

Supporting Information

Visible-Light-Induced Cyclization of Cyclic *N*-Sulfonyl Ketimines to *N*-Sulfonamides fused imidazolidines

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1. General Information

1.1 Materials and instruments

All the chemicals were purchased from commercial suppliers, and used directly without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All the ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz operating at 400 MHz, 101 MHz, and 376 MHz, respectively. Proton chemical shifts δ were given in ppm using tetramethylsilane as internal standard. All NMR spectra were recorded in CDCl_3 or DMSO-d_6 at room temperature (20 ± 3 °C). High-resolution mass spectra (HRMS) were taken with a 3000-mass spectrometer, using Waters Q-ToF MS/MS system with the ESI technique. Emission intensities were recorded using an F-4600 FL spectrophotometer. The cyclic N-sulfonyl ketimines and phenylglycines are synthesized according to the reported procedure.^{1,2}

1.2 The spectrum of the lamp and the visible-light irradiation instrument

Photochemical reaction was carried out under visible light irradiation by a white LED at 25 °C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 10W white LEDs were equipped in this Photo reactor. The reaction vessel is a borosilicate glass test tube and the distance between it and the lamp is 15 mm, no filter applied.

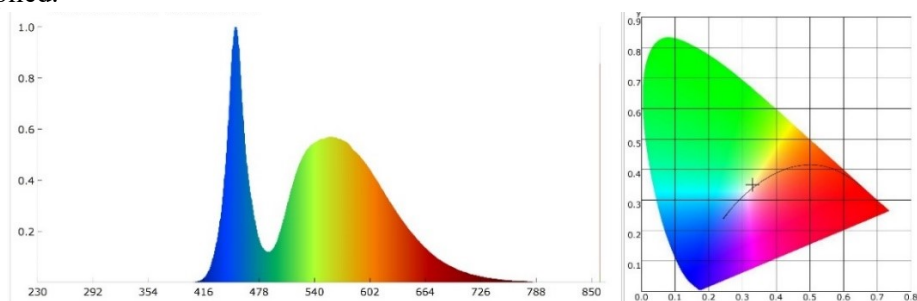


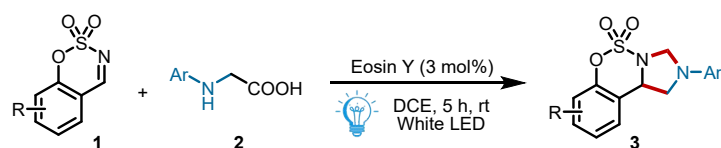
Figure S1. The spectrum of our lamp (white LED)



Figure S2. The visible-light irradiation instrument

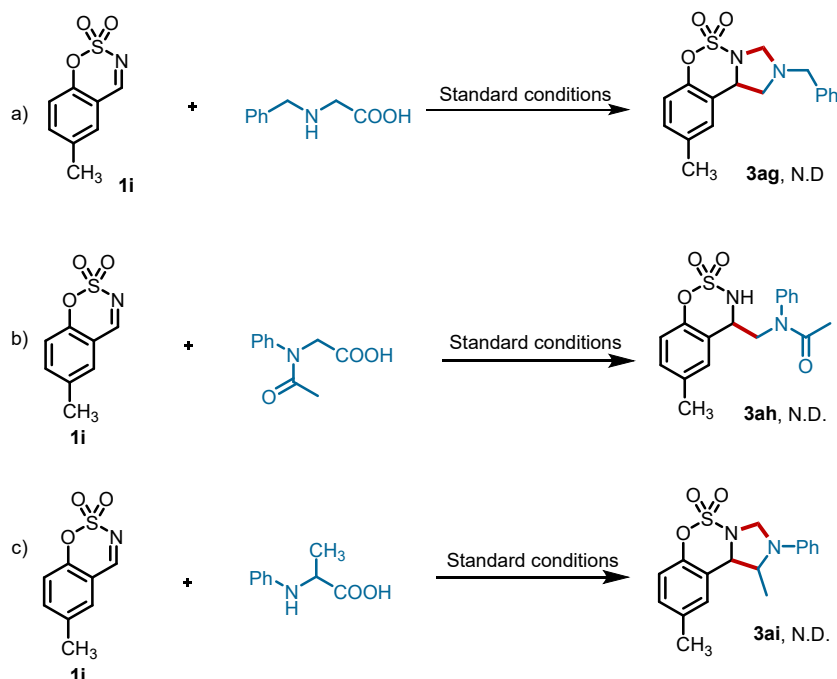
2. Experimental procedures

2.1 General experimental procedures for the to the desired product 3



The mixture of cyclic *N*-sulfonyl ketimines **1** (0.1 mmol), phenylglycines **2** (0.3 mmol), Eosin Y (3 mol%) and DCE (1.5 mL) were sequentially added in a 25 mL reaction vessel. Then the reaction vessel was exposed to 5 W white LED irradiation at room temperature for 5 h. After the reaction, the solvent was evaporated under vacuum, all the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate (v/v = 15/1) as eluting solvent to give the desired products.

2.2. Unsuccessful substrates

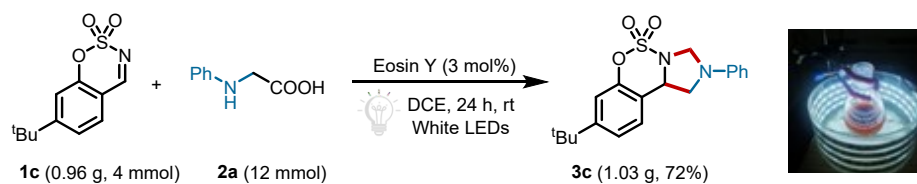


N-phenyl glycine, glycine bearing *N*-benzyl, *N*-acetyl, α -methyl groups did not give the desired products, in which the starting materials were fully recovered.

2.3 Large scale synthesis under the irradiation of White LEDs

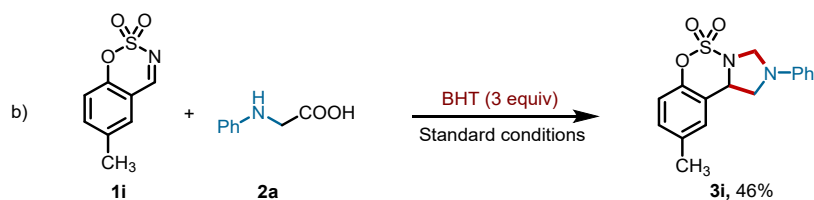
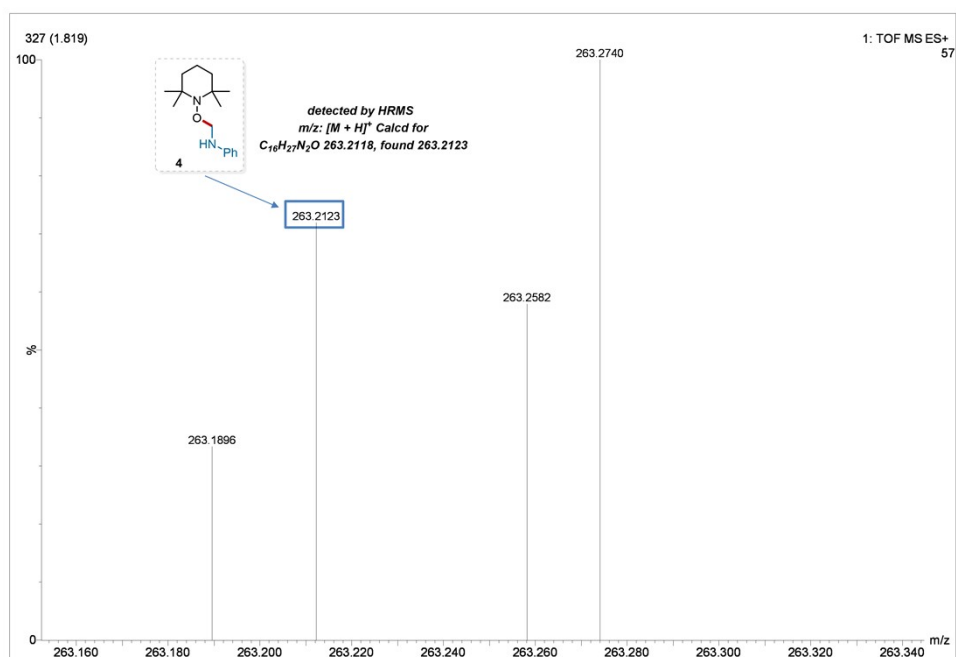
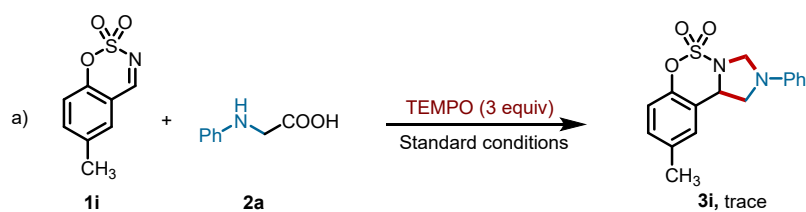
A 100 mL round bottom flask was charged with 6-(tert-butyl)benzo[e][1,2,3]oxathiazine 2,2-dioxide **1c** (4 mmol), *N*-phenylglycine **2a** (12 mmol) and Eosin Y (3 mol%), which were dissolved in DCE (25 mL). And then the reaction system was carried out under White LEDs for 24 h. After reaction, the residue was quenched with saturated NaHCO₃ solution (8 mL), and the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na₂SO₄. The residue was purified by silica gel

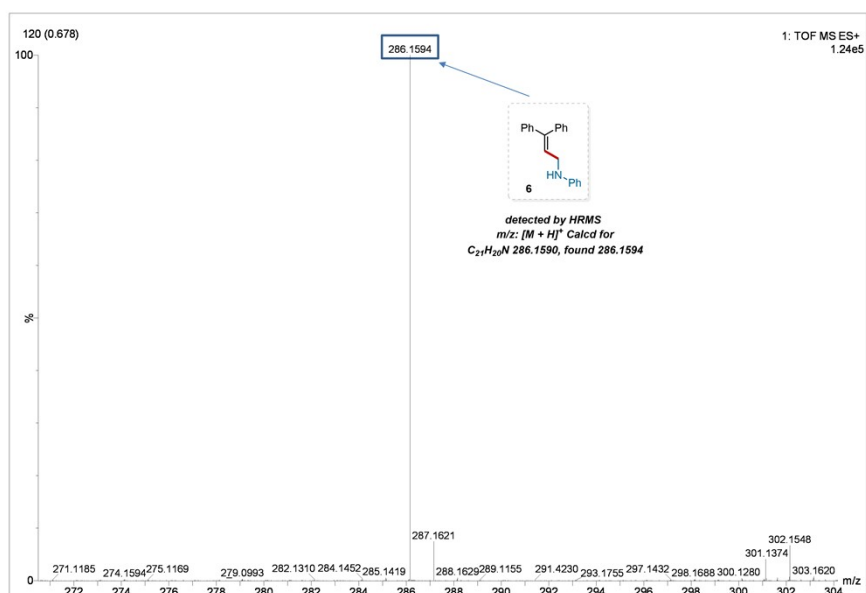
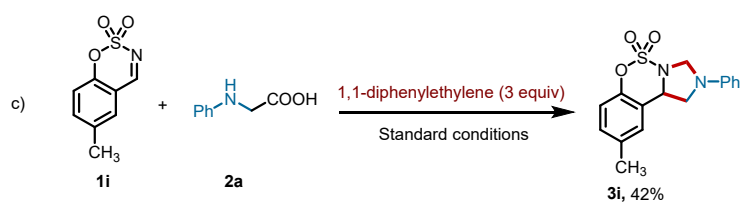
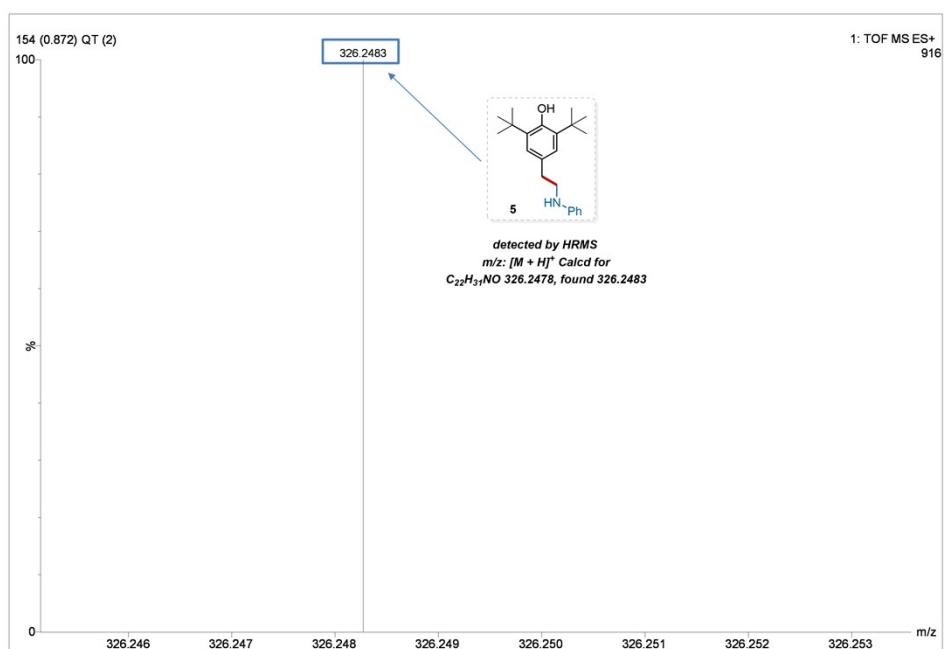
chromatography (petroleum ether/ethyl acetate = 15/1) to afford the desired product (1.03 g, 72%).



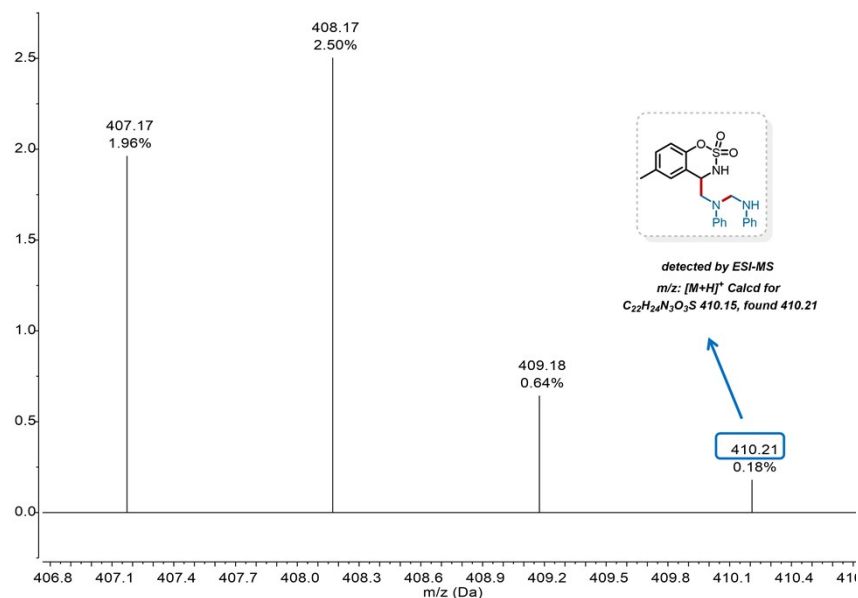
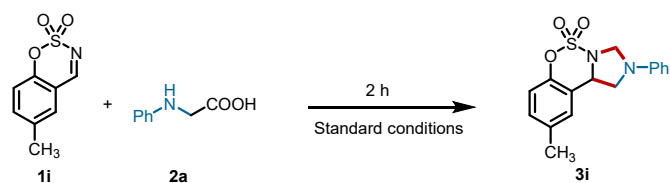
Scheme S1. Gram-scale synthesis of **3c**

2.4 HRMS data analysis





2.5 ESI-MS data analysis



2.6 Procedure for emission quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 5×10^{-5} M solution of Eosin Y in degassed anhydrous DCE added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 470 nm and fluorescence was measured from 500 nm to 700 nm. The studies were conducted by mixing Eosin Y with **1a**, **2a**, respectively. As a result, a significant luminescence quenching effect was detected when Eosin Y was mixed with **2a** (Figure S3), As shown in Figure S4, a linear relationship between the concentration of 2a and I_0/I (I_0 and I are the fluorescence intensities before and after adding **2a**) was observed. The results indicated that **2a** was an effective quencher of Eosin Y.

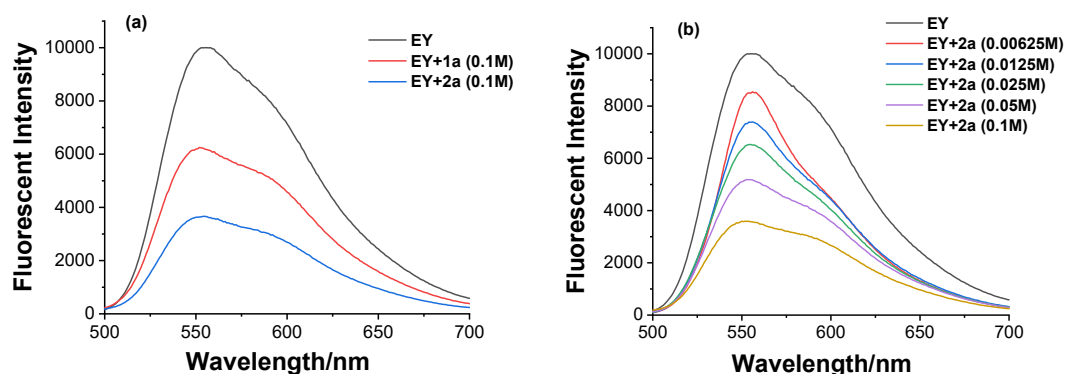


Figure S3. Luminescence quenching study: **(a)** the emission spectra of a 5×10^{-5} M solution of Eosin Y with reactants in degassed anhydrous DCE excited at 470 nm; **(b)** the emission spectra of a 5×10^{-5} M solution of Eosin Y with various concentrations of **2a** in degassed anhydrous DCE excited at 470 nm.

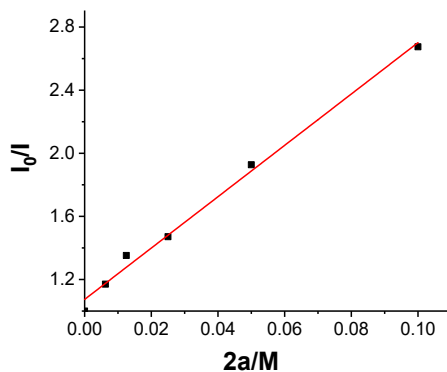
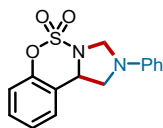


Figure S4. the linear relationship between I_0/I and the concentration of **2a**

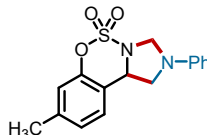
3. Characterization Data for Products

2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3a)



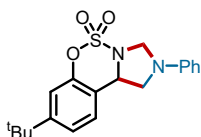
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3a**. White solid (25.4 mg, 84%); m.p. 77.2 – 78.8 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.57 (d, $J = 7.4$ Hz, 1H), 7.44 – 7.39 (m, 1H), 7.34 (td, $J = 7.5, 1.2$ Hz, 1H), 7.25 – 7.16 (m, 3H), 6.80 (t, $J = 7.3$ Hz, 1H), 6.73 (d, $J = 7.9$ Hz, 2H), 5.56 (d, $J = 5.6$ Hz, 1H), 4.96 (d, $J = 5.4$ Hz, 1H), 4.60 (d, $J = 5.4$ Hz, 1H), 4.14 – 4.08 (m, 1H), 3.85 (dd, $J = 9.9, 5.9$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 150.9, 145.8, 130.2, 129.6, 128.0, 126.6, 121.7, 119.3, 118.8, 114.2, 66.4, 62.1, 54.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_3\text{S}$, 303.0798; Found: 303.0807.

8-methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3b)



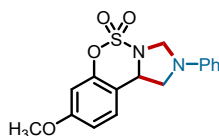
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3b**. White solid (25.9 mg, 82%); m.p. 169.8 – 170.9 °C; ^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.31 – 7.27 (m, 2H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.09 – 7.06 (m, 1H), 6.90 – 6.85 (m, 2H), 6.60 (d, $J = 7.9$ Hz, 2H), 5.44 (t, $J = 3.3$ Hz, 1H), 4.96 (d, $J = 4.7$ Hz, 1H), 4.68 (d, $J = 4.7$ Hz, 1H), 3.98 – 3.93 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $\text{Chloroform-}d$) δ 150.8, 145.1, 140.4, 129.5, 126.9, 126.2, 119.20, 119.16, 117.6, 113.1, 66.0, 61.8, 54.5, 21.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$, 317.0954; Found: 317.0963.

8-(tert-butyl)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3c)



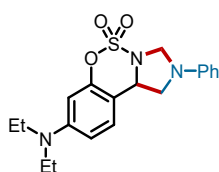
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3c**. White solid (27.9 mg, 78%); m.p. 182.1 – 183.5 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 1.9 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 5.45 (t, *J* = 3.5 Hz, 1H), 4.96 (d, *J* = 4.7 Hz, 1H), 4.69 (d, *J* = 4.7 Hz, 1H), 3.98 (d, *J* = 3.6 Hz, 2H), 1.32 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.8, 150.8, 145.0, 129.5, 126.1, 123.3, 119.1, 117.5, 115.8, 113.1, 65.9, 61.7, 54.4, 34.8, 31.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₃N₂O₃S, 359.1424; Found: 359.1432.

8-methoxy-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3d)



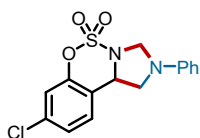
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3d**. White solid (27.6 mg, 83%); m.p. 100.1 – 101.2 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.63 – 6.57 (m, 3H), 5.42 (dd, *J* = 5.0, 2.1 Hz, 1H), 4.96 (d, *J* = 4.7 Hz, 1H), 4.68 (d, *J* = 4.7 Hz, 1H), 3.97 – 3.92 (m, 2H), 3.81 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.5, 151.7, 145.1, 129.5, 127.1, 119.2, 113.1, 113.0, 112.4, 103.6, 65.9, 61.5, 55.7, 54.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₇N₂O₄S, 333.0904; Found: 333.0912.

8-(diethylamino)-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3e)



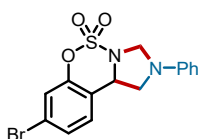
Purification by flash column chromatography (PE:EA, 100:1~10:1 v/v) to provide **3e**. Yellow solid (21.6 mg, 58%); m.p. 183.7 – 185.0 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 6.52 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.25 (d, *J* = 2.6 Hz, 1H), 5.38 (t, *J* = 4.0 Hz, 1H), 4.93 (d, *J* = 4.5 Hz, 1H), 4.68 (d, *J* = 4.6 Hz, 1H), 3.94 – 3.88 (m, 2H), 3.33 (q, *J* = 7.1 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 152.1, 148.8, 145.2, 129.4, 126.9, 118.8, 112.9, 109.5, 105.8, 100.4, 65.8, 61.5, 54.3, 44.5, 12.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₄N₃O₃S, 374.1533; Found: 374.1541.

8-chloro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3f)



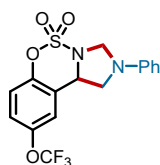
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3f**. White solid (25.5 mg, 76%); m.p. 140.1 – 140.9 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 3H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.62 – 6.59 (m, 2H), 5.43 (dd, *J* = 5.0, 1.5 Hz, 1H), 4.98 (d, *J* = 4.8 Hz, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 3.99 – 3.92 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.4, 144.9, 135.1, 129.5, 127.5, 126.3, 119.6, 119.5, 119.3, 113.4, 66.1, 61.7, 54.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄ClN₂O₃S, 337.0408; Found: 337.0418.

8-bromo-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3g)



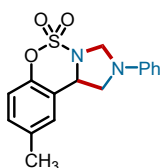
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3g**. White solid (29.3 mg, 77%); m.p. 143.7 – 145.2 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.17 – 7.12 (m, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.64 – 6.59 (m, 2H), 5.44 – 5.38 (m, 1H), 4.98 (d, *J* = 4.8 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 1H), 3.98 – 3.92 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.4, 144.9, 129.5, 129.2, 127.7, 122.6, 122.2, 120.0, 119.6, 113.4, 66.1, 61.7, 54.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄⁷⁹BrN₂O₃S, 380.9903; Found: 380.9913.

2-phenyl-9-(trifluoromethoxy)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3h)



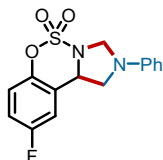
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3h**. White solid (22.4 mg, 58%); m.p. 130.2 – 131.1 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.23 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 2H), 5.46 (d, *J* = 5.7 Hz, 1H), 5.00 (d, *J* = 4.9 Hz, 1H), 4.69 (d, *J* = 4.9 Hz, 1H), 4.02 – 3.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.2, 146.3 (q, *J* = 2.1 Hz), 144.8, 129.6, 122.62, 122.57, 120.6, 120.3 (q, *J* = 258.4 Hz), 119.7, 119.3, 113.4, 66.2, 61.8, 54.6. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -58.17. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄F₃N₂O₄S, 387.0621; Found: 387.0630.

9-methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3i)



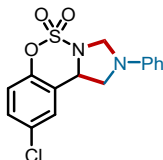
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3i**. White solid (26.9 mg, 85%); m.p. 155.6 – 157.5 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.16 – 7.12 (m, 1H), 7.05 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.64 – 6.59 (m, 2H), 5.43 (t, *J* = 3.6 Hz, 1H), 4.96 (d, *J* = 4.7 Hz, 1H), 4.68 (d, *J* = 4.7 Hz, 1H), 3.97 (d, *J* = 3.7 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.9, 145.1, 135.9, 130.4, 129.5, 126.7, 120.3, 119.2, 118.7, 113.2, 66.0, 61.9, 54.4, 20.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₇N₂O₃S, 317.0954; Found: 317.0963.

9-fluoro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3j)



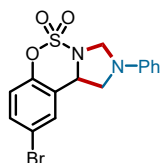
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3j**. White solid (21.8 mg, 68%); m.p. 152.1 – 153.5 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.07 – 7.06 (m, 2H), 7.02 – 6.97 (m, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.65 – 6.60 (m, 2H), 5.43 (d, *J* = 4.5 Hz, 1H), 4.98 (d, *J* = 4.8 Hz, 1H), 4.68 (d, *J* = 4.8 Hz, 1H), 4.00 – 3.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.7 (d, *J* = 246.7 Hz), 147.0 (d, *J* = 2.8 Hz), 144.9, 129.6, 122.5 (d, *J* = 7.0 Hz), 120.6 (d, *J* = 8.4 Hz), 119.6, 116.9 (d, *J* = 23.6 Hz), 113.4, 113.2 (d, *J* = 24.8 Hz), 66.1, 61.8 (d, *J* = 1.7 Hz), 54.5. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.72. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄FN₂O₃S, 321.0704; Found: 321.0713.

9-chloro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3k)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3k**. White solid (24.2 mg, 72%); m.p. 180.8 – 182.1 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.65 – 6.61 (m, 2H), 5.43 (t, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 4.8 Hz, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 3.99 – 3.94 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.6, 144.9, 131.3, 129.9, 129.5, 126.5, 122.5, 120.4, 119.7, 113.4, 66.1, 61.7, 54.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄ClN₂O₃S, 337.0408; Found: 337.0417.

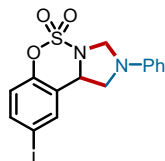
9-bromo-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3l)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3l**. White solid (27.4 mg, 72%); m.p. 170.5 – 172.3 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.45 (m, 1H), 7.42 (dd, *J* = 2.2, 0.7 Hz, 1H), 7.33 – 7.28 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.66 – 6.60 (m, 2H), 5.44 (t, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 4.8 Hz, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 3.96 (d, *J* = 3.6 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.2, 144.9, 132.8, 129.5, 129.4, 122.9, 120.7, 119.7,

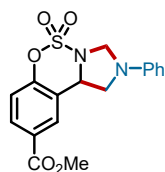
118.7, 113.4, 66.1, 61.6, 54.5. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{15}H_{14}^{79}BrN_2O_3S$, 380.9903; Found: 380.9913.

9-iodo-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3m)



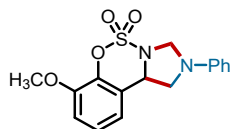
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3m**. White solid (26.1 mg, 61%); m.p. 190.8 – 191.9 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.63 (m, 1H), 7.59 (dd, $J = 2.0, 0.8$ Hz, 1H), 7.33 – 7.28 (m, 2H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 1H), 6.66 – 6.60 (m, 2H), 5.42 (t, $J = 4.0$ Hz, 1H), 4.98 (d, $J = 4.8$ Hz, 1H), 4.67 (d, $J = 4.8$ Hz, 1H), 3.98 – 3.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.0, 144.9, 138.7, 135.3, 129.5, 123.3, 120.9, 119.7, 113.4, 89.2, 66.1, 61.4, 54.5. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{15}H_{14}IN_2O_3S$, 428.9764; Found: 428.9772.

Methyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine-9-carboxylate 5,5-dioxide (3n)



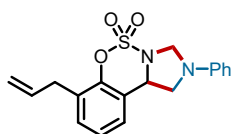
Purification by flash column chromatography (PE:EA, 100:1~10:1 v/v) to provide **3n**. White solid (28.4 mg, 79%); m.p. 174.2 – 175.4 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.00 (m, 2H), 7.31 – 7.27 (m, 2H), 7.15 – 7.10 (m, 1H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.64 – 6.60 (m, 2H), 5.50 (d, $J = 5.4$ Hz, 1H), 5.00 (d, $J = 4.8$ Hz, 1H), 4.68 (d, $J = 4.8$ Hz, 1H), 4.06 – 3.97 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 154.3, 144.9, 131.1, 129.5, 128.5, 128.0, 121.1, 119.6, 119.2, 113.4, 66.1, 61.8, 54.6, 52.5. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O_5S$, 361.0853; Found: 361.0860.

7-methoxy-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3o)



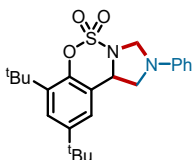
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3o**. White solid (28.6 mg, 86%); m.p. 138.7 – 139.5 °C; 1H NMR (400 MHz, DMSO-*d*₆) δ 7.29 – 7.19 (m, 3H), 7.12 (d, $J = 7.7$ Hz, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 6.80 (t, $J = 7.3$ Hz, 1H), 6.75 – 6.69 (m, 2H), 5.53 (d, $J = 5.6$ Hz, 1H), 4.94 (d, $J = 5.4$ Hz, 1H), 4.59 (d, $J = 5.4$ Hz, 1H), 4.06 (dd, $J = 9.9, 1.2$ Hz, 1H), 3.87 – 3.82 (m, 4H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 148.4, 145.8, 140.1, 129.6, 126.3, 122.5, 119.3, 118.6, 114.3, 112.8, 66.4, 62.2, 56.5, 54.9. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_4S$, 333.0904; Found: 333.0908.

7-allyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (**3p**)



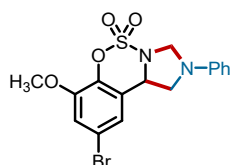
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3p**. White solid (28.4 mg, 83%); m.p. 105.6 – 107.3 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 (d, *J* = 6.8 Hz, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.01 – 5.91 (m, 1H), 5.47 (d, *J* = 4.8 Hz, 1H), 5.19 – 5.07 (m, 2H), 4.98 (d, *J* = 4.8 Hz, 1H), 4.70 (d, *J* = 4.8 Hz, 1H), 4.02 – 3.95 (m, 2H), 3.52 – 3.40 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.1, 145.1, 135.0, 130.43, 130.37, 129.5, 125.6, 124.5, 120.8, 119.3, 116.9, 113.2, 66.2, 62.0, 54.8, 33.3. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₁₉N₂O₃S, 343.1111; Found: 343.1119.

7,9-di-*tert*-butyl-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (**3q**)



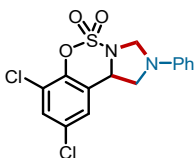
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3q**. White solid (31.9 mg, 77%); m.p. 196.5 – 198.2 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 2.2 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.44 (d, *J* = 5.6 Hz, 1H), 4.98 (d, *J* = 4.9 Hz, 1H), 4.75 (d, *J* = 4.9 Hz, 1H), 4.05 (dd, *J* = 9.0, 6.4 Hz, 1H), 3.90 (dd, *J* = 9.1, 1.8 Hz, 1H), 1.45 (s, 9H), 1.33 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.2, 147.9, 145.2, 139.4, 129.5, 124.5, 121.1, 120.5, 119.2, 113.3, 66.5, 62.2, 55.3, 35.1, 34.8, 31.4, 30.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₃H₃₁N₂O₃S, 415.2050; Found: 415.2056.

9-bromo-7-methoxy-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (**3r**)



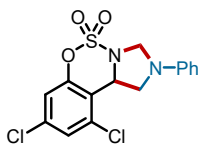
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3r**. White solid (25.8 mg, 63%); m.p. 193.3 – 194.8 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 2.1, 0.7 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.66 – 6.59 (m, 2H), 5.42 (t, *J* = 3.6 Hz, 1H), 4.99 (d, *J* = 4.8 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 1H), 3.94 (d, *J* = 3.7 Hz, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.6, 144.9, 140.0, 129.5, 123.4, 120.2, 119.6, 118.4, 115.5, 113.4, 66.2, 61.8, 56.5, 54.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆⁷⁹BrN₂O₄S, 411.0009; Found: 411.0016.

7,9-dichloro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (**3s**)



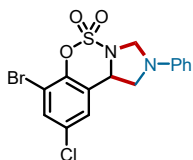
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3s**. White solid (27.4 mg, 74%); m.p. 154.6 – 155.4 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 2.1 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.19 – 7.16 (m, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 5.43 (t, *J* = 4.0 Hz, 1H), 5.03 (d, *J* = 4.9 Hz, 1H), 4.67 (d, *J* = 4.9 Hz, 1H), 3.99 – 3.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.9, 144.7, 130.9, 130.3, 129.6, 125.1, 124.8, 124.1, 120.0, 113.6, 66.3, 61.9, 54.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃Cl₂N₂O₃S, 371.0018; Found: 371.0024.

8,10-dichloro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3t)



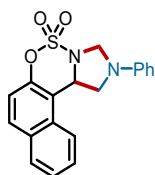
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3t**. White solid (31.1 mg, 84%); m.p. 131.4 – 133.2 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 3H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.72 – 6.68 (m, 2H), 5.45 (dd, *J* = 6.7, 2.5 Hz, 1H), 5.04 (d, *J* = 5.6 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 1H), 4.08 (dd, *J* = 10.1, 6.7 Hz, 1H), 4.00 (dd, *J* = 10.1, 2.6 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.9, 144.9, 135.3, 133.3, 129.5, 127.4, 120.3, 119.5, 118.6, 114.2, 67.4, 61.3, 54.6. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃Cl₂N₂O₃S, 371.0018; Found: 371.0027.

7-bromo-9-chloro-2-phenyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3u)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3u**. White solid (33.5 mg, 81%); m.p. 202.7 – 204.4 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.22 (d, *J* = 2.2 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H), 5.43 (t, *J* = 4.0 Hz, 1H), 5.03 (d, *J* = 4.9 Hz, 1H), 4.66 (d, *J* = 4.9 Hz, 1H), 3.99 – 3.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.8, 144.7, 133.2, 131.3, 129.6, 125.5, 124.1, 120.0, 113.7, 113.6, 66.4, 62.0, 54.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃⁷⁹BrClN₂O₃S, 414.9513; Found: 414.9522.

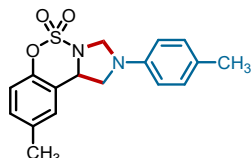
2-phenyl-1,2,3,12c-tetrahydroimidazo[1,5-c]naphtho[1,2-e][1,2,3]oxathiazine 5,5-dioxide (3v)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3v**. White solid (21.8

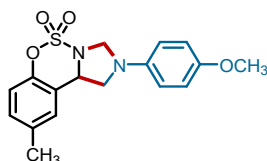
mg, 62%); m.p. 151.2 – 152.3 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.59 – 7.55 (m, 1H), 7.29 – 7.24 (m, 2H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 2H), 5.96 (dd, *J* = 7.0, 2.4 Hz, 1H), 5.07 (d, *J* = 5.2 Hz, 1H), 4.82 (d, *J* = 5.2 Hz, 1H), 4.31 – 4.27 (m, 1H), 3.99 (dd, *J* = 9.3, 2.6 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.7, 145.1, 140.2, 131.7, 130.9, 130.0, 129.4, 127.9, 125.9, 122.5, 119.7, 118.4, 115.3, 113.8, 67.0, 61.0, 55.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₇N₂O₃S, 353.0954; Found: 353.0958.

9-methyl-2-(p-tolyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3w)



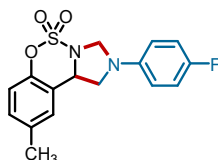
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3w**. White solid (27.7 mg, 84%); m.p. 120.5 – 121.8 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.11 (dd, *J* = 14.4, 8.3 Hz, 3H), 7.04 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 2H), 5.40 (s, 1H), 4.95 (d, *J* = 4.7 Hz, 1H), 4.63 (d, *J* = 4.7 Hz, 1H), 3.93 (d, *J* = 3.7 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.0, 143.1, 135.8, 130.3, 129.9, 128.7, 126.7, 120.5, 118.7, 113.4, 66.4, 61.9, 55.0, 20.9, 20.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₉N₂O₃S, 331.1111; Found: 331.1120.

2-(4-methoxyphenyl)-9-methyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3x)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3x**. White solid (28.3 mg, 82%); m.p. 148.9 – 150.3 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.4 Hz, 1H), 7.03 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.89 – 6.84 (m, 2H), 6.64 – 6.58 (m, 2H), 5.38 (t, *J* = 4.0 Hz, 1H), 4.95 (d, *J* = 4.9 Hz, 1H), 4.59 (d, *J* = 4.9 Hz, 1H), 3.92 – 3.86 (m, 2H), 3.78 (s, 3H), 2.36 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.5, 149.0, 139.7, 135.8, 130.2, 126.6, 120.7, 118.7, 114.98, 114.96, 67.1, 61.9, 55.8, 55.7, 20.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₉N₂O₄S, 347.1060; Found: 347.1068.

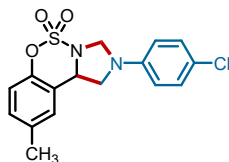
2-(4-fluorophenyl)-9-methyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3y)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3y**. White solid (24.7 mg, 74%); m.p. 168.6 – 170.5 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.4 Hz, 1H), 7.04 – 6.95 (m, 4H), 6.59 – 6.53 (m, 2H), 5.44 – 5.39 (m, 1H), 4.94 (d, *J* = 4.7 Hz, 1H), 4.61 (d, *J* = 4.7 Hz, 1H), 3.95 – 3.89 (m, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.8 (d, *J* = 238.4 Hz),

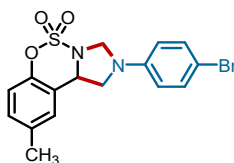
148.9, 141.8 (d, $J = 2.2$ Hz), 136.0, 130.4, 126.7, 120.4, 118.7, 116.0 (d, $J = 22.6$ Hz), 114.4 (d, $J = 7.7$ Hz), 66.6, 61.9, 55.3, 20.9. ^{19}F NMR (376 MHz, Chloroform- d) δ -125.21. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{FN}_2\text{O}_3\text{S}$, 335.0860; Found: 335.0869.

2-(4-chlorophenyl)-9-methyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3z)



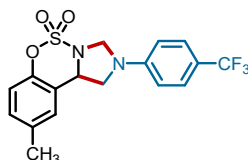
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3z**. White solid (26.6 mg, 76%); m.p. 187.8 – 189.2 °C; ^1H NMR (400 MHz, Chloroform- d) δ 7.26 – 7.21 (m, 2H), 7.17 – 7.13 (m, 1H), 7.06 – 7.03 (m, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.55 – 6.50 (m, 2H), 5.43 (d, $J = 5.4$ Hz, 1H), 4.91 (d, $J = 4.7$ Hz, 1H), 4.65 (d, $J = 4.7$ Hz, 1H), 3.98 – 3.91 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 148.9, 143.7, 136.0, 130.5, 129.3, 126.7, 124.3, 120.1, 118.7, 114.3, 66.0, 61.9, 54.6, 20.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{ClN}_2\text{O}_3\text{S}$, 351.0565; Found: 351.0566.

2-(4-bromophenyl)-9-methyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3aa)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3aa**. Yellow solid (24.8 mg, 63%); m.p. 112.1 – 113.3 °C; ^1H NMR (400 MHz, Chloroform- d) δ 7.40 – 7.34 (m, 2H), 7.17 – 7.13 (m, 1H), 7.04 (s, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.50 – 6.45 (m, 2H), 5.43 (d, $J = 5.4$ Hz, 1H), 4.90 (d, $J = 4.7$ Hz, 1H), 4.64 (d, $J = 4.7$ Hz, 1H), 3.98 – 3.90 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 148.9, 144.0, 136.0, 132.2, 130.5, 126.7, 120.0, 118.7, 114.7, 111.4, 65.8, 61.8, 54.4, 20.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}^{79}\text{BrN}_2\text{O}_3\text{S}$, 395.0060; Found: 395.0065.

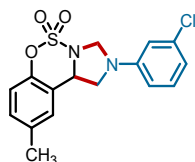
9-methyl-2-(4-(trifluoromethyl)phenyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (3ab)



Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3ab**. White solid (25.7 mg, 67%); m.p. 213.7 – 215.3 °C; ^1H NMR (400 MHz, Chloroform- d) δ 7.52 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.06 (s, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 6.61 (d, $J = 8.5$ Hz, 2H), 5.48 (d, $J = 5.7$ Hz, 1H), 4.92 (d, $J = 4.7$ Hz, 1H), 4.75 (d, $J = 4.7$ Hz, 1H), 4.11 – 3.99 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 148.8, 147.1, 136.2, 130.7, 126.8 (q, $J = 4.2$ Hz), 124.6 (q, $J = 271.7$ Hz), 120.7 (q, $J = 32.9$ Hz), 119.7, 118.8, 114.2, 112.3, 65.2, 61.8, 53.9, 20.9. ^{19}F NMR (376 MHz,

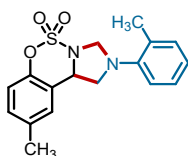
Chloroform-*d* δ -61.36. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₅F₃N₂O₃S, 385.0828; Found: 385.0835.

2-(3-chlorophenyl)-9-methyl-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (**3ac**)



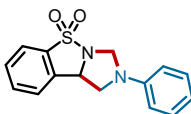
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3ac**. White solid (13.0 mg, 37%); m.p. 167.4 – 168.9 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 2H), 7.06 – 7.02 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.88 – 6.80 (m, 1H), 6.59 (t, *J* = 2.1 Hz, 1H), 6.47 – 6.44 (m, 1H), 5.44 (d, *J* = 5.7 Hz, 1H), 4.90 (d, *J* = 4.7 Hz, 1H), 4.68 (d, *J* = 4.7 Hz, 1H), 4.02 – 3.92 (m, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.8, 145.9, 136.0, 135.3, 130.6, 130.5, 126.7, 119.9, 119.0, 118.7, 113.1, 111.2, 65.6, 61.8, 54.2, 20.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆ClN₂O₃S, 351.0565; Found: 351.0574.

9-methyl-2-(*o*-tolyl)-1,2,3,10b-tetrahydrobenzo[e]imidazo[1,5-c][1,2,3]oxathiazine 5,5-dioxide (**3ad**)



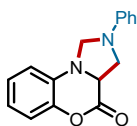
Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3ad**. White solid (9.2 mg, 28%); m.p. 98.1 – 99.9 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.04 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 1.5 Hz, 1H), 5.20 – 5.15 (m, 1H), 4.84 (d, *J* = 7.3 Hz, 1H), 4.61 (d, *J* = 7.3 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.58 (dd, *J* = 10.8, 4.6 Hz, 1H), 2.34 (s, 3H), 2.26 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.6, 145.8, 135.8, 132.3, 131.5, 129.8, 126.9, 126.7, 124.5, 121.9, 118.81, 118.80, 70.3, 60.7, 60.3, 20.8, 18.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₉N₂O₃S, 331.1111; Found: 331.1124.

2-phenyl-1,2,3,9b-tetrahydrobenzo[d]imidazo[1,5-b]isothiazole 5,5-dioxide (**3ae**)



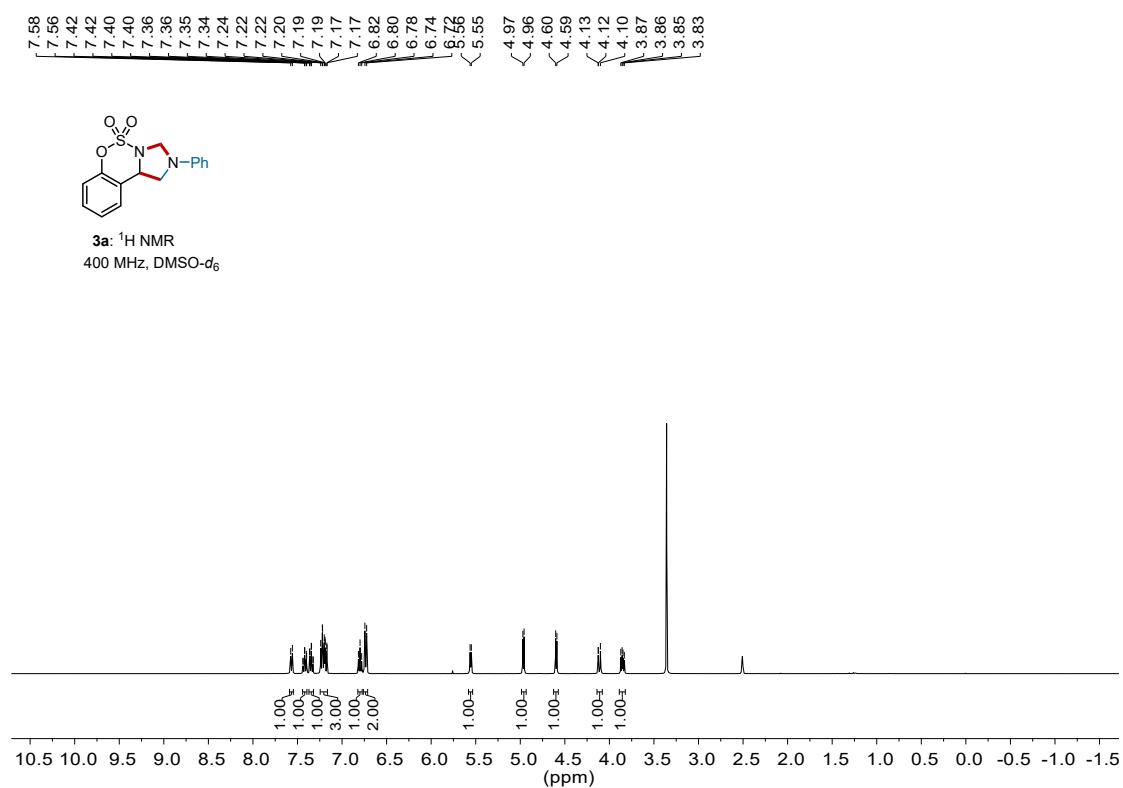
Purification by flash column chromatography (PE:EA, 100:1~10:1 v/v) to provide **3ae**. Yellow solid (23.5 mg, 82%); m.p. 112.3 – 113.4 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.26 (m, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 2H), 5.39 – 5.29 (m, 2H), 4.43 (d, *J* = 7.5 Hz, 1H), 3.80 – 3.74 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.4, 138.5, 135.5, 133.7, 130.0, 129.4, 124.0, 121.7, 119.7, 114.4, 65.1, 63.2, 53.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₅N₂O₂S, 287.0849; Found: 287.0858.

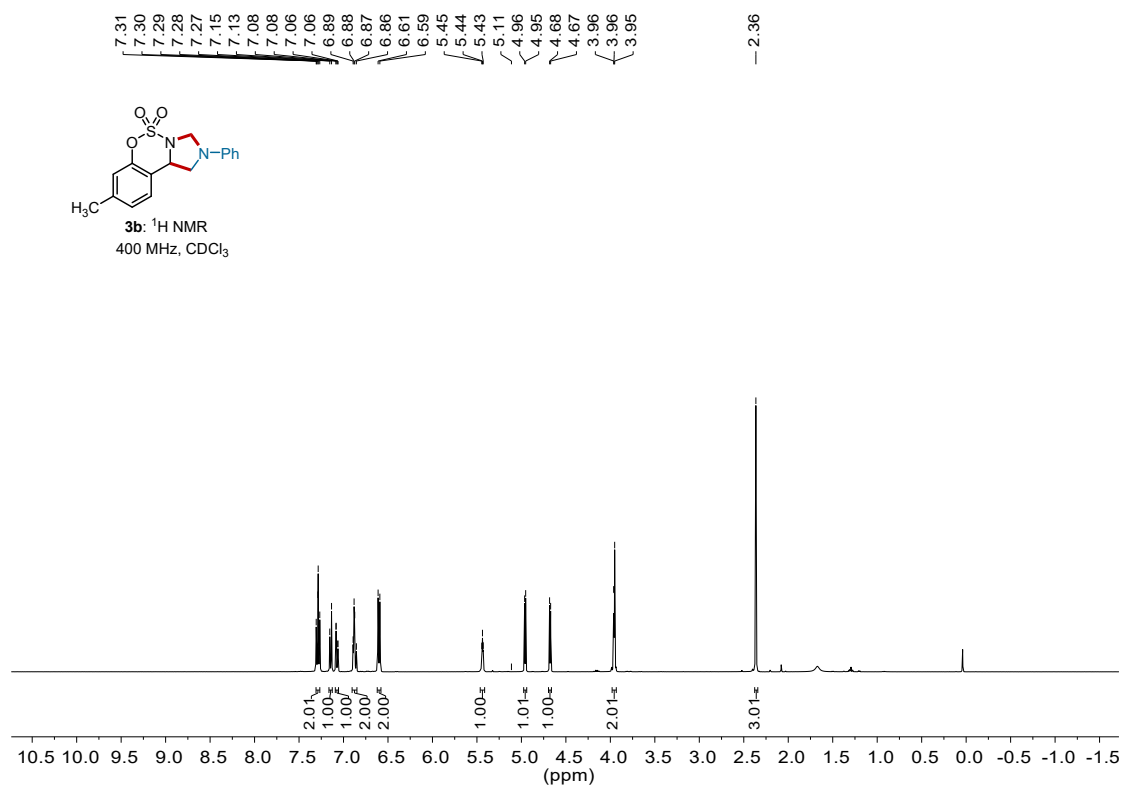
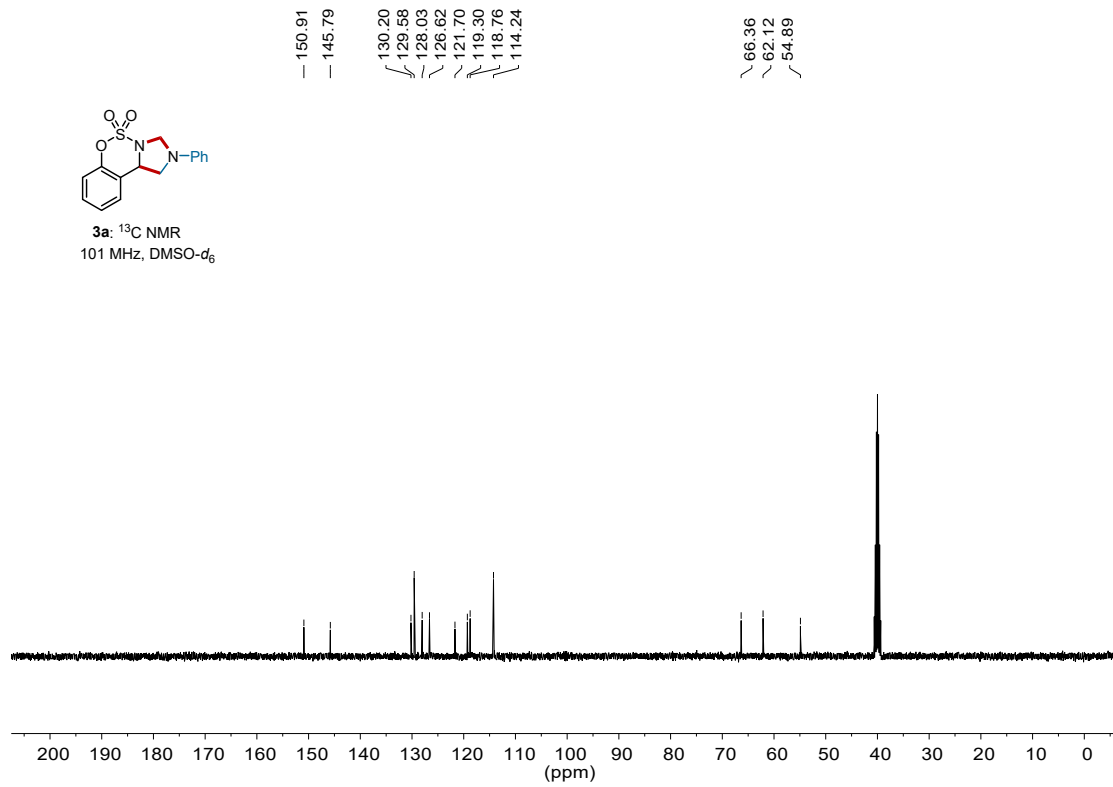
2-phenyl-1,2,3,3a-tetrahydro-4H-benzo[b]imidazo[1,5-d][1,4]oxazin-4-one (**3af**)

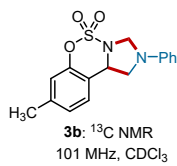


Purification by flash column chromatography (PE:EA, 100:1~15:1 v/v) to provide **3af**. Yellow solid (11.2 mg, 42%); m.p. 114.3 – 116.0 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 8.0 Hz, 2H), 7.19 – 7.15 (m, 2H), 6.99 (td, *J* = 7.9, 1.2 Hz, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.80 – 6.78 (m, 1H), 6.66 (d, *J* = 8.1 Hz, 2H), 4.80 (d, *J* = 3.4 Hz, 1H), 4.69 (d, *J* = 3.3 Hz, 1H), 4.10 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.96 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.84 (t, *J* = 8.6 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 145.4, 142.4, 132.2, 129.5, 125.4, 121.0, 118.1, 116.9, 113.4, 112.0, 64.9, 57.2, 47.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₅N₂O₂, 267.1128; Found: 267.1137.

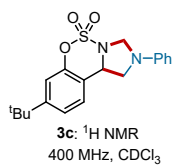
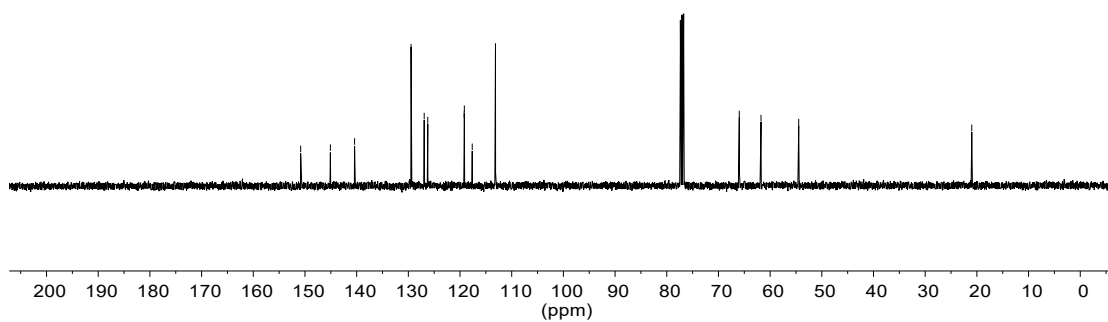
4. NMR Copies of Products



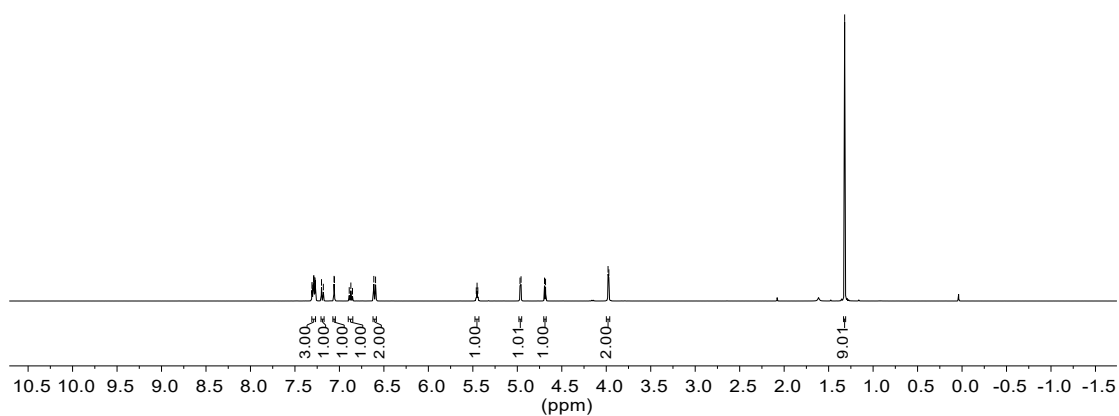


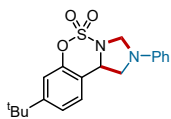


150.83
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 140.40
 129.47
 126.93
 126.24
 119.20
 119.16
 117.64
 113.14
 65.97
 61.77
 54.47
 20.99



7.31
 7.30
 7.30
 7.29
 7.29
 7.29
 7.28
 7.28
 7.27
 7.27
 7.20
 7.18
 7.06
 7.06
 6.89
 6.87
 6.85
 6.61
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 4.96
 4.69
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 3.98
 3.97
 1.32



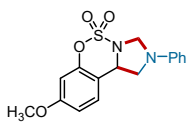
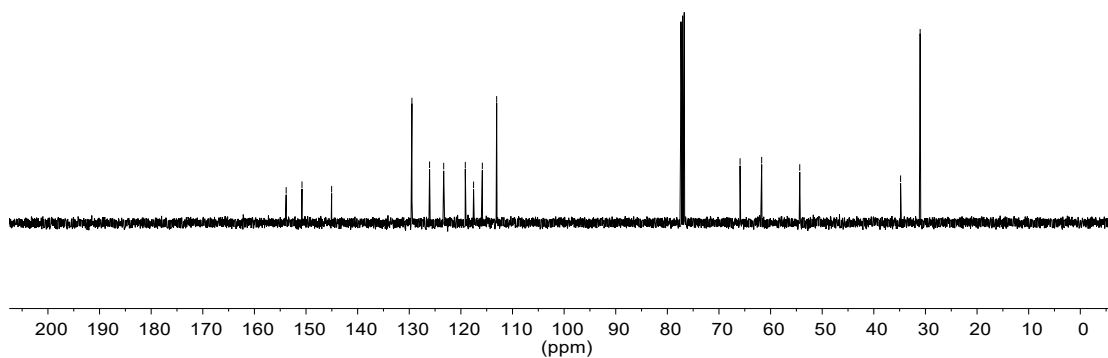


3c: ^{13}C NMR
101 MHz, CDCl_3

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150.78
145.04
129.49
126.07
123.33
119.14
117.54
115.84
113.07

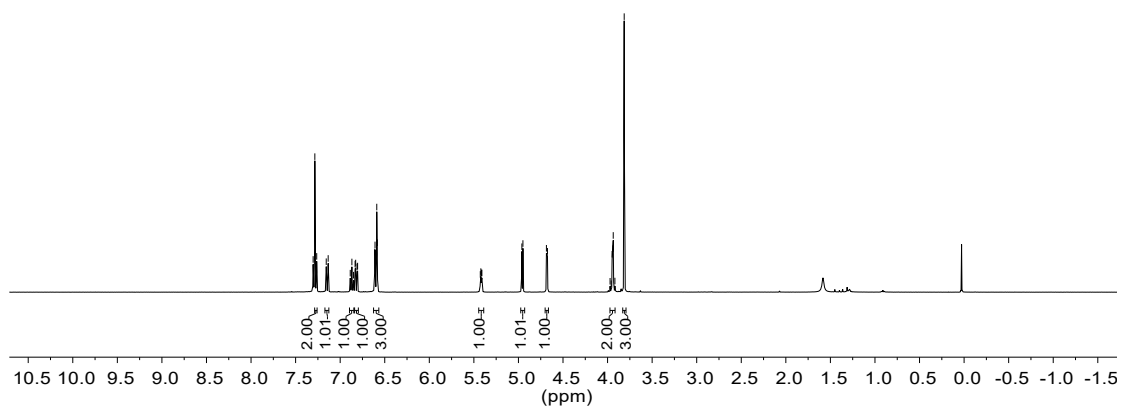
65.91
61.73
54.35

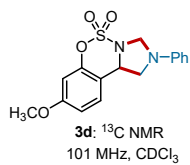
34.81
31.03



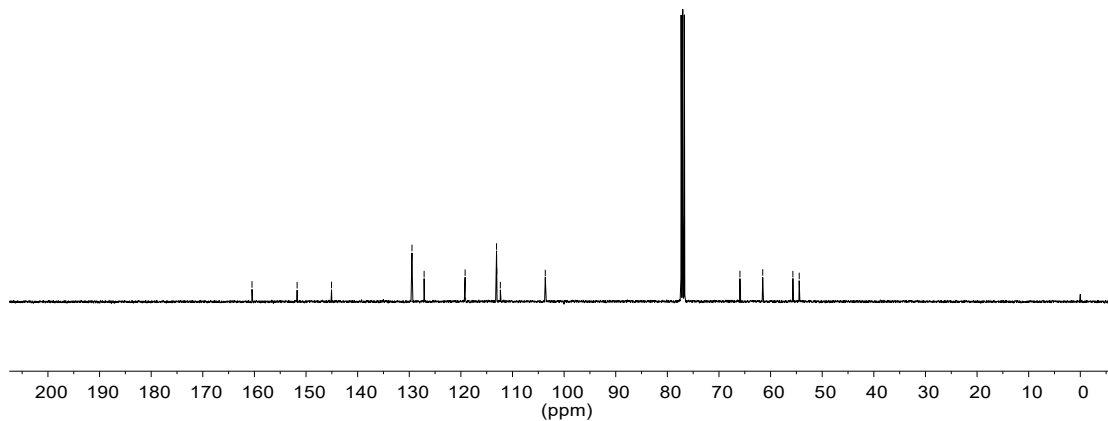
3d: ^1H NMR
400 MHz, CDCl_3

7.30
7.30
7.28
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7.16
7.13
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6.85
6.83
6.81
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3.81

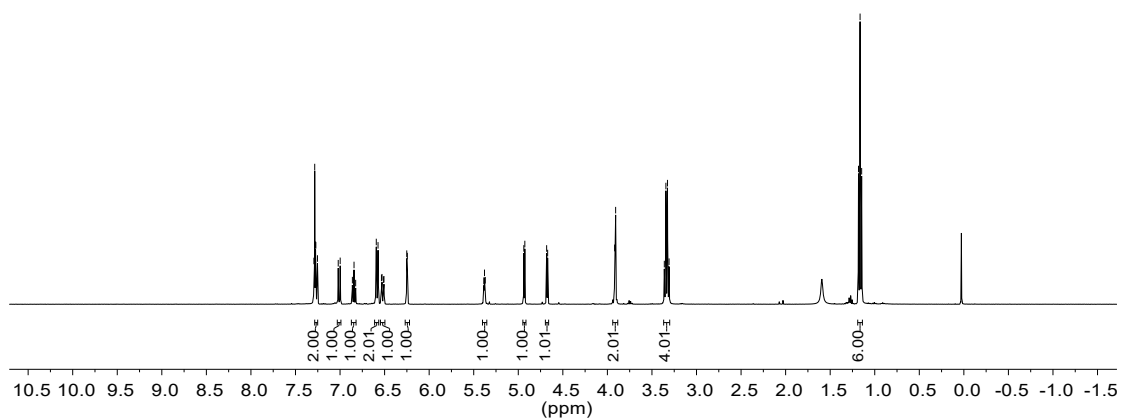
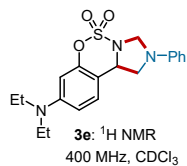


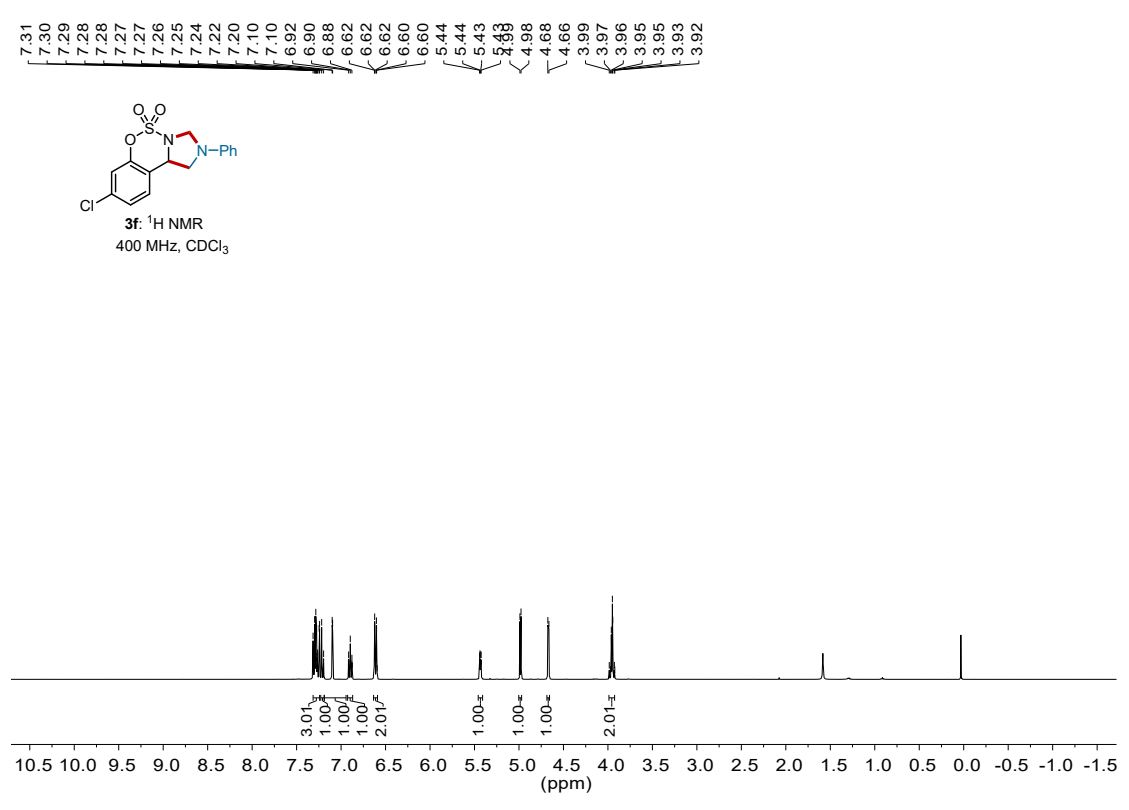
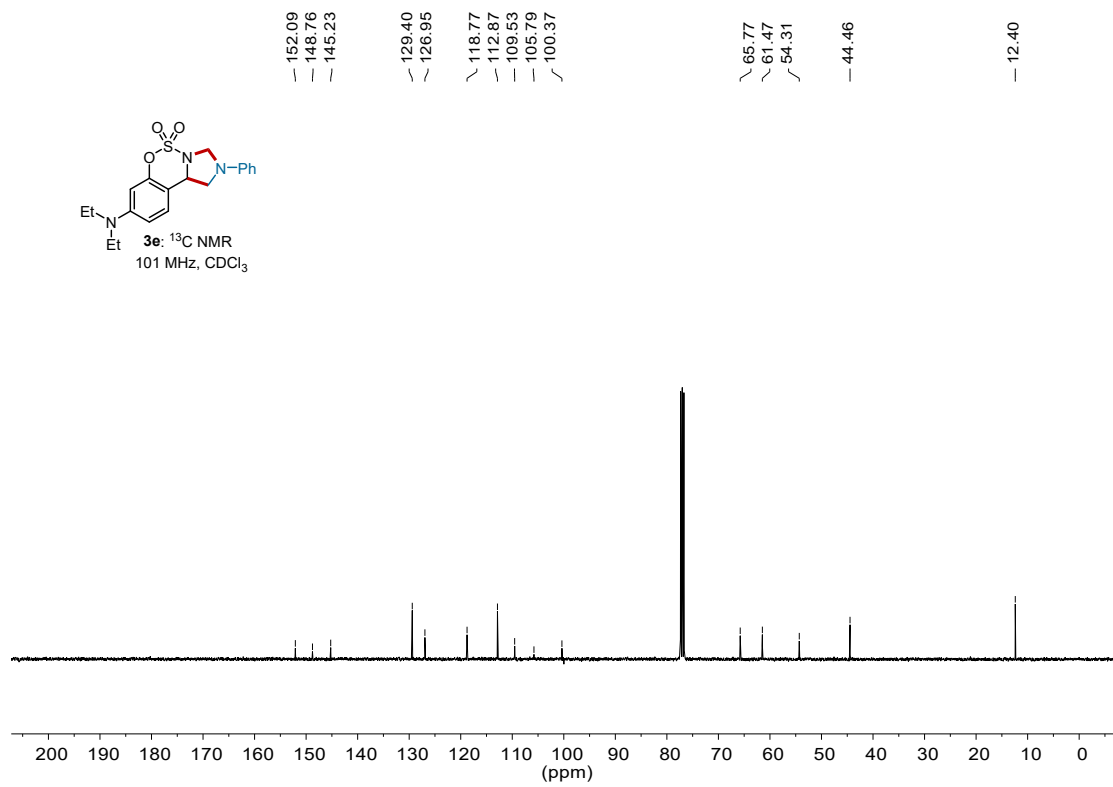


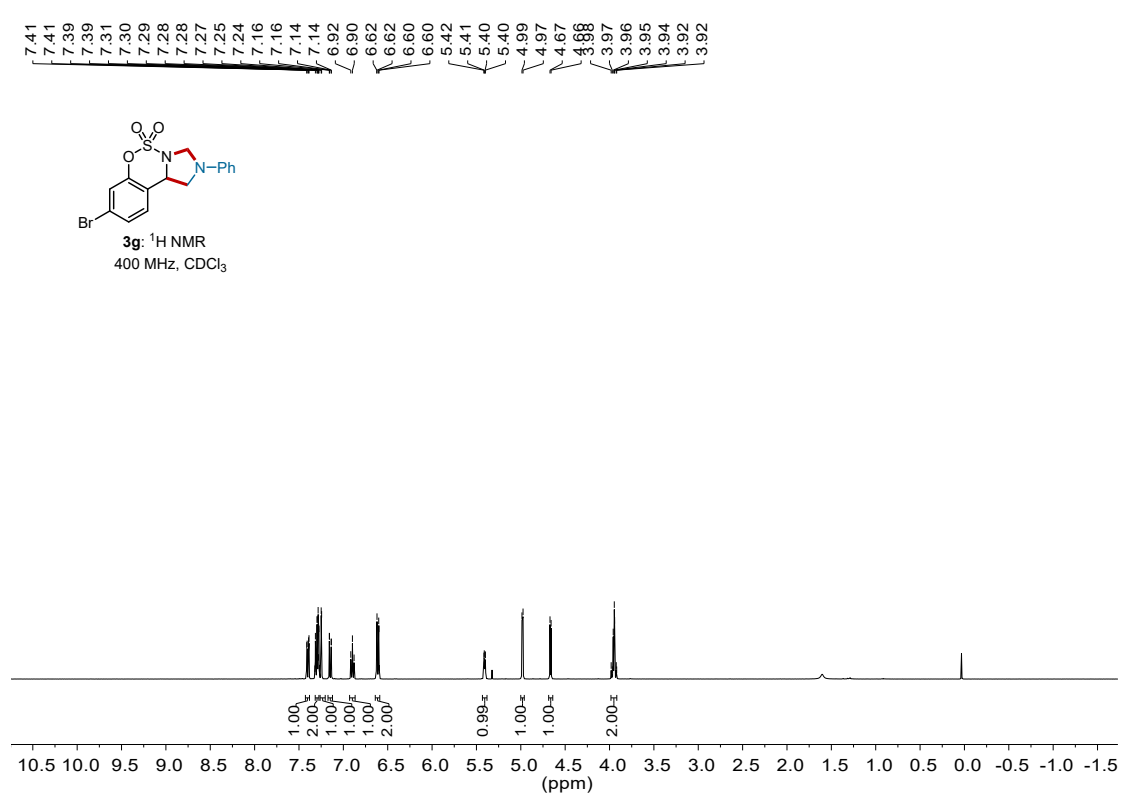
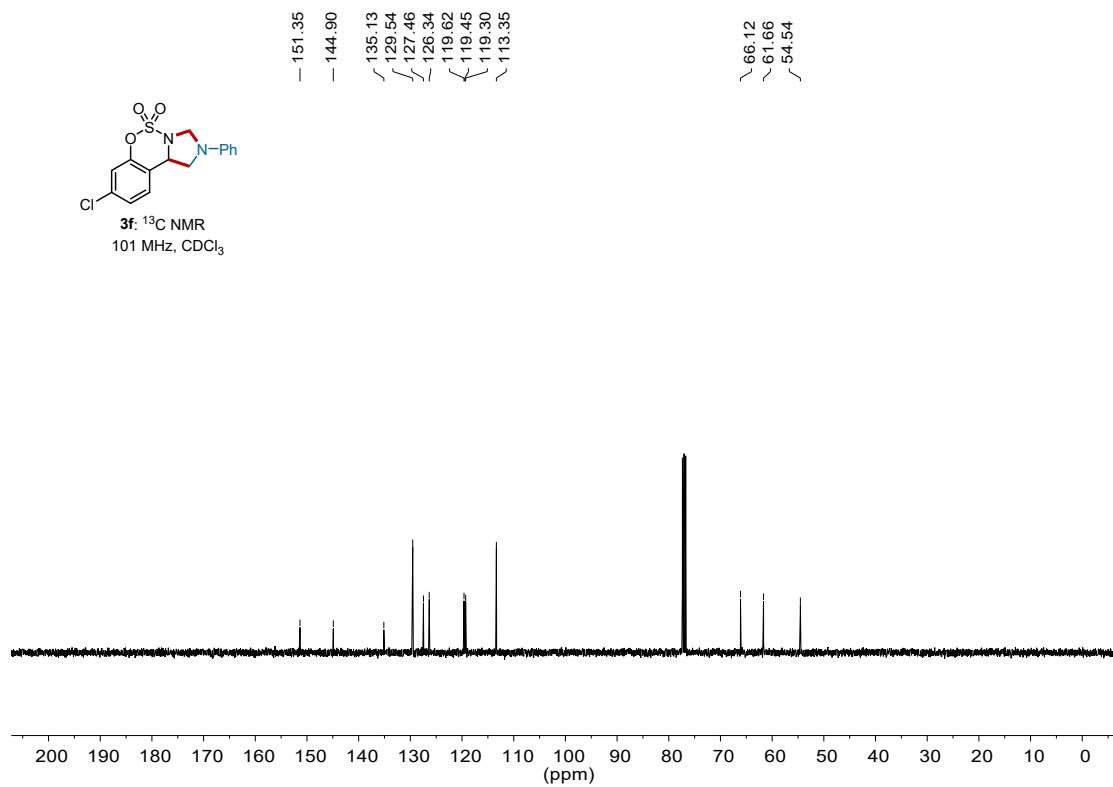
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 — 151.73
 — 145.06
 — 129.48
 — 127.12
 — 119.18
 — 113.09
 — 113.05
 — 112.35
 — 103.65
 — 65.94
 — 61.52
 — 55.68
 — 54.45

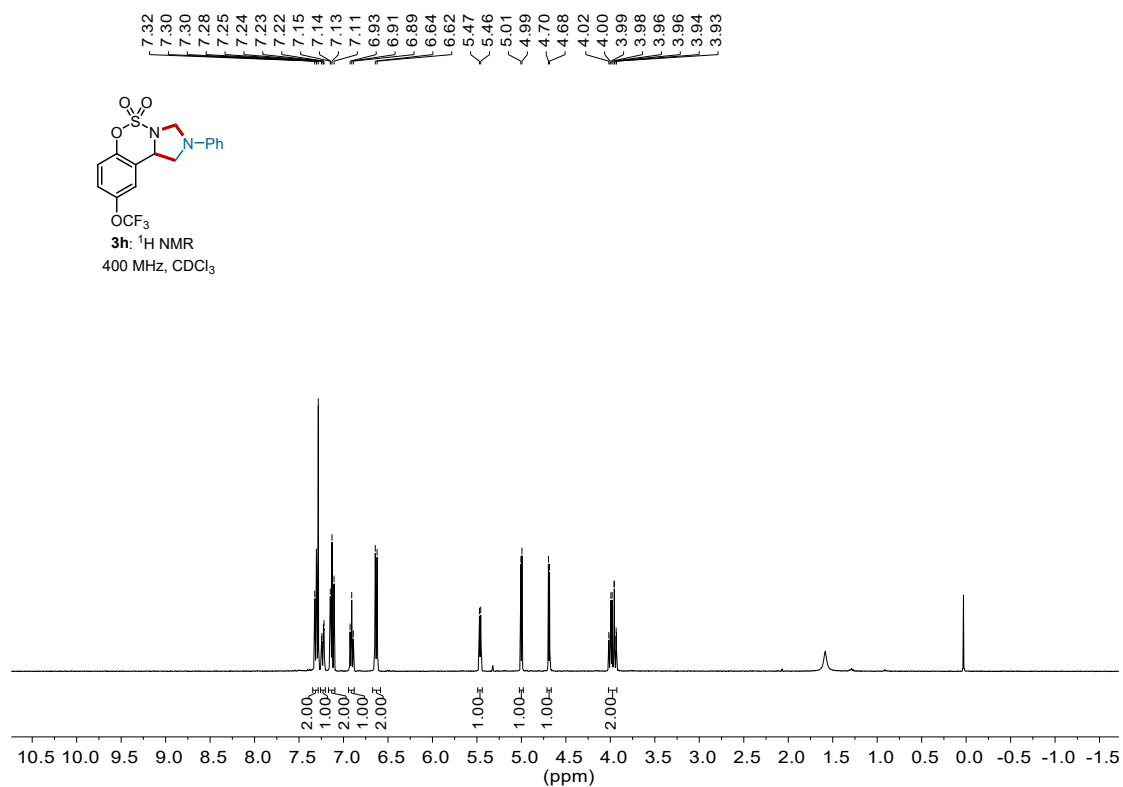
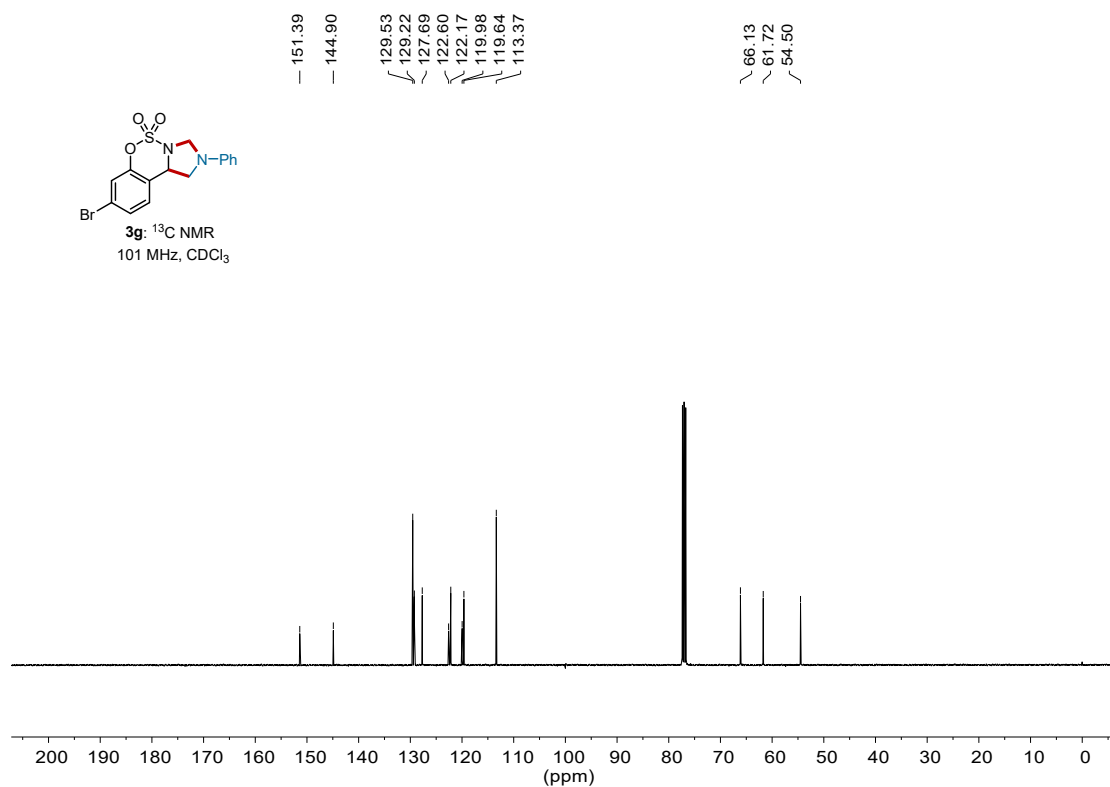


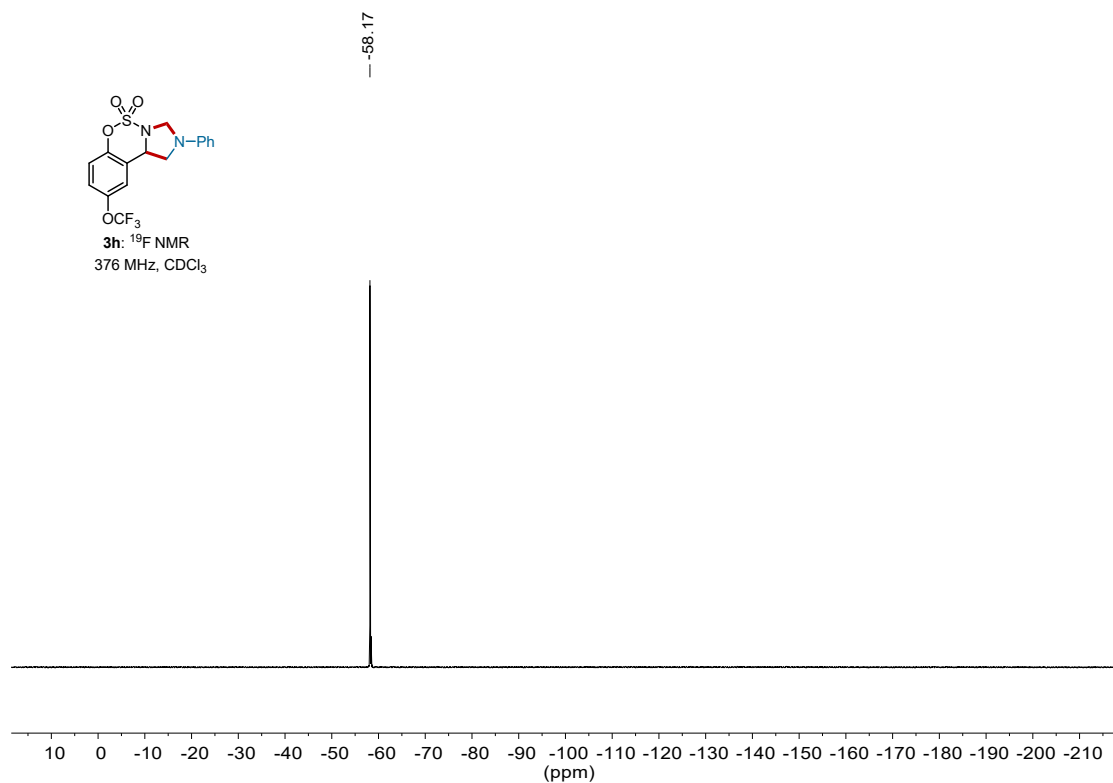
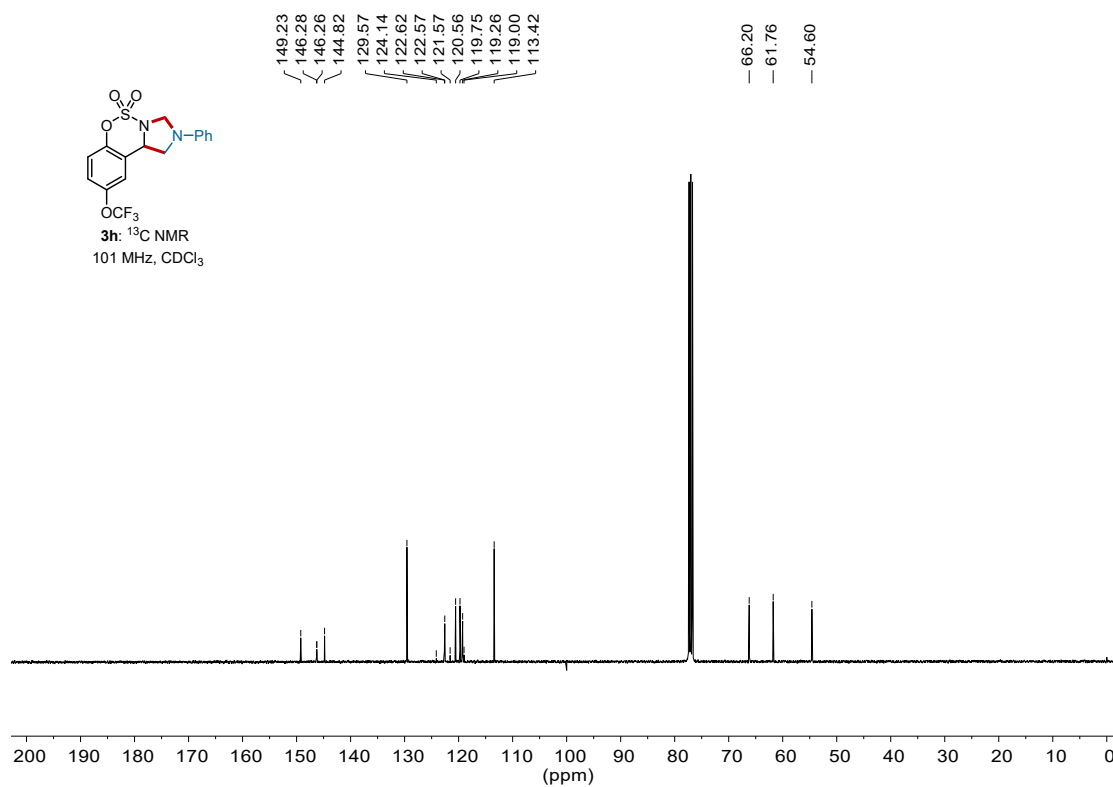
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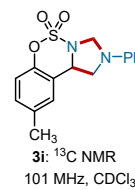
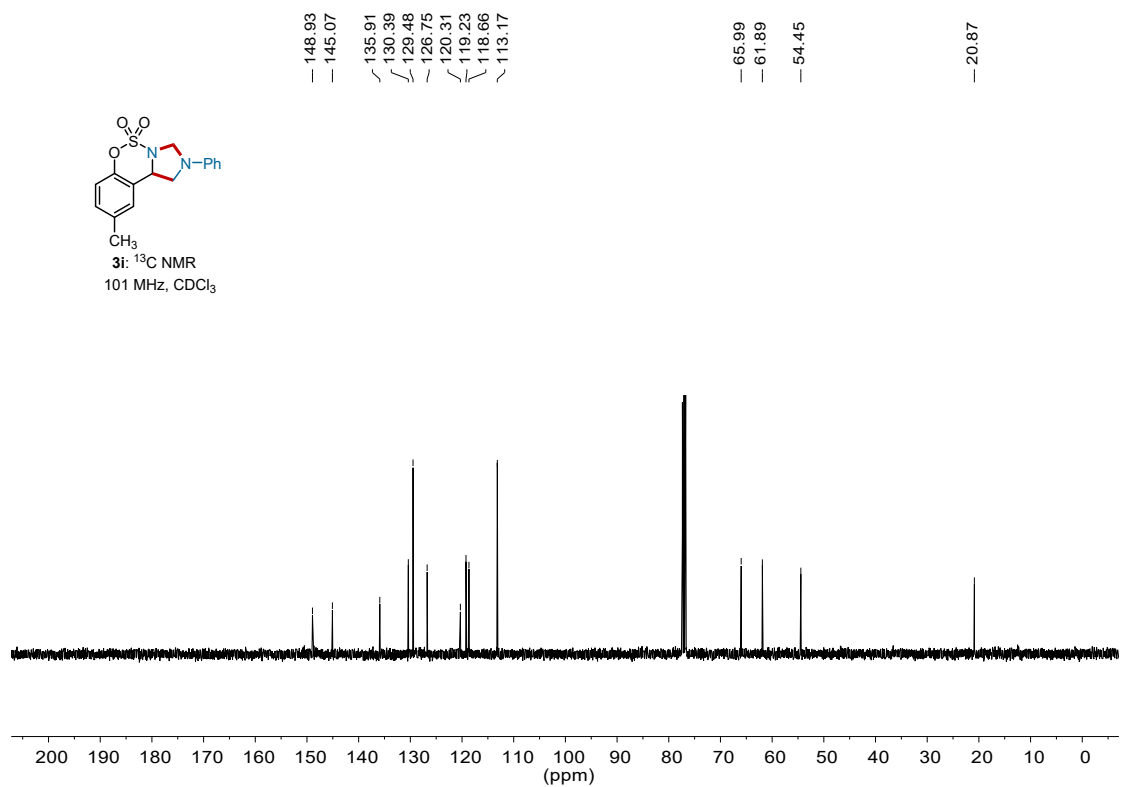
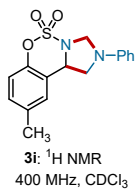
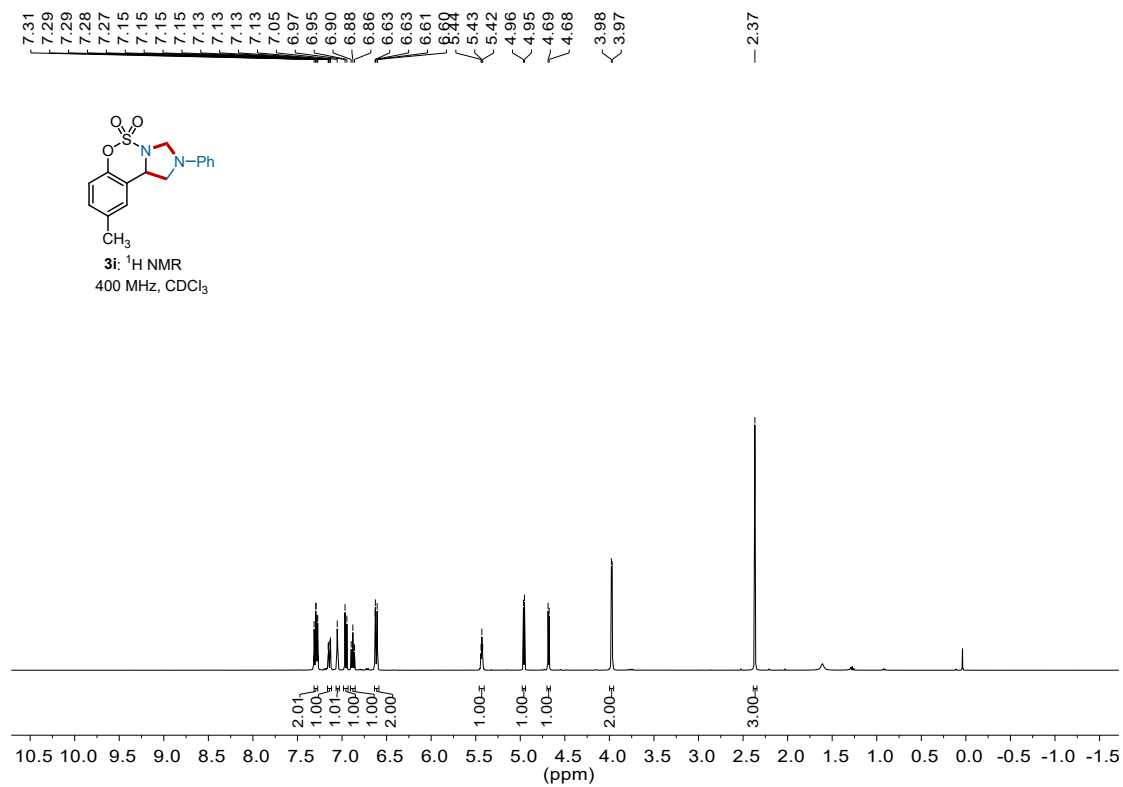




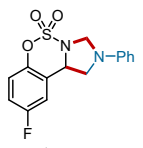




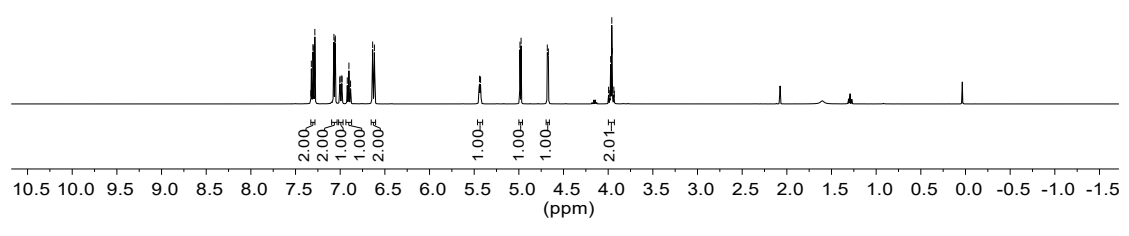




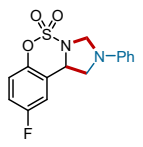
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6.64
6.64
6.62
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3.97
3.96
3.95
3.94
3.93



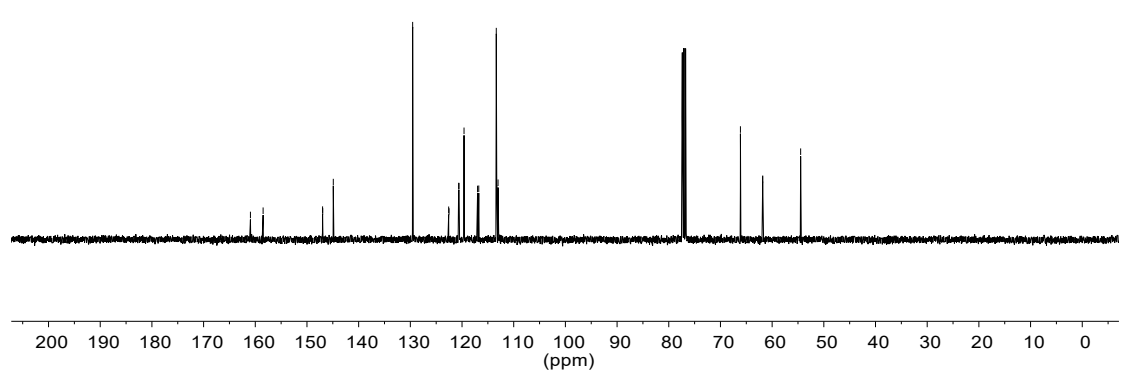
3j: ¹H NMR
400 MHz, CDCl₃

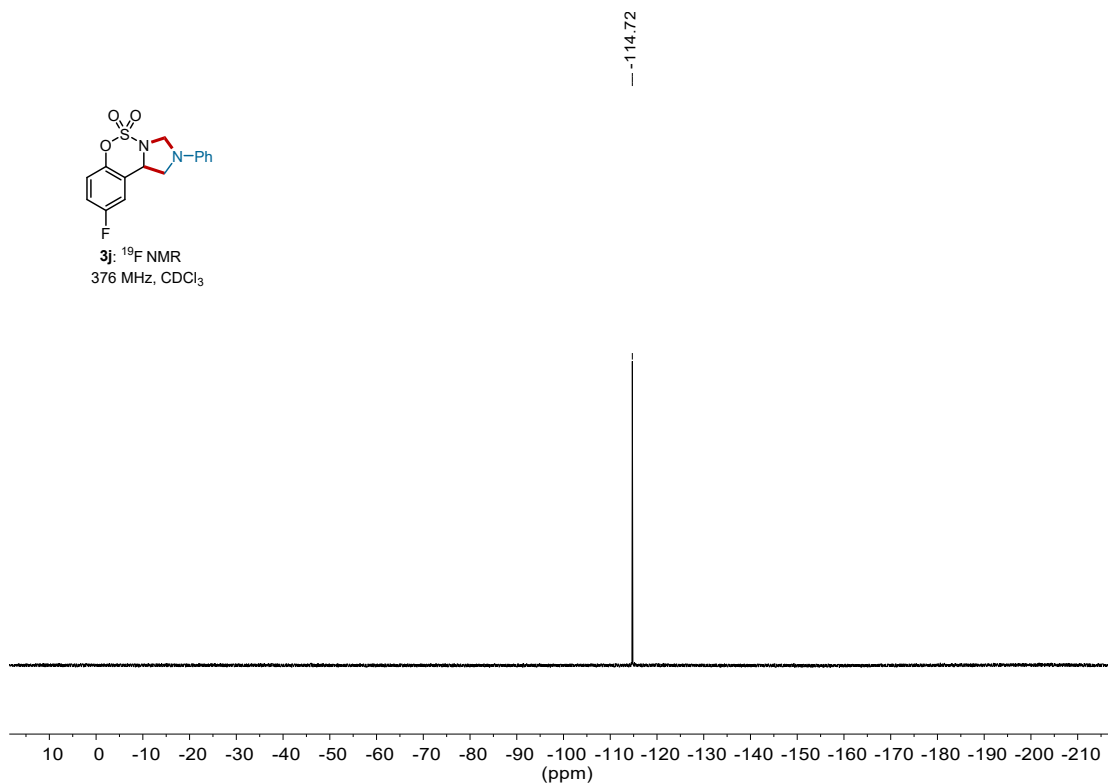
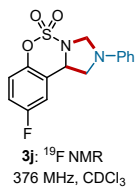


160.94
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146.95
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120.56
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113.28
113.03
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61.82
54.48

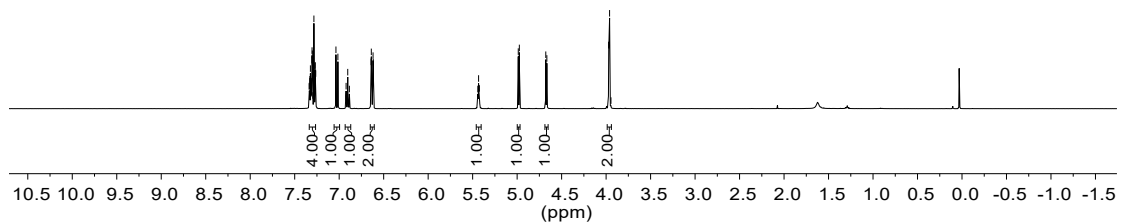
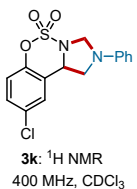


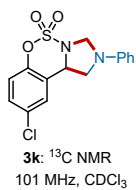
3j: ¹³C NMR
101 MHz, CDCl₃



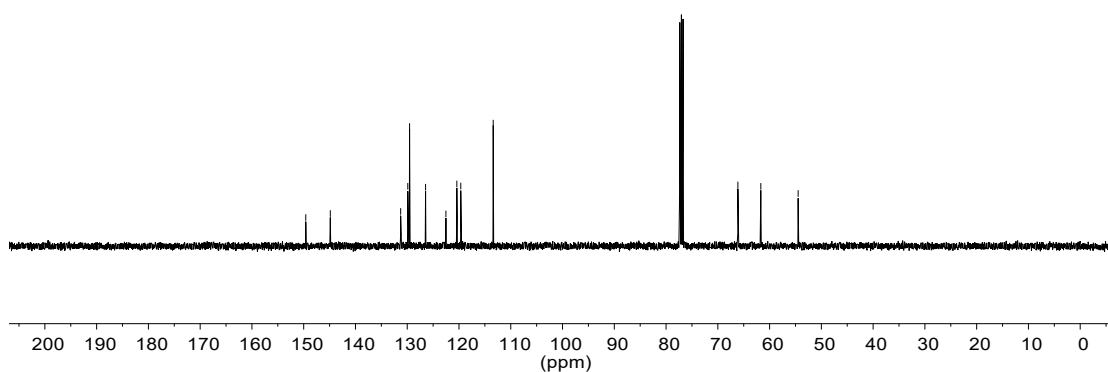


7.34
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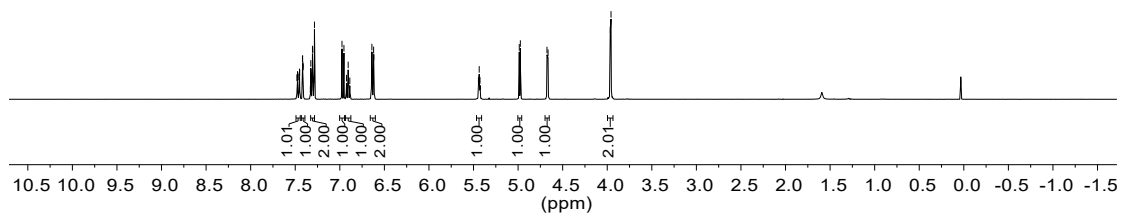
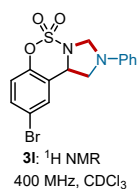


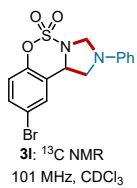


— 149.60
 — 144.86
 { 131.27
 { 129.89
 { 129.55
 { 126.46
 { 122.53
 { 120.42
 { 119.66
 { 113.39
 { 66.12
 { 61.70
 { 54.49



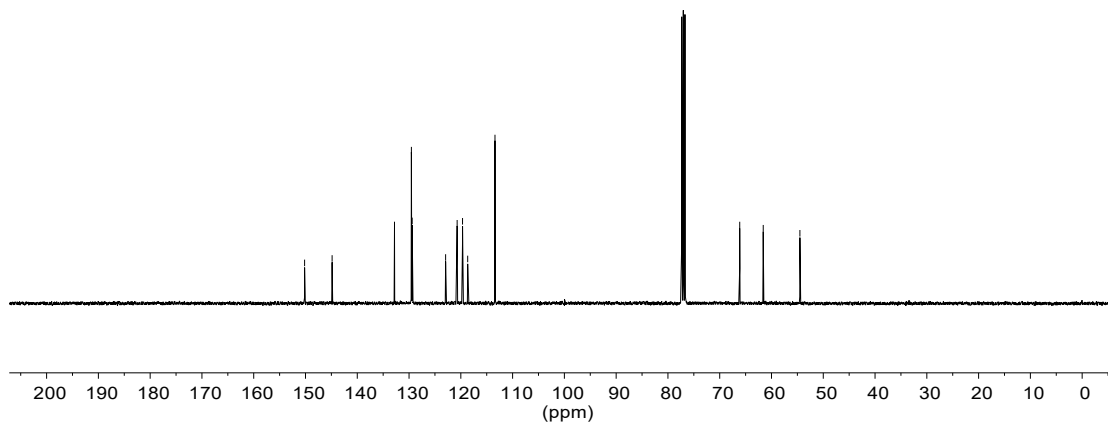
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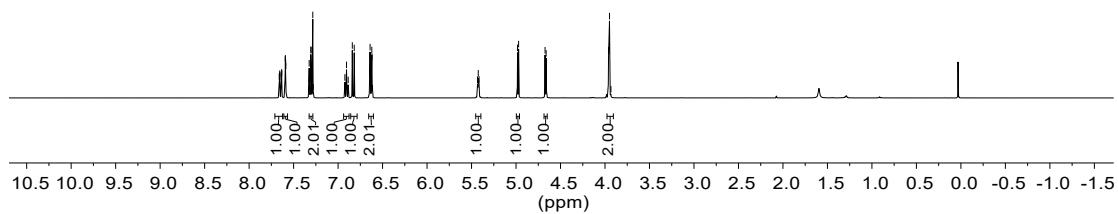
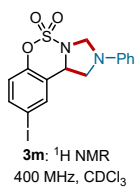


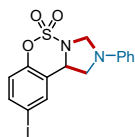
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 — 144.86
 / 132.81
 / 129.55
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/ 66.13
 / 61.60
 / 54.51

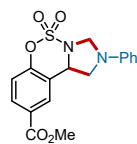
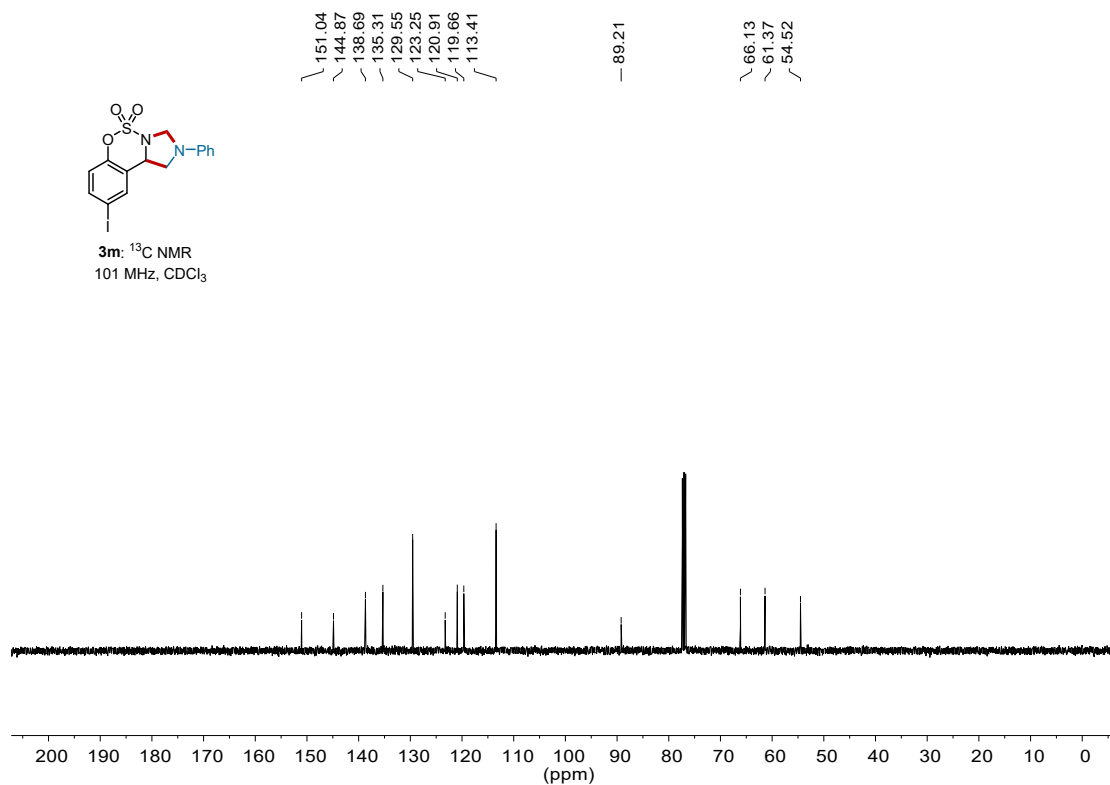


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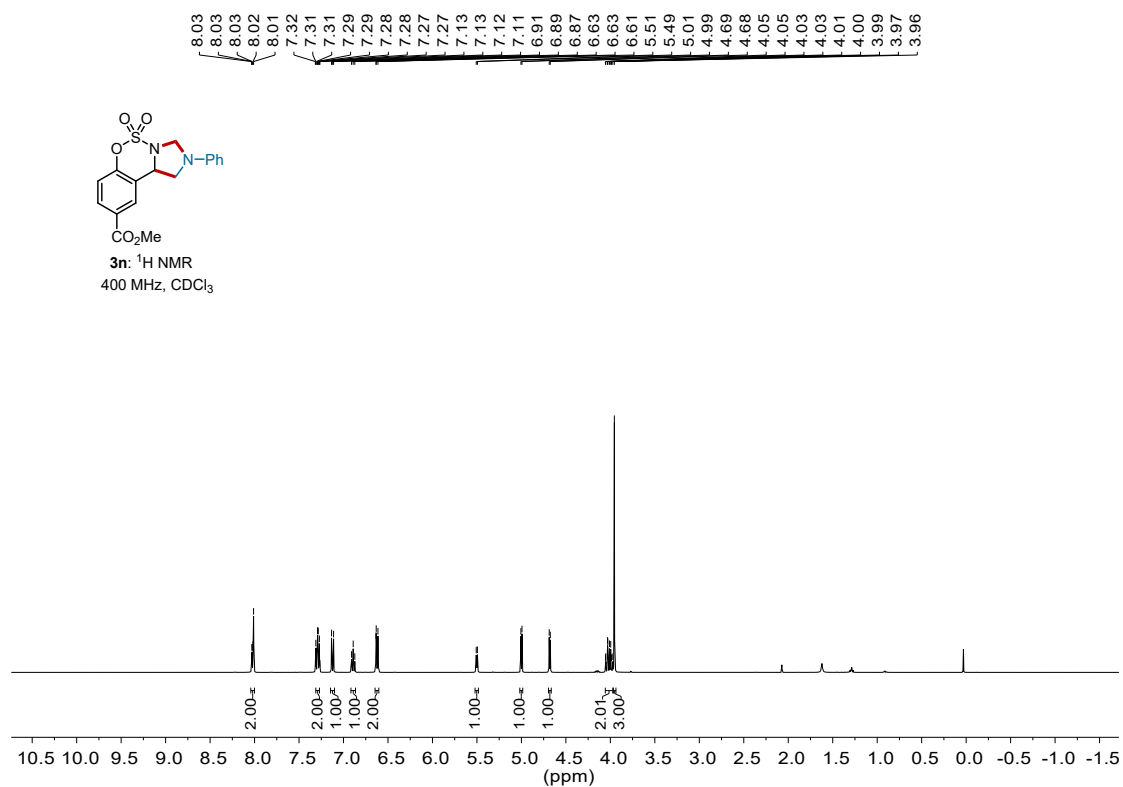


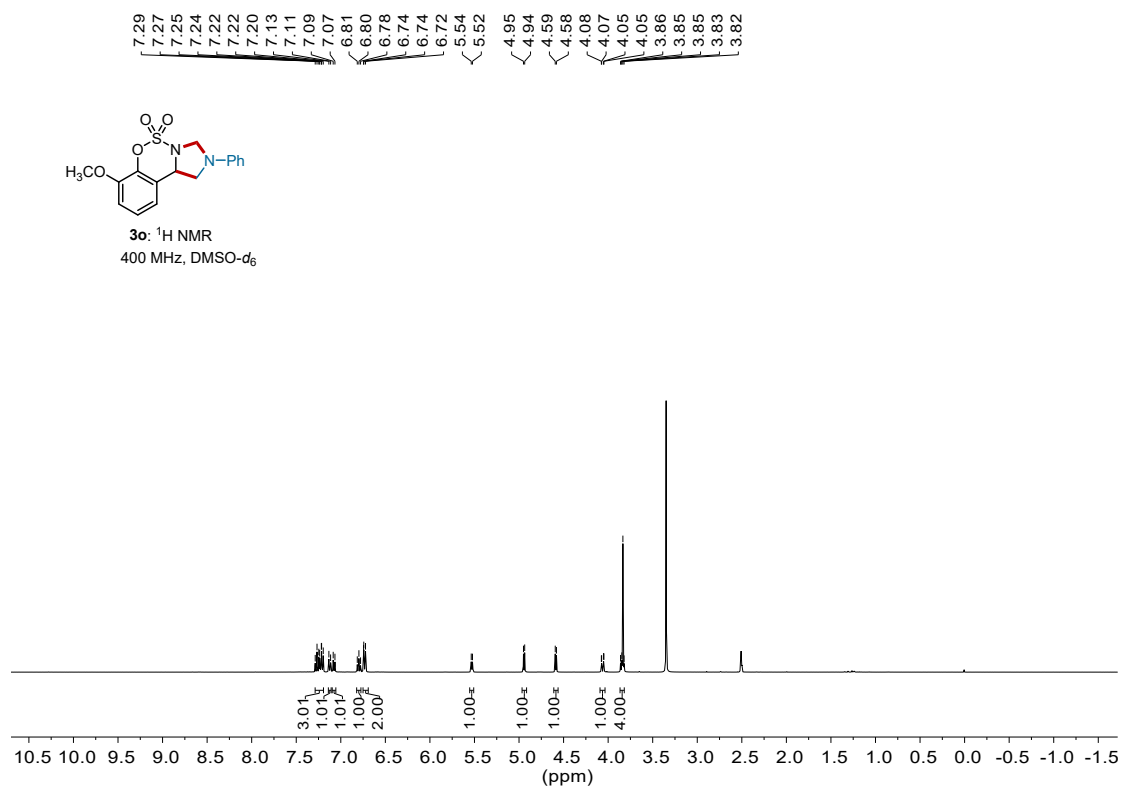
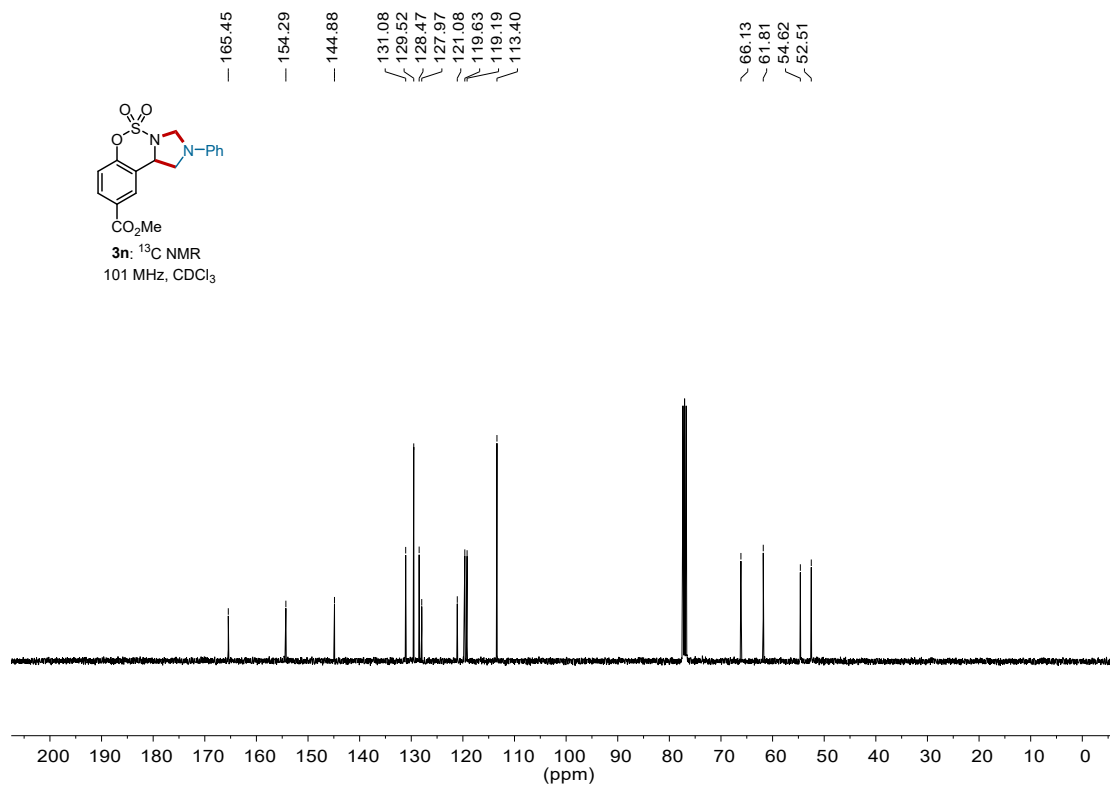


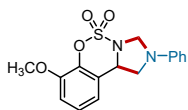
3m: ^{13}C NMR
101 MHz, CDCl_3



3n: ^1H NMR
400 MHz, CDCl_3



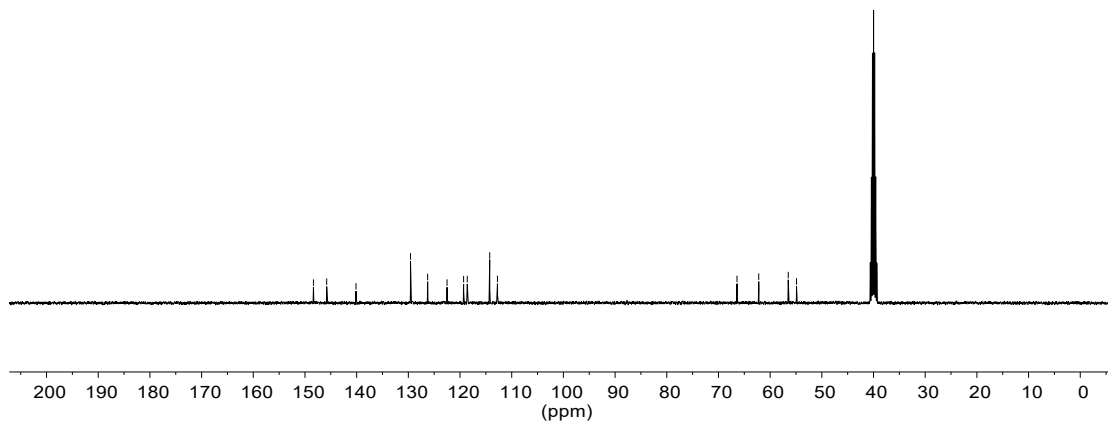




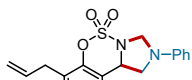
3o: ¹³C NMR
101 MHz, DMSO-*d*₆

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114.26
112.76

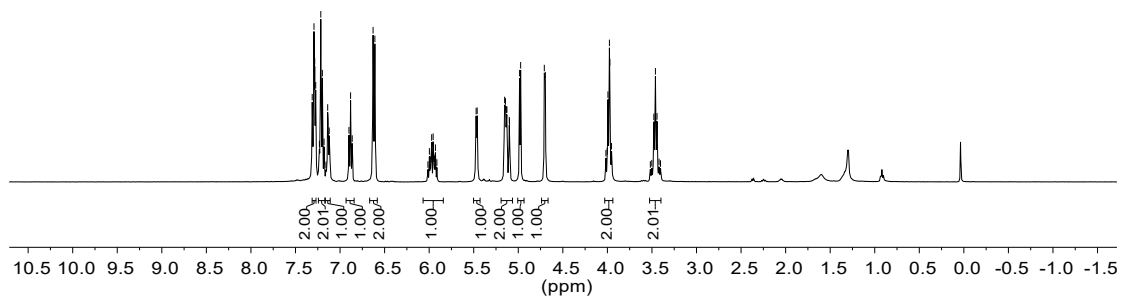
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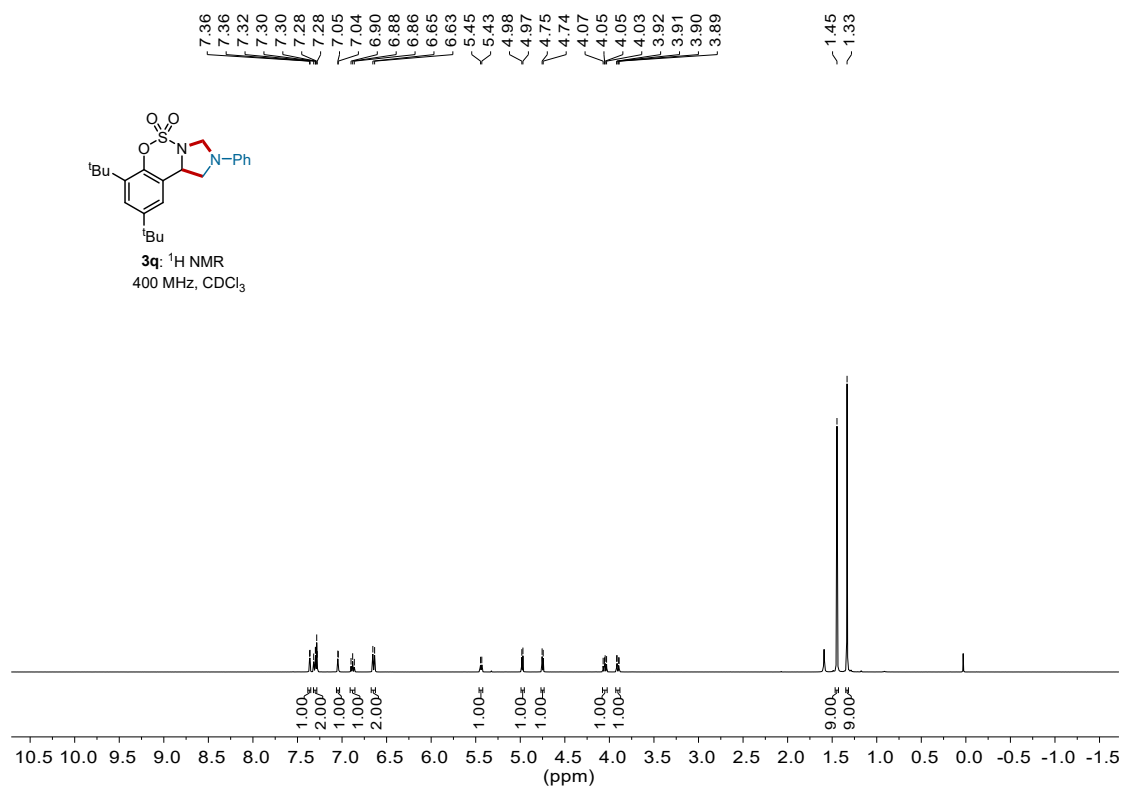
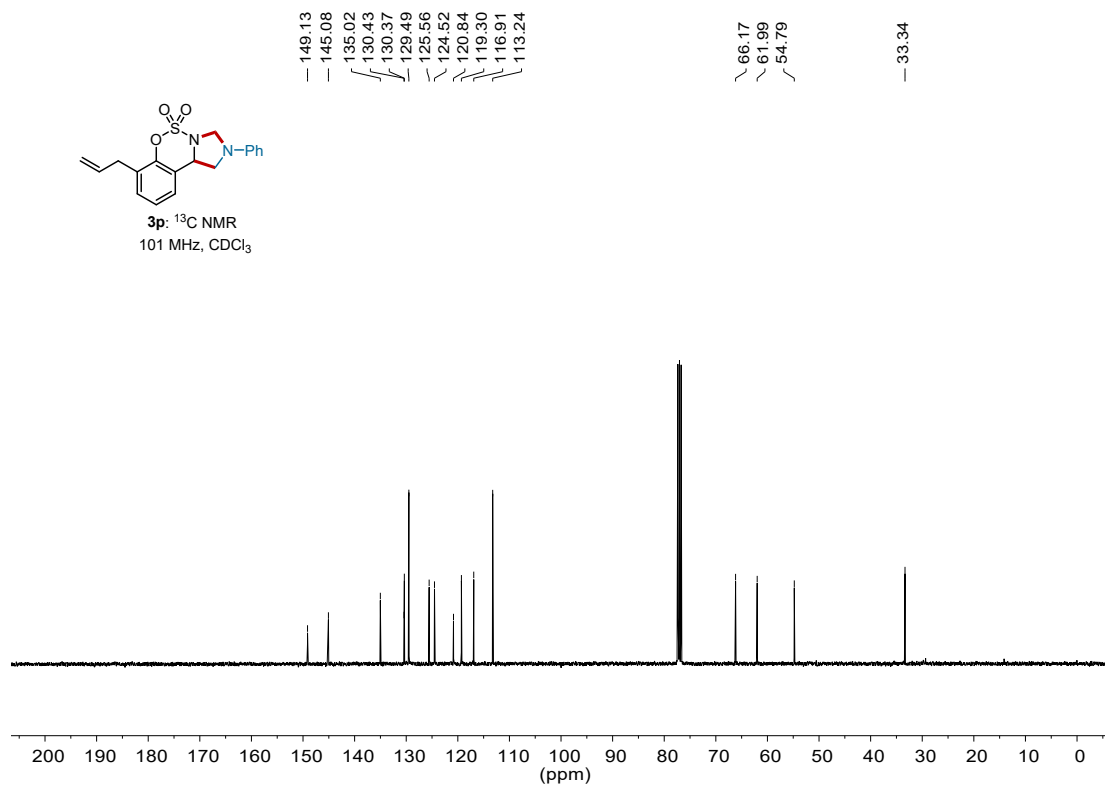


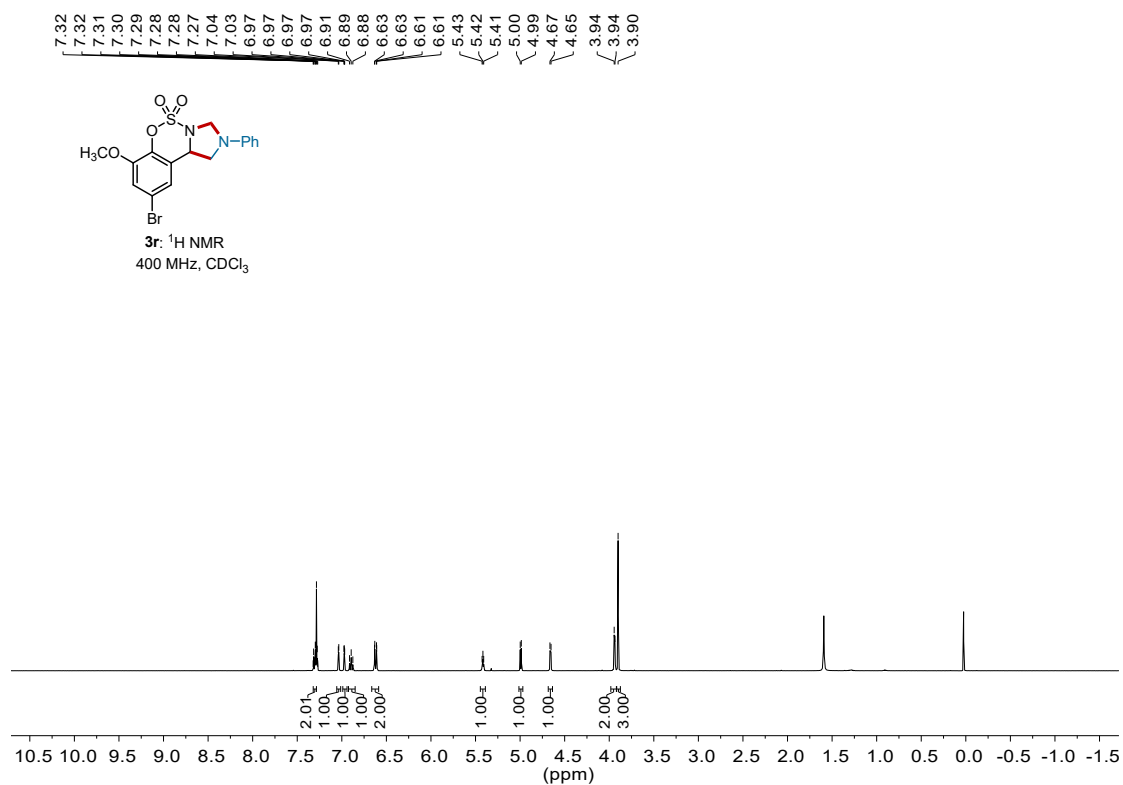
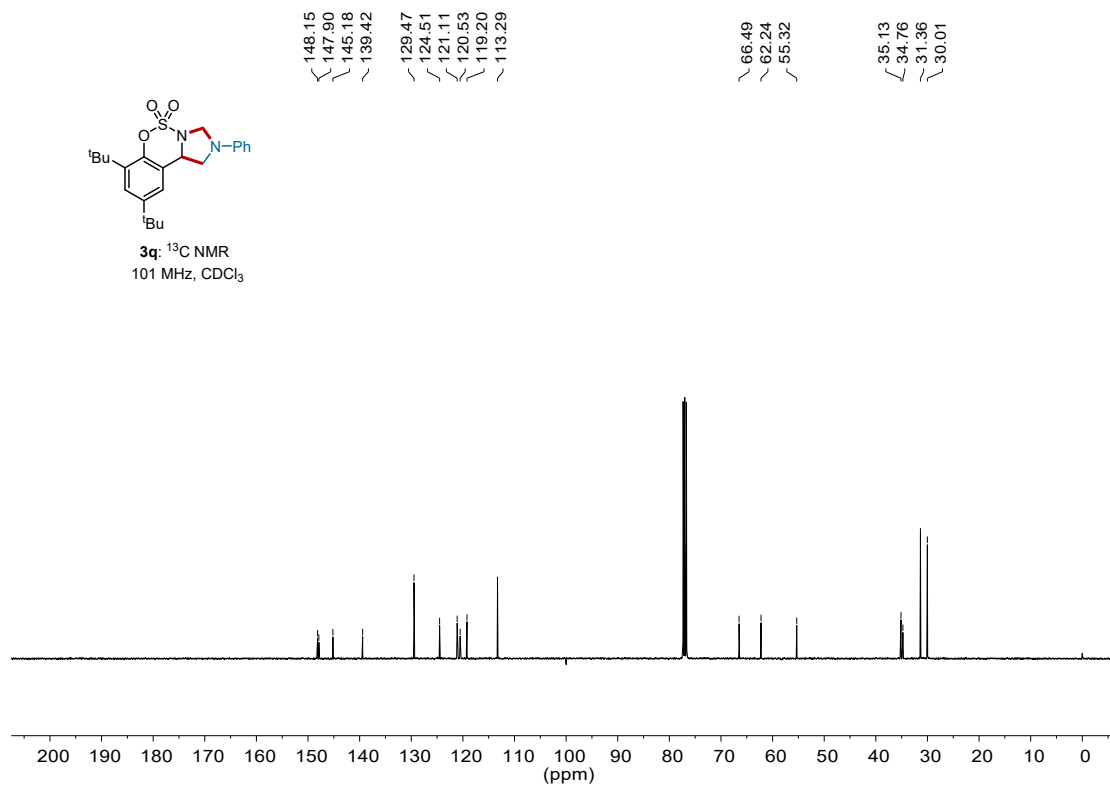
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6.61
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5.97
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5.95
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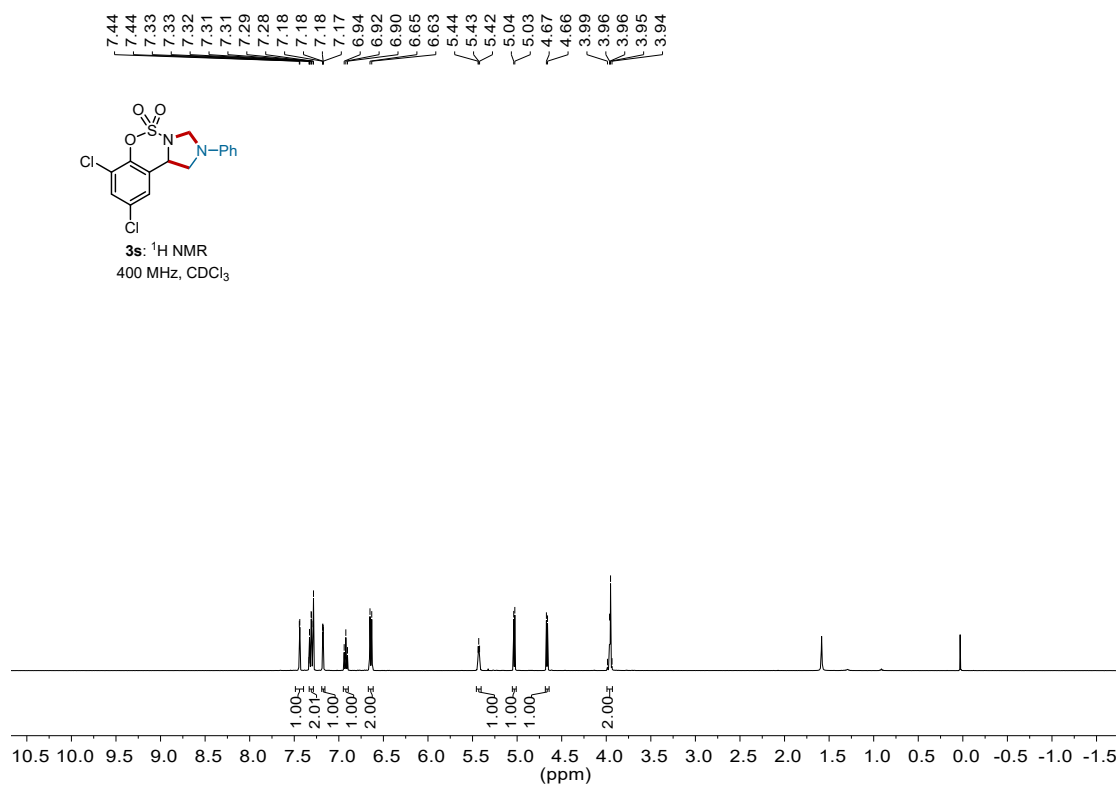
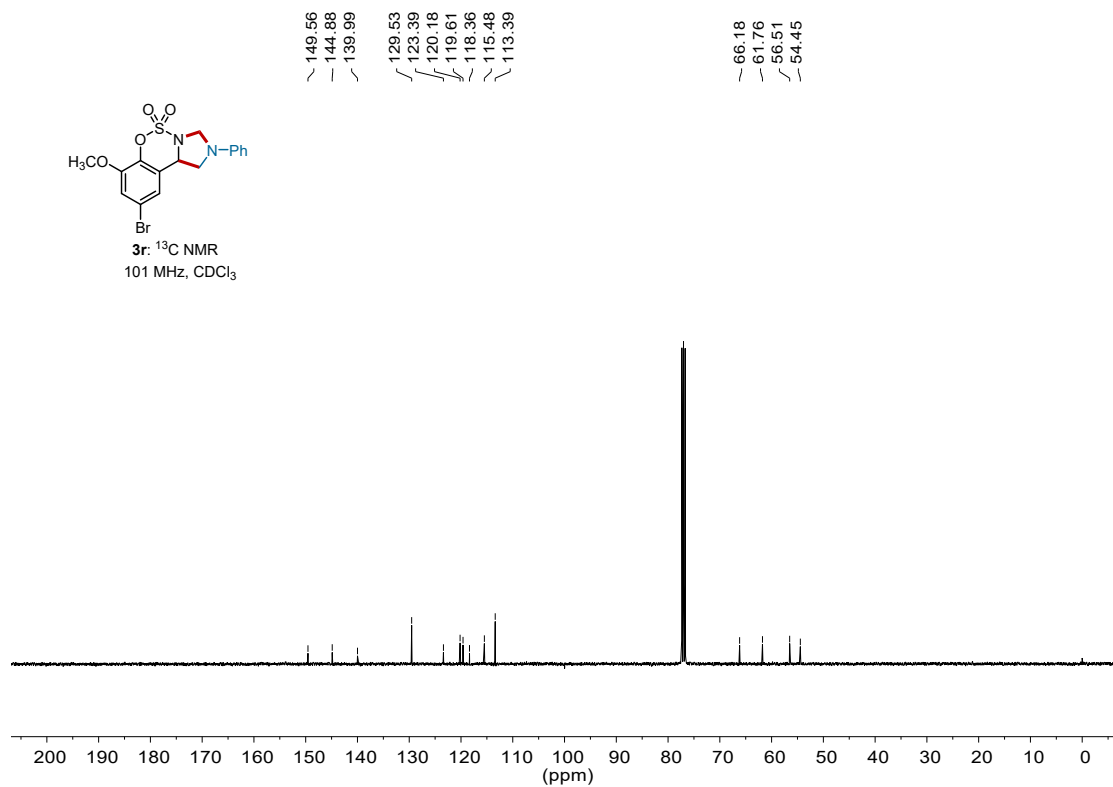


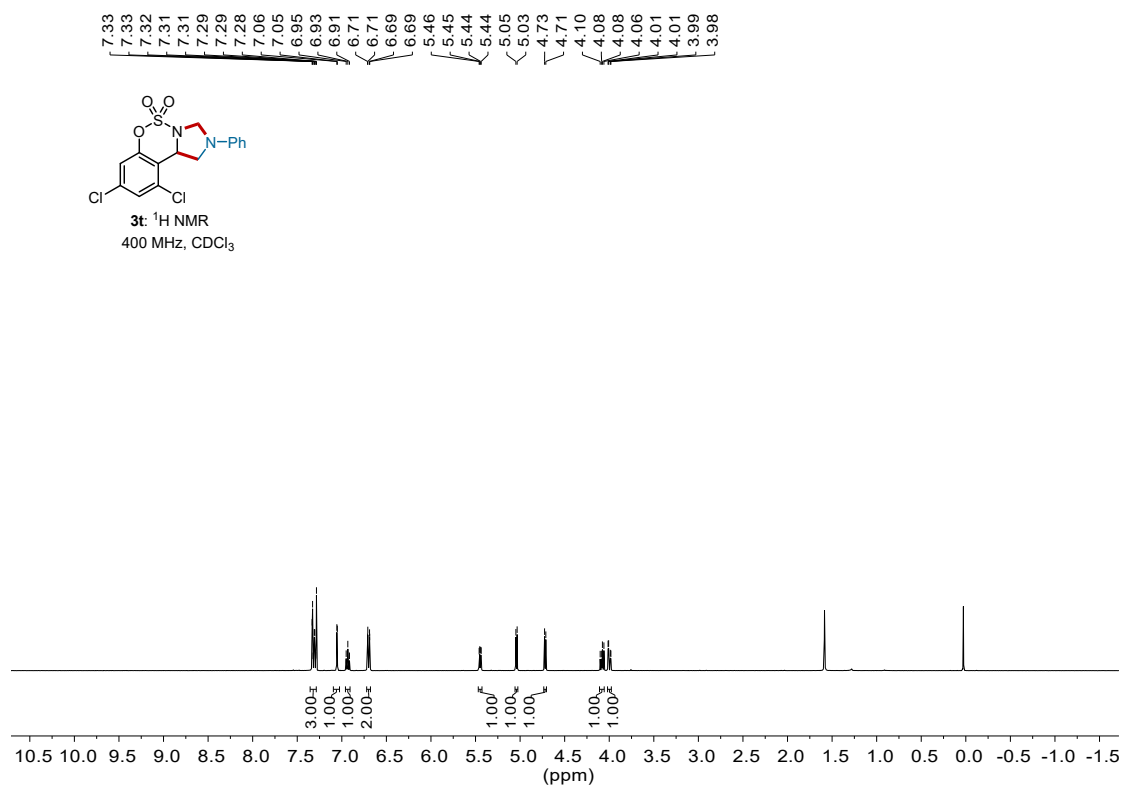
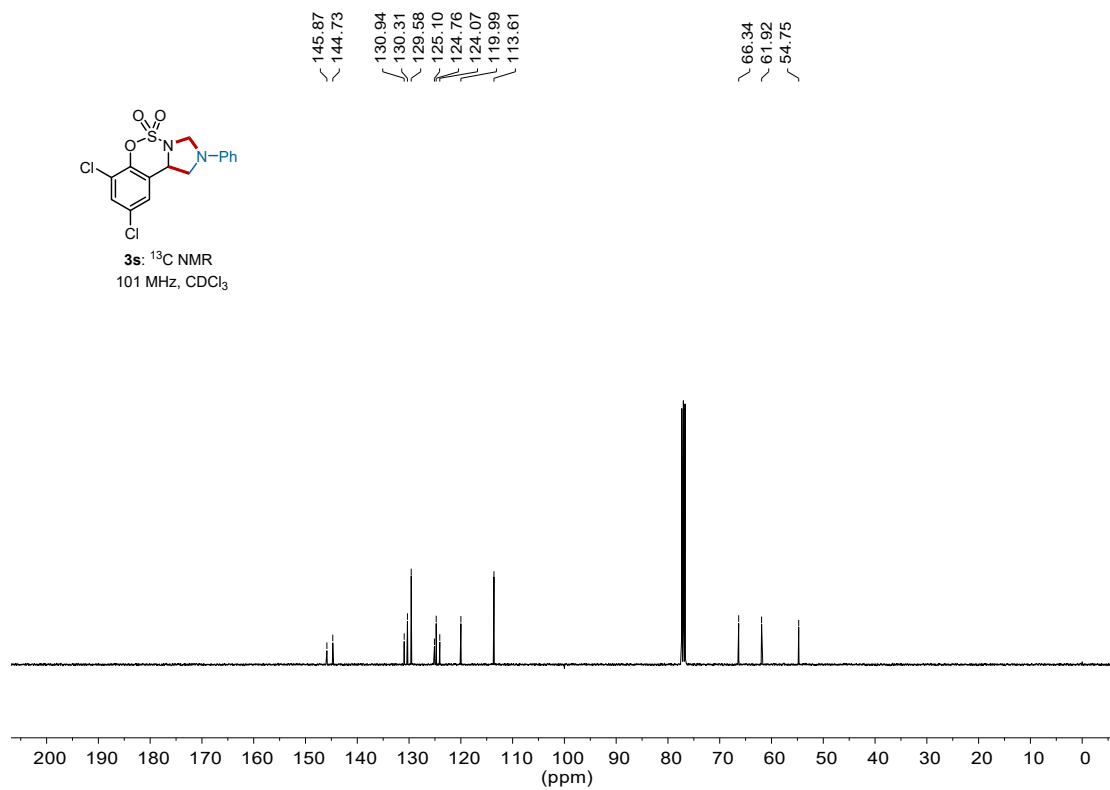
3p: ¹H NMR
400 MHz, CDCl₃

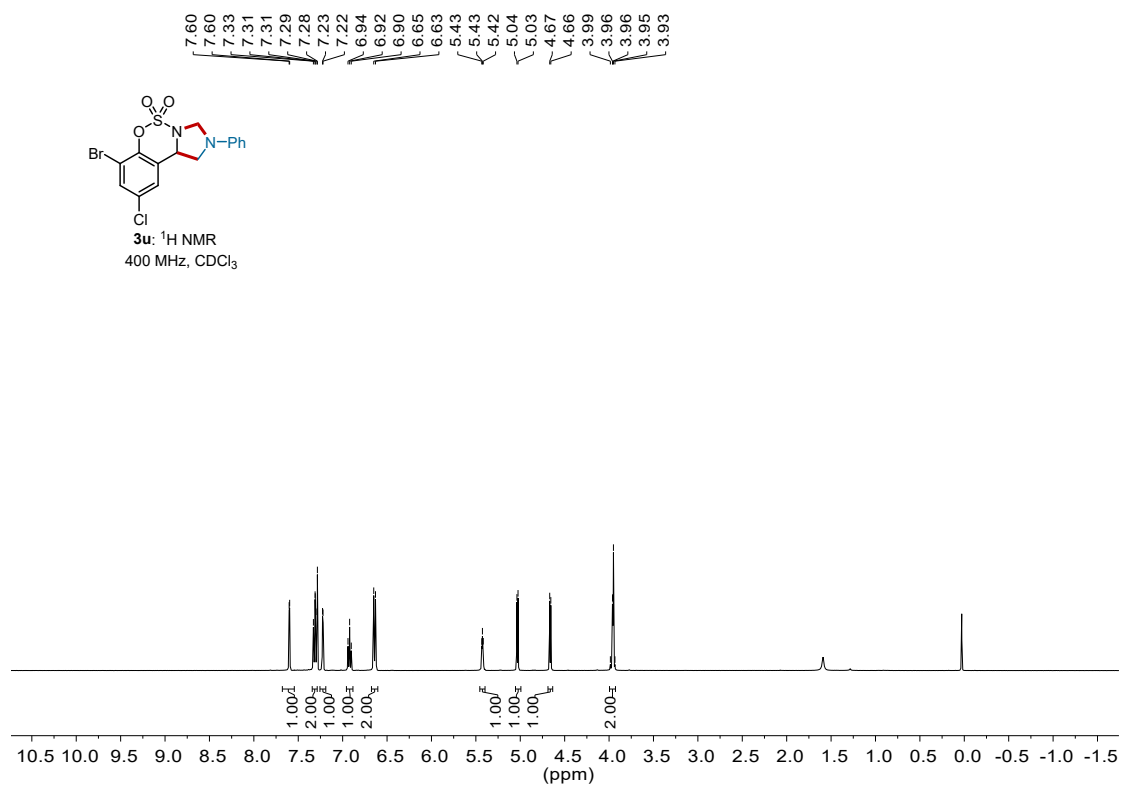
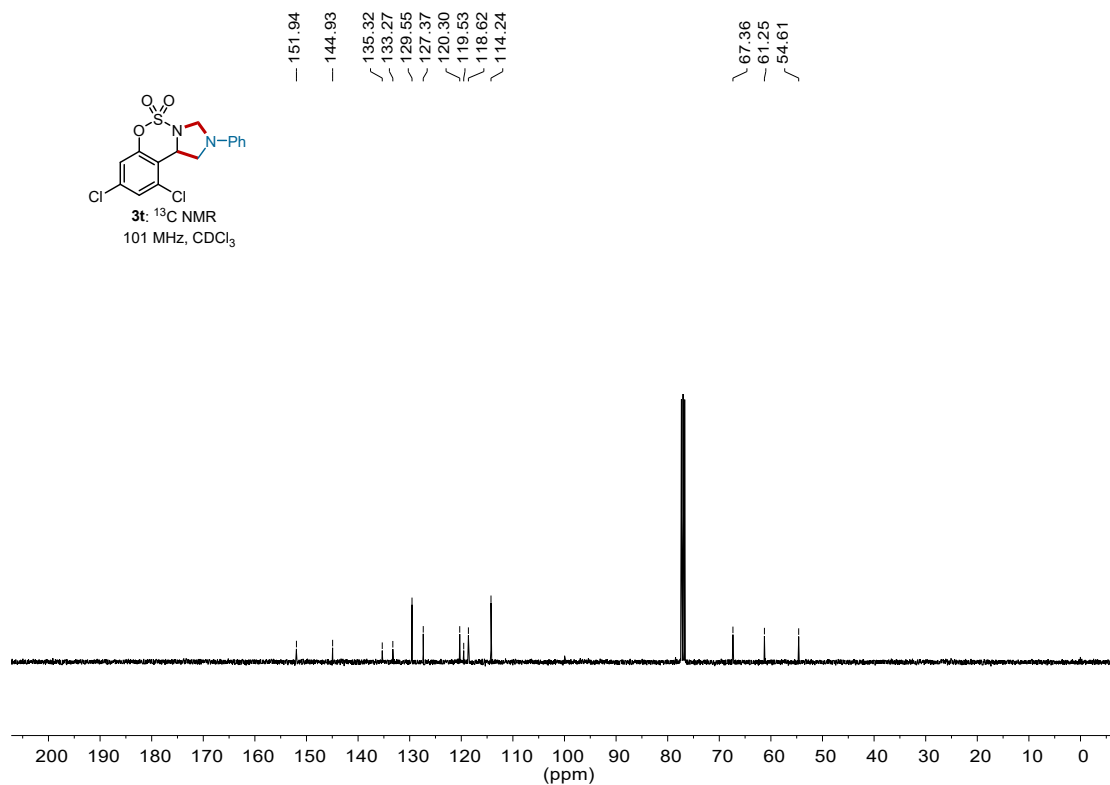


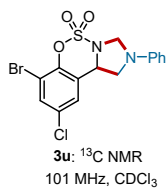






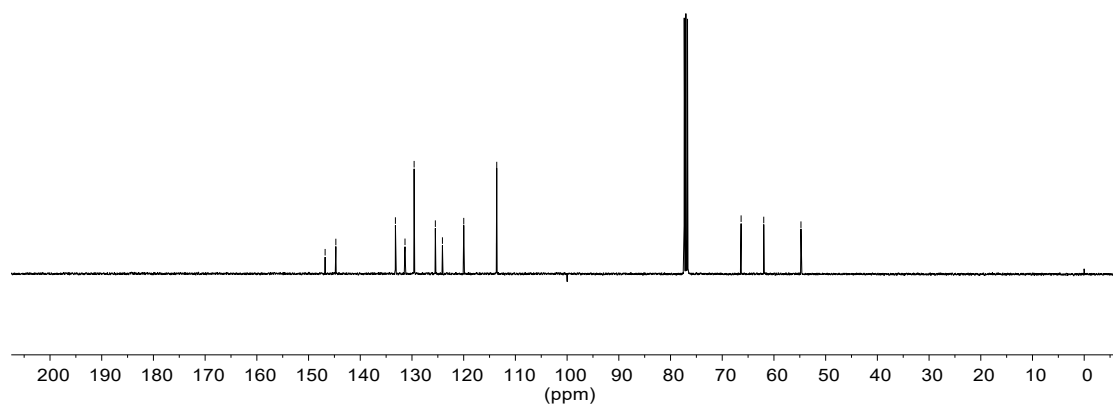




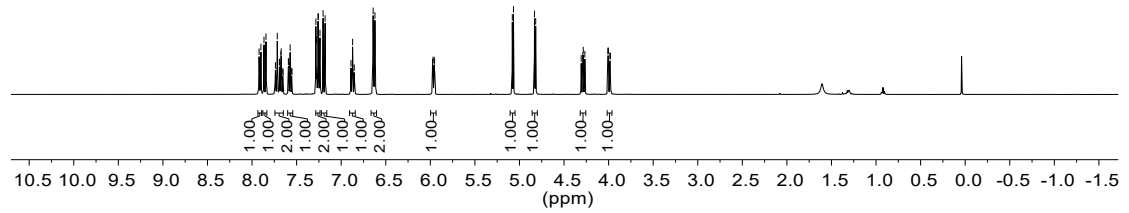
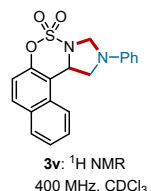


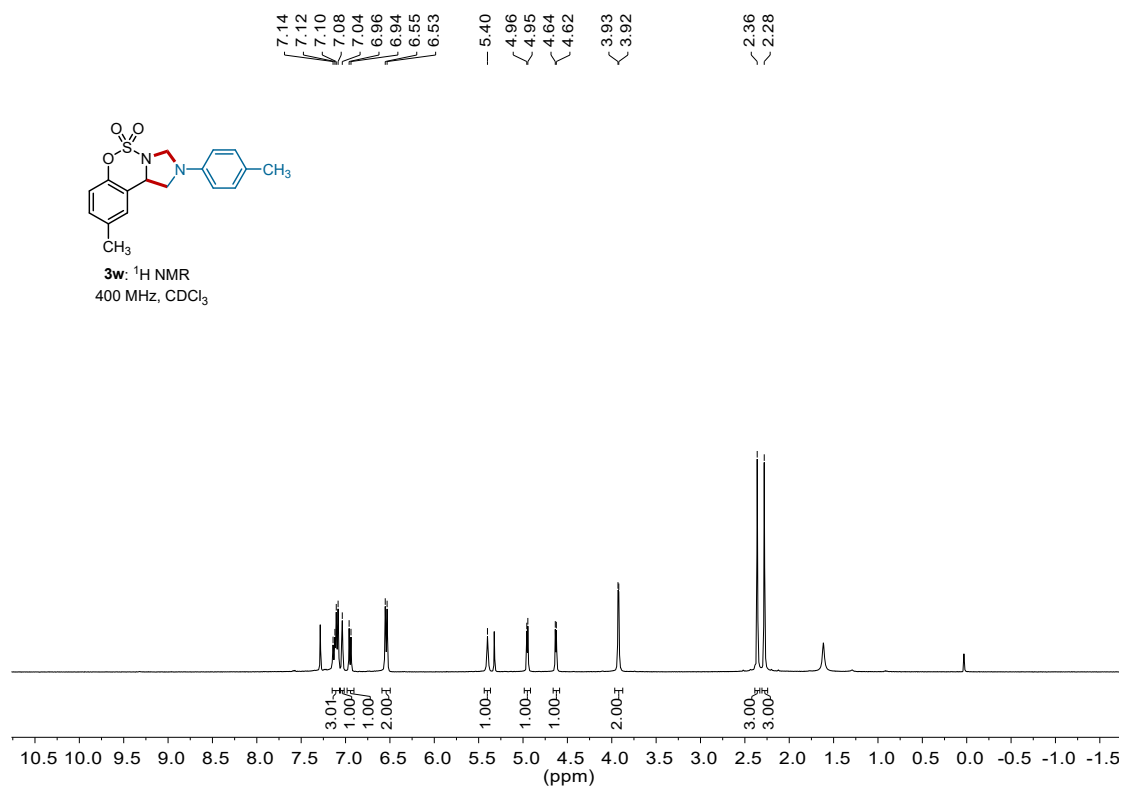
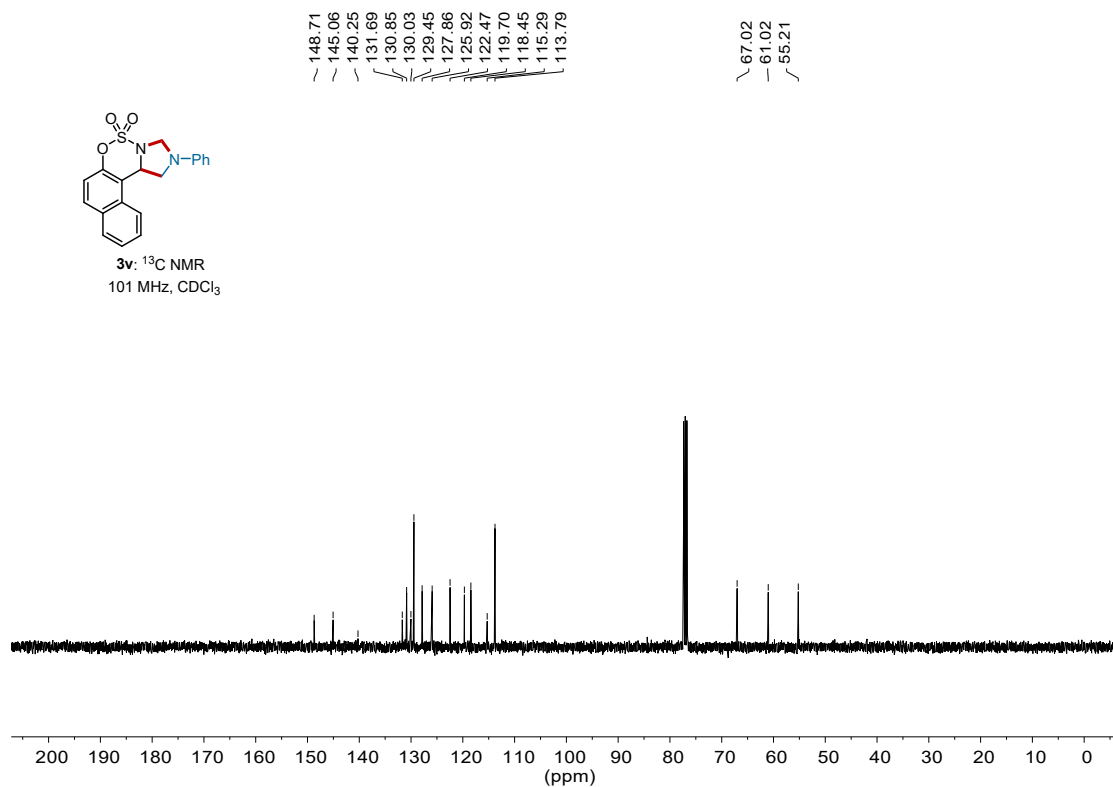
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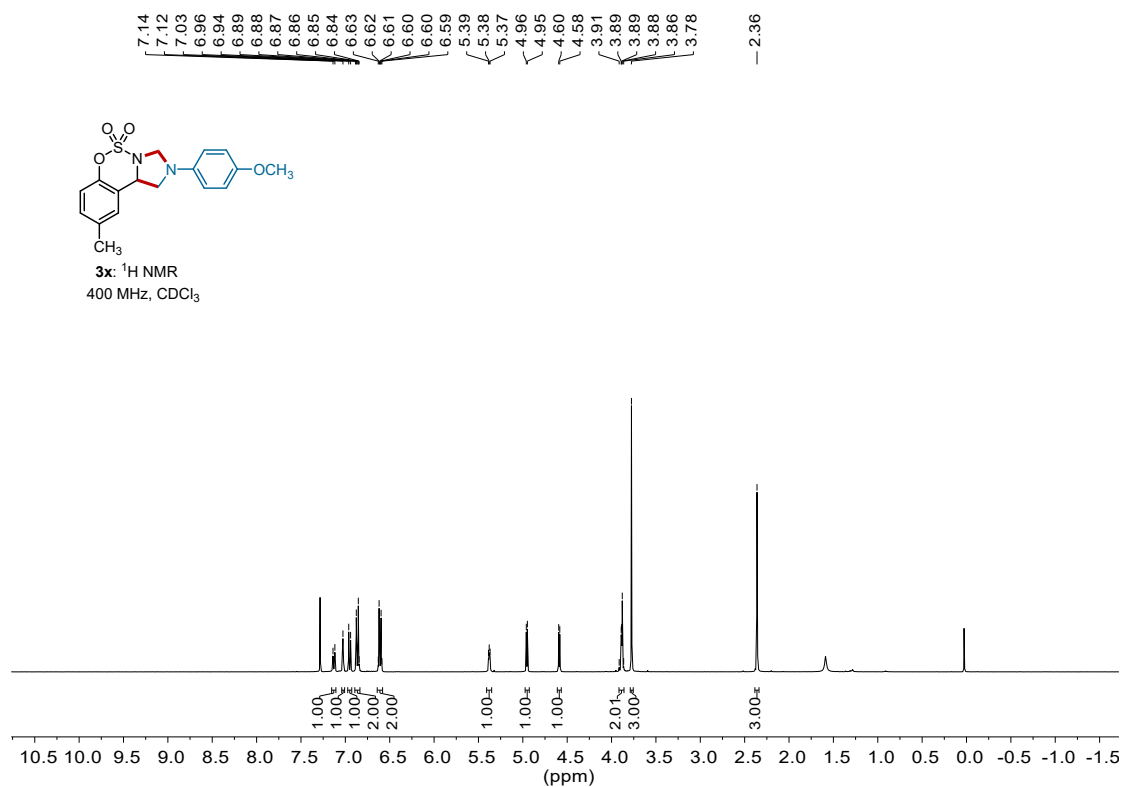
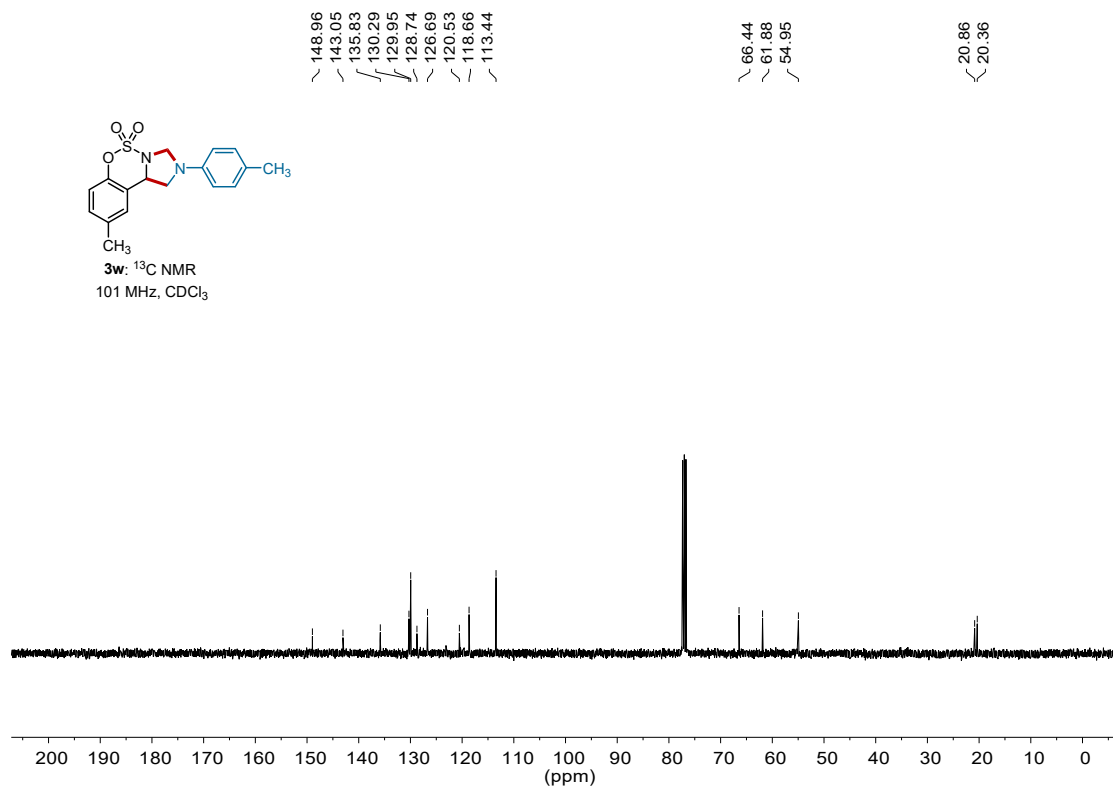
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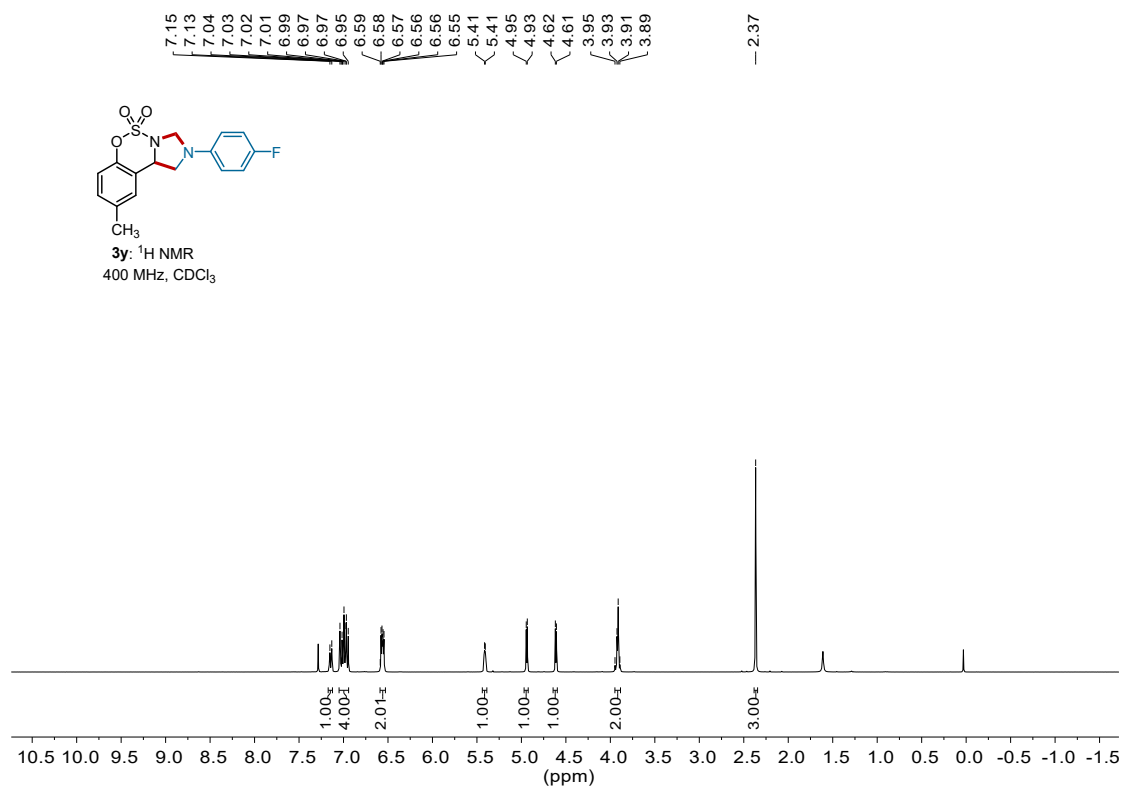
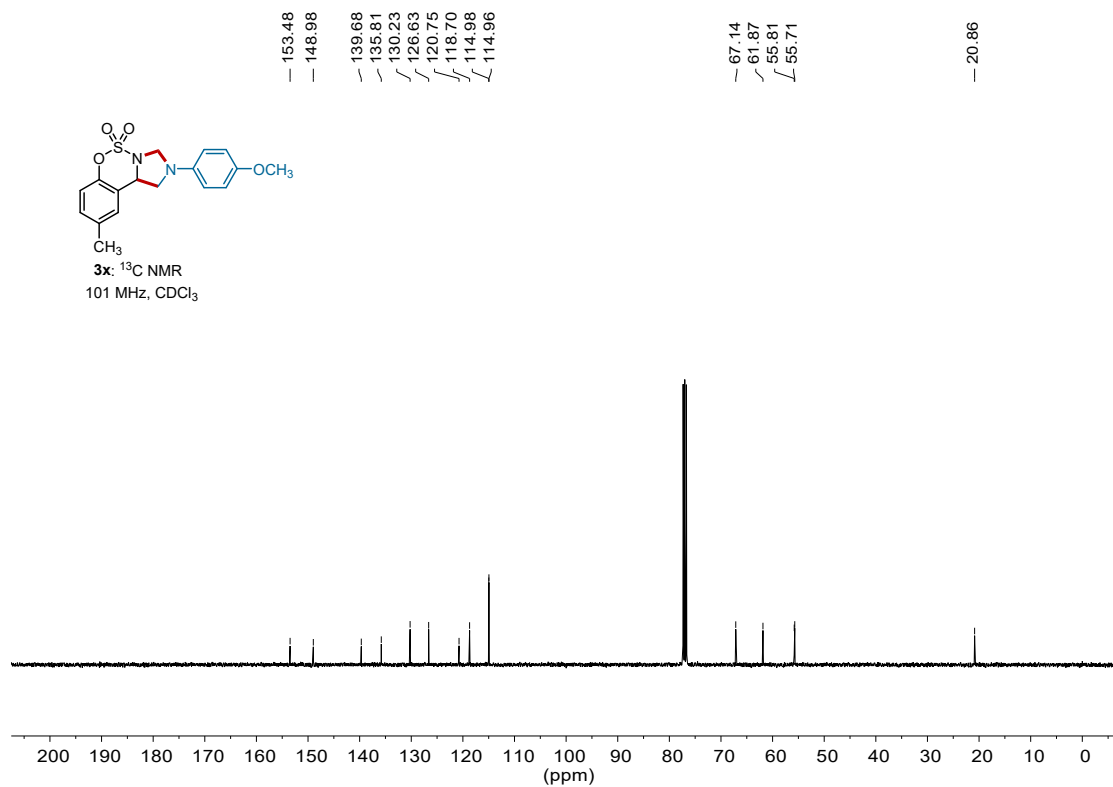


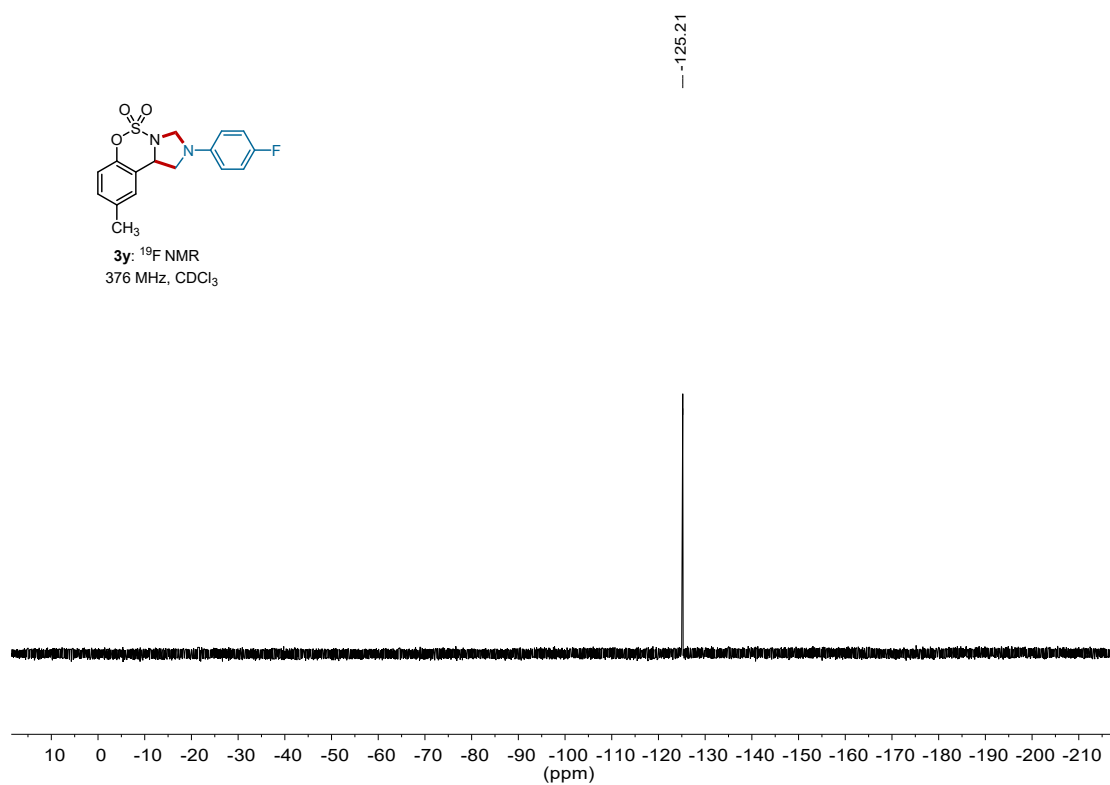
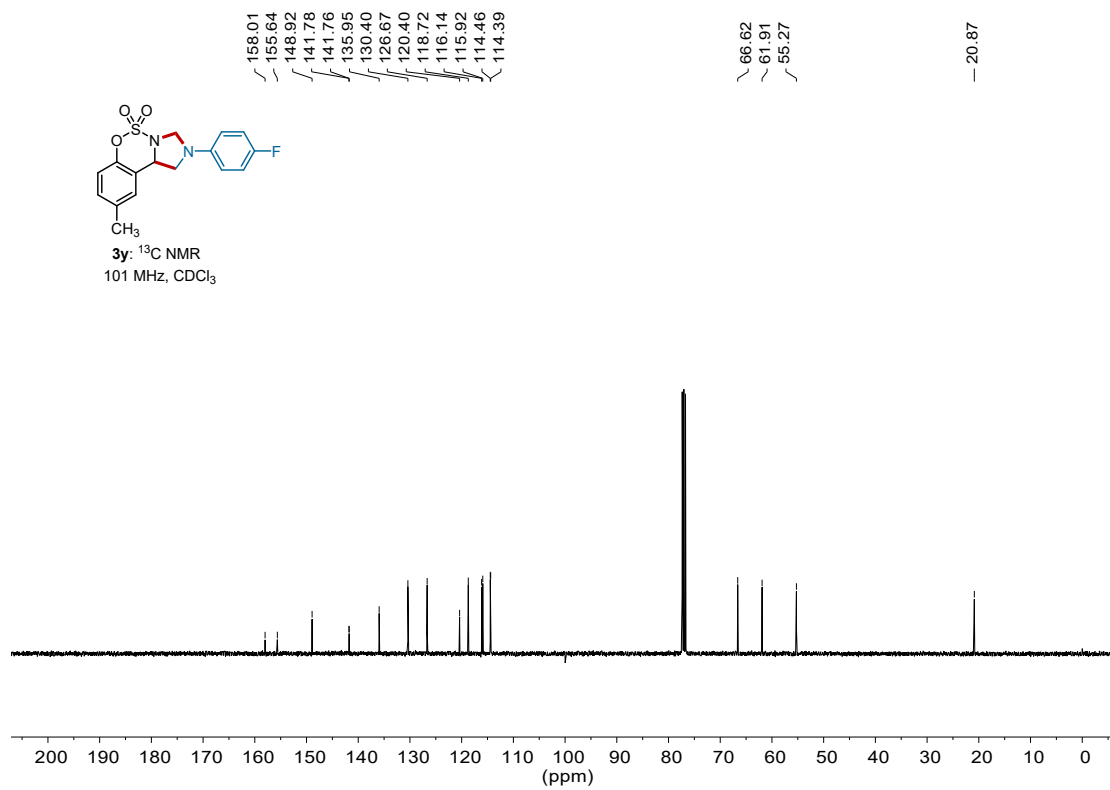
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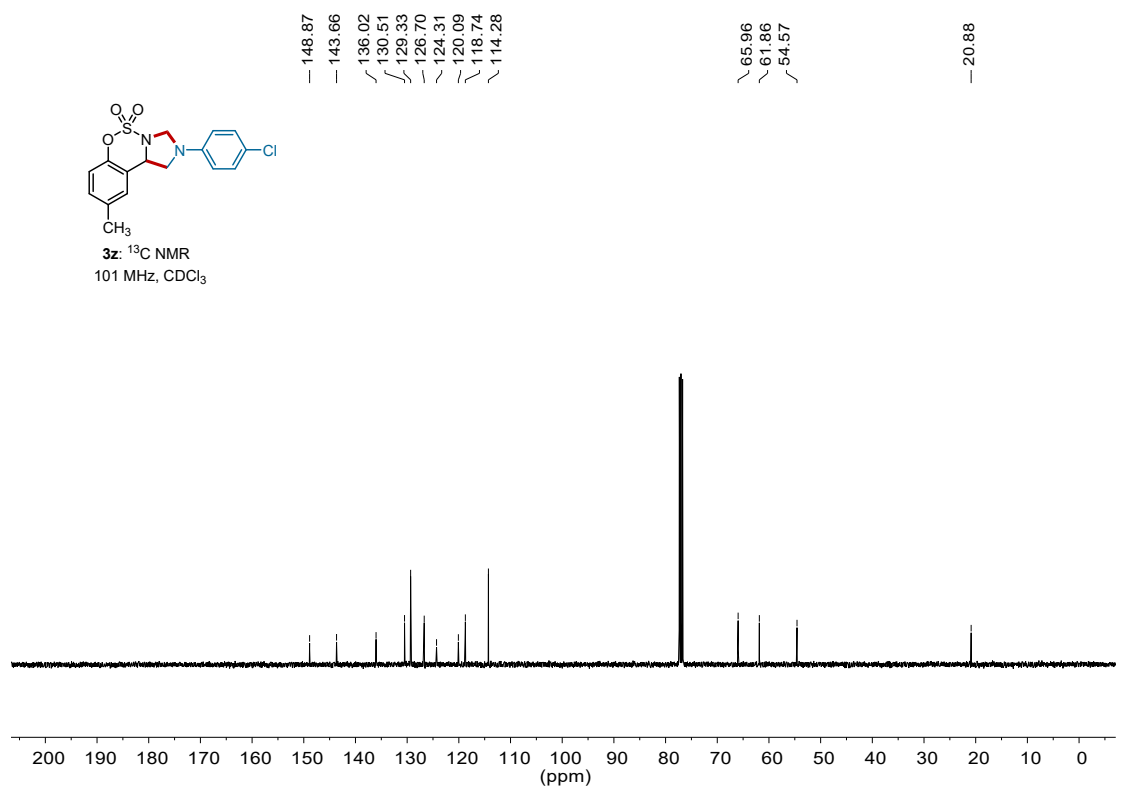
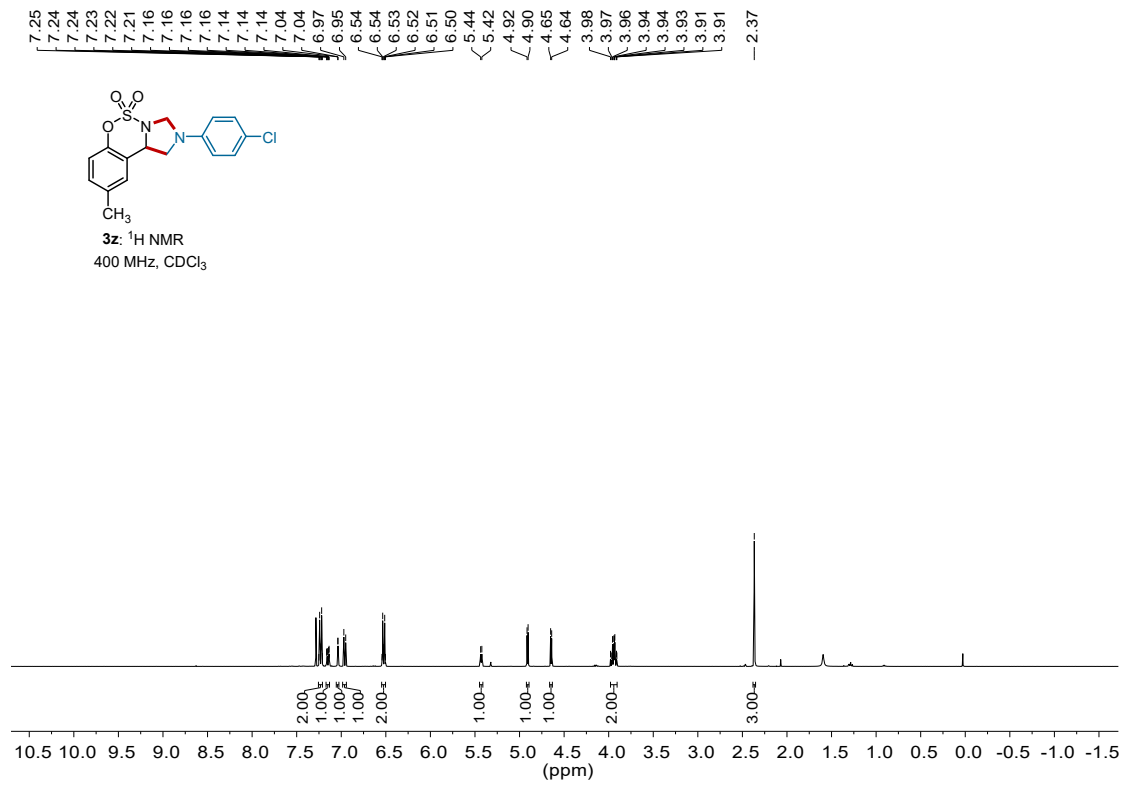


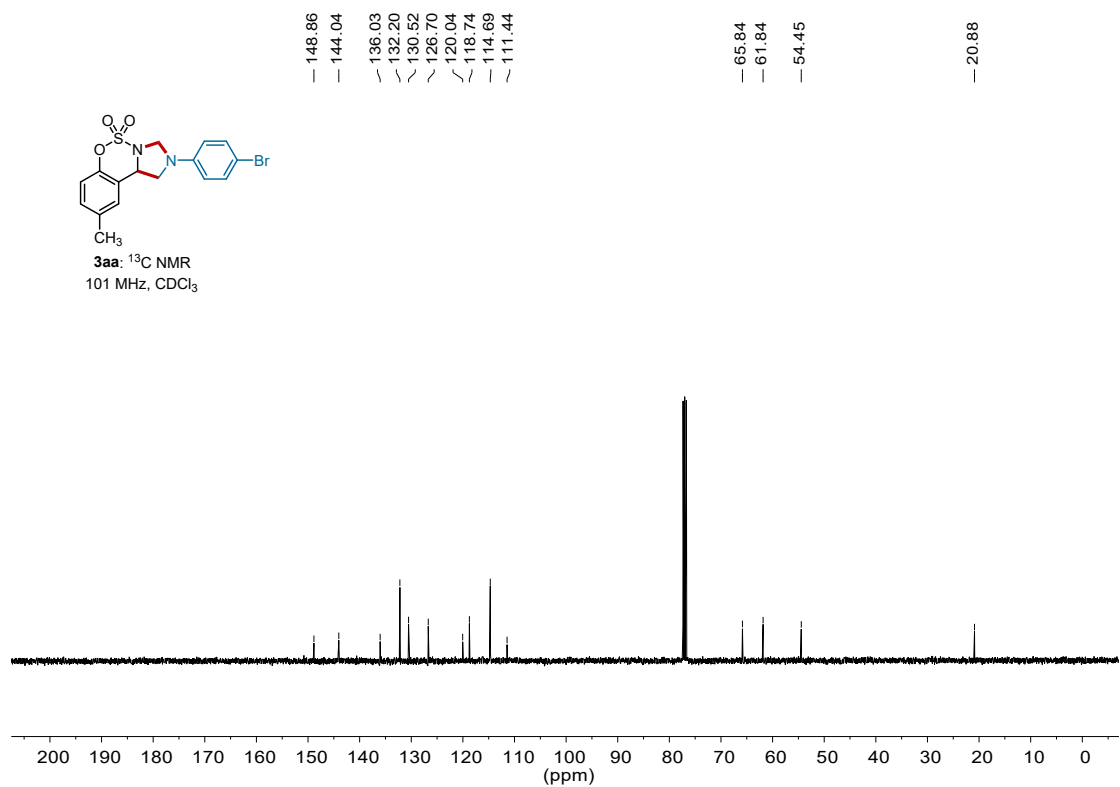
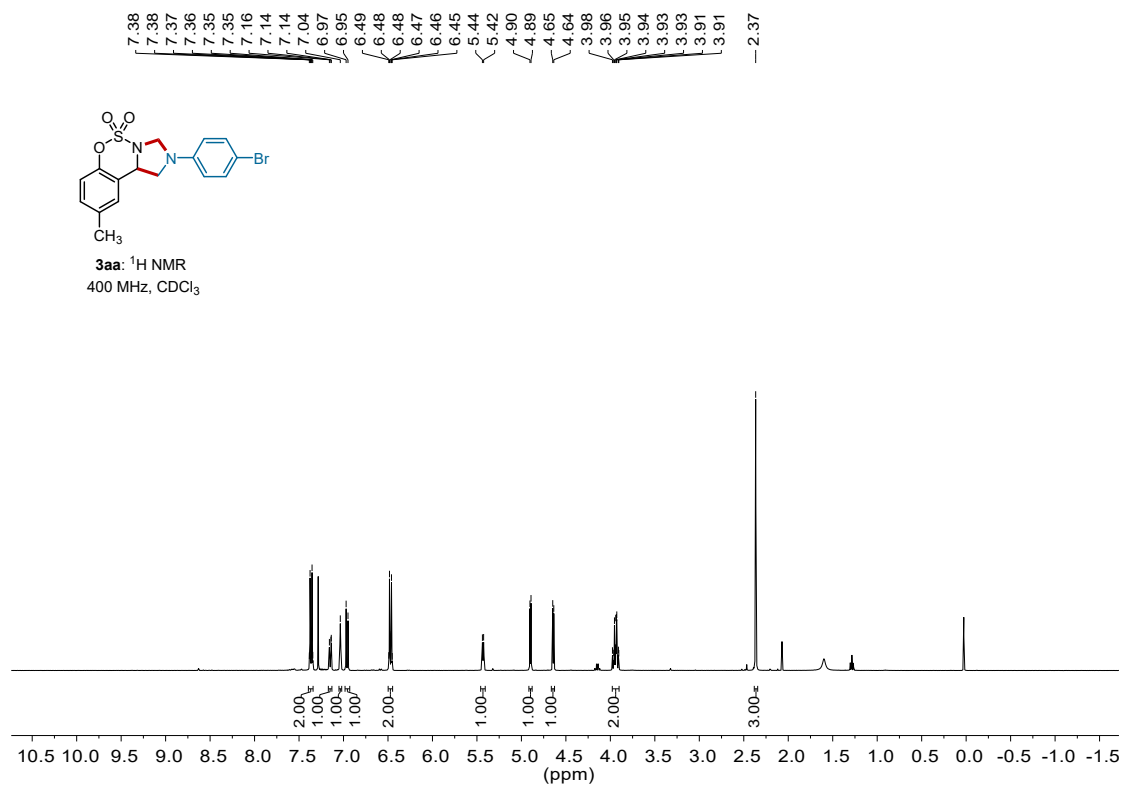


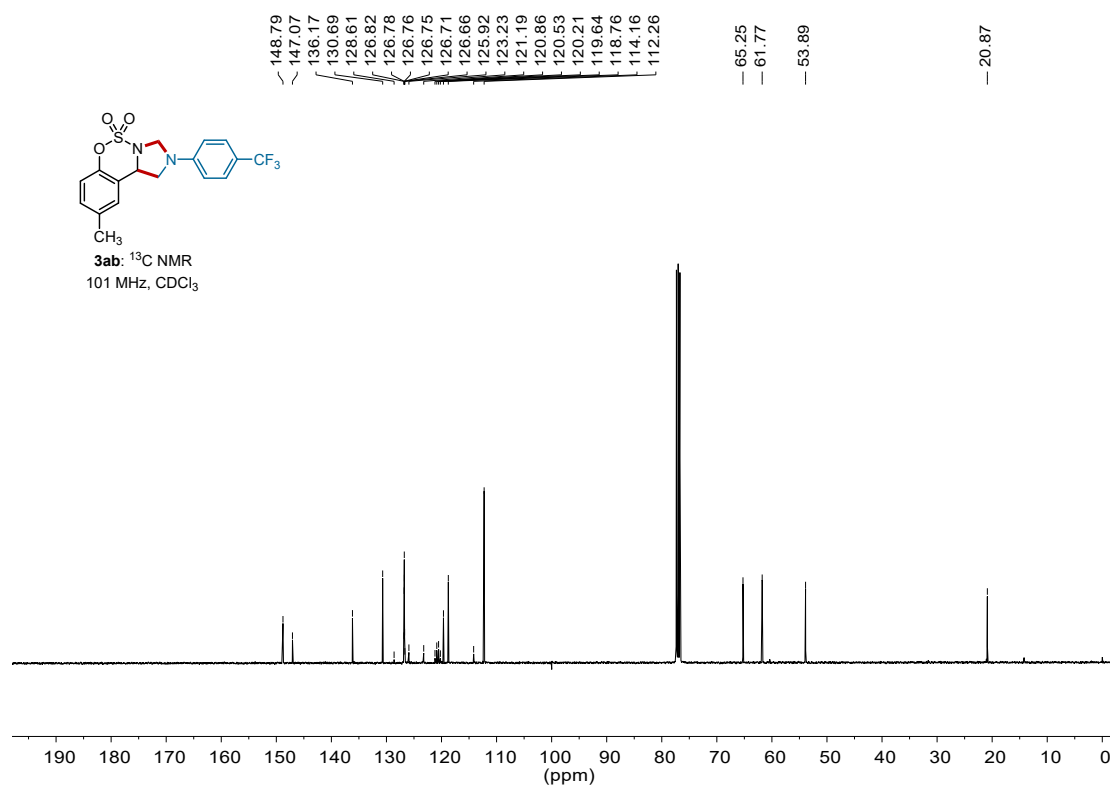
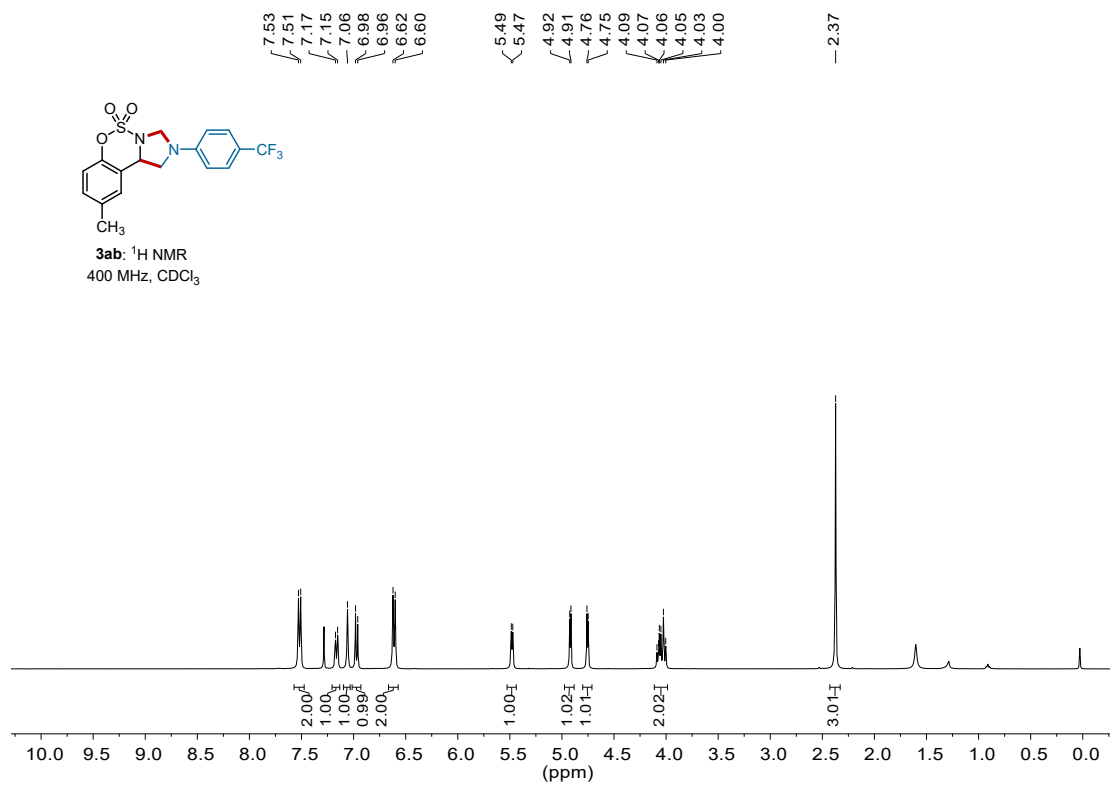


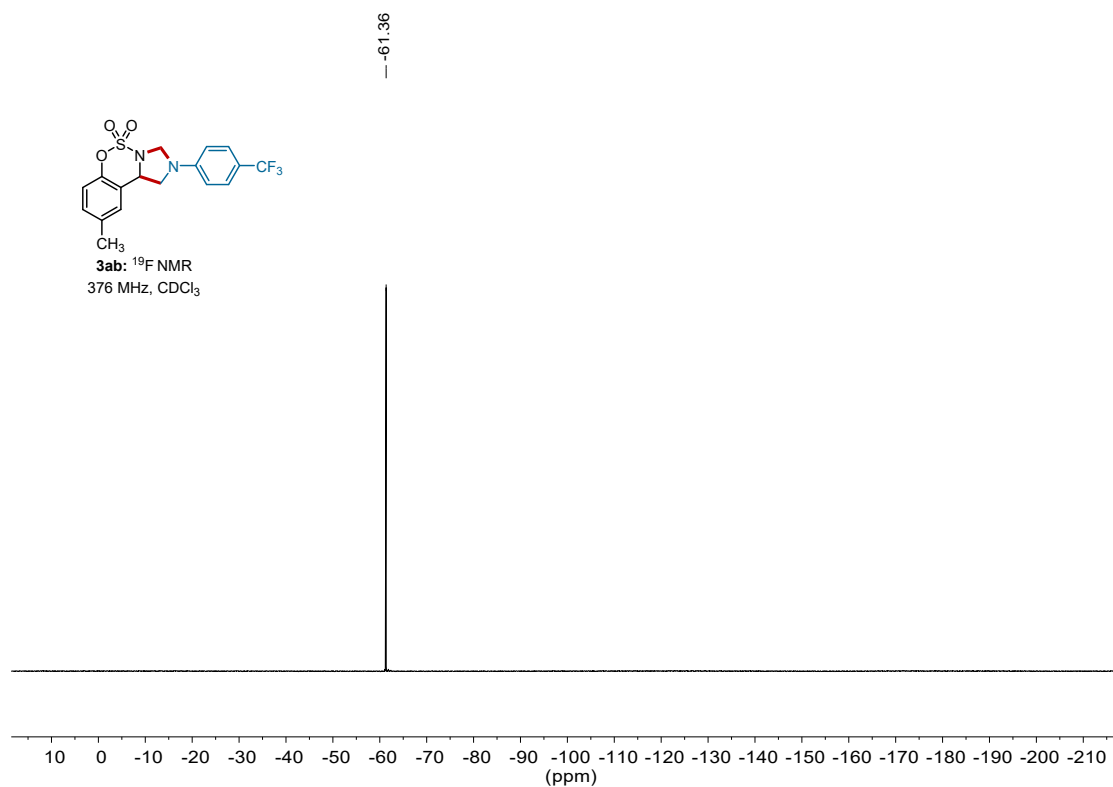




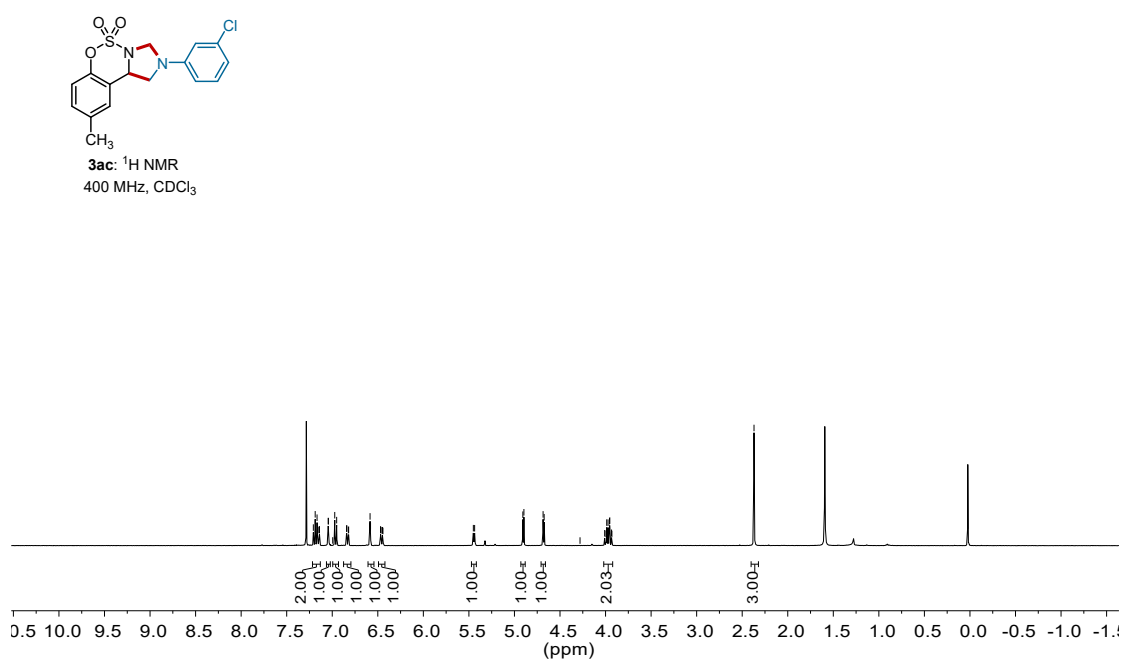


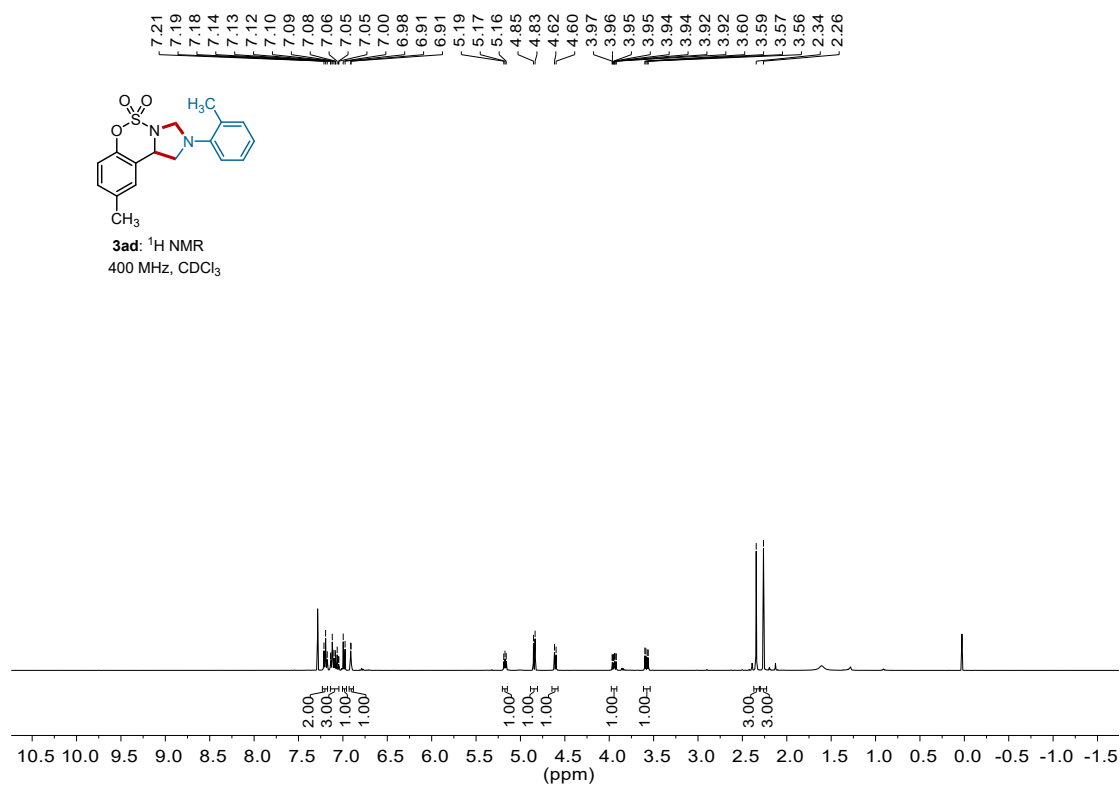
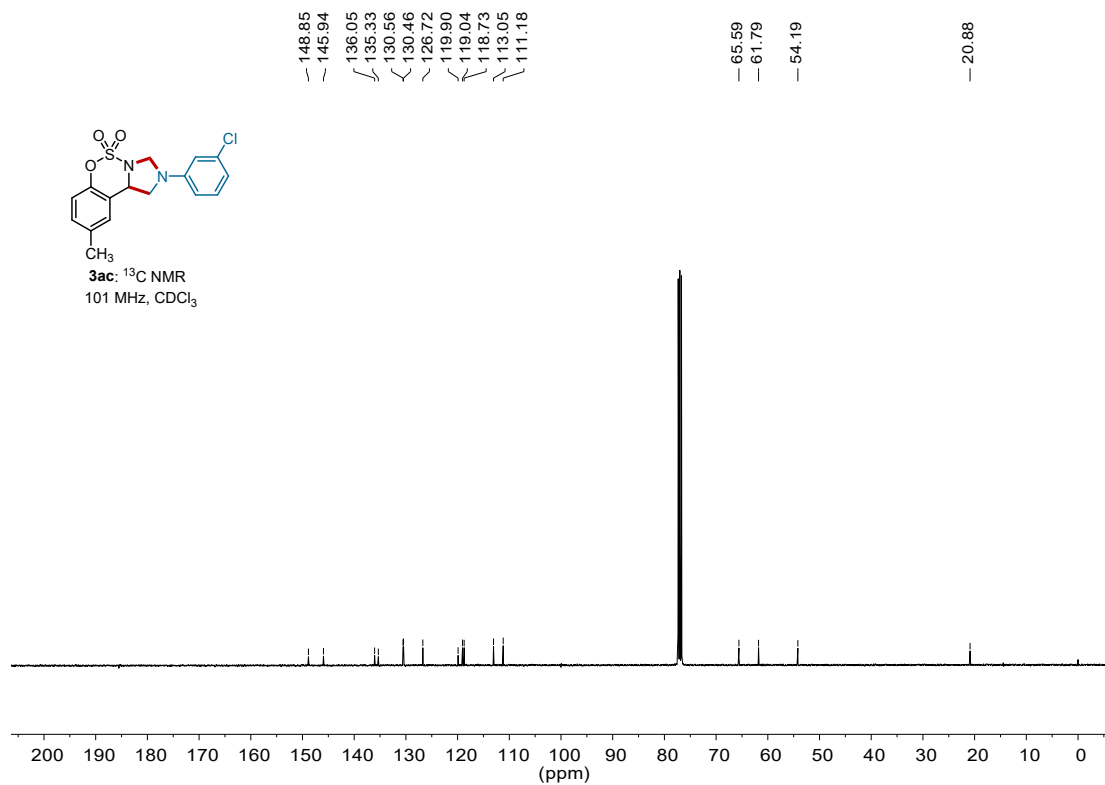


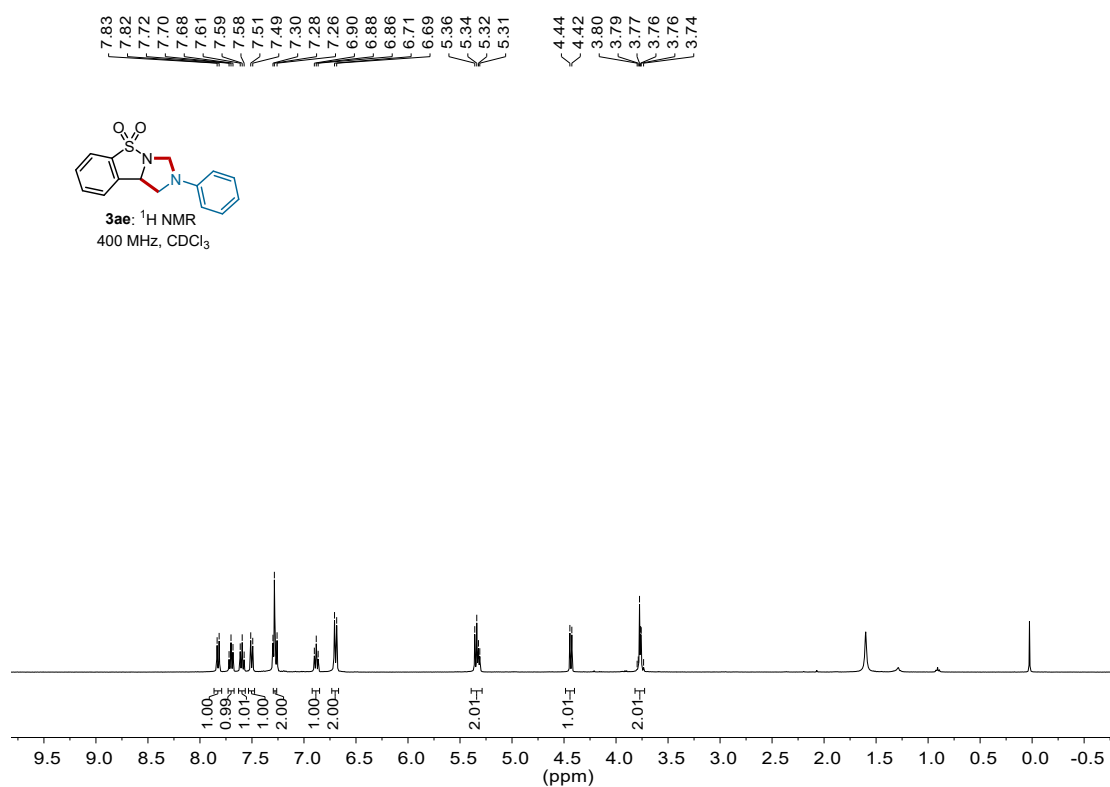
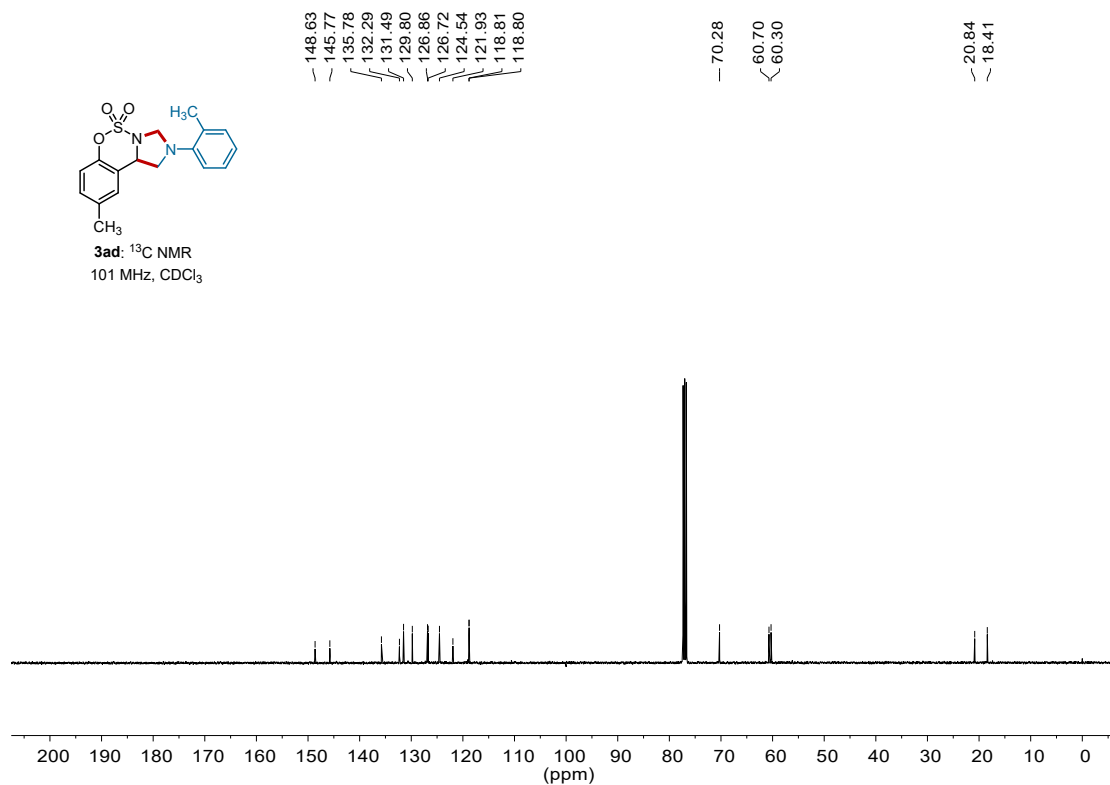


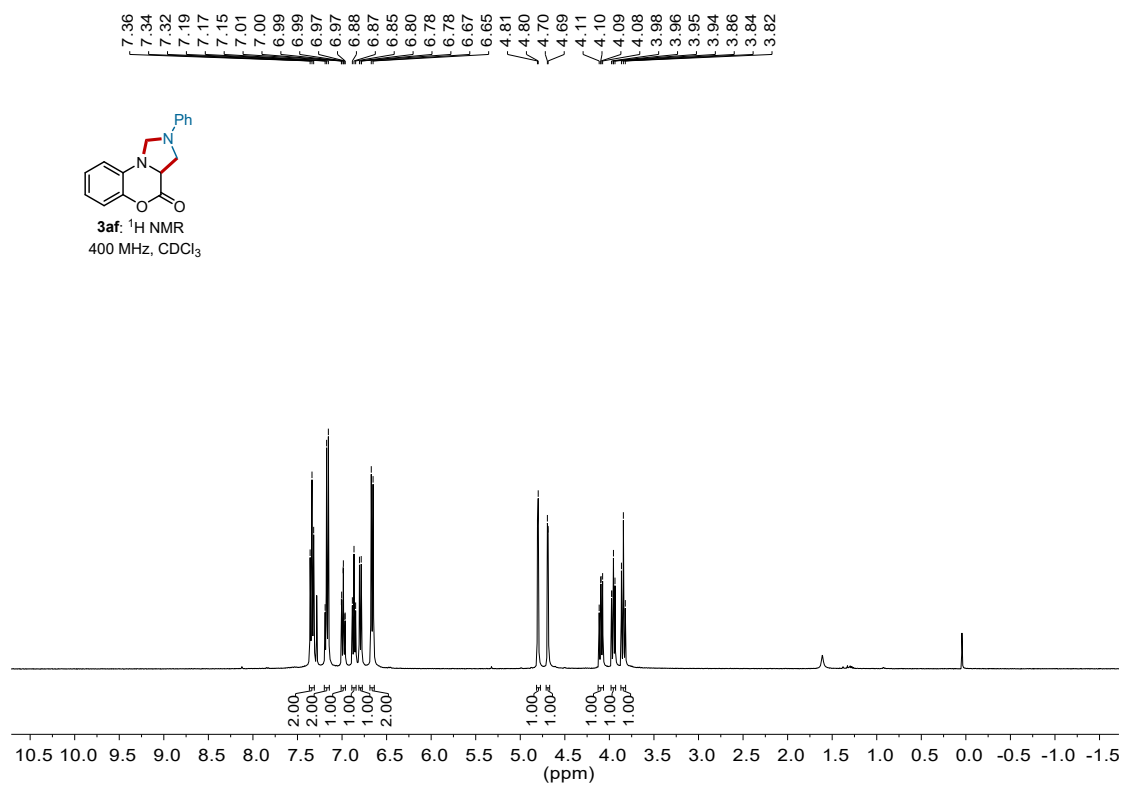
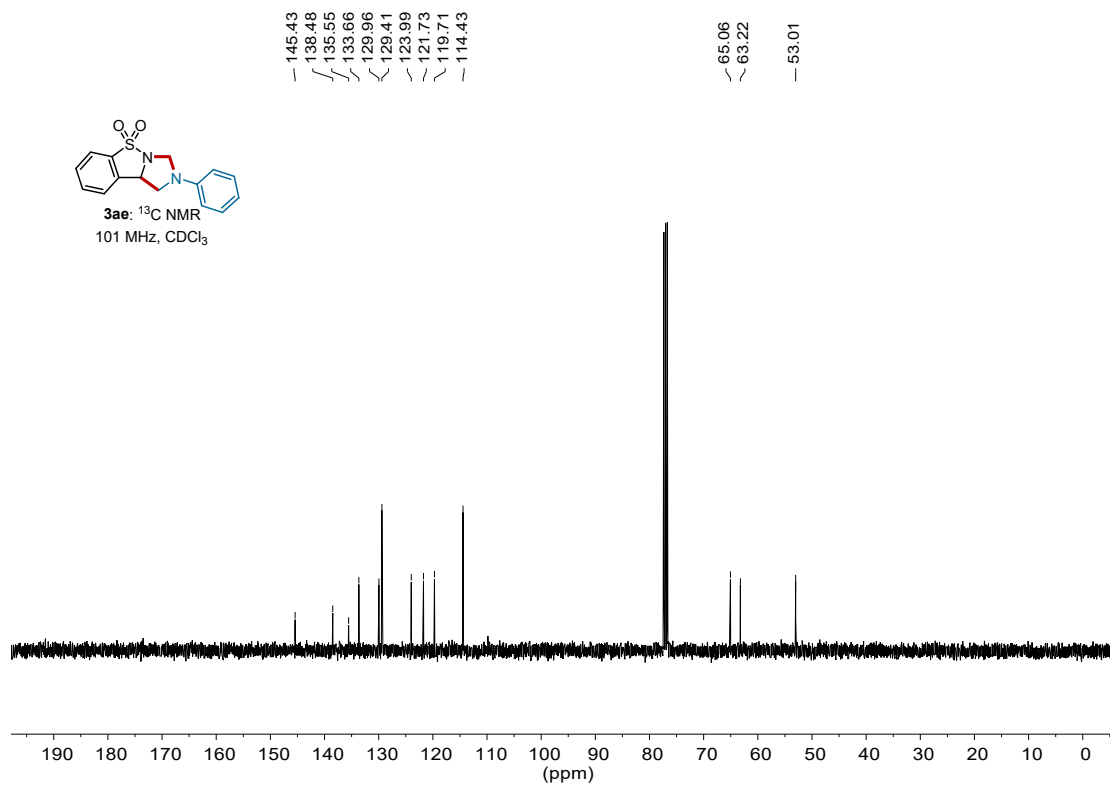


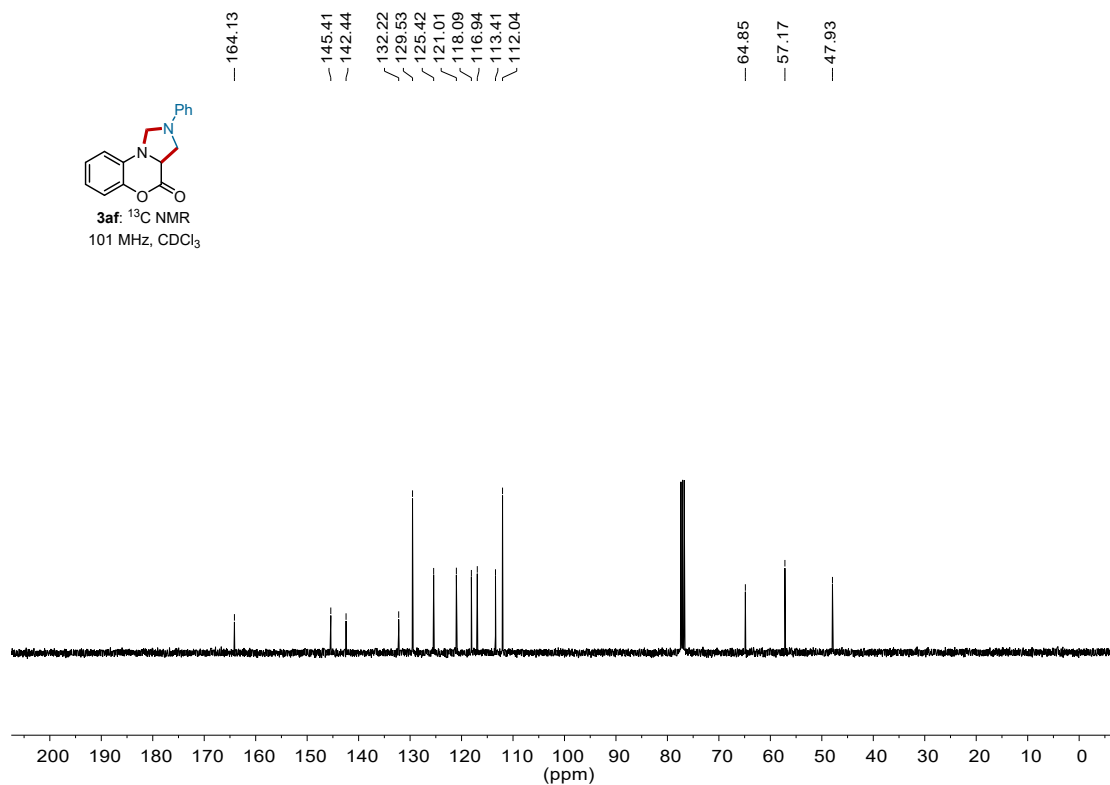
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— 2.37











5. Reference

1. Yan, Z.; Wu, B.; Gao, X.; Chen, M.-W.; Zhou, Y.-G., Enantioselective Synthesis of α -Amino Phosphonates via Pd-Catalyzed Asymmetric Hydrogenation. *Org. Lett.* **2016**, *18* (4), 692-695.
2. Duan, Y.; Zhang, M.; Ruzi, R.; Wu, Z.; Zhu, C., The direct decarboxylative allylation of N-arylglycine derivatives by photoredox catalysis. *Org. Chem. Front.* **2017**, *4* (4), 525-528.