

## Supporting Information

### **Base mediated aza-[2+1] annulation and regioselective aziridines ring-opening cascade: mild synthesis of functionalized $\beta$ -amino ketones from cyclic *N*-sulfonyl aldimines and $\alpha$ -carbonyl sulfonium salts**

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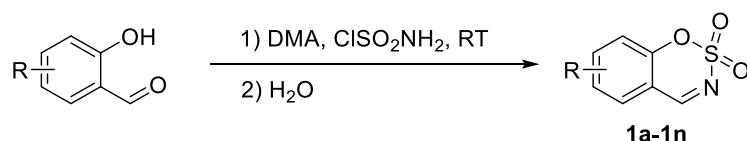
## 1. General Information

All reactions were monitored by Thin Layer Chromatography on plates (GF<sub>254</sub>) supplied by Yantai Chemicals (China) using UV light as visualizing agent and an ethanolic solution of Potassium permanganate, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).

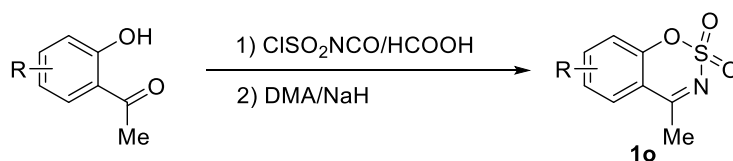
**NMR spectra** were recorded on Bruker AV400 and Bruker AV500 instrument. Solvent signal was used as internal standard for <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm) and <sup>13</sup>C NMR (CDCl<sub>3</sub>, 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triple doublet, m = multiplet. **High Resolution Mass Spectrometry (HRMS):** All were recorded on Waters Xevo G2 QTOF MS using a positive electrospray ionization (ESI+). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope. **Infrared spectra (IR)** were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer and reported as wavelength numbers (cm<sup>-1</sup>). **Melting points** were determined using a Stanford Research Systems DigiMelt MPA-160 capillary melting point apparatus. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (<sup>1</sup>H NMR) homogeneous materials.

## 2. General Experimental Procedures

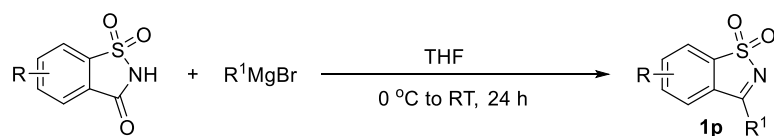
### (1) General procedure for the synthesis of *N*-sulfonyl aldimines



**General Procedure A:**<sup>[1]</sup> To a solution of substituted salicylaldehyde (15.0 mmol) in DMA (100 mL) at room temperature was carefully added freshly prepared ClSO<sub>2</sub>NH<sub>2</sub> (4.62 g, 40.0 mmol) in small portions and the resulting solution was stirred for 18 h. The reaction was quenched carefully with ice-cold H<sub>2</sub>O (100 mL) and the mixture was transferred to a separating funnel containing CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL), and the combined organic layers were washed with saturated NaHCO<sub>3</sub> solution (100 mL), H<sub>2</sub>O (3 x 100 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered through a short pad of silica using CH<sub>2</sub>Cl<sub>2</sub> as eluent and concentrated in vacuo. The residue was further purified by flash column chromatography over silica gel (hexane:ethyl acetate = 4:1) to afford the desired *N*-sulfonyl aldimines **1a-1n**.

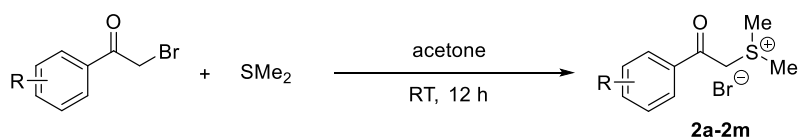


**General Procedure B:**<sup>[2]</sup> Anhydrous formic acid (20.0 mmol, 921 mg, 0.75 mL) was dropwise added to neat chlorosulfonyl isocyanate (20.0 mmol, 2.83 g, 1.74 mL) at 0 °C ice bath with rapid stirring. Vigorous gas evolution was observed during the addition process. The resulting viscous suspension was stirred at room temperature until gas evolution ceased (1-2 h). To the resulting sulfamoyl chloride (ClSO<sub>2</sub>NH<sub>2</sub>) was added 2'-hydroxyacetophenone (10.0 mmol). After the mixture was cooled under ice-cooling, 15 mL of DMA (*N,N*-dimethyl acetamide) was slowly added. Caution: a mild exotherm was noted upon combining these reagents. After the icecooling was moved, the mixture was stirring for 10 min, and sodium hydride (480 mg of 60% dispersion in mineral oil, 12.0 mmol) was added in portions. After stirring for 30 min at room temperature another sodium hydride (480 mg of 60% dispersion in mineral oil, 12.0 mmol) was added in portions again. After stirring for 1 h at room temperature, the reaction mixture was allowed to stir overnight (8-12 h) at 50 °C with oil bath. The reaction was quenched by the addition of 30 mL H<sub>2</sub>O and the aqueous layer was extracted with EtOAc (20 mL x 3). The combined organic layers were washed with 40 mL H<sub>2</sub>O and 40 mL brine, and concentrated under reduced pressure. Purification by chromatography on silica gel (PE/EtOAc = 10:1 to 5:1) to afford the desired imine **1o**.



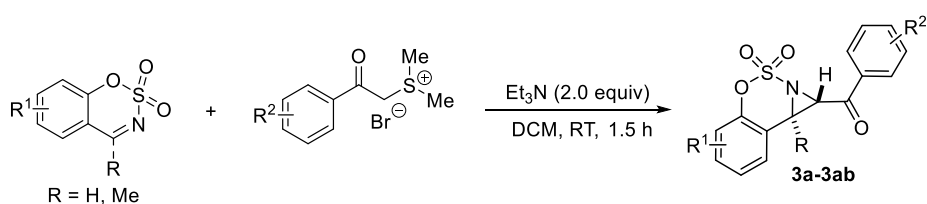
**General Procedure C:**<sup>[2]</sup> To a solution of saccharin (1.83g, 10.0 mmol, 1.0 equiv) in THF (20 mL) was slowly added  $R^1MgBr$  (3.0 equiv, 30 mmol, in 30 mL THF) at 0 °C, and the mixture was stirred at room temperature for 24 h, then acidified with 1 M HCl to pH= 2 and diluted with water (30 mL). The mixture was extracted with EtOAc (20 mL x 3). The combined organic layers were dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (or recrystallized from hot absolute ethanol) to give the product **1p**.

## (2) General procedure for the synthesis of $\alpha$ -carbonyl sulfonium salts



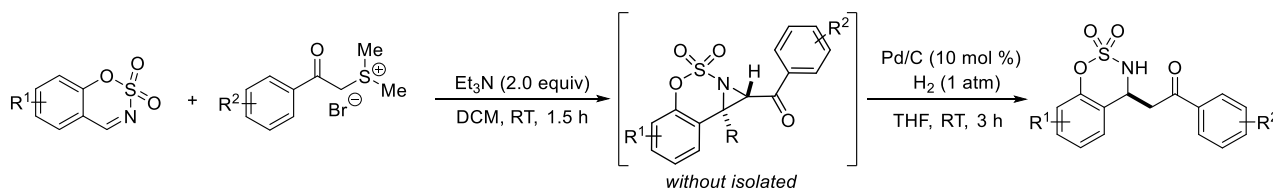
**General Procedure D:**<sup>[3]</sup> Dimethyl sulfide (10 mmol) was added to a solution of 2-bromoacetophenone (10 mmol) in acetone (15 mL). After the mixture had been stirred for 12 h, the residue was filtered and washed with acetone. The solid product was used as sulfonium salts without further purification. **2a-2m** was prepared by the general procedure.

## (3) General procedure for the base-promoted [2+1] annulation of *N*-sulfonyl aldimines with $\alpha$ -carbonyl sulfonium salts



**General Procedure E:** To a solution of sulfamate-derived cyclic aldimine (0.4 mmol, 1.0 equiv) and  $\alpha$ -carbonyl sulfonium salts (0.6 mmol, 1.5 equiv) in dry dichloromethane (3.0 mL) was added trimethylamine (0.6 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred at this temperature for 1.5 h until complete consumption of starting material (detected by TLC). After filtration through a plug of celite, the combined organic concentrated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to give the aziridines **3a-3ab**.

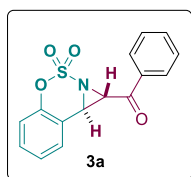
## (4) General procedure for the synthesis of $\beta$ -amino ketones from *N*-sulfonyl aldimines and $\alpha$ -carbonyl sulfonium salts by one-pot procedure



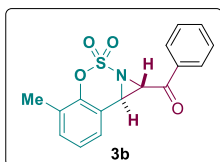
**General Procedure F:** To a solution of *N*-sulfonyl aldimine (0.4 mmol, 1.0 equiv) and  $\alpha$ -carbonyl sulfonium salts (0.6 mmol, 1.5 equiv) in dry dichloromethane (3.0 mL) was added trimethylamine (0.6 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred at this temperature for 1.5 h until complete consumption of starting material (detected by TLC). Then, the solvent dichloromethane was evaporated and the crude product was redissolved in tetrahydrofuran (3.0 mL), the reaction mixture was further stirred at room temperature for 3~4 h in the presence of Pd/C (10 mol %) under hydrogen atmosphere (one atmospheric pressure) until complete consumption of starting material (detected by TLC). After filtration through a plug of celite, the organic was concentrated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:4) to give  $\beta$ -amino ketones.

### 3. Characterization Data

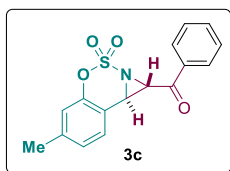
Note: The fused tri-substituted aziridines **3a-3ab** are new compounds, and their spectroscopic data are provided below. The  $\beta$ -amino ketones **4a-4d**,<sup>[4]</sup> **4e-4f**,<sup>[5]</sup> **4g**,<sup>[4]</sup> **4h**,<sup>[5]</sup> **4j**,<sup>[5]</sup> **4l**,<sup>[5]</sup> **4m**,<sup>[4]</sup> **4o**,<sup>[4]</sup> **4p**,<sup>[5]</sup> **4q**,<sup>[4]</sup> **4u-4y**,<sup>[4]</sup> **4z**,<sup>[5]</sup> **5**,<sup>[5]</sup> and **6**<sup>[6]</sup> are known compounds, the  $\beta$ -amino ketones **4i**, **4k**, **4n**, **4v-4t**, **4x**, **6'**, **7**, and **8** are new compounds, and their spectroscopic data are provided below.



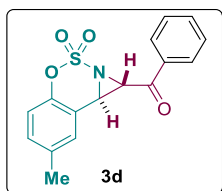
**(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3a)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (238.6 mg, 0.792 mmol, 99 %). **Mp**: 112.3-112.0 °C; **IR**  $\nu_{\max}$  (film): 3056, 2842, 1680, 1394, 1194, 918, 855, 754  $\text{cm}^{-1}$ ; **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**:  $\delta$  = 8.10 (dd,  $J$  = 8.5, 1.0 Hz, 2H), 7.77-7.60 (m, 1H), 7.58-7.50 (m, 3H), 7.44 (td,  $J$  = 8.1, 1.6 Hz, 1H), 7.33 (td,  $J$  = 7.5, 1.0 Hz, 1H), 7.17 (d,  $J$  = 8.0 Hz, 1H), 4.70 (d,  $J$  = 3.5 Hz, 1H), 4.29 (d,  $J$  = 3.5 Hz, 1H) ppm; **<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)**:  $\delta$  = 189.3, 150.0, 135.2, 134.9, 130.9, 129.7, 129.3, 129.1, 127.2, 119.7, 118.3, 47.9, 45.3 ppm; **HRMS (ESI)**:  $m/z$  calcd for C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>NS [M + H]<sup>+</sup>: 302.0482; found: 302.0483.



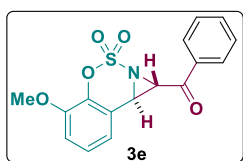
**(5-methyl-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3b)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (62.5 mg, 0.198 mmol, 99 %). **Mp**: 189.0-189.5 °C; **IR**  $\nu_{\max}$  (film): 3016, 2906, 1683, 1470, 1389, 1187, 869, 776  $\text{cm}^{-1}$ ; **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 800 MHz)**:  $\delta$  = 8.09 (d,  $J$  = 7.2 Hz, 2H), 7.67 (t,  $J$  = 6.8 Hz, 1H), 7.54 (t,  $J$  = 7.2 Hz, 2H), 7.34 (d,  $J$  = 7.2 Hz, 1H), 7.29 (d,  $J$  = 6.4 Hz, 1H), 7.21 (q,  $J$  = 6.9 Hz, 1H), 4.70 (d,  $J$  = 2.4 Hz, 1H), 4.24 (d,  $J$  = 2.4 Hz, 1H), 2.33 (s, 3H) ppm; **<sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz)**:  $\delta$  = 189.4, 148.4, 135.2, 134.8, 132.5, 129.3, 129.2, 129.0, 127.3, 126.6, 117.8, 48.1, 45.1, 14.9 ppm; **HRMS (ESI)**:  $m/z$  calcd for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>NS [M + H]<sup>+</sup>: 316.0638; found: 316.0635.



**(6-methyl-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3c):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (59.2 mg, 0.188 mmol, 94 %). **Mp:** 192.4-192.9 °C; **IR**  $\nu_{\text{max}}$  (film): 3044, 2924, 1687, 1599, 1506, 1450, 1393, 1194, 1033, 798, 720  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 800 MHz):**  $\delta$  = 8.09 (d,  $J$  = 7.2 Hz, 2H), 7.67 (t,  $J$  = 7.2 Hz, 1H), 7.54 (t,  $J$  = 7.6 Hz, 2H), 7.39 (d,  $J$  = 7.2 Hz, 1H), 7.13 (d,  $J$  = 8.0 Hz, 1H), 6.98 (s, 1H), 4.67 (d,  $J$  = 3.2 Hz, 1H), 4.24 (d,  $J$  = 3.2 Hz, 1H), 2.39 (s, 3H) ppm;  **$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 200 MHz):**  $\delta$  = 189.4, 149.9, 141.9, 135.2, 134.9, 129.4, 129.3, 129.1, 127.9, 120.1, 114.9, 48.0, 45.4, 21.4 ppm; **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{NS}$  [ $\text{M} + \text{H}$ ] $^+$ : 316.0638; found: 316.0638.



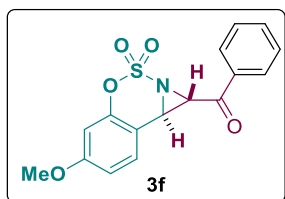
**(7-methyl-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3d):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (48.4 mg, 0.153 mmol, 77 %). **Mp:** 114.7-115.8 °C; **IR**  $\nu_{\text{max}}$  (film): 3071, 2927, 1681, 1498, 1392, 1174, 829, 714  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  = 8.21-7.94 (m, 2H), 7.66 (t,  $J$  = 7.3 Hz, 1H), 7.53 (t,  $J$  = 7.8 Hz, 2H), 7.31 (s, 1H), 7.21 (dd,  $J$  = 8.3, 1.1 Hz, 1H), 7.03 (d,  $J$  = 8.5 Hz, 1H), 4.67 (d,  $J$  = 3.5 Hz, 1H), 4.21 (d,  $J$  = 3.5 Hz, 1H), 2.37 (s, 3H) ppm;  **$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  = 189.3, 147.8, 137.3, 135.2, 134.8, 131.2, 130.1, 129.2, 129.0, 119.3, 117.7, 48.0, 45.4, 20.9 ppm; **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{NS}$  [ $\text{M} + \text{H}$ ] $^+$ : 316.0638; found: 316.0638.



**(5-methoxy-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3e):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (49.0 mg, 0.148 mmol, 74 %). **Mp:** 167.9-168.7 °C; **IR**  $\nu_{\text{max}}$  (film): 3013, 2905, 1686, 1488, 1387, 1284, 1068, 934, 689  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 800 MHz):**  $\delta$  = 8.09 (d,  $J$  = 8.0 Hz, 2H), 7.67 (t,  $J$  = 7.6 Hz, 1H), 7.53 (t,  $J$  = 7.6 Hz, 2H), 7.25 (t,  $J$  = 8.4 Hz, 1H), 7.07 (d,  $J$  = 8.0 Hz, 1H), 7.03 (d,  $J$  = 8.0 Hz, 1H), 4.73 (d,  $J$  = 3.2 Hz, 1H), 4.24 (d,  $J$  = 3.2 Hz, 1H), 3.90 (s, 3H) ppm;  **$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 200 MHz):**  $\delta$  = 189.3, 149.5, 138.9, 135.2, 134.9,

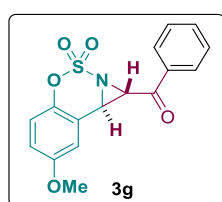


129.2, 129.1, 127.2, 120.7, 119.2, 114.0, 56.5, 48.0, 45.1 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $C_{16}H_{14}O_5NS$   $[M + H]^+$ : 332.0587; found: 332.0584.



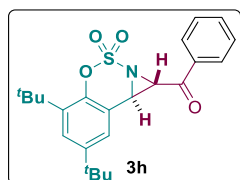
**(6-methoxy-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3f):**

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (48.0 mg, 0.145 mmol, 72%). **Mp**: 165.3-166.1 °C; **IR**  $\nu_{max}$  (film): 2914, 2836, 1692, 1504, 1394, 1089, 797, 691  $cm^{-1}$ ;  **$^1H$  NMR (CDCl<sub>3</sub>, 800 MHz)**:  $\delta$  = 8.09 (d,  $J$  = 8.0 Hz, 2H), 7.67 (t,  $J$  = 7.2 Hz, 1H), 7.54 (t,  $J$  = 8.0 Hz, 2H), 7.41-7.39 (m, 1H), 6.85 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 6.71 (d,  $J$  = 2.4 Hz, 1H), 4.66 (d,  $J$  = 3.2 Hz, 1H), 4.23 (d,  $J$  = 3.2 Hz, 1H), 3.84 (s, 3H) ppm;  **$^{13}C$  NMR (CDCl<sub>3</sub>, 200 MHz)**:  $\delta$  = 189.5, 161.6, 151.0, 135.3, 134.9, 130.3, 129.3, 129.1, 113.1, 109.6, 105.6, 56.0, 48.1, 45.5 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $C_{16}H_{14}O_5NS$   $[M + H]^+$ : 332.0587; found: 332.0587.



**(7-methoxy-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3g):**

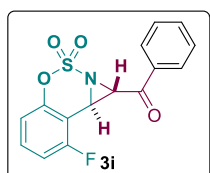
The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (64.4 mg, 0.195 mmol, 97%). **Mp**: 141.4-142.1 °C; **IR**  $\nu_{max}$  (film): 2950, 2822, 1682, 1498, 1399, 1171, 922, 685  $cm^{-1}$ ;  **$^1H$  NMR (CDCl<sub>3</sub>, 800 MHz)**:  $\delta$  = 8.09 -8.07 (m, 2H), 7.66 (t,  $J$  = 7.2 Hz, 1H), 7.53 (t,  $J$  = 7.6 Hz, 2H), 7.07 (d,  $J$  = 8.8 Hz, 1H), 7.01 (d,  $J$  = 2.4 Hz, 1H), 6.91 (dd,  $J$  = 9.2, 2.8 Hz, 1H), 4.68 (d,  $J$  = 3.2 Hz, 1H), 4.20 (d,  $J$  = 4.0 Hz, 1H), 3.81 (s, 3H) ppm;  **$^{13}C$  NMR (CDCl<sub>3</sub>, 200 MHz)**:  $\delta$  = 189.3, 158.1, 143.3, 135.1, 134.9, 129.2, 129.1, 120.6, 118.9, 115.7, 114.8, 56.0, 47.9, 45.3 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $C_{16}H_{14}O_5NS$   $[M + H]^+$ : 332.0587; found: 332.0587.



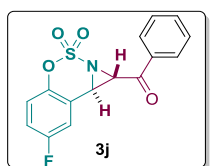
**(5,7-di-tert-butyl-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3h):**

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (81.8 mg, 0.198 mmol, 99%). **Mp**: 198.3-198.8 °C; **IR**  $\nu_{max}$  (film): 2952, 1683, 1405, 1195, 848, 684  $cm^{-1}$ ;  **$^1H$  NMR (CDCl<sub>3</sub>, 800 MHz)**:  $\delta$  = 8.13 (d,  $J$  = 8.0 Hz, 2H), 7.67 (t,  $J$  = 7.2 Hz,

1H), 7.55 (t,  $J = 7.6$  Hz, 2H), 7.44 (d,  $J = 1.6$  Hz, 1H), 7.35 (d,  $J = 1.6$  Hz, 1H), 4.73 (d,  $J = 3.2$  Hz, 1H), 4.26 (d,  $J = 3.2$  Hz, 1H), 1.44 (s, 9H), 1.33 (s, 9H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 189.7, 149.6, 147.0, 140.5, 135.3, 134.8, 129.2, 129.1, 125.6, 124.9, 117.7, 48.8, 45.0, 35.2, 35.0, 31.4, 30.2$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 414.1734; found: 414.1731.

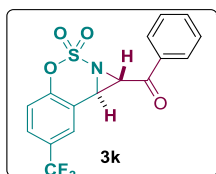


**(8-fluoro-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3i):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (56.2 mg, 0.176 mmol, 88 %). **Mp:** 102.5-107.2 °C; **IR**  $\nu_{\text{max}}$  (film): 3057, 2945, 1682, 1594, 1404, 1195, 971, 796  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 800 MHz):  $\delta = 8.09$  (d,  $J = 8.0$  Hz, 2H), 7.70-7.67 (m, 1H), 7.55 (t,  $J = 7.6$  Hz, 2H), 7.44-7.40 (m, 1H), 7.09 (t,  $J = 8.4$  Hz, 1H), 6.99 (d,  $J = 8.0$  Hz, 1H), 4.71 (d,  $J = 4.0$  Hz, 1H), 4.56 (d,  $J = 4.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 188.7, 161.3$  (d,  $J_{\text{F-C}} = 253.5$  Hz), 150.7 (d,  $J_{\text{F-C}} = 4.6$  Hz), 135.1, 135.0, 131.6 (d,  $J_{\text{F-C}} = 9.2$  Hz), 129.3, 129.1, 115.4 (d,  $J_{\text{F-C}} = 2.8$  Hz), 114.3 (d,  $J_{\text{F-C}} = 20.5$  Hz), 107.2 (d,  $J_{\text{F-C}} = 17.7$  Hz), 44.7, 42.5 (d,  $J_{\text{F-C}} = 5.0$  Hz) ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta = -116.71$  - - 116.75 (m) ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{NFS}$   $[\text{M} + \text{H}]^+$ : 320.0387; found: 320.0389.

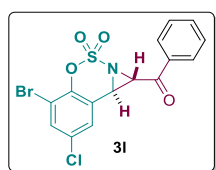


**(7-fluoro-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3j):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (48.5 mg, 0.152 mmol, 76 %). **Mp:** 128.3-129.0 °C; **IR**  $\nu_{\text{max}}$  (film): 3038, 2900, 1682, 1494, 1394, 1201, 1155, 836, 687  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 800 MHz):  $\delta = 8.08$  (d,  $J = 7.2$  Hz, 2H), 7.68 (t,  $J = 7.2$  Hz, 1H), 7.54 (t,  $J = 7.6$  Hz, 2H), 7.26 (dd,  $J = 7.2, 2.4$  Hz, 1H), 7.16-7.11 (m, 2H), 4.71 (d,  $J = 4.0$  Hz, 1H), 4.24 (d,  $J = 3.2$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 188.9, 160.4$  (d,  $J_{\text{F-C}} = 248.0$  Hz), 145.8, 135.0, 135.0, 129.3, 129.1, 121.3 (d,  $J_{\text{F-C}} = 8.0$  Hz), 120.0 (d,  $J_{\text{F-C}} = 8.0$  Hz), 117.6 (d,  $J_{\text{F-C}} = 24.0$  Hz), 116.8 (d,  $J_{\text{F-C}} = 26.0$  Hz),

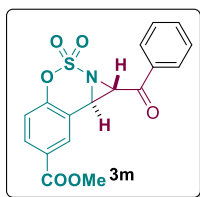
47.2, 45.1 ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta = -112.83$ -  $-112.84$ (m) ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{NFS}$   $[\text{M} + \text{H}]^+$ : 320.0387; found: 320.0384.



**3,3-dioxido-7-(trifluoromethyl)-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl(phenyl)methanone (3k):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white oil (31.6 mg, 0.086 mmol, 43 %). IR  $\nu_{\text{max}}$  (film): 3067, 2926, 1689, 1404, 1337, 1120, 825, 711  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 8.11$  (d,  $J = 8.4$  Hz, 2H), 7.83 (s, 1H), 7.71 (dd,  $J = 13.0$ , 7.1 Hz, 2H), 7.56 (t,  $J = 7.7$  Hz, 2H), 7.31 (d,  $J = 8.6$  Hz, 1H), 4.74 (d,  $J = 3.6$  Hz, 1H), 4.38 (d,  $J = 3.6$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 188.6$ , 152.2, 135.1, 135.0, 129.8 (q,  $J_{\text{F-C}} = 33.8$  Hz), 129.4, 129.2, 128.1 (q,  $J_{\text{F-C}} = 3.8$  Hz), 127.2 (q,  $J_{\text{F-C}} = 3.8$  Hz), 123.1 (q,  $J_{\text{F-C}} = 270.8$  Hz), 120.5, 119.4, 47.2, 45.1 ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 470 MHz):  $\delta = -62.46$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_9\text{O}_4\text{NF}_3\text{S}$   $[\text{M-H}]^-$ : 368.0203; found: 368.0210.

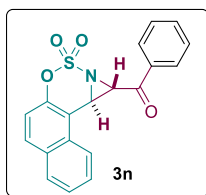


**(5-bromo-7-chloro-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl(phenyl)methanone (3l):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (58.4 mg, 0.141 mmol, 71 %). Mp: 216.1-217.0  $^{\circ}\text{C}$ ; IR  $\nu_{\text{max}}$  (film): 3061, 2901, 1673, 1411, 1200, 915, 802  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 800 MHz):  $\delta = 8.10$  (d,  $J = 7.2$  Hz, 2H), 7.70 (t,  $J = 7.2$  Hz, 1H), 7.66 (d,  $J = 2.4$  Hz, 1H), 7.56 (t,  $J = 7.6$  Hz, 2H), 7.49 (d,  $J = 2.4$  Hz, 1H), 4.72 (d,  $J = 4.0$  Hz, 1H), 4.25 (d,  $J = 3.2$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 188.5$ , 145.6, 135.2, 134.9, 134.0, 133.0, 129.4, 129.2, 128.8, 121.3, 114.4, 47.0, 44.7 ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{10}\text{O}_4\text{NBr}$   $[\text{M} + \text{H}]^+$ : 413.9197; found: 413.9194.

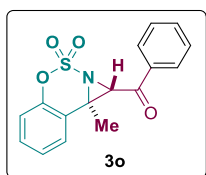


**Methyl-1-benzoyl-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazine-7-carboxylate 3,3-dioxide (3m):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (33.5 mg, 0.093 mmol, 93 %). Mp: 124.5-125.5  $^{\circ}\text{C}$ ; IR  $\nu_{\text{max}}$  (film): 3050, 2960, 1719, 1408, 1281, 1170, 914,

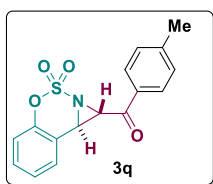
841, 782  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 8.23$  (d,  $J = 2.0$  Hz, 1H), 8.12 - 8.07 (m, 3H), 7.67 (t,  $J = 7.5$  Hz, 1H), 7.54 (t,  $J = 7.8$  Hz, 2H), 7.22 (d,  $J = 8.5$  Hz, 1H), 4.71 (d,  $J = 3.5$  Hz, 1H), 4.35 (d,  $J = 3.5$  Hz, 1H), 3.94 (s, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 188.7, 165.1, 153.0, 135.1, 135.0, 132.3, 131.3, 129.3, 129.1, 119.9, 118.5, 52.8, 47.5, 45.2$  ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_6\text{NS}$   $[\text{M} + \text{H}]^+$ : 360.0536; found: 360.0537.



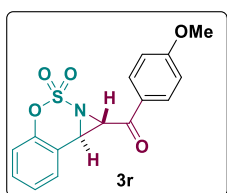
**(3,3-dioxido-1,10c-dihydroazirino[1,2-c]naphtho[1,2-e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3n)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (67.0mg, 0.191 mmol, 96 %). **Mp**: 152.5-152.8  $^{\circ}\text{C}$ ; **IR**  $\nu_{\text{max}}$  (film): 3056, 1683, 1397, 1192, 953, 810, 733  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 800 MHz):  $\delta = 8.12$  (d,  $J = 6.4$  Hz, 2H), 8.05 (d,  $J = 8.0$  Hz, 1H), 7.93-7.91 (m, 2H), 7.66 (d,  $J = 6.4$  Hz, 2H), 7.59-7.57 (m, 3H), 7.27-7.25 (m, 1H), 4.96 (d,  $J = 4.0$  Hz, 1H), 4.79 (d,  $J = 4.0$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 189.5, 148.5, 135.1, 135.0, 131.8, 131.3, 129.4, 129.3, 129.1, 128.7, 126.95, 122.1, 118.2, 112.3, 45.9, 45.0$  ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 352.0638; found: 332.0636.



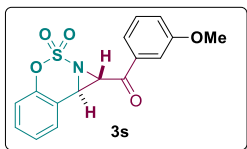
**(8b-methyl-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(phenyl)methanone (3o)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (22.0 mg, 0.070 mmol, 12 %). **Mp**: 60.1-61.2  $^{\circ}\text{C}$ ; **IR**  $\nu_{\text{max}}$  (film): 3010, 2930, 1692, 1398, 1203, 1171, 984, 852, 731  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 7.99$  (d,  $J = 7.5$  Hz, 2H), 7.65 (t,  $J = 7.54$  Hz, 1H), 7.60-7.44 (m, 4H), 7.38 (t,  $J = 7.5$  Hz, 1H), 7.18 (d,  $J = 8.1$  Hz, 1H), 4.58 (s, 1H), 1.73 (s, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 189.4, 149.4, 135.3, 134.7, 131.1, 129.2, 128.8, 128.2, 127.2, 122.3, 119.9, 53.5, 52.4, 17.7$  ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 316.0638; found: 316.0638.



**(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(p-tolyl)methanone(3q):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (116.1 mg, 0.368 mmol, 92 %). **Mp:** 160.8-162.3 °C; **IR**  $\nu_{\max}$  (film): 3101, 3017, 1672, 1489, 1393, 1181, 911, 804, 770  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 8.00 (d,  $J$  = 8.0 Hz, 2H), 7.52 (d,  $J$  = 7.5 Hz, 1H), 7.44 (t,  $J$  = 7.8 Hz, 1H), 7.33 (t,  $J$  = 7.0 Hz, 3H), 7.17 (d,  $J$  = 8.0 Hz, 1H), 4.69 (d,  $J$  = 3.5 Hz, 1H), 4.28 (d,  $J$  = 3.0 Hz, 1H), 2.45 (s, 3H) ppm;  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 188.7, 150.0, 146.2, 132.8, 130.8, 130.0, 129.7, 129.2, 127.1, 119.6, 118.3, 47.9, 45.2, 22.0 ppm; **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 316.0638; found: 316.0635.

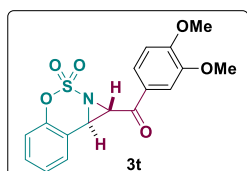


**(3,3-dioxido-1,8b-dihydroazirino[1,2c]benzo[e][1,2,3]-Oxathiazin-1-yl)(4-methoxyphenyl)methanone(3r):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (128.3 mg, 0.387 mmol, 97 %). **Mp:** 128.4-130.2 °C; **IR**  $\nu_{\max}$  (film): 2997, 2820, 1682, 1598, 1395, 1242, 1169, 864, 761  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 800 MHz):  $\delta$  = 8.08 (d,  $J$  = 8.8 Hz, 2H), 7.52 (d,  $J$  = 7.2 Hz, 1H), 7.43 (t,  $J$  = 7.6 Hz, 1H), 7.32 (t,  $J$  = 7.2 Hz, 1H), 7.15 (d,  $J$  = 8.0 Hz, 1H), 6.99 (d,  $J$  = 8.8 Hz, 2H), 4.67 (d,  $J$  = 2.4 Hz, 1H), 4.28 (d,  $J$  = 2.4 Hz, 1H), 3.89 (s, 3H) ppm;  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 187.4, 165.0, 150.0, 131.6, 130.7, 129.7, 128.2, 127.1, 119.6, 118.4, 114.5, 55.8, 47.8, 45.2 ppm; **HRMS (ESI):**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_5\text{NS}$   $[\text{M} + \text{H}]^+$ : 332.0587; found: 332.0595.



**(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(3-methoxyphenyl)methanone (3s):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (131.3 mg, 0.396 mmol, 99 %). **Mp:** 149.3-149.7 °C; **IR**  $\nu_{\max}$  (film): 2903, 2821, 1693, 1392, 1268, 1191, 1018, 914, 753  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 800 MHz):  $\delta$  = 7.65 (d,  $J$  = 8.0 Hz, 1H), 7.56

(s, 1H), 7.51 (d,  $J = 7.2$  Hz, 1H), 7.43-7.40 (m, 2H), 7.32 (t,  $J = 7.2$  Hz, 1H), 7.20-7.18 (m, 1H), 7.13 (d,  $J = 8.0$  Hz, 1H), 4.68 (d,  $J = 4.0$  Hz, 1H), 4.25 (d,  $J = 4.0$  Hz, 1H), 3.84 (s, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 189.0, 160.1, 149.8, 136.3, 130.8, 130.2, 129.7, 127.1, 121.6, 121.6, 119.5, 118.0, 112.8, 55.6, 47.9, 45.4$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_5\text{NS}$   $[\text{M} + \text{H}]^+$ : 332.0587; found: 332.0584.



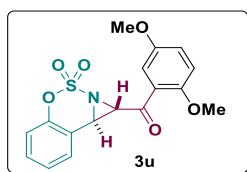
(3,4-dimethoxyphenyl)(3,3-dioxido-1,8b-

dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-

yl)methanone (3t): The product was purified by flash column

chromatography (ethyl acetate/petroleum ether = 1:5) as a white

solid (72.1 mg, 0.1997 mmol, 99 %). **Mp**: 166.7-167.1 °C; **IR**  $\nu_{\text{max}}$  (film): 2922, 2820, 1674, 1596, 1274, 1022, 894, 764, 663  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 800 MHz):  $\delta = 7.78$  (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.59 (d,  $J = 1.6$  Hz, 1H), 7.52 (d,  $J = 7.2$  Hz, 1H), 7.43-7.42 (m, 1H), 7.31 (t,  $J = 7.6$  Hz, 1H), 7.13 (d,  $J = 8.0$  Hz, 1H), 6.94 (d,  $J = 8.0$  Hz, 1H), 4.66 (d,  $J = 4.0$  Hz, 1H), 4.28 (d,  $J = 3.2$  Hz, 1H), 3.94 (d,  $J = 15.2$  Hz, 6H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 187.4, 154.9, 149.9, 149.5, 130.7, 129.7, 128.3, 127.1, 124.5, 119.5, 118.3, 110.7, 110.5, 56.3$  (d,  $J = 9.6$  Hz), 56.2, 47.64 (d,  $J = 10.4$  Hz), 45.3 ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_6\text{NS}$   $[\text{M} + \text{H}]^+$ : 362.0693; found: 362.0690.



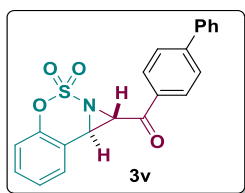
(2,5-dimethoxyphenyl)(3,3-dioxido-1,8b-dihydroazirino[1,2-

c]benzo[e][1,2,3]oxathiazin-1-yl)methanone (3u): The product

was purified by flash column chromatography (ethyl

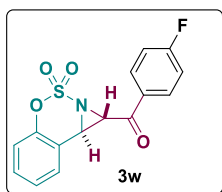
acetate/petroleum ether = 1:5) as a yellow solid (137.6 mg, 0.381 mmol, 95 %). **Mp**: 184.9-185.7 °C; **IR**  $\nu_{\text{max}}$  (film): 3062, 2951, 2840, 1672, 1498, 1390, 1193, 1033, 821, 760  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 800 MHz):  $\delta = 7.45$  (d,  $J = 36.0$  Hz, 2H), 7.30 (s, 2H), 7.13 (d,  $J = 8.0$  Hz, 2H), 6.92 (d,  $J = 5.6$  Hz, 1H), 4.91 (s, 1H), 4.14 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 190.4, 154.4, 153.9, 150.1, 130.5, 129.4, 126.8, 125.8, 123.0, 119.6, 119.0, 113.88, 113.4, 56.3, 56.05$  (d,  $J = 9.6$  Hz), 49.44, 48.62 (d,  $J = 12.0$  Hz) ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_6\text{NS}$   $[\text{M}$

+ H]<sup>+</sup>: 362.0693; found: 362.0693.



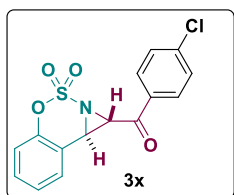
**[1,1'-biphenyl]-4-yl(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)methanone (3v)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid

(141.1 mg, 0.374 mmol, 94 %). **Mp**: 172.5-173.2 °C; **IR**  $\nu_{\text{max}}$  (film): 3010, 1687, 1602, 1386, 1186, 864, 733, 698  $\text{cm}^{-1}$ ; **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 800 MHz)**:  $\delta$  = 8.18 (s, 2H), 7.76 (s, 2H), 7.64 (s, 2H), 7.49-7.44 (m, 5H), 7.34 (s, 1H), 7.18 (d,  $J$  = 7.2 Hz, 1H), 4.74 (s, 1H), 4.32 (s, 1H) ppm; **<sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz)**:  $\delta$  = 188.8, 150.0, 147.6, 139.4, 133.8, 130.9, 129.7, 129.2, 128.8, 127.8, 127.5, 127.2, 119.7, 118.2, 47.9, 45.3 ppm; **HRMS (ESI)**:  $m/z$  calcd for C<sub>21</sub>H<sub>16</sub>O<sub>4</sub>NS [M + H]<sup>+</sup>: 378.0795; found: 378.0790.



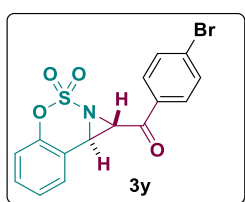
**(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)(4-fluorophenyl)methanone (3w)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (61.4 mg,

0.192 mmol, 96 %). **Mp**: 142.0-144.4 °C; **IR**  $\nu_{\text{max}}$  (film): 3328, 3123, 1681, 1596, 1398, 1193, 912, 808, 759  $\text{cm}^{-1}$ ; **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**:  $\delta$  = 8.16 -8.11 (m, 2H), 7.53 (dd,  $J$  = 7.5, 1.5 Hz, 1H), 7.44 (td,  $J$  = 8.0, 1.5 Hz, 1H), 7.33 (td,  $J$  = 7.5, 1.0 Hz, 1H), 7.23-7.18 (m, 2H), 7.15 (dd,  $J$  = 8.0, 0.5 Hz, 1H), 4.65 (d,  $J$  = 4.0 Hz, 1H), 4.27 (d,  $J$  = 3.5 Hz, 1H) ppm; **<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)**:  $\delta$  = 187.7, 166.8 (d,  $J_{\text{F-C}}$  = 258.7 Hz), 149.9, 132.0 (d,  $J_{\text{F-C}}$  = 9.7 Hz), 131.6 (d,  $J_{\text{F-C}}$  = 2.8 Hz), 130.9, 129.7, 127.2, 119.6, 118.0, 116.6 (d,  $J_{\text{F-C}}$  = 22.3 Hz), 47.8, 45.3 ppm; **<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)**:  $\delta$  = -101.33 - -101.29 (m) ppm; **HRMS (ESI)**:  $m/z$  calcd for C<sub>15</sub>H<sub>11</sub>O<sub>4</sub>NFS [M + H]<sup>+</sup>: 320.0387; found: 320.0383.



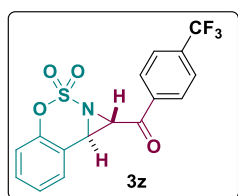
**(4-chlorophenyl)(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)methanone (3x)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (46.6 mg, 0.139

mmol, 70 %). **Mp**: 154.0-155.7 °C; **IR**  $\nu_{\max}$  (film): 3078, 2909, 1678, 1588, 1399, 1192, 922, 760, 669  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 8.06 (d,  $J$  = 8.5 Hz, 2H), 7.52 (d,  $J$  = 8.0 Hz, 3H), 7.45 (t,  $J$  = 7.5 Hz, 1H), 7.34 (t,  $J$  = 7.5 Hz, 1H), 7.17 (d,  $J$  = 8.0 Hz, 1H), 4.64 (d,  $J$  = 3.5 Hz, 1H), 4.29 (d,  $J$  = 3.5 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 188.3, 149.9, 141.7, 133.4, 131.0, 130.5, 129.8, 129.7, 127.2, 119.7, 118.0, 47.8, 45.2 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{NCIS}$   $[\text{M} + \text{H}]^+$ : 336.0092; found: 336.0089.



**(4-bromophenyl)(3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl)methanone (3y)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (90.7 mg, 0.239

mmol, 80 %). **Mp**: 167.9-170.0 °C; **IR**  $\nu_{\max}$  (film): 3031, 1683, 1585, 1393, 1190, 909, 860, 759  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 800 MHz):  $\delta$  = 7.97 (d,  $J$  = 8.0 Hz, 2H), 7.69 (d,  $J$  = 8.8 Hz, 2H), 7.53 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 7.45 (td,  $J$  = 7.8, 1.1 Hz, 1H), 7.34 (td,  $J$  = 7.6, 0.8 Hz, 1H), 7.17 (d,  $J$  = 8.0 Hz, 1H), 4.64 (d,  $J$  = 3.2 Hz, 1H), 4.28 (d,  $J$  = 3.2 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  = 188.5, 149.9, 133.8, 132.7, 131.0, 130.6, 130.5, 129.8, 127.2, 119.7, 118.0, 47.8, 45.2 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{O}_4\text{NBrS}$   $[\text{M} + \text{H}]^+$ : 379.9587; found: 379.9576.

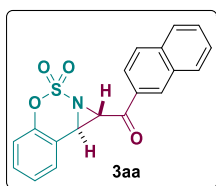


**3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[e][1,2,3]oxathiazin-1-yl(4-(trifluoromethyl)phenyl)methanone (3z)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (30.4 mg, 0.082

mmol, 41 %). **Mp**: 141.1-142.7 °C; **IR**  $\nu_{\max}$  (film): 2919, 1699, 1401, 1325, 1192, 1123, 1067, 810, 761  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.23 (d,  $J$  = 8.1 Hz, 2H), 7.81 (d,  $J$  = 8.1 Hz, 2H), 7.54 (d,  $J$  = 7.5 Hz, 1H), 7.46 (t,  $J$  = 7.8 Hz, 1H), 7.35 (t,  $J$  = 7.5 Hz, 1H), 7.18 (d,  $J$  = 8.1 Hz, 1H), 4.67 (d,  $J$  = 3.3 Hz, 1H), 4.30 (d,  $J$  = 3.2 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 188.8, 150.0, 137.7 (q,  $J_{\text{F-C}}$  = 1.3 Hz), 136.0 (q,  $J_{\text{F-C}}$  = 32.5 Hz), 131.1, 129.8, 129.5, 127.3, 126.4 (q,  $J_{\text{F-C}}$  = 3.8 Hz), 123.4 (q,  $J_{\text{F-C}}$  =



272.0 Hz), 119.8, 117.9, 47.9, 45.4 ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 470 MHz):  $\delta = -63.25$  ppm; HRMS (ESI)  $m/z$ :  $[\text{M}-\text{H}]^-$  calcd for  $\text{C}_{16}\text{H}_9\text{O}_4\text{NF}_3\text{S}$  368.0203; found: 368.0210.

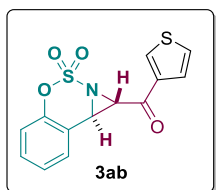


**(3,3-dioxido-1,8b-dihydroazirino[1,2-**

**c]benzo[e][1,2,3]oxathiazin-1-yl)(naphthalen-2-yl)methanone**

**(3aa)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (137.6 mg, 0.392 mmol, 98 %).

**Mp**: 185.0-186.1 °C; **IR**  $\nu_{\text{max}}$  (film): 2907, 2836, 1682, 1399, 1195, 933, 811, 746  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 8.69$  (s, 1H), 8.07 (d,  $J = 9.0$  Hz, 1H), 8.01 (d,  $J = 8.0$  Hz, 1H), 7.93 (d,  $J = 8.5$  Hz, 1H), 7.89 (d,  $J = 8.0$  Hz, 1H), 7.66 (t,  $J = 7.5$  Hz, 1H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.54 (d,  $J = 7.5$  Hz, 1H), 7.45 (t,  $J = 7.8$  Hz, 1H), 7.34 (t,  $J = 7.5$  Hz, 1H), 7.19 (d,  $J = 8.0$  Hz, 1H), 4.85 (d,  $J = 3.5$  Hz, 1H), 4.35 (d,  $J = 3.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 189.1, 150.0, 136.3, 132.5, 131.9, 130.9, 130.1, 129.8, 129.7, 129.3, 128.0, 127.4, 127.2, 123.7, 119.7, 118.3, 48.0, 45.4$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 352.0547; found: 352.0552.

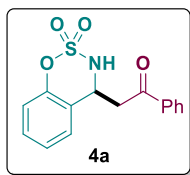


**(3,3-dioxido-1,8b-dihydroazirino[1,2-**

**c]benzo[e][1,2,3]oxathiazin-1-yl)(thiophen-2-yl)methanone**

**(3ab)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (60.4 mg, 0.197 mmol, 98 %).

**Mp**: 181.2-188.3 °C; **IR**  $\nu_{\text{max}}$  (film): 3117, 3078, 1654, 1384, 1191, 1058, 918, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 8.09$  (dd,  $J = 4.0, 1.0$  Hz, 1H), 7.83 (dd,  $J = 5.0, 1.0$  Hz, 1H), 7.52 (dd,  $J = 7.5, 1.5$  Hz, 1H), 7.45 (td,  $J = 8.0, 1.5$  Hz, 1H), 7.34 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.23 (dd,  $J = 4.5, 4.0$  Hz, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 4.55 (d,  $J = 3.5$  Hz, 1H), 4.28 (d,  $J = 4.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 181.8, 150.0, 141.8, 136.8, 135.1, 130.9, 129.8, 129.1, 127.2, 119.7, 118.2, 47.9, 46.1$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{O}_4\text{NS}_2$   $[\text{M} + \text{H}]^+$ : 308.0046; found: 308.0047.

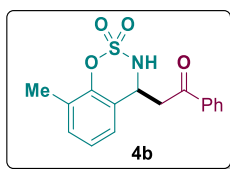


**2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (4a):**

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid

(24.6 mg, 0.081 mmol, 82 %). **Mp:** 186 °C; **IR**  $\nu_{\max}$  (film): 3333,

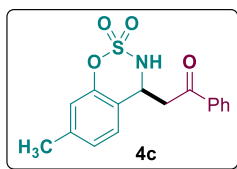
2915, 1676, 1484, 1400, 1172, 918, 840, 796  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 800 MHz):**  $\delta$  = 7.96 (d,  $J$  = 8.0 Hz, 2H), 7.62 (t,  $J$  = 7.2 Hz, 1H), 7.48 (t,  $J$  = 7.6 Hz, 2H), 7.32-7.29 (m, 1H), 7.15 (s, 2H), 7.04 (d,  $J$  = 8.8 Hz, 1H), 5.99 (d,  $J$  = 8.0 Hz, 1H), 5.42 (td,  $J$  = 7.7, 3.6 Hz, 1H), 4.28 (dd,  $J$  = 18.0, 7.6 Hz, 1H), 3.40 (dd,  $J$  = 18.0, 3.6 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  = 198.0, 151.3, 136.2, 134.3, 129.7, 129.0, 128.4, 126.2, 125.6, 121.7, 119.2, 53.7, 42.0 ppm; **HRMS (ESI):**  $m/z$  calcd for C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>NS [M + H]<sup>+</sup>: 304.0638; found: 304.0639.



**2-(8-methyl-2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (4b):**

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5)

as a white solid (46.1 mg, 0.145 mmol, 73 %). **Mp:** 135 °C; **IR**  $\nu_{\max}$  (film): 3306, 2967, 1683, 1455, 1364, 1151, 879, 759, 730  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  = 7.97 (d,  $J$  = 7.5 Hz, 2H), 7.62 (t,  $J$  = 7.3 Hz, 1H), 7.49 (t,  $J$  = 7.8 Hz, 2H), 7.16 (d,  $J$  = 7.5 Hz, 1H), 7.03 (t,  $J$  = 7.8 Hz, 1H), 6.97 (d,  $J$  = 8.0 Hz, 1H), 5.88 (d,  $J$  = 8.0 Hz, 1H), 5.39 (td,  $J$  = 7.6, 3.7 Hz, 1H), 4.26 (dd,  $J$  = 18.3, 7.3 Hz, 1H), 3.40 (dd,  $J$  = 18.0, 3.5 Hz, 1H), 2.30 (s, 3H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  = 198.0, 149.9, 136.3, 134.2, 131.2, 129.0, 128.7, 128.4, 124.9, 123.5, 121.6, 53.9, 42.0, 15.7 ppm; **HRMS (ESI):**  $m/z$  calcd for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>NS [M + H]<sup>+</sup>: 318.0795; found: 318.0791 .



**2-(7-methyl-2,2-dioxido-3,4-**

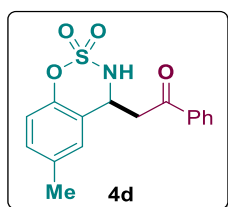
**dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one**

**(4c):** The product was purified by flash column chromatography

(ethyl acetate/petroleum ether = 1:5) as a white solid (59.2 mg, 0.187 mmol, 93 %).

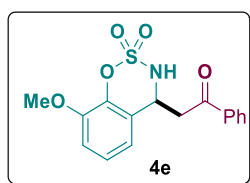
**Mp:** 141 °C; **IR**  $\nu_{\max}$  (film): 3314, 1678, 1401, 1191, 1106, 954, 798, 686  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  = 8.00-7.95 (m, 2H), 7.62 (t,  $J$  = 7.5 Hz, 1H), 7.49 (t,  $J$  = 7.8 Hz,

2H), 7.02 (d,  $J = 8.0$  Hz, 1H), 6.95 (d,  $J = 8.0$  Hz, 1H), 6.87 (s, 1H), 5.83 (d,  $J = 8.20$ Hz, 1H), 5.36 (td,  $J = 7.6, 3.7$  Hz, 1H), 4.24 (dd,  $J = 18.3, 7.3$  Hz, 1H), 3.39 (dd,  $J = 18.3, 3.8$  Hz, 1H), 2.33 (s, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 198.0, 151.2, 140.3, 136.4, 134.3, 129.0, 128.4, 126.5, 125.7, 119.5, 118.6, 53.7, 41.8, 21.1$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 318.0795; found: 318.0785.



**2-(6-methyl-2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (4d)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (43.4 mg, 0.137 mmol, 69 %). **Mp**: 134-136 °C;

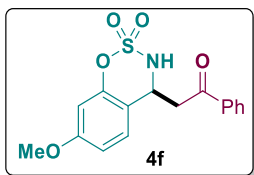
**IR**  $\nu_{\text{max}}$  (film): 3299, 2938, 1675, 1493, 1361, 1206, 863, 764, 681  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.98\text{-}7.95$  (m, 2H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.48 (t,  $J = 7.8$  Hz, 2H), 7.09 (d,  $J = 5.8$  Hz, 1H), 6.95-6.91 (m, 2H), 5.86 (d,  $J = 7.9$  Hz, 1H), 5.38 (td,  $J = 7.8, 3.6$  Hz, 1H), 4.25 (dd,  $J = 18.1, 7.8$  Hz, 1H), 3.38 (dd,  $J = 18.1, 3.7$  Hz, 1H), 2.28 (s, 3H). ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 198.0, 149.2, 136.4, 135.4, 134.2, 130.1, 129.0, 128.4, 126.5, 121.3, 118.9, 53.8, 42.4, 20.9$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 318.0795; found: 318.0803.



**2-(8-methoxy-2,2-dioxido-3,4-**

**dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (4e)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (46.5 mg,

0.140 mmol, 70 %). **Mp**: 172-175 °C; **IR**  $\nu_{\text{max}}$  (film): 3334, 2943, 1674, 1580, 1437, 1269, 1158, 865, 283  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.97$  (d,  $J = 8.0$  Hz, 2H), 7.62 (t,  $J = 7.5$ Hz, 1H), 7.49 (t,  $J = 7.8$  Hz, 2H), 7.07 (t,  $J = 8.0$  Hz, 1H), 6.89 (d,  $J = 8.5$  Hz, 1H), 6.70 (d,  $J = 7.5$  Hz, 1H), 5.85 (d,  $J = 8.0$  Hz, 1H), 5.40 (td,  $J = 7.5, 3.5$  Hz, 1H), 4.27 (dd,  $J = 18.0, 7.5$  Hz, 1H), 3.88 (s, 3H), 3.39 (dd,  $J = 18.3, 3.8$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 197.9, 149.2, 141.1, 136.3, 134.3, 129.0, 128.4, 125.3, 122.8, 117.1, 112.1, 56.4, 54.0, 41.9$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{NS}$   $[\text{M} + \text{H}]^+$ : 334.0744; found: 334.0745.

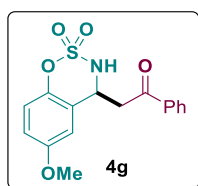


#### 2-(7-methoxy-2,2-dioxido-3,4-

#### dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one

(**4f**): The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (31.0 mg,

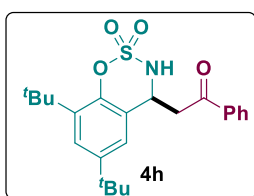
0.093 mmol, 47 %). **Mp**: 163 °C; **IR**  $\nu_{\max}$  (film): 3191, 1675, 1441, 1358, 1199, 1103, 802, 744, 685  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.97 (d,  $J$  = 7.5 Hz, 2H), 7.62 (t,  $J$  = 7.5 Hz, 1H), 7.50 (t,  $J$  = 7.8 Hz, 2H), 7.03 (d,  $J$  = 9.0 Hz, 1H), 6.70 (dd,  $J$  = 9.0, 2.5 Hz, 1H), 6.58 (d,  $J$  = 3.0 Hz, 1H), 5.85 (d,  $J$  = 8.0 Hz, 1H), 5.34 (td,  $J$  = 7.8, 3.8 Hz, 1H), 4.22 (dd,  $J$  = 18.0, 7.0 Hz, 1H), 3.79 (s, 3H), 3.38 (dd,  $J$  = 18.0, 4.0 Hz, 1H) ppm;  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 198.1, 160.5, 152.1, 136.4, 134.3, 129.1, 128.4, 126.6, 113.4, 112.5, 104.0, 55.8, 53.5, 41.8 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{NS}$  [ $\text{M} + \text{H}$ ] $^+$ : 334.0744; found: 334.0736.



#### 2-(6-methoxy-2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (**4g**):

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (62.2 mg, 0.187 mmol, 93 %). **Mp**: 170 °C; **IR**  $\nu_{\max}$  (film):

3202, 2963, 1674, 1489, 1374, 1175, 854, 758, 688  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.97 (d,  $J$  = 7.0 Hz, 2H), 7.62 (t,  $J$  = 7.3 Hz, 1H), 7.50 (t,  $J$  = 7.8 Hz, 2H), 6.99 (d,  $J$  = 9.0 Hz, 1H), 6.84 (dd,  $J$  = 9.0, 3.0 Hz, 1H), 6.64 (d,  $J$  = 2.5 Hz, 1H), 5.75 (d,  $J$  = 8.0 Hz, 1H), 5.37 (td,  $J$  = 7.6, 3.87 Hz, 1H), 4.25 (dd,  $J$  = 18.0, 7.5 Hz, 1H), 3.73 (s, 3H), 3.40 (dd,  $J$  = 18.0, 4.0 Hz, 1H) ppm;  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 197.8, 156.9, 145.1, 136.3, 134.3, 129.1, 128.4, 122.6, 120.1, 114.8, 111.3, 55.9, 53.9, 42.1 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{NS}$  [ $\text{M} + \text{H}$ ] $^+$ : 334.0744; found: 334.0744.



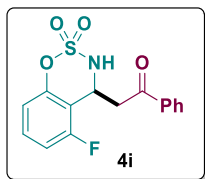
#### 2-(6,8-di-tert-butyl-2,2-dioxido-3,4-

#### dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one

(**4h**): The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (66.8 mg,

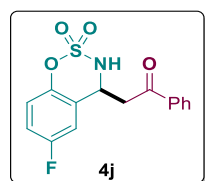
0.161 mmol, 80 %). **Mp**: 158 °C; **IR**  $\nu_{\max}$  (film): 3337, 2972, 2875, 1674, 1377, 1088, 1045, 880, 740  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.98 (d,  $J$  = 7.5 Hz, 2H), 7.61

(t,  $J = 7.5$  Hz, 1H), 7.49 (t,  $J = 7.8$  Hz, 2H), 7.34 (d,  $J = 2.0$  Hz, 1H), 6.98 (d,  $J = 2.0$  Hz, 1H), 5.72 (d,  $J = 7.5$  Hz, 1H), 5.39 (td,  $J = 7.8, 3.8$  Hz, 1H), 4.28 (dd,  $J = 18.0, 8.0$  Hz, 1H), 3.34 (dd,  $J = 17.8, 3.8$  Hz, 1H), 1.43 (s, 9H), 1.24 (s, 9H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 198.2, 148.3, 147.8, 139.7, 136.6, 134.1, 129.0, 128.4, 124.5, 122.1, 121.1, 54.3, 42.9, 35.3, 34.8, 31.4, 30.2$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{30}\text{O}_4\text{NS}$  [ $\text{M} + \text{H}$ ] $^+$ : 416.1890; found: 416.1890.



**2-(5-fluoro-2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (4i):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (35.1 mg, 0.109 mmol, 55 %). **Mp:** 138 °C; **IR**  $\nu_{\text{max}}$  (film):

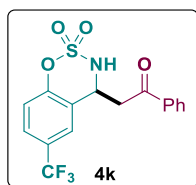
3646, 3579, 3182, 1675, 1582, 1460, 1179, 1002, 918, 825  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.97$  (d,  $J = 7.5$  Hz, 2H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.48 (t,  $J = 7.8$  Hz, 2H), 7.33 (dd,  $J = 14.8, 8.3$  Hz, 1H), 6.92 (dd,  $J = 18.3, 8.8$  Hz, 2H), 5.91 (d,  $J = 7.0$  Hz, 1H), 5.58 (t,  $J = 7.3$  Hz, 1H), 4.41 (dd,  $J = 18.0, 9.0$  Hz, 1H), 3.34 (dd,  $J = 18.3, 2.3$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 197.7, 159.3$  (d,  $J_{\text{F-C}} = 248.0$  Hz), 152.1 (d,  $J_{\text{F-C}} = 6.4$  Hz), 136.3, 134.1, 130.3 (d,  $J_{\text{F-C}} = 10.3$  Hz), 129.0, 128.4, 115.0 (d,  $J_{\text{F-C}} = 3.3$  Hz), 112.5 (d,  $J_{\text{F-C}} = 22.1$  Hz), 110.6 (d,  $J_{\text{F-C}} = 19.5$  Hz), 50.9, 41.2 (d,  $J_{\text{F-C}} = 4.2$  Hz) ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta = -112.53$ -  $-112.57$  (m) ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{NFS}$  [ $\text{M} + \text{H}$ ] $^+$ : 322.0544; found: 322.0536.



**2-(6-fluoro-2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one (4j):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (60.8 mg, 0.189 mmol, 95 %). **Mp:** 146.2-147.1 °C; **IR**  $\nu_{\text{max}}$  (film):

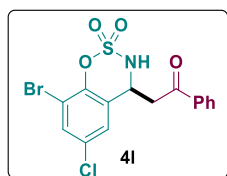
3266, 2945, 1666, 1489, 1364, 1207, 1156, 861, 758, 680  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.96$  (d,  $J = 7.9$  Hz, 2H), 7.63 (t,  $J = 7.1$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.02 (d,  $J = 5.3$  Hz, 2H), 6.88 (d,  $J = 8.1$  Hz, 1H), 5.93 (d,  $J = 8.1$  Hz, 1H), 5.38 (td,  $J = 7.6, 4.1$  Hz, 1H), 4.22 (dd,  $J = 18.2, 7.1$  Hz, 1H), 3.42 (dd,  $J = 18.2, 3.6$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 197.6, 159.5$  (d,  $J_{\text{F-C}} = 247.0$  Hz),

147.3, 136.1, 134.4, 129.1, 128.4, 123.4 (d,  $J_{F-C} = 7.1$  Hz), 120.8 (d,  $J_{F-C} = 8.3$  Hz), 116.7 (d,  $J_{F-C} = 23.7$  Hz), 112.8 (d,  $J_{F-C} = 24.9$  Hz), 53.6, 42.0 ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , **376 MHz**):  $\delta = -115.48$ -  $-115.50$  (m) ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{NFS}$   $[\text{M} + \text{H}]^+$ : 322.0544; found: 322.0550.



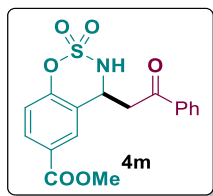
**2-(2,2-dioxido-6-(trifluoromethyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one**

**(4k)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid white oil (22.9 mg, 0.062 mmol, 31 %). **IR**  $\nu_{\text{max}}$  (film): 3263, 2924, 1678, 1427, 1330, 1116, 831, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , **300 MHz**):  $\delta = 7.96$  (d,  $J = 7.3$  Hz, 2H), 7.73-7.56 (m, 2H), 7.48 (dd,  $J = 16.3, 8.9$  Hz, 3H), 7.17 (d,  $J = 8.6$  Hz, 1H), 6.04 (d,  $J = 8.1$  Hz, 1H), 5.46 (td,  $J = 7.7, 3.7$  Hz, 1H), 4.31 (dd,  $J = 18.2, 7.3$  Hz, 1H), 3.45 (dd,  $J = 18.2, 3.7$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , **125 MHz**):  $\delta = 197.6, 153.7$  (q,  $J_{F-C} = 1.3$  Hz), 136.0, 134.6, 129.2, 128.4, 128.0 (q,  $J_{F-C} = 33.8$  Hz), 127.0 (q,  $J_{F-C} = 3.8$  Hz), 123.6 (q,  $J_{F-C} = 3.8$  Hz), 123.4 (q,  $J_{F-C} = 271.3$  Hz), 122.5, 120.1, 53.7, 41.7 ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , **470 MHz**):  $\delta = -62.20$  ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{11}\text{O}_4\text{NF}_3\text{S}$   $[\text{M}-\text{H}]^-$ : 370.0358; found: 370.0366.



**2-(8-bromo-6-chloro-2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-phenylethan-1-one**

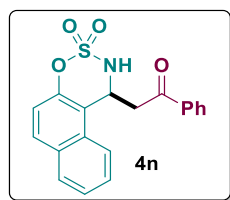
**(4l)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (54.1 mg, 0.130 mmol, 65 %). **Mp**: 147.3-148.2 °C; **IR**  $\nu_{\text{max}}$  (film): 3227, 1667, 1447, 1375, 1201, 1156, 839, 759, 683  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , **500 MHz**):  $\delta = 7.97$ -7.86 (m, 2H), 7.65 (t,  $J = 7.4$  Hz, 1H), 7.56-7.55 (m, 1H), 7.51 (t,  $J = 7.8$  Hz, 2H), 7.11-7.09 (m, 1H), 5.95 (d,  $J = 8.4$  Hz, 1H), 5.38 (td,  $J = 7.8, 3.9$  Hz, 1H), 4.24 (dd,  $J = 18.3, 6.9$  Hz, 1H), 3.45 (dd,  $J = 18.3, 3.9$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , **125 MHz**):  $\delta = 197.3, 147.1, 136.0, 134.6, 133.2, 131.0, 129.2, 128.4, 125.1, 124.9, 113.8, 53.8, 41.8$  ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{15}\text{H}_{10}\text{O}_4\text{NBrClS}$   $[\text{M} + \text{H}]^+$ : 413.9208; found: 413.9213.



### Methyl-4-(2-oxo-2-phenylethyl)-3,4-

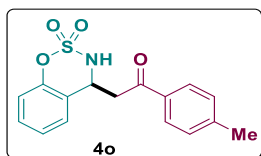
### dihydrobenzo[e][1,2,3]oxathiazine-6-carboxylate 2,2-dioxide

**(4m)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (67.2 mg, 0.186 mmol, 93 %). **Mp**: 147.1-147.9 °C; **IR**  $\nu_{\max}$  (film): 3245, 2952, 1727, 1663, 1434, 1368, 1123, 842, 762  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.96-7.93 (m, 3H), 7.88 (d,  $J$  = 0.9 Hz, 1H), 7.60 (t,  $J$  = 7.4 Hz, 1H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.06 (d,  $J$  = 8.6 Hz, 1H), 6.20 (d,  $J$  = 8.2 Hz, 1H), 5.44 (td,  $J$  = 7.9, 3.5 Hz, 1H), 4.32 (dd,  $J$  = 18.2, 7.6 Hz, 1H), 3.86 (s, 3H), 3.44 (dd,  $J$  = 18.2, 3.5 Hz, 1H) ppm;  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 75 MHz): 197.7, 165.7, 154.7, 136.1, 134.5, 131.2, 129.1, 128.4, 127.9, 127.5, 121.8, 119.5, 53.8, 52.6, 41.3 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_6\text{NS}$   $[\text{M} - \text{H}]^-$ : 360.0547; found: 360.0553.



### 2-(3,3-dioxido-1,2-dihydronaphtho[1,2-e][1,2,3]oxathiazin-1-yl)-1-phenylethan-1-one

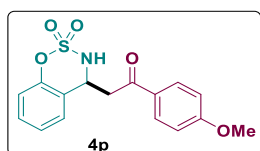
**(4n)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (43.9 mg, 0.124 mmol, 62 %). **Mp**: 173 °C; **IR**  $\nu_{\max}$  (film): 3331, 1682, 1406, 1184, 1073, 817, 750, 686  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.99-7.97 (m, 2H), 7.86 (dd,  $J$  = 17.5, 8.5 Hz, 2H), 7.67 (d,  $J$  = 8.5 Hz, 1H), 7.59-7.54 (m, 2H), 7.51 (t,  $J$  = 7.0 Hz, 1H), 7.44 (t,  $J$  = 8.0 Hz, 2H), 7.17 (d,  $J$  = 9.0 Hz, 1H), 6.14-6.10 (m, 1H), 5.73 (d,  $J$  = 6.5 Hz, 1H), 4.68 (dd,  $J$  = 18.5, 10.5 Hz, 1H), 3.29 (dd,  $J$  = 18.5, 1.5 Hz, 1H) ppm;  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 197.9, 149.3, 136.4, 134.1, 131.4, 131.0, 129.5, 129.4, 128.9, 128.6, 128.3, 126.0, 122.2, 118.6, 114.4, 52.3, 42.0 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_4\text{NS}$   $[\text{M} + \text{H}]^+$ : 354.0795; found: 354.0794.



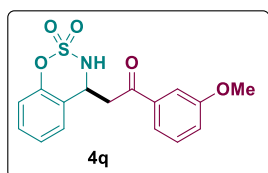
### 2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-(p-tolyl)ethan-1-one

**(4o)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (20.4 mg, 0.064 mmol, 64 %). **Mp**: 174 °C; **IR**  $\nu_{\max}$  (film): 3181, 2912, 1668, 1442, 1376, 1168, 919, 839, 759  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  =

7.87 (d,  $J = 8.2$  Hz, 2H), 7.33-7.28 (m, 3H), 7.14 (d,  $J = 4.2$  Hz, 2H), 7.06 (d,  $J = 8.2$  Hz, 1H), 5.89 (d,  $J = 8.3$  Hz, 1H), 5.39 (td,  $J = 7.6, 3.8$  Hz, 1H), 4.24 (dd,  $J = 18.1, 7.0$  Hz, 1H), 3.39 (dd,  $J = 18.1, 3.8$  Hz, 1H), 2.43 (s, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 197.5, 151.4, 145.4, 133.9, 129.8, 128.5, 126.0, 125.6, 121.9, 119.3, 54.0, 41.4, 21.9$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{NS}$   $[\text{M}+\text{H}]^+$ : 318.0795; found: 318.0795.



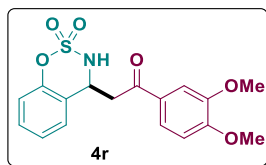
**2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-(4-methoxyphenyl)ethan-1-one (4p):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (33.7 mg, 0.101 mmol, 51 %). **Mp:** 152 °C; **IR**  $\nu_{\text{max}}$  (film): 3335, 3226, 1601, 1257, 1167, 1019, 917, 827  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.97$  -7.93 (m, 2H), 7.33-7.28 (m, 1H), 7.16-7.12 (m, 2H), 7.06 (d,  $J = 8.25$  Hz, 1H), 6.98-6.94 (m, 2H), 5.93 (d,  $J = 8.5$  Hz, 1H), 5.37 (td,  $J = 7.5, 3.7$  Hz, 1H), 4.21 (dd,  $J = 17.8, 6.8$  Hz, 1H), 3.89 (s, 3H), 3.36 (dd,  $J = 18.0, 4.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 196.3, 164.5, 151.4, 130.8, 129.7, 129.4, 126.0, 125.5, 121.9, 119.3, 114.2, 55.7, 54.1, 41.1$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{NS}$   $[\text{M}+\text{H}]^+$ : 334.0744; found: 334.0746.



**2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-(3-methoxyphenyl)ethan-1-one (4q):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (46.0 mg, 0.138 mmol, 69 %). **Mp:** 147 °C; **IR**  $\nu_{\text{max}}$  (film): 3270, 2837, 1673, 1485, 1258, 1162, 1020, 836, 769  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.56$  (d,  $J = 7.5$  Hz, 1H), 7.48 -7.47 (m, 1H), 7.40 (t,  $J = 8.0$  Hz, 1H), 7.34 -7.30 (m, 1H), 7.18 -7.13 (m, 3H), 7.06 (d,  $J = 8.0$  Hz, 1H), 5.83 (d,  $J = 8.25$  Hz, 1H), 5.40 (td,  $J = 7.7, 3.5$  Hz, 1H), 4.26 (dd,  $J = 18.0, 7.0$  Hz, 1H), 3.86 (s, 3H), 3.40 (dd,  $J = 18.0, 3.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 197.7, 160.2, 151.4, 137.6, 130.1, 129.8, 126.0, 125.6, 121.7, 121.0, 120.9, 119.3, 112.5, 55.7, 53.9, 41.9$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{NS}$   $[\text{M}+\text{H}]^+$ :

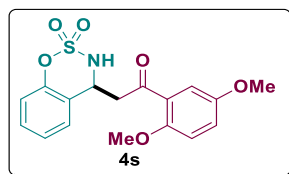


334.0744; found: 334.0734.



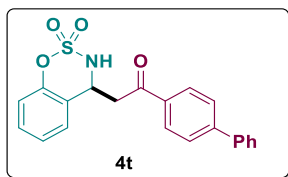
**1-(3,4-dimethoxyphenyl)-2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)ethan-1-one (4r):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (43.8 mg, 0.121

mmol, 60 %). **Mp:** 173 °C; **IR**  $\nu_{\max}$  (film): 3210, 3002, 2942, 1655, 1586, 1281, 1153, 817, 765  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  = 7.63 (dd,  $J$  = 8.5, 2.0 Hz, 1H), 7.49 (d,  $J$  = 1.5 Hz, 1H), 7.32-7.28 (m, 1H), 7.17-7.13 (m, 2H), 7.05 (d,  $J$  = 8.0 Hz, 1H), 6.91 (d,  $J$  = 8.5 Hz, 1H), 5.98 (d,  $J$  = 8.0 Hz, 1H), 5.39 (td,  $J$  = 7.7, 4.0 Hz, 1H), 4.25 (dd,  $J$  = 17.8, 7.3 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 3.33 (dd,  $J$  = 18.0, 4.0 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  = 196.4, 154.4, 151.4, 149.4, 129.7, 129.6, 126.1, 125.6, 123.5, 121.9, 119.3, 110.4, 110.3, 56.3, 56.2, 54.2, 41.1 ppm; **HRMS (ESI):**  $m/z$  calcd for C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>NS [M+H]<sup>+</sup>: 364.0849; found: 364.0850.



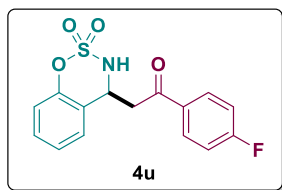
**1-(2,5-dimethoxyphenyl)-2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)ethan-1-one (4s):** The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (61.0 mg,

0.167 mmol, 84 %). **Mp:** 123 °C; **IR**  $\nu_{\max}$  (film): 3268, 2952, 1668, 1495, 1372, 1164, 920, 759  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  = 7.31-7.27 (m, 1H), 7.23 (d,  $J$  = 3.5 Hz, 1H), 7.15-7.12 (m, 2H), 7.09 (dd,  $J$  = 9.3, 3.3 Hz, 1H), 7.04 (d,  $J$  = 8.0 Hz, 1H), 6.95 (d,  $J$  = 9.0 Hz, 1H), 5.98 (d,  $J$  = 9.0 Hz, 1H), 5.30-5.26 (m, 1H), 4.23 (dd,  $J$  = 18.8, 6.7 Hz, 1H), 3.92 (s, 3H), 3.76 (s, 3H), 3.53 (dd,  $J$  = 18.5, 3.5 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  = 199.1, 153.9, 153.8, 151.6, 129.5, 126.9, 125.8, 125.4, 122.2, 122.0, 119.1, 113.9, 113.4, 56.3, 56.0, 54.3, 46.1 ppm; **HRMS (ESI):**  $m/z$  calcd for C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>NS [M+H]<sup>+</sup>: 364.0849; found: 364.0848.



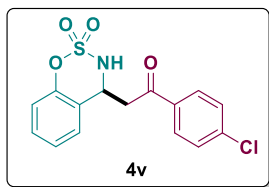
**1-([1,1'-biphenyl]-4-yl)-2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)ethan-1-one (4t):**

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (31.3 mg, 0.083 mmol, 41 %). **Mp:** 187 °C; **IR**  $\nu_{\max}$  (film): 3333.1, 1675, 1485, 1400, 1172, 1091, 919, 840, 764  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  = 8.05 (d,  $J$  = 8.5 Hz, 2H), 7.72 (d,  $J$  = 8.5 Hz, 2H), 7.63 (d,  $J$  = 7.5 Hz, 2H), 7.48 (t,  $J$  = 7.5 Hz, 2H), 7.42 (t,  $J$  = 7.5 Hz, 1H), 7.34-7.30 (m, 1H), 7.18-7.14 (m, 2H), 7.08 (d,  $J$  = 8.5 Hz, 1H), 5.87 (d,  $J$  = 8.0 Hz, 1H), 5.43 (td,  $J$  = 7.5, 3.8 Hz, 1H), 4.31 (dd,  $J$  = 18.0, 7.0 Hz, 1H), 3.45 (dd,  $J$  = 18.0, 4.0 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  = 197.4, 151.4, 147.1, 139.7, 135.0, 129.8, 129.2, 129.0, 128.7, 127.7, 127.5, 126.0, 125.6, 121.8, 119.3, 53.9, 41.8 ppm; **HRMS (ESI):**  $m/z$  calcd for **HRMS (ESI):**  $m/z$  calcd for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>NS [M+H]<sup>+</sup>: 380.0951; found: 380.0938.



**2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-(4-fluorophenyl)ethan-1-one (4u) :**

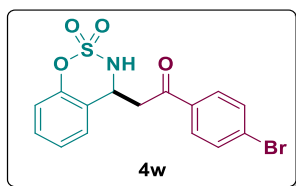
The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (41.4 mg, 0.129 mmol, 65 %). **Mp:** 133 °C; **IR**  $\nu_{\max}$  (film): 3664, 3203, 1675, 1594, 1379, 1167, 926, 834, 762  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  = 8.00 (dd,  $J$  = 9.0, 5.5 Hz, 2H), 7.34-7.30 (m, 1H), 7.18-7.13 (m, 4H), 7.05 (d,  $J$  = 8.5 Hz, 1H), 5.88 (d,  $J$  = 8.0 Hz, 1H), 5.42 (td,  $J$  = 7.9, 3.7 Hz, 1H), 4.26 (dd,  $J$  = 18.0, 8.0 Hz, 1H), 3.35 (dd,  $J$  = 18.0, 4.0 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  = 196.2, 166.4 (d,  $J_{\text{F-C}}$  = 257.3 Hz), 151.2, 132.7 (d,  $J_{\text{F-C}}$  = 2.9 Hz), 131.1 (d,  $J_{\text{F-C}}$  = 9.6 Hz), 129.7, 126.1, 125.5, 121.5, 119.19, 116.2 (d,  $J_{\text{F-C}}$  = 22.1 Hz), 53.7, 42.1 ppm;  **$^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 376 MHz):**  $\delta$  = -102.91- -102.99 (m) ppm; **HRMS (ESI):**  $m/z$  calcd for **HRMS (ESI):**  $m/z$  calcd for C<sub>15</sub>H<sub>13</sub>O<sub>4</sub>NFS [M+H]<sup>+</sup>: 322.0544; found: 322.0545.



#### 1-(4-chlorophenyl)-2-(2,2-dioxido-3,4-

#### dihydrobenzo[e][1,2,3]oxathiazin-4-yl)ethan-1-one (4v) :

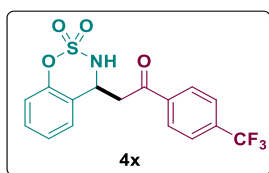
The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (43.4 mg, 0.129 mmol, 64 %). **Mp**: 169.1-171.4 °C; **IR**  $\nu_{\max}$  (film): 3190, 1674, 1590, 1378, 1188, 1092, 834, 763  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)**:  $\delta$  = 7.91 (d,  $J$  = 8.5 Hz, 2H), 7.47 (d,  $J$  = 8.5 Hz, 2H), 7.34-7.30 (m, 1H), 7.18-7.13 (m, 2H), 7.06 (d,  $J$  = 8.3 Hz, 1H), 5.76 (d,  $J$  = 7.9 Hz, 1H), 5.42 (td,  $J$  = 7.8, 3.7 Hz, 1H), 4.25 (dd,  $J$  = 18.1, 7.7 Hz, 1H), 3.35 (dd,  $J$  = 18.0, 3.7 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)**:  $\delta$  = 196.64, 151.35, 140.91, 134.67, 129.86, 129.81, 129.42, 126.16, 125.68, 121.60, 119.35, 53.81, 42.27 ppm; **HRMS (ESI)**:  $m/z$  calcd for **HRMS (ESI)**:  $m/z$  calcd for C<sub>15</sub>H<sub>13</sub>O<sub>4</sub>NCIS [M+H]<sup>+</sup>: 338.0248; found: 338.0249.



#### 1-(4-bromophenyl)-2-(2,2-dioxido-3,4-

#### dihydrobenzo[e][1,2,3]oxathiazin-4-yl)ethan-1-one (4w):

The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (21.2 mg, 0.056 mmol, 56 %). **Mp**: 158 °C; **IR**  $\nu_{\max}$  (film): 3193, 2913, 1676, 1582, 1439, 1376, 1155, 916, 841, 760  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 300 MHz)**:  $\delta$  = 7.86-7.77 (m, 2H), 7.66-7.61 (m, 2H), 7.36-7.30 (m, 1H), 7.20-7.10 (m, 2H), 7.06 (d,  $J$  = 8.1 Hz, 1H), 5.76 (d,  $J$  = 8.1 Hz, 1H), 5.42 (td,  $J$  = 7.8, 3.6 Hz, 1H), 4.26 (dd,  $J$  = 18.0, 7.8 Hz, 1H), 3.35 (dd,  $J$  = 18.0, 3.6 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 75 MHz)**:  $\delta$  = 196.8, 151.3, 135.0, 132.4, 129.9, 129.7, 126.2, 125.7, 121.5, 119.4, 5.75, 42.2 ppm ; **HRMS (ESI)**:  $m/z$  calcd for **HRMS (ESI)**:  $m/z$  calcd for C<sub>15</sub>H<sub>13</sub>O<sub>4</sub>NBrS [M+H]<sup>+</sup>: 382.0246; found: 382.0249.

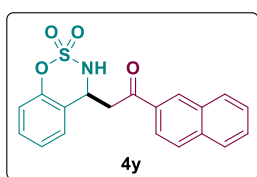


#### 2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-

#### 1-(4-(trifluoromethyl)phenyl)ethan-1-one (4x):

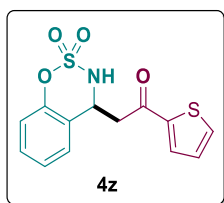
The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid (22.2 mg, 0.060

mmol, 30 %). **Mp**: 159.1-159.5 °C; **IR**  $\nu_{\max}$  (film): 3243, 1681, 1327, 1169, 1066, 865, 749  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.09 (d,  $J$  = 8.2 Hz, 2H), 7.77 (d,  $J$  = 8.3 Hz, 2H), 7.42-7.28 (m, 1H), 7.22-7.13 (m, 2H), 7.08 (d,  $J$  = 8.6 Hz, 1H), 5.63 (d,  $J$  = 7.9 Hz, 1H), 5.46 (td,  $J$  = 7.9, 3.7 Hz, 1H), 4.34 (dd,  $J$  = 18.2, 7.8 Hz, 1H), 3.40 (dd,  $J$  = 18.2, 3.7 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 175 MHz):  $\delta$  = 196.8, 151.3, 138.9, 135.5 (q,  $J_{\text{F-C}}$  = 31.5 Hz), 130.0, 128.8, 126.2, 126.2 (q,  $J_{\text{F-C}}$  = 5.3 Hz), 125.8, 123.5 (q,  $J_{\text{F-C}}$  = 271.3 Hz), 121.4, 119.4, 53.7, 42.8 ppm;  **$^{19}\text{F}$  NMR** ( $\text{CDCl}_3$ , 470 MHz):  $\delta$  = -63.15 ppm; **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{11}\text{O}_4\text{NF}_3\text{S}$   $[\text{M-H}]^-$ : 370.0358; found: 370.0366.



**2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-(naphthalen-2-yl)ethan-1-one (4y)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (50.3 mg, 0.142

mmol, 71 %). **Mp**: 167 °C; **IR**  $\nu_{\max}$  (film): 3295, 2923, 1669, 1392, 1166, 915, 837, 774  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 8.51 (s, 1H), 8.02-7.96 (m, 2H), 7.90 (dd,  $J$  = 12.5, 8.5 Hz, 2H), 7.66-7.62 (m, 1H), 7.60-7.56 (m, 1H), 7.34-7.30 (m, 1H), 7.20 (d,  $J$  = 6.5 Hz, 1H), 7.17-7.13 (m, 1H), 7.08 (dd,  $J$  = 8.3, 0.7 Hz, 1H), 5.91 (d,  $J$  = 8.0 Hz, 1H), 5.47 (td,  $J$  = 7.6, 3.8 Hz, 1H), 4.44 (dd,  $J$  = 18.0, 7.5 Hz, 1H), 3.54 (dd,  $J$  = 18.0, 4.0 Hz, 1H) ppm;  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 197.8, 151.4, 136.2, 133.7, 132.6, 130.6, 129.9, 129.8, 129.3, 129.0, 128.0, 127.3, 126.1, 125.6, 123.6, 121.8, 119.3, 54.0, 41.9 ppm; **HRMS (ESI)**:  $m/z$  calcd for **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_4\text{NS}$   $[\text{M+H}]^+$ : 354.0795; found: 354.0795.

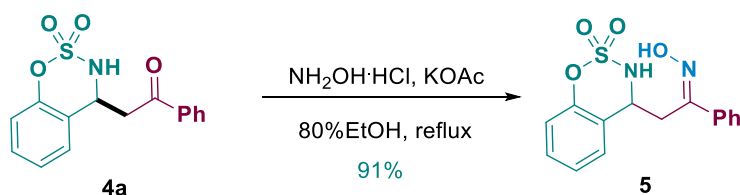


**2-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)-1-(thiophen-2-yl)ethan-1-one (4z)**: The product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid (51.2 mg, 0.166 mmol, 83 %). **Mp**: 179 °C; **IR**  $\nu_{\max}$

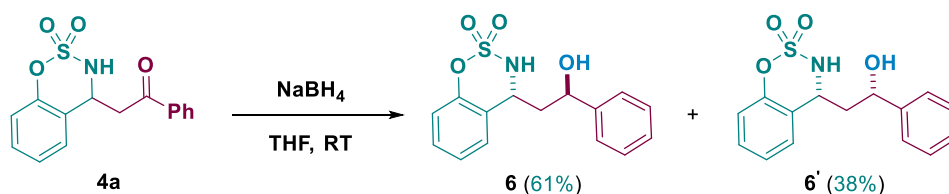
(film): 3258, 3102, 1635, 1481, 1415, 1178, 1072, 851, 762, 665  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.81 (dd,  $J$  = 4.0, 1.0 Hz, 1H), 7.73 (dd,  $J$  = 5.0, 1.0 Hz, 1H), 7.34-7.30 (m, 1H), 7.19-7.16 (m, 3H), 7.06 (d,  $J$  = 8.5 Hz, 1H), 5.80 (d,  $J$  = 8.0 Hz,

1H), 5.39 (td,  $J = 7.8, 3.7$  Hz, 1H), 4.19 (dd,  $J = 17.5, 7.5$  Hz, 1H), 3.35 (dd,  $J = 17.5, 4.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 190.4, 151.4, 143.5, 135.5, 133.4, 129.9, 128.7, 126.1, 125.7, 121.4, 119.4, 54.1, 42.4$  ppm; HRMS (ESI):  $m/z$  calcd for HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{NS}_2$   $[\text{M}+\text{H}]^+$ : 310.0202; found: 310.0202.

#### 4. Further transformations of products

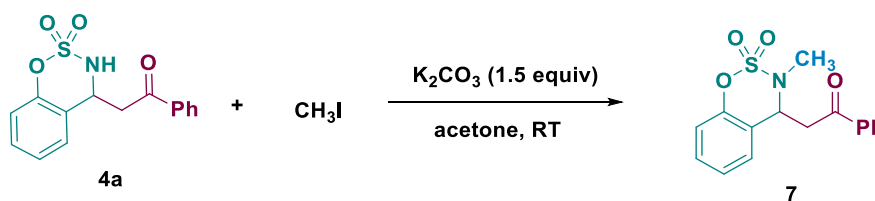


A mixture of **4a** (30.3 mg, 0.1 mmol), hydroxylamine hydrochloride (24.3 mg, 0.35 mmol) and KOAc (24.5 mg, 0.25 mmol) in 80% aqueous EtOH (2 mL) was heated gently to reflux for 2.5 hours. After the reaction mixture was cooled to room temperature, the solvent was concentrated in vacuo and the residue was further purified by flash column chromatography over silica gel (hexane:ethyl acetate = 4:1) to afford the desired **5**<sup>[5]</sup> as a white solid (28.8 mg, 0.905 mmol, 91%). **Mp**: 161 °C; **IR**  $\nu_{\text{max}}$  (film): 3332, 3065, 1581, 1422, 1169, 930, 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 7.67$  -7.65 (m, 2H), 7.44-7.39 (m, 3H), 7.34 -7.30 (m, 2H), 7.21 -7.17 (m, 1H), 7.04-7.01 (m, 1H), 5.40 (d,  $J = 8.0$  Hz, 1H), 5.23-5.17 (m, 1H), 3.70 (dd,  $J = 14.0, 11.0$  Hz, 1H), 3.44 (dd,  $J = 13.8, 4.3$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta = 156.8, 151.0, 134.5, 130.3, 129.9, 129.1, 126.8, 126.7, 125.6, 121.8, 119.3, 55.4, 32.0$  ppm; HRMS (ESI):  $m/z$  calcd for HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 319.0747; found: 319.0747.



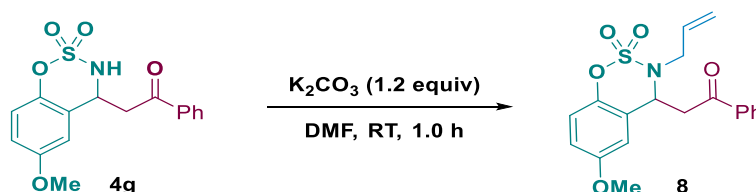
To a solution of **4a** (30.3 mg, 0.1 mmol) in THF (1 mL),  $\text{NaBH}_4$  (7.6 mg, 0.2 mmol) was added at room temperature. After stirred at RT for 20 min, the mixture was

quenched with water. The aqueous layer was extracted with EtOAc (3 x 30 mL), and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was concentrated in vacuo and the residue was further purified by flash column chromatography over silica gel (dichloromethane) to afford the desired **6** as a white solid (18.7 mg, 0.061 mmol, 61%) and **6'** as a yellow solid (12.0 mg, 0.039 mmol, 38%). For **6**,<sup>[6]</sup> **Mp**: 146.7-147.2 °C; **IR**  $\nu_{\max}$  (film): 3263, 3035, 1485, 1367, 1165, 847, 755, 698 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, **300 MHz**):  $\delta$  = 7.41-7.29 (m, 6H), 7.26-7.22 (m, 2H), 7.09-7.05 (m, 1H), 6.41 (d, *J* = 8.7 Hz, 1H), 5.17-5.10 (m, 1H), 4.90 (dd, *J* = 9.9, 3.0 Hz, 1H), 2.54-2.36 (m, 2H), 2.21 (s, 1H) ppm; **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, **75 MHz**):  $\delta$  = 152.1, 143.5, 129.6, 129.0, 128.4, 126.3, 125.5, 121.4, 119.5, 71.5, 56.0, 40.6 ppm; **HRMS (ESI)**: *m/z* calcd for **HRMS (ESI)**: *m/z* calcd for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>NS [M+H]<sup>+</sup>: 306.0232; found: 306.0239; For **6'**, **Mp**: 126.9-127.5 °C; **IR**  $\nu_{\max}$  (film): 3550, 3272, 3066, 1486, 1453, 1369, 1166 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, **300 MHz**):  $\delta$  = 7.38 (d, *J* = 4.2 Hz, 4H), 7.36-7.27 (m, 2H), 7.17-7.07 (m, 2H), 7.02-6.99 (m, 1H), 5.67 (d, *J* = 6.2 Hz, 1H), 5.04 (dd, *J* = 7.5, 5.6 Hz, 1H), 4.83-4.76 (m, 1H), 2.62-2.23 (m, 3H) ppm; **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, **75 MHz**):  $\delta$  = 151.0, 143.1, 129.6, 129.1, 128.7, 126.5, 126.0, 125.5, 122.6, 119.2, 77.6, 77.2, 76.7, 73.1, 56.2, 43.0 ppm; **HRMS (ESI)**: *m/z* calcd for **HRMS (ESI)**: *m/z* calcd for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>NS [M+H]<sup>+</sup>: 306.0242; found: 306.0238



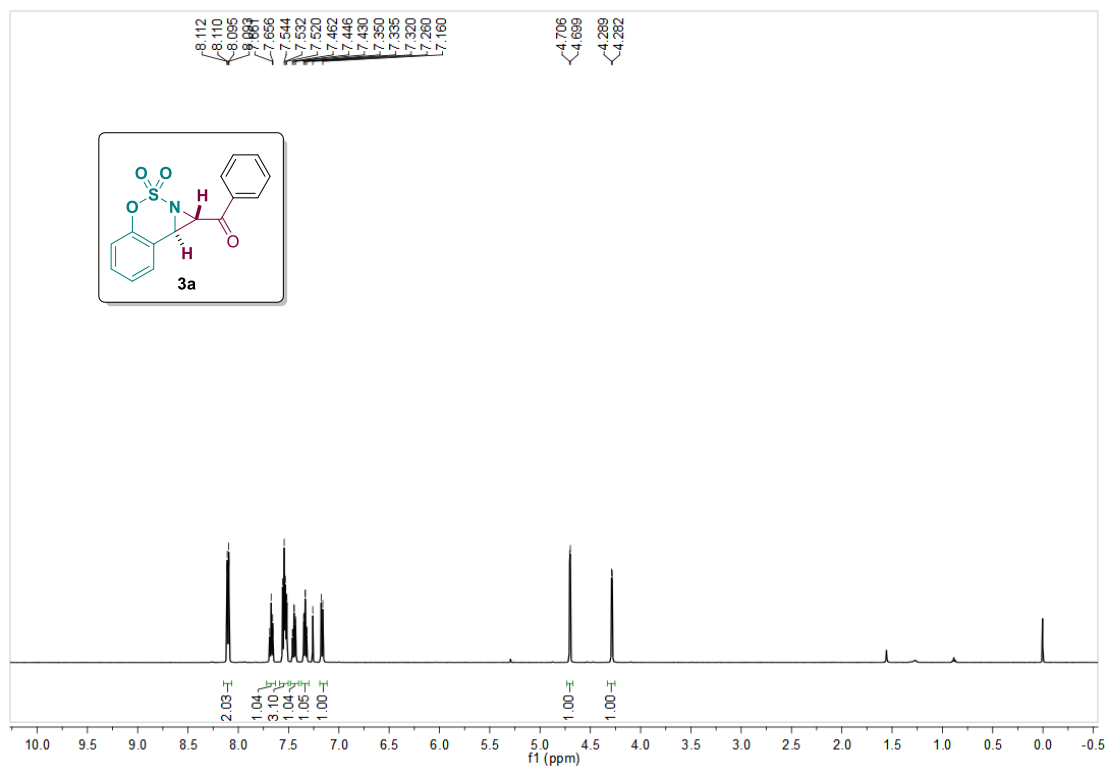
To a solution of **4a** (30.3 mg, 0.1 mmol) in THF (1 mL), iodomethane (17.0 mg, 0.12 mmol) and K<sub>2</sub>CO<sub>3</sub> (20.7 mg, 0.15 mmol) were added at room temperature. The mixture was stirred at RT for 3h. After completion of the reaction (monitored by TLC), the crude reaction mixture was filtered through celite and washed with EtOAc (~ 10 mL). The solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 5/1) to afford the desired product **7** (31.5 mg, 0.993mmol, 99.3%) as a white solid. **Mp**: 88.1-88.7 °C; **IR**  $\nu_{\max}$  (film): 3061,

1678, 1451, 1388, 1159, 839, 749  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.02-7.98 (m, 2H), 7.63-7.57 (m, 1H), 7.51-7.45 (m, 2H), 7.37-7.28 (m, 1H), 7.20 (d,  $J$  = 3.9 Hz, 2H), 7.04 (d,  $J$  = 8.1 Hz, 1H), 5.37 (dd,  $J$  = 9.0, 4.2 Hz, 1H), 4.48 (dd,  $J$  = 18.3, 9.0 Hz, 1H), 3.29 (dd,  $J$  = 18.2, 4.1 Hz, 1H), 3.10 (s, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 197.3, 150.6, 136.5, 133.9, 129.5, 128.9, 128.5, 127.8, 125.8, 120.6, 118.9, 61.6, 45.5, 40.7 ppm; **HRMS (ESI)**:  $m/z$  calcd for **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{NS}$   $[\text{M}+\text{H}]^+$ : 317.0782; found: 317.0780.

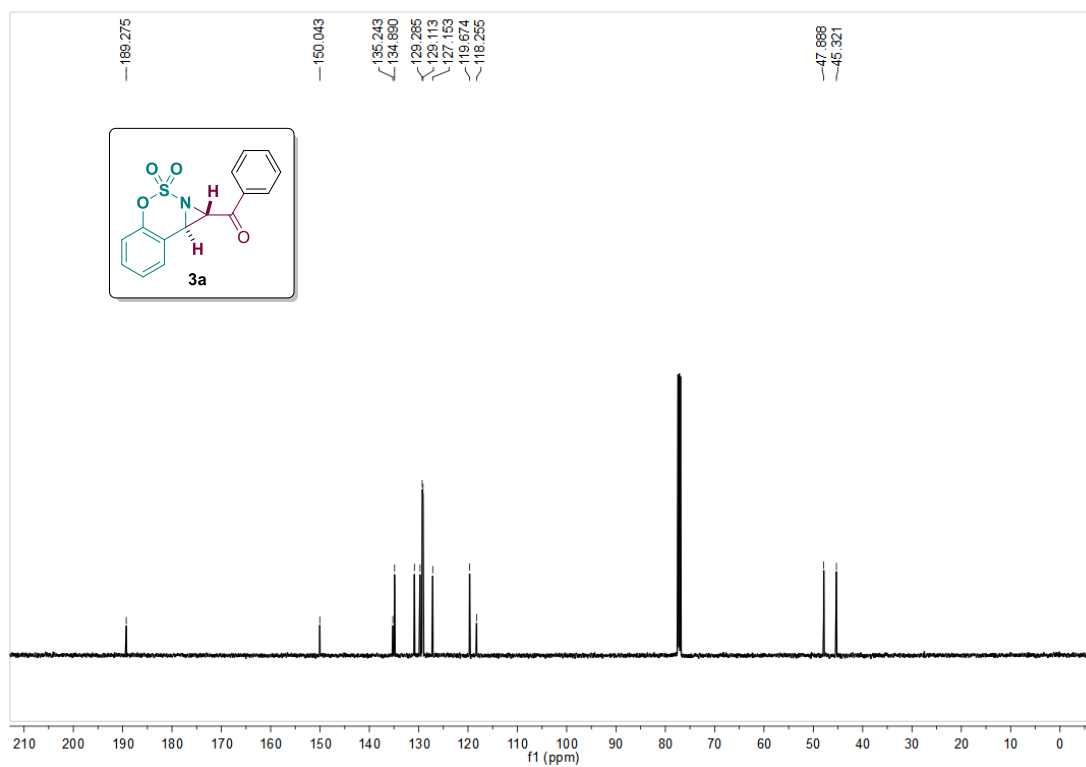


To a mixture of **4g** (133.2 mg, 0.4 mmol) and  $\text{K}_2\text{CO}_3$  (66.3 mg, 0.48 mmol) in DMF (2 mL) was added allyl bromide (96.8 mg, 0.8 mmol). The mixture was stirred at room temperature for 1 hour and then diluted with water, extracted with dichloromethane (3 x 40 mL). The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$ . The solvent was concentrated in vacuo and the residue was further purified by flash column chromatography over silica gel (dichloromethane) to afford the desired product **8** (143.5 mg, 0.385 mmol, 96%) as colorless transparent oil. **IR**  $\nu_{\text{max}}$  (film): 3071, 2941, 1682, 1492, 1388, 1167, 1033, 844, 752  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.99 (dd,  $J$  = 5.3, 3.3 Hz, 2H), 7.62-7.55 (m, 1H), 7.50-7.44 (m, 2H), 6.94 (d,  $J$  = 9.0 Hz, 1H), 6.83 (dd,  $J$  = 9.0, 2.9 Hz, 1H), 6.69 (d,  $J$  = 2.8 Hz, 1H), 5.86 (ddt,  $J$  = 16.9, 10.0, 6.8 Hz, 1H), 5.43 (dd,  $J$  = 8.4, 4.4 Hz, 1H), 5.32-5.21 (m, 2H), 4.44 (dd,  $J$  = 18.1, 8.5 Hz, 1H), 4.09 (dd,  $J$  = 14.9, 6.9 Hz, 1H), 3.91 (dd,  $J$  = 14.9, 6.7 Hz, 1H), 3.75 (s, 3H), 3.32 (dd,  $J$  = 18.1, 4.4 Hz, 1H). ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 197.4, 156.9, 144.4, 136.5, 133.8, 131.2, 128.9, 128.4, 122.5, 121.2, 119.7, 115.1, 111.8, 58.0, 56.0, 55.8, 45.9 ppm; **HRMS (ESI)**:  $m/z$  calcd for **HRMS (ESI)**:  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_5\text{NS}$   $[\text{M}+\text{H}]^+$ : 374.0747; found: 374.0739.

## 5. NMR Spectra

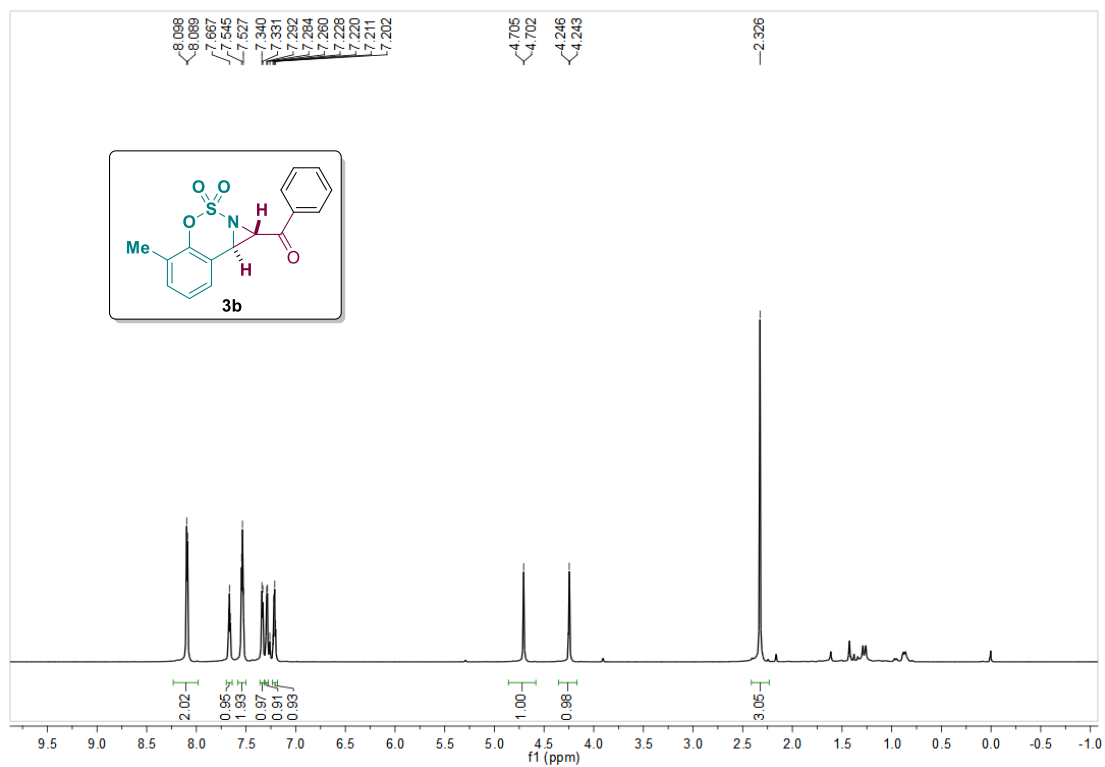


<sup>1</sup>H NMR Spectrum for **3a** (CDCl<sub>3</sub>, 500 MHz)

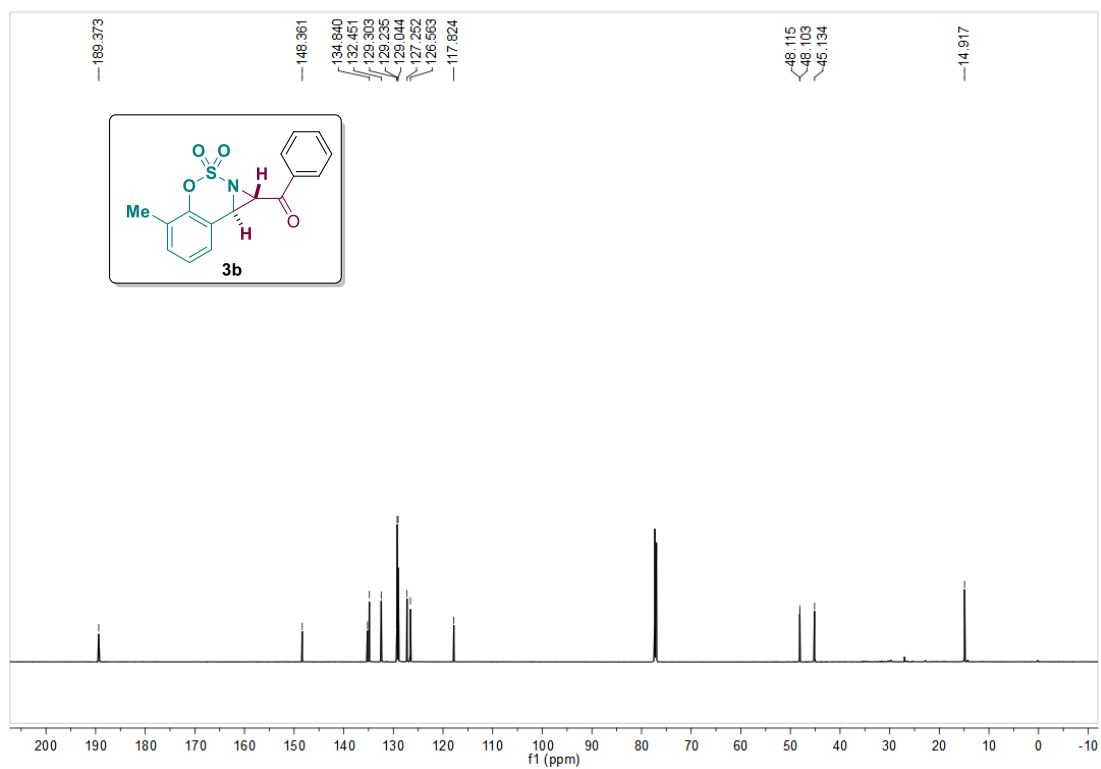


<sup>13</sup>C NMR Spectrum for **3a** (CDCl<sub>3</sub>, 125 MHz)

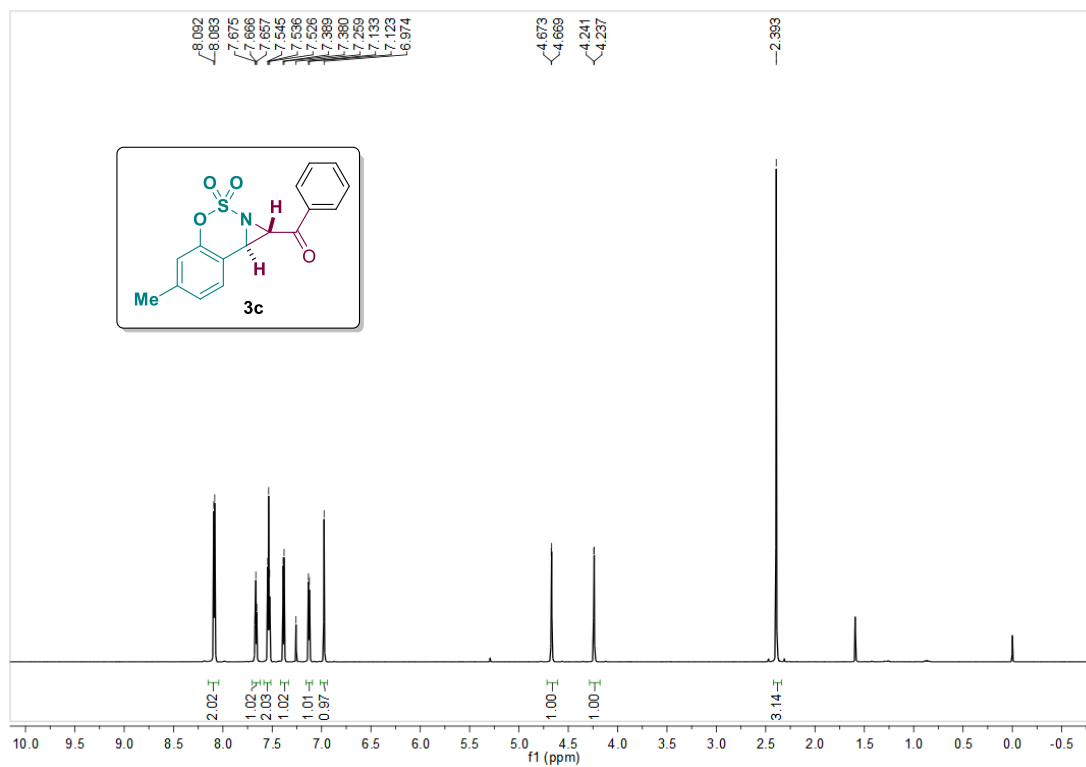




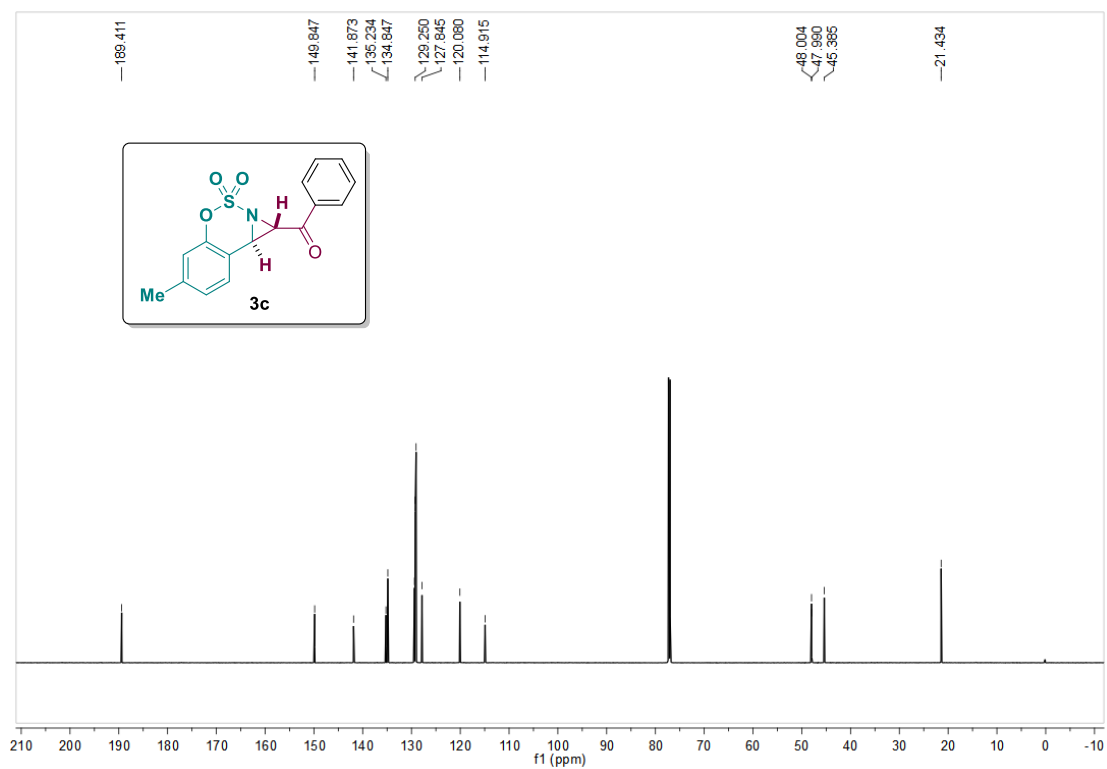
**<sup>1</sup>H NMR Spectrum for **3b** (CDCl<sub>3</sub>, 800 MHz)**



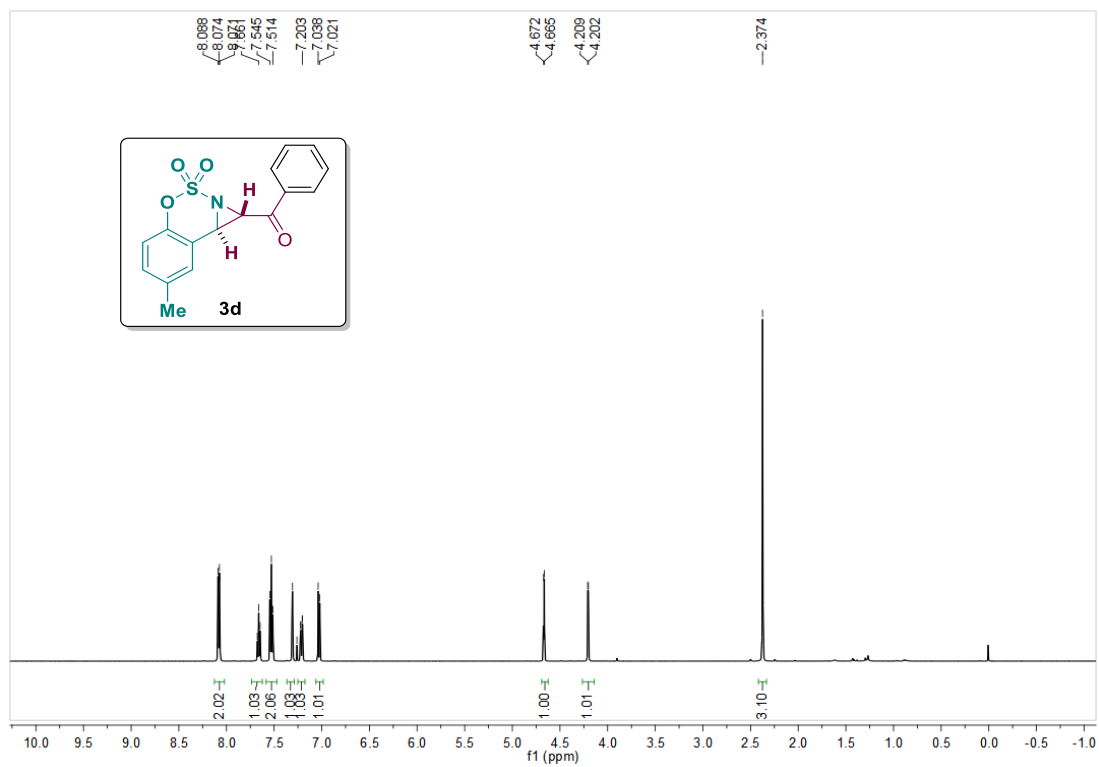
**<sup>13</sup>C NMR Spectrum for **3b** (CDCl<sub>3</sub>, 200 MHz)**



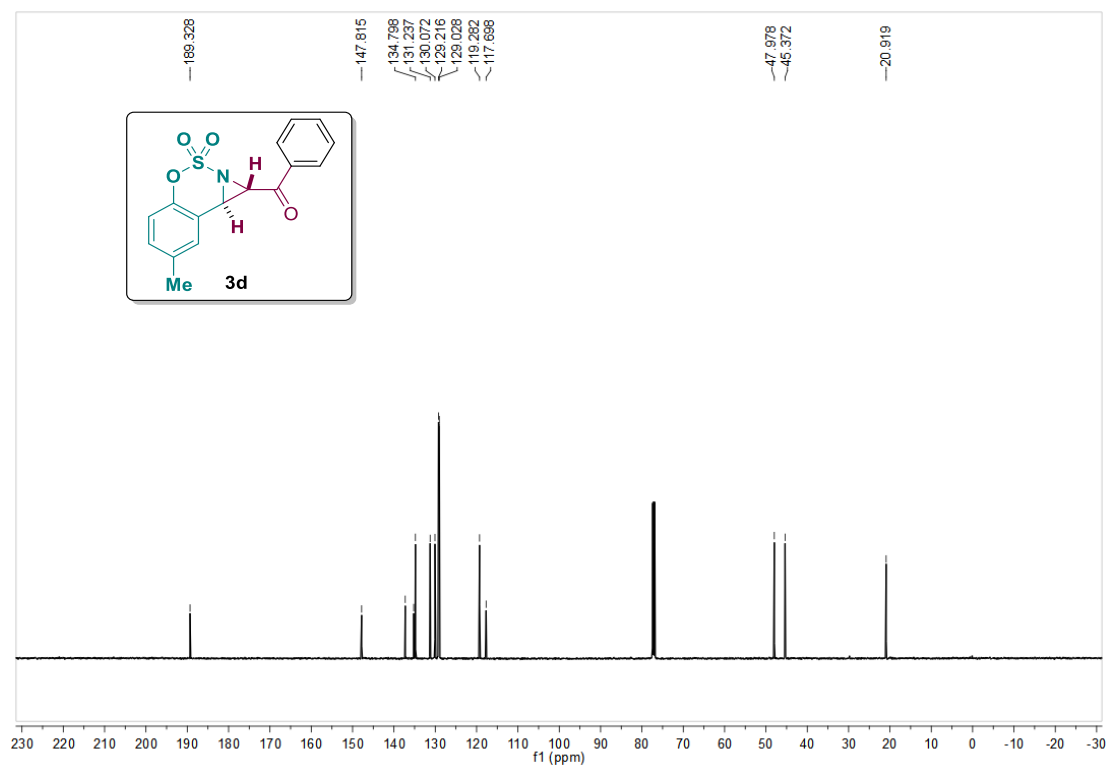
<sup>1</sup>H NMR Spectrum for 3c (CDCl<sub>3</sub>, 800 MHz)



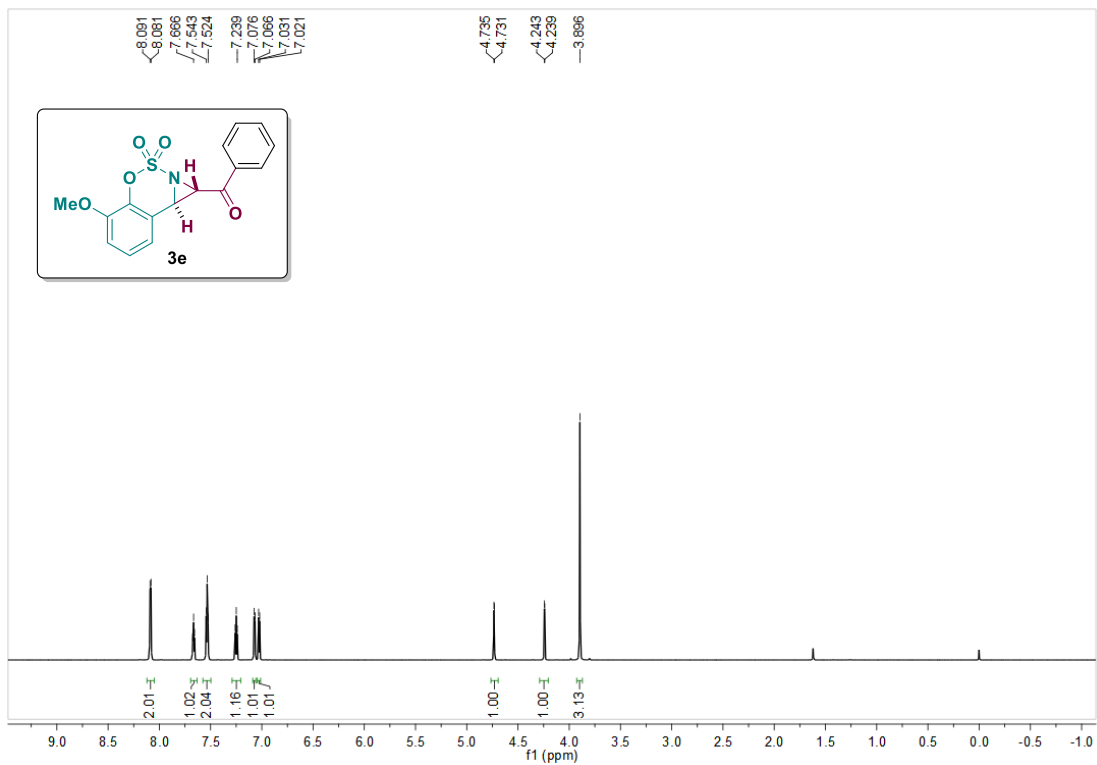
<sup>13</sup>C NMR Spectrum for 3c (CDCl<sub>3</sub>, 200 MHz)



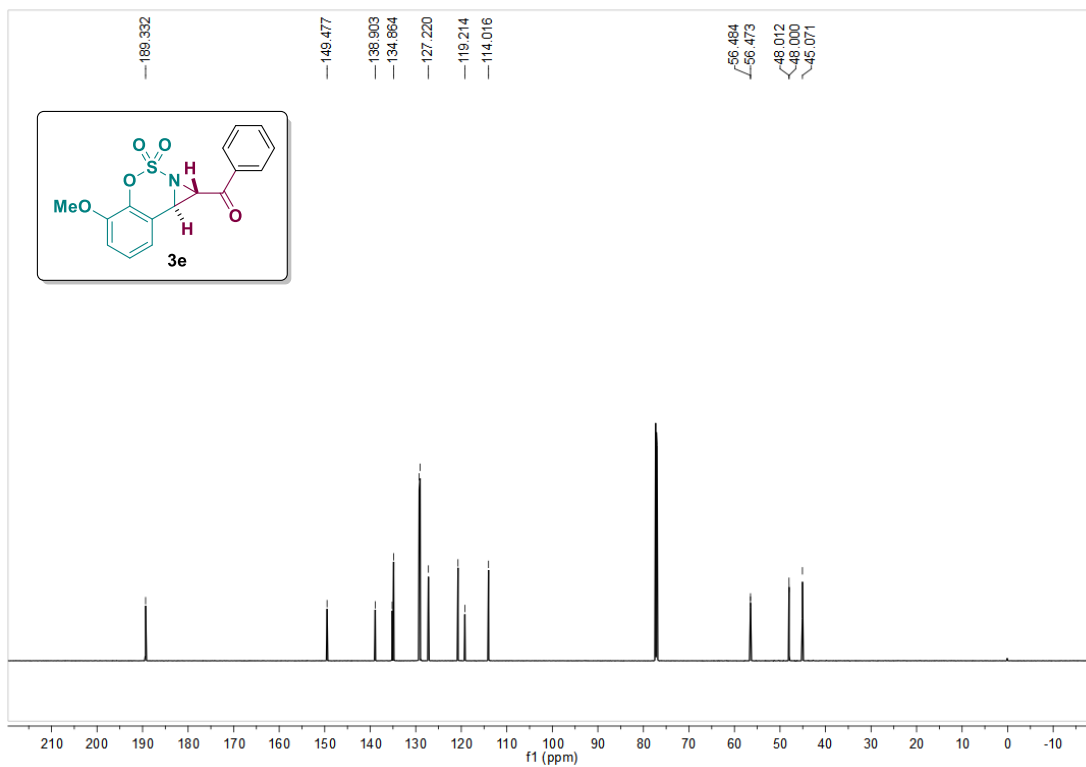
<sup>1</sup>H NMR Spectrum for 3d (CDCl<sub>3</sub>, 500 MHz)



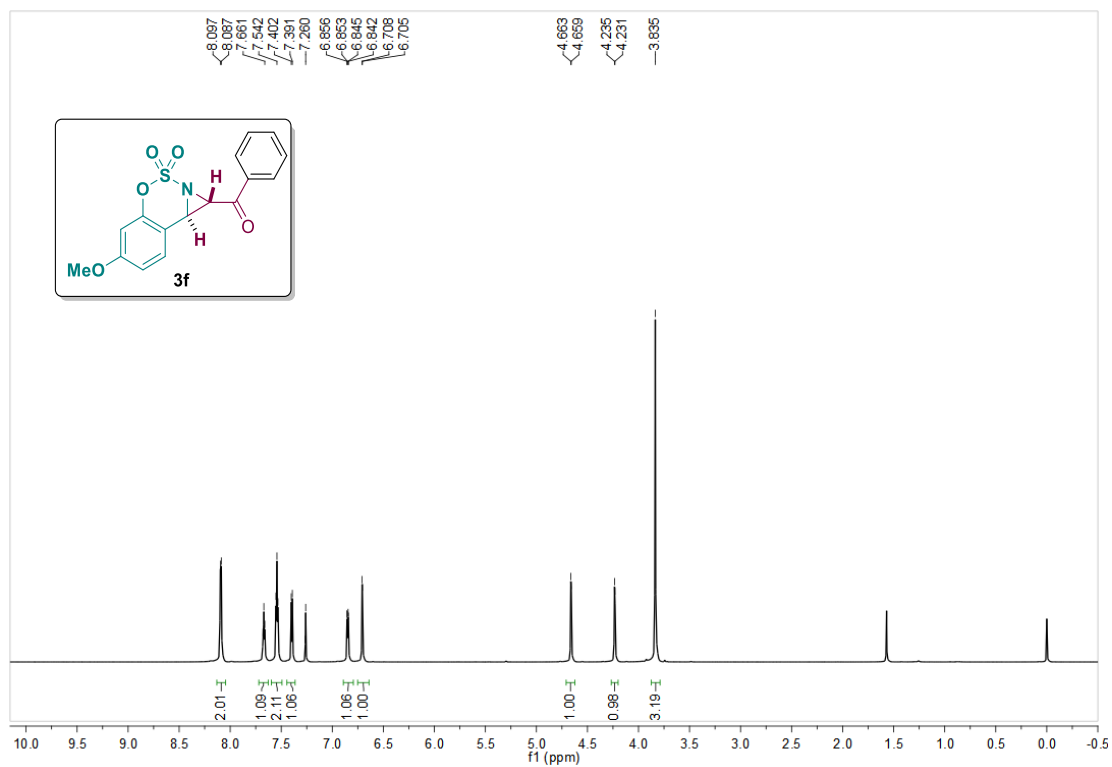
<sup>13</sup>C NMR Spectrum for 3d (CDCl<sub>3</sub>, 125 MHz)



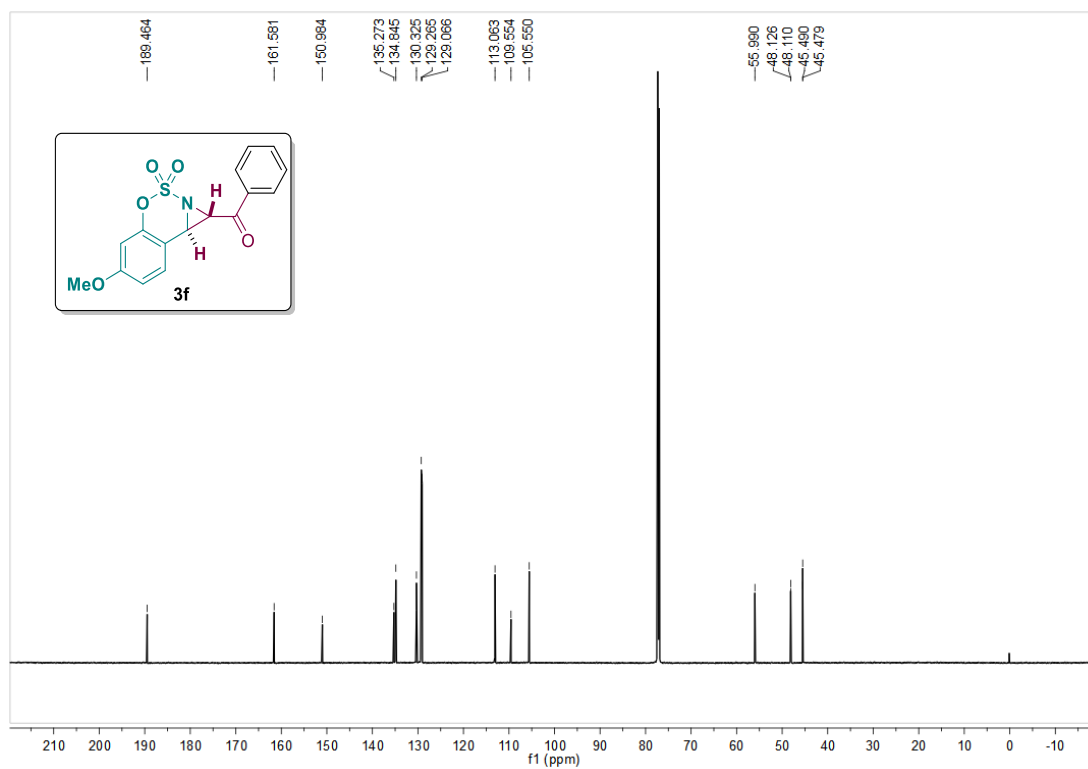
<sup>1</sup>H NMR Spectrum for **3e** (CDCl<sub>3</sub>, 800 MHz)



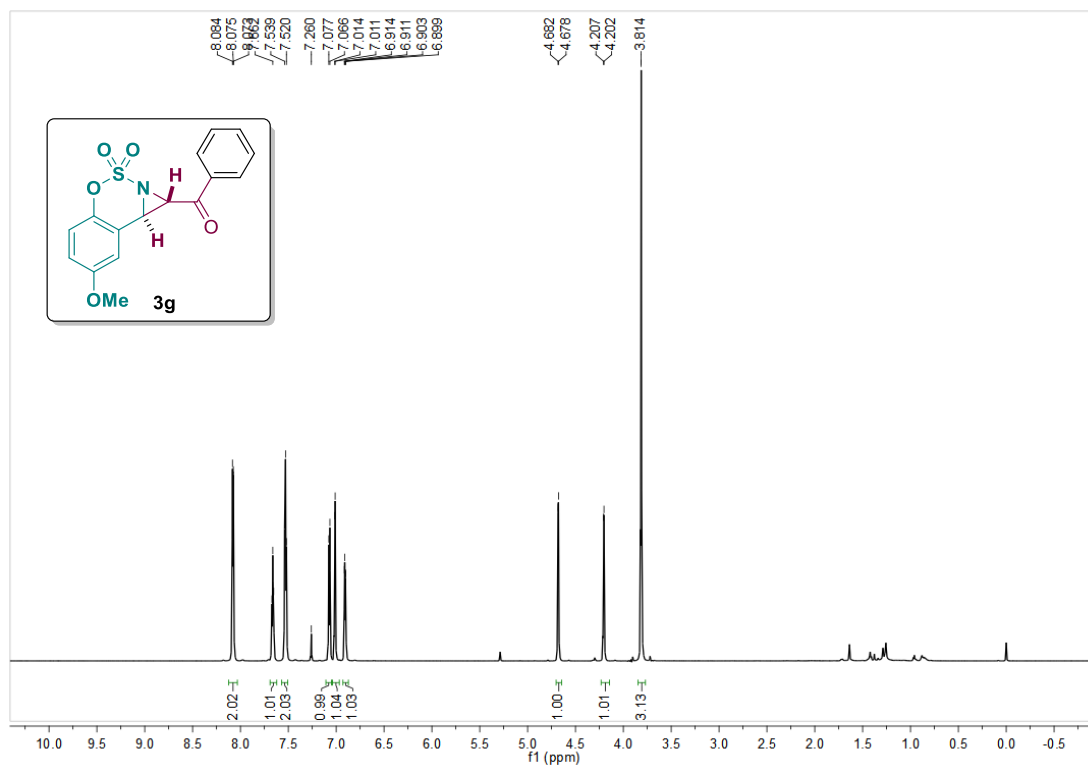
<sup>13</sup>C NMR Spectrum for **3e** (CDCl<sub>3</sub>, 200 MHz)



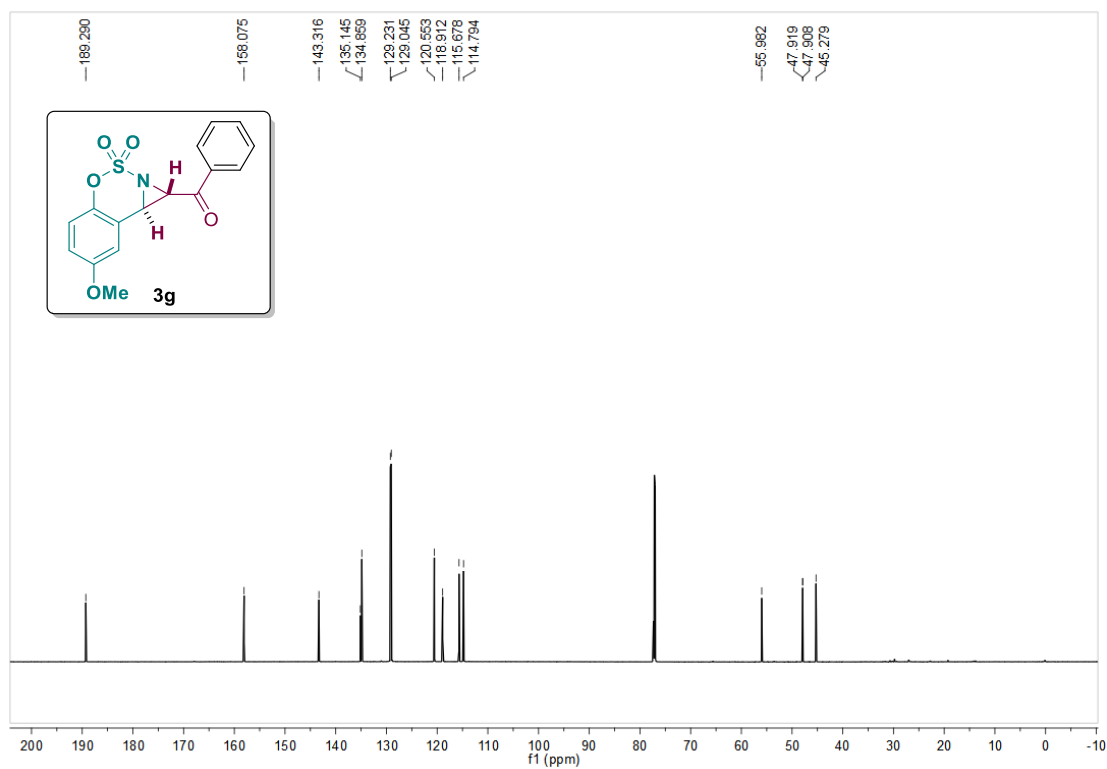
**<sup>1</sup>H NMR Spectrum for 3f (CDCl<sub>3</sub>, 800 MHz)**



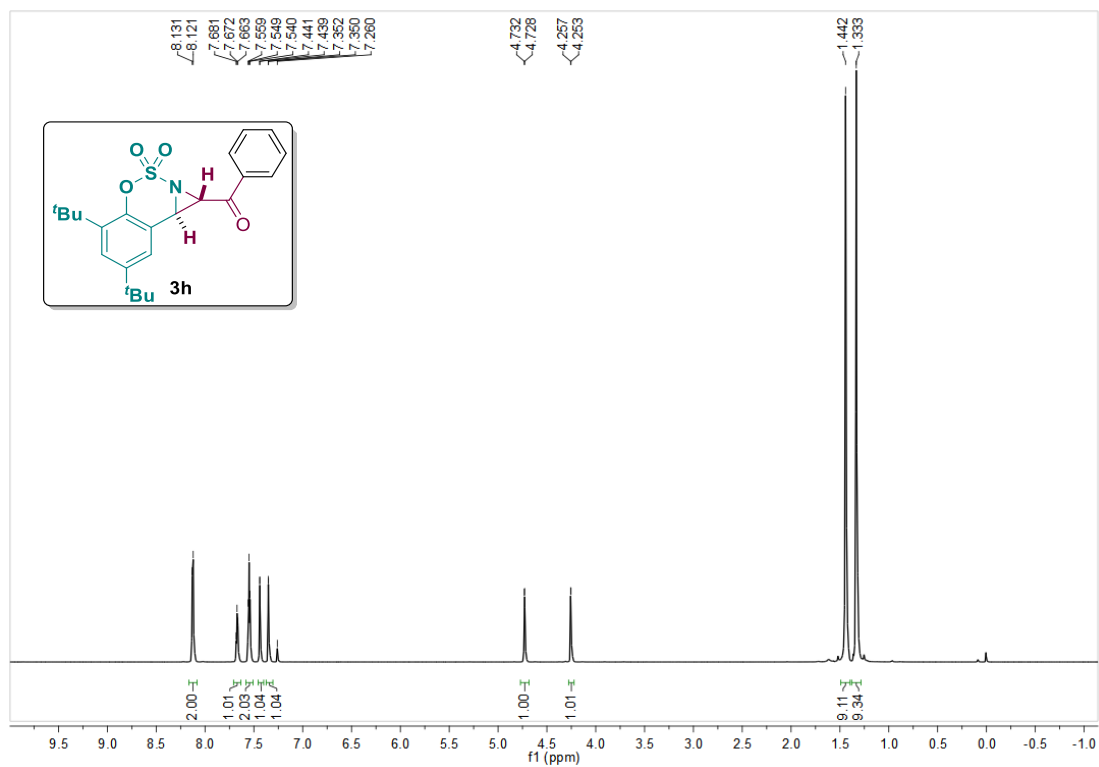
**<sup>13</sup>C NMR Spectrum for 3f (CDCl<sub>3</sub>, 200 MHz)**



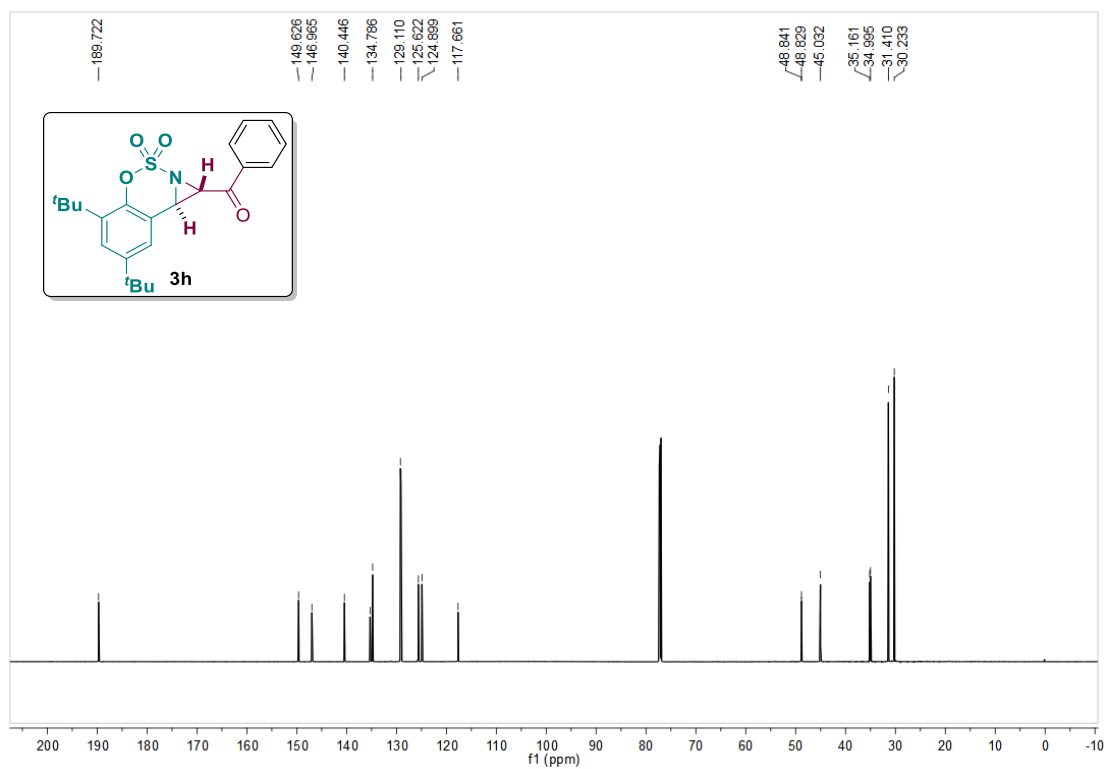
**<sup>1</sup>H NMR Spectrum for **3g** (CDCl<sub>3</sub>, 800 MHz)**



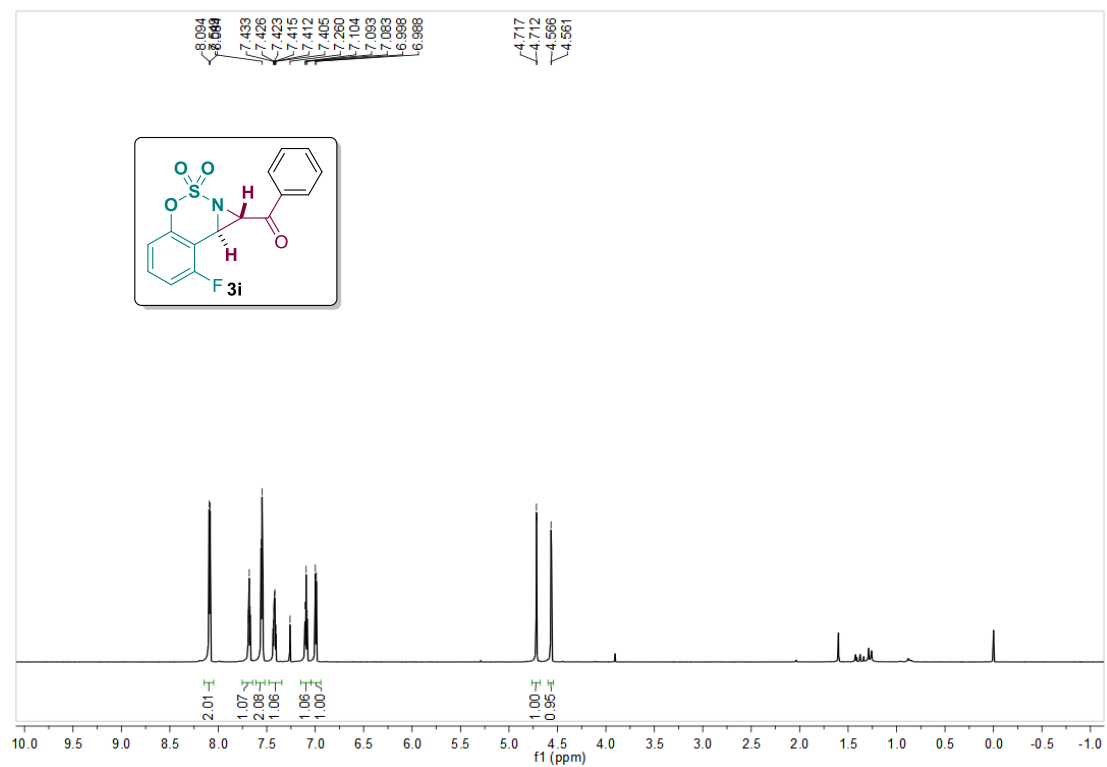
**<sup>13</sup>C NMR Spectrum for **3g** (CDCl<sub>3</sub>, 200 MHz)**



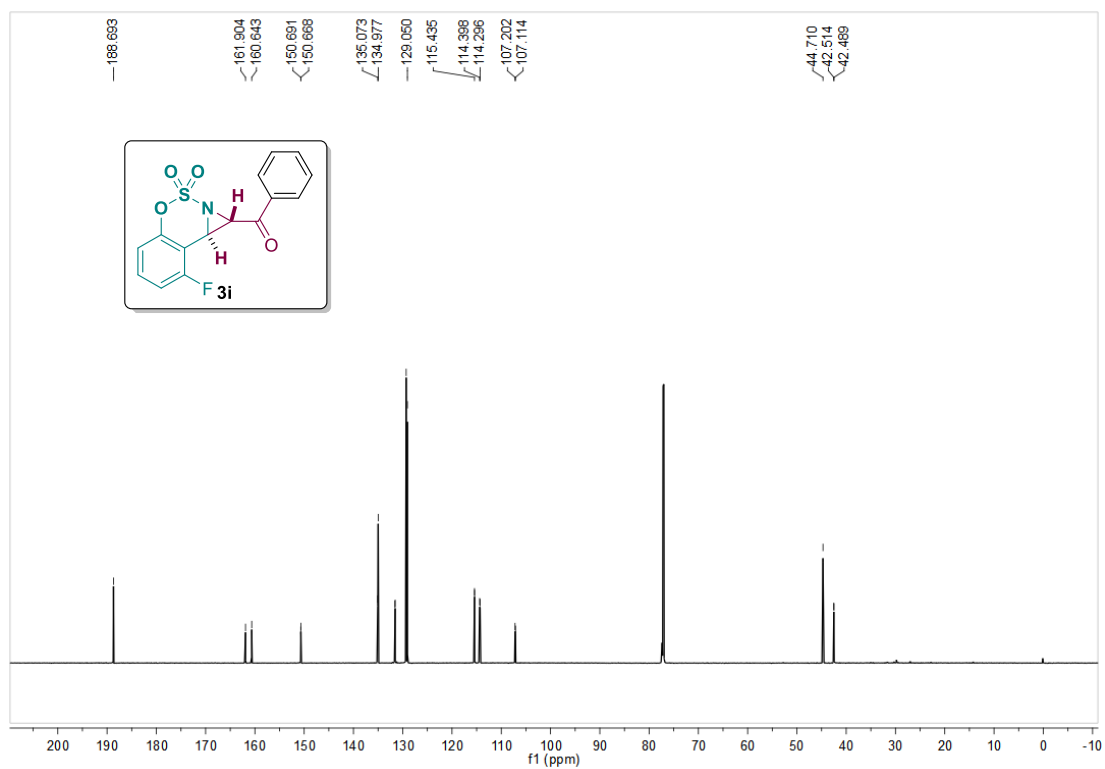
**<sup>1</sup>H NMR Spectrum for **3h** (CDCl<sub>3</sub>, 800 MHz)**



**<sup>13</sup>C NMR Spectrum for **3h** (CDCl<sub>3</sub>, 200 MHz)**

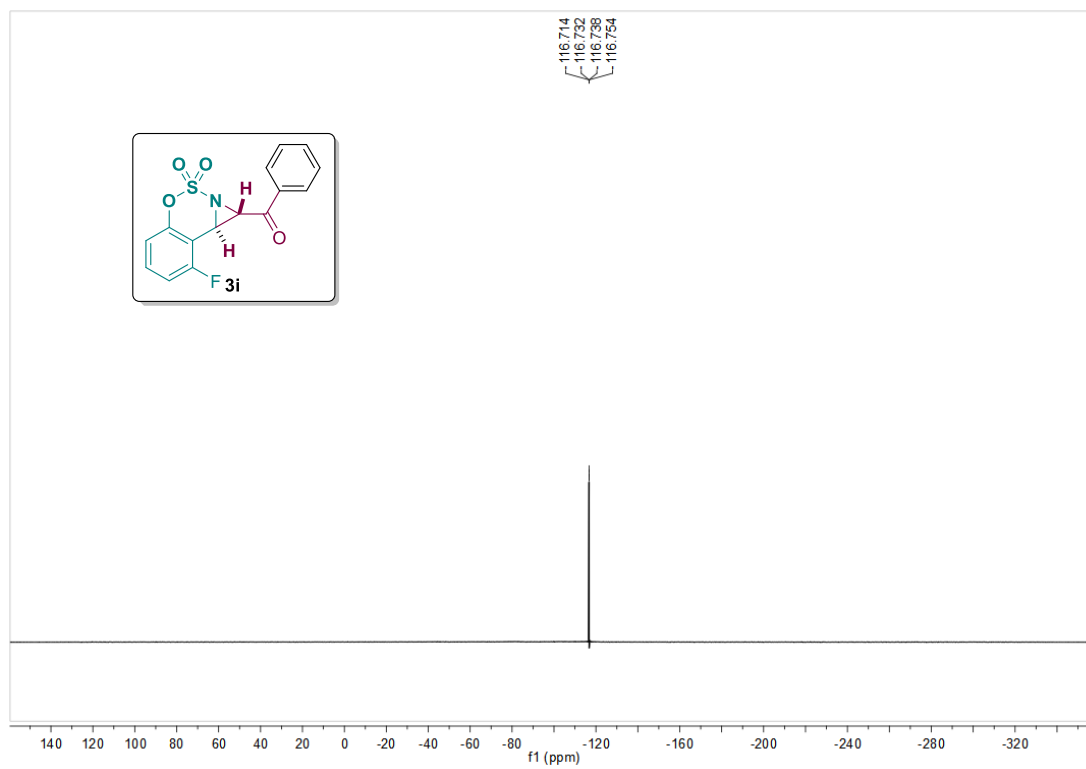


<sup>1</sup>H NMR Spectrum for **3i** (CDCl<sub>3</sub>, 800 MHz)

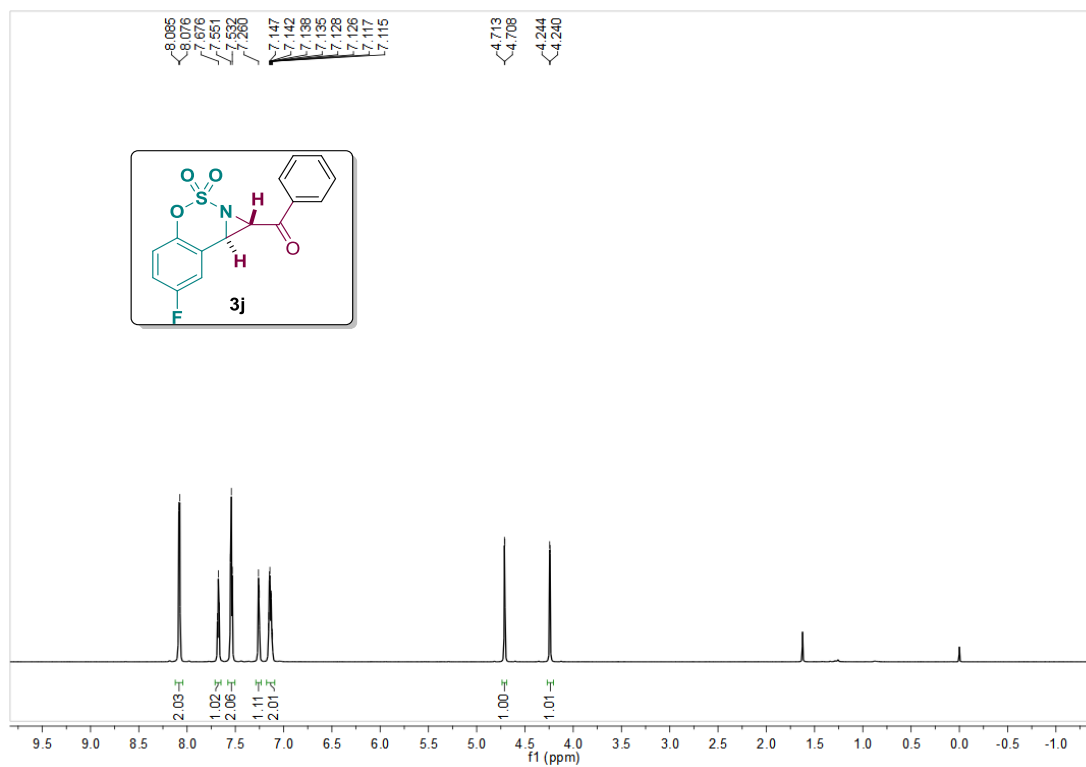


<sup>13</sup>C NMR Spectrum for **3i** (CDCl<sub>3</sub>, 200 MHz)

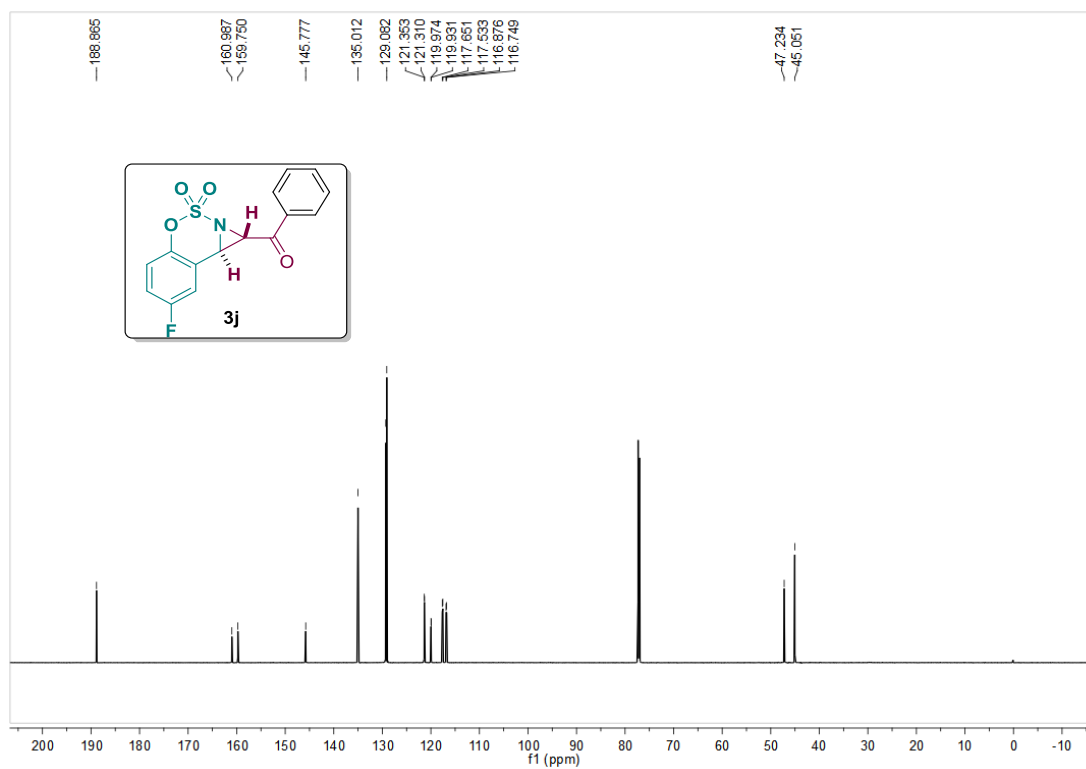




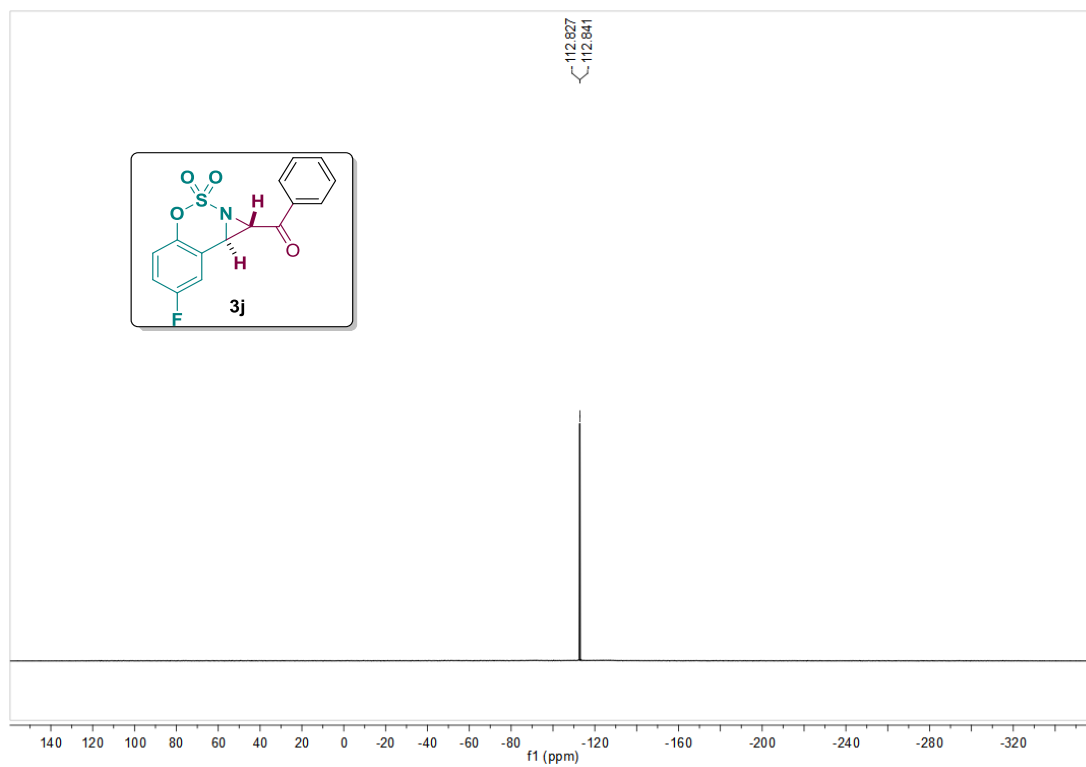
$^{19}\text{F}$  NMR Spectrum for **3i** ( $\text{CDCl}_3$ , 376 MHz)



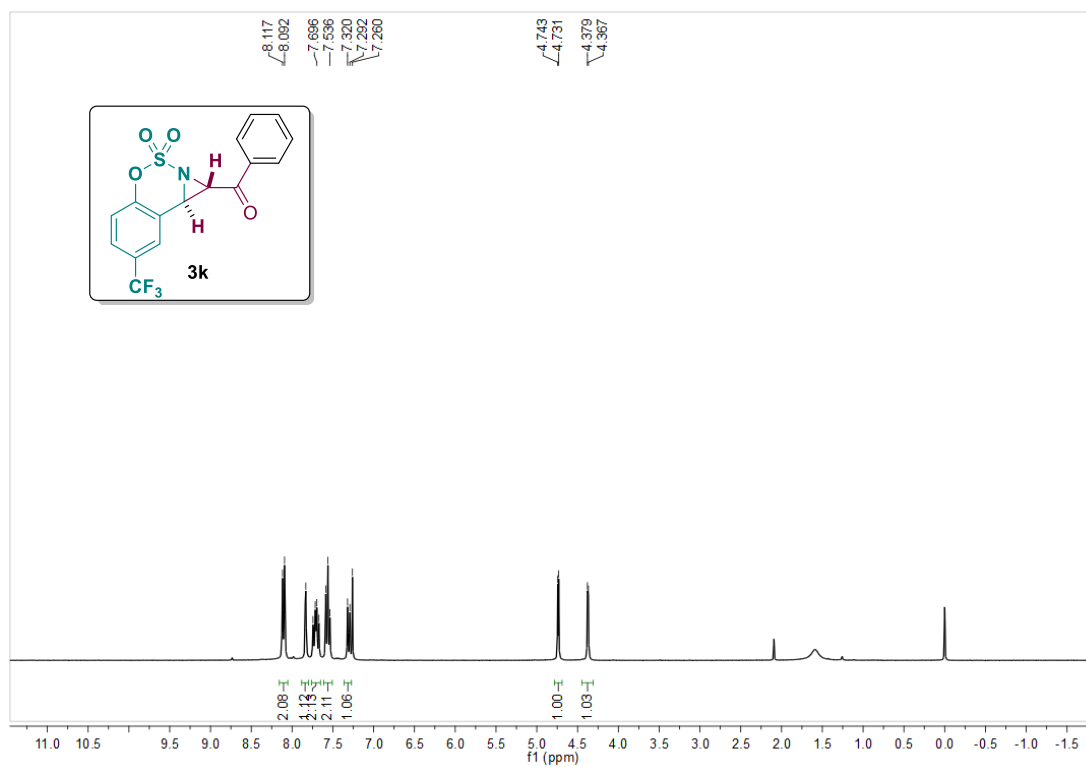
<sup>1</sup>H NMR Spectrum for 3j (CDCl<sub>3</sub>, 800 MHz)



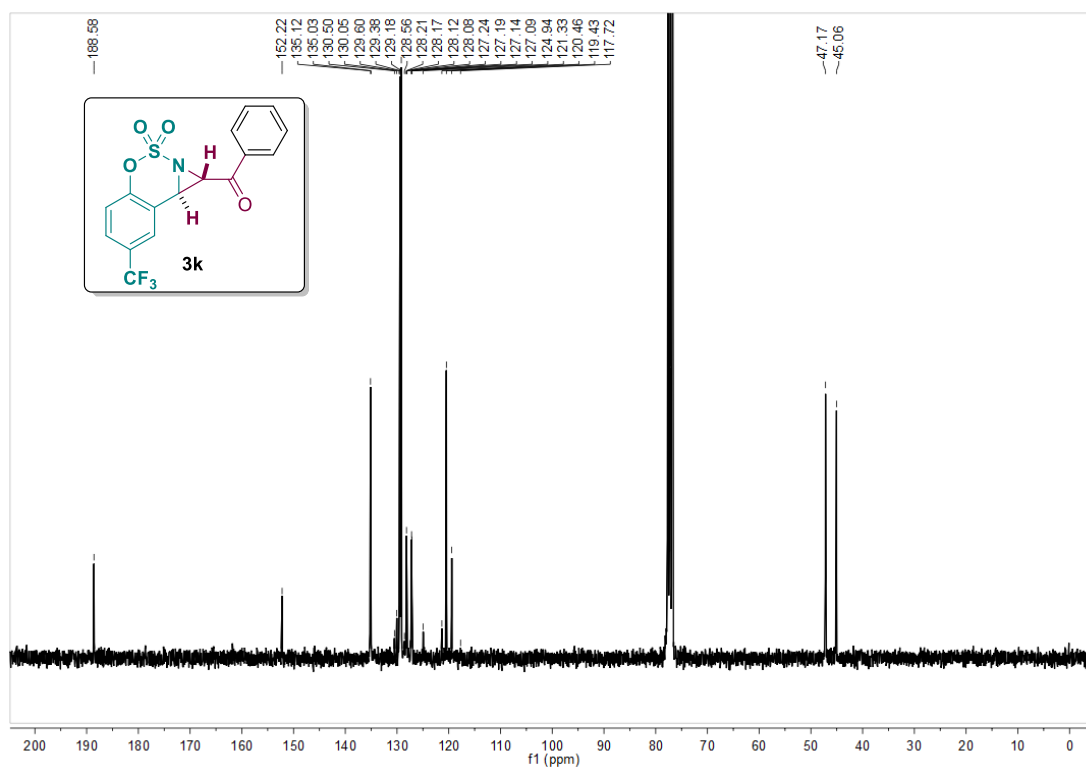
<sup>13</sup>C NMR Spectrum for 3j (CDCl<sub>3</sub>, 200 MHz)



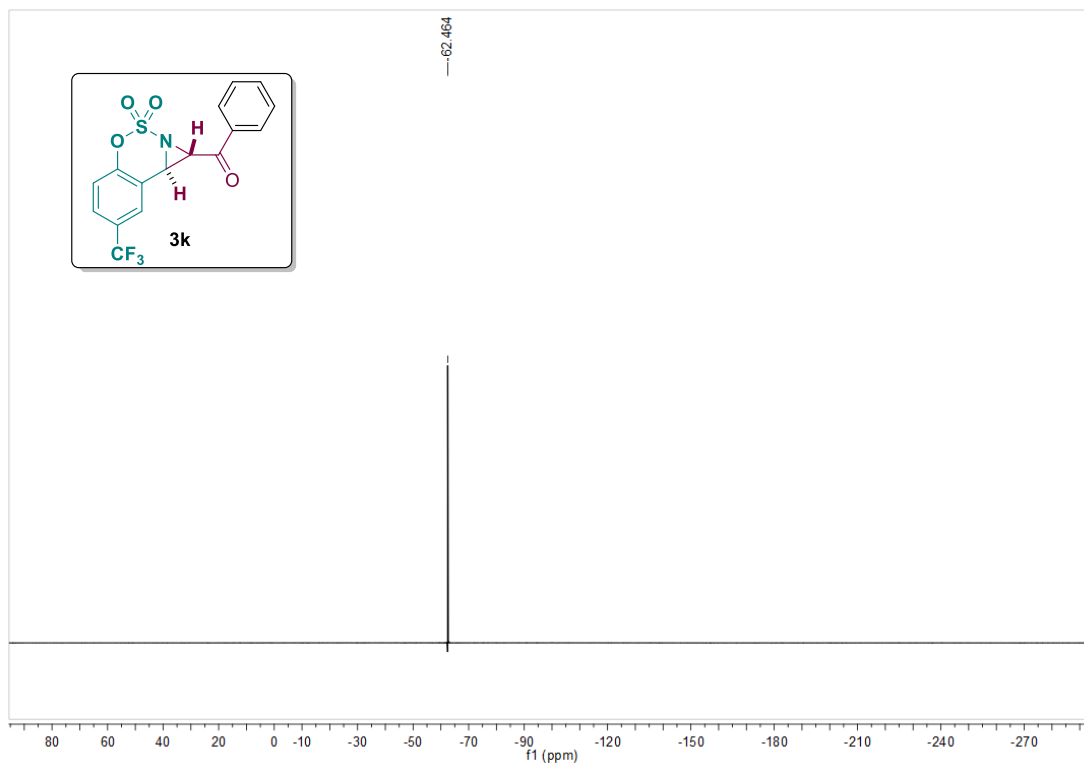
$^{19}\text{F}$  NMR Spectrum for **3j** ( $\text{CDCl}_3$ , 376 MHz)



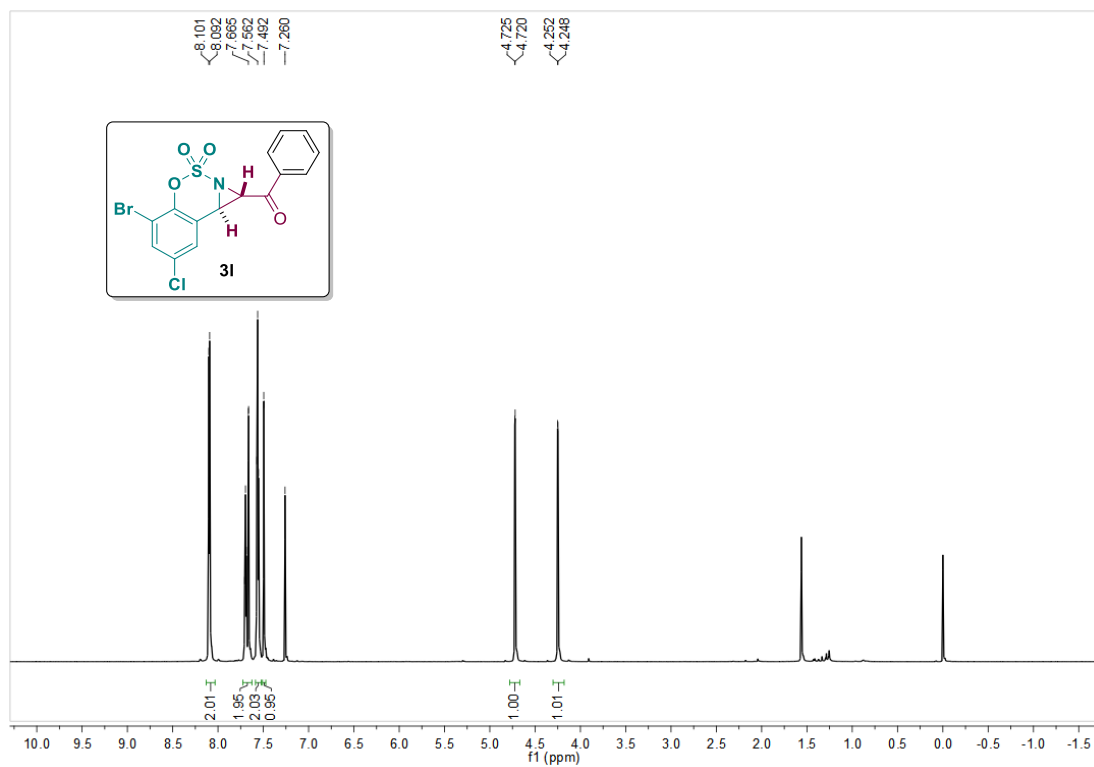
<sup>1</sup>H NMR Spectrum for **3k** (CDCl<sub>3</sub>, 300 MHz)



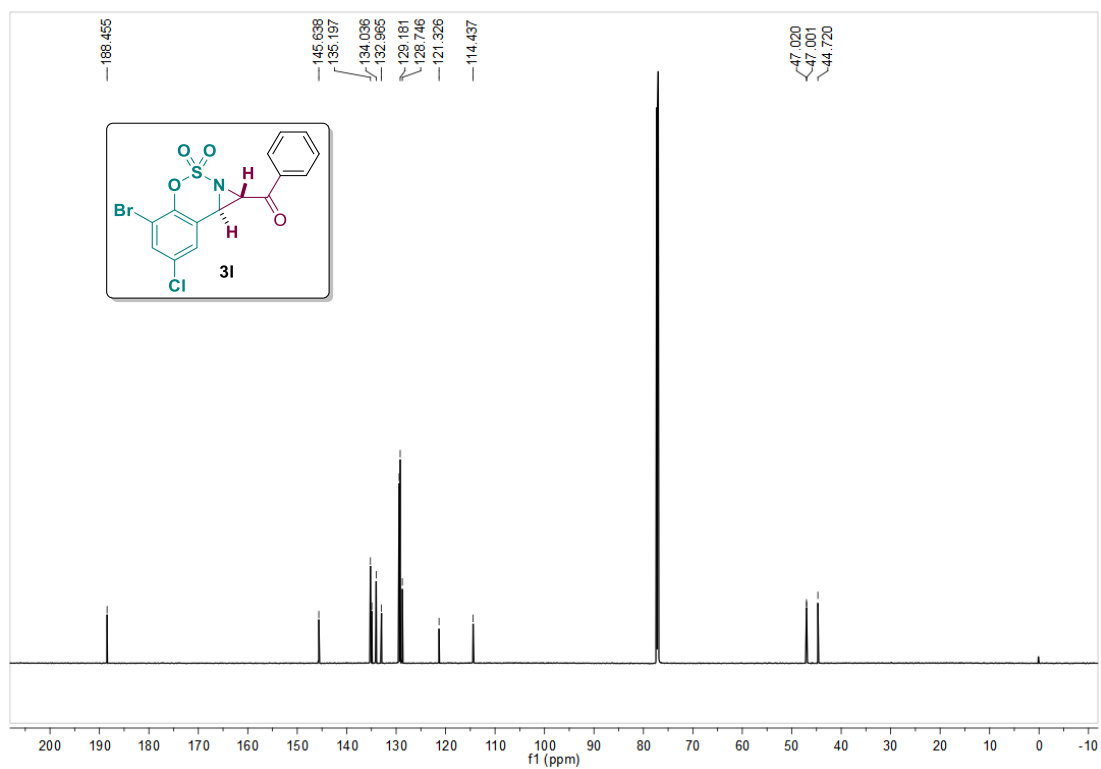
<sup>13</sup>C NMR Spectrum for **3k** (CDCl<sub>3</sub>, 75 MHz)



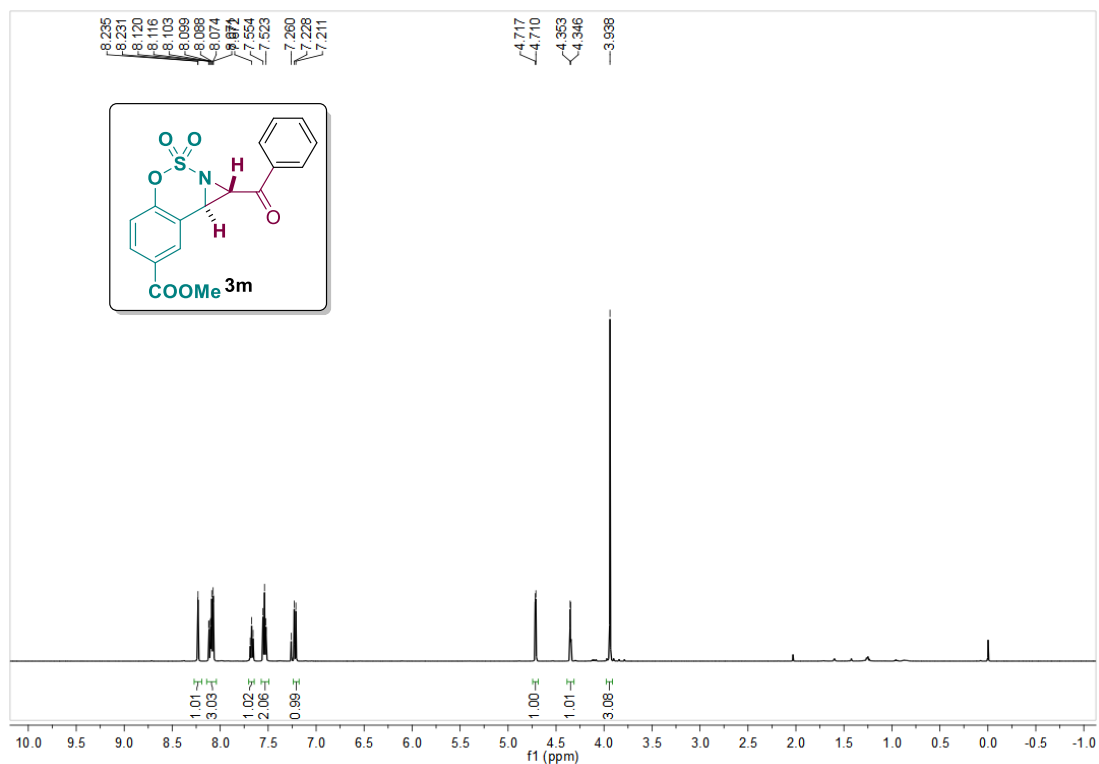
$^{19}\text{F}$  NMR Spectrum for **3k** ( $\text{CDCl}_3$ , 470 MHz)



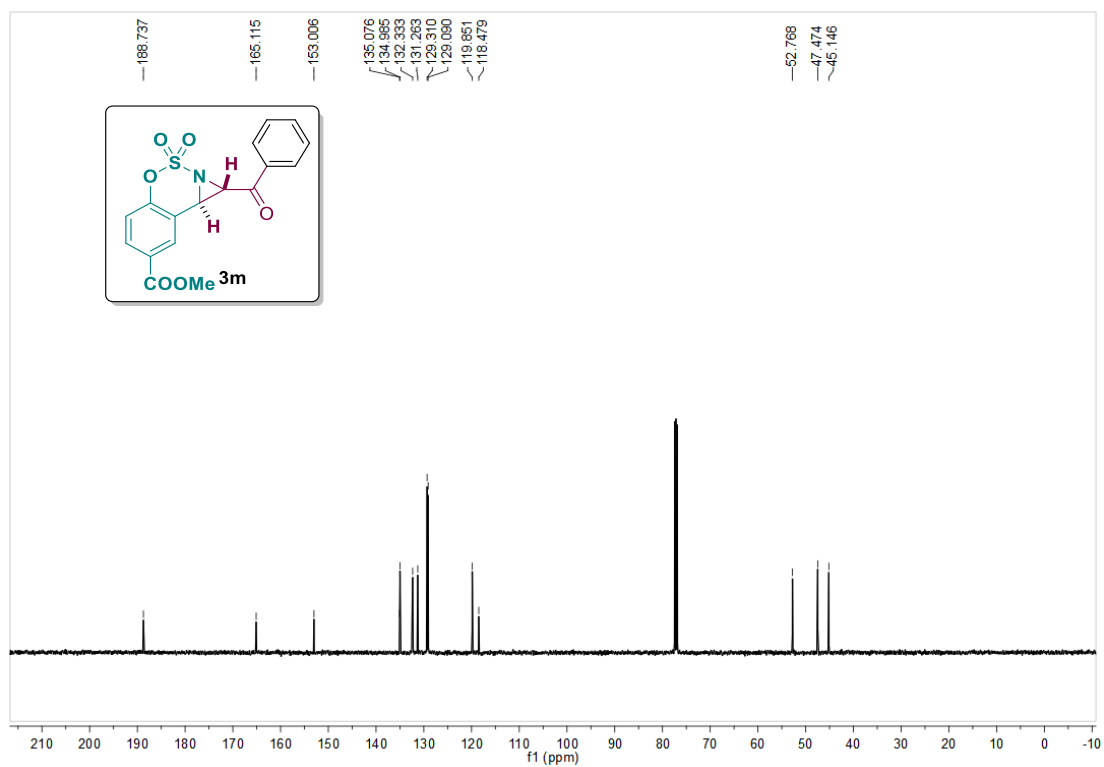
$^1\text{H}$  NMR Spectrum for **31** ( $\text{CDCl}_3$ , 800 MHz)



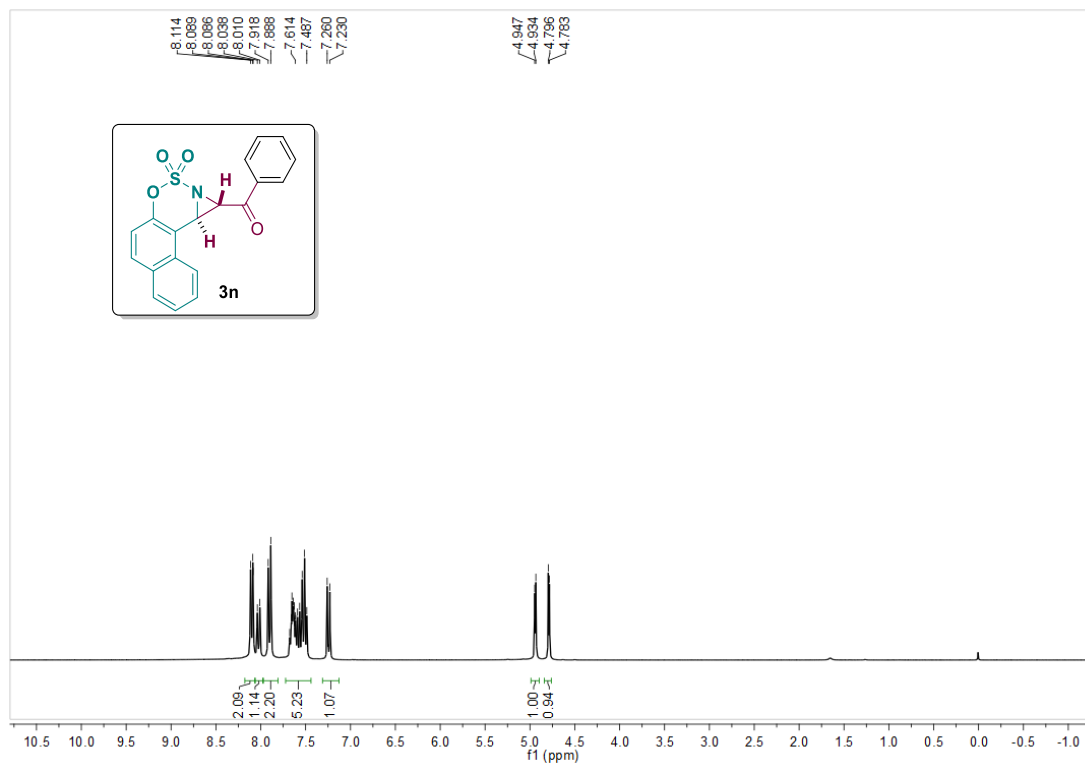
$^{13}\text{C}$  NMR Spectrum for **31** ( $\text{CDCl}_3$ , 200 MHz)



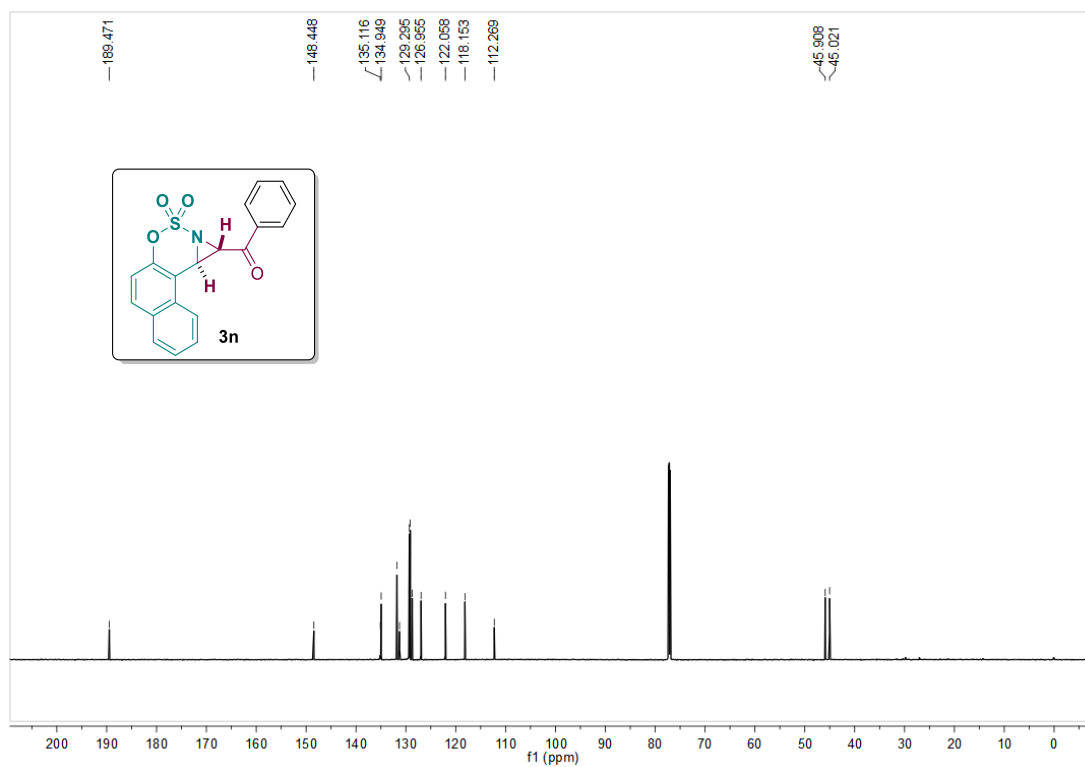
**<sup>1</sup>H NMR Spectrum for **3m** (CDCl<sub>3</sub>, 500 MHz)**



**<sup>13</sup>C NMR Spectrum for **3m** (CDCl<sub>3</sub>, 125 MHz)**

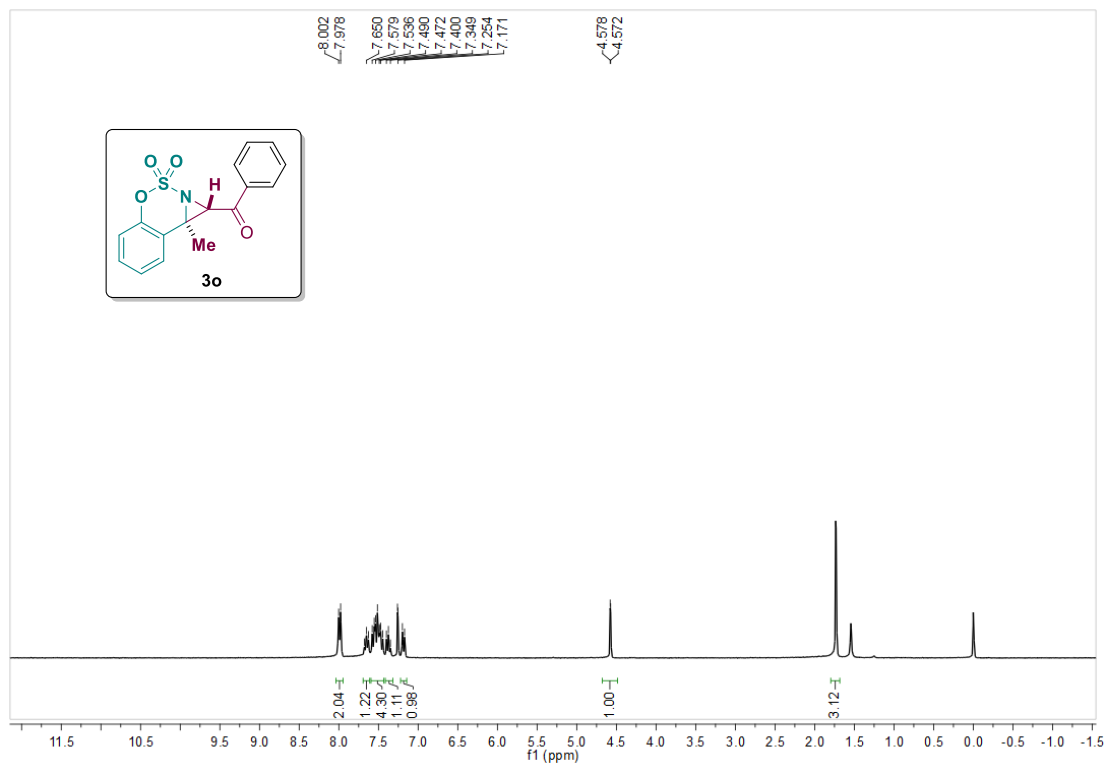


**<sup>1</sup>H NMR Spectrum for 3n (CDCl<sub>3</sub>, 800 MHz)**

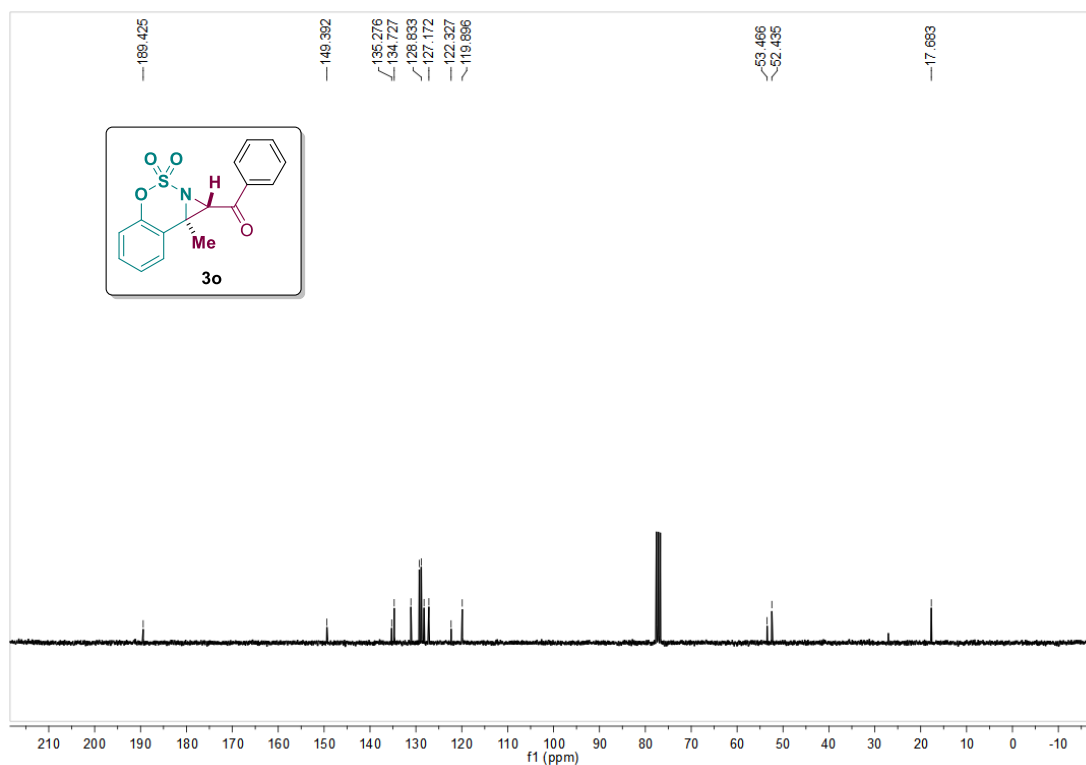


**<sup>13</sup>C NMR Spectrum for 3n (CDCl<sub>3</sub>, 200 MHz)**

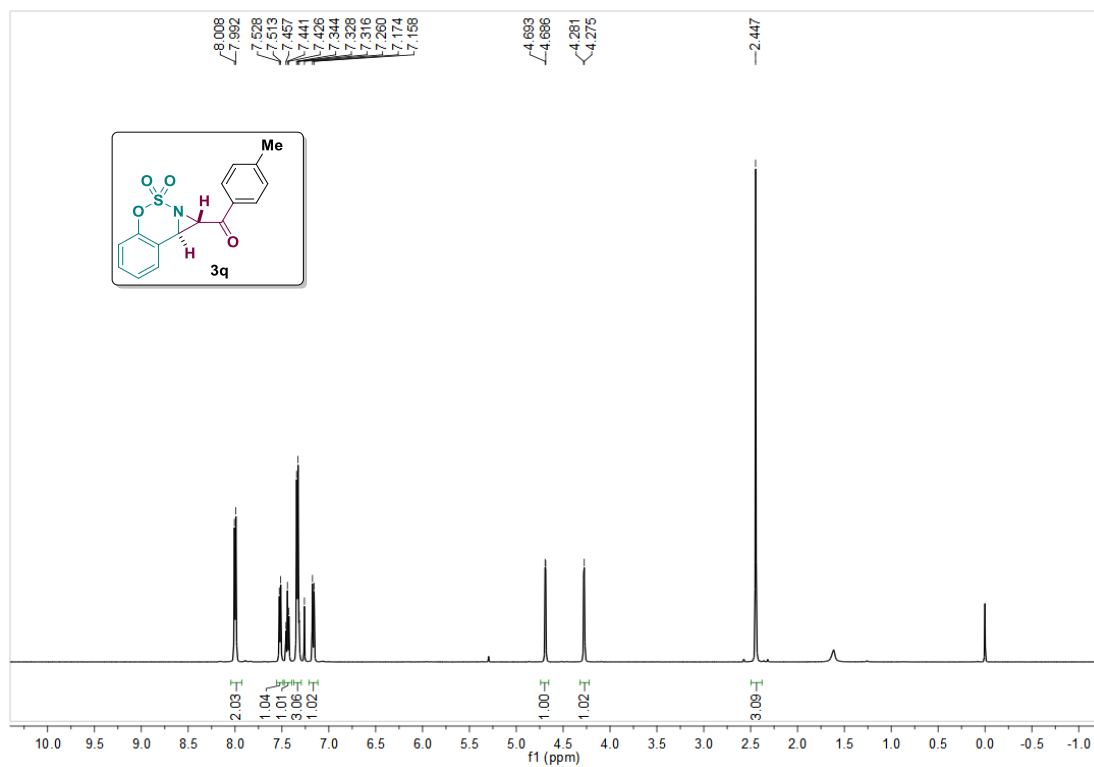




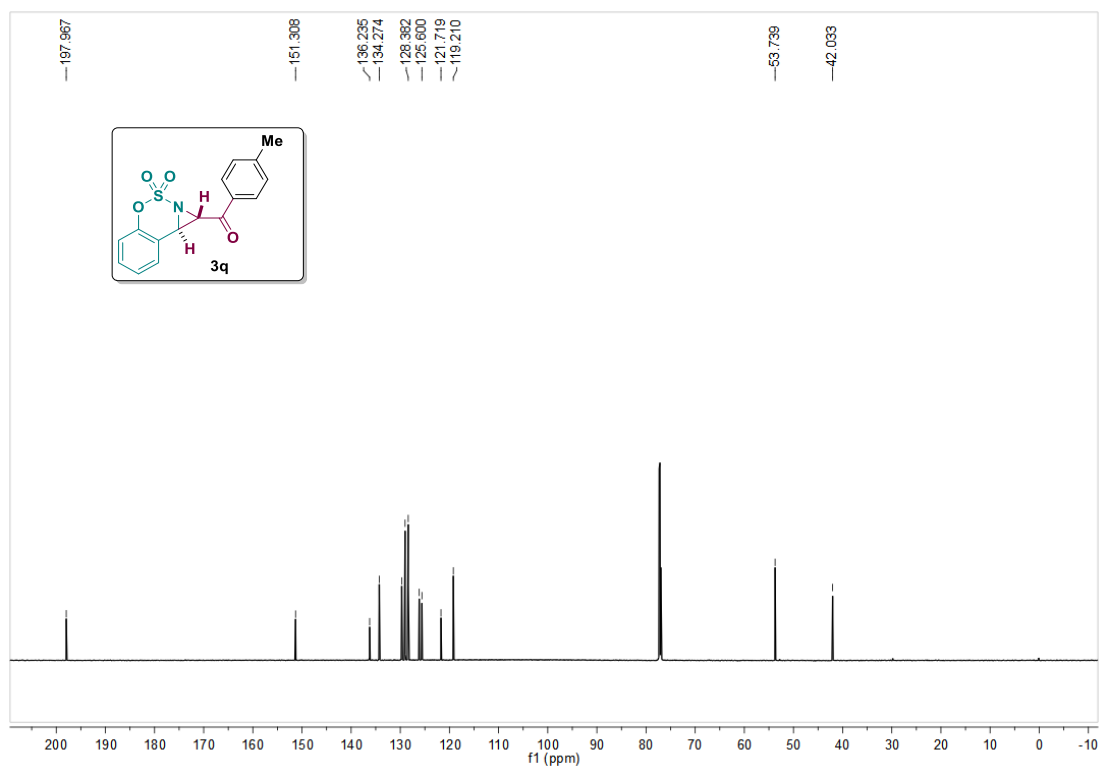
<sup>1</sup>H NMR Spectrum for 3o (CDCl<sub>3</sub>, 300 MHz)



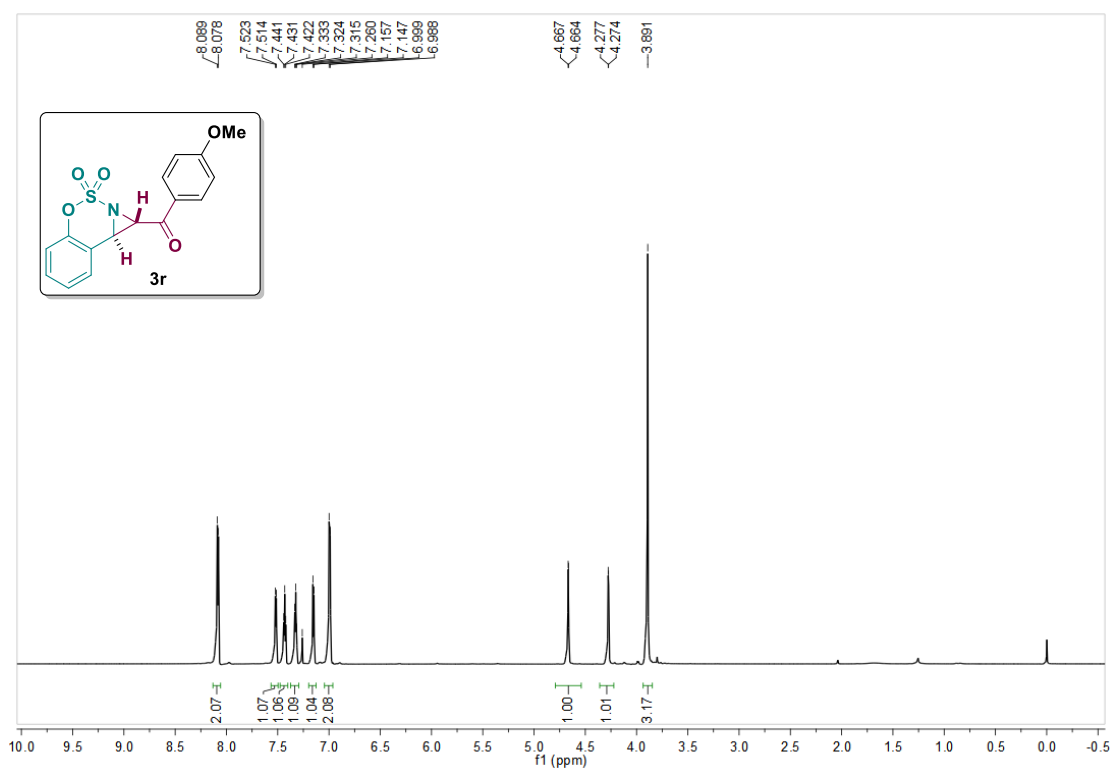
<sup>13</sup>C NMR Spectrum for 3o (CDCl<sub>3</sub>, 75 MHz)



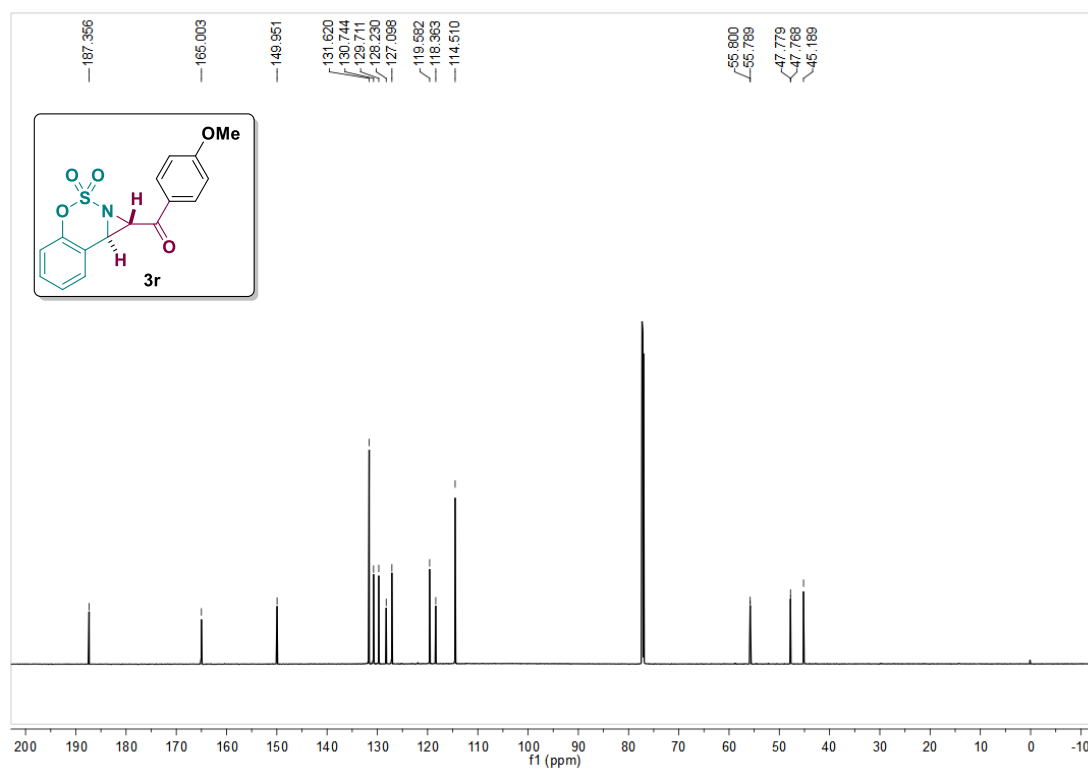
**<sup>1</sup>H NMR Spectrum for **3q** (CDCl<sub>3</sub>, 500 MHz)**



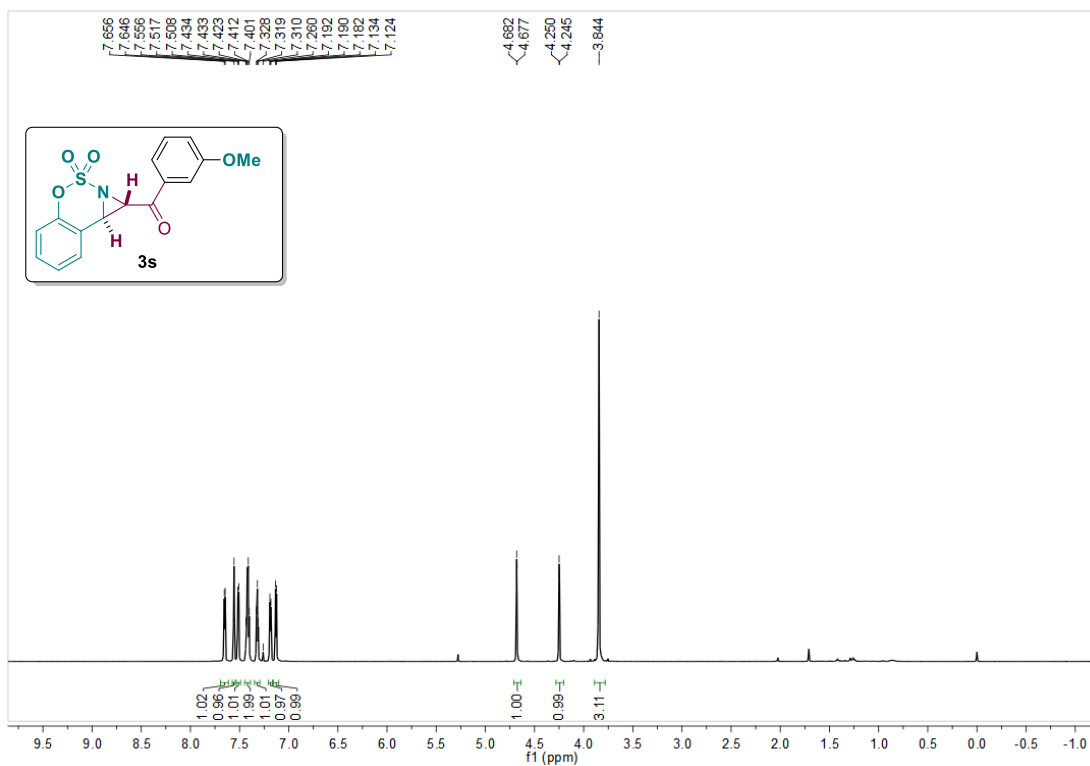
**<sup>13</sup>C NMR Spectrum for **3q** (CDCl<sub>3</sub>, 125 MHz)**



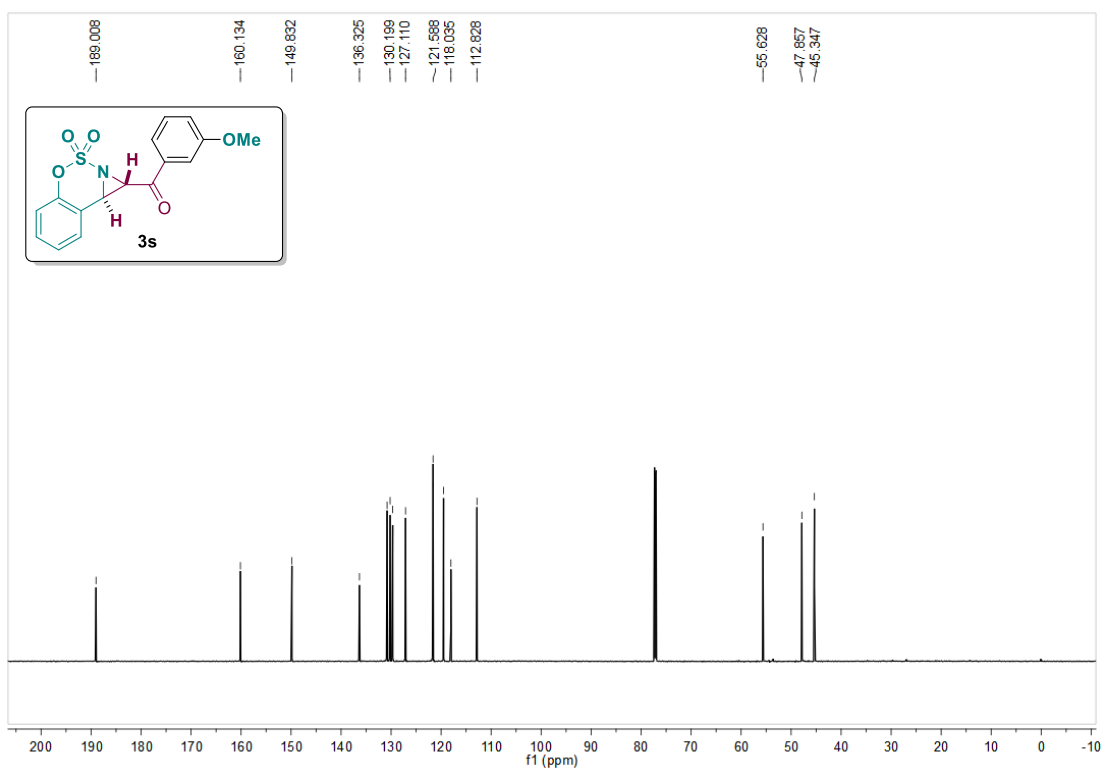
**<sup>1</sup>H NMR Spectrum for 3r (CDCl<sub>3</sub>, 800 MHz)**



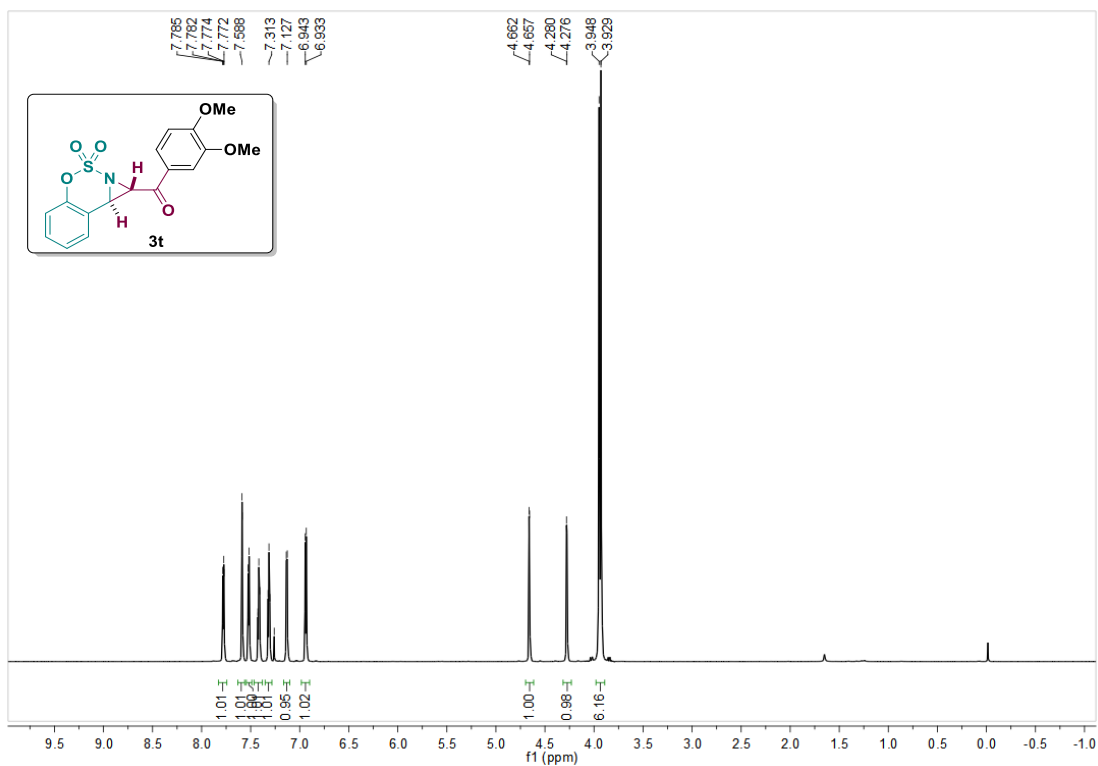
**<sup>13</sup>C NMR Spectrum for 3r (CDCl<sub>3</sub>, 200 MHz)**



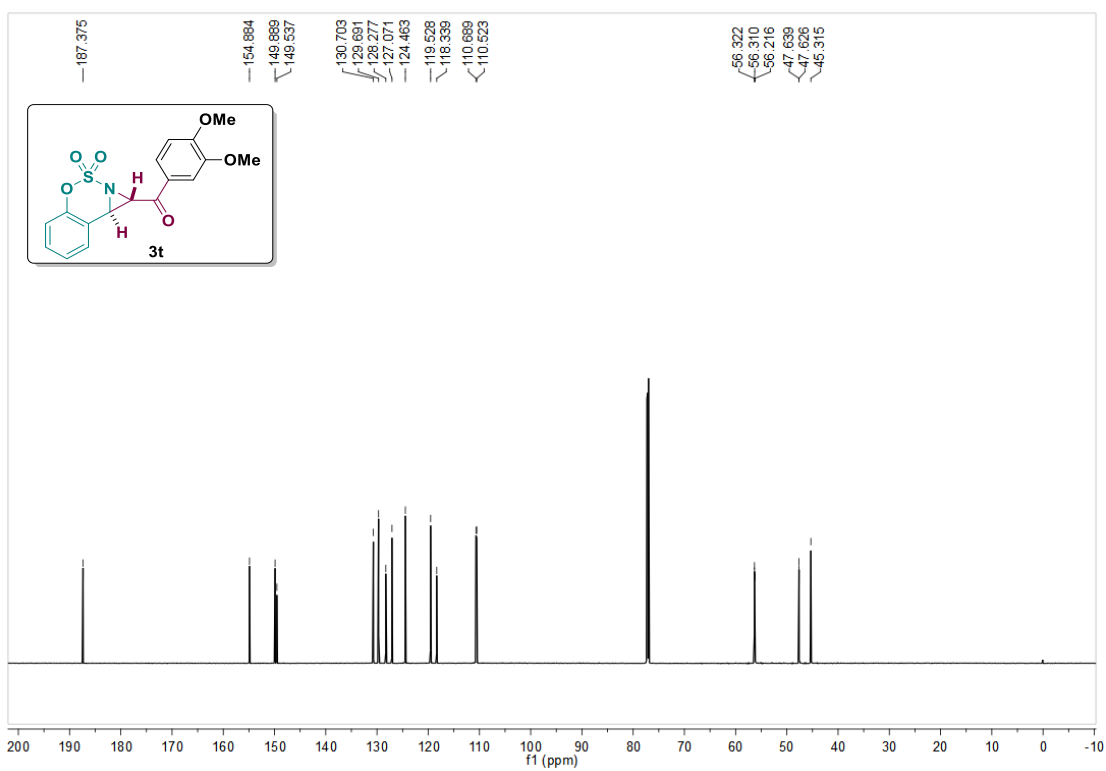
<sup>1</sup>H NMR Spectrum for **3s** (CDCl<sub>3</sub>, 800 MHz)



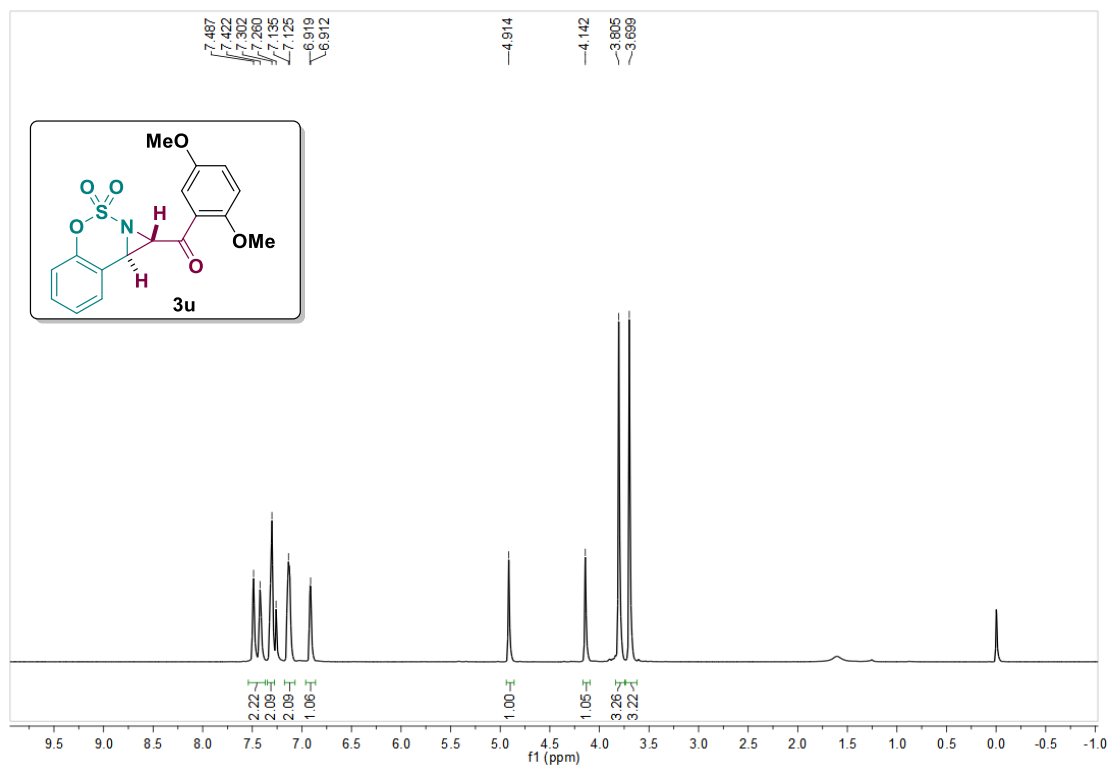
<sup>13</sup>C NMR Spectrum for **3s** (CDCl<sub>3</sub>, 200 MHz)



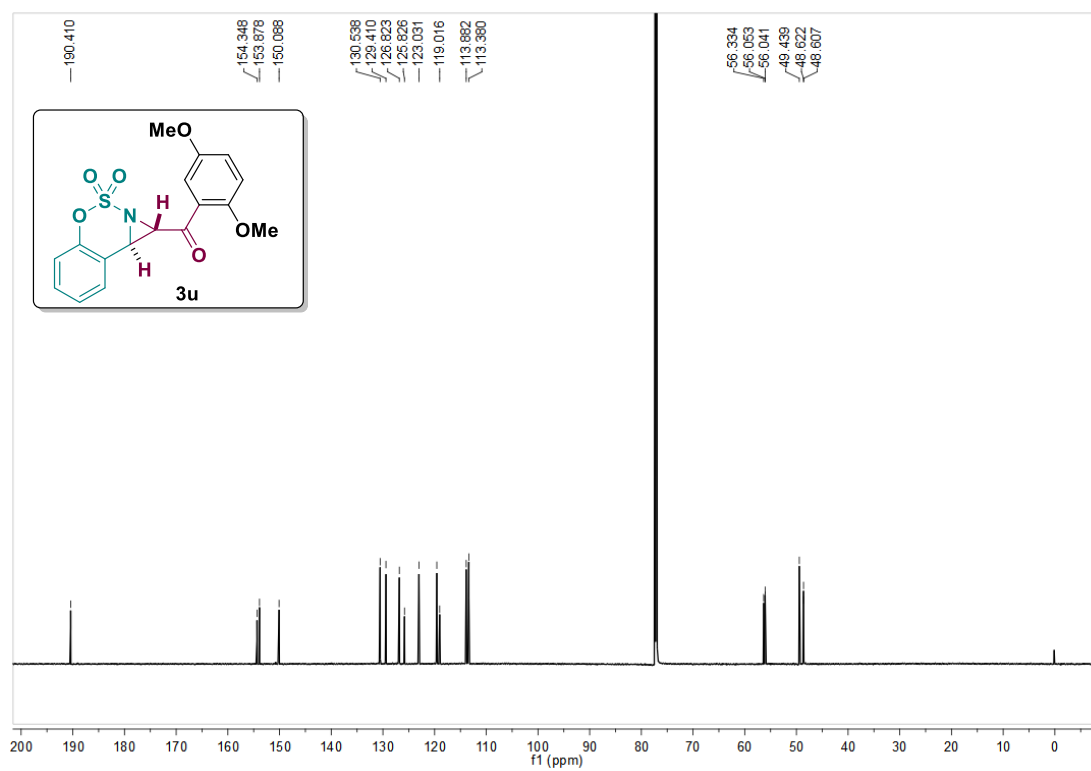
**<sup>1</sup>H NMR Spectrum for 3t (CDCl<sub>3</sub>, 800 MHz)**



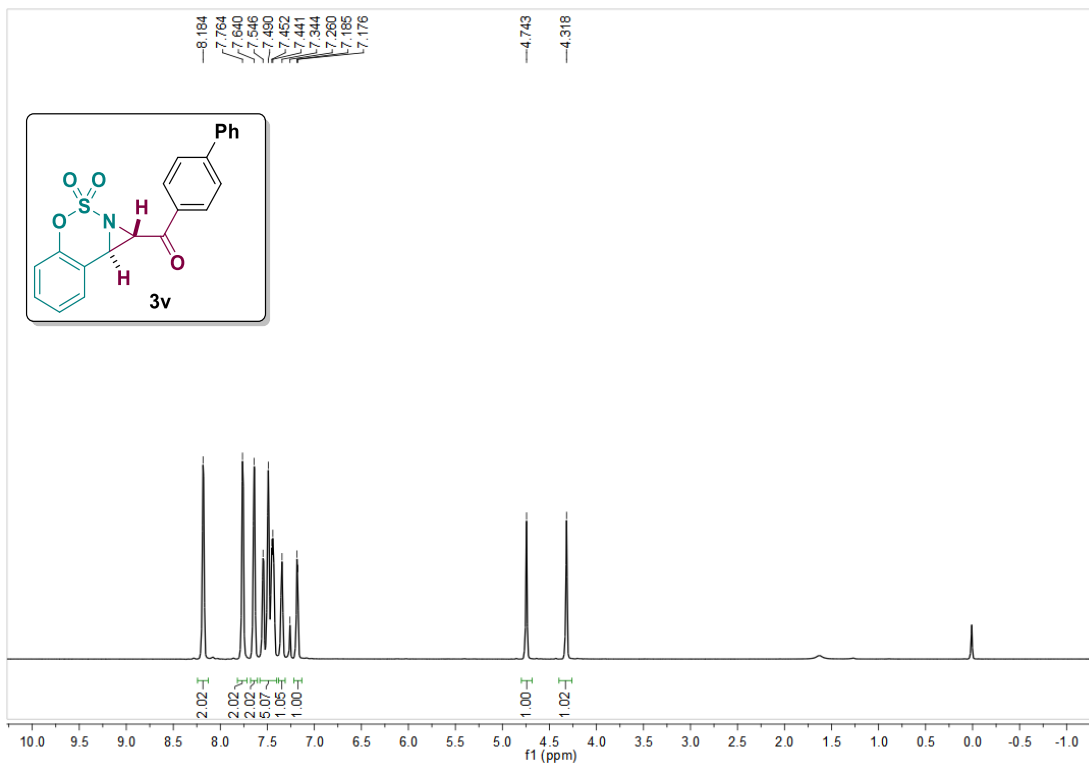
**<sup>13</sup>C NMR Spectrum for 3t (CDCl<sub>3</sub>, 200 MHz)**



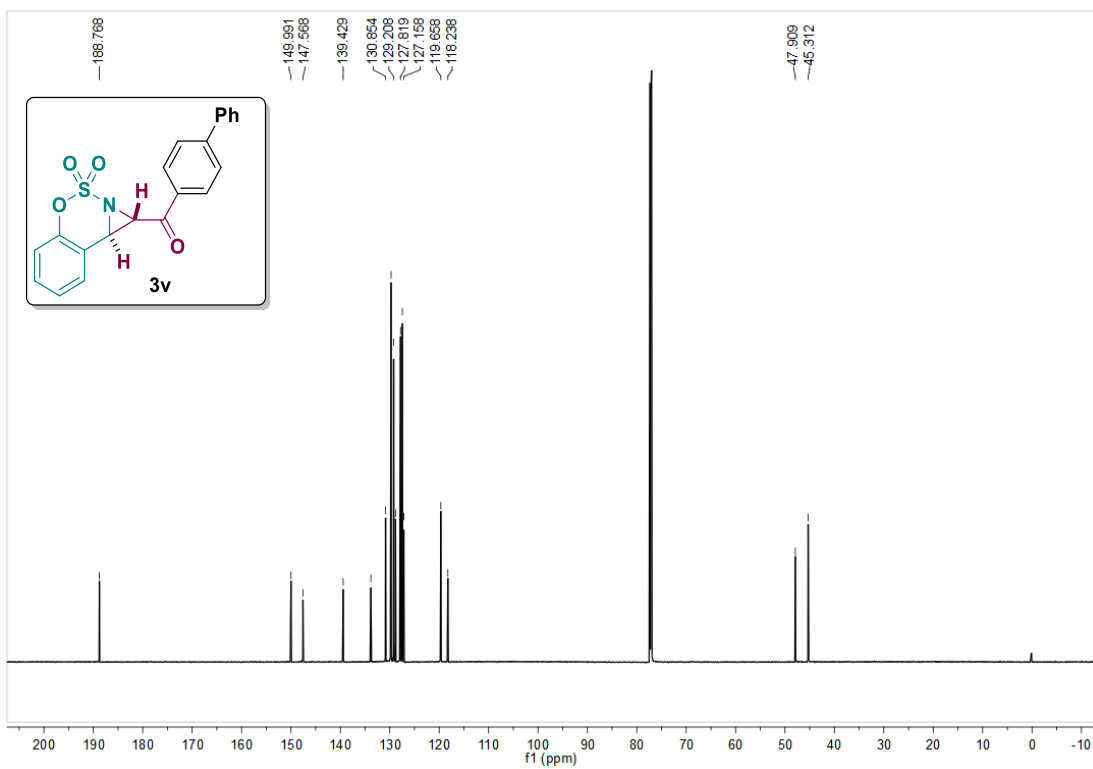
**<sup>1</sup>H NMR Spectrum for **3u** (CDCl<sub>3</sub>, 800 MHz)**



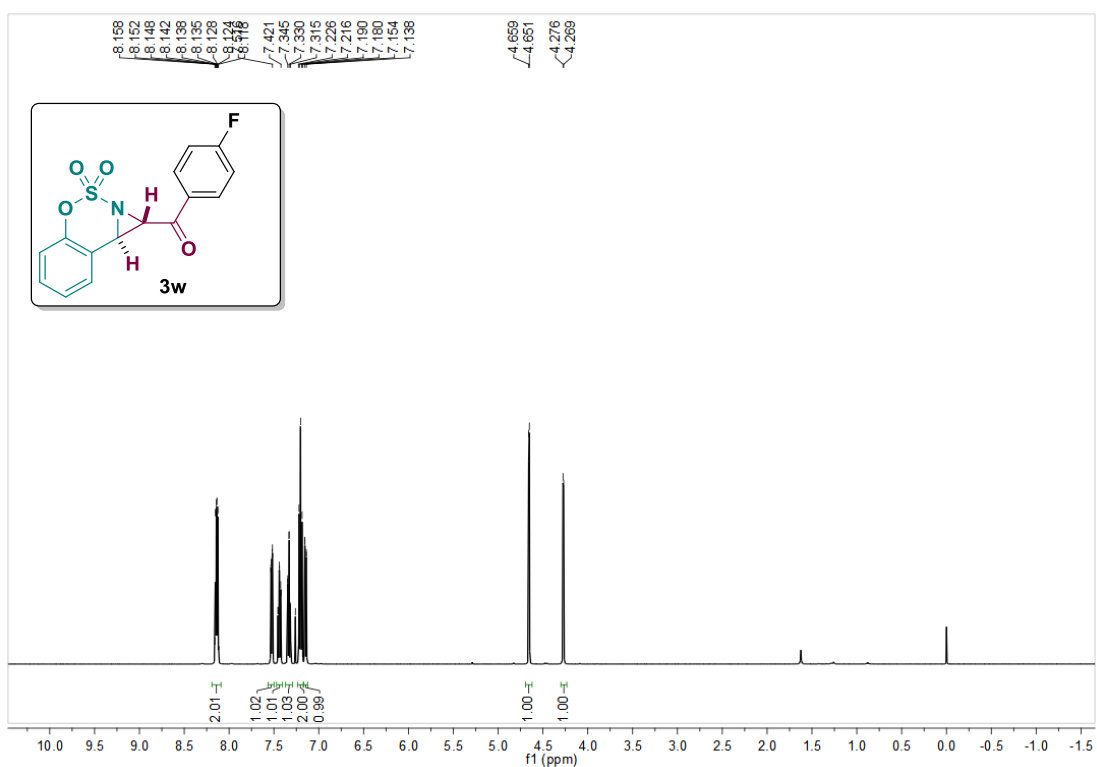
**<sup>13</sup>C NMR Spectrum for **3u** (CDCl<sub>3</sub>, 200 MHz)**



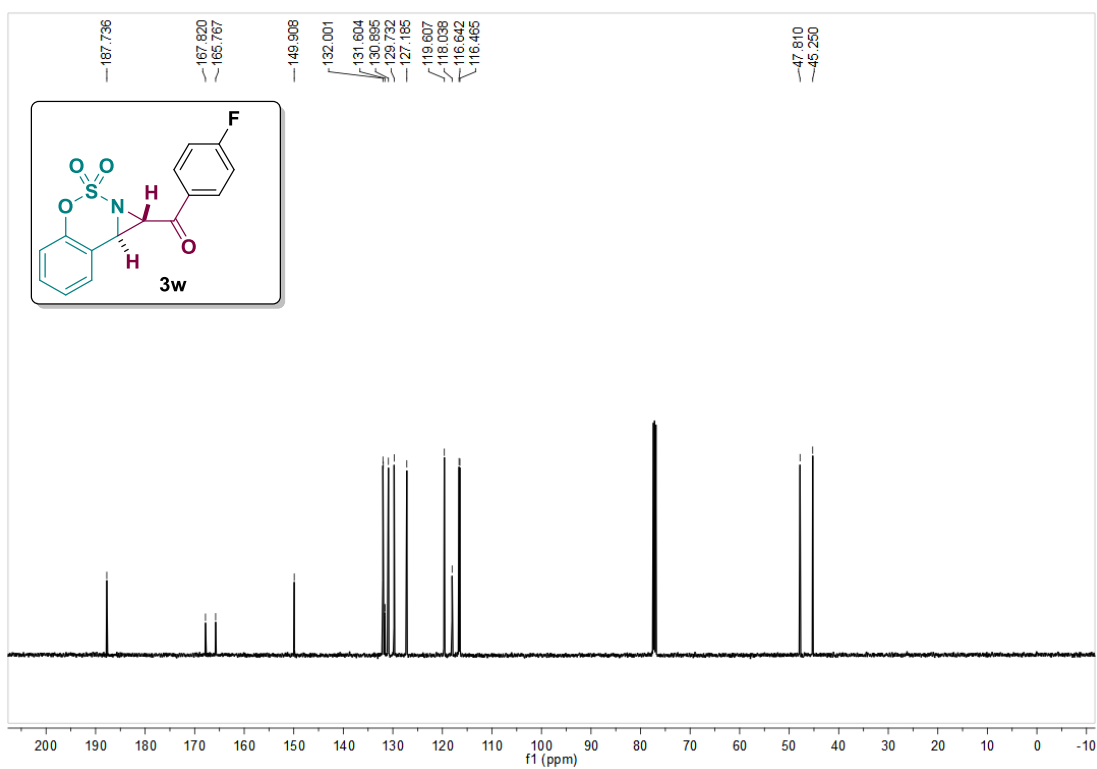
<sup>1</sup>H NMR Spectrum for **3v** (CDCl<sub>3</sub>, 800 MHz)



<sup>13</sup>C NMR Spectrum for **3v** (CDCl<sub>3</sub>, 200 MHz)

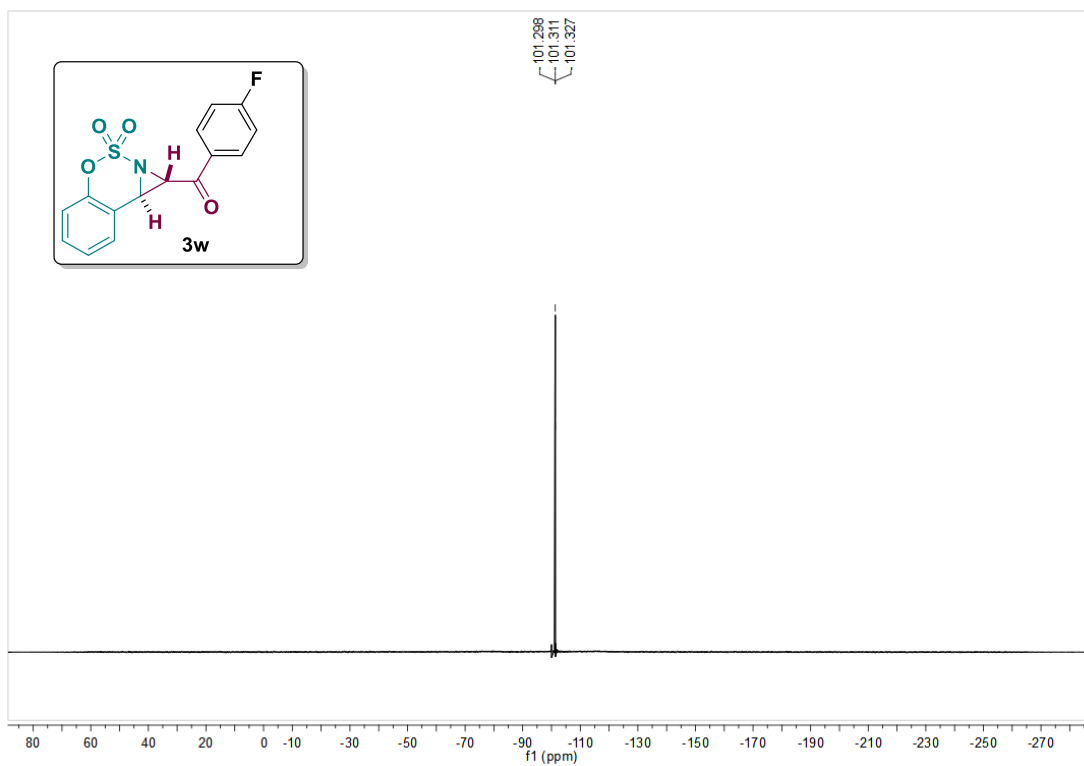


**<sup>1</sup>H NMR Spectrum for **3w** (CDCl<sub>3</sub>, 500 MHz)**

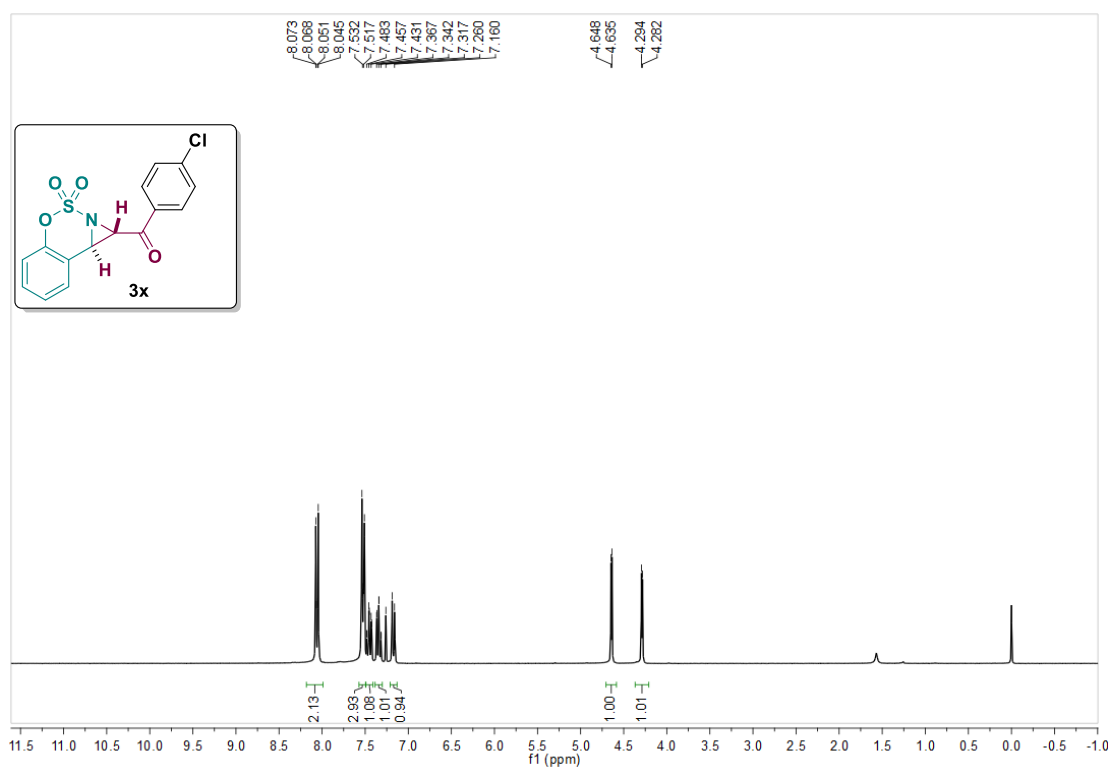


**<sup>13</sup>C NMR Spectrum for **3w** (CDCl<sub>3</sub>, 125 MHz)**

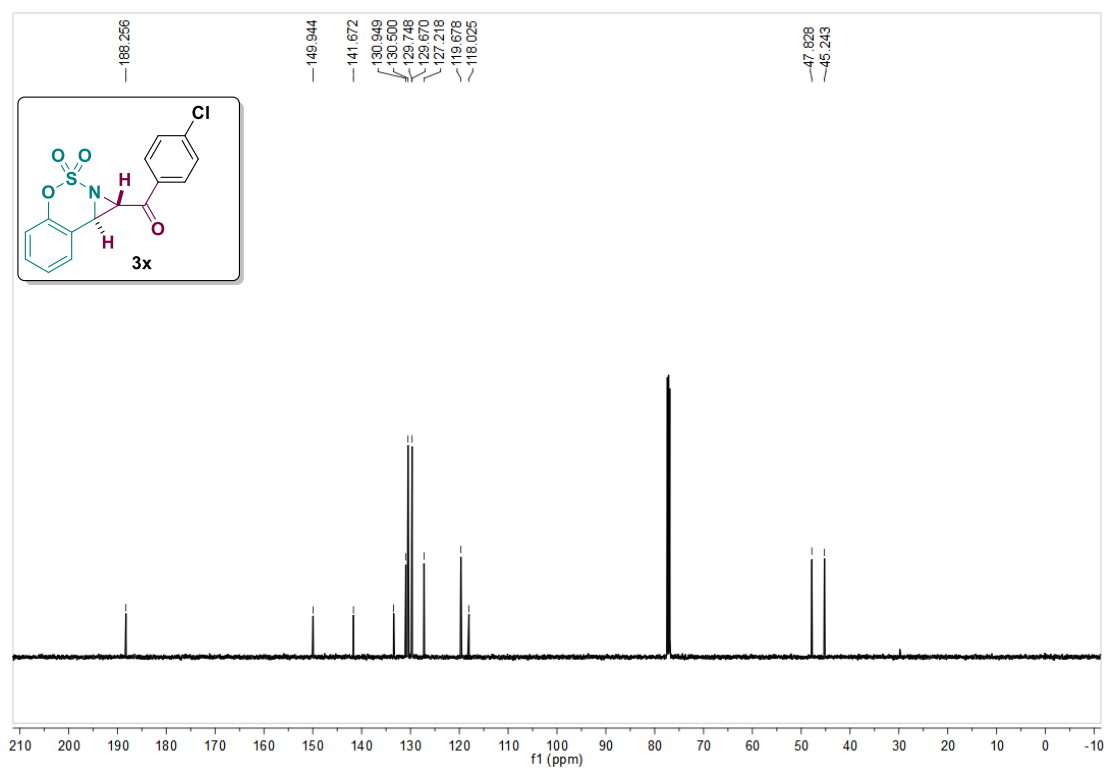




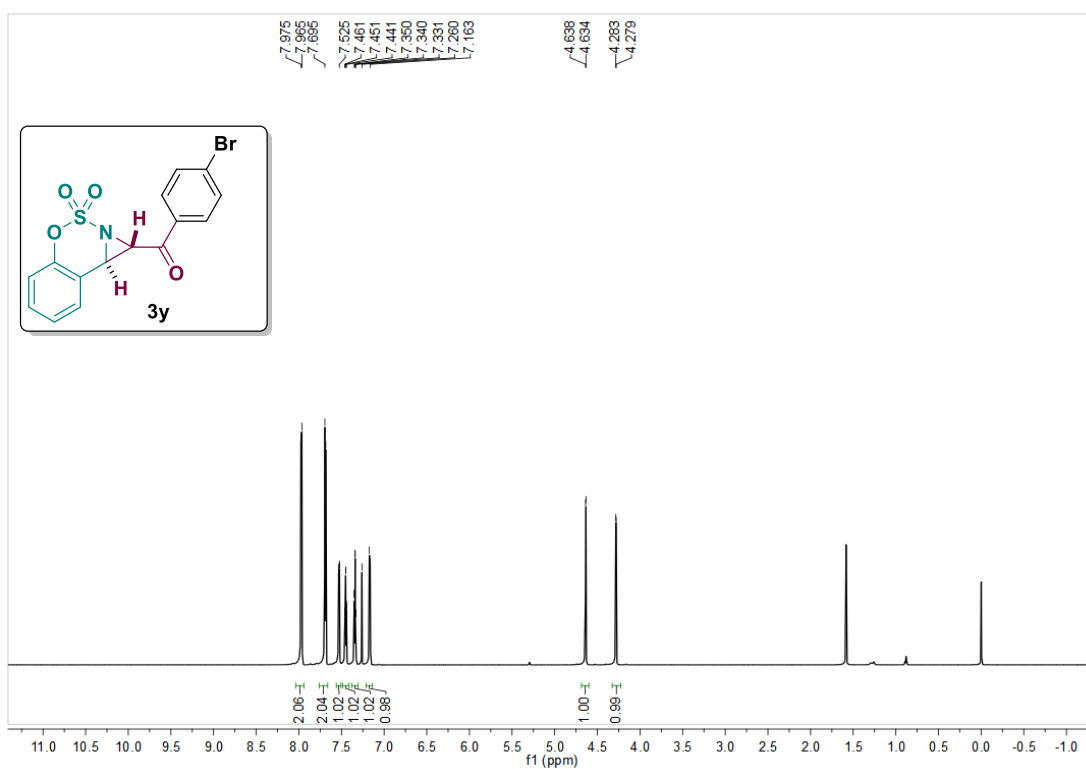
$^{19}\text{F}$  NMR Spectrum for **3w** ( $\text{CDCl}_3$ , 376 MHz)



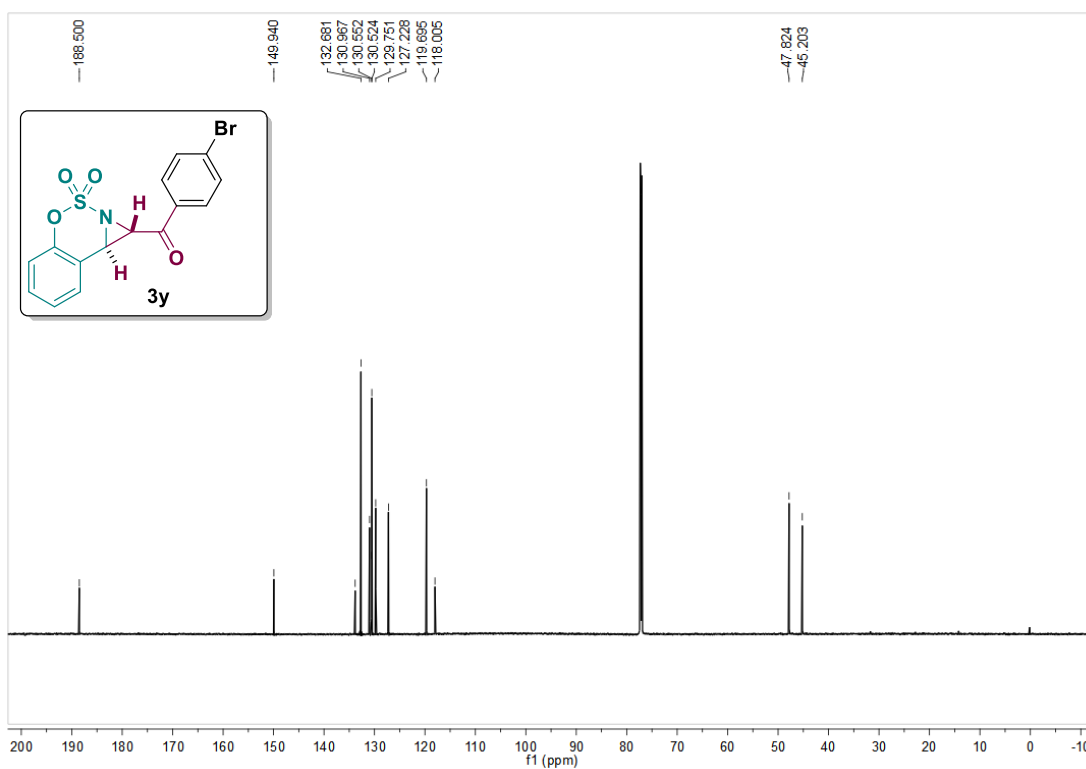
<sup>1</sup>H NMR Spectrum for 3x (CDCl<sub>3</sub>, 500 MHz)



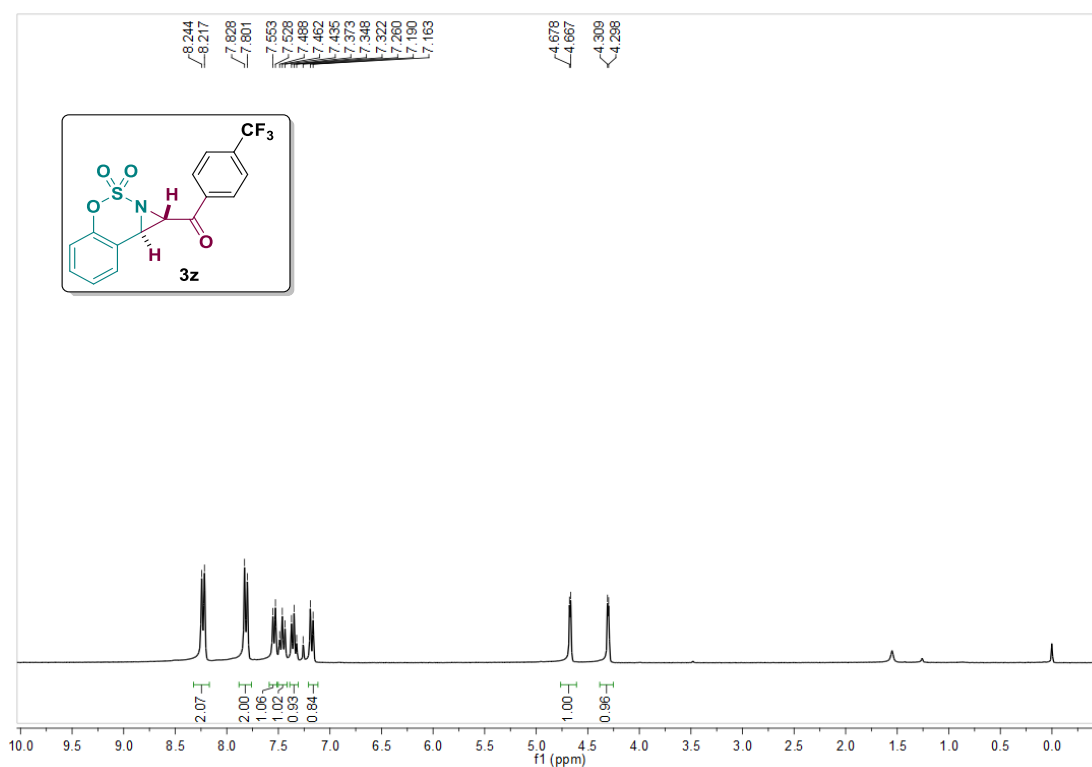
<sup>13</sup>C NMR Spectrum for 3x (CDCl<sub>3</sub>, 125 MHz)



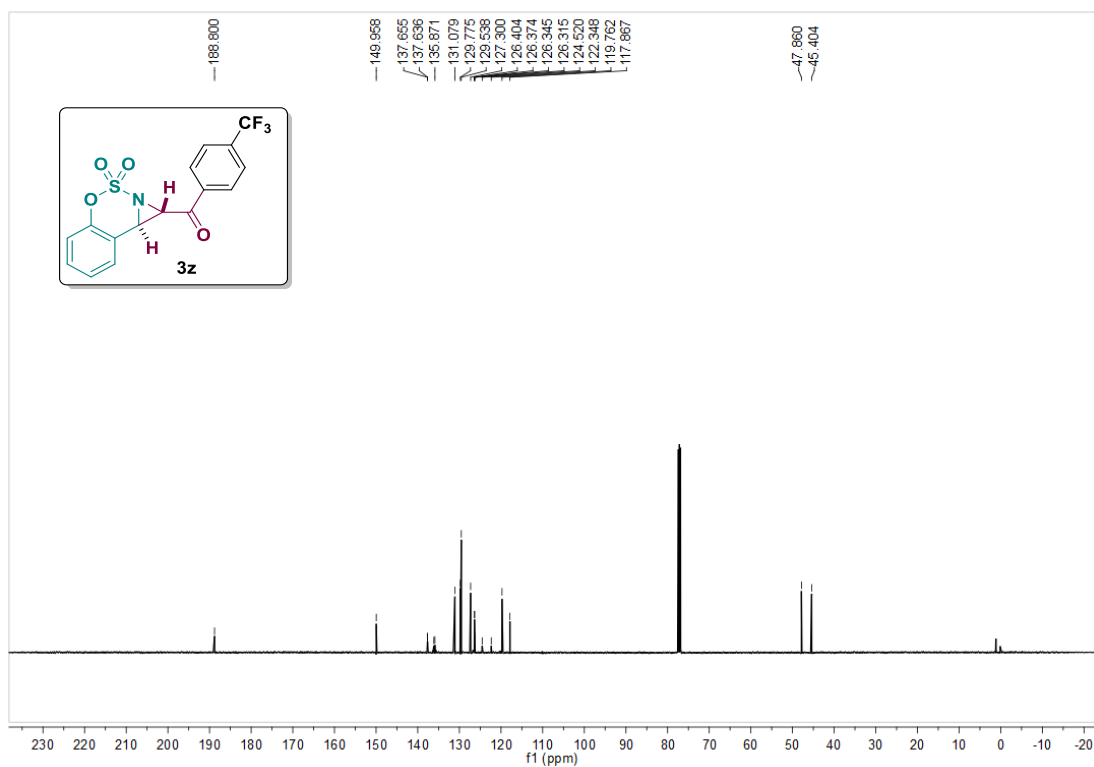
<sup>1</sup>H NMR Spectrum for 3y (CDCl<sub>3</sub>, 800 MHz)



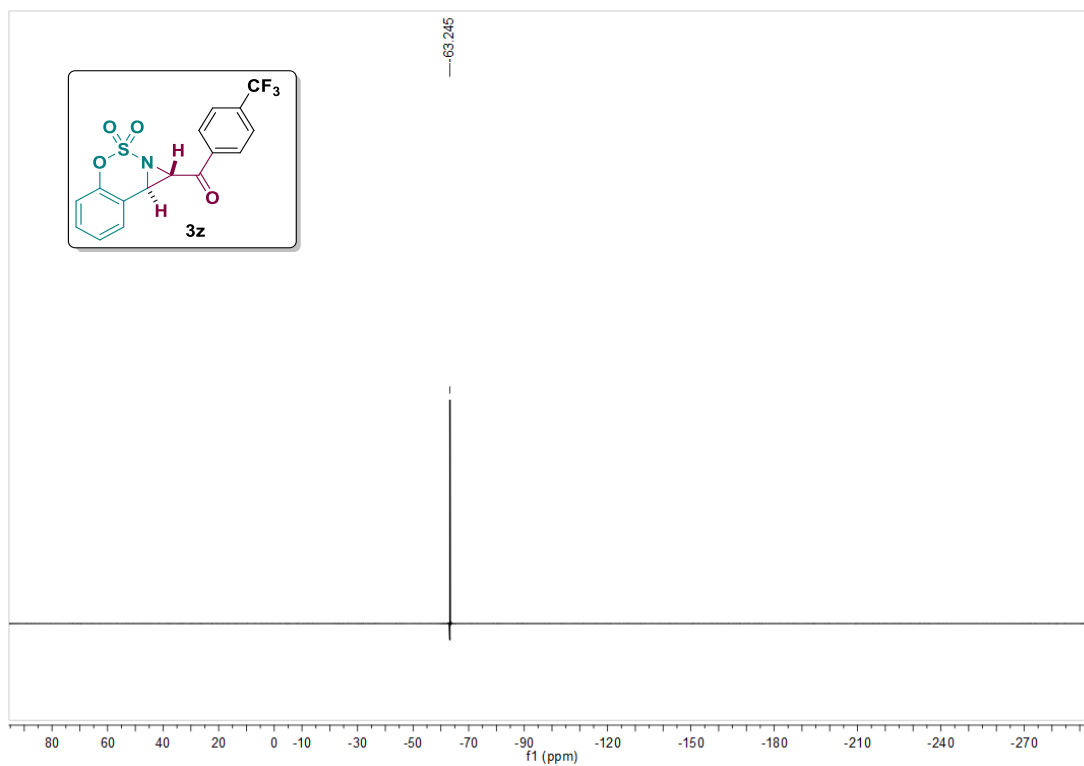
<sup>13</sup>C NMR Spectrum for 3y (CDCl<sub>3</sub>, 200 MHz)



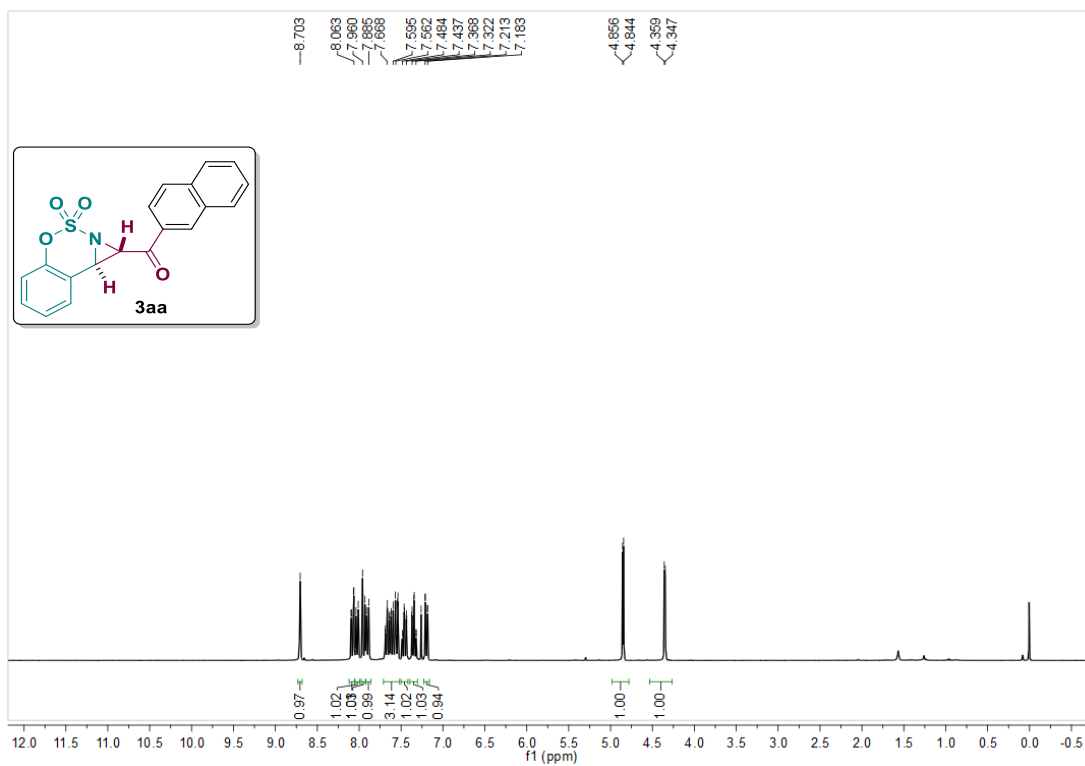
**<sup>1</sup>H NMR Spectrum for **3z** (CDCl<sub>3</sub>, 300 MHz)**



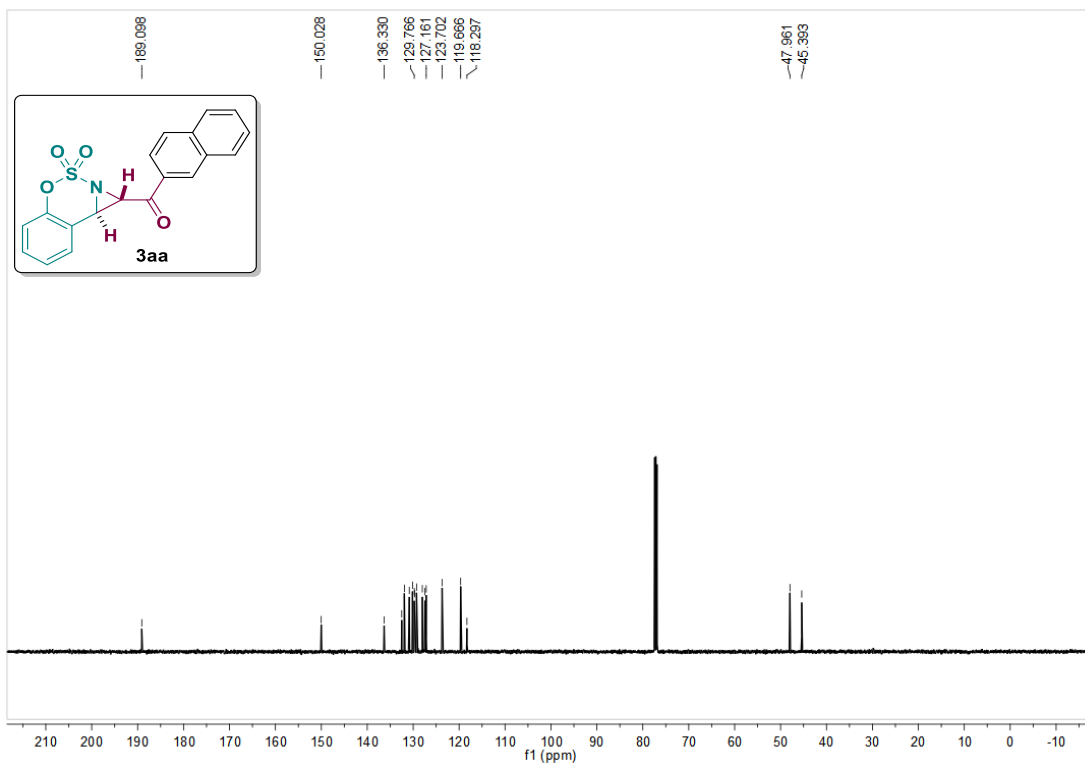
**<sup>13</sup>C NMR Spectrum for **3z** (CDCl<sub>3</sub>, 125 MHz)**



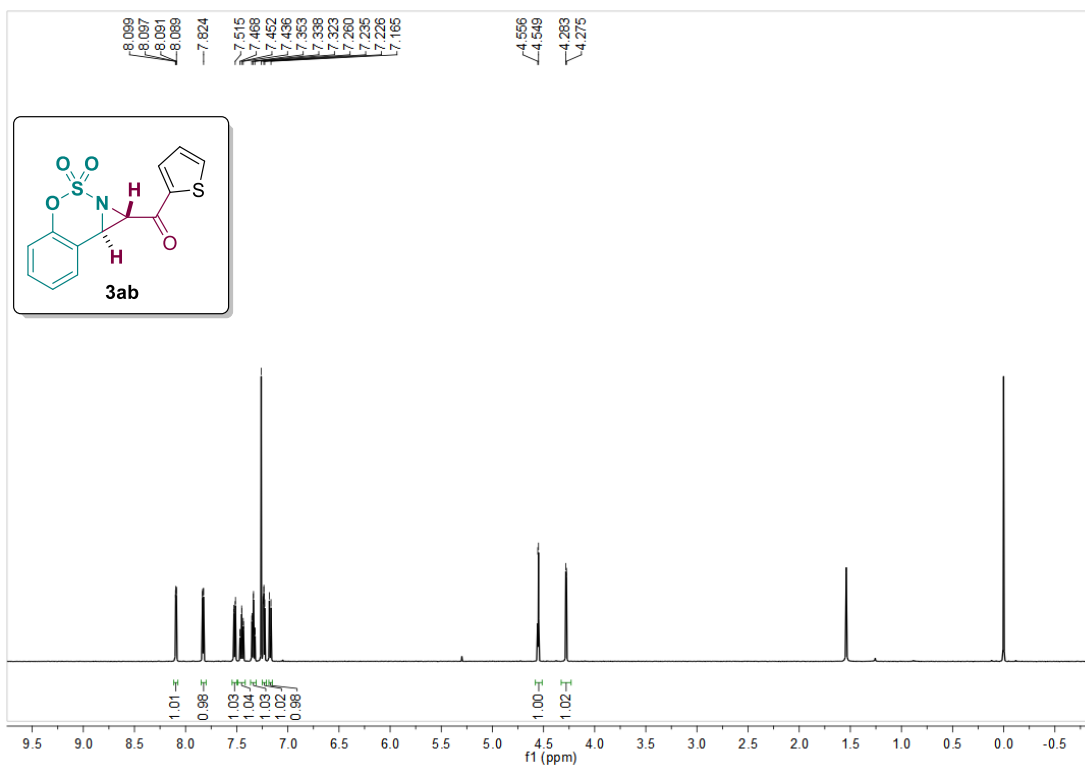
$^{19}\text{F}$  NMR Spectrum for **3z** ( $\text{CDCl}_3$ , 470 MHz)



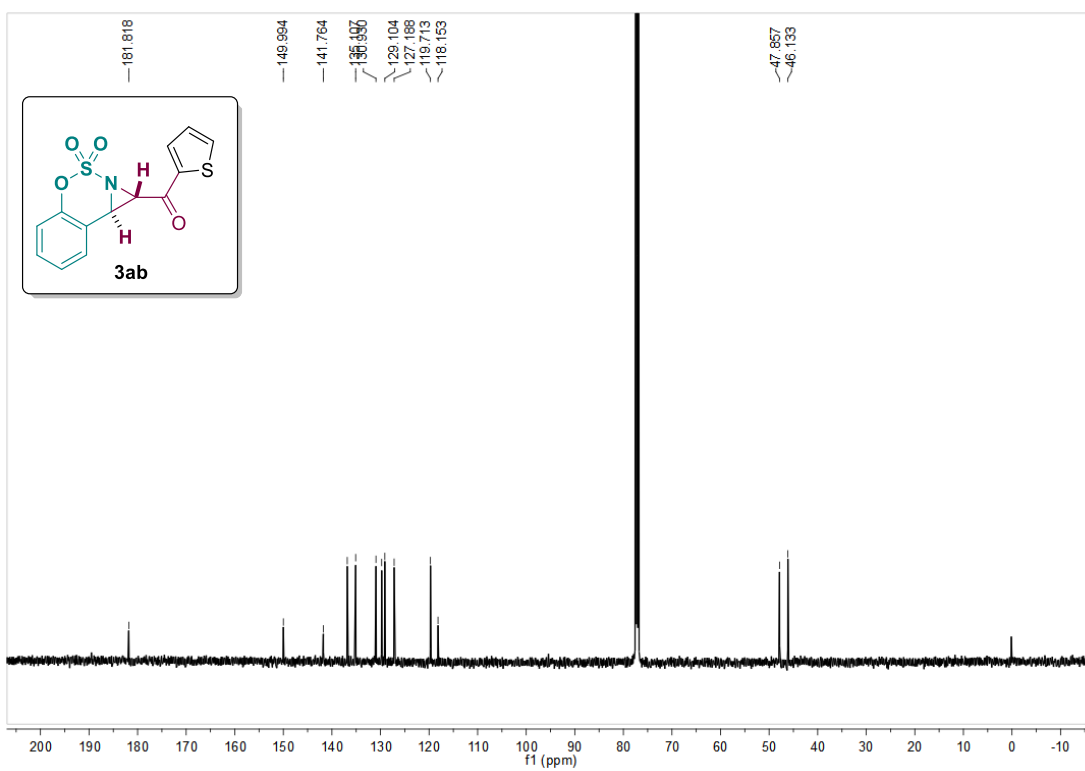
**<sup>1</sup>H NMR Spectrum for 3aa (CDCl<sub>3</sub>, 500 MHz)**



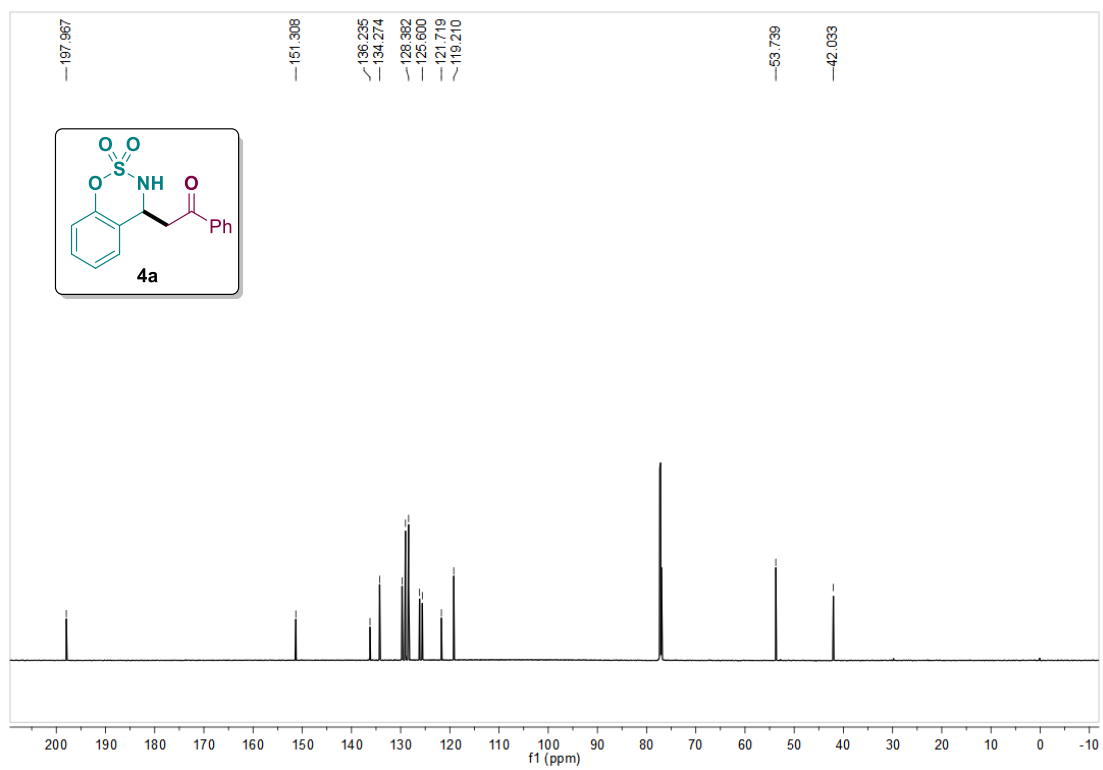
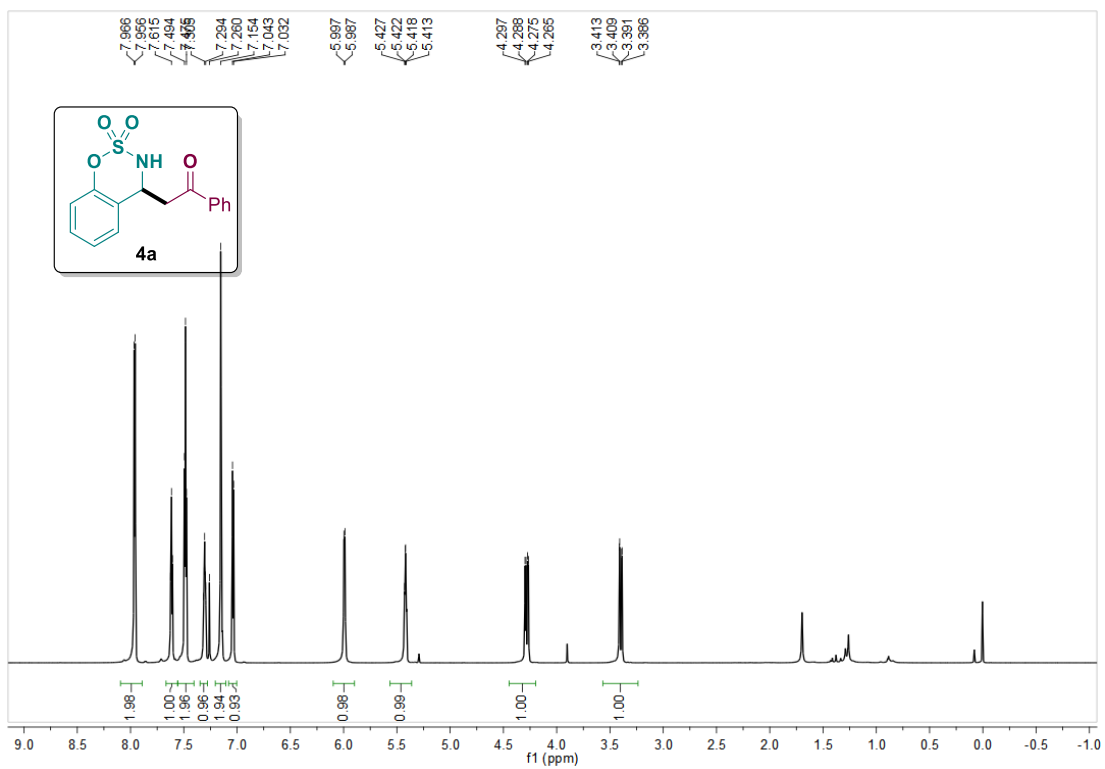
**<sup>13</sup>C NMR Spectrum for 3aa (CDCl<sub>3</sub>, 125 MHz)**



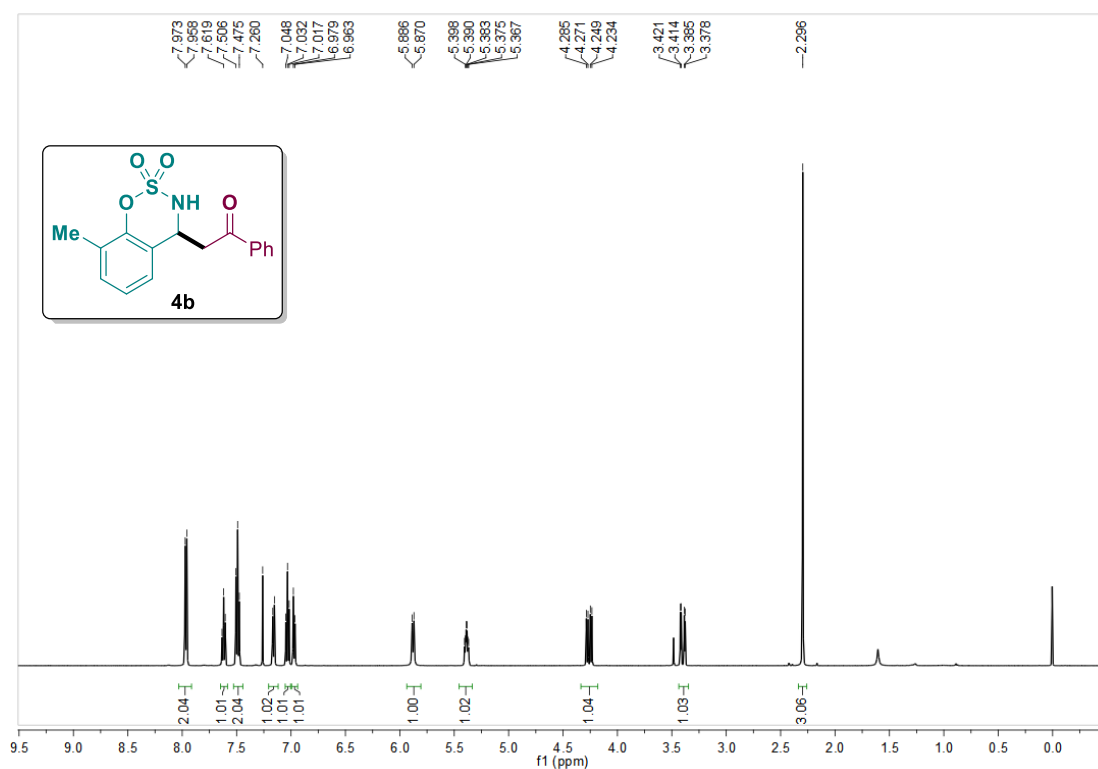
<sup>1</sup>H NMR Spectrum for **3ab** (CDCl<sub>3</sub>, 500 MHz)



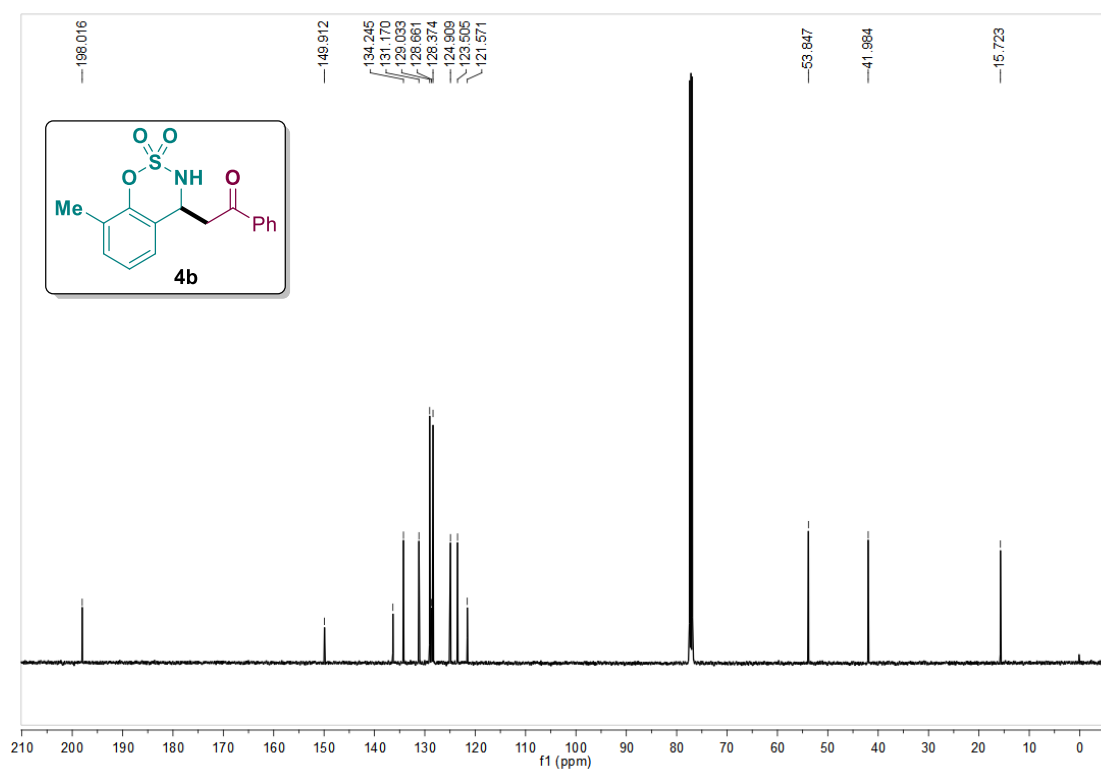
<sup>13</sup>C NMR Spectrum for **3ab** (CDCl<sub>3</sub>, 125 MHz)



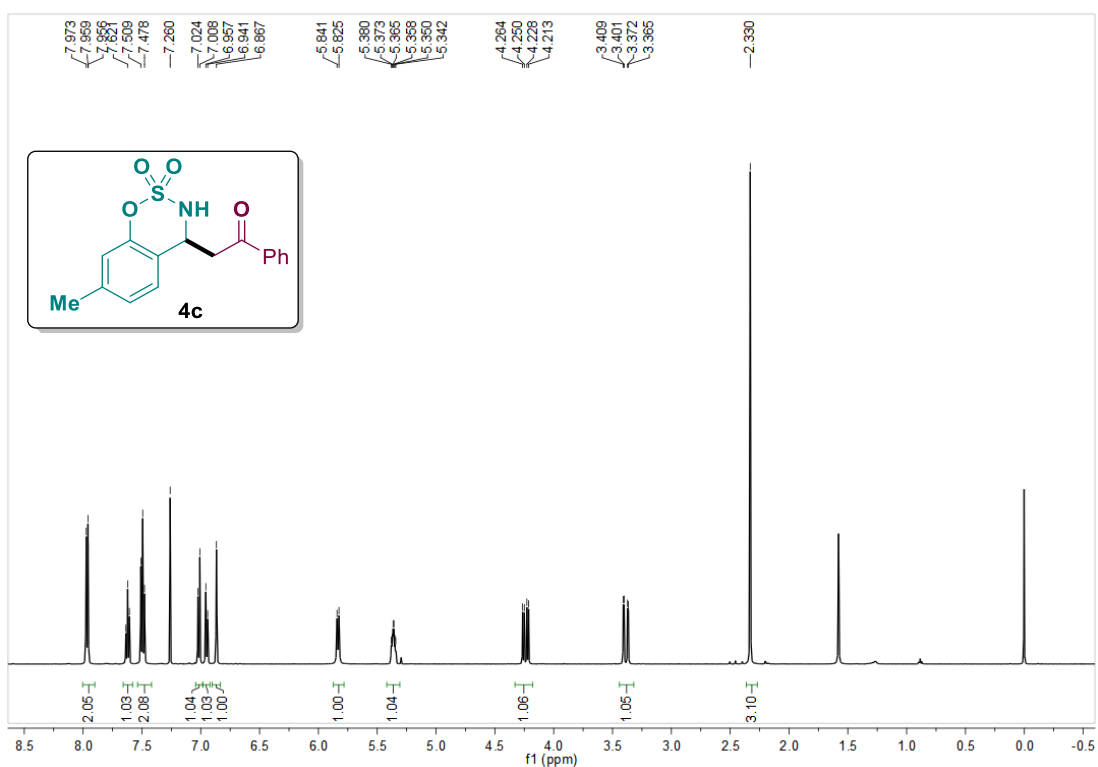




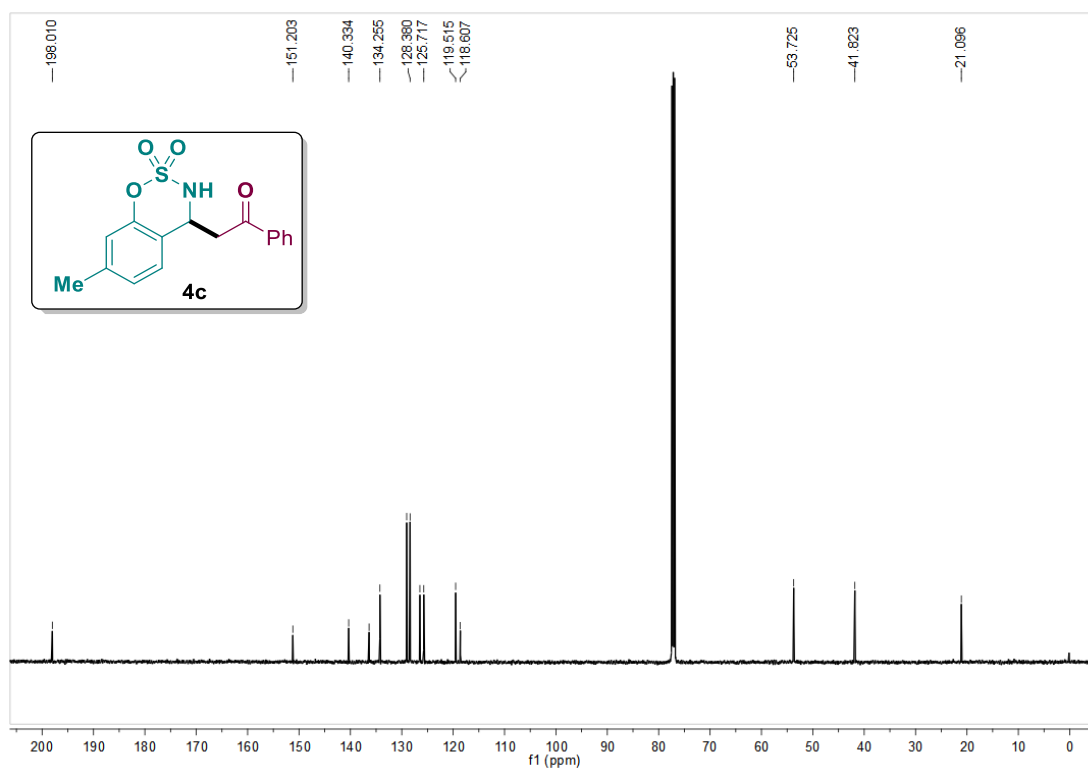
**<sup>1</sup>H NMR Spectrum for 4b (CDCl<sub>3</sub>, 500 MHz)**



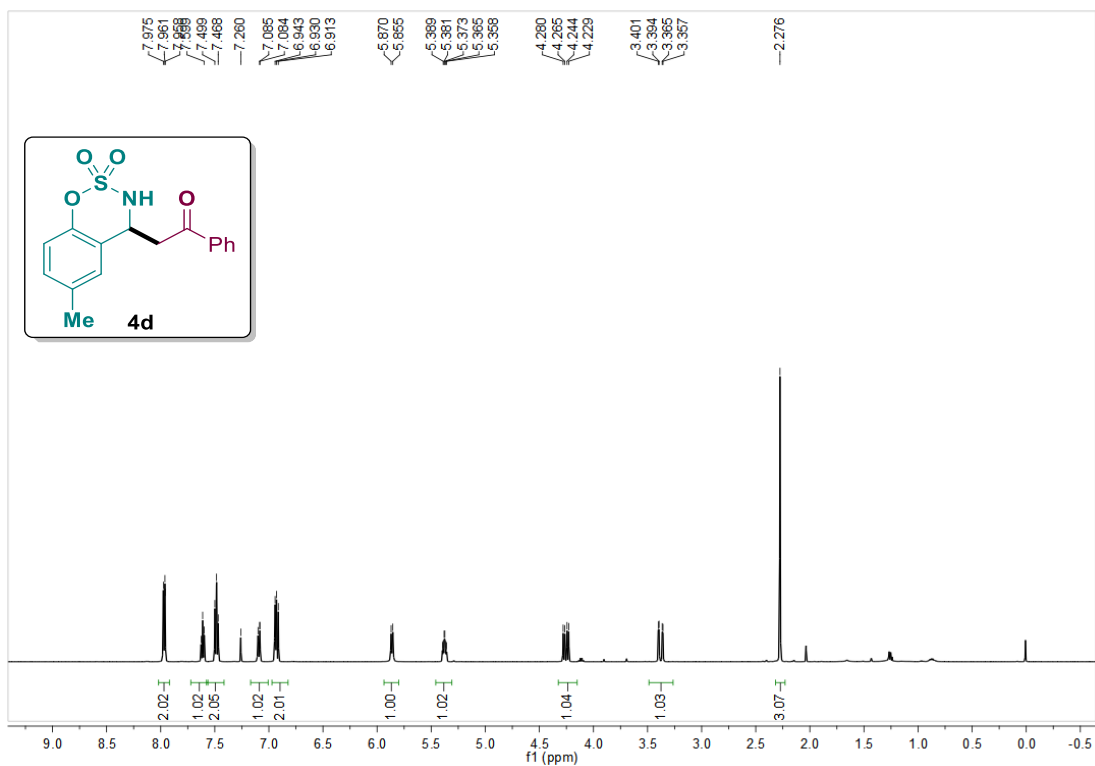
**<sup>13</sup>C NMR Spectrum for 4b (CDCl<sub>3</sub>, 125 MHz)**



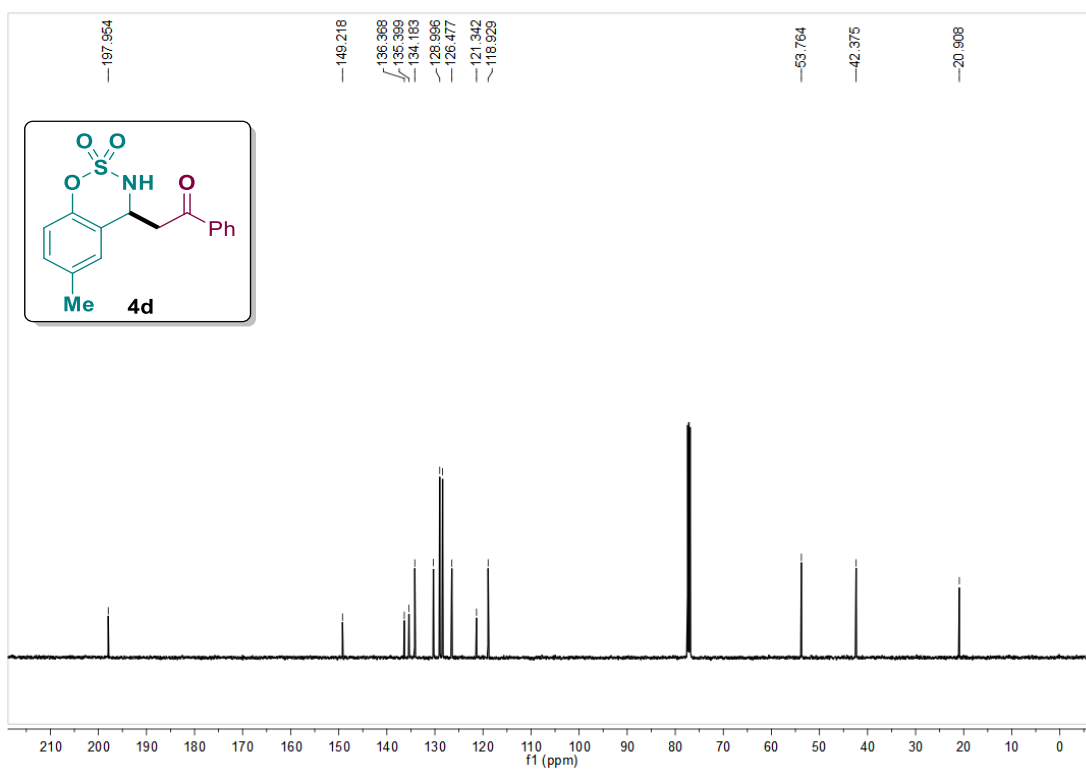
<sup>1</sup>H NMR Spectrum for **4c** (CDCl<sub>3</sub>, 500 MHz)



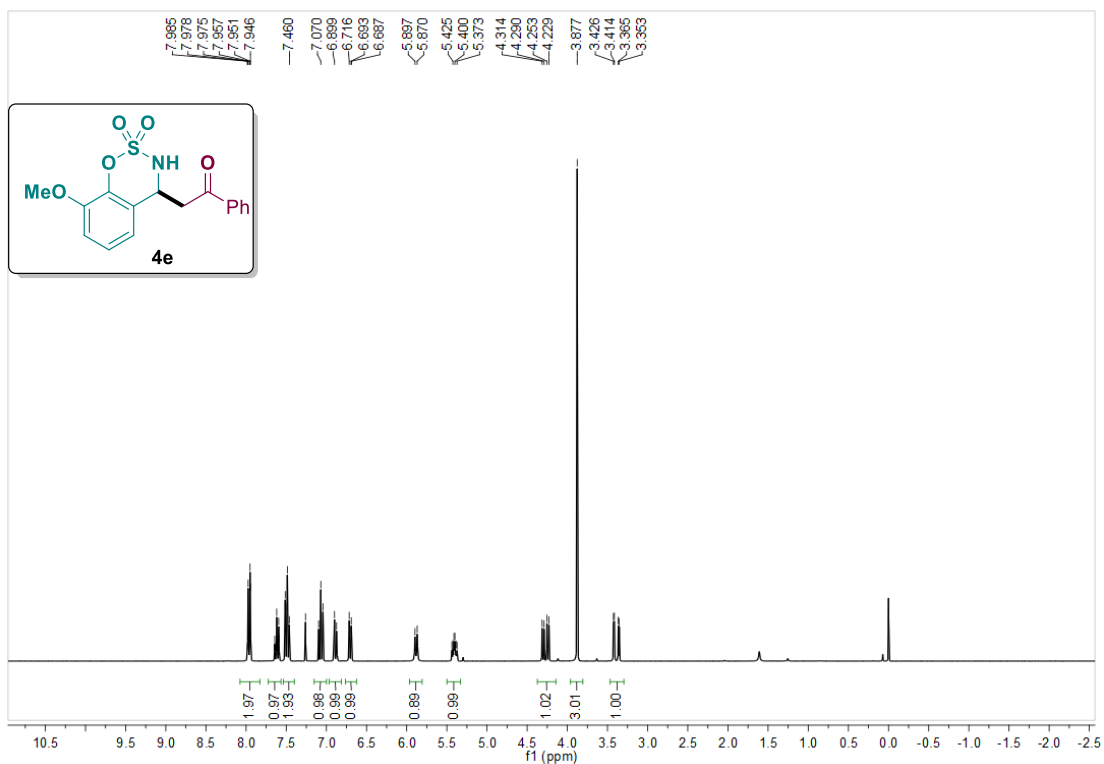
<sup>13</sup>C NMR Spectrum for **4c** (CDCl<sub>3</sub>, 125 MHz)



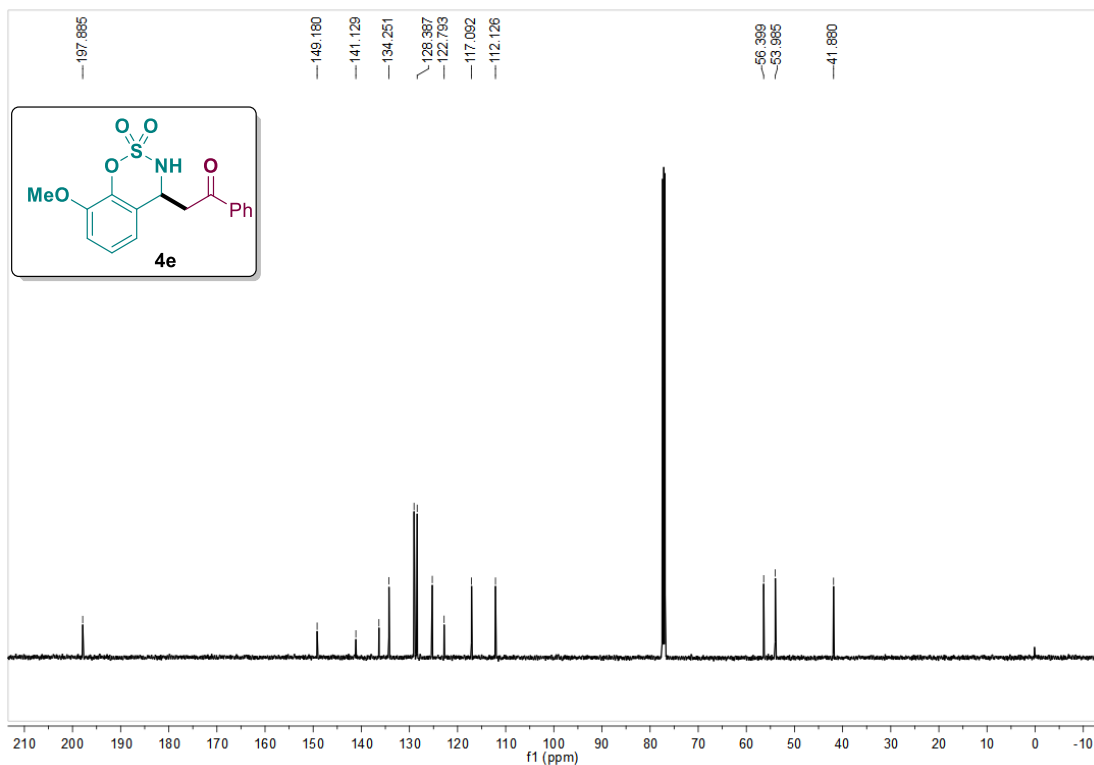
<sup>1</sup>H NMR Spectrum for **4d** (CDCl<sub>3</sub>, 500 MHz)



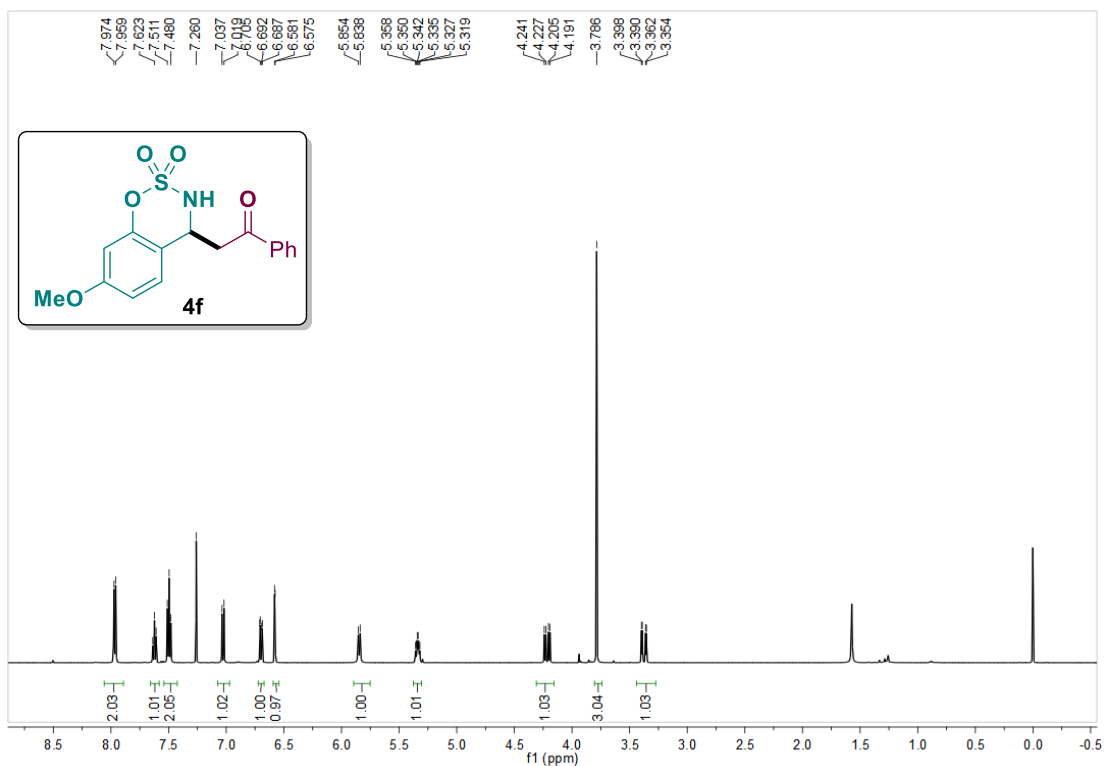
<sup>13</sup>C NMR Spectrum for **4d** (CDCl<sub>3</sub>, 125 MHz)



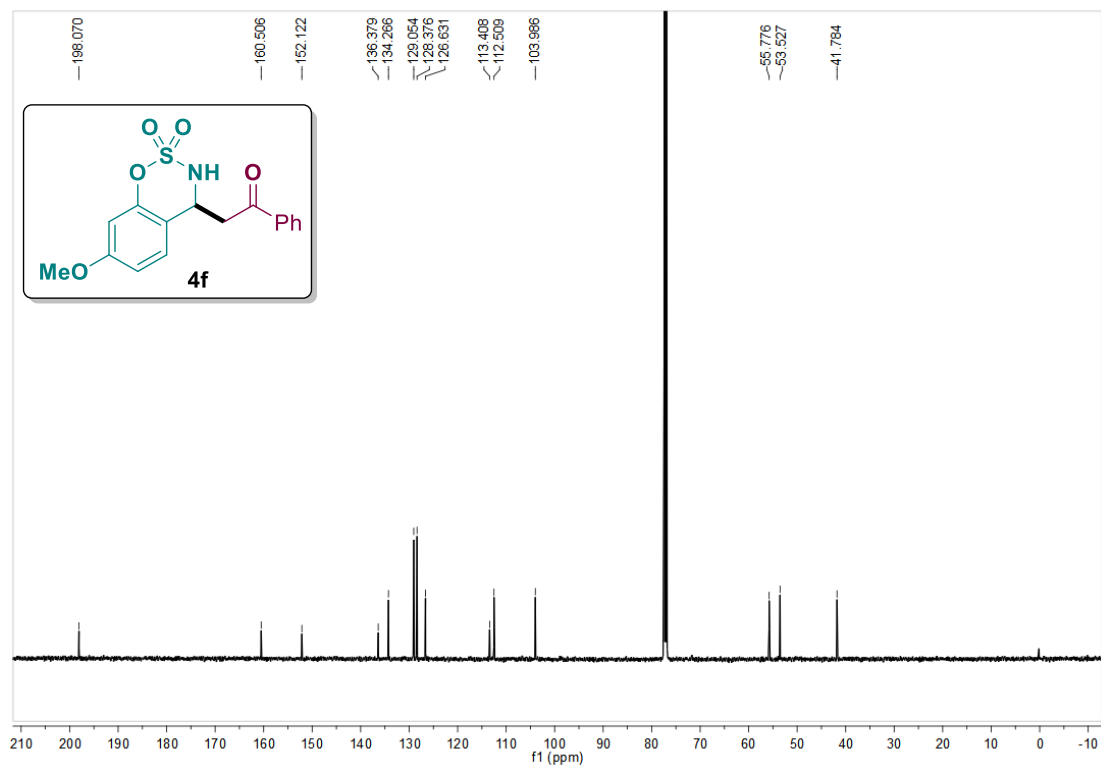
<sup>1</sup>H NMR Spectrum for 4e (CDCl<sub>3</sub>, 500 MHz)



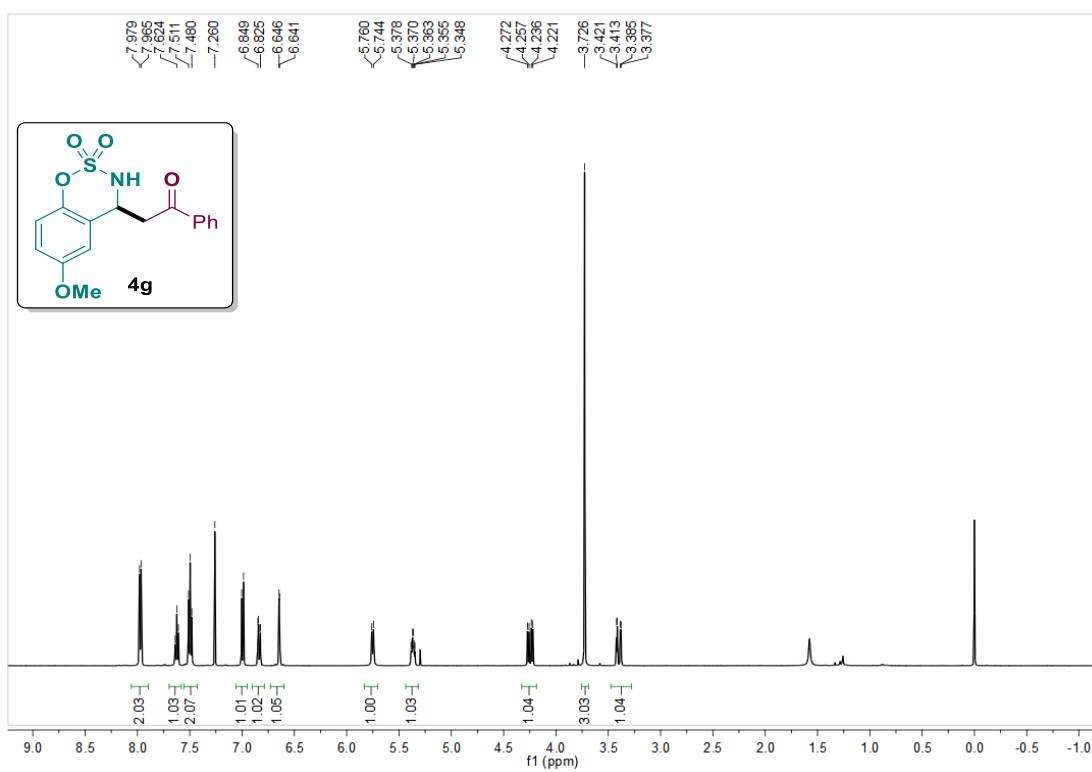
<sup>13</sup>C NMR Spectrum for 4e (CDCl<sub>3</sub>, 125 MHz)



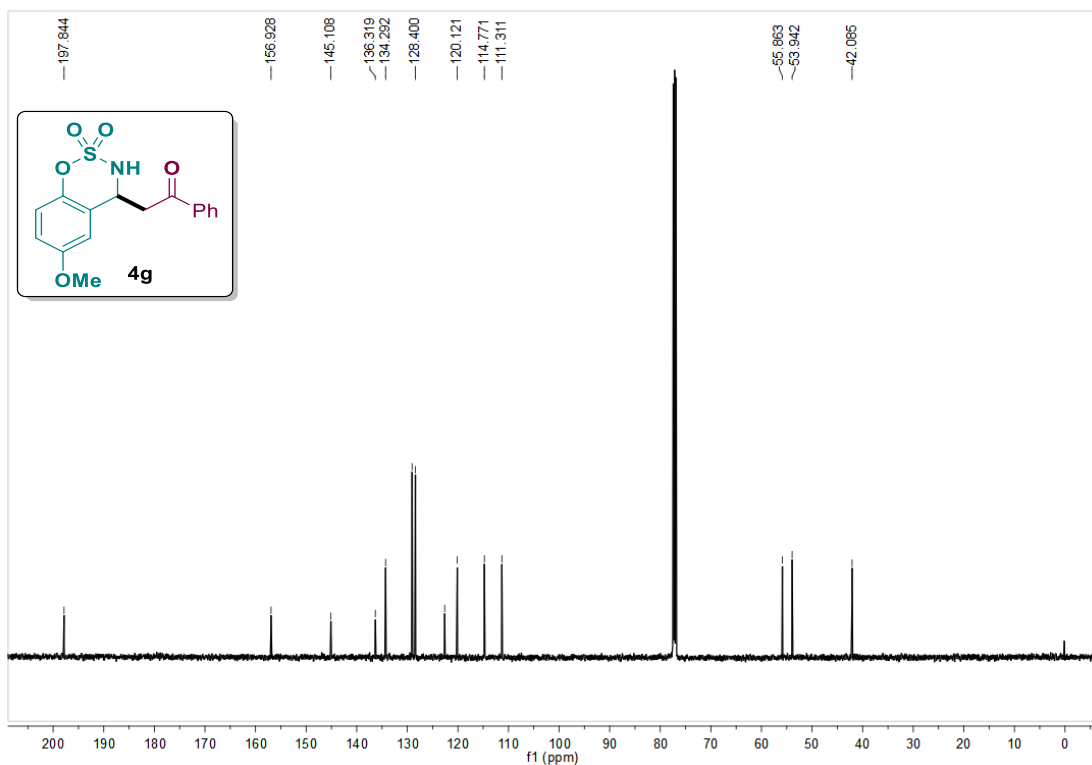
<sup>1</sup>H NMR Spectrum for **4f** (CDCl<sub>3</sub>, 500 MHz)



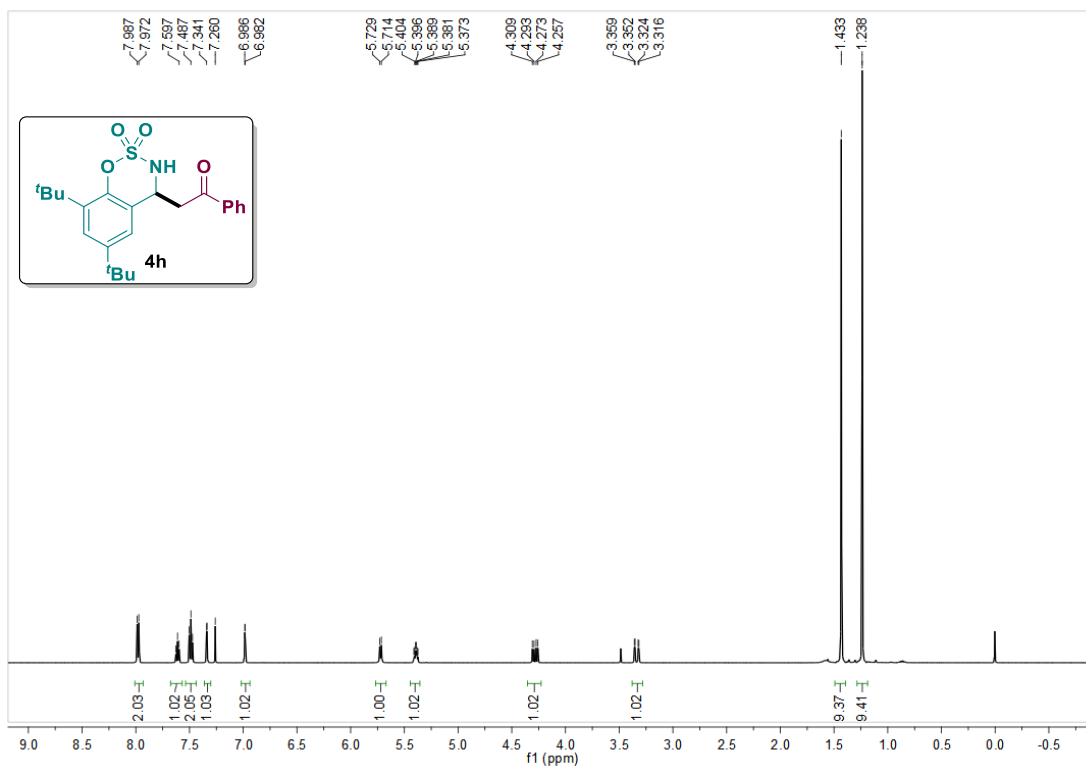
<sup>13</sup>C NMR Spectrum for **4f** (CDCl<sub>3</sub>, 125 MHz)



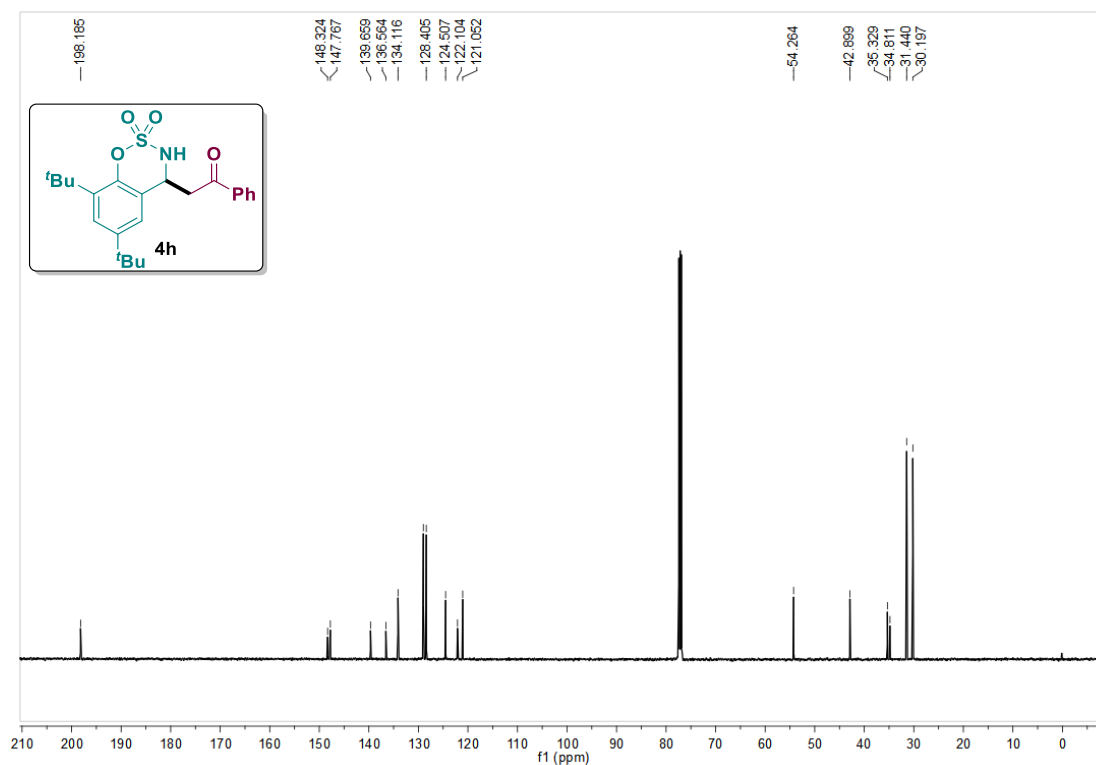
$^1\text{H}$  NMR Spectrum for **4g** ( $\text{CDCl}_3$ , 500 MHz)



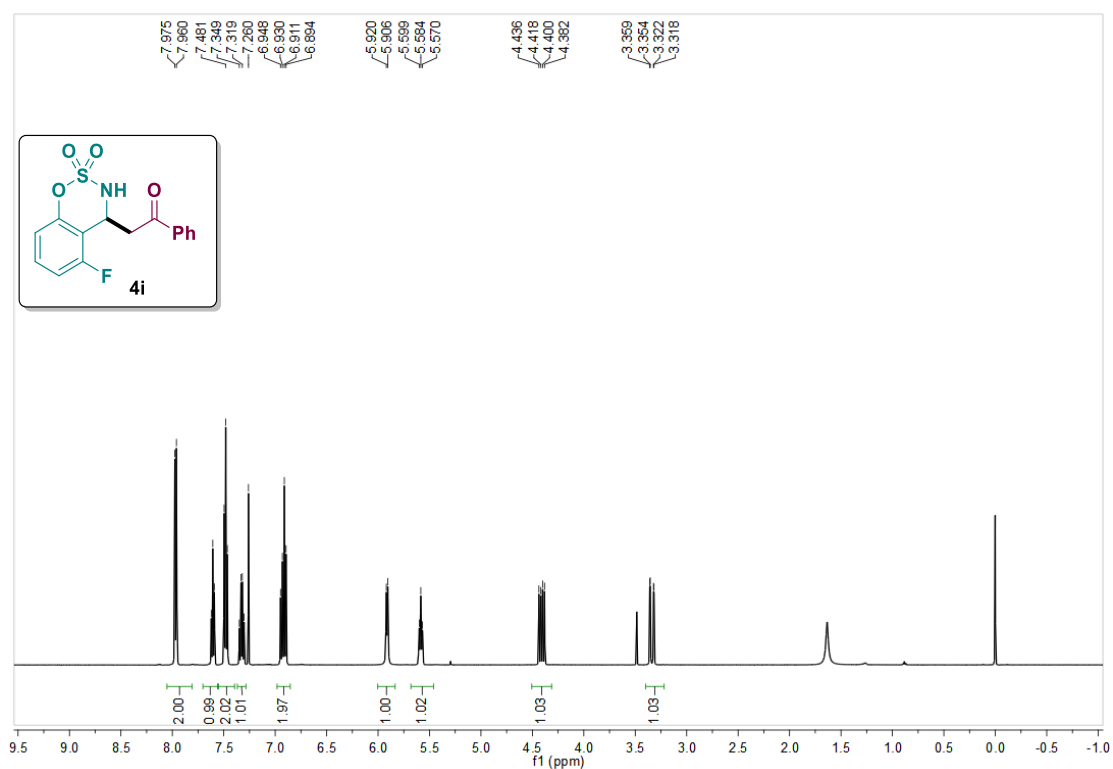
$^{13}\text{C}$  NMR Spectrum for **4g** ( $\text{CDCl}_3$ , 125 MHz)



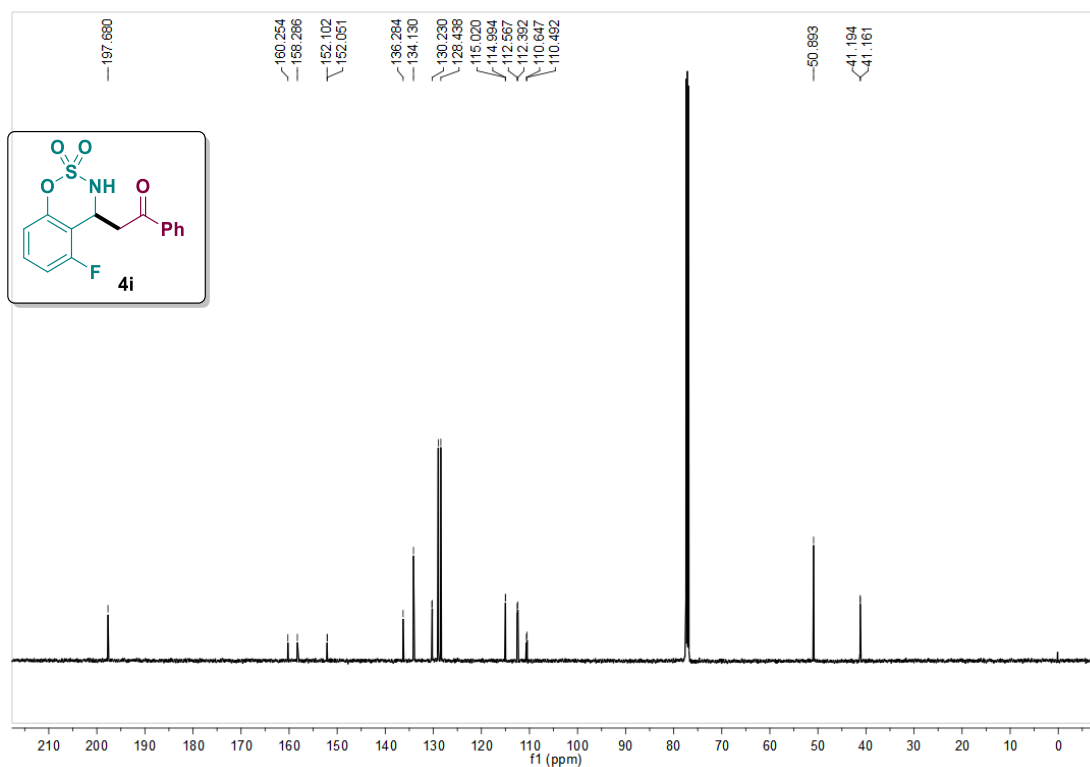
<sup>1</sup>H NMR Spectrum for **4h** (CDCl<sub>3</sub>, 500 MHz)



<sup>13</sup>C NMR Spectrum for **4h** (CDCl<sub>3</sub>, 125 MHz)

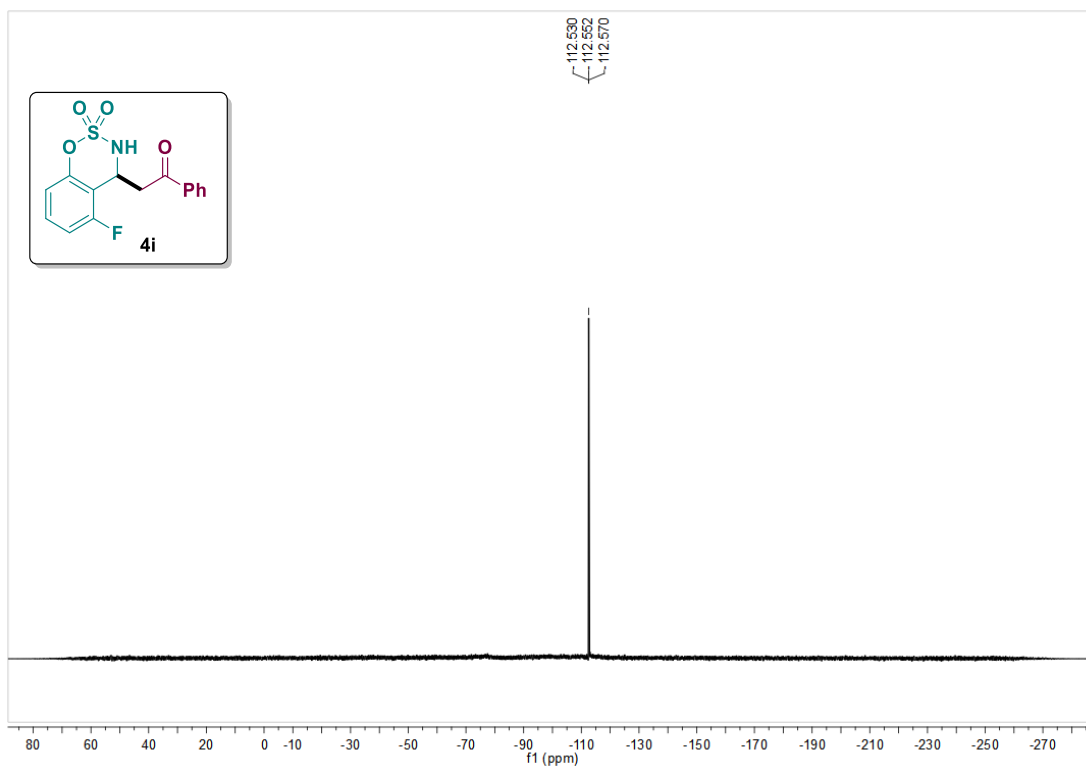


<sup>1</sup>H NMR Spectrum for 4i (CDCl<sub>3</sub>, 500 MHz)

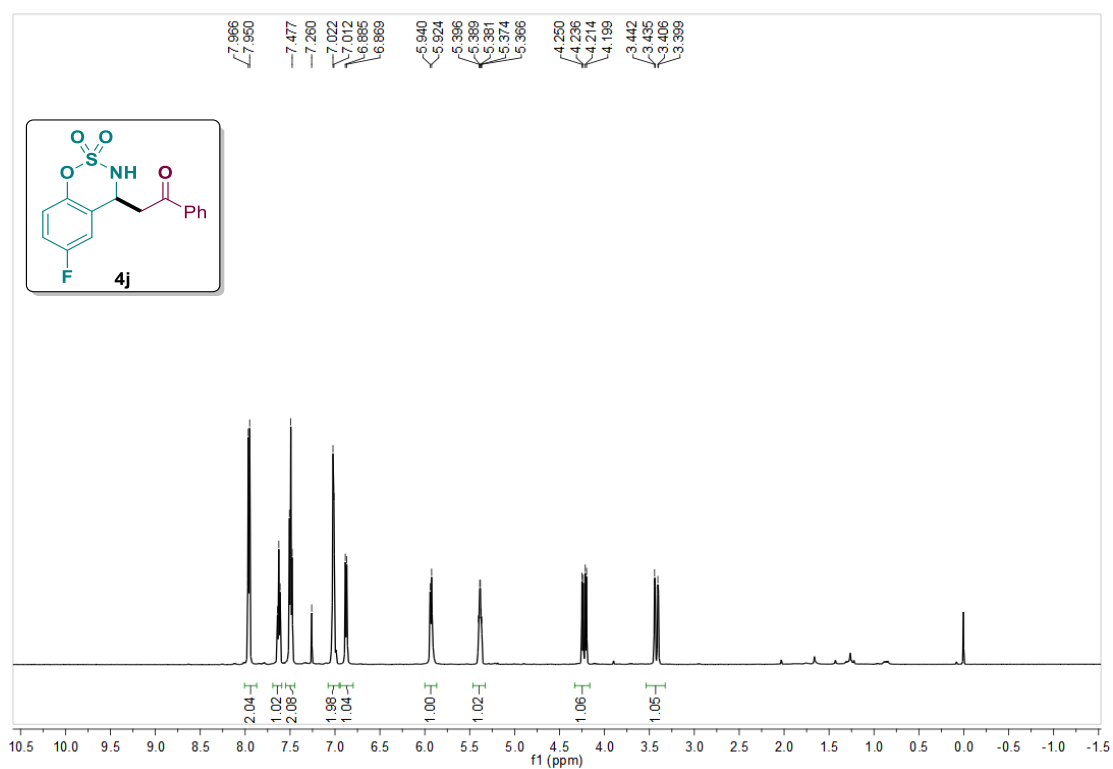


<sup>13</sup>C NMR Spectrum for 4i (CDCl<sub>3</sub>, 125 MHz)

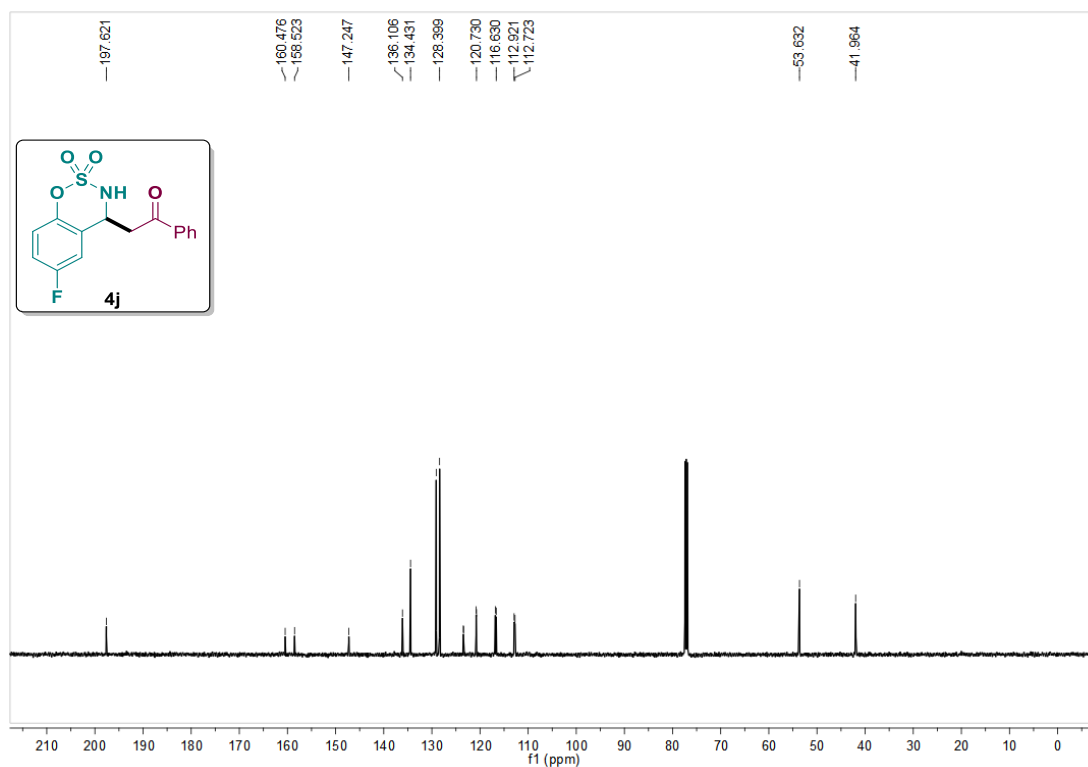




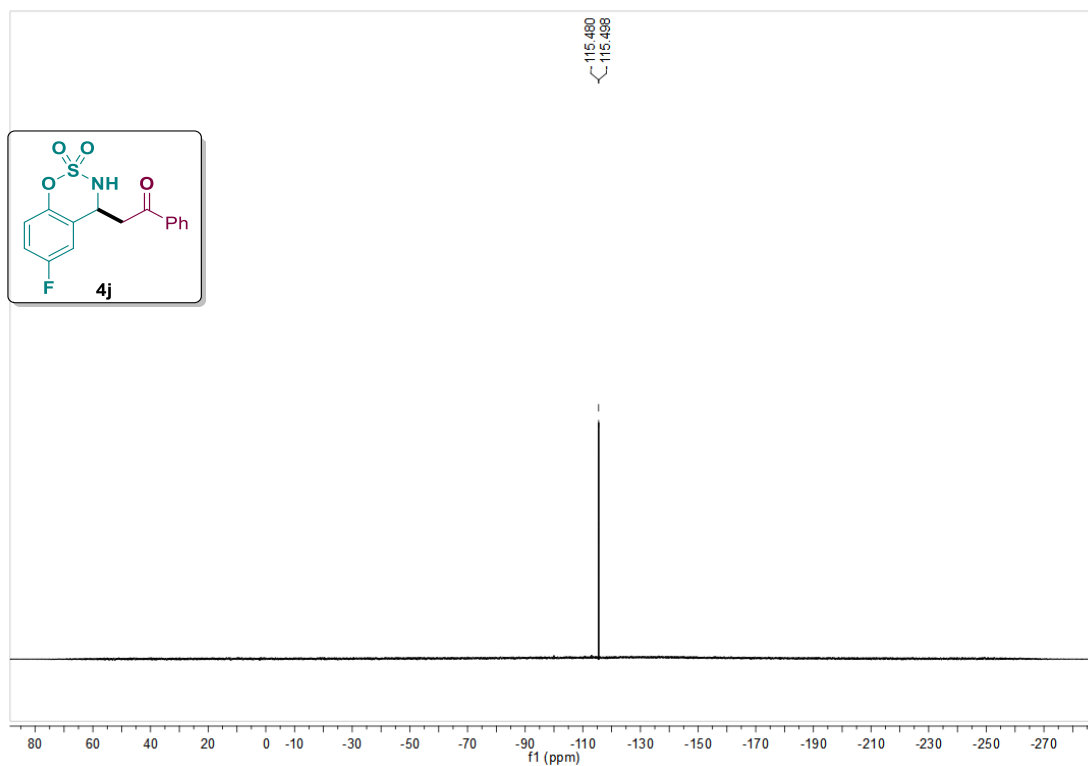
$^{19}\text{F}$  NMR Spectrum for **4i** ( $\text{CDCl}_3$ , 376 MHz)



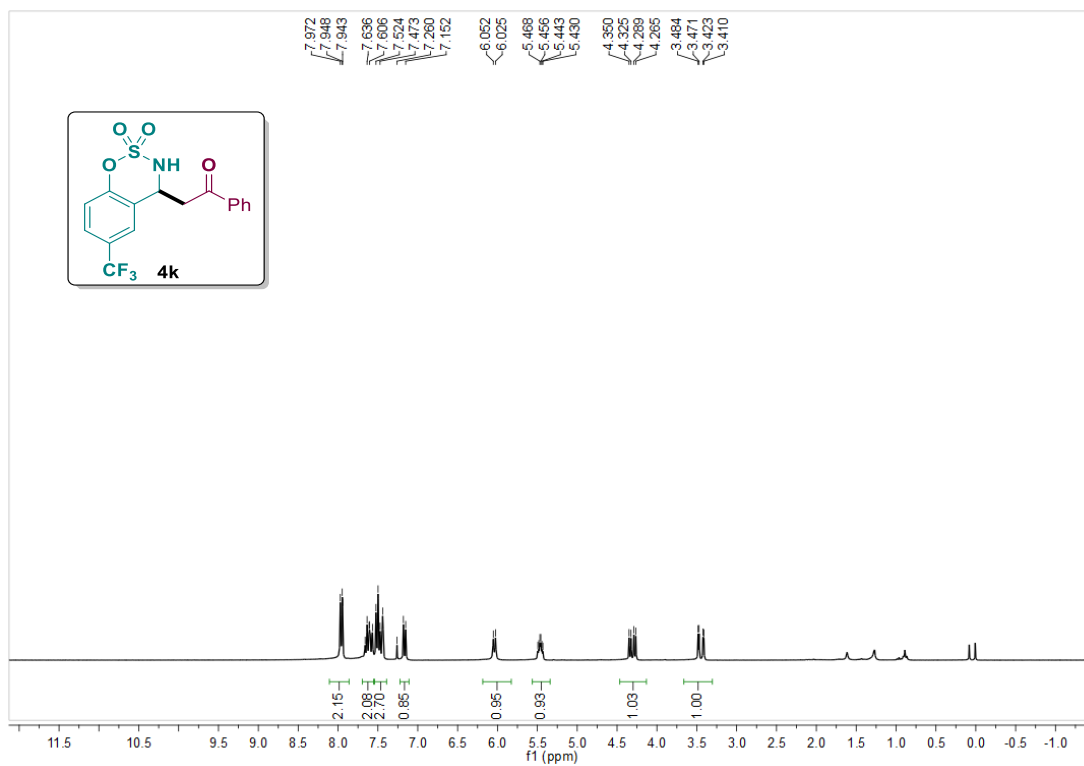
$^1\text{H}$  NMR Spectrum for **4j** ( $\text{CDCl}_3$ , 500 MHz)



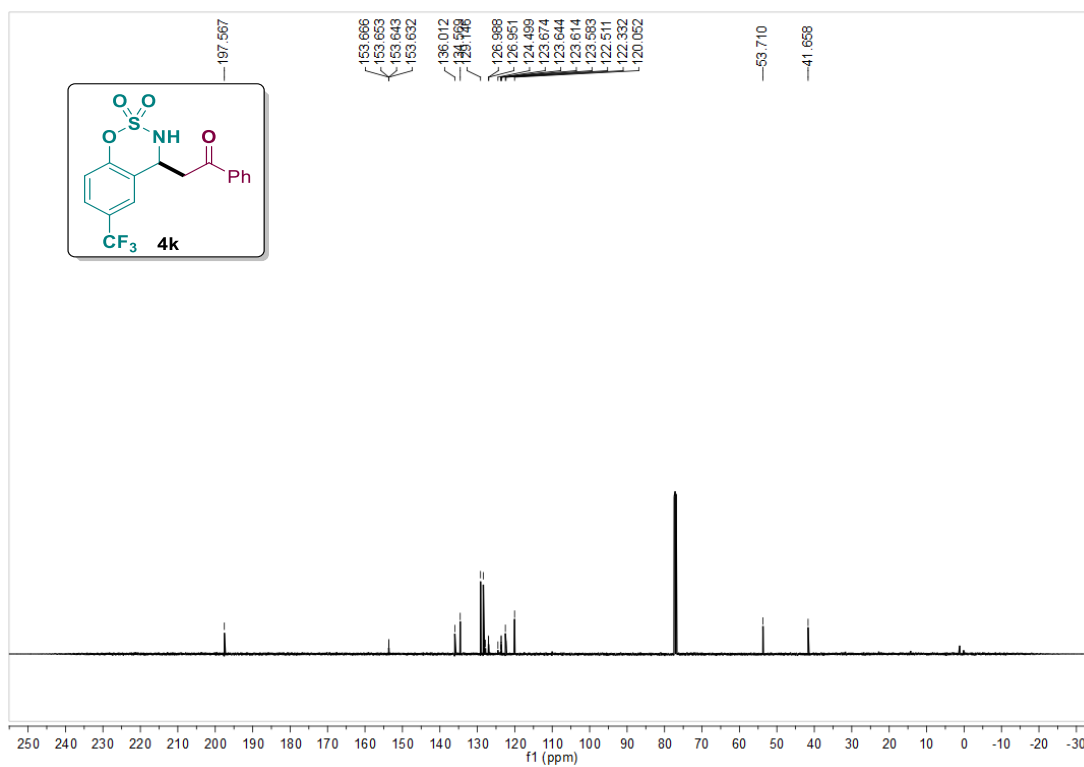
$^{13}\text{C}$  NMR Spectrum for **4j** ( $\text{CDCl}_3$ , 125 MHz)



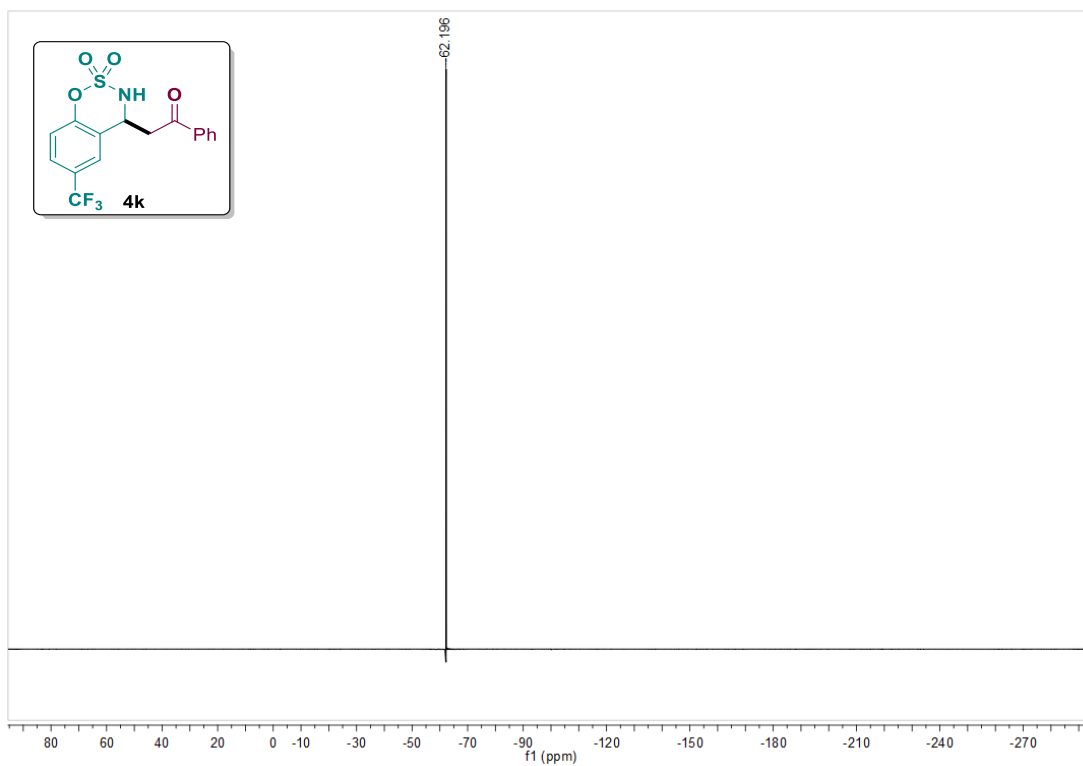
$^{19}\text{F}$  NMR Spectrum for **4j** ( $\text{CDCl}_3$ , 376 MHz)



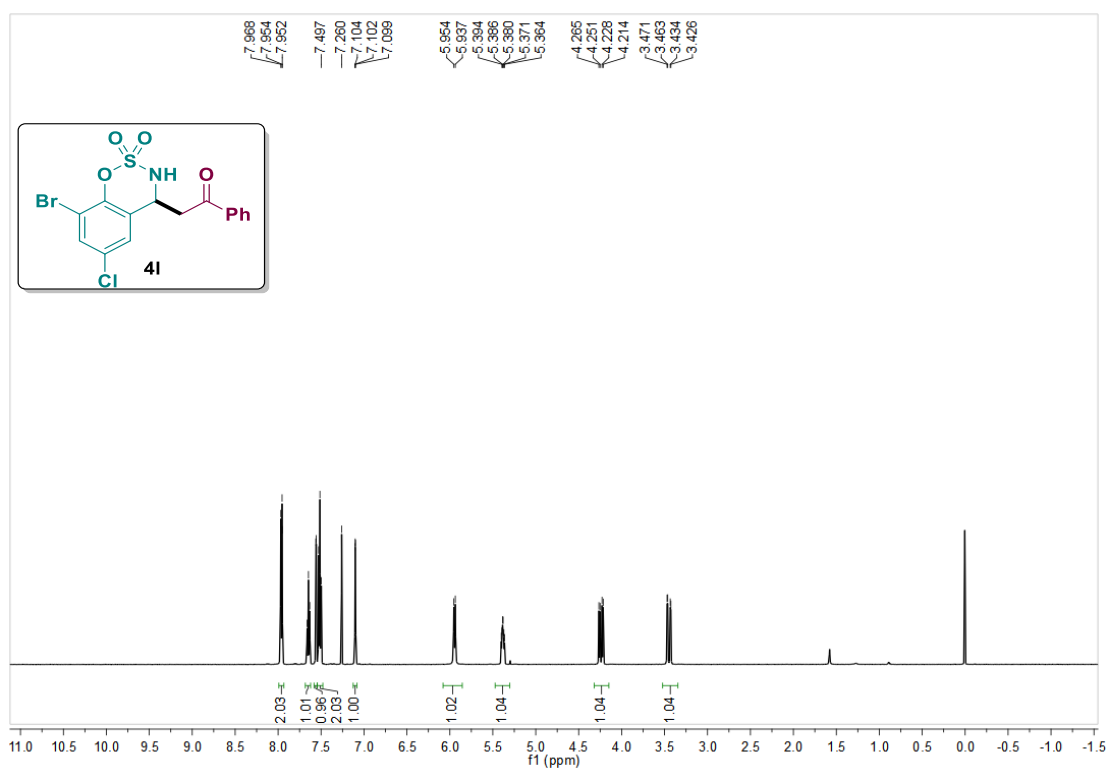
<sup>1</sup>H NMR Spectrum for 4k (CDCl<sub>3</sub>, 300 MHz)



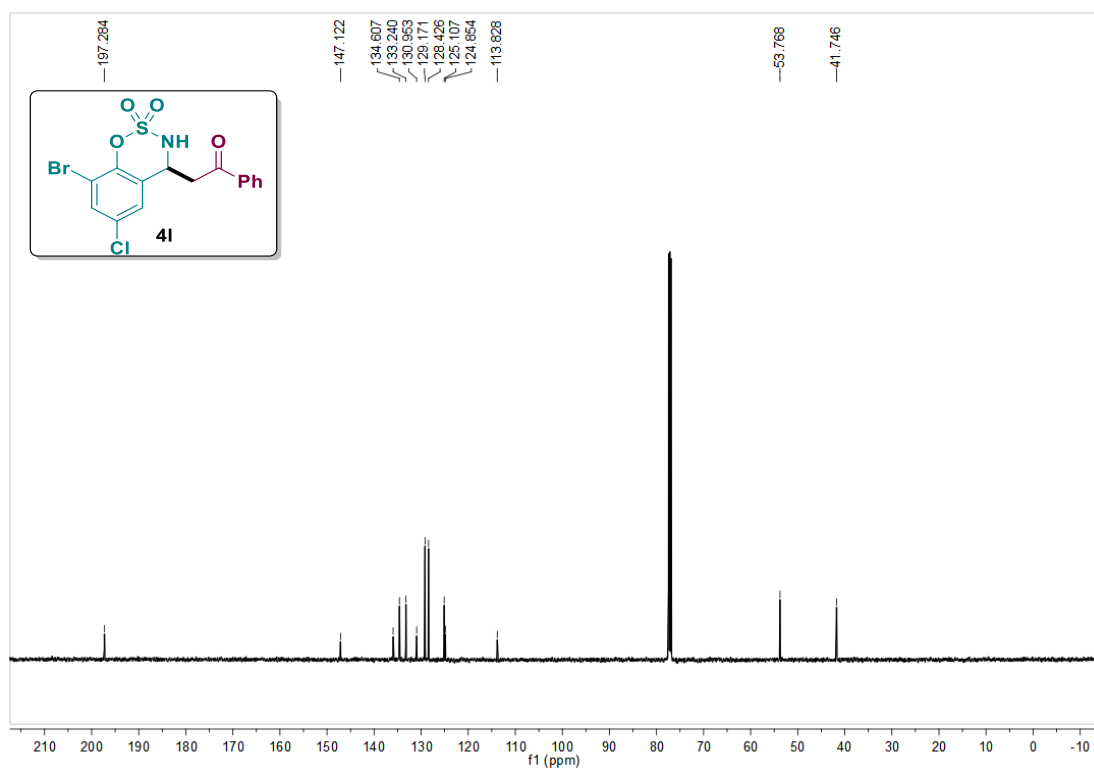
<sup>13</sup>C NMR Spectrum for 4k (CDCl<sub>3</sub>, 125 MHz)



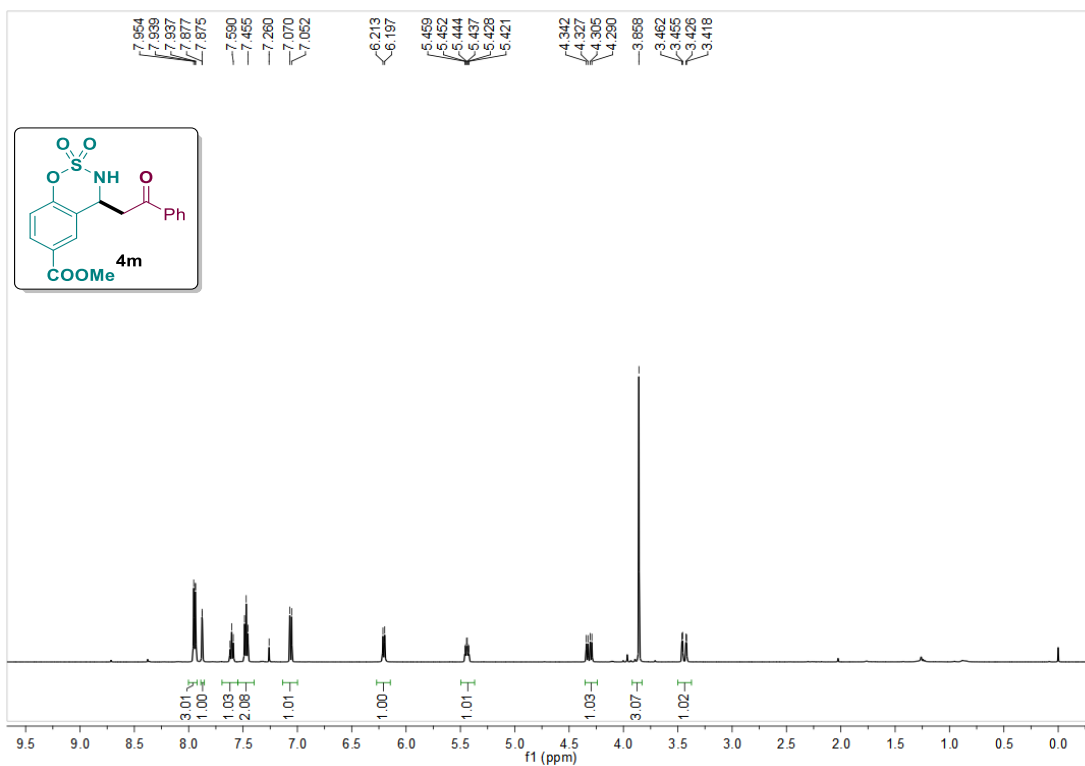
$^{19}\text{F}$  NMR Spectrum for **4k** ( $\text{CDCl}_3$ , 470 MHz)



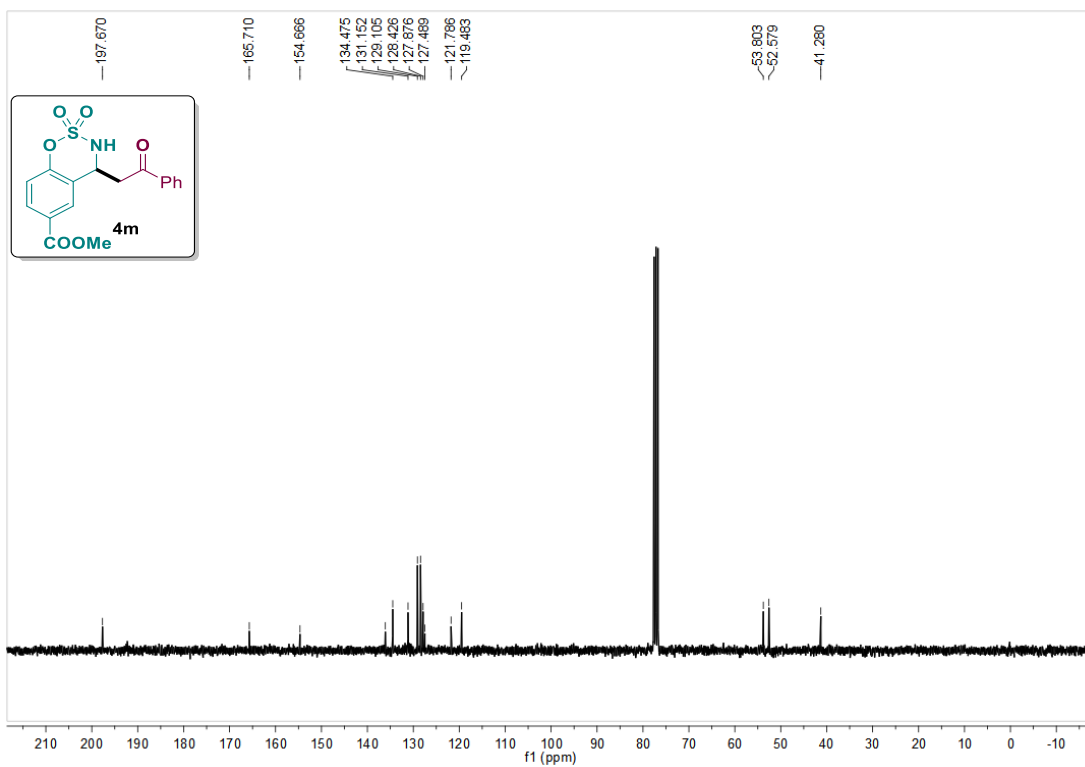
<sup>1</sup>H NMR Spectrum for **4I** (CDCl<sub>3</sub>, 500 MHz)



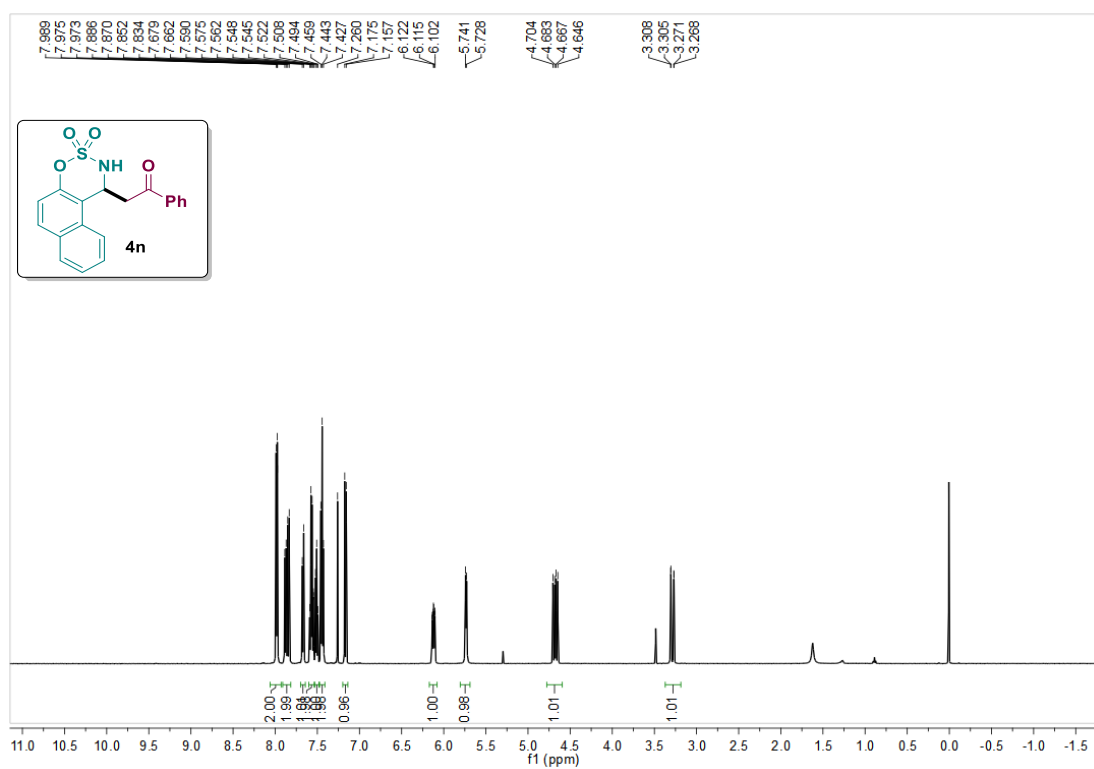
<sup>13</sup>C NMR Spectrum for **4I** (CDCl<sub>3</sub>, 125 MHz)



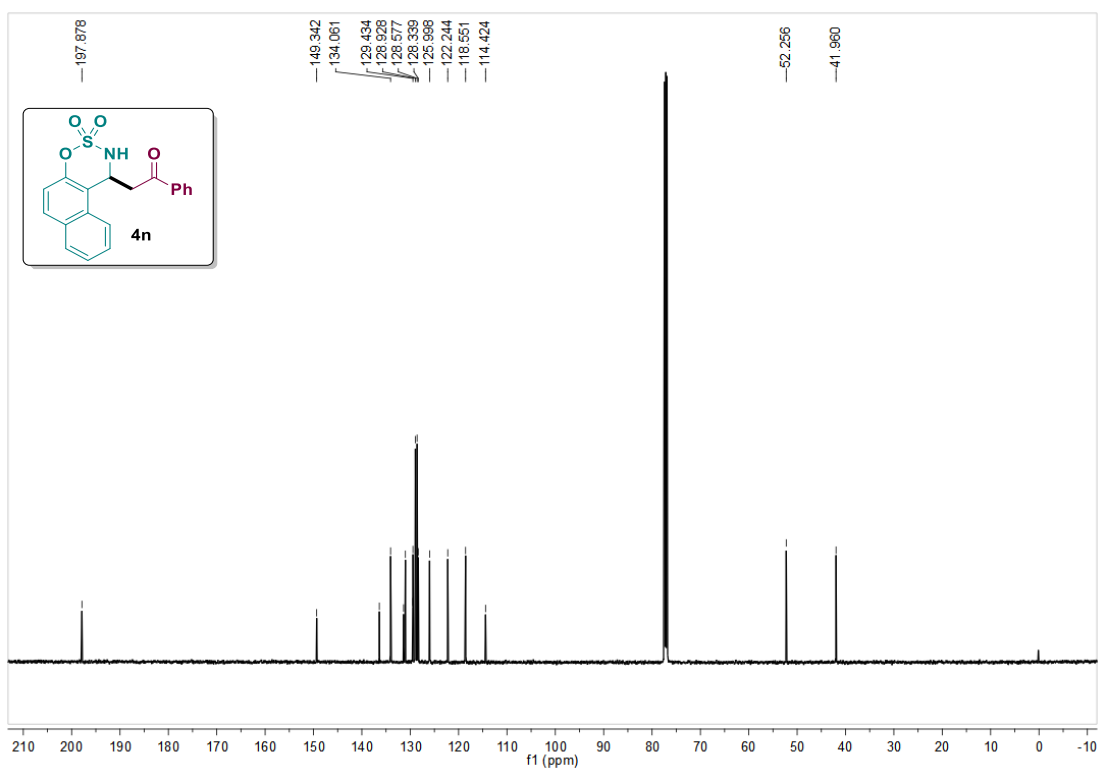
<sup>1</sup>H NMR Spectrum for **4m** (CDCl<sub>3</sub>, 500 MHz)



<sup>13</sup>C NMR Spectrum for **4m** (CDCl<sub>3</sub>, 75 MHz)

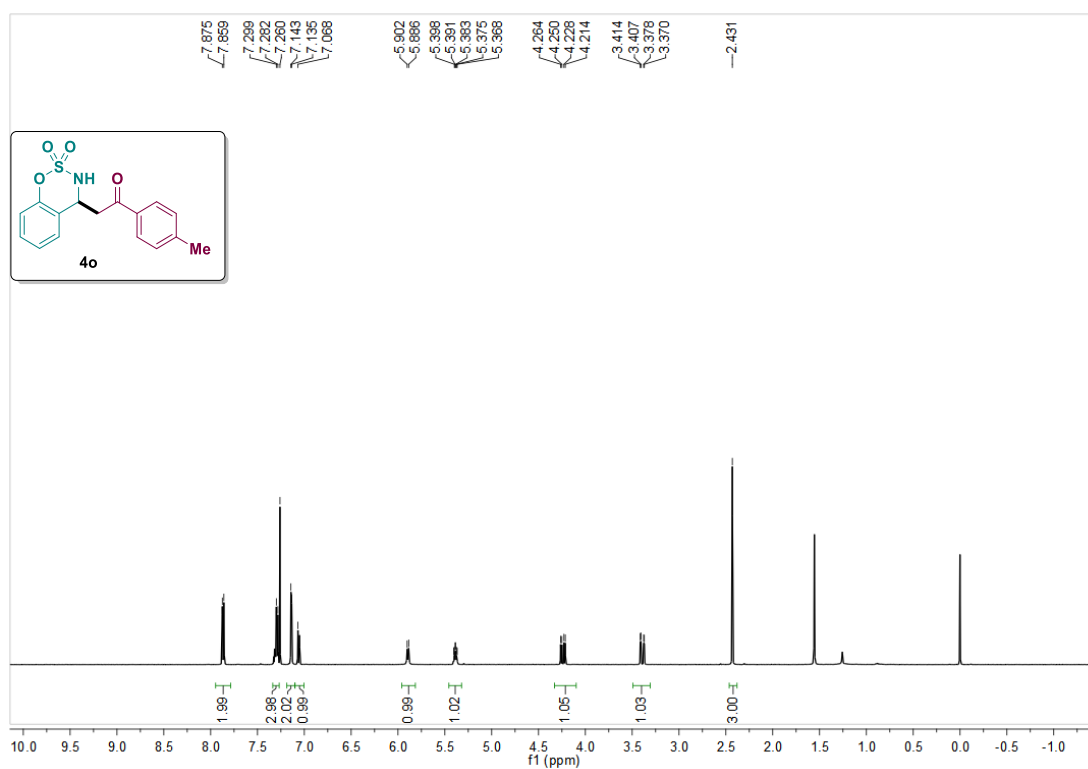


<sup>1</sup>H NMR Spectrum for 4n (CDCl<sub>3</sub>, 500 MHz)

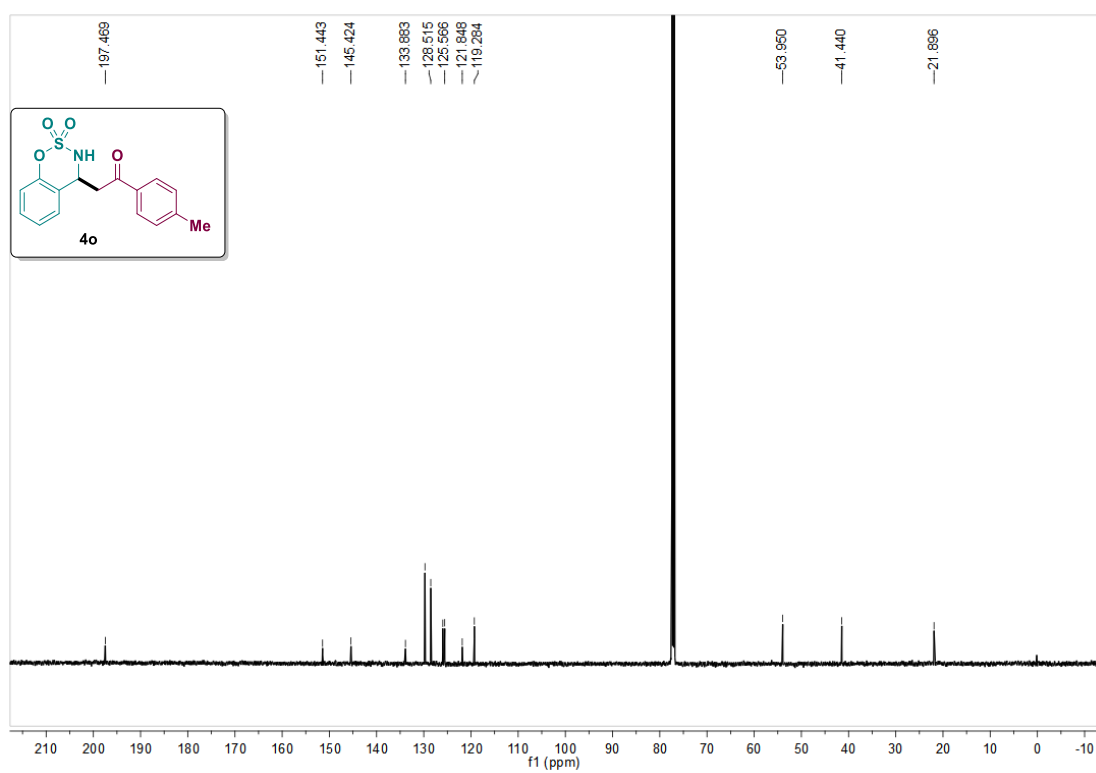


<sup>13</sup>C NMR Spectrum for 4n (CDCl<sub>3</sub>, 125 MHz)

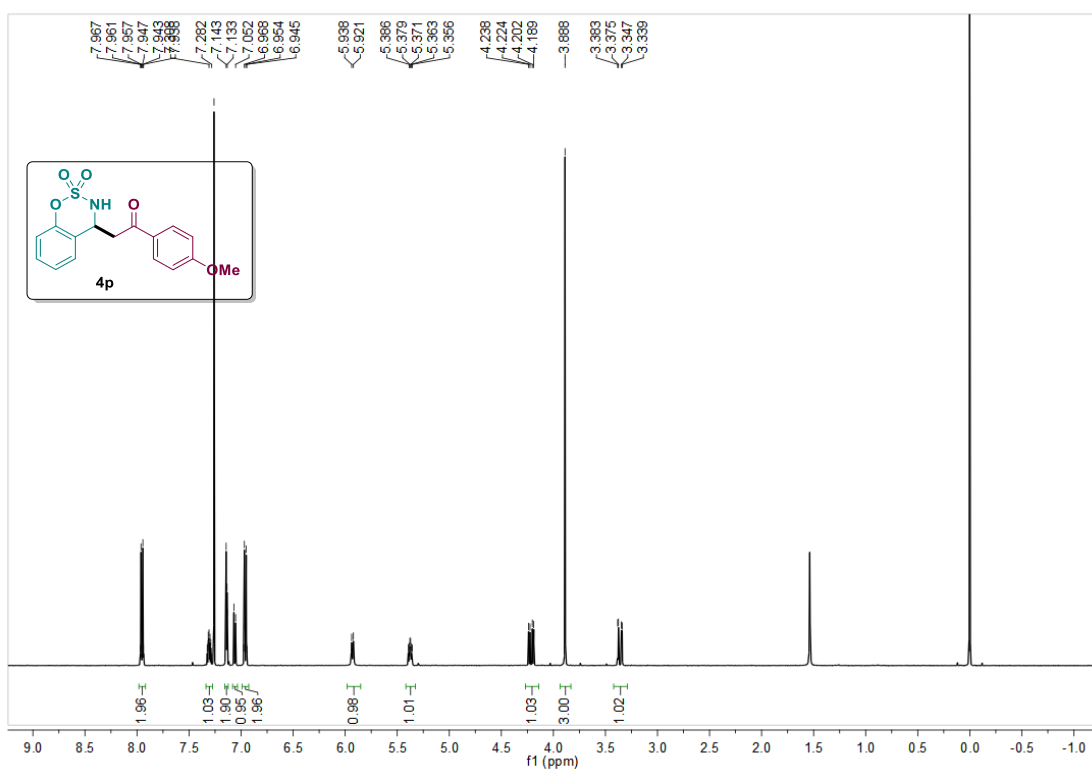




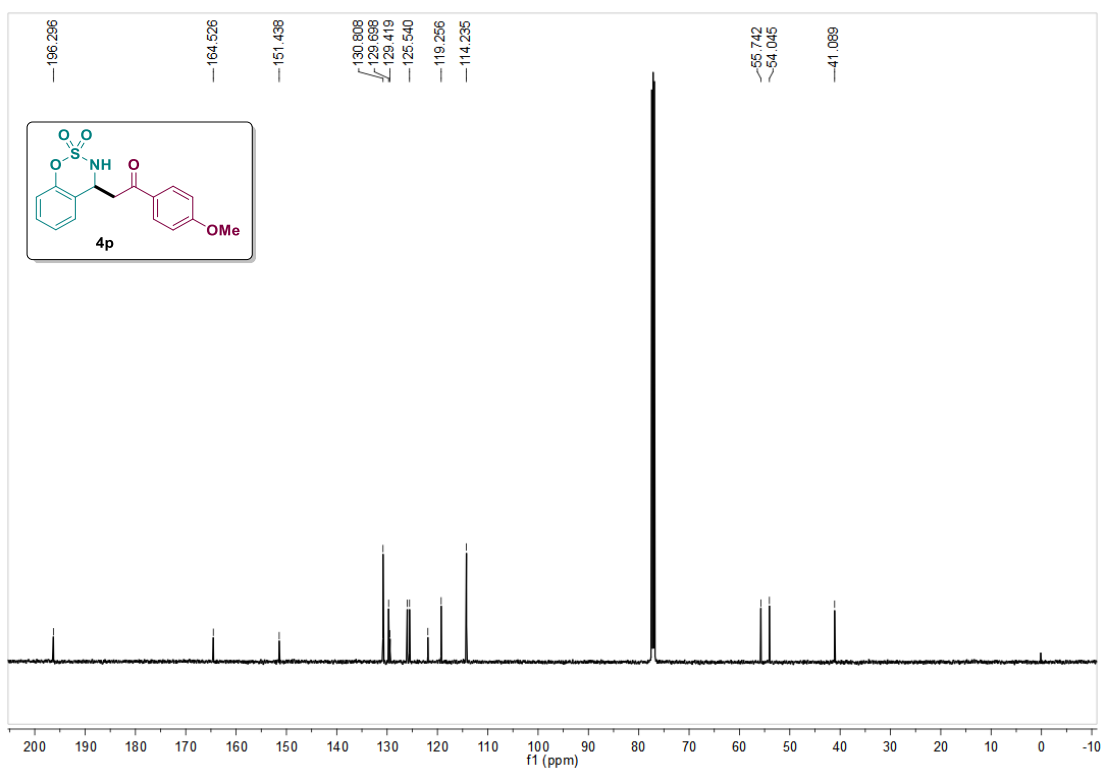
<sup>1</sup>H NMR Spectrum for **4o** (CDCl<sub>3</sub>, 500 MHz)



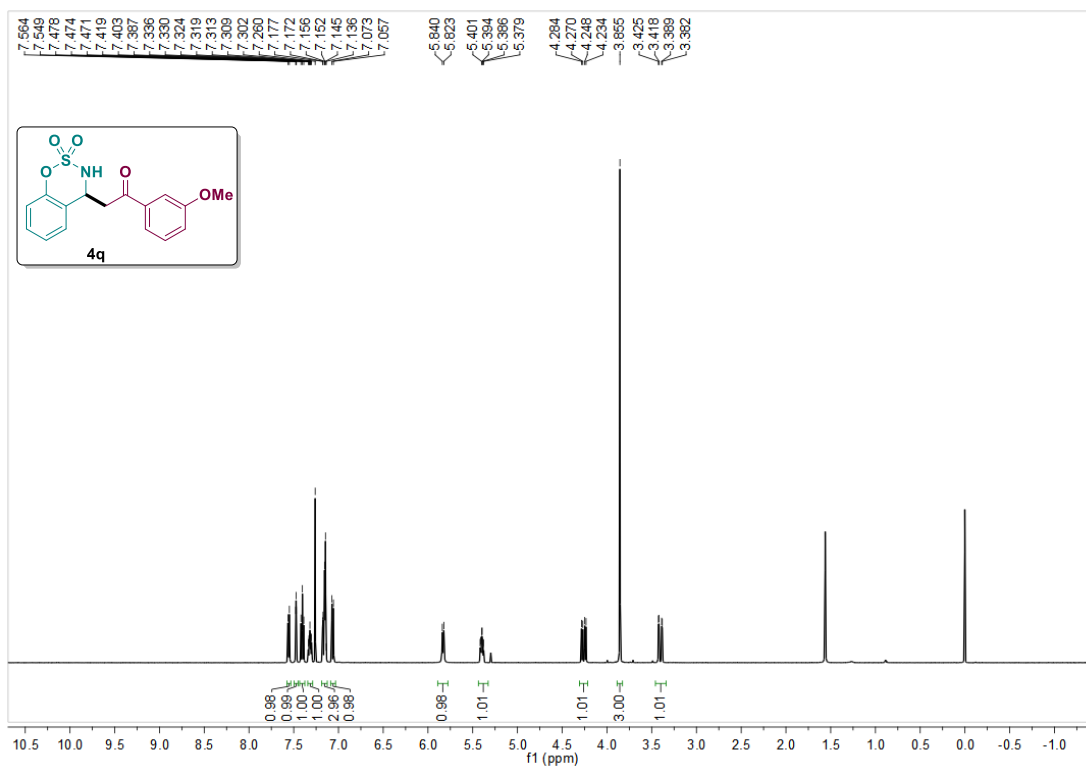
<sup>13</sup>C NMR Spectrum for **4o** (CDCl<sub>3</sub>, 125 MHz)



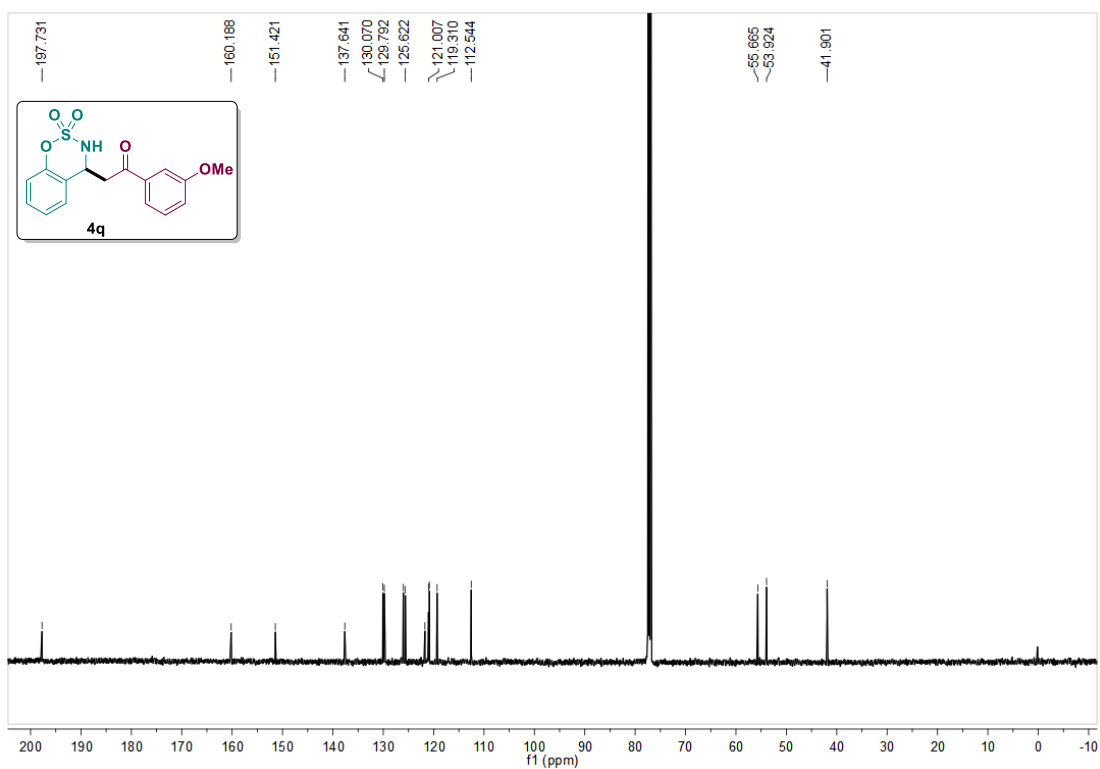
**<sup>1</sup>H NMR Spectrum for 4p (CDCl<sub>3</sub>, 500 MHz)**



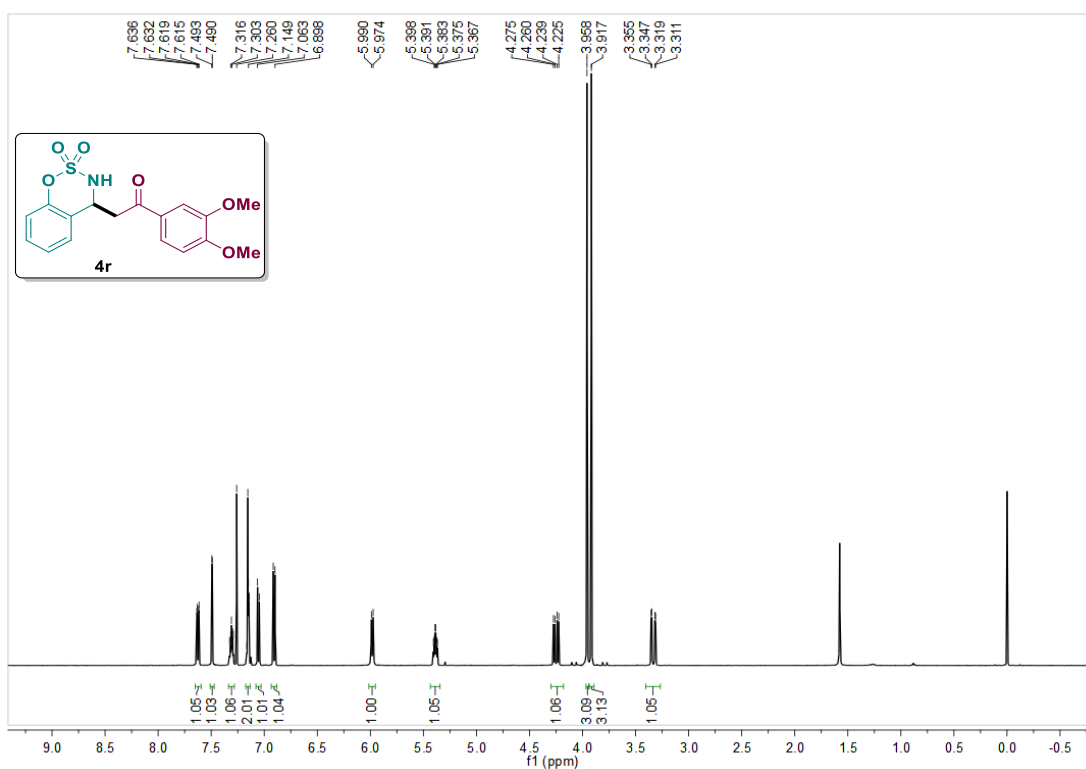
**<sup>13</sup>C NMR Spectrum for 4p (CDCl<sub>3</sub>, 125 MHz)**



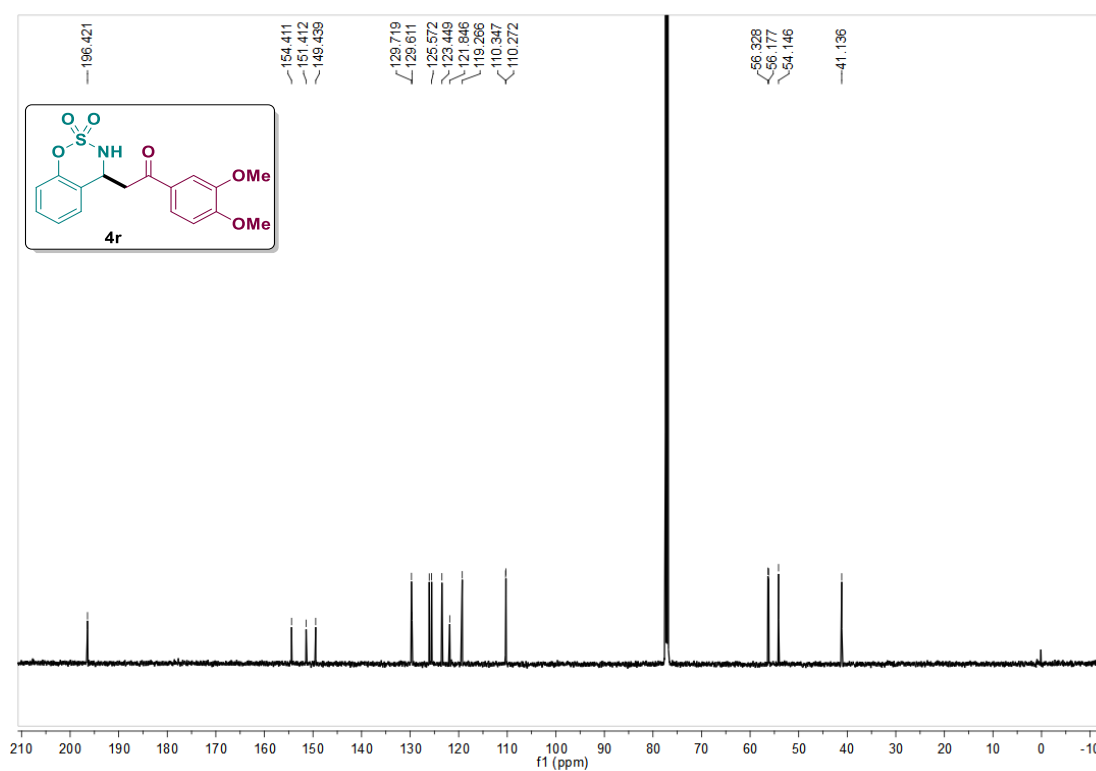
<sup>1</sup>H NMR Spectrum for **4q** (CDCl<sub>3</sub>, 500 MHz)



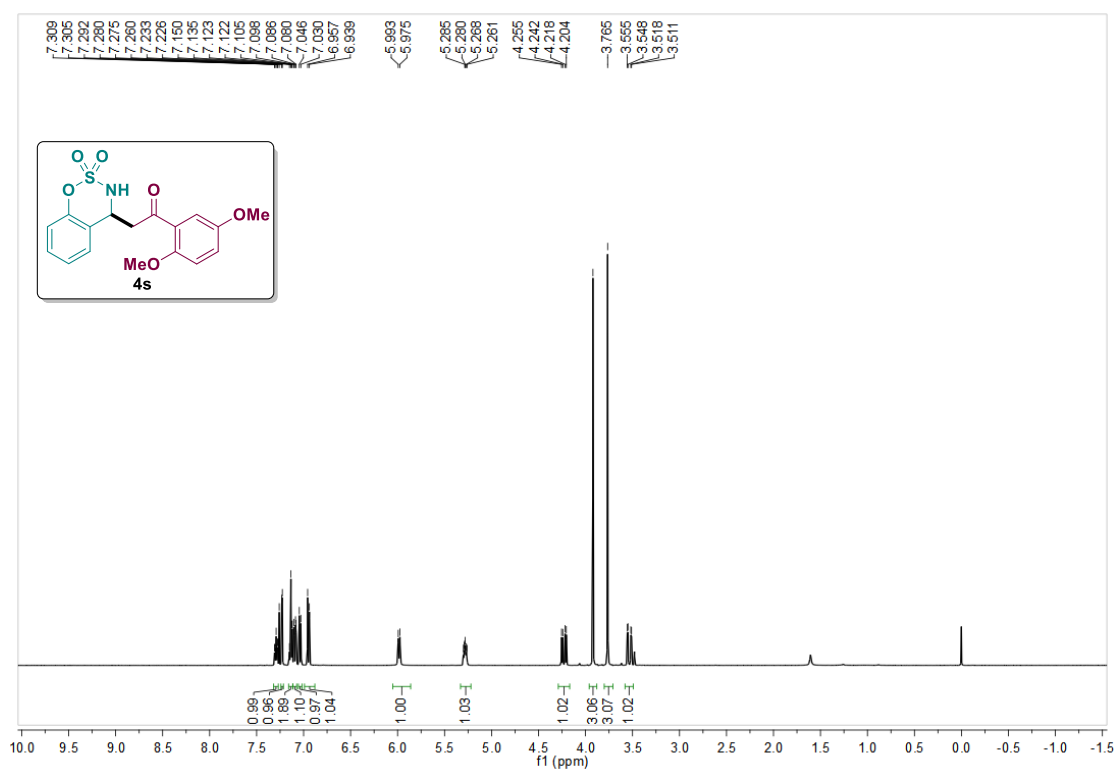
<sup>13</sup>C NMR Spectrum for **4q** (CDCl<sub>3</sub>, 125 MHz)



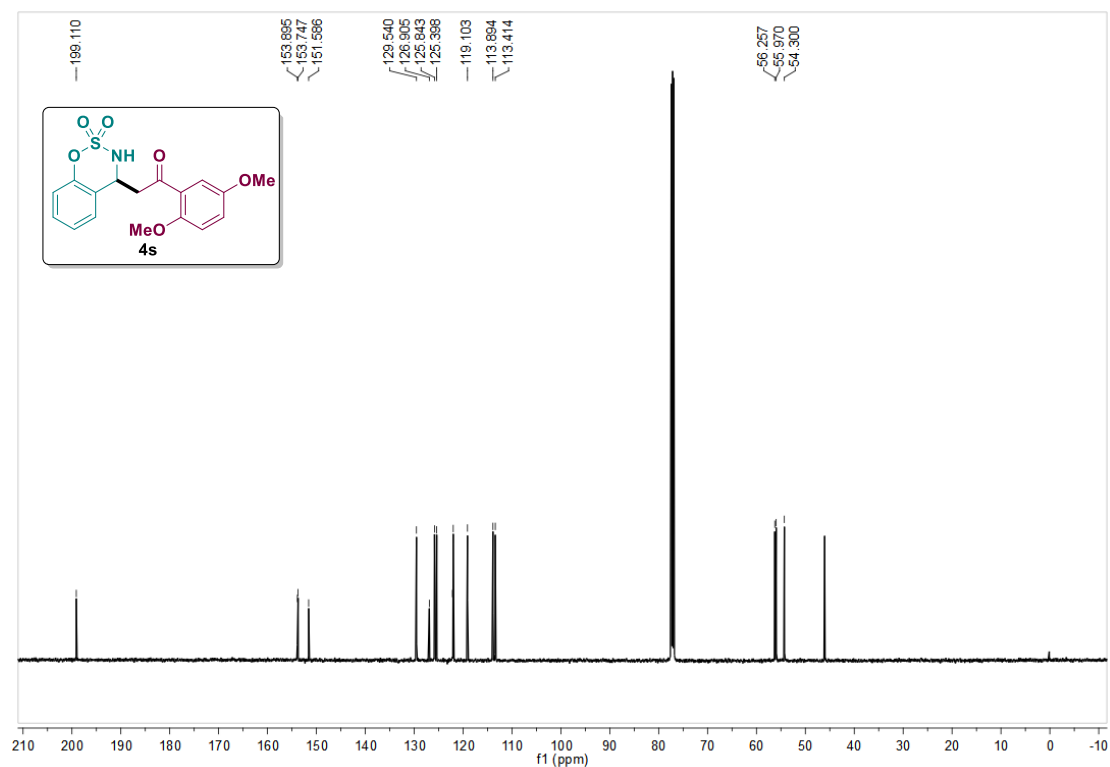
**<sup>1</sup>H NMR Spectrum for 4r (CDCl<sub>3</sub>, 500 MHz)**



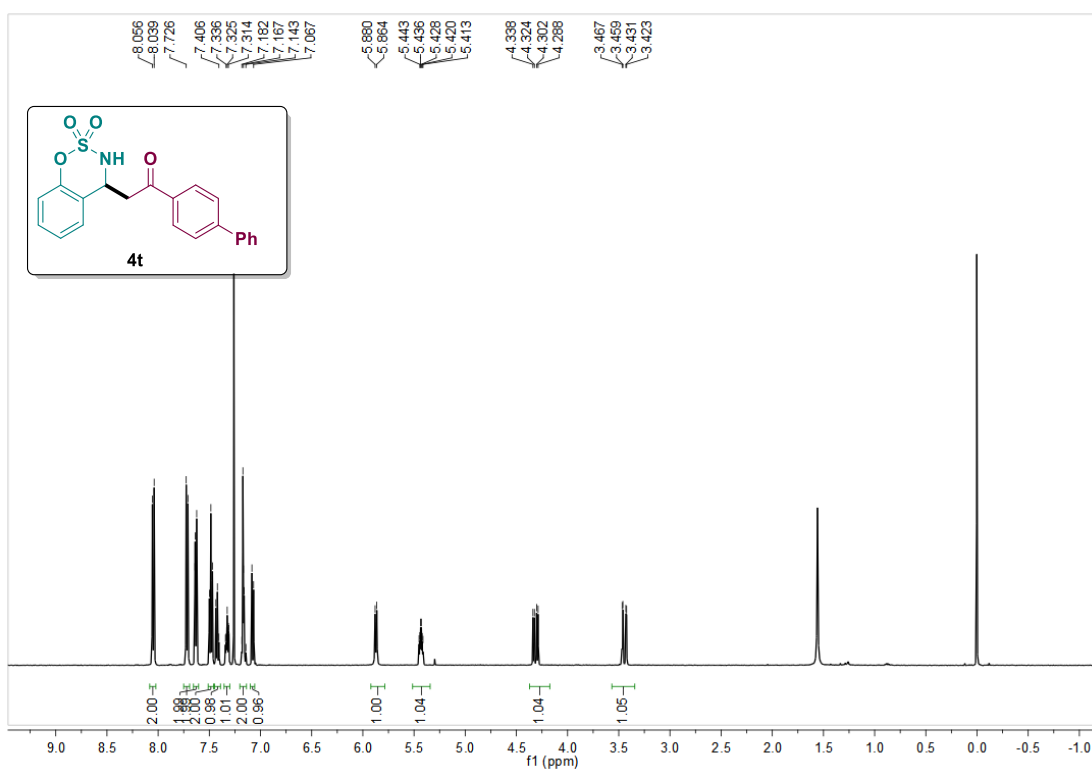
**<sup>13</sup>C NMR Spectrum for 4r (CDCl<sub>3</sub>, 125 MHz)**



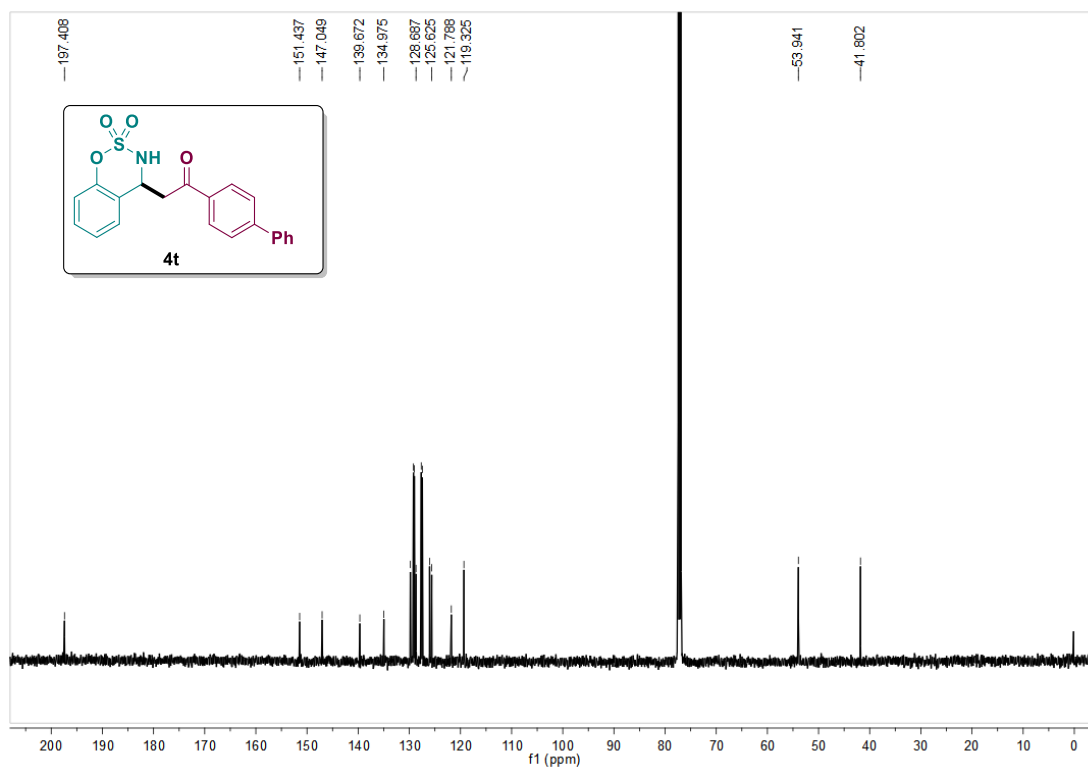
<sup>1</sup>H NMR Spectrum for 4s (CDCl<sub>3</sub>, 500 MHz)



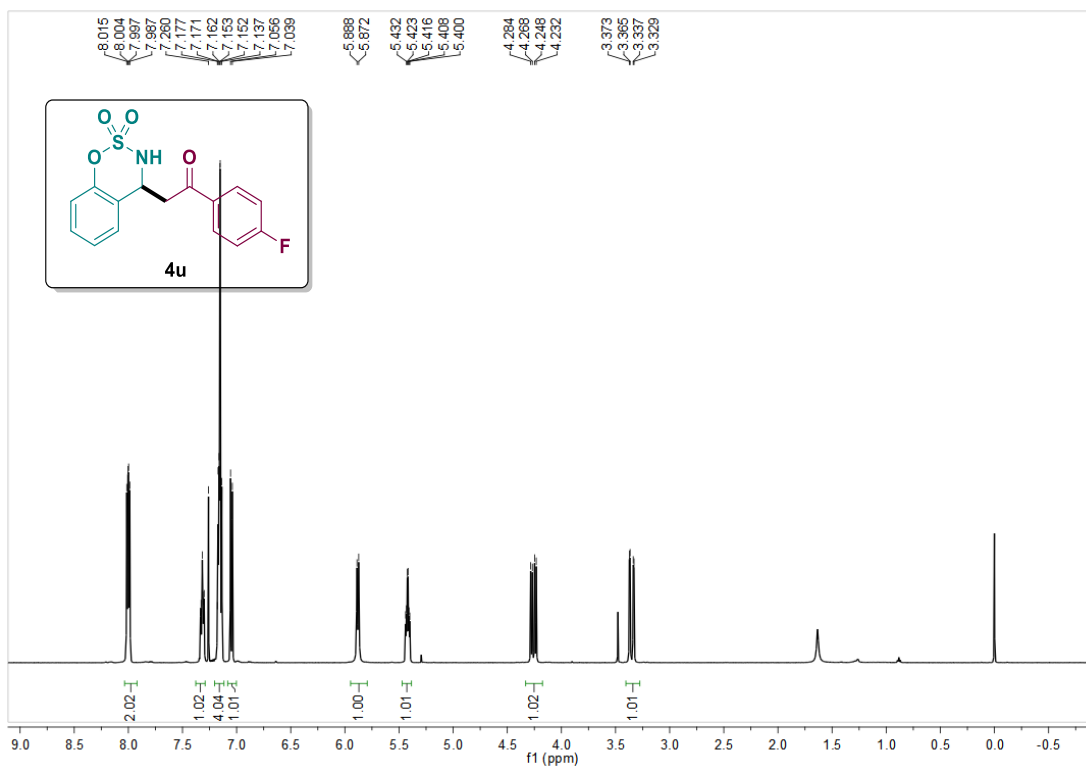
<sup>13</sup>C NMR Spectrum for 4s (CDCl<sub>3</sub>, 125 MHz)



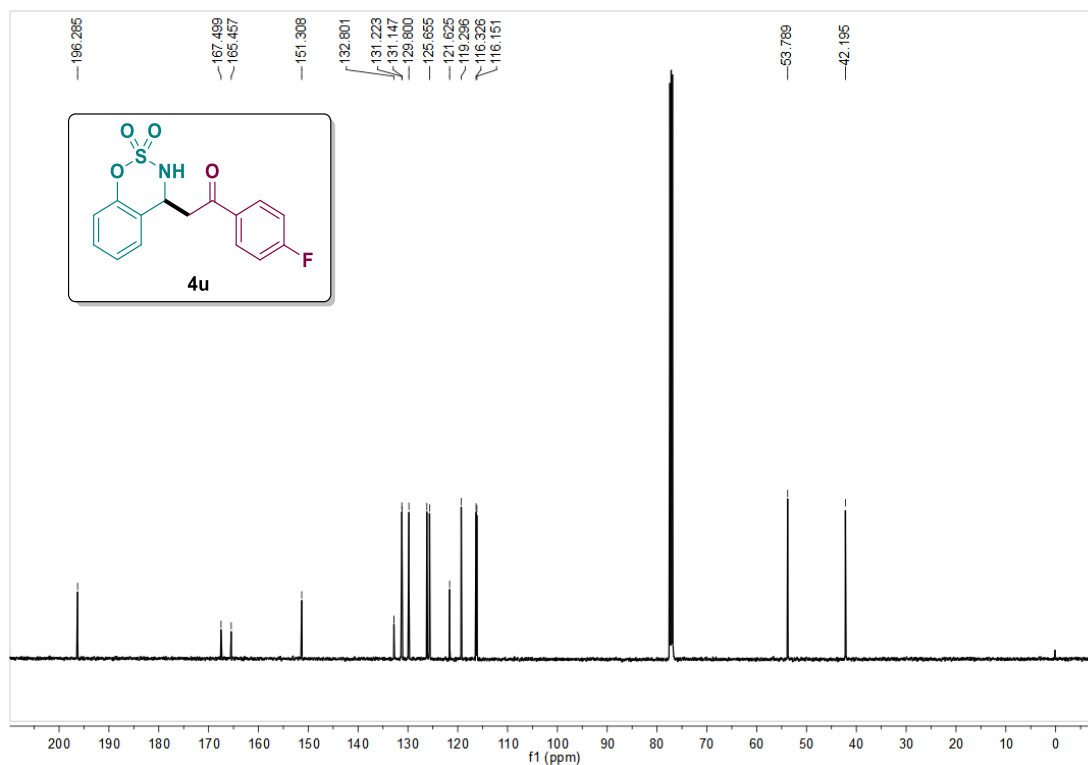
<sup>1</sup>H NMR Spectrum for 4t (CDCl<sub>3</sub>, 500 MHz)



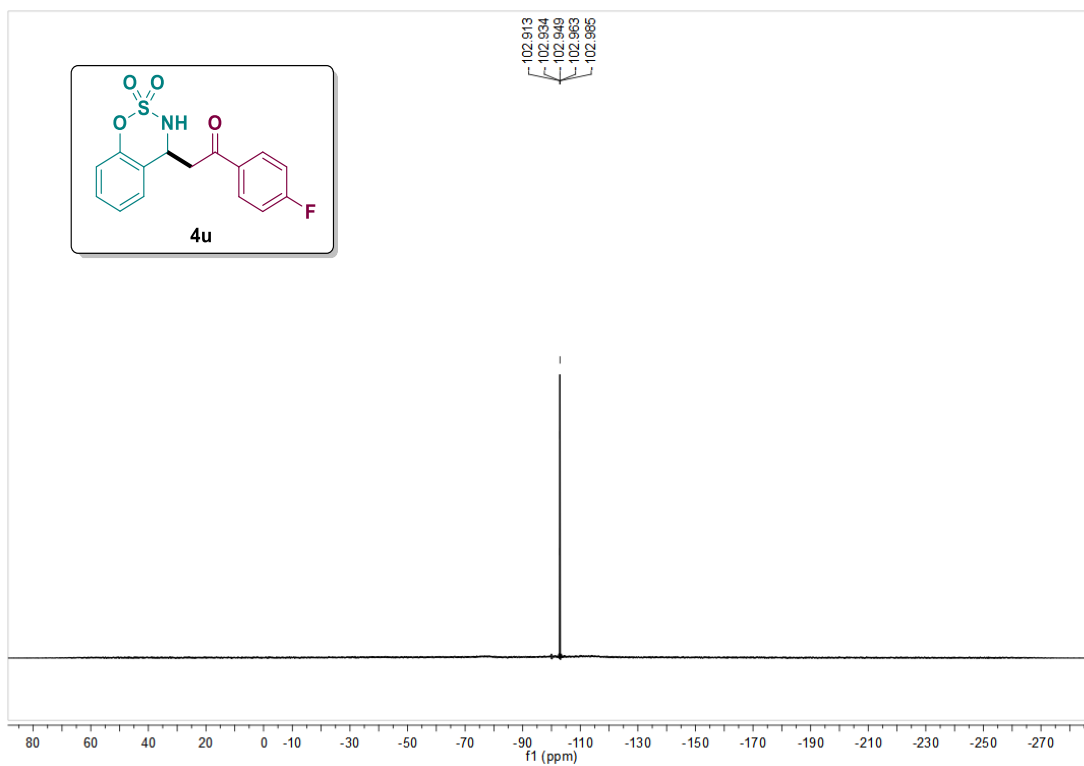
<sup>13</sup>C NMR Spectrum for 4t (CDCl<sub>3</sub>, 125 MHz)



<sup>1</sup>H NMR Spectrum for 4u (CDCl<sub>3</sub>, 500 MHz)

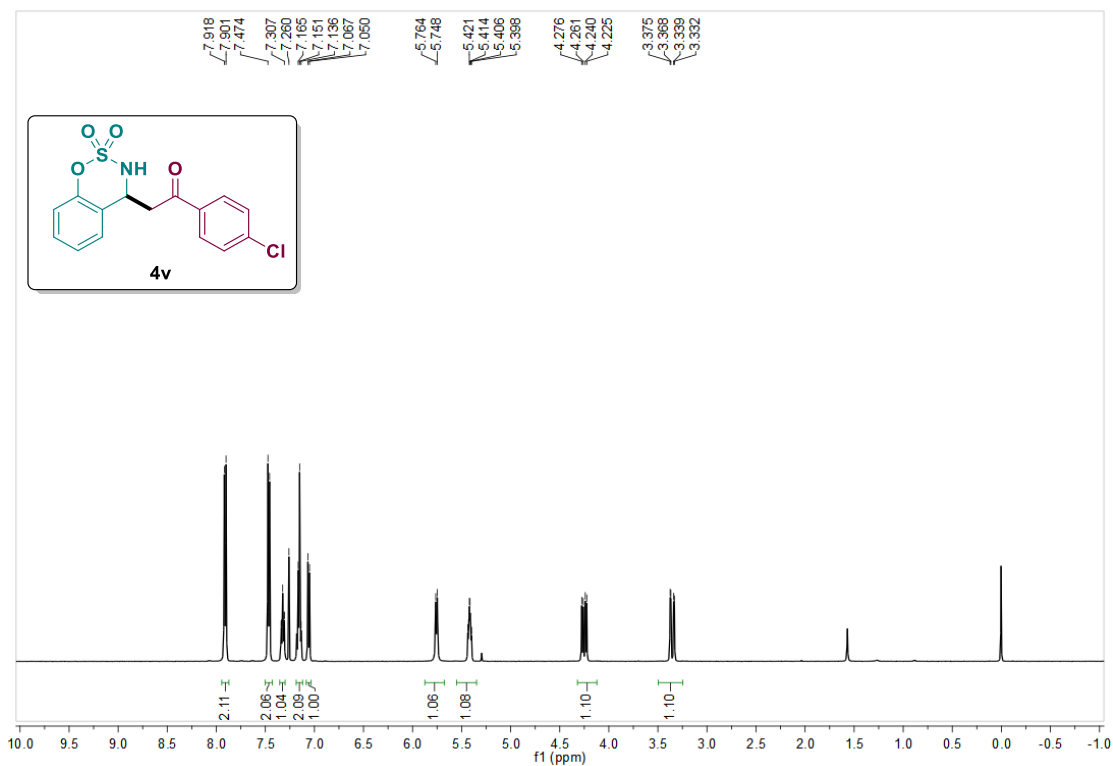


<sup>13</sup>C NMR Spectrum for 4u (CDCl<sub>3</sub>, 125 MHz)

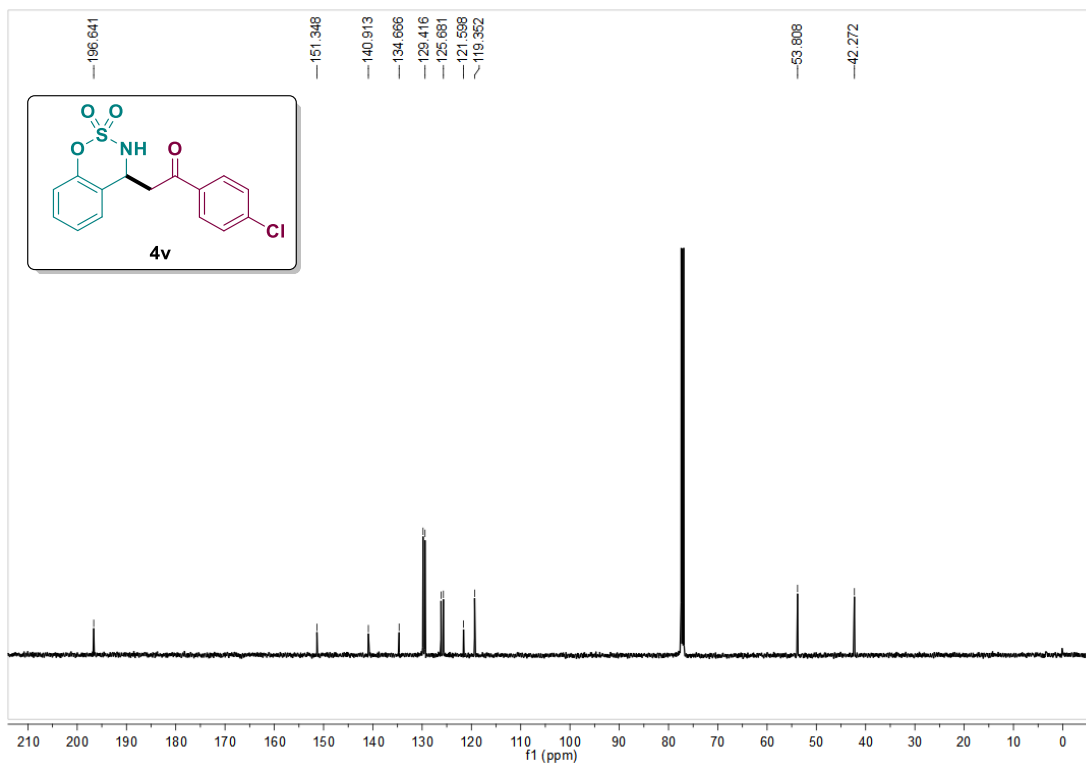


$^{19}\text{F}$  NMR Spectrum for **4u** ( $\text{CDCl}_3$ , 376 MHz)

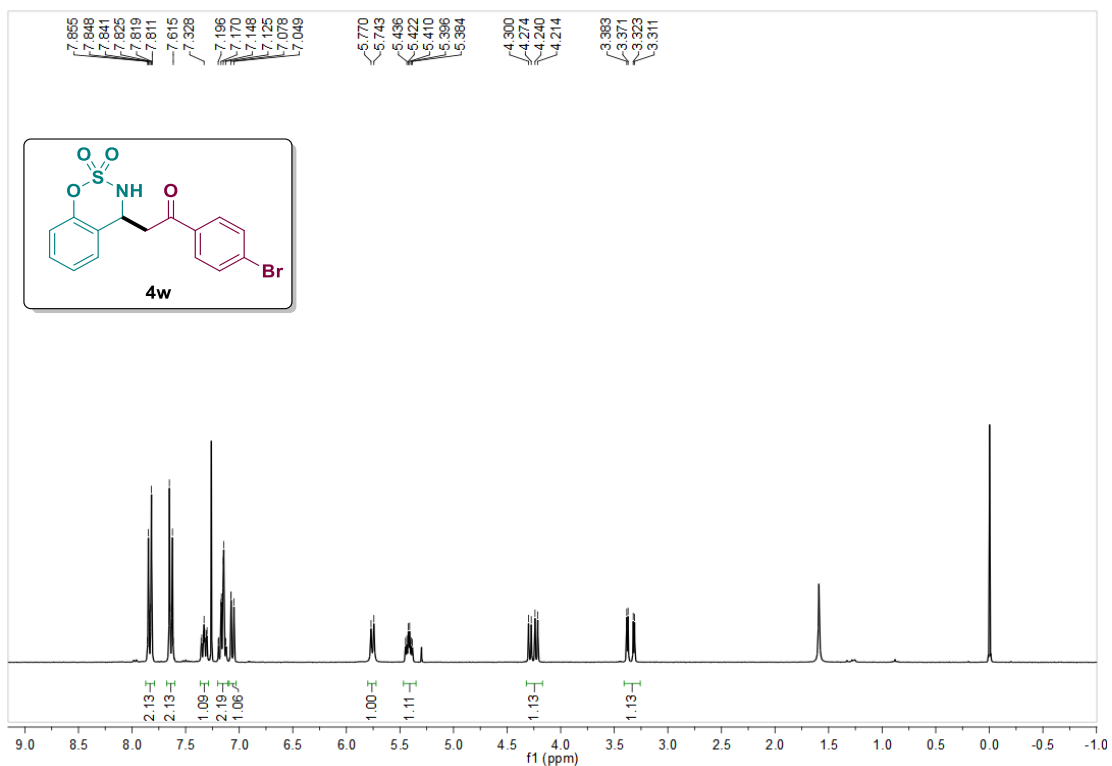




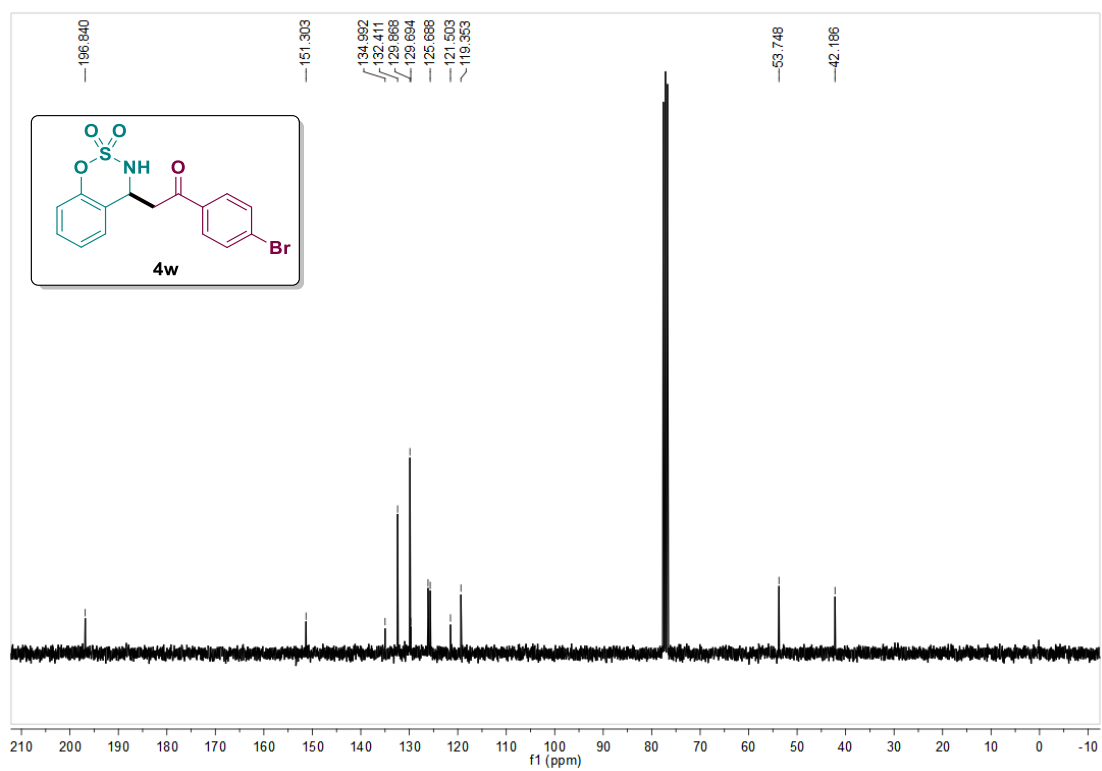
<sup>1</sup>H NMR Spectrum for **4v** (CDCl<sub>3</sub>, 500 MHz)



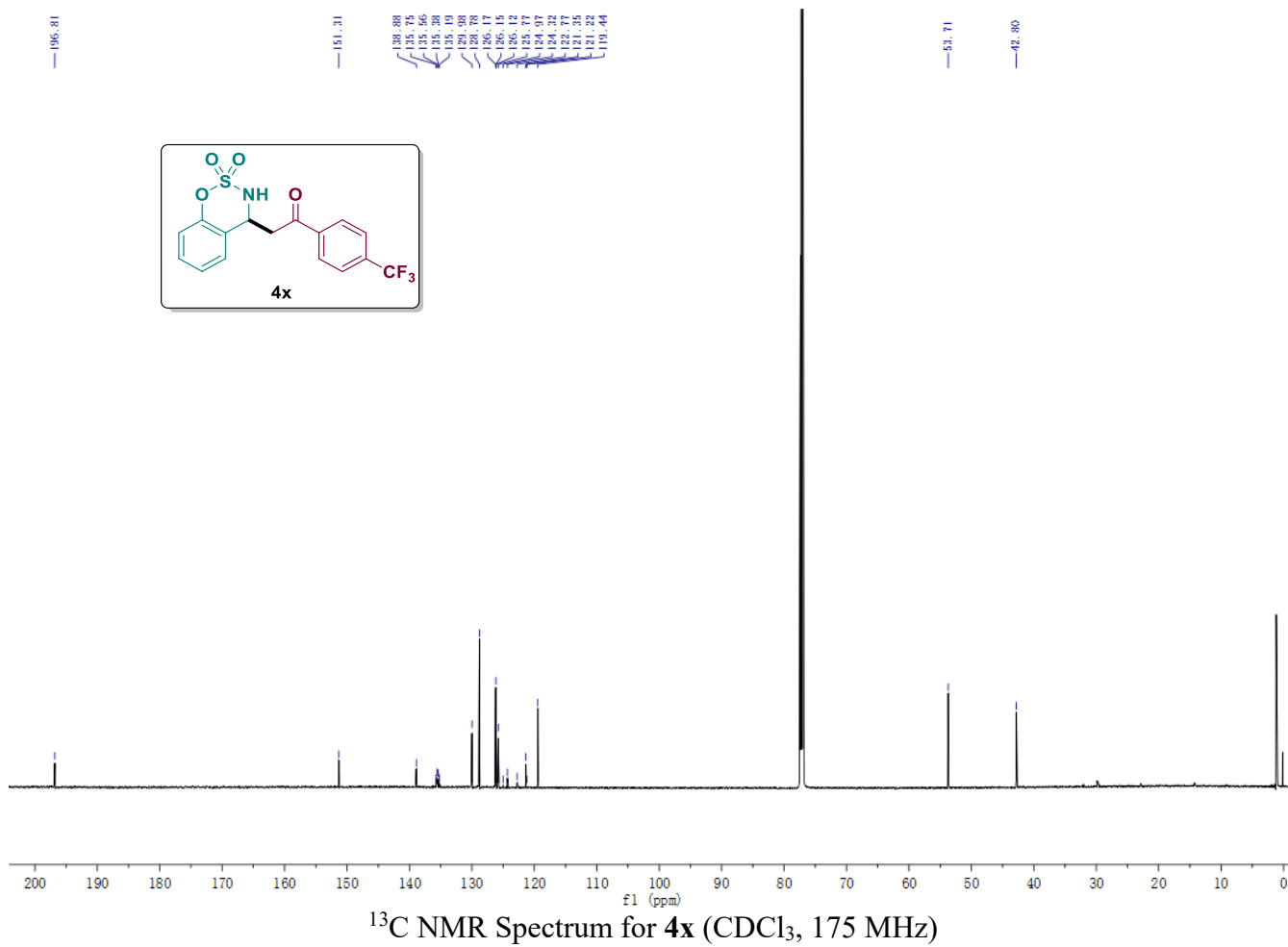
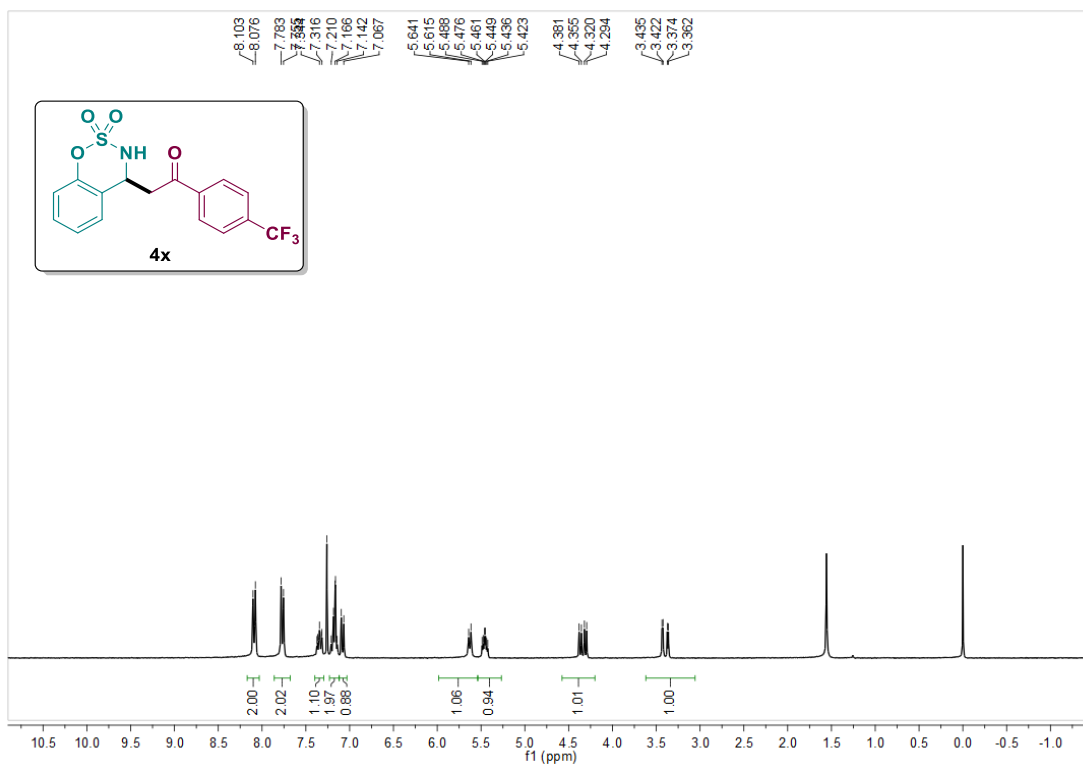
<sup>13</sup>C NMR Spectrum for **4v** (CDCl<sub>3</sub>, 125 MHz)

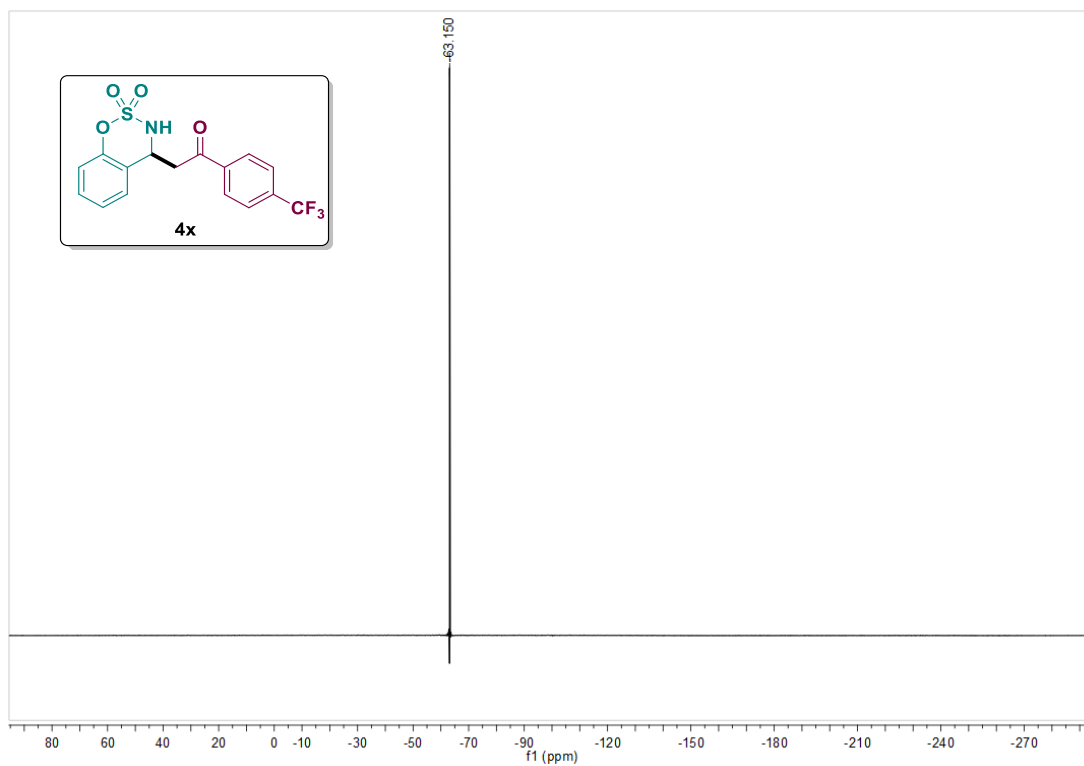


<sup>1</sup>H NMR Spectrum for **4w** (CDCl<sub>3</sub>, 300 MHz)

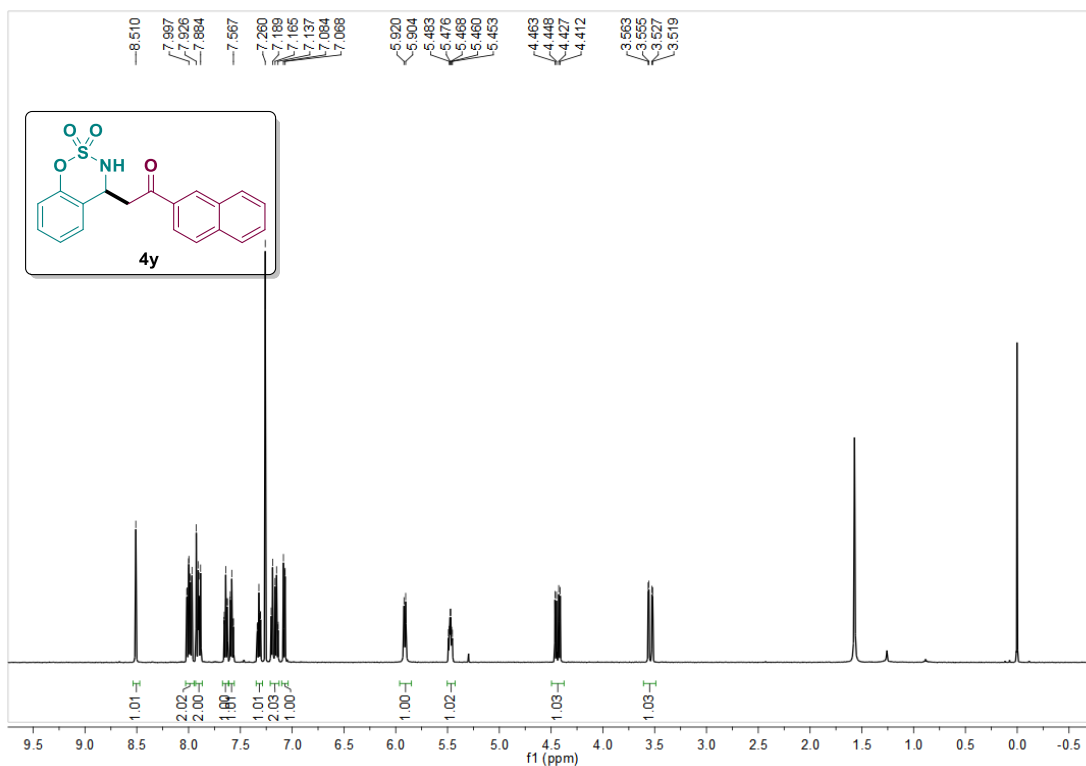


<sup>13</sup>C NMR Spectrum for **4w** (CDCl<sub>3</sub>, 75 MHz)

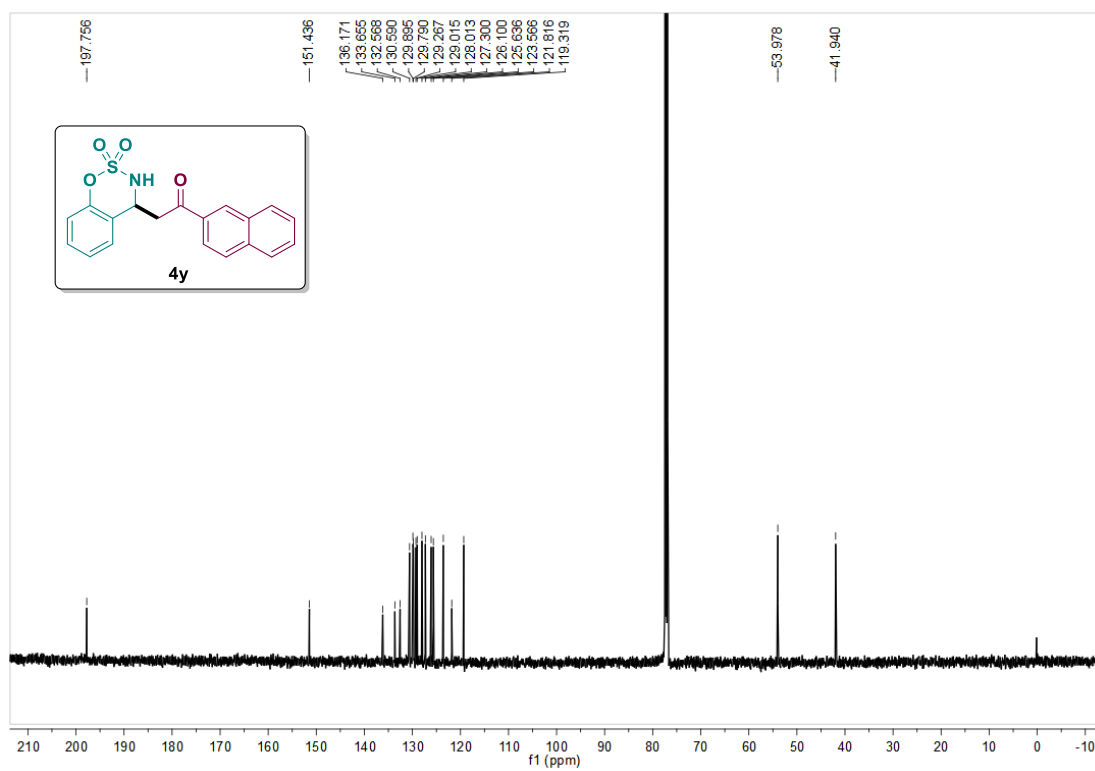




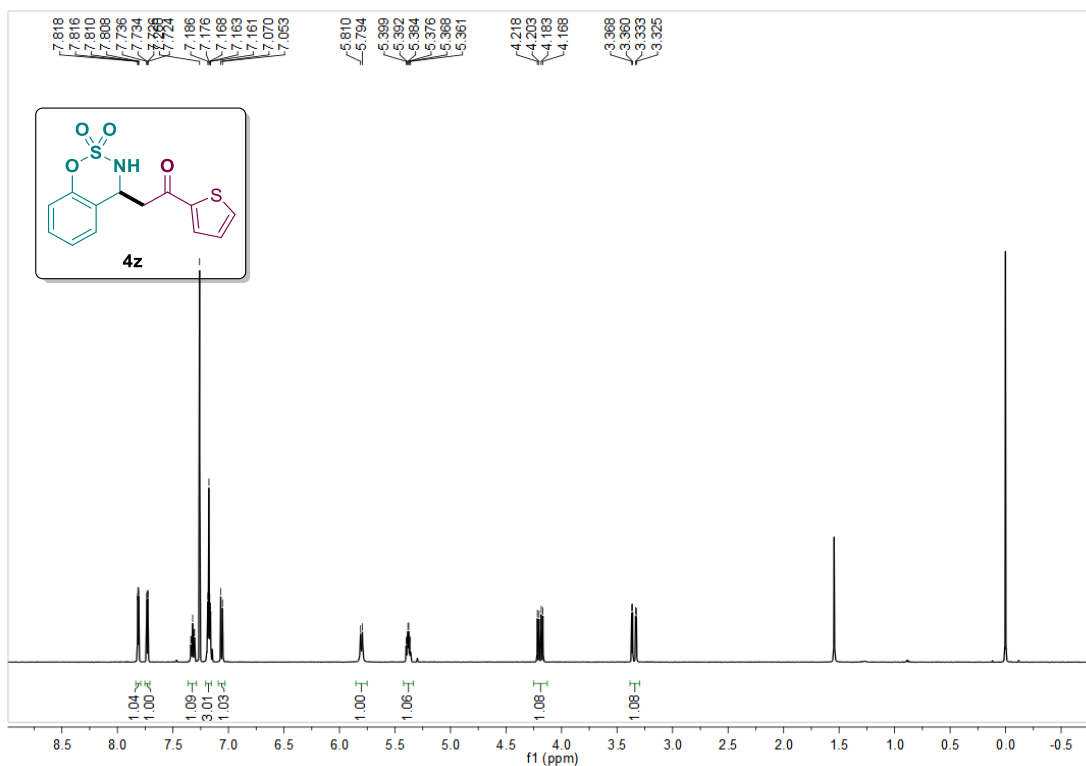
$^{19}\text{F}$  NMR Spectrum for **4x** ( $\text{CDCl}_3$ , 470 MHz)



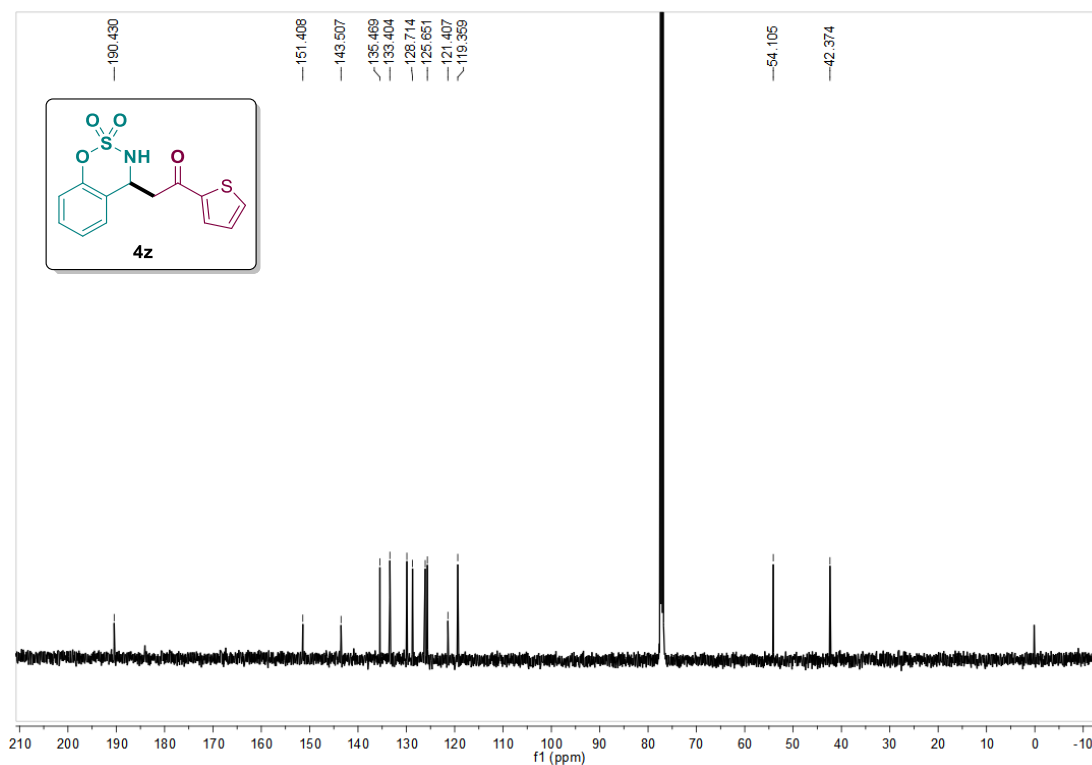
<sup>1</sup>H NMR Spectrum for **4y** (CDCl<sub>3</sub>, 500 MHz)



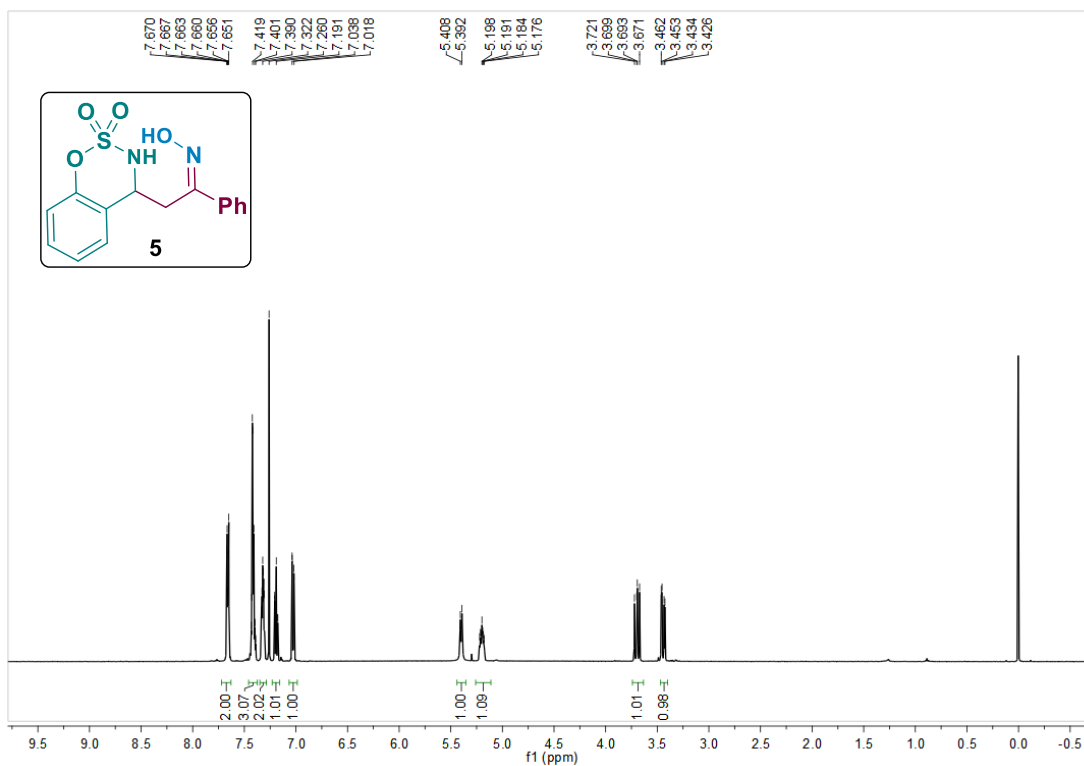
<sup>13</sup>C NMR Spectrum for **4y** (CDCl<sub>3</sub>, 125 MHz)



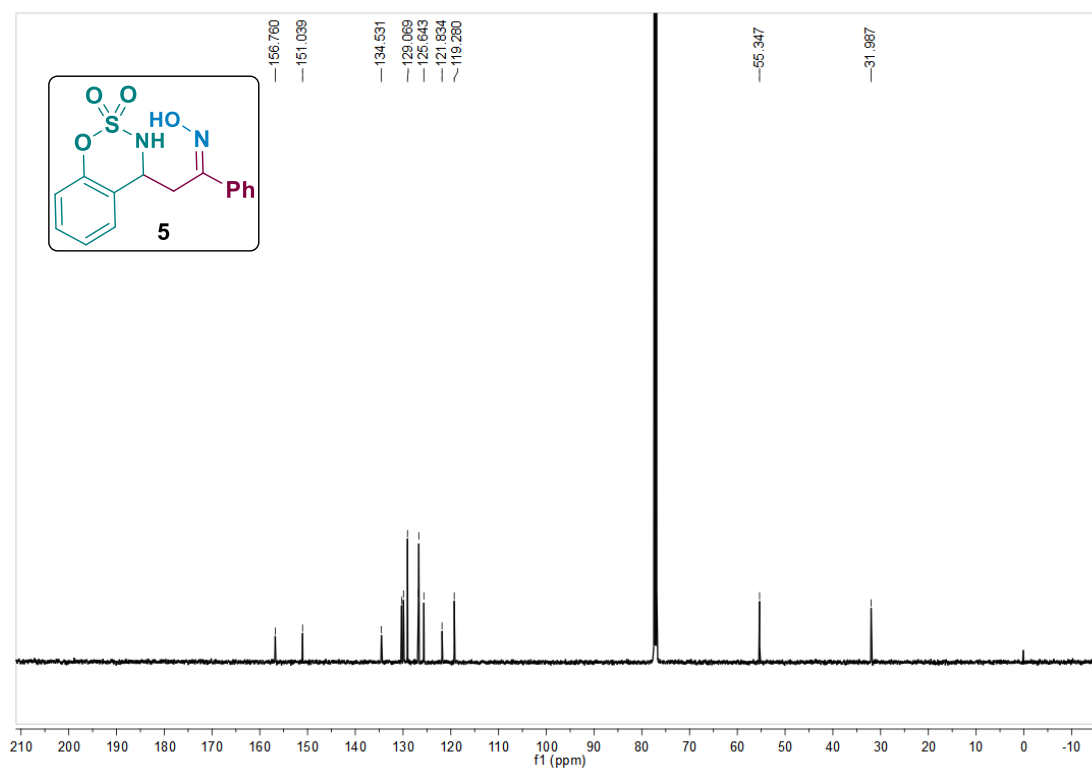
<sup>1</sup>H NMR Spectrum for **4z** (CDCl<sub>3</sub>, 500 MHz)



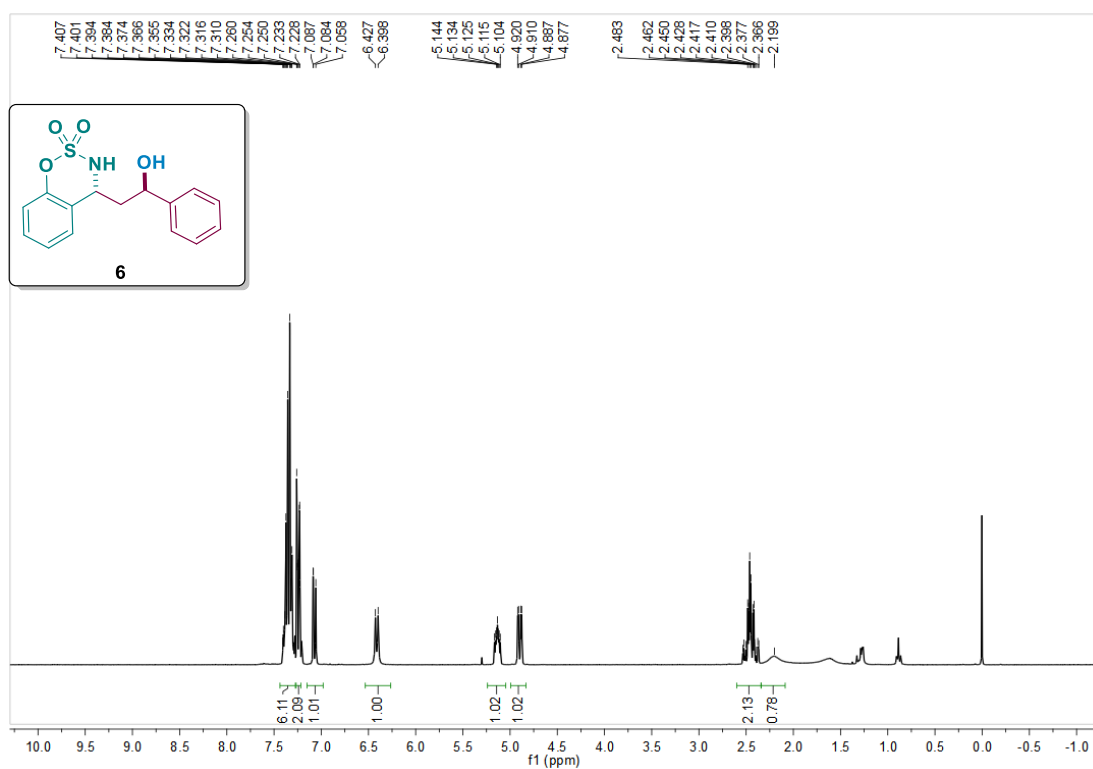
<sup>13</sup>C NMR Spectrum for **4z** (CDCl<sub>3</sub>, 125 MHz)



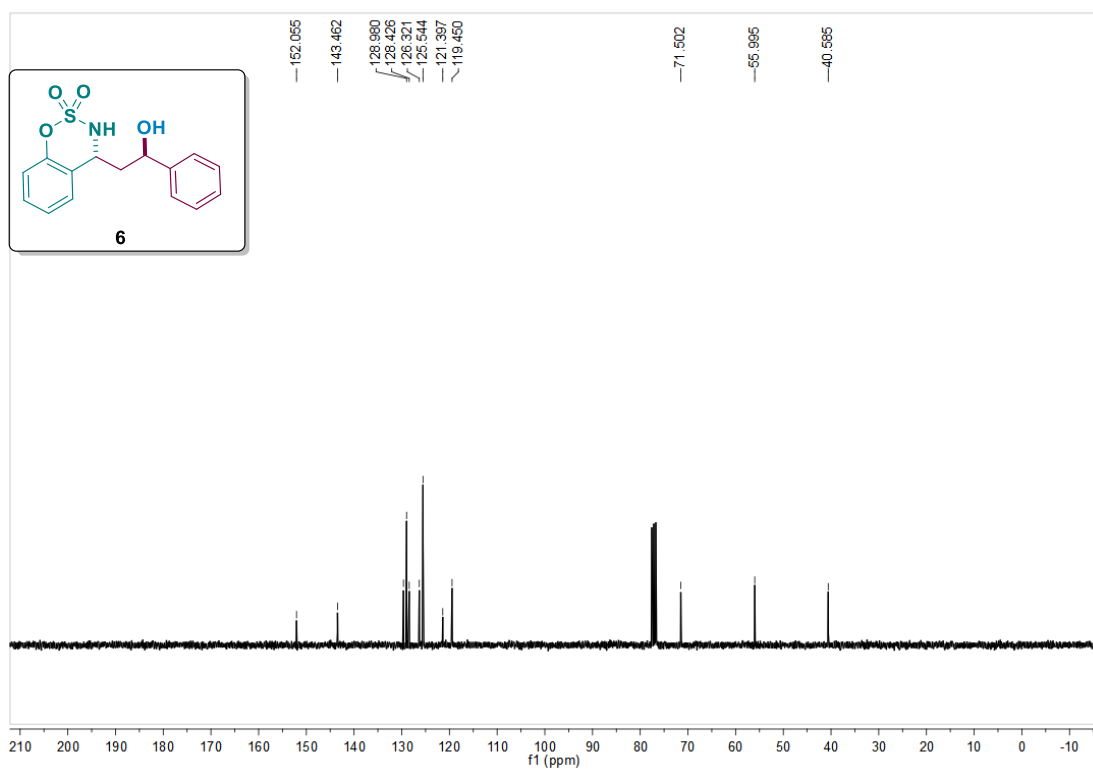
<sup>1</sup>H NMR Spectrum for 5 (CDCl<sub>3</sub>, 500 MHz)



<sup>13</sup>C NMR Spectrum for 5 (CDCl<sub>3</sub>, 125 MHz)

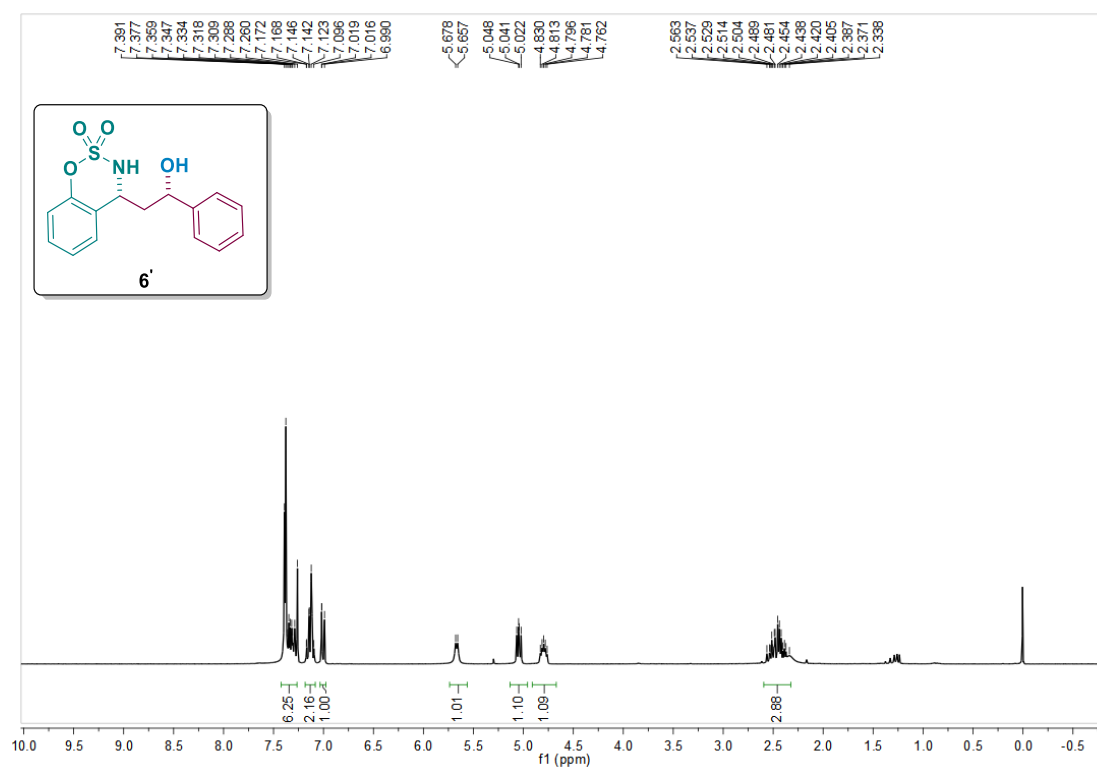


<sup>1</sup>H NMR Spectrum for **6** (CDCl<sub>3</sub>, 300 MHz)

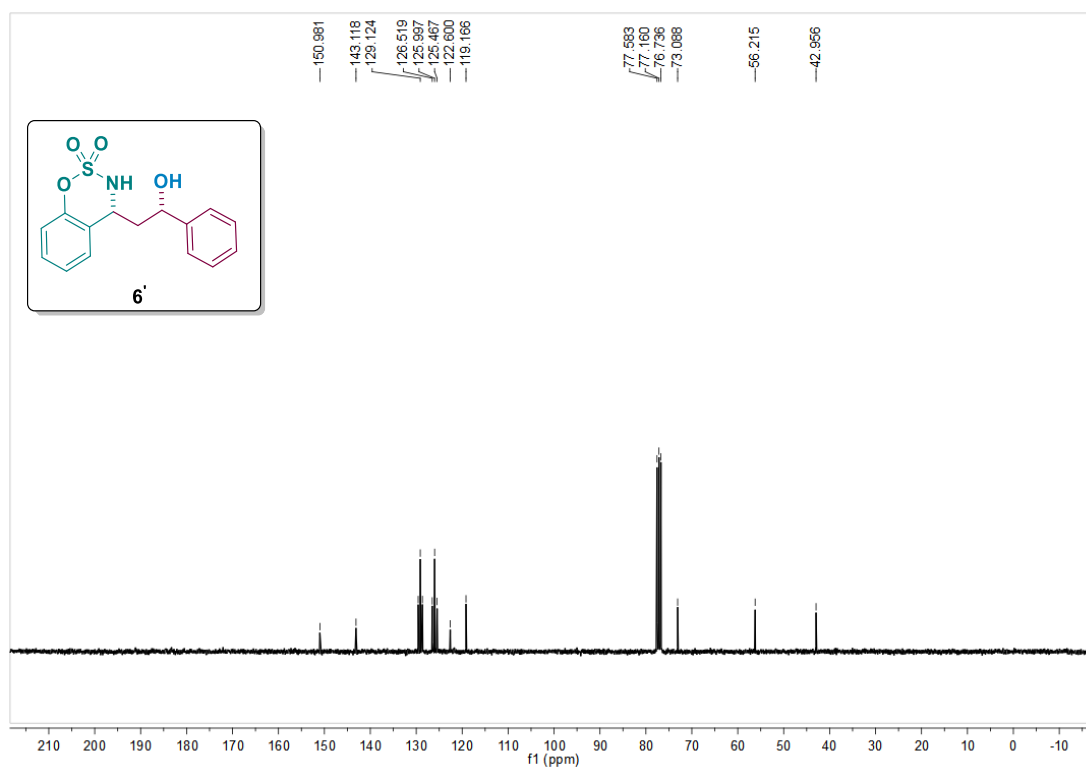


<sup>13</sup>C NMR Spectrum for **6a** (CDCl<sub>3</sub>, 75 MHz)

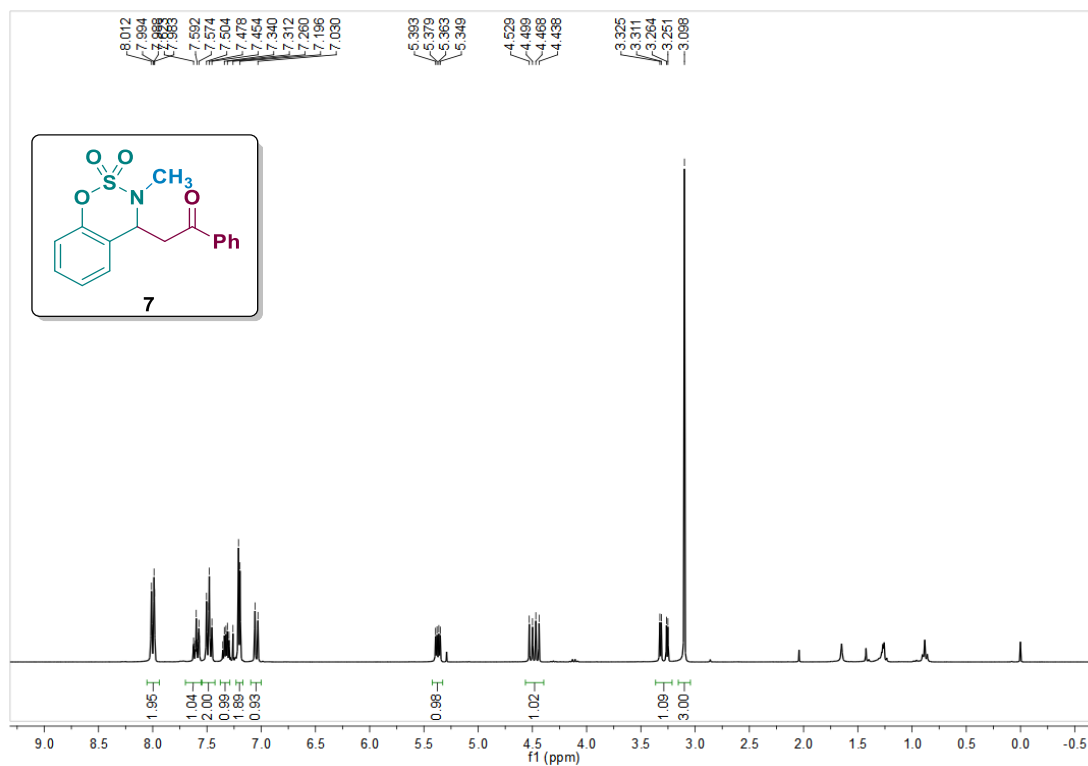




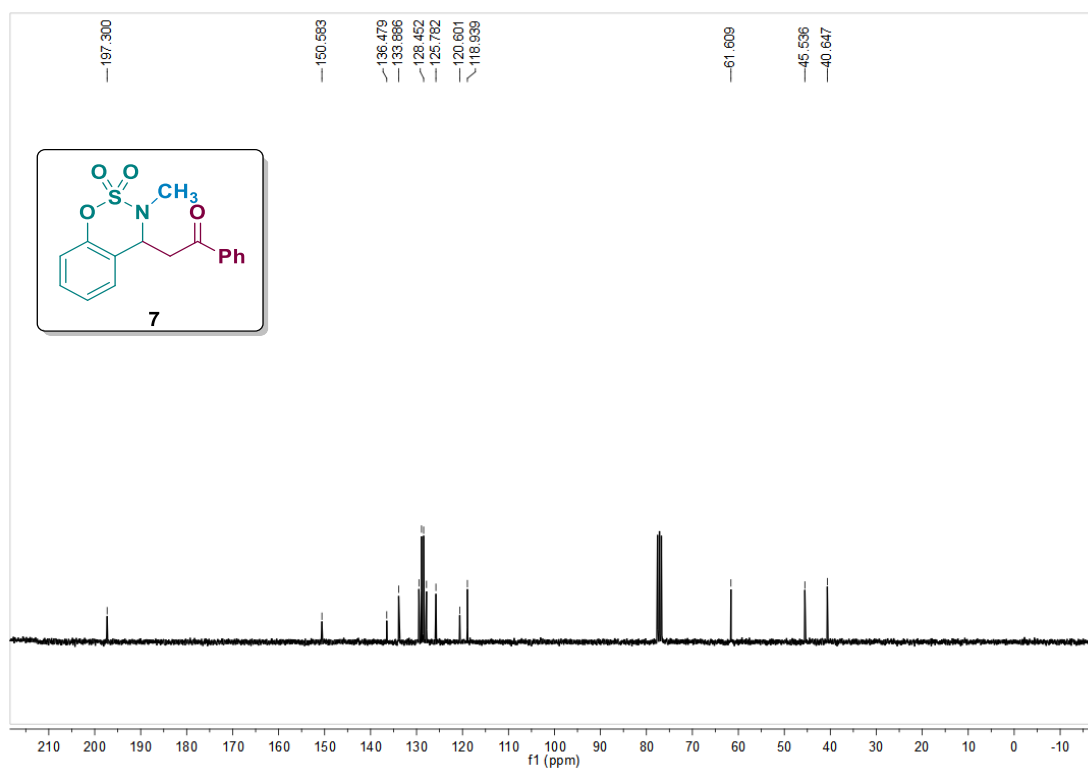
**<sup>1</sup>H NMR Spectrum for 6' (CDCl<sub>3</sub>, 300 MHz)**



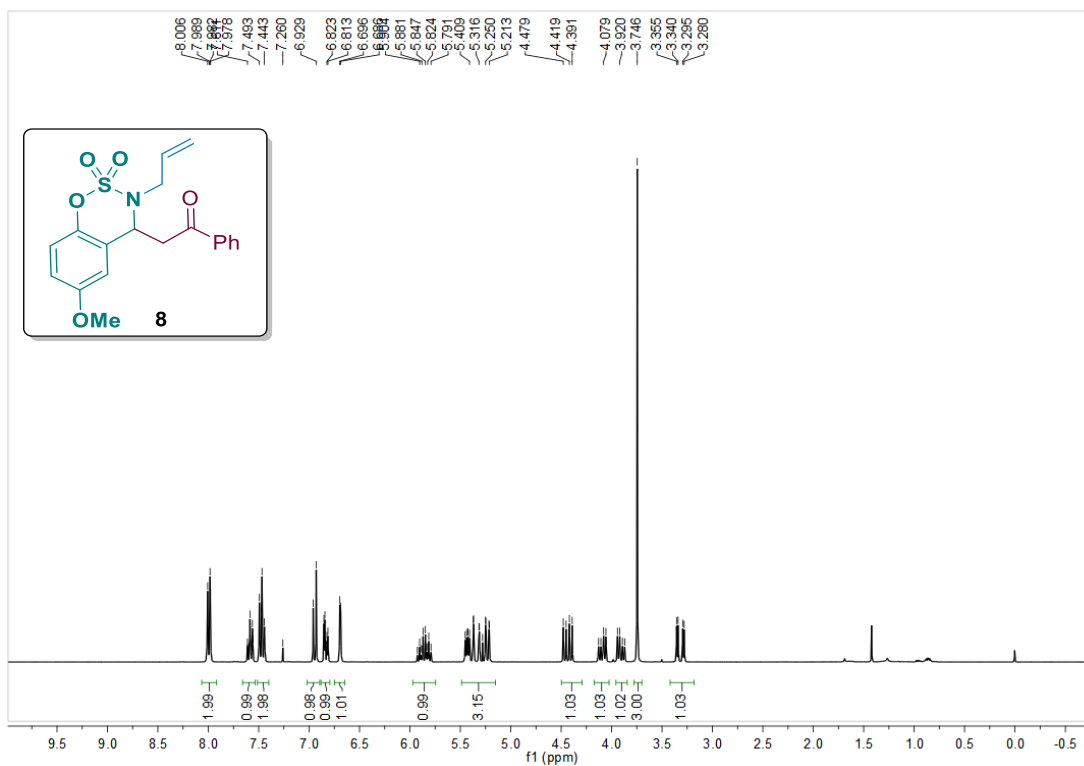
**<sup>13</sup>C NMR Spectrum for 6' (CDCl<sub>3</sub>, 75 MHz)**



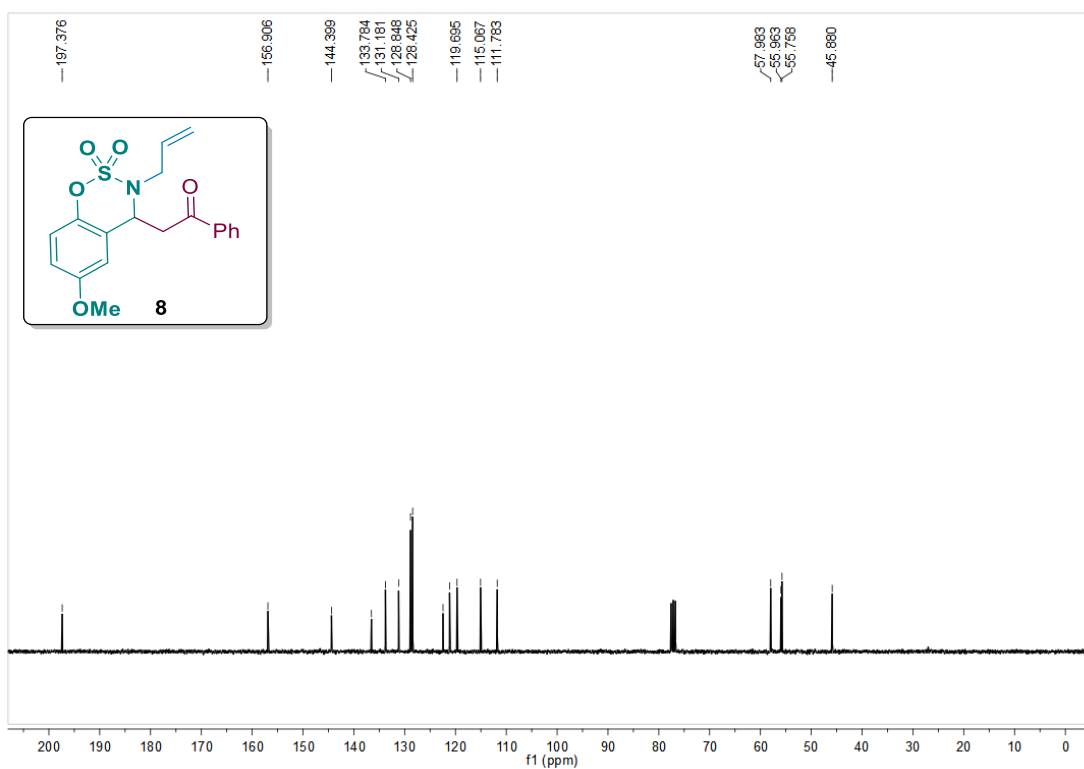
<sup>1</sup>H NMR Spectrum for 7 (CDCl<sub>3</sub>, 300 MHz)



<sup>13</sup>C NMR Spectrum for 7 (CDCl<sub>3</sub>, 75 MHz)



<sup>1</sup>H NMR Spectrum for **8** (CDCl<sub>3</sub>, 300 MHz)



<sup>13</sup>C NMR Spectrum for **8** (CDCl<sub>3</sub>, 75 MHz)



## 7. References

- [1] (a) Y. Luo, R. J. Carnell, H. W. Lam, *Angew. Chem. Int. Ed.* **2012**, *51*, 6762; (b) J. Zhou, H. Zhang, X.-L. Chen, Y.-L. Qu, Q. Zhu, C.-G. Feng, and Y.-J. Chen, *J. Org. Chem.* **2019**, *84*, 9179.
- [2] L.-M. Zhang, W. Luo, J. Fu, Y. Liu, and J. Zhang, *ACS Catal.* **2023**, *13*, 8830.
- [3] Z. Yuan, X. Fang, X. Li, J. Wu, H. Yao, and A. Lin. *J. Org. Chem.* **2015**, *80*, 11123.
- [4] H.-X. Zhang, J. Nie, H. Cai, and J.-A. Ma, *Org. Lett.* **2014**, *16*, 2542.
- [5] X.-Y. Cui, H.-X. Duan, Y. Zhang, and Y.-Q. Wang, *Chem. Asian J.* **2016**, *11*, 3118.
- [6] Y. Tang, K. Liu, Y. Wu, S. Zhou, T. Cheng, and G. Liu, *Adv. Synth. Catal.* **2022**, *364*, 994.