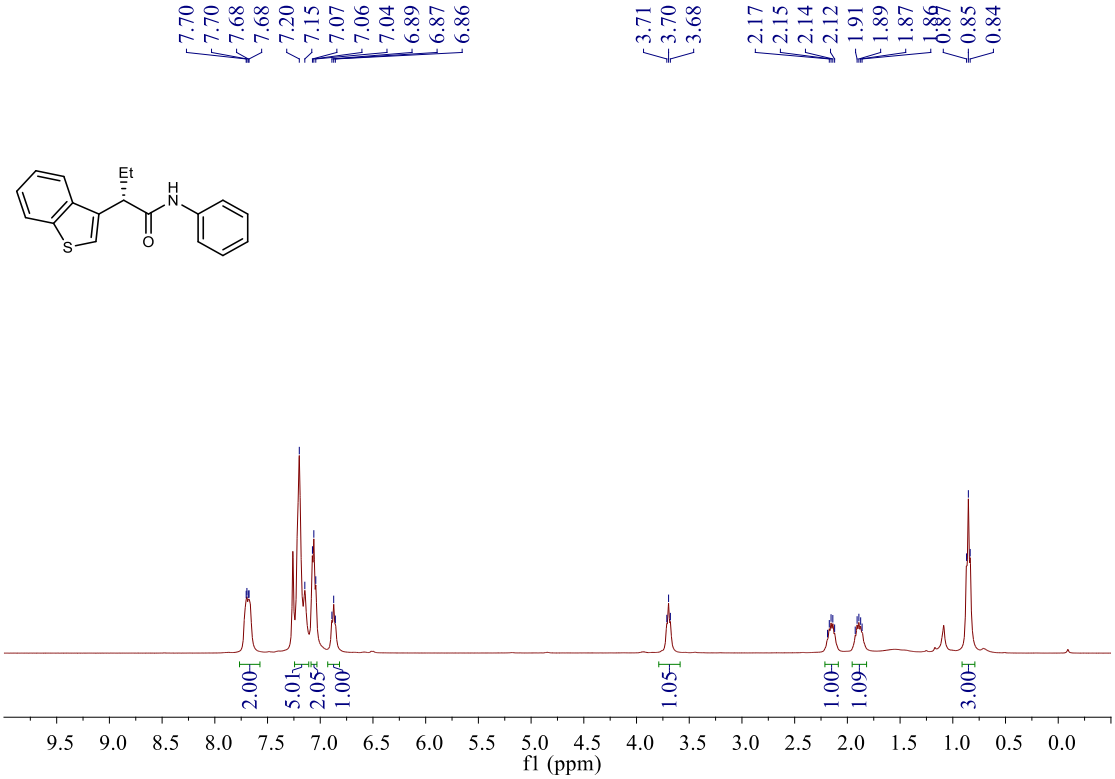


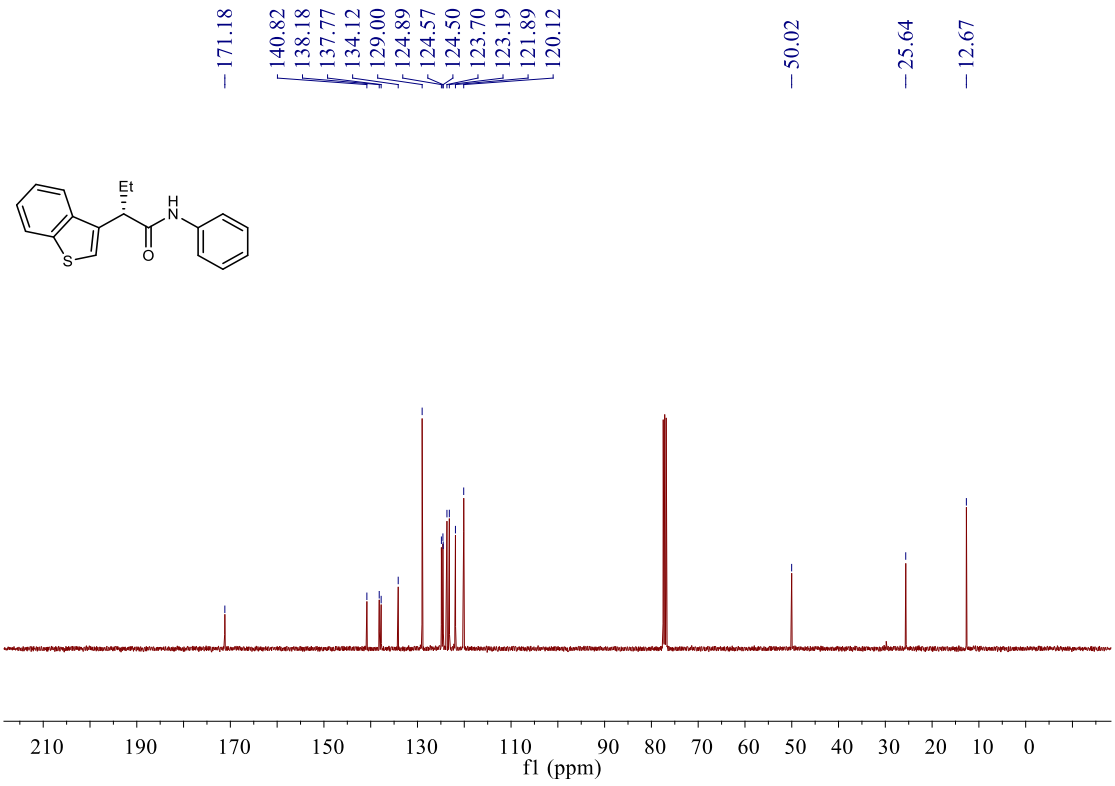
Compound 24 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



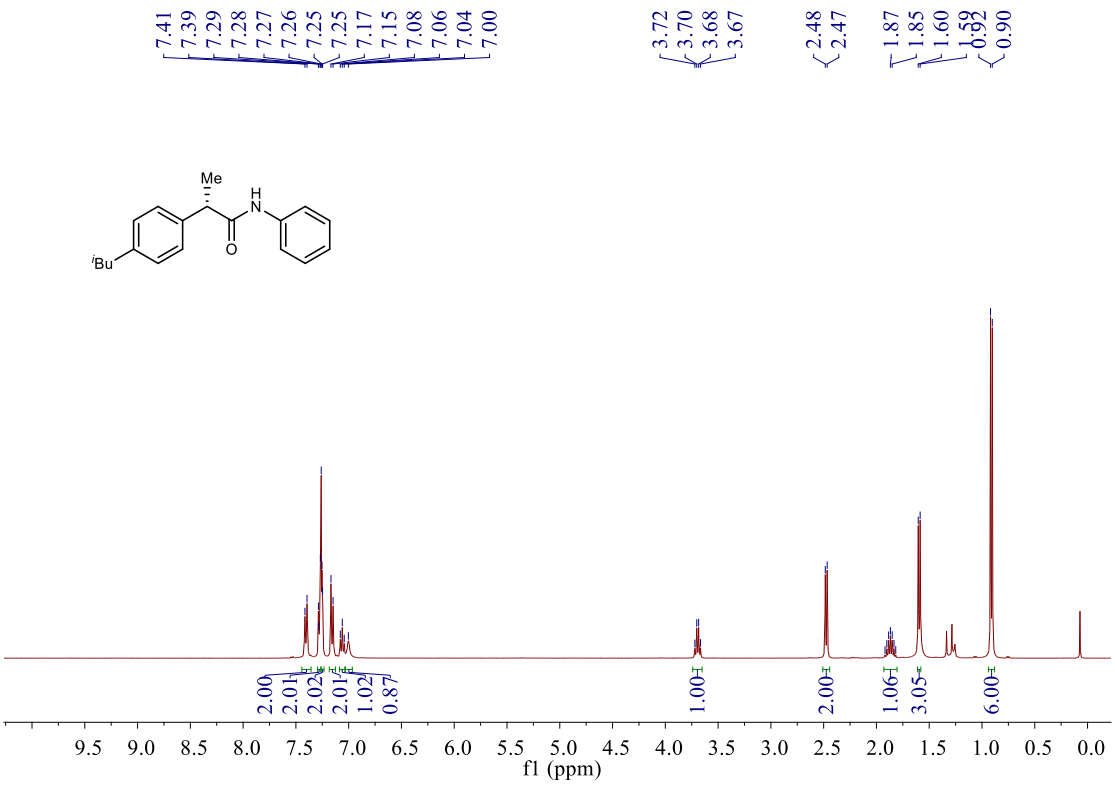


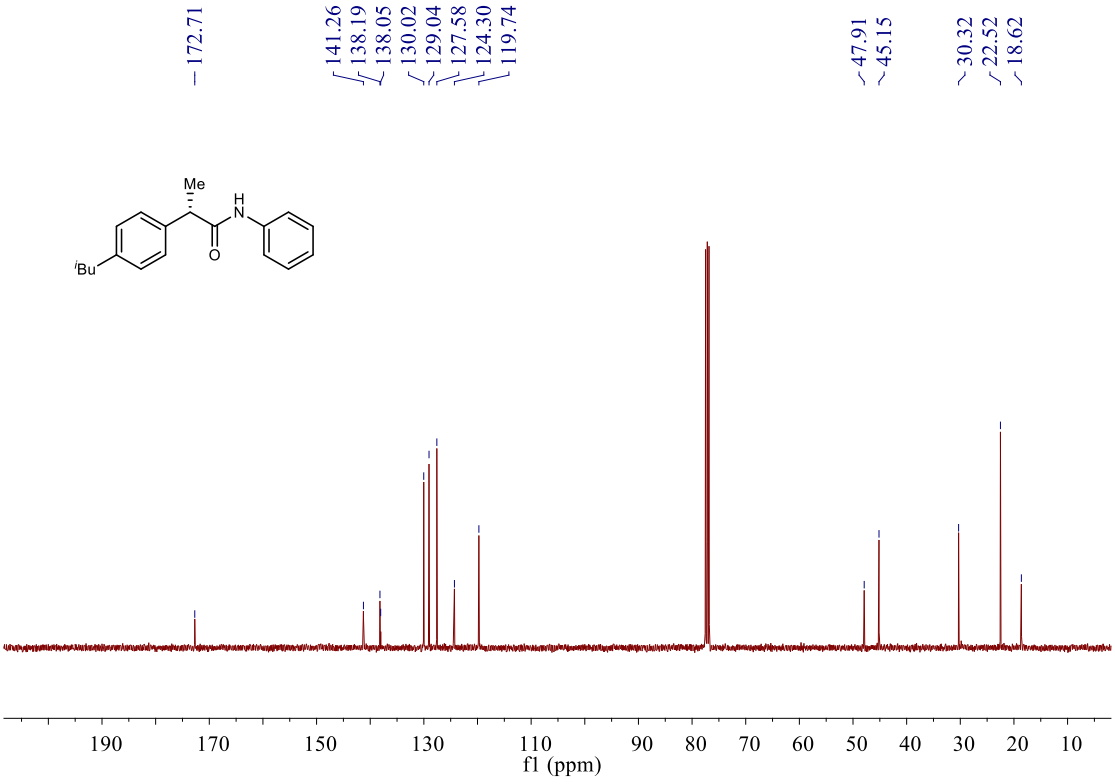
Compound 25 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



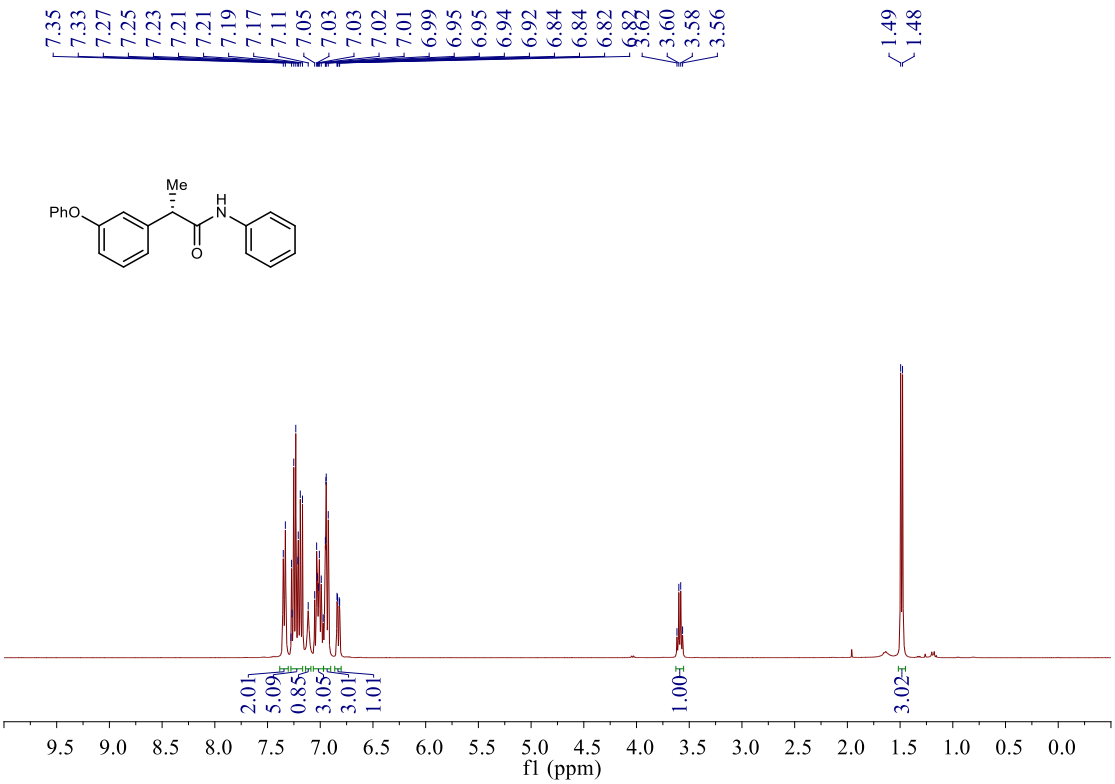


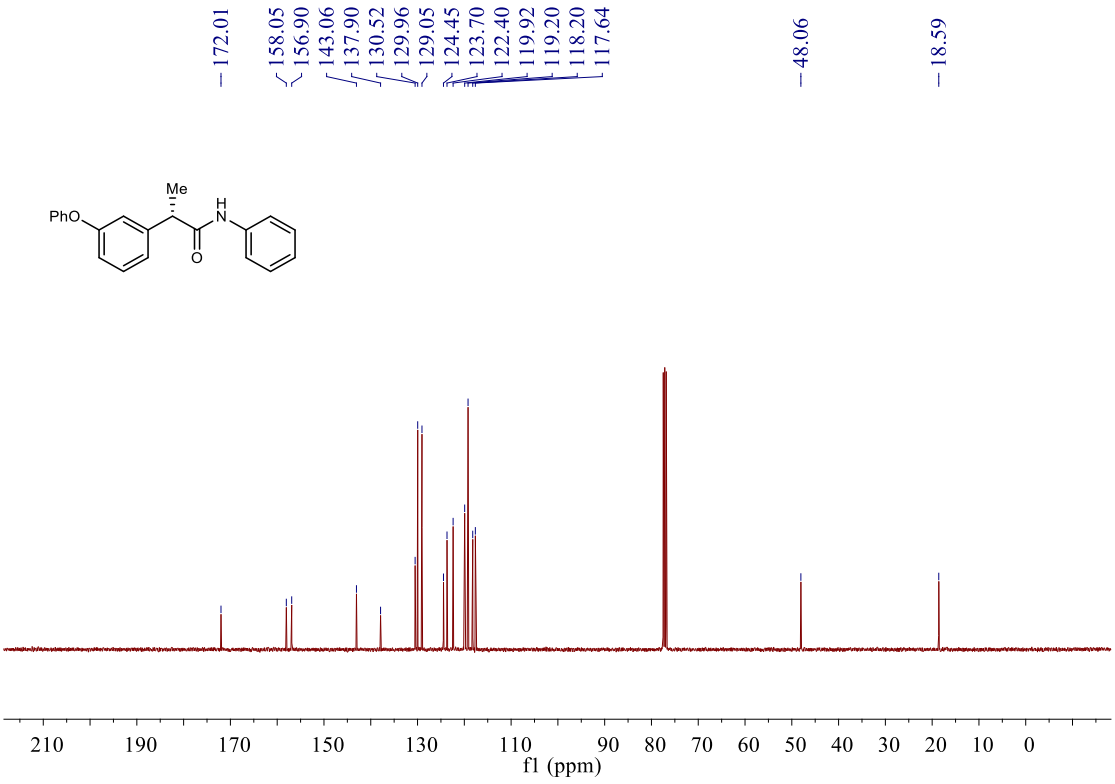
Compound 26 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)


7.41
7.39
7.29
7.28
7.27
7.26
7.25
7.25
7.17
7.15
7.08
7.06
7.04
7.00
3.72
3.70
3.68
3.67
2.48
2.47
1.87
1.85
1.60
1.59
0.92
0.90
Me
H
N
O
iBu
2.00
2.01
2.02
2.01
1.02
0.87
1.00
2.00
1.06
3.05
6.00
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)

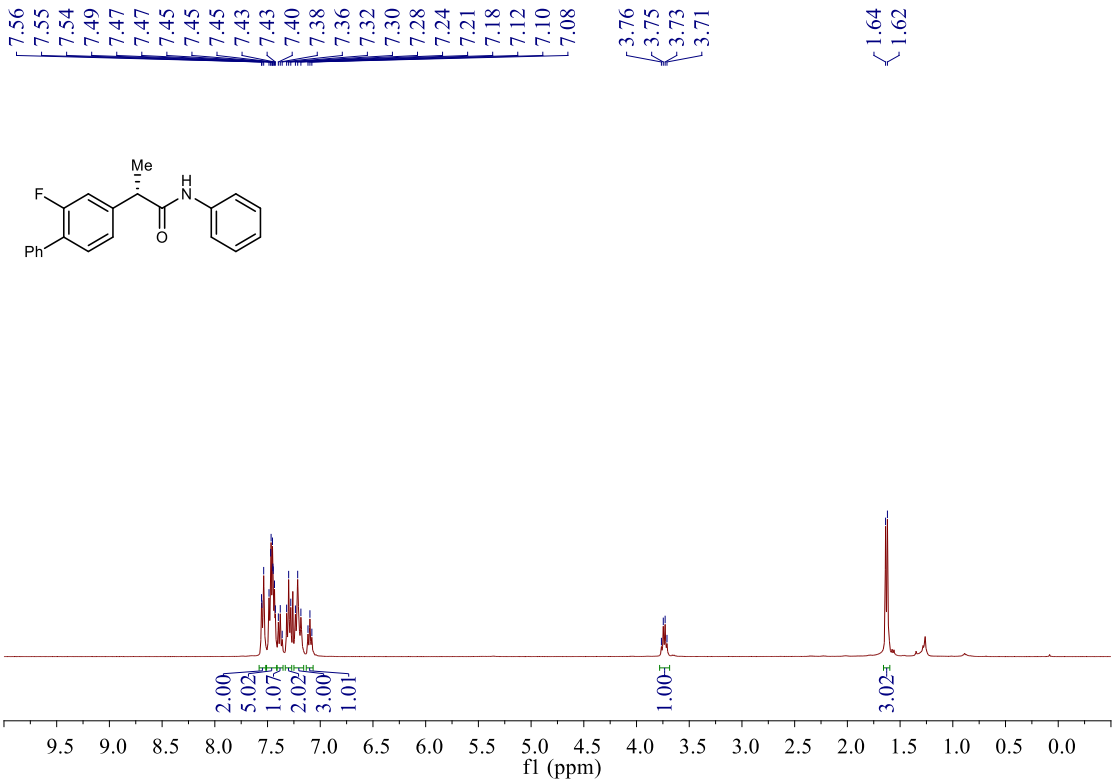

172.71
141.26
138.19
138.05
130.02
129.04
127.58
124.30
119.74
47.91
45.15
30.32
22.52
18.62
Me
H
N
O
iBu
190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)

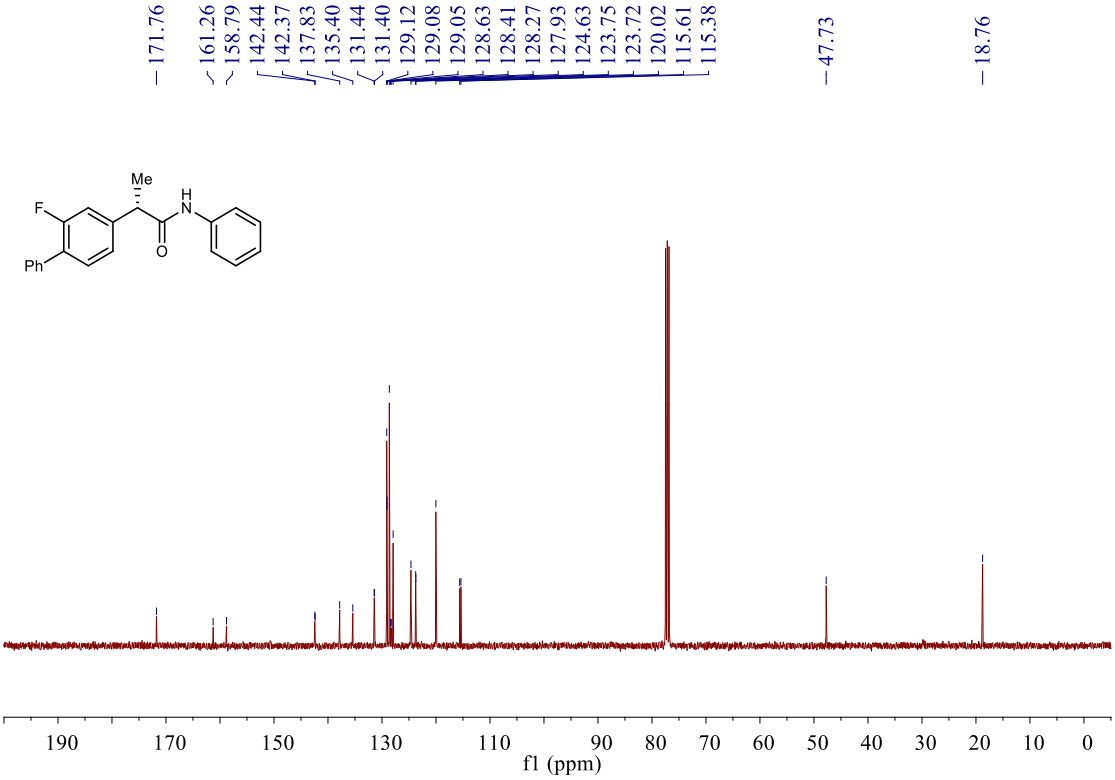
Compound 27 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

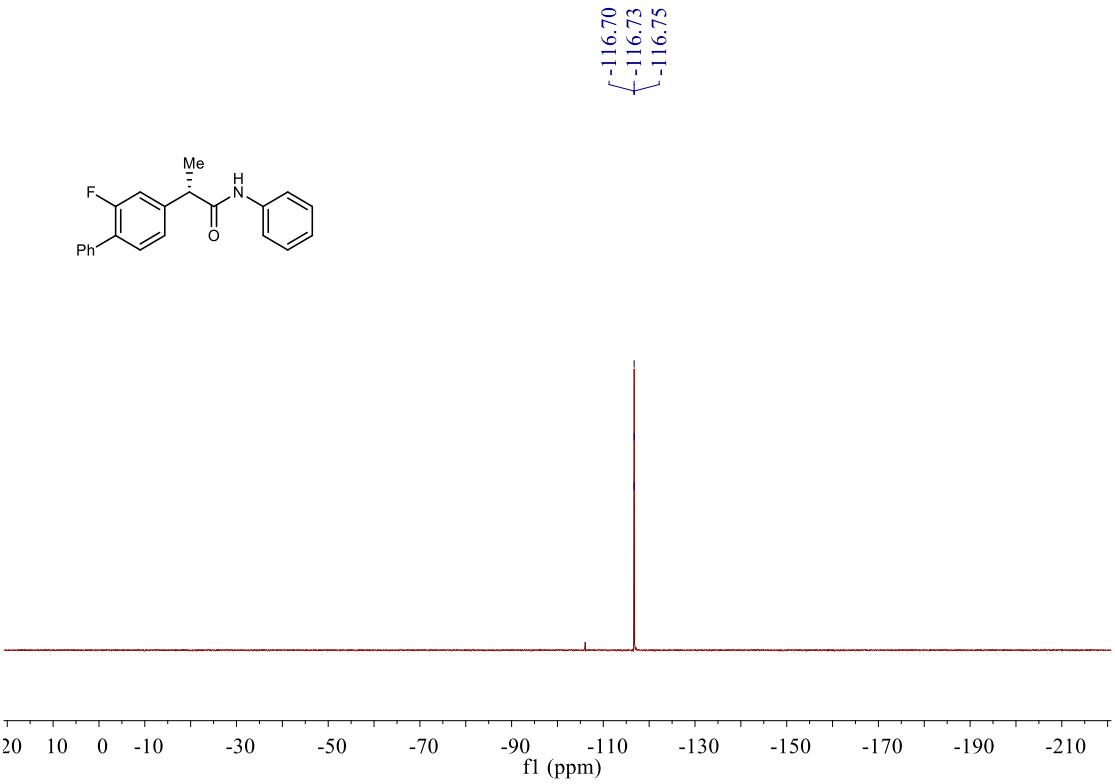




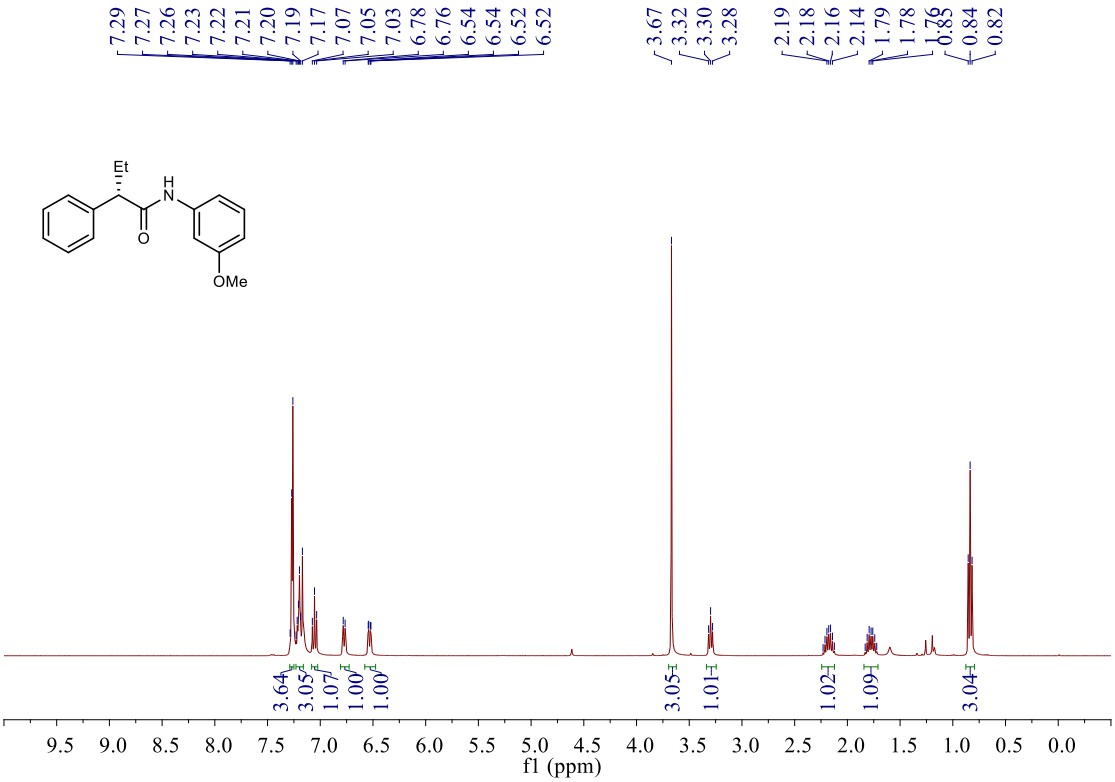
Compound 28 (^{1}H NMR, ^{13}C NMR and ^{19}F NMR, $CDCl_3$, 400 MHz, 101 MHz and 377 MHz respectively)

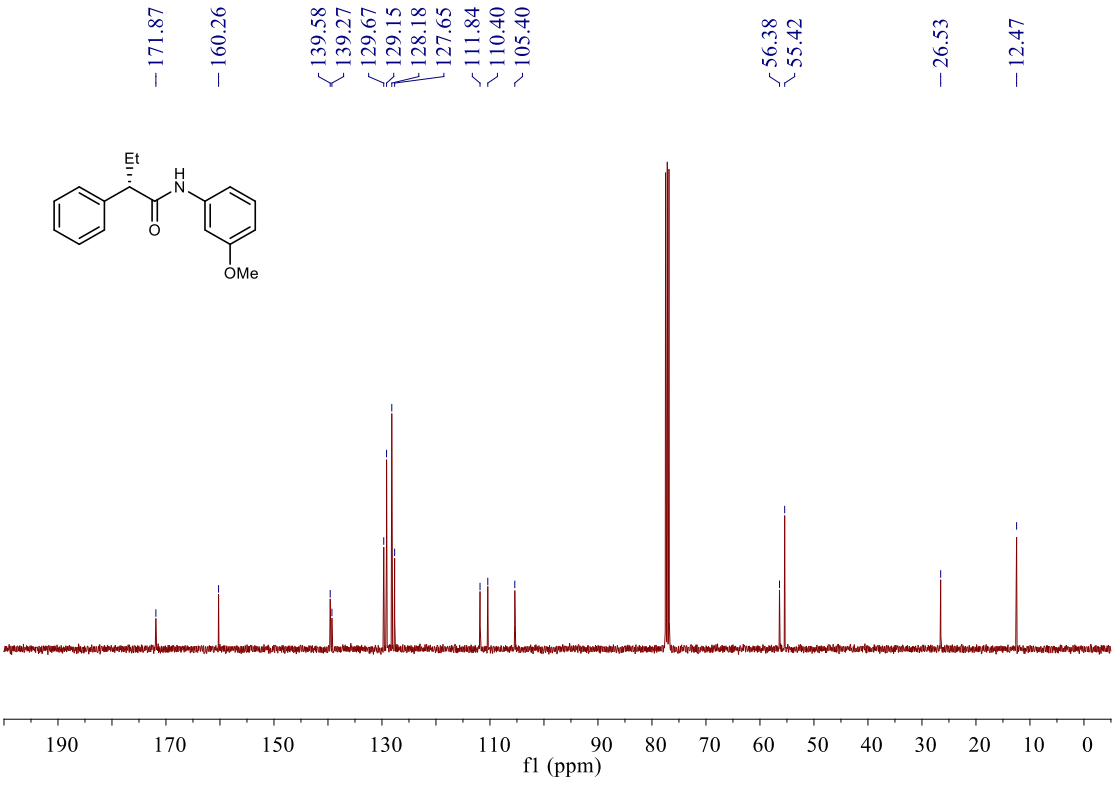



171.76
161.26
158.79
142.44
142.37
137.83
135.40
131.44
131.40
129.12
129.08
129.05
128.63
128.41
128.27
127.93
124.63
123.75
123.72
120.02
115.61
115.38
47.73
18.76
Me
H
N
F
Ph
O
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

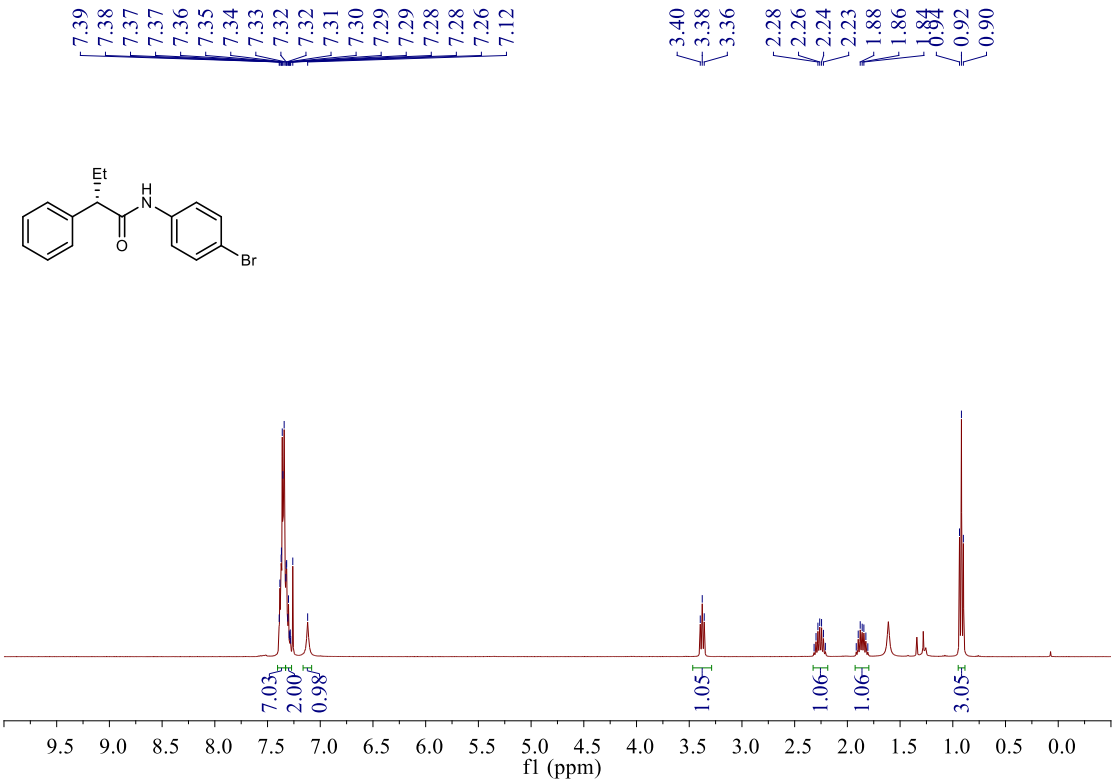

-116.70
-116.73
-116.75
Me
H
N
F
Ph
O
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

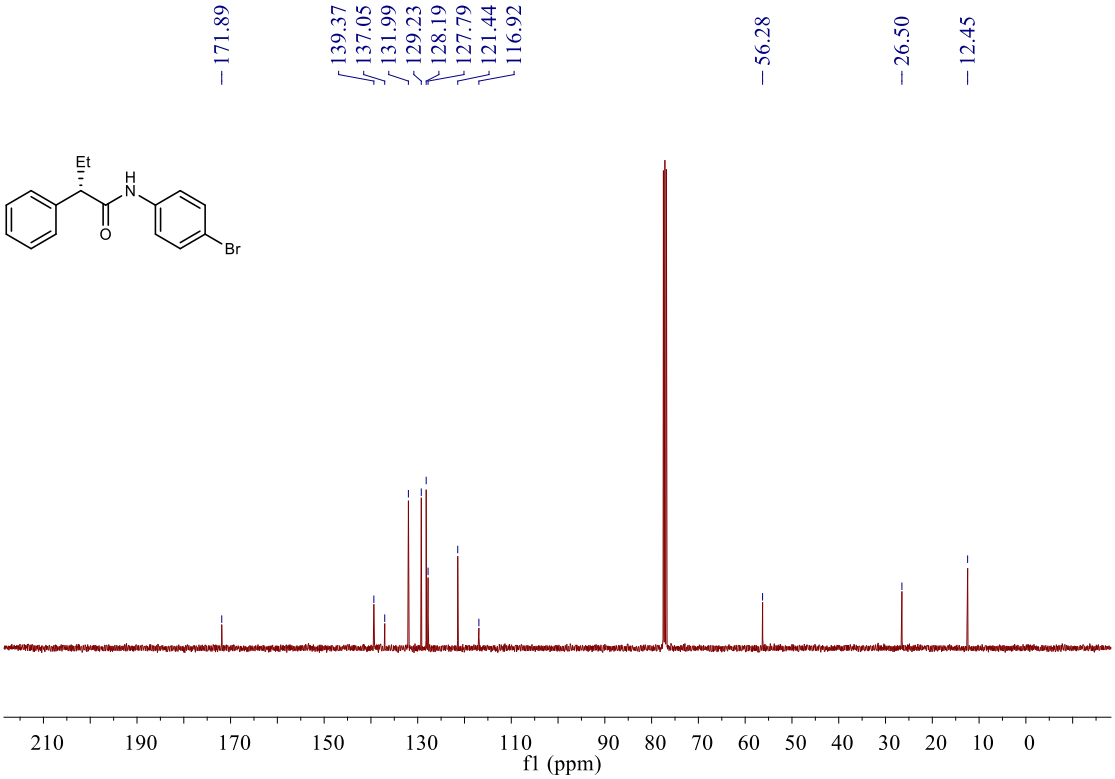
Compound 29 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



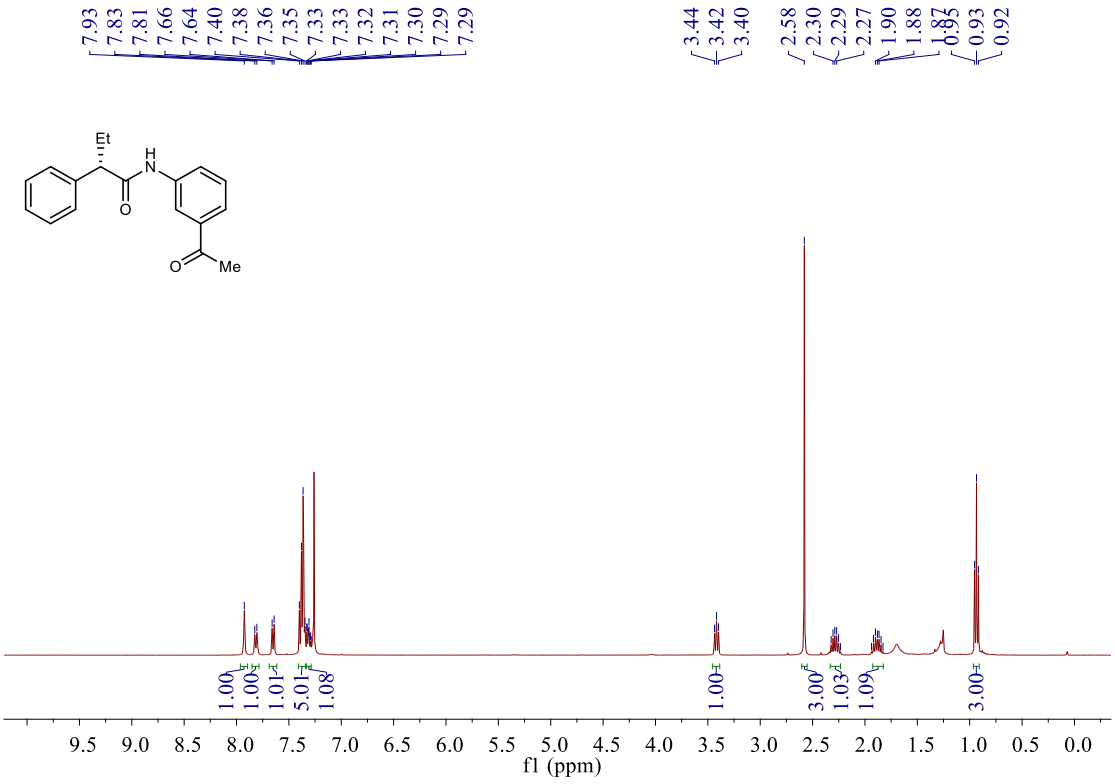


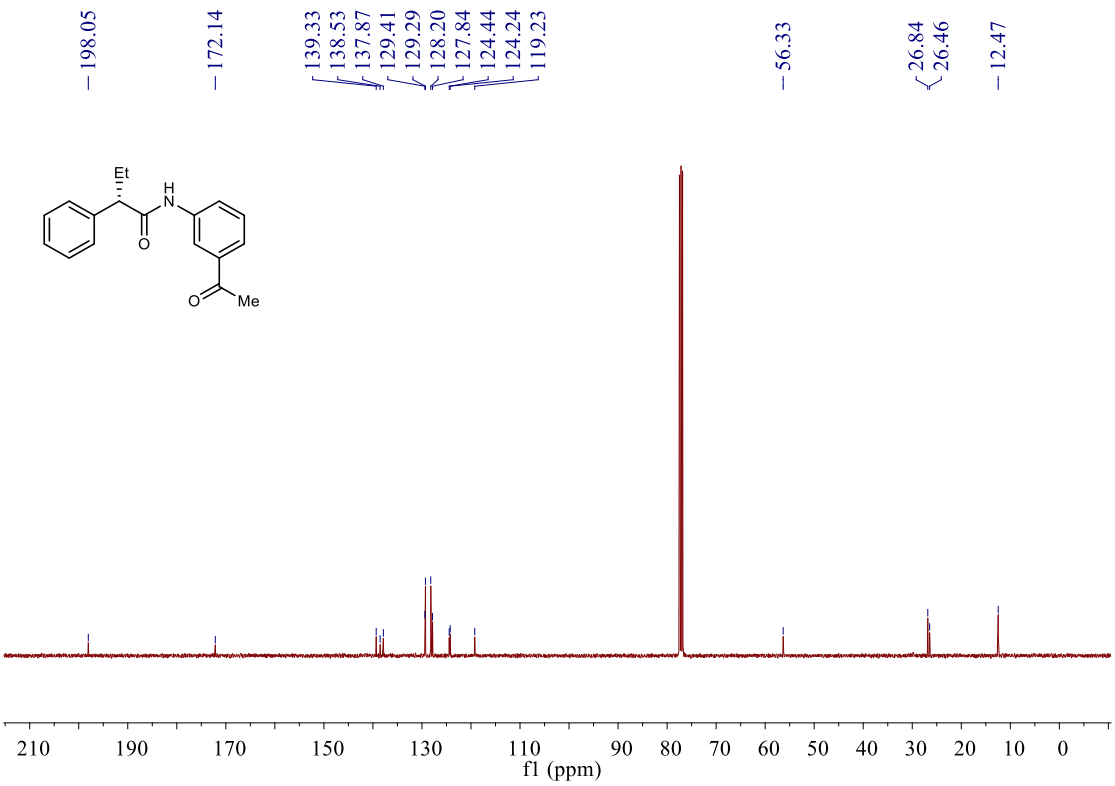
Compound 30 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



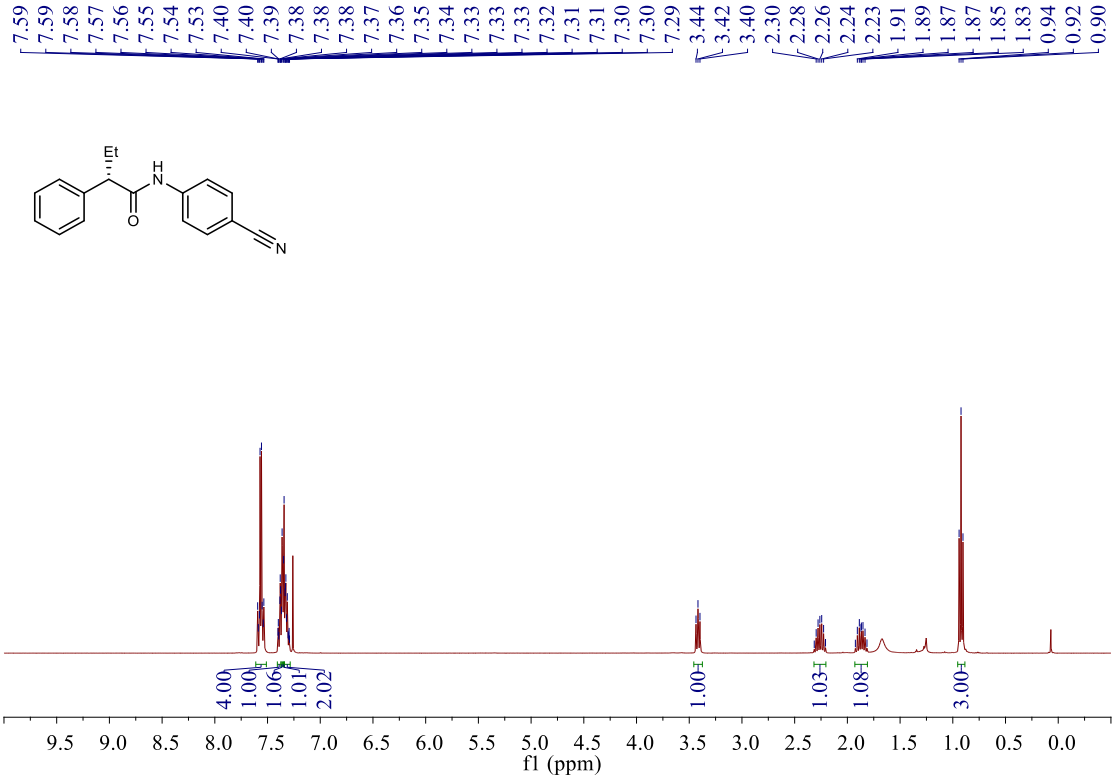


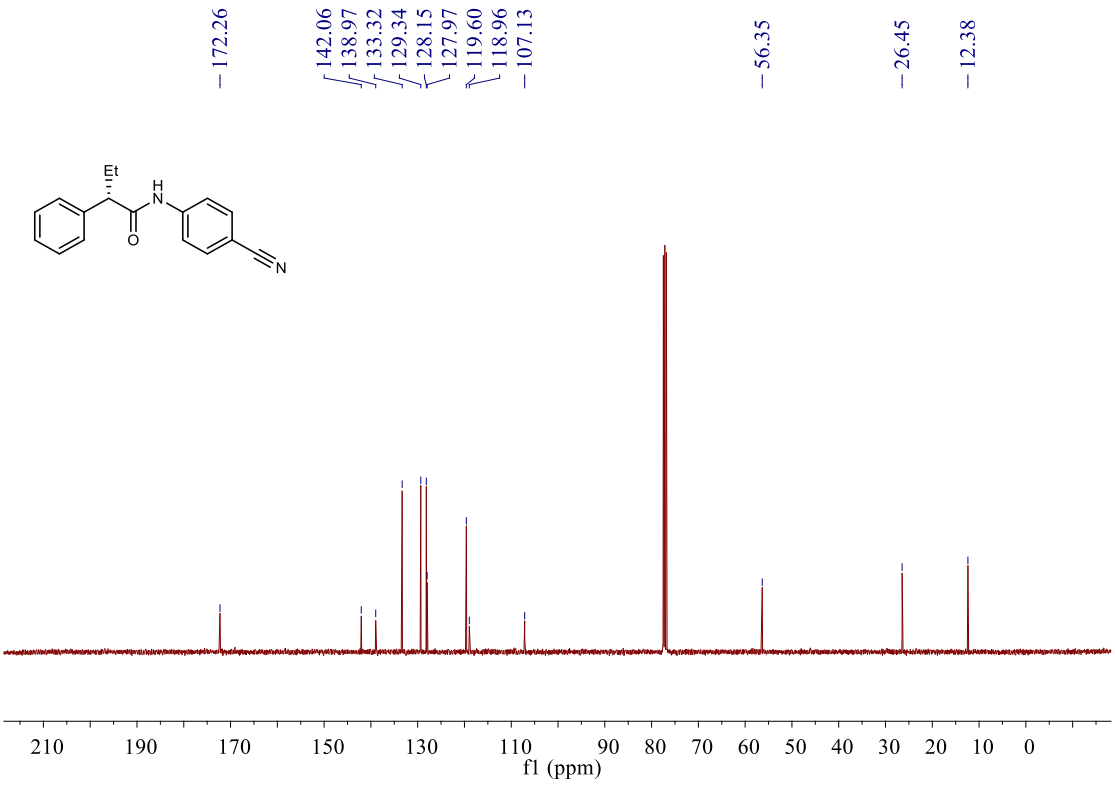
Compound 31 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



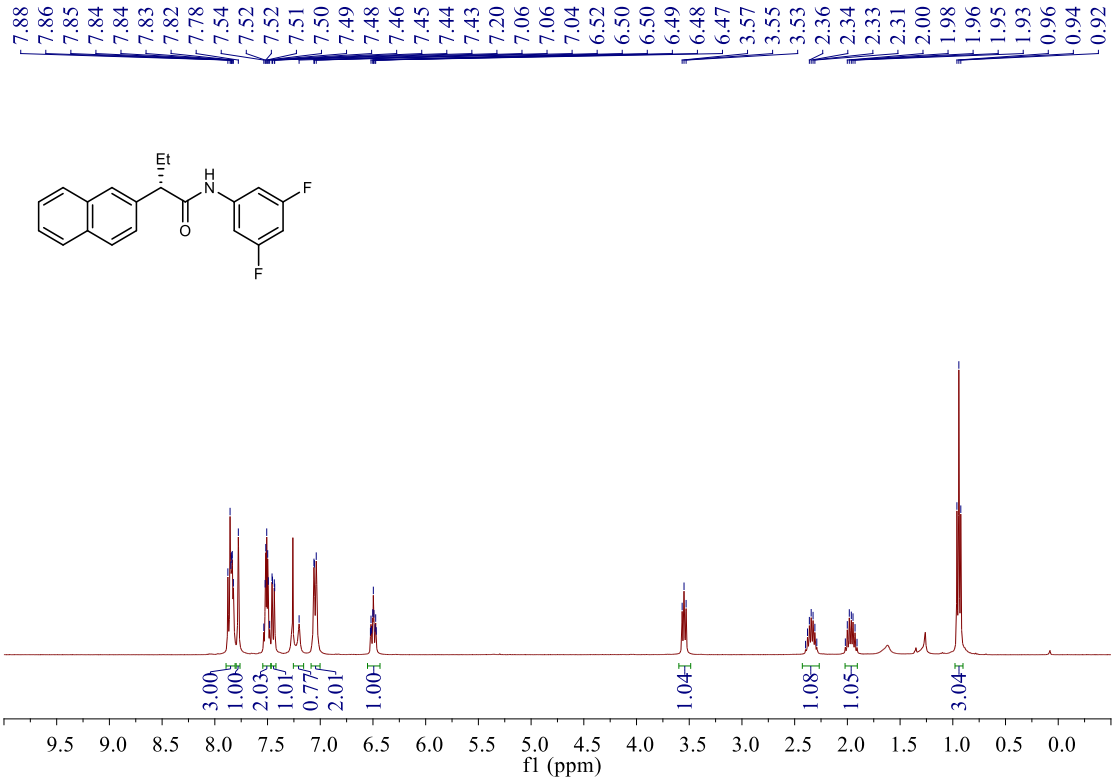


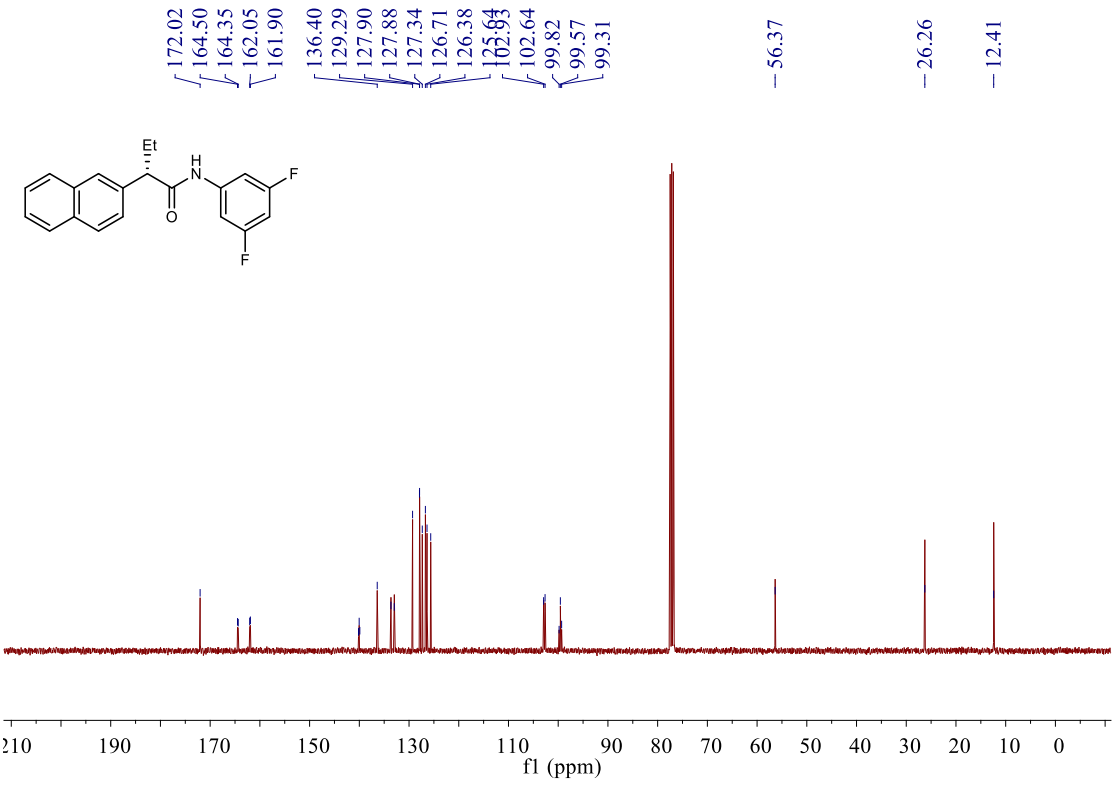
Compound 32 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

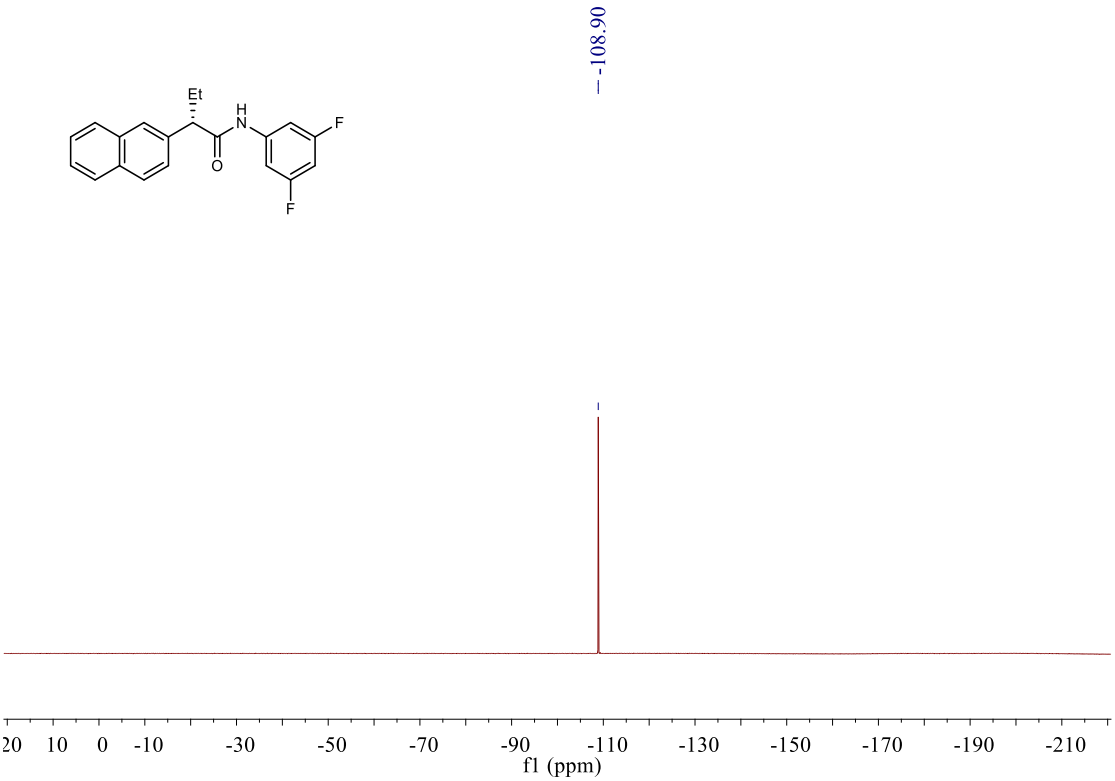




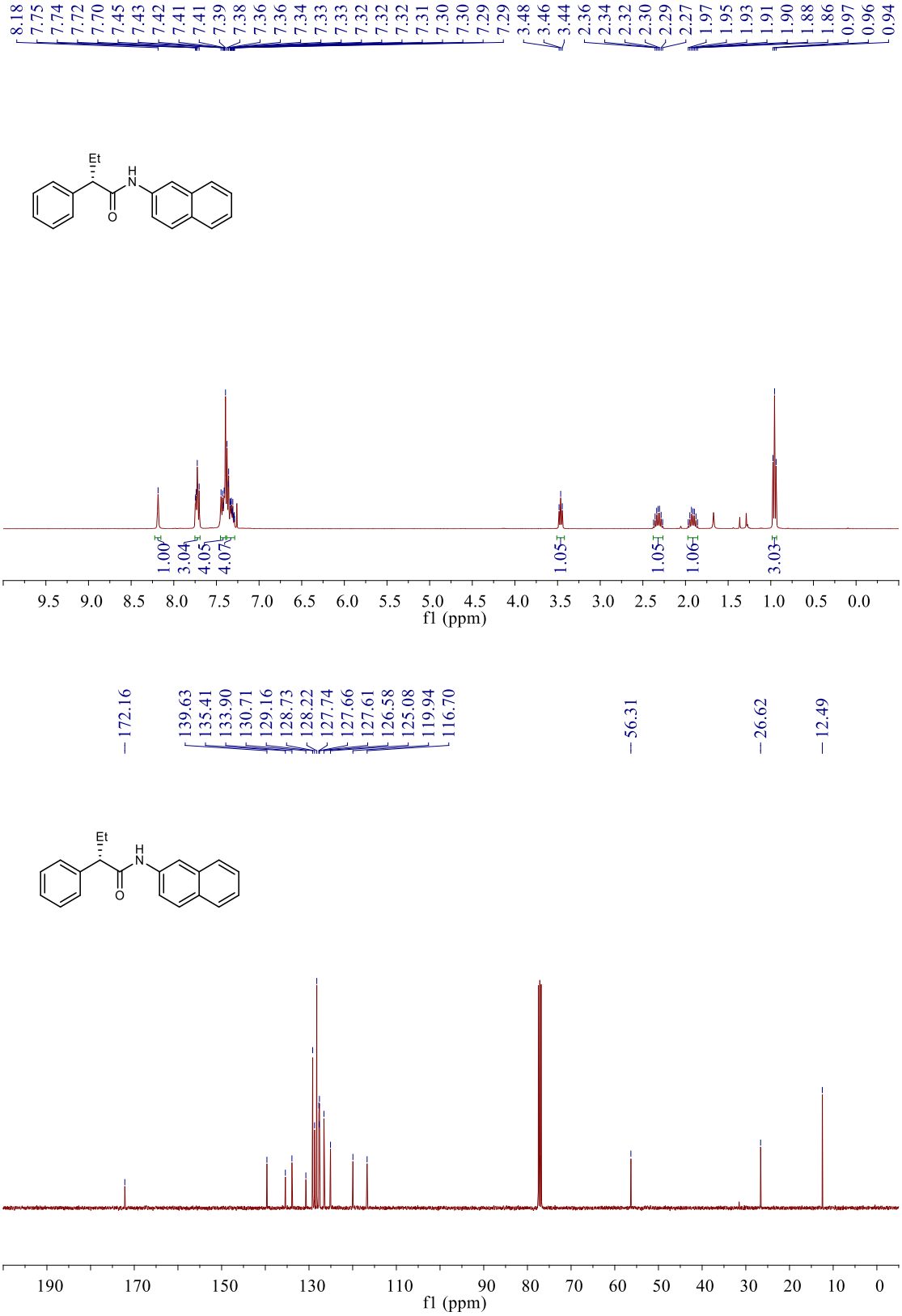
Compound 33 (^{1}H NMR, ^{13}C NMR and ^{19}F NMR, $CDCl_3$, 400 MHz, 101 MHz and 377 MHz respectively)


7.88
7.86
7.85
7.84
7.84
7.83
7.82
7.78
7.54
7.52
7.52
7.51
7.50
7.49
7.48
7.46
7.45
7.44
7.43
7.20
7.06
7.06
7.04
6.52
6.50
6.50
6.49
6.48
6.47
3.57
3.55
3.53
2.36
2.34
2.33
2.31
2.00
1.98
1.96
1.95
1.93
0.96
0.94
0.92
Et
H
N
O
F
F
3.00
1.00
2.03
1.01
0.77
2.01
1.00
1.04
1.08
1.05
3.04
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)

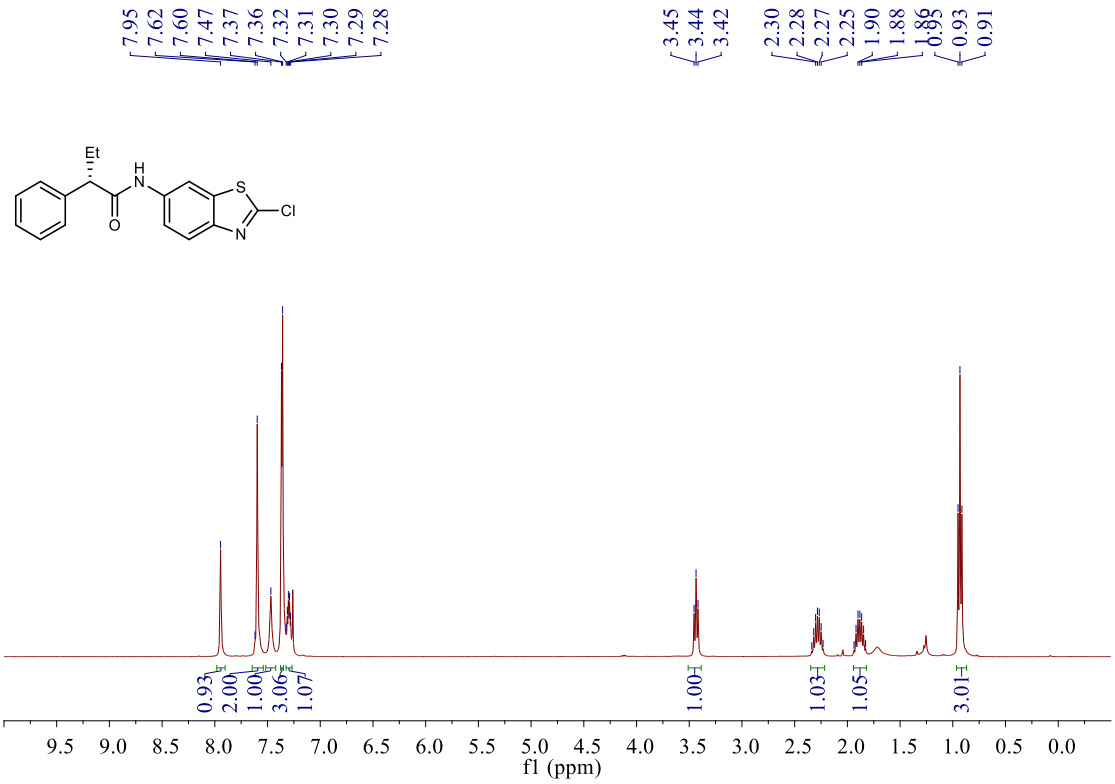

172.02
164.50
164.35
162.05
161.90
136.40
129.29
127.90
127.88
127.34
126.71
126.38
125.64
102.93
102.64
99.82
99.57
99.31
56.37
26.26
12.41
Et
H
N
O
F
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

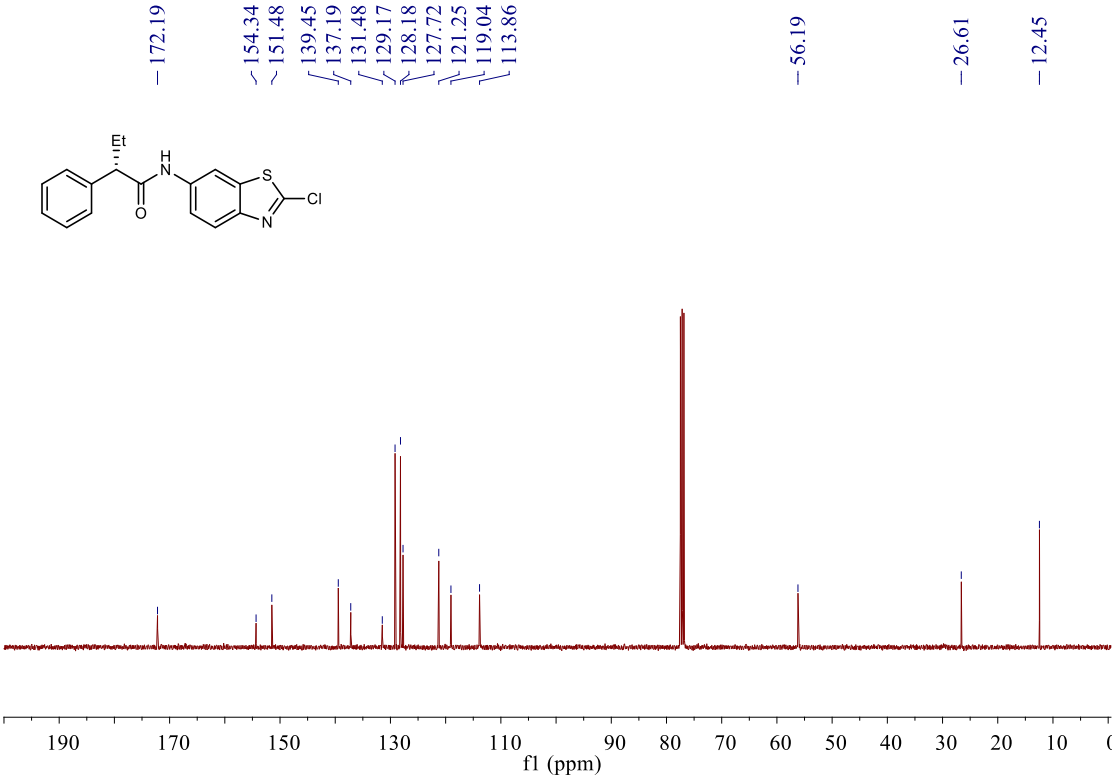

-108.90
Et
H
N
O
F
F
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Compound 34 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

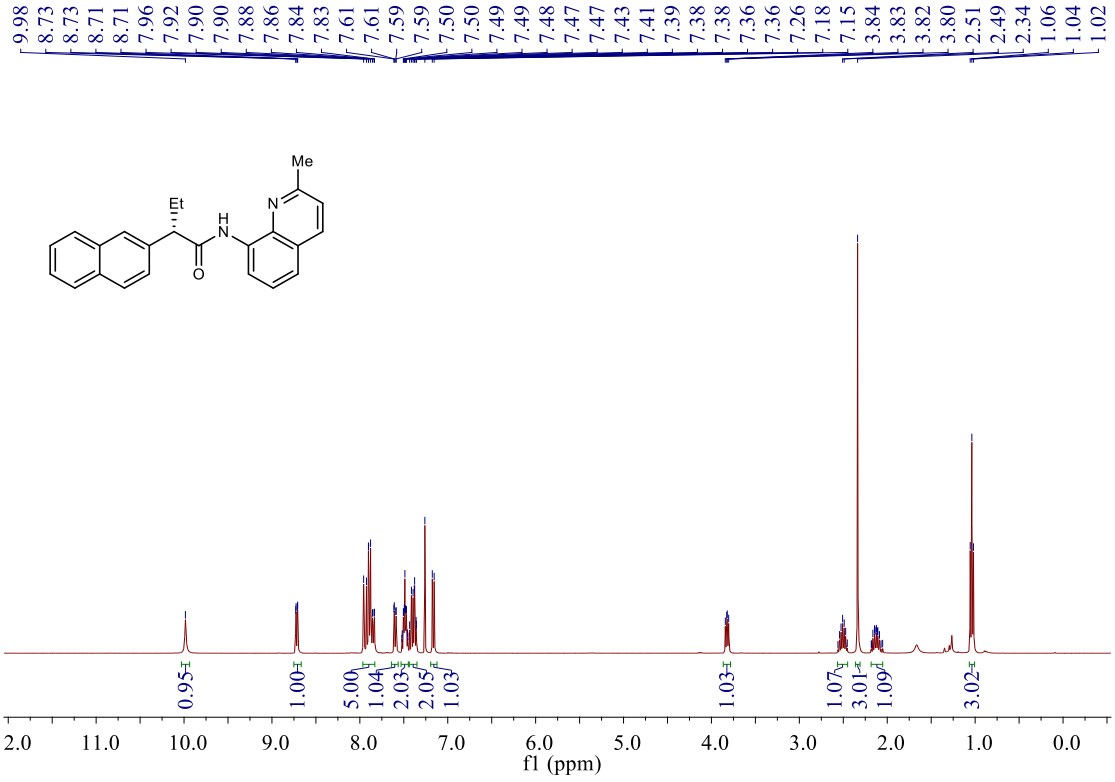


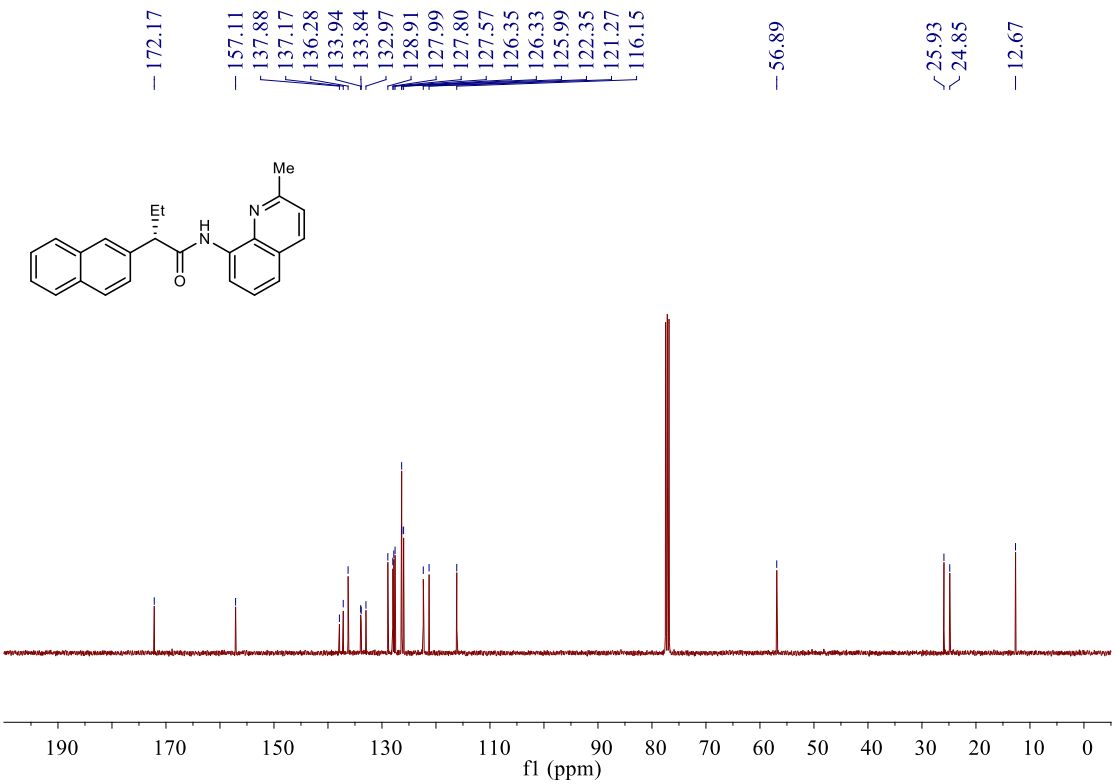
Compound 35 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



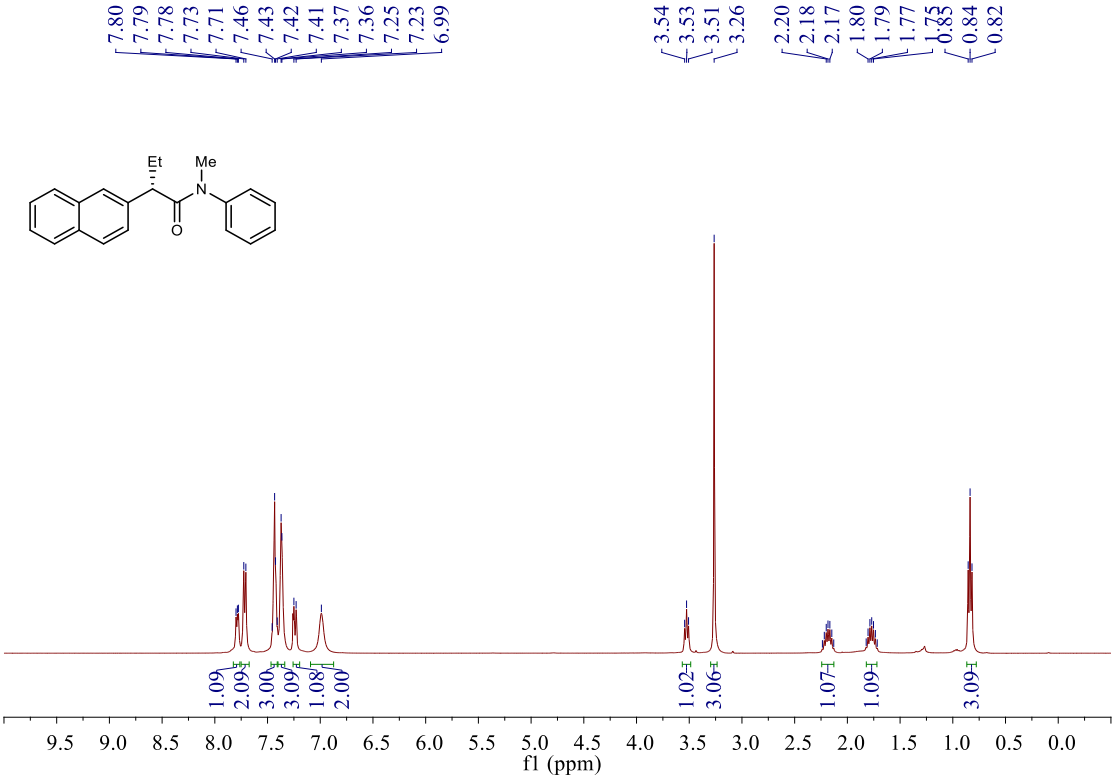


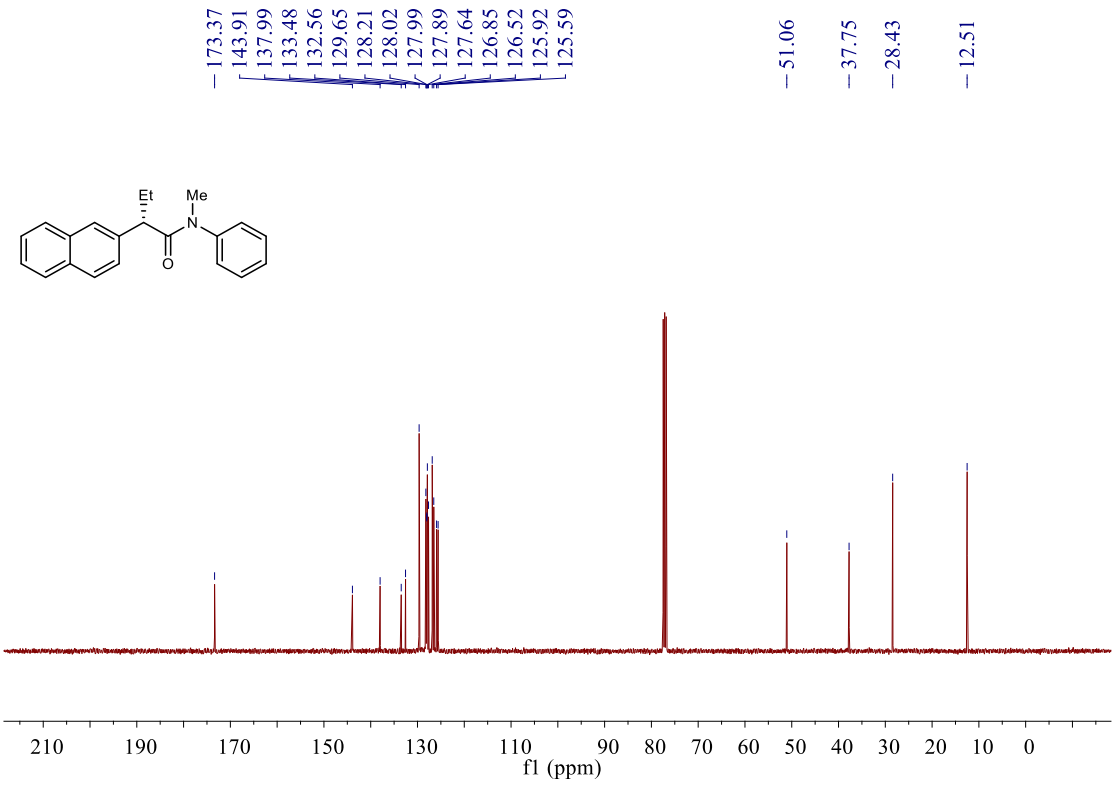
Compound 36 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



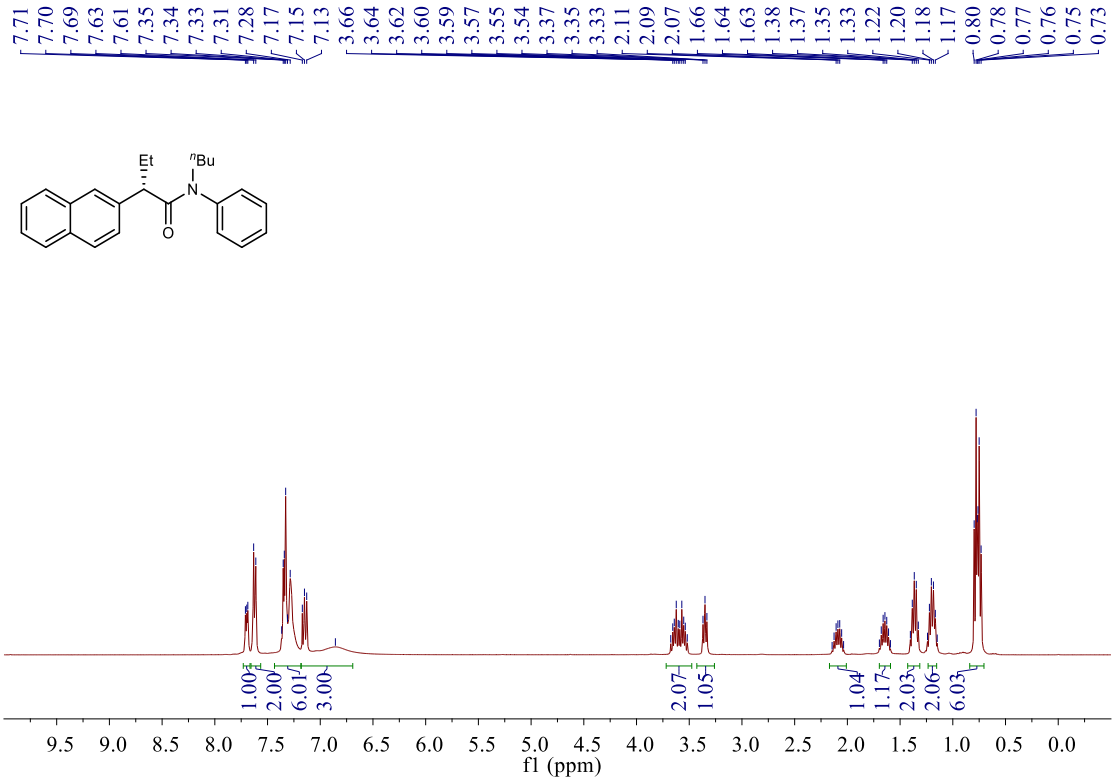


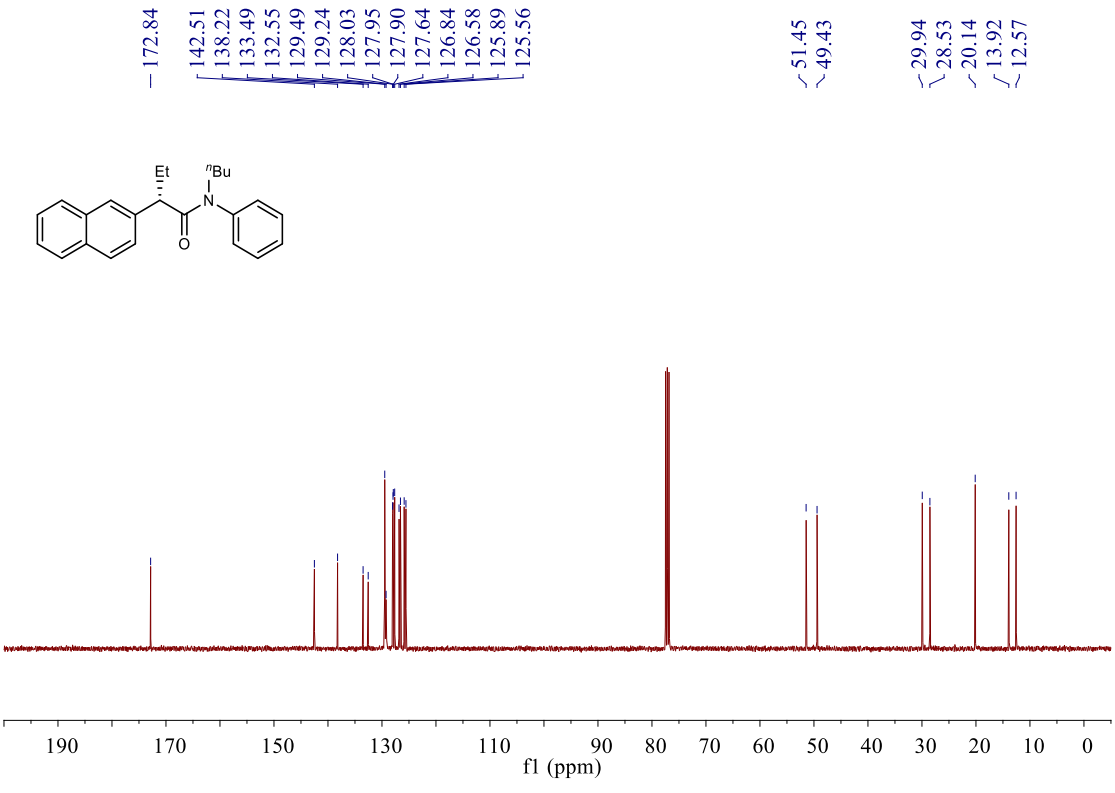
Compound 37 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



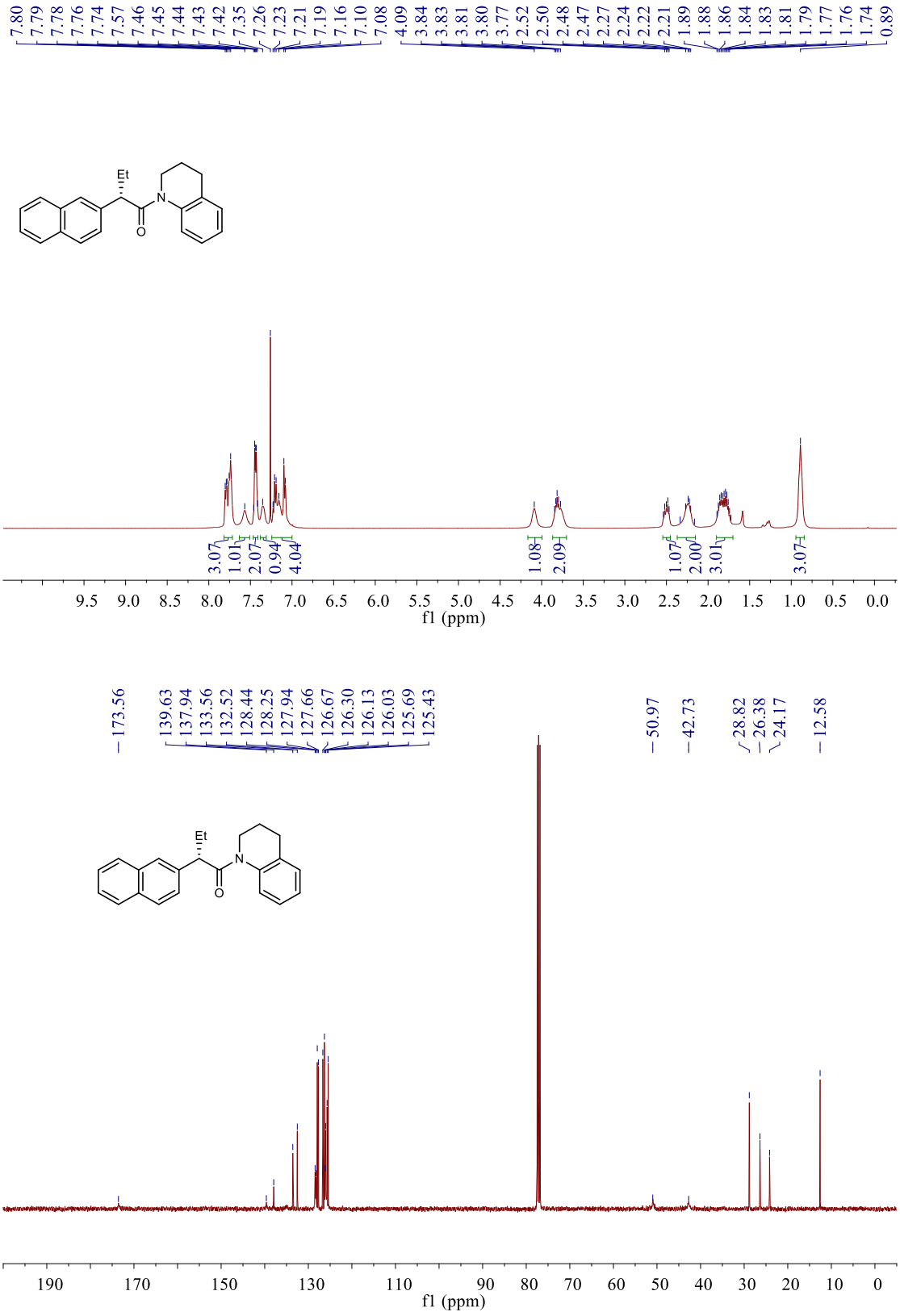


Compound 38 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

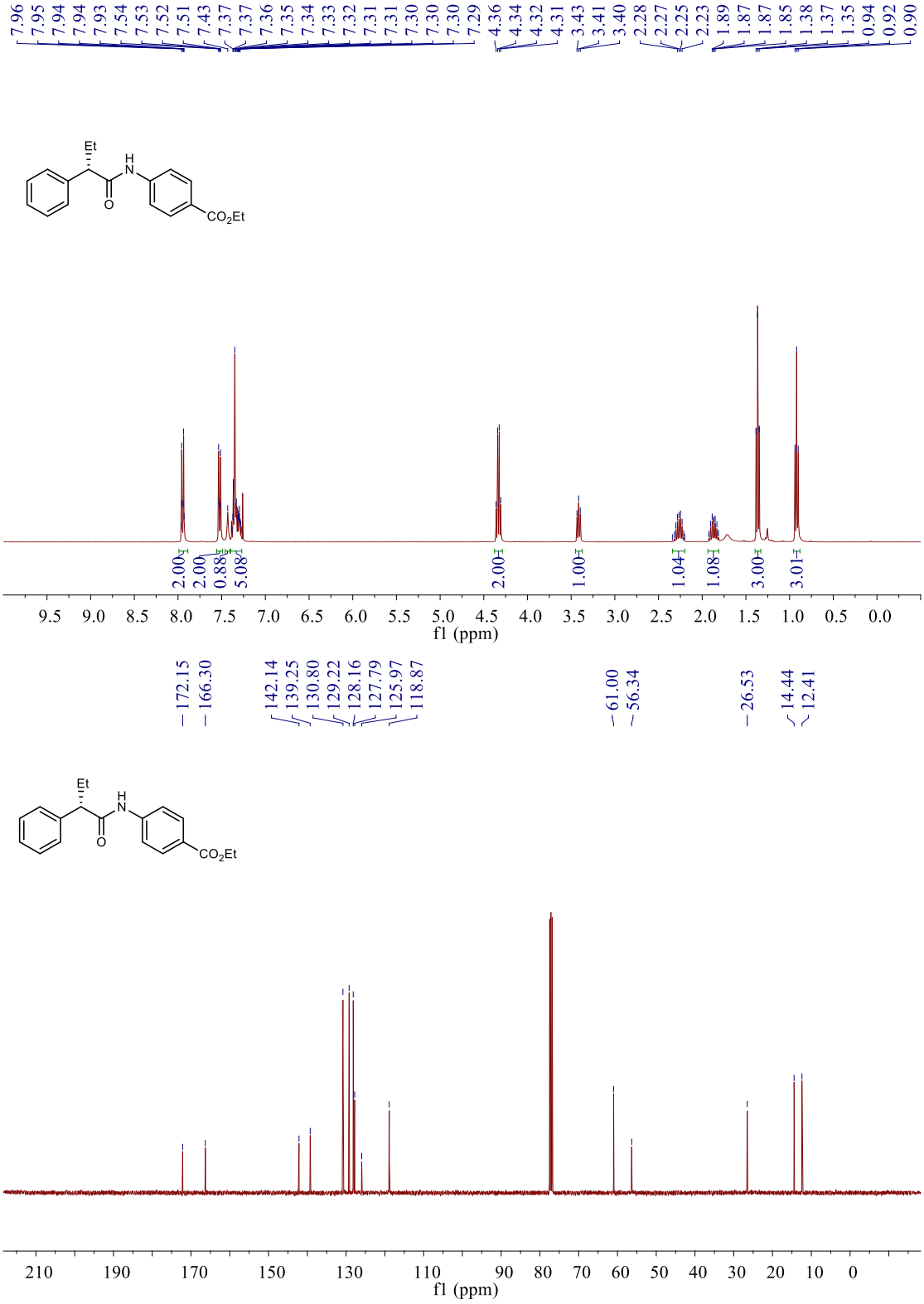

7.71
7.70
7.69
7.63
7.61
7.35
7.34
7.33
7.31
7.28
7.17
7.15
7.13
3.66
3.64
3.62
3.60
3.59
3.57
3.55
3.54
3.37
3.35
3.33
2.11
2.09
2.07
1.66
1.64
1.63
1.38
1.37
1.35
1.33
1.22
1.20
1.18
1.17
0.80
0.78
0.77
0.76
0.75
0.73
Et
nBu
N
O
1.00
2.00
6.01
3.00
2.07
1.05
1.04
1.17
2.03
2.06
6.03
9.5 9.0 8.5 8.0 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)


172.84
142.51
138.22
133.49
132.55
129.49
129.24
128.03
127.95
127.90
127.64
126.84
126.58
125.89
125.56
51.45
49.43
29.94
28.53
20.14
13.92
12.57
Et
nBu
N
O
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

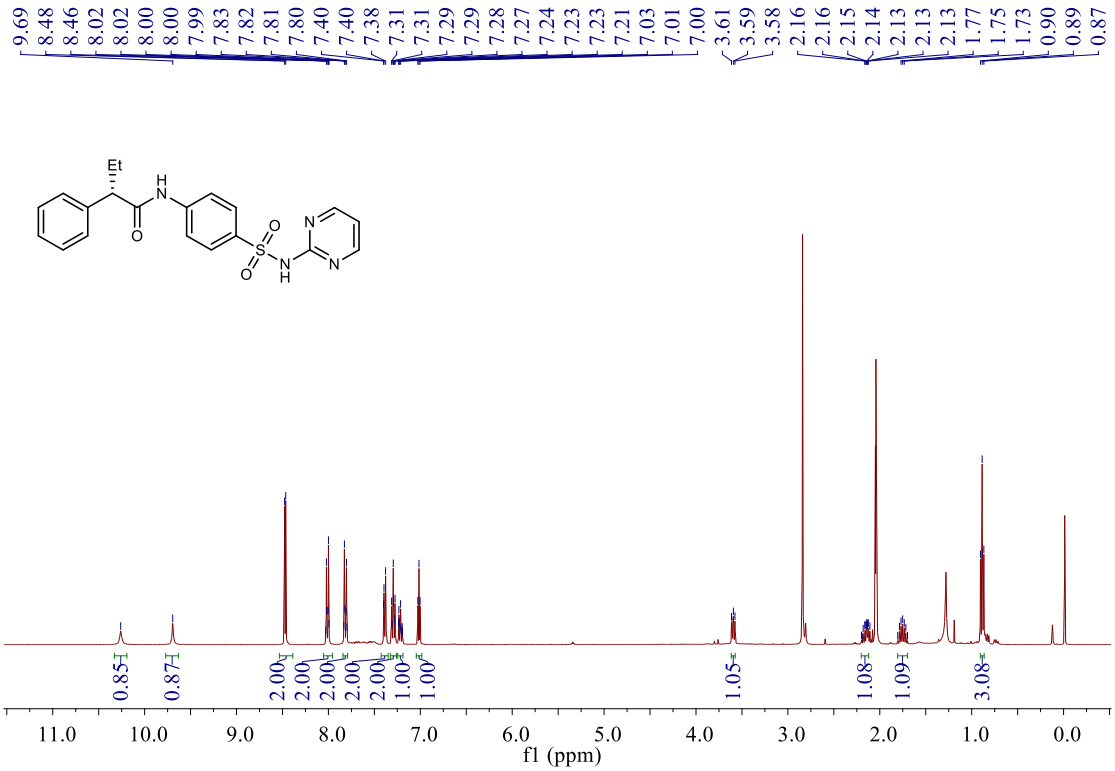
Compound 39 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

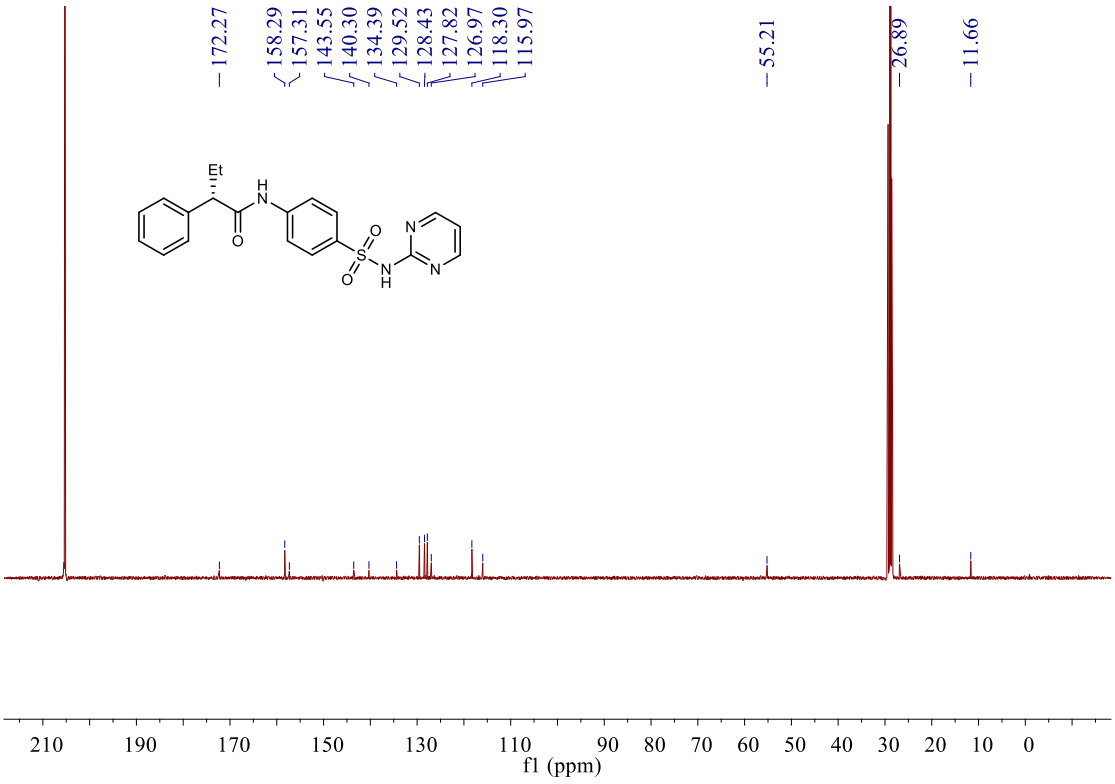


Compound 40 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

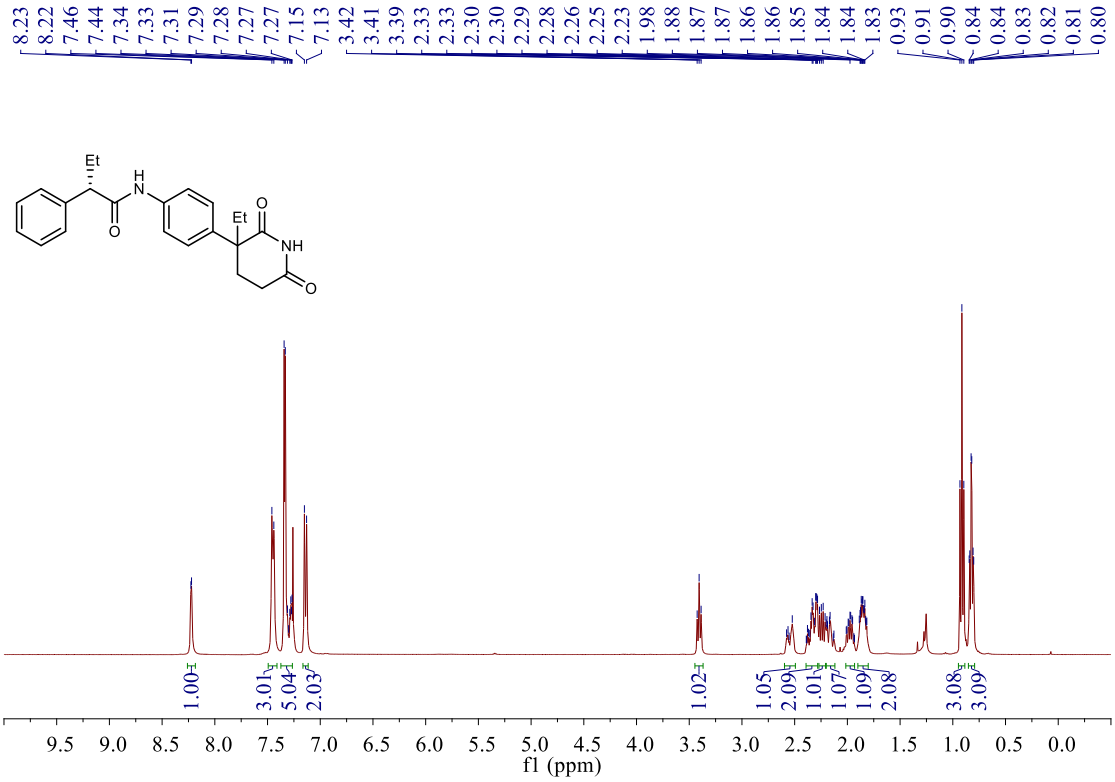


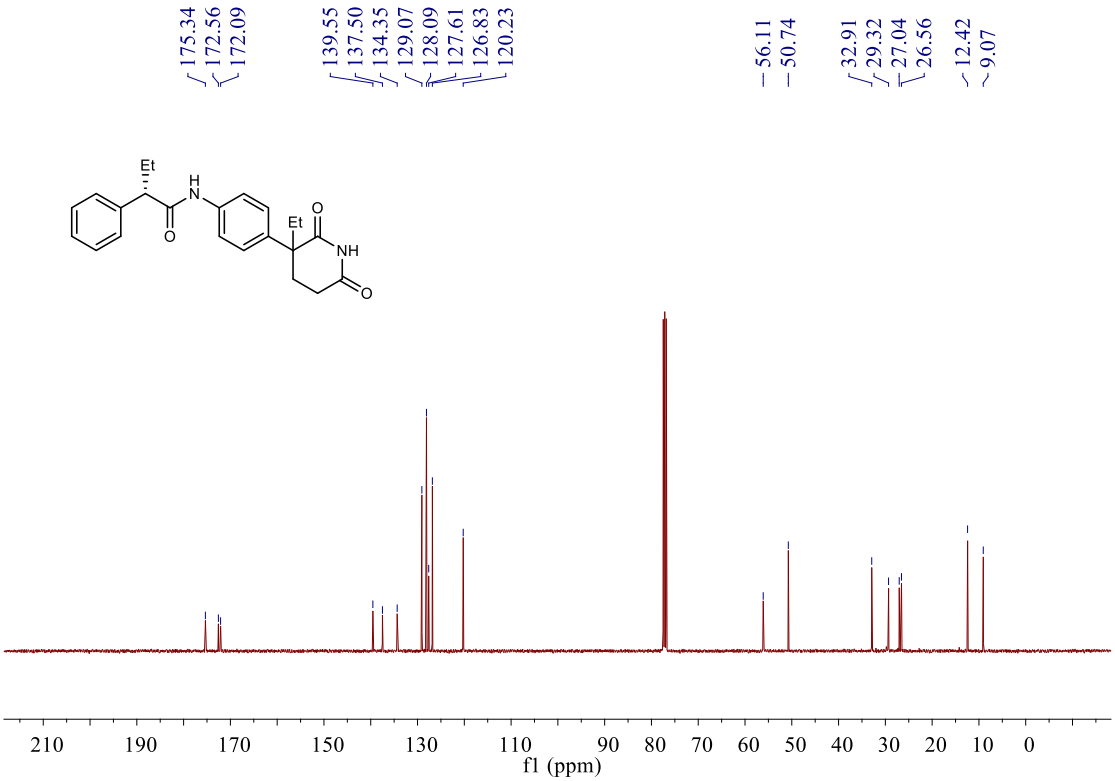
Compound 41 (^{1}H NMR and ^{13}C NMR, Acetone-d_6, 400 MHz and 101 MHz respectively)



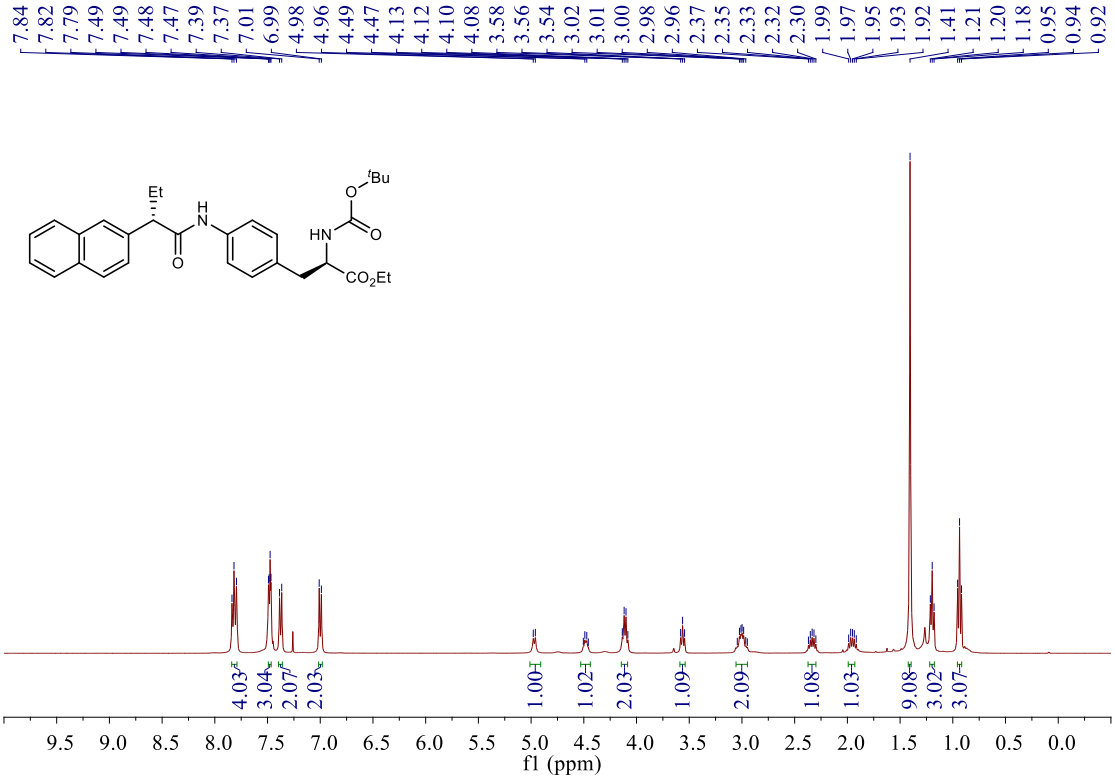


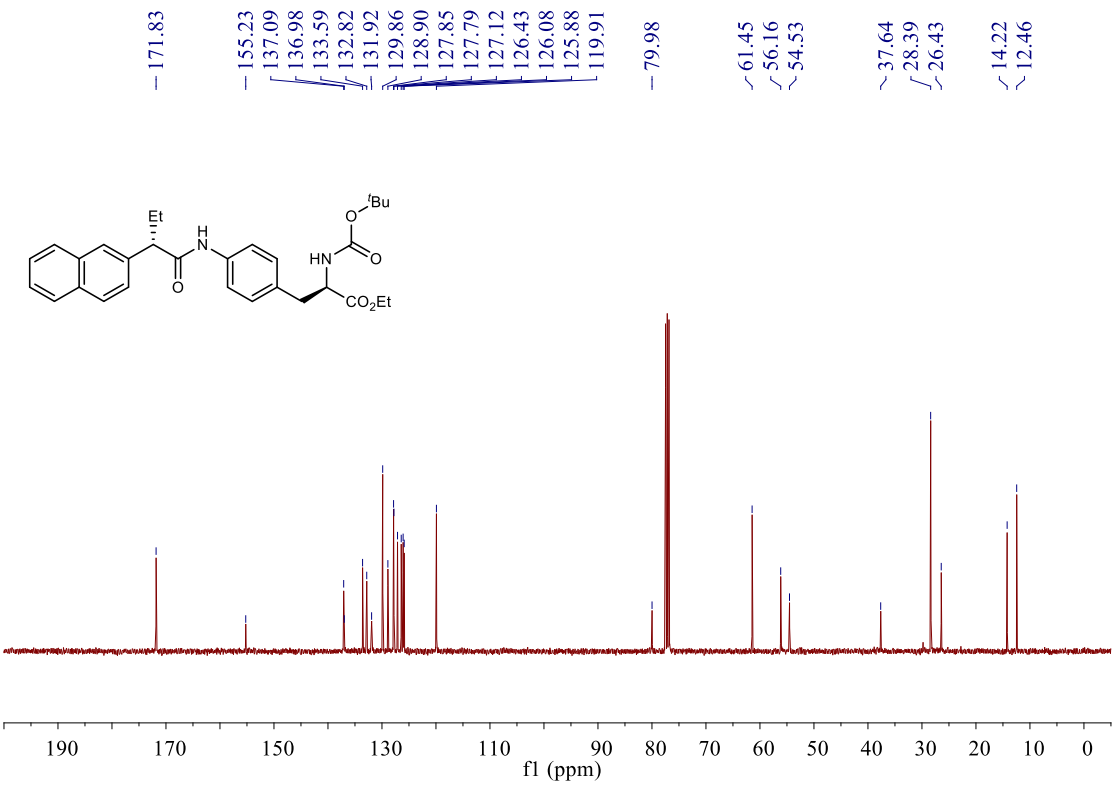
Compound 42 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



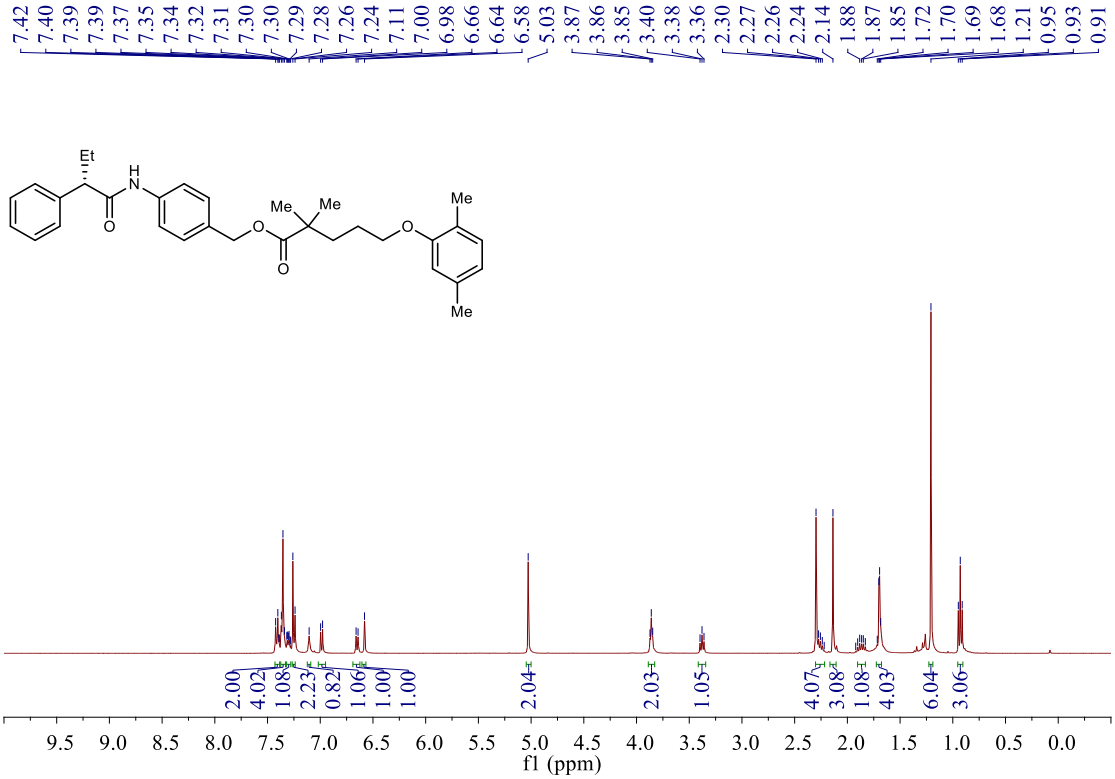


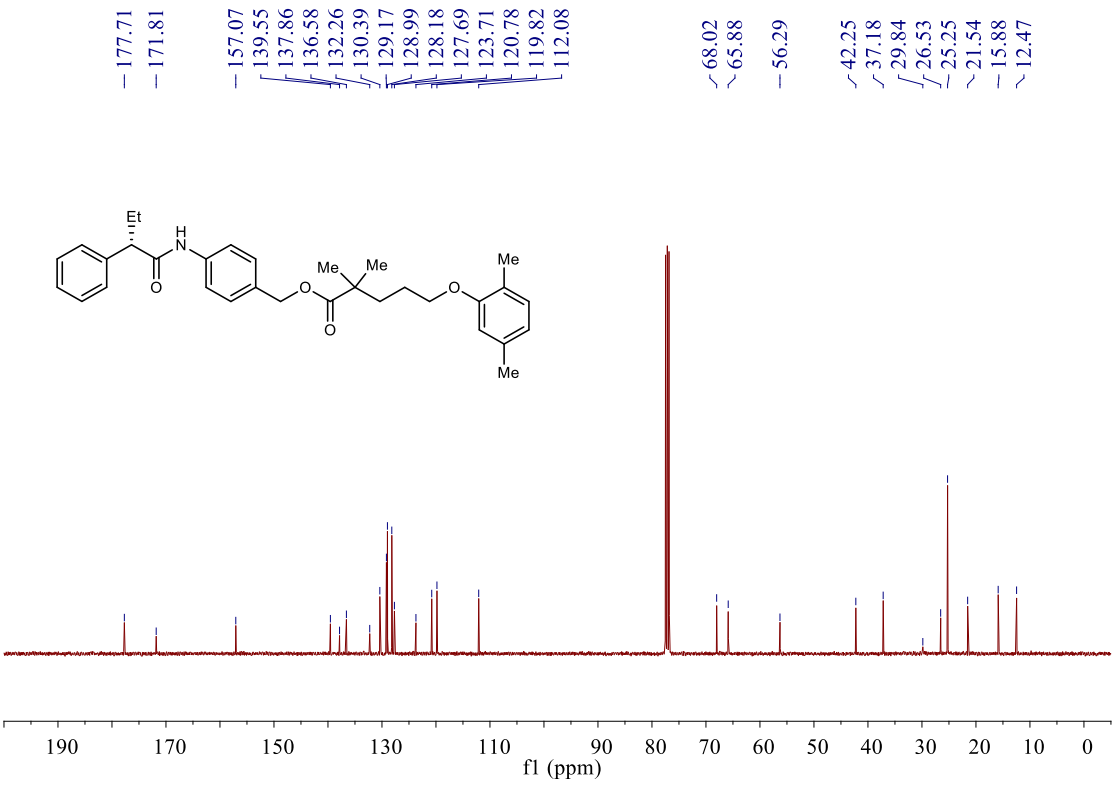
Compound 43 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



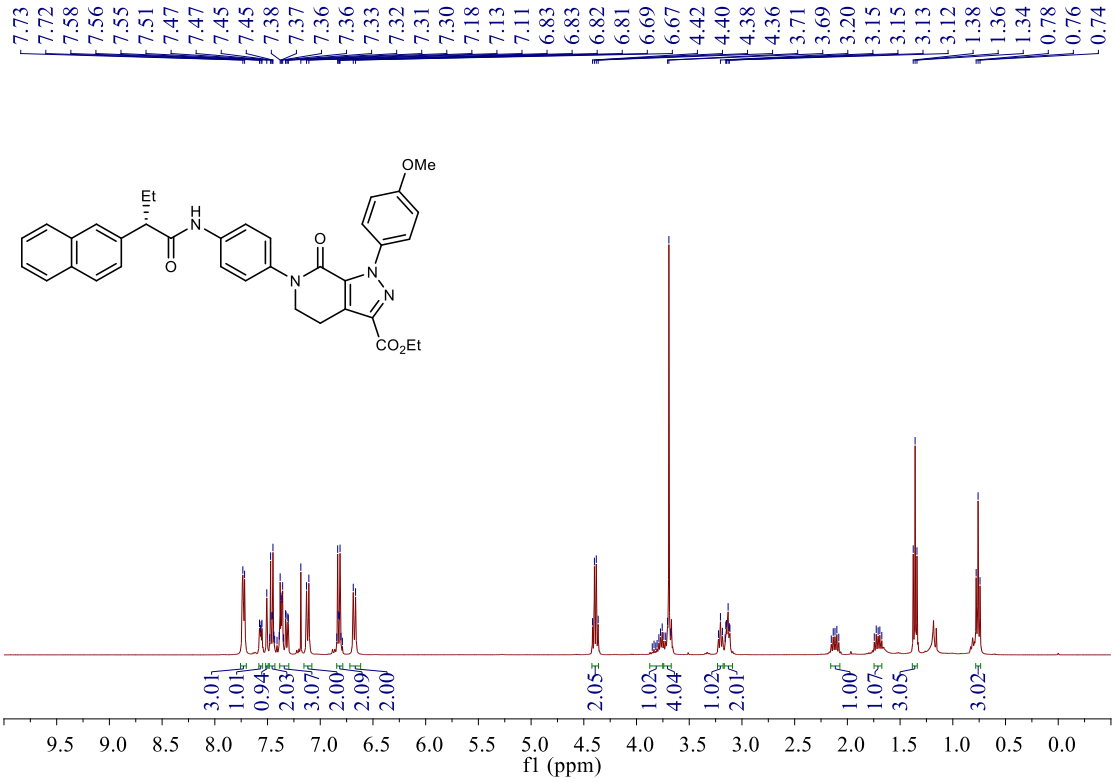


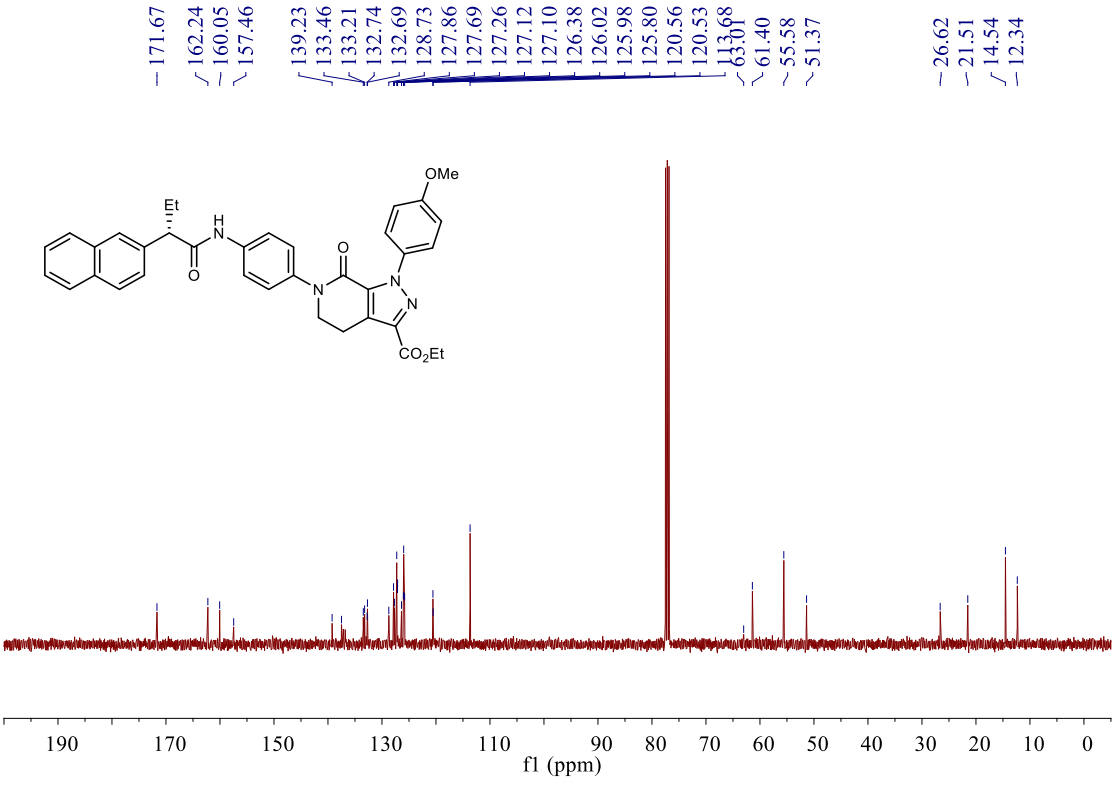
Compound 44 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



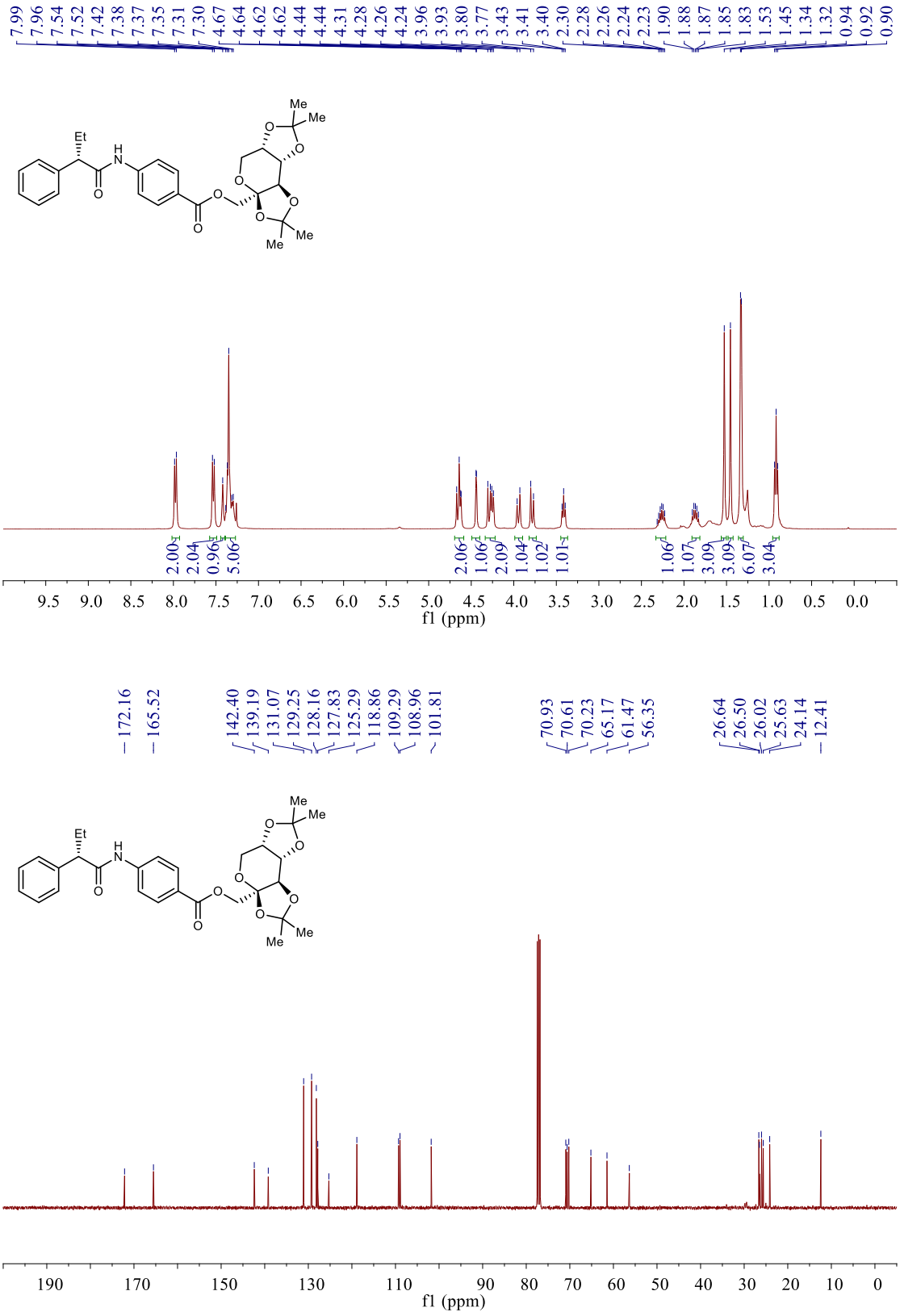


Compound 45 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

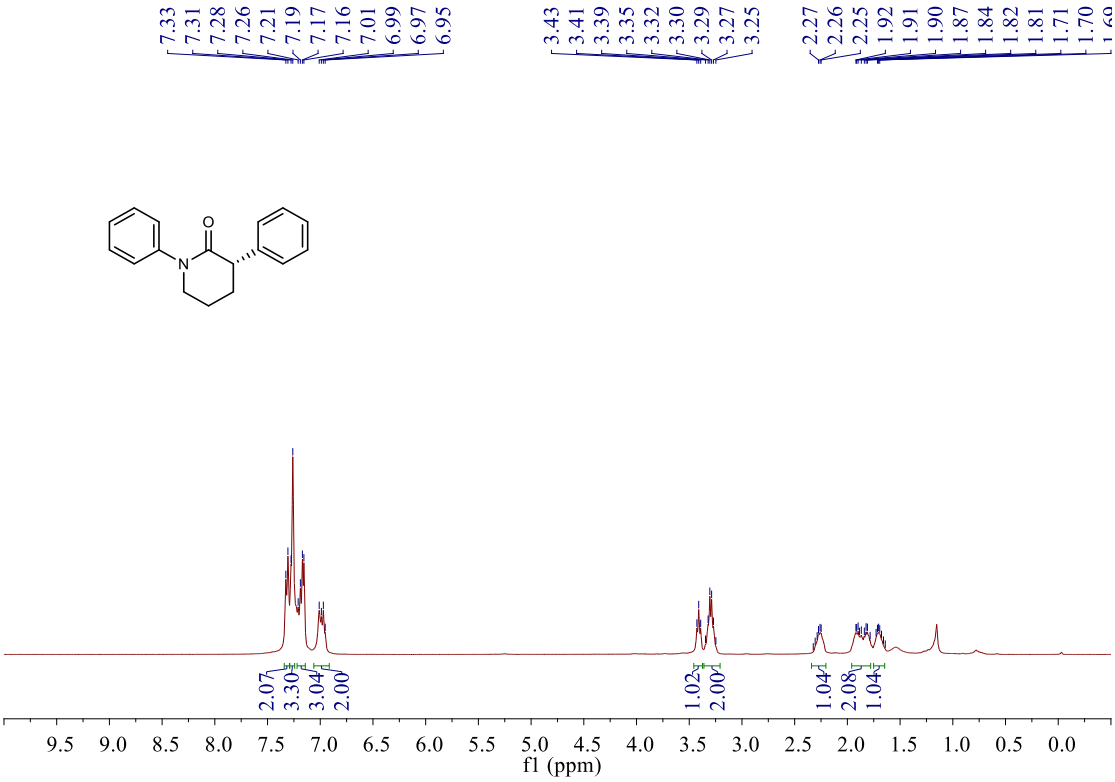

7.73
7.72
7.58
7.56
7.55
7.51
7.47
7.47
7.45
7.45
7.38
7.37
7.36
7.36
7.33
7.32
7.31
7.30
7.18
7.13
7.11
6.83
6.83
6.82
6.81
6.69
6.67
4.42
4.40
4.38
4.36
3.71
3.69
3.20
3.15
3.15
3.13
3.12
1.38
1.36
1.34
0.78
0.76
0.74
OMe
Et
H
N
O
O
N
N
N
CO2Et
3.01
1.01
0.94
2.03
3.07
2.00
2.09
2.00
2.05
1.02
4.04
1.02
2.01
1.00
1.07
3.05
3.02
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)

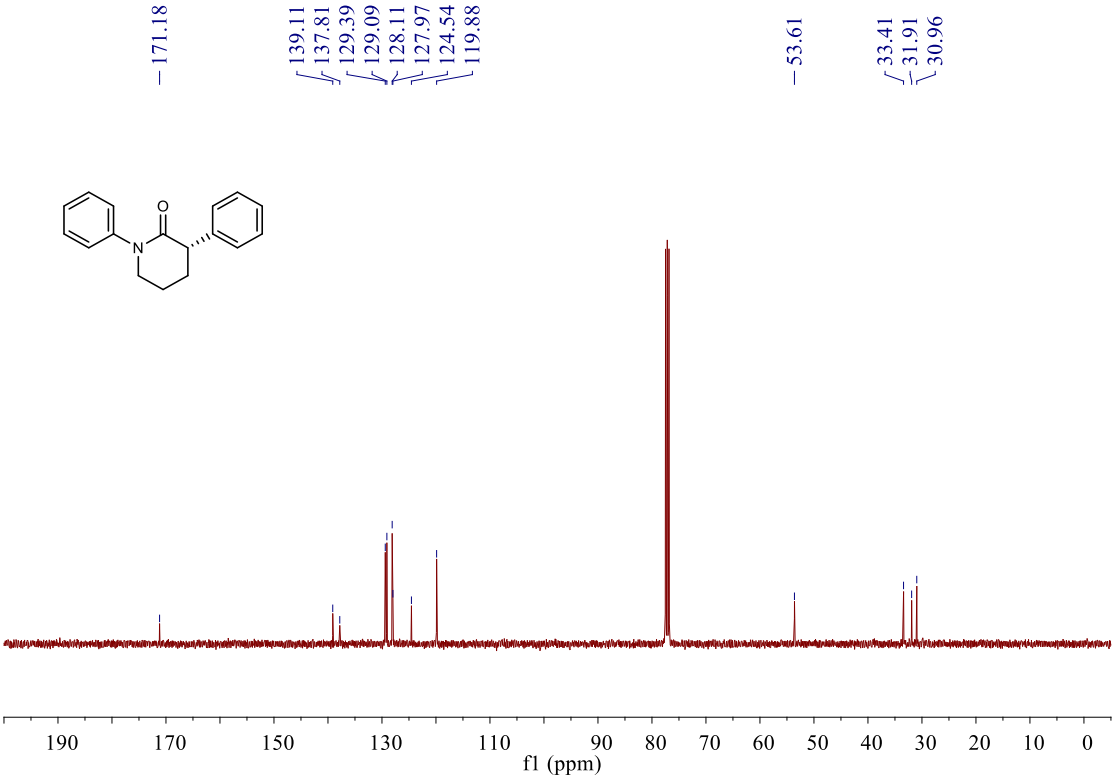

171.67
162.24
160.05
157.46
139.23
133.46
133.21
132.74
132.69
128.73
127.86
127.69
127.26
127.12
127.10
126.38
126.02
125.98
125.80
120.56
120.53
113.68
63.01
61.40
55.58
51.37
26.62
21.51
14.54
12.34
OMe
Et
H
N
O
O
N
N
N
CO2Et
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Compound 46 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

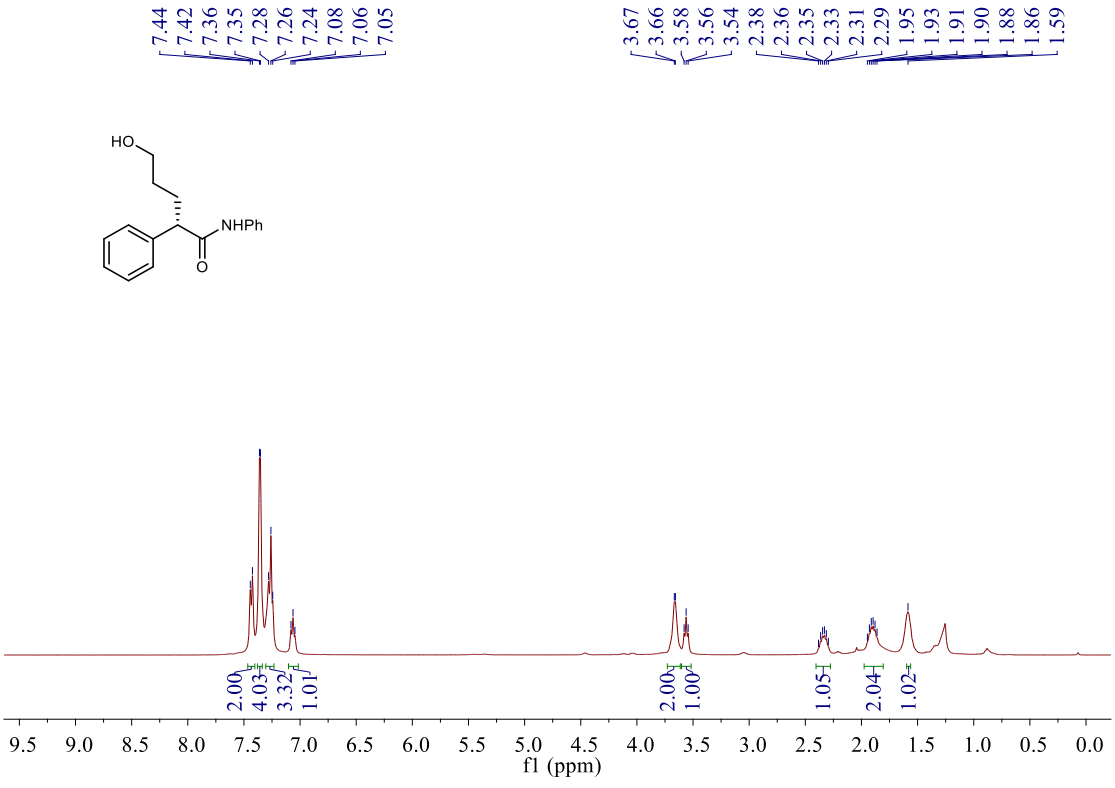


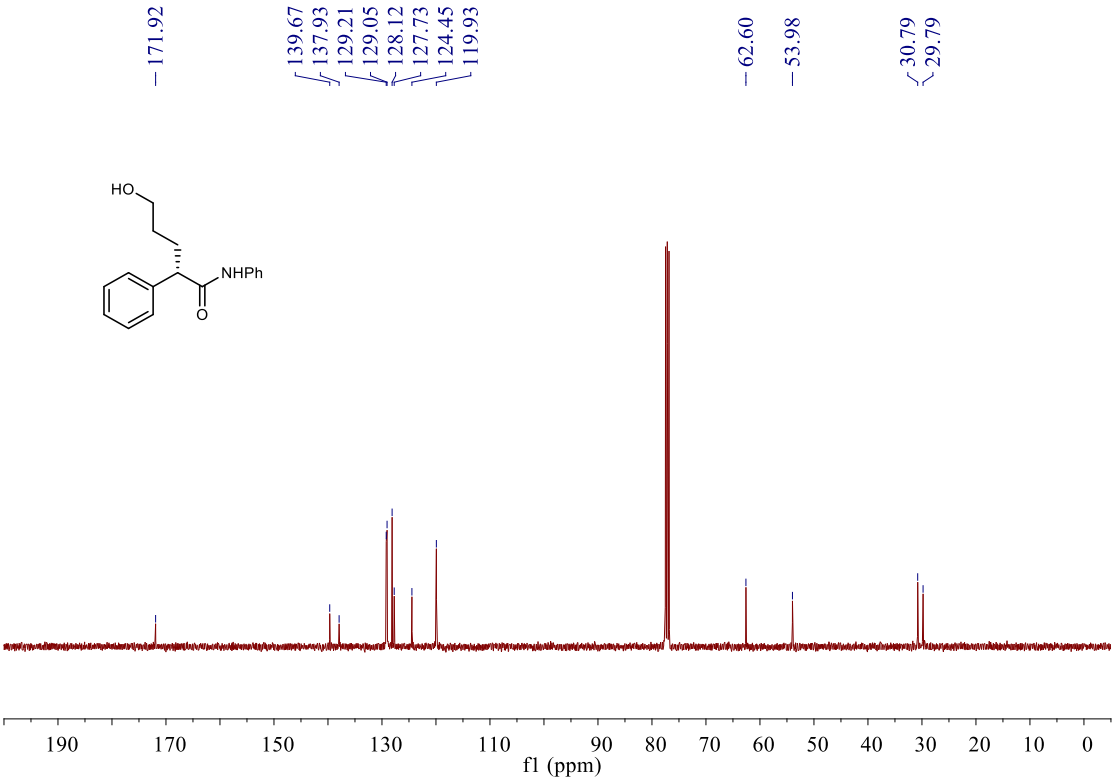
Compound 47 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



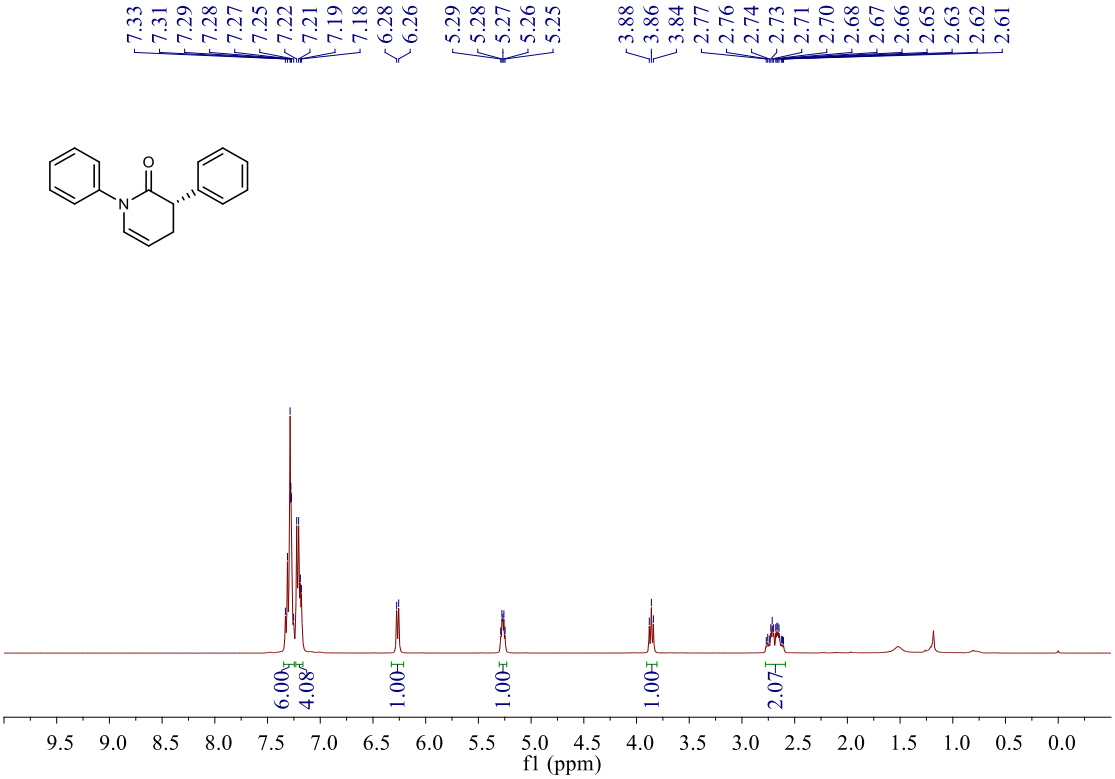


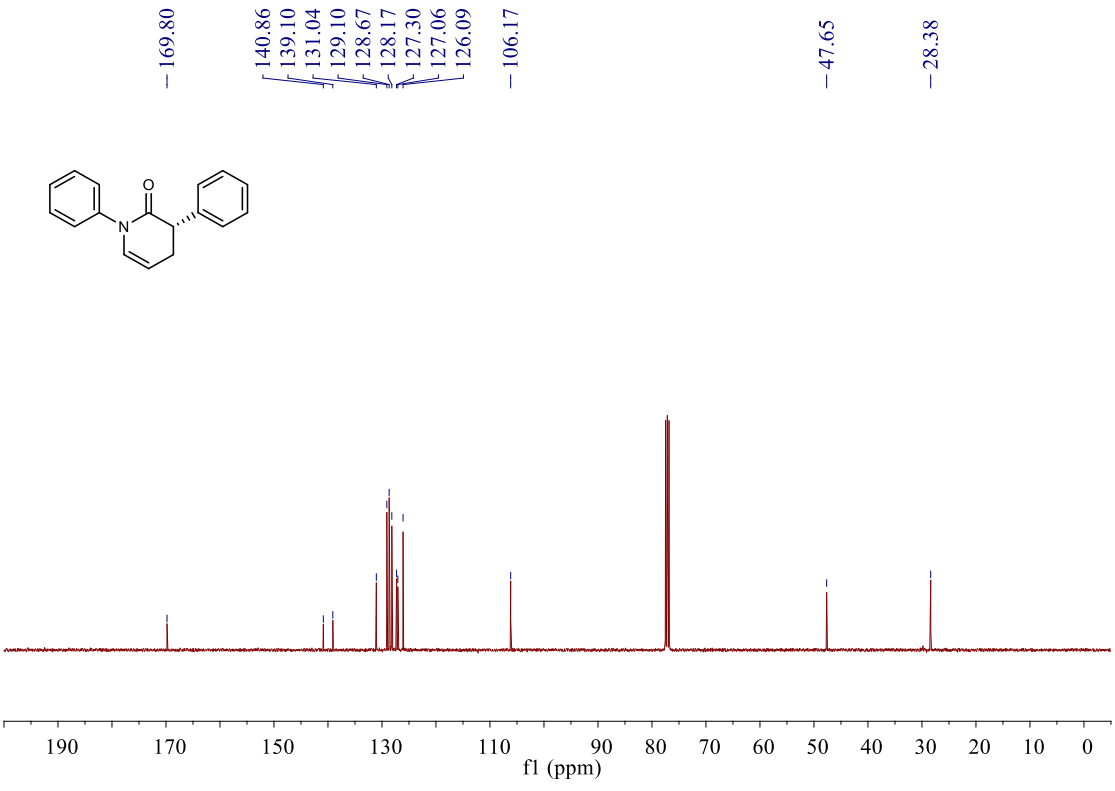
Compound 48 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



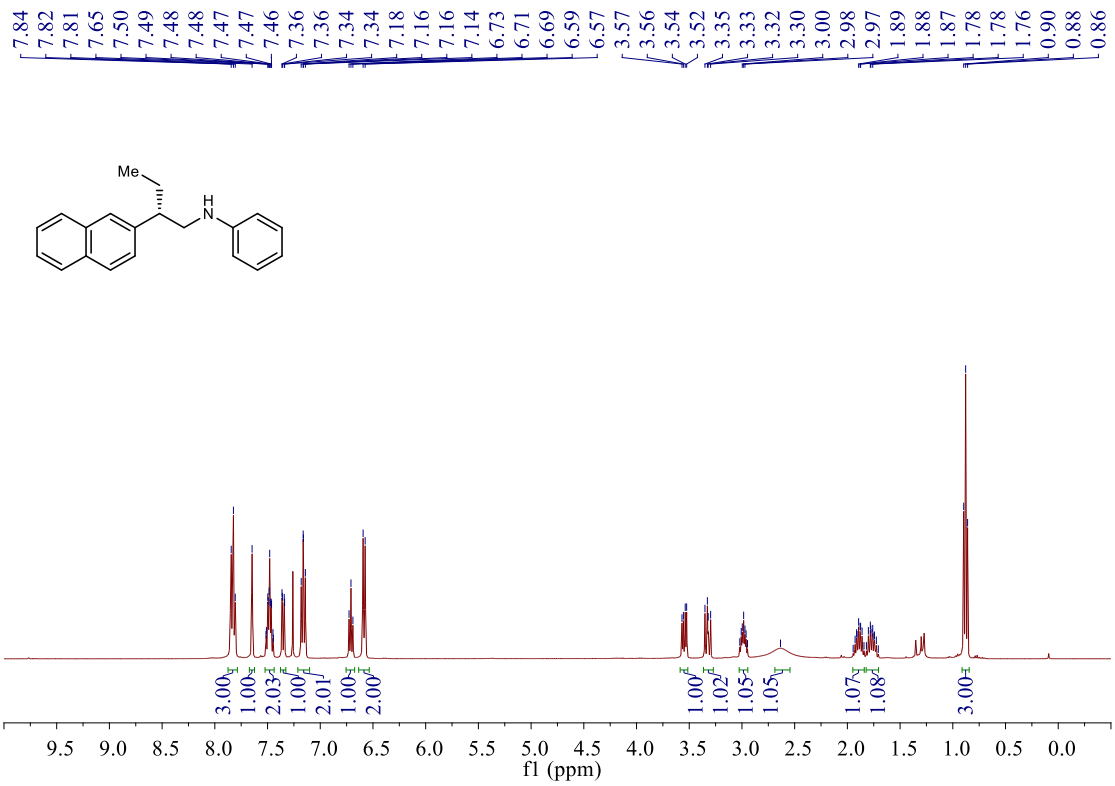


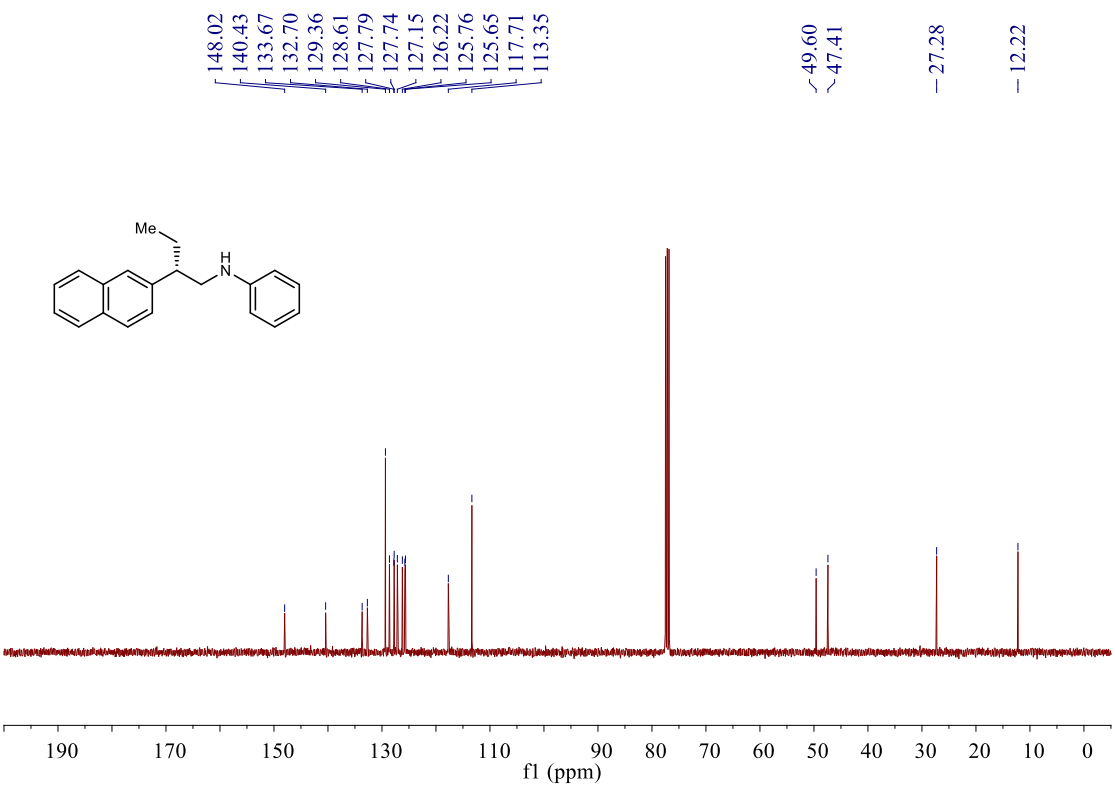
Compound 49 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



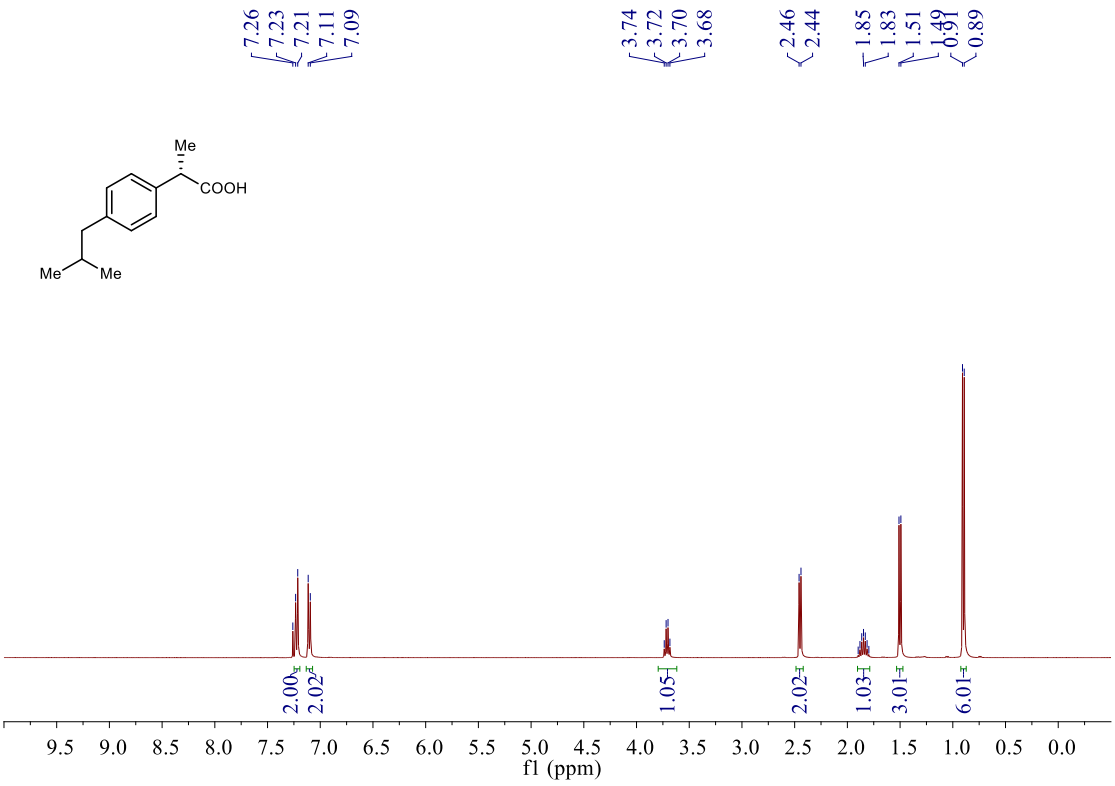


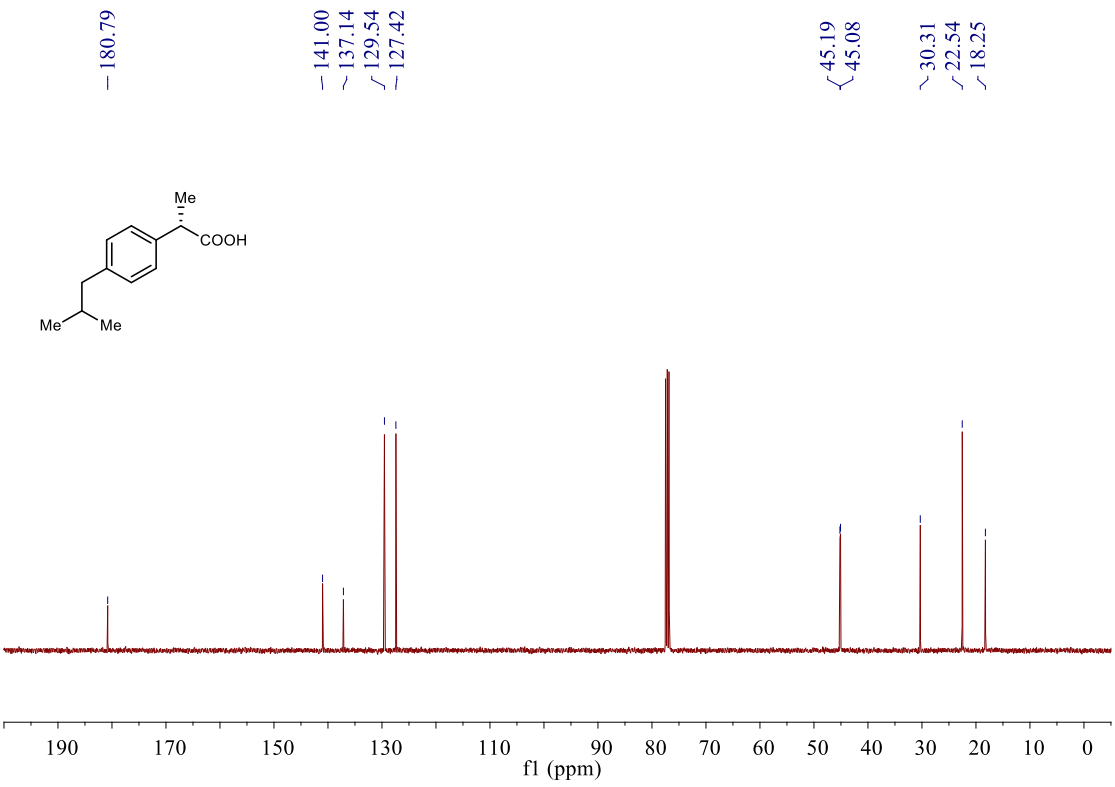
Compound 50 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)


7.84
7.82
7.81
7.65
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.36
7.36
7.34
7.34
7.18
7.16
7.16
7.14
6.73
6.71
6.69
6.59
6.57
3.57
3.56
3.54
3.52
3.35
3.33
3.32
3.30
3.00
2.98
2.97
1.89
1.88
1.87
1.78
1.78
1.76
0.90
0.88
0.86
Me
H
N
3.00
1.00
2.03
1.00
2.01
1.00
2.00
1.00
1.02
1.05
1.05
1.07
1.08
3.00
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)

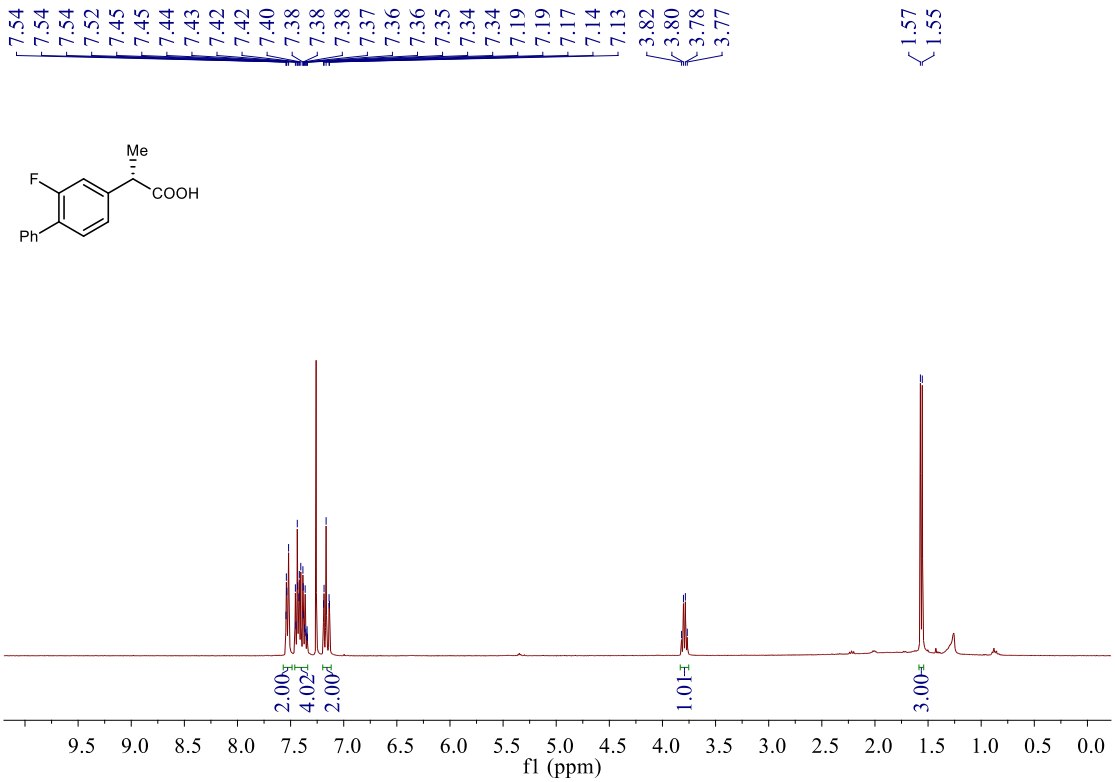

148.02
140.43
133.67
132.70
129.36
128.61
127.79
127.74
127.15
126.22
125.76
125.65
117.71
113.35
49.60
47.41
27.28
12.22
Me
H
N
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

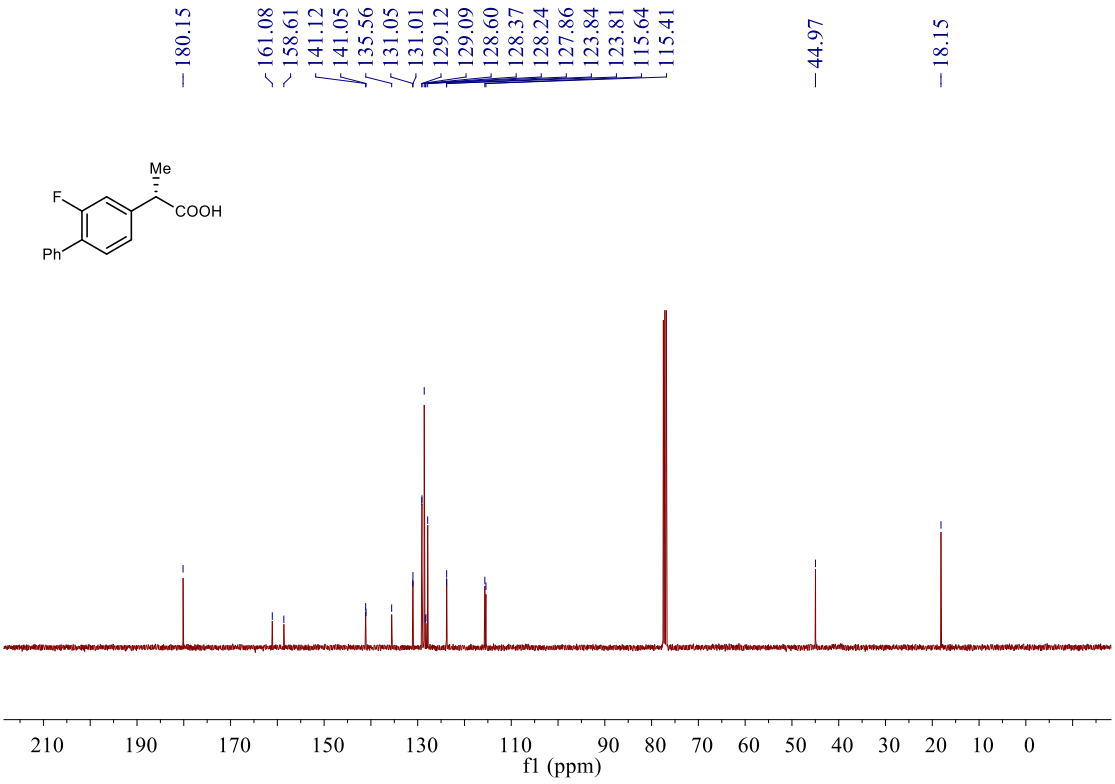
Compound 51 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

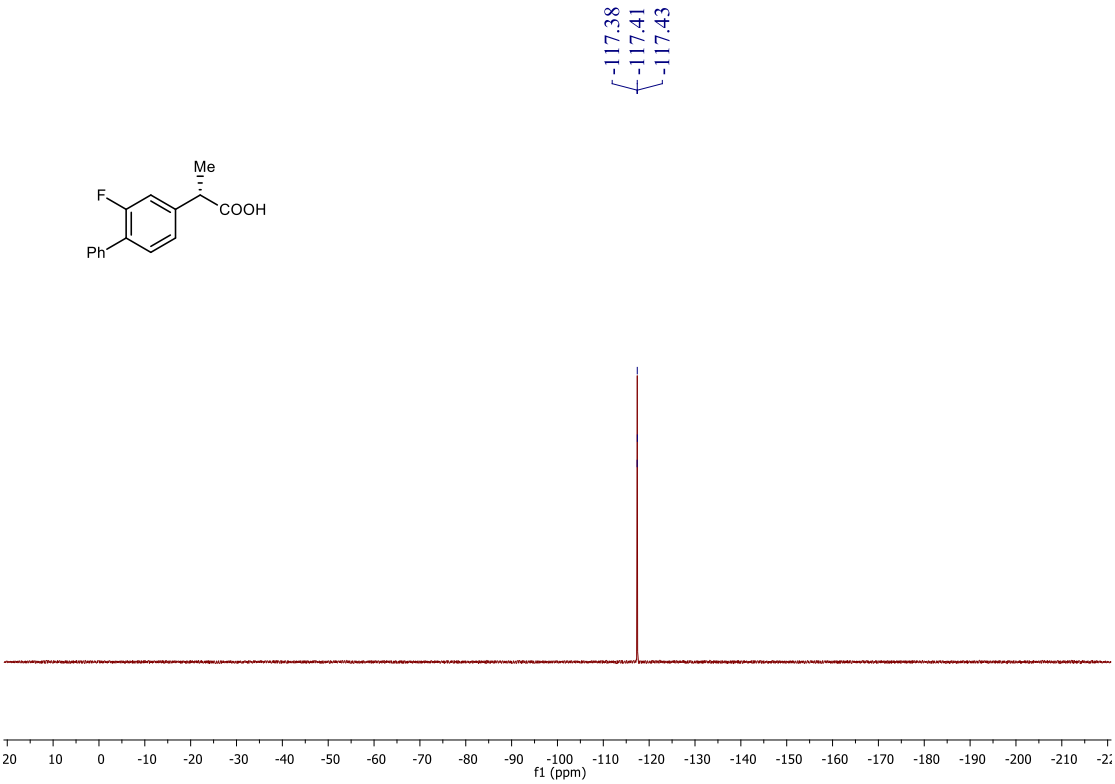




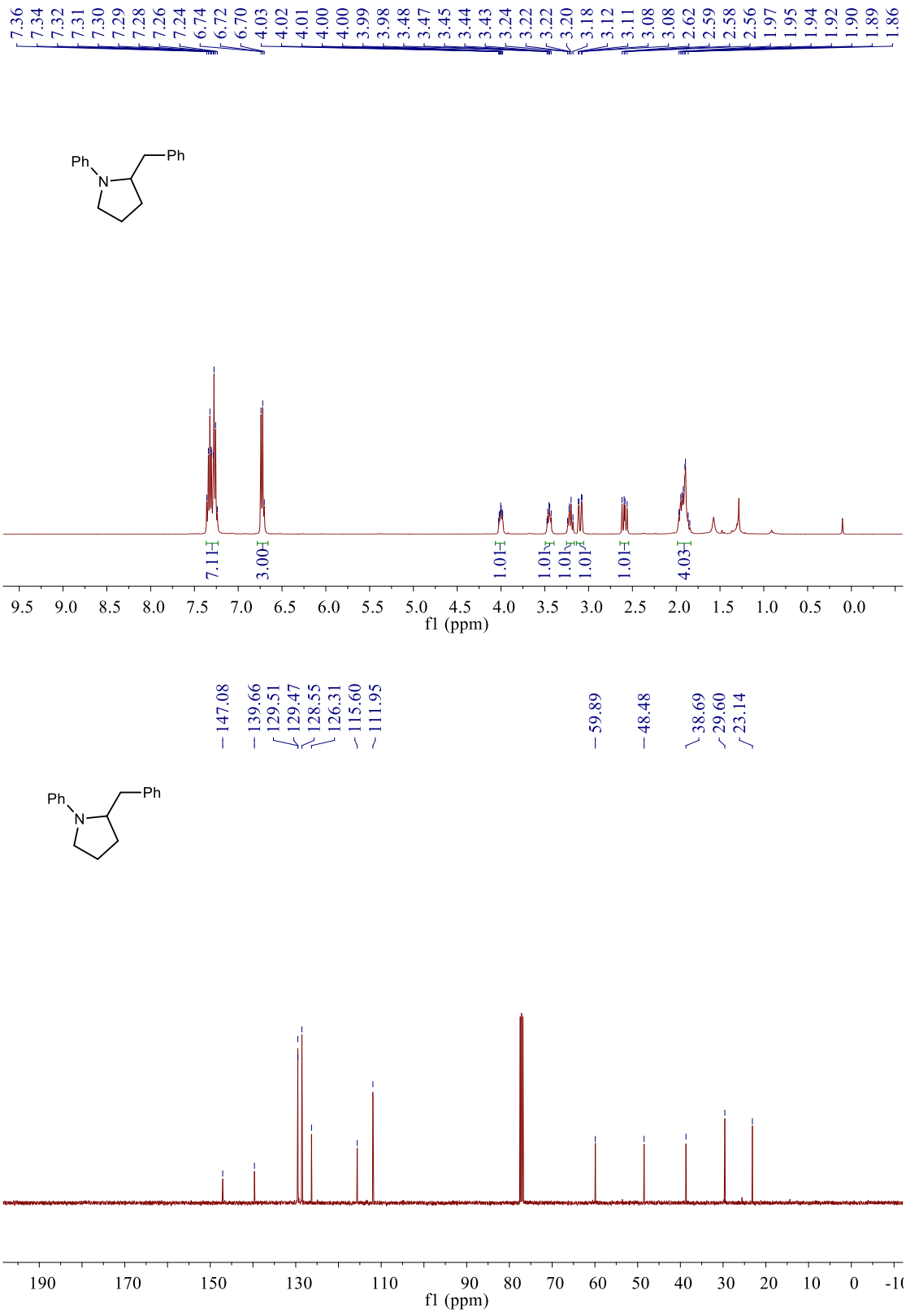
Compound 52 (^{1}H NMR, ^{13}C NMR and ^{19}F NMR, $CDCl_3$, 400 MHz, 101 MHz and 376 MHz respectively)



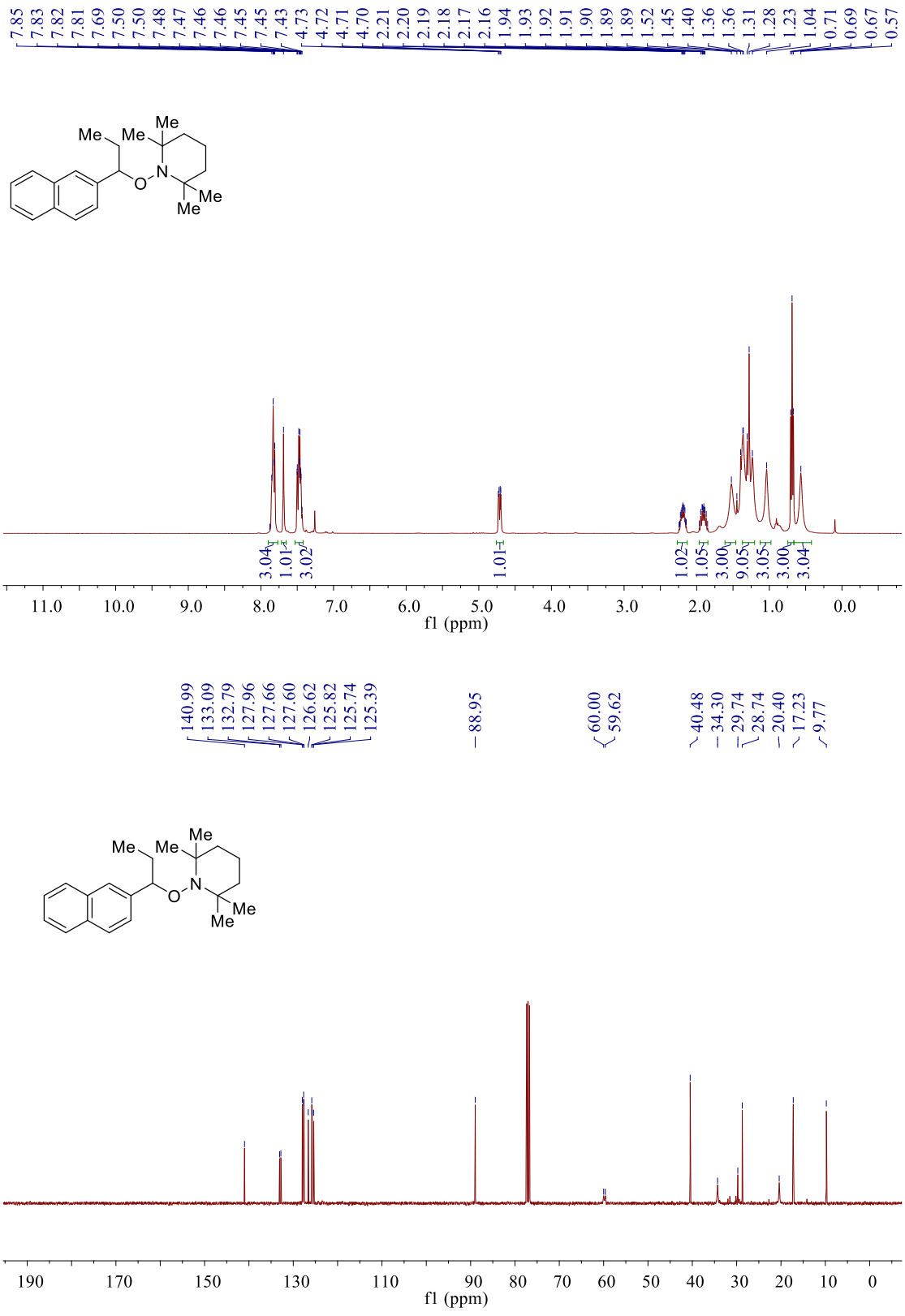



-117.38
-117.41
-117.43
Me
F
COOH
Ph
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

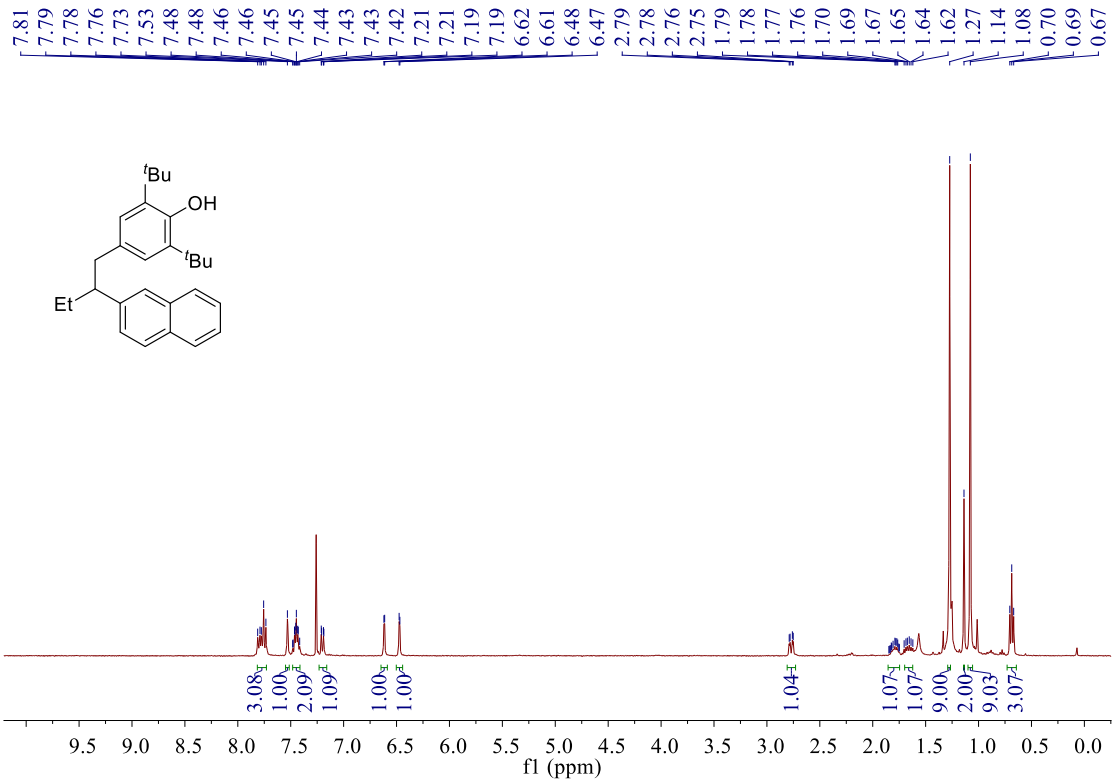
Compound 5 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)



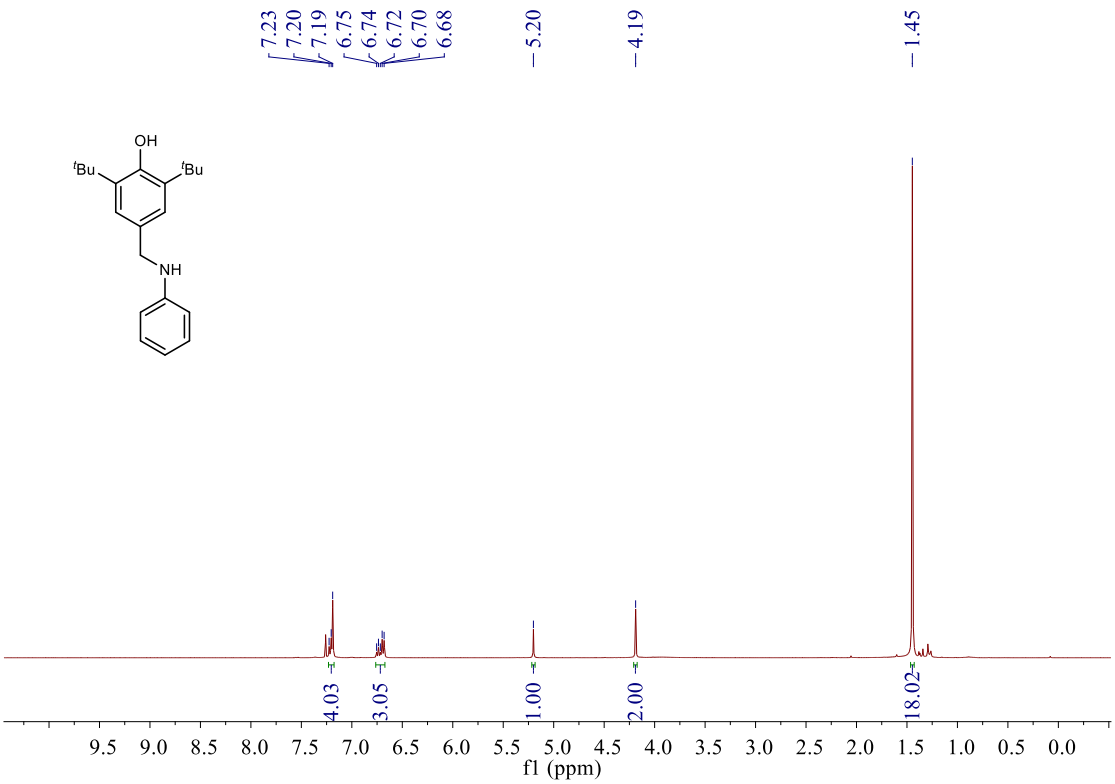
Compound 7 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

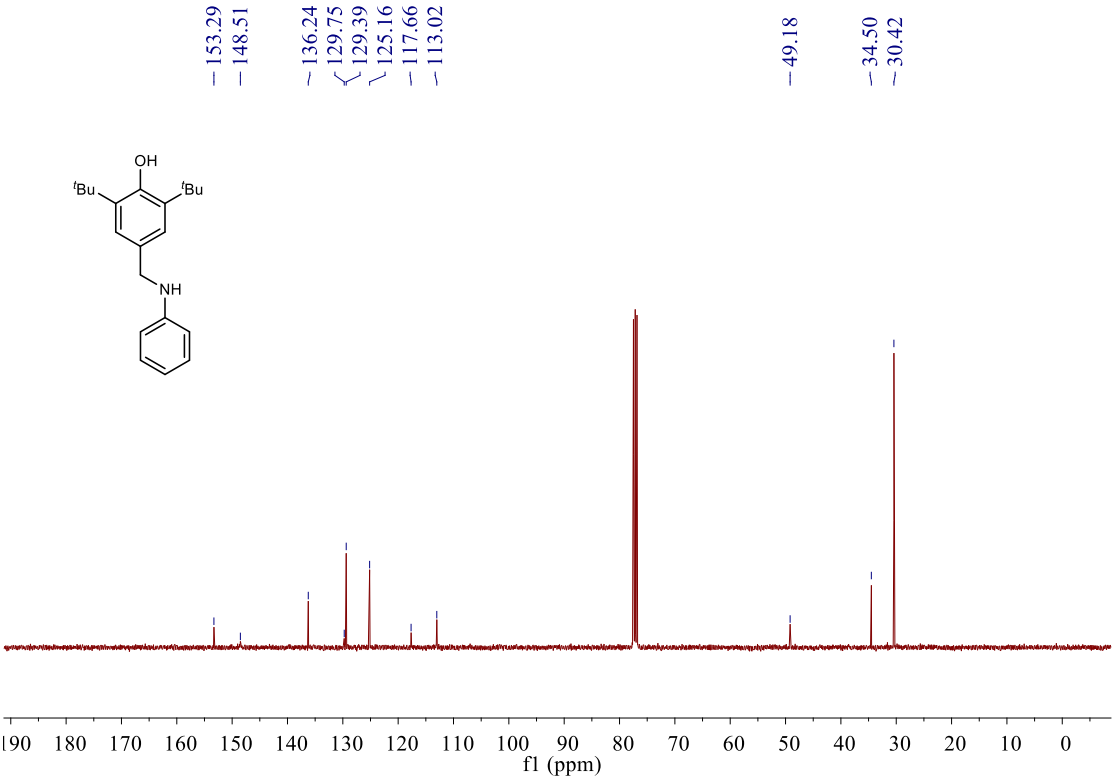


Compound 54 (^{1}H NMR, $CDCl_3$, 400 MHz)

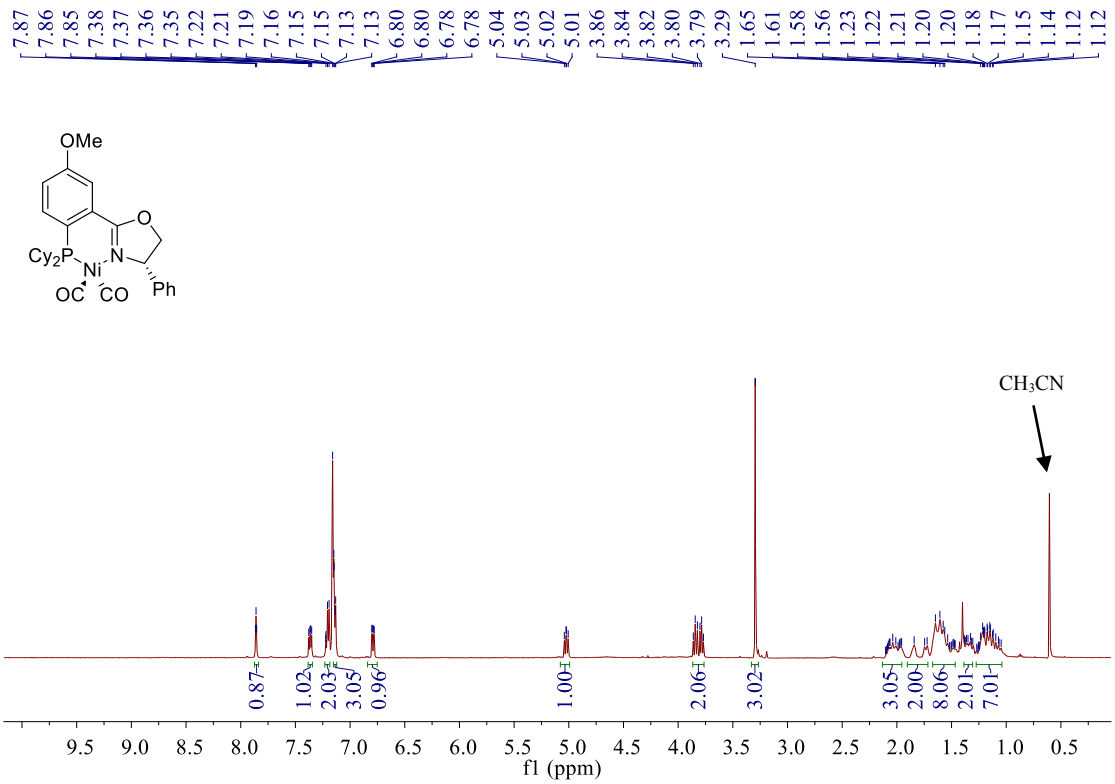


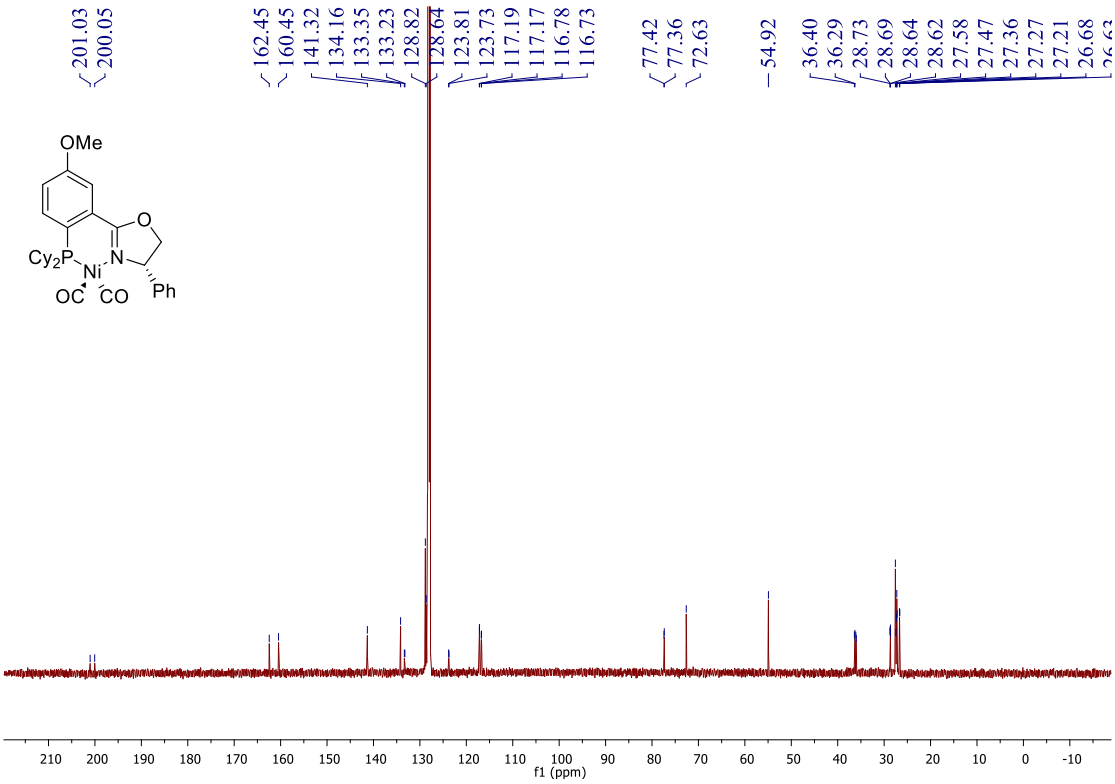
Compound 55 (^{1}H NMR and ^{13}C NMR, $CDCl_3$, 400 MHz and 101 MHz respectively)

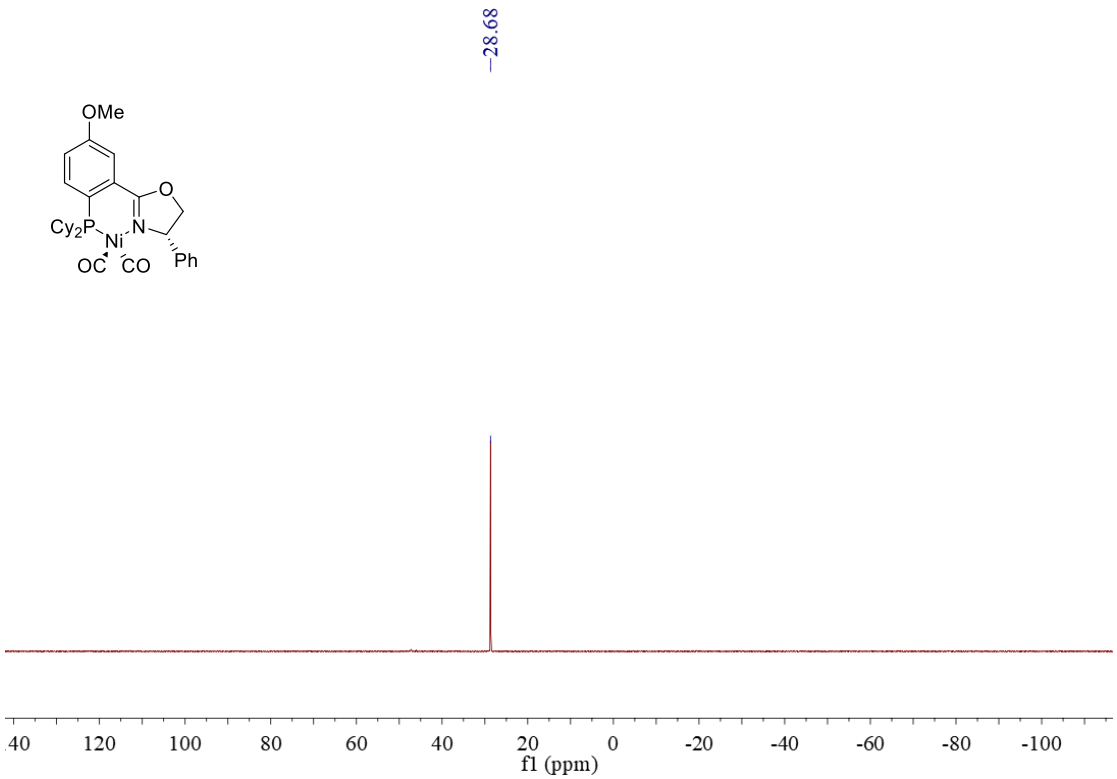




Compound (L5)Ni(CO)$_2$ B (^{1}H NMR, ^{13}C NMR and ^{31}P NMR, C_6D_6, 400 MHz, 126 MHz and 162 MHz respectively)






28.68
OMe
O
Cy2P
Ni
N
OC
CO
Ph
40
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

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