Supporting Information

Photocatalyzed Formal Carbooxygenation of Terminal Alkynes

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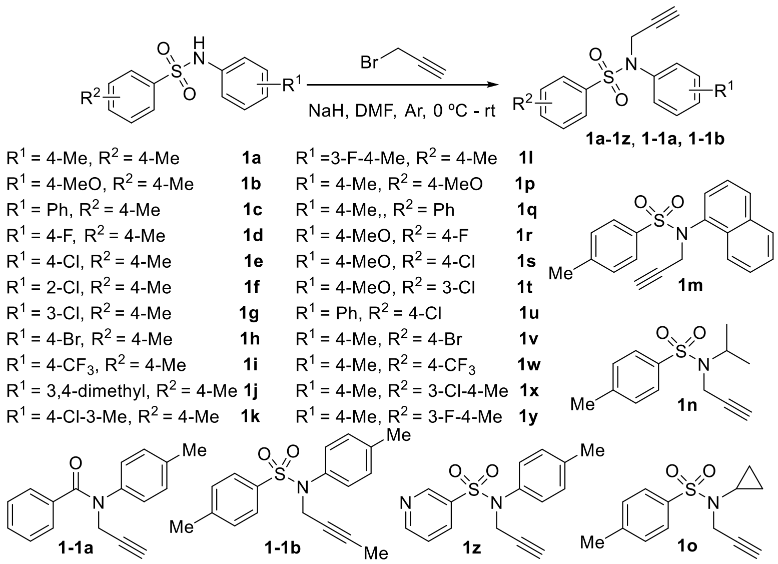
I. General Experimental Information

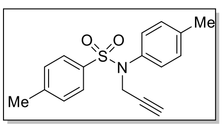
All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under in air using flash column techniques. All of the reagents were used directly as obtained commercially and used without further purification. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 or 500 MHz for ^{1}H NMR and 101 or 126 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HR-MS) were recorded on an IF-TOF spectrometer (Micromass).

II. Preparation and characterization of *N*-aryl substituted *N*-tosylpropargylamines and *N*-benzamido-substituted propargylamines (1a-1z, 1-1a, 1-1b)

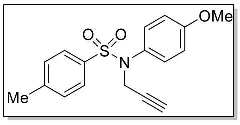
1. Preparation of *N*-aryl substituted *N*-tosylpropargylamine and *N*-benzamido-substituted propargylamines



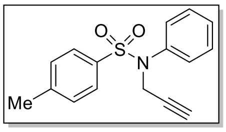
These starting materials were prepared by using the reported method.[1,2] To a solution of amides (1.0 equiv) in anhydrous DMF (20 mL) was added sodium hydride (60% dispersion in mineral oil, 1.1 equiv) at 0 °C under Ar. The reaction was stirred for 15 minutes at the same temperature and then 3-bromo-propyne (1.2 equiv) was slowly added *via* a syringe. The mixture was stirred at room temperature until the reaction completed and then quenched with a saturated solution of NH_4Cl (20 mL). The organic phases were washed with water (3 × 20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated to obtain the corresponding residue, which was then purified through flash chromatography on silica gel with ethyl acetate/petroleum (v/v = 50/1) as the eluent to afford the desired products.



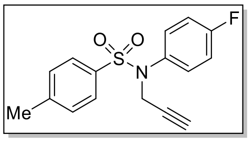
4-Methyl-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1a)[1]: light yellow solid (807 mg, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.06 (m, 4H), 4.41 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 2.15 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 138.3, 136.6, 135.8, 129.7, 129.3, 128.4, 128.1, 78.2, 73.7, 41.2, 21.6, 21.2.



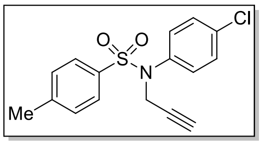
***N*-(4-Methoxyphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b)[1]:** yellow solid (756 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.1 Hz, 2H), 7.16 (d, J = 5.8 Hz, 2H), 7.03 (d, J = 6.7 Hz, 2H), 6.73 (d, J = 6.7 Hz, 2H), 4.32 (s, 2H), 3.71 (s, 3H), 2.34 (s, 3H), 2.08 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 143.6, 135.7, 131.8, 130.1, 129.3, 128.1, 114.2, 78.3, 73.7, 55.4, 41.4, 21.6.



4-Methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c)[2]: yellow solid (726 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 2H), 7.30 (s, 3H), 7.23 (d, J = 7.2 Hz, 4H), 4.44 (s, 2H), 2.41 (s, 3H), 2.16 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 139.4, 135.6, 129.3, 129.0, 128.5, 128.2, 128.1, 78.1, 73.8, 41.1, 21.6.

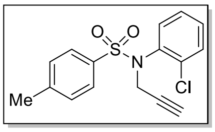


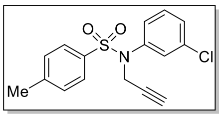
***N*-(4-Fluorophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1d)[1]:** yellow solid (799 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.22 – 7.17 (m, 2H), 6.99 (t, J = 8.0 Hz,2H), 4.41 (s, 2H), 2.42 (s, 3H), 2.18 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, J = 247 Hz, $^{1}J_{CF}$), 143.9, 135.4, 135.2, 135.1, 130.6 (d, J = 8 Hz, $^{3}J_{CF}$), 129.4, 128.0, 116.0 (d, J = 22 Hz, $^{2}J_{CF}$), 77.9, 74.1, 41.2, 21.6.



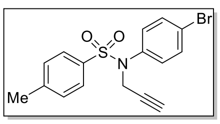
***N*-(4-Chlorophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1e)[1]:** yellow solid (861 mg, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 4.43 (s, 2H), 2.43 (s, 3H), 2.20 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 137.9, 135.2, 134.1, 129.7, 129.5, 129.3, 128.0, 77.8, 77.4, 77.1, 76.8, 74.2, 74.2, 40.9, 21.6.

***N*-(2-Chlorophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1f)[1]:** yellow solid (717 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 7.9 Hz, 1H), 7.35 – 7.22 (m, 5H), 4.94 – 3.96 (m, 2H), 2.43 (s, 3H), 2.17 (d, J = 2.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 136.8, 135.7, 135.1, 132.6, 130.6, 130.1, 129.5, 127.9, 127.3, 77.8, 73.8, 40.1, 21.6.

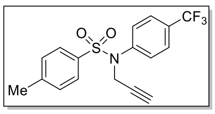




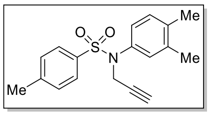
***N*-(3-Chlorophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1g)[1]:** yellow solid (736 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 2H), 7.34 – 7.24 (m, 5H), 7.20 – 7.15 (m, 1H), 4.44 (d, J = 2.5 Hz, 2H), 2.44 (s, 3H), 2.21 (t, J = 2.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 140.6, 135.2, 134.4, 129.9, 129.5, 128.5, 128.4, 128.0, 126.4, 77.7, 74.3, 40.9, 21.6.



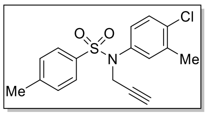
***N*-(4-Bromophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1h)[1]:** yellow solid (890 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 4.40 (d, J = 2.4 Hz, 2H), 2.41 (s, 3H), 2.18 (t, J = 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 138.4, 135.2, 132.2, 130.0, 129.5, 128.0, 122.1, 77.7, 74.2, 40.9, 21.6.



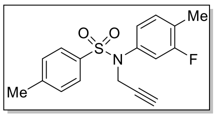
4-Methyl-*N*-(prop-2-yn-1-yl)-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (1i)[1]: yellow solid (794 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.46 (d, *J* = 2.3 Hz, 2H), 2.40 (s, 3H), 2.20 (d, *J* = 2.2 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 144.3, 142.7, 137.9, 135.1, 129.9, 129.6, 128.0, 127.9 (d, *J* = 5 Hz, $^{3}J_{CF}$), 126.1 (q, *J* = 4 Hz, $^{3}J_{CF}$), 123.8 (d, *J* = 270 Hz, $^{1}J_{CF}$),77.5, 74.4, 40.6, 21.5.



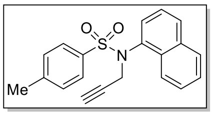
***N*-(3,4-Dimethylphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1j)[1]:** yellow solid (788 mg, 84%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.90 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.42 (d, *J* = 2.4 Hz, 2H), 2.44 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.18 (t, *J* = 2.3 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 143.6, 137.5, 137.0, 136.9, 135.9, 130.1, 129.9, 129.2, 128.1, 125.5, 78.3, 73.6, 41.2, 21.6, 19.8, 19.5.



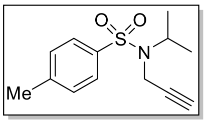
***N*-(4-Chloro-3-methylphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1k)[1]:** yellow solid (789 mg, 79%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 3H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.42 (d, *J* = 2.5 Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 2.19 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 143.9, 137.7, 137.1, 135.4, 134.3, 131.2, 129.5, 129.4, 128.0, 126.7, 77.9, 74.0, 41.0, 21.6, 20.1.



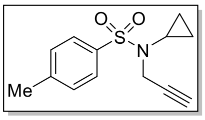
***N*-(3-Fluoro-4-methylphenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1l)[1]:** yellow solid (827 mg, 87%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 9.2 Hz, 2H), 4.43 (d, *J* = 1.4 Hz, 2H), 2.44 (s, 3H), 2.28 (s, 3H), 2.20 (s, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 160.7 (d, *J* =245 Hz, $^{1}J_{CF}$), 143.9, 138.2 (d, *J* =10 Hz, $^{3}J_{CF}$), 135.4, 131.4 (d, *J* =6 Hz, $^{3}J_{CF}$), 129.4, 128.0, 125.2 (d, *J* =17 Hz, $^{2}J_{CF}$), 123.8 (d, *J* =4 Hz, $^{3}J_{CF}$), 115.2 (d, *J* =24 Hz, $^{2}J_{CF}$), 77.9, 74.0, 41.0, 21.6, 14.3.



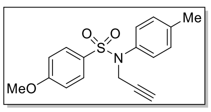
4-Methyl-*N*-(naphthalen-1-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1m)[1]: yellow solid (502 mg, 50%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.58 – 7.45 (m, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 4.80 (d, *J* = 17.8 Hz, 1H), 4.29 (d, *J* = 17.8 Hz, 1H), 2.43 (s, 3H), 2.11 (s, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 143.8, 136.2, 135.5, 134.8, 132.5, 129.5, 129.4, 128.3, 128.1, 127.2, 127.1, 126.6, 124.9, 123.7, 78.2, 73.9, 41.7, 21.6.



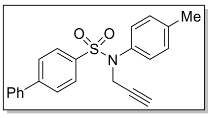
***N*-Isopropyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1n)[1]:** yellow liquid (647 mg, 86%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.29 (d, 2H), 4.14 (dd, *J* = 13.6, 6.8 Hz, 1H), 4.09 (d, *J* = 2.5 Hz, 2H), 2.43 (s, 3H), 2.17 (t, *J* = 2.5 Hz, 1H), 1.17 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 143.2, 137.9, 129.4, 127.4, 80.4, 72.2, 49.8, 31.3, 21.5, 20.8.



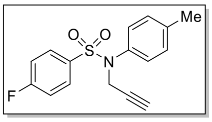
***N*-Cyclopropyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1o)[1]:** yellow solid (575 mg, 77%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.12 (d, *J* = 2.5 Hz, 2H), 2.43 (s, 3H), 2.20 (tt, *J* = 6.9, 3.6 Hz, 1H), 2.04 – 1.96 (m, 1H), 0.95 – 0.90 (m, 2H), 0.79 – 0.70 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 143.7, 135.0, 129.3, 128.4, 77.1, 73.8, 39.8, 29.3, 21.6, 7.7.



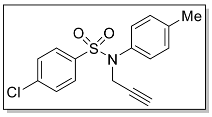
4-Methoxy-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1p)[1]: yellow solid (765 mg, 81%); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.10 (s, 4H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.39 (s, 2H), 3.84 (s, 3H), 2.32 (s, 3H), 2.17 (s, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 163.1, 138.2, 136.7, 130.2, 130.2, 129.7, 128.4, 113.8, 78.3, 73.8, 55.6, 41.1, 21.2.



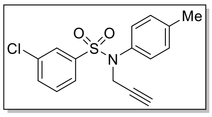
***N*-(Prop-2-yn-1-yl)-*N*-(*p*-tolyl)-[1,1'-biphenyl]-4-sulfonamide (1q)[1]:** yellow solid (758 mg, 70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.0 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.16 – 7.08 (m, 4H), 4.45 (s, 2H), 2.33 (s, 3H), 2.17 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 139.3, 138.4, 137.3, 136.6, 129.8, 129.1, 128.6, 128.6, 128.5, 127.3, 127.2, 78.2, 73.9, 41.3, 21.2.



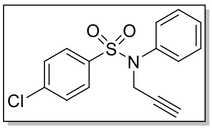
4-Fluoro-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1r)[1]: yellow solid (718 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.19 – 7.03 (m, 6H), 4.43 (s, 2H), 2.35 (s, 3H), 2.18 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2 (d, J = 253 Hz, $^{1}J_{CF}$), 138.6, 136.5, 134.8 (d, J = 4 Hz, $^{3}J_{CF}$), 134.8, 130.8 (d, J = 9 Hz, $^{3}J_{CF}$), 129.9, 128.4, 115.9 (d, J = 23 Hz, $^{2}J_{CF}$), 78.1, 74.0, 41.3, 21.2.



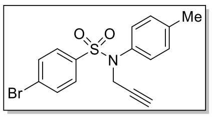
4-Chloro-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1s)[1]: yellow solid (765 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.12 (s, 4H), 4.43 (s, 2H), 2.34 (s, 3H), 2.19 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 138.6, 137.3, 136.4, 129.9, 129.5, 128.9, 128.4, 78.0, 74.1, 41.4, 21.2.



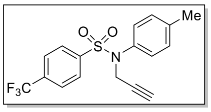
3-Chloro-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1t)[1]: yellow solid (727 mg, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.15 – 7.07 (m, 4H), 4.43 (s, 2H), 2.34 (s, 3H), 2.21 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 138.8, 136.3, 134.8, 132.9, 130.0, 129.9, 128.4, 128.1, 126.2, 77.9, 74.2, 41.5, 21.2.



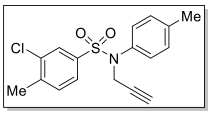
4-Chloro-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1u)[2]: yellow solid (677 mg, 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 2.5 Hz, 3H), 7.26 (d, J = 2.3 Hz, 2H), 4.46 (s, 2H), 2.20 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.4, 139.2, 137.2, 129.5, 129.2, 128.9, 128.5, 128.4, 77.9, 74.2, 41.3.



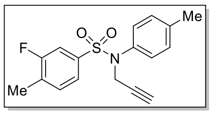
4-Bromo-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1v)[1]: yellow solid (857 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.15 – 7.08 (m, 4H), 4.42 (s, 2H), 2.34 (s, 3H), 2.19 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 137.9, 136.4, 131.9, 129.9, 129.6, 128.4, 127.9, 78.0, 74.1, 41.4, 21.2.



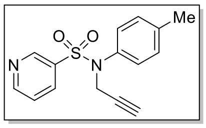
***N*-(Prop-2-yn-1-yl)-*N*-(*p*-tolyl)-4-(trifluoromethyl)benzenesulfonamide (1w)[1]:** yellow solid (847 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.18 – 7.06 (m, 4H), 4.46 (s, 2H), 2.35 (s, 3H), 2.18 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 138.9, 136.3, 134.4 (d, J = 32 Hz, $^{2}J_{CF}$), 130.0, 128.6, 128.3, 125.8 (q, J = 4 Hz, $^{3}J_{CF}$), 123.3 (q, J = 271 Hz, $^{1}J_{CF}$), 77.8, 74.2, 41.5, 21.2.



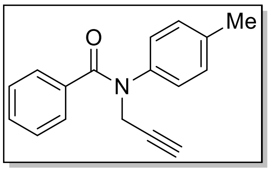
3-Chloro-4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1x)[1]: yellow solid (819 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.15 – 7.08 (m, 4H), 4.42 (s, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 2.21 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 138.6, 137.7, 136.4, 134.8, 131.0, 129.9, 128.6, 128.4, 126.2, 78.0, 74.0, 41.4, 21.2, 20.3.



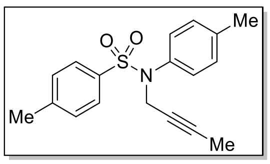
3-Fluoro-4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1y)[1]: yellow solid (1.093 g, 69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.18 – 7.11 (m, 4H), 4.45 (s, 2H), 2.37 (s, 6H), 2.22 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ160.5 (d, *J* = 248 Hz, $^{31}J_{CF}$), 138.6, 137.9 (d, *J* = 7 Hz, $^3J_{CF}$), 136.4, 131.7 (d, *J* = 5 Hz, $^3J_{CF}$), 130.7 (d, *J* = 17 Hz, $^2J_{CF}$), 129.8, 128.4, 123.6 (d, *J* = 4 Hz, $^3J_{CF}$), 114.9 (d, *J* = 26 Hz, $^2J_{CF}$), 78.0, 73.9, 41.4, 21.2, 14.8.



***N*-(Prop-2-yn-1-yl)-*N*-(*p*-tolyl)pyridine-3-sulfonamide (1z)[1]:** brown solid (729 mg, 51%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.78 (d, *J* = 3.1 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.14 (s, 4H), 4.46 (s, 2H), 2.34 (s, 3H), 2.23 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.2, 148.7, 138.9, 136.2, 135.8, 135.5, 130.0, 128.2, 123.3, 77.8, 74.5, 41.5, 21.1.

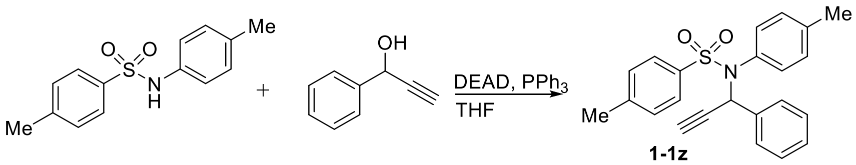


***N*-(Prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzamide (1-1a)[1]:** white solid (821 mg, 66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.3 Hz, 2H), 7.24 (t, 1H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.02 (q, *J* = 8.3 Hz, 4H), 4.65 (s, 2H), 2.27 (s, 3H), 2.24 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 140.2, 137.1, 135.3, 129.9, 128.8, 127.7, 127.5, 79.2, 77.4, 72.2, 39.9, 21.1.

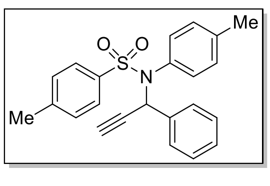


***N*-(But-2-yn-1-yl)-4-methyl-*N*-(*p*-tolyl)benzenesulfonamide (1-1b):** yellow solid (1.283g, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.10 (s, 4H), 4.35 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 137.9, 137.2, 136.1, 129.6, 129.1, 128.3, 128.1, 81.5, 73.5, 41.8, 21.6, 21.1, 3.5; **HR-MS (ESI)** calcd for $[M + Na]^+$: $C_{18}H_{19}NO_2SNa$: 336.1029, found: 336.1055.

2. Procedure for the preparation of 4-methyl-*N*-(1-phenylprop-2-yn-1-yl)-*N*-(*p*-tolyl)benzene sulfonamide (1-1z)[3]

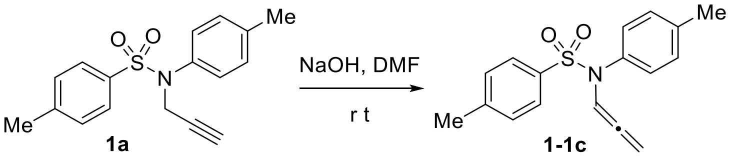


This starting material **1-1z** was prepared by using the reported method.[3] To a mixture of 4-methyl -*N*- (*p*-tolyl)benzenesulfonamide (0.9 mmol), PPh_3 (1.0 mmol), and 1-phenylprop-2-yn-1-ol (1.0 mmol) in THF (5.0 mL) was added DEAD (2.20 M in toluene, 1.0 mmol) at 0 ºC. The mixture was stirred at reflux for 6 h and cooled to room temperature. After THF was removed under reduced pressure, the residue was chromatographed on silica gel (hexane-ethyl acetate) to afford 4-methyl-*N*-(1-phenylprop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide **1-1z**.

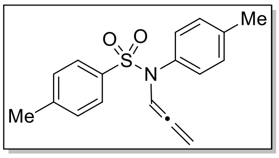


4-Methyl-*N*-(1-phenylprop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1-1z): yellow solid (562 mg, 30%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.41 (s, 2H), 7.33 – 7.24 (m, 5H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 2H), 6.56 (s, 1H), 2.51 (s, 1H), 2.47 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 138.6, 137.0, 135.9, 132.7, 131.5, 129.3, 129.1, 128.6, 128.3, 128.2, 128.1, 79.8, 54.8, 21.6, 21.2; **HR-MS (ESI)** calcd for $[M + Na]^+$: $C_{23}H_{21}NO_2SNa$: 398.1185, found: 398.1224.

3. Procedure for the preparation of propa-1,2-dien-1-amine (1-1c) [4]



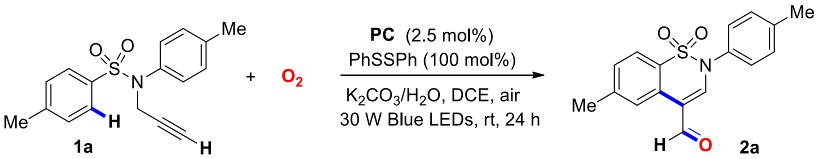
This starting material **1-1c** was prepared by using the reported method.[4] A flame-dried flask filled with argon was charged with corresponding 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzene sulfon amide **1a** (1.0 equiv), and the flask was then closed by a septum. Back-filled with a flow of argon. Argon atmosphere was ensured by argon balloon. Solid was dissolved in DMF (10 mL), and then sodium hydroxide (1.2 equiv) was added quickly. After 12 hours, the solution was neutralized with adding of saturated solution of ammonium chloride (30 mL), the corresponding aqueous phase was extracted with CH_2Cl_2 (3 ×20 mL). The combined organic solution was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was then purified by flash column chromatography to obtain corresponding allenamide **1-1c**.

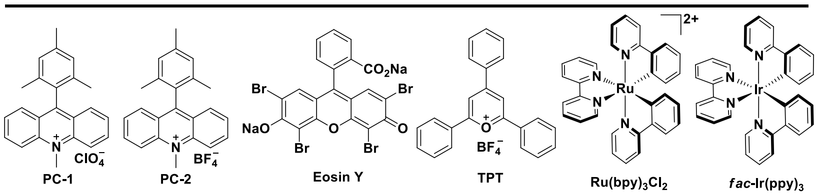


4-Methyl-*N*-(propa-1,2-dien-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (1-1c): white solid (822 mg, 55%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 10.1 Hz, 3H), 6.87 (d, *J* = 7.4 Hz, 2H), 5.05 – 5.00 (m, 2H), 2.44 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.1, 143.9, 138.7, 135.3, 134.5, 129.6, 129.5, 129.3, 127.7, 102.5, 87.5, 21.7, 21.2; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{18}NO_2S$: 300.1053, found: 300.1078.

III. Screening the reaction conditions

Table S-1. The Effect of photocatalysts on the intramolecular carbo-oxygenation of alkyne 1a[a]

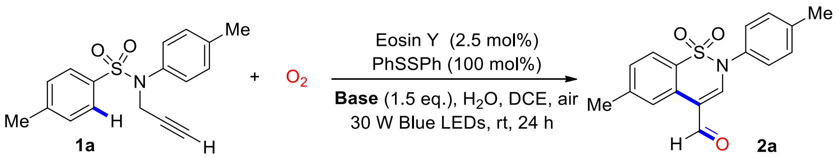




Entry	Photocatalyst	Yield (%)[b]
1	PC-1	32
2	PC-2	29
3	Eosin Y	75
4	TPT	65
5	$Ru(bpy)_3Cl_2$	10
6	*fac*-$Ir(ppy)_3$	30

[a]0.10 mmol of *N*-propargyl-*N*-tosylamide (**1a**) (29.9 mg), H_2O (0.50 mmol), photocatalyst (2.5 mol %), K_2CO_3 (1.5 equiv.), and PhSSPh (0.10 mmol) in DCE (2.0 mL) under an air atmosphere at room temperature for 24 h, blue LED light. [b]Isolated yield.

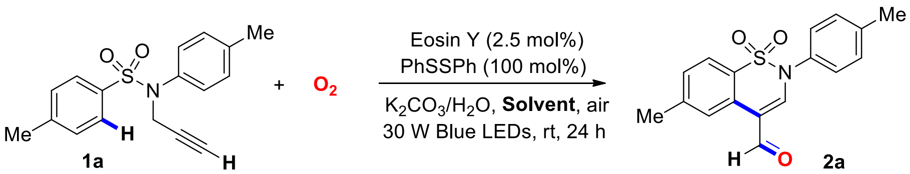
Table S-2. The Effect of bases on the intramolecular carbo-oxygenation of alkyne 1a[a]



Entry	Base	Yield (%)[b]
1	CH_3COOK	34
2	Na_2CO_3	40
3	CH_3COONa	0
4	K_3PO_4	54
5	KPF_6	14
6	^{t}BuONa	60
7	Cs_2CO_3	36
8	Li_2CO_3	10

[a]0.10 mmol of *N*-propargyl-*N*-tosylamide (**1a**) (29.9 mg), H_2O (0.50 mmol), Eosin Y (2.5 mol %), base (1.5 equiv.), and PhSSPh (0.10 mmol) in DCE (2.0 mL) under an air atmosphere at room temperature for 24 h, blue LED light. [b]Isolated yield.

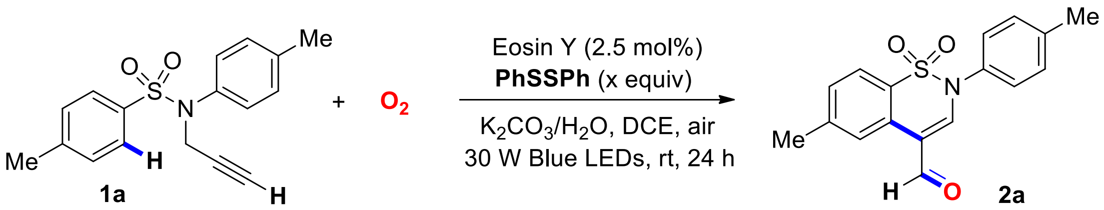
Table S-3. The Effect of solvents on the intramolecular carbo-oxygenation of alkyne 1a[a]



Entry	Base	Yield (%)[b]
1	Toluene	40
2	CH_3CN	50
3	THF	0
4	DCM	0
5	$CHCl_3$	0
6	$CHCl_2CHCl_2$	0
7	CH_2BrCH_2Br	0

[a]0.10 mmol of *N*-propargyl-*N*-tosylamide (**1a**) (29.9 mg), H_2O (0.50 mmol), Eosin Y (2.5 mol %), K_2CO_3 (1.5 equiv.), and PhSSPh (0.10 mmol) in solvent (2.0 mL) under an air atmosphere at room temperature for 24 h, blue LED light. [b]Isolated yield.

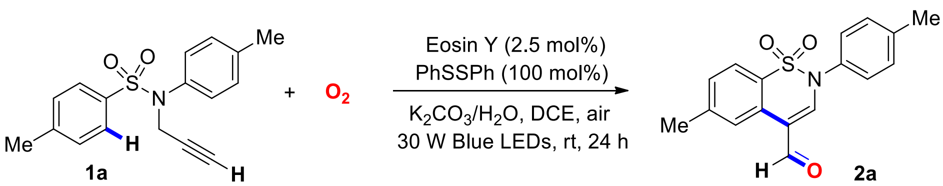
Table S-4. The Effect of the dosage of PhSSPh on the intramolecular carbo-oxygenation of alkyne 1a[a]



Entry	PhSSPh (x equiv.)	Yield (%)[b]
1	0.1	15
2	0.3	31
3	0.5	47
4	1.0	75

[a]0.10 mmol of *N*-propargyl-*N*-tosylamide (**1a**) (29.9 mg), H_2O (0.50 mmol), Eosin Y (2.5 mol %), K_2CO_3 (1.5 equiv.), and PhSSPh (0.10 -1.0 mmol) in DCE (2.0 mL) under an air atmosphere at room temperature for 24 h, blue LED light. [b]Isolated yield.

Table S-5. Control experiments[a]

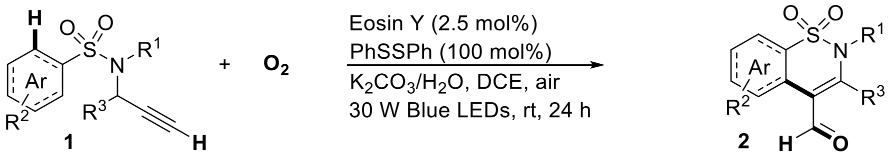


Entry	Changes to standard conditions	Yield (%)[b]
1	none	75
2	no photocatalyst	48
3	no PhSSPh	0
4	no light	0
5	no base	0
6	Ar instead of O_2	0
7	without H_2O	48

[a]0.10 mmol of *N*-propargyl-*N*-tosylamide (**1a**) (29.9 mg), H_2O (0.50 mmol), Eosin Y (2.5 mol %), K_2CO_3 (1.5 equiv.), and PhSSPh (1.0 equiv) in DCE (2.0 mL) under an air atmosphere at room temperature for 24 h, blue LED light. [b]Isolated yield.

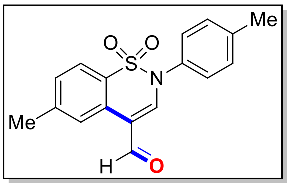
IV. General Procedure and Characterization Data of the Products

1. Procedure for the photocatalyzed intramolecular carbo-oxygenation of alkynes

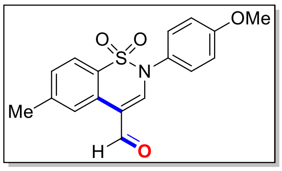


A flame-dried 5 mL Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with *N*-propargyl-*N*-tosylamides (**1**, 0.10 mmol, 29.9 mg), Eosin Y (2.5 mol %, 1.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg), PhSSPh (0.10 mmol, 21.8 mg) and H_2O (0.50 mmol, 9.0 uL), followed by the addition of DCE (2.0 mL) under air. Then the mixture was stirred and irradiated with 2 × 30 W blue LEDs at room temperature for 24 h. The residue was purified by flash column chromatography on silica gel (petrol ether/EtOAc = 20/1) to afford the desired products **2**.

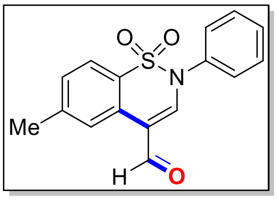
2. Spectroscopic data of formyl-substituted *N*-heterocycles



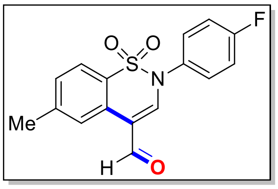
6-Methyl-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2a): yellow solid (23.5 mg, 75%); m.p. 168.5-169.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.68 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.39 (dd, *J* = 17.5, 8.9 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2, 150.0, 144.3, 140.3, 133.7, 130.6, 129.6, 129.3, 127.4, 127.3, 126.2, 122.6, 115.9, 22.1, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{16}NO_3S$: 314.0845, found: 314.0843.



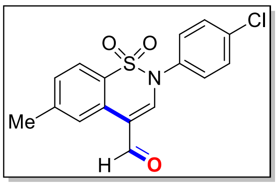
2-(4-Methoxyphenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2b): yellow solid (22.4 mg, 68%); m.p. 163.5-165.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.69 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.34 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 160.8, 150.3, 144.3, 129.6, 129.3, 129.3, 128.7, 127.2, 126.2, 122.7, 115.7, 115.1, 55.7, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{16}NO_4S$: 330.0795, found: 330.0793.



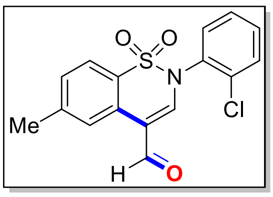
6-Methyl-2-phenyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2c): yellow solid (17.6 mg, 59%); m.p. 163.5-164.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.68 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.47 (m, 5H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.38 (s, 1H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2, 149.6, 144.4, 136.4, 130.0, 129.8, 129.7, 129.2, 127.5, 127.4, 126.2, 122.6, 116.2, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{14}NO_3S$: 300.0689, found: 300.0687.



2-(4-Fluorophenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2d): yellow solid (19.7 mg, 62%); m.p. 140.5-141.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.58 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.41 (s, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.26 (s, 1H), 7.12 (t, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 163.2 (d, *J* = 250 Hz, $^1J_{CF}$), 149.5, 144.5, 132.1 (d, *J* = 4 Hz, $^3J_{CF}$), 129.9, 129.8, 129.1, 127.2, 126.3, 122.6, 117.0 (d, *J* = 23 Hz, $^2J_{CF}$), 116.2, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}FNO_3S$: 318.0595, found: 318.0594.

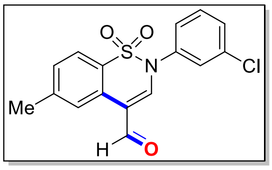


2-(4-Chlorophenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2e): yellow solid (21.6 mg, 65%); m.p. 165.5-167.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.69 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.43 (m, 3H), 7.36 (s, 1H), 2.55 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.0, 149.0, 144.6, 136.0, 134.8, 130.2, 129.8, 129.1, 128.8, 127.3, 126.4, 122.6, 116.6, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}ClNO_3S$: 334.0299, found: 334.0297.

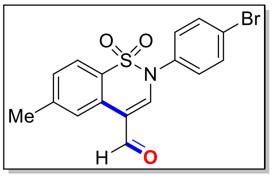


2-(2-Chlorophenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2f): yellow solid (17.0 mg, 51%); m.p. 160.7-161.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.71 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.31 (s, 1H), 2.55 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$)

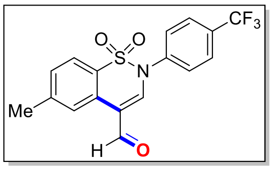
δ 188.2, 149.9, 144.4, 133.8, 133.3, 131.7, 131.2, 131.2, 129.7, 129.2, 128.2, 127.9, 126.5, 122.4, 116.5, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}ClNO_3S$: 334.0299, found: 334.0302.



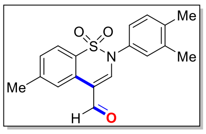
2-(3-Chlorophenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2g): yellow solid (21.6 mg, 65%); m.p. 130.5-131.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.68 (s, 1H), 7.89 (dd, *J* = 21.3, 8.2 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 3H), 7.38 (s, 1H), 2.55 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 148.8, 144.6, 137.3, 135.6, 130.8, 130.02, 129.9, 129.0, 127.6, 127.4, 126.4, 125.6, 122.6, 116.8, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}ClNO_3S$: 334.0299, found: 334.0301.



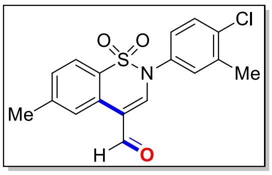
2-(4-Bromophenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2h): yellow solid (24.1 mg, 64%); m.p. 182.5-184.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.68 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.36 (s, 1H), 2.54 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 148.9, 144.6, 135.3, 133.2, 129.8, 129.1, 129.0, 127.3, 126.4, 124.0, 122.6, 116.6, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}BrNO_3S$: 377.9794, found: 377.9794.



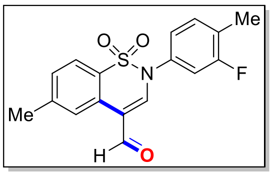
6-Methyl-2-(4-(trifluoromethyl)phenyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2i): yellow solid (20.2 mg, 55%); m.p. 168.5-169.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.66 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 2.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.0, 148.2, 144.7, 139.4,131.6 (d, *J* = 33 Hz, $^2J_{CF}$), 130.0, 129.0, 127.5, 127.4, 127.6 (q, *J* = 4 Hz, $^3J_{CF}$), 126.7, 126.5, 122.6, 117.3, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{13}F_3NO_3S$: 368.0563, found: 368.0560.



2-(3,4-Dimethylphenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2j): yellow solid (21.9 mg, 67%); m.p. 164.5-165.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.70 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 7.31 – 7.24 (m, 3H), 2.53 (s, 3H), 2.34 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2, 150.1, 144.2, 139.0, 138.7, 133.9, 130.9, 129.6, 129.3, 128.5, 127.3, 126.1, 124.9, 122.6, 115.7, 22.1, 22.1, 19.8, 19.6; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{18}H_{18}NO_3S$: 328.1002, found: 328.0996.

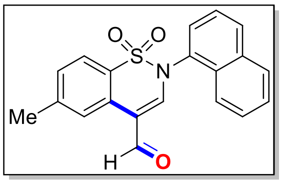


2-(4-Chloro-3-methylphenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2k): yellow solid (22.2 mg, 64%); m.p. 152.5-154.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.56 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.25 (s, 1H), 7.20 – 7.16 (m, 1H), 2.42 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 149.3, 144.5, 138.3, 136.1, 134.6, 130.4, 129.8, 129.1, 127.3, 126.3, 126.1, 122.6, 116.3, 22.1, 20.2; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{15}ClNO_3S$: 348.0456, found: 348.0456.

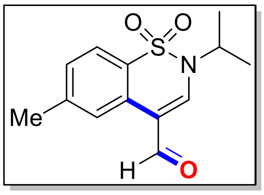


2-(3-Fluoro-4-methylphenyl)-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2l): yellow solid (20.9 mg, 63%); m.p. 147.5-148.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.57 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.14 – 7.08 (m, 2H), 2.43 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (101

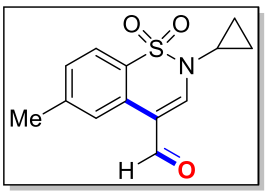
MHz, $CDCl_3$) δ 188.1, 161.1 (d, *J* = 247 Hz, $^1J_{CF}$), 149.3, 144.5, 134.8, 134.7, 132.4 (d, *J* = 6 Hz, $^3J_{CF}$), 129.8, 129.1, 127.4, 127.3, 127.2, 126.3, 123.0 (d, *J* = 3 Hz, $^3J_{CF}$), 122.6, 116.4, 114.7 (d, *J* = 24 Hz, $^2J_{CF}$), 22.1, 14.4; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{15}FNO_3S$: 332.0751, found: 332.0748.



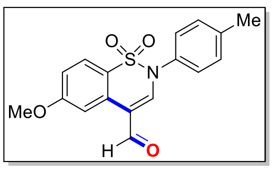
6-Methyl-2-(naphthalen-1-yl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2m): yellow solid (14.3 mg, 41%); m.p. 167.5-168.3 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.79 (s, 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 7.98 (t, *J* = 5.7 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.55 (m, 3H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.42 (s, 1H), 2.59 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2, 151.2, 144.4, 134.7, 132.3, 131.2, 131.1, 129.8, 129.3, 128.6, 128.3, 128.2, 127.5, 127.2, 126.4, 125.5, 122.7, 122.5, 116.0, 22.1; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{20}H_{16}NO_3S$: 350.0845, found: 350.0843.



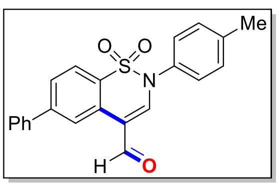
2-Isopropyl-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2n): yellow solid (15.9 mg, 60%); m.p. 93.5-95.3 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.62 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 4.91 – 4.78 (m, 1H), 2.49 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.0, 145.4, 144.0, 129.3, 129.1, 126.7, 125.7, 122.1, 115.9, 49.3, 22.9, 22.0; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{13}H_{16}NO_3S$: 266.0845, found: 266.0846.



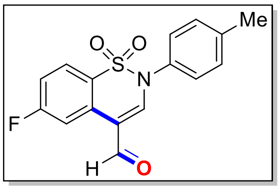
2-Cyclopropyl-6-methyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2o): yellow solid (17.6 mg, 67%); m.p. 109.5-110.3 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.60 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.27 (m, 2H), 3.56 – 3.12 (m, 1H), 2.48 (s, 3H), 1.22 – 1.03 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.0, 150.7, 144.2, 129.4, 129.0, 127.0, 125.8, 122.3, 115.4, 30.4, 22.0, 6.8; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{13}H_{14}NO_3S$: 264.0689, found: 264.0689.



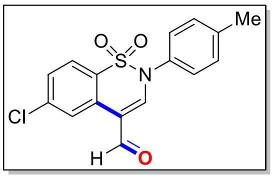
6-Methoxy-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2p): yellow solid (23.0 mg, 70%); m.p. 150.5-151.3 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.43 (s, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.9 Hz, 1H), 3.93 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2, 150.1, 146.4, 140.4, 139.3, 133.7, 130.6, 129.8, 129.1, 128.7, 128.3, 127.6, 127.5, 127.4, 124.6, 123.2, 116.1, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{16}NO_4S$: 330.0795, found: 330.0792.



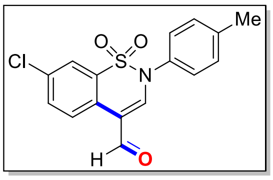
6-Phenyl-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2q): yellow solid (25.1 mg, 67%); m.p. 170.5-171.3 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.13 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 6.2 Hz, 3H), 7.33 (d, *J* = 7.7 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.2, 150.1, 146.4, 140.4, 139.3, 133.7, 130.6, 129.8, 129.1, 128.7, 128.3, 127.6, 127.5, 127.4, 124.6, 123.2, 116.1, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{22}H_{18}NO_3S$: 376.1002, found: 376.0998.



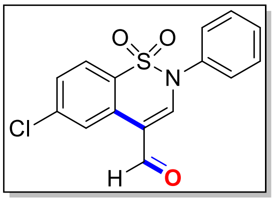
6-Fluoro-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2r): yellow solid (21.9 mg, 69%); m.p. 135.5-137.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.66 (d, *J* = 10.7 Hz, 1H), 8.09 – 7.99 (m, 1H), 7.45 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.8, 165.3 (d, *J* = 252 Hz, $^1J_{CF}$) 150.6, 140.6, 133.3,132.1 (d, *J* = 11 Hz, $^3J_{CF}$), 130.7, 127.4, 125.9 (d, *J* = 3 Hz, $^3J_{CF}$), 125.5 (d, *J* = 10 Hz, $^3J_{CF}$), 125.5, 116.5 (d, *J* = 24 Hz, $^2J_{CF}$), 115.0 (d, *J* = 3 Hz, $^3J_{CF}$),113.0 (d, *J* = 26 Hz, $^2J_{CF}$), 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}FNO_3S$: 318.0595, found: 318.0593.



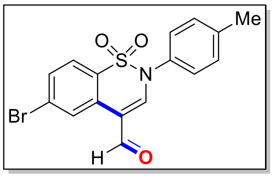
6-Chloro-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2s): yellow solid (22.3 mg, 67%); m.p. 177.5-178.3 ºC; **^{1}H NMR** (400 MHz, DMSO) δ 9.62 (s, 1H), 8.82 (s, 1H), 8.29 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.44 (dd, *J* = 20.2, 7.2 Hz, 4H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 190.2, 153.0, 140.5, 139.2, 133.4, 131.2, 130.8, 129.5, 128.1, 127.9, 125.3, 125.1, 114.2, 21.2; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}ClNO_3S$: 334.0299, found: 334.0301.



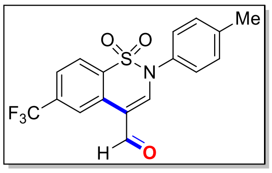
7-Chloro-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2t): yellow solid (13.3 mg, 40%); m.p. 159.5-161.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.88 (d, *J* = 8.8 Hz, 1H), 8.01 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 5.5 Hz, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.9, 149.6, 140.6, 134.7, 133.5, 133.4, 130.9, 130.7, 127.8, 127.7, 127.5, 122.5, 115.7, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}ClNO_3S$: 334.0299, found: 334.0299.



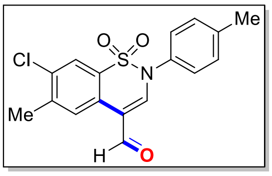
6-Chloro-2-phenyl-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2u): yellow solid (17.5 mg, 55%); m.p. 202.5-203.3 ºC; **^{1}H NMR** (400 MHz, DMSO) δ 9.65 (s, 1H), 8.83 (d, *J* = 1.9 Hz, 1H), 8.36 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.66 – 7.57 (m, 5H); **^{13}C NMR** (101 MHz, DMSO) δ 190.3, 152.9, 139.2, 136.0, 131.2, 130.5, 130.4, 129.5, 128.2, 128.0, 125.3, 125.2, 114.4; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{15}H_{11}ClNO_3S$: 320.0143, found: 320.0143.



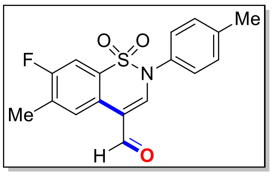
6-Bromo-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2v): yellow solid (24.1 mg, 64%); m.p. 187.5-188.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 9.11 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.44 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.7, 150.5, 140.7, 133.3, 131.9, 130.8, 130.7, 128.9, 128.6, 128.4, 127.4, 124.1, 114.9, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{16}H_{13}BrNO_3S$: 377.9794, found: 377.9796.



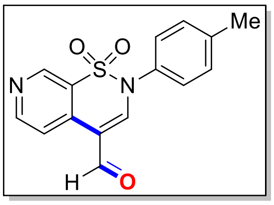
2-(*p*-Tolyl)-6-(trifluoromethyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2w): yellow solid (22.0 mg, 60%); m.p. 161.5-162.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 9.26 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.50 (s, 1H), 7.38 (dd, *J* = 18.0, 8.2 Hz, 4H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.7, 150.4, 140.8, 135.3, 135.0, 133.2, 132.2, 130.7, 130.1, 127.4, 125.4 (q, J = 4 Hz, $^3J_{CF}$), 123.6, 123.3 (d, J = 272 Hz, $^1J_{CF}$), 115.4, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{13}F_3NO_3S$: 368.0563, found: 368.0559.



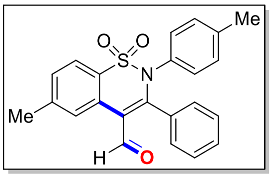
7-Chloro-6-methyl-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2x): yellow solid (19.1 mg, 55%); m.p. 191.5-193.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.79 (s, 1H), 7.97 (s, 1H), 7.38 (s, 1H), 7.35 (d, J = 4.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.53 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.0, 149.9, 142.5, 140.5, 135.0, 133.5, 130.6, 128.6, 128.2, 127.6, 127.5, 123.0, 115.6, 21.2, 20.8; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{15}ClNO_3S$: 348.0456, found: 348.0454.



7-Fluoro-6-methyl-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2y): yellow solid (18.9 mg, 57%); m.p. 199.5-200.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.77 (d, J = 6.9 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 5.4 Hz, 3H), 2.43 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 161.7, 149.4, 140.5, 133.5, 132.0 (d, J = 18 Hz, $^2J_{CF}$), 130.6, 129.6 (d, J = 5 Hz, $^3J_{CF}$), 128.8 (d, J = 7 Hz, $^3J_{CF}$), 125.4 (d, J = 4 Hz, $^3J_{CF}$), 109.2 (d, J = 27 Hz, $^2J_{CF}$), 21.3, 15.2; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{17}H_{15}FNO_3S$: 332.0751, found: 332.0746.

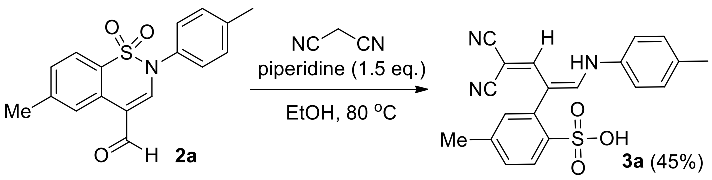


2-(*p*-Tolyl)-2H-pyrido[4,3-e][1,2]thiazine-4-carbaldehyde 1,1-dioxide (2z): yellow solid (15.0 mg, 50%); m.p. 141.5-142.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 9.05 – 8.89 (m, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.91 (s, 1H), 7.53 – 7.47 (m, 1H), 7.33 (q, J = 8.0 Hz, 4H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.9, 153.5, 148.6, 142.1, 140.6, 133.3, 131.4, 130.6, 127.5, 125.6, 122.2, 114.7, 21.3; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{15}H_{13}N_2O_3S$: 301.0641, found: 301.0635.



6-Methyl-3-phenyl-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine-4-carbaldehyde1,1-dioxide (2-1z): light yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.15 (d, J = 8.6 Hz, 1H), 8.06 (s, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H), 2.27 (s, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 150.8, 145.6, 135.5, 135.3, 134.8, 132.0, 130.2, 130.0, 129.7, 128.9, 128.3, 128.1, 127.7, 127.5, 127.0, 126.2, 121.9, 121.2, 114.9, 21.6, 21.4; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{23}H_{20}NO_3S$: 390.1158, found: 390.1148.

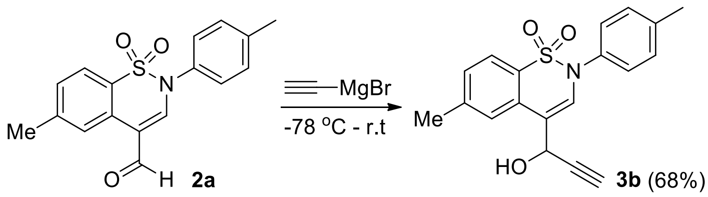
3. Synthetic applications of this transformation



Preparation of 2-(4,4-dicyano-1-(*p*-tolylamino)buta-1,3-dien-2-yl)-4-methylbenzenesulfonica cid 3a.[5]

A mixture of compound **2a** (0.30 mmol), piperidine (0.5 mL) and malononitrile (0.30 mmol) in ethanol (5.0 mL) was heated under reflux for 3 hours. The mixture was then cooled to 25-30 °C and condensed under reduced pressure to form the corresponding oil. The residue was purified by flash column chromatography on silica gel to afford the desired product **3a**. Yellow solid (17.1 mg, 45%); m.p. 173.5-1474.3 °C; **^{1}H NMR** (400 MHz, DMSO) δ 12.66 (s, 1H), 9.93 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 2.5 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.18 (s, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 160.0, 150.4, 143.9, 141.4, 135.9, 135.0, 134.8, 134.3, 133.4, 130.3, 130.0, 129.6, 120.0, 116.9, 116.3, 102.8, 21.1, 20.7; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{20}H_{18}N_3O_3S$: 380.1063, found: 380.1060.

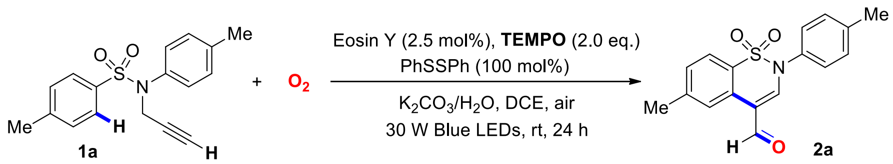
Preparation of 4-(1-hydroxyprop-2-yn-1-yl)-6-methyl-2-(*p*-tolyl)-2H-benzo[e][1,2]thiazine1,1-dioxide 3b.[6]



To an ice-cold solution of **2a** (0.2 mmol) in anhydrous THF (5 mL) under Ar atmosphere was added ethynylmagnesium bromide (1.5 eq., 0.5 M in THF), and the reaction mixture was stirred for 4 h (monitored by TLC analysis) at 0 °C. Reaction mixture was diluted with saturated aq. NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (10:1, hexane: EtOAc) gave the corresponding product **3b** in 68 % yields. Yellow solid (23.1 mg, 68%); m.p. 141.5-142.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.60 (s, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.17 (dd, *J* = 18.5, 8.1 Hz, 4H), 7.08 (s, 1H), 5.55 (s, 1H), 2.86 (s, 1H), 2.58 (s, 1H), 2.40 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 138.8, 134.7, 132.0, 131.3, 130.1, 129.0, 128.8, 127.1, 124.8, 122.6, 116.9, 81.8, 76.2, 61.0, 22.0, 21.2; **HR-MS (ESI)** calcd for $[M + H]^+$: $C_{19}H_{19}NO_3S$: 340.1007, found: 340.0817.

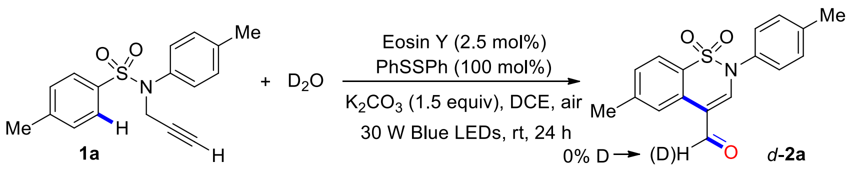
V. Control experiments for mechanistic investigation

1. The effect of the radical trapper TEMPO on the intramolecular carbo-oxygenation of alkyne 1a



An oven dried reaction tube containing a PTFE-coated stir bar was charged sequentially with **TEMPO** (2.0 equiv, 31.2 mg), *N*-propargyl-*N*-tosylamide **1a** (0.10 mmol, 29.9 mg), Eosin Y (2.5 mol %, 1.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg), PhSSPh (0.10 mmol, 21.8 mg) and H_2O (0.50 mmol, 9 uL), followed by the addition of DCE (2.0 mL) under air. Then the mixture was stirred and irradiated by 2 × 30 W blue LEDs at room temperature for 24 h. No desired product **2a** was detected, and the reaction was completely inhibited.

2. H/D exchange about the intramolecular carbo-oxygenation of alkyne 1a



N-Propargyl-*N*-tosylamide (**1a**, 0.10 mmol, 29.9 mg), Eosin Y (2.5 mol %, 1.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg), PhSSPh (0.10 mmol, 21.8 mg) and **D_2O** (0.50 mmol, 9 uL), followed by the addition of DCE (2.0 mL) under air, and the reaction vessel was irradiated with 2 × 30 W blue LED at room temperature for 24 h. After the reaction was complete, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography and preparative TLC to afford the corresponding product **2a**, ^{1}H NMR spectrum of *d*-**2a** indicated that no H/D exchange of formyl Csp^2-H bond was observed (**Figure S-1**).

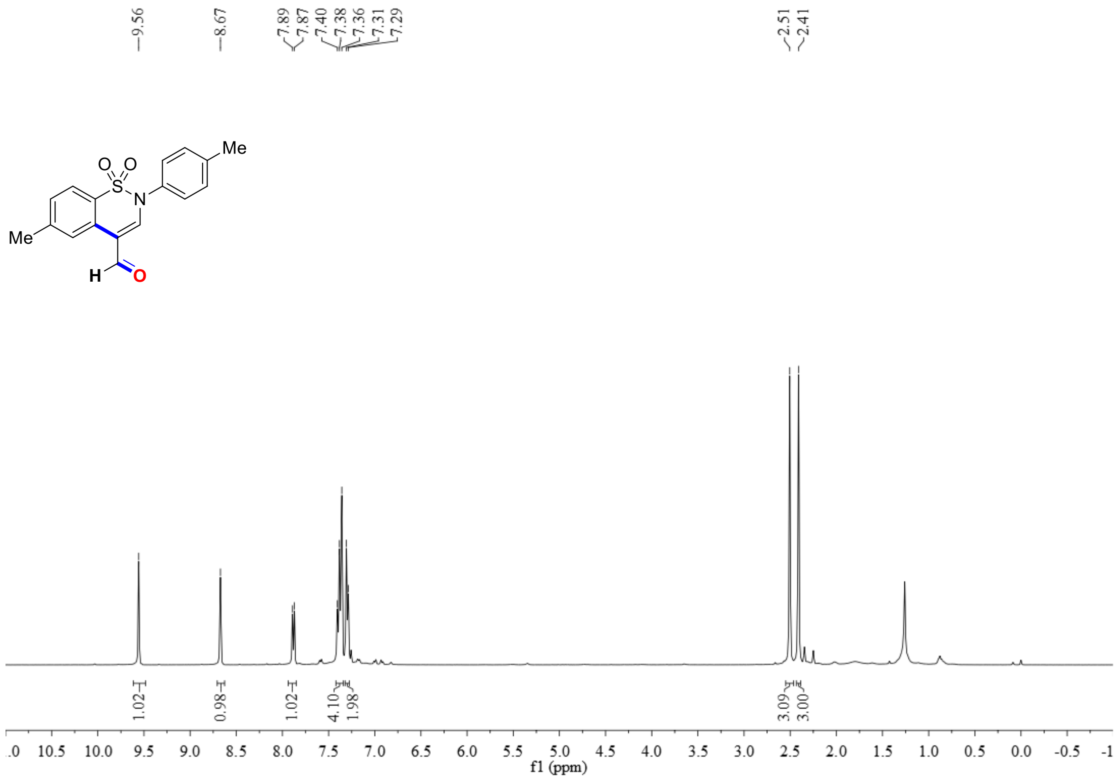
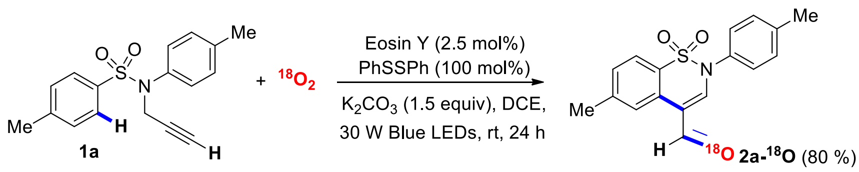


Figure S-1. **^{1}H NMR** analysis of *d*-**2a**

3. ^{18}O Isotope tracing experiment



N-Propargyl-*N*-tosylamide (**1a**, 0.10 mmol, 29.9 mg), Eosin Y (2.5 mol %, 1.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg), PhSSPh (0.10 mmol, 21.8 mg) and H_2O (0.50 mmol, 9 uL), followed by the addition of DCE (2.0 mL), and the reaction vessel was irradiated with 2 × 30 W blue LED at room temperature for 24 h under the atmosphere of **$^{18}O_2$**. After the reaction was complete, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography and preparative TLC to afford the corresponding product **2a-^{18}O**, which was characterized by **^{1}H NMR** (**Figure S-2**), **^{13}C NMR** (**Figure S-3**) and **HR-MS** (**Figure S-4**).

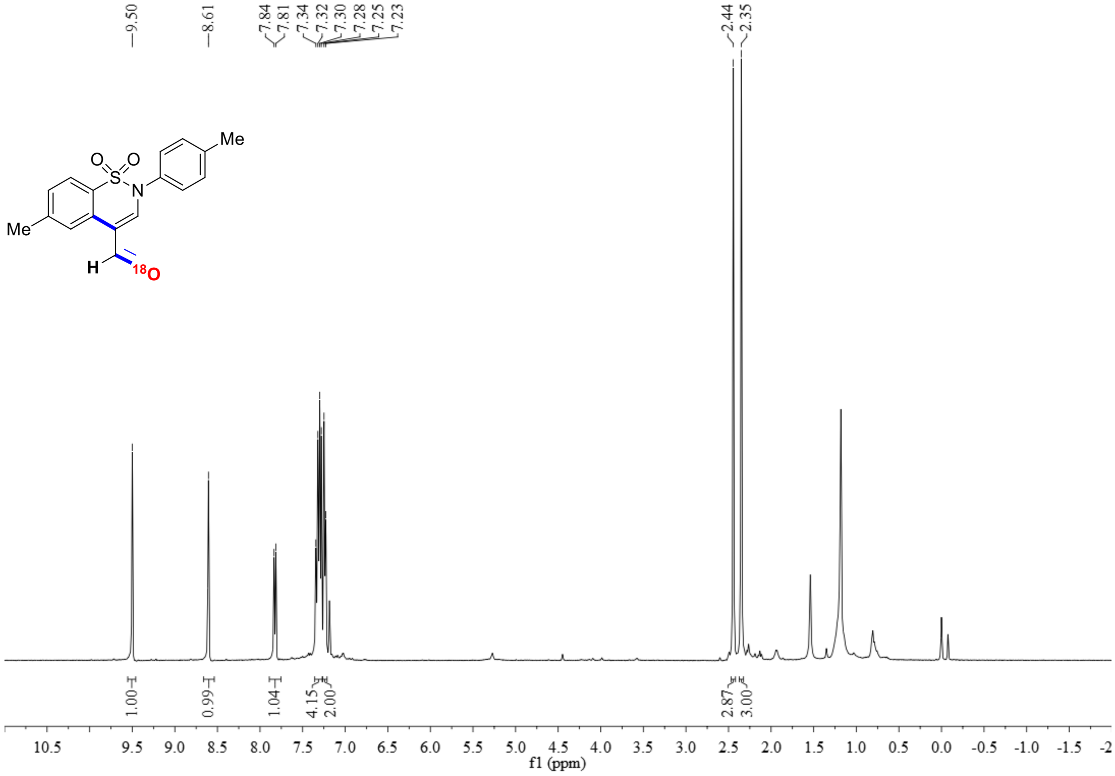


Figure S-2. **^{1}H NMR** analysis of **2a-^{18}O** isotopic labeled product

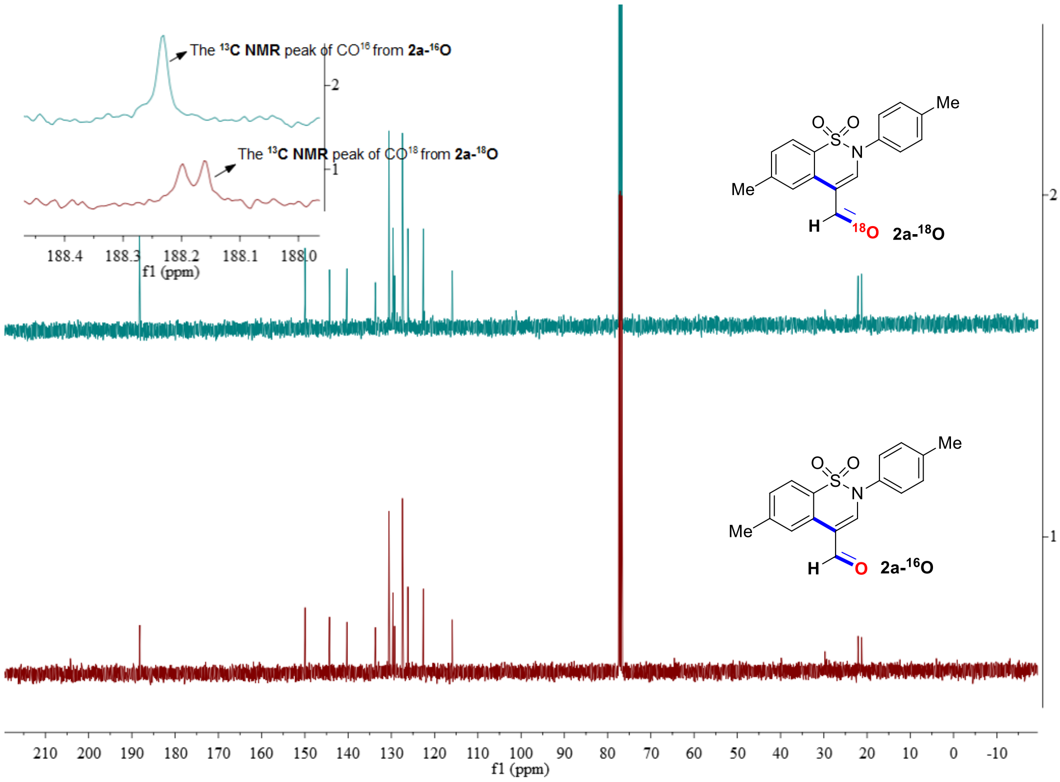


Figure S-3. **^{13}C NMR** analysis of **2a-^{16}O** and **2a-^{18}O**

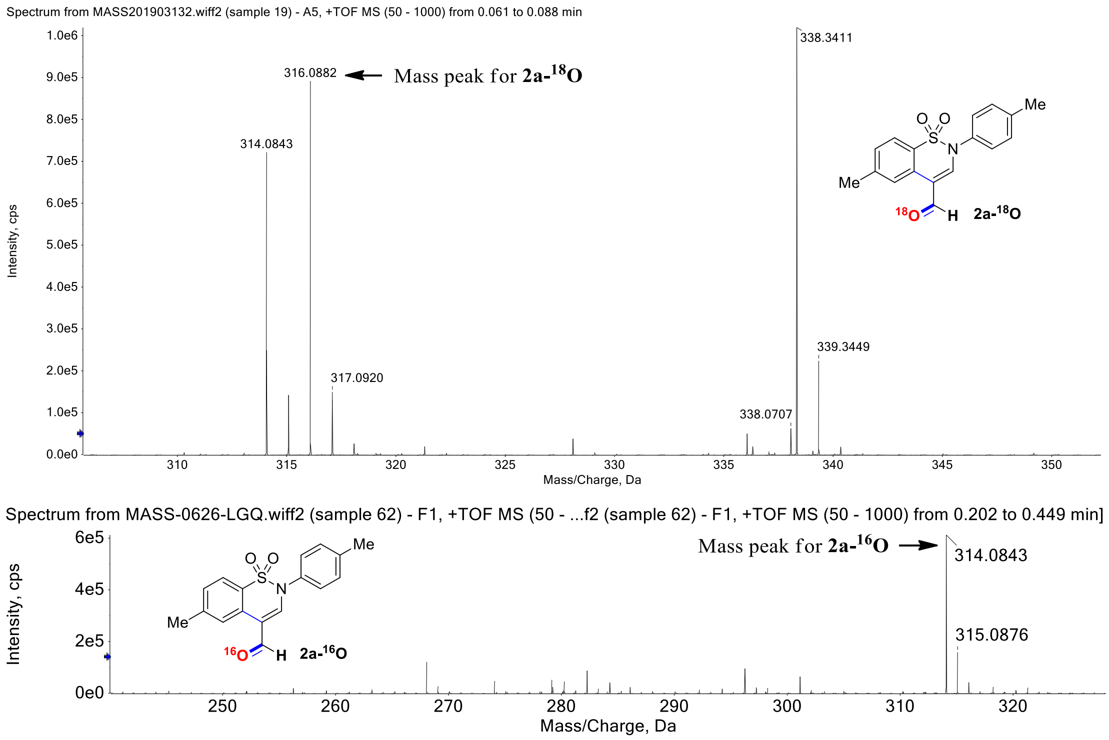
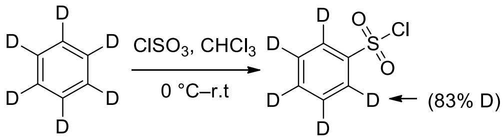
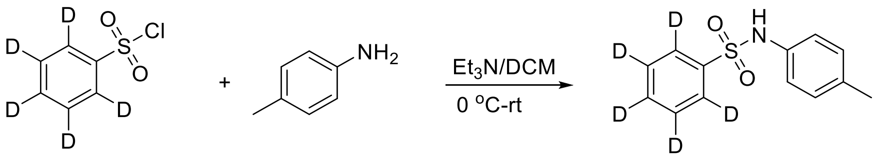


Figure S-4. **HR-MS** analysis of **2a-^{16}O** and **2a-^{18}O**

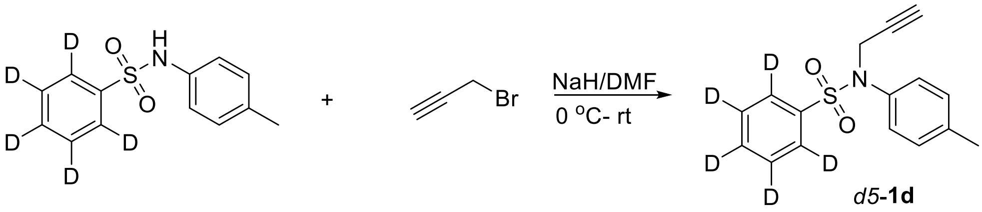
4. The procedure for the preparation of *d5*-1d



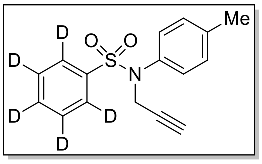
Benzene-d_6 (2.0 g, 25 mmol) (99.5% isotopic purity) was dissolved in 10 mL of $CHCl_3$, and cooled under argon to 0 °C. Chlorosulfuric acid (13 mL) was added during 10 min at the same temperature. The ice-salt bath was removed and the mixture was still stirred for 45 min at room temperature. The mixture was then diluted with 50 mL of CH_2Cl_2 and poured onto 100 mL of ice water. The organic layer was separated, washed with water (2 × 40 mL), dried with $MgSO_4$, and evaporated to give a colorless oil. Purification was carried out by distillation to give d_5-benzenesulfonyl chloride as clear colorless oil.[7]



To a solution of the aniline (1.0 equiv) in anhydrous DCM (20 mL) at 0 °C was added triethylamine (1.2 equiv) and d_5-benzenesulfonyl chloride (1.1 equiv). The reaction mixture was stirred at room temperature until the reaction was completed (monitored by TLC). Then water (50 mL) was carefully added, and the mixture was extracted by DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to dryness under reduced pressure to obtain a residue, then purified through flash chromatography on silica gel with ethyl acetate/petroleum (v/v = 25/1) as the eluent to afford the desired d_5-amides.



Finally to a solution of d_5-amides (1.0 equiv) in anhydrous DMF (20 mL) was added sodium hydride (60% dispersion in mineral oil, 1.1 equiv) at 0 °C under Ar. The reaction was stirred for 15 minutes at the same temperature and then 3-bromo-propyne (1.2 equiv) was slowly added *via* a syringe. The mixture was stirred at room temperature until the reaction completed and then quenched with a saturated solution of NH_4Cl (20 mL). The combined organic phases were washed with water (3 × 20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated to obtain the corresponding residue, which was then purified through flash chromatography on silica gel with ethyl acetate/petroleum (v/v = 50/1) as the eluent to afford the desired product *d5*-**1d**.



***N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (*d5*-1d): ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 0.32H), 7.56 (s, 0.17H), 7.44 (s, 0.33H), 7.15 – 7.04 (m, 4H), 4.42 (s, 2H), 2.33 (s, 3H), 2.15 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.5, 129.8, 128.42, 78.1, 73.8, 41.3, 21.2; **HR-MS (ESI)** calcd for $[M + Na]^+$: $C_{16}H_{10}D_5NO_2SNa$: 313.1030, found: 313.1057.

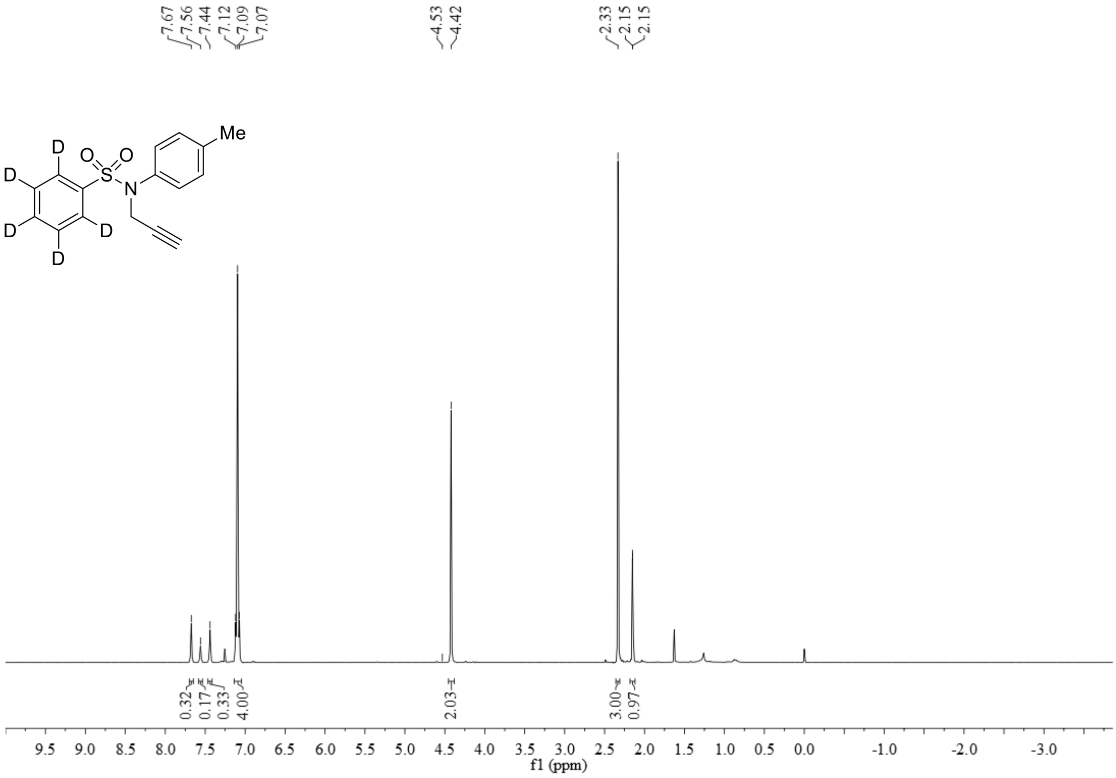
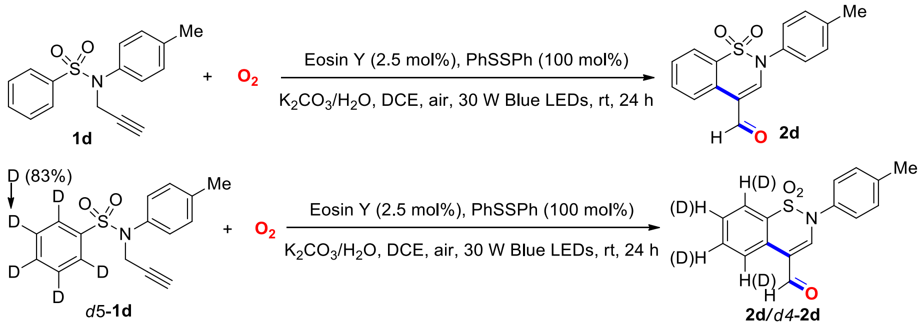


Figure S-5. **^{1}H NMR** analysis of *d5*-**1d**

5. Kinetic isotope effect for this transformation



A flame-dried 5 ml Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with *N*-propargyl-*N*-tosylamide (**1d**: 0.10 mmol, 28.5 mg or *d*5-**1d**: 0.1 mmol, 29.9 mg), Eosin Y (2.5 mol %, 1.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg), PhSSPh (0.10 mmol, 21.8 mg) and H_2O (0.50 mmol, 9.0 uL), followed by the addition of DCE (2.0 mL) under air. Then the mixture was stirred and irradiated with 2 x 30 W blue LEDs at room temperature. An aliquot of each reaction mixture was taken at 2 h, 4 h, 6 h, 8 h and 10 h. After the solvent of each aliquot (0.5 mL) was removed under reduced pressure conditions and analyzed by ^{1}H NMR spectrum (see **Figure S-4** and **Figure S-5**). The relative **^{1}H NMR** yield of **1d** and *d*5-**1d** were shown in **Table 1-6**. A sample plot of the initial rate data for the reaction of both **1d** and *d*5-**1d** was shown in **Figure S-6** and **Figure S-7**. The reaction progress in the early stage (0-10 h) indicated a kinetic isotope effect (KIE) of 1.0.

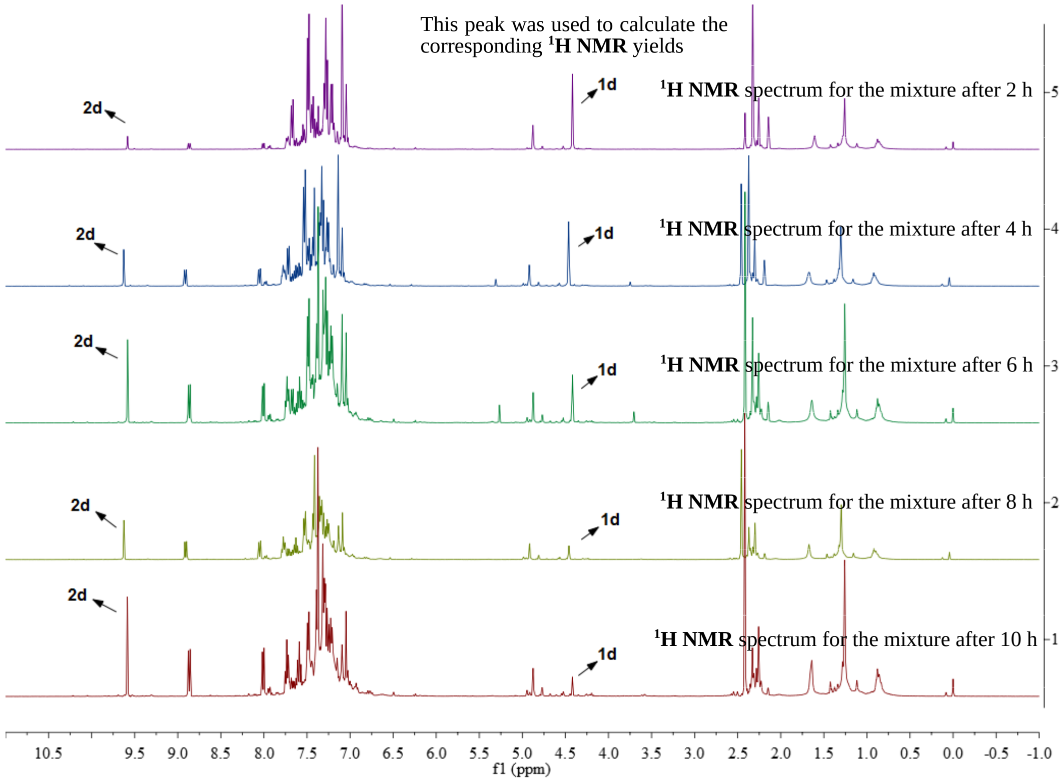


Figure S-6. The conversion of **1d** was monitored by **^{1}H NMR** method

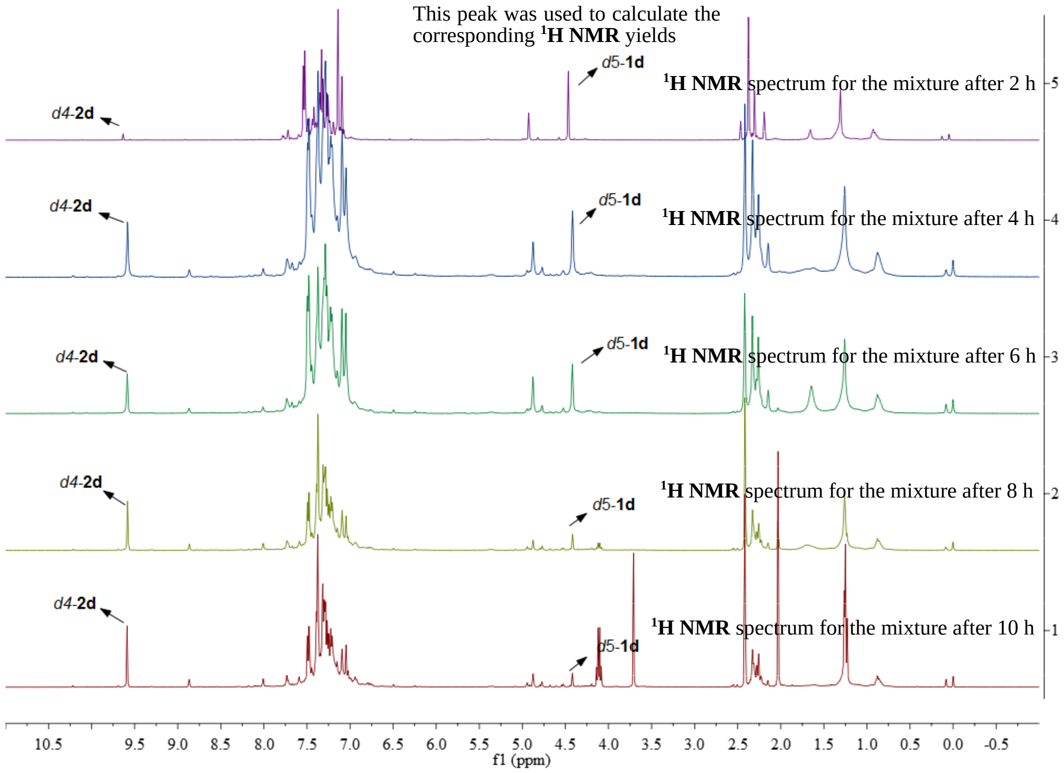


Figure S-7. The conversion of *d*5-**1d** was monitored by ^{1}**H NMR** method

Table S-6. The relative yields (%) of **2d** and *d*4-**2d** was monitored by ^{1}**H-NMR** method

Time (h)	0	2	4	6	8	10
^{1}H NMR yield of **2d** from **1d** (%)	0	9.9	28.6	56.1	66.7	79.2
^{1}H NMR yield of *d*4-**2d** from *d*5-**1d** (%)	0	7.4	39.8	41.5	72.7	79.1

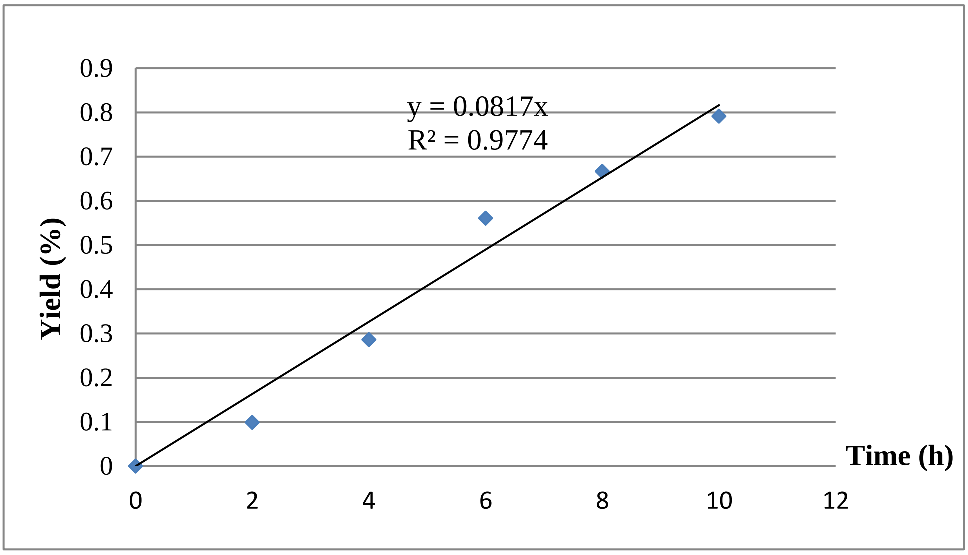


Figure S-8 The plot of initial rates for the conversion of **1d**

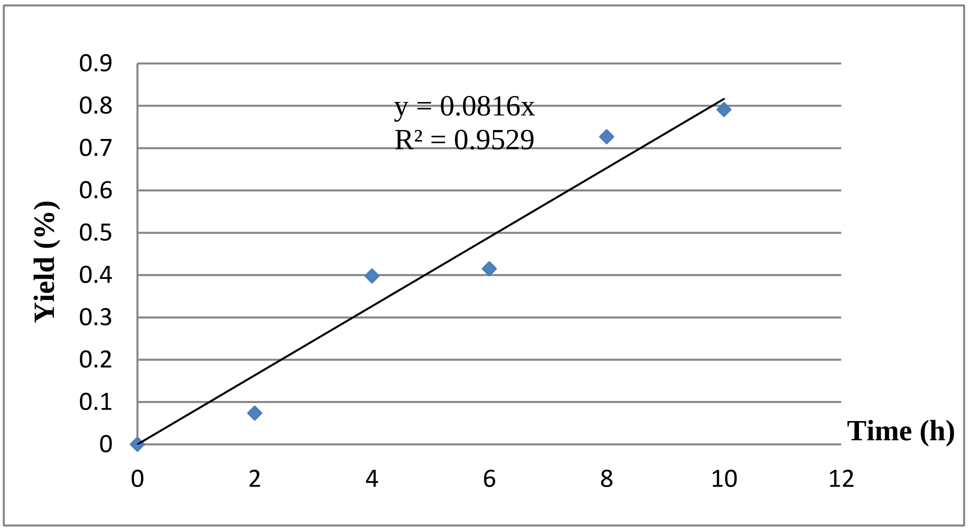
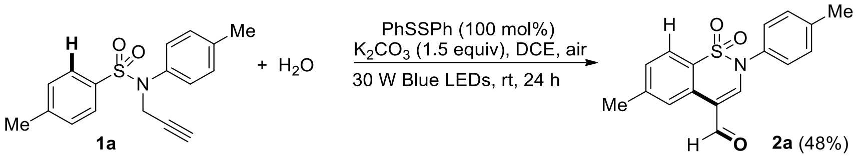


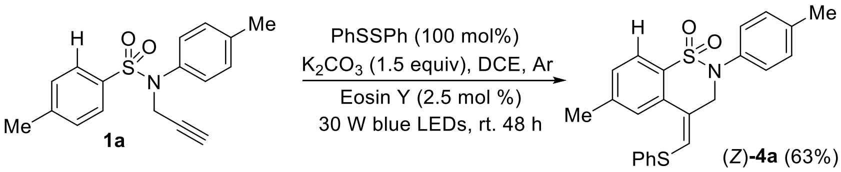
Figure S-9. The plot of initial rates for the conversion of *d*5-**1d**

6. The PhSSPh-promoted intramolecular carbooxygenation of alkyne 1a



An oven dried reaction tube containing a PTFE-coated stir bar was charged sequentially with *N*-propargyl-*N*-tosylamide (**1a**, 0.10 mmol, 30 mg), PhSSPh (0.10 mmol, 21.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg) and H_2O (0.50 mmol, 9.0 uL), followed by the addition of DCE (2.0 mL) under air. Then the mixture was stirred and irradiated with 2 × 30 W blue LEDs at room temperature for 24 h. The solvent was then evaporated to dryness, and the resulting residue was purified by silica gel column chromatography to provide pure product **2a** in 48% yield.

7. The photocatalyzed intramolecular carbooxygenation of alkynes 1a under argon



A flame-dried 5 mL Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with *N*-propargyl-*N*-tosylamides (**1**, 0.10 mmol, 29.9 mg), Eosin Y (2.5 mol %, 1.8 mg), K_2CO_3 (1.5 equiv, 20.7 mg), PhSSPh (0.10 mmol, 21.8 mg) and H_2O (0.50 mmol, 9.0 uL), followed by the addition of DCE (2.0 mL) under argon. Then the mixture was stirred and irradiated with 2 × 30 W blue LEDs at room temperature for 48 h. The residue was purified by flash column chromatography on silica gel (petrol ether/EtOAc = 50/1) to afford the vinyl thioether *(Z)*-**4a**. A yellow liquid (25.6 mg, 63%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.30 (m, 3H), 7.20 (m, 3H), 7.03 (s, 2H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.95 (d, *J* = 1.0 Hz, 1H), 6.23 (s, 1H), 4.51 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.2, 138.9, 137.1, 134.2, 133.8, 130.8, 130.6, 129.6, 129.5, 128.6, 128.0, 126.4, 125.5, 124.9, 124.7, 53.6, 21.8, 21.0; **HR-MS (ESI)** calcd for $[M + Na]^+$: $C_{23}H_{21}NO_2S_2Na$: 430.0911, found: 430.0909.

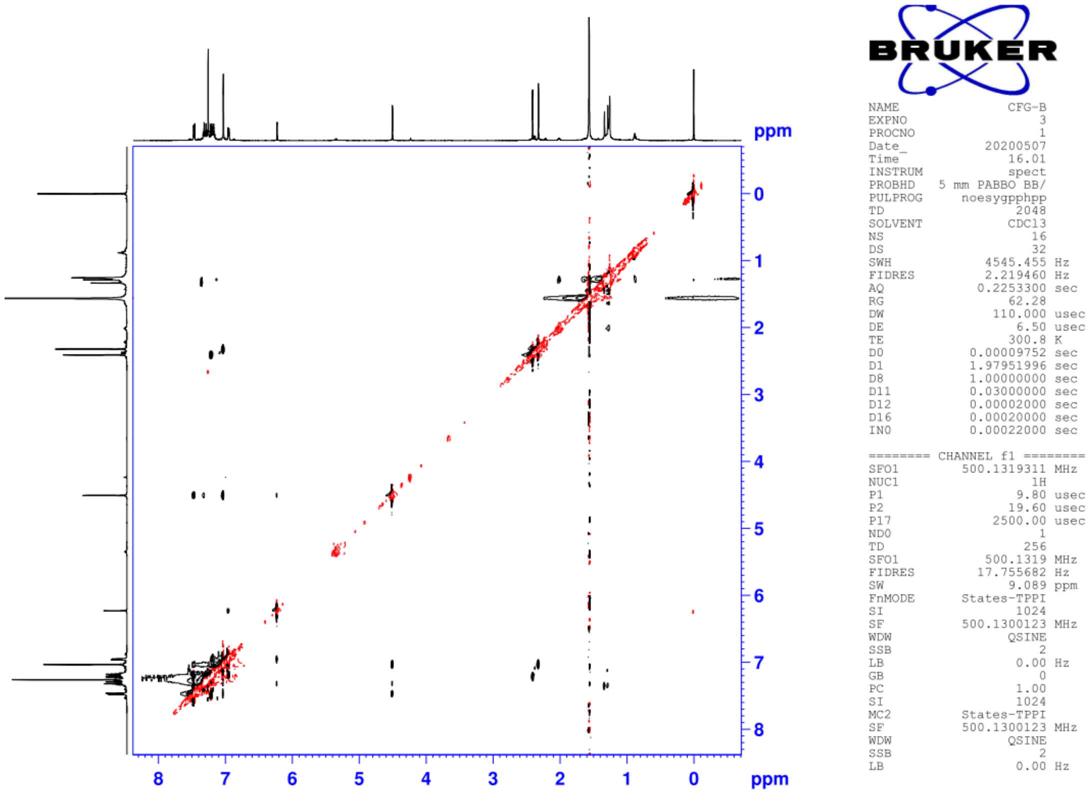
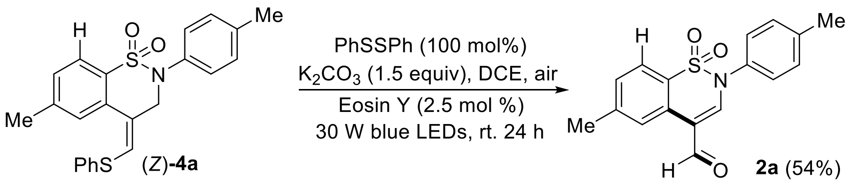


Figure S-10. The ^{1}H-^{1}H NOE spectrum of (*Z*)-**4a**

8. The vinyl thioether (*Z*)-4a converted to target compound 2a under standard conditions



The vinyl thioether (*Z*)-**4a** (40.7 mg, 0.1 mmol), Eosin Y (2.5 mol %, 1.8 mg), PhSSPh (21.8 mg, 0.1 mmol) and K_2CO_3 (20.7 mg, 1.5 equiv) were taken in an oven dried round bottom flask with a magnetic stir, and then, dry DCE (2 mL) was added. Then the mixture was stirred and irradiated with 2 × 30 W blue LEDs at room temperature for 24 h. The residue was purified by flash column chromatography on silica gel (petrol ether/EtOAc = 20/1) to afford the target compound **2a** (54% yield).

9. Luminescence Quenching Experiments

Fluorescence spectra was collected on Hitachi Fluorescence Spectrophotometer F-7000 for all experiments. All Eosin Y solutions were excited at 539 nm[8] and the emission intensity was collected at 450 nm. In a typical experiment, the emission spectrum of a 1×10^{-4} M solution of Eosin Y in CH_3CN was collected. The significant decrease of Eosin Y luminescence could be observed in the presence of PhSSPh and O_2. On the contrary, only a slightly decrease of Eosin Y luminescence was observed in the presence of substrate **1a** and O_2 (see **Figure S-11**).

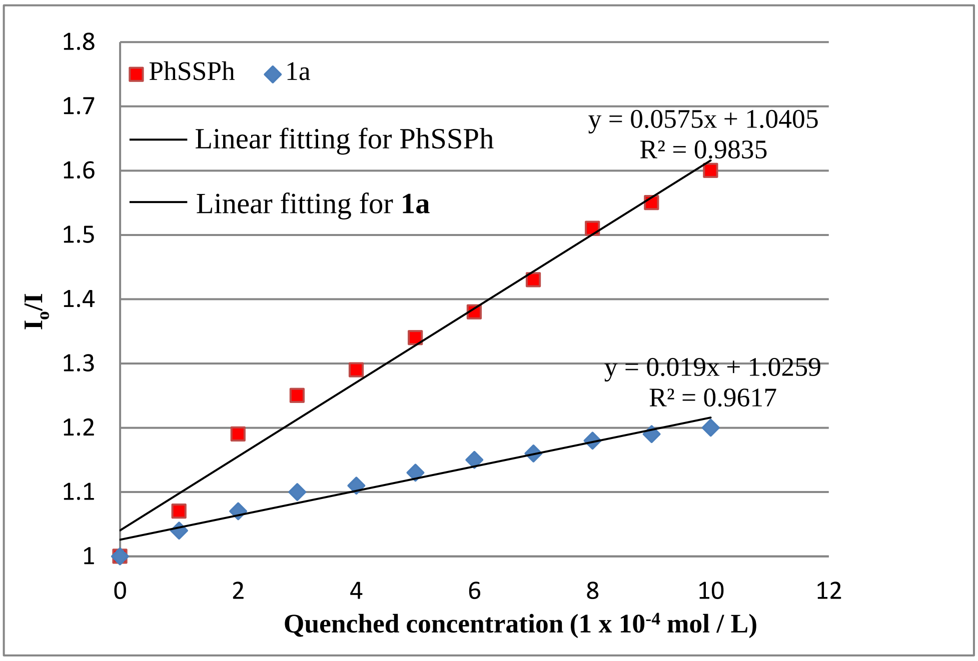
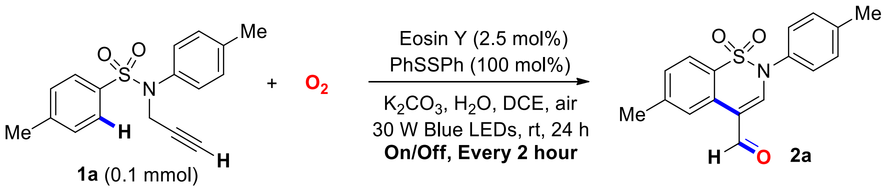


Figure S-11. Eosin Y emission quenching by **1a** and **PhSSPh**

10. Light On/Off Experiments

We performed the light ON/OFF experiments on the model reaction using 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide **1a** and the result are shown below.



The data showed that the formation of the desired product was halted during the lighf off period and product formation only occurred during constant irradiation with blue light. This experimental may indicate that a extended radical chain process is not likely and it manisfests the photoredox catalytic mechanism.

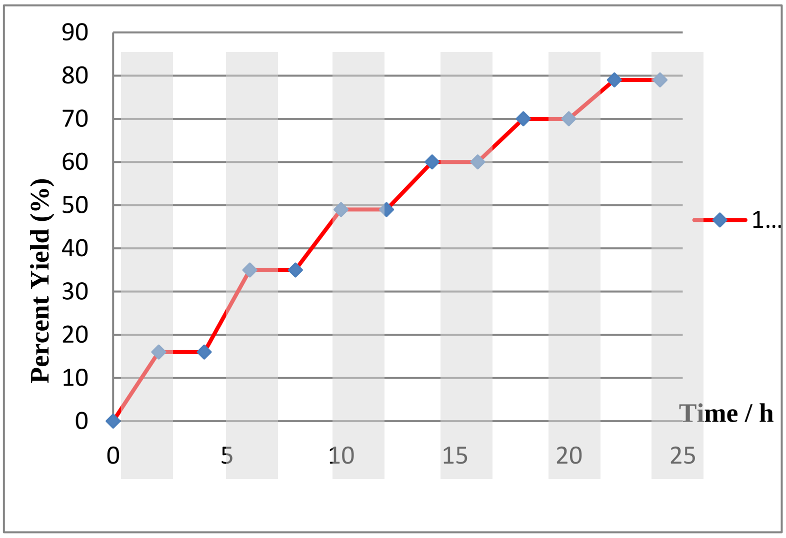


Figure S-12. Light ON/OFF experiment for the reaction of **1a**

VI. Single Crystal Structure and Crystallographic Data for 2u

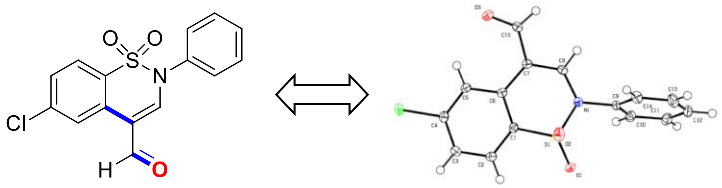


Figure S-13. The single crystal structure of **2u** (the ellipsoid contour probability level is 30%)

Table S-7. Crystal data and structure refinement for **2u**

Identification code	C1
Empirical formula	$C_{15}H_{10}ClNO_3S$
Formula weight	319.75
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.0797(4)
b/Å	8.5758(5)
c/Å	10.9983(6)
α/°	93.142(5)
β/°	91.207(4)
γ/°	91.822(5)
Volume/Å^3	666.24(7)
Z	2
ρ_{calc}g/cm^3	1.594
μ/mm^{-1}	0.452
F(000)	328.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.76 to 58.876
Index ranges	$-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $-13 \leq l \leq 15$
Reflections collected	9057
Independent reflections	3225 [R_{int} = 0.0439, R_{sigma} = 0.0571]
Data/restraints/parameters	3225/0/190

VII. Reference

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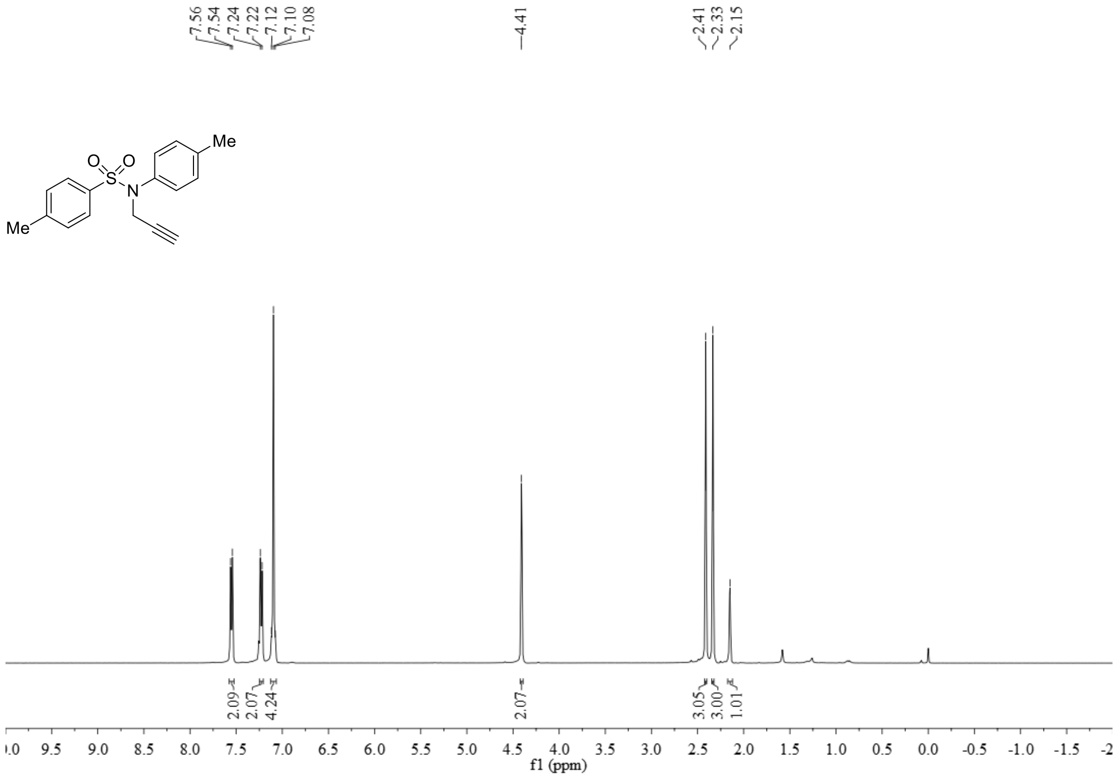
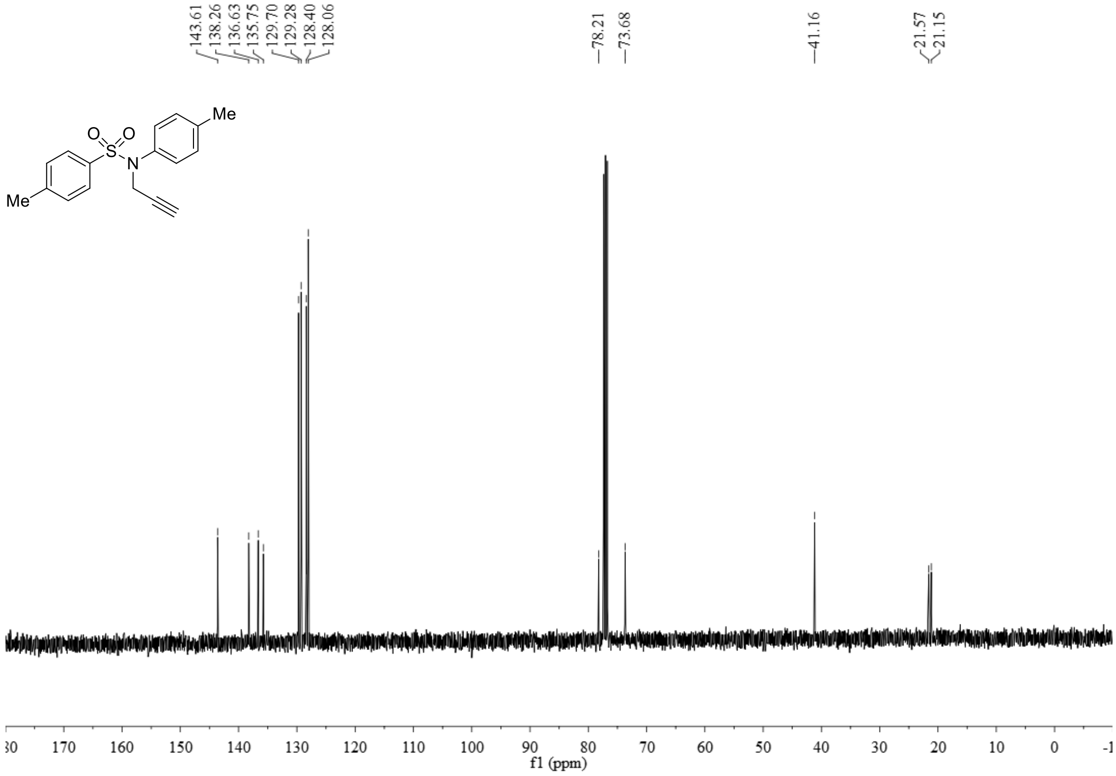
Appendix II: Spectral copies of ^{1}H and ^{13}C NMR of compounds

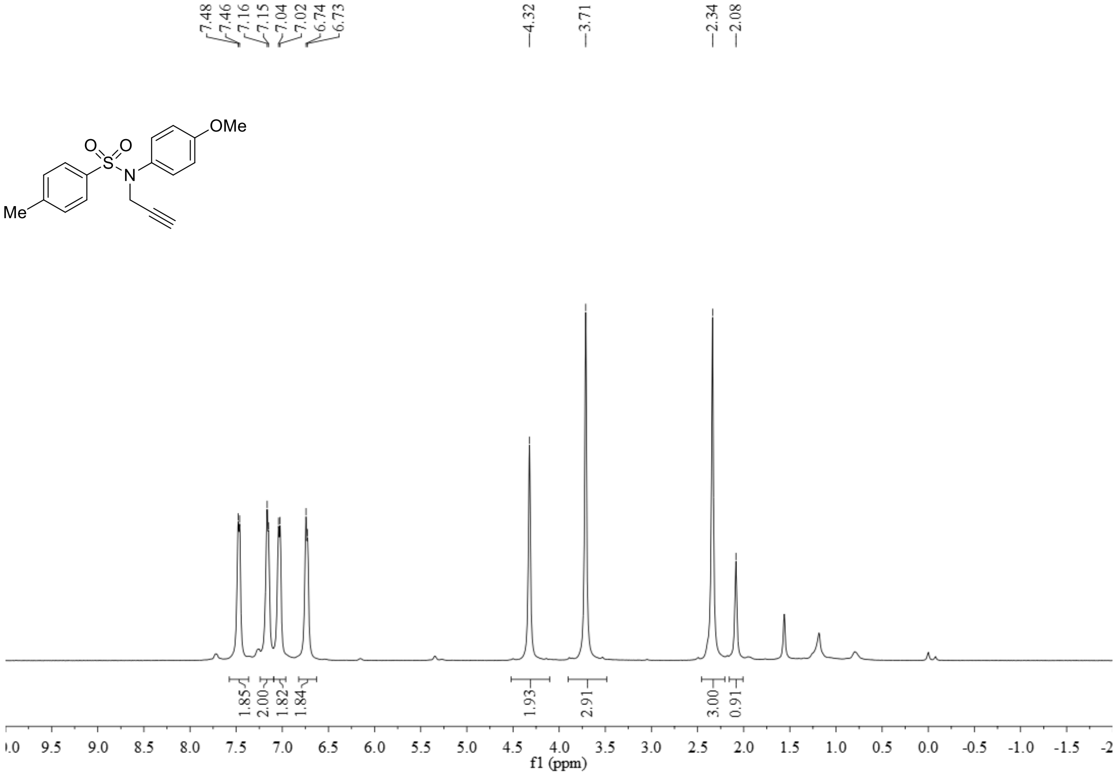
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**



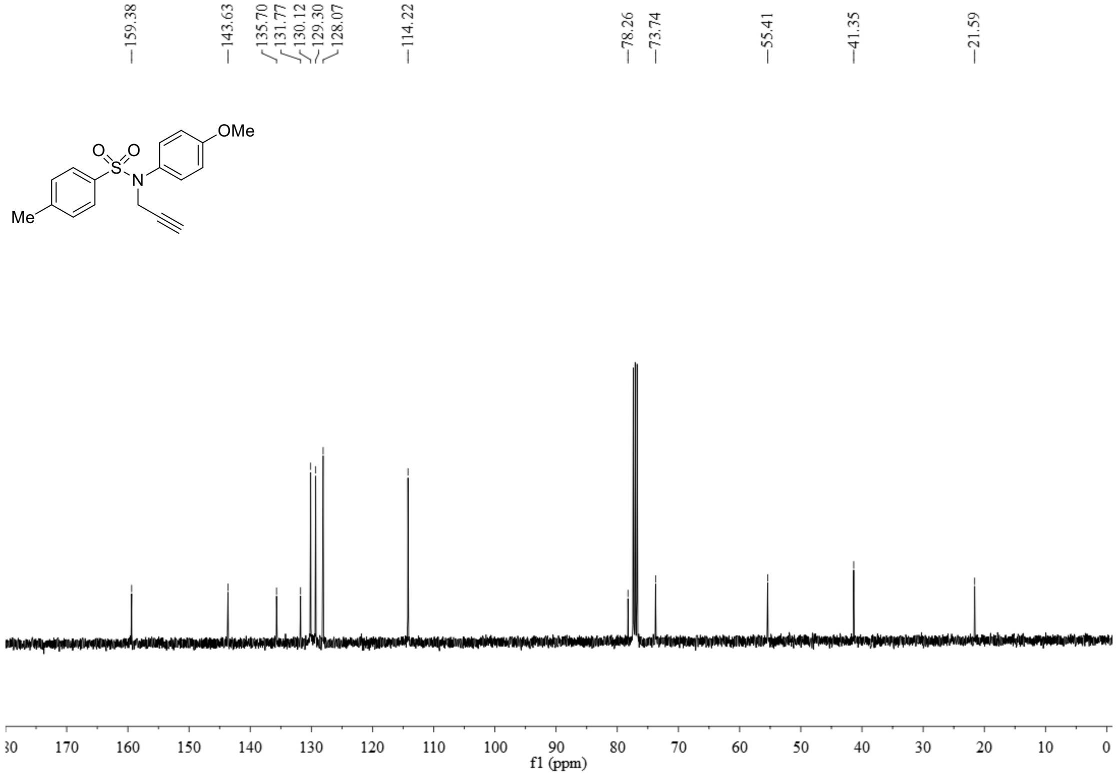
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1a**



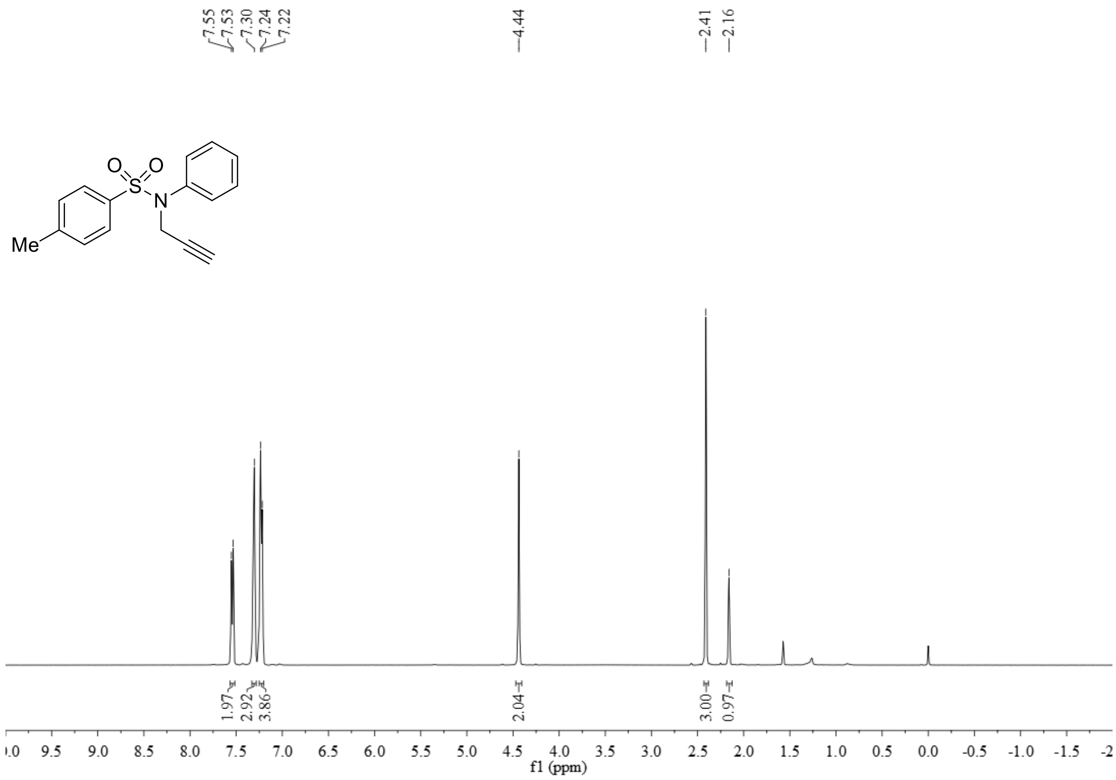
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**



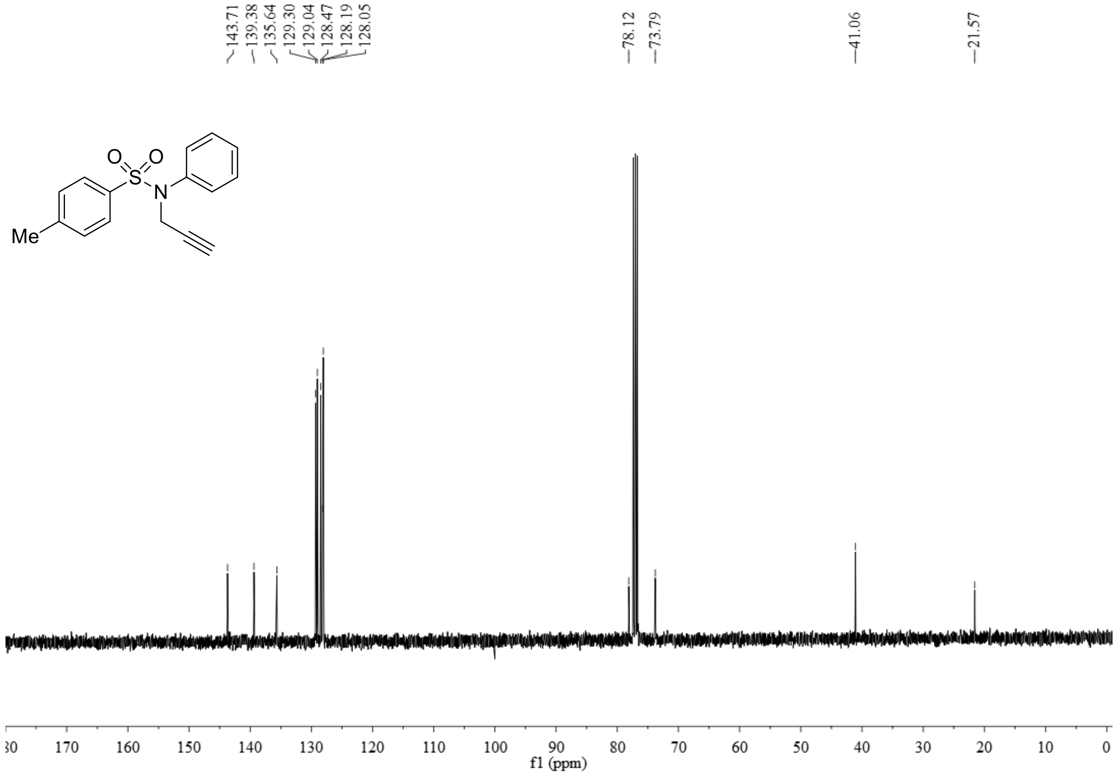
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1b**



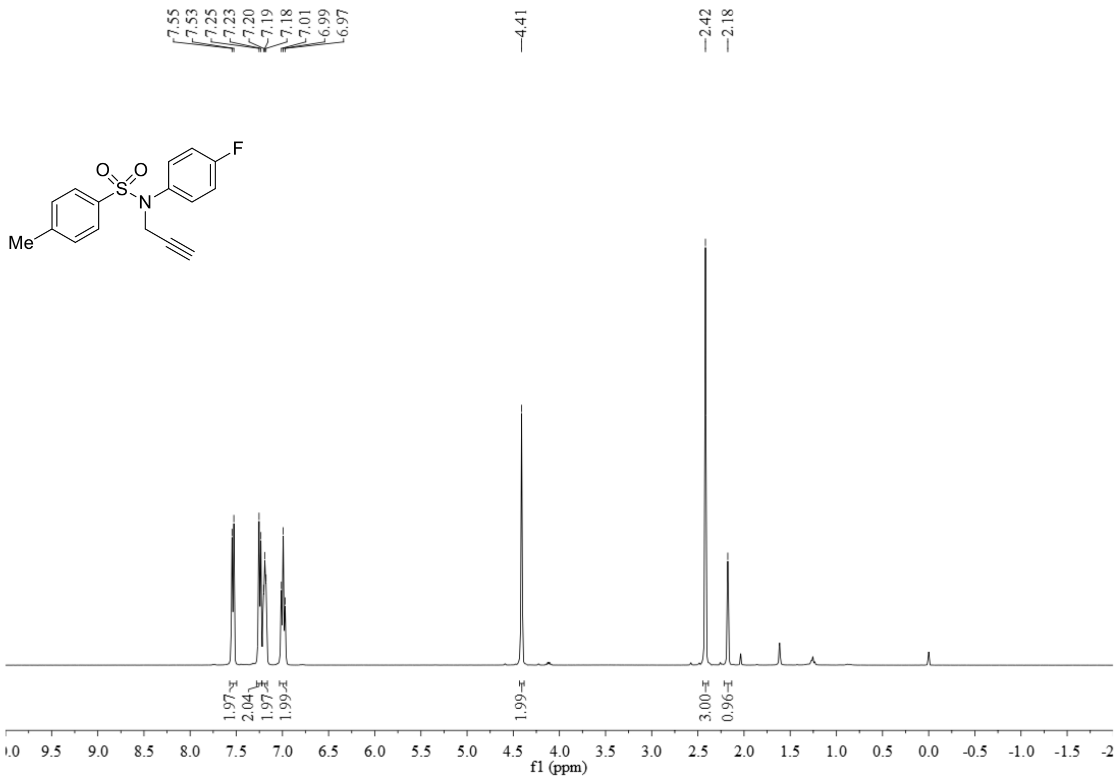
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1c**



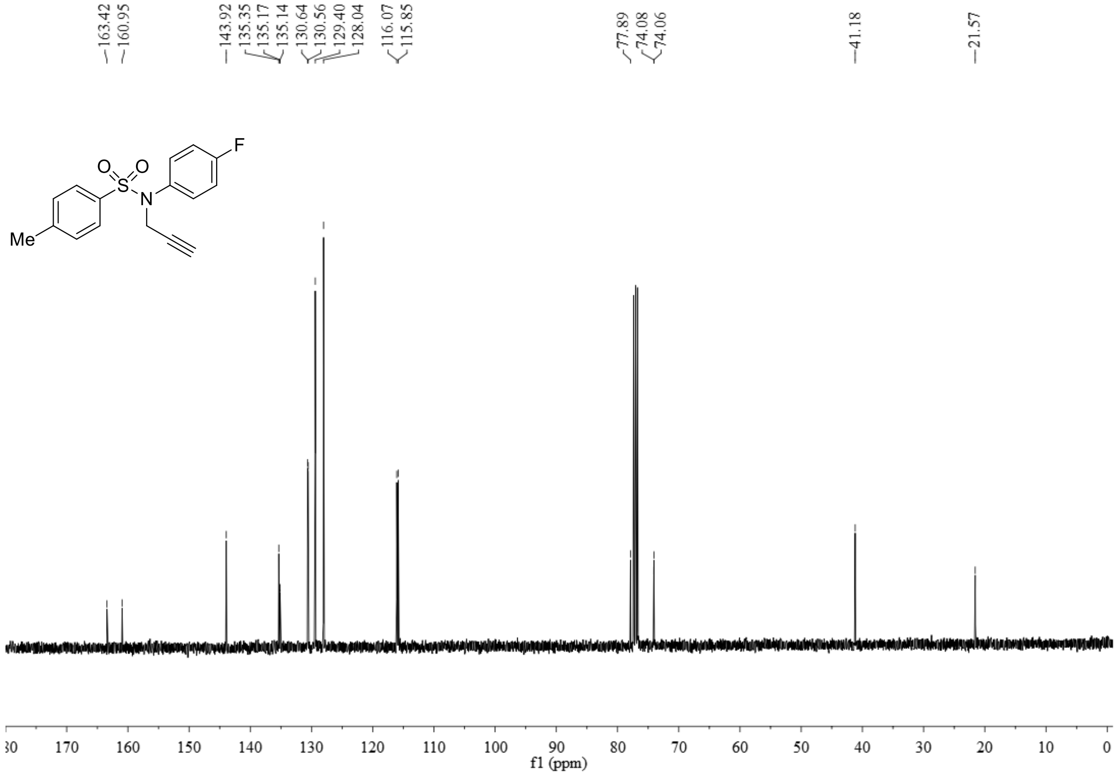
[13]C NMR spectrum (100 MHz, $CDCl_3$) of **1c**



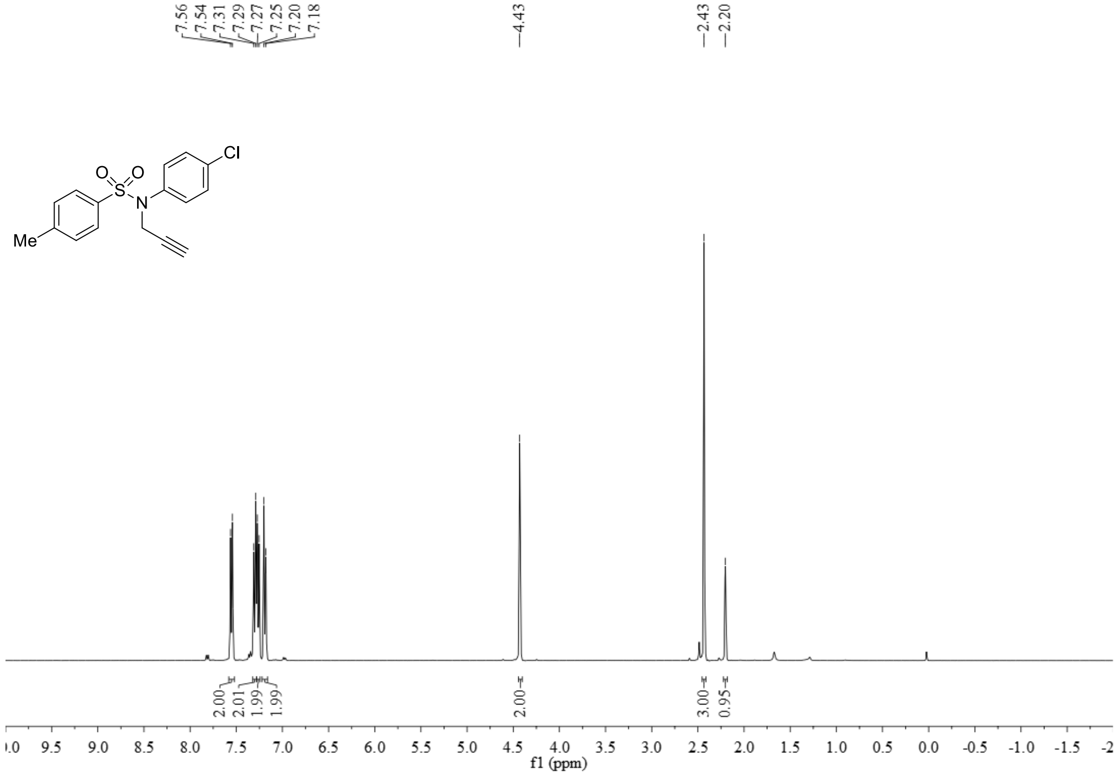
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1d**



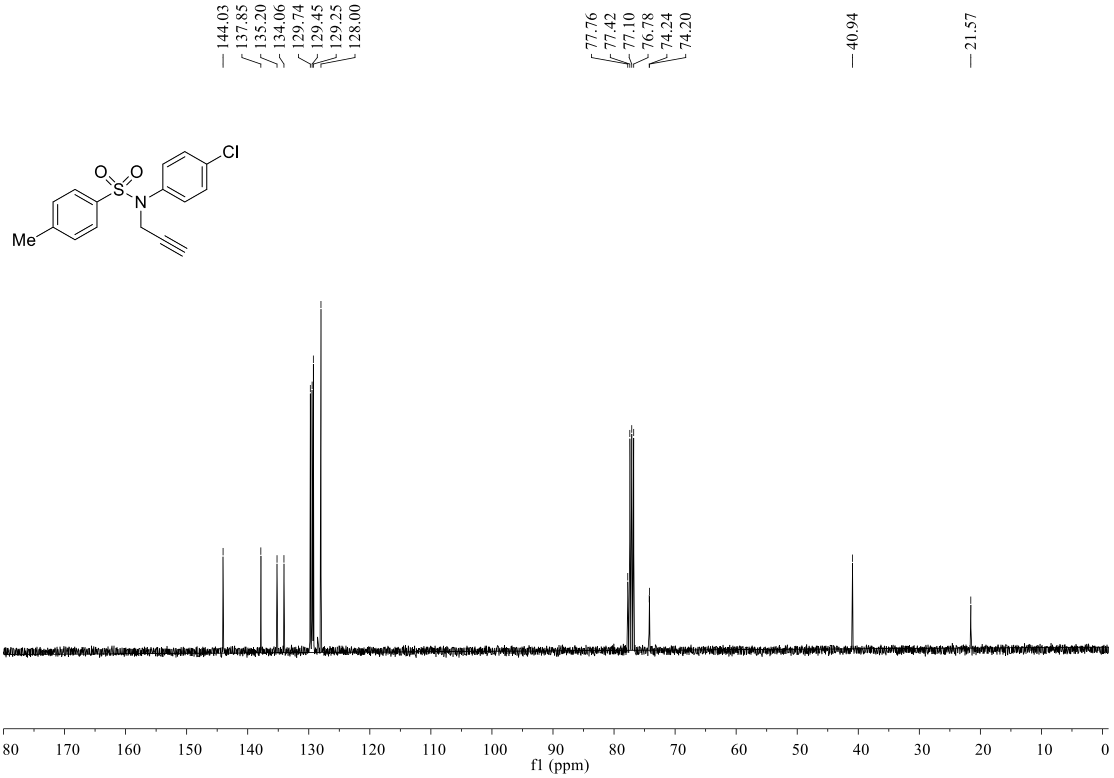
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1d**



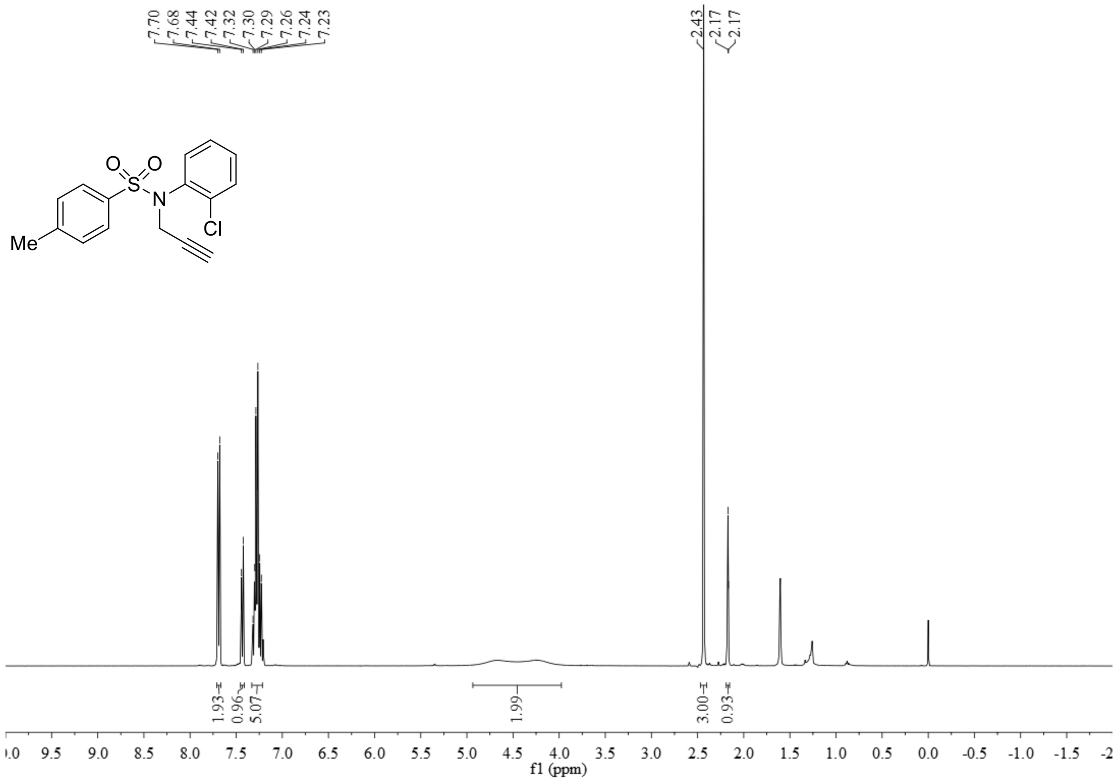
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1e**



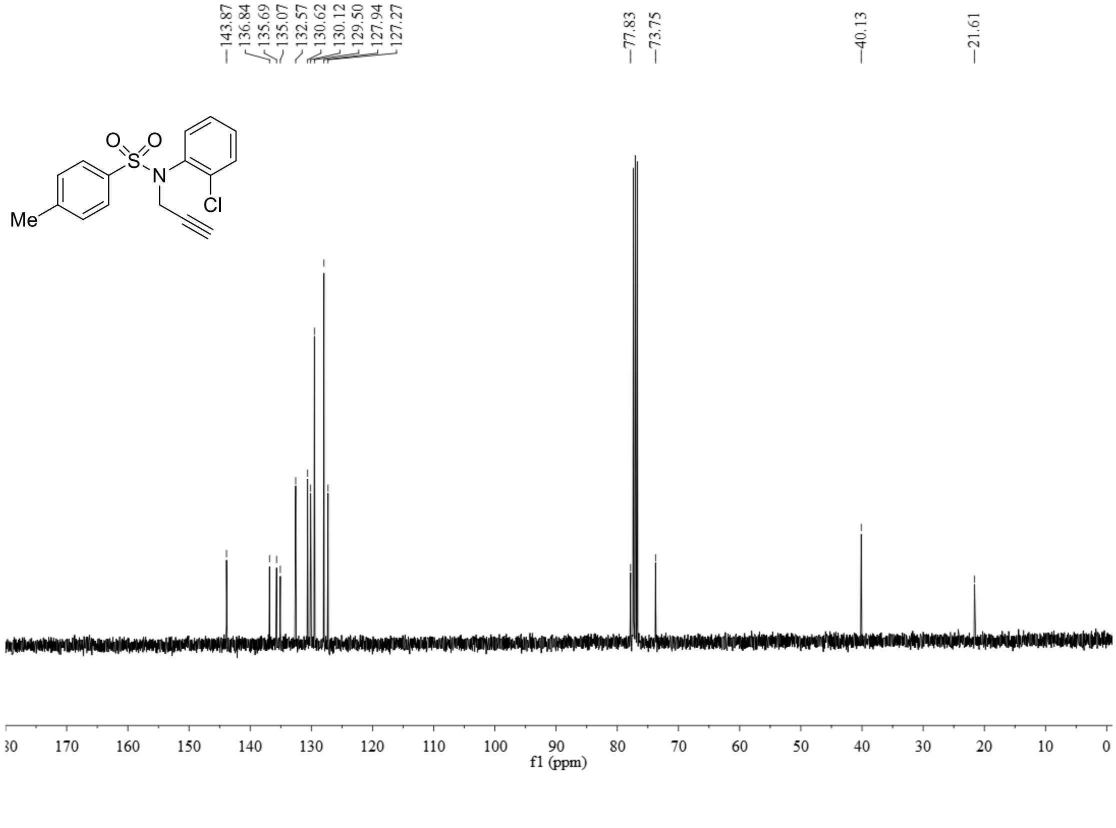
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1e**



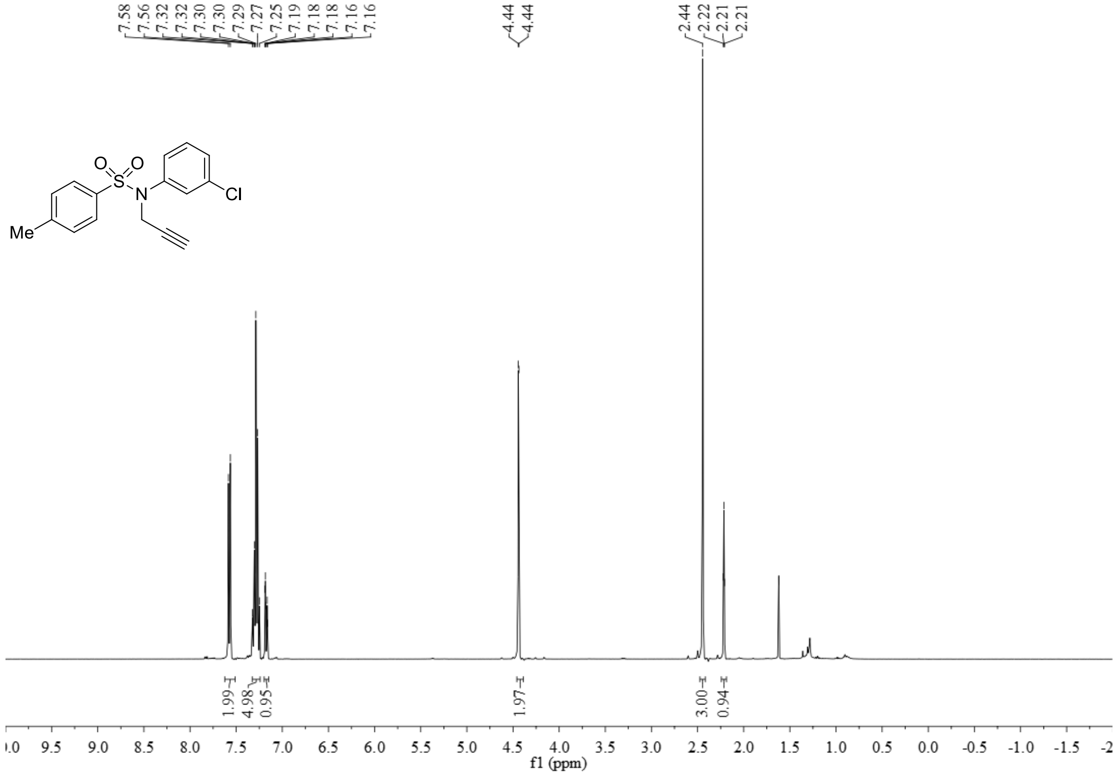
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1f**



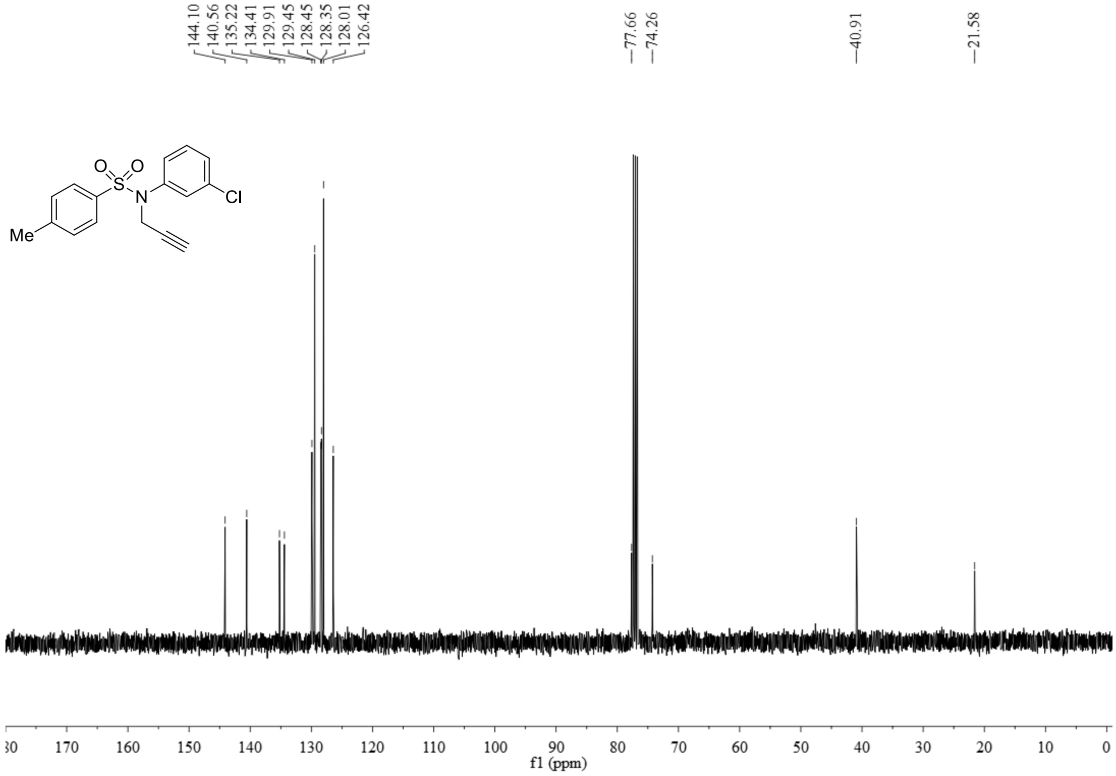
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1f**



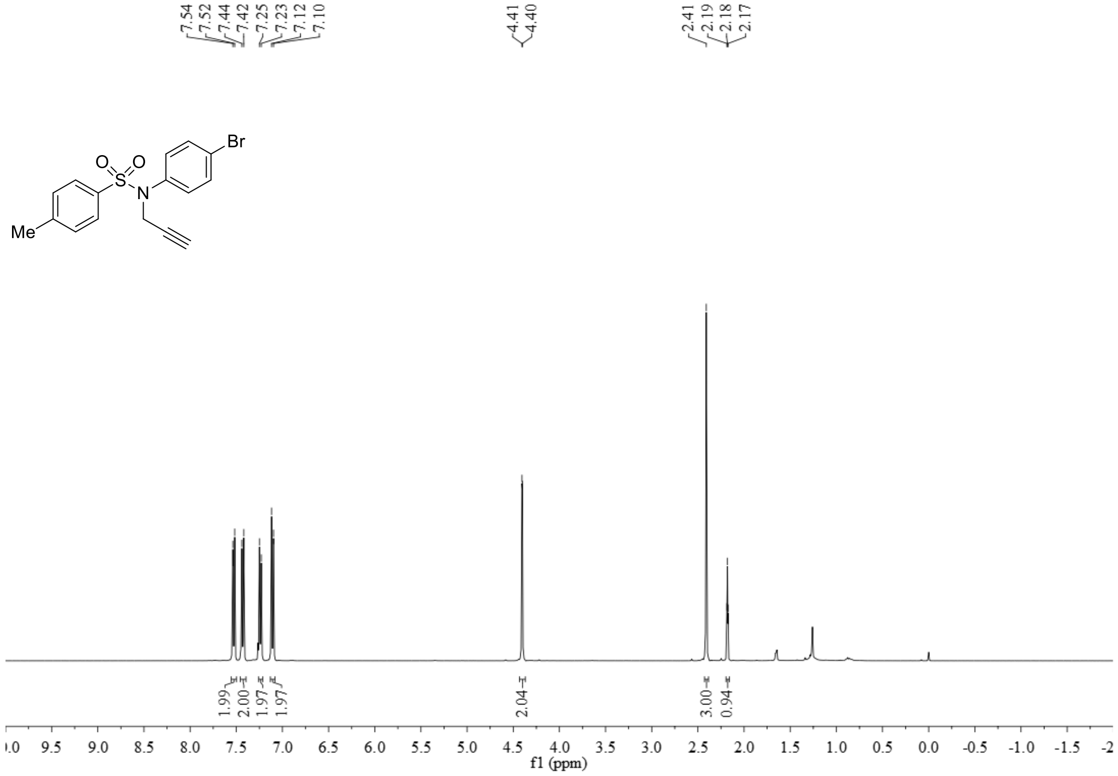
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1g**



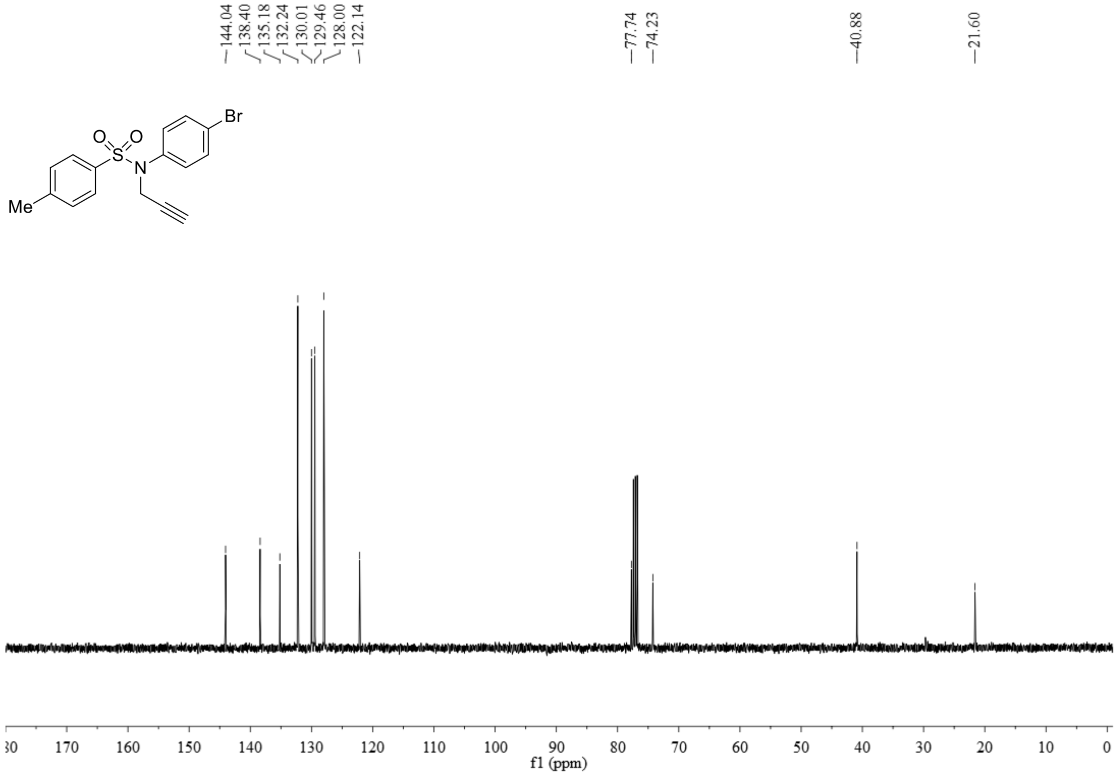
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1g**



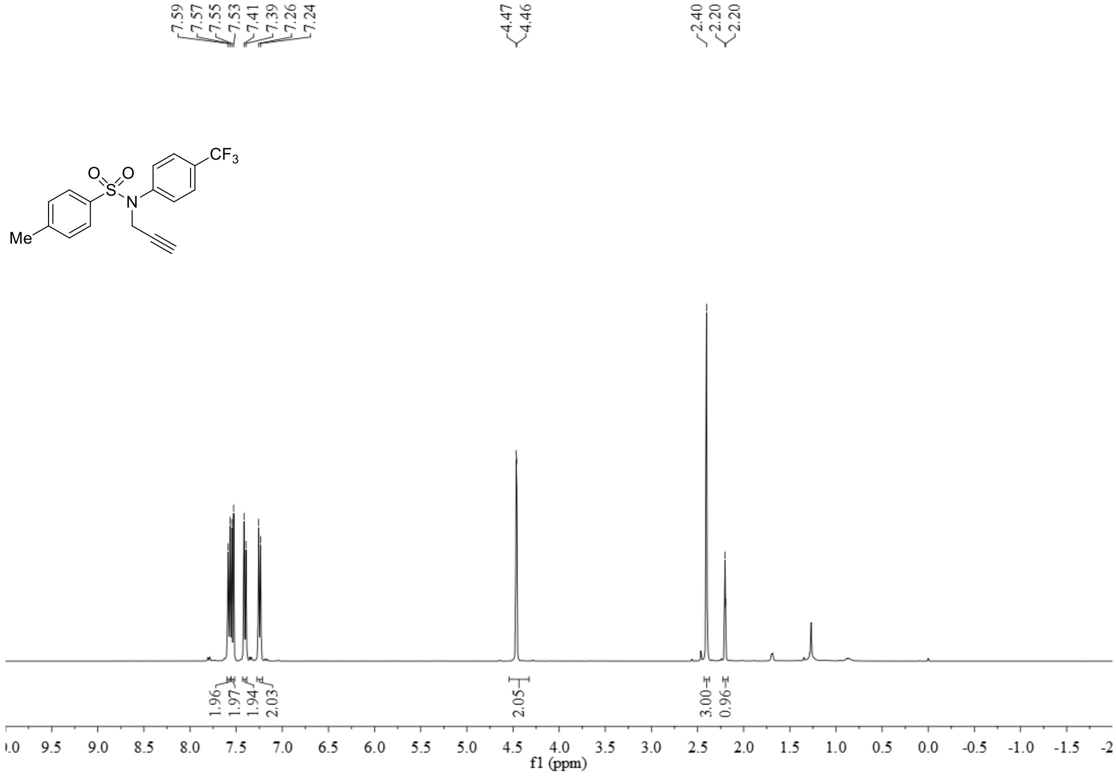
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1h**



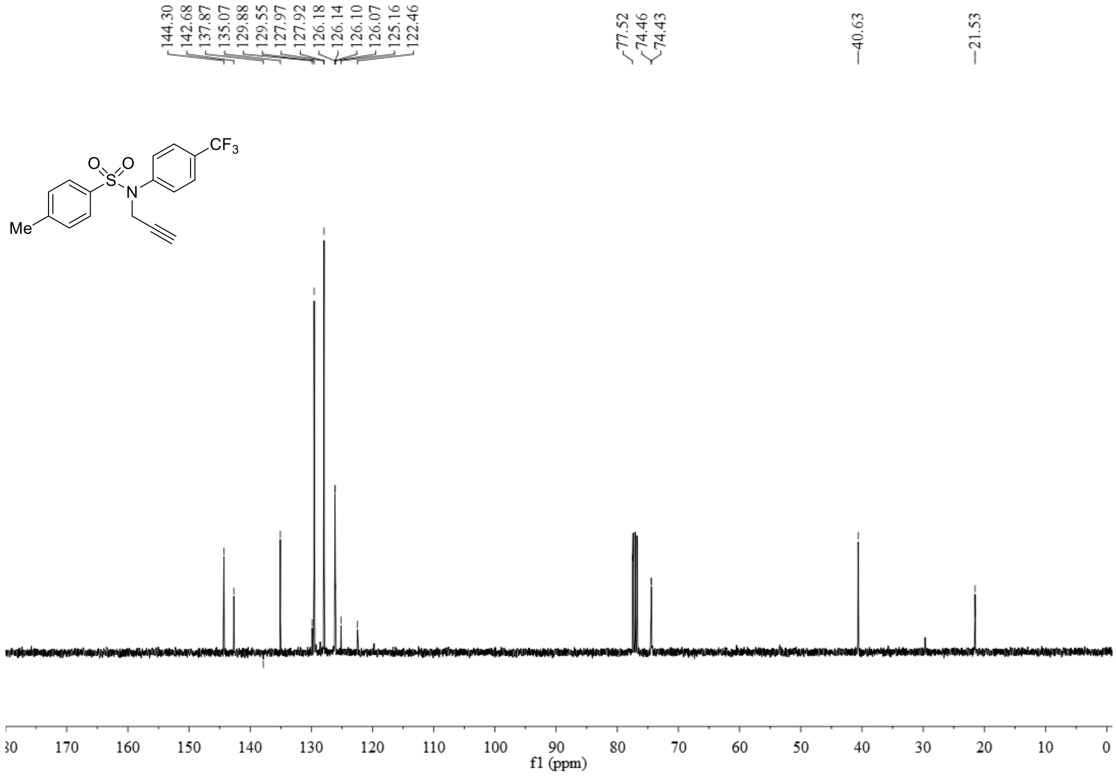
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1h**



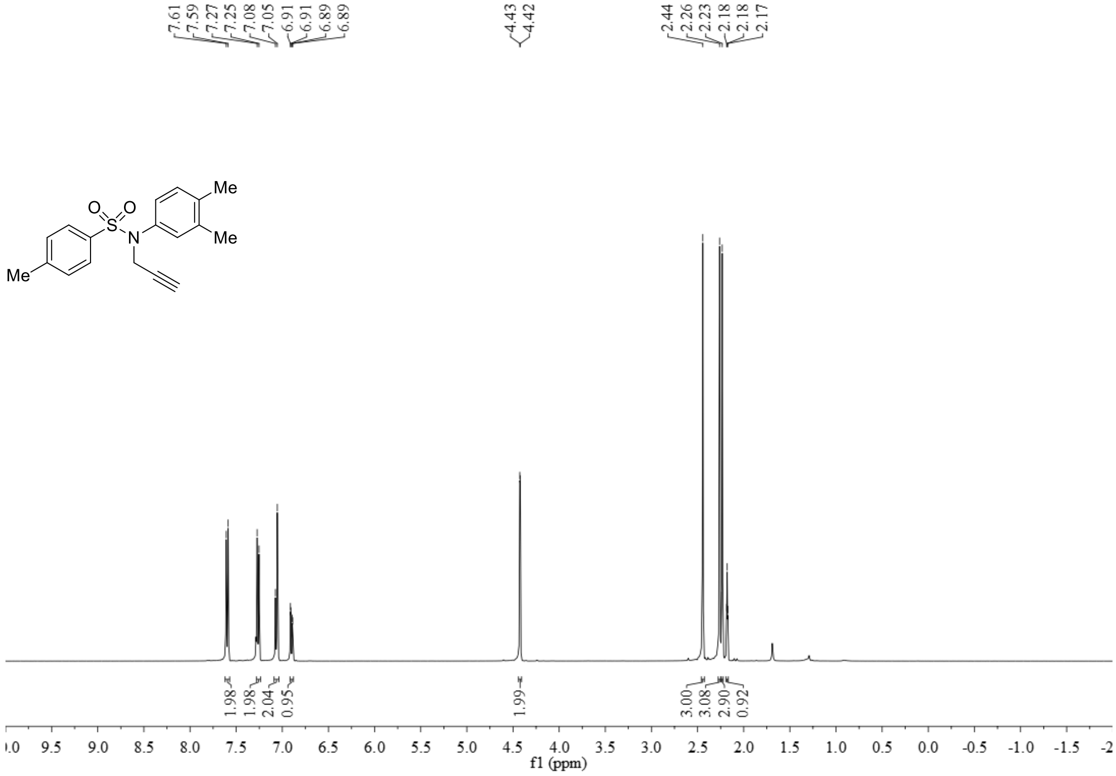
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1i**



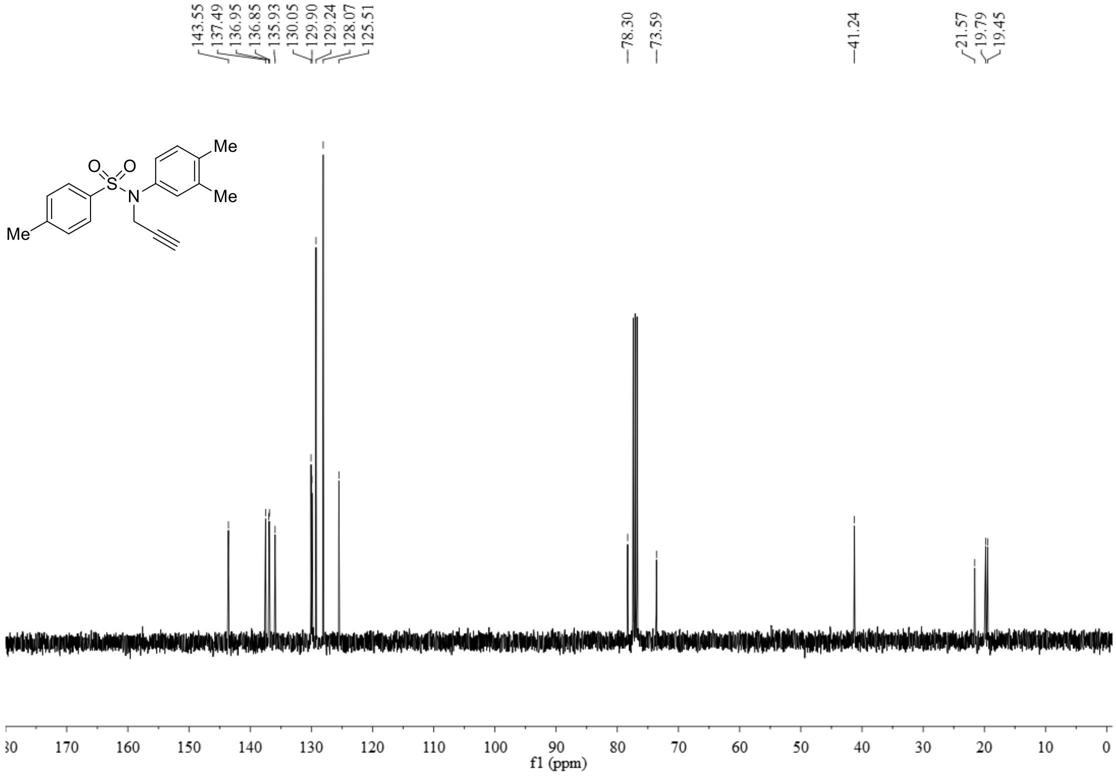
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1i**



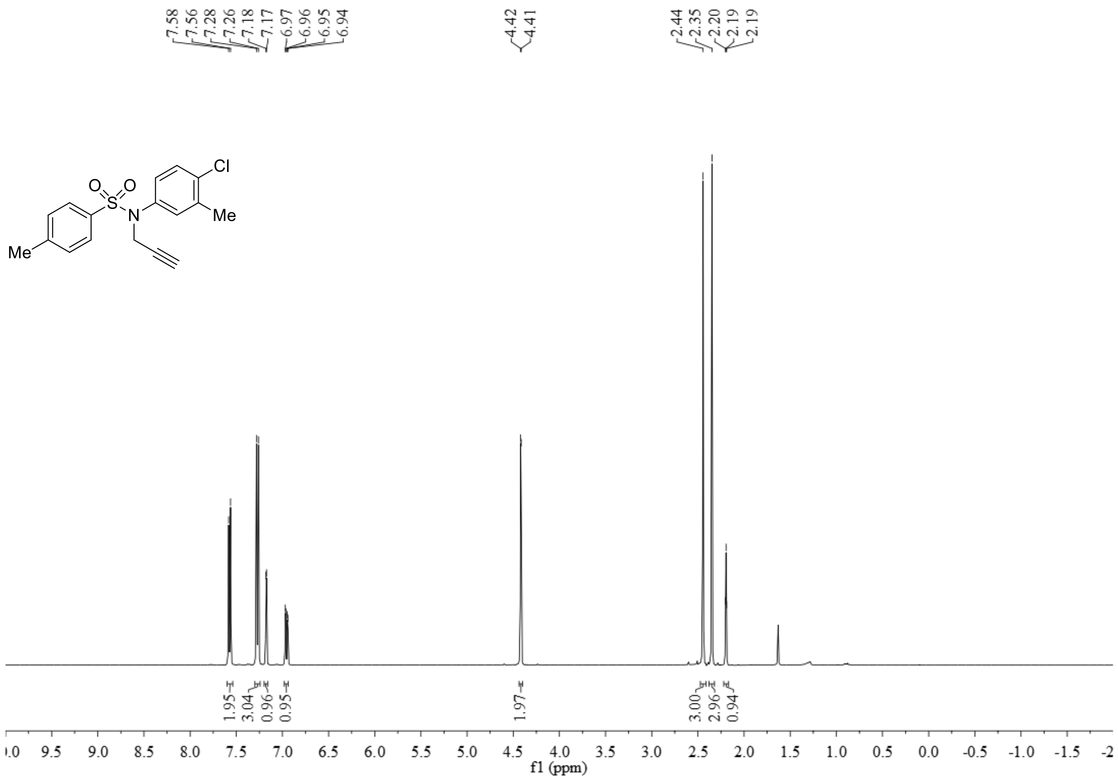
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1j**



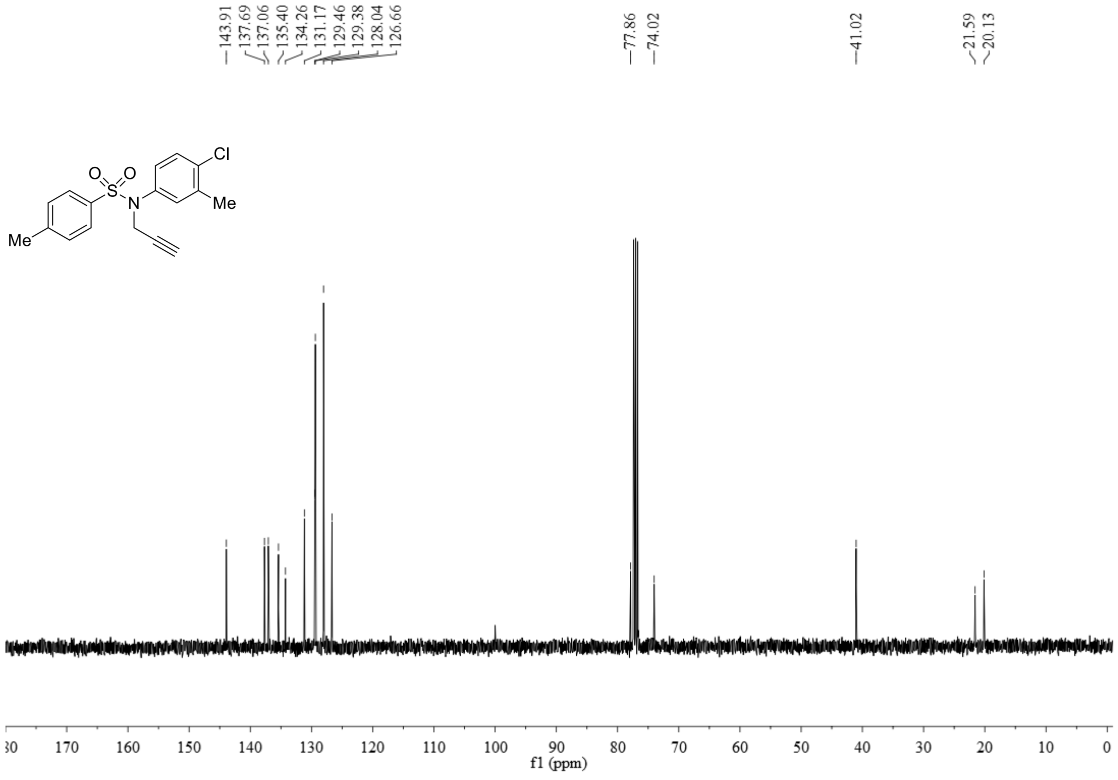
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1j**



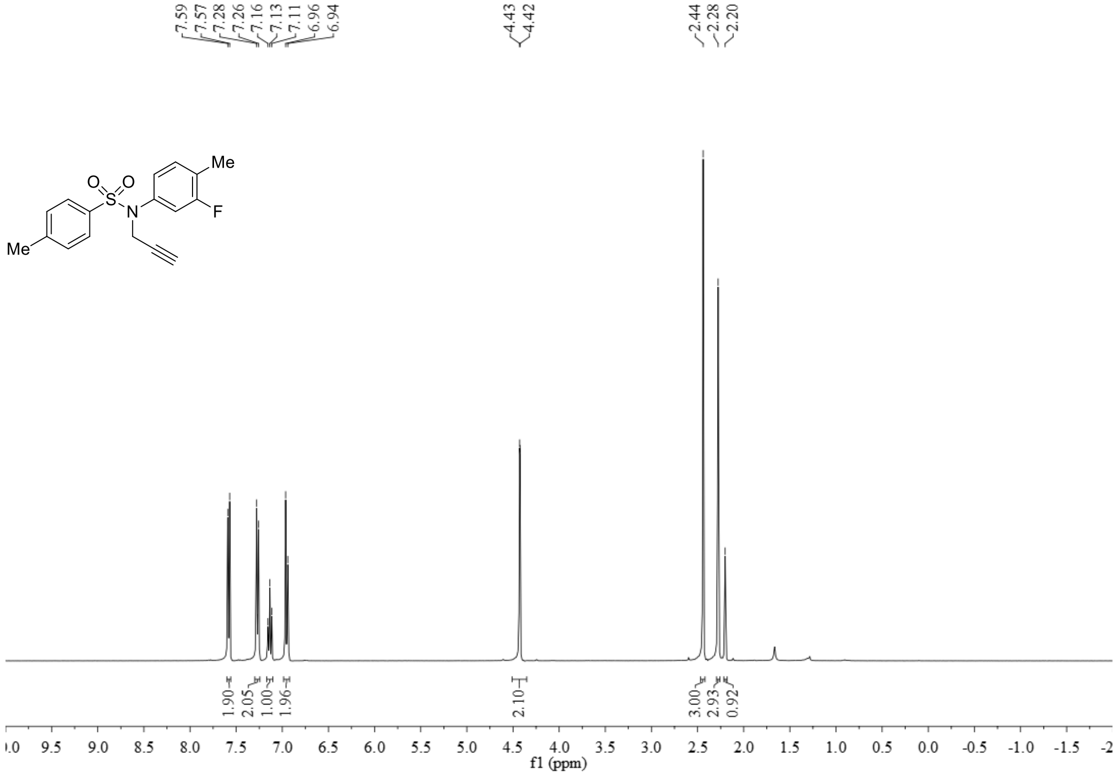
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1k**



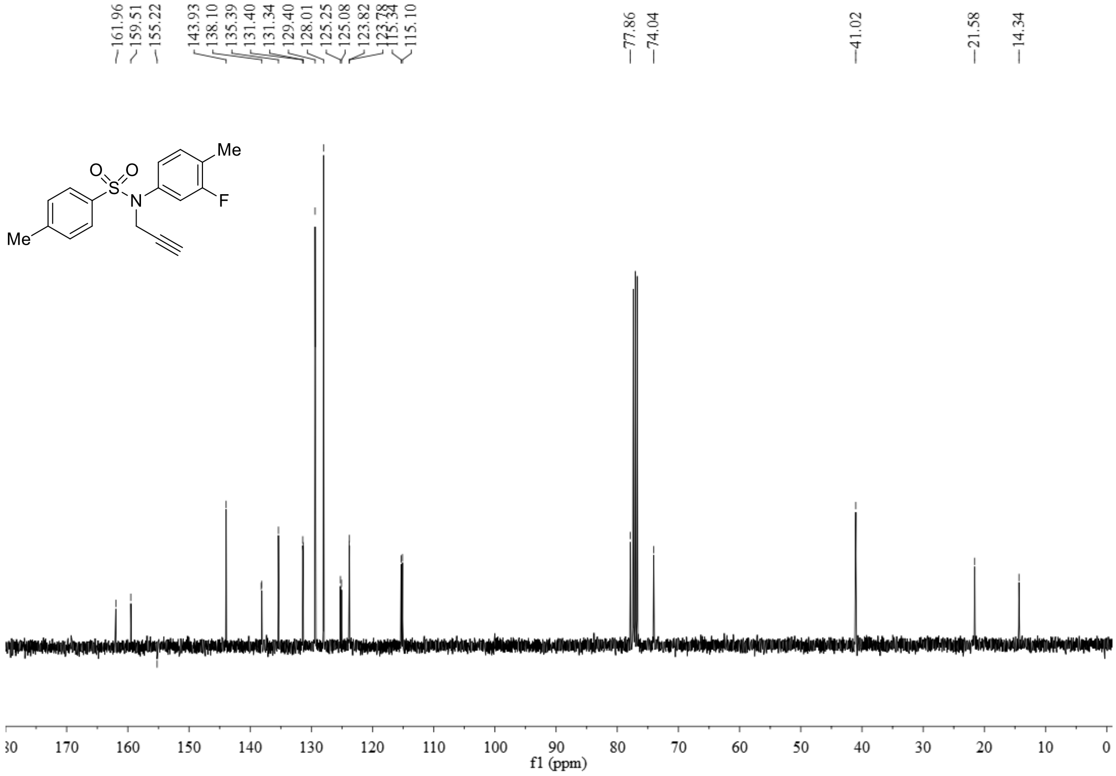
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1k**



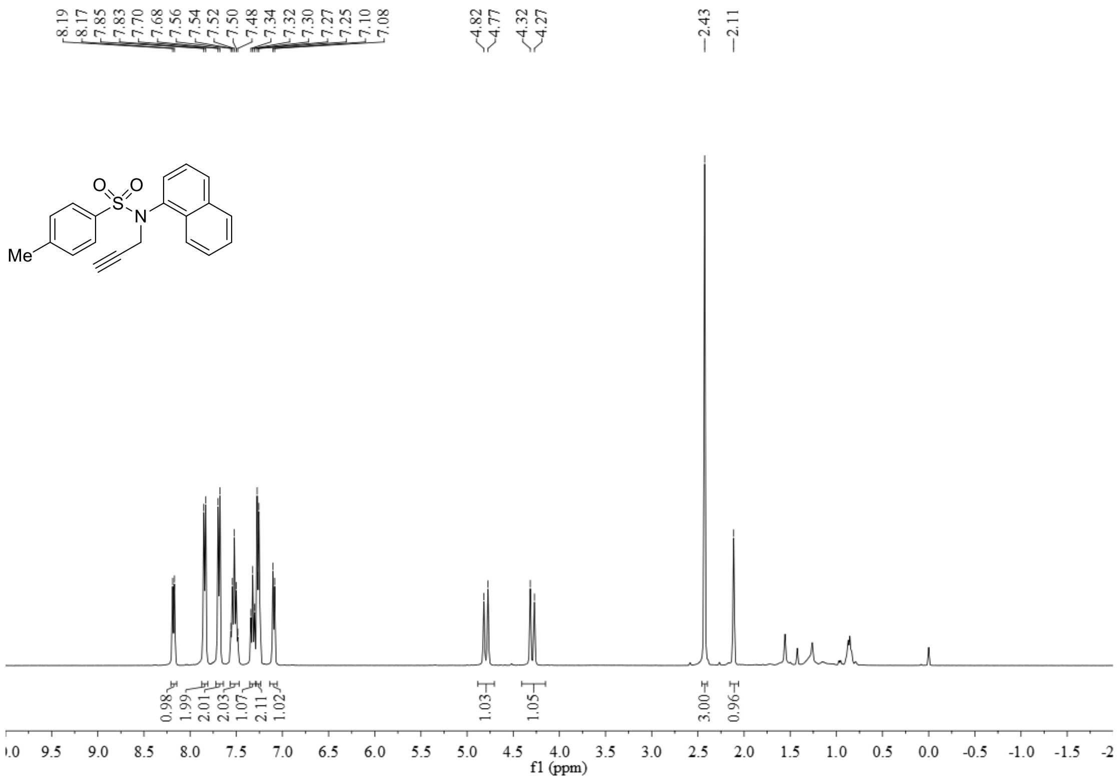
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1l**



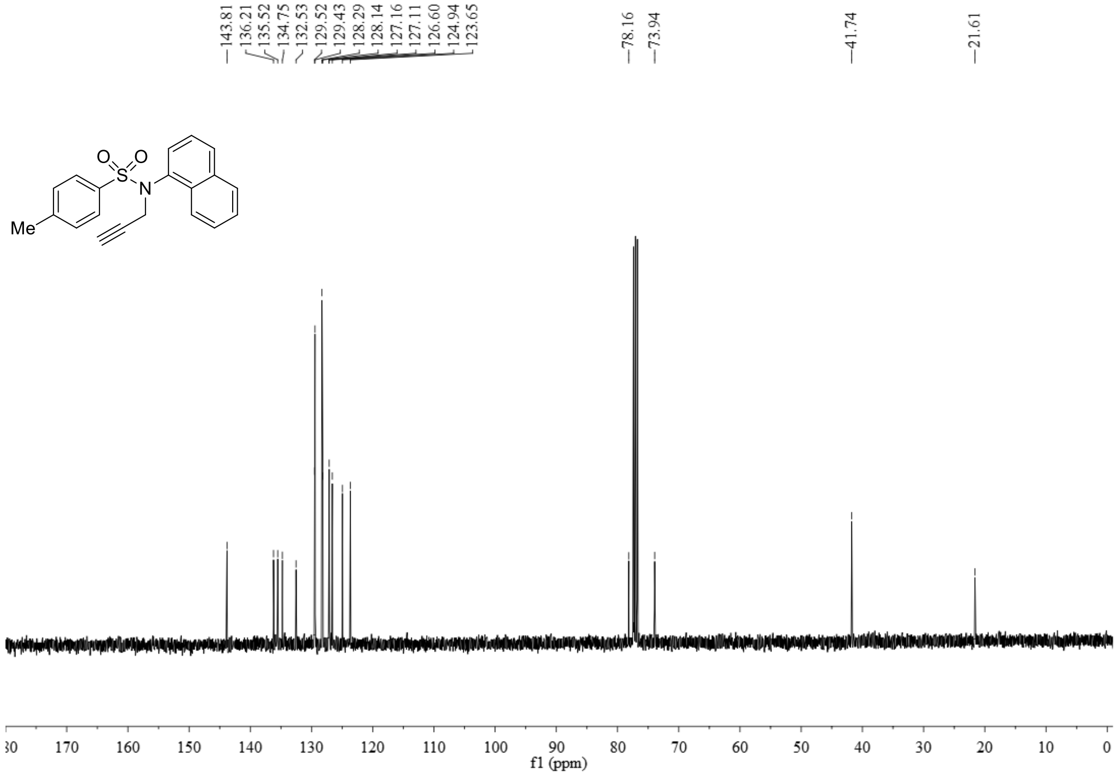
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1l**



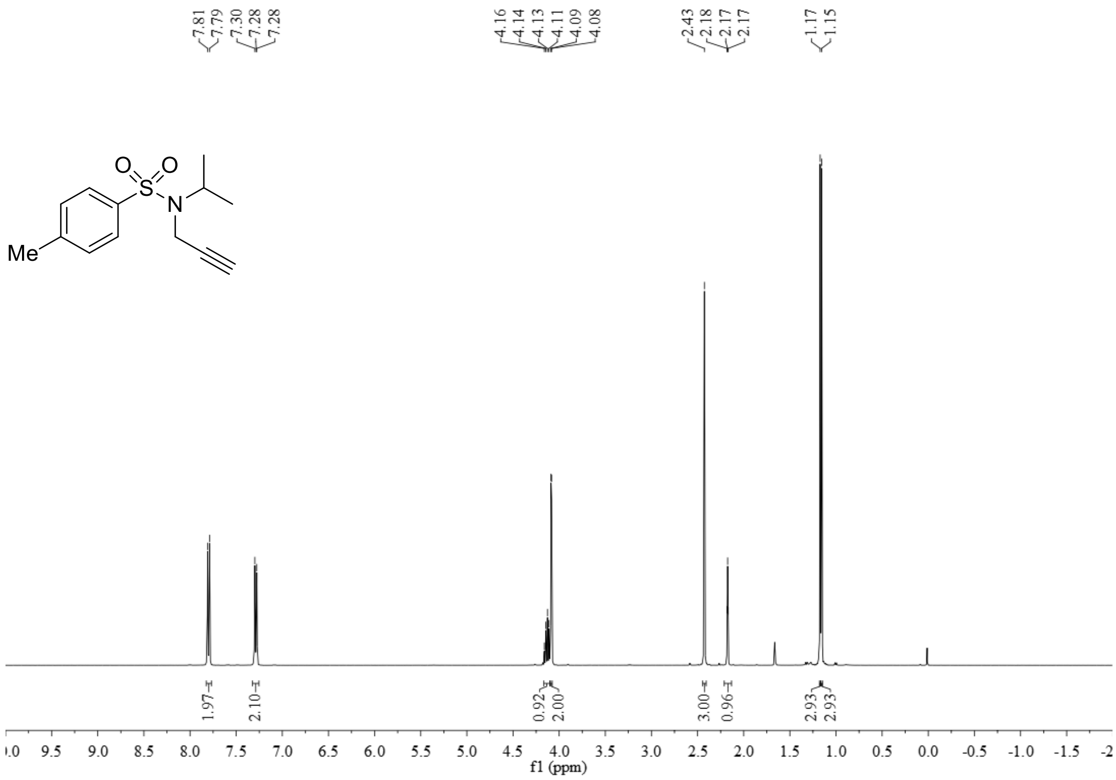
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1m**



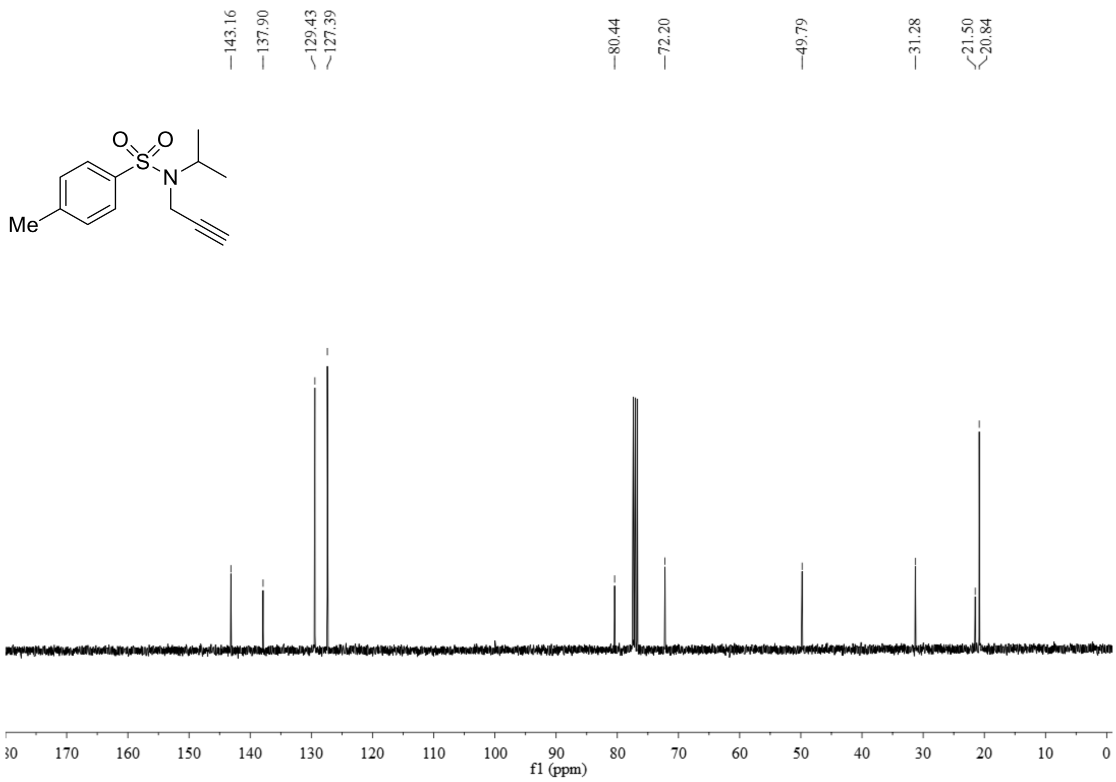
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1m**



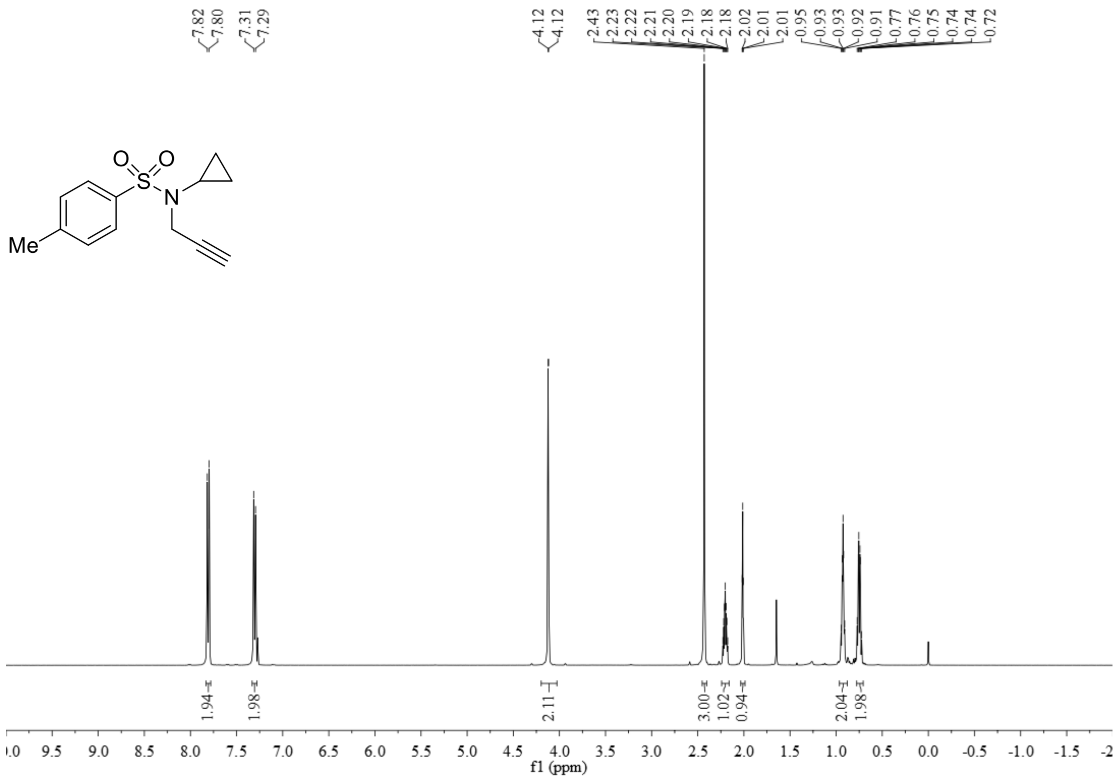
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **1n**



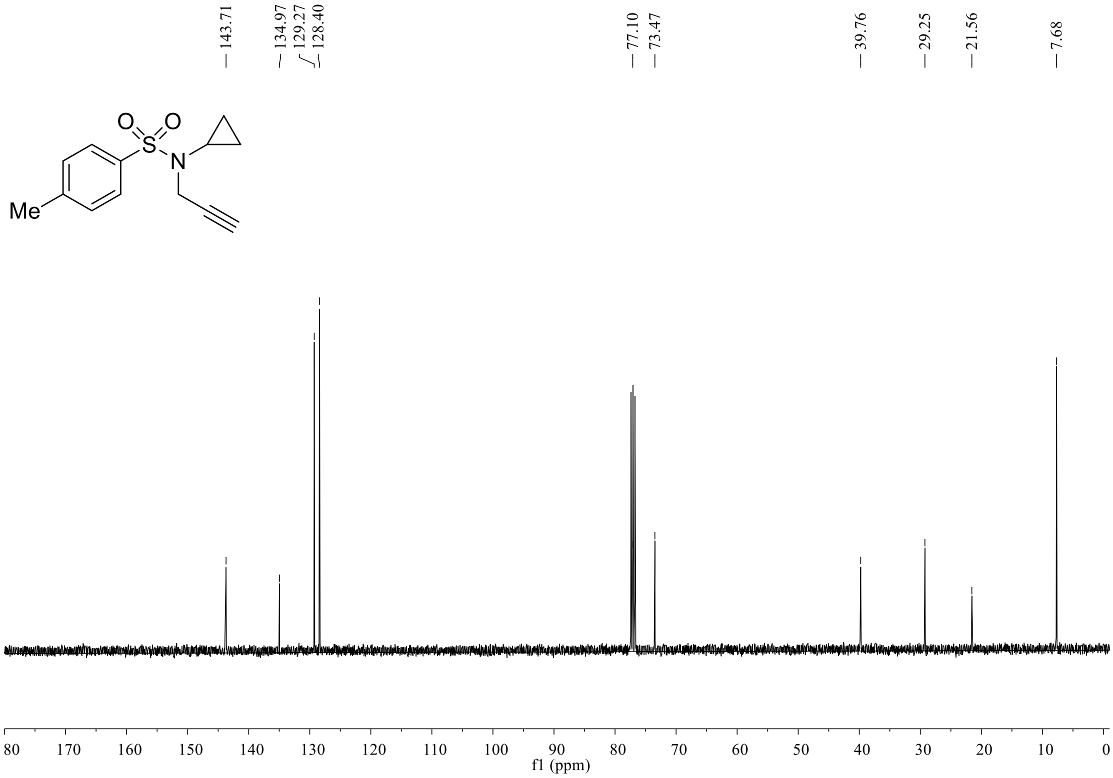
^{13}C NMR spectrum (400 MHz, CDCl$_3$) of **1n**



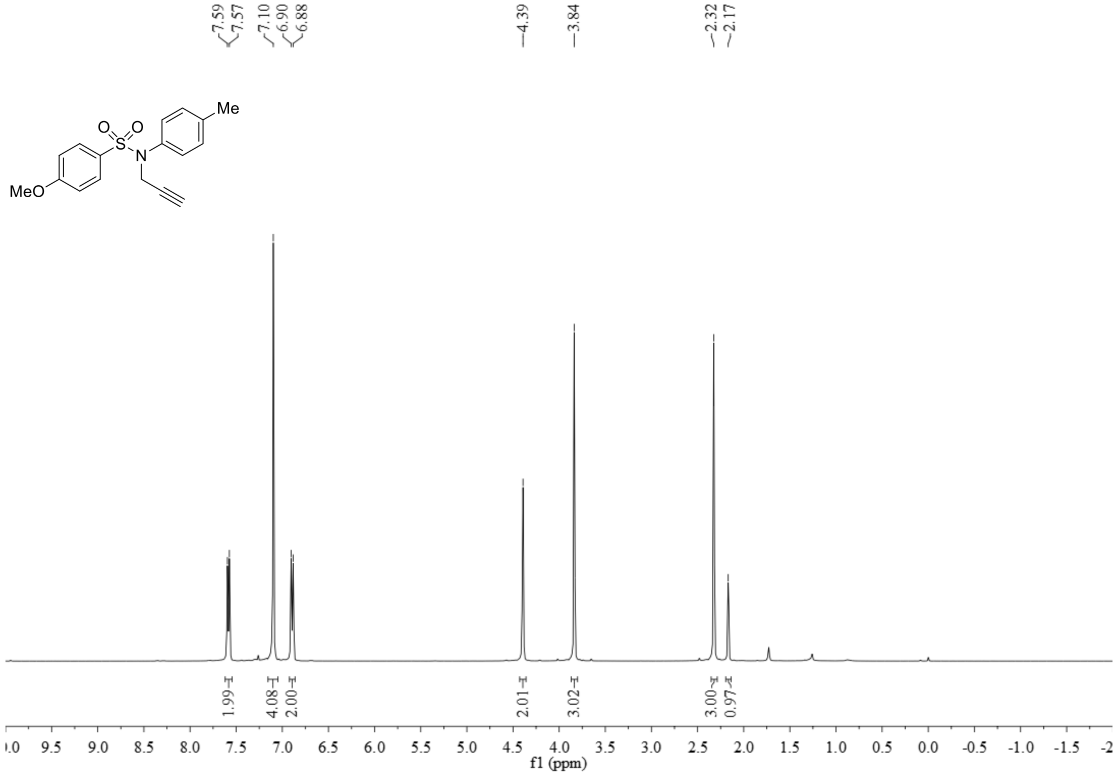
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1o**



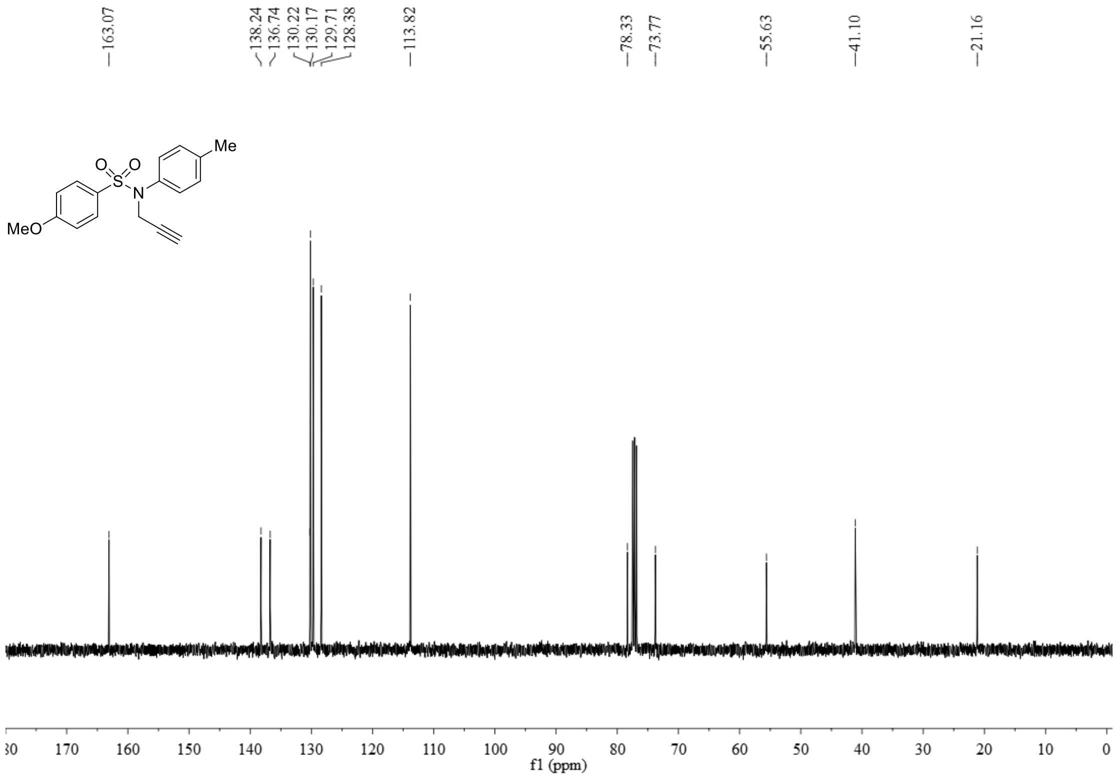
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1o**



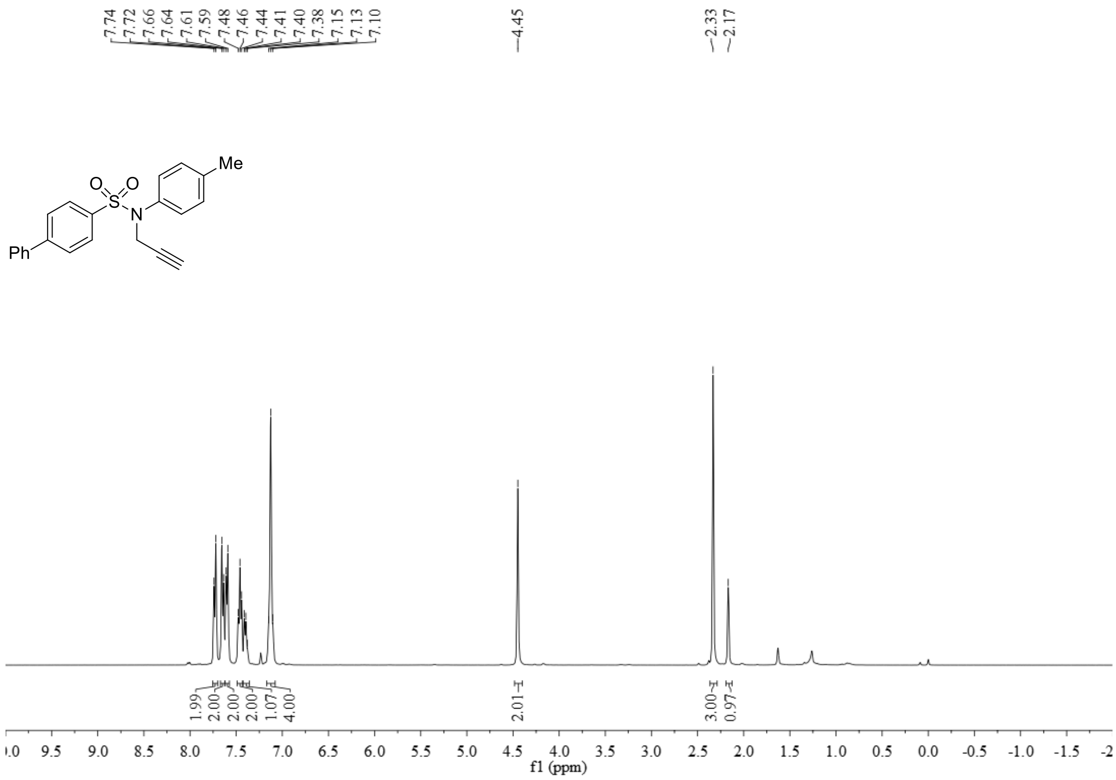
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1p**



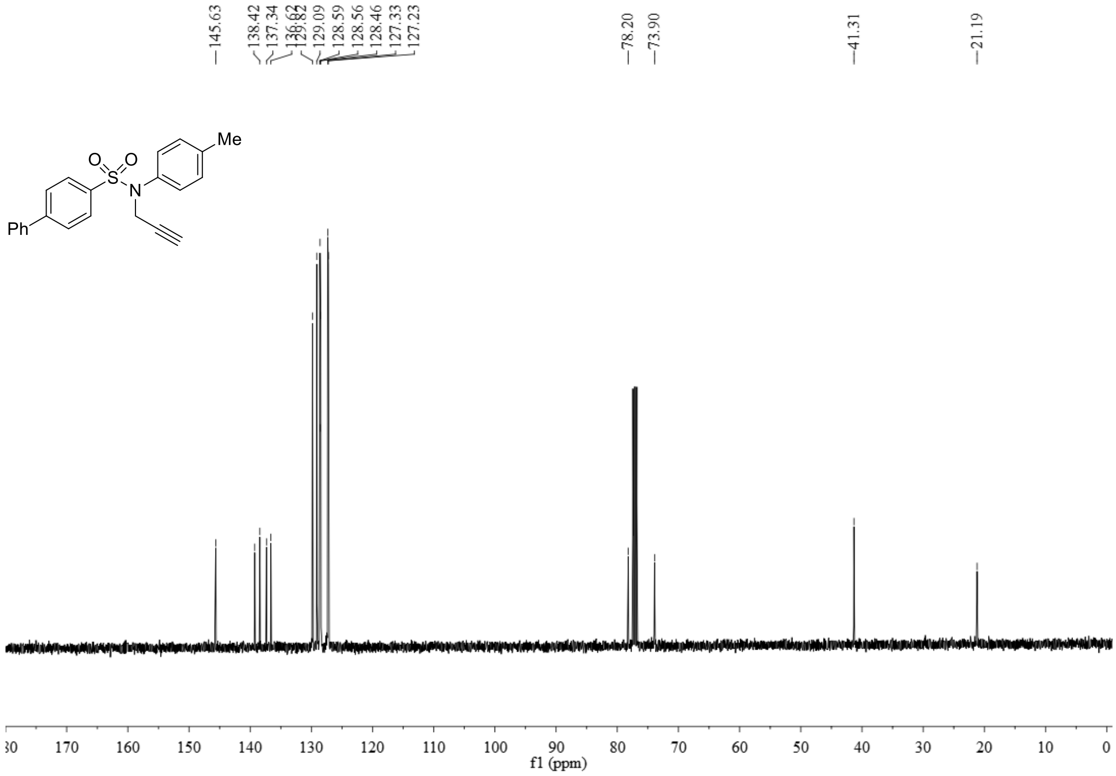
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1p**



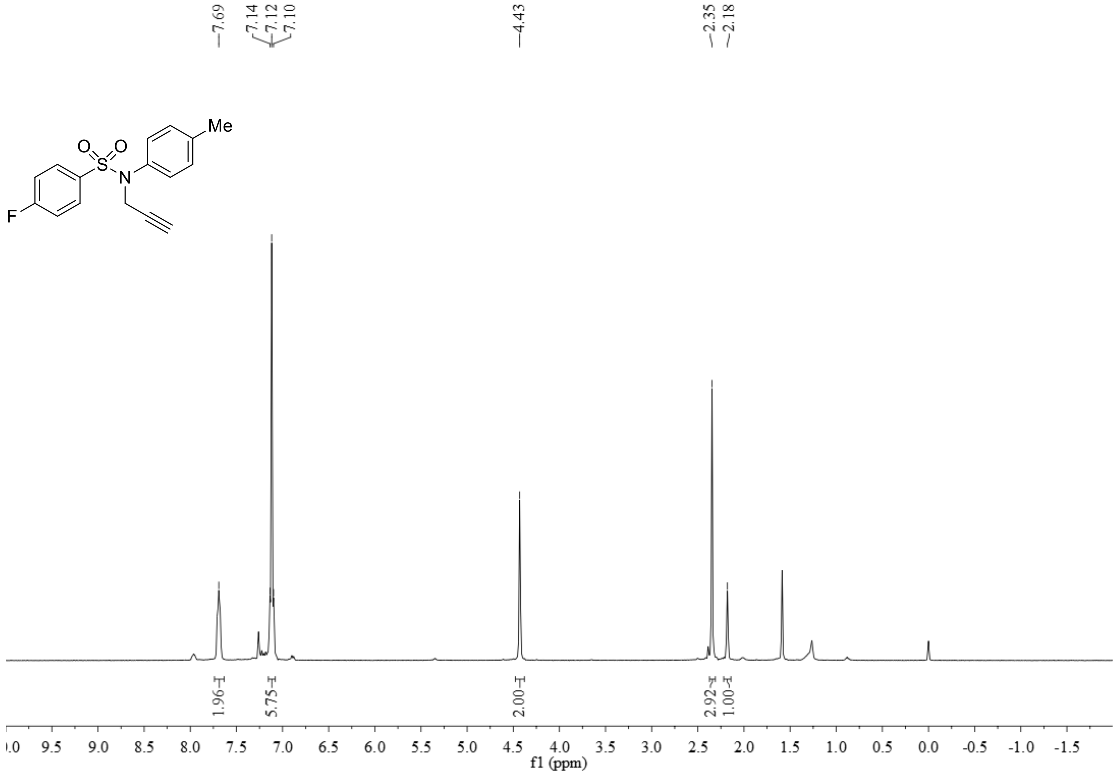
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1q**



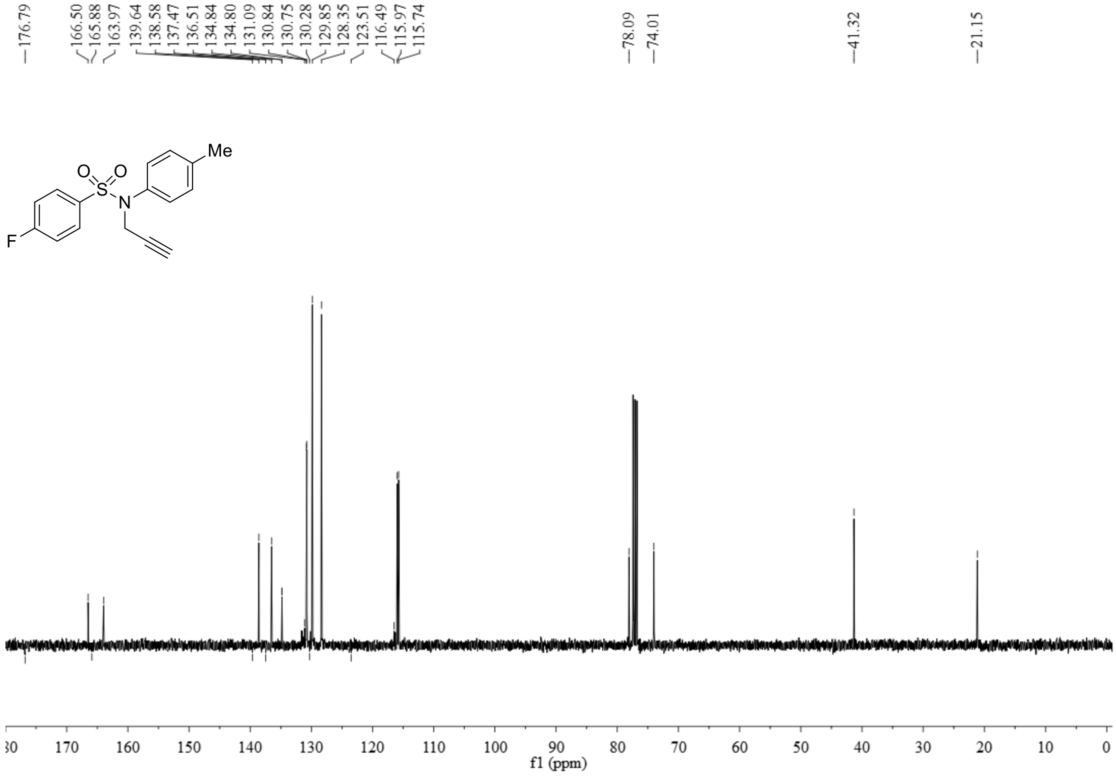
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1q**



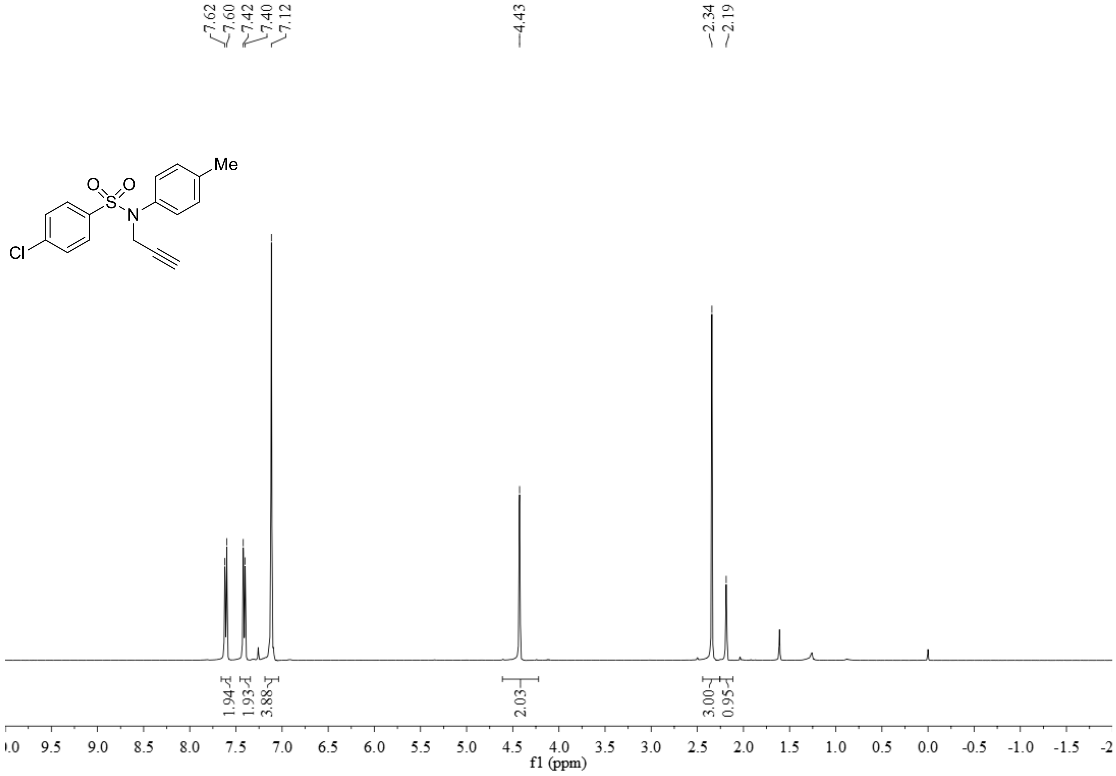
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1r**



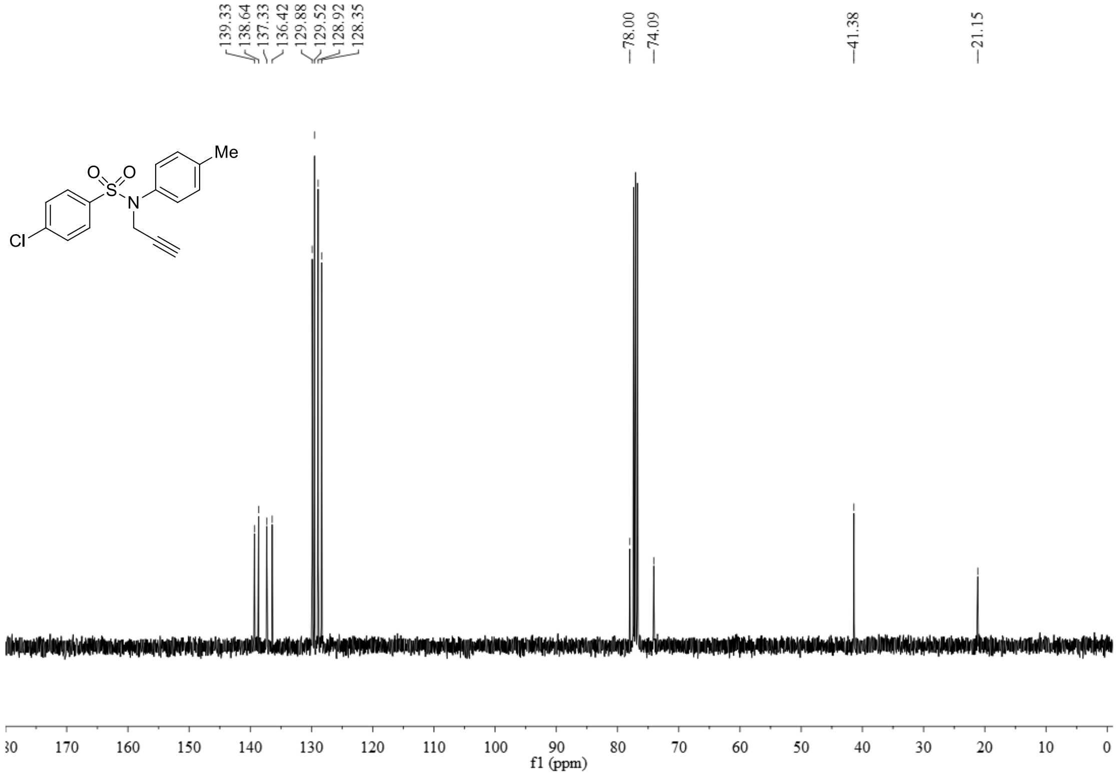
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1r**



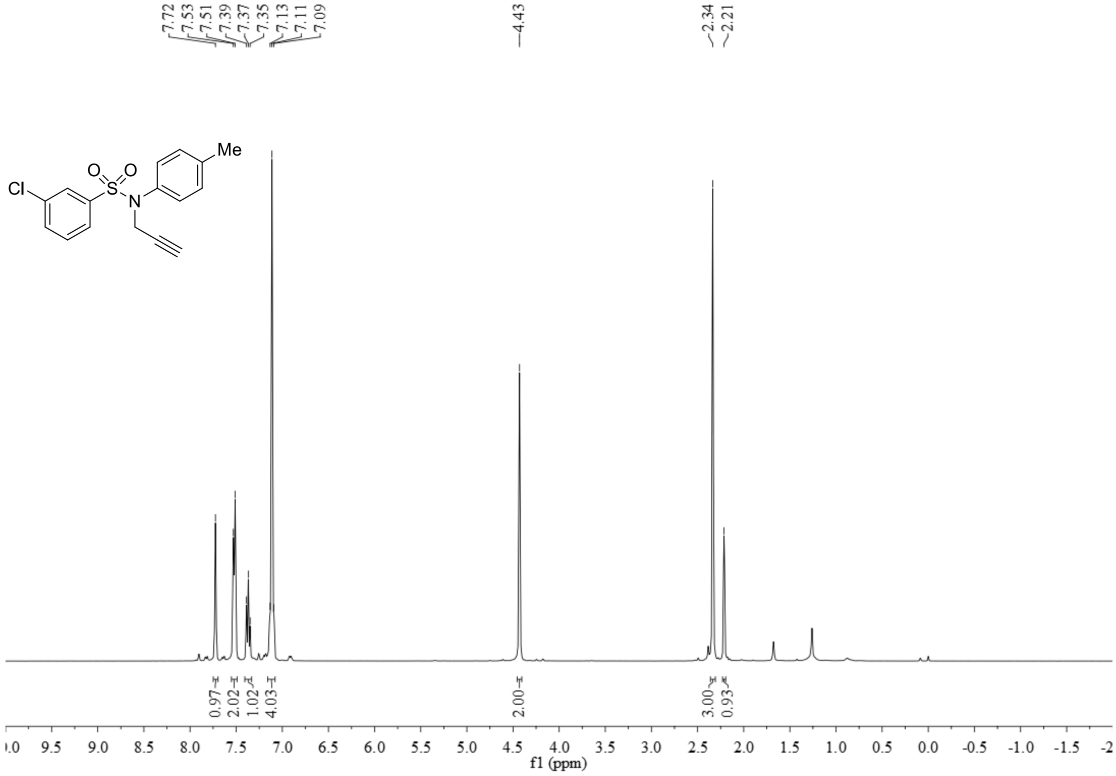
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1s**



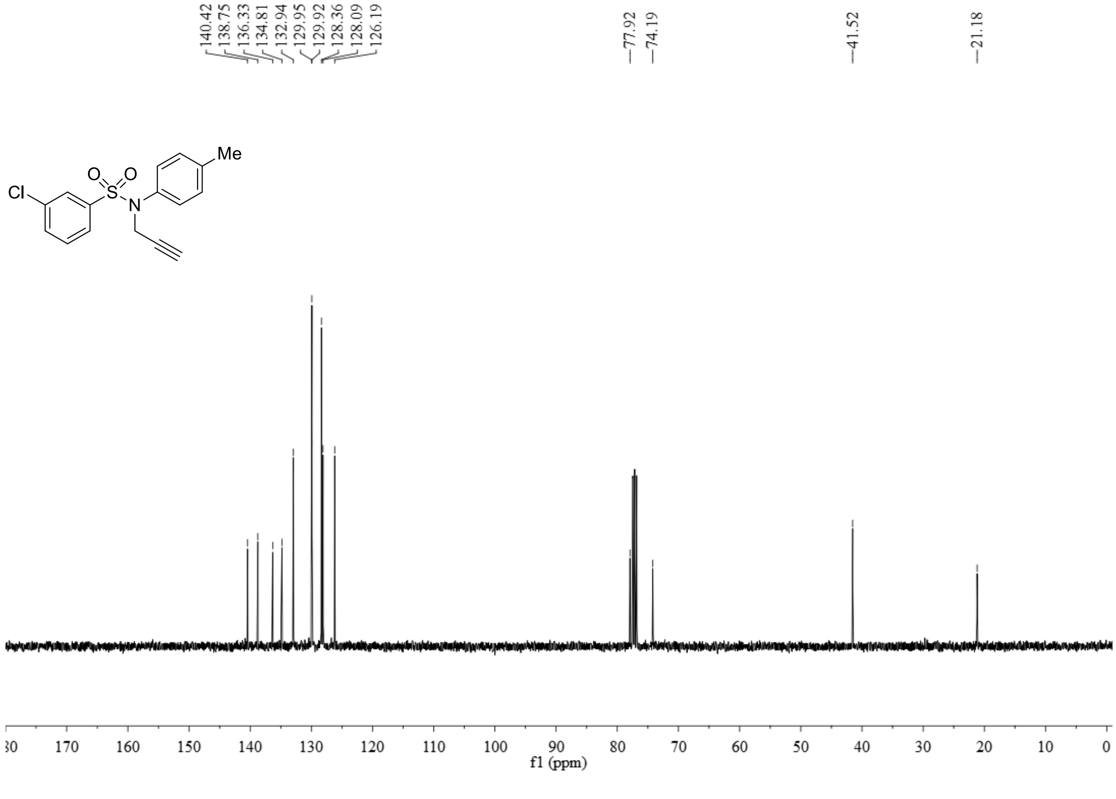
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1s**



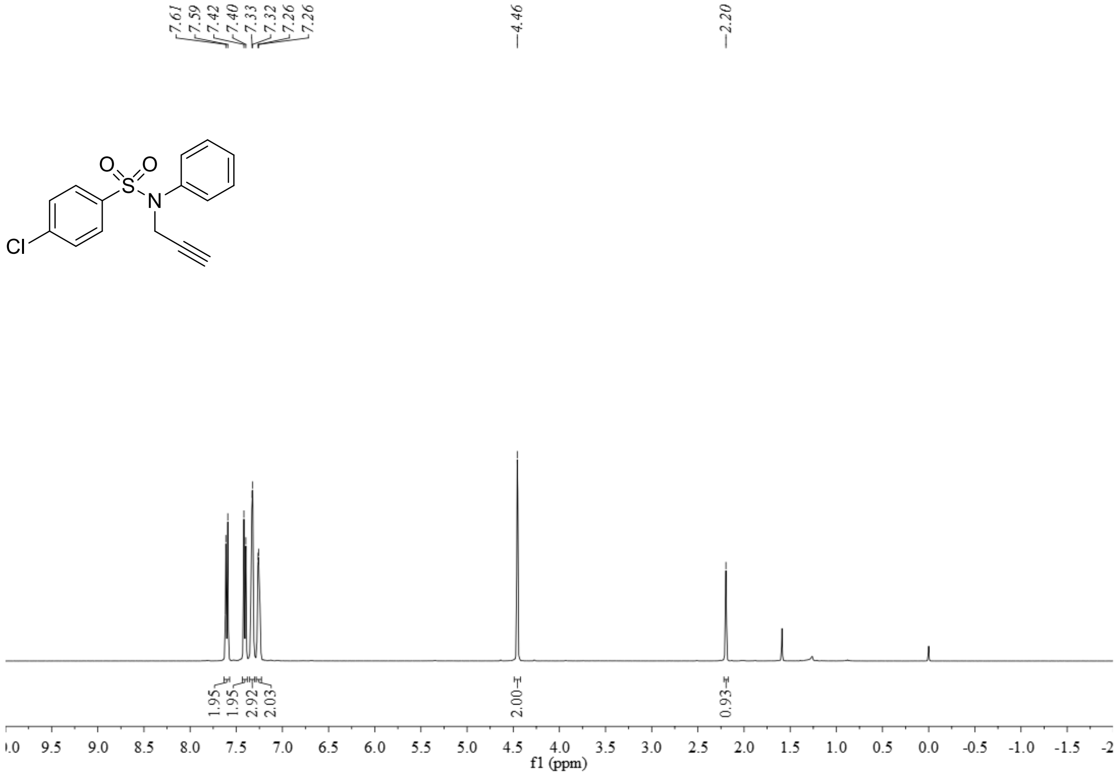
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1t**



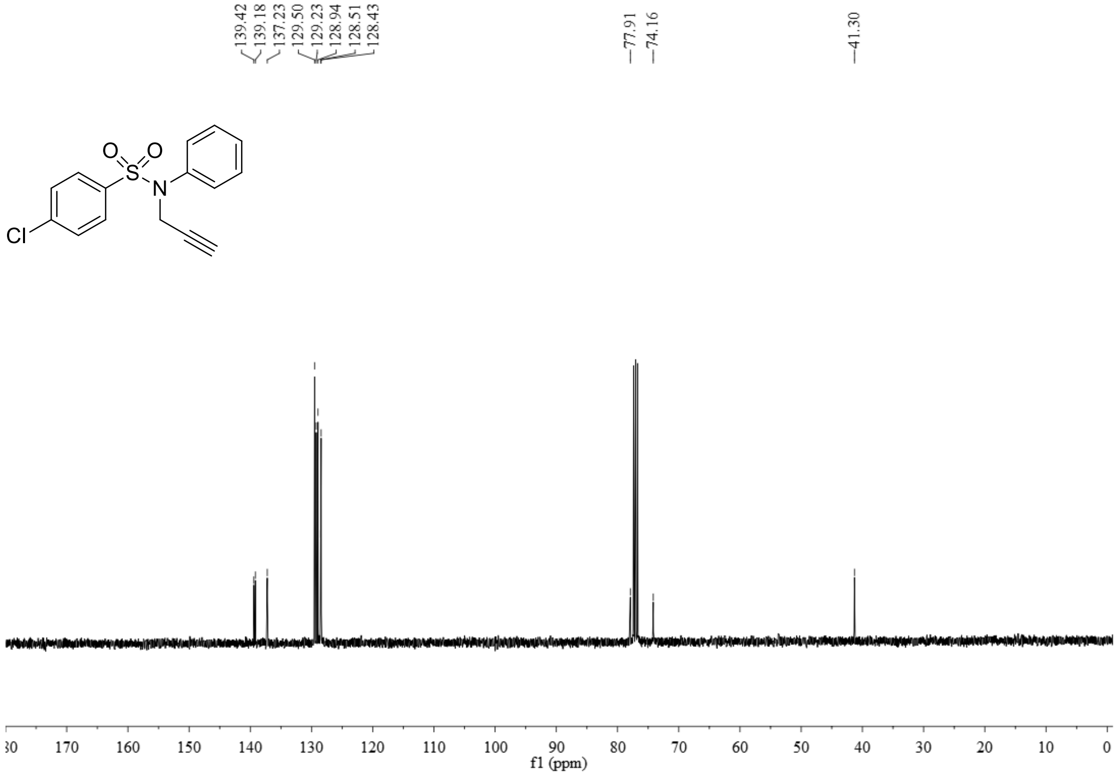
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1t**



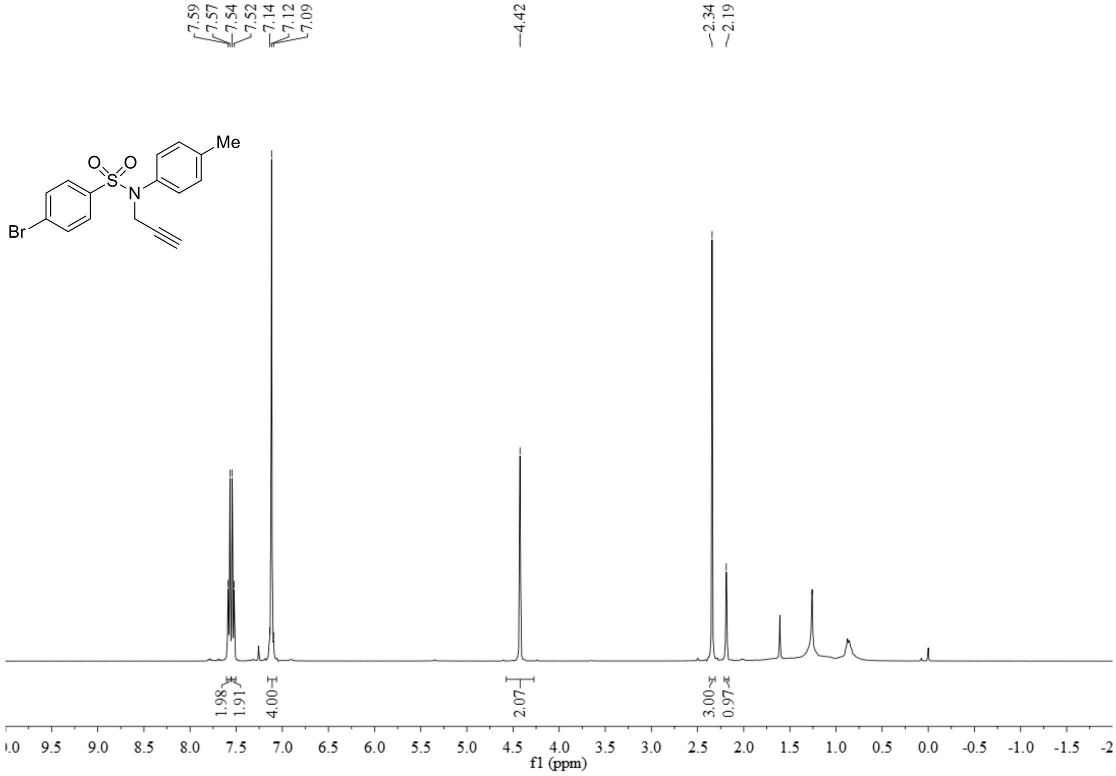
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1u**



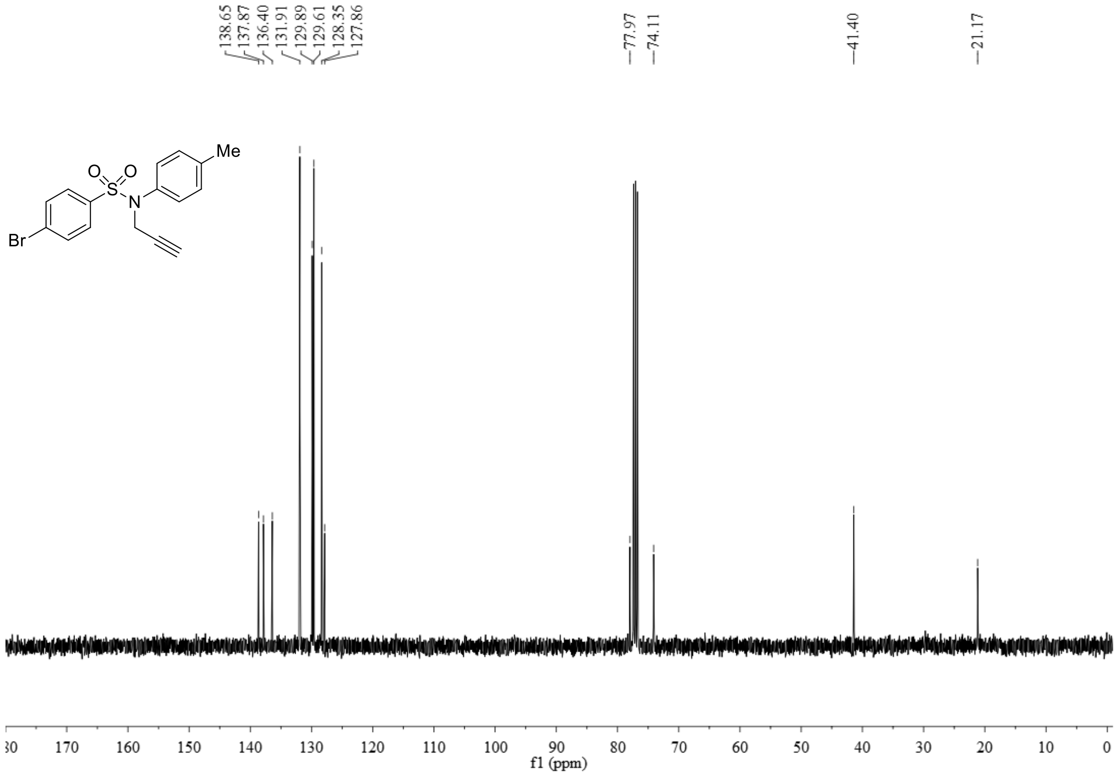
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1u**



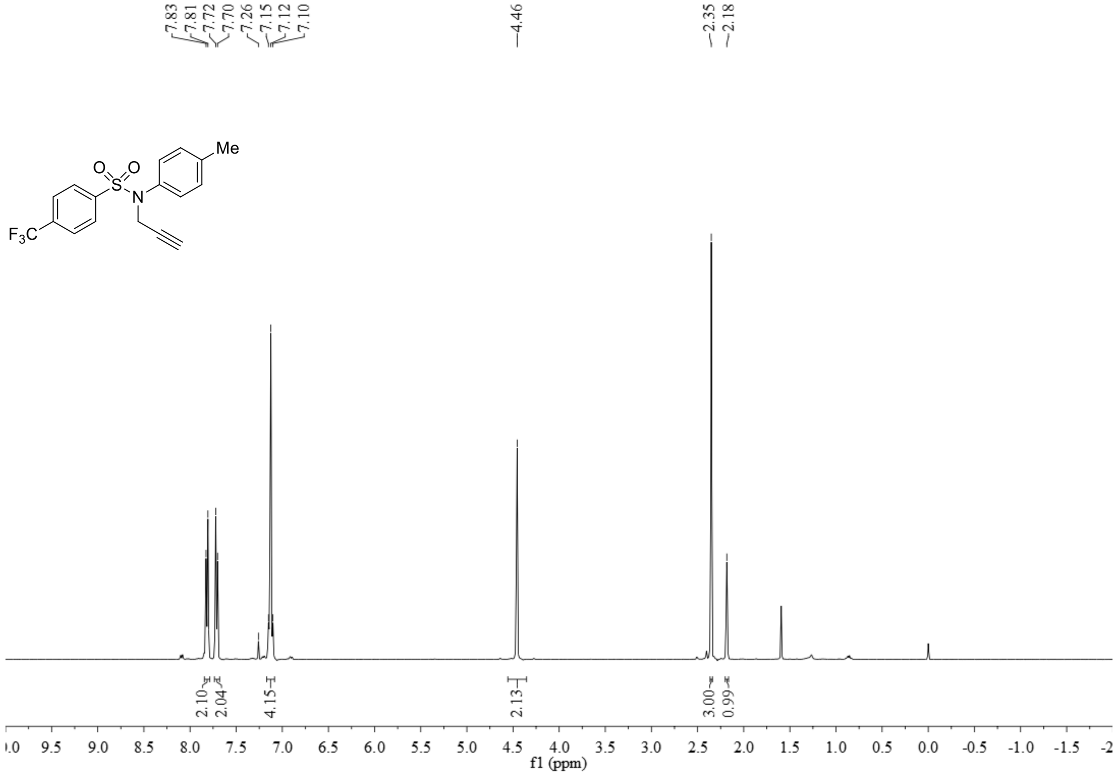
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1v**



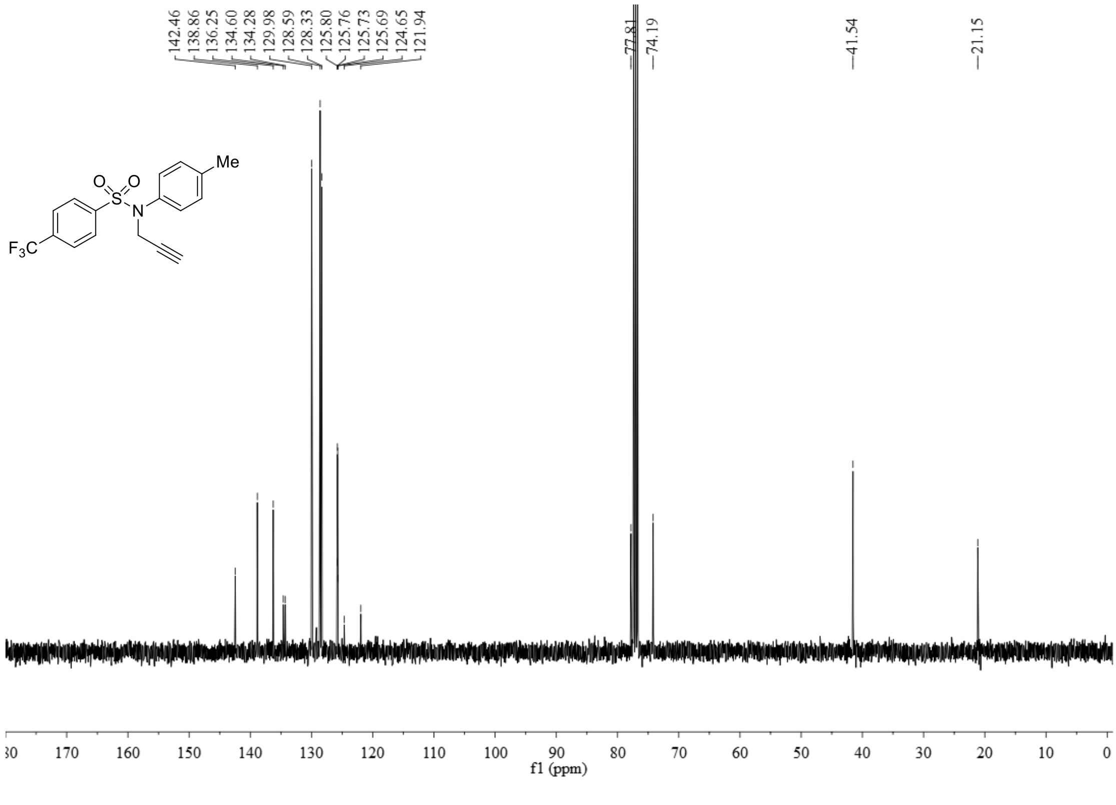
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1v**



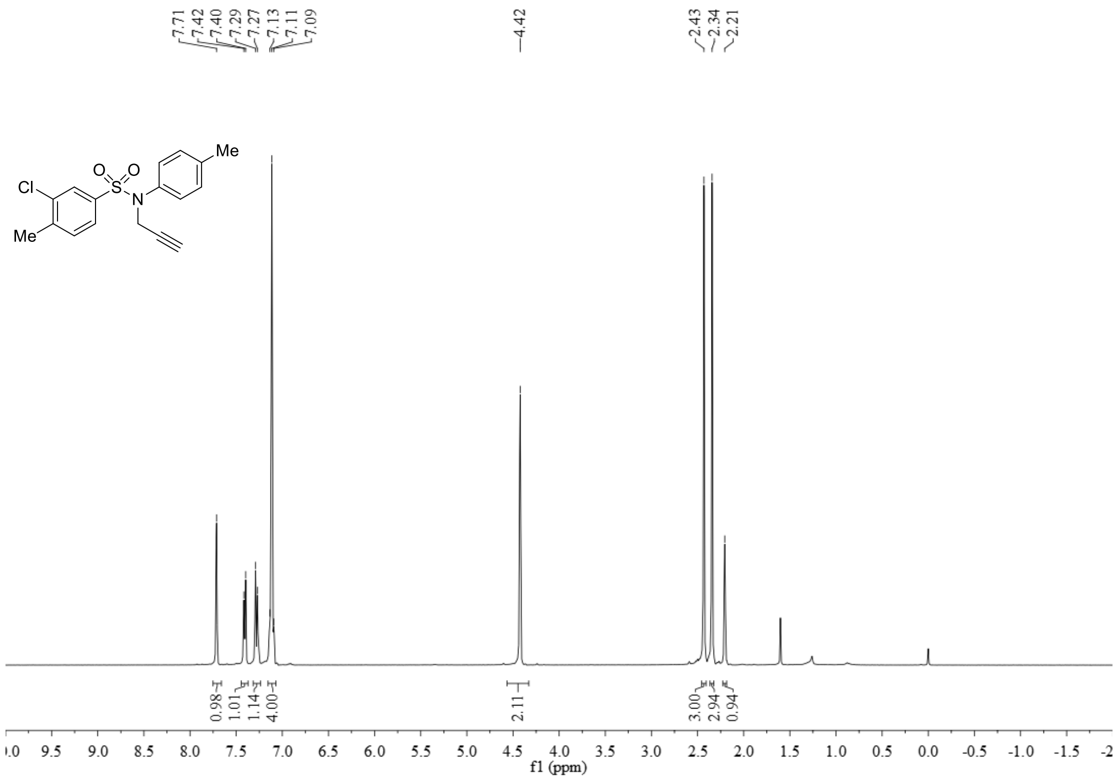
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1w**



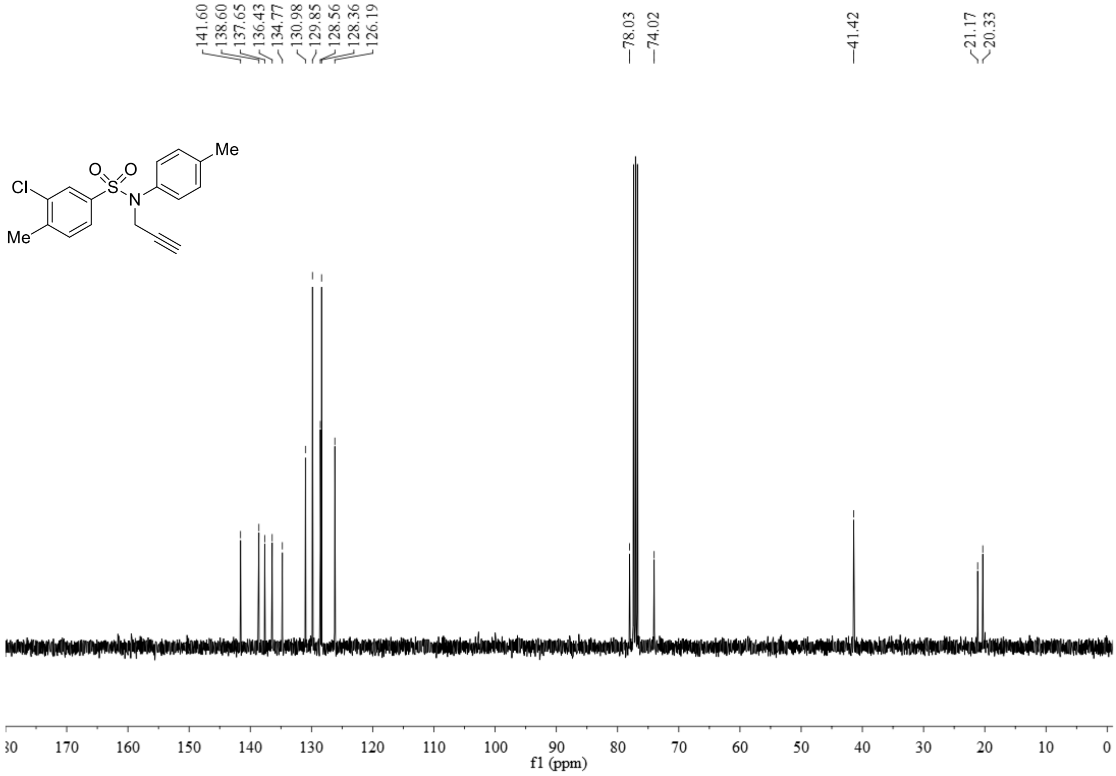
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1w**



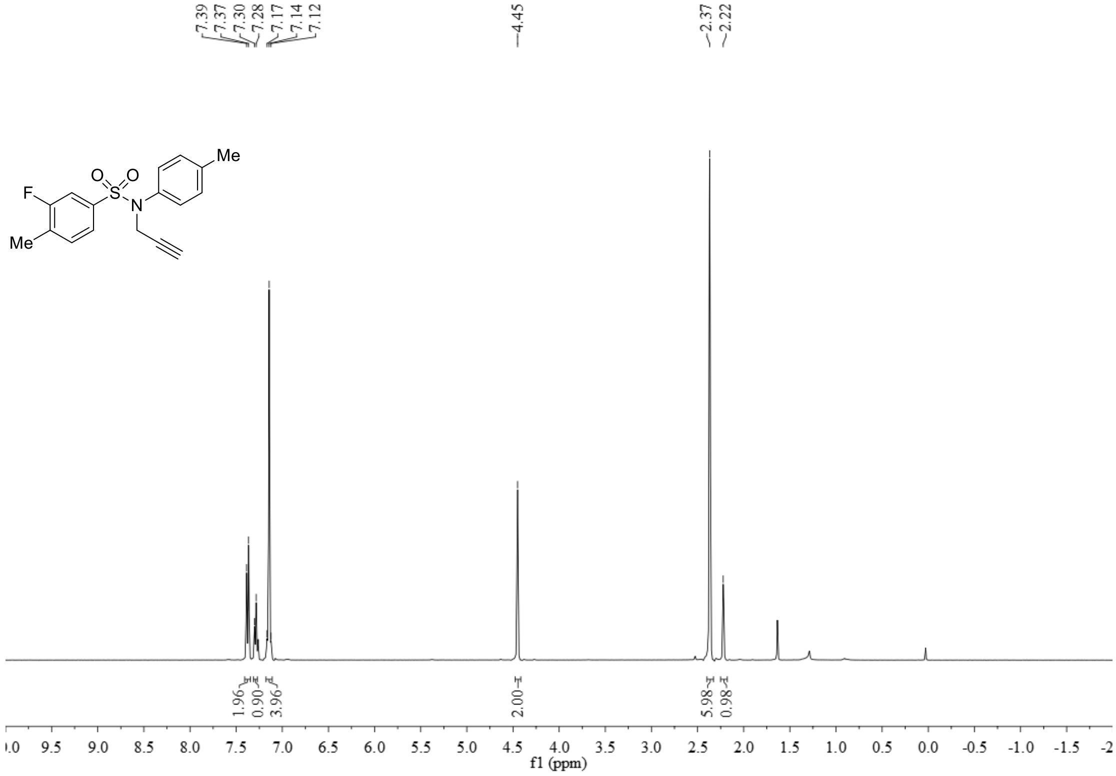
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1x**



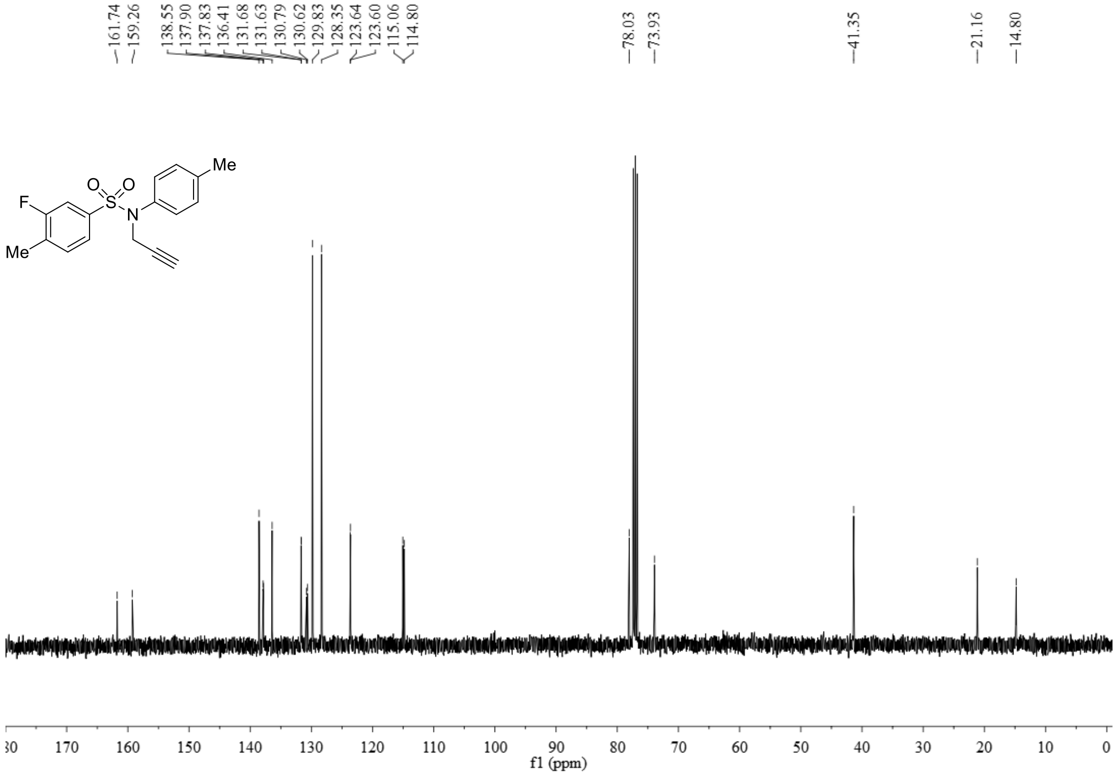
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1x**



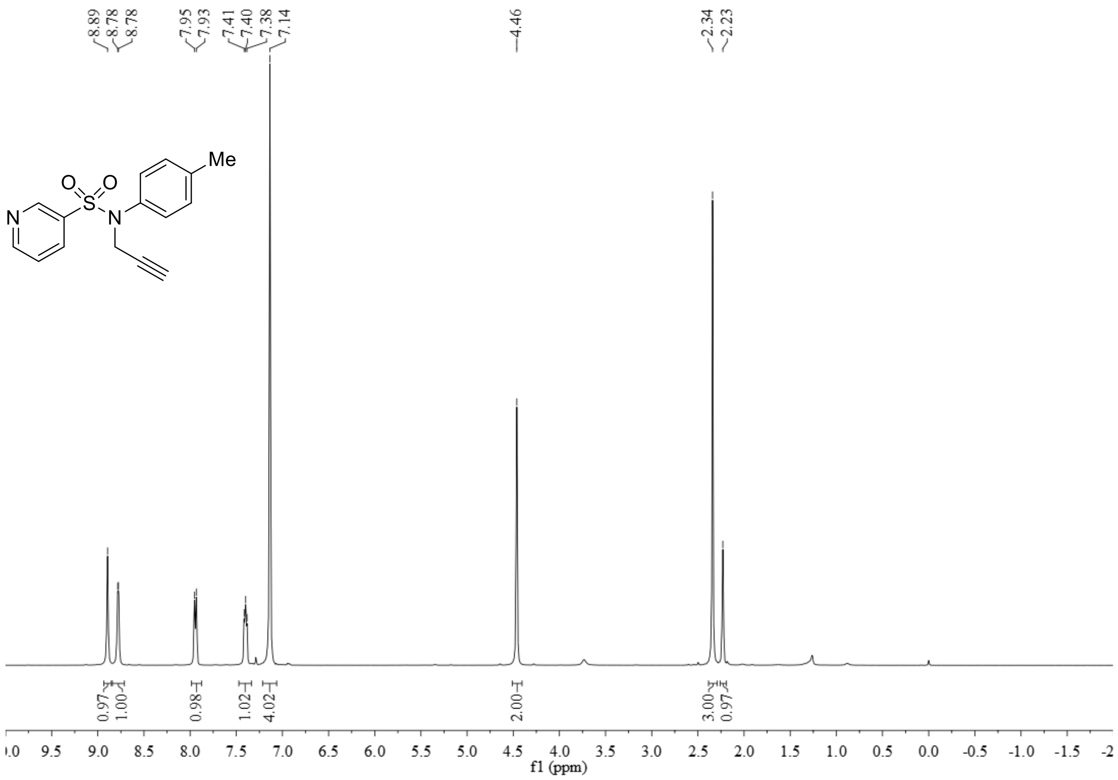
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1y**



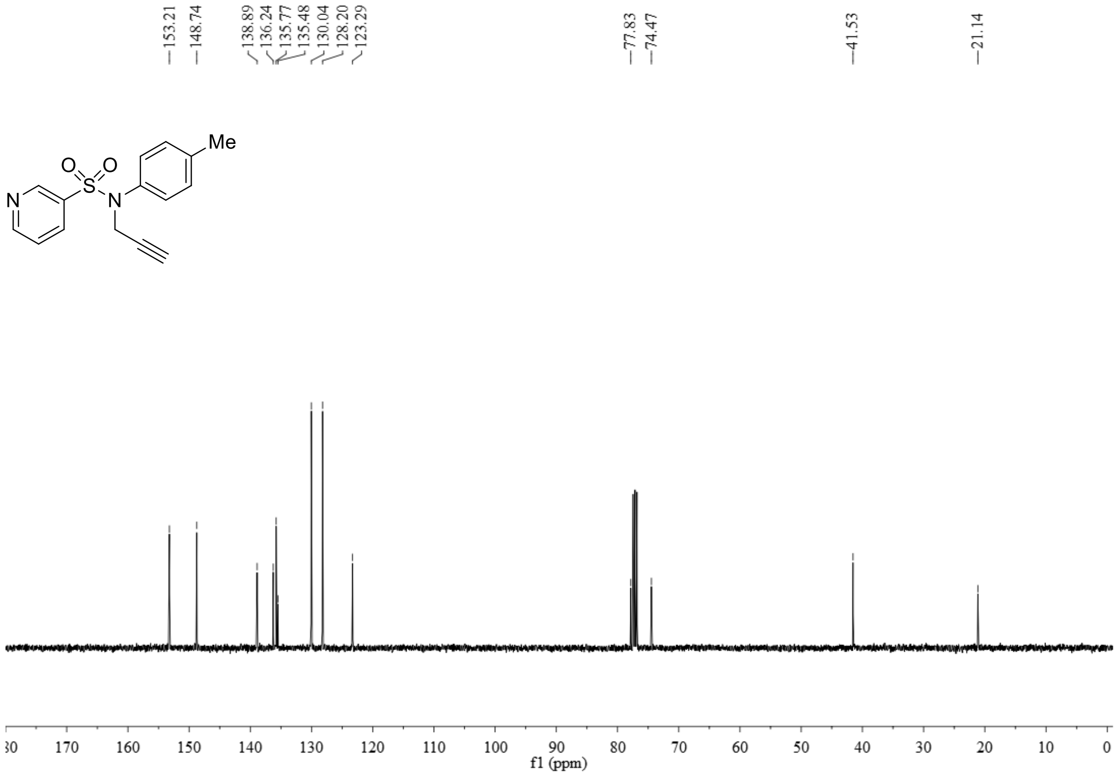
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1y**



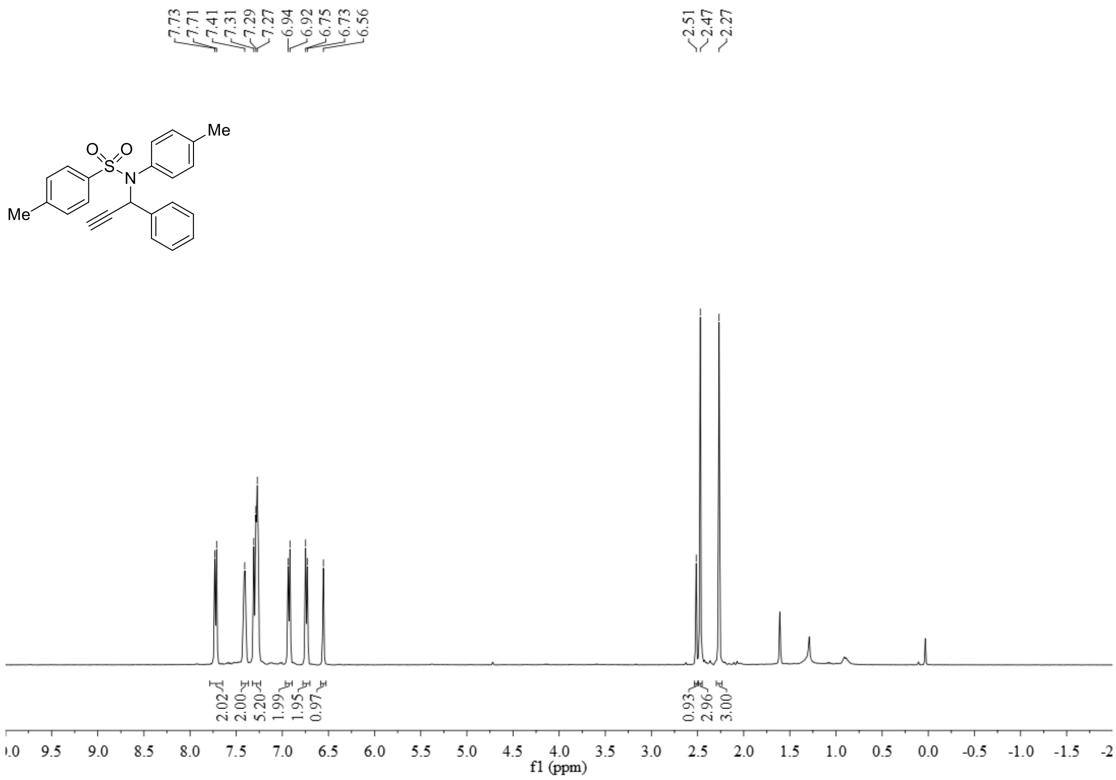
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1z**



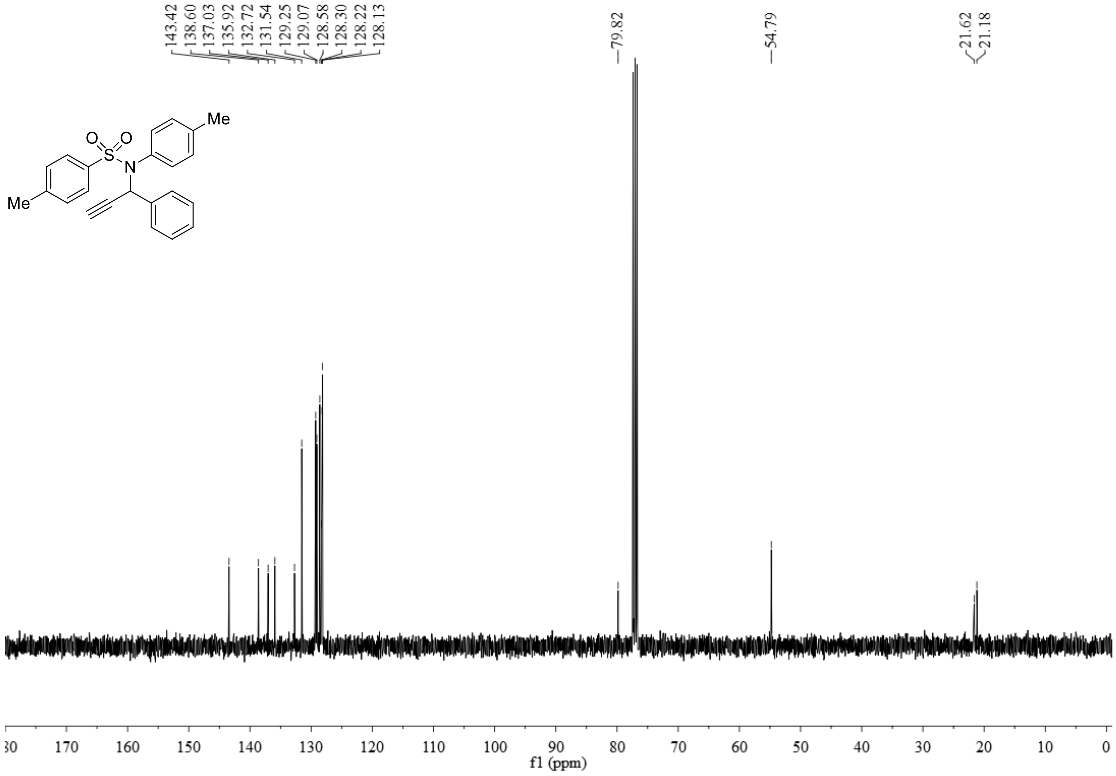
^{13}CNMR spectrum (400 MHz, $CDCl_3$) of **1z**



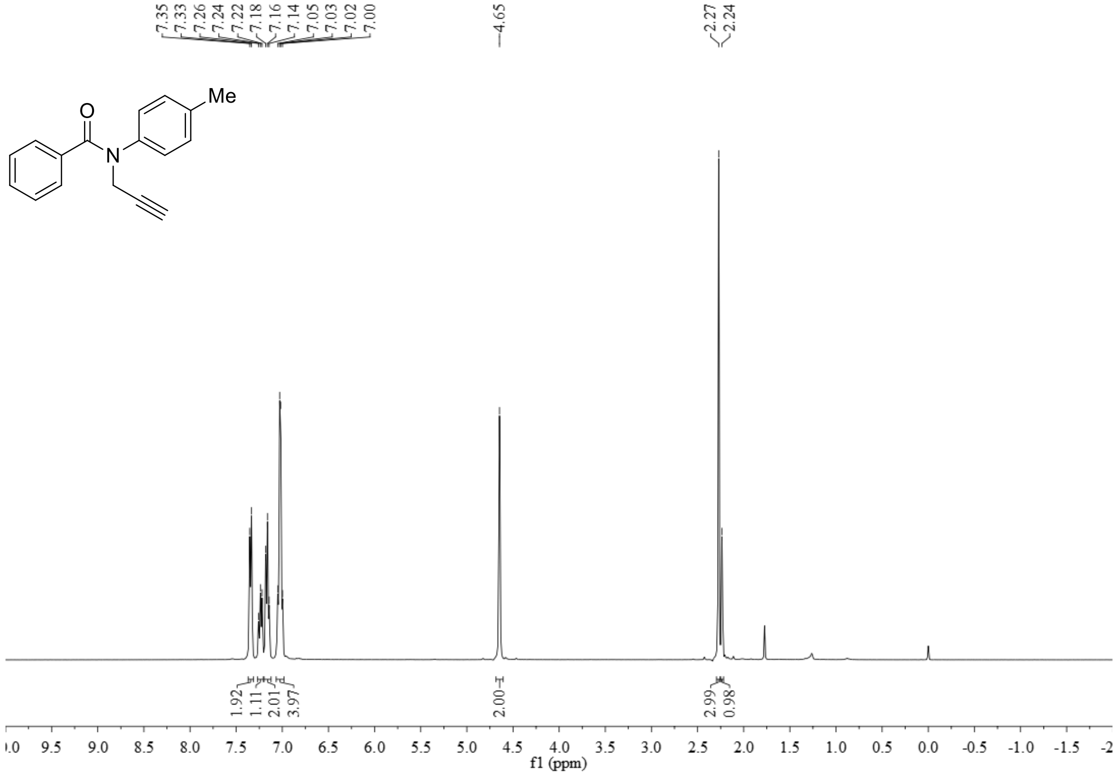
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1-1z**



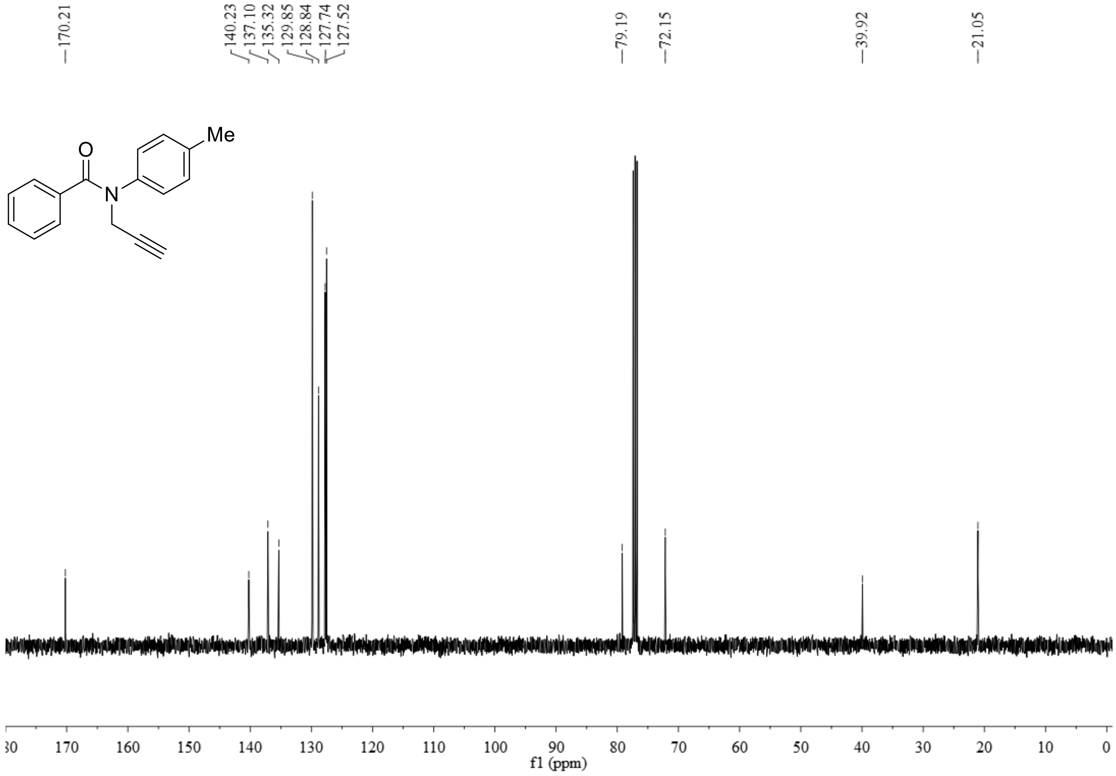
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1-1z**



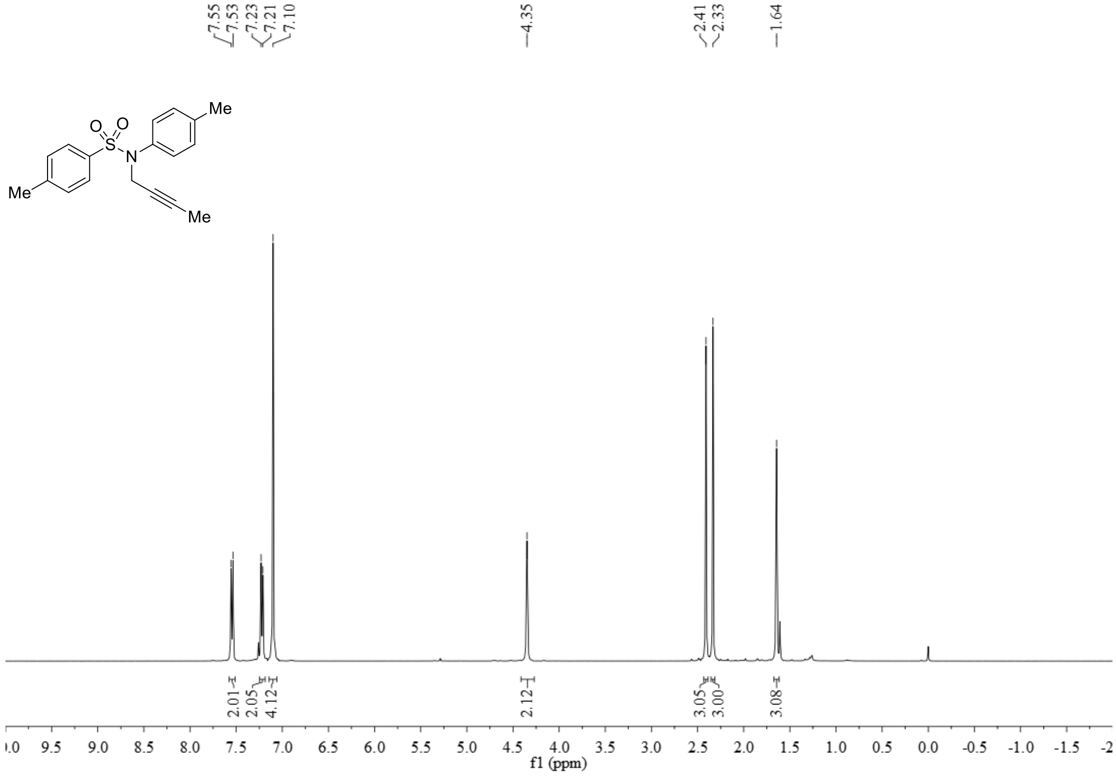
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **1-1a**



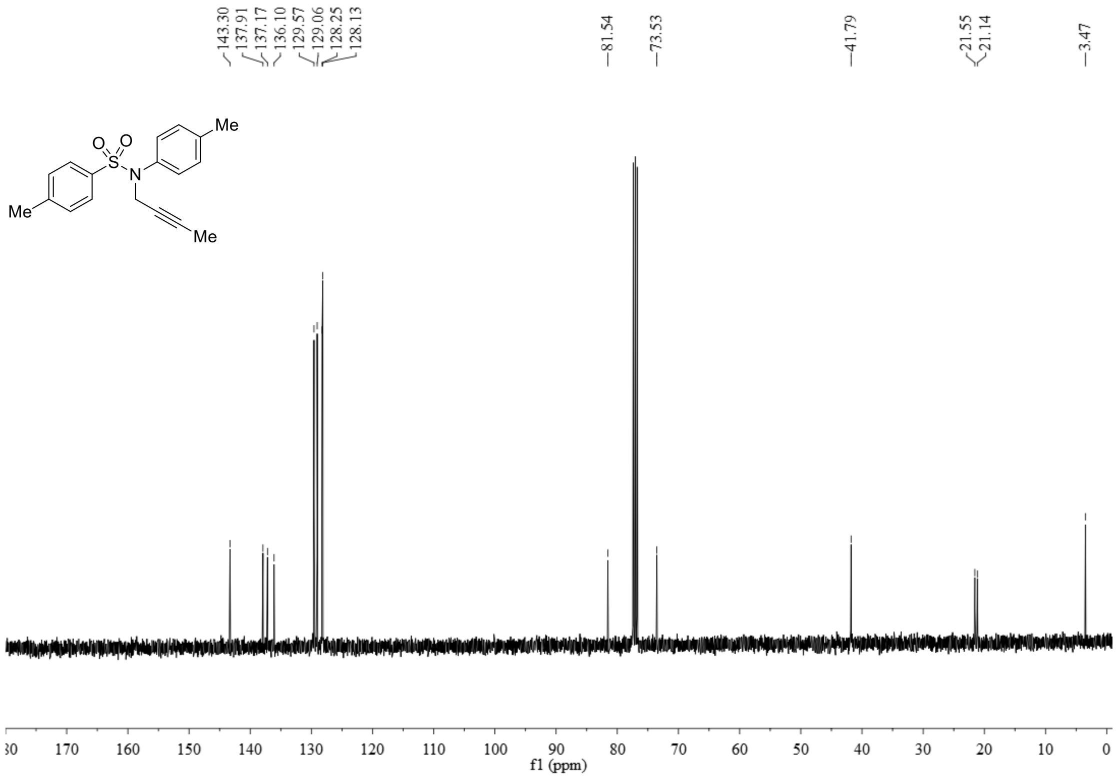
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **1-1a**



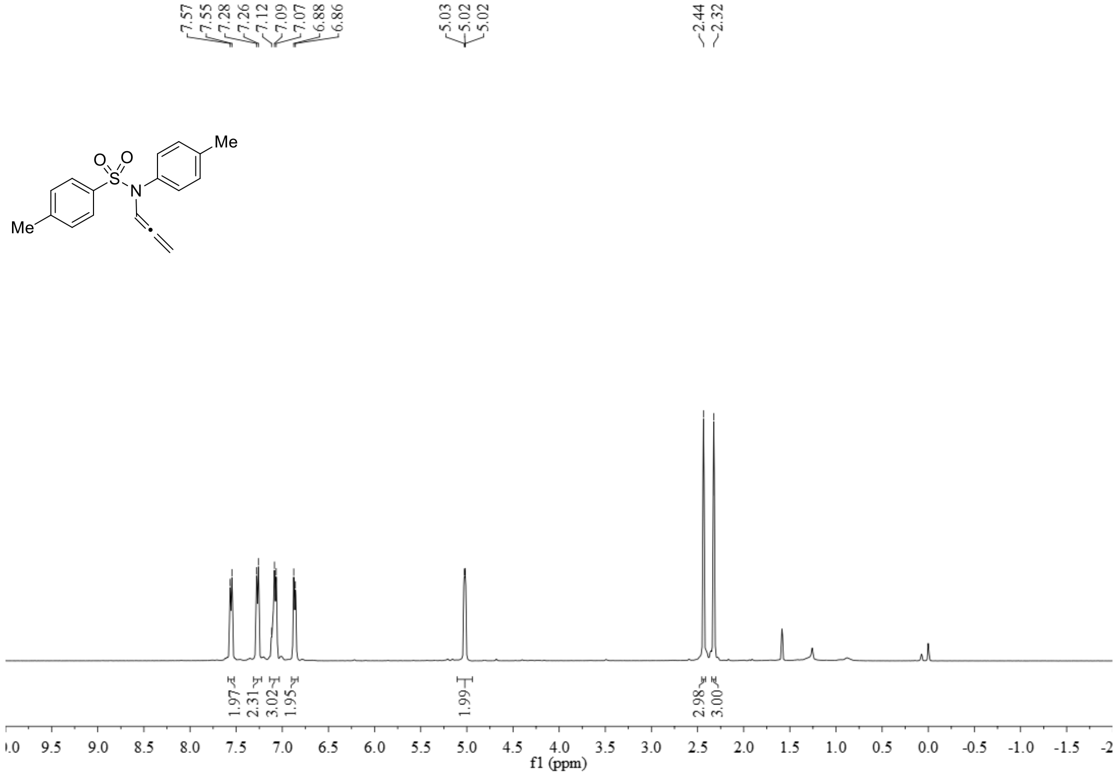
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1-1b**



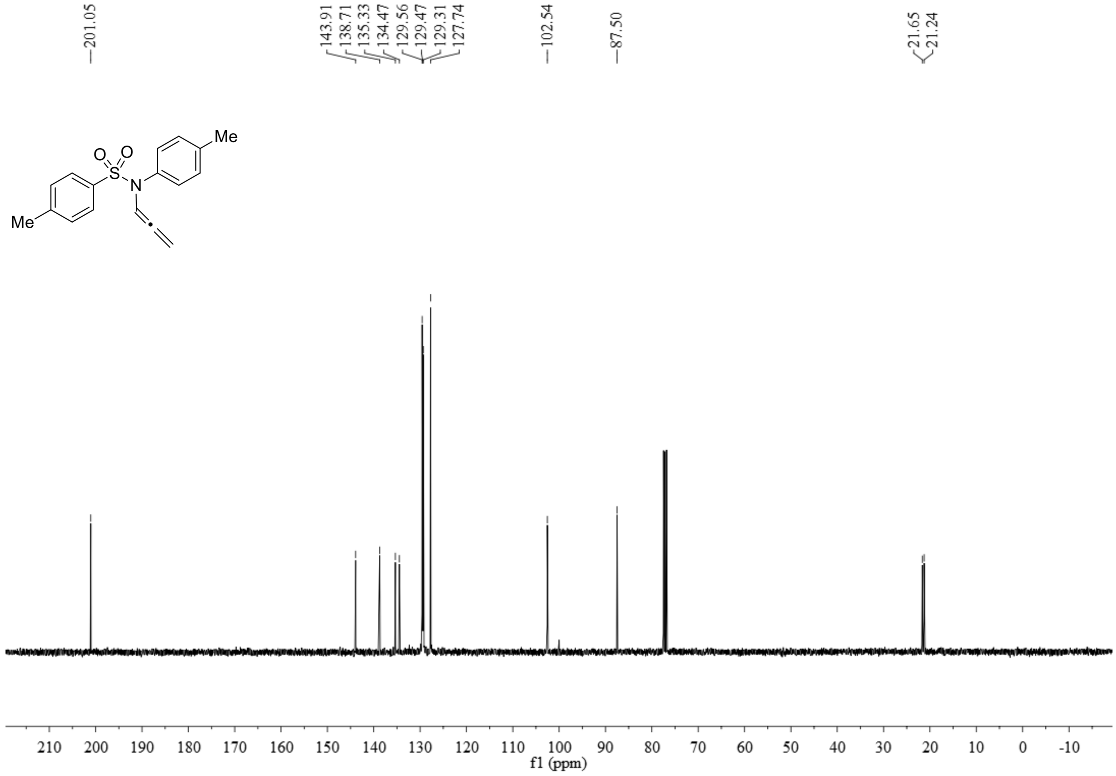
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1-1b**



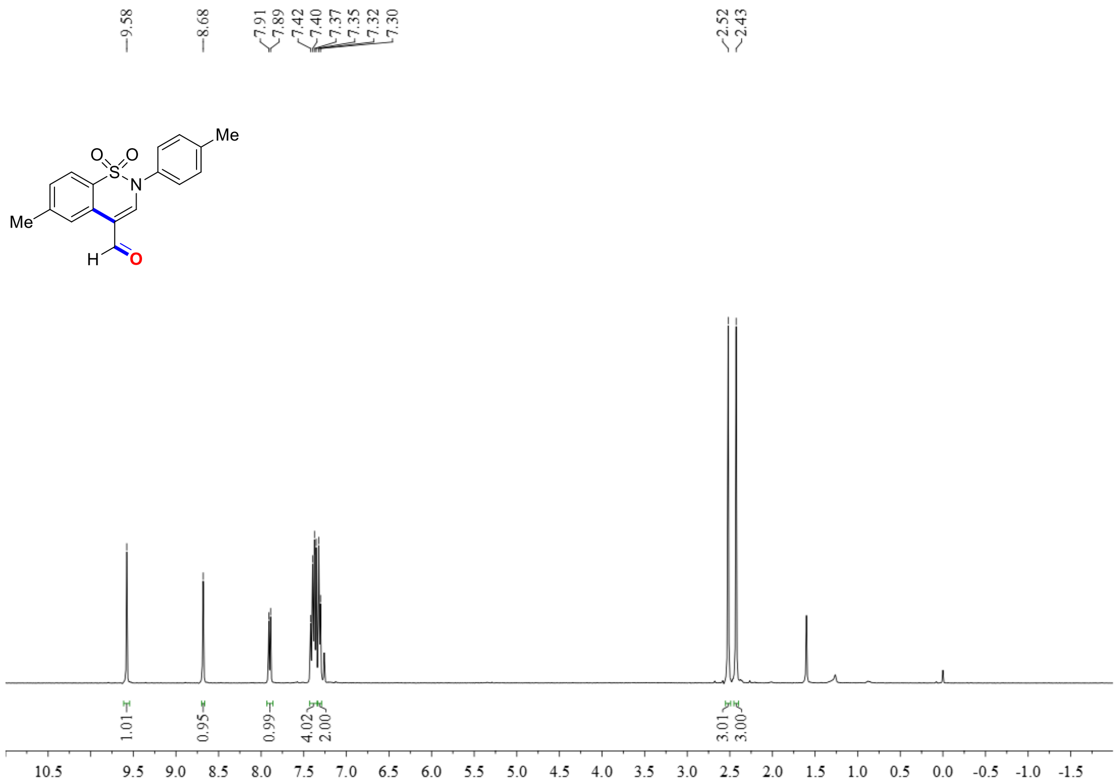
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1-1c**



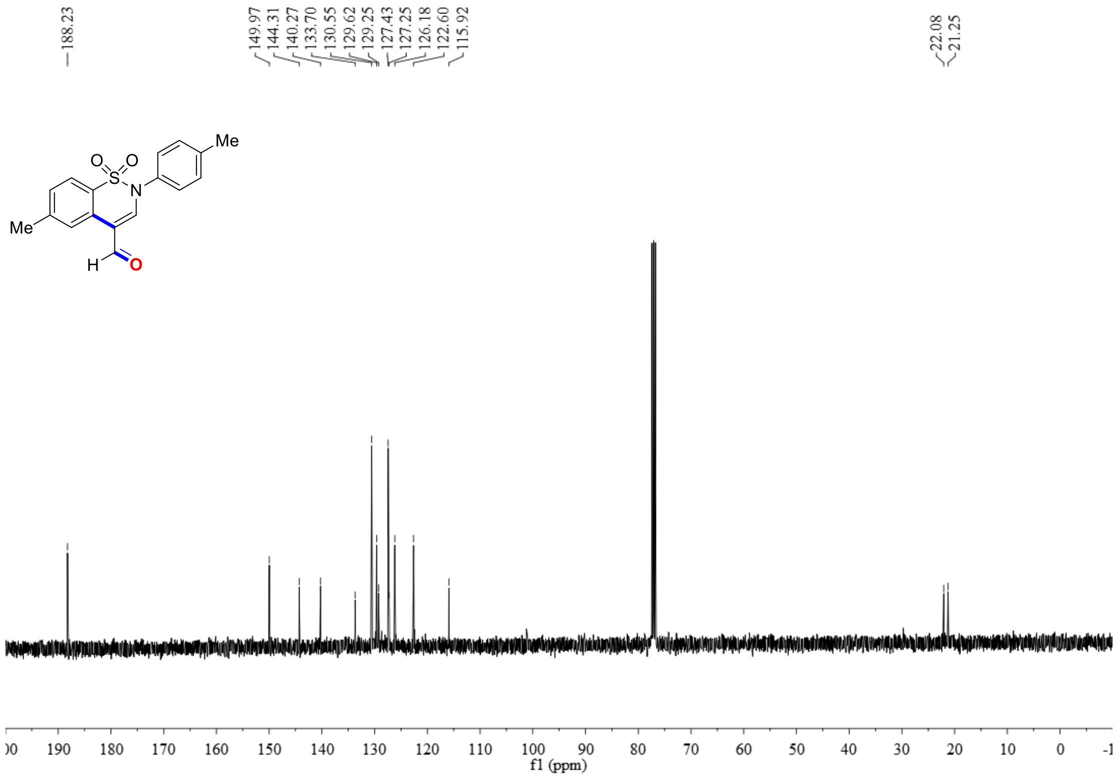
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **1-1c**



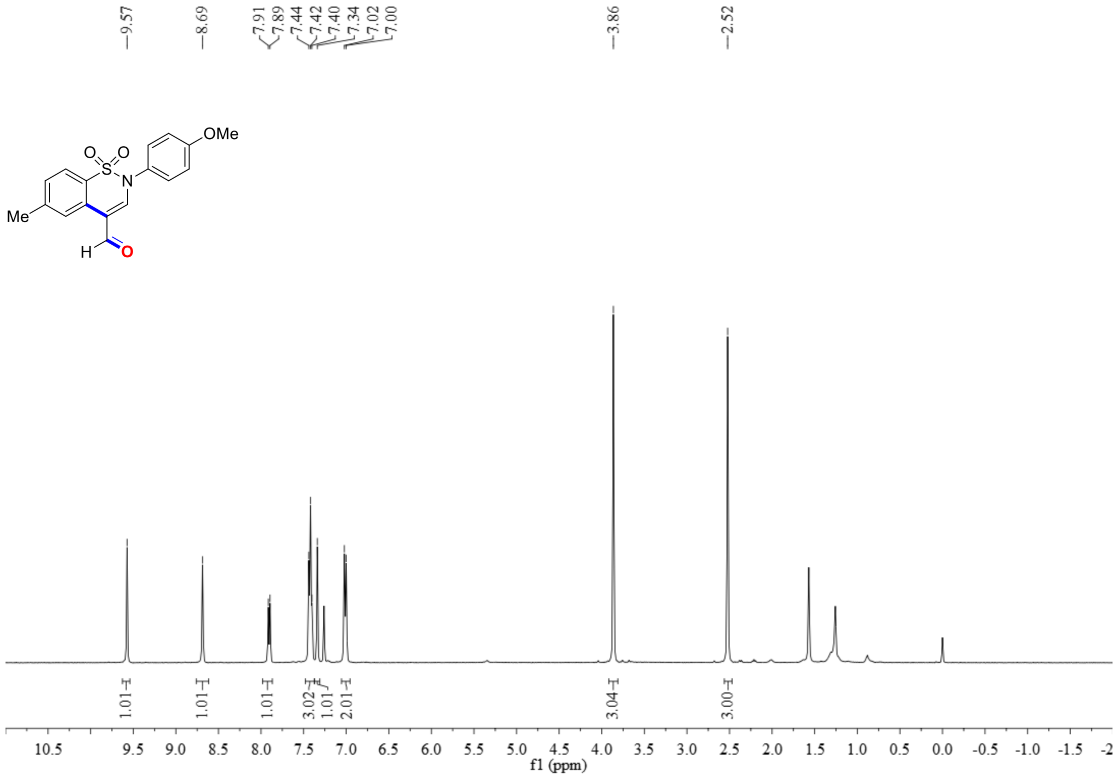
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**



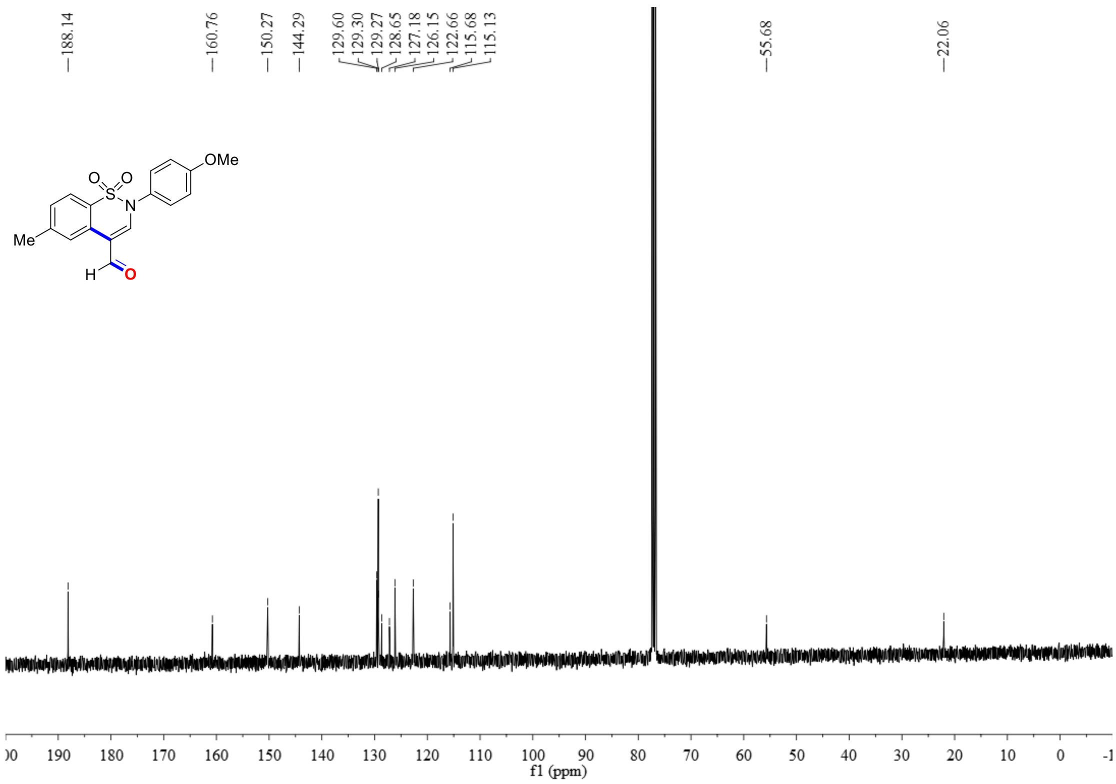
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2a**



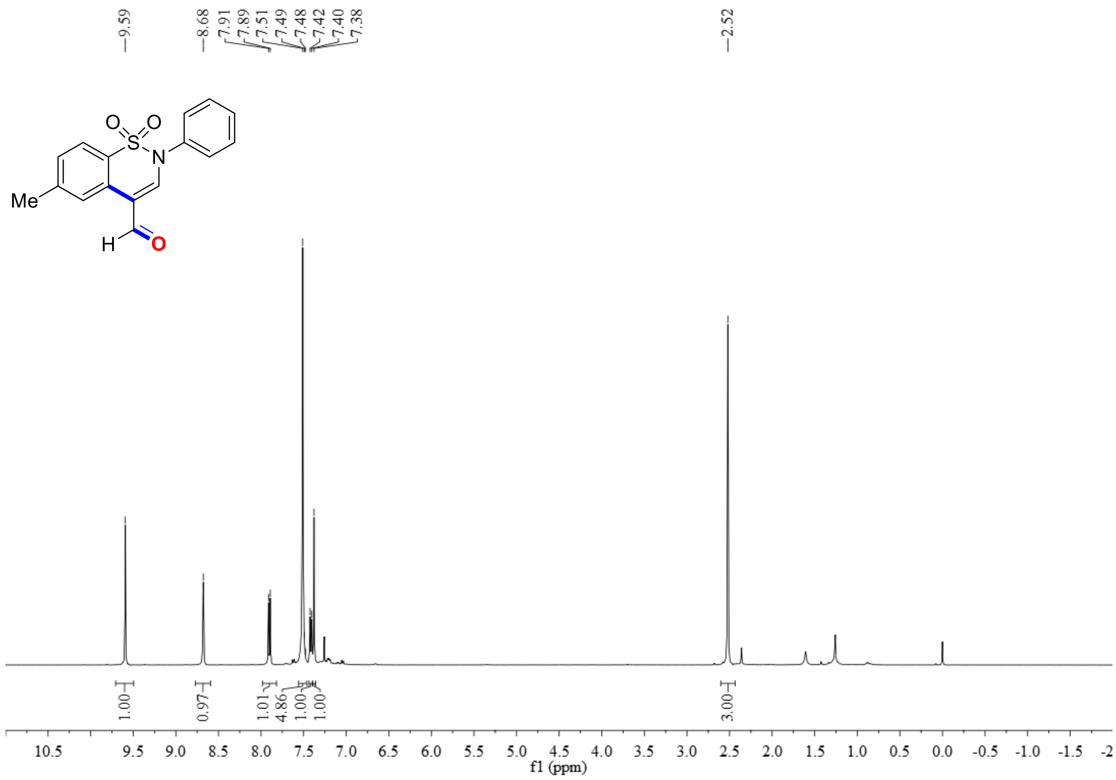
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b**



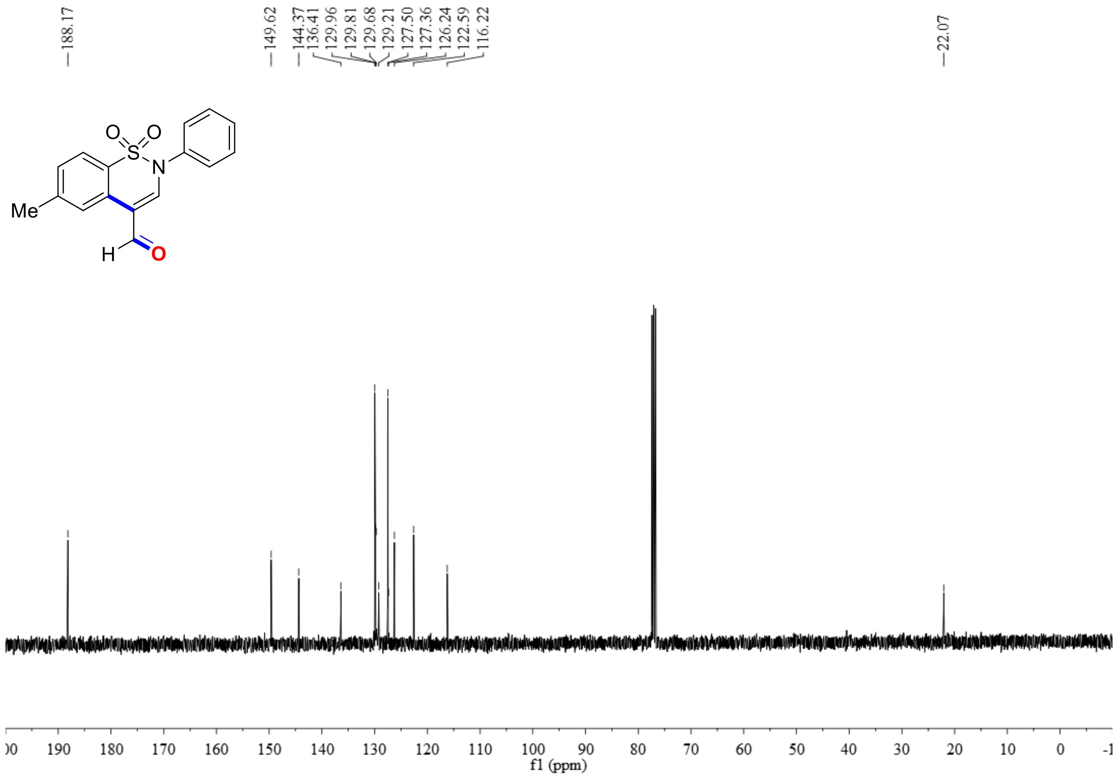
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2b**



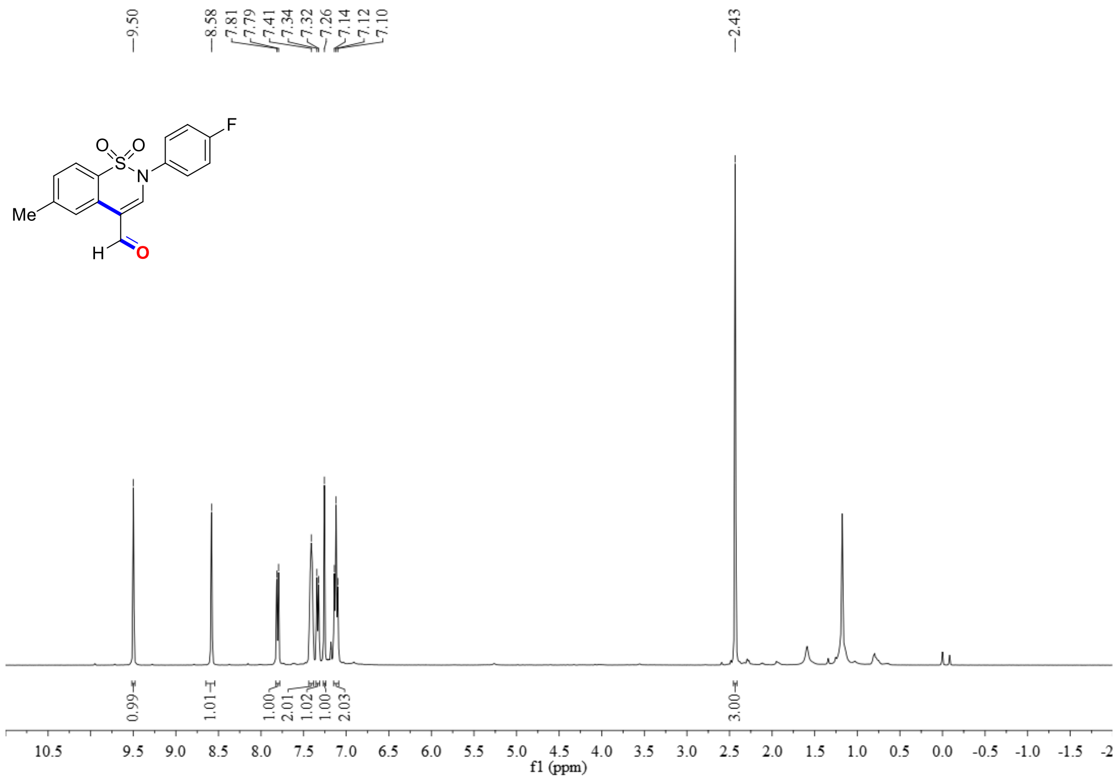
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**



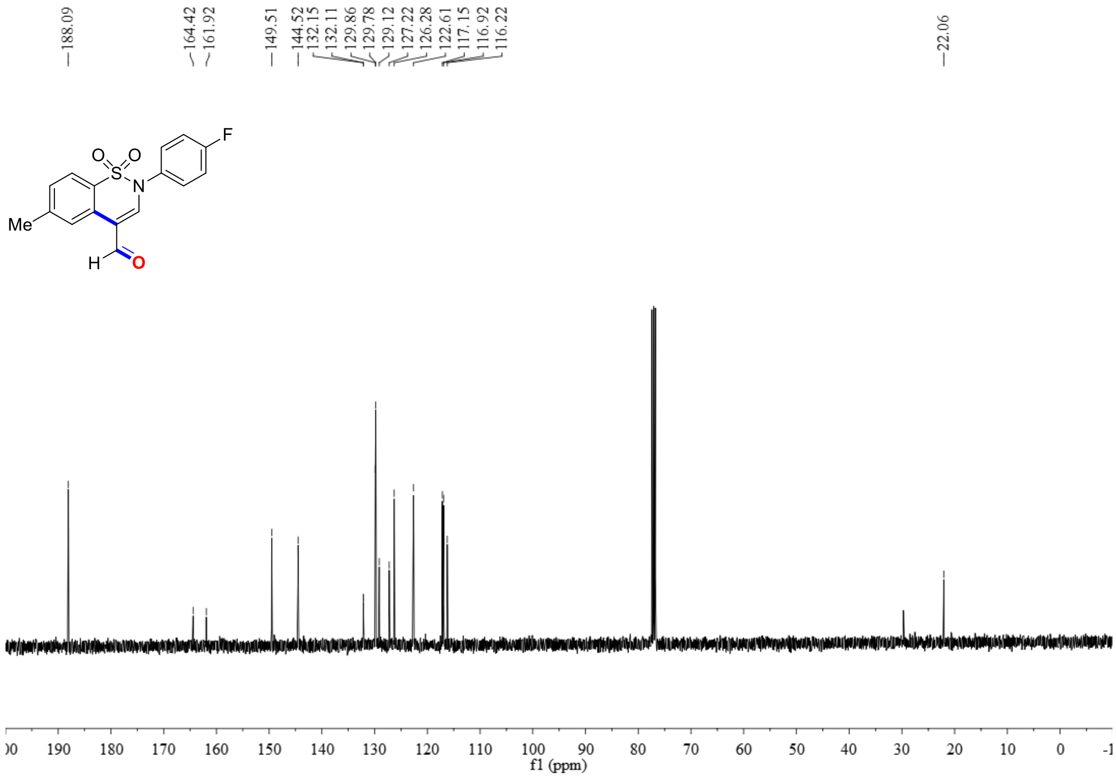
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2c**



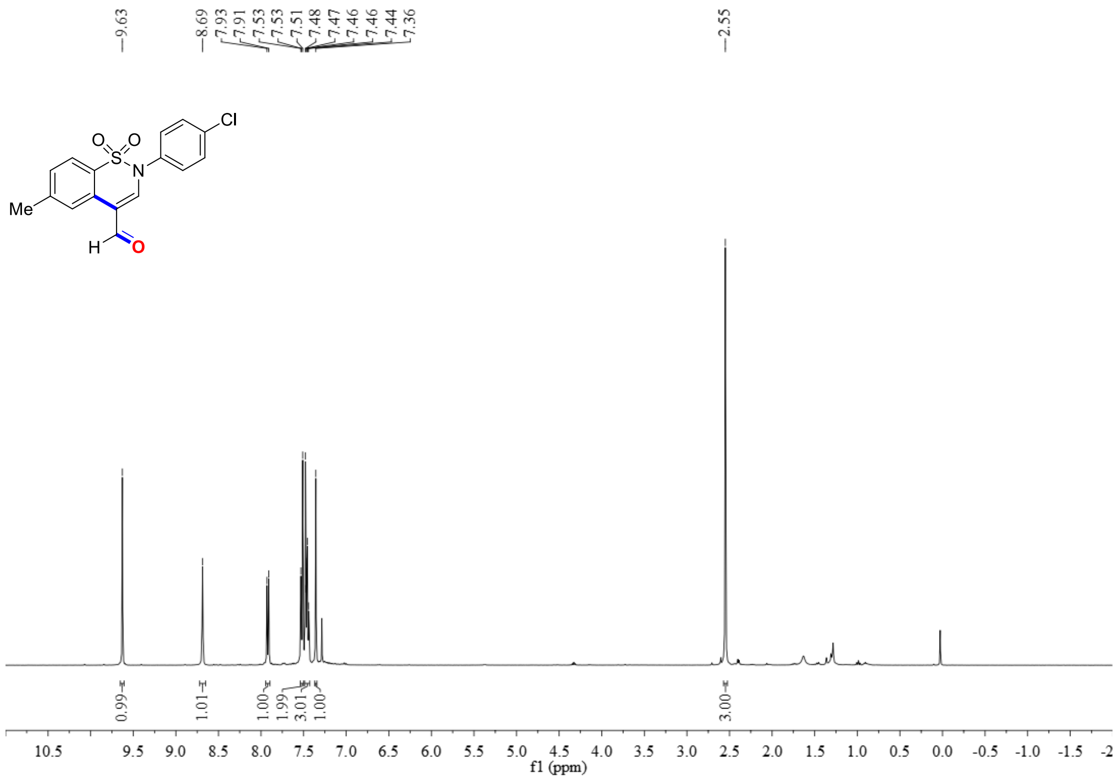
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**



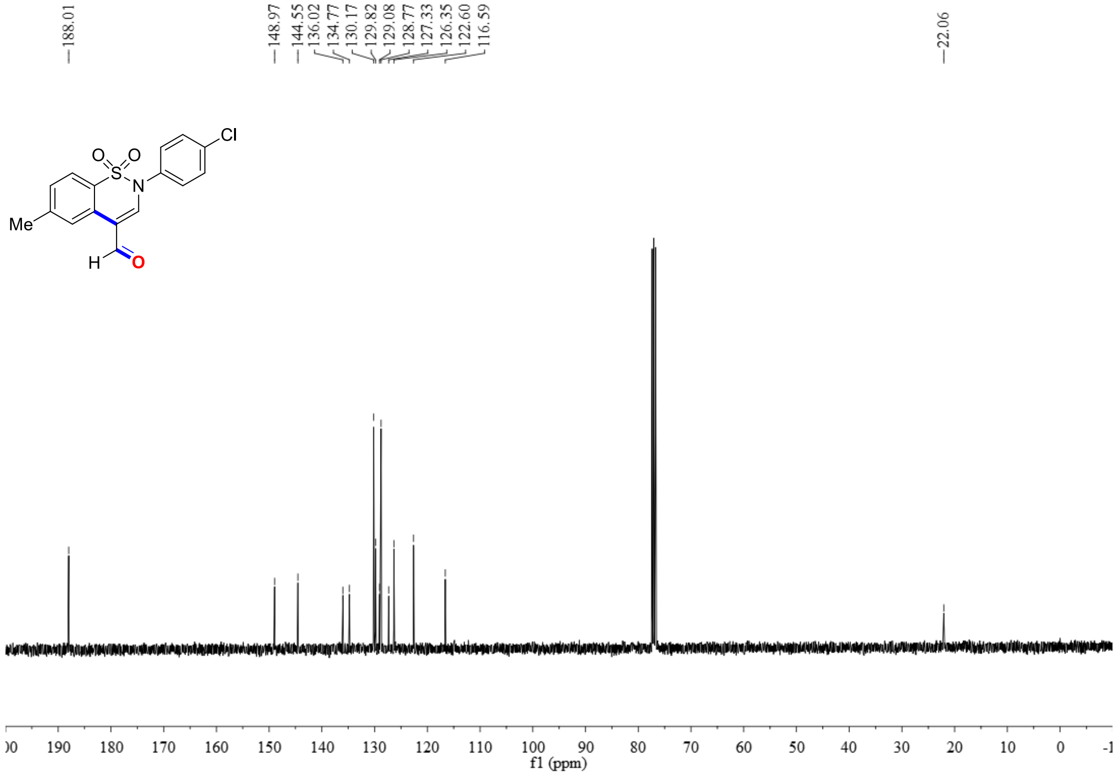
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2d**



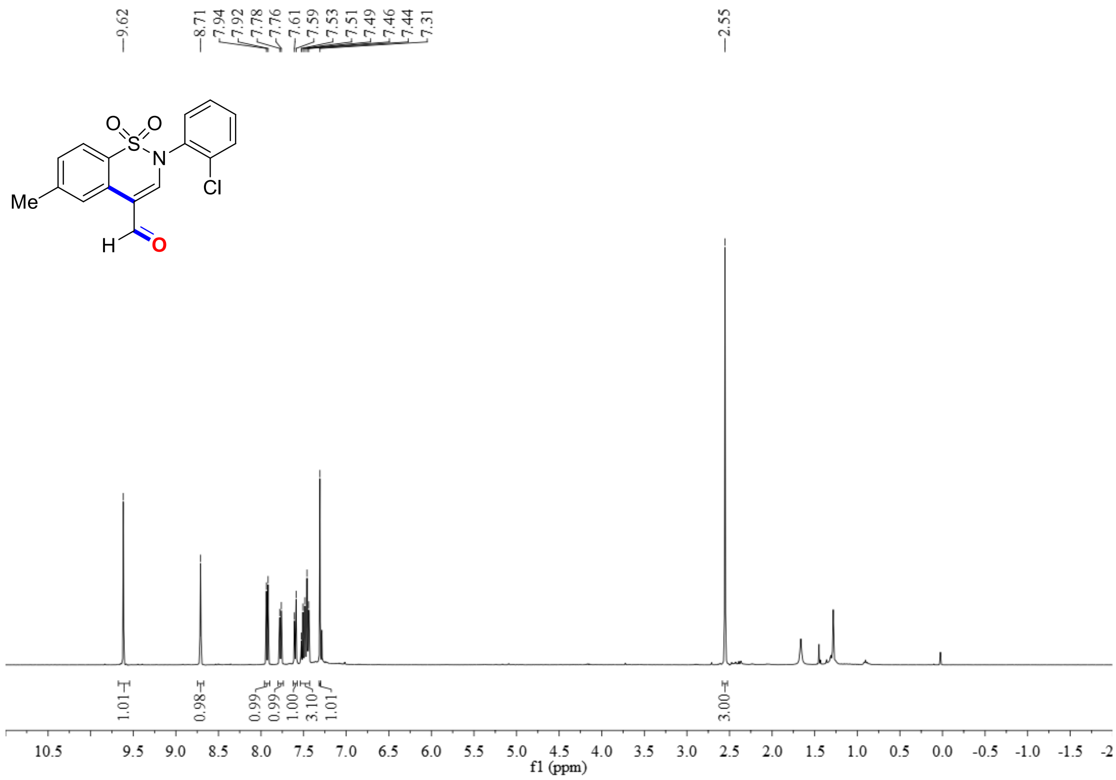
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **2e**



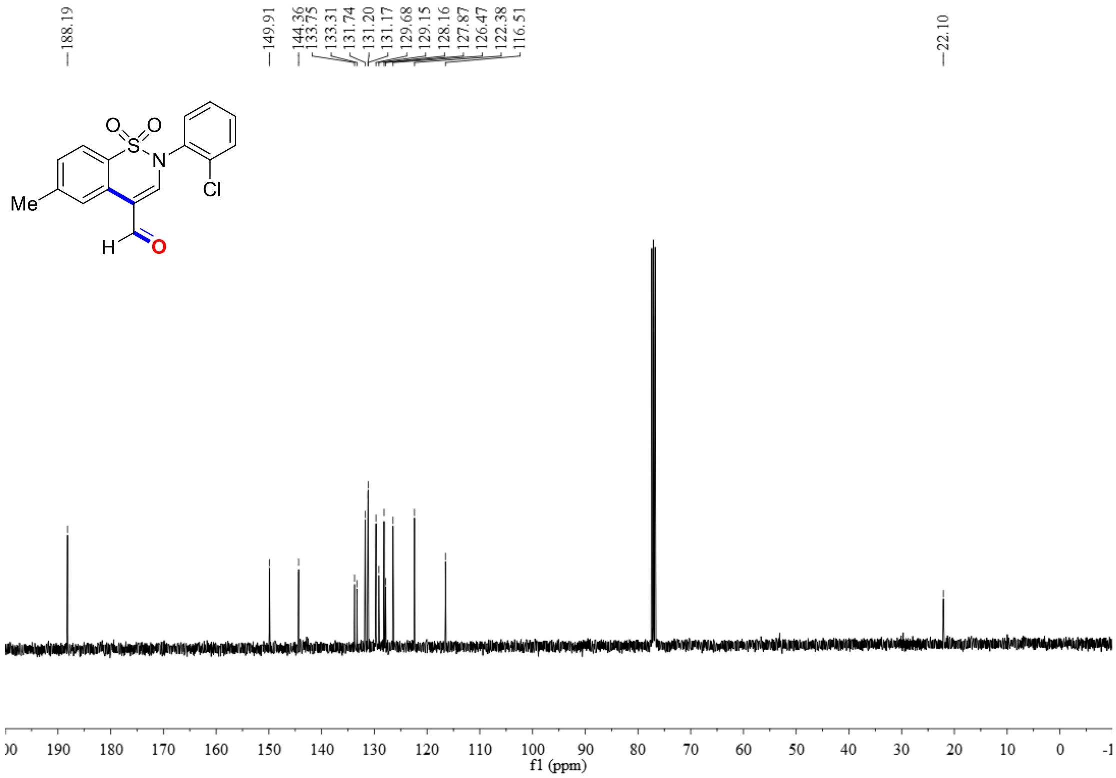
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **2e**



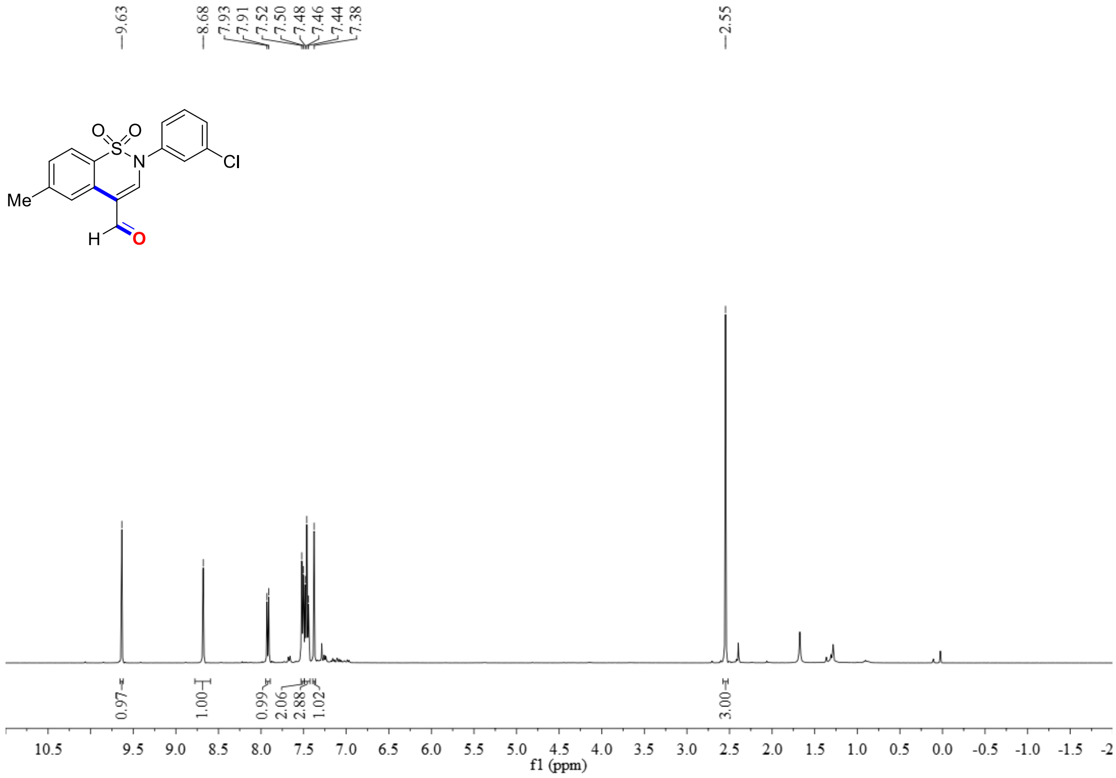
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2f**



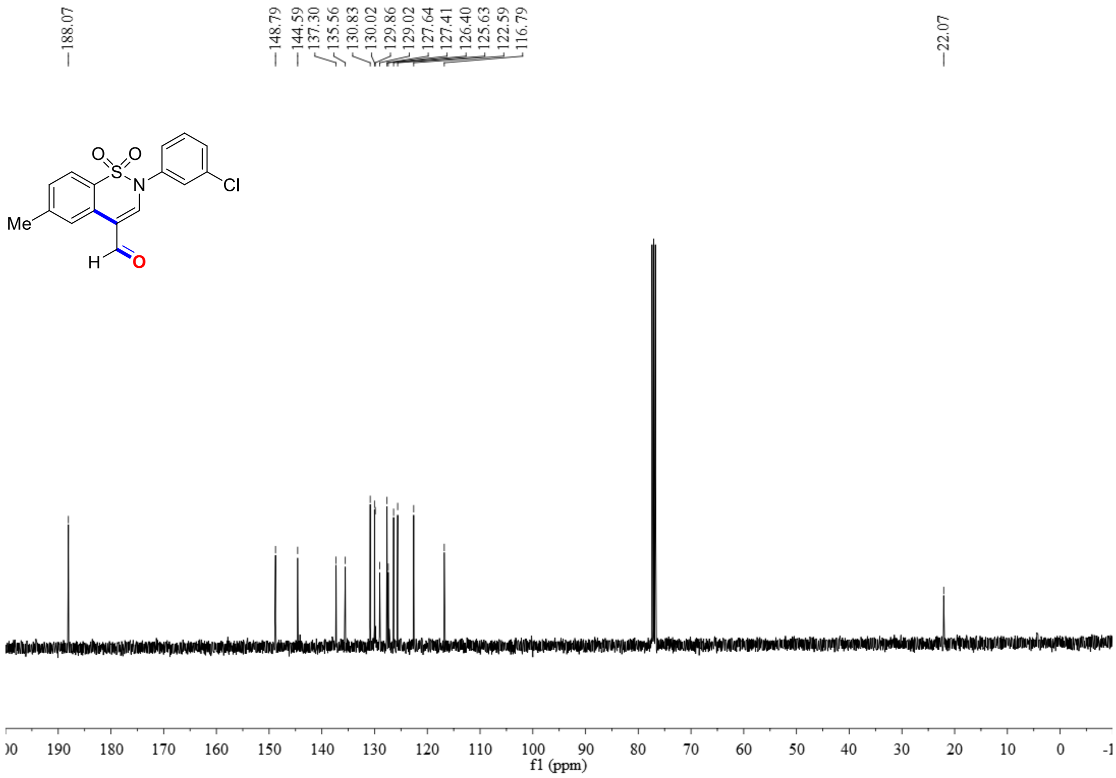
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2f**



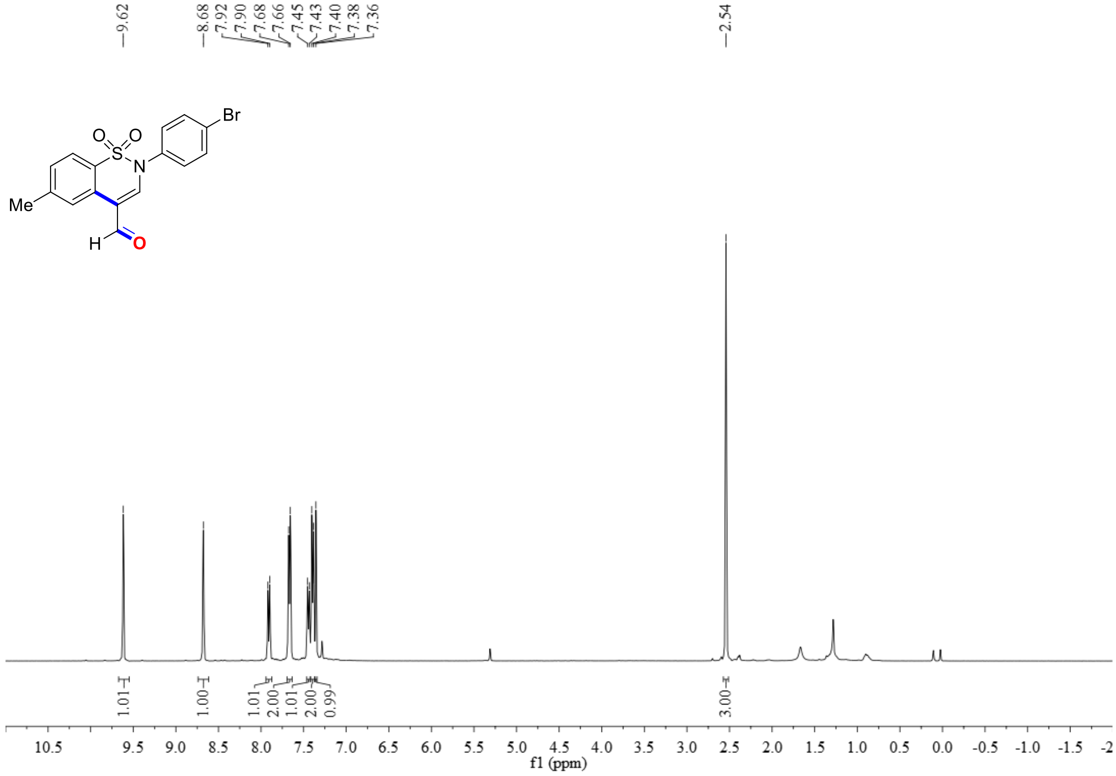
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **2g**



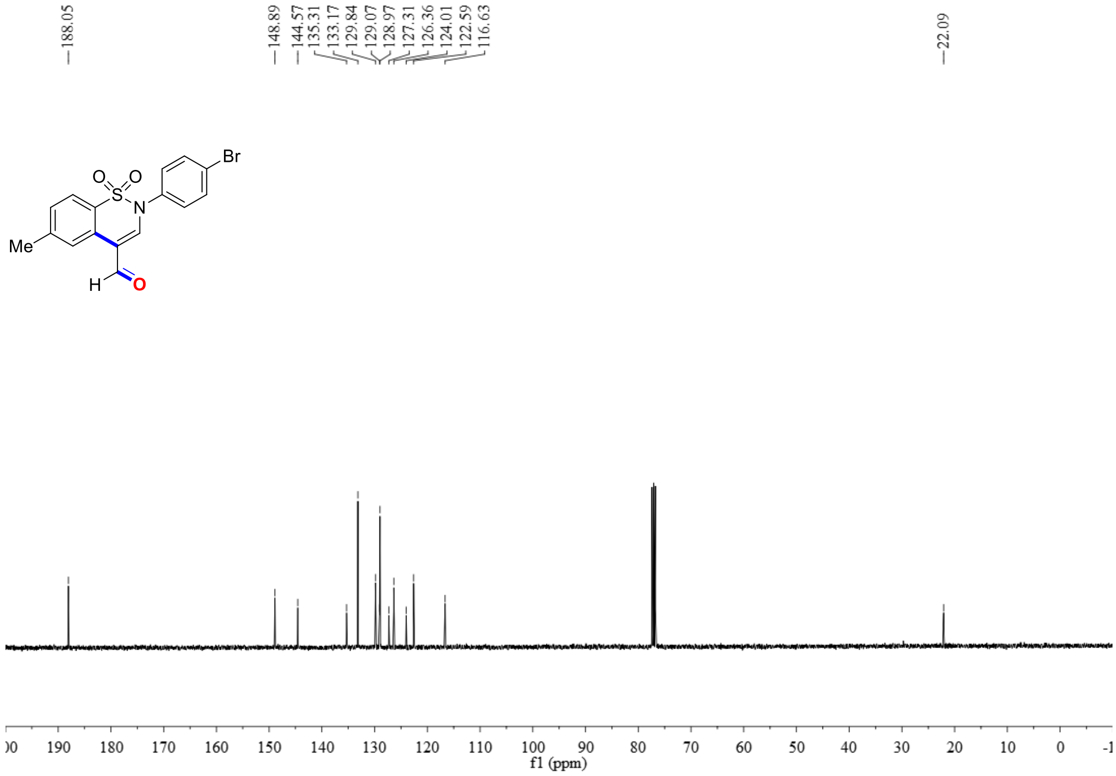
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **2g**



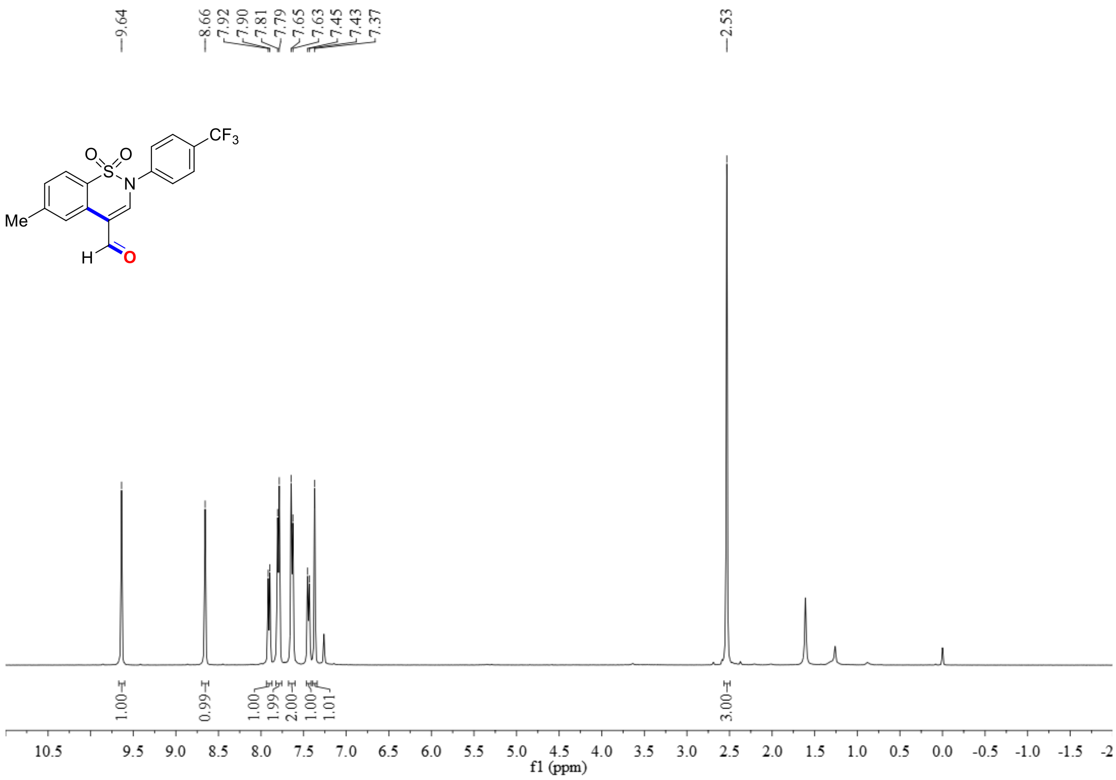
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2h**



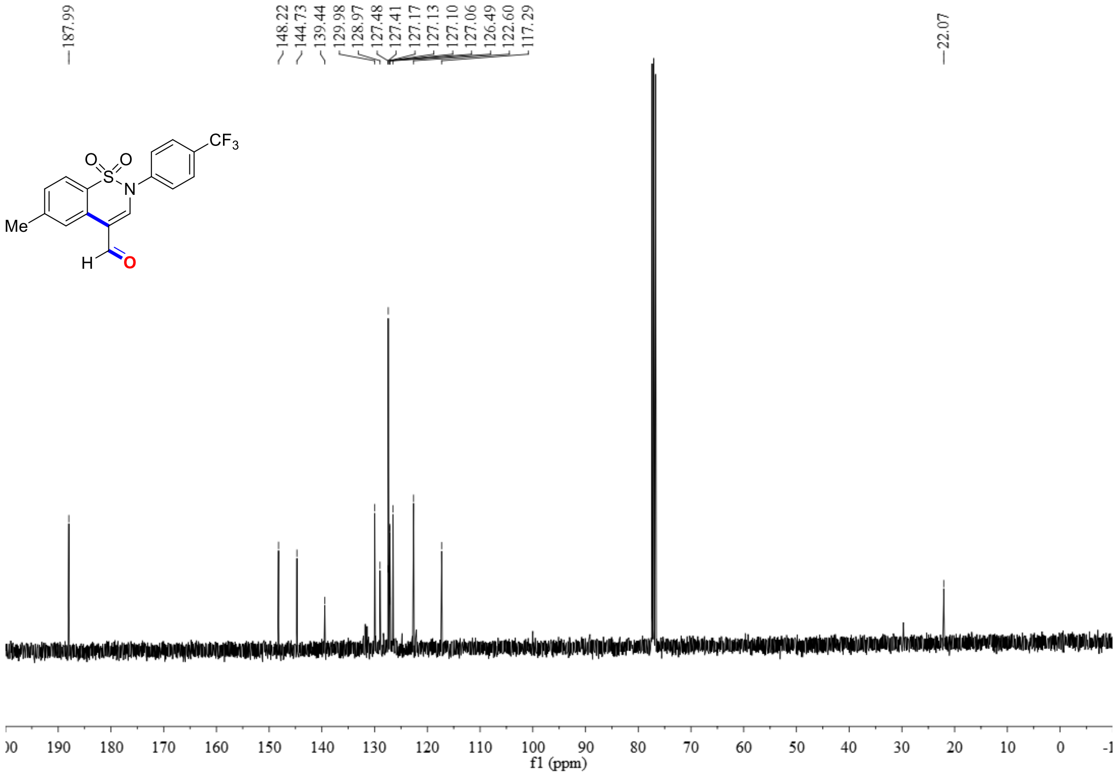
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2h**



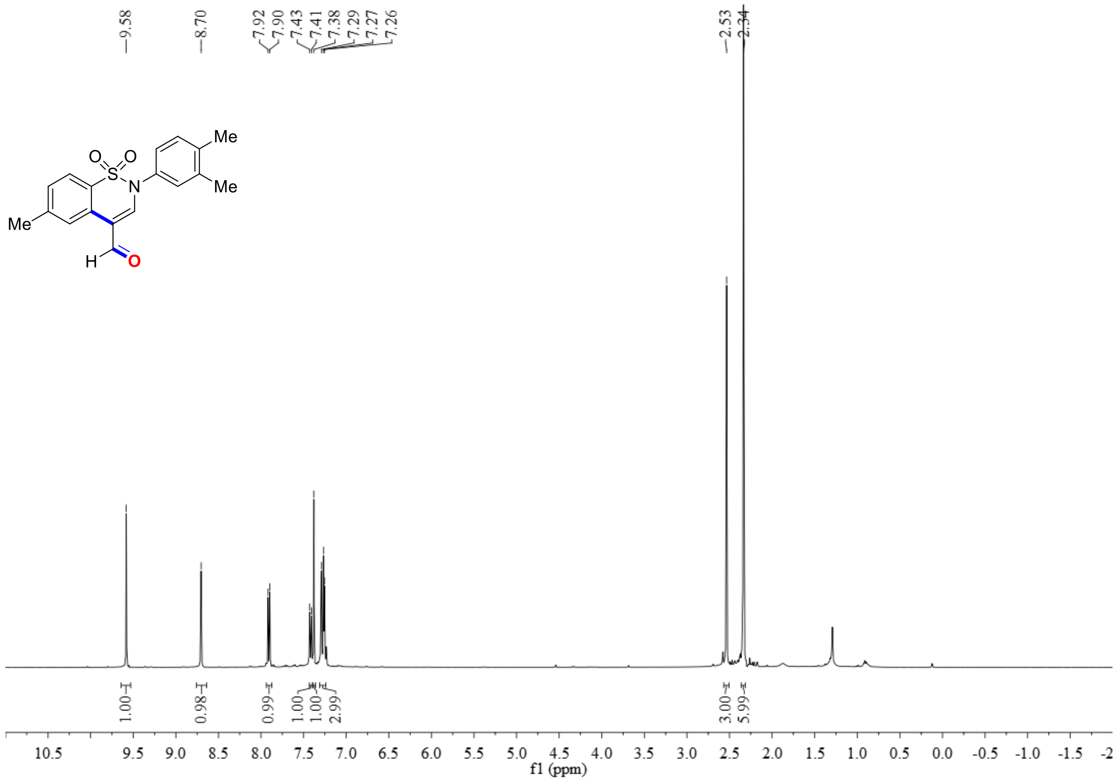
^1H NMR spectrum (400 MHz, $CDCl_3$) of **2i**



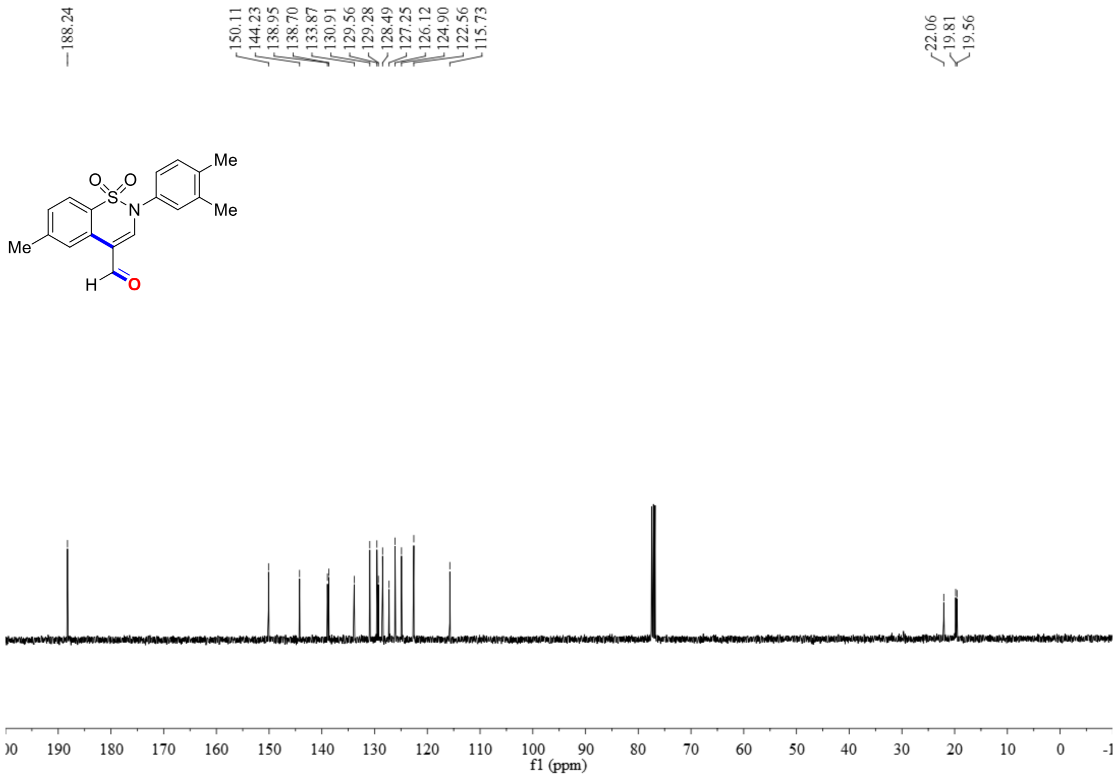
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2i**



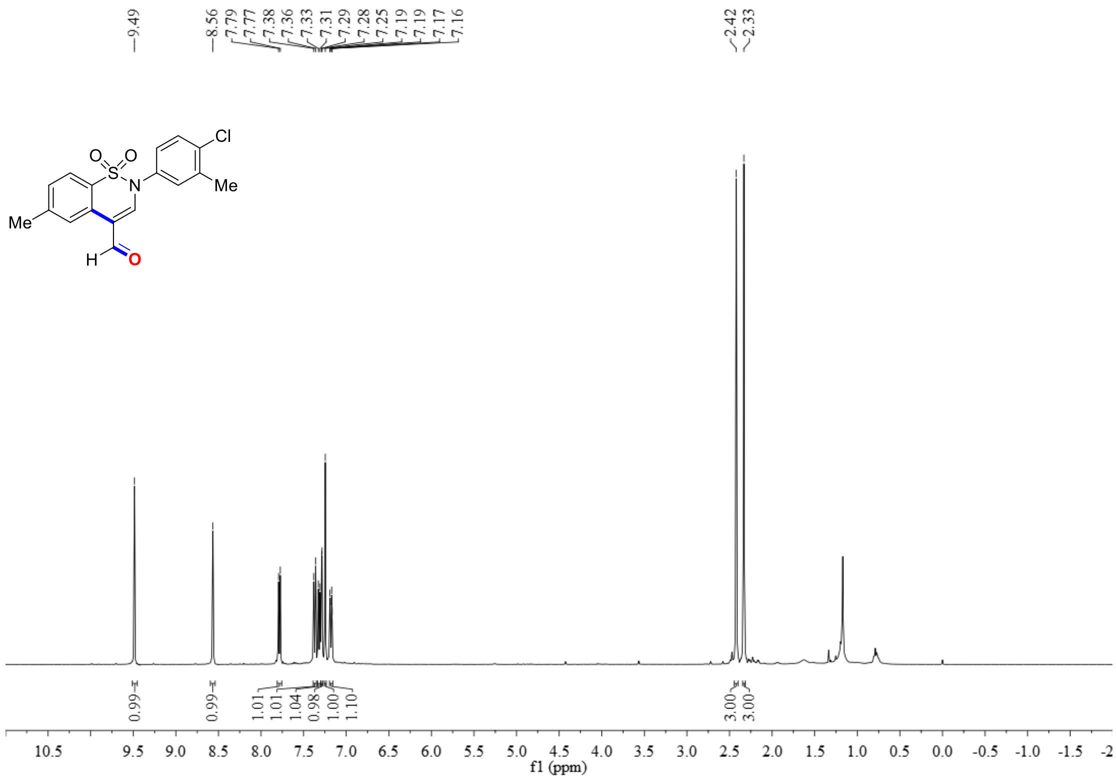
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **2j**



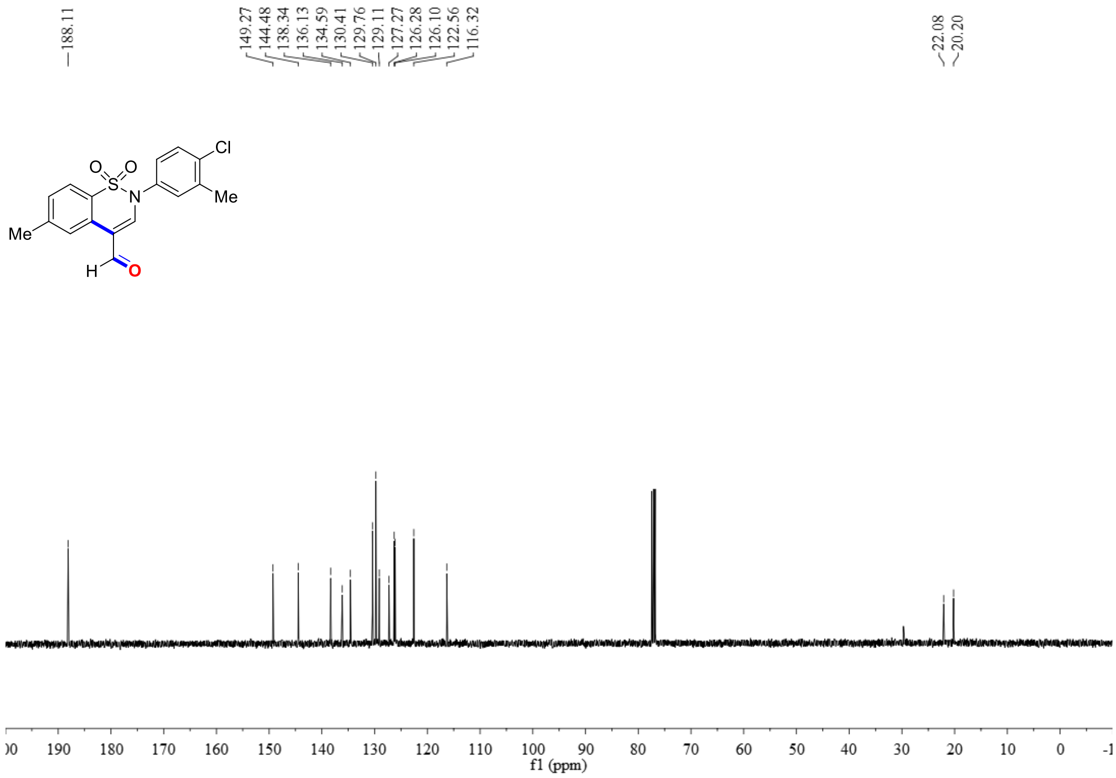
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **2j**



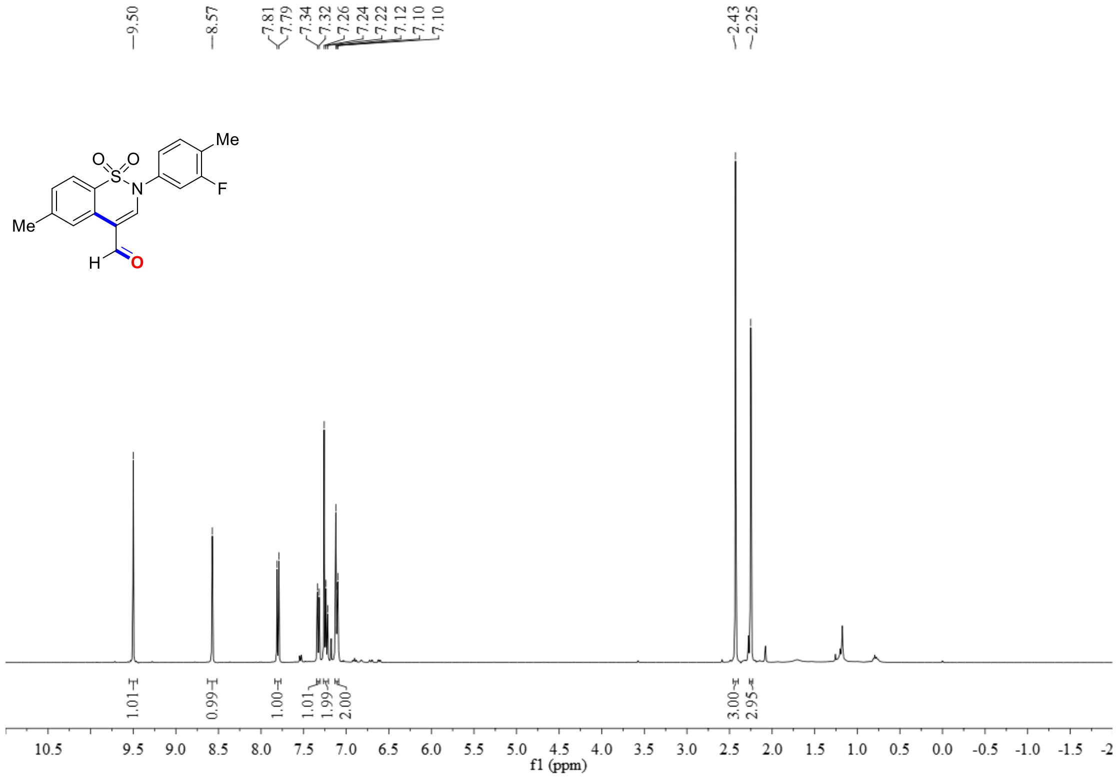
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **2k**



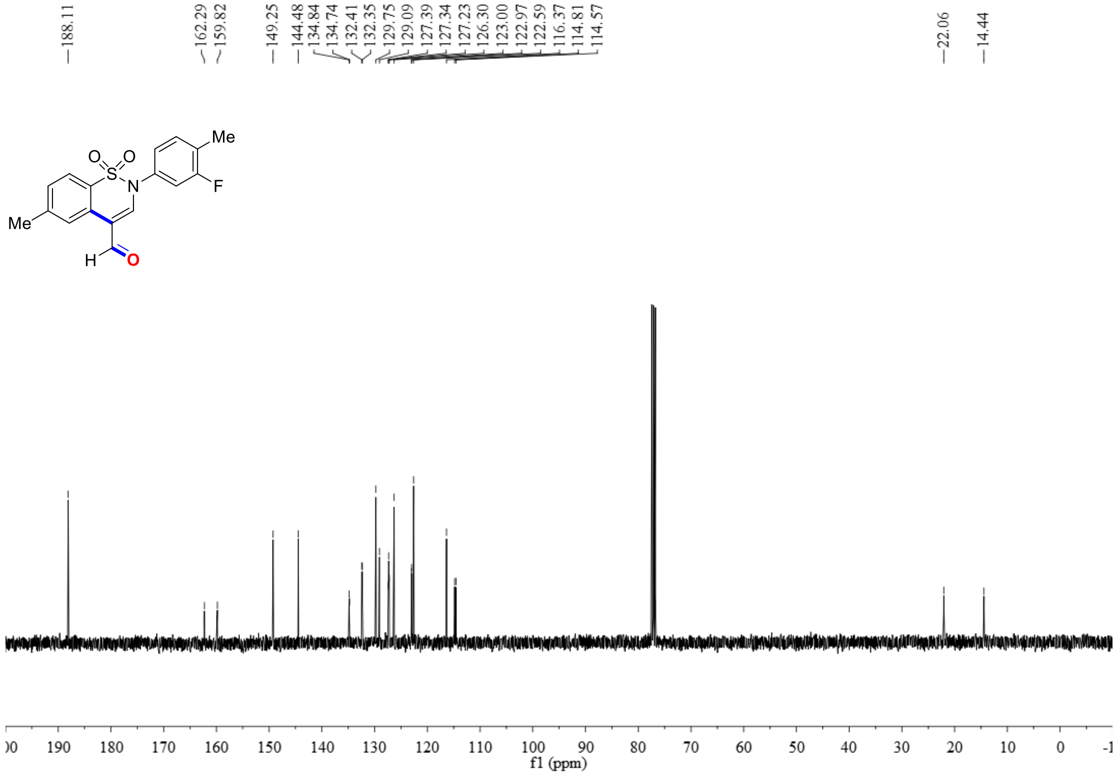
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **2k**



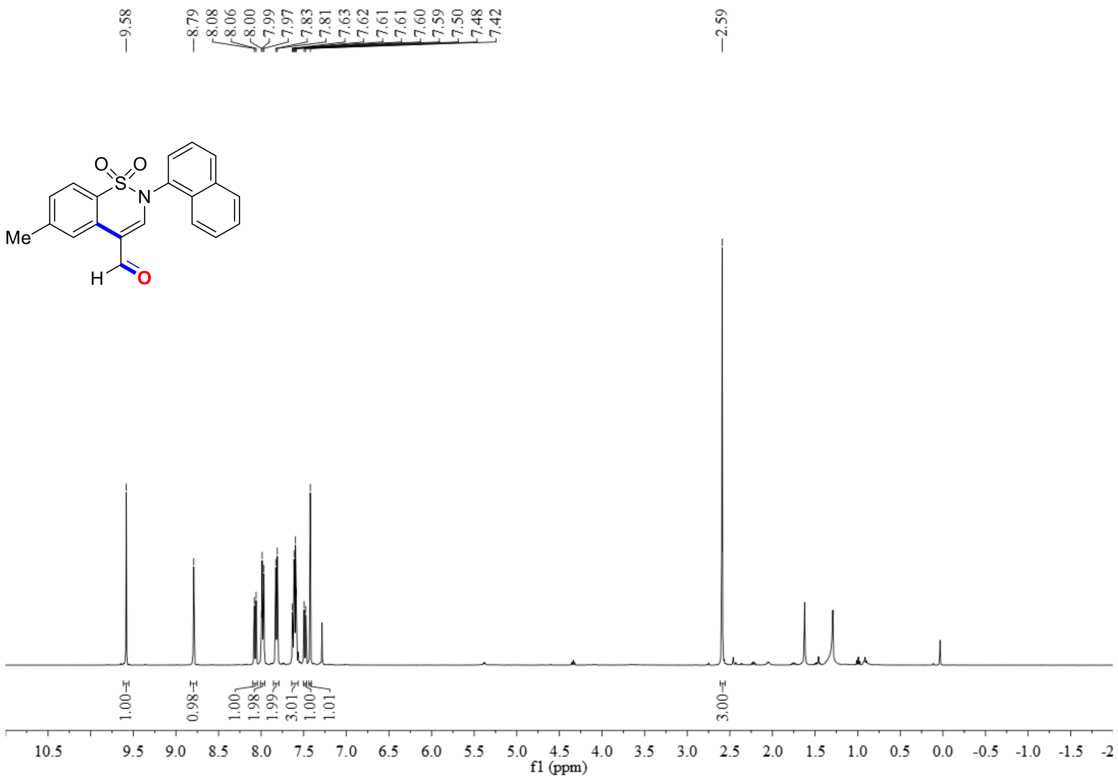
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2l**



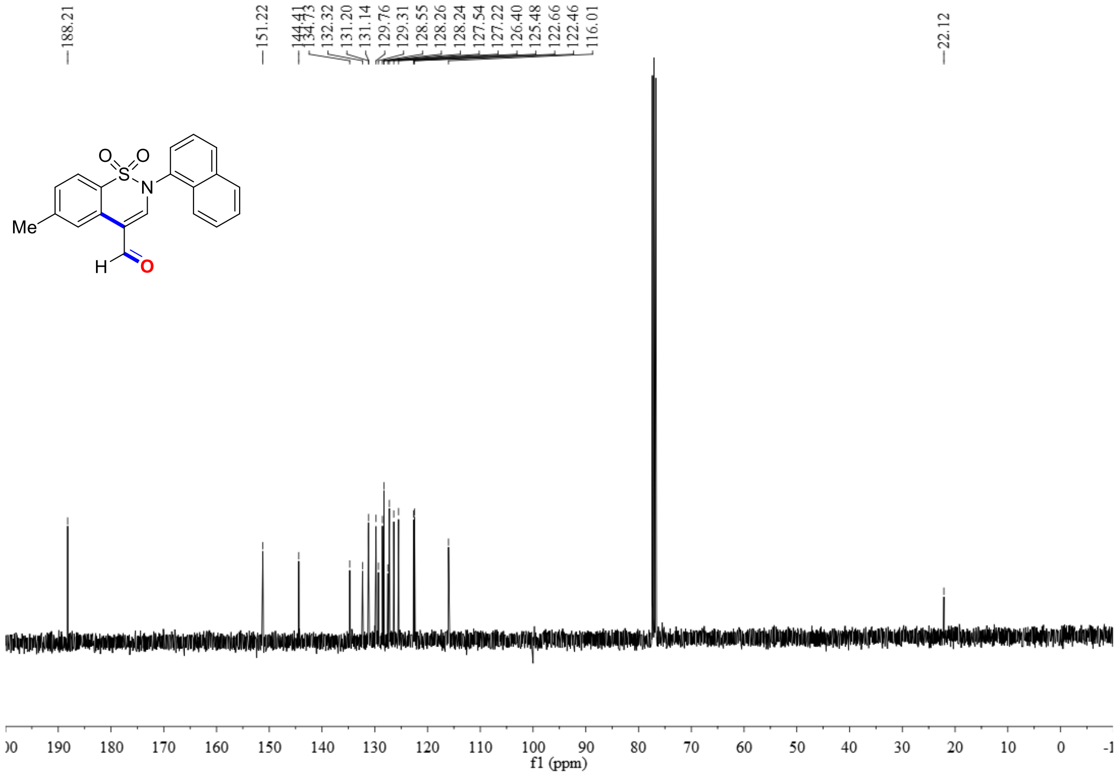
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2l**



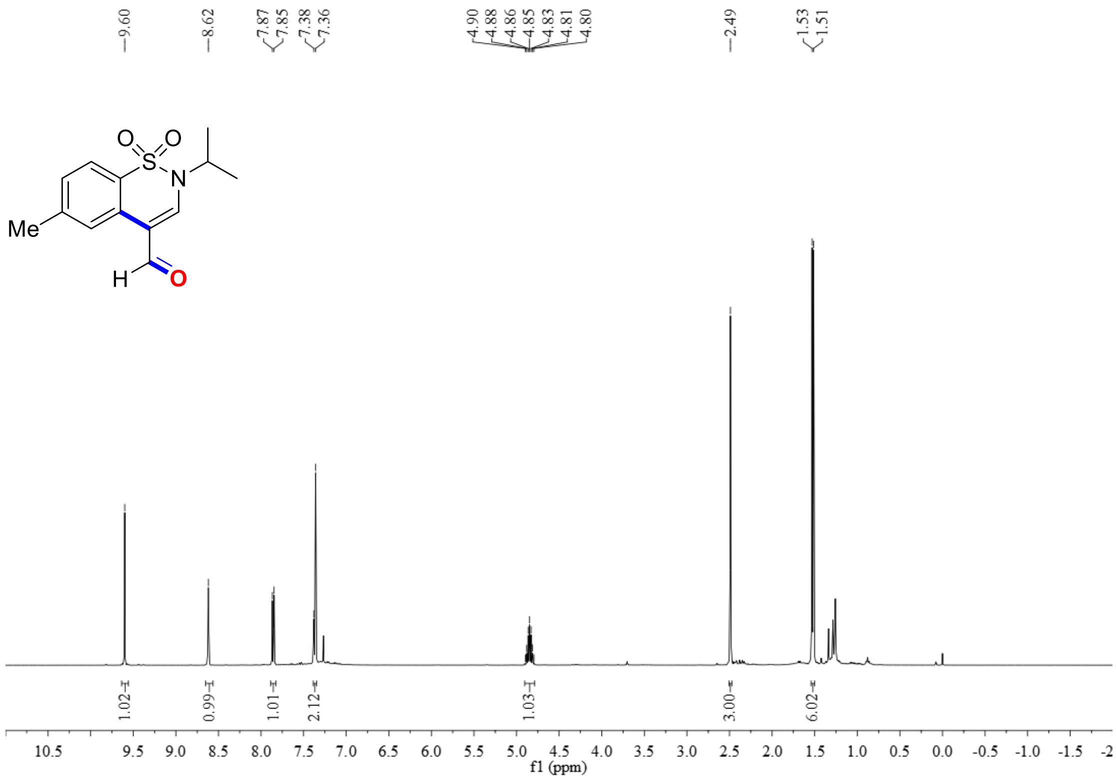
[1]H NMR spectrum (400 MHz, $CDCl_3$) of **2m**



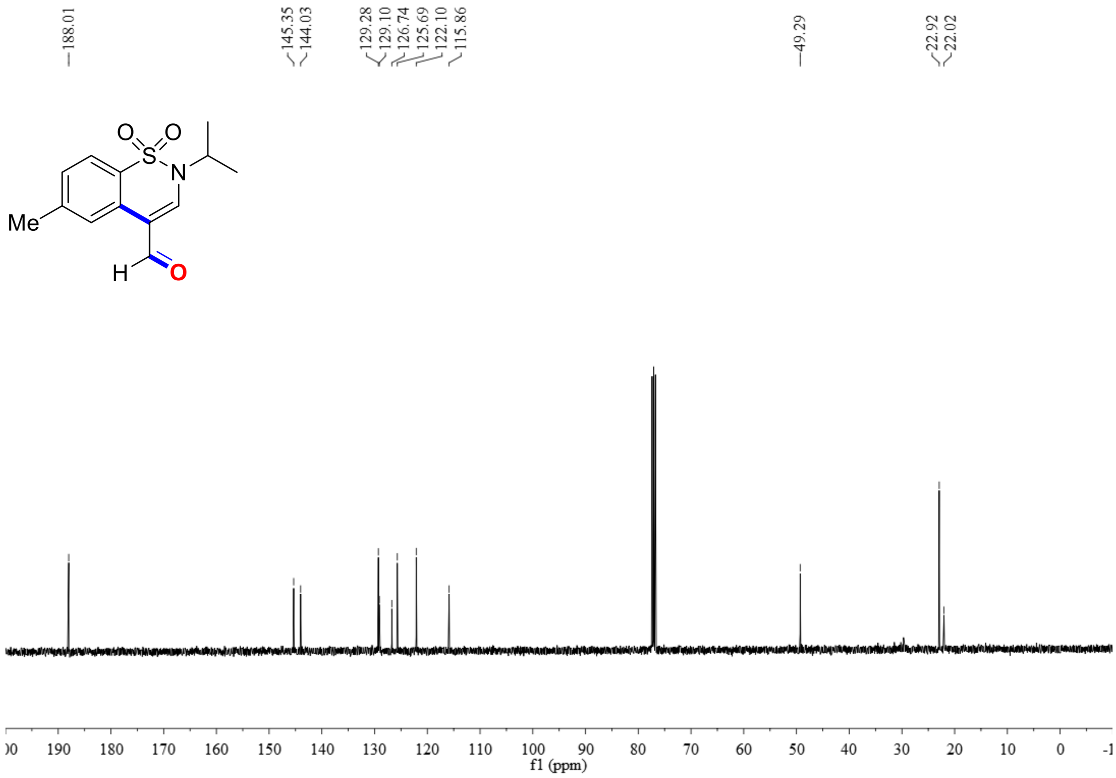
[13]C NMR spectrum (400 MHz, $CDCl_3$) of **2m**



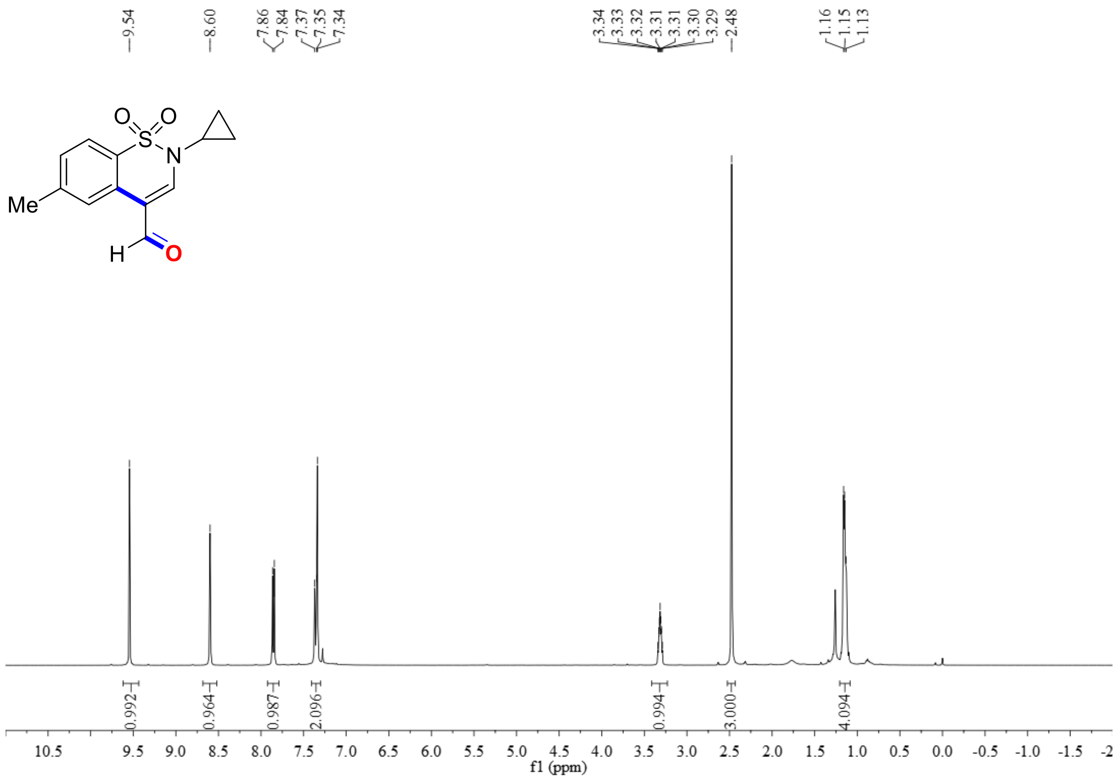
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2n**



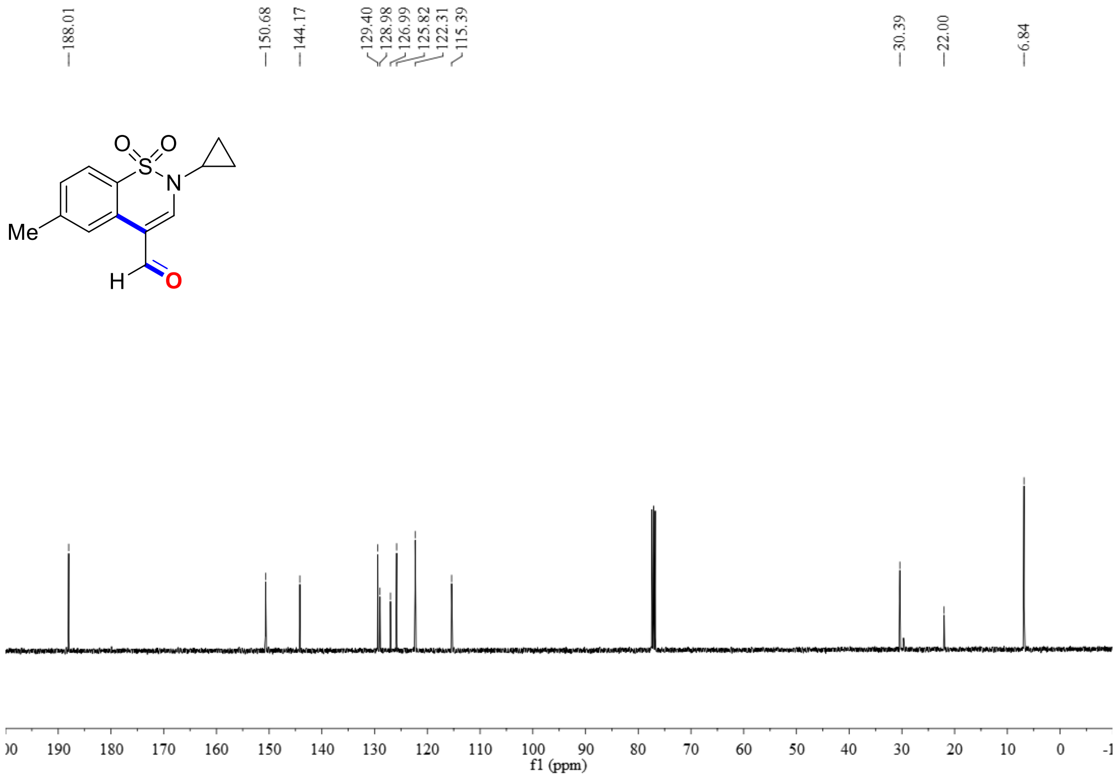
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2n**



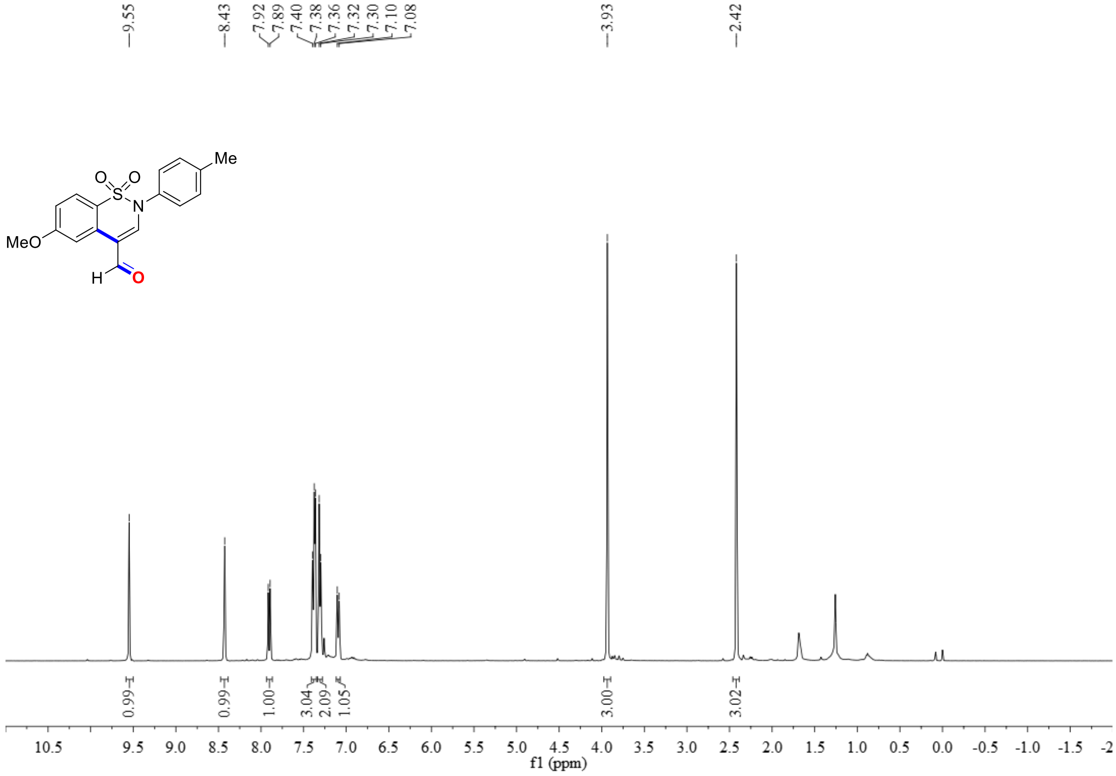
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2o**



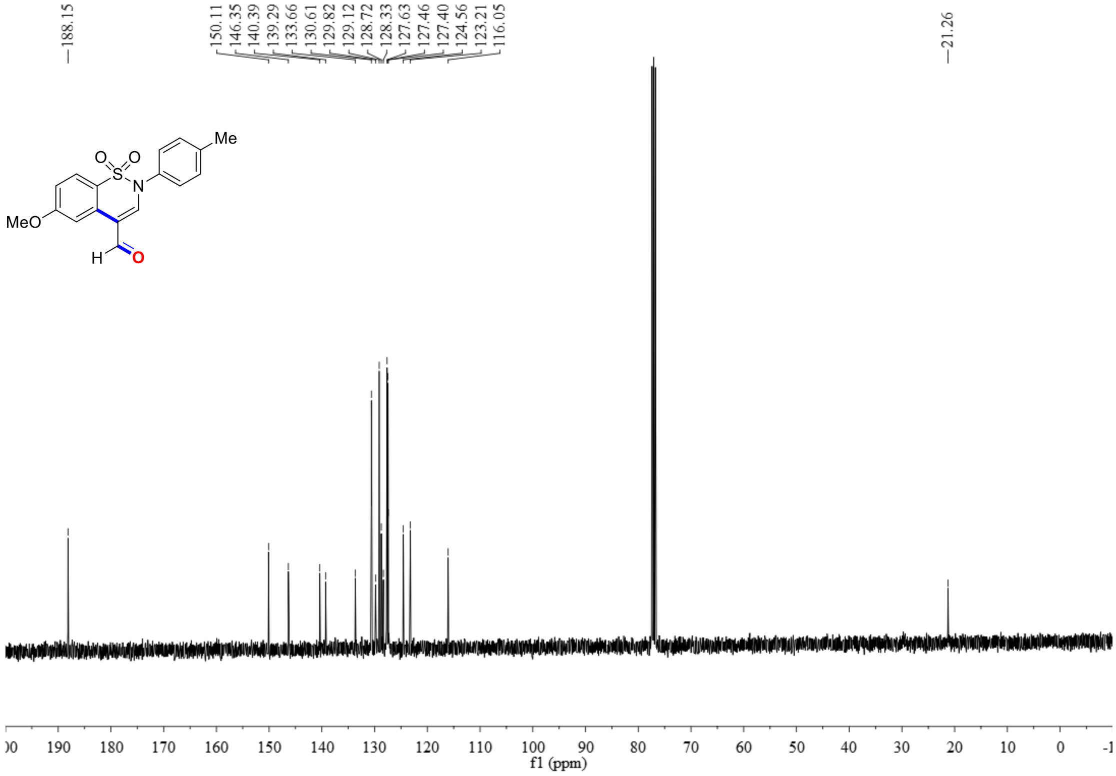
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2o**



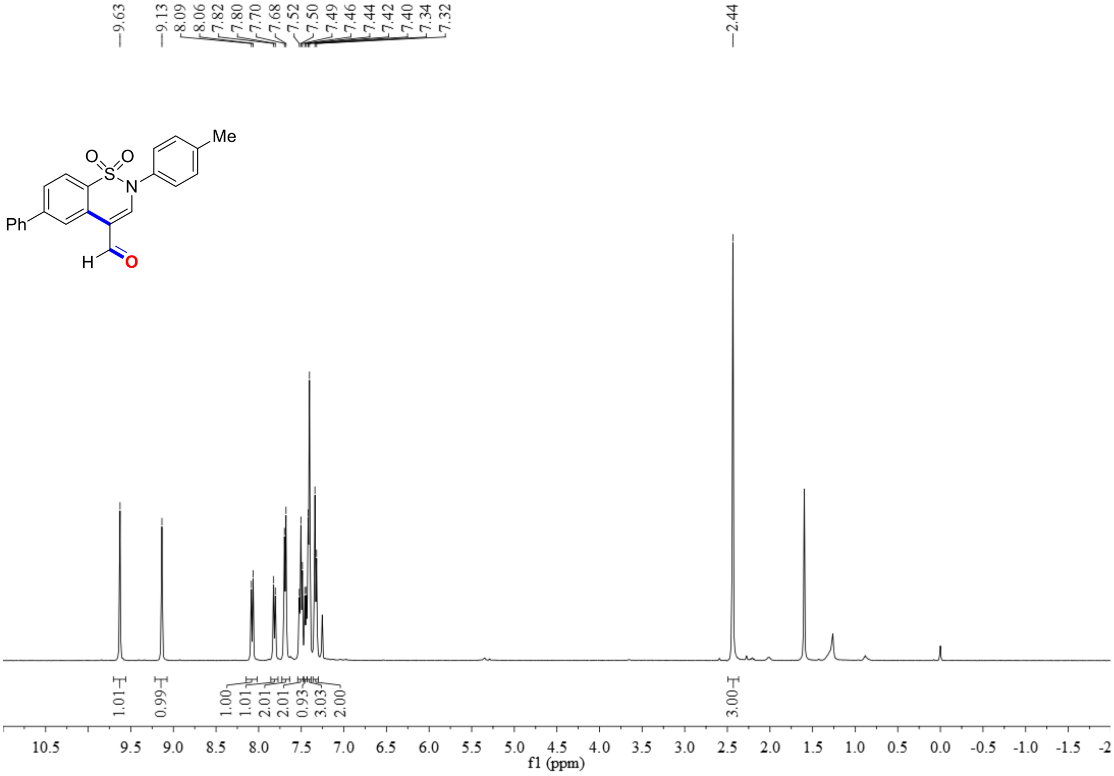
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2p**



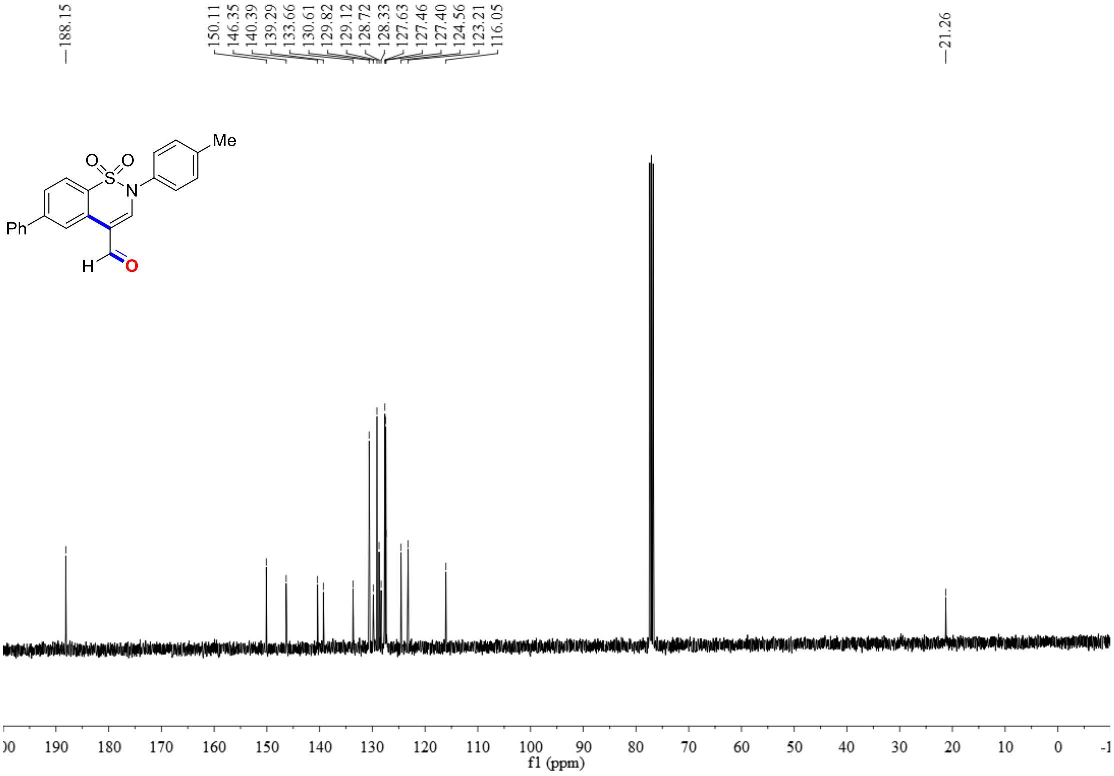
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2p**



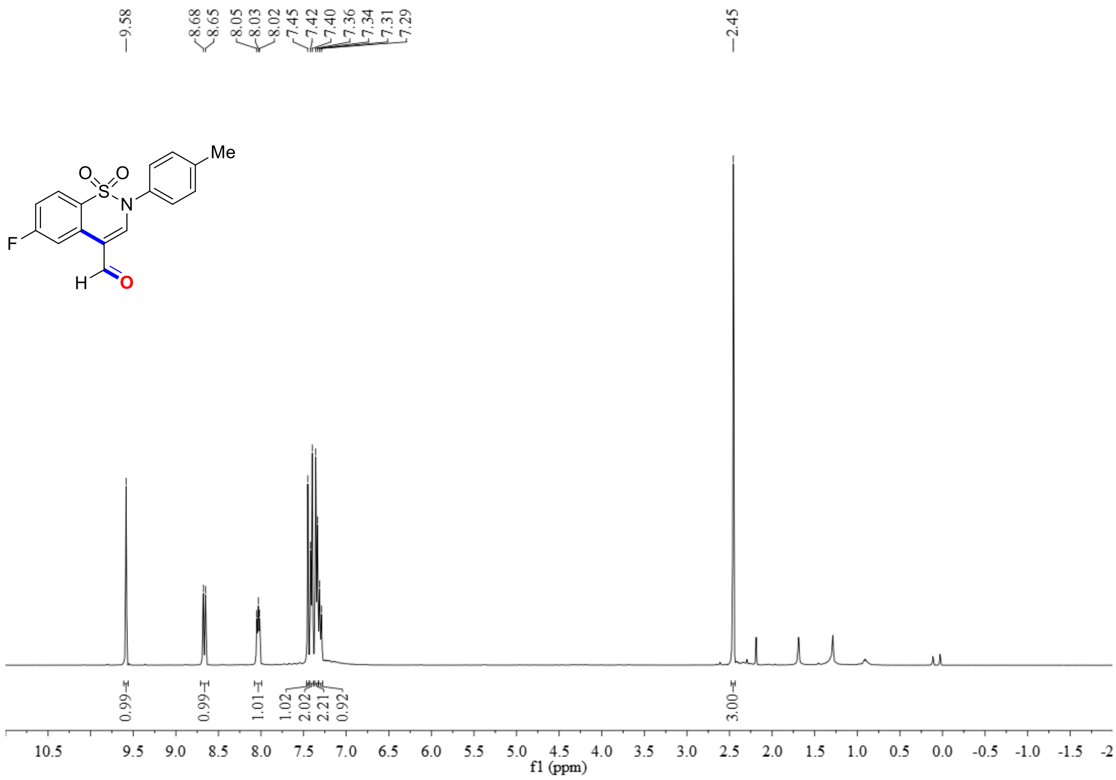
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2q**



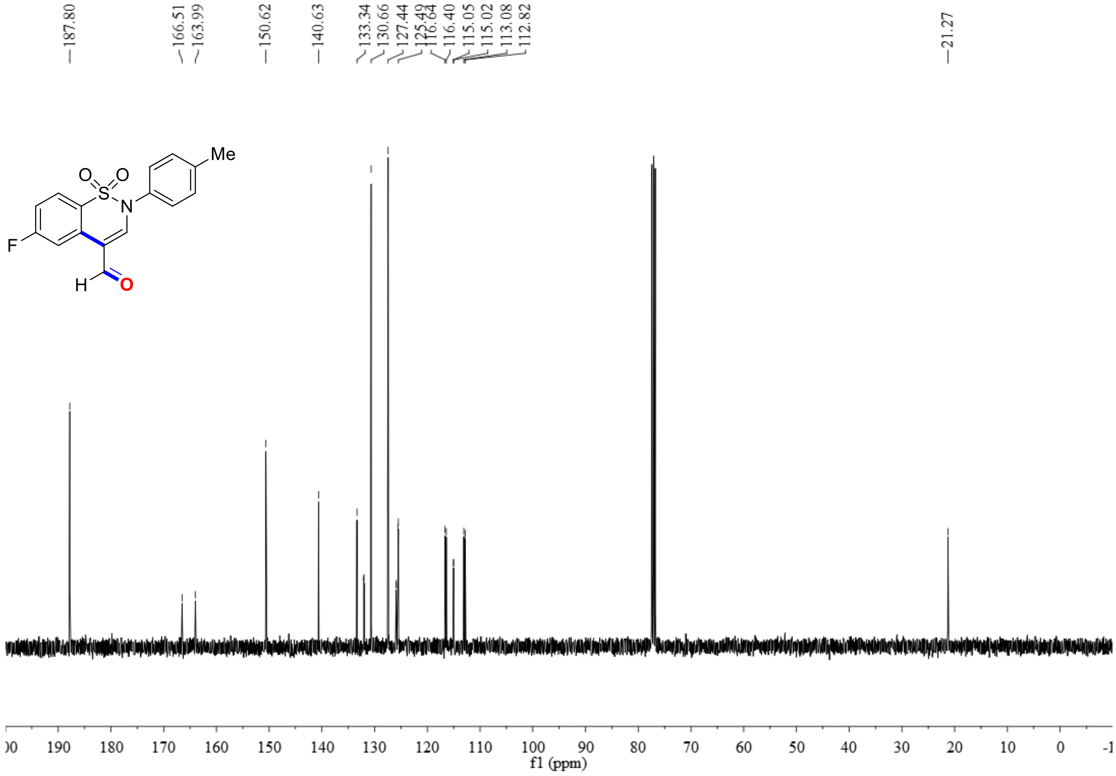
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2q**



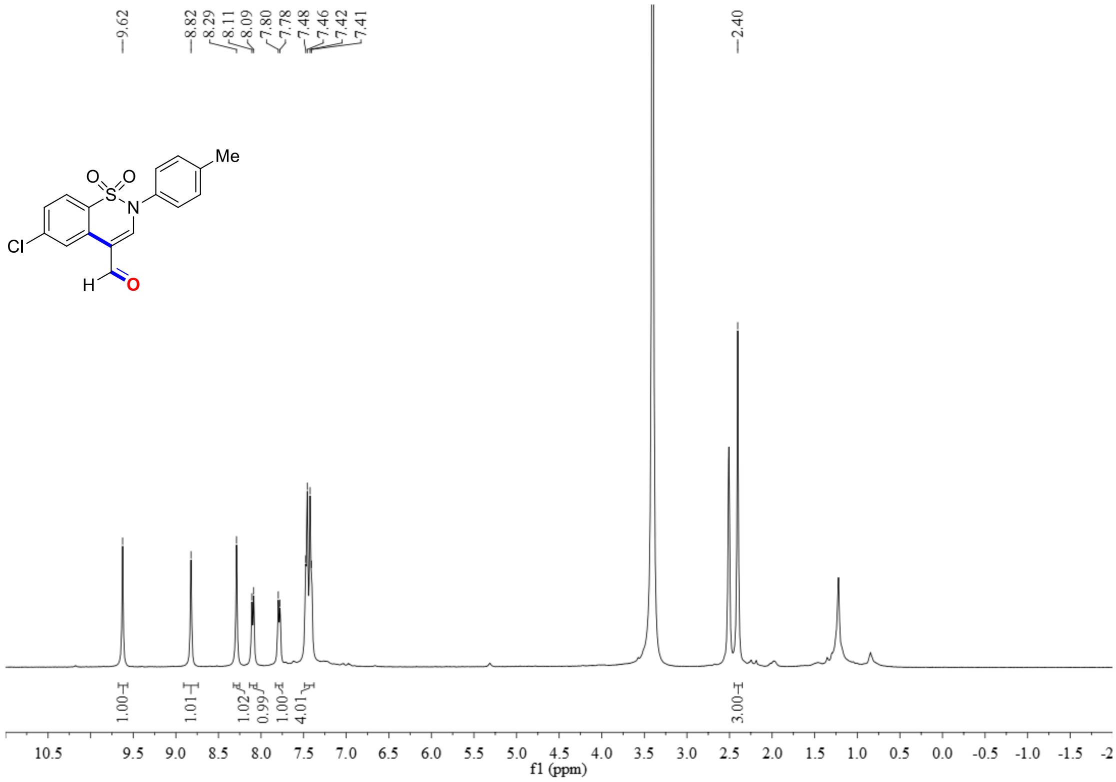
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2r**



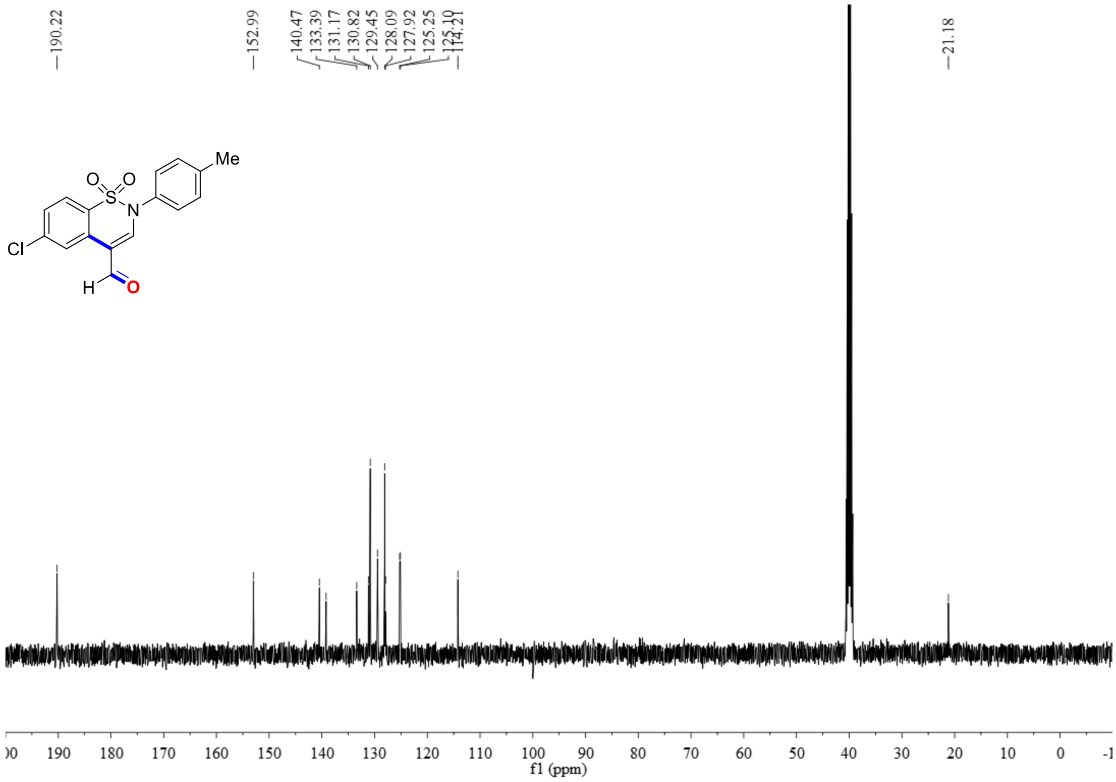
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2r**



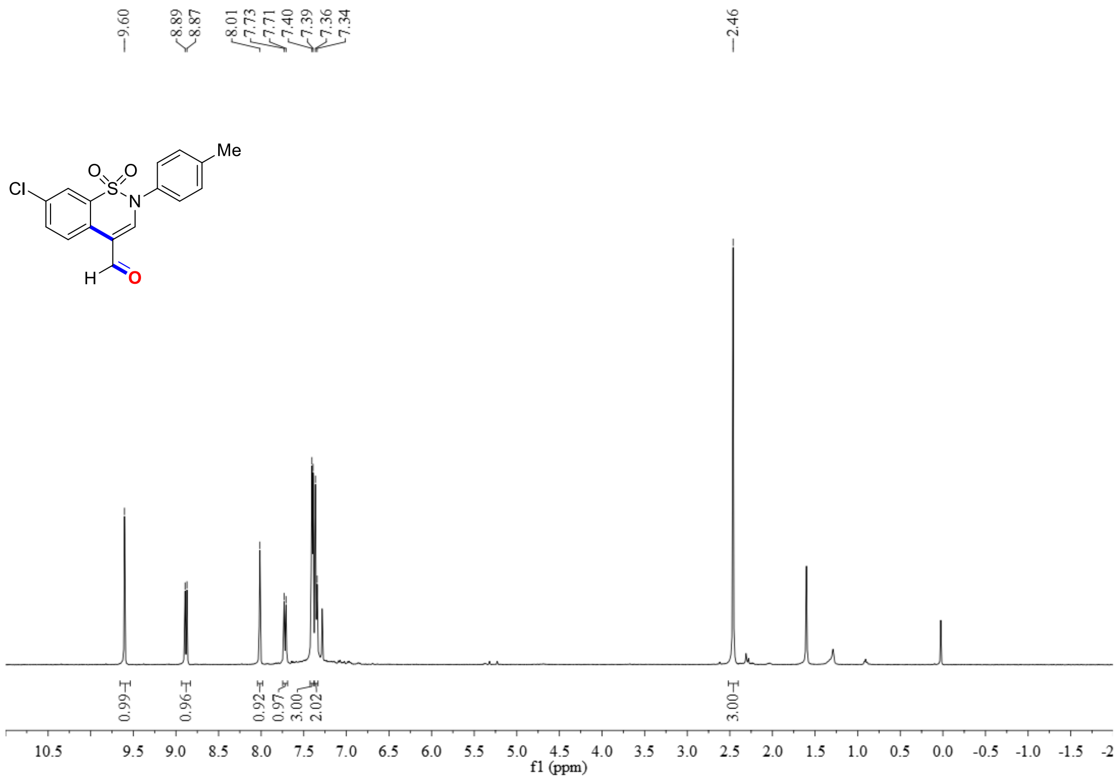
[1]H NMR spectrum (400 MHz, DMSO) of **2s**



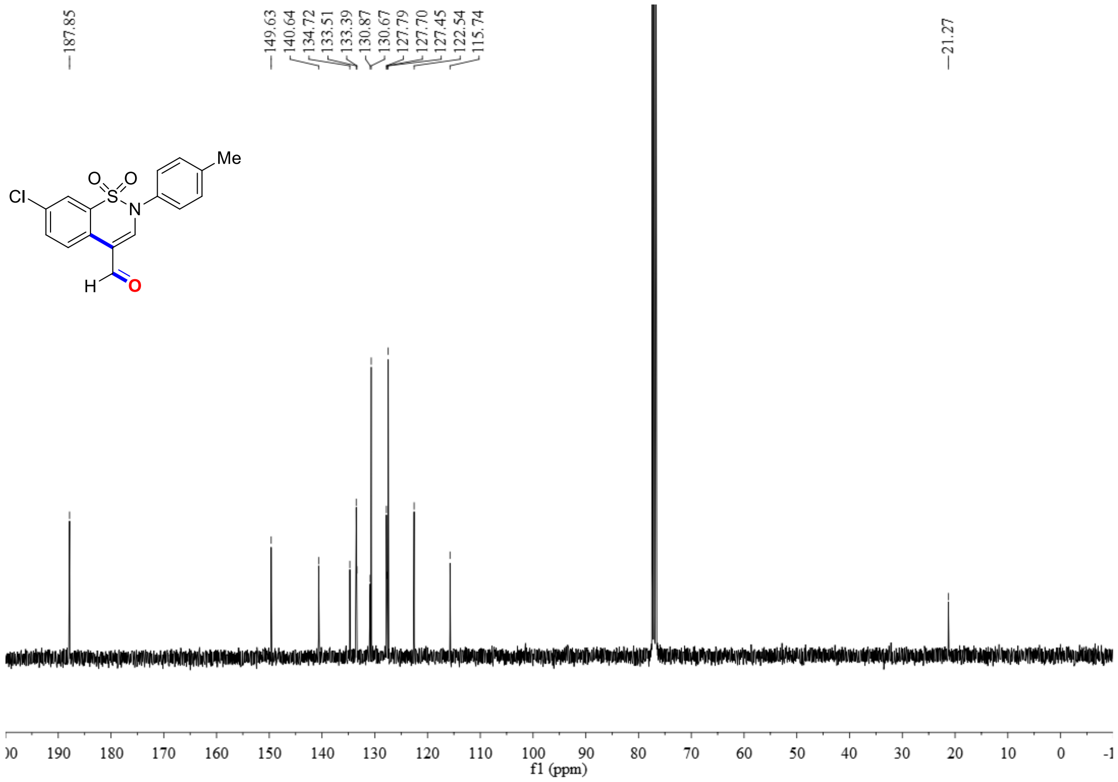
[13]C NMR spectrum (400 MHz, DMSO) of **2s**



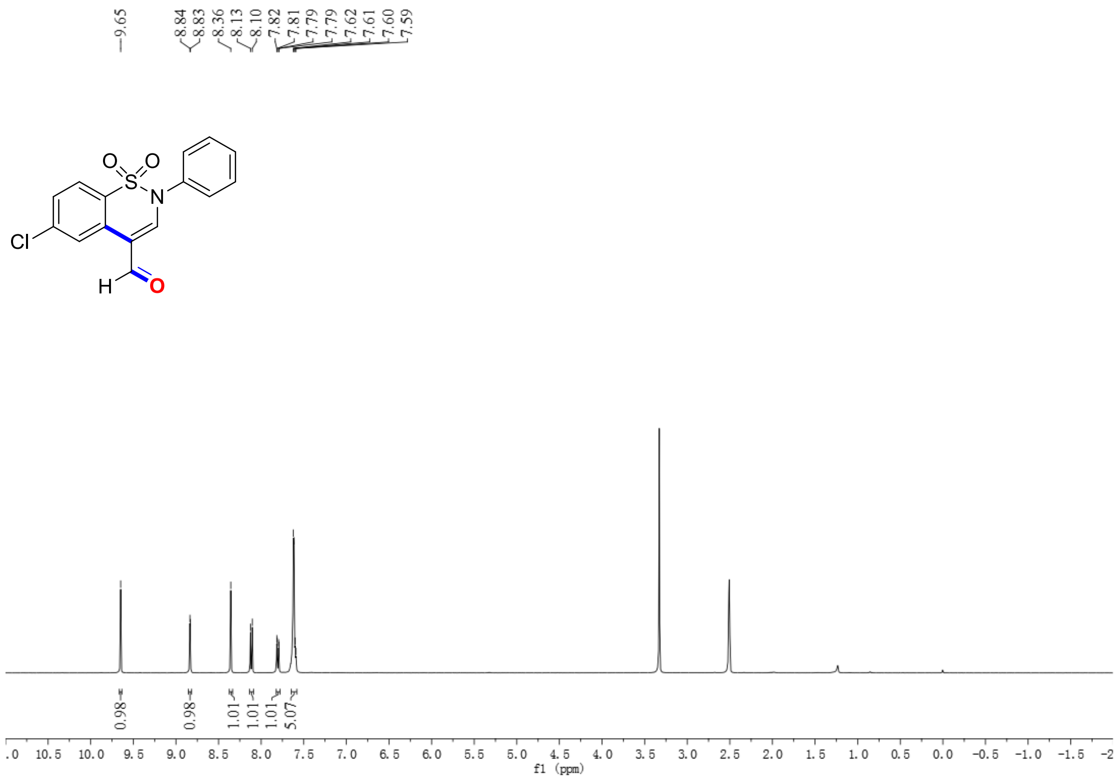
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2t**



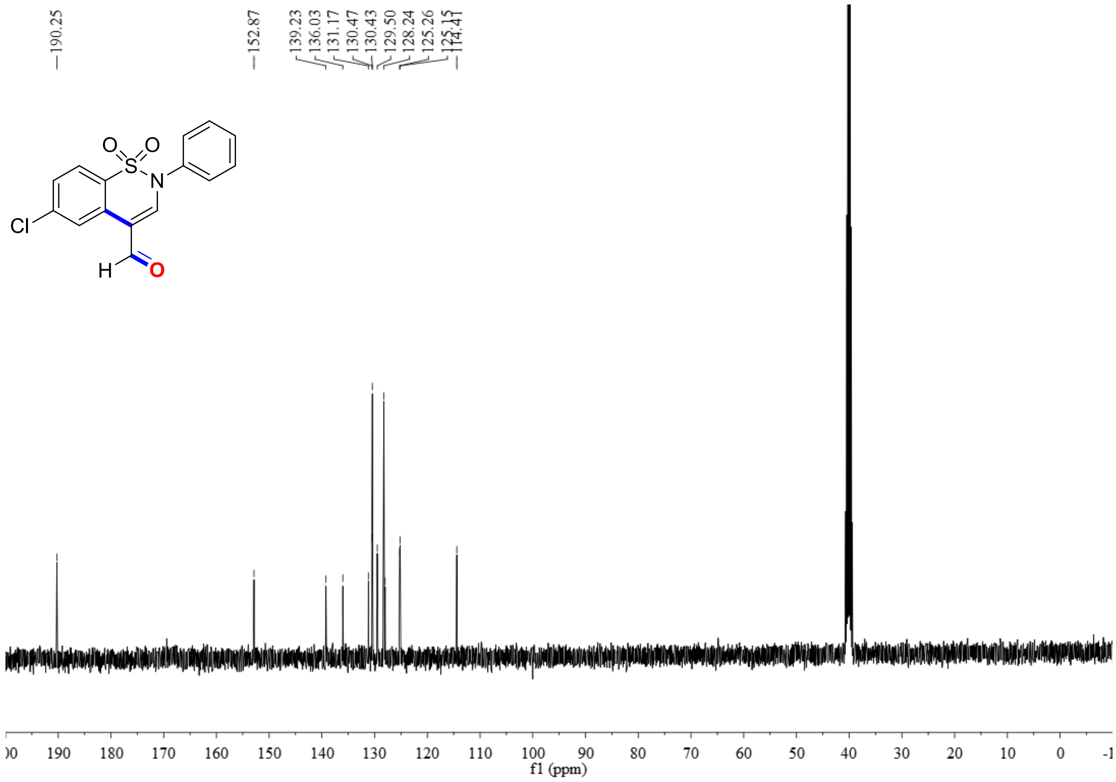
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2t**



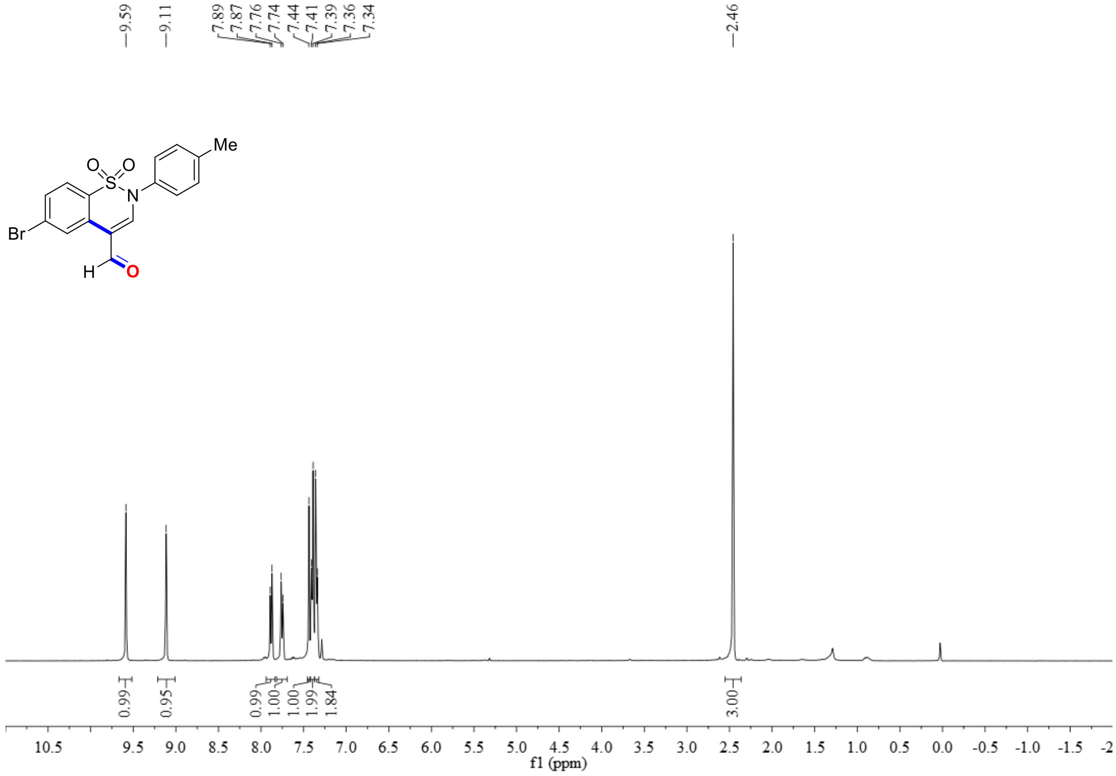
[1]H NMR spectrum (400 MHz, DMSO) of **2u**



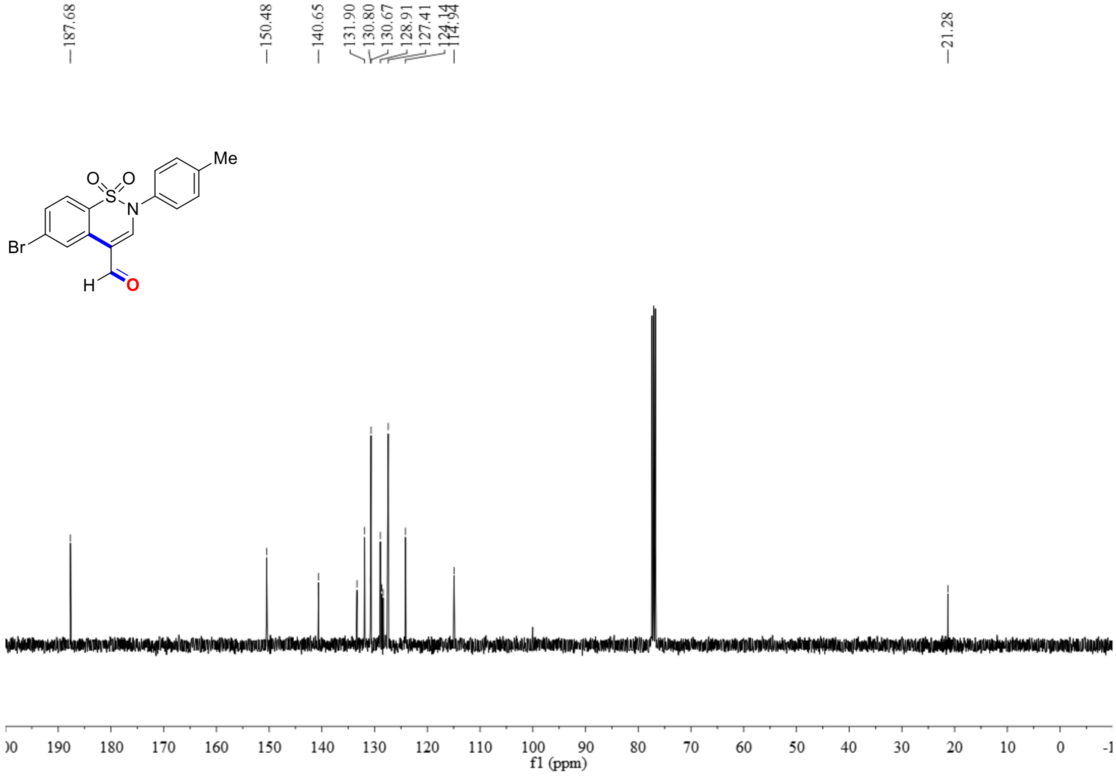
[13]C NMR spectrum (400 MHz, DMSO) of **2u**



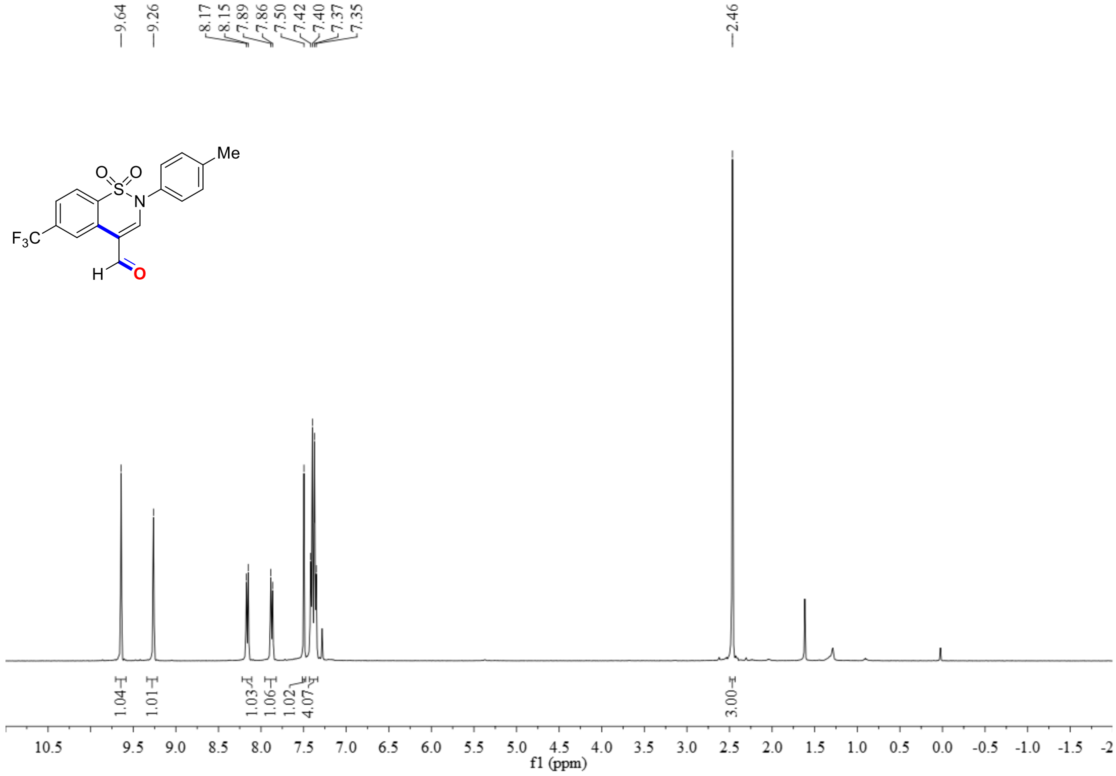
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2v**



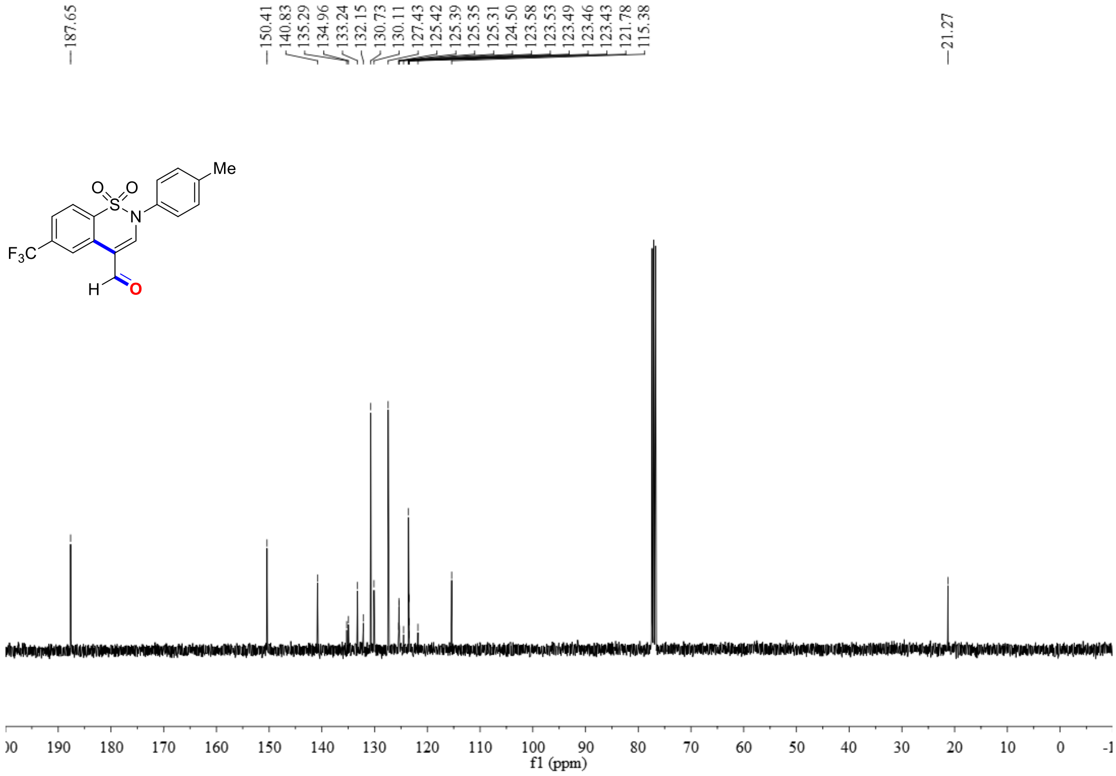
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2v**



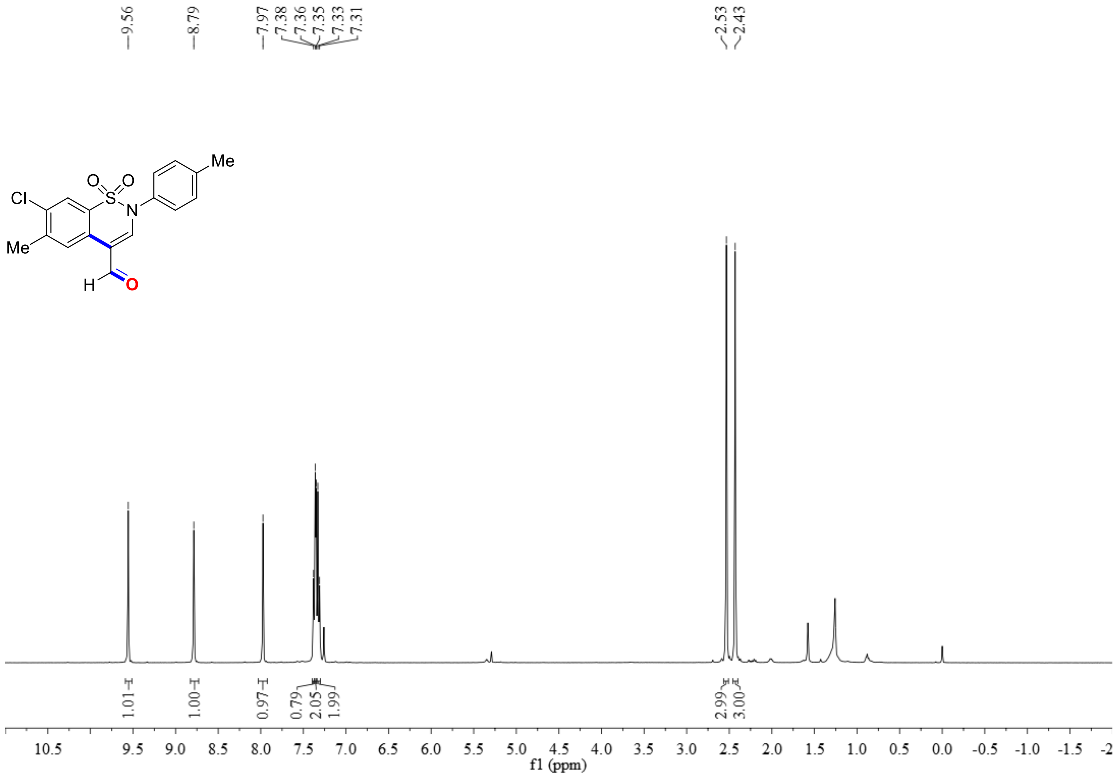
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2w**



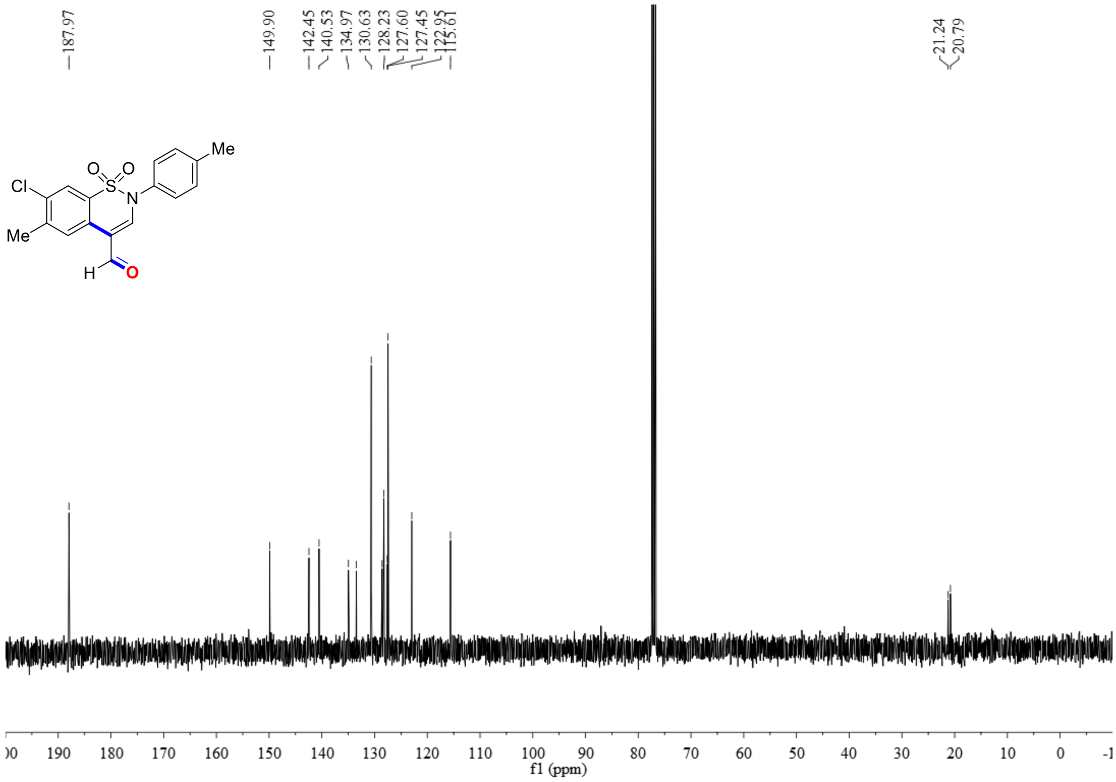
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2w**



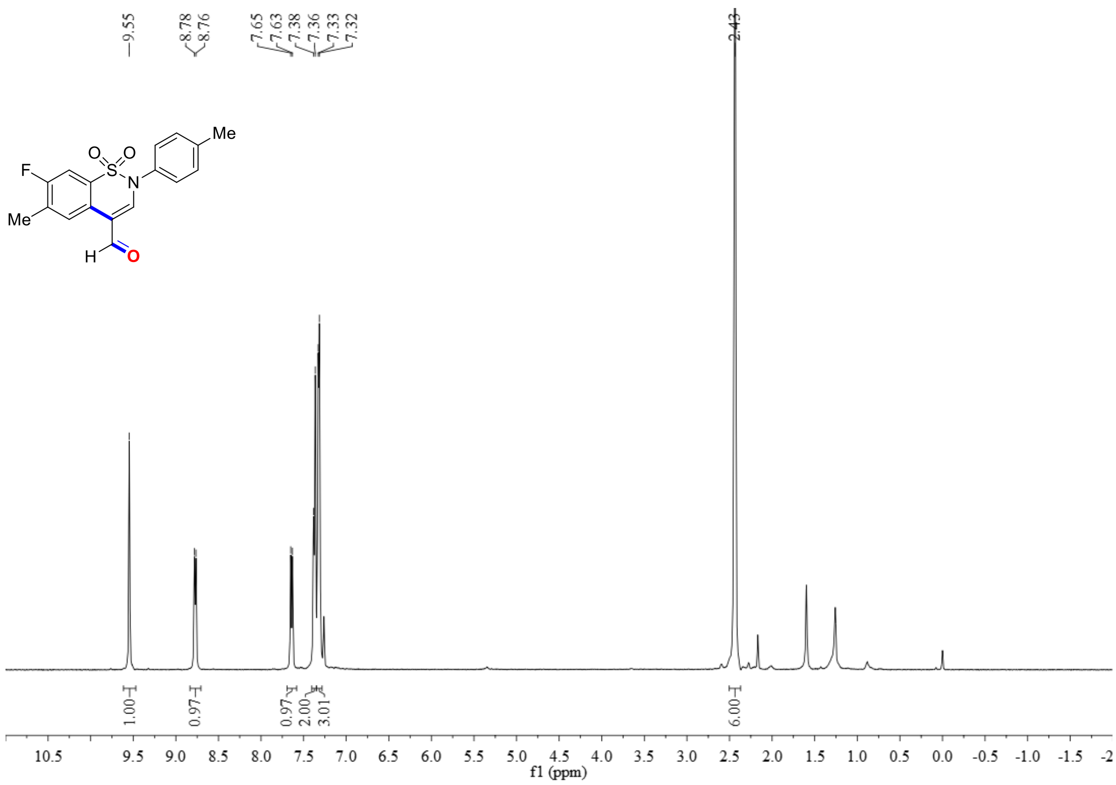
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2x**



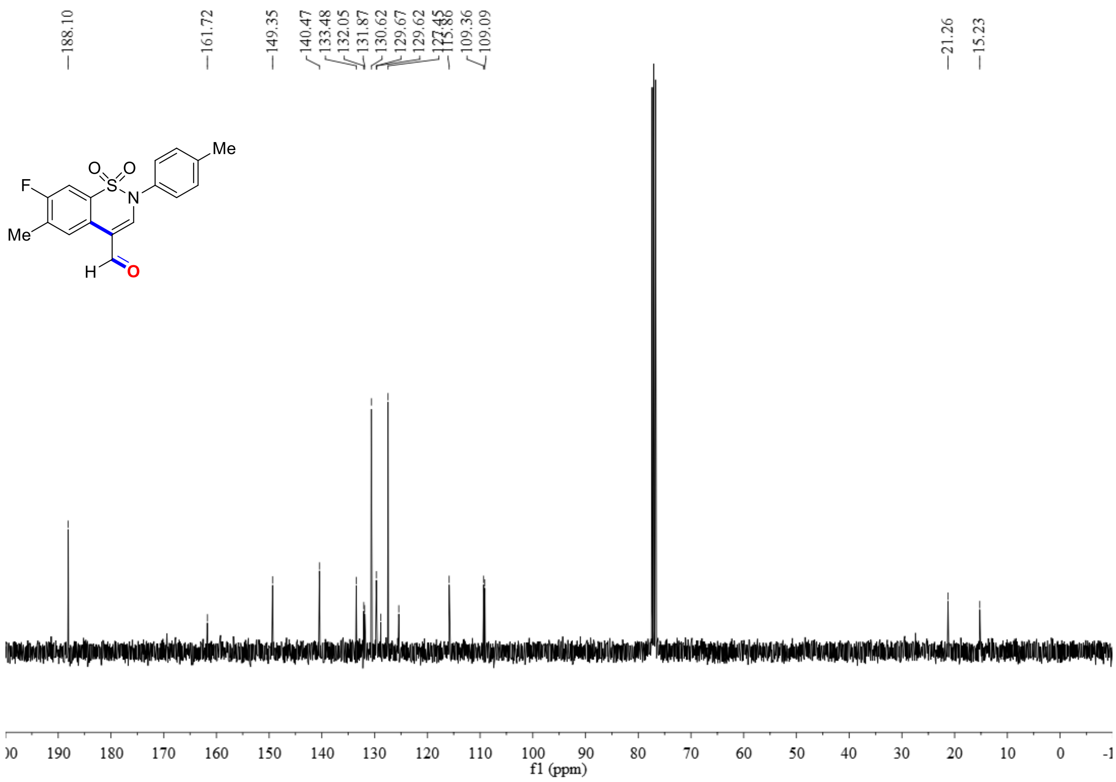
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2x**



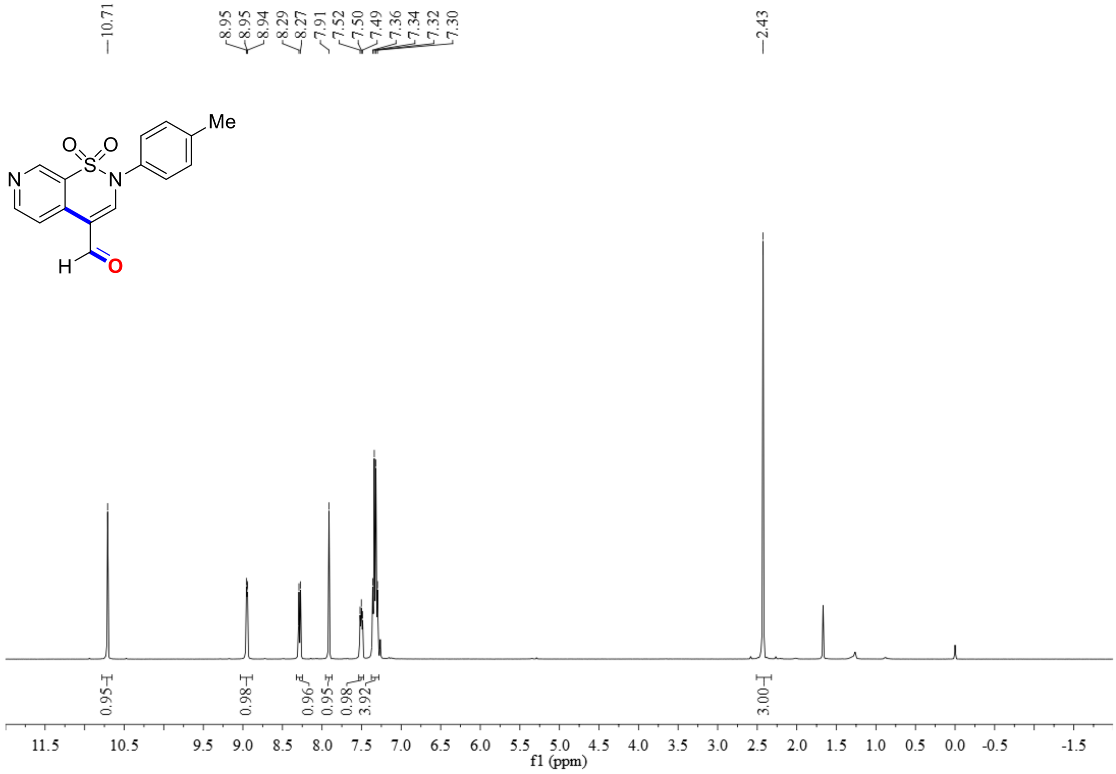
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2y**



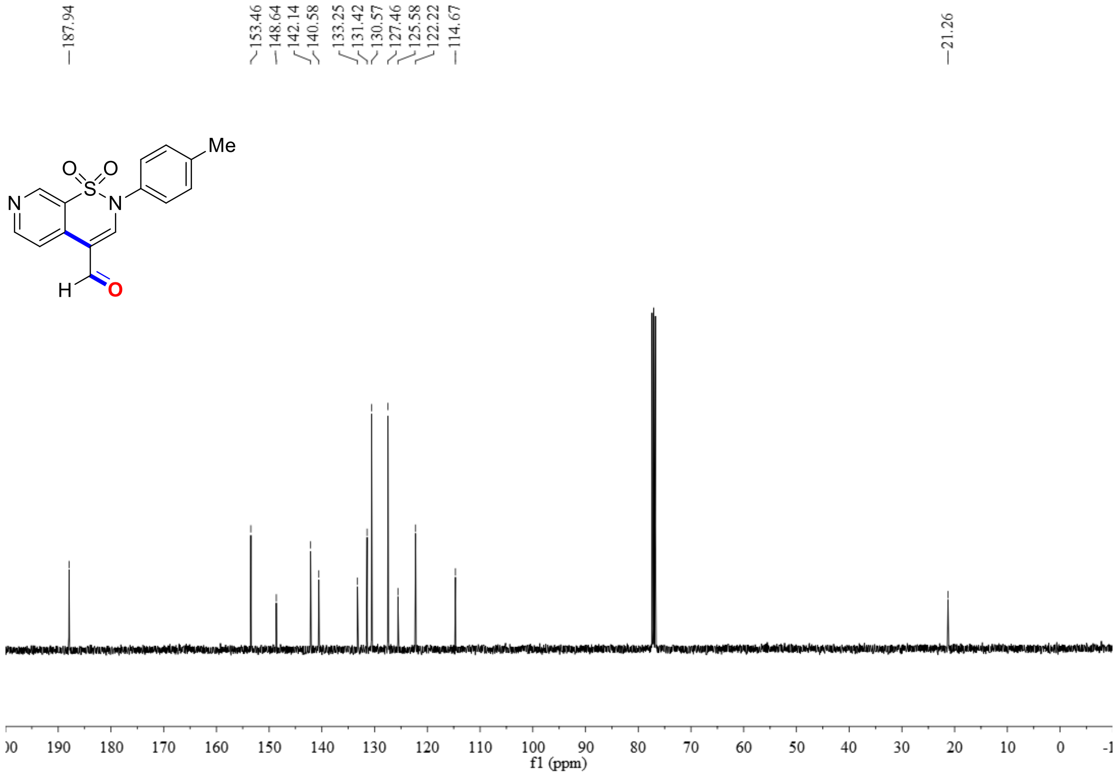
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2y**



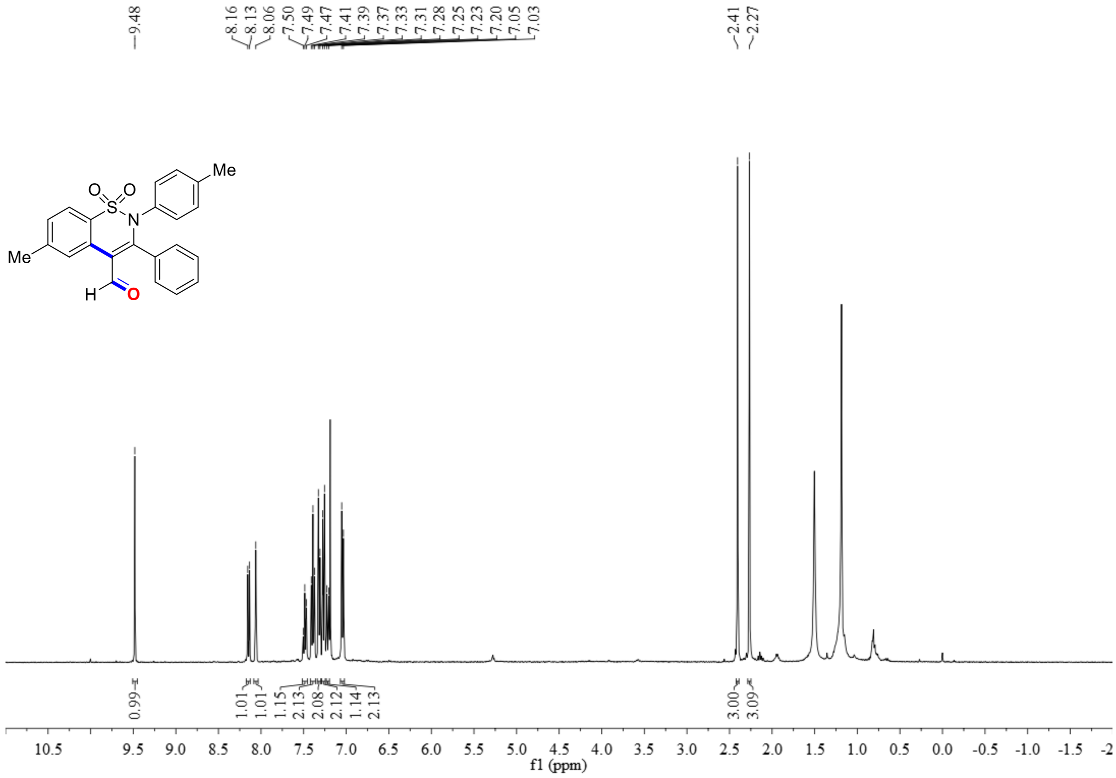
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2z**



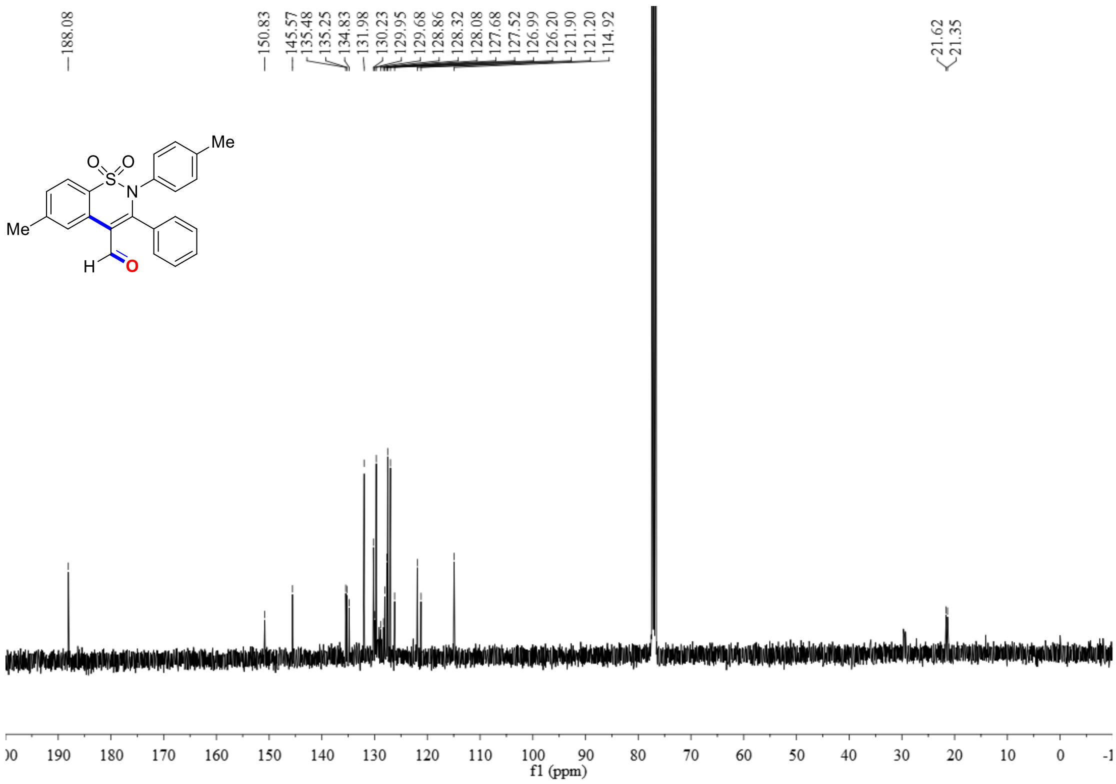
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2z**



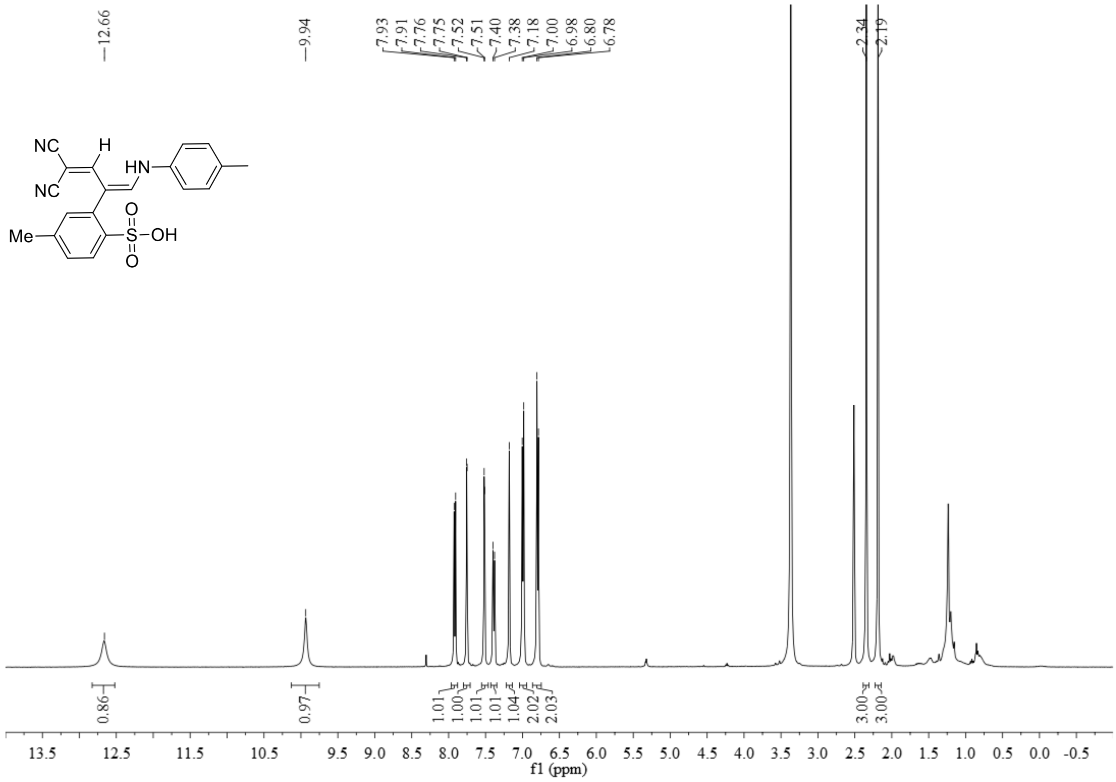
^1H NMR spectrum (400 MHz, $CDCl_3$) of **2-1z**



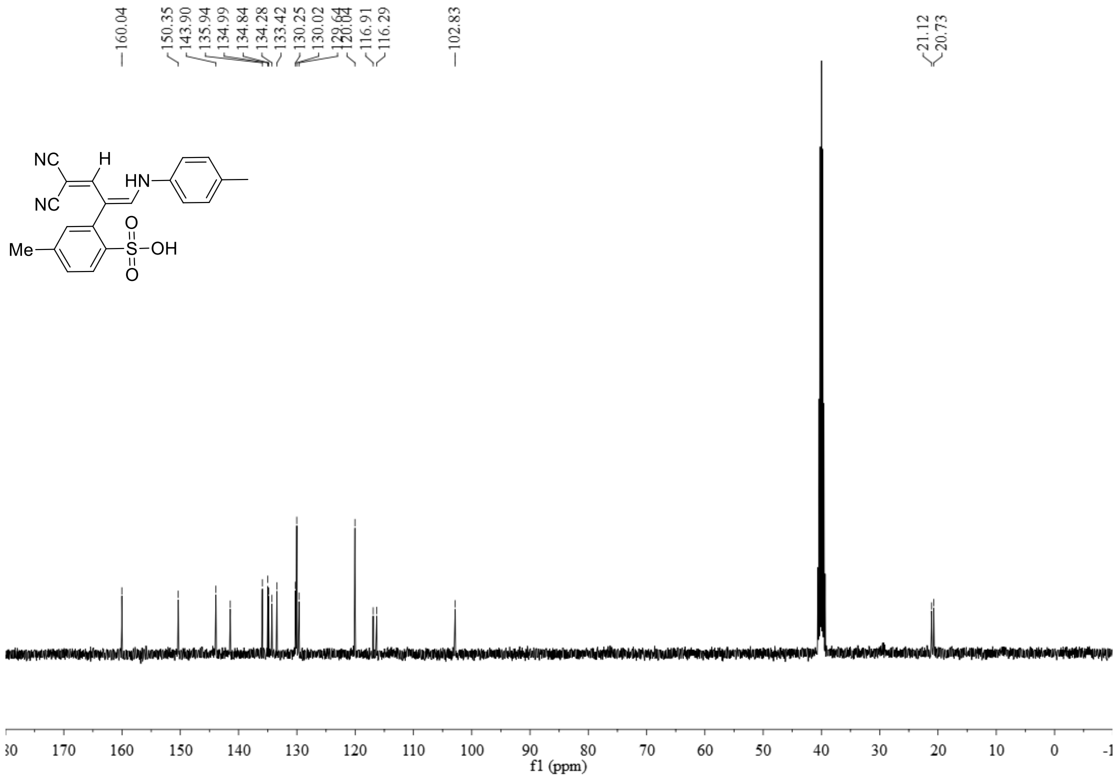
^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2-1z**



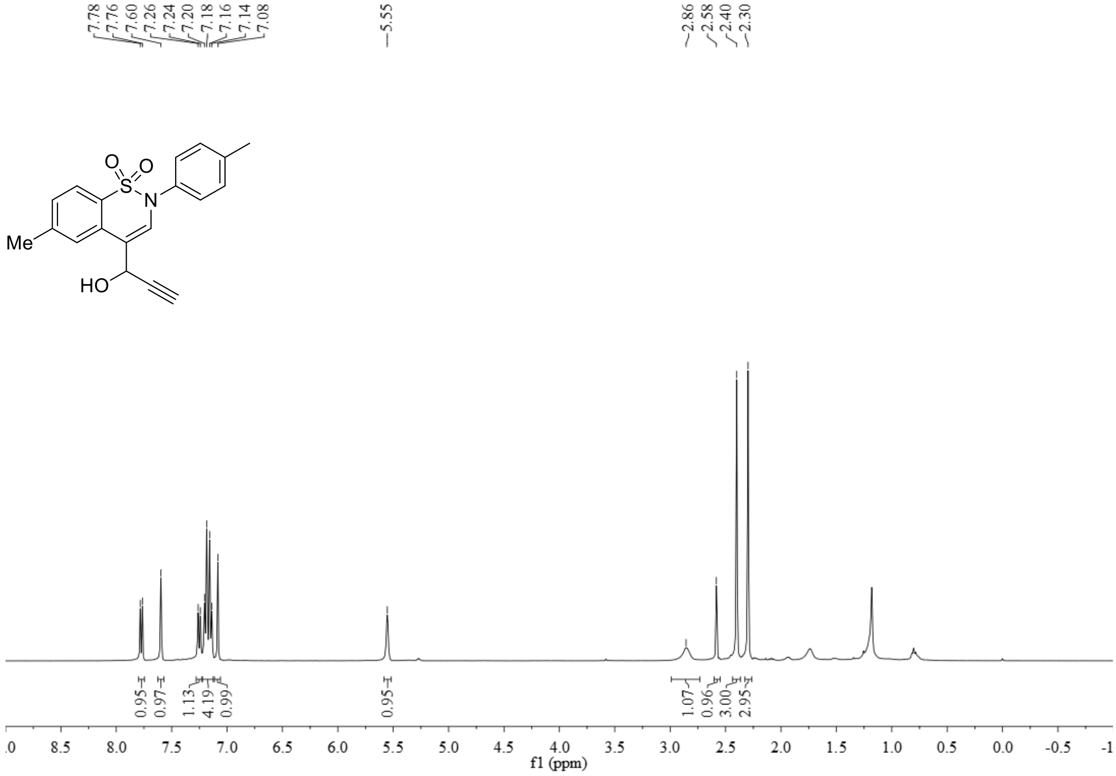
[1]H NMR spectrum (400 MHz, DMSO) of **3a**



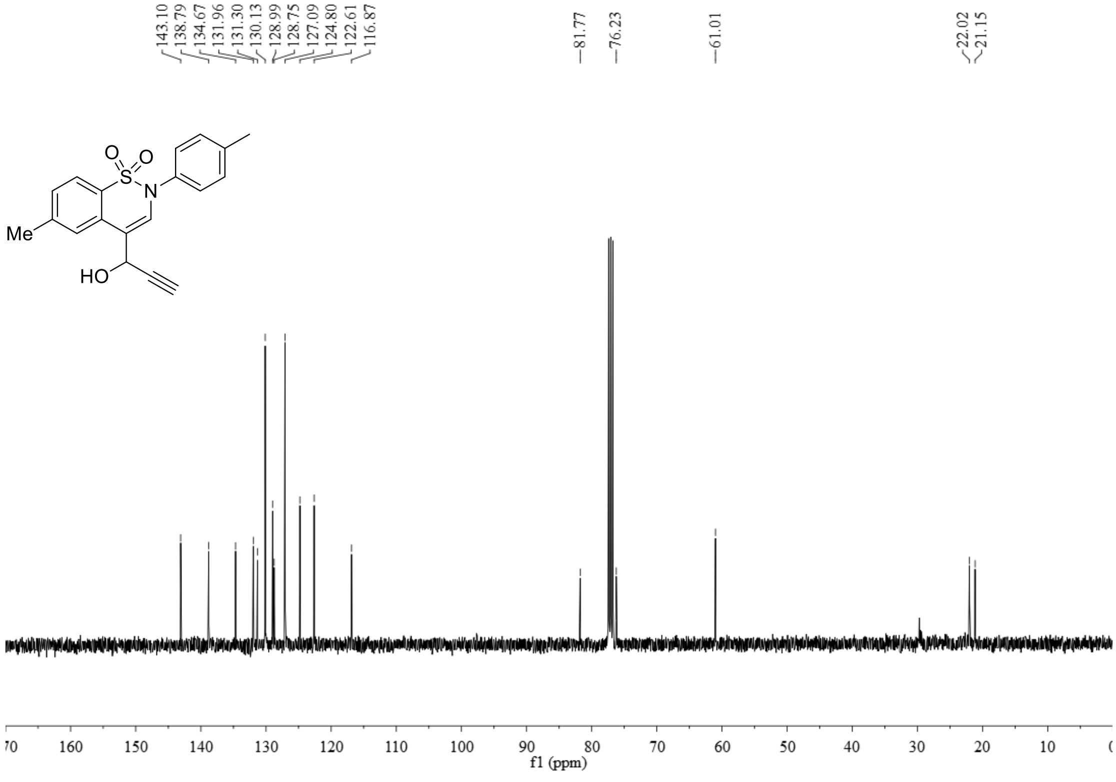
[13]C NMR spectrum (400 MHz, DMSO) of **3a**



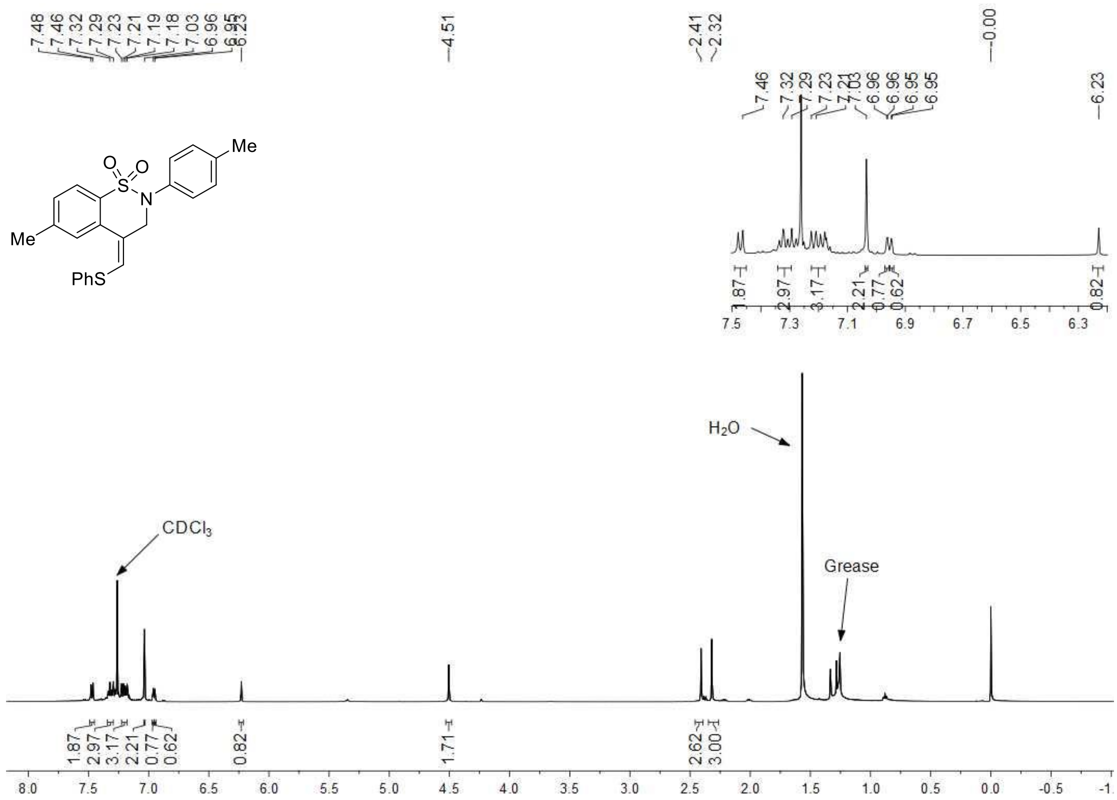
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **3b**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (*Z*)-**4a**



^{13}C NMR spectrum (500 MHz, $CDCl_3$) of (*Z*)-**4a**