

Visible-Light-Induced Anti-Markovnikov Hydrosulfonation of Styrene Derivatives

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Supplementary Information

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1. General information

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 spectrometer at 25 °C in solvents as indicated. Chemical shift values are reported in ppm with the solvent resonance referred to the standard position (CDCl_3 ; ^1H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.16$). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants J are reported in Hertz (Hz). IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm^{-1} . HRMS were obtained on a QTOF micro spectrometer.

All reactions were conducted in oven-dried Schlenk-tube under an atmosphere of nitrogen. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Conversion of the reactions was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an ethanolic vanillin/sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh). The photocatalyst 4CzIPN¹, sulfonates² and styrenes³ were prepared according to previous reported procedures.

2. Optimization of the reaction conditions

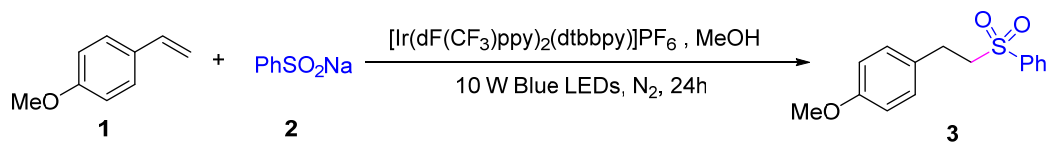
2.1 Solvent screening^a



Entry ^a	Solvent	Yield (%) ^b
1	MeOH	66
2	THF+H ₂ O (9:1)	40
3	DMF	n.r. ^c
4	DMSO	n.r. ^c
5	MeOH+CH ₃ CN (1:1)	63
6	MeOH+THF (1:1)	44
7	CH ₃ CN +H ₂ O (9:1)	37
8	CH ₃ CN +H ₂ O (8:2)	40
9	CH ₃ CN +H ₂ O (7:3)	36
10	CH ₃ CN +H ₂ O (6:4)	n.r. ^c
11	CH ₃ CN +H ₂ O (5:5)	n.r. ^c

^a Conditions: **1** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.) and 1 mol% of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ in the indicated solvents (2 mL), irradiated with 10 W blue LEDs light for 24 h. ^b Yield of isolated product. ^c n.r. = no reaction.

2.2 Light intensity investigation^a

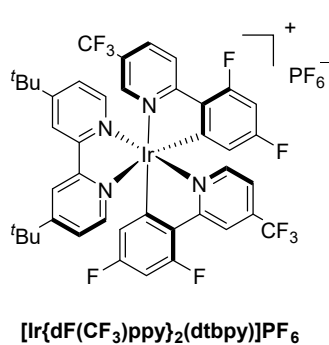
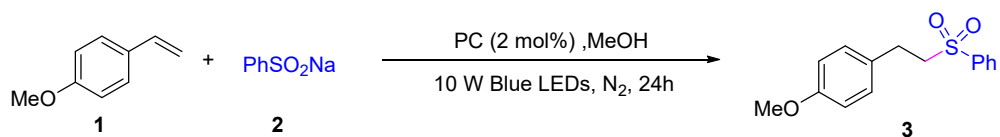


Entry ^a	Power of light (W)	Yield (%) ^b
1	6	26
2	10	37
3	30	29

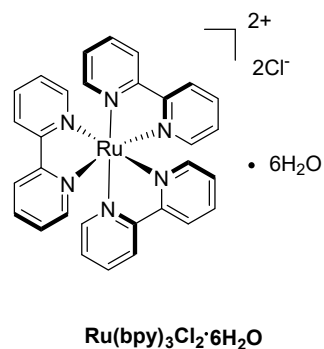
^a Conditions: **1** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.) and 1mol% of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ in MeOH (2 mL), irradiated with the indicated blue LEDs light for 24 h.

^b Yield of isolated product.

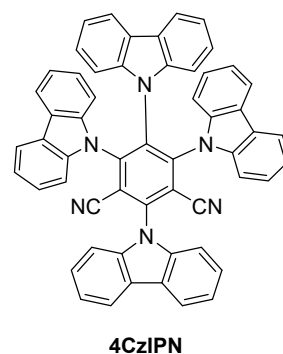
2.3 Catalysts screening^a



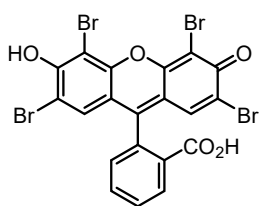
66%



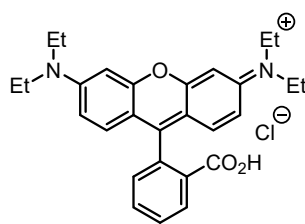
18%



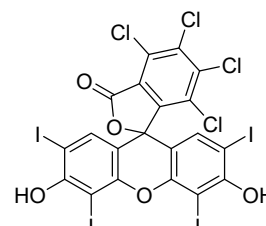
trace



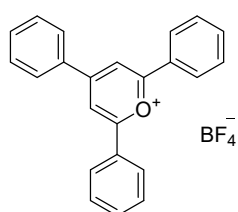
n.r.



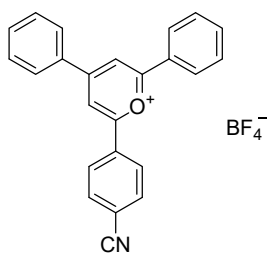
trace



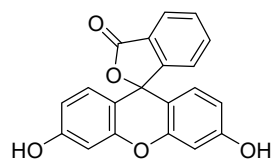
trace



18%



n.r.



trace

^a Conditions: **1** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.) and 1 mol% of the indicated photocatalyst in MeOH (2 mL), irradiated with 10 W blue LEDs light for 24 h, isolated yield are given and n.r. = no reaction.

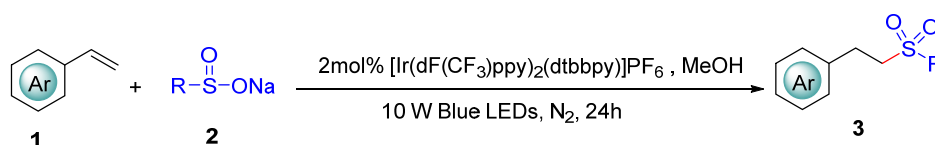
2.4 Concentration Screening



Entry	Concentration (mol/L)	Yield (%) ^e
1 ^a	0.1	63
2 ^b	0.1	69
3 ^c	0.05	94
4 ^d	0.05	73

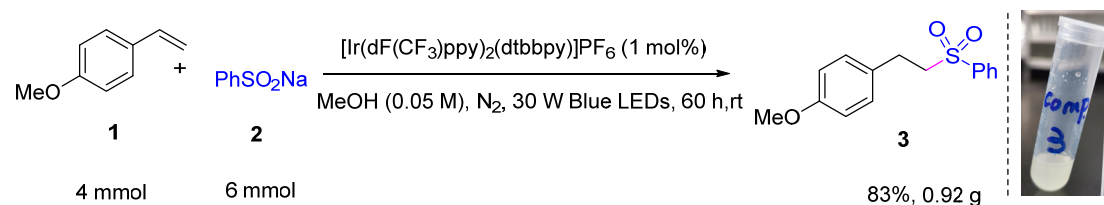
^a Conditions: **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv) and 1 mol% of catalyst in CH_3OH (2 mL), irradiated with 10 W blue LEDs light for 24 h. ^b In the presence of 2 mol% of catalyst in 2 mL CH_3OH . ^c In the presence of 2 mol% of catalyst in 4 mL CH_3OH . ^d In the presence of 1 mol% of catalyst in the 2 mL CH_3OH .

3. General procedures



A 5 mL dry Schlenk-tube containing a PTFE-coated stirring bar was sequentially charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.02 mmol, 2 mol%), sulfinate **2** (0.3 mmol, 1.5 equiv) and styrene **1** (0.2 mmol, if solid). The vessel was then evacuated and filled with nitrogen three times. Then, MeOH (4 mL) was added followed by the addition of **1** (0.2 mmol, if liquid) at 25 °C under nitrogen flow. Finally, the tube was sealed and placed 2 cm away from a 10 W blue LEDs light irradiation under fan cooling (to maintain the temperature at 25 °C). After 24 hours, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of Celite. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate mixtures to give the corresponding products in yields listed in Scheme 2 and 3.

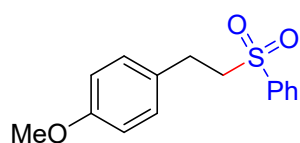
4. Procedure for Scale-up reaction



A 150 mL dry Schlenk-tube containing a PTFE-coated stirring bar was sequentially charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.04 mmol, 1 mol%), sulfinate **2** (0.98g, 6 mmol). Then, MeOH (80 mL) was added and the vessel was subjected to freeze-pump-thaw three times, followed by the addition of **1** (536 μL , 4 mmol) at 25 °C under nitrogen flow. Finally, the tube was sealed and placed 2 cm away from two 30 W blue LEDs light irradiation under fan cooling (to maintain the temperature at 25 °C). The reaction time was elongated to 60 hours to ensure the smooth proceeding of this transformation. After 60 hours, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of Celite. The solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (5:1) mixtures to give product **3** (0.92g) in 83% yield.

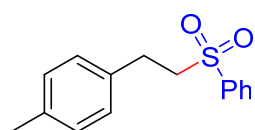
5. Characterization of products

1-Methoxy-4-(2-(phenylsulfonyl)ethyl)benzene (**3**)



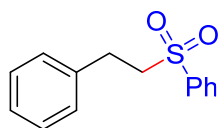
Obtained as a yellow oil (94%, 51.9 mg); $R_f = 0.25$ (EtOAc:petroleum ether 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.3$ Hz, 2H), 7.66 (d, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.03 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.6$ Hz, 2H), 3.76 (s, 3H), 3.37 – 3.29 (m, 2H), 3.04 – 2.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 139.2, 133.9, 129.5, 129.5, 129.4, 128.2, 114.3, 57.9, 55.4, 28.0 ppm. IR (neat): ν_{max} 3621, 3063, 2940, 2838, 1613, 1513, 1452, 1408, 1305, 1249, 1146, 1089, 1032, 824, 746. HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 299.0712, Found: 299.0711.

1-Methyl-4-(2-(phenylsulfonyl)ethyl)benzene (**4**)



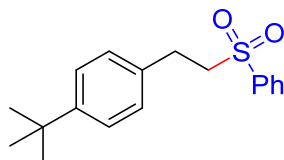
Obtained as a yellow oil (91%, 47.3 mg); $R_f = 0.20$ (EtOAc:petroleum ether 1:5); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 – 7.89 (m, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 3.39 – 3.26 (m, 2H), 3.07 – 2.93 (m, 2H), 2.29 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.2, 136.7, 134.5, 133.9, 129.6, 129.5, 128.3, 128.2, 57.8, 28.4, 21.1 ppm. IR (neat): ν_{max} 3627, 3016, 2925, 1905, 1515, 1447, 1407, 1306, 1148, 1089, 1023, 804, 745. HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 283.0763, Found: 283.0764.

(Phenethylsulfonyl)benzene (5)



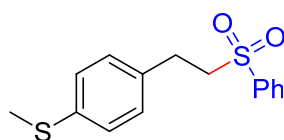
Obtained as a yellow oil (82%, 40.4 mg); $R_f = 0.30$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 – 7.90 (m, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.29 – 7.18 (m, 3H), 7.25 -7.17 (m, 2H), 7.11 (d, $J = 7.0$ Hz, 2H), 3.41 – 3.29 (m, 2H), 3.10 – 3.00 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.1, 137.6, 134.0, 129.5, 129.0, 128.4, 128.2, 127.1, 57.7, 28.9 ppm. IR (neat): ν_{max} 3830, 3740, 3604, 3062, 2961, 1696, 1493, 1448, 1403, 1303, 1268, 1144, 1084, 1023, 796, 752. HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 269.0607, Found: 269.0603.

1-(*tert*-Butyl)-4-(2-(phenylsulfonyl)ethyl)benzene (6)



Obtained as a yellow oil (65%, 39.3 mg); $R_f = 0.35$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.2$ Hz, 2H), 7.72 - 7.63 (m, 1H), 7.62 -7.53 (m, 2H), 7.33 – 7.24 (m, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 3.43 – 3.29 (m, 2H), 3.43 -3.31 (m, 2H), 1.28 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.0, 139.2, 134.4, 133.9, 129.4, 128.2, 128.1, 125.8, 57.7, 34.5, 31.4, 28.3 ppm. IR (neat): ν_{max} 3739, 3061, 2960, 2870, 1696, 1514, 1450, 1404, 1360, 1309, 1148, 1091, 1020, 820, 747. HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 325.1233, Found: 325.1239.

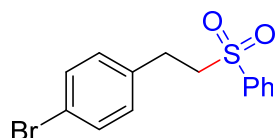
Methyl 4-(2-(phenylsulfonyl)ethyl)phenyl)sulfane (7)



Obtained as a white solid (60%, 35.0 mg); $R_f = 0.18$ (EtOAc:petroleum ether 1:4); m.p. 65 – 66 °C; ^1H

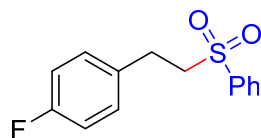
NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 7.3 Hz, 2H), 7.72 – 7.63 (m, 1H), 7.57 (t, J = 7.1 Hz, 2H), 7.19 – 7.11 (m, 2H), 7.03 (d, J = 6.7 Hz, 2H), 3.44 – 3.27 (m, 2H), 3.09 – 2.94 (m, 2H), 2.52 – 2.34 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 139.1, 137.2, 134.4, 134.0, 129.5, 128.9, 128.2, 127.2, 57.6, 28.3, 16.1. IR (neat): ν_{\max} 3741, 3624, 2963, 2920, 1716, 1494, 1442, 1300, 1145, 1088, 1019, 801, 750. HRMS (ESI-MS): Calcd. for C₁₆H₁₅O₂S₂Na [M+Na]⁺: 315.0484, Found: 315.0486.

1-Bromo-4-(2-(phenylsulfonyl)ethyl)benzene (8)



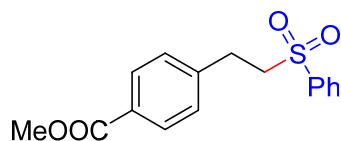
Obtained as a yellow oil (85%, 55.1 mg); R_f = 0.18 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.85 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 3.40 – 3.22 (m, 2H), 3.09 – 2.89 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 136.5, 134.0, 132.0, 130.2, 129.5, 128.1, 120.9, 57.3, 28.3. IR (neat): ν_{\max} 3735, 3059, 2930, 1899, 1582, 1485, 1446, 1403, 1306, 1148, 1081, 1013, 804, 737. HRMS (ESI-MS): Calcd. for C₁₄H₁₃BrO₂SNa [M+Na]⁺: 346.9712, Found: 346.9714.

1-Fluoro-4-(2-(phenylsulfonyl)ethyl)benzene (9)



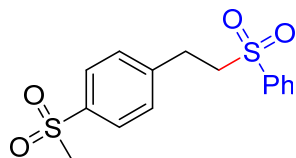
Obtained as a yellow oil (59%, 31.2 mg); R_f = 0.30 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.88 (m, 2H), 7.71 – 7.63 (m, 1H), 7.63 – 7.53 (m, 2H), 7.14 – 7.04 (m, 2H), 7.00 – 6.91 (m, 2H), 3.40 – 3.26 (m, 2H), 3.10 – 2.98 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 161.9 (d, J = 244.0 Hz), 139.1, 134.0, 133.2 (d, J = 3.2 Hz), 130.0 (d, J = 7.9 Hz), 129.5, 128.2, 115.8 (d, J = 21.3 Hz), 57.7, 28.1 ppm. IR (neat): ν_{\max} 3624, 3066, 2961, 1719, 1602, 1510, 1447, 1408, 1306, 1226, 1148, 1087, 1018, 822, 742. HRMS (ESI-MS): Calcd. for C₁₄H₁₃FO₂SNa [M+Na]⁺: 287.0512, Found: 287.0514.

Methyl 4-(2-(phenylsulfonyl)ethyl)benzoate (10)



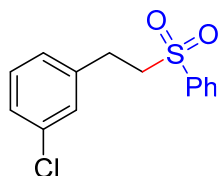
Obtained as a white solid (56%, 34.1 mg); $R_f = 0.38$ (EtOAc:petroleum ether 1:4); m.p. 110 – 111 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.88 (m, 4H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 3.88 (s, 3H), 3.43 – 3.31 (m, 2H), 3.16 – 3.05 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 142.8, 139.0, 134.1, 130.2, 129.6, 129.1, 128.5, 128.2, 57.1, 52.3, 28.8 ppm. IR (neat): ν_{max} 2957, 1718, 1612, 1443, 1281, 1147, 1100, 1021, 749. HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 327.0662, Found: 327.0669.

1-(Methylsulfonyl)-4-(2-(phenylsulfonyl)ethyl)benzene (11)



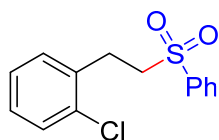
Obtained as a white solid (53%, 34.3 mg); $R_f = 0.12$ (EtOAc:petroleum ether 1:3); m.p. 126.2 – 126.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.90 (m, 2H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 3.44 – 3.29 (m, 2H), 3.21 – 3.12 (m, 2H), 3.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 139.4, 138.8, 134.2, 129.6, 129.5, 128.2, 128.1, 56.9, 44.6, 28.7 ppm. IR (neat): ν_{max} 3829, 3740, 3603, 2963, 1702, 1518, 1446, 1405, 1295, 1147, 1092, 1017, 960, 756. HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_4\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 347.0382, Found: 347.0392.

1-Chloro-3-(2-(phenylsulfonyl)ethyl)benzene (12)



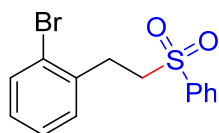
Obtained as a white solid (70%, 39.2 mg); $R_f = 0.25$ (EtOAc:petroleum ether 1:4); m.p. 75 – 76 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.71 – 7.63 (m, 1H), 7.58 (t, $J = 7.8$ Hz, 2H), 7.22 – 7.15 (m, 2H), 7.09 (s, 1H), 7.04 – 6.98 (m, 1H), 3.42 – 3.25 (m, 2H), 3.11 – 2.95 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.5, 139.0, 134.7, 134.1, 130.2, 129.5, 128.6, 128.2, 127.3, 126.7, 57.3, 28.5 ppm. IR (neat): ν_{max} 3830, 3739, 3619, 3063, 2383, 2312, 1697, 1567, 1467, 1441, 1146, 1085, 1015, 872, 751. HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{13}\text{ClO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 303.0217, Found: 303.0223.

1-Chloro-2-(2-(phenylsulfonyl)ethyl)benzene (13)



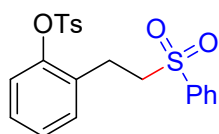
Obtained as a yellow oil (90%, 50.4 mg); $R_f = 0.25$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 – 7.91 (m, 2H), 7.70 – 7.63 (m, 1H), 7.62 – 7.55 (m, 2H), 7.32 – 7.27 (m, 1H), 7.21 – 7.13 (m, 3H), 3.43 – 3.33 (m, 2H), 3.17 – 3.08 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.9, 135.3, 134.0, 133.9, 130.8, 129.9, 129.5, 128.7, 128.2, 127.4, 55.4, 27.4 ppm. IR (neat): ν_{max} 3634, 3064, 2928, 2870, 1816, 1585, 1573, 1476, 1447, 1404, 1305, 1258, 1233, 1153, 1109, 1087, 1071, 1036, 999, 969, 945, 842, 787, 753, 723. HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{13}\text{ClO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 303.0217, Found: 303.0222.

1-Bromo-2-(2-(phenylsulfonyl)ethyl)benzene (14)



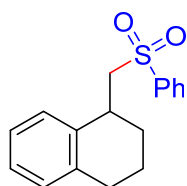
Obtained as a yellow oil (88%, 57.0 mg); $R_f = 0.22$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.1$ Hz, 2H), 7.73 – 7.65 (m, 1H), 7.64 – 7.54 (m, 2H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.25 – 7.17 (m, 2H), 7.14–7.03 (m, 1H), 3.44 – 3.28 (m, 2H), 3.21 – 3.07 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.8, 137.0, 134.0, 133.2, 130.8, 129.5, 129.0, 128.3, 128.1, 124.2, 55.5, 29.9 ppm. IR (neat): ν_{max} 3623, 3062, 2962, 1916, 1697, 1576, 1442, 1404, 1307, 1147, 1088, 1026, 753. HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{13}\text{BrO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 346.9712, Found: 346.9714.

2-(2-(Phenylsulfonyl)ethyl)phenyl 4-methylbenzenesulfonate (15)



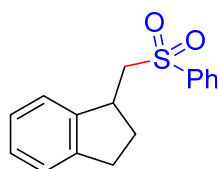
Obtained as a yellow oil (28%, 23.3 mg); $R_f = 0.25$ (EtOAc:petroleum ether 1:3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 – 7.88 (m, 2H), 7.69 (t, $J = 8.1$ Hz, 3H), 7.60 (t, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.21 – 7.13 (m, 3H), 7.06 – 7.02 (m, 1H), 3.37 – 3.24 (m, 2H), 2.92 – 2.82 (m, 2H), 2.46 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.8, 145.9, 138.9, 133.9, 132.6, 131.1, 131.0, 130.1, 129.5, 128.6, 128.5, 128.3, 127.6, 123.0, 55.8, 23.9, 21.9 ppm. IR (neat): ν_{max} 3831, 3738, 3605, 2956, 2860, 1706, 1495, 1450, 1371, 1306, 1265, 1152, 1089, 1024, 872, 810, 759. HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_5\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 439.0644, Found: 439.0640.

1-((Phenylsulfonyl)methyl)-1,2,3,4-tetrahydronaphthalene (16)⁴



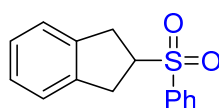
Obtained as a yellow oil (67%, 38.3 mg); $R_f = 0.30$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 – 7.94 (m, 2H), 7.72 – 7.65 (m, 1H), 7.60 (t, $J = 7.5$ Hz, 2H), 7.11 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 6.96 – 6.91 (m, 1H), 3.54 – 3.27 (m, 3H), 2.79 – 2.67 (m, 2H), 2.16 – 2.06 (m, 1H), 2.00 – 1.90 (m, 1H), 1.84 – 1.71 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.0, 137.7, 137.4, 133.9, 129.6, 129.5, 128.7, 128.1, 126.7, 126.4, 62.9, 32.9, 29.2, 27.6, 18.9 ppm. IR (neat): ν_{max} 3061, 3016, 2929, 2866, 1490, 1447, 1403, 1303, 1260, 1147, 1085, 1023, 797, 737, 689. HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 309.0920, Found: 309.0922.

1-((Phenylsulfonyl)methyl)-2,3-dihydro-1H-indene (17)



Obtained as a yellow oil (43%, 23.4 mg); $R_f = 0.34$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.72 – 7.64 (m, 1H), 7.64 – 7.56 (m, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.09 (m, 3H), 3.73 – 3.63 (m, 1H), 3.73 – 3.63 (m, 1H), 3.61 – 3.52 (m, 1H), 3.00 – 2.80 (m, 2H), 2.53 – 2.41 (m, 1H), 2.00 – 1.89 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 143.8, 143.7, 140.0, 133.9, 129.5, 128.1, 127.5, 126.7, 124.9, 123.4, 61.4, 39.5, 32.5, 31.5 ppm. IR (neat): ν_{max} 3831, 3740, 3618, 3002, 1705, 1519, 1381, 1282, 1202, 956, 756. HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 295.0763, Found: 295.0765.

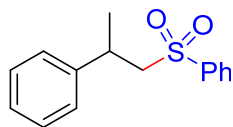
2-(Phenylsulfonyl)-2,3-dihydro-1H-indene (18)



Obtained as a yellow oil (72%, 37.2 mg); $R_f = 0.30$ (EtOAc:petroleum ether 1:4); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.1$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 2H), 7.20 – 7.14 (m, 4H), 4.09 – 3.98 (m, 1H), 3.51 (d, $J = 7.9$ Hz, 1H), 3.47 (d, $J = 7.9$ Hz, 1H), 3.21 (d, $J = 8.8$ Hz, 1H), 3.17 (d, $J = 8.9$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.6, 138.3, 133.9, 129.4, 128.7, 127.3, 124.5,

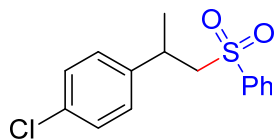
63.6, 33.8 ppm. IR (neat): ν_{\max} 3067, 2958, 2906, 2851, 1732, 1584, 1478, 1461, 1447, 1434, 1302, 1279, 1260, 1234, 1212, 1142, 1083, 1023, 987, 968, 916, 871, 799, 756, 736, 714. HRMS (ESI-MS): Calcd. for $C_{15}H_{15}O_2S$ $[M+H]^+$: 295.0787, Found: 295.0783.

((2-Phenylpropyl)sulfonyl)benzene (19) ⁴



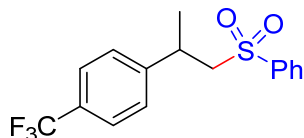
Obtained as a white solid (83%, 43.2 mg); m.p. 87 – 88°C; R_f = 0.30 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 2H), 7.63 – 7.53 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.24 – 7.14 (m, 3H), 7.07 (d, J = 7.0 Hz, 2H), 3.48 – 3.30 (m, 3H), 1.44 (d, J = 6.3 Hz, 3H). ¹³C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.0, 133.6, 129.3, 128.9, 128.0, 127.0, 126.8, 63.5, 35.2, 22.3 ppm. IR (neat): ν_{\max} 3830, 3740, 3604, 3062, 2971, 1697, 1500, 1449, 1398, 1296, 1144, 1083, 1008, 843, 752. HRMS (ESI-MS): Calcd. for $C_{15}H_{16}O_2SNa$ $[M+Na]^+$: 283.0763, Found: 283.0767.

1-Chloro-4-(1-(phenylsulfonyl)propan-2-yl)benzene (20) ⁴



Obtained as a white solid (68%, 40.0 mg); m.p. 75 – 76 °C; R_f = 0.20 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.9 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.20 – 7.11 (m, 2H), 7.00 (d, J = 8.3 Hz, 2H), 3.48 – 3.27 (m, 3H), 1.40 (d, J = 6.5 Hz, 3H). ¹³C NMR (100 MHz, $CDCl_3$) δ 142.3, 139.9, 133.6, 132.8, 129.3, 128.9, 128.3, 127.9, 63.3, 34.7, 22.4 ppm. IR (neat): ν_{\max} 3830, 3741, 3622, 3063, 2972, 1698, 1490, 1450, 1406, 1300, 1145, 1090, 1009, 831, 750. HRMS (ESI-MS): Calcd. for $C_{15}H_{15}ClO_2SNa$ $[M+Na]^+$: 317.0373, Found: 317.0375.

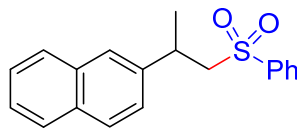
1-(1-(Phenylsulfonyl)propan-2-yl)-4-(trifluoromethyl)benzene (21)



Obtained as a white solid (51%, 33.5 mg); m.p. 113 – 114 °C; R_f = 0.25 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.61 – 7.52 (m, 1H), 7.49 – 7.37 (m, 4H), 7.18 (d, J = 8.1 Hz, 2H), 3.54 – 3.34 (m, 3H), 1.43 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, $CDCl_3$) δ 147.9, 139.7, 133.7, 129.3, 129.3 (q, J = 16.1 Hz), 128.8, 127.9, 125.7 (q, J = 3.7 Hz), 124.1 (q, J = 270 Hz), 62.9, 35.2, 22.5 ppm. IR (neat): ν_{\max} 3743, 2970, 1926, 1618, 1416, 1324, 1295, 1126, 1017, 878, 833,

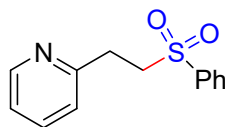
798, 747. HRMS (ESI-MS): Calcd. for $C_{16}H_{15}F_3O_2SNa$ $[M+Na]^+$: 351.0637, Found: 351.0631.

2-(1-(Phenylsulfonyl)propan-2-yl)naphthalene (22)⁴



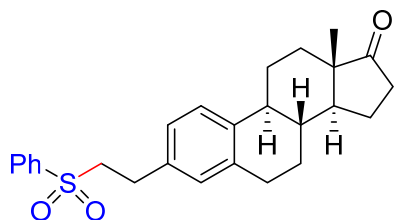
Obtained as a yellow oil (44%, 27.3 mg); $R_f = 0.25$ (EtOAc:petroleum ether 1:4); 1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 3H), 7.72 – 7.65 (m, 2H), 7.53 – 7.41 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 1H), 3.63 – 3.54 (m, 1H), 3.51 – 3.37 (m, 2H), 1.53 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.9, 133.5, 133.5, 132.5, 129.1, 128.7, 128.0, 127.7, 127.7, 126.4, 125.9, 125.6, 124.9, 63.4, 35.4, 22.3 ppm. IR (neat): ν_{max} 3740, 3623, 3055, 2966, 1715, 1509, 1449, 1388, 1300, 1145, 1087, 1020, 98, 859, 812, 746. HRMS (ESI-MS): Calcd. for $C_{19}H_{18}O_2SNa$ $[M+Na]^+$: 333.0920, Found: 333.0930.

2-(2-(Phenylsulfonyl)ethyl)pyridine (23)



Obtained as a yellow oil (91%, 45.0 mg); $R_f = 0.25$ (EtOAc:petroleum ether 2:5); 1H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.39 (m, 1H), 7.98 – 7.83 (m, 2H), 7.72 – 7.46 (m, 4H), 7.17 (d, $J = 7.8$ Hz, 1H), 7.12 (dd, $J = 7.1, 5.3$ Hz, 1H), 3.71 – 3.54 (m, 2H), 3.34 – 3.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.3, 139.2, 137.0, 133.9, 129.4, 128.3, 123.5, 122.1, 55.3, 30.8 ppm. IR (neat): ν_{max} 3602, 3062, 2961, 1585, 1476, 1441, 1306, 1146, 1087, 1024, 793, 754. HRMS (ESI-MS): Calcd. for $C_{13}H_{14}NO_2S$ $[M+H]^+$: 248.0740, Found: 248.0741.

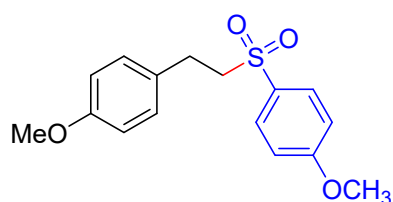
(8R,9S,13S,14S)-13-Methyl-3-(2-(phenylsulfonyl)ethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (24)



Obtained as a colorless oil (34 %, 28.7 mg); $R_f = 0.30$ (EtOAc:petroleum ether 1:4); 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J = 7.2$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.85 (s, 1H), 3.43 – 3.28 (m, 2H), 3.03 – 2.93 (m, 2H), 2.89 –

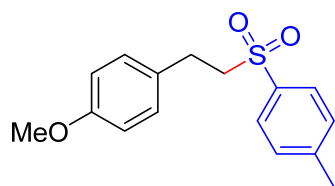
2.78 (m, 2H), 2.56 – 2.41 (m, 1H), 2.43 – 2.33 (m, 1H), 2.19 – 2.09 (m, 1H), 2.19 – 2.09 (m, 1H), 2.08 – 1.93 (m, 3H), 1.64 – 1.54 (m, 2H), 1.53 – 1.40 (m, 4H), 0.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 221.0, 139.2, 138.6, 137.1, 135.0, 133.9, 129.5, 129.1, 128.2, 126.0, 125.8, 57.7, 50.6, 48.1, 44.4, 38.2, 36.0, 31.7, 29.4, 28.3, 26.5, 25.8, 21.7, 13.9 ppm. IR (neat): ν_{max} 2928, 1730, 1503, 1448, 1404, 1373, 1339, 1310, 1260, 1145, 1083, 1010, 903, 885, 799, 760, 739, 710, 689. HRMS (ESI-MS): Calcd. for C₂₆H₃₀O₄SNa [M+Na]⁺: 445.1808, Found 445.1810.

1-Methoxy-4-((4-methoxyphenethyl)sulfonyl)benzene (27)



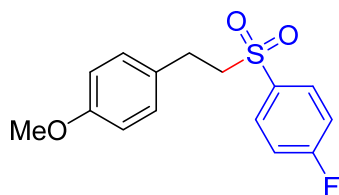
Obtained as a white solid (53%, 32.4 mg); m.p. 81 – 82 °C; R_f = 0.23 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.79 (m, 2H), 7.02 (dd, *J* = 8.6, 1.4 Hz, 4H), 6.84 – 6.75 (m, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 3.36 – 3.20 (m, 2H), 3.01 – 2.89 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 158.6, 130.7, 130.4, 129.6, 129.4, 114.6, 114.3, 58.2, 55.8, 55.4, 28.2 ppm. IR (neat): ν_{max} 3830, 3741, 3623, 2956, 2838, 1897, 1756, 1586, 1506, 1453, 1304, 1254, 1140, 1093, 1025, 816, 743. HRMS (ESI-MS): Calcd. for C₁₆H₁₈O₄SNa [M+Na]⁺: 329.0818, Found: 329.0828.

1-Methoxy-4-(2-tosylethyl)benzene (28)



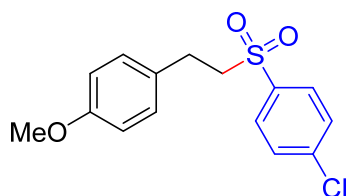
Obtained as a white solid (87%, 50.4 mg); m.p. 107 – 108 °C; R_f = 0.25 (EtOAc:petroleum ether 1:4); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.38 – 3.15 (m, 2H), 3.03 – 2.90 (m, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 144.9, 136.2, 130.1, 129.6, 129.4, 128.2, 114.3, 58.0, 55.4, 28.1, 21.8 ppm. IR (neat): ν_{max} 3741, 2959, 2921, 2836, 1599, 1510, 1450, 1394, 1296, 1254, 1142, 1095, 1031, 812, 744. HRMS (ESI-MS): Calcd. for C₁₆H₁₈O₃SNa [M+Na]⁺: 313.0869, Found: 313.0872.

1-Fluoro-4-((4-methoxyphenethyl)sulfonyl)benzene (29)



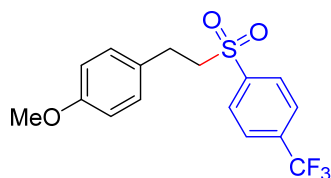
Obtained as a white solid (65%, 38.2 mg); m.p. 78 – 79 °C; $R_f = 0.28$ (EtOAc:petroleum ether 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.84 (m, 2H), 7.26 – 7.19 (m, 2H), 7.02 (d, $J = 8.7$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 3.76 (s, 3H), 3.41 – 3.21 (m, 2H), 3.03 – 2.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.8 (d, $J = 254.8$ Hz), 158.6, 135.2 (d, $J = 3.2$ Hz), 131.0 (d, $J = 9.5$ Hz), 129.3, 129.2, 116.7 (d, $J = 22.5$ Hz), 114.2, 57.9, 55.3, 28.0 ppm. IR (neat): ν_{max} 3740, 3623, 3069, 2955, 2839, 1910, 1774, 1593, 1505, 1455, 1405, 1300, 1243, 1146, 1092, 1027, 826, 741. HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{15}\text{FO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 317.0618, Found: 317.0619.

1-Chloro-4-((4-methoxyphenethyl)sulfonyl)benzene (30)



Obtained as a white solid (63%, 39.1 mg); m.p. 106 – 107 °C; $R_f = 0.25$ (EtOAc:petroleum ether 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.79 (m, 2H), 7.58 – 7.44 (m, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.5$ Hz, 2H), 3.76 (s, 3H), 3.42 – 3.23 (m, 2H), 3.02 – 2.90 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 140.6, 137.6, 129.8, 129.7, 129.4, 129.2, 114.3, 57.9, 55.4, 28.0 ppm. IR (neat): ν_{max} 3831, 3742, 2959, 2838, 1706, 1614, 1574, 1511, 1467, 1395, 1311, 1250, 1146, 1088, 1025, 812, 759. HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{15}\text{ClO}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 333.0323, Found: 333.0320.

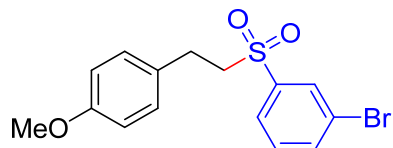
1-Methoxy-4-(2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)benzene (31)



Obtained as a white solid (41%, 28.2 mg); m.p. 99 – 100 °C; $R_f = 0.15$ (EtOAc:petroleum ether 1:5); ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.2$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 6.80 – 6.74 (m, 2H), 3.76 (s, 3H), 3.41 – 3.31 (m, 2H), 3.07 – 2.95 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 142.8, 135.6 (q, $J = 33.3$ Hz), 129.5, 128.9, 128.9, 126.6 (q, $J = 3.7$ Hz), 123.2 (q, $J = 271.4$ Hz), 114.4, 57.8, 55.4, 28.0 ppm. IR (neat): ν_{max} 3829, 3742, 3623, 2961, 1705, 1512, 1455, 1400,

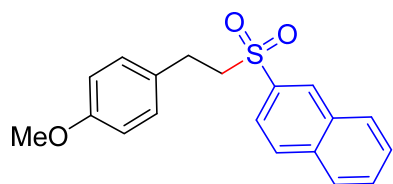
1318, 1254, 1161, 1097, 1061, 1024, 808, 754. HRMS (ESI-MS): Calcd. for $C_{16}H_{15}F_3O_3SNa$ $[M+Na]^+$: 367.0586, Found: 367.0583.

1-Bromo-4-((4-methoxyphenethyl)sulfonyl)benzene (32)



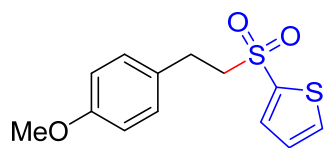
Obtained as yellow oil (60%, 42.5 mg); $R_f = 0.25$ (EtOAc:petroleum ether 1:4); 1H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, $J = 1.8$ Hz, 1H), 7.87 – 7.82 (m, 1H), 7.80 – 7.75 (m, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 7.03 (d, $J = 8.6$ Hz, 2H), 6.84 – 6.72 (m, 2H), 3.77 (s, 3H), 3.43 – 3.24 (m, 2H), 3.08 – 2.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 141.1, 137.0, 131.2, 131.0, 129.5, 129.1, 126.8, 123.5, 114.3, 57.9, 55.4, 28.0 ppm. IR (neat): ν_{max} 3831, 3740, 3606, 2960, 2835, 1706, 1615, 1511, 1454, 1404, 1309, 1252, 1145, 1092, 1026, 804. HRMS (ESI-MS): Calcd. for $C_{15}H_{15}BrO_3SNa$ $[M+Na]^+$: 376.9817, Found: 376.9812.

1-((4-Methoxyphenethyl)sulfonyl)naphthalene (33)



Obtained as a yellow oil (60%, 39.1 mg); $R_f = 0.23$ (EtOAc:petroleum ether 1:4); 1H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.01 (t, $J = 6.9$ Hz, 2H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.88 (dd, $J = 8.7, 1.8$ Hz, 1H), 7.73 – 7.60 (m, 2H), 7.05 – 6.94 (m, 2H), 6.78 – 6.71 (m, 2H), 3.72 (s, 3H), 3.47 – 3.34 (m, 2H), 3.08 – 2.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 135.9, 135.3, 132.2, 130.0, 129.7 (two peaks overlapped), 129.5, 129.3, 128.0, 127.8, 122.7, 114.2 (two peaks overlapped), 57.8, 55.2, 28.1 ppm. IR (neat): ν_{max} 3830, 3741, 3604, 2960, 2837, 1703, 1614, 1510, 1453, 1305, 1253, 1138, 1027, 859, 813, 750. HRMS (ESI-MS): Calcd. for $C_{19}H_{18}O_3SNa$ $[M+Na]^+$: 349.0869, Found: 349.0871.

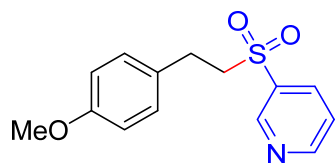
2-((4-Methoxyphenethyl)sulfonyl)thiophene (34)



Obtained as a yellow oil (63%, 35.5 mg); $R_f = 0.15$ (EtOAc:petroleum ether 1:4); 1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.59 (m, 2H), 7.21 – 7.12 (m, 1H), 7.10 – 7.00 (m, 2H), 6.85 – 6.78 (m, 2H), 3.77 (s,

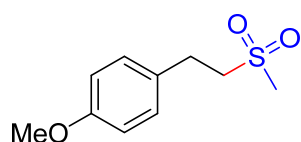
3H), 3.49 – 3.28 (m, 2H), 3.10 – 2.98 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 140.1, 134.3, 134.1, 129.4, 129.2, 128.0, 114.2, 59.2, 55.3, 28.3 ppm. IR (neat): ν_{max} 3831, 3740, 3604, 3093, 2960, 2837, 1698, 1615, 1510, 1452, 1399, 1308, 1250, 1138, 1092, 1022, 805, 740. HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 305.0277, Found: 305.0278.

4-((4-Methoxyphenethyl)sulfonyl)pyridine (35)



Obtained as a yellow oil (64%, 35.5 mg); R_f = 0.20 (EtOAc:petroleum ether 1:3); ^1H NMR (400 MHz, CDCl_3) δ 9.12 (d, J = 1.9 Hz, 1H), 8.87 (dd, J = 4.9, 1.5 Hz, 1H), 8.23 – 8.11 (m, 1H), 7.56 – 7.45 (m, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.83 – 6.69 (m, 2H), 3.75 (s, 3H), 3.45 – 3.34 (m, 2H), 3.07 – 2.97 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 154.1, 149.0, 136.1, 135.8, 129.3, 128.7, 123.9, 114.3, 58.1, 55.3, 27.8 ppm. IR (neat): ν_{max} 3615, 2958, 2840, 1613, 1574, 1513, 1457, 1413, 1311, 1251, 1153, 1104, 1028, 813, 752, 706. HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{16}\text{NO}_3\text{S}$ $[\text{M} + \text{H}]^+$: 278.0845, Found: 278.0844.

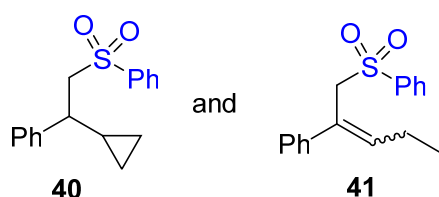
1-Methoxy-4-(2-(methylsulfonyl)ethyl)benzene (36)



Obtained as a white solid (93%, 39.8 mg); R_f = 0.10 (EtOAc:petroleum ether 1:4); m.p. 92.2 – 92.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, J = 8.7 Hz, 2H), 6.91 – 6.81 (m, 2H), 3.79 (s, 3H), 3.30 – 3.18 (m, 2H), 3.15 – 3.05 (m, 2H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 129.5, 129.3, 114.4, 56.4, 55.3, 41.1, 27.8 ppm. IR (neat): ν_{max} 3603, 3017, 2957, 2844, 2046, 1894, 1613, 1514, 1457, 1296, 1256, 1182, 1131, 1027, 972, 820. HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 237.0556, Found: 237.0558.

(1-Cyclopropyl-2-(phenylsulfonyl)ethyl)benzene (40) and

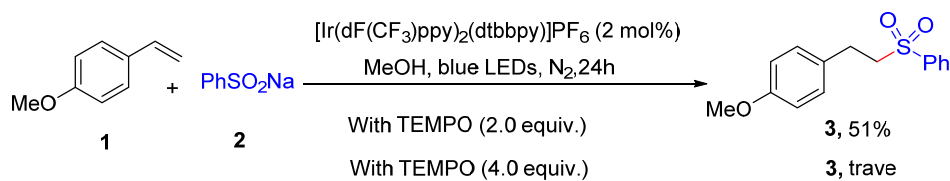
((2-Phenylpent-2-en-1-yl)sulfonyl)benzene (41)



Inseparable mixture of **40** and **41** was isolated as colorless oil (32%, 18.3 mg) with a ratio of 3: 1. $R_f = 0.20$ (EtOAc:petroleum ether 1:9); Due to the peak overlap of these two compound, recognizable peaks for **40** (major) are reported here: $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.66 (d, $J = 7.1$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.19 – 7.10 (m, 3H), 7.03 (dd, $J = 7.7, 1.6$ Hz, 3H), 3.68 – 3.60 (m, 2H), 2.57 – 2.45 (m, 1H), 1.10 – 0.97 (m, 1H), 0.66 – 0.55 (m, 1H), 0.44 – 0.37 (m, 1H), 0.36 – 0.28 (m, 1H), 0.22 – 0.12 (m, 1H). recognizable peaks for **41** (minor) are reported herein: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.0$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 5.59 (t, $J = 7.5$ Hz, 1H), 4.13 (s, 2H), 2.03 – 1.95 (m, 2H), 0.86 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 141.6, 140.5, 140.1, 138.9, 138.4, 133.5, 133.3, 129.0, 129.0, 128.7, 128.6, 128.6, 128.3, 127.9, 127.6, 127.6, 127.3, 127.0, 65.1, 62.3, 45.9, 29.8, 22.9, 18.3, 14.0, 6.0, 5.0 ppm. IR (neat): ν_{max} 2965, 2919, 1585, 1496, 1447, 1398, 1307, 1274, 1244, 1168, 1137, 1083, 1042, 1021, 958, 907, 861, 828, 780, 764, 745, 699, 685, 596, 580. HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 309.0920, Found: 309.0915.

6. Control experiments

6.1 TEMPO inhibition

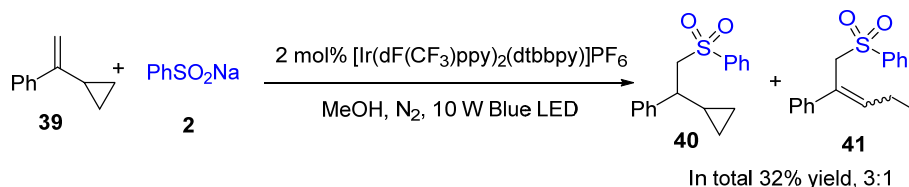


A 5 mL dry Schlenk-tube containing a PTFE-coated stirring bar was sequentially charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.02 mmol, 2 mol%), sulfinate **2** (0.3 mmol, 1.5 equiv), styrene **1** (0.2 mmol) and the indicated equiv. of TEMPO. The vessel was then evacuated and filled with nitrogen three times. Then, CH_3OH (4 mL) was added at 25 °C under nitrogen flow. Finally, the tube was sealed and placed 2 cm away from a 10 W blue LEDs light irradiation under fan cooling (to maintain the temperature at 25 °C). After 24 hours, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of Celite. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate mixtures to

give the corresponding products in pure form.

Conclusion: *The reaction proceeds through a radical process since radical scavenger, TEMPO, could suppress the transformation.*

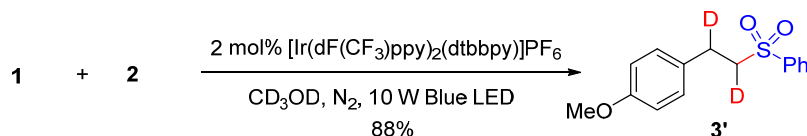
6.2 Radical clock reaction



A 5 mL dry Schlenk-tube containing a PTFE-coated stirring bar was sequentially charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.02 mmol, 2 mol%) and sulfinate **2** (0.3 mmol, 1.5 equiv). The vessel was then evacuated and filled with nitrogen three times. Then, CH_3OH (4 mL) was added followed by the addition of **39** (0.2 mmol) at 25 °C under nitrogen flow. Finally, the tube was sealed and placed 2 cm away from a 10 W blue LEDs light irradiation under fan cooling (to maintain the temperature at 25 °C). After 24 hours, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of Celite. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate mixtures to give the inseparable isomers **40** and **41** in total 32% of yield with a ratio of 2.7:1, which is determined from $^1\text{H-NMR}$ spectroscopy.

Conclusion: *radical process was involved in this transformation, which is consistent with the TEMPO inhibition experiment.*

6.3 Deuterium exchange experiments



Followed the general procedure for the reaction of styrene **1** and sulfinate **2** while CD_3OD was used as the solvent instead of MeOH . The product was isolated and confirmed to be **3'**. Deuterium was not only introduced into the expected benzylic position but also the α -position of sulfone.

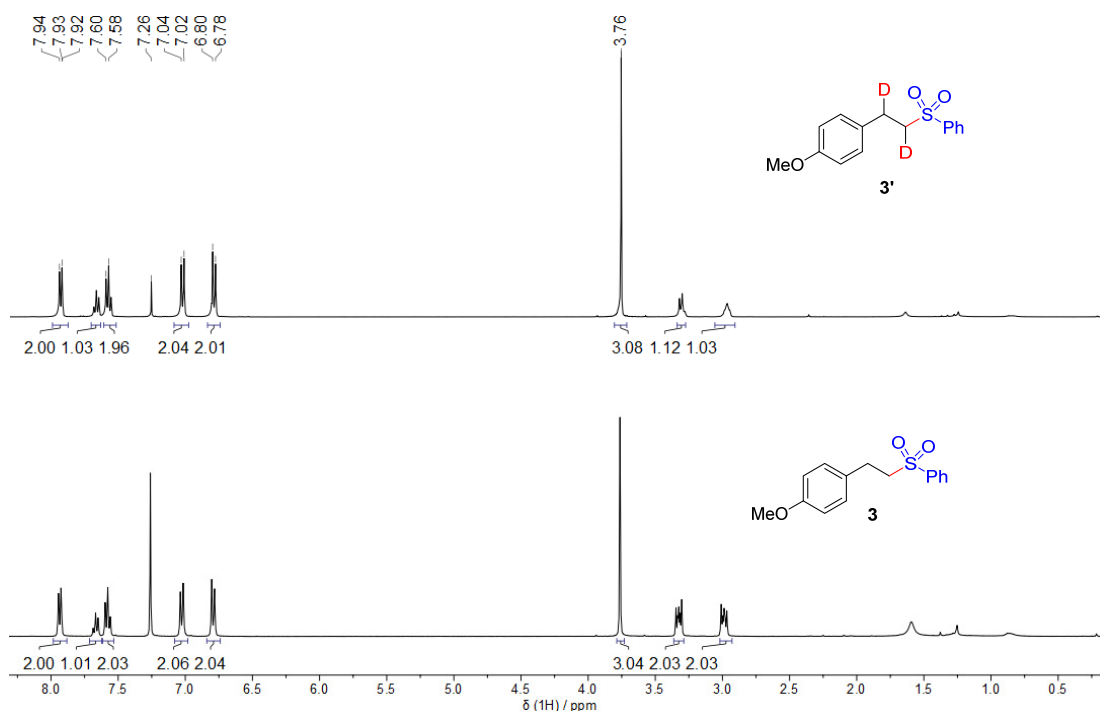


Figure S1. $^1\text{H-NMR}$ spectra of compound **3** and **3'**

To gain information about the α -position deuteration of the product, further proton/deuterium exchange experiment was carried out with compound **3**.



A 5 mL dry Schlenk-tube containing a PTFE-coated stirring bar was sequentially charged with compound **3** (0.1 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.02 mmol, 2 mol%) and sulfinate **2** (0.3 mmol, 1.5 equiv) or sodium methoxide (0.11 mmol, 1.1 equiv.), respectively in N_2 filled glove box. Then, the vessel was moved out and CD_3OD (4 mL) was added followed by the at 25 °C under nitrogen flow. Finally, the tube was sealed and placed 2 cm away from a 10 W blue LEDs light irradiation under fan cooling (to maintain the temperature at 25 °C). After 24 hours, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of Celite. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate mixtures and the product were confirmed by $^1\text{H-NMR}$ spectroscopy.

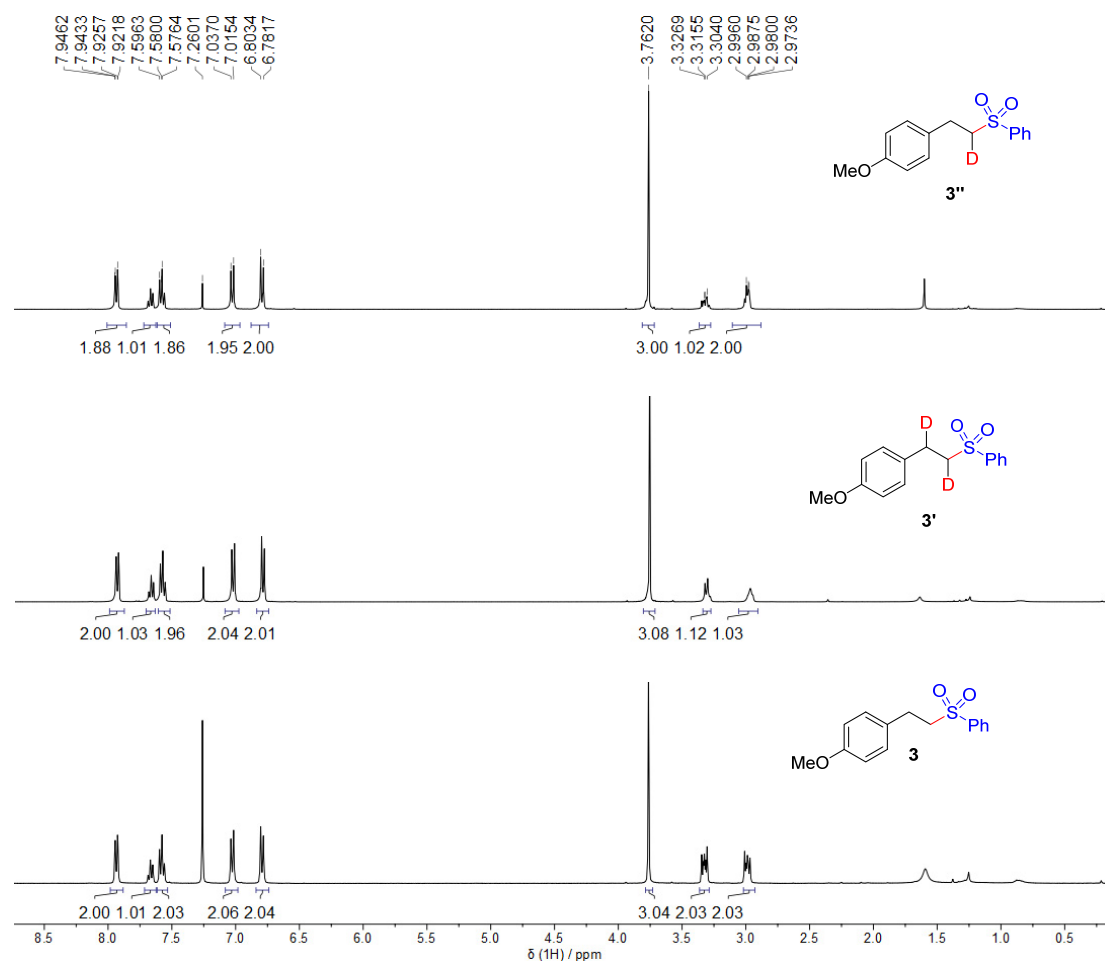
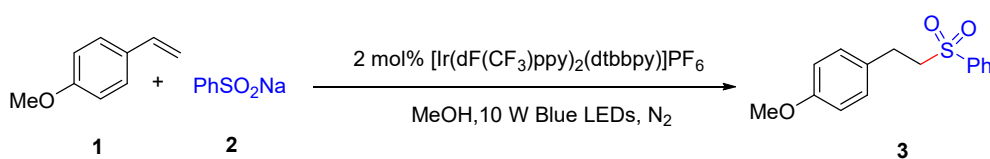


Figure S2. $^1\text{H-NMR}$ spectra of compound **3**, **3'** and **3''**

Conclusion:

- 1) The formation of unexpected α -position deuteration **3'** was probably attributed to the basic conditions formed during the reaction, which enabled the D/H exchange through a deprotonation and/deuteration process.
- 2) Benzenesulfinate **2** was not able to deprotonate product **3** while addition of sodium methoxide as a base led to the deuterium exchange under the reaction conditions

7. Light on/off experiment



Following the general procedure, six reactions were set up in parallel. Sequentially, the reactions were stopped and quenched after the indicated reaction times. The yields of the product were measured

by $^1\text{H-NMR}$ with mesitylene as internal standard. The yields of the target product were plotted against reaction time in figure S3.

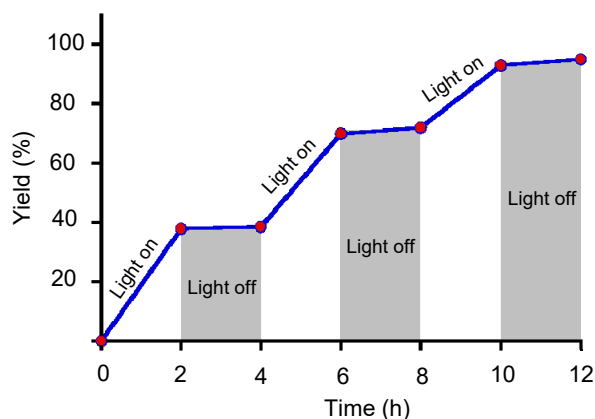


Figure S3. Light on/off experiment on the cross-coupling reaction of **1** and **2**

8. Quantum yield measurement

8.1 Determination of the light intensity at 436 nm

The photon flux of the spectrophotometer was determined by chemical actinometry using potassium ferrioxalate. The solution of 0.15 M ferrioxalate and buffered solution of phenanthroline were prepared as same as literature procedures.⁵ Both solutions were stored in the dark. The fraction of light absorbed (f) by this solution was calculated using eq 1, where A is the measured absorbance at 436 nm. (**Figure S4**, $A = 3.3950$). Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions. l is the path length (1.00 cm), and ϵ is the molar absorptivity at 510 nm ($11,100 \text{ L mol}^{-1} \text{ cm}^{-1}$). Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at $\lambda = 436 \text{ nm}$).⁶ t is the time (90.0 s). The photon flux was calculated (average of three experiments) to be $4.40 \times 10^{-10} \text{ einstein s}^{-1}$.

$$f = 1 - 10^{-A} \quad \text{eq 1}$$

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \epsilon} \quad \text{eq 2}$$

$$\text{photo flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f} \quad \text{eq 3}$$

Sample calculation:

$$f = 1 - 10^{-3.3950}$$

$$= 0.9999$$

$$\text{mol Fe}^{2+} = \frac{0.00235 \text{L}^{-1} \times 0.201}{1.000 \text{ cm} \times 11100 \text{L mol}^{-1} \text{cm}^{-1}}$$

$$= 4.26 \times 10^{-8} \text{ mol}$$

$$\text{photo flux} = \frac{4.26 \times 10^{-8}}{1.01 \times 90 \times 0.9999}$$

$$= 4.71 \times 10^{-10} \text{ einstein s}^{-1}$$

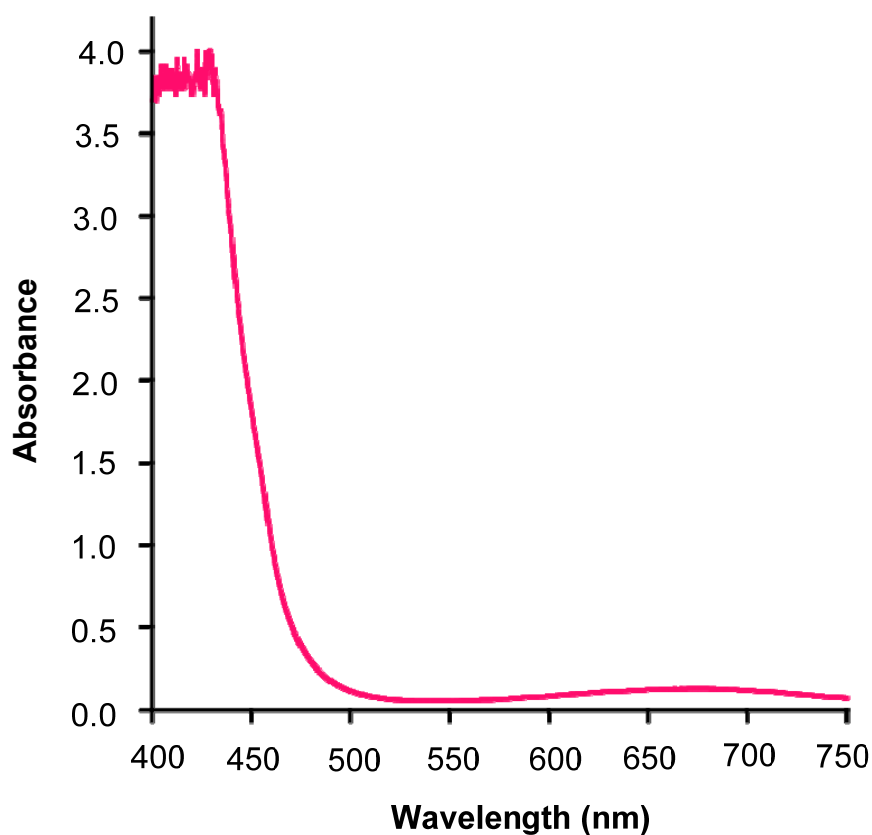
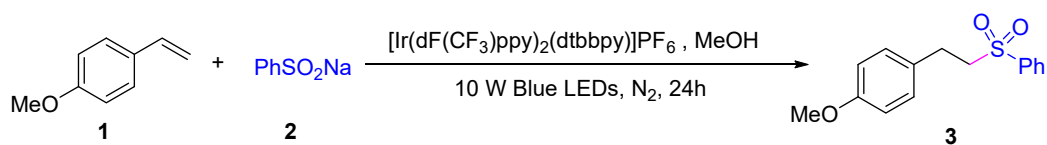


Figure S4. Absorbance of the Ferrioxalate Actinometer Solution.

8.2 Determination of Quantum Yield



The above reaction was set up in a glove box. Sulfinate **2** (0.15 mmol, 1.5 equiv), $[\text{Ir}(\text{dF}-\text{CF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$ (0.002 mmol, 0.02 equiv), styrene **1** (0.1 mmol, 1.0 equiv) and 2.0 mL of MeOH. The cuvette sealed with a cap and septa and irradiated ($\lambda = 436 \text{ nm}$) for 68400 s (19 h). After irradiation, the mixture was concentrated under reduced pressure and subjected to crude ^1H -NMR analysis with 1,3,5-methoxybenzene was used as the internal standard. 1.3 mg of the product **3** formed based on the crude ^1H NMR spectroscopy.

The absorbance of $[\text{Ir}(\text{dF}-\text{CF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$ in CH_3OH was measured at the reaction concentration of $1.0 \times 10^{-3} \text{ M}$ (**Figure S5**, Absorbance = 1.163). Therefore, fraction of light absorbed is 0.99.

$$\begin{aligned}\text{Quantum Yield} &= \frac{\text{numbers of moles of product}}{\text{flux} \times f \times t} \\ &= \frac{1.3/276.08/1000}{4.71 \times 10^{-10} \times 0.99 \times 68400} \\ &= 0.15\end{aligned}$$

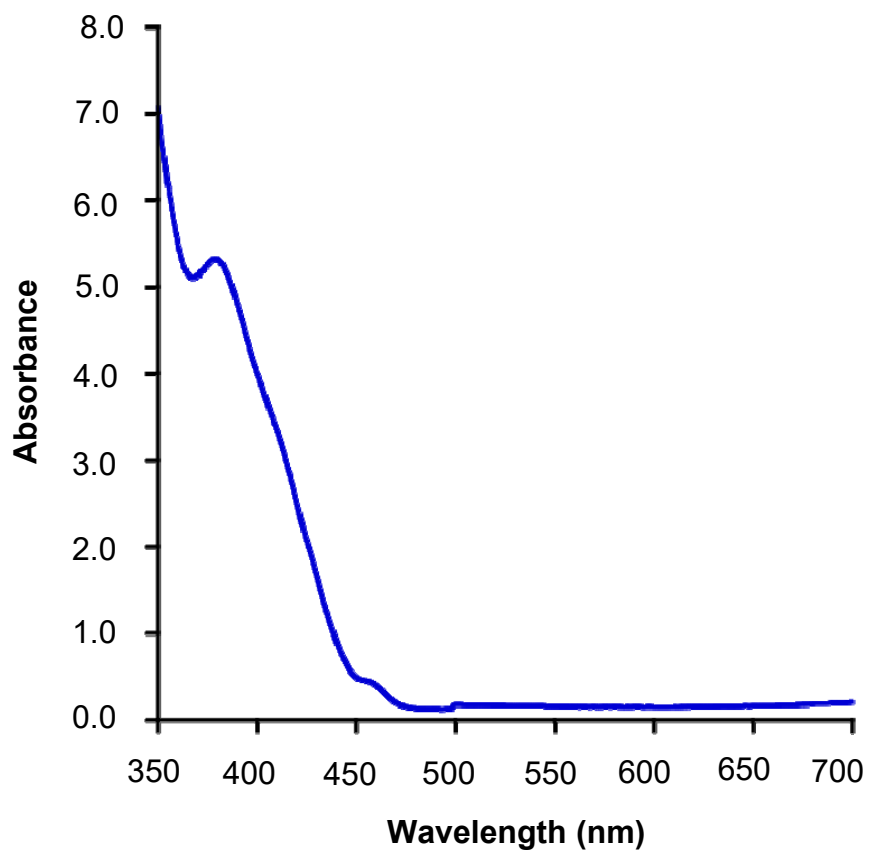
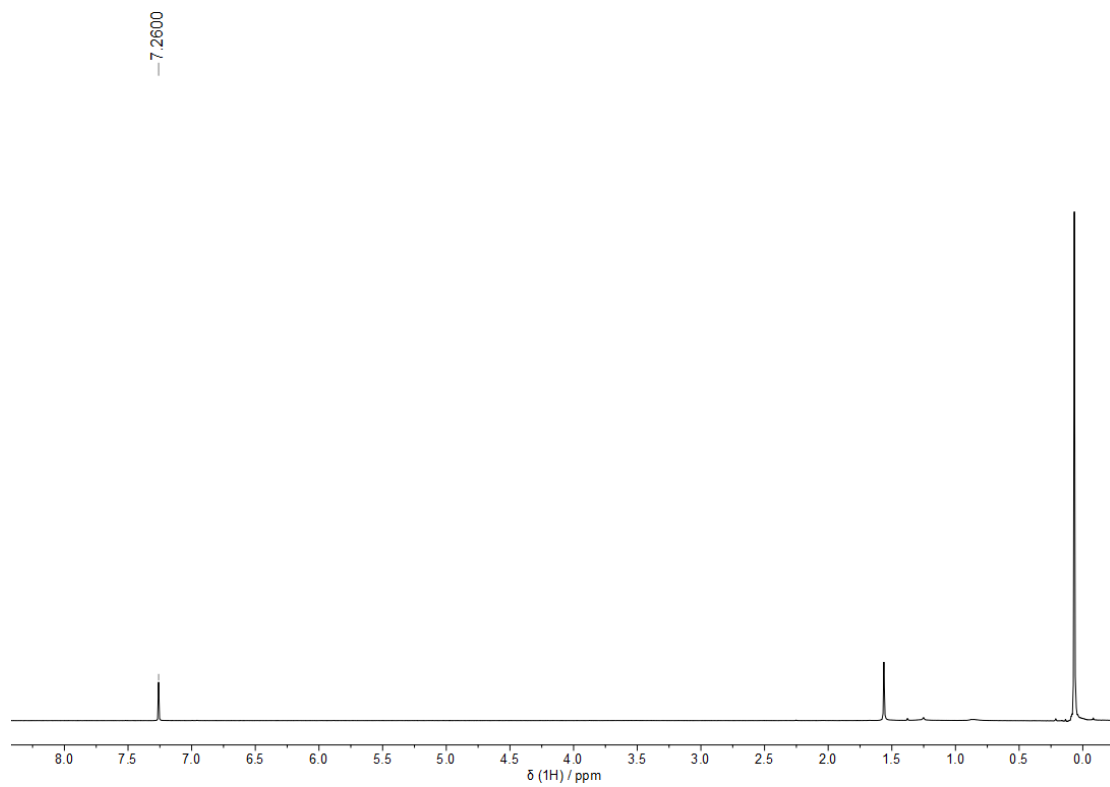


Figure S5. Absorbance of the Ir(dF-CF₃ppy)₂dtbbpyPF₆ under the Reaction Conditions.

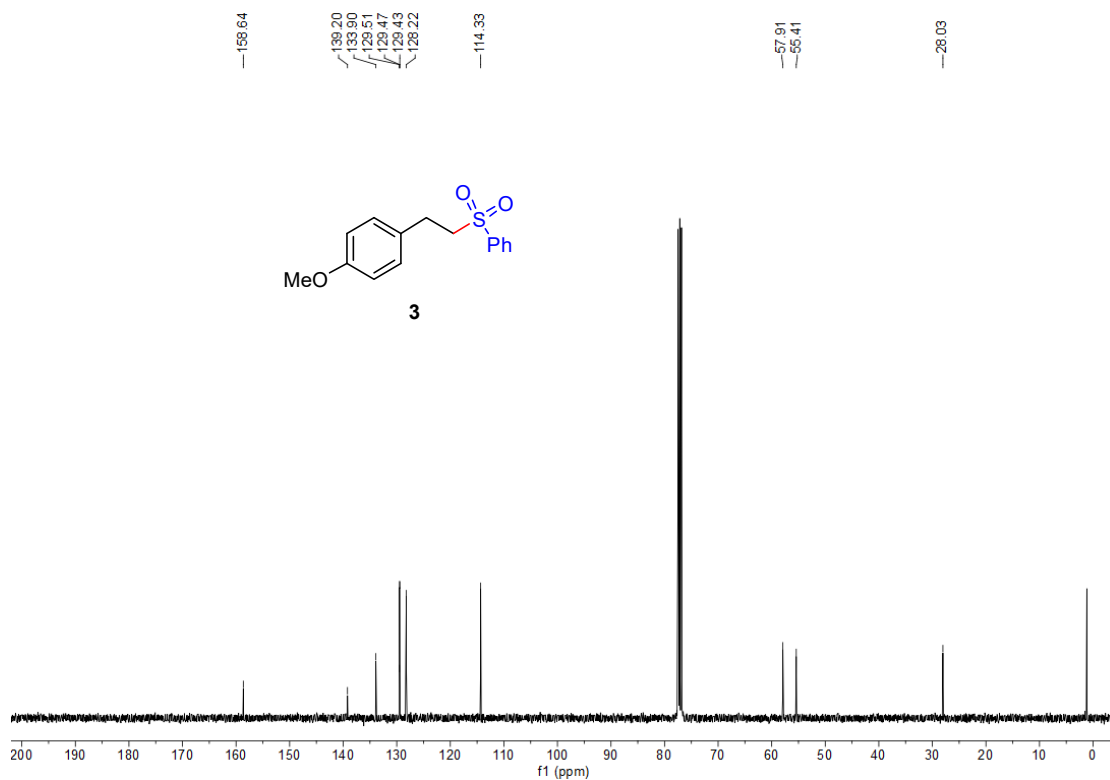
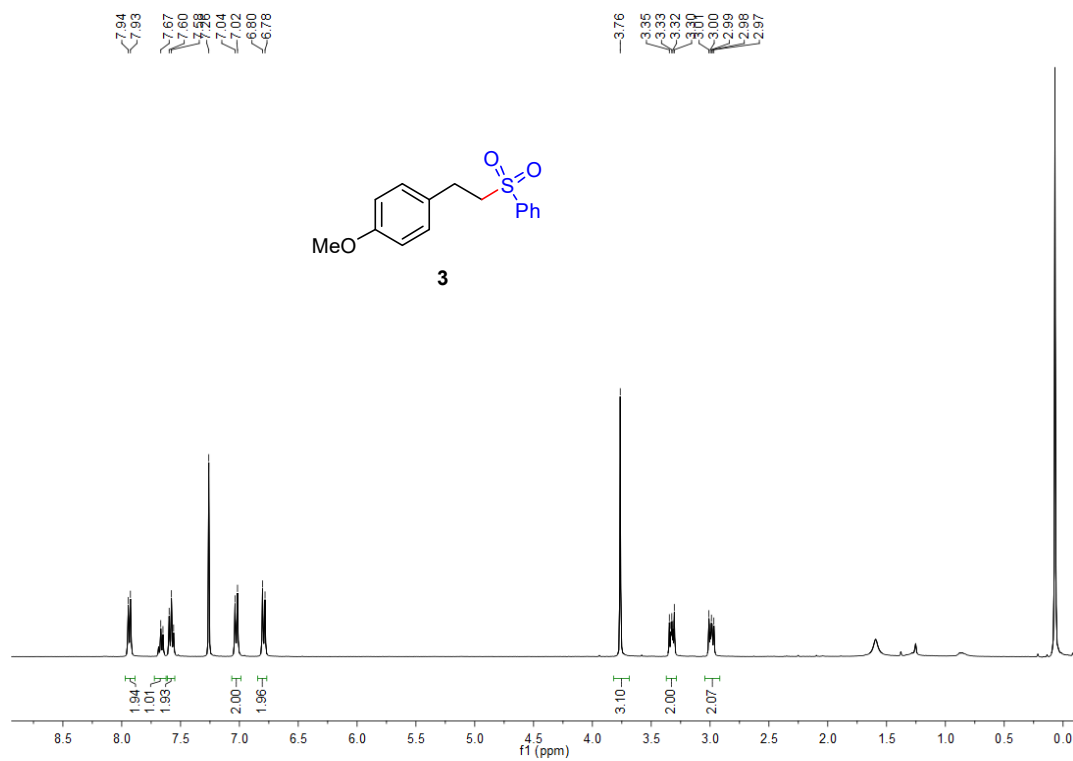
9. Reference

- 1) J. Luo and J. Zhang, Donor–Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic C(sp³)–C(sp²) Cross-Coupling, *ACS Catal.* 2016, **6**, 873-877.
- 2) For the synthesis of sulfinate: a) J. M. Lopchuk, K. Fjelbye, Y. Kawamata, L. R. Malins, C. Pan, R. Gianatassio, J. Wang, L. Prieto, J. Bradow, T. A. Brandt, M. R. Collins, J. Elleraas, J. Ewanicki, W. Farrell, O. O. Fadeyi, G. M. Gallego, J. Mousseau, R. Oliver, N. W. Sach, J. K. Smith, J. E. Spangler, H. Zhu, J. Zhu and P. S. Baran, Strain-Release Heteroatom Functionalization: Development, Scope, and Stereospecificity. *J. Am. Chem. Soc.* 2017, **139**, 3209; b) R. Melngailė, A. Sperga, K. Baldrige, J. Veliks, Diastereoselective Monofluorocyclopropanation Using Fluoromethylsulfonium Salts. *Org. Lett.* 2019, **21**, 7174; c) R. Wu, W. Chen and D. Yang, Platinum-catalyzed syn-stereocontrolled ring-opening of oxabicyclic alkenes with sodium arylsulfonates. *Org. Chem. Front.* 2017, **4**, 1921.
- 3) For the synthesis of styrenes, see: a) X. Li, Q. Gu, X. Dong, X. Meng and X. Liu, A Copper Catalyst with a Cinchona-Alkaloid-Based Sulfonamide Ligand for Asymmetric Radical Oxytrifluoromethylation of Alkenyl Oximes. *Angew. Chem. Int. Ed.* 2018, **57**, 7668; b) D. Kawauchi, H. Ueda and H. Tokuyama, Double Functionalization of Styrenes by Cu-Mediated Assisted Tandem Catalysis. *Eur. J. Org. Chem.* 2019, 2056; c) F. Scheidt, J. Neufeld, M. Schafer, C. Thiehoff and R. Gilmour, Catalytic Geminal Difluorination of Styrenes for the Construction of Fluorine-rich Bioisosteres. *Org. Lett.* 2018, **20**, 8073; d) M. Ratushnyy, M. Kamenova and V. Gevorgyan, A mild light-induced cleavage of the S–O bond of aryl sulfonate esters enables efficient sulfonylation of vinylarenes. *Chem. Sci.* 2018, **9**, 7193.
- 4) J. N. Dersiers and A. B. Charette, Catalytic Enantioselective Reduction of β , β -Disubstituted Vinyl Phenyl Sulfones by Using Bisphosphine Monoxide Ligands. *Angew. Chem. Int. Ed.* 2007, **46**, 5955.
- 5) M. A. Cismesia, T. P. Yoon, Characterizing chain processes in visible light photoredox catalysis. *Chem. Sci.* **2015**, **6**, 5426-5434.
- 6) C. G. Hatchard, C. A. Parker, A new sensitive chemical actinometer - II. Potassium ferrioxalate as a standard chemical actinometer. *Proc. R. Soc.* **1956**, **235**, 518-536.

10. NMR-spectra

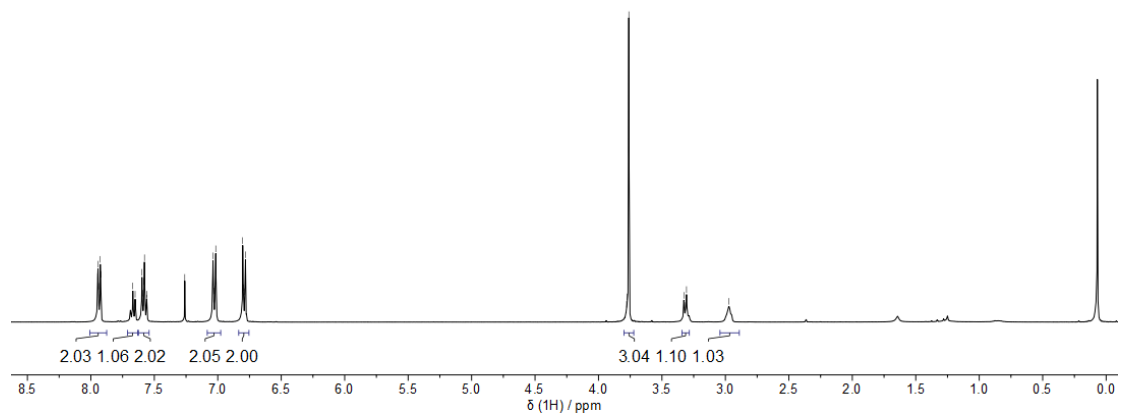
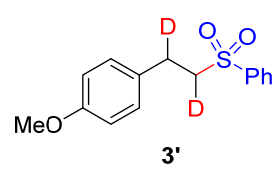


¹H-NMR spectrum of the CDCl₃ used for the characterization of all the products.



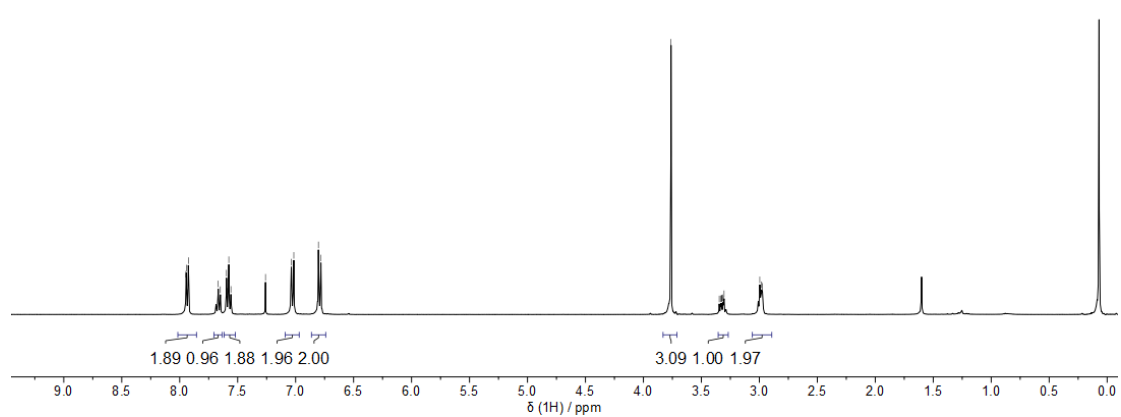
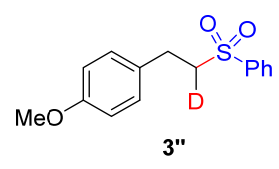
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6.7818

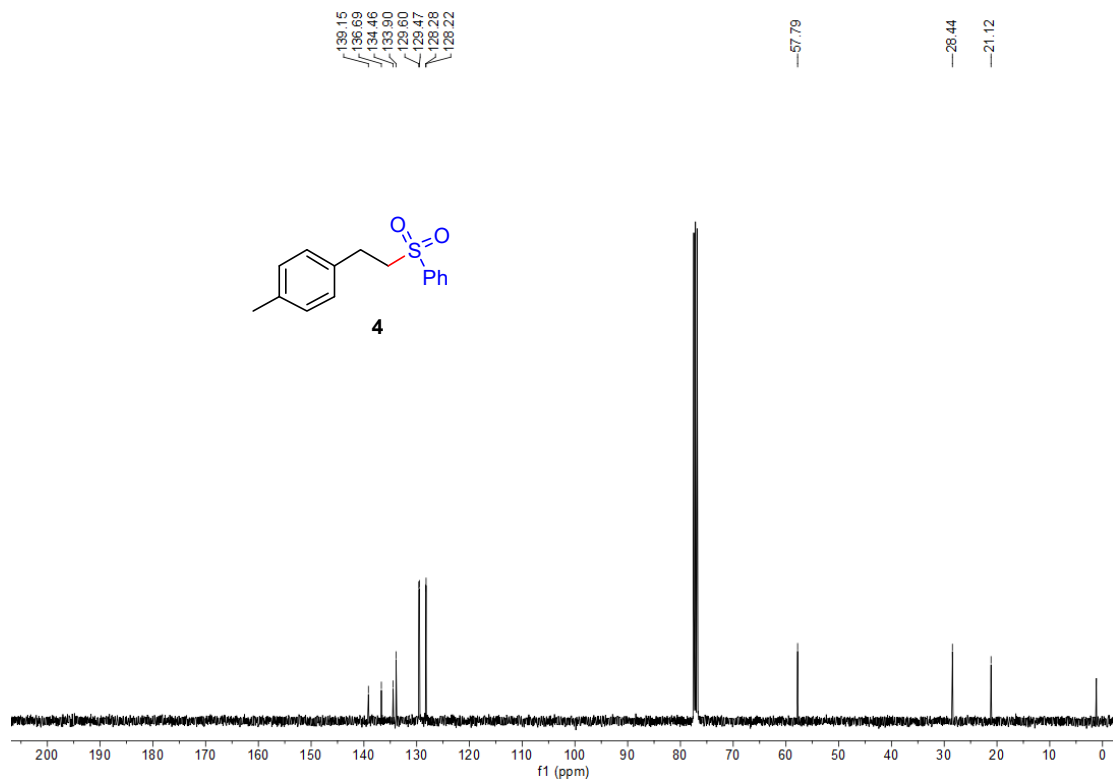
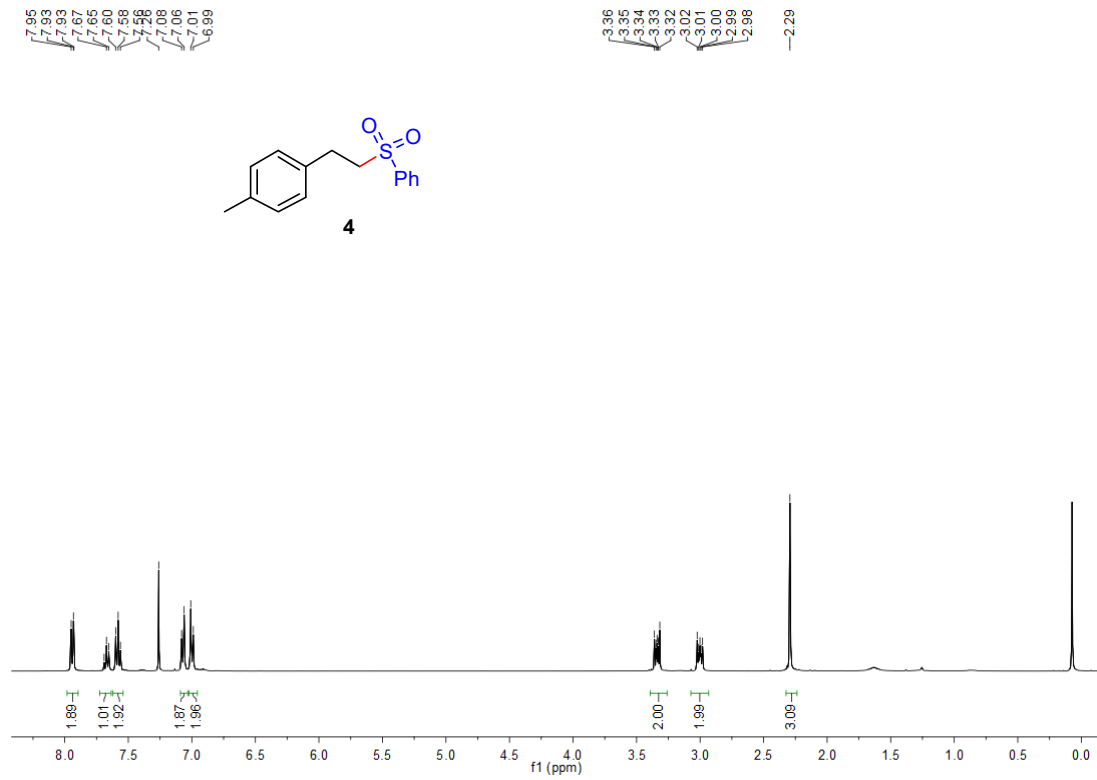
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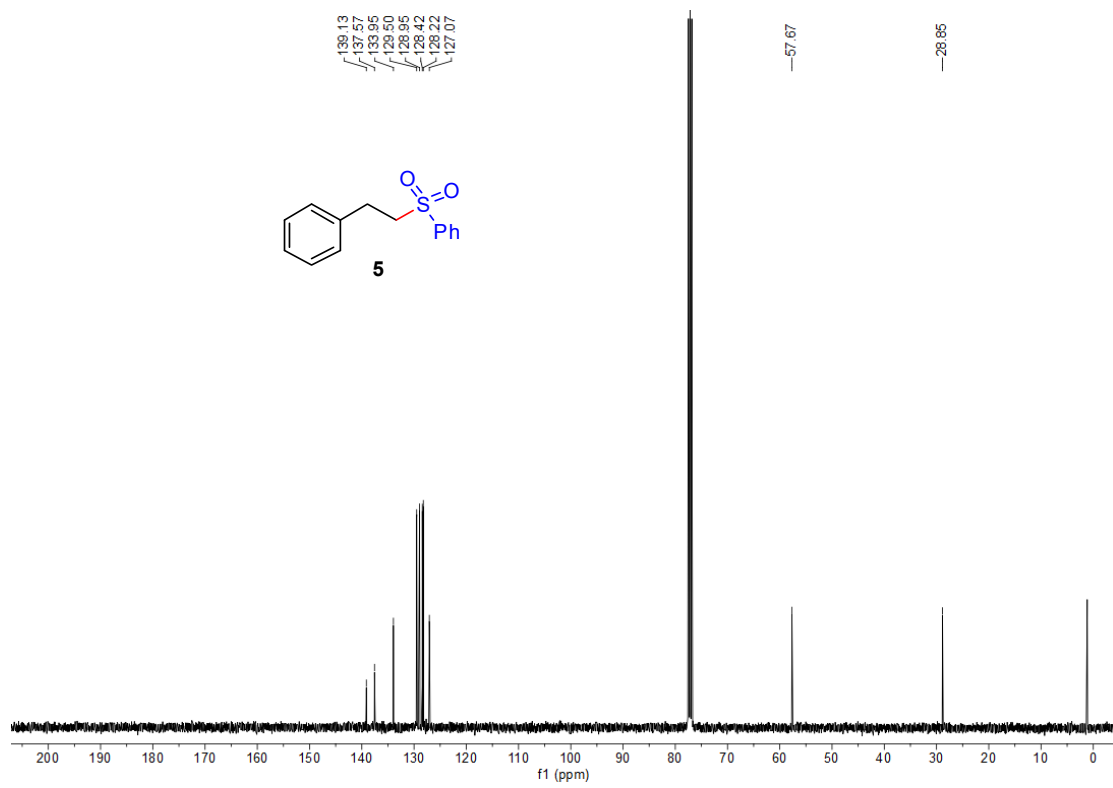
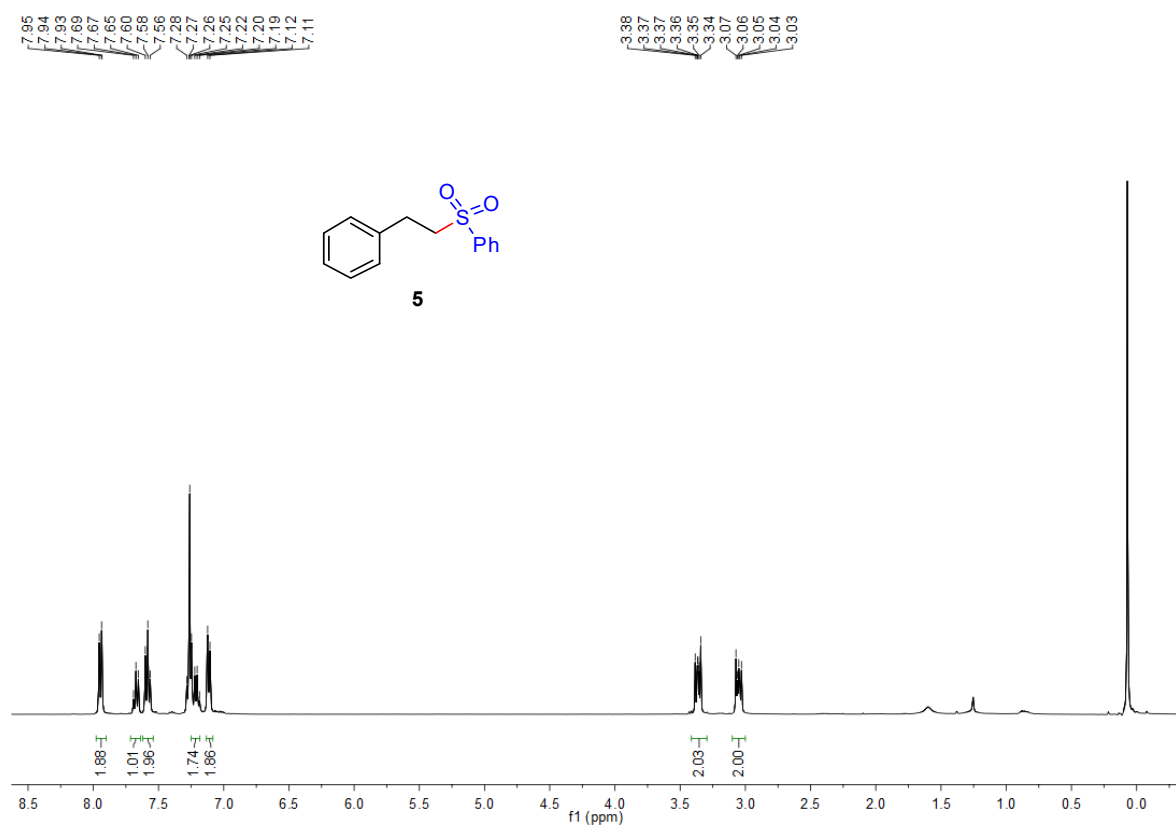


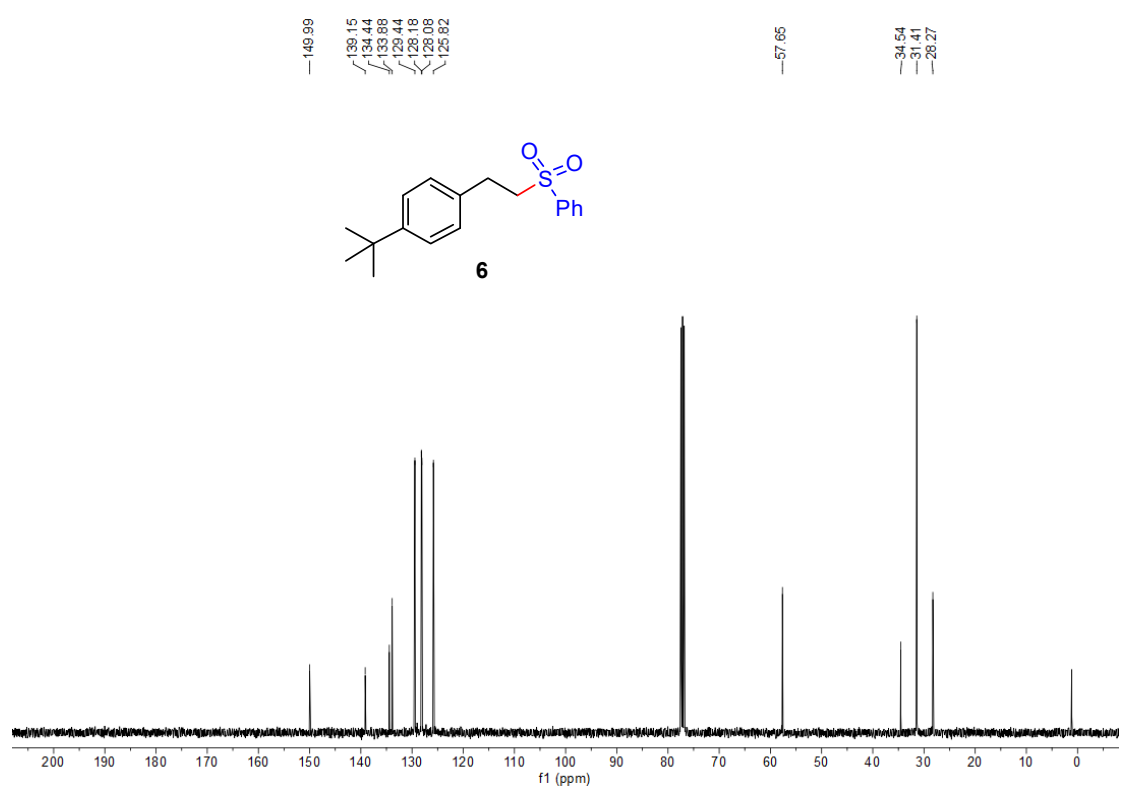
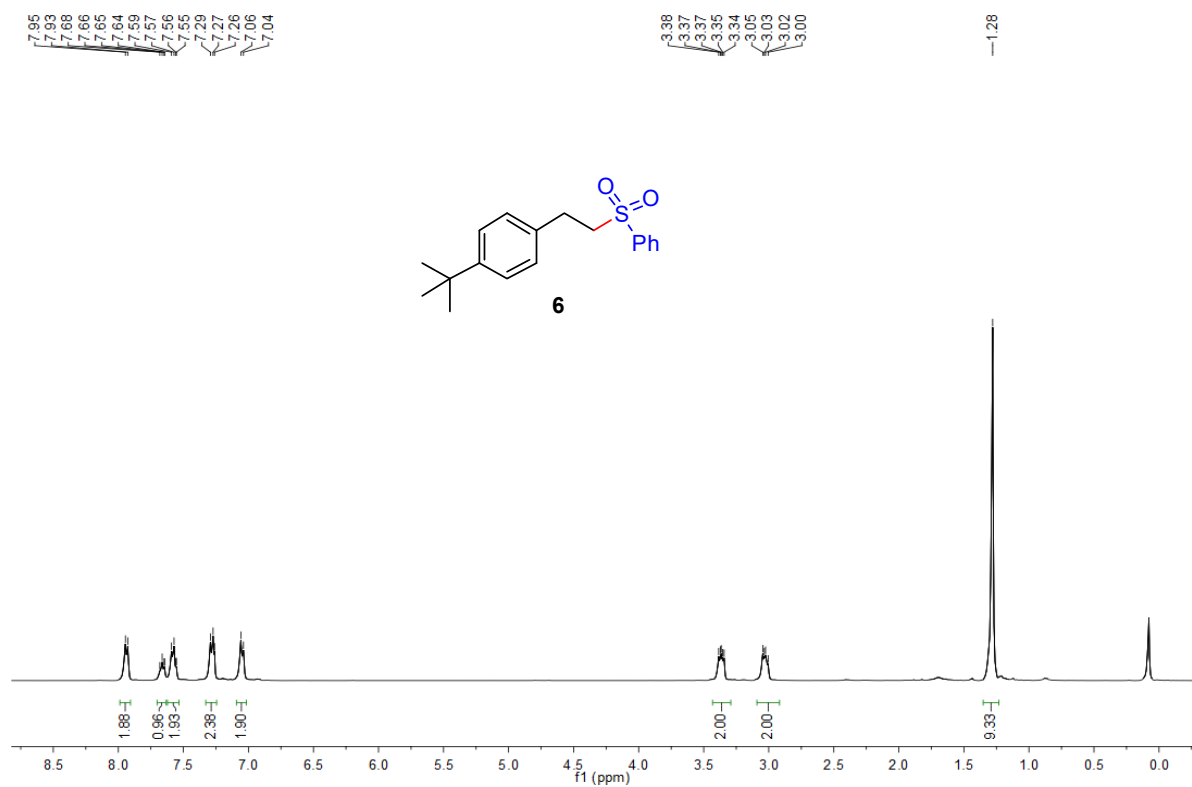
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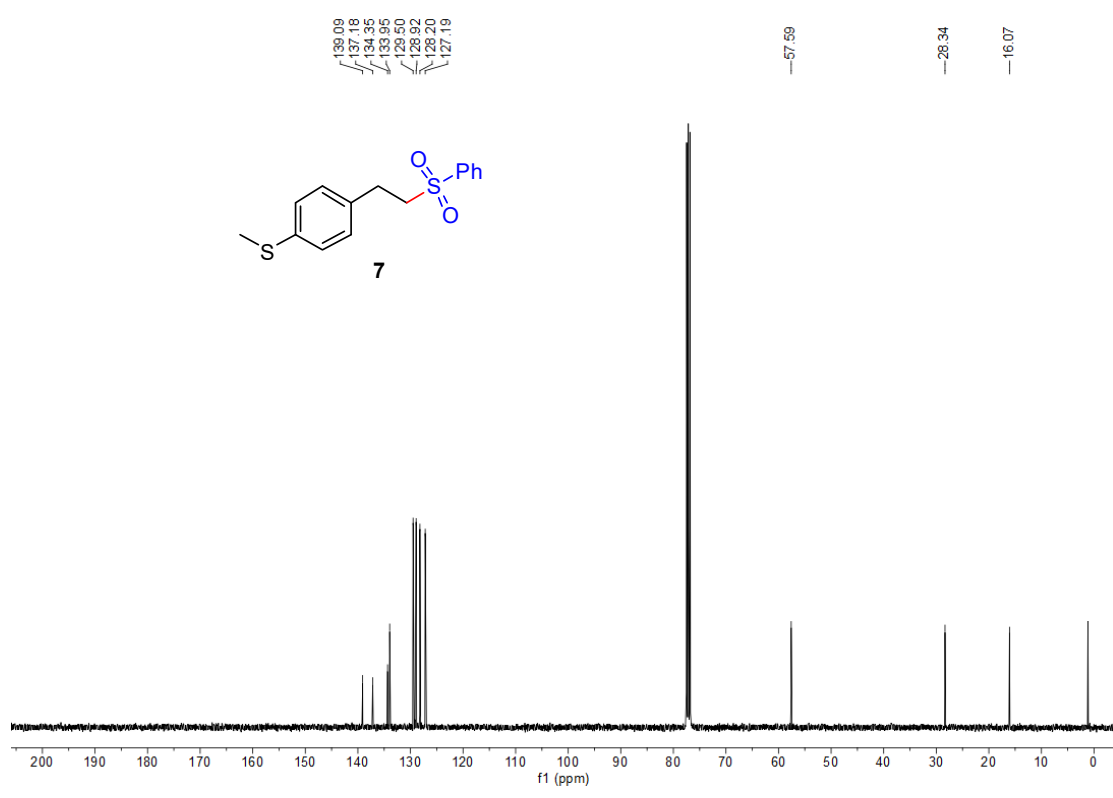
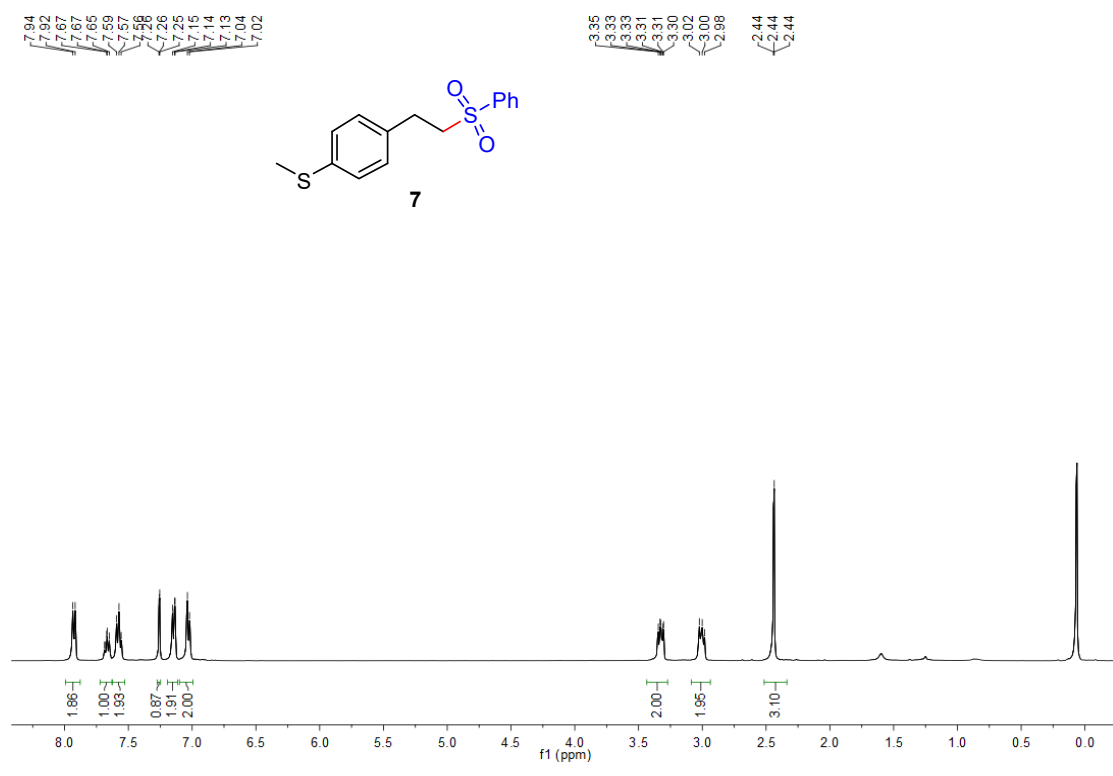
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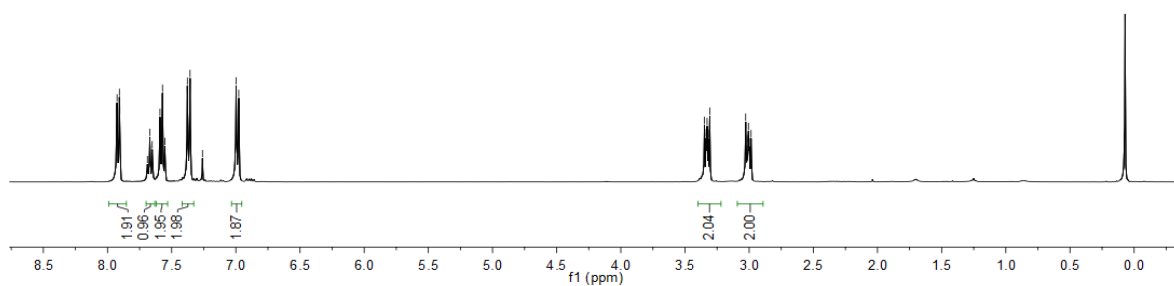
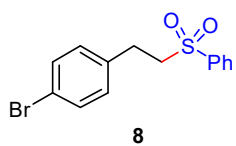






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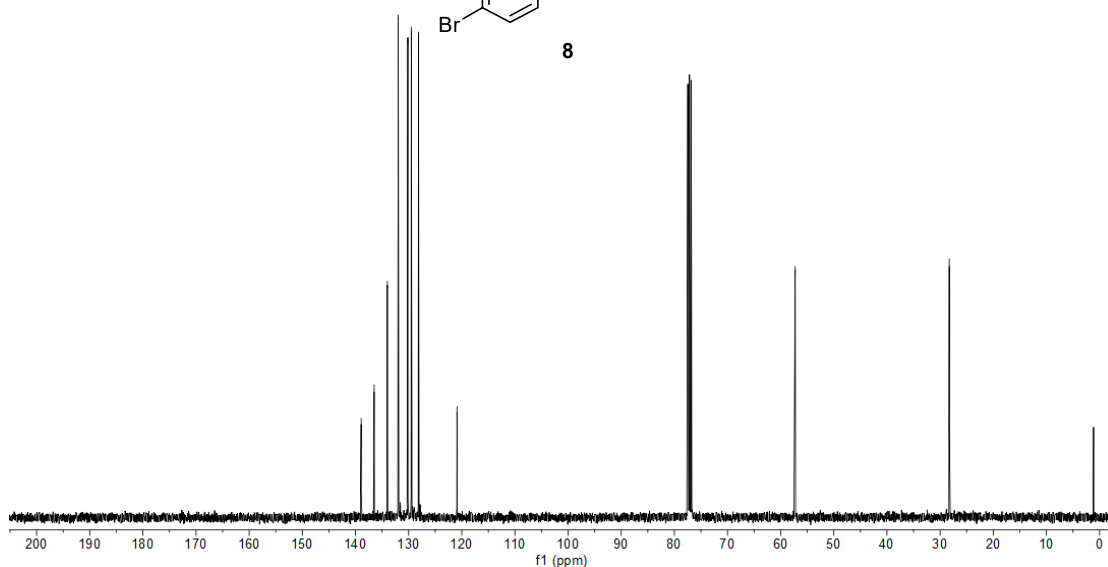
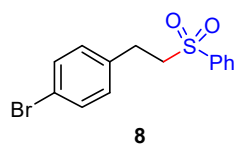
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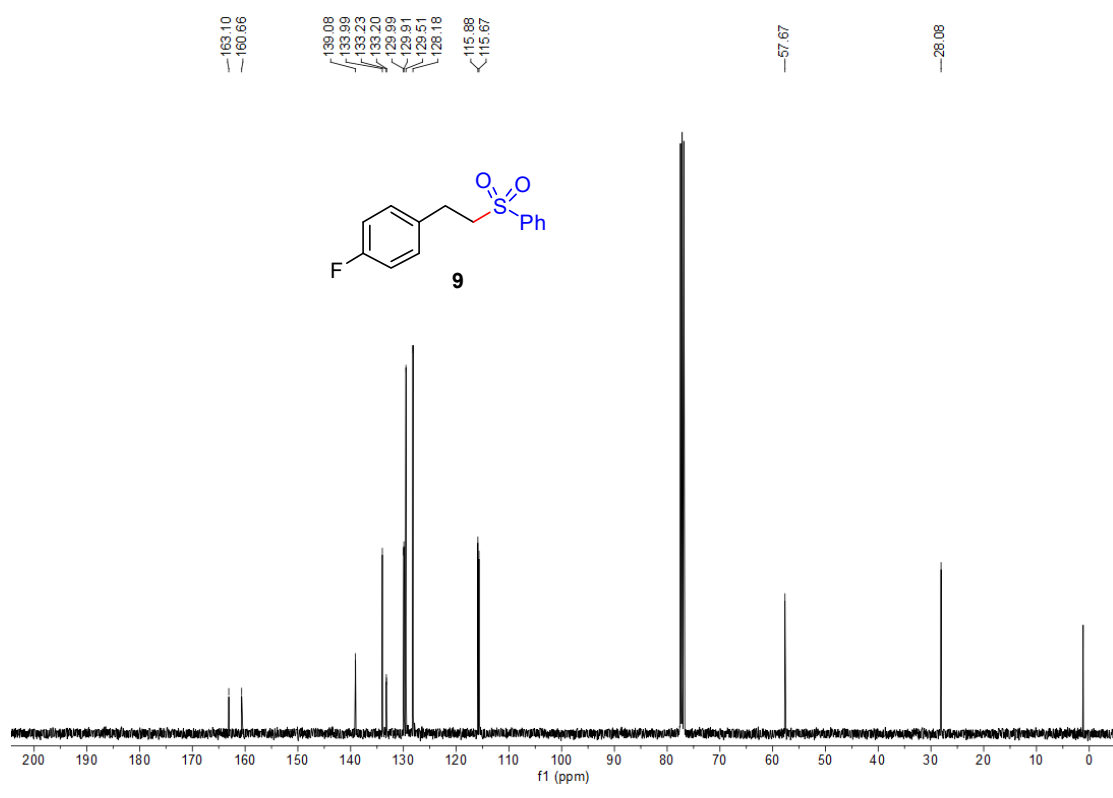
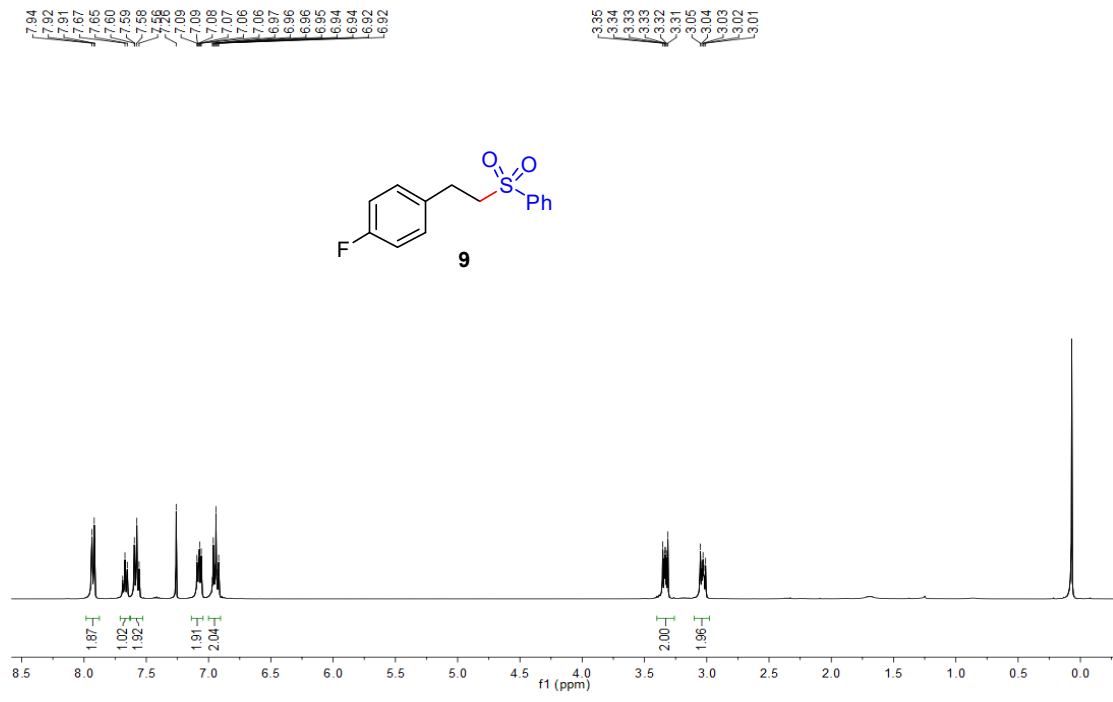


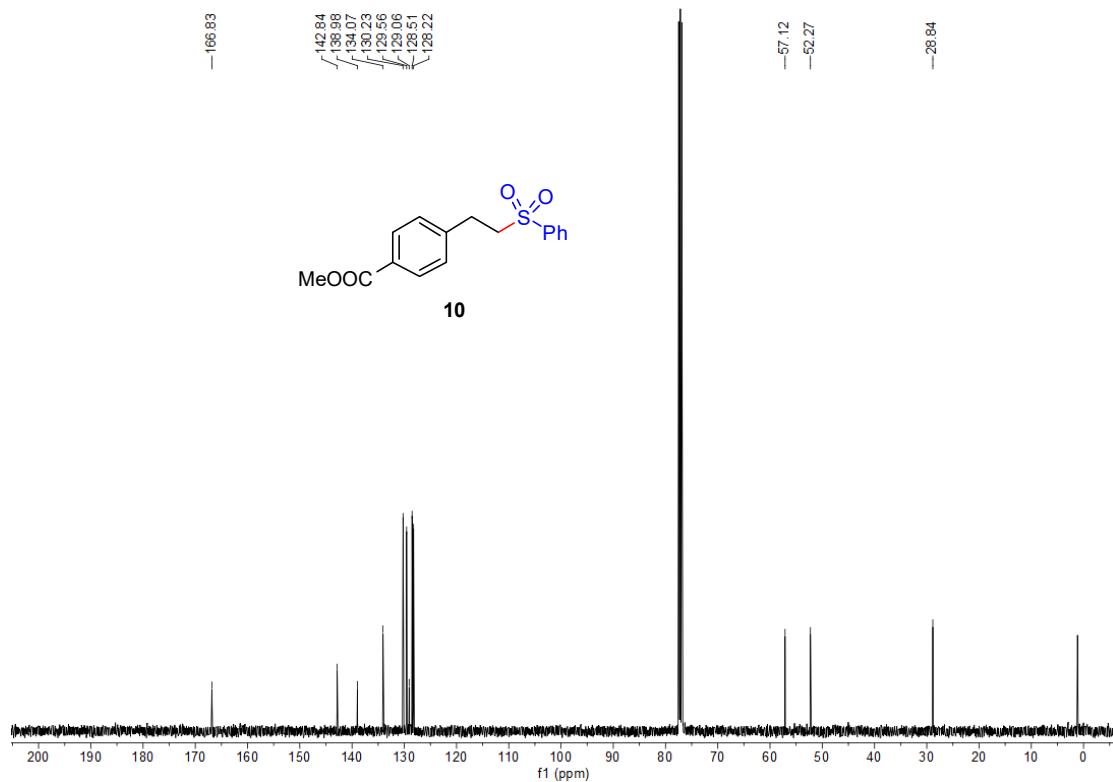
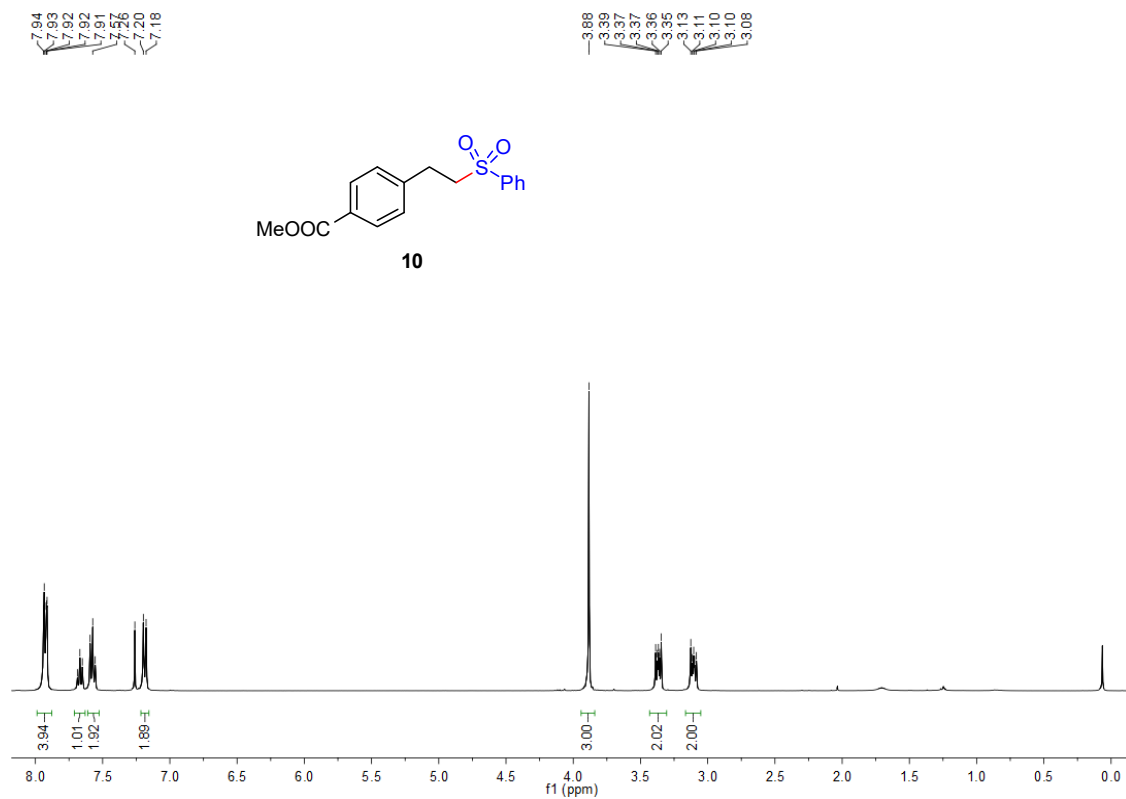
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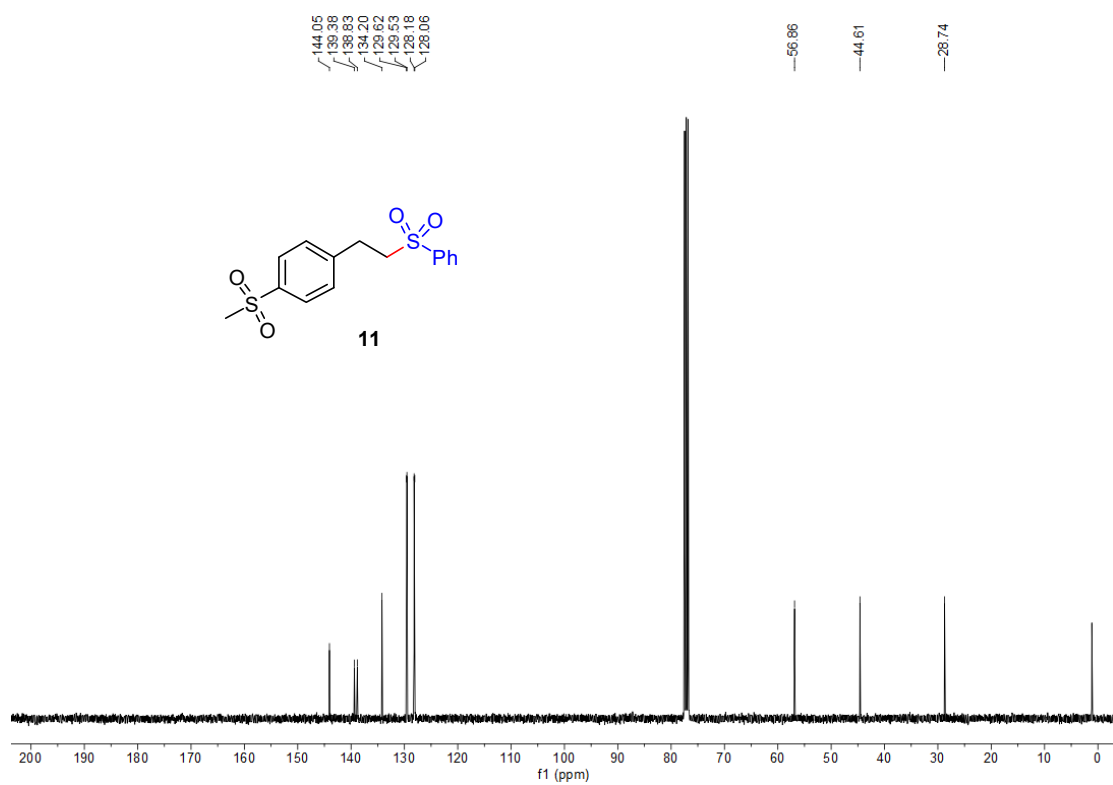
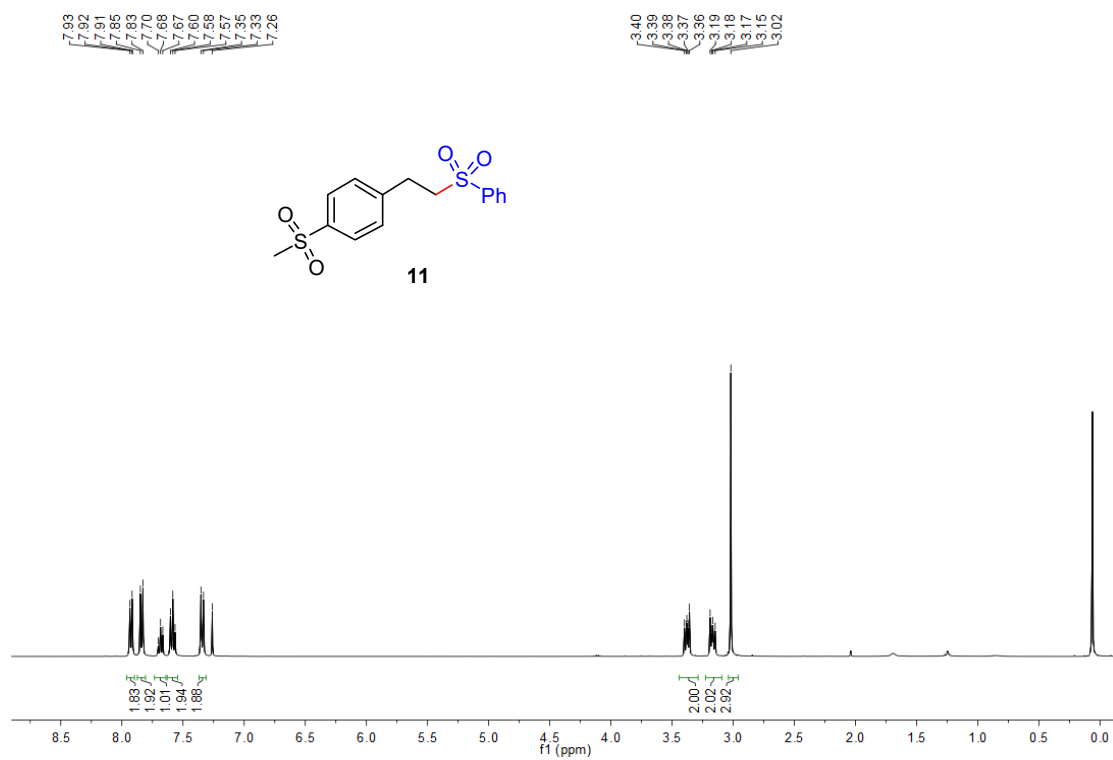
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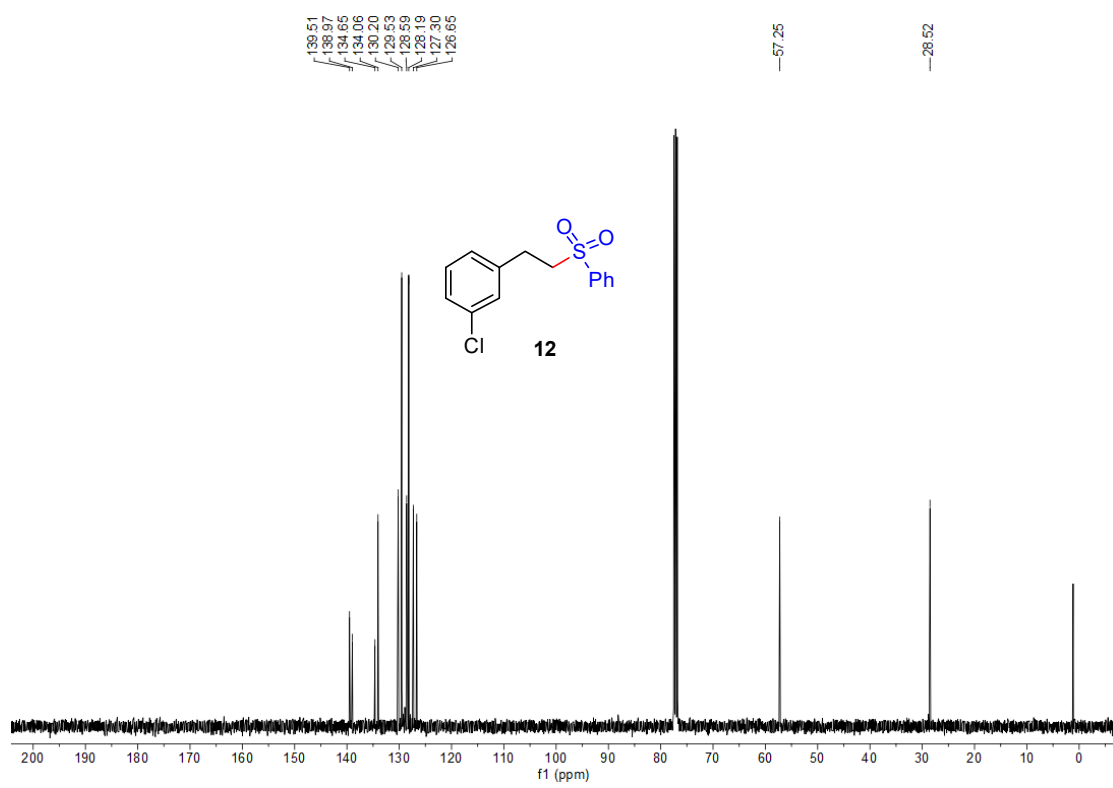
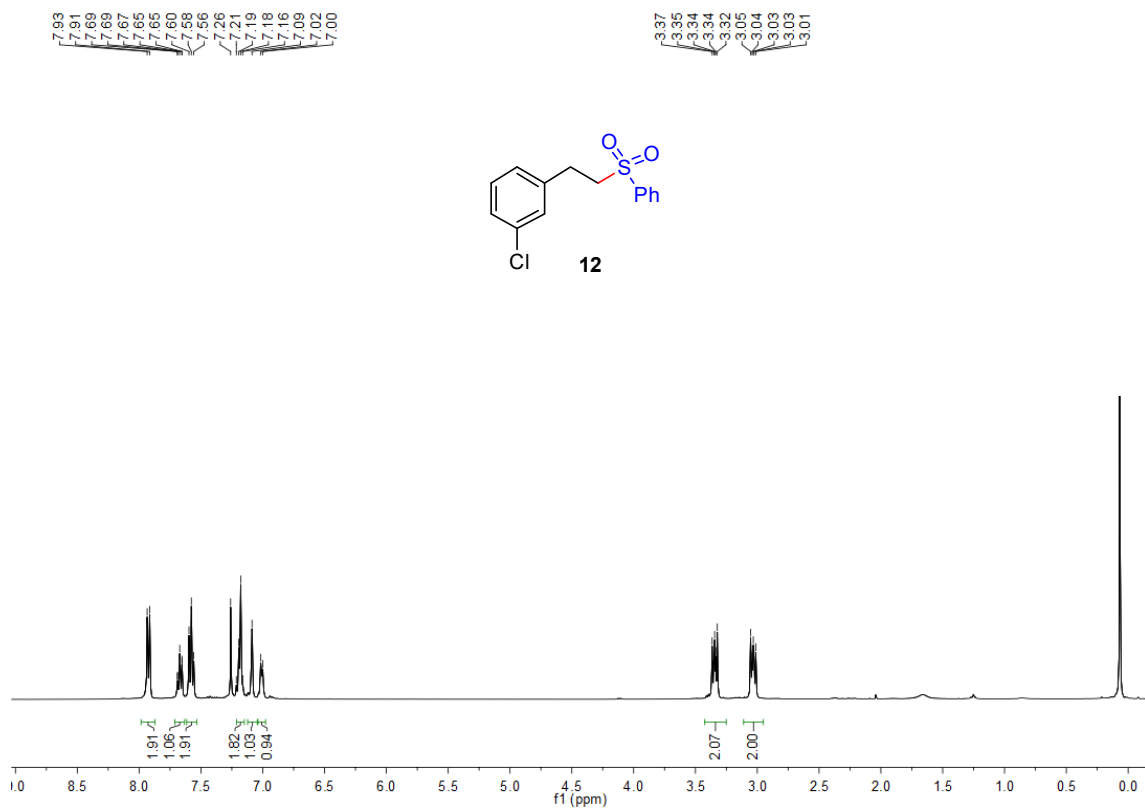
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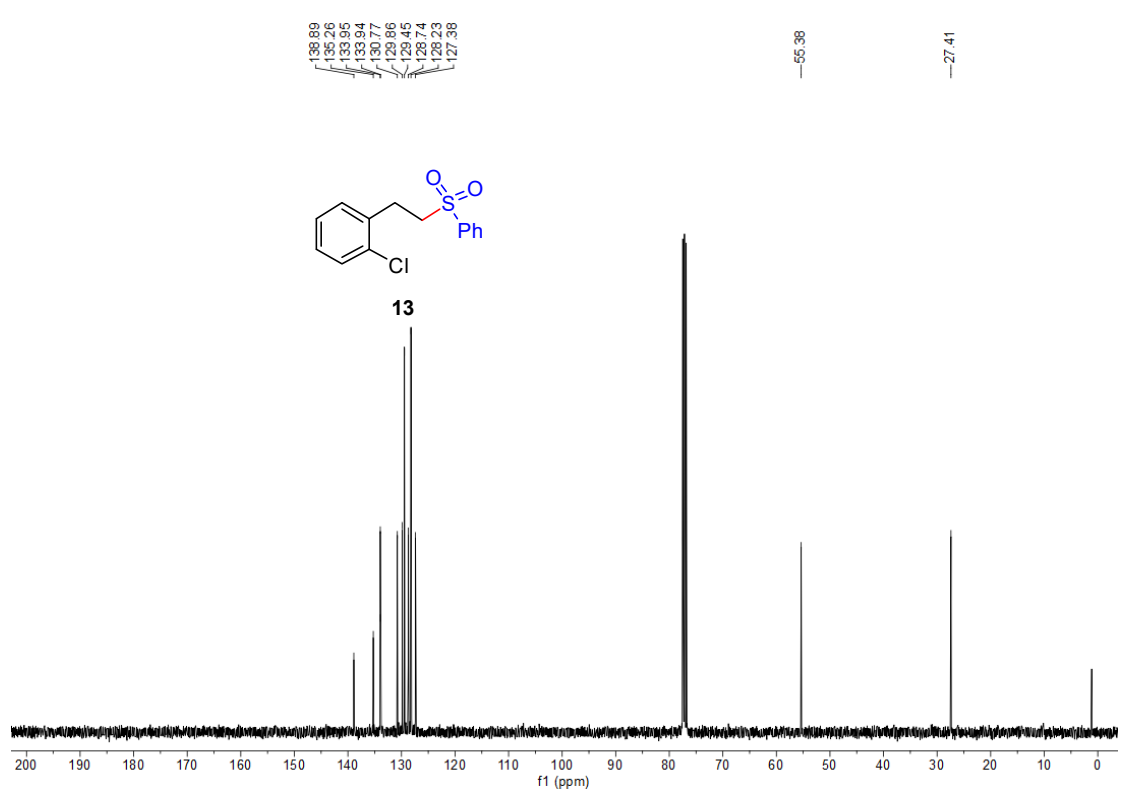
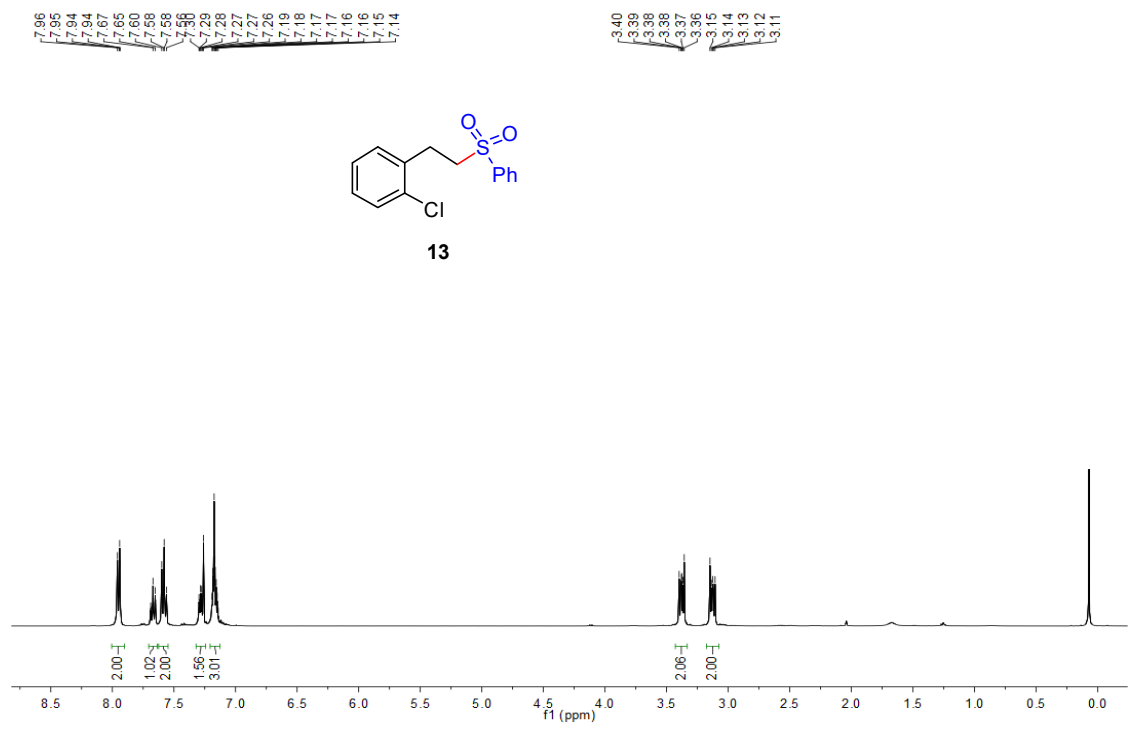


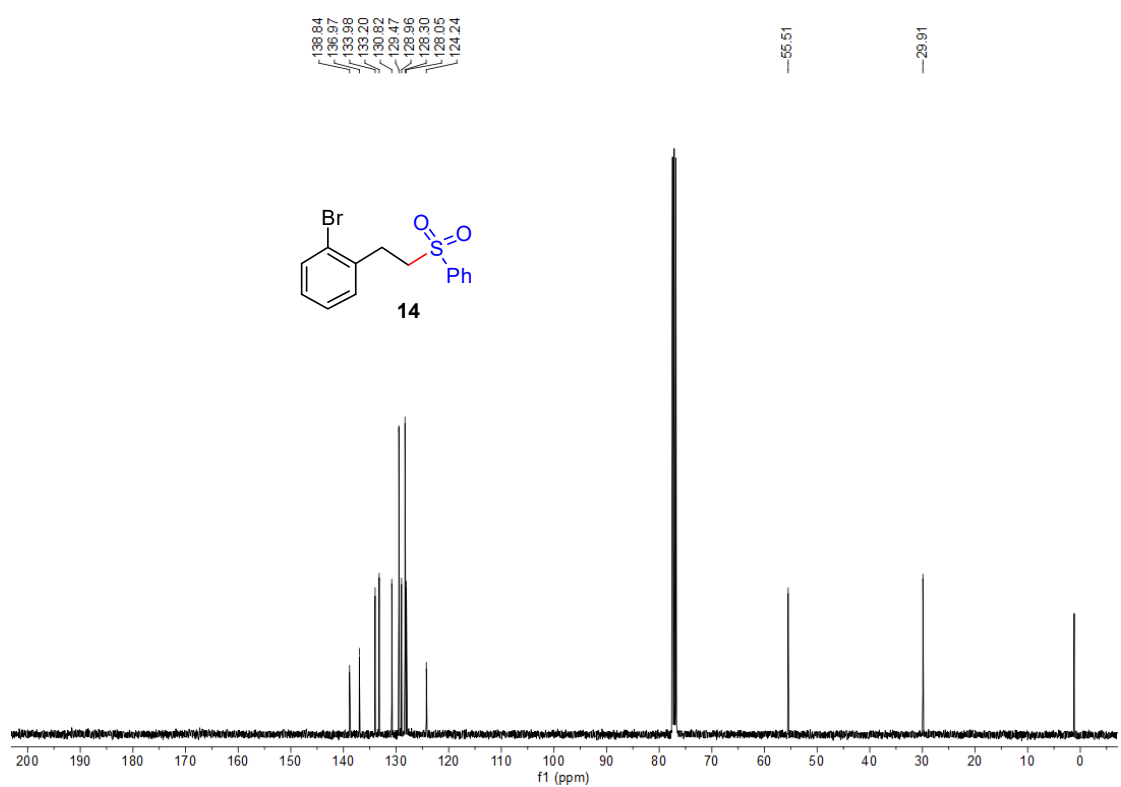
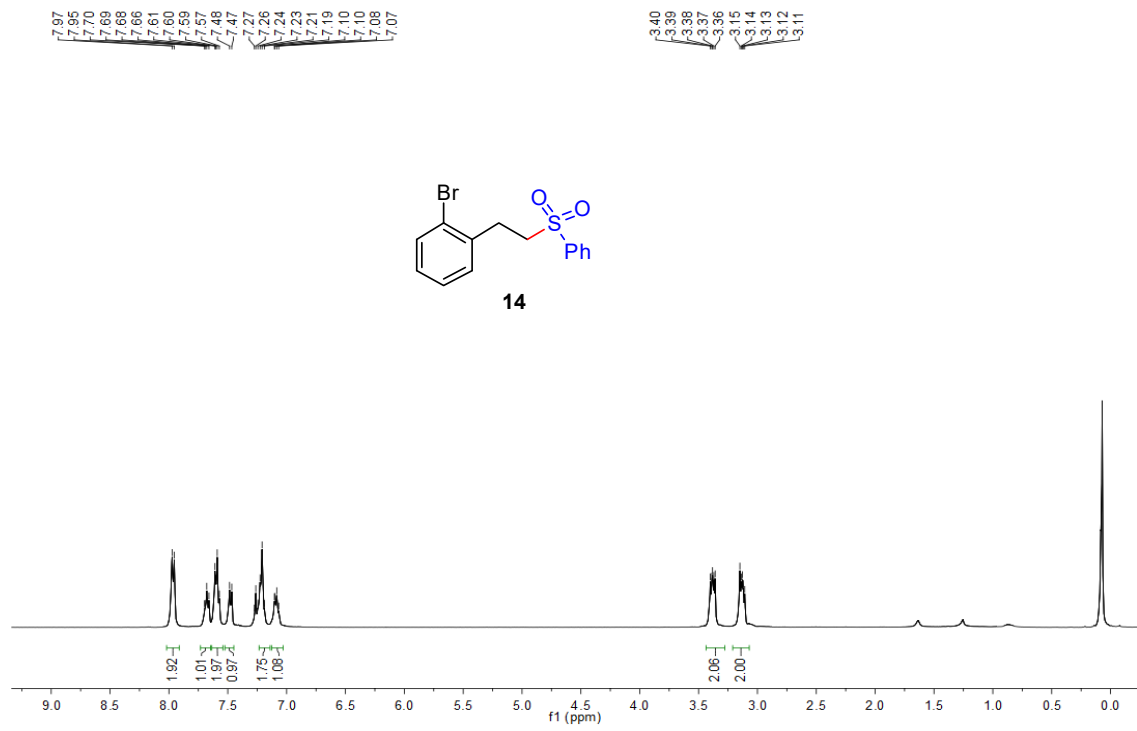






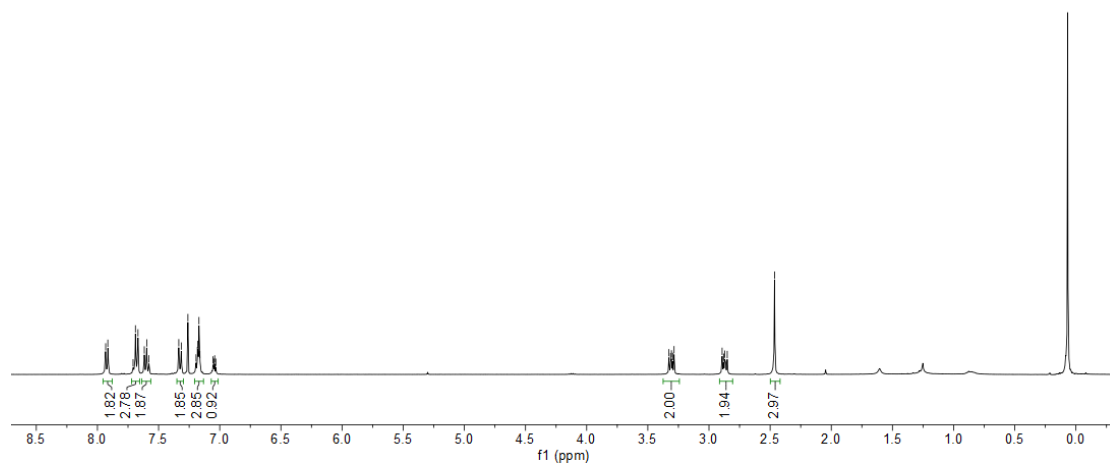
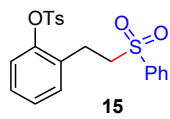






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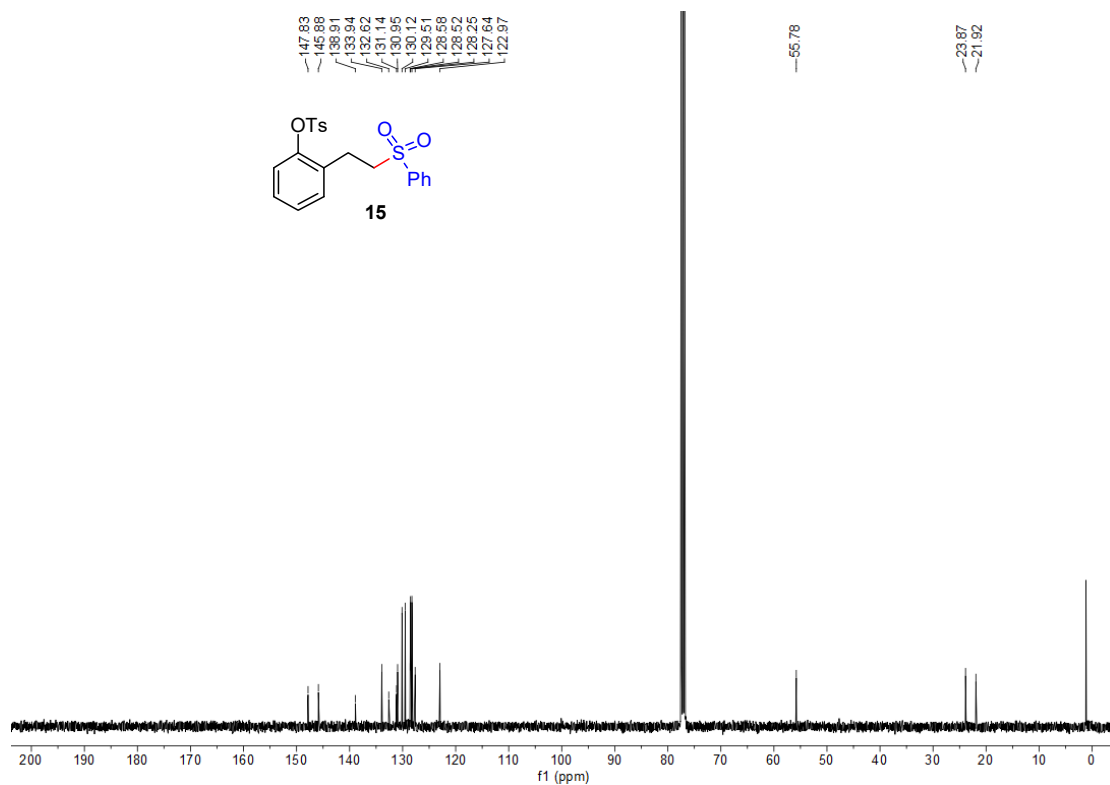
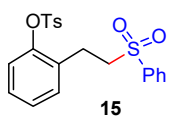
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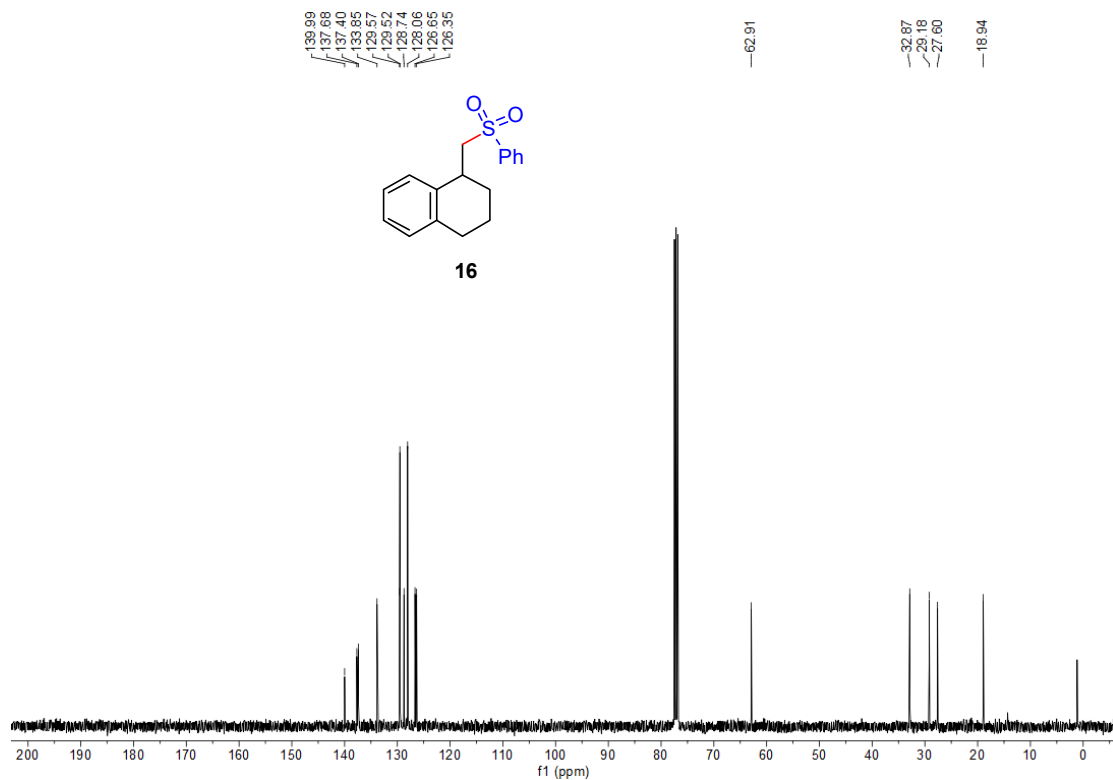
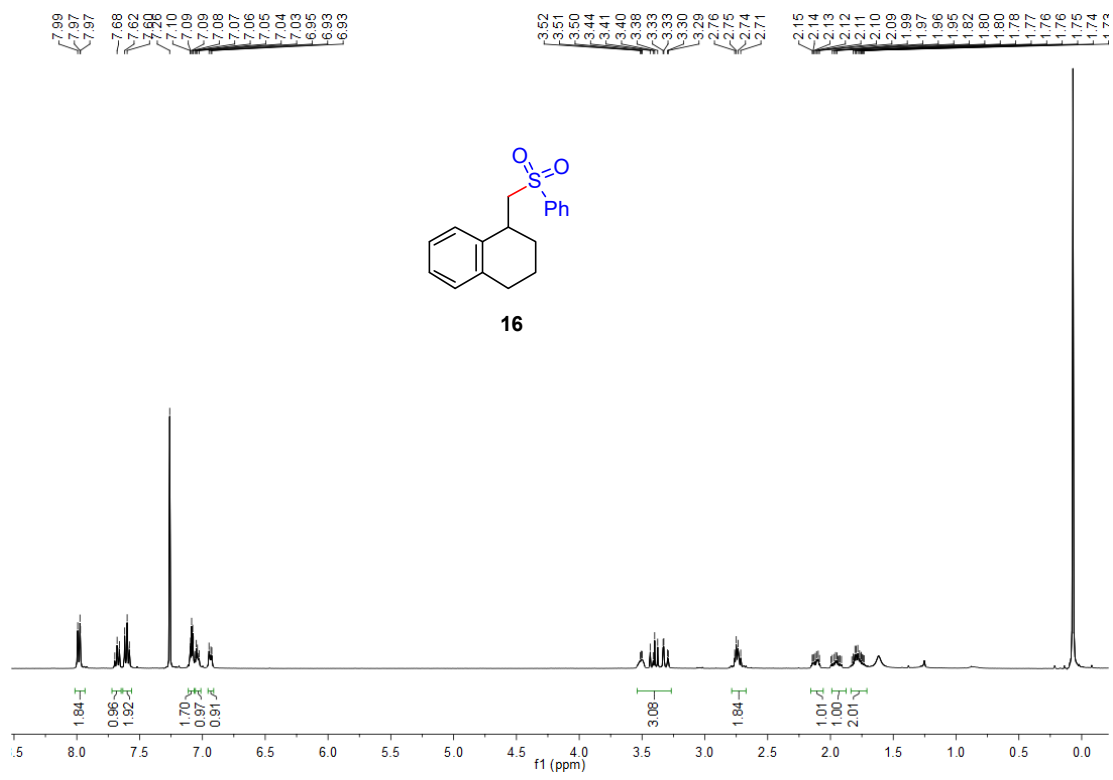


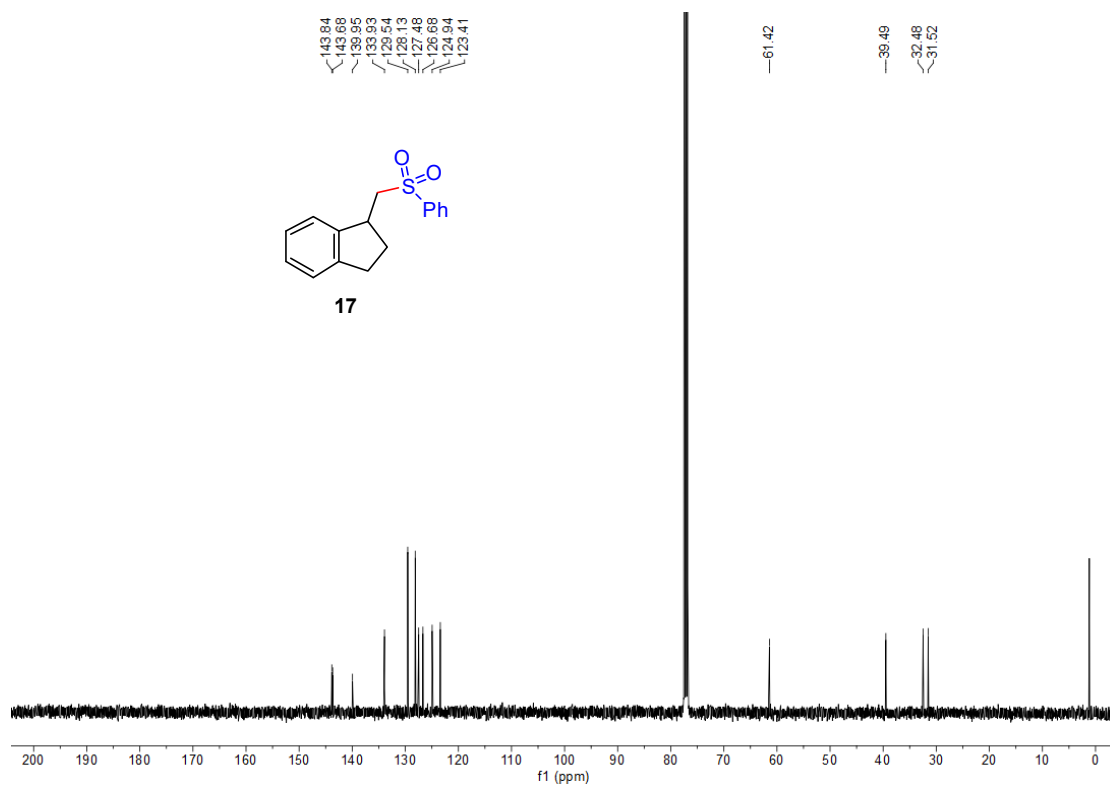
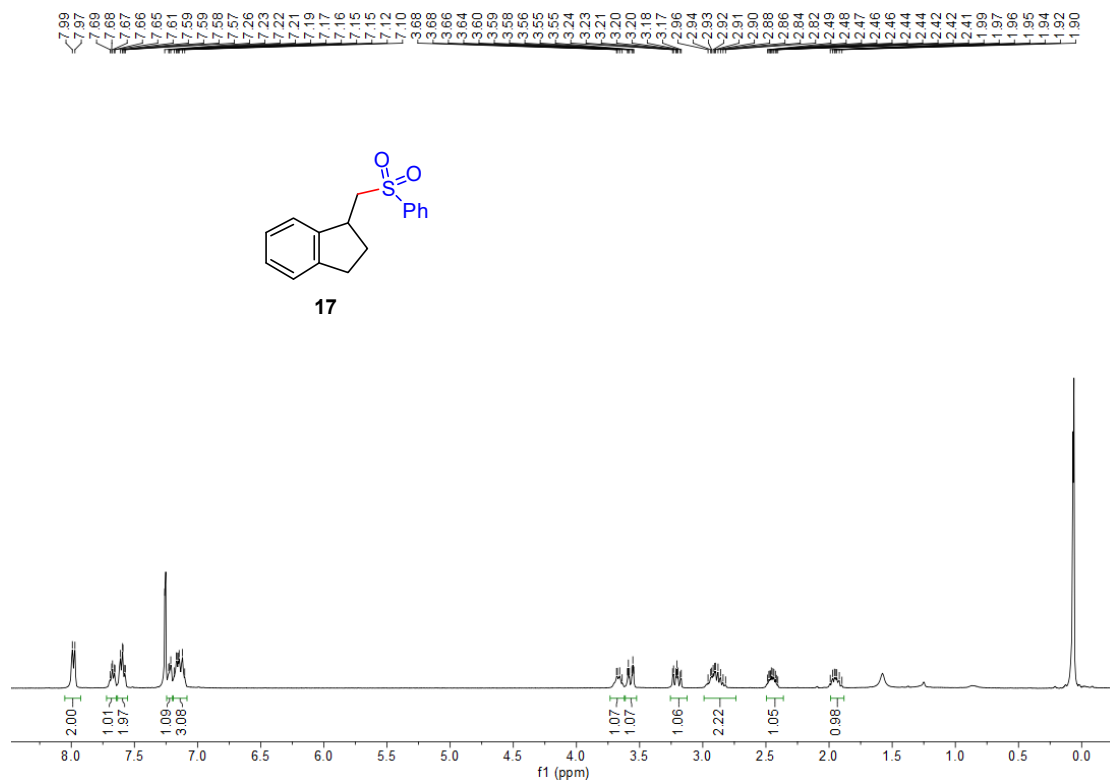
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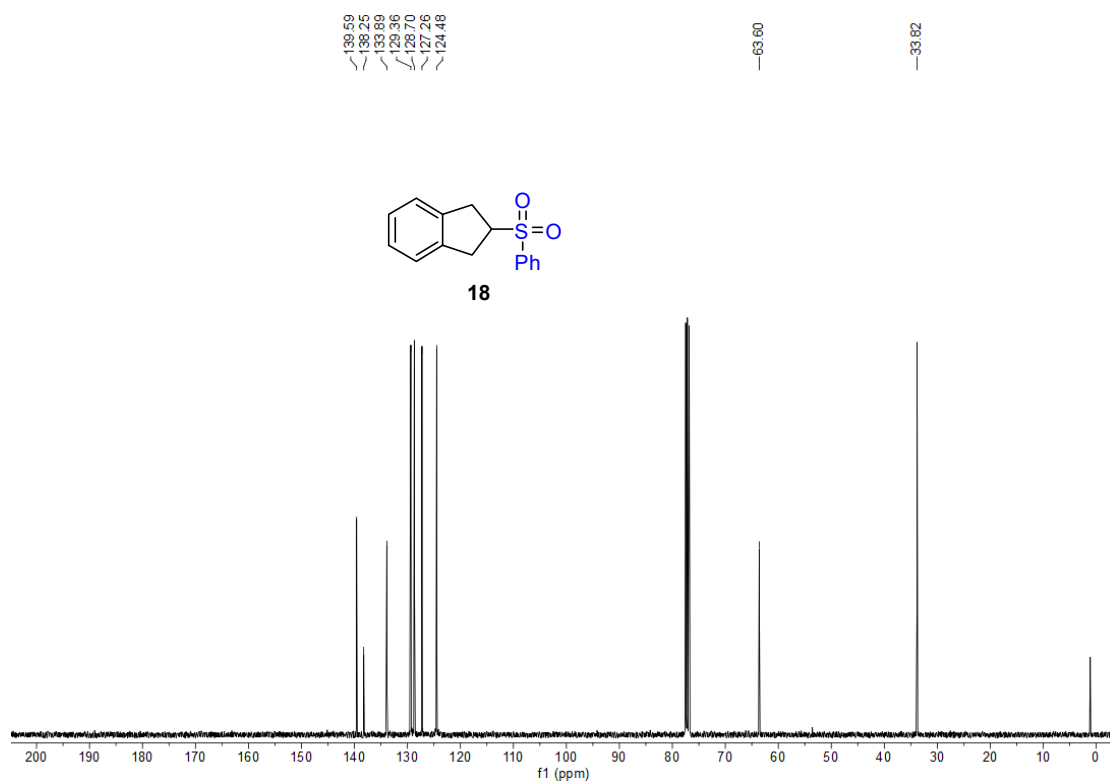
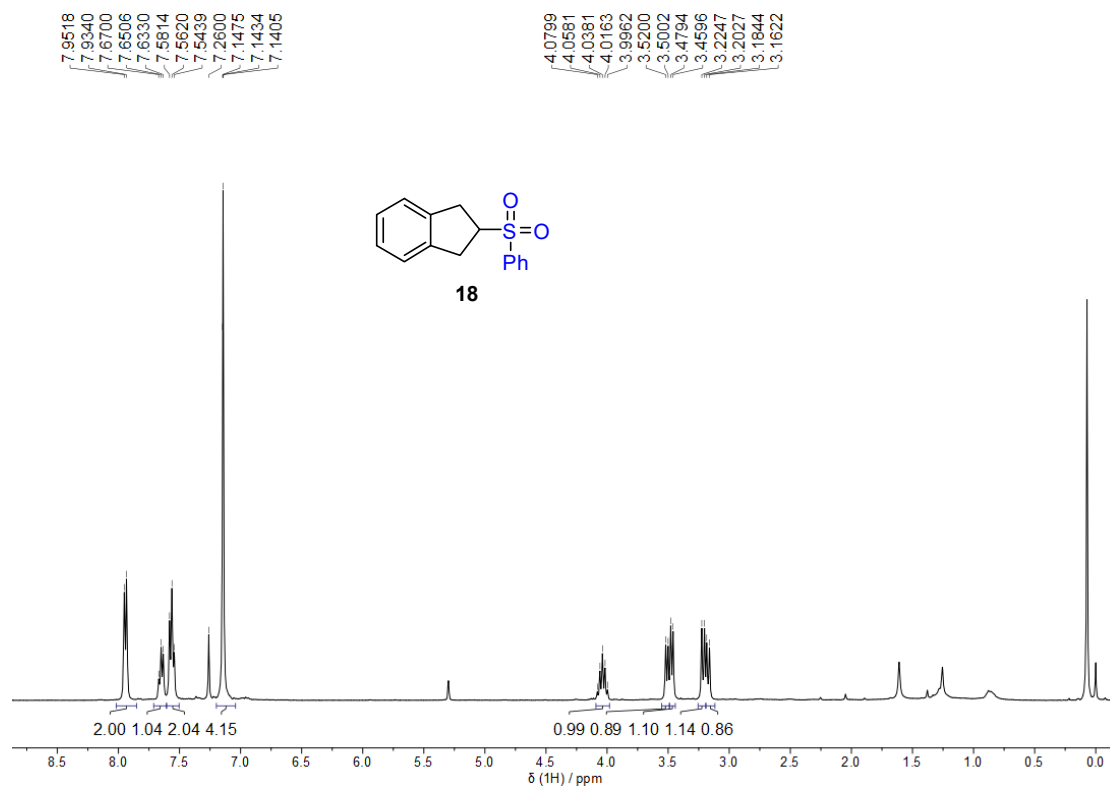
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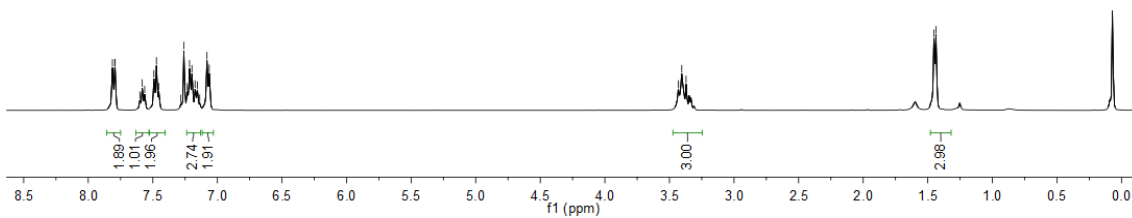
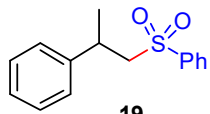




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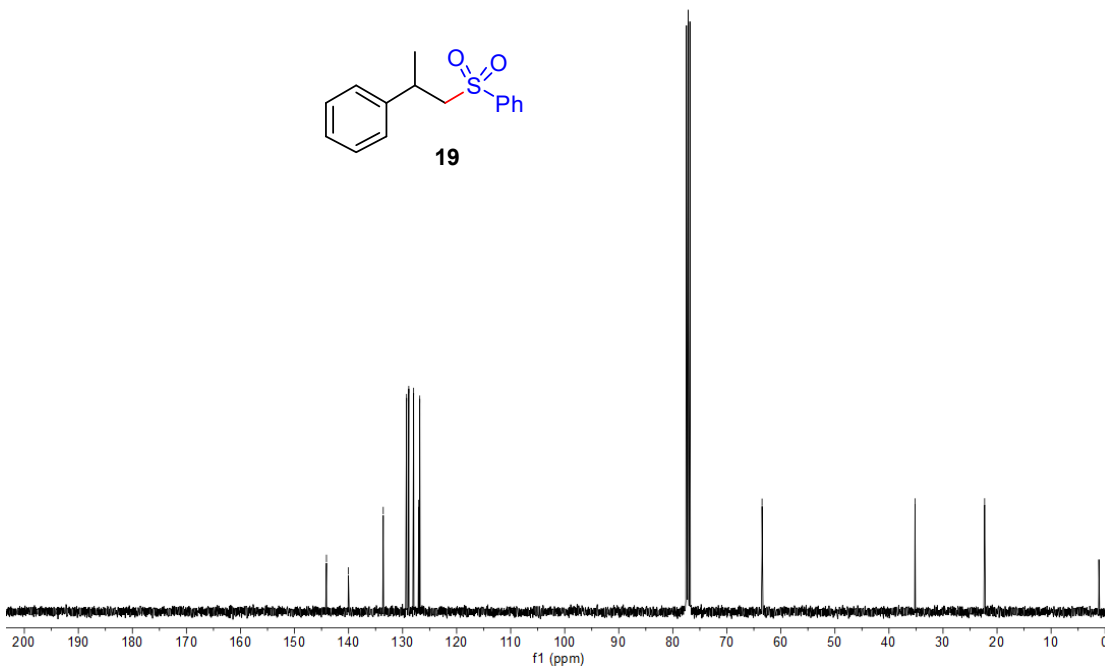
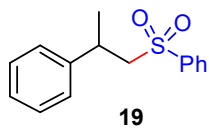


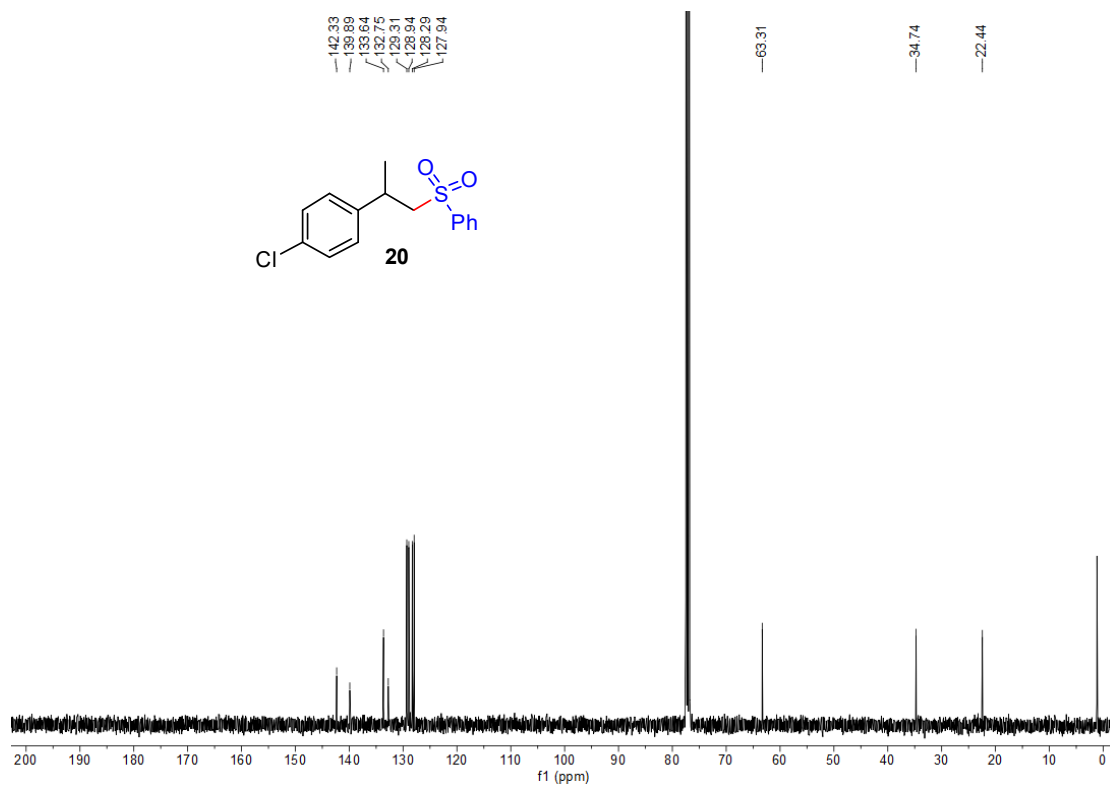
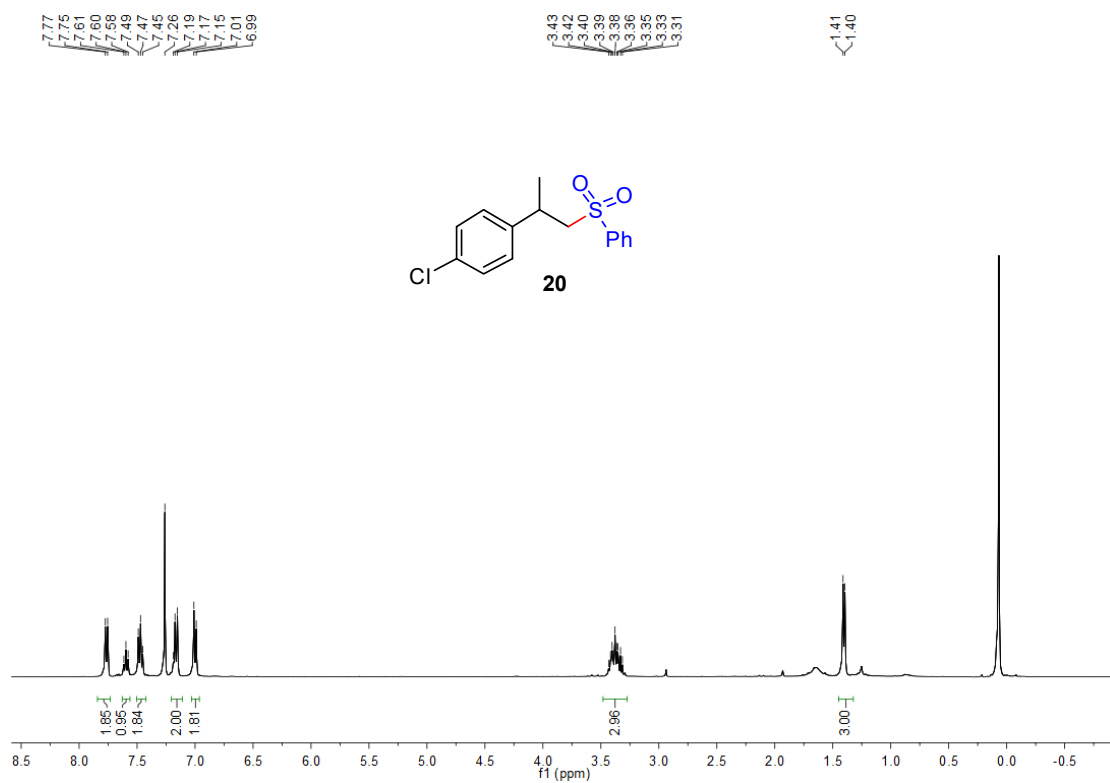
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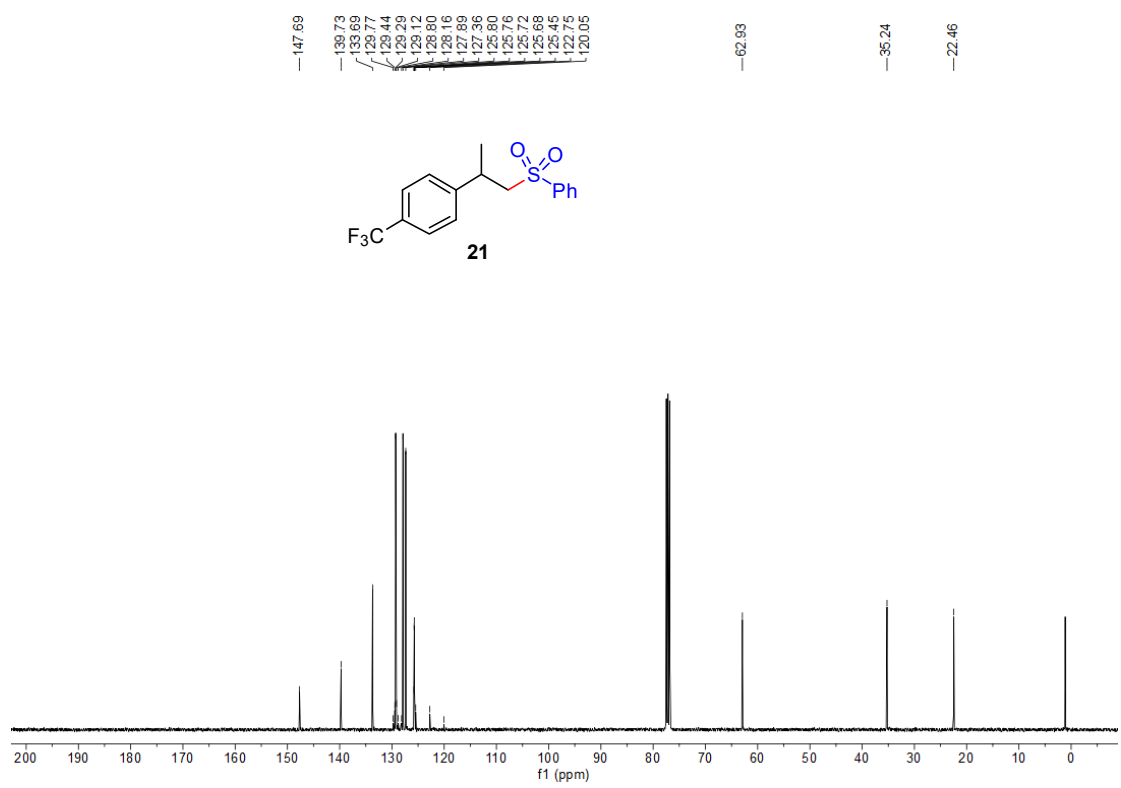
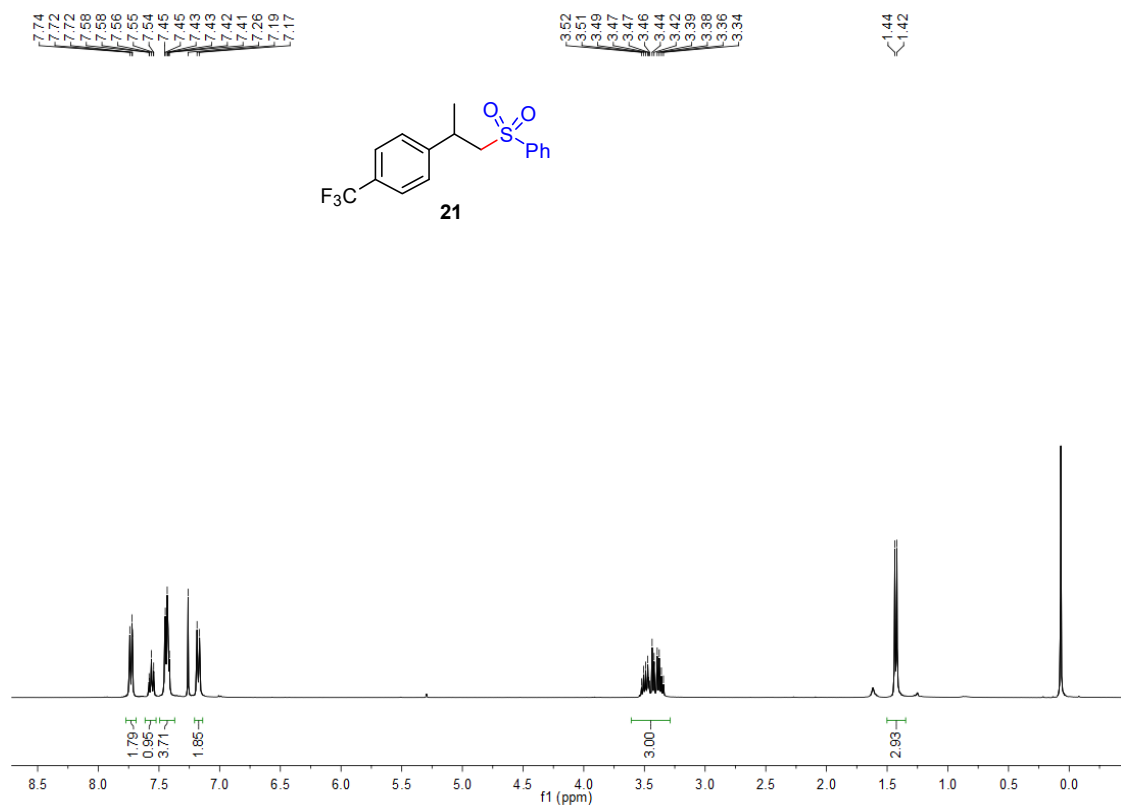
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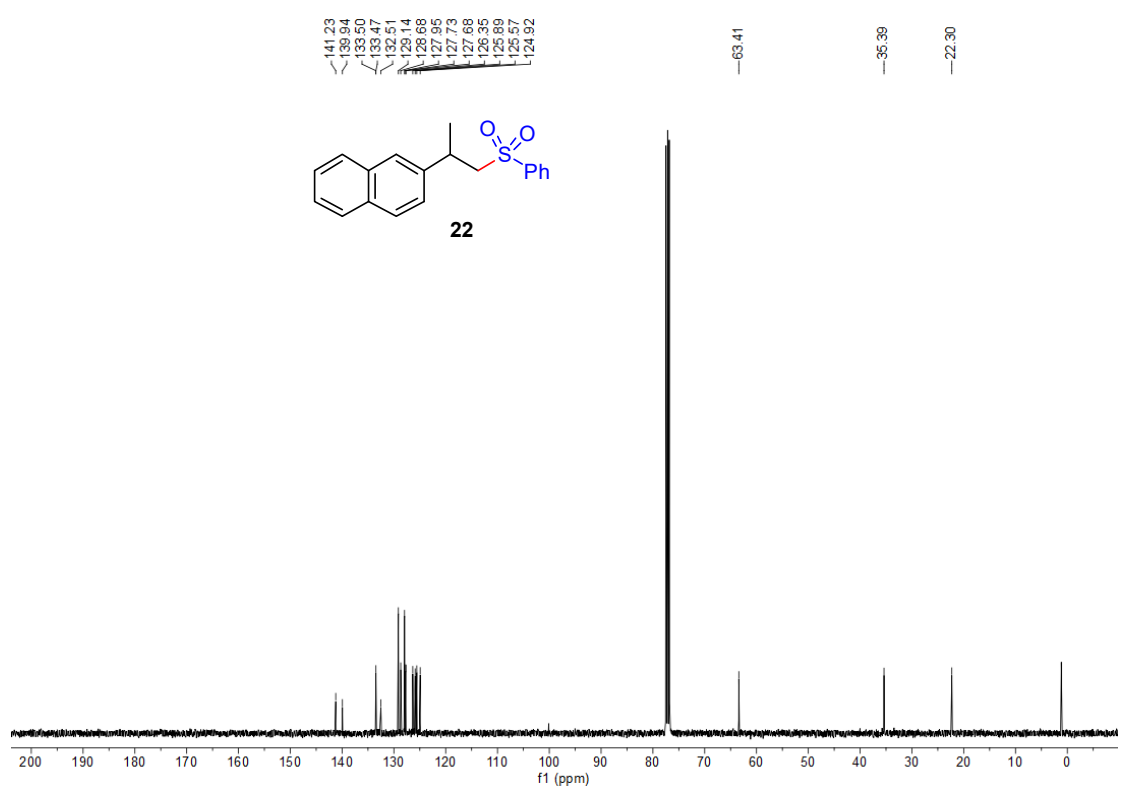
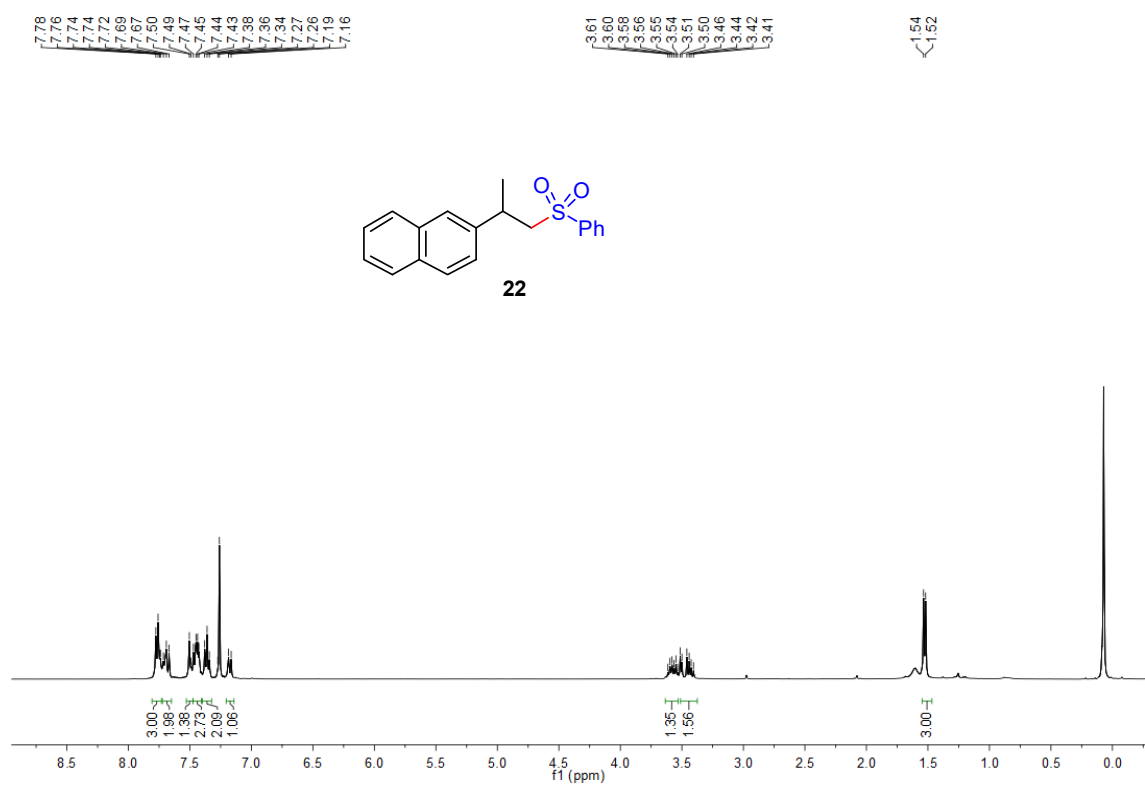
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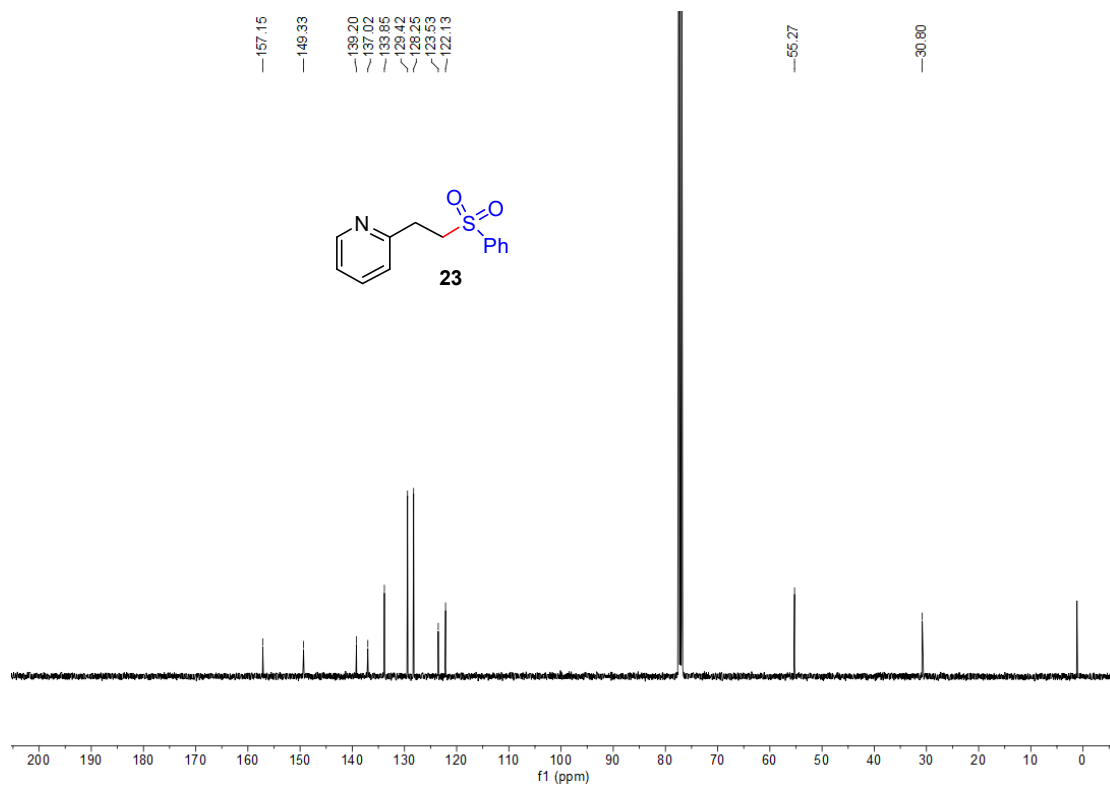
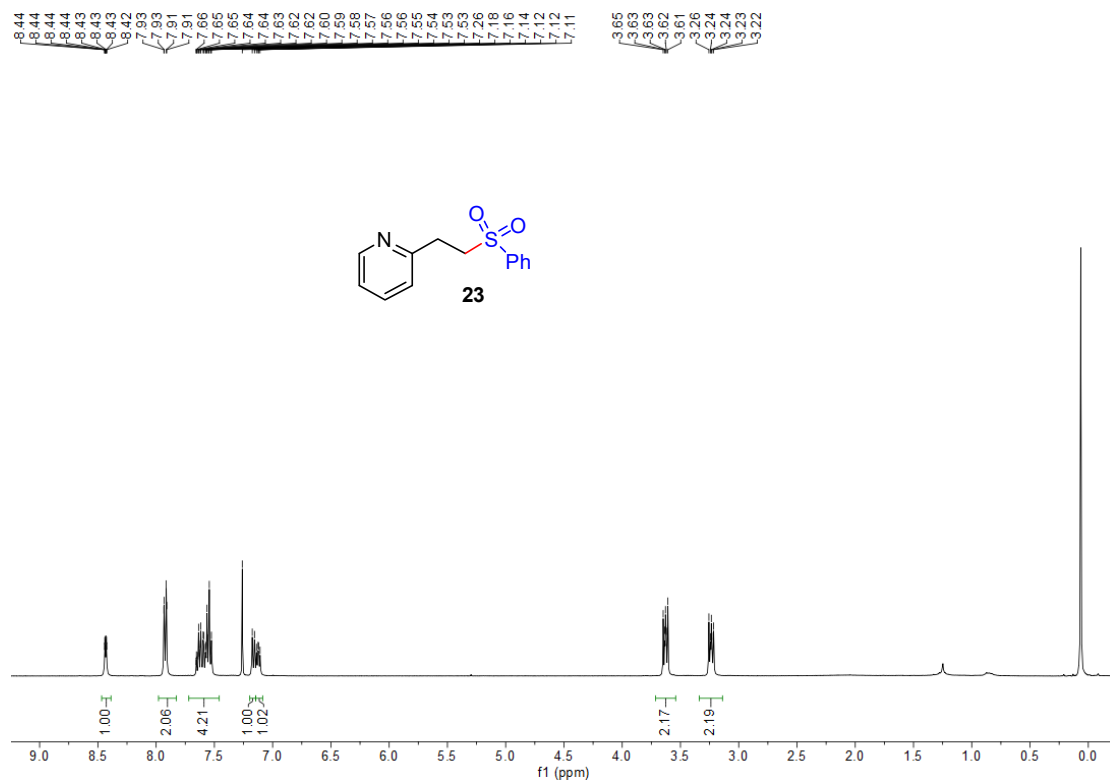
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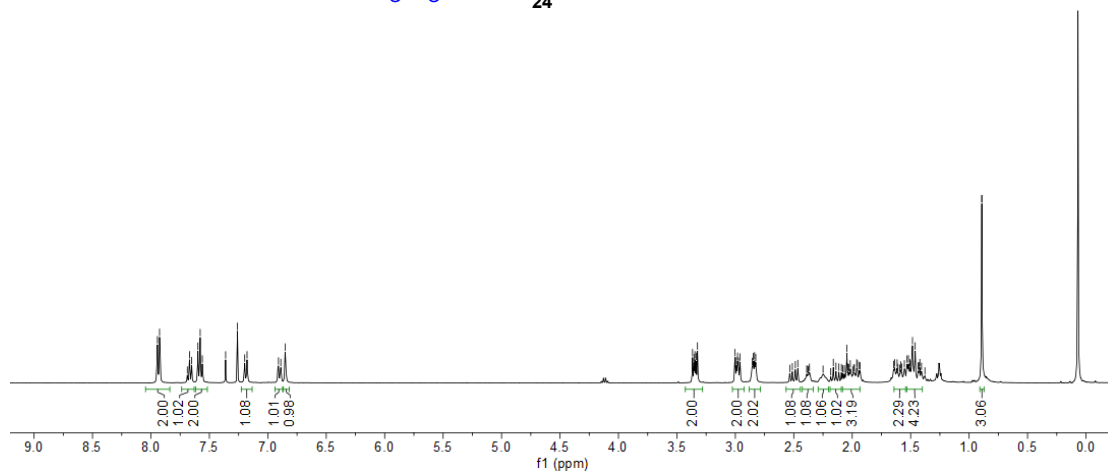
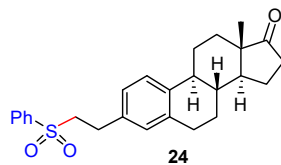








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