Supplementary Information

Iron/Photoredox Dual-Catalyzed Redox-Neutral Double Decarboxylative C(sp^3)–C(sp^3) Cross-Coupling

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1. General Information

Commercially Reagents: Commercially reagents were purchased from Sigma Aldrich, Energy Chemical, TCI, Bidepharm or Adamas and used without further purification. All experiments were performed in oven-dried glassware under an atmosphere of N_2. Tert-butyl methyl ether, acetonitrile were extra-dry solvents with molecular sieve (MS) purchased from Energy Chemical and stored within a N_2 filled glove box.

NMR Spectra: ^{1}H NMR spectra were recorded on a 400 or 600 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm，d_6-DMSO: 2.50 ppm). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm, t；d_6-DMSO: 39.6 ppm). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment.

High Resolution Mass Spectrometer (HRMS): All HRMS were recorded on high resolution Fourier transform mass spectrometer with BrukerDaltonics SolariX 7.0T from The United States of America, and the detector is FT-MS.

Gas Chromatograph-Mass Spectrometer (GC-MS): All GC-MS were recorded on Shimadzu GCMS-QP2020 NX. Measured values are reported to 3 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

Gas Chromatograph (GC): All GC were recorded on Fuli GC9790II.

Infra-Red Spectrometer (IR): All IR were recorded on Bruker INVENIO-R.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualization

was realized by ultraviolet fluorescence (λ = 254 nm) and/or staining with phosphomolybdic acid or potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

UV/Vis: Measurements were made on Shanghai JiaPeng technology co. ZF-7 Spectro Fluorophotometer.

Photoreactor: The light source used in this research were purchased from Changji engineering lighting fixtures, IP66 (Figure S1: 50W blue LEDs).

The material of the crystallizing dish with water is borosilicate glass, and the material of 12 mL reaction vial is borosilicate glass. The reaction mixture is irradiated with a 50 W blue LEDs lamp (the distance was about 0.6 cm), and the crystallizing dish with water is maintained at 40 ℃.

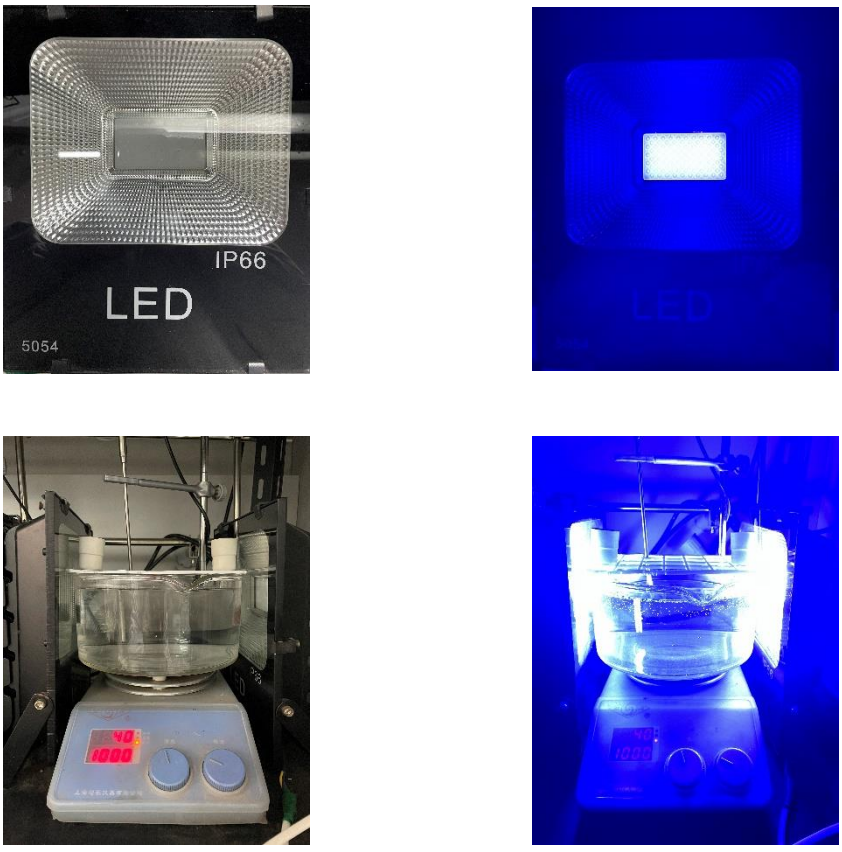


Figure S1. Photoreactor used in this research (50 W blue LEDs)

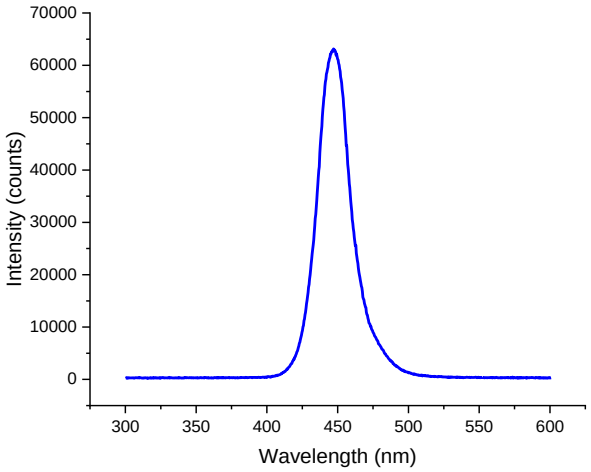
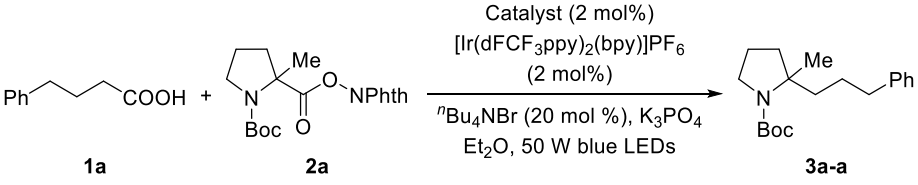


Figure S2. Emission spectra of the 50W blue LEDs, its emission wavelength range is from 405 nm to 510 nm, and its maximum emission wavelength is 447 nm. (The emission spectra were recorded on a Marine optical spectrometer USB2000+)

2. Detailed Optimization of Reaction Conditions

2.1 Detailed Optimization of Reaction Conditions

Table S1. Screening of Catalysts[a]

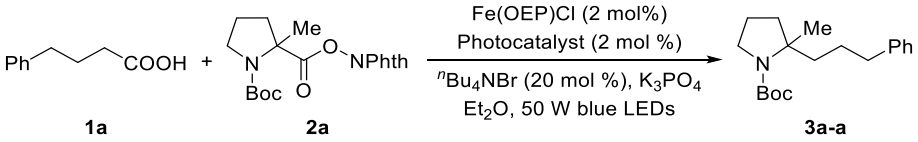


1a **2a** **3a-a**

Entry	Catalyst	Yield (%)[b]
1	None	3
2	Ni(TPP)Cl	Trace
3	Co(TPP)Cl	Trace
4	Fe(TPP)Cl	4
5	Fe(OEP)Cl	26

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), Et_2O (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), catalyst (2 mol %), $[Ir(dFCF_3ppy)_2(bpy)]PF_6$ (2 mol %), $^nBu_4NBr$ (20 mol %), Et_2O (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S2. Screening of Photocatalysts[a]

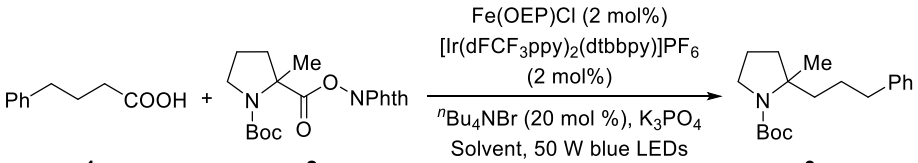


1a **2a** **3a-a**

Entry	Photocatalyst	Yield (%)[b]
1	4CzIPN	Trace
2	$[Ir(dFCF_3ppy)_2(bpy)]PF_6$	26
3	$[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$	39
4	$[Ir(dFFppy)_2(dtbbpy)]PF_6$	17
5	$[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$	Trace
6	$[Ir(dFF(Me)ppy)_2(dtbbpy)]PF_6$	20
7	$[Ir\ (dFCF_3(CF_3)ppy_2(dtbbpy)]PF_6$	Trace
8	$[Ir(dFCF_3ppy)_2(5,5'\text{-}CF_3bpy)]PF_6$	Trace

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), Et_2O (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), Fe(OEP)Cl (2 mol %), photocatalyst (2 mol %), $^nBu_4NBr$ (20 mol %), Et_2O (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S3. Screening of Solvents[a]

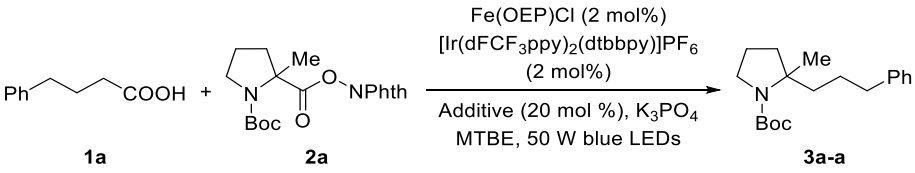


1a **2a** **3a-a**

Entry	Solvent	Yield (%)[b]
1	DMSO	Trace
2	DMF	Trace
3	MeCN	Trace
4	DCM	5
5	EA	53
6	PhCl	50
7	THF	9
8	Et_2O	39
9	MTBE	71

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), Et_2O (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), Fe(OEP)Cl (2 mol %), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2 mol %), $^nBu_4NBr$ (20 mol %), solvent (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S4. Screening of Additives[a]

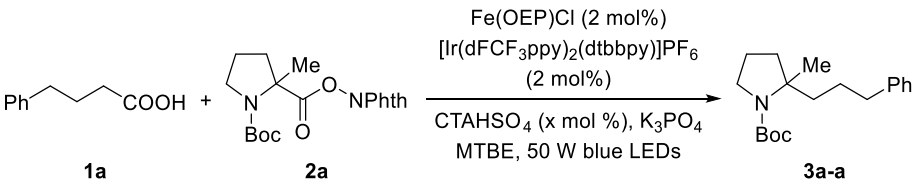


1a **2a** **3a-a**

Entry	Additives	Yield (%)[b]
1	$^{n}Bu_4NBr$	71
2	$^{n}Bu_4NCl$	66
3	$^{n}Bu_4NOAc$	68
4	$^{n}Bu_4NPF_6$	8
5	$^{n}Bu_4NBF_4$	62
6	$^{n}Bu_4NHSO_4$	79
7	Me_4NHSO_4	55
8	$^{n}Pr_4NHSO_4$	71
9	$(Me_4N)_2SO_4$	39
10	$CTAHSO_4$	85
11	CTABr	70
12	$CTABF_4$	65
13	$CTAClO_4$	35
14	$CTAPF_6$	42

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), Et_2O (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), Fe(OEP)Cl (2 mol %), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2 mol %), additive (20 mol %), MTBE (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S5. Amount of $CTAHSO_4$[a]

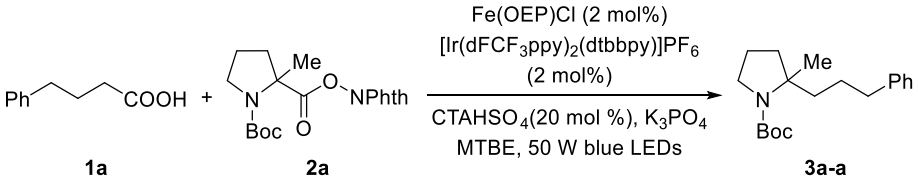


1a **2a** **3a-a**

Entry	$CTAHSO_4$ (x mol %)	Yield (%)[b]
1	10	70
2	20	85
3	50	66

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), Et_2O (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), Fe(OEP)Cl (2 mol %), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2 mol %), $CTAHSO_4$ (x mol %), MTBE (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S6. Screening of Solvents[a]

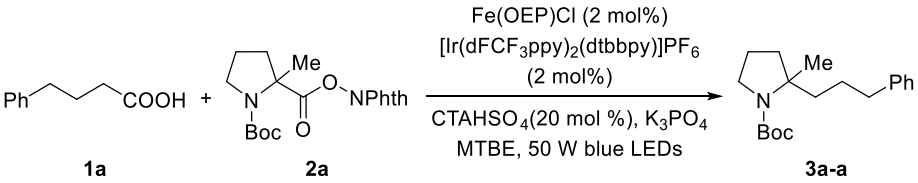


Entry	Solvent	Yield (%)[b]
1	THF	76
2	Et_2O	83
3	MTBE	85(82[c])

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), solvent (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), Fe(OEP)Cl (2 mol %), [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %), $CTAHSO_4$ (20 mol %), MTBE (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard. [c]Isolated yield.

2.2 Control Experiments

Table S7. Control Experiments[a]

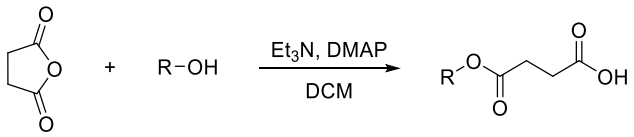


Entry	Light	PC	Fe(OEP)Cl	$CTANHSO_4$	Yield (%)[b]
1	×	√	√	√	N.D.
2	√	×	√	√	N.D.
3	√	√	×	√	8
4	√	√	√	×	20
5	√	√	√	√	85

[a]Standard procedure: **1a** (0.20 mmol), K_3PO_4 (0.20 mmol, 1.0 equiv.), MTBE (3.0 mL), 30 min. After removing solvent *in vacuo*, then **2a** (0.40 mmol, 2.0 equiv.), Fe(OEP)Cl (2 mol %), [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %), $CTAHSO_4$ (20 mol %), MTBE (3.0 mL), 50 W blue LED irradiation for 12 h. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

3. Preparation and Characterization Data of Substrates

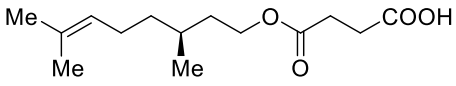
3.1 Preparation of Carboxylic Acids



Carboxylic acids **1ab, 1ac** were prepared according to the following **procedure**: A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with the corresponding alcohol (5.0 mmol), succinic anhydride (0.51 g, 5.0 mmol), Et_3N (0.76 g, 1.04 mL, 7.5 mmol), and DMAP (0.67 g, 0.55 mmol) in DCM (40 mL) under an atmosphere of N_2. The mixture was left stirring for 8 hours at room temperature. The mixture was removed *in vacuo*, the residue was subjected to *high vacuo* for 15 min, dissolved in $CHCl_3$ (100 mL) and stirred with 4% aq. HCl (15 mL) for 15 min. The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (75 mL). The combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Purification of the residue by column chromatography gave the desired carboxylic acid.[1]

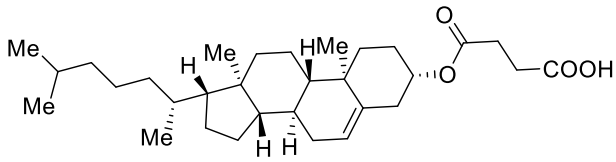
3.2 Characterization Data of Carboxylic Acids

(S)-4-((3,7-Dimethyloct-6-en-1-yl)oxy)-4-oxobutanoic acid (1ab): Synthesized according to the procedure. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 1:1) as a colorless oil (1.09 g, 85% yield). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.07 (t, *J* = 6.7 Hz, 1H), 4.17 – 4.07 (m, 2H), 2.66 (t, *J* = 6.6 Hz, 2H), 2.60 (t, *J* = 6.7 Hz, 2H), 2.03 – 1.89 (m, 2H), 1.70 – 1.62 (m, 4H), 1.58 (s, 3H), 1.56 – 1.49 (m, 1H), 1.46 – 1.38 (m, 1H), 1.36 – 1.29 (m, 1H), 1.20 – 1.12 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 178.3, 172.4, 131.4, 124.7, 63.6, 37.1, 35.5, 29.5, 29.1, 29.0, 25.8, 25.5, 19.5, 17.7. **IR (ATR)**: ν = 1739, 1686 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{14}H_{24}O_4^+$: 257.1744, found: 257.1747.



1ab

4-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-4-oxobutanoic acid (1ac): Synthesized according to the procedure.

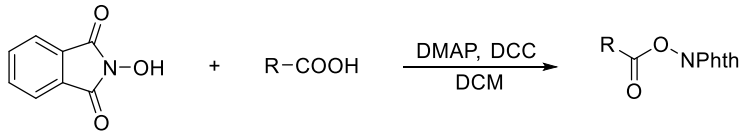


1ac

The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 1:1) as a white solid (1.85 g, 76% yield).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.37 (d, *J* = 3.9 Hz, 1H), 4.69 – 4.56 (m, 1H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.59 (t, *J* = 6.3 Hz, 2H), 2.31 (d, *J* = 7.8 Hz, 2H), 2.05 – 1.91 (m, 2H), 1.90 – 1.77 (m, 3H), 1.64 – 1.41 (m, 7H), 1.38 – 1.23 (m, 4H), 1.22 – 0.96 (m, 13H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.88 – 0.83 (m, 6H), 0.67 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 178.3, 171.7, 139.6, 122.9, 74.7, 56.8, 56.3, 50.1, 42.4, 39.9, 39.7, 38.1, 37.1, 36.7, 36.3, 35.9, 32.0, 32.0, 29.4, 29.2, 28.4, 28.2, 27.8, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0. **Mp** 82 – 83 ºC. **IR (ATR)**: ν = 1725, 1607 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{31}H_{50}O_4^+$: 485.3636, found: 485.3632.

3.3 Preparation of Redox-Active Esters

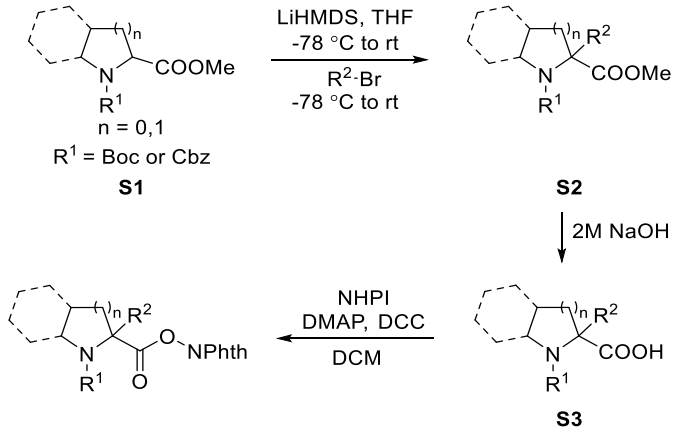
Procedure A:



Redox-active esters **2a, 2g, 2h, 2i, 2j, 2l, 2m, 2n** were prepared according to the above **procedure A**: To a DCM (30 mL) solution of the corresponding carboxylic acid (12 mmol) were added *N*-hydroxyphthalimide (1.67 g, 10 mmol), and 4-dimethylaminopyridine (62.3 mg, 0.50 mmol) sequentially. Then a solution of *N*, *N*′-dicyclohexylcarbodiimide (2.48 g, 12 mmol) in DCM (10 mL) was added slowly. The reaction was stirred at rt for 3 h, as monitored by TLC for completion. Upon completion, the reaction mixture was poured into water and the aqueous layer was extracted with DCM (30 mL × 3), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The

mixture was purified by flash column chromatography on silica gel to afford the corresponding redox-active esters.[2]

Procedure B:



Redox-active esters **2b, 2c, 2d, 2e, 2f, 2k** were prepared according to the above **procedure B**: To an oven-dried 100 mL round bottom flask with a magnetic stir bar was added the corresponding methyl ester **S1** (10 mmol) and dry THF (30 mL) under nitrogen. The reaction was cooled to -78 ℃, followed by the slow addition of LiHMDS (1 M in THF) (15 mL, 15 mmol). The resulting solution was stirred at -78°C for 1.5 hours. Then, alkyl bromide (20 mmol) was added dropwise. After being allowed to warm up to room temperature, the reaction was stirred for 18 hours. The reaction was quenched with saturated NH_4Cl solution (30 mL) and the mixture was extracted with EtOAc (20 mL × 3), dried over anhydrous Na_2SO_4. Concentration of the solvent under reduced pressure would afford the crude material **S2**.[3]

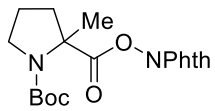
The methyl ester **S2** was hydrolyzed by using 2 M NaOH aqueous solution (10 mL, 20 mmol) in EtOH (20 mL). The reaction was stirred at 50 ℃ for 16 hours. Upon completion, 1 M HCl was added to the reaction until pH was adjusted to 3-4. The solution was extracted with EtOAc (20 mL × 3). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration, all the volatiles were removed under vacuum to afford the carboxylic acid **S3**, which was used for redox-active ester synthesis without further purification.

To a DCM (30 mL) solution of the corresponding carboxylic acid were added N-hydroxyphthalimide (1.67 g, 10 mmol), and 4-dimethylaminopyridine (62.3 mg, 0.50

mmol) sequentially. Then a solution of N, N′-dicyclohexylcarbodiimide (2.48 g, 12 mmol) in DCM (10 mL) was added slowly. The reaction was stirred at rt for 3 h, as monitored by TLC for completion. Upon completion, the reaction mixture was poured into water and the aqueous layer was extracted with DCM (30 mL × 3), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The mixture was purified by flash column chromatography on silica gel to afford the corresponding redox-active esters.

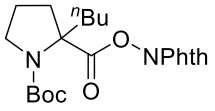
3.4 Characterization Data of Redox-Active Ester

1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) 2-methylpyrrolidine-1,2-dicarboxylate (2a): Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.43 g, 92% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.90 – 7.80 (m, 2H), 7.76 (dd, *J* = 5.2, 3.0 Hz, 2H), 3.71 – 3.64 (m, 1H), 3.61 – 3.54 (m, 1H), 2.71 – 2.63 (m, 1H), 2.17 – 2.01 (m, 2H), 1.99 – 1.86 (m, 1H), 1.68 (s, 3H), 1.51 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 171.4, 161.7(2C), 153.4, 134.8(2C), 129.0(2C), 123.9(2C), 81.4, 64.2, 48.0, 41.5, 28.1(3C), 23.5, 22.7. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.90 – 7.80 (m, 2H), 7.73 (dd, *J* = 5.1, 3.1 Hz, 2H), 3.61 – 3.54 (m, 1H), 3.53 – 3.48 (m, 1H), 2.59 (dd, *J* = 12.8, 6.2 Hz, 1H), 2.17 – 2.01 (m, 2H), 1.99 – 1.86 (m, 1H), 1.70 (s, 3H), 1.49 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 171.0, 161.7(2C), 153.7, 134.7(2C), 129.1(2C), 123.8(2C), 80.3, 64.5, 47.9, 39.6, 28.5(3C), 23.6, 22.5. **Mp** 80 – 81 ºC. **IR (ATR)**: ν = 1812, 1785, 1742, 1686 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{19}H_{22}N_2O_6^+$: 375.1551, found: 375.1546.



2a

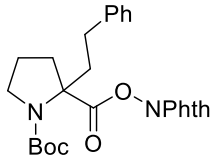
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) 2-butylpyrrolidine-1,2-dicarboxylate (2b): Synthesized according to the procedure B. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (2.21 g, 53% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 – 7.82 (m, 2H), 7.82 – 7.71 (m, 2H), 3.86 – 3.76 (m, 1H), 3.51 – 3.39 (m, 1H),



2b

2.58 – 2.49 (m, 1H), 2.45 – 2.34 (m, 1H), 2.33 – 2.23 (m, 1H), 2.14 – 2.05 (m, 1H), 1.99 – 1.86 (m, 2H), 1.52 (s, 9H), 1.44 – 1.27 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.6, 162.1(2C), 153.6, 134.8(2C), 129.1(2C), 124.0(2C), 81.3, 67.0, 48.8, 38.4, 34.5, 28.2(3C), 25.1, 22.9, 22.6, 14.2. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 – 7.82 (m, 2H), 7.82 – 7.71 (m, 2H), 3.74 – 3.65 (m, 1H), 3.51 – 3.39 (m, 1H), 2.58 – 2.49 (m, 1H), 2.45 – 2.34 (m, 1H), 2.33 – 2.23 (m, 1H), 2.14 – 2.05 (m, 1H), 1.99 – 1.86 (m, 2H), 1.50 (s, 9H), 1.44 – 1.27 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 162.1(2C), 153.7, 134.7(2C), 129.2(2C), 123.9(2C), 80.3, 67.4, 48.6, 36.5, 33.6, 28.6(3C), 25.5, 23.6, 22.9, 14.2. **Mp** 117 – 118 °C. **IR (ATR)**: ν = 1814, 1787, 1742, 1688 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{22}H_{28}N_2O_6^+$: 417.2020, found: 417.2017.

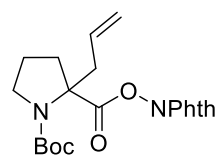
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) 2-phenethylpyrrolidine-1,2-dicarboxylate (2c): Synthesized according to the procedure B. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (2.09 g, 45% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 – 7.85 (m, 2H), 7.85 – 7.74 (m, 2H), 7.37 – 7.19 (m, 5H), 3.97 – 3.86 (m, 1H), 3.63 – 3.48 (m, 1H), 2.85 – 2.56 (m, 4H), 2.52 – 2.38 (m, 1H), 2.38 – 2.27 (m, 1H), 2.26 – 2.10 (m, 1H), 2.06 – 1.95 (m, 1H), 1.58 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.3, 162.1(2C), 153.6, 141.3, 134.9(2C), 129.1, 128.7(2C), 128.5(2C), 126.3(2C), 124.0(2C), 81.7, 67.0, 48.9, 38.5, 37.1, 29.7, 28.2(3C), 22.7. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 – 7.85 (m, 2H), 7.85 – 7.74 (m, 2H), 7.37 – 7.19 (m, 5H), 3.82 – 3.73 (m, 1H), 3.63 – 3.48 (m, 1H), 2.85 – 2.56 (m, 4H), 2.52 – 2.38 (m, 1H), 2.38 – 2.27 (m, 1H), 2.26 – 2.10 (m, 1H), 2.06 – 1.95 (m, 1H), 1.56 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.9, 161.9(2C), 153.6, 141.3, 134.7(2C), 129.2, 128.6(2C), 128.5(2C), 126.0(2C), 124.0(2C), 80.5, 67.3, 48.6, 36.6, 36.2, 30.1, 28.6(3C), 23.6. **Mp** 137 – 139 °C. **IR (ATR)**: ν = 1814, 1785, 1739, 1685 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{26}H_{28}N_2O_6^+$: 465.2020,



2c

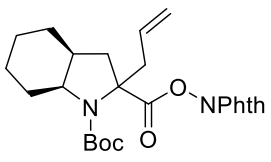
found: 465.2026.

1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) 2-allylpyrrolidine-1,2-dicarboxylate (2d): Synthesized according to the procedure B. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (1.88 g, 47% yield). **The major rotamer**:**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 – 7.82 (m, 2H), 7.81 – 7.73 (m, 2H), 5.81 – 5.66 (m, 1H), 5.25 – 5.18 (m, 2H), 3.84 – 3.73 (m, 1H), 3.48 – 3.34 (m, 1H), 3.14 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.68 (dd, *J* = 14.1, 8.0 Hz, 1H), 2.59 – 2.42 (m, 1H), 2.39 – 2.19 (m, 1H), 2.14 – 2.00 (m, 1H), 1.93 – 1.84 (m, 1H), 1.53 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.1, 161.9(2C), 153.3, 134.9(2C), 131.8, 129.0(2C), 124.0(2C), 120.3, 81.6, 66.4, 48.7, 39.2, 38.0, 28.1(3C), 22.5. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 – 7.82 (m, 2H), 7.81 – 7.73 (m, 2H), 5.81 – 5.66 (m, 1H), 5.18 – 5.11 (m, 2H), 3.71 – 3.61 (m, 1H), 3.48 – 3.34 (m, 1H), 3.28 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.68 (dd, *J* = 14.1, 8.0 Hz, 1H), 2.59 – 2.42 (m, 1H), 2.39 – 2.19 (m, 1H), 2.14 – 2.00 (m, 1H), 1.93 – 1.84 (m, 1H), 1.50 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.8, 161.8(2C), 153.7, 134.7(2C), 132.4, 129.1(2C), 123.9(2C), 119.9, 80.4, 66.9, 48.5, 38.2, 36.0, 28.5(3C), 23.4. **Mp** 109 – 111 ºC. **IR (ATR)**: ν = 1818, 1794, 1748, 1696 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{21}H_{24}N_2O_6^+$: 401.1707, found: 401.1701.



2d

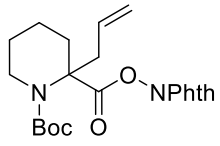
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) 2-allyloctahydro-1*H*-indole-1,2-dicarboxylate (2e): Synthesized according to the procedure B. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil (1.40 g, 32% yield). **The major rotamer**: **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.02 – 7.91 (m, 4H), 5.88 – 5.75 (m, 1H), 5.31 – 5.08 (m, 2H), 3.89 – 3.79 (m, 1H), 2.96 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.80 – 2.52 (m, 2H), 2.22 – 1.97 (m, 2H), 1.68 – 1.54 (m, 3H), 1.49 – 1.36 (m, 11H), 1.34 – 0.99 (m, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 171.3, 161.9(2C), 151.7, 135.6(2C), 132.9,



2e

128.3(2C), 124.1(2C), 119.6, 80.3, 66.1, 58.3, 38.5, 37.6, 33.6, 27.7(3C), 26.2, 25.1, 23.0, 20.2. **The minor rotamer**: **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.02 – 7.91 (m, 4H), 5.88 – 5.75 (m, 1H), 5.31 – 5.08 (m, 2H), 3.79 – 3.69 (m, 1H), 3.08 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.80 – 2.52 (m, 2H), 2.22 – 1.97 (m, 2H), 1.68 – 1.54 (m, 3H), 1.49 – 1.36 (m, 11H), 1.34 – 0.99 (m, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 170.7, 161.9(2C), 152.6, 135.6(2C), 132.9, 128.3(2C), 124.0(2C), 119.4, 79.4, 66.4, 58.3, 38.5, 37.6, 34.7, 28.1(3C), 27.0, 25.2, 23.2, 20.2. **IR (ATR)**: ν = 1813, 1787, 1744, 1693 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{25}H_{30}N_2O_6^+$: 455.2177, found: 455.2168.

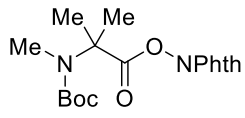
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) 2-allylpiperidine-1,2-dicarboxylate (2f):



2f

Synthesized according to the procedure B. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (1.61 g, 39% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.00 – 7.89 (m, 4H), 5.94 – 5.76 (m, 1H), 5.16 (dd, *J* = 23.9, 13.5 Hz, 2H), 3.73 (d, *J* = 12.7 Hz, 1H), 3.16 – 2.87 (m, 2H), 2.66 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.14 – 1.94 (m, 2H), 1.76 – 1.54 (m, 4H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 170.6, 161.8(2C), 154.5, 135.5(2C), 132.8, 128.3(2C), 123.9(2C), 119.5, 80.9, 61.9, 31.8, 27.8(3C), 22.2, 20.8, 16.7, 14.2. Mp 114 – 116 °C. **IR (ATR)**: ν = 1811, 1785, 1735, 1686 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{22}H_{26}N_2O_6^+$: 415.1864, found: 415.1858.

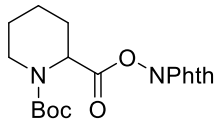
1,3-Dioxoisoindolin-2-yl 2-((tert-butoxycarbonyl)(methyl)amino)-2-methylpropanoate (2g): Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (2.93 g, 81% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.0, 3.1 Hz, 2H), 2.98 (s, 3H), 1.66 (s, 6H), 1.54 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.5, 161.9(2C), 155.2, 134.7(2C), 129.1(2C), 123.9(2C), 82.2, 60.2, 29.6(2C), 28.2(3C), 22.5. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.0, 3.1 Hz, 2H), 2.98 (s, 3H), 1.66 (s, 6H), 1.54 (s, 9H). **^{13}C**



2g

NMR (101 MHz, Chloroform-*d*) δ 171.5, 161.9(2C), 155.2, 134.2(2C), 129.1(2C), 123.4(2C), 82.2, 60.2, 29.6(2C), 28.2(3C), 22.5. This compound is known.[4]

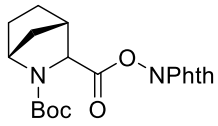
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) piperidine-1,2-dicarboxylate (2h):



2h

Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.34 g, 89% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.92 – 7.83 (m, 2H), 7.82 – 7.74 (m, 2H), 5.12 (s, 1H), 4.06 (d, *J* = 12.5 Hz, 1H), 3.02 (t, *J* = 10.7 Hz, 1H), 2.35 – 2.30 (m, 1H), 1.92 – 1.81 (m, 3H), 1.48 – 1.42 (m, 11H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 168.9, 161.8(2C), 155.2, 134.9(2C), 129.0(2C), 124.1(2C), 81.1, 53.7, 41.3, 28.2(3C), 27.3, 24.5, 20.4. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.92 – 7.83 (m, 2H), 7.82 – 7.74 (m, 2H), 5.37 (s, 1H), 3.97 (d, *J* = 11.2 Hz, 1H), 3.08 (t, *J* = 10.7 Hz, 1H), 2.35 – 2.30 (m, 1H), 1.82 – 1.72 (m, 3H), 1.53 – 1.48 (m, 11H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 168.7, 161.8(2C), 155.5, 134.9(2C), 129.0(2C), 124.1(2C), 80.7, 52.7, 42.3, 28.4(3C), 27.3, 24.9, 20.7. This compound is known.[5]

2-(*tert*-Butyl) 3-(1,3-dioxoisoindolin-2-yl) (1R,3S,4S)-2-azabicyclo[2.2.1]heptane-2,3-dicarboxylate (2i): Synthesized according to the procedure A. The title compound

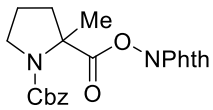


2i

was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.12 g, 81% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 – 7.84 (m, 2H), 7.83 – 7.74 (m, 2H), 4.40 (s, 1H), 4.11 (s, 1H), 3.05 – 2.98 (m, 1H), 2.01 (d, *J* = 10.0 Hz, 1H), 1.89 – 1.76 (m, 2H), 1.73 – 1.59 (m, 2H), 1.48 (s, 9H), 1.40 (d, *J* = 10.5 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.7, 161.8(2C), 153.0, 134.9(2C), 129.1(2C), 124.1(2C), 81.1, 62.4, 56.5, 43.6, 35.1, 30.4, 28.3(3C), 28.0. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 – 7.84 (m, 2H), 7.83 – 7.74 (m, 2H), 4.25 (s, 1H), 4.22 (s, 1H), 3.05 – 2.98 (m, 1H), 2.01 (d, *J* = 10.0 Hz, 1H), 1.89 – 1.76 (m, 2H), 1.73 – 1.59 (m, 2H), 1.47 (s, 9H), 1.40 (d, *J* = 10.5 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ

167.5, 161.7(2C), 153.0, 134.8(2C), 129.1(2C), 124.1(2C), 80.4, 62.2, 57.8, 42.7, 35.9, 30.6, 28.6(3C), 27.7. This compound is known.[3]

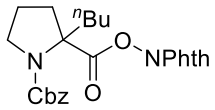
1-Benzyl 2-(1,3-dioxoisoindolin-2-yl) 2-methylpyrrolidine-1,2-dicarboxylate (2j):



2j

Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.21 g, 79% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.87 – 7.75 (m, 2H), 7.74 – 7.65 (m, 2H), 7.34 – 7.19 (m, 5H), 5.15 – 5.03 (m, 2H), 3.75 – 3.49 (m, 2H), 2.69 – 2.48 (m, 1H), 2.12 – 1.97 (m, 2H), 1.95 – 1.85 (m, 1H), 1.58 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.1, 161.8(2C), 154.2, 136.5, 134.9(2C), 129.0, 128.5(2C), 128.3(2C), 128.0(2C), 124.0(2C), 67.6, 64.5, 48.6, 41.1, 23.5, 22.9. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 – 7.75 (m, 2H), 7.74 – 7.65 (m, 2H), 7.34 – 7.19 (m, 5H), 5.41 (d, *J* = 12.3 Hz, 2H), 3.75 – 3.49 (m, 2H), 2.69 – 2.48 (m, 1H), 2.12 – 1.97 (m, 2H), 1.95 – 1.85 (m, 1H), 1.73 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.7, 161.8(2C), 154.3, 136.8, 134.8(2C), 129.1, 128.5(2C), 128.1(2C), 128.0(2C), 124.0(2C), 67.2, 65.2, 47.8, 39.8, 23.4, 22.4. This compound is known.[3]

1-Benzyl 2-(1,3-dioxoisoindolin-2-yl) 2-butylpyrrolidine-1,2-dicarboxylate (2k):

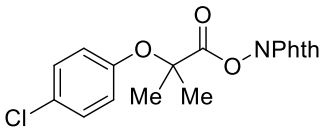


2k

Synthesized according to the procedure B. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (2.07 g, 46% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 – 7.84 (m, 2H), 7.84 – 7.75 (m, 2H), 7.43 – 7.27 (m, 5H), 5.53 – 5.20 (m, 2H), 3.95 – 3.83 (m, 1H), 3.58 – 3.46 (m, 1H), 2.35 – 2.21 (m, 3H), 2.00 – 1.86 (m, 3H), 1.39 – 1.09 (m, 4H), 0.78 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.3, 161.9(2C), 154.4, 136.5, 134.9(2C), 129.1, 128.5(2C), 128.5(2C), 128.1(2C), 124.0(2C), 67.6, 67.3, 49.4, 38.1, 34.6, 25.2, 22.9, 22.7, 14.0.**The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 – 7.84 (m, 2H), 7.84 – 7.75 (m, 2H), 7.43 – 7.27 (m, 5H), 5.20 – 5.03 (m, 2H), 3.83 – 3.74 (m, 1H),

3.58 – 3.46 (m, 1H), 2.59 – 2.50 (m, 3H), 2.17 – 2.04 (m, 3H), 1.39 – 1.09 (m, 4H), 0.94 – 0.86 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.8, 161.9(2C), 154.3, 136.9, 134.8(2C), 129.2, 128.5(2C), 128.5(2C), 128.0(2C), 124.0(2C), 68.2, 67.2, 48.6, 36.4, 33.4, 25.5, 23.4, 22.9, 14.2. **Mp** 95 – 97 ºC. **IR (ATR)**: ν = 1787, 1744, 1701 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{25}H_{26}N_2O_6^+$: 451.1864, found: 451.1858.

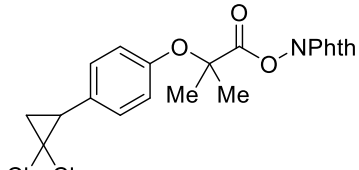
1,3-Dioxoisoindolin-2-yl 2-(4-chlorophenoxy)-2-methylpropanoate (2l):



2l

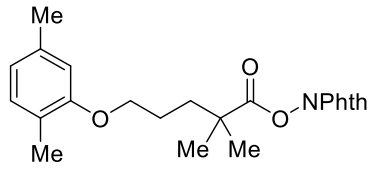
Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.05 g, 85% yield). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.89 (dd, *J* = 5.0, 2.9 Hz, 2H), 7.80 (dd, *J* = 4.9, 2.9 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 1.77 (s, 6H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 170.7, 161.9(2C), 153.3, 135.0(2C), 129.5(2C), 129.0(2C), 128.6, 124.2(2C), 121.8(2C), 79.1, 25.7(2C). This compound is known.[4]

1,3-Dioxoisoindolin-2-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (2m): Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.78 g, 87% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.07 – 7.92 (m, 4H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 3.07 (dd, *J* = 8.9, 1.5 Hz, 1H), 2.14 (t, *J* = 8.2 Hz, 1H), 2.05 (dd, *J* = 10.9, 7.9 Hz, 1H), 1.70 (s, 6H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 170.8, 161.9(2C), 153.6, 135.8(2C), 130.0(2C), 129.5, 128.3(2C), 124.2(2C), 119.8(2C), 78.5, 62.0, 34.0, 25.2, 25.2, 24.9. This compound is known.[6]



2m

1,3-Dioxoisoindolin-2-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (2n):



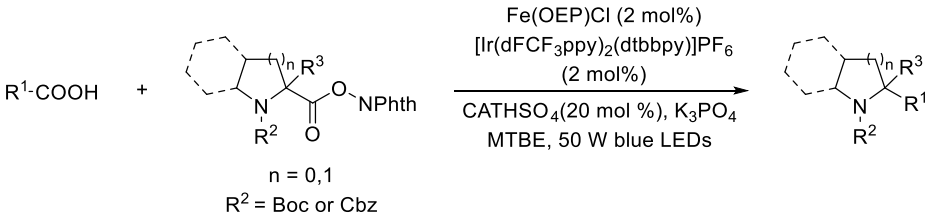
2n

Synthesized according to the procedure A. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil white solid (3.57 g, 91% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.00 – 7.90 (m, 4H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.73 (s, 1H), 6.62 (d, *J* = 7.3 Hz, 1H), 3.97 (t, *J* = 4.7 Hz, 2H), 2.25 (s, 3H), 2.09 (s, 3H), 1.86 (s, 4H), 1.36 (s, 6H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 173.9, 162.1(2C), 156.5, 136.2, 135.7(2C), 130.1, 128.3(2C), 124.1(2C), 122.6, 120.7, 112.2, 67.4, 41.5, 36.5, 24.7(2C), 24.6, 21.1, 15.6. This compound is known.[6]

4. General Procedure and Characterization Data of Products

4.1 General Procedure for Double Decarboxylation Coupling

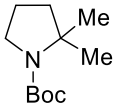


1 **2** **3**

A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1** (0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2** (0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 ℃ by a water bath, and stirred for 12 hours. After completion of the reaction, the solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product.

4.2 Characterization Data of Products

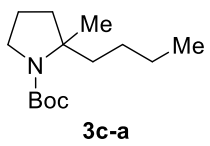
***tert*-Butyl 2,2-dimethylpyrrolidine-1-carboxylate (3b-a)**: Synthesized according to the general procedure from carboxylic acid **1b** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (27.8 mg, 70% yield). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 3.40 (t, *J* = 6.1 Hz, 2H), 1.80



3b-a

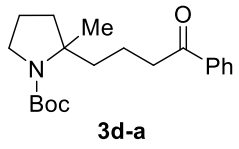
– 1.67 (m, 4H), 1.45 (s, 9H), 1.33 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.3, 78.9, 59.8, 48.2, 42.7, 28.7(3C), 26.9, 21.9(2C). This compound is known.[7]

***tert*-Butyl 2-butyl-2-methylpyrrolidine-1-carboxylate (3c-a)**: Synthesized according to the general procedure from carboxylic acid **1c** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (35.2 mg, 73% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 3.60 – 3.47 (m, 1H), 3.35 – 3.19 (m, 1H), 1.95 – 1.77 (m, 2H), 1.76 – 1.50 (m, 4H), 1.44 (s, 9H), 1.34 – 1.17 (m, 6H), 1.15 – 1.05 (m, 1H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.6, 79.1, 62.3, 48.7, 39.3, 39.2, 28.7(3C), 26.6, 26.4, 23.3, 21.8, 14.3. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 3.46 – 3.37 (m, 1H), 3.35 – 3.19 (m, 1H), 1.95 – 1.77 (m, 2H), 1.76 – 1.50 (m, 4H), 1.44 (s, 9H), 1.34 – 1.17 (m, 6H), 1.15 – 1.05 (m, 1H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 78.3, 62.9, 48.6, 38.3, 38.1, 28.7(3C), 27.1, 24.9, 23.2, 22.2, 14.3. **IR (ATR)**: ν = 1696 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{14}H_{27}NO_2^+$: 242.2115, found: 242.2109.



3c-a

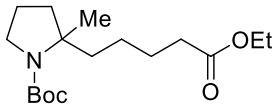
***tert*-Butyl 2-methyl-2-(4-oxo-4-phenylbutyl)pyrrolidine-1-carboxylate (3d-a)**: Synthesized according to the general procedure from carboxylic acid **1d** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (56.3 mg, 85% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.39 (m, 2H), 3.50 – 3.40 (m, 1H), 3.37 – 3.21 (m, 1H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.03 – 1.57 (m, 8H), 1.41 (s, 9H), 1.33 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 200.5, 153.6, 137.1, 133.1, 128.7(2C), 128.1(2C), 78.5, 62.8, 48.6, 39.1, 38.9, 38.2, 28.7(3C), 24.9, 22.2, 19.6. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.39 (m, 2H), 3.60 – 3.50 (m, 1H), 3.37 – 3.21 (m, 1H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.03 – 1.57 (m, 8H), 1.44 (s, 9H), 1.28 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 200.1,



3d-a

154.5, 137.1, 133.0, 128.6(2C), 128.1(2C), 79.2, 62.2, 48.6, 39.3, 38.8, 38.0, 28.7(3C), 26.1, 21.8, 19.6. **IR (ATR)**: ν = 1700, 1688 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{20}H_{29}NO_3^+$: 332.2220, found: 332.2221.

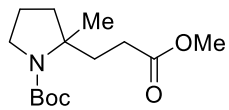
***tert*-Butyl 2-(5-ethoxy-5-oxopentyl)-2-methylpyrrolidine-1-carboxylate (3e-a)**:



3e-a

Synthesized according to the general procedure from carboxylic acid **1e** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (48.9 mg, 78% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.10 (q, *J* = 5.7, 4.3 Hz, 2H), 3.59 – 3.48 (m, 1H), 3.32 – 3.17 (m, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.95 – 1.55 (m, 8H), 1.44 (s, 9H), 1.31 – 1.12 (m, 8H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.7, 154.5, 79.2, 62.2, 60.3, 48.7, 39.3, 39.2, 34.4, 28.7(3C), 26.3, 25.5, 24.1, 21.8, 14.3. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.10 (q, *J* = 5.7, 4.3 Hz, 2H), 3.47 – 3.37 (m, 1H), 3.32 – 3.17 (m, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.95 – 1.55 (m, 8H), 1.40 (s, 9H), 1.31 – 1.12 (m, 8H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.9, 153.5, 78.4, 62.8, 60.2, 48.5, 38.3, 37.9, 34.5, 28.7(3C), 25.4, 24.9, 24.3, 22.2, 14.3. **IR (ATR)**: ν = 1737, 1695 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{17}H_{31}NO_4^+$: 314.2326, found: 314.2327.

***tert*-Butyl 2-(3-methoxy-3-oxopropyl)-2-methylpyrrolidine-1-carboxylate (3f-a)**:

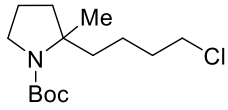


3f-a

Synthesized according to the general procedure from carboxylic acid **1f** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (37.2 mg, 68% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 3.65 (s, 3H), 3.60 – 3.50 (m, 1H), 3.34 – 3.20 (m, 1H), 2.29 – 2.16 (m, 3H), 1.96 – 1.60 (m, 5H), 1.45 (s, 9H), 1.29 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 174.3, 154.3, 79.7, 61.7, 51.7, 48.7, 39.1, 34.4, 29.7, 28.6(3C), 26.2, 21.6. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 3.65 (s, 3H), 3.50 – 3.39 (m, 1H), 3.34 – 3.20 (m, 1H), 2.29 – 2.16 (m, 3H), 1.96 – 1.60 (m, 5H), 1.45 (s, 9H), 1.33 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 174.3, 153.5,

78.8, 62.3, 51.7, 48.5, 38.2, 33.3, 30.0, 28.6(3C), 24.8, 22.0. **IR (ATR)**: ν = 1741, 1697 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{14}H_{25}NO_4^+$: 272.1856, found: 272.1855.

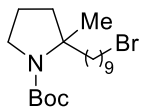
***tert*-Butyl 2-(4-chlorobutyl)-2-methylpyrrolidine-1-carboxylate (3g-a)**:



3g-a

Synthesized according to the general procedure from carboxylic acid **1g** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (39.6 mg, 72% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 3.62 – 3.40 (m, 3H), 3.35 – 3.19 (m, 1H), 1.96 – 1.80 (m, 2H), 1.78 – 1.53 (m, 6H), 1.49 – 1.35 (m, 10H), 1.34 – 1.19 (m, 4H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.5, 79.2, 62.2, 48.7, 44.9, 39.3, 38.7, 33.1, 28.7(3C), 26.3, 21.8, 21.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 3.62 – 3.40 (m, 3H), 3.35 – 3.19 (m, 1H), 1.96 – 1.80 (m, 2H), 1.78 – 1.53 (m, 6H), 1.49 – 1.35 (m, 10H), 1.34 – 1.19 (m, 4H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.5, 78.5, 62.7, 48.6, 45.2, 38.2, 37.5, 32.9, 28.7(3C), 24.9, 22.2, 22.0. **IR (ATR)**: ν = 1693, 740 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{14}H_{26}ClNO_2^+$: 276.1725, found: 276.1726.

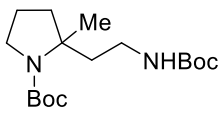
***tert*-Butyl 2-(9-bromononyl)-2-methylpyrrolidine-1-carboxylate (3h-a)**:



3h-a

Synthesized according to the general procedure from carboxylic acid **1h** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (36.3 mg, 47% yield). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 3.58 – 3.44 (m, 1H), 3.38 (t, *J* = 6.9 Hz, 2H), 3.34 – 3.20 (m, 1H), 1.96 – 1.54 (m, 8H), 1.49 – 1.36 (m, 11H), 1.34 – 1.19 (m, 12H), 1.17 – 1.06 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.4, 78.8, 62.6, 48.7, 39.1(2C), 34.1, 32.9, 30.1, 29.7, 29.5, 28.9, 28.7(3C), 28.3, 26.1, 24.5, 22.0. **IR (ATR)**: ν = 1695, 646 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{19}H_{36}BrNO_2^+$: 390.2002, found: 390.1996.

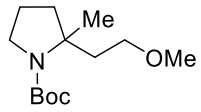
***tert*-Butyl 2-(2-((*tert*-butoxycarbonyl)amino)ethyl)-2-methylpyrrolidine-1-carboxylate (3i-a)**: Synthesized according to the general procedure from carboxylic acid **1i** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (48.6 mg, 74% yield).



3i-a

The major rotamer: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.70 (s, 1H), 3.42 (s, 1H), 3.34 – 3.05 (m, 2H), 2.96 (s, 1H), 2.15 – 1.82 (m, 3H), 1.77 – 1.59 (m, 3H), 1.54 – 1.34 (m, 18H), 1.29 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 156.1, 154.3, 79.5, 78.8, 61.8, 48.4, 39.6, 38.7, 37.0, 28.7(3C), 28.5(3C), 25.0, 22.0. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.54 (s, 1H), 3.51 (s, 1H), 3.34 – 3.05 (m, 2H), 2.96 (s, 1H), 2.15 – 1.82 (m, 3H), 1.77 – 1.59 (m, 3H), 1.54 – 1.34 (m, 18H), 1.27 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 155.9, 153.8, 79.2, 78.9, 61.2, 48.4, 39.5, 38.1, 37.0, 28.7(3C), 28.5(3C), 26.1, 21.7. **Mp** 72 – 74 ºC. **IR (ATR)**: ν = 3369, 1712, 1676, 1515 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{17}H_{32}N_2O_4^+$: 329.2435, found: 329.2436.

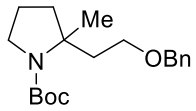
***tert*-Butyl 2-(2-methoxyethyl)-2-methylpyrrolidine-1-carboxylate (3j-a)**: Synthesized according to the general procedure from carboxylic acid **1j** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (30.7 mg, 63% yield).



3j-a

The major rotamer: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 3.53 – 3.17 (m, 7H), 2.16 – 1.84 (m, 3H), 1.72 – 1.58 (m, 3H), 1.42 (s, 9H), 1.25 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.4, 79.4, 69.7, 61.1, 58.7, 48.4, 39.8, 38.7, 28.6(3C), 26.4, 21.7. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 3.53 – 3.17 (m, 7H), 2.16 – 1.84 (m, 3H), 1.72 – 1.58 (m, 3H), 1.38 (s, 9H), 1.30 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 78.5, 69.9, 61.7, 58.5, 48.3, 39.0, 37.4, 28.6(3C), 25.1, 22.1. **IR (ATR)**: ν = 1694, 1253 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{13}H_{25}NO_3^+$: 244.1907, found: 244.1906.

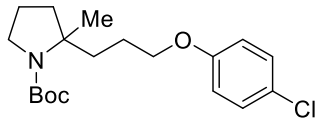
***tert*-Butyl 2-(2-(benzyloxy)ethyl)-2-methylpyrrolidine-1-carboxylate (3k-a)**:



3k-a

Synthesized according to the general procedure from carboxylic acid **1k** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (40.9 mg, 64% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.35 – 7.13 (m, 5H), 4.41 (s, 2H), 3.52 – 3.14 (m, 4H), 2.22 – 1.87 (m, 3H), 1.71 – 1.55 (m, 3H), 1.38 (s, 9H), 1.23 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5, 138.5, 128.5(2C), 127.6(3C), 79.4, 73.2, 67.4, 61.2, 48.5, 40.0, 38.9, 28.7(3C), 26.5, 21.7. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.35 – 7.13 (m, 5H), 4.41 (s, 2H), 3.52 – 3.14 (m, 4H), 2.22 – 1.87 (m, 3H), 1.71 – 1.55 (m, 3H), 1.35 (s, 9H), 1.29 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.6, 138.7, 128.4(2C), 127.6(2C), 127.5, 78.6, 73.0, 67.7, 61.9, 48.4, 39.1, 37.6, 28.7(3C), 25.2, 22.2. **IR (ATR)**: ν = 1693, 1253 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{19}H_{29}NO_3^+$: 320.2220, found: 320.2219.

***tert*-Butyl 2-(3-(4-chlorophenoxy)propyl)-2-methylpyrrolidine-1-carboxylate (3l-a)**:

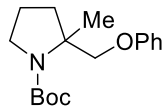


3l-a

Synthesized according to the general procedure from carboxylic acid **1l** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (51.5 mg, 73% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.15 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.91 (t, *J* = 5.8 Hz, 2H), 3.63 – 3.53 (m, 1H), 3.38 – 3.22 (m, 1H), 2.07 – 1.63 (m, 8H), 1.47 (s, 9H), 1.30 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.7, 154.4, 129.4(2C), 125.5, 115.8(2C), 79.3, 68.6, 62.0, 48.7, 39.3, 36.0, 28.7(3C), 26.4, 24.5, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.15 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.91 (t, *J* = 5.8 Hz, 2H), 3.52 – 3.42 (m, 1H), 3.38 – 3.22 (m, 1H), 2.07 – 1.63 (m, 8H), 1.43 (s, 9H), 1.35 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.7, 153.6, 129.3(2C), 125.3, 115.8(2C), 78.6, 68.6, 62.6, 48.6, 38.3, 34.5, 28.7(3C), 24.9, 24.7, 22.2. **IR (ATR)**: ν = 1693, 1254 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{19}H_{28}ClNO_3^+$: 354.1830, found:

354.1831.

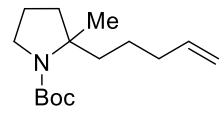
***tert*-Butyl 2-methyl-2-(phenoxymethyl)pyrrolidine-1-carboxylate (3m-a)**:



3m-a

Synthesized according to the general procedure from carboxylic acid **1m** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (29.2 mg, 50% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.11 (m, 2H), 6.92 – 6.76 (m, 3H), 4.02 (d, *J* = 8.6 Hz, 1H), 3.89 (d, *J* = 8.6 Hz, 1H), 3.55 – 3.29 (m, 2H), 2.28 – 2.14 (m, 1H), 1.82 – 1.66 (m, 3H), 1.34 (s, 9H), 1.32 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.2, 154.4, 129.5(2C), 120.8, 114.7(2C), 79.7, 71.9, 61.9, 48.9, 38.4, 28.7(3C), 23.3, 21.7. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.11 (m, 2H), 6.92 – 6.76 (m, 3H), 4.24 (d, *J* = 8.8 Hz, 1H), 3.98 (d, *J* = 8.8 Hz, 1H), 3.55 – 3.29 (m, 2H), 2.28 – 2.14 (m, 1H), 1.82 – 1.66 (m, 3H), 1.38 (s, 3H), 1.34 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.3, 153.8, 129.4(2C), 120.6, 115.0(2C), 78.9, 71.4, 62.6, 48.8, 37.4, 28.7(3C), 22.3, 22.2. **IR (ATR)**: ν = 1694, 1246 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{17}H_{25}NO_3^+$: 292.1907, found: 292.1902.

***tert*-Butyl 2-methyl-2-(pent-4-en-1-yl)pyrrolidine-1-carboxylate (3n-a)**:

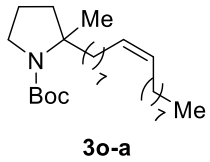


3n-a

Synthesized according to the general procedure from carboxylic acid **1n** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (29.9 mg, 59% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.85 – 5.73 (m, 1H), 5.05 – 4.87 (m, 2H), 3.60 – 3.49 (m, 1H), 3.35 – 3.20 (m, 1H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.96 – 1.78 (m, 2H), 1.75 – 1.67 (m, 2H), 1.67 – 1.51 (m, 2H), 1.45 (s, 9H), 1.36 – 1.22 (m, 5H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.6, 138.9, 114.7, 79.2, 62.3, 48.7, 39.3, 39.0, 34.3, 28.7(3C), 26.3, 23.9, 21.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.85 – 5.73 (m, 1H), 5.05 – 4.87 (m, 2H), 3.48 – 3.37 (m, 1H), 3.35 – 3.20 (m, 1H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.96 – 1.78 (m, 2H), 1.75 – 1.67 (m, 2H), 1.67 – 1.51 (m, 2H), 1.42 (s, 9H), 1.36 – 1.22 (m, 5H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.5, 139.2, 114.4,

78.4, 62.9, 48.6, 38.4, 37.9, 34.2, 28.7(3C), 25.0, 24.3, 22.2. **IR (ATR)**: ν = 3077, 1696, 1642, 992, 909 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{15}H_{27}NO_2{}^+$: 254.2115, found: 254.2114.

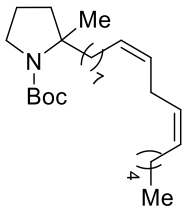
***tert*-Butyl (Z)-2-(heptadec-8-en-1-yl)-2-methylpyrrolidine-1-carboxylate (3o-a)**:



3o-a

Synthesized according to the general procedure from carboxylic acid **1o** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (53.6 mg, 64% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.45 – 5.25 (m, 2H), 3.53 (s, 1H), 3.27 (s, 1H), 2.04 – 1.58 (m, 9H), 1.44 (s, 9H), 1.38 – 1.00 (m, 26H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.6, 130.1, 129.9, 79.1, 62.4, 48.7, 39.6, 39.3, 32.0, 30.3, 29.9(2C), 29.7, 29.7, 29.4(3C), 28.7(3C), 27.3(2C), 26.4, 24.4, 22.8, 21.8, 14.2. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.45 – 5.25 (m, 2H), 3.45 (s, 1H), 3.27 (s, 1H), 2.04 – 1.58 (m, 9H), 1.44 (s, 9H), 1.38 – 1.00 (m, 26H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.5, 130.0, 130.0, 78.4, 63.0, 48.6, 38.4(2C), 32.0, 30.1, 29.9(2C), 29.7, 29.7, 29.4(3C), 28.7(3C), 27.3(2C), 25.0, 24.8, 22.8, 22.3, 14.2. **IR (ATR)**: ν = 3059, 1698, 724 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{27}H_{51}NO_2{}^+$: 422.3993, found: 422.3983.

***tert*-Butyl 2-((8E,11E)-heptadeca-8,11-dien-1-yl)-2-methylpyrrolidine-1-carboxylate (3p-a)**: Synthesized according to the general procedure from carboxylic acid **1p** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (49.5 mg, 59% yield).

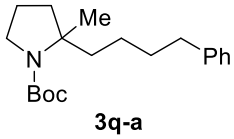


3p-a

The major rotamer: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.41 – 5.27 (m, 4H), 3.58 – 3.51 (m, 1H), 3.33 – 3.21 (m, 1H), 2.76 (t, *J* = 6.9 Hz, 2H), 2.04 (q, *J* = 6.9 Hz, 4H), 1.95 – 1.77 (m, 2H), 1.73 – 1.68 (m, 2H), 1.65 – 1.50 (m, 2H), 1.46 (s, 9H), 1.36 – 1.22 (m, 19H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.6, 130.3(2C), 128.1, 128.0, 79.1, 62.4, 48.7, 39.6, 39.3, 31.7, 30.3, 29.8, 29.7, 29.5, 29.5, 28.8(3C), 27.4, 27.3, 26.4, 25.8, 24.4, 22.7, 21.8, 14.2. **The**

minor rotamer: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.41 – 5.27 (m, 4H), 3.46 – 3.40 (m, 1H), 3.33 – 3.21 (m, 1H), 2.76 (t, *J* = 6.9 Hz, 2H), 2.04 (q, *J* = 6.9 Hz, 4H), 1.95 – 1.77 (m, 2H), 1.73 – 1.68 (m, 2H), 1.65 – 1.50 (m, 2H), 1.42 (s, 9H), 1.36 – 1.22 (m, 19H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.5, 130.2(2C), 128.1, 128.0, 78.4, 63.0, 48.6, 38.4, 38.4, 31.7, 30.1, 29.8, 29.8, 29.5, 29.4, 28.8(3C), 27.4, 27.3, 25.8, 25.0, 24.8, 22.7, 22.3, 14.2. **IR (ATR)**: ν = 3078, 1696, 980 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{27}H_{49}NO_2^+$: 420.3836, found: 420.3828.

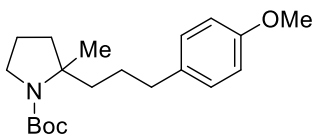
***tert*-Butyl 2-methyl-2-(4-phenylbutyl)pyrrolidine-1-carboxylate (3q-a)**:



3q-a

Synthesized according to the general procedure from carboxylic acid **1q** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (43.1 mg, 68% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.22 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 3H), 3.61 – 3.50 (m, 1H), 3.37 – 3.19 (m, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.97 – 1.58 (m, 8H), 1.45 (s, 9H), 1.35 – 1.16 (m, 5H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5, 142.7, 128.4(2C), 128.4(2C), 125.8, 79.1, 62.3, 48.7, 39.4, 39.3, 36.1, 32.2, 28.7(3C), 26.3, 24.2, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.22 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 3H), 3.49 – 3.39 (m, 1H), 3.37 – 3.19 (m, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.97 – 1.58 (m, 8H), 1.43 (s, 9H), 1.35 – 1.16 (m, 5H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 142.9, 128.5(2C), 128.3(2C), 125.6, 78.4, 62.9, 48.6, 38.3, 38.1, 36.1, 31.9, 28.7(3C), 25.0, 24.5, 22.2. **IR (ATR)**: ν = 1695 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{20}H_{31}NO_2^+$: 318.2428, found: 318.2429.

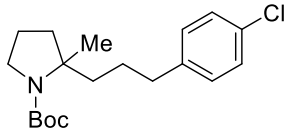
***tert*-Butyl 2-(3-(4-methoxyphenyl)propyl)-2-methylpyrrolidine-1-carboxylate (3r-a)**: Synthesized according to the general procedure from carboxylic acid **1r** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (60.1 mg, 81% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.07 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.77 (s, 3H), 3.59



3r-a

– 3.50 (m, 1H), 3.35 – 3.17 (m, 1H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.02 – 1.49 (m, 8H), 1.42 (s, 9H), 1.25 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.8, 154.5, 134.6, 129.4(2C), 113.8(2C), 79.1, 62.2, 55.3, 48.6, 39.3, 39.1, 35.5, 28.7(3C), 26.7, 26.3, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.07 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.77 (s, 3H), 3.48 – 3.40 (m, 1H), 3.35 – 3.17 (m, 1H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.02 – 1.49 (m, 8H), 1.44 (s, 9H), 1.33 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.7, 153.5, 135.1, 129.3(2C), 113.8(2C), 78.4, 62.8, 55.3, 48.6, 38.3, 38.1, 35.5, 28.7(3C), 27.3, 25.0, 22.2. **IR (ATR)**: ν = 1692, 1247 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^{+}$ calcd for $C_{20}H_{31}NO_3^{+}$: 334.2377, found: 334.2372.

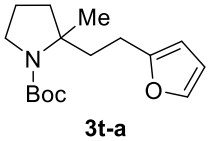
***tert*-Butyl 2-(3-(4-chlorophenyl)propyl)-2-methylpyrrolidine-1-carboxylate (3s-a)**:



3s-a

Synthesized according to the general procedure from carboxylic acid **1s** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (50.6 mg, 75% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.62 – 3.37 (m, 1H), 3.34 – 3.16 (m, 1H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.99 – 1.80 (m, 2H), 1.78 – 1.46 (m, 6H), 1.41 (s, 9H), 1.27 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5, 140.9, 131.6, 129.9(2C), 128.5(2C), 79.1, 62.1, 48.7, 39.4, 39.0, 35.8, 28.7(3C), 26.3(2C), 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.62 – 3.37 (m, 1H), 3.34 – 3.16 (m, 1H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.99 – 1.80 (m, 2H), 1.78 – 1.46 (m, 6H), 1.41 (s, 9H), 1.27 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 141.4, 131.4, 129.9(2C), 128.5(2C), 78.5, 62.8, 48.6, 38.3, 38.0, 35.8, 28.7(3C), 26.9, 25.0, 22.2. **IR (ATR)**: ν = 1678 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^{+}$ calcd for $C_{19}H_{28}ClNO_2^{+}$: 338.1881, found: 338.1878.

***tert*-Butyl 2-(2-(furan-2-yl)ethyl)-2-methylpyrrolidine-1-carboxylate (3t-a)**:

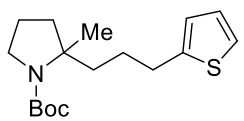


3t-a

Synthesized according to the general procedure from carboxylic acid **1t** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl

acetate (PE/EA = 10:1) as a colorless oil (29.8 mg, 53% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 (s, 1H), 6.27 (s, 1H), 5.96 (d, *J* = 2.4 Hz, 1H), 3.69 – 3.53 (m, 1H), 3.41 – 3.25 (m, 1H), 2.63 – 2.46 (m, 2H), 2.29 – 2.19 (m, 1H), 2.08 – 1.86 (m, 2H), 1.80 – 1.66 (m, 3H), 1.46 (s, 9H), 1.33 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 156.3, 140.9, 110.2(2C), 104.6, 79.5, 62.0, 48.7, 39.2, 37.6, 28.7(3C), 26.3, 23.4, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 (s, 1H), 6.27 (s, 1H), 5.96 (d, *J* = 2.4 Hz, 1H), 3.53 – 3.42 (m, 1H), 3.41 – 3.25 (m, 1H), 2.63 – 2.46 (m, 2H), 2.29 – 2.19 (m, 1H), 2.08 – 1.86 (m, 2H), 1.80 – 1.66 (m, 3H), 1.46 (s, 9H), 1.33 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.5, 140.7, 110.2(2C), 104.6, 78.7, 62.6, 48.6, 38.3, 36.5, 28.7(3C), 24.8, 23.7, 22.2. **IR (ATR)**: ν = 1689 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{16}H_{25}NO_3{}^+$: 280.1907, found: 280.1903.

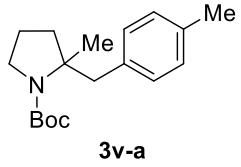
***tert*-Butyl 2-methyl-2-(3-(thiophen-2-yl)propyl)pyrrolidine-1-carboxylate (3u-a)**:



3u-a

Synthesized according to the general procedure from carboxylic acid **1u** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (47.6 mg, 77% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.09 (d, *J* = 5.0 Hz, 1H), 6.90 (dd, *J* = 4.9, 3.5 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 3.59 – 3.40 (m, 1H), 3.37 – 3.21 (m, 1H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.00 – 1.82 (m, 2H), 1.78 – 1.53 (m, 6H), 1.44 (s, 9H), 1.29 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.5, 145.3, 126.8, 124.2, 123.0, 79.2, 62.1, 48.6, 39.4, 39.0, 30.4, 28.7(3C), 26.9, 26.2, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.09 (d, *J* = 5.0 Hz, 1H), 6.90 (dd, *J* = 4.9, 3.5 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 3.59 – 3.40 (m, 1H), 3.37 – 3.21 (m, 1H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.00 – 1.82 (m, 2H), 1.78 – 1.53 (m, 6H), 1.44 (s, 9H), 1.29 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.5, 145.9, 126.7, 124.1, 122.8, 78.5, 62.7, 48.6, 38.3, 37.9, 30.4, 28.7(3C), 27.4, 25.0, 22.2. **IR (ATR)**: ν = 1693 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{17}H_{27}NO_2S^+$: 310.1835, found: 310.1835.

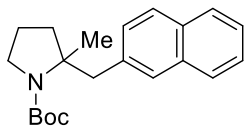
***tert*-Butyl 2-methyl-2-(4-methylbenzyl)pyrrolidine-1-carboxylate (3v-a)**:



3v-a

Synthesized according to the general procedure from carboxylic acid **1v** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (47.4 mg, 82% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.10 – 6.98 (m, 4H), 3.48 – 3.36 (m, 1H), 3.35 – 3.28 (m, 1H), 3.25 – 3.12 (m, 1H), 2.80 – 2.67 (m, 1H), 2.31 (s, 3H), 2.04 – 1.94 (m, 1H), 1.63 – 1.48 (m, 11H), 1.46 (s, 3H), 1.25 – 1.16 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.8, 135.9, 135.8, 130.2(2C), 128.7(2C), 78.6, 63.1, 48.6, 43.9, 37.8, 28.8(3C), 26.0, 21.8, 21.1. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.10 – 6.98 (m, 4H), 3.48 – 3.36 (m, 1H), 3.25 – 3.12 (m, 1H), 3.07 – 2.94 (m, 1H), 2.80 – 2.67 (m, 1H), 2.31 (s, 3H), 2.04 – 1.94 (m, 1H), 1.63 – 1.48 (m, 11H), 1.40 (s, 3H), 1.25 – 1.16 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.5, 135.7, 135.5, 130.4(2C), 128.9(2C), 79.5, 63.6, 48.6, 42.7, 39.0, 28.8(3C), 27.1, 21.4, 21.1. **IR (ATR)**: ν = 1699 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{18}H_{27}NO_2^+$: 290.2115, found: 290.2117.

***tert*-Butyl 2-methyl-2-(naphthalen-2-ylmethyl)pyrrolidine-1-carboxylate (3w-a)**:

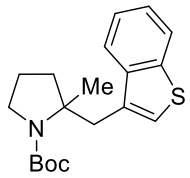


3w-a

Synthesized according to the general procedure from carboxylic acid **1w** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (55.9 mg, 85% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 (dd, *J* = 17.9, 7.7 Hz, 2H), 7.63 (d, *J* = 26.0 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 3.70 (d, *J* = 13.3 Hz, 1H), 3.37 – 3.29 (m, 1H), 3.01 – 2.90 (m, 2H), 2.13 – 2.06 (m, 1H), 1.65 – 1.46 (m, 14H), 1.24 – 1.14 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.9, 136.7, 133.5, 132.2, 129.0, 128.9, 127.6(2C), 127.6, 125.8, 125.3, 78.7, 63.7, 48.6, 43.3, 37.9, 28.8(3C), 26.2, 21.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 (dd, *J* = 17.9, 7.7 Hz, 2H), 7.63 (d, *J* = 26.0 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.50

– 3.39 (m, 2H), 3.23 – 3.14 (m, 1H), 3.01 – 2.90 (m, 1H), 2.13 – 2.06 (m, 1H), 1.65 – 1.46 (m, 14H), 1.24 – 1.14 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.5, 136.4, 133.5, 132.2, 129.3, 128.8, 127.6(2C), 127.3, 125.9, 125.4, 79.6, 63.2, 48.6, 44.6, 39.1, 28.8(3C), 27.2, 21.4. This compound is known.[8]

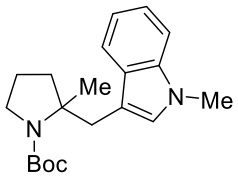
***tert*-Butyl 2-(benzo[*b*]thiophen-3-ylmethyl)-2-methylpyrrolidine-1-carboxylate (3x-a)**: Synthesized according to the general procedure from carboxylic acid **1x** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (59.6 mg, 89% yield).



3x-a

The major rotamer: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.91 – 7.75 (m, 2H), 7.41 – 7.29 (m, 2H), 7.10 (d, *J* = 13.9 Hz, 1H), 3.65 (d, *J* = 14.2 Hz, 1H), 3.37 – 3.32 (m, 1H), 3.21 (d, *J* = 14.2 Hz, 1H), 3.10 – 3.02 (m, 1H), 2.01 – 1.89 (m, 1H), 1.64 – 1.47 (m, 14H), 1.25 – 1.16 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.8, 140.3, 140.0, 133.8, 123.9, 123.8(2C), 122.7, 122.4, 78.8, 63.9, 48.5, 38.6, 35.2, 28.8(3C), 26.0, 21.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.91 – 7.75 (m, 2H), 7.41 – 7.29 (m, 2H), 7.10 (d, *J* = 13.9 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.39 (d, *J* = 14.5 Hz, 1H), 3.27 – 3.16 (m, 2H), 2.01 – 1.89 (m, 1H), 1.64 – 1.47 (m, 14H), 1.33 – 1.25 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.4, 140.2, 140.0, 133.3, 124.0, 123.9(2C), 122.9, 121.9, 79.7, 63.3, 48.7, 39.6, 36.3, 28.8(3C), 27.0, 21.4. **IR (ATR)**: ν = 1665 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{19}H_{25}NO_2S^+$: 332.1679, found: 332.1679.

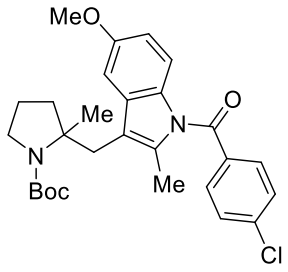
***tert*-Butyl 2-methyl-2-((1-methyl-1*H*-indol-3-yl)methyl)pyrrolidine-1-carboxylate (3y-a)**: Synthesized according to the general procedure from carboxylic acid **1y** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 3:1) as a colorless oil (31.8 mg, 48% yield). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 3.76 (s, 3H), 3.54 – 3.08 (m, 4H), 2.08 – 2.01 (m, 1H), 1.65 – 1.60 (m,



3y-a

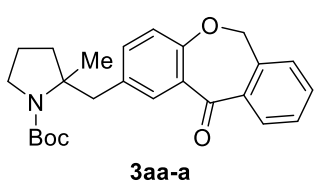
2H), 1.57 (s, 9H), 1.48 (s, 3H), 1.45 – 1.39 (m, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.3, 136.6, 129.3, 128.1, 121.3, 119.2, 118.8, 111.4, 109.1, 79.2, 63.9, 48.8, 39.1, 33.5, 32.8, 28.9(3C), 26.3, 21.7. **IR (ATR)**: ν = 1690, 1328 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{20}H_{28}N_2O_2^+$: 329.2224, found: 329.2224.

***tert*-Butyl 2-((1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)-2-methylpyrrolidine-1-carboxylate (3z-a)**: Synthesized according to the general procedure from carboxylic acid **1z** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil (86.0 mg, 86% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.86 (m, 2H), 6.64 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.82 (s, 3H), 3.53 – 2.93 (m, 4H), 2.31 (s, 3H), 2.08 – 1.94 (m, 1H), 1.69 – 1.39 (m, 15H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.4, 156.0, 153.8, 139.1, 136.0, 134.3, 132.5, 131.2(2C), 131.0, 129.1(2C), 117.6, 114.7, 110.8, 102.7, 78.9, 64.9, 55.9, 48.5, 39.1, 31.7, 28.7(3C), 26.2, 22.3, 14.3. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.86 (m, 2H), 6.64 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.82 (s, 3H), 3.53 – 2.93 (m, 4H), 2.31 (s, 3H), 2.08 – 1.94 (m, 1H), 1.69 – 1.39 (m, 15H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.4, 156.0, 154.4, 139.2, 135.8, 134.2, 132.2, 131.2(2C), 131.0, 129.2(2C), 117.4, 114.9, 111.4, 102.1, 79.7, 64.4, 55.9, 48.5, 39.9, 32.8, 28.8(3C), 27.1, 21.7, 14.3. **IR (ATR)**: ν = 1739, 1684, 1223 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{28}H_{33}ClN_2O_4^+$: 497.2202, found: 497.2196.



3z-a

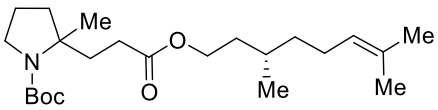
***tert*-Butyl 2-methyl-2-((11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)methyl)pyrrolidine-1-carboxylate (3aa-a)**: Synthesized according to the general procedure from carboxylic acid **1aa** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (66.9 mg, 82% yield). **The major rotamer**: **^{1}H**



3aa-a

NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.15 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.08 (s, 2H), 3.45 – 2.83 (m, 3H), 2.73 (d, *J* = 13.4 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.57 – 1.30 (m, 14H), 1.24 – 1.12 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 191.1, 159.9, 153.7, 140.7, 137.7, 135.7, 133.2(2C), 132.6, 129.5, 129.2, 127.8, 124.8, 120.3, 78.7, 73.6, 63.4, 48.5, 42.2, 37.7, 28.7(3C), 25.9, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.15 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.08 (s, 2H), 3.45 – 2.83 (m, 3H), 2.73 (d, *J* = 13.4 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.57 – 1.30 (m, 14H), 1.24 – 1.12 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 191.0, 160.1, 154.4, 140.5, 137.1, 135.7, 132.8, 132.7, 132.5, 129.6, 129.2, 127.8, 124.9, 120.6, 79.7, 73.7, 62.9, 48.6, 43.4, 39.0, 28.8(3C), 26.9, 21.4. **IR (ATR)**: ν = 1738, 1689, 1242 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{25}H_{29}NO_4^+$: 408.2169, found: 408.2165.

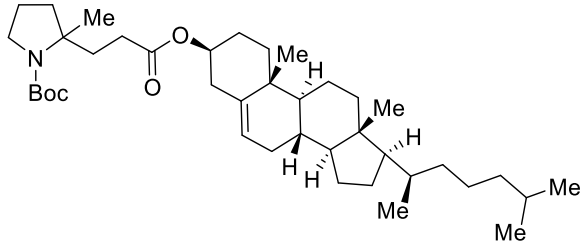
***tert*-Butyl 2-(3-(((S)-3,7-dimethyloct-6-en-1-yl)oxy)-3-oxopropyl)-2-methylpyrrolidine-1-carboxylate (3ab-a)**: Synthesized according to the general procedure from carboxylic acid **1ab** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (33.7 mg, 49% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.07 (t, *J* = 6.5 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.60 – 3.51 (m, 1H), 3.34 – 3.21 (m, 1H), 2.27 – 2.15 (m, 3H), 2.02 – 1.81 (m, 4H), 1.77 – 1.62 (m, 7H), 1.58 (s, 3H), 1.55 – 1.50 (m, 1H), 1.47 – 1.40 (m, 10H), 1.36 – 1.27 (m, 4H), 1.21 – 1.12 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 173.9, 154.3, 131.4, 124.7, 79.6, 63.1, 61.8, 48.6, 39.1, 37.1, 35.6, 34.4, 30.0, 29.6, 28.7(3C), 26.2, 25.8, 25.5, 21.6, 19.5, 17.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.07 (t, *J* = 6.5 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.50 – 3.40 (m, 1H), 3.34 – 3.21 (m, 1H), 2.27 – 2.15 (m, 3H), 2.02 – 1.81 (m, 4H), 1.77 – 1.62 (m, 7H), 1.58 (s, 3H), 1.55 – 1.50 (m, 1H), 1.47 – 1.40 (m, 10H), 1.36 – 1.27 (m, 4H), 1.21 – 1.12 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-**



3ab-a

***d*)** δ 173.9, 153.5, 131.4, 124.7, 78.8, 63.1, 62.3, 48.6, 38.2, 37.1, 35.6, 33.3, 30.2, 29.6, 28.7(3C), 25.8, 25.5, 24.8, 22.1, 19.5, 17.8. **IR (ATR)**: ν = 1736, 1687 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{23}H_{41}NO_4{}^+$: 396.3108, found: 396.3104.

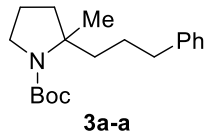
***tert*-Butyl 2-(3-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxopropyl)-2-methylpyrrolidine-1-carboxylate (3ac-a)**: Synthesized according to the general procedure from carboxylic acid **1ac** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (65.2 mg, 52% yield).



3ac-a

The major rotamer: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.36 (d, *J* = 3.2 Hz, 1H), 4.66 – 4.52 (m, 1H), 3.64 – 3.50 (m, 1H), 3.36 – 3.21 (m, 1H), 2.34 – 2.12 (m, 5H), 2.03 – 1.66 (m, 10H), 1.61 – 1.38 (m, 17H), 1.37 – 1.22 (m, 7H), 1.17 – 1.05 (m, 6H), 1.04 – 0.93 (m, 6H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.87 – 0.81 (m, 6H), 0.66 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.3, 154.4, 139.7, 122.8, 79.6, 74.0, 61.8, 56.8, 56.2, 50.1, 48.6, 42.4, 39.8, 39.6, 39.0, 38.2, 37.1, 36.7, 36.3, 35.9, 34.5, 32.0, 32.0, 30.3, 28.7(3C), 28.3, 28.1, 27.9, 26.2, 24.4, 23.9, 22.9, 22.7, 21.7, 21.1, 19.4, 18.8, 12.0. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.36 (d, *J* = 3.2 Hz, 1H), 4.66 – 4.52 (m, 1H), 3.50 – 3.39 (m, 1H), 3.36 – 3.21 (m, 1H), 2.34 – 2.12 (m, 5H), 2.03 – 1.66 (m, 10H), 1.61 – 1.38 (m, 17H), 1.37 – 1.22 (m, 7H), 1.17 – 1.05 (m, 6H), 1.04 – 0.93 (m, 6H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.87 – 0.81 (m, 6H), 0.66 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.3, 153.5, 139.7, 122.8, 78.7, 74.0, 62.3, 56.8, 56.2, 50.1, 48.6, 42.4, 39.8, 39.6, 39.0, 38.2, 37.1, 36.7, 36.3, 35.9, 33.2, 32.0, 32.0, 30.5, 28.7(3C), 28.3, 28.1, 27.9, 24.8, 24.4, 23.9, 22.9, 22.7, 22.0, 21.1, 19.4, 18.8, 12.0. **IR (ATR)**: ν = 1732, 1679 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{40}H_{67}NO_4{}^+$: 626.5143, found: 626.5136.

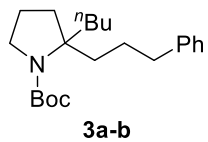
***tert*-Butyl 2-methyl-2-(3-phenylpropyl)pyrrolidine-1-carboxylate (3a-a)**:



3a-a

Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (49.7 mg, 82% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 3.59 – 3.49 (m, 1H), 3.34 – 3.18 (m, 1H), 2.60 (t, *J* = 7.1 Hz, 2H), 2.05 – 1.51 (m, 8H), 1.41 (s, 9H), 1.25 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5, 142.5, 128.5(2C), 128.4(2C), 125.9, 79.1, 62.2, 48.7, 39.4, 39.2, 36.5, 28.7(3C), 26.5, 26.3, 21.8. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 3.49 – 3.39 (m, 1H), 3.34 – 3.18 (m, 1H), 2.60 (t, *J* = 7.1 Hz, 2H), 2.05 – 1.51 (m, 8H), 1.44 (s, 9H), 1.33 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 143.0, 128.5(2C), 128.4(2C), 125.7, 78.5, 62.9, 48.6, 38.3, 38.2, 36.5, 28.7(3C), 27.2, 25.1, 22.2. **IR (ATR)**: ν = 1695 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{19}H_{29}NO_2^+$: 304.2271, found: 304.2268.

***tert*-Butyl 2-butyl-2-(3-phenylpropyl)pyrrolidine-1-carboxylate (3a-b)**:

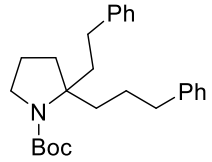


3a-b

Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2b**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (52.4 mg, 76% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.23 (m, 2H), 7.22 – 7.10 (m, 3H), 3.42 (t, *J* = 6.9 Hz, 2H), 2.59 (t, *J* = 5.3 Hz, 2H), 2.08 – 1.48 (m, 10H), 1.40 (s, 9H), 1.32 – 1.09 (m, 4H), 0.89 (t, *J* = 5.5 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5, 142.5, 128.5(2C), 128.4(2C), 125.8, 79.1, 65.0, 49.2, 39.1, 36.6(2C), 36.3, 28.6(3C), 26.5, 26.4, 23.4, 22.2, 14.3. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.23 (m, 2H), 7.22 – 7.10 (m, 3H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.59 (t, *J* = 5.3 Hz, 2H), 2.08 – 1.48 (m, 10H), 1.44 (s, 9H), 1.32 – 1.09 (m, 4H), 0.87 (t, *J* = 4.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 143.1, 128.5(2C), 128.4(2C), 125.7, 78.4, 65.7, 49.1, 39.1, 37.7, 37.6, 34.9, 28.7(3C), 26.9, 26.8, 23.3, 22.5, 14.4. **IR (ATR)**:

ν = 1694 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{22}H_{35}NO_2^+$: 346.2741, found: 346.2735.

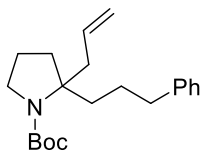
***tert*-Butyl 2-phenethyl-2-(3-phenylpropyl)pyrrolidine-1-carboxylate (3a-c)**:



3a-c

Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2c**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (58.3 mg, 74% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.23 – 7.14 (m, 4H), 7.14 – 7.03 (m, 6H), 3.41 (t, *J* = 6.9 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.48 – 2.33 (m, 2H), 2.11 – 2.01 (m, 1H), 1.99 – 1.62 (m, 7H), 1.56 – 1.44 (m, 2H), 1.34 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.4, 142.7, 142.3, 128.6(4C), 128.4(2C), 128.4(2C), 125.9, 125.8, 79.4, 64.9, 49.3, 41.7, 39.0, 36.6, 36.5, 31.0, 28.7(3C), 26.4, 22.2. **The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.23 – 7.14 (m, 4H), 7.14 – 7.03 (m, 6H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.48 – 2.33 (m, 2H), 2.28 – 2.17 (m, 1H), 1.99 – 1.62 (m, 7H), 1.56 – 1.44 (m, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 142.9, 142.9, 128.5(4C), 128.4(2C), 128.4(2C), 125.8, 125.7, 78.6, 65.7, 49.1, 40.2, 37.7, 36.6, 35.0, 31.2, 28.7(3C), 26.9, 22.6. **IR (ATR)**: ν = 1690 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{26}H_{35}NO_2^+$: 394.2741, found: 394.2737.

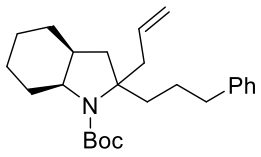
***tert*-Butyl 2-allyl-2-(3-phenylpropyl)pyrrolidine-1-carboxylate (3a-d)**: Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2d**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (40.2 mg, 61% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.34 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 5.74 (dd, *J* = 15.8, 7.8 Hz, 1H), 5.15 – 5.00 (m, 2H), 3.49 – 3.39 (m, 2H), 2.73 – 2.58 (m, 3H), 2.30 – 2.23 (m, 1H), 1.98 – 1.90 (m, 2H), 1.82 – 1.64 (m, 4H), 1.63 – 1.54 (m, 2H), 1.45 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 154.4, 142.4, 134.8, 128.5(2C), 128.4(2C), 125.9, 117.9, 79.4, 64.7, 49.2, 43.7, 38.7, 36.5, 36.0, 28.7(3C),



3a-d

26.2, 21.9. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.34 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 5.74 (dd, *J* = 15.8, 7.8 Hz, 1H), 5.15 – 5.00 (m, 2H), 3.38 – 3.30 (m, 2H), 2.83 (dd, *J* = 12.4, 6.3 Hz, 1H), 2.73 – 2.58 (m, 2H), 2.38 – 2.31 (m, 1H), 2.12 (t, *J* = 12.3 Hz, 1H), 1.90 – 1.82 (m, 2H), 1.82 – 1.64 (m, 3H), 1.63 – 1.54 (m, 2H), 1.48 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.5, 143.0, 135.0, 128.5(2C), 128.4(2C), 125.8, 117.8, 78.6, 65.5, 49.1, 42.2, 37.7, 36.5, 34.6, 28.7(3C), 26.8, 22.4. **IR (ATR)**: ν = 3074, 1692, 1639, 999, 914 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{21}H_{31}NO_2^+$: 330.2428, found: 330.2428.

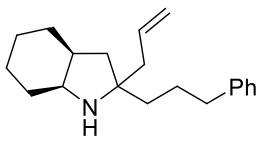
***tert*-Butyl 2-allyl-2-(3-phenylpropyl)octahydro-1*H*-indole-1-carboxylate (3a-e)**:



3a-e

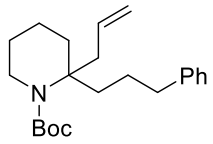
Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2e**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (38.4 mg, 50% yield, dr > 20:1). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.85 – 5.69 (m, 1H), 5.16 – 5.04 (m, 2H), 3.71 – 3.64 (m, 1H), 2.83 (dd, *J* = 13.0, 5.6 Hz, 1H), 2.67 – 2.54 (m, 2H), 2.48 – 2.41 (m, 1H), 2.32 – 2.26 (m, 1H), 2.14 – 2.03 (m, 1H), 2.02 – 1.92 (m, 2H), 1.78 – 1.50 (m, 8H), 1.47 (s, 9H), 1.28 – 1.07 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.3, 143.0, 135.7, 128.5(2C), 128.4(2C), 125.8, 117.8, 78.4, 65.6, 58.5, 42.6, 37.7, 36.7, 36.1, 33.5, 28.7(3C), 28.5, 28.0, 26.3, 24.2, 21.0. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.85 – 5.69 (m, 1H), 5.16 – 5.04 (m, 2H), 3.87 – 3.79 (m, 1H), 2.67 – 2.54 (m, 3H), 2.38 – 2.26 (m, 2H), 2.14 – 2.03 (m, 1H), 2.02 – 1.92 (m, 2H), 1.87 – 1.80 (m, 1H), 1.78 – 1.50 (m, 7H), 1.42 (s, 9H), 1.28 – 1.07 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.9, 142.4, 135.5, 128.6(2C), 128.4(2C), 125.9, 117.9, 79.2, 64.9, 58.6, 44.0, 38.9, 37.4, 36.8, 33.0, 28.7(3C), 27.6, 27.4, 26.2, 23.9, 21.0. **IR (ATR)**: ν = 3072, 1688, 1639, 1000, 913 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{25}H_{37}NO_2^+$: 384.2897, found: 384.2892.

(3aS,7aS)-2-Allyl-2-(3-phenylpropyl)octahydro-1H-indole (3a-e-NH): In order to distinguish the diastereoisomers from the rotamers, the Boc group was removed from the product **3a-e** according to the following procedure. A solution of **3a-e** in DCM (0.20 mL) was treated with trifluoroacetic acid (0.20 mL) at 0 ℃ and the mixture was stirred for 1 h at the same temperature. After dilution with DCM (5.0 mL), pH of the solution was adjusted to 7-8 using saturated aqueous $NaHCO_3$ solution. The combined organic extract was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography to afford the product **3a-e-NH** (PE/EA = 3:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.25 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 3H), 5.87 – 5.73 (m, 1H), 5.07 (d, *J* = 6.1 Hz, 1H), 5.04 (s, 1H), 3.09 (q, *J* = 5.5 Hz, 1H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.28 (d, *J* = 6.2 Hz, 2H), 2.05 (q, *J* = 6.4 Hz, 1H), 1.68 – 1.57 (m, 5H), 1.53 – 1.38 (m, 7H), 1.34 – 1.22 (m, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 142.8, 135.5, 128.5(2C), 128.4(2C), 125.8, 117.5, 62.8, 56.9, 46.4, 41.6, 41.1, 38.6, 36.7, 29.2, 28.0, 26.5, 23.6, 22.2.



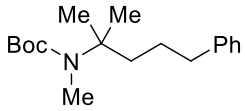
3a-e-NH

***tert*-Butyl 2-allyl-2-(3-phenylpropyl)piperidine-1-carboxylate (3a-f)**: Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2f**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (33.7 mg, 49% yield). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.31 – 7.26 (m, 2H), 7.21 – 7.13 (m, 3H), 5.83 – 5.70 (m, 1H), 5.09 – 5.00 (m, 2H), 3.49 – 3.31 (m, 2H), 2.78 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.67 – 2.52 (m, 2H), 2.39 (dd, *J* = 13.5, 7.7 Hz, 1H), 2.18 – 2.05 (m, 1H), 1.66 – 1.52 (m, 9H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.0, 142.8, 135.2, 128.5(2C), 128.4(2C), 125.8, 117.6, 79.4, 59.5, 42.2, 42.0, 37.7, 36.7, 30.9, 28.7(3C), 26.3, 23.3, 17.8. **IR (ATR)**: ν = 3005, 1687, 1638, 997, 911 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{22}H_{33}NO_2^+$: 344.2584, found: 344.2576.



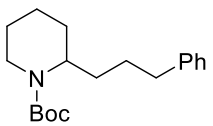
3a-f

***tert*-Butyl methyl(2-methyl-5-phenylpentan-2-yl)carbamate (3a-g)**: Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2g.** The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (30.2 mg, 52% yield). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.17 (m, 2H), 7.15 – 7.05 (m, 3H), 2.76 (s, 3H), 2.51 (t, *J* = 7.7 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.53 – 1.43 (m, 2H), 1.36 (s, 9H), 1.23 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.2, 142.8, 128.5(2C), 128.4(2C), 125.8, 79.3, 57.5, 40.8, 36.5, 32.2, 28.7(3C), 27.9(2C), 26.6. **IR (ATR)**: ν = 1696 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{18}H_{29}NO_2^+$: 292.2271, found: 292.2262.



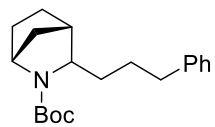
3a-g

***tert*-Butyl 2-(3-phenylpropyl)piperidine-1-carboxylate (3a-h)**: Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2h**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (58.3 mg, 52% yield). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.32 – 7.27 (m, 2H), 7.20 (d, *J* = 5.5 Hz, 3H), 4.27 (s, 1H), 3.98 (s, 1H), 2.78 – 2.61 (m, 3H), 1.77 – 1.71 (m, 1H), 1.68 – 1.53 (m, 7H), 1.48 – 1.38 (m, 11H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 155.3, 142.6, 128.5(2C), 128.4(2C), 125.8, 79.2, 50.3, 38.9, 35.8, 29.3, 28.6(4C), 28.1, 25.8, 19.2. This compound is known.[9]



3a-h

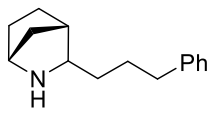
***tert*-Butyl 3-(3-phenylpropyl)-2-azabicyclo[2.2.1]heptane-2-carboxylate (3a-i)**: Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2i.** The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (33.4 mg, 53% yield, dr = 4:1). **The major diastereoisomer 3a-i-1**: **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.29 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 3H), 4.26 – 3.94 (m, 1H), 3.35 – 2.99 (m, 1H), 2.78 – 2.52 (m, 2H), 2.32 (s, 1H), 1.85 – 1.59 (m, 6H), 1.50 – 1.35 (m, 10H), 1.33 – 1.19 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.4, 142.8,



3a-i

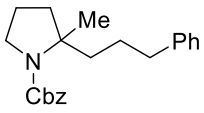
128.5(4C), 125.7, 79.0, 64.8, 57.6, 40.1, 36.2, 34.9, 33.8, 30.5, 29.1, 28.7(3C), 27.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.29 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 3H), 4.26 – 3.94 (m, 1H), 3.35 – 2.99 (m, 1H), 2.78 – 2.52 (m, 2H), 2.32 (s, 1H), 1.85 – 1.59 (m, 6H), 1.50 – 1.35 (m, 10H), 1.33 – 1.19 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.9, 142.5, 128.4(2C), 128.4(2C), 125.9, 79.1, 64.8, 56.6, 40.8, 36.1, 34.3, 34.0, 30.0, 28.9, 28.6(3C), 28.0. **The minor diastereoisomer 3a-i-2**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.31 – 7.26 (m, 2H), 7.18 (d, *J* = 7.1 Hz, 3H), 4.37 – 4.17 (m, 1H), 3.62 – 3.37 (m, 1H), 2.76 – 2.51 (m, 2H), 2.45 (s, 1H), 2.35 – 2.02 (m, 1H), 1.64 – 1.26 (m, 18H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.9, 142.5, 128.5(2C), 128.4(2C), 125.9, 78.9, 60.8, 58.6, 57.8, 40.2, 39.7, 38.5, 36.2, 30.1, 28.7(3C), 21.3. **IR (ATR)**: ν = 1693 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{20}H_{29}NO_2^+$: 316.2271, found: 316.2269.

(1R,4S)-3-(3-Phenylpropyl)-2-azabicyclo[2.2.1]heptane (3a-i-1-NH): In order to distinguish the diastereoisomers from the rotamers, the Boc group was removed from the product **3a-i-1** according to the following procedure. A solution of compound **3a-i-1** in DCM (0.20 mL) was treated with trifluoroacetic acid (0.20 mL) at 0 ℃ and the mixture was stirred for 1 h at the same temperature. After dilution with DCM (5.0 mL), pH of the solution was adjusted to 7 – 8 using saturated aqueous $NaHCO_3$ solution. The combined organic extract was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography to afford the product **3a-i-1-NH**. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.23 (m, 2H), 7.19 – 7.12 (m, 3H), 3.65 (s, 1H), 3.03 (t, *J* = 6.6 Hz, 1H), 2.57 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 1H), 1.85 (d, *J* = 10.9 Hz, 1H), 1.72 – 1.44 (m, 8H), 1.37 (d, *J* = 10.9 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 141.9, 128.5(2C), 128.5(2C), 126.0, 63.6, 57.2, 40.3, 35.6, 34.9, 33.5, 28.3(2C), 27.3.



3a-i-1-NH

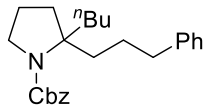
Benzyl 2-methyl-2-(3-phenylpropyl)pyrrolidine-1-carboxylate (3a-j): Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2j**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate



3a-j

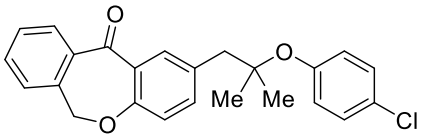
(PE/EA = 15:1) as a colorless oil (49.2 mg, 70% yield). **The major rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.37 – 7.22 (m, 7H), 7.20 – 7.06 (m, 3H), 5.18 – 5.02 (m, 2H), 3.59 – 3.51 (m, 1H), 3.42 – 3.30 (m, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.97 – 1.83 (m, 2H), 1.82 – 1.41 (m, 6H), 1.37 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.7, 142.8, 137.5, 128.5(2C), 128.4(4C), 128.3, 127.7(2C), 125.8, 66.0, 63.5, 48.2, 38.1, 38.1, 36.4, 27.0, 24.8, 22.4.**The minor rotamer**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.37 – 7.22 (m, 7H), 7.20 – 7.06 (m, 3H), 5.18 – 5.02 (m, 2H), 3.65 – 3.59 (m, 1H), 3.42 – 3.30 (m, 1H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.97 – 1.83 (m, 2H), 1.82 – 1.41 (m, 6H), 1.26 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.0, 142.4, 137.0, 128.5(2C), 128.5(4C), 128.0, 127.8(2C), 125.8, 66.8, 62.9, 49.3, 39.3, 39.1, 36.2, 26.4, 26.3, 22.0. **IR (ATR)**: ν = 1700 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{22}H_{27}NO_2^+$: 338.2115, found: 338.2112.

Benzyl 2-butyl-2-(3-phenylpropyl)pyrrolidine-1-carboxylate (3a-k): Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2k**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (59.3 mg, 78% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.29 – 7.13 (m, 7H), 7.10 – 6.99 (m, 3H), 5.07 – 4.95 (m, 2H), 3.36 (t, *J* = 6.9 Hz, 2H), 2.55 – 2.44 (m, 2H), 2.00 – 1.91 (m, 1H), 1.90 – 1.83 (m, 1H), 1.79 – 1.34 (m, 8H), 1.22 – 0.95 (m, 4H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 153.6, 142.8, 137.6, 128.4(4C), 128.3(3C), 127.6(2C), 125.7, 66.3, 65.9, 48.7, 37.6, 37.5, 36.5, 34.7, 26.8, 26.7, 23.2, 22.7, 14.3. **The minor rotamer: ^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.29 – 7.13 (m, 7H), 7.10 – 6.99 (m, 3H), 5.07 – 4.95 (m, 2H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.42 – 2.35 (m, 2H), 1.79 – 1.34 (m, 10H), 1.22 – 0.95 (m, 4H), 0.73 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 155.0, 142.4, 137.0, 128.5(2C), 128.4(2C), 128.3(2C), 128.0, 127.7(2C), 125.8, 66.7, 65.7, 49.8, 38.9, 38.9, 36.3, 36.1, 26.5, 26.3, 23.2, 22.3, 14.2. **IR (ATR)**: ν = 1702 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{25}H_{33}NO_2^+$: 380.2584, found: 380.2588.



3a-k

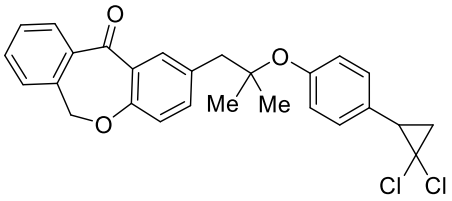
2-(2-(4-Chlorophenoxy)-2-methylpropyl)dibenzo[*b*,*e*]oxepin-11(6*H*)-one (3aa-l):



3aa-l

Synthesized according to the general procedure from carboxylic acid **1aa** and redox-active ester **2l**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 20:1) as a colorless oil (37.6 mg, 48% yield). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (d, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.19 (s, 2H), 2.98 (s, 2H), 1.25 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 191.2, 160.2, 153.9, 140.7, 138.0, 135.7, 133.4, 132.8, 131.8, 129.6, 129.3, 129.0(2C), 128.7, 127.9, 125.4(2C), 124.8, 120.3, 81.0, 73.7, 47.9, 26.3(2C). **IR (ATR)**: ν = 1648, 1262, 1221, 733 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{24}H_{21}ClO_3^+$: 391.1106, found: 391.1110.

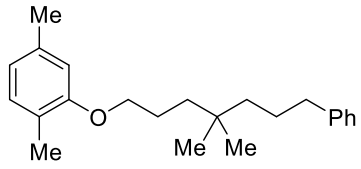
2-(2-(4-(2,2-Dichlorocyclopropyl)phenoxy)-2-methylpropyl)dibenzo[*b*,*e*]oxepin-11(6*H*)-one (3aa-m): Synthesized according to the general procedure from carboxylic acid **1aa** and redox-active ester **2m**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 20:1) as a colorless oil (41.2 mg, 44% yield).



3aa-m

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.19 (s, 2H), 3.00 (s, 2H), 2.89 – 2.81 (m, 1H), 1.94 (dd, *J* = 10.3, 7.6 Hz, 1H), 1.79 (t, *J* = 7.8 Hz, 1H), 1.27 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 191.2, 160.2, 154.8, 140.7, 138.1, 135.8, 133.4, 132.8, 132.0, 129.6, 129.5(3C), 129.3, 127.9, 124.8, 123.8(2C), 120.3, 80.7, 73.7, 61.0, 48.0, 35.0, 26.4(2C), 26.0. **IR (ATR)**: ν = 1648, 1262, 1221, 733 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{27}H_{24}Cl_2O_3^+$: 465.1031, found: 465.1030.

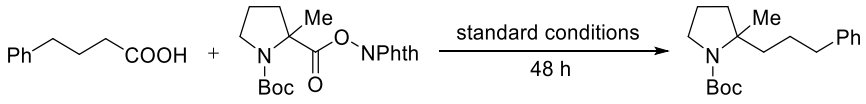
2-((4,4-Dimethyl-7-phenylheptyl)oxy)-1,4-dimethylbenzene (3an): Synthesized according to the general procedure from carboxylic acid **1a** and redox-active ester **2n**. The title compound was isolated by column chromatography eluting with petroleum ether as a colorless oil (29.8 mg, 46% yield).



3an

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H), 2.18 (s, 3H), 1.77 – 1.66 (m, 2H), 1.65 – 1.57 (m, 2H), 1.38 – 1.32 (m, 2H), 1.31 – 1.25 (m, 2H), 0.89 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.2, 143.0, 136.6, 130.4, 128.5(2C), 128.4(2C), 125.8, 123.7, 120.7, 112.1, 68.8, 41.7, 38.1, 37.0, 32.6, 27.4(2C), 26.3, 24.4, 21.6, 16.0. **IR (ATR)**: ν = 1265 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^{+}$ calcd for $C_{23}H_{32}O^{+}$: 325.2526, found: 325.2520.

5. Gram-Scale Reaction



1a (6 mmol) **2a** **3a-a** 1.03 g, 57%

An 250 mL flask equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1a** (0.98 g, 6.0 mmol), K_3PO_4 (1.3 g, 6.0 mmol), and dry MTBE (90 mL) was added. Then the reaction mixture was stirred at room temperature for 1 hours before removing the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2a** (4.5 g, 12 mmol), Fe(OEP)Cl (72.0 mg, 0.12 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (0.13 g, 0.12 mmol), $CTAHSO_4$ (0.47 g, 1.2 mmol), and MTBE (90 mL) were added. The reaction mixture was transferred out of the glovebox and irradiated with a 50 W blue LEDs lamp, then stirred for 48 hours. After completion of the reaction, the solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **3a-a** (1.03 g, 57% yield).

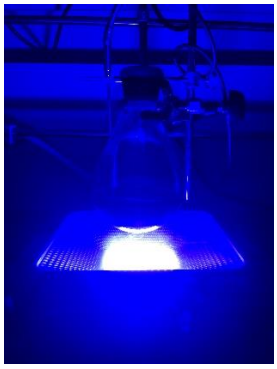
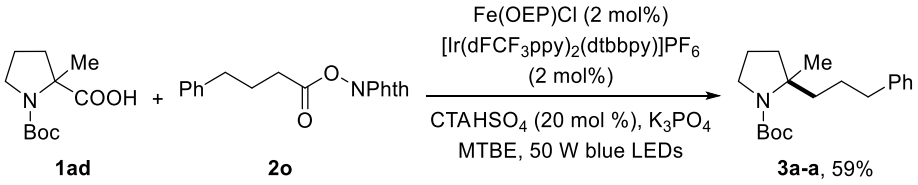


Figure S3. Gram-Scale Reaction.

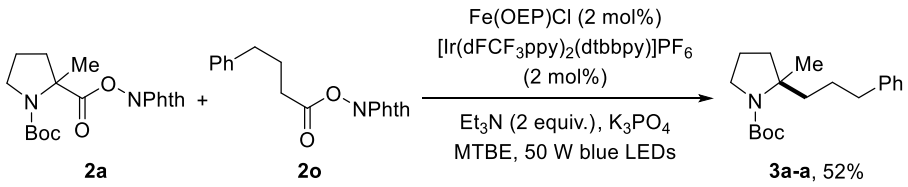
6. Other Methods for Double Decarboxylative Coupling

6.1 Double Decarboxylative Coupling of N-Boc α-Methylproline and Redox-Active Ester



A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1ad** (46.8 mg, 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2o** (0.13 g, 0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 ℃ by a water bath, and stirred for 12 hours. After completion of the reaction, the solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **3a-a**.

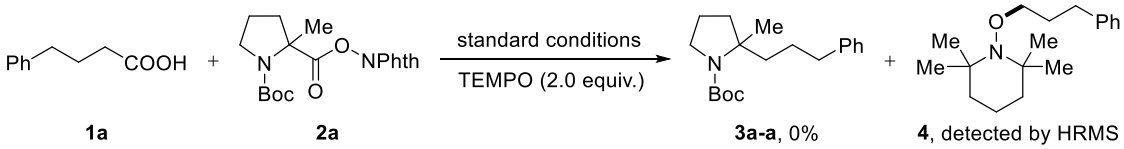
6.2 Double Decarboxylative Coupling of Redox-Active Esters



In a N_2-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **2a** (75.0 mg, 0.20 mmol), **2o** (62.0 mg, 0.20 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), Et_3N (41.0 mg, 56 μL, 0.40 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 ℃ by a water bath, and stirred for 24 hours. After completion of the reaction, the solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **3a-a**.

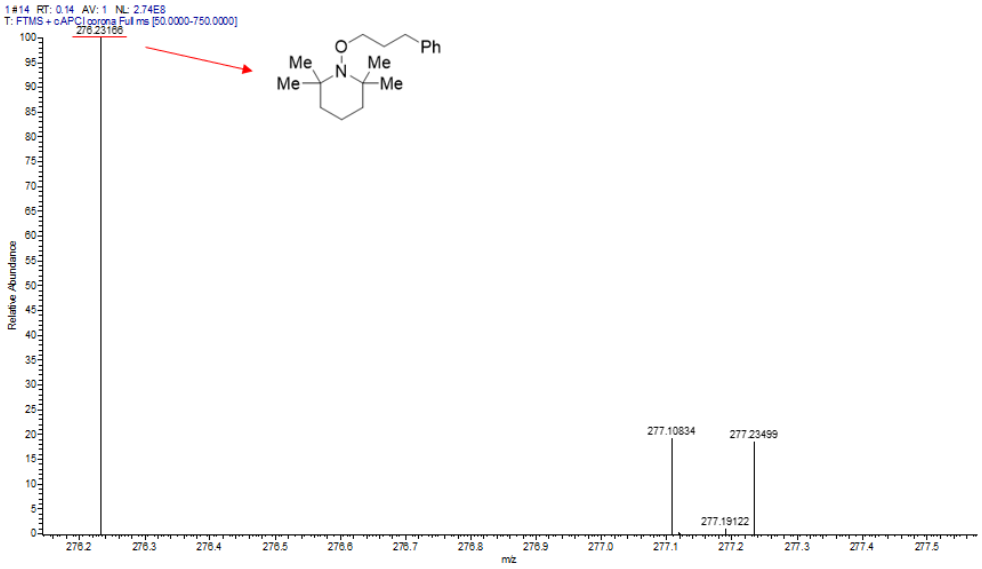
7. Mechanism Studies

7.1 Radical Trapping Experiments

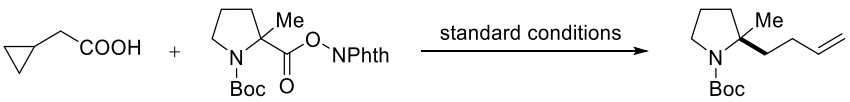


A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1a** (0.20 mmol, 32.8 mg), K_3PO_4 (0.20 mmol, 43.4 mg), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2a** (0.15 g, 0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), TEMPO (62.5 mg, 0.40 mmol), and MTBE (3.0 mL). The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 ℃ by a water bath, and stirred for 12 hours. The reaction mixture was detected by GC-MS analysis. This result showed that the standard reaction was completely

inhibited, and the TEMPO trapped phenylpropyl radical could be identified by HRMS (APCI). Calcd for $C_{18}H_{29}NO$ [M + H]$^+$: 276.2322, found: 276.2317.



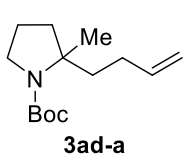
7.2 Radical Clock Experiments



1ad **2a** **3ad-a**, 43%

A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1ad** (20.2 mg, 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2a** (0.15 g, 0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 °C by a water bath, and stirred for 12 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **3ad-a**.

***tert*-Butyl 2-(but-3-en-1-yl)-2-methylpyrrolidine-1-carboxylate (3ad-a)**: The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (20.6 mg, 43% yield). **The major rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.84 – 5.74 (m, 1H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.94 – 4.85 (m, 1H), 3.60 – 3.49 (m, 1H), 3.36 – 3.16 (m, 1H), 2.01 – 1.87 (m, 4H), 1.76 – 1.58 (m, 4H), 1.44 (s, 9H), 1.27 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5, 138.8, 114.3, 79.3, 62.2, 48.7, 39.2, 38.6, 28.9, 28.7(3C), 26.4, 21.8. **The minor rotamer**: **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 5.84 – 5.74 (m, 1H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.94 – 4.85 (m, 1H), 3.49 – 3.37 (m, 1H), 3.36 – 3.16 (m, 1H), 2.01 – 1.87 (m, 4H), 1.76 – 1.58 (m, 4H), 1.44 (s, 9H), 1.32 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.5, 139.1, 114.1, 78.5, 62.7, 48.6, 38.3, 37.6, 29.4, 28.7(3C), 25.0, 22.2. **IR (ATR)**: ν = 3077, 1696, 1642, 995, 908 cm^{-1}. **HRMS (APCI)**: m/z [M + H]$^+$ calcd for $C_{14}H_{25}NO_2^+$: 240.1958, found: 240.1956.



3ad-a

7.3 Light On-Off Experiments

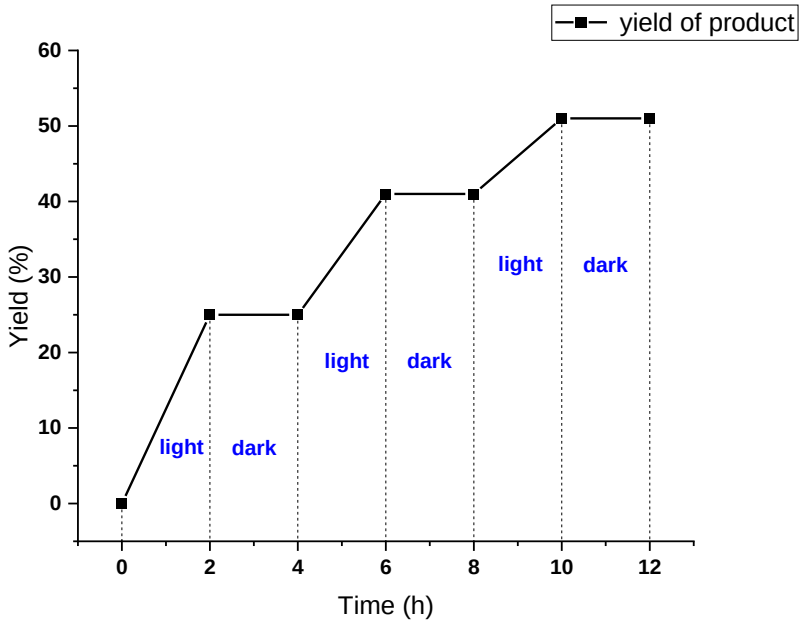


Figure S4. Light on-off experiments.

A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially

with carboxylic acid **1a** (32.8 mg, 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2a** (0.15 g, 0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and internal standard 1,2,4,5-tetramethylbenzene (27.4 mg, 0.20 mmol) in the solvent of MTBE (3.0 mL). The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 ℃ by a water bath, and stirred for 2 hours. The vial was wrapped in tin foil and a 20 μL sample of the reaction mixture was taken with a syringe and measured by GC. After being stirred for 2 hours at 40 ℃ in dark, a 20 μL sample of the reaction mixture was taken with a syringe and measured by GC. The reaction mixture was then irradiated with a 50 W blue LEDs lamp, maintained at 40 ℃, and stirred for 2 hours. This process was repeated for three times.

7.4 Measurement of Quantum Yields

The photon flux of blue LED was determined by standard ferrioxalate actinometry. 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.33 g, 0.75 mmol) in 5.0 mL of 0.20 M aqueous sulfuric acid. 0.15 M buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.30 mmol) and sodium acetate (1.23 g, 15 mmol) in 20 mL of 0.20 M aqueous sulfuric acid.

The actinometry measurements were done as follows:

To a 4-mL borosilicate vial equipped with a stir bar was added 0.25 mL of the ferrioxalate solution. The vial was sealed and placed 2 cm away from a 10 W blue LEDs. After irradiation for 10 seconds, 0.75 mL of the aqueous sulfuric acid and 1.0 mL of the buffered solution was added to the vial. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 μL of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 M aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette (l = 1.0 cm)

at 510 nm was measured by UV-Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as follows:

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

where V is the total volume (0.12 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11,100 L/mol•cm).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 M solution at λ = 457.9 nm) , t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.9931).

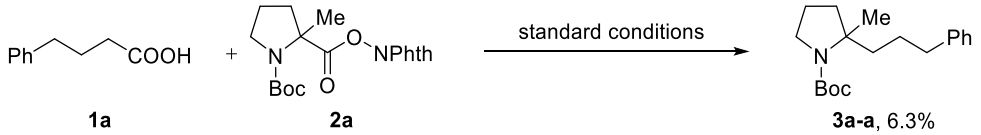
The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (2.163) of the 0.15 M solution of potassium ferrioxalate at 450 nm.

The photo flux is 1.92×10^{-7} Einstein/s.

Determination of quantum yield:



1a **2a** **3a-a**, 6.3%

A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1a** (32.8 mg, 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the

solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2a** (0.15 g, 0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox, and placed 2 cm away from 10 W blue LEDs. After irradiation for 1 hour. The moles of product **3a-a** formed for the model reaction were determined by GC measurement using 1,2,4,5-tetramethylbenzene as internal standard, and revealed 6.3 % yield of **3a-a** (1.3×10^{-6} mol).

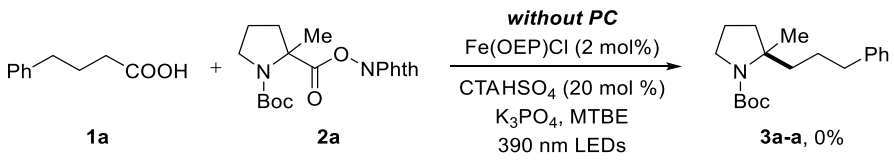
The quantum yield was calculated as follows:

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

where flux is the photon flux determined by ferrioxalate actinometry (1.92×10^{-7} Einstein/s), t is the time (3600 s), and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 5.475. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-5.475} = 0.999997$.

The quantum yield was calculated: **Φ = 0.018**

7.5 Reaction under 390nm Light Irradiation without Photocatalyst



A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1a** (0.20 mmol, 32.8 mg), K_3PO_4 (0.20 mmol, 43.4 mg), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then **2a** (0.15 g, 0.40 mmol), Fe(OEP)Cl (2.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL). The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 ℃ by a water bath, and stirred for 12 hours. The reaction mixture was detected by

GC-MS analysis.

7.6 Luminescence Quenching Experiments

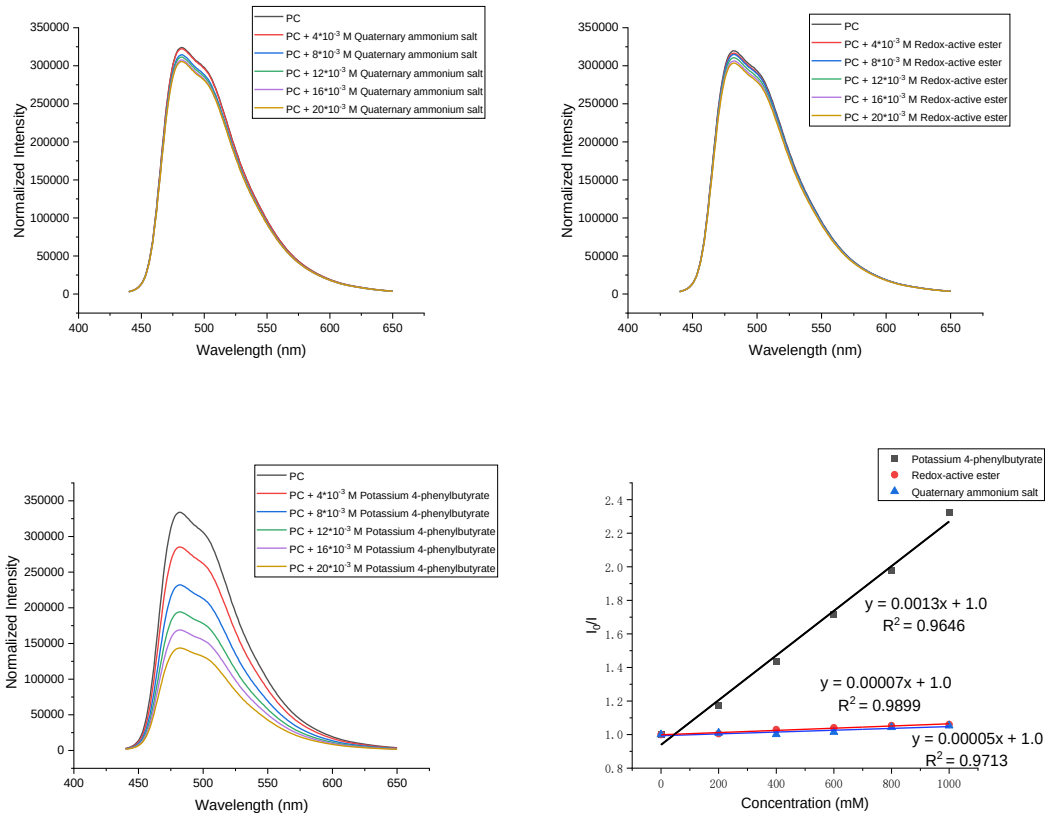
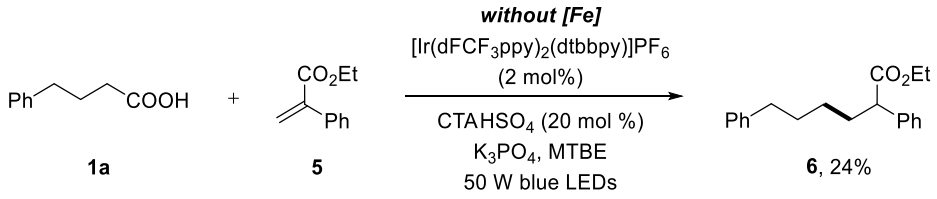


Figure S5. Fluorescence quenching of **PC**.

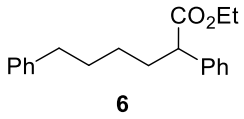
Fluorescence spectra was collected on Shimadzu Fluorescence Spectrophotometer RF-6000 for all experiments. All **PC** solutions were excited at 420 nm and the emission intensity was collected at 482 nm. In a typical experiment, the emission spectrum of a 2×10^{-5} M solution of **PC** in DMSO was collected. The significant decrease of **PC** luminescence could be observed in the presence of potassium 4-phenylbutyrate. No decrease of **PC** luminescence could be observed in the presence of redox-active ester or quaternary ammonium salt.

7.7 Exploration of Phenylpropyl Radical with α-Aryl Acrylate



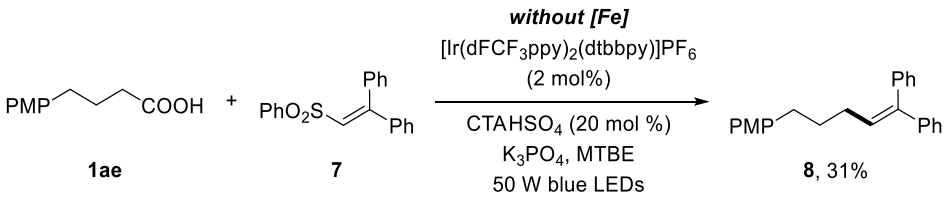
A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1a** (32.8 mg, 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then α-aryl acrylate **5** (71.0 mg, 0.40 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp, maintained at 40 ℃ by a water bath, and stirred for 12 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **6**.

Ethyl 2,6-diphenylhexanoate (6): The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 20:1) as a colorless oil (14.2 mg, 24% yield). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 3H), 7.23 – 7.15 (m, 3H), 4.22 – 4.07 (m, 2H), 3.55 (t, J = 7.5 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 2.19 – 2.10 (m, 1H), 1.87 – 1.79 (m, 1H), 1.73 – 1.63 (m, 2H), 1.40 – 1.31 (m, 2H), 1.23 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.2, 142.6, 139.5, 128.7(2C), 128.5(2C), 128.4(2C), 128.0(2C), 127.2, 125.8, 60.8, 51.8, 35.8, 33.6, 31.3, 27.4, 14.3. **IR (ATR)**: ν = 1732 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{20}H_{24}O_2^+$: 297.1849, found: 297.1853.



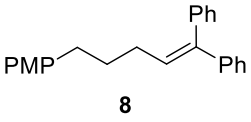
6

7.8 Exploration of Phenylpropyl Radical with Vinyl Sulfone



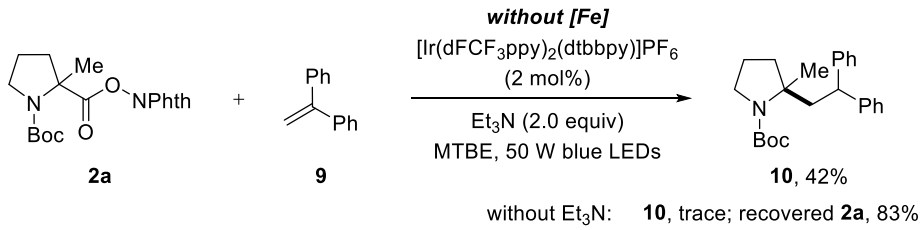
A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1ae** (39.2 mg. 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into a N_2-filled glovebox, then vinyl sulfone **7** (128.8 mg, 0.40 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol), and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp, maintained at 40 ℃ by a water bath, and stirred for 12 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **8**.

(5-(4-Methoxyphenyl)pent-1-ene-1,1-diyl)dibenzene (8): The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (20.3 mg, 31% yield). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.24 – 7.12 (m, 6H), 7.08 (d, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.01 (t, *J* = 7.5 Hz, 1H), 3.70 (s, 3H), 2.46 (t, *J* = 7.7 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.71 – 1.60 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.8, 143.0, 142.0, 140.3, 134.6, 130.1(2C), 129.9, 129.4(2C), 128.3(2C), 128.2(2C), 127.4(2C), 127.0, 127.0, 113.8(2C), 55.4, 34.7, 32.1, 29.5. **IR (ATR)**: ν = 1649, 1261, 1223, 733 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{24}H_{24}O^+$: 329.1900, found: 329.1904.



8

7.9 Exploration of α-Amino Radical with 1,1-Diphenylethylene

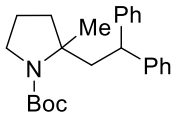


2a **9** **10**, 42%

without Et_3N: **10**, trace; recovered **2a**, 83%

In a N_2-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **2a** (75.0 mg, 0.20 mmol), 1,1-Diphenylethylene **9** (73.4 mg, 0.40 mmol), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), and Et_3N (40.5 mg, 56 μL, 0.40 mmol) or not in the solvent of MTBE (3.0 mL). The vial was sealed with a headspace cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp, maintained at 40 °C by a water bath, and stirred for 24 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **10** and **2a**.

***tert*-Butyl 2-(2,2-diphenylethyl)-2-methylpyrrolidine-1-carboxylate (10)**: The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 15:1) as a colorless oil (30.5 mg, 42% yield). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.25 – 7.14 (m, 8H), 7.11 – 7.01 (m, 2H), 3.88 (dd, *J* = 7.7, 5.1 Hz, 1H), 3.49 – 3.34 (m, 1H), 3.24 – 3.06 (m, 1H), 2.67 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.50 (dd, *J* = 14.1, 4.6 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.60 – 1.44 (m, 2H), 1.43 – 1.36 (m, 1H), 1.32 (s, 9H), 1.19 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.1, 146.6, 146.0, 128.6(2C), 128.5(2C), 128.1(2C), 127.7(2C), 126.2, 126.0, 79.1, 63.2, 48.6, 48.5, 44.1, 38.8, 28.7(3C), 26.4, 21.9. **IR (ATR)**: ν = 1689 cm^{-1}. **HRMS (APCI)**: m/z $[M + H]^+$ calcd for $C_{24}H_{31}NO_2^+$: 366.2428, found: 366.2436.

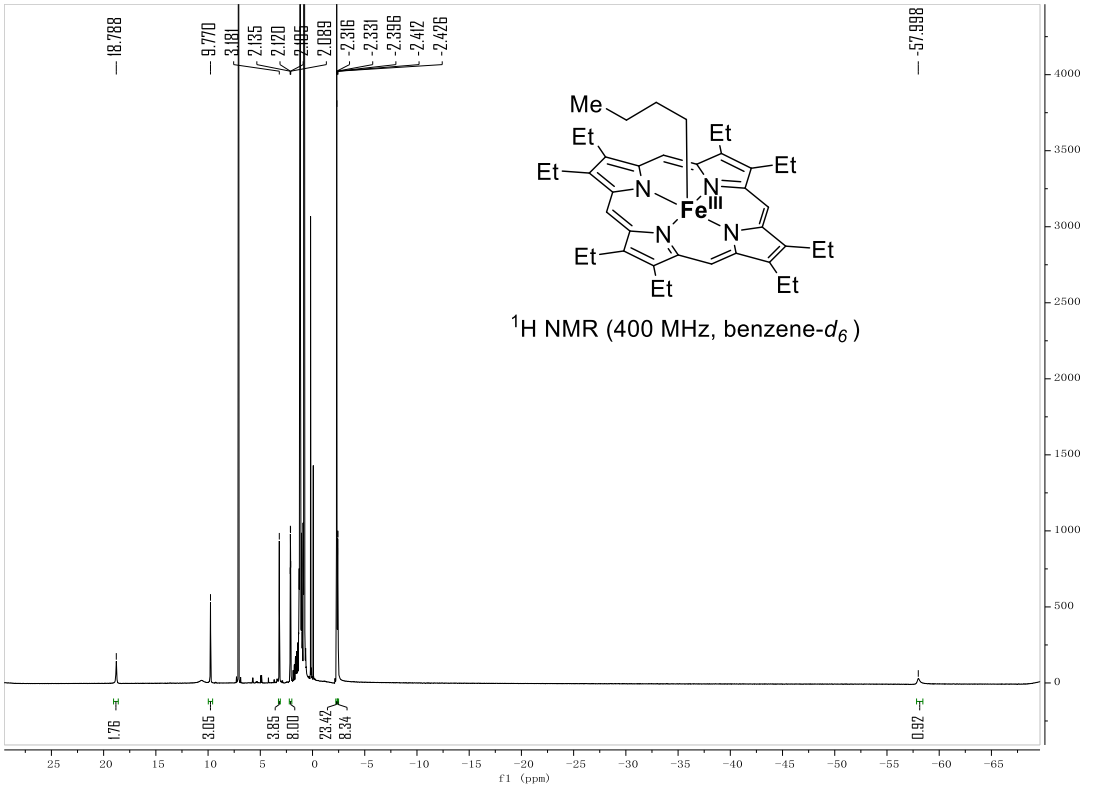


10

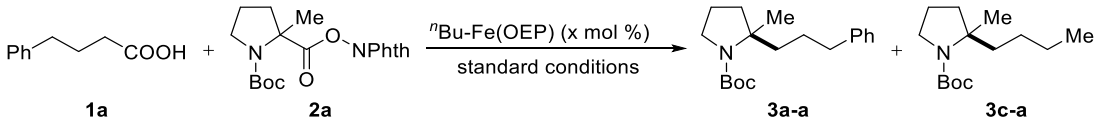
7.10 ^{n}Bu–Fe(OEP) Precatalyst Studies

In a N_2-filled glovebox, an oven-dried 10 mL Schlenk flask equipped with a magnetic stir bar was charged sequentially with Fe(OEP)Cl (29.0 mg, 0.050 mmol), and benzene-d_6 (1.0 mL). Then stirred at room temperature for 15 minutes, ^{n}BuLi (1.6

M in hexanes, 31 μL, 0.050 mmol) was added dropwise, resulting in an immediate color change of the solution to dark red. The resulting solution was stirred for 1 h at room temperature. Then filter with nylon filter membrane (0.2 μm × 47 mm), add to the NMR tube, and isolate oxygen with Parafilm. ^{1}H-NMR spectra are consistent with literature data.



7.11 Direct use of ^{n}Bu–Fe(OEP) Complex as Precatalyst



A 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with carboxylic acid **1a** (32.8 mg, 0.20 mmol), K_3PO_4 (43.4 mg, 0.20 mmol), and MTBE (3.0 mL). Then stirred at room temperature for 30 minutes and remove the solvent *in vacuo*. The system was transferred into the glovebox, then **2a** (0.15 g, 0.40 mmol), ^{n}Bu-Fe(OEP) (x mol %), $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (4.4 mg, 0.0040 mmol), $CTAHSO_4$ (15.8 mg, 0.040 mmol) and MTBE (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp maintained at 40 °C by a water bath, and stirred

for 12 hours. These reactions were analyzed by GC, and yields were determined using 1,2,4,5-tetramethylbenzene as an internal standard.

^{n}Bu-Fe(OEP) (x mol %)	Yield of **3a-a**	Yield of **3c-a**
2	79%	trace
10	5%	8%

8. References

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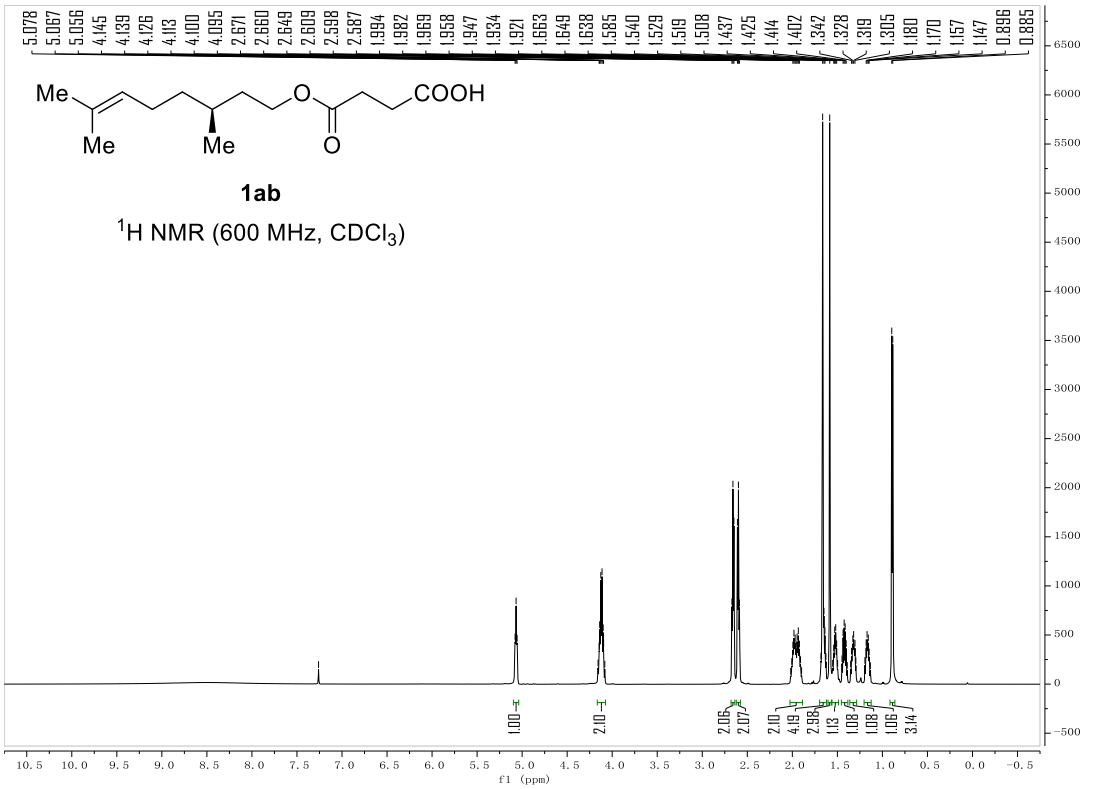
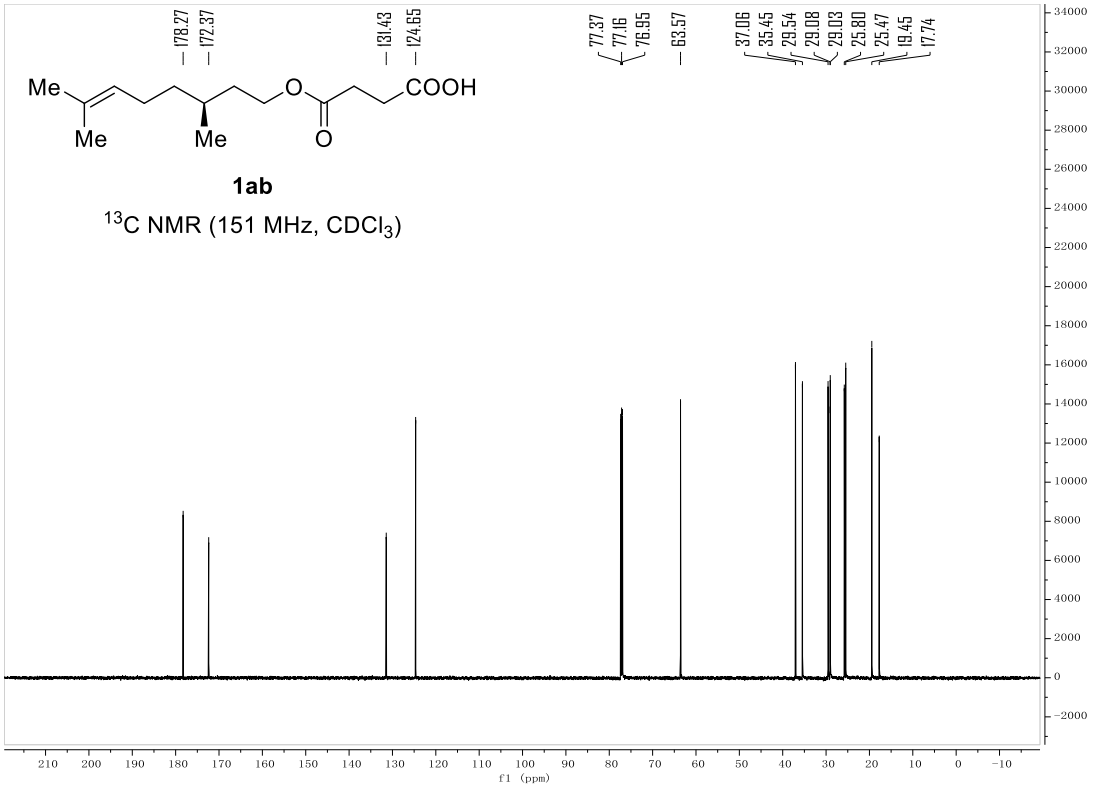
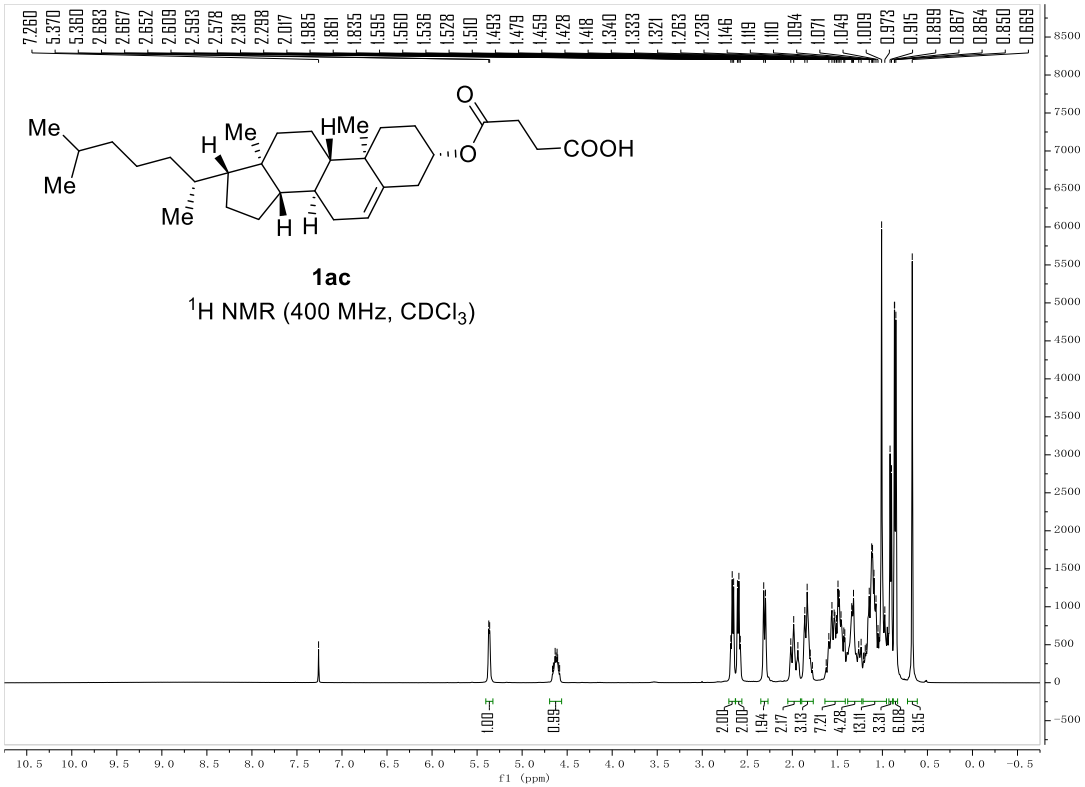
9. NMR Spectra

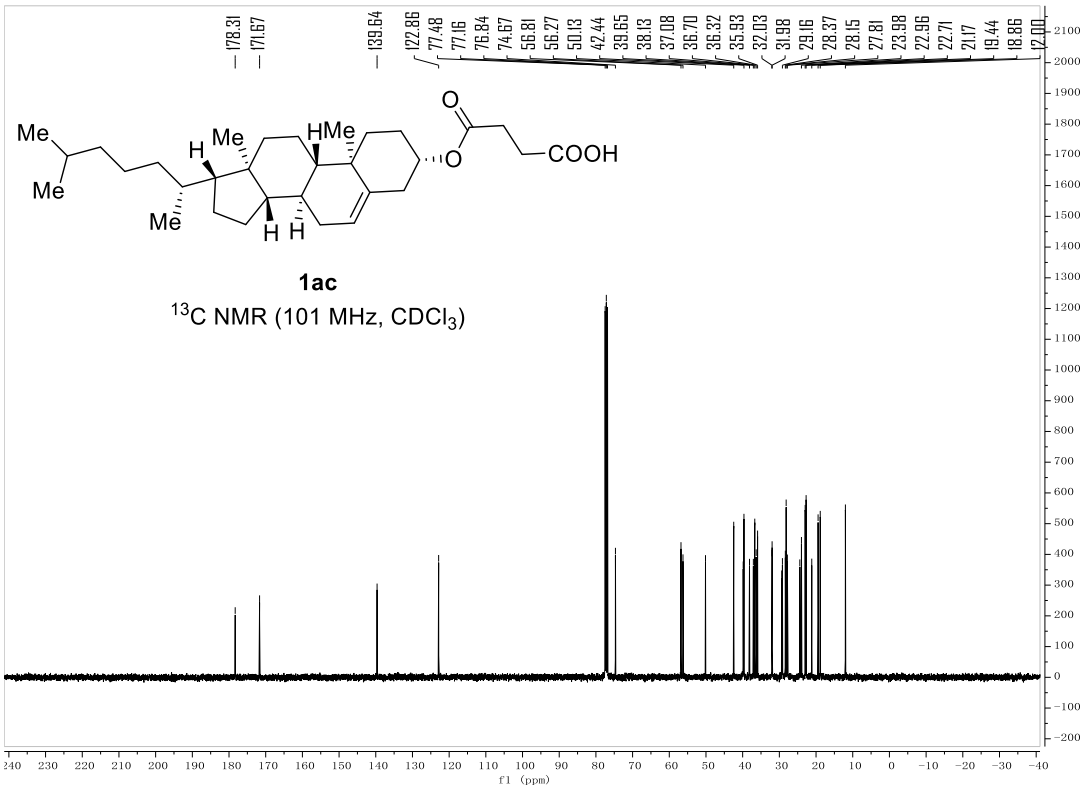






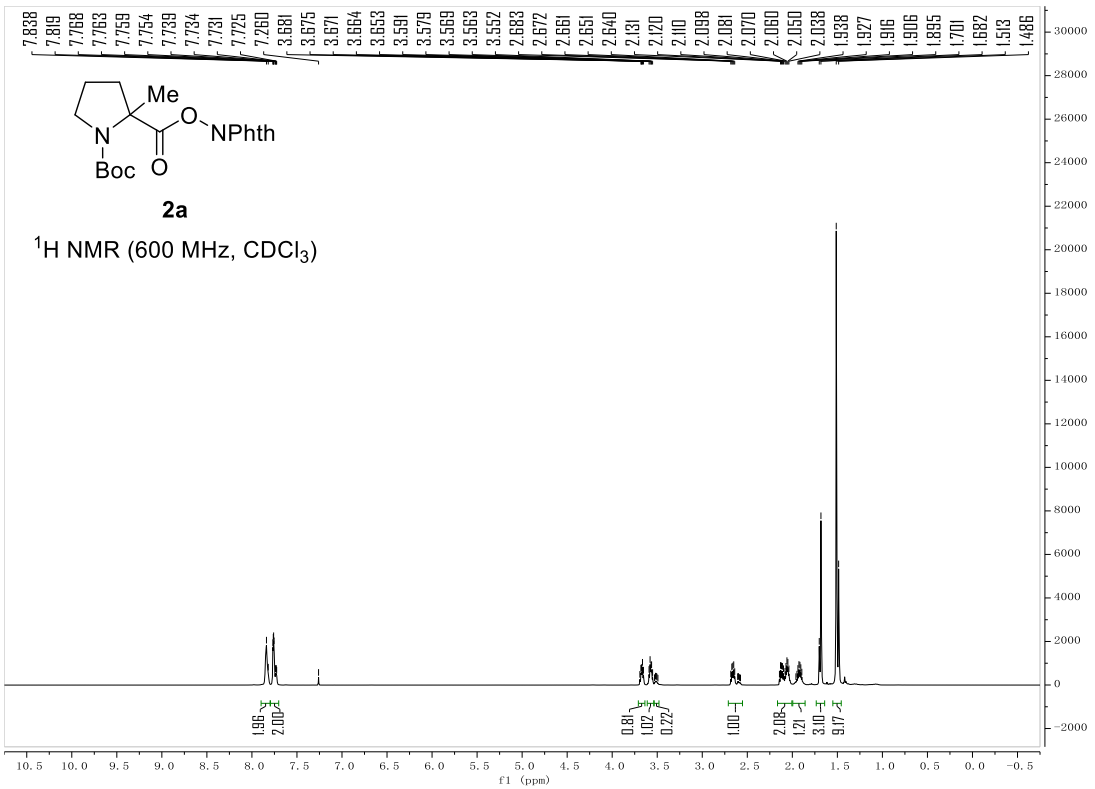
1ac

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



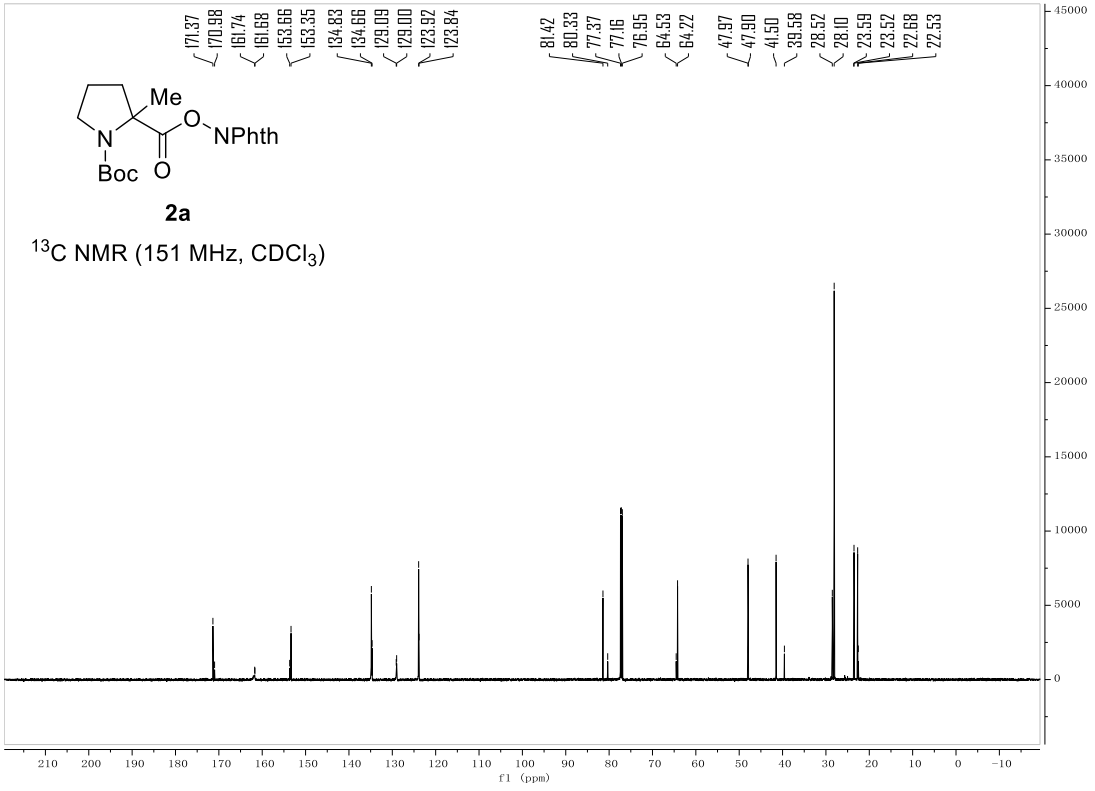
1ac

^{13}C NMR (101 MHz, $CDCl_3$)



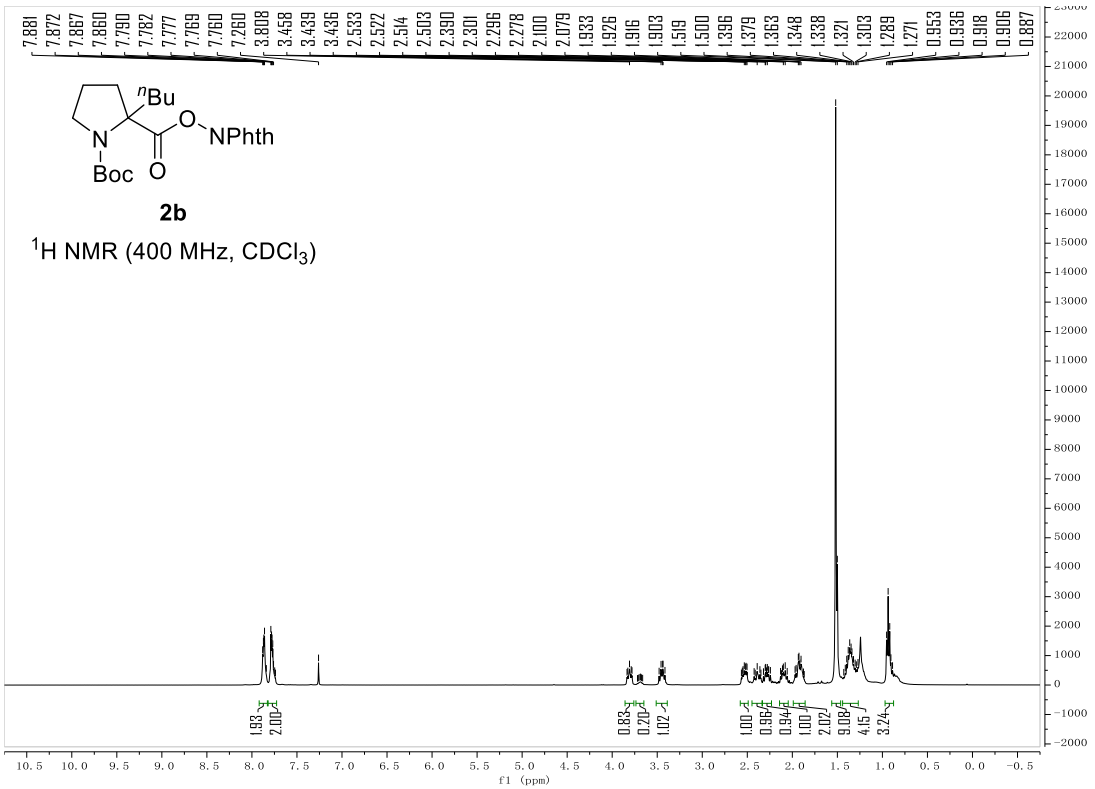
2a

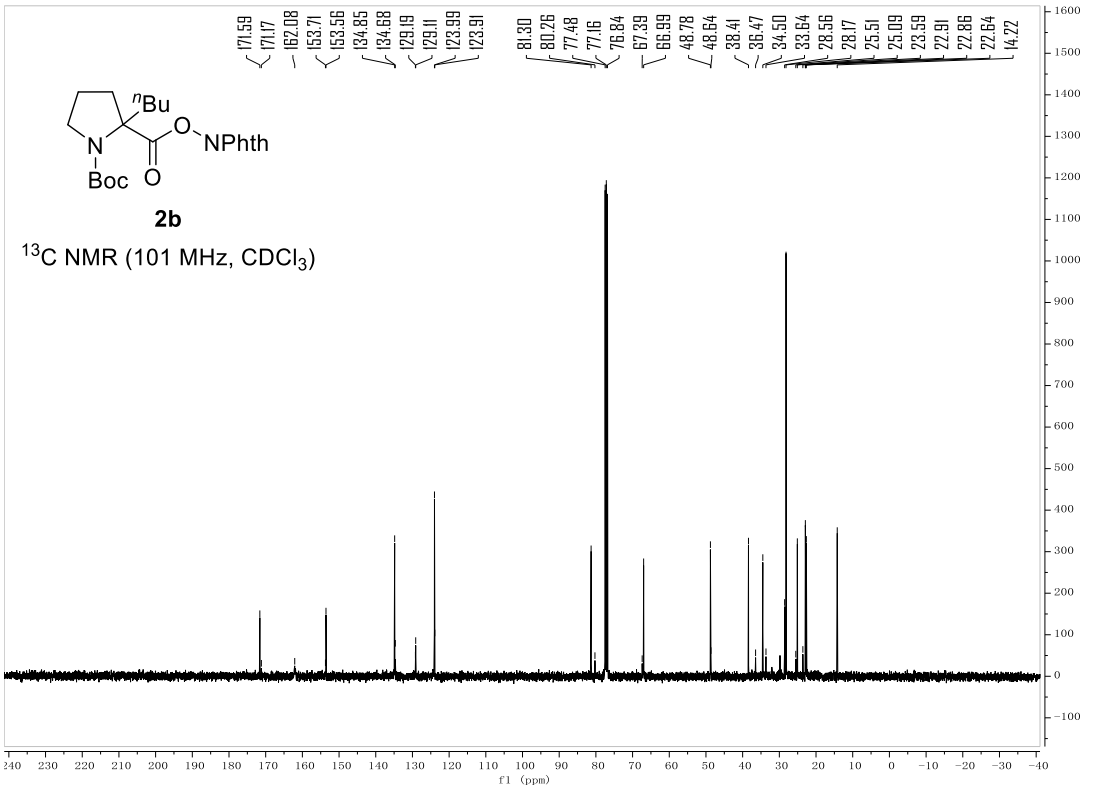
^{1}H NMR (600 MHz, $CDCl_3$)

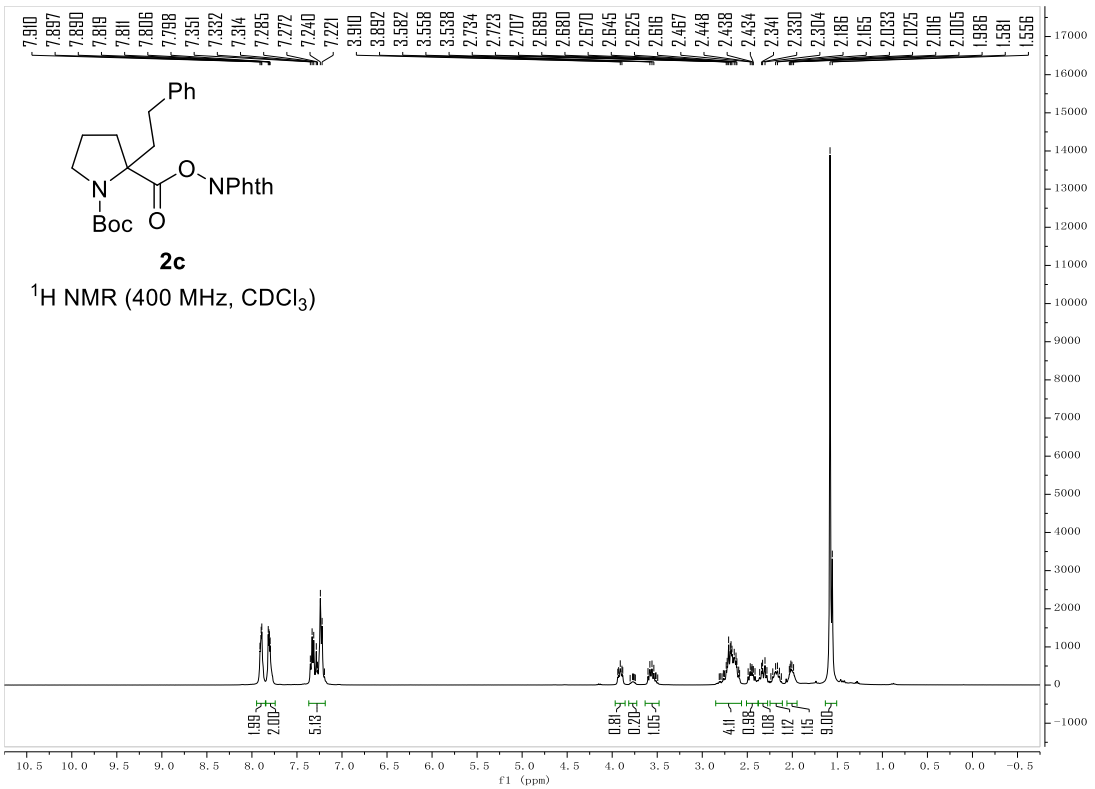


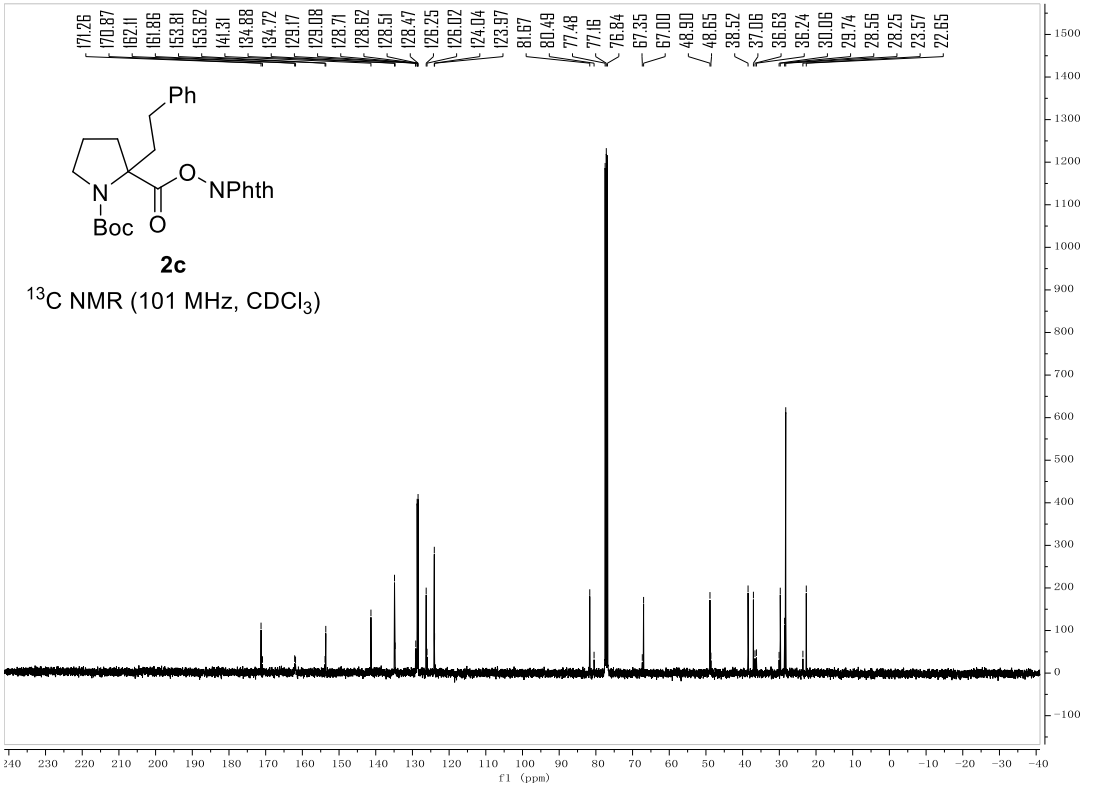
2a

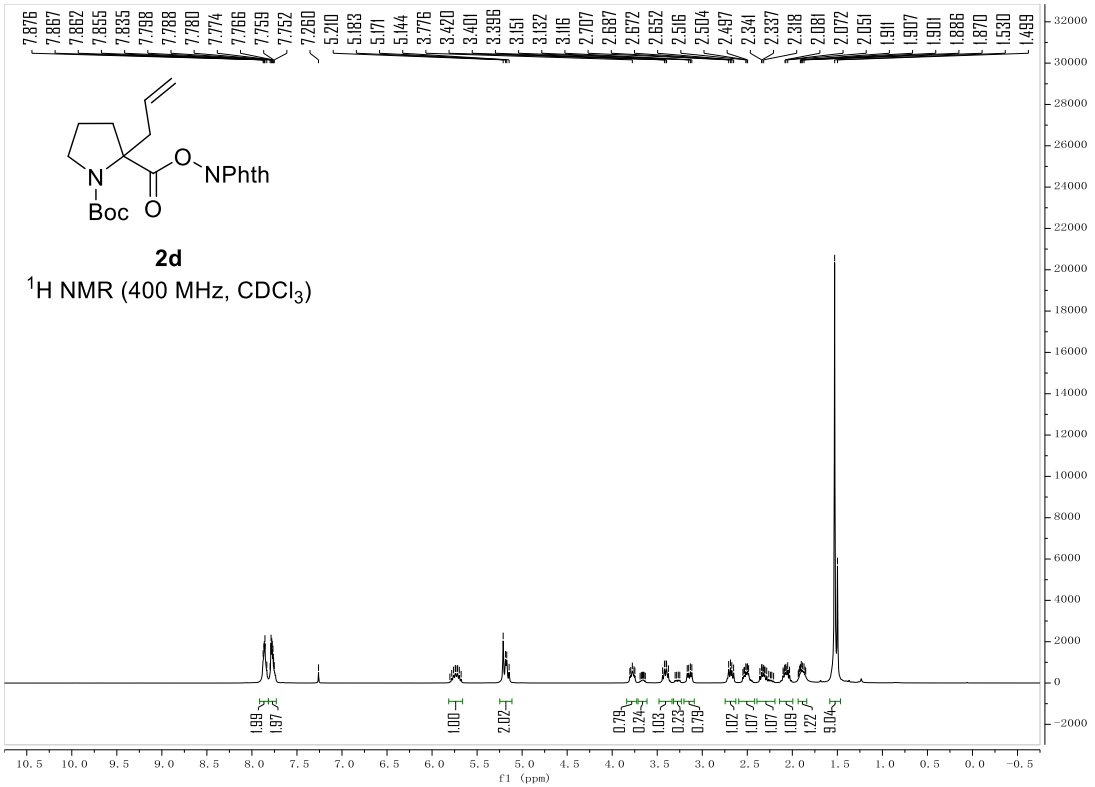
^{13}C NMR (151 MHz, $CDCl_3$)


nBu
O
N
NPhth
Boc
O
2b
1H NMR (400 MHz, CDCl3)
f1 (ppm)


nBu
O
N
NPhth
Boc
O
2b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

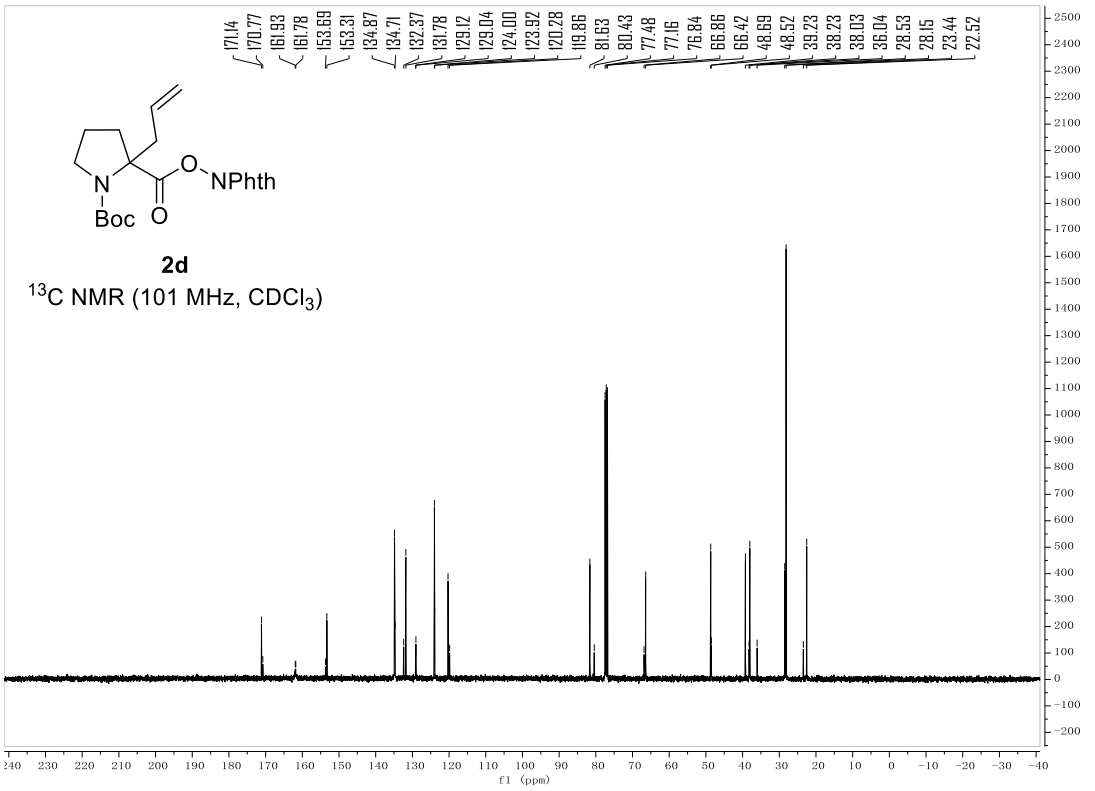

Ph
N
O
NPhth
Boc
O
2c
1H NMR (400 MHz, CDCl3)


Ph
N
O
NPhth
Boc
O
2c
13C NMR (101 MHz, CDCl3)



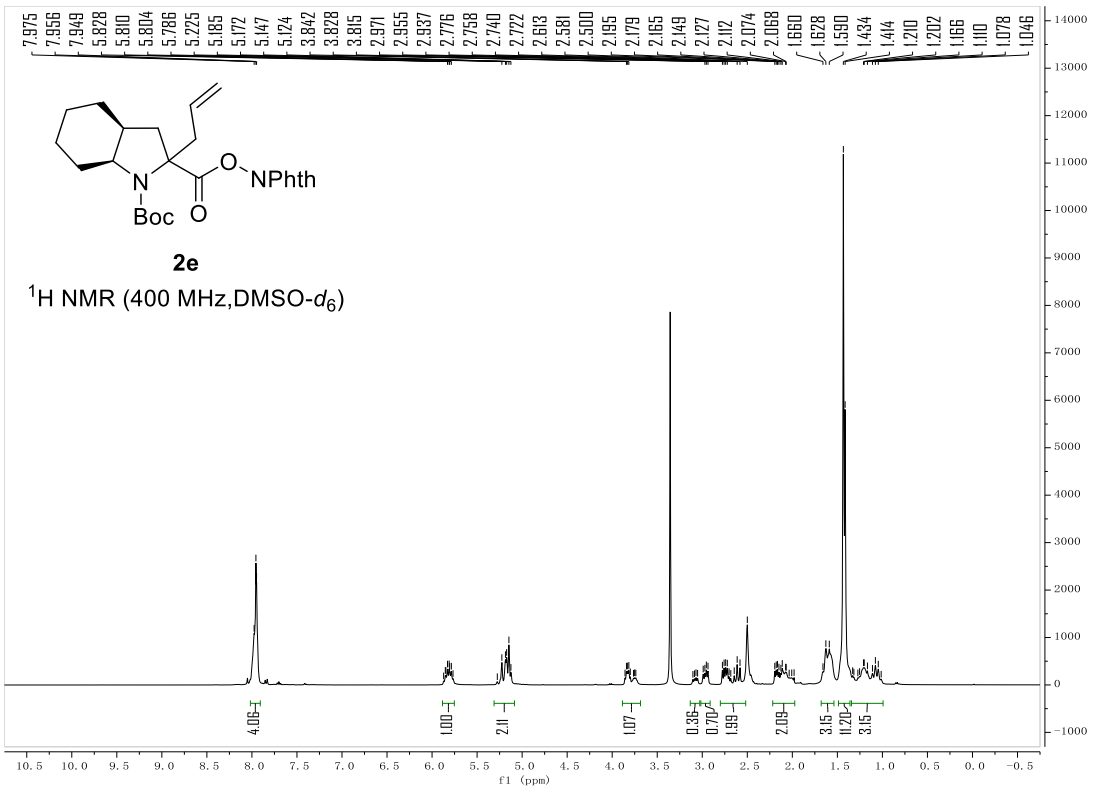
2d

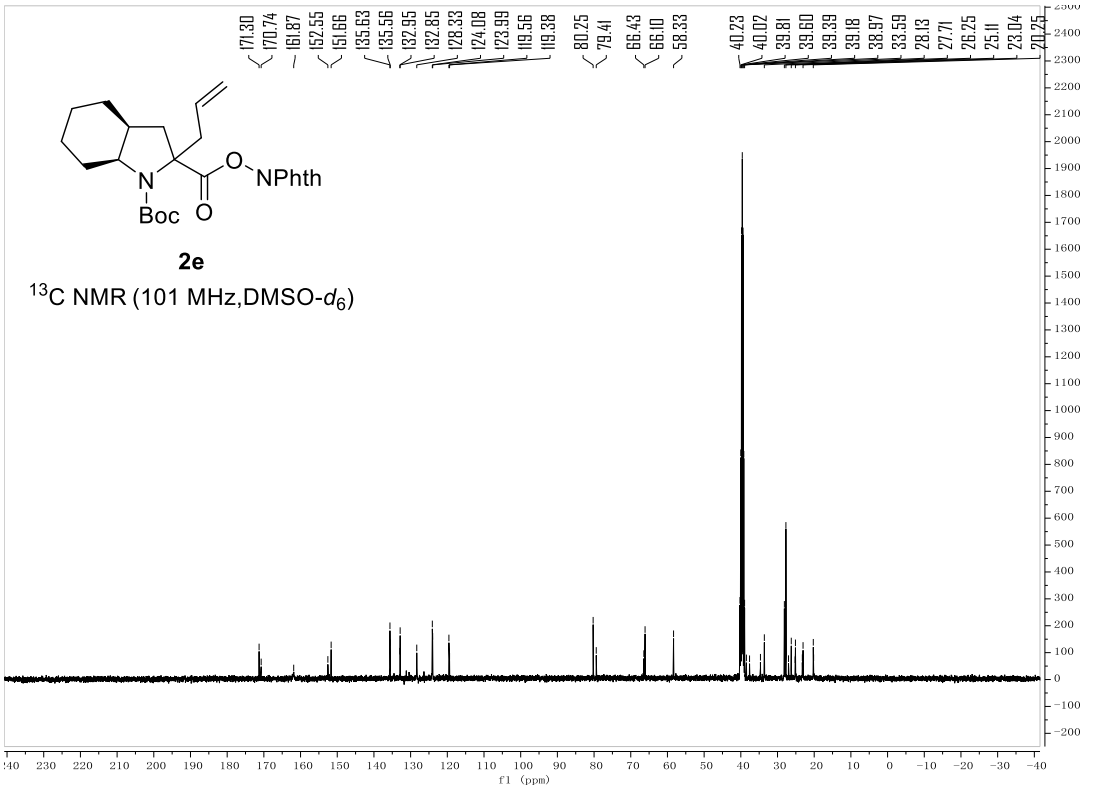
^{1}H NMR (400 MHz, $CDCl_3$)

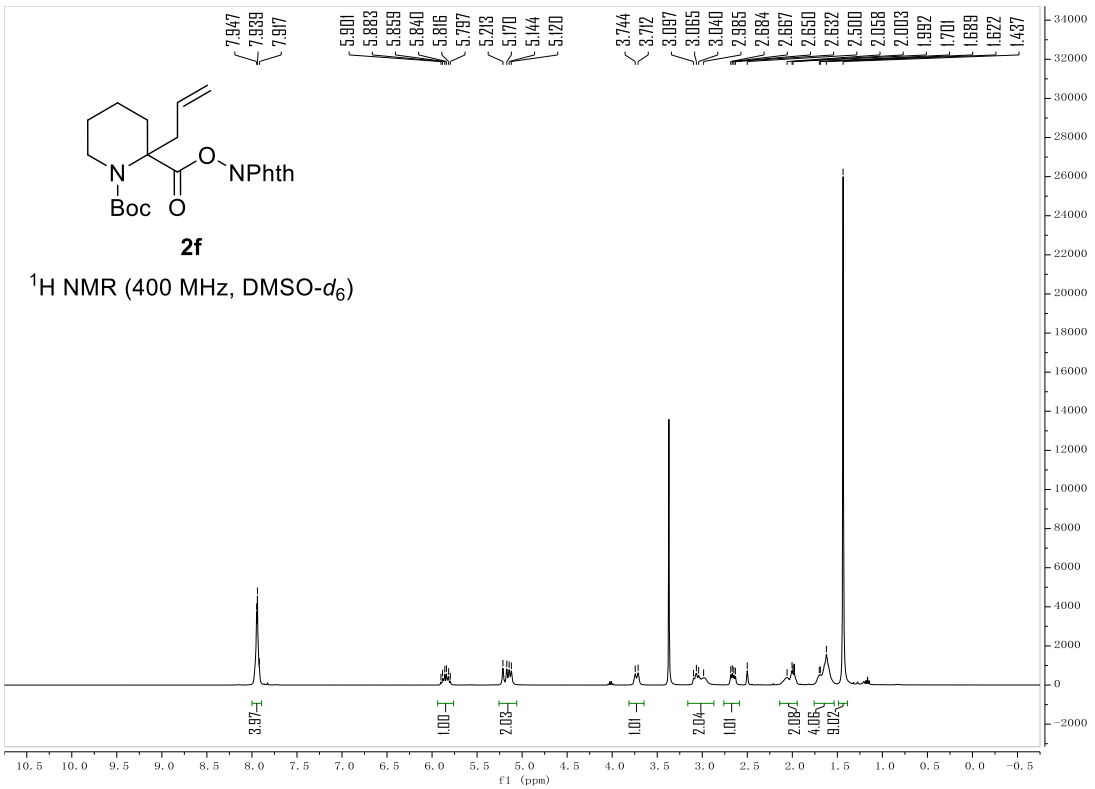


2d

^{13}C NMR (101 MHz, $CDCl_3$)

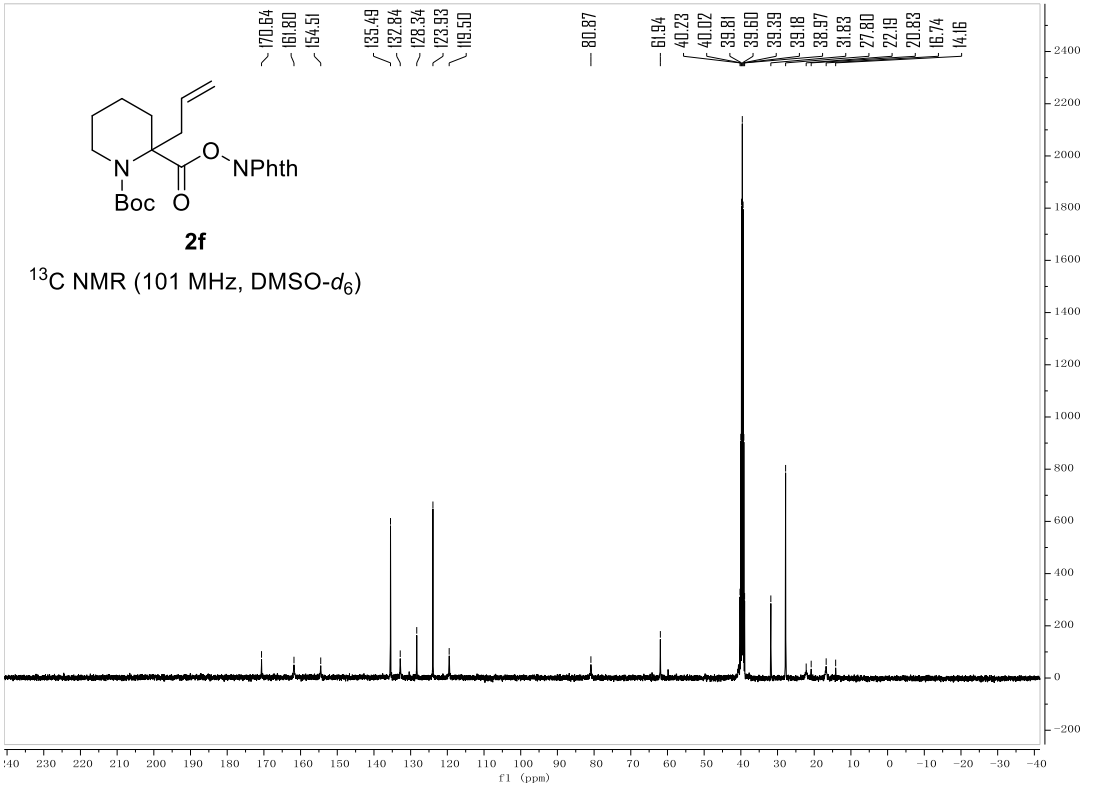

NPhth
Boc
2e
1H NMR (400 MHz,DMSO-d6)
f1 (ppm)


NPhth
Boc
2e
13C NMR (101 MHz,DMSO-d6)
f1 (ppm)



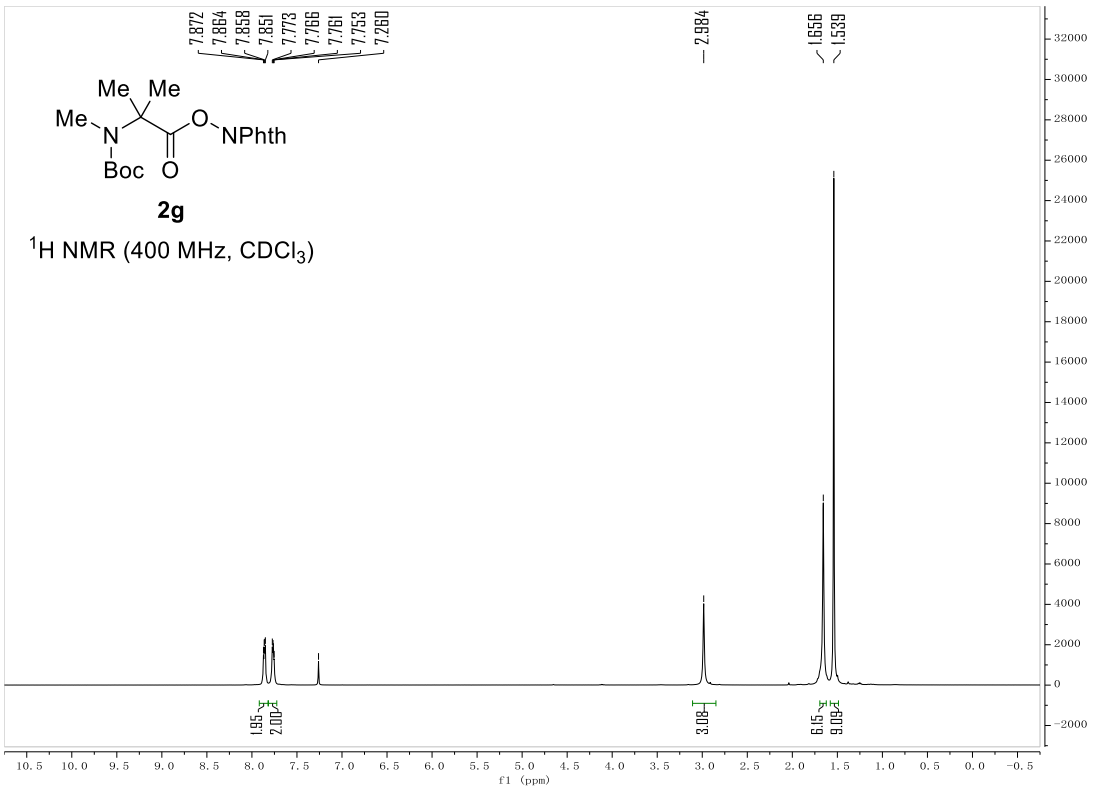
2f

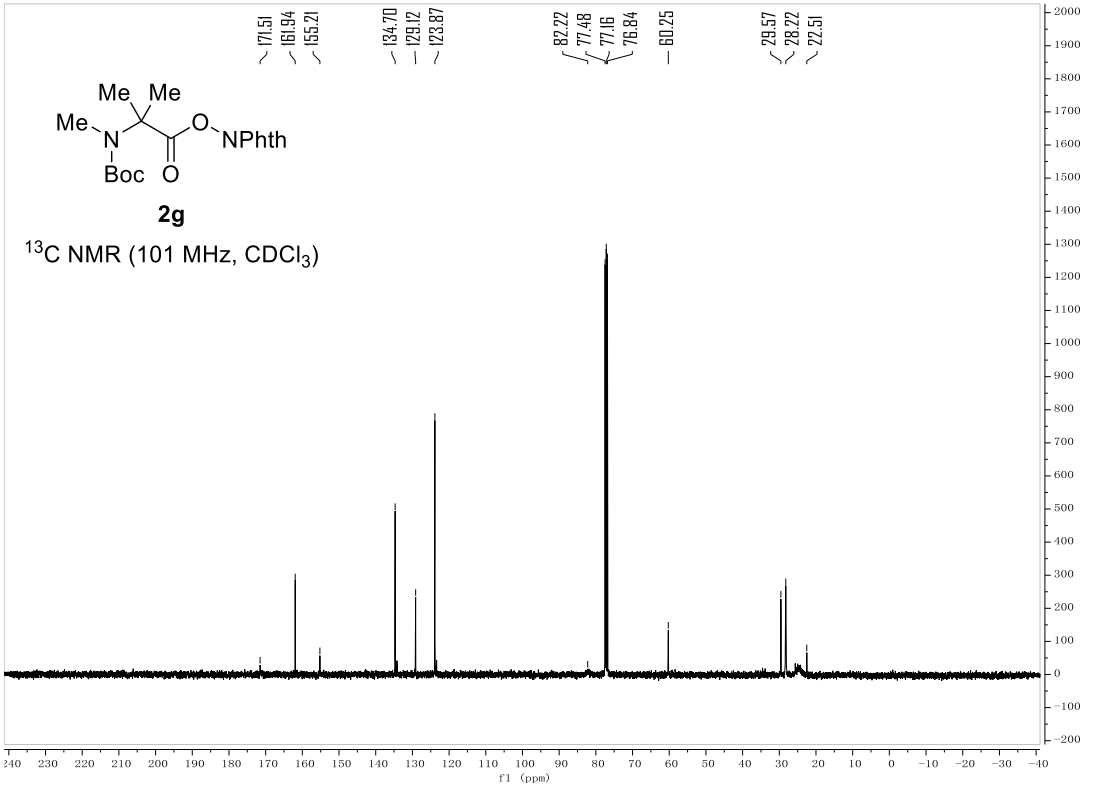
^{1}H NMR (400 MHz, DMSO-d_6)

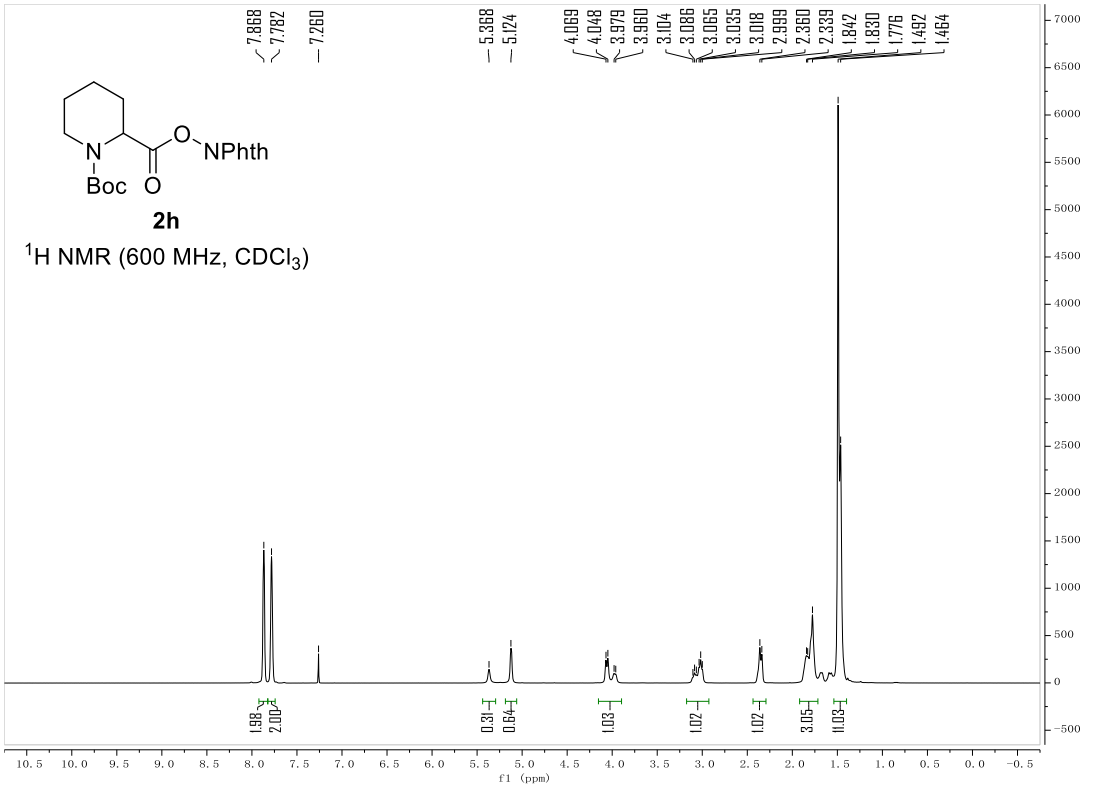


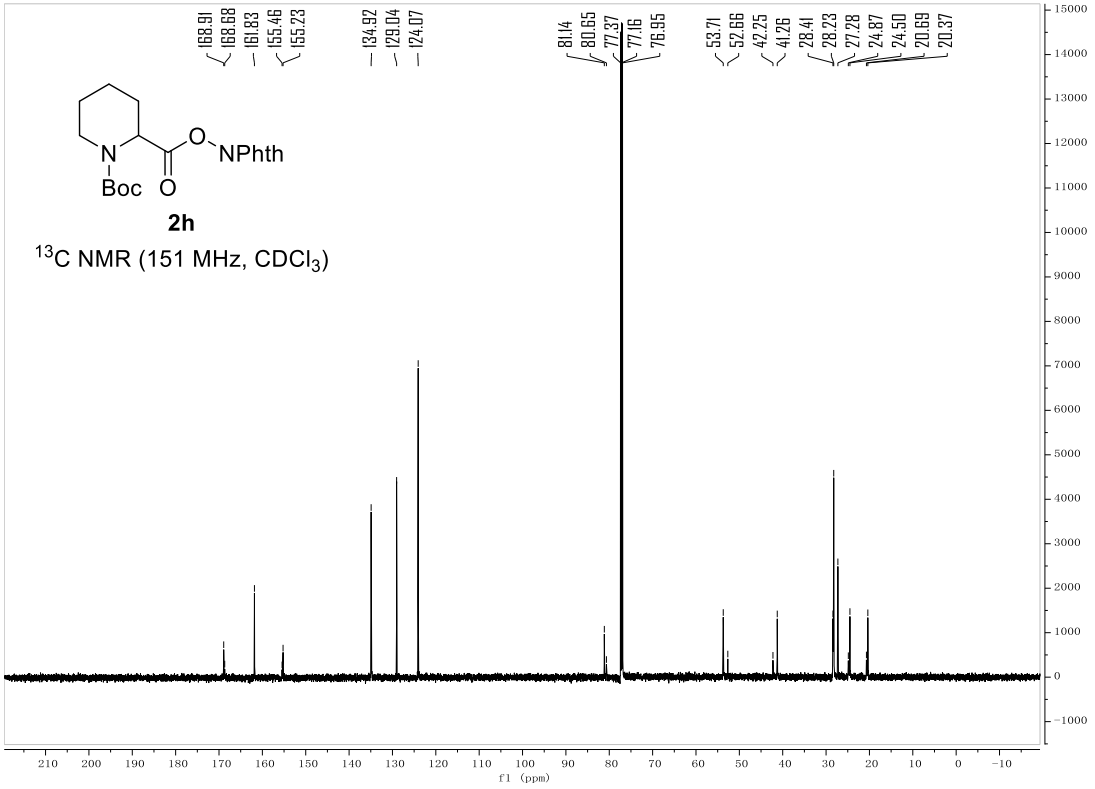
2f

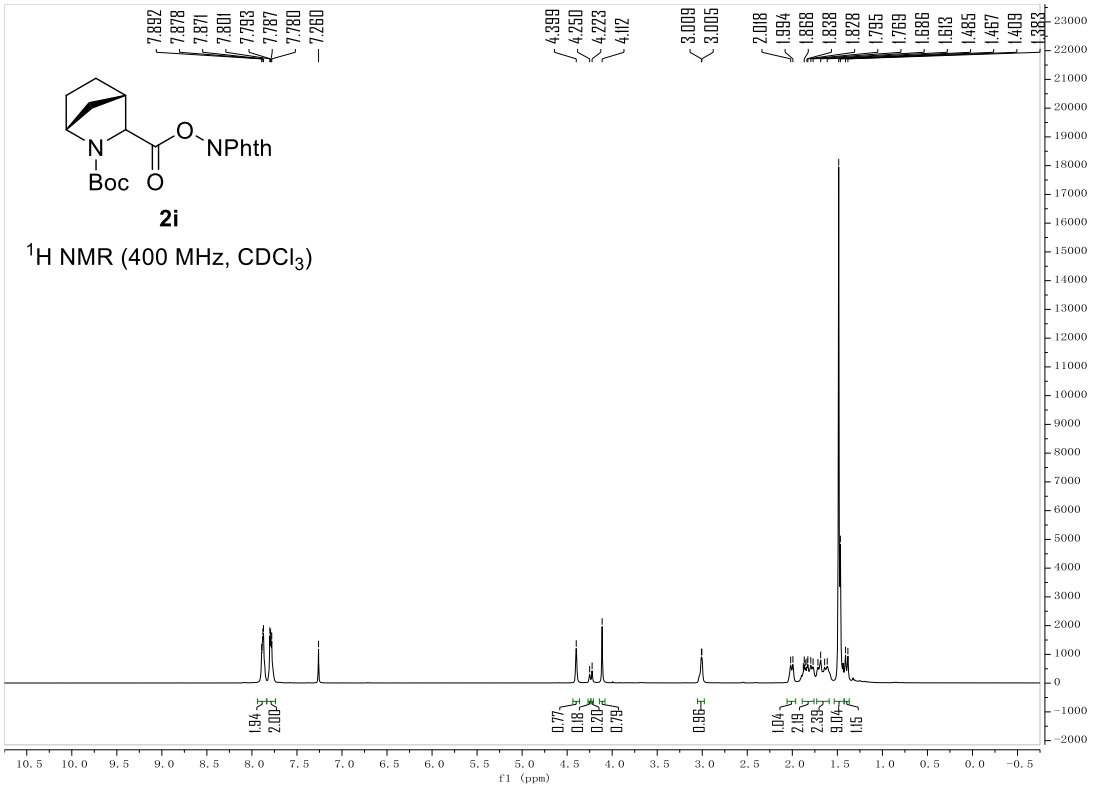
^{13}C NMR (101 MHz, DMSO-d_6)

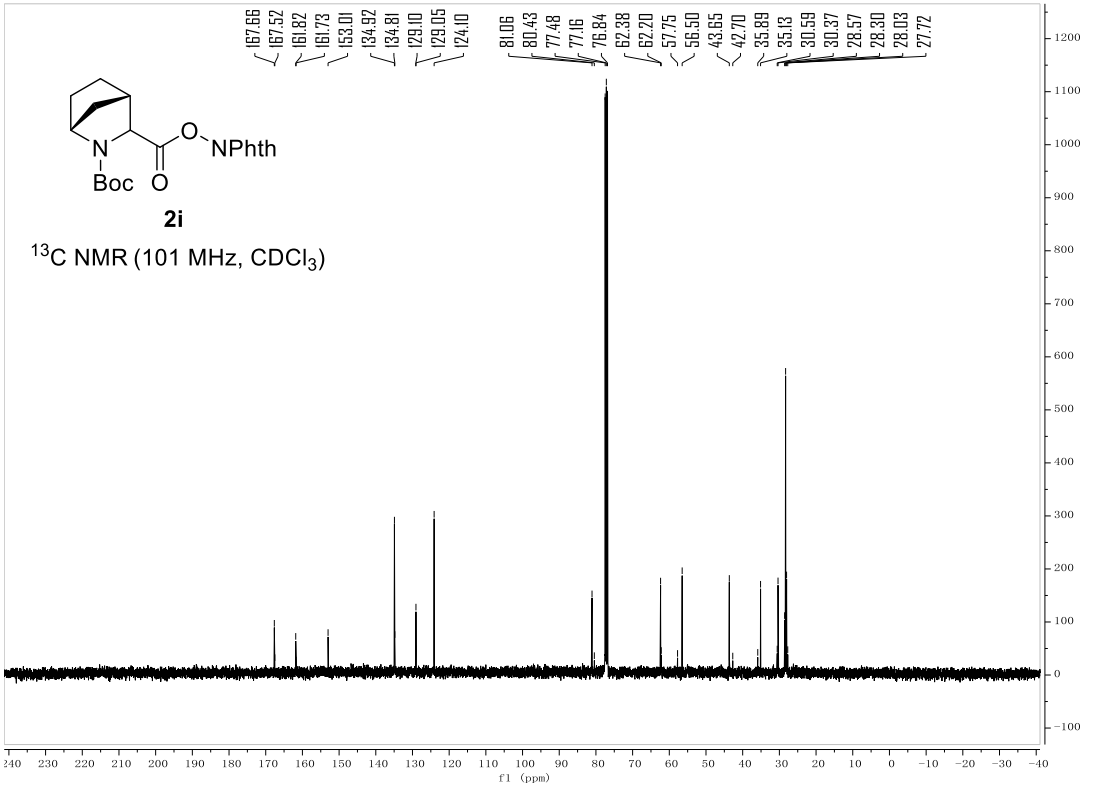

7.872
7.864
7.858
7.851
7.773
7.766
7.761
7.753
7.260
2.984
1.656
1.539
Me Me
Me N O NPhth
Boc O
2g
1H NMR (400 MHz, CDCl3)
1.95
2.00
3.08
6.15
9.09
f1 (ppm)

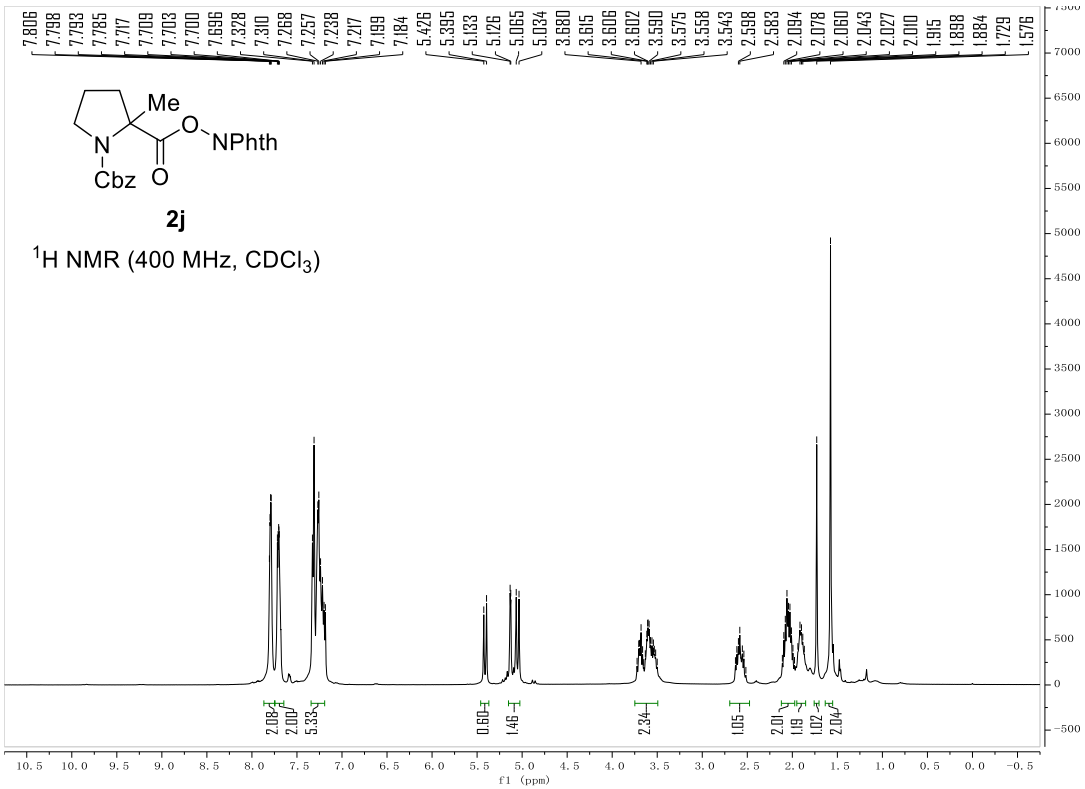

171.51
161.94
155.21
134.70
129.12
123.87
82.22
77.48
77.16
76.84
60.25
29.57
28.22
22.51
Me Me
Me N O NPhth
Boc O
2g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

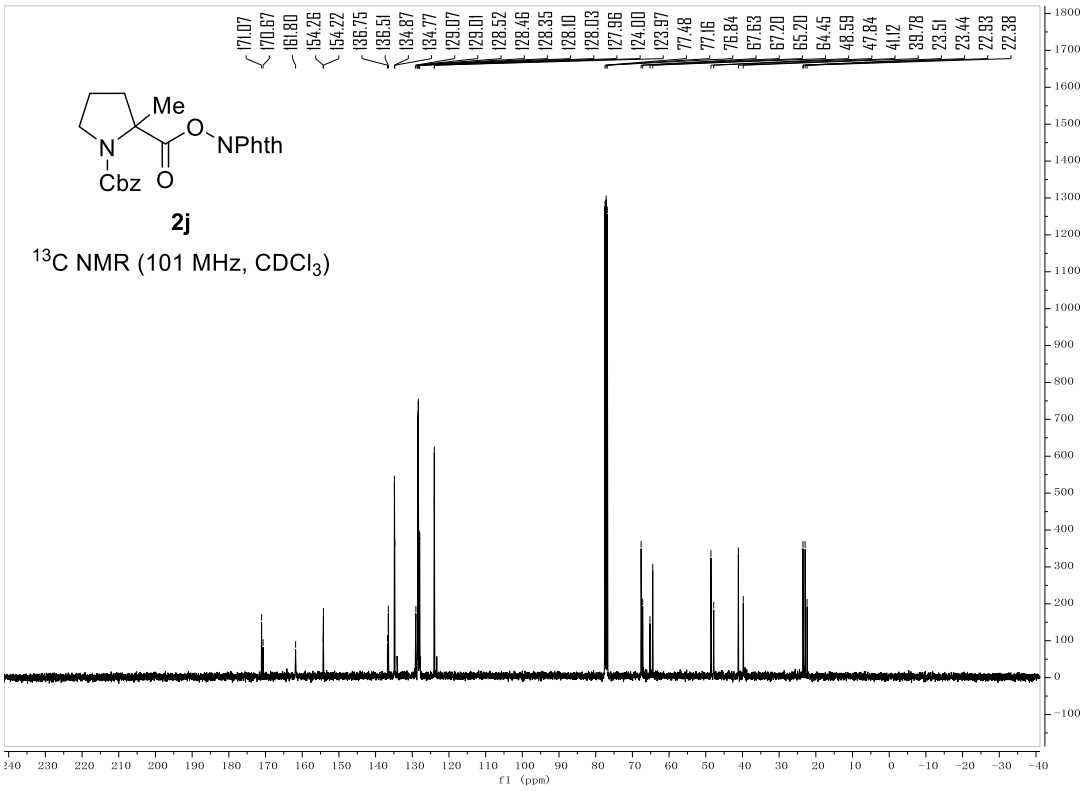

7.888
7.782
7.260
5.368
5.124
4.069
4.048
3.979
3.960
3.104
3.086
3.065
3.035
3.018
2.999
2.360
2.339
1.842
1.830
1.776
1.492
1.464
O
NPhth
N
Boc
O
2h
1H NMR (600 MHz, CDCl3)
1.98
2.00
0.31
0.64
1.03
1.02
1.02
3.05
11.03
f1 (ppm)

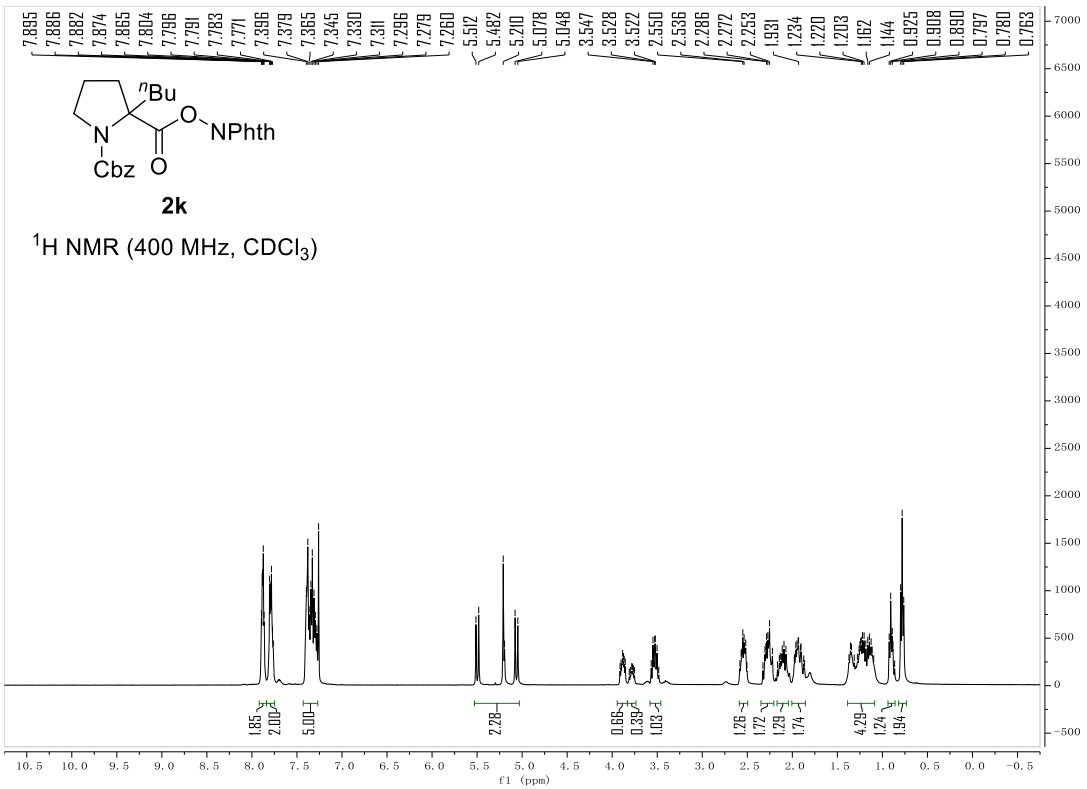

168.91
168.68
161.83
155.46
155.23
134.92
129.04
124.07
81.14
80.65
77.37
77.16
76.95
53.71
52.66
42.25
41.26
28.41
28.23
27.28
24.87
24.50
20.69
20.37
O
NPhth
N
Boc
O
2h
13C NMR (151 MHz, CDCl3)
f1 (ppm)

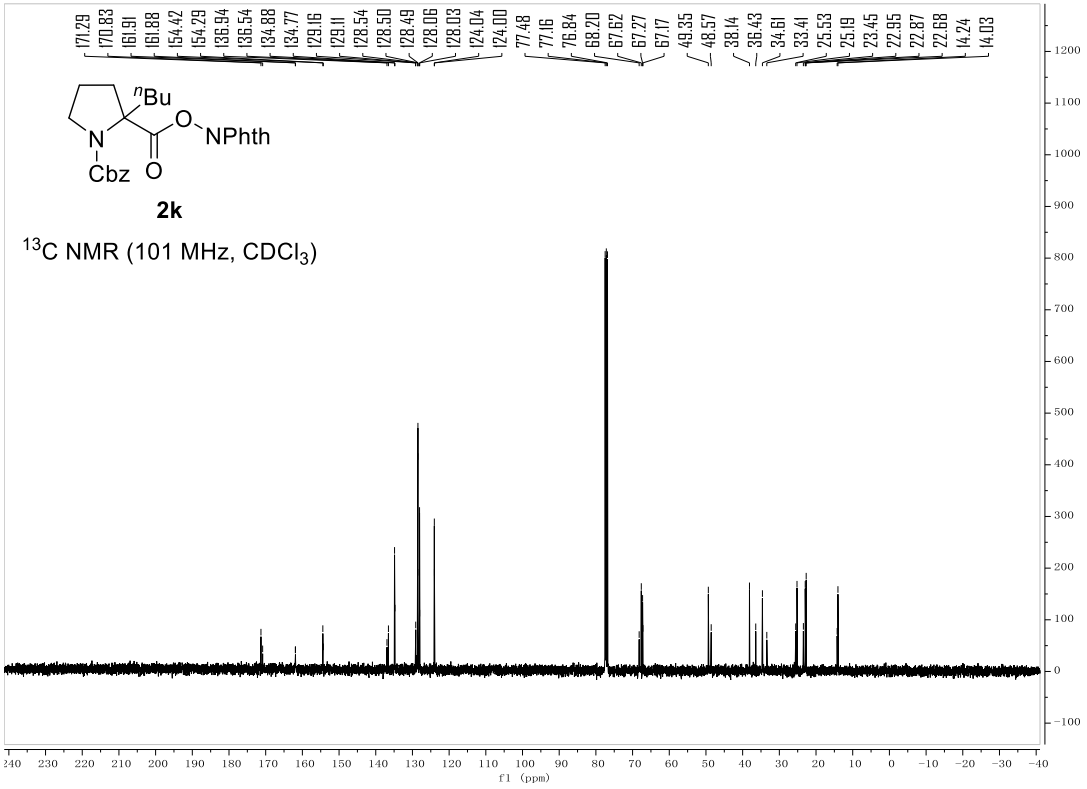

7.892
7.878
7.871
7.801
7.793
7.787
7.780
7.260
4.399
4.250
4.223
4.112
3.009
3.005
2.018
1.994
1.868
1.838
1.828
1.795
1.769
1.686
1.613
1.485
1.467
1.409
1.383
O
NPhth
N
Boc
O
2i
1H NMR (400 MHz, CDCl3)
1.94
2.00
0.77
0.18
0.20
0.79
0.96
1.04
2.19
2.39
9.04
1.15
f1 (ppm)

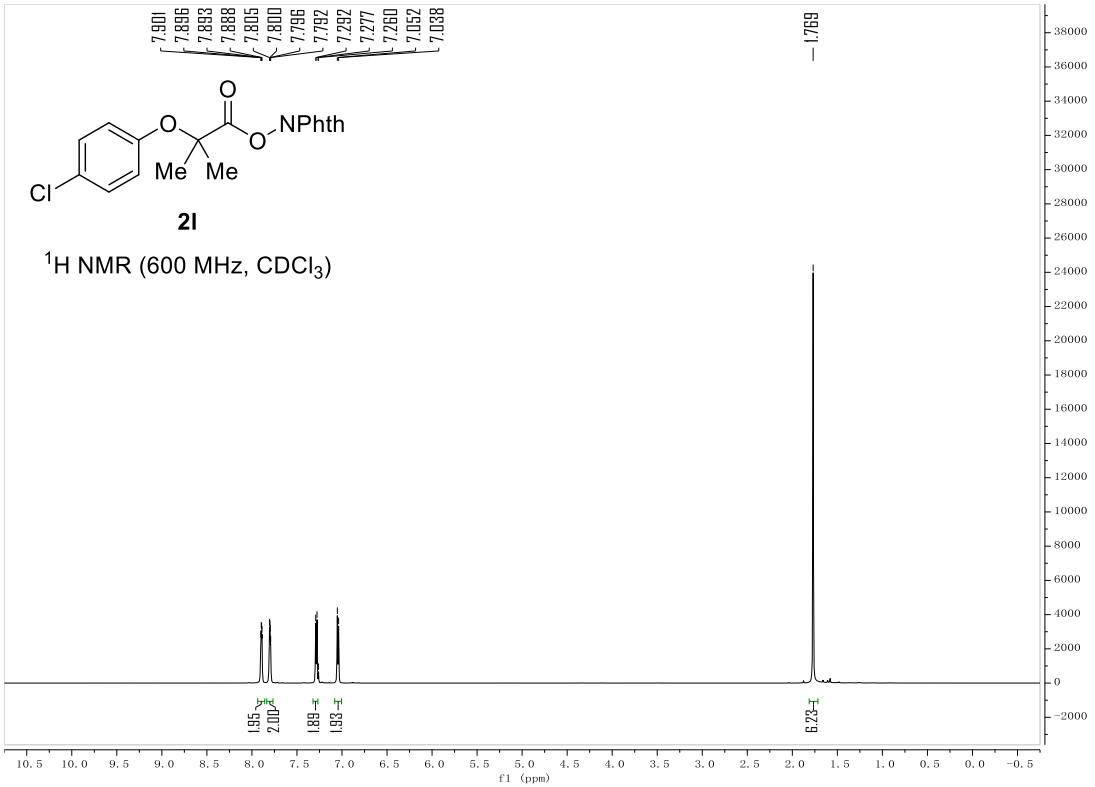

167.66
167.52
161.82
161.73
153.01
134.92
134.81
129.10
129.05
124.10
81.06
80.43
77.48
77.16
76.84
62.38
62.20
57.75
56.50
43.65
42.70
35.89
35.13
30.59
30.37
28.57
28.30
28.03
27.72
O
NPhth
N
Boc
O
2i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

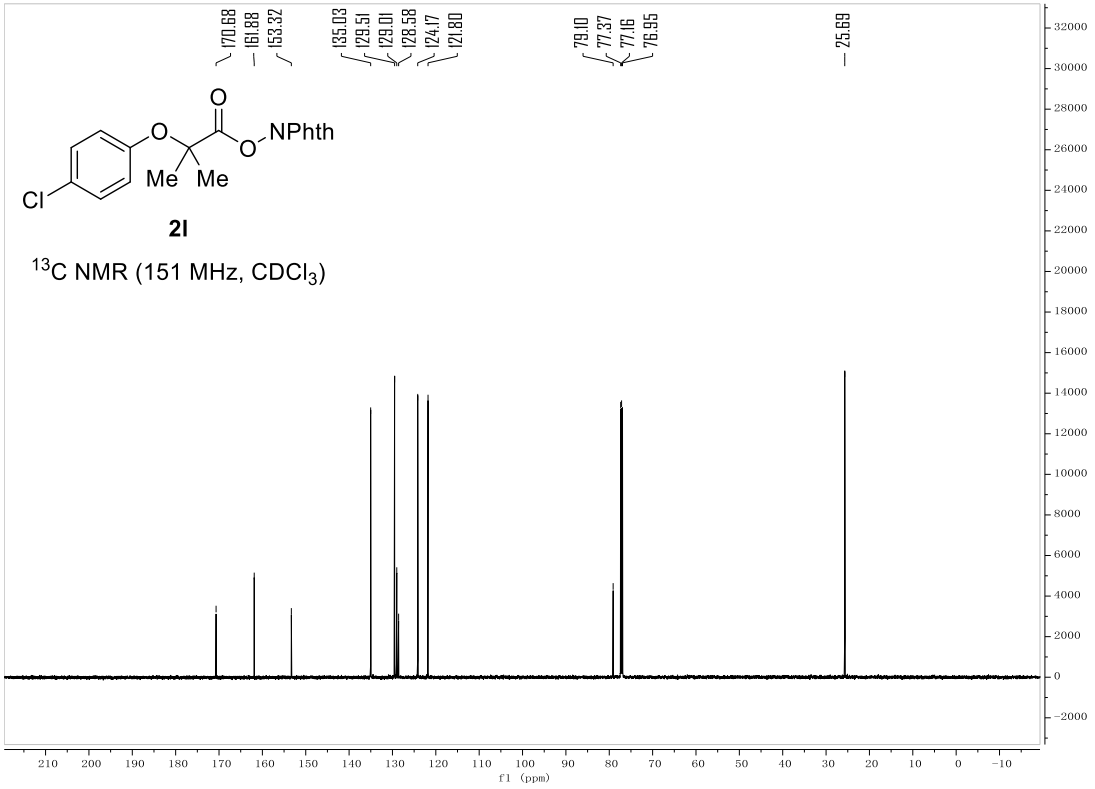

Me
O
NPhth
N
Cbz
O
2j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

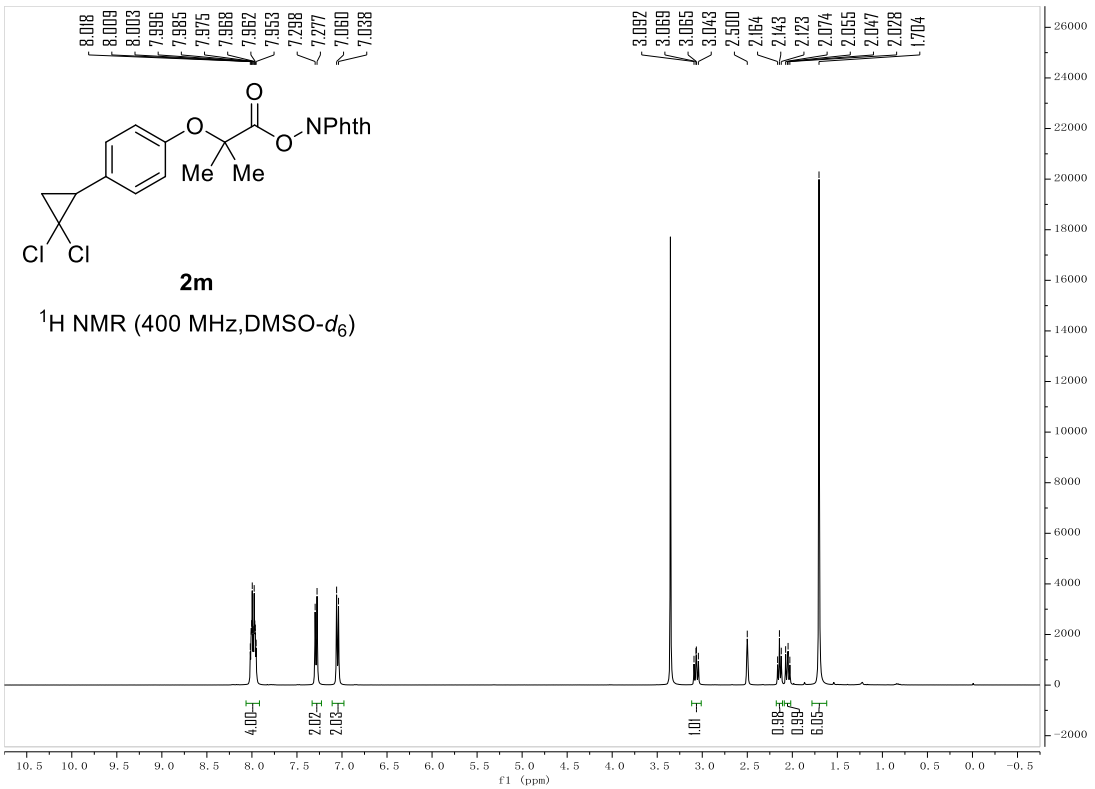

Me
O
NPhth
N
Cbz
O
2j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

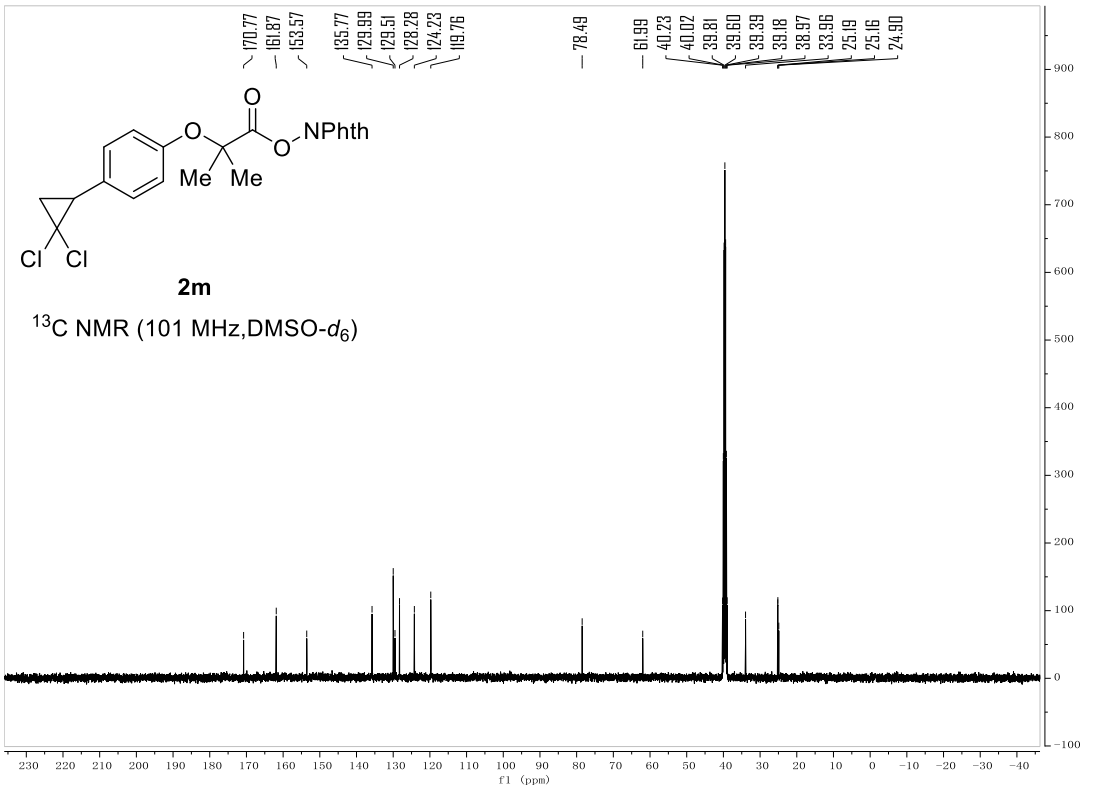

7.885
7.886
7.882
7.874
7.865
7.804
7.796
7.791
7.783
7.771
7.396
7.379
7.365
7.345
7.330
7.311
7.296
7.279
7.260
5.512
5.482
5.210
5.078
5.048
3.547
3.528
3.522
2.550
2.536
2.286
2.272
2.253
1.931
1.234
1.220
1.203
1.162
1.144
0.925
0.908
0.890
0.797
0.780
0.763
nBu
O
NPhth
N
Cbz
O
2k
1H NMR (400 MHz, CDCl3)
1.85
2.00
5.00
2.28
0.66
0.39
1.03
1.26
1.72
1.29
1.74
4.29
1.24
1.94
f1 (ppm)

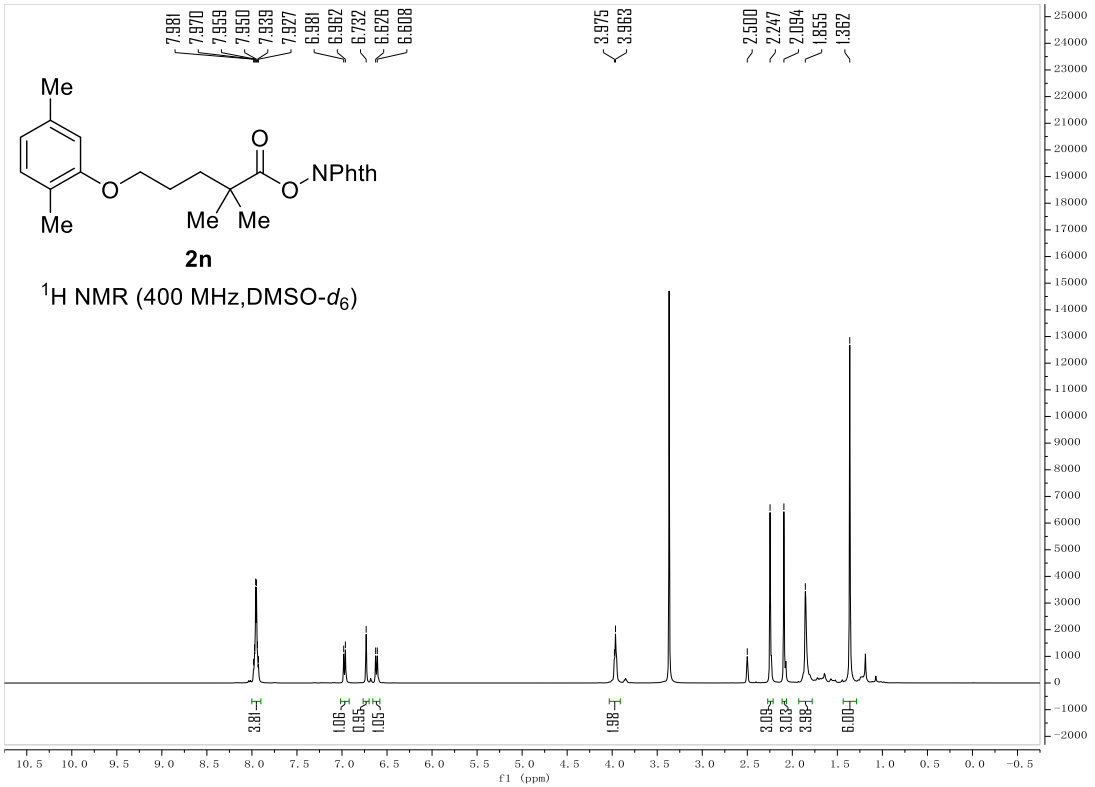

171.29
170.83
161.91
161.88
154.42
154.29
136.94
136.54
134.88
134.77
129.16
129.11
128.54
128.50
128.49
128.06
128.03
124.04
124.00
77.48
77.16
76.84
68.20
67.62
67.27
67.17
49.35
48.57
38.14
36.43
34.61
33.41
25.53
25.19
23.45
22.95
22.87
22.68
14.24
14.03
nBu
O
NPhth
N
Cbz
O
2k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

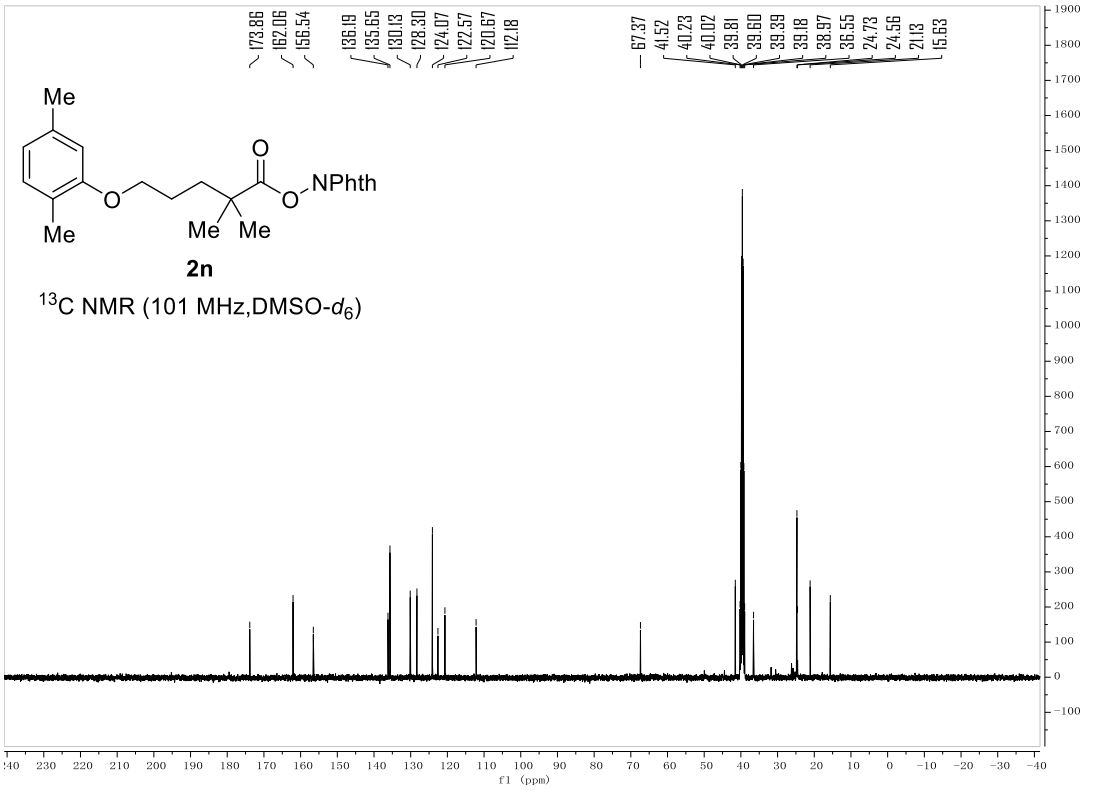

7.911
7.896
7.893
7.888
7.805
7.800
7.796
7.792
7.292
7.277
7.280
7.052
7.038
1.769
O
O
NPhth
O
Me
Me
Cl
2l
1H NMR (600 MHz, CDCl3)
1.95
2.00
1.89
1.93
6.23
f1 (ppm)

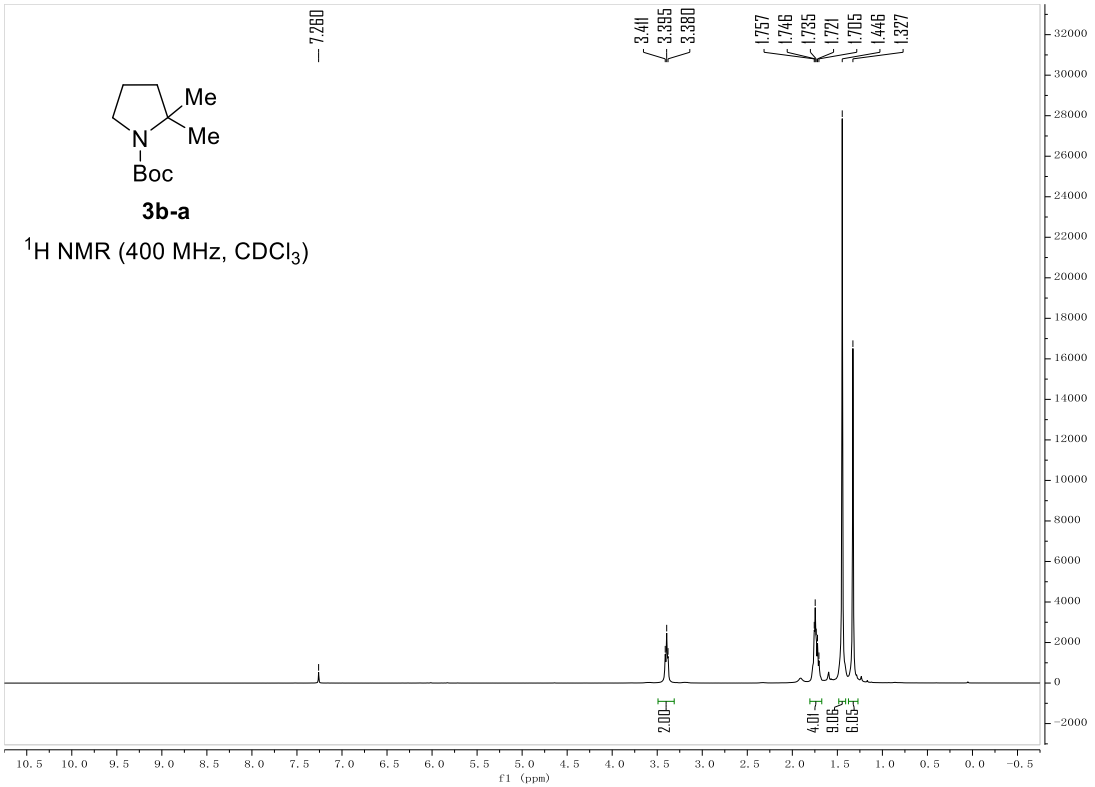

170.68
161.88
153.32
135.03
129.51
129.01
128.58
124.17
121.80
79.10
77.37
77.16
76.95
25.69
O
O
NPhth
O
Me
Me
Cl
2l
13C NMR (151 MHz, CDCl3)
f1 (ppm)


8.018
8.009
8.003
7.996
7.985
7.975
7.968
7.962
7.953
7.298
7.277
7.060
7.038
3.092
3.069
3.065
3.043
2.500
2.164
2.143
2.123
2.074
2.055
2.047
2.028
1.704
O
O
O
NPhth
Me
Me
Cl
Cl
2m
1H NMR (400 MHz,DMSO-d6)
4.00
2.02
2.03
1.01
0.98
0.99
6.05
f1 (ppm)


170.77
161.87
153.57
135.77
129.99
129.51
128.28
124.23
119.76
78.49
61.99
40.23
40.02
39.81
39.60
39.39
39.18
38.97
33.96
25.19
25.16
24.90
O
O
O
NPhth
Me
Me
Cl
Cl
2m
13C NMR (101 MHz,DMSO-d6)
f1 (ppm)

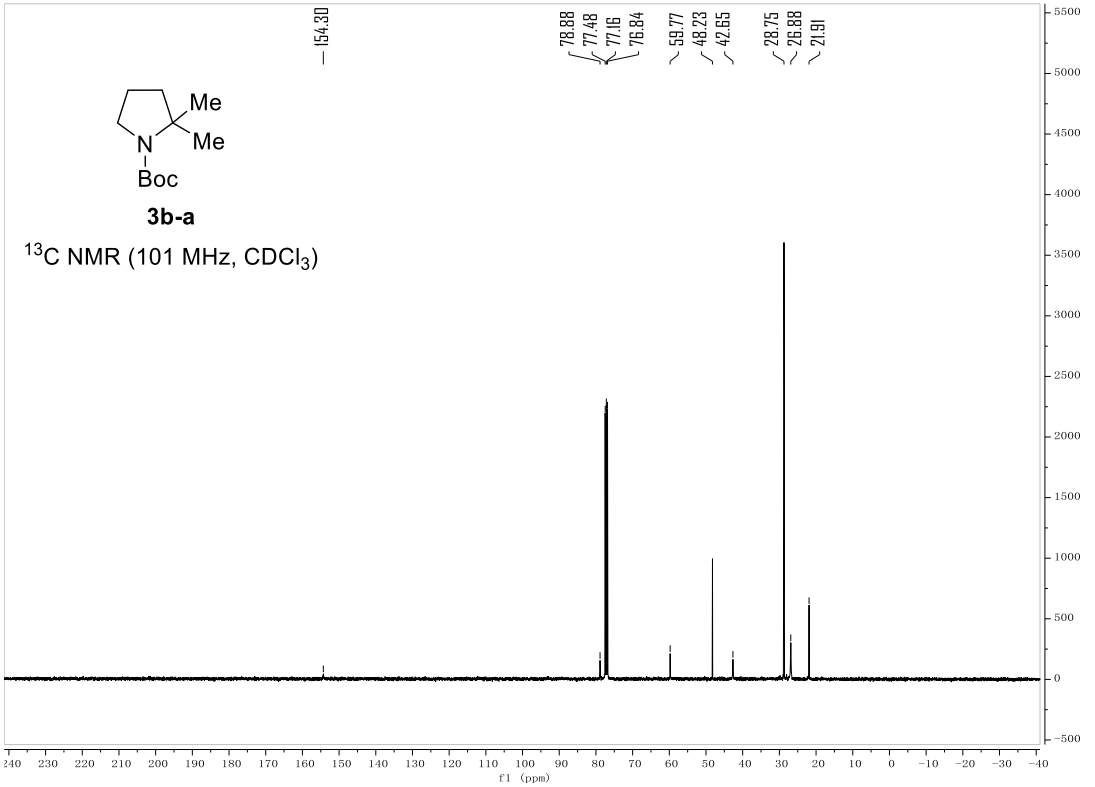

Me
O
NPhth
O
Me
Me
Me
2n
1H NMR (400 MHz,DMSO-d6)
7.981
7.970
7.959
7.950
7.939
7.927
6.981
6.962
6.732
6.626
6.608
3.975
3.963
2.500
2.247
2.094
1.855
1.362
3.81
1.06
0.95
1.05
1.98
3.09
3.03
3.98
6.00
f1 (ppm)


Me
O
NPhth
O
Me
Me
Me
2n
13C NMR (101 MHz,DMSO-d6)
173.86
162.06
156.54
136.19
135.65
130.13
128.30
124.07
122.57
120.67
112.18
67.37
41.52
40.23
40.02
39.81
39.60
39.39
39.18
38.97
36.55
24.73
24.56
21.13
15.63
f1 (ppm)



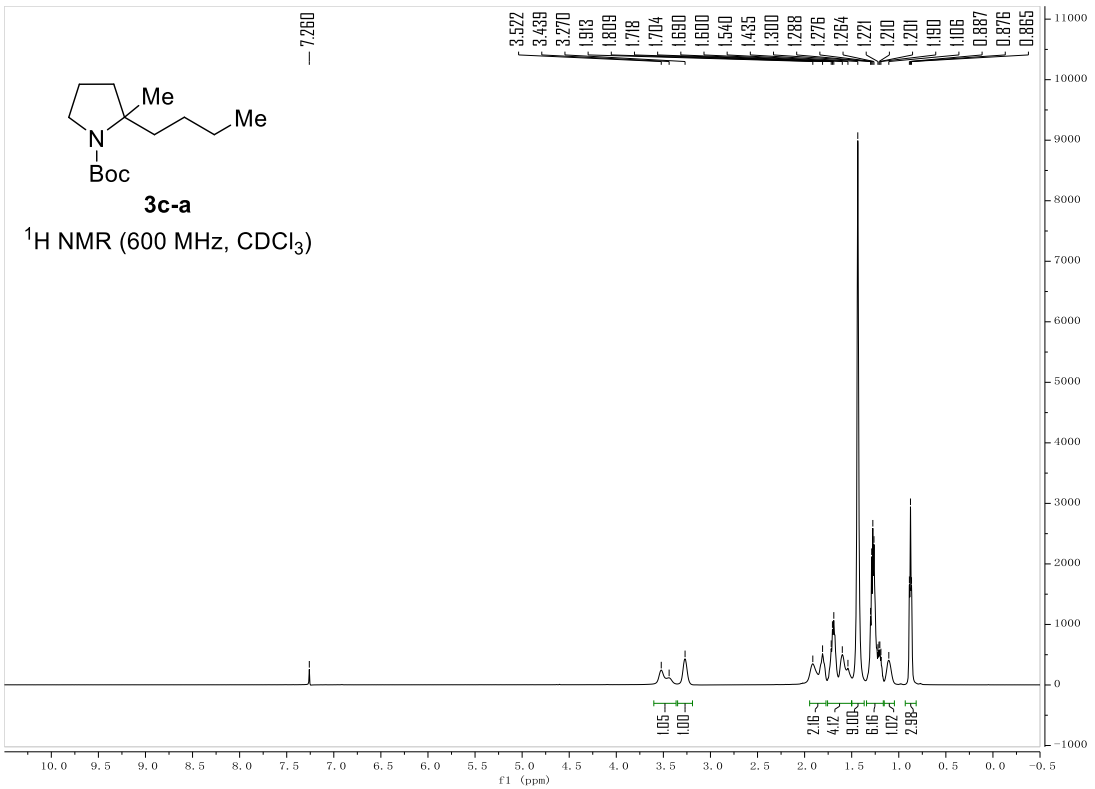
3b-a

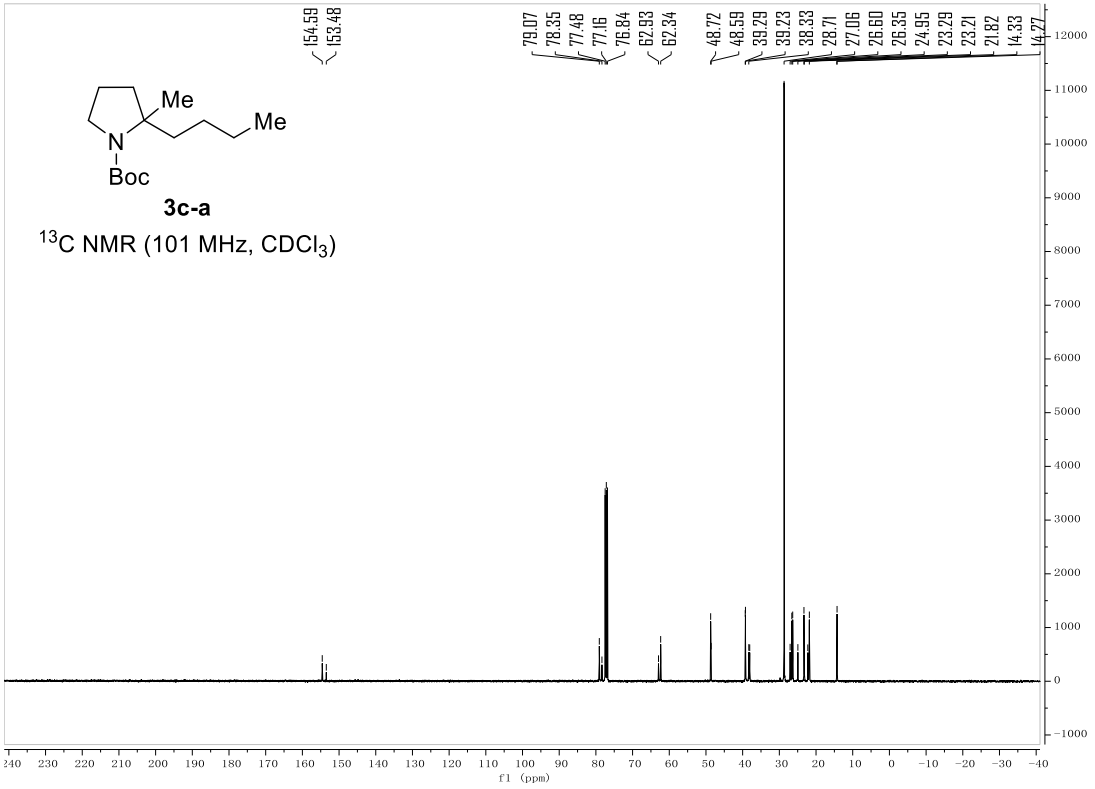
^{1}H NMR (400 MHz, $CDCl_3$)

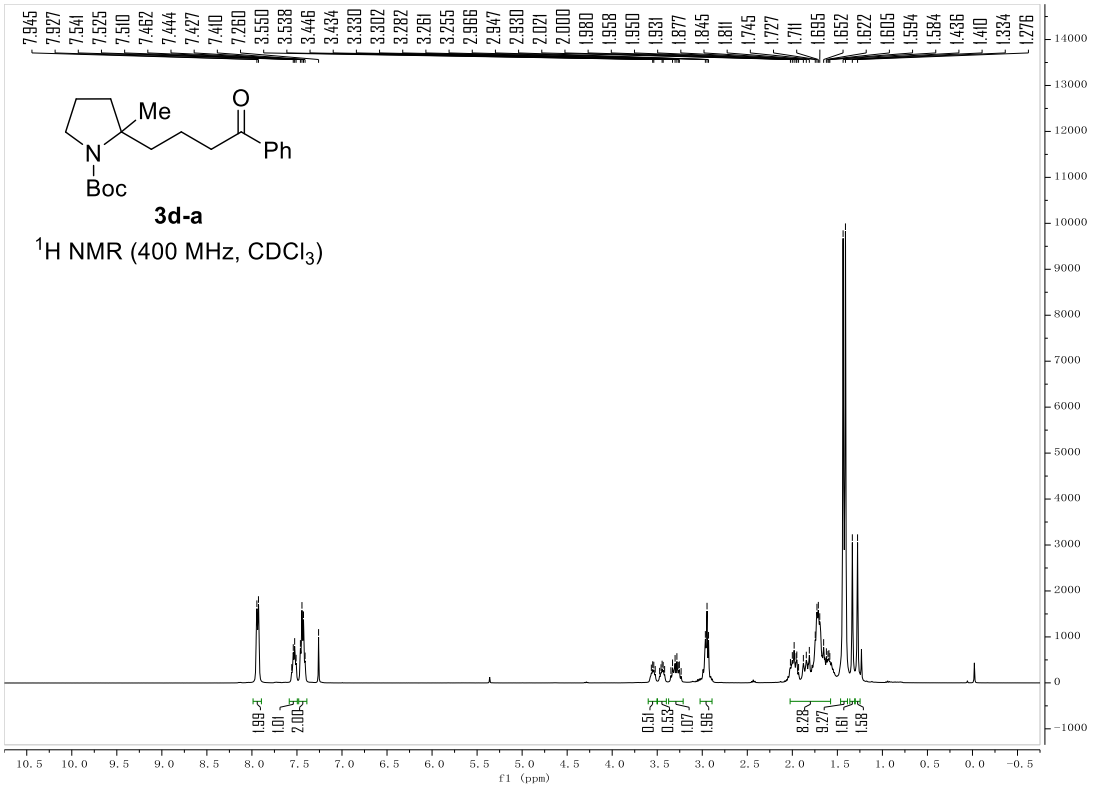


3b-a

^{13}C NMR (101 MHz, $CDCl_3$)

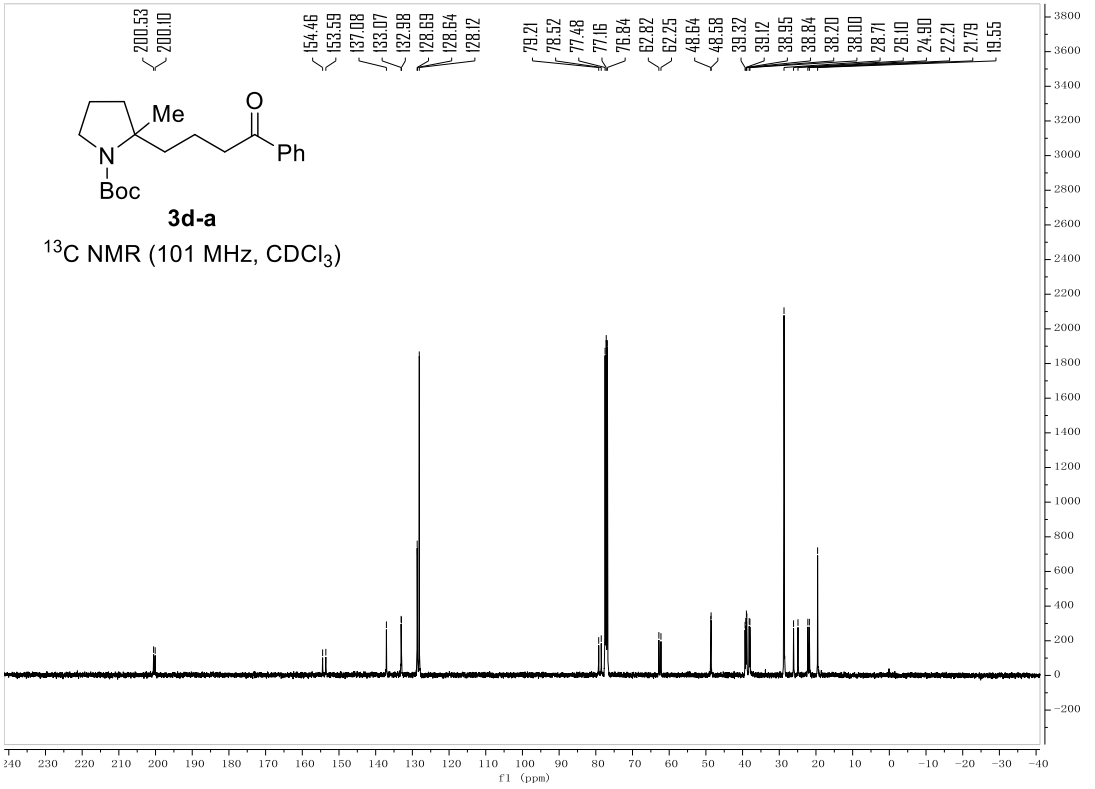

Me
Me
N
Boc
3c-a
1H NMR (600 MHz, CDCl3)
7.260
3.522
3.439
3.270
1.913
1.809
1.718
1.704
1.690
1.600
1.540
1.435
1.300
1.288
1.276
1.264
1.221
1.210
1.201
1.190
1.106
0.887
0.876
0.865
1.05
1.00
2.16
4.12
9.00
6.16
1.02
2.98
f1 (ppm)


Me
Me
N
Boc
3c-a
13C NMR (101 MHz, CDCl3)
154.59
153.48
79.07
78.35
77.48
77.16
76.84
62.93
62.34
48.72
48.59
39.29
39.23
38.33
28.71
27.06
26.60
26.35
24.95
23.29
23.21
21.82
14.33
14.27
f1 (ppm)



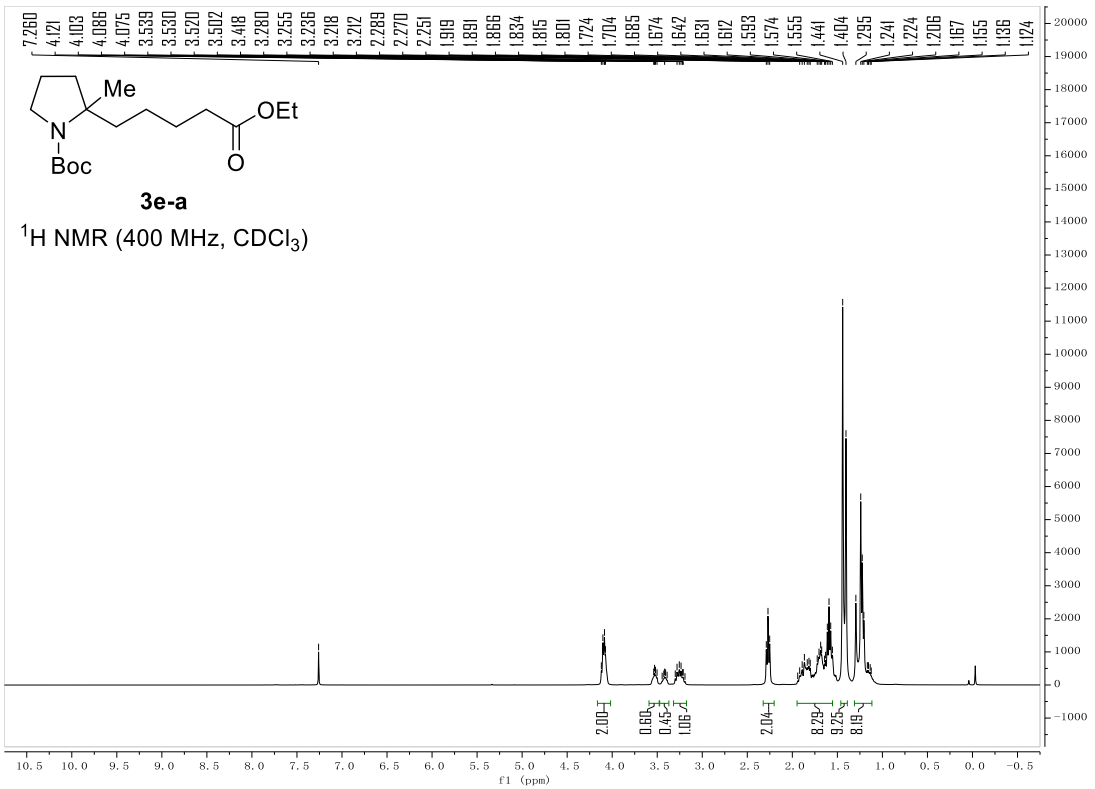
3d-a

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



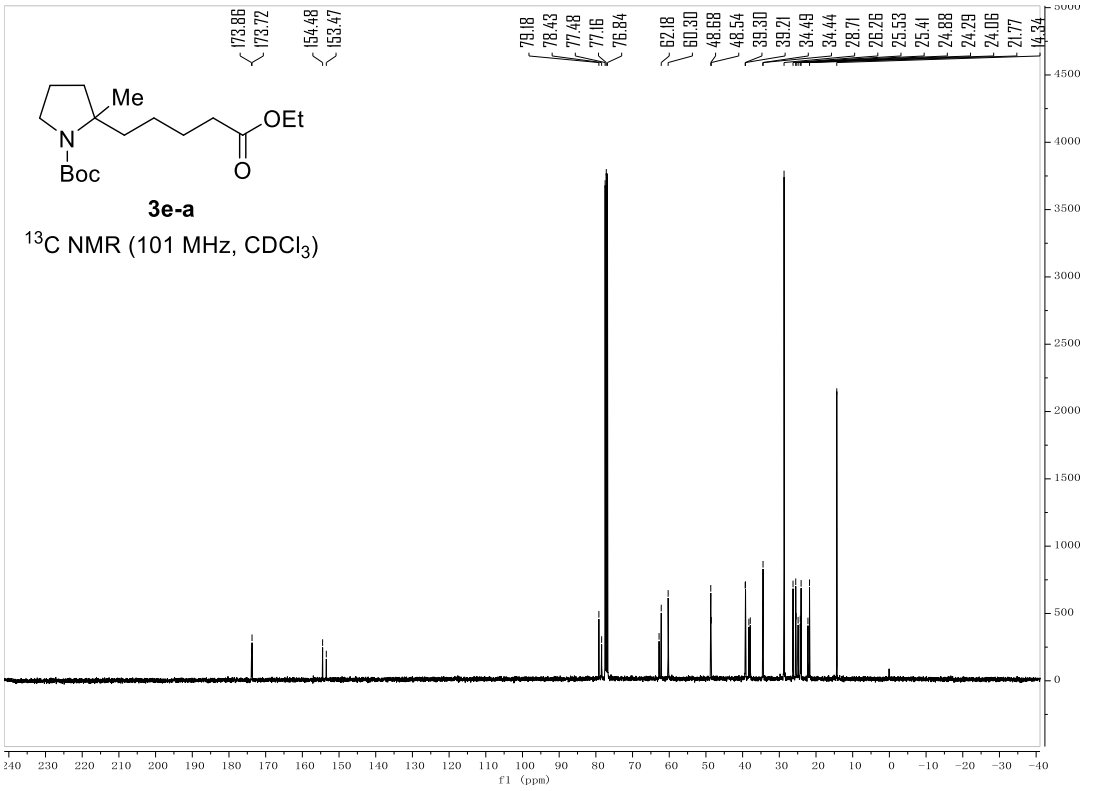
3d-a

^{13}C NMR (101 MHz, $CDCl_3$)



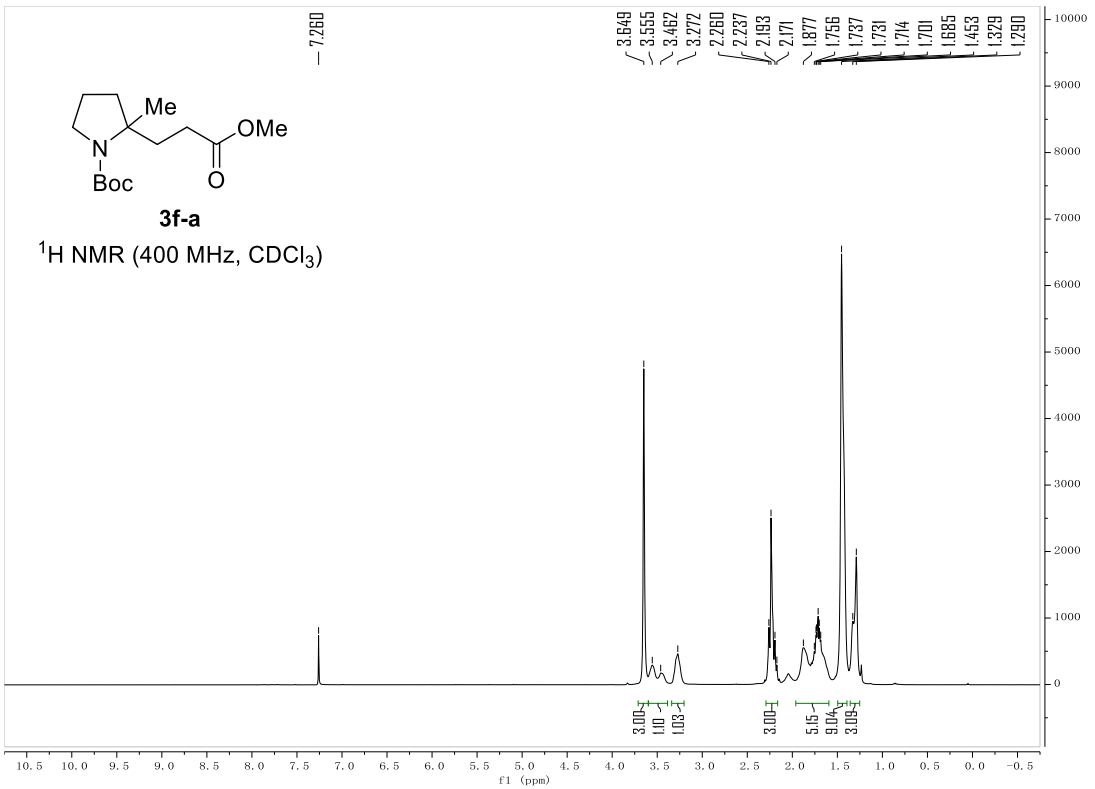
3e-a

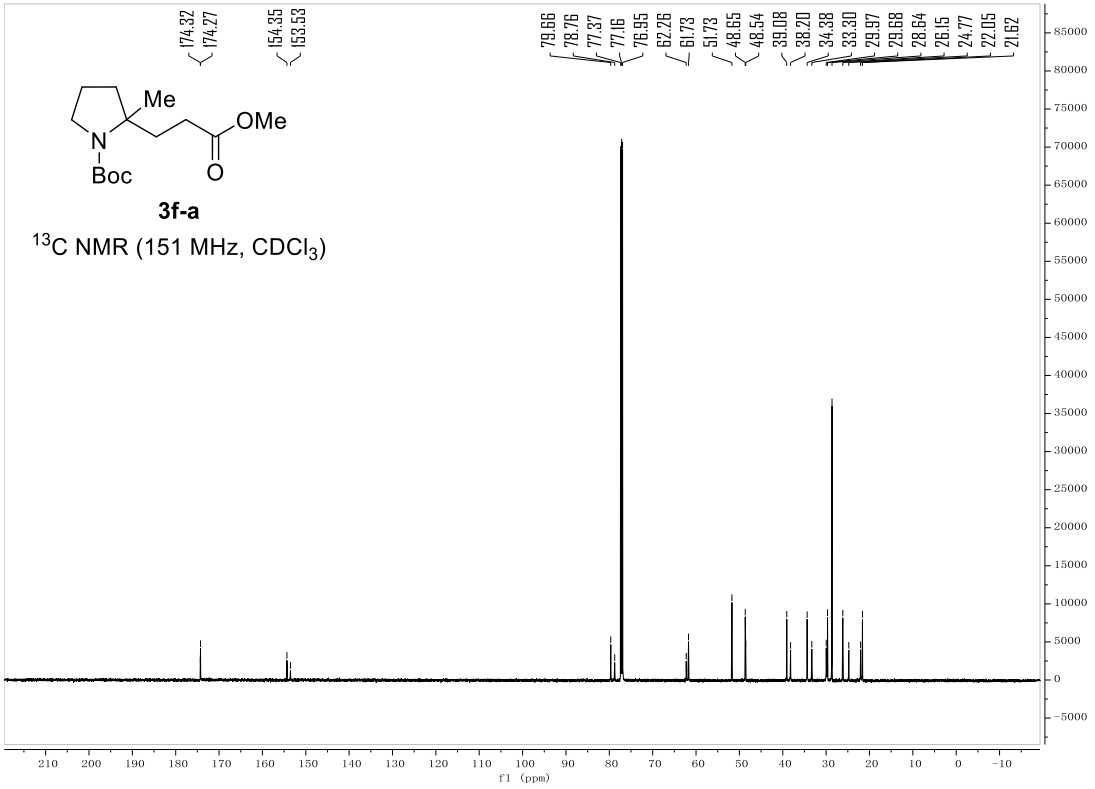
^{1}H NMR (400 MHz, $CDCl_3$)

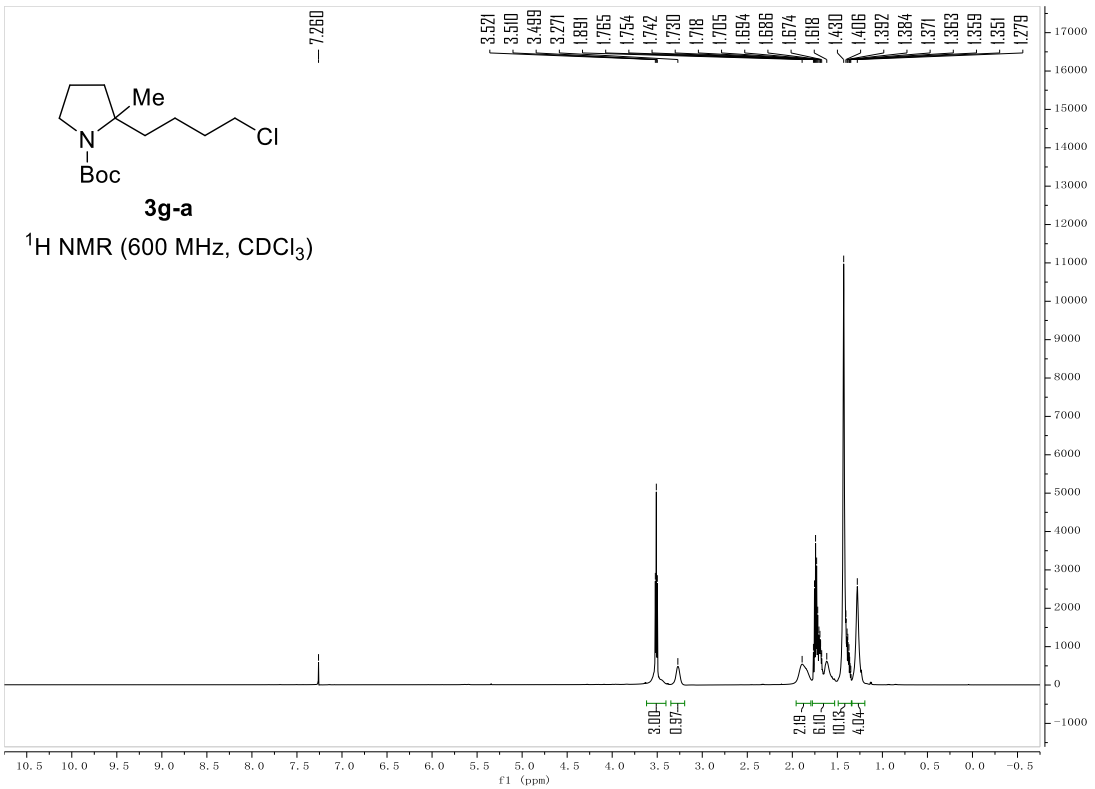


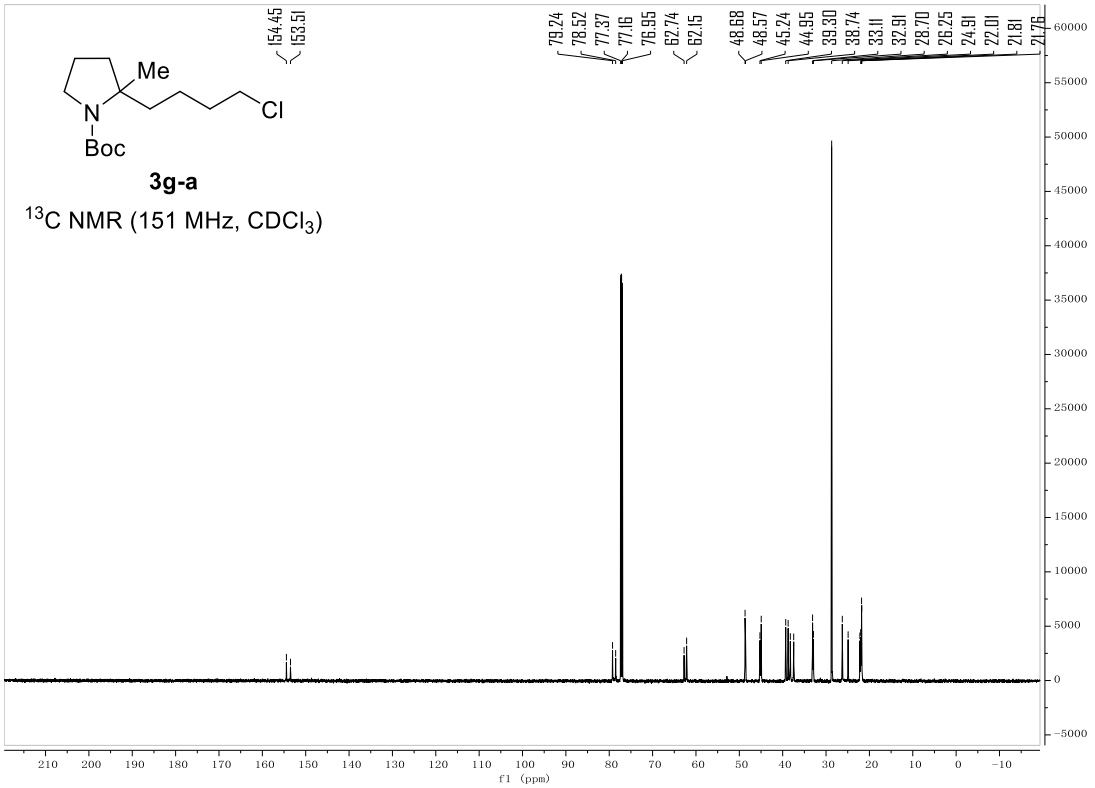
3e-a

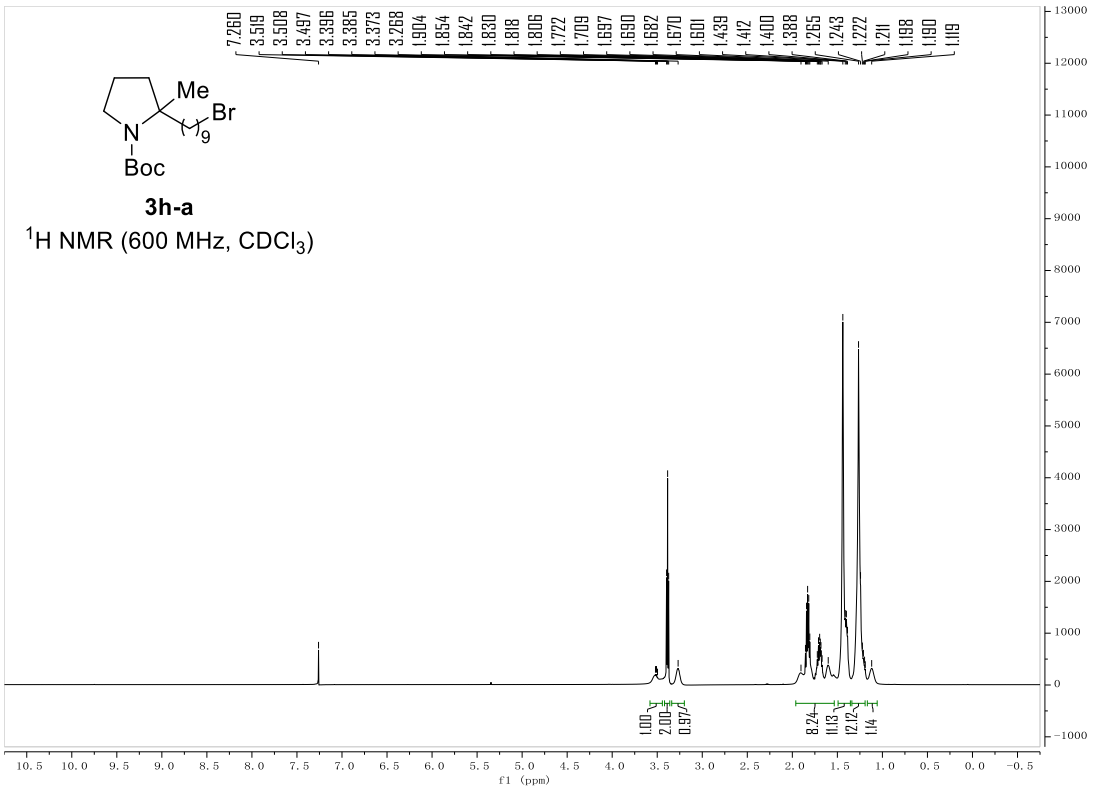
^{13}C NMR (101 MHz, $CDCl_3$)

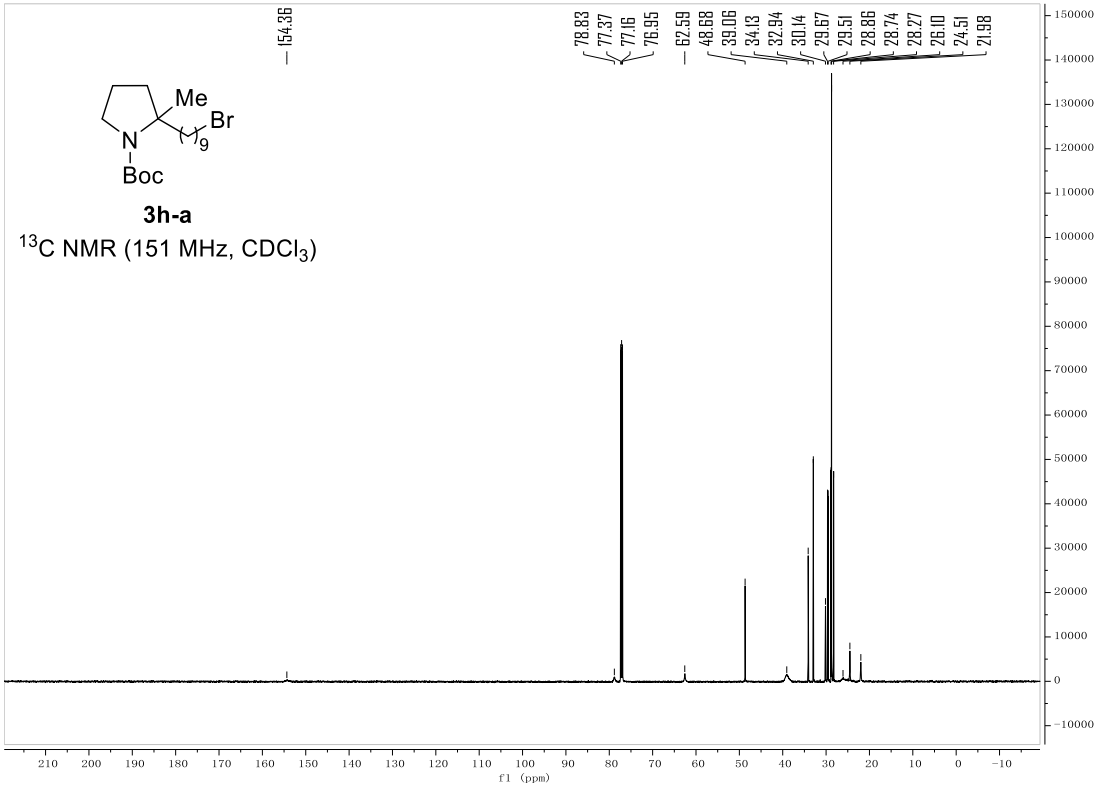

7.260
3.649
3.555
3.462
3.272
2.260
2.237
2.193
2.171
1.877
1.756
1.737
1.731
1.714
1.701
1.685
1.453
1.329
1.290
Me
OMe
N
Boc
O
3f-a
1H NMR (400 MHz, CDCl3)
3.00
1.10
1.03
3.00
5.15
9.04
3.09
f1 (ppm)

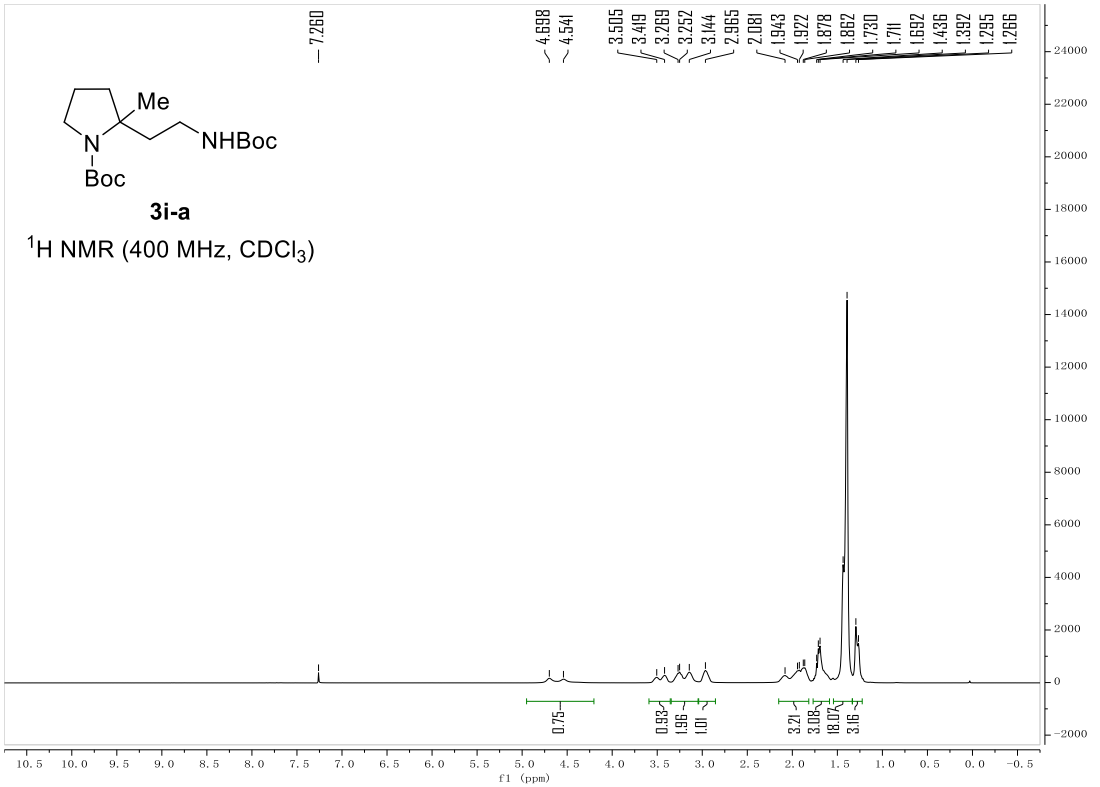

174.32
174.27
154.35
153.53
79.66
78.76
77.37
77.16
76.95
62.26
61.73
51.73
48.65
48.54
39.08
38.20
34.38
33.30
29.97
29.68
28.64
26.15
24.77
22.05
21.62
Me
OMe
N
Boc
O
3f-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.260
3.521
3.510
3.499
3.271
1.891
1.765
1.754
1.742
1.730
1.718
1.705
1.694
1.686
1.674
1.618
1.430
1.406
1.392
1.384
1.371
1.363
1.359
1.351
1.279
Me
N
Cl
Boc
3g-a
1H NMR (600 MHz, CDCl3)
3.00
0.97
2.19
6.10
10.13
4.04
f1 (ppm)


154.45
153.51
79.24
78.52
77.37
77.16
76.95
62.74
62.15
48.68
48.57
45.24
44.95
39.30
38.74
33.11
32.91
28.70
26.25
24.91
22.01
21.81
21.76
Me
N
Cl
Boc
3g-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

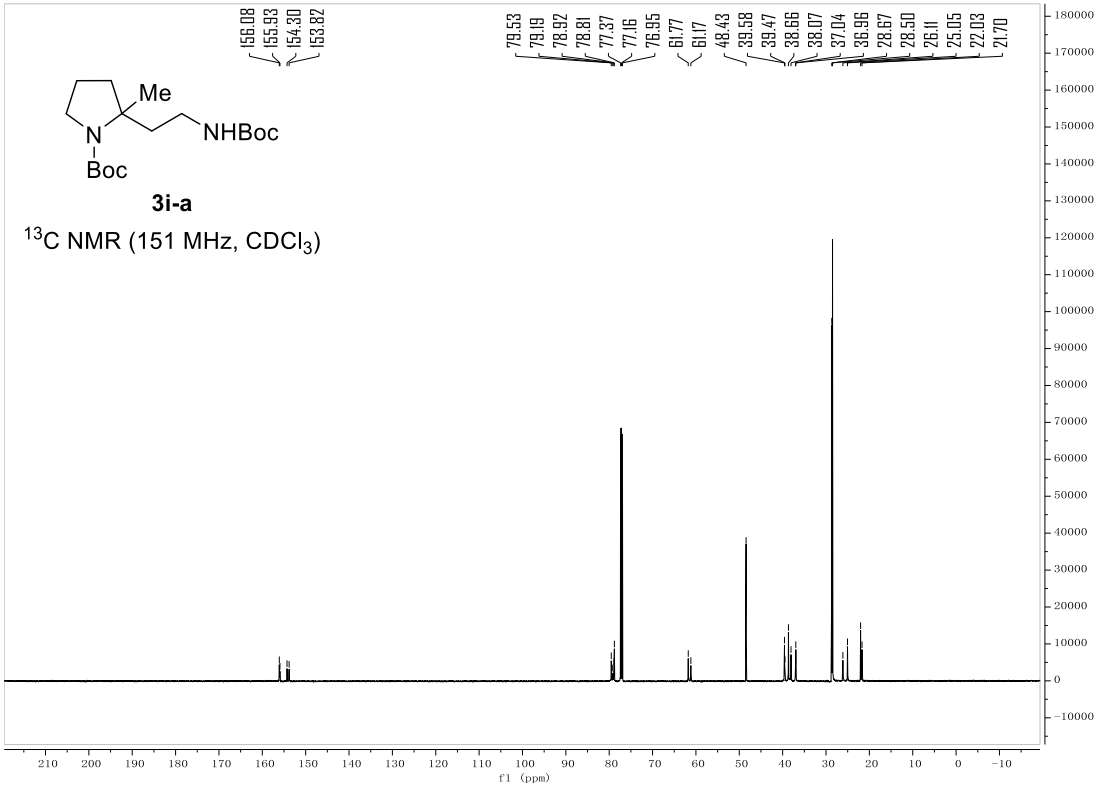

7.260
3.519
3.508
3.497
3.396
3.385
3.373
3.268
1.904
1.854
1.842
1.830
1.818
1.806
1.722
1.709
1.697
1.690
1.682
1.670
1.601
1.439
1.412
1.400
1.388
1.265
1.243
1.222
1.211
1.198
1.190
1.119
Me
Br
N
9
Boc
3h-a
1H NMR (600 MHz, CDCl3)
1.00
2.00
0.97
8.24
11.13
12.12
1.14
f1 (ppm)


154.36
78.83
77.37
77.16
76.95
62.59
48.68
39.06
34.13
32.94
30.14
29.67
29.51
28.86
28.74
28.27
26.10
24.51
21.98
Me
Br
N
9
Boc
3h-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



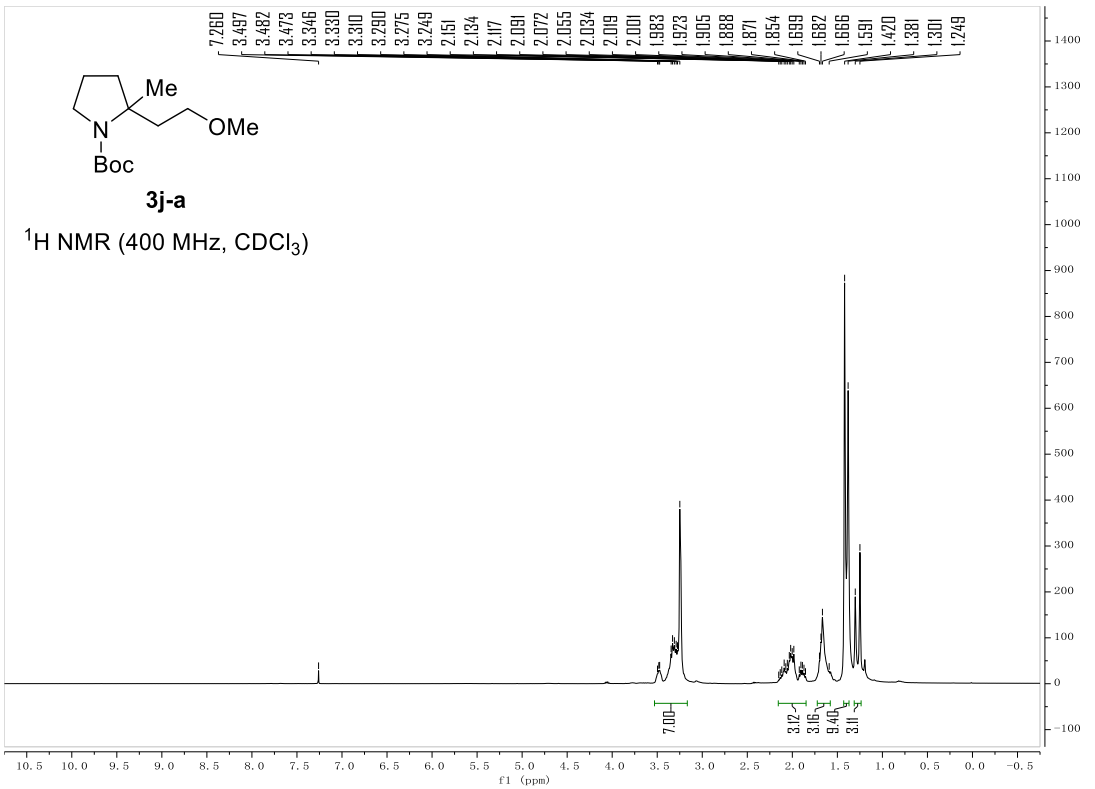
3i-a

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



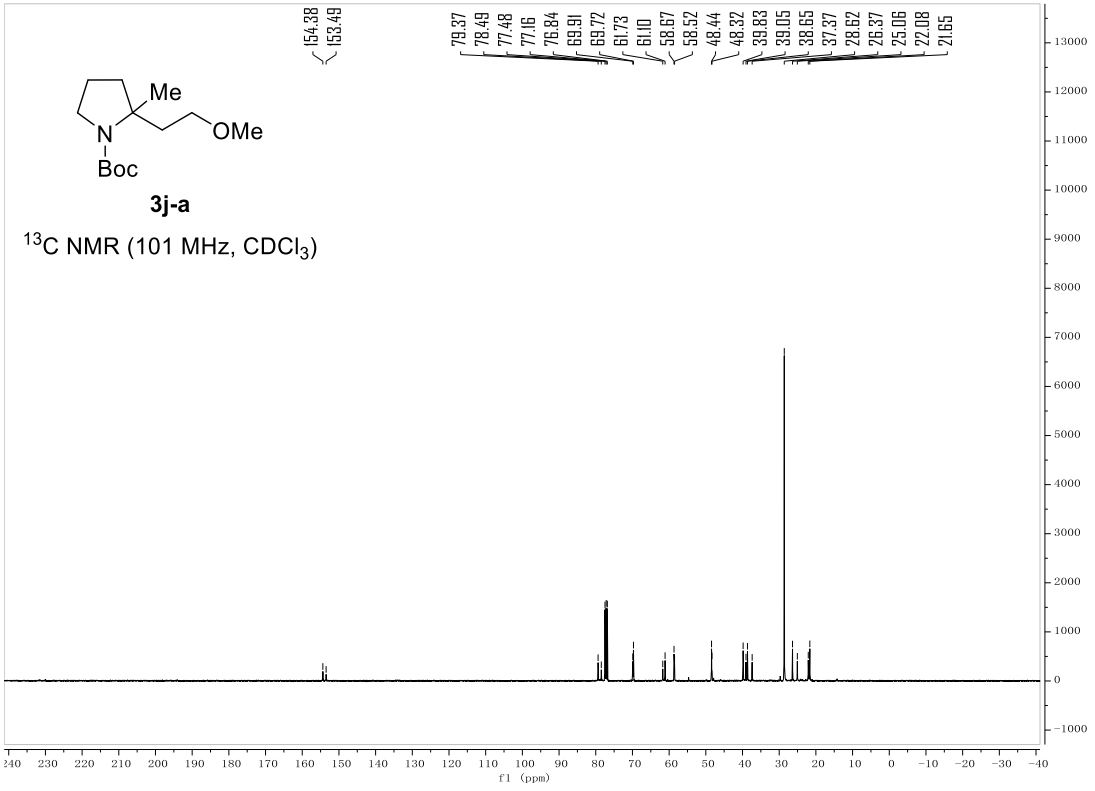
3i-a

^{13}C NMR (151 MHz, $CDCl_3$)



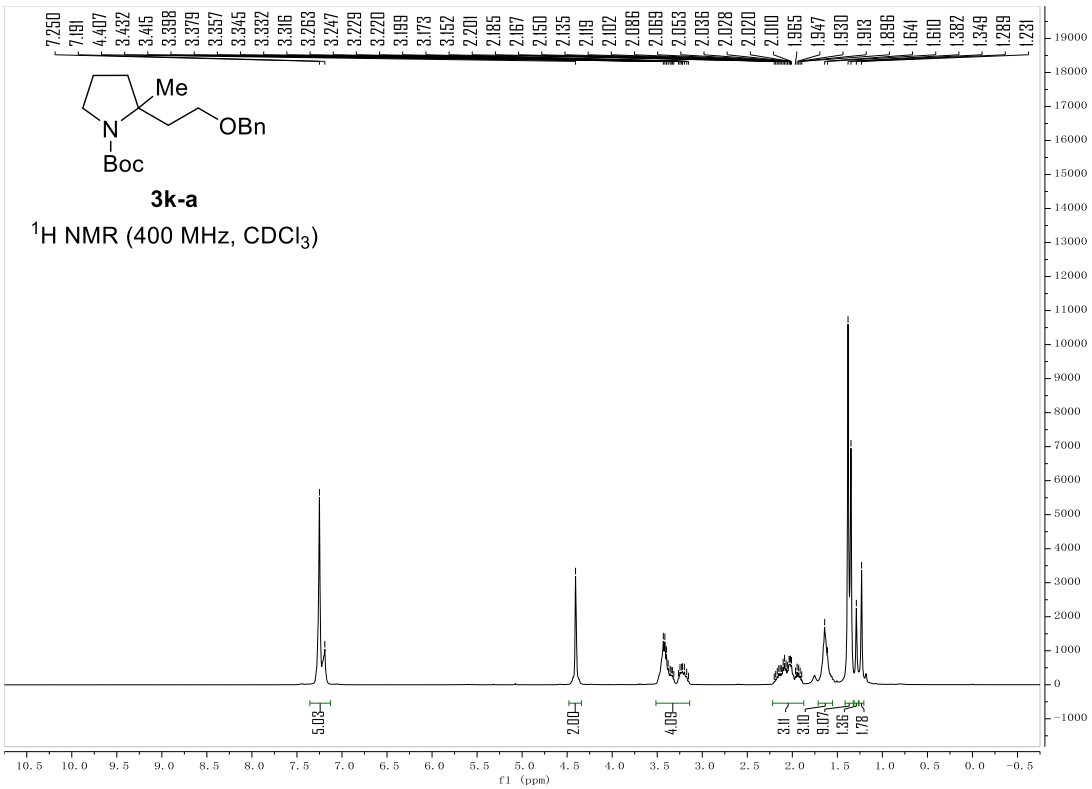
3j-a

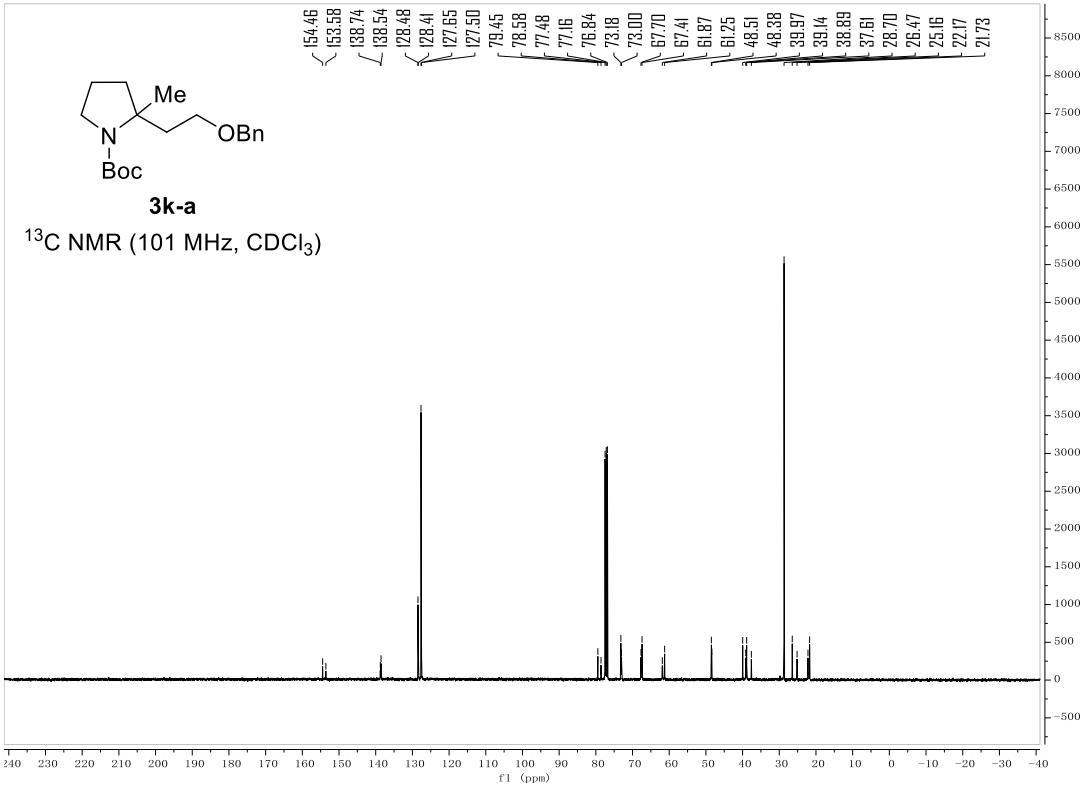
^{1}H NMR (400 MHz, $CDCl_3$)

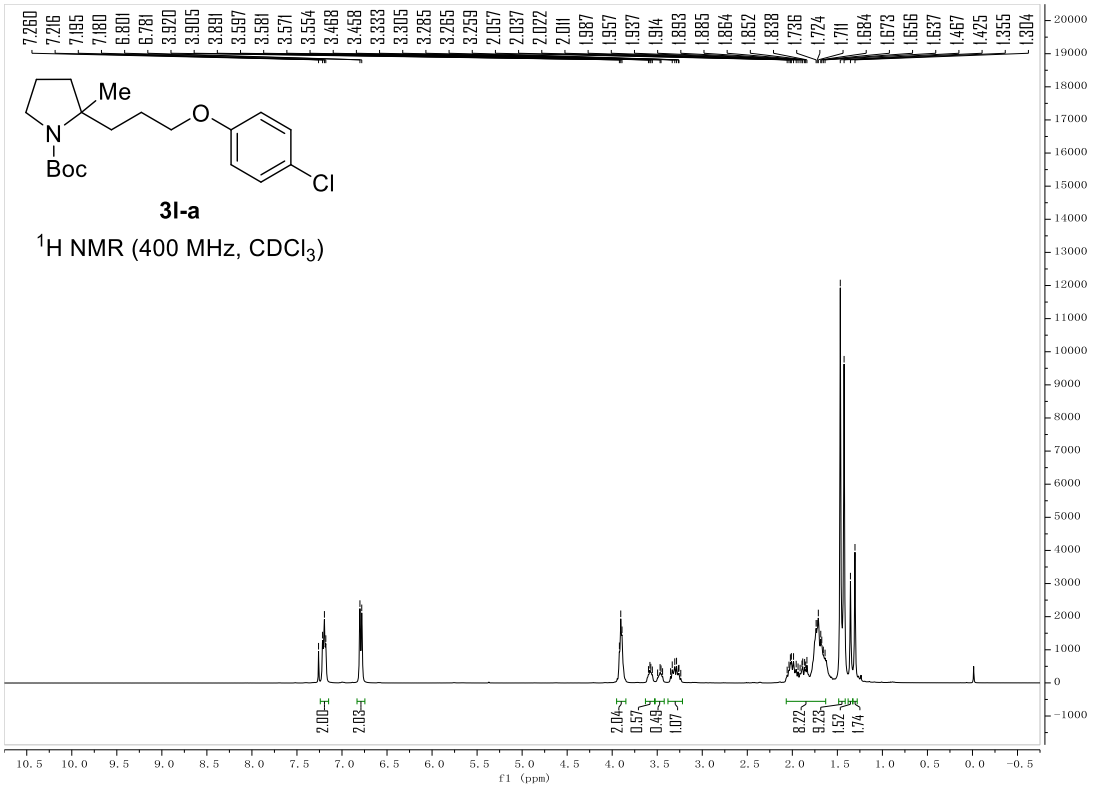


3j-a

^{13}C NMR (101 MHz, $CDCl_3$)

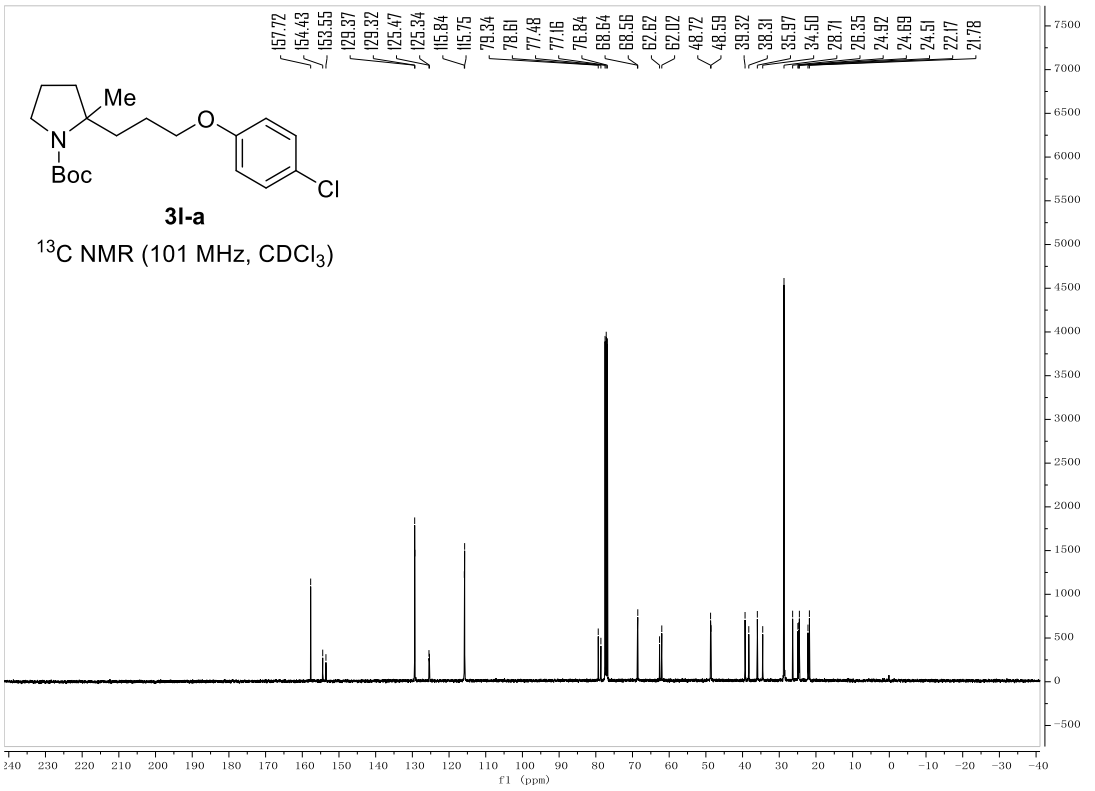

Me
N
OBn
Boc
3k-a
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
N
OBn
Boc
3k-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)



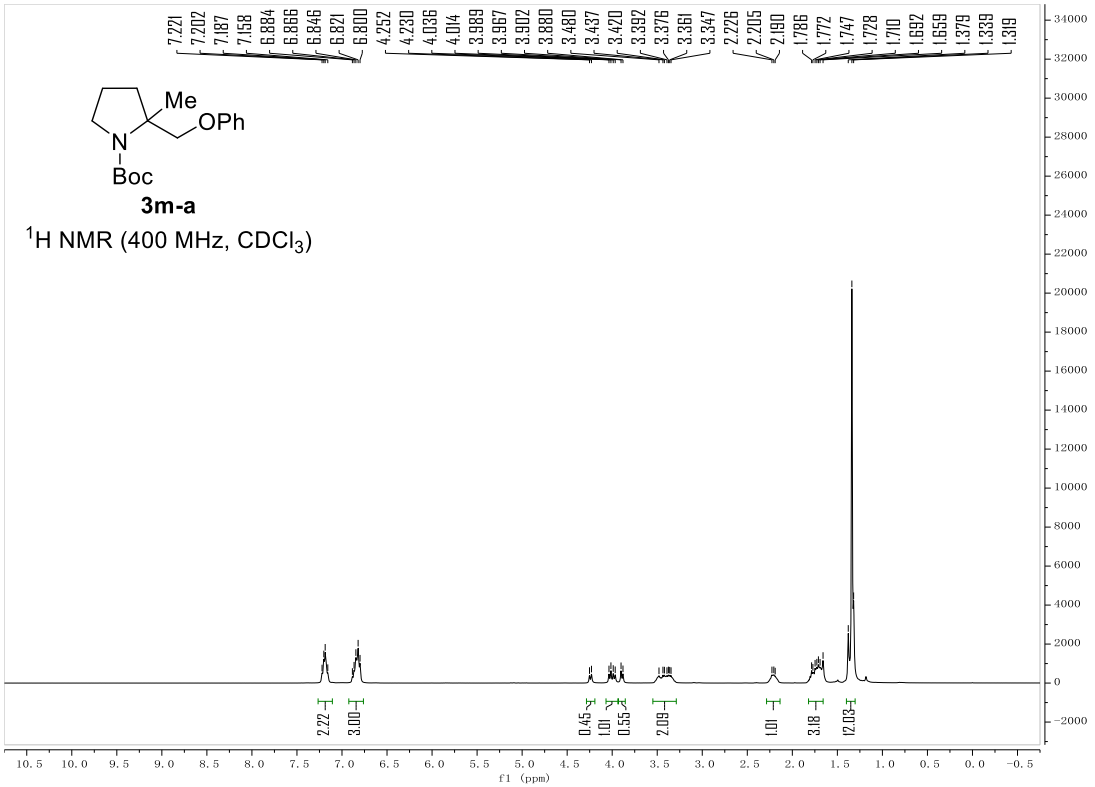
3l-a

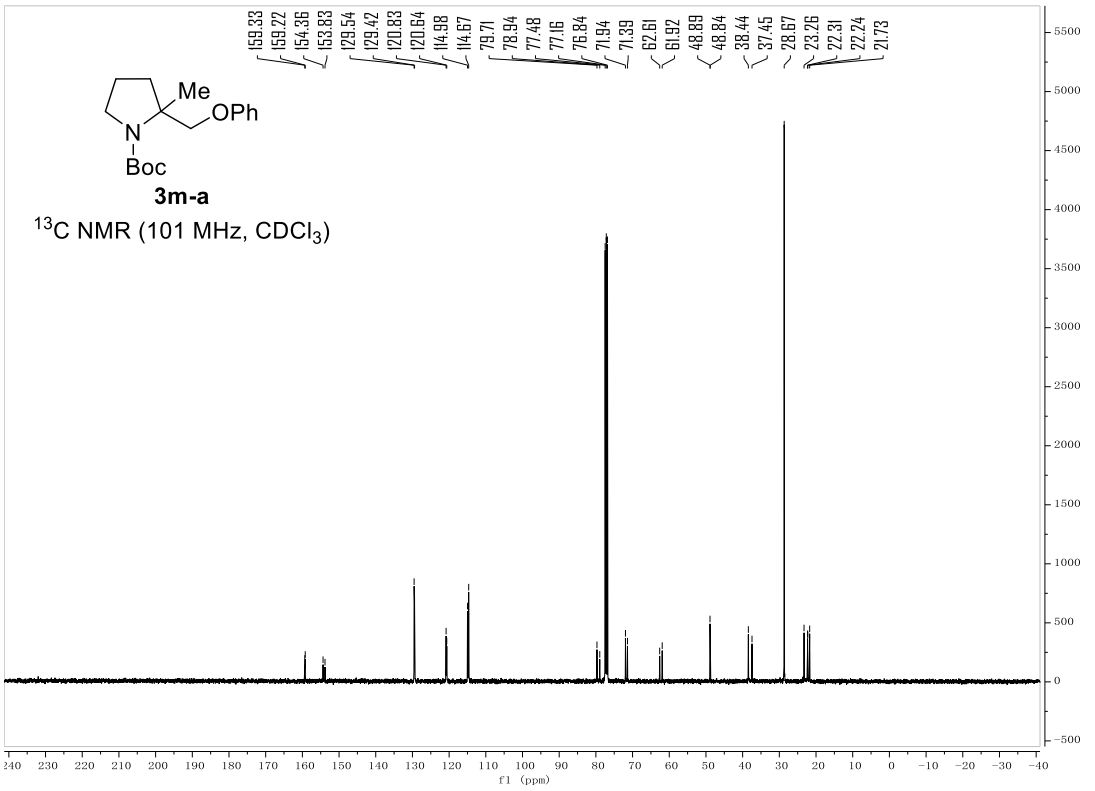
^{1}H NMR (400 MHz, $CDCl_3$)

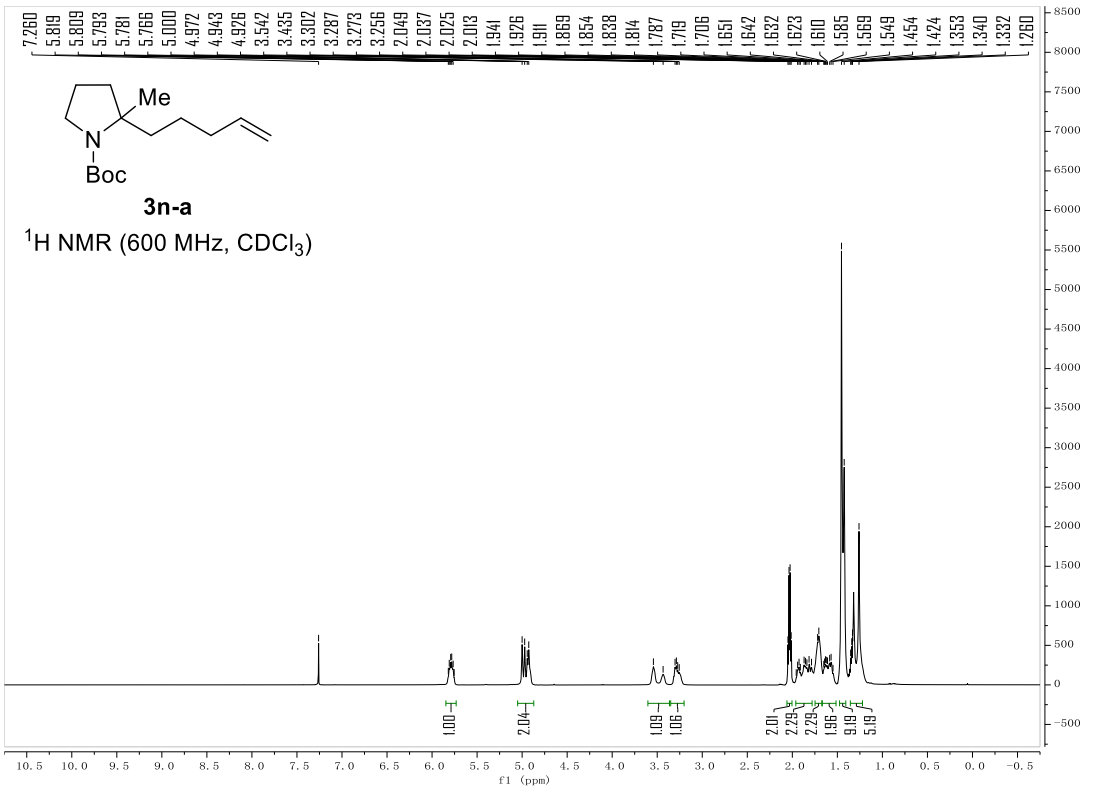


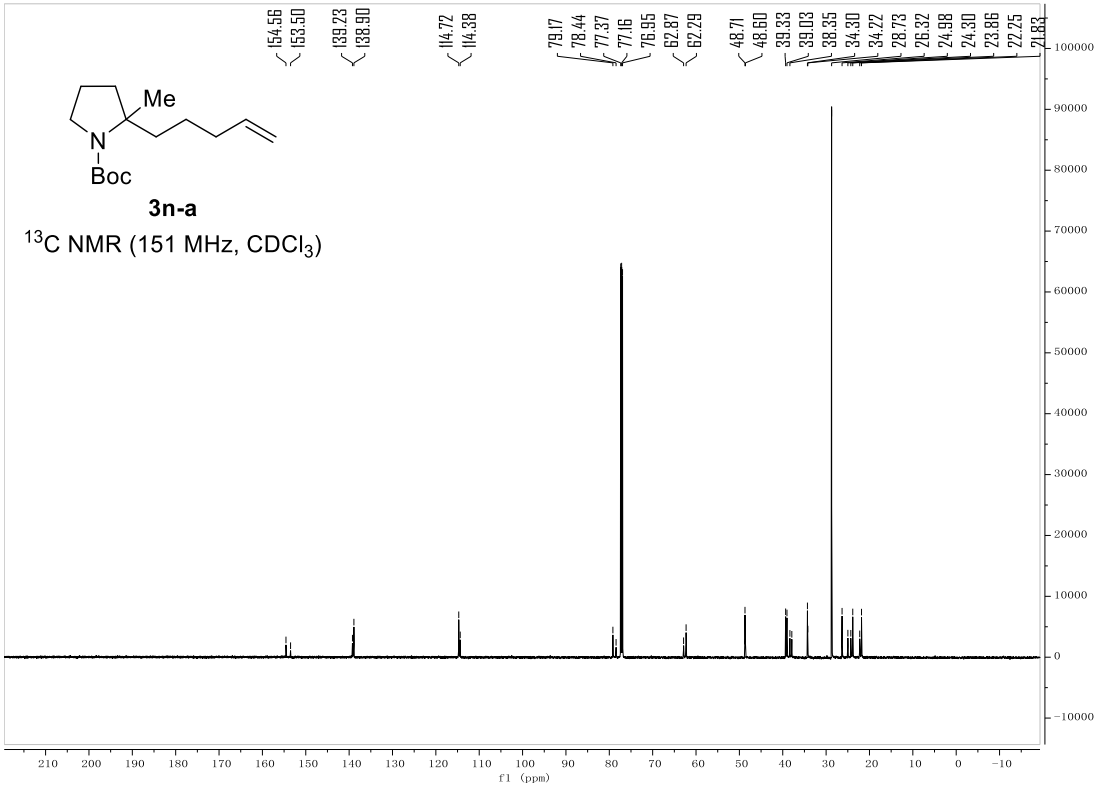
3l-a

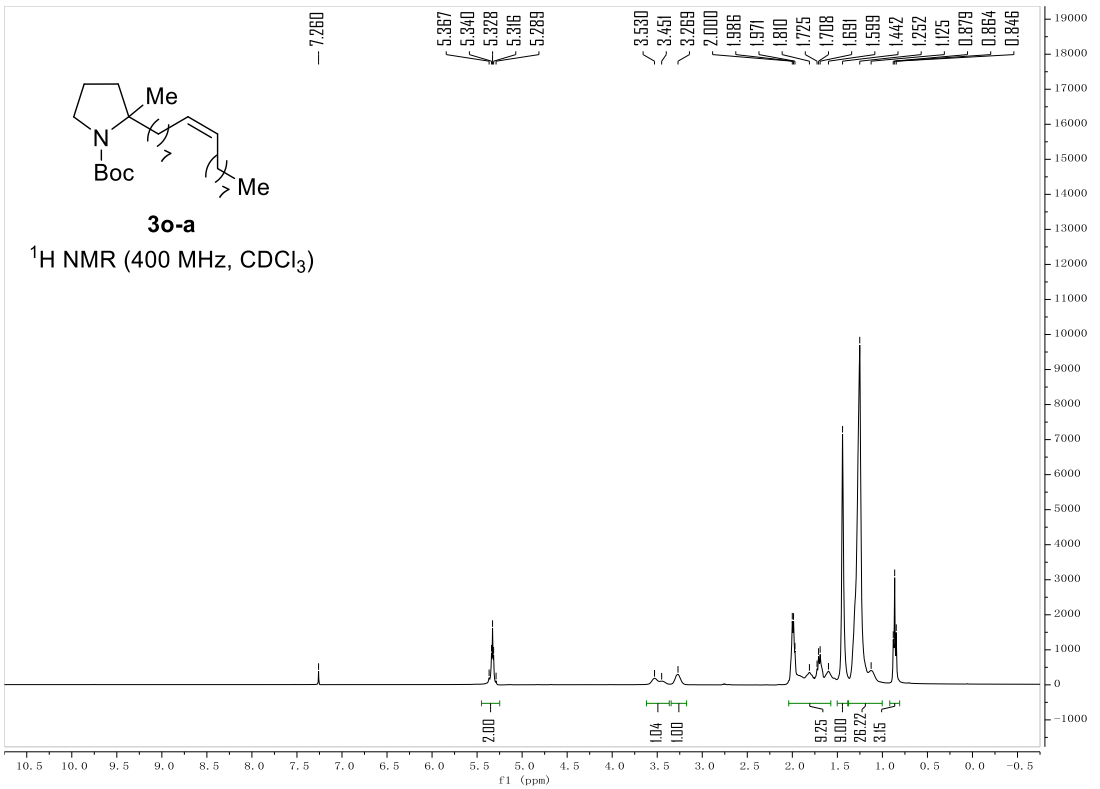
^{13}C NMR (101 MHz, $CDCl_3$)


7.221
7.202
7.187
7.158
6.884
6.866
6.846
6.821
6.800
4.252
4.230
4.036
4.014
3.989
3.967
3.902
3.880
3.480
3.437
3.420
3.392
3.376
3.361
3.347
2.226
2.205
2.190
1.786
1.772
1.747
1.728
1.710
1.692
1.659
1.378
1.339
1.319
Me
OPh
N
Boc
3m-a
1H NMR (400 MHz, CDCl3)
2.22
3.00
0.45
1.01
0.55
2.09
1.01
3.18
12.03
f1 (ppm)


159.33
159.22
154.36
153.83
129.54
129.42
120.83
120.64
114.98
114.67
79.71
78.94
77.48
77.16
76.84
71.94
71.39
62.61
61.92
48.89
48.84
38.44
37.45
28.67
23.26
22.31
22.24
21.73
Me
OPh
N
Boc
3m-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

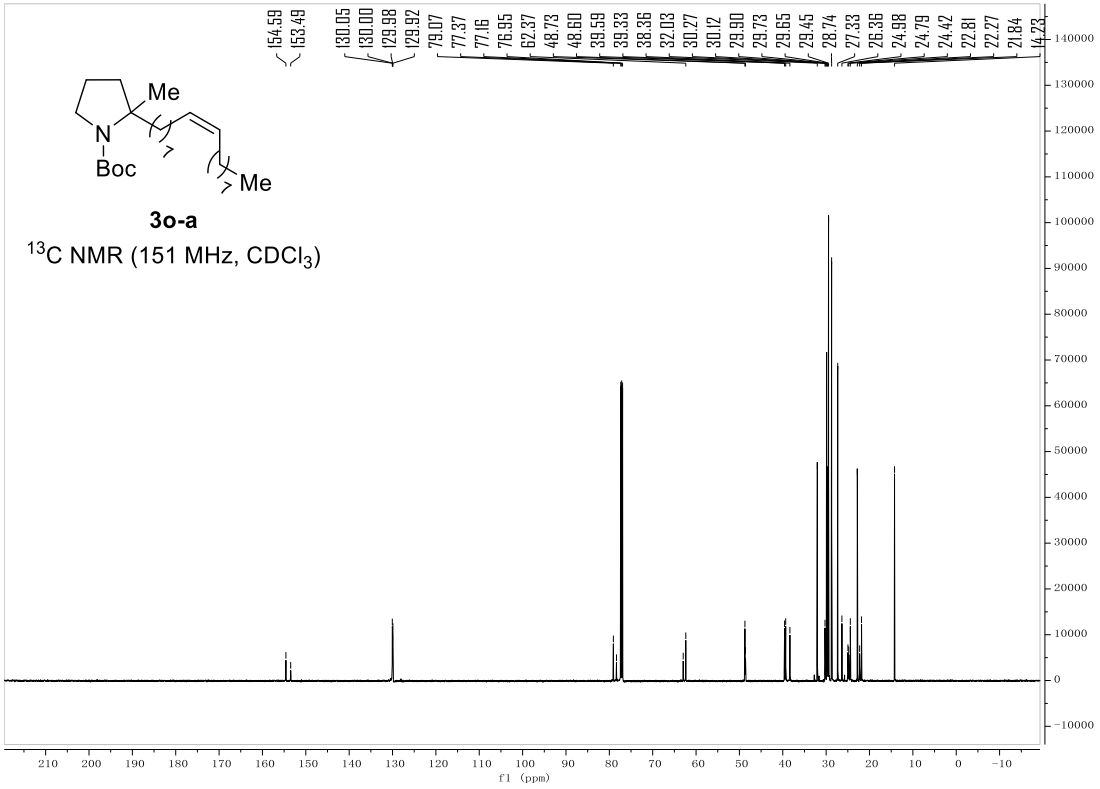

Me
N
Boc
3n-a
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Me
N
Boc
3n-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



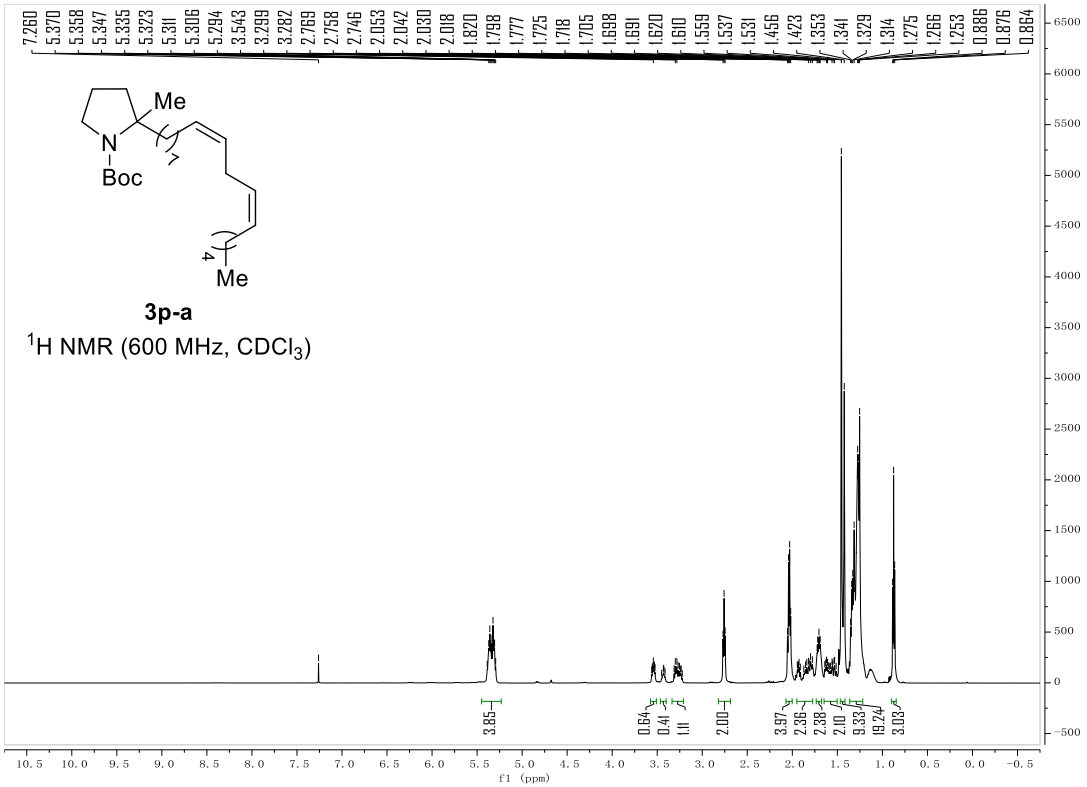
3o-a

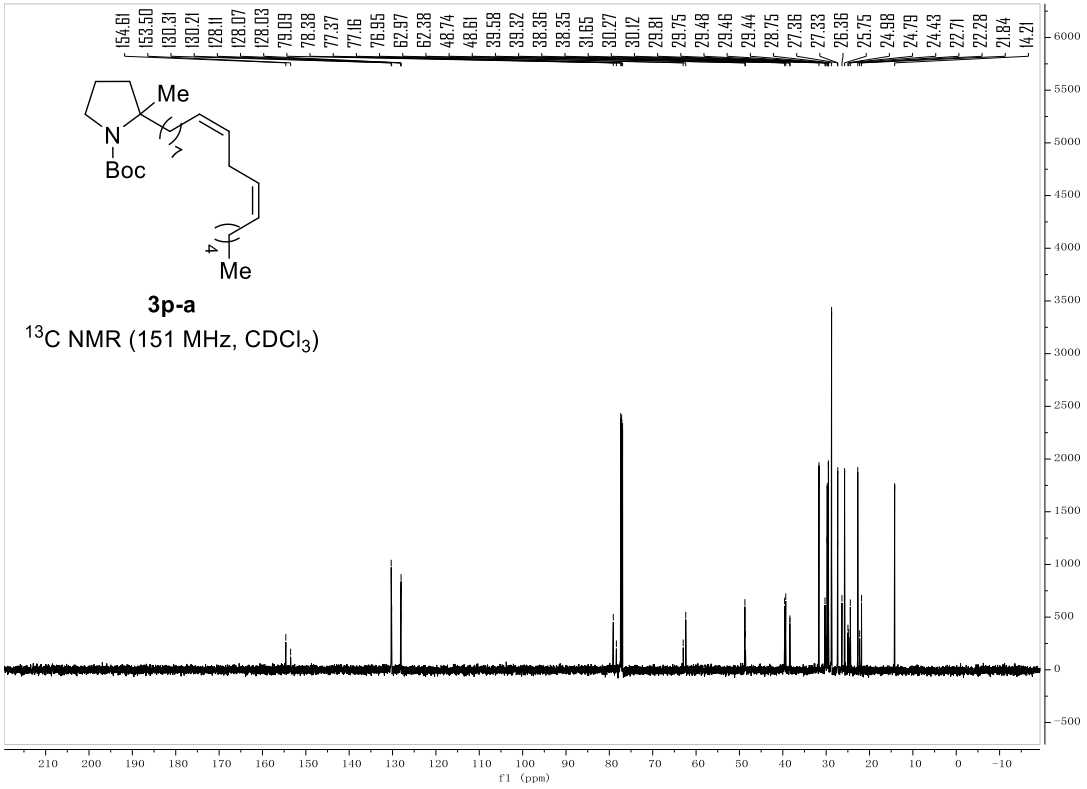
^{1}H NMR (400 MHz, $CDCl_3$)

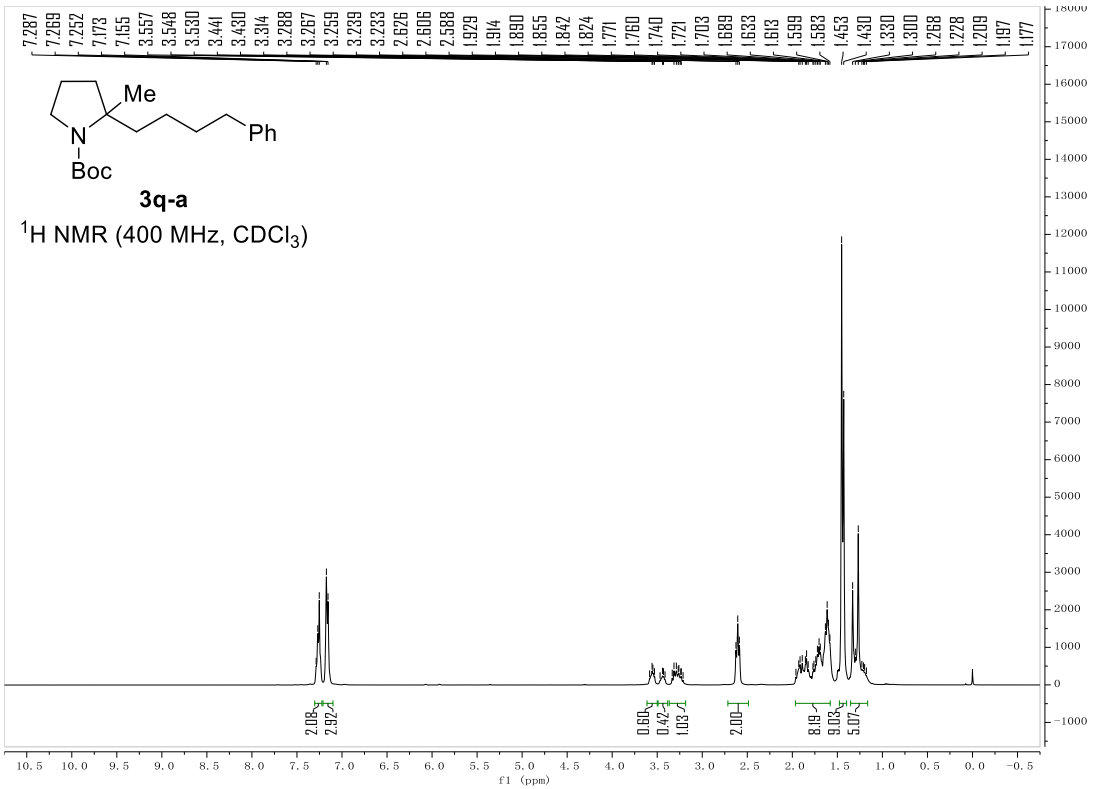


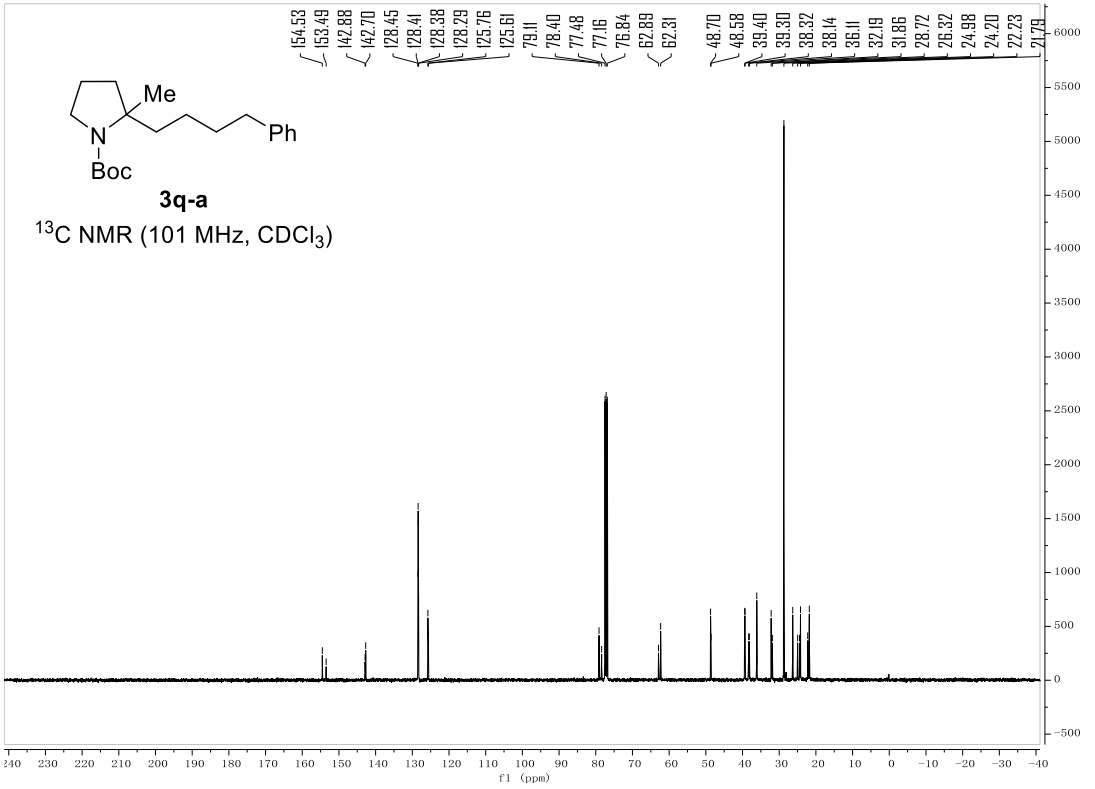
3o-a

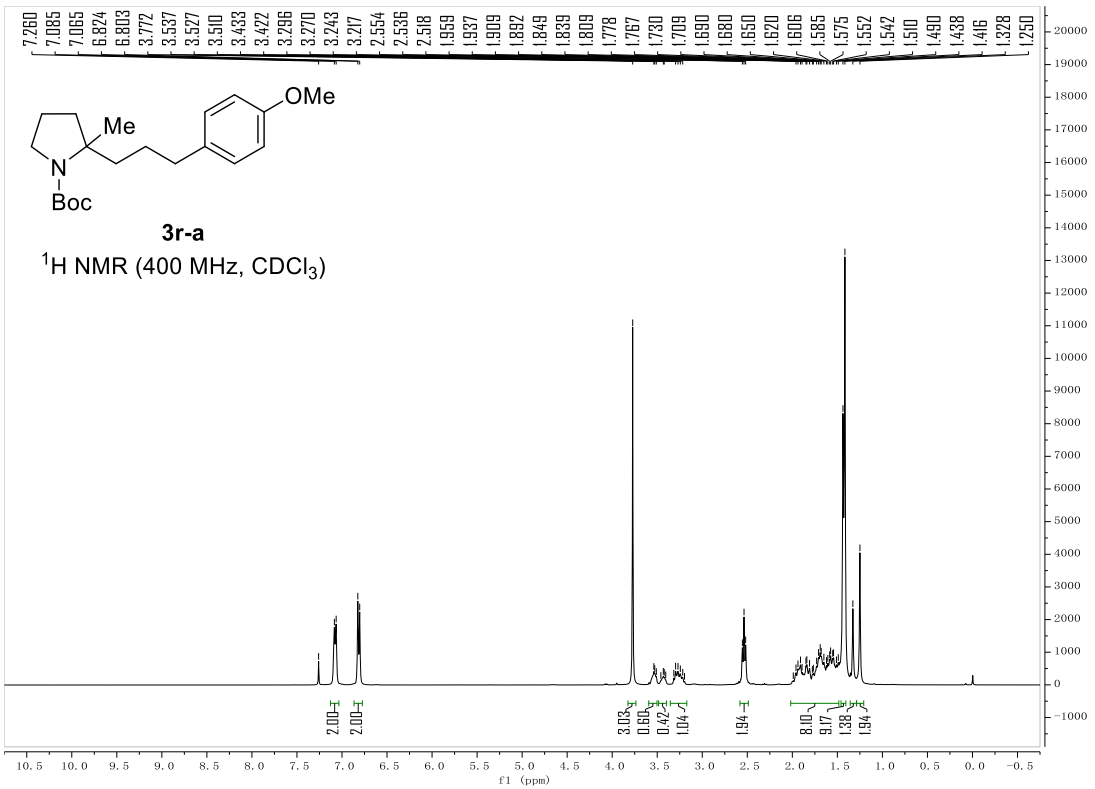
^{13}C NMR (151 MHz, $CDCl_3$)

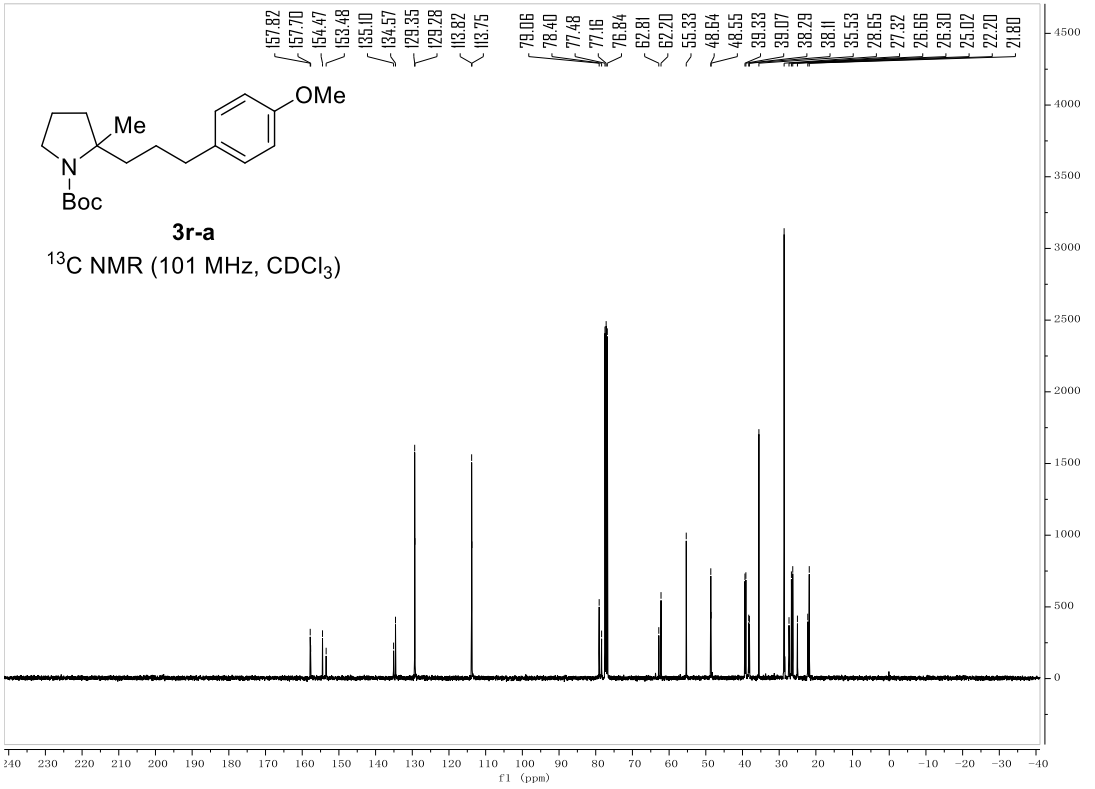

Me
N
Boc
4
Me
3p-a
1H NMR (600 MHz, CDCl3)
f1 (ppm)

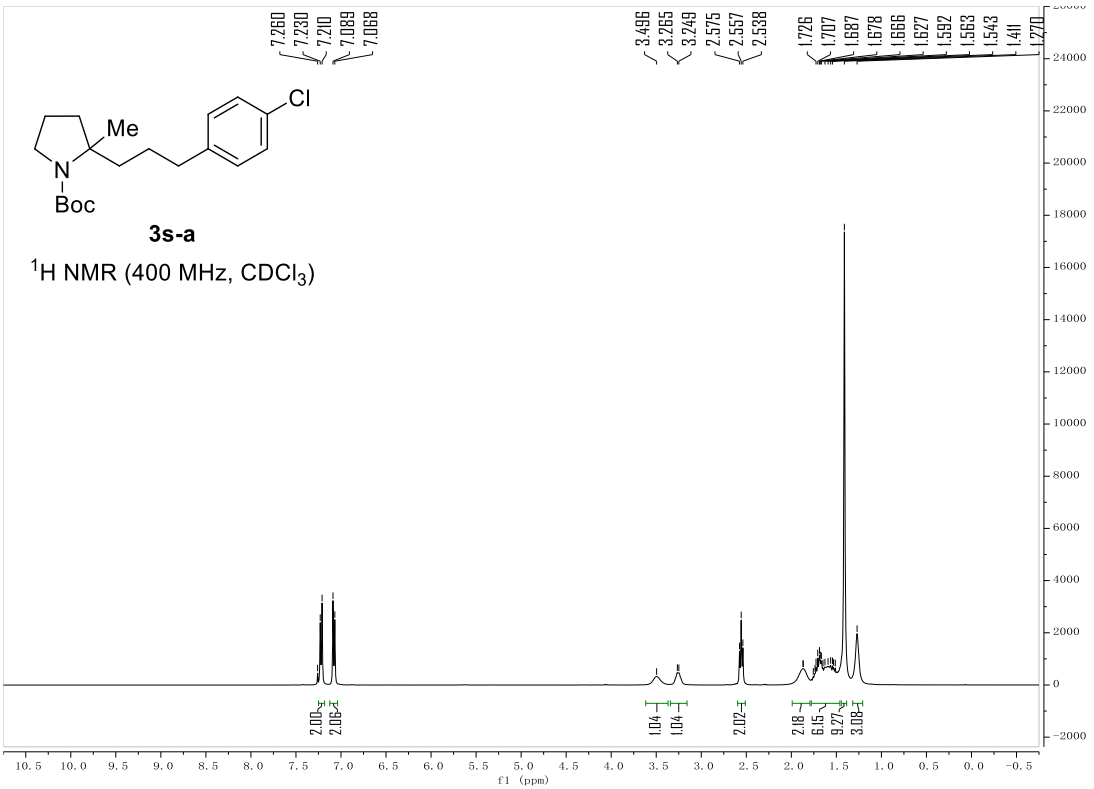

Me
N
Boc
4
Me
3p-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

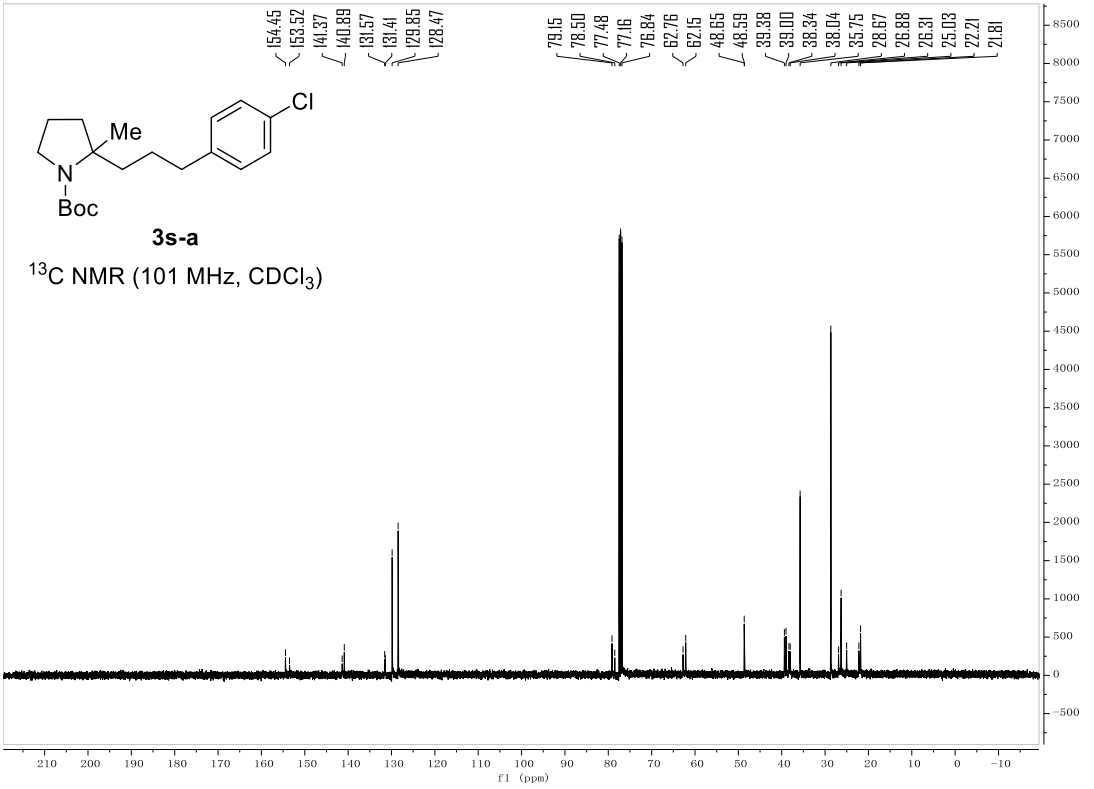

Me
N
Boc
Ph
3q-a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

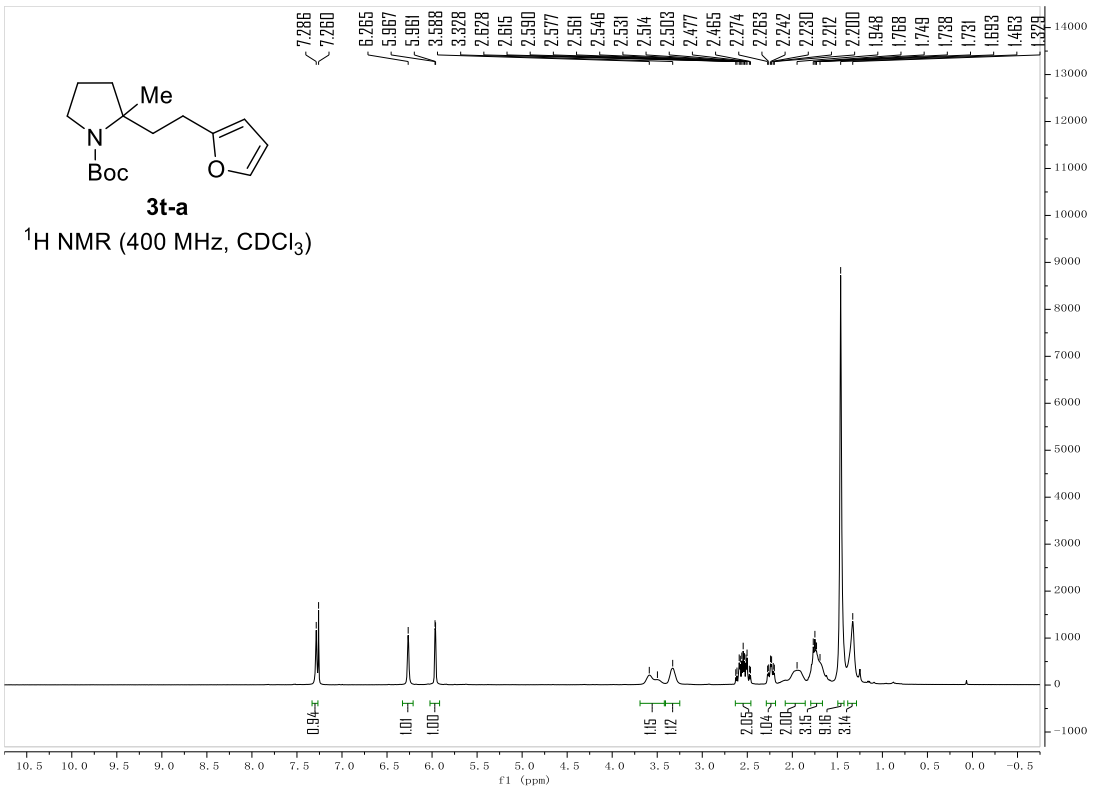

Me
N
Boc
Ph
3q-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

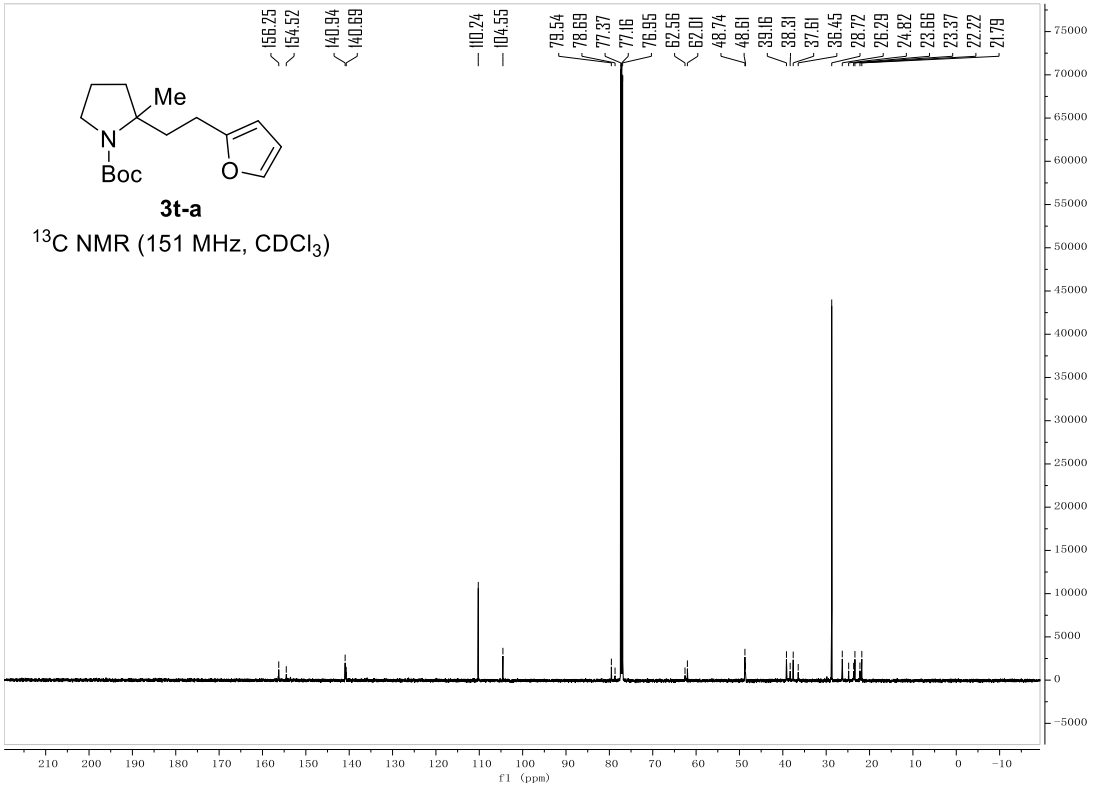

OMe
Me
N
Boc
3r-a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

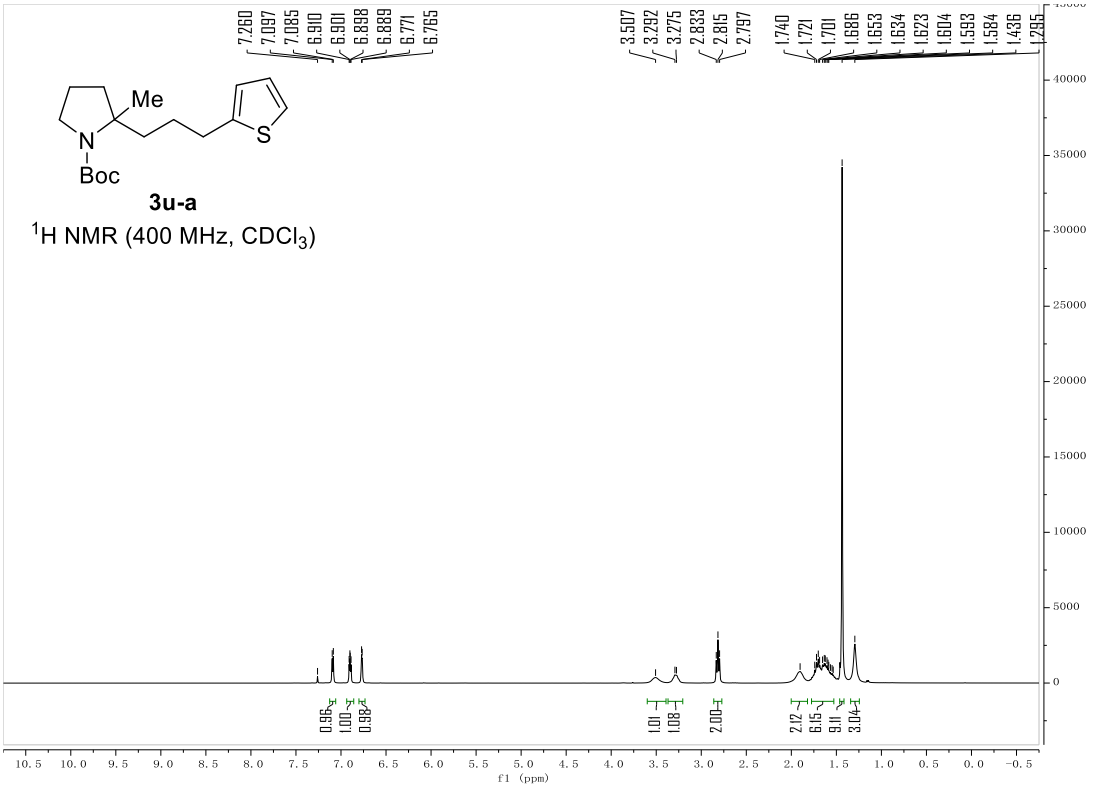

OMe
Me
N
Boc
3r-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

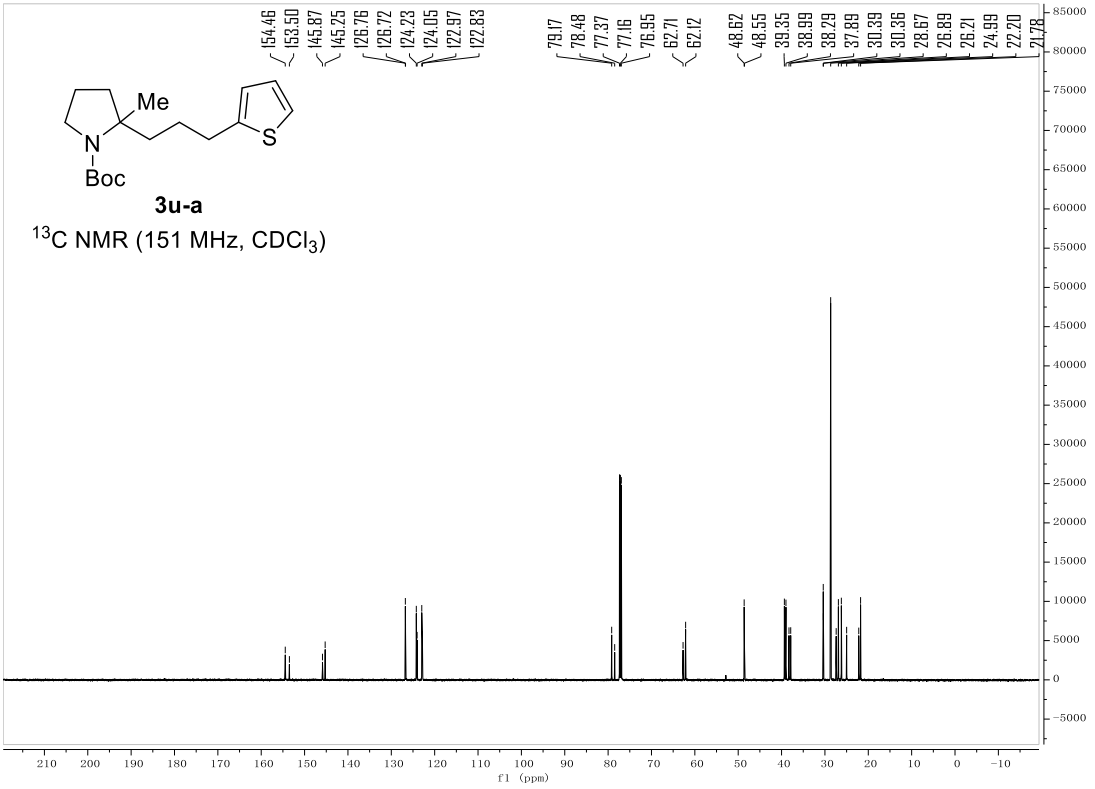

7.280
7.230
7.210
7.089
7.068
3.496
3.265
3.249
2.575
2.557
2.538
1.726
1.707
1.687
1.678
1.666
1.627
1.592
1.563
1.543
1.411
1.270
Cl
Me
N
Boc
3s-a
1H NMR (400 MHz, CDCl3)
2.00
2.06
1.04
1.04
2.02
2.18
6.15
9.27
3.08
f1 (ppm)

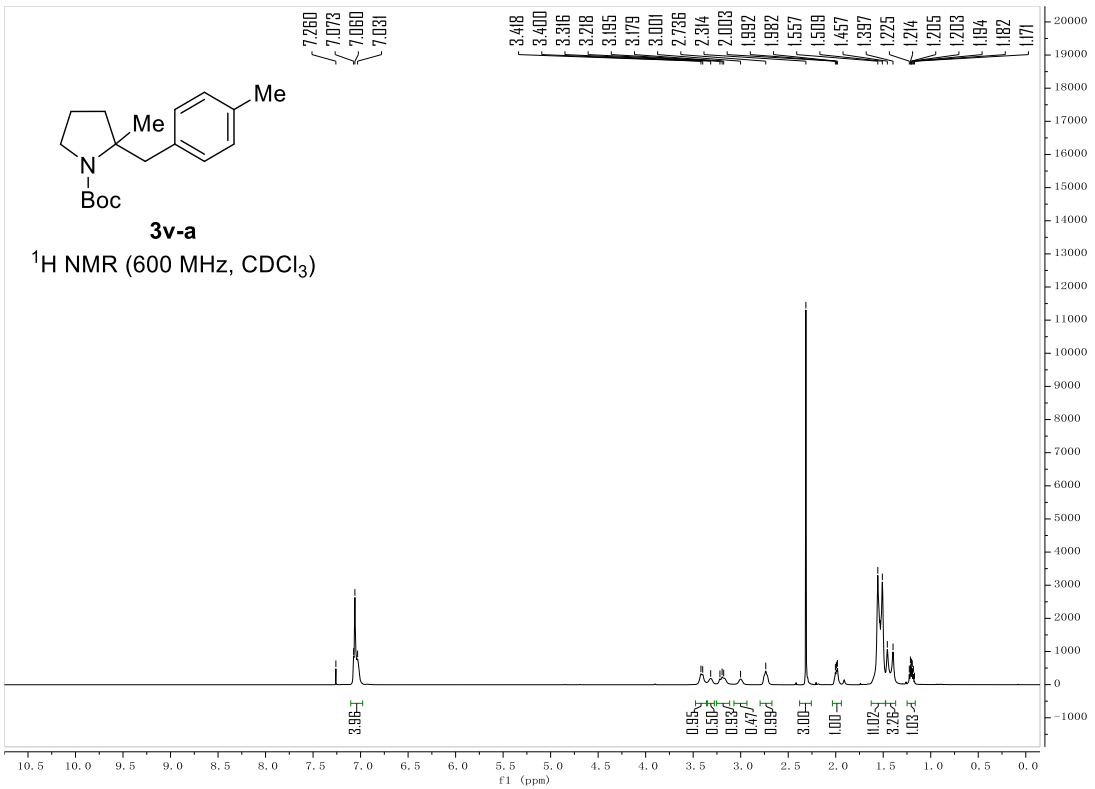

154.45
153.52
141.37
140.89
131.57
131.41
129.85
128.47
79.15
78.50
77.48
77.16
76.84
62.76
62.15
48.65
48.59
39.38
39.00
38.34
38.04
35.75
28.67
26.88
26.31
25.03
22.21
21.81
Cl
Me
N
Boc
3s-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

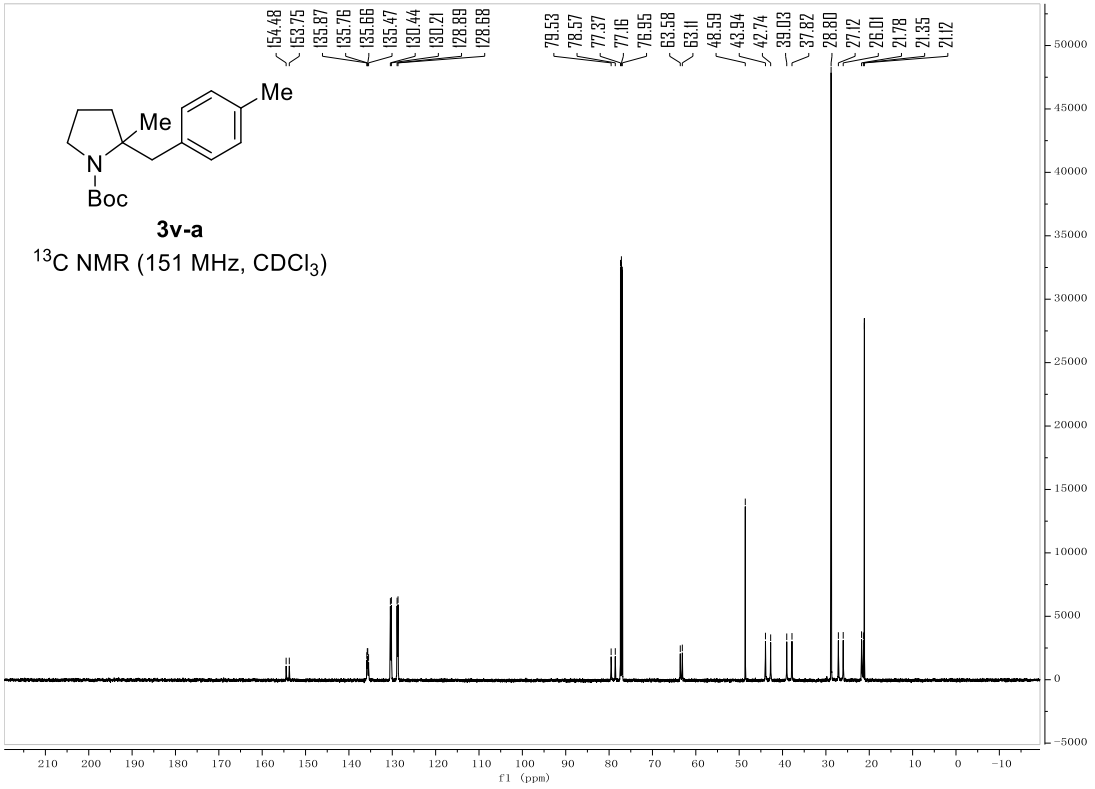

Me
N
Boc
O
3t-a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

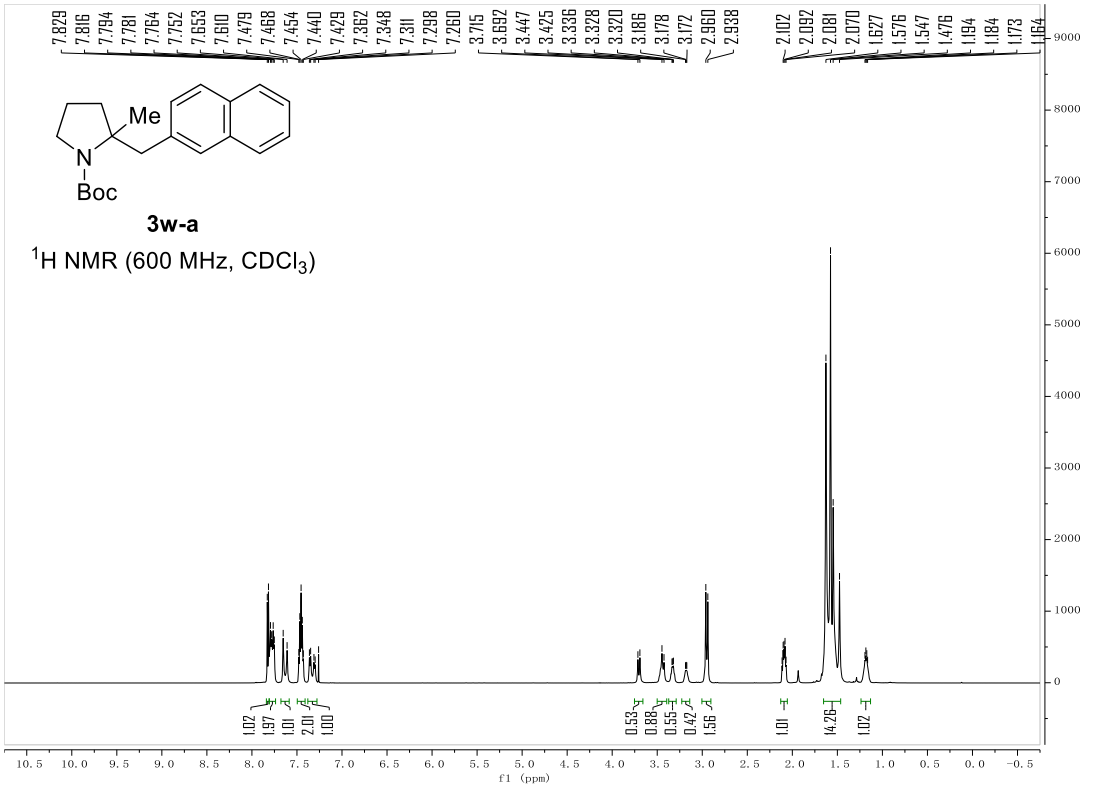

Me
N
Boc
O
3t-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

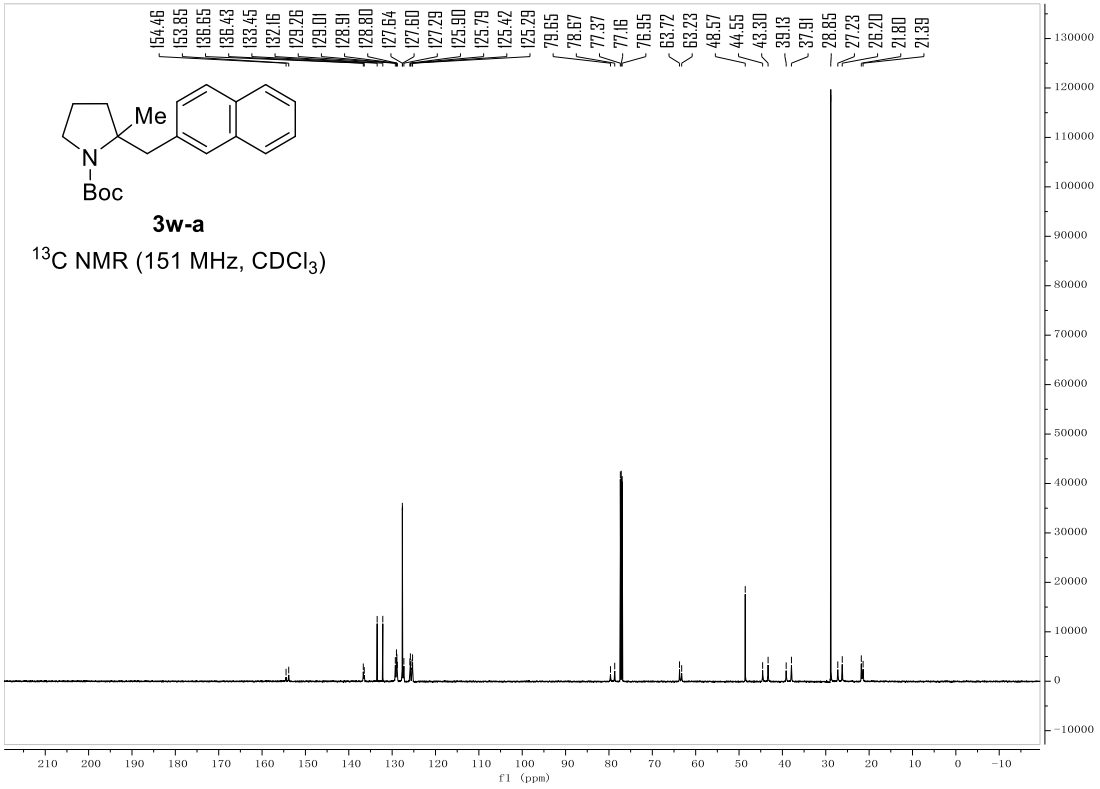

7.260
7.097
7.085
6.910
6.901
6.898
6.889
6.771
6.765
3.507
3.292
3.275
2.833
2.815
2.797
1.740
1.721
1.701
1.686
1.653
1.634
1.623
1.604
1.583
1.584
1.436
1.295
Me
N
Boc
S
3u-a
^{1}H NMR (400 MHz, $CDCl_3$)
0.96
1.00
0.98
1.01
1.08
2.00
2.17
6.15
9.11
3.04
f1 (ppm)

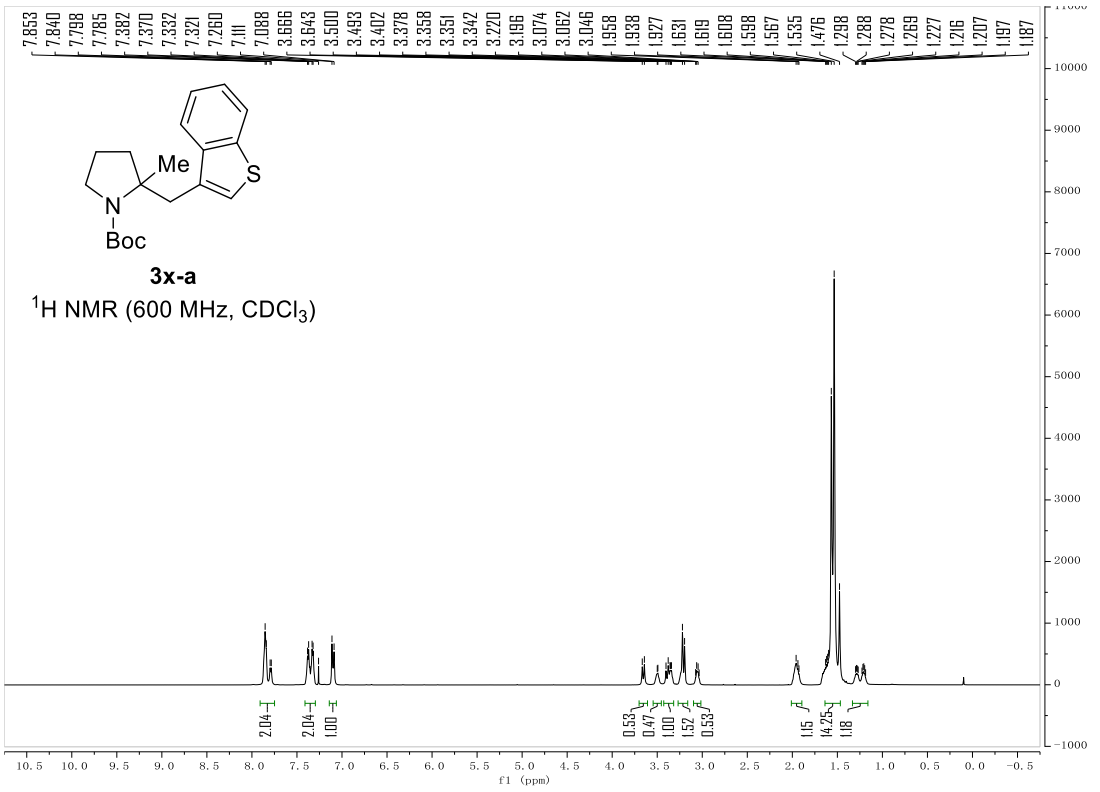

154.46
153.50
145.87
145.25
126.76
126.72
124.23
124.05
122.97
122.83
79.17
78.48
77.37
77.16
76.95
62.71
62.12
48.62
48.55
39.35
38.99
38.29
37.89
30.39
30.36
28.67
26.89
26.21
24.99
22.20
21.78
Me
N
Boc
S
3u-a
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)

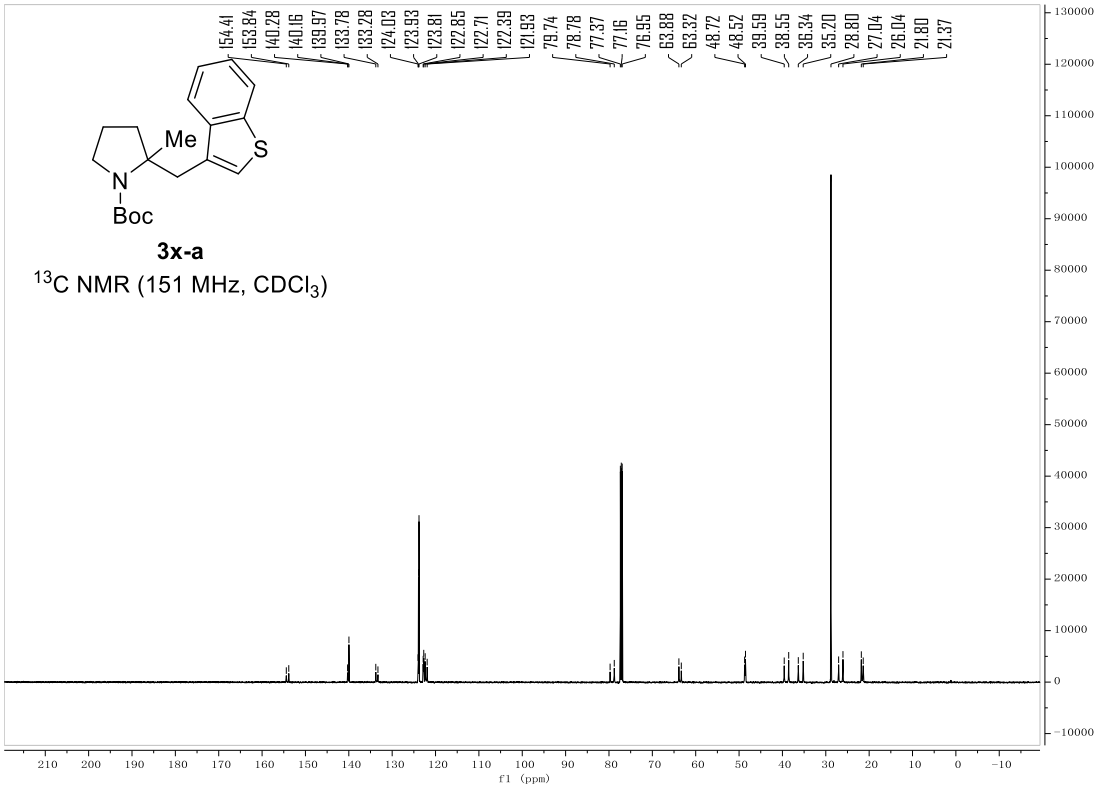

Me
Me
N
Boc
3v-a
1H NMR (600 MHz, CDCl3)

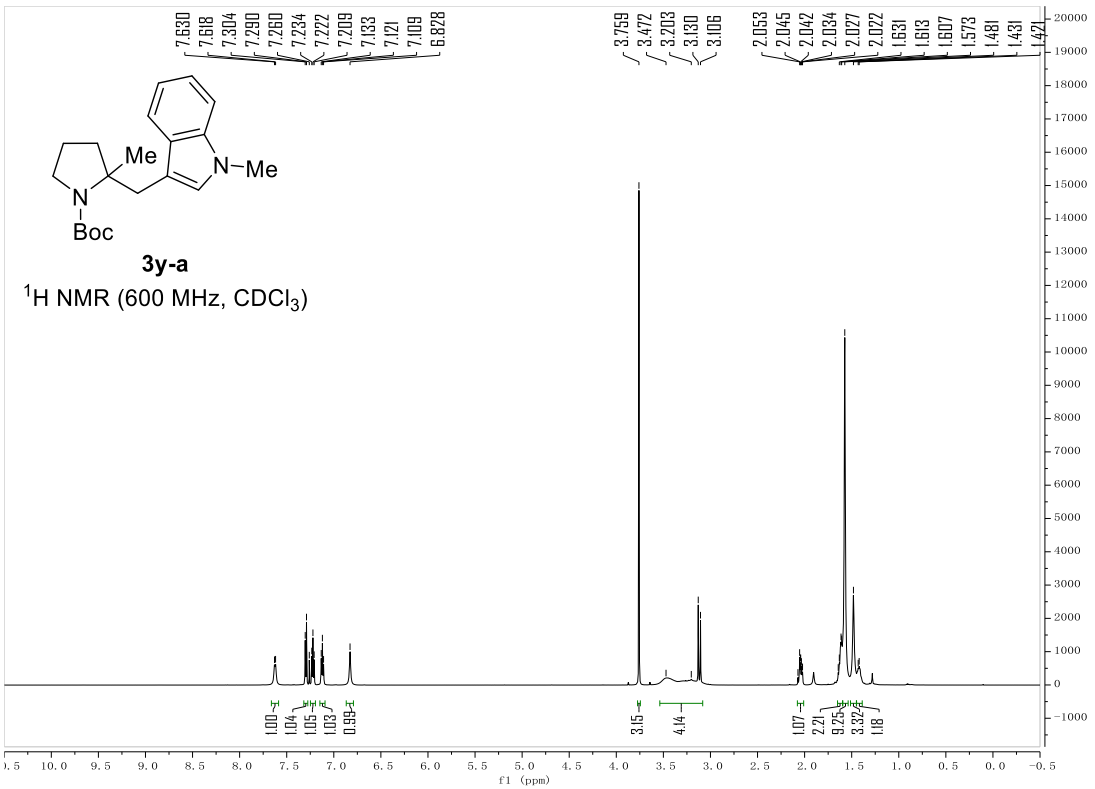

Me
Me
N
Boc
3v-a
13C NMR (151 MHz, CDCl3)


Me
N
Boc
3w-a
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Me
N
Boc
3w-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

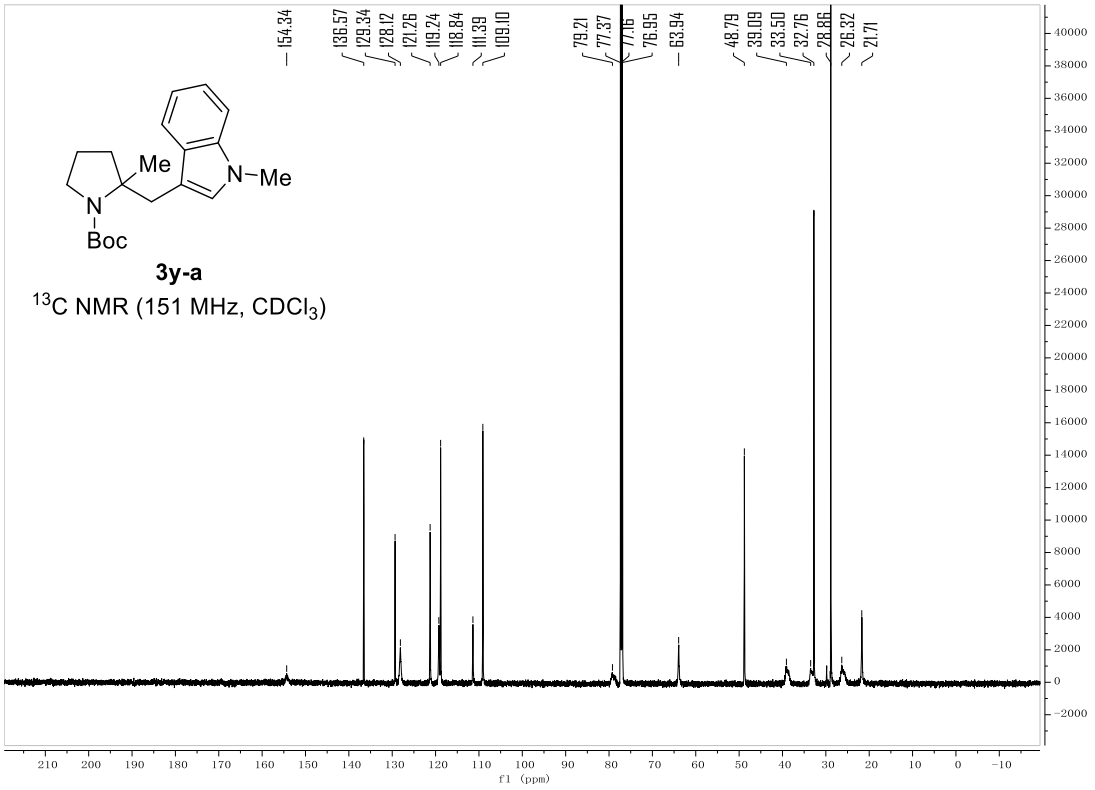

Me
S
N
Boc
3x-a
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Me
S
N
Boc
3x-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



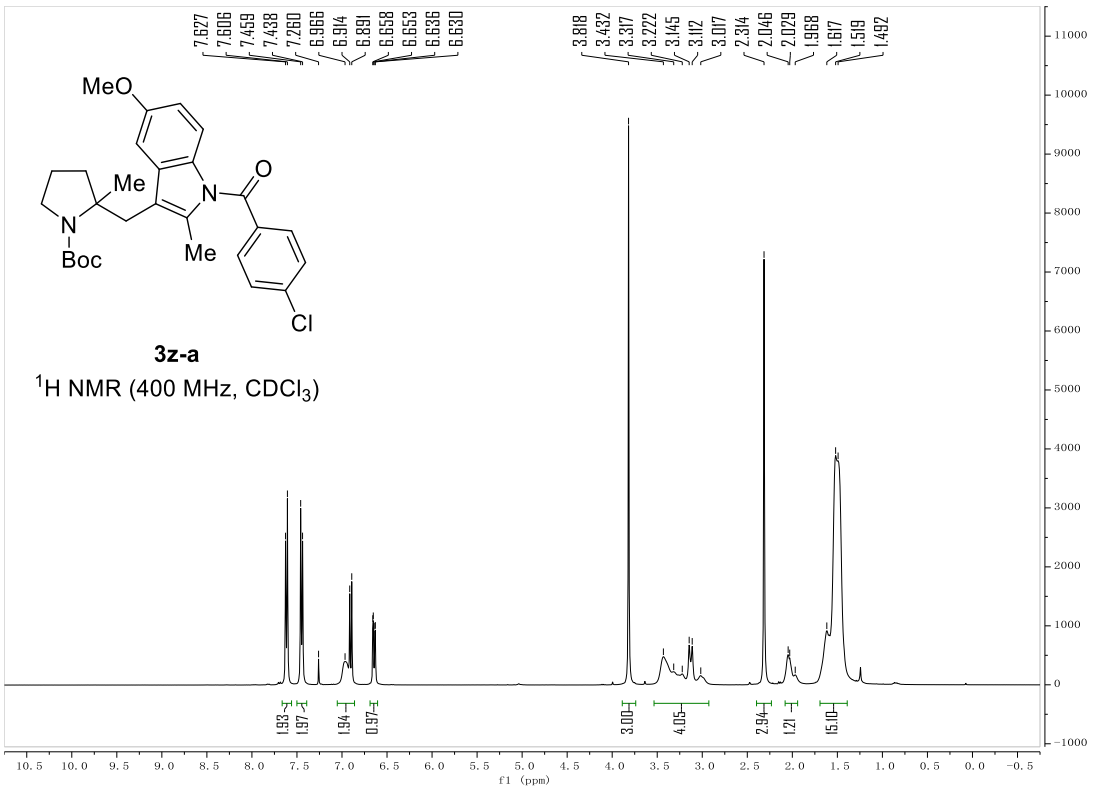
3y-a

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



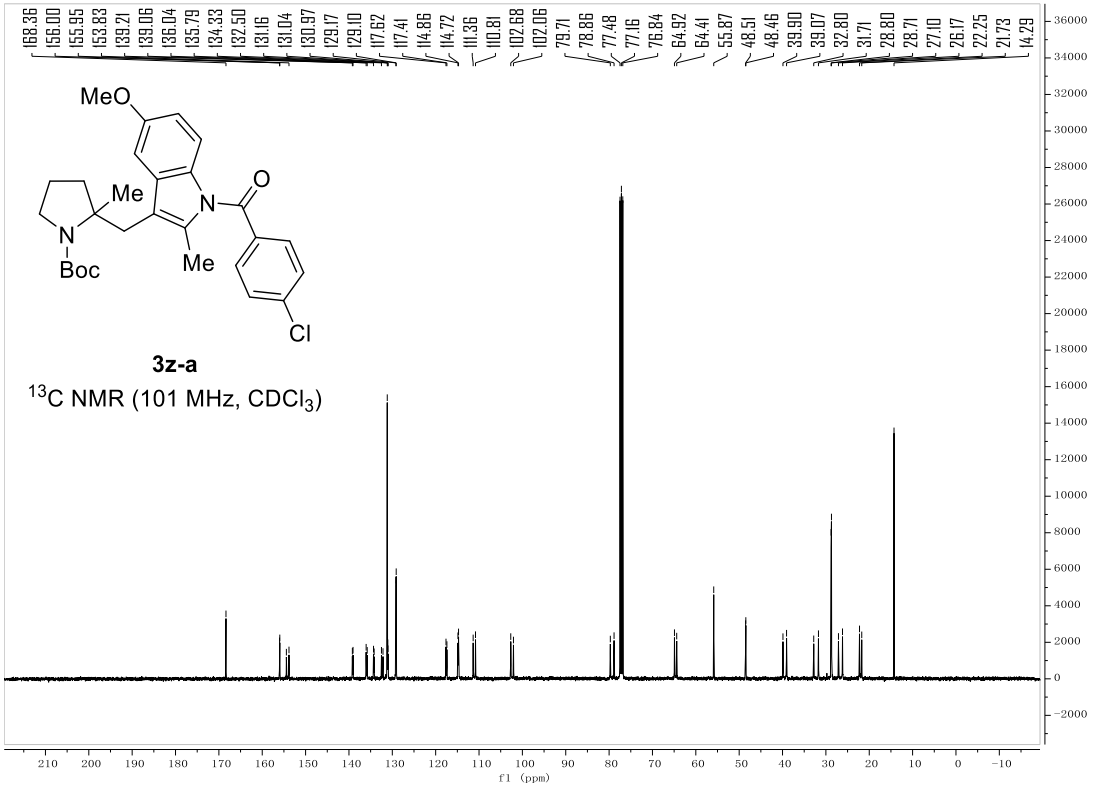
3y-a

^{13}C NMR (151 MHz, $CDCl_3$)



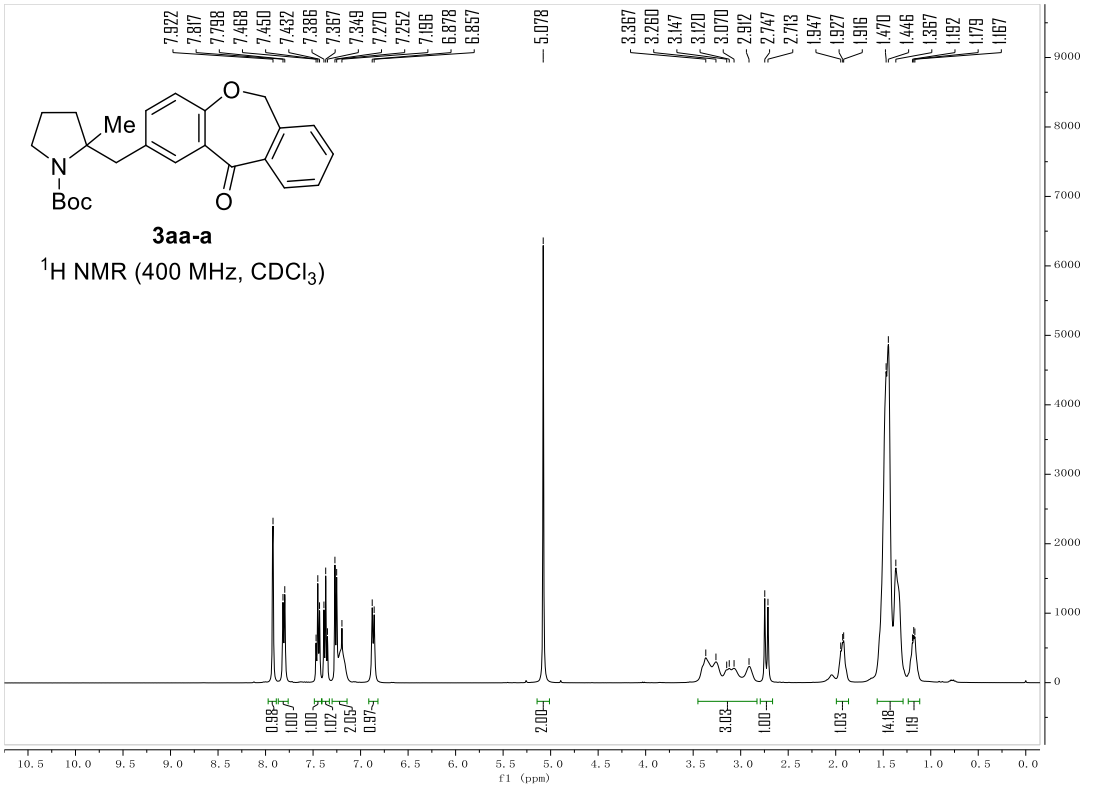
3z-a

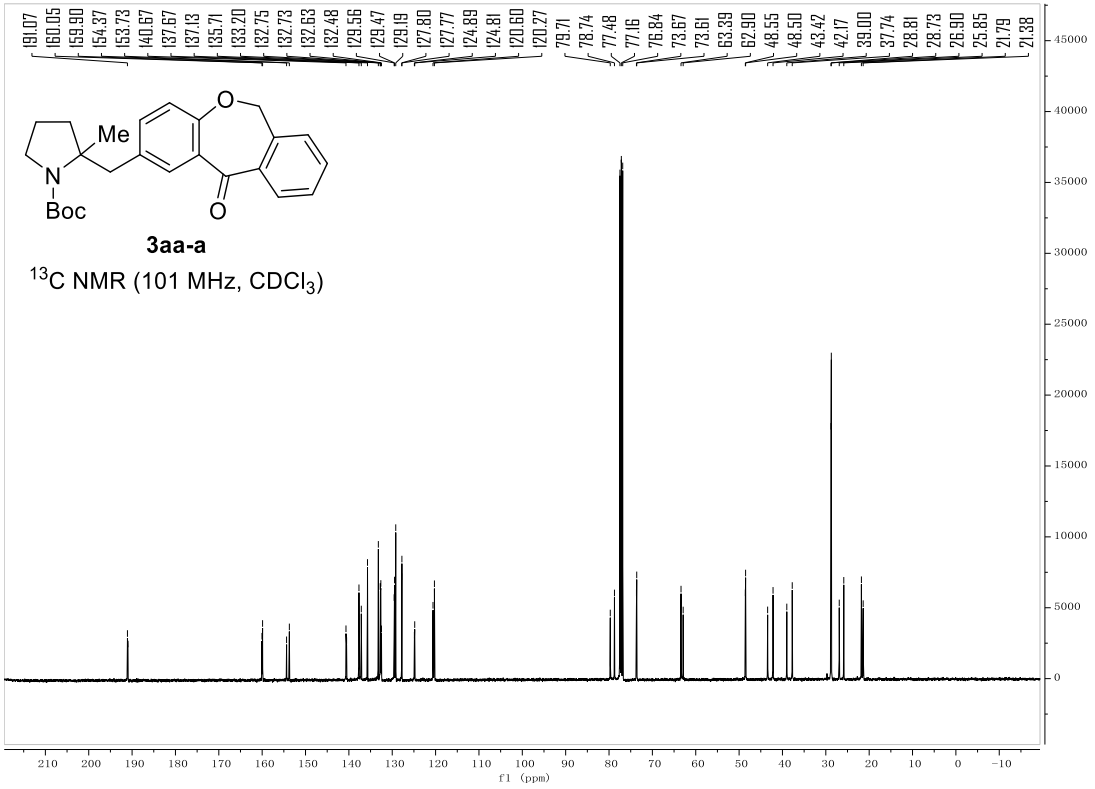
^{1}H NMR (400 MHz, $CDCl_3$)

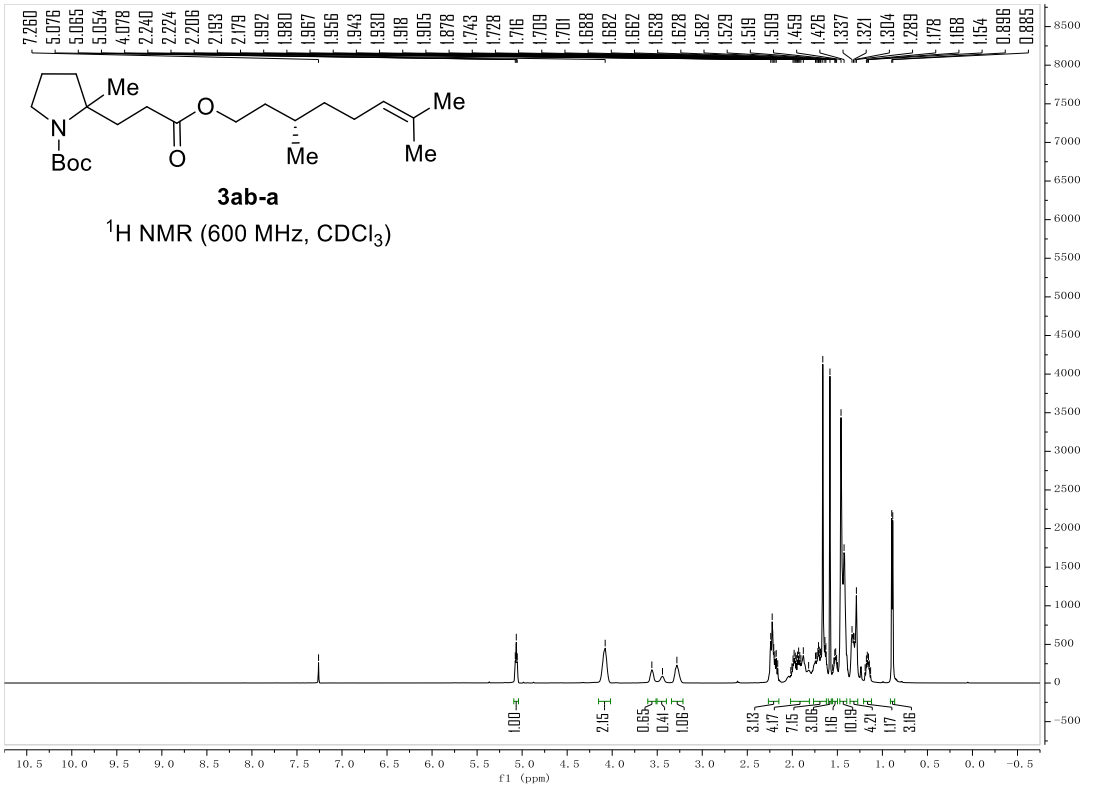


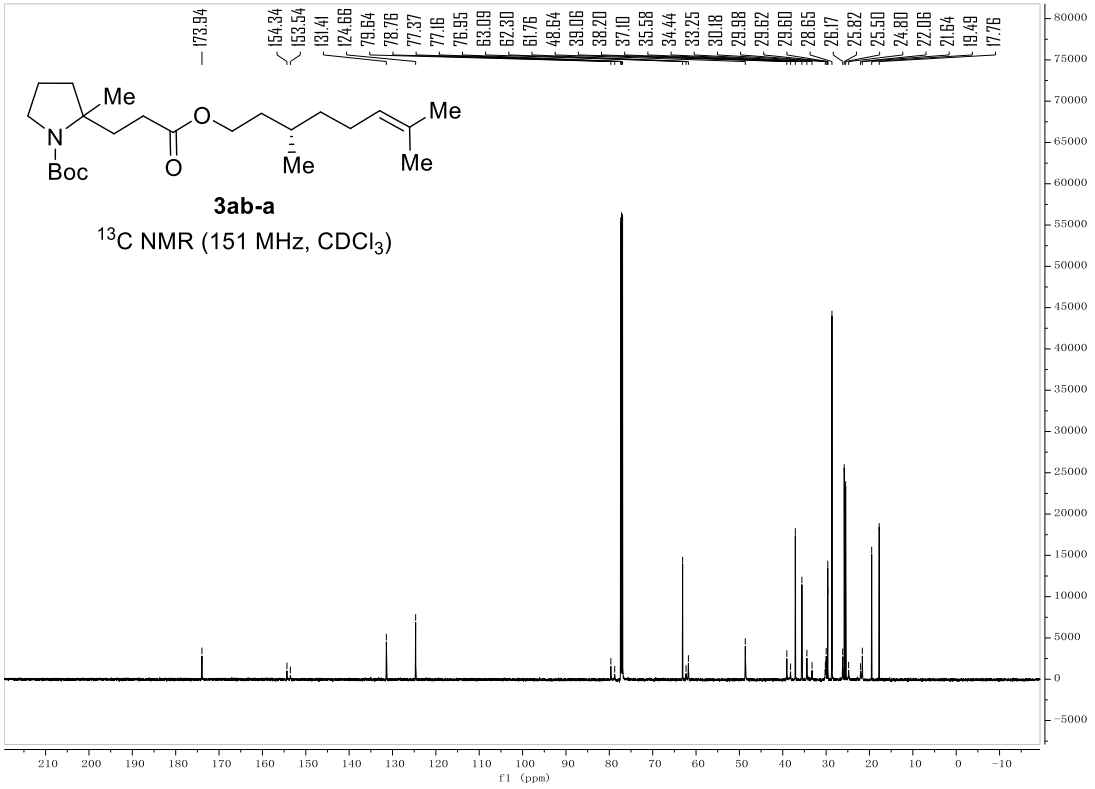
3z-a

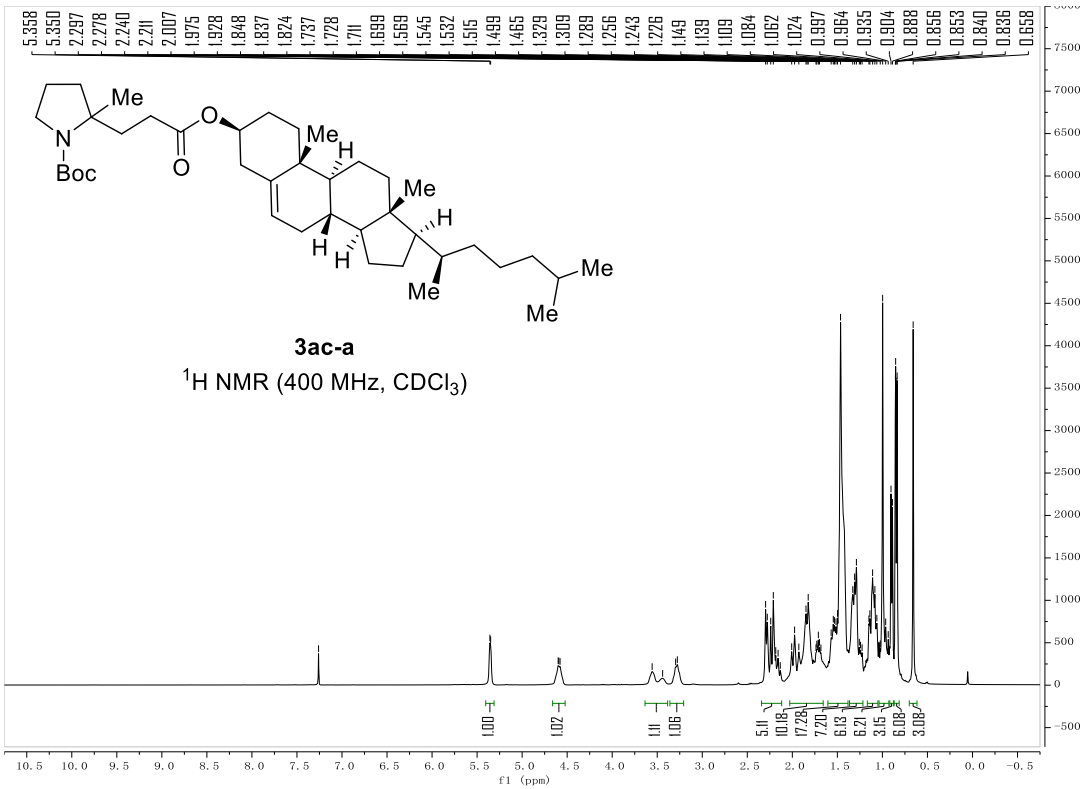
^{13}C NMR (101 MHz, $CDCl_3$)


7.922
7.817
7.798
7.468
7.450
7.432
7.386
7.367
7.349
7.270
7.252
7.196
6.878
6.857
5.078
3.387
3.260
3.147
3.120
3.070
2.912
2.747
2.713
1.947
1.927
1.916
1.470
1.446
1.367
1.192
1.179
1.167
Me
N
Boc
O
O
3aa-a
1H NMR (400 MHz, CDCl3)
0.98
1.00
1.00
1.02
2.05
0.97
2.00
3.03
1.00
1.03
14.18
1.19
f1 (ppm)


191.07
160.05
159.90
154.37
153.73
140.67
137.67
137.13
135.71
133.20
132.75
132.73
132.63
132.48
129.56
129.47
129.19
127.80
127.77
124.89
124.81
120.60
120.27
79.71
78.74
77.48
77.16
76.84
73.67
73.61
63.39
62.90
48.55
48.50
43.42
42.17
39.00
37.74
28.81
28.73
26.90
25.85
21.79
21.38
Me
N
Boc
O
O
3aa-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

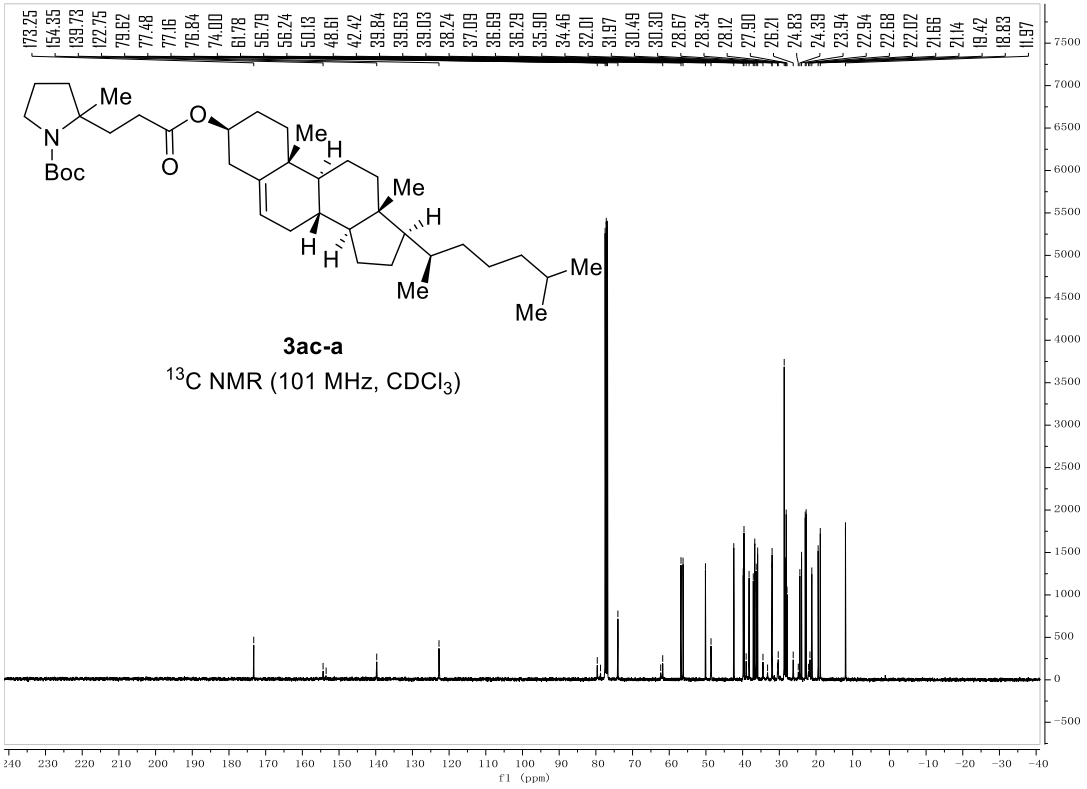

Me
N
Boc
O
O
Me
Me
Me
3ab-a
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Me
N
Boc
O
O
Me
Me
Me
3ab-a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



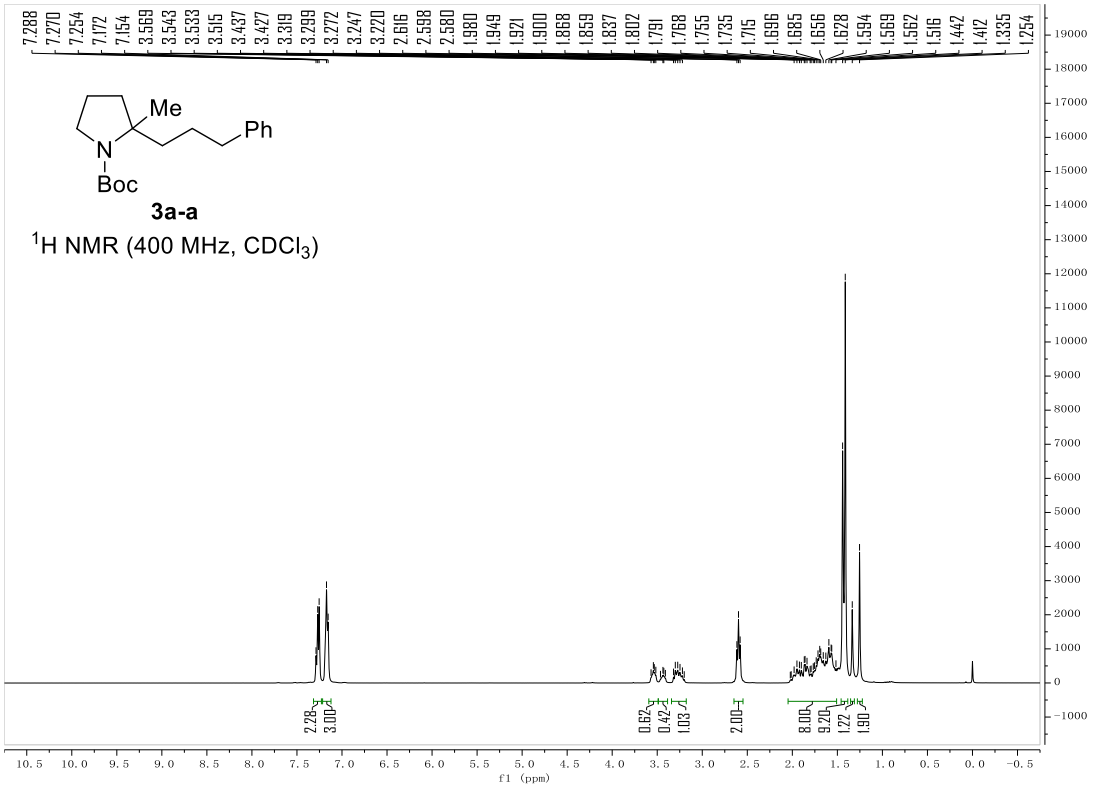
3ac-a

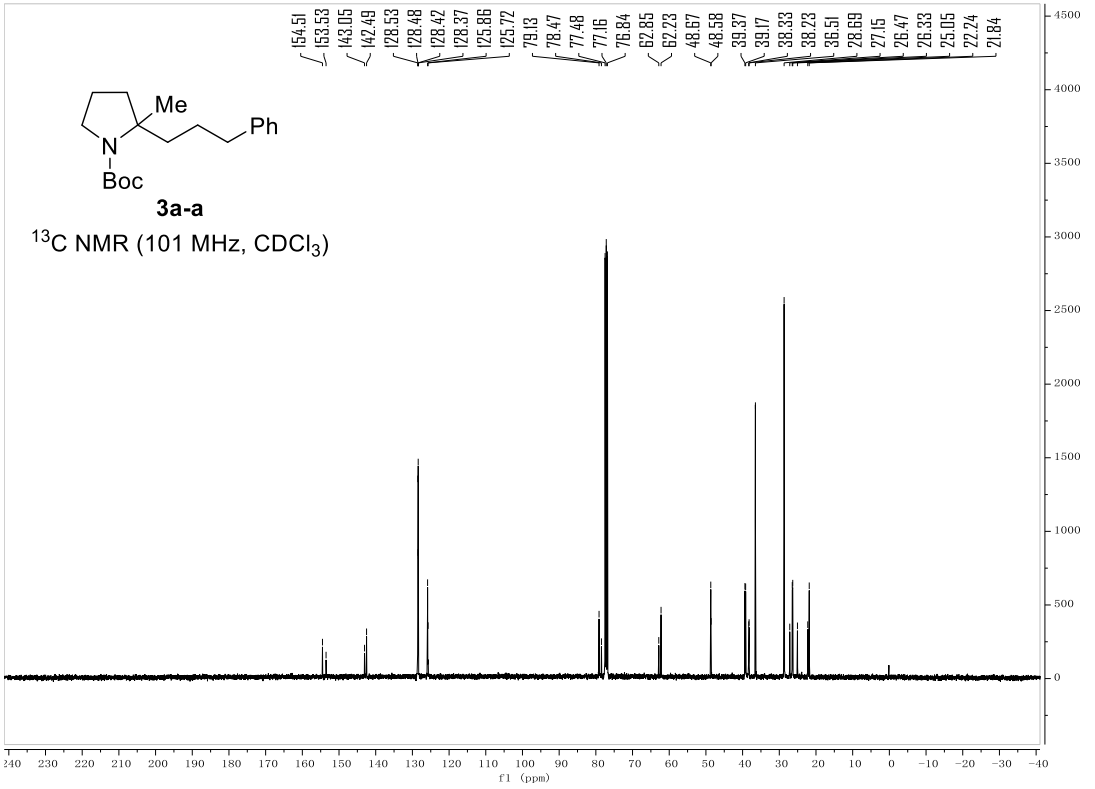
^{1}H NMR (400 MHz, $CDCl_3$)

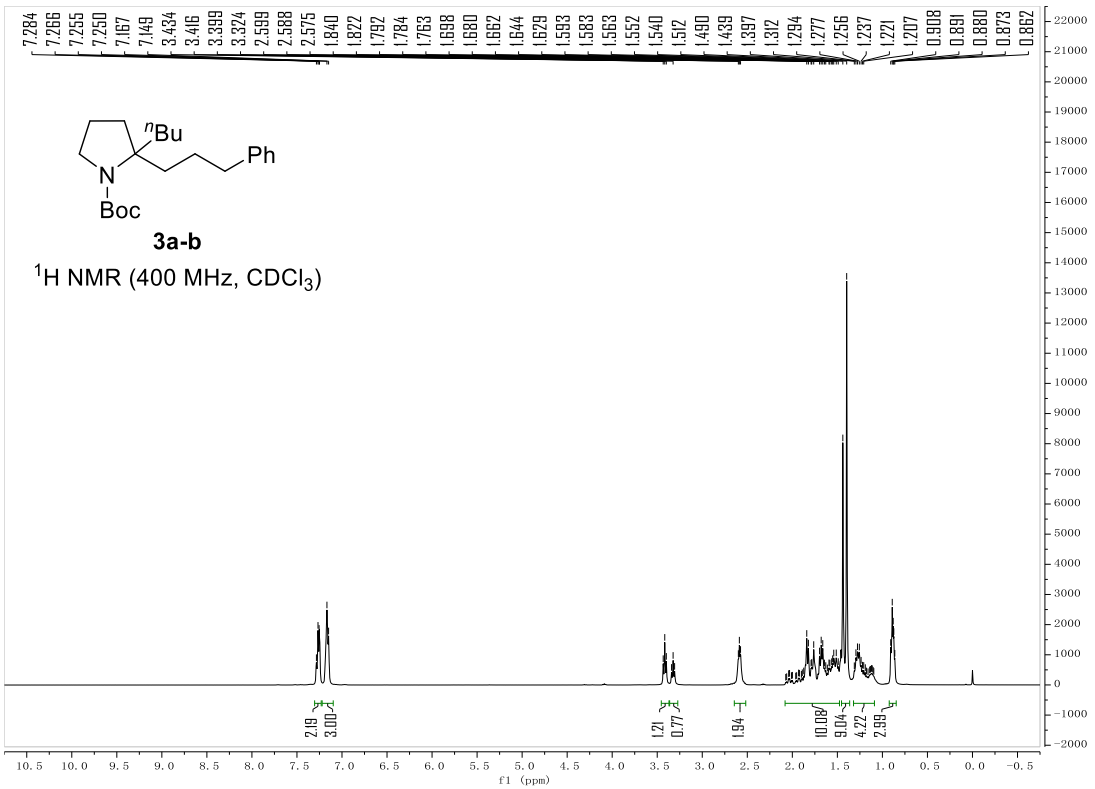


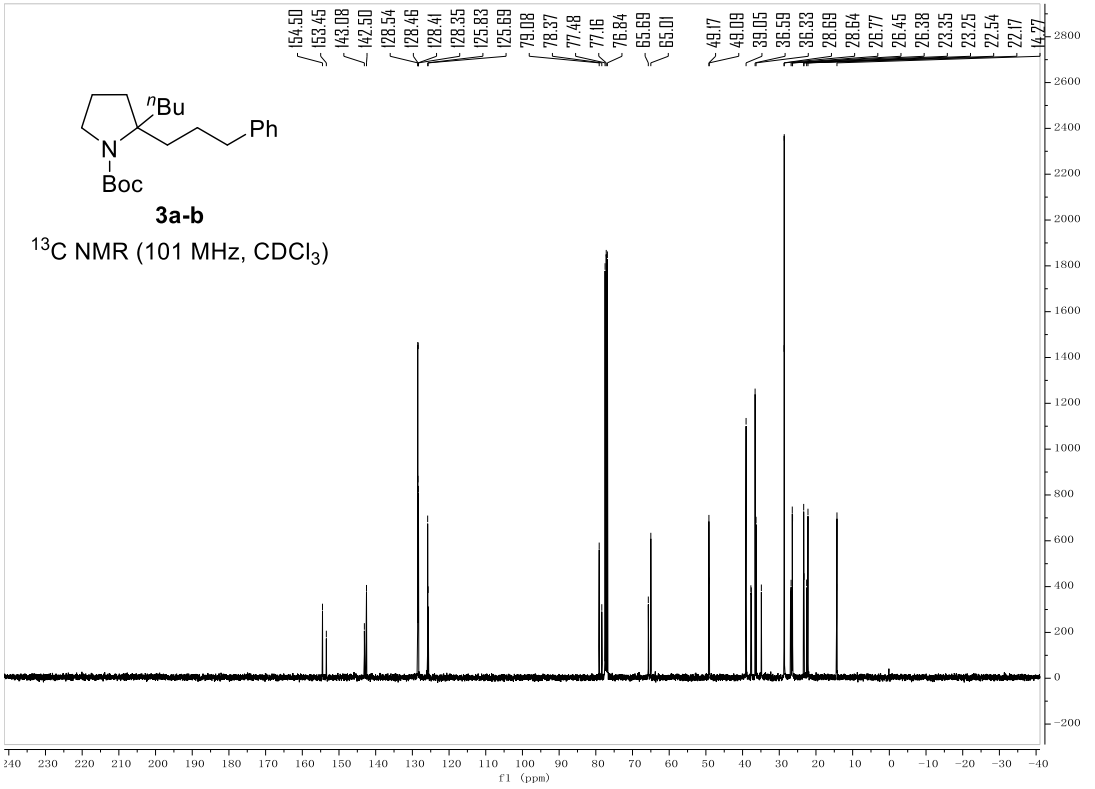
3ac-a

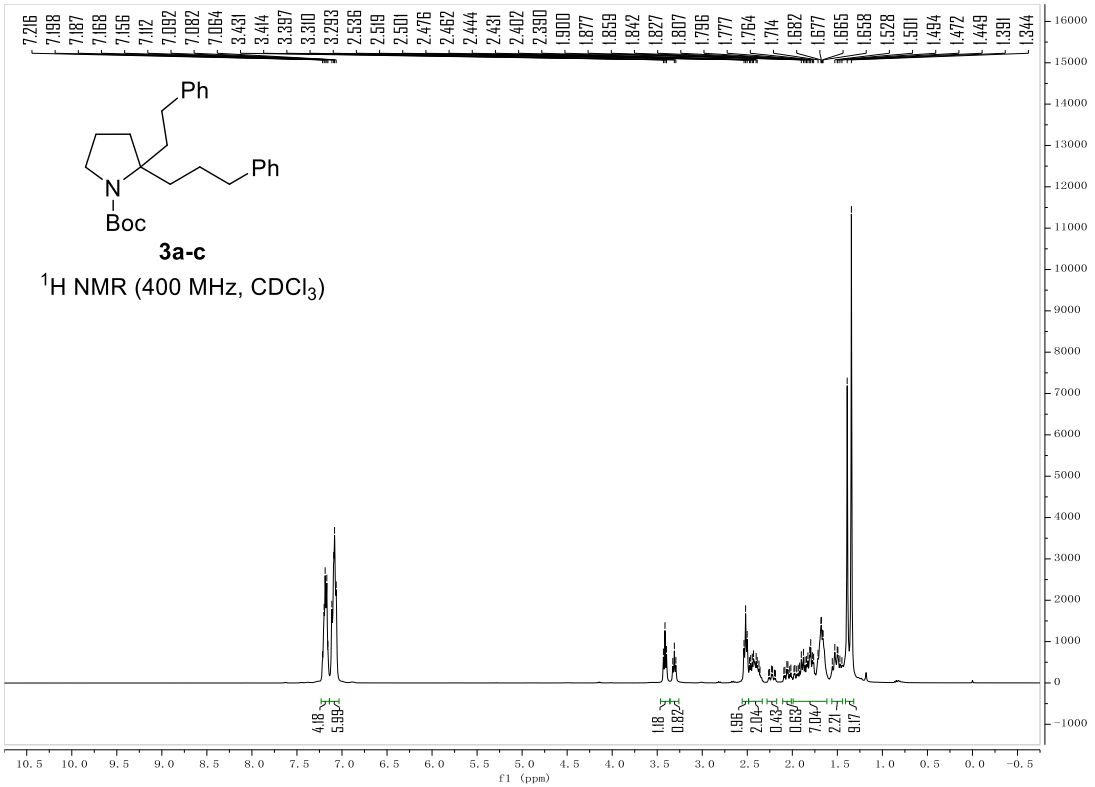
^{13}C NMR (101 MHz, $CDCl_3$)

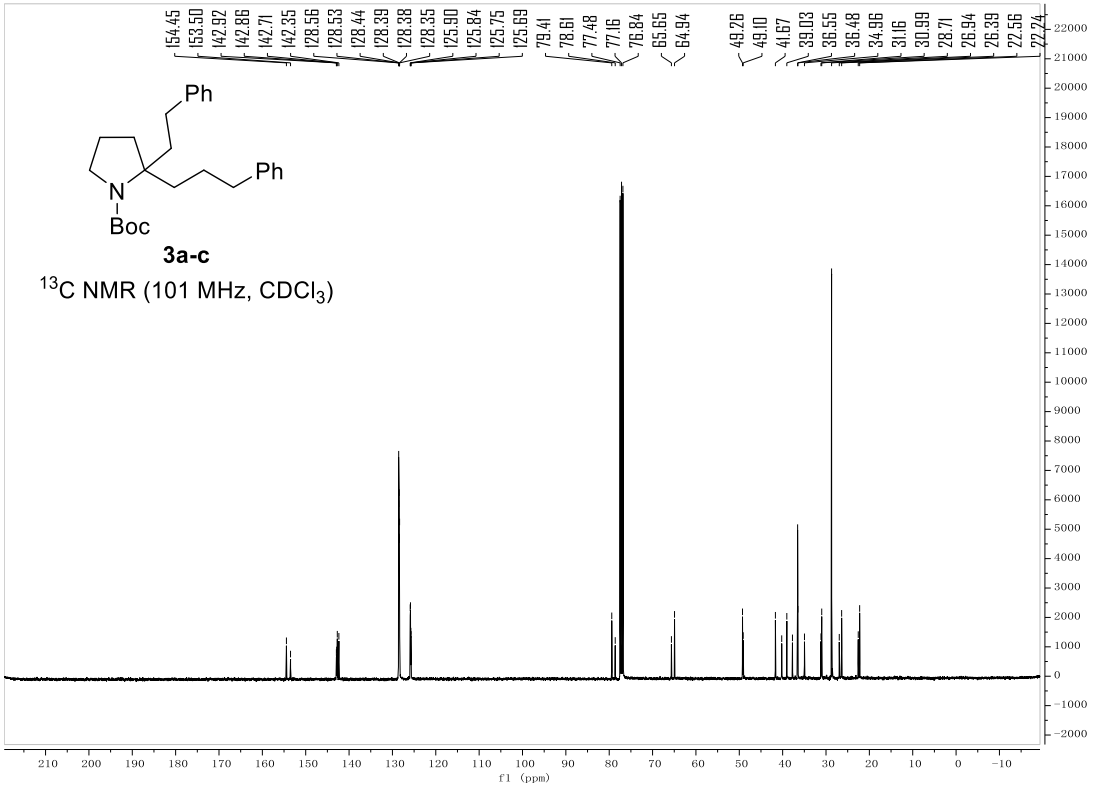

Me
Ph
N
Boc
3a-a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

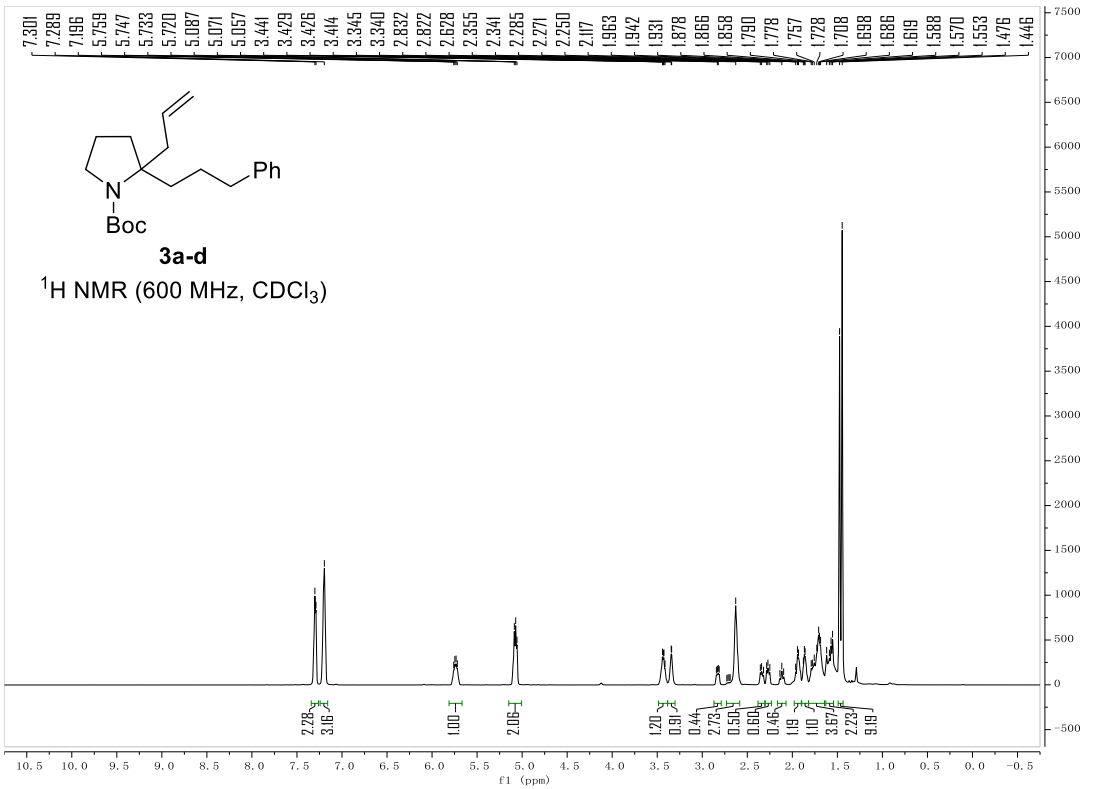

Me
Ph
N
Boc
3a-a
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.284
7.266
7.255
7.250
7.167
7.149
3.434
3.416
3.399
3.324
2.599
2.588
2.575
1.840
1.822
1.792
1.784
1.763
1.698
1.680
1.662
1.644
1.629
1.593
1.583
1.563
1.552
1.540
1.512
1.490
1.439
1.397
1.312
1.294
1.277
1.256
1.237
1.221
1.207
0.908
0.891
0.880
0.873
0.862
nBu
Ph
N
Boc
3a-b
1H NMR (400 MHz, CDCl3)
2.19
3.00
1.21
0.77
1.94
10.08
9.04
4.22
2.99
f1 (ppm)


154.50
153.45
143.08
142.50
128.54
128.46
128.41
128.35
125.83
125.69
79.08
78.37
77.48
77.16
76.84
65.69
65.01
49.17
49.09
39.05
36.59
36.33
28.69
28.64
26.77
26.45
26.38
23.35
23.25
22.54
22.17
14.27
nBu
Ph
N
Boc
3a-b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

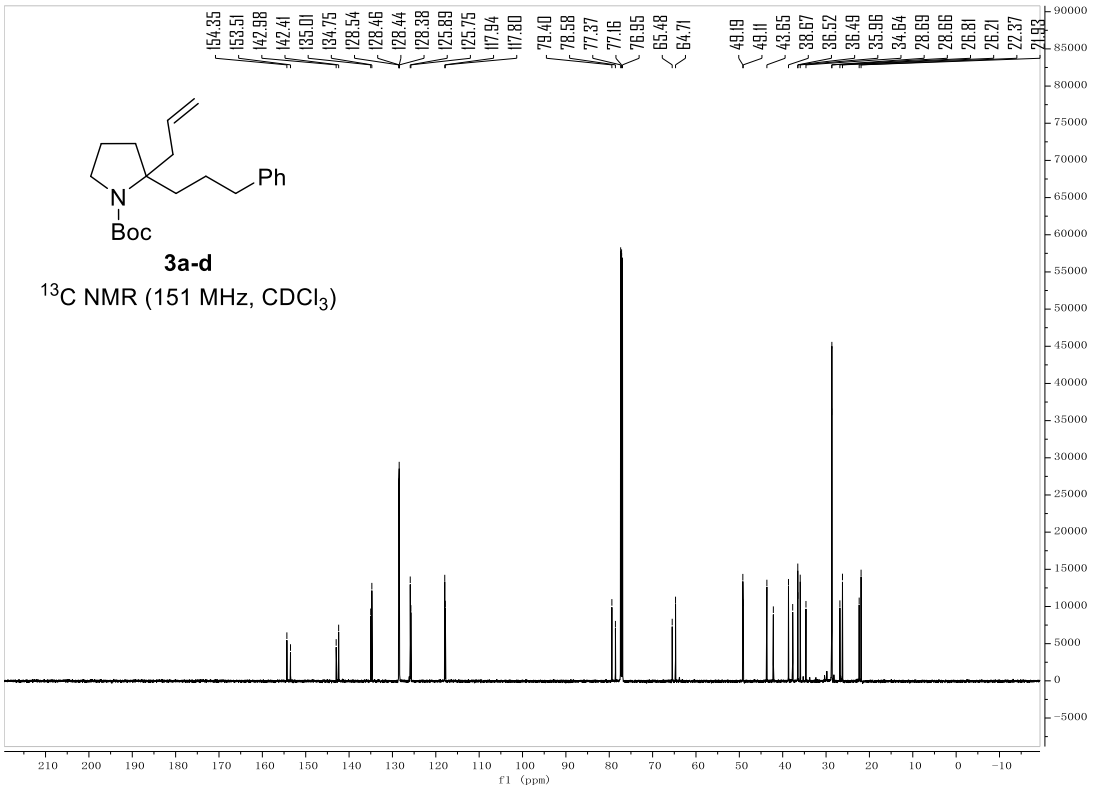

Ph
Ph
N
Boc
3a-c
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Ph
Ph
N
Boc
3a-c
13C NMR (101 MHz, CDCl3)
f1 (ppm)



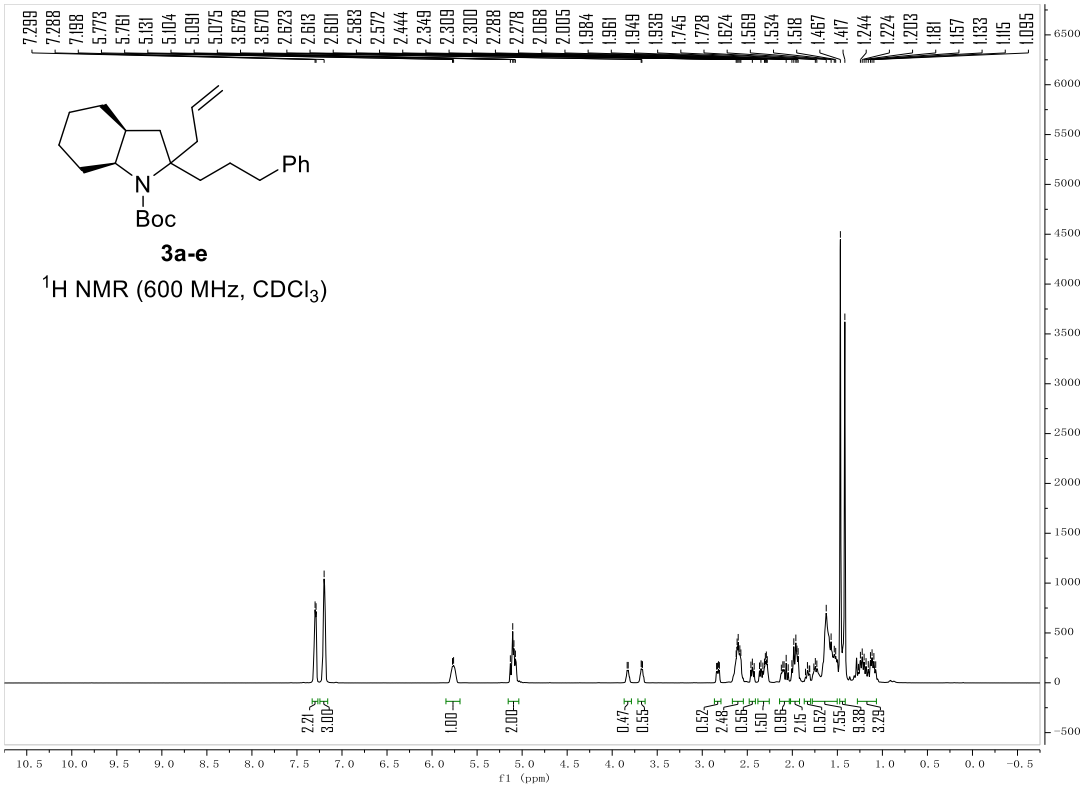
3a-d

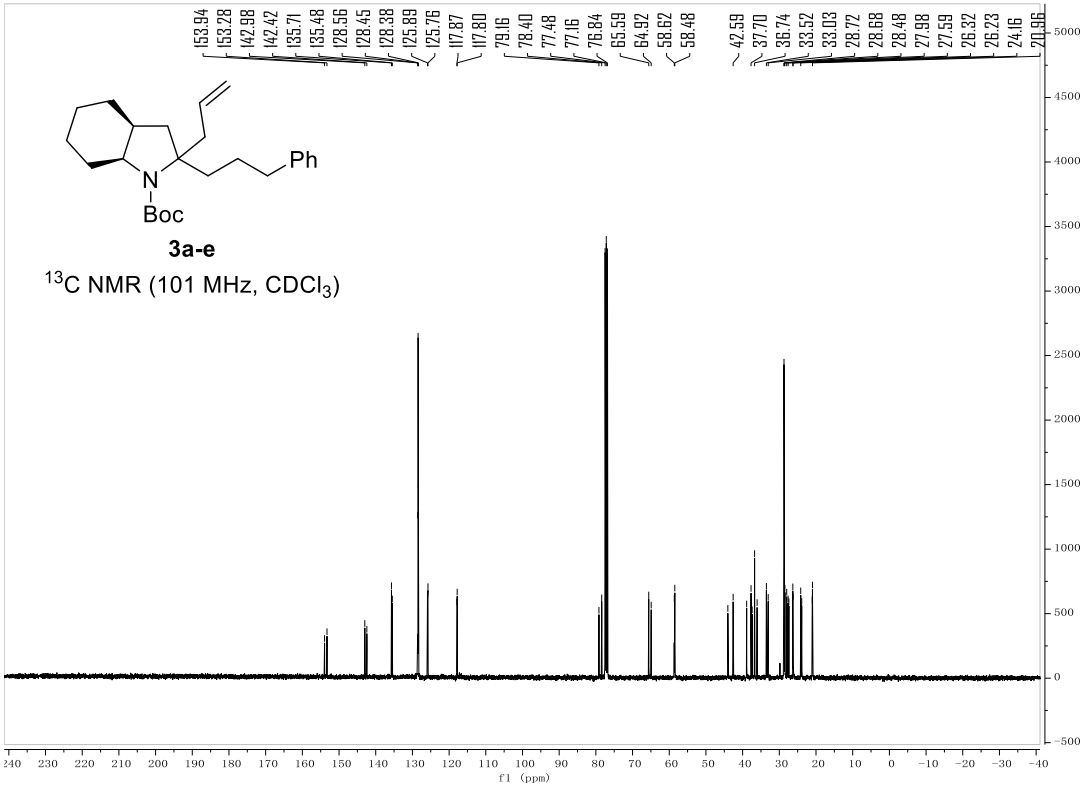
^{1}H NMR (600 MHz, $CDCl_3$)

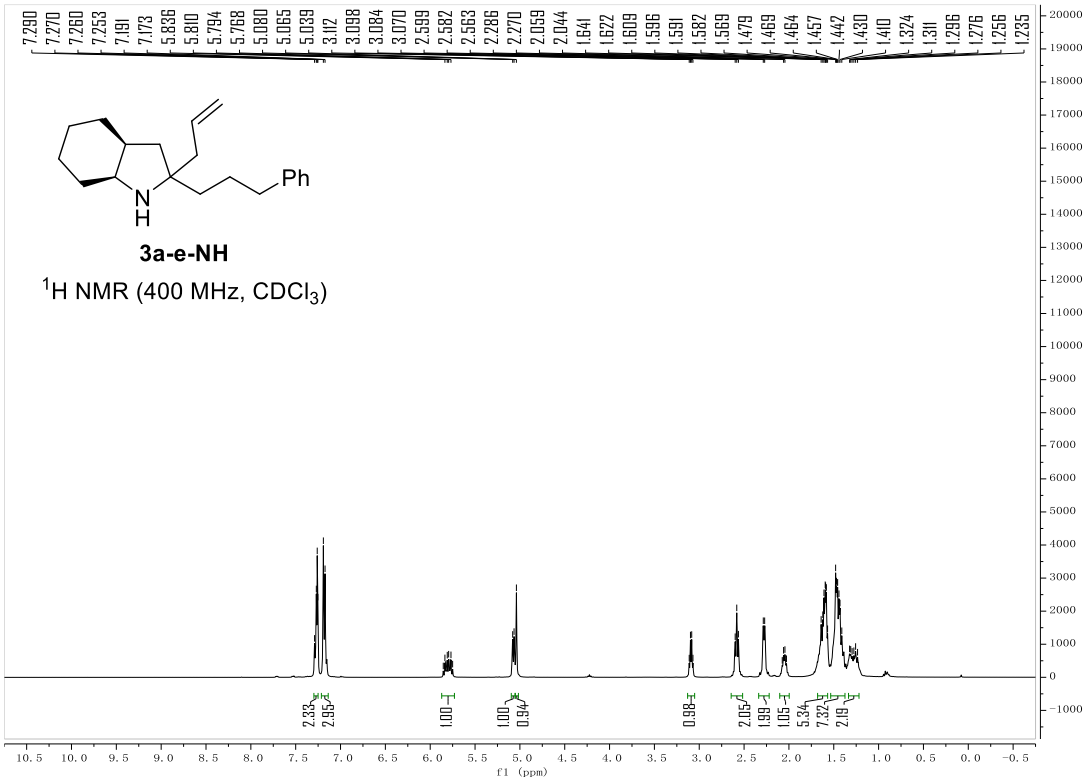


3a-d

^{13}C NMR (151 MHz, $CDCl_3$)

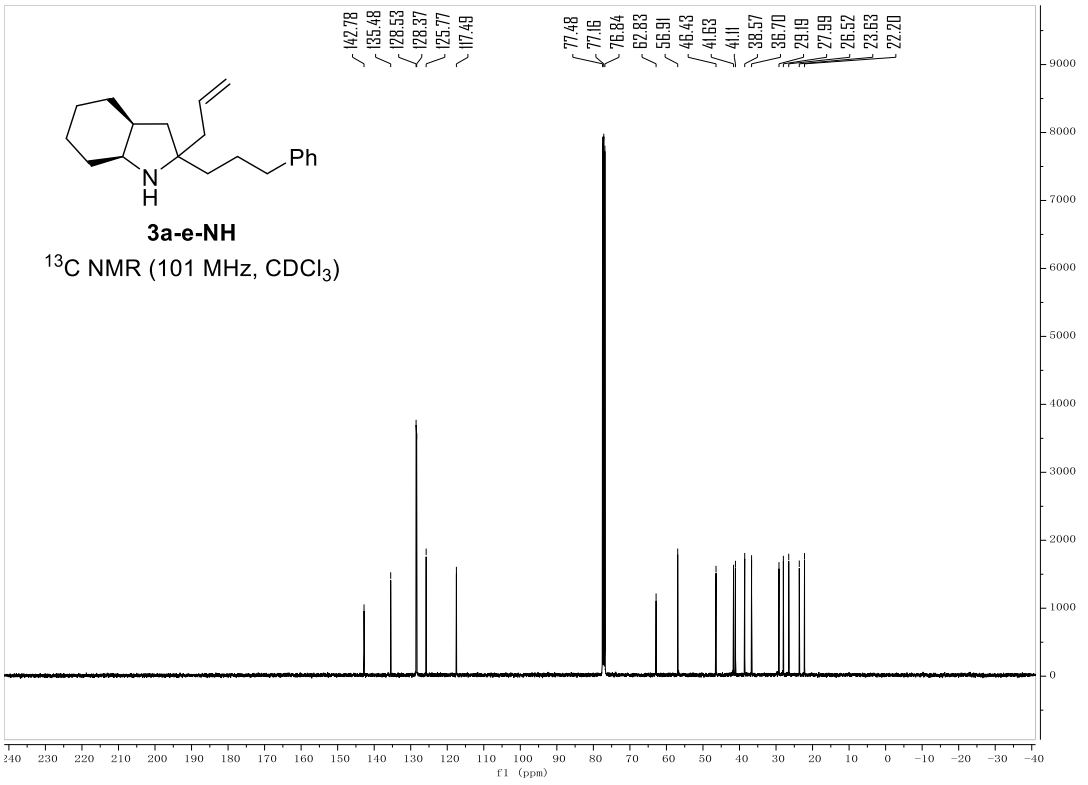

Ph
N
Boc
3a-e
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Ph
N
Boc
3a-e
13C NMR (101 MHz, CDCl3)
f1 (ppm)



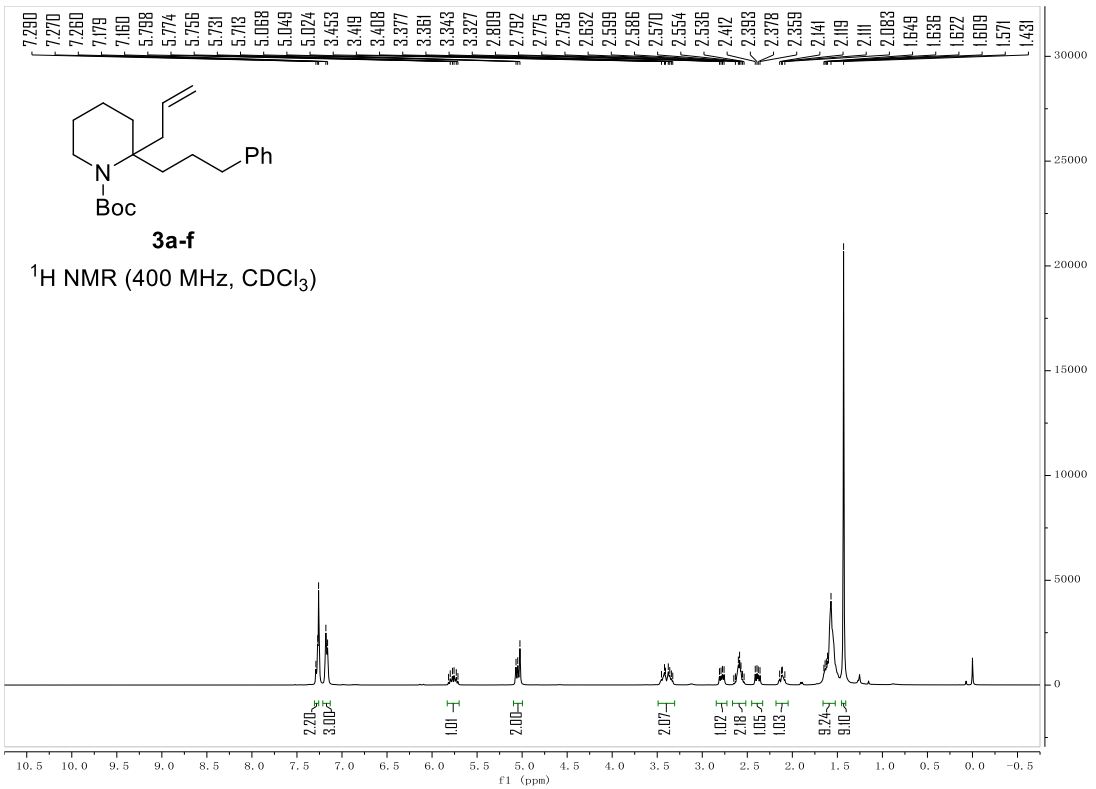
3a-e-NH

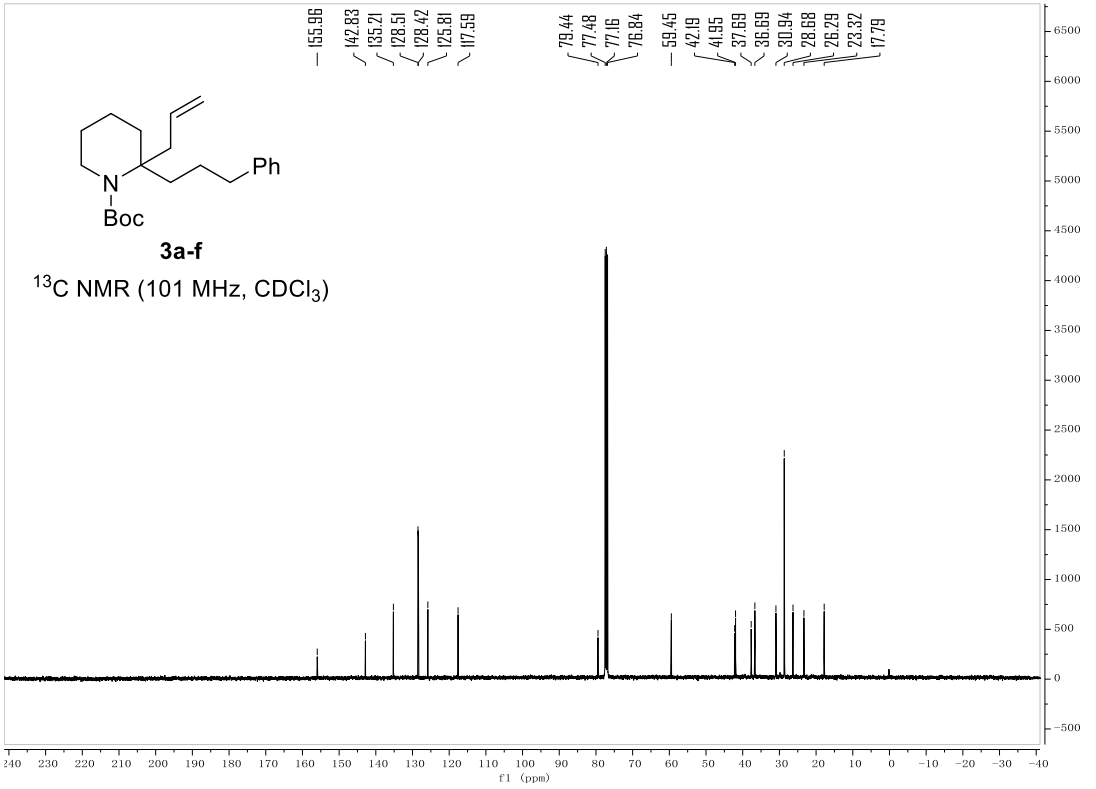
^{1}H NMR (400 MHz, $CDCl_3$)

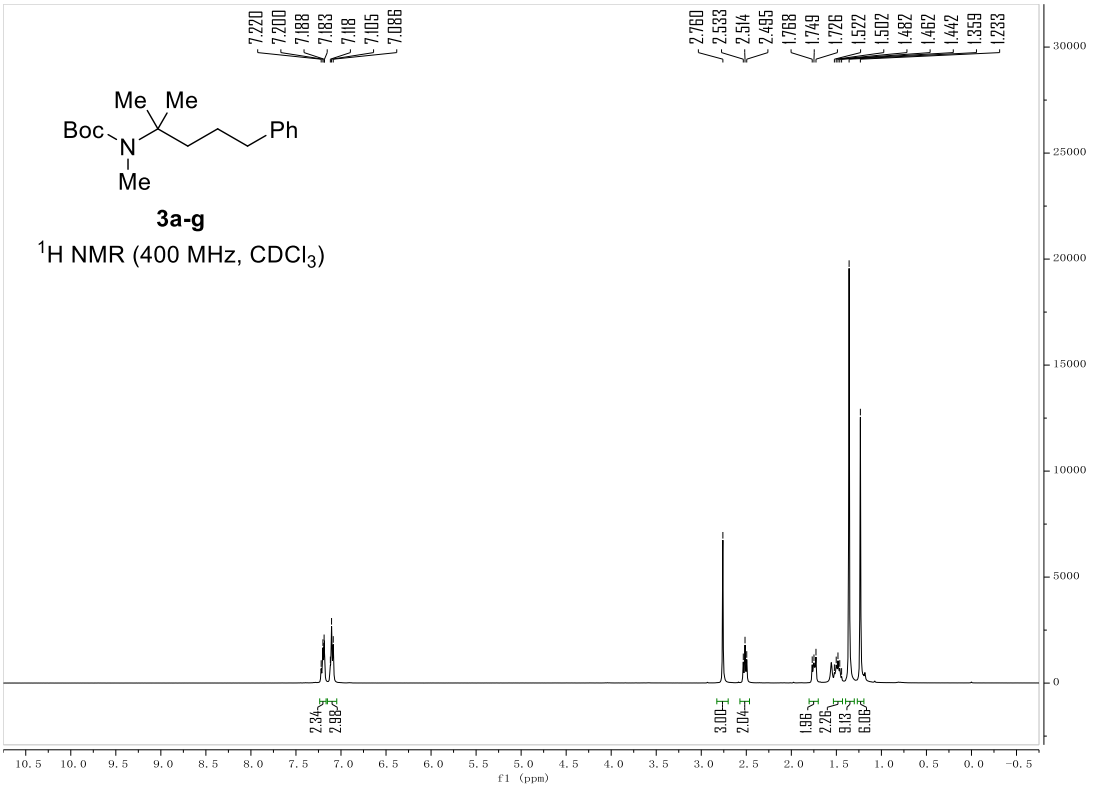


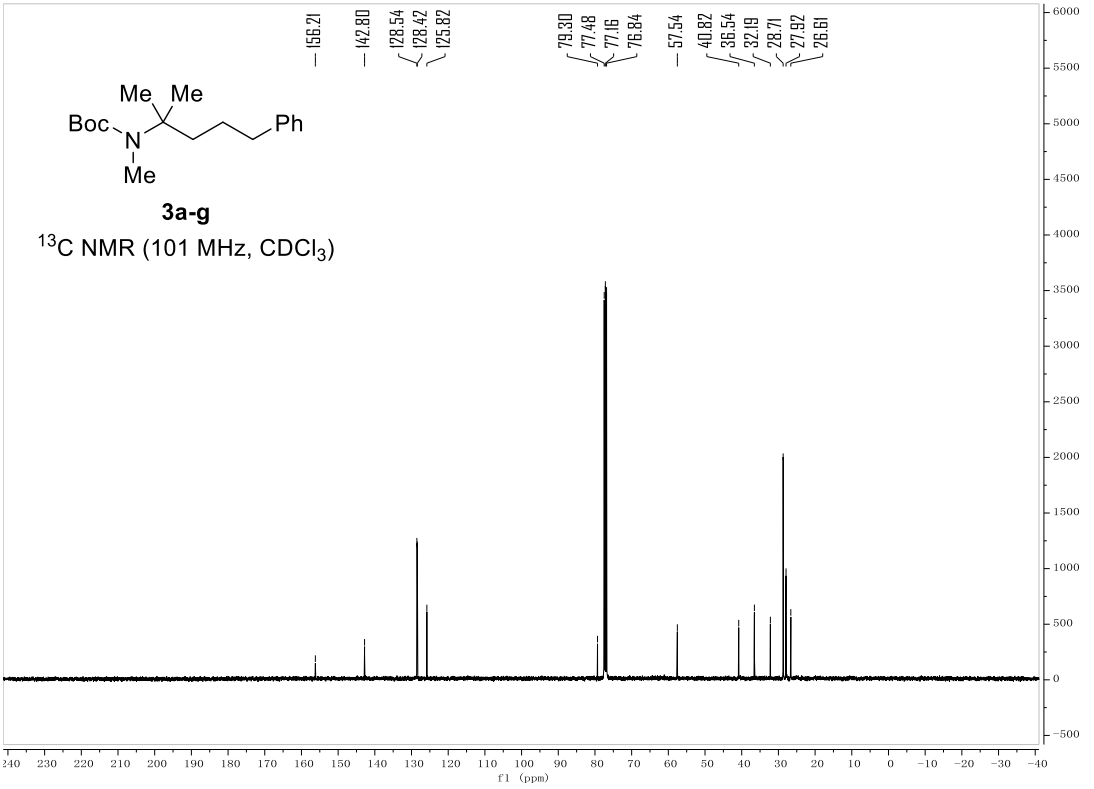
3a-e-NH

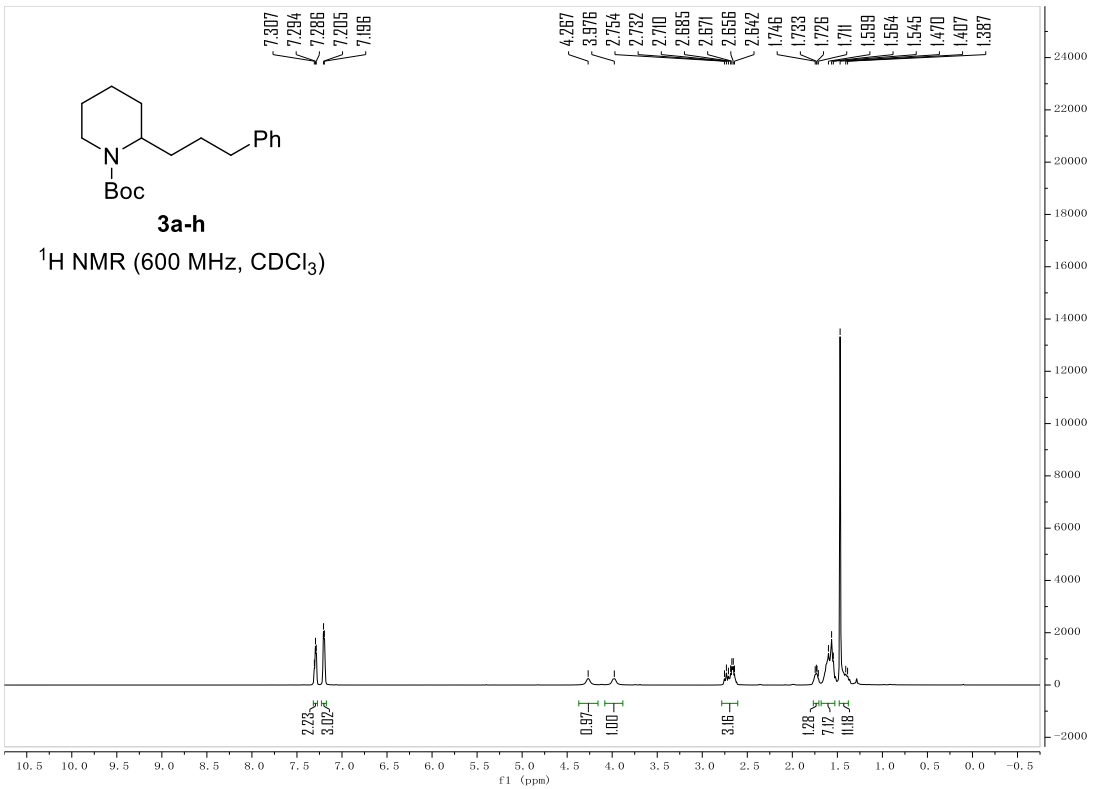
^{13}C NMR (101 MHz, $CDCl_3$)


7.290
7.270
7.260
7.179
7.160
5.798
5.774
5.756
5.731
5.713
5.068
5.049
5.024
3.453
3.419
3.408
3.377
3.361
3.343
3.327
2.809
2.792
2.775
2.758
2.632
2.599
2.586
2.570
2.554
2.536
2.412
2.393
2.378
2.359
2.141
2.119
2.111
2.083
1.649
1.636
1.622
1.609
1.571
1.431
Ph
N
Boc
3a-f
1H NMR (400 MHz, CDCl3)
2.20
3.00
1.01
2.00
2.07
1.02
2.18
1.05
1.03
9.24
9.10
f1 (ppm)


155.96
142.83
135.21
128.51
128.42
125.81
117.59
79.44
77.48
77.16
76.84
59.45
42.19
41.95
37.69
36.69
30.94
28.68
26.29
23.32
17.79
Ph
N
Boc
3a-f
13C NMR (101 MHz, CDCl3)
f1 (ppm)

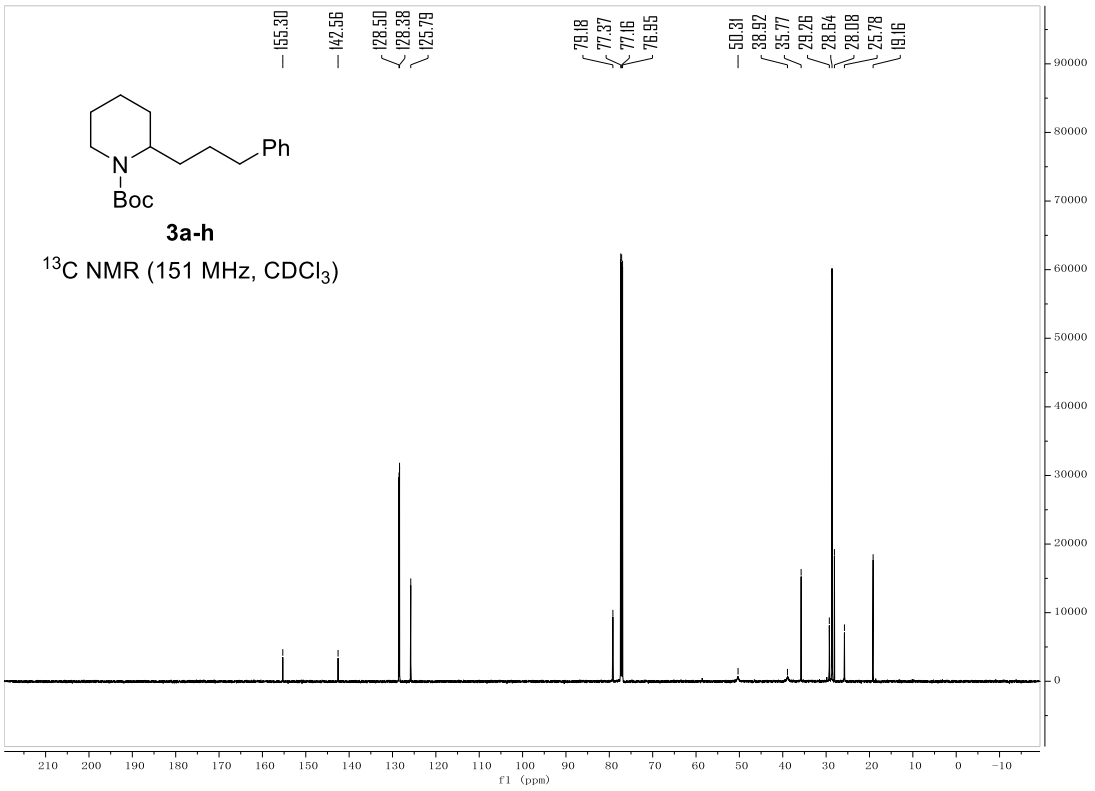

7.220
7.200
7.188
7.183
7.118
7.105
7.086
2.760
2.533
2.514
2.495
1.768
1.749
1.726
1.522
1.502
1.482
1.462
1.442
1.359
1.233
Me Me
Boc
N
Ph
Me
3a-g
1H NMR (400 MHz, CDCl3)
2.34
2.98
3.00
2.04
1.96
2.26
9.13
6.06
f1 (ppm)


156.21
142.80
128.54
128.42
125.82
79.30
77.48
77.16
76.84
57.54
40.82
36.54
32.19
28.71
27.92
26.61
Me Me
Boc
N
Ph
Me
3a-g
13C NMR (101 MHz, CDCl3)
f1 (ppm)



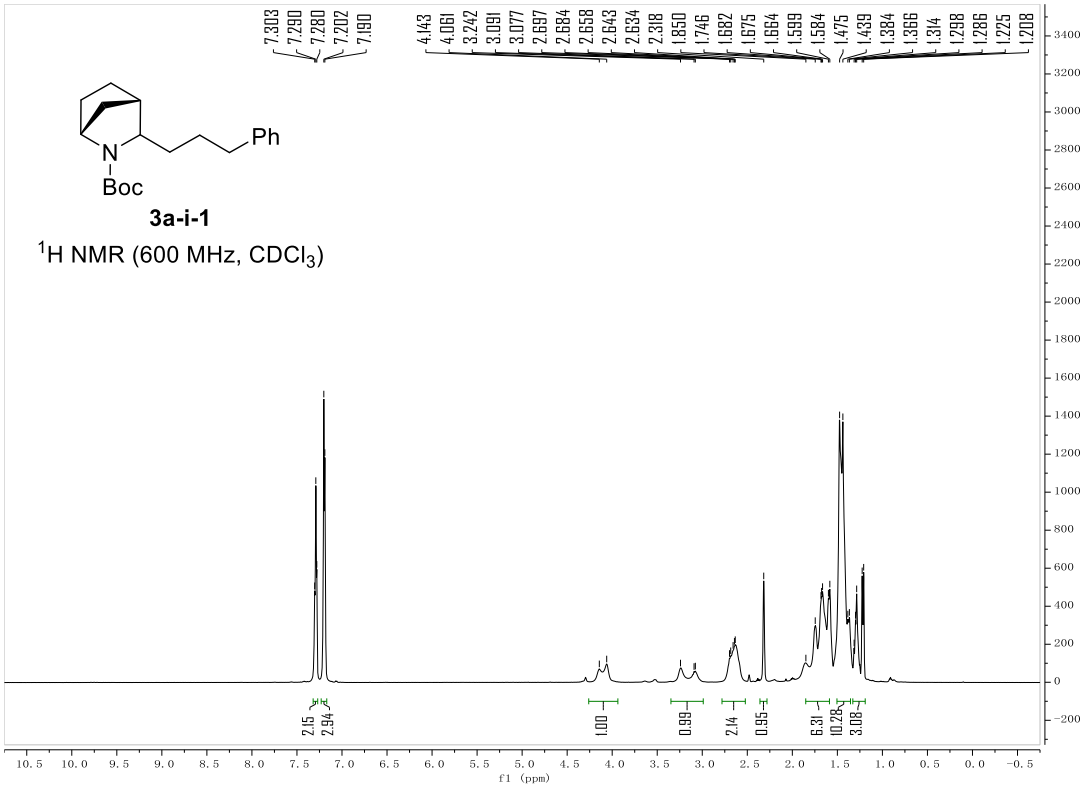
3a-h

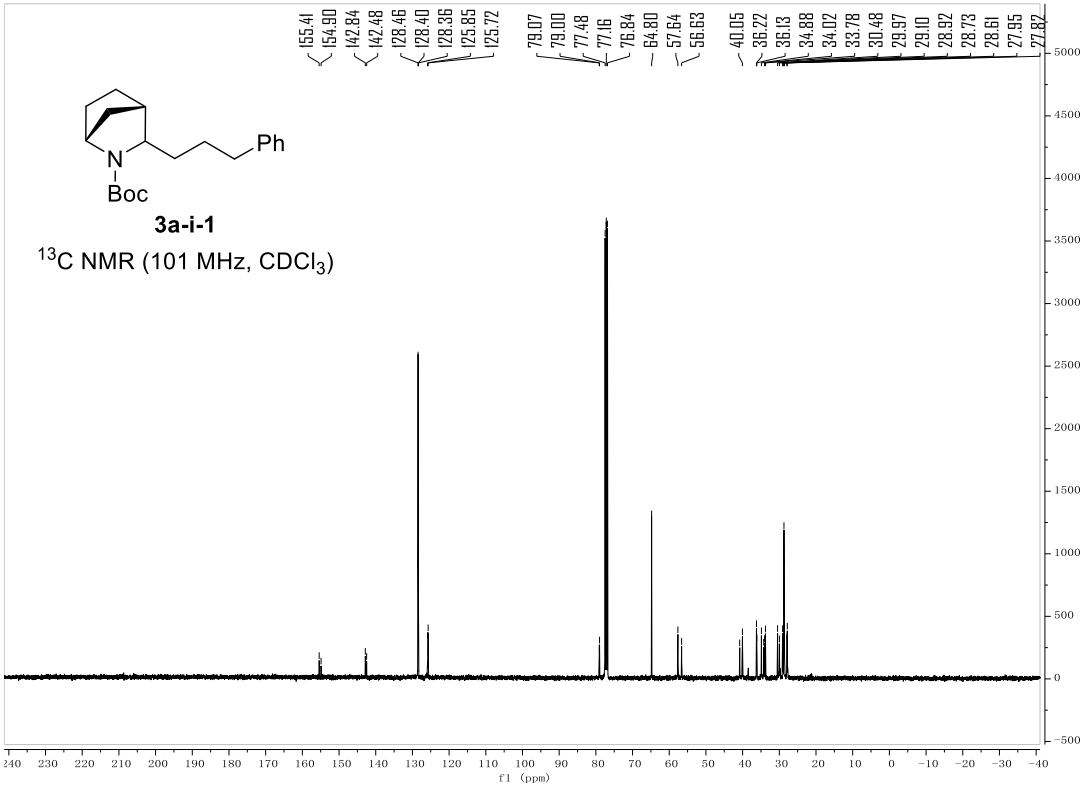
^{1}H NMR (600 MHz, $CDCl_3$)

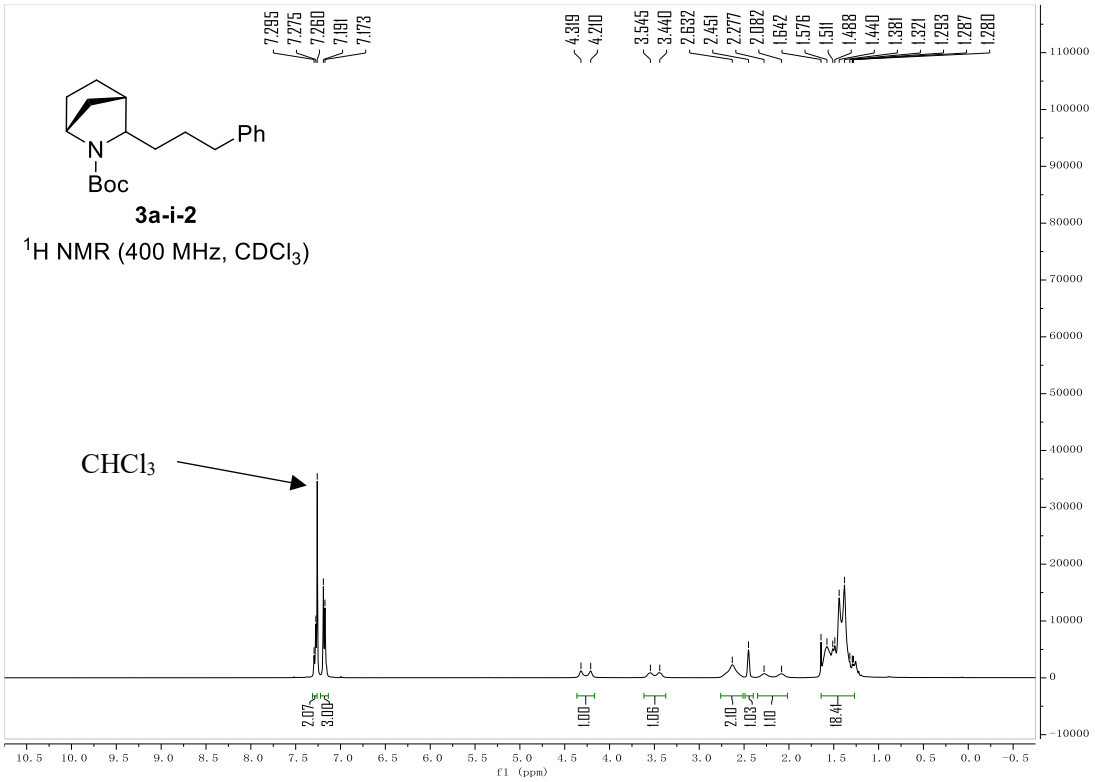


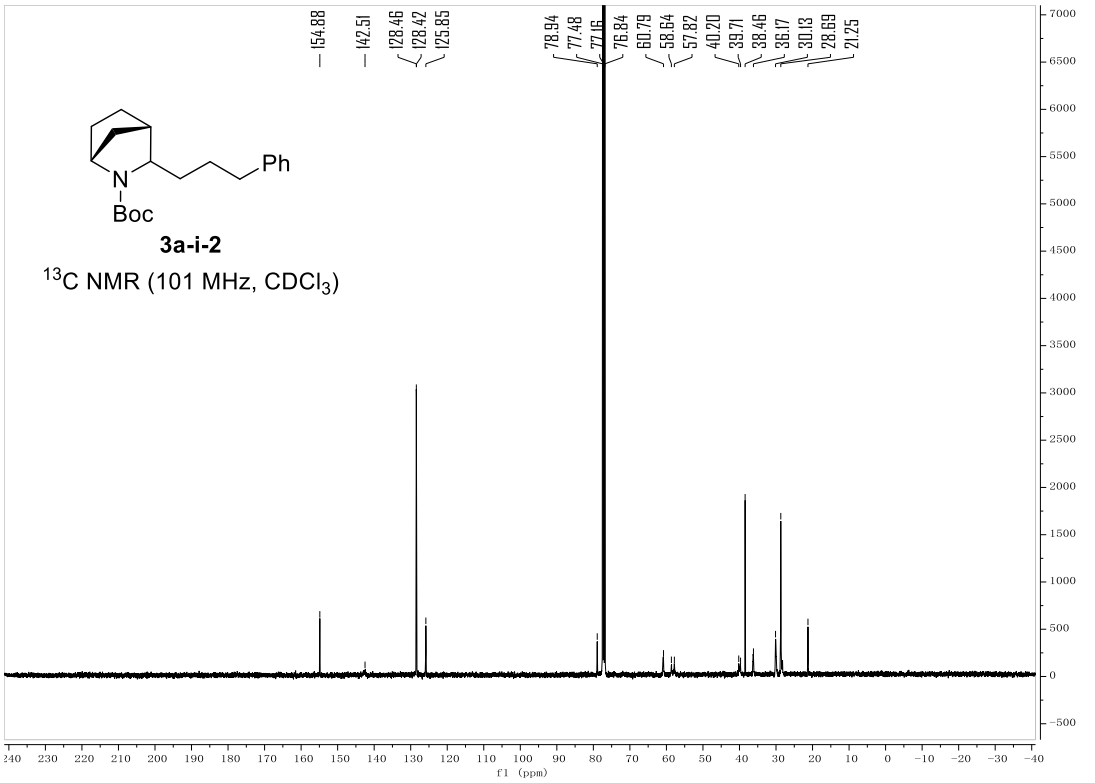
3a-h

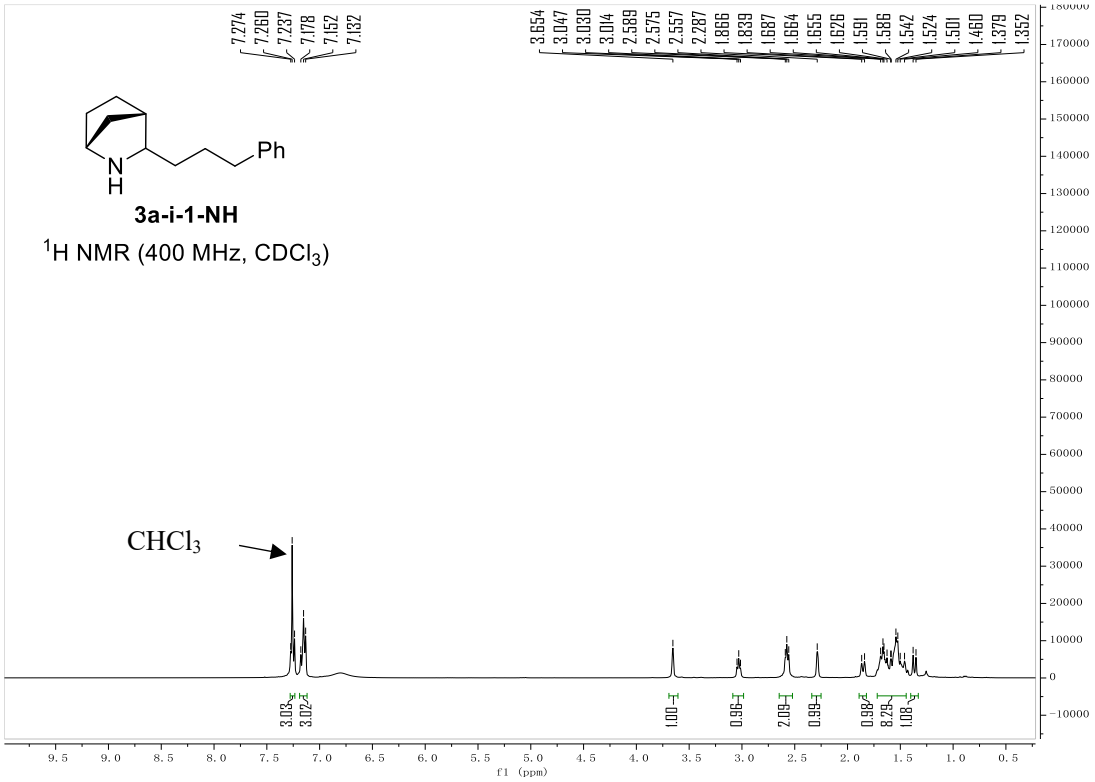
^{13}C NMR (151 MHz, $CDCl_3$)

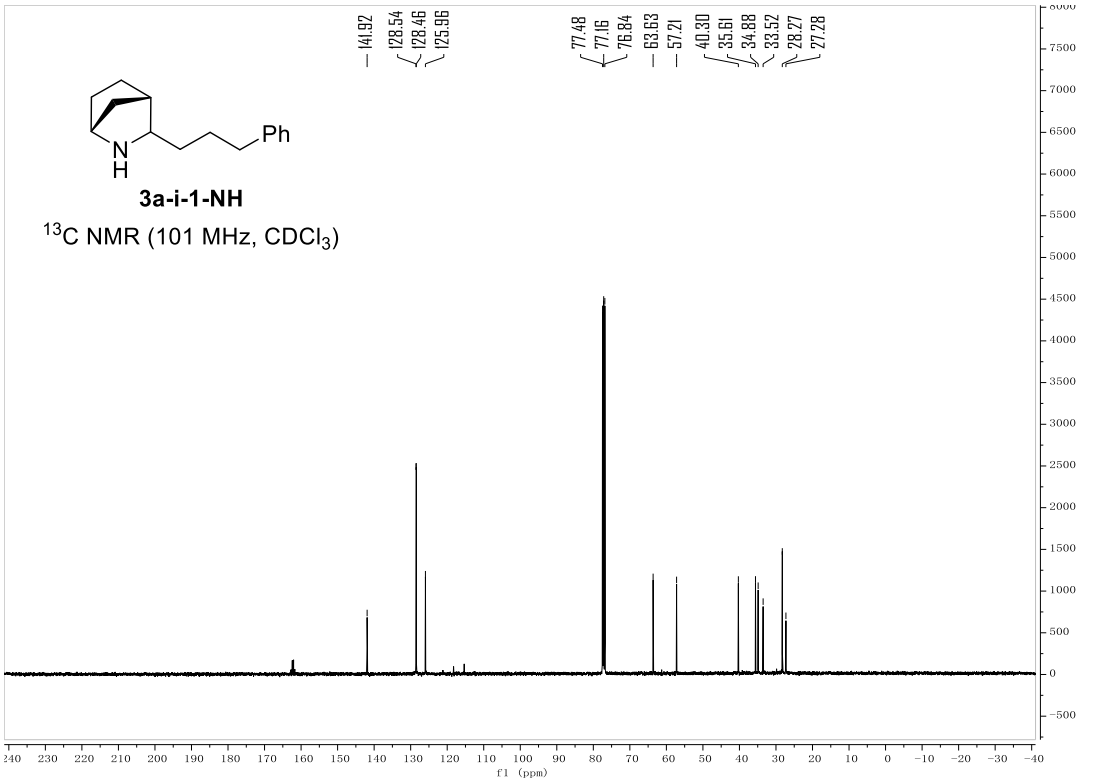

7.303
7.290
7.280
7.202
7.190
4.143
4.061
3.242
3.091
3.077
2.697
2.684
2.658
2.643
2.634
2.318
1.850
1.746
1.682
1.675
1.664
1.599
1.584
1.475
1.439
1.384
1.366
1.314
1.298
1.286
1.225
1.208
Ph
N
Boc
3a-i-1
1H NMR (600 MHz, CDCl3)
2.15
2.94
1.00
0.99
2.14
0.95
6.31
10.28
3.08
f1 (ppm)

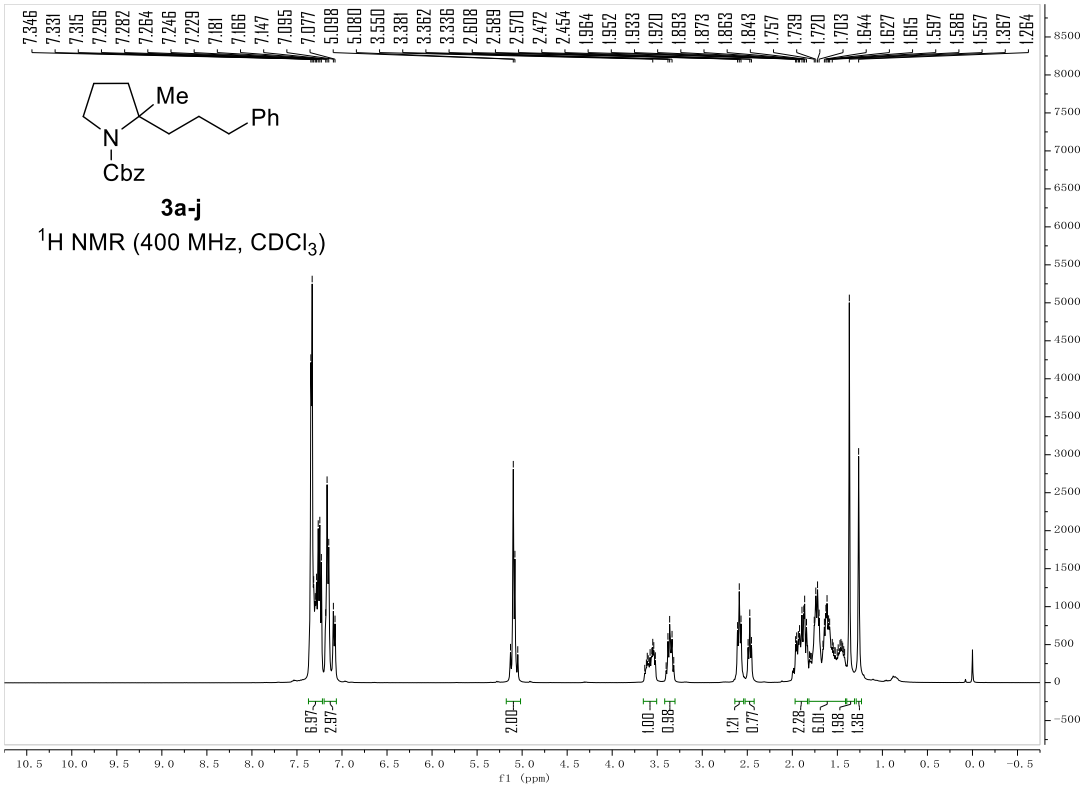

155.41
154.90
142.84
142.48
128.46
128.40
128.36
125.85
125.72
79.07
79.00
77.48
77.16
76.84
64.80
57.64
56.63
40.05
36.22
36.13
34.88
34.02
33.78
30.48
29.97
29.10
28.92
28.73
28.61
27.95
27.82
Ph
N
Boc
3a-i-1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

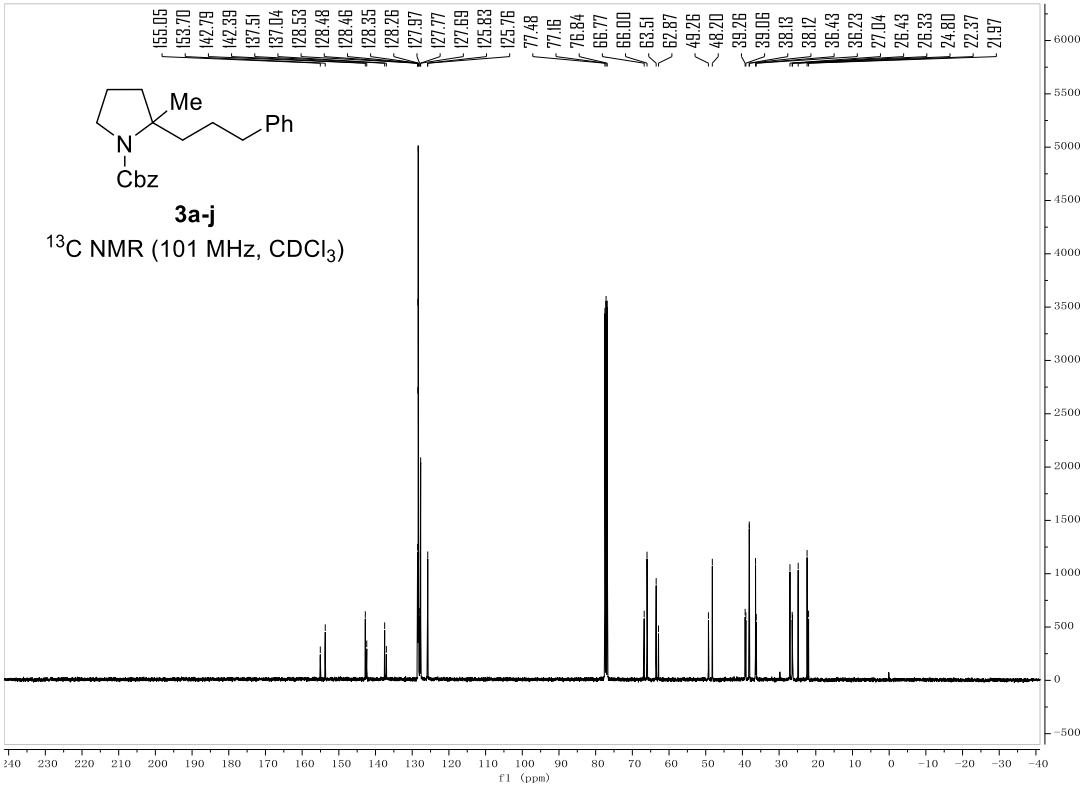

7.295
7.275
7.260
7.191
7.173
4.319
4.210
3.545
3.440
2.632
2.451
2.277
2.082
1.642
1.576
1.511
1.488
1.440
1.381
1.321
1.293
1.287
1.280
Ph
N
Boc
3a-i-2
1H NMR (400 MHz, CDCl3)
CHCl3
2.07
3.00
1.00
1.06
2.10
1.03
1.10
18.41
f1 (ppm)

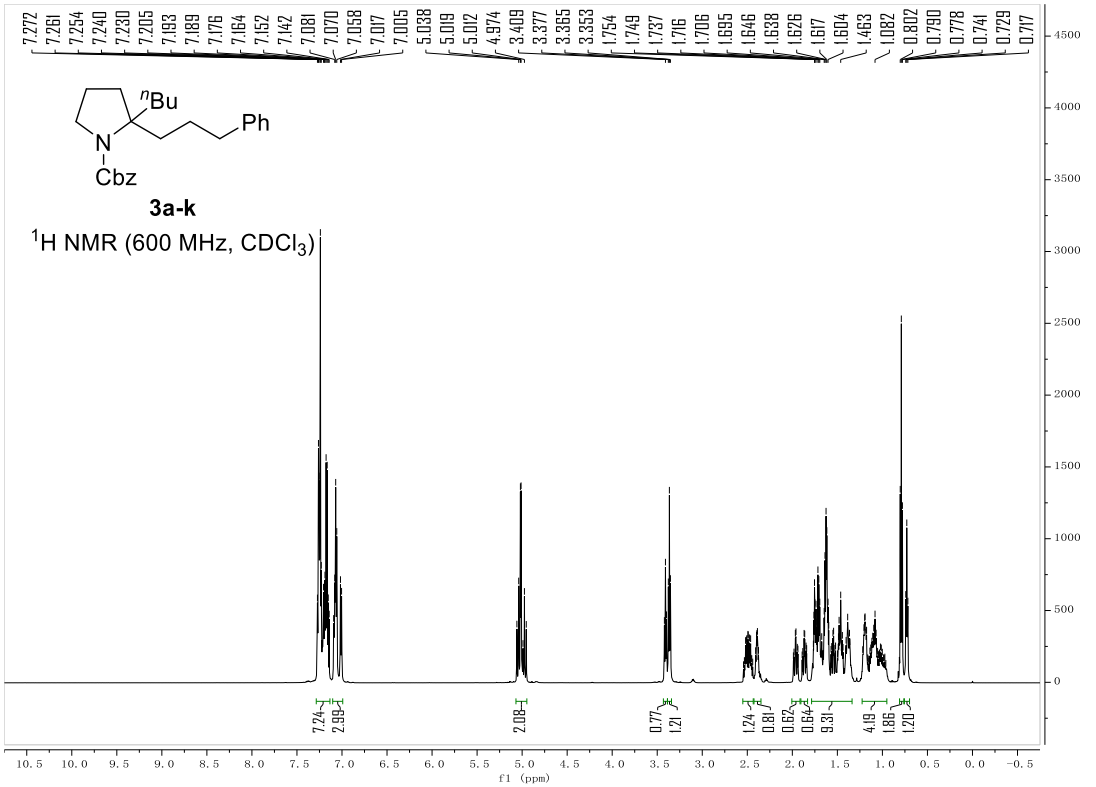

154.88
142.51
128.46
128.42
125.85
78.94
77.48
77.16
76.84
60.79
58.64
57.82
40.20
39.71
38.46
36.17
30.13
28.69
21.25
Ph
N
Boc
3a-i-2
13C NMR (101 MHz, CDCl3)
f1 (ppm)

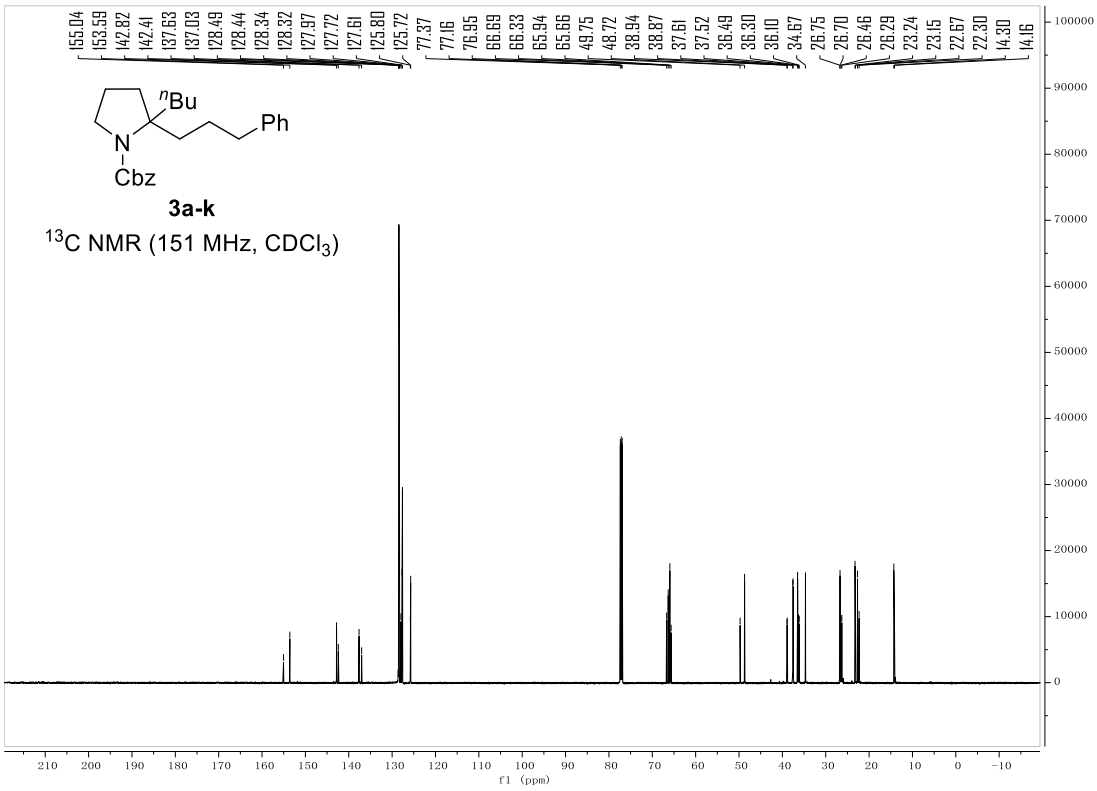

7.274
7.260
7.237
7.178
7.152
7.132
3.654
3.047
3.030
3.014
2.589
2.575
2.557
2.287
1.866
1.839
1.687
1.664
1.655
1.626
1.591
1.586
1.542
1.524
1.501
1.460
1.379
1.352
Ph
N
H
3a-i-1-NH
1H NMR (400 MHz, CDCl3)
CHCl3
3.03
3.02
1.00
0.96
2.09
0.99
0.98
8.29
1.08
f1 (ppm)

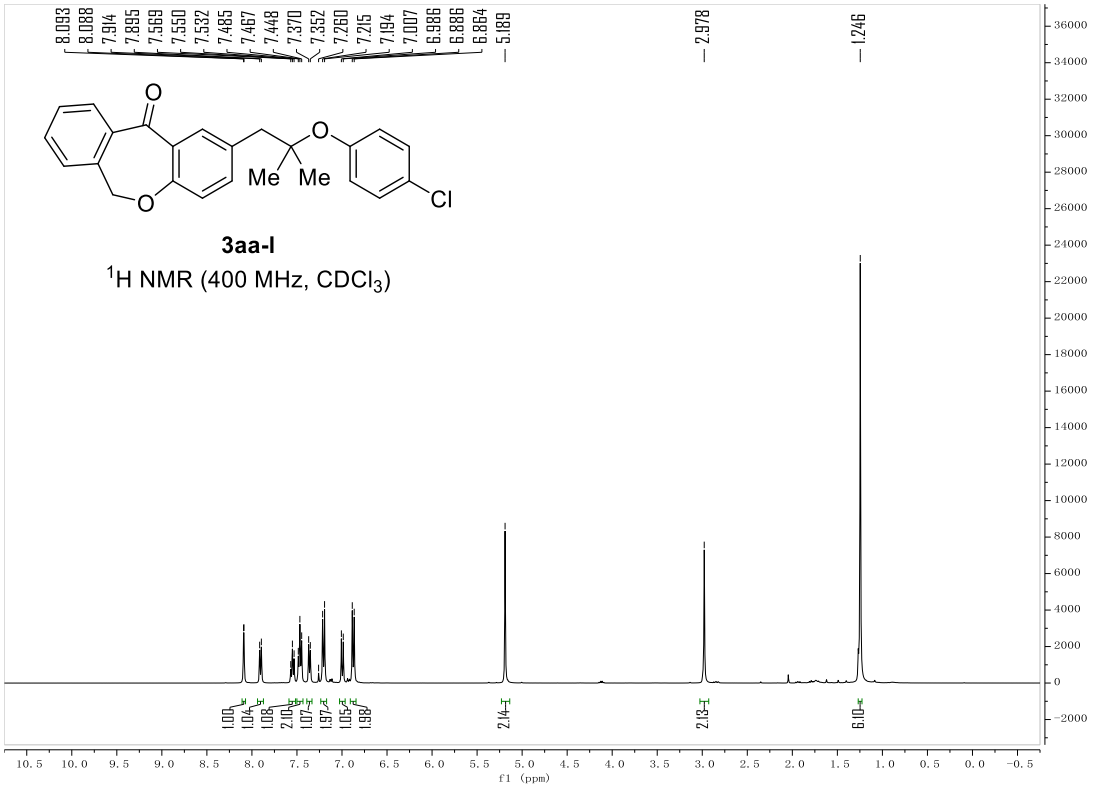

141.92
128.54
128.45
125.96
77.48
77.16
76.84
63.63
57.21
40.30
35.61
34.88
33.52
28.27
27.28
Ph
N
H
3a-i-1-NH
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Me
Ph
N
Cbz
3a-j
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
Ph
N
Cbz
3a-j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

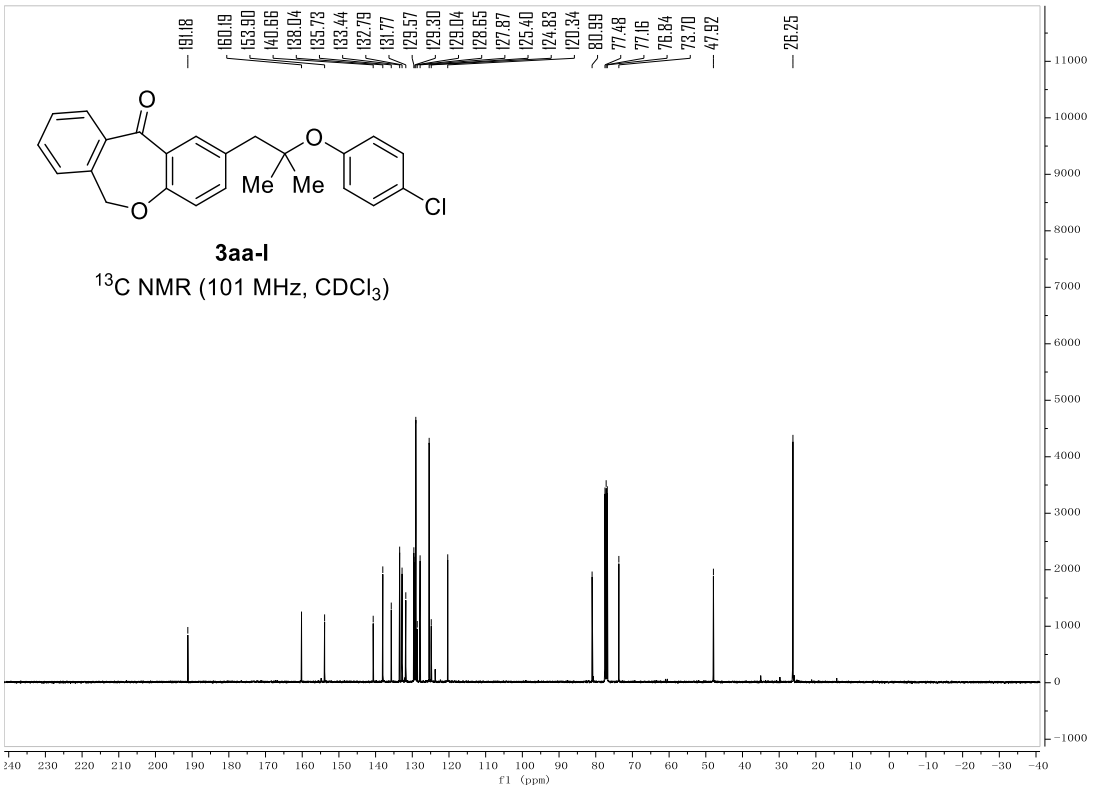

7.272
7.261
7.254
7.240
7.230
7.205
7.193
7.189
7.176
7.164
7.152
7.142
7.081
7.070
7.058
7.017
7.005
5.038
5.019
5.012
4.974
3.409
3.377
3.365
3.353
1.754
1.749
1.737
1.716
1.706
1.695
1.646
1.638
1.626
1.617
1.604
1.463
1.082
0.802
0.790
0.778
0.741
0.729
0.717
nBu
Ph
N
Cbz
3a-k
1H NMR (600 MHz, CDCl3)
7.24
2.99
2.08
0.77
1.21
1.24
0.81
0.62
0.64
9.31
4.19
1.86
1.20
f1 (ppm)


155.04
153.59
142.82
142.41
137.63
137.03
128.49
128.44
128.34
128.32
127.97
127.72
127.61
125.80
125.72
77.37
77.16
76.95
66.69
66.33
65.94
65.66
49.75
48.72
38.94
38.87
37.61
37.52
36.49
36.30
36.10
34.67
26.75
26.70
26.46
26.29
23.24
23.15
22.67
22.30
14.30
14.16
nBu
Ph
N
Cbz
3a-k
13C NMR (151 MHz, CDCl3)
f1 (ppm)



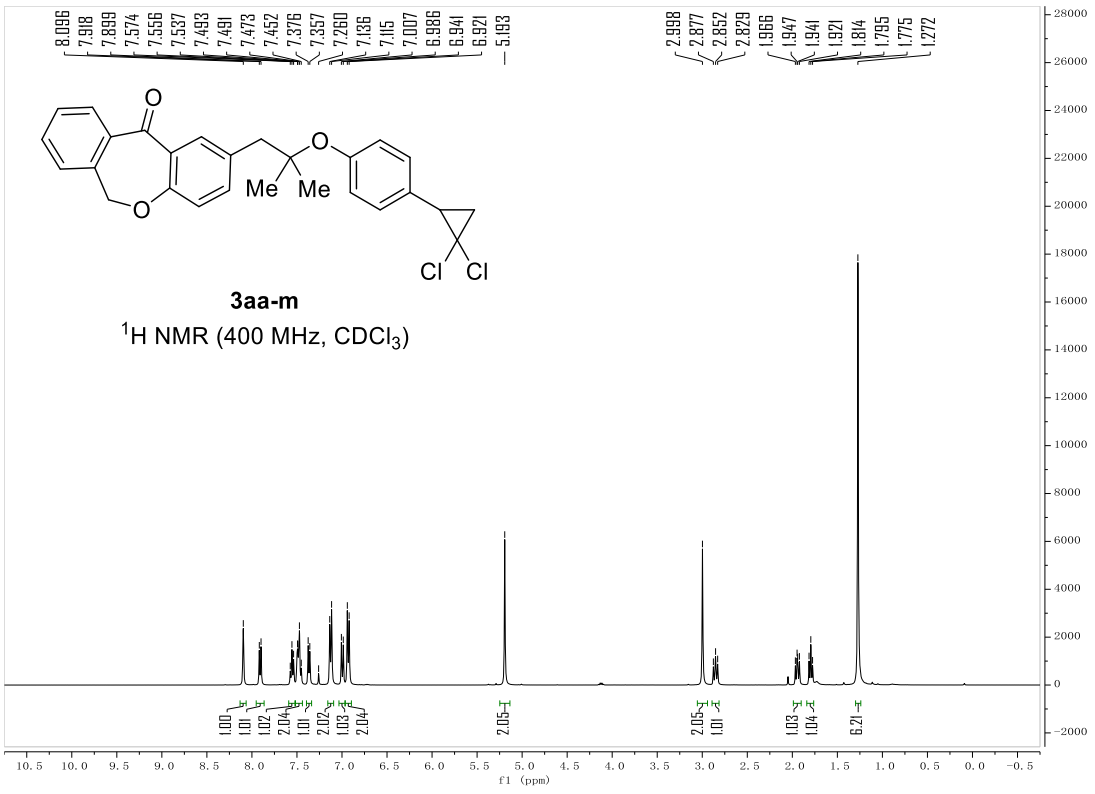
3aa-I

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



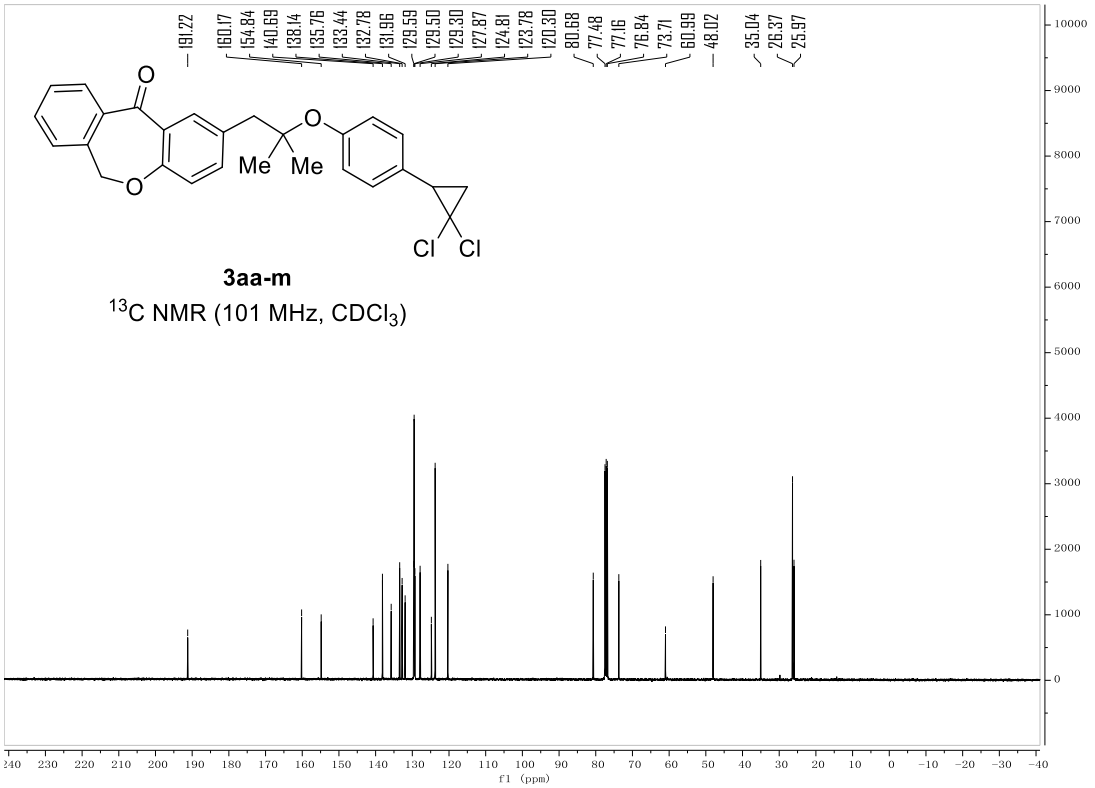
3aa-I

^{13}C NMR (101 MHz, $CDCl_3$)



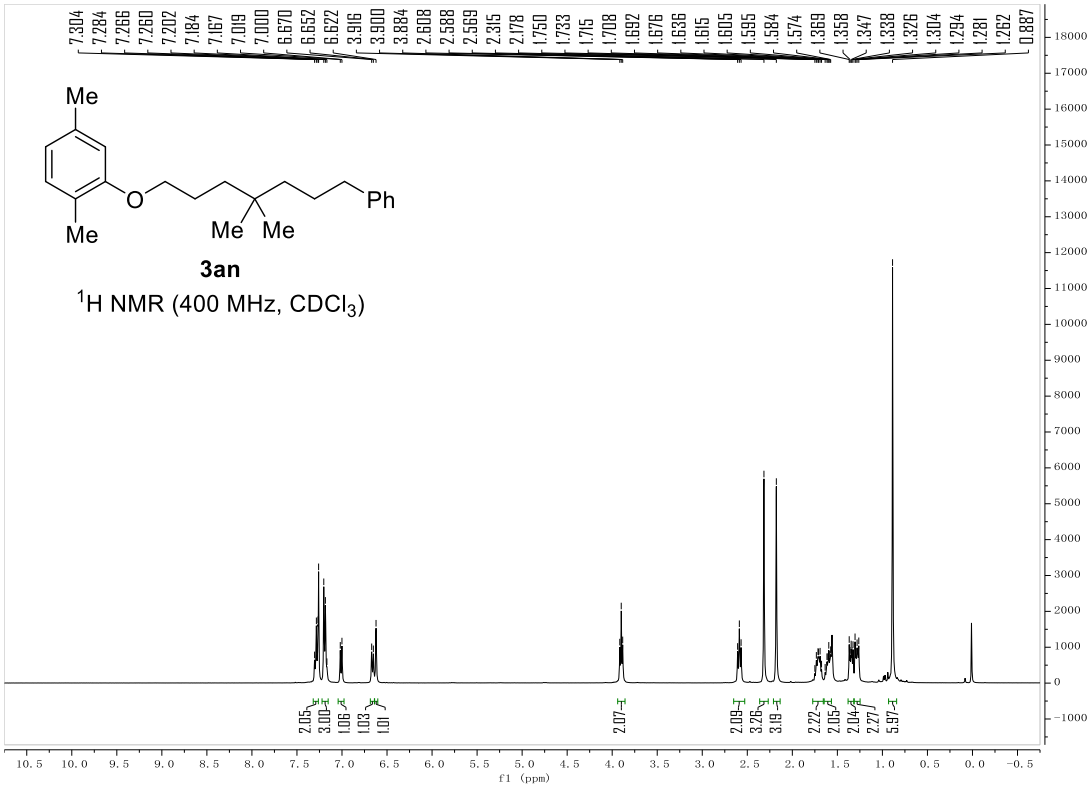
3aa-m

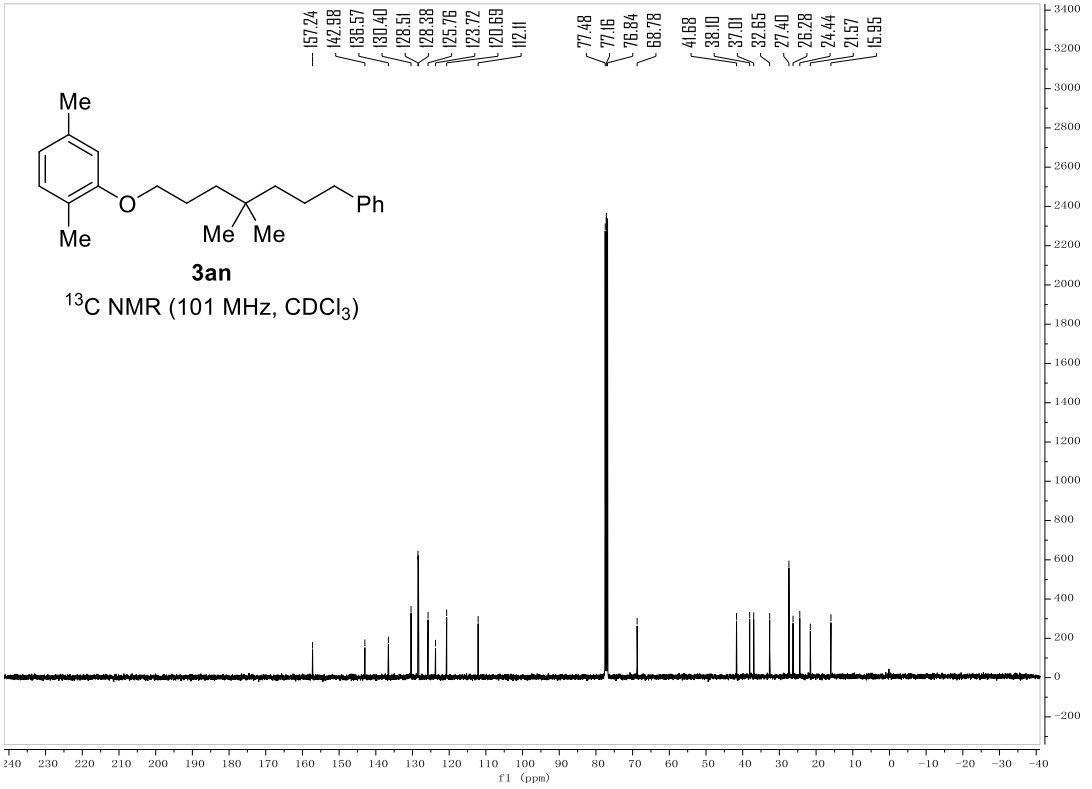
^{1}H NMR (400 MHz, $CDCl_3$)

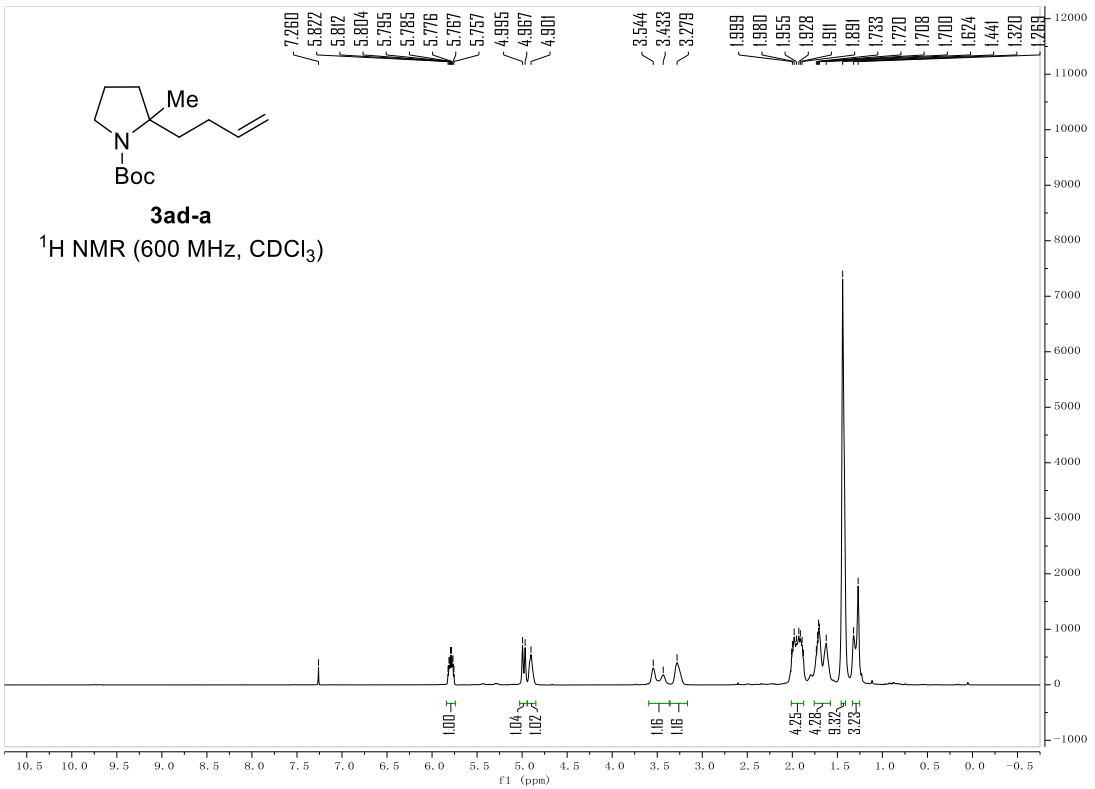


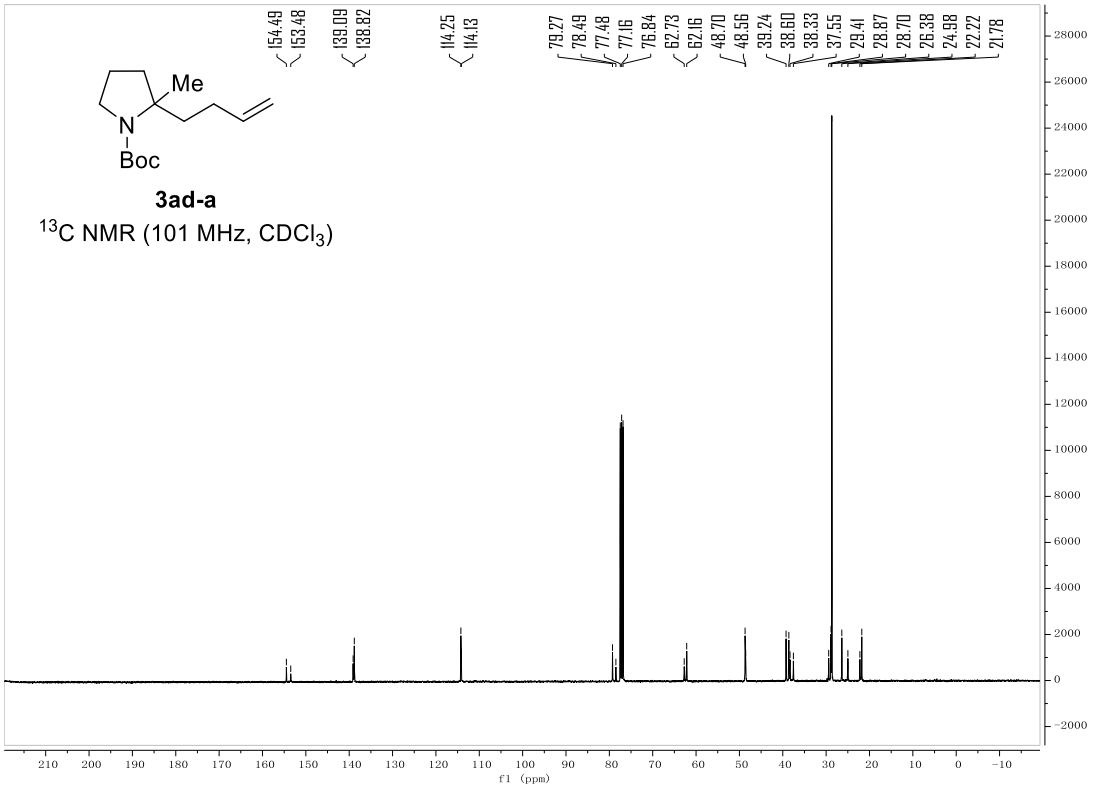
3aa-m

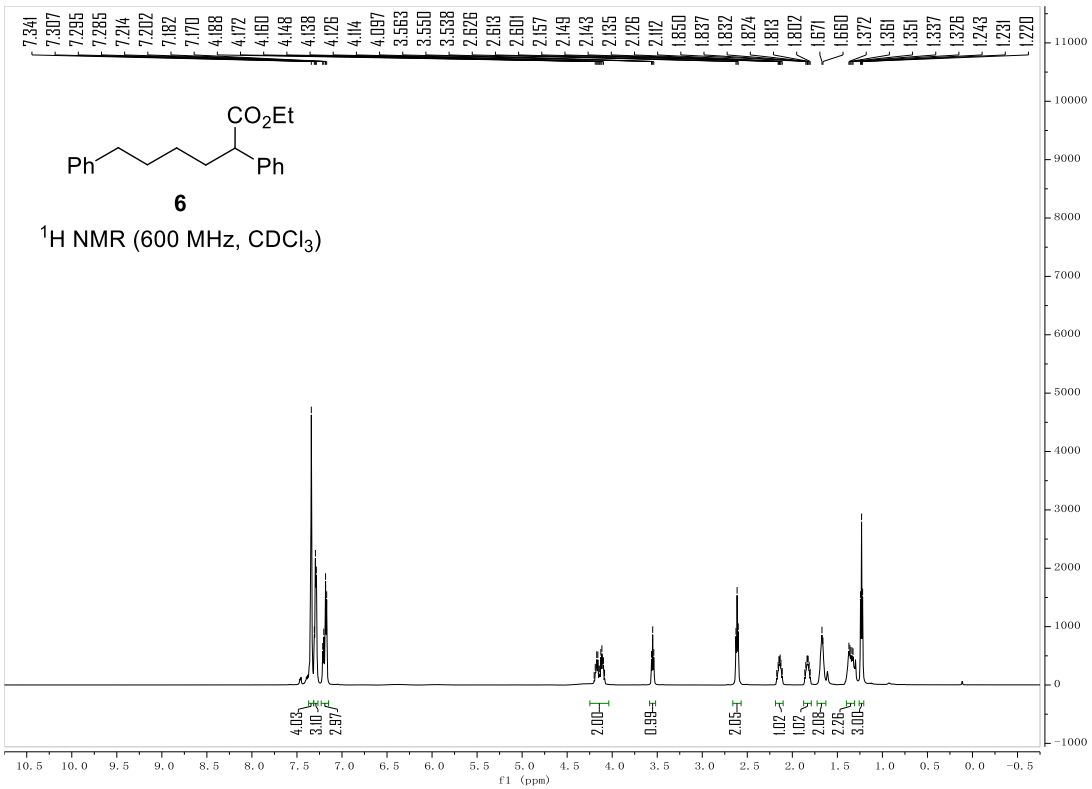
^{13}C NMR (101 MHz, $CDCl_3$)

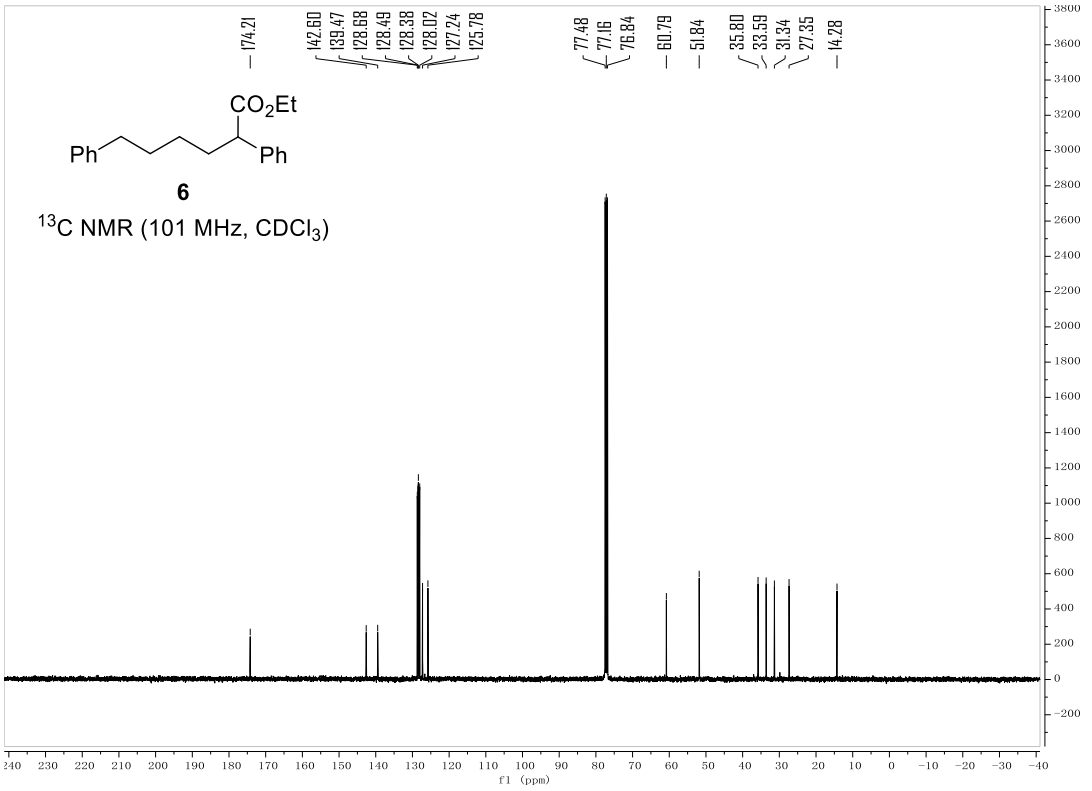

7.304
7.284
7.266
7.260
7.202
7.184
7.167
7.019
7.000
6.670
6.652
6.622
3.916
3.900
3.884
2.608
2.588
2.569
2.315
2.178
1.750
1.733
1.715
1.708
1.692
1.676
1.636
1.615
1.605
1.595
1.584
1.574
1.369
1.358
1.347
1.338
1.326
1.304
1.294
1.281
1.262
0.887
Me
O
Me
Me
Me
Ph
3an
1H NMR (400 MHz, CDCl3)
2.05
3.00
1.06
1.03
1.01
2.07
2.09
3.26
3.19
2.22
2.05
2.04
2.27
5.97
f1 (ppm)

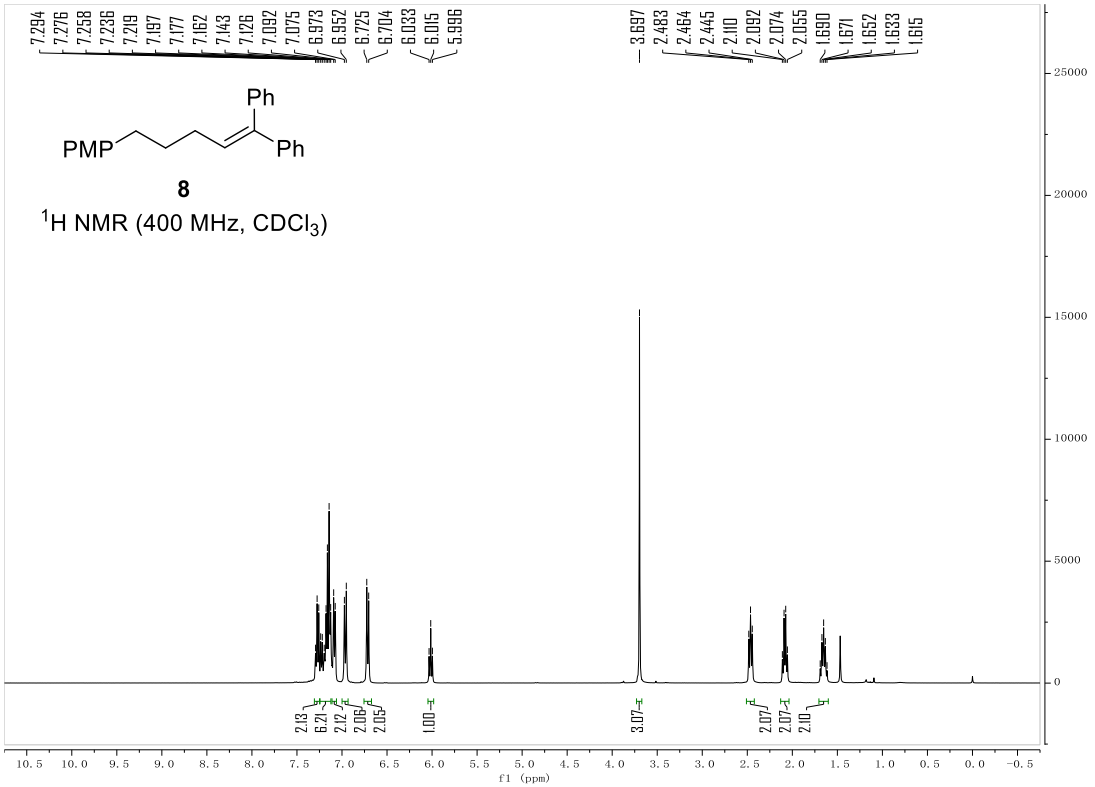

157.24
142.98
136.57
130.40
128.51
128.38
125.76
123.72
120.69
112.11
77.48
77.16
76.84
68.78
41.68
38.10
37.01
32.65
27.40
26.28
24.44
21.57
15.95
Me
O
Me
Me
Me
Ph
3an
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Me
N
Boc
3ad-a
1H NMR (600 MHz, CDCl3)
7.260
5.822
5.812
5.804
5.795
5.785
5.776
5.767
5.757
4.995
4.967
4.901
3.544
3.433
3.279
1.999
1.980
1.955
1.928
1.911
1.891
1.733
1.720
1.708
1.700
1.624
1.441
1.320
1.269
1.00
1.04
1.02
1.16
1.16
4.25
4.28
9.32
3.23
f1 (ppm)


Me
N
Boc
3ad-a
13C NMR (101 MHz, CDCl3)
154.49
153.48
139.09
138.82
114.25
114.13
79.27
78.49
77.48
77.16
76.84
62.73
62.16
48.70
48.56
39.24
38.60
38.33
37.55
29.41
28.87
28.70
26.38
24.98
22.22
21.78
f1 (ppm)

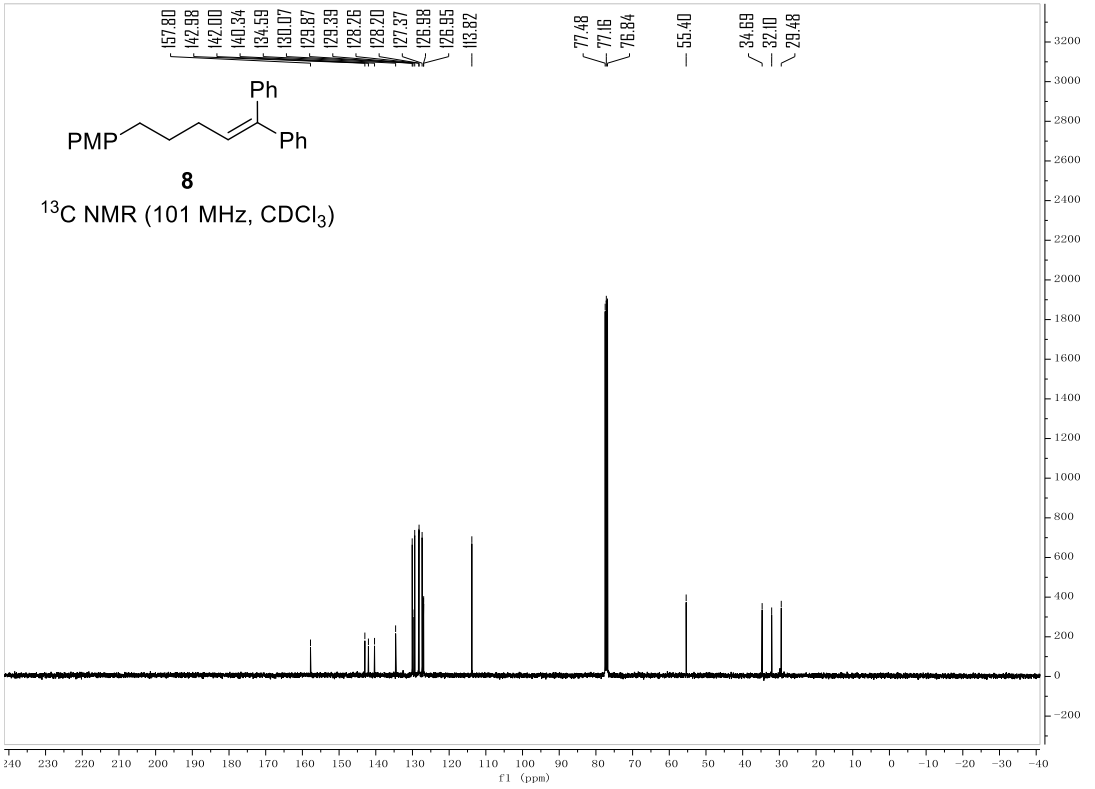

7.341
7.307
7.295
7.285
7.214
7.202
7.182
7.170
4.188
4.172
4.160
4.148
4.138
4.126
4.114
4.097
3.563
3.550
3.538
2.626
2.613
2.601
2.157
2.149
2.143
2.135
2.126
2.112
1.850
1.837
1.832
1.824
1.813
1.802
1.671
1.660
1.372
1.361
1.351
1.337
1.326
1.243
1.231
1.220
CO2Et
Ph
Ph
6
1H NMR (600 MHz, CDCl3)
4.03
3.10
2.97
2.00
0.99
2.05
1.02
1.02
2.08
2.26
3.00
f1 (ppm)


174.21
142.60
139.47
128.68
128.49
128.38
128.02
127.24
125.78
77.48
77.16
76.84
60.79
51.84
35.80
33.59
31.34
27.35
14.28
CO2Et
Ph
Ph
6
13C NMR (101 MHz, CDCl3)
f1 (ppm)



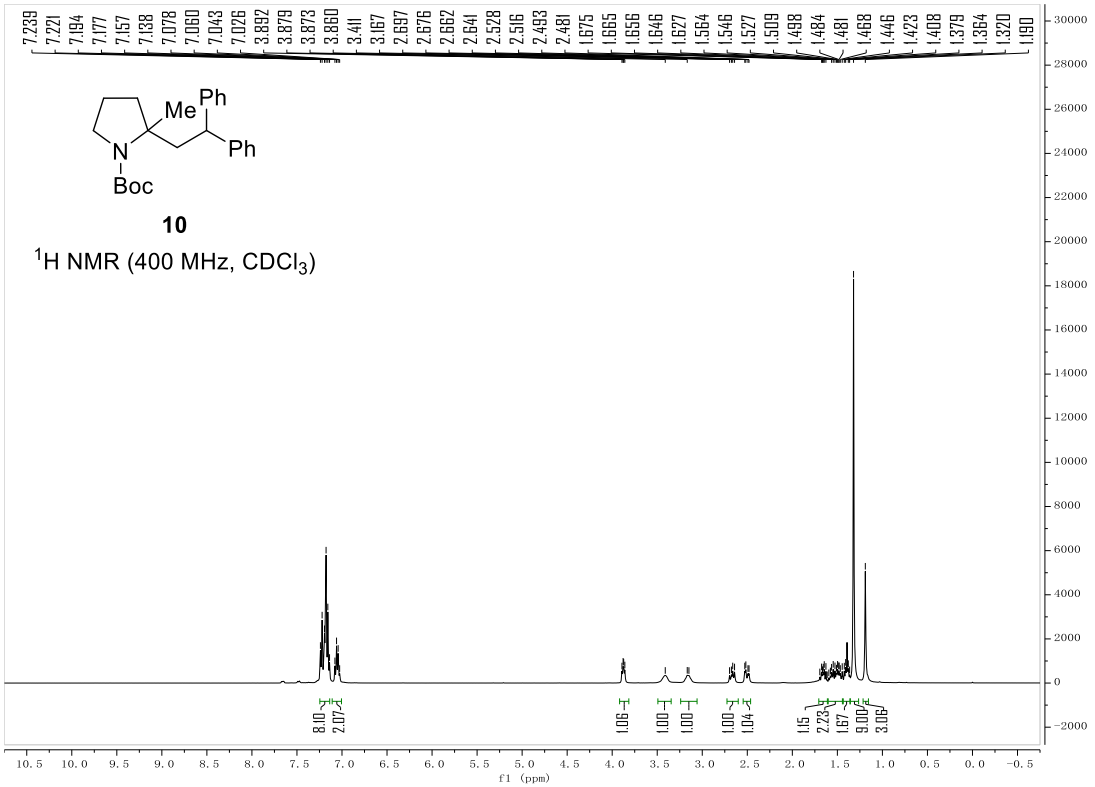
8

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



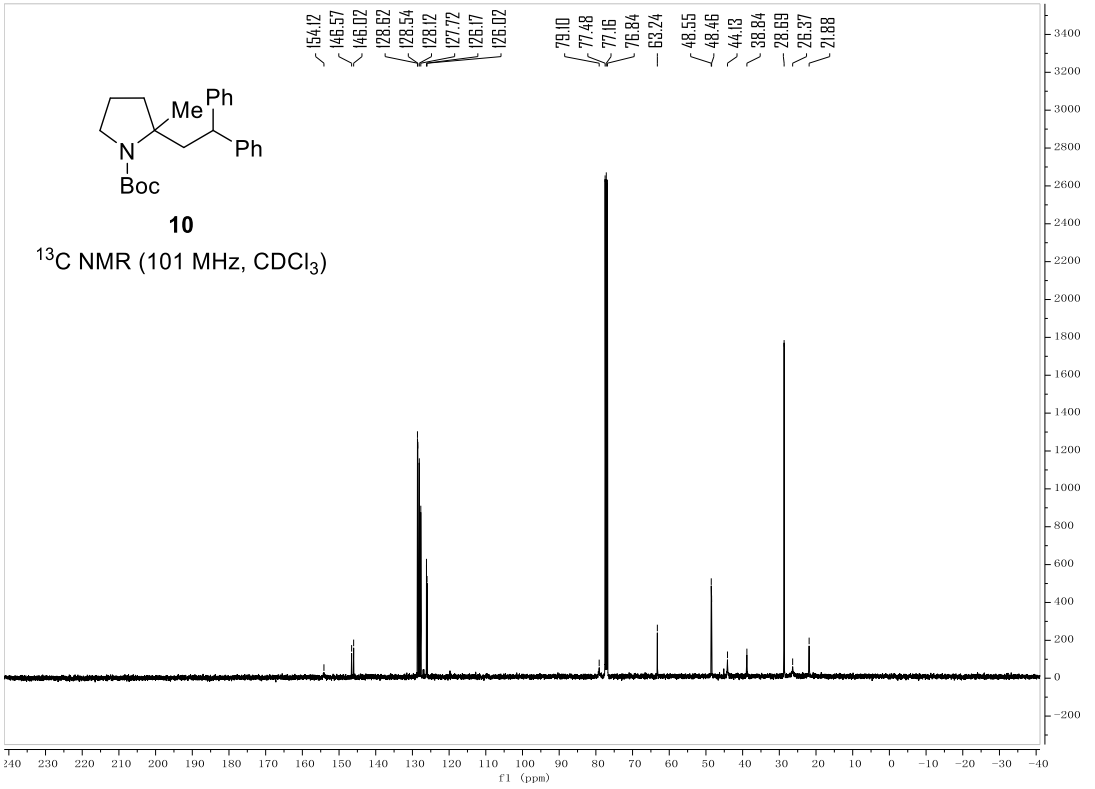
8

^{13}C NMR (101 MHz, $CDCl_3$)



10

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



10

^{13}C NMR (101 MHz, $CDCl_3$)