Supporting Information for

Atom-economic Synthesis of β-Ketosulfones Based on Gold-catalyzed Highly Regioselective Hydration of Alkynylsulfones

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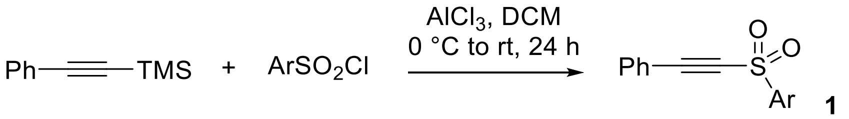
1 General Remarks

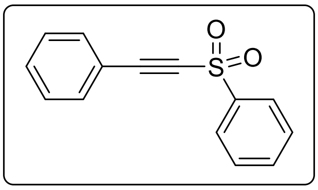
NMR spectra were recorded at ambient temperature with a Bruker Avance III 400 instrument at 400.13 MHz (^{1}H NMR) and 100.61 MHz (^{13}C NMR) in $CDCl_3$. Chemical shifts (δ) are given in ppm relative to resonances of the solvents (^{1}H: δ = 7.26 for residual $CHCl_3$ peak, δ = 2.50 for residual DMSO peak; ^{13}C: δ = 77.2 for $CDCl_3$, δ = 39.5 for DMSO-d_6). Mass-spectra were recorded on Bruker MicroTOF (ESI) and Bruker maXis HRMS-ESI-QTOF instruments. Chromatographic separation was carried out on Macherey–Nagel silica gel 60 M (0.04–0.063 mm). Analytical TLC was performed on unmodified Merck ready-to-use plates (TLC silica gel 60 F254); detection was achieved with a UV lamp. Melting points were measured with Stuart smp30 apparatus. Gold complexes were synthesized accordingly to our previously published protocols.[1] Known alkynylsulfones **1** were prepared by the literature procedures.[2–4] The solvents were purified using standard techniques and stored over activated 4 Å molecular sieves before use. Other reagents were purchased from commercial vendors and were used as received. For known compounds **1b**, **1e**, **1g–h**, **1l–m**, **2a–h**, **2j**, **2l–m**, **2z**, **2a–c**, **4**, **6**, **8**, **10**, **11**, **12** the ^{1}H and ^{13}C NMR spectra are consistent with previously reported literature.

2 Preparation of the Starting Materials

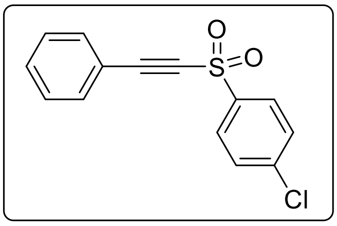
2.1. General Procedure for the Synthesis of Starting Alkynylsulfones 1 from Arylsulfonyl Chlorides



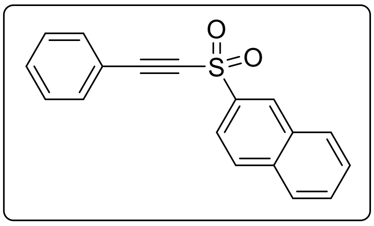
$AlCl_3$ (160 mg, 1.2 mmol, 1.2 equiv) was added to a solution of arylsulfonyl chloride (1.0 mmol) in DCM (5 mL) under argon atmosphere. The resulting mixture was stirred for 30 min and cooled to 0 °C. A solution of trimethyl(phenylethynyl)silane (209 mg, 1.2 mmol, 1.2 equiv) in DCM (5 mL) was then added dropwise. Upon completion, the reaction mixture was warmed to room temperature and stirred overnight. The reaction was carefully quenched with 10% HCl aqueous solution (30 ml) and extracted with DCM (2×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc to afford alkynylsulfone **1**.



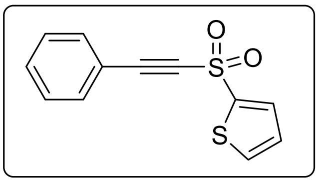
((Phenylethynyl)sulfonyl)benzene[2] (**1b**): brown solid (102 mg, 42%); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–8.05 (m, 2H, Ar), 7.68 (t, J = 7.4 Hz, 1H, Ar), 7.59 (t, J = 7.6 Hz, 2H, Ar), 7.53–7.43 (m, 3H, Ar), 7.35 (t, J = 7.6 Hz, 2H, Ar); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 134.3, 132.7, 131.7, 129.5, 128.7, 127.4, 117.8, 93.6, 85.4; **HRMS** (ESI): m/z [M + Na]$^+$ calcd. for $C_{14}H_{10}NaO_2S^+$: 265.0294; found: 265.0286.



1-Chloro-4-((phenylethynyl)sulfonyl)benzene[2] (**1e**): colorless solid (122 mg, 44%); R_f 0.45 (hexane/EtOAc 4:1); R_f 0.45 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.7 Hz, 2H, Ar), 7.57 (d, J = 8.7 Hz, 2H, Ar), 7.54–7.46 (m, 3H, Ar), 7.38 (t, J = 7.6 Hz, 2H, Ar); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.1, 140.4, 132.9, 131.9, 129.9, 129.0, 128.9, 117.7, 94.1, 85.2; **HRMS** (ESI): m/z [M + Na]$^+$ calcd. for $C_{14}H_9ClNaO_2S^+$: 298.9904; found: 298.9907.

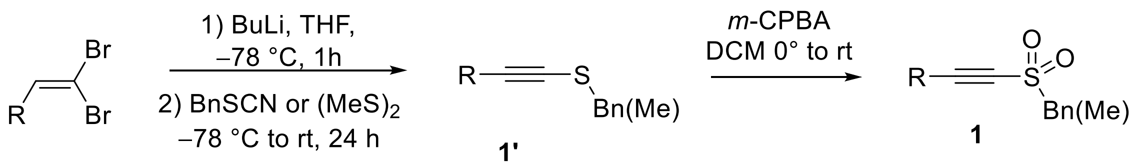


2-((Phenylethynyl)sulfonyl)naphthalene[5] (**1g**): brown solid (135 mg, 46%); R_f 0.30 (hexane/EtOAc 4:1); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (s, 1H, Ar), 8.09–8.00 (m, 3H, Ar), 7.94 (d, J = 8.4 Hz, 1H, Ar), 7.72–7.61 (m, 2H, Ar), 7.53–7.50 (m, 2H, Ar), 7.45 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H, Ar); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 138.7, 135.6, 132.8, 132.2, 131.7, 129.9, 129.7, 129.7, 129.3, 128.8, 128.1, 128.0, 122.2, 118.0, 93.8, 85.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{18}H_{12}NaO_2S^+$: 315.0450; found: 315.0453.



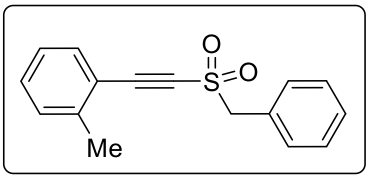
2-((Phenylethynyl)sulfonyl)thiophene (**1v**): brown solid 84.3 mg, 34%); mp 75.0–77.0 °C (hexane/EtOAc); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.89 (dd, *J* = 3.8, 1.4 Hz, 1H, Ar), 7.79 (dd, *J* = 4.9, 1.4 Hz, 1H, Ar), 7.57–7.49 (m, 2H, Ar), 7.51 (t, *J* = 7.5 Hz, 1H, Ar), 7.40 (t, *J* = 7.6 Hz, 2H, Ar), 7.20 (dd, *J* = 5.0, 3.8 Hz, 1H, Ar); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.0, 135.0, 134.4, 132.9, 131.8, 128.8, 128.1, 117.9, 93.4, 85.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{12}H_8NaO_2S_2^+$: 270.9858; found: 270.9856.

2.2. General Procedure for the Synthesis of Starting Alkynylsulfones 1 from Alkenyldibromides

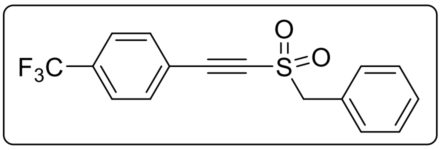


To a dry and degassed 3-necked round bottom flask was charged alkenyldibromide **1''** (1.0 mmol, prepared by the reported procedure[6]) and anhydrous THF (10 mL). The solution was cooled to –78 °C under dry argon atmosphere, and *n*-butyllithium (2.5 M in hexanes, 0.88 mL, 2.2 equiv) was added dropwise. The reaction mixture was stirred for 1 h at –78 °C, and a solution of benzyl thiocyanate (179 mg, 1.2 mmol, 1.2 equiv) or dimethyl disulfide (113 mg, 1.2 mmol, 1.2 equiv) in anhydrous THF (2 mL) were added dropwise. The reaction was allowed to warm to room temperature and stirred 24 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (30 ml) and extracted with DCM (3×20 ml). The combined organic extracts were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude alkynylsulfide **1'**.

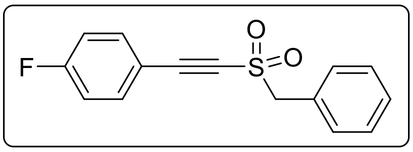
Most of alkynylsulfides **1'** were difficult to purify due to similar R_fs to the starting materials and various impurities, therefore **1'** were immediately oxidized to the corresponding alkynylsulfones **1**. *m*-Chloroperoxybenzoic acid (77%, 672 mg, 3.0 mmol, 3.0 equiv) was added portionwise to a stirred solution of the crude alkynylsulfide **1'** in dichloromethane (10 mL) at 0 °C. Then, the reaction was stirred at room temperature for 24 h. Next, aqueous K_2CO_3 (10%, 50 mL) was added, and the emulsion was extracted by DCM (3 × 50 mL). The combined organic extracts were dried over anhydrous K_2CO_3. After filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc to afford alkynylsulfone **1**.



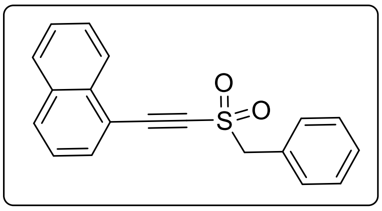
1-((Benzylsulfonyl)ethynyl)-2-methylbenzene (1n): colorless solid (243 mg, 90%); mp 77.5–79.5 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 6.6, 2.9 Hz, 2H, Ar), 7.44–7.38 (m, 4H, Ar), 7.38–7.34 (m, 1H, Ar), 7.21 (d, J = 7.8 Hz, 1H, Ar), 7.18 (t, J = 7.9 Hz, 1H, Ar), 4.51 (s, 2H, CH_2), 2.29 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 133.2, 131.7, 131.2, 129.9, 129.3, 128.8, 127.4, 125.9, 117.2, 93.5, 86.2, 64.5, 20.3; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{14}NaO_2S^+$: 293.0607; found: 293.0603.



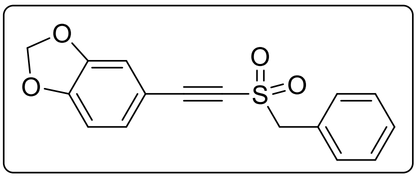
1-((Benzylsulfonyl)ethynyl)-4-(trifluoromethyl)benzene (1o): colorless solid (350 mg, 89%); mp 123.5–125.5 °C (hexane/EtOAc); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H, Ar), 7.57 (d, J = 8.1 Hz, 2H, Ar), 7.49–7.41 (m, 5H, Ar), 4.52 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.4 (q, J_F = 33.1 Hz), 133.2, 131.4, 129.7, 129.1, 127.1, 125.9 (q, J_F = 3.7 Hz), 123.4 (q, J_F = 272.7 Hz), 121.5, 91.8, 84.4, 64.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.34; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{11}F_3NaO_2S^+$: 347.0324; found: 347.0322.



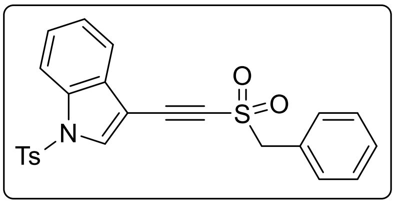
1-((Benzylsulfonyl)ethynyl)-4-fluorobenzene (1p): colorless solid (222 mg, 81%); mp 93.0–95.0 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.39 (m, 7H, Ar), 7.09 (t, J = 8.6 Hz, 2H, Ar), 4.50 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6 (d, J_F = 255.5 Hz, CF), 135.3 (d, J_F = 9.2 Hz, CH), 131.4, 129.6, 129.0, 127.4, 116.6 (d, J_F = 22.5 Hz, CH), 113.8 (d, J_F = 3.5 Hz, C), 93.2, 82.8 (d, J_F = 1.8 Hz, C), 64.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.05; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{15}H_{11}FNaO_2S^+$: 297.0356; found: 297.0352.



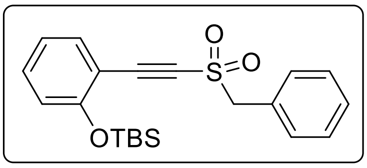
1-((Benzylsulfonyl)ethynyl)naphthalene (**1t**): yellow solid (156 mg, 51%); mp 78.0–80.0 °C (hexane/EtOAc); R$_f$ 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H, Ar), 7.92–7.85 (m, 2H, Ar), 7.74 (dd, J = 7.2, 1.2 Hz, 1H, Ar), 7.58–7.52 (m, 4H, Ar), 7.51–7.42 (m, 4H, Ar), 4.58 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.5, 133.3, 133.0, 132.6, 131.4, 129.5, 129.1, 128.7, 128.2, 127.5, 127.3, 125.6, 125.1, 115.1, 93.2, 87.2, 64.9; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{19}H_{14}NaO_2S^+$: 329.0607; found: 329.0597.



5-((Benzylsulfonyl)ethynyl)benzo[*d*][1,3]dioxole (**1w**): yellow solid (180 mg, 60%); mp 100.0–102.0 °C (hexane/EtOAc); R$_f$ 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49–7.37 (m, 5H, Ar), 7.02 (dd, J = 8.1, 1.7 Hz, 1H, Ar), 6.83 (d, J = 1.7 Hz, 1H, Ar), 6.79 (d, J = 8.1 Hz, 1H, Ar), 6.01 (s, 2H, CH_2), 4.48 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 147.8, 131.3, 129.4, 129.0, 128.9, 127.5, 112.0, 110.3, 109.0, 102.1, 94.9, 81.5, 64.7; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{16}H_{12}NaO_4S^+$: 323.0349; found: 323.0342.

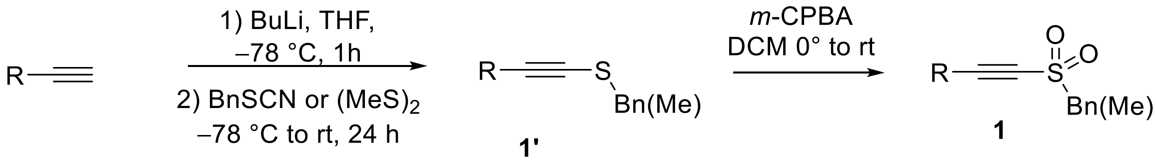


3-((Benzylsulfonyl)ethynyl)-1-tosyl-1*H*-indole (**1x**): orange oil (157 mg, 35%); R$_f$ 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 1H, Ar), 7.92 (s, 1H, Ar), 7.80 (d, J = 8.2 Hz, 2H, Ar), 7.52–7.46 (m, 2H, Ar), 7.46–7.36 (m, 5H, Ar), 7.31–7.26 (m, 3H, Ar), 4.53 (s, 2H, CH_2), 2.36 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 134.3, 133.9, 133.5, 131.3, 130.4, 129.5, 129.4, 129.0, 127.4, 127.2, 126.3, 124.5, 120.6, 113.8, 99.4, 87.7, 87.0, 64.8, 21.7; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{24}H_{19}NNaO_4S_2^+$: 247.0648; found: 472.0643.



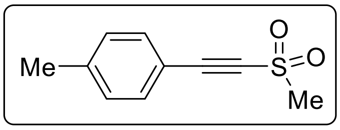
(2-((Benzylsulfonyl)ethynyl)phenoxy)(*tert*-butyl)dimethylsilane (**1ae**): colorless oil (73 mg, 19%); R$_f$ 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H, Ar), 7.41–7.38 (m, 3H, Ar), 7.37–7.33 (m, 2H, Ar), 6.95 (d, J = 7.6 Hz, 1H, Ar), 6.86 (d, J = 8.2 Hz, 1H, Ar), 4.48 (s, 2H, CH_2), 1.02 (s, 9H, Me), 0.23 (s, 6H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 134.6, 133.3, 131.4, 129.4, 128.9, 127.3, 121.5, 120.0, 110.3, 92.6, 86.2, 64.7, 25.7, 18.3, -4.3; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{21}H_{26}NaO_3SSi^+$: 409.1264; found: 409.1262.

2.3. General Procedure for the Synthesis of Starting Alkynylsulfones 1 from Terminal Alkynes

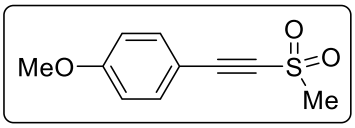


To a dry and degassed 3-necked round bottom flask was charged terminalalkyne (1.0 mmol) and anhydrous THF (10 mL). The solution was cooled to –78 °C under dry argon atmosphere, and *n*-butyllithium (2.5 M in hexanes, 0.44 mL, 1.1 equiv) was added dropwise. The reaction mixture was stirred for 1 h at –78 °C, and a solution of benzyl thiocyanate (179 mg, 1.2 mmol, 1.2 equiv) or dimethyl disulfide (113 mg, 1.2 mmol, 1.2 equiv) in anhydrous THF (2 mL) were added dropwise. The reaction was allowed to warm to room temperature and stirred 24 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (30 ml) and extracted with DCM (3×20 ml). The combined organic extracts were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude alkynylsulfide **1'**.

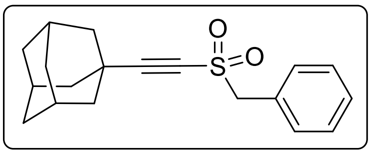
Most of alkynylsulfides **1'** were difficult to purify due to similar R_fs to the starting materials and various impurities, therefore **1'** were immediately oxidized to the corresponding alkynylsulfones **1**. *m*-Chloroperoxybenzoic acid (77%, 672 mg, 3.0 mmol, 3.0 equiv) was added portionwise to a stirred solution of the crude alkynylsulfide **1'** in dichloromethane (10 mL) at 0 °C. Then, the reaction was stirred at room temperature for 24 h. Next, aqueous K_2CO_3 (10%, 50 mL) was added, and the emulsion was extracted by DCM (3 × 50 mL). The combined organic extracts were dried over anhydrous K_2CO_3. After filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc to afford alkynylsulfone **1**.



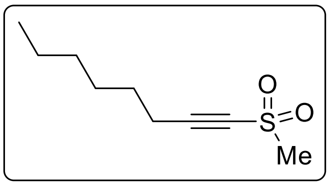
1-Methyl-4-((methylsulfonyl)ethynyl)benzene[7] (**1l**): colorless solid (66 mg, 34%); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H, Ar), 7.22 (d, J = 7.6 Hz, 2H, Ar), 3.29 (s, 3H, Me), 2.40 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 132.9, 129.7, 114.5, 92.4, 84.2, 47.0, 21.9; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{10}H_{10}NaO_2S^+$: 217.0294; found: 217.0290.



1-Methoxy-4-((methylsulfonyl)ethynyl)benzene[7] (**1m**): colorless solid (133 mg, 32%); mp 55.0–57.0 °C (hexane/EtOAc); R$_f$ 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.8 Hz, 2H, Ar), 6.88 (d, J = 8.8 Hz, 2H, Ar), 3.81 (s, 3H, Me), 3.26 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 134.8, 114.6, 109.0, 92.7, 83.8, 55.5, 46.9; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{10}H_{10}NaO_3S^+$: 233.0243; found: 233.0242.

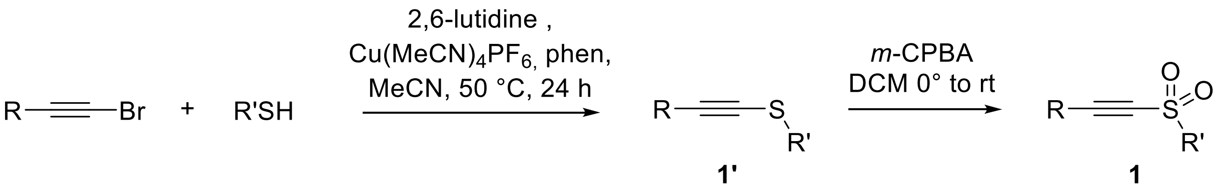


1-((Benzylsulfonyl)ethynyl)adamantine (**1u**): colorless solid (201 mg, 64%); mp 115.0–117.0 °C (hexane/EtOAc); R$_f$ 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (br. s, 5H, Ar), 4.36 (s, 2H, CH_2), 1.97 (br. s, 3H, CH), 1.81 (d, J = 2.3 Hz, 6H, CH_2), 1.68 (q, J = 12.4 Hz, 6H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.3, 129.4, 128.9, 127.8, 103.8, 74.2, 64.6, 40.9, 36.0, 30.0, 27.4; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{19}H_{22}NaO_2S^+$: 337.1233; found: 337.1225.



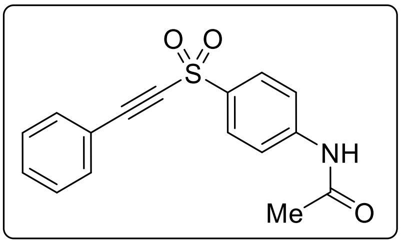
1-(Methylsulfonyl)oct-1-yne (**1z**): colorless oil (180 mg, 48%); R$_f$ 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.10 (s, 3H, Me), 2.34 (t, J = 7.2 Hz, 2H, CH_2), 1.53 (p, J = 7.2 Hz, 2H, CH_2), 1.37–1.29 (m, 2H, CH_2), 1.28–1.17 (m, 4H, CH_2), 0.82 (t, J = 6.8 Hz, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 95.6, 77.2, 46.6, 30.9, 28.3, 26.8, 22.2, 18.5, 13.8; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_9H_{16}NaO_2^+$: 211.0763; found: 211.0765.

2.4. General Procedure for the Synthesis of Starting Alkynylsulfones 1 from Alkynyl Bromides

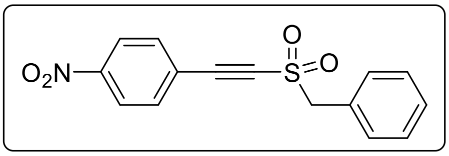


A 50 mL round-bottom flask was charged with alkynylbromide **1''** (1.0 mmol, prepared by the reported procedures[8,9]), $Cu(MeCN)_4PF_6$ (74.5 mg, 0.2 mmol, 20 mol %), and 1,10-phenanthroline monohydrate (39.6 mg, 0.2 mmol, 20 mol %). The flask was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry degassed acetonitrile (10 mL), 2,6-lutidine (214 mg, 2.0 mmol, 2.0 equiv) and the corresponding mercaptan (1.5 mmol, 1.5 equiv) were next added and the dark red suspension was heated at 50 °C for 24 h with stirring. After completion, all volatile components were removed in vacuum, the dark green residue was suspended in DCM (50 mL) and filtered through a short pad of silica gel. The solvent was evaporated under reduced pressure to afford a crude alkynylsulfide **1'**.

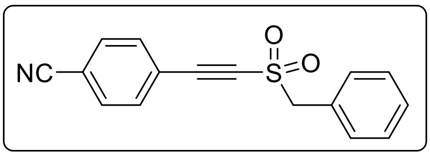
Most of alkynylsulfides **1'** were difficult to purify due to similar R_fs to the starting materials and various impurities, therefore **1'** were immediately oxidized to the corresponding alkynylsulfones **1**. *m*-Chloroperoxybenzoic acid (77%, 672 mg, 3.0 mmol, 3.0 equiv) was added portionwise to a stirred solution of the crude alkynylsulfide **1'** in dichloromethane (10 mL) at 0 °C. Then, the reaction was stirred at room temperature for 24 h. Next, aqueous K_2CO_3 (10%, 50 mL) was added, and the emulsion was extracted by DCM (3 × 50 mL). The combined organic extracts were dried over anhydrous K_2CO_3. After filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc to afford alkynylsulfone **1**.



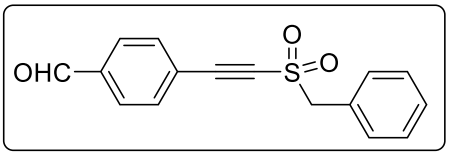
***N*-(4-((Phenylethynyl)sulfonyl)phenyl)acetamide**[10] (**1h**): colorless oil (182 mg, 61%); R_f 0.40 (hexane/EtOAc 1:2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.48 (m, 4H, Ar), 7.44 (d, J = 8.8 Hz, 2H, Ar), 7.35–7.32 (m, 3H, Ar), 7.26 (br. s, 1H, NH), 2.18 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 136.9, 131.9, 128.8, 128.5, 127.9, 127.5, 123.0, 120.9, 97.7, 75.9, 24.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{13}NNaO_3S^+$: 322.0508; found: 322.0510.



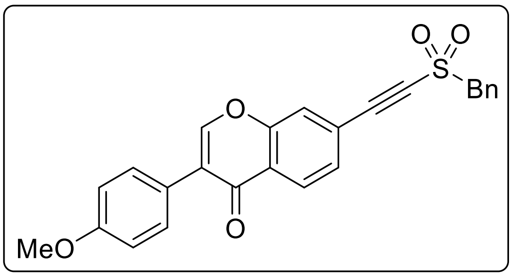
1-((Benzylsulfonyl)ethynyl)-4-nitrobenzene (**1q**): colorless solid (181 mg, 60%); mp 135.5–137.5 °C (hexane/EtOAc); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H, Ar), 7.62 (d, J = 8.8 Hz, 2H, Ar), 7.53–7.36 (m, 5H, Ar), 4.53 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 133.8, 131.4, 129.8, 129.2, 127.0, 124.2, 124.0, 90.6, 86.3, 64.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{15}H_{11}NNaO_4S^+$: 324.0301; found: 324.0298.



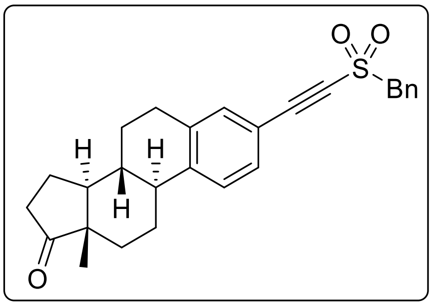
4-((Benzylsulfonyl)ethynyl)benzonitrile (**1r**): colorless solid (177 mg, 63%); mp 125.0–126.0 °C (hexane/EtOAc); R_f 0.60 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H, Ar), 7.53 (d, J = 8.3 Hz, 2H, Ar), 7.50–7.39 (m, 5H, Ar), 4.52 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.2, 132.4, 131.3, 129.7, 129.1, 126.9, 122.3, 117.6, 115.2, 91.0, 85.7, 64.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{11}NNaO_2S^+$: 304.0403; found: 304.0405.



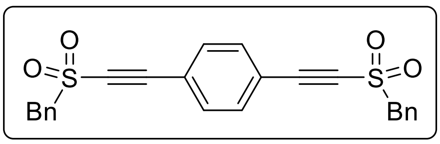
4-((Benzylsulfonyl)ethynyl)benzaldehyde (1s): colorless oil (22.7 mg, 8%); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.05 (s, 1H, CH), 7.89 (d, *J* = 8.3 Hz, 2H, Ar), 7.61 (d, *J* = 8.2 Hz, 2H, Ar), 7.51–7.39 (m, 5H, Ar), 4.53 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.0, 137.9, 133.4, 131.4, 129.7 (×2), 129.1, 127.1, 123.4, 92.1, 85.3, 64.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{12}NaO_3S^+$: 307.0399; found: 307.0400.



7-((Benzylsulfonyl)ethynyl)-3-(4-methoxyphenyl)-4*H*-chromen-4-one (1aa): colorless oil; (138 mg, 32%); R_f 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.2 Hz, 1H, Ar), 8.02 (s, 1H, Ar), 7.59 (d, *J* = 1.5 Hz, 1H, Ar), 7.51–7.41 (m, 8H, Ar), 6.98 (d, *J* = 8.8 Hz, 2H, Ar), 4.54 (s, 2H, CH_2), 3.85 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 160.1, 155.5, 152.9, 131.4, 130.2, 129.8, 129.2, 128.4, 127.4, 127.1, 126.4, 126.0, 123.4, 123.0, 122.5, 114.3, 91.4, 85.1, 64.8, 55.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{25}H_{18}NaO_5S^+$: 453.0767; found: 453.0757.



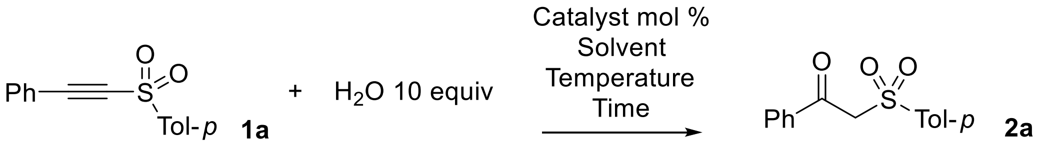
(8*R*,9*S*,13*S*,14*S*)-3-((Benzylsulfonyl)ethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (1ab): colorless oil (221 mg, 51%); R_f 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H, Ar), 7.42–7.38 (m, 3H, Ar), 7.30 (d, *J* = 8.2 Hz, 1H, Ar), 7.24–7.21 (m, 2H, Ar), 4.48 (s, 2H, CH_2), 2.89 (dd, *J* = 8.6, 3.9 Hz, 2H, CH_2), 2.55–2.48 (m, 1H, CH), 2.43–2.38 (m, 1H, CH), 2.35–2.28 (m, 1H, CH), 2.50–1.95 (m, 4H, CH), 1.68–1.40 (m, 6H, CH), 0.91 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.4, 144.5, 137.5, 133.4, 131.4, 130.2, 129.5, 129.0, 127.5, 126.0, 114.8, 95.0, 82.3, 64.8, 50.6, 47.9, 44.7, 37.8, 35.9, 31.6, 29.1, 26.2, 25.6, 21.7, 13.9; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{27}H_{28}NaO_3S^+$: 455.1651; found: 455.1644.



1,4-Bis((benzylsulfonyl)ethynyl)benzene (1ad): colorless solid (200 mg, 46%); mp 188.0–189.0 °C

(DCM); R_f 0.45 (DCM/MeOH 99:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.75 (s, 4H, Ar), 7.54–7.51 (m, 4H, Ar), 7.47–7.42 (m, 6H, Ar), 4.98 (s, 4H, CH_2); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 133.1, 131.5, 129.1, 128.6, 127.9, 119.9, 90.9, 85.5, 63.0; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{24}H_{19}O_4S_2^+$: 435.0719; found: 435.0710.

3 Complete Optimization Studies



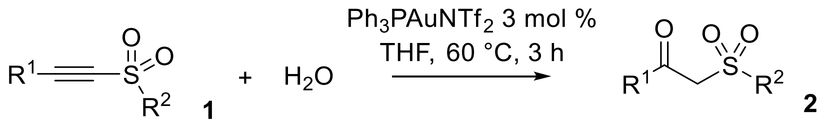
Entry[a]	Catalyst	mol %	Solvent	Temperature, °C	Time, h	Yield,[b] %
1	–	–	Dioxane	100	12	–
2	–	–	THF	60	6	–
3	–	–	MeOH	60	6	–
4	–	–	Acetone	60	6	–
5	–	–	H_2O	60	6	–
6	$Hg(OTf)_2$	5	THF	rt	24	95
7	MsOH	5	THF	rt	24	–
8	TfOH	5	THF	rt	24	–
9	Tf_2NH	5	THF	rt	24	–
10	TfOH	150	Dioxane	100	8	26
11	$Zn(OTf)_2$	5	THF	rt	24	–
12	$Cu(OTf)_2$	5	THF	rt	24	–
13	AgOTf	5	THF	rt	24	17
14	$PtCl_2$	5	THF	rt	24	28
15	$Ph_3PAuNTf_2$	5	THF	rt	24	97
16	$IPrAuNTf_2$	5	THF	rt	24	96
17	$JohnPhosAuNTf_2$	5	THF	rt	24	97
18	$PicAuCl_2$	5	THF	rt	24	50
19	$Ph_3PAuCl/AgNTf_2$	5	THF	rt	24	96
20	$Ph_3PAuCl/AgOTf$	5	THF	rt	24	57
21	Ph_3PAuCl /$AgSbF_6$	5	THF	rt	24	63
22	$Ph_3PAuNTf_2$	5	Dioxane	rt	24	95
23	$Ph_3PAuNTf_2$	5	MeCN	rt	24	50
24	$Ph_3PAuNTf_2$	5	MeOH	rt	24	94
25	$Ph_3PAuNTf_2$	5	EtOH	rt	24	92

26	$Ph_3PAuNTf_2$	5	H_2O	rt	24	29
27	$Ph_3PAuNTf_2$	5	H_2O	60	6	85
28	$Ph_3PAuNTf_2$	3	THF	rt	24	96
29	**$Ph_3PAuNTf_2$**	**3**	**THF**	**60**	**3**	**98**
30	$Ph_3PAuNTf_2$	1.5	THF	rt	24	30
31	$Ph_3PAuNTf_2$	0.5	THF	rt	24	6
31	$Ph_3PAuNTf_2$	0.5	THF	60	24	65

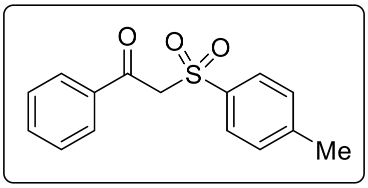
[a]All reactions were carried out on a 0.1 mmol scale (0.2 *M*); [b]Estimated by ^{1}H NMR spectroscopy using durene as an internal standard.

4 Experimental Procedures and Characterization Data

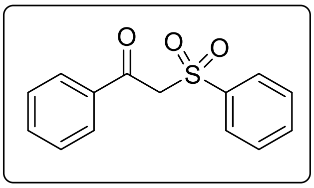
4.1.General Procedure for the Gold(I)-Catalyzed Hydration of Alkynylsulfones



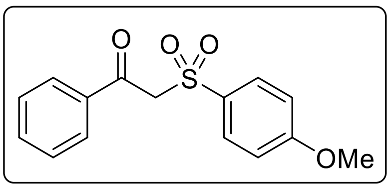
$Ph_3PAuNTf_2$ (4.4 mg, 6.0 μmol, 3 mol %) was added to the solution of alkynylsulfones (**1**, 0.2 mmol) and water (36 μL, 2.0 mmol, 10 equiv) in tetrahydrofuran (1.0 mL). The resulting mixture was stirred at 60 °C for 3 h. After completion, all volatile components were removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford β-ketosulfones **2**. 5 mol % of $Ph_3PAuNTf_2$ was used for the preparation of β-ketosulfones **2o**, **2q**–**s**, and **2ab**.



1-Phenyl-2-tosylethan-1-one[11] (**2a**): colorless solid (54.6 mg, 96%); mp 109.0–111.0 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.4, 1.3 Hz, 2H, Ar), 7.76 (d, J = 8.4 Hz, 2H, Ar), 7.61 (t, J = 7.4 Hz, 1H, Ar), 7.47 (t, J = 7.8 Hz, 2H, Ar), 7.33 (d, J = 8.1 Hz, 2H, Ar), 4.71 (s, 2H, CH_2), 2.44 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.3, 145.5, 136.0, 135.9, 134.4, 130.0, 129.5, 129.0, 128.7, 63.7, 21.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd. for $C_{15}H_{14}NaO_3S^+$: 297.0556; found: 297.0554.

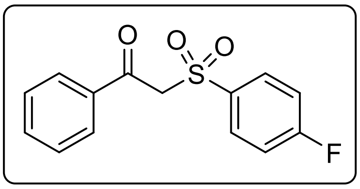


1-Phenyl-2-(phenylsulfonyl)ethan-1-one[11] (**2b**): colorless solid (48.9 mg, 94%); mp 92.0–93.0 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.86 (m, 4H, Ar), 7.68–7.58 (m, 2H, Ar), 7.53 (t, J = 7.8 Hz, 2H, Ar), 7.51–7.42 (m, 2H, Ar), 4.74 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.1, 138.9, 135.9, 134.5, 134.3, 129.4, 129.3, 129.0, 128.7, 63.5; **HRMS** (ESI): m/z [M + Na]$^+$ calcd. for $C_{14}H_{12}NaO_3S^+$: 283.0399; found: 283.0399.

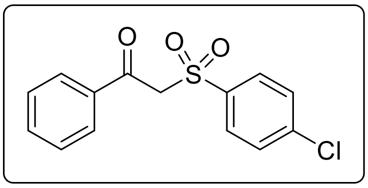


2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one[11] (**2c**): colorless solid (56.9 mg, 98%); mp 106.5–108.5 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.3 Hz, 2H, Ar), 7.80 (d, J = 8.9 Hz, 2H, Ar), 7.61 (t, J = 7.4 Hz, 1H, Ar), 7.48 (t, J = 7.7 Hz, 2H, Ar), 6.98 (d, J =

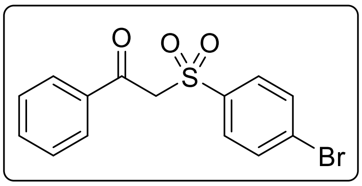
9.0 Hz, 2H, Ar), 4.71 (s, 2H, CH_2), 3.87 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.4, 164.3, 135.9, 134.4, 131.0, 130.4, 129.4, 129.0, 114.5, 63.9, 55.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{15}H_{14}NaO_4S^+$: 313.0505; found: 313.0506.



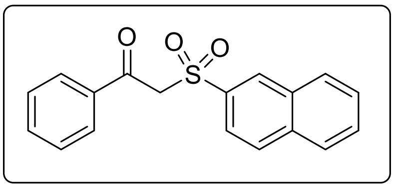
2-((4-Fluorophenyl)sulfonyl)-1-phenylethan-1-one[11] (**2d**): colorless solid (52.8 mg, 95%); mp 148.0–150.0 °C (hexane/EtOAc); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.86 (m, 4H, Ar), 7.62 (t, J = 7.4 Hz, 1H, Ar), 7.48 (t, J = 7.8 Hz, 2H, Ar), 7.21 (t, J = 8.5 Hz, 2H, Ar), 4.74 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.1, 166.2 (d, J_F = 257.3 Hz, CF), 135.7, 134.8 (d, J_F = 3.2 Hz, C), 134.6, 131.8 (d, J_F = 9.7 Hz, CH), 129.4, 129.0, 116.7 (d, J_F = 22.8 Hz, CH), 63.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{14}H_{11}FNaO_3S^+$: 301.0305; found: 301.0301.



2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one[11] (**2e**): colorless solid (54.7 mg, 69%); mp 129.0–131.0 °C (hexane/EtOAc); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 2H, Ar), 7.83 (d, J = 8.7 Hz, 2H, Ar), 7.63 (t, J = 7.5 Hz, 1H, Ar), 7.55–7.44 (m, 4H, Ar), 4.74 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0, 141.2, 137.3, 135.7, 134.6, 130.3, 129.6, 129.4, 129.1, 63.4; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{14}H_{11}ClNaO_3S^+$: 314.0010; found: 317.0009.

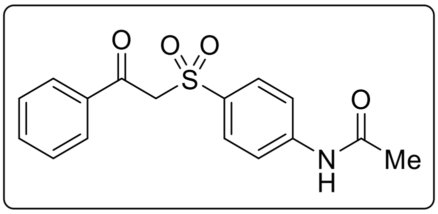


2-((4-Bromophenyl)sulfonyl)-1-phenylethan-1-one[11] (**2f**): colorless solid (67.1 mg, 99%); mp 104.0–105.0 °C (hexane/EtOAc); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.1 Hz, 2H, Ar), 7.76 (d, J = 8.7 Hz, 2H, Ar), 7.69 (d, J = 8.7 Hz, 2H, Ar), 7.64 (t, J = 7.5 Hz, 1H, Ar), 7.49 (t, J = 7.8 Hz, 2H, Ar), 4.73 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0, 137.8, 135.7, 134.7, 132.7, 130.4, 129.9, 129.4, 129.1, 63.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{14}H_{11}BrNaO_3S^+$: 360.9504; found: 360.9499.

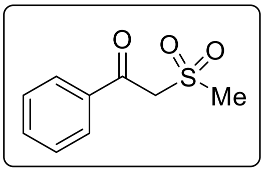


2-(Naphthalen-2-ylsulfonyl)-1-phenylethan-1-one[11] (**2g**): colorless solid (57.7 mg, 93%); mp 132.5–133.5 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H, Ar), 8.02–7.84 (m, 6H, Ar), 7.70–7.66 (m, 1H, Ar), 7.65–7.55 (m, 2H, Ar), 7.46 (t, J = 7.8 Hz, 2H, Ar), 4.81 (s, 2H, CH_2);

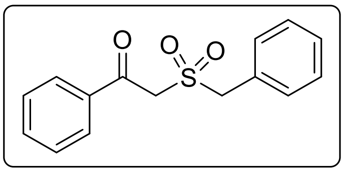
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 135.9, 135.8, 135.7, 134.5, 132.2, 130.8, 129.7, 129.7, 129.7, 129.4, 129.0, 128.2, 127.9, 123.1, 63.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{18}H_{14}NaO_3S^+$: 333.0556; found: 333.0554.



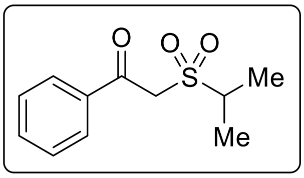
***N*-(4-((2-Oxo-2-phenylethyl)sulfonyl)phenyl)acetamide**[12] (**2h**): colorless solid (62.8 mg, 99%); mp 158.5–160.0 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 1:2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.38 (s, 1H, NH), 7.95 (d, *J* = 7.4 Hz, 2H, Ar), 7.82–7.76 (m, 4H, Ar), 7.66 (t, *J* = 7.4 Hz, 1H, Ar), 7.51 (t, *J* = 7.8 Hz, 2H, Ar), 5.23 (s, 2H, CH_2), 2.10 (s, 3H, Me); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 189.1, 169.1, 144.1, 135.8, 134.1, 132.8, 129.4, 129.1, 128.7, 118.4, 62.5, 24.2; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{15}NNaO_4S^+$: 340.0614; found: 340.0616.



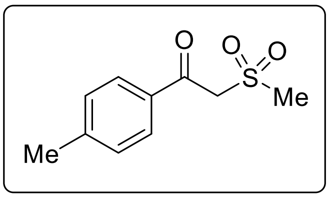
2-(Methylsulfonyl)-1-phenylethan-1-one (**2i**): colorless solid (37.6 mg, 95%); mp 107.0–108.0 °C (hexane/EtOAc); R_f 0.25 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03–7.96 (m, 2H, Ar), 7.66 (t, *J* = 7.4 Hz, 1H, Ar), 7.52 (t, *J* = 7.8 Hz, 2H, Ar), 4.60 (s, 2H, CH_2), 3.15 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4, 135.8, 134.8, 129.4, 129.2, 61.4, 42.0; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_9H_{10}NaO_3S^+$: 221.0243; found: 221.0242.



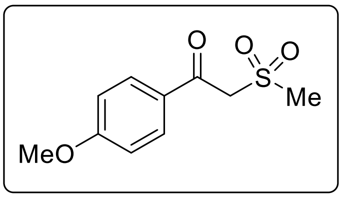
2-(Benzylsulfonyl)-1-phenylethan-1-one[13] (**2j**): colorless solid (51.5 mg, 94%); mp 109.0–110.0 °C (hexane/EtOAc); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H, Ar), 7.65 (t, *J* = 7.5 Hz, 1H, Ar), 7.56–7.49 (m, 4H, Ar), 7.42–7.39 (m, 3H, Ar), 4.55 (s, 2H, CH_2), 4.39 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7, 136.0, 134.7, 131.2, 129.4, 129.2 (×2), 129.1, 128.0, 60.0, 56.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{15}H_{14}NaO_3S^+$: 297.0556; found: 297.0550.



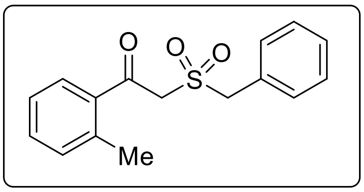
2-(Isopropylsulfonyl)-1-phenylethan-1-one (2k): colorless solid (43.0 mg, 95%); mp 61.0–63.0 °C (hexane/EtOAc); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H, Ar), 7.65 (d, *J* = 7.4 Hz, 1H, Ar), 7.52 (t, *J* = 7.8 Hz, 2H, Ar), 4.58 (s, 2H, CH_2), 3.61–3.50 (m, 1H, CH), 1.46 (d, *J* = 6.9 Hz, 6H, 2Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4, 136.0, 134.7, 129.5, 129.1, 57.1, 53.8, 15.3; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{11}H_{14}NaO_3S^+$: 249.0556; found: 249.0552.



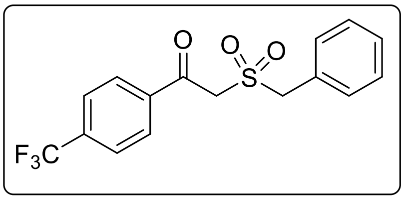
2-(Methylsulfonyl)-1-(*p*-tolyl)ethan-1-one[14] (**2l**): colorless solid (39.4 mg, 93%); mp 101.0–103.0 °C (hexane/EtOAc); R_f 0.45 (hexane/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H, Ar), 7.31 (d, J = 8.0 Hz, 2H, Ar), 4.57 (s, 2H, CH_2), 3.13 (s, 3H, Me), 2.43 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.8, 146.1, 133.3, 129.8, 129.5, 61.3, 41.9, 21.9; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{10}H_{12}NaO_3S^+$: 235.0399; found: 235.0395.



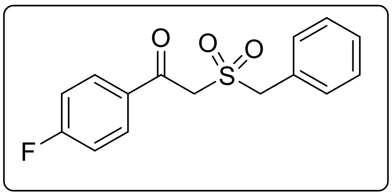
1-(4-Methoxyphenyl)-2-(methylsulfonyl)ethan-1-one[15] (**2m**): colorless solid (43.3 mg, 95%); mp 138.0–140.0 °C (hexane/EtOAc); R_f 0.30 (hexane/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 2H, Ar), 6.97 (d, J = 8.9 Hz, 2H, Ar), 4.54 (s, 2H, CH_2), 3.88 (s, 3H, Me), 3.12 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.5, 165.0, 132.0, 128.8, 114.4, 61.3, 55.8, 41.9; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{10}H_{12}NaO_4S^+$: 251.0349; found: 251.0347.



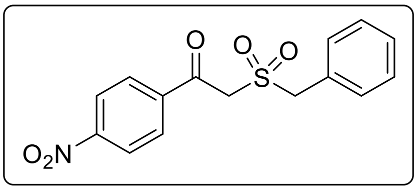
2-(Benzylsulfonyl)-1-(*o*-tolyl)ethan-1-one (**2n**): colorless solid (50.7 mg, 88%); mp 68.0–70.0 °C (hexane/EtOAc); R_f 0.25 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 1H, Ar), 7.55 (dd, J = 6.5, 2.8 Hz, 2H, Ar), 7.48–7.39 (m, 4H, Ar), 7.30 (t, J = 6.7 Hz, 2H, Ar), 4.57 (s, 2H, CH_2), 4.34 (s, 2H, CH_2), 2.58 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 140.1, 136.1, 133.1, 132.6, 131.2, 130.2, 129.4, 129.2, 128.1, 126.2, 60.0, 59.0, 21.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{16}NaO_3S^+$: 311.0712; found: 311.0707.



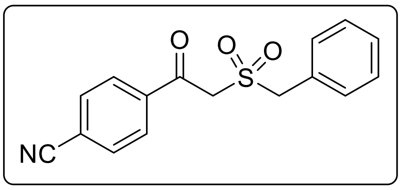
2-(Benzylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2o**): colorless solid (63.6 mg, 93%); mp 178.0–180.0 °C (hexane/EtOAc); R_f 0.25 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.1 Hz, 2H, Ar), 7.78 (d, J = 8.1 Hz, 2H, Ar), 7.57–7.51 (m, 2H, Ar), 7.45–7.39 (m, 3H, Ar), 4.52 (s, 2H, CH_2), 4.41 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.0, 138.6, 135.8 (q, J_F = 32.9 Hz, C), 131.2, 129.7, 129.6, 129.2, 127.7, 126.2 (q, J_F = 3.7 Hz, CH), 123.4 (q, J_F = 273.0 Hz, CF_3), 60.0, 57.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.36; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{13}F_3NaO_3S^+$: 365.0430; found: 365.0433.



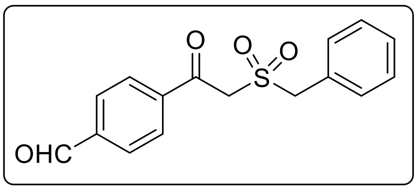
2-(Benzylsulfonyl)-1-(4-fluorophenyl)ethan-1-one (2p): colorless solid (53.1 mg, 91%); mp 146.0–147.0 °C (hexane/EtOAc); R$_f$ 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–7.95 (m, 2H, Ar), 7.56–7.50 (m, 2H, Ar), 7.45–7.38 (m, 3H, Ar), 7.18 (t, J = 8.5 Hz, 2H, Ar), 4.52 (s, 2H, CH_2), 4.36 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.1, 166.8 (d, J_F = 258.1 Hz, CF), 132.5 (d, J_F = 3.0 Hz, C), 132.2 (d, J_F = 9.8 Hz, CH), 131.2, 129.5, 129.3, 127.8, 116.4 (d, J_F = 22.2 Hz, CH), 60.0, 57.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –101.91; **HRMS** (ESI): m/z $[M + Na]^+$ calcd. for $C_{15}H_{13}FNaO_3S^+$: 315.0462; found: 315.0464.



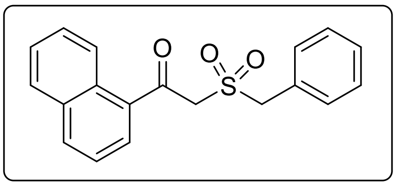
2-(Benzylsulfonyl)-1-(4-nitrophenyl)ethan-1-one (2q): colorless solid (61.9 mg, 97%); mp 179.0–181.0 °C (hexane/EtOAc); R$_f$ 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.37 (d, J = 8.7 Hz, 2H, Ar), 8.26 (d, J = 8.5 Hz, 2H, Ar), 7.42 (br. s, 5H, Ar), 5.12 (s, 2H, CH_2), 4.69 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 189.2, 150.4, 140.4, 131.3, 130.5, 128.7, 128.6, 127.7, 123.8, 59.4, 59.2; **HRMS** (ESI): m/z $[M + Na]^+$ calcd. for $C_{15}H_{13}NNaO_5S^+$: 342.0407; found: 342.0409.



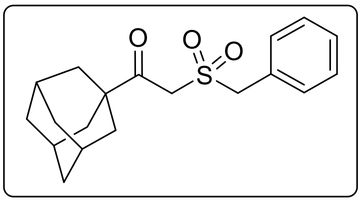
4-(2-(Benzylsulfonyl)acetyl)benzonitrile (2r): colorless solid (50.8 mg, 85%); mp 141.0–143.0 °C (hexane/EtOAc); R$_f$ 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H, Ar), 7.81 (d, J = 8.4 Hz, 2H, Ar), 7.57–7.50 (m, 2H, Ar), 7.46–7.39 (m, 3H, Ar), 4.51 (s, 2H, CH_2), 4.40 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.7, 138.8, 132.9, 131.2, 129.7, 129.6, 129.4, 127.5, 117.9, 117.6, 60.1, 57.1; **HRMS** (ESI): m/z $[M + Na]^+$ calcd. for $C_{16}H_{13}NNaO_3S^+$: 322.0508; found: 322.0505.



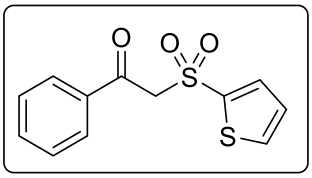
4-(2-(Benzylsulfonyl)acetyl)benzaldehyde (2s): colorless solid (58.0 mg, 96%); mp 129.0–131.0 °C (hexane/EtOAc); R$_f$ 0.25 (hexane/EtOAc 2:1); R$_f$ 0.25 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.12 (s, 1H, CH), 8.12 (d, J = 8.3 Hz, 2H, Ar), 8.01 (d, J = 8.3 Hz, 2H, Ar), 7.57–7.50 (m, 2H, Ar), 7.44–7.39 (m, 3H, Ar), 4.53 (s, 2H, CH_2), 4.43 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.3, 189.3, 140.0, 131.2, 130.1, 129.8, 129.6, 129.3 (×2), 127.7, 60.0, 57.2; **HRMS** (ESI): m/z $[M + Na]^+$ calcd. for $C_{16}H_{14}NaO_4S^+$: 325.0505; found: 325.0503.



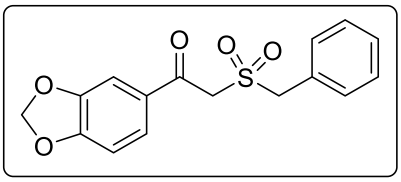
2-(Benzylsulfonyl)-1-(naphthalen-1-yl)ethan-1-one (**2t**): colorless solid (54.4 mg, 84%); mp 106.0–108.0 °C (hexane/EtOAc); R*f* 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.78 (d, *J* = 8.4 Hz, 1H, Ar), 8.08 (d, *J* = 8.2 Hz, 1H, Ar), 7.96 (d, *J* = 7.3 Hz, 1H, Ar), 7.91 (d, *J* = 8.1 Hz, 1H, Ar), 7.71–7.65 (m, 1H, Ar), 7.63–7.57 (m, 3H, Ar), 7.53 (t, *J* = 7.8 Hz, 1H, Ar), 7.46–7.40 (m, 3H, Ar), 4.64 (s, 2H, CH_2), 4.50 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 192.2, 135.0, 134.1, 133.8, 131.2, 130.7, 130.4, 129.4, 129.3, 129.1, 128.9, 128.1, 127.1, 125.6, 124.5, 60.1, 59.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{19}H_{16}NaO_3S^+$: 347.0712; found: 347.0714.



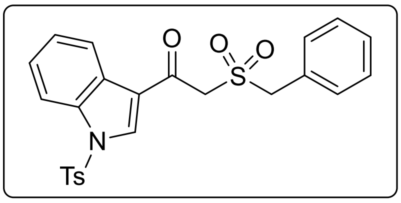
1-(Adamantan-1-yl)-2-(benzylsulfonyl)ethan-1-one (**2u**): colorless solid (59.8 mg, 90%); mp 122.0–124.0 °C (hexane/EtOAc); R*f* 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.50–7.44 (m, 2H, Ar), 7.42–7.36 (m, 3H, Ar), 4.52 (s, 2H, CH_2), 3.88 (s, 2H, CH_2), 2.07 (br. s, 3H, CH), 1.83–1.63 (m, 12H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 204.7, 131.0, 129.3, 129.1, 128.4, 60.1, 54.3, 47.8, 37.4, 36.3, 27.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{19}H_{24}NaO_3S^+$: 355.1338; found: 355.1334.



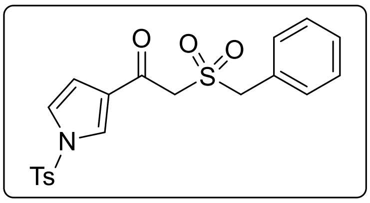
1-Phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one[11] (**2v**): yellow oil (47.4 mg, 89%); R*f* 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.95 (d, *J* = 8.3 Hz, 2H, Ar), 7.74 (dd, *J* = 5.0, 1.5 Hz, 1H, Ar), 7.69 (dd, *J* = 3.9, 1.4 Hz, 1H, Ar), 7.63 (t, *J* = 7.4 Hz, 1H, Ar), 7.49 (t, *J* = 7.8 Hz, 2H, Ar), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H, Ar), 4.82 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 187.9, 139.6, 135.8, 135.6, 135.1, 134.6, 129.4, 129.1, 128.1, 64.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{12}H_{10}NaO_3S_2^+$: 288.9964; found: 288.9966.



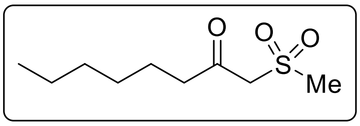
1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(benzylsulfonyl)ethan-1-one (**2w**): colorless solid (57.9 mg, 91%); mp 96.0–98.0 °C (hexane/EtOAc); R*f* 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.57–7.50 (m, 3H, Ar), 7.45 (d, *J* = 1.6 Hz, 1H, Ar), 7.42–7.37 (m, 3H, Ar), 6.88 (d, *J* = 8.2 Hz, 1H, Ar), 6.08 (s, 2H, CH_2), 4.52 (s, 2H, CH_2), 4.31 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 187.4, 153.4, 148.8, 131.3, 130.9, 129.4, 129.2, 128.0, 126.7, 108.5, 108.4, 102.4, 59.9, 56.9; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{16}H_{14}NaO_5S^+$: 341.0454; found: 341.0451.



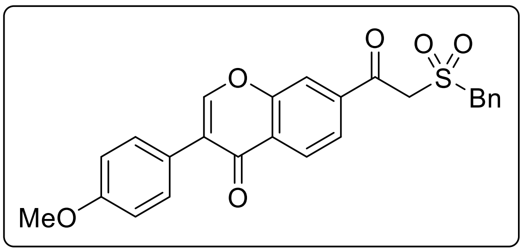
2-(Benzylsulfonyl)-1-(1-tosyl-1*H*-indol-3-yl)ethan-1-one (**2x**): yellowish solid (77.5 mg, 83%); mp 216.0–218.0 °C (hexane/EtOAc); R$_f$ 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H, Ar), 8.36–8.32 (m, 1H, Ar), 7.94 (dd, *J* = 6.7, 2.0 Hz, 1H, Ar), 7.86 (d, *J* = 8.4 Hz, 2H, Ar), 7.58 (dd, *J* = 6.5, 2.8 Hz, 2H, Ar), 7.45–7.36 (m, 5H, Ar), 7.29 (d, *J* = 8.2 Hz, 2H, Ar), 4.52 (s, 2H, CH_2), 4.32 (s, 2H, CH_2), 2.36 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.9, 146.4, 135.2, 135.0, 134.2, 131.4, 130.5, 129.4, 129.2, 127.8, 127.6, 127.3, 126.4, 125.4, 123.1, 121.0, 113.4, 59.9, 58.9, 21.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{24}H_{21}NNaO_5S_2^+$: 490.0753; found: 490.0748.



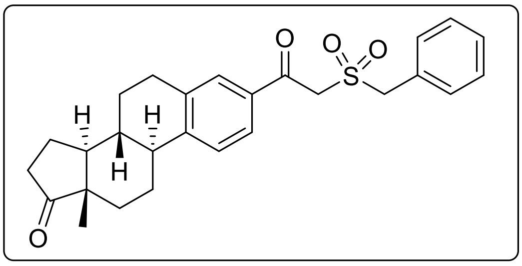
2-(Benzylsulfonyl)-1-(1-tosyl-1*H*-pyrrol-3-yl)ethan-1-one (**2y**): colorless oil (78.4 mg, 94%); R$_f$ 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.76 (m, 3H, Ar), 7.55–7.47 (m, 2H, Ar), 7.41–7.37 (m, 3H, Ar), 7.35 (d, *J* = 8.1 Hz, 2H, Ar), 7.15 (dd, *J* = 3.3, 2.1 Hz, 1H, Ar), 6.71 (dd, *J* = 3.3, 1.7 Hz, 1H, Ar), 4.48 (s, 2H, CH_2), 4.14 (s, 2H, CH_2), 2.43 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7, 146.5, 134.7, 131.3, 130.6, 129.4, 129.2, 128.4, 127.8, 127.6, 126.8, 122.3, 112.6, 59.9, 58.3, 21.9; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{19}NNaO_5S_2^+$: 440.0597; found: 440.0594.



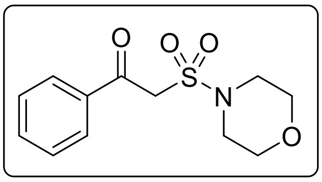
1-(Methylsulfonyl)octan-2-one[16] (**2z**): colorless solid (40.0 mg, 97%); mp 43.0–45.0 °C (hexane/EtOAc); R$_f$ 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.02 (s, 2H, CH_2), 3.03 (s, 3H, Me), 2.68 (t, *J* = 7.3 Hz, 2H, CH), 1.59 (p, *J* = 7.3 Hz, 2H, CH), 1.33–1.23 (m, 6H, CH), 0.90–0.82 (m, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.9, 64.6, 45.0, 41.6, 31.6, 28.6, 23.0, 22.5, 14.1; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_9H_{18}NaO_3S^+$: 229.0869; found: 229.0866.



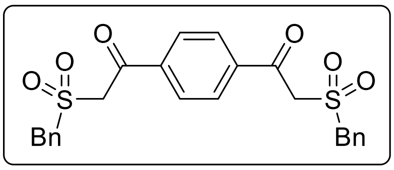
7-(2-(Benzylsulfonyl)acetyl)-3-(4-methoxyphenyl)-4*H*-chromen-4-one (2aa): colorless solid (73.6 mg, 82%); mp 204.5–206.5 °C (benzene/EtOAc); R$_f$ 0.30 (benzene/EtOAc 5:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.64 (s, 1H, Ar), 8.38 (s, 1H, Ar), 8.27 (d, *J* = 8.3 Hz, 1H, Ar), 8.04 (d, *J* = 6.9 Hz, 1H, Ar), 7.57 (d, *J* = 8.8 Hz, 2H, Ar), 7.45–7.41 (m, 5H, Ar), 7.02 (d, *J* = 8.8 Hz, 2H, Ar), 5.17 (s, 2H, CH_2), 4.71 (s, 2H, CH_2), 3.80 (s, 3H, Me); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 189.2, 174.9, 159.2, 155.3, 155.0, 139.8, 131.3, 130.1, 128.7, 128.6, 127.7, 126.9, 126.2, 124.4, 124.2, 123.6, 120.4, 113.7, 59.5, 59.1, 55.2; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{25}H_{20}NaO_6S^+$: 471.0873; found: 471.0856.



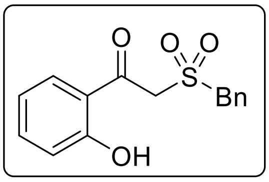
(8*R*,9*S*,13*S*,14*S*)-3-(2-(Benzylsulfonyl)acetyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2ab): colorless solid (77.4 mg, 86%); colorless oil (77.4 mg, 86%); R$_f$ 0.25 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76–7.67 (m, 2H, Ar), 7.54 (dd, *J* = 6.4, 2.8 Hz, 2H, Ar), 7.46–7.37 (m, 4H, Ar), 4.53 (s, 2H, CH_2), 4.36 (s, 2H, CH_2), 3.05–2.87 (m, 2H, CH), 2.52 (dd, *J* = 18.7, 8.7 Hz, 1H, CH), 2.48–2.30 (m, 2H, CH), 2.21–2.03 (m, 3H, CH), 2.03–1.96 (m, 1H, CH), 1.68–1.44 (m, 6H, CH), 0.92 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.4, 189.4, 147.6, 137.7, 133.7, 131.2, 129.9, 129.3, 129.2, 128.0, 126.7, 126.2, 59.9, 56.7, 50.6, 48.0, 44.9, 37.8, 35.9, 31.6, 29.4, 26.3, 25.6, 21.7, 13.9; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{27}H_{30}NaO_4S^+$: 473.1757; found: 473.1747.



2-(Morpholinosulfonyl)-1-phenylethan-1-one[17] (**2ac**): colorless solid (45.8 mg, 85%); mp 130.5–132.5 °C (hexane/EtOAc); R$_f$ 0.50 (hexane/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H, Ar), 7.65 (t, *J* = 7.4Hz, 1H, Ar), 7.52 (t, *J* = 7.8 Hz, 2H, Ar), 4.57 (s, 2H, CH_2), 3.73–3.71 (m, 4H, CH_2), 3.37–3.35 (m, 4H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.2, 135.9, 134.6, 129.5, 129.1, 66.7, 57.5, 46.3; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{12}H_{15}NNaO_4S^+$: 292.0614; found: 292.0622.

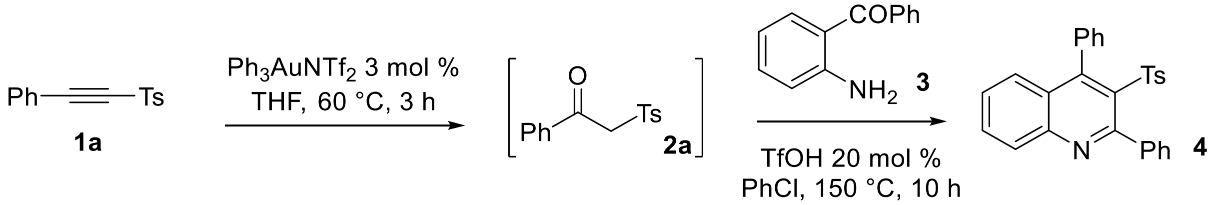


1,1'-(1,4-Phenylene)bis(2-(benzylsulfonyl)ethan-1-one) (**2ad**): colorless solid (88.5 mg, 94%); mp 227.0–229.0 °C (DCM); R$_f$ 0.40 (benzene/EtOAc 3:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.18 (s, 4H, Ar), 7.44–7.39 (m, 10H, Ar), 5.10 (s, 4H, CH_2), 4.69 (s, 4H, CH_2); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 189.7, 139.6, 131.3, 129.4, 128.7, 128.6, 127.8, 59.4, 59.0; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{24}H_{22}NaO_6S_2^+$: 493.0750; found: 493.0758.

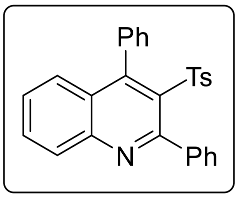


2-(Benzylsulfonyl)-1-(2-hydroxyphenyl)ethan-1-one (**2ae**): colorless solid (48.1 mg, 93%); mp 103.0–105.0 °C (hexane/EtOAc); R_f 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.74 (s, 1H, OH), 7.65 (dd, J = 8.1, 1.2 Hz, 1H), 7.58–7.52 (m, 3H, Ar), 7.43–7.40 (m, 3H, Ar), 7.04 (d, J = 8.3 Hz, 1H, Ar), 6.95 (t, J = 7.6 Hz, 1H, Ar), 4.54 (s, 2H, CH_2), 4.40 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.6, 163.6, 138.4, 131.3, 131.2, 129.6, 129.3, 127.7, 119.8, 119.5, 119.1, 60.4, 56.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd. for $C_{15}H_{14}NNaO_4S^+$: 313.0505; found: 313.0507.

4.2.One-pot Synthesis of Quinoline 4

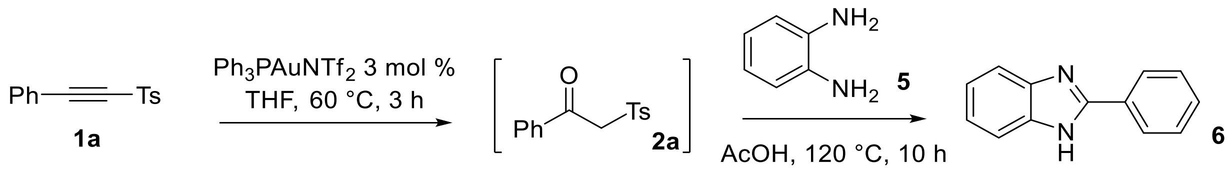


$Ph_3PAuNTf_2$ (4.4 mg, 6.0 μmol, 3 mol %) was added to the solution of 1-methyl-4-((phenylethynyl)sulfonyl)benzene (**1a**, 51.3 mg, 0.2 mmol) and water (36 μL, 2.0 mmol, 10 equiv) in tetrahydrofuran (1.0 mL). The resulting mixture was stirred at 60 °C for 3 h. After completion, all volatile components were removed in vacuum. Then chlorobenzene (1.0 mL), (2-aminophenyl)(phenyl)methanone (**3**, 59.2 mg, 0.3 mmol, 1.5 equiv), and triflic acid (6.0 mg, 40 μmol, 20 mol %) were added in this sequence. The resulting mixture was stirred at 150 °C for 10 h. Finally, all volatile components were removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford quinoline **4**.

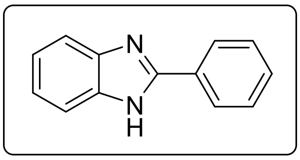


2,4-Diphenyl-3-tosylquinoline[18] (**4**): colorless solid (82.7 mg, 95%); mp 181.0–182.0 °C (hexane/EtOAc); R_f 0.60 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H, Ar), 7.85–7.77 (m, 1H, Ar), 7.59–7.53 (m, 2H, Ar), 7.51–7.34 (m, 8H, Ar), 7.27 (d, J = 7.1 Hz, 2H, Ar), 6.97 (d, J = 8.3 Hz, 2H, Ar), 6.88 (d, J = 8.2 Hz, 2H, Ar), 2.30 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 151.4, 147.7, 143.0, 141.1, 139.3, 135.1, 133.5, 132.2, 130.3, 129.7, 129.6, 129.0, 128.6, 128.6, 127.9, 127.8, 127.7, 127.5, 127.3, 126.8, 21.6; **HRMS** (ESI): m/z [M + Na]$^+$ calcd. for $C_{28}H_{21}NNaO_2S^+$: 458.1185; found: 458.1177.

4.3.One-pot Synthesis of Benzimidazole 6

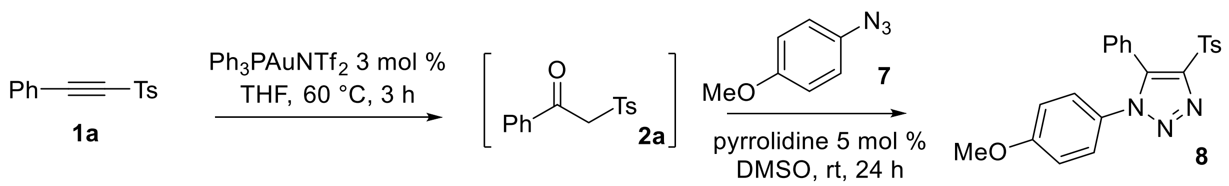


$Ph_3PAuNTf_2$ (4.4 mg, 6.0 μmol, 3 mol %) was added to the solution of 1-methyl-4-((phenylethynyl)sulfonyl)benzene (**1a**, 51.3 mg, 0.2 mmol) and water (36 μL, 2.0 mmol, 10 equiv) in tetrahydrofuran (1.0 mL). The resulting mixture was stirred at 60 °C for 3 h. After completion, all volatile components were removed in vacuum. Then acetic acid (1.0 mL) and *o*-phenylendiamine (**5**, 38.2 mg, 0.2 mmol, 1.0 equiv) were added in this sequence. The resulting mixture was stirred at 120 °C for 10 h. Finally, all volatile components were removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford benzimidazole **6**.

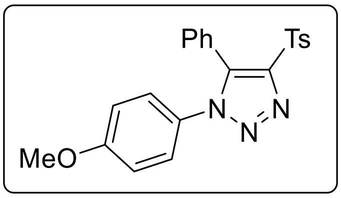


2-Phenyl-1*H*-benzo[*d*]imidazole[19] (**6**): colorless solid (35.3 mg, 91%); mp 289.0–291.0 °C (hexane/EtOAc); R_f 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.91 (br. s, 1H, NH), 8.23–8.15 (m, 2H, Ar), 7.69–7.44 (m, 5H, Ar), 7.21 (dq, J = 6.9, 3.8 Hz, 2H, Ar); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.2, 130.2, 129.8, 128.9, 126.4, 122.1 (two signals are merged with others); **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{13}H_{11}N_2^+$: 195.0917; found: 195.0921.

4.4.One-pot Synthesis of Triazole 8

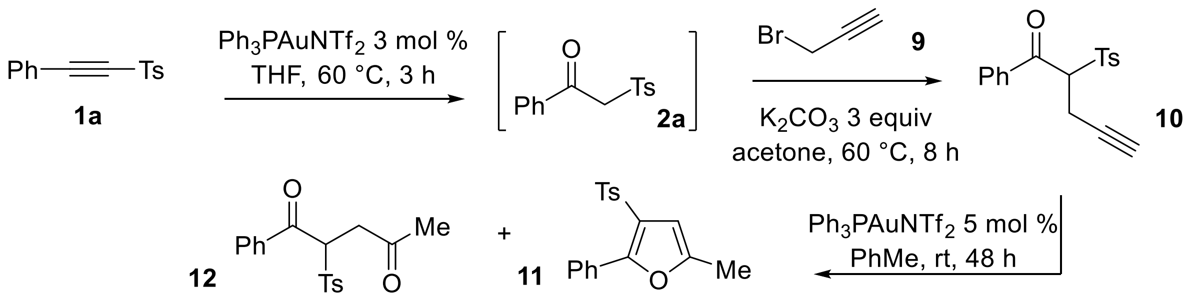


$Ph_3PAuNTf_2$ (4.4 mg, 6.0 μmol, 3 mol %) was added to the solution of 1-methyl-4-((phenylethynyl)sulfonyl)benzene (**1a**, 51.3 mg, 0.2 mmol) and water (36 μL, 2.0 mmol, 10 equiv) in tetrahydrofuran (1.0 mL). The resulting mixture was stirred at 60 °C for 3 h. After completion, all volatile components were removed in vacuum. Then DMSO (1.0 mL), 1-azido-4-methoxybenzene (**7**, 32.8 mg, 0.22 mmol, 1.1 equiv) and pyrrolidine (0.7 mg, 10 μmol, 5 mol %) were added in this sequence. The resulting mixture was stirred at room temperature for 24 h. Finally, all volatile components were removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford triazole **8**.



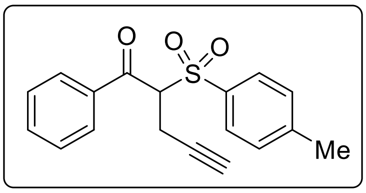
1-(4-Methoxyphenyl)-5-phenyl-4-tosyl-1*H*-1,2,3-triazole[20] (**8**): colorless solid (78.6 mg, 97%); mp 198.0–199.0 °C (hexane/EtOAc); R*f* 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H, Ar), 7.45 (t, *J* = 7.4 Hz, 1H, Ar), 7.38 (t, *J* = 7.5 Hz, 2H, Ar), 7.26–7.24 (m, 4H, Ar), 7.12 (d, *J* = 9.0 Hz, 2H, Ar), 6.83 (d, *J* = 9.0 Hz, 2H, Ar), 3.78 (s, 3H, Me), 2.39 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 146.0, 144.9, 138.6, 137.9, 130.6, 130.5, 129.8, 128.6, 128.4, 128.3, 126.6, 124.6, 114.6, 55.7, 21.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{22}H_{19}N_3NaO_3S^+$: 428.1039; found: 428.1034.

4.5.One-pot Propargylation of 2a. Synthesis of Furane 11 and Diketone 12

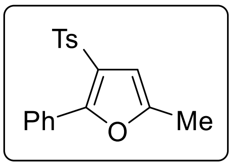


$Ph_3PAuNTf_2$ (4.4 mg, 6.0 μmol, 3 mol %) was added to the solution of 1-methyl-4-((phenylethynyl)sulfonyl)benzene (**1a**, 51.3 mg, 0.2 mmol) and water (36 μL, 2.0 mmol, 10 equiv) in tetrahydrofuran (1.0 mL). The resulting mixture was stirred at 60 °C for 3 h. After completion, all volatile components were removed in vacuum. Then acetone (1.0 mL), propargyl bromide (**9**, 80% wt. solution in toluene, 32.7 mg, 0.22 mmol, 1.1 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3 equiv) were added in this sequence. The resulting mixture was stirred at 60 °C for 8 h. Finally, all volatile components were removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford **10**.

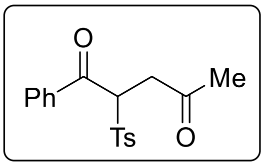
$Ph_3PAuNTf_2$ (3.7 mg, 5.0 μmol, 5 mol %) was added to the solution of **10** (31.2 mg, 0.1 mmol) in dry toluene (1.0 mL). The resulting mixture was stirred at room temperature for 48 h. After completion, all the solvent was removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford **11** and **12**.



1-Phenyl-2-tosylpent-4-yn-1-one[21] (**10**): colorless solid (53.0 mg, 85%); mp 110.0–112.0 °C (hexane/EtOAc); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H, Ar), 7.66–7.56 (m, 3H, Ar), 7.47 (t, J = 7.8 Hz, 2H, Ar), 7.30 (d, J = 8.1 Hz, 2H, Ar), 5.26 (dd, J = 8.6, 6.1 Hz, 1H, CH), 2.97 (t, J = 2.7 Hz, 1H, CH), 2.95 (d, J = 2.7 Hz, 1H, CH), 2.42 (s, 3H, Me), 1.89 (t, J = 2.7 Hz, 1H, CH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.0, 146.0, 137.0, 134.2, 133.0, 129.9, 129.8, 129.3, 128.9, 78.4, 71.3, 68.4, 21.8, 18.4; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{18}H_{16}NaO_3S^+$: 335.0712; found: 335.0707.



5-Methyl-2-phenyl-3-tosylfuran[21] (**11**): yellowish oil (40.6 mg, 65%); R_f 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H, Ar), 7.68 (d, J = 8.4 Hz, 2H, Ar), 7.43–7.38 (m, 3H, Ar), 7.20 (d, J = 8.0 Hz, 2H, Ar), 6.42 (d, J = 1.0 Hz, 1H, Ar), 2.35 (s, 3H, Me), 1.89 (d, J = 0.8 Hz, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 151.7, 144.1, 139.4, 129.7, 129.7, 128.7, 128.6, 128.3, 127.2, 124.6, 108.5, 21.6, 13.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{18}H_{16}NaO_3S^+$: 335.0712; found: 335.0709.



1-Phenyl-2-tosylpentane-1,4-dione[21] (**12**): yellowish oil (19.8 mg, 30%); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.3 Hz, 2H, Ar), 7.58–7.54 (m, 3H, Ar), 7.41 (t, J = 7.8 Hz, 2H, Ar), 7.24 (d, J = 8.1 Hz, 2H, Ar), 5.51 (dd, J = 10.8, 3.0 Hz, 1H, CH), 3.49 (dd, J = 18.1, 10.8 Hz, 1H, CH), 3.29 (dd, J = 18.1, 3.0 Hz, 1H, CH), 2.40 (s, 3H, Me), 2.16 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.9, 191.8, 145.7, 136.8, 133.8, 133.8, 129.8, 129.5, 129.3, 128.6, 65.8, 42.0, 29.7, 21.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{18}H_{18}Na_3O_4S^+$: 353.0818; found: 353.0824.

5 References

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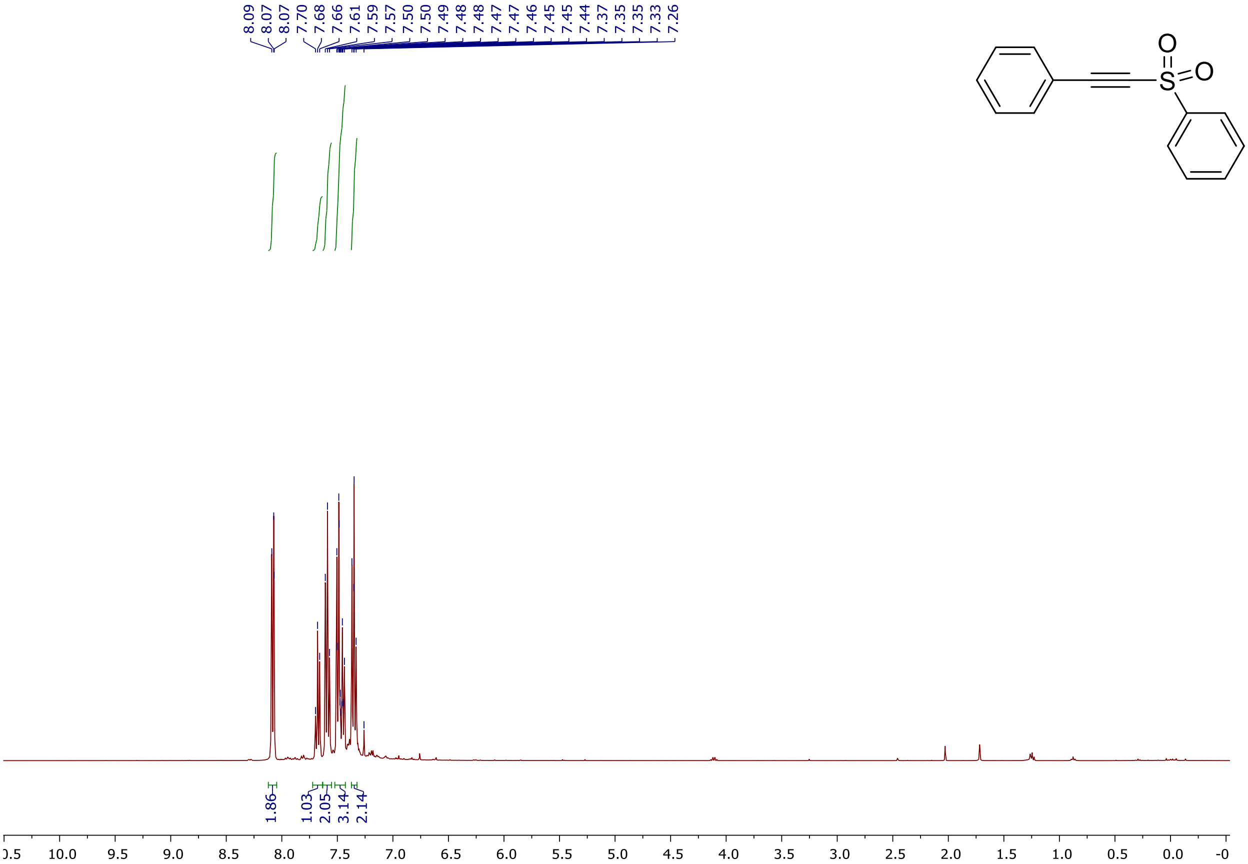
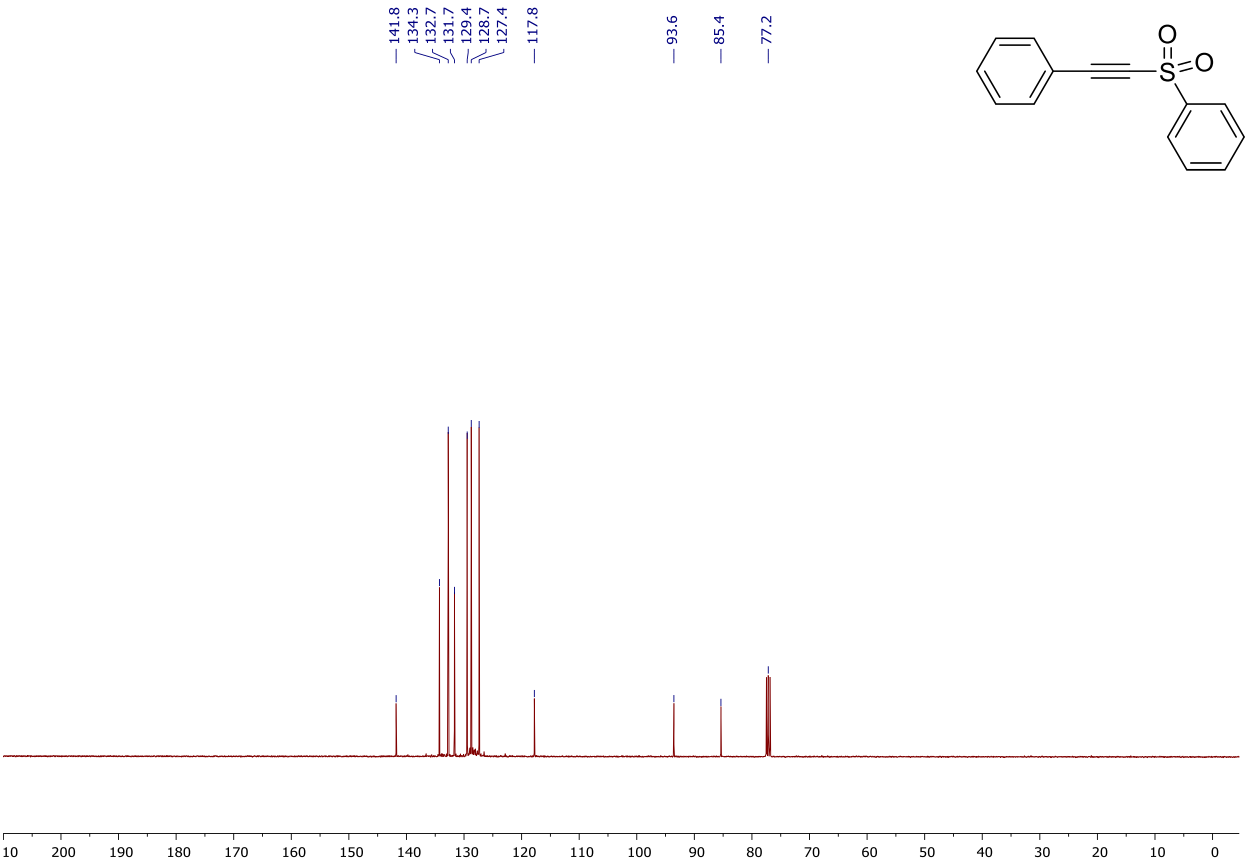
6 NMR Spectra

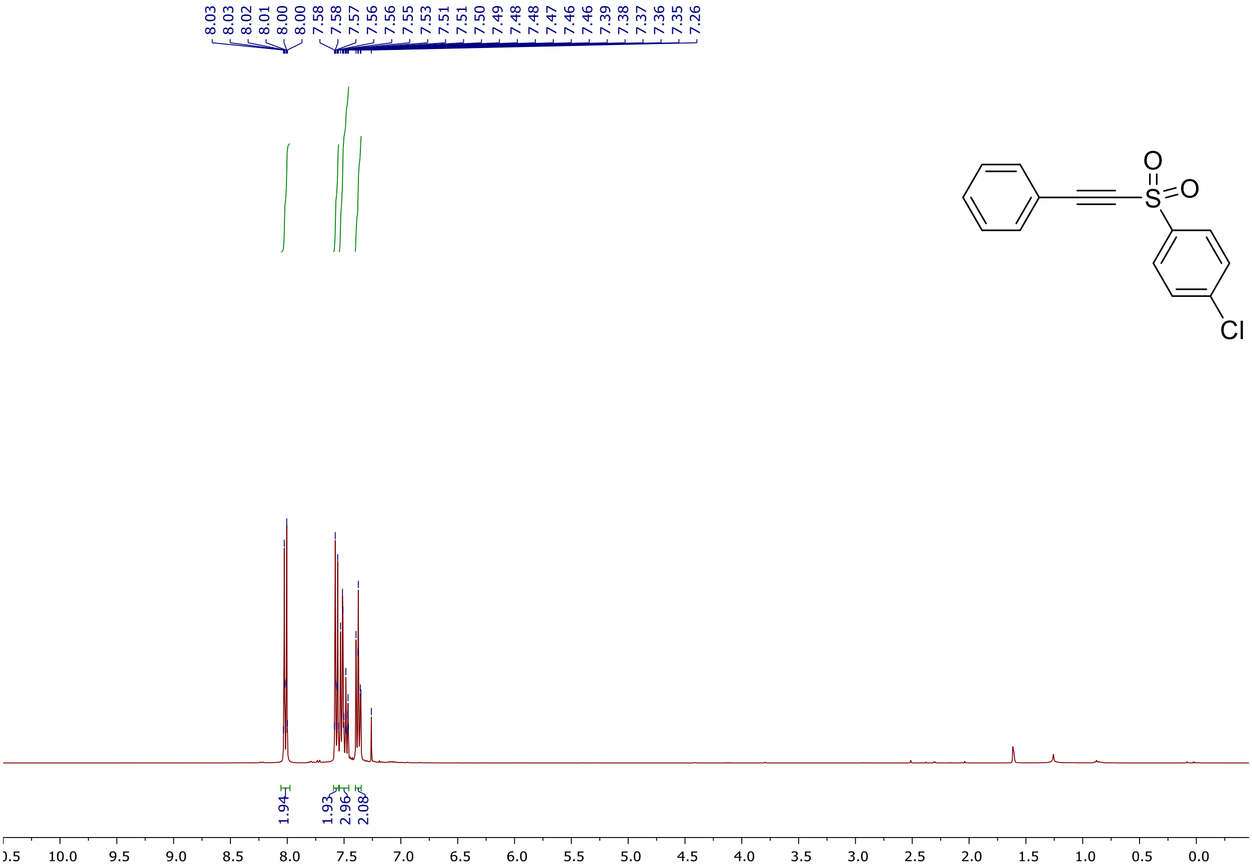
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



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



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



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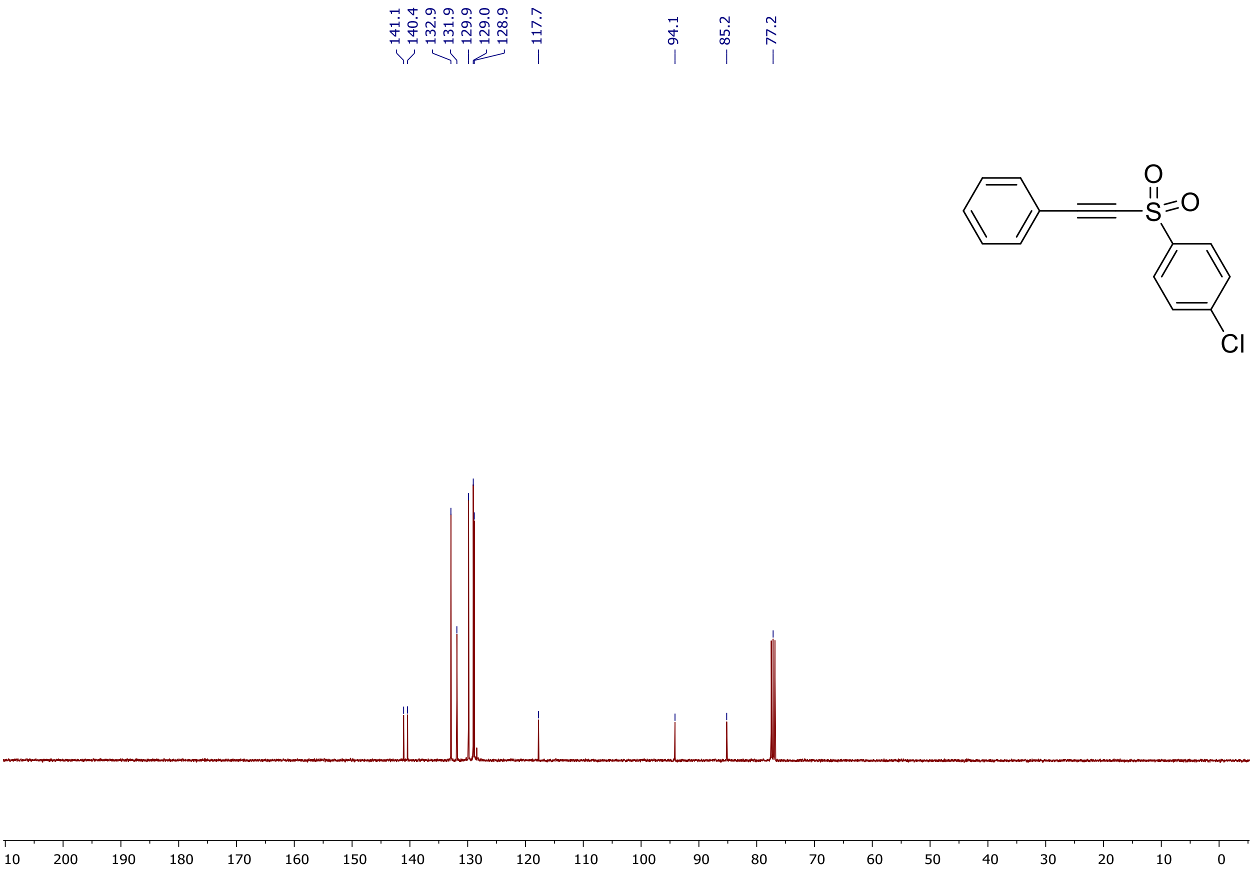

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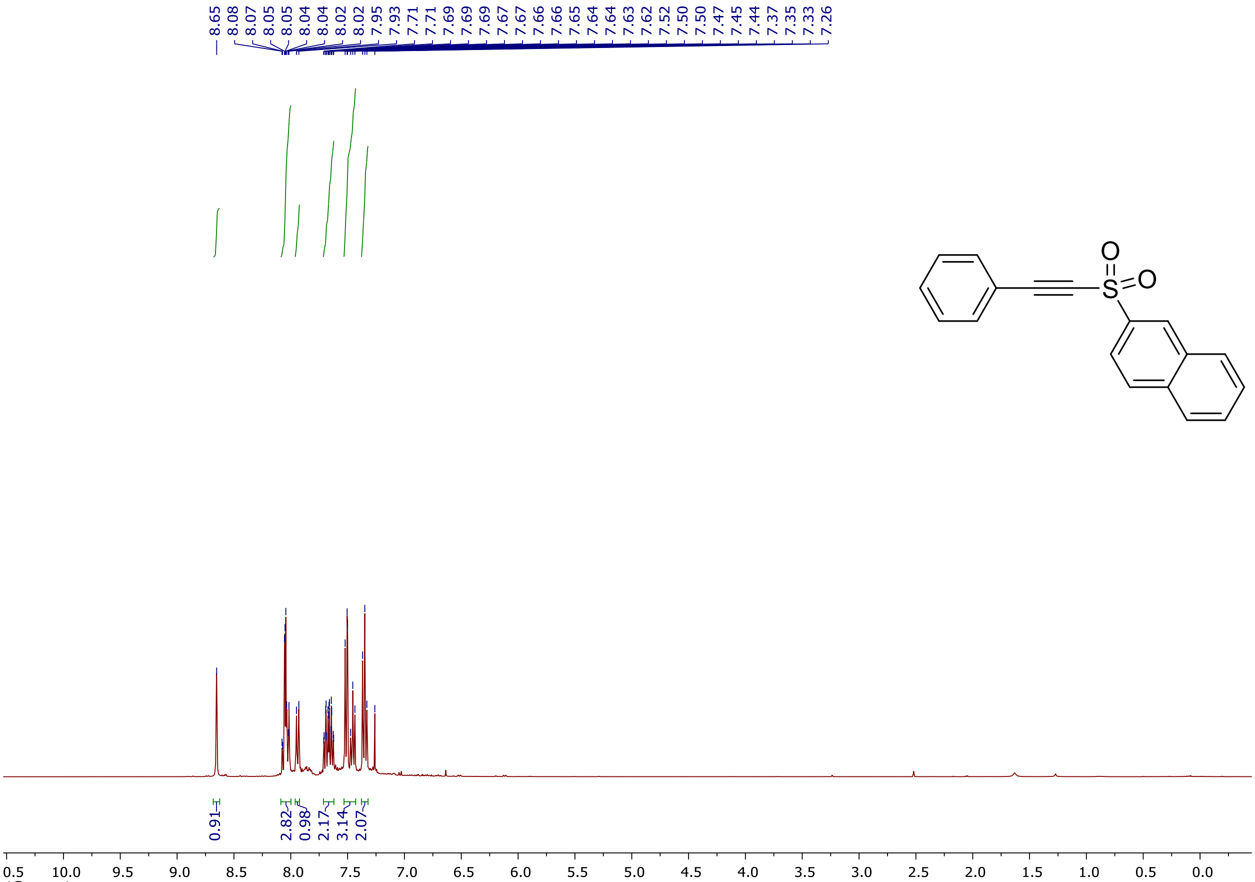
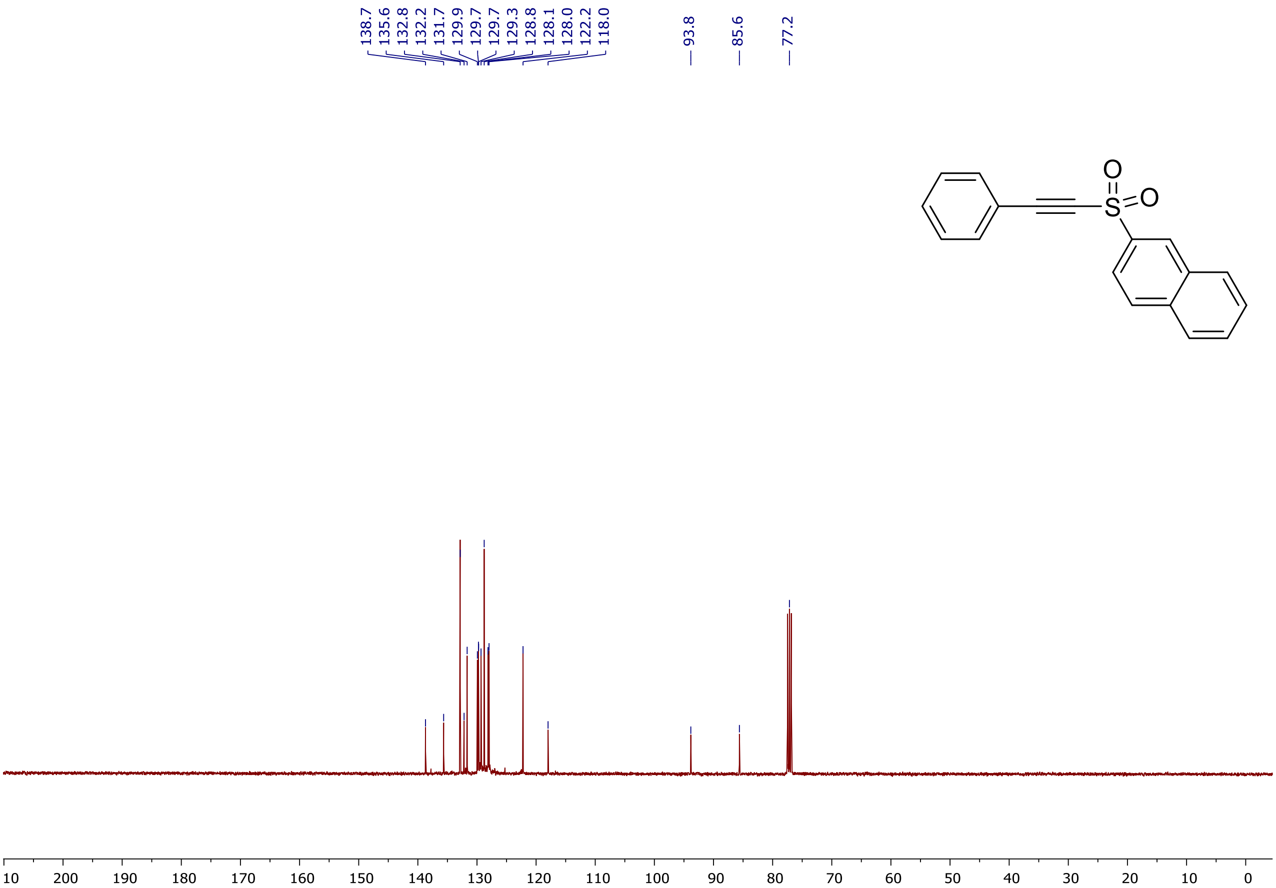


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1g**



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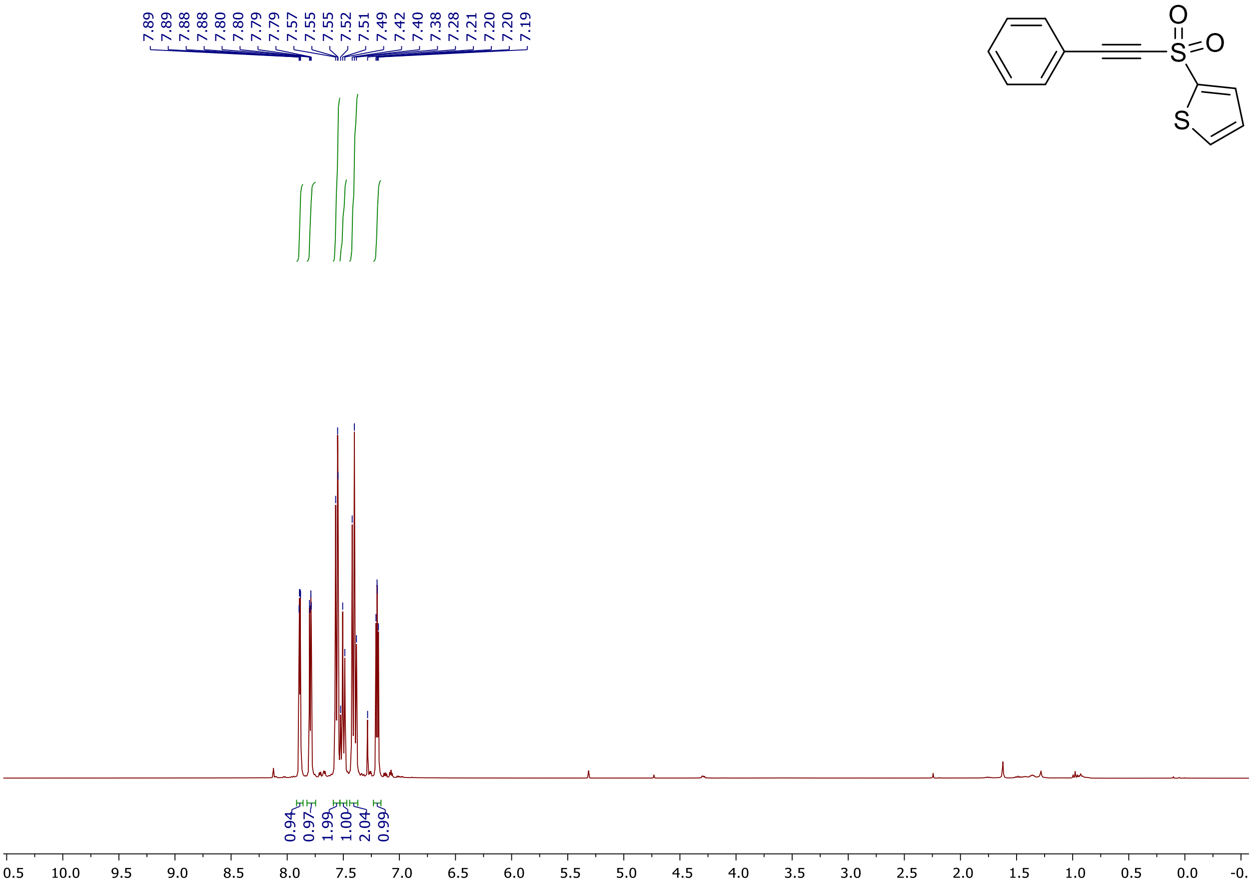
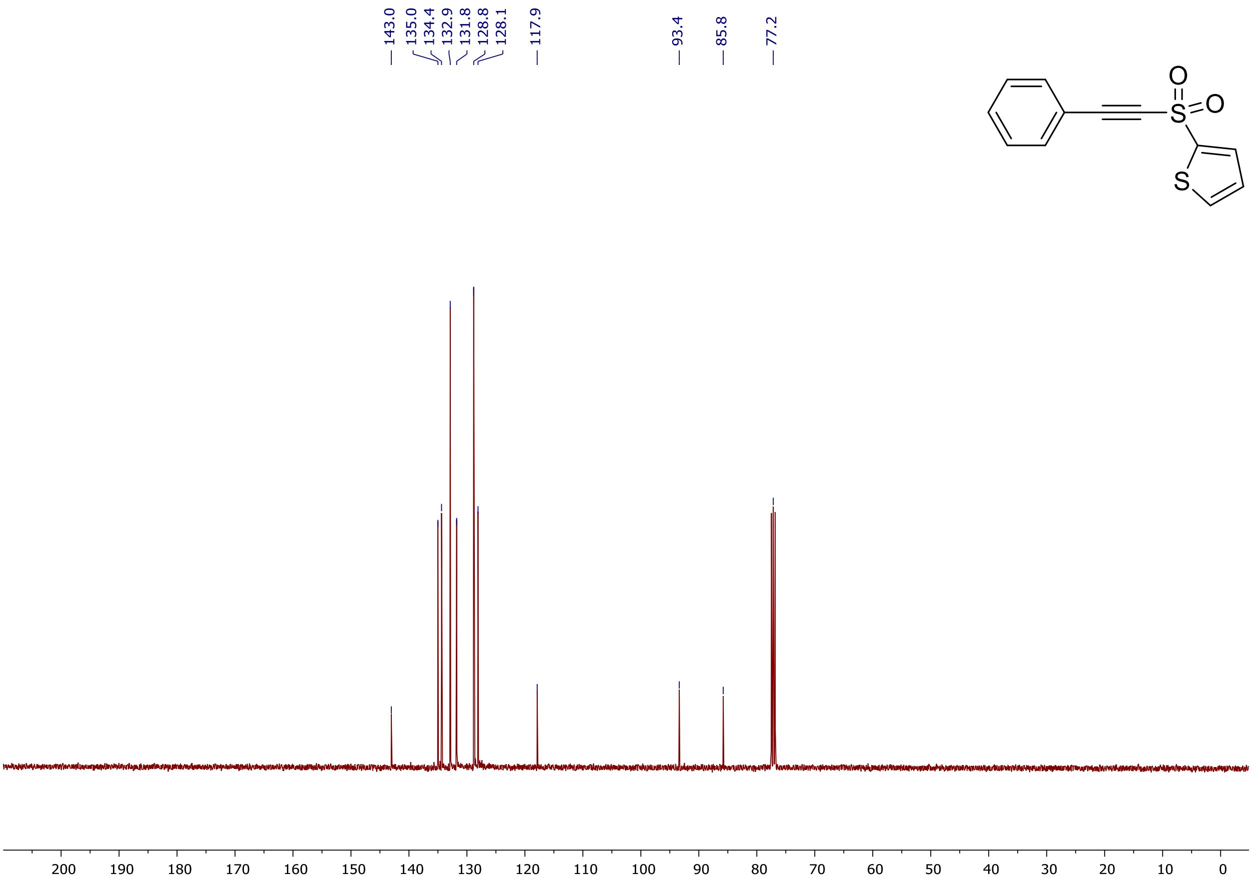
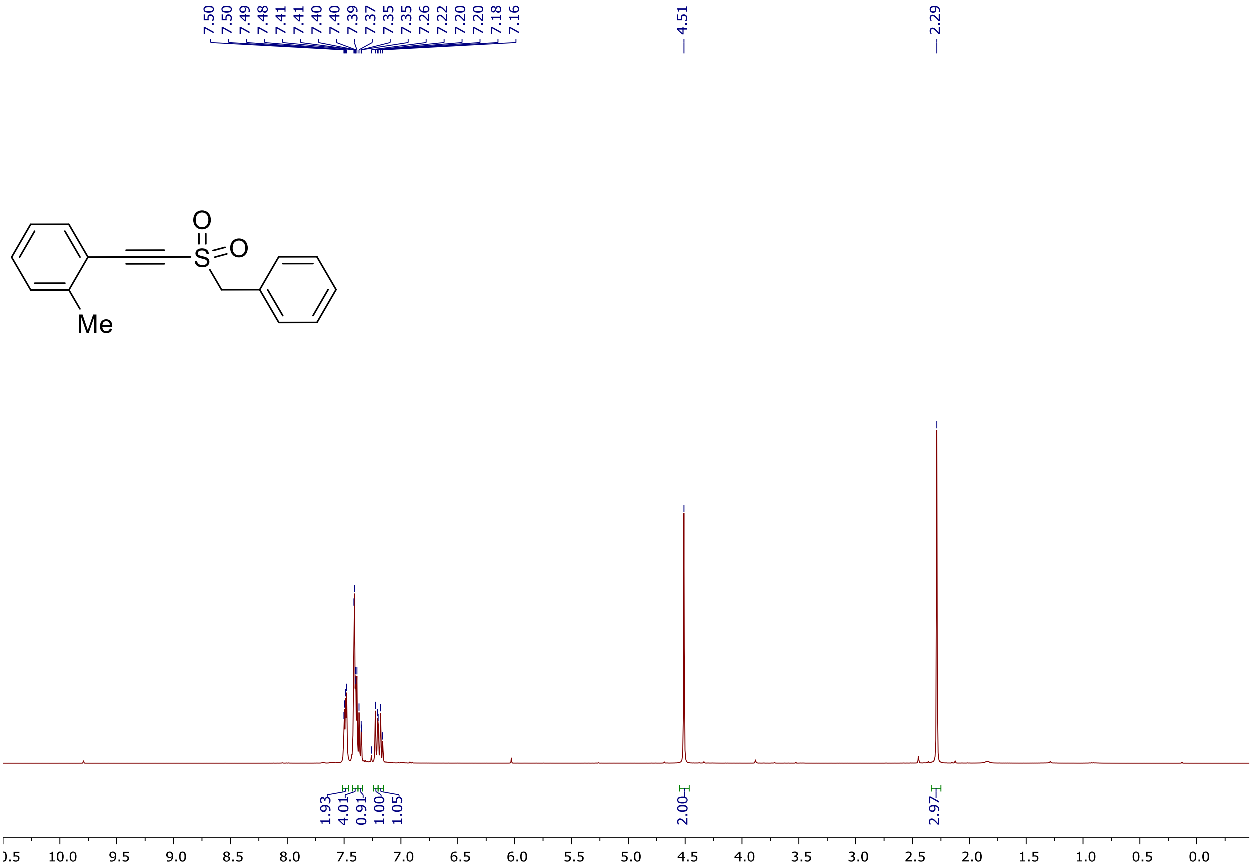


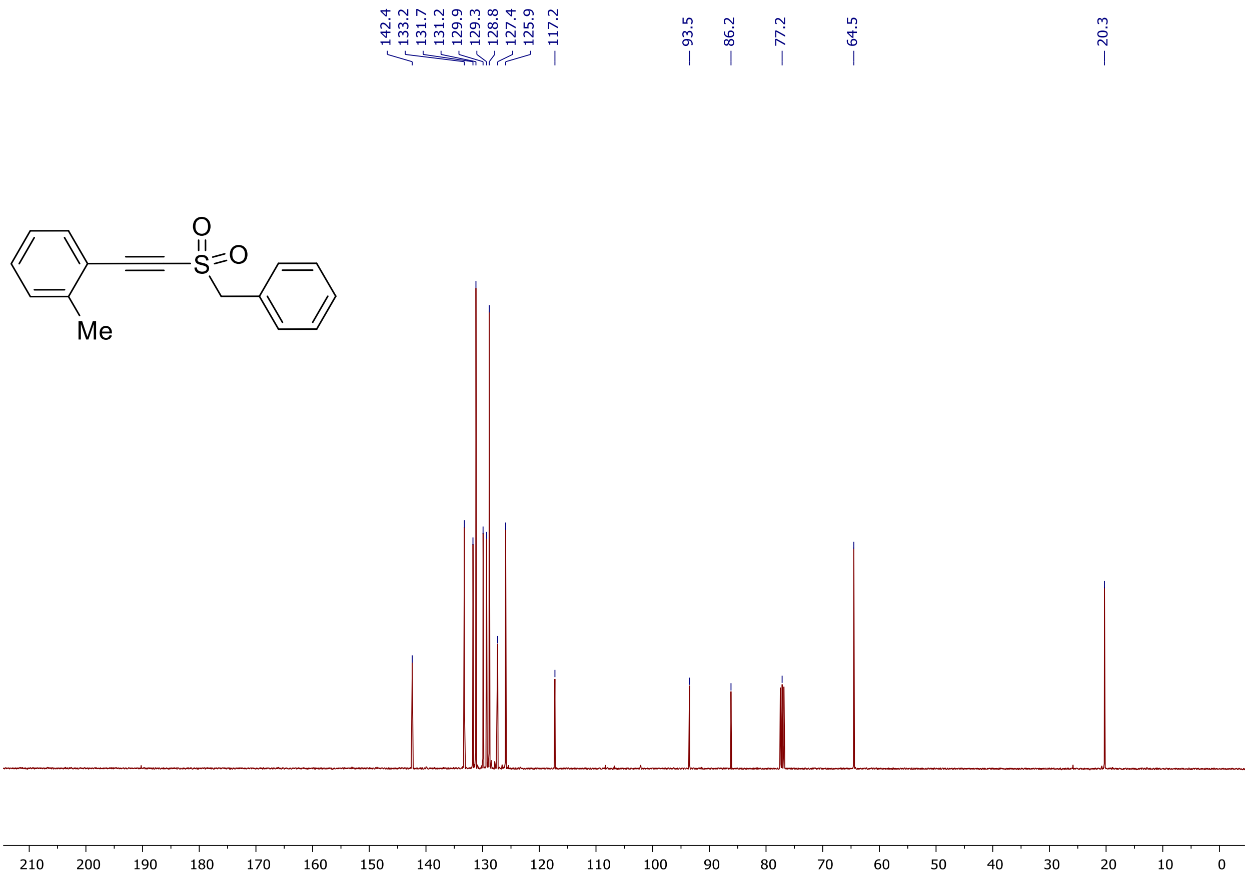
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1v**



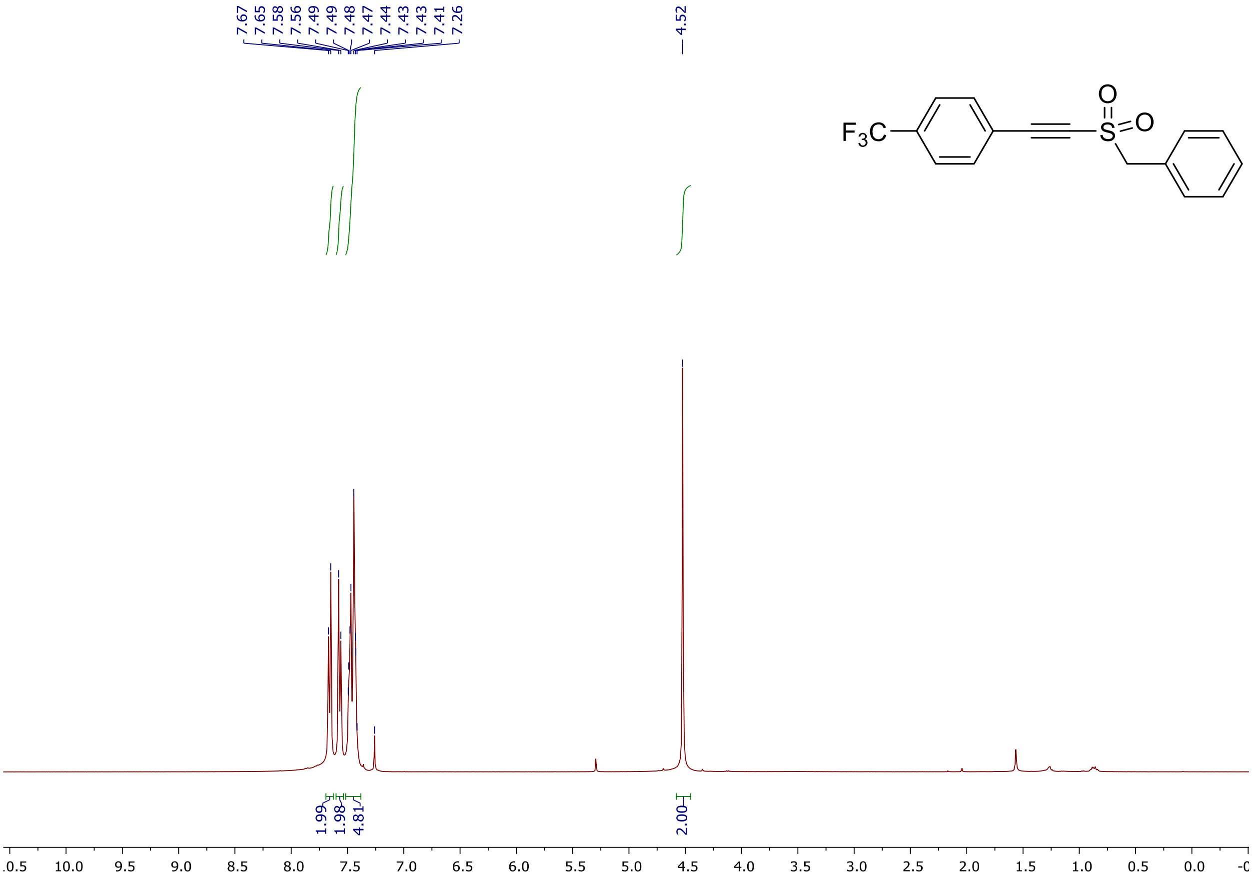
^{1}H NMR (400 MHz, $CDCl_3$) of **1n**



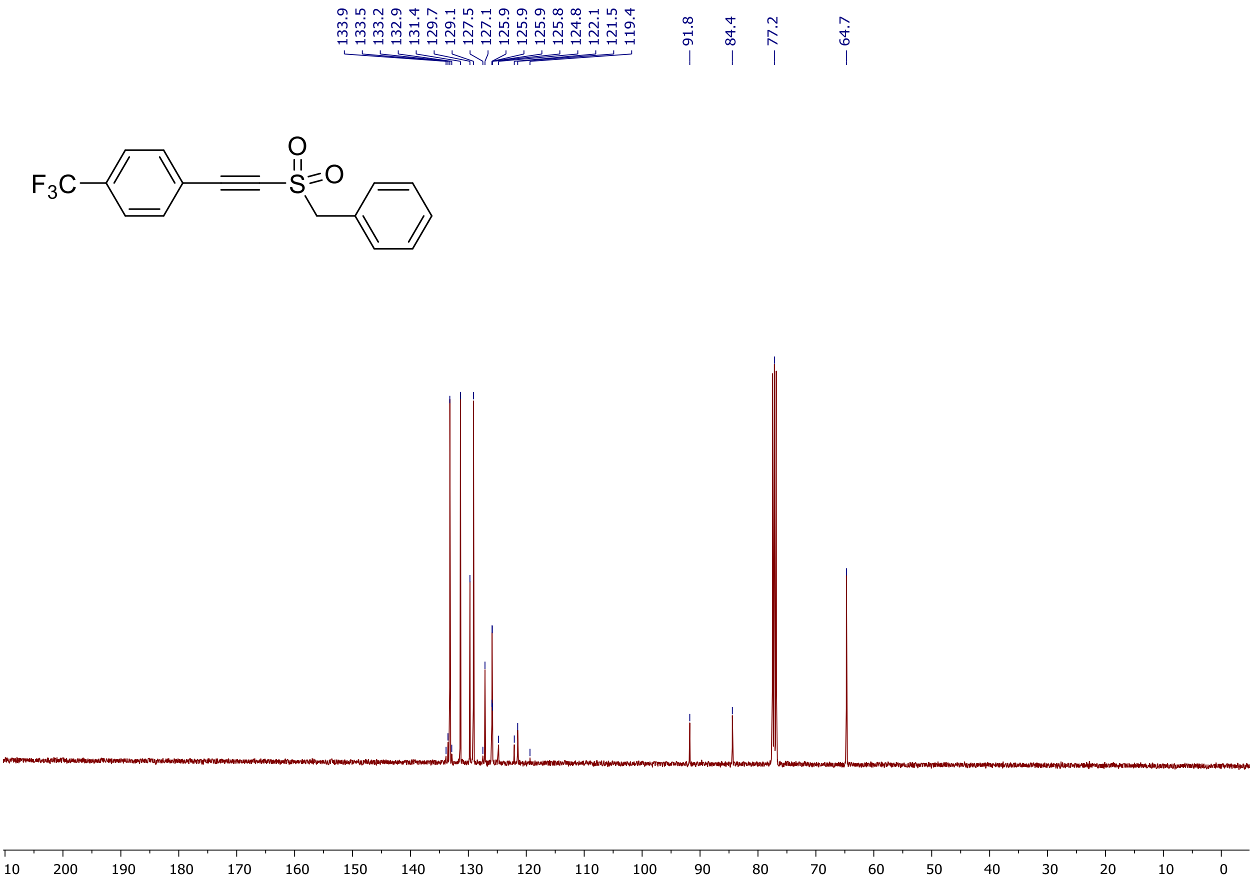
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1n**



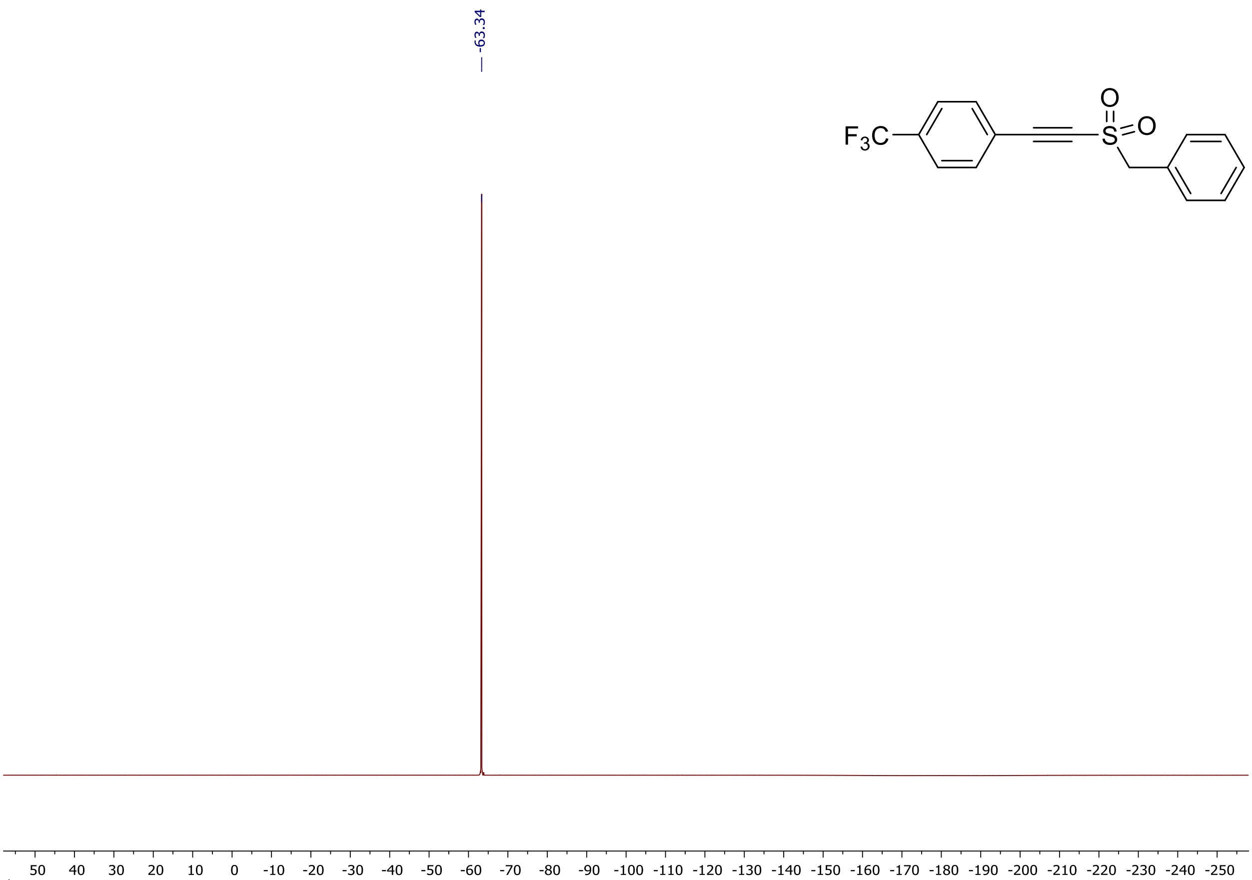
[1]H NMR (400 MHz, $CDCl_3$) of **1o**



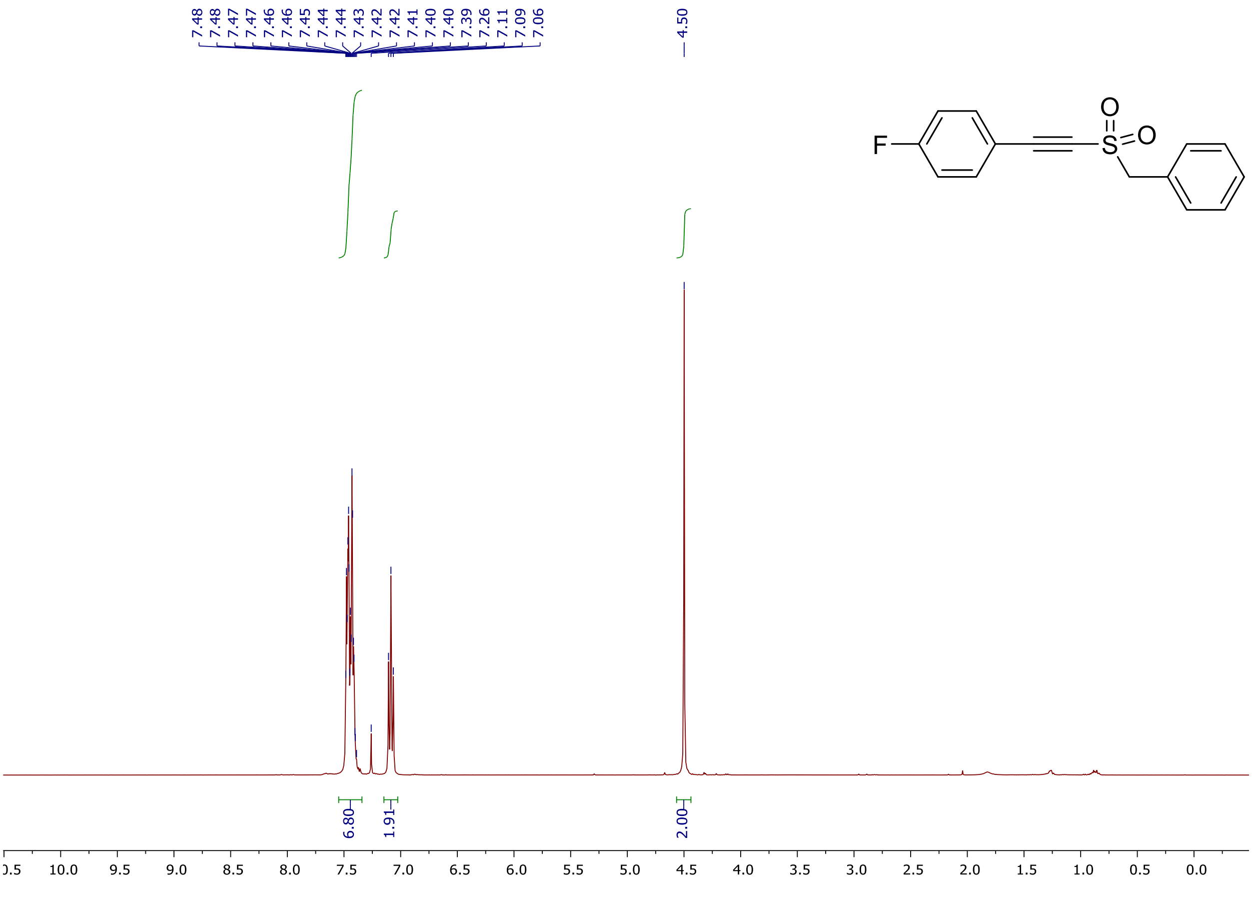
[13]C{[1]H} NMR (100 MHz, $CDCl_3$) of **1o**



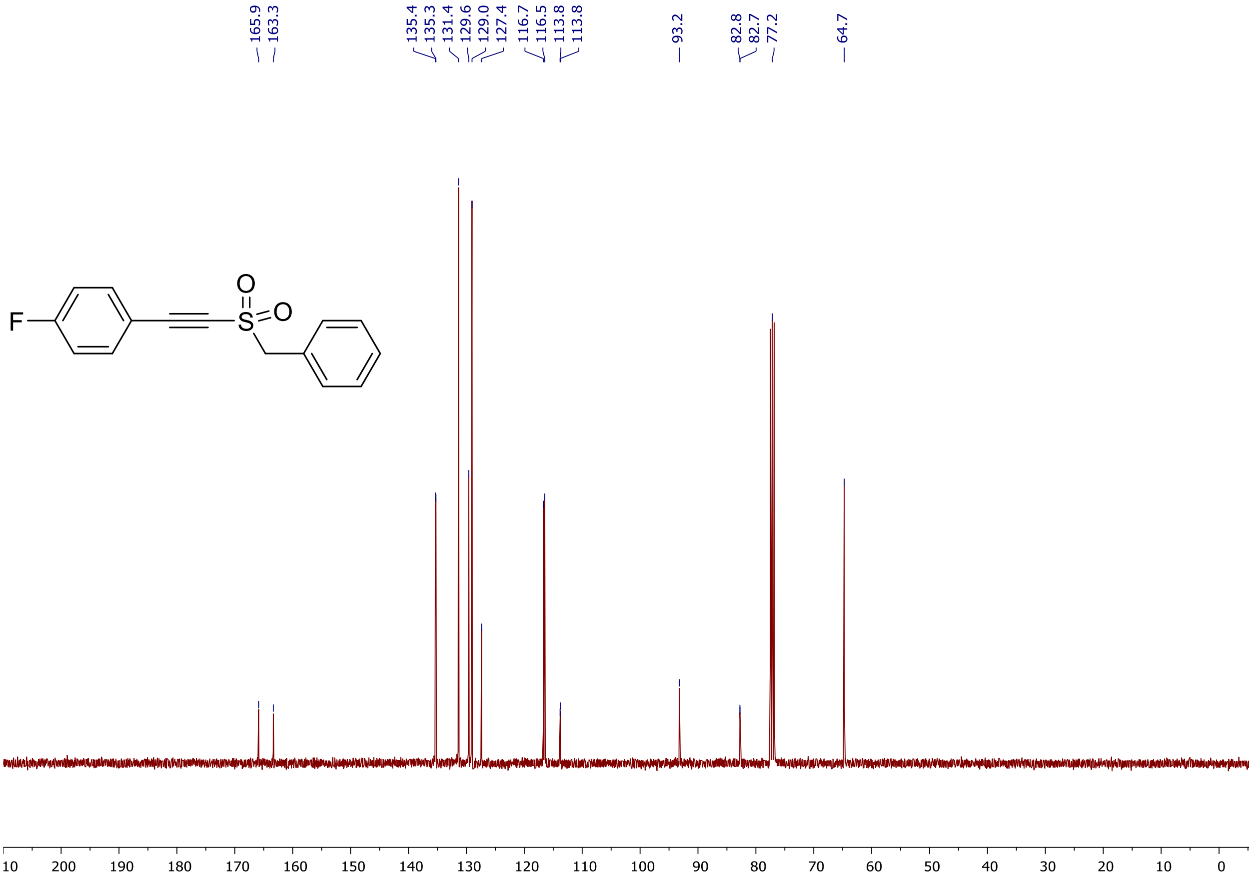
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **1o**



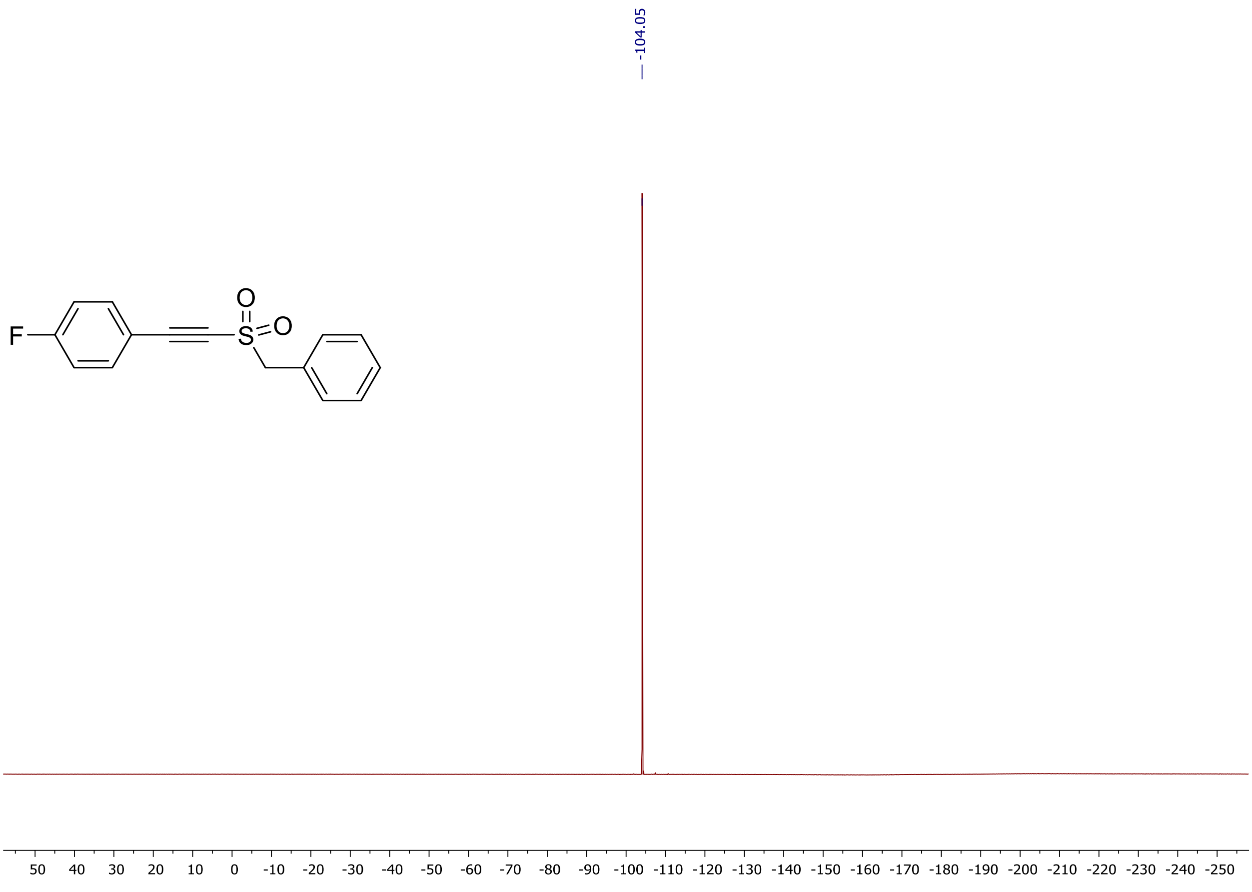
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



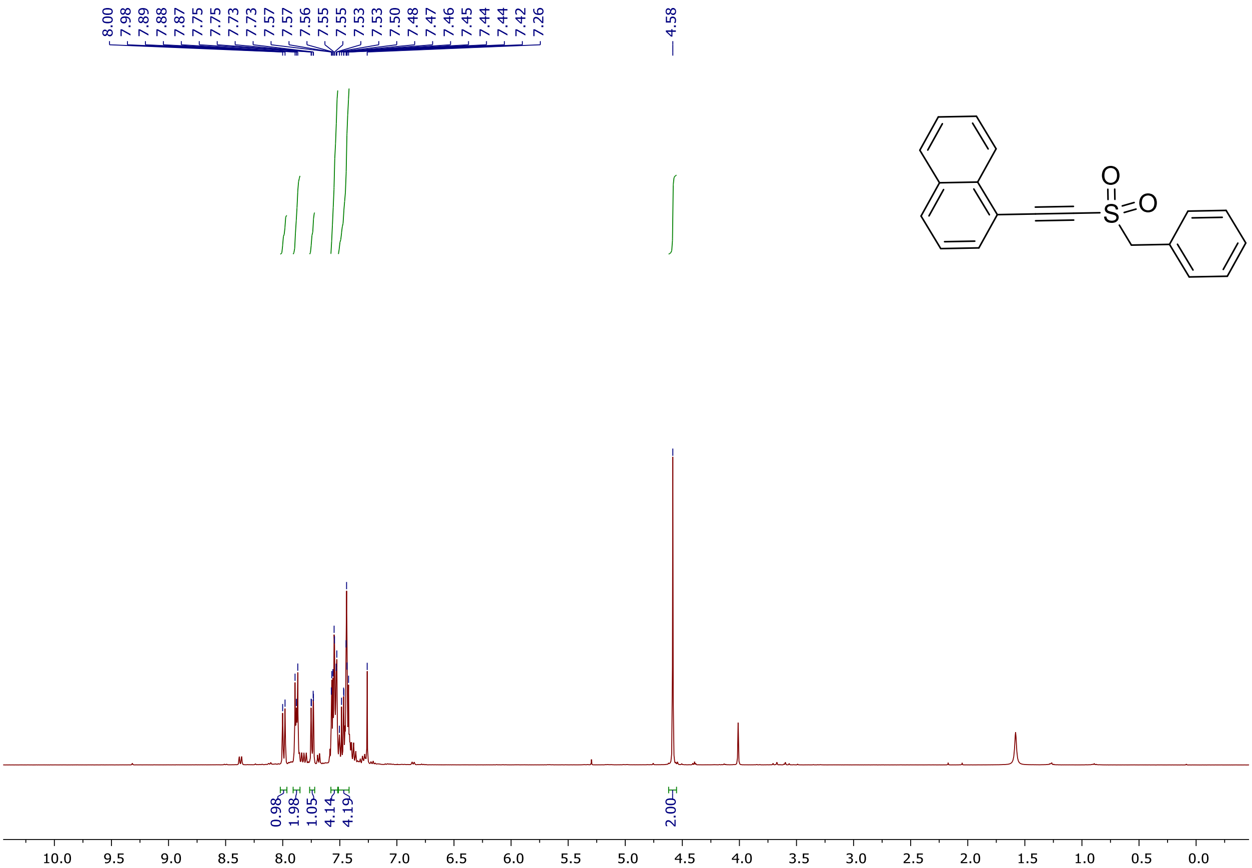
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of **1p**



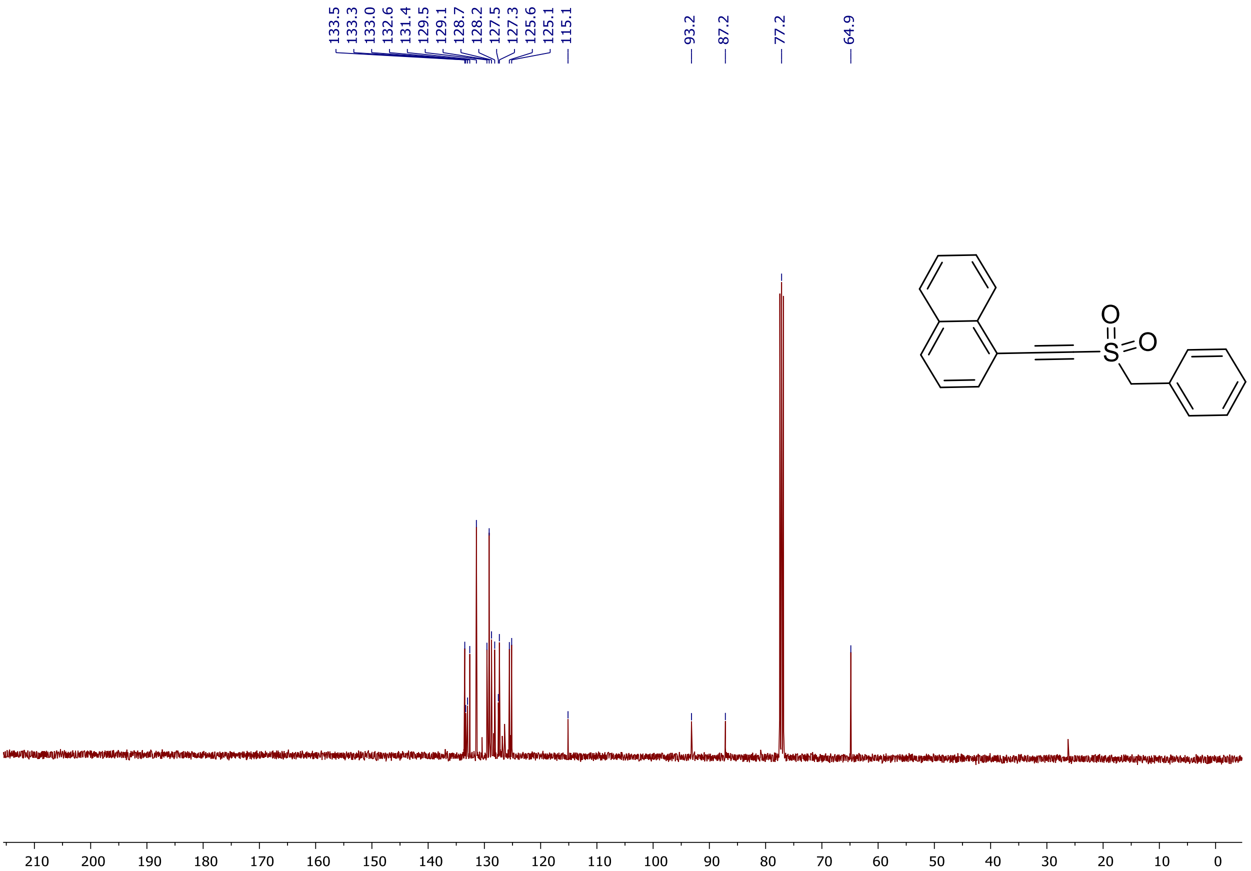
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) of **1p**



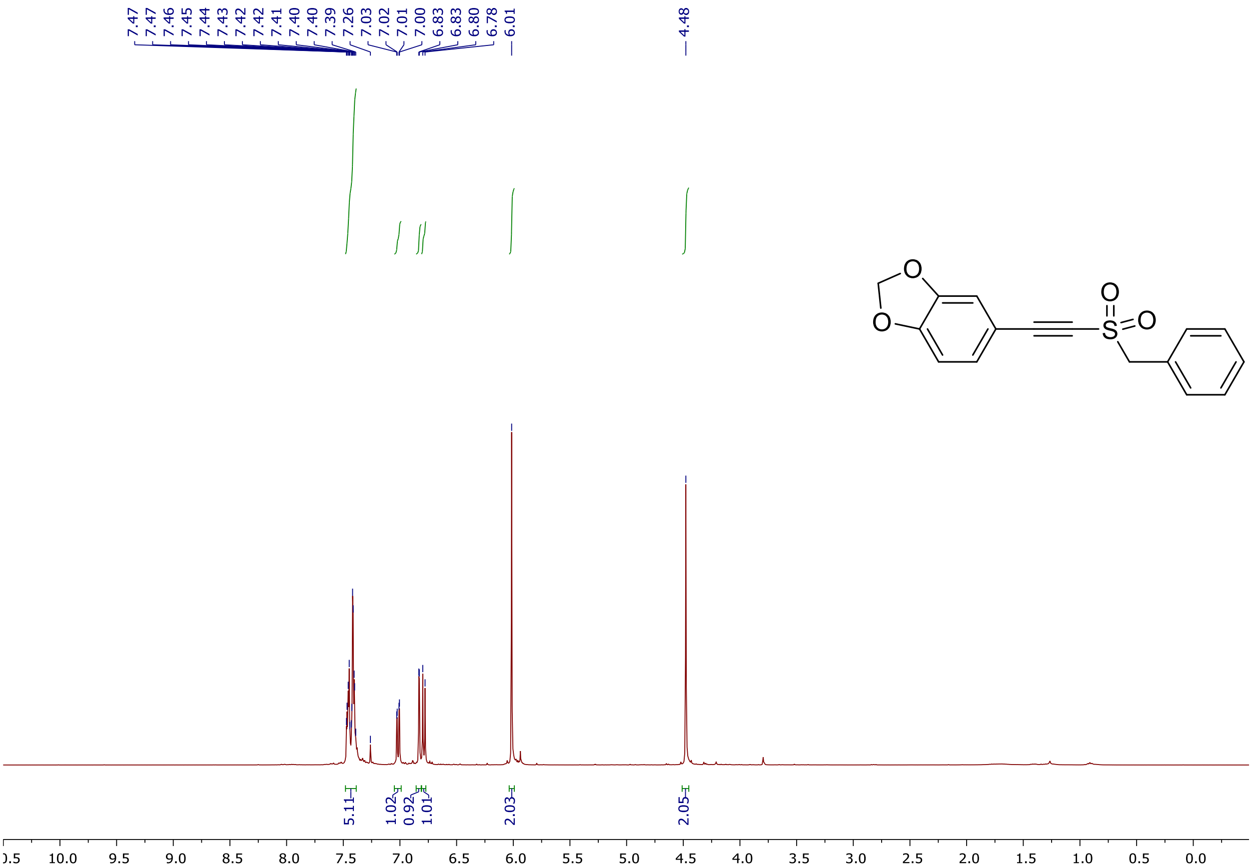
^{1}H NMR (400 MHz, $CDCl_3$) of **1t**



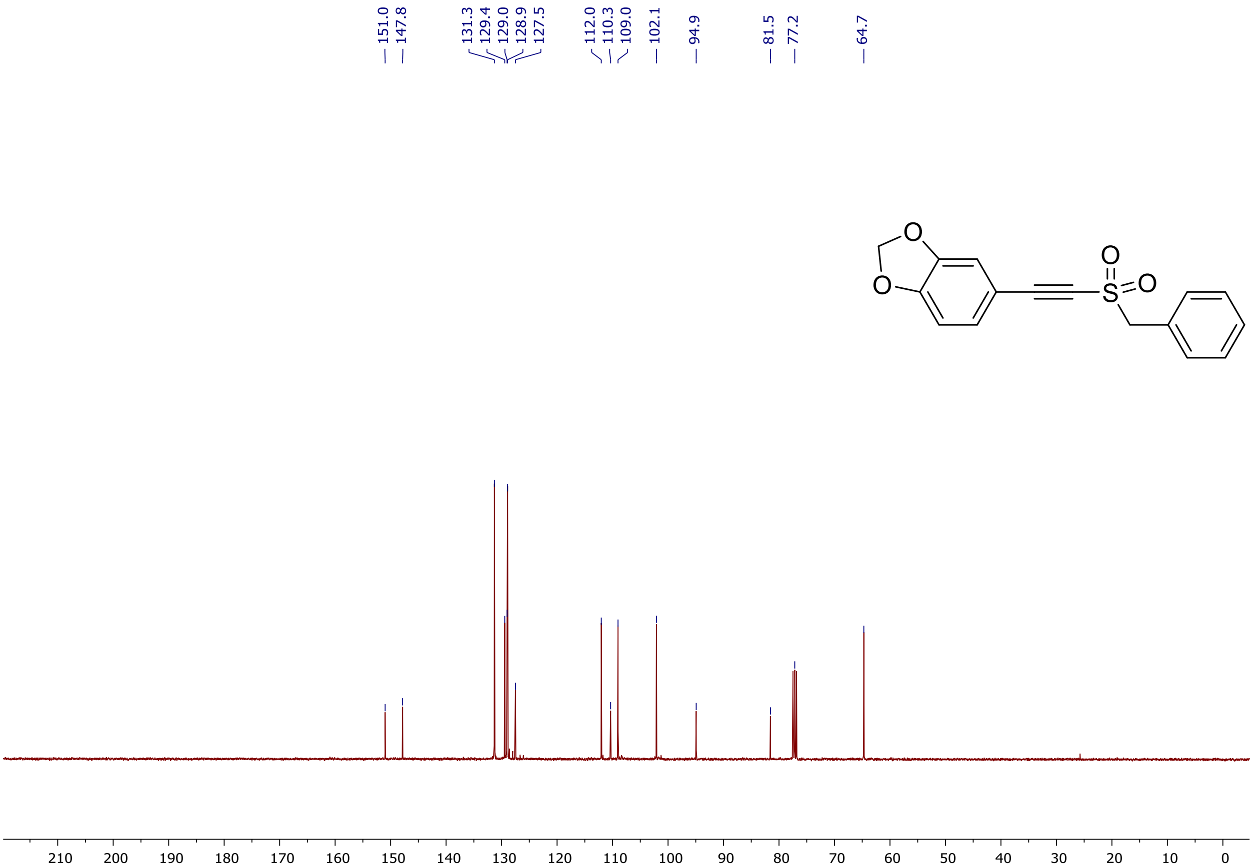
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1t**



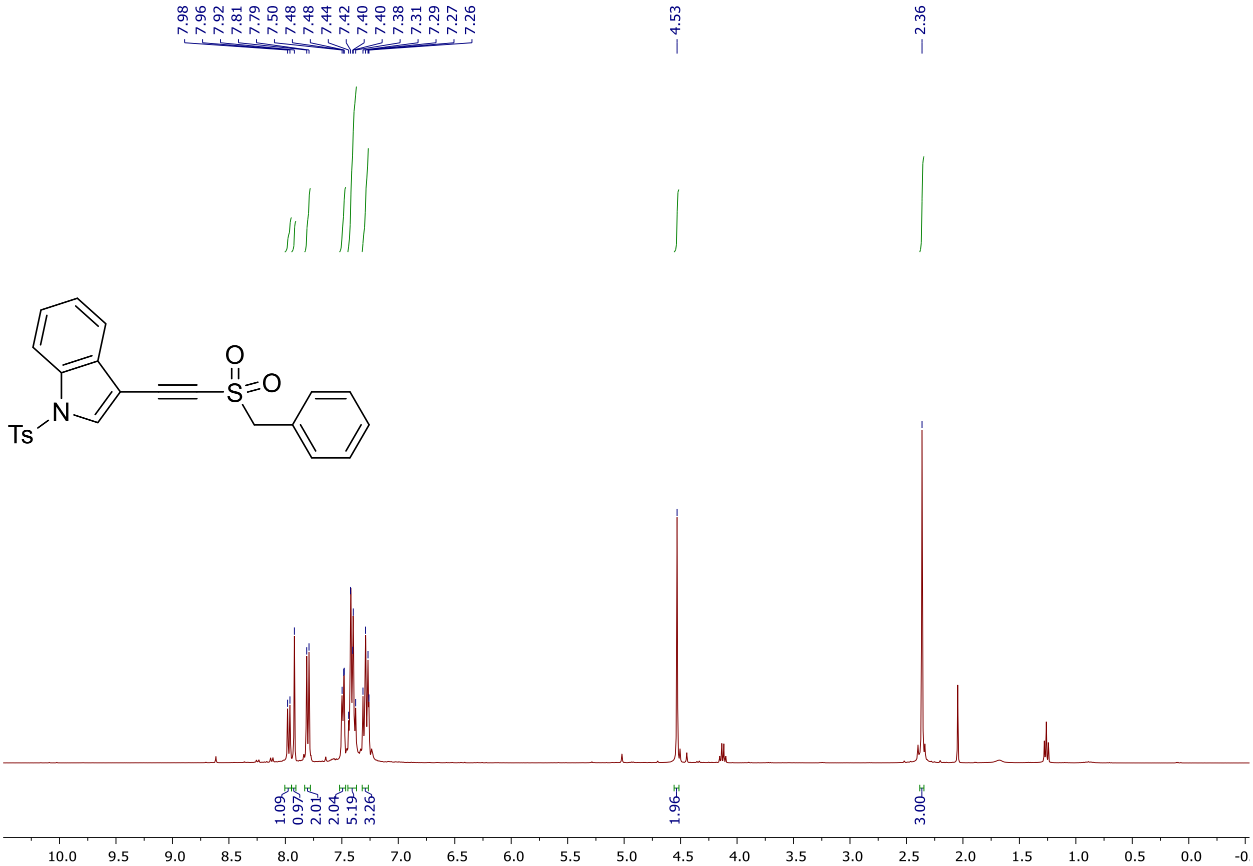
[1]H NMR (400 MHz, $CDCl_3$) of **1w**



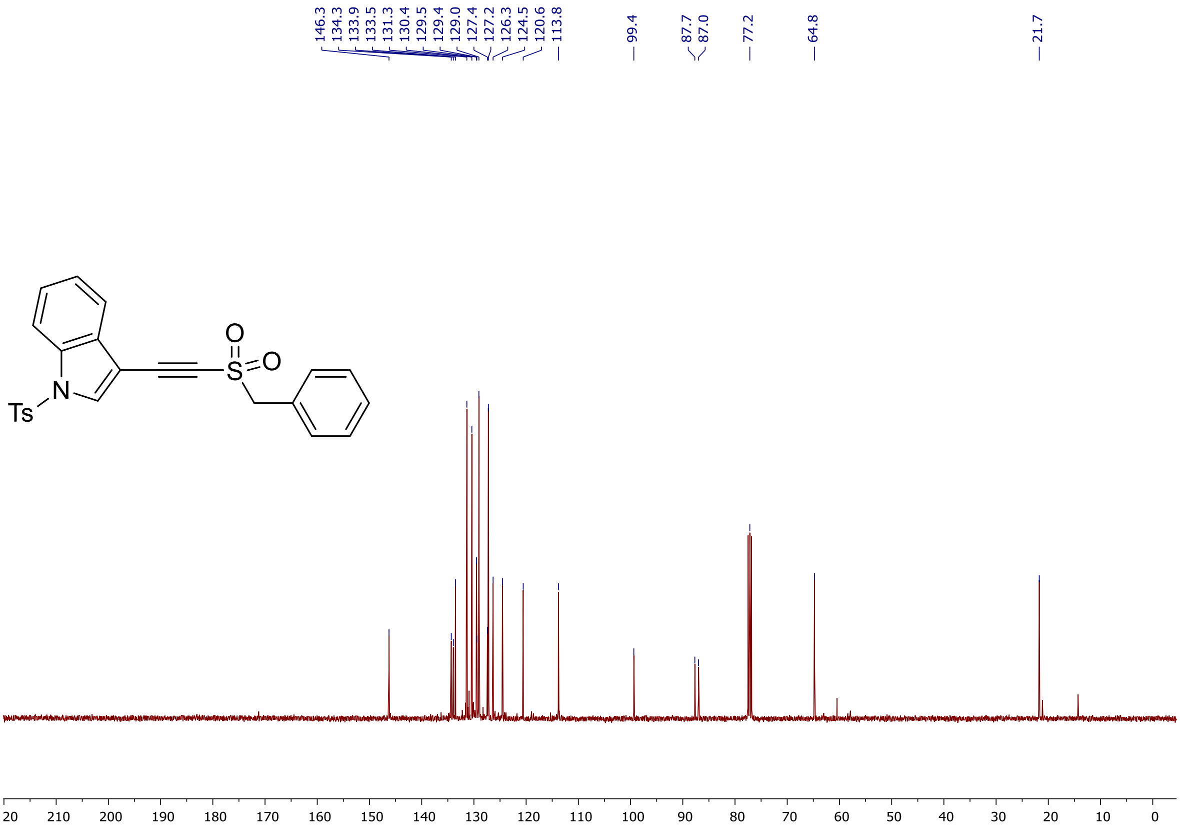
[13]C{[1]H} NMR (100 MHz, $CDCl_3$) of **1w**



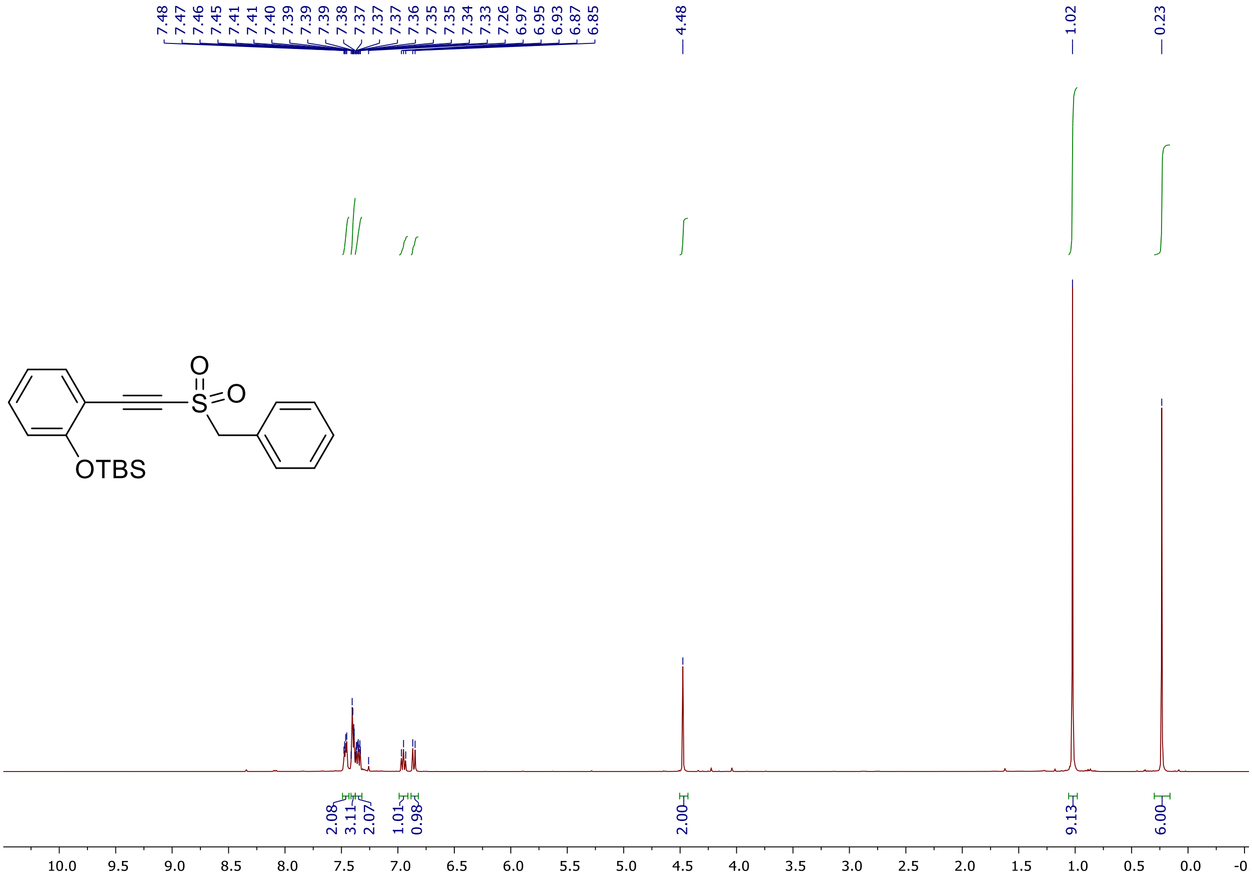
^{1}H NMR (400 MHz, $CDCl_3$) of **1x**



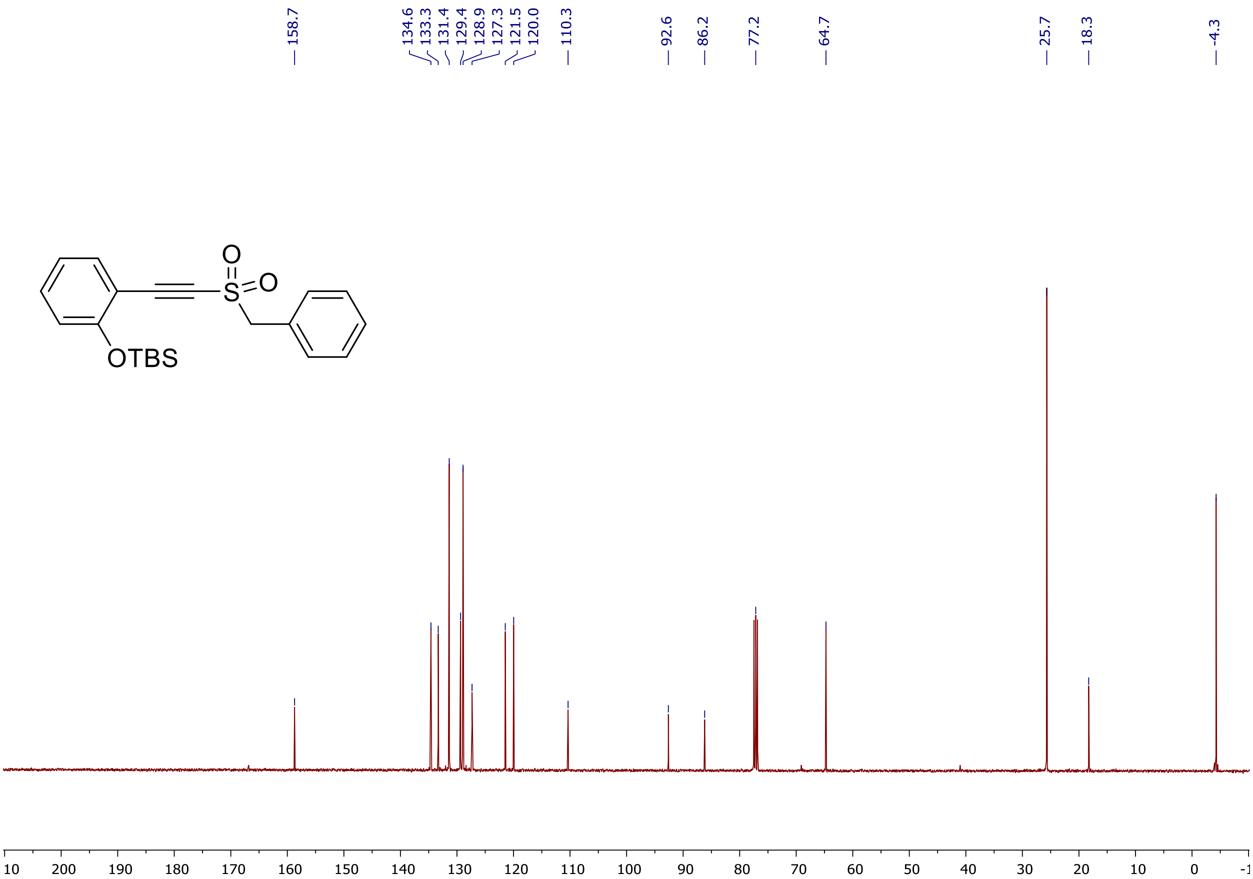
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1x**



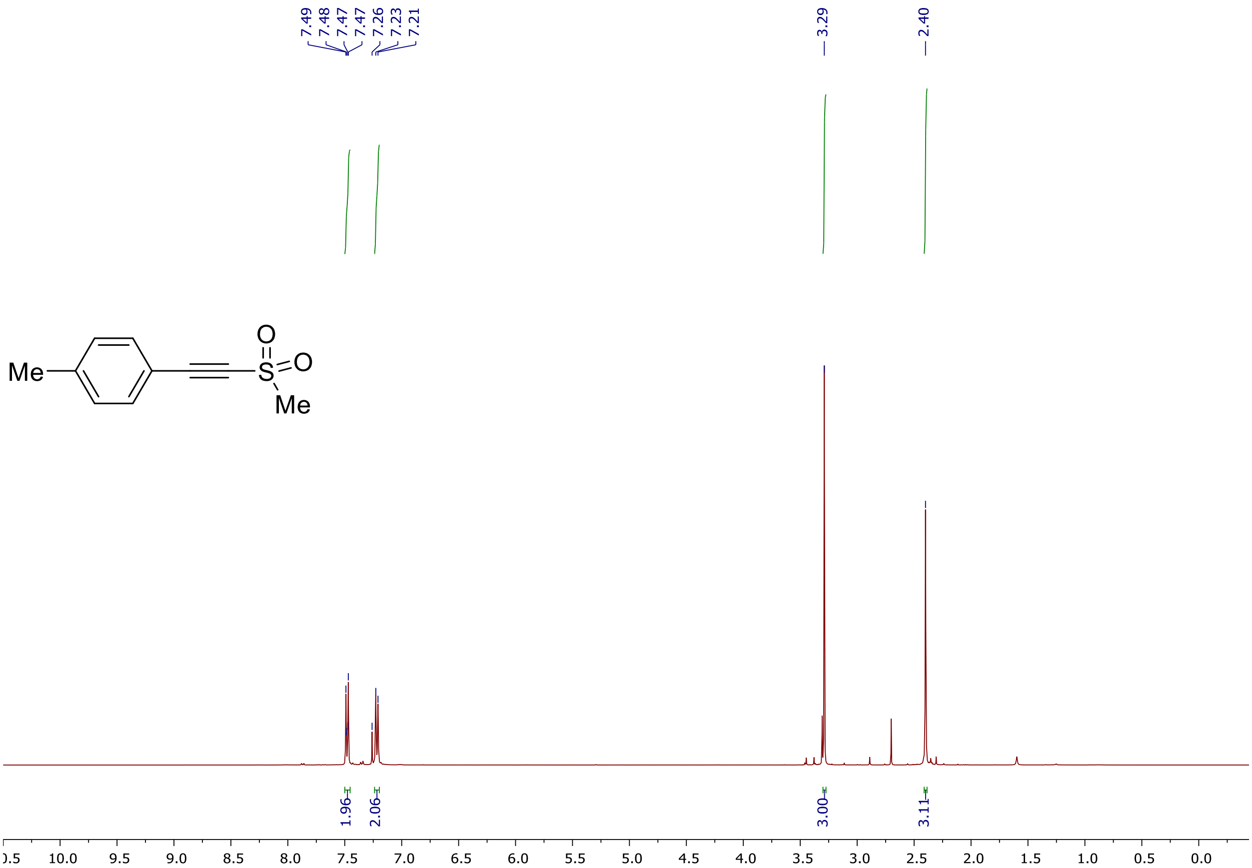
^{1}H NMR (400 MHz, $CDCl_3$) of **1ae**



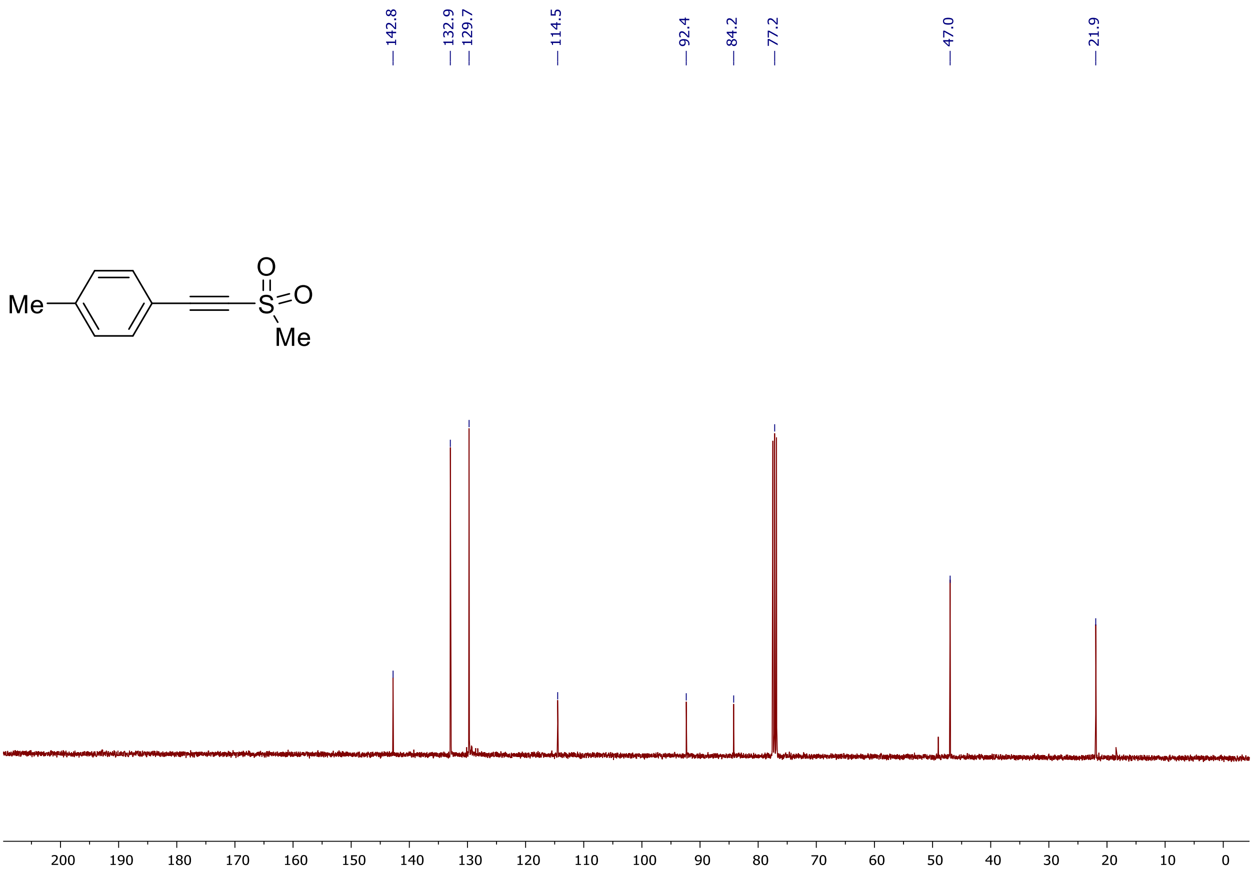
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1ae**



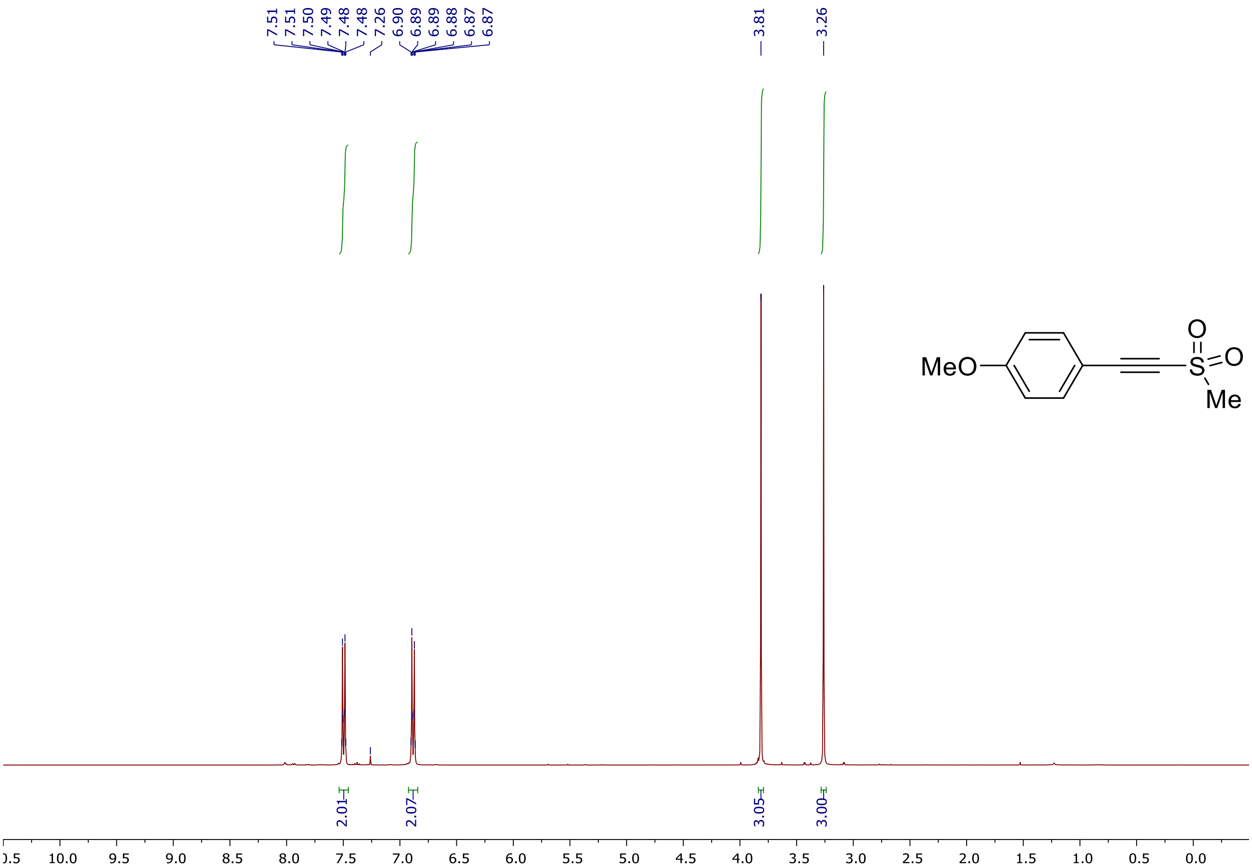
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



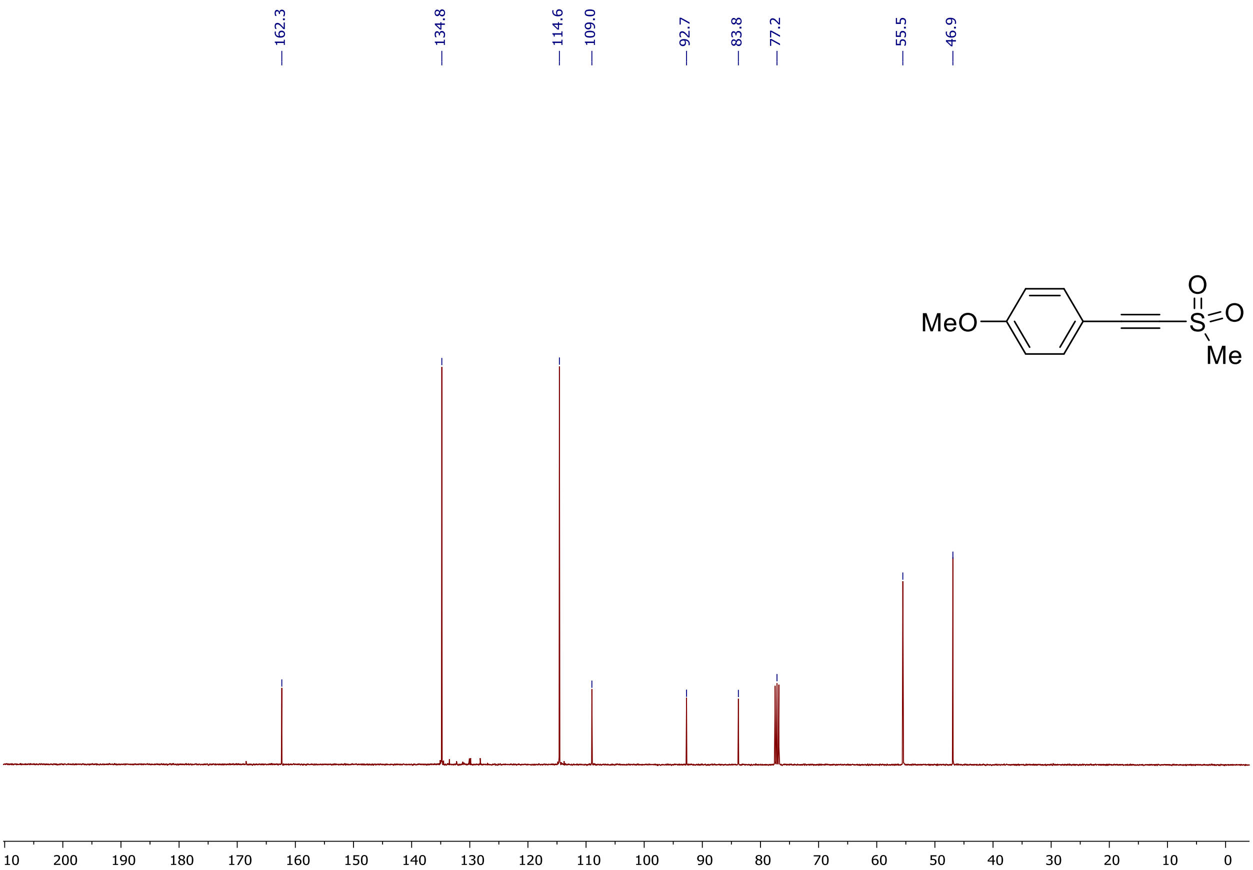
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1l**



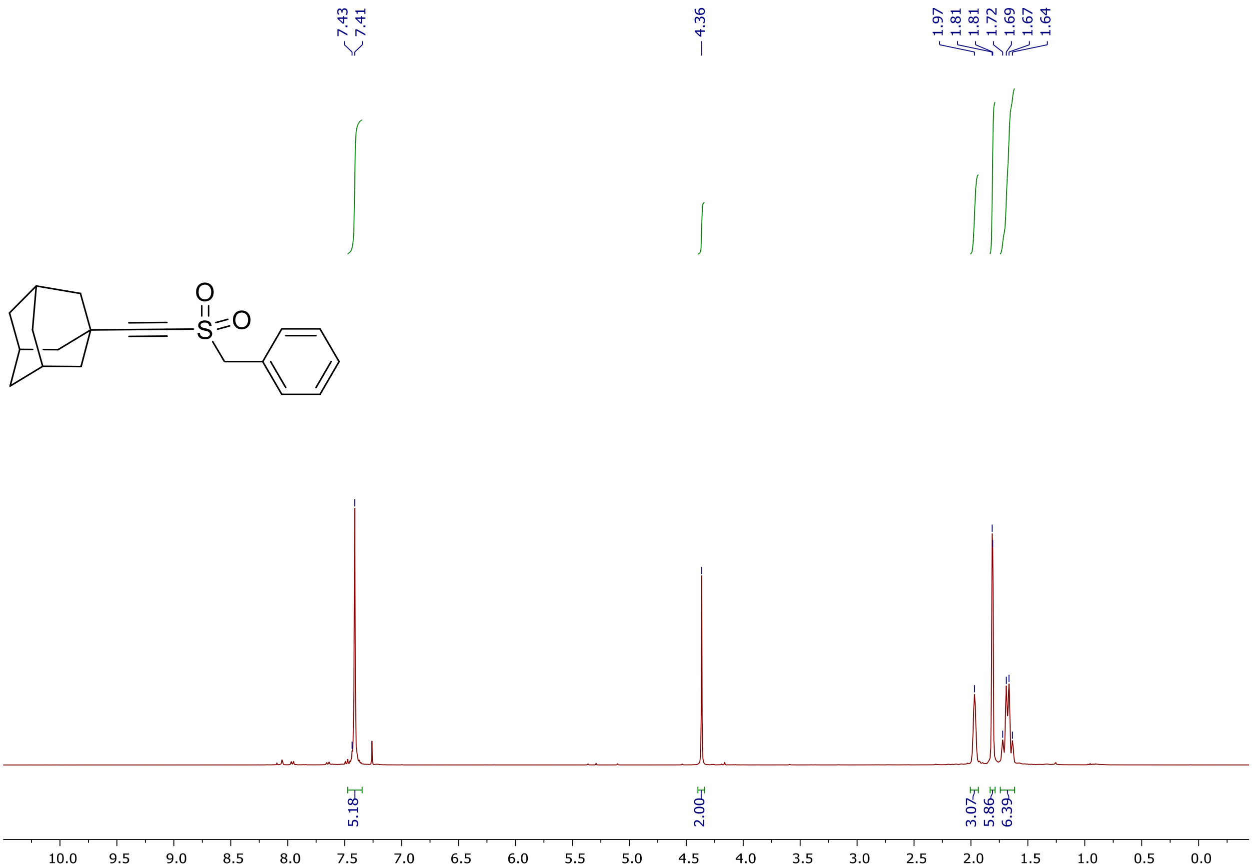
^{1}H NMR (400 MHz, $CDCl_3$) of **1m**



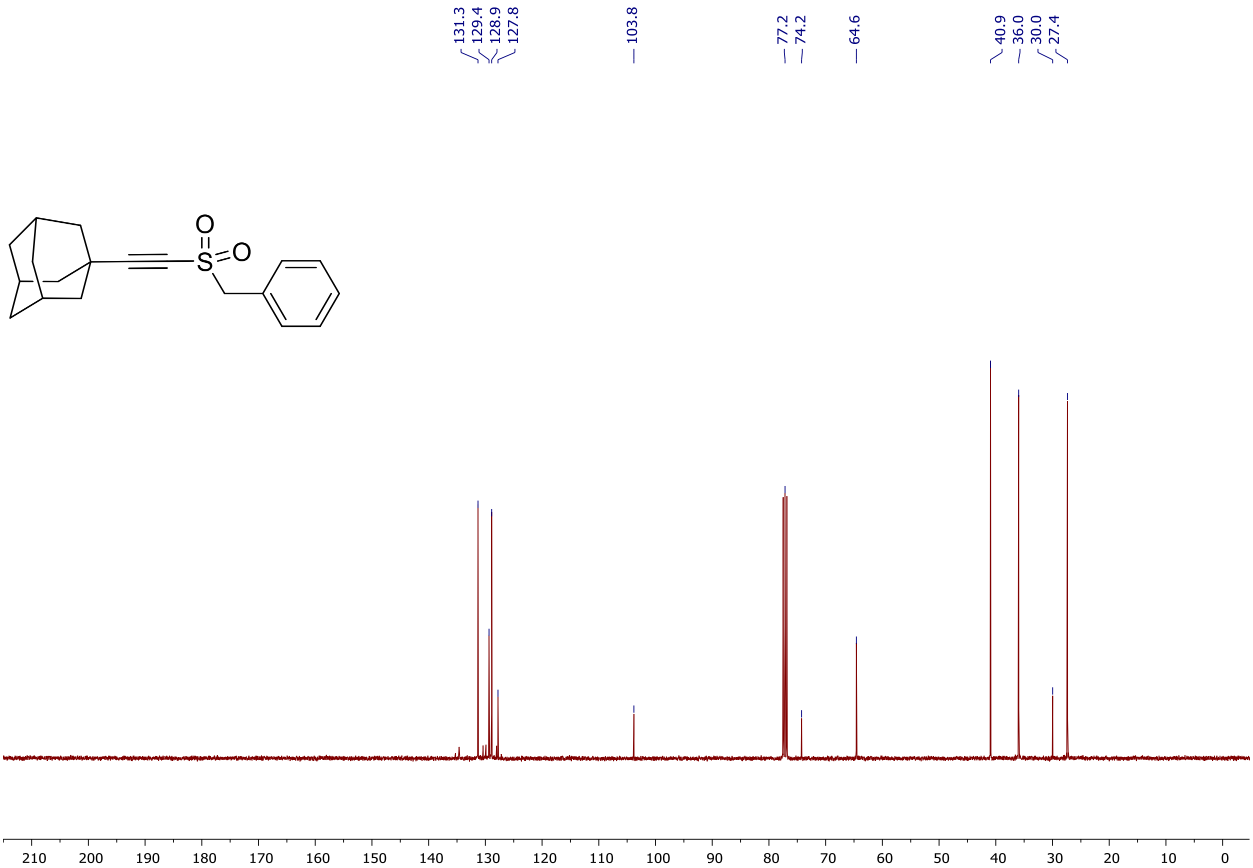
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1m**



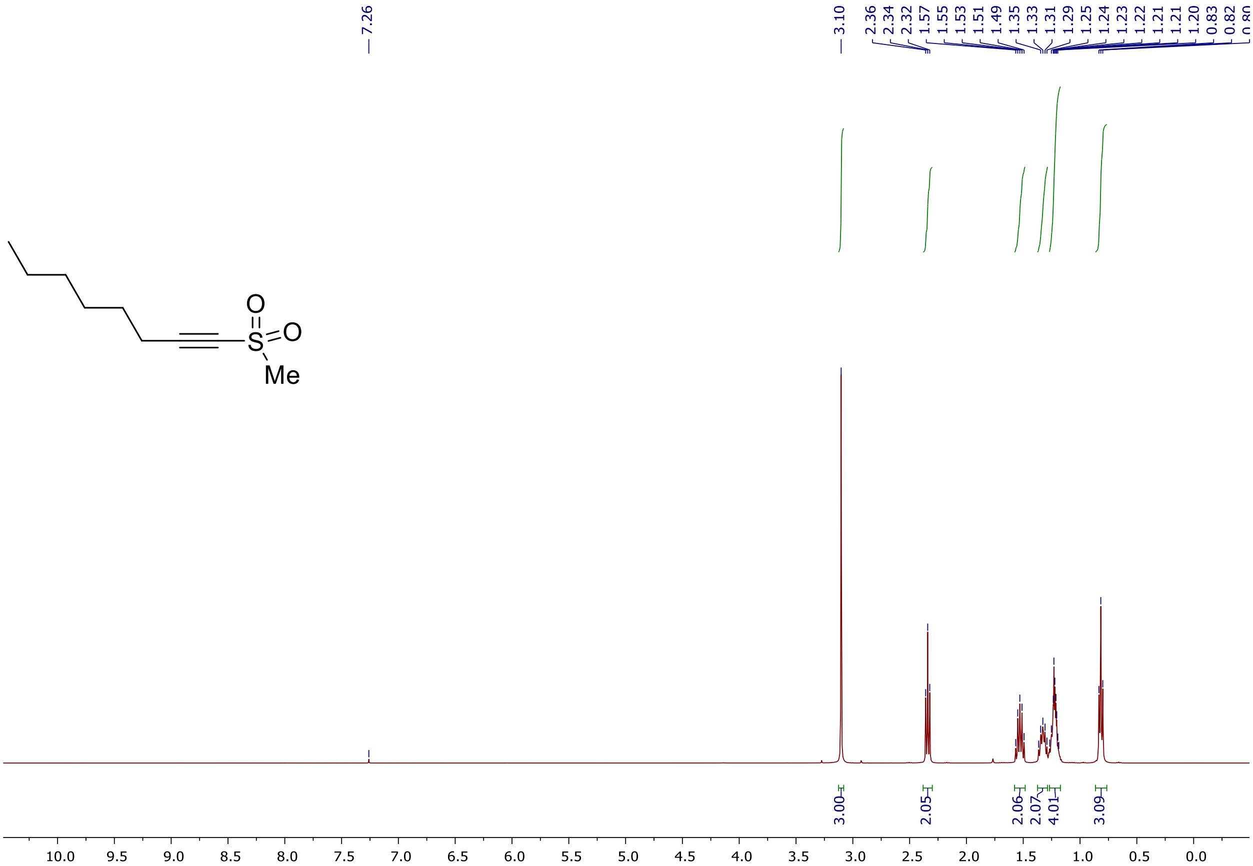
^{1}H NMR (400 MHz, $CDCl_3$) of **1u**



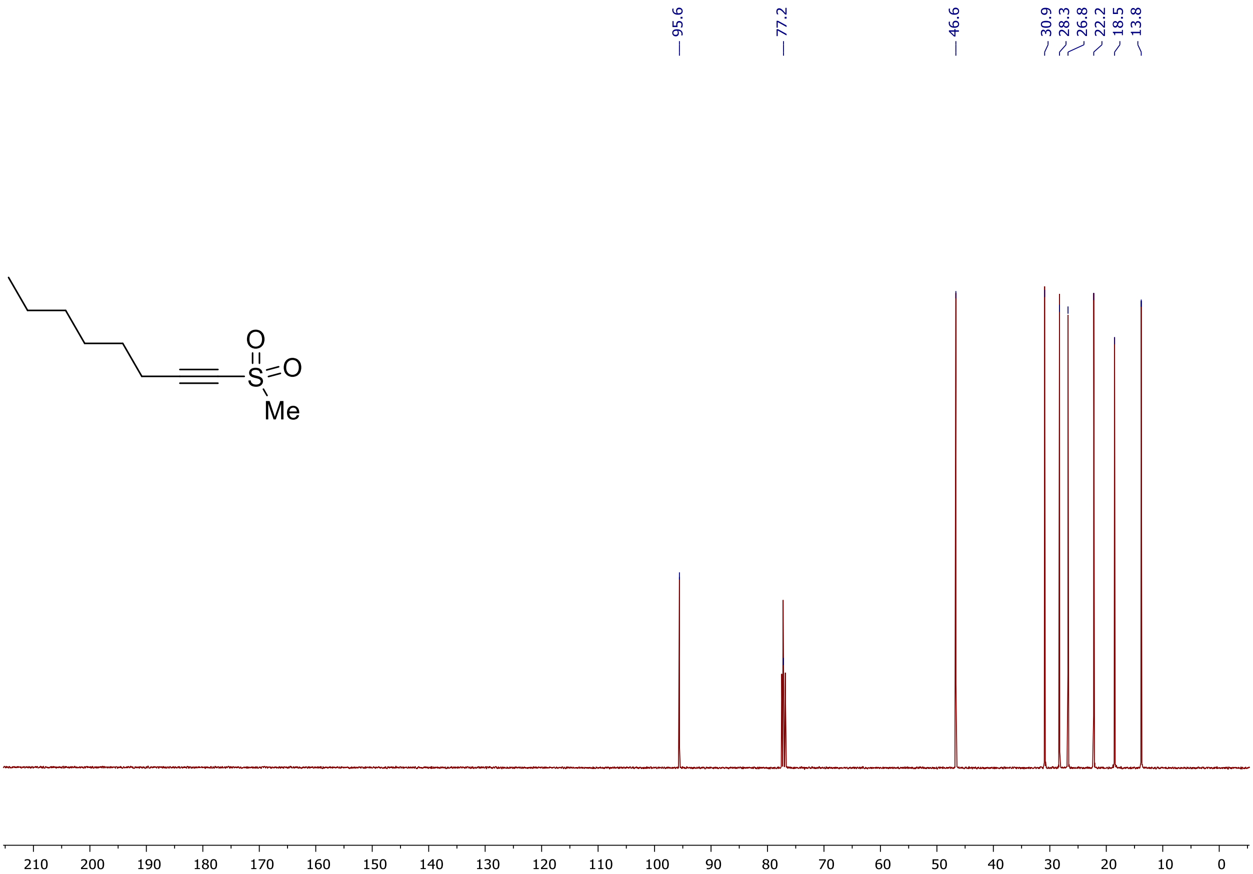
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1u**



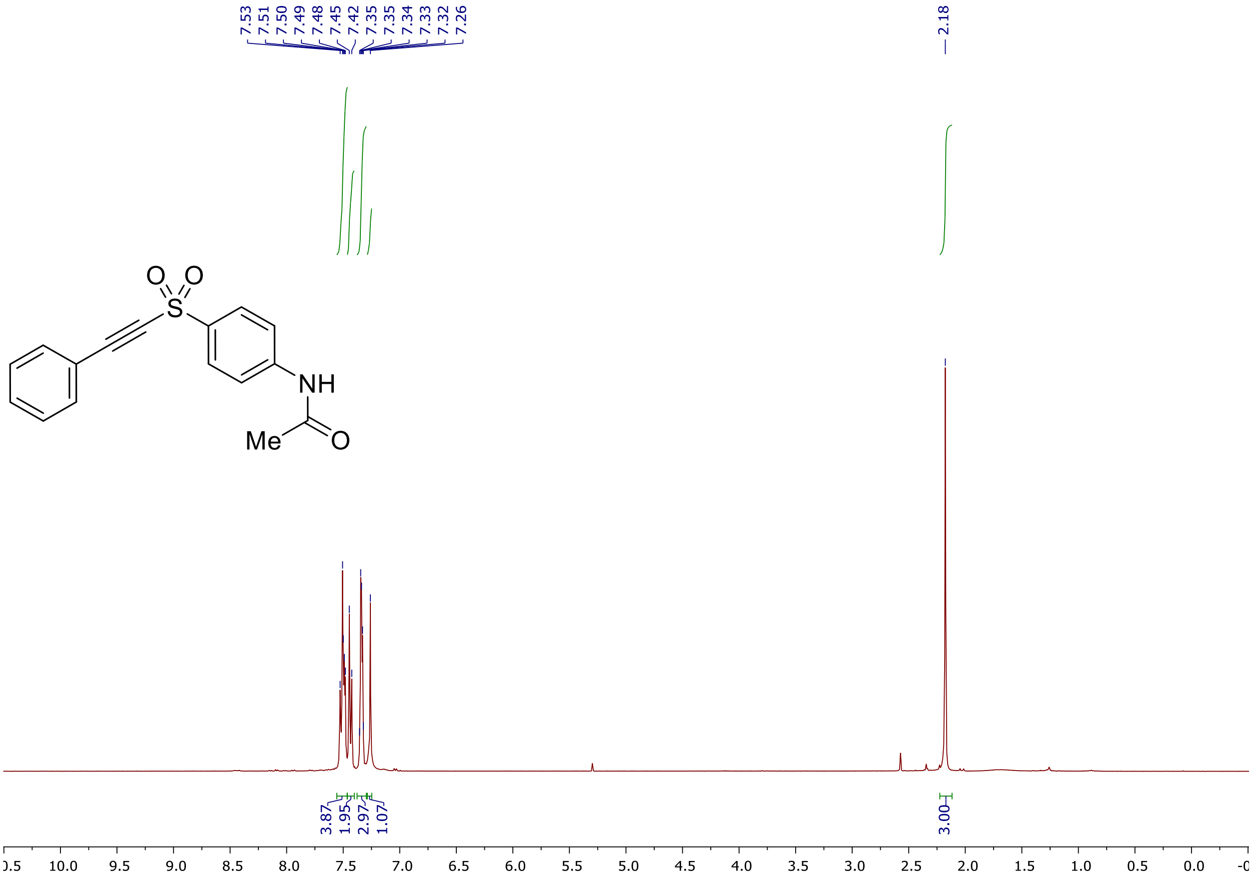
^{1}H NMR (400 MHz, $CDCl_3$) of **1z**



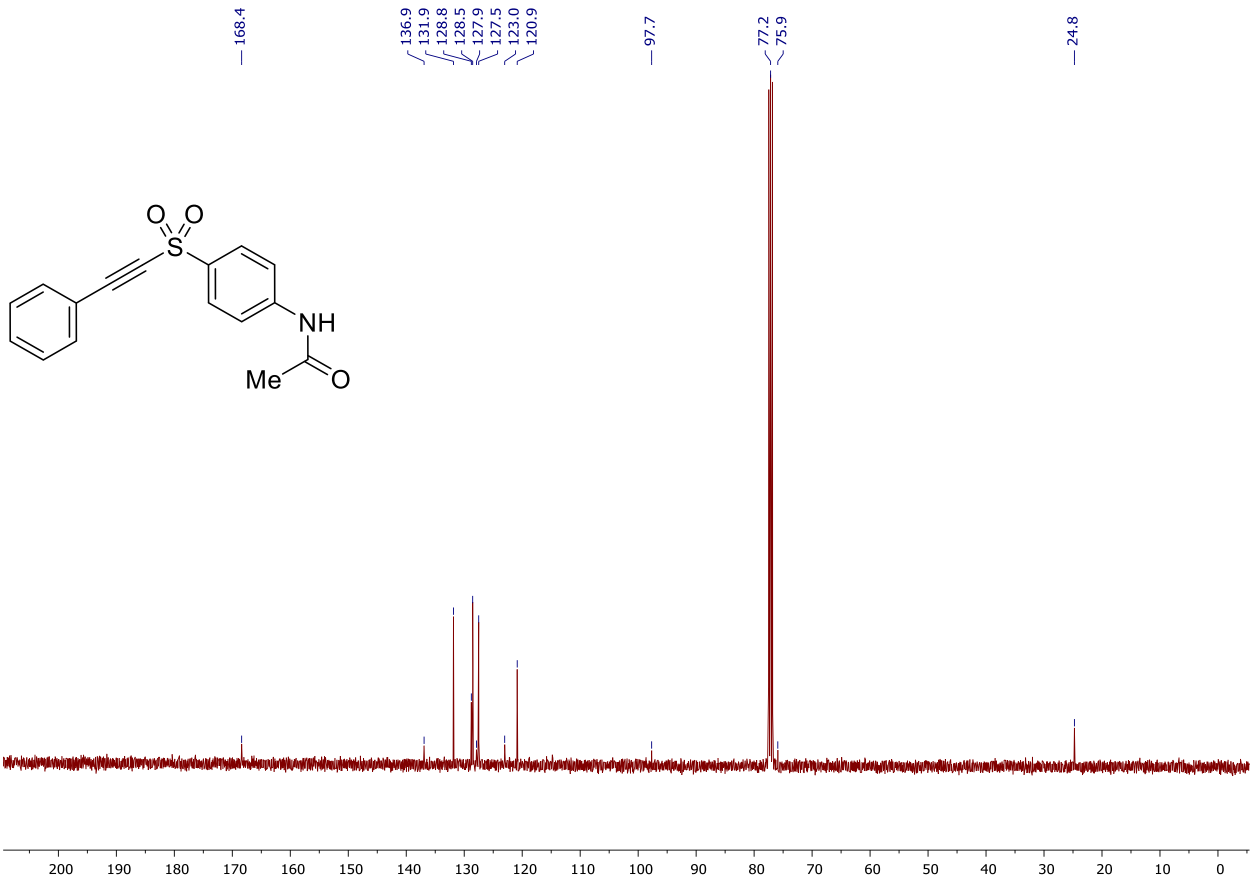
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **1z**



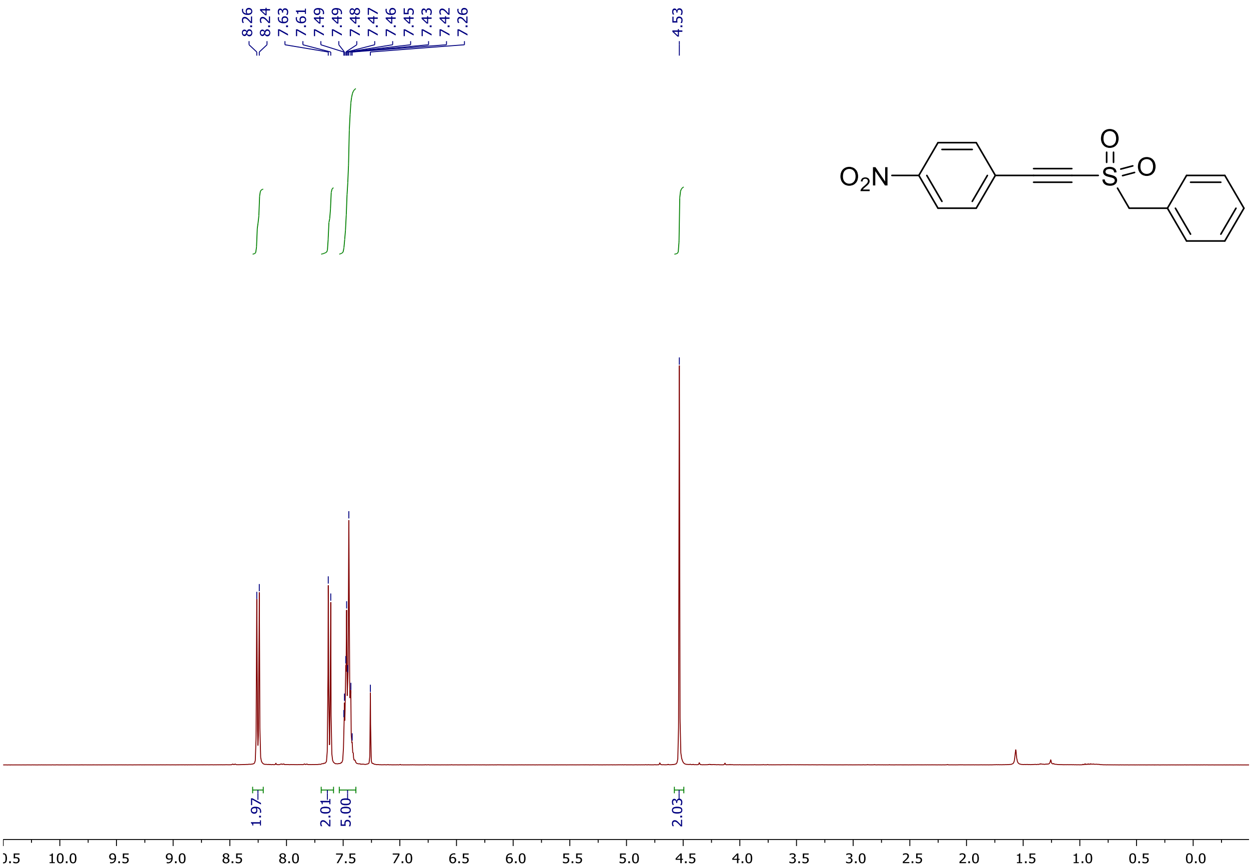
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



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



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



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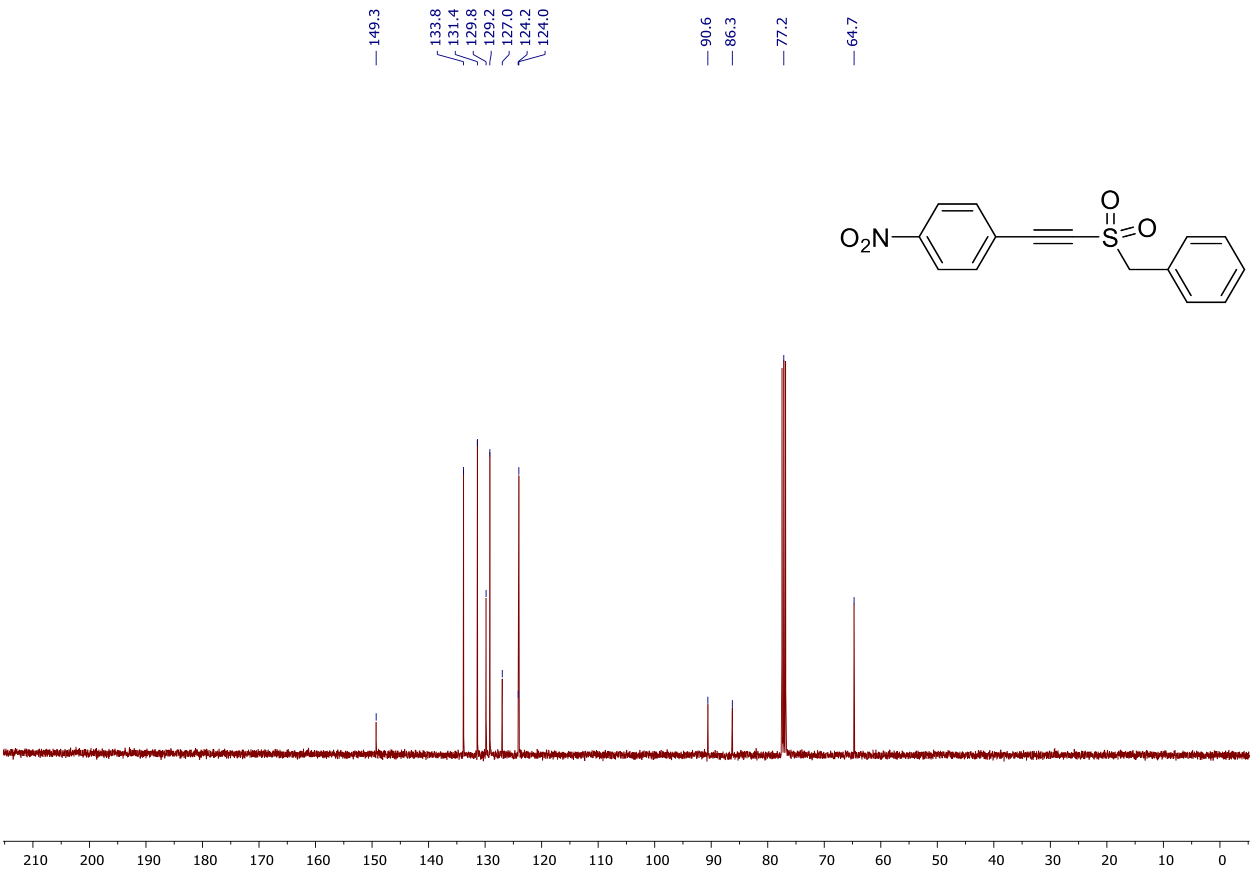

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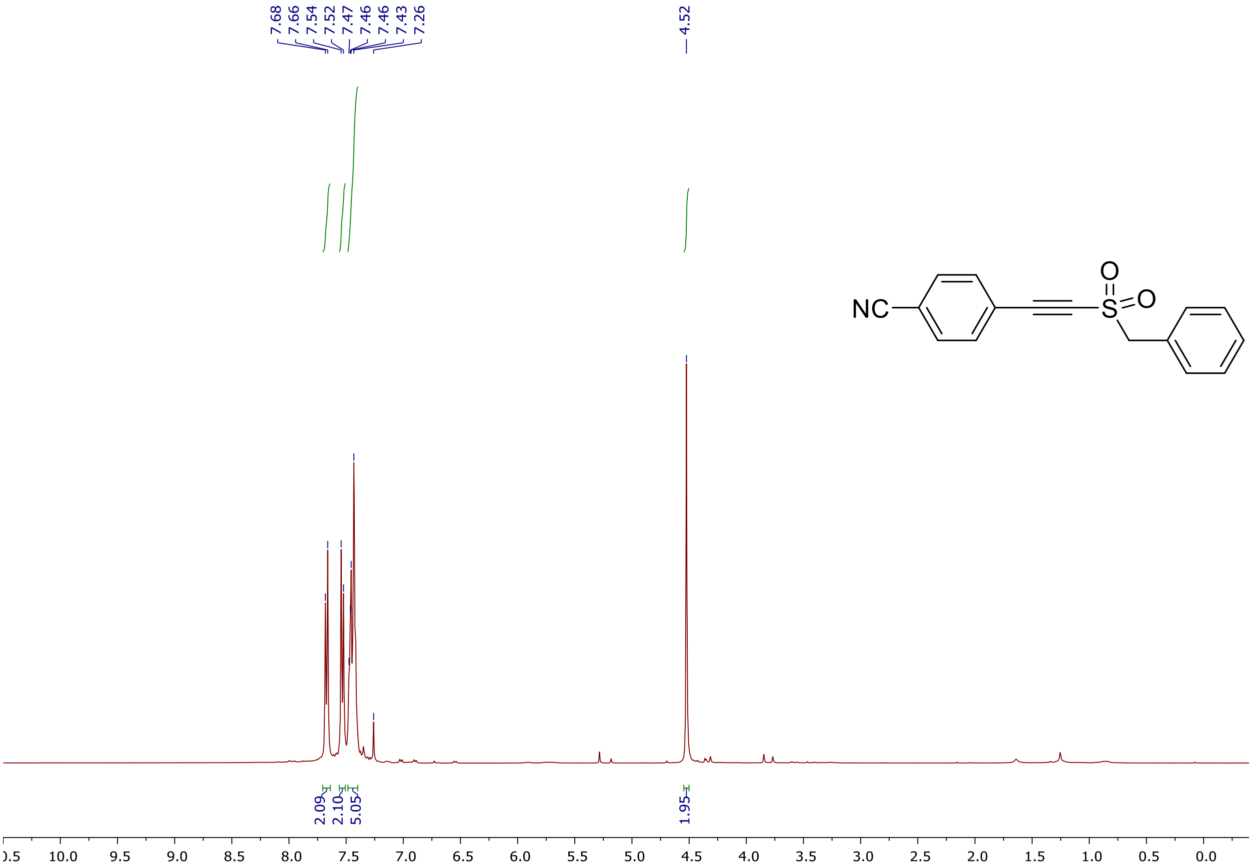

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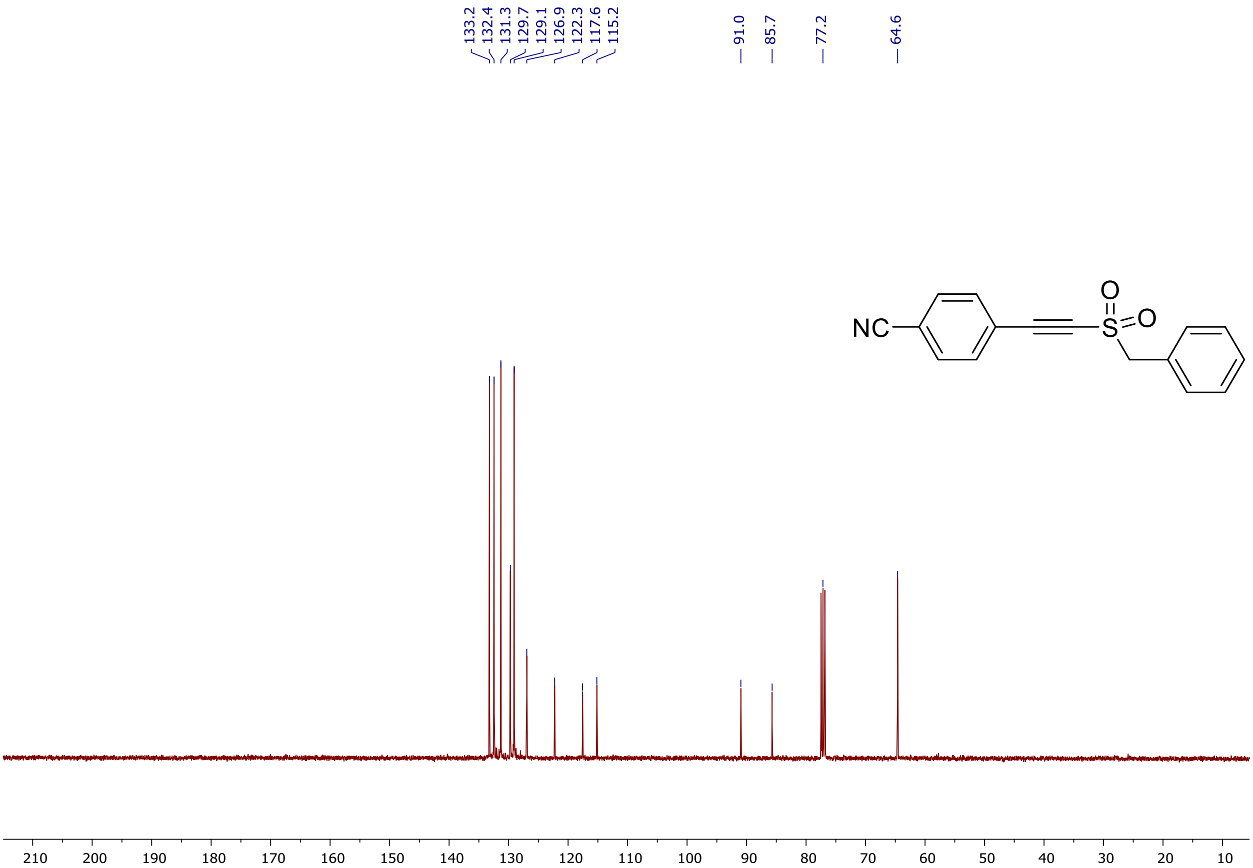

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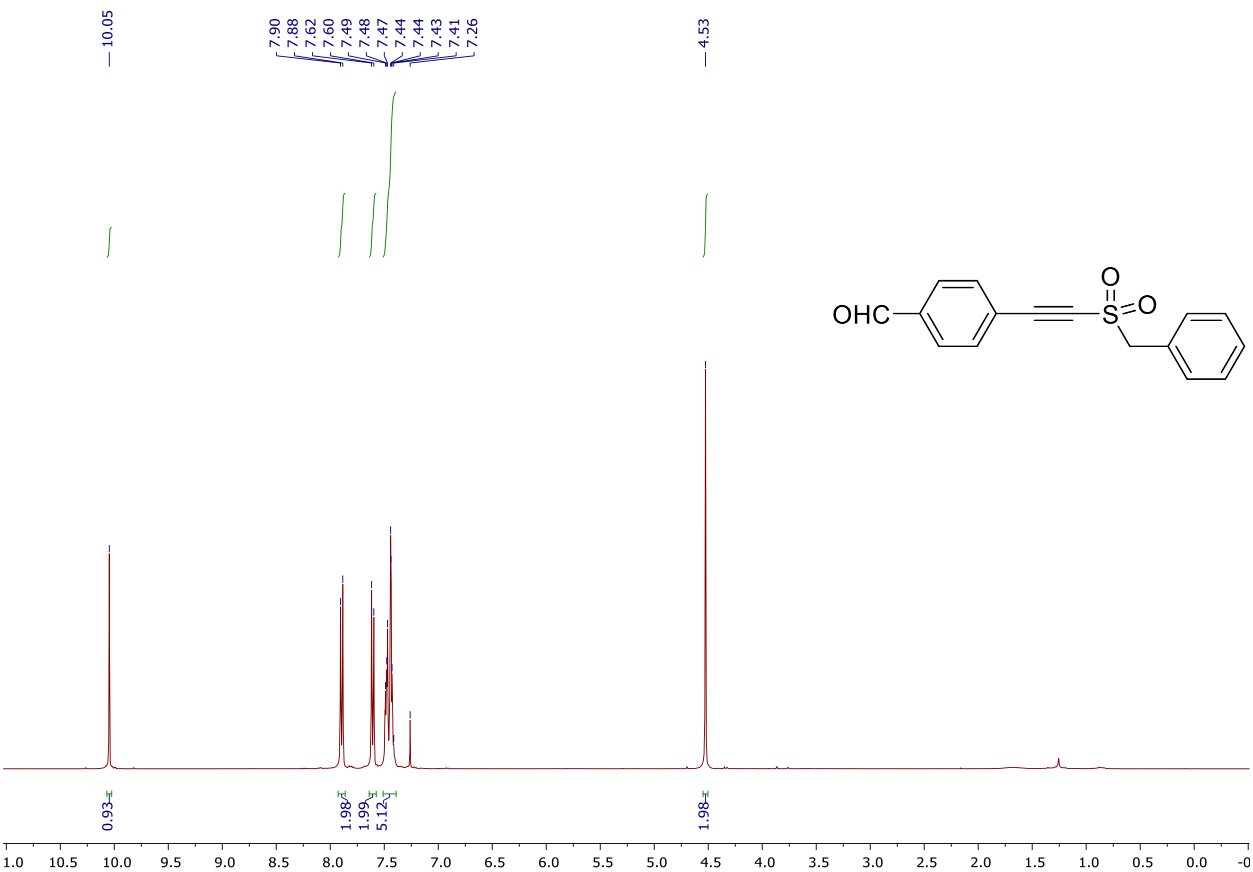

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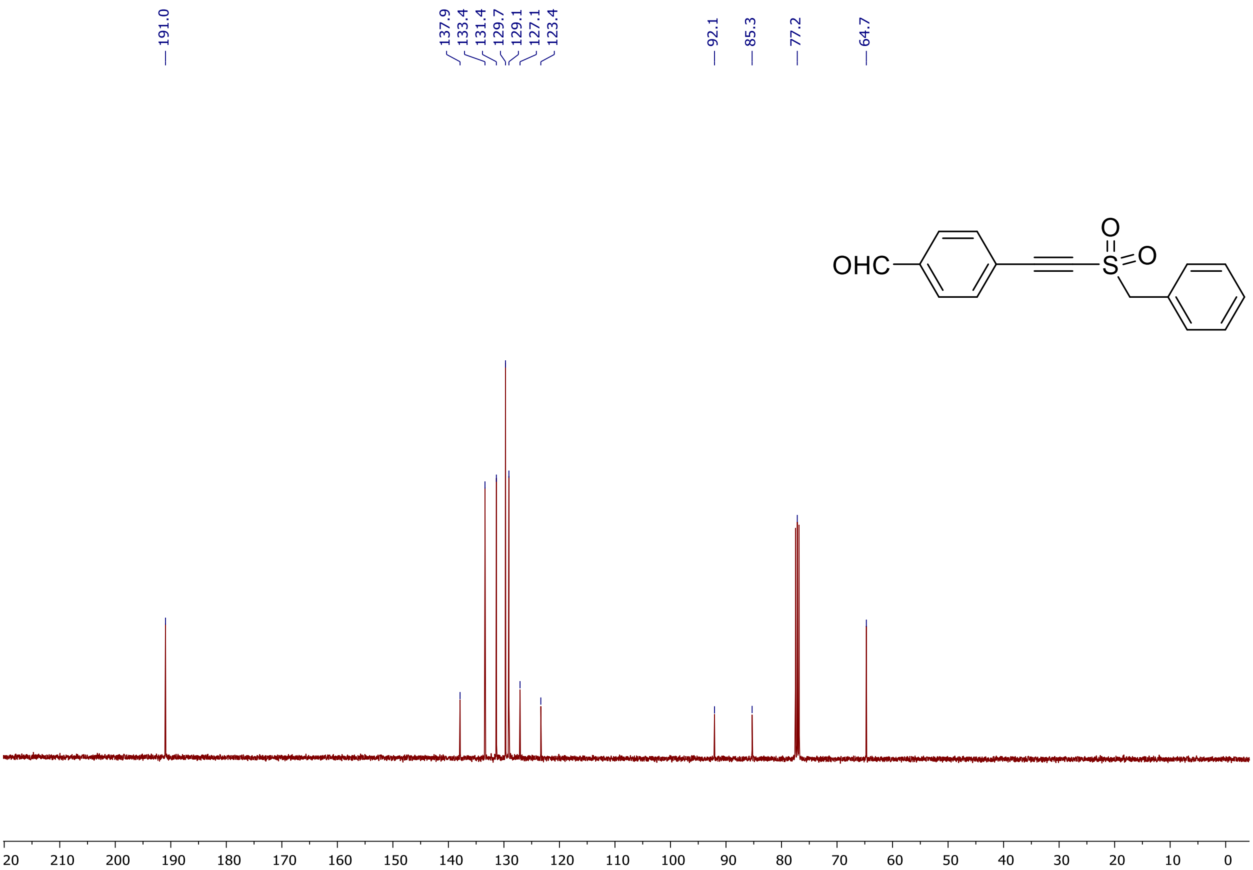

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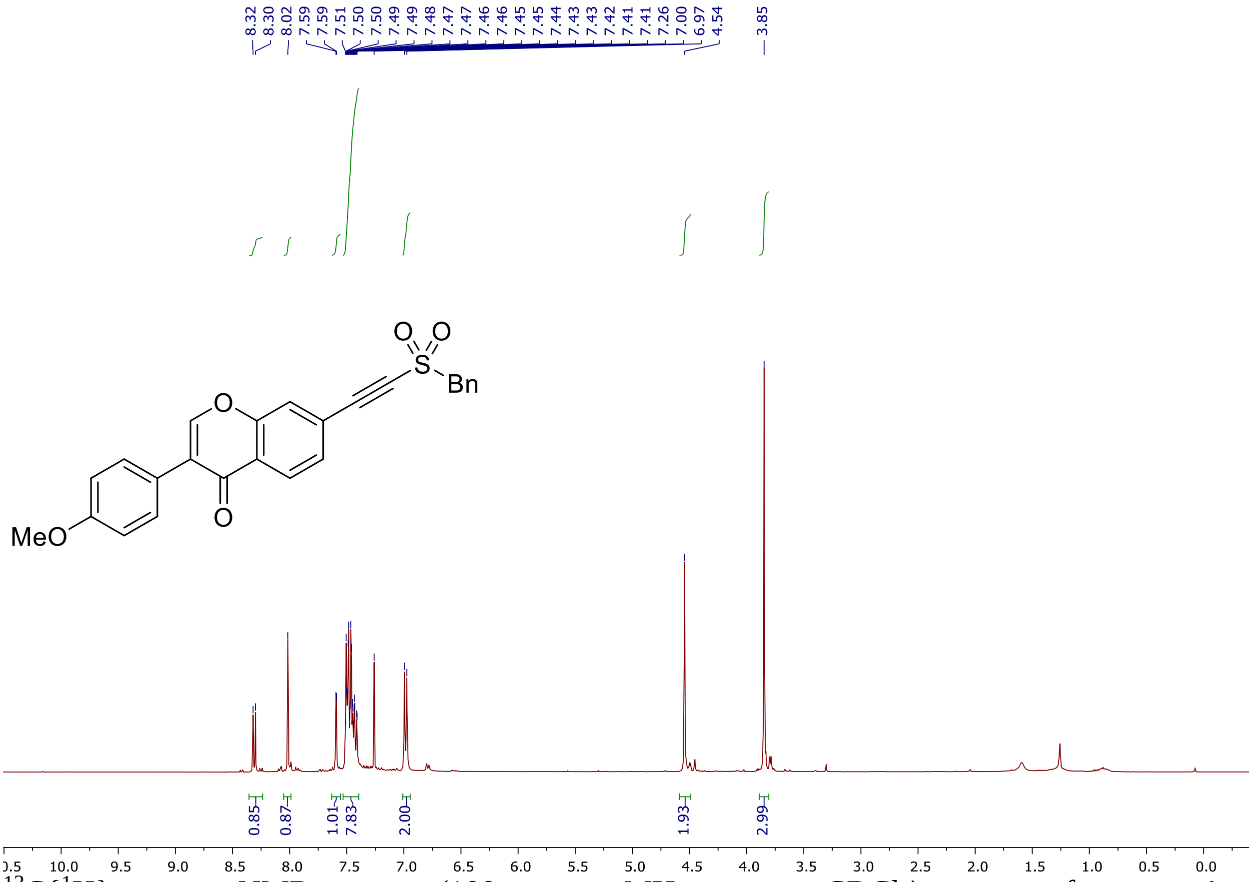

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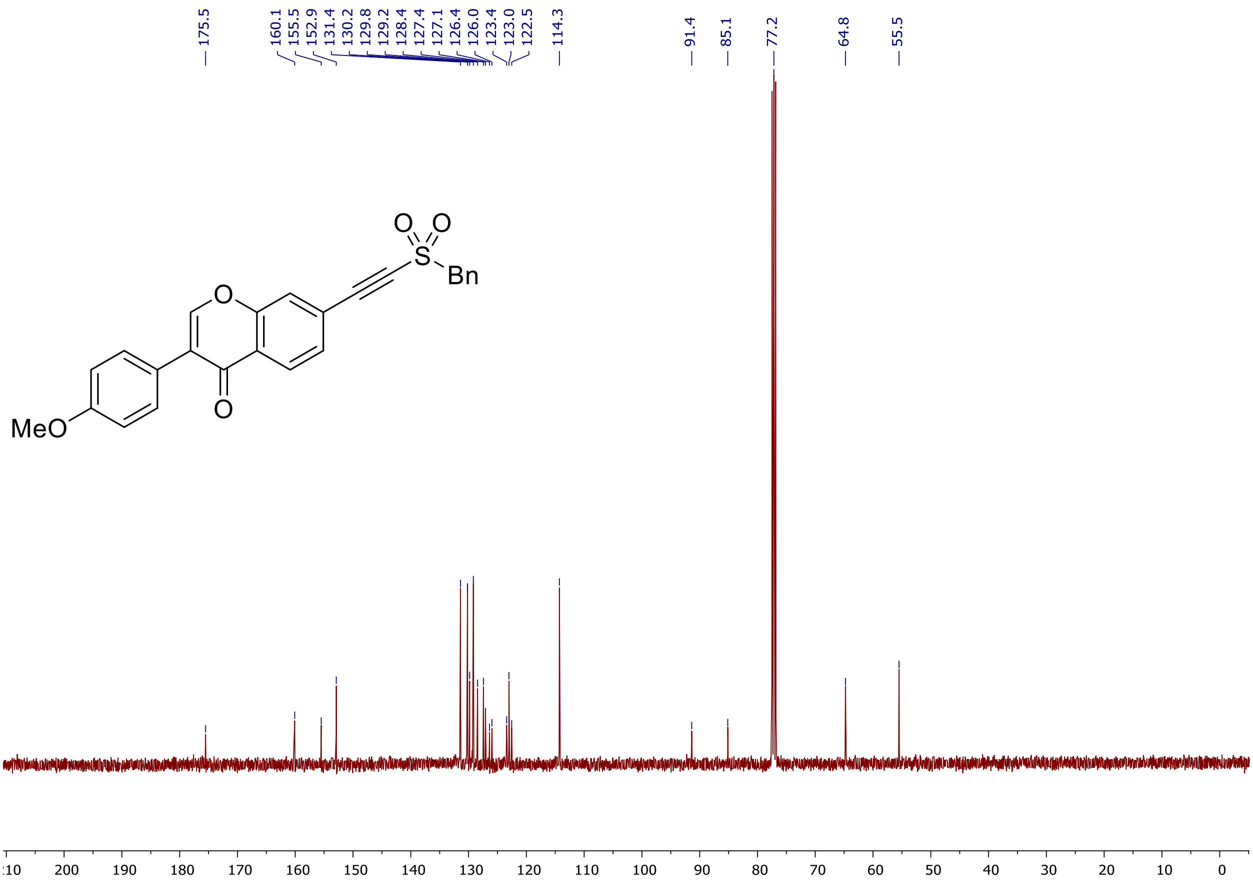

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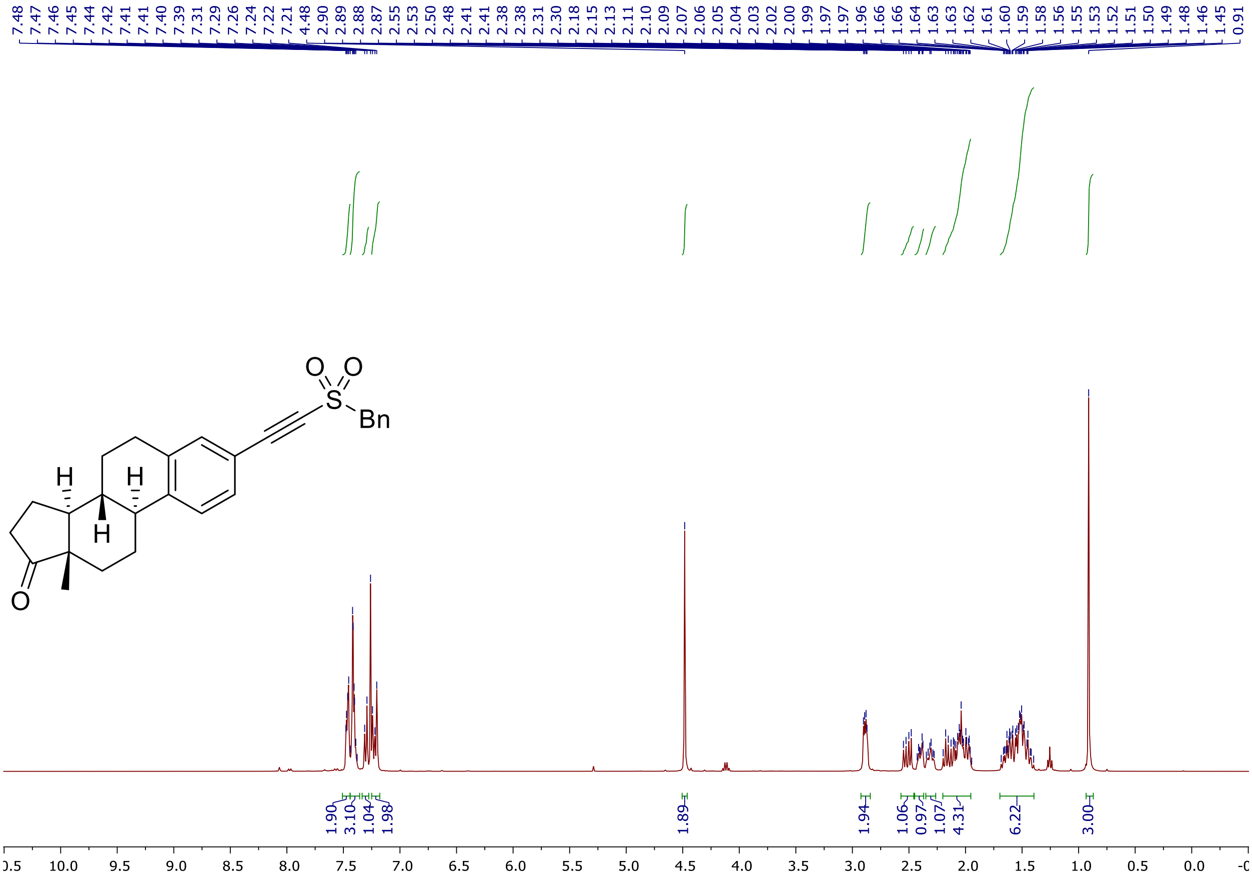

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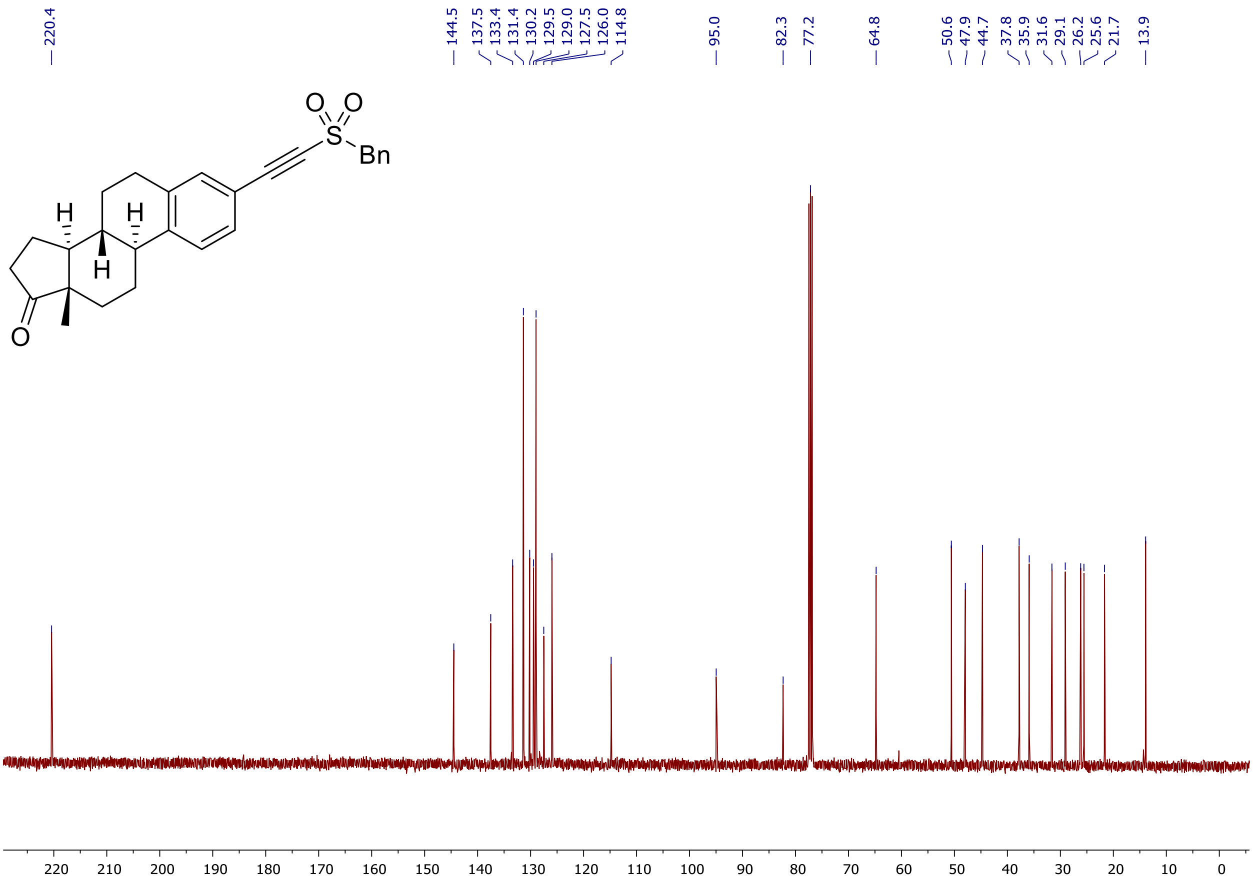

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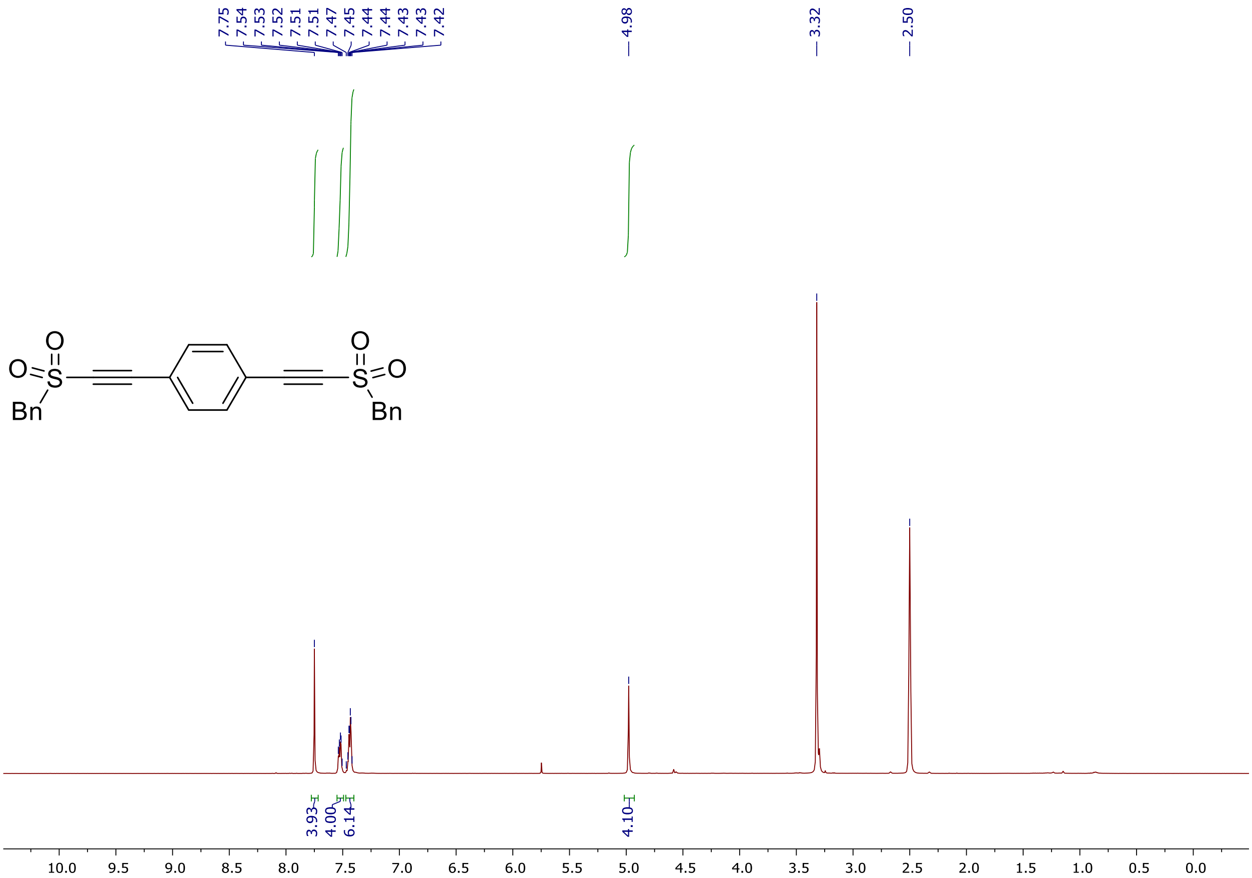

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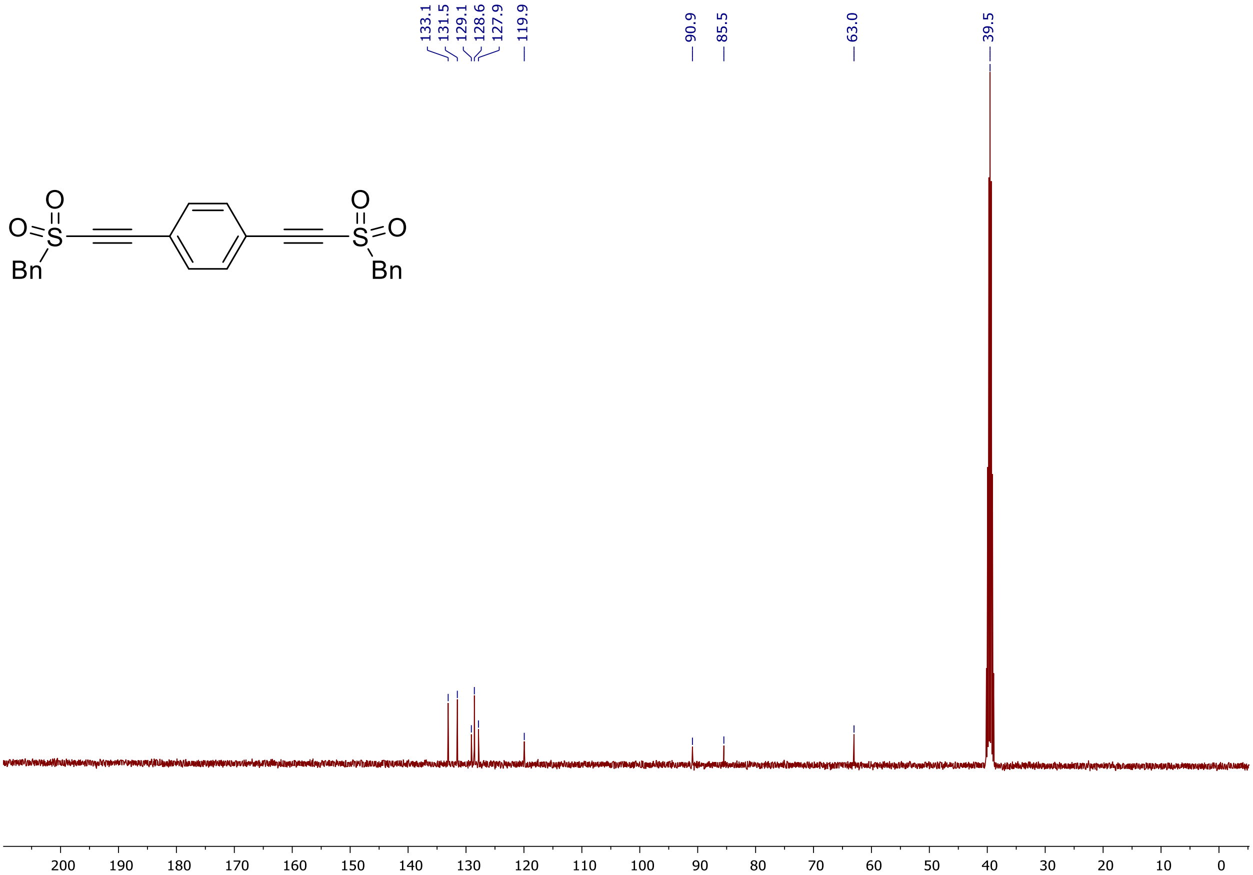

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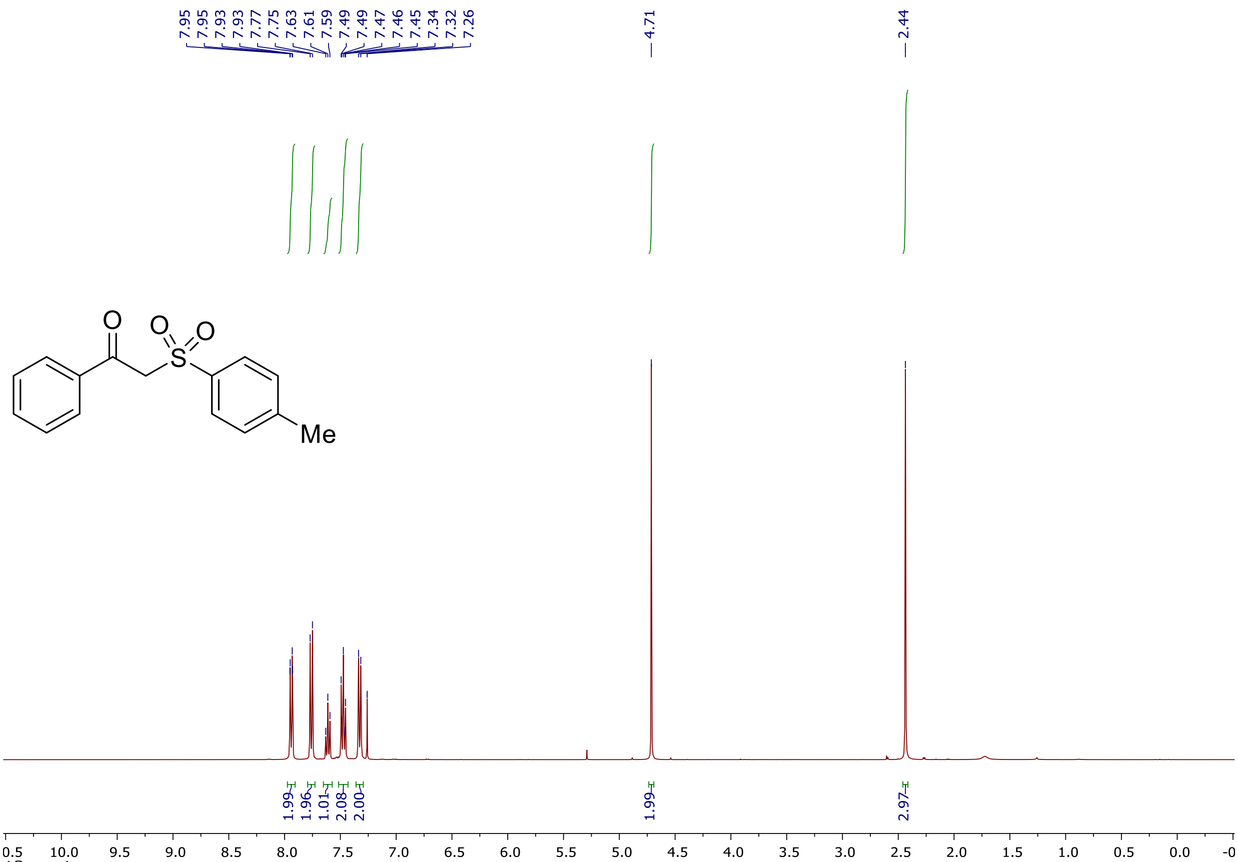

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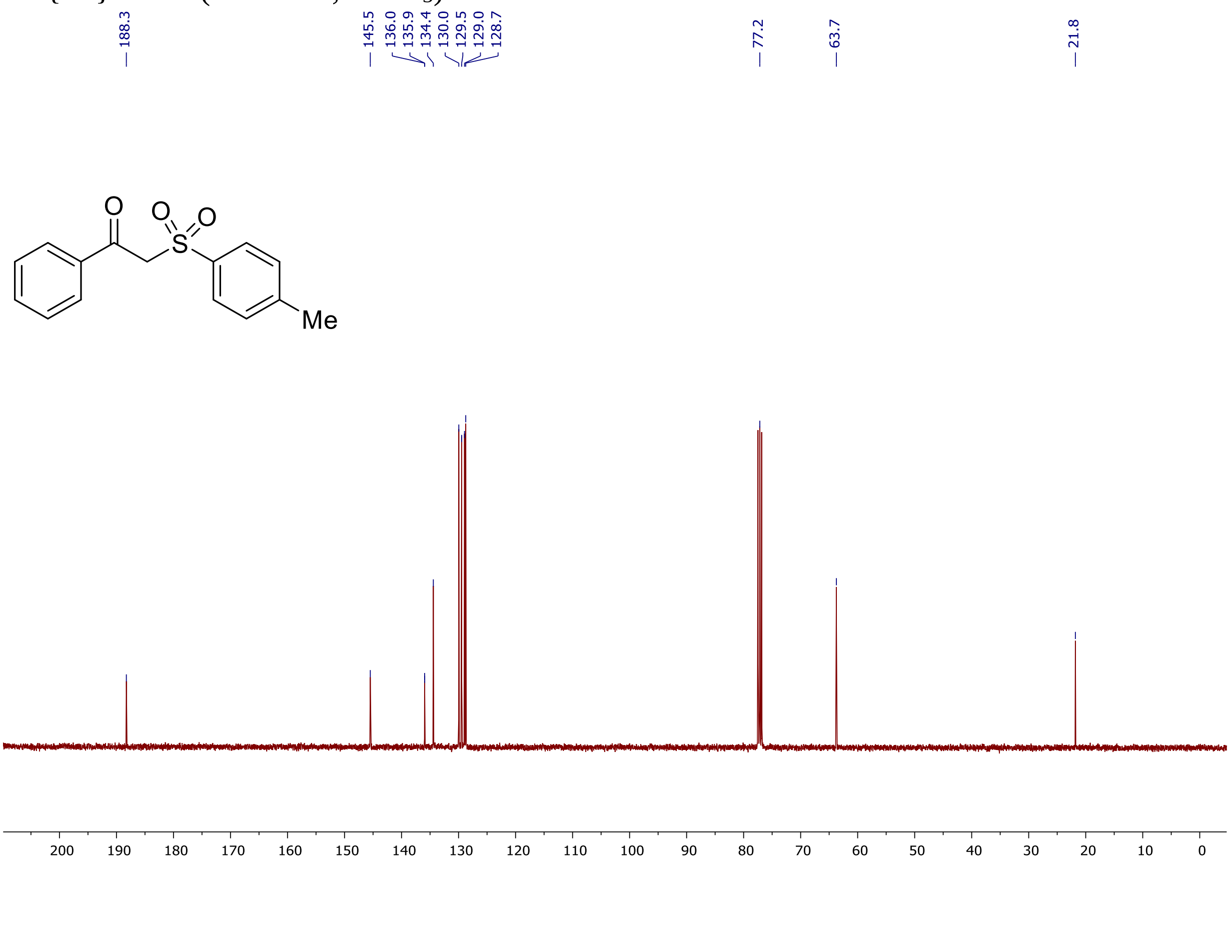

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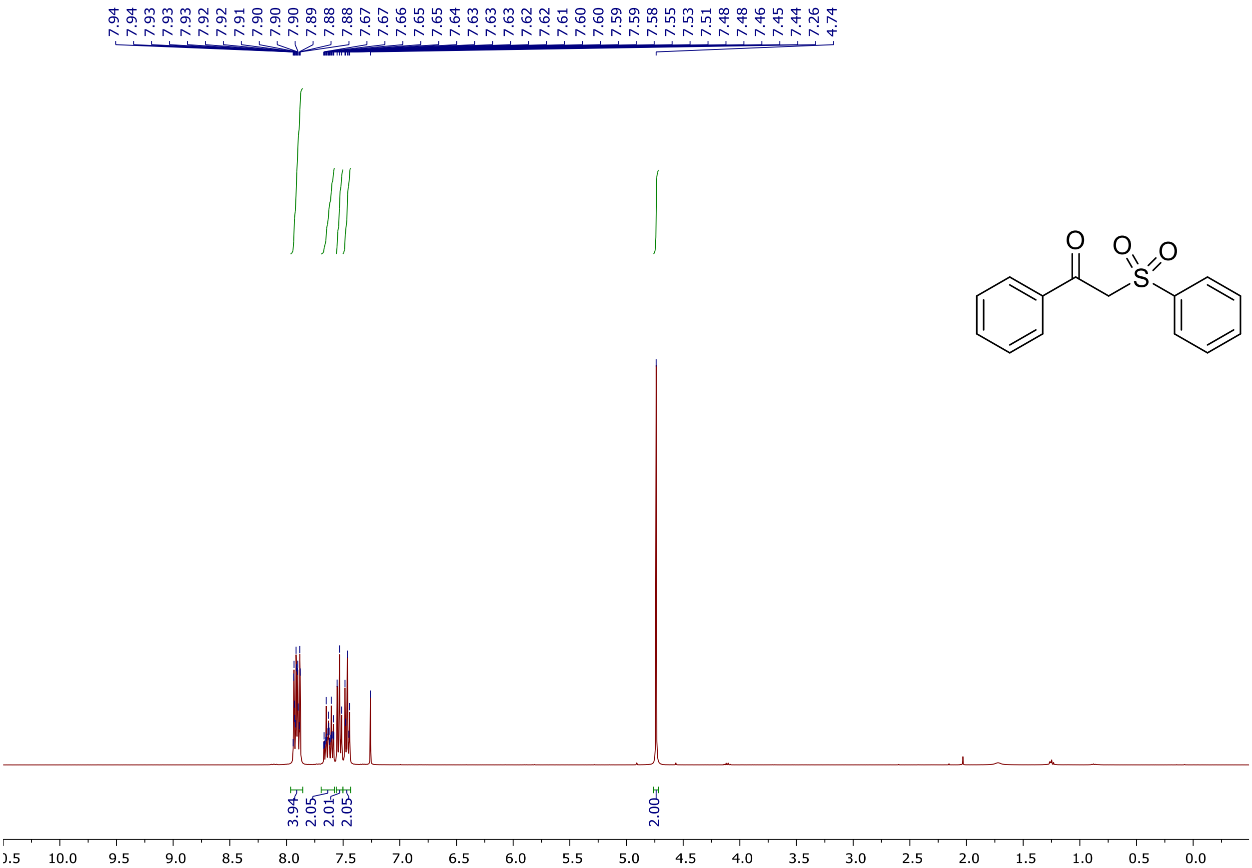

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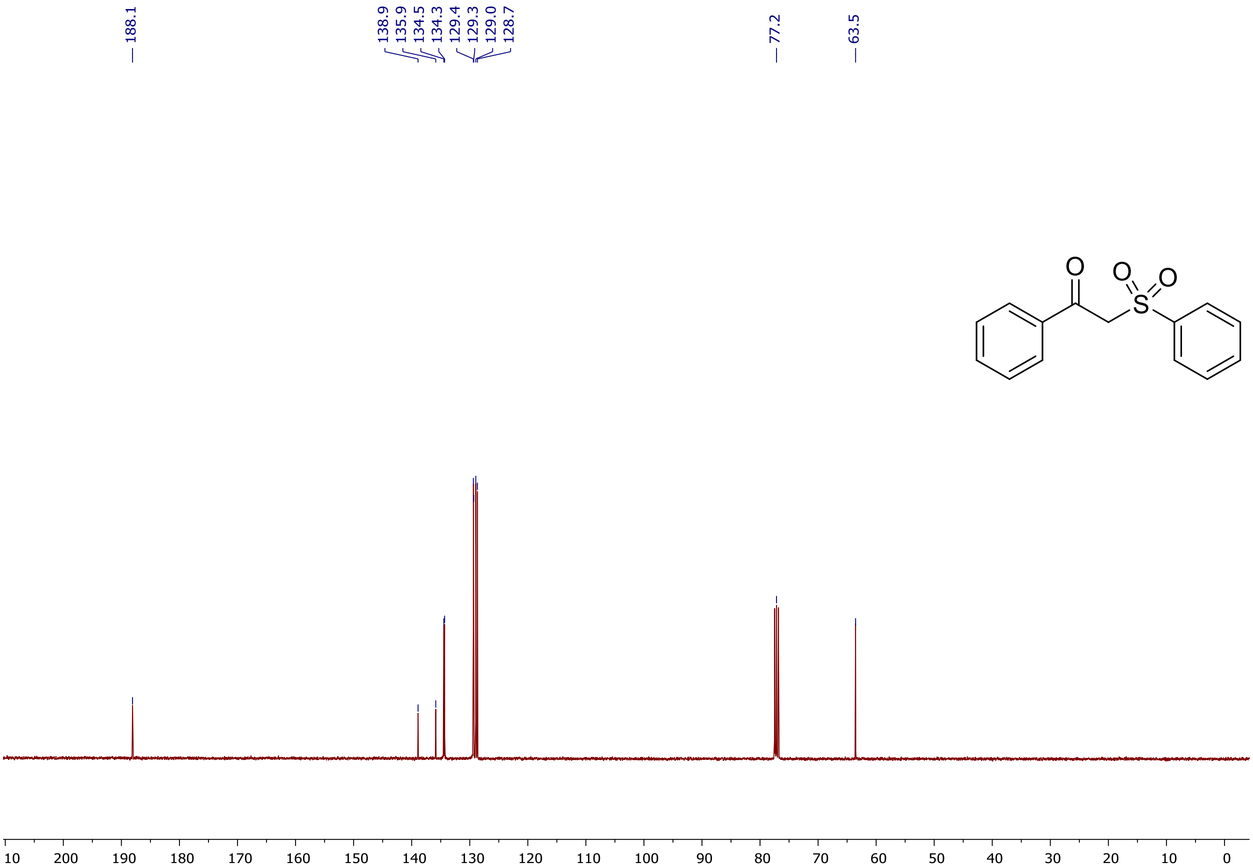

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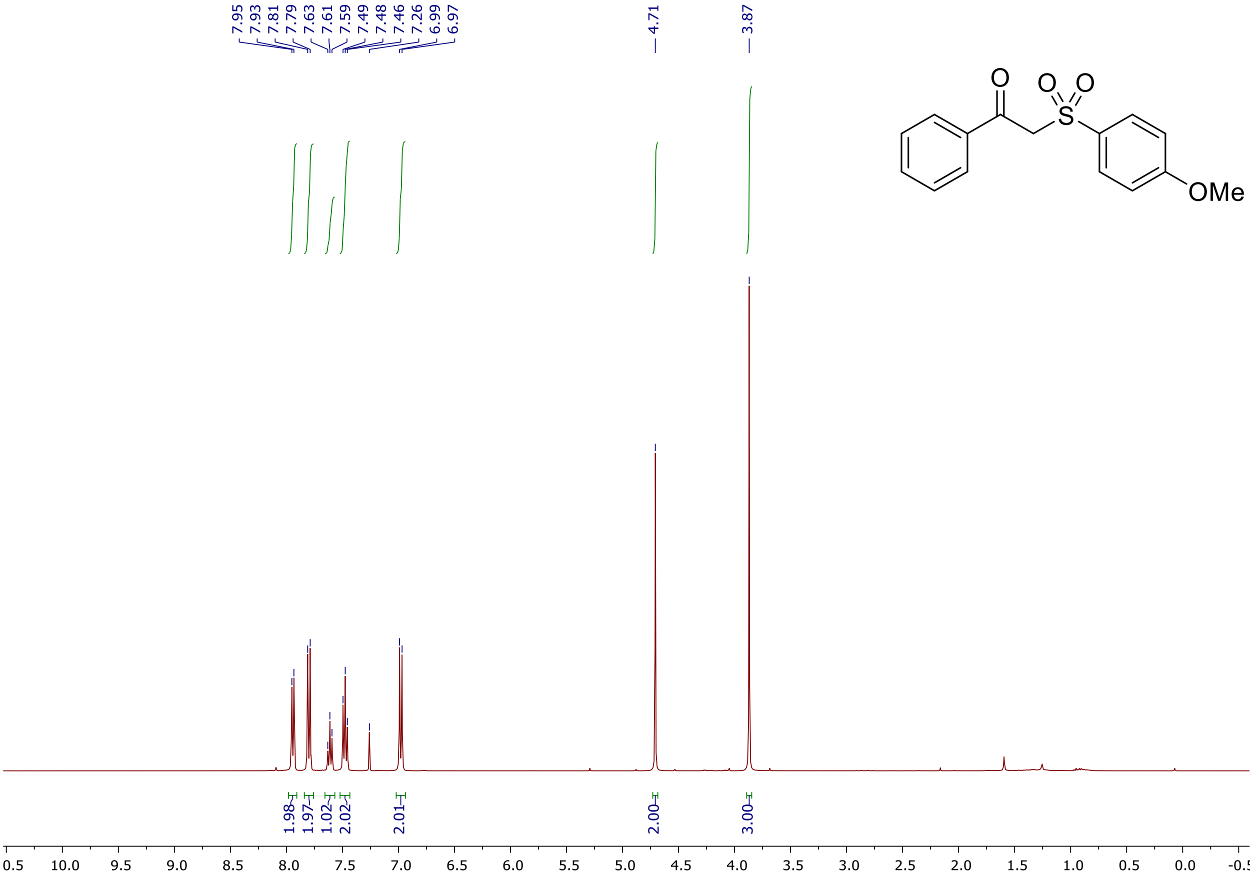

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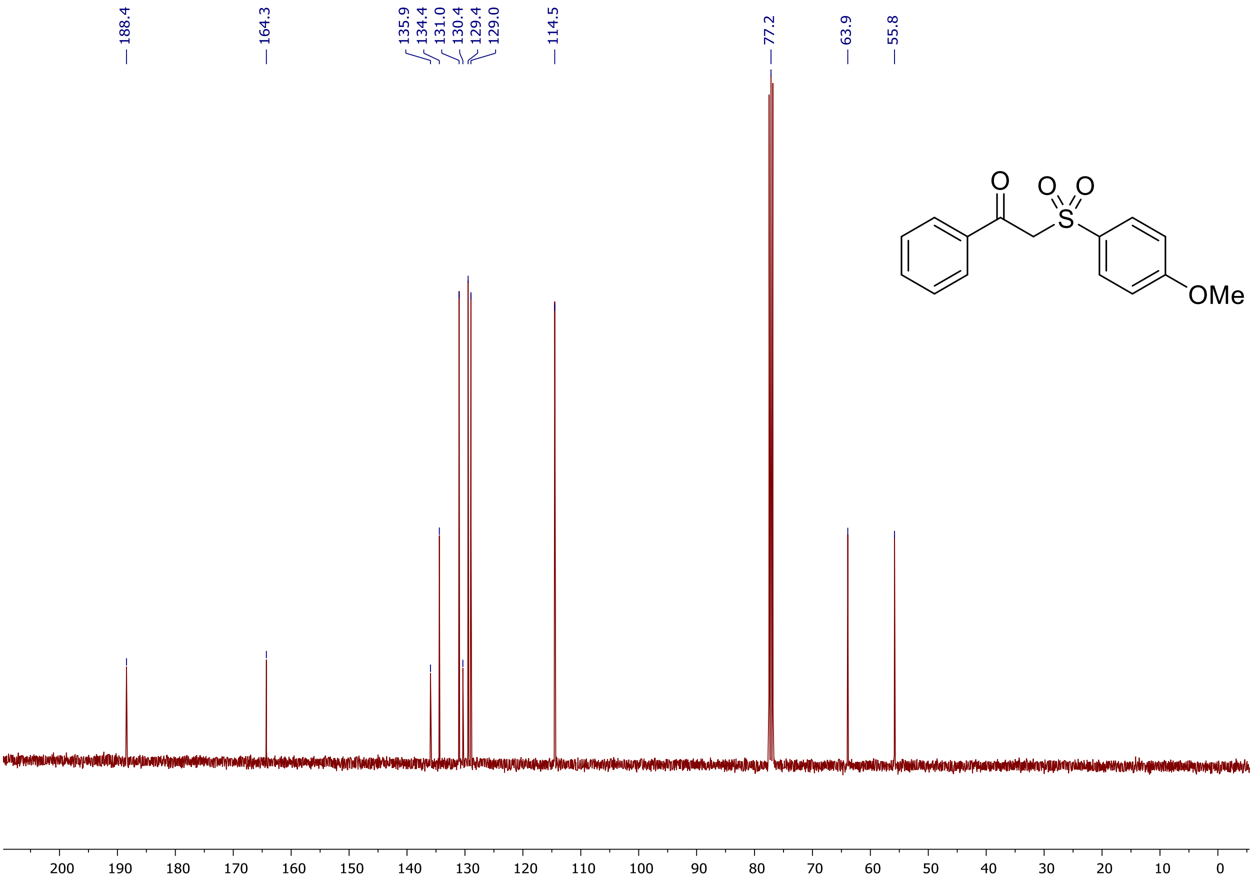

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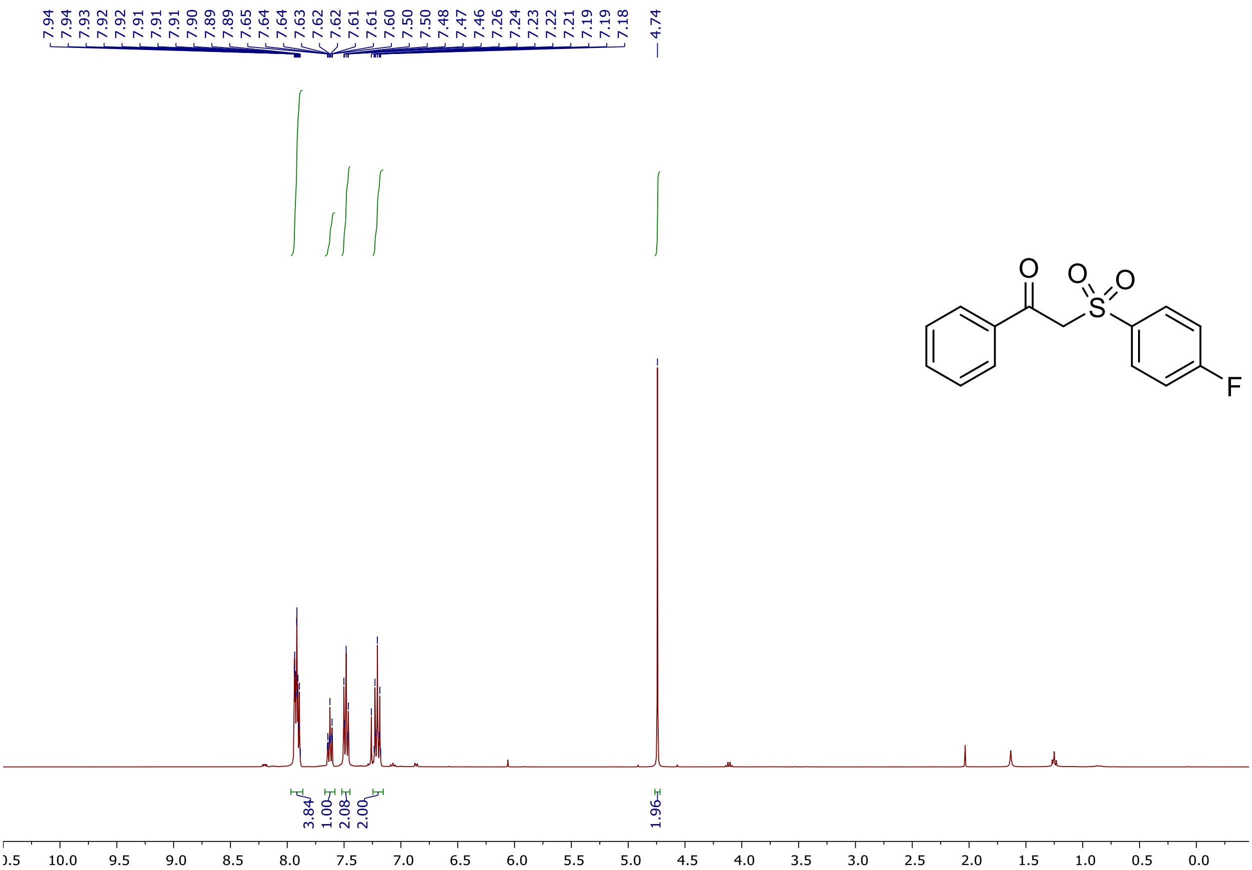

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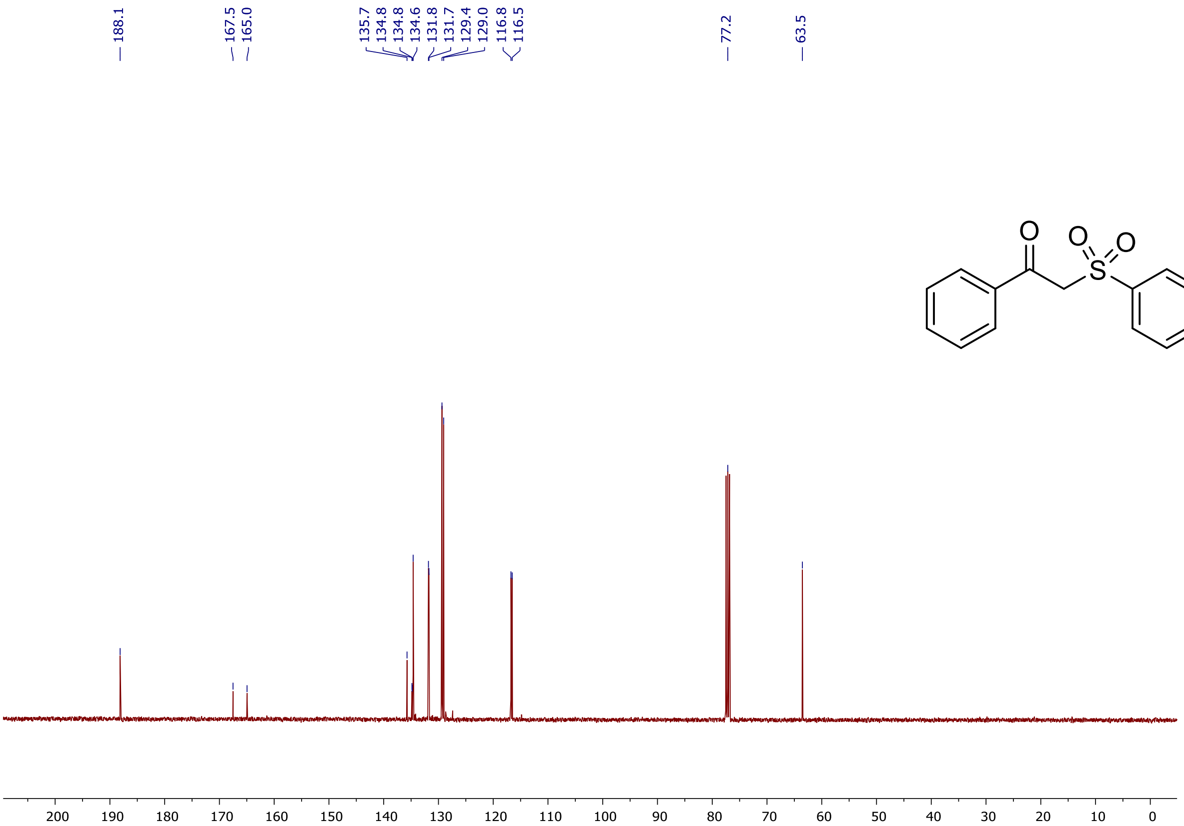

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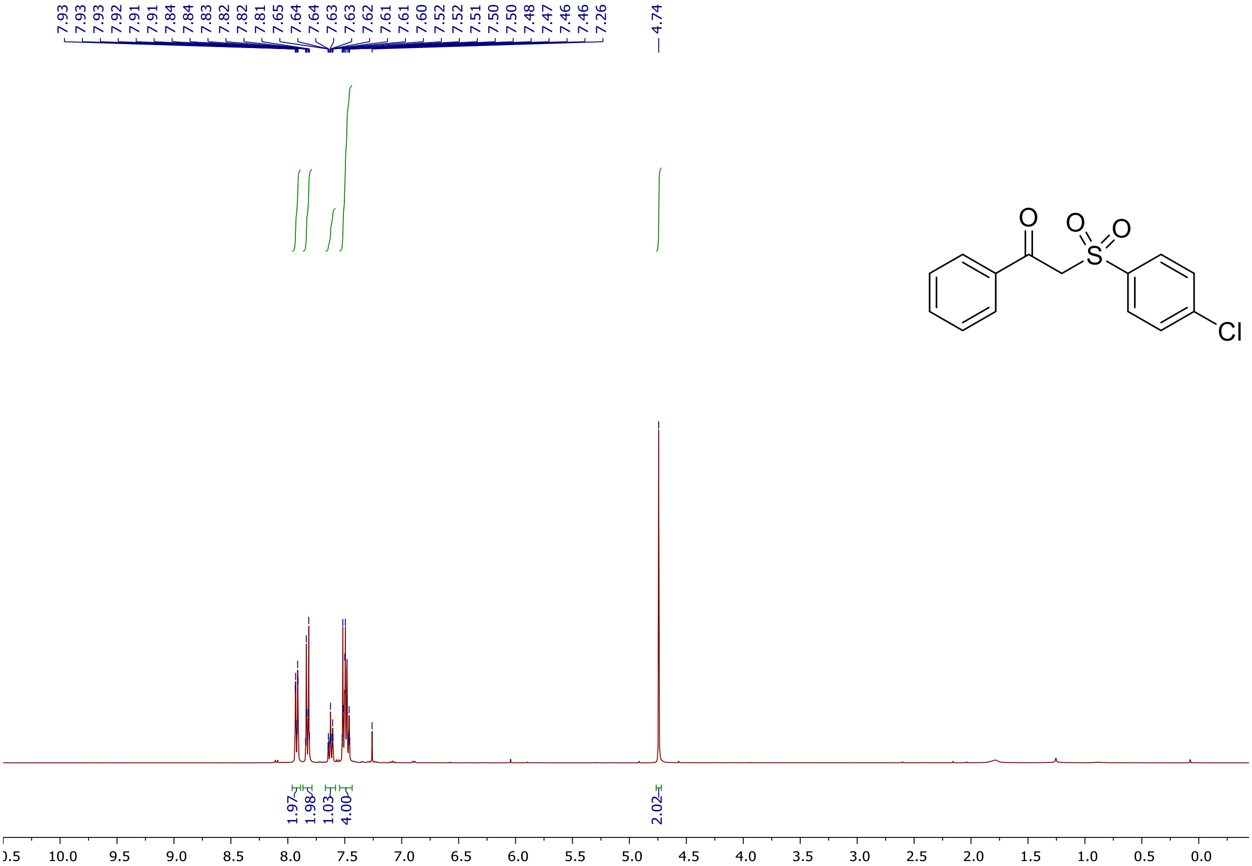

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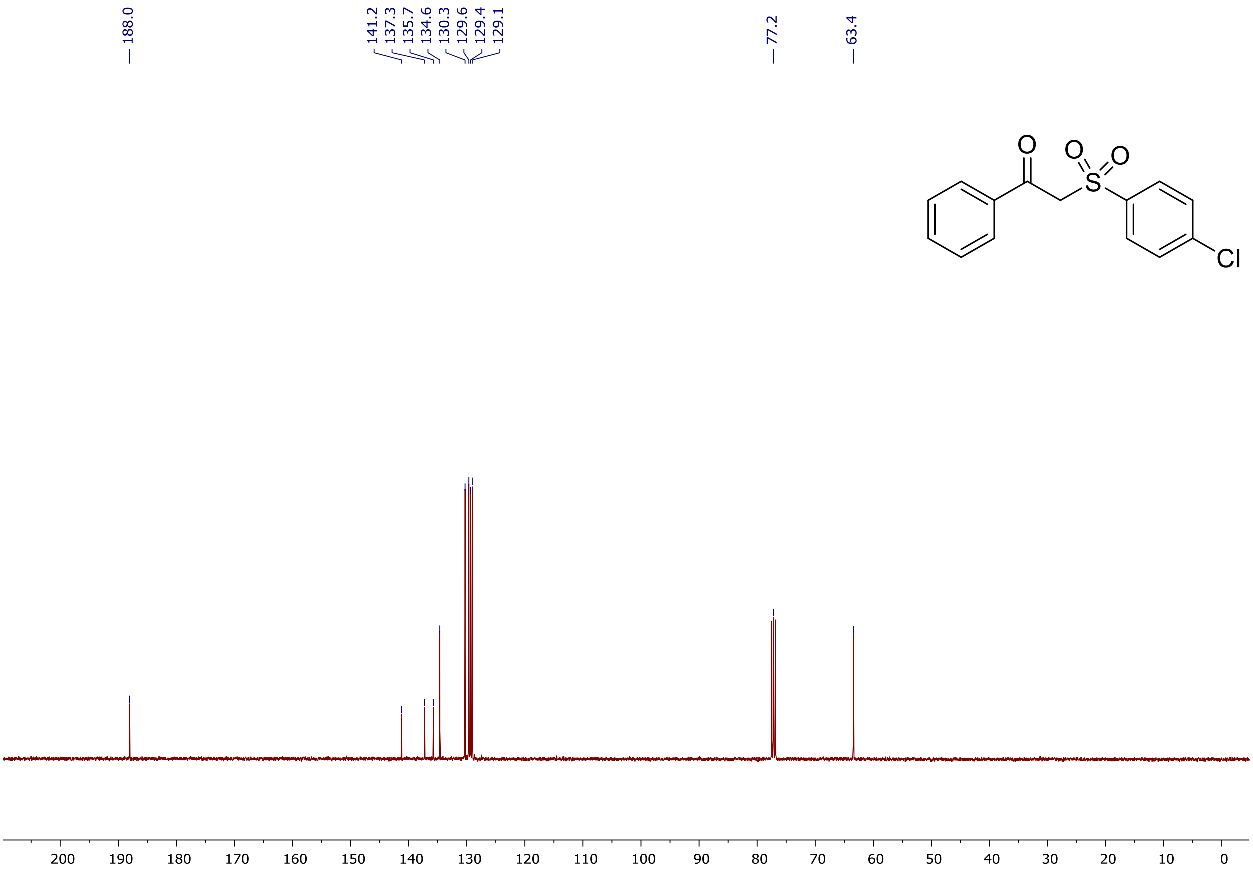
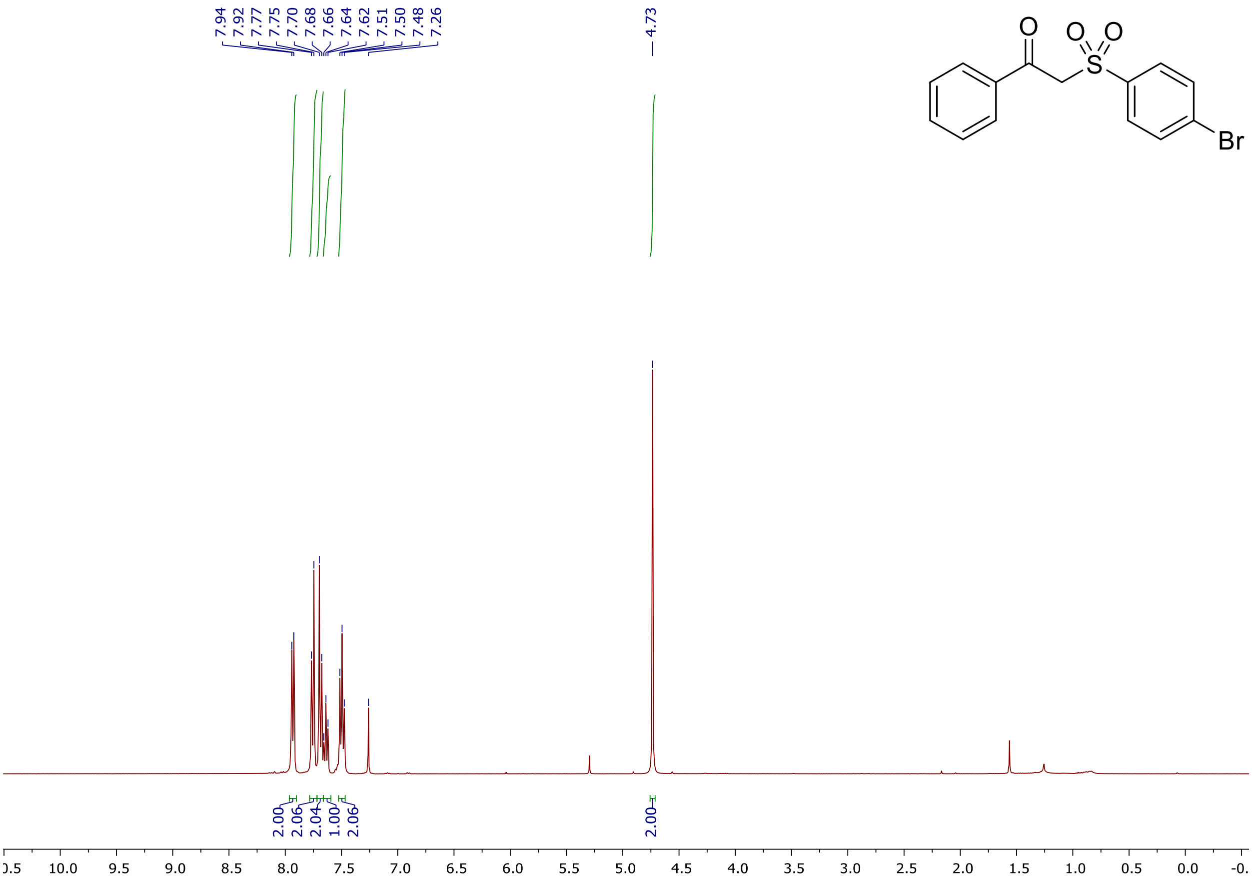
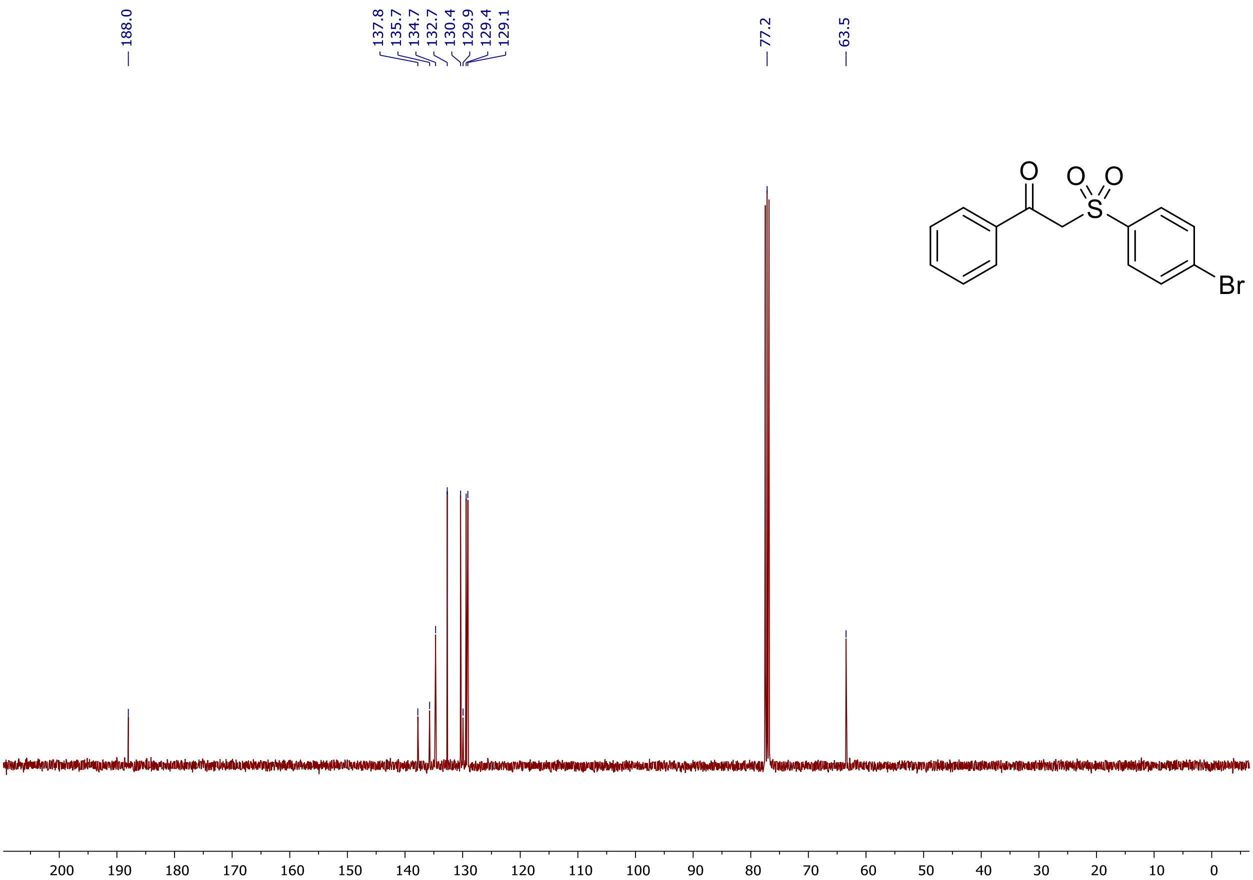


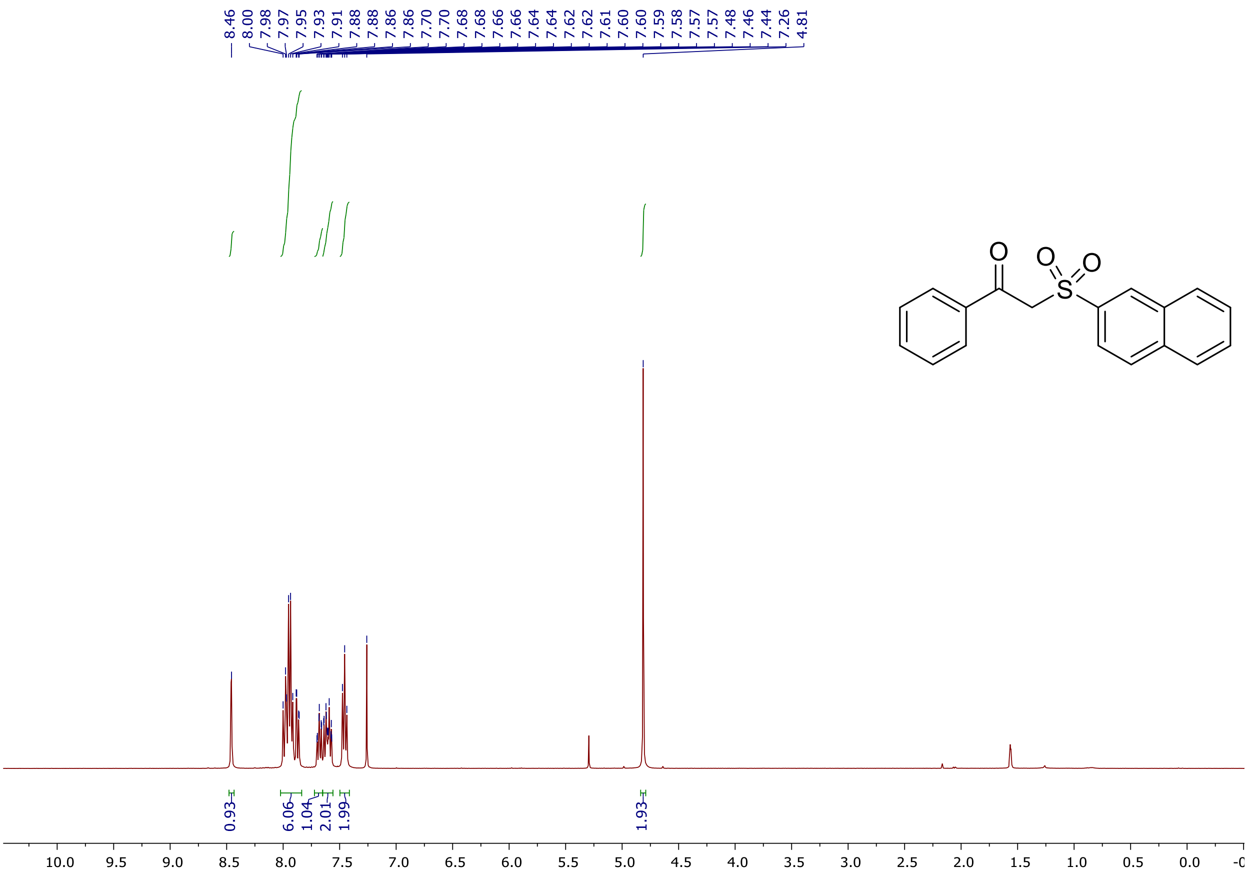
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



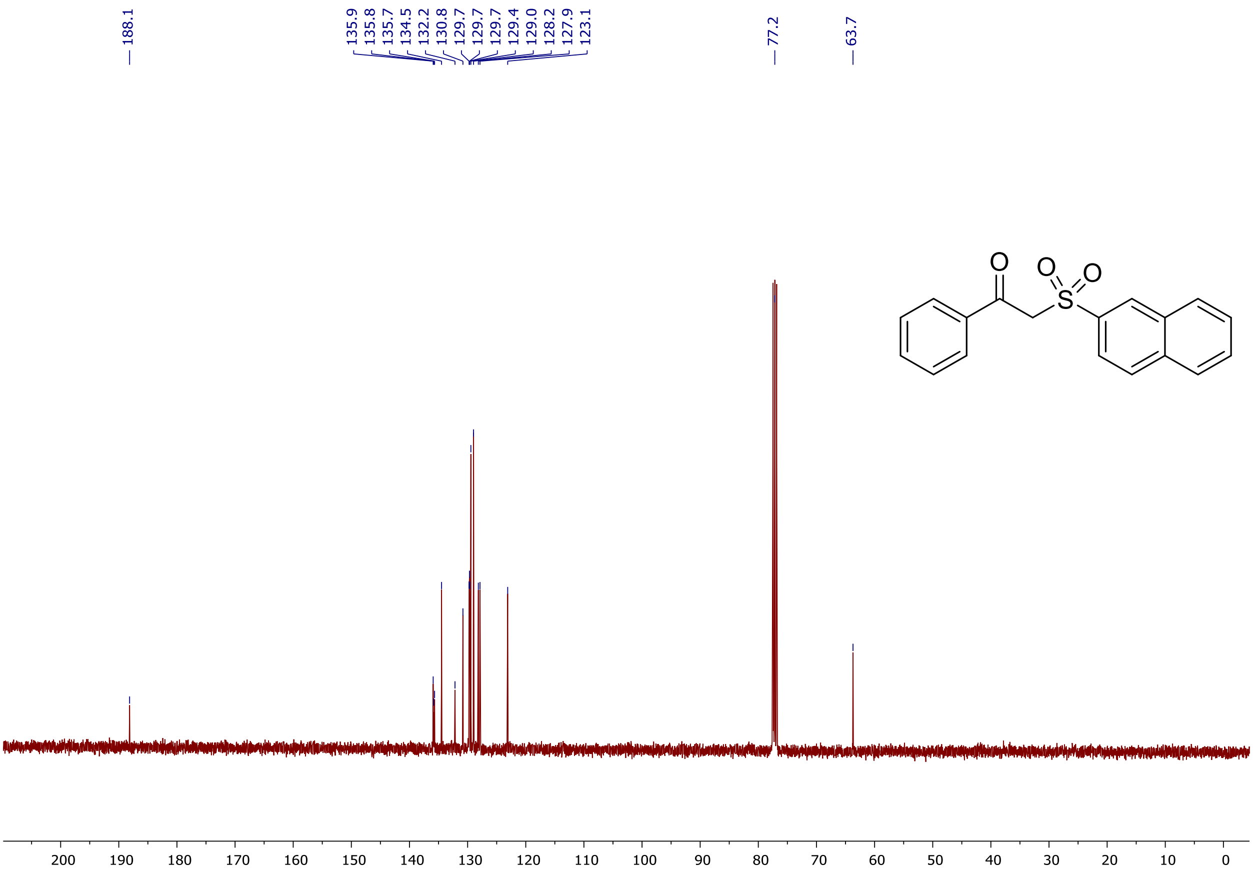
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2f**



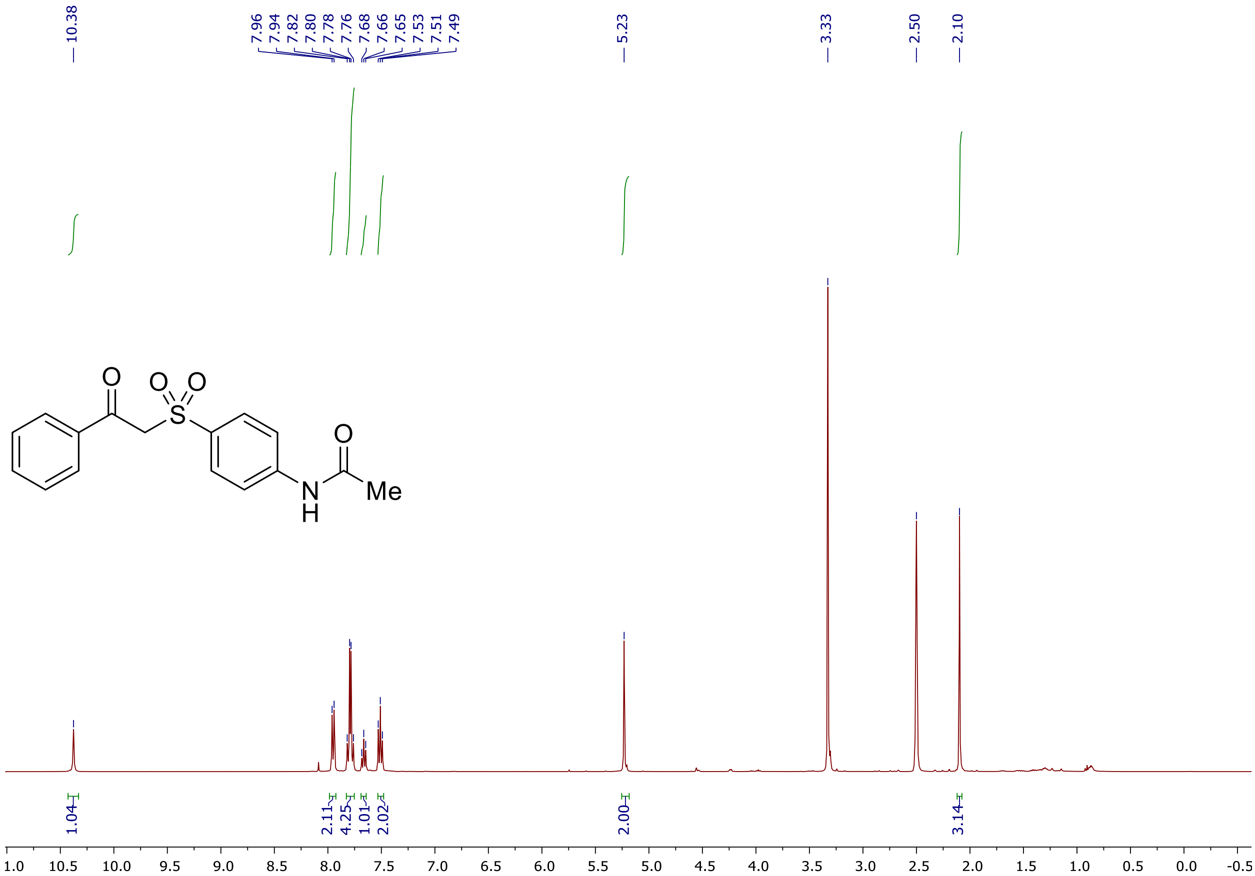
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



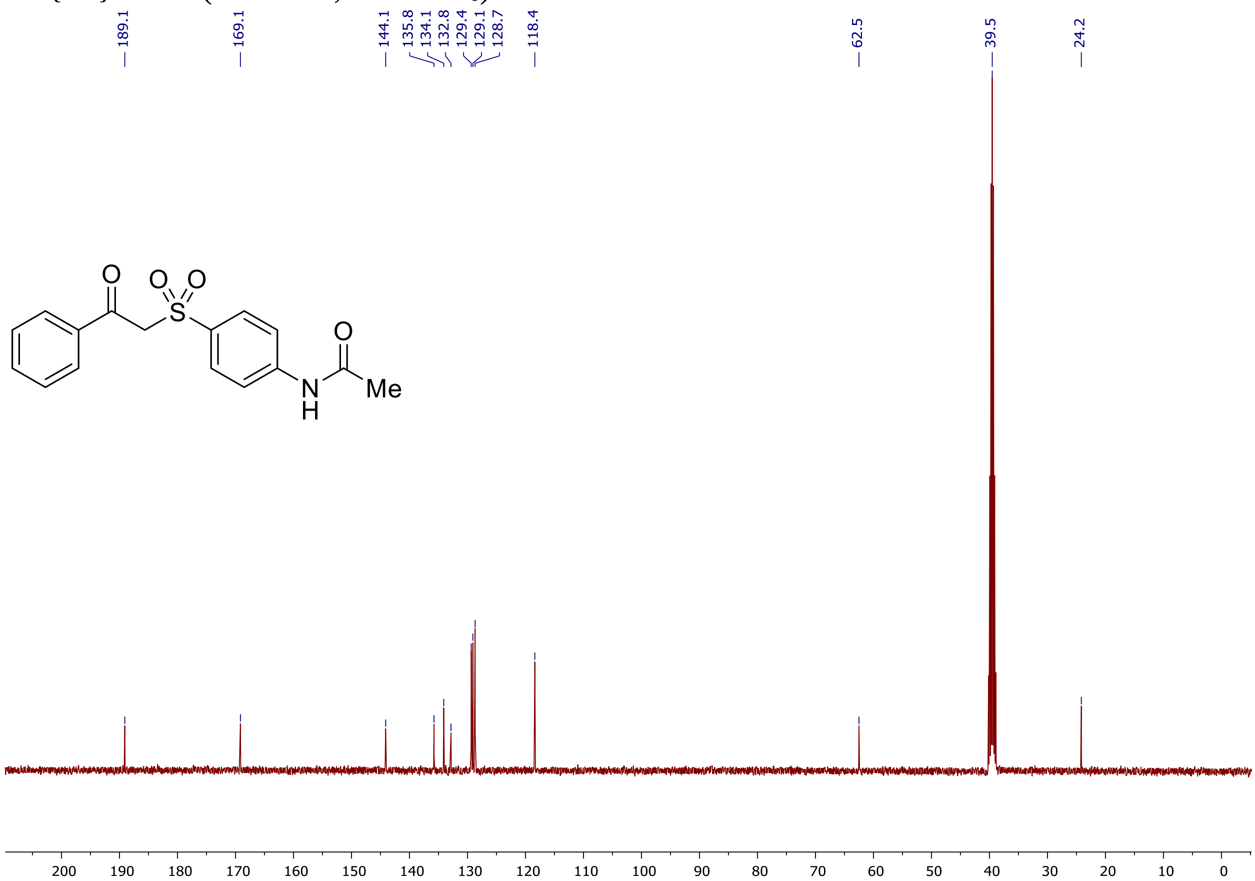
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2g**



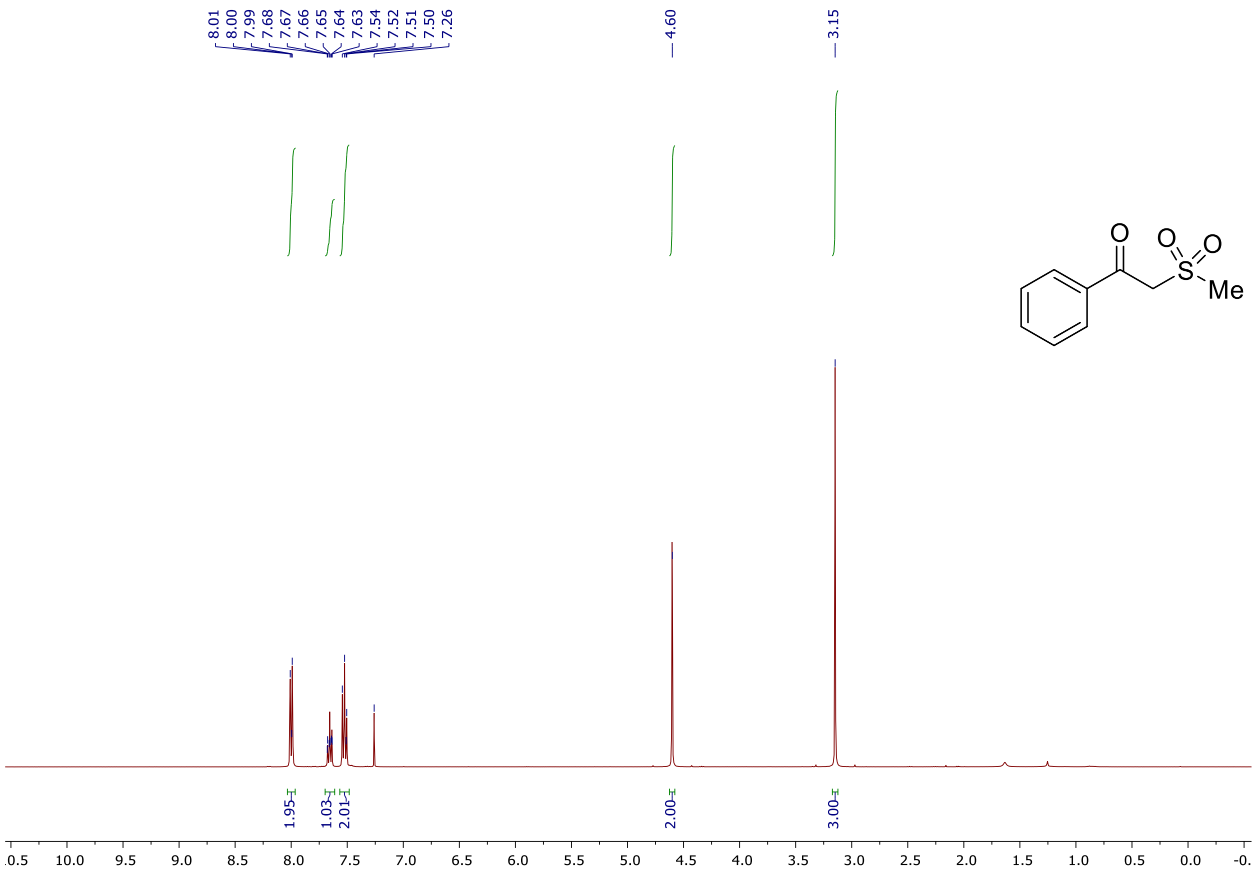
[1]H NMR (400 MHz, DMSO-d_6) of **2h**



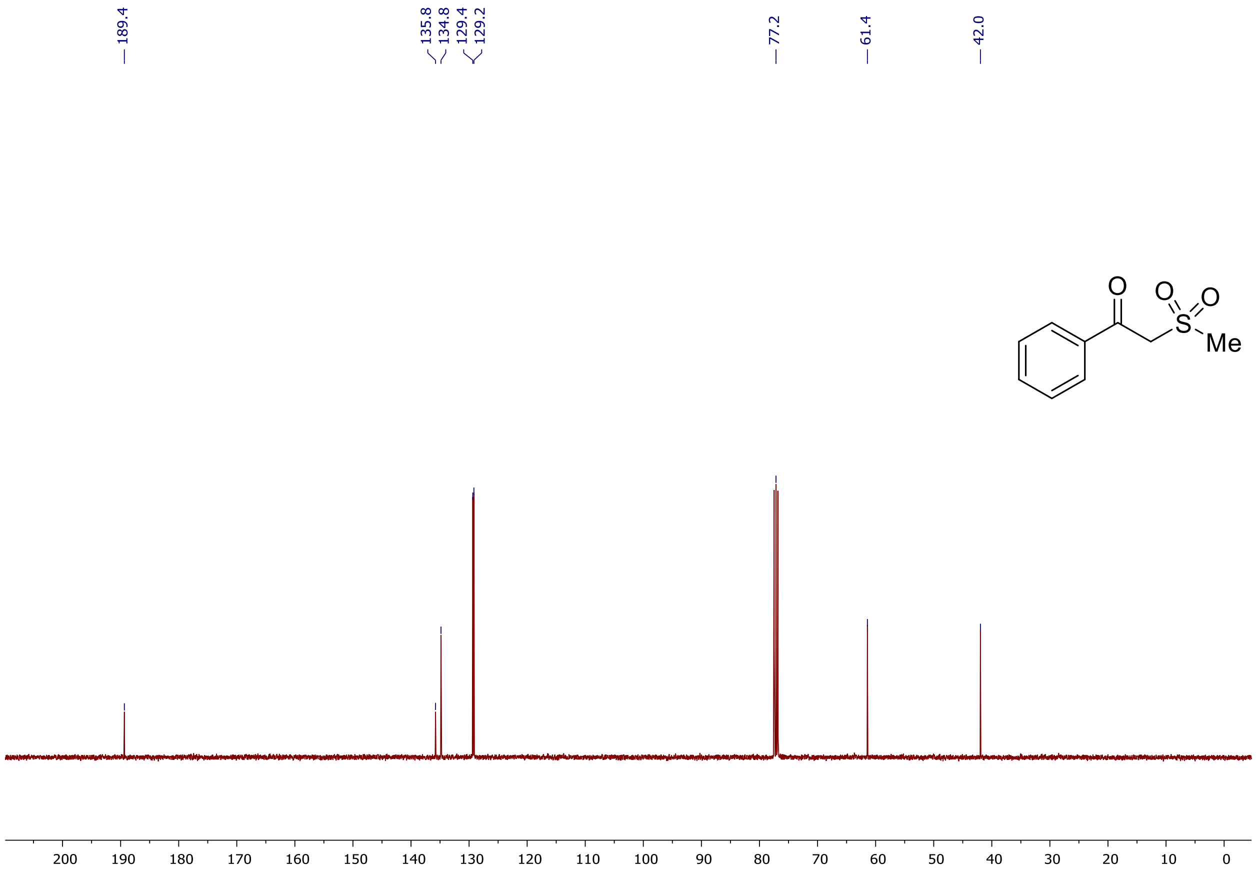
[13]C{[1]H} NMR (100 MHz, DMSO-d_6) of **2h**



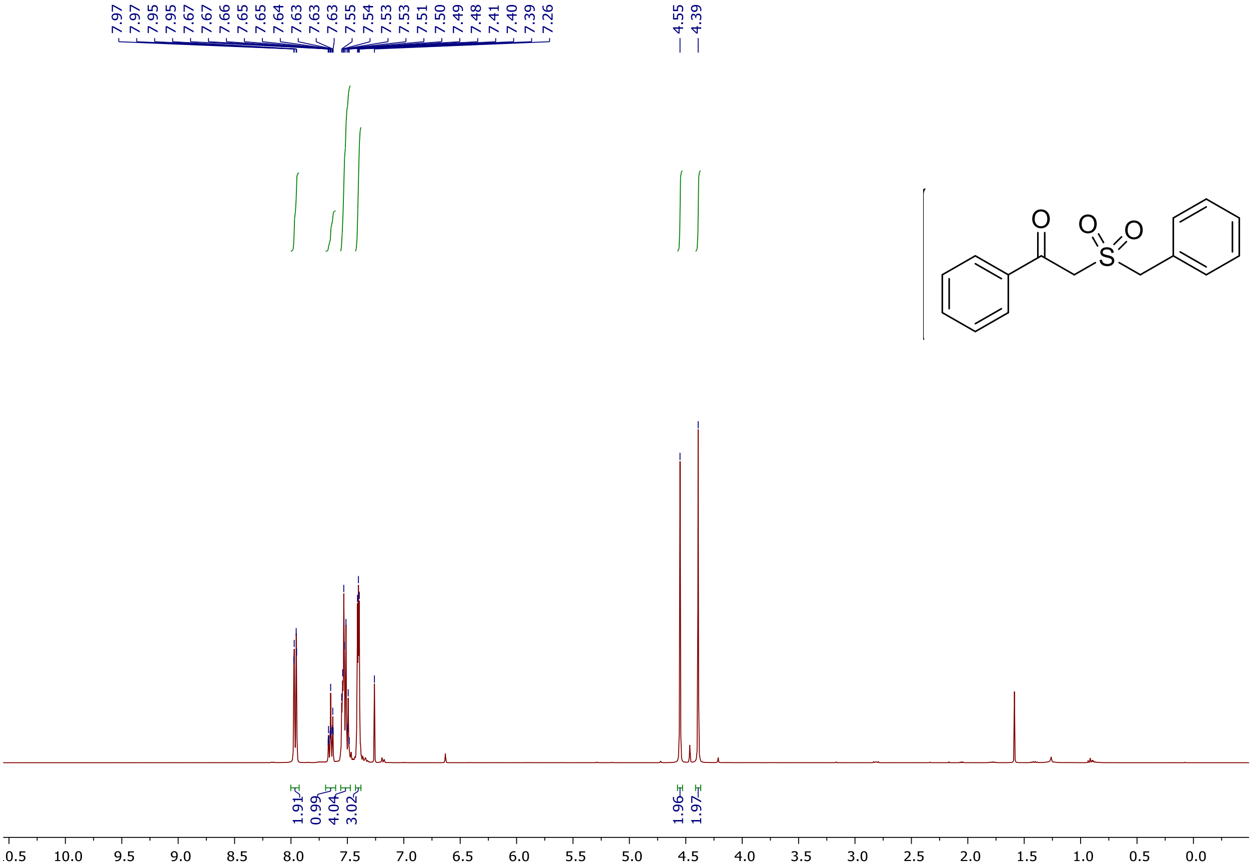
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



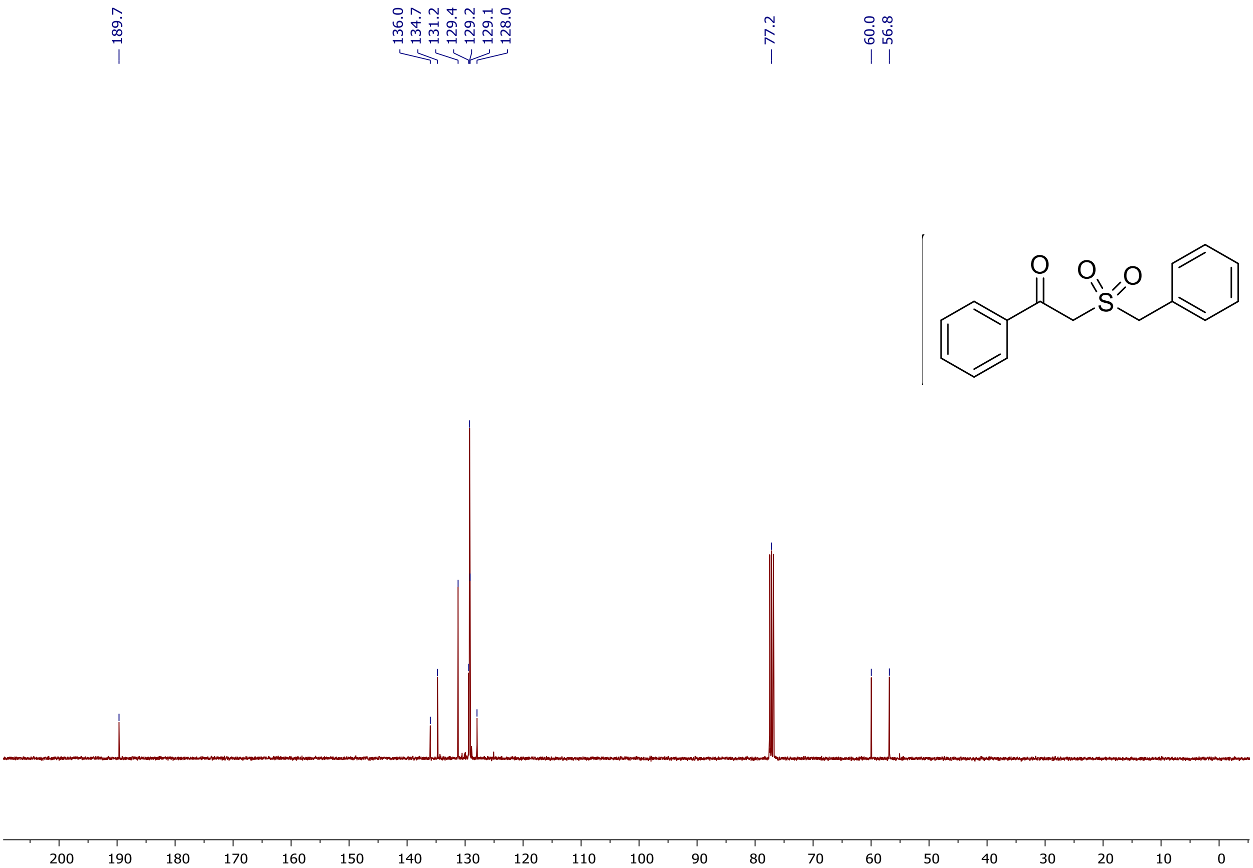
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2i**



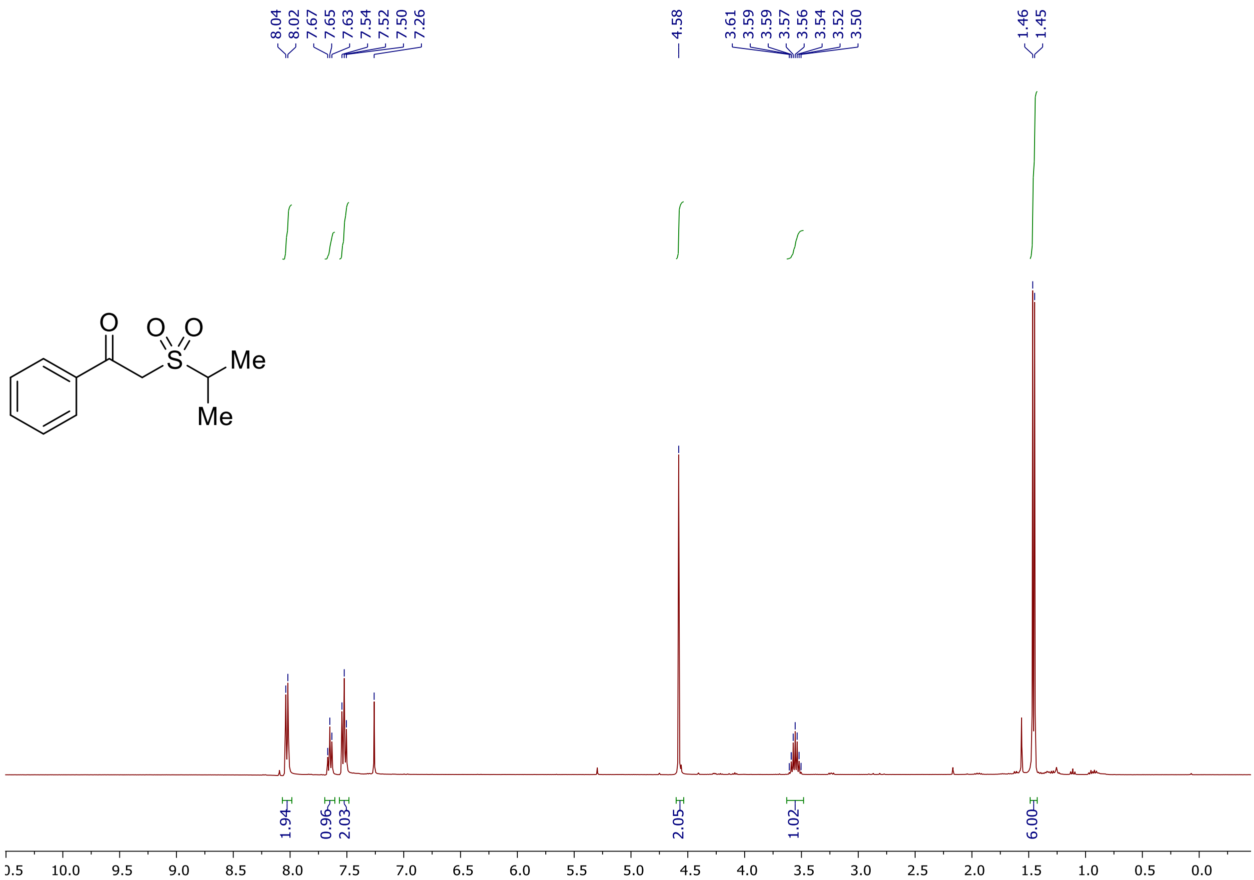
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



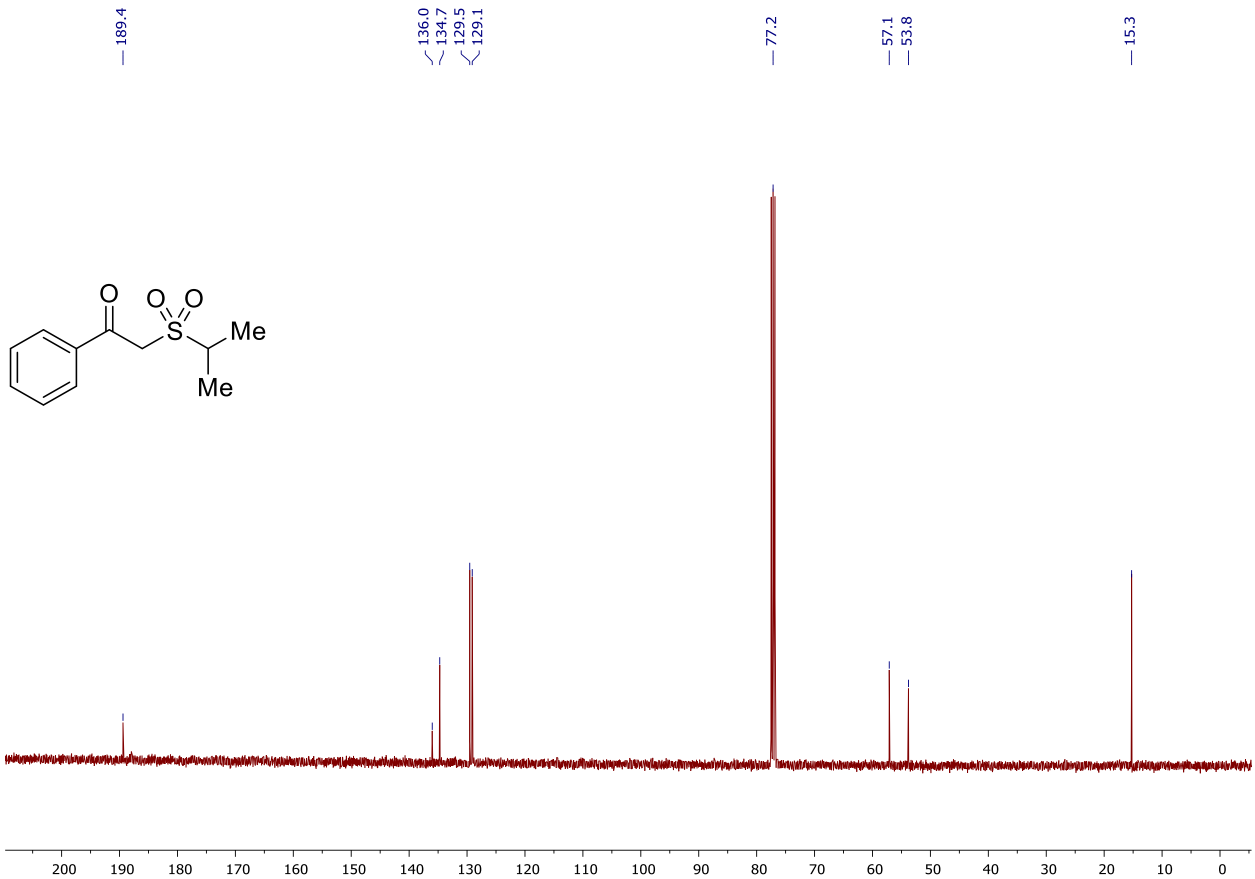
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2j**



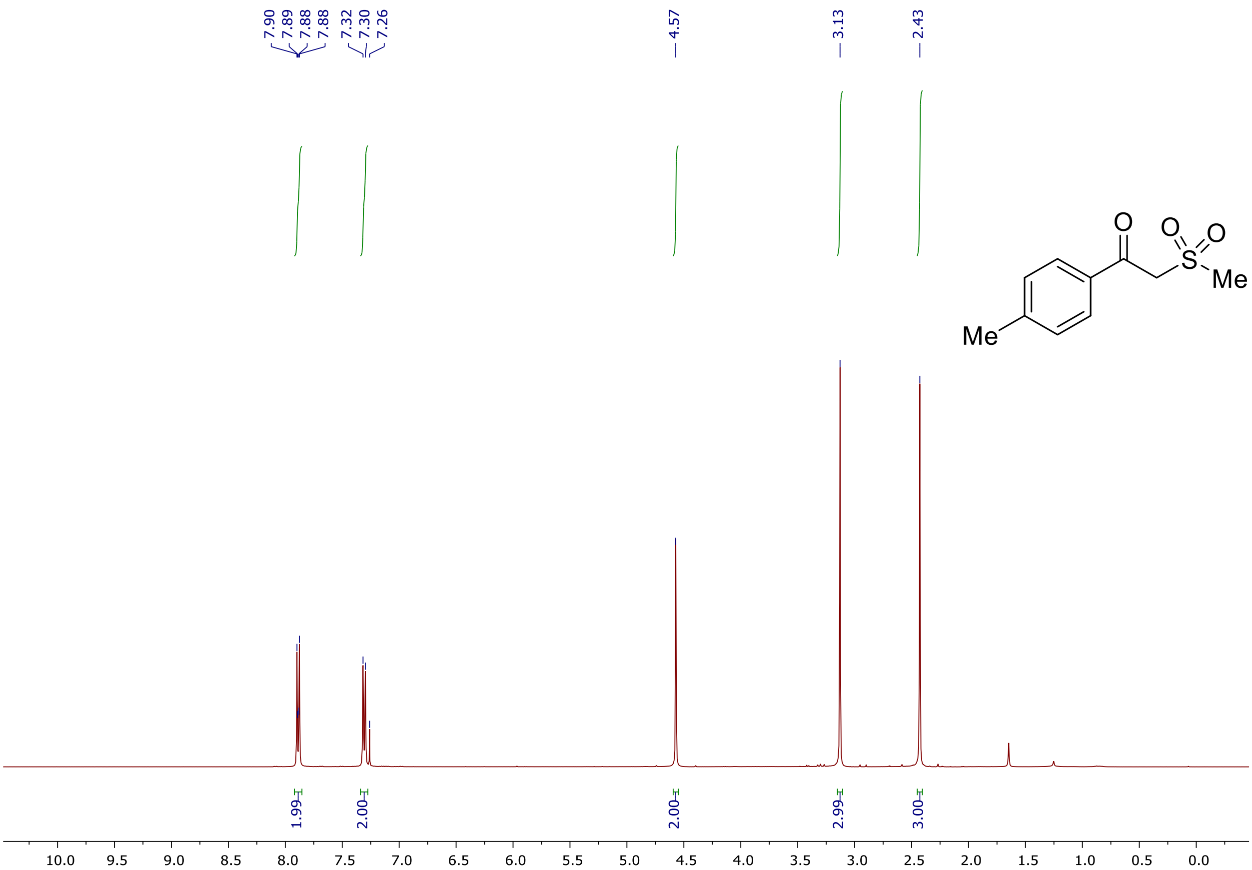
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



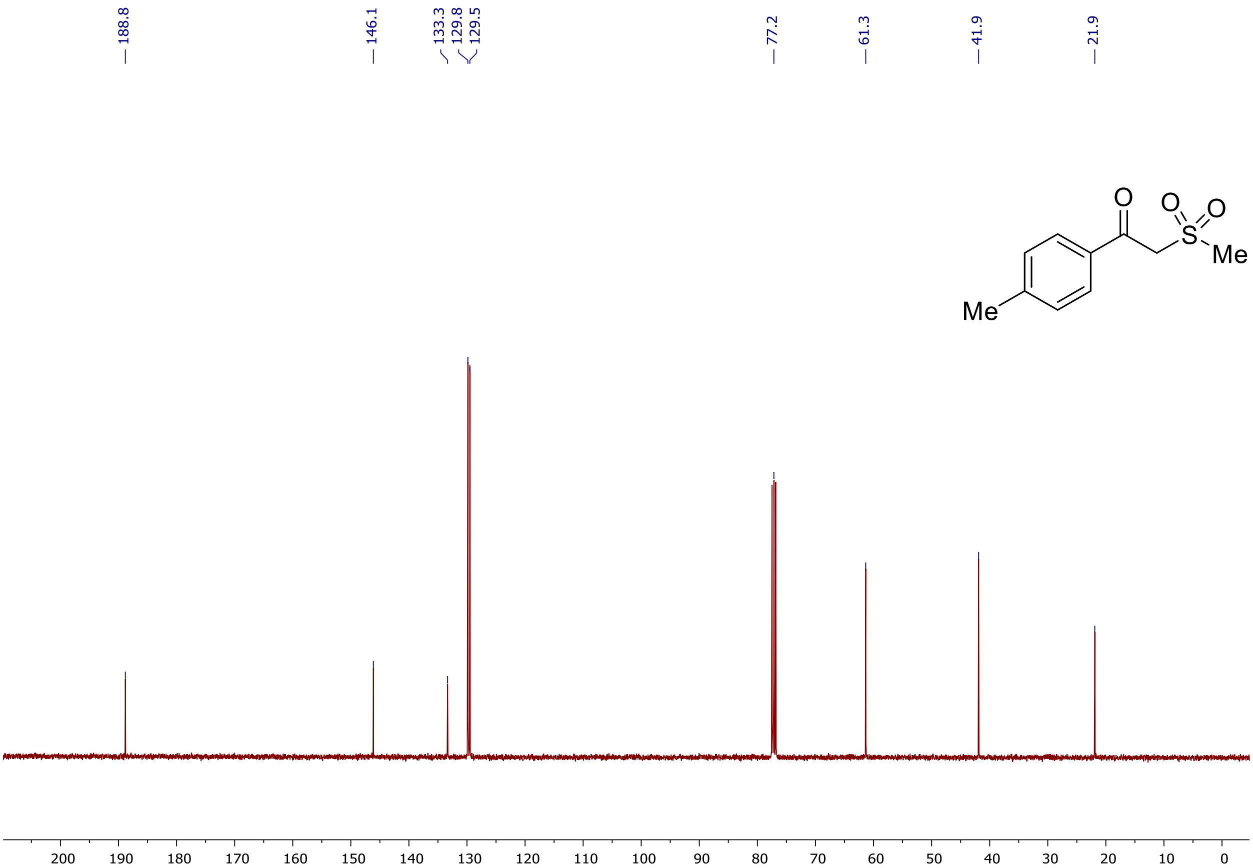
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2k**



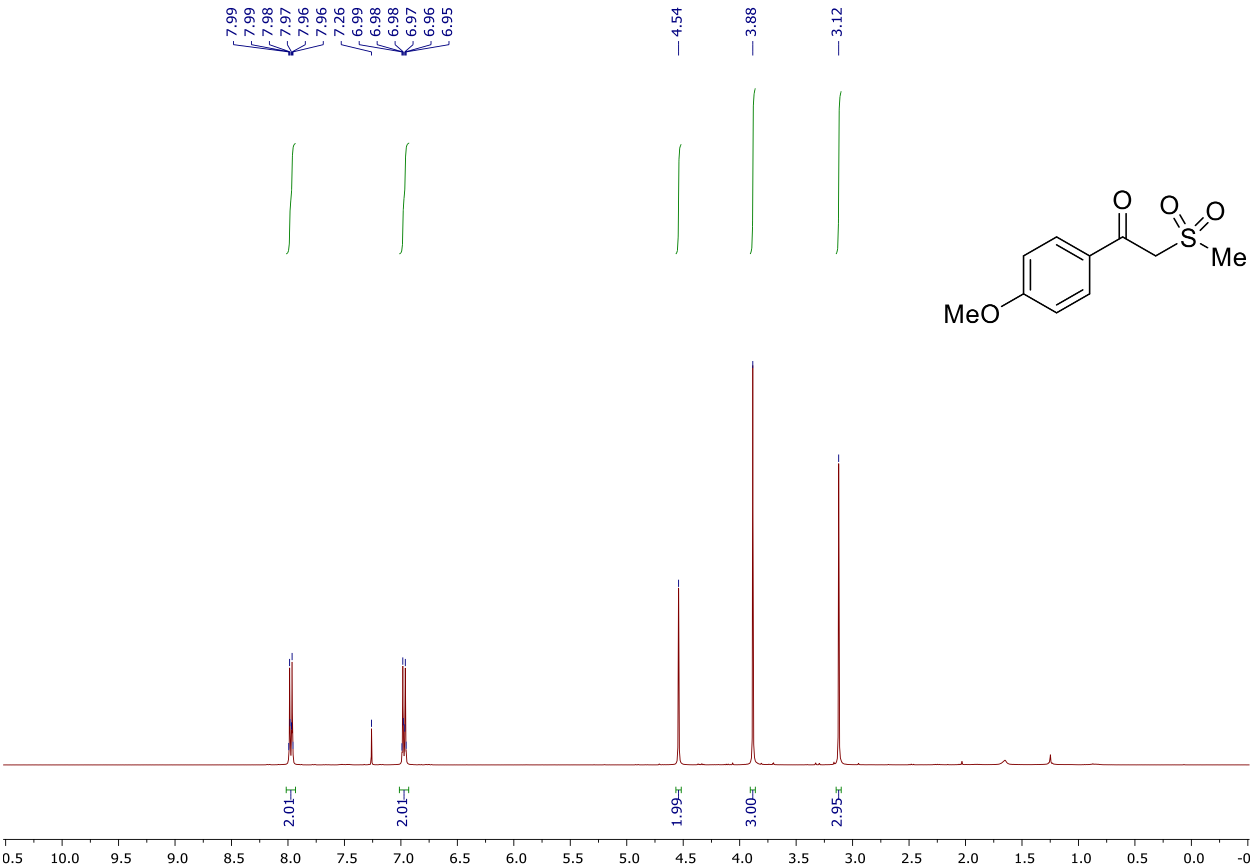
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



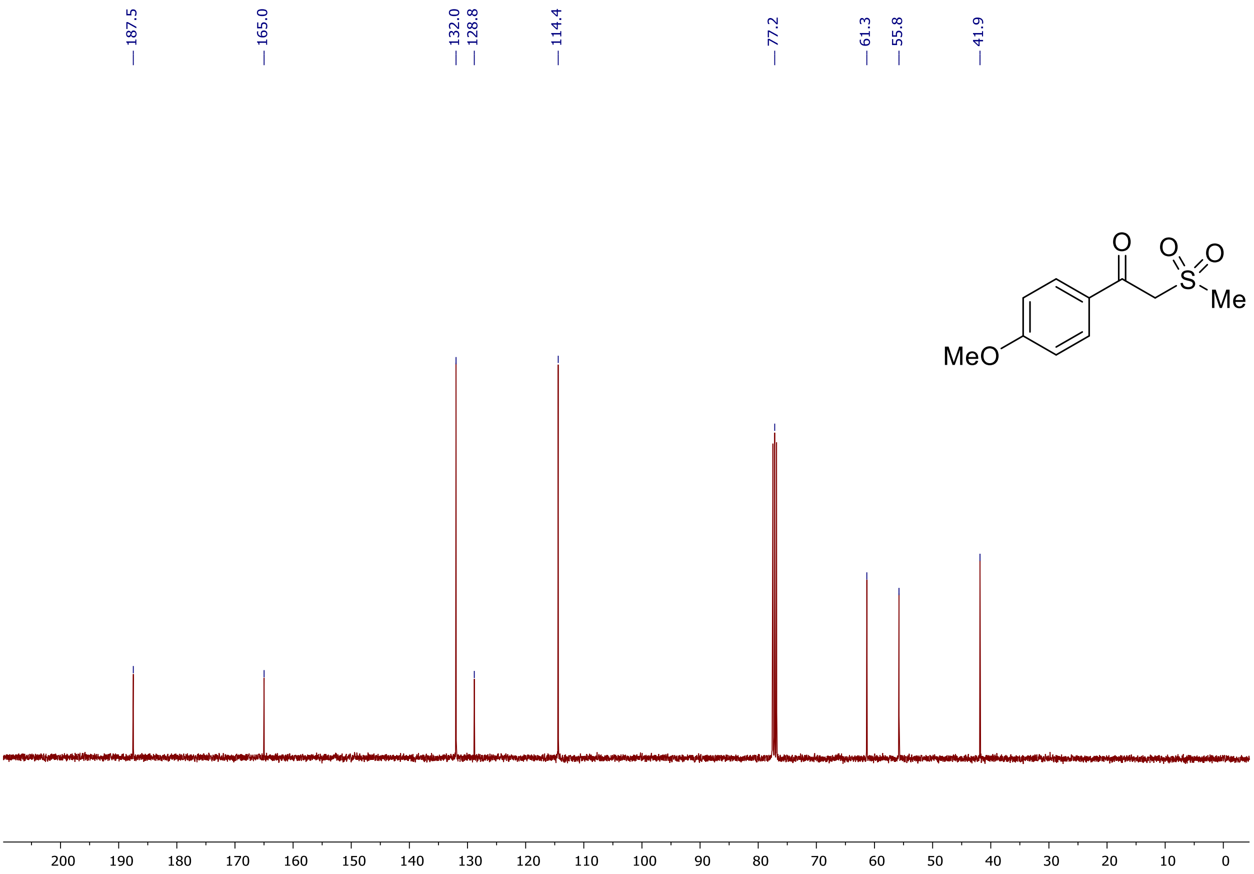
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2l**



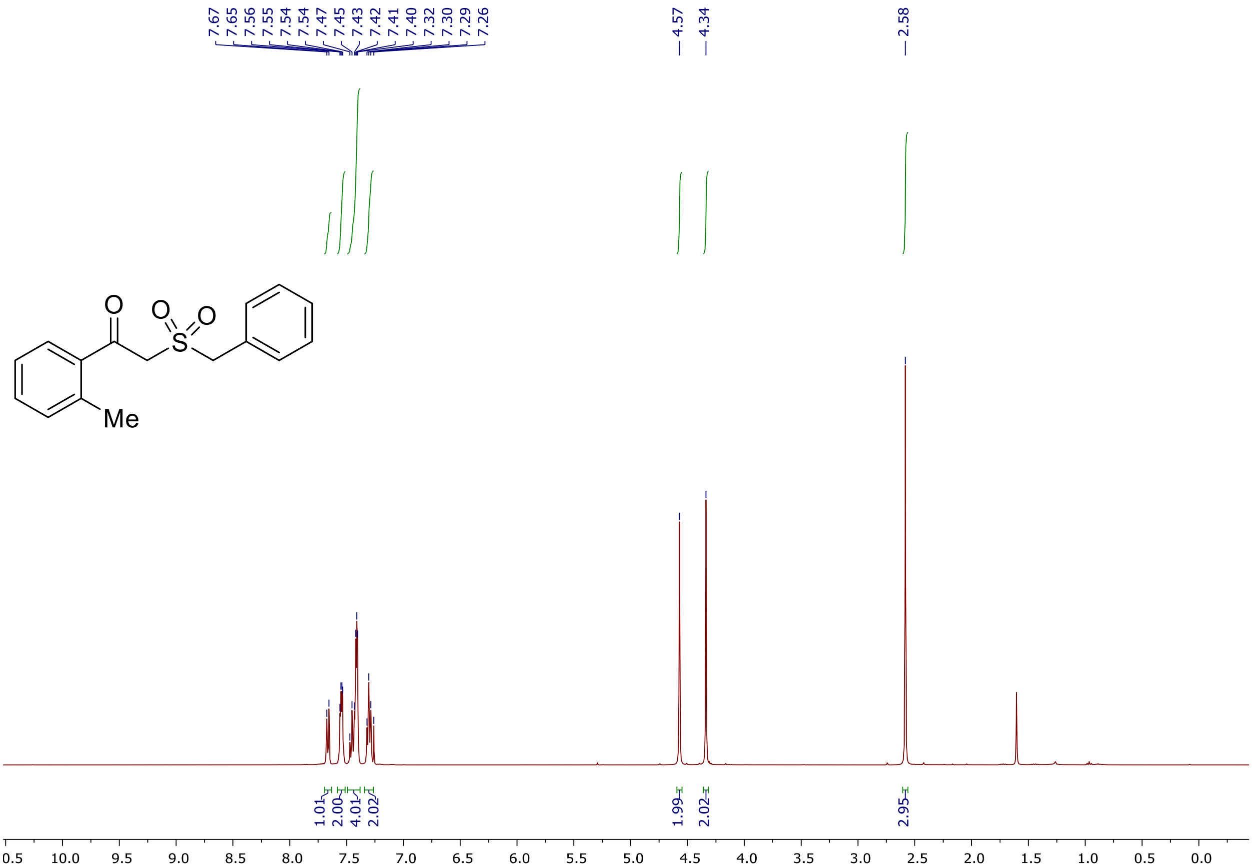
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



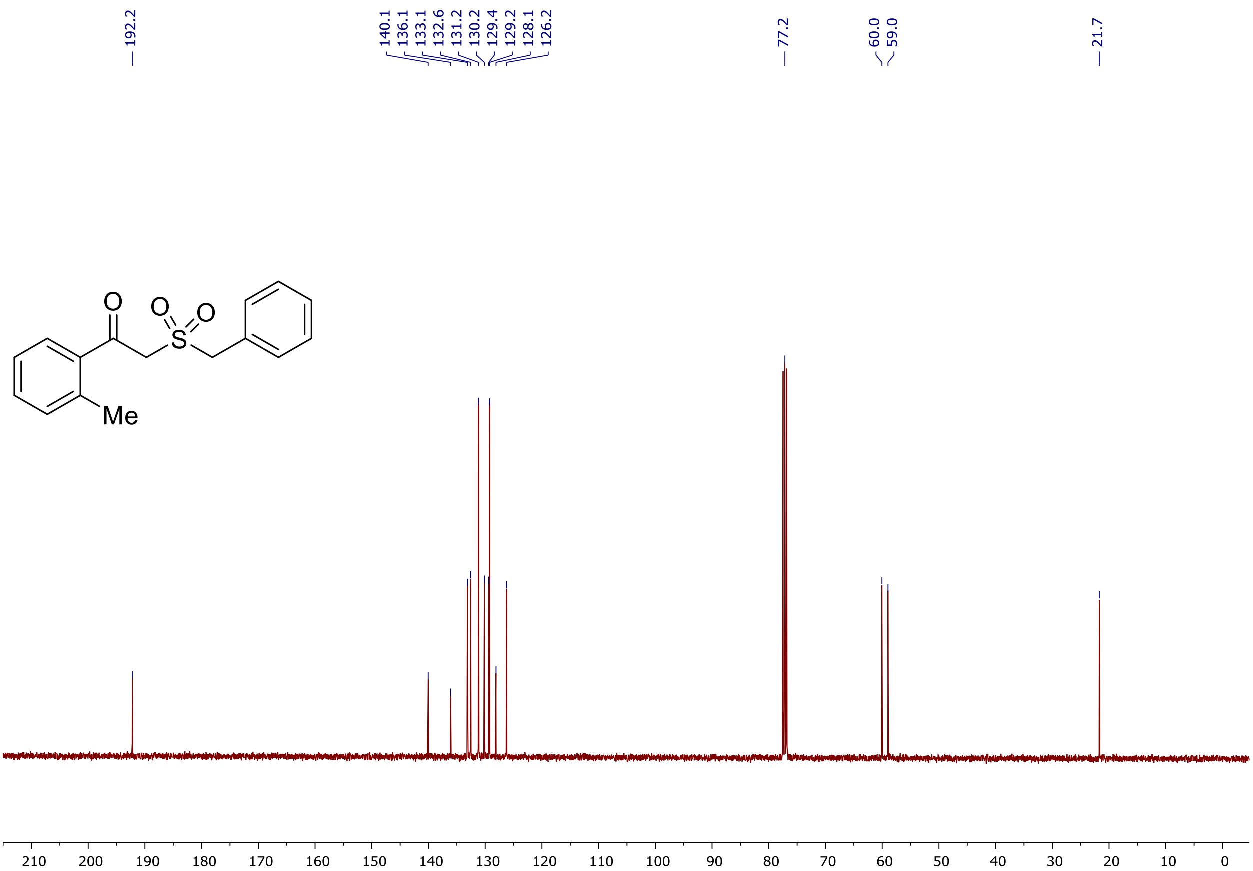
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2m**



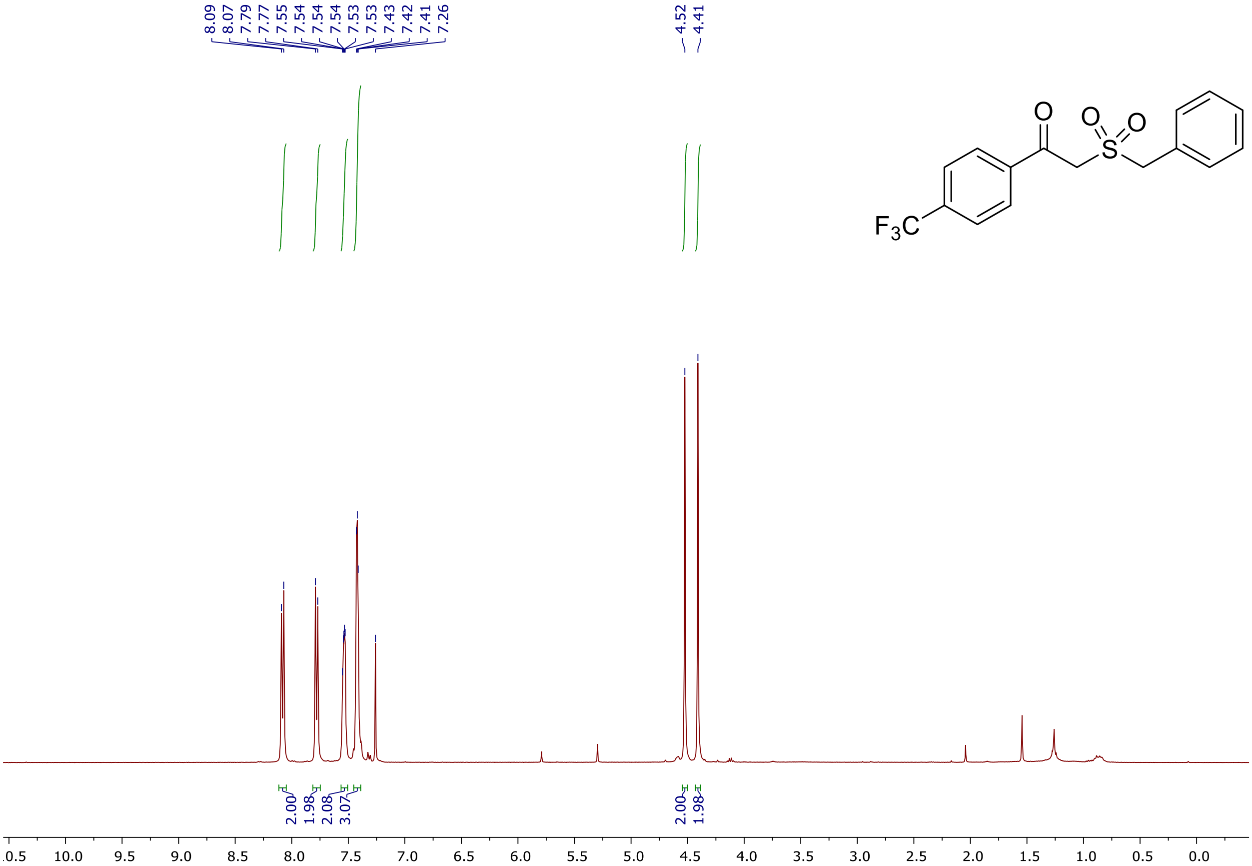
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



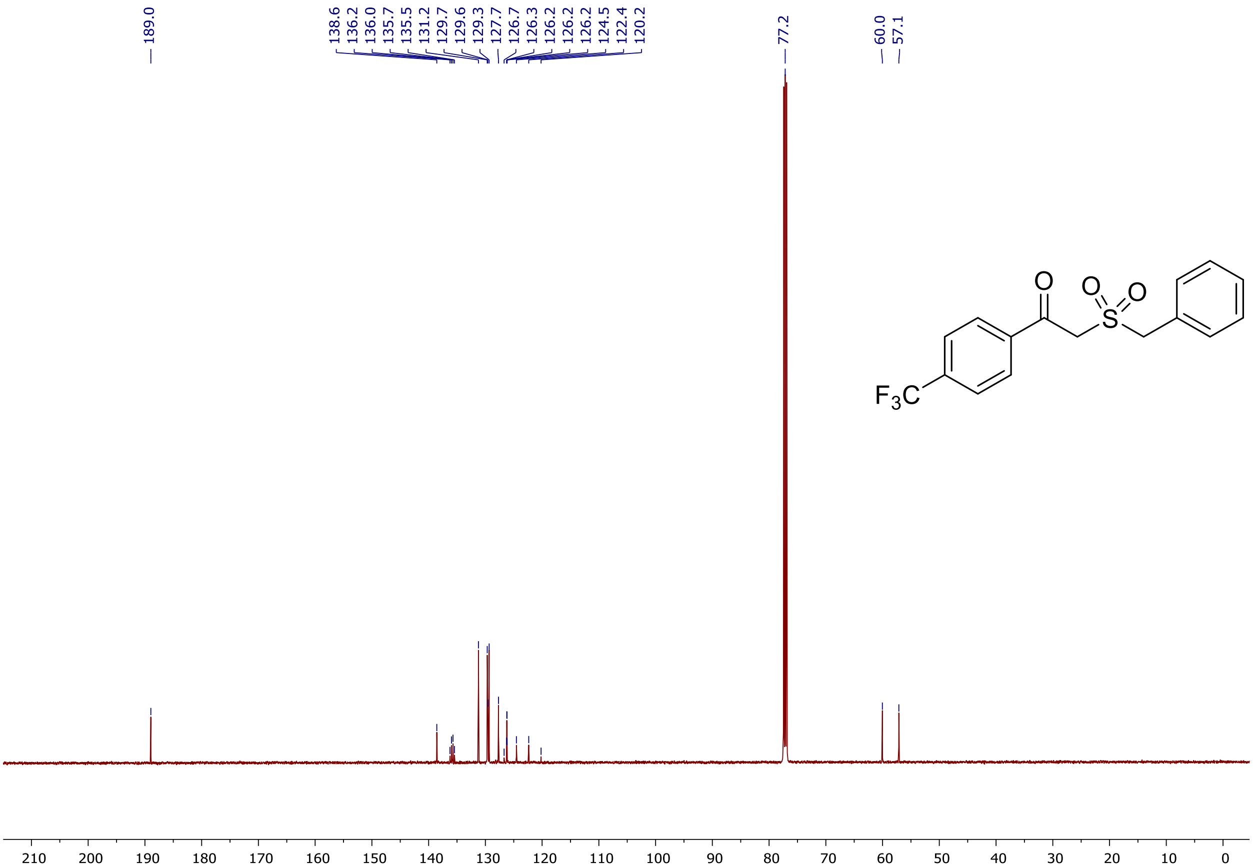
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2n**



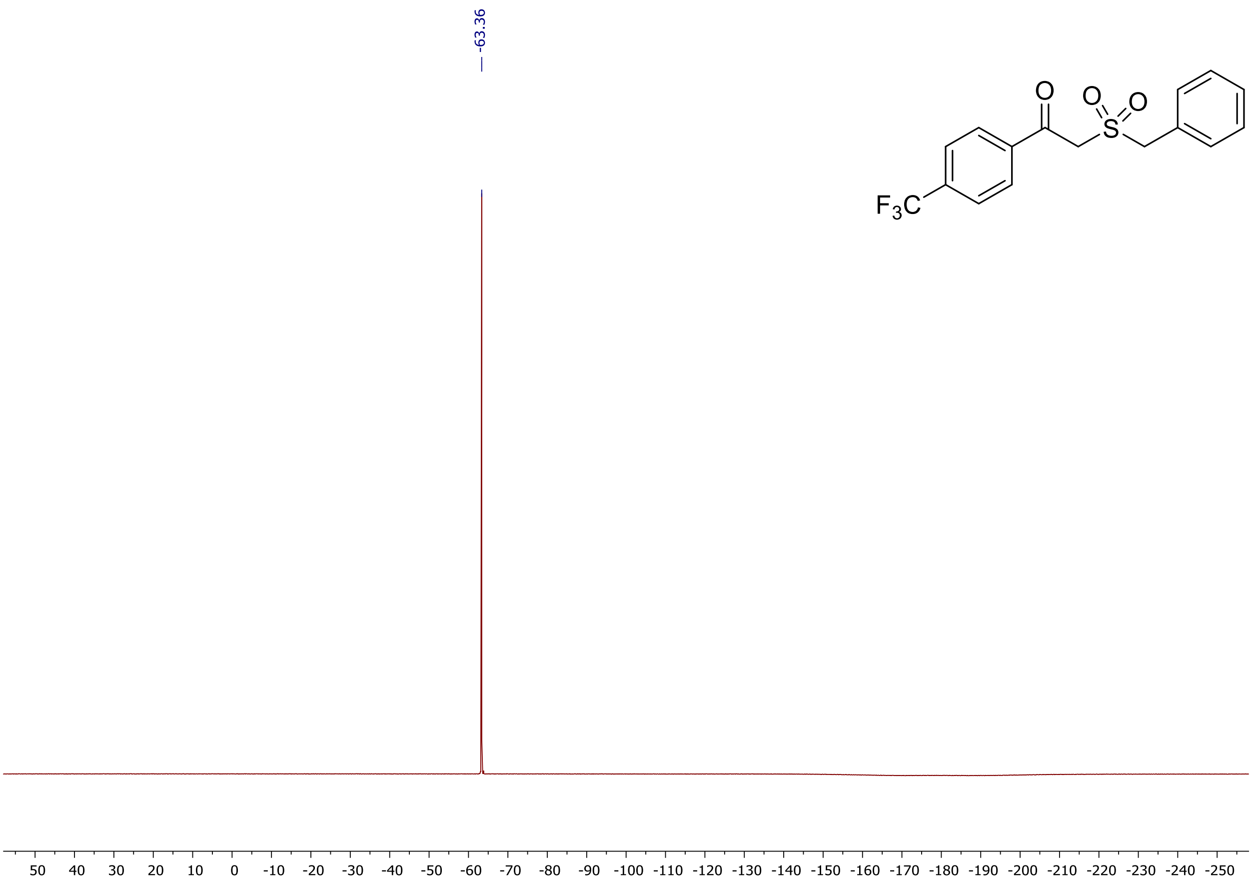
^{1}H NMR (400 MHz, $CDCl_3$) of **2o**



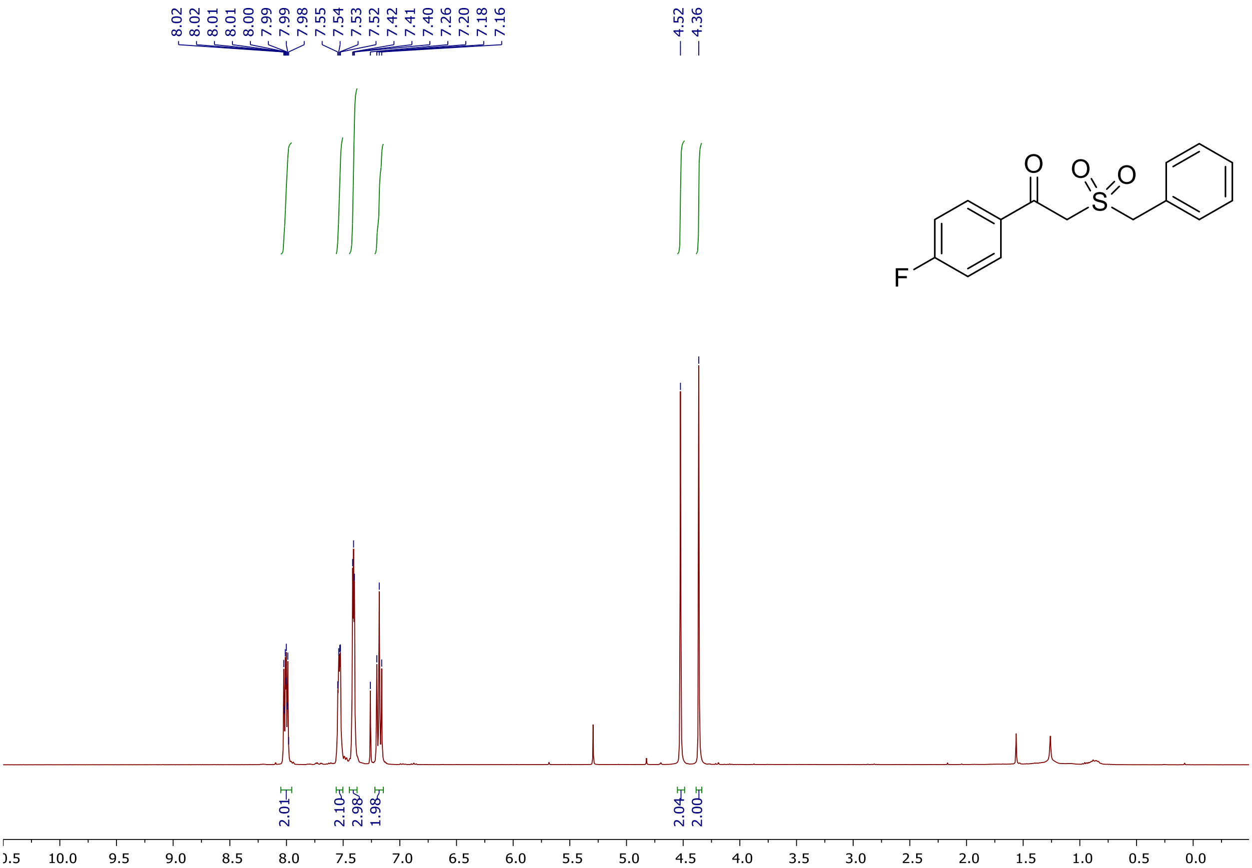
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2o**



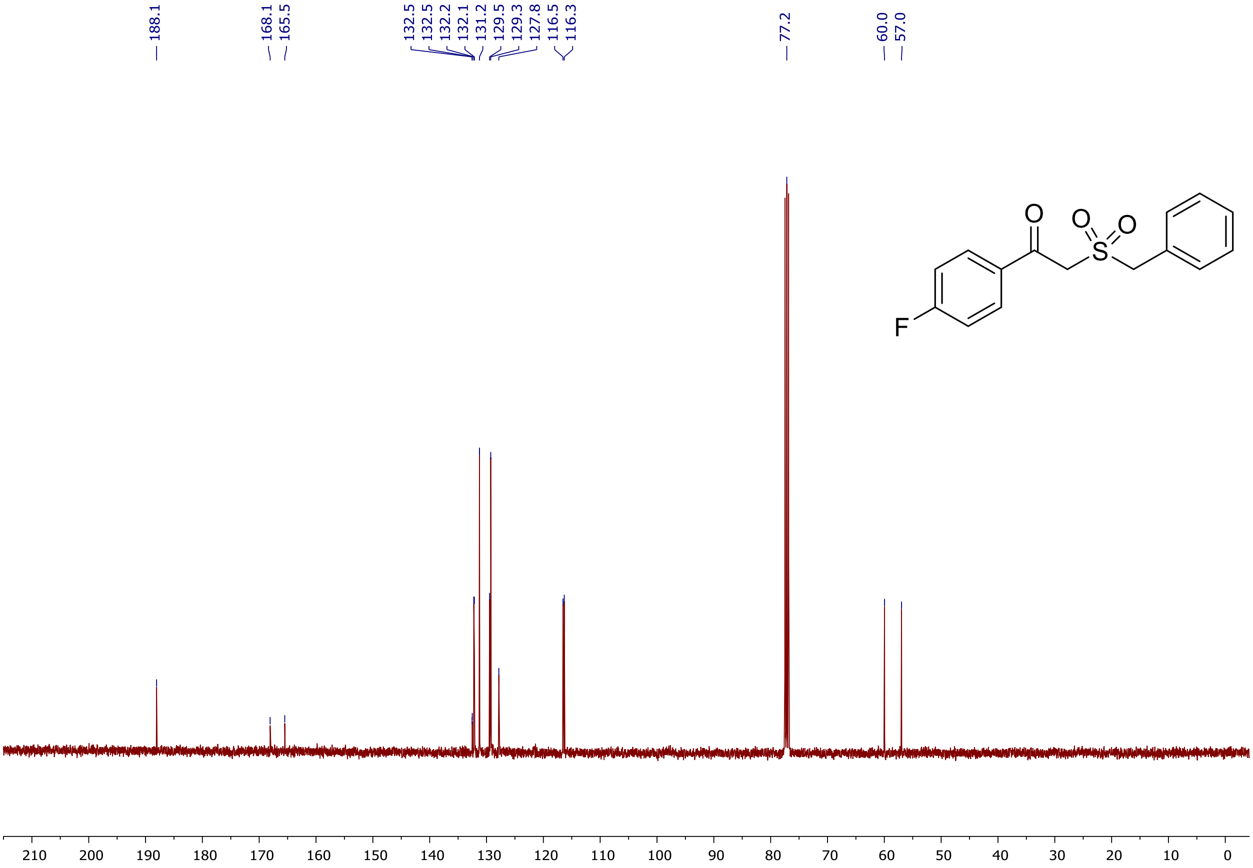
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **2o**



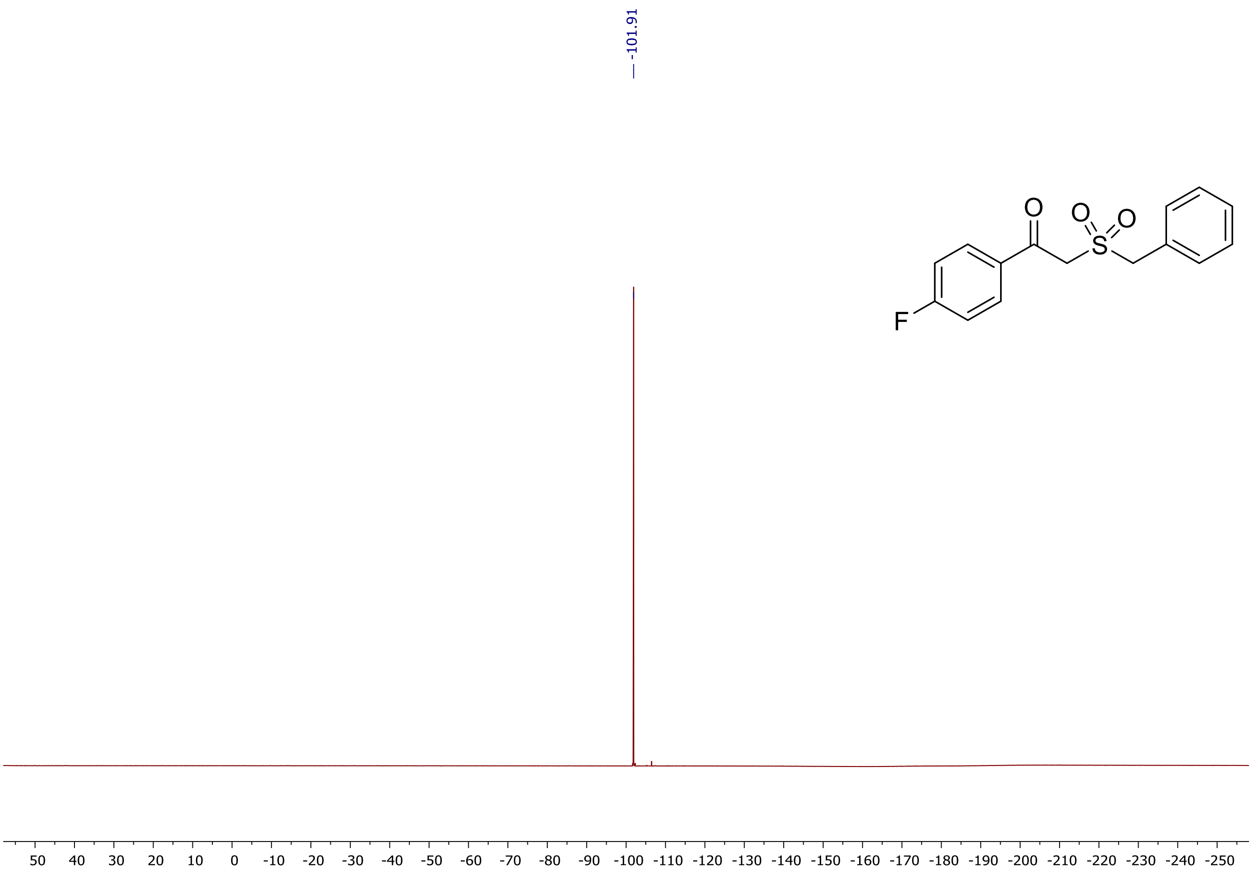
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



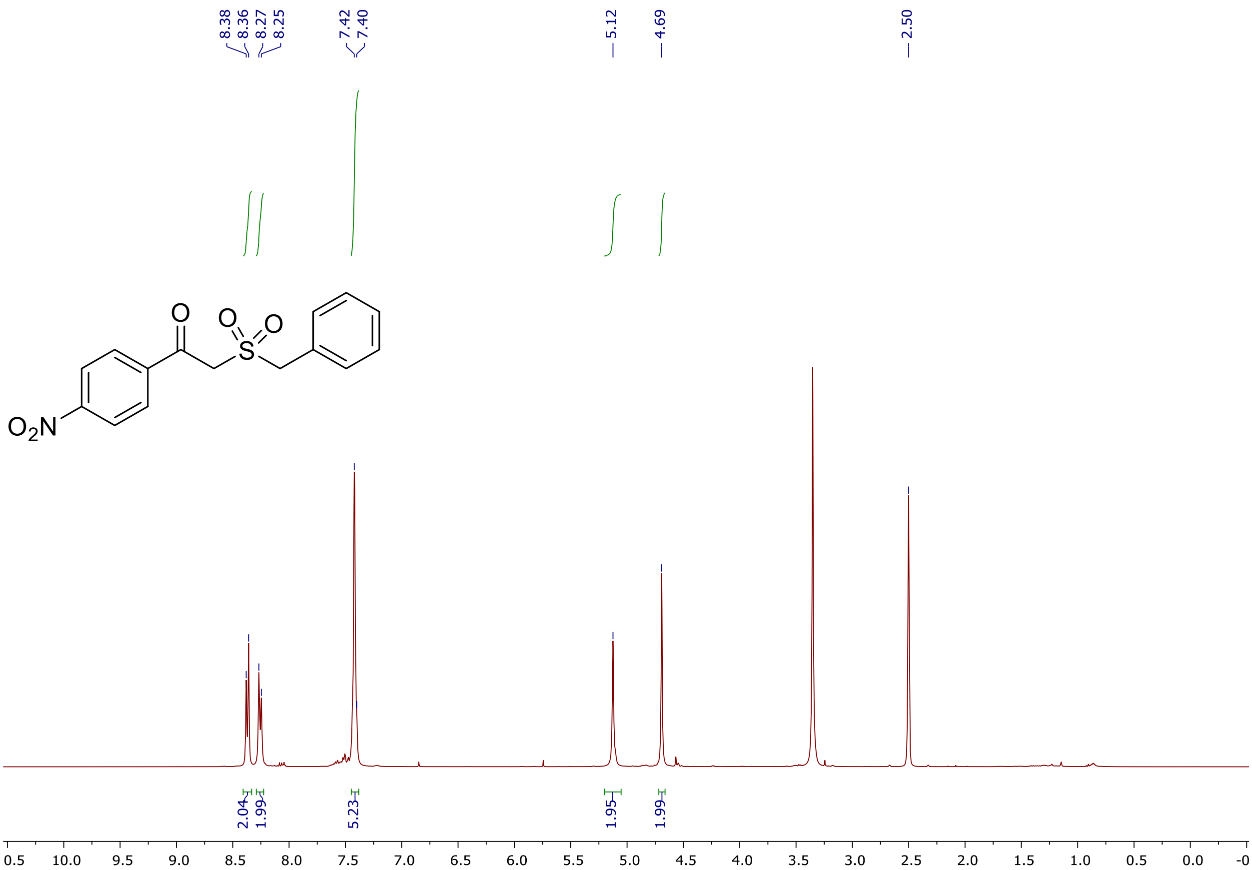
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2p**



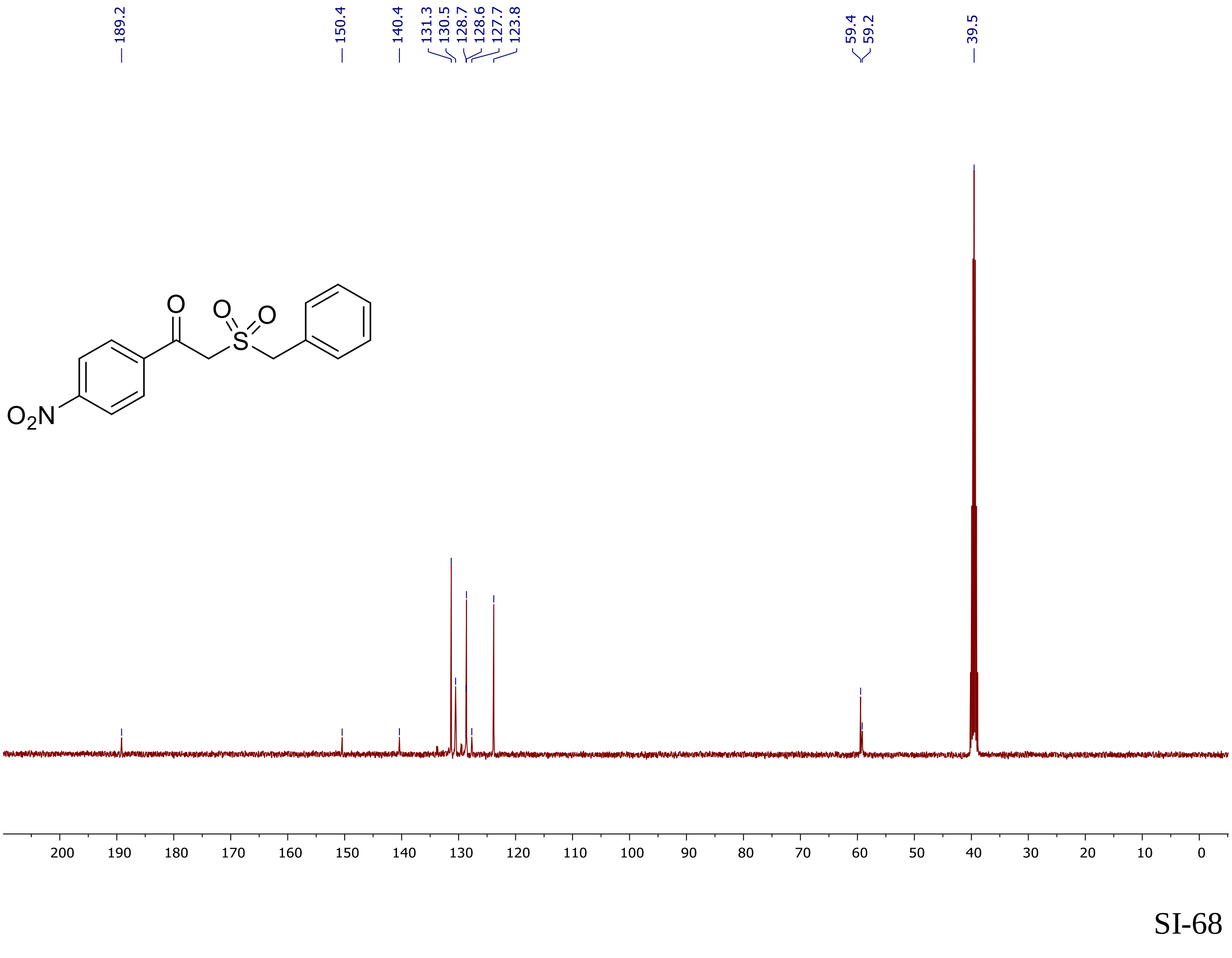
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **2p**



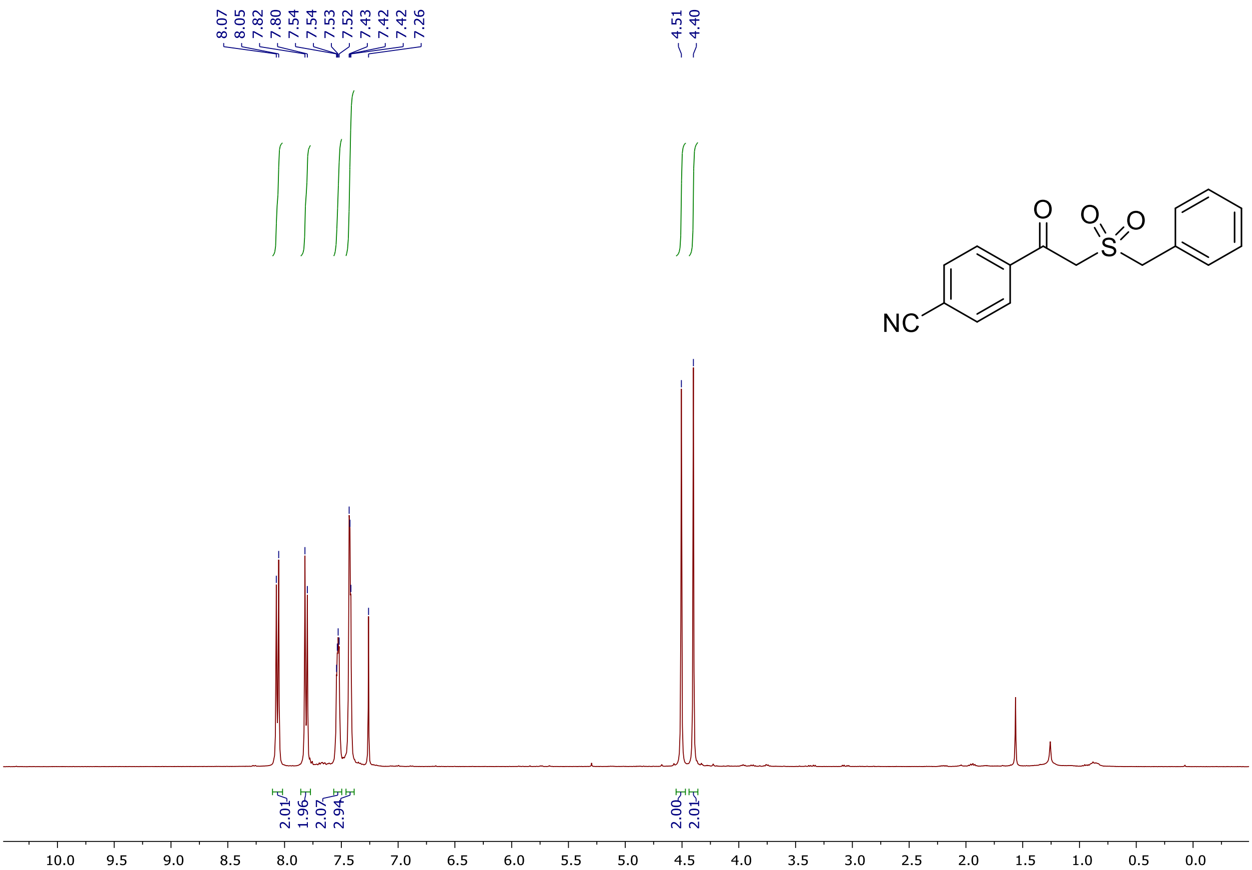
^{1}H NMR (400 MHz, DMSO-d_6) of **2q**



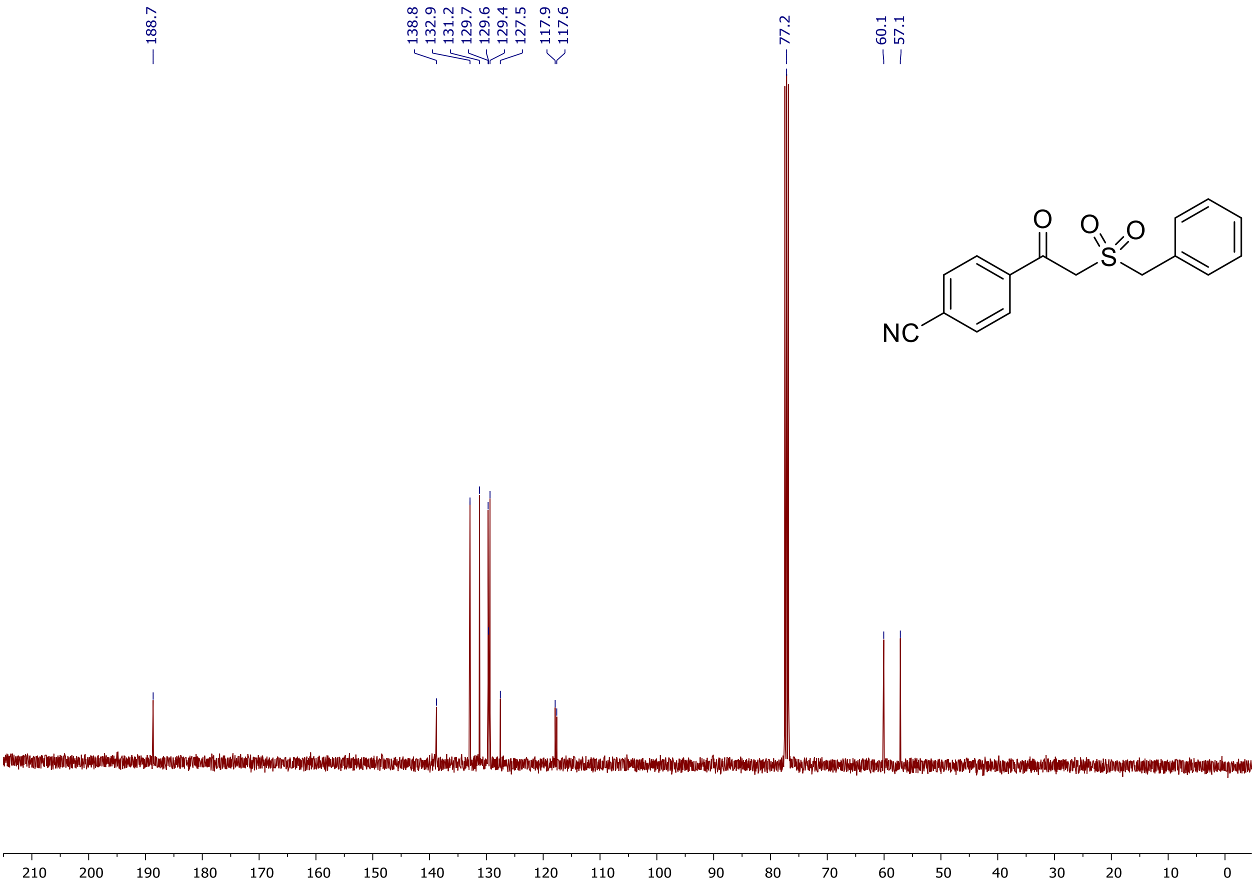
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **2q**



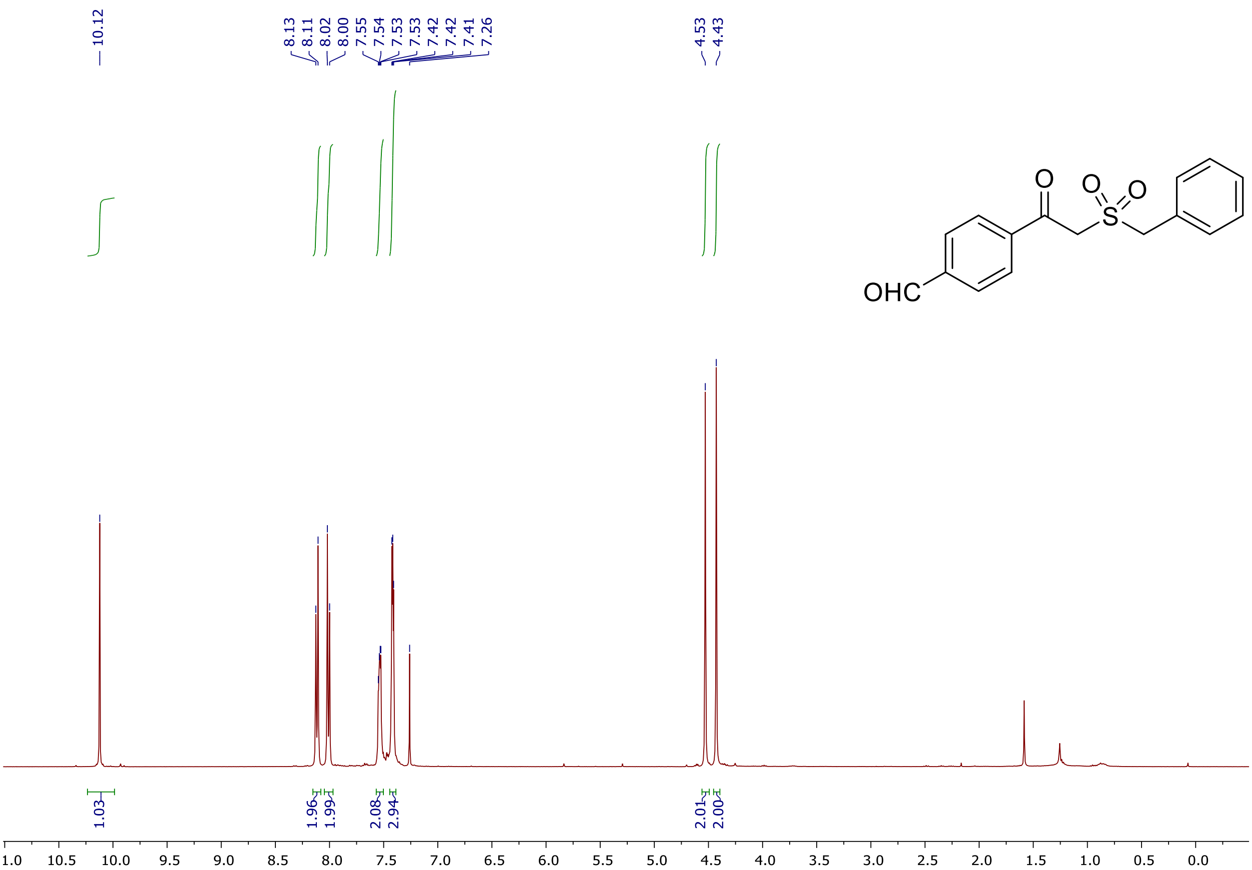
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**



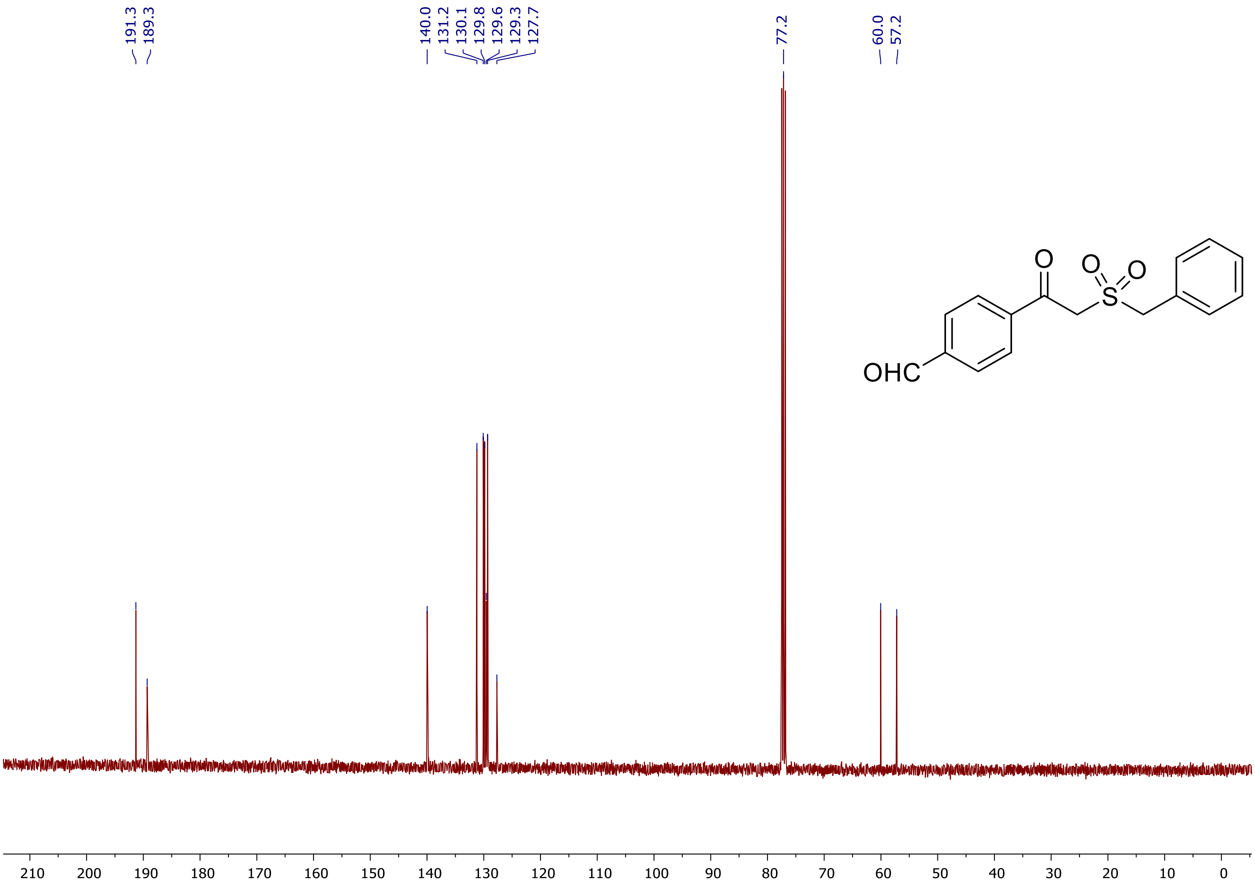
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2r**



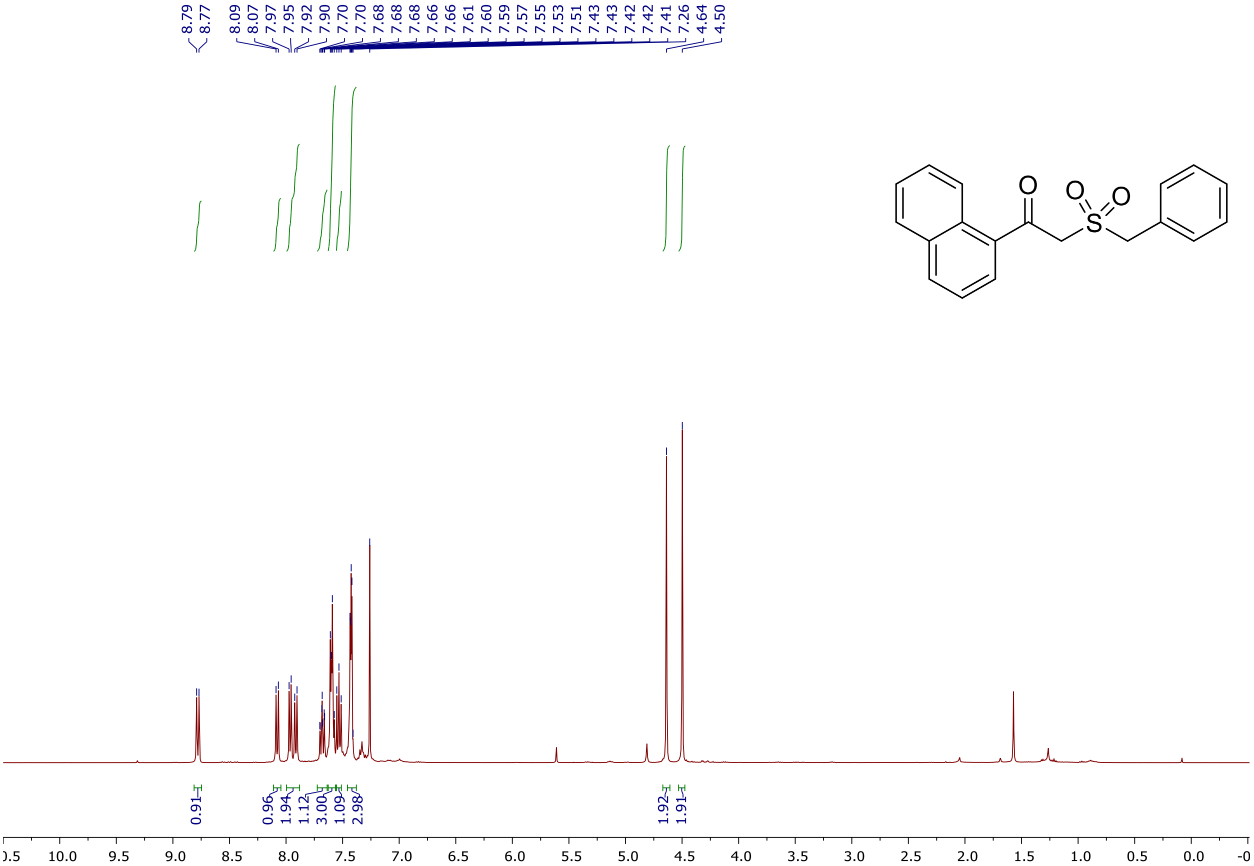
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



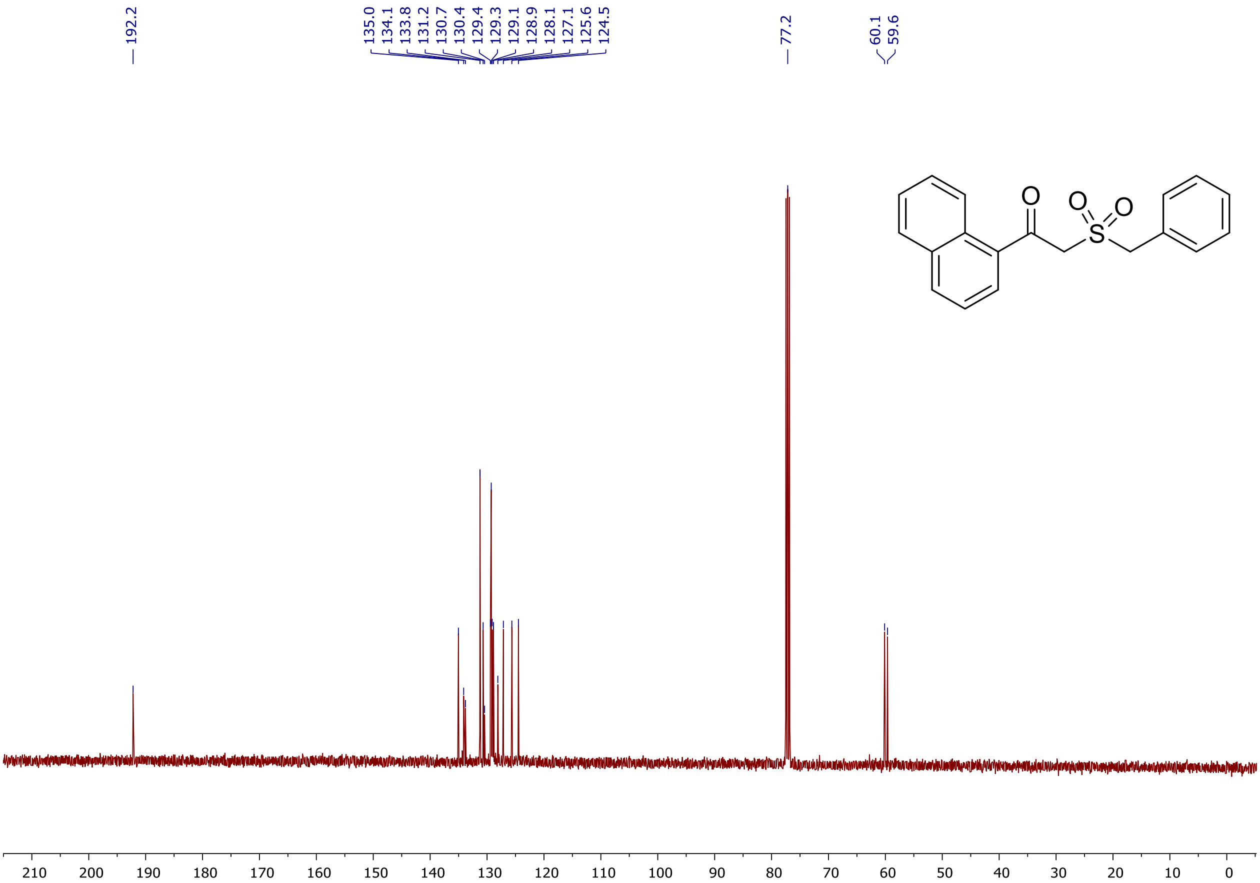
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2s**



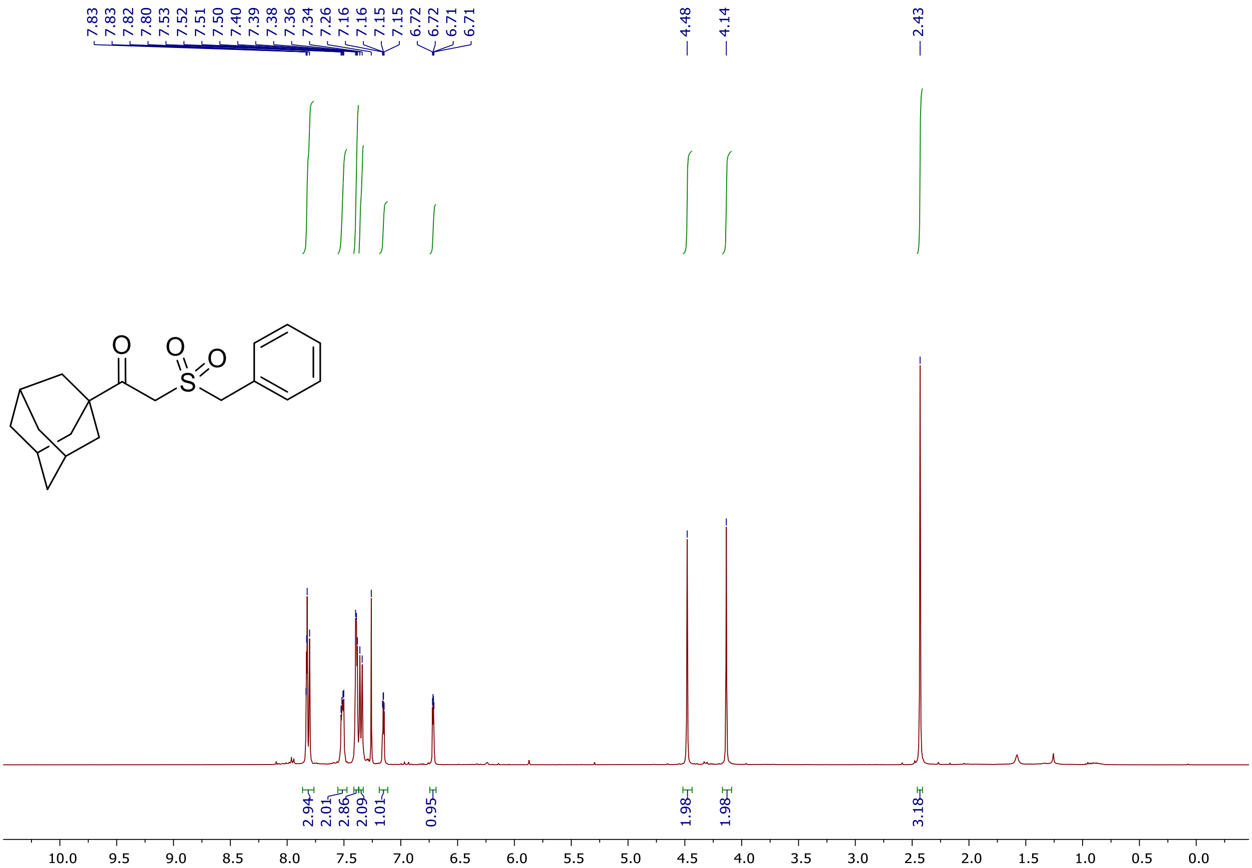
[1]H NMR (400 MHz, $CDCl_3$) of **2t**



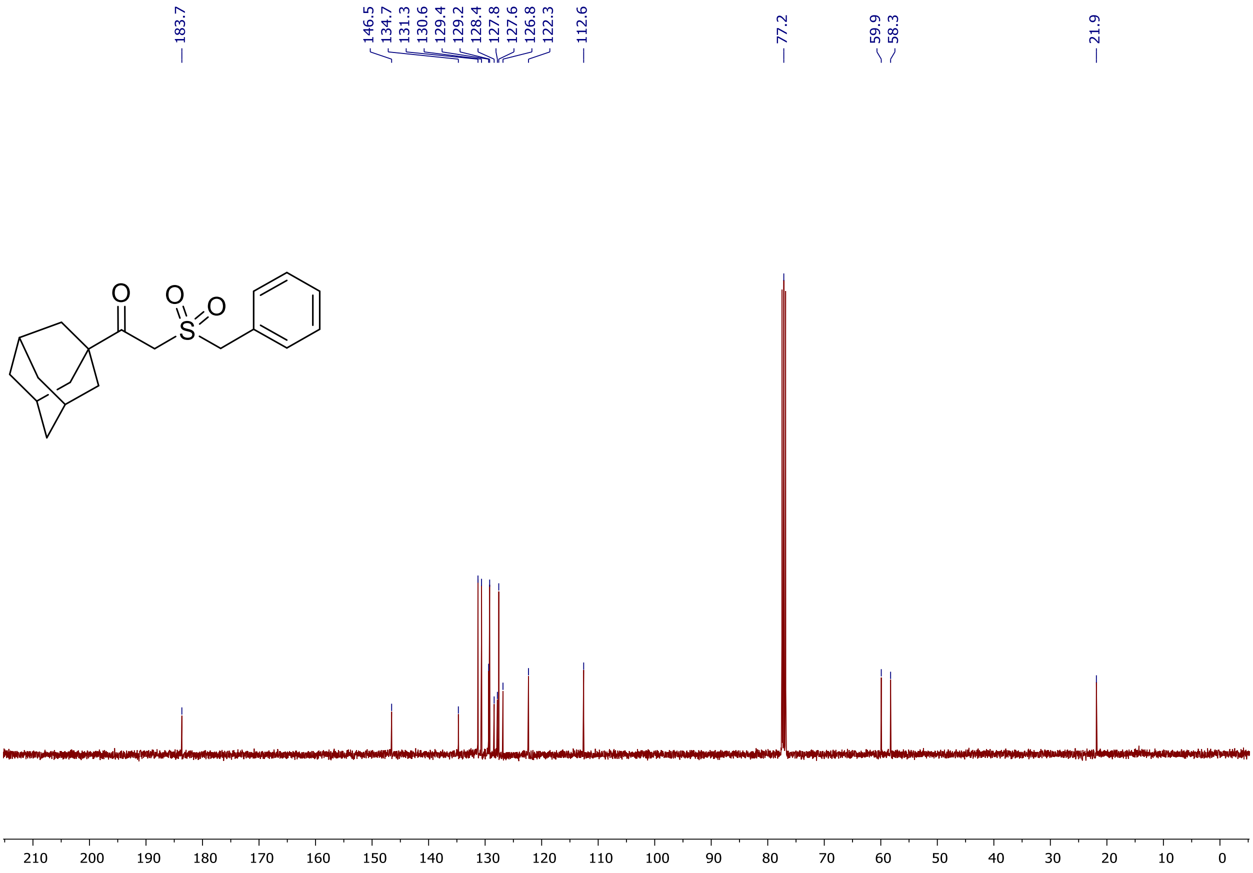
[13]C{[1]H} NMR (100 MHz, $CDCl_3$) of **2t**



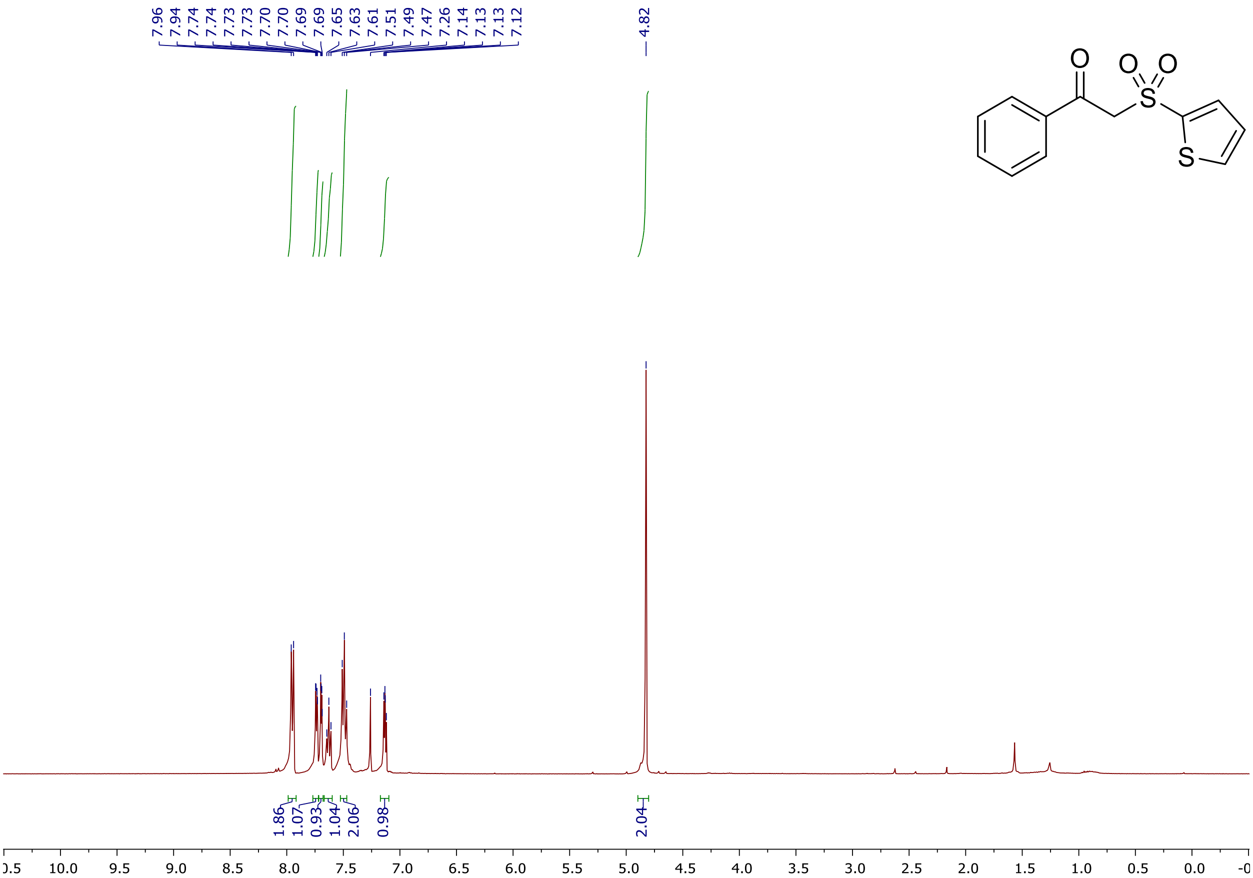
[1]H NMR (400 MHz, $CDCl_3$) of **2u**



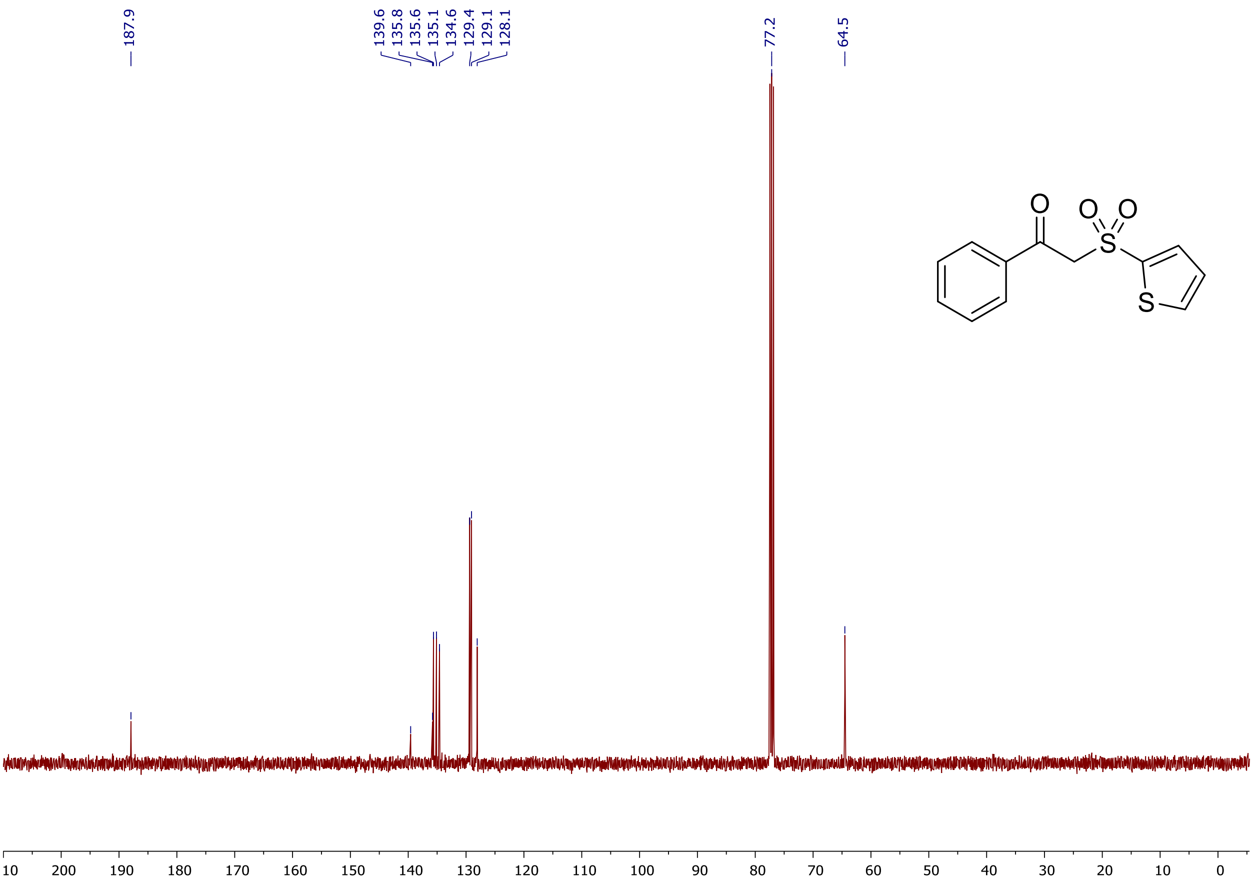
[13]C{[1]H} NMR (100 MHz, $CDCl_3$) of **2u**



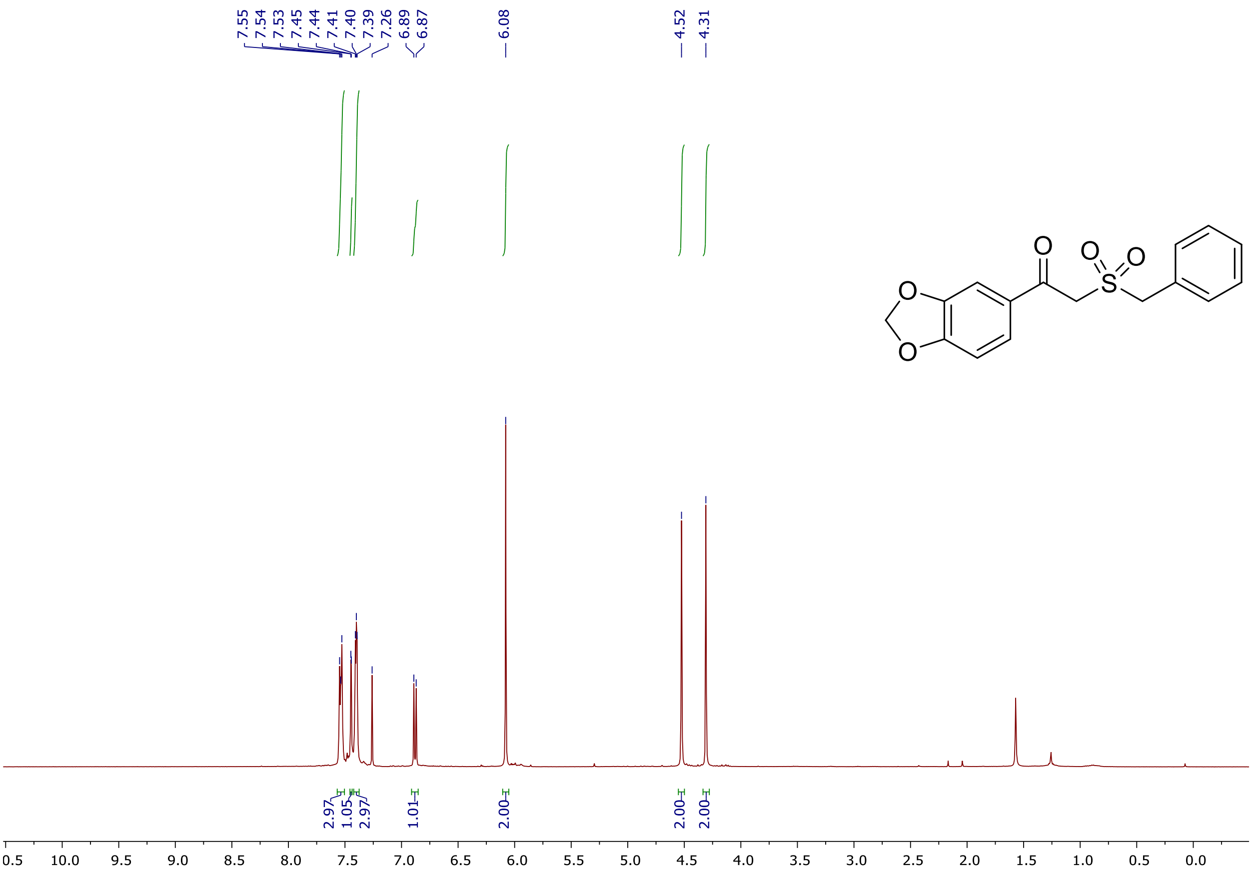
^{1}H NMR (400 MHz, $CDCl_3$) of **2v**



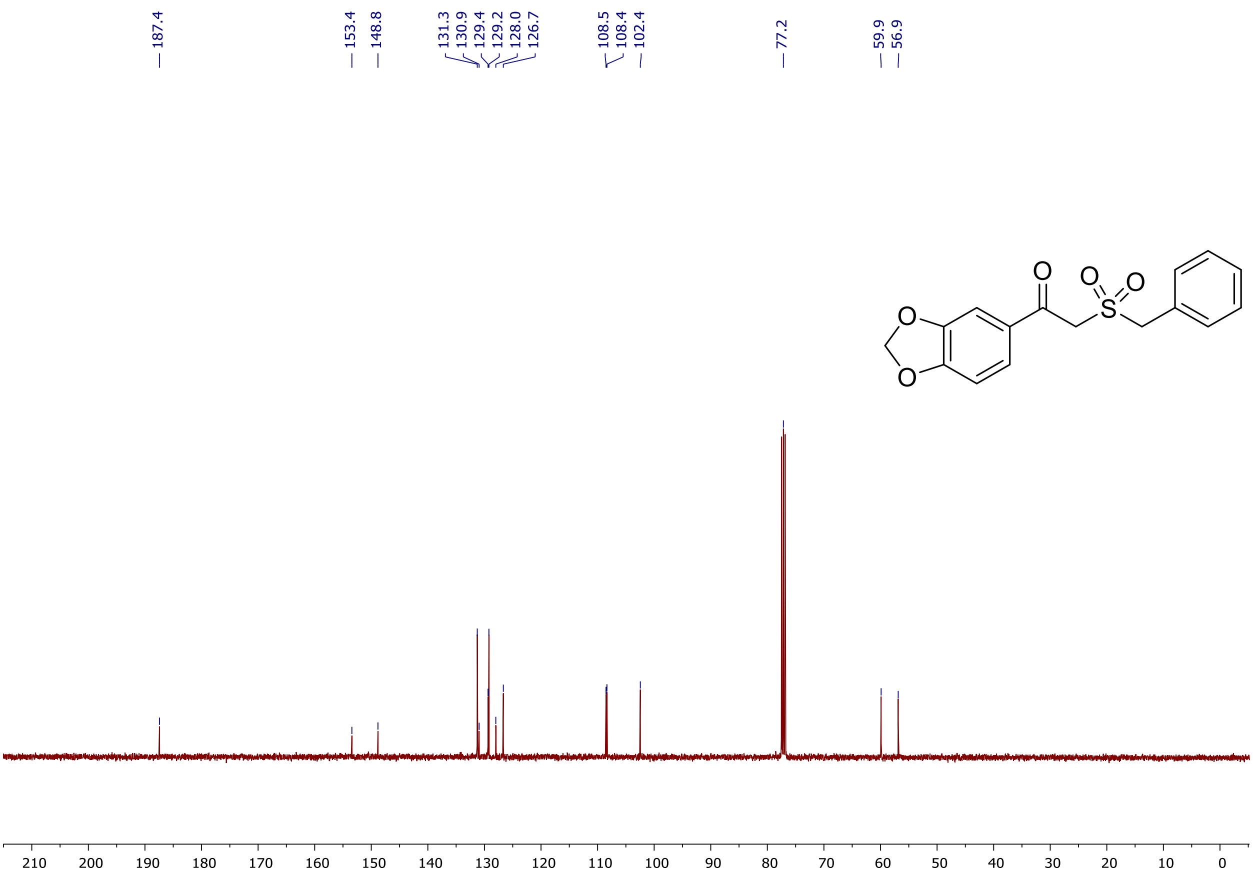
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2v**



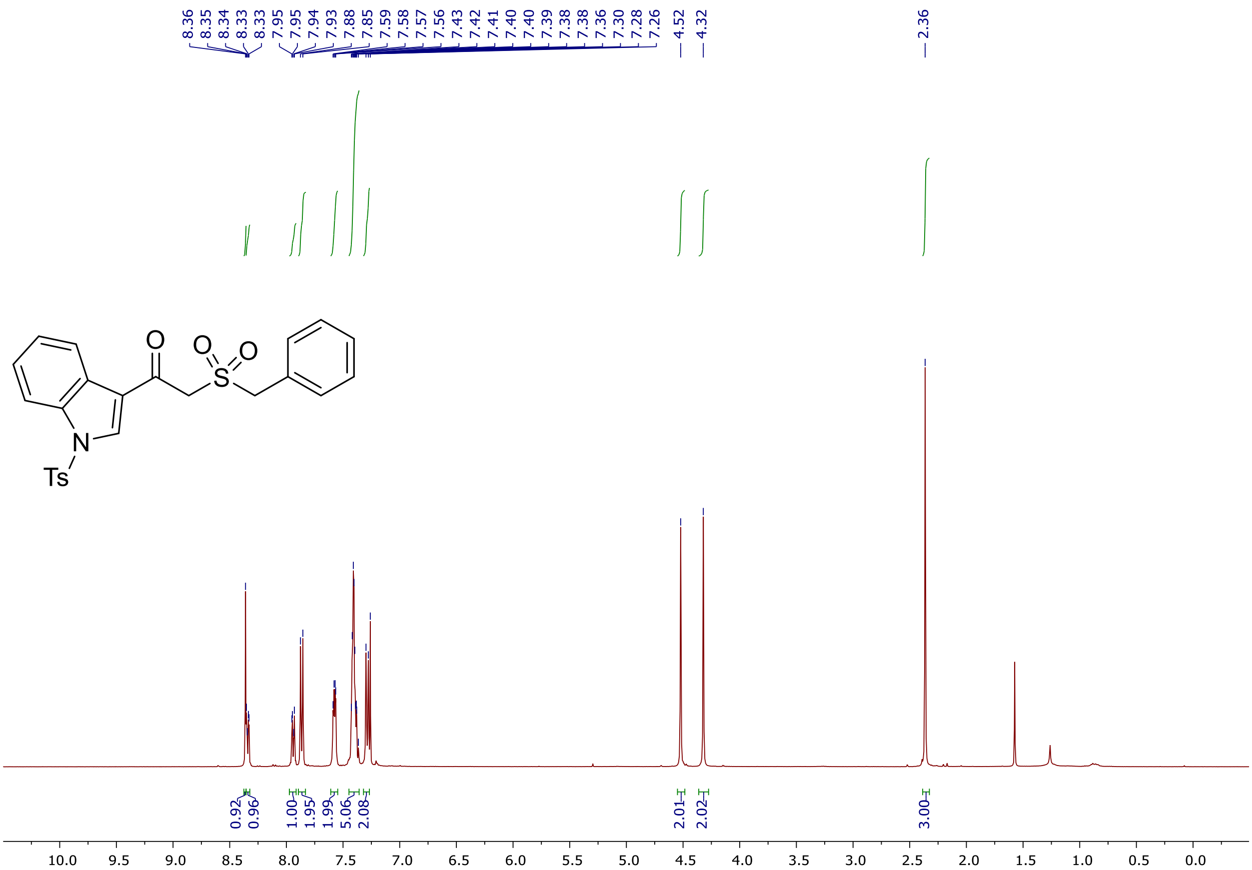
[1]H NMR (400 MHz, $CDCl_3$) of **2w**



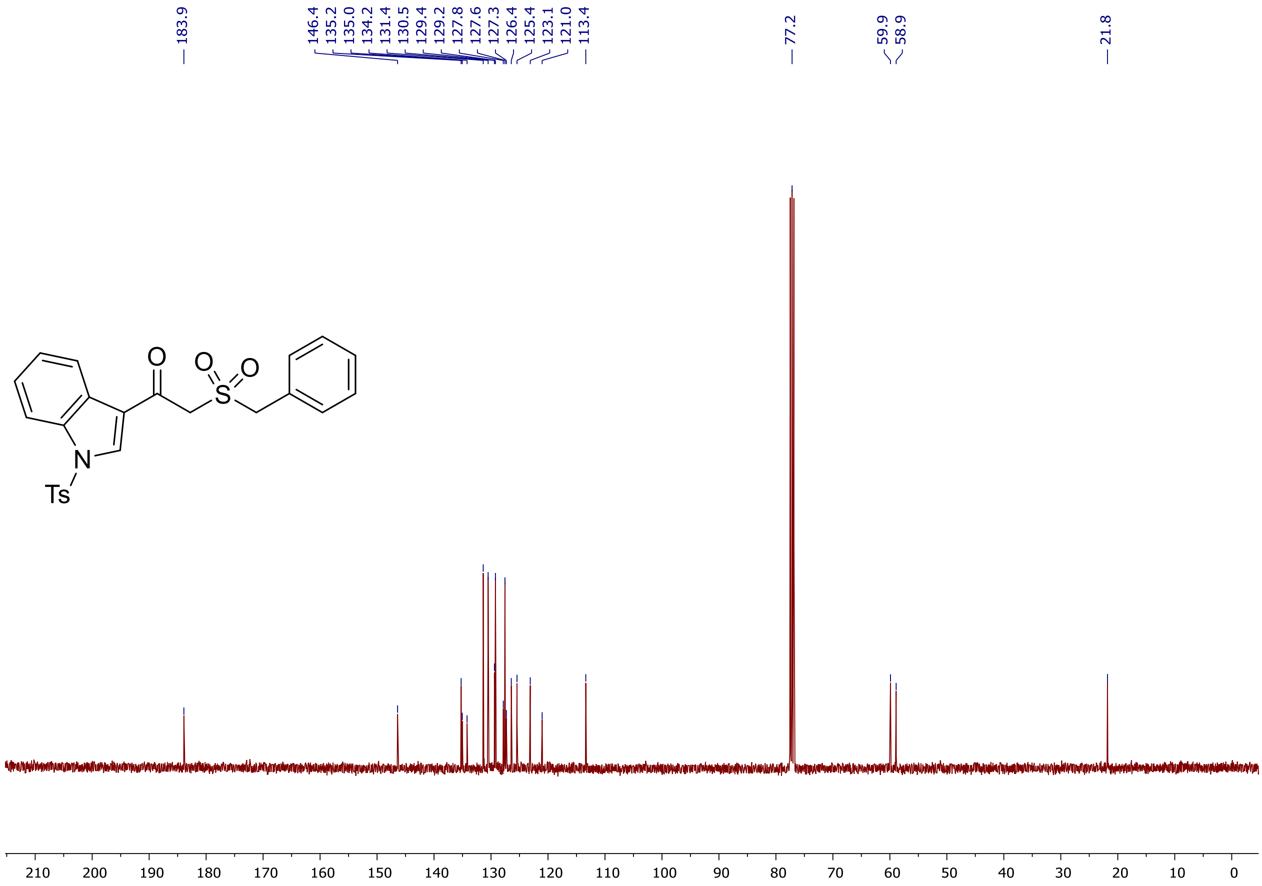
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of **2w**



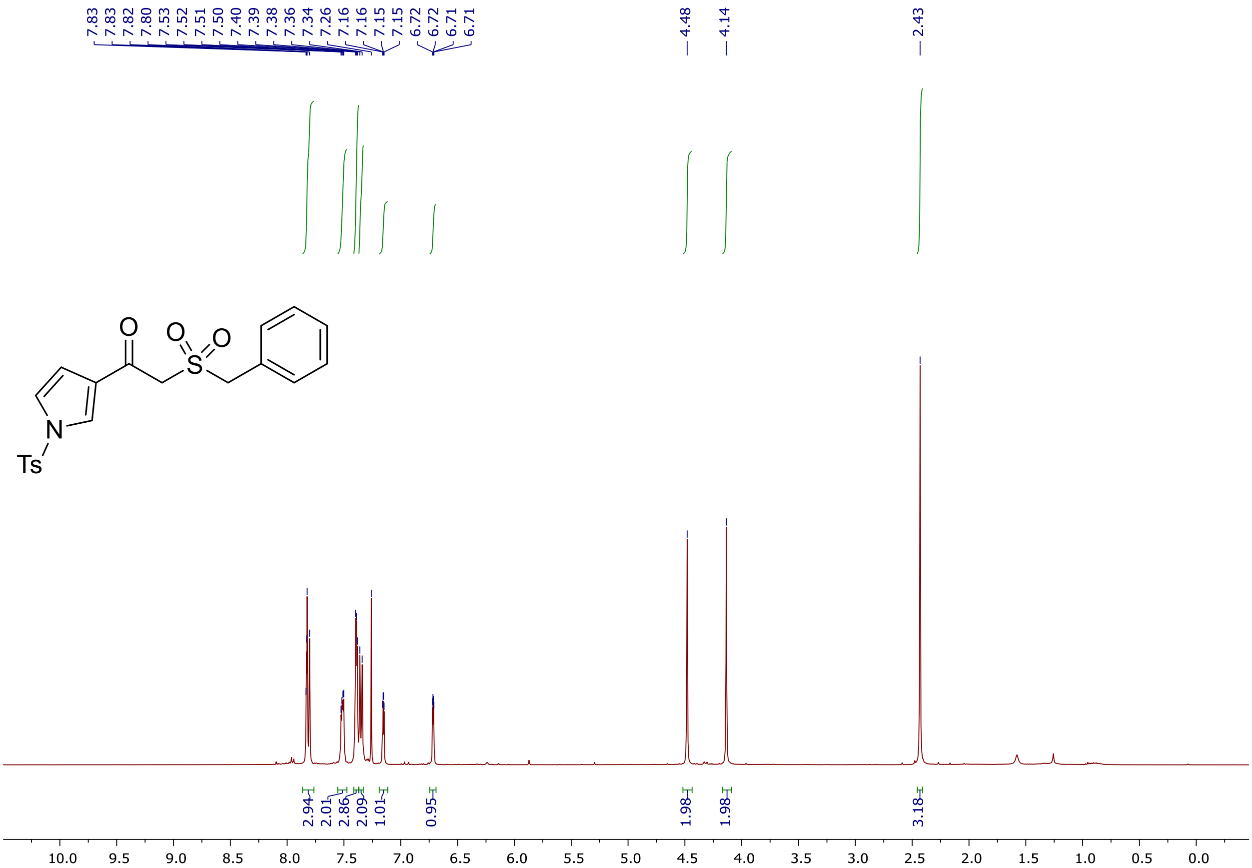
^{1}H NMR (400 MHz, $CDCl_3$) of **2x**



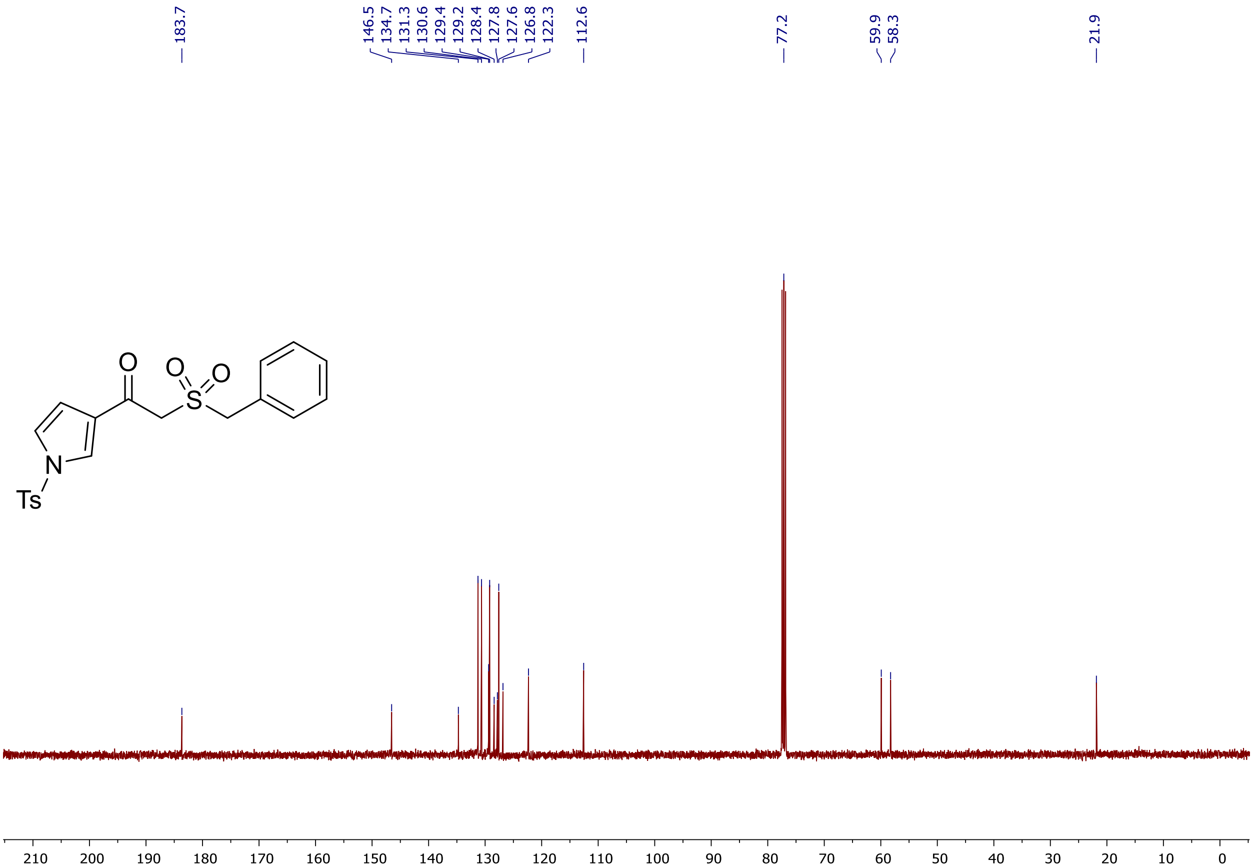
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2x**



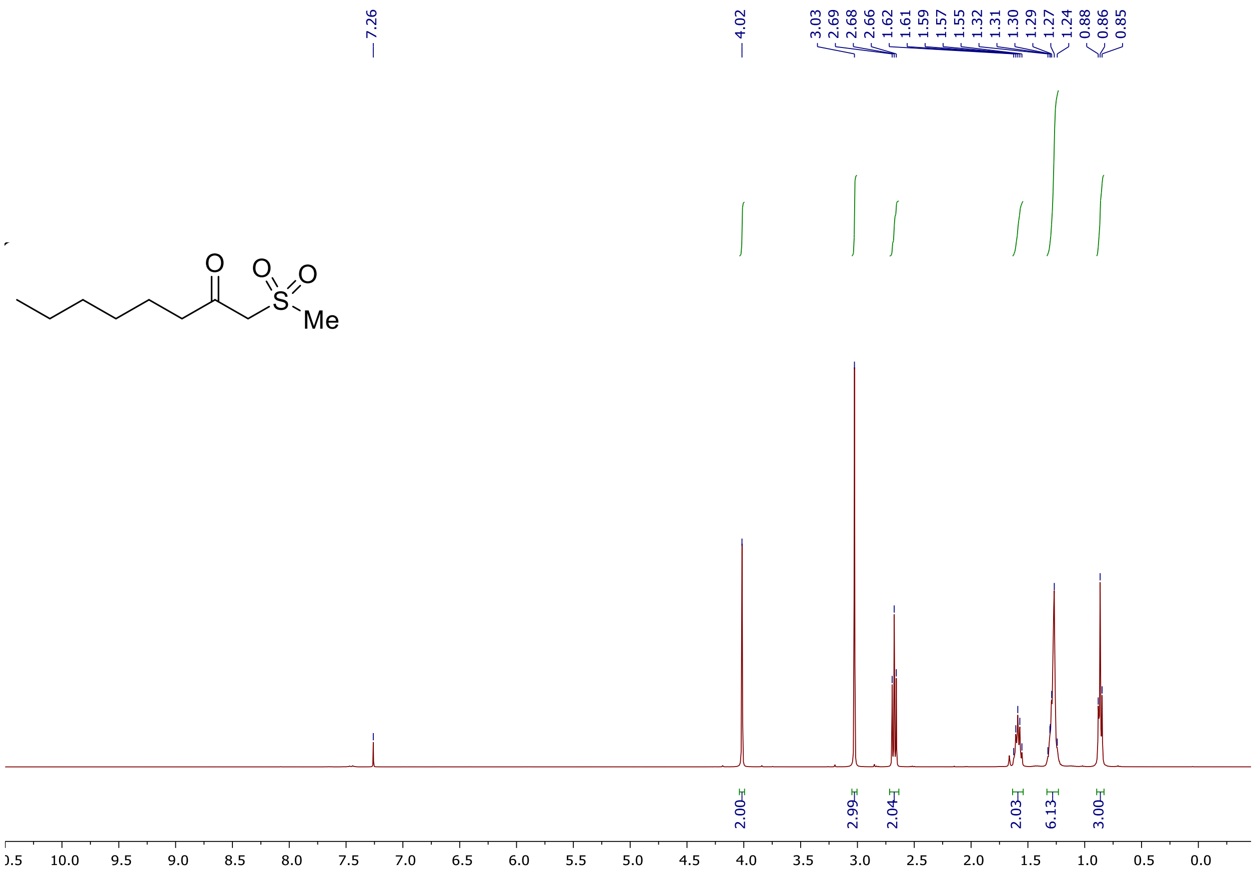
^{1}H NMR (400 MHz, $CDCl_3$) of **2y**



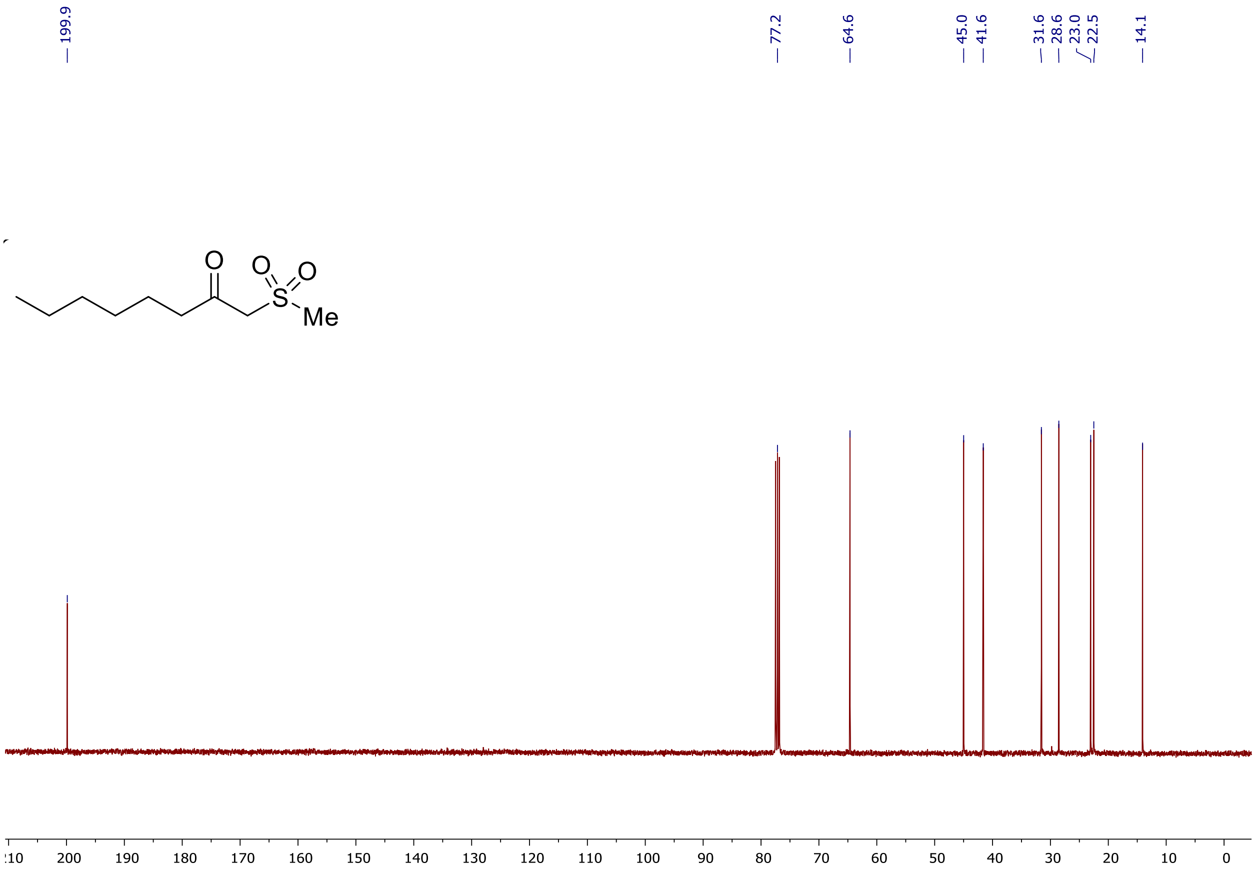
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2y**



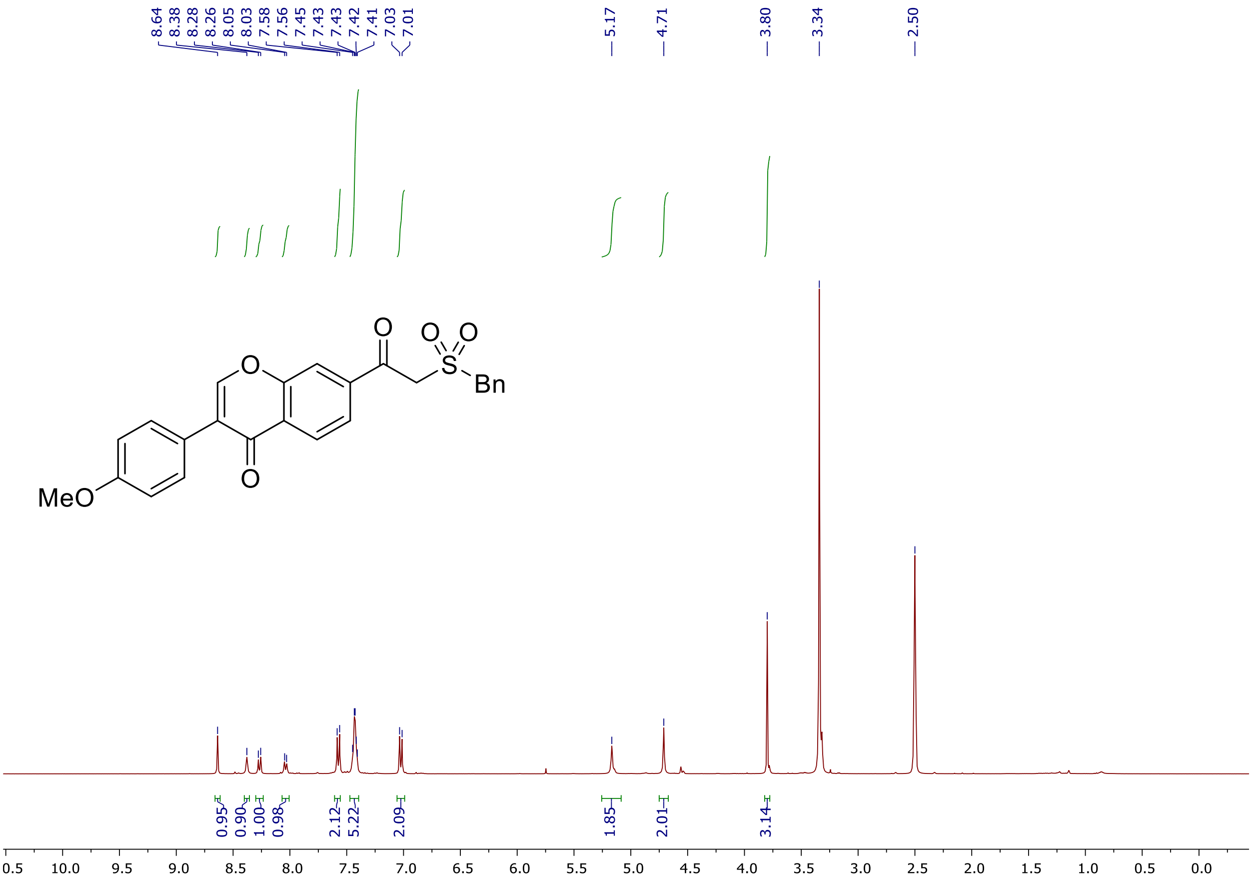
^{1}H NMR (400 MHz, $CDCl_3$) of **2z**



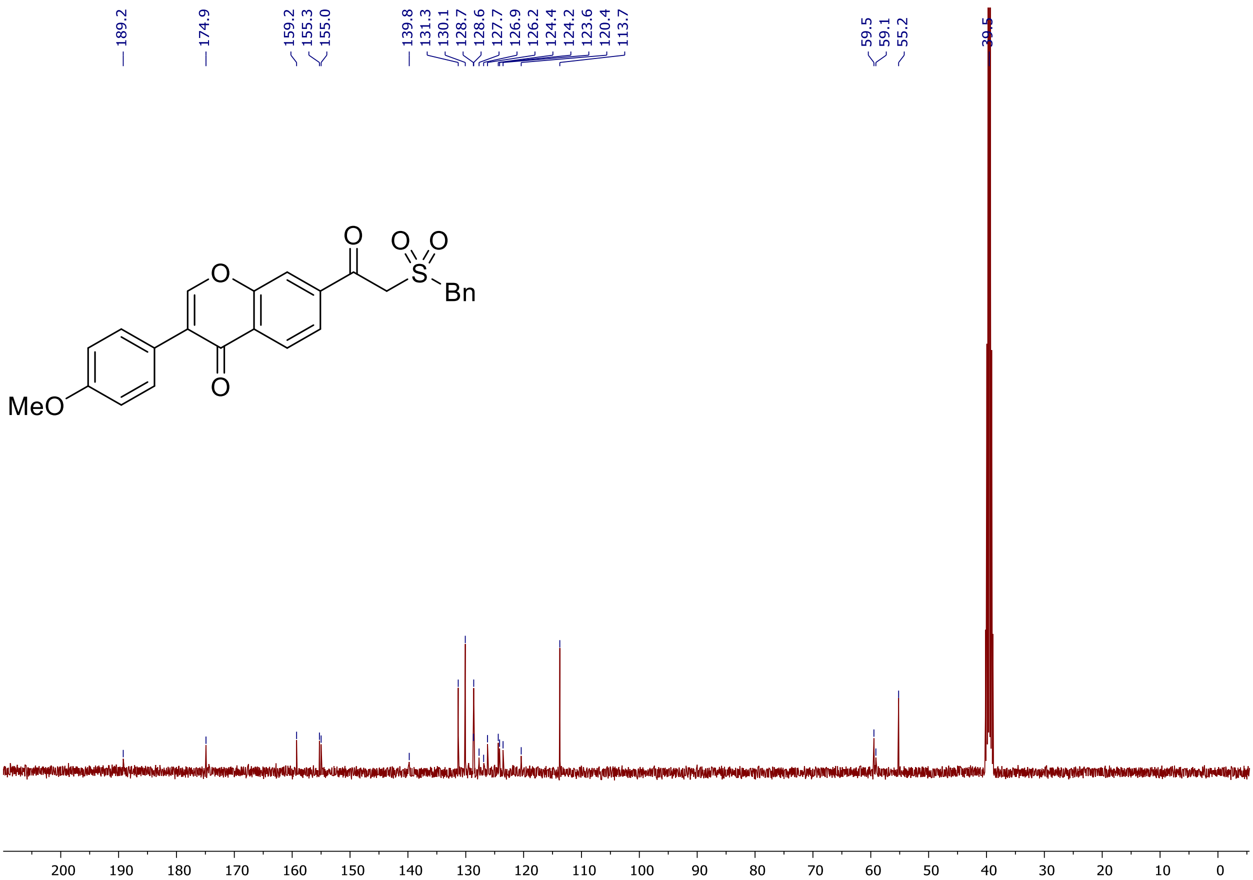
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2z**



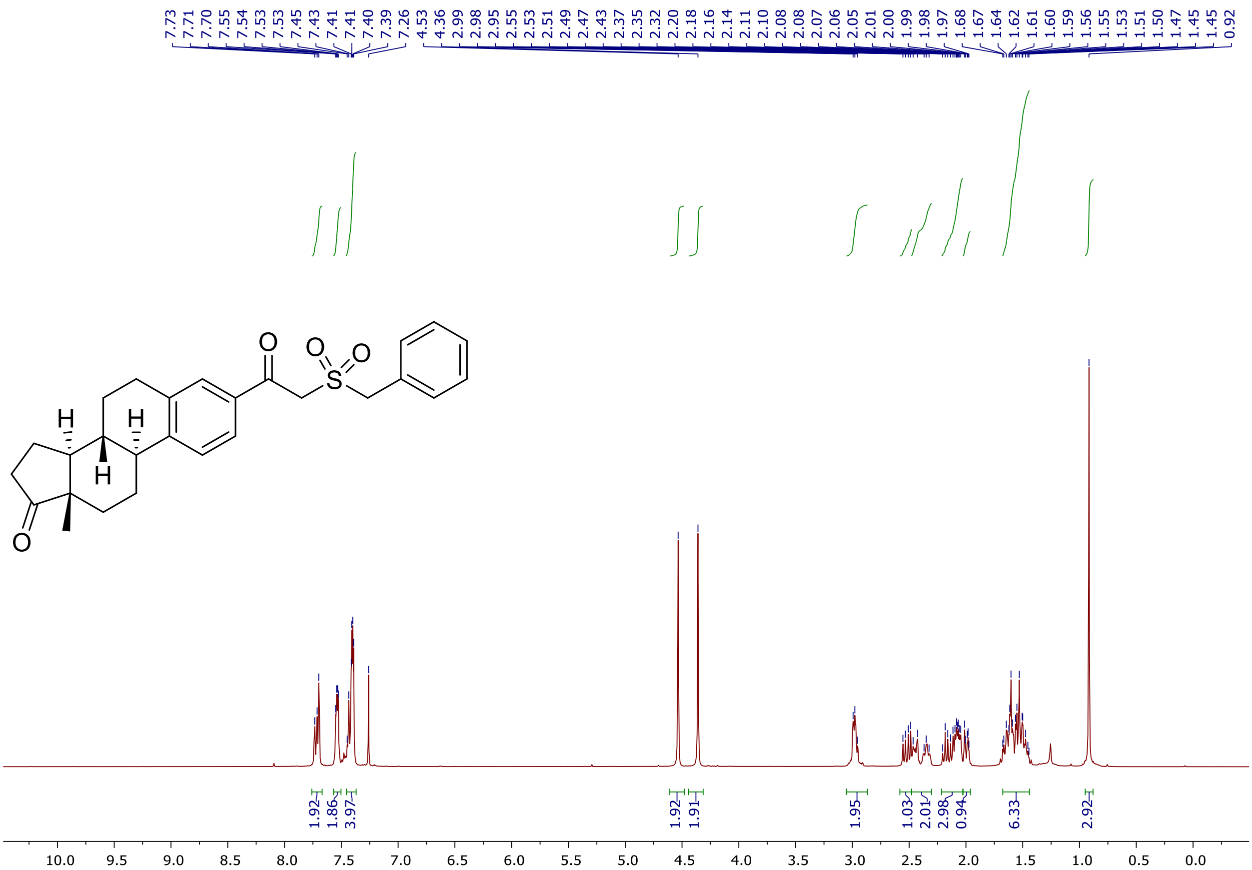
^{1}H NMR (400 MHz, DMSO-d_6) of **2aa**



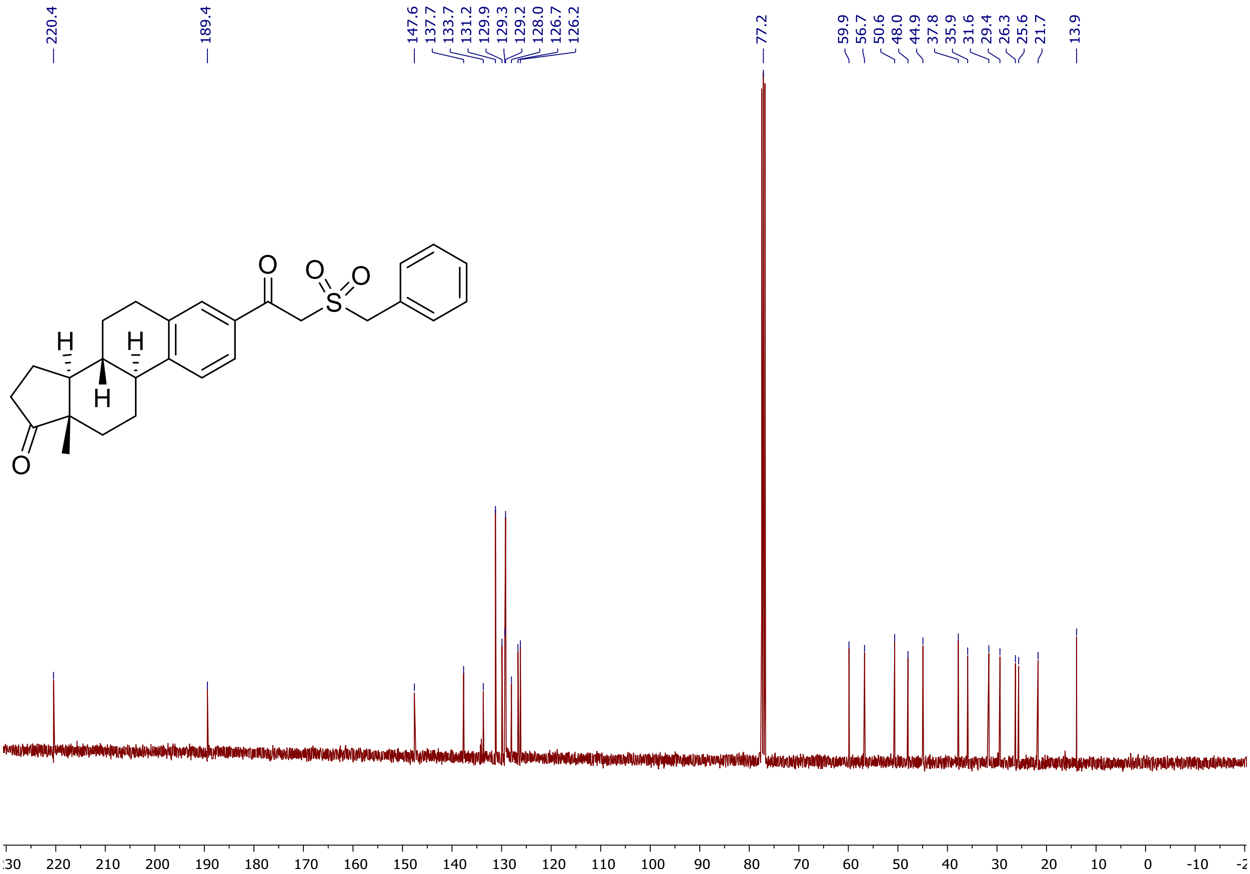
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **2aa**



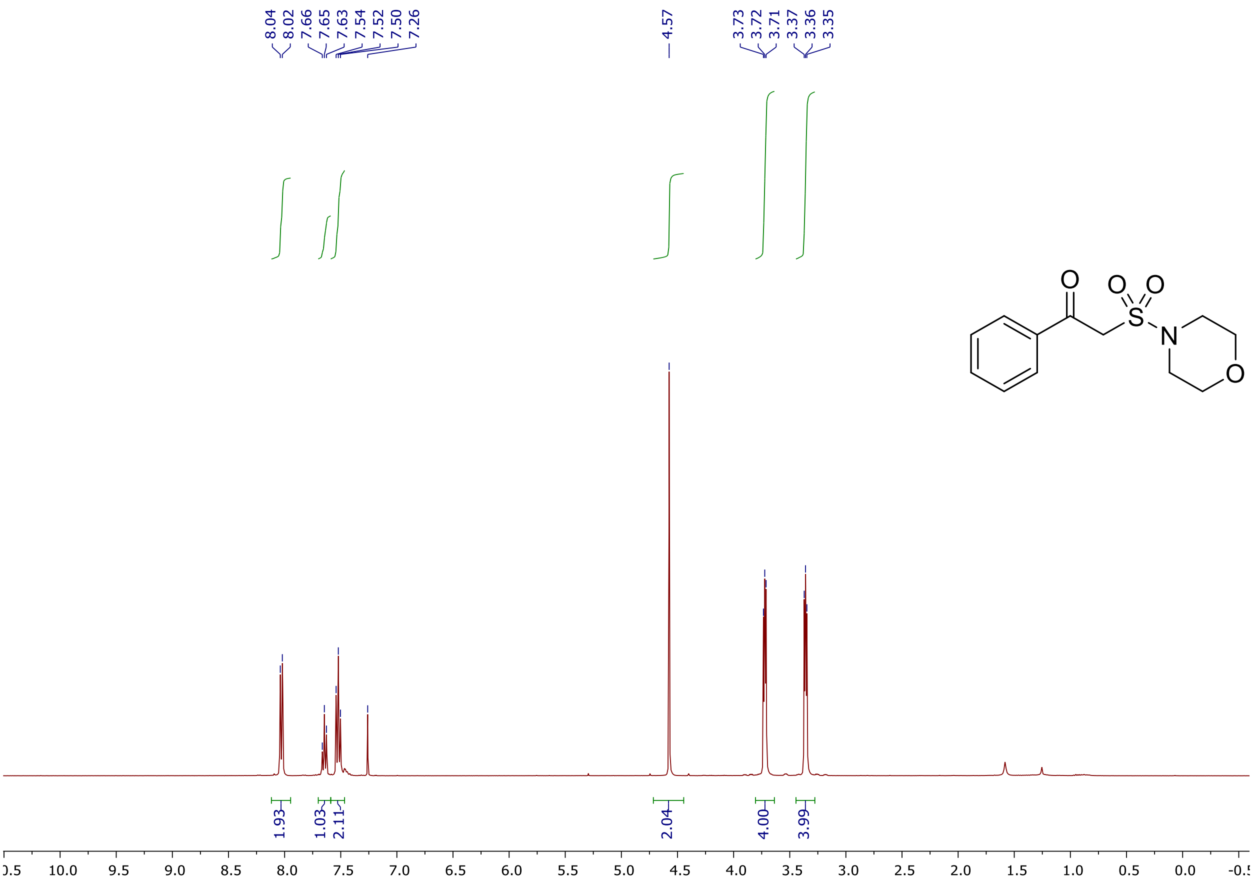
[1]H NMR (400 MHz, $CDCl_3$) of **2ab**



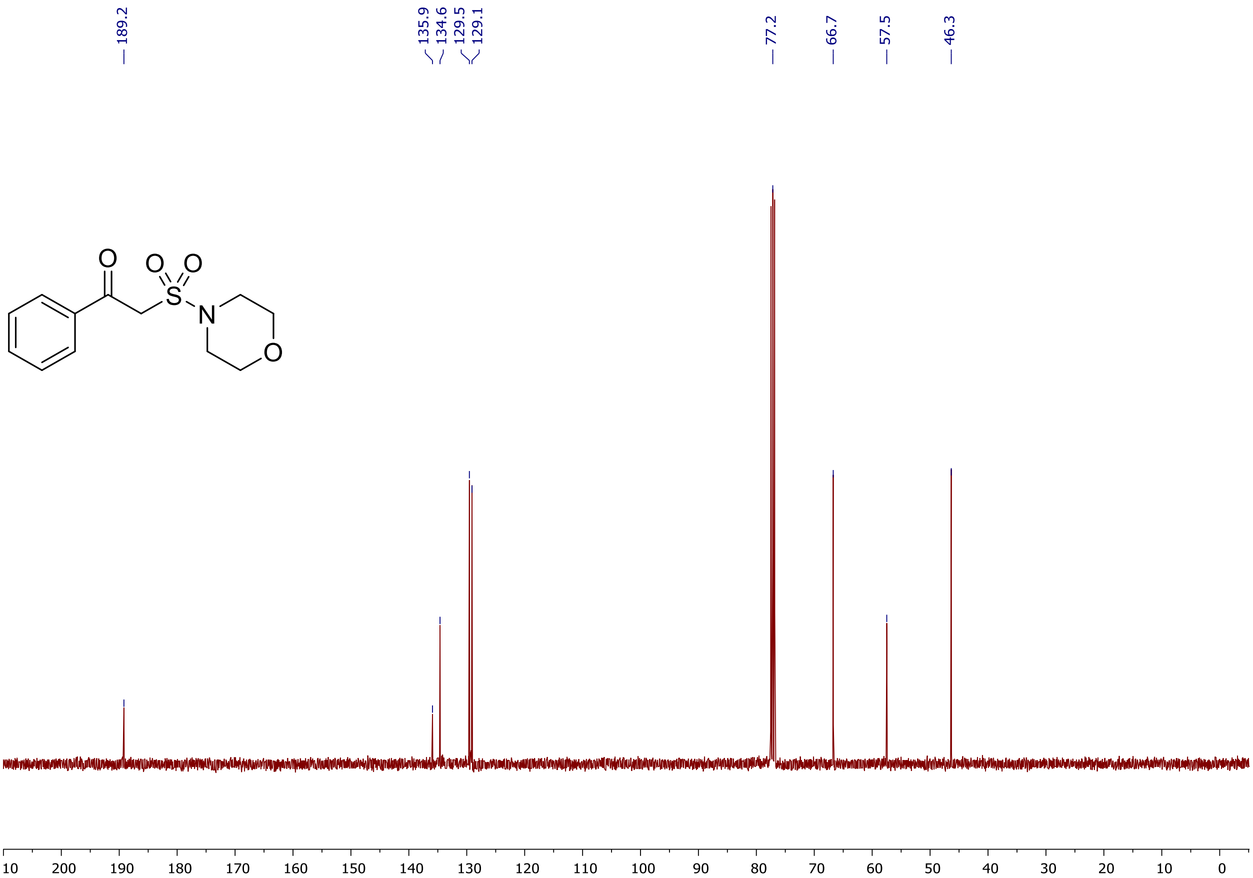
[13]C{[1]H} NMR (100 MHz, $CDCl_3$) of **2ab**



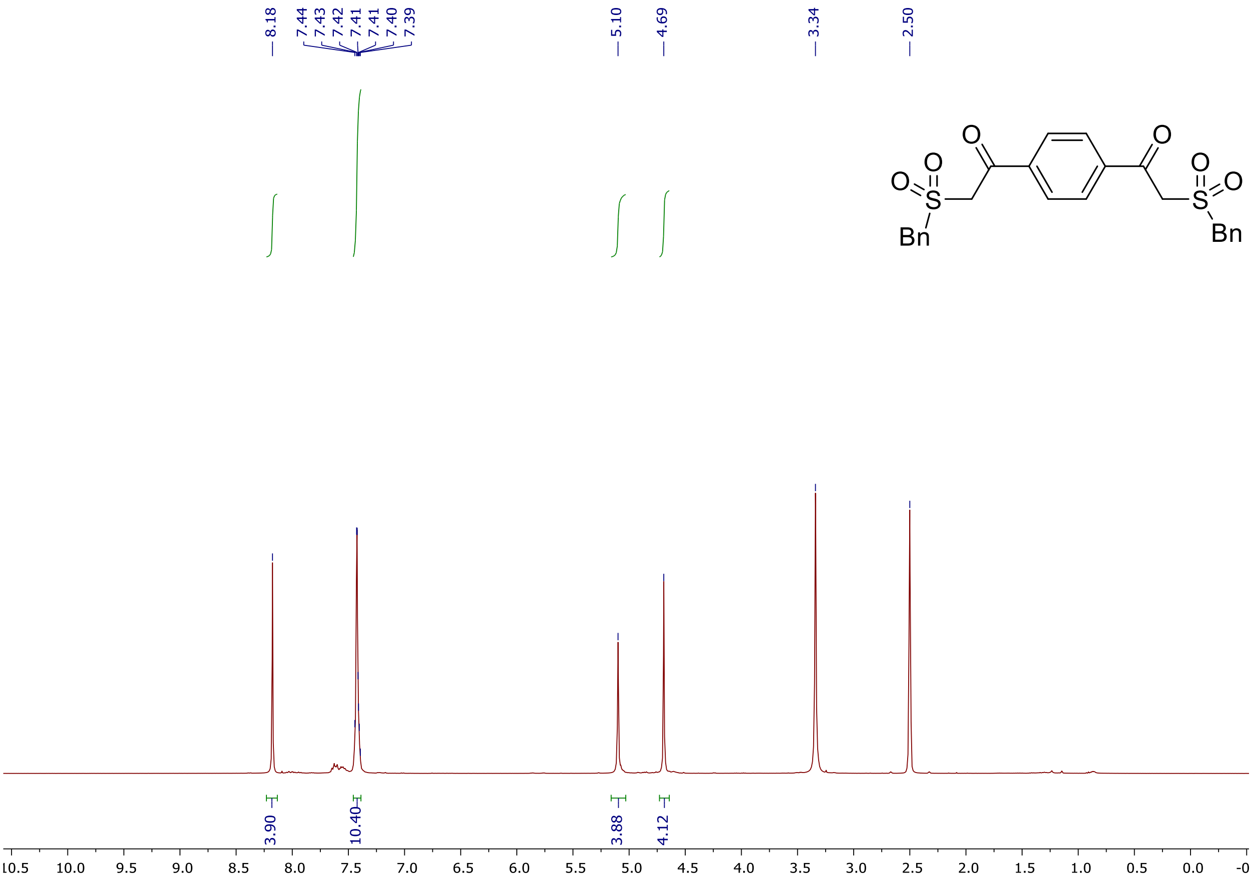
^{1}H NMR (400 MHz, $CDCl_3$) of **2ac**



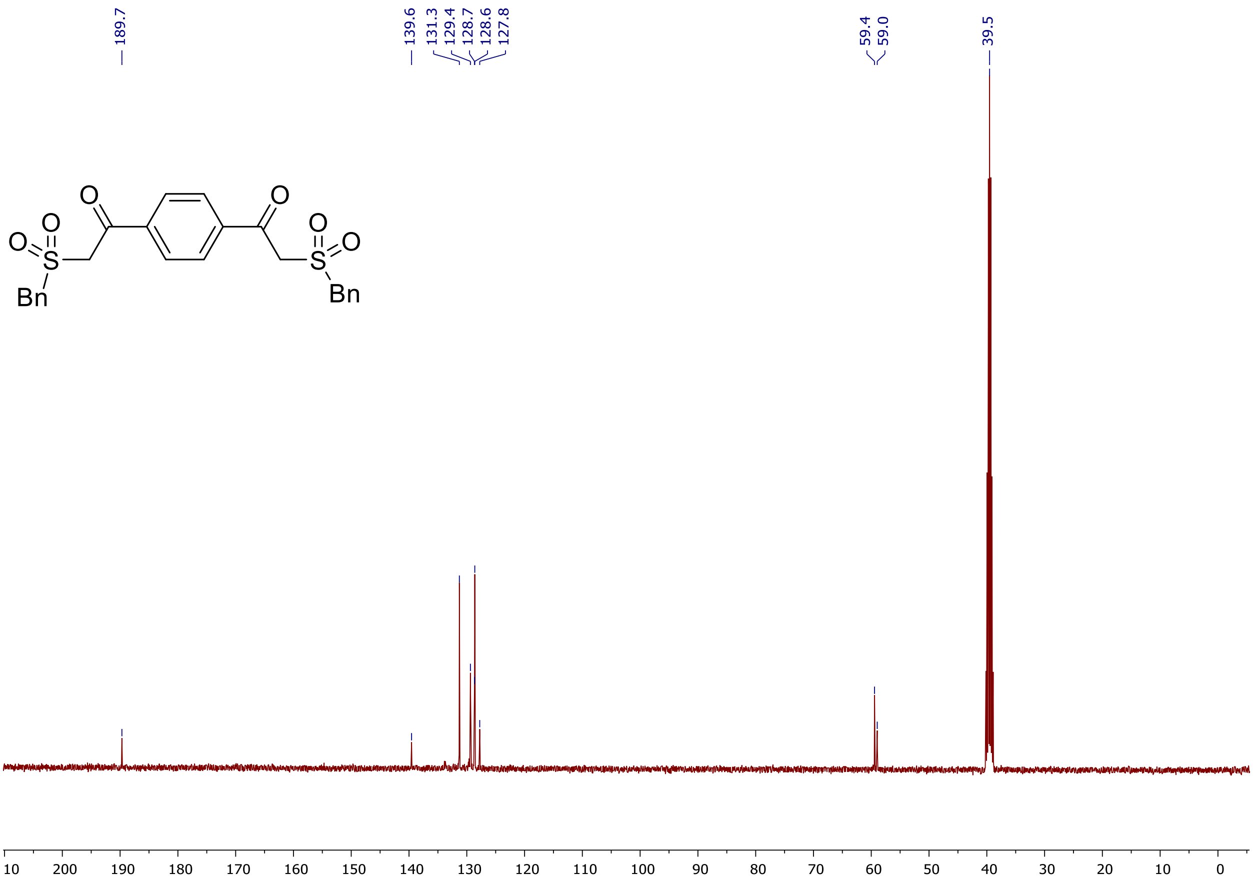
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **2ac**



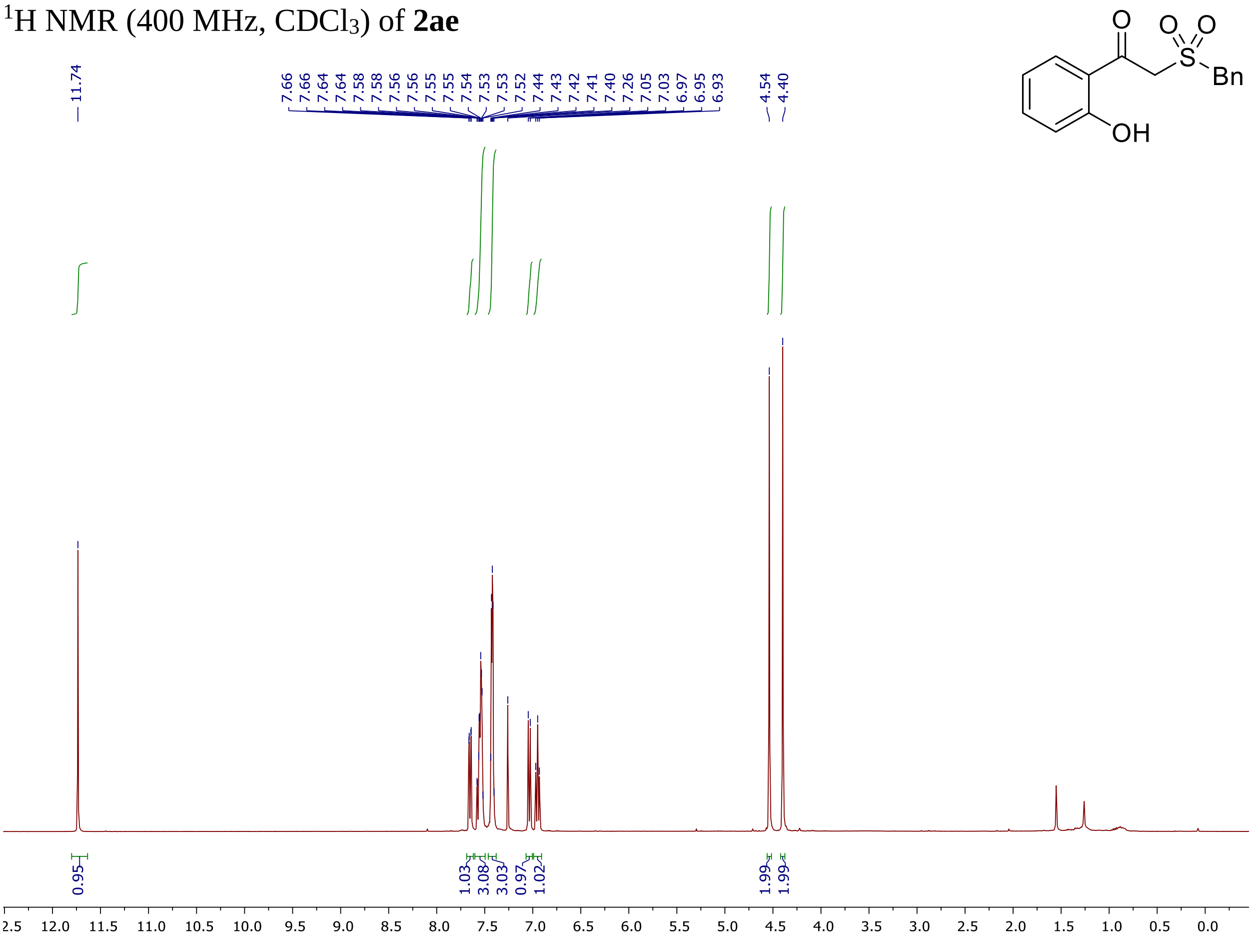
[1]H NMR (400 MHz, DMSO-d_6) of **2ad**



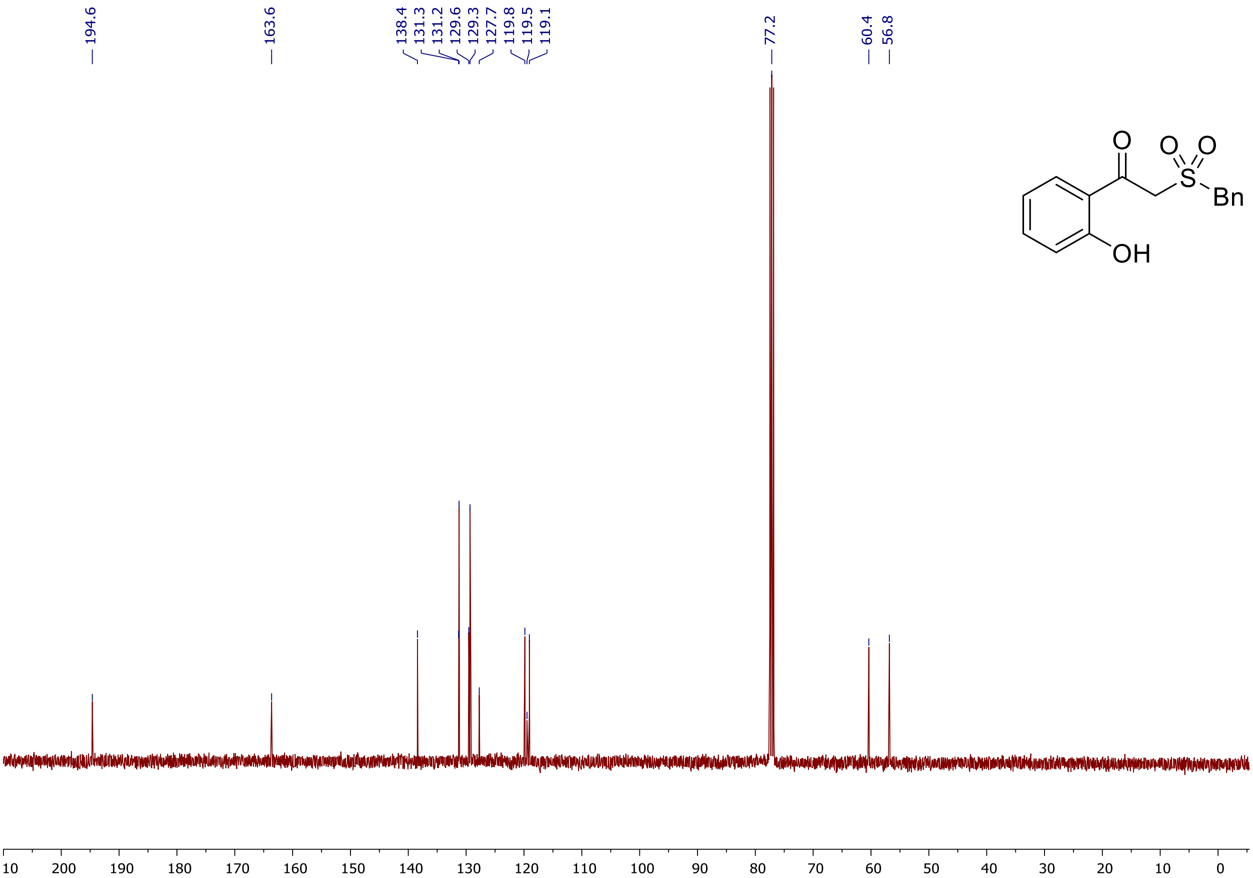
[13]C{[1]H} NMR (100 MHz, DMSO-d_6) of **2ad**



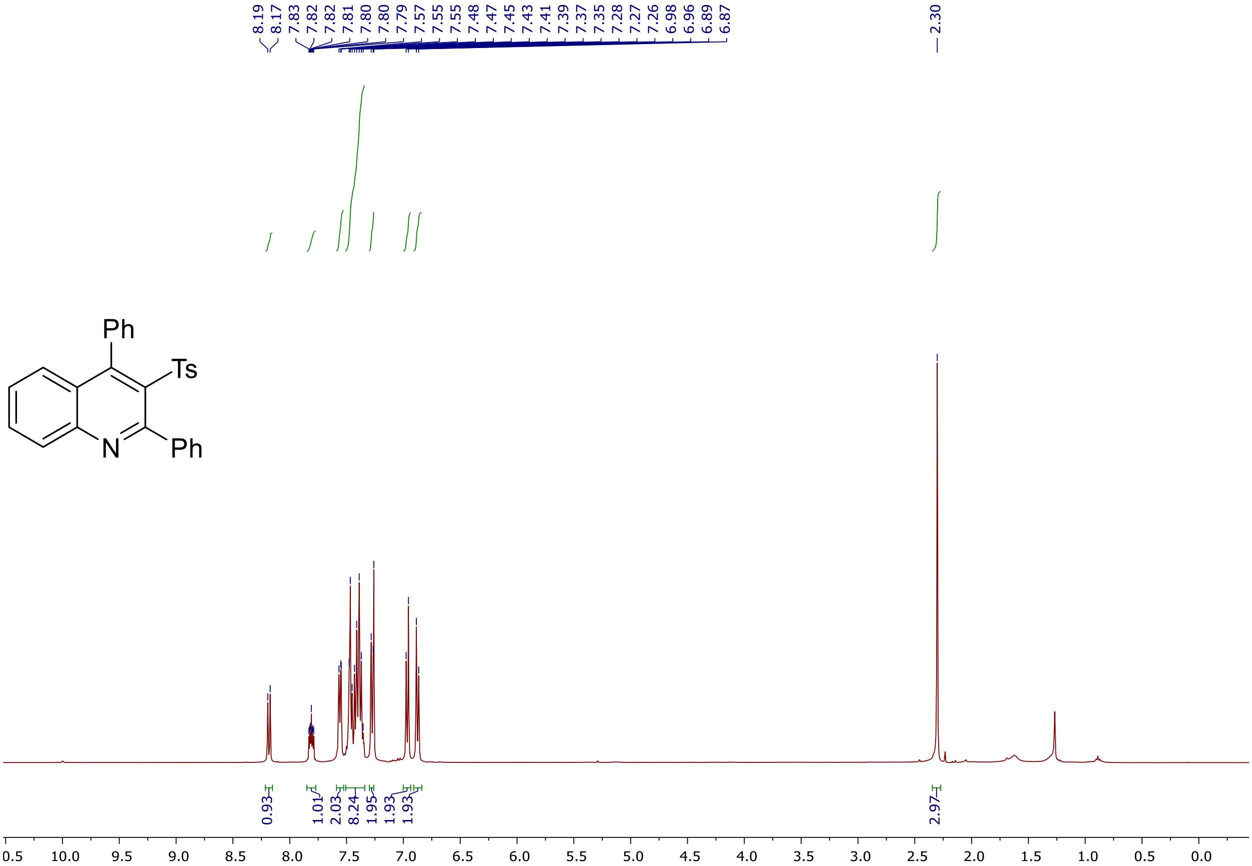
^{1}H NMR (400 MHz, $CDCl_3$) of **2ae**



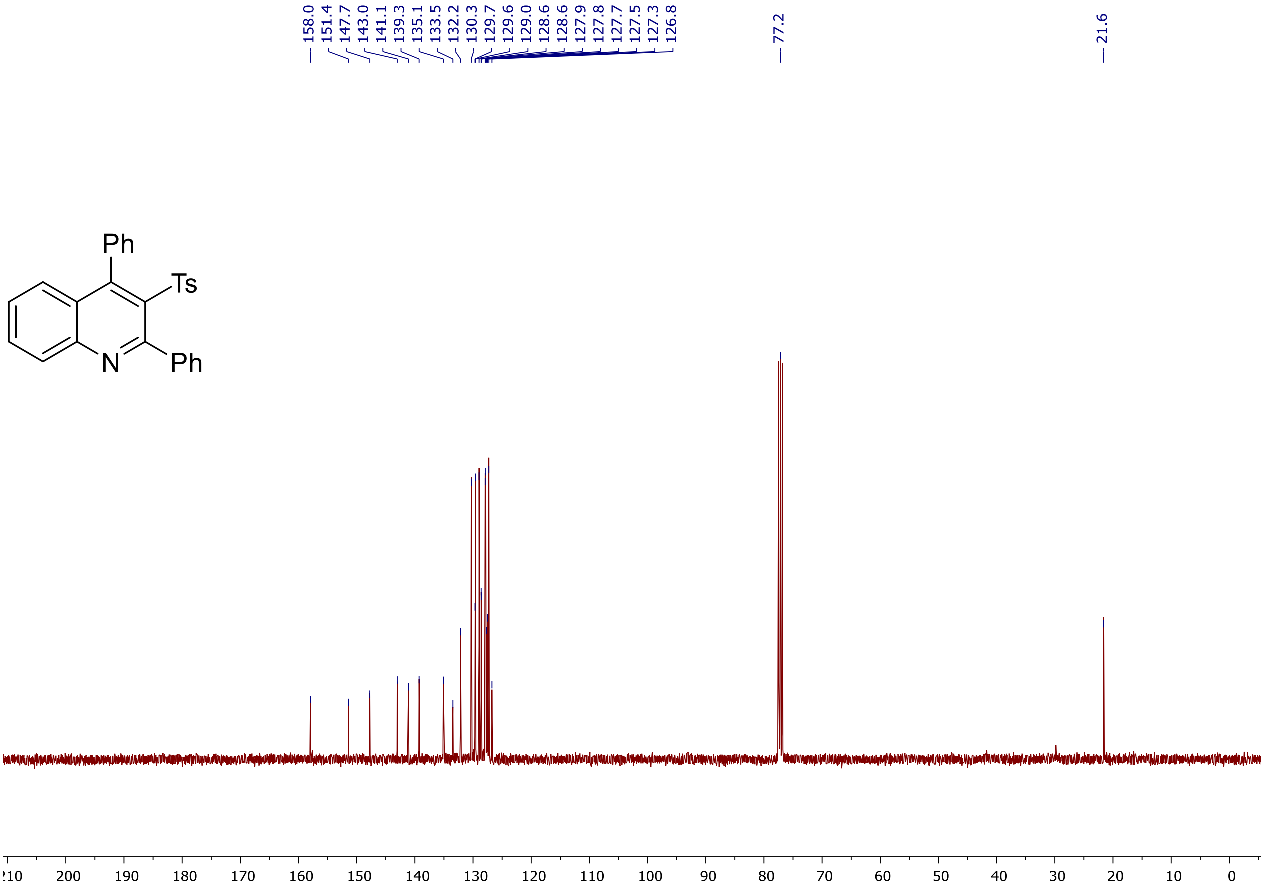
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2ae**



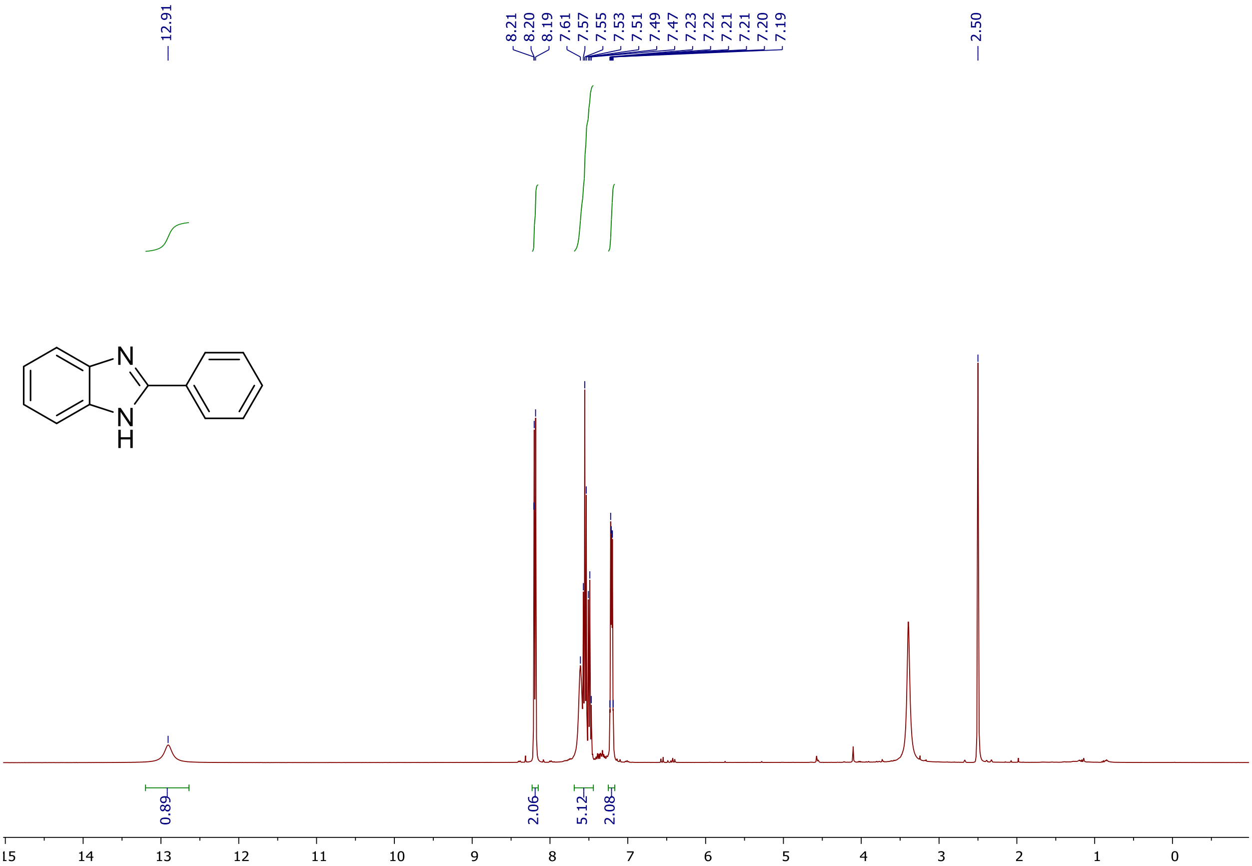
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



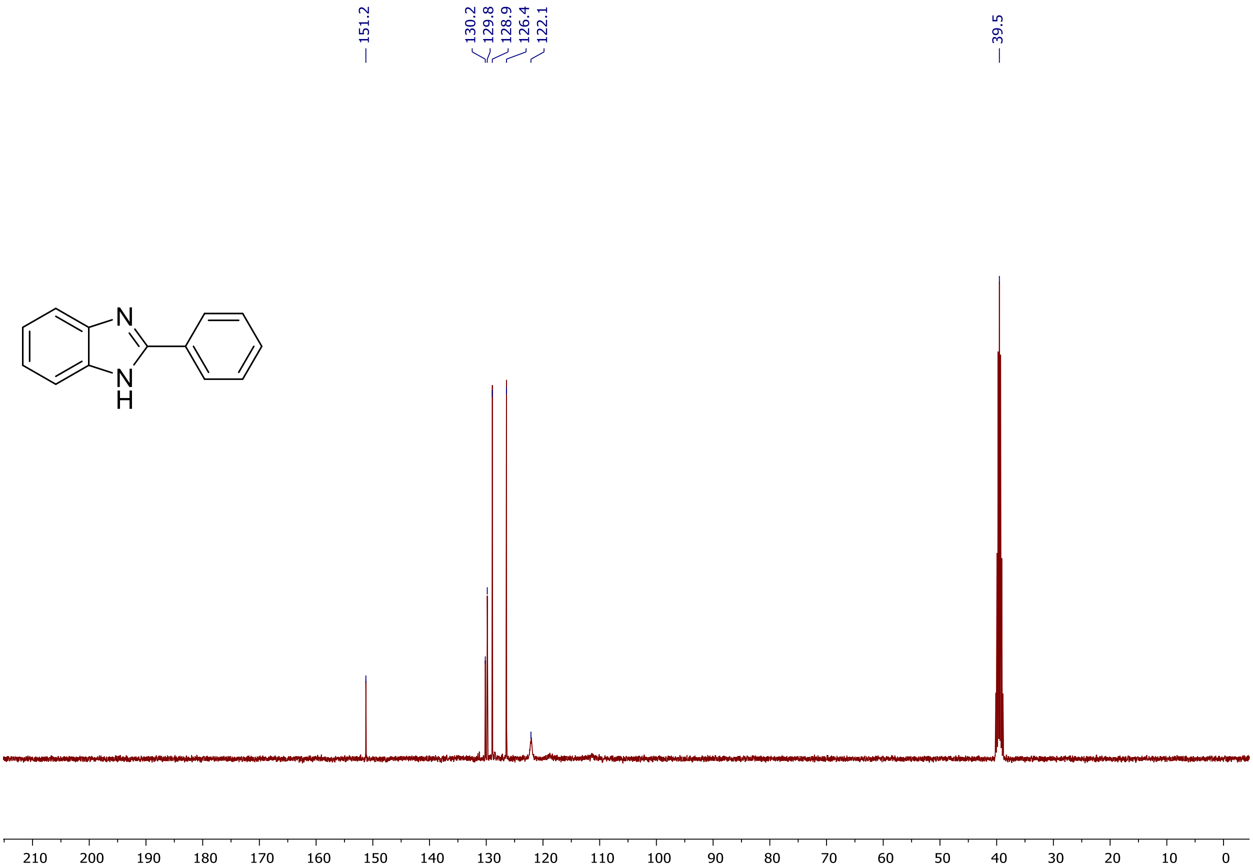
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **4**



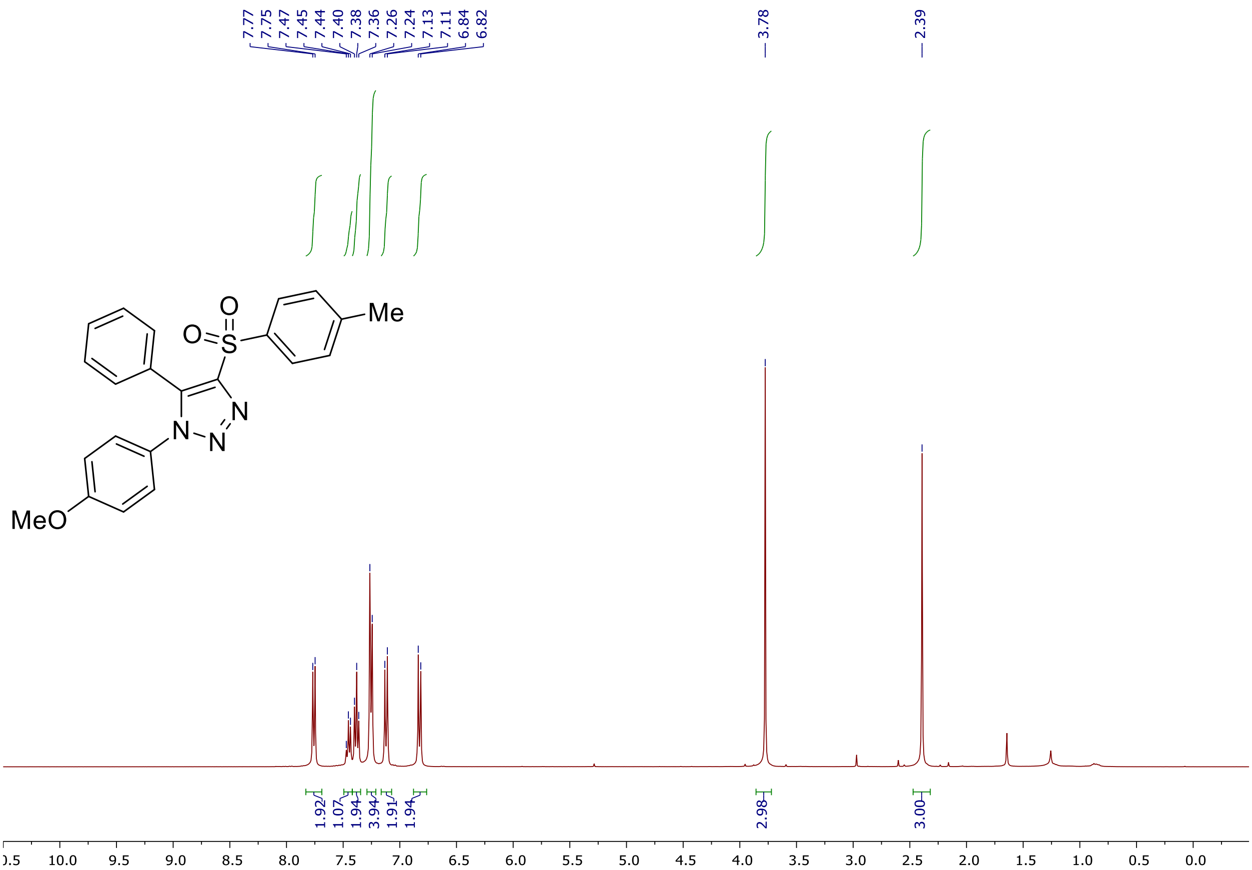
^{1}H NMR (400 MHz, DMSO-d_6) of **6**



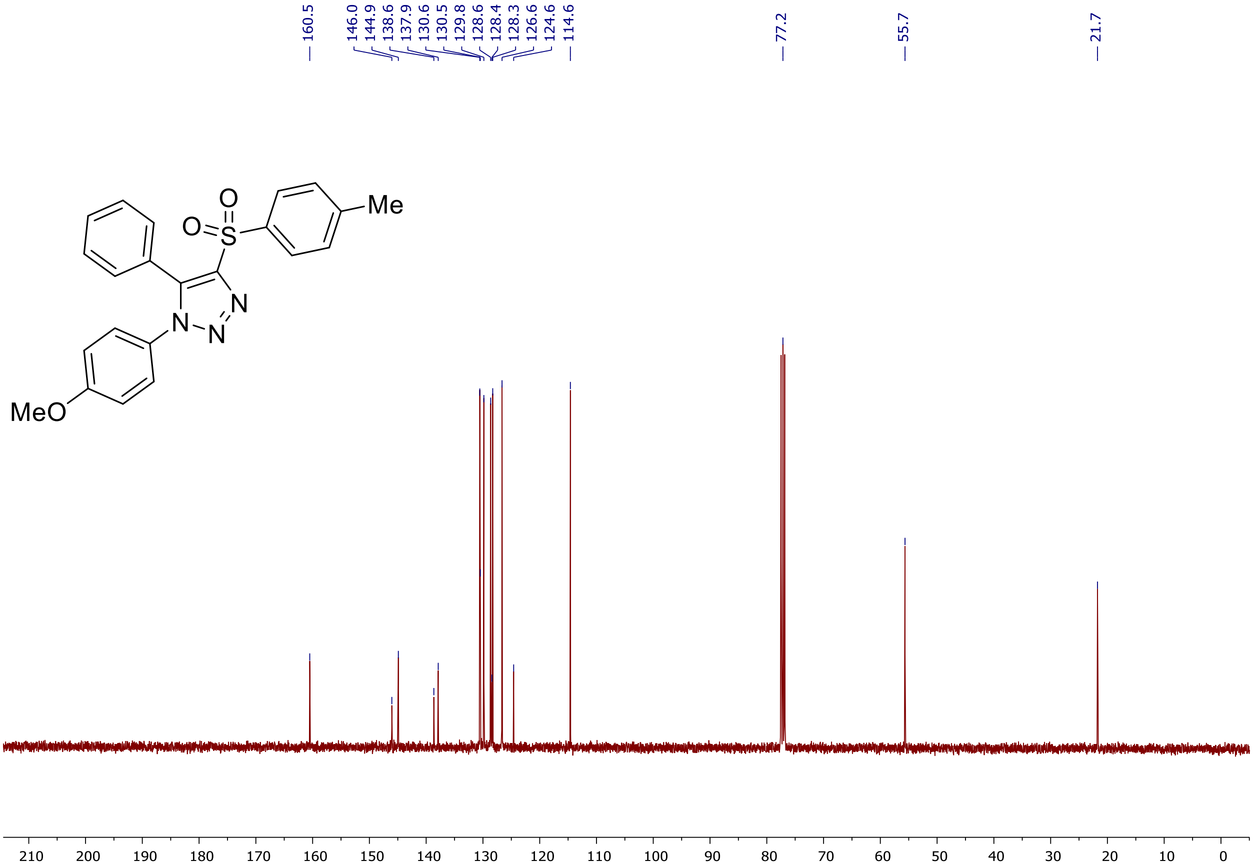
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **6**



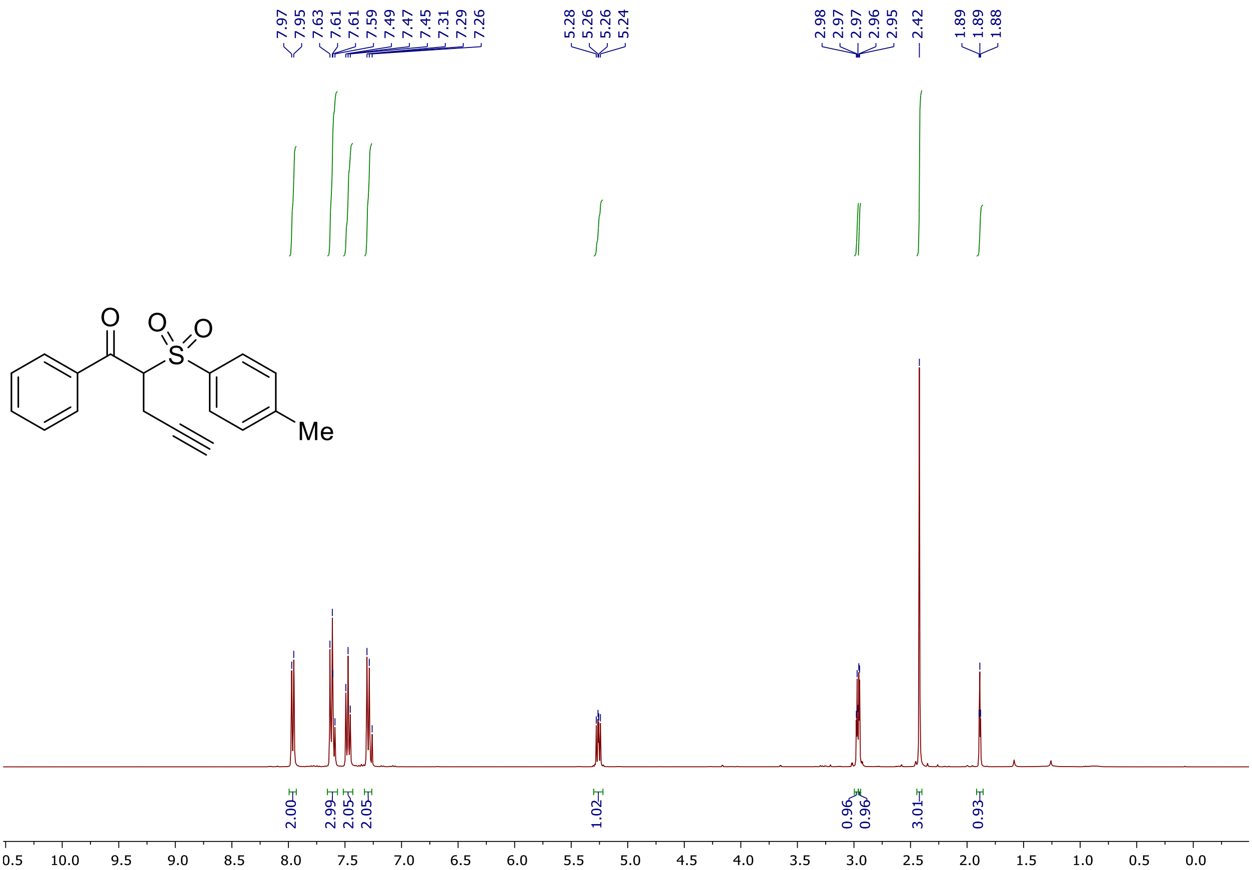
^{1}H NMR (400 MHz, CDCl$_3$) of **8**



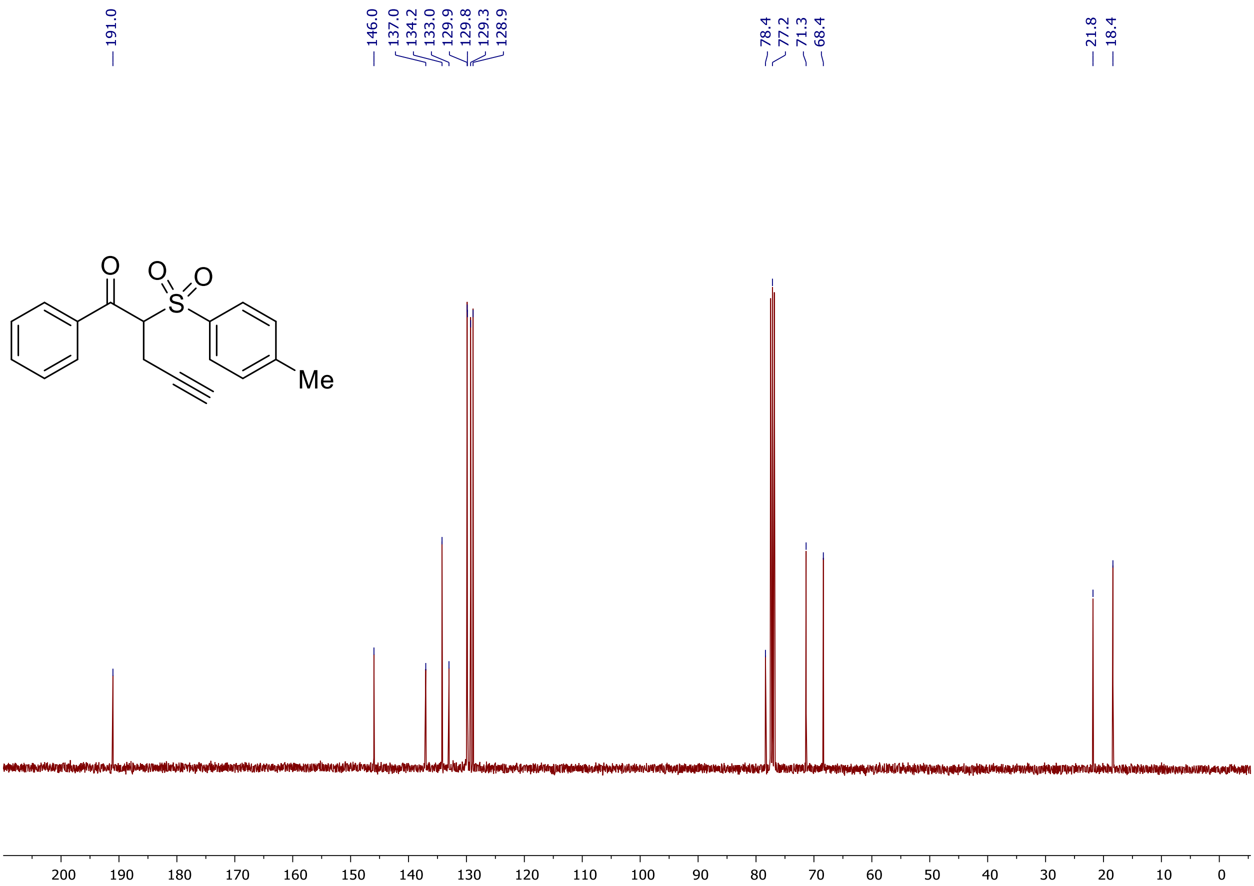
^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of **8**



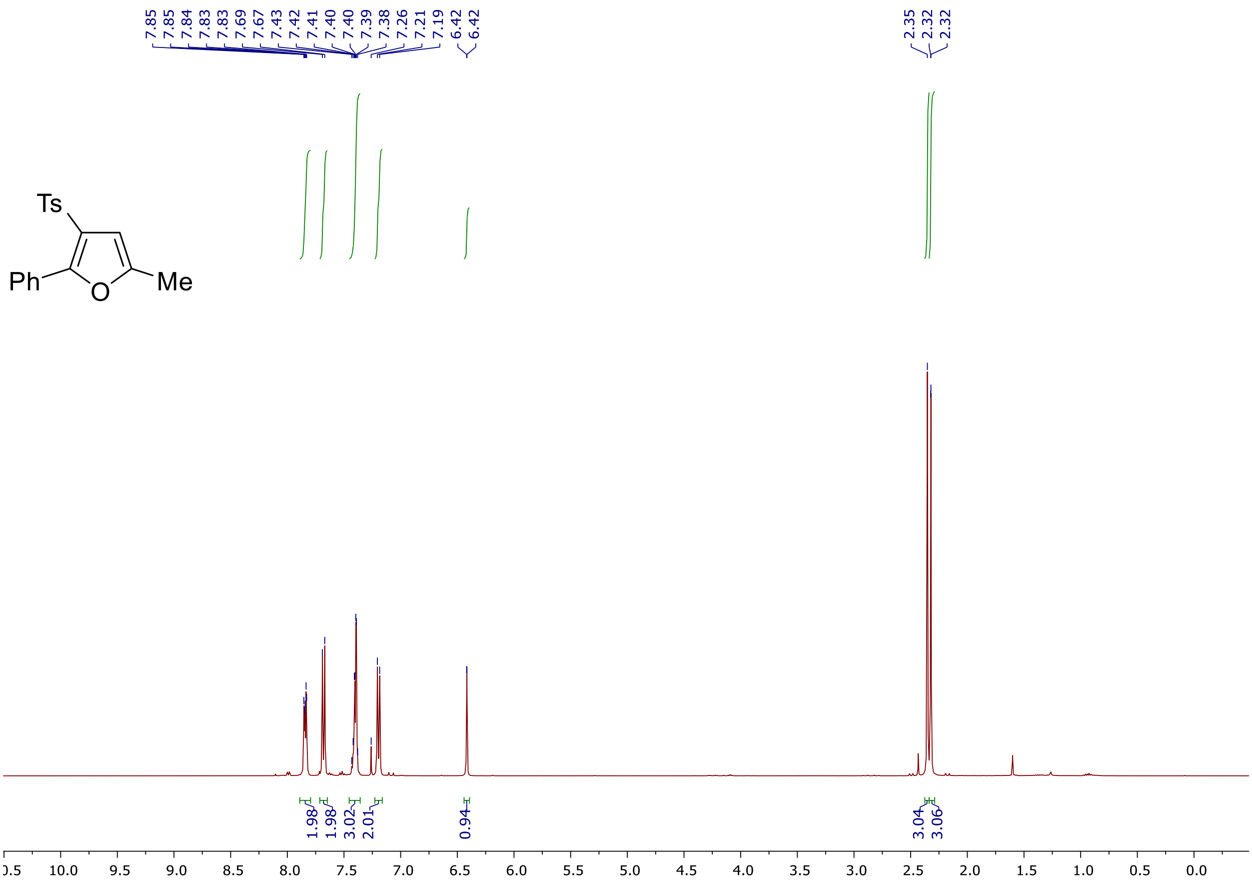
^{1}H NMR (400 MHz, $CDCl_3$) of **10**



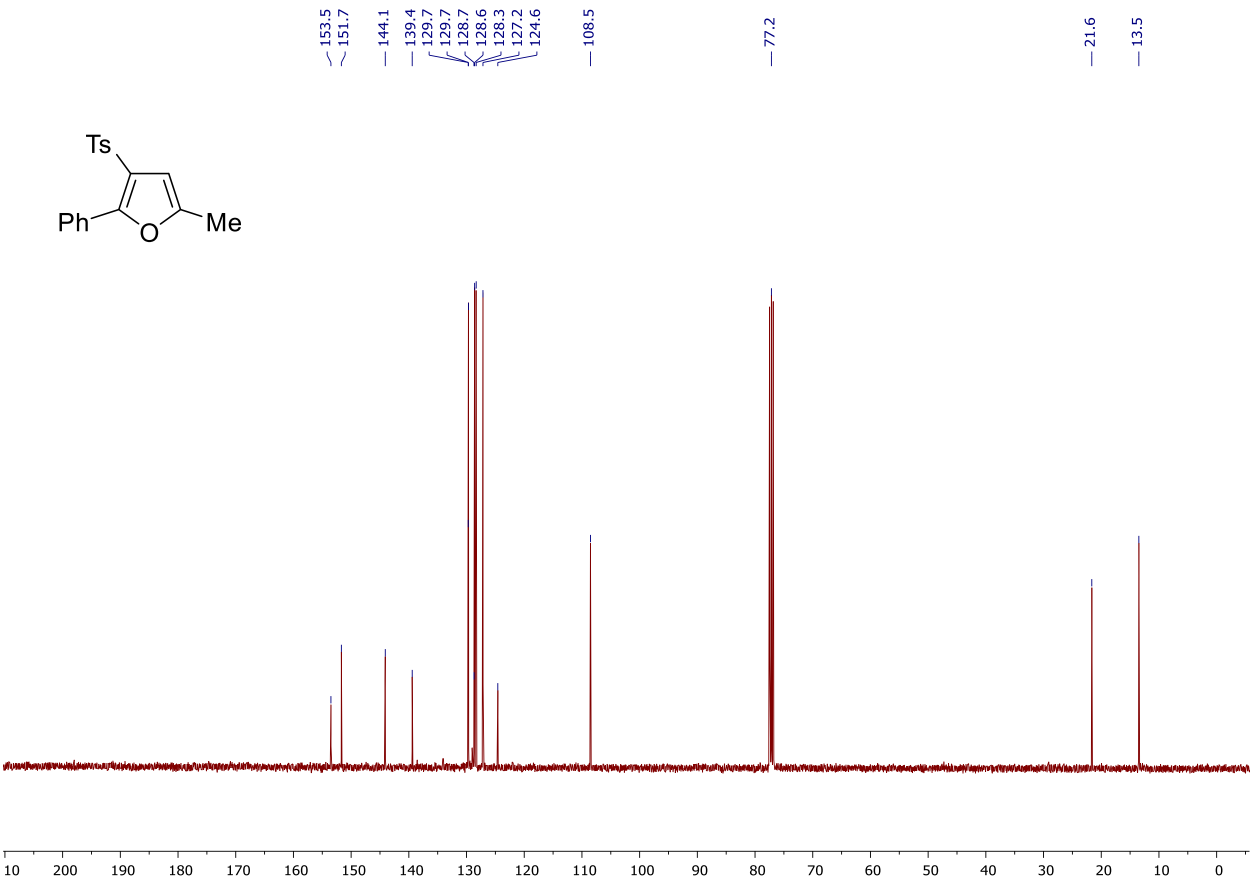
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **10**



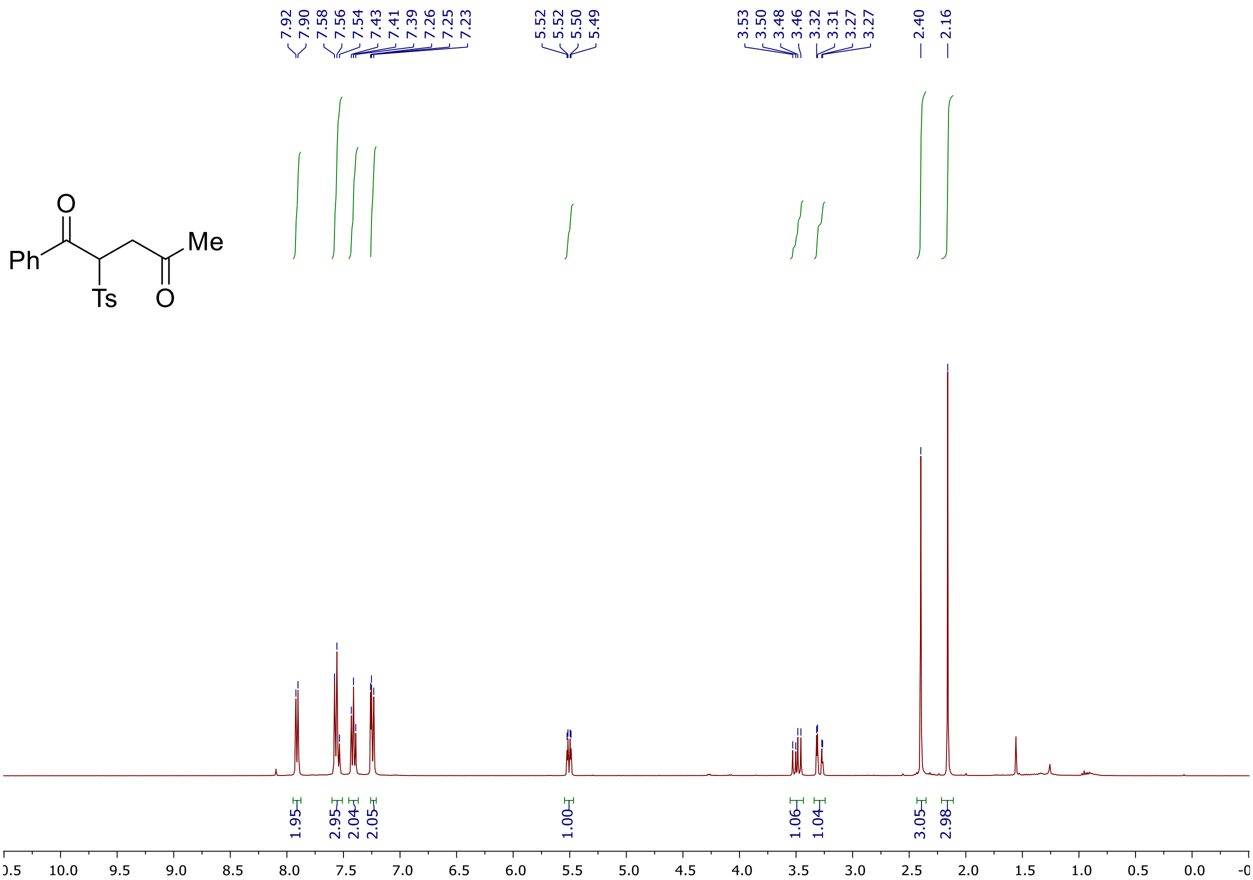
^{1}H NMR (400 MHz, $CDCl_3$) of **11**



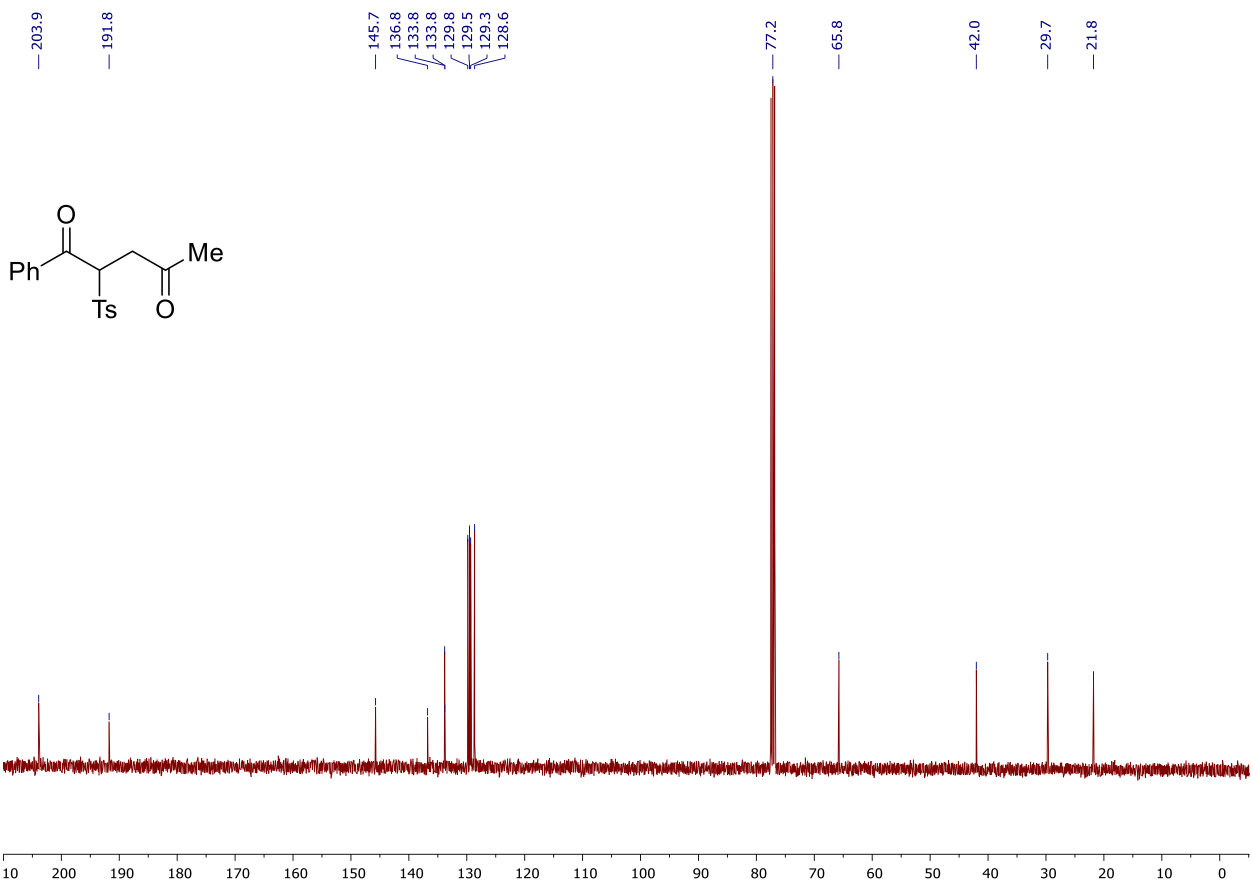
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **11**



^{1}H NMR (400 MHz, CDCl$_3$) of **12**



^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of **12**



7 XRD Single Crystal Structures of 2q

The crystal was prepared by slow evaporation of solutions of **2q** in acetonitrile at room temperature. For single crystal X-ray diffraction experiment the crystals were fixed on a micro mount and placed on a SuperNova, Single source at offset/far, HyPix3000 diffractometer using Cu Kα monochromated radiation. The crystals were kept at 100(2) K during data collection. The structures have been solved by ShelXT [G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2015, *71*, 3-8] structure solution programs using Intrinsic Phasing, respectively, and refined by means of the SHELXL program [G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, *71*, 3-8] incorporated in the OLEX2 program package [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, *42*, 339-341].

Crystal data and structure refinement

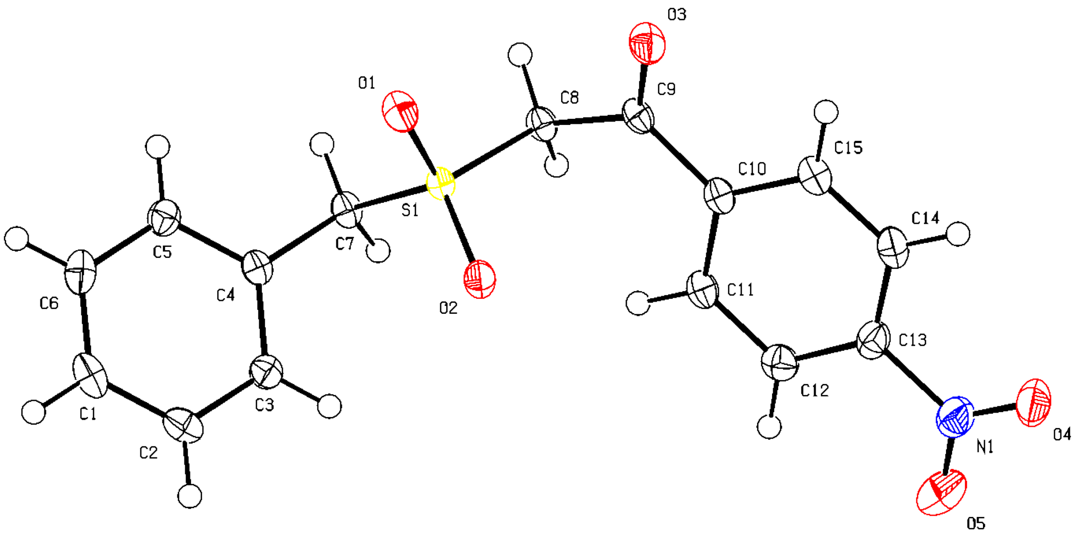
Bond precision:	C-C = 0.0018 A		Wavelength=1.54184
Cell:	a=6.5529(1)	b=7.7286(1)	c=27.9324(2)
	alpha=90	beta=93.449(1)	gamma=90
Temperature:	100 K		

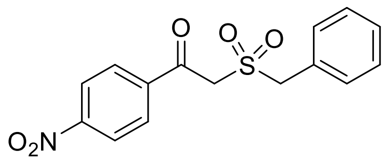
	Calculated	Reported
Volume	1412.07(3)	1412.07(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C15 H13 N O5 S	C15 H13 N O5 S
Sum formula	C15 H13 N O5 S	C15 H13 N O5 S
Mr	319.32	319.32
Dx,g cm-3	1.502	1.502
Z	4	4
Mu (mm-1)	2.272	2.272
F000	664.0	664.0
F000'	667.45	
h,k,lmax	8,9,35	8,9,35
Nref	3076	3009
Tmin,Tmax	0.643,0.893	0.794,1.000
Tmin'	0.578	

Correction method= # Reported T Limits: Tmin=0.794 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.978	Theta(max)= 79.832
R(reflections)= 0.0319(2881)	wR2(reflections)= 0.0878(3009)
S = 1.088	Npar= 199

Molecular structure of **2q** (50% probability amplitude displacement ellipsoids).

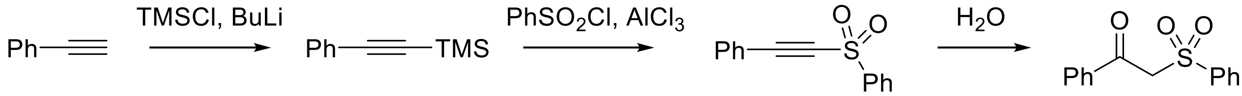

O1
O2
O3
O4
O5
S1
N1
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15


O
O
O
S
O2N

8 Calculations of Atom-economy

Calculations of atom-economy are given for equivalent quantities of reagents that are needed for a full material balance. Also, it is assumed that all chemical reactions proceed quantitatively, auxiliary reagents and additives are not taken into account.

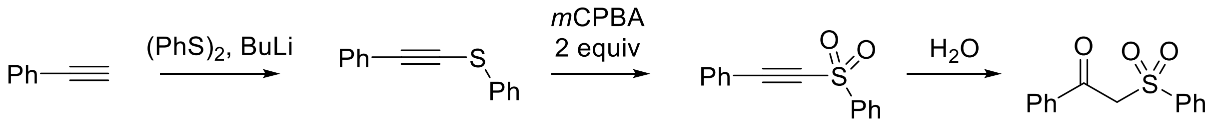
Our method 1:



2b

$$\text{Atom economy} = \frac{M(2b)}{M(PhC{\equiv}CH)+M(TMSCl)+M(BuLi)+M(PhSO2Cl)+M(AlCl3)+M(H2O)} \times 100\% = 43\%$$

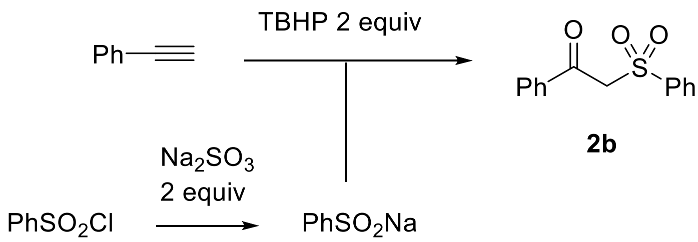
Our method 2:



2b

$$\text{Atom economy} = \frac{M(2b)}{M(PhC{\equiv}CH)+M(PhSSPh)+M(BuLi)+2M(mCPBA)+M(H2O)} \times 100\% = 35\%$$

Yavari's method [I. Yavari and S. Shaabanzadeh, Electrochemical Synthesis of β-Ketosulfones from Switchable Starting Materials, *Org. Lett.*, 2020, **22**, 464–467]:



2b

$$\text{Atom economy} = \frac{M(2b)}{M(PhC{\equiv}CH)+M(PhSO2Cl)+2M(Na2SO3)+2M(TBHP)} \times 100\% = 37\%$$