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Supporting Information for

$B(C_6F_5)_3$-Catalyzed Stepwise 1,5-Hydride Migration/Cyclization: Diastereoselective Construction of Carbocyclic β-Amino Acid Derivatives.

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Table of Contents

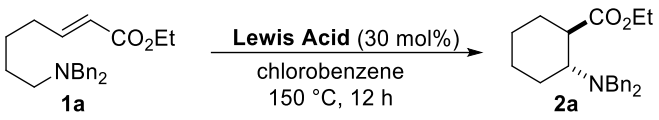
1. General Information

All non-aqueous reactions and manipulations were using standard Schlenk techniques. NMR spectra were recorded on BRUKER Avence III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. Coupling constants (J) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI). Single crystal X-ray diffraction analyses were recorded on Bruker SMART APEX II. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Adamas-beta, J&K Scientfic or Energy Chemical. The reactions were monitored by thin-layer chromatography using TLC plates and visualized by short-wave ultraviolet light. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh).

2. Optimization of the Reaction Conditions

Ethyl (*E*)-7-(dibenzylamino) hept-2-enoate **1a** (105 mg, 0.3 mmol, 1 equiv.), Lewis Acid, solvent (4 mL) were added to a 25 mL flame-dried Young-type tube in the glove box under nitrogen atomsphere. The mixture was stirred at designed temperature in an oil bath for 12 hours. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product.

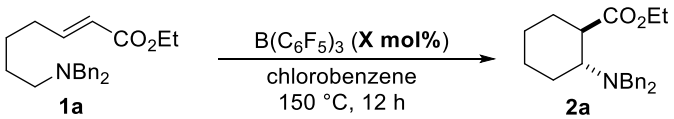
2.1 Screening of Lewis Acid.[a]



entry	Lewis Acid (30 mol%)	**2a** yield (%)
1	$AlCl_3$	33
2	$BF_3 \bullet Et_2O$	0
3	$TiCl_4$	0
4	$Sc(OTf)_3$	0
5	$Yb(OTf)_3$	0
6	$Zn(OTf)_2$	0
7	$FeCl_3$	0
8	$AgSbF_6$	0
9	$B(C_6F_5)_3$	60

[a] Reaction conditions: **1a** (105 mg, 0.3 mmol), Lewis Acid (0.09 mmol, 30 mol%), chlorobenzene (4.0 mL), 150 ℃, 12 h; isolated yield.

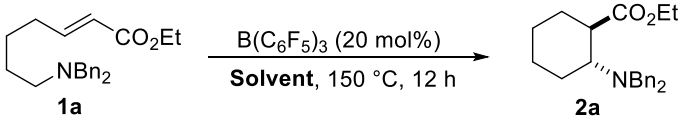
2.2 Effect of the Loading of $B(C_6F_5)_3$.[a]



entry	$B(C_6F_5)_3$ (X mol%)	**2a** yield (%)
1	30	60
2	20	80
3	10	57

[a] Reaction conditions: **1a** (105 mg, 0.3 mmol), $B(C_6F_5)_3$, chlorobenzene (4.0 mL), 150 ℃, 12 h; isolated yield.

2.3 Screening of Solvent.[a]

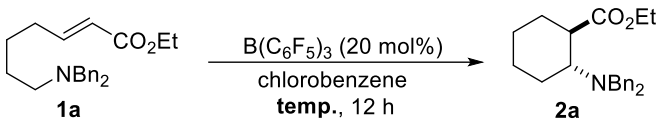


entry	Solvent	**2a** yield (%)

1	Mesitylene	77
2	chlorobenzene	80
3	toluene	69
4	benzotrifluoride	62
5	$CHCl_3$	trace
6	DCM	0
7	DCE	55

[a] Reaction conditions: **1a** (105 mg, 0.3 mmol), $B(C_6F_5)_3$ (0.06mmol, 20 mol%), solvent (4.0 mL), 150 °C, 12 h; isolated yield.

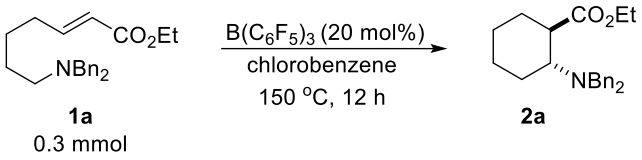
2.4 Effect of Temperature.[a]



entry	temp. (°C)	**2a** yield (%)
1	150	80
2	130	0
3	110	0

[a] Reaction conditions: **1a** (105 mg, 0.3 mmol), $B(C_6F_5)_3$ (0.06mmol, 20 mol%), chlobenzene (4.0 mL), 12 h; isolated yield.

3. General Procedure for the Catalytic Reaction



1a
0.3 mmol

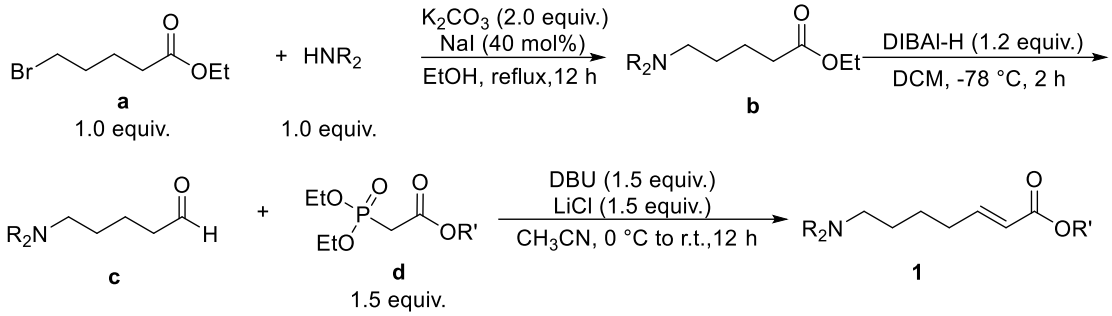
2a

To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $B(C_6F_5)_3$ (0.06 mmol, 20 mol%), acrylate **1** (0.30 mmol) and chlorobenzene (4.0 mL) in the glove box. Then the mixture was removed from glove box and heated to 150 °C in an oil bath and stirred for 12 hours. After the reaction mixture was cooled to room temperature, the solvent was evaporaed under reduced pressure and the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product.

4. Experimental Characterization Data

4.1 Preparation and Spectral Data of Substrates

General Procedure A: Synthesis of Substrate 1a~1r and 1t~1u.



Step 1.

A flame-dried two-neck flask (250 mL) equipped with a reflux condenser and a stirring bar was charged with **a** (9.5 mmol, 1.0 equiv.), potassium carbonate (2.6 g, 19.1 mmol, 2.0 equiv.) and sodium iodide (0.57 g, 3.8 mmol, 0.4 equiv.) in EtOH (50 mL, 0.2 M). Corresponding amine (9.5 mmol, 1.0 equiv.) was added dropwise to the mixture by syringe under nitrogen atmosphere at room temperature over 10 minutes. The reaction mixture was heated to 93 °C in an oil bath and stirred for 12 hours. Then the reaction flask was cooled to room temperature. Next 1 mL water was added to quench the reaction and the solution was concentrated in vacuo to remove EtOH. The aqueous layer was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was obtained and used directly for the next step without further purification.

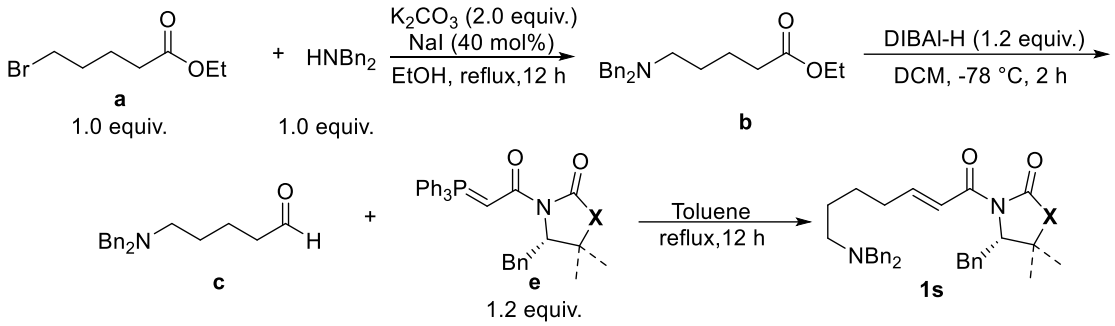
Step 2.

A flame-dried single-neck flask (250 mL) with stirring bar was charged with corresponding amine **b** (9.5 mmol, 1.0 equiv.) in anhydrous dichloromethane (50 mL, 0.2 M). DIBAL-H (11.4 mL, 11.4 mmol, 1.0 M in hexane, 1.2 equiv.) was added to the mixture in portions under nitrogen atmosphere at -78 °C over 10 minutes. The heterogeneous reaction mixture was stirred at same temperature for 2 hours. The resulting mixture was quenched by 20 mL saturated potassium sodium tartrate solution slowly. After stirring for an additional 30 minutes, the resulting solution was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was obtained and used directly for the next step without further purification.

Step 3.

A flame-dried single-neck flask (250 mL) with stirring bar was charged with corresponding phosphate **d** (14.5 mmol, 1.5 equiv.), DBU (2.1 mL, 14.3 mmol, 1.5 equiv.) and LiCl (0.61 g, 14.3 mmol, 1.5 equiv.) in anhydrous CH_3CN (25 mL, 0.2 M) under nitrogen atomsphere in 0 °C ice bath and then stirred at same temperature for 1 hour. Corresponding aldehyde (9.5 mmol, 1.0 equiv.) was added to the mixture via syringe, and stirred at room temperature for another 12 hours. Then reaction mixture was quenched by 5 mL saturated sodium carbonate solution slowly. the resulting solution was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. The resulting organic phase was concentrated under reduced pressure and the residue was purified by chromatography.

General Procedure B: Synthesis of Substrate 1s and 1v



Step 1.

A flame-dried two-neck flask (250 mL) equipped with a reflux condenser and a stirring bar was charged with **a** (2.0 g, 9.5 mmol, 1.0 equiv.), potassium carbonate (2.6 g, 19.1 mmol, 2.0 equiv.) and sodium iodide (0.57 g, 3.8 mmol, 0.4 equiv.) in EtOH (50 mL, 0.2 M). Corresponding amine (9.5 mmol, 1.0 equiv.) was added dropwise to the mixture by syringe under nitrogen atmosphere at room temperature over 10 minutes. The reaction mixture was heated to 93 °C in an oil bath and stirred for 12 hours. Then the reaction flask was cooled to room temperature. Next 1 mL water was added to quench the reaction and the solution was concentrated in vacuo to remove EtOH. The aqueous layer was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was obtained and used directly for the next step without further purification.

Step 2.

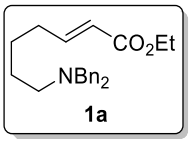
A flame-dried single-neck flask (250 mL) with stirring bar was charged with corresponding amine **b** (9.5 mmol, 1.0 equiv.) in anhydrous dichloromethane (50 mL, 0.2 M). DIBAL-H (11.4 mL, 11.4 mmol, 1.0 M in hexane, 1.2 equiv.) was added to the mixture in portions under nitrogen atmosphere at -78 °C over 10 minutes. The heterogeneous reaction mixture was stirred at same temperature for 2 hours. The resulting mixture was quenched by 20 mL saturated potassium sodium tartrate solution slowly. After stirring for an additional 30 minutes, the resulting solution was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was obtained and used directly for the next step without further purification.

Step 3.

A flame-dried single-neck flask (100 mL) with stirring bar was charged with 1-(2-(triphenyl-λ^5-phosphaneylidene)acetyl)pyrrolidin-2-one (2.3 g, 6.0 mmol, 1.2 equiv.) in anhydrous toluene (20 mL) under nitrogen atmosphere, then **c** (1.4 g, 5 mmol, 1.0 equiv.) was added to the mixture via syringe, and stirred at 110 °C for 12 hours. Then reaction mixture was quenched by 5 mL water slowly. The resulting solution was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4. The resulting organic phase was concentrated under reduced pressure and the residue was purified by chromatography.

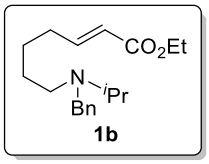
4.2 Substrates Characterization

Ethyl (*E*)-7-(dibenzylamino)hept-2-enoate (1a)



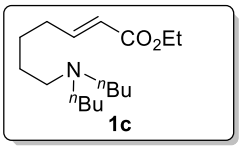
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.5 g, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.43 – 7.26 (m, 8H), 7.27 – 7.19 (m, 2H), 6.91 (dt, *J* = 15.7, 6.6 Hz, 1H), 5.75 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.54 (s, 4H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.14 – 2.01 (m, 2H), 1.68 – 1.38 (m, 4H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.9, 149.4, 140.1, 128.9, 128.3, 126.9, 121.5, 60.3, 58.6, 53.0, 32.0, 26.7, 25.7, 14.4. **HRMS** (ESI) calcd for $C_{23}H_{30}NO_2$ $[M+H]^+$: 352.2272, found: 352.2280.

Ethyl (*E*)-7-(benzyl(isopropyl)amino)hept-2-enoate (1b)



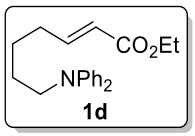
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.1 g, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.26 (m, 4H), 7.24 – 7.16 (m, 1H), 6.92 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.76 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.53 (s, 2H), 2.97 – 2.87 (m, 1H), 2.40 (t, *J* = 6.5 Hz, 2H), 2.17 – 2.06 (m, 2H), 1.51 – 1.35 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 166.9, 149.6, 141.7, 128.5, 128.2, 126.6, 121.4, 60.3, 54.1, 49.5, 49.0, 32.2, 28.1, 25.8, 18.0, 14.4. **HRMS** (ESI) calcd for $C_{19}H_{30}NO_2$ $[M+H]^+$: 304.2277, found: 304.2274.

Ethyl (*E*)-7-(dibutylamino)hept-2-enoate (1c)



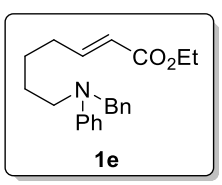
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.0 g, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.95 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.55 – 2.28 (m, 6H), 2.25 – 2.17 (m, 2H), 1.48 – 1.42 (m, 4H), 1.43 – 1.34 (m, 4H), 1.33 – 1.23 (m, 7H), 0.90 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 167.0, 149.4, 121.5, 60.3, 54.04, 53.94, 32.3, 29.4, 26.8, 26.2, 21.0, 14.4, 14.3. **HRMS** (ESI) calcd for $C_{12}H_{34}NO_2$ $[M+H]^+$: 284.2590, found: 284.2594.

Ethyl (*E*)-7-(diphenylamino)hept-2-enoate (1d)



The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.0 g, 65% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.30 – 7.19 (m, 4H), 7.06 – 6.84 (m, 7H), 5.79 (dt, *J* = 15.6, 1.7 Hz, 1H), 4.18 (q, *J* = 6.8 Hz, 2H), 3.70 (t, *J* = 7.6 Hz, 2H), 2.21 (q, *J* = 7.4 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.60 – 1.48 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 166.8, 148.8, 148.1, 129.4, 121.8, 121.3, 121.0, 60.3, 52.1, 32.1, 27.2, 25.7, 14.4. **HRMS** (ESI) calcd for $C_{21}H_{27}NO_2$ $[M+H]^+$: 324.1964, found: 324.1973.

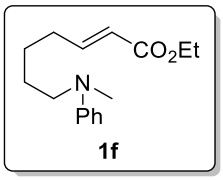
Ethyl (*E*)-7-(benzyl(phenyl)amino)hept-2-enoate (1e)



The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.4 g, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.28 (m, 2H), 7.26 – 7.15 (m, 5H), 6.95 (dt, *J* = 15.9, 6.9 Hz, 1H), 6.73 – 6.64 (m, 3H), 5.82 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.54 (s, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.40 (t, 2H), 2.32 – 2.14 (m, 2H), 1.81 – 1.64 (m, 2H), 1.55 – 1.45 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 148.8, 148.6, 139.1, 129.4, 128.7, 126.9,

126.7, 121.8, 116.3, 112.3, 60.3, 54.7, 51.0, 32.2, 26.9, 25.7, 14.4. **HRMS** (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found: 338.2129.

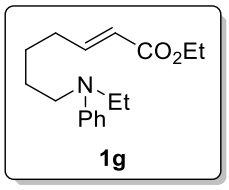
Ethyl (*E*)-7-(methyl(phenyl)amino)hept-2-enoate (1f)



1f

The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.9 g, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.25 – 7.17 (m, 2H), 6.95 (dt, *J* = 15.5, 6.5 Hz, 1H), 6.75 – 6.63 (m, 3H), 5.82 (dt, *J* = 15.6, 1.4 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.3 Hz, 2H), 2.92 (s, 3H), 2.27 – 2.20 (m, 2H), 1.67 – 1.56 (m, 2H), 1.55 – 1.45 (m, 2H), 1.28 – 2.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 149.4, 148.9, 129.3, 121.7, 116.2, 112.3, 60.3, 52.6, 38.5, 32.2, 26.5, 25.8, 14.4. **HRMS** (ESI) calcd for $C_{16}H_{24}NO_2$ $[M+H]^+$: 262.1807, found: 262.1808.

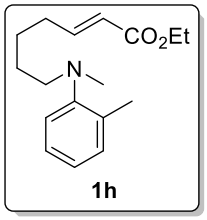
Ethyl (*E*)-7-(ethyl(phenyl)amino)hept-2-enoate (1g)



1g

The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.1 g, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.25 – 7.17 (m, 2H), 6.96 (dt, *J* = 15.0, 7.0 Hz, 1H), 6.70 – 6.60 (m, 3H), 5.89 – 5.76 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.35 (q, *J* = 7.0 Hz, 2H), 3.29 – 3.22 (m, 2H), 2.25 (qd, *J* = 7.1, 1.6 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.56 – 1.46 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 148.9, 148.0, 129.4, 121.7, 115.6, 112.0, 60.3, 50.2, 45.1, 32.2, 27.3, 25.8, 14.4, 12.4. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1964.

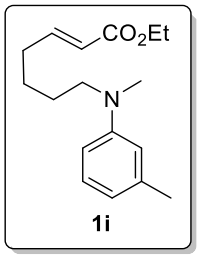
Ethyl (*E*)-7-(methyl(o-tolyl)amino)hept-2-enoate (1h)



1h

The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.9 g, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.20 – 7.11 (m, 2H), 7.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.99 – 6.88 (m, 2H), 5.80 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.92 – 2.76 (m, 2H), 2.64 (s, 3H), 2.30 (s, 3H), 2.23 – 2.14 (m, 2H), 1.64 – 1.40 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.9, 152.4, 149.2, 133.4, 131.2, 126.5, 123.0, 121.5, 120.1, 60.3, 55.9, 42.1, 32.2, 27.2, 25.7, 18.4, 14.4. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1962.

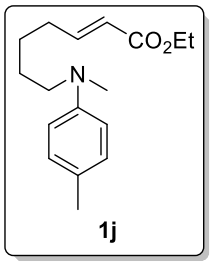
Ethyl (*E*)-7-(methyl(m-tolyl)amino)hept-2-enoate (1i)



1i

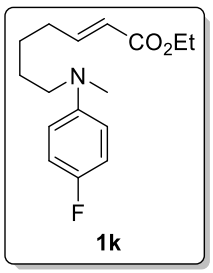
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.9 g, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.11 (t, *J* = 7.9 Hz, 1H), 6.94 (dt, *J* = 15.6, 7.0, Hz, 1H), 6.58 – 6.47 (m, 3H), 5.82 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.91 (s, 3H), 2.31 (s, 3H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.63 – 1.58 (m, 2H), 1.56 – 1.39 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 166.8, 149.4, 149.0, 139.0, 129.2, 121.7, 117.1, 113.0, 109.5, 60.3, 52.7, 38.6, 32.2, 26.5, 25.8, 22.1, 14.4. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1969.

Ethyl (*E*)-7-(methyl(p-tolyl)amino)hept-2-enoate (1j)



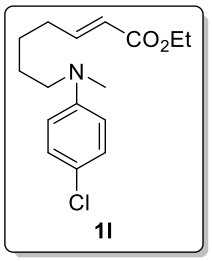
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.0 g, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.09 – 7.00 (m, 2H), 6.95 (dt, *J* = 15.6, 7.0 Hz, 1H), 6.71 – 6.54 (m, 2H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.24 (m, 2H), 2.88 (s, 3H), 2.39 – 2.10 (m, 5H), 1.64 – 1.54 (m, 2H), 1.53 – 1.43 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 149.0, 147.5, 129.8, 125.5, 121.7, 112.8, 60.3, 53.0, 38.7, 32.2, 26.4, 25.8, 20.3, 14.4. **HRMS** (ESI) calcd for $C_{18}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1954.

Ethyl (*E*)-7-((4-fluorophenyl)(methyl)amino)hept-2-enoate (1k)



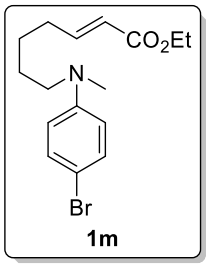
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.7 g, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.99 – 6.89 (m, 3H), 6.74 – 6.44 (m, 2H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.26 (t, *J* = 7.2 Hz, 2H), 2.87 (s, 3H), 2.27 – 2.20 (m, 2H), 1.63 – 1.54 (m, 2H), 1.53 – 1.43 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 155.4 (d, *J* = 234.8 Hz), 148.8, 146.3 (d, *J* = 1.7 Hz), 121.8, 115.6 (d, *J* = 21.9 Hz), 113.6 (d, *J* = 7.3 Hz), 60.4, 53.4, 39.0, 32.2, 26.3, 25.8, 14.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -129.6. **HRMS** (ESI) calcd for $C_{16}H_{23}FNO_2$ $[M+H]^+$: 280.1713, found: 280.1711.

Ethyl (*E*)-7-((4-chlorophenyl)(methyl)amino)hept-2-enoate (1l)



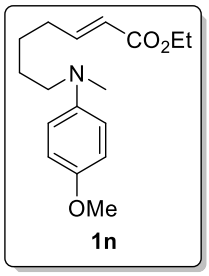
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.9 g, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.19 – 7.11 (m, 2H), 6.94 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.62 – 6.53 (m, 2H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.25 (m, 2H), 2.89 (s, 3H), 2.28 – 2.16 (m, 2H), 1.63 – 1.54 (m, 2H), 1.53 – 1.43 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 148.7, 148.0, 129.1, 121.9, 121.0, 113.4, 60.4, 52.7, 38.6, 32.2, 26.4, 25.7, 14.4. **HRMS** (ESI) calcd for $C_{16}H_{23}ClNO_2$ $[M+H]^+$: 296.1417, found:296.1414.

Ethyl (*E*)-7-((4-bromophenyl)(methyl)amino)hept-2-enoate (1m)



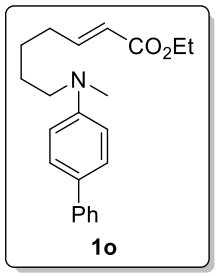
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.0 g, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.32 – 7.23 (m, 2H), 6.93 (dt, *J* = 15.6, 7.0 Hz, 1H), 6.60 – 6.47 (m, 2H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.36 – 3.19 (m, 2H), 2.89 (s, 3H), 2.28 – 2.17 (qd, *J* = 7.1, 1.6 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.52 – 1.43 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 148.7, 148.3, 131.9, 121.8, 113.8, 108.0, 60.4, 52.6, 38.6, 32.2, 26.3, 25.7, 14.4. **HRMS** (ESI) calcd for $C_{16}H_{23}BrNO_2$ $[M+H]^+$: 340.0912, found: 340.0921.

Ethyl (*E*)-7-((4-methoxyphenyl)(methyl)amino)hept-2-enoate (1n)



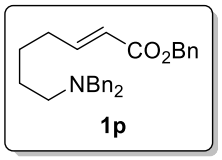
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.7 g, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.95 (dt, *J* = 15.4, 7.0 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.75 – 6.63 (m, 2H), 5.81 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.22 (t, *J* = 7.2 Hz, 2H), 2.84 (s, 3H), 2.28 – 2.15 (m, 2H), 1.76 – 1.52 (m, 2H), 1.52 – 1.42 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 151.7, 148.9, 144.5, 121.7, 114.9, 114.7, 60.3, 55.9, 53.8, 39.2, 32.2, 26.3, 25.8, 14.4. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_3$ $[M+H]^+$: 292.1913, found: 292.1907.

Ethyl (*E*)-7-((4-methoxyphenyl)(methyl)amino)hept-2-enoate (1o)



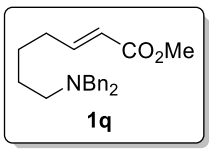
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.5 g, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.60 – 7.53 (m, 2H), 7.53 – 7.46 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.20 (m, 1H), 6.96 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.84 – 6.62 (m, 2H), 5.83 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 7.3 Hz, 2H), 2.97 (s, 3H), 2.29 – 2.20 (m, 2H), 1.72 – 1.60 (m, 2H), 1.59 – 1.47 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.8, 148.8, 148.7, 141.4, 128.9, 128.8, 128.0, 126.4, 126.1, 121.8, 112.4, 60.4, 52.6, 38.6, 32.2, 26.6, 25.8, 14.4. **HRMS** (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found: 338.2120.

Benzyl (*E*)-7-(dibenzylamino)hept-2-enoate (1p)



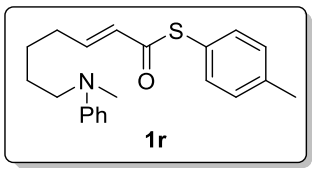
The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.2 g, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.41 – 7.28 (m, 13H), 7.25 – 7.19 (m, 2H), 6.95 (dt, *J* = 14.0, 6.9 Hz, 1H), 5.80 (dt, *J* = 15.7, 1.3 Hz, 1H), 5.18 (s, 2H), 3.53 (s, 4H), 2.40 (t, *J* = 6.7 Hz, 2H), 2.18 – 1.92 (m, 2H), 1.56 – 1.33 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.7, 150.2, 140.0, 136.3, 128.9, 128.7, 128.34, 128.30, 126.9, 121.1, 66.1, 58.5, 52.9, 32.1, 26.6, 25.6. **HRMS** (ESI) calcd for $C_{28}H_{32}NO_2$ $[M+H]^+$: 414.2433, found: 414.2426.

Methyl (*E*)-7-(dibenzylamino)hept-2-enoate (1q)



The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 2.1 g, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.28 (m, 8H), 7.25 – 7.18 (m, 2H), 6.92 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.75 (dt, *J* = 15.6, 1.6 Hz, 1H), 3.73 (s, 3H), 3.53 (s, 4H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.12 – 2.02 (m, 2H), 1.56 – 1.48 (m, 2H), 1.48 – 1.40 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 167.3, 149.8, 140.0, 128.9, 128.3, 127.0, 121.0, 58.5, 52.9, 51.5, 32.0, 26.6, 25.6. **HRMS** (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found: 338.2118.

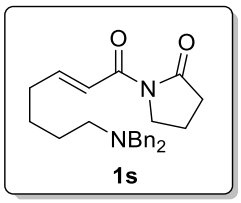
Methyl (*E*)-7-(dibenzylamino)hept-2-enoate (1r)



The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.9 g, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.28 (m, 2H), 7.27 – 7.18 (m, 4H), 6.95 (dt, *J* = 15.4, 7.0 Hz, 1H), 6.77 – 6.58 (m, 3H), 6.18 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.33 (t, *J* = 7.2 Hz, 2H), 2.93 (s, 3H), 2.38 (s, 3H), 2.26 (q, *J* = 7.1, 1.5 Hz, 2H), 1.72 – 1.57 (m, 2H), 1.56 – 1.45 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 188.7, 149.3, 146.1,

139.8, 134.8, 130.2, 129.4, 128.2, 124.1, 116.2, 112.3, 52.6, 38.5, 32.3, 26.5, 25.7, 21.5. **HRMS** (ESI) calcd for $C_{21}H_{26}NOS$ $[M+H]^+$: 340.1735, found: 340.1742.

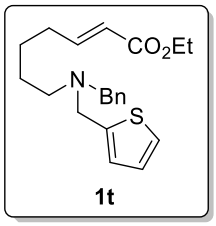
(*E*)-1-(7-(Dibenzylamino)hept-2-enoyl)pyrrolidin-2-one (1s)



1s

The title compound was prepared according to the general procedure **B** and purified by column chromatography to give a colorless oil, 2.4 g, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.41 – 7.34 (m, 4H), 7.34 – 7.28 (m, 4H), 7.25 – 7.16 (m, 3H), 7.13 – 6.97 (m, 1H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.54 (s, 4H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.42 (t, *J* = 6.7 Hz, 2H), 2.16 (q, *J* = 7.1 Hz, 2H), 2.08 – 1.94 (m, 2H), 1.60 – 1.40 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.6, 166.4, 150.7, 140.0, 128.9, 128.3, 126.9, 122.3, 58.5, 53.0, 45.8, 34.1, 32.5, 26.7, 25.9, 17.3. **HRMS** (ESI) calcd for $C_{25}H_{31}N_2O_2$ $[M+H]^+$: 391.2386, found: 391.2381.

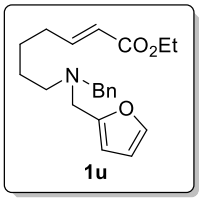
Ethyl (*E*)-7-(benzyl(thiophen-2-ylmethyl)amino)hept-2-enoate (1t)



1t

The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.7 g, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.40 – 7.28 (m, 4H), 7.26 – 7.19 (m, 2H), 6.99 – 6.84 (m, 3H), 5.76 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 2H), 3.58 (s, 2H), 2.45 (t, *J* = 6.7 Hz, 2H), 2.18 – 2.05 (m, 2H), 1.57 – 1.43 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.9, 149.4, 143.5, 139.7, 128.9, 128.3, 127.0, 126.5, 125.5, 124.8, 121.5, 60.3, 58.1, 52.7, 52.6, 32.1, 26.7, 25.6, 14.4. **HRMS** (ESI) calcd for $C_{21}H_{28}NO_2S$ $[M+H]^+$: 358.1841, found: 358.1836.

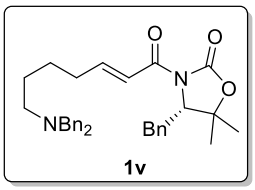
Ethyl (*E*)-7-(benzyl(furan-2-ylmethyl)amino)hept-2-enoate (1u)



1u

The title compound was prepared according to the general procedure **A** and purified by column chromatography to give a colorless oil, 1.6 g, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38 – 7.29 (m, 5H), 7.26 – 7.20 (m, 1H), 6.93 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.16 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.78 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.61 (s, 2H), 3.59 (s, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.14 (qd, *J* = 7.1, 1.6 Hz, 2H), 1.56 – 1.42 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.9, 152.9, 149.4, 142.0, 139.6, 129.0, 128.4, 127.0, 121.5, 110.1, 108.6, 60.3, 58.3, 52.9, 49.7, 32.0, 26.8, 25.7, 14.4. **HRMS** (ESI) calcd for $C_{21}H_{28}NO_3$ $[M+H]^+$: 342.2069, found: 342.2068.

(*S*,*E*)-4-Benzyl-3-(7-(dibenzylamino)hept-2-enoyl)-5,5-dimethyloxazolidin-2-one (1v)

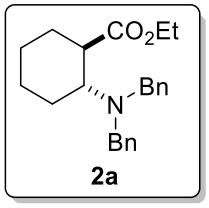


1v

The title compound was prepared according to the general procedure **B** and purified by column chromatography to give a colorless oil, 3.2 g, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 – 7.27 (m, 12H), 7.24 – 7.19 (m, 4H), 7.08 (dt, *J* = 15.4, 6.8 Hz, 1H), 4.54 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.53 (s, 4H), 3.21 (dd, *J* = 14.4, 3.5 Hz, 1H), 2.86 (dd, *J* = 14.4, 9.8 Hz, 1H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.21 – 2.10 (m, 2H), 1.59 – 1.45 (m, 4H), 1.35 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 165.5, 152.7, 151.5, 140.0, 137.2, 129.1, 128.9, 128.8, 128.7, 128.3, 128.2, 126.9, 126.8, 120.8, 82.2, 63.8, 58.4, 52.9, 35.3, 32.5, 28.6, 26.7, 25.8, 22.4. **HRMS** (ESI) calcd for $C_{33}H_{39}N_2O_3$ $[M+H]^+$: 511.2961, found: 511.2958.

4.3 Products Characterization

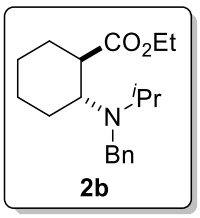
Ethyl-*trans*-2-(dibenzylamino)cyclohexane-1-carboxylate (2a)



2a

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 85 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31 – 7.17 (m, 10H), 4.25 – 4.16 (m, 1H), 4.07 – 3.96 (m, 1H), 3.82 (d, *J* = 13.6 Hz, 2H), 3.38 (d, *J* = 13.6 Hz, 2H), 2.83 (td, *J* = 11.2, 3.4 Hz, 1H), 2.59 (td, *J* = 11.5, 3.6 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.89 – 1.76 (m, 2H), 1.68 – 1.65 (m, 1H), 1.50 – 1.40 (m, 1H), 1.27 – 1.10 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.2, 140.2, 129.1, 128.1, 126.8, 60.2, 59.3, 53.7, 48.6, 29.9, 25.44, 25.39, 23.7, 14.2. **HRMS** (ESI) calcd for $C_{23}H_{30}NO_2$ $[M+H]^+$: 352.2277, found:352.2291.

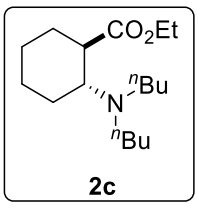
Ethyl-*trans*-2-(benzyl(isopropyl)amino)cyclohexane-1-carboxylate (2b)



2b

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 45 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.23 (m, 4H), 7.22 – 7.16 (m, 1H), 4.24 – 4.12 (m, 1H), 4.11 – 4.01 (m, 1H), 3.83 (d, *J* = 14.3 Hz, 1H), 3.54 (d, *J* = 14.3 Hz, 1H), 3.00 – 2.83 (m, 2H), 2.48 (td, *J* = 11.5, 3.7 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.91 – 1.83 (m, 1H), 1.83 – 1.75 (m, 1H), 1.73 – 1.64 (m, 1H), 1.61 – 1.46 (m, 2H), 1.43 – 1.28 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 – 1.06 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.8, 141.8, 128.7, 128.0, 126.6, 60.0, 58.1, 49.6, 49.5, 48.5, 30.2, 29.2, 26.0, 25.3, 22.4, 18.7, 14.3. **HRMS** (ESI) calcd for $C_{19}H_{30}NO_2$ $[M+H]^+$: 304.2277, found: 304.2278.

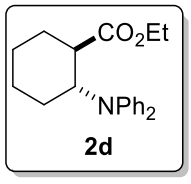
Ethyl-*trans*-2-(dibutylamino)cyclohexane-1-carboxylate (2c)



2c

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 51 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.13 (q, *J* = 7.1 Hz, 2H), 2.51 – 2.34 (m, 6H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.89 – 1.73 (m, 1H), 1.66 – 1.56 (m, 2H), 1.49 – 1.36 (m, 6H), 1.32 – 1.17 (m, 8H), 0.97 – 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 173.9, 60.3, 54.0, 53.8, 34.5, 29.3, 26.7, 23.2, 20.9, 14.4, 14.3. **HRMS** (ESI) calcd for $C_{17}H_{34}NO_2$ $[M+H]^+$: 284.2590, found: 284.2594.

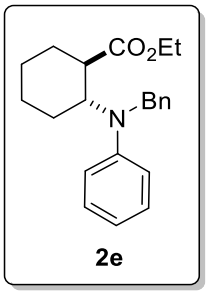
Ethyl-*trans*-2-(diphenylamino)cyclohexane-1-carboxylate (2d)



2d

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 50 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.26 – 7.21 (m, 4H), 7.00 – 6.94 (m, 2H), 6.95 – 6.85 (m, 4H), 4.35 (td, *J* = 11.5, 3.8 Hz, 1H), 4.08 – 3.87 (m, 2H), 2.51 – 2.37 (m, 1H), 2.08 – 2.00 (m, 1H), 2.00 – 1.92 (m, 1H), 1.84 – 1.75 (m, 1H), 1.73 – 1.66 (m, 1H), 1.64 – 1.53 (m, 1H), 1.50 – 1.38 (m, 1H), 1.32 – 1.23 (m, 1H), 1.07 (t, *J* = 7.2 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.1, 146.7, 129.2, 123.4, 122.0, 60.5, 58.1, 49.3, 30.6, 30.5, 25.8, 24.9, 14.1. **HRMS** (ESI) calcd for $C_{21}H_{26}NO_2$ $[M+H]^+$: 324.1964, found: 324.1966.

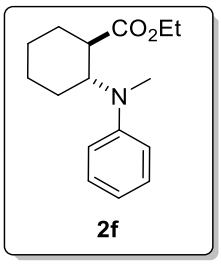
Ethyl-*trans*-2-(benzyl(phenyl)amino)cyclohexane-1-carboxylate (2e)



2e

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 72 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.26 – 7.19 (m, 4H), 7.19 – 7.05 (m, 3H), 6.88 – 6.79 (m, 2H), 6.68 (tt, *J* = 7.1, 1.0 Hz, 1H), 4.45 (q, *J* = 17.1 Hz, 2H), 4.16 (td, *J* = 11.2, 3.8 Hz, 1H), 3.94 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.82 (dq, *J* = 10.8, 7.2 Hz, 1H), 2.67 (td, *J* = 11.5, 3.7 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.98 – 1.90 (m, 1H), 1.87 – 1.73 (m, 2H), 1.72 – 1.60 (m, 1H), 1.54 – 1.33 (m, 2H), 1.28 – 1.12 (m, 1H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.0, 148.9, 139.8, 128.9, 128.3, 126.8, 126.5, 117.8, 115.8, 61.1, 60.5, 48.4, 48.0, 30.1, 29.3, 25.7, 25.0, 14.0. **HRMS** (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found: 338.2120.

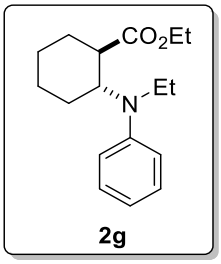
Ethyl-*trans*-2-(diphenylamino)cyclohexane-1-carboxylate (2f)



2f

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 67 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.24 – 7.16 (m, 2H), 6.88 – 6.82 (m, 2H), 6.70 (tt, *J* = 7.2, 1.1 Hz, 1H), 4.06 – 3.78 (m, 3H), 2.75 (s, 3H), 2.69 – 2.61 (m, 1H), 2.07 – 1.94 (m, 1H), 1.87 – 1.68 (m, 3H), 1.67 – 1.57 (m, 1H), 1.55 – 1.12 (m, 4H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.0, 150.5, 129.0, 117.3, 114.4, 61.0, 60.4, 48.2, 31.1, 29.7, 28.0, 25.6, 25.0, 14.2. **HRMS** (ESI) calcd for $C_{16}H_{24}NO_2$ $[M+H]^+$: 262.1807, found: 262.1808.

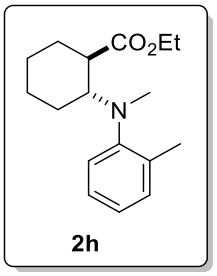
Ethyl-*trans*-2-(ethyl(phenyl)amino)cyclohexane-1-carboxylate (2g)



2g

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 74 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.23 – 7.17 (m, 2H), 6.89 – 6.83 (m, 2H), 6.73 – 6.67 (m, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.88 (td, *J* = 11.3, 3.5 Hz, 1H), 3.27 – 3.18 (m, 2H), 2.64 (td, *J* = 11.5, 3.7 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.83 – 1.72 (m, 3H), 1.65 – 1.59 (m, 1H), 1.44 – 1.16 (m, 4H), 1.11 – 1.06 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.2, 148.6, 129.0, 117.4, 115.6, 61.8, 60.4, 48.4, 38.0, 29.9, 28.9, 25.8, 25.0, 14.2, 14.1. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1964.

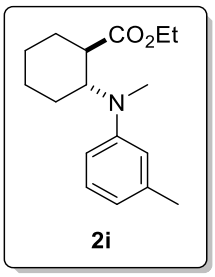
Ethyl-*trans*-2-(ethyl(phenyl)amino)cyclohexane-1-carboxylate (2h)



2h

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 59 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.14 – 7.06 (m, 2H), 6.99 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.90 (td, *J* = 7.3, 1.4 Hz, 1H), 4.07 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.86 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.24 – 3.15 (m, 1H), 2.75 (s, 3H), 2.59 – 2.67 (m, 1H), 2.24 (s, 3H), 1.96 – 1.88 (m, 1H), 1.83 – 1.75 (m, 2H), 1.73 – 1.66 (m, 1H), 1.62 – 1.51 (m, 2H), 1.32 – 1.16 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.2, 151.6, 133.0, 131.4, 125.9, 122.5, 122.1, 62.3, 60.2, 48.2, 33.6, 29.9, 26.5, 25.5, 25.2, 18.8, 14.1. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1972.

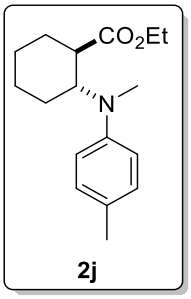
Ethyl *trans*-2-(methyl(m-tolyl)amino)cyclohexane-1-carboxylate (2i)



2i

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 61 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.14 – 7.04 (m, 1H), 6.71 – 6.61 (m, 2H), 6.54 (d, *J* = 7.4 Hz, 1H), 4.06 – 3.81 (m, 3H), 2.73 (s, 3H), 2.65 (td, *J* = 11.5, 3.6 Hz, 1H), 2.30 (s, 3H), 2.00 (d, *J* = 13.4 Hz, 1H), 1.87 – 1.61 (m, 4H), 1.53 – 1.30 (m, 2H), 1.29 – 1.14 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.0, 150.7, 138.6, 128.8, 118.3, 115.3, 111.7, 61.1, 60.4, 48.2, 31.1, 29.7, 27.9, 25.6, 25.0, 22.0, 14.2. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1972.

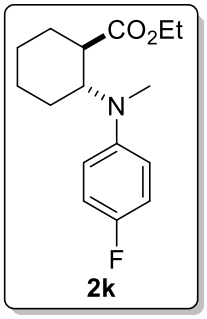
Ethyl *trans*-2-(methyl(p-tolyl)amino)cyclohexane-1-carboxylate (2j)



2j

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 58 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.06 – 6.95 (m, 2H), 6.82 – 6.71 (m, 2H), 4.05 – 3.92 (m, 2H), 3.82 (td, *J* = 11.3, 3.6 Hz, 1H), 2.71 (s, 3H), 2.67 – 2.61 (m, 1H), 2.24 (s, 3H), 2.03 – 1.96 (m, 1H), 1.81 – 1.61 (m, 4H), 1.45 – 1.21 (m, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.1, 148.5, 129.5, 126.7, 115.0, 61.8, 60.3, 48.2, 31.2, 29.7, 27.5, 25.6, 25.0, 20.4, 14.3. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, found: 276.1962.

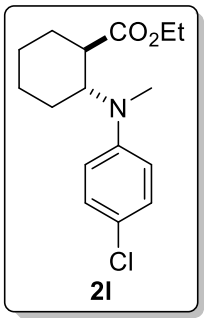
Ethyl *trans*-2-(methyl(p-tolyl)amino)cyclohexane-1-carboxylate (2k)



2k

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 64 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.95 – 6.85 (m, 2H), 6.83 – 6.73 (m, 2H), 4.09 – 3.89 (m, 2H), 3.75 (td, *J* = 11.3, 3.7 Hz, 1H), 2.70 (s, 3H), 2.67 – 2.59 (m, 1H), 2.12 – 1.92 (m, 1H), 1.86 – 1.54 (m, 4H), 1.51 – 1.14 (m, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.0, 155.9 (d, *J* = 237.4 Hz), 147.3 (d, *J* = 2.02 Hz), 116.1 (d, *J* = 7.1 Hz), 115.3 (d, *J* = 22.2 Hz), 62.3, 60.4, 48.1, 31.5, 29.8, 27.5, 25.6, 25.0, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -128.0. **HRMS**(ESI) calcd for $C_{16}H_{23}FNO_2$ $[M+H]^+$: 280.1713, found: 280.1709.

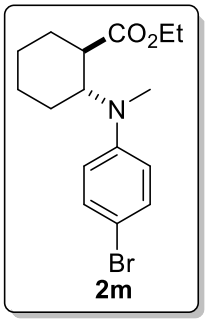
Ethyl *trans*-2-((4-chlorophenyl)(methyl)amino)cyclohexane-1-carboxylate (2l)



2l

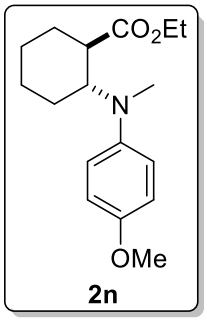
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 37 mg, 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.16 – 7.01 (m, 2H), 6.82 – 6.67 (m, 2H), 4.03 – 3.89 (m, 2H), 3.83 (td, *J* = 11.3, 3.6 Hz, 1H), 2.72 (d, *J* = 1.4 Hz, 3H), 2.69 – 2.54 (m, 1H), 2.06 – 1.90 (m, 1H), 1.87 – 1.55 (m, 4H), 1.52 – 1.30 (m, 2H), 1.26 – 1.14 (m, 1H), 1.08 (td, *J* = 7.1, 1.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 174.8, 149.0, 128.7, 121.9, 115.3, 61.1, 60.4, 48.0, 31.2, 29.6, 28.0, 25.5, 24.9, 14.2 ppm. **HRMS** (ESI) calcd for $C_{16}H_{23}ClNO_2$ $[M+H]^+$: 296.1417, found: 296.1410.

Ethyl *trans*-2-((4-bromophenyl)(methyl)amino)cyclohexane-1-carboxylate (2m)



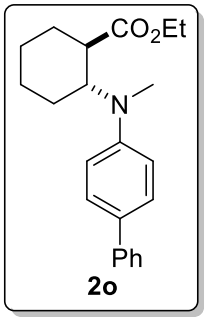
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 50 mg, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.16 – 7.01 (m, 2H), 6.82 – 6.67 (m, 2H), 4.03 – 3.89 (m, 2H), 3.83 (td, *J* = 11.3, 3.6 Hz, 1H), 2.72 (d, *J* = 1.4 Hz, 3H), 2.69 – 2.54 (m, 1H), 2.06 – 1.90 (m, 1H), 1.87 – 1.55 (m, 4H), 1.52 – 1.30 (m, 2H), 1.26 – 1.14 (m, 1H), 1.08 (td, *J* = 7.1, 1.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 174.8, 149.4, 131.7, 115.8, 109.1, 60.9, 60.5, 48.0, 31.2, 29.7, 28.1, 25.6, 24.9, 14.2 ppm. **HRMS** (ESI) calcd for $C_{16}H_{23}BrNO_2$ $[M+H]^+$: 340.0912, found: 340.0916.

Ethyl *trans*-2-((4-methoxyphenyl)(methyl)amino)cyclohexane-1-carboxylate (2n)



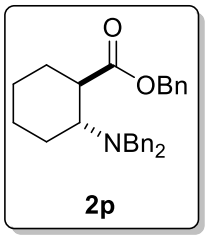
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 68 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.97 – 6.66 (m, 4H), 4.13 – 3.86 (m, 2H), 3.75 (s, 3H), 3.70 (td, *J* = 11.3, 3.6 Hz, 1H), 2.69 (s, 3H), 2.64 (td, *J* = 11.6, 3.7 Hz, 1H), 2.07 – 1.93 (m, 1H), 1.85 – 1.53 (m, 5H), 1.50 – 1.17 (m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 152.3, 145.3, 117.0, 114.4, 62.9, 60.3, 55.8, 48.3, 31.6, 29.8, 27.06, 25.6, 25.1, 14.3 ppm. **HRMS** (ESI) calcd for $C_{17}H_{26}NO_3$ $[M+H]^+$: 292.1913, found: 292.1907.

Ethyl *trans*-2-([1,1'-biphenyl]-4-yl(methyl)amino)cyclohexane-1-carboxylate (2o)



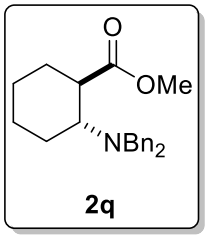
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 67 mg, 66% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.57 – 7.52 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.35 (m, 2H), 7.25 – 7.21 (m, 1H), 6.96 – 6.86 (m, 2H), 4.05 – 3.89 (m, 3H), 2.80 (s, 3H), 2.68 (td, *J* = 11.5, 3.6 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.81 (ddt, *J* = 34.1, 12.1, 3.3 Hz, 3H), 1.71 – 1.63 (m, 1H), 1.54 – 1.47 (m, 1H), 1.45 – 1.35 (m, 1H), 1.22 (ddd, *J* = 16.8, 8.7, 3.5 Hz, 1H), 1.08 (td, *J* = 7.1, 1.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 174.9, 149.9, 141.4, 129.9, 128.8, 127.6, 126.4, 126.1, 114.4, 60.8, 60.4, 48.2, 31.2, 29.7, 28.2, 25.7, 25.0, 14.2. **HRMS** (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found: 338.2119.

Benzyl *trans*-2-(dibenzylamino)cyclohexane-1-carboxylate (2p)



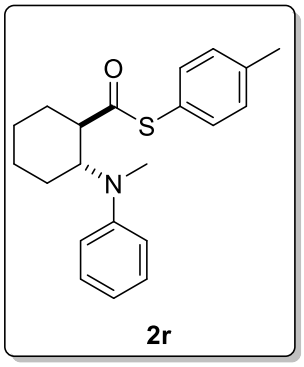
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 95 mg, 77% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.35 – 7.29 (m, 3H), 7.28 – 7.21 (m, 10H), 7.20 – 7.15 (m, 2H), 5.22 (d, *J* = 12.5 Hz, 1H), 5.04 – 4.96 (m, 1H), 3.81 (d, *J* = 13.5 Hz, 2H), 3.38 (d, *J* = 13.5 Hz, 2H), 2.89 (td, *J* = 11.2, 3.1 Hz, 1H), 2.67 (td, *J* = 11.4, 3.4 Hz, 1H), 2.02 (dd, *J* = 12.2, 3.4 Hz, 1H), 1.91 – 1.86 (m, 1H), 1.83 – 1.76 (m, 1H), 1.69 – 1.63 (m, 1H), 1.51 – 1.43 (m, 1H), 1.29 – 1.13 (m, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 175.0, 140.1, 136.4, 129.1, 128.6, 128.3, 128.1, 128.1, 126.9, 66.0, 59.4, 53.8, 48.6, 30.0, 25.4, 25.4, 23.9 ppm. **HRMS** (ESI) calcd for $C_{28}H_{31}NO_2$ $[M+H]^+$: 414.2433, found: 414.2425.

Methyl *trans*-2-(dibenzylamino)cyclohexane-1-carboxylateBenzyl (2q)



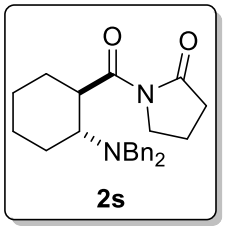
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 62 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31 – 7.24 (m, 8H), 7.23 – 7.17 (m, 2H), 3.81 (d, *J* = 13.5 Hz, 2H), 3.62 (s, 3H), 3.36 (d, *J* = 13.5 Hz, 2H), 2.80 (td, *J* = 11.3, 3.3 Hz, 1H), 2.62 (td, *J* = 11.5, 3.7 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.91 – 1.78 (m, 2H), 1.70 – 1.62 (m, 1H), 1.48 – 1.39 (m, 1H), 1.25 – 1.09 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.6, 140.1, 129.1, 128.1, 126.9, 59.3, 53.7, 51.4, 48.6, 29.8, 25.5, 25.4, 23.6. **HRMS** (ESI) calcd for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found: 338.2124.

S-(p-tolyl) *trans* -2-(methyl(phenyl)amino)cyclohexane-1-carbothioate (2r)



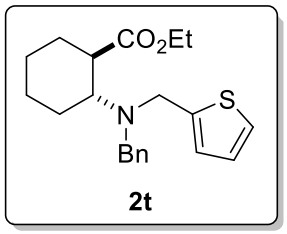
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 80 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.25 – 7.18 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.77 – 6.70 (m, 1H), 4.04 (td, *J* = 11.3, 3.7 Hz, 1H), 3.00 (td, *J* = 11.4, 3.7 Hz, 1H), 2.85 (s, 3H), 2.32 (s, 3H), 2.14 – 2.05 (m, 1H), 1.85 – 1.63 (m, 4H), 1.59 – 1.50 (m, 1H), 1.41 – 1.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 200.0, 150.5, 139.5, 134.5, 130.0, 129.1, 124.3, 117.4, 114.4, 61.3, 55.6, 31.4, 30.3, 28.4, 25.5, 25.2, 21.4. **HRMS** (ESI) calcd for $C_{21}H_{26}NOS$ $[M+H]^+$: 340.1735, found: 340.1743.

1-(*trans* -2-(Dibenzylamino)cyclohexane-1-carbonyl)pyrrolidin-2-one (2s)



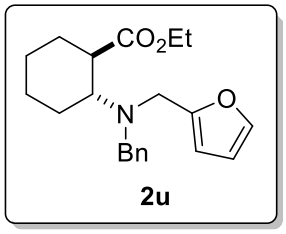
The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 81 mg, 69% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.27 (m, 8H), 7.22 – 7.17 (m, 2H), 4.20 (td, *J* = 11.3, 3.6 Hz, 1H), 3.92 – 3.81 (m, 4H), 3.47 (d, *J* = 14.5 Hz, 2H), 3.04 (td, *J* = 11.4, 3.4 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.14 – 2.06 (m, 1H), 2.02 – 1.96 (m, 1H), 1.95 – 1.76 (m, 4H), 1.69 – 1.62 (m, 1H), 1.45 – 1.36 (m, 1H), 1.32 – 1.13 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 176.8, 175.4, 140.3, 128.3, 128.1, 126.7, 60.6, 54.2, 46.1, 45.8, 33.9, 30.0, 25.5, 25.4, 23.6, 16.7. **HRMS** (ESI) calcd for $C_{25}H_{31}N_2O_2$ $[M+H]^+$: 391.2386, found: 391.2378.

Ethyl *trans*-2-(benzyl(thiophen-2-ylmethyl)amino)cyclohexane-1-carboxylate (2t)



The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 74 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: δ 7.35 – 7.26 (m, 4H), 7.24 – 7.16 (m, 2H), 6.93 – 6.85 (m, 2H), 4.26 – 4.08 (m, 2H), 3.97 – 3.81 (m, 2H), 3.70 (d, *J* = 14.3 Hz, 1H), 3.45 (d, *J* = 13.7 Hz, 1H), 2.93 – 2.83 (m, 1H), 2.61 – 2.53 (m, 1H), 1.98 – 1.84 (m, 2H), 1.83 – 1.74 (m, 1H), 1.70 – 1.63 (m, 1H), 1.53 – 1.42 (m, 1H), 1.26 – 1.10 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 175.1, 144.4, 139.8, 129.0, 128.2, 127.0, 126.3, 125.6, 124.8, 60.3, 59.6, 53.3, 48.60, 48.59, 29.9, 25.5, 25.4, 24.3, 14.3. **HRMS** (ESI) calcd for $C_{21}H_{28}NO_2S$ $[M+H]^+$: 358.1841, found: 358.1841.

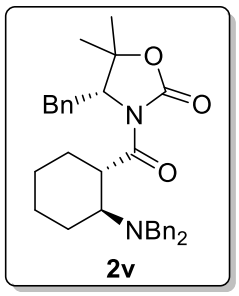
Ethyl *trans*-2-(benzyl(furan-2-ylmethyl)amino)cyclohexane-1-carboxylate (2u)



2u

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 59 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 – 7.25 (m, 5H), 7.23 – 7.18 (m, 1H), 6.29 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.12 (d, *J* = 3.1 Hz, 1H), 4.22 – 4.07 (m, 2H), 3.86 (d, *J* = 13.8 Hz, 1H), 3.65 (d, *J* = 15.0 Hz, 1H), 3.51 (t, *J* = 14.4 Hz, 2H), 2.95 (td, *J* = 11.2, 3.4 Hz, 1H), 2.54 (td, *J* = 11.6, 3.7 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.78 – 1.65 (m, 3H), 1.56 – 1.45 (m, 1H), 1.27 – 1.08 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 175.5, 154.0, 141.5, 140.2, 128.9, 128.2, 126.8, 110.3, 107.8, 61.3, 60.2, 52.8, 48.9, 46.9, 30.0, 25.6, 25.4, 25.2, 14.3. **HRMS** (ESI) calcd for $C_{21}H_{28}NO_3$ $[M+H]^+$: 342.2069, found: 342.2075.

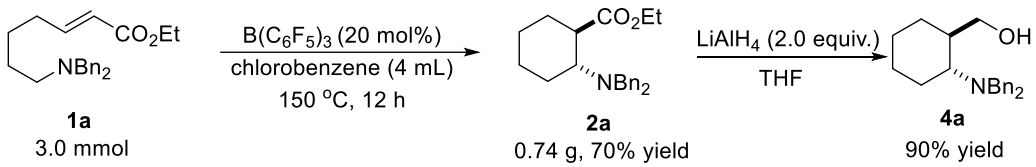
(*S*)-4-benzyl-3-(*trans*-2-(dibenzylamino)cyclohexane-1-carbonyl)-5,5-dimethyloxazolidin-2-one (2v)



2v

The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil, 110 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.32 – 7.18 (m, 15H), 4.58 (dd, *J* = 9.9, 2.8 Hz, 1H), 4.14 (td, *J* = 10.9, 3.6 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 2H), 3.48 (d, *J* = 14.0 Hz, 2H), 3.20 – 3.06 (m, 2H), 2.83 (dd, *J* = 14.5, 10.1 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.80 – 1.73 (m, 1H), 1.69 – 1.60 (m, 1H), 1.36 – 1.12 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.3, 152.5, 140.0, 137.3, 129.2, 128.8, 128.7, 128.1, 126.78, 126.76, 81.6, 63.8, 59.0, 54.0, 45.1, 35.2, 30.9, 28.8, 25.5, 25.4, 24.4, 22.7. **HRMS** (ESI) calcd for $C_{33}H_{39}N_2O_3$ $[M+H]^+$: 511.2961, found: 511.2962. $[\alpha]_D^{20}$= +15.8 ($CHCl_3$, c 1.0)].

4.4 Procedure for Gram-Scale Reaction[1]



1a
3.0 mmol

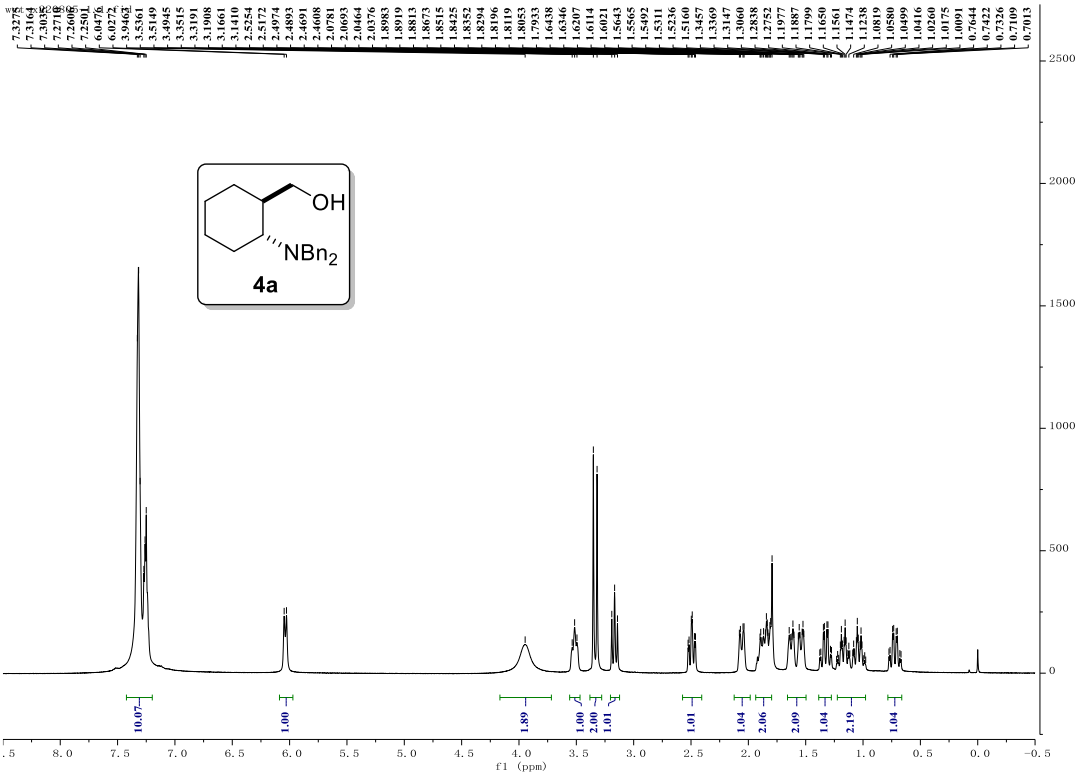
2a
0.74 g, 70% yield

4a
90% yield

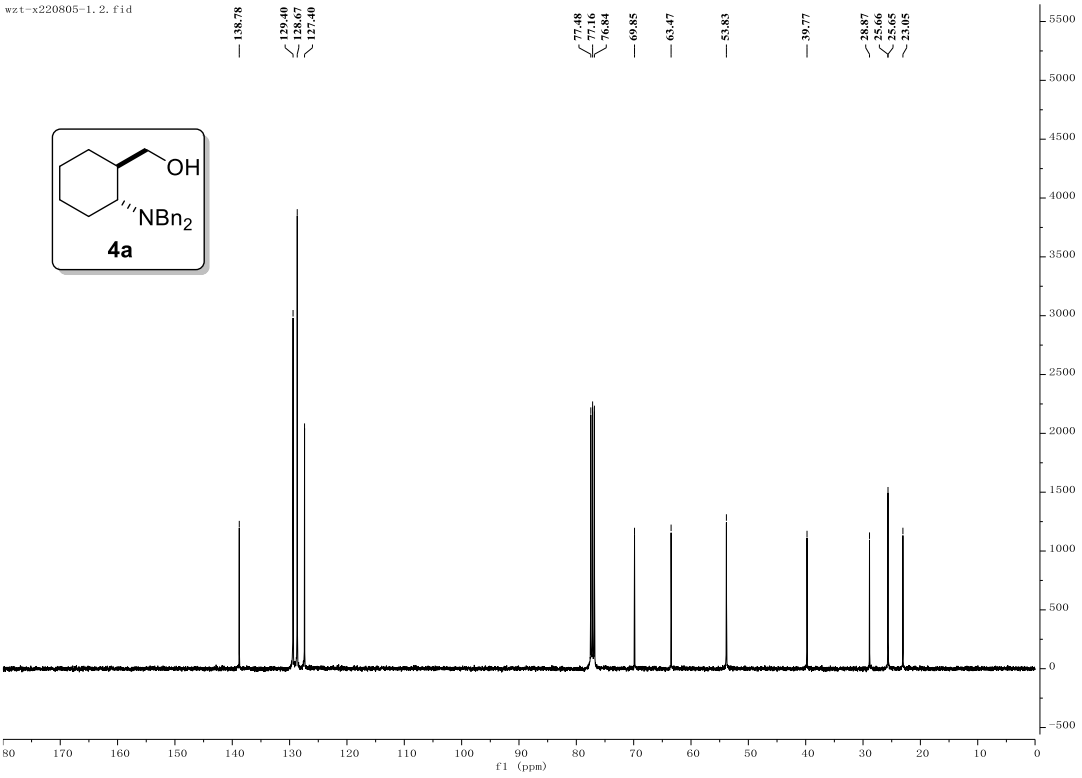
To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $B(C_6F_5)_3$ (30.7 mg, 0.6 mmol, 20 mol%), Ethyl (*E*)-7-(dibenzylamino) hept-2-enoate **1a** (1.05 g ,3.0 mmol) and chlorobenzene (40.0 mL) in the glove box. Then the mixture was heated to 150 °C in an oil bath and stirred for 12 hours. After the reaction mixture was cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product **2a** (0.74 g, 70% yield) as a colorless oil.

A suspension of $LiAlH_4$ (2.0 equiv., 22.8 mg, 0.6 mmol) in dry THF (2 mL) was stirred at 0 °C under nitrogen atmosphere. A solution of **2a** (105.3 mg, 0.3 mmol) in dry THF (1 mL) was carefully added dropwise to the solution. After the addition was complete, the cooling equipment was removed, and the reaction mixture was stirred at room temperature for 4 hours. The resulting mixture was quenched by 2 mL saturated potassium sodium tartrate solution slowly. After stirring for an additional 30 minutes, the resulting solution was extracted with ethyl acetate (3 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 5/1) on silica gel to give the desired product **3a** (83.1 mg, 90% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.43 – 7.18 (m, 10H), 6.04 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 2H), 3.52 (t, *J* = 8.3 Hz, 1H), 3.34 (d, *J* = 13.0 Hz, 2H), 3.17 (t, *J* = 9.9 Hz, 1H), 2.49 (td, *J* = 11.3, 3.3 Hz, 1H), 2.06 (dd, *J* = 12.7, 3.5 Hz, 1H), 1.94 – 1.80 (m, 2H), 1.66 – 1.50 (m, 2H), 1.39 – 1.28 (m, 1H), 1.22 – 0.98 (m, 2H), 0.79 – 0.64 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 138.8, 129.4, 128.7, 127.4, 69.9, 63.5, 53.8, 39.8, 28.9, 25.66, 25.65, 23.1.

^{1}H NMR (400 MHz, $CDCl_3$) spectra for the 4a



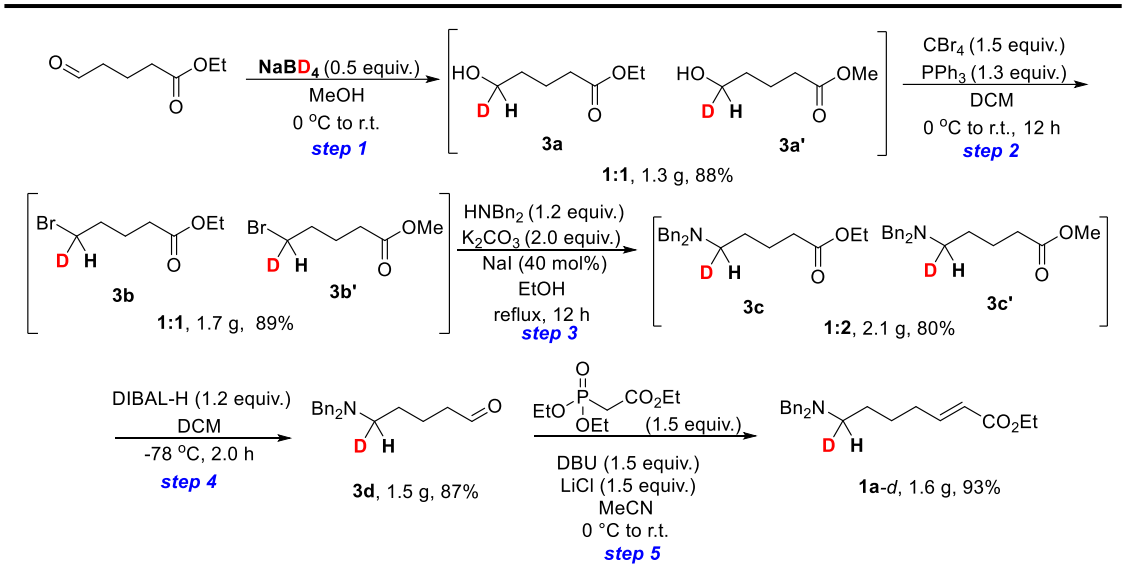
^{13}C NMR (101 MHz, $CDCl_3$) spectra for the 4a



4.5 Procedure for Gram-Scale Reaction

4.5.1 Deuterium-Labeling Experiments of 1a-*d*.

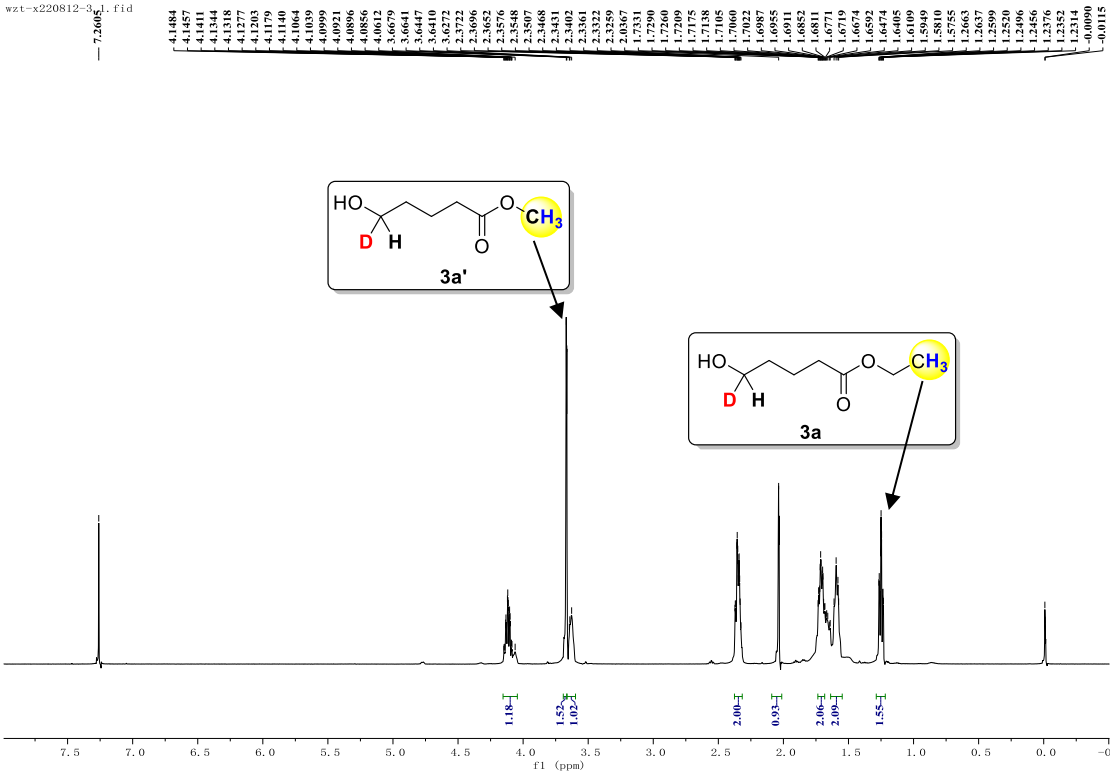
Synthesis of Ethyl (*E*)-7-(dibenzylamino) hept-2-enoate 1a-*d*.



Step 1.

A flame-dried two-neck flask (100 mL) equipped with a stirring bar was charged with ethyl 5-oxopentanoate (1.44 g, 10 mmol, 1.0 equiv.) in MeOH (20 mL, 0.5 M). $NaBD_4$ (209 mg, 5 mmol, 0.5 equiv.) was added to the mixture in portions at 0 °C over 10 minutes. The heterogeneous reaction mixture was stirred at room temperature for 2 hours. Next 2 mL water was added to quench the reaction and the solution was concentrated in vacuo to remove MeOH. The aqueous layer was extracted with ethyl acetate (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to give out the mixture of **3a** and **3a'** (1:1, 1.3 g, 88% yield) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 4.15 – 4.04 (m, 1H), 3.67 (s, 1.5H), 3.65 – 3.60 (m, 1H), 2.38 – 2.32 (m, 2H), 2.04 (s, 1H), 1.74 – 1.68 (m, 2H), 1.62 – 1.65 (m, 2H), 1.29 – 1.22 (m, 1.5H).

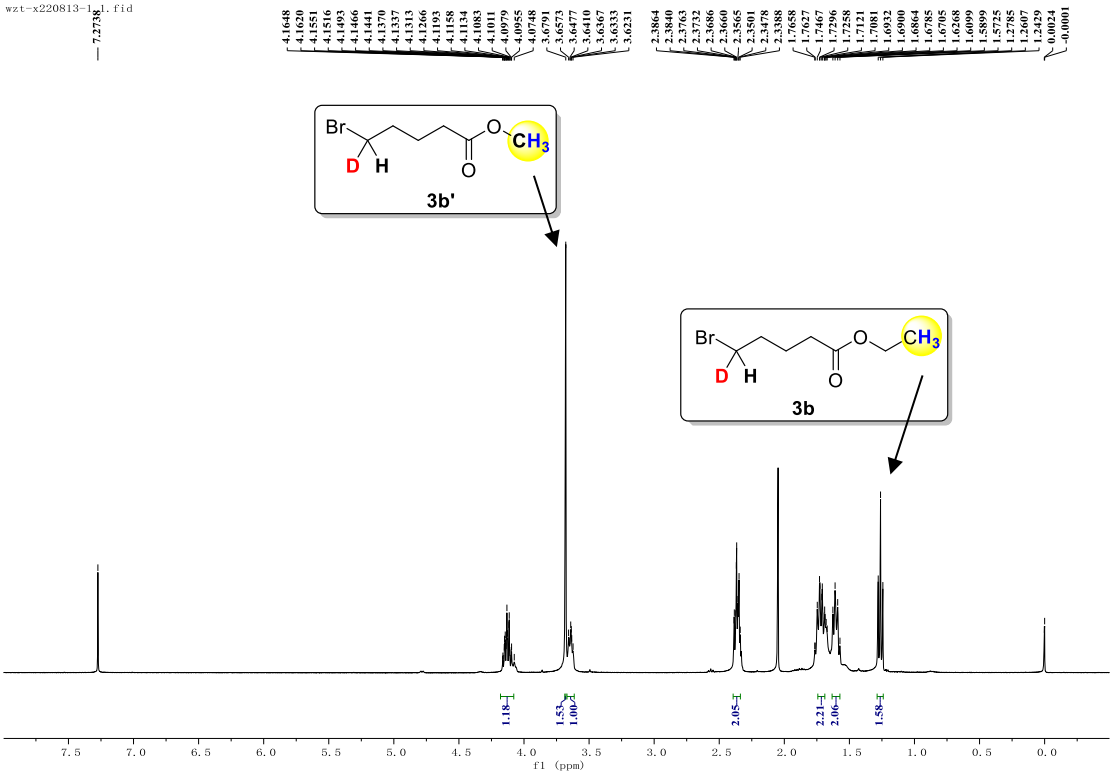
^{1}H NMR (500 MHz, $CDCl_3$) spectra for the mixture of 3a and 3a'



Step 2.

A flame-dried two-neck flask (100 mL) equipped with a stirring bar was charged with the mixture of **3a** and **3a'** (1.3 g, 8.8 mmol, 1.0 equiv.) and PPh_3 (3.0 g, 11.4 mmol, 1.3 equiv.) in anhydrous dichloromethane (20 mL). CBr_4 (4.4 g, 13.2 mmol, 1.5 equiv.) was added to the mixture in portions at 0 °C over 10 minutes. Then the heterogeneous reaction mixture was stirred at room temperature for overnight. Next 2 mL water was added to quench the reaction and the solution was concentrated in vacuo to remove dichloromethane. The aqueous layer was extracted with ethyl acetate (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to give out the mixture of **3b** and **3b'** (1:1, 1.7 g, 89% yield) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.18 – 4.08 (m, 1H), 3.68 (s, 1.5H), 3.67 – 3.61 (m, 1H), 2.40 – 2.31 (m, 2H), 1.74 – 1.69 (m, 2H), 1.64 – 1.55 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 1.5H).

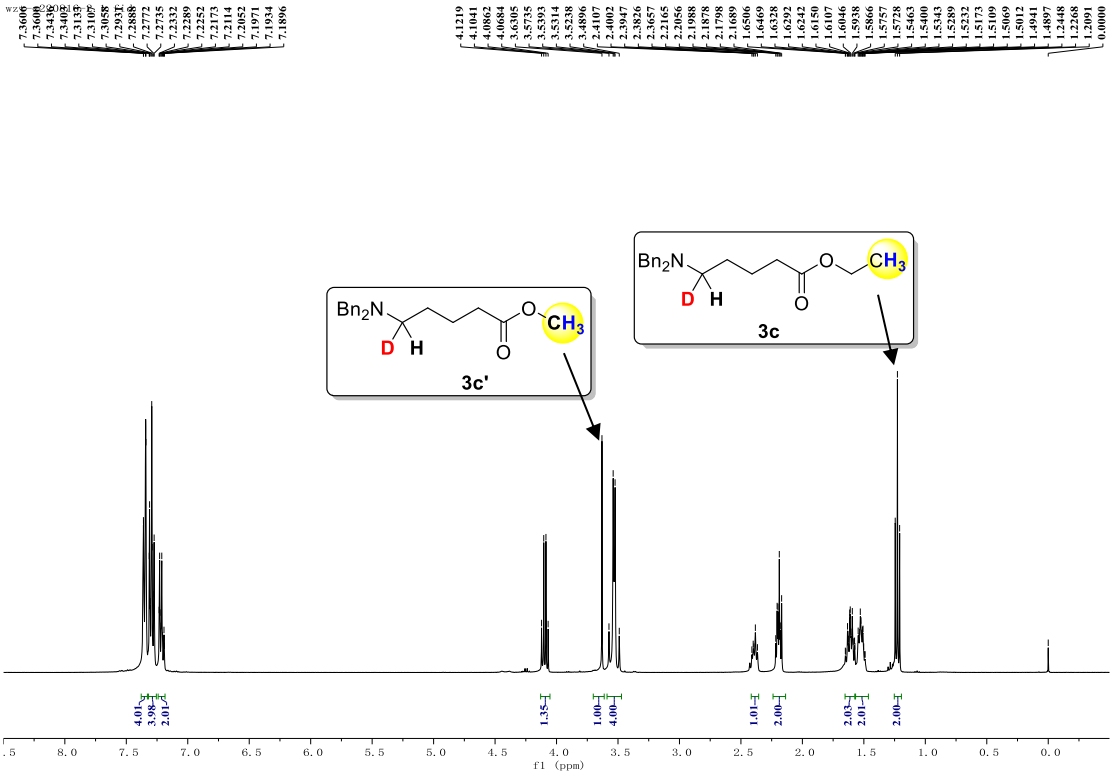
^{1}H NMR (400 MHz, $CDCl_3$) spectra for the mixture of 3b and 3b'



Step 3.

A flame-dried two-neck flask (100 mL) equipped with a reflux condenser and a stirring bar was charged with the mixture of **3b** and **3b'** (1.7 g, 7.8 mmol, 1.0 equiv.), potassium carbonate (2.1 g, 15.6 mmol, 2.0 equiv.) and sodium iodide (0.47 g, 3.1 mmol, 0.4 equiv.) in EtOH (20 mL). Dibenzylamine (1.7 g, 8.5 mmol, 1.1 equiv.) was added dropwise to the mixture by syringe under nitrogen atmosphere at room temperature over 10 minutes. The reaction mixture was heated to 93 °C in an oil bath and stirred for 12 hours. Then the reaction flask was cooled to room temperature. Next 1 mL water was added to quench the reaction and the solution was concentrated in vacuo to remove EtOH. The aqueous layer was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to give out the mixture of **3c** and **3c'** (1:2, 2.1 g, 80% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38 – 7.33 (m, 4H), 7.32 – 7.26 (m, 4H), 7.24 – 7.18 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 1.3H), 3.63 (s, 1H), 3.59 – 3.47 (m, 4H), 2.42 – 2.36 (m, 1H), 2.23 – 2.14 (m, 2H), 1.65 – 1.57 (m, 2H), 1.55 – 1.47 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 2H).

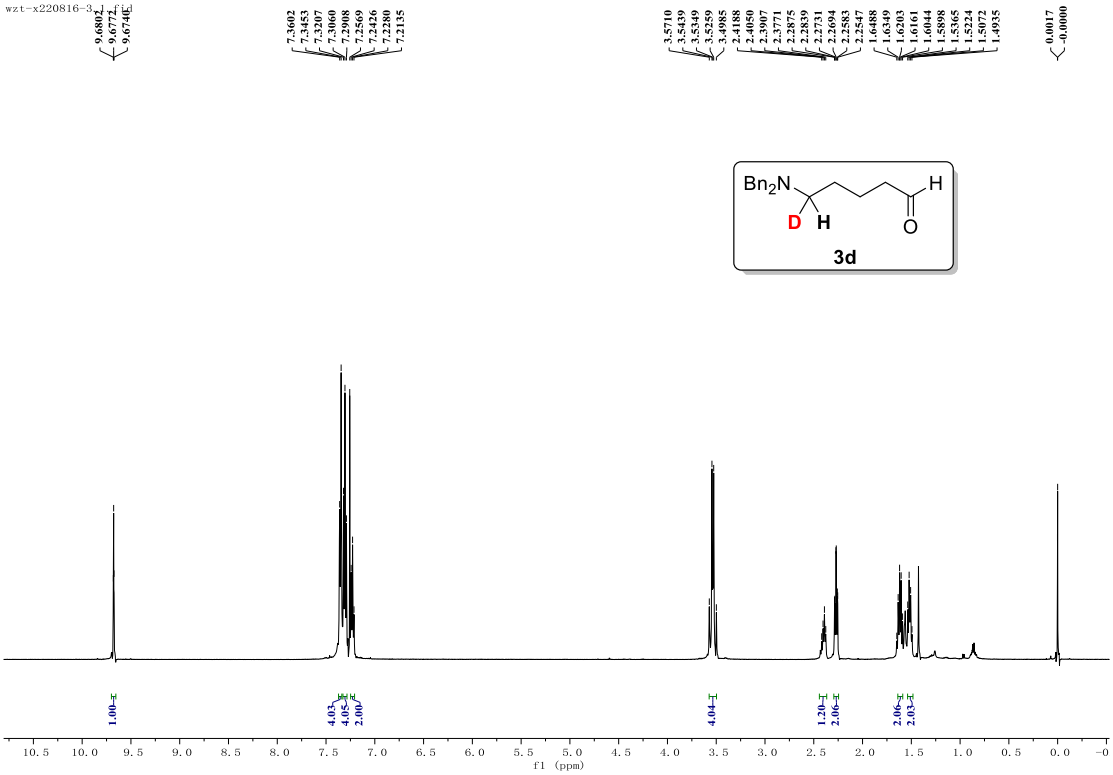
^{1}H NMR (400 MHz, $CDCl_3$) spectra for the mixture of 3c and 3c'



Step 4.

A flame-dried single-neck flask (100 mL) with stirring bar was charged with corresponding the mixture of **3c** and **3c'** (2.1 g, 6.2 mmol, 1.0 equiv.) in anhydrous dichloromethane (30 mL, 0.2 M). DIBAL-H (7.4 mmol, 1.2 equiv.) was added to the mixture in portions under nitrogen atmosphere at -78 °C over 10 minutes. The heterogeneous reaction mixture was stirred at same temperature for 2 hours. The resulting mixture was quenched by 10 mL saturated potassium sodium tartrate solution slowly. After stirring for an additional 30 minutes, the resulting solution was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 1 hour. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to give out the aldehyde **3d** (1.5 g, 87% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.68 (t, *J* = 1.6 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 4H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.23 (t, *J* = 7.3 Hz, 2H), 3.57 – 3.50 (m, 4H), 2.47 – 2.35 (m, 1.2 H), 2.27 (td, *J* = 7.3, 1.8 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.54 – 1.48 (m, 2H).

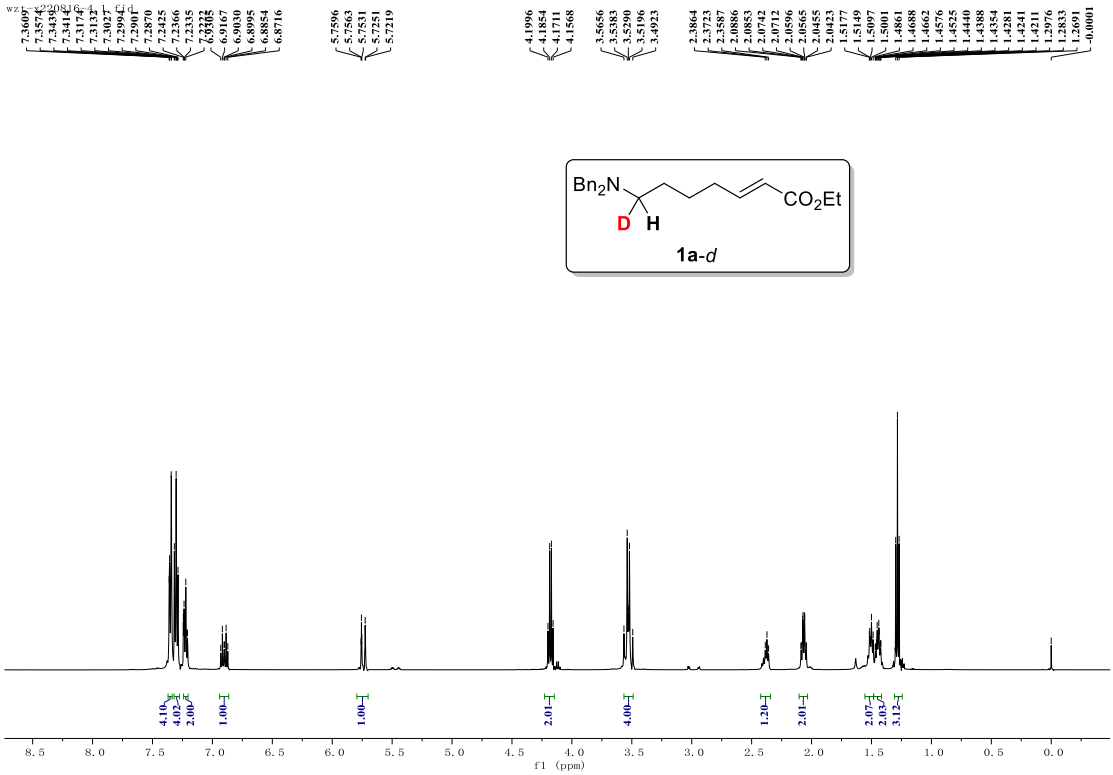
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3d



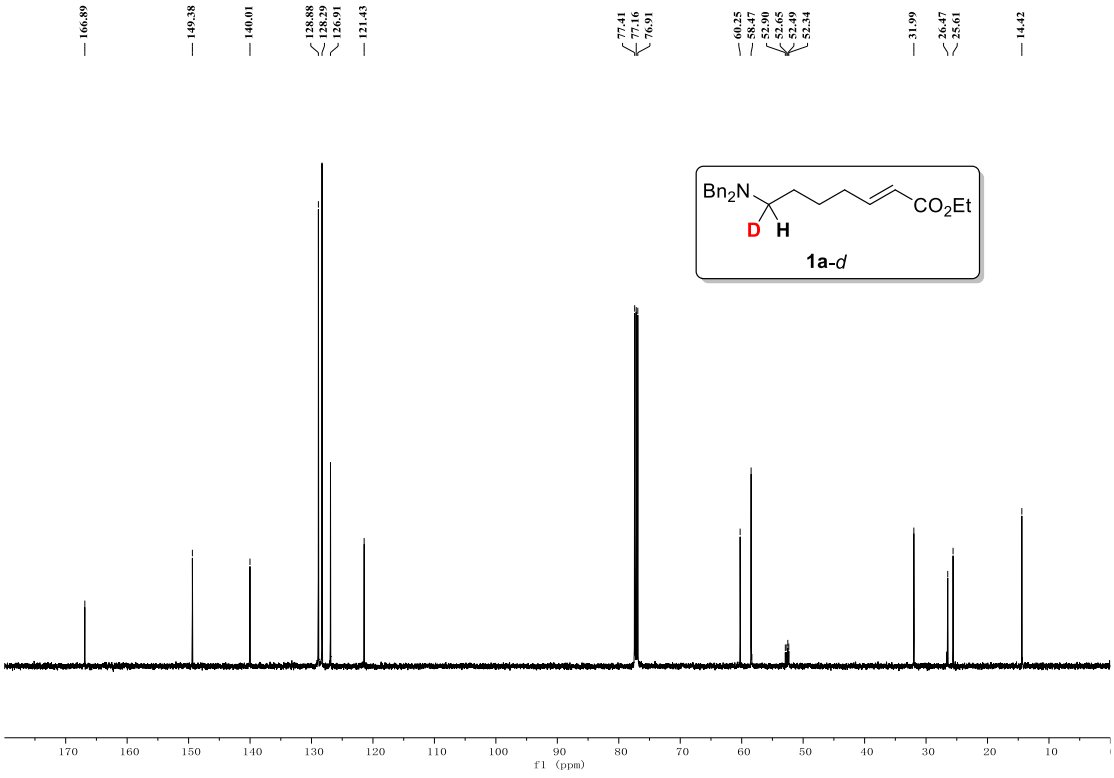
Step 5.

A flame-dried single-neck flask (100 mL) with stirring bar was charged with ethyl 2-(diethoxyphosphoryl) acetate (1.2 g, 5.4 mmol, 1.5 equiv.), DBU (1.2 g, 8.1 mmol, 1.5 equiv.) and LiCl (0.34 g, 8.1 mmol, 1.5 equiv.) in anhydrous CH_3CN (25 mL) under nitrogen atomsphere at 0 ºC ice bath and then stirred at same temperature for 1 hour. Then the **3d** (1.5 g, 5.4 mmol, 1.0 equiv.) was added to the mixture via syringe, and stirred at room temperature for another 12 hours. Then reaction mixture was quenched by 1 mL water slowly. the resulting solution was extracted with dichloromethane (20 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4. The resulting organic phase was concentrated under reduced pressure and the residue was purified by chromatography to give out the **1a**-*d* (1.6 g, D: ≈ 80%, 93% yield) as a colorless oil. **1H NMR** (500 MHz, $CDCl_3$) δ: 7.37 – 7.34 (m, 4H), 7.30 (dd, J = 8.4, 6.8 Hz, 4H), 7.24 – 7.20 (m, 2H), 6.90 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.79 – 5.70 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.57 – 3.49 (m, 4H), 2.45 – 2.31 (m, 1.2 H), 2.07 (qd, *J* = 7.1, 1.6 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.48 – 1.42 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 166.9, 149.4, 140.0, 128.9, 128.3, 126.9, 121.4, 60.3, 58.5, 52.9, 52.5 (t, *J* = 20.2 Hz), 32.0, 26.5, 25.6, 14.4.

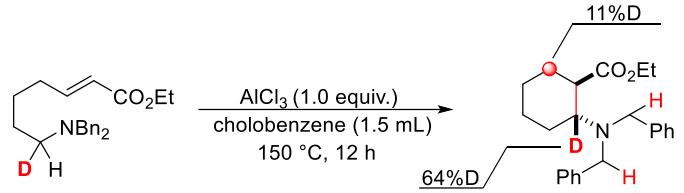
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1a-*d*



^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1a-*d*



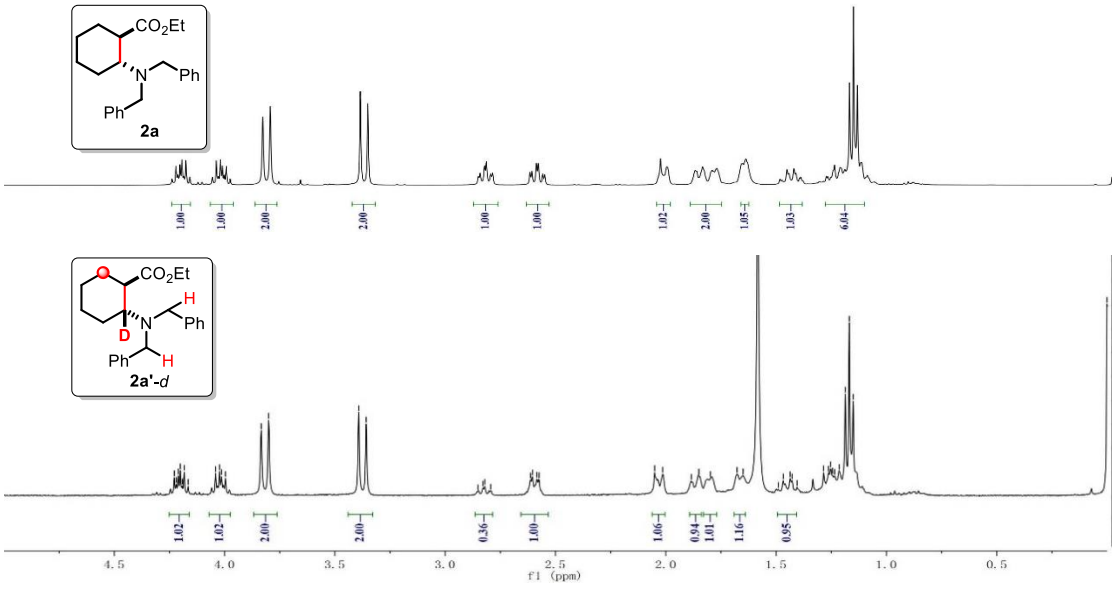
Deuteration study with 1a-*d*.

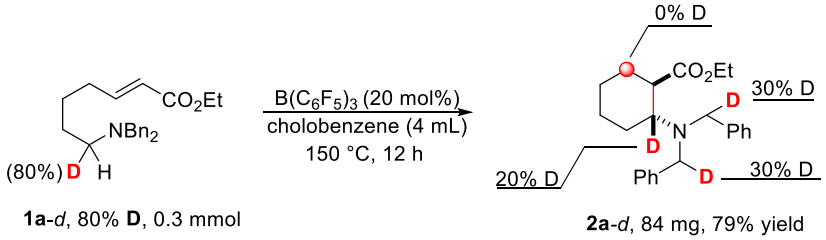


1a-*d*, 80% **D**, 0.2 mmol　　**2a'**-*d*, 21.8 mg, 31% yield

To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $AlCl_3$ (0.2 mmol, 1.0 equiv.), Ethyl (*E*)-7-(dibenzylamino)hept-2-enoate **1a**-*d* (70.4 mg ,0.2 mmol) and chlorobenzene (1.5 mL) in the glove box. Then the mixture was heated to 150 ºC in an oil bath stirred for 12 hours. After the reaction mixture was cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product **2a'**-*d* (21.8 mg, 31% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2a and 2a'-*d*



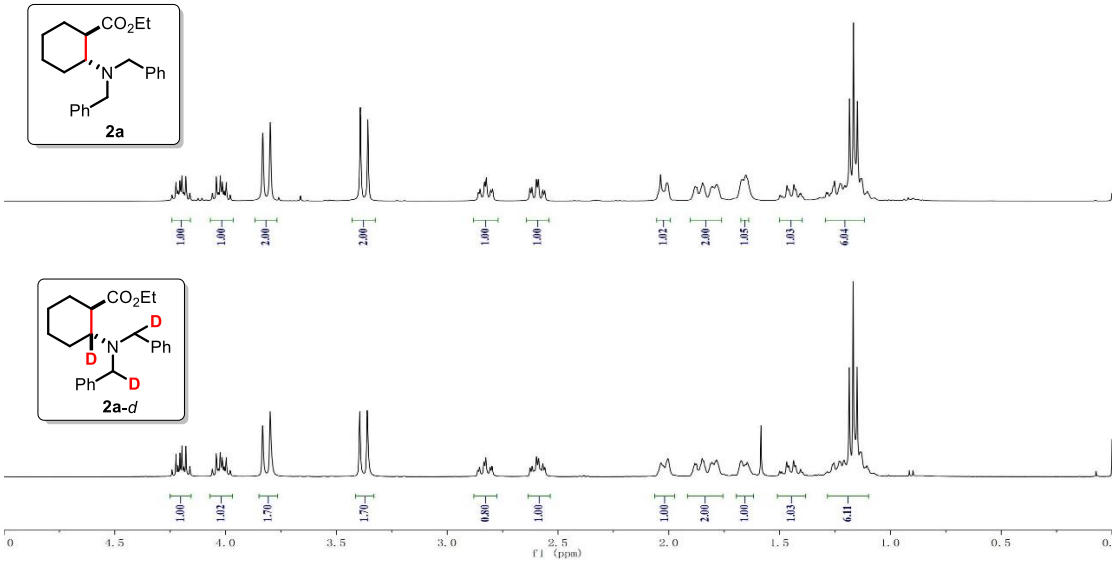


1a-*d*, 80% **D**, 0.3 mmol　　**2a**-*d*, 84 mg, 79% yield

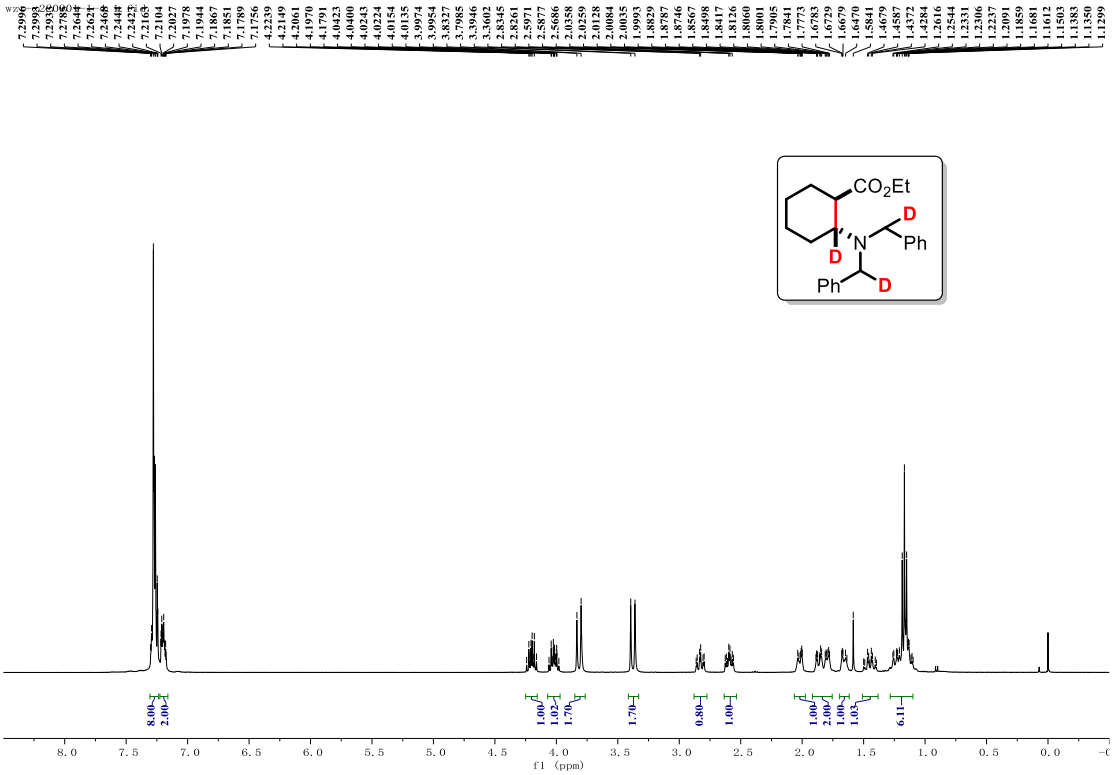
To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $B(C_6F_5)_3$ (0.06 mmol, 20 mol%), Ethyl (*E*)-7-(dibenzylamino)hept-2-enoate **1a**-*d* (105.6 mg ,0.3 mmol) and chlorobenzene (4.0 mL) in the glove box. Then the mixture was heated to 150 ºC in an oil bath stirred for 12 hours. After the reaction mixture was cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product **2a**-*d* (84 mg, 79% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31 – 7.24 (m, 8H), 7.23 – 7.16 (m, 2H), 4.25 – 4.15 (m, 1H), 4.07 – 3.97 (m, 1H), 3.82 (d,

J = 13.7 Hz, 1.7H), 3.38 (d, *J* = 13.8 Hz, 1.7H), 2.83 (td, *J* = 11.2, 3.4 Hz, 0.8 H), 2.59 (td, *J* = 11.5, 3.7 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.92 – 1.76 (m, 2H), 1.70 – 1.62 (m, 1H), 1.45 (qd, *J* = 12.8, 3.7 Hz, 1H), 1.28 – 1.10 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 175.2, 140.2, 129.1, 128.1, 126.8, 60.2, 59.4, 53.7, 48.7, 29.9, 25.5, 25.4, 23.8, 23.7 (t, *J* = 8.1 Hz, 1H), 14.2.

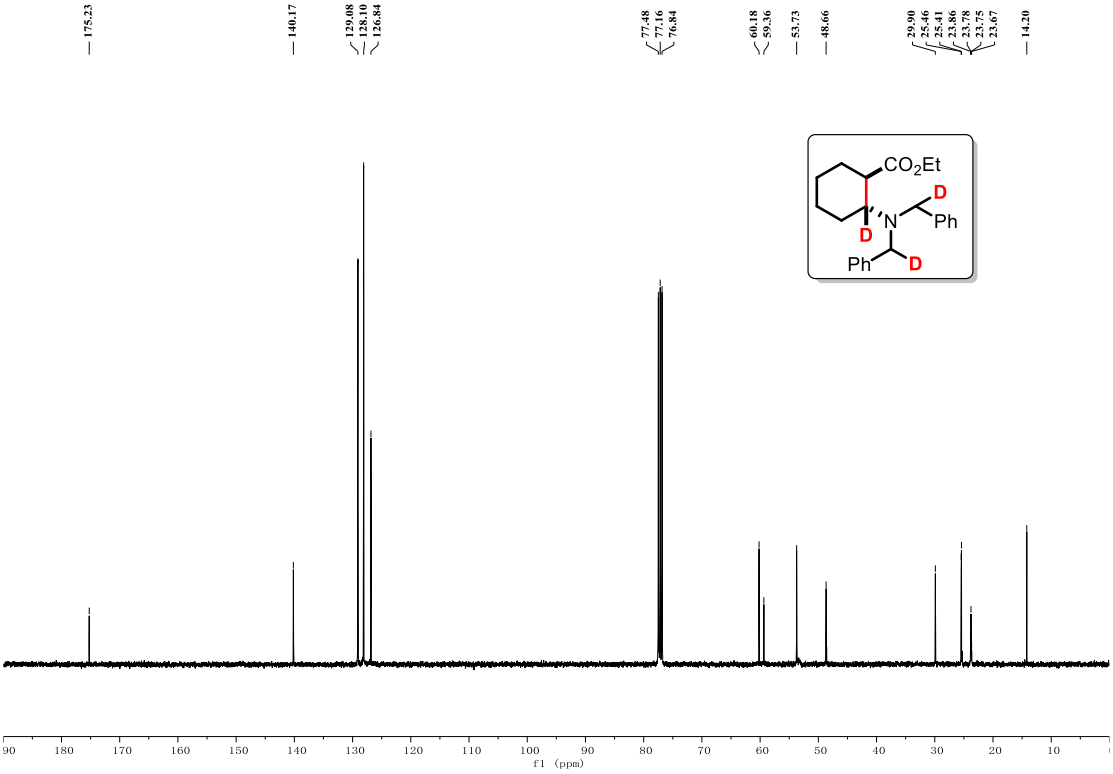
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2a and 2a-*d*



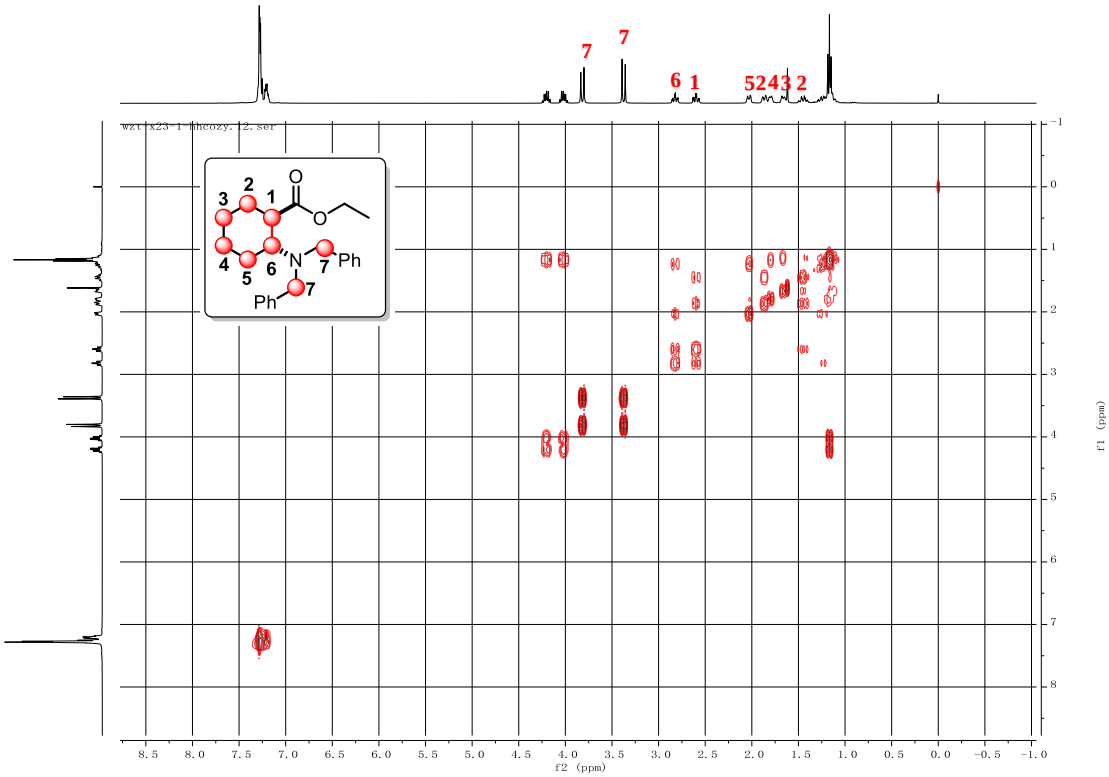
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2a-*d*



^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2a-*d*

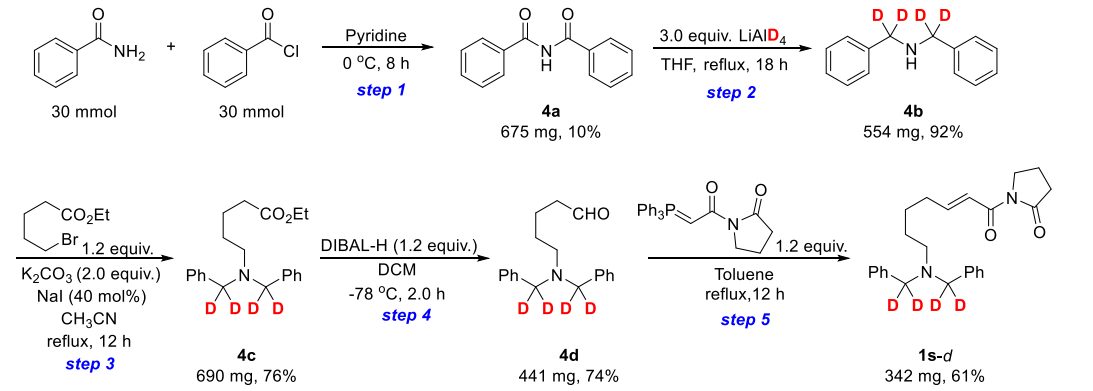


^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$) spectra for 2a



4.5.2 Deuterium-Labeling Experiments of 1s-*d*.

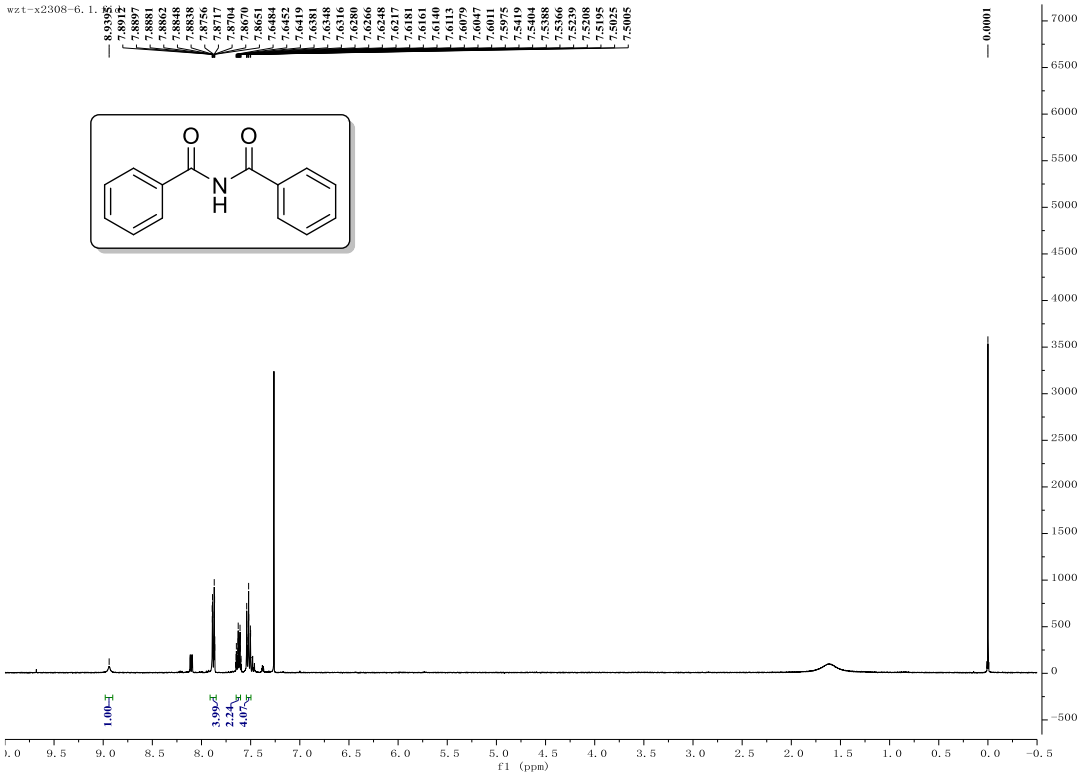
Synthesis of Ethyl (*E*)-7-(dibenzylamino) hept-2-enoate 1s-*d*.



Step 1.

Benzamide (3.7 g, 30 mmol) was dissolved in pyridine (18 mL) and cooled to 0°C. After the dropwise addition of benzoyl chloride (17.5 mL, 125 mmol) the reaction mixture was stirred at 0 °C for 8 h, then H_2O (73mL) was added in one portion to the reaction. The reaction mixture was extracted with Et_2O (2 x 24 mL). The combined organic phases were washed with 10% aqueous H_2SO_4 (2 x) leading to the formation of a colorless crystalline precipitate, which was collected by filtration. A second crop of crystals can be obtained from the organic layer upon standing. The combined precipitate was recrystallized from EtOAc to afford N-benzoylbenzamide (675 mg, 10% yield) as colorless needles. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.94 (s, 1H), 7.91 – 7.85 (m, 4H), 7.65 – 7.60 (m, 2H), 7.54 – 7.50 (m, 4H). Data consistent with literature.[2]

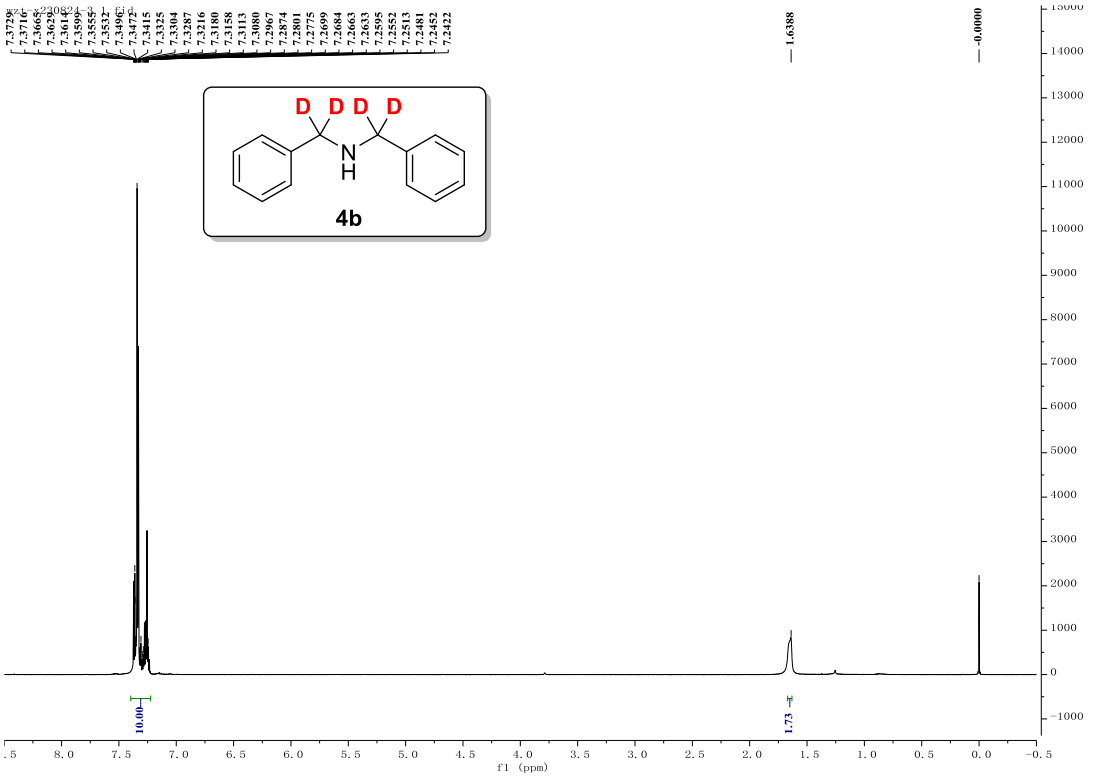
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4a



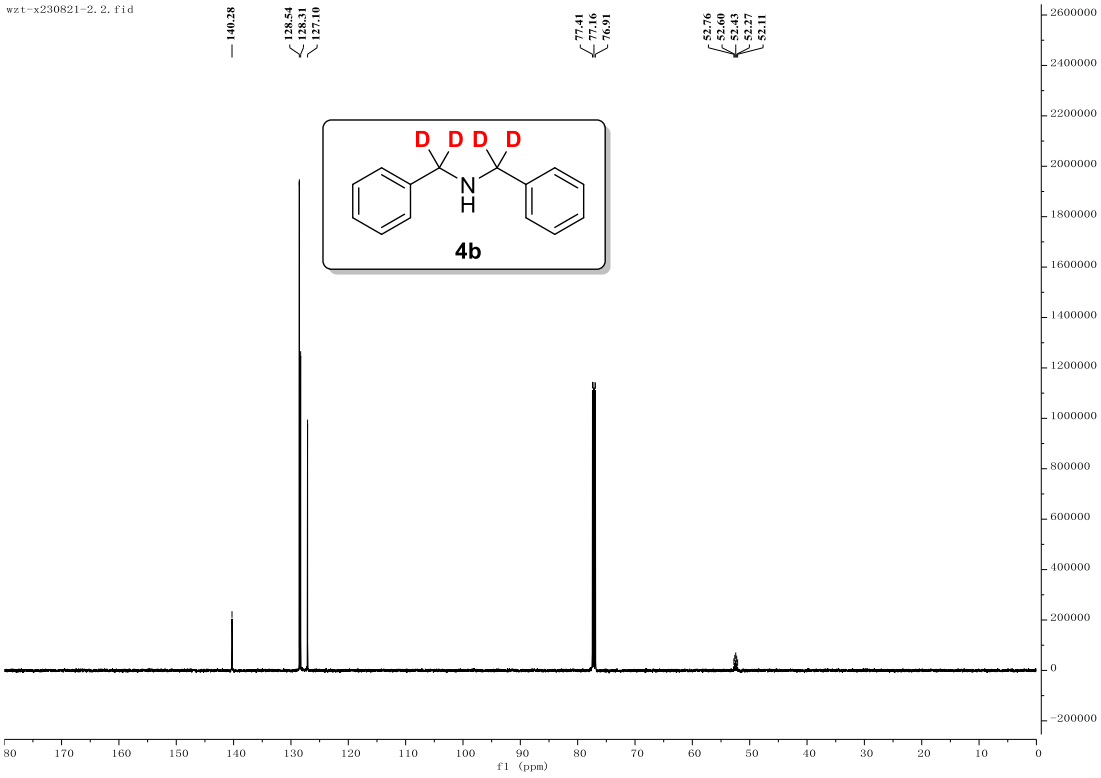
Step 2.

N-benzoylbenzamide (675 mg, 3.0 mmol) was dissolved in THF (30 mL). After careful addition of lithium aluminium deuteride (378 mg, 9.0 mmol) the reaction mixture was heated to reflux with stirring for 18 h. The purple solution was allowed to cool to ambient temperature and then quenched by slow addition of solid sodium sulphate hexahydrate under vigorous stirring. The resulting slurry was diluted with Et_2O and filtered. The colorless filtrate was concentrated *in vacuo*. The resulting oil was purified using flash column chromatography (50% EtOAc in P.E.) to afford bis(phenylmethyl-d_2) amine (554 mg, 92%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.24 (m, 10H), 1.70 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): 140.3, 128.5, 128.3, 127.1, 52.4 (quint, J = 20.2 Hz). Data consistent with literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4b



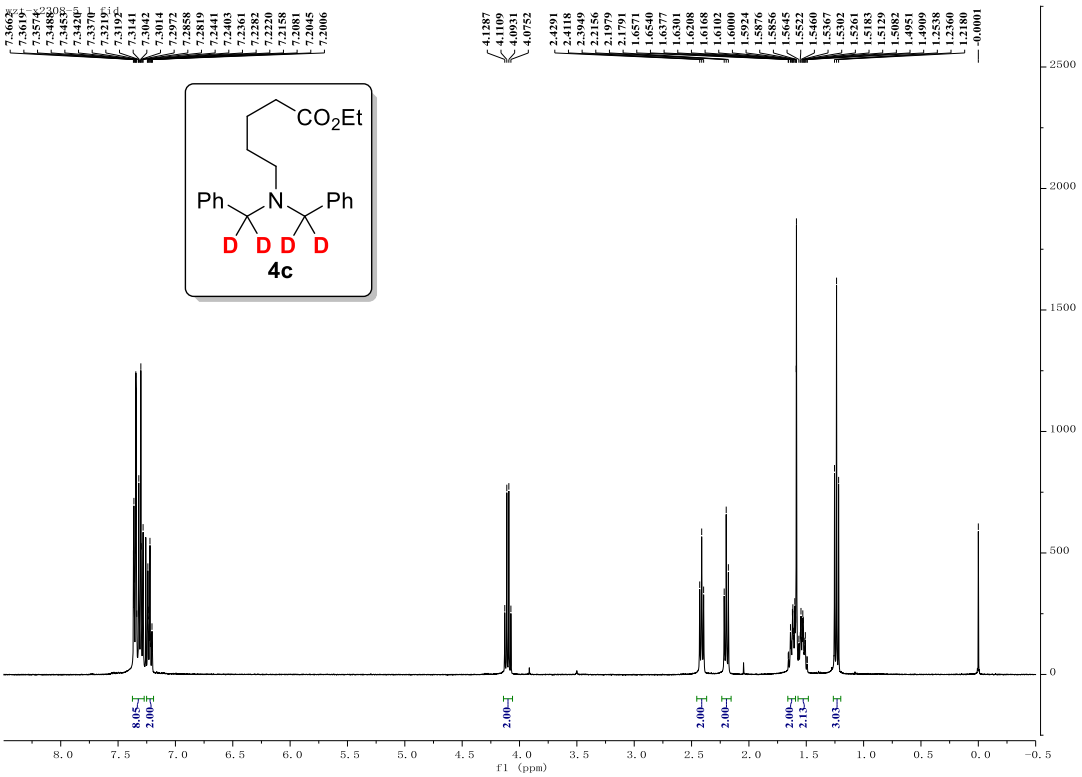
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 4b



Step 3.

A flame-dried two-neck flask (50 mL) equipped with a reflux condenser and a stirring bar was charged with Ethyl 5-bromovalerate (1.1 g, 5.4mmol, 1.2 equiv.), potassium carbonate (773.9 mg, 5.6 mmol, 2.0 equiv.) and sodium iodide (180 mg, 1.2 mmol, 0.4 equiv.) in CH_3CN (5 mL). **4b** (554 mg, 2.8 mmol, 1.0 equiv.) was added dropwise to the mixture by syringe under nitrogen atmosphere at room temperature over 2 minutes. The reaction mixture was heated to 88°C in an oil bath and stirred for 12 hours. Then the reaction flask was cooled to room temperature. Next 0.2 mL water was added to quench the reaction and the solution was concentrated in vacuo to remove the solvent. The aqueous layer was extracted with EtOAc (4 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 0.5 hour. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to give out the **4c** (690 mg, 76% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 – 7.27 (m, 8H), 7.25 – 7.19 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.20 (t, *J* = 7.3 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.57 – 1.48 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

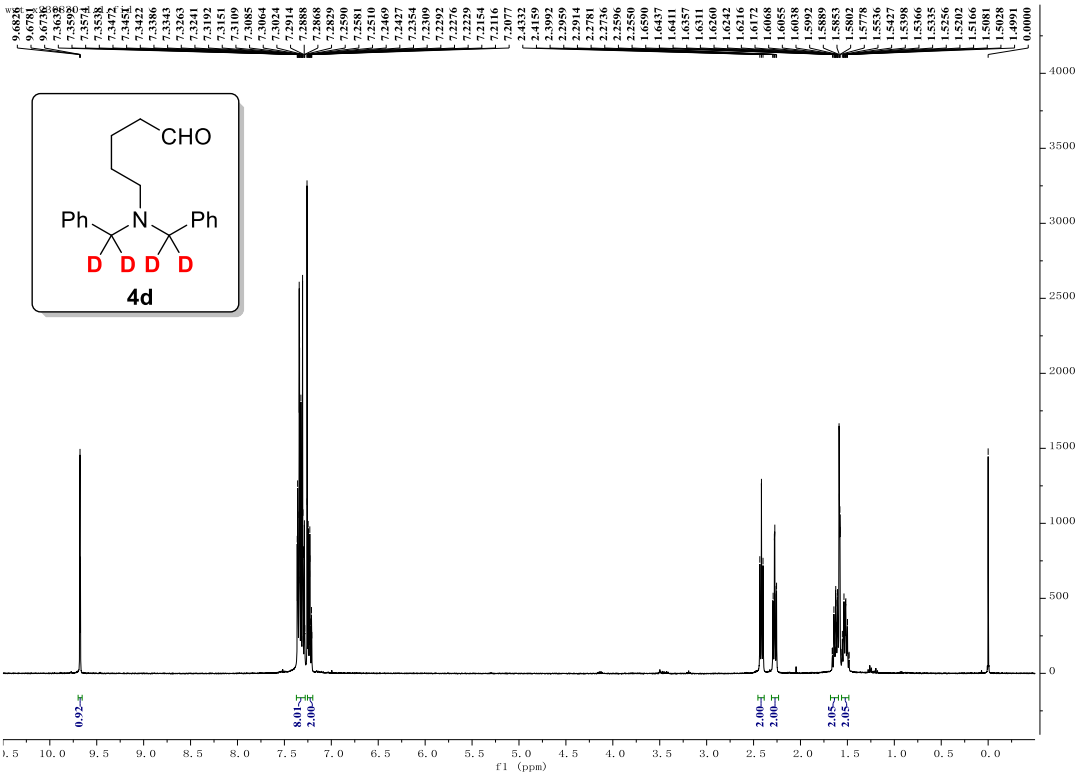
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4c



Step 4.

A flame-dried single-neck flask (50 mL) with stirring bar was charged with corresponding the mixture of **4c** (690 mg, 2.1 mmol, 1.0 equiv.) in anhydrous dichloromethane (10 mL, 0.2 M). DIBAL-H (4.2 mmol, 1.2 equiv.) was added to the mixture in portions under nitrogen atmosphere at -78 ºC over 5 minutes. The heterogeneous reaction mixture was stirred at same temperature for 2 hours. The resulting mixture was quenched by 10 mL saturated potassium sodium tartrate solution slowly. After stirring for an additional 30 minutes, the resulting solution was extracted with dichloromethane (10 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4 for 0.5 hour. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to give out the aldehyde **4d** (441 mg, 74% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.68 (t, *J* = 1.8 Hz, 1H), 7.37 – 7.28 (m, 8H), 7.25 – 7.20 (m, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.28 (td, *J* = 7.3, 1.8 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.56 – 1.48 (m, 2H).

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4d

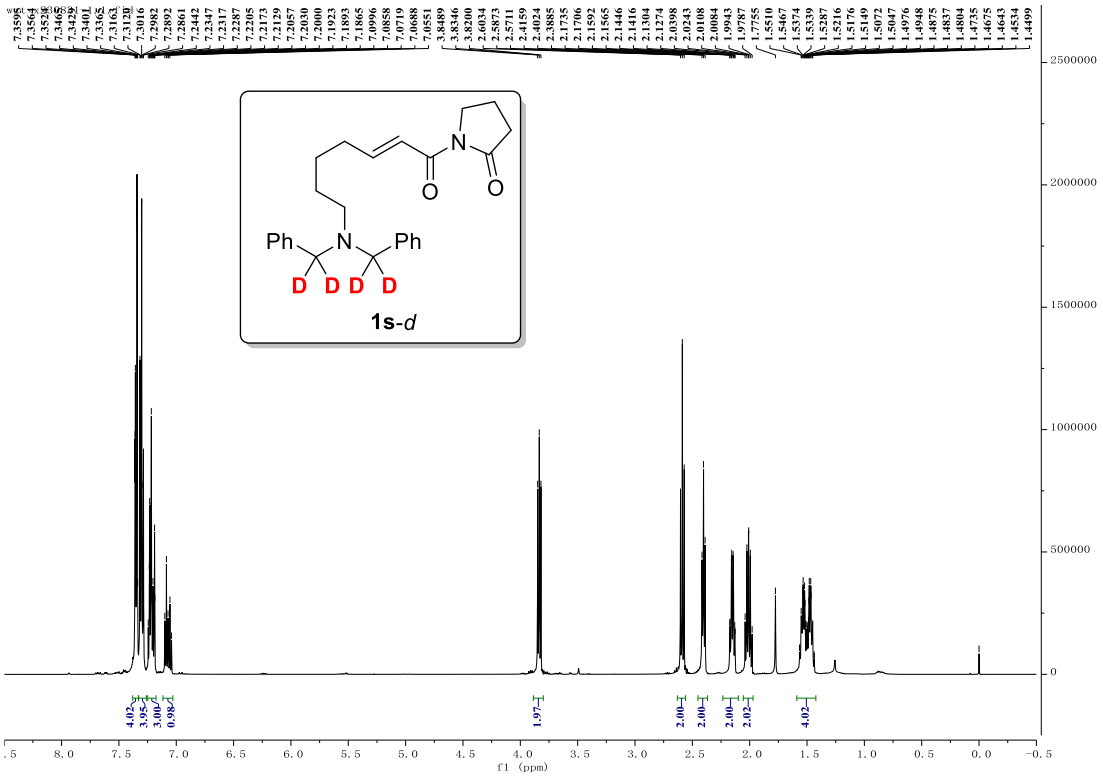


Step 5.

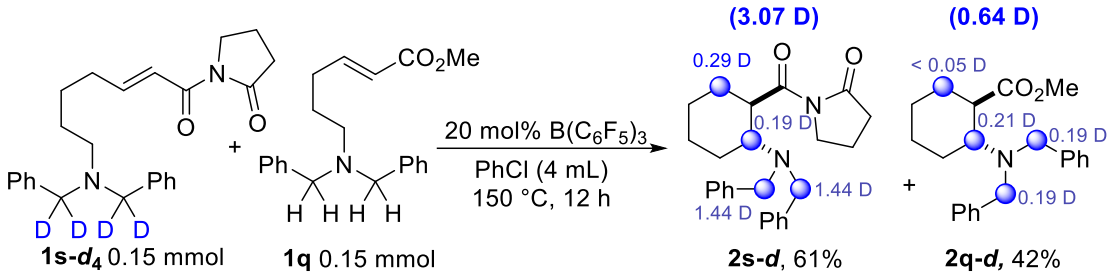
A flame-dried single-neck flask (50 mL) with stirring bar was charged with 1-(2-(triphenyl-l5-phosphaneylidene)acetyl)pyrrolidin-2-one (735 mg, 1.9 mmol, 1.2 equiv.) in anhydrous toluene (10 mL) under nitrogen atmosphere, then the **4d** (441 mg, 1.6 mmol, 1.0 equiv.) was added to the mixture via syringe, and stirred at 110 ºC for 12 hours. Then reaction mixture was quenched by 0.5 mL water slowly. the resulting solution was extracted with dichloromethane (10 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4. The resulting organic phase was concentrated under reduced pressure and the residue was purified by chromatography to give out the **1S**-*d* (342 mg, D > 99%, 61% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.38 – 7.33 (m, 4H), 7.33 – 7.26 (m, 4H), 7.25 – 7.18 (m, 3H), 7.11 – 7.03 (m, 1H),

3.89 – 3.80 (m, 2H), 2.59 (t, *J* = 8.1 Hz, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.15 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.06 – 1.97 (m, 2H), 1.59 – 1.42 (m, 4H).

^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1s-*d*

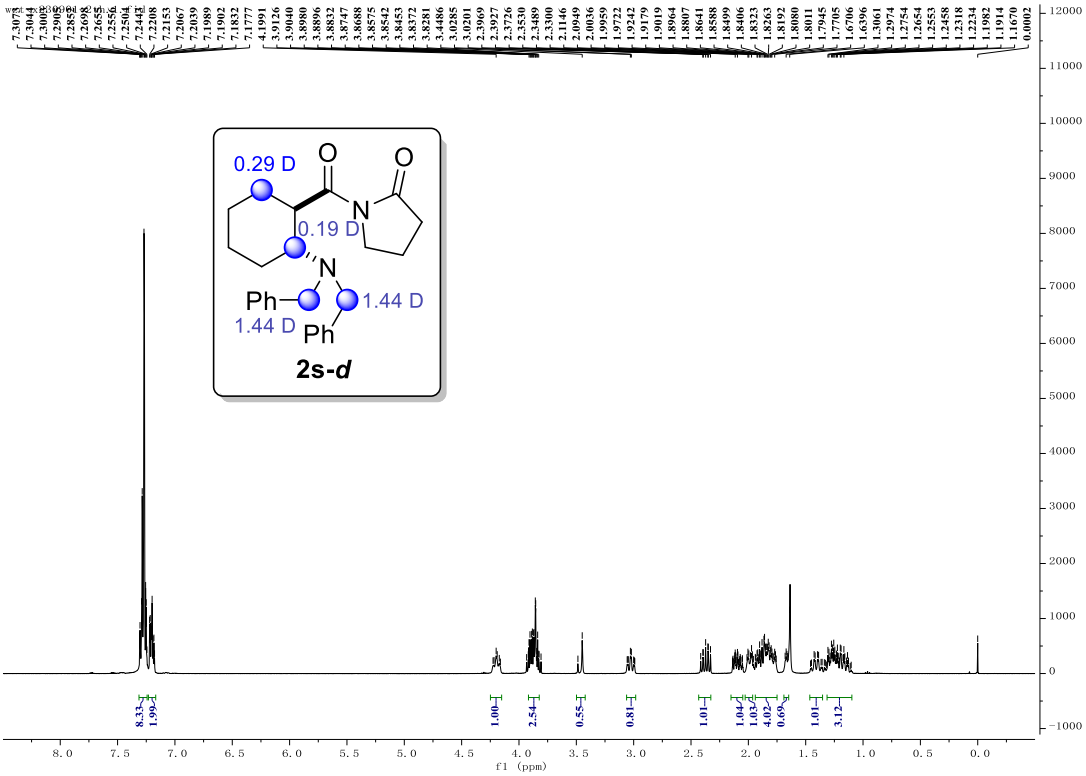


Deuteration study with 1s-d_4.

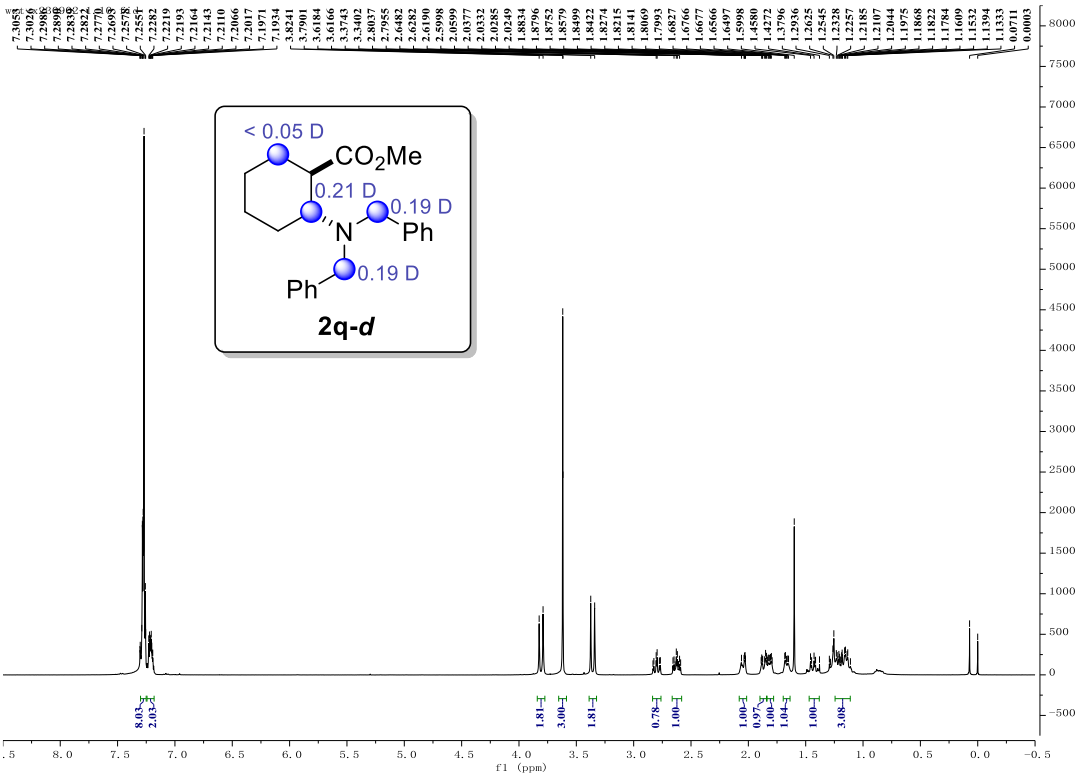


To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $B(C_6F_5)_3$ (30.7 mg, 0.06 mmol, 20 mol%), (*E*)-1-(7-(dibenzylamino)hept-2-enoyl)pyrrolidin-2-one **1s**-d_4 (58.5 mg ,0.15 mmol) and Methyl (*E*)-7-(dibenzylamino)hept-2-enoate (**1q**) chlorobenzene (3.0 mL) in the glove box. Then the mixture was heated to 150 °C in an oil bath stirred for 12 hours. After the reaction mixture was cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product **2s**-*d* (35.6 mg, 61% yield) and **2q**-*d* (21.2 mg, 42% yield).

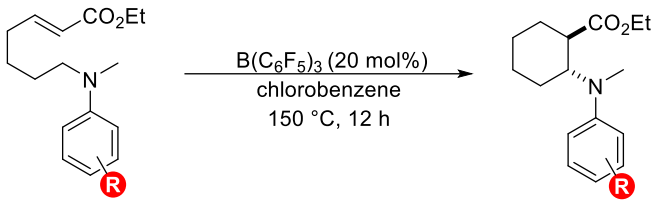
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2s-*d*



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2q-*d*

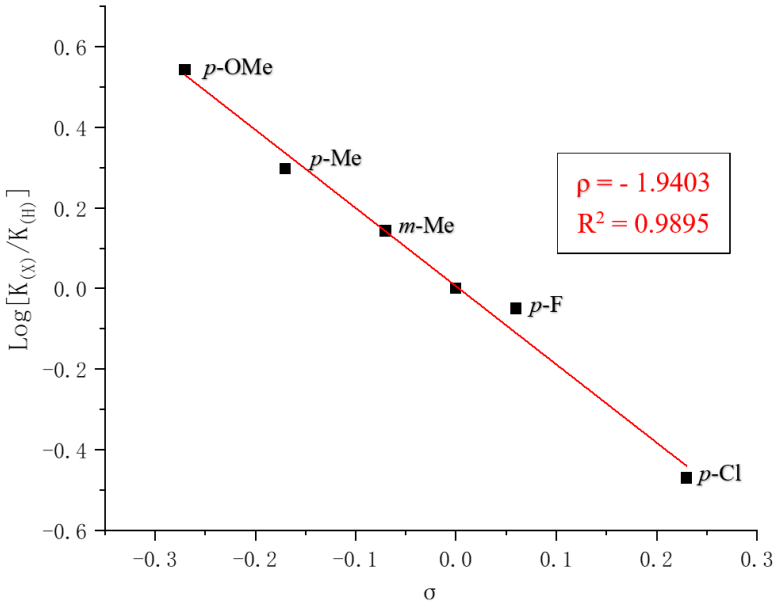


4.5.3 Hammett Studies[3]



A Hammett value for the reaction of *N*-aryl substituted starting material (**2f**, **1i** – **1l**, **1n**) was monitored by the ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $B(C_6F_5)_3$ (0.03 mmol, 20 mol%), and added different starting material (**1i** – **1l**, **1n**) (0.07 mmol) separately, **1f** (18.3 mg ,0.07 mmol) and chlorobenzene (1.5 mL) in the glove box. Then the mixture was heated to 150 ℃ in an oil bath stirred for 40 minutes. After the reaction mixture was cooled to room temperature, evaporation of the solvent under reduced pressure, then added the internal standard. The data were processed using MestReNova software and peak integrations.

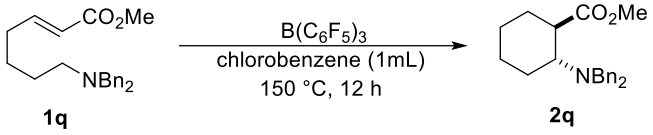
	Peak area (X/H)	$K_{(X)}/K_{(H)}$	$Log[K_{(X)}/K_{(H)}]$	Hammett constant σ
p-OMe	3.480	3.480	0.542	-0.27
p-Me	1.980	1.980	0.297	-0.17
m-Me	1.390	1.390	0.143	-0.07
H	1	1	0	0
p-F	0.891	0.891	-0.050	0.06
p-Cl	0.339	0.339	-0.470	0.23



4.5.4 Kinetic Experiments

Determination of Reaction Order of $B(C_6F_5)_3$

A kinetic study was conducted following the procedure for time course reaction monitoring by 1H NMR (using CH_2Br_2 as the internal standard) while varying the concentration of $B(C_6F_5)_3$ (Figure **S1**). There is an induction period due to the reaction (in the period of 15-30 minutes), so the initial-rate kinetic analysis, which was determined from the data points in the period of 35-65 minutes, demonstrates first-order kinetics of $B(C_6F_5)_3$ in the reaction (Figure **S2**).



1q **2q**

To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added and the following amounts of $B(C_6F_5)_3$ (10.0, 15.0, 20.0 and 30.0 mol%). and added starting material (**1q**) (0.1 mmol), and chlorobenzene (1.0 mL) in the glove box. Then the mixture was heated to 150 °C in an oil bath stirred for corresponding time. After the reaction mixture was cooled to room temperature, evaporation of the solvent under reduced pressure, then added the internal standard (**0.1 mmol CH_2Br_2**). The data were processed using MestReNova software and peak integrations.

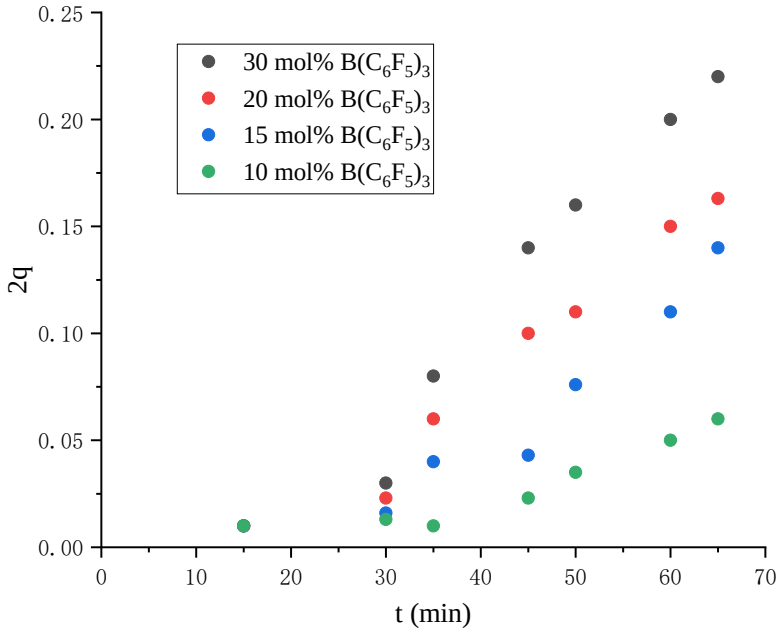


Figure **S1**. Monitoring the formation of **2q** using different concentrations of $B(C_6F_5)_3$.

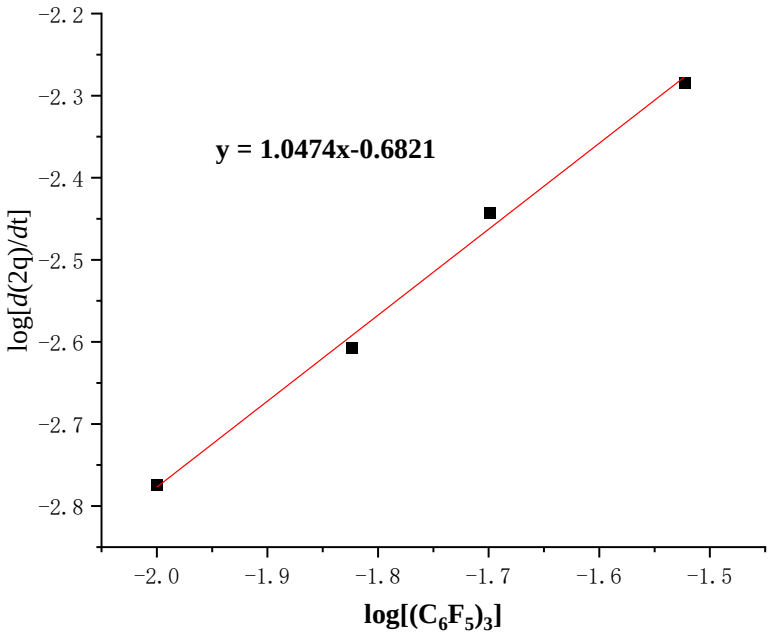
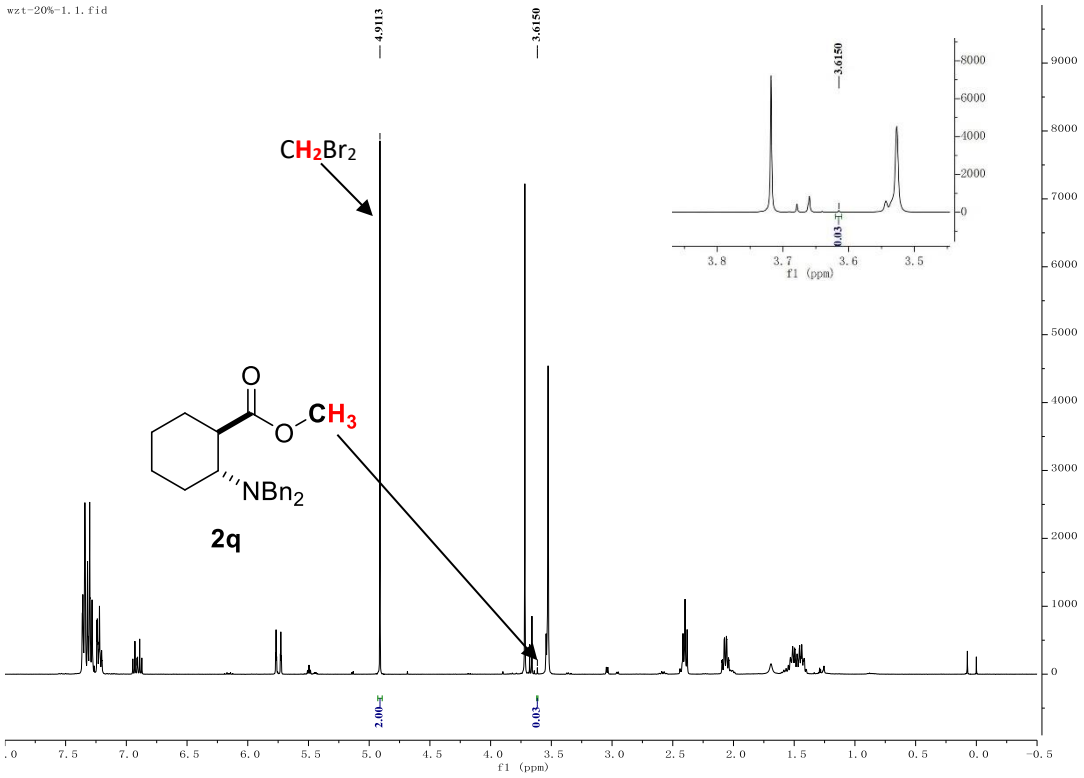


Figure **S2**. Log(rate) *vs* Log[$B(C_6F_5)_3$] plot is employed to determine the reaction order for $B(C_6F_5)_3$. The result suggests that there is approximately first-order dependency on the concentration of $B(C_6F_5)_3$.

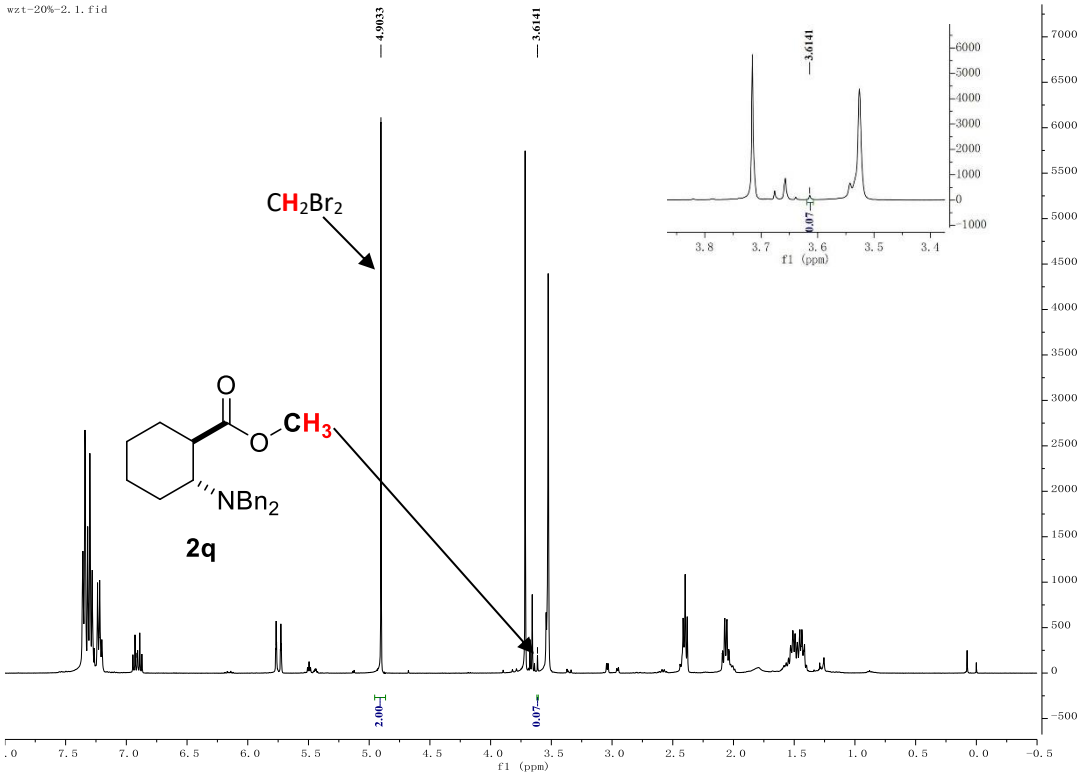
For example:

Crude ^{1}H-NMR of 2p Catalyzed by 20% mol $B(C_6F_6)_3$ Using CH_2Br_2 as Internal Standard:

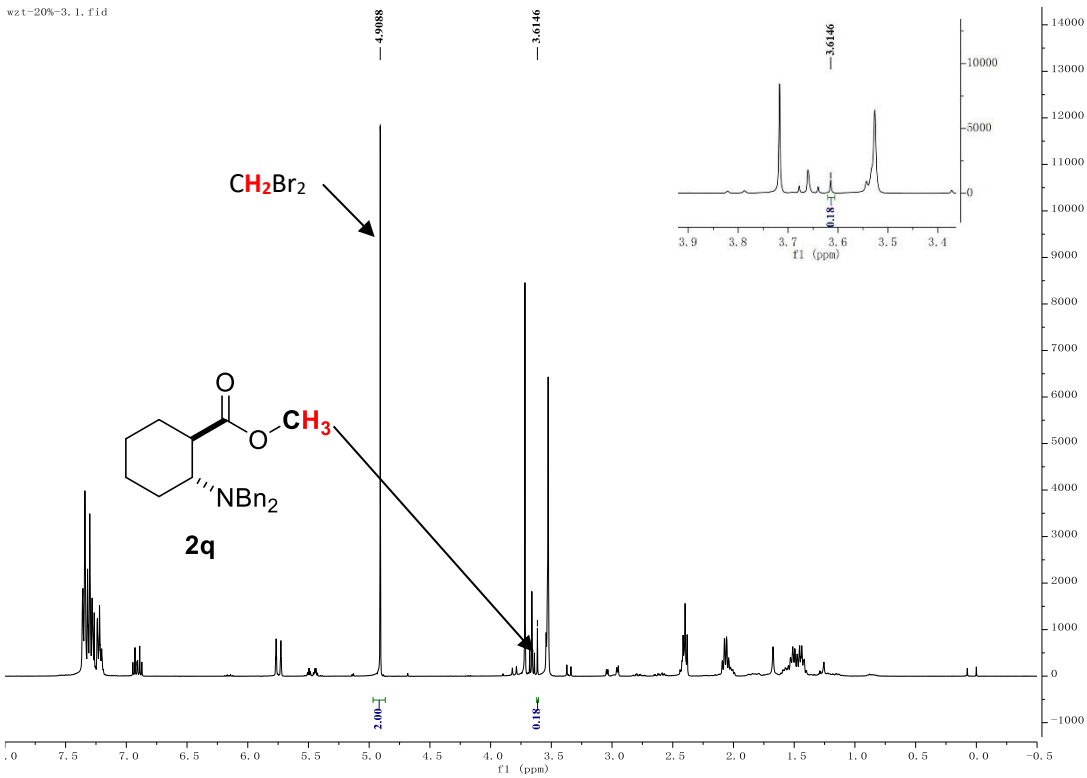
Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 15 min



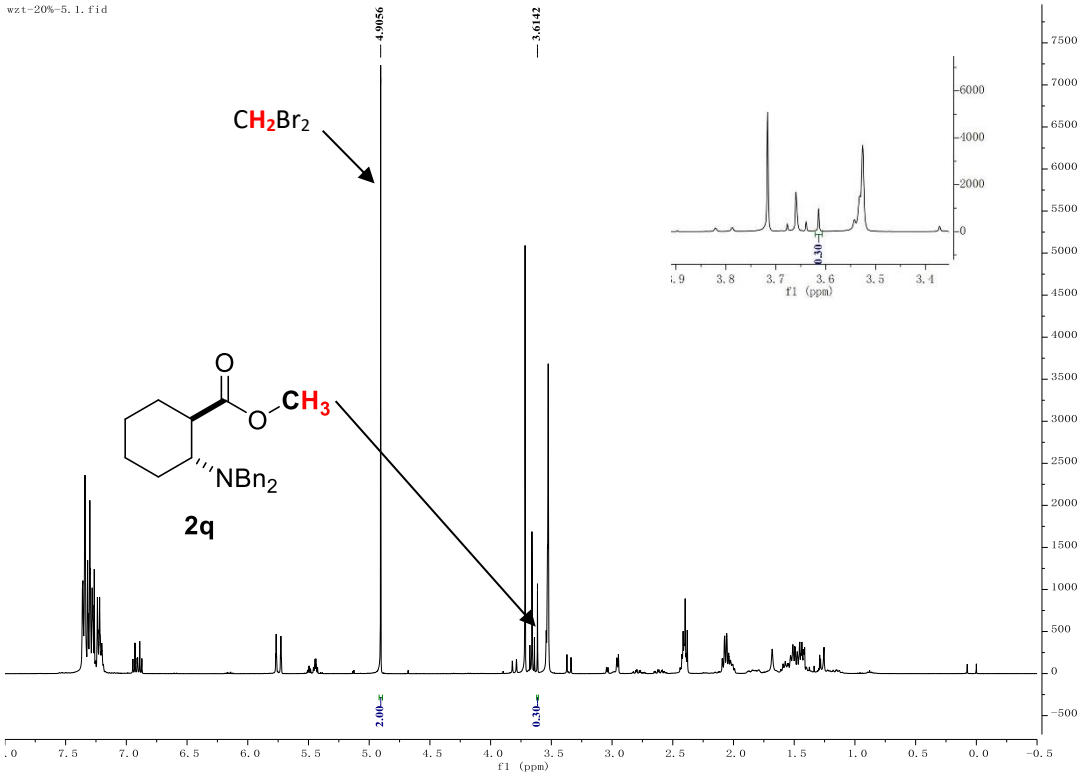
Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 30 min



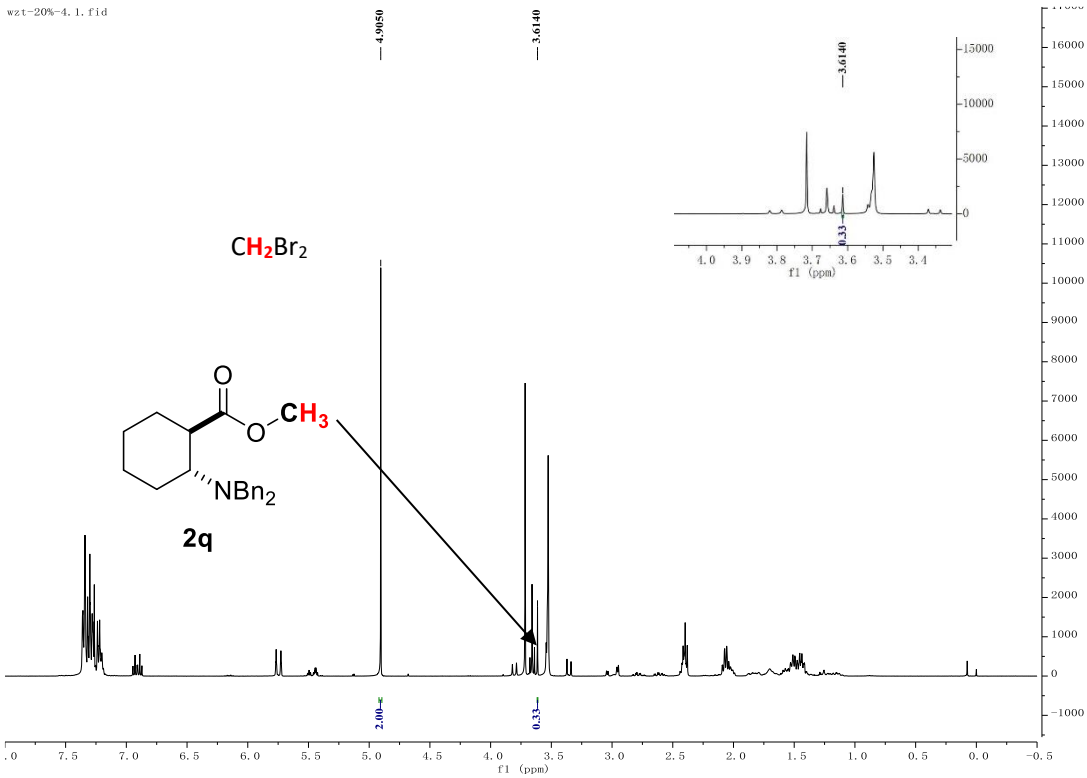
Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 35 min



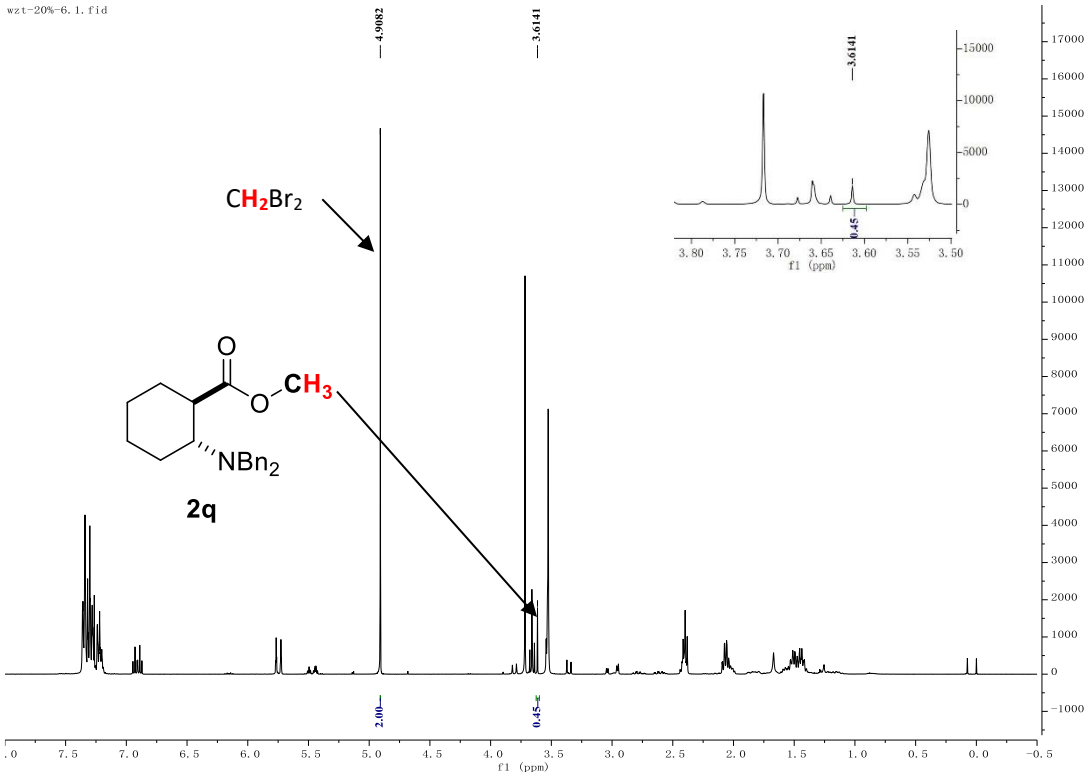
Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 45 min



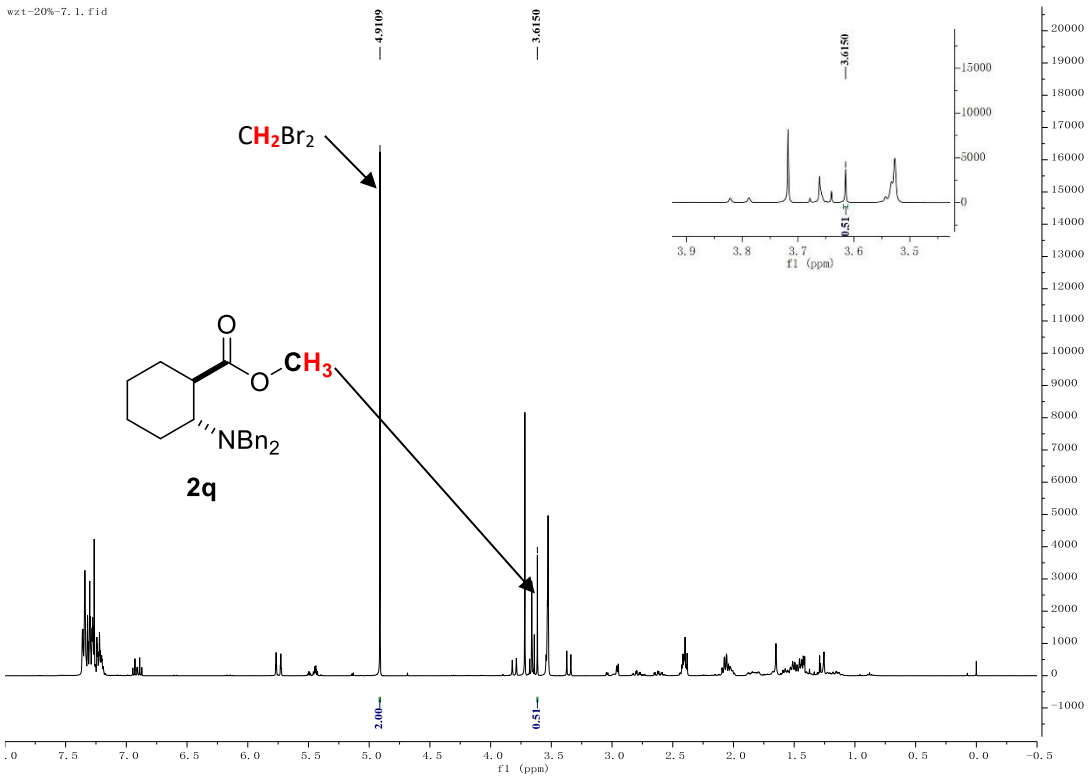
Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 50 min



Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 60 min

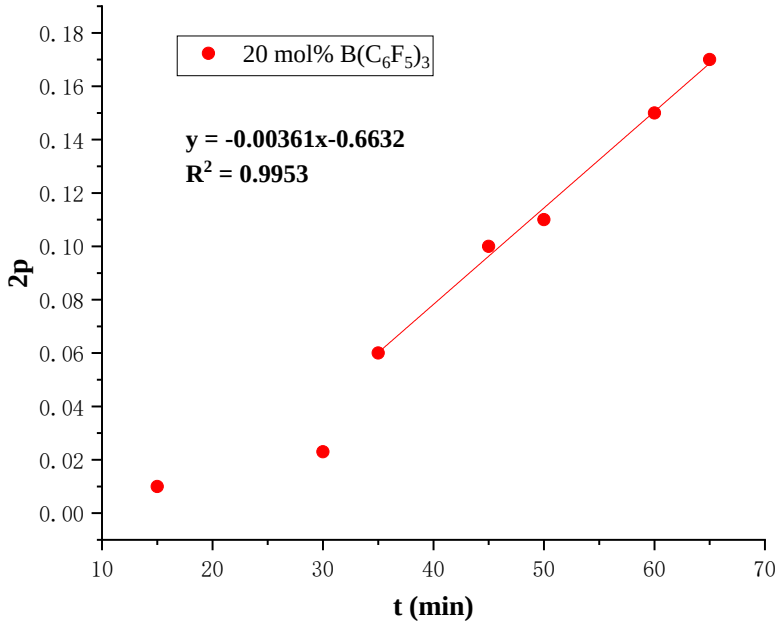


Crude ^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2p at 65 min



Data processing and analysis of this reaction catalyzed by 20% mol $B(C_6F_6)_3$ Using CH_2Br_2 as Internal Standard:

Time (min)	Peak area in 3.61 ppm	Yield (%)
15	0.03	1
30	0.07	2.3
35	0.18	6
45	0.30	10
50	0.33	11
60	0.45	15
65	0.51	17



Data processing and analysis of Log(rate) *vs* Log[$B(C_6F_5)_3$] plot:

$B(C_6F_5)_3$ (mol%)	Rate (slope)	Log(rate)	Log[$B(C_6F_5)_3$]
30	0.00520	-2.2840	-1.523
20	0.00361	-2.4424	-1.699
15	0.00247	-2.6073	-1.824
10	0.00168	-2.7747	-2

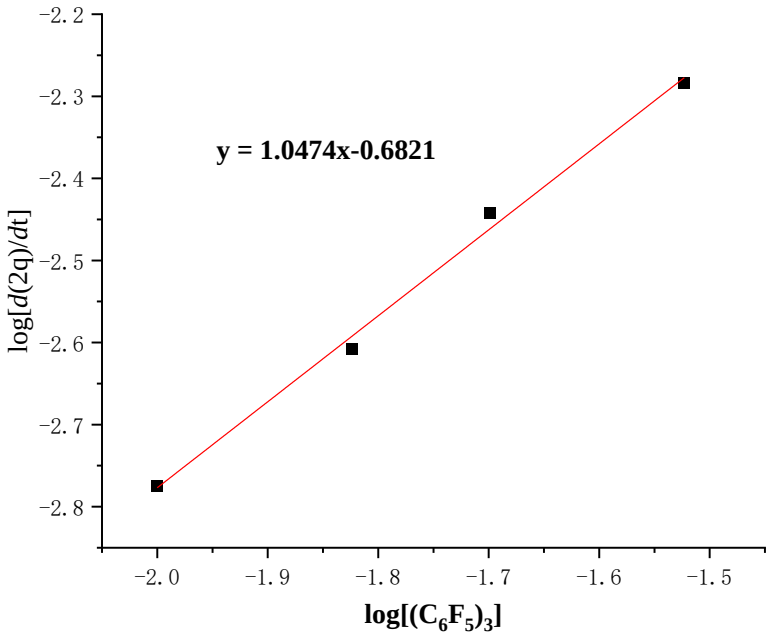
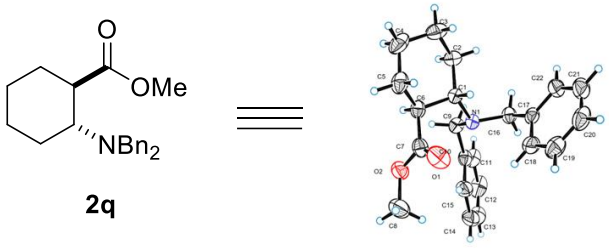


Figure **S2**. Log(rate) *vs* Log[$B(C_6F_5)_3$] plot is employed to determine the reaction order for $B(C_6F_5)_3$. The result suggests that there is approximately first-order dependency on the concentration of $B(C_6F_5)_3$.

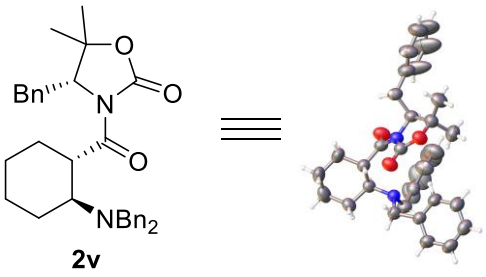
5. X-ray Crystallographic Date



2q

CCDC: 2269106

Identification code	WZT-1_auto
Empirical formula	$C_{22}H_{27}NO_2$
Formula weight	337.44
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.5717(3)
b/Å	9.8552(4)
c/Å	10.5251(3)
α/°	90.752(3)
β/°	90.752(3)
γ/°	102.176(3)
Volume/Å^3	970.31(6)
Z	2
ρ_{calc}g/cm^3	1.155
μ/mm^{-1}	0.572
F(000)	364.0
Crystal size/mm^3	0.18 × 0.15 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.402 to 145.872
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 11, -9 ≤ l ≤ 13
Reflections collected	7024
Independent reflections	3741 [R_{int} = 0.0156, R_{sigma} = 0.0166]
Data/restraints/parameters	3741/0/228
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1585
Final R indexes [all data]	R_1 = 0.0581, wR_2 = 0.1647
Largest diff. peak/hole / e Å^{-3}	0.29/-0.17



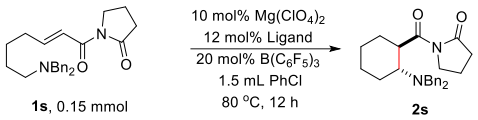
2v

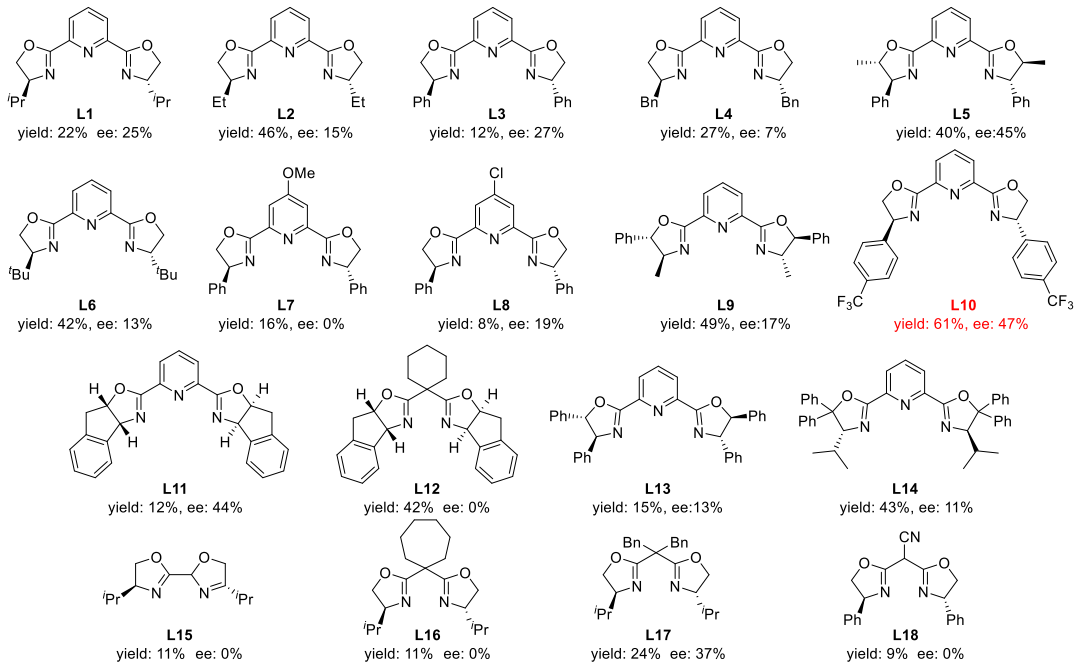
CCDC: 2311722

Identification code	WZT-1202_auto
Empirical formula	$C_{33}H_{38}N_2O_3$
Formula weight	510.65
Temperature/K	300
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.80990(10)
b/Å	8.93610(10)
c/Å	18.6704(2)
α/°	90
β/°	99.5870(10)
γ/°	90
Volume/Å^3	1449.32(3)
Z	2
ρ_{calc}g/cm^3	1.170
μ/mm^{-1}	0.586
F(000)	548.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.608 to 145.816
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected	27277
Independent reflections	5690 [R_{int} = 0.0365, R_{sigma} = 0.0205]
Data/restraints/parameters	5690/13/346
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1131
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1169
Largest diff. peak/hole / e Å^{-3}	0.15/-0.19
Flack parameter	0.03(8)

6. Asymmetric Synthesis of 2s

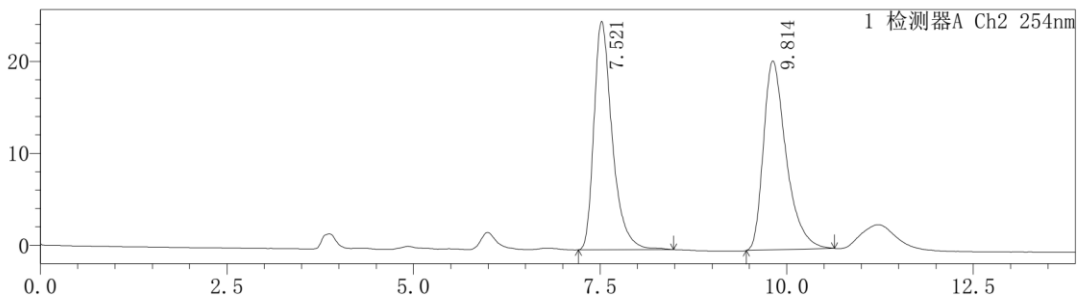
6.1. Screening of chiral ligands





To an oven-dried 25 mL flame-dried Young-type tube equipped with a stir bar was added $B(C_6F_5)_3$ (0.03mmol, 20 mol%), $Mg(ClO_4)_2$ (3.3 mg, 10 mol%), ligand (12 mol%), (*E*)-1-(7-(dibenzylamino) hept-2-enoyl) pyrrolidin-2-one **1s** (58.5 mg ,0.15 mmol) and PhCl (1.5 mL) in the glove box. Then the mixture was heated to 80 ºC in an oil bath and refluxed for 12 h. After the reaction mixture was cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted with petroleum ether / ethyl acetate = 20/1 ~ 10/1) on silica gel to give the desired product **2s** as a white solid, by chiral HPLC analysis [Chiralcel IA column, Hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 10.397 min (minor), t_R = 7.302 min (major)].

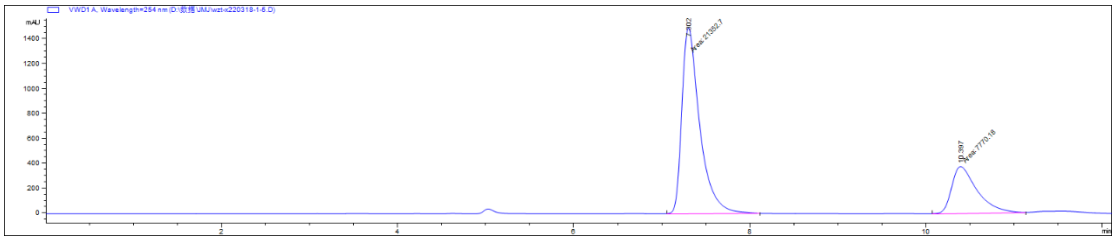
6.2. HPLC analyses of the chiral product



Peak Table

检测器A Ch1 220nm

eakNumbe	RetTime	Area	Height	Tab	Area%
1	7.519	5686450	330315	M	48.873
2	9.812	5948655	274843	M	51.127
总计		11635105	605158		100.000



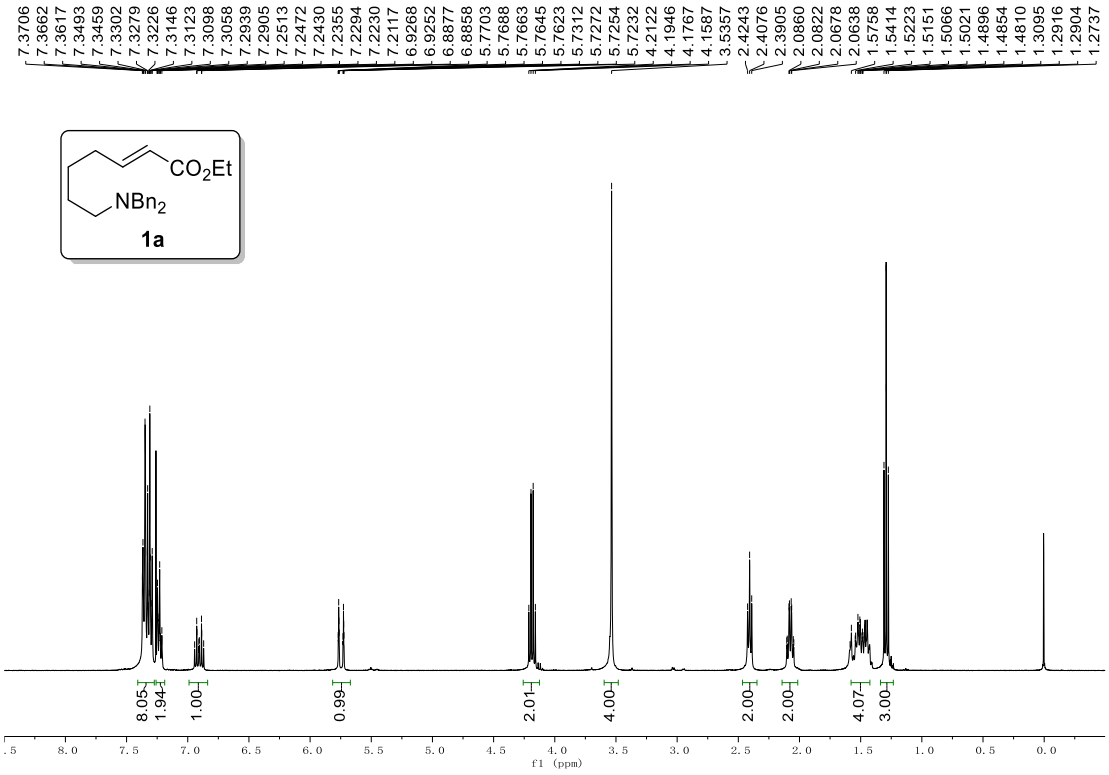
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.302	MM	0.2377	2.13527e4	1496.95313	73.3193
2	10.397	MM	0.3404	7770.17725	380.48300	26.6807
Totals :				2.91229e4	1877.43613	

7. Reference

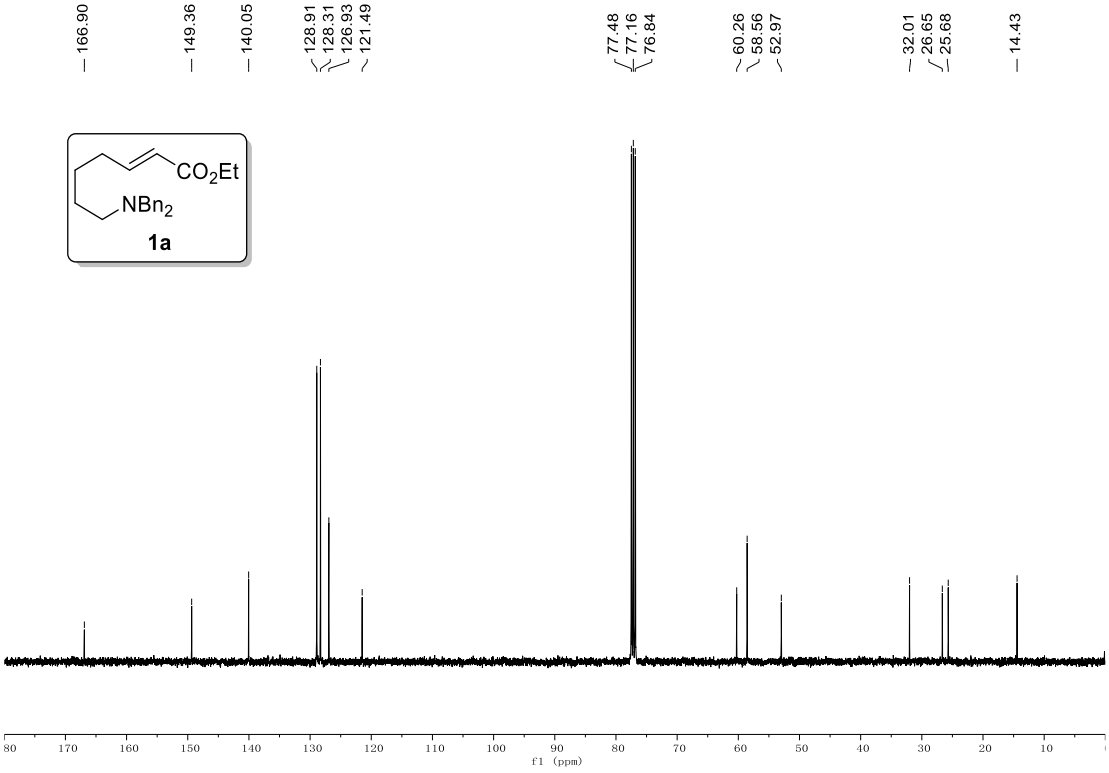
1. C. Joannesse, C. P. Johnston, L. C. Morrill, P. A. Woods, M. Kieffer, D.-C. T. A. Nigst, H. Mayr, T. Lebl, D. Philp, R. A. Bragg and A. D. Smith, *Chem. Eur. J.*, 2012, **18**, 2398-2408.
2. A. Trowbridge, D. Reich and M. J. Gaunt, *Nature*, 2018, **561**, 522–527.
3 Y. Chang, M. Cao, J. Z. Chan, C. Zhao, Y. Wang, R. yang and M. Wasa, *J. Am. Chem. Soc.*, 2021, **143**, 2441-2455.

8. NMR Spectra of Materials and Products

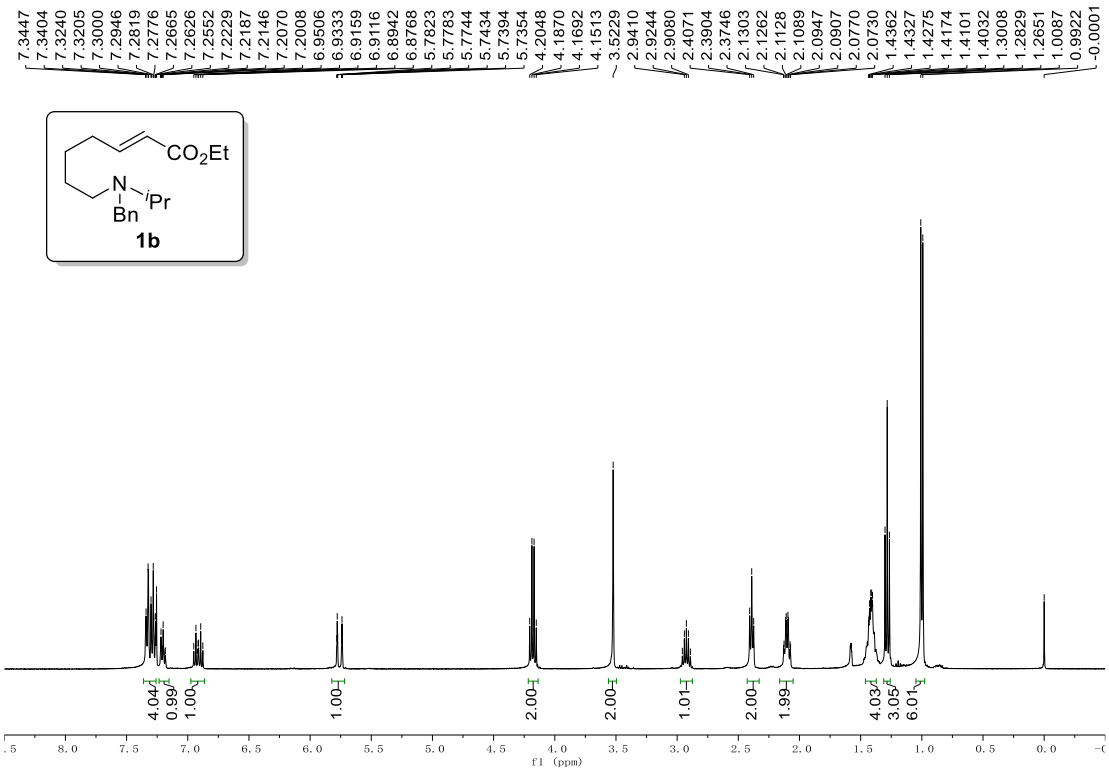
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1a



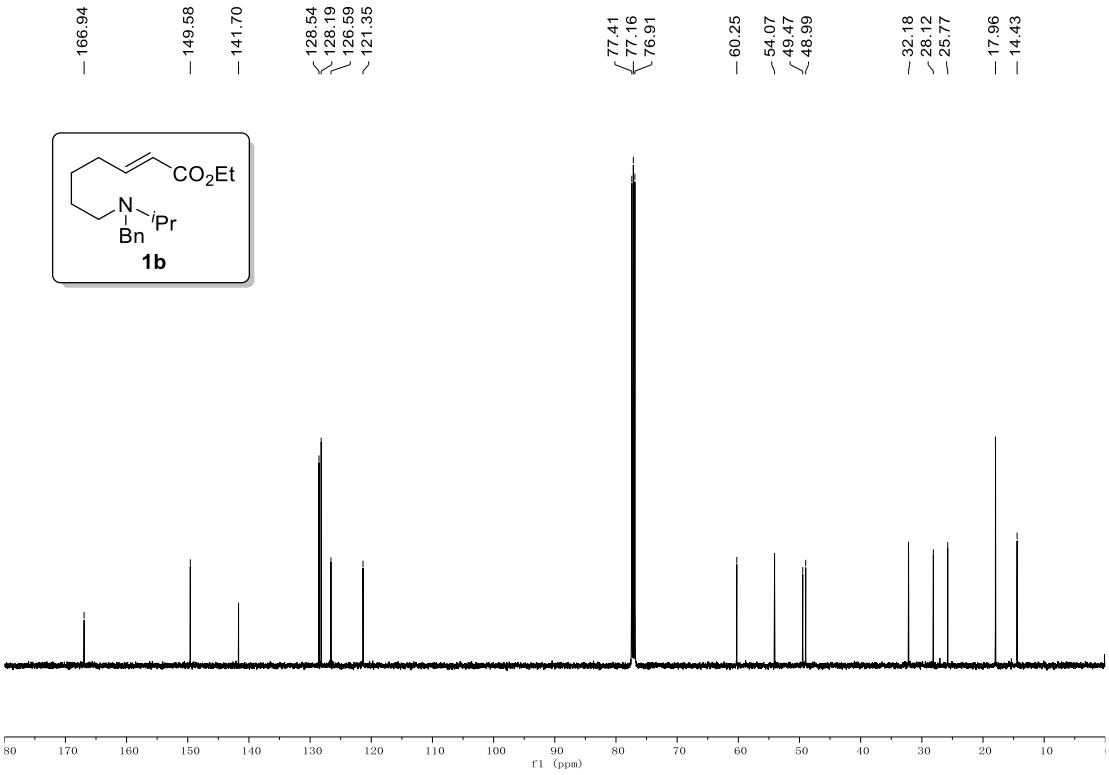
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1a



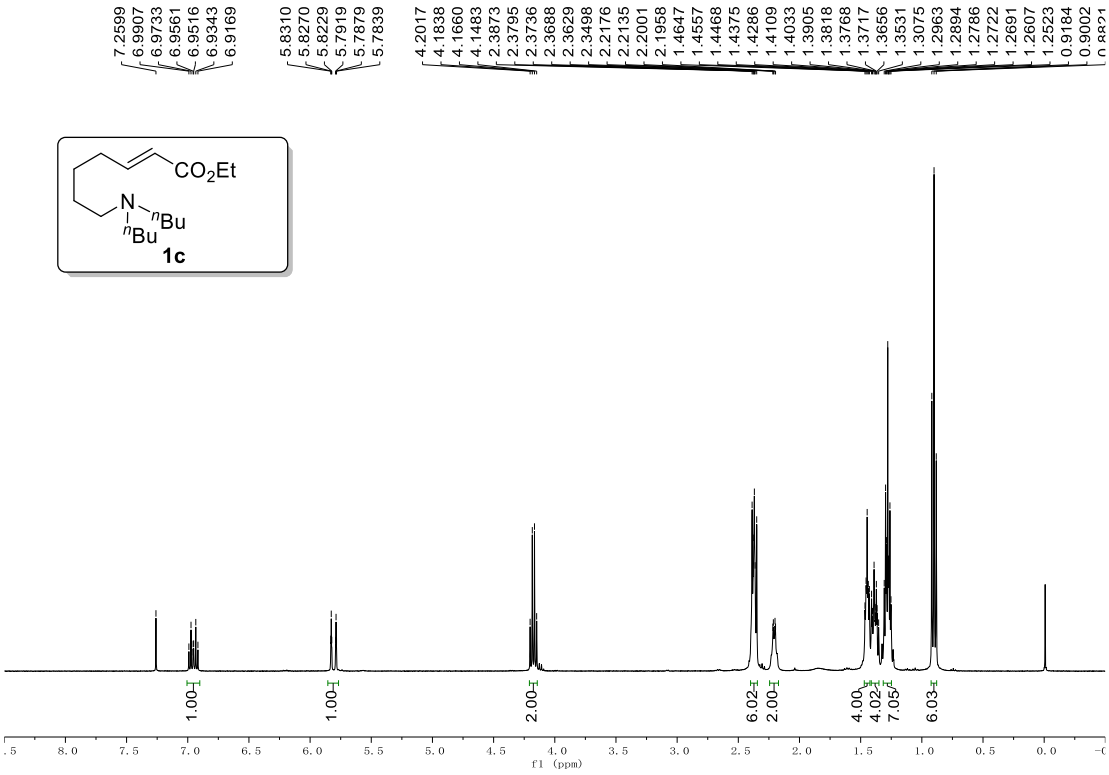
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1b



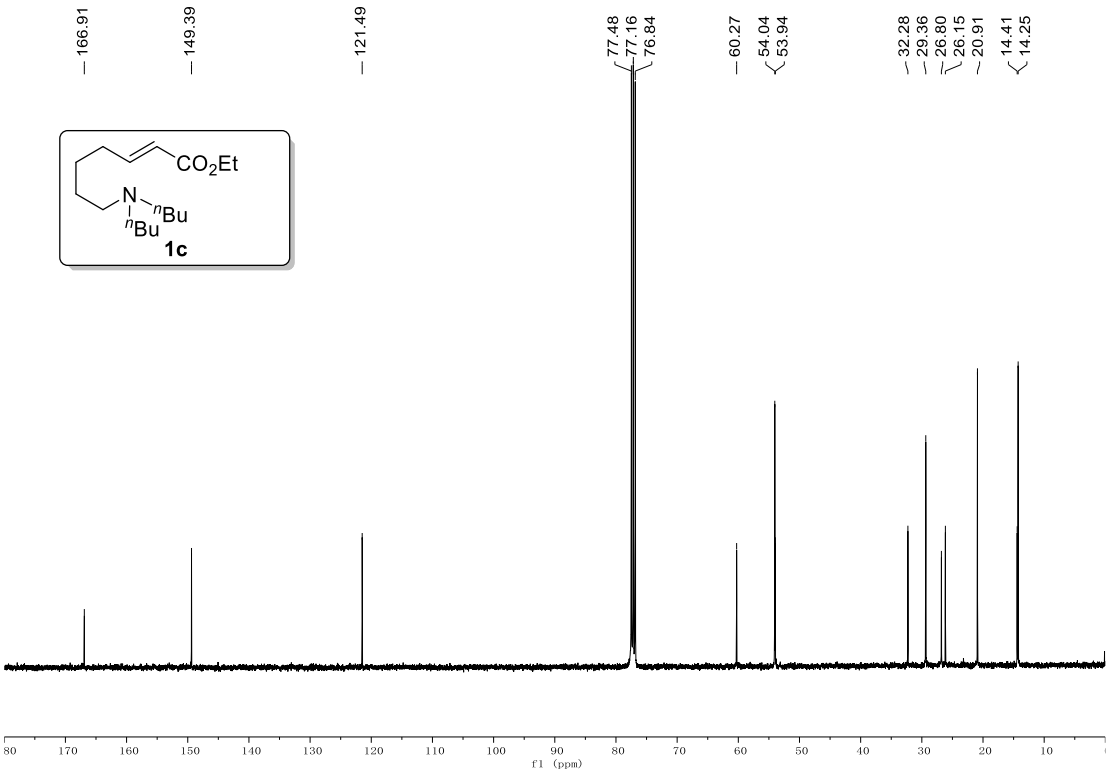
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1b



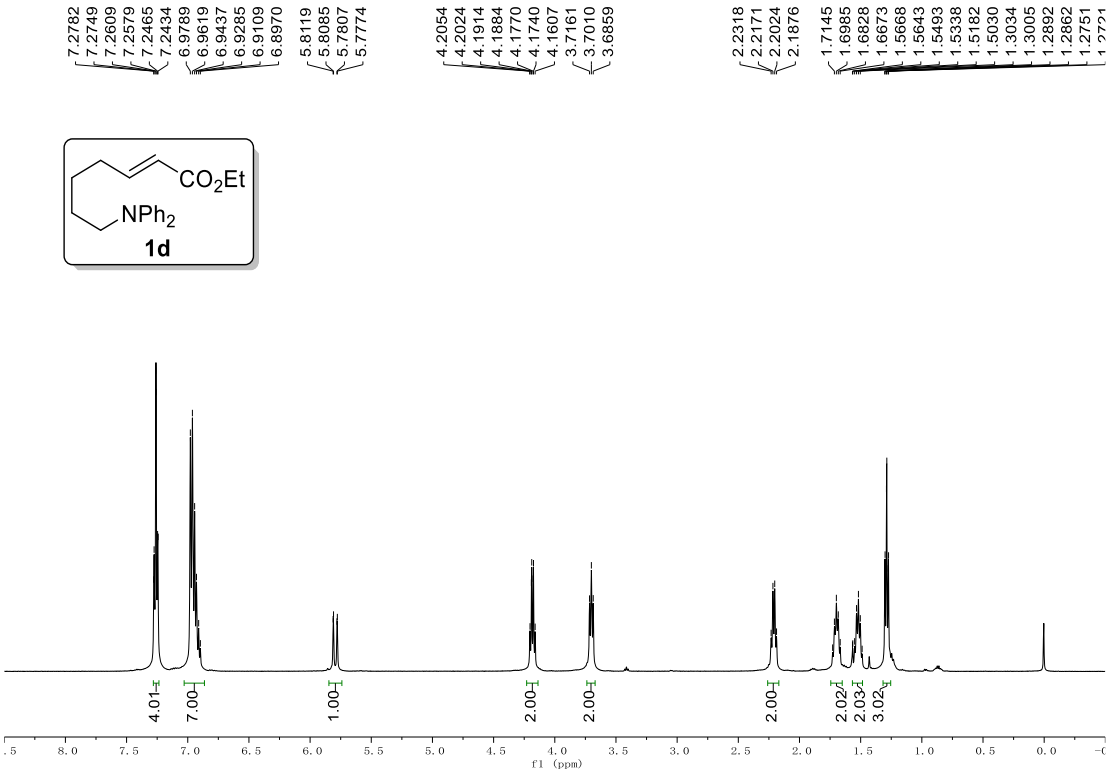
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1c



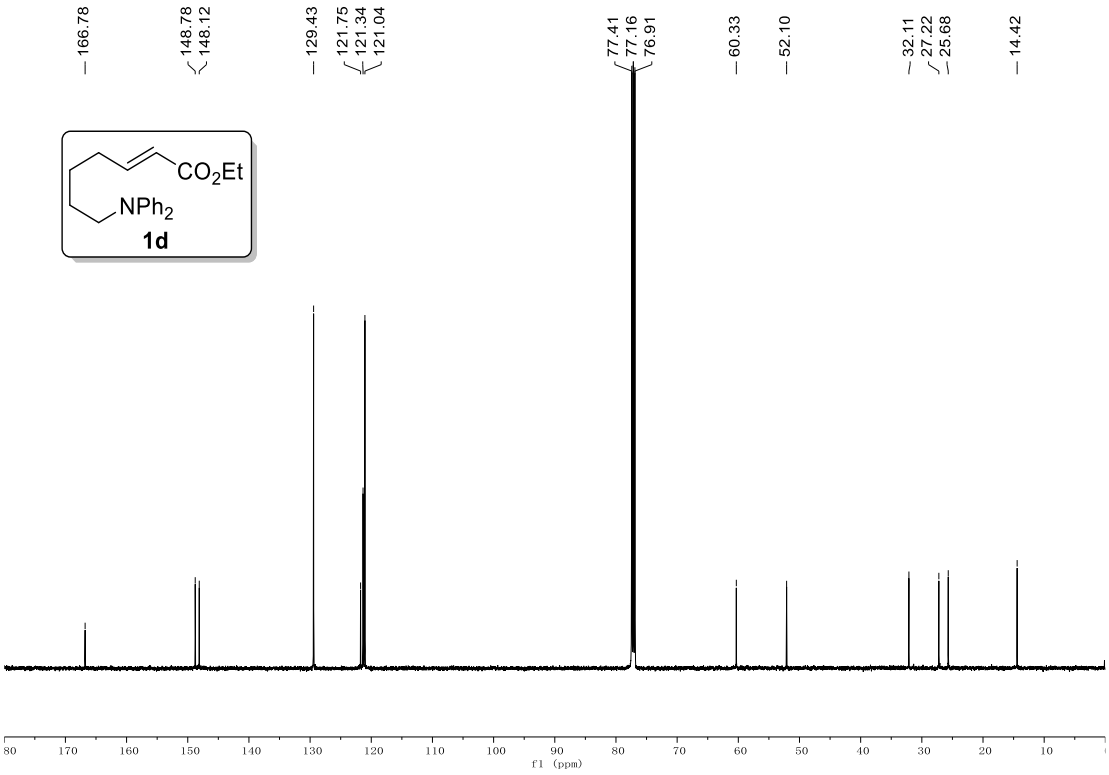
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1c



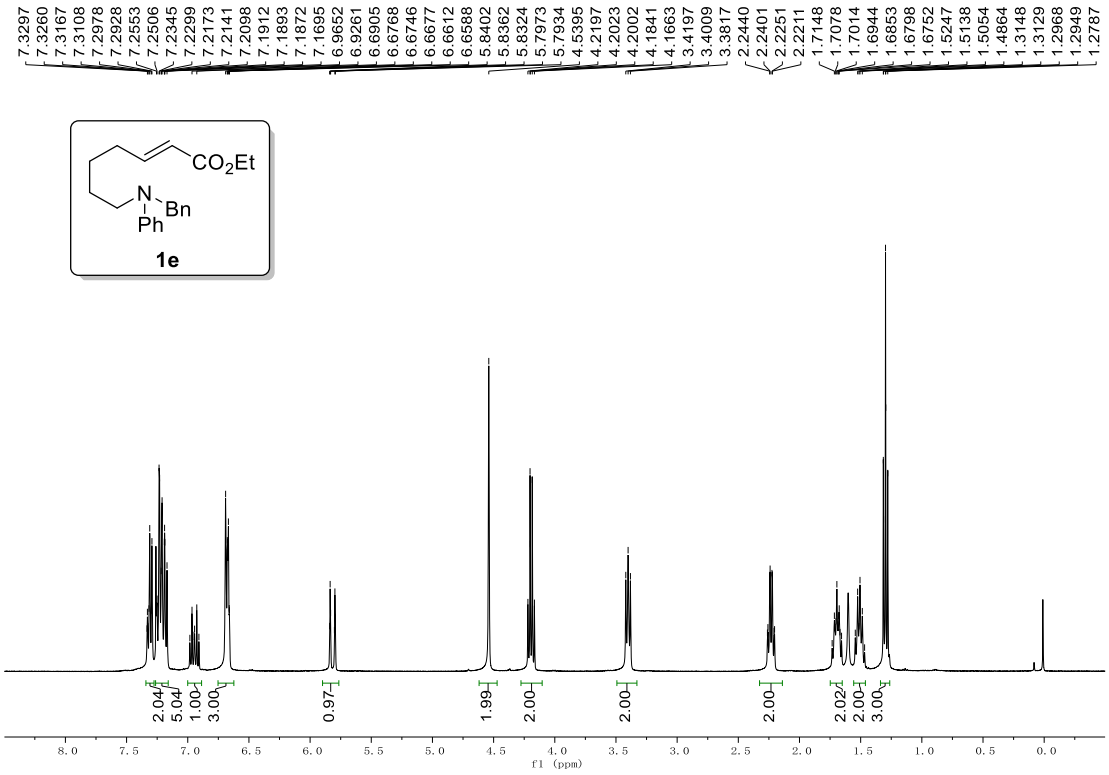
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1d



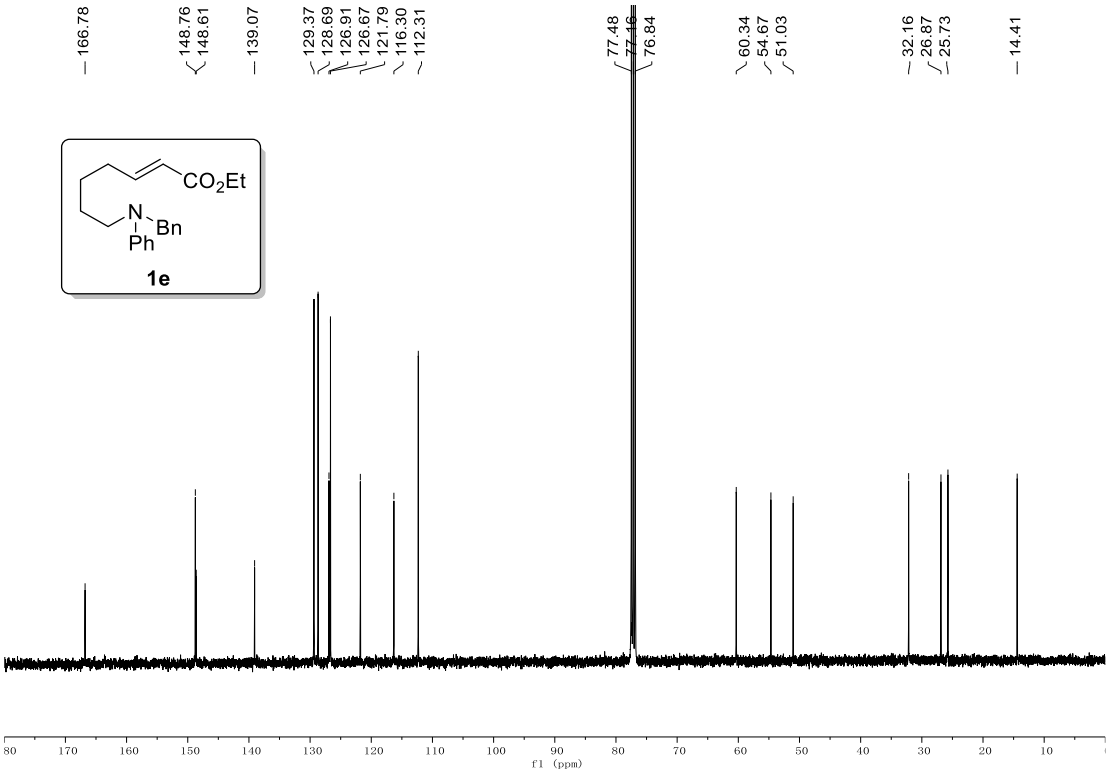
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1d



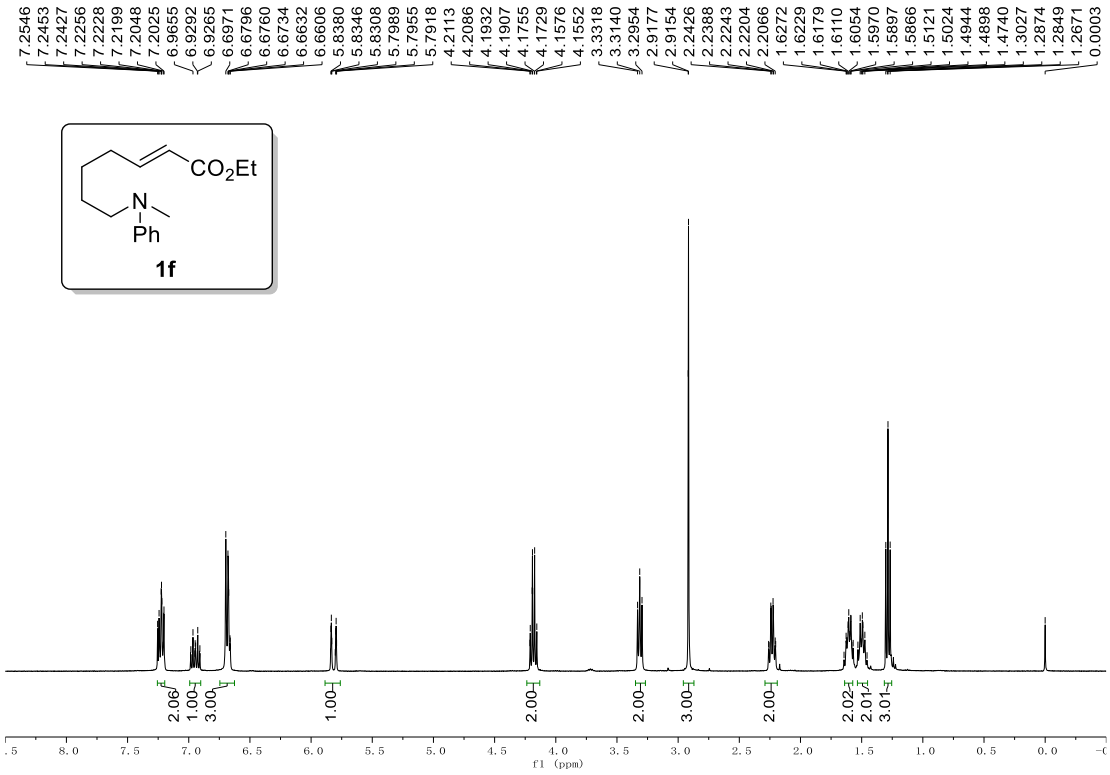
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1e



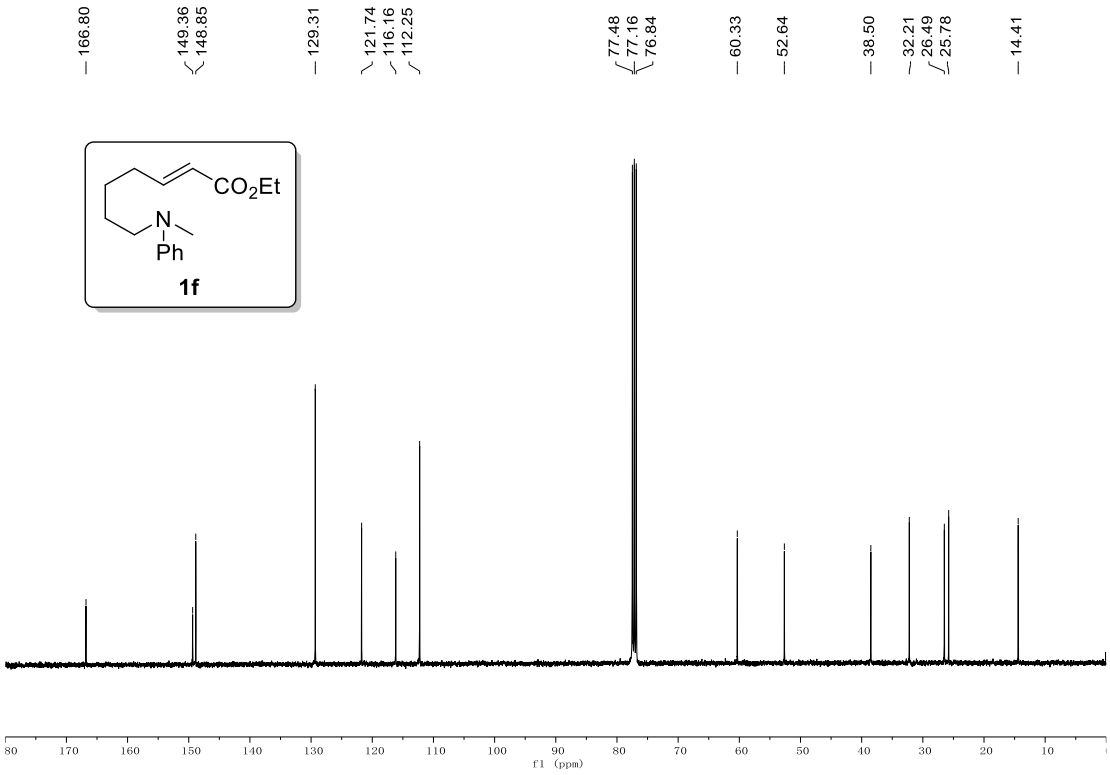
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1e



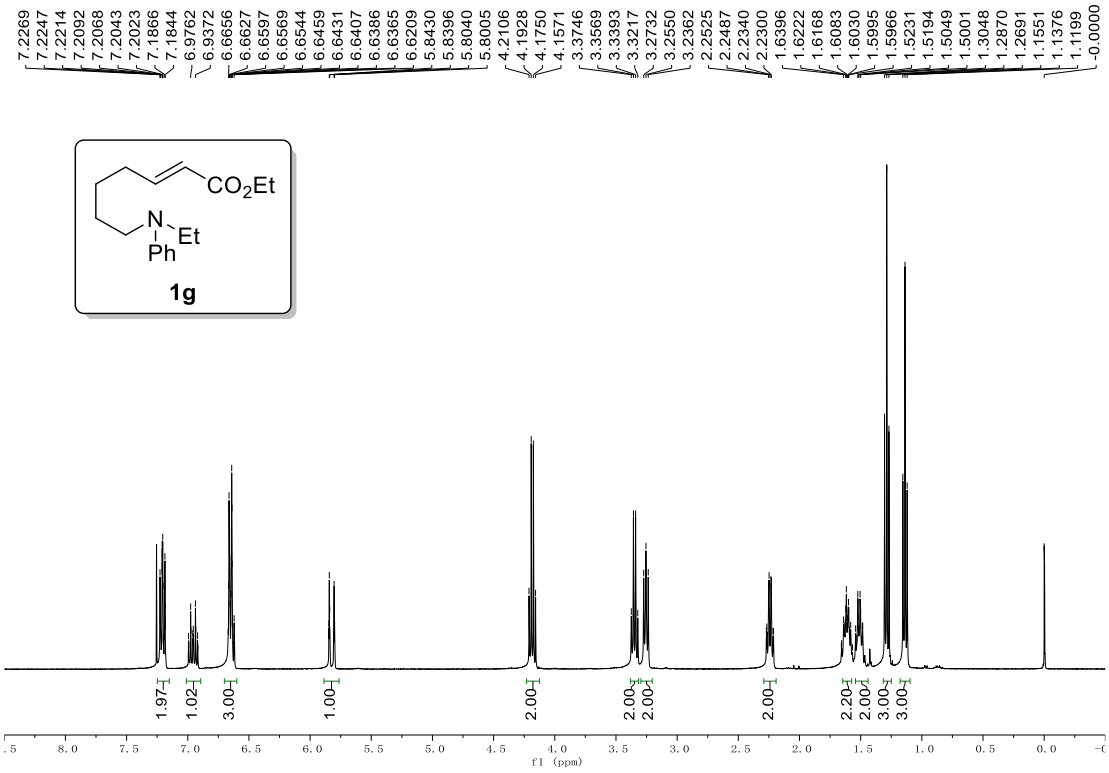
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1f



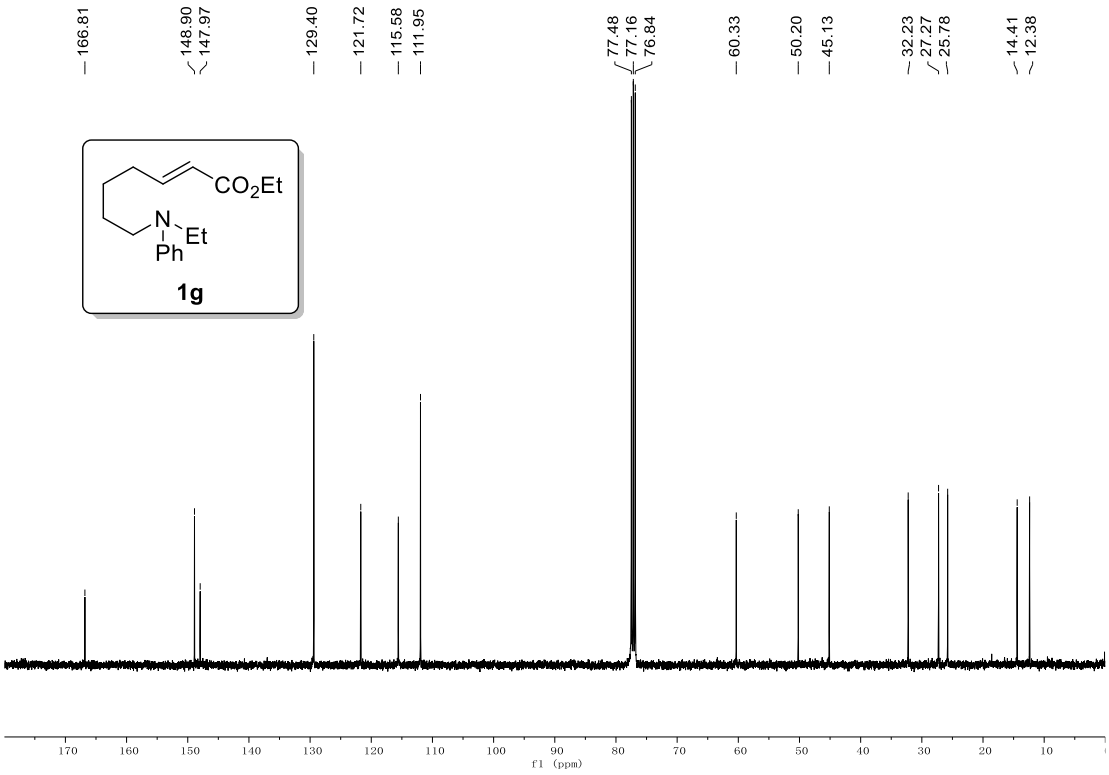
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1f



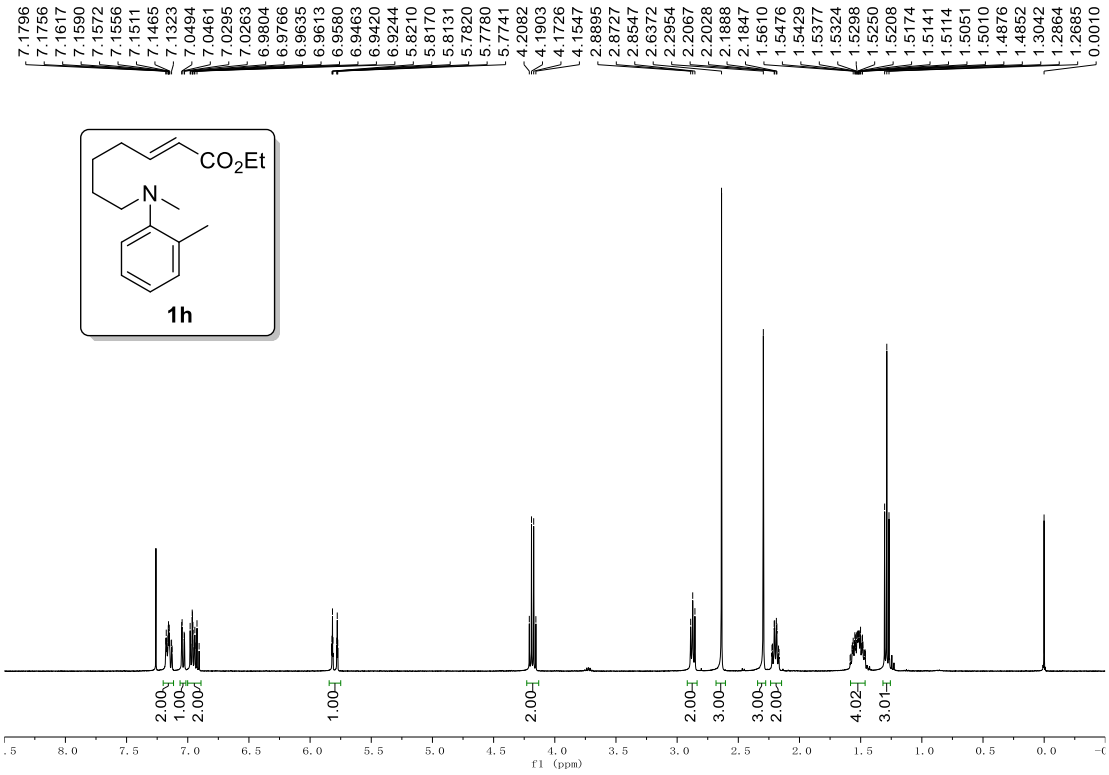
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1g



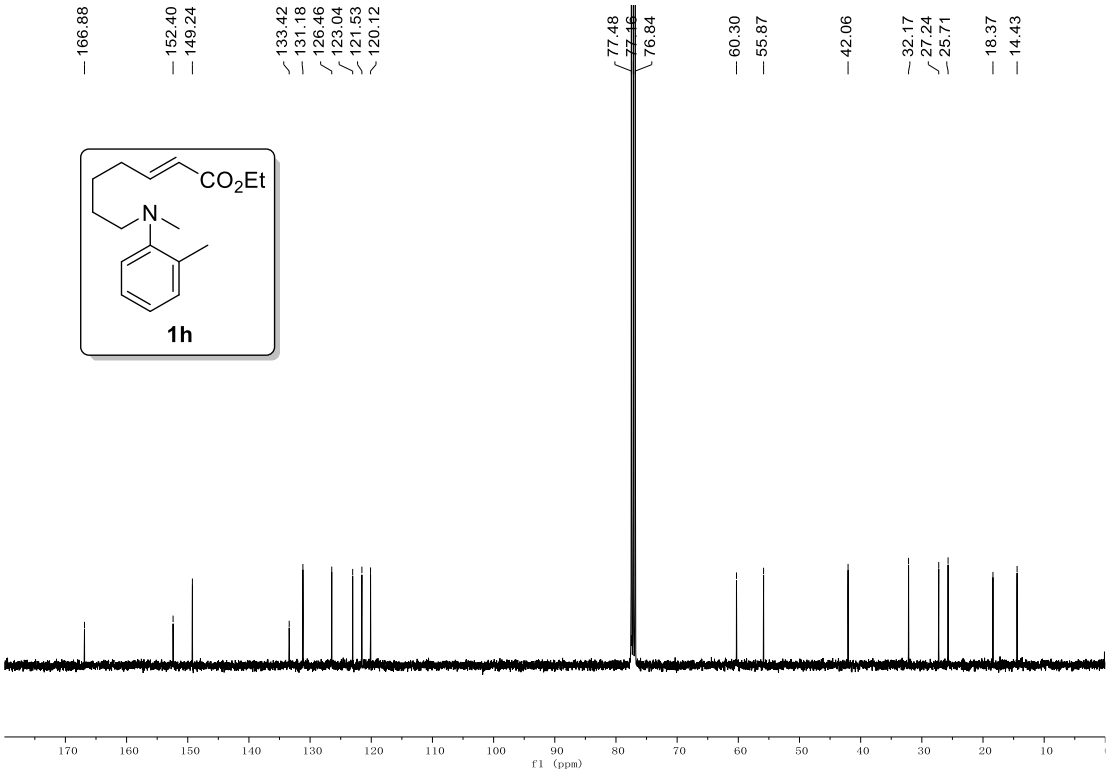
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1g



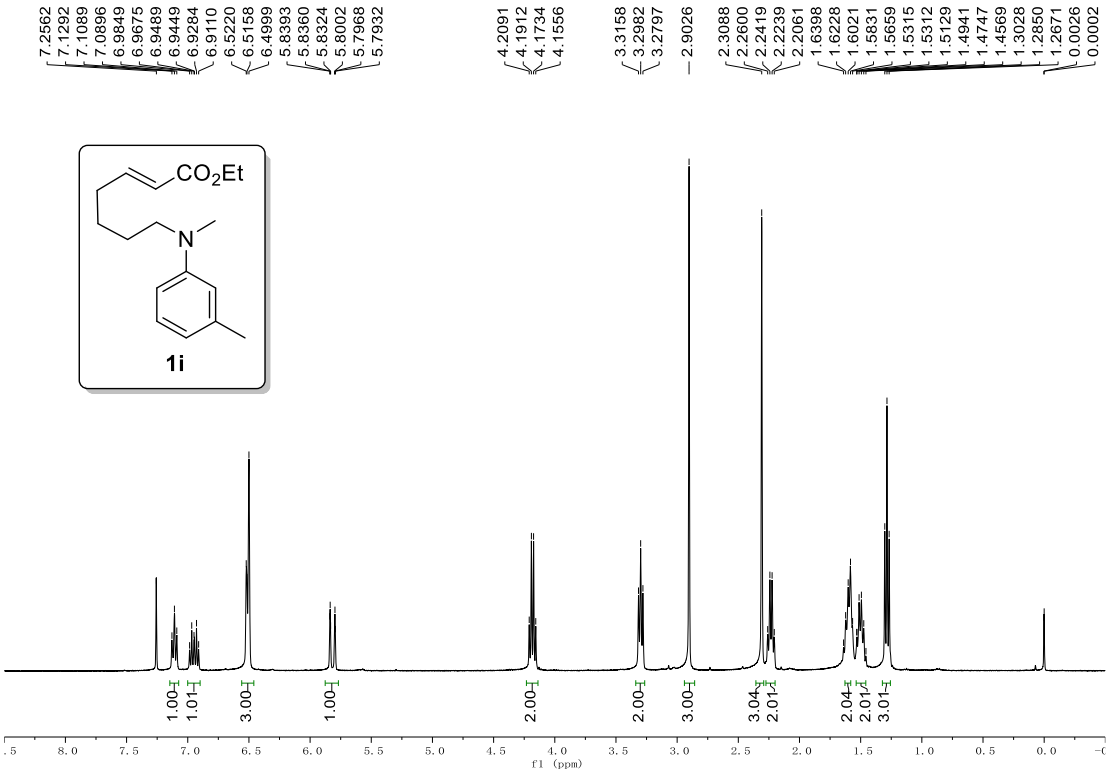
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1h



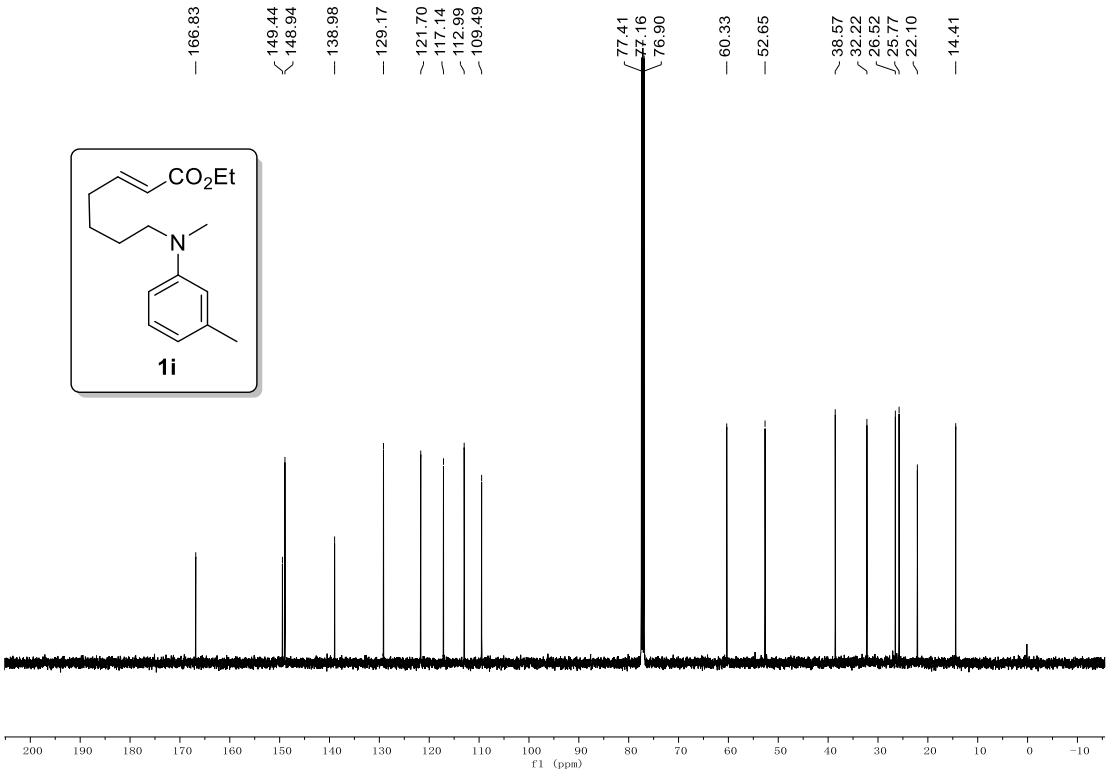
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1h



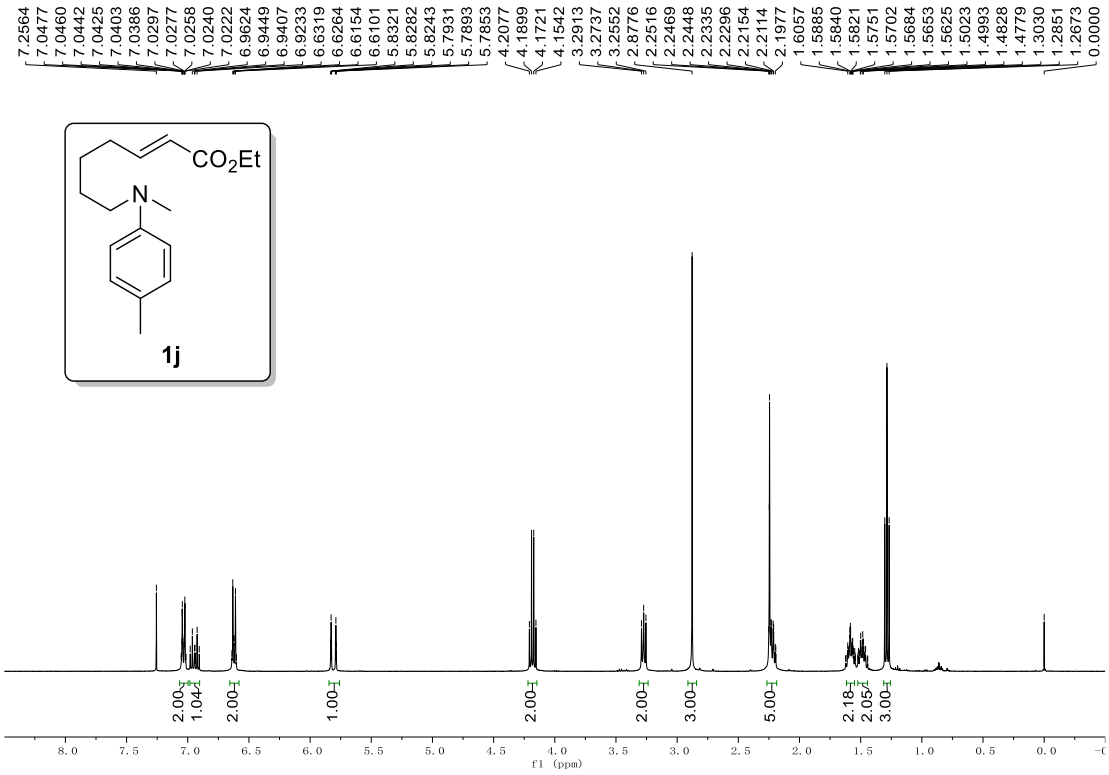
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1i



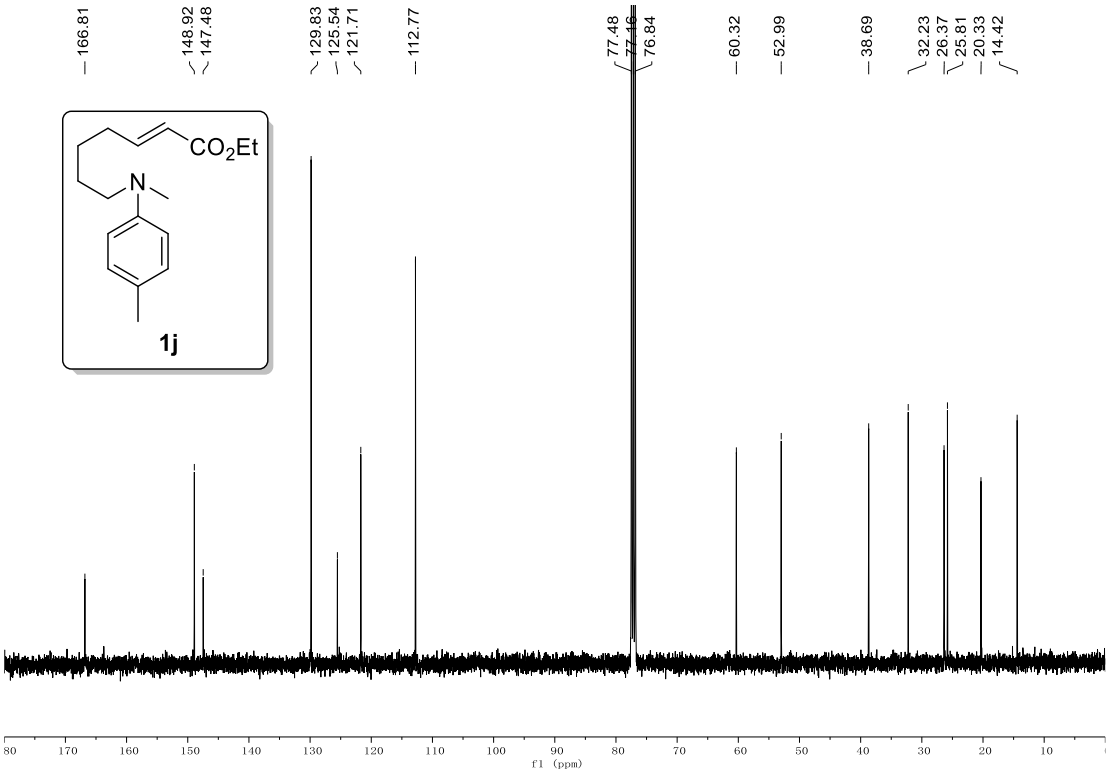
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1i



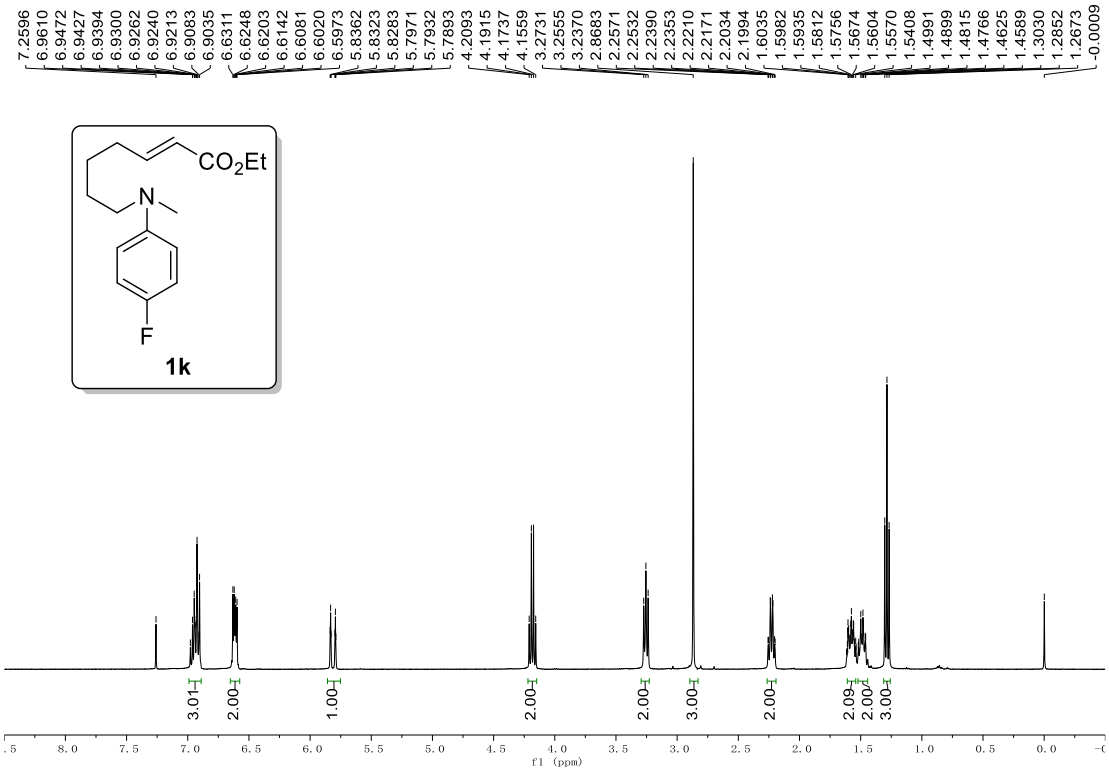
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1j



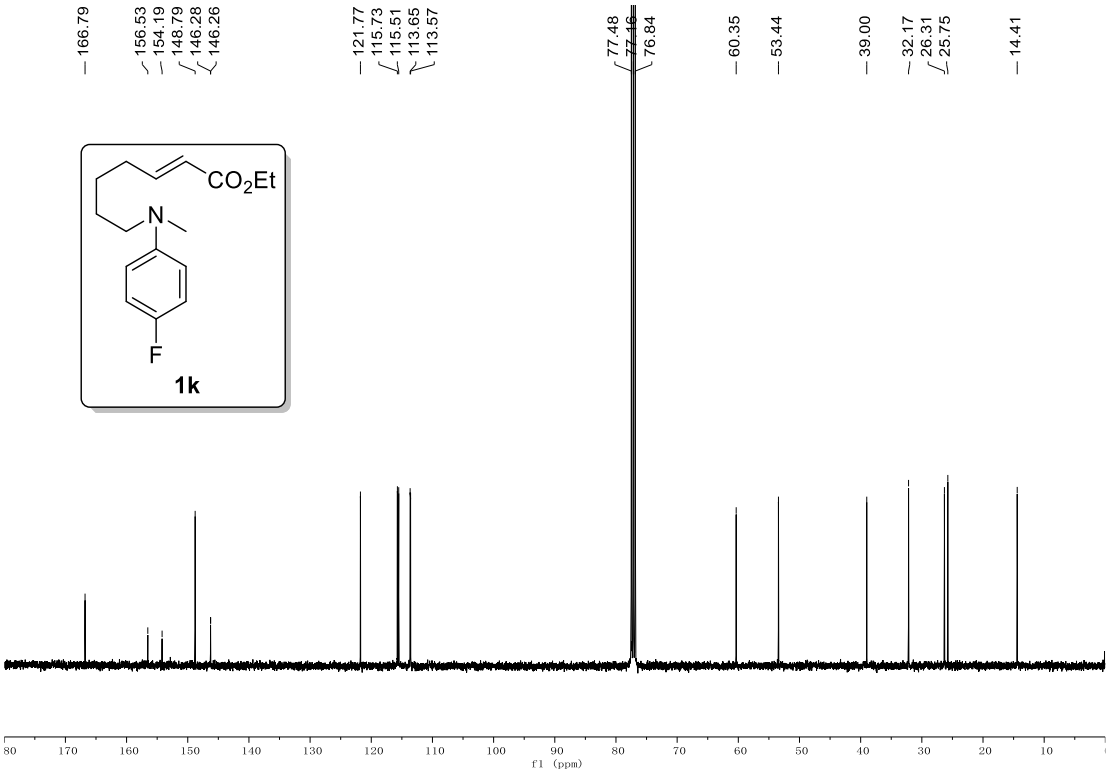
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1j



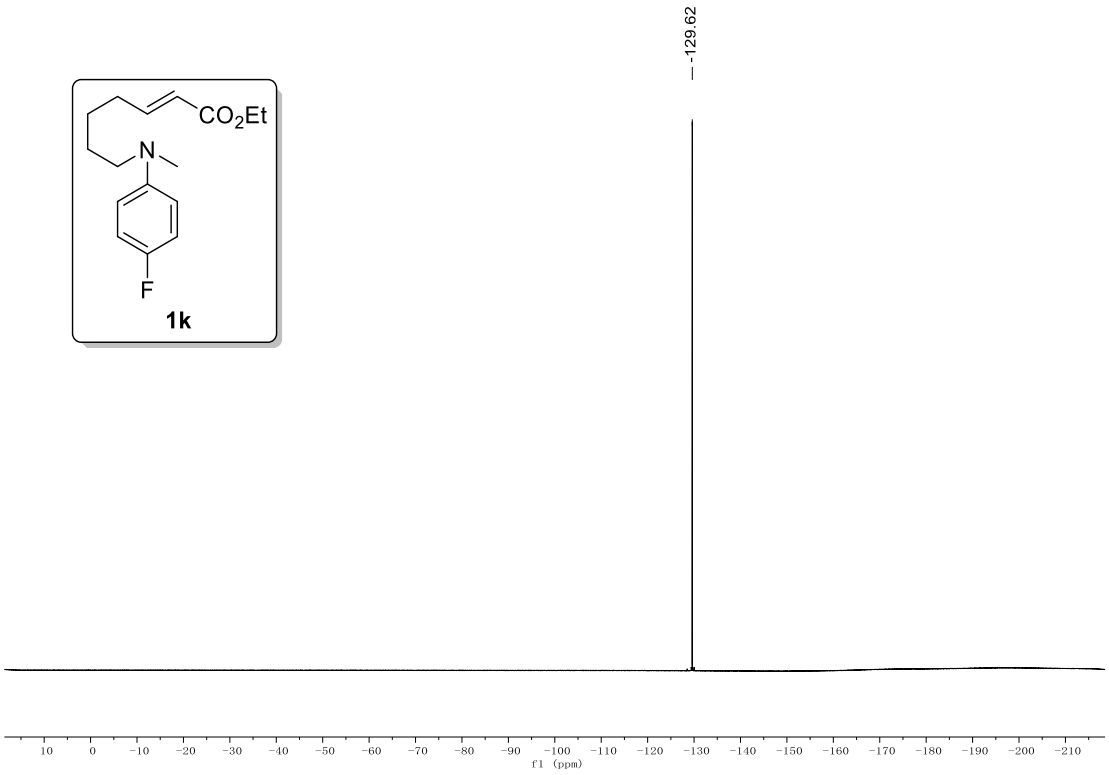
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1k



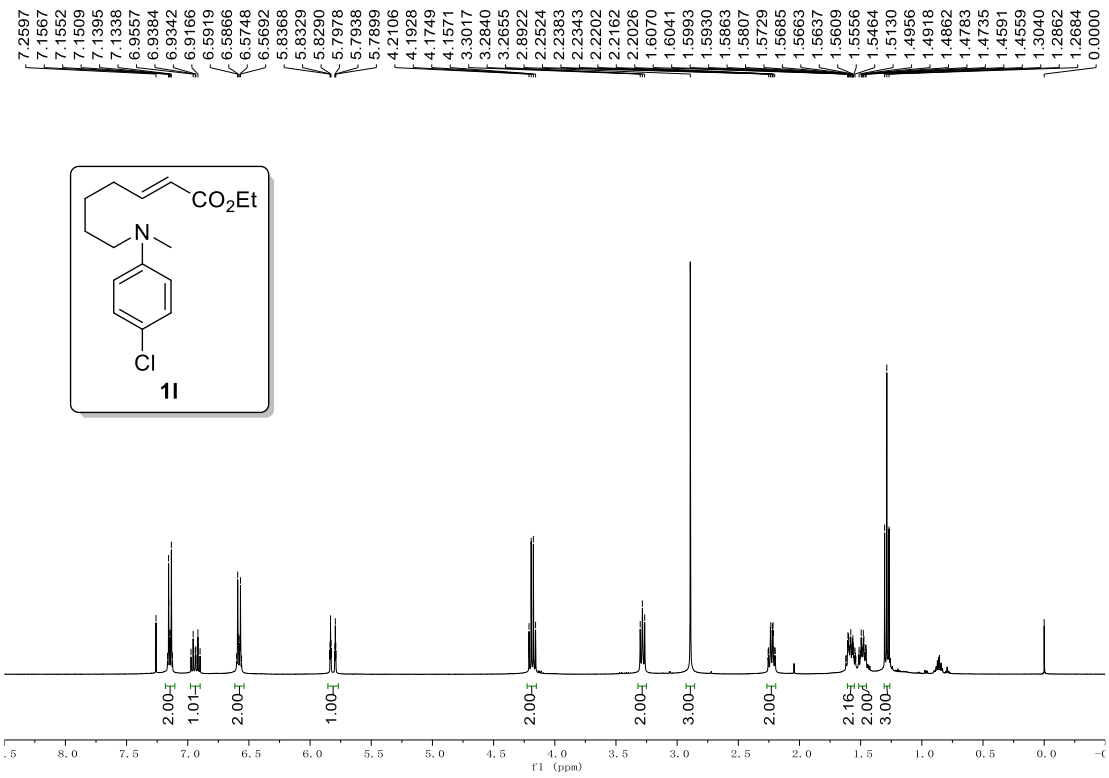
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1k



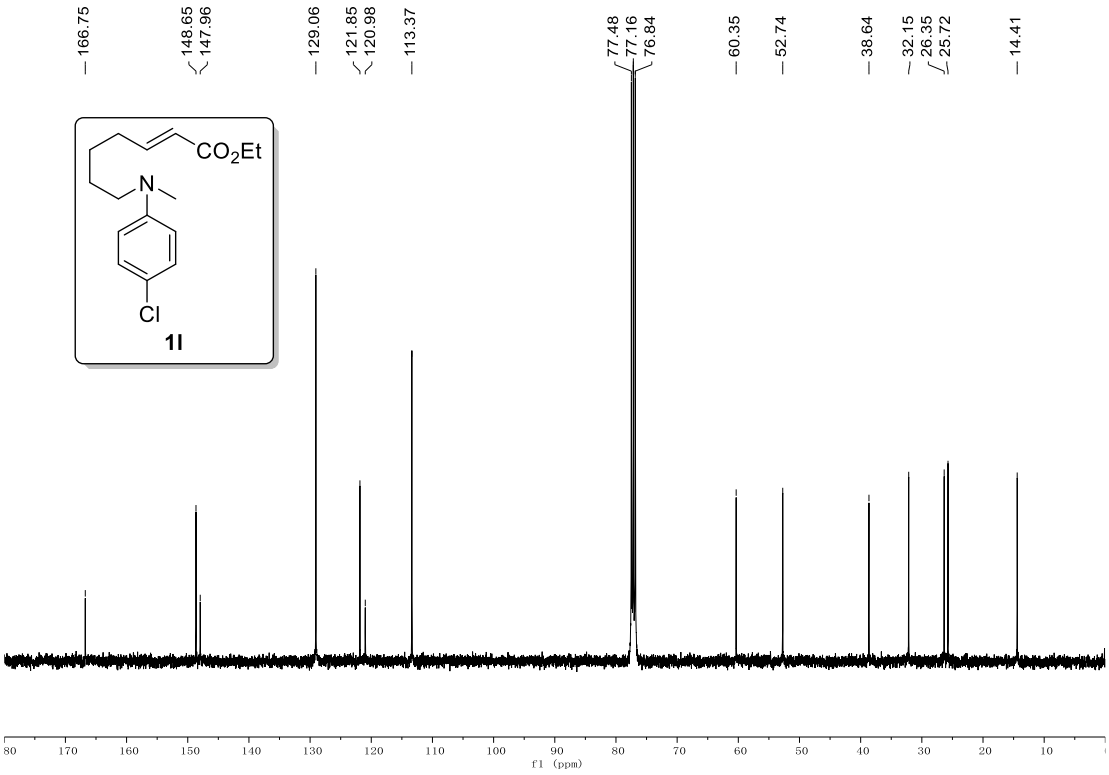
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1k



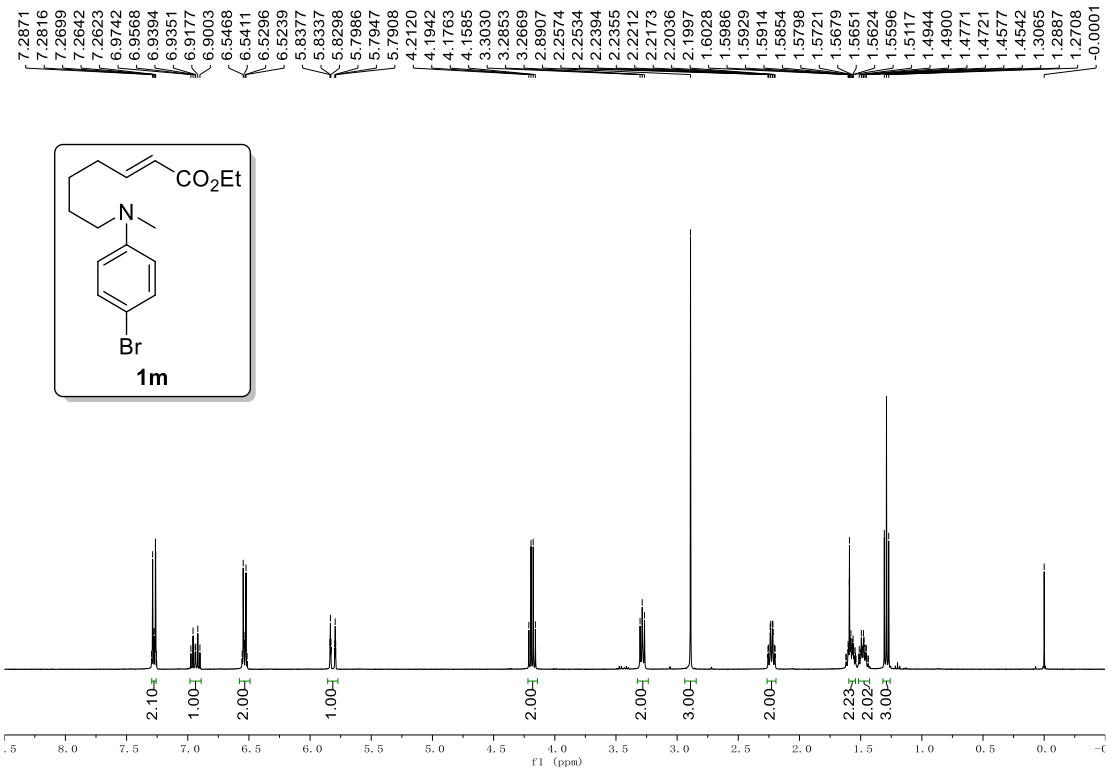
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1l



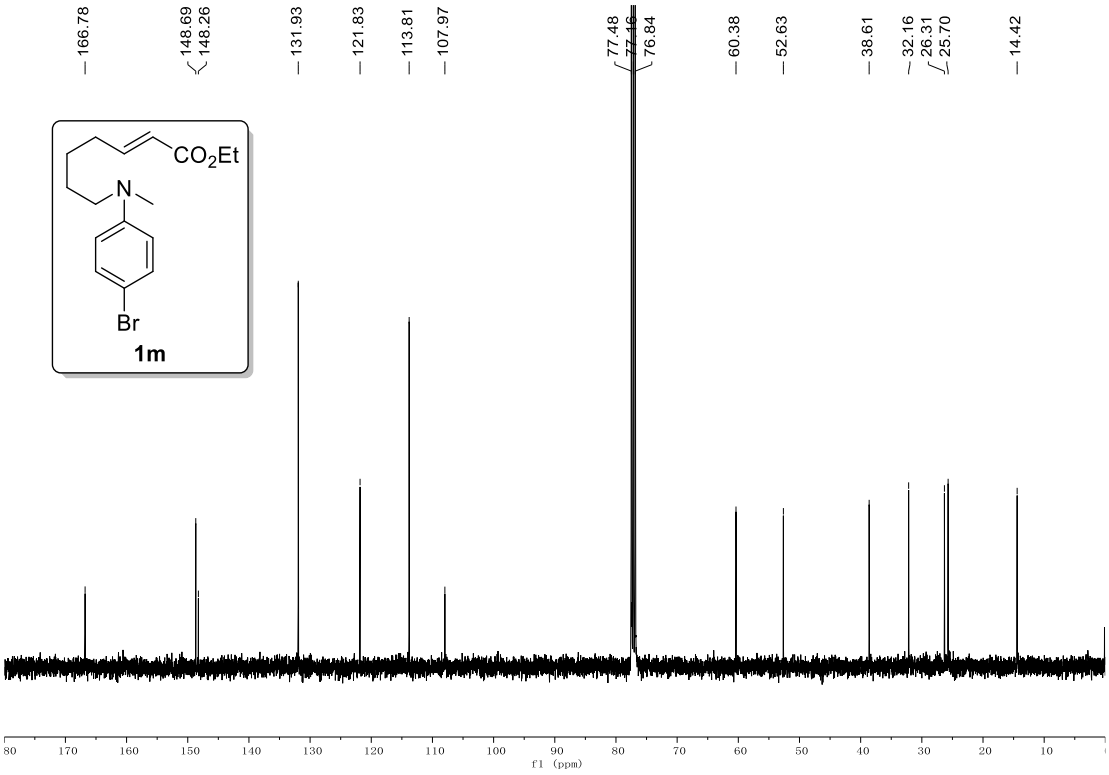
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1l



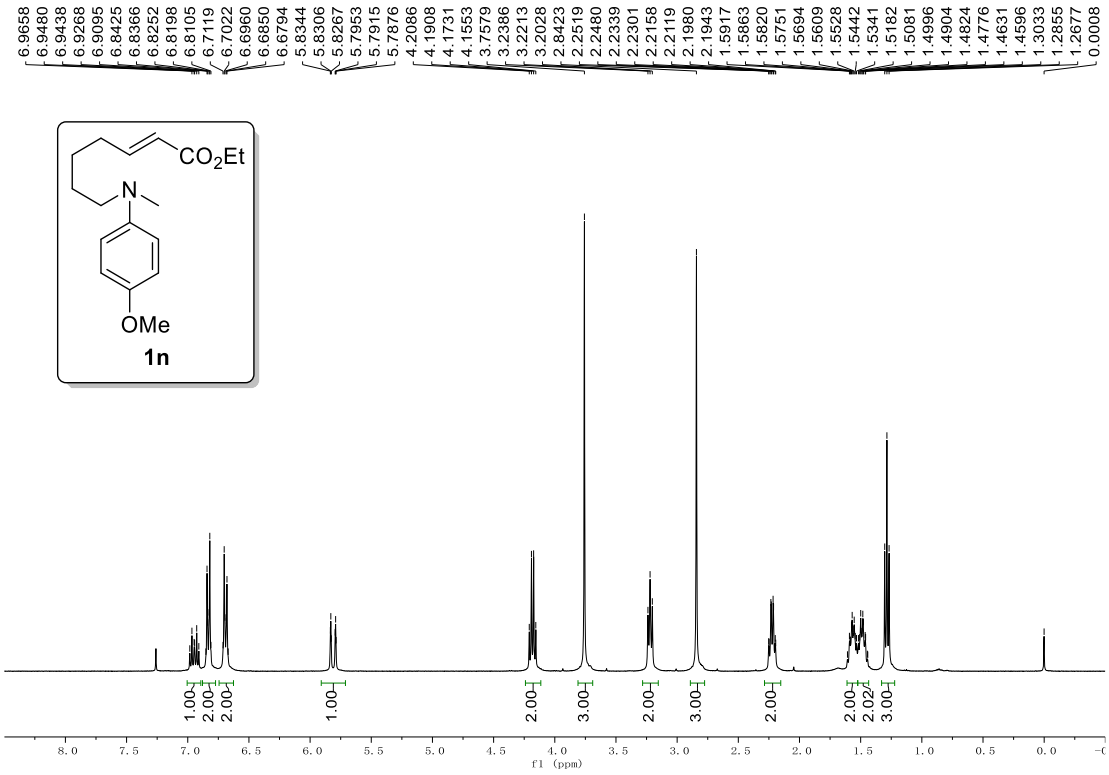
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1m



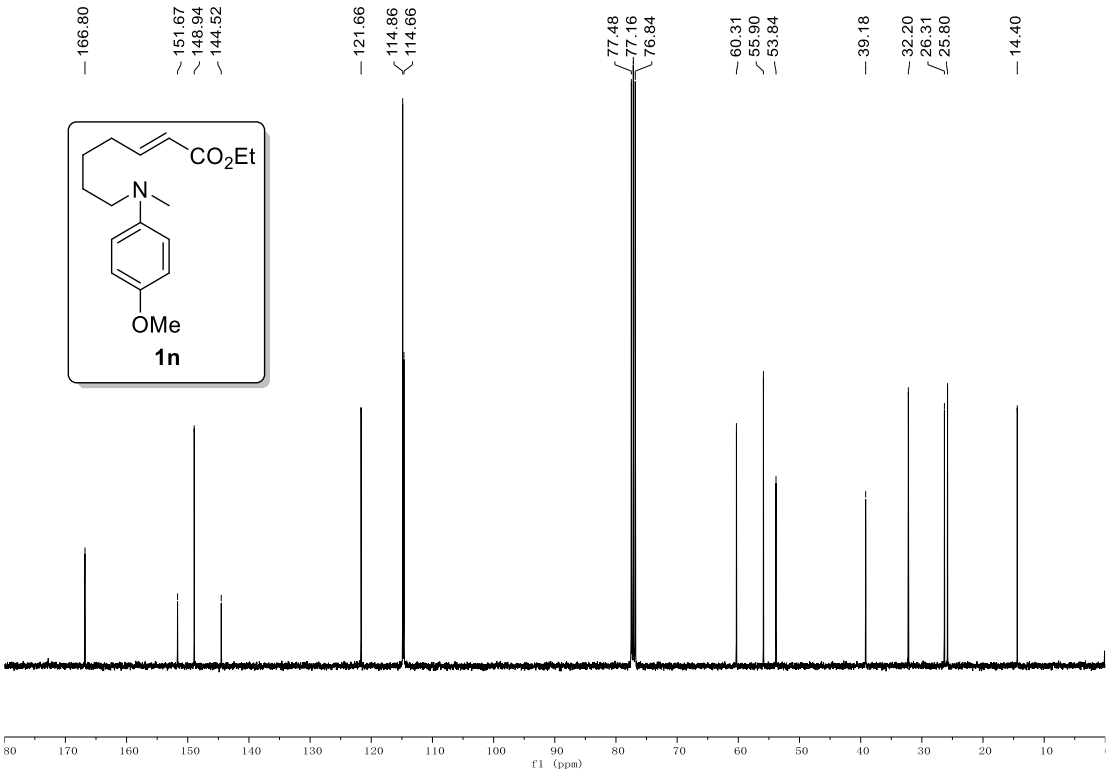
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1m



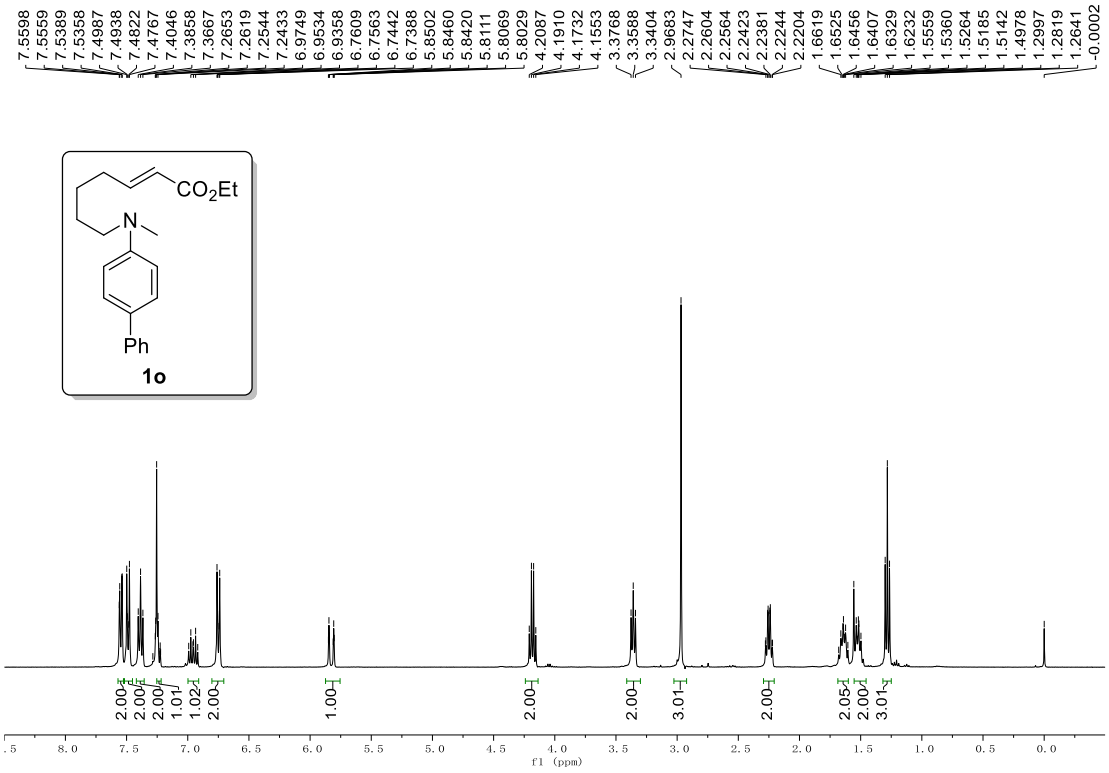
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1n



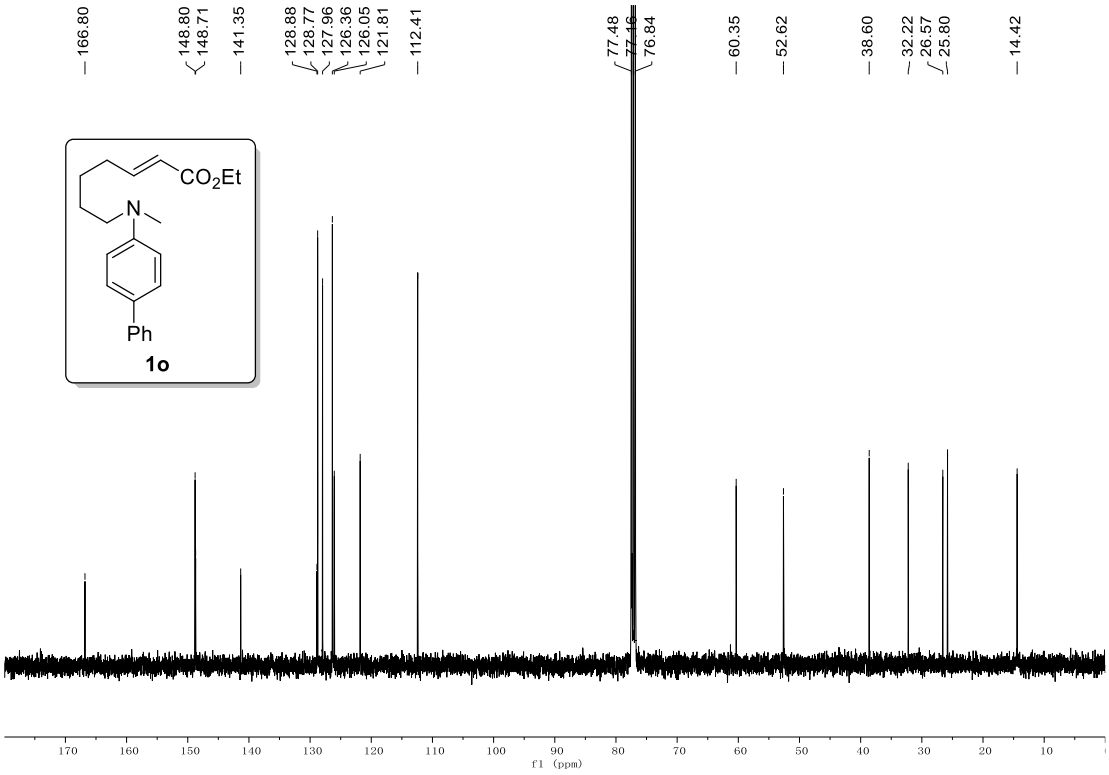
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1n



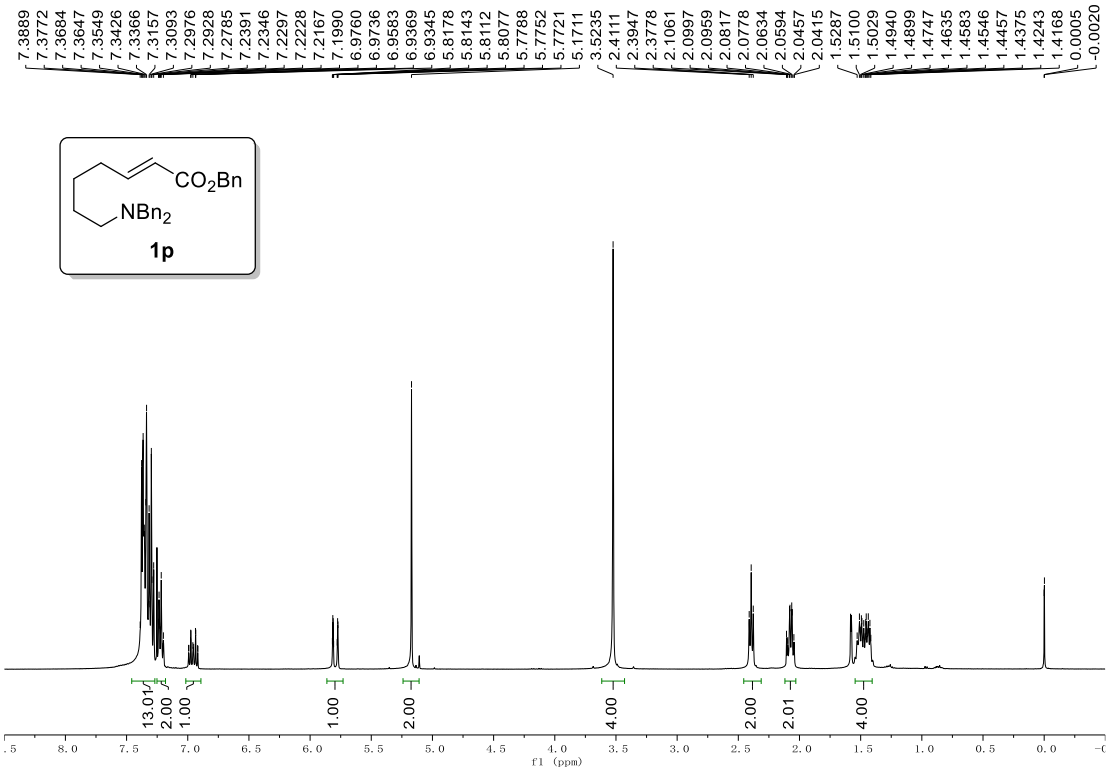
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1o



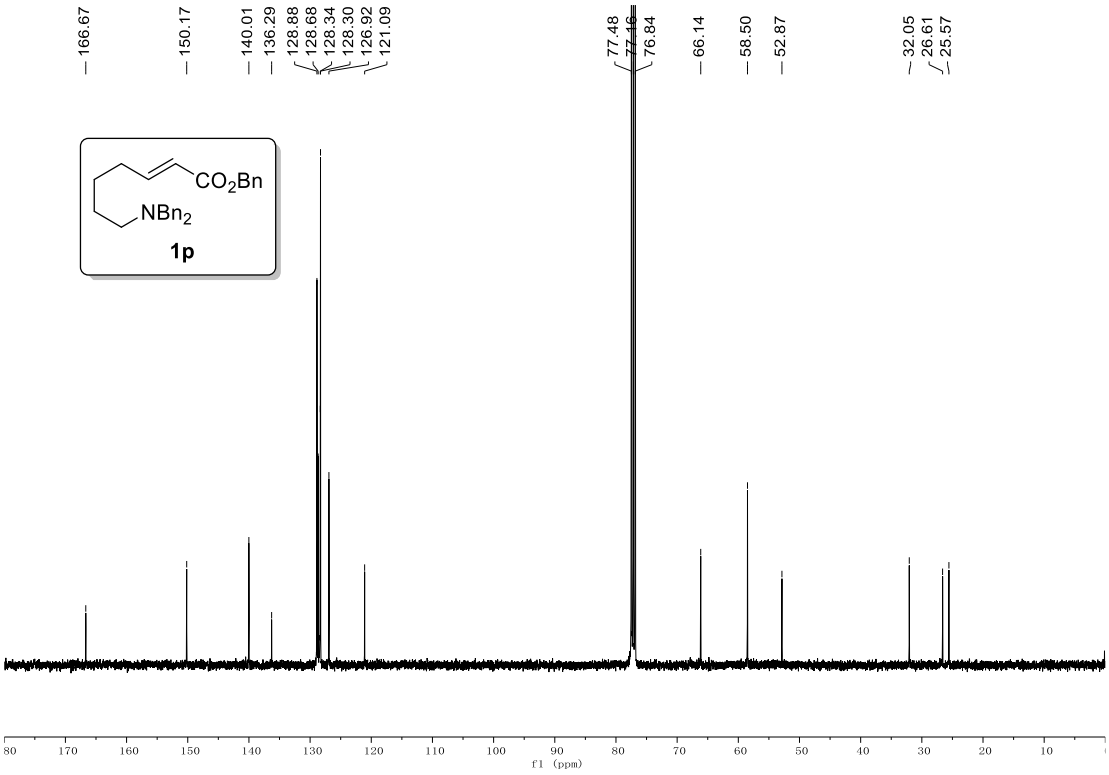
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1o



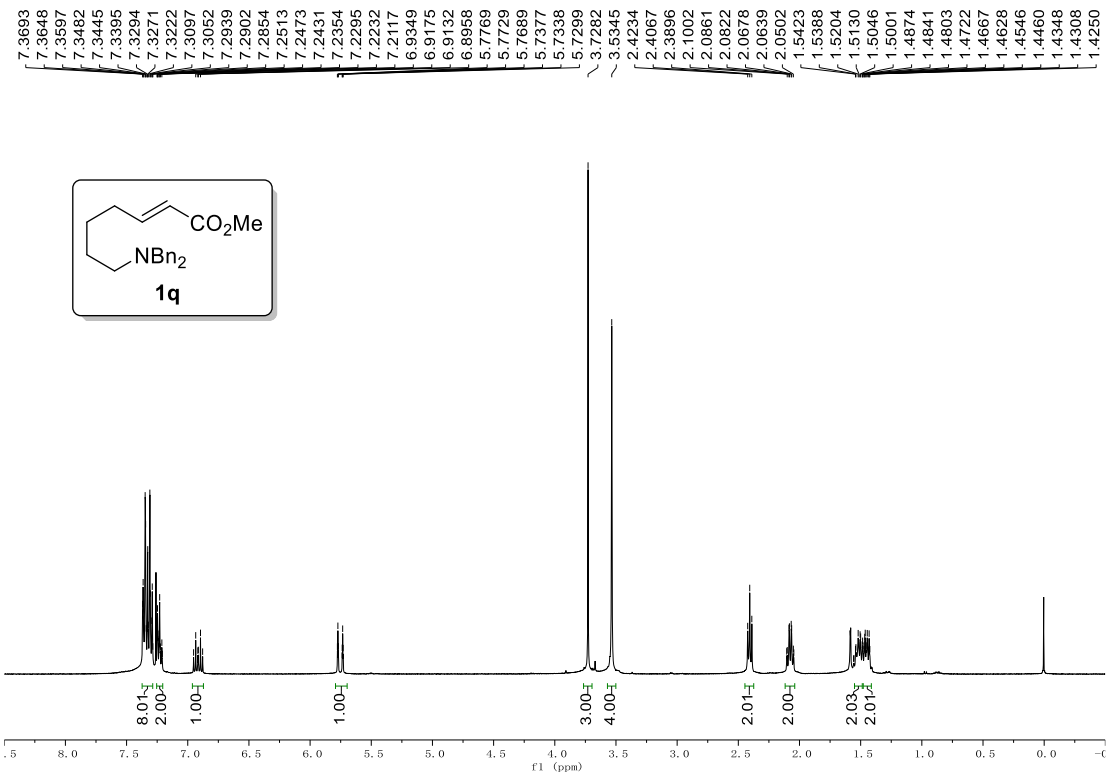
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1p



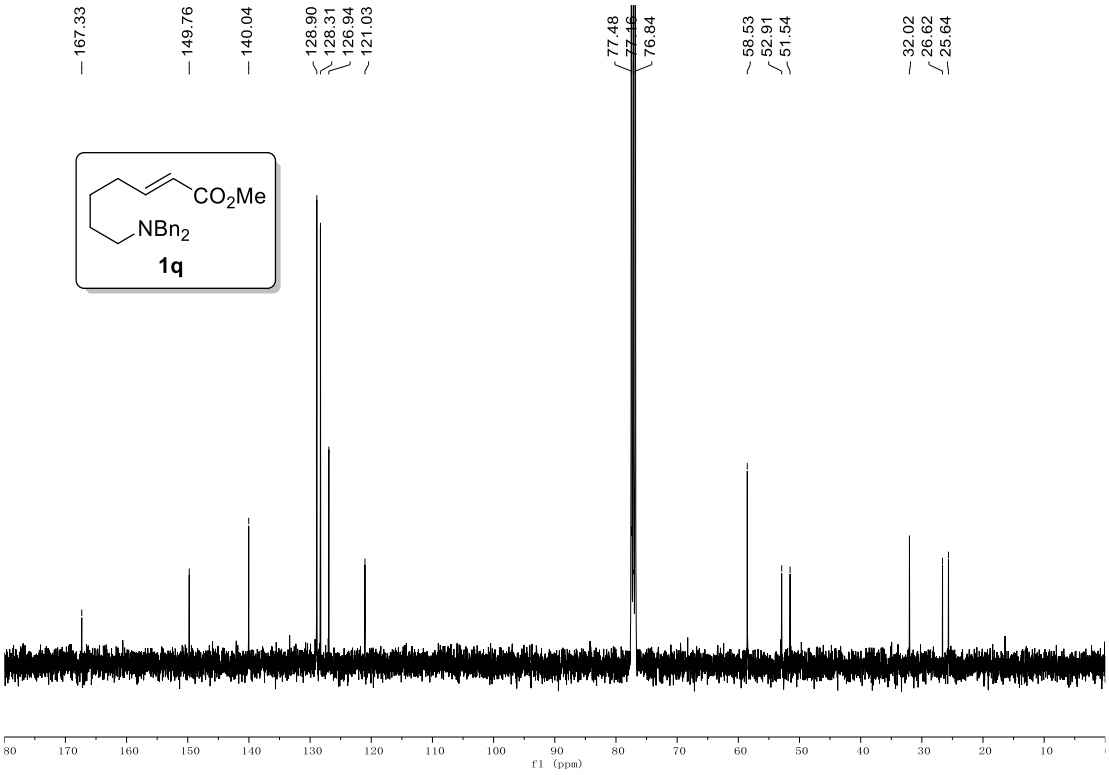
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1p



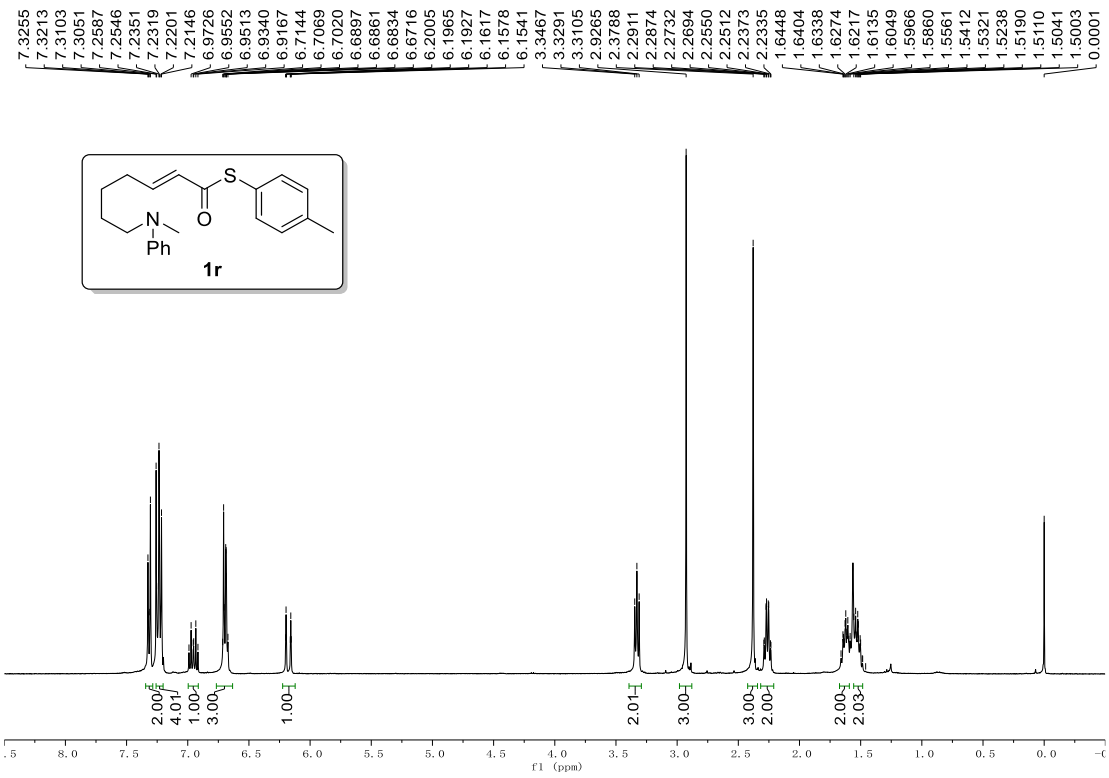
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1q



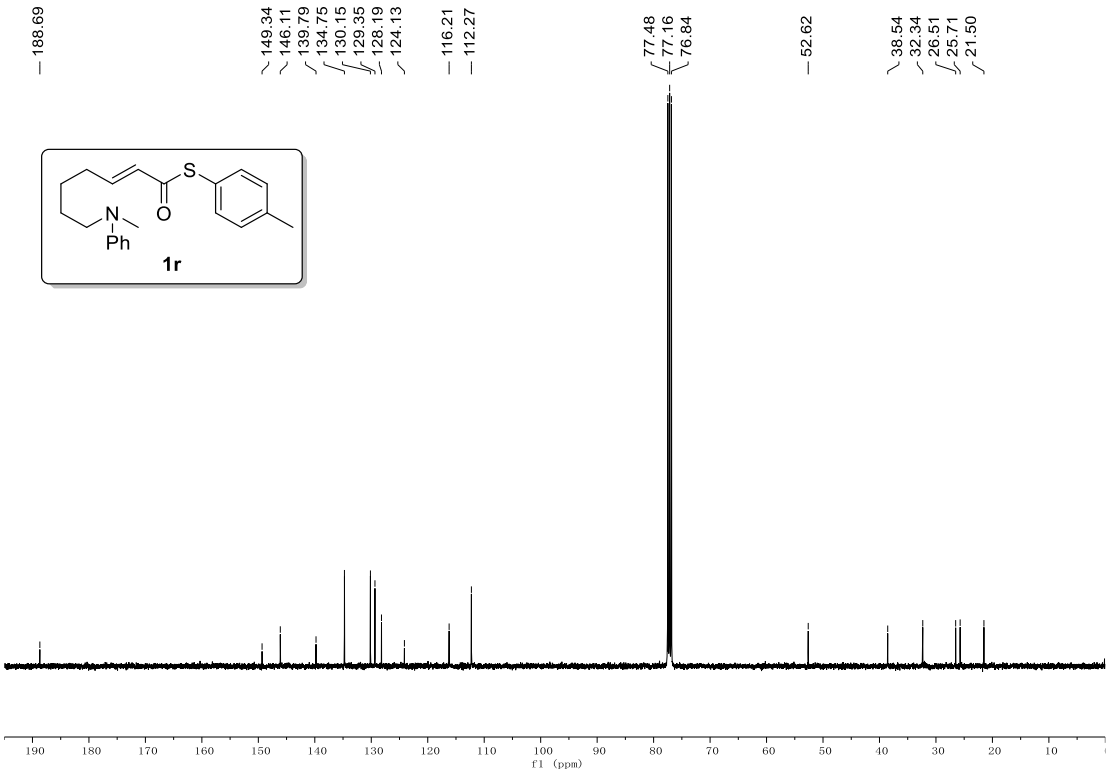
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1q



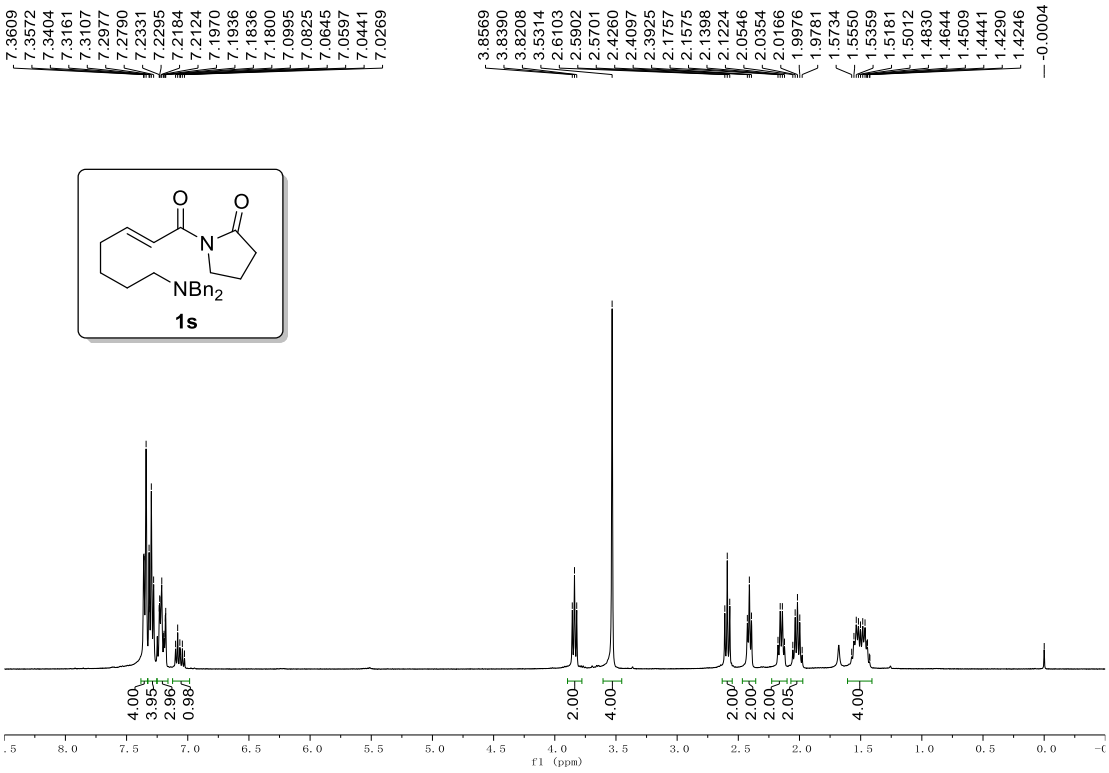
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1r



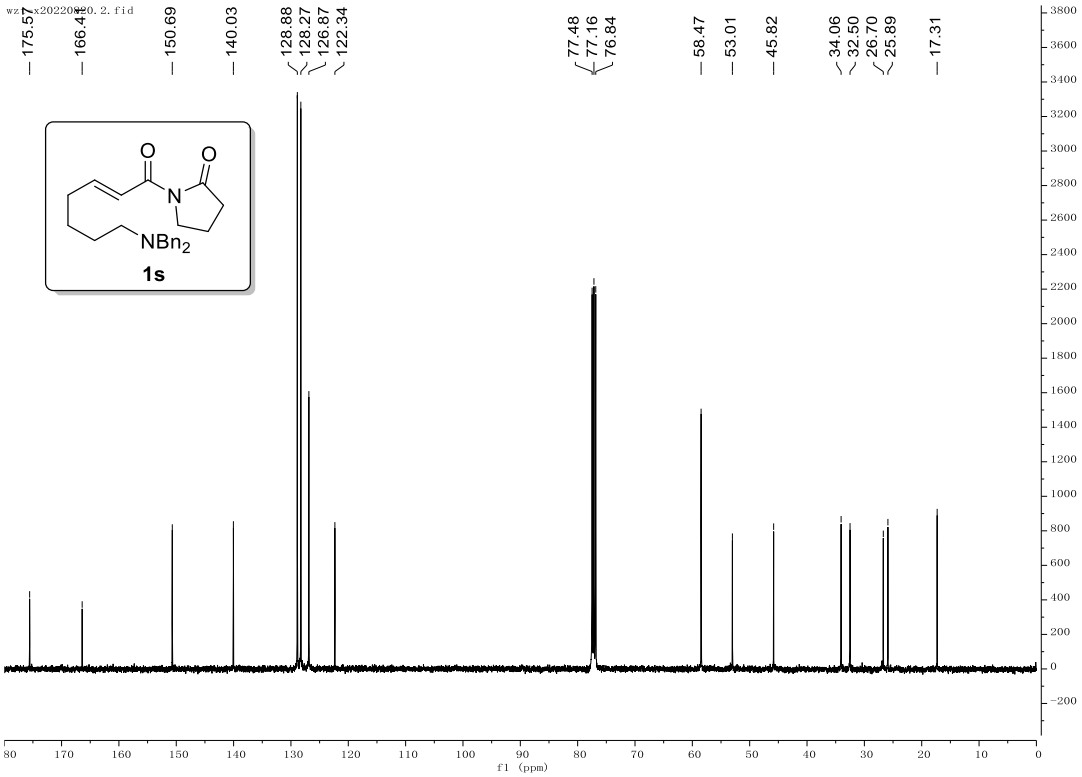
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1r



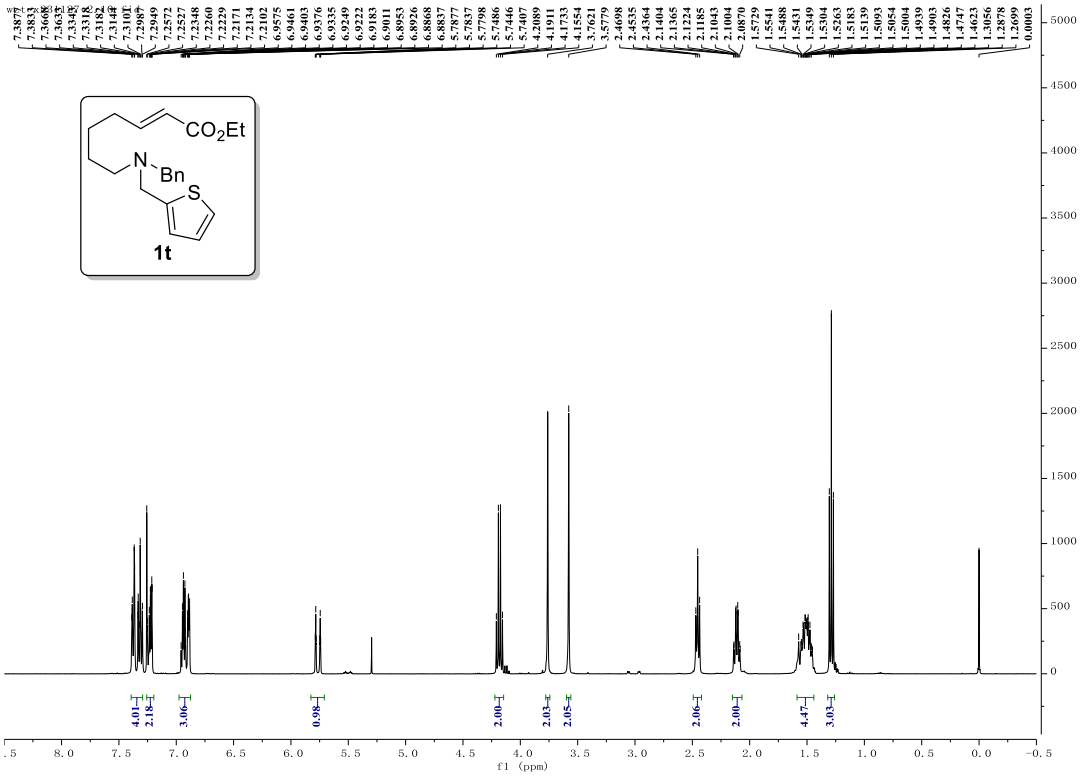
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1s



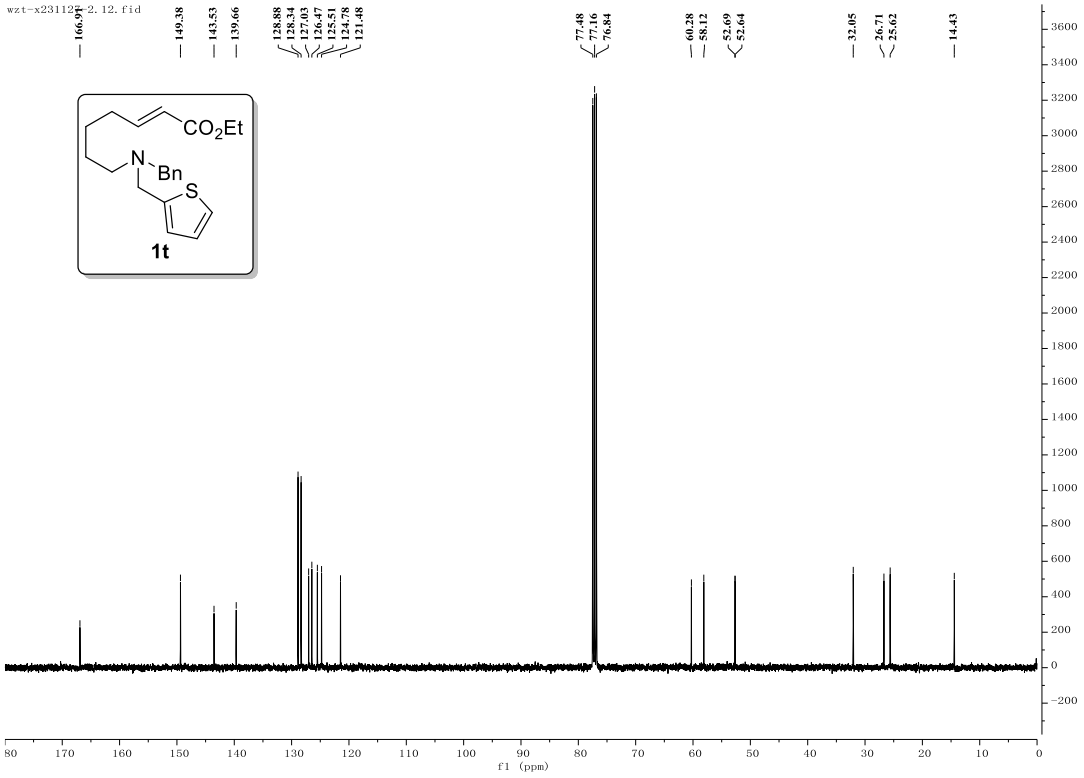
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1s



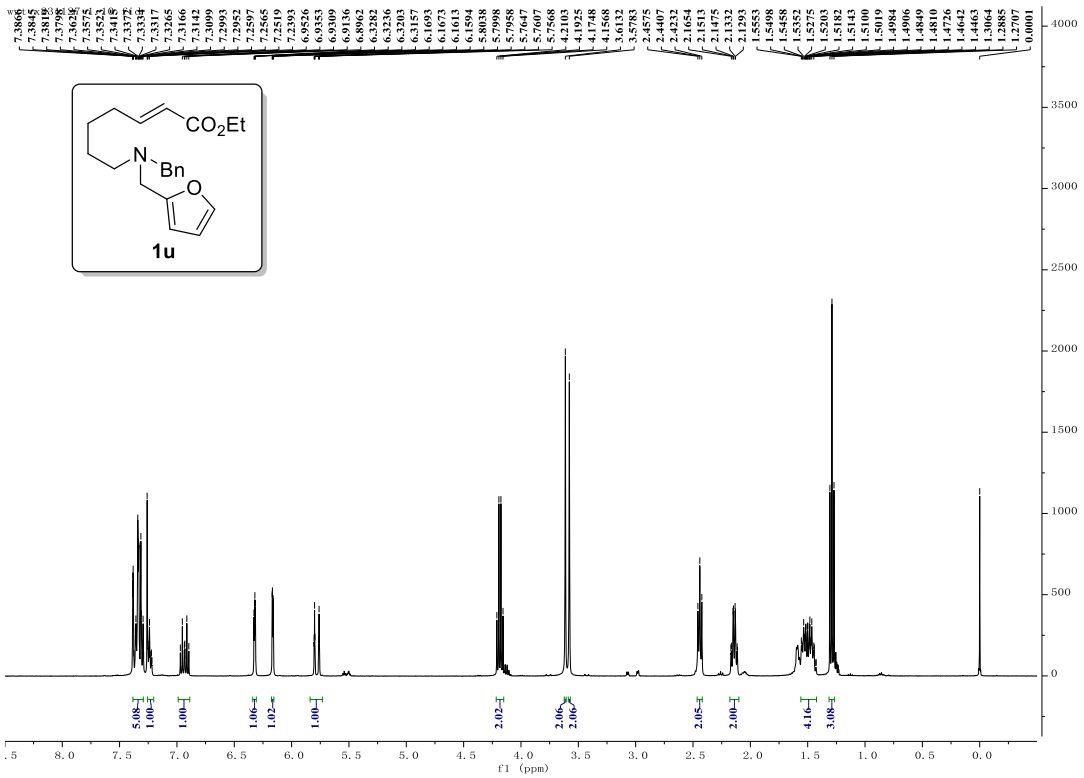
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1t



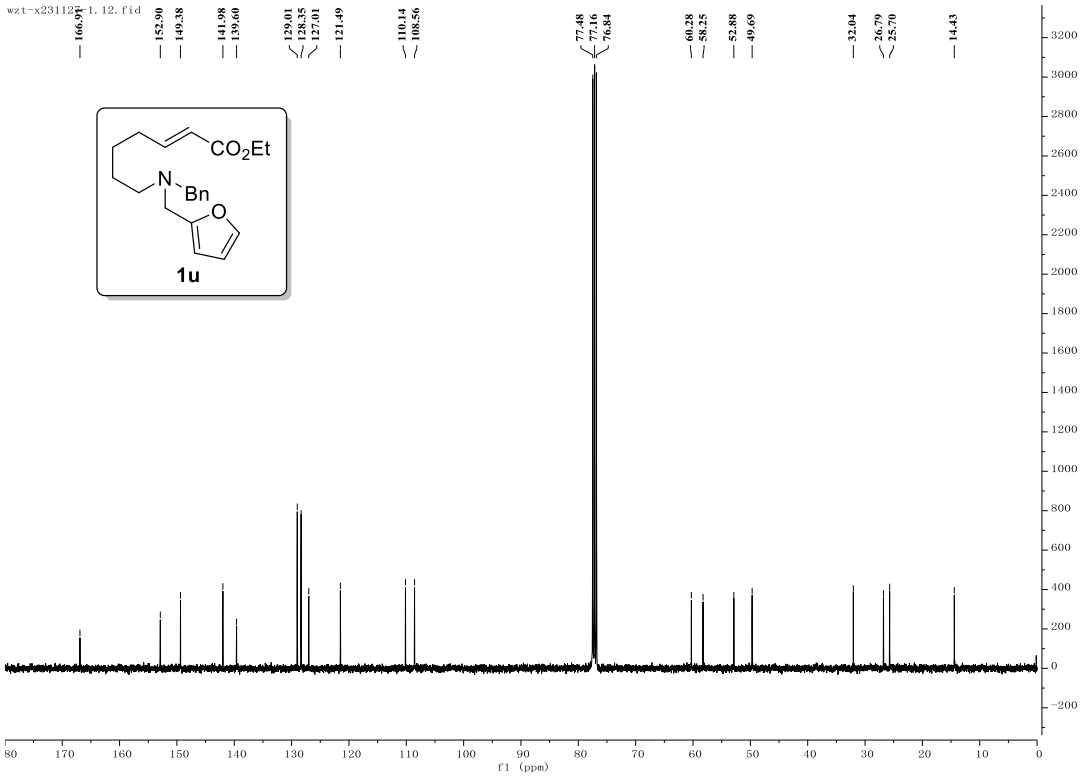
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1t



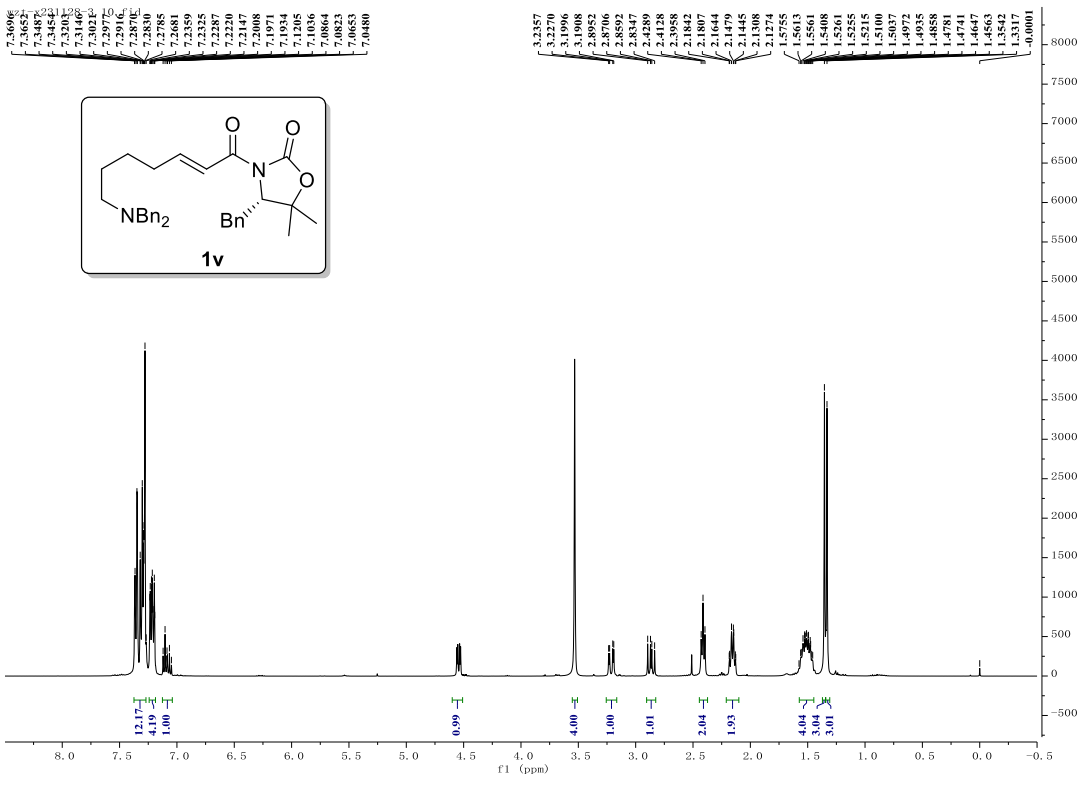
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1u



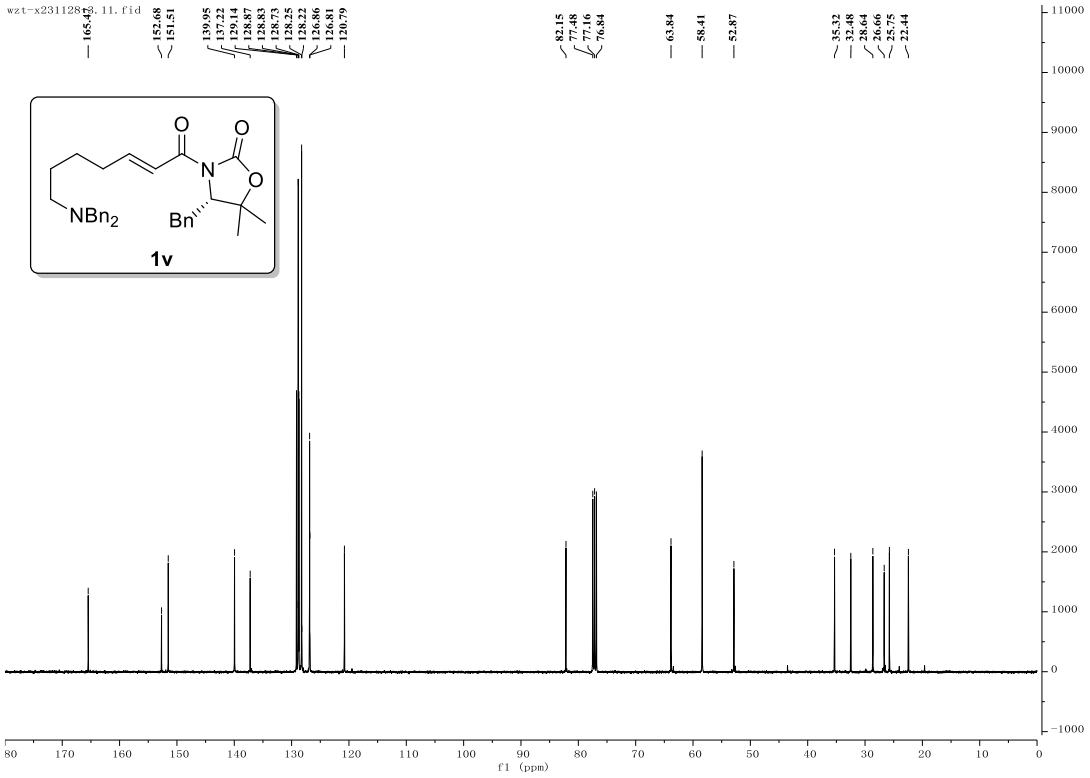
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1u



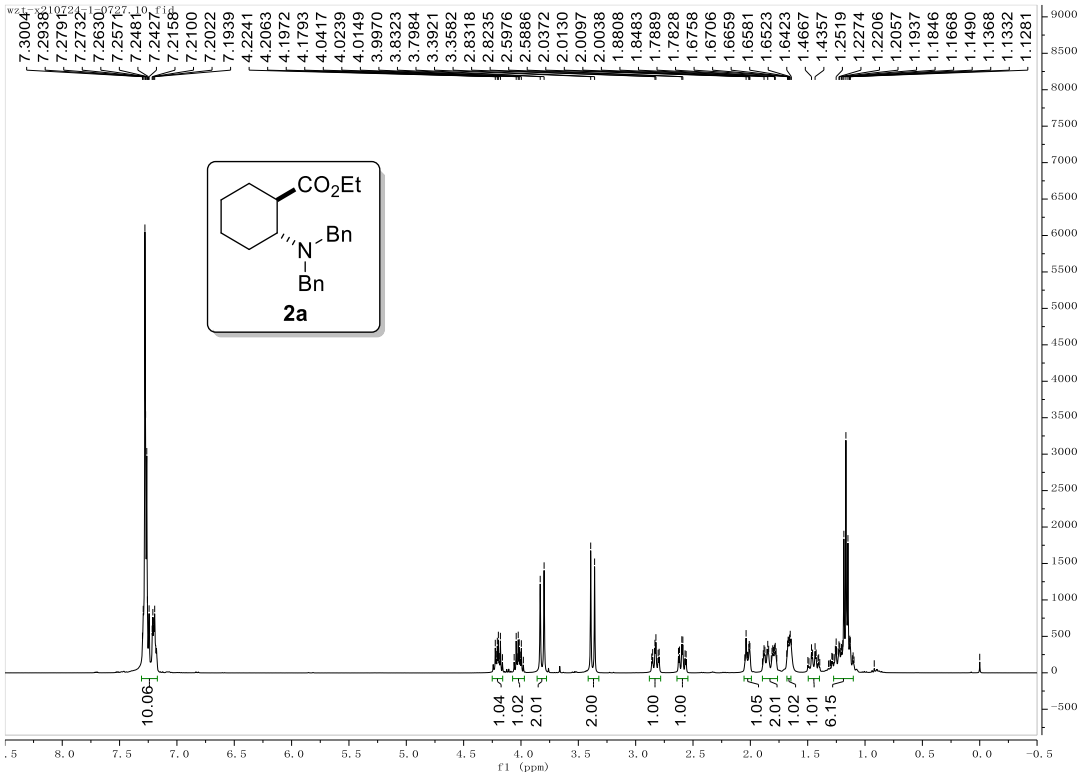
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1v



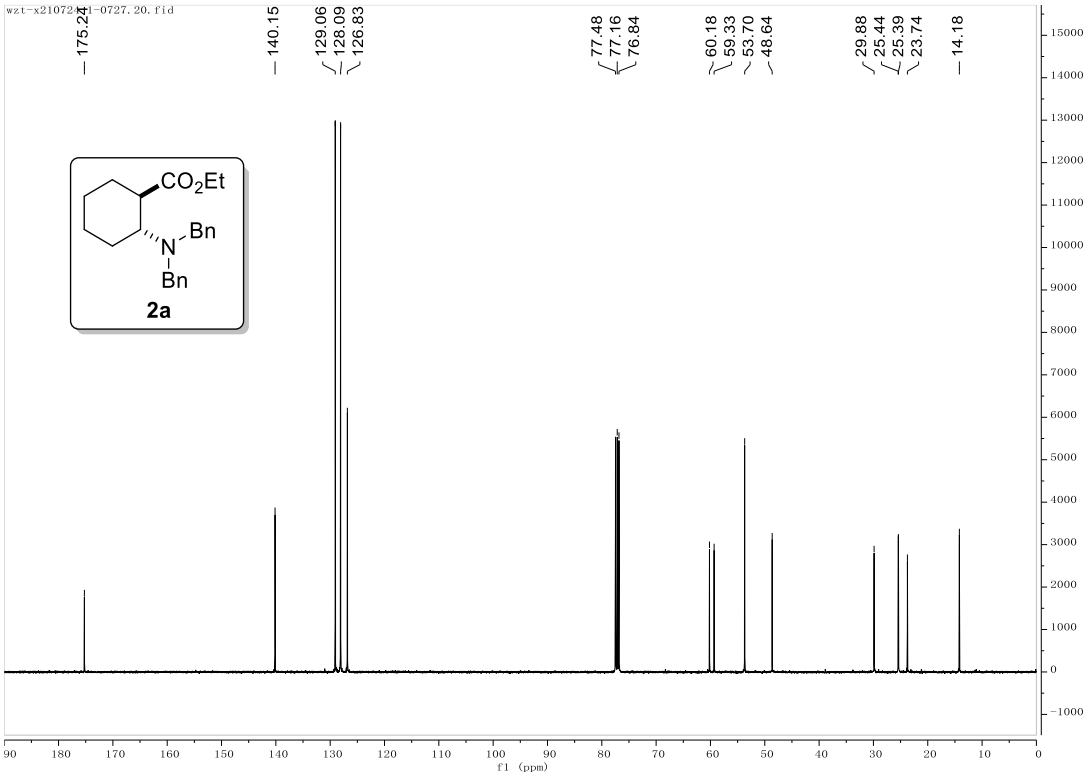
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 1v



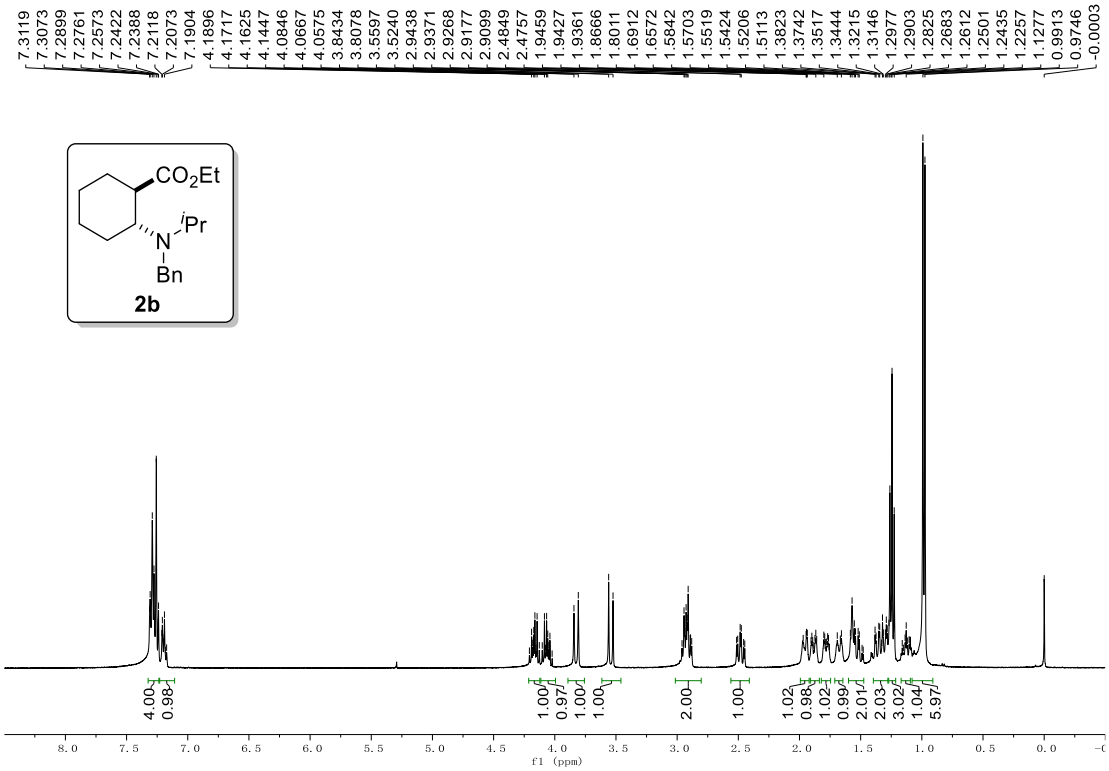
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2a



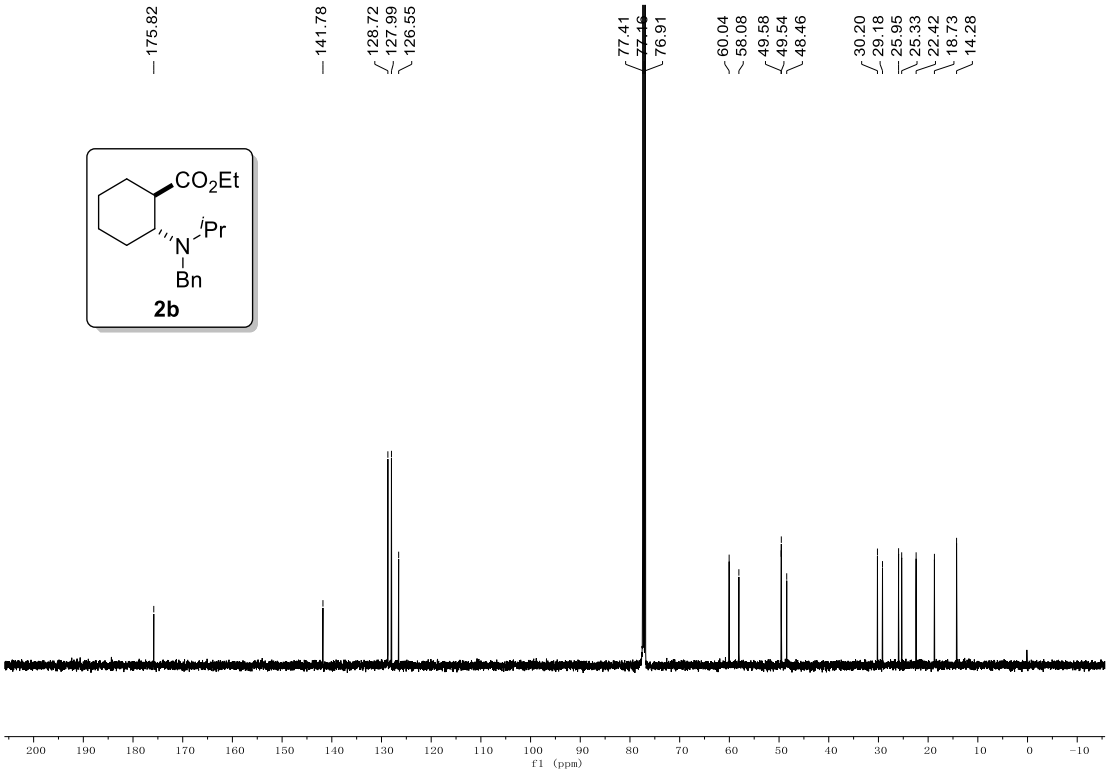
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2a



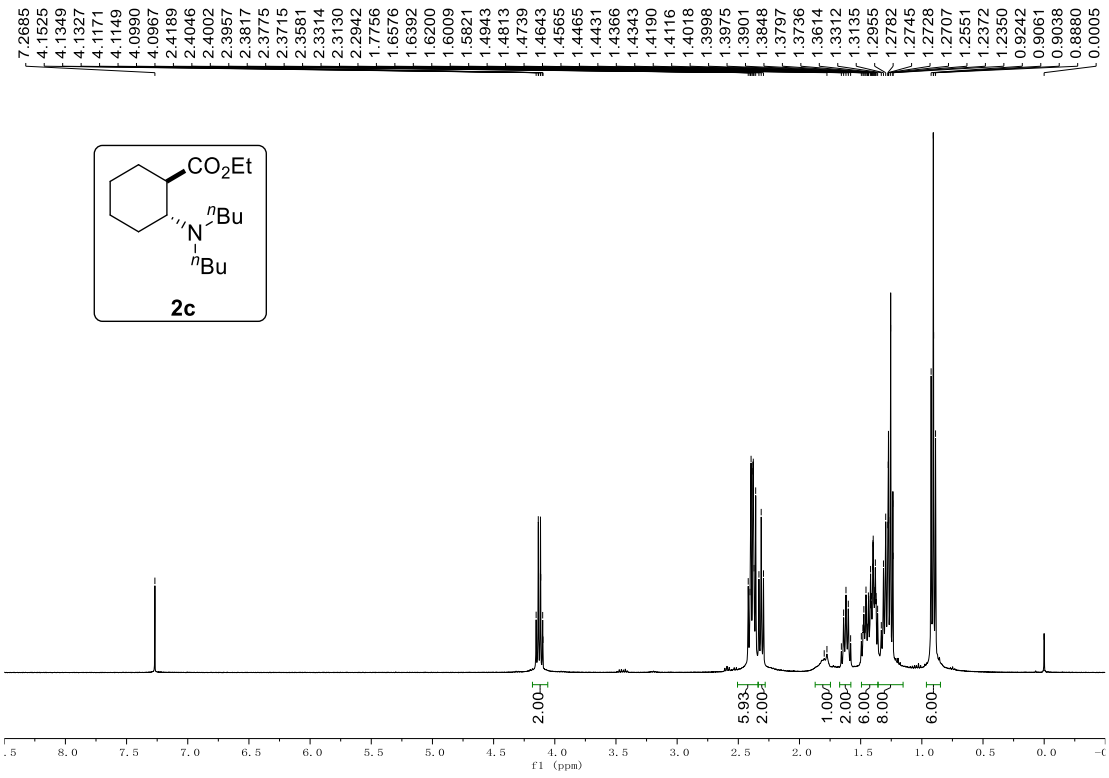
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2b



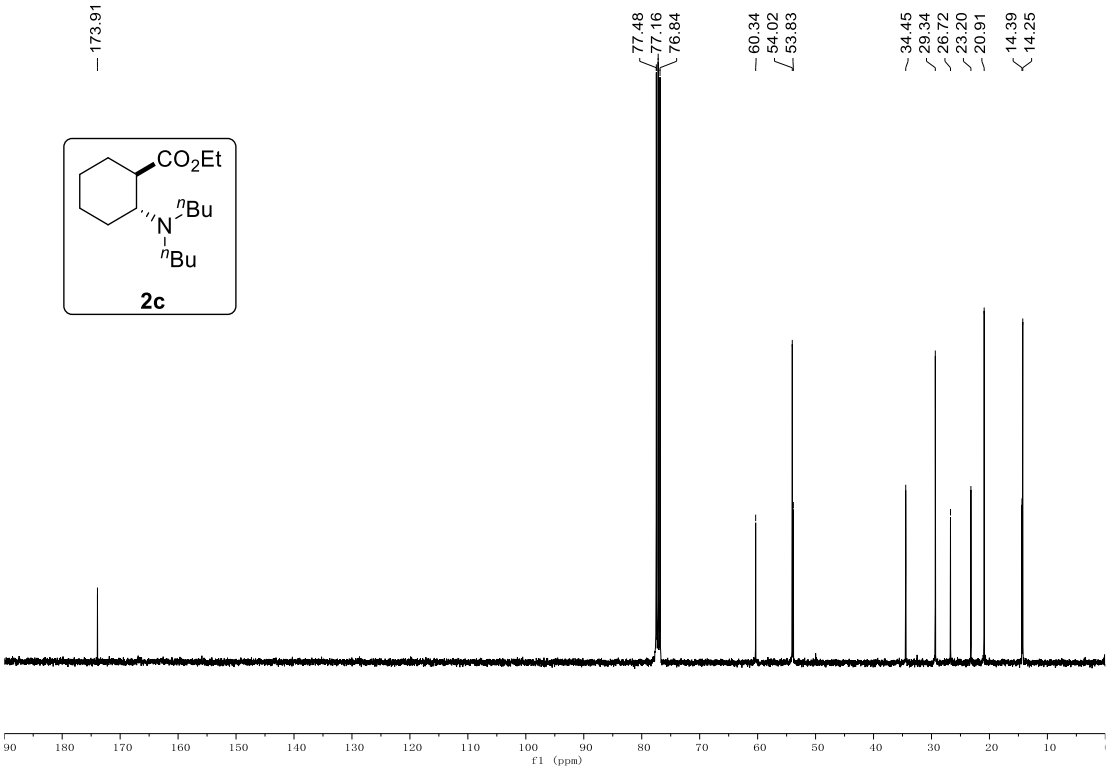
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2b



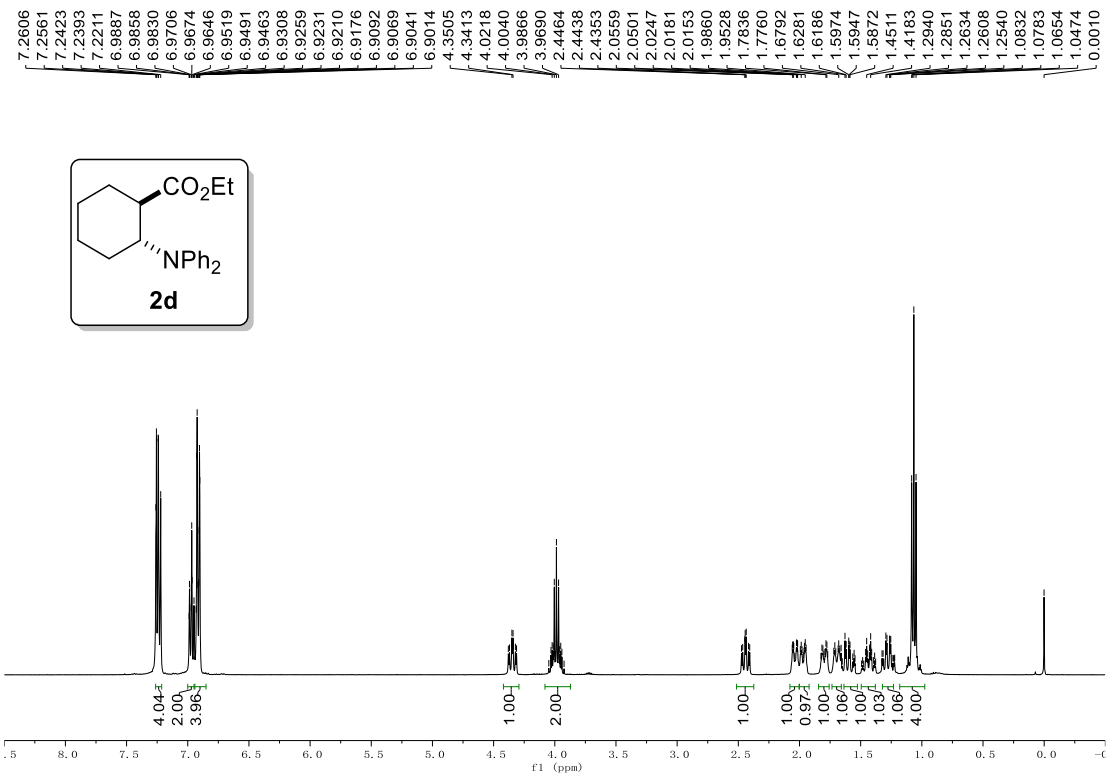
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2c



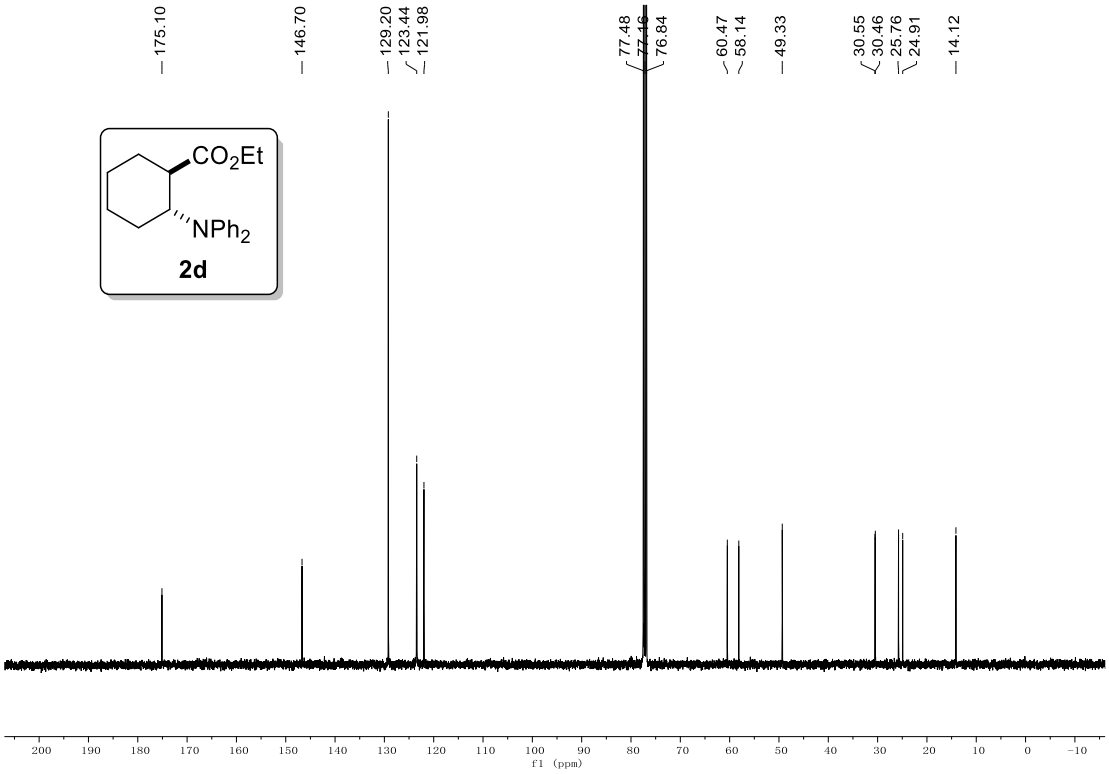
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2c



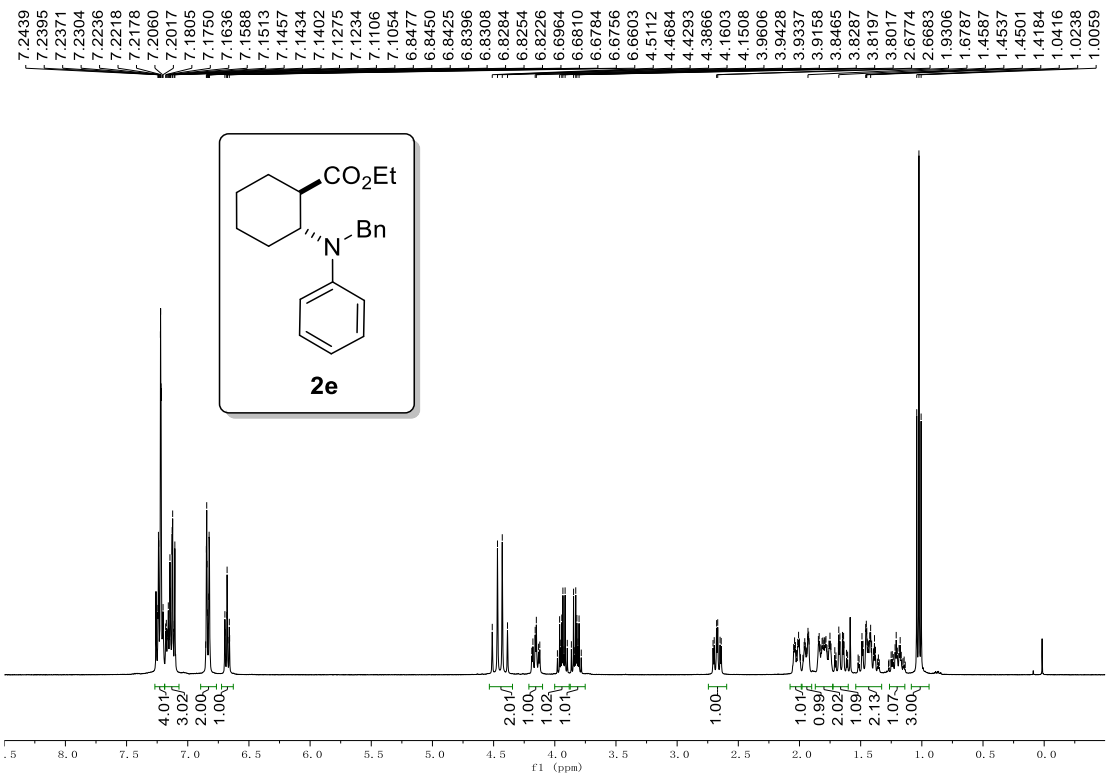
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2d



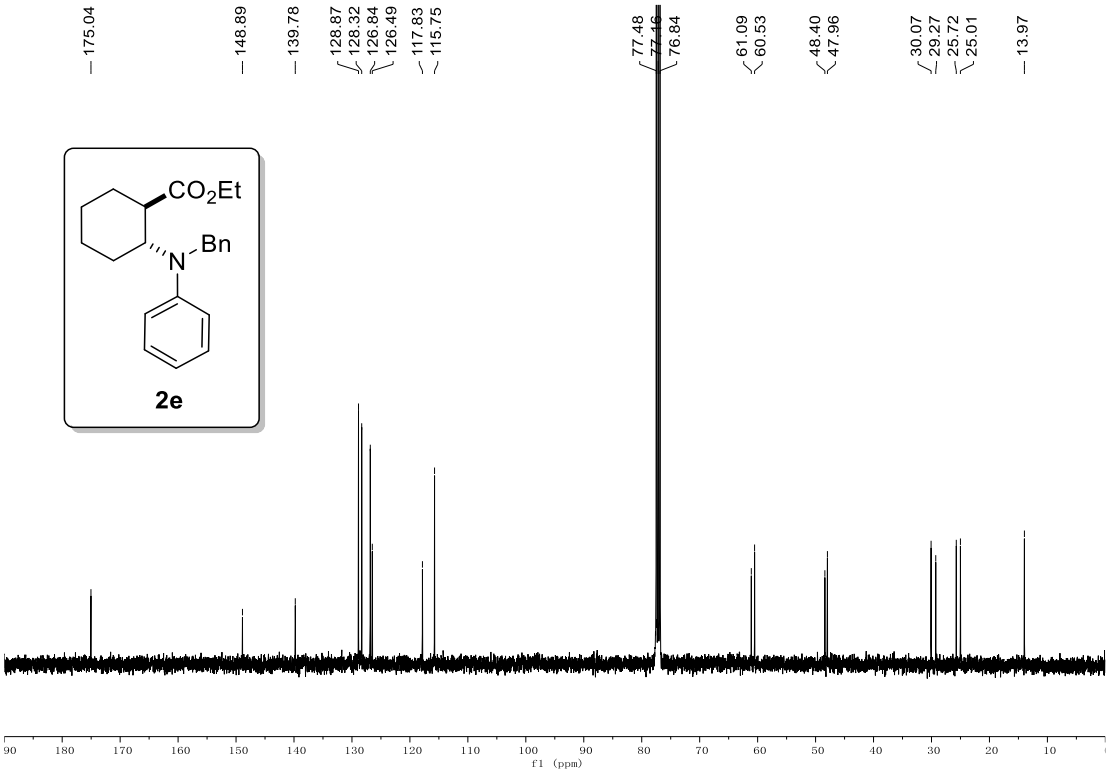
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2d



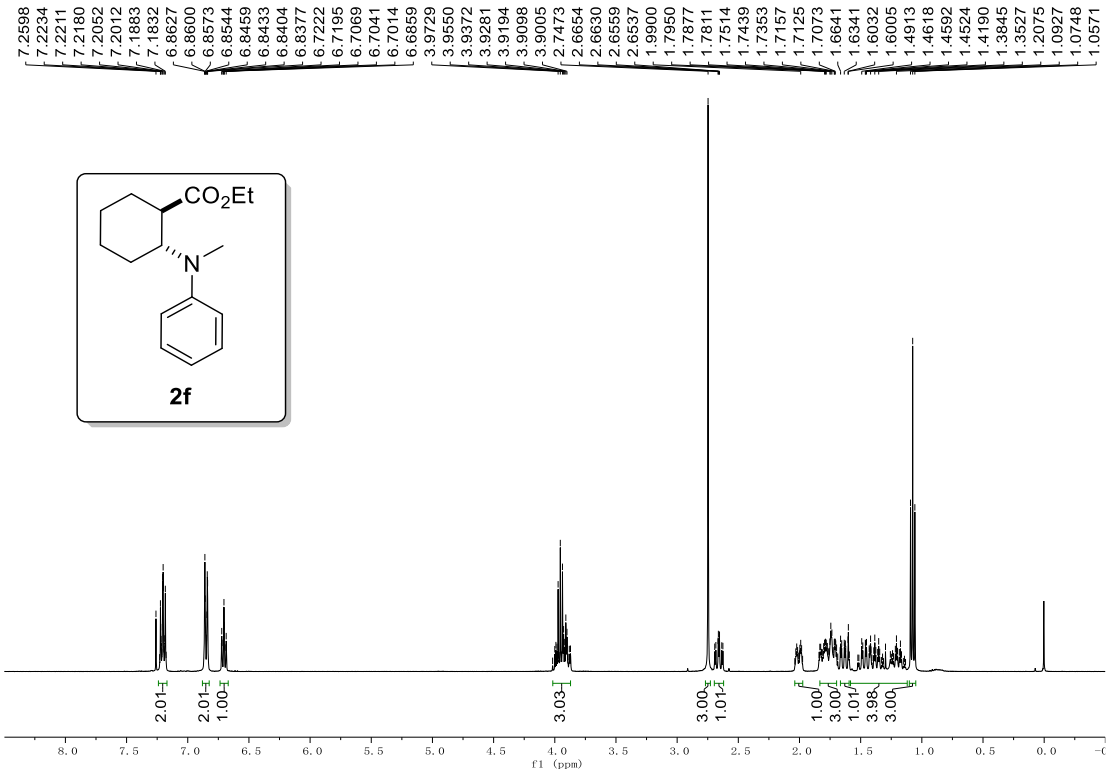
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2e



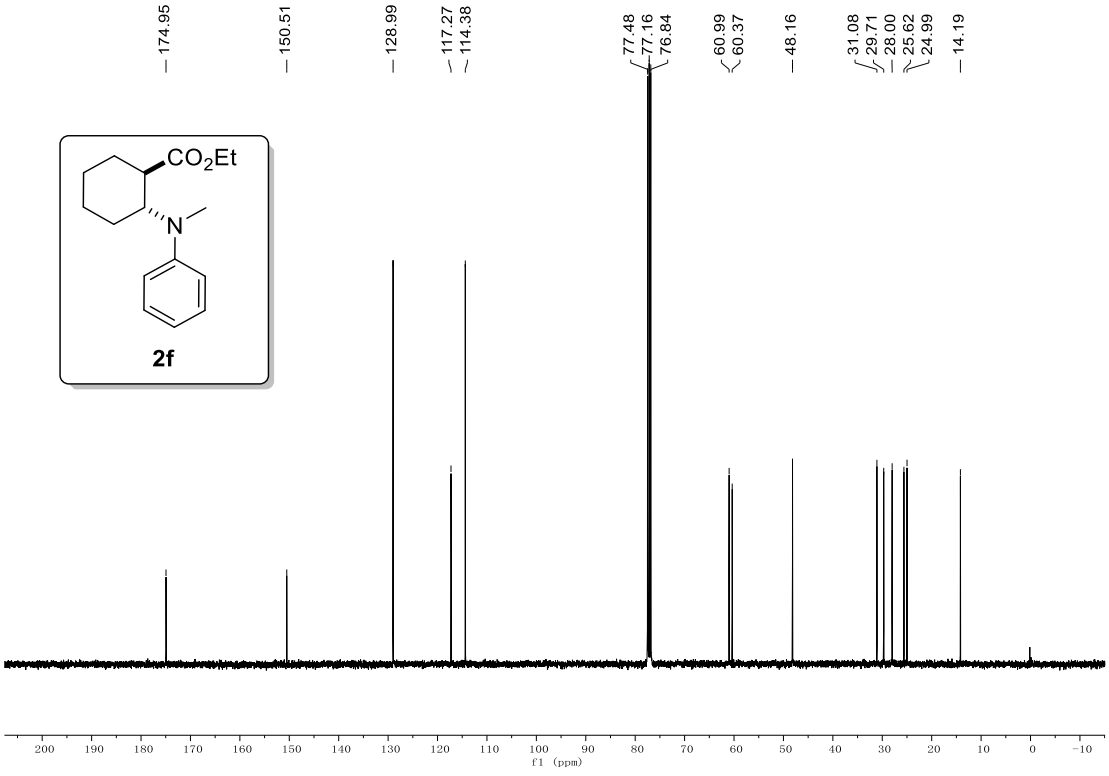
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2e



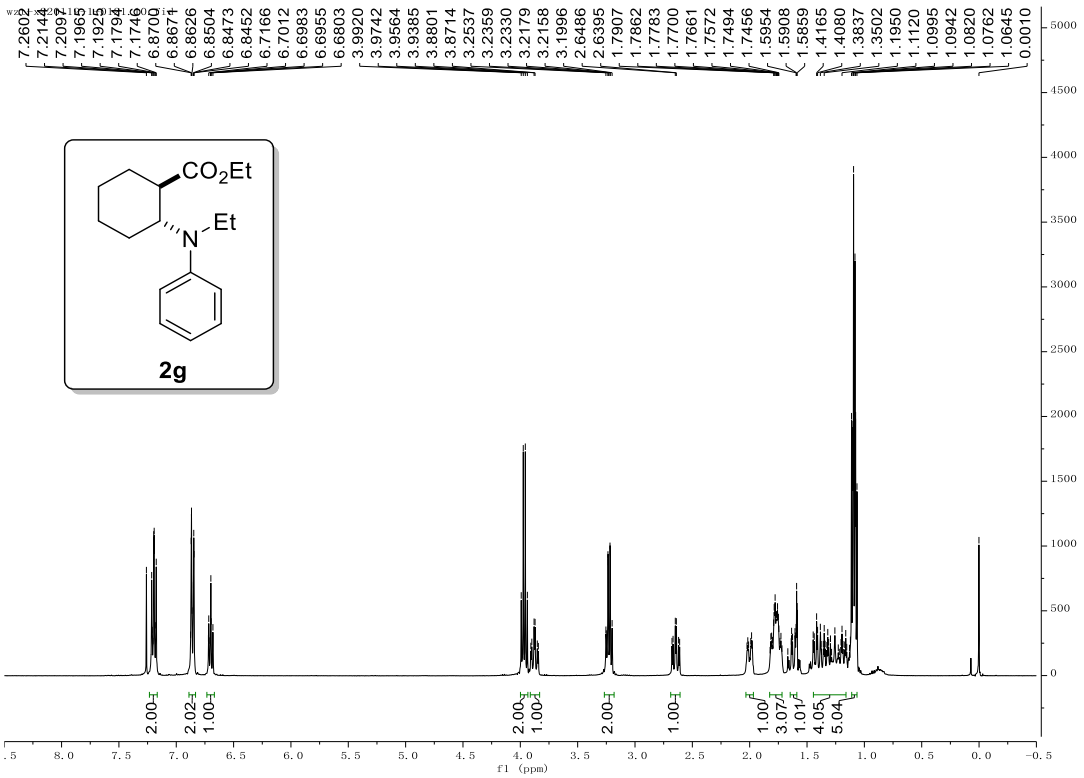
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2f



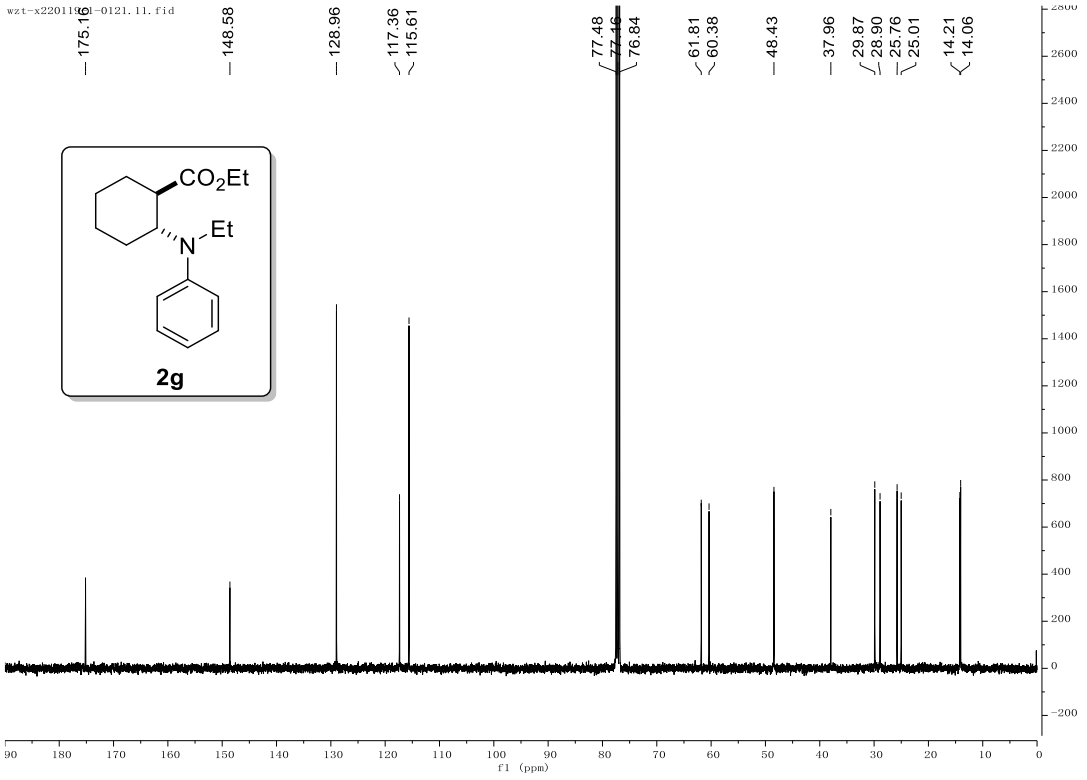
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2f



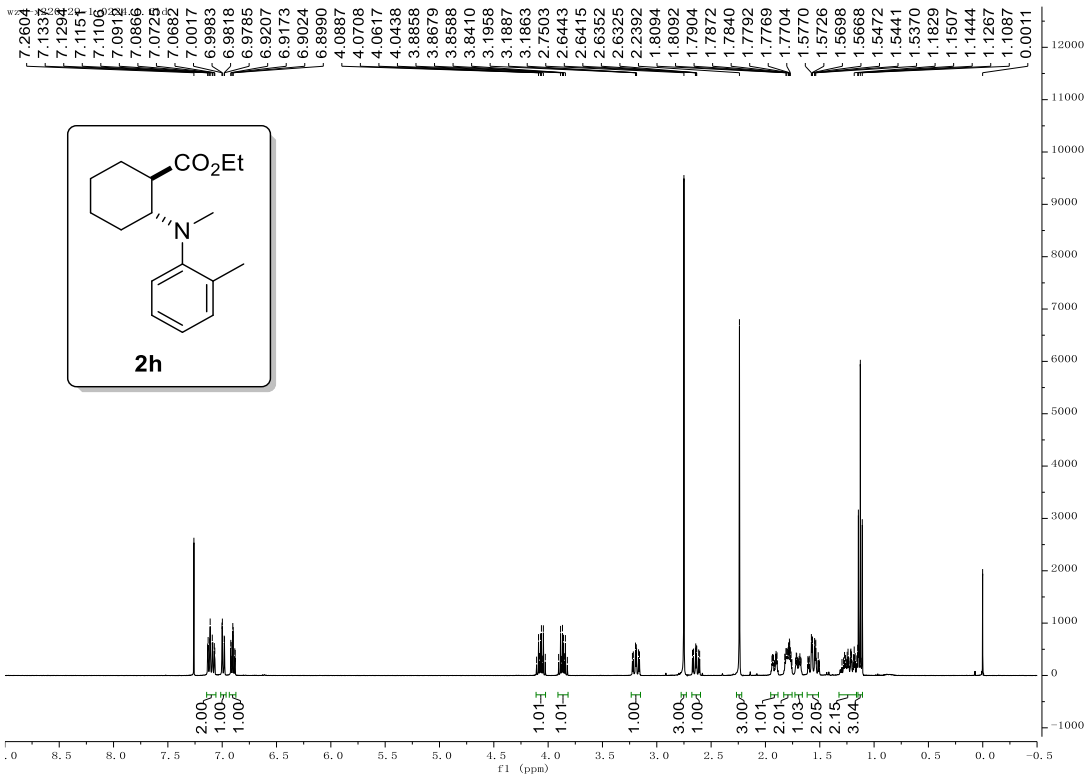
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2g



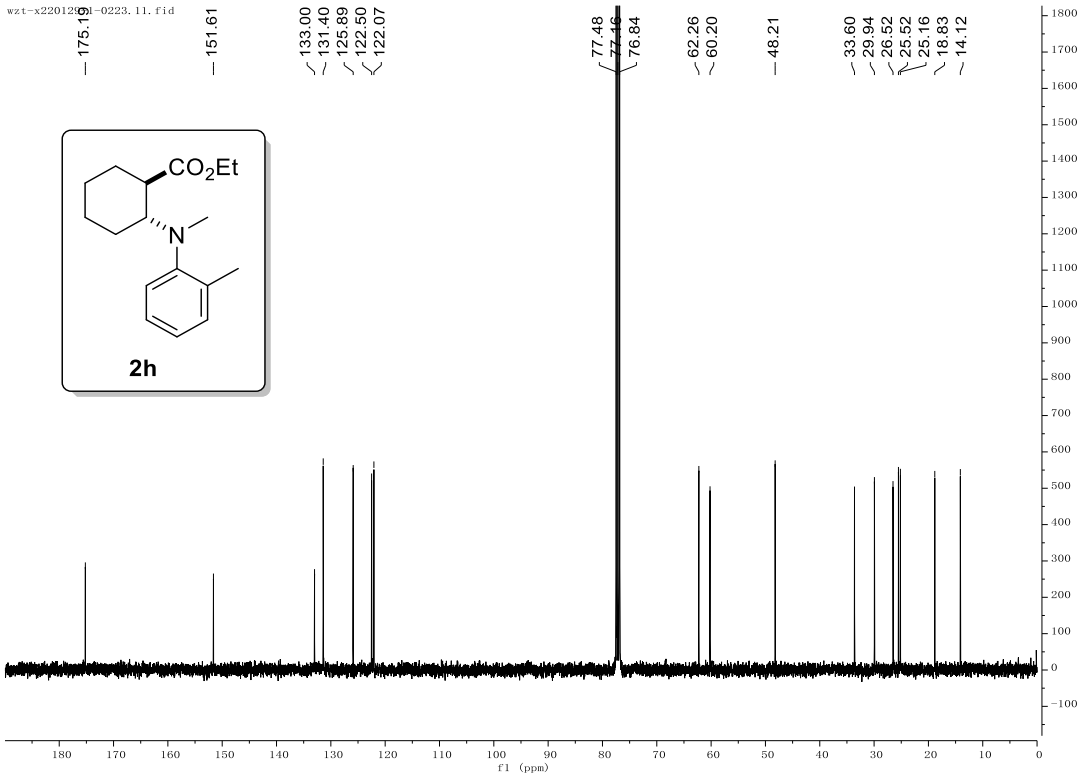
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2g



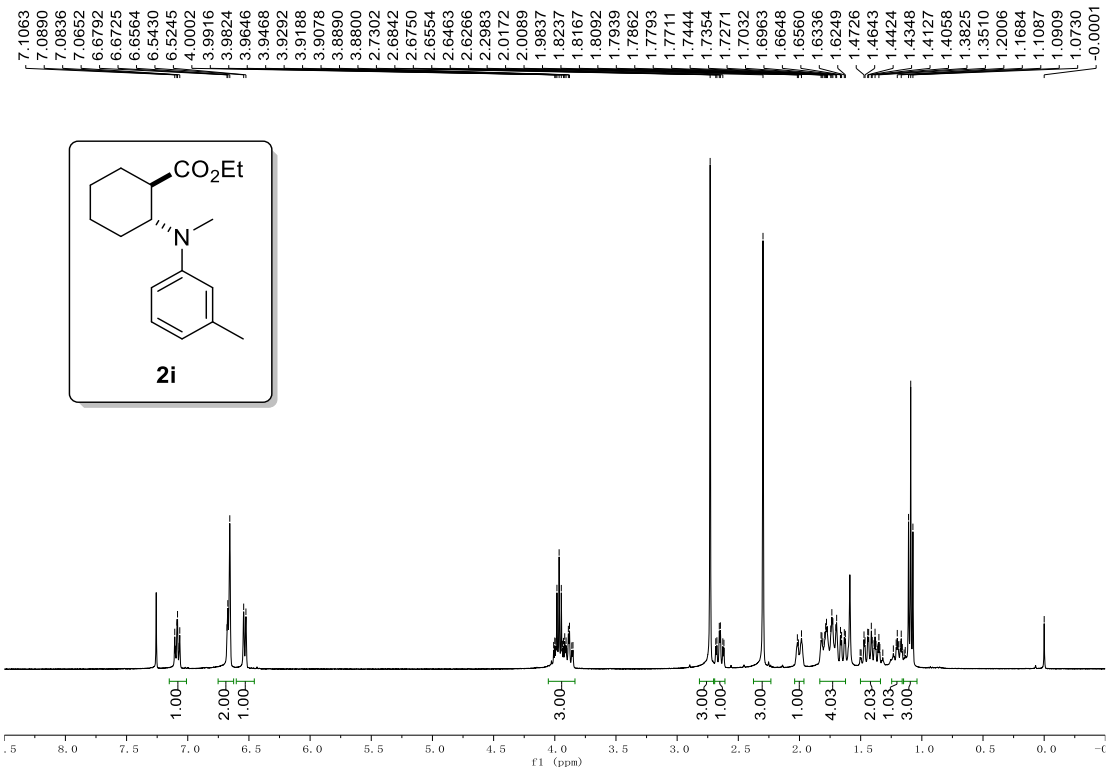
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2h



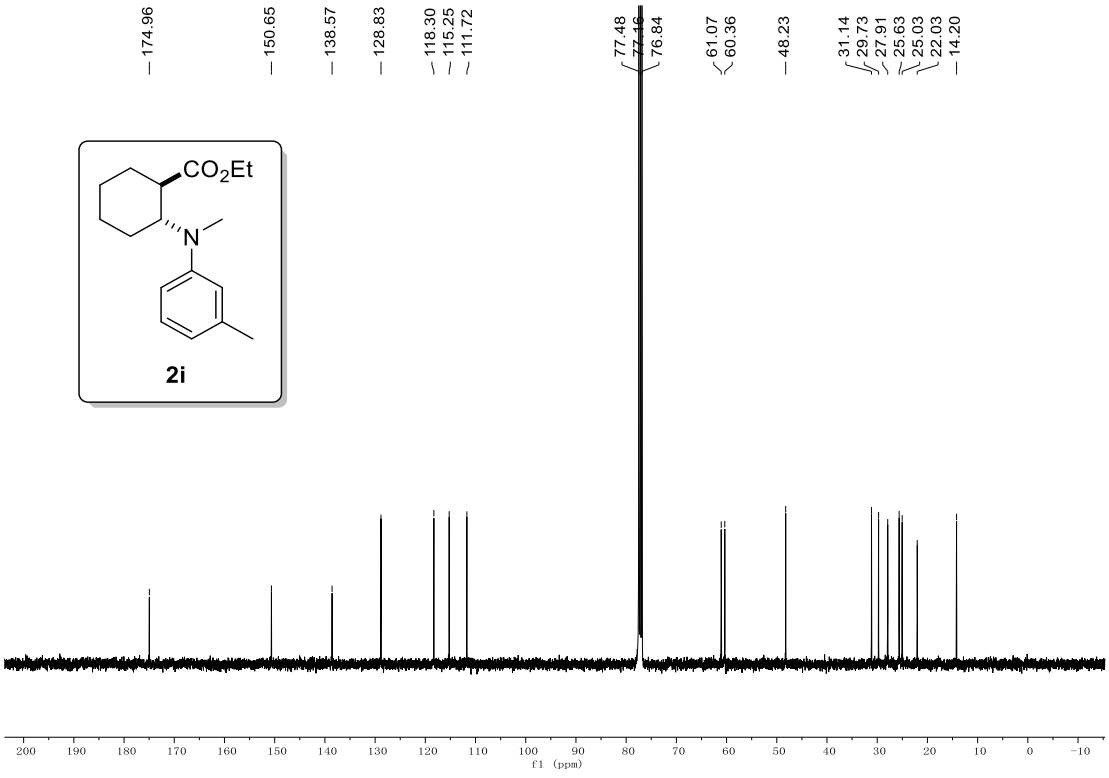
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2h



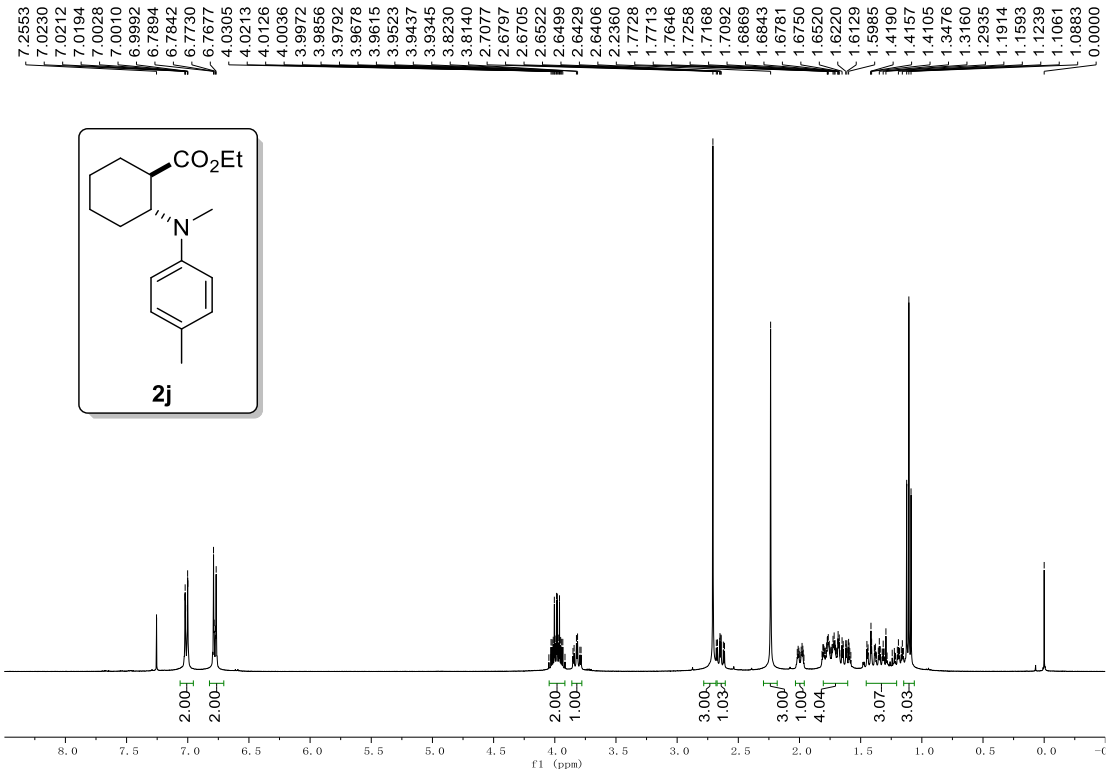
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2i



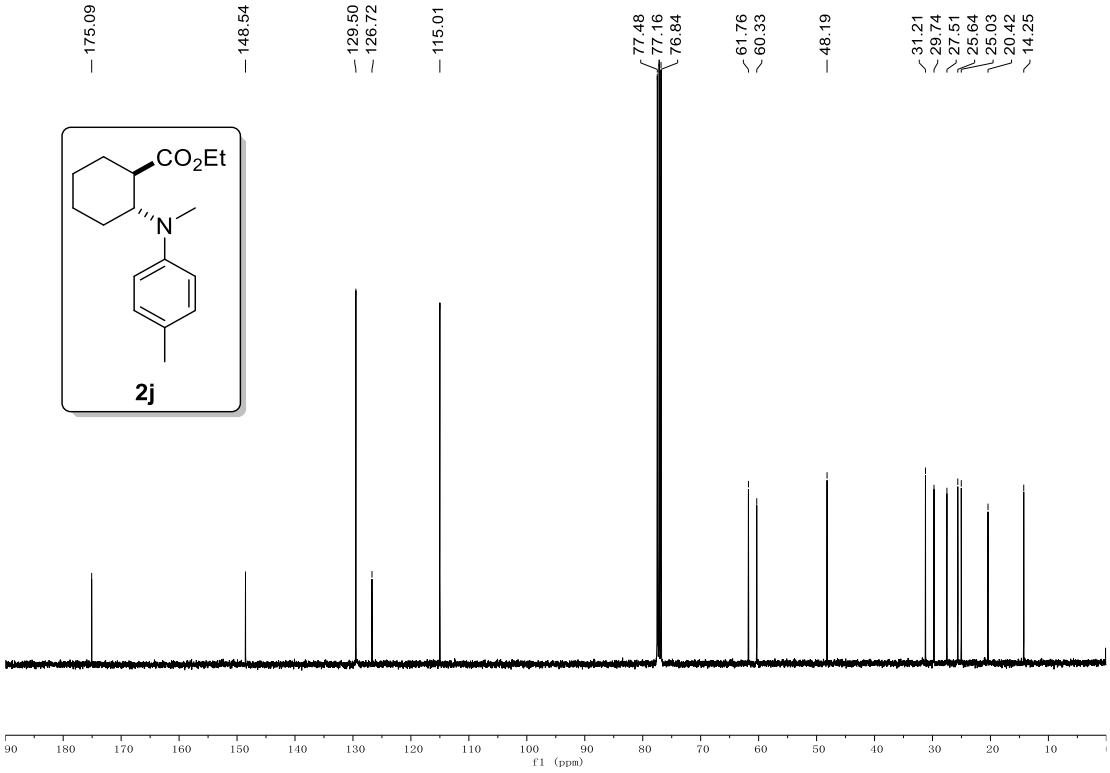
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2i



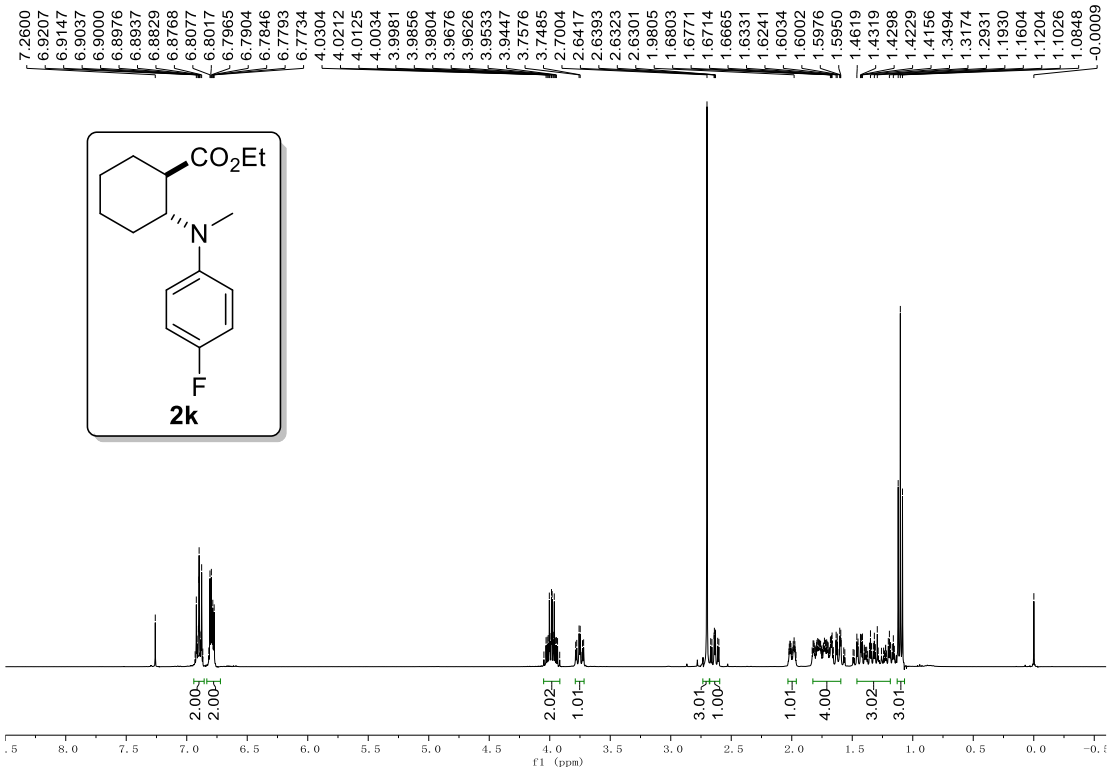
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2j



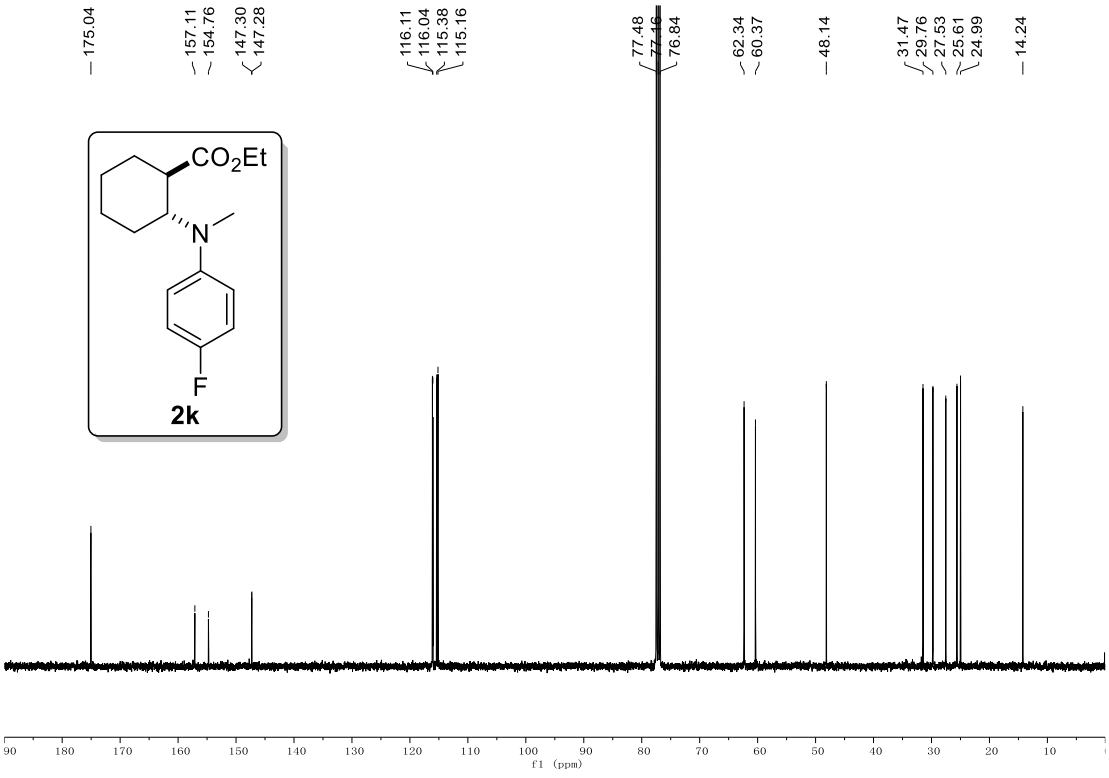
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2j



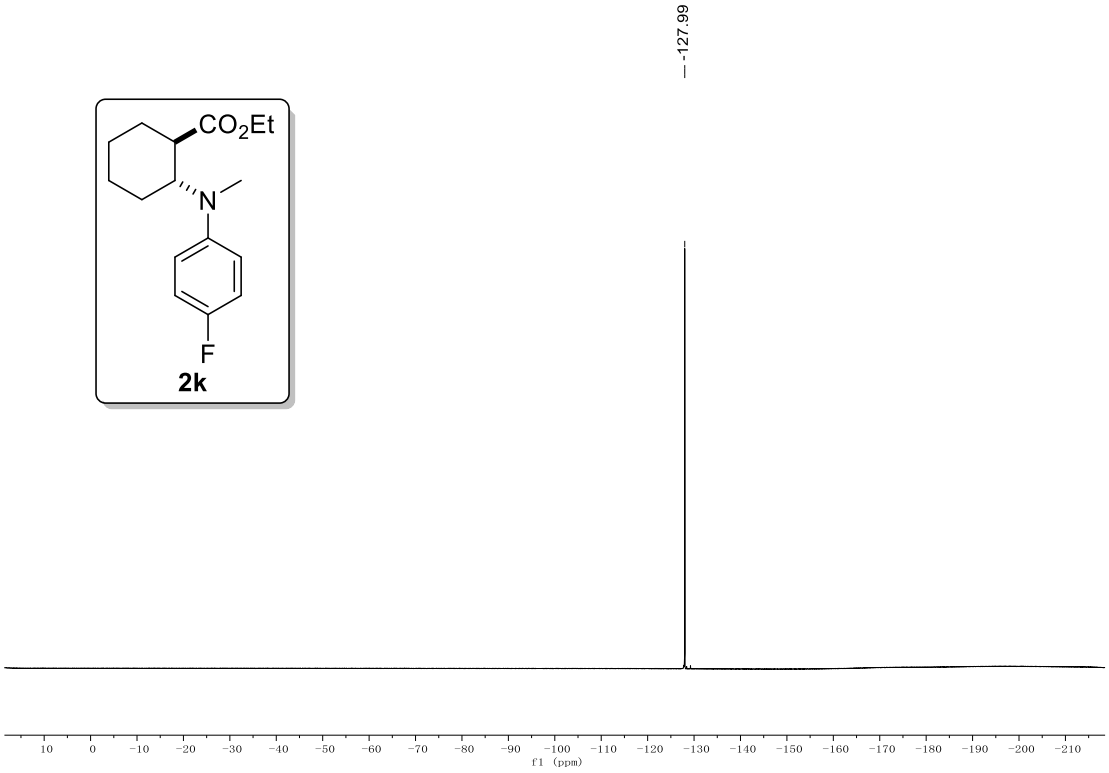
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2k



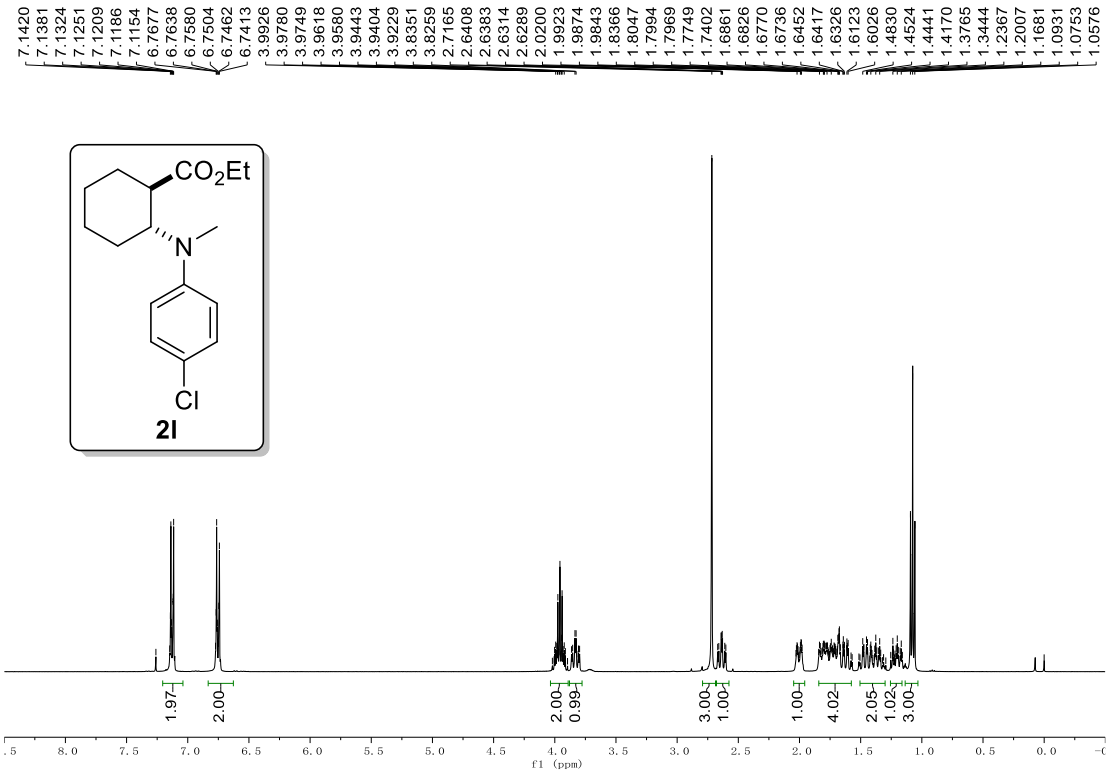
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2k



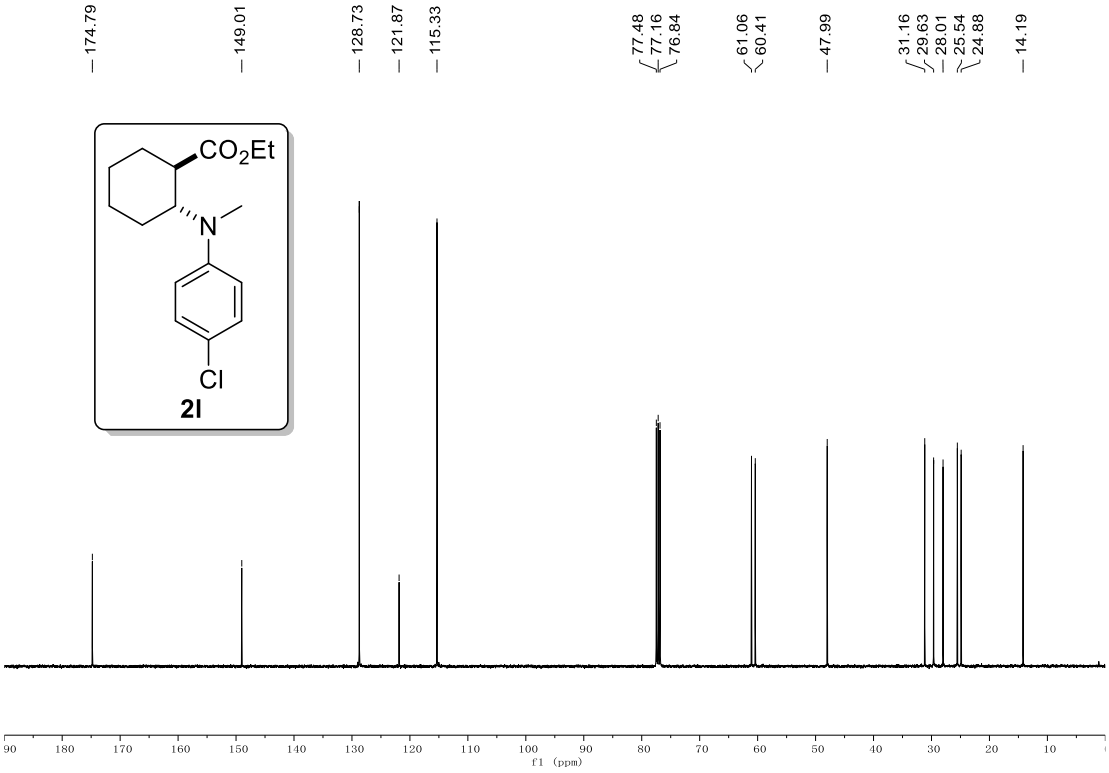
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 2k



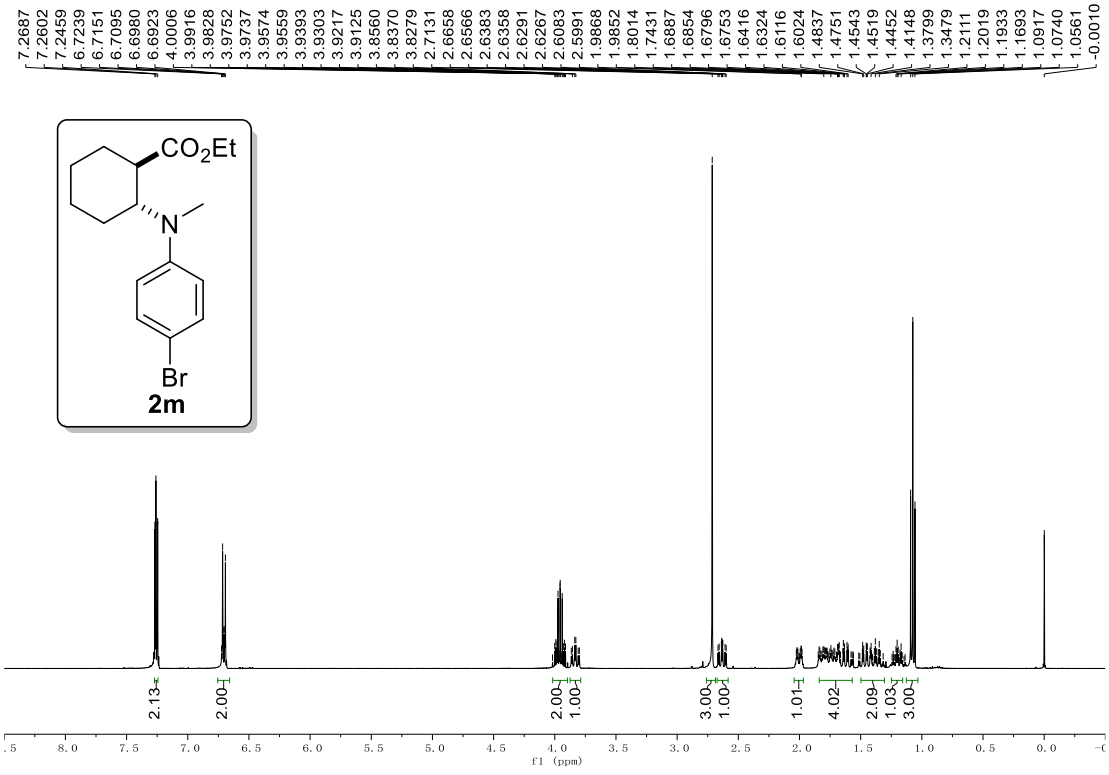
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2l



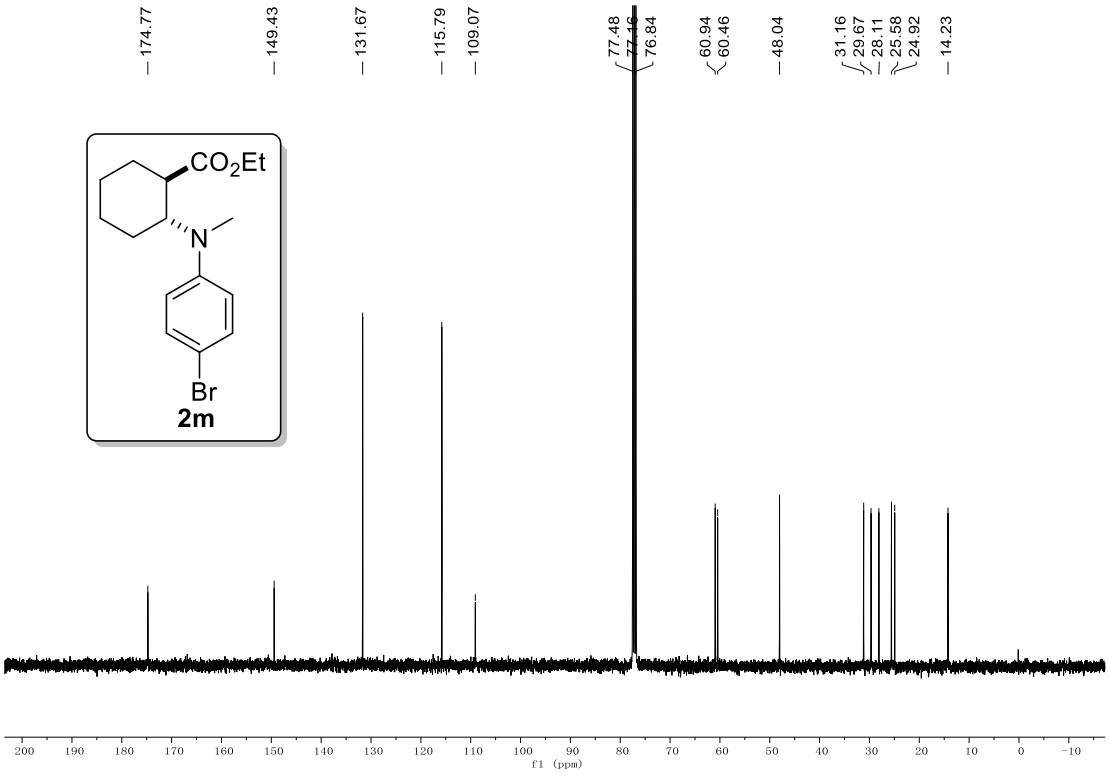
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2l



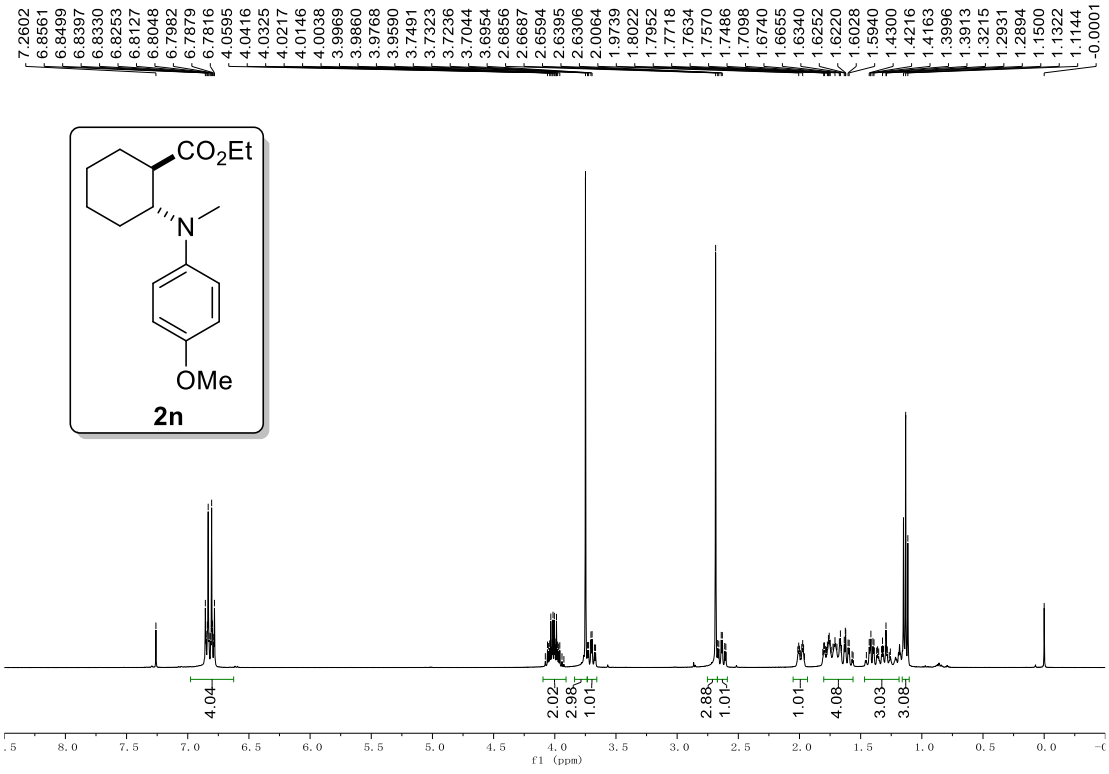
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2m



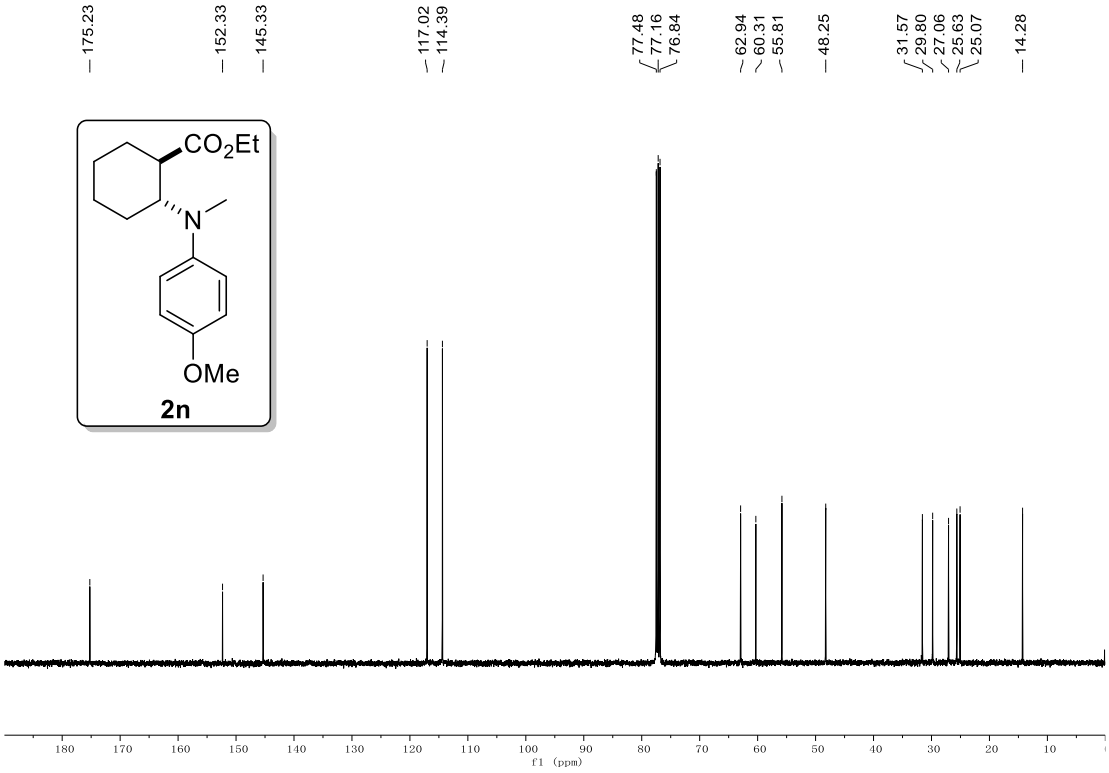
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2m



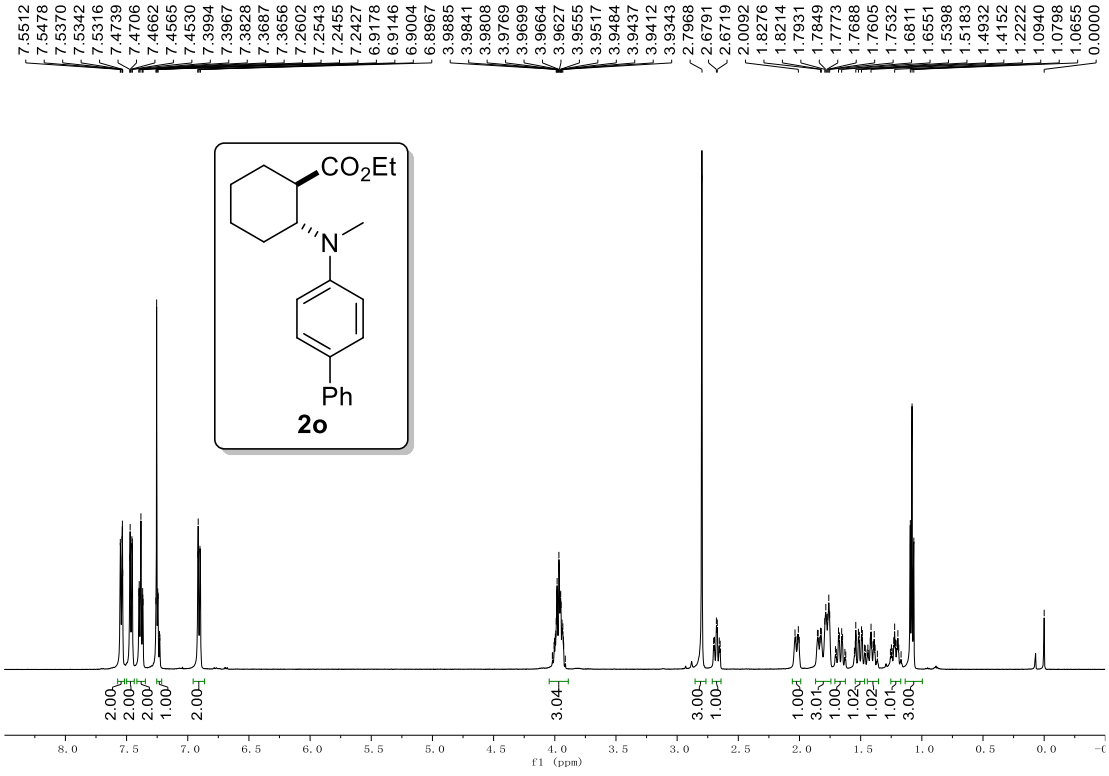
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2n



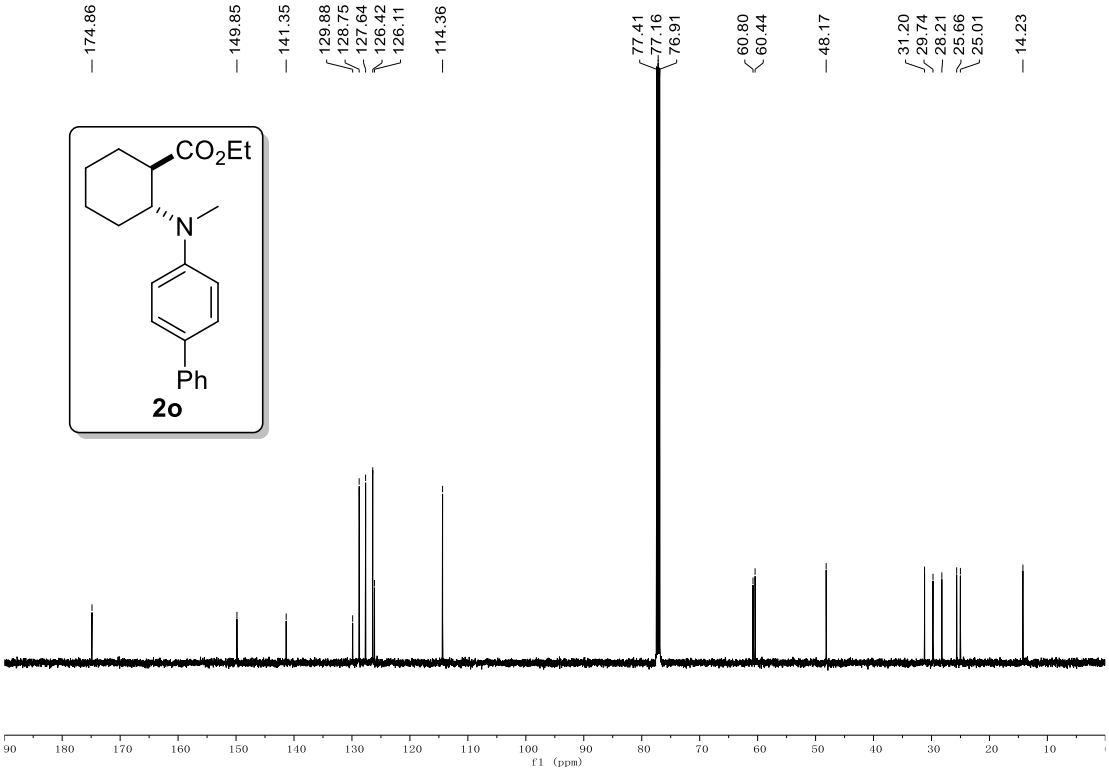
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2n



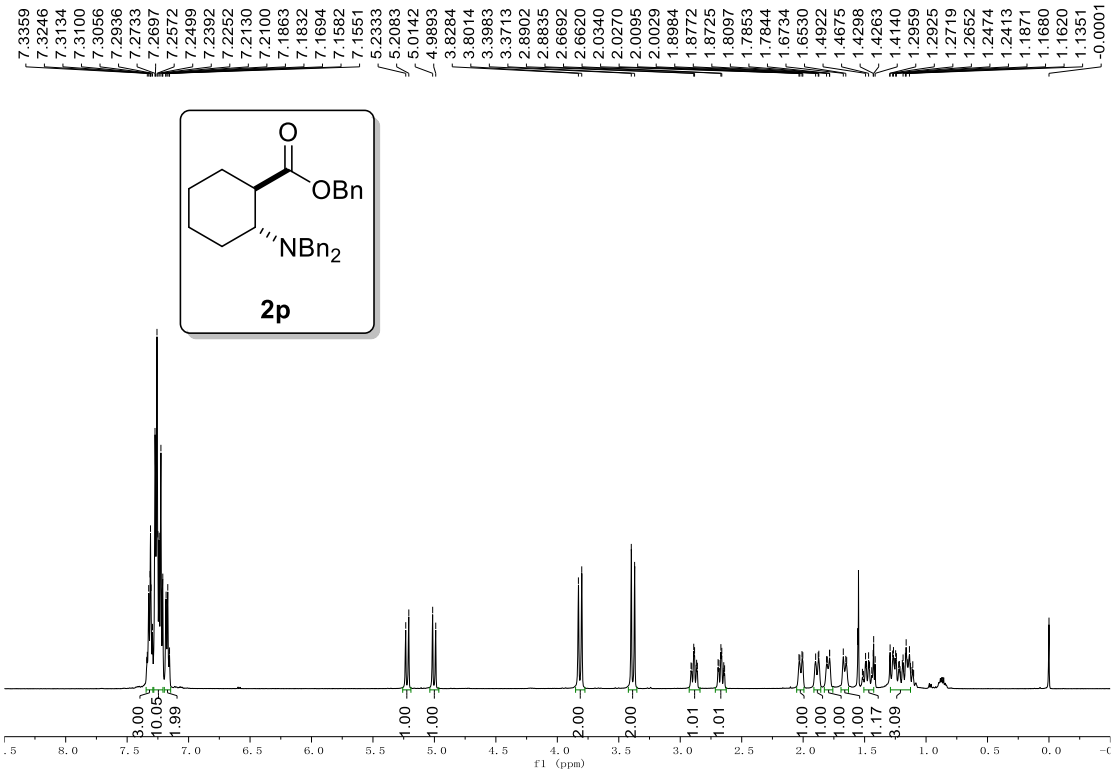
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 2o



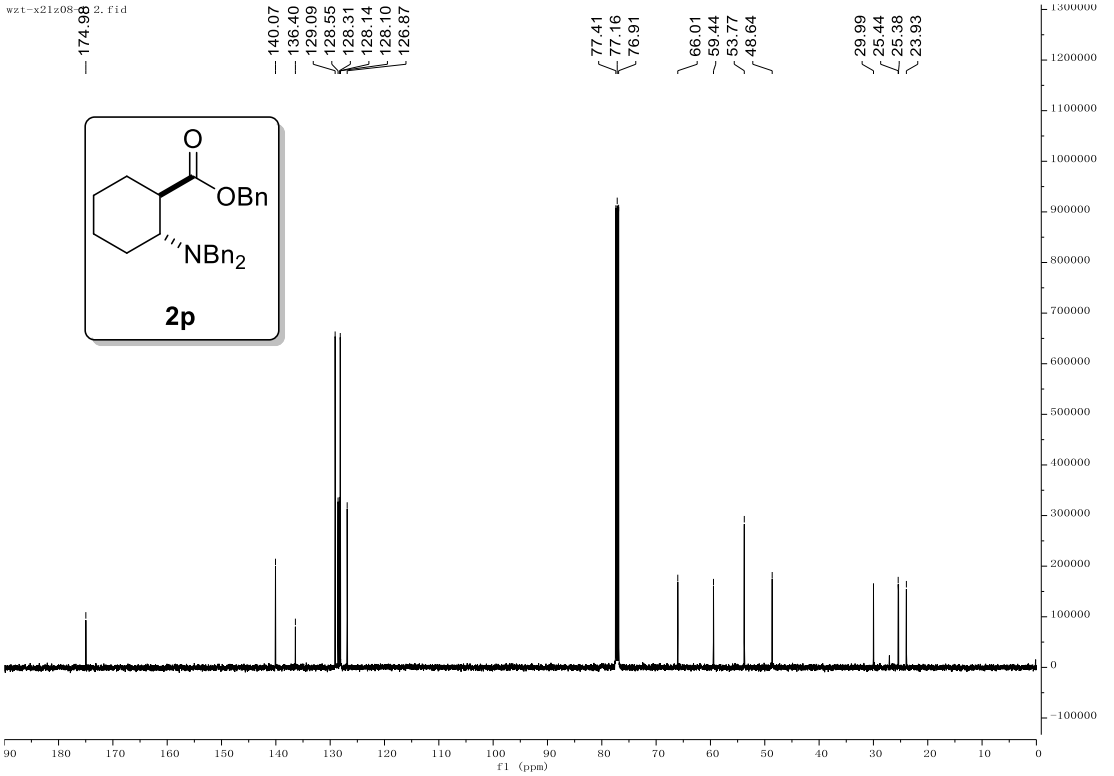
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 2o



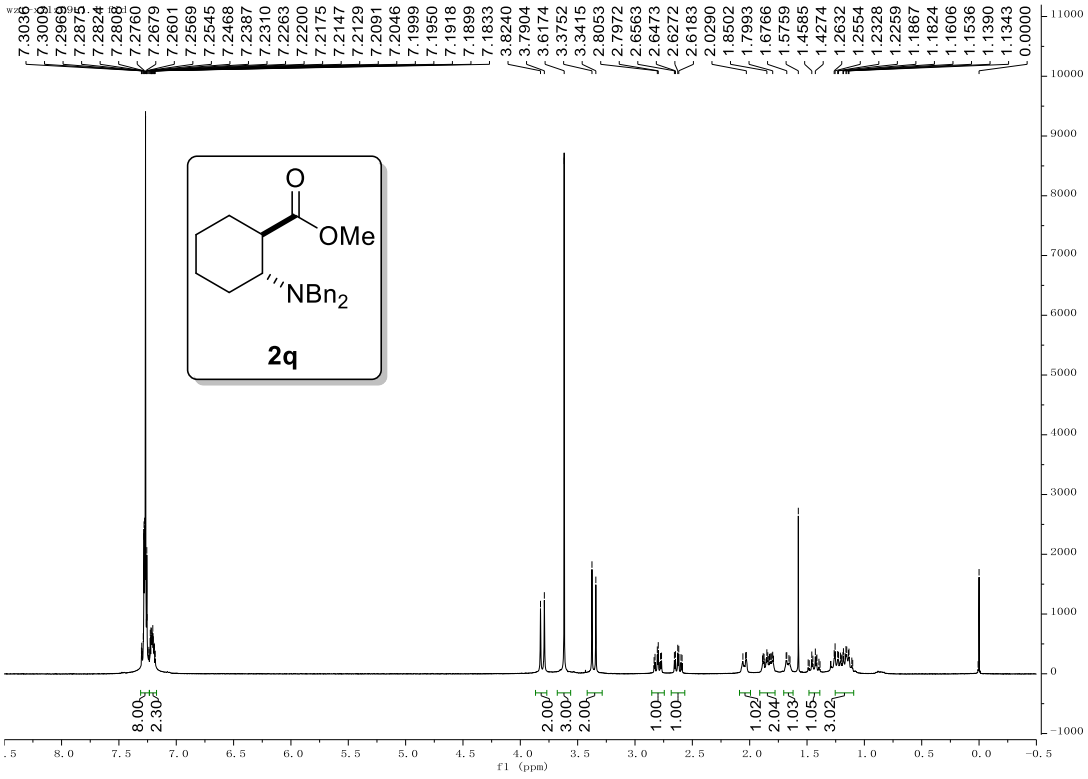
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 2p



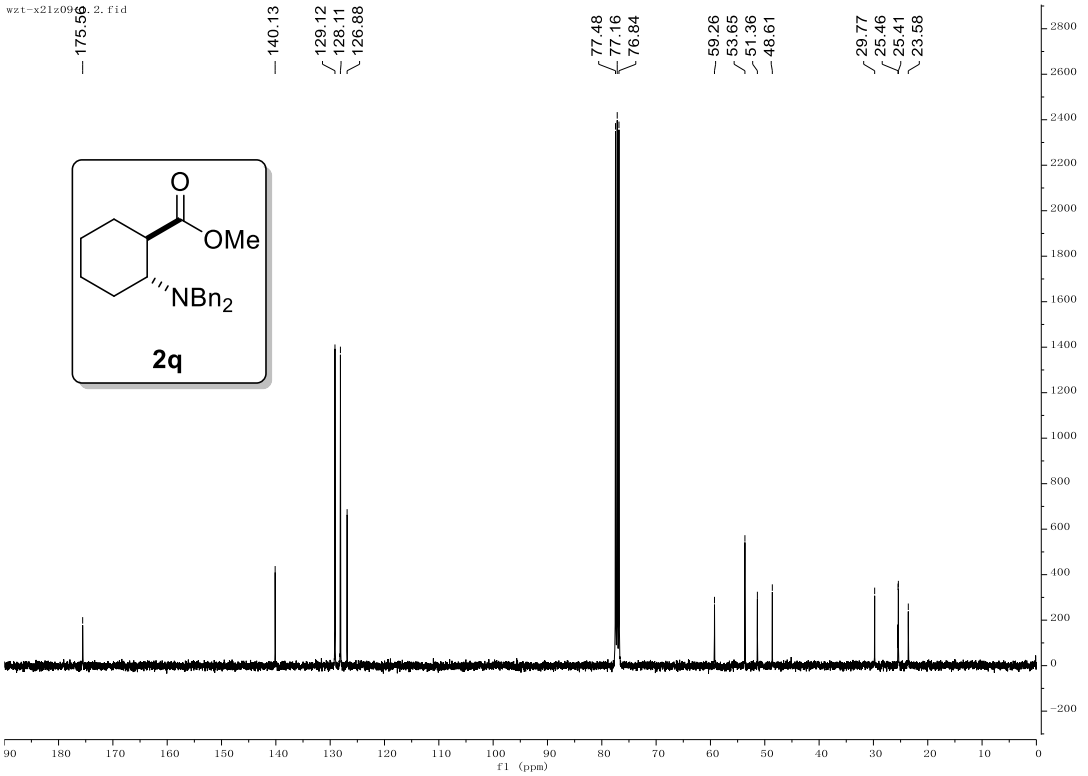
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 2p



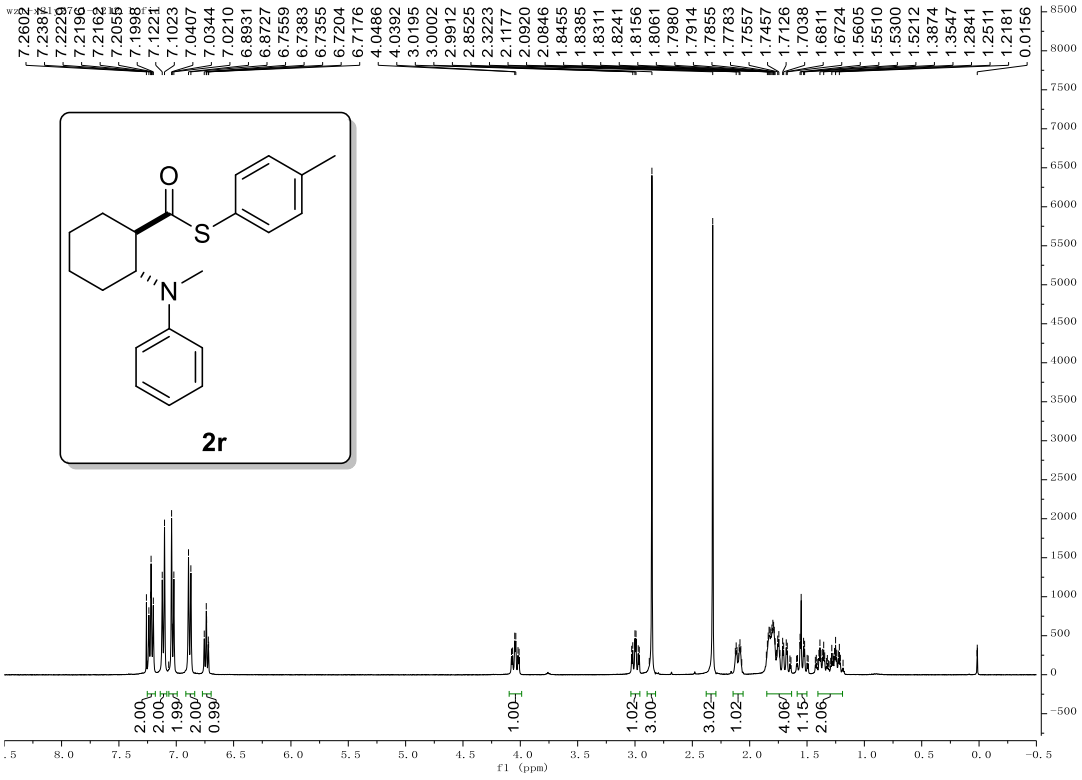
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2q



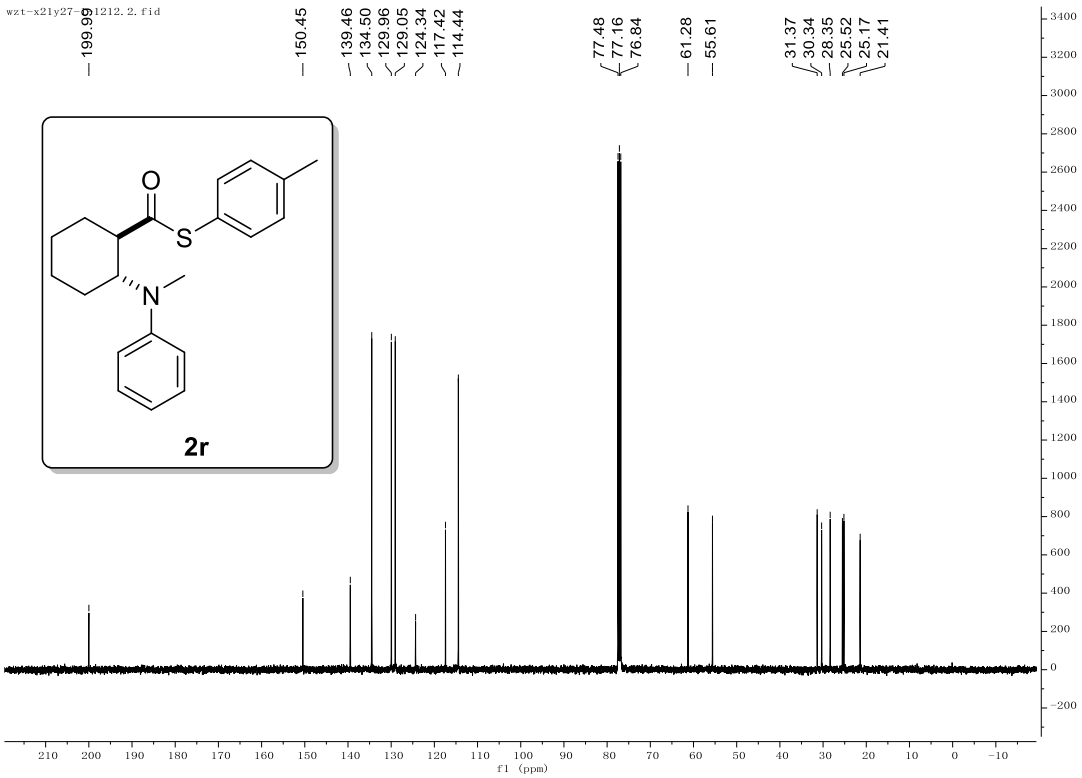
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2q



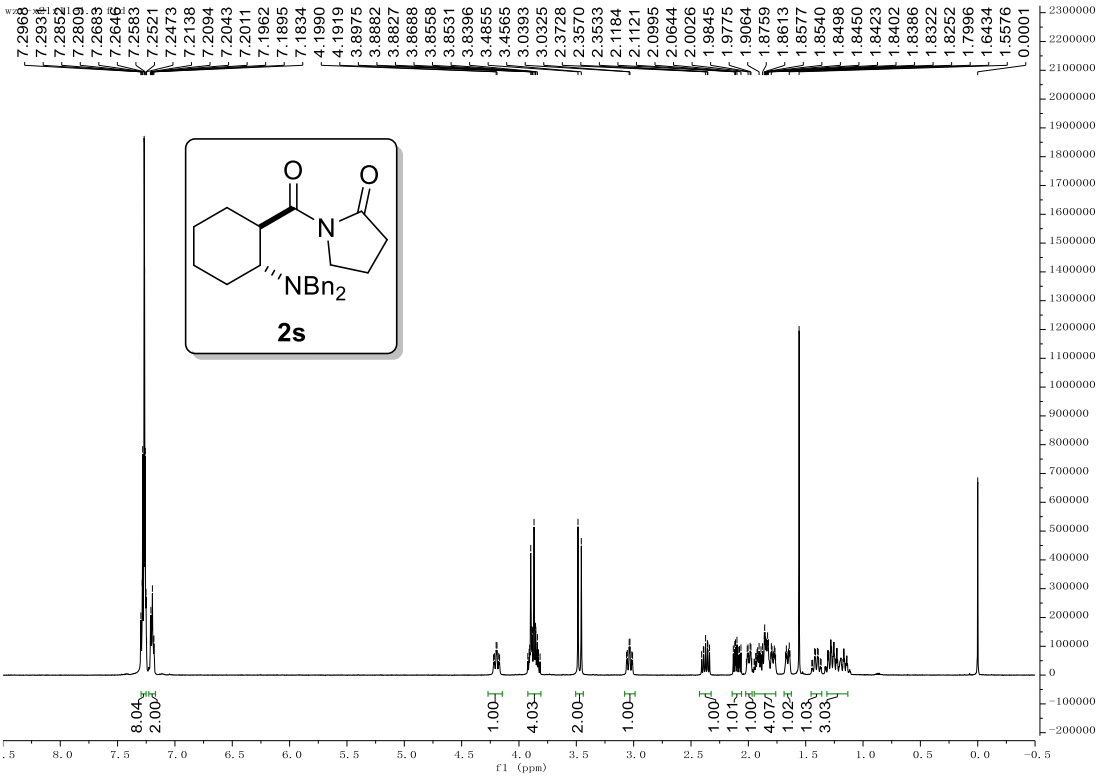
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2r



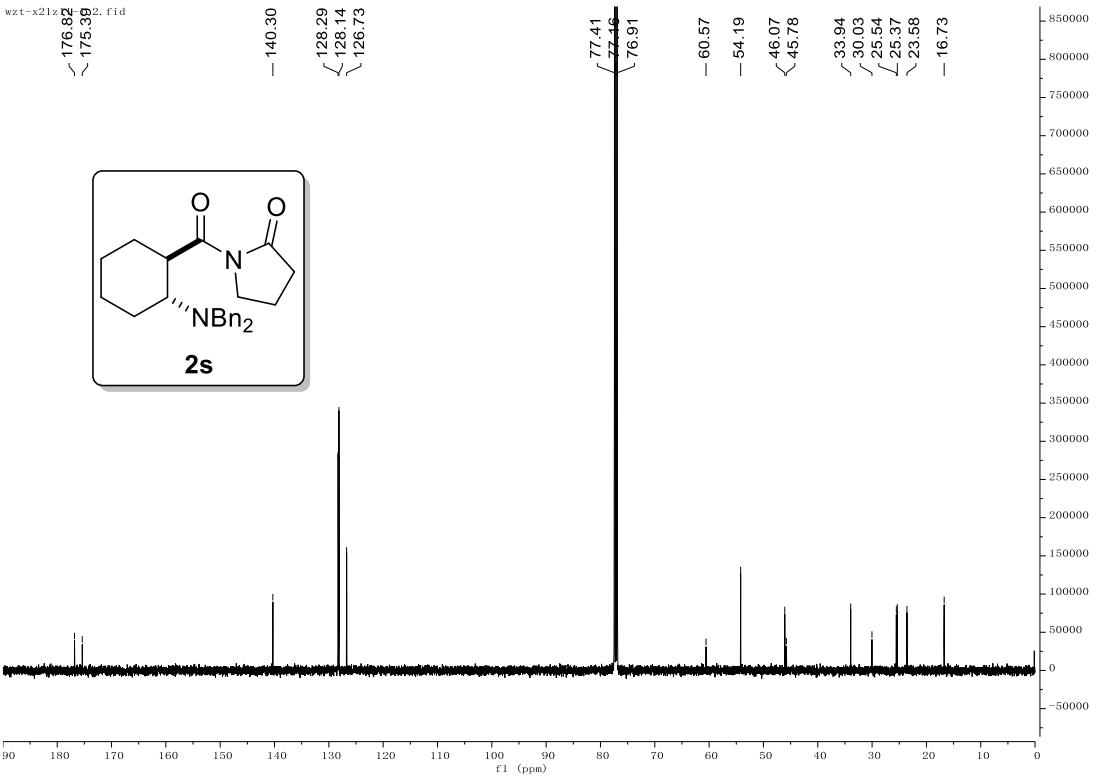
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2r



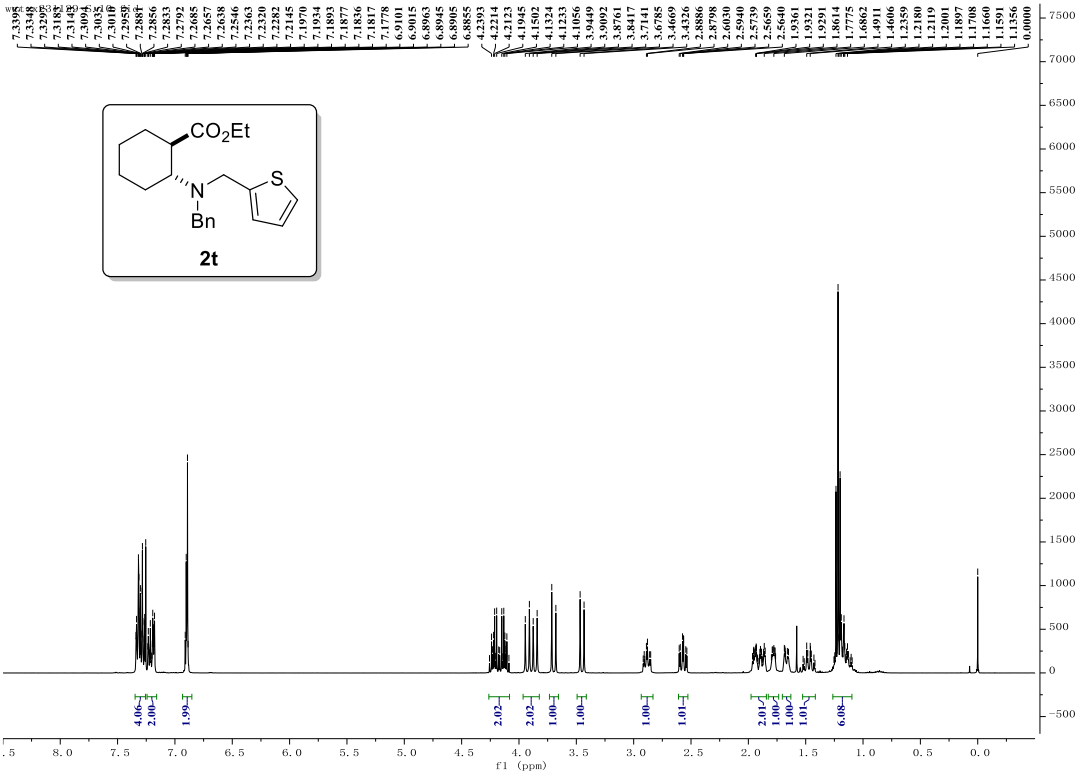
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 2s



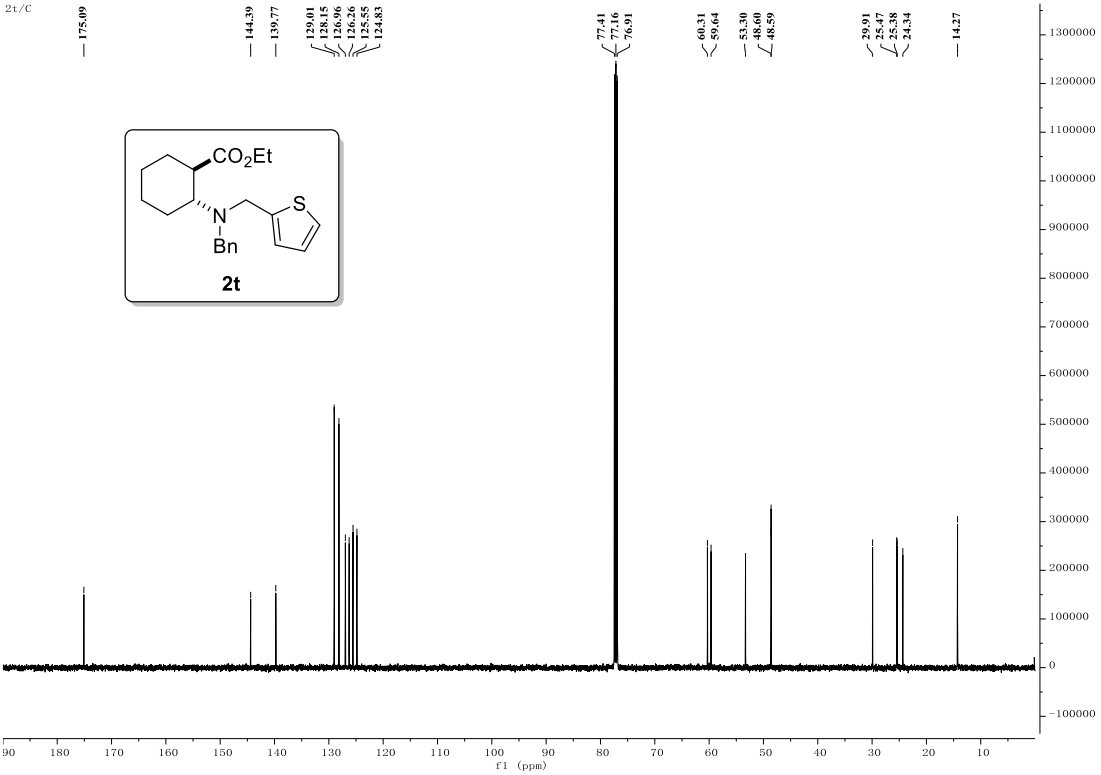
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 2s



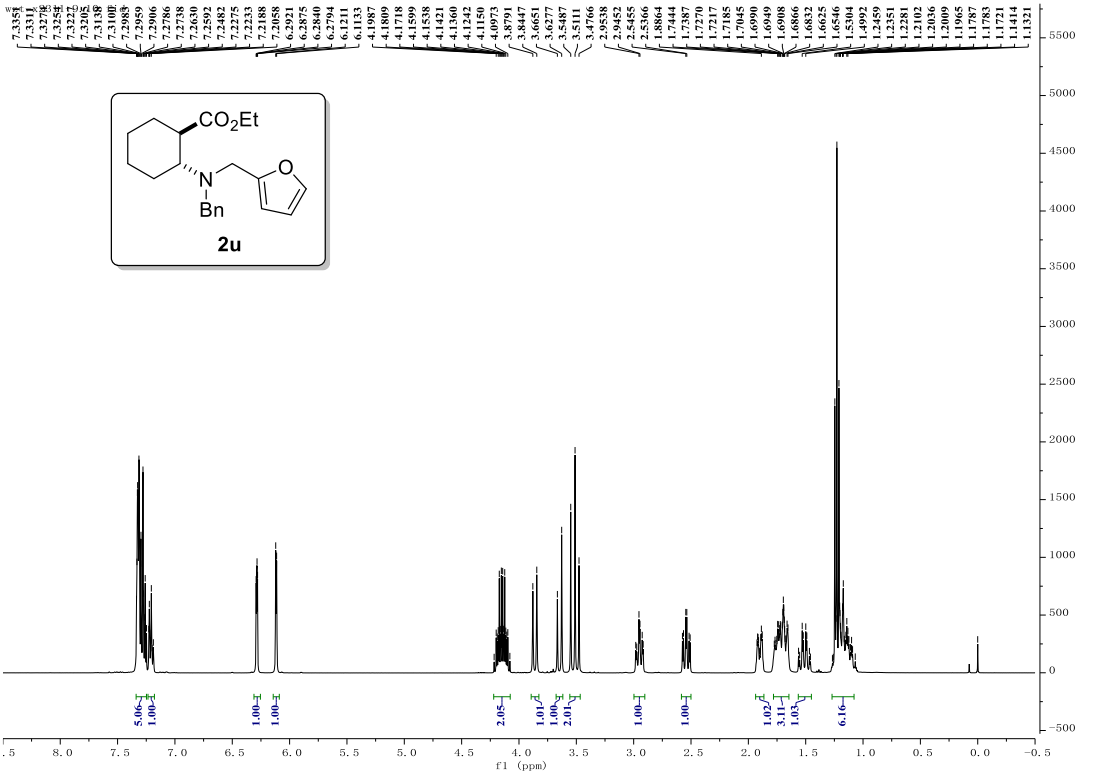
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2t



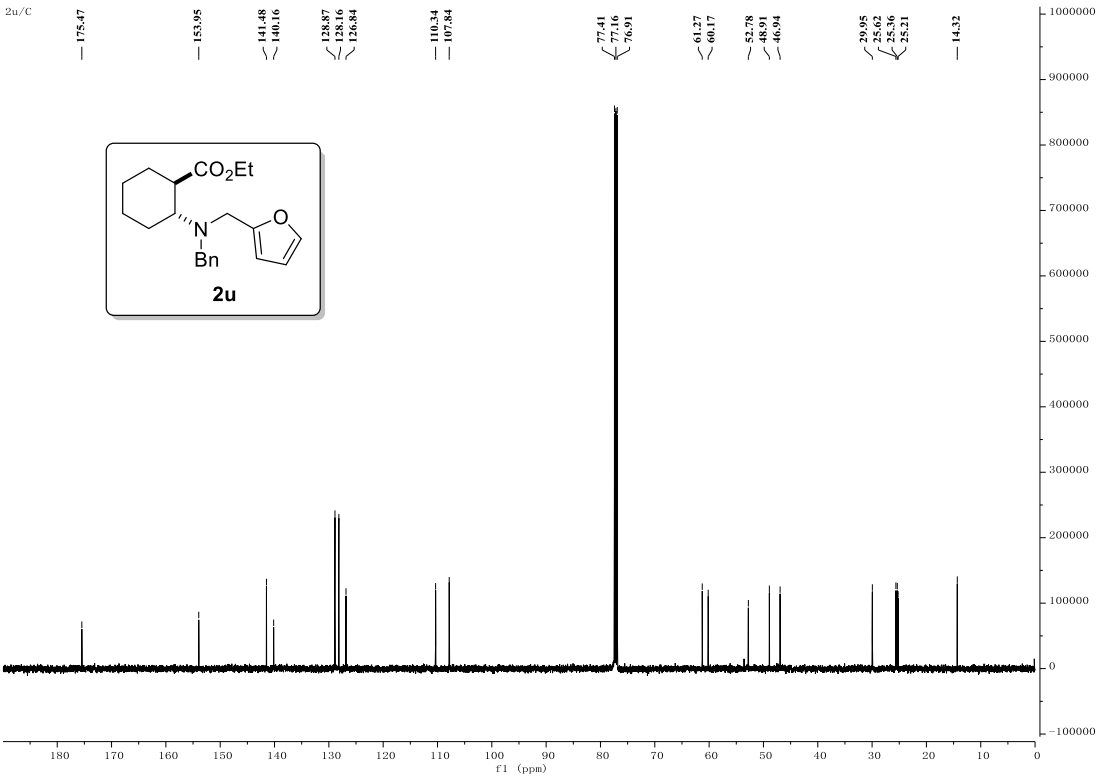
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 2t



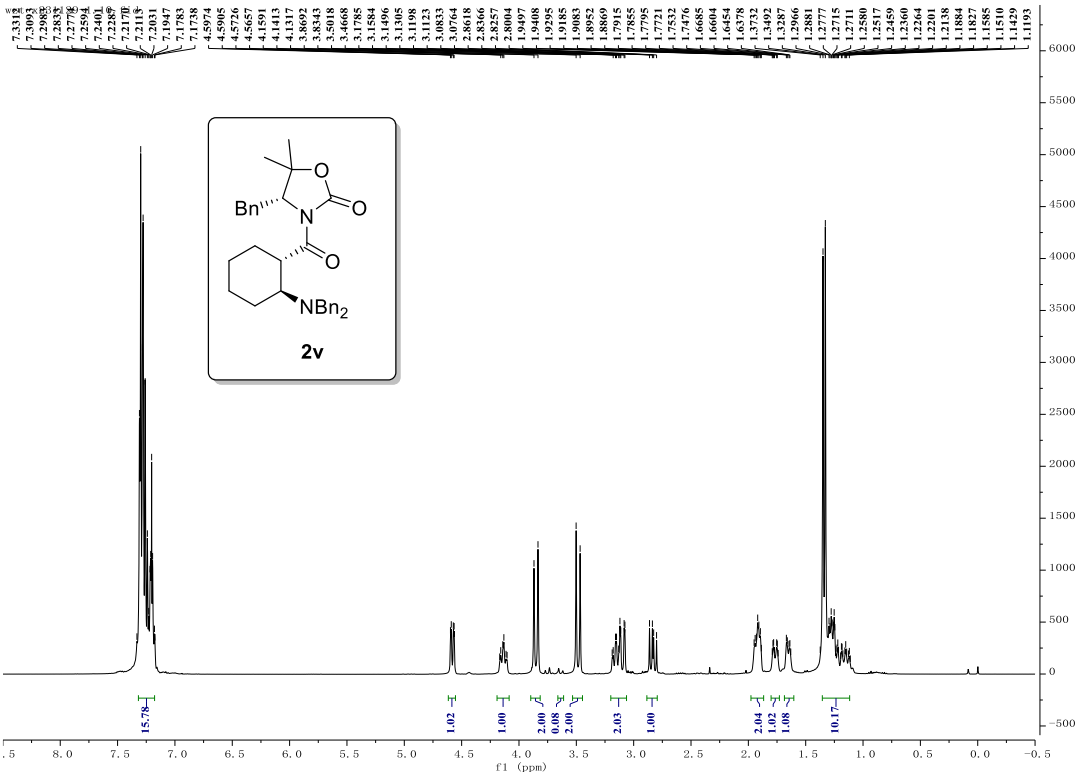
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2u



^{13}C NMR (126 MHz, $CDCl_3$) spectra for 2u



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2v



^{13}C NMR (101 MHz, $CDCl_3$) spectra for 2v