Supporting Information

EtOH-catalyzed Electrosynthesis of Imidazolidine-Fused Sulfamidates from *N*-Sulfonyl Ketimines, *N*-Arylglycines and Formaldehyde

Yu-Han Lu[a,b], Si-Yu Mu[a], Hong-Xia Li[a], Jun Jiang[b], Chao Wu[b], Min-Hang Zhou[b], Wen-Tao Ouyang[b], Wei-Min He[b*]

[a]Hengyang Medical School, University of South China, Hengyang 421001, China

[b]School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China.

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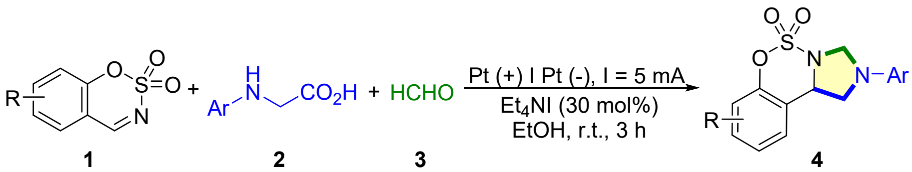
1. General Information

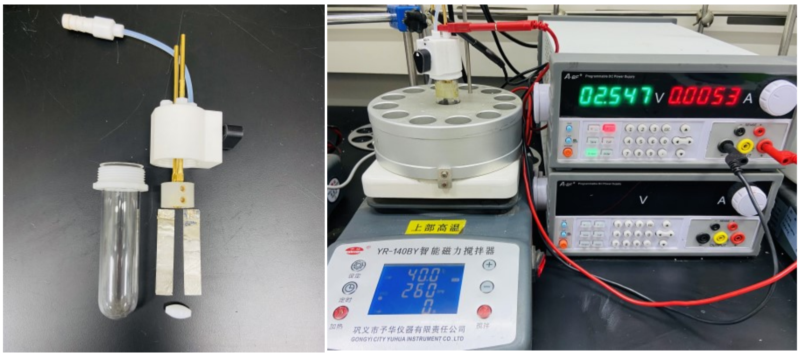
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Pt electrode is 15 mm × 10 mm × 0.1 mm. The instrument for cyclic voltammetrys is CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in EtOH) as counter and reference electrode. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. ^{1}H NMR spectra were recorded at 500 MHz, ^{13}C NMR spectra were recorded at 126 MHz and ^{19}F NMR spectra were recorded at 471 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1}H NMR: $CDCl_3$ 7.26 ppm, ^{13}C NMR: $CDCl_3$ 77.0 ppm), the chemical shifts (δ) were expressed in ppm and J values were given in Hz. HRMS were performed on a spectrometer operating on ESI-TOF.

2. Experimental Section

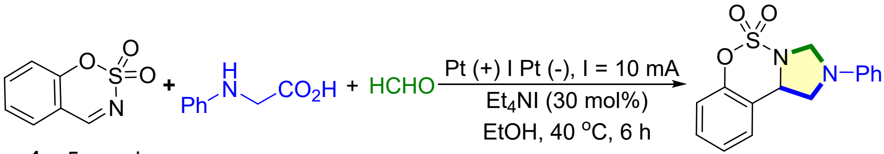
2.1 General Procedure for Compounds 4



In an undivided flask (25 mL) equipped with a stir bar, *N*-sulfonyl ketimines **1** (0.2 mmol), *N*-phenylglycines **2** (0.2 mmol), formaldehyde **3** (0.2 mmol), Et_4NI (0.06 mmol) and EtOH (7 mL) were added. The flask was equipped with platinum anode (15 mm × 10 mm × 0.1 mm) and platinum cathode (15 mm × 10 mm × 0.1 mm). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under 40 ^{o}C for 3 h. After completion, the solvent was concentrated under reduced pressure, and the pure products **4** were obtained by flash chromatography on silica gel.



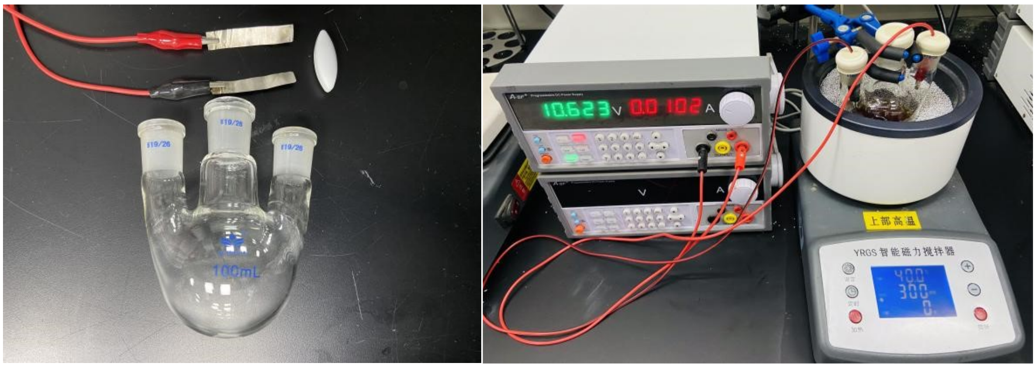
2.2 Large Scale Synthesis of 4aa



1a, 5 mmol

4aa, 81%, 1.22 g

The large scale reaction was performed in an oven-dried 100-mL three-necked flask equipped with a stir bar, the platinum (15 mm × 15 mm × 0.2 mm) as the anode and platinum (15 mm × 15 mm × 0.2 mm) as cathode, *N*-sulfonyl ketimine **1a** (5 mmol, 915 mg), *N*-phenylglycine **2a** (5 mmol, 755 mg) , formaldehyde **3** (5 mmol, 150 mg), Et_4NI (1.5 mmol, 385.5 mg) and EtOH (30 mL) were added. The reaction mixture was stirred at 40 °C at a constant current of 10 mA for 6 h. The resulting mixture was purified by column chromatography on silica gel (eluted with EA/PE = 1:15) to afford the desired product **4aa** (81%, 1.22 g).



2.3 Cyclic Voltammetry Experiments

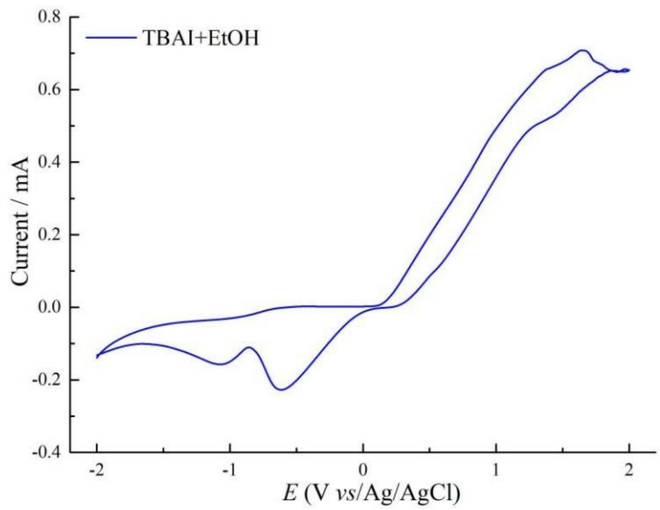


Figure S1. Cyclic voltammogram experiments of TBAI (0.1 M) as electrolyte in EtOH from -2.0 V to +2.0 V at room temperature

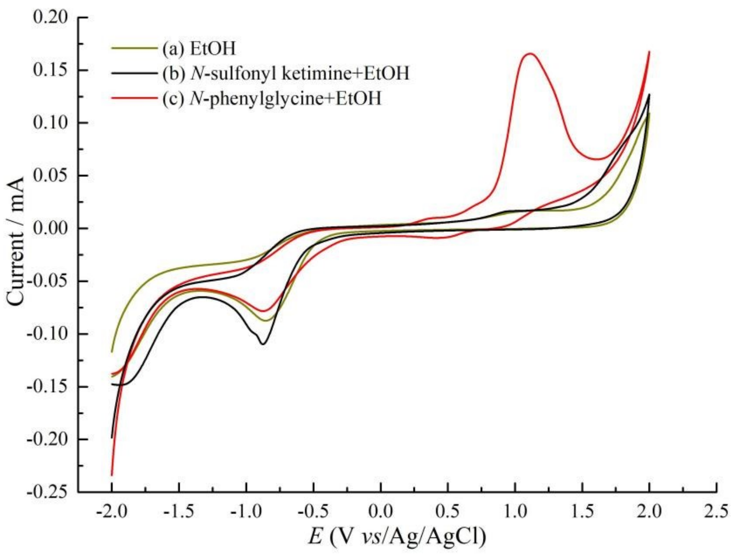


Figure S2. Cyclic voltammogram experiments of blank, **1a** and **2a** in an electrolyte of $LiClO_4$ (0.1 M) in EtOH from -2.0 V to +2.0 V at room temperature

CV measurements were performed on a CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl as counter and reference electrode. As shown in the Figure S1, TBAI (0.1 M) as elctrolyte in 10 mL EtOH. And in the Figure S2, cyclic voltammograms of reactants and their mixtures in 0.1 M $LiClO_4$ glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in EtOH) as counter and reference electrode at 100 mV/s scan rate: 1) EtOH (10 mL) (green line), (2) 10 mM of **1a** in EtOH (10 mL) (black line), (3) 10 mM of **2a** in EtOH (10 mL) (red line).

2.4 ON-OFF Experiment

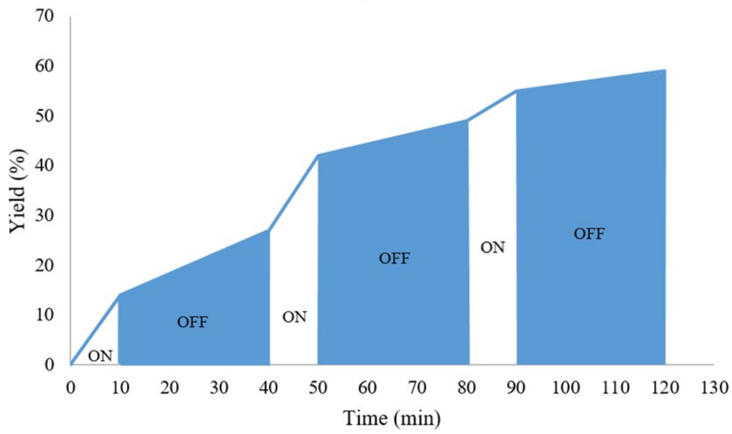
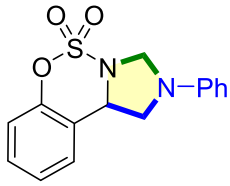


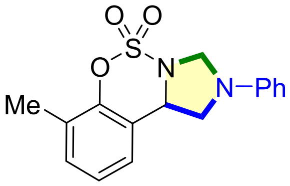
Figure S3. ON-OFF Experiment

As shown in the Figure S3, the reaction between **1a**, **2a** and **3** was conducted under the standard conditons on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under electrolyzing under air at a constant current 5 mA with 10 mins and followed by stirring in the absence of electricity with 30 mins. Compared to the OFF periods, the reaction system was rapidly continued during the ON period. The mixture was then purifide with chromatography column on silica gel (EtOAc: petroleum ether = 10:1) to give the corresponding products **4aa**.

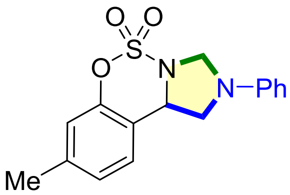
3. Characterization Data for Products



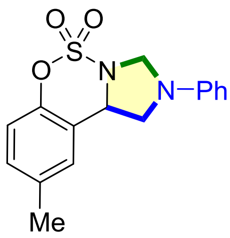
(R)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4aa)[1]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.26 (d, *J* = 9.6 Hz, 4H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 5.47 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.97 (d, *J* = 4.7 Hz, 1H), 4.68 (d, *J* = 4.7 Hz, 1H), 3.98 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.08, 145.04, 129.78, 129.51, 126.52, 126.05, 120.87, 119.33, 119.01, 113.21, 66.04, 61.91, 54.53.



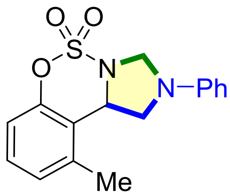
(R)-7-methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ba)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.43 (d, *J* = 5.4 Hz, 1H), 4.96 (d, *J* = 4.7 Hz, 1H), 4.67 (d, *J* = 4.7 Hz, 1H), 3.99 – 3.91 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.50, 144.04, 130.13, 128.45, 127.37, 124.28, 122.92, 119.56, 118.23, 112.17, 65.07, 60.92, 53.70, 14.42.



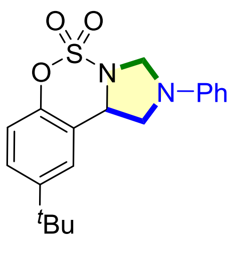
(R)-8-methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ca)[1]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 5.8 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.42 (t, *J* = 3.6 Hz, 1H), 4.94 (dd, *J* = 4.7, 1.3 Hz, 1H), 4.65 (d, *J* = 4.6 Hz, 1H), 3.93 (d, *J* = 3.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.81, 144.05, 139.37, 128.44, 125.89, 125.19, 118.17, 118.15, 116.60, 112.10, 76.25, 64.93, 60.73, 53.43, 19.95.



(R)-9-methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4da)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.02 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 5.40 (t, *J* = 3.8 Hz, 1H), 4.93 (d, *J* = 4.7 Hz, 1H), 4.65 (d, *J* = 4.6 Hz, 1H), 3.94 (d, *J* = 3.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.90, 144.03, 134.87, 129.36, 128.45, 125.71, 119.27, 118.19, 117.63, 112.13, 64.94, 60.85, 53.40, 19.83.

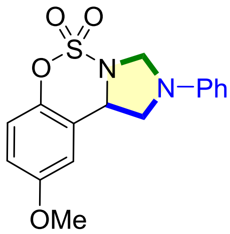


(R)-10-methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ea)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.85 (m, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.44 (dd, *J* = 7.2, 3.5 Hz, 1H), 4.95 (d, *J* = 5.4 Hz, 1H), 4.77 (d, *J* = 5.4 Hz, 1H), 4.11 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.66 (dd, *J* = 9.4, 3.5 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.99, 144.19, 134.97, 128.47, 128.18, 127.42, 119.78, 118.86, 116.06, 113.00, 66.02, 59.92, 53.83, 18.40.

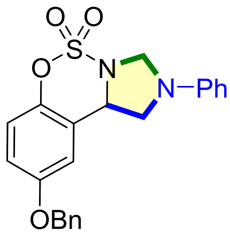


(R)-9-(tert-butyl)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4fa)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 8.7, 2.0 Hz, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.19 (s, 1H), 6.97 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 5.45 (d, *J* = 6.0 Hz, 1H), 4.95 (dd, *J* = 4.6, 1.5 Hz, 1H), 4.68 (dd, *J* = 4.6, 1.5 Hz, 1H), 4.00 (ddd, *J* = 7.8, 6.1, 1.6 Hz, 1H), 3.93 (dd, *J* = 8.9, 1.6 Hz, 1H), 1.31 (d, *J* = 1.6 Hz, 9H). ^{13}C NMR (126 MHz,

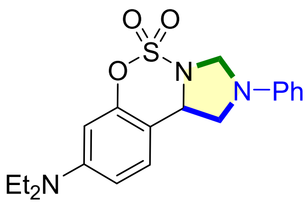
$CDCl_3$) δ 148.23, 147.68, 144.03, 128.47, 126.01, 121.97, 118.82, 118.17, 117.39, 112.11, 65.00, 61.04, 53.59, 33.60, 30.28.



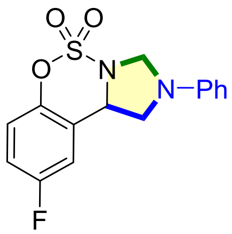
(R)-9-methoxy-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ga)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 2.3 Hz, 2H), 6.91 (d, J = 9.0 Hz, 1H), 6.81-6.75 (m, 2H), 6.65 (d, J = 2.8 Hz, 1H), 6.52 (d, J = 8.1 Hz, 2H), 5.35-5.30 (m, 1H), 4.86 (d, J = 4.7 Hz, 1H), 4.58 (d, J = 4.7 Hz, 1H), 3.90-3.85 (m, 2H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.21, 144.02, 143.71, 128.47, 120.62, 118.84, 118.30, 113.86, 112.20, 110.53, 65.03, 60.96, 54.78, 53.47.



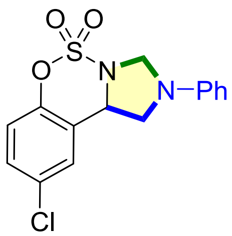
(R)-9-(benzyloxy)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ha): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 4.3 Hz, 4H), 7.20-7.16 (m, 3H), 7.05 (d, J = 8.7 Hz, 1H), 6.81-6.74 (m, 2H), 6.56 (d, J = 2.5 Hz, 1H), 6.50 (d, J = 8.1 Hz, 2H), 5.32 (dd, J = 4.9, 2.1 Hz, 1H), 4.96 (d, J = 1.5 Hz, 2H), 4.86 (d, J = 4.6 Hz, 1H), 4.58 (d, J = 4.6 Hz, 1H), 3.87-3.82 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.55, 150.65, 144.02, 134.93, 128.46, 127.72, 127.28, 126.42, 126.14, 118.16, 112.66, 112.06, 111.62, 103.68, 69.43, 64.90, 60.51, 53.40. HRMS: calcd for $C_{22}H_{21}N_2O_4S^+$ $[M+H]^+$, 409.1217, found 409.1220.



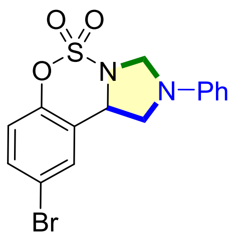
(R)-7-(diethylamino)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3ia)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 7.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 1H), 6.82 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 8.0 Hz, 2H), 6.49 (dd, J = 8.8, 2.6 Hz, 1H), 6.22 (d, J = 2.6 Hz, 1H), 5.38 – 5.33 (m, 1H), 4.91 (d, J = 4.5 Hz, 1H), 4.65 (d, J = 4.5 Hz, 1H), 3.89 (d, J = 4.0 Hz, 2H), 3.31 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.05, 147.71, 144.18, 128.39, 125.93, 117.73, 111.83, 108.47, 104.69, 99.28, 64.73, 60.45, 53.25, 43.43, 11.36.



(R)-9-fluoro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ja)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 6.0 Hz, 2H), 6.97 (d, J = 8.2 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 5.41 (d, J = 5.1 Hz, 1H), 4.96 (d, J = 4.7 Hz, 1H), 4.65 (d, J = 4.7 Hz, 1H), 3.94 (d, J = 5.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ158.68 (d, J = 248.2 Hz), 145.95 (d, J = 3.8 Hz), 143.85, 128.52, 121.49 (d, J = 6.3 Hz), 119.60 (d, J = 8.82 Hz), 118.59, 115.85 (d, J = 22.68 Hz), 112.32, 112.08 (d, J = 25.2 Hz), 65.09, 60.79 (d, J = 12.6 Hz), 53.45. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.71.

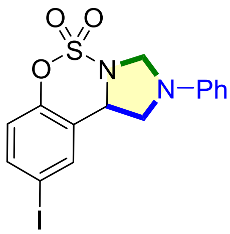


(R)-9-chloro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ka)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 3H), 7.24 (d, J = 2.5 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 7.9 Hz, 2H), 5.44 – 5.39 (m, 1H), 4.96 (d, J = 4.7 Hz, 1H), 4.65 (d, J = 4.8 Hz, 1H), 3.94 (d, J = 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.58, 143.83, 130.26, 128.87, 128.53, 125.42, 121.50, 119.41, 118.64, 112.35, 65.09, 60.67, 53.45.

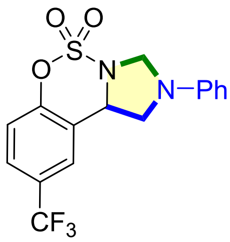


(R)-9-bromo-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4la)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.8, 2.3 Hz, 1H), 7.26 (d, J = 2.3 Hz, 1H), 7.15

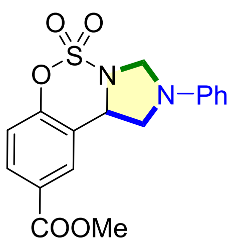
(t, J = 7.8 Hz, 2H), 6.81 (d, J = 8.7 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 8.0 Hz, 2H), 5.28 (t, J = 3.6 Hz, 1H), 4.82 (d, J = 4.8 Hz, 1H), 4.51 (d, J = 4.8 Hz, 1H), 3.80 (d, J = 3.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.14, 143.82, 131.78, 128.37, 121.89, 119.68, 118.63, 117.65, 112.36, 65.09, 60.56, 53.46.



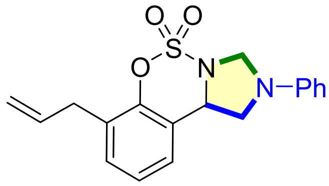
(R)-9-iodo-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ma)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 6.84 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 5.37 (t, J = 3.6 Hz, 1H), 4.92 (d, J = 4.7 Hz, 1H), 4.61 (d, J = 4.7 Hz, 1H), 3.90 (d, J = 3.6 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 150.01, 143.81, 137.66, 134.26, 128.52, 122.20, 119.89, 118.62, 112.35, 88.17, 65.08, 60.34, 53.46.



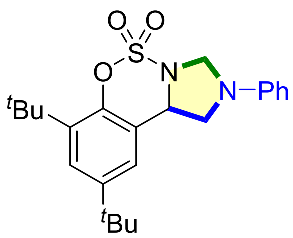
(R)-2-phenyl-9-(trifluoromethyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4na)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.6 Hz, 1H), 7.54 (s, 1H), 7.32 – 7.24 (m, 2H), 7.18 (d, J = 8.6 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 5.49 (d, J = 5.1 Hz, 1H), 5.00 (d, J = 4.8 Hz, 1H), 4.67 (d, J = 4.8 Hz, 1H), 3.98 (t, J = 3.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.43, 152.38, 143.75, 128.56, 127.44 (q, J = 32.76 Hz), 125.98 (q, J = 3.78 Hz), 122.98 (q, J = 3.78 Hz), 120.83, 120.18, 118.82, 112.46, 65.21, 60.78, 53.63. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.31.



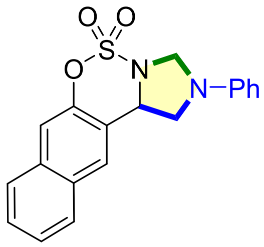
Methyl (R)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine-9-carboxylate 5,5-dioxide (3oa)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.11 – 7.05 (m, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 5.46 (d, *J* = 5.6 Hz, 1H), 4.96 (d, *J* = 4.7 Hz, 1H), 4.64 (d, *J* = 4.8 Hz, 1H), 4.03 – 3.92 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.44, 153.28, 143.82, 130.07, 128.51, 127.44, 126.92, 120.02, 118.60, 118.19, 112.34, 65.09, 60.79, 53.56, 51.50.



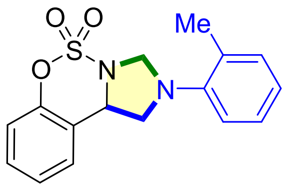
(R)-7-allyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4pa)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 7.08 (dd, *J* = 7.3, 2.2 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.60 – 6.54 (m, 2H), 5.91 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.42 (dd, *J* = 5.7, 1.8 Hz, 1H), 5.13 – 5.03 (m, 2H), 4.93 (d, *J* = 4.7 Hz, 1H), 4.65 (d, *J* = 4.8 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.48 – 3.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.09, 144.04, 133.98, 129.39, 129.33, 128.45, 124.52, 123.49, 119.80, 118.27, 115.88, 112.20, 65.13, 60.94, 53.75, 32.29.



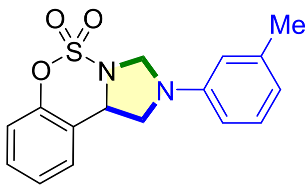
(R)-7,9-di-tert-butyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4qa)[2]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.6 Hz, 1H), 7.24 (d, *J* = 6.7 Hz, 2H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 2H), 5.39 (d, *J* = 6.2 Hz, 1H), 4.92 (d, *J* = 4.8 Hz, 1H), 4.69 (d, *J* = 4.8 Hz, 1H), 4.00 (dd, *J* = 9.0, 6.4 Hz, 1H), 3.85 (dd, *J* = 9.1, 1.9 Hz, 1H), 1.39 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.14, 146.89, 144.16, 138.40, 128.46, 123.50, 120.09, 119.51, 118.19, 112.27, 65.47, 61.22, 54.29, 34.10, 33.73, 30.34, 28.99.



(R)-2-phenyl-1,2,3,12b-tetrahydroimidazo[1,5-c]naphtho[2,3-e][1,2,3]oxathiazine 5,5-dioxide (4ra)[2]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 14.5, 6.8 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 2H), 5.94 (dd, *J* = 7.2, 2.4 Hz, 1H), 5.05 (d, *J* = 5.2 Hz, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 4.26 (dd, *J* = 9.2, 7.1 Hz, 1H), 3.98 (dd, *J* = 9.3, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.68, 144.01, 130.66, 129.82, 128.99, 128.43, 128.41, 126.82, 124.89, 121.43, 118.66, 117.41, 114.25, 112.74, 65.98, 59.98, 54.15.

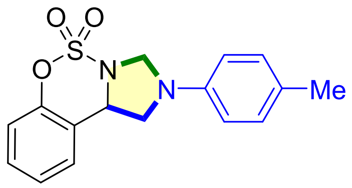


(R)-2-(o-tolyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ab): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 8.5, 4.4 Hz, 1H), 7.24 (d, *J* = 4.5 Hz, 2H), 7.15 (t, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 6.7 Hz, 2H), 5.44 (t, *J* = 3.6 Hz, 1H), 4.95 (d, *J* = 4.7 Hz, 1H), 4.66 (d, *J* = 4.7 Hz, 1H), 3.95 (d, *J* = 3.8 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.04, 144.04, 138.40, 128.70, 128.32, 125.49, 124.99, 119.87, 119.19, 117.94, 112.96, 109.33, 65.02, 60.87, 53.51, 20.64. HRMS: calcd for $C_{16}H_{17}N_2O_3S^+$ $[M+H]^+$, 317.0955, found 317.0953.

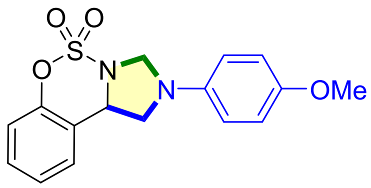


(R)-2-(m-tolyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ac): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 8.5, 4.4 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 7.1 Hz, 2H), 5.45 (s, 1H), 4.95 (d, *J* = 4.7 Hz, 1H), 4.66 (d, *J* = 4.6 Hz, 1H), 3.95 (d, *J* = 3.6 Hz, 2H), 2.32 (s, 3H). ^{13}C

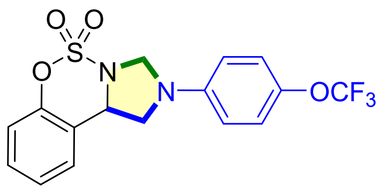
NMR (126 MHz, $CDCl_3$) δ 150.02, 144.03, 138.38, 128.69, 128.31, 125.50, 124.98, 119.86, 119.17, 117.92, 112.95, 109.32, 65.01, 60.86, 53.49, 20.64. HRMS: calcd for $C_{16}H_{17}N_2O_3S^+$ $[M+H]^+$, 317.0955, found 317.0956.



(R)-2-(p-tolyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ad): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (ddd, *J* = 8.6, 6.1, 2.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 9.0 Hz, 2H), 5.40 (dd, *J* = 5.2, 2.4 Hz, 1H), 4.95 (d, *J* = 4.9 Hz, 1H), 4.57 (d, *J* = 4.9 Hz, 1H), 3.90 – 3.85 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.49, 150.06, 138.59, 128.58, 125.40, 124.96, 120.26, 117.98, 113.98, 113.96, 66.15, 60.86, 54.86, 54.67. HRMS: calcd for $C_{16}H_{17}N_2O_3S^+$ $[M+H]^+$, 317.0955, found 317.0963.

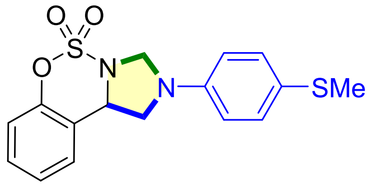


(R)-2-(4-methoxyphenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ae): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 1H), 7.29-7.24 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.87 (dd, *J* = 9.0, 1.1 Hz, 2H), 6.64-6.58 (m, 2H), 5.43 (dd, *J* = 5.2, 2.5 Hz, 1H), 4.99 (dd, *J* = 4.9, 1.1 Hz, 1H), 4.60 (dd, *J* = 4.9, 1.0 Hz, 1H), 3.92-3.87 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.48, 150.06, 138.58, 128.59, 125.39, 124.96, 120.25, 117.98, 113.97, 113.95, 66.14, 60.86, 54.85, 54.67. HRMS: calcd for $C_{16}H_{17}N_2O_4S^+$ $[M+H]^+$, 333.0904, found 333.0912.

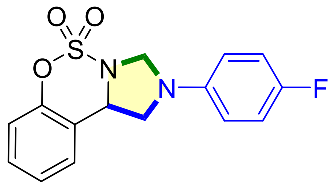


(R)-2-(4-(trifluoromethoxy)phenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4af): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 8.6, 6.4, 2.6 Hz, 1H), 7.25-7.20 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 9.0 Hz, 2H), 5.46 (d, *J* = 5.7 Hz, 1H), 4.91 (d, *J* = 4.7 Hz, 1H), 4.64 (d, *J* = 4.7 Hz, 1H), 4.01-3.88 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.96, 142.72, 140.80, 128.90, 125.46, 125.14, 121.61, 119.56 (q,

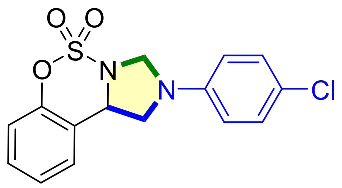
J = 257.1 Hz), 119.53, 118.03, 112.64, 64.94, 60.88, 53.63. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.46. HRMS: calcd for $C_{16}H_{14}F_3N_2O_4S^+$ [M+H]$^+$, 387.0621, found 387.0620.



(R)-2-(4-(methylthio)phenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ag): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 1H), 7.24 (t, J = 5.8 Hz, 4H), 7.04 (d, J = 8.2 Hz, 1H), 6.53 (d, J = 8.3 Hz, 2H), 5.44 (d, J = 5.6 Hz, 1H), 4.92 (d, J = 4.8 Hz, 1H), 4.64 (d, J = 4.7 Hz, 1H), 3.94 (dd, J = 7.1, 3.6 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.99, 142.50, 129.56, 128.80, 126.37, 125.47, 125.06, 119.71, 118.00, 112.86, 65.00, 60.84, 53.61, 17.24. HRMS: calcd for $C_{16}H_{17}N_2O_3S_2^+$ [M+H]$^+$, 349.0676, found 349.0678.

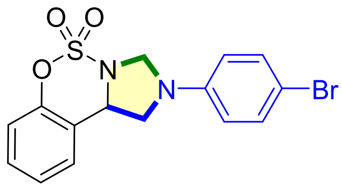


(R)-2-(4-fluorophenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ah): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 1H), 7.26 (d, J = 3.8 Hz, 2H), 7.06 (d, J = 8.2 Hz, 1H), 6.97 (t, J = 8.6 Hz, 2H), 6.54 (dd, J = 9.1, 4.2 Hz, 2H), 5.44 (d, J = 5.6 Hz, 1H), 4.94 (d, J = 4.8 Hz, 1H), 4.61 (d, J = 4.7 Hz, 1H), 3.96-3.86 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.82 (d, J = 238.1 Hz), 150.01, 140.67 (d, J = 2.52 Hz), 128.76, 125.23 (d, J = 44.1 Hz), 120.90 (d, J = 875.7 Hz), 119.87, 118.03, 115.04 (d, J = 22.6 Hz), 113.41 (d, J = 7.5 Hz), 65.61, 60.89, 54.29. ^{19}F NMR (471 MHz, $CDCl_3$) δ -125.08. HRMS: calcd for $C_{15}H_{14}FN_2O_3S^+$ [M+H]$^+$, 321.0704, found 321.0709.



(R)-2-(4-bromophenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4ai): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.2 Hz, 1H), 6.48 (d, J = 8.4 Hz, 2H), 5.45 (d, J = 5.8 Hz, 1H), 4.90 (d, J = 4.7 Hz, 1H), 4.62 (d, J = 4.6 Hz, 1H), 3.94 (dd, J = 9.0, 5.9 Hz, 1H), 3.90 (d, J = 9.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.97, 142.59, 128.86, 128.33, 125.47, 125.11, 123.38, 119.59, 118.04, 113.28, 64.98, 60.85, 53.61. HRMS: calcd for $C_{15}H_{14}ClN_2O_3S^+$ $[M+H]^+$, 337.0408, found 337.0409.



(R)-2-(4-chlorophenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (4aj): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.22 (m, 3H), 7.19-7.13 (m, 2H), 6.99-6.94 (m, 1H), 6.35 (d, J = 8.9 Hz, 2H), 5.37 (d, J = 5.8 Hz, 1H), 4.81 (d, J = 4.7 Hz, 1H), 4.54 (d, J = 4.7 Hz, 1H), 3.89-3.79 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.94, 142.97, 131.19, 128.88, 125.49, 125.13, 119.54, 118.02, 113.70, 110.49, 64.84, 60.82, 53.47. HRMS: calcd for $C_{15}H_{14}BrN_2O_3S^+$ $[M+H]^+$, 380.9904, found 380.9907.

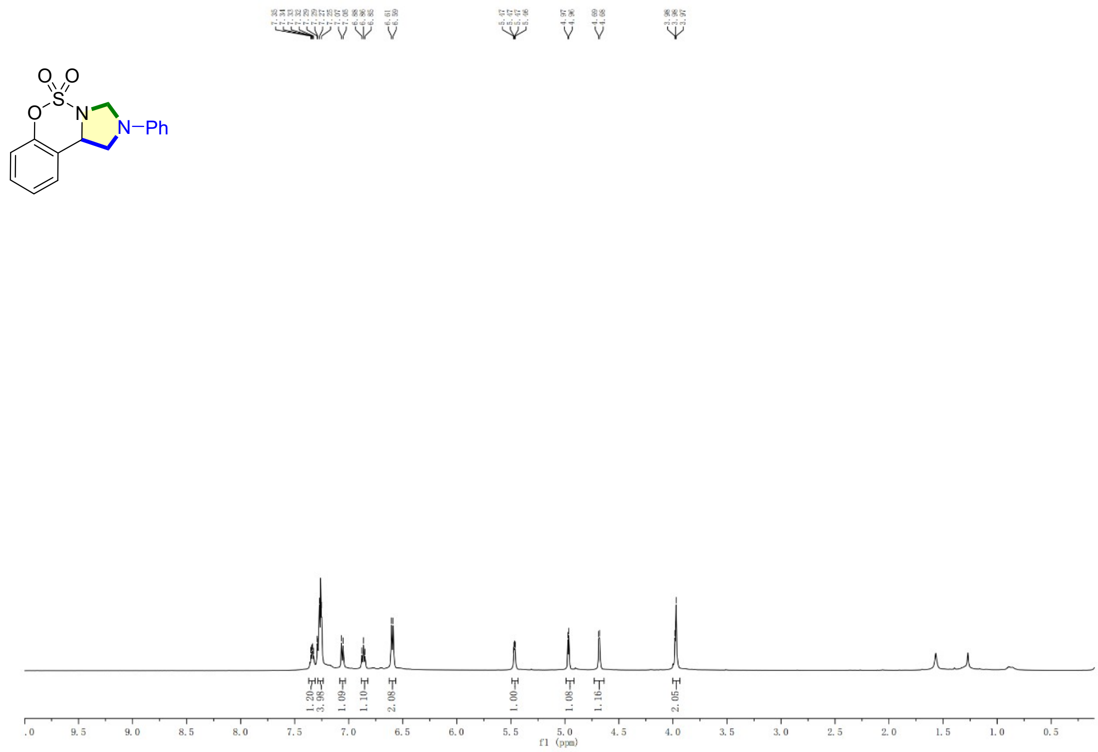
4. Reference

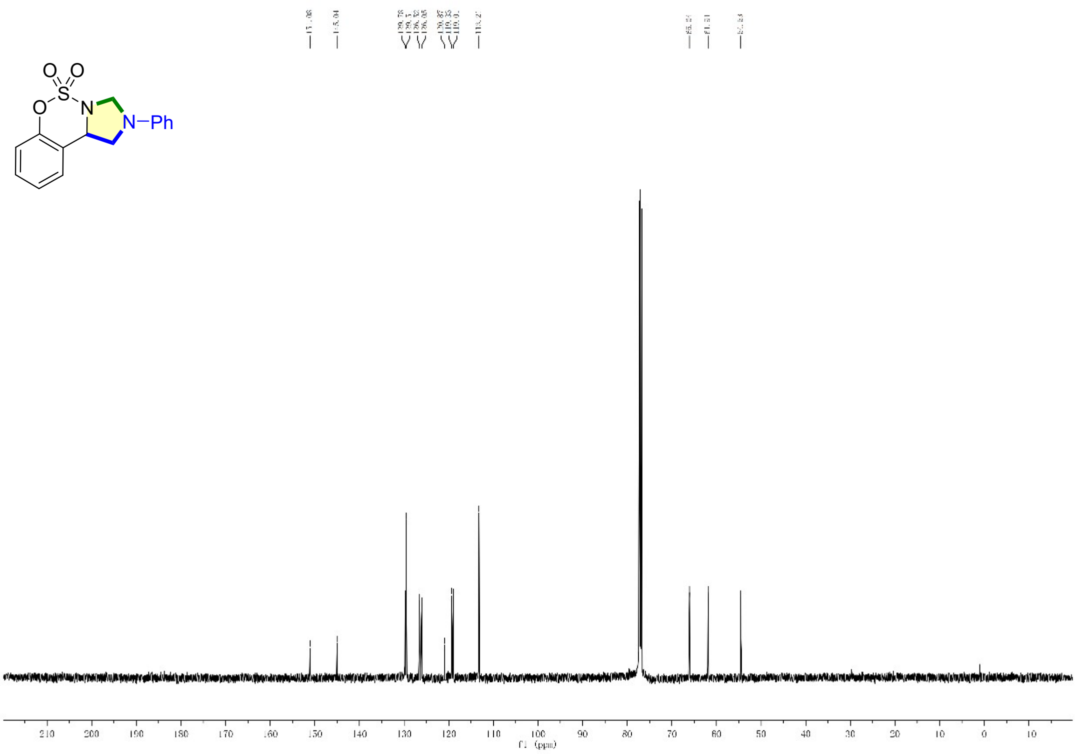
1. Wang, X.; Shi, A.; Huang, X.-Q.; Chen, X.; Li, T.; Qu, L.; Yu, B., *Org. Biomol. Chem.*, **2022,** *20*, 3798-3802.

2. Shi, A.; Sun, K.; Chen, X.; Qu, L.; Zhao, Y.; Yu, B., *Org. Lett.,* **2022,** *24*, 299-303.

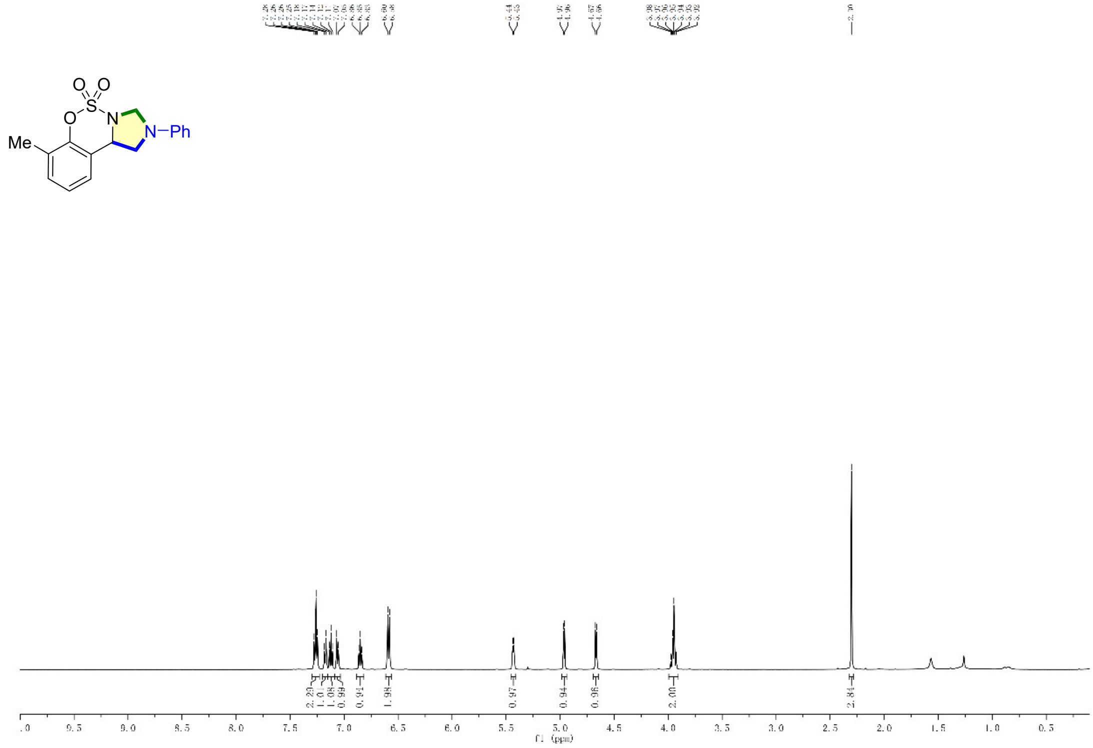
5. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Products

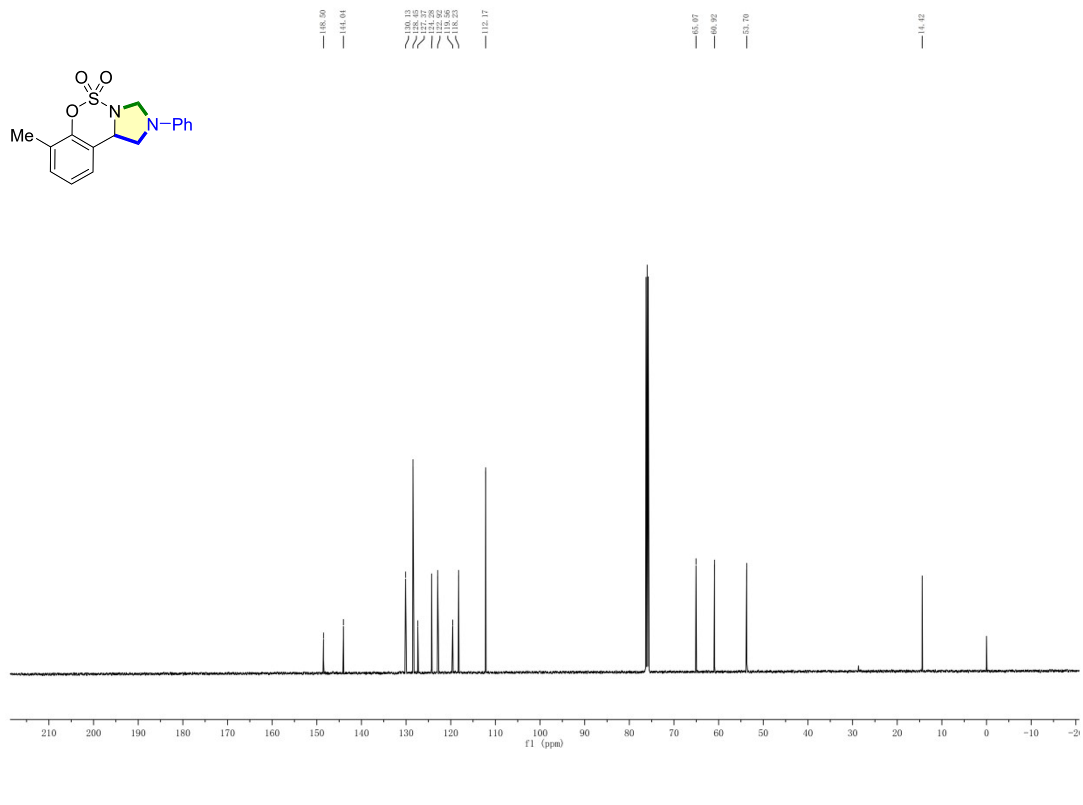
4aa ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



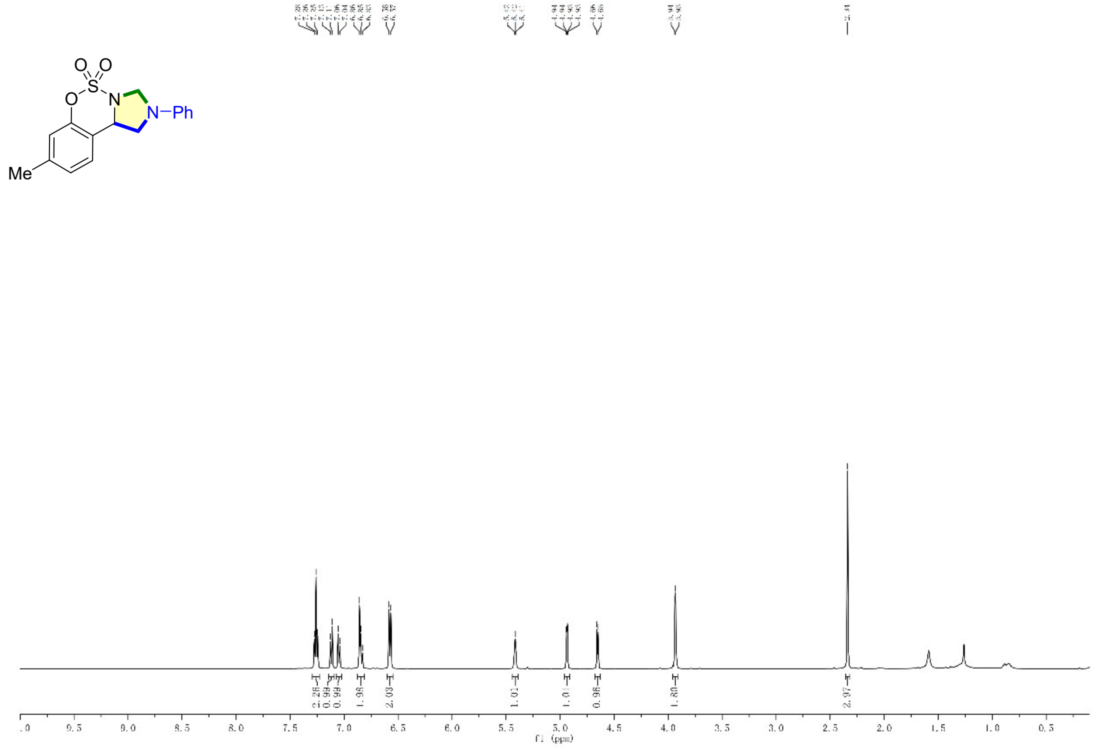


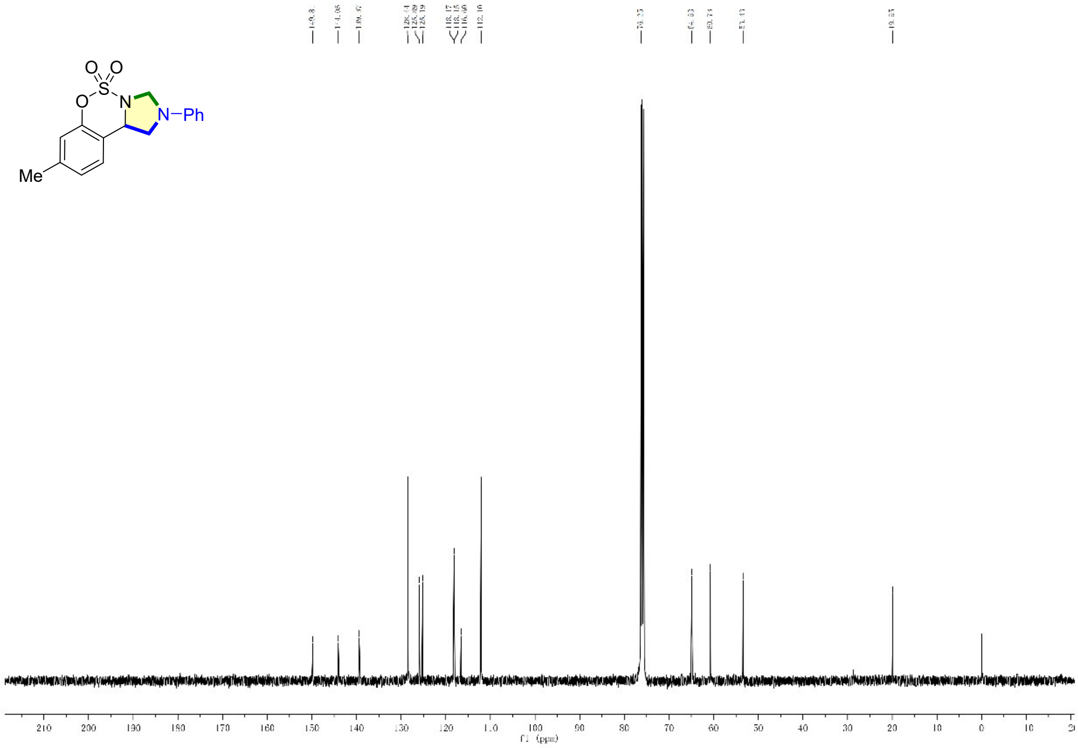
4ba ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



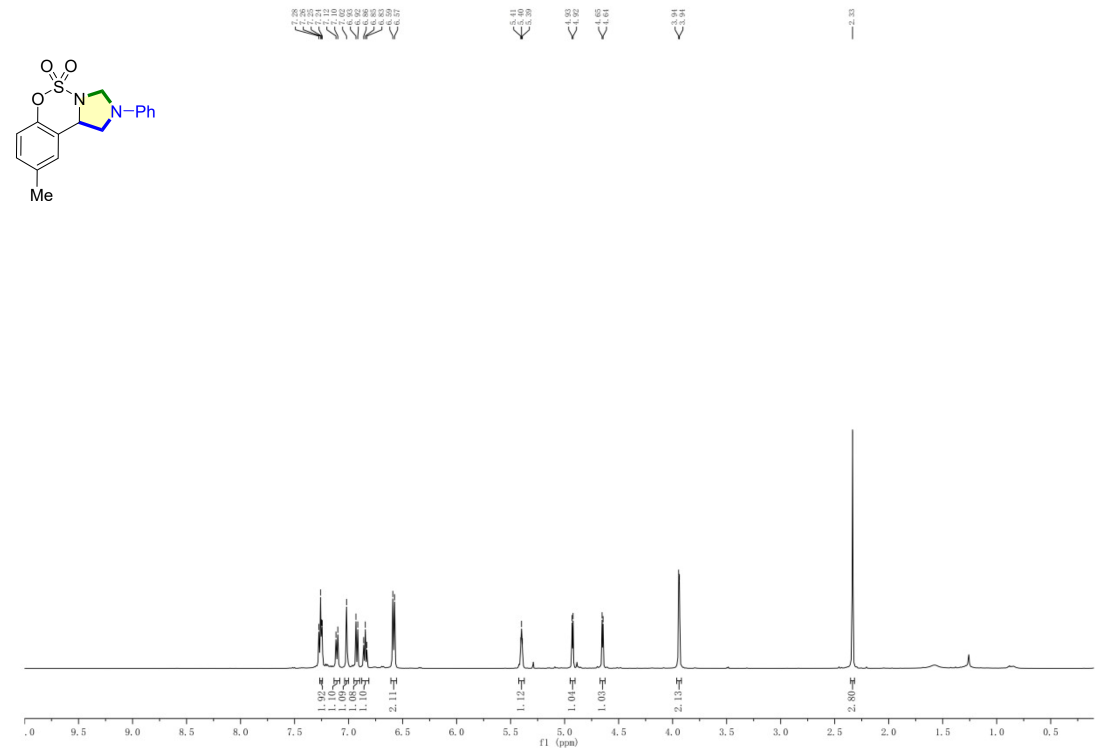


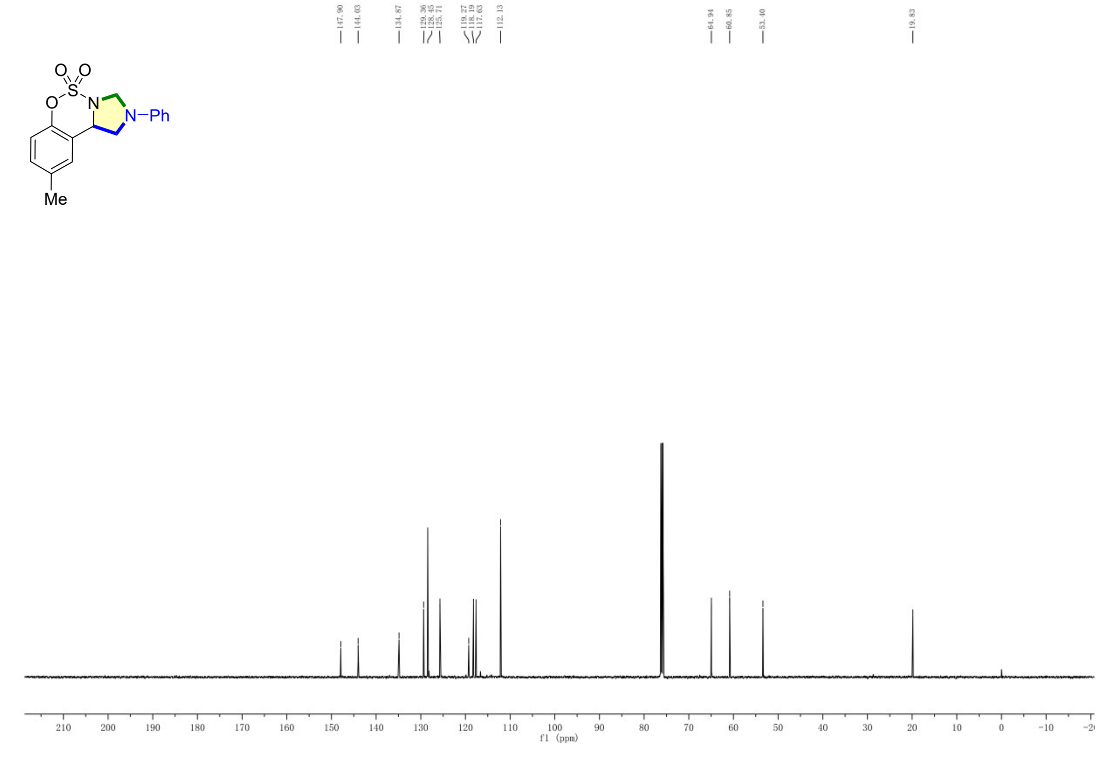
4ca ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



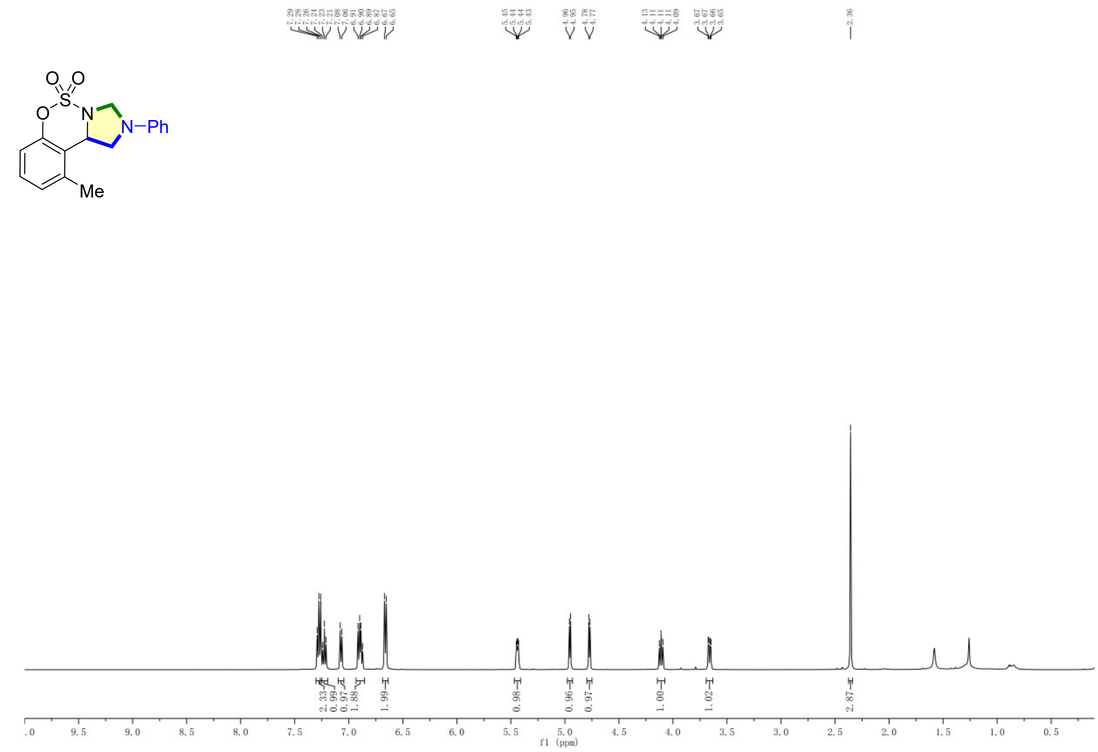


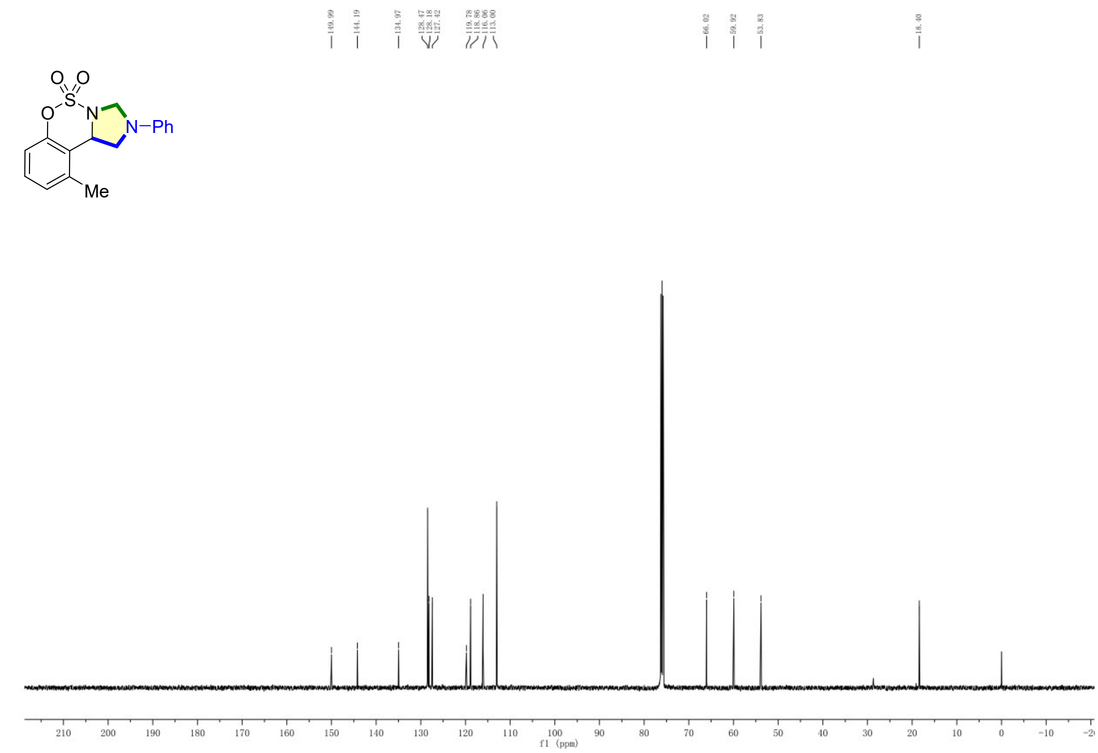
4da ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



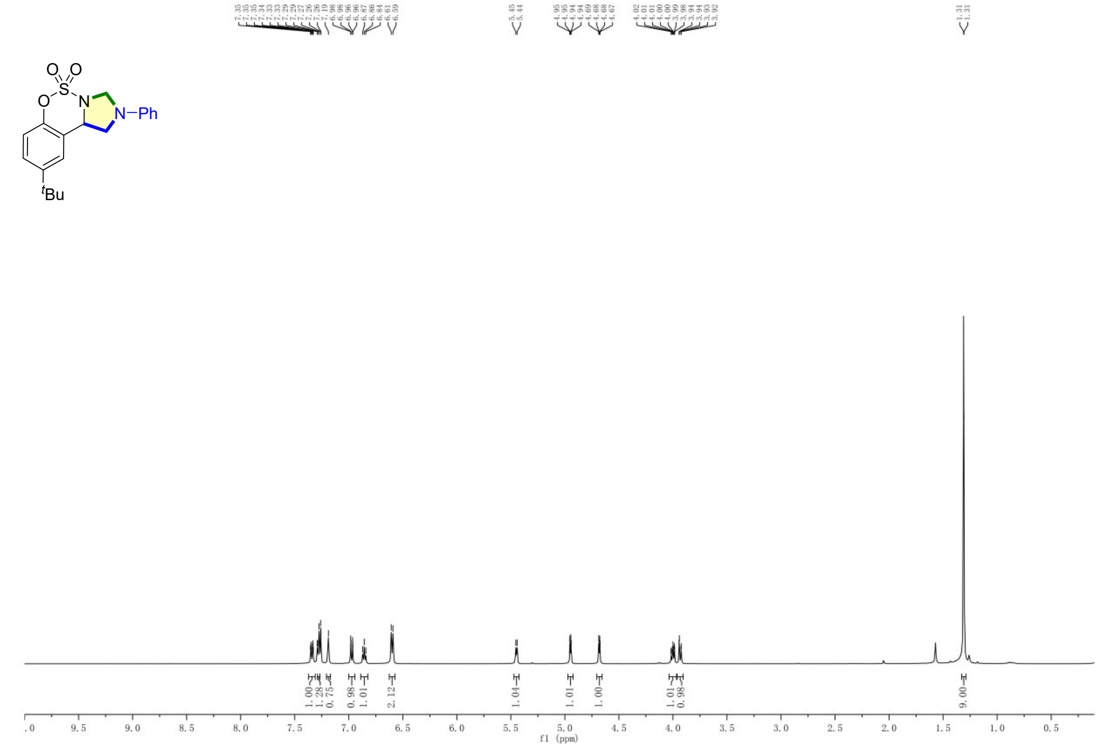


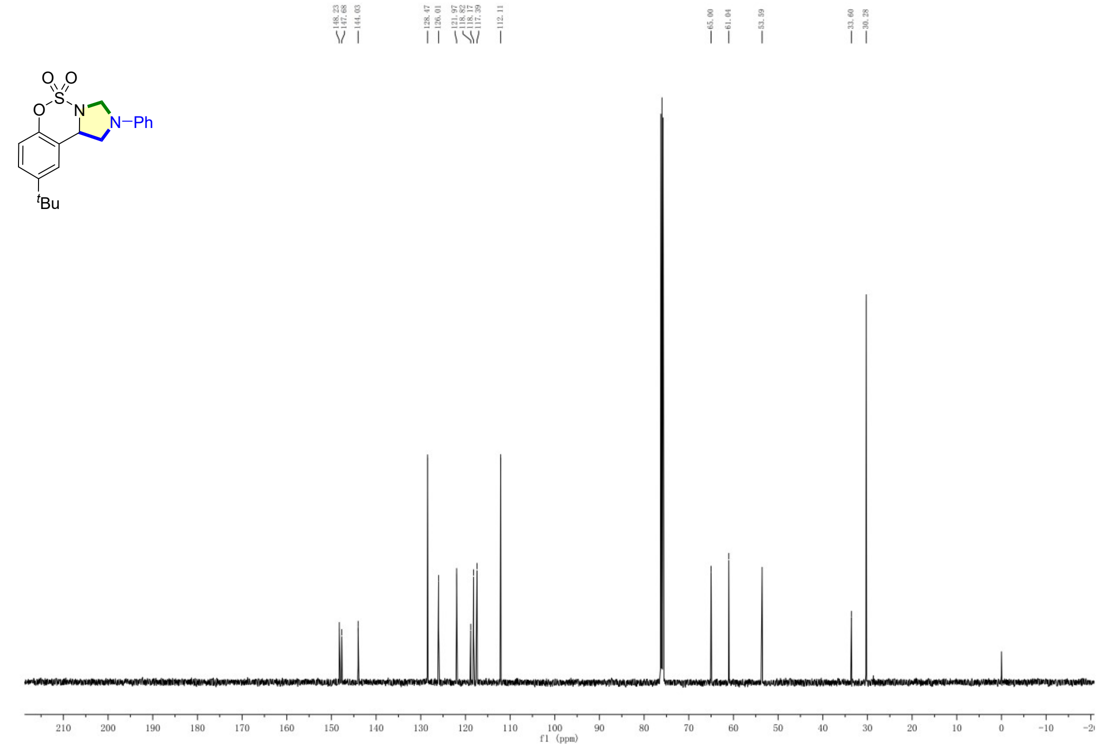
4ea ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



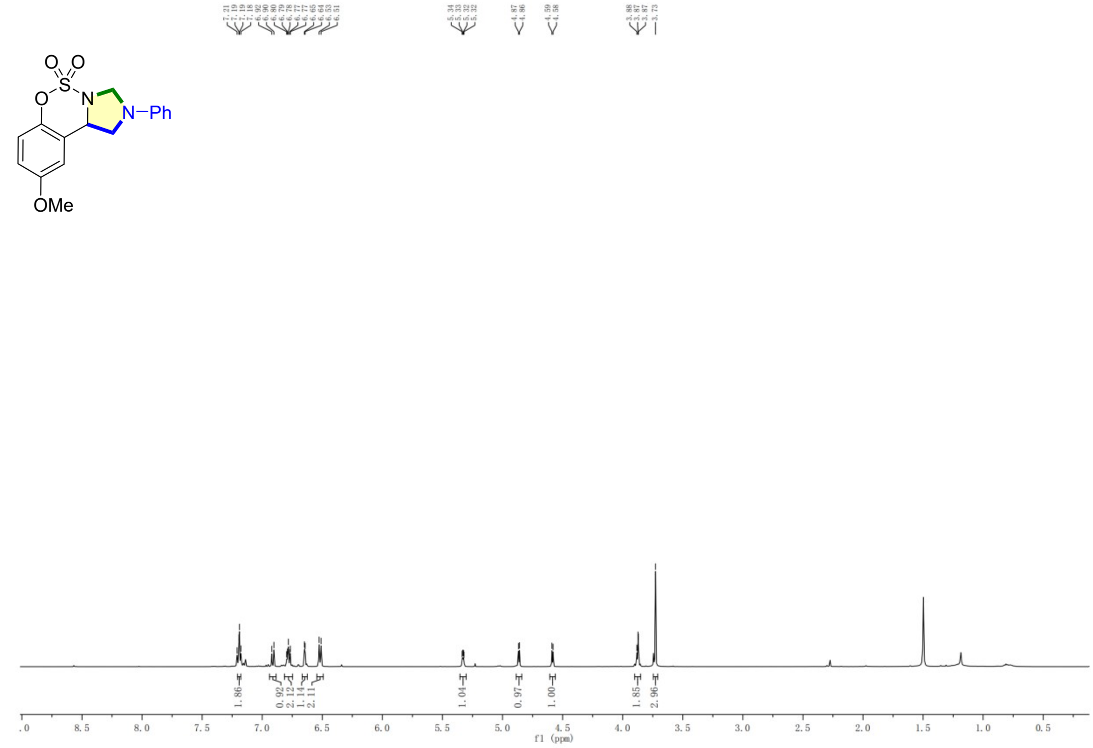


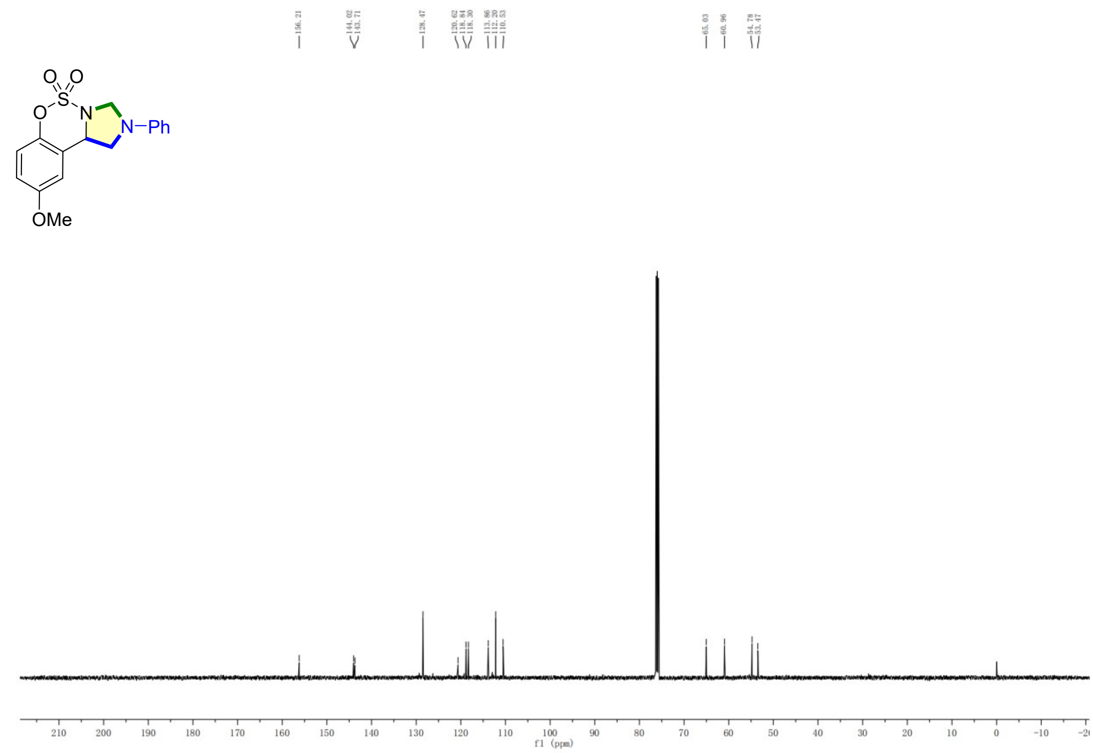
4fa ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



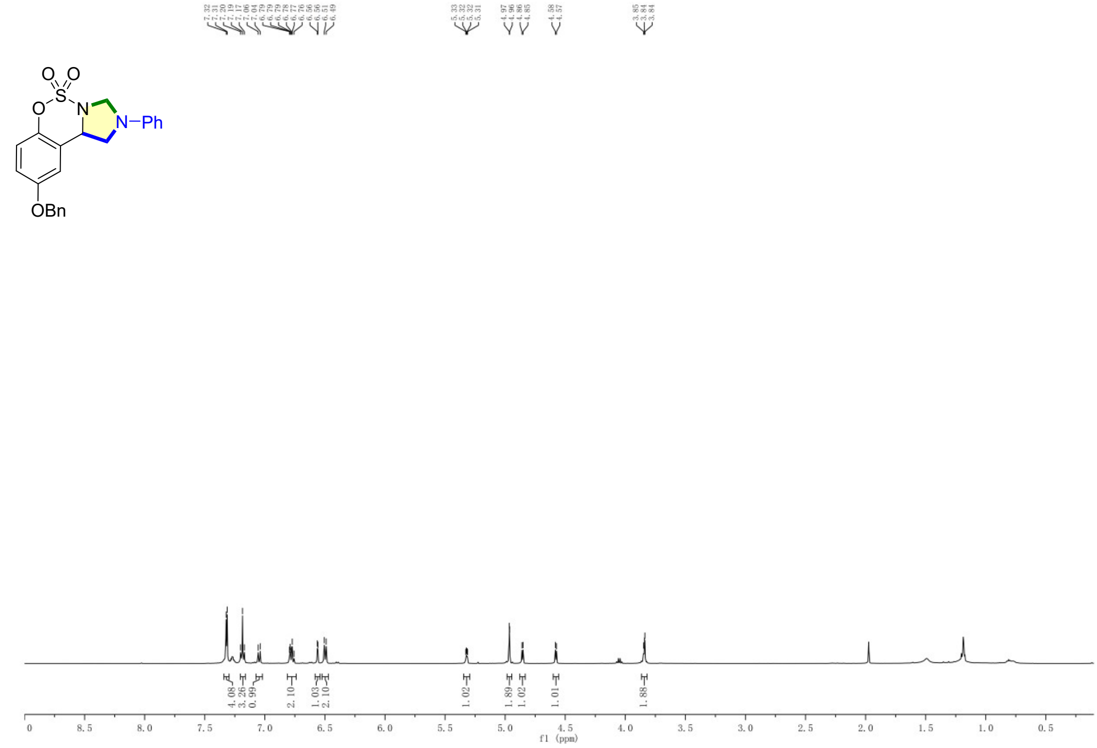


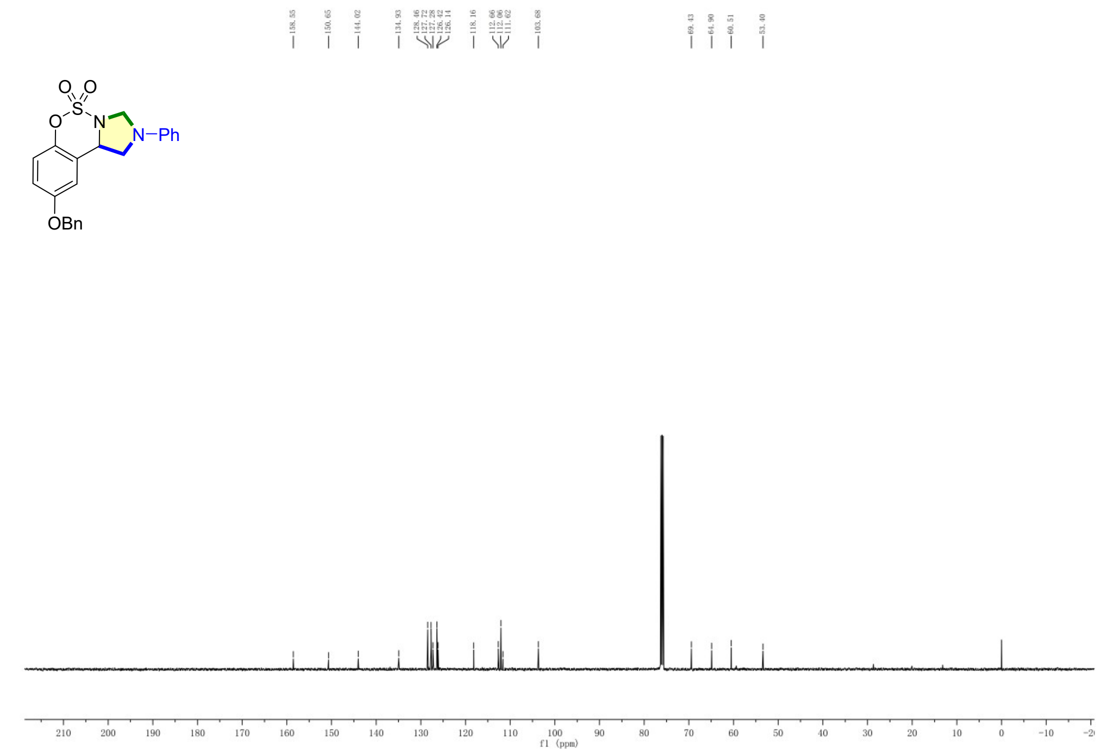
4ga ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



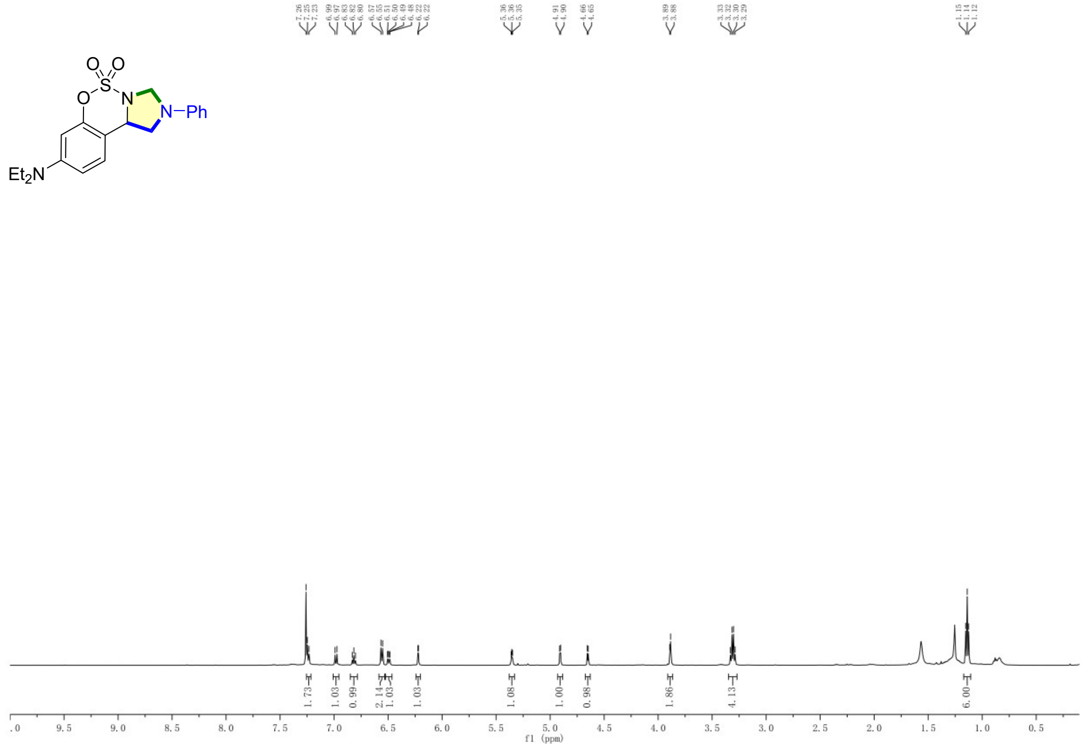


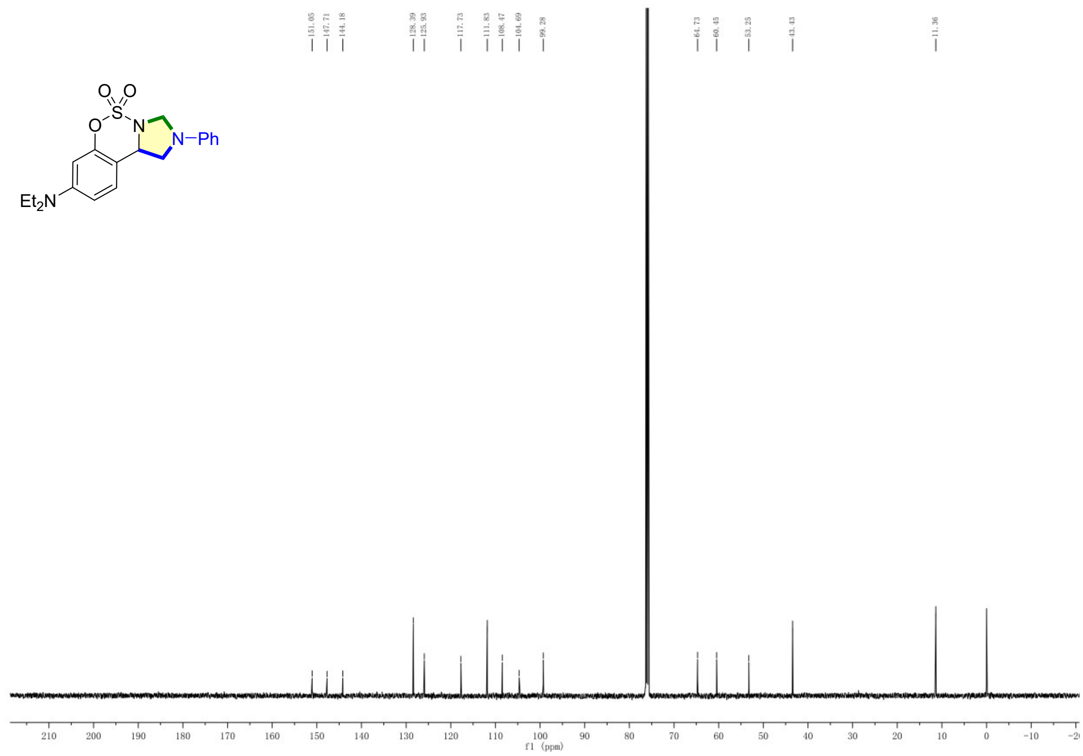
4ha ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



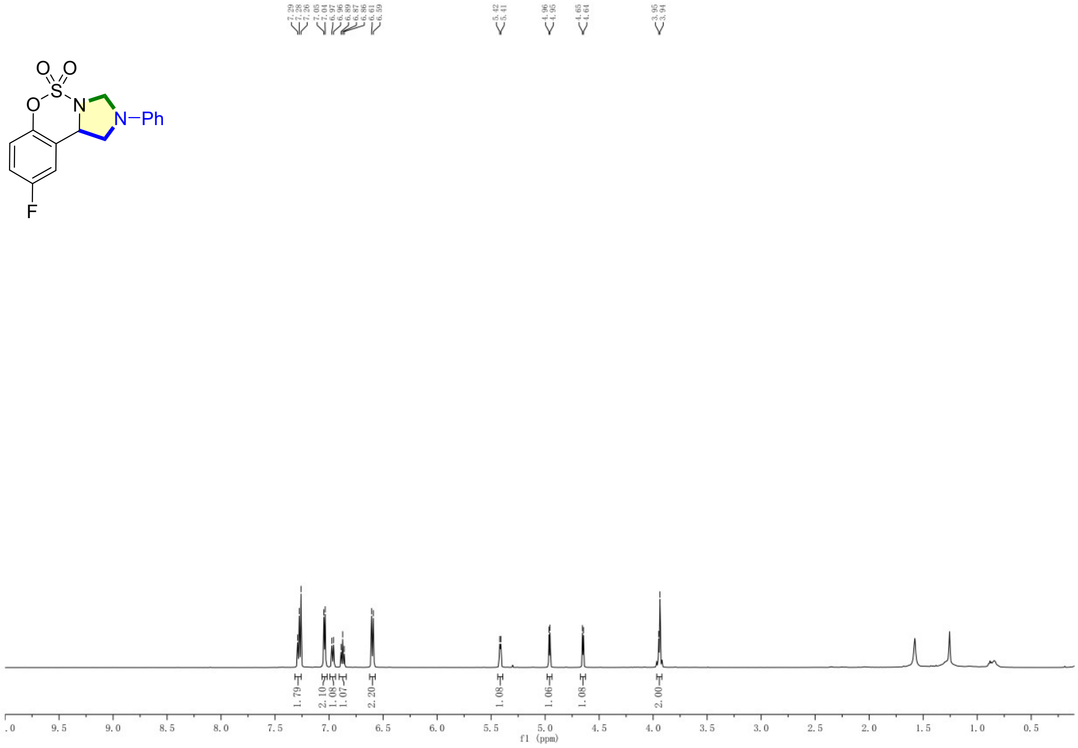


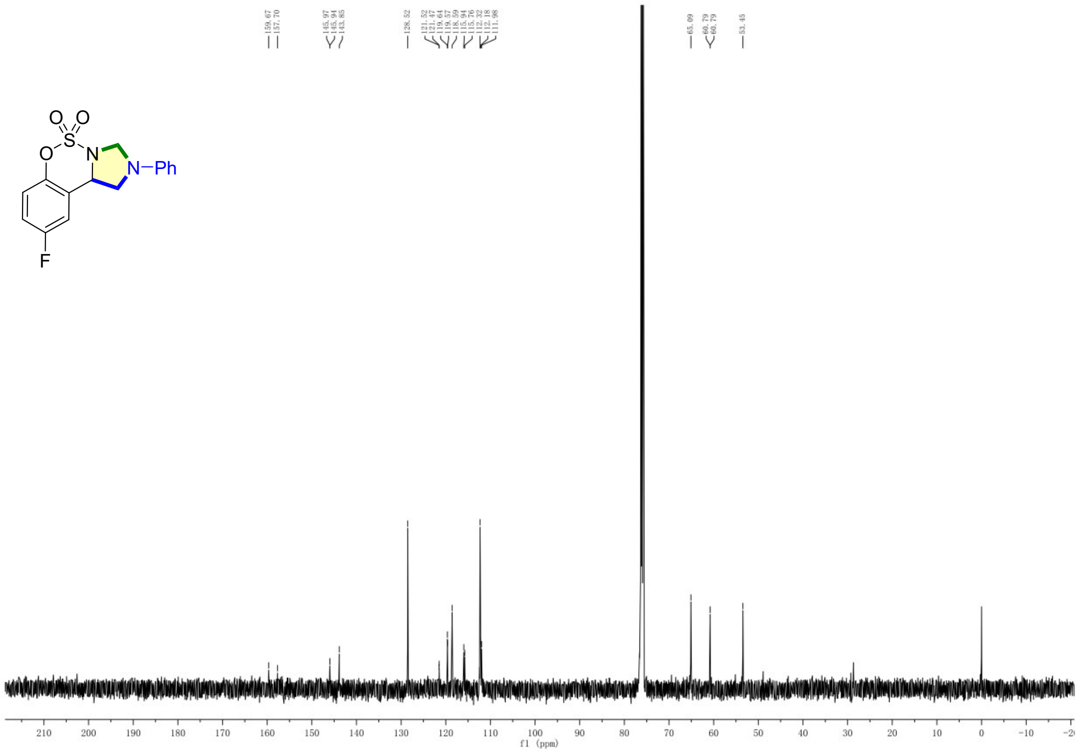
4ia ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)

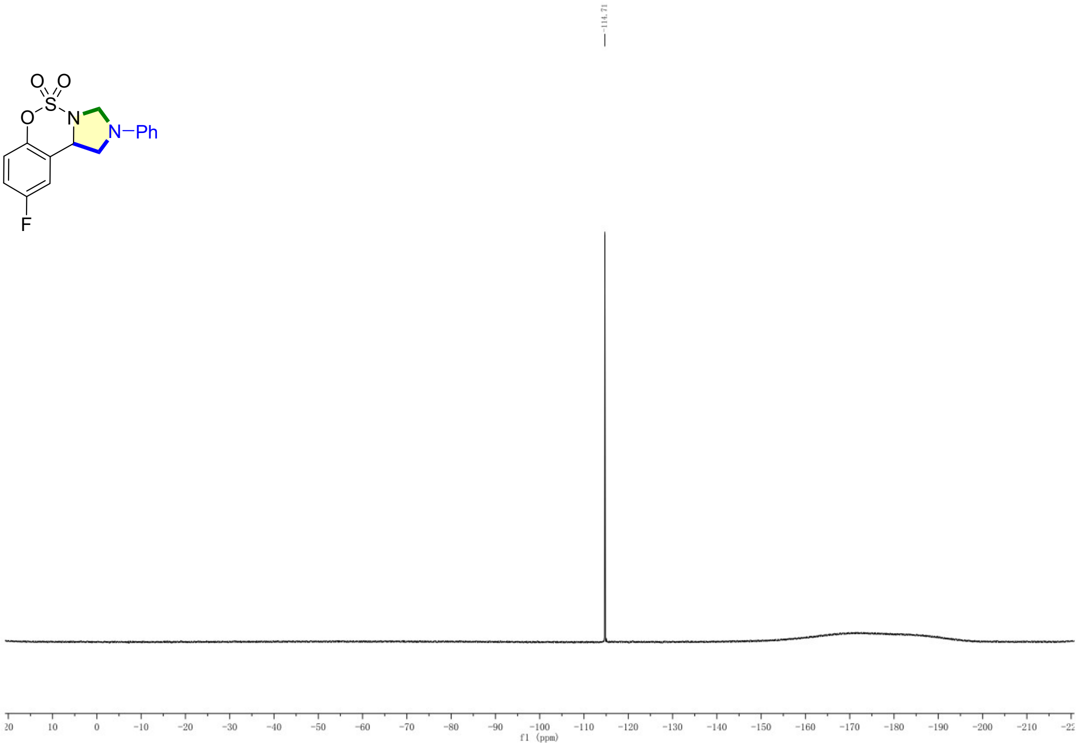




4ja ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{19}F NMR (471 MHz)


N−Ph
F
f1 (ppm)


N−Ph
F
f1 (ppm)



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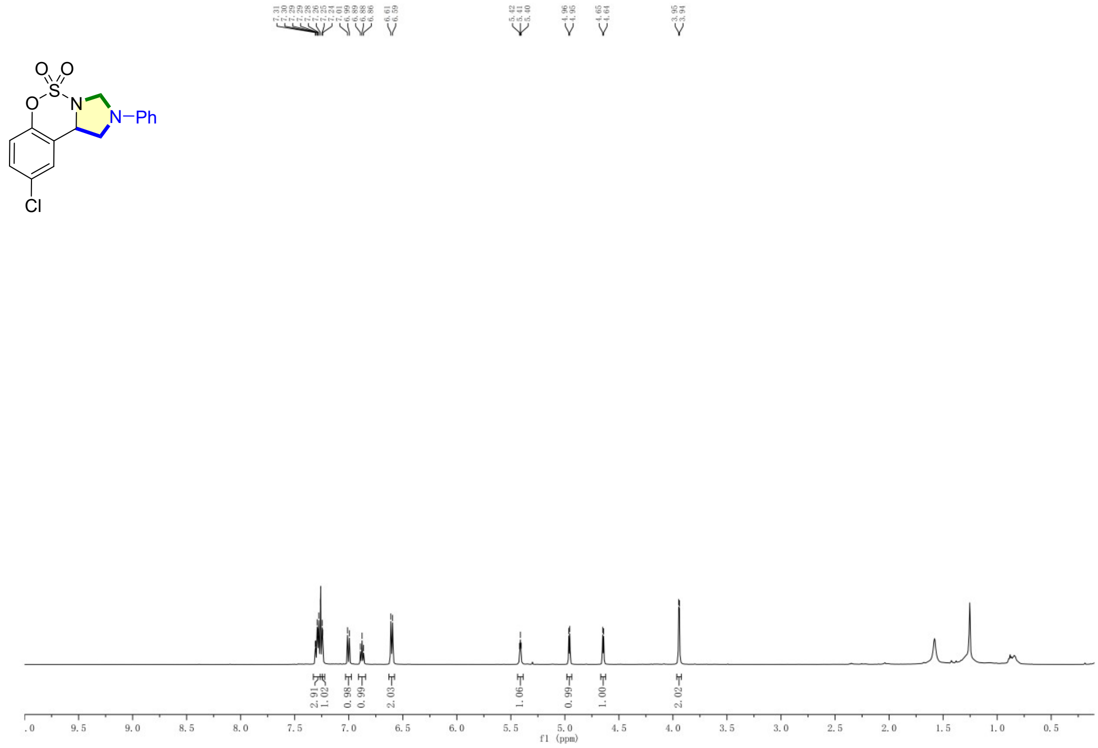

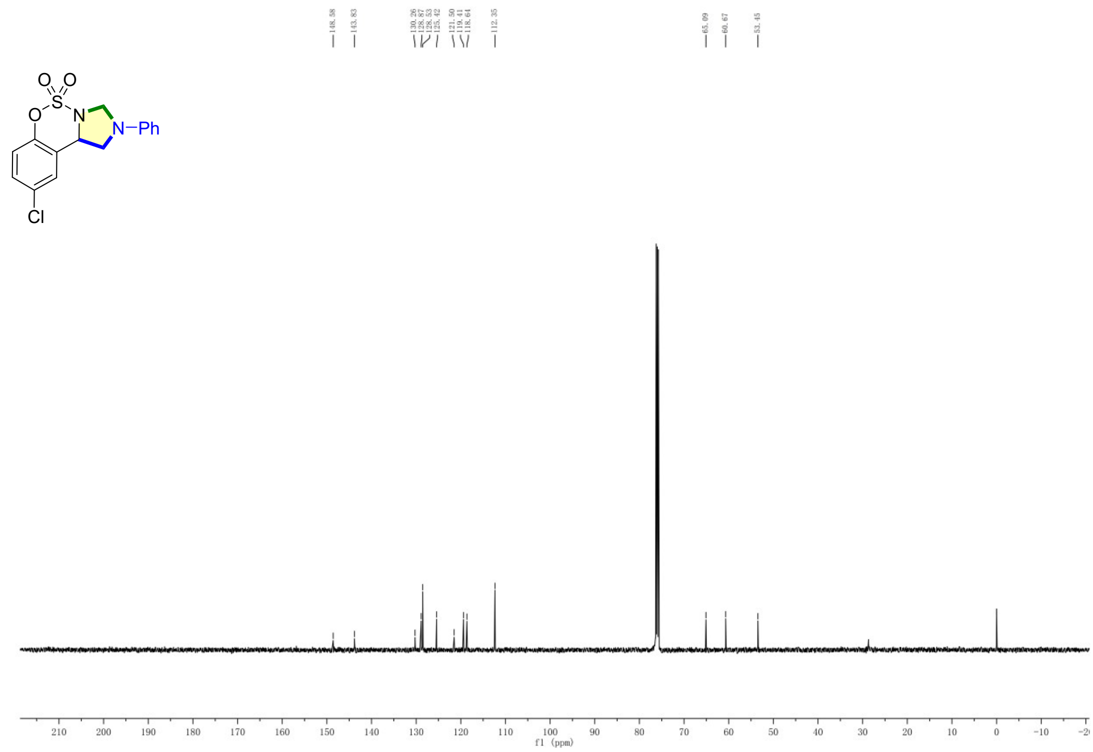

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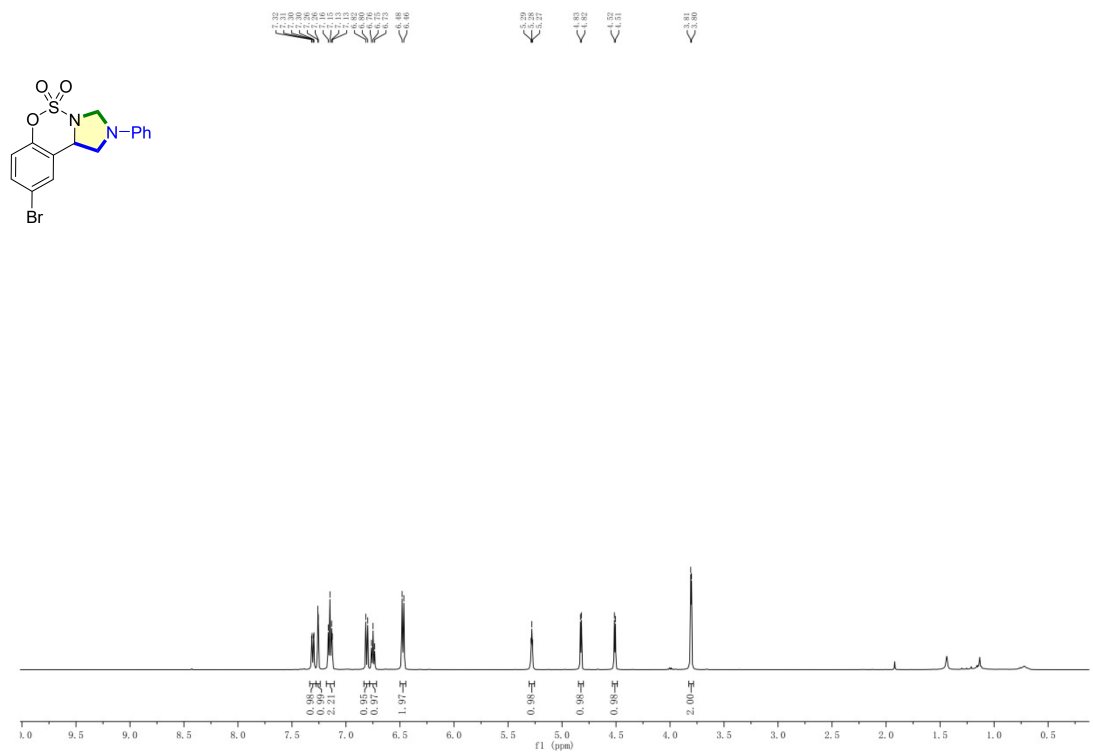
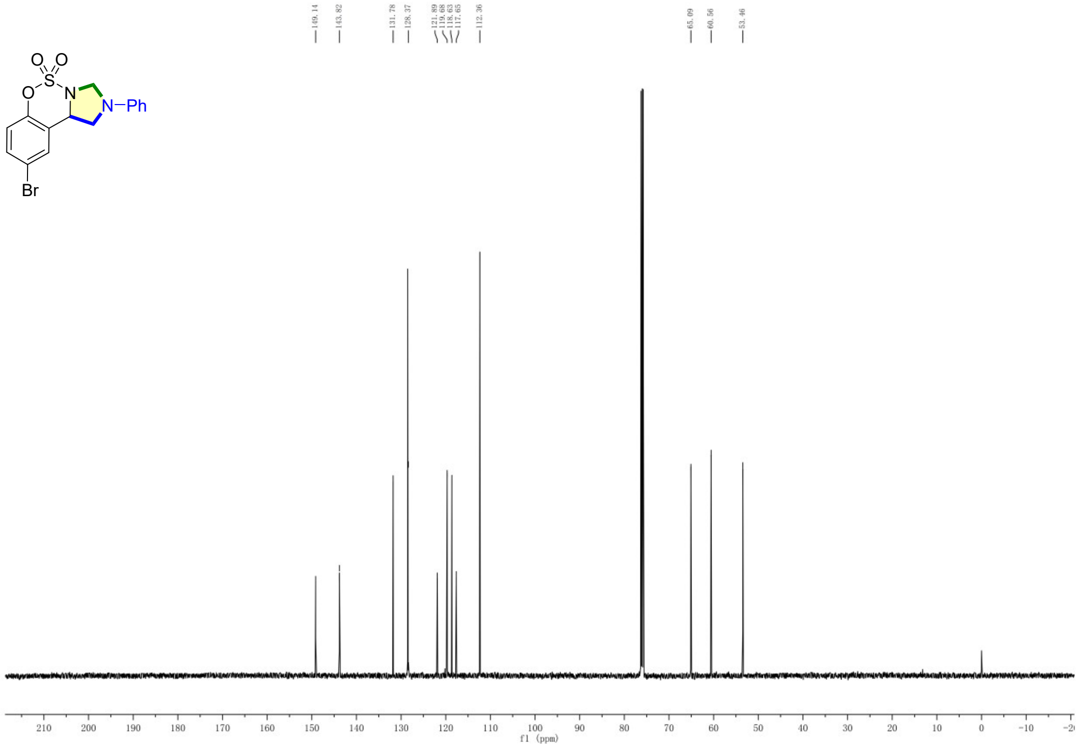
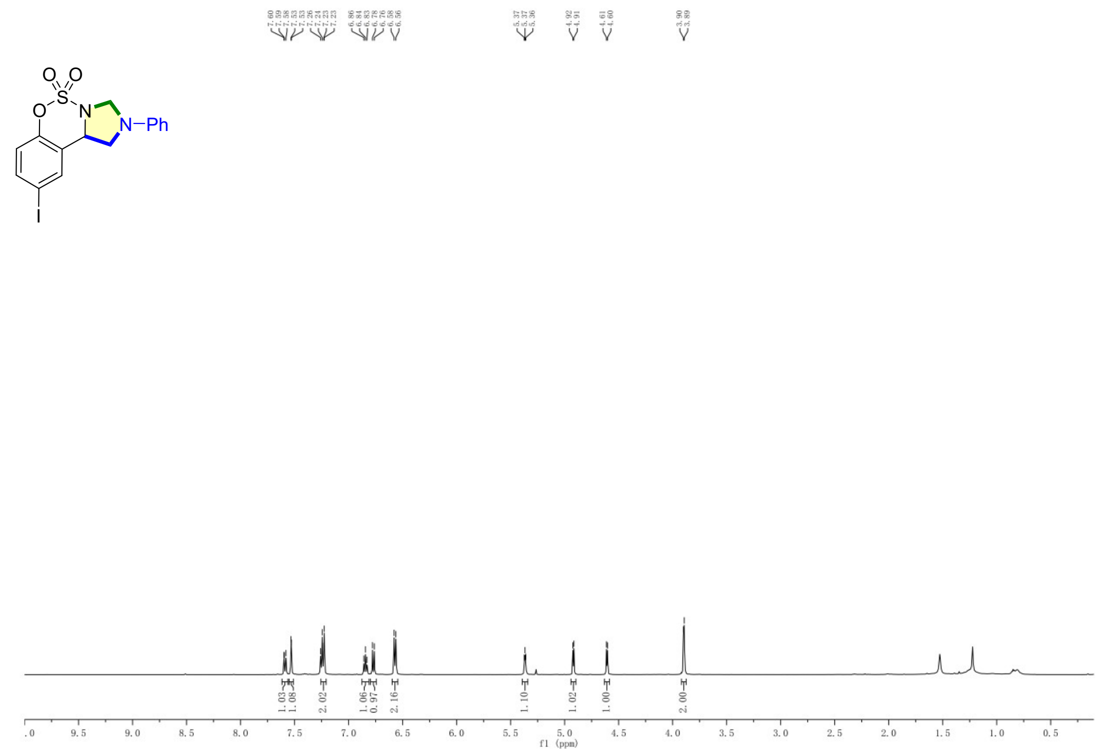
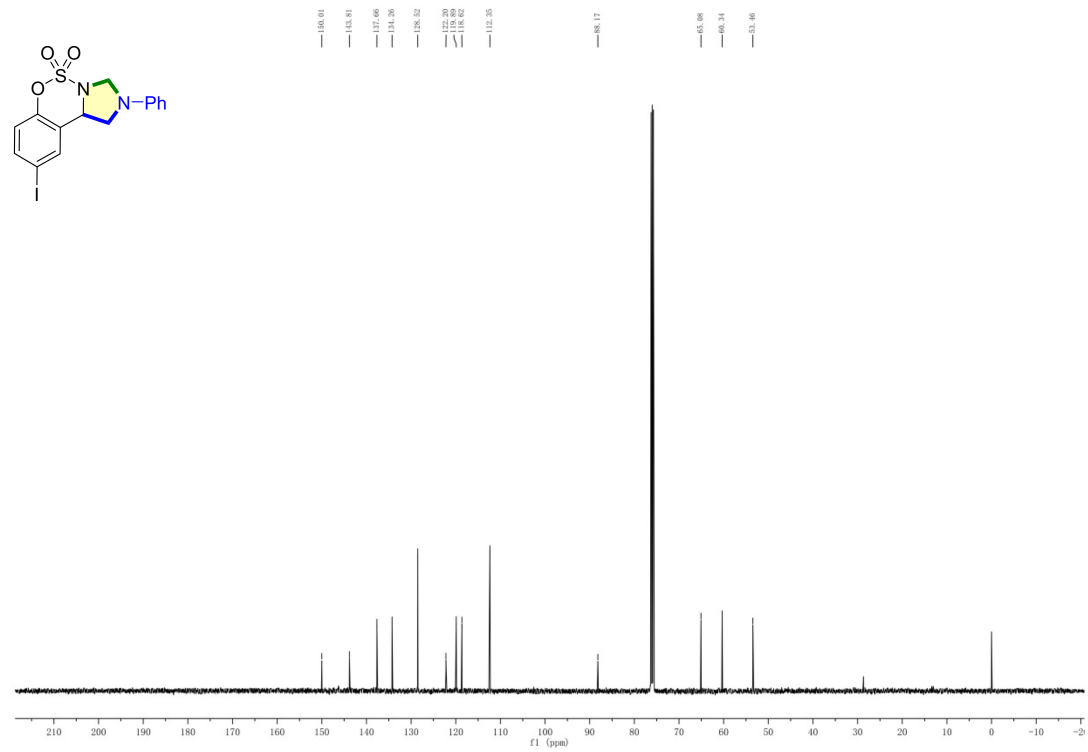


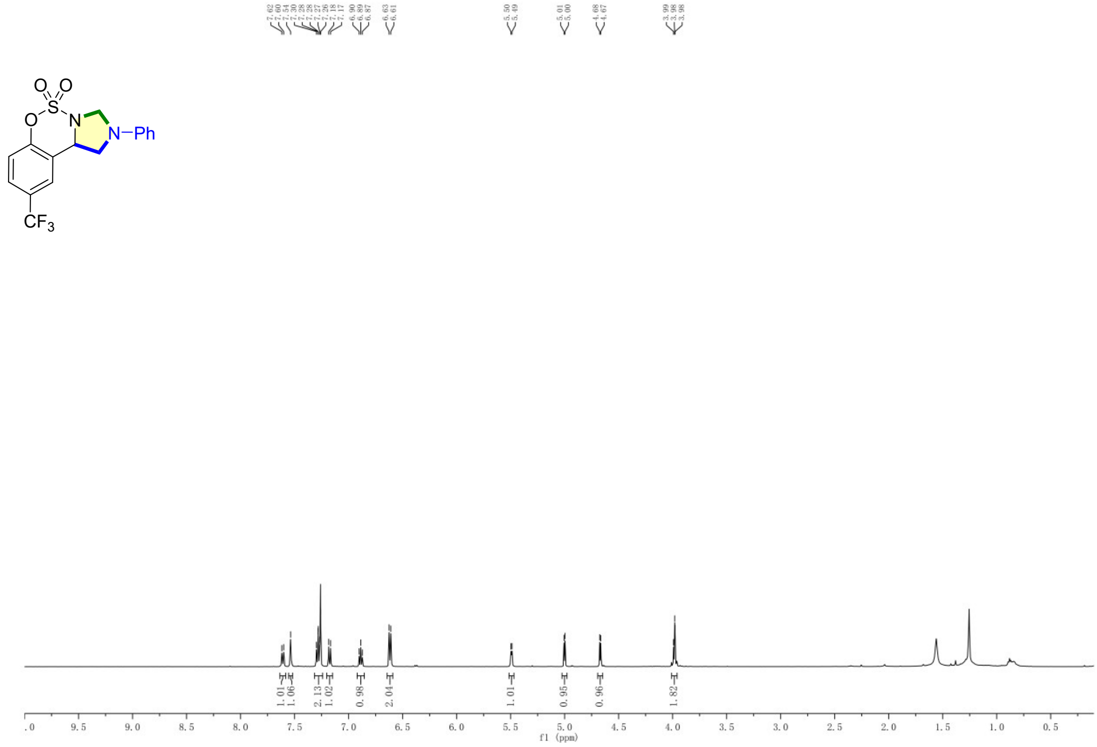


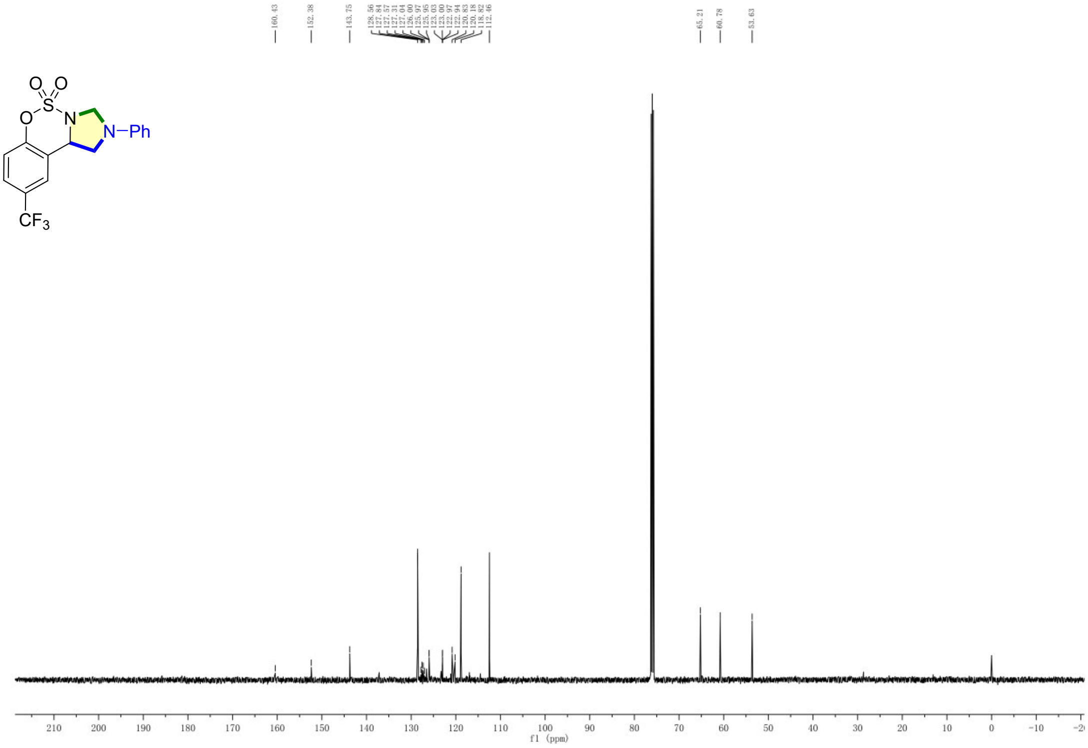
4ma ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)

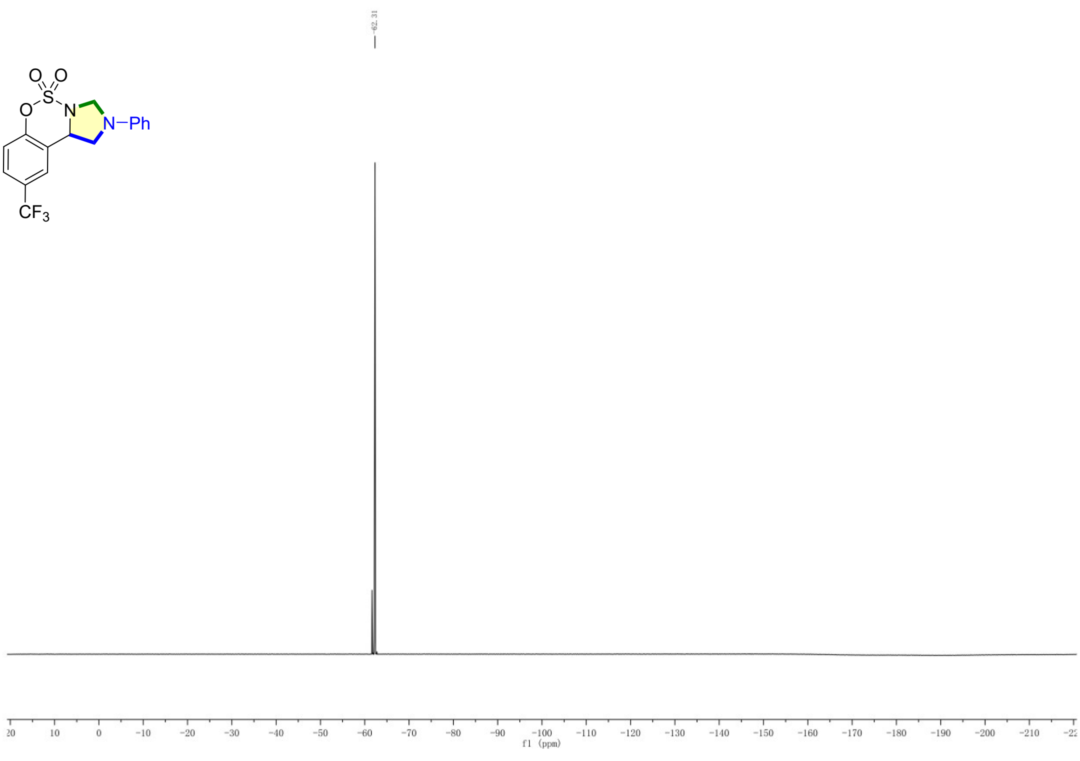




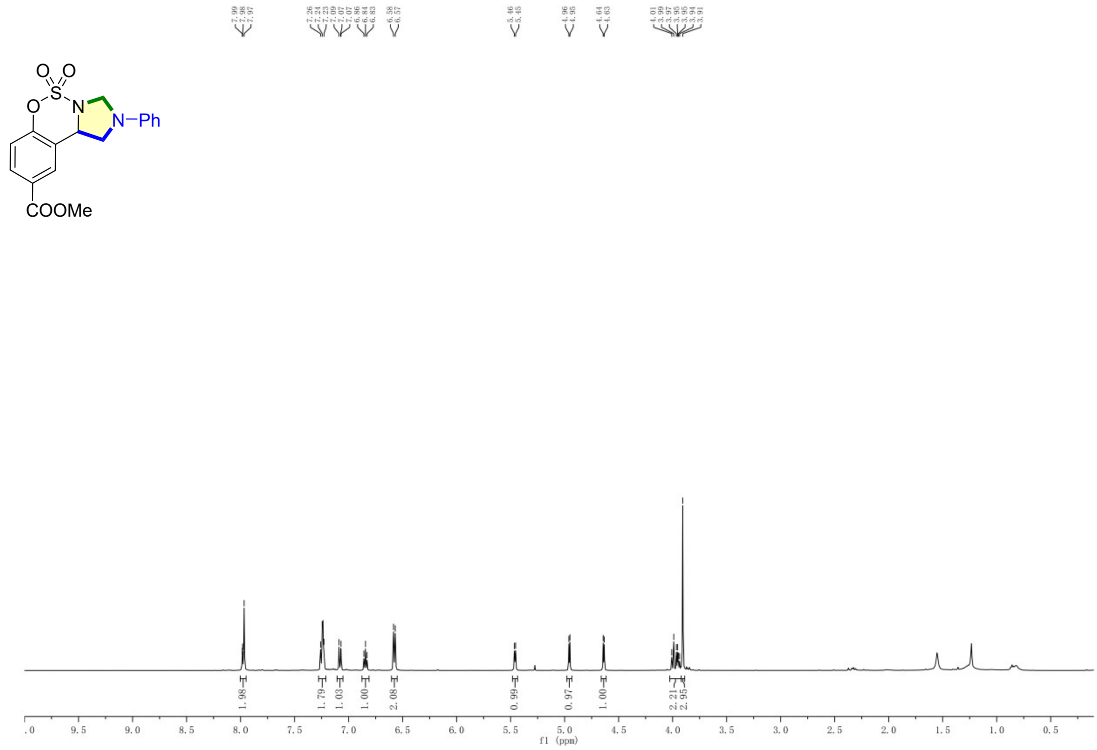
4na ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) and ^{19}F NMR (471 MHz)

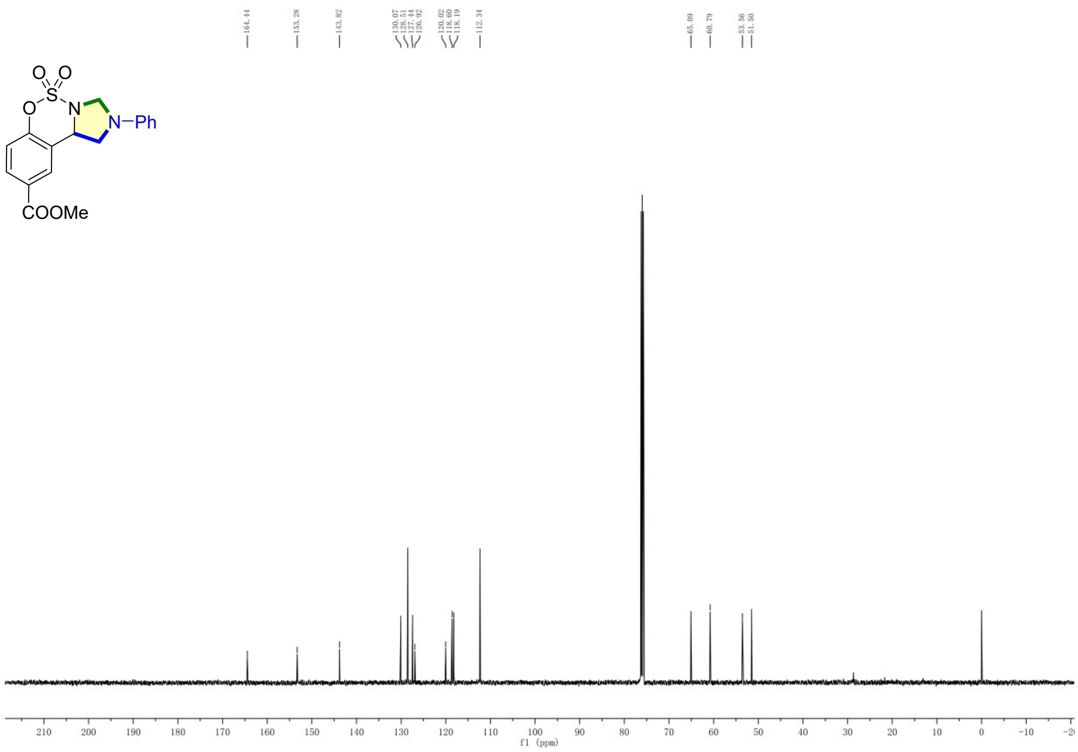




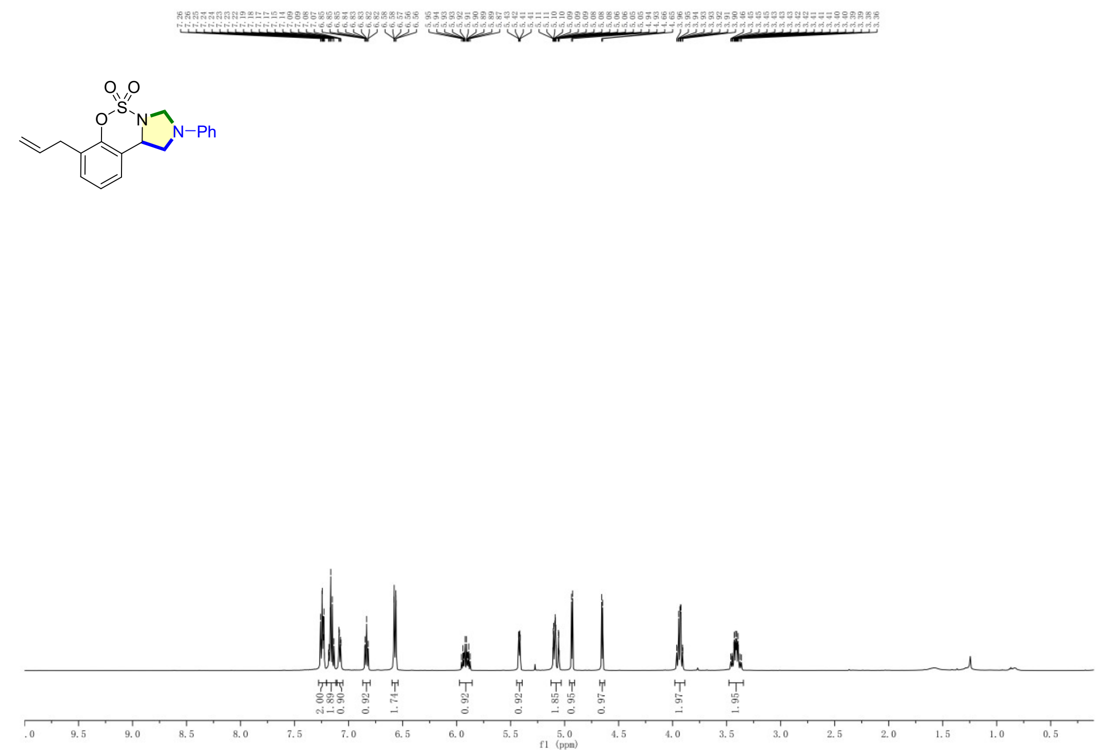


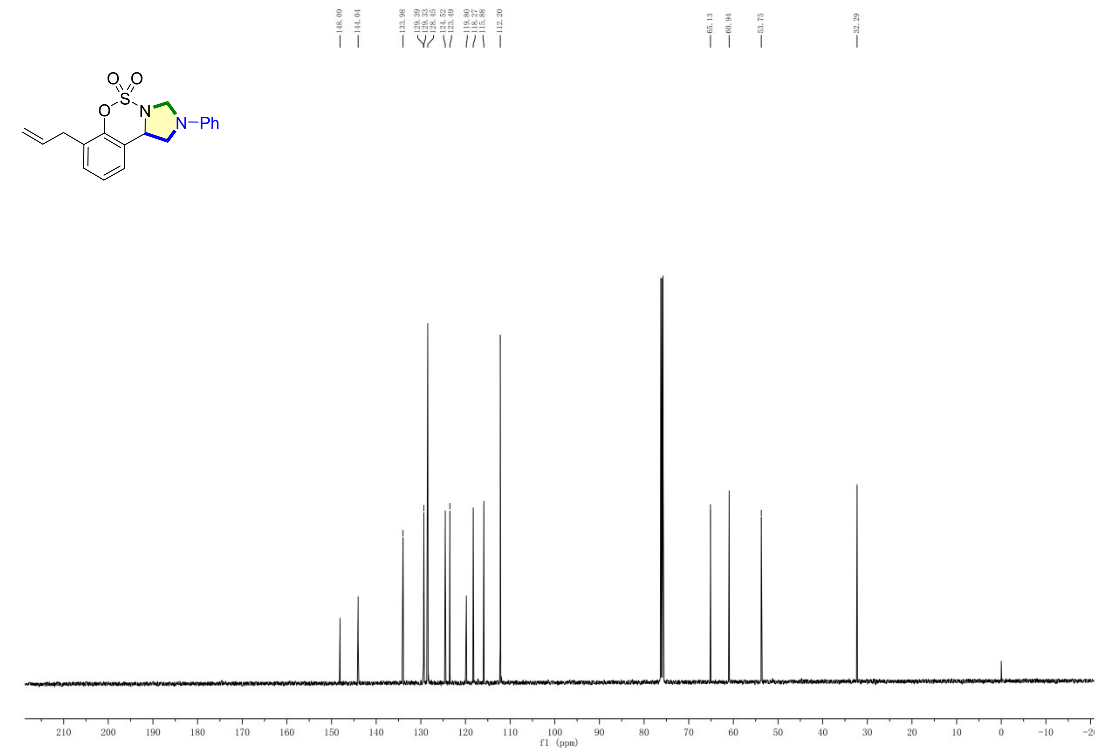
4oa ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



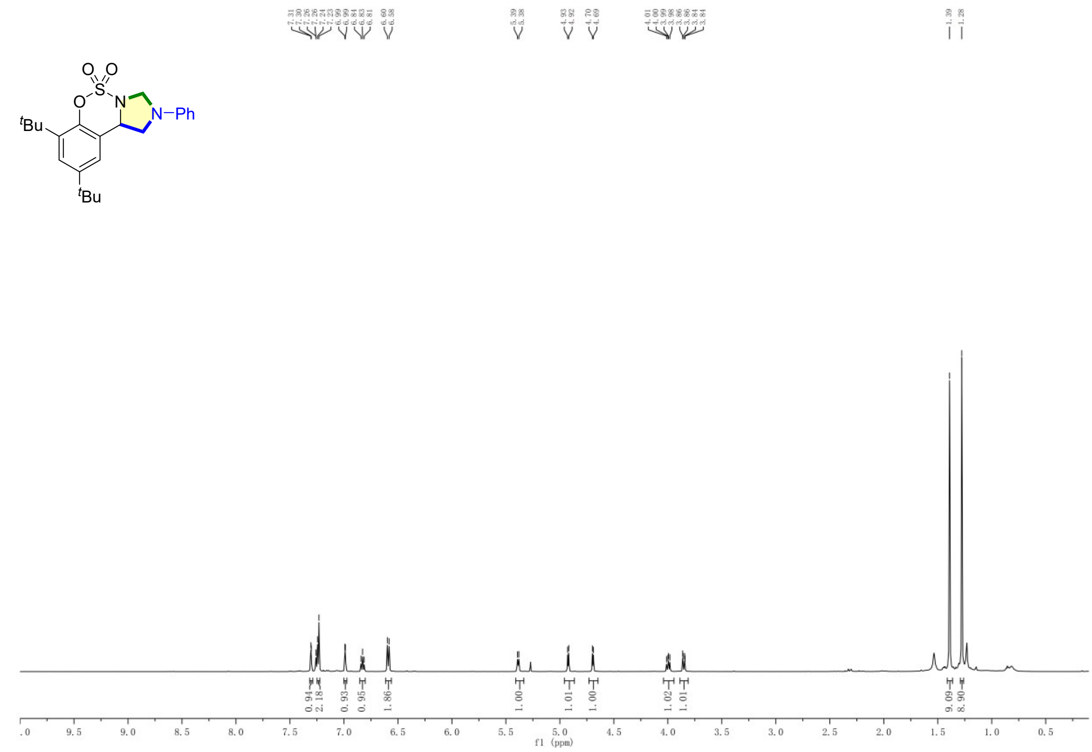


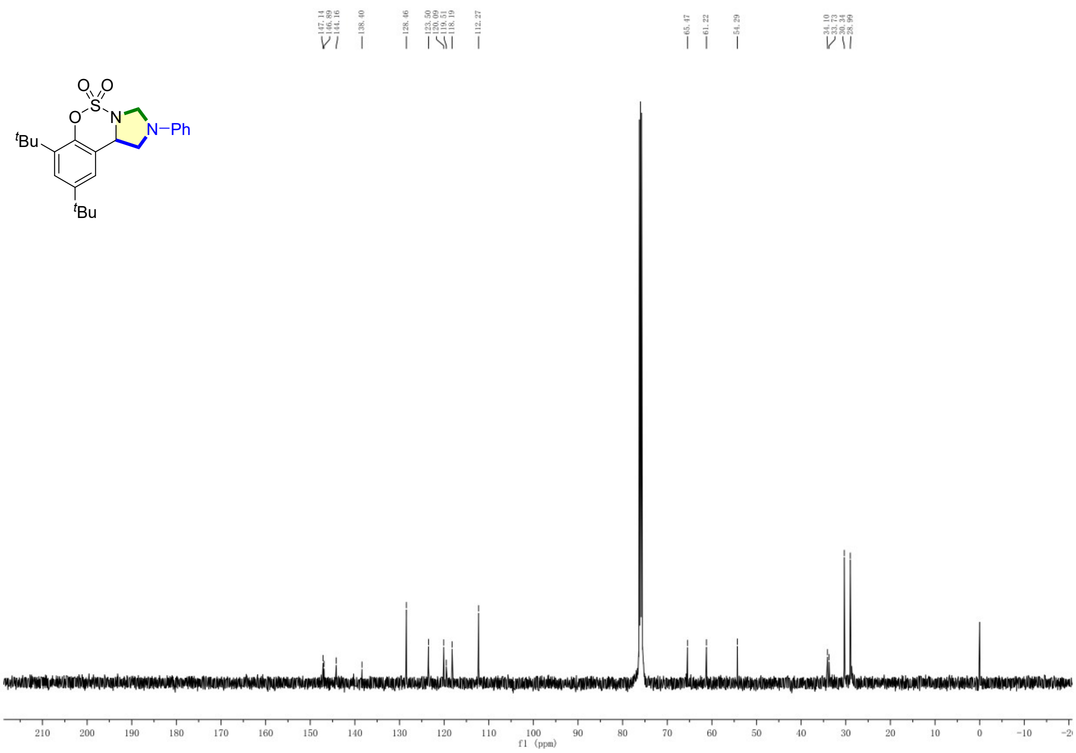
4pa ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



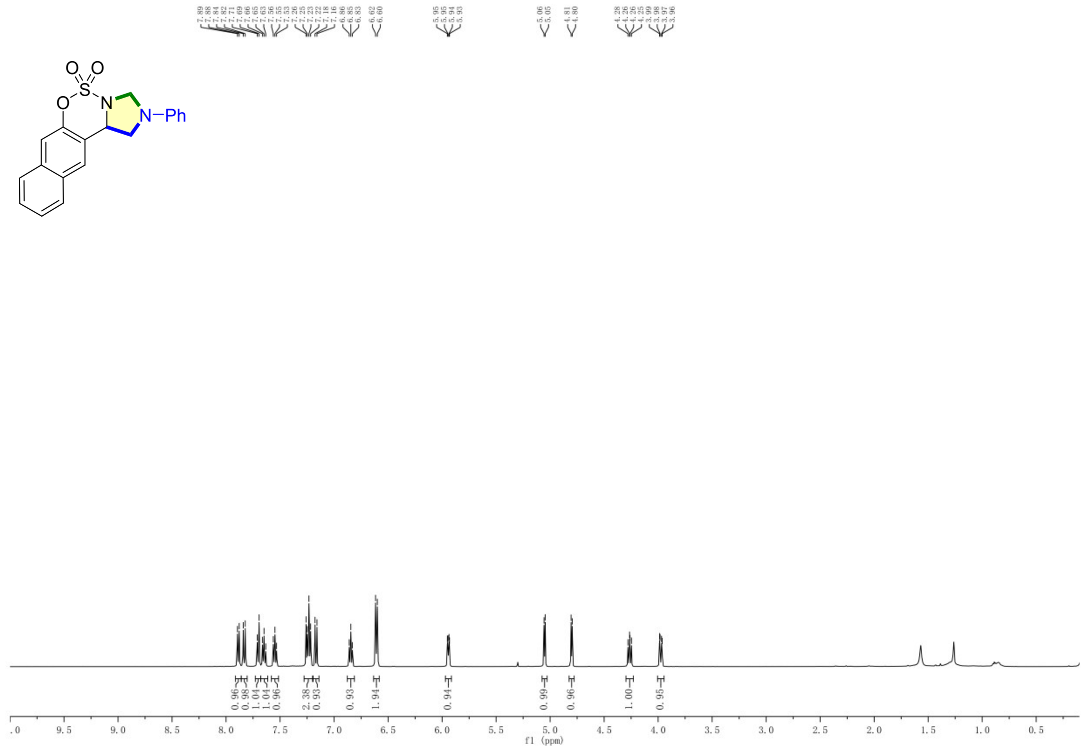


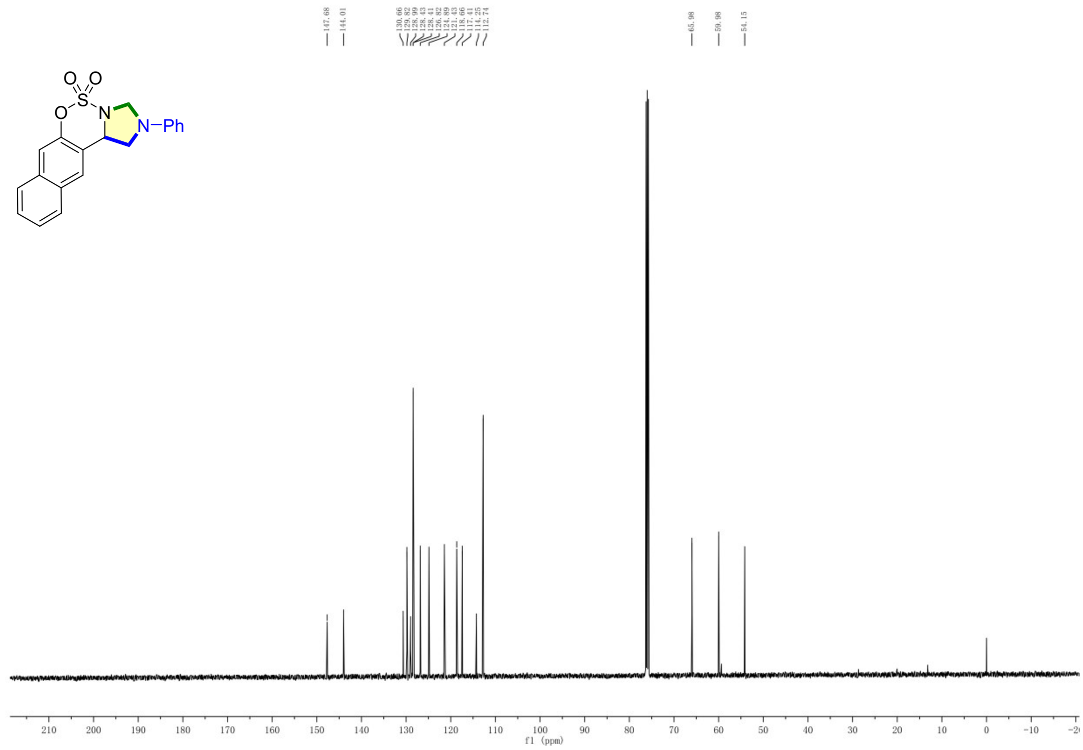
4qa ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



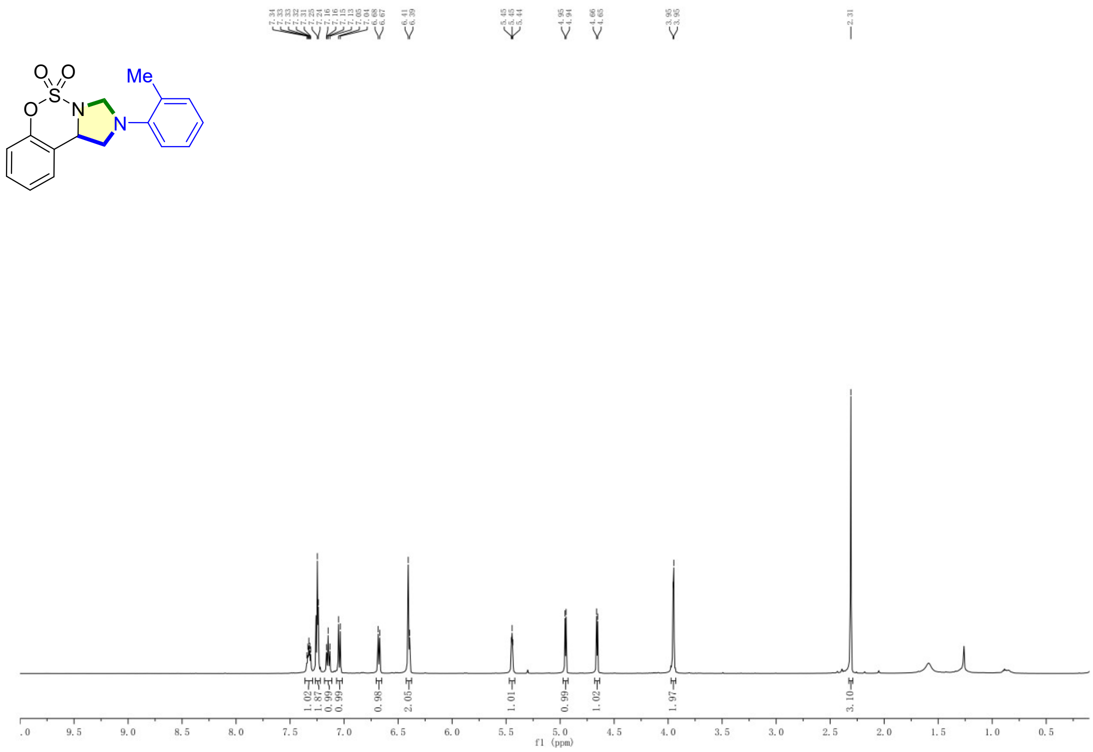


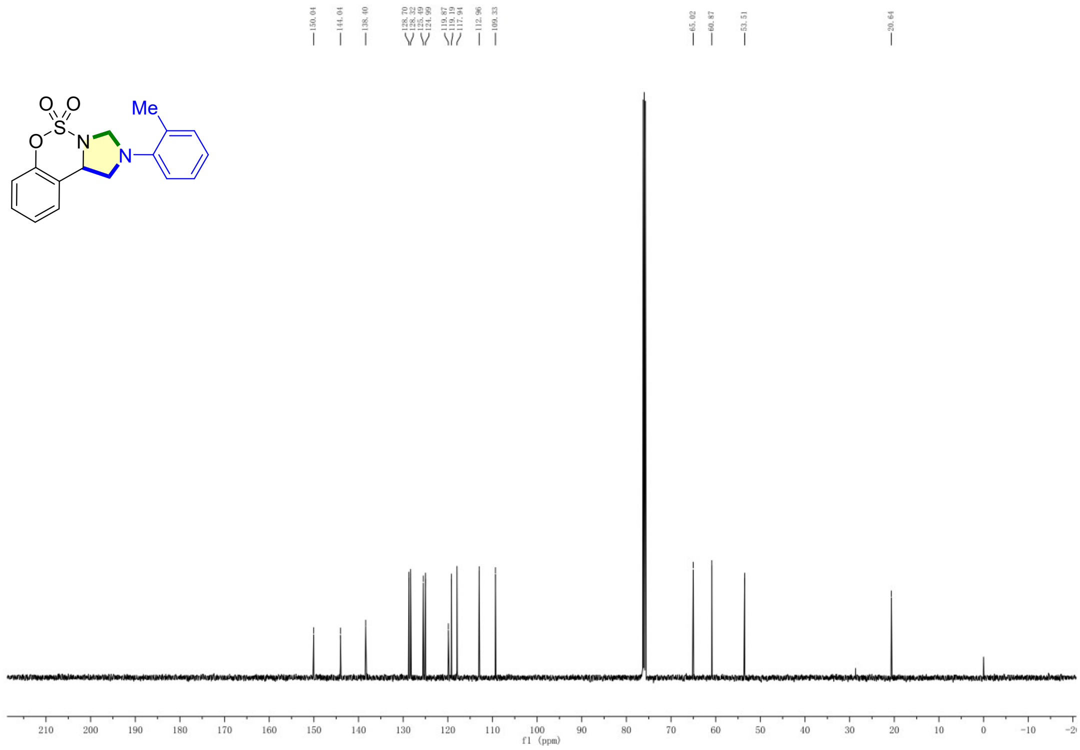
4ra ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz)



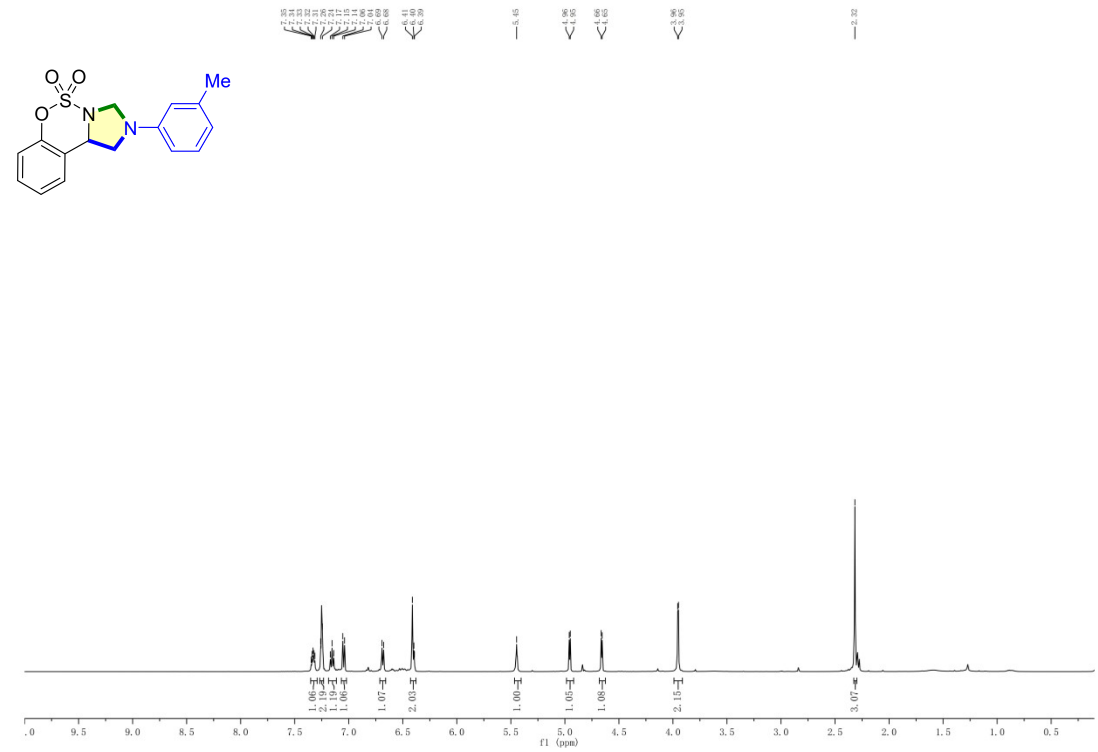


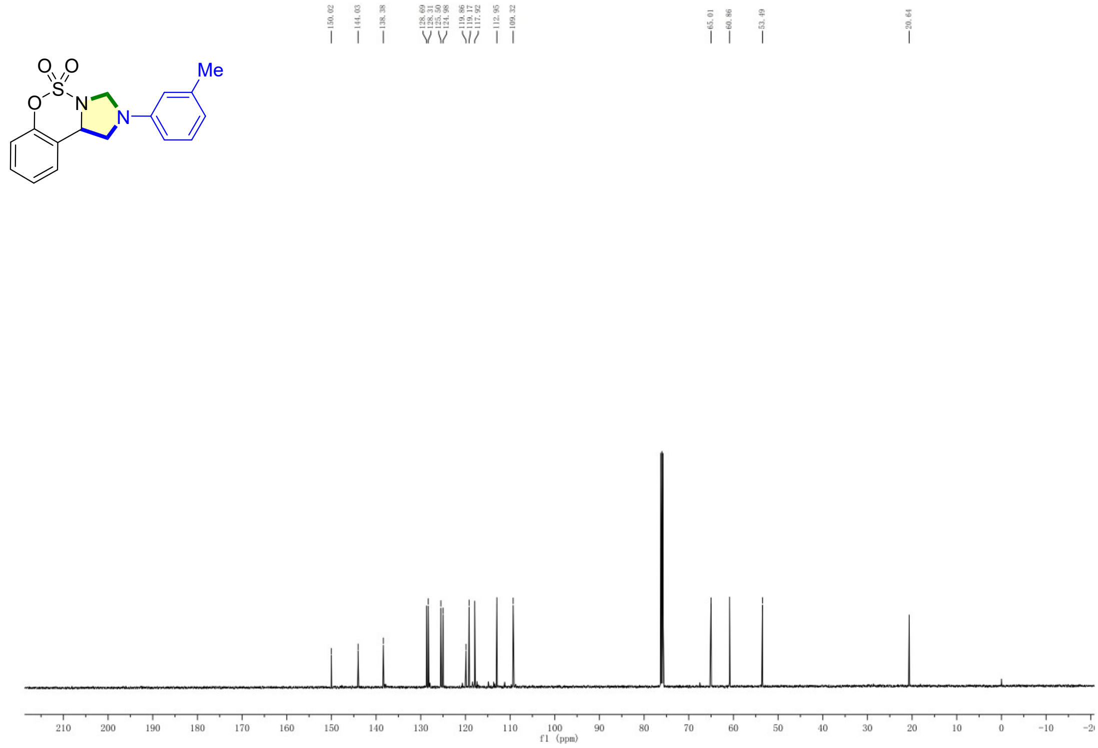
4ab ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH)



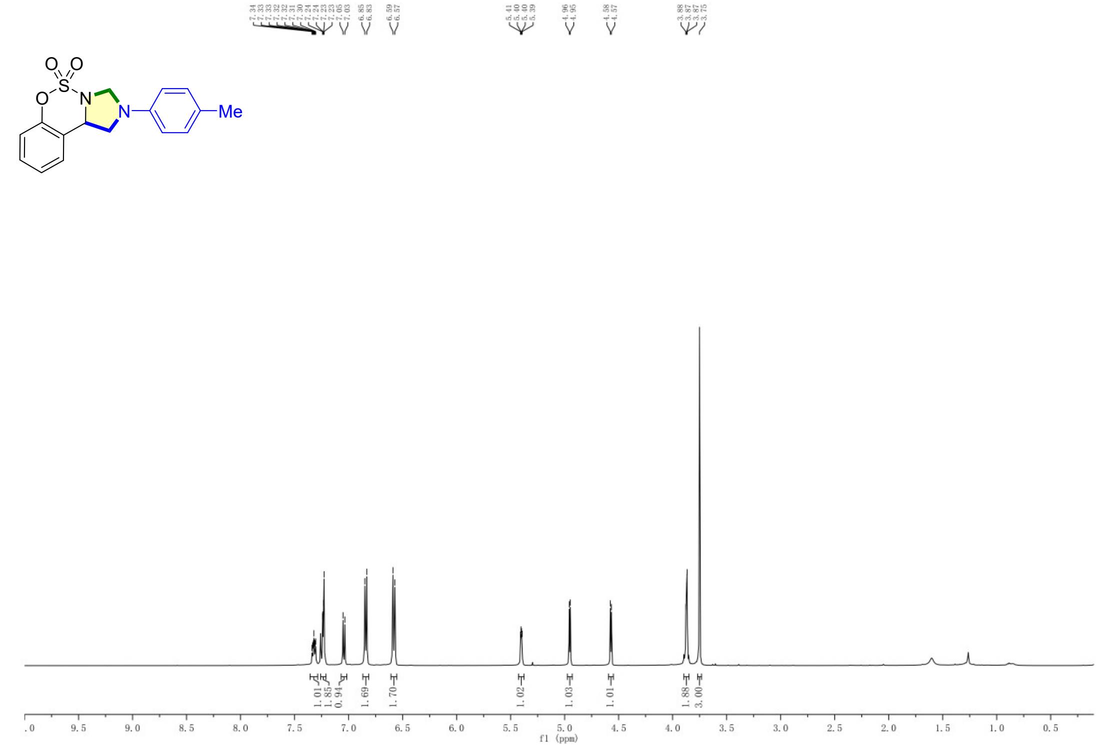


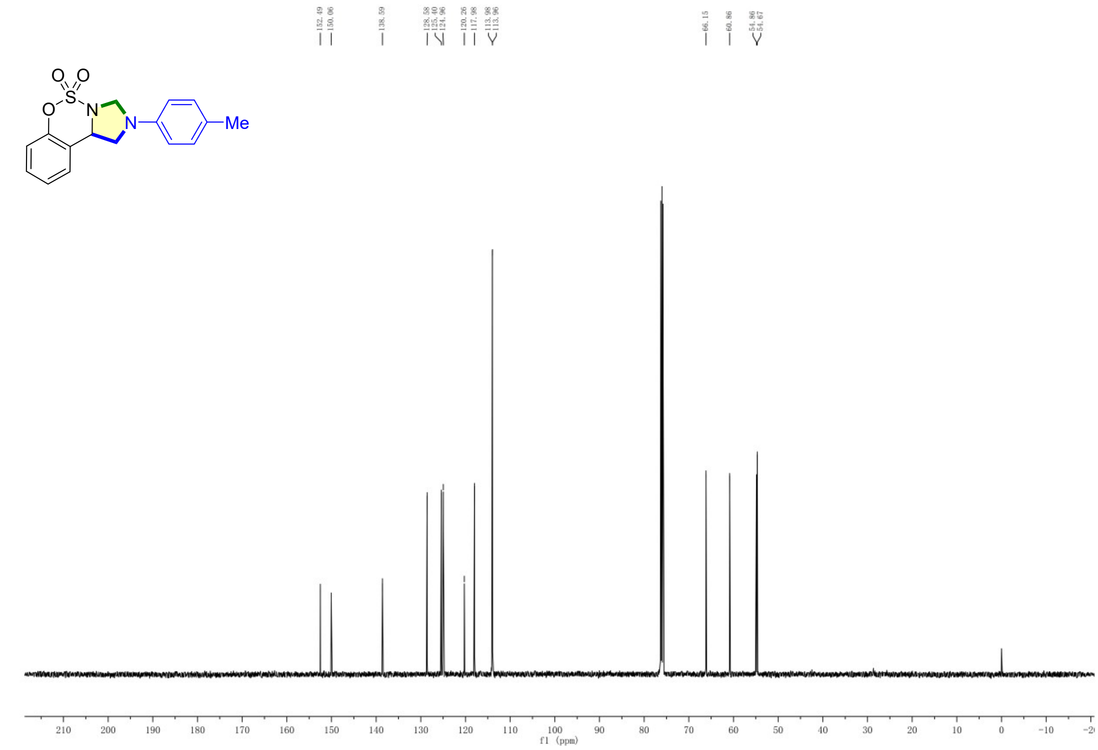
4ac ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH)



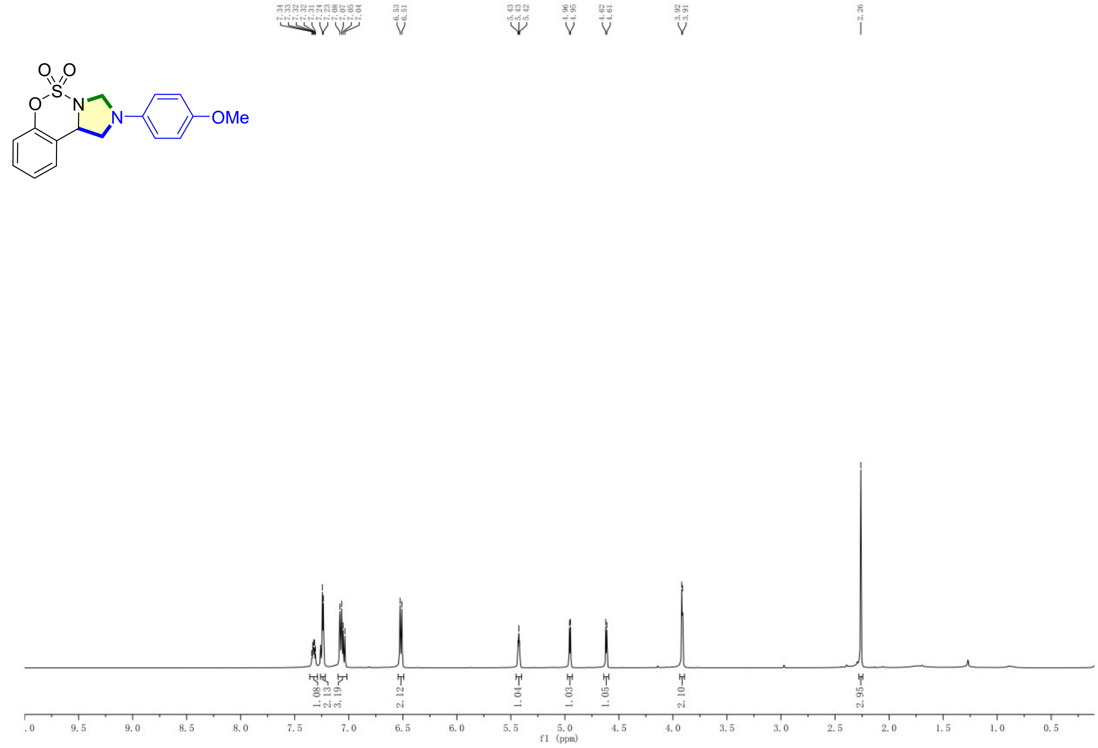


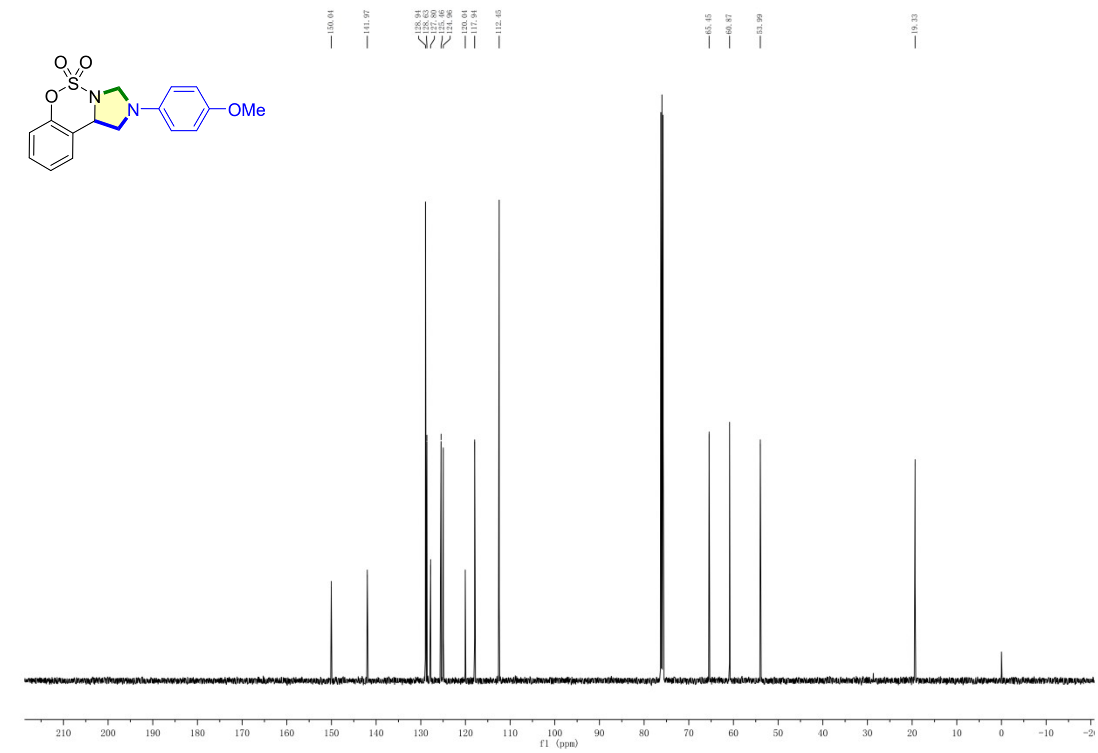
4ad [1]H NMR (500 MHz) and [13]C NMR (126 MH)



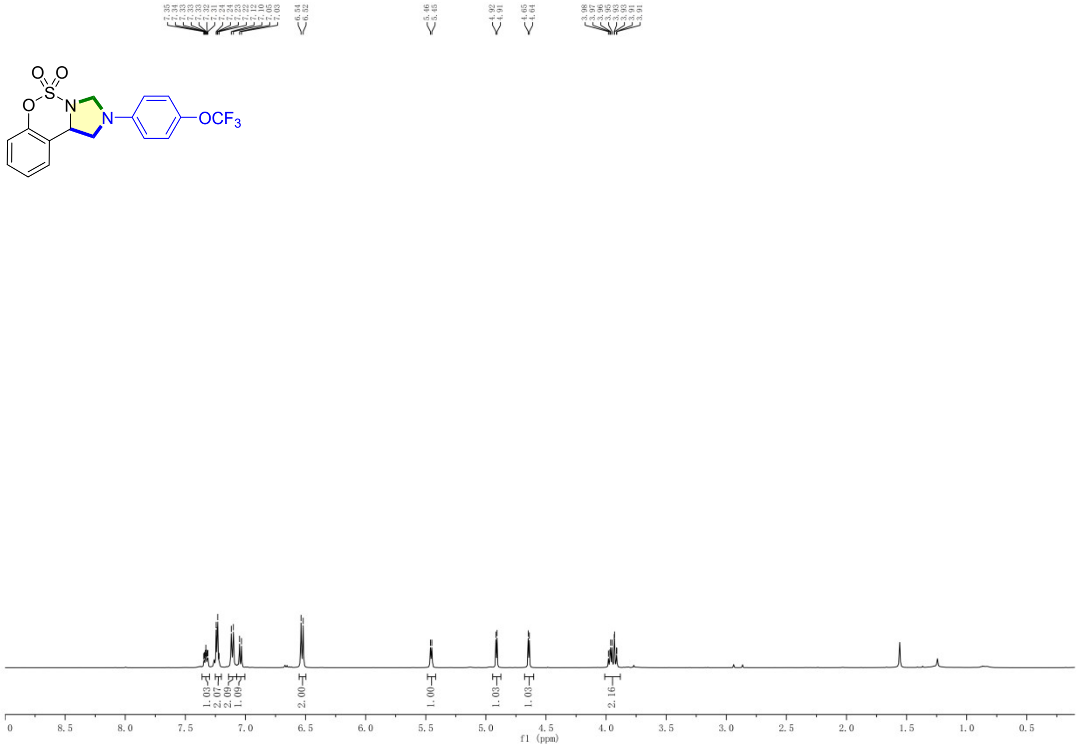


4ae ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH)

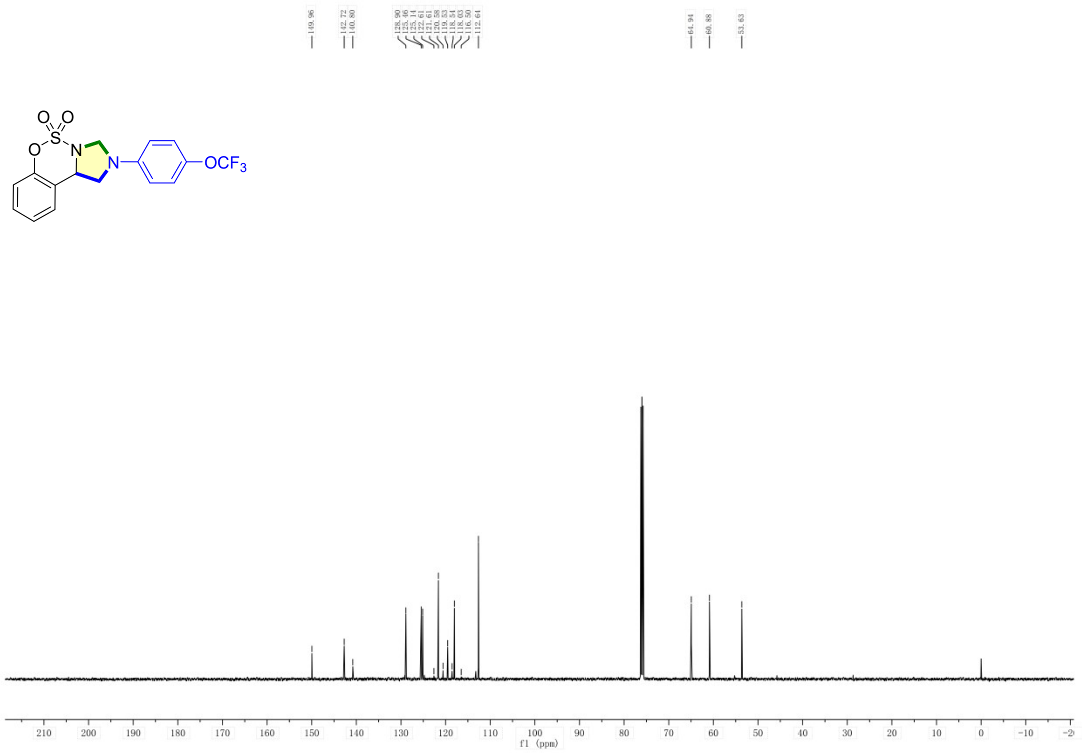




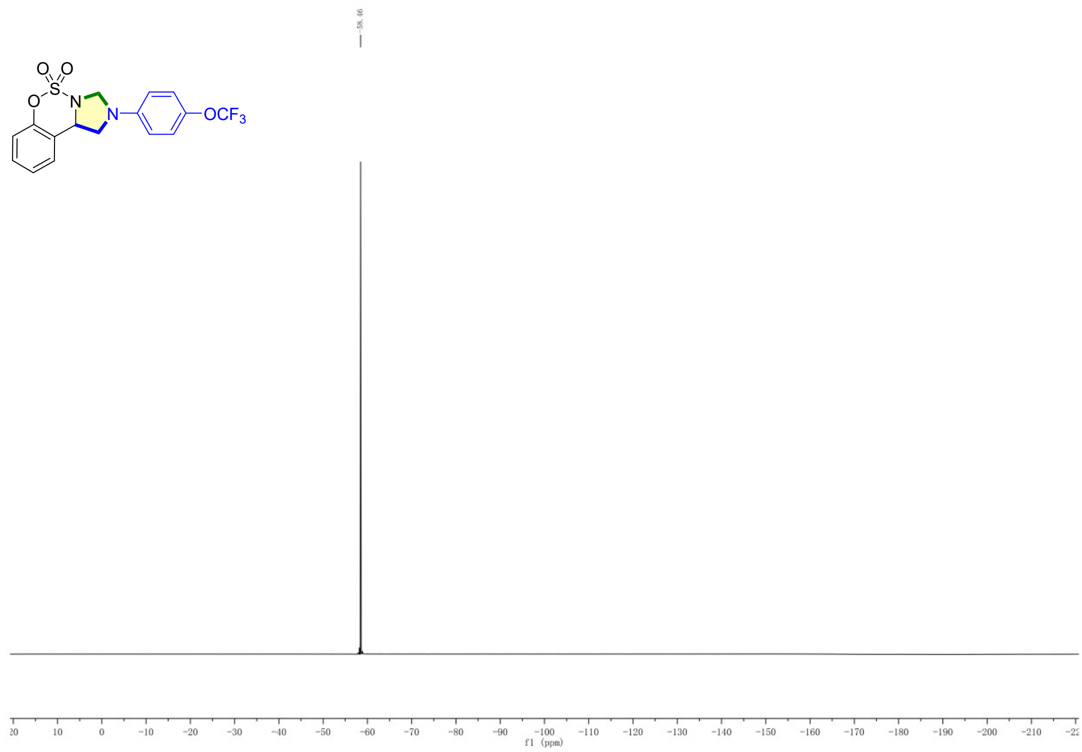
4af ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH) and ^{19}F (471 MHz)



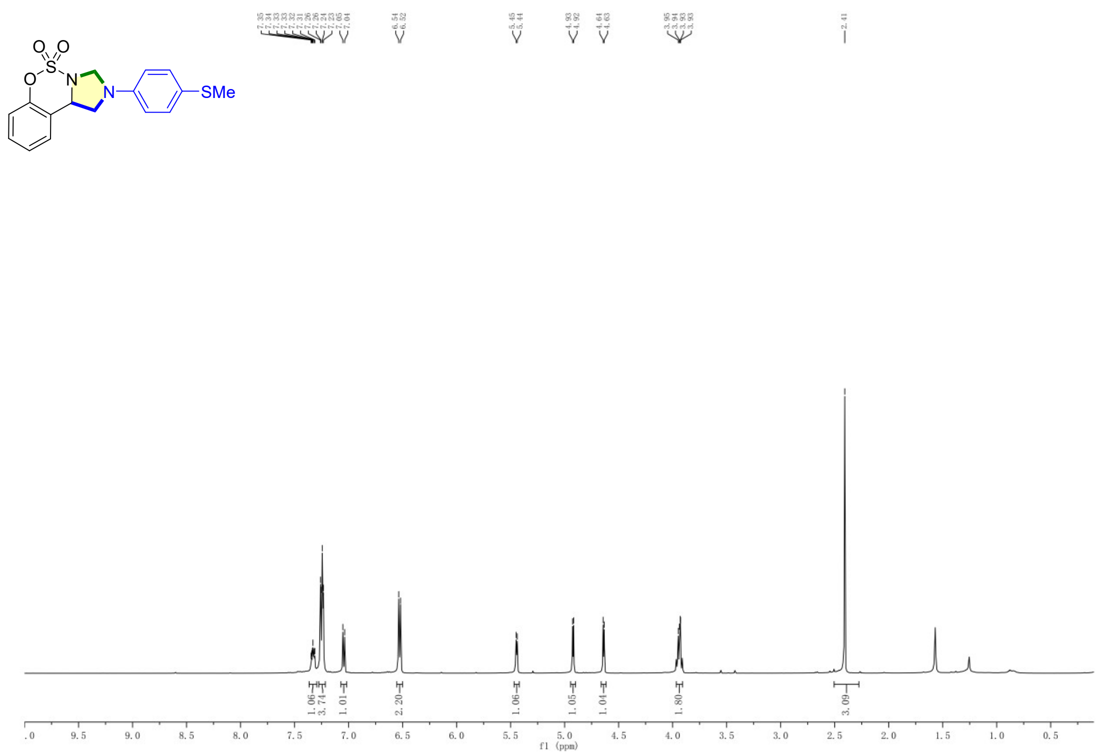
OCF3
f1 (ppm)

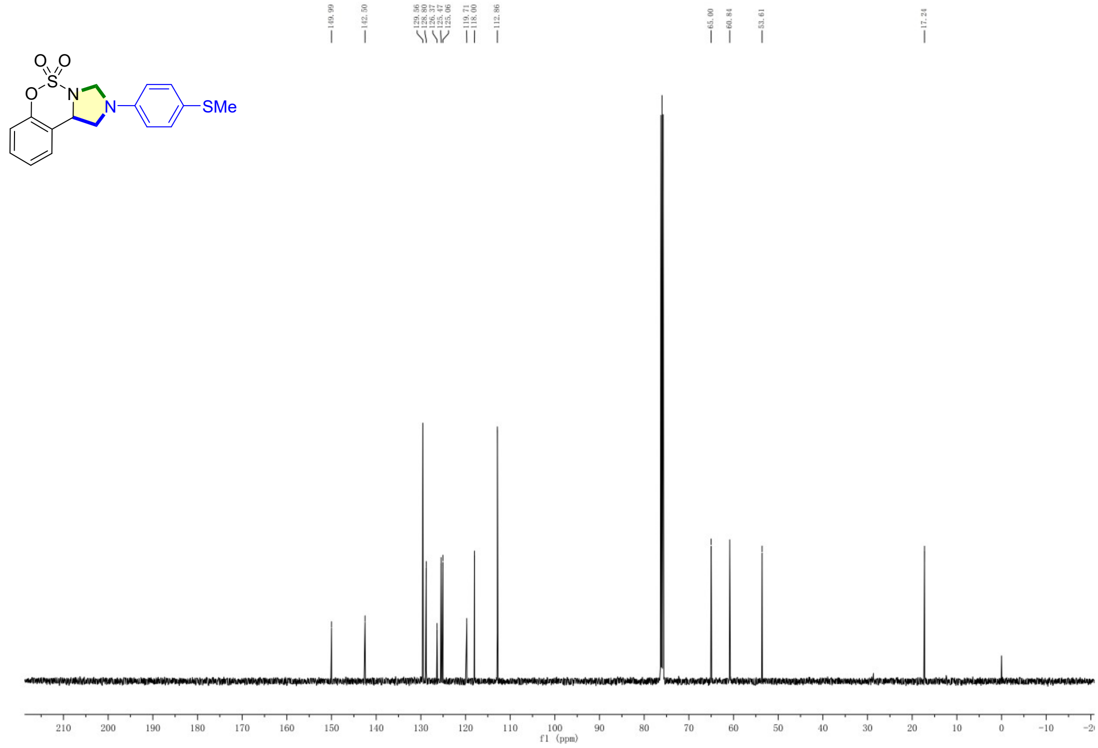


OCF3
f1 (ppm)

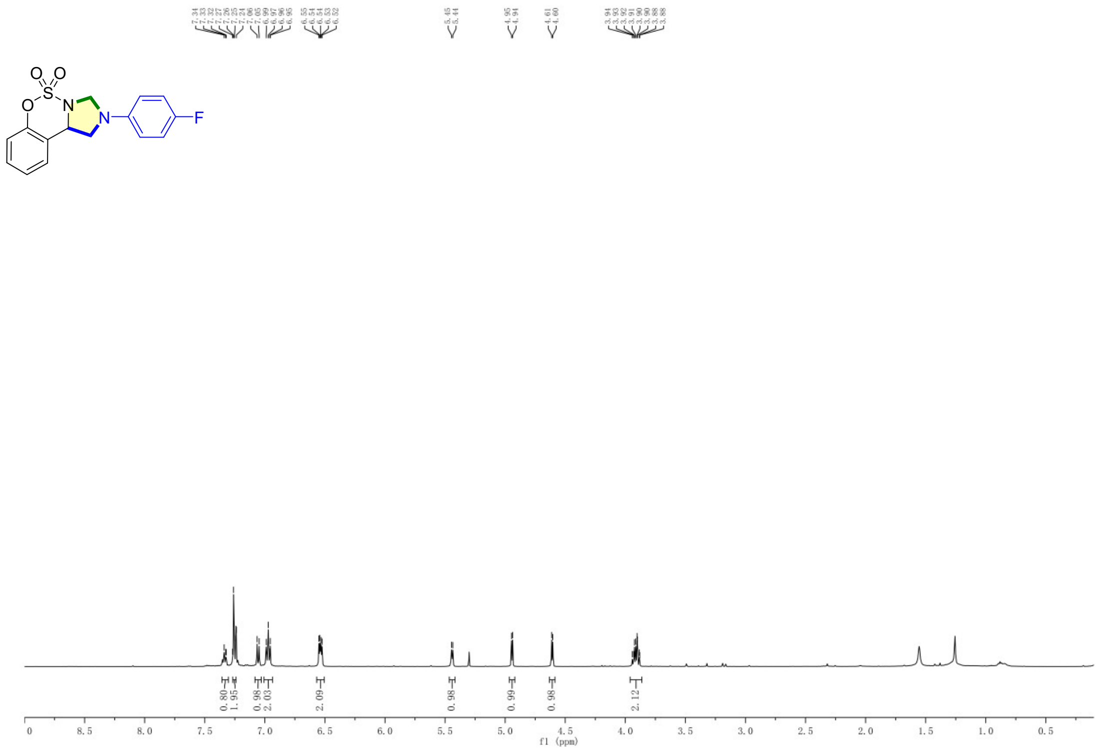


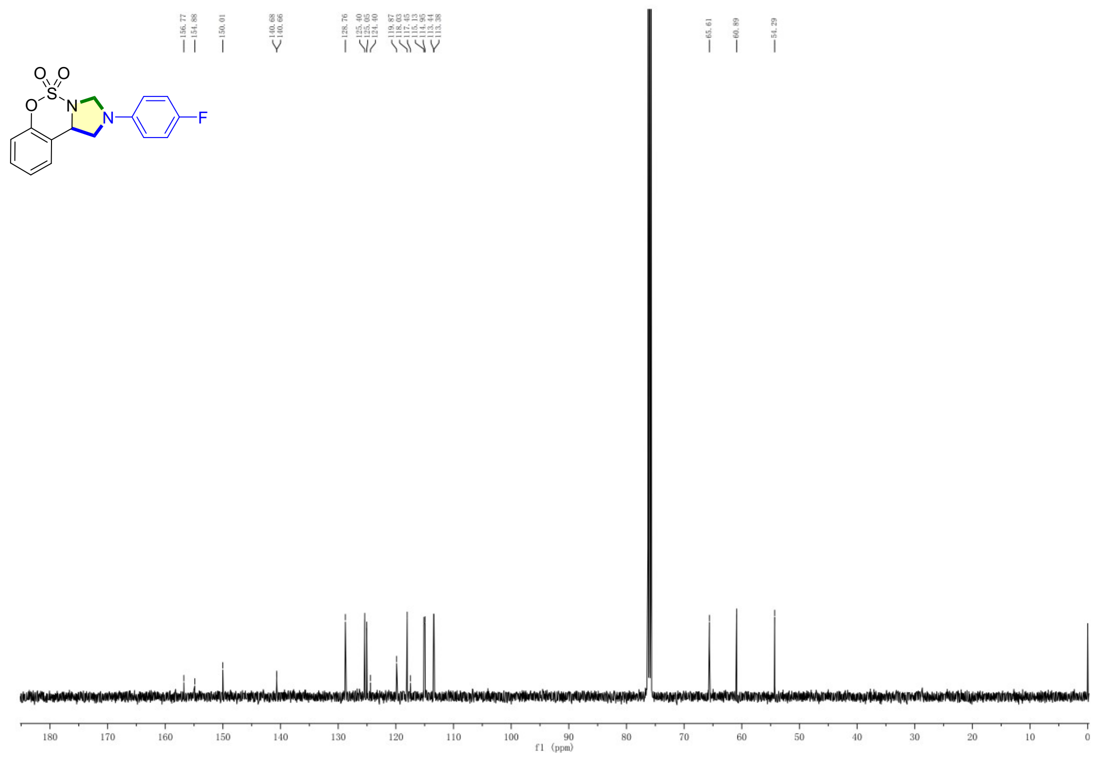
4ag [1]H NMR (500 MHz) and [13]C NMR (126 MH)

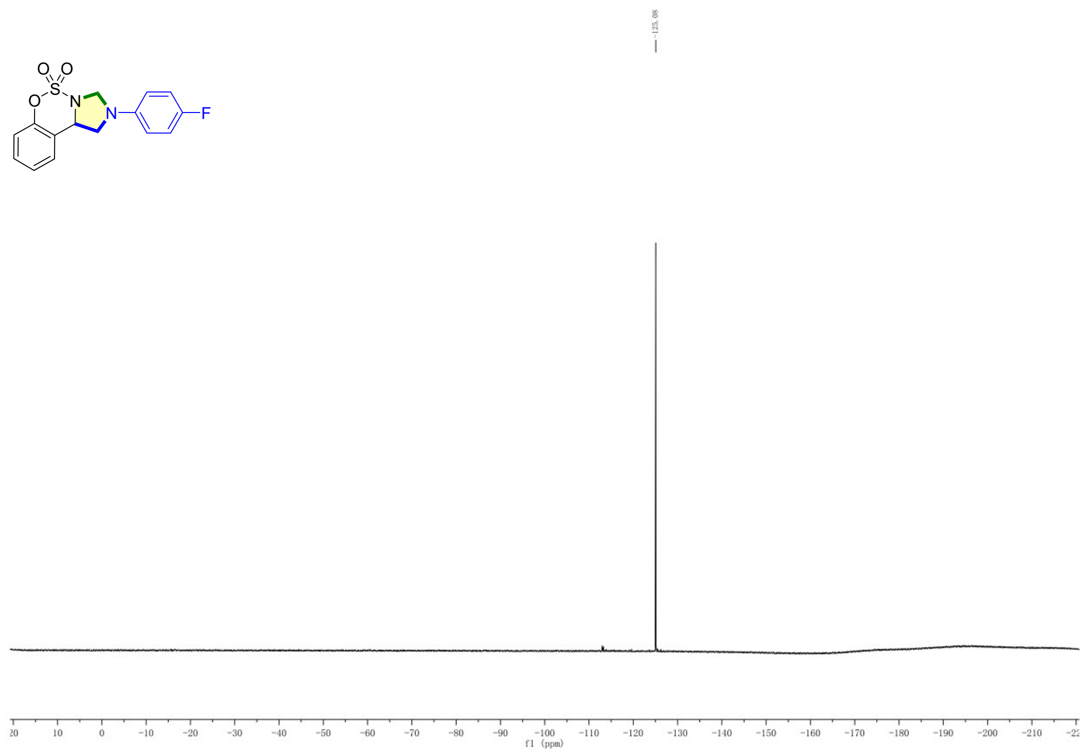




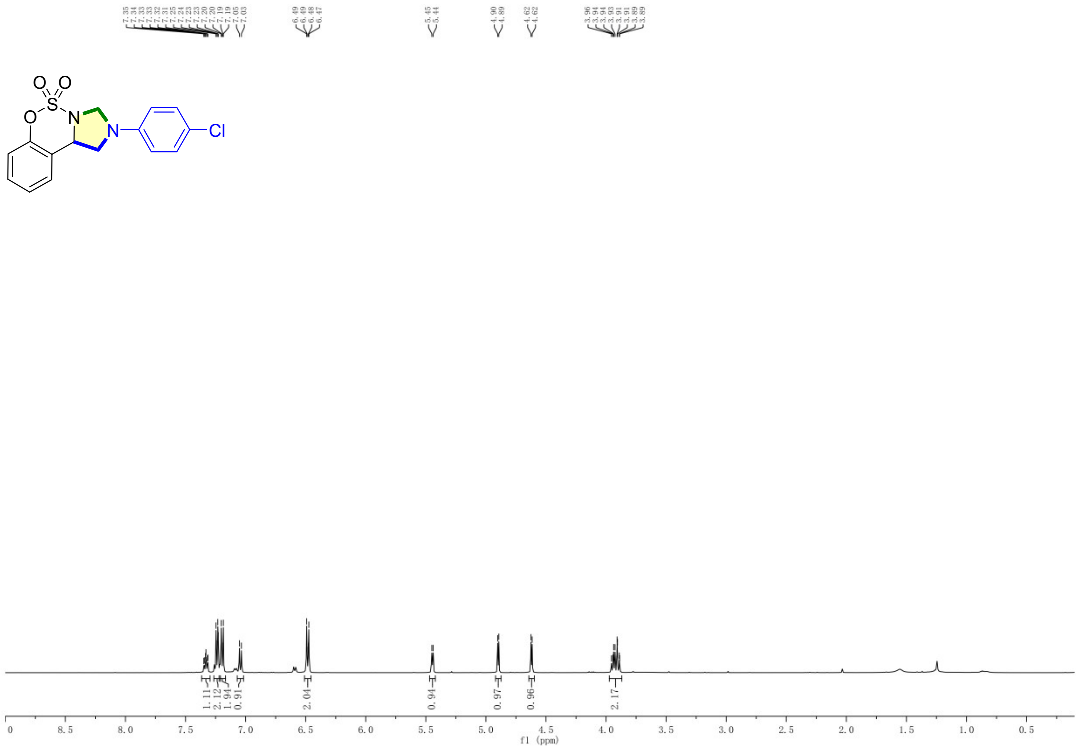
4ah ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH) and ^{19}F (471 MHz)

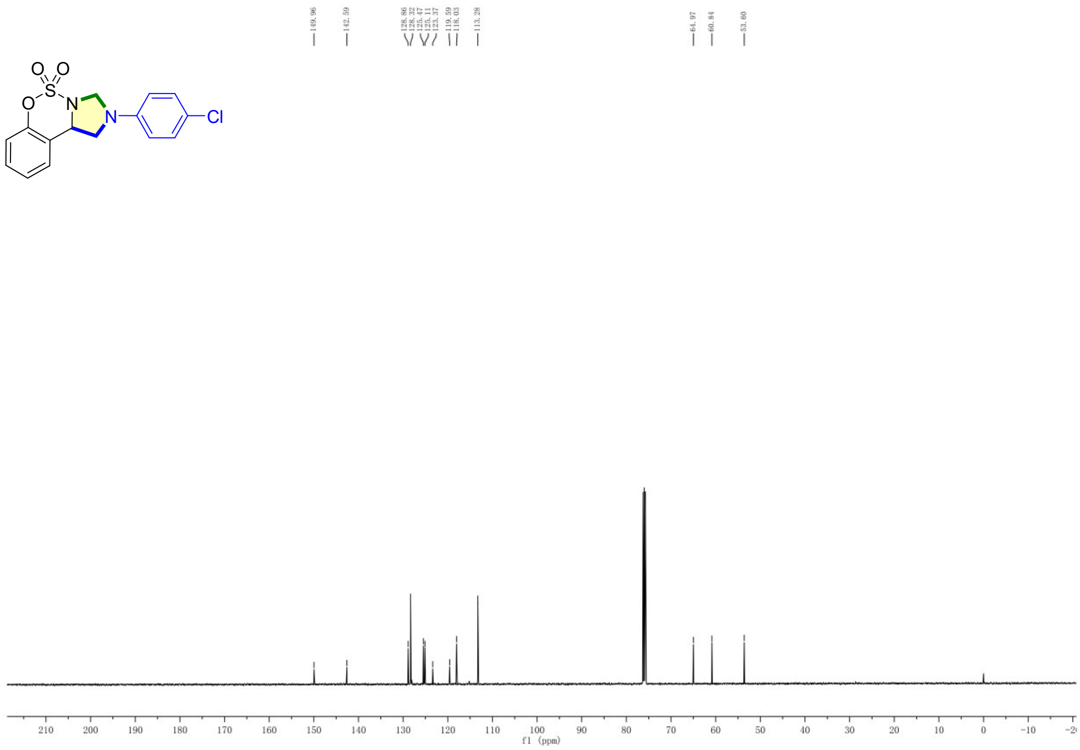






4ai ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH)





4aj ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MH)