Supporting Information

For

I_2-Mediated Oxidative Bicyclization of 4-Pentenamines to Prolinol Carbamates with CO_2 Incorporating Oxyamination of C=C Bond

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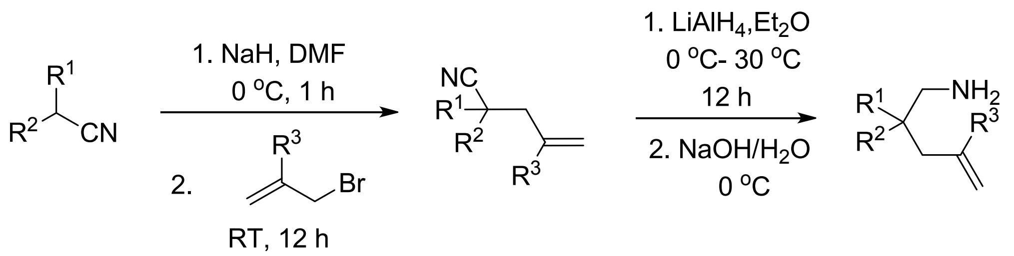
General information

MeCN, DMF (*N*,*N*-dimethylformamide), DCM (dichloromethane) were dried by 4 Å molecular sieves. THF and Et_2O were purified by solvent purification system. Unless otherwise mentioned, reagents purchased were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded with 600 MHz, 400 MHz and 300 MHz spectrometer. $CDCl_3$ was selected as the solvent and residual proton resonance of $CDCl_3$ was referenced using the 7.26 ppm in ^{1}H NMR and 77.16 ppm in ^{13}C NMR. Coupling constants (J) were obtained in Hertz (Hz). The abbreviation of s, d, t and m means singlet, doublet, triplet, and multiplet, respectively. HRMS were recorded with ESI in positive ion mode on IT-TOF instrument. Pent-4-en-1-amine (1q) was prepared according reported literature.[1]

Experiment procedure

Synthesis of substrate 1a, 1f, 1n



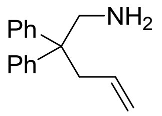
1a R^1= R^2= Ph, R^3= H
1j R^1= Ph R^2= H, R^3= H
1n R^1= R^2= Ph, R^3= Me

Representative procedure[2]

100 mL Schlenk tube with NaH (22 mmol) was evacuated and back-filled with N_2 and 25 mL DMF was added. A solution of 2,2-diphenylacetonitrile (20mmol) in 10 mL DMF was injected via syringe. Mixture was stirred at room temperature for 1 h and turned yellow. Then Schlenk tube was cooled to 0 °C followed by addition of allyl bromide (22 mmol). The reaction was warmed to room temperature and stirred for 12 h, diluted with ice water and extracted with EtOAc for 3 times. Organic layer combined was washed with saturated NaCl solution, dried by Na_2SO_4, evaporated and isolated by silica gel flash chromatography (petroleum ether/ EtOAc).

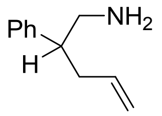
100mL Schlenk tube containing $LiAlH_4$ (64 mmol) was evacuated and back-filled with

N_2 followed by addition of 30mL ether. The purified nitrile (16 mmol) in 10 mL ether was added to suspension at 0 °C. Then the reaction was stirred at 30 °C for 12 h followed by addition of 5M NaOH slowly in 0 °C to quench the reaction. After extraction with EtOAc for 3 times, combined organic layer was washed with saturated NaCl solution, dried by Na_2SO_4, evaporated and purified by silica gel flash chromatography (petroleum ether/ EtOAc).



2,2-Diphenylpent-4-en-1-amine(1a)[3]

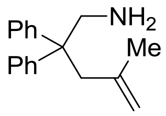
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.30 (m, 4H), 7.17-7.21 (m, 6H), 5.36-5.43 (m, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 3.32 (s, 2H), 2.93 (d, 2H, *J* = 6.0 Hz), 1.01 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 146.4, 134.7, 128.4, 128.2, 126.1, 117.9, 51.5, 48.6, 41.3.



2-Phenylpent-4-en-1-amine(1j)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 7.25-7.15 (m, 3H), 5.69 (ddt, *J* = 17.3, 10.1, 7.0 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 2.96 (dd, *J* = 12.6, 5.2 Hz, 1H), 2.85 (dd, *J* = 12.7, 8.7 Hz, 1H), 2.75-2.62 (m, 1H), 2.47-2.30 (m, 2H), 1.08-0.95 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 143.2, 136.7, 128.6, 128.1, 126.6, 116.2, 49.5, 47.6, 38.5.

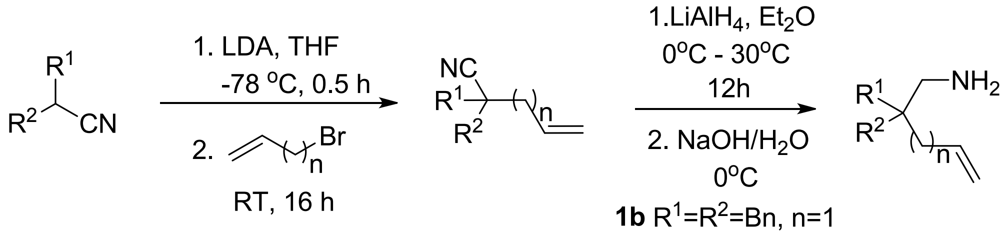


4-Methyl-2,2-diphenylpent-4-en-1-amine(1n)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 4H), 7.22-7.14 (m, 6H), 4.84-4.79 (m, 1H), 4.59 (s, 1H), 3.41 (s, 2H), 2.92 (s, 2H), 1.07 (s, 3H), 0.74 (s, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 147.0, 143.0, 128.5, 128.1, 126.1, 115.3, 51.4, 48.0, 44.1, 24.5.

Synthesis of 1b, 1h, 1i, 1k, 1p

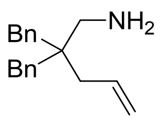


1b R^1=R^2=Bn, n=1
1h R^1=R^2=$(CH_2)_4$, n=1
1i R^1=R^2=$(CH_2)_5$, n=1
1k R^1=Ph, R^2=Me, n=1
1p R^1=R^2=Ph, n=2

Representative procedure[2]

100 mL Schlenk tube was evacuated and back-filled with N_2 with addition of ${}^{i}Pr_2NH$ (20 mmol) in 20 mL THF. The reaction was cooled to -78 °C followed by addition of *n*BuLi (1.6 M, 20 mmol) and stirred for 15 min. Then solution of cyclopentanecarbonitrile (20 mmol) in 10 mL THF was injected to LDA solution with stirring at -78 °C for 30 minutes. After dropwise addition of Allyl bromide (22 mmol), the resulting solution was warmed to room temperature and stirred for 16 h. Then the mixture was treated with saturated solution of NH_4Cl and extracted with EtOAc for 3 times. The combined organic layer was washed with saturated NaCl solution, dried by Na_2SO_4, evaporated and purified by silica gel flash chromatography.

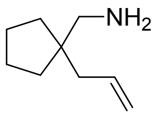
100mL Schlenk tube containing $LiAlH_4$ (60 mmol) was evacuated and back-filled with N_2 followed by addition of 30mL ether. Solution of purified nitrile (15 mmol) in 10 mL ether was added to suspension at 0 °C. Then the reaction was stirred at 30 °C for 12 h followed by addition of 5M NaOH at 0 °C to quench the reaction. After extraction with EtOAc for 3 times, the combined organic layer was washed with saturated NaCl solution, dried by Na_2SO_4, concentrated and purified by silica gel flash chromatography (petroleum ether/ EtOAc).



2,2-Dibenzylpent-4-en-1-amine(1b)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.22 (m, 10H), 6.10-6.02 (m, 1H), 5.24-5.10 (m, 2H), 2.72 (dd, J = 5.5, 2.0 Hz, 4H), 2.53 (d, J = 1.6 Hz, 2H), 2.11-2.06 (m, 2H), 1.10 (s, 2H).

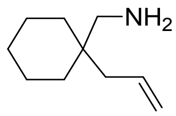
^{13}C NMR (101 MHz, CDCl$_3$) δ 138.7, 135.2, 130.8, 128.2, 126.2, 118.1, 47.0, 42.7, 41.7, 38.7.



(1-Allylcyclopentyl)methanamine (1h)[4]

^{1}H NMR (400 MHz, CDCl$_3$) δ5.84-5.71 (m, 1H), 5.10-4.97 (m, 2H), 2.47 (s, 2H), 2.07-2.01 (m, 2H), 1.53-1.59 (m, 4H), 1.33-1.39 (m, 4H), 1.09 (s, 2H).

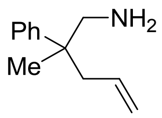
^{13}C NMR (101 MHz, CDCl$_3$) δ135.6, 116.0, 49.2, 46.0, 40.9, 34.1, 24.9.



(1-Allylcyclohexyl)methanamine (1i)[3]

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.87-5.74 (m, 1H), 5.11-4.98 (m, 2H), 2.58-2.48 (m, 2H), 2.12-2.05 (m, 2H), 1.48-1.25 (m, 11H), 0.97 (s, 2H).

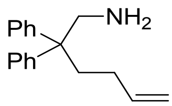
^{13}C NMR (101 MHz, CDCl$_3$) δ 135.1, 116.9, 48.9, 39.9, 37.1, 33.3, 26.5, 21.6.



2-Methyl-2-phenylpent-4-en-1-amine (1k)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36-7.28 (m, 4H), 7.21-7.17 (m, 1H), 5.61-5.48 (m, 1H), 5.03-4.91 (m, 2H), 2.95 (d, J = 13.1 Hz, 1H), 2.72 (d, J = 13.1 Hz, 1H), 2.50 (dd, J = 13.8, 6.4 Hz, 1H), 2.27 (dd, J = 13.8, 8.1 Hz, 1H), 1.29 (s, 3H), 1.01 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.3, 134.7, 128.3, 126.7, 125.9, 117.3, 53.4, 44.6, 43.0, 22.2.

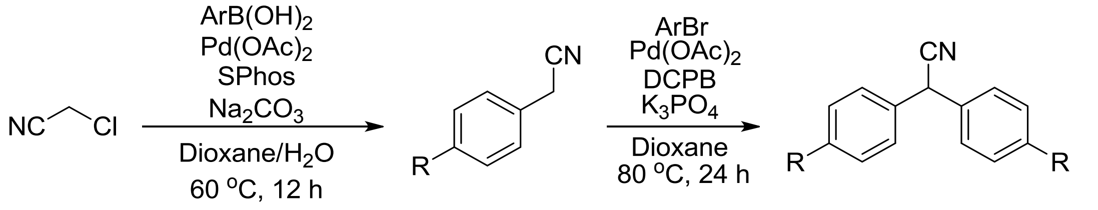


2,2-Diphenylhex-5-en-1-amine(1p)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 4H), 7.23-7.17 (m, 6H), 5.84-5.69 (m, 1H), 5.03-4.87 (m, 2H), 3.34 (s, 2H), 2.25-2.14 (m, 2H), 1.76 (dt, *J* = 10.5, 6.7 Hz, 2H), 0.80 (s, 2H).

^{13}C NMR (400 MHz, $CDCl_3$) 23.4, 34.2, 35.9, 49.1, 51.7, 114.6, 125.9, 128.0, 128.2, 138.6, 146.5

Synthesis of S-1d, S-1e, S-1f



S-1d Ar= Tol
S-1e Ar= *p*-F-Ph
S-1f Ar= 3-thiophene

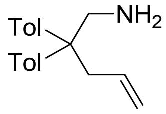
Representative procedure[5]

250mL sealed tube containing $Pd(OAc)_2$ (0.5 mmol) and SPhos (1.0 mmol) was evacuated and back-filled with N_2 for 3 times. After injection of dry dioxane under N_2 flows, the resulting solution was stirred at room temperature for 30 min. The tube was added chloroacetonitrile (20 mmol), phenylboronic acid (30 mmol), Na_2CO_3 (45 mmol) and H_2O (6 mL) in 50 mL dioxane via syringe and sealed after addition. Then the reaction was stirred at 60 °C for 12 h and cooled to room temperature. The mixture was filtrated with a pad of silica gel using EtOAc. After concentration under reduced pressure, the crude product was purified by silica gel flash chromatography (petroleum ether/ EtOAc).

100mL sealed tube containing $Pd(OAc)_2$ (0.25 mmol), 2,2'-bis(dicyclohexylphosphino)-1,1'-biphenyl (DCPB) (0.5 mmol) was evacuated and back-filled with N_2 for 3 times, followed by addition of 10 mL dry dioxane and stirring for 30 min at room temperature. Then arylacetonitrile (5 mmol), aryl brimide (7.5 mmol), K_3PO_4 (15 mmol) in dry dioxane (20 mL) were added under N_2 flow and the reaction was conducted at 80 °C for 24 h. After cooling to room temperature, the mixture was filtrated with a pad of silica gel with EtOAc. The filtrate was concentrated and purified by silica gel flash chromatography (petroleum ether/ EtOAc).

Synthesis of substrate 1d, 1e, 1f

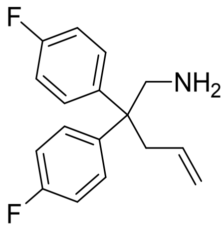
Procedure follows the synthesis of **1b**, **1h**, **1i**, **1k**, **1p**



2,2-Di-p-tolylpent-4-en-1-amine (1d)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12-7.04 (m, 8H), 5.46-5.39 (m, 1H), 5.06 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.01-4.95 (m, 1H), 3.29 (d, *J* = 1.3 Hz, 2H), 2.90 (d, *J* = 7.0 Hz, 2H), 2.33 (s, 6H), 0.85 (s, 2H).

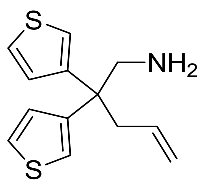
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 135.5, 135.0, 128.9, 128.1, 117.6, 50.8, 48.8, 41.3, 21.0.



2,2-Bis(4-fluorophenyl)pent-4-en-1-amine (1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (ddd, *J* = 8.9, 5.4, 2.7 Hz, 4H), 6.96 (t, *J* = 8.7 Hz, 4H), 5.35 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.02 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.97 (d, *J* = 10.1 Hz, 1H), 3.26 (s, 2H), 2.86 (d, *J* = 7.0 Hz, 2H), 0.77 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.24 (d, *J* = 245.4 Hz), 141.87 (d, *J* = 3.1 Hz), 134.1, 129.7 (d, *J* = 7.7 Hz), 118.2, 115.0 (d, *J* = 21.0 Hz), 50.6, 48.8, 41.4.

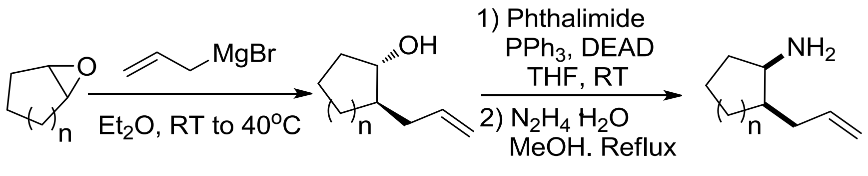


2,2-Di(thiophen-3-yl)pent-4-en-1-amine (1f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 2H), 7.03-6.99 (m, 2H), 6.81 (d, *J* = 5.0 Hz, 2H), 5.48 (ddt, *J* = 17.1, 10.0, 7.0 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 3.20 (s, 2H), 2.83 (d, *J* = 6.9 Hz, 2H), 1.06 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 134.5, 127.7, 125.4, 121.0, 117.9, 49.5, 48.5, 41.9.

Representative Synthesis procedure of substrates 1l, 1m[6]

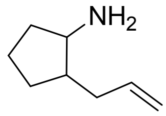


1l n=1
1m n=2

100mL schlenk tube was evacuated and backfilled with N_2 3 times. Allyl magnesium bromide (30 mmol) was injected and diluted with Et_2O. The reaction was added cyclopentene oxide (10 mmol) dropwise at room temperature over 15 min and refluxed for 3h.After cooling to room temperature, the solution was quenched with saturated NH_4Cl solution and extracted with EtOAc for 3 times. The combined organic layer was washed with brine, dried by Na_2SO_4, concentrated for next step without further purification.

Then 250 mL Schlenk tube with phthalimide (12.35 mmol) and PPh_3 (12.35 mmol) was evacuated and backfilled with N_2 for 3 times followed by addition of alcohol in THF (60 mL) and DEAD (40% solution in toluene, 13.3 mmol). The mixture was stirred at room temperature for 22 h. After removal of solvent in vaccum, the residue was triturated with PE/Et_2O (2:1) until complete precipitation of the solid. The solid was filtered off and washed with the same mixture of solvents. The combined organic layers were evaporated in vaccum and purified by silica gel flash chromatography (petroleum ether/ EtOAc).

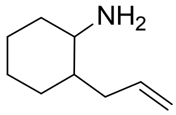
To a solution of phthalimide (8 mmol) in MeOH (10 mL) was added a solution of hydrazine monohydrate (9.6 mmol) in methanol (10 mL). The resulting solution was refluxed for 3 h. Then the reaction was evaporated followed by addition of CH_2Cl_2 and white solid appeared. The suspension was filtrated and the separated organic layer was mixed with water and acidified (pH < 2) with 1 M HCl. After separation, the aqueous phase basified with solid KOH (pH > 10) and extracted with EtOAc for 3 times, dried by Na_2SO_4, evaporated and product was obtained without further purification.



2-Allylcyclopentanamine (1l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H), 5.09-5.00 (m, 1H), 4.98-4.91 (m, 1H), 3.32-3.24 (m, 1H), 2.18 (dt, J = 14.3, 7.1 Hz, 1H), 2.04 (dt, J = 14.3, 7.2 Hz, 1H), 1.86-1.65 (m, 4H), 1.52 (ddt, J = 9.5, 7.4, 4.5 Hz, 1H), 1.44-1.31 (m, 2H), 1.11 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 115.0, 54.2, 44.4, 34.8, 34.1, 28.7, 21.9.

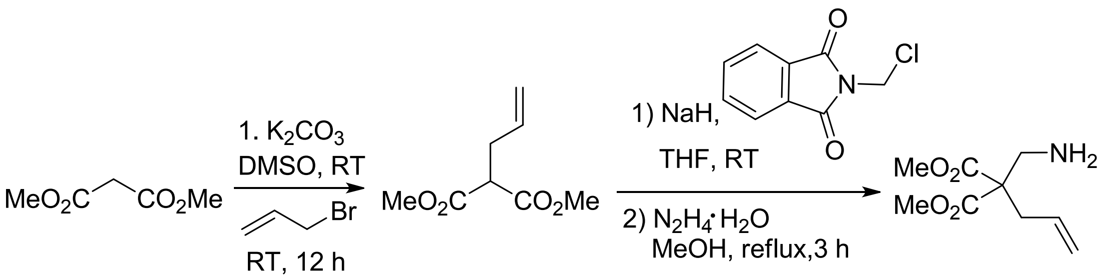


2-Allylcyclohexanamine (1m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80-5.67 (m, 1H), 5.02-4.91 (m, 2H), 2.99-2.91 (m, 1H), 2.08-2.00 (m, 1H), 1.98-1.89 (m, 1H), 1.61-1.46 (m, 5H), 1.39-1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 115.5, 49.5, 41.0, 36.3, 33.4, 26.4, 24.8, 21.0.

Synthesis procedure of substrate 1g[7]

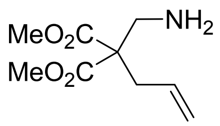


250 mL sealed tube was evacuated and back-filled with N_2 for 3 times. Dimethyl malonate (20 mmol) in 80mL DMSO was added to sealed tube under N_2 flows. Then K_2CO_3 was added and the reaction was stirred at room temperature for 10 minutes. After completion of basification, allyl bromide (24 mmol) in 20 mL DMSO was added dropwise. Stirred at room temperature for 14 h, the reaction was quenched with water, extracted with EtOAc for 3 times, dried by Na_2SO_4, evaporated and purified by silica gel flash chromatography (petroleum ether/ EtOAc).

100mL Schlenk tube containing NaH (9.9 mmol) was evacuated and back-filled with

N_2 for 3 times followed by addition of 30 mL THF. After addition of dimethyl 2-allylmalonate (9 mmol), the suspension was stirred for 30 min at 0 ^oC. Then the mixture was added N-chloromethylphthalimide (9 mmol) and stirred at room temperature for 16 h. After quenching by saturated NH_4Cl solution, the mixture was extracted with EtOAc for 3 times and combined organic layer was dried by Na_2SO_4 and evaporated under vacuum. Petroleum ether was added to afford unsolvable white solid, and crude product was obtained after filtration.

Crude dimethyl 2-allyl-2-((1,3-dioxoisoindolin-2-yl)methyl)malonate (8 mmol) was added to a solution of hydrazine monohydrate (9.6 mmol) in methanol (20 mL). And the resulting solution was refluxed for 3 h. Then the reaction was evaporated followed by addition of CH_2Cl_2 and eliminated white solid after filtration. The organic layer was acidified (pH < 2) with 1 M HCl. After separation, the aqueous phase was basified with solid KOH (pH > 10) and extracted with EtOAc for 3 times. The organic layers was combined, washed with saturated NaCl solution, dried by Na_2SO_4 and dimethyl 2-allyl-2-(aminomethyl)malonate was obtained after evaporation.



Dimethyl 2-allyl-2-(aminomethyl)malonate (1g)

^1H NMR (600 MHz, $CDCl_3$) δ 5.62-5.53 (m, 1H), 5.05-4.96 (m, 2H), 3.63 (s, 6H), 2.99 (s, 2H), 2.56 (d, J = 7.4 Hz, 2H), 1.14 (s, 2H).

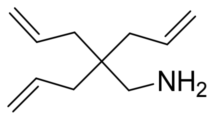
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 132.3, 119.0, 59.9, 52.3, 44.9, 36.5.

Synthesis procedure of 1c[8]

250 mL Schlenk tube was evacuated and back-filled with N_2, *i*PrNH$_2$ (60 mml, 8.4mL) and THF (45mL) was added. The resulting solution was injected *n*BuLi (1.6M in hexane, 60 mmol) via syringe at -78^oC and stirred for 30min. Then the LDA solution was stored at 0 ^oC. Another 250 mL Schlenk tube was evacuated and back-filled with N_2followed by addition of MeCN (20 mmol) and THF (10 mL). The resulting solution cooled to -78 ^oC followed by addition of a third of prepared LDA solution (30.3 mL) and stirred for 15 min. Allyl bromide (20mmol) was added and the mixture was warmed

to room temperature with stirring for 30 min. The reaction was cooled to -78 °C again with addition of another equivalent LDA solution and stirred for 15 min. Then the reaction was added allyl bromide (20mmol) again and warmed to room temperature with stirring. The reaction was cooled to -78 °C once more followed by addition remaining LDA solution with 15 min stirring. The mixture was added allyl bromide (20 mmol) and warmed to room with stirring for 12 h and quenched with water. After extraction with EtOAc for 3 times, combined organic layer was washed with brine and dried by Na_2SO_4 followed by removal of solvent under vacuum and purified by silica gel flash chromatography (petroleum ether/ EtOAc).

100mL Schlenk tube containing $LiAlH_4$ (20 mmol) was evacuated and back-filled with N_2 followed by addition of 15mL ether. Solution of purified nitrile (5 mmol) in 5 mL ether was added to suspension at 0 °C. Then the reaction was stirred at 30 °C for 12 h and slowly quenched by 5M NaOH at 0°C. After extraction with EtOAc for 3 times, combined organic layer was washed with saturated NaCl solution and dried by Na_2SO_4, evaporated and purified by silica gel flash chromatography (petroleum ether/ EtOAc).



2,2-Diallylpent-4-en-1-amine(1c)[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.76 (m, 3H), 5.09-5.02 (m, 6H), 2.49 (d, *J* = 1.4 Hz, 2H), 2.04-1.98 (m, 6H), 1.06 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 117.7, 47.5, 40.7, 39.2.

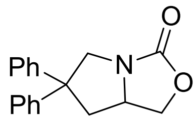
General procedure for oxyamination in MeCN

25 mL Schlenk tube was evacuated and backfilled with CO_2 for 3 times. Amine (0.5 mmol) in MeCN (5 mL) was added under flow of CO_2, followed by addition of DBU (1.0 mmol). After stirring for 10 min, I_2 (0.5 mmol) was added and the reaction was conducted at room temperature for 16 h. Quenched with water, the reaction was extracted with EtOAc for 3 times and washed with saturated $Na_2S_2O_3$ solution and brine. The combined organic layer was dried by Na_2SO_4, evaporated and isolated by silica gel flash chromatography (petroleum ether/ EtOAc).

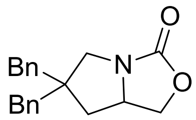
General procedure for oxyamination in EtOH or EtOAc

25 mL Schlenk tube was evacuated and backfilled with CO_2 for 3 times. Amine (0.5 mmol) in EtOH or EtOAc (5 mL) was added under flow of CO_2, followed by addition of DBU (1.0 mmol). After stirring for 10 min, I_2 (0.5 mmol) was added and the reaction was conducted at room temperature for 16 h. The reaction was monitored by NMR in $CDCl_3$ with CH_2Br_2 as internal standard.

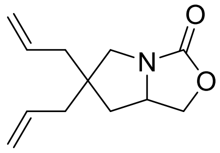
Spectrum data



6,6-Diphenyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (2a)[9]: White solid, yield: 84%, 117 mg, R_f= 0.30 (PE : EA=3:1), mp: 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, *J* = 9.2, 5.0, 1.8 Hz, 4H), 7.24-7.17 (m, 6H), 4.48 (t, *J* = 8.6 Hz, 1H), 4.21 (d, *J* = 11.4 Hz, 1H), 4.16 (dd, *J* = 8.9, 4.8 Hz, 1H), 4.05 (ddt, *J* = 10.0, 8.6, 4.9 Hz, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 2.54 (dd, *J* = 11.8, 5.1 Hz, 1H), 2.37 (dd, *J* = 11.7, 10.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 145.5, 128.7, 128.6, 127.0, 126.9, 126.8, 126.7, 68.0, 58.1, 57.8, 57.2, 43.7. IR (neat) ν_{max} cm^{-1} 1754; HRMS (ESI) calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1332, found: 280.1334

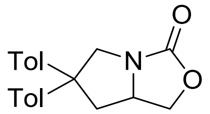


6,6-Dibenzyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one(2b): Colorless oil, yield: 65%, 100 mg, R_f= 0.28 (PE:EA=3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.25 (m, 6H), 7.20 (d, 7.5 Hz, 2H), 7.14 (d, 7.5 Hz, 2H), 4.31 (t, *J* = 8.4 Hz, 1H), 3.98 (dd, *J* = 8.8, 4.3 Hz, 1H), 3.69 (d, *J* = 11.7 Hz, 1H), 3.51-3.45 (m, 1H), 3.21 (d, *J* = 11.7 Hz, 1H), 2.86-2.73 (m, 4H), 2.03 (dd, *J* = 12.7, 6.2 Hz, 1H), 1.54 (dd, *J* = 12.7, 9.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 137.3, 130.7, 130.6, 128.6, 128.5, 126.9, 68.5, 58.3, 54.0, 50.0, 46.1, 44.2, 41.1. IR (neat) ν_{max} cm^{-1} 1747; HRMS (ESI) calcd for $C_{20}H_{21}NO_2$ $[M+H]^+$ 308.1645, found: 308.1643.

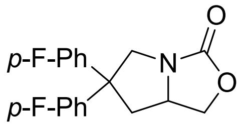


6,6-Diallyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (2c): White solid, yield: 83%, 86 mg, R_f= 0.29 (PE:EA=3:1), mp: 29-31 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.78-5.62 (m, 2H), 5.13-5.01 (m, 4H), 4.42 (t, *J* = 8.3 Hz, 1H), 4.08-3.99 (m, 2H), 3.45 (d, *J* = 11.8 Hz, 1H), 2.91 (d, *J* = 11.8 Hz, 1H), 2.17-2.10 (m, , 4H), 1.88 (dd, *J* = 12.8, 6.5 Hz, 1H), 1.39 (dd, *J* = 12.8, 9.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 133.6, 133.5, 119.0, 118.9, 68.1, 58.2, 55.2, 47.8, 43.0, 42.1, 41.5. IR (neat) ν_{max} cm^{-1} 1746;

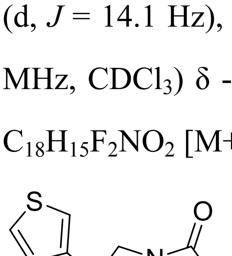
HRMS (ESI) calcd for $C_{12}H_{17}NO_2$ $[M+H]^+$ 208.1332 found: 208.1331.



6,6-Di-p-tolyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (2d): White solid, yield: 88%, 135 mg, R_f= 0.28 (PE:EA=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.07 (m, *J* = 3.7, 3.1 Hz, 8H), 4.45 (t, *J* = 8.6 Hz, 1H), 4.19-4.12 (m, 2H), 4.09-4.00 (m, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 2.53 (dd, *J* = 11.8, 5.2 Hz, 1H), 2.40-2.33 (m, 1H), 2.31 (d, *J* = 1.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 142.7, 136.3, 136.2, 129.2, 129.2, 126.7, 126.4, 68.0, 58.0, 57.3, 57.1, 43.6, 20.9, 20.8. IR (neat) ν_{max} cm^{-1} 1755; HRMS (ESI) calcd for $C_{20}H_{21}NO_2$ $[M+H]^+$ 308.1645, found: 308.1644.

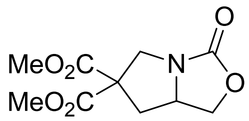


6,6-Bis(4-fluorophenyl)tetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (2e): Light yellow oil, yield: 65 %, 102 mg, R_f= 0.32 (PE:EA=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dt, *J* = 8.3, 5.3 Hz, 4H), 6.99 (td, *J* = 8.5, 5.7 Hz, 4H), 4.52 (t, *J* = 8.7 Hz, 1H), 4.19 (dd, *J* = 9.0, 4.9 Hz, 1H), 4.14 (d, *J* = 11.5 Hz, 1H), 4.05 (tt, *J* = 10.0, 5.0 Hz, 1H), 3.86 (d, *J* = 11.5 Hz, 1H), 2.49 (dd, *J* = 11.8, 5.2 Hz, 1H), 2.40-2.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ, 161.8, 161.7 (d, *J* = 248.5 Hz) , 161.6 (d, *J* = 248.5 Hz), 141.3 (d, *J* = 2.9 Hz), 141.1 (d, *J* = 3.1 Hz), 128.6 (d, *J* = 7.9 Hz), 128.3 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 14.1 Hz), 115.5 (d, *J* = 14.2 Hz), 68.1, 58.1, 57.5, 57.0, 43.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.18 , -115.63. IR (neat) ν_{max} cm^{-1} 1754; HRMS (ESI) calcd for $C_{18}H_{15}F_2NO_2$ $[M+Na]^+$ 338.0963, found: 338.0967.

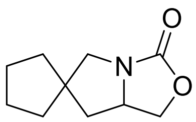


6,6-Di(thiophen-3-yl)tetrahydropyrrolo[1,2-c]oxazol-3(1H)-one(2f): White solid, yield: 68 %, 99 mg, R_f= 0.19 (PE:EA=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), δ 7.04 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.01 (dd, *J* = 2.9, 1.4 Hz, 1H), 6.91-6.83 (m, 2H), 4.49 (t, *J* = 8.1 Hz, 1H), 4.19-4.02 (m, 3H), 3.91 (d, *J* = 11.6 Hz, 1H), 2.62 (dd, *J*

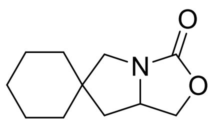
= 12.3, 5.6 Hz, 1H), 2.31 (dd, *J* = 12.3, 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.56 , 146.34 , 145.84 , 127.11 , 126.82 , 126.75 , 126.60 , 120.51 , 120.41 , 68.06 , 58.48 , 58.22 , 52.71 , 44.83 . IR (neat) ν_{max} cm^{-1} 1748; HRMS (ESI) calcd for $C_{14}H_{13}NO_2S_2$ $[M+H]^+$ 292.0460, found: 292.0463.



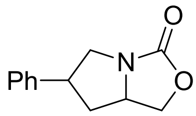
Dimethyl 3-oxotetrahydropyrrolo[1,2-c]oxazole-6,6(1H)-dicarboxylate (2g): Light yellow oil, yield: 47 %, 57 mg, R_f= 0.33 (PE:EA=1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53-4.48 (m, 1H), 4.26-4.20 (m, 2H), 4.14-4.06 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.66 (d, *J* = 12.8 Hz, 1H), 2.59 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.21 (dd, *J* = 13.4, 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 170.3, 161.0, 67.6, 60.8, 58.5, 53.6, 53.5, 52.5, 38.9. IR (neat) ν_{max} cm^{-1} 1728; HRMS (ESI) calcd for $C_{10}H_{13}NO_2$ $[M+H]^+$ 244.0816, found: 244.0817.



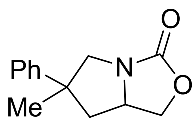
Dihydro-1'H-spiro[cyclopentane-1,6'-pyrrolo[1,2-c]oxazol]-3'(5'H)-one (2h): Colorless oil, yield: 81%, 73 mg, R_f= 0.23 (PE:EA=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51-4.44 (m, 1H), 4.11-4.01 (m, 2H), 3.45 (dd, *J* = 11.2, 3.5 Hz, 1H), 2.99 (dd, *J* = 11.2, 3.7 Hz, 1H), 1.94-1.87 (m, 1H), 1.67-1.47 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 68.4, 58.9, 57.9, 52.5, 43.9, 38.4, 38.3, 24.3, 24.2. IR (neat) ν_{max} cm^{-1} 1744; HRMS (ESI) calcd for $C_{10}H_{15}NO_2$ $[M+H]^+$ 182.1176 found: 182.1178.



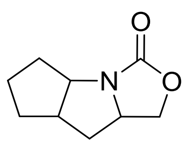
Dihydro-1'H-spiro[cyclohexane-1,6'-pyrrolo[1,2-c]oxazol]-3'(5'H)-one (2i): Light yellow oil, yield: 70%, 68 mg, R_f= 0.30 (PE:EA=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (t, *J* = 8.2 Hz, 1H), 4.10-4.06 (m, 1H), 4.05-4.00 (m, 1H), 3.44 (d, *J* = 11.5 Hz, 1H), 2.94 (d, *J* = 11.5 Hz, 1H), 1.92 (dd, *J* = 12.5, 6.3 Hz, 1H), 1.52-1.32 (m, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 68.4, 58.1, 57.2, 45.6, 44.0, 38.1, 36.4, 25.6, 24.0, 23.3. IR (neat) ν_{max} cm^{-1} 1755; HRMS (ESI) calcd for $C_{11}H_{17}NO_2$ $[M+H]^+$ 196.1332, found: 196.1330.



6-Phenyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (2j): Yellow oil, yield: 46%, 47 mg, R_f= 0.45 (PE:EA=1:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (dd, *J* = 10.3, 7.3 Hz, 3H), 4.54 (t, *J* = 8.5 Hz, 1H), 4.27 (dd, *J* = 9.0, 3.2 Hz, 1H), 4.13-4.07 (m, 1H), 3.72-3.62 (m, 2H), 3.61-3.57 (m, 1H), 2.39 (dt, *J* = 10.8, 5.2 Hz, 1H), 1.70 (q, *J* = 11.2 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 128.9, 127.2, 127.1, 67.4, 60.3, 52.9, 46.6, 40.1. IR (neat) ν_{max} cm^{-1} 1750; HRMS (ESI) calcd for $C_{12}H_{13}NO_2$ $[M+H]^+$ 204.1019, found: 204.1020.



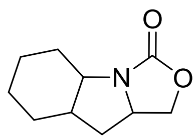
6-Methyl-6-phenyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one 4-63 (2k): Light yellow oil, yield: 69%, mg, R_f= 0.35 (PE:EA=3:1), major:minor=5:4. ^{1}H NMR (600 MHz, $CDCl_3$) major product: δ 7.36-7.30 (m, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.25-7.20 (t, *J* = 8.2 Hz, 2H), 4.58-4.54 (m, 1H), 4.29 (ddd, *J* = 12.7, 10.5, 4.7 Hz, 1H), 4.21-4.12 (m, 1H), 3.93 (d, *J* = 11.0 Hz, 1H), 3.40 (d, *J* = 11.0 Hz, 1H), 2.23 (dd, *J* = 11.9, 5.3 Hz, 1H), 1.95 (t, *J* = 11.3 Hz, 1H), 1.46 (s, 3H); minor product: δ 7.36-7.30 (m, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.25-7.20 (t, *J* = 8.2 Hz, 2H), 4.21-4.12 (m, 2H) , 3.78 (d, *J* = 11.6 Hz, 1H), ,3.55 (d, *J* = 11.6 Hz, 1H) , 2.45 (dd, *J* = 12.9, 7.2 Hz, 1H) , 1.86 (dd, *J* = 12.8, 7.0 Hz, 1H) , 1.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) major product: δ 161.6, 128.7, 126.6, 125.6, 68.11, 59.3, 58.7, 49.4, 44.8, 29.8. minor product: δ 162.06 , 146.70 , 128.8, 126.7, 125.8, 69.5, 58.6, 58.2, 49.1, 45.7, 29.5. IR (neat) ν_{max} cm^{-1} 1745



Hexahydro-1H-cyclopenta[4,5]pyrrolo[1,2-c]oxazol-3(4aH)-one (2l):

Compound 2l-1, colorless oil, yield: 50 %, 42 mg, R_f=0.62(PE:EA=1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49-4.42 (m, 1H), 4.33 (td, *J* = 7.4, 3.7 Hz, 1H), 4.09 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.958-3.91 (m, 1H), 2.83-2.75 (m, 1H), 1.98-1.93 (m, 1H), 1.90-1.81 (m, 2H), 1.68-1.57 (m, 3H), 1.57-1.46 (m, 1H), 1.38-1.30 (m, , 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 67.5, 63.8, 58.6, 44.1, 38.5, 34.4, 32.7, 26.4. IR (neat) ν_{max} cm^{-1} 1744; HRMS (ESI) calcd for $C_9H_{13}NO_2$ [M+H]$^+$ 168.1019, found: 168.1018.

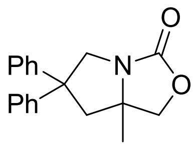
Compound 2l-2, colorless oil, yield: 25 %, 21 mg, R_f=0.52(PE:EA=1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43-4.37 (m, 1H), 4.18-4.09 (m, 1H), 3.98 (t, *J* = 7.9 Hz, 1H), 3.91 (t, *J* = 7.2 Hz, 1H), 3.02-2.94 (m, 1H), 2.53 (dt, *J* = 7.1, 3.0 Hz, 1H), 2.21-2.15 (m, 1H), 1.68-1.53 (m, 5H), 1.23-1.14 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 68.3, 61.6, 60.6, 47.7, 38.0, 31.7, 28.3, 24.4. IR (neat) ν_{max} cm^{-1} 1744; HRMS (ESI) calcd for $C_9H_{13}NO_2$ [M+H]$^+$ 168.1019, found: 168.1016.



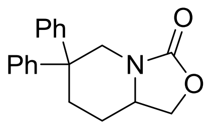
Octahydrooxazolo[3,4-a]indol-3(1H)-one (2m):

Compound 2m-1, Coloreless oil, yield: 38 %, 34 mg, R_f=0.52(PE:EA=1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (t, *J* = 8.6 Hz, 1H), 4.29-4.24 (m, 1H), 4.04 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.85 (dt, *J* = 8.7, 5.9 Hz, 1H), 2.34 (dt, *J* = 13.9, 7.0 Hz, 1H), 2.04 -1.99(m, 1H), 1.81-1.75 (m, 1H), 1.71-1.68 (m, 2H), 1.63-1.57 (m, 2H), 1.54-1.50 (m, 1H), 1.43 (m, 2H), 1.35-1.31 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 70.3, 59.1, 56.7, 38.5, 35.5, 27.6, 26.3, 22.7, 21.1. IR (neat) ν_{max} cm^{-1} 1744; HRMS (ESI) calcd for $C_{10}H_{15}NO_2$ [M+H]$^+$ 182.1176, found: 182.1177.

Compound 2m-2, Coloreless oil, yield: 26 %, 24 mg, R_f=0.45(PE:EA=1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.49 (t, *J* = 8.3 Hz, 1H), 4.26-4.19 (m, 1H), 4.00 (t, *J* = 9.0 Hz, 1H), 3.57 (dt, *J* = 9.6, 6.3 Hz, 1H), 2.53 (dt, *J* = 11.3, 5.8 Hz, 1H), 2.48-2.42 (m, 1H), 1.86 (dt, *J* = 11.8, 5.9 Hz, 1H), 1.72-1.65 (m, 4H), 1.50-1.46 (m, 1H), 1.36-1.19 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 71.1, 59.7, 55.1, 41.5, 33.4, 27.4, 26.7, 23.1, 21.6. IR (neat) ν_{max} cm^{-1} 1742; HRMS (ESI) calcd for $C_{10}H_{15}NO_2$ [M+H]$^+$ 182.1176, found: 182.1178.



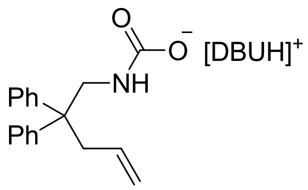
7a-Methyl-6,6-diphenyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (2n): White solid, yield: 40%, 59 mg, R_f=0.39 (PE:EA=3:1), mp: 176-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 6H), 7.21-7.13 (m, 4H), 4.80 (dd, *J* = 12.7, 1.1 Hz, 1H), 3.98 (d, *J* = 8.5 Hz, 1H), 3.71 (d, *J* = 8.4 Hz, 1H), 3.57 (d, *J* = 12.7 Hz, 1H), 2.88 (dd, *J* = 13.7, 1.1 Hz, 1H), 2.66 (d, *J* = 13.7 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 146.1, 144.3, 129.0, 128.8, 126.9, 126.8, 126.7, 76.0, 64.8, 58.6, 55.1, 49.9, 27.9. IR (neat) ν_{max} cm^{-1} 1746; HRMS (ESI) calcd for $C_{19}H_{19}NO_2$ [M+H]$^+$ 294.1489, found: 294.1486.



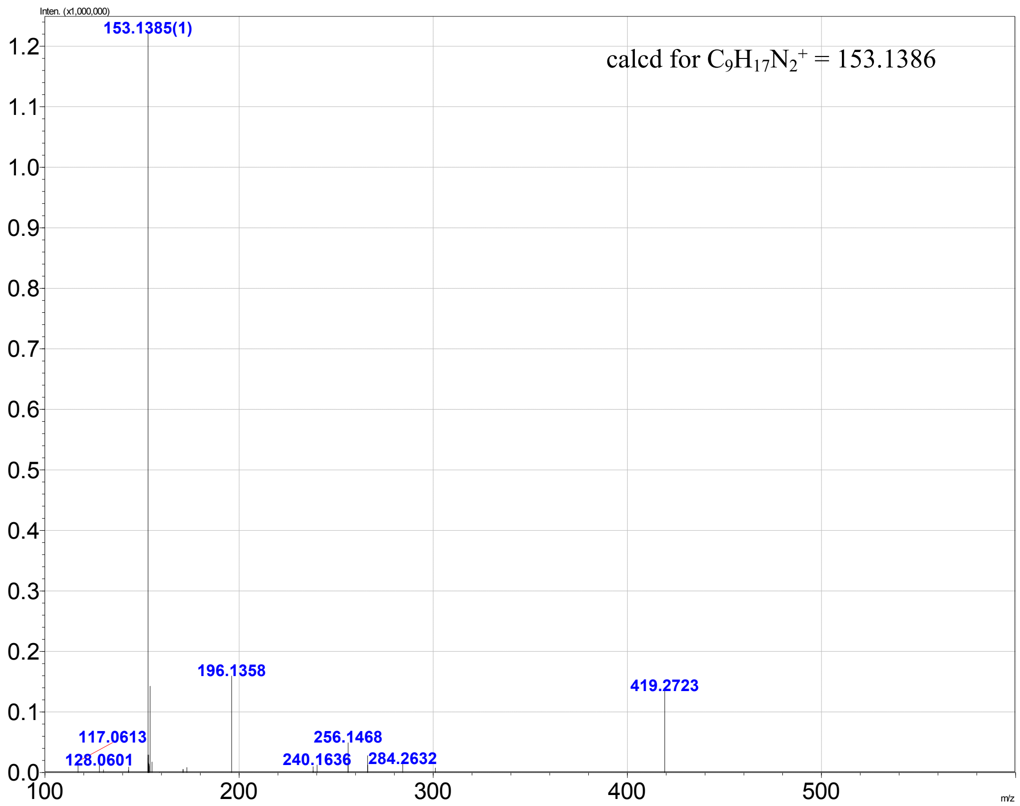
6,6-Diphenyltetrahydro-1H-oxazolo[3,4-a]pyridin-3(5H)-one: White solid, yield: 24%, 35 mg, R_f=0.32 (PE:EA=3:1), mp:115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 4.3 Hz, 4H), 7.28-7.24 (m, 2H), 7.21-7.16 (m, 4H), 4.72 (dd, *J* = 13.9, 2.5 Hz, 1H), 4.45 (t, *J* = 7.7 Hz, 1H), 3.85-3.70 (m, 2H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.73 (dq, *J* = 13.6, 2.9 Hz, 1H), 2.33 (td, *J* = 13.4, 3.0 Hz, 1H), 1.85 (dq, *J* = 13.0, 3.4 Hz, 1H), 1.25-1.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 146.7, 143.5, 128.9, 128.7, 127.7, 126.8, 126.5, 126.4, 68.6, 54.2, 49.3, 45.9, 33.9, 26.8. IR (neat) ν_{max} cm^{-1} 1744; HRMS (ESI) calcd for $C_{19}H_{19}NO_2$ [M+H]$^+$ 294.1489, found: 294.1487.

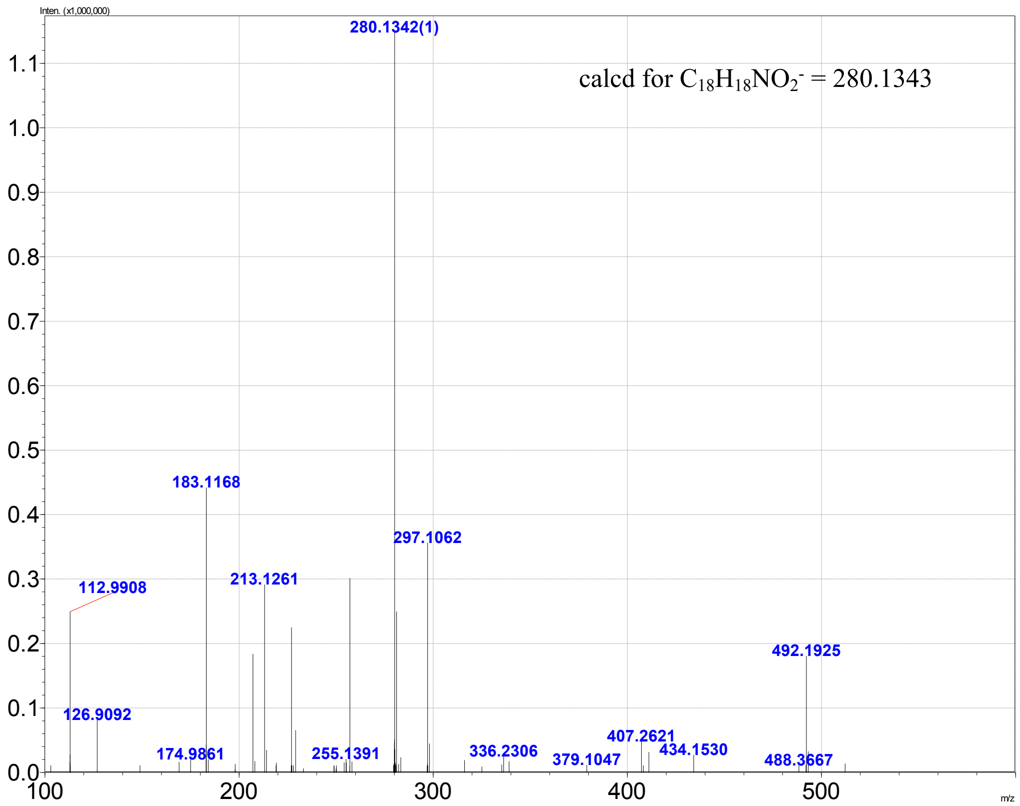
Mechanistic studies

25 mL Schlenk tube with 2,2-diphenylpent-4-en-1-amine (0.1 mmol) was evacuated and backfilled with CO_2. CD_3CN (1mL) was added under flow of CO_2 followed by addition of DBU (1 equiv.). The resulting solution was stirred for 1 h.



^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 12.30 (s, 1H), 7.34-7.28 (m, 4H), 7.26-7.20 (m, 6H), 5.62-5.52 (m, 1H), 5.07-5.01 (m, 1H), 4.92 (dd, J = 10.2, 2.3 Hz, 1H), 4.49 (s, 1H), 3.85 (d, J = 5.9 Hz, 2H), 3.50-3.43 (m, 2H), 3.40 (t, J = 5.9 Hz, 2H), 3.22 (t, J = 5.7 Hz, 2H), 2.98 (d, J = 7.1 Hz, 2H), 2.77-2.69 (m, 2H), 1.95-1.86 (m, 2H), 1.76-1.68 (m, 2H), 1.68-1.57 (m, 4H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ166.5, 162.7, 147.8, 136.1, 129.0, 128.8, 126.8, 118.1, 54.5, 51.2, 49.1, 48.9, 42.1, 38.9, 32.4, 29.7, 27.4, 24.9, 20.4.





Radical scavenger experiment

25 mL Schlenk tube with 2,2-diphenylpent-4-en-1-amine (0.5 mmol) was evacuated and backfilled with CO_2. CH_3CN 5mL was added under flow of CO_2, followed by addition of DBU (2 equiv.). The solution was stirred for 10 min with addition of TEMPO and I_2 (1 equiv.).

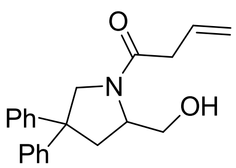
Extension of prolinol carbamates synthesis

Synthesis of 2a in gram scale

The 250 mL Schlenk tube with **1a** (5 mmol) was evacuated and backfilled with CO_2 for 3 times followed by addition of MeCN (50 mL). The DBU (5mmol) was injected via syringe and the resulting solution was stirred for 30 min. Then I_2 was added with stirring for 24 h at room temperature. The reaction was quenched with water, extracted with EtOAc and washed with saturated $Na_2S_2O_3$ and brine. Combined organic layer was dried by Na_2SO_4, evaporated and isolated by silica gel flash chromatography (petroleum ether/ EtOAc).

Synthesis of 3

The 25 mL Schlenk tube with **2a** (0.4 mmol) was evacuated and back-filled with N_2 followed by addition THF 4 mL. The allyl magnesium bromide (1 M in ether, 0.4 mmol) was injected via syringe at -78 °C. With stirring for 4 h, the reaction was warmed to room temperature and quenched with saturated NH_4Cl solution and was extracted with EtOAc (3×5 mL), dried by Na_2SO_4, evaporated and purified by silica gel flash chromatography (petroleum ether/ EtOAc).

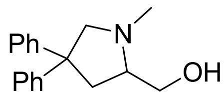


1-(2-(hydroxymethyl)-4,4-diphenylpyrrolidin-1-yl)but-3-en-1-one (3)

^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 4H), 7.19 (q, *J* = 7.3, 5.9 Hz, 6H), 5.93 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.37-5.32 (m, 1H), 5.23-5.12 (m, 2H), 4.46-4.37 (m, 1H), 4.15-4.05 (m, 1H), 3.88 (d, *J* = 10.9 Hz, 1H), 3.76-3.69 (m, 1H), 3.62 (dd, *J* = 10.7, 7.4 Hz, 1H), 3.20 (d, *J* = 6.6 Hz, 2H), 2.86-2.78 (m, 1H), 2.21 (dd, *J* = 12.7, 10.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 145.0, 144.2, 130.6, 128.9, 128.8, 127.0, 127.0, 126.6, 126.4, 118.8, 66.9, 61.7, 58.2, 52.5, 40.6, 40.2.

Synthesis of 4

25 mL Schlenk tube containing $LiAlH_4$ (1.6 mmol) was evacuated and back-filled with N_2 followed by addition of THF 4 mL. **2a** (0.4 mmol) in THF (4 mL) was added to the suspension at 0 °C. Then the reaction was warmed to 30°C with stirring for 12 h. The mixture was cooled to 0 °C and quenched by 5M NaOH slowly. After extraction with EtOAc for 3 times, combined organic layer was washed with saturated NaCl solution and dried by Na_2SO_4, evaporated and generate pure product without further purification.



(1-methyl-4,4-diphenylpyrrolidin-2-yl)methanol (4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.23 (q, *J* = 7.7, 7.2 Hz, 6H), 7.17-7.07 (m, 2H), 3.90 (d, *J* = 9.9 Hz, 1H), 3.57 (dd, *J* = 11.1, 3.7 Hz, 1H), 3.37 (dd, *J* = 11.0, 2.3 Hz, 1H), 2.99 (d, *J* = 9.9 Hz, 1H), 2.79 (dd, *J* = 12.4, 8.6 Hz, 1H), 2.68 (ddt, *J* = 8.7, 6.4, 3.0 Hz, 1H), 2.59 (dd, *J* = 12.4, 6.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 148.3, 128.5, 128.4, 127.2, 127.1, 126.1, 125.9, 68.3, 66.8, 61.6, 53.1, 41.8, 41.0.

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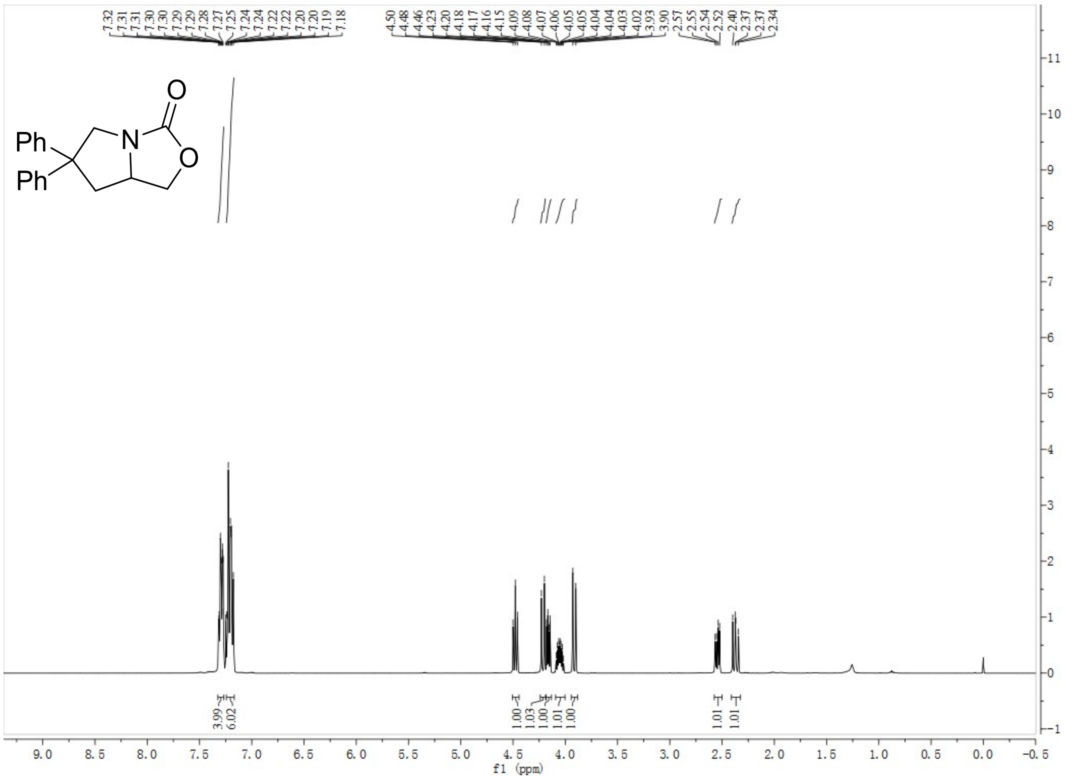
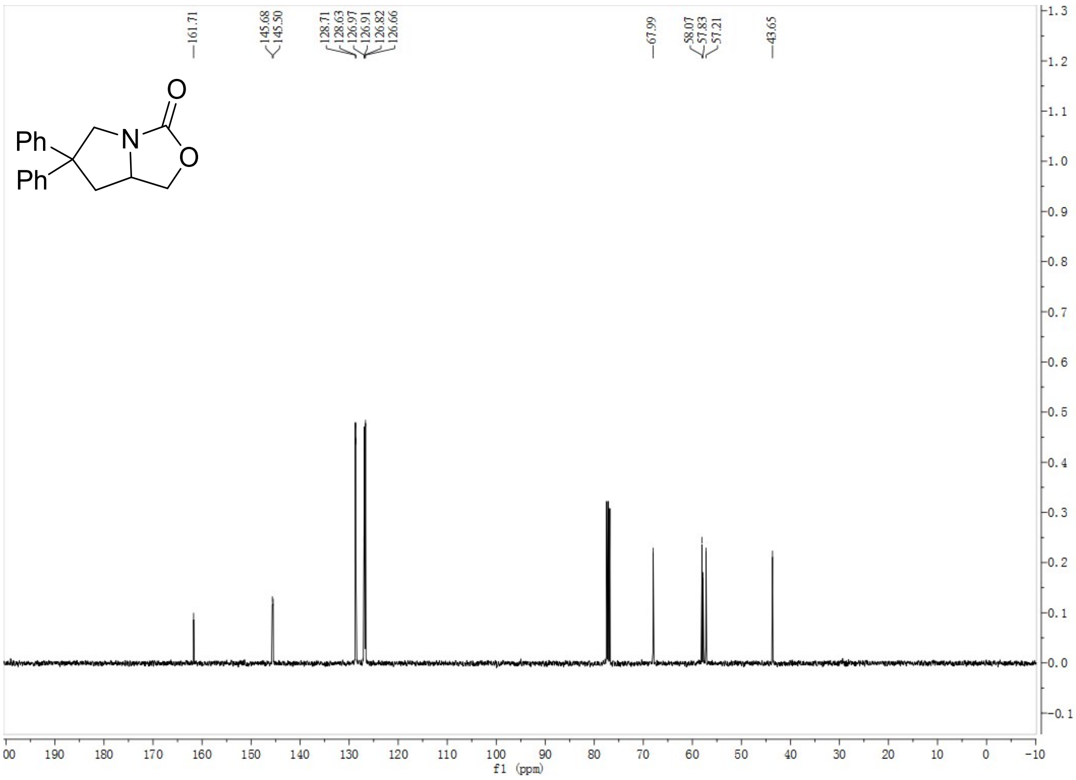
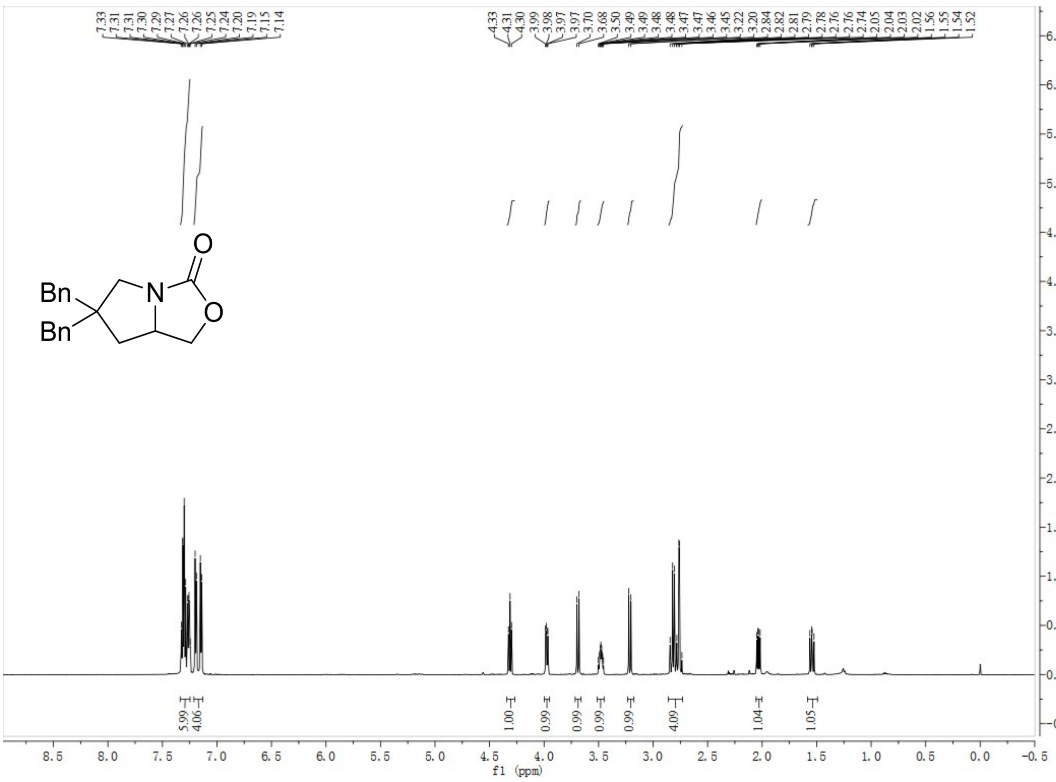
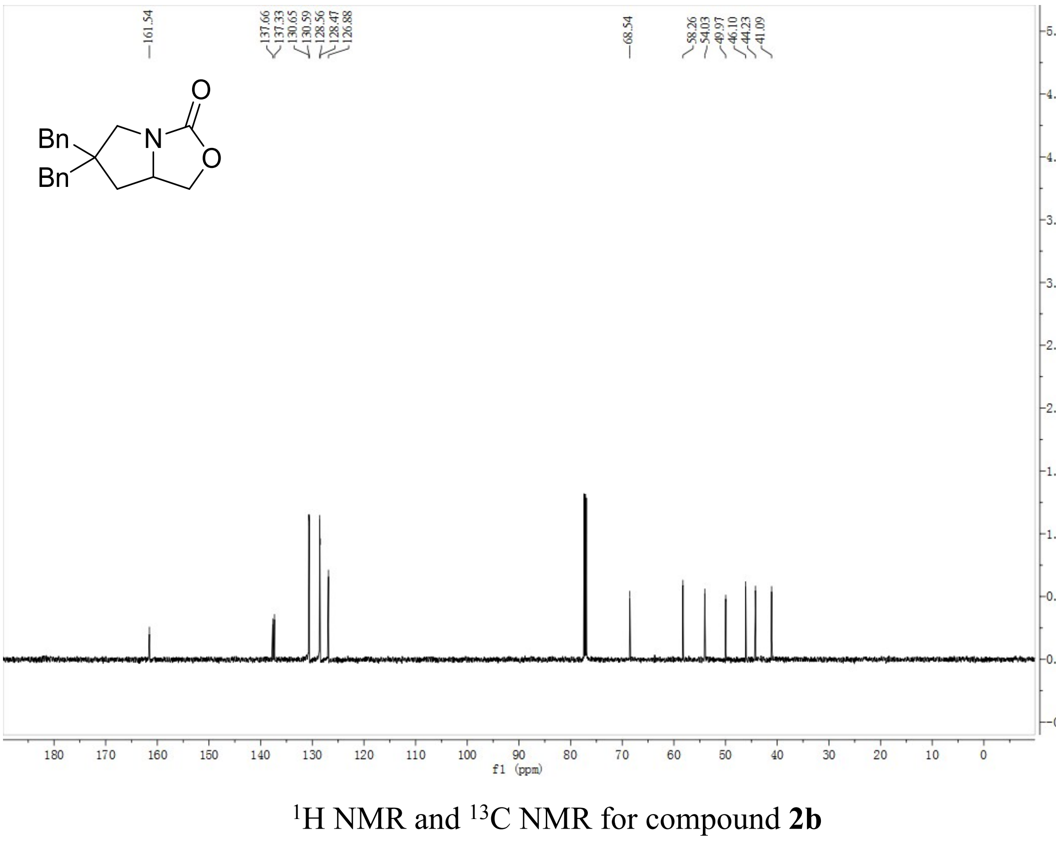
[1] H NMR, [13]C NMR and [19]F NMR Spectra



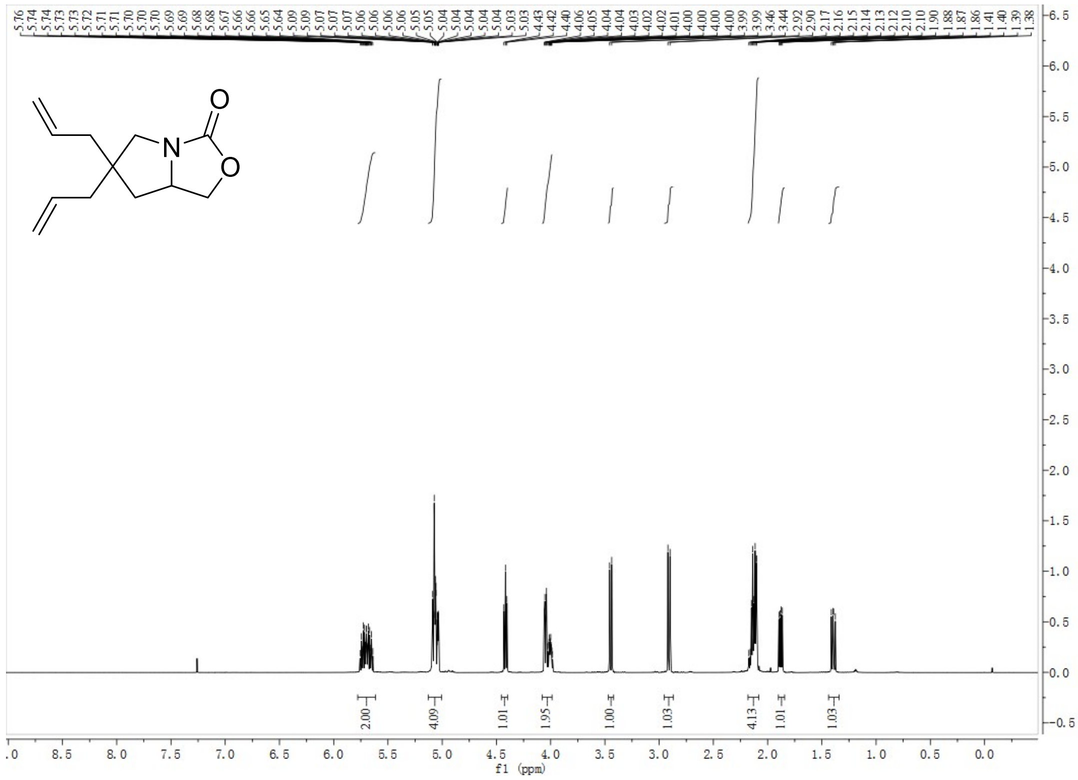


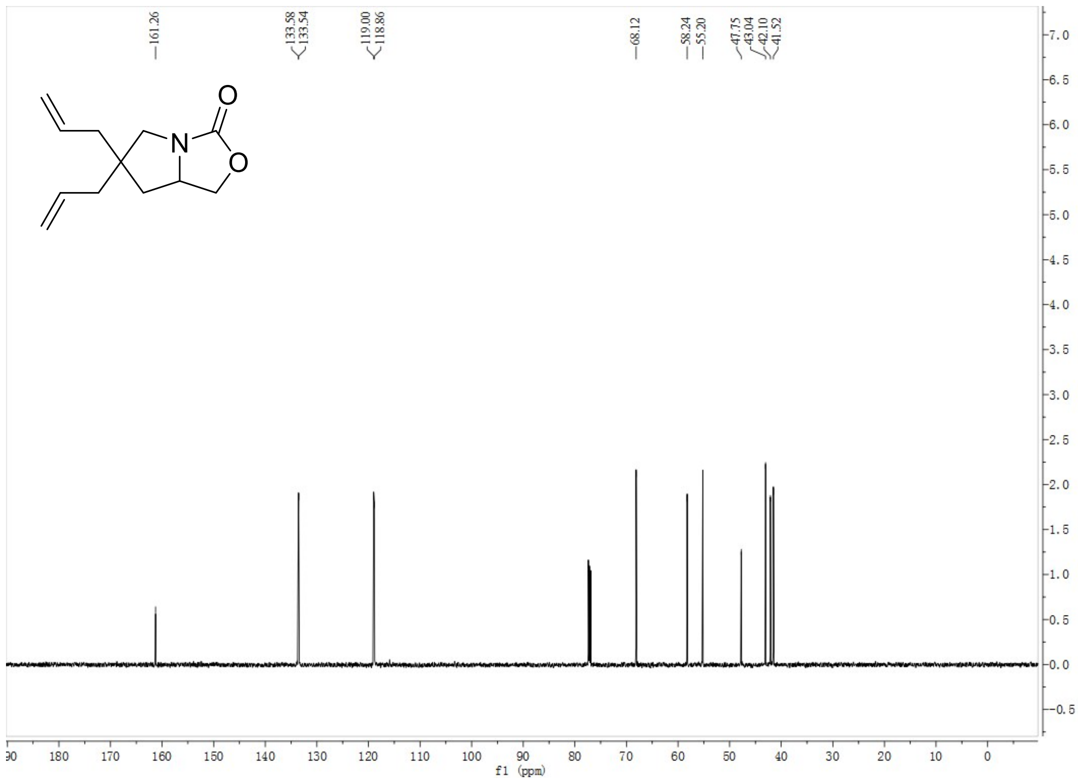
^{1}H NMR and ^{13}C NMR for compound **2a**



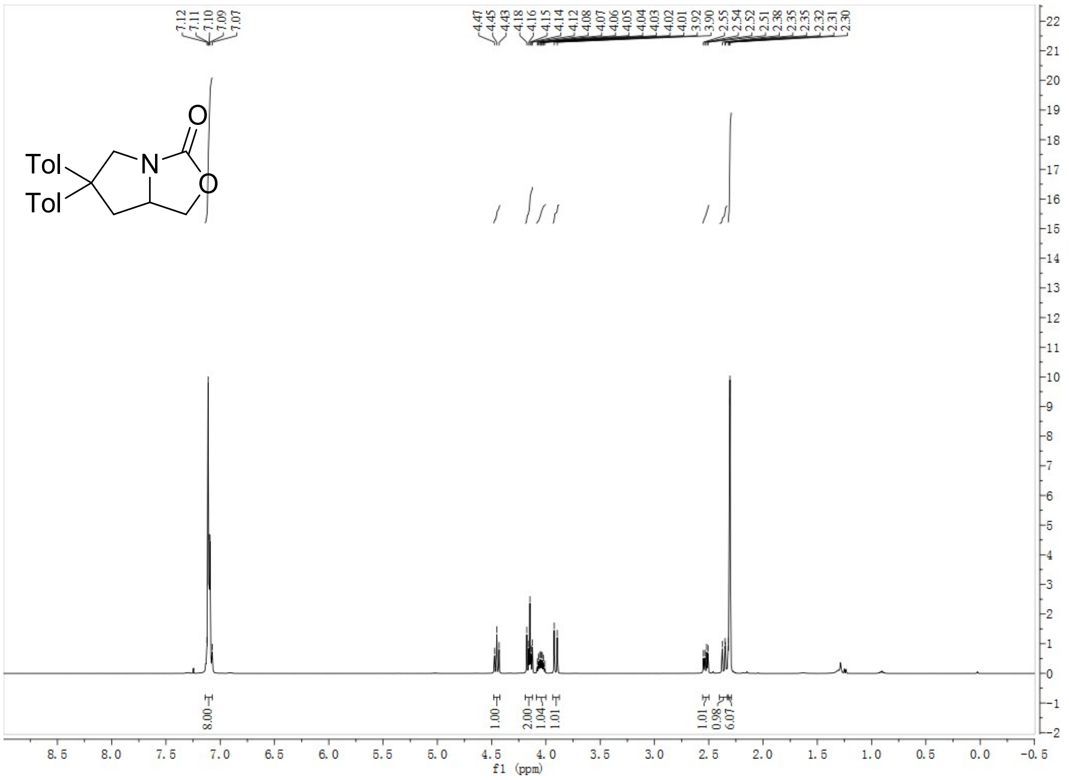


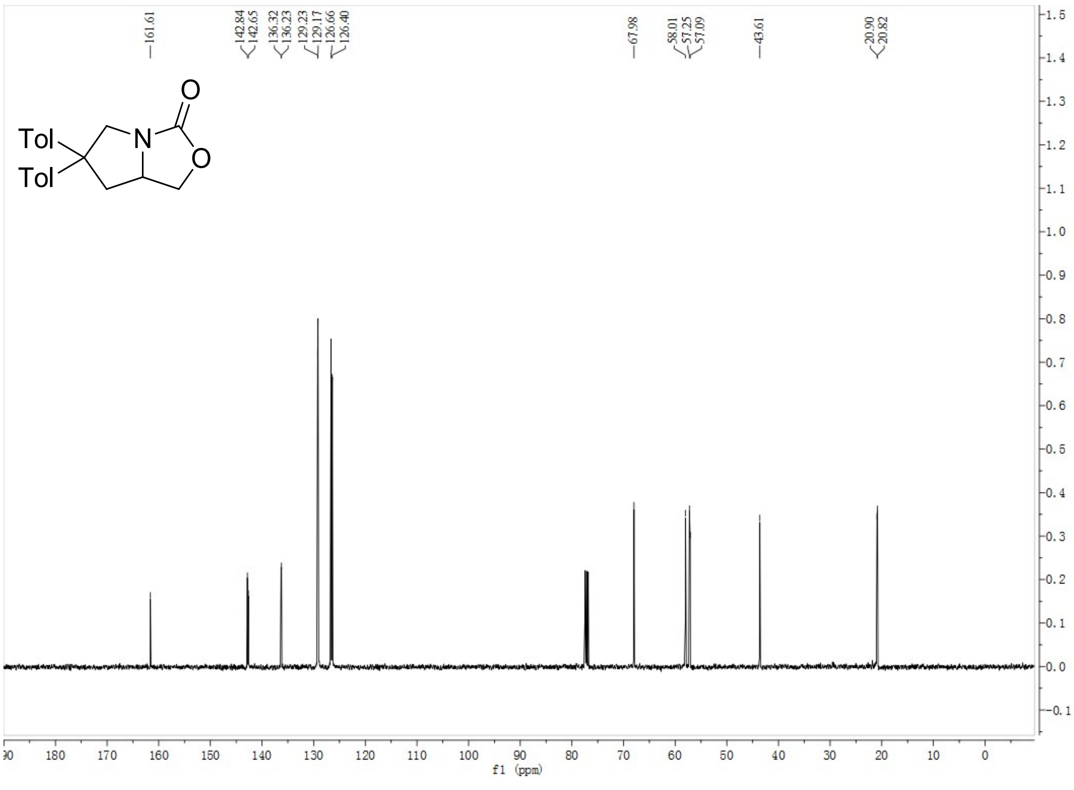
[1]H NMR and [13]C NMR for compound **2b**



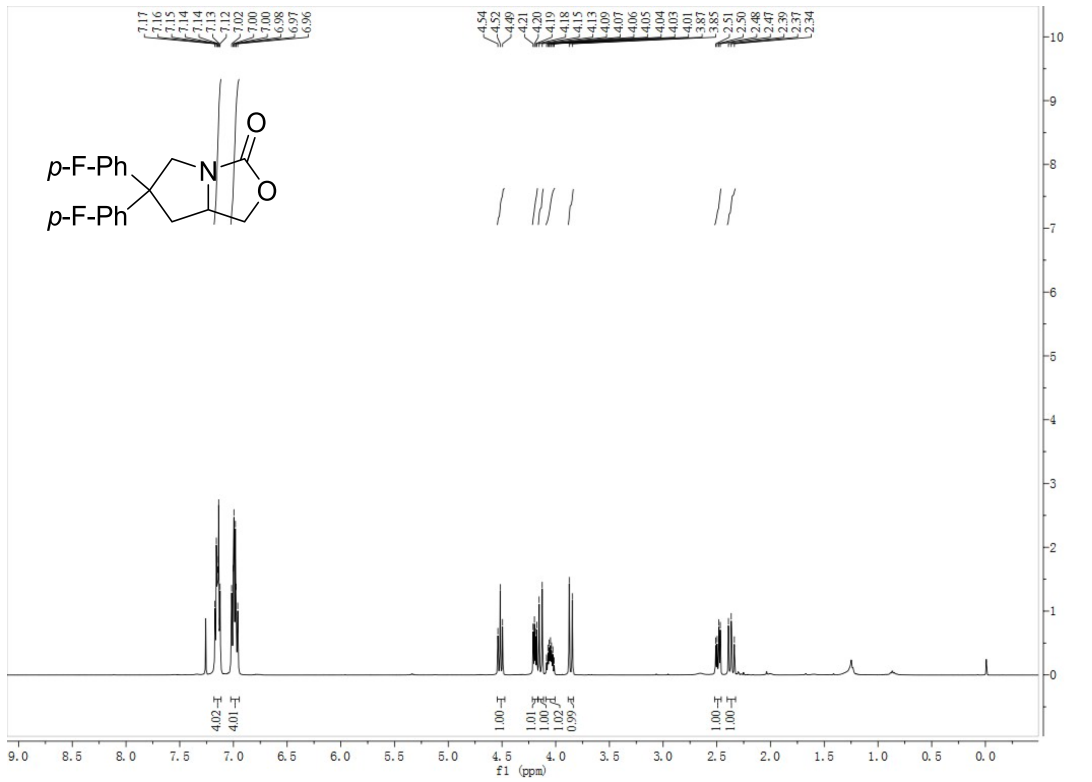


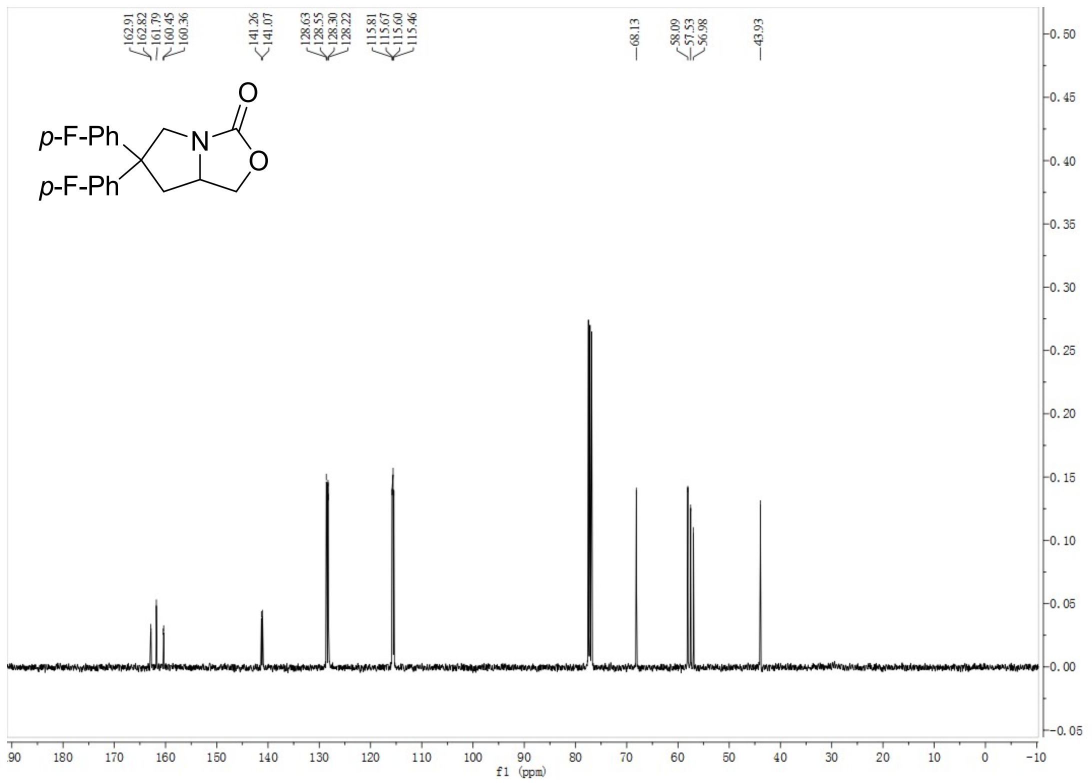
^{1}H NMR and ^{13}C NMR for compound **2c**

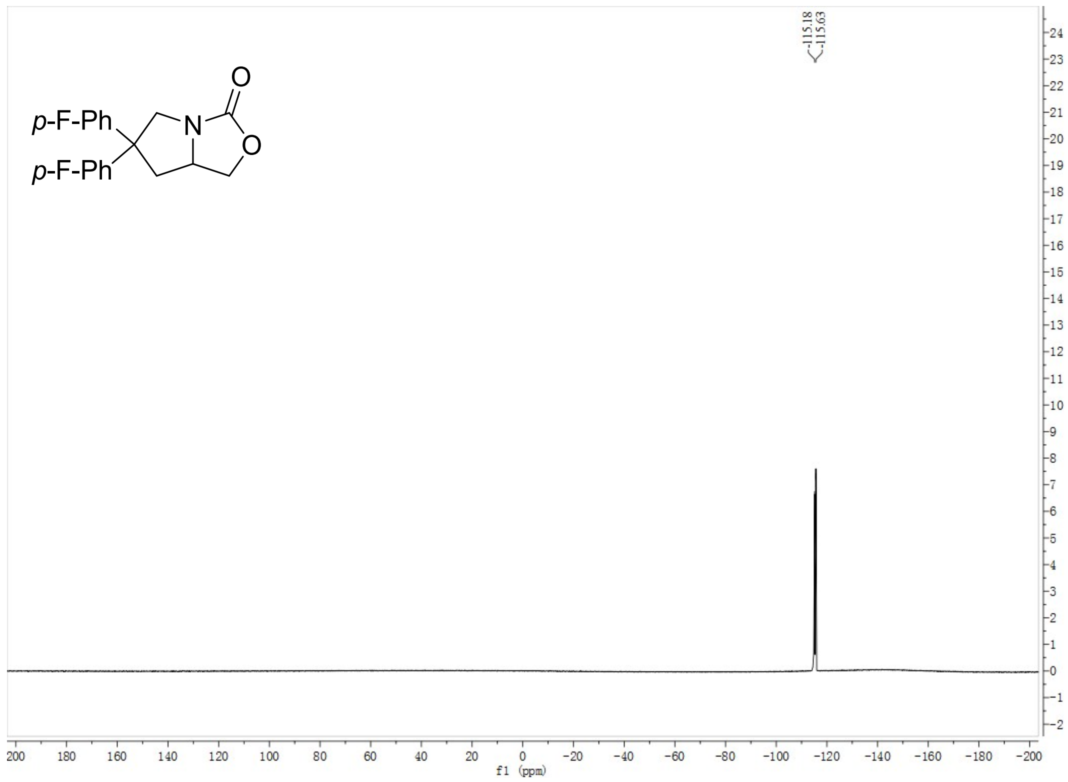




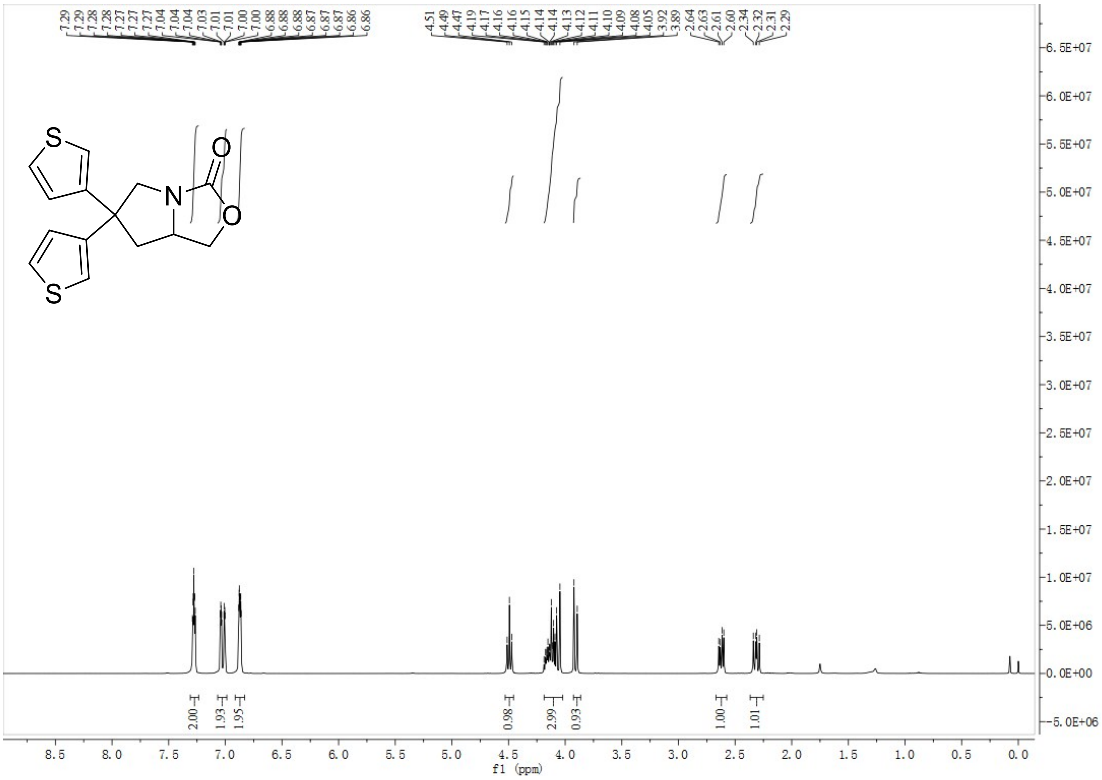
^{1}H NMR and ^{13}C NMR for compound **2d**

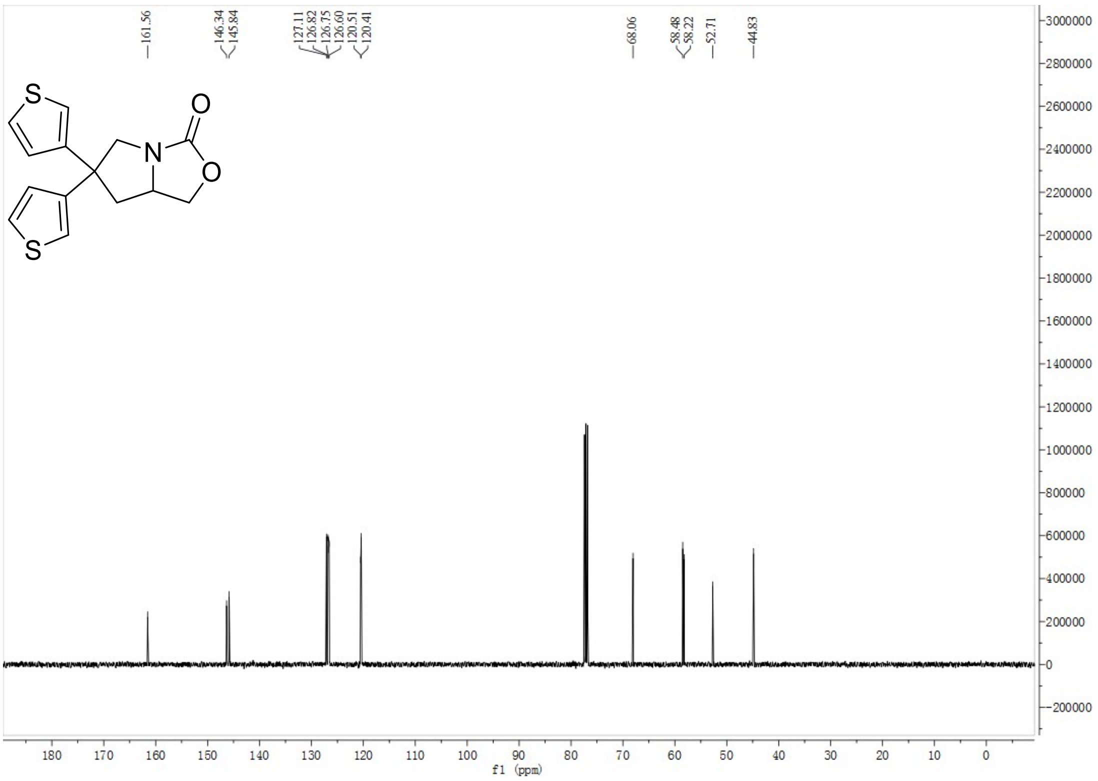




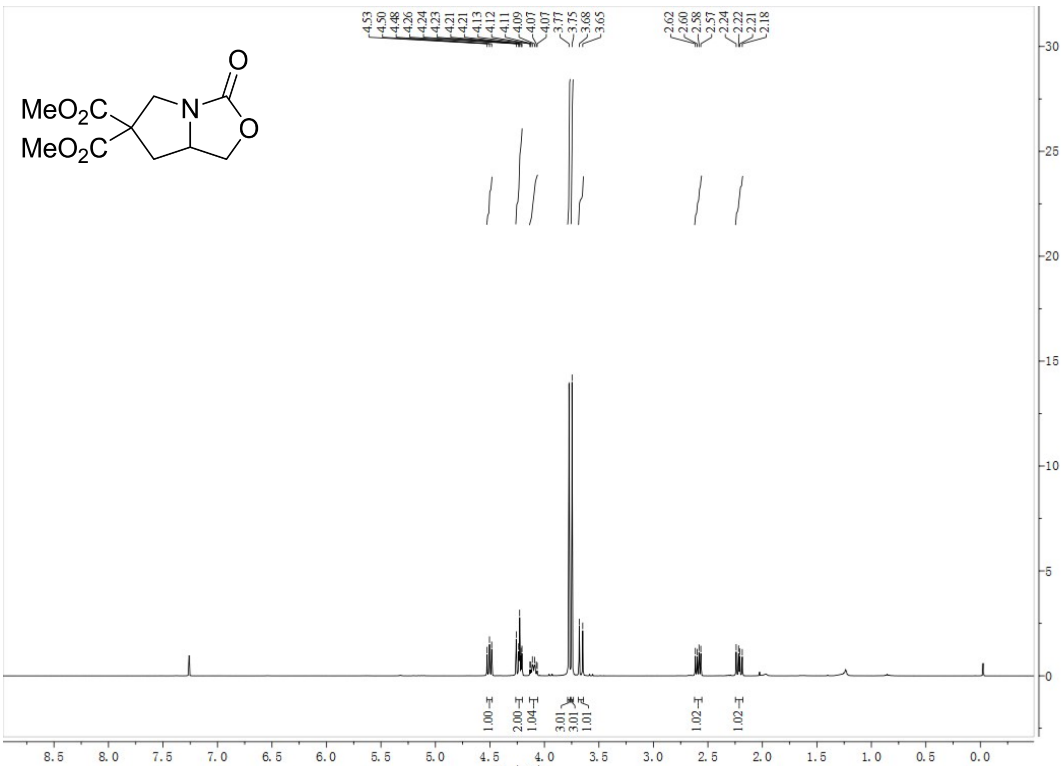


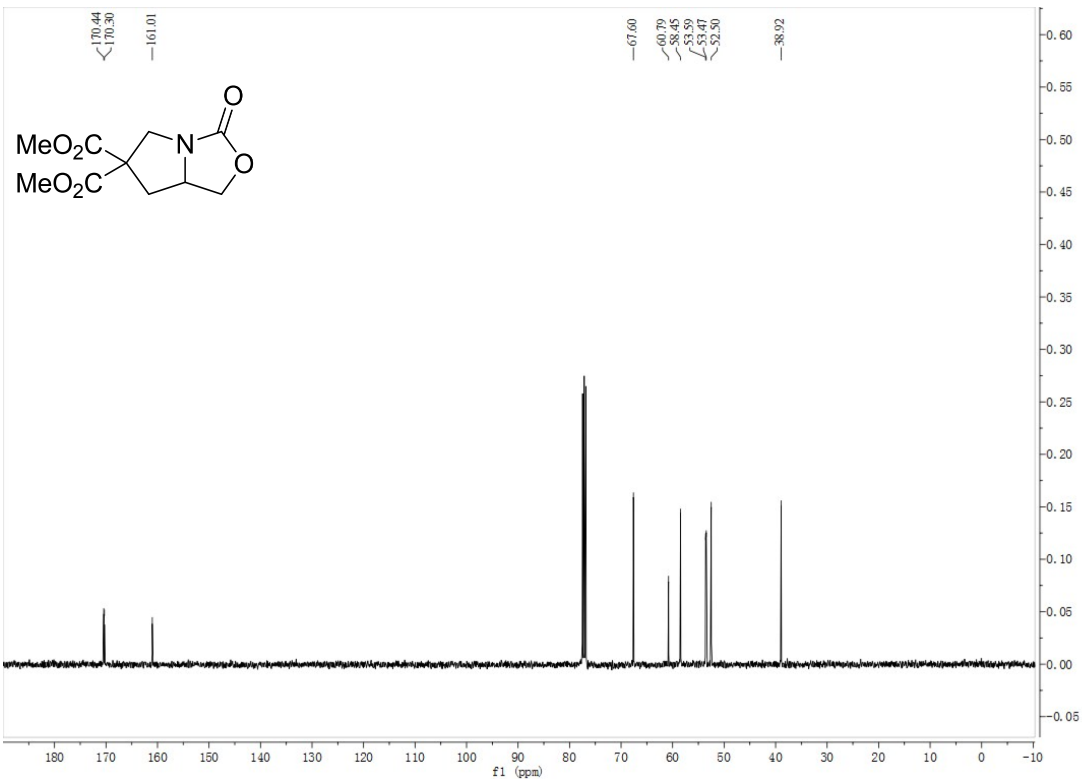
^{1}H NMR, ^{13}C NMR and ^{19}F NMR for compound **2e**



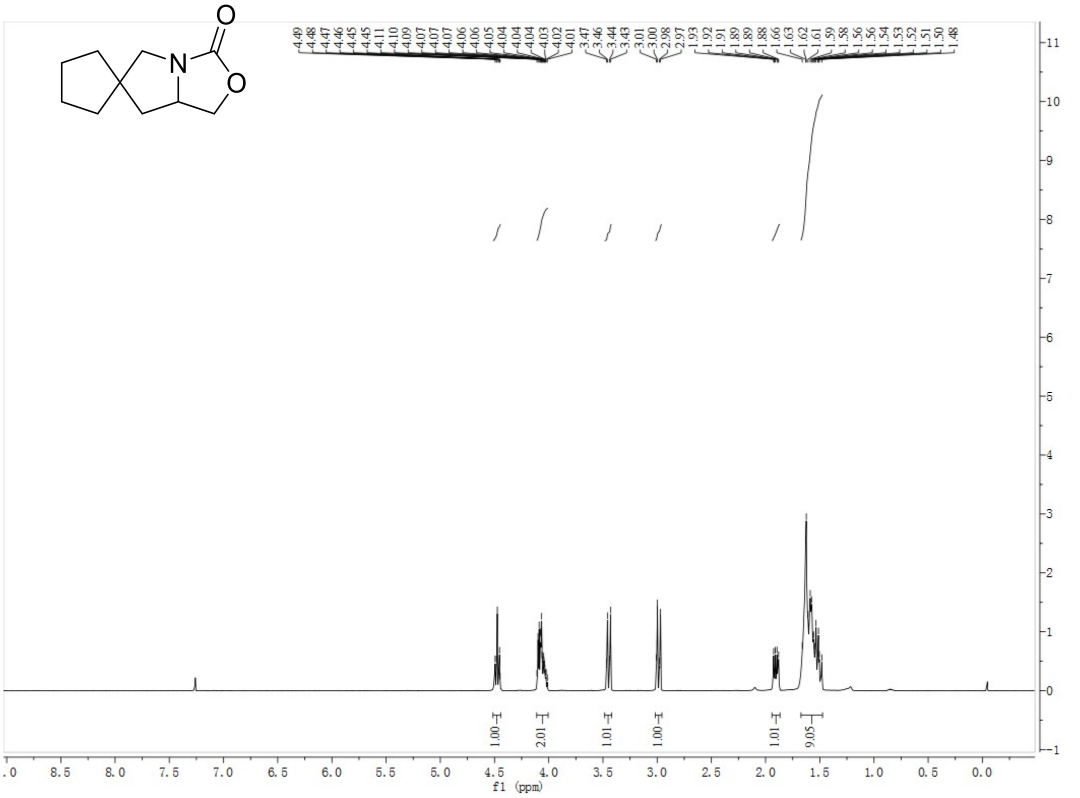


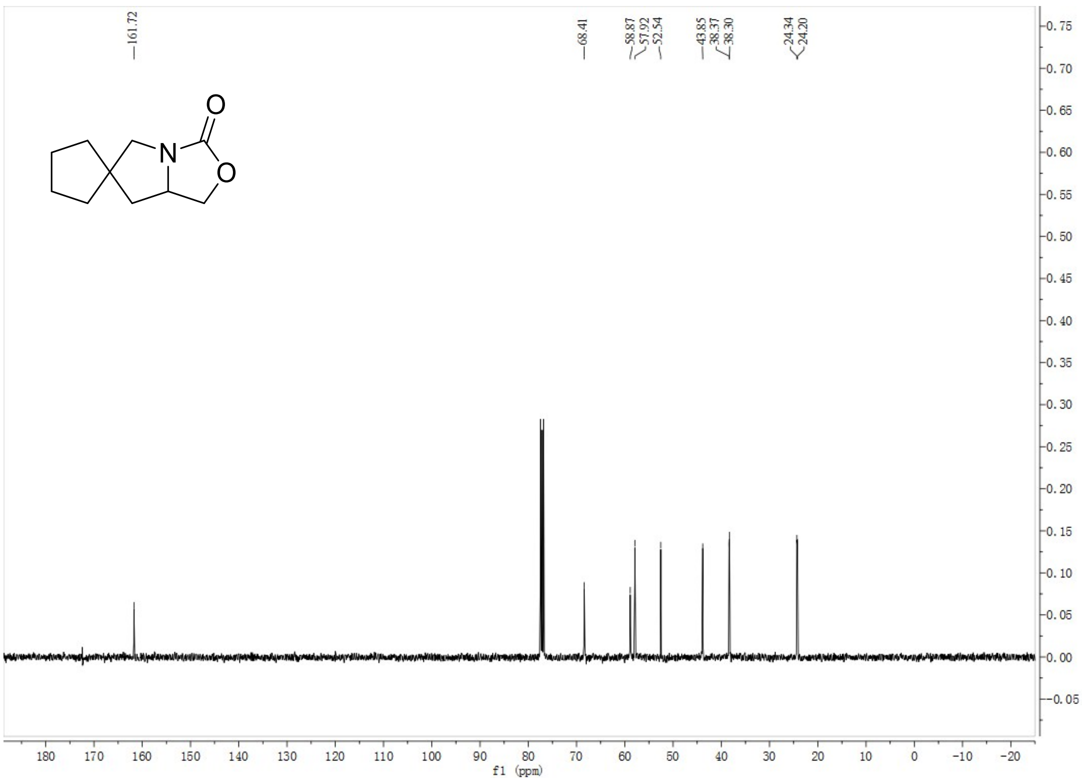
^{1}H NMR and ^{13}C NMR for compound **2f**



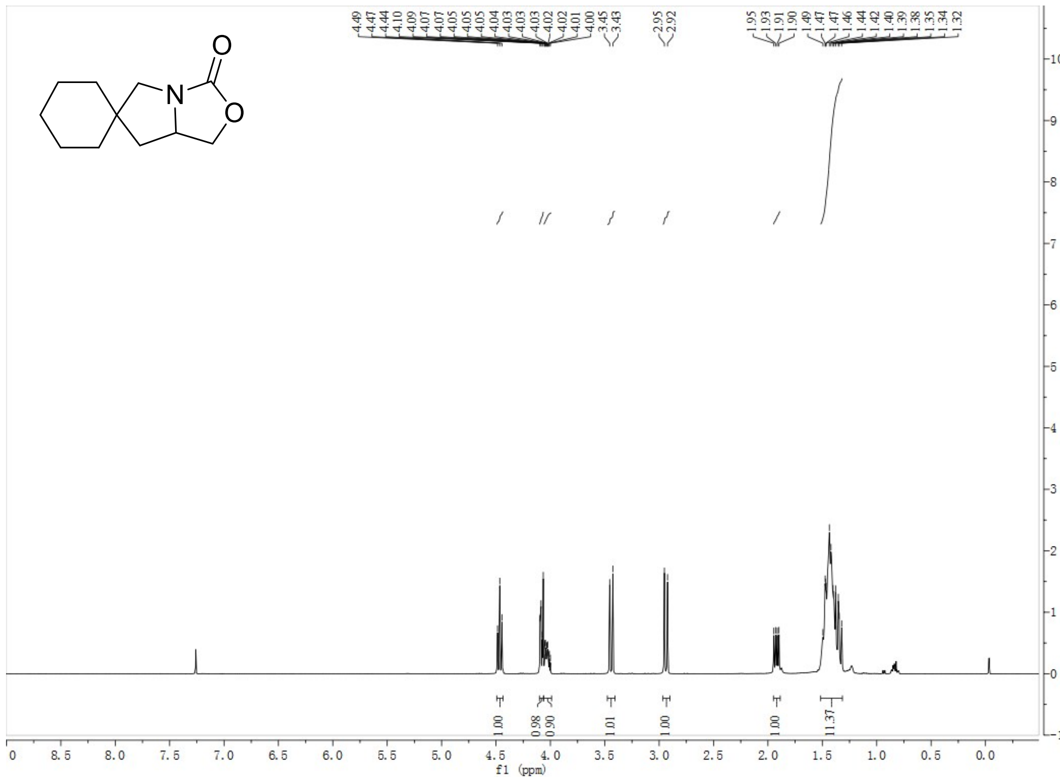


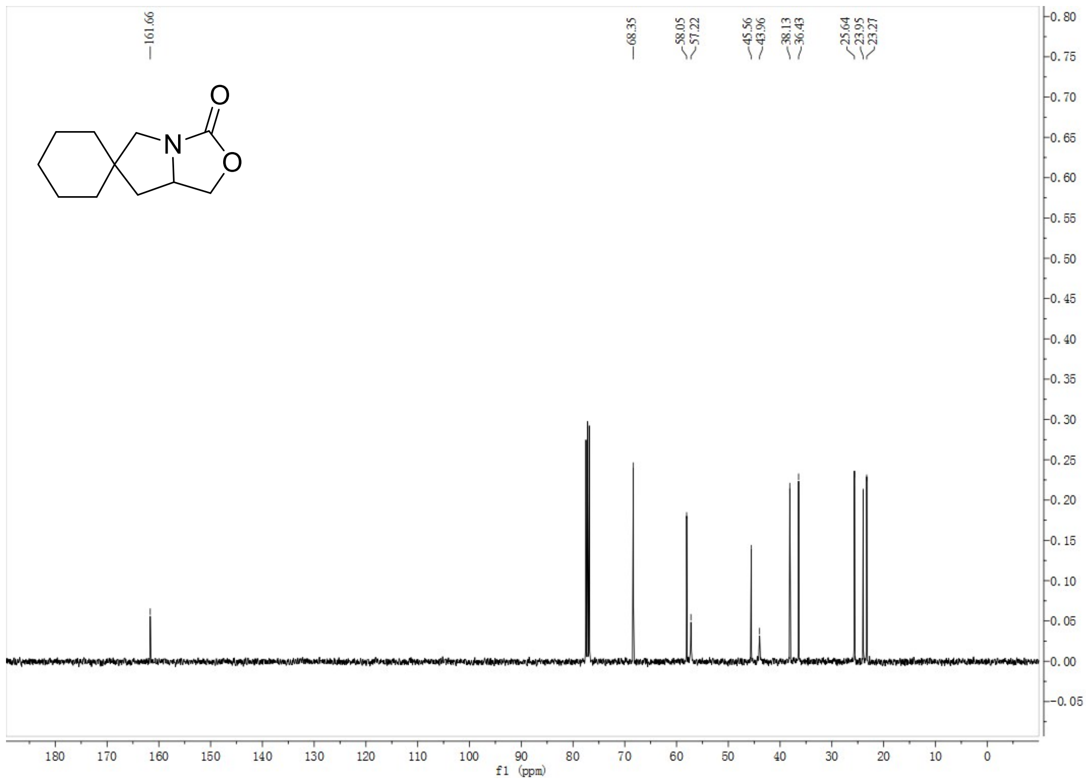
^{1}H NMR and ^{13}C NMR for compound **2g**



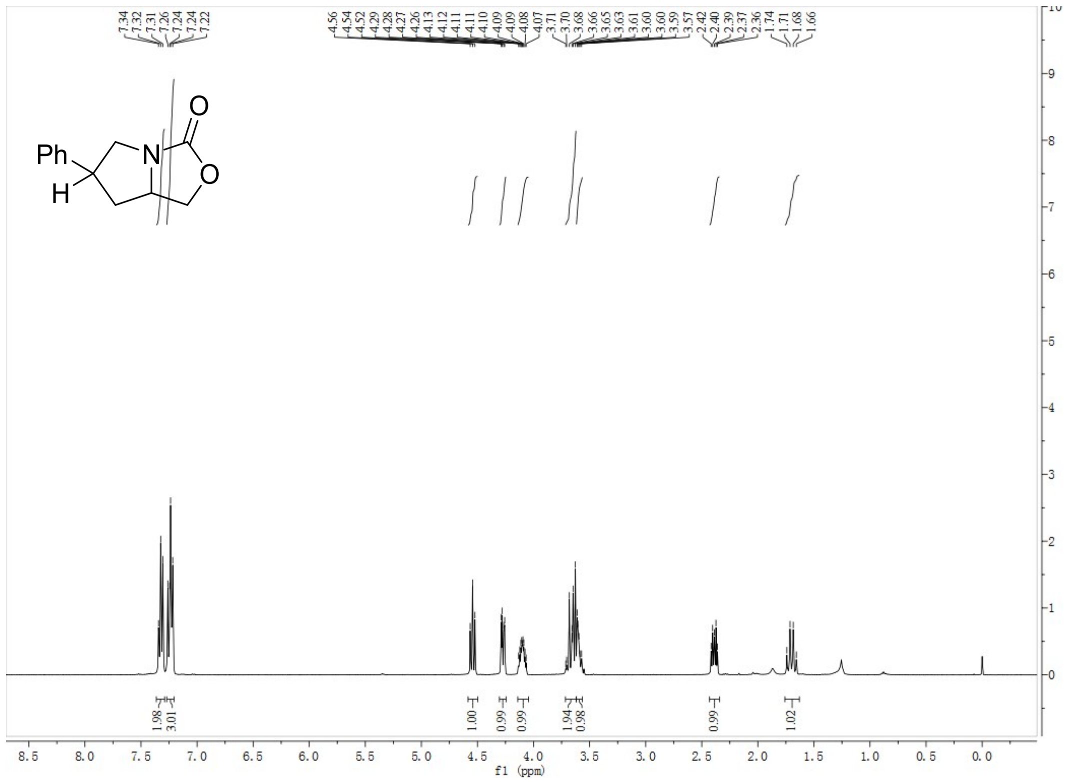


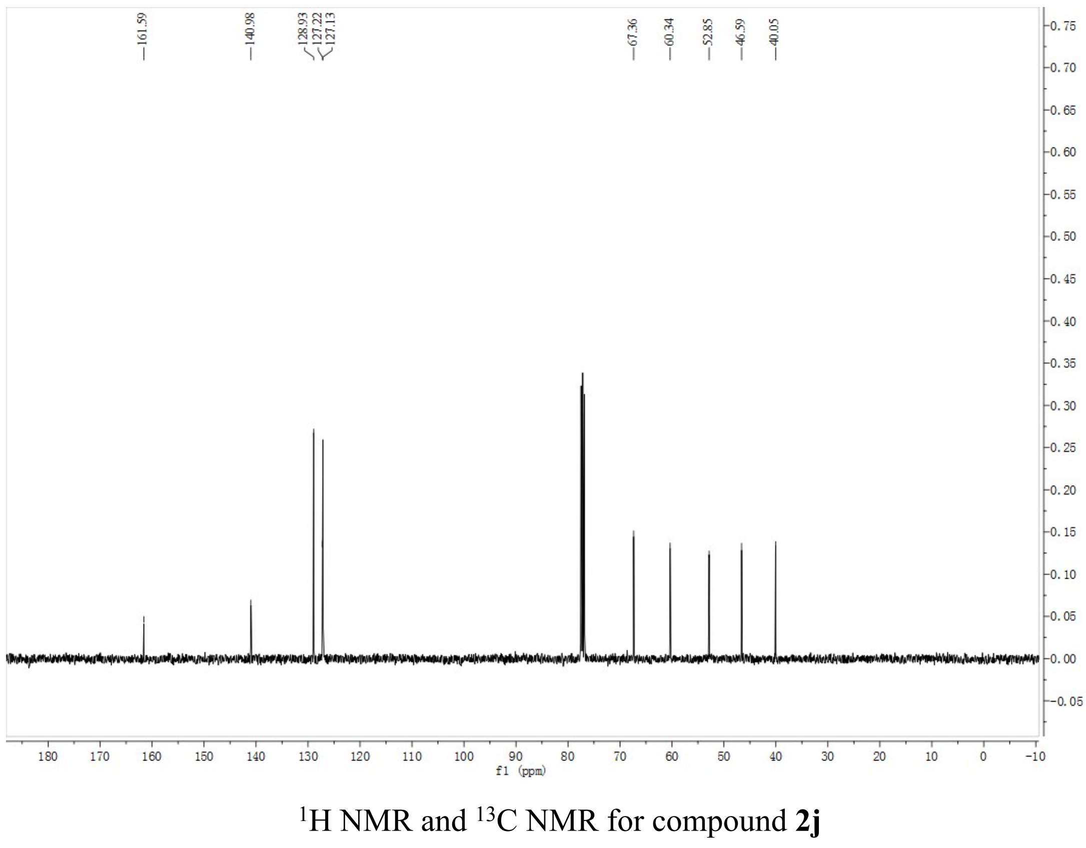
[1]H NMR and [13]C NMR for compound **2h**



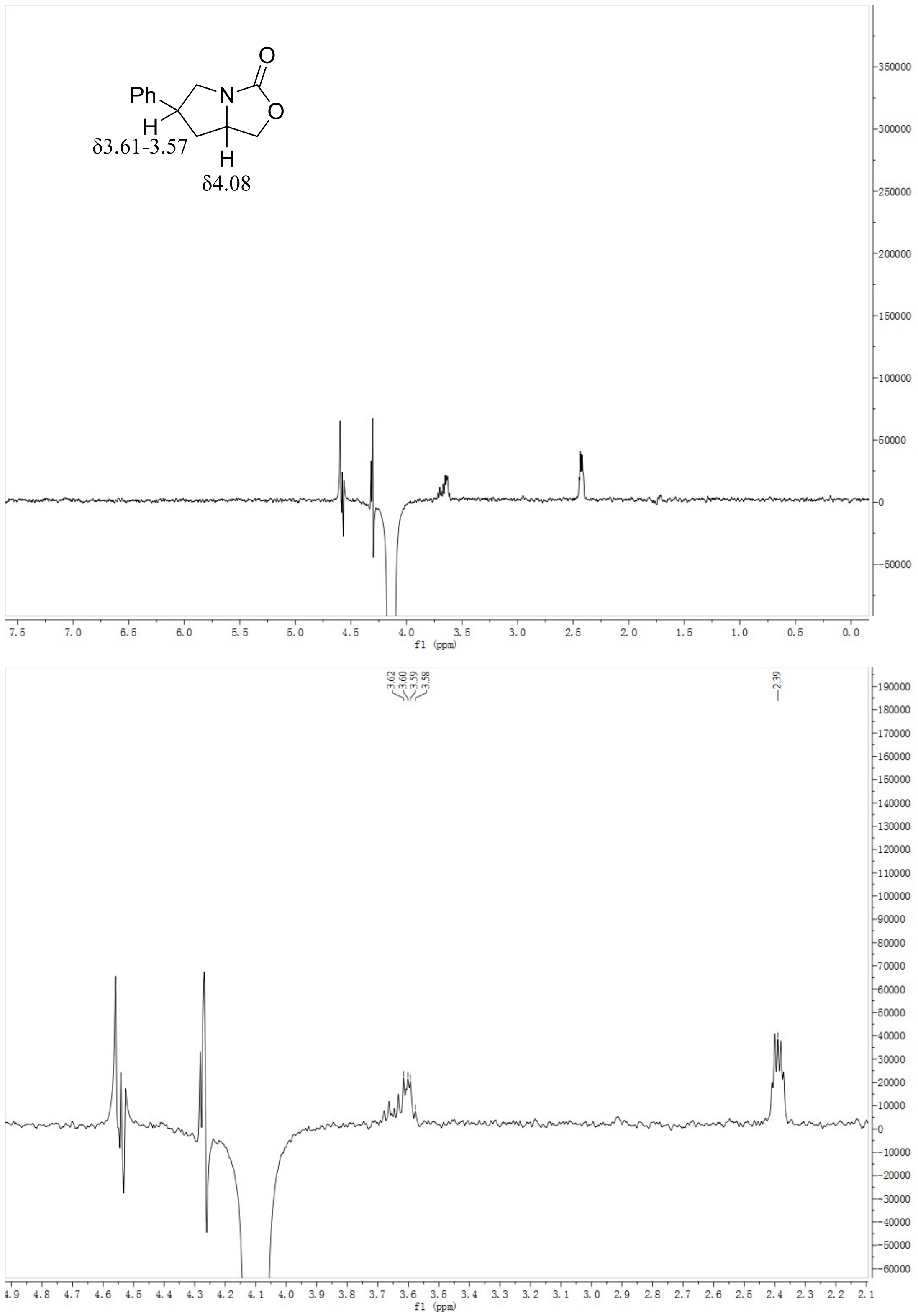


^{1}H NMR and ^{13}C NMR for compound **2i**

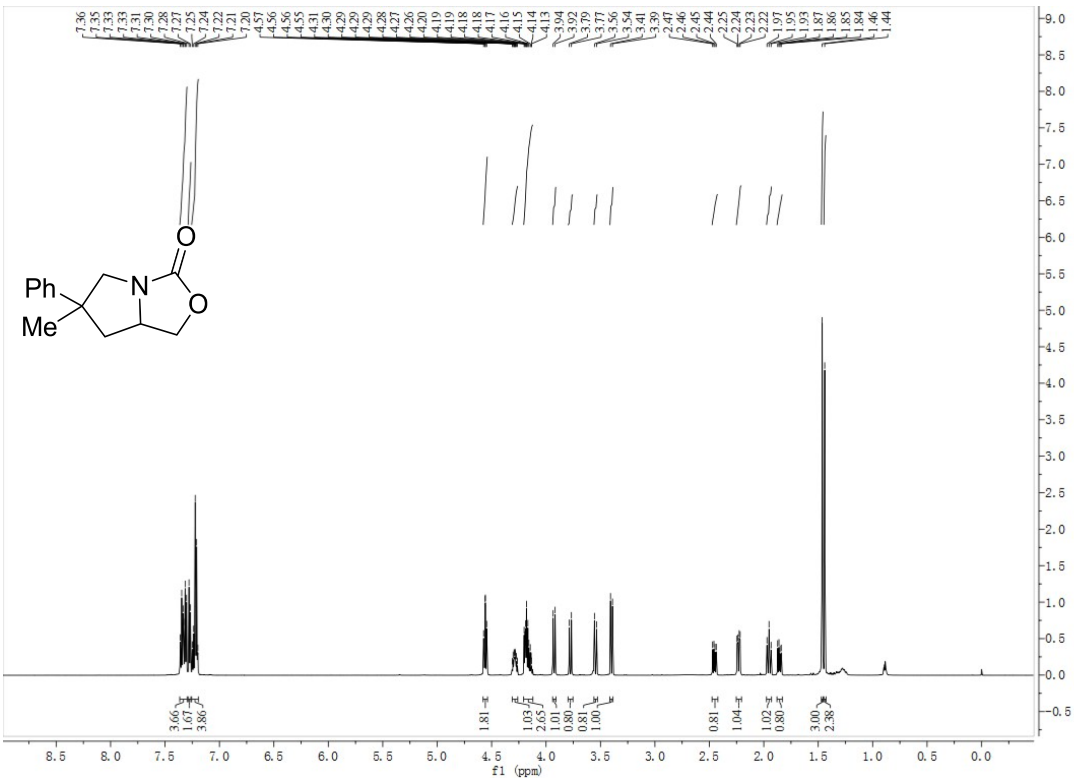


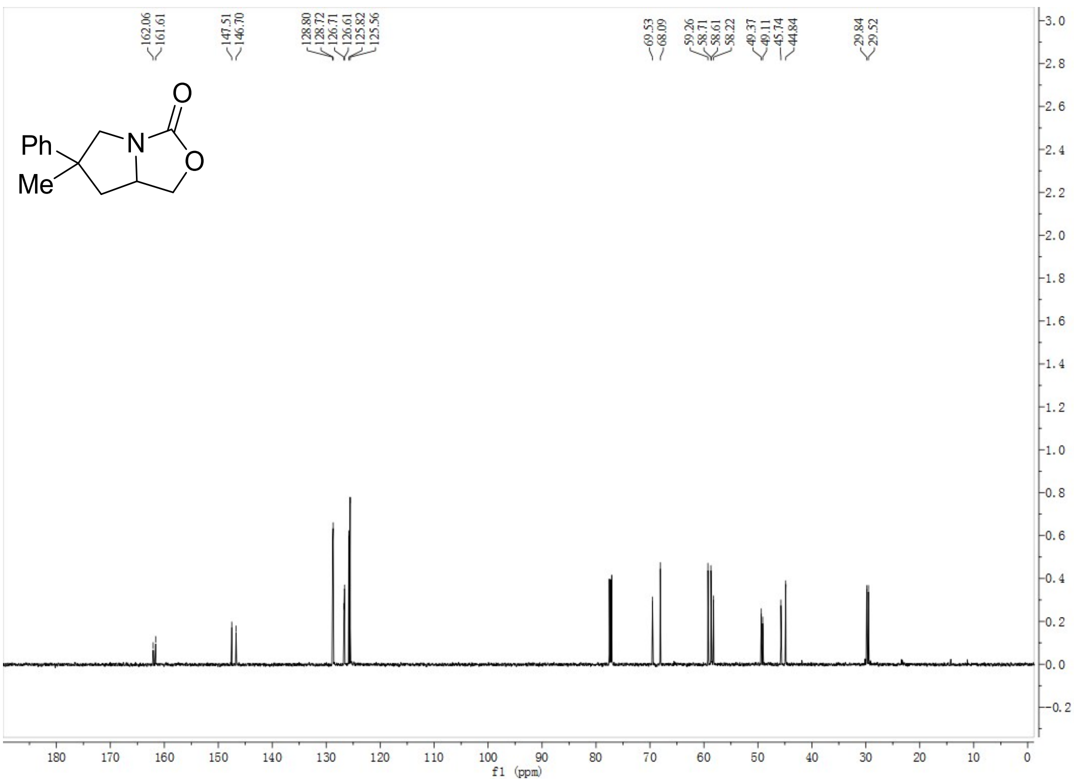


^{1}H NMR and ^{13}C NMR for compound **2j**

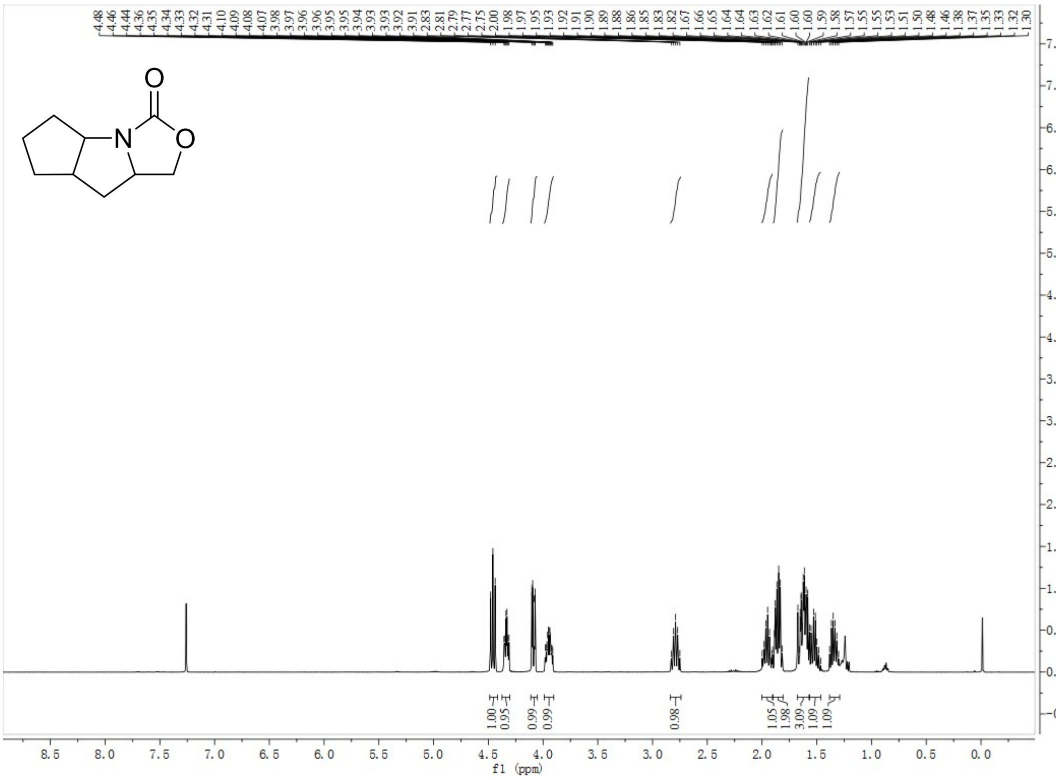


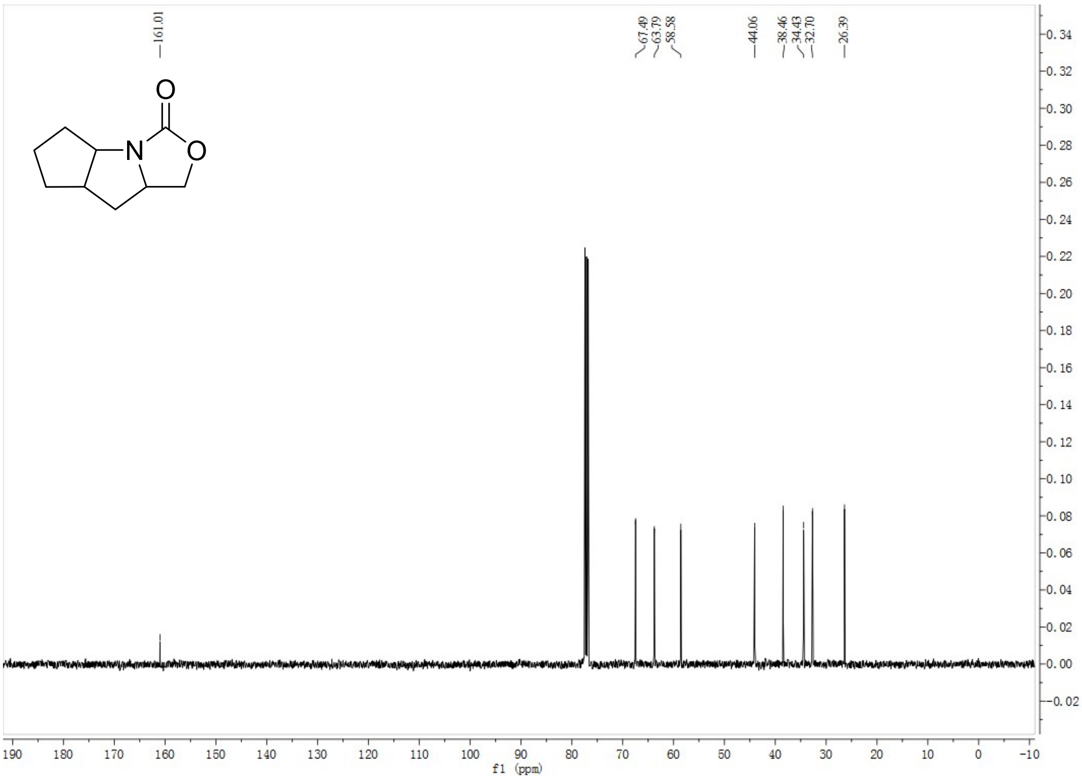
The NOE spectrum of **2j** with irradiation at δ 4.08



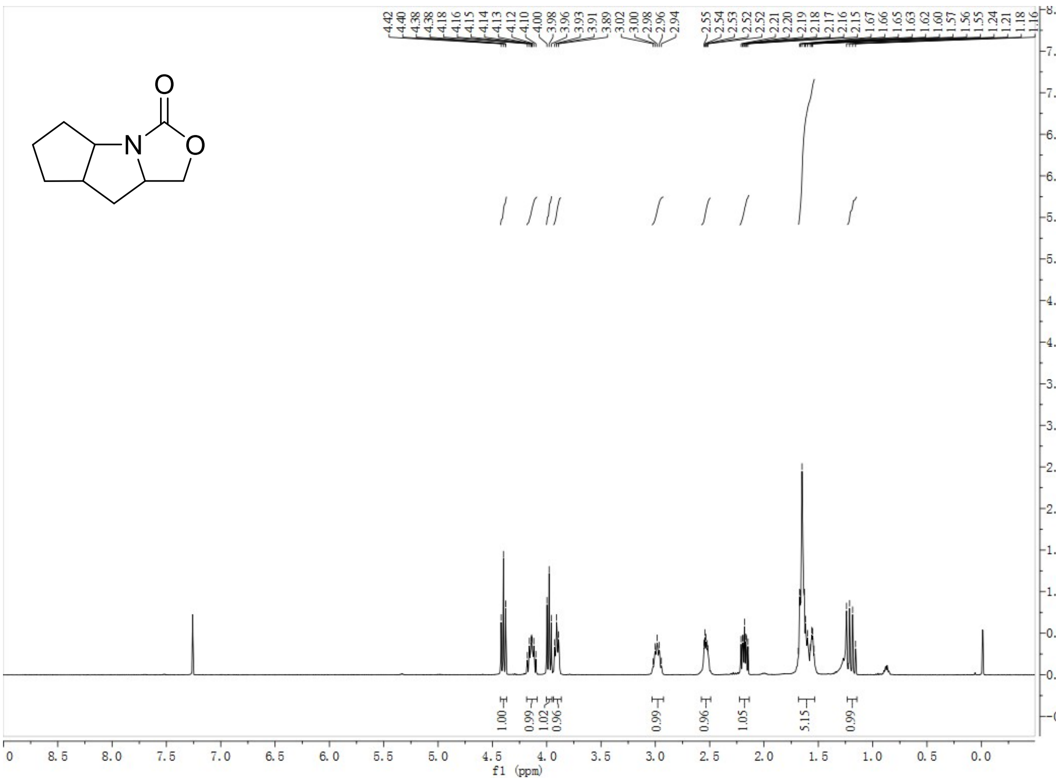


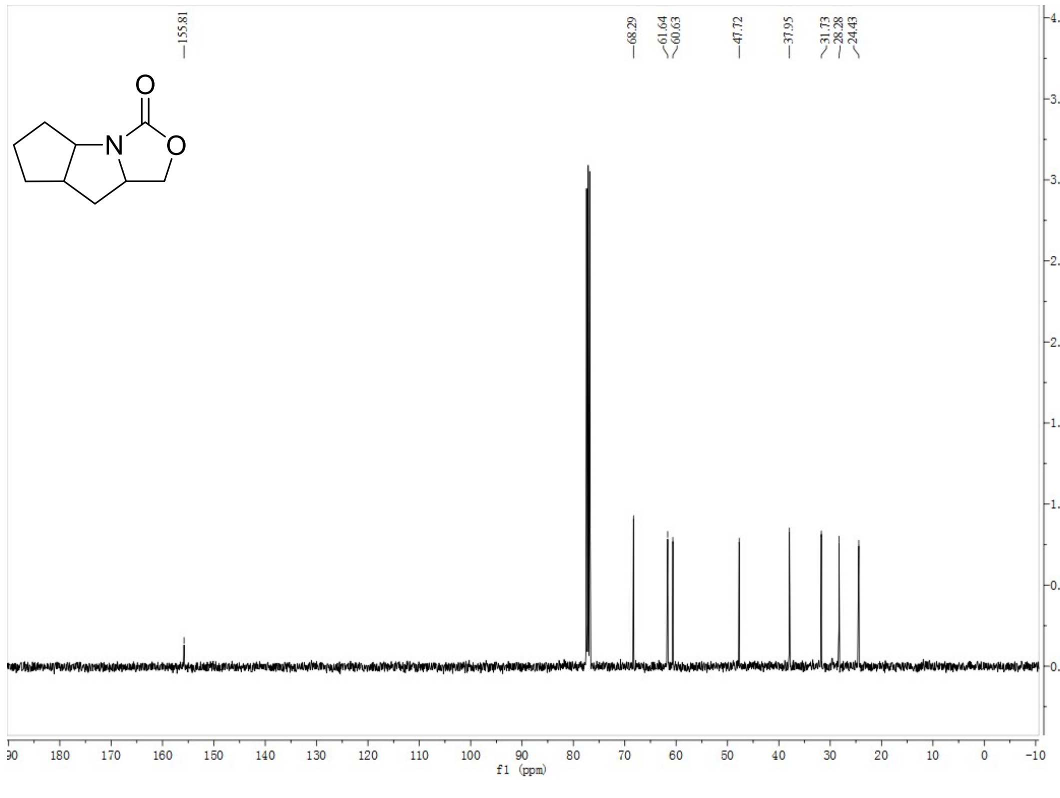
^{1}H NMR and ^{13}C NMR for compound **2k**



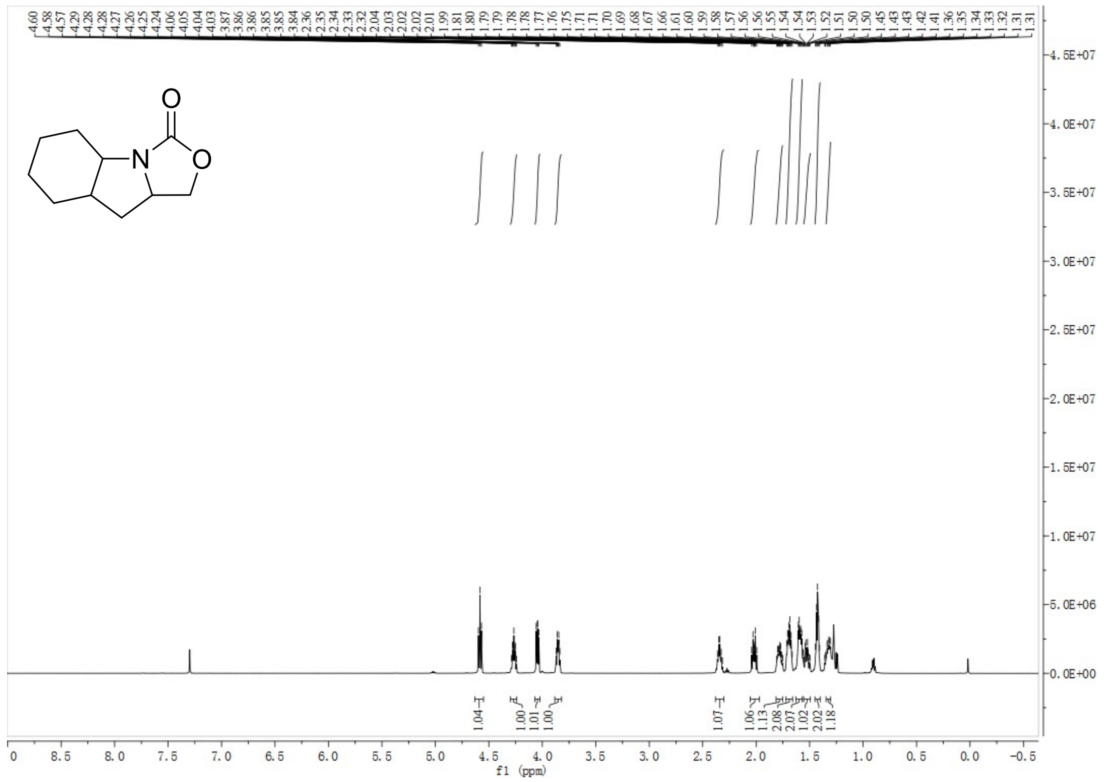


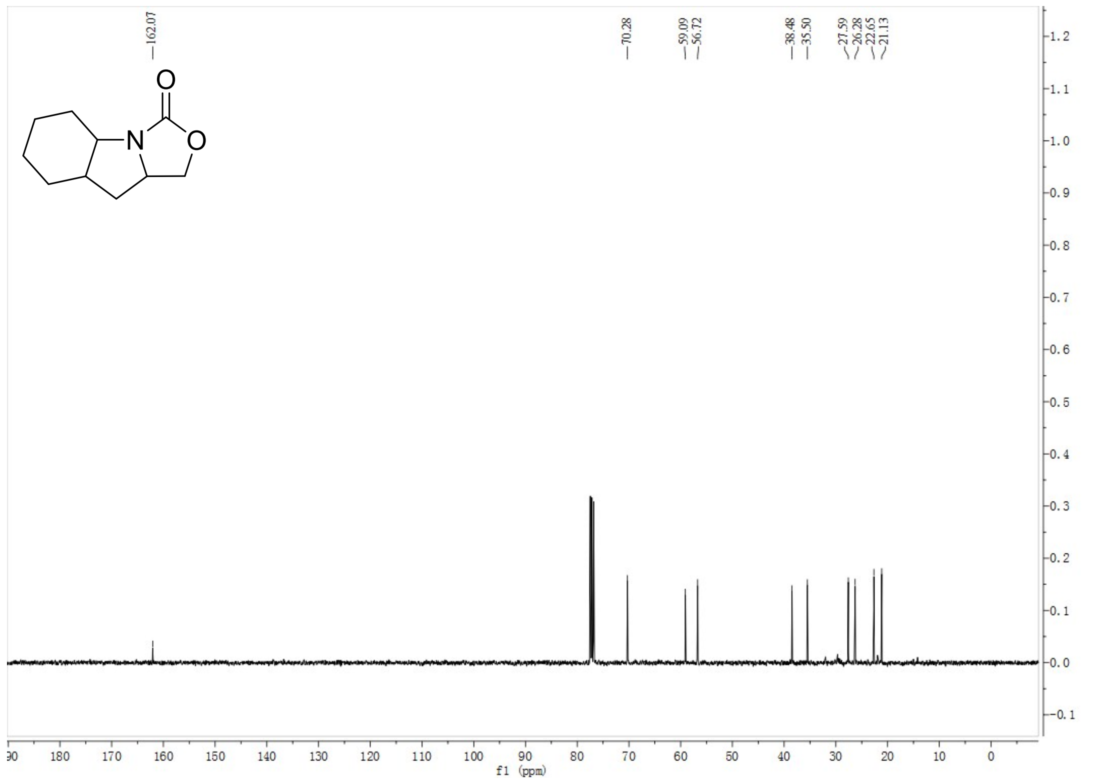
[1]H NMR and [13]C NMR for compound **2l-1**



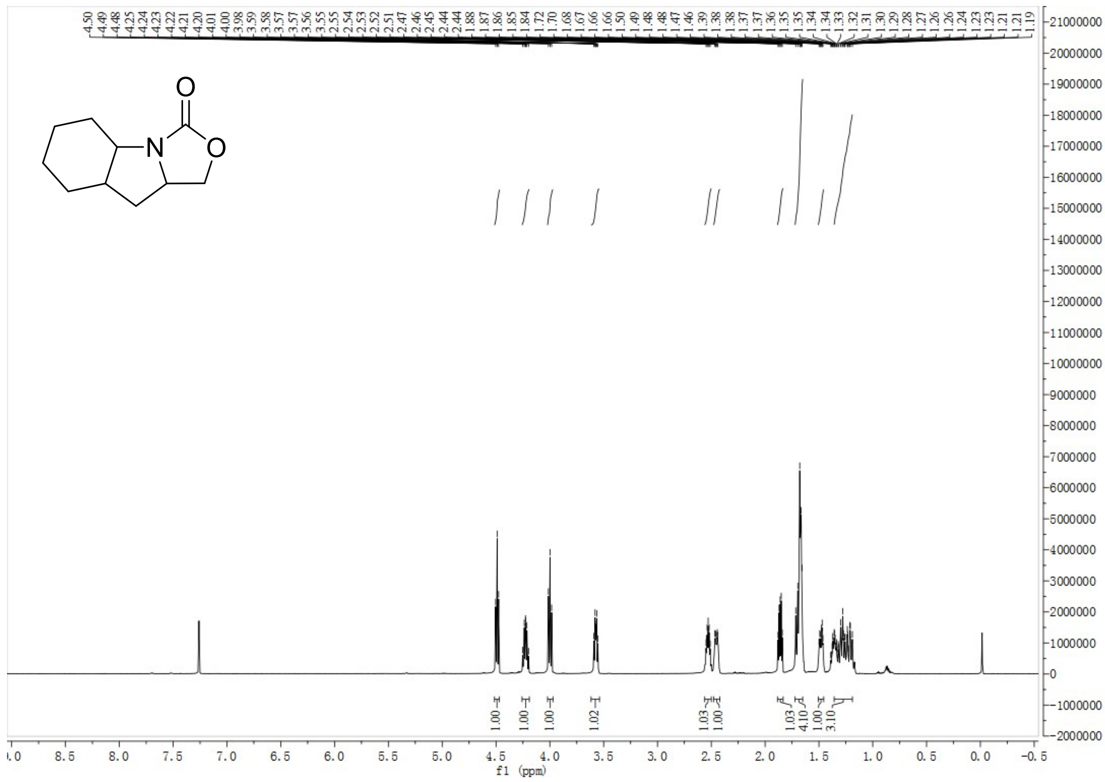


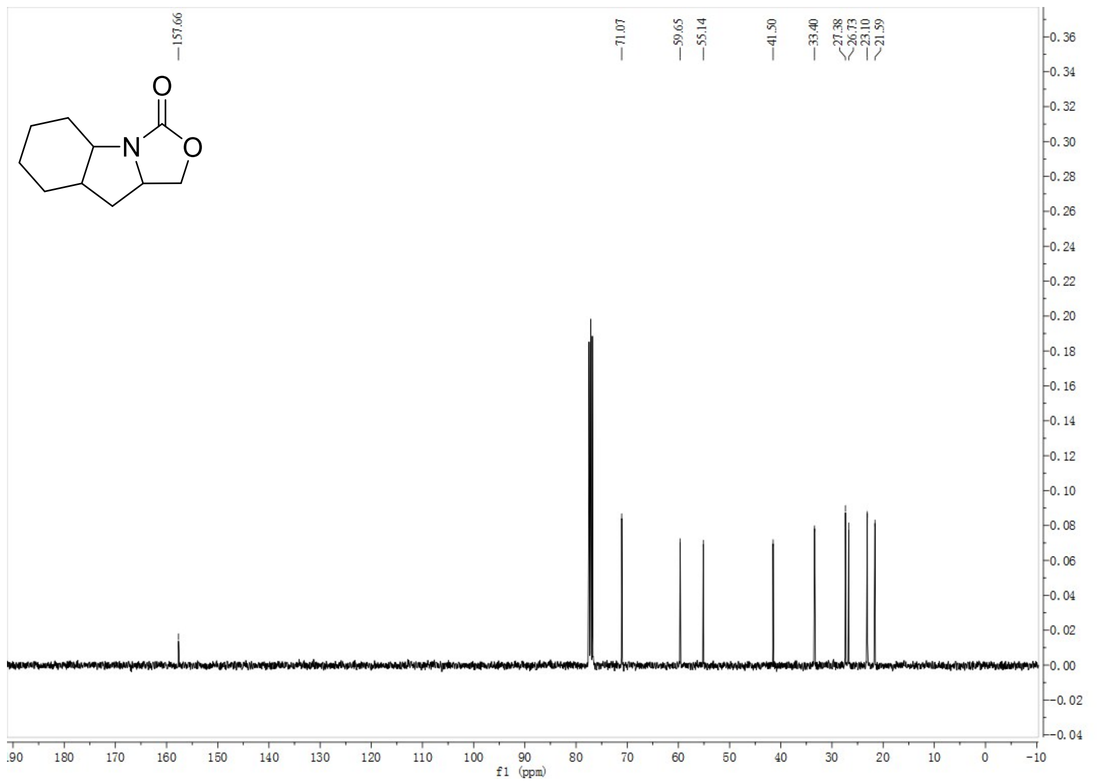
[1]H NMR and [13]C NMR for compound **2l-2**



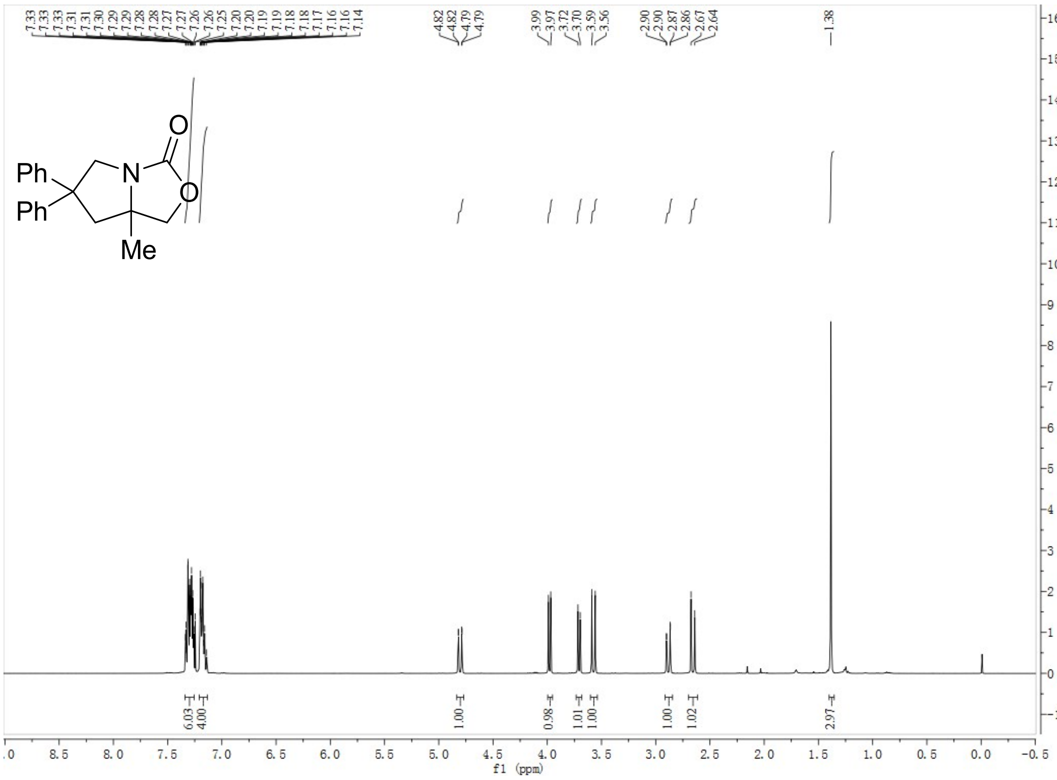


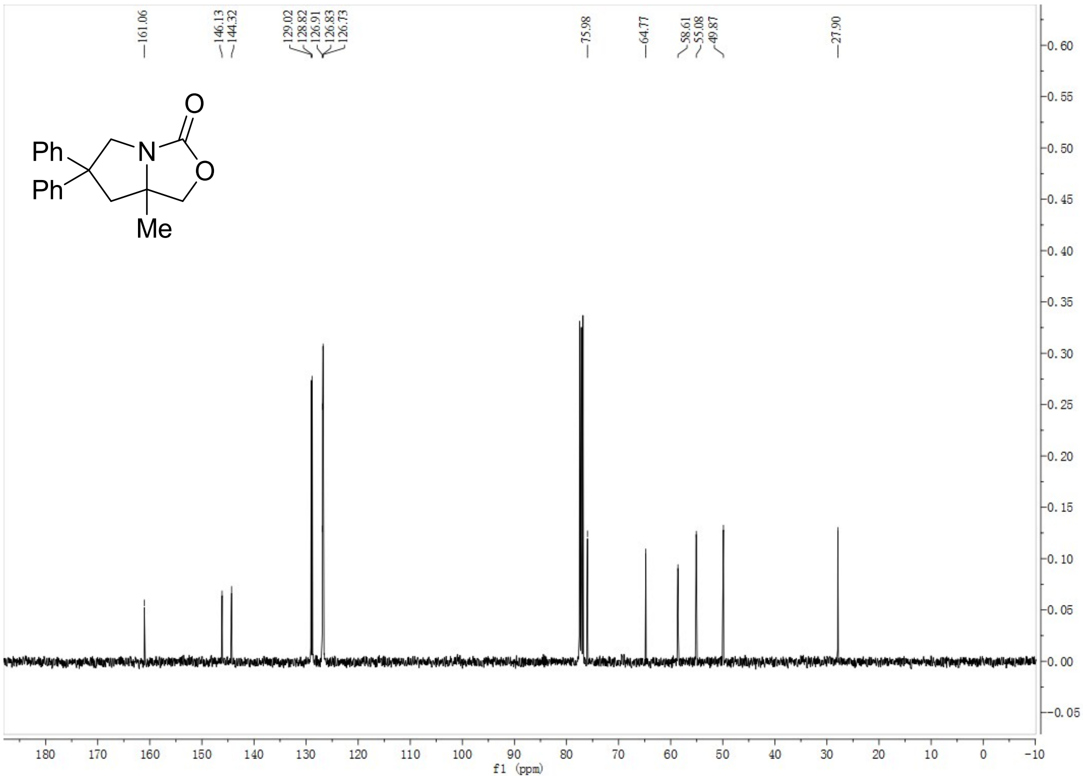
[1]H NMR and [13]C NMR for compound **2m-1**



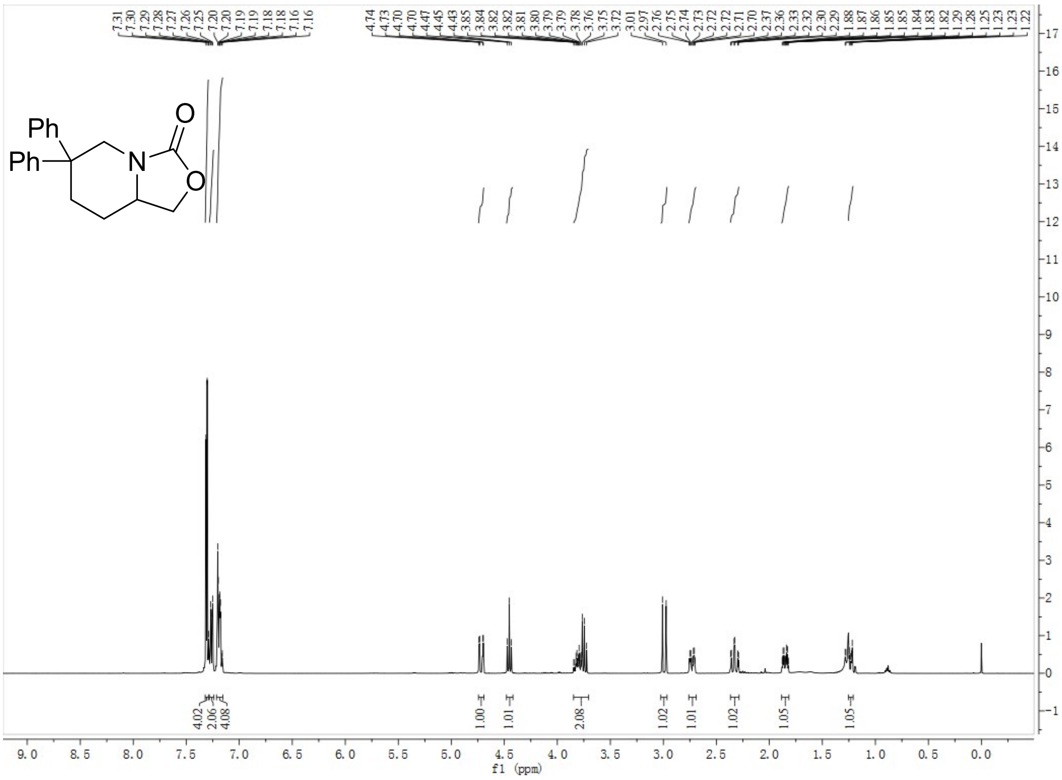


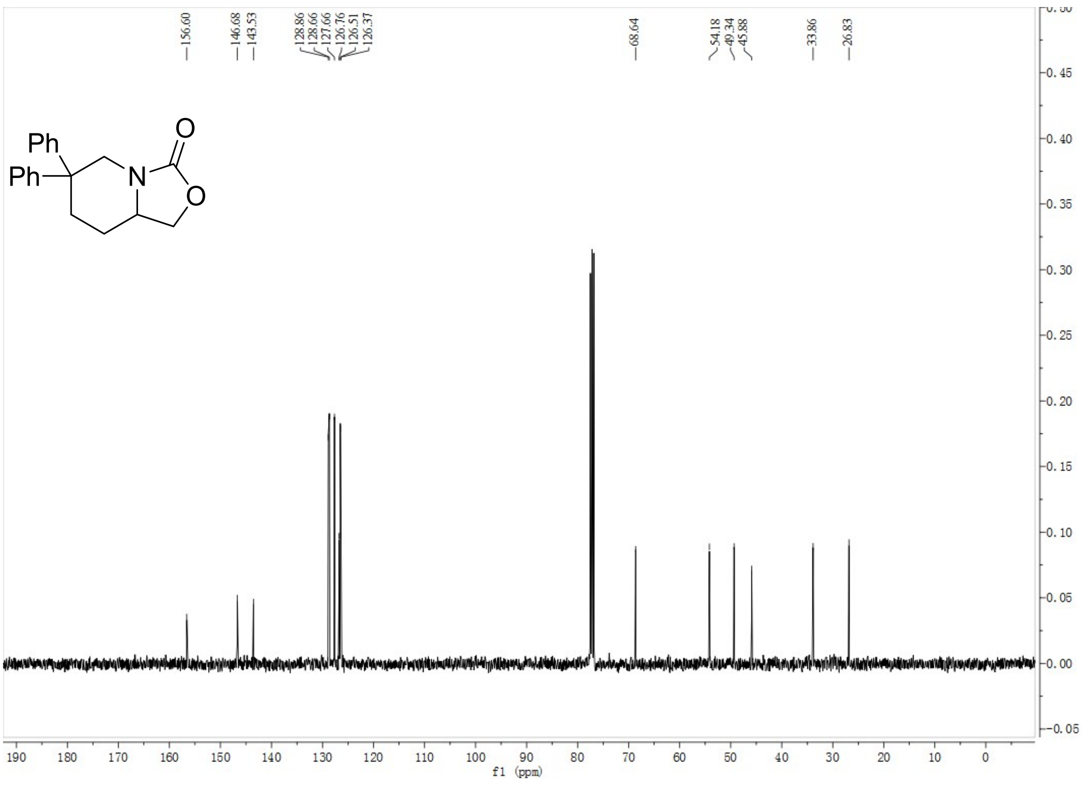
[1]H NMR and [13]C NMR for compound **2m-2**



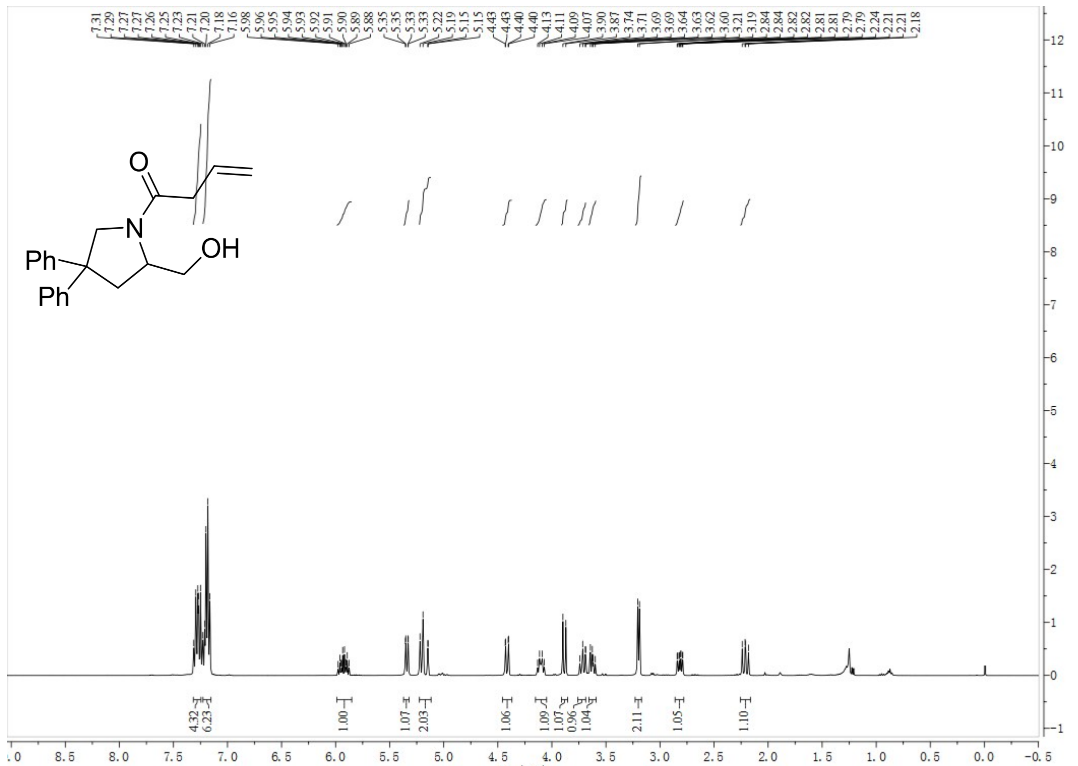


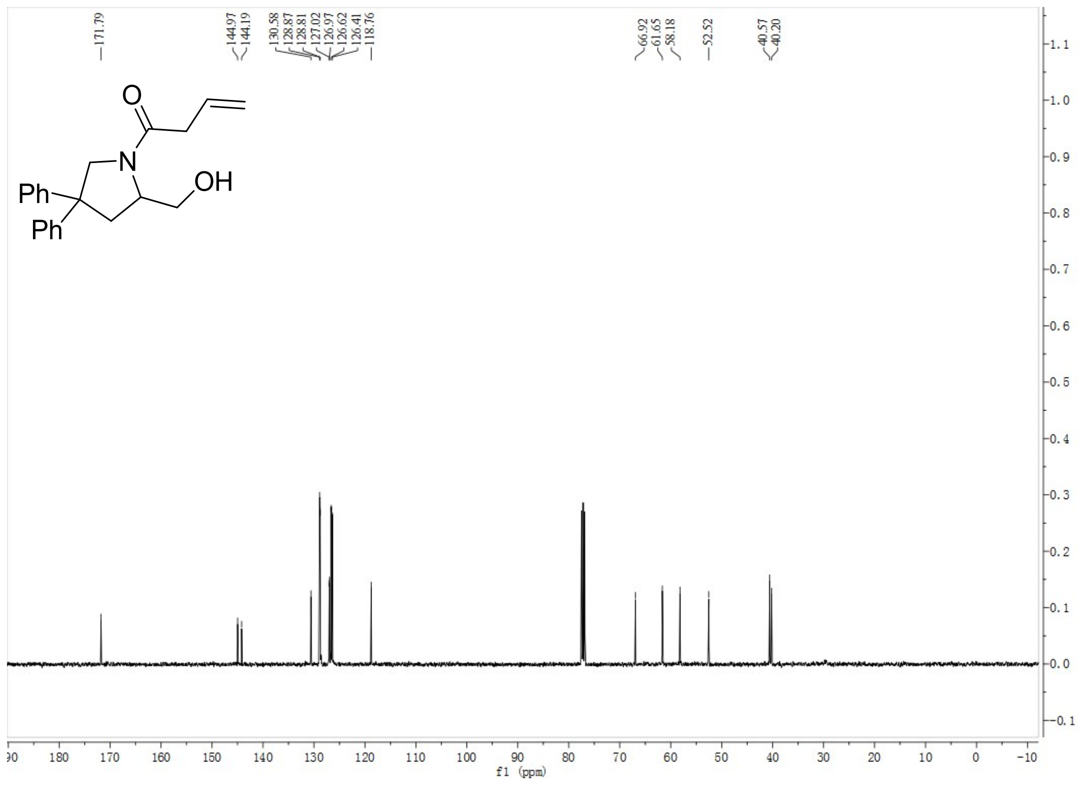
^{1}H NMR and ^{13}C NMR for compound **2n**



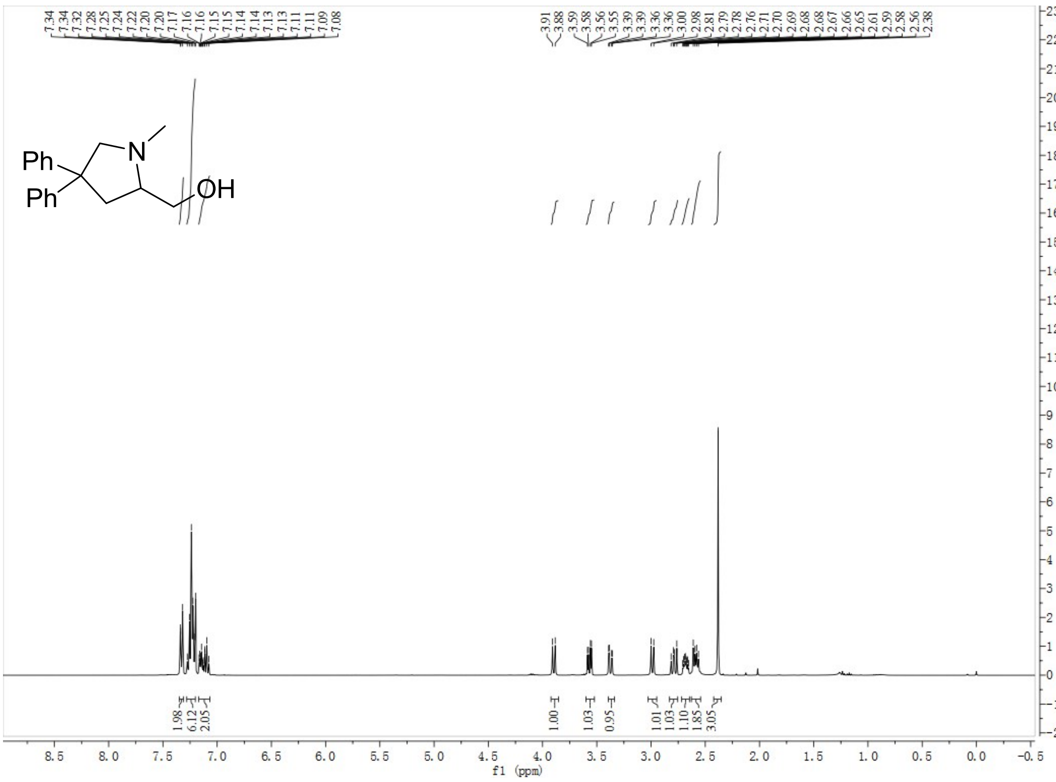


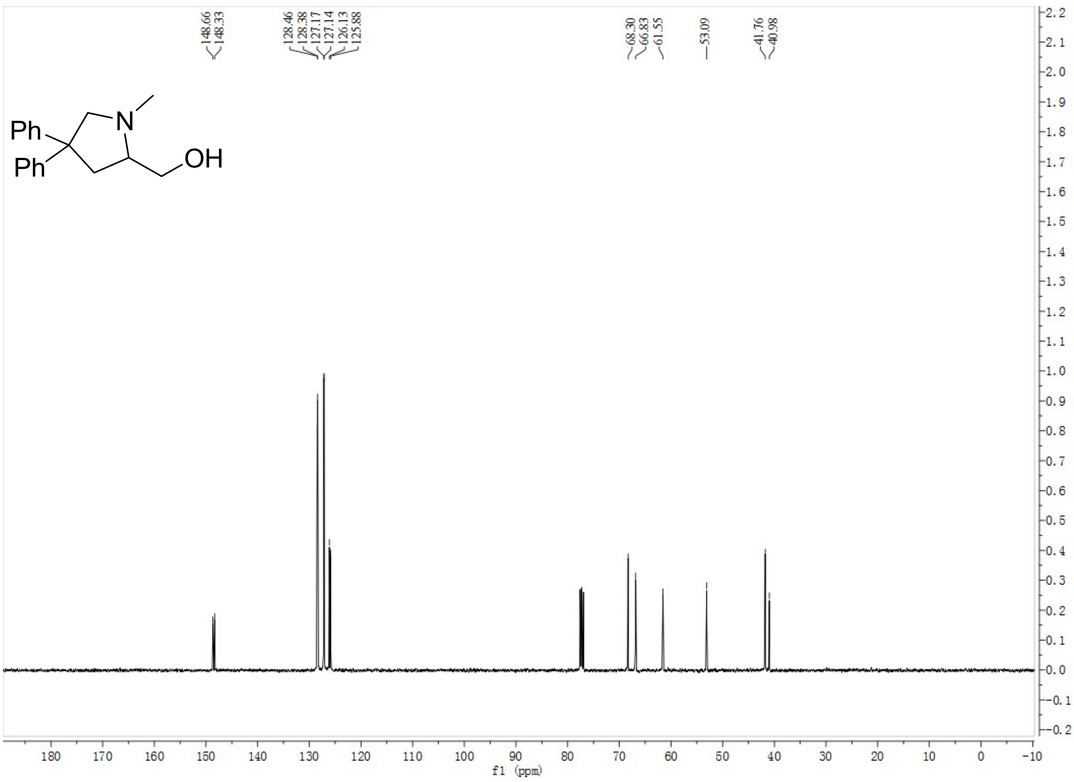
[1]H NMR and [13]C NMR for compound **2p**





^{1}H NMR and ^{13}C NMR for compound **3**





^{1}H NMR and ^{13}C NMR for compound **4**

Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_{18}H_{17}NO_2$
Formula weight	279.33
Temperature/K	173.15
Crystal system	triclinic
Space group	P-1
a/Å	6.3952(13)
b/Å	9.4580(19)
c/Å	12.085(2)
α/°	102.98(3)
β/°	94.15(3)
γ/°	90.64(3)
Volume/Å^3	710.1(2)
Z	2
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	0.085
F(000)	296
Crystal size/mm^3	0.415 × 0.332 × 0.197
Radiation	MoKα (λ = 0.710747)
Theta range for data collection/°	3.46 to 54.98
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	9148
Independent reflections	3206 [R_{int} = 0.0267, R_{sigma} = 0.0214]
Data/restraints/parameters	3206/0/190
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.1070

Largest diff. peak/hole / e Å^{-3} 0.29/-C14:D330.17