- Supporting Information -

Visible-Light Photoredox/Nickel Dual Catalysis for the Cross-Coupling of Sulfinic Acid Salts with Aryl Iodides

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1 General Information

Reactions

Unless otherwise mentioned, all reactions were carried out under an argon atmosphere in flame dried glassware applying standard Schlenk techniques. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR. Irradiation experiments were performed at λ = 445 or 530 nm using commercially available High Power 10 W LED. For each irradiation reaction the light source was placed ≈ 1-2 cm away from the reaction vessels. A custom-made photoreactor box with an incorporated magnetic stirrer was used with 3 interchangeable heatsinks with mounted LEDs arranged around the reactions vessels (Figure S1). The temperature inside the box was maintained below 30 °C (internal reaction temperature ≥30 °C) with an integrated fan. All experiments for the determination of the chemical quantum yield were performed at λ = 436 nm using commercially available High Power 3 W LED.

Figure S1 Pictures of the custom-made photoreactor box used for reaction performed under visible-light irradiation. Reproduced with permission from *Adv. Synth. Catal.* **2018**, *359*, 1308-1319. Copyright 2017 Wiley-VCH.

Chromatography

Column chromatography was performed with Silica 60 (0.04-0.063 mm, 230-400 mesh) and the specified solvent mixture. Thin layer chromatography was performed on aluminum sheets coated with SiO_2 (TLC silica gel 60 F254). The spots were visualized by ultraviolet light.

Solvents

Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. All anhydrous solvents were purchased from

commercial suppliers and stored over MS 4 Å under an atmosphere of argon. Solvents for column chromatography were technical standard.

Materials

All starting materials, which were obtained from commercial sources, were used without further purification. $NiCl_2$·dme and $NiBr_2$·dme was prepared according to the literature.[1] Non-commercially available sulfinic acid sodium salts were prepared from the corresponding sulfonyl chlorides according to Deng et al.[2] 5-(2-Ethoxy-5-iodo-phenyl)-1-methyl-3-propyl-6H-pyrazolo[4,3-d]pyrimidin-7-one (**7**) was prepared according to literature.[3] The two photoredox catalyst $[Ru(bpz)](PF_6)_2$[4] and $Cu(dpp)_2PF_6$[5] were prepared according to Yoon et al. and Ollivier et al., respectively.

SO_2 (sulfur dioxide, purity 3.8) was used directly without further purification. SO_2 is a toxic and corrosive gas! It should be handled with care only in a well-ventilated fume-hood with the necessary precaution! All reactions were performed with a defined amount of liquid SO_2. Therefore, SO_2 was condensed into a dry and Ar-filled Schlenk-flask, cooled to -78 °C. Because of its high heat of evaporation, liquid and cooled SO_2 can be easily handled, measured and transferred with syringes. For small-scale reactions, we recommend this procedure.

NMR spectroscopy

Proton nuclear magnetic resonance spectra (^{1}H NMR), carbon spectra (^{13}C NMR) and fluorine spectra (^{19}F NMR) were recorded at 400 MHz, 300 MHz, 250 MHz (^{1}H), 151 MHz, 126 MHz, 75 MHz (^{13}C), 471 MHz, 282 MHz (^{19}F), respectively. Chemical shifts are reported as δ - values relative to the residual $CDCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C). Coupling constants (J) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartett; m = multiplet; dd = doublet of doublets; dt = doublet of triplets; tt = triplet of triplets and ddd= doublet of doublet of doublet.

Melting points

Melting points are reported uncorrected. The solvent given in brackets after the melting point is the last solvent the compound was treated with (e.g. for transfer of the compound into a smaller flask).

Mass spectrometry

Mass spectra (MS) were measured using electrospray ionization (ESI) techniques. High resolution mass spectra (HRMS) were measured using matrix-assisted laser desorption/ionization (MALDI) techniques.

Infrared spectroscopy

Infrared spectra (IR) of neat substances were recorded on a FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm^{-1}) and classified in weak (w), medium (m) and strong (s).

Fluorescence spectroscopy

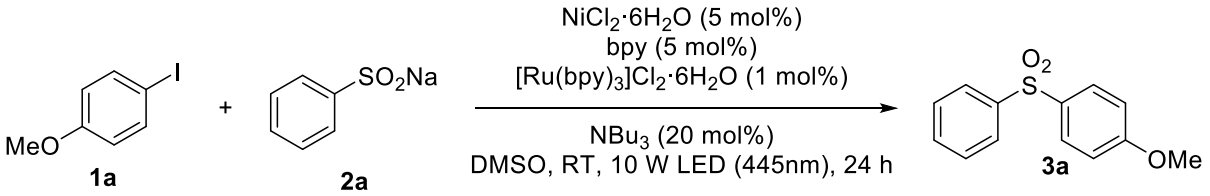
Fluorescence measurements were performed at 20 °C. The excitation wavelength was λ = 436 nm. The emission was recorded at λ = 542 nm.

UV-Vis spectroscopy

UV-Vis spectra were recorded at 20 °C.

2 Further Optimization data

Table SI1: Extended optimization data for the formation of sulfone **3a** from aryl iodide **1a** and sulfinate **2a** via photoredox/nickel catalysis.[a]



Entry	Variation from standard conditions	Yield (%)[b]
1	None	87 (85)[c]
2	With $Ru(bpz)_3(PF_6)_2$ instead of $Ru(bpy)_3Cl_2{\cdot}6H_2O$	trace
3	With Eosin Y[d] instead of $Ru(bpy)_3Cl_2{\cdot}6H_2O$	12
4	With $Ir(ppy)_3$ instead of $Ru(bpy)_3Cl_2{\cdot}6H_2O$	32
5	With $Cu(dpp)_2PF_6$ instead of $Ru(bpy)_3Cl_2{\cdot}6H_2O$	trace
6	With $Ir(dtbbpy)(ppy)_2PF_6$ instead of $Ru(bpy)_3Cl_2{\cdot}6H_2O$	60
7	With $NiBr_2{\cdot}3H_2O$ instead of $NiCl_2{\cdot}6H_2O$	84
8	With $NiBr_2{\cdot}dme$ instead of $NiCl_2{\cdot}6H_2O$	85
9	With $NiCl_2{\cdot}dme$ instead of $NiCl_2{\cdot}6H_2O$	86
10	With $[Ni(PPh_3)_2(1\text{-naphthyl})Br]$ instead of $NiCl_2{\cdot}6H_2O$	17
11	With dtbbpy instead of bpy	75
12	With phen instead of bpy	40
13	With PPh_3 instead of bpy	56
14	With $t Bu_3P{\cdot}HBF_4$ instead of bpy	31

15	With dppe instead of bpy	5
16	With IMes·HCl instead of bpy	22
17	With DMF instead of DMSO	40
18	With NMP instead of DMSO	31
19	Not degassed	38
20	Without NBu_3	58
21	With NEt_3 instead of NBu_3	67
22	With DABCO instead of NBu_3	73
23	With 1.5 eq. of **2a**	64
24	Without bpy	58
25	Without $NiCl_2{\cdot}6H_2O$	trace
26	Without $Ru(bpy)_3Cl_2{\cdot}6H_2O$	11
27	Without irradiation	-

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), $NiCl_2{\cdot}6H_2O$ (0.025 mmol), bpy (0.025 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.005 mmol), degased DMSO (2 mL), room temperature, irradiation with blue LED (10 W LED, 445 nm). [b]Yield determined by GC using biphenyl as internal standard. [c]Isolated yield. [d]Irradiation with green LED (10 W LED, 520 nm).

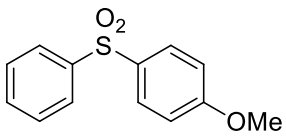
3 General procedures

TP1: Typical procedure for the synthesis of Sulfones from (hetero)aryl iodides and sodium sulfinates via photoredox/nickel catalysis

A 10 mL tube was charged with a stirring bar, $NiCl_2 \cdot 6\ H_2O$ (6 mg, 5.0 mol%), 2,2'-bipyridine (4 mg, 5.0 mol%), $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ (4 mg, 1.0 mol%), sulfinate (1 mmol, 2.0 eq.) and aryl iodide (0.5 mmol, 1.0 eq.). DMSO (2mL) and afterwards NBu_3 (24 µL, 19 mg, 20 mol%) were added. Then the tube was closed with a rubber septum and sparged with nitrogen for 5 min. The resulting mixture was irradiated (445 nm, 10 W LED) for 24 h. Then H_2O (15 mL) and sat. aq. NaCl (15 mL) were added and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with sat. aq. NH_4Cl (25 mL), sat. aq. NaCl (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (*n*-hexane/EtOAc) afforded the analytically pure product.

4 Experimental procedures and Analytical Data

Preparation of 4-Methoxyphenylphenylsulfone (3a)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3a** as a white solid (105 mg, 85%). On a 2 mmol scale **3a** was obtained as a white solid (440 mg, 89%).

3a was also prepared starting from benzene (**11**) via the corresponding lithium sulfinate (**10b**):

A dry and Ar-flushed Schlenk-tube equipped with a magnetic stirrer and a rubber septum was charged with *n*-BuLi (0.44 mL, 2.40 M in hexane, 1.05 mmol) and TMEDA (0.15 mL, 1.0 mmol). Benzene (**11**, 89 µL, 1.0 mmol) was added at 25 °C and the reaction stirred for 3 h at this temperature. The resulting mixture was cooled to –40 °C and liquid SO_2 (0.22 mL, 5 mmol) was added and the reaction mixture was allowed to warm to room temperature over 90 min. Then solvents and excess SO_2 were removed under reduced pressure (**Caution!** Excess sulfur dioxide should be collected in a cooled trap and quenched with aq. NaOH) to afford the crude lithium benzenesulfinate (**10b**) as an off-white solid. This solid was suspended in EtOAc (7.5 mL) by stirring for 15 min. Stirring was discontinued and the solids were allowed to settle down. Then the supernatant liquid was taken of carefully and discarded. This step was repeated three times. Afterwards the remaining solid was dried under high vakuum (1 mbar) for 2 h. This procedure affords sulfinate **10b** sufficiently pure for the following transformation. A quantitative formation of the sulfinate is assumed (≡ 1 mmol **10b**).

$NiCl_2 \cdot 6\ H_2O$ (6 mg, 5.0 mol%), 2,2'-bipyridine (4 mg, 5.0 mol%), $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ (4 mg, 1.0 mol%), and 4-iodoanisol (**1a**, 117 mg, 0.5 mmol) were added to the crude sulfinate (1 mmol). Then DMSO (2ml) and afterwards NBu_3 (24 µL, 19 mg, 20 mol%) were added. The tube was closed with a rubber septum and sparged with nitrogen for 5 min. The resulting mixture was irradiated (445 nm, 10 W LED) for 24 h. Then H_2O (15 mL) and sat. aq. NaCl (15 mL) were added and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with sat. aq. NH_4Cl (25 mL), sat. aq. NaCl (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3a** as a yellowish solid (31 mg, 25%).

Analytical data are consistent with the literature.[6]

R_f = 0.44 (*n*-hexane/EtOAc 7:3)

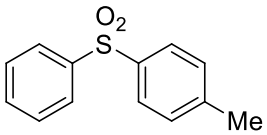
m.p. = 86.3 °C (DCM, decomposed)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 14.9, 8.0 Hz, 4H), 7.60 – 7.43 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 142.5, 133.3, 133.0, 130.0, 129.3, 127.4, 114.7, 55.8 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{13}O_3S$ $[M+H]^+$ = 249.1; found: 249.0.

Preparation of 4-Methylphenylphenylsulfone (3b)



Prepared from 4-iodotoluene (**1b**, 109 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3b** as an off-white solid (81 mg, 70%).

Analytical data are consistent with the literature.[6]

R_f = 0.59 (*n*-hexane/EtOAc 7:3)

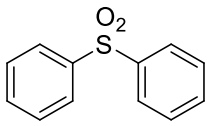
m.p. = 126.4 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.87 – 7.79 (m, 2H), 7.58 – 7.43 (m, 3H), 7.33 – 7.26 (m, 2H), 2.39 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 142.1, 138.8, 133.1, 130.0, 129.4, 127.9, 127.6, 21.7 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{13}O_2S$ $[M+H]^+$ = 233.1; found: 233.0.

Preparation of Diphenylsulfone (3c)



Prepared from iodobenzene (102 mg, 56 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3c** as an off-white solid (77 mg, 70%).

Analytical data are consistent with the literature.[6]

R_f = 0.55 (*n*-hexane/EtOAc 7:3)

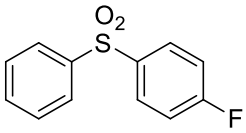
m.p. = 126.3 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 4H), 7.59 – 7.44 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 133.3, 129.4, 127.8 ppm.

MS (ESI): m/z calcd. for $C_{12}H_{11}O_2S$ $[M+H]^+$ = 219.0; found: 219.0.

Preparation of 4-Fluorophenylphenylsulfone (3d)



Prepared from 1-fluoro-4-iodobenzene (111 mg, 58 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3d** as a yellowish white solid (79 mg, 67%).

Analytical data are consistent with the literature.[6]

R_f = 0.59 (*n*-hexane/EtOAc 7:3)

m.p. = 115.3 °C (DCM)

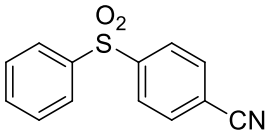
^{1}H NMR (250 MHz, $CDCl_3$) δ 8.03 – 7.88 (m, 4H), 7.64 – 7.43 (m, 3H), 7.23 – 7.12 (m, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 163.9, 141.6, 137.8 (d, J = 3.2 Hz), 133.4, 130.6 (d, J = 9.6 Hz), 129.5, 127.7, 116.8 (d, J = 22.7 Hz) ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -104.2 ppm.

MS (ESI): m/z calcd. for $C_{12}H_{10}FO_2S$ $[M+H]^+$ = 237.0; found: 237.0.

Preparation of 4-(Phenylsulfonyl)benzonitrile (3e)



Prepared from 4-iodobenzonitril (115 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3e** as a white solid (100 mg, 82%).

Analytical data are consistent with the literature.[6]

R_f = 0.52 (*n*-hexane/EtOAc 7:3)

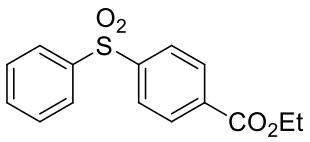
m.p. = 130.4 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.09–8.01 (m, 2H), 7.99–7.88 (m, 2H), 7.83–7.73 (m, 2H), 7.67–7.48 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 140.3, 134.1, 133.2, 129.8, 128.4, 128.1, 117.3, 117.0 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{10}NO_2S$ $[M+H]^+$ = 244.0; found: 244.1.

Preparation of Ethyl 4-(Phenylsulfonyl)benzoate (3f)



Prepared from ethyl 4-iodobenzoate (138 mg, 83 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**,164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3f** as a white solid (117 mg, 81%).

Analytical data are consistent with the literature.[6]

R_f = 0.52 (*n*-hexane/EtOAc 7:3)

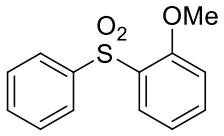
m.p. = 68-69 °C (DCM)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.22 – 8.09 (m, 2H), 8.06 – 7.89 (m, 4H), 7.64 – 7.46 (m, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 145.5, 141.0, 134.8, 133.7, 130.5, 129.6, 128.0, 127.8, 61.9, 14.4 ppm.

MS (ESI): m/z calcd. for $C_{15}H_{15}O_4S$ $[M+H]^+$ = 291.1; found: 291.0.

Preparation of 2-Methoxyphenylphenylsulfone (3g)



Prepared from 2-iodoanisole (117 mg, 65 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3g** as a yellowish solid (94 mg, 76%).

Analytical data are consistent with the literature.[7]

R_f = 0.30 (*n*-hexane/EtOAc 7:3)

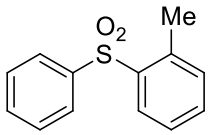
m.p. = 142.2 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.02–7.93 (m, 2H), 7.62 – 7.43 (m, 4H), 7.16 – 7.04 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 141.6, 135.7, 133.0, 130.0, 129.1, 128.6, 128.5, 120.7, 112.6, 56.0 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{13}O_3S$ $[M+H]^+$ = 249.1; found: 249.0.

Preparation of 2-Methylphenylphenylsulfone (3h)



Prepared from 1-iodo-2-methylbenzene (109 mg, 64 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3h** as an off-white solid (37 mg, 32%).

Analytical data are consistent with the literature.[8]

R_f = 0.63 (*n*-hexane/EtOAc 7:3)

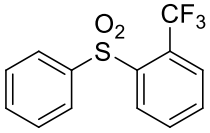
m.p. = 70-71 °C (DCM)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.92–7.82 (m, 2H), 7.63 – 7.34 (m, 5H), 7.29 – 7.18 (m, 1H), 2.44 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 138.9, 138.1, 133.8, 133.2, 132.8, 129.6, 129.2, 127.8, 126.6, 20.3 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{13}O_2S$ $[M+H]^+$ = 233.1; found: 233.0.

Preparation of 2-Trifluoromethylphenylphenylsulfone (3i)



Prepared from 2-iodobenzotrifluoride (136 mg, 70 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3i** as an off-white solid (60 mg, 42%).

Analytical data are consistent with the literature.[9]

R_f = 0.51 (*n*-hexane/EtOAc 7:3)

m.p. = 89-90 °C (DCM)

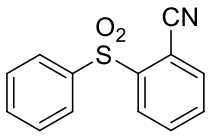
^{1}H NMR (250 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.91–7.69 (m, 5H), 7.63 – 7.44 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 140.0, 133.7, 133.5, 132.7, 132.6, 129.4, 129.1, 128.7 (q, *J* = 6.3 Hz), 127.9, 127.8, 122.6 (q, *J* = 274.4 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$) δ -56.6 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{10}F_3O_2S$ $[M+H]^+$ = 287.0; found: 287.0.

Preparation of 2-(Phenylsulfonyl)benzonitrile (3j)



Prepared from 2-iodobenzonitril (115 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3j** as a yellowish oil (49 mg, 40 %).

Analytical data are consistent with the literature.[10]

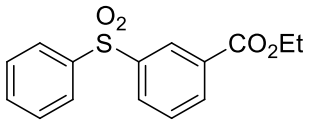
R_f = 0.40 (*n*-hexane/EtOAc 7:3)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.39–8.29 (m, 1H), 8.12–8.01 (m, 2H), 7.87–7.75 (m, 2H), 7.73–7.49 (m, 4H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 139.6, 135.8, 134.3, 133.5, 133.4, 129.9, 129.5, 128.7, 115.7, 111.5 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{10}NO_2S$ $[M+H]^+$ = 244.0; found: 244.4.

Preparation of Ethyl 3-(Phenylsulfonyl)benzoate (3k)



Prepared from ethyl 2-Iodobenzoate (138 mg, 83 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3k** as a white solid (127 mg, 87%).

Analytical data are consistent with the literature.[6]

R_f = 0.49 (*n*-hexane/EtOAc 7:3)

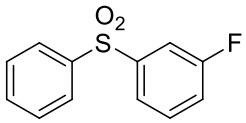
m.p. = 77.8 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.22 (dd, *J* = 7.6, 0.8 Hz, 1H), 8.17–8.07 (m, 1H), 8.01–7.93 (m, 2H), 7.64–7.46 (m, 4H), 4.46 – 4.32 (m, 2H), 1.46 – 1.34 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 142.4, 141.2, 134.2, 133.6, 132.1, 131.7, 129.7, 129.7, 129.6, 128.8, 61.9, 14.4 ppm.

MS (ESI): m/z calcd. for $C_{15}H_{15}O_4S$ $[M+H]^+$ = 291.1; found: 291.1.

Preparation of 3-Fluorophenylphenylsulfone (3l)



Prepared from 1-fluoro-3-iodoanisole (111 mg, 58 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3l** as an off-white solid (89 mg, 75%).

Analytical data are consistent with the literature.[11]

R_f = 0.40 (*n*-hexane/EtOAc 7:3)

m.p. = 101.9 °C (DCM, decomposed)

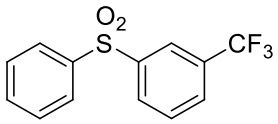
^{1}H NMR (250 MHz, $CDCl_3$) δ 7.98–7.91 (m, 2H), 7.77–7.70 (m, 1H), 7.67–7.44 (m, 5H), 7.30–7.20 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 161.6, 143.8 (d, *J* = 6.4 Hz), 141.0, 133.7, 131.3 (d, *J* = 7.7 Hz), 128.7 (d, *J* = 208.1 Hz), 123.6 (d, *J* = 3.4 Hz), 120.6 (d, *J* = 21.3 Hz), 115.1 (d, *J* = 24.3 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.1 ppm.

MS (ESI): m/z calcd. for $C_{12}H_{10}FO_2S$ $[M+H]^+$ = 237.0; found: 237.0.

Preparation of 3-Trifluoromethyphenylphenylsulfone (3m)



Prepared from 3-iodobenzotrifluoride (136 mg, 72 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3m** as an off-white solid (127 mg, 89%).

Analytical data are consistent with the literature.[6]

R_f = 0.23 (*n*-hexane/EtOAc 7:3)

m.p. = 83.1 °C (DCM)

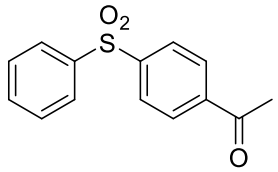
^{1}H NMR (250 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.48 (m, 4H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 140.7, 133.9, 132.1 (q, *J* = 33.6 Hz), 131.1, 130.3, 130.1, 129.7, 128.0, 124.8 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 273.0 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.8 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{10}F_3O_2S$ $[M+H]^+$ = 287.0; found: 287.0.

Preparation of 4-(Phenylsulfonyl)acetophenone (3n)



Prepared from 4-iodoacetophenone (123 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3n** as an off-white solid (93 mg, 78%).

Analytical data are consistent with the literature.[8]

R_f = 0.42 (*n*-hexane/EtOAc 7:3)

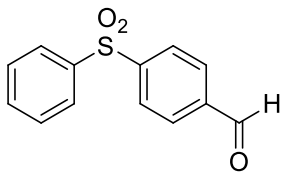
m.p. = 131.7 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.08–8.00 (m, 4H), 7.99 – 7.92 (m, 2H), 7.64 – 7.47 (m, 3H), 2.61 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 145.6, 141.0, 140.5, 133.8, 129.6, 129.2, 128.1, 128.0, 27.0 ppm.

MS (ESI): m/z calcd. for $C_{14}H_{13}O_3S$ $[M+H]^+$ = 261.1; found: 261.0.

Preparation of 4-(Phenylsulfonyl)benzaldehyde (3o)



Prepared from 4-iodobenzaldehyde (116 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3o** as an off-white solid (18 mg, 14%).

Analytical data are consistent with the literature.[12]

R_f = 0.21 (*n*-hexane/EtOAc 7:3)

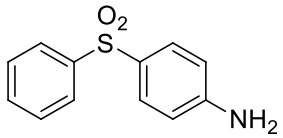
m.p. = 93.8 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) *δ* 10.06 (s, 1H), 8.43 (t, *J* = 1.7 Hz, 1H), 8.23–8.17 (m, 1H), 8.08 (dt, *J* = 7.7, 1.3 Hz, 1H), 8.02–7.95 (m, 2H), 7.75–7.66 (m, 1H), 7.62–7.49 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 190.3, 143.4, 140.9, 137.3, 133.8, 133.0, 130.4, 129.7, 128.0 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{11}O_3S$ $[M+H]^+$ = 247.0; found: 247.0.

Preparation of 4-(Phenylsulfonyl)aniline (3p)



Prepared from 4-iodoaniline (110 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3p** as an off-white solid (63 mg, 54%).

Analytical data are consistent with the literature.[8]

R_f = 0.22 (*n*-hexane/EtOAc 7:3)

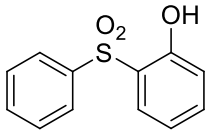
m.p. = 168.5°C (DCM)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.94–7.83 (m, 2H), 7.75–7.64 (m, 2H), 7.57–7.38 (m, 3H), 6.70–6.60 (m, 2H), 4.17 (s, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 143.1, 132.6, 130.0, 129.6, 129.2, 127.2, 114.3 ppm.

MS (ESI): m/z calcd. for $C_{12}H_{12}NO_2S$ $[M+H]^+$ = 234.1; found: 234.0.

Preparation of 2-(Phenylsulfonyl)phenole (3q)



Prepared from 2-iodophenol (110 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3q** as a white solid (104 mg, 89%).

Analytical data are consistent with the literature.[13]

R_f = 0.44 (*n*-hexane/EtOAc 7:3)

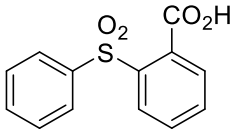
m.p. = 100.4 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.00–7.85 (m, 2H), 7.70–7.37 (m, 5H), 7.03–6.90 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 141.7, 136.3, 133.9, 129.6, 129.3, 126.9, 123.6, 120.9, 119.3 ppm.

MS (ESI): m/z calcd. for $C_{12}H_{11}O_3S$ $[M+H]^+$ = 235.0; found: 235.0.

Preparation of 2-(Phenylsulfonyl)benzoic acid (3r)



Prepared from 2-Iodobenzoic acid (124 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc/AcOH 4:1:0.01→1:1:0.01) afforded **3r** as a white solid (88 mg, 67%).

Analytical data are consistent with the literature.[14]

R_f = 0.26 (*n*-hexane/EtOAc 7:3)

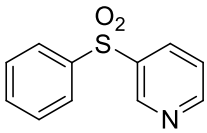
m.p. = 145.7 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.29–8.20 (m, 1H), 8.04–7.95 (m, 2H), 7.79–7.64 (m, 3H), 7.61–7.46 (m, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 141.3, 139.6, 133.5, 133.5, 132.3, 131.7, 130.5, 130.1, 129.1, 128.2 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{10}NaO_4S$ $[M+Na]^+$ = 285.0; found: 285.0.

Preparation of 3-(Phenylsulfonyl)pyridine (3s)



Prepared from 3-iodopyridine (103 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3u** as an off-white solid (92 mg, 84 %).

Analytical data are consistent with the literature.[6]

R_f = 0.21 (*n*-hexane/EtOAc 7:3)

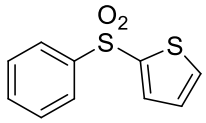
m.p. = 102.5 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 9.14 (d, *J* = 2.3 Hz, 1H), 8.78 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.26 – 8.16 (m, 1H), 8.01 – 7.91 (m, 2H), 7.66 – 7.50 (m, 3H), 7.49 – 7.40 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 148.9, 140.9, 138.4, 135.4, 134.0, 129.7, 127.9, 124.0 ppm.

MS (ESI): m/z calcd. for $C_{11}H_{10}NO_2S$ $[M+H]^+$ = 220.0; found: 220.0.

Preparation of Phenyl(2-thienyl)sulfone (3t)



Prepared from 2-iodothiophene (105 mg, 55 µL, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3t** as an off-white solid (73 mg, 65%).

Analytical data are consistent with the literature.[7]

R_f = 0.53 (*n*-hexane/EtOAc 7:3)

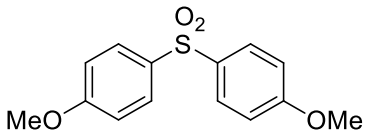
m.p. = 118-120 °C (DCM)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.03–7.95 (m, 2H), 7.70 (dt, *J* = 3.8, 1.1 Hz, 1H), 7.66–7.62 (m, 1H), 7.59–7.47 (m, 3H), 7.08 (ddd, *J* = 4.8, 3.8, 0.9 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 142.2, 134.0, 133.5, 133.4, 129.5, 128.0, 127.5 ppm.

MS (ESI): m/z calcd. for $C_{10}H_9O_2S_2$ $[M+H]^+$ = 225.0; found: 225.0.

Preparation of Di-(4-methoxyphenyl)sulfone (4a)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 4-methoxybenzenesulfinic acid sodium salt (194 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4a** as an off-white solid (96 mg, 69%).

Analytical data are consistent with the literature.[15]

R_f = 0.30 (*n*-hexane/EtOAc 7:3)

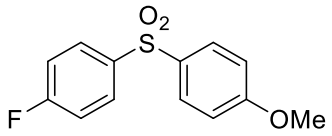
m.p. = 131.1 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.89–7.80 (m, 4H), 7.01–6.90 (m, 4H), 3.83 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 134.2, 129.7, 114.6, 55.8 ppm.

MS (ESI): m/z calcd. for $C_{14}H_{15}O_4S$ $[M+H]^+$ = 279.1; found: 279.1.

Preparation of 1-Fluoro-4-((4-Methoxyphenyl)sulfonyl)benzene (4b)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 4-fluorobenzenesulfinic acid sodium salt (182 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4b** as an off-white solid (63 mg, 42%).

Analytical data are consistent with the literature.[16]

R_f = 0.50 (*n*-hexane/EtOAc 7:3)

m.p. = 100.0 °C (DCM)

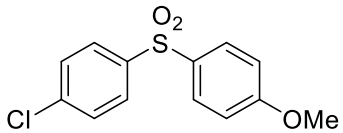
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.9, 5.1 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.10 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 163.7 (d, *J* = 3.4 Hz), 138.7 (d, *J* = 3.2 Hz), 133.1, 130.3 (d, *J* = 9.5 Hz), 130.0, 116.6 (d, *J* = 22.6 Hz), 114.7, 55.8 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -104.9 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{12}FO_3S$ $[M+H]^+$ = 267.0; found: 267.0.

Preparation of 1-Chloro-4-((4-Methoxyphenyl)sulfonyl)benzene (4c)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 4-chlorobenzenesulfinic acid sodium salt (198 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4c** as an off-white solid (45 mg, 32%).

Analytical data are consistent with the literature.[17]

R_f = 0.43 (*n*-hexane/EtOAc 7:3)

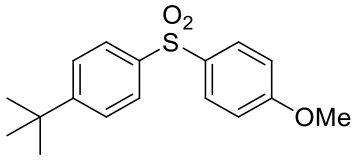
m.p. = 104.3 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.90–7.81 (m, 1H), 7.48–7.42 (m, 1H), 7.00–6.94 (m, 1H), 3.85 (s, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 141.0, 139.6, 132.8, 130.0, 129.6, 128.9, 114.8, 55.8 ppm.

MS (ESI): m/z calcd. for $C_{13}H_{12}ClO_3S$ $[M+H]^+$ = 283.0; found: 283.0.

Preparation of 1-(Tert-butyl)-4-((4-Methoxyphenyl)sulfonyl)benzene (4d)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 4-*tert*-butylbenzenesulfinic acid sodium salt (220 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4d** as an off-white solid (99 mg, 56%).

R_f = 0.52 (*n*-hexane/EtOAc 7:3)

m.p. = 134.7 °C (DCM, decomposed)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 21.3, 8.7 Hz, 4H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 1.30 (s, 9H) ppm.

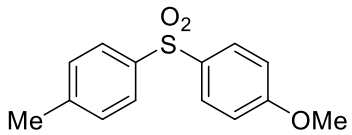
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 156.8, 139.5, 133.7, 129.9, 127.3, 126.4, 114.6, 55.8, 35.2, 31.2 ppm.

MS (ESI): m/z calcd. for $C_{17}H_{21}O_3S$ $[M+H]^+$ = 305.1; found: 305.0.

MS (HRMS): m/z calcd. for $C_{17}H_{21}O_3S$ $[M+H]^+$ = 305.1205; found: 305.3033.

IR (cm^{-1}): 2962 (s), 1594 (m), 1496 (s), 1464 (s), 1319 (m), 1304 (m), 1291 (m), 1261 (m), 1152 (w), 1117 (m), 1109 (m), 1095 (w), 1074 (m), 1015 (m), 1005 (s), 836 (m), 828 (m), 803 (m), 755 (w), 668 (w), 628 (m), 610 (w), 568 (w), 551 (w), 534 (m).

Preparation of 1-Methoxy-4-Tosylbenzene (4e)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 4-tolylsulfinic acid sodium salt (178 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4e** as an off-white solid (93 mg, 71%).

4e was also prepared starting from 4-iodotolune (**1b**) via the corresponding lithium sulfinate (**10a**):

A dry and Ar-flushed Schlenk-tube equipped with a magnetic stirrer and a rubber septum was charged with 4-iodotolune (**1b**, 218 mg, 1.0 mmol) and Et_2O (2 mL). The resulting solution was cooled to 0 °C and *n*-BuLi (0.42 mL, 2.40 M in hexane, 1.0 mmol) was added dropwise. The reaction was stirred for 30 min at this temperature. After cooling to – 40 °C and liquid SO_2 (0.22 mL, 5.0 mmol) was added and the reaction mixture was allowed to warm to room temperature over 90 min. Then solvents and excess SO_2 were removed under reduced pressure (**Caution!** Excess sulfur dioxide should be collected in a cooled trap and quenched with aq. NaOH) to afford the crude lithium sulfinate (**10a**) as an off-white solid. This solid was suspended in EtOAc (7.5 mL) by stirring for 15 min. Stirring was discontinued and the solids were allowed to settle down. Then the supernatant liquid was taken of carefully and discarded. This step was repeated three times. Afterwards the remaining solid was dried under high vakuum (1 mbar) for 2 h. This procedure affords sulfinate **10a** sufficiently pure for the following transformation. A quantitative formation of the sulfinate is assumed (≡ 1 mmol **10a**).

$NiCl_2 \cdot 6\ H_2O$ (6 mg, 5.0 mol%), 2,2'-bipyridine (4 mg, 5.0 mol%), $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ (4 mg, 1.0 mol%), and 4-iodoanisol (**1a**, 117 mg, 0.5 mmol) were added to the crude sulfinate (1 mmol). Then DMSO (2ml) and afterwards NBu_3 (24 µL, 19 mg, 20 mol%) were added. The tube was closed with a rubber septum and sparged with nitrogen for 5 min. The resulting mixture was irradiated (445 nm, 10 W LED) for 24 h. Then H_2O (15 mL) and sat. aq. NaCl (15 mL) were added and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with sat. aq. NH_4Cl (25 mL), sat. aq. NaCl (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4a** as a yellowish solid (117 mg, 89%).

Analytical data are consistent with the literature.[8]

R_f = 0.54 (*n*-hexane/EtOAc 7:3)

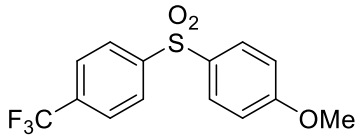
m.p. = 105.5 °C (DCM)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.83 (dd, J = 16.1, 8.5 Hz, 4H), 7.32 – 7.23 (m, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 143.8, 139.5, 133.6, 129.9, 129.8, 127.5, 114.6, 55.7, 21.6 ppm.

MS (ESI): m/z calcd. for $C_{14}H_{15}O_3S$ $[M+H]^+$ = 263.1; found: 263.0.

Preparation of 1-Methoxy-4-((4-(Trifluoromethyl)phenyl)sulfonyl)benzene (4f)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 4-trifluoromethylbenzenesulfinic acid sodium salt (232 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4f** as an off-white solid (36 mg, 23%).

Analytical data are consistent with the literature.[18]

R_f = 0.58 (*n*-hexane/EtOAc 7:3)

m.p. = 111.0 °C (DCM)

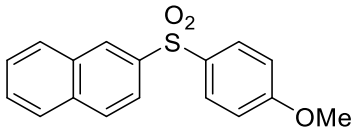
^{1}H NMR (250 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.93 – 7.84 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.03 – 6.94 (m, 1H), 3.86 (s, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 146.1, 134.6 (q, *J* = 33.1 Hz), 132.1, 130.3, 128.0, 126.5 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 273.0 Hz), 114.9, 55.9 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.2 ppm.

MS (ESI): m/z calcd. for $C_{14}H_{12}F_3O_3S$ $[M+H]^+$ = 317.0; found: 317.1.

Preparation of 2-Anisolenaphthalenesulfone (4g)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and 2-napthalenesulfinic acid sodium salt (214 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4g** as an off-white solid (76 mg, 51%).

Analytical data are consistent with the literature.[19]

R_f = 0.49 (*n*-hexane/EtOAc 7:3)

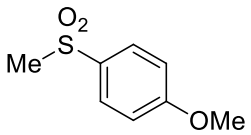
m.p. = 138.6 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.03 – 7.78 (m, 6H), 7.67 – 7.53 (m, 2H), 7.00 – 6.92 (m, 2H), 3.83 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 139.2, 134.9, 133.2, 132.3, 130.0, 129.6, 129.4, 129.0, 128.6, 127.9, 127.6, 122.6, 114.5, 55.6 ppm.

MS (ESI): m/z calcd. for $C_{17}H_{15}O_3S$ $[M+H]^+$ = 299.1; found: 299.0.

Preparation of 1-Methoxy-4-(Methylsulfonyl)benzene (4h)



Prepared from 4-iodoanisole (**1a**, 117 mg, 0.5 mmol) and methylsulfinic acid sodium salt (102 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **4h** as an off-white solid (59 mg, 63%).

Analytical data are consistent with the literature.[20]

R_f = 0.26 (*n*-hexane/EtOAc 7:3)

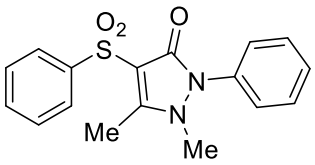
m.p. = 119.8 °C (DCM, decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.94–7.82 (m, 2H), 7.08–6.97 (m, 2H), 3.89 (s, 3H), 3.03 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 132.4, 129.6, 114.6, 55.8, 45.0 ppm.

MS (ESI): m/z calcd. for $C_8H_{11}NaO_3S$ $[M+Na]^+$ = 209.0; found: 209.0.

Preparation of 1,5-Dimethyl-2-phenyl-4-(phenylsulfonyl)-1,2-dihydro-3H-pyrazol-3-one (6)



Prepared from Iodoantipyrine (**5**, 157 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (**2a**, 164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **6** as an off-white solid (62 mg, 38%).

R_f = 0.04 (*n*-hexane/EtOAc 1:1)

m.p. = 98.1 °C (DCM. decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.19–8.11 (m, 2H), 7.57–7.35 (m, 6H), 7.26–7.21 (m, 2H), 3.30 (s, 3H), 2.69 (s, 3H) ppm.

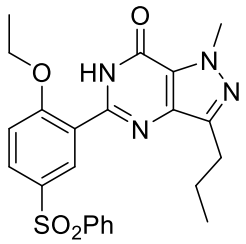
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 153.1, 142.5, 133.1, 133.1, 129.7, 128.9, 128.7, 127.5, 126.3, 107.0, 34.4, 11.9 ppm.

MS (ESI): m/z calcd. for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$ = 329.1; found: 329.0.

MS (HRMS): m/z calcd. for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$ = 329.0954; found: 329.0957.

IR (cm^{-1}): 2924 (s), 2854 (s), 1687 (m), 1683 (m), 1667 (m), 1662 (m), 1652 (m), 1594 (s), 1540 (s), 1524 (m), 1521 (m), 1516 (m), 1506 (m), 1489 (m), 1456 (m), 1446 (m), 1408 (m), 1344 (m), 1303 (m), 1291 (m), 1234 (s), 1147 (w), 1081 (m), 1070 (m), 1044 (s), 1021 (m), 998 (s), 924 (s), 902 (s), 801 (m), 7459 (m), 719 (w), 688 (m), 669 (m), 642 (m), 615 (m), 580 (w), 555 (w), 502 (s).

Preparation of 5-(2-Ethoxy-5-(phenylsulfonyl)phenyl)-1-methyl-3-propyl-1H-pyrazolo[4,3-d]pyrimidin-7(6H)-one (8)



Prepared from 5-(2-ethoxy-5-iodo-phenyl)-1-methyl-3-propyl-6*H*-pyrazolo[4,3-d]pyrimidin-7-one (**7**, 219 mg, 0.5 mmol) and benzenesulfinic acid sodium salt (164 mg, 1.0 mmol) according to TP1. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **8** as an off-white solid (75 mg, 33 %).

R_f = 0.16 (*n*-hexane/EtOAc 1:1)

m.p. = 144.5-167.8 °C (DCM. decomposed)

^{1}H NMR (250 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.96 (d, *J* = 2.5 Hz, 1H), 8.06–7.90 (m, 3H), 7.66–7.42 (m, 3H), 7.12 (d, *J* = 8.9 Hz, 1H), 4.33 (q, *J* = 7.0 Hz, 2H), 4.25 (s, 3H), 2.99–2.89 (m, 2H), 1.96–1.78 (m, 2H), 1.60 (t, *J* = 7.0 Hz, 3H), 1.10–1.01 (m, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 153.7, 147.2, 146.5, 141.8, 138.5, 135.1, 133.4, 131.6, 129.5, 127.8, 124.6, 121.6, 113.5, 66.3, 38.3, 27.9, 22.4, 14.6, 14.2 ppm.

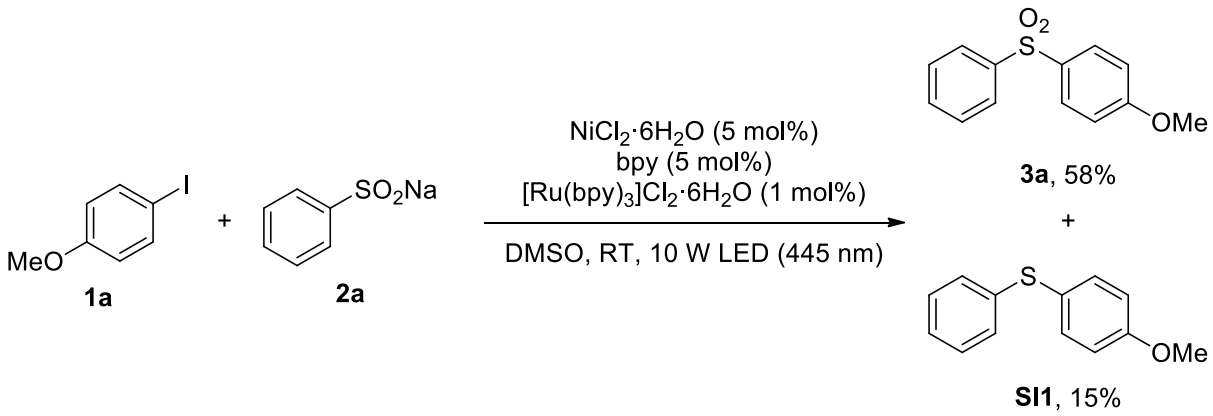
MS (ESI): m/z calcd. for $C_{23}H_{25}N_4O_4S$ $[M+H]^+$ = 453.2; found: 453.1.

MS (HRMS): m/z calcd. for $C_{23}H_{25}N_4O_4S$ $[M+H]^+$ = 453.1591; found: 453.1592.

IR (cm^{-1}): 3302 (w), 2935(w), 1703(w), 1687(s), 1683 (s), 1653 (m), 1598 (w), 1578 (w), 1555 (w), 1489 (m), 1464 (m), 1446 (m), 1390 (m), 1357 (w), 1322 (m), 1272 (m), 1245 (m), 1158 (m), 1148 (s), 1105 (m), 1081 (m), 1028 (m), 1000 (m), 924 (m), 887 (w), 819 (m), 788 (w), 774 (m), 761 (m), 737 (m), 685 (s), 651 (s), 625 (m), 608 (m), 595 (s), 573 (s), 553 (s), 527 (s), 513 (m), 493 (m), 476 (m), 457(m).

5 Mechanistic Experiments

Reaction without the addition of NBu_3



A 10 mL tube was charged with a stirring bar, $NiCl_2 \cdot 6\ H_2O$ (6 mg, 5.0 mol%), 2,2'-bipyridine (4 mg, 5.0 mol%), $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ (4 mg, 1.0 mol%), $PhSO_2Na$ (**2a**, 164 mg, 1 mmol, 2.0 eq.) and 4-iodoanisole (**1a**, 117 mg, 0.5 mmol, 1.0 eq.). DMSO (2mL) was added. Then the tube was closed with a rubber septum and sparged with nitrogen for 5 min. The resulting mixture was irradiated (445 nm, 10 W LED) for 24 h. Then H_2O (15 mL) and sat. aq. NaCl (15 mL) were added and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with sat. aq. NH_4Cl (25 mL), sat. aq. NaCl (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (*n*-hexane/EtOAc, 20:1→1:3) afforded two products **3a** (70 mg, 58%) and **SI1** (16 mg, 14 %) as an off-white solids.

Analytical data of **3a** are in agreement with the data of **3a** prepared from TP1 with the addition of NBu_3 (see pages 5 and 6) and with the literature.[6]

Analytical data of **SI1** are consistent with the literature.[21]

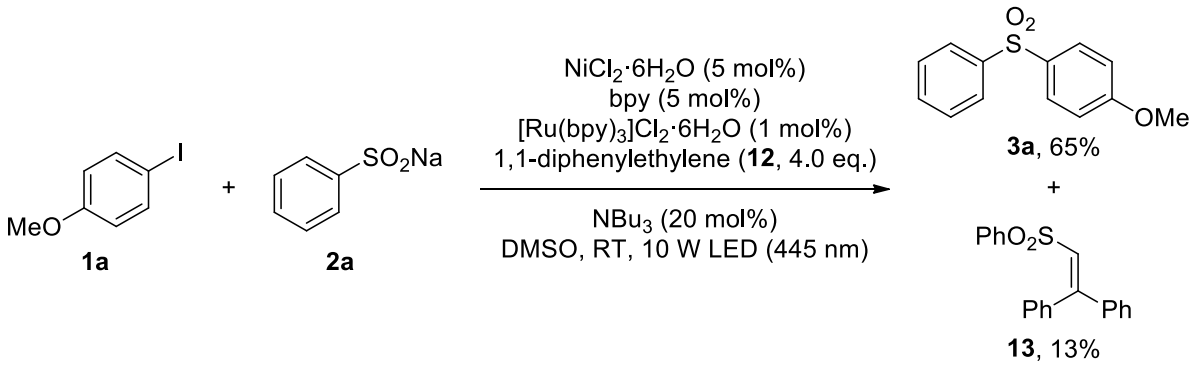
R_f = 0.66 (*n*-hexane/EtOAc 7:3)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.46–7.36 (m, 2H), 7.29–7.07 (m, 5H), 6.95–6.82 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 138.7, 135.5, 129.0, 128.4, 125.9, 124.5, 115.2, 55.5.

MS (EI, 70 eV): m/z calcd. for $C_{13}H_{12}OS$ [M] = 216.0; found: 216.3.

Radical Trap Experiment with 1,1-Diphenylethylene (12)



A 10 mL tube was charged with a stirring bar, $NiCl_2 \cdot 6\ H_2O$ (6 mg, 5.0 mol%), 2,2'-bipyridine (4 mg, 5.0 mol%), $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ (4 mg, 1.0 mol%), $PhSO_2Na$ (**2a**, 164 mg, 1 mmol, 2.0 eq.), 4-iodoanisole (**1a**, 117 mg, 0.5 mmol, 1.0 eq.) and 1,1-diphenylethylene (**12**, 360 mg, 353 µL, 2 mmol, 4.0 eq). DMSO (2mL) and afterwards NBu_3 (24 µL, 19 mg, 20 mol%) were added. Then the tube was closed with a rubber septum and sparged with nitrogen for 5 min. The resulting mixture was irradiated (445 nm, 10 W LED) for 24 h. Then H_2O (15 mL) and sat. aq. NaCl (15 mL) were added and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with sat. aq. NH_4Cl (25 mL), sat. aq. NaCl (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (*n*-hexane/EtOAc, 50:1→1:1) afforded **3a** (81 mg, 63%) and **13** (21 mg, 13%) as a pale-yellow oil.

Analytical data of **3a** are in agreement with the data of **3a** prepared from TP1 with the addition of NBu_3 (see pages 5 and 6) and with the literature.[6]

Analytical data of **13** are consistent with the literature.[22]

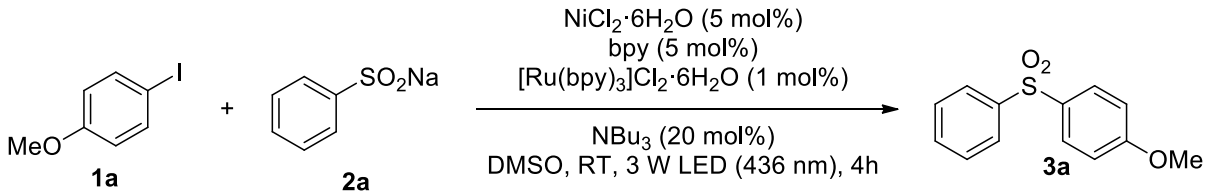
^{1}H NMR (250 MHz, $CDCl_3$) δ 7.85–7.78 (m, 2H), 7.76–7.67 (m, 1H), 7.63–7.40 (m, 11H), 7.35–7.28 (m, 2H) ppm.

MS (ESI): m/z calcd. for $C_{20}H_{17}O_2S$ $[M+H]^+$ = 321.1; found: 321.0.

6 Chemical Quantum Yield measurements

All experiments for the determination of the chemical quantum yield were performed at λ = 436 nm using commercially available High Power blue 3 W LED. The photon flux of the LED was determined with standard ferrioxlate actinometry using the protocol from Yoon.[23,24] The conversion of potassium ferrioxalate was kept below 5%. The photon flux interaction with the sample was determined to be $1.27 \cdot 10^{-7}$ einstein s^{-1}. The fraction of light absorbed at 436 nm by $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was determined to be f = 0.996632 (2.5 mM, reaction concentration). The substrate conversion was determined by quantative GC/FID analysis with biphenyl as an internal standard. The chemical quantum yield was calculated according to equation (1).

$$\Phi = \frac{(mol\ of\ product)}{(photon\ flux)\ \cdot (irradiation\ time)\ \cdot (incident\ light\ absorbed\ by\ PDI1)} \qquad (1)$$



Φ (5%) = 0.015

A 3 mL cuvette was charged with a stirring bar, $NiCl_2 \cdot 6\ H_2O$ (6 mg, 5.0 mol%), 2,2'-bipyridine (4 mg, 5.0 mol%), $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ (4 mg, 1.0 mol%), $PhSO_2Na$ (**2a**, 164 mg, 1 mmol, 2.0 eq.) , 4-iodoanisole (**1a**,117 mg, 0.5 mmol, 1.0 eq.) and biphenyl (20 mg). DMSO (2mL) and afterwards NBu_3 (24 µL, 19 mg, 20 mol%) were added. Then the cuvette was closed with a rubber septum and sparged with nitrogen for 5 min. The resulting mixture was irradiated (436 nm, 3 W LED) for 14400 s (4 h). Next a small amount was taken, quenched with sat. aq. NH_4Cl and extracted with EtOAc and filtered through Na_2SO_4 directly into a GC vial. The substrate conversion was determined by quantative GC/FID analysis with biphenyl as an internal standard.

Yield 5%, Φ(5%) = 0.015

7 Steady-state fluorescence quenching experiments

A nitrogen sparged solution of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in DMSO (50 µM) containing the appropriate amount of quencher is excited at λ = 451 nm and the emission intensities are recorded at λ = 600 nm. Measurements are conducted in 10 mm quartz cuvettes under an nitrogen atmosphere. Plots are created according to the Stern-Volmer equation for a single-step reaction (2).[23,25]

$$\frac{I_0}{I} - 1 = k_q \tau_o [Q] \qquad (2)$$

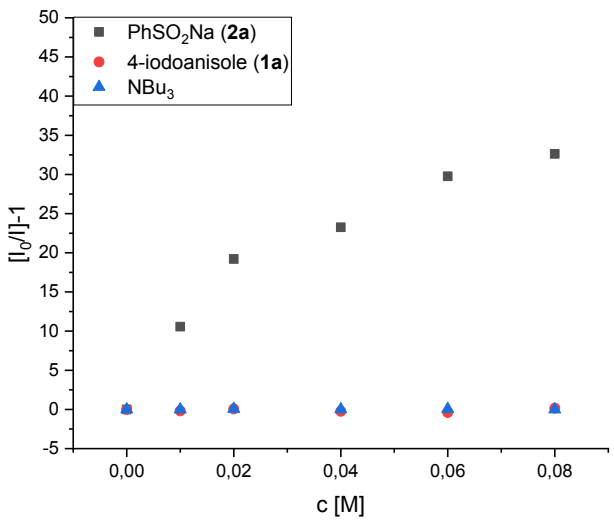


Figure SI2: Plots of Stern-Volmer quenching experiments.

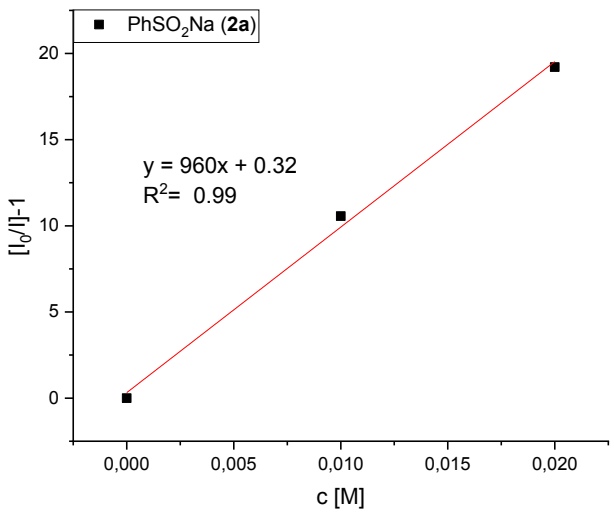


Figure SI3: Plot of Stern-Volmer quenching experiments with $PhSO_2Na$ (**2a**).

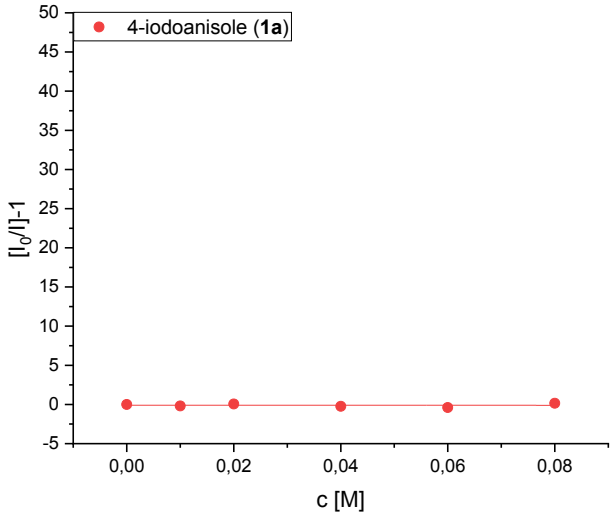


Figure SI4: Plot of Stern-Volmer quenching experiments with 4-iodoanisole (**1a**).

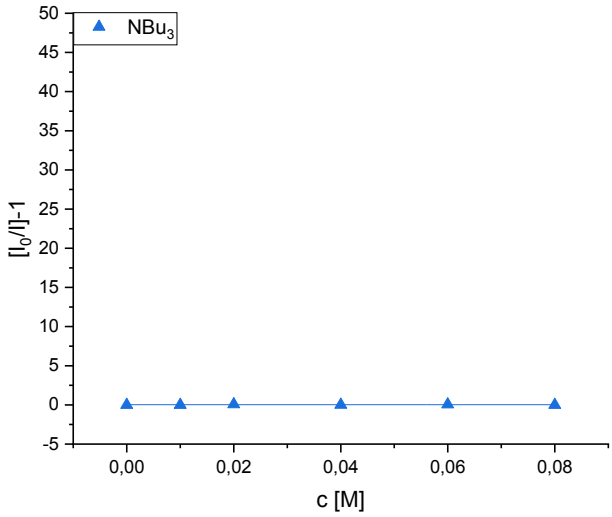


Figure SI5: Plot of Stern-Volmer quenching experiments with NBu_3.

The measurements with $PhSO_2Na$ (**1a**) concentration higher than 0.04 M were unsuited to be taken into account for a linear fit, because higher concentrations showed mostly saturation. Also the measurements with NBu_3 have to be considered with caution since NBu_3 poorly dissolves in DMSO.[26]

8 Full mechanistic discussion

A brief mechanistic discussion based control experiments, spectroscopic studies and previous reports is provided in the article (see also Figure SI6). The following pathway is proposed. Irradiation of the Ru^{II}-photocatalyst generates a long-lived excited state $*Ru^{II}$. Single-electron-transfer (SET) oxidation of the sulfinate **I** leads to a sulfonyl radical **II** and a Ru^{I}-complex. Facile addition of the sulfonyl radical **II** to the Ni^{0}-catalyst, furnishes a Ni^{I}-intermediate **III**, which can undergo an oxidative addition into the aryl iodide. The formed Ni^{III}-complex **IV** is prone to reductive elimination, affording the sulfone product **V** and a Ni^{I}-I-species **VI**. Single-electron-transfer reduction of the **VI** by the Ru^{I} produces the Ni^{0}-catalyst along with the ground state Ru^{II}-complex, closing both the photoredox and the cross-coupling cycle.

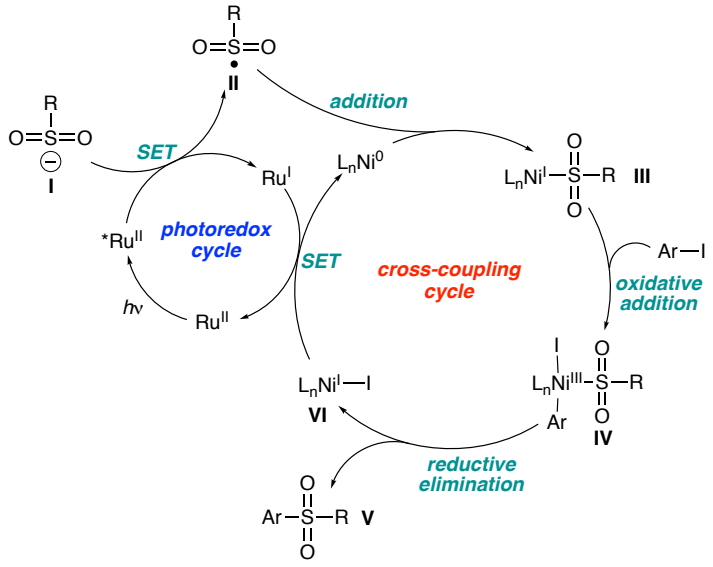


Figure SI6: Simplified catalytic cycle.

However, this catalytic cycle fails to explain the beneficial role of an amine additive. The exact role of the amine remains unclear so far. Control experiments show, that the amine additive suppresses the formation of the thioether side product **SI1** (Figure SI7 and page 23). Interestingly, 20 mol% of the amine additive are sufficient. Increasing the amount of NBu_3 does not lead to further improvements, indicating a catalytic role of the amine additive.

The formation of the side product could be rationalized with the two following hypotheses. One the one hand the sulfinate **I** could be reduced either by the Ru^{I}-complex or the Ni^{I}-species **VI**, which both can serve as strong reductants, affording the either a thiol (**SI2**), a disulfide (**SI3**) or a sulfenyl halide (**SI4**) (Figure SI7a).[27] **SI2**-**SI4** can serve as precursors for the formation of thiyl radicals **SI5**, which can

undergo an analogous nickel-catalyzed coupling with the aryl iodide.[28] Alternatively, in the absence of a suitable trap the sulfonyl radical **I** can undergo disproportionation reactions[29] to form disulfides **SI3** or a thiosulfonates **SI6**, which are both competent precursors for thiyl radicals **SI4**.

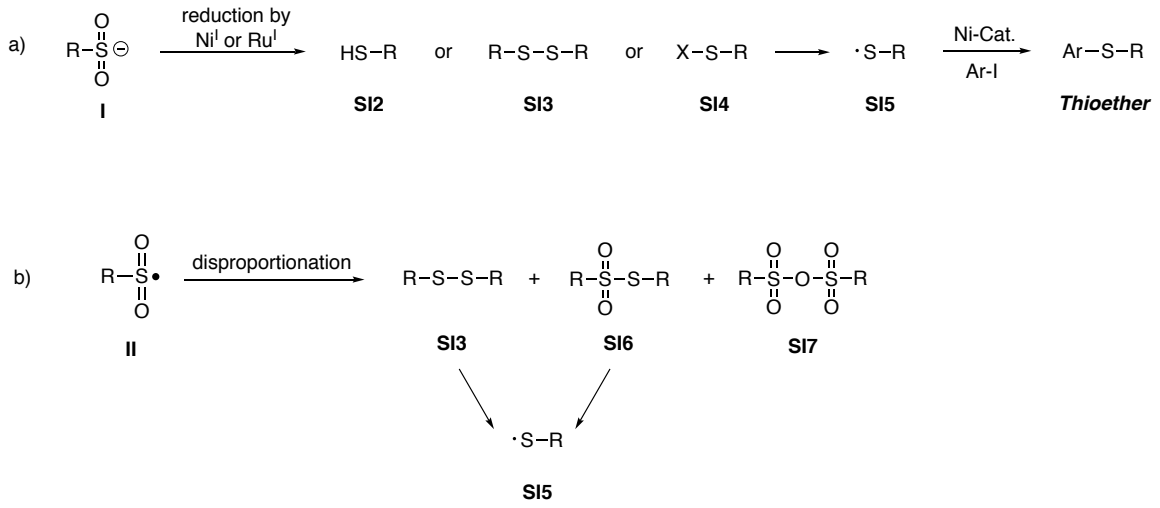


Figure SI7: Possible pathways to the thioether side product.

We assume, that NBu_3 can serve as a mediator for a more efficient electron-transfer between the Ni- and the Ru-cycle, thereby avoiding the formation of these side products (Figure SI8). Single-electron-transfer oxidation of the amine **VII** by the Ni^{I}-I-complex **VI** leads to the formation of a radical cation **VIII**. This radical cation then undergoes a single-electron-transfer reduction by the Ru^{I}-complex, affording the ground state photocatalyst and amine **VII**. This pathway might provide a faster reduction of the reactive Ni^{I}-I-species **VI** and could decrease the formation of the thioether side product (**SI1**)

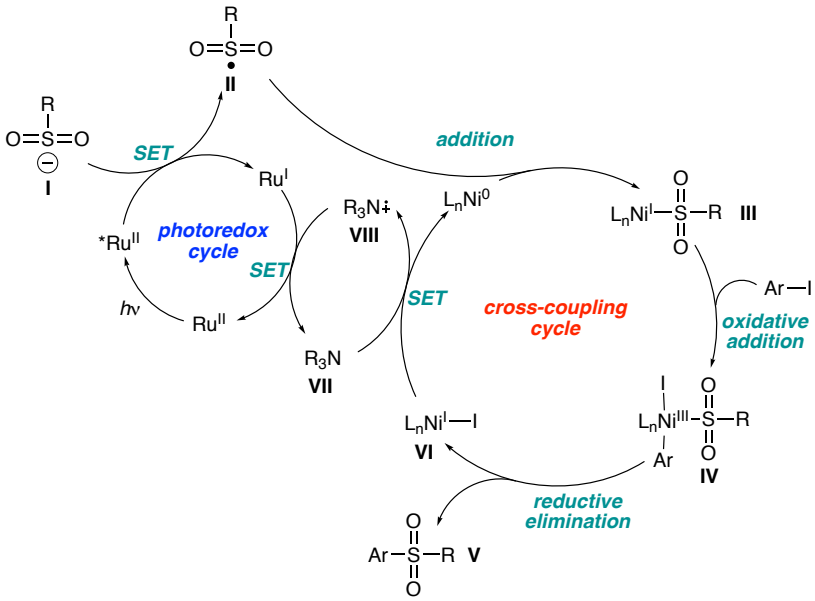


Figure SI8: Catalytic cycle with amine as electron-transfer mediator.

9 References

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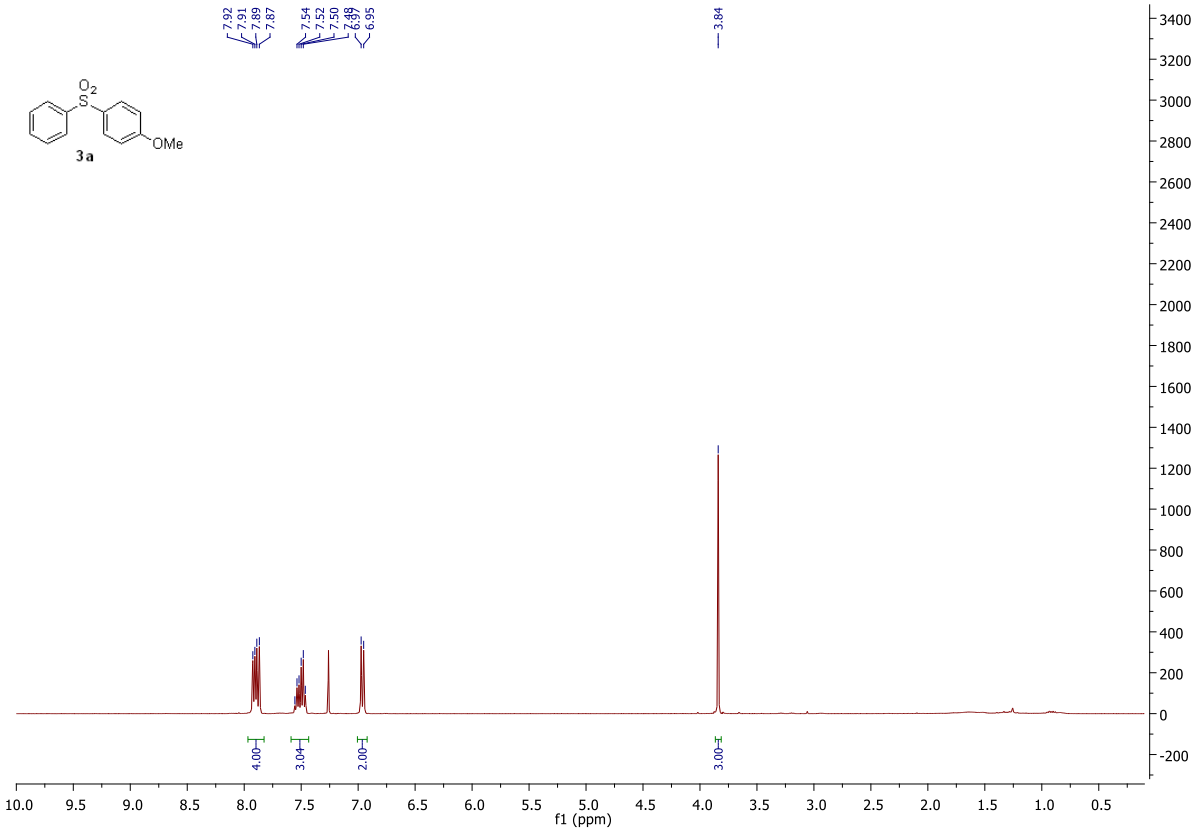
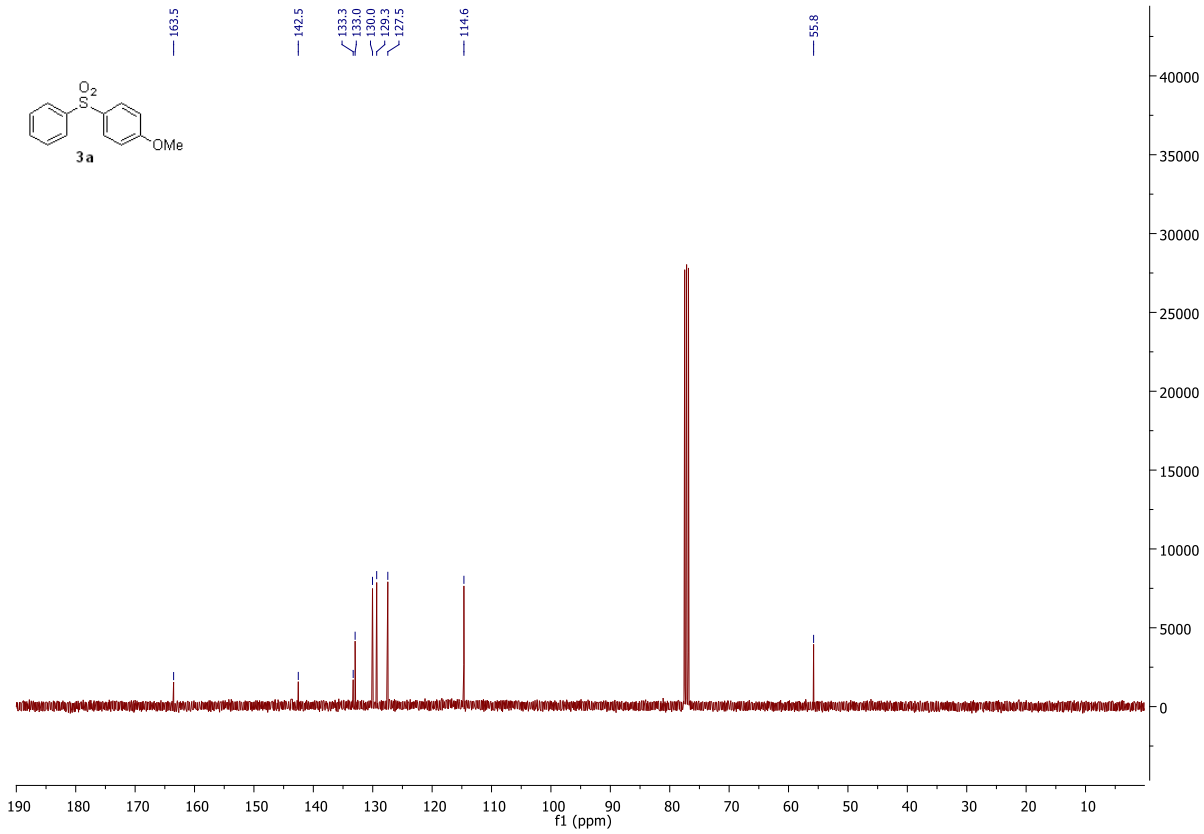
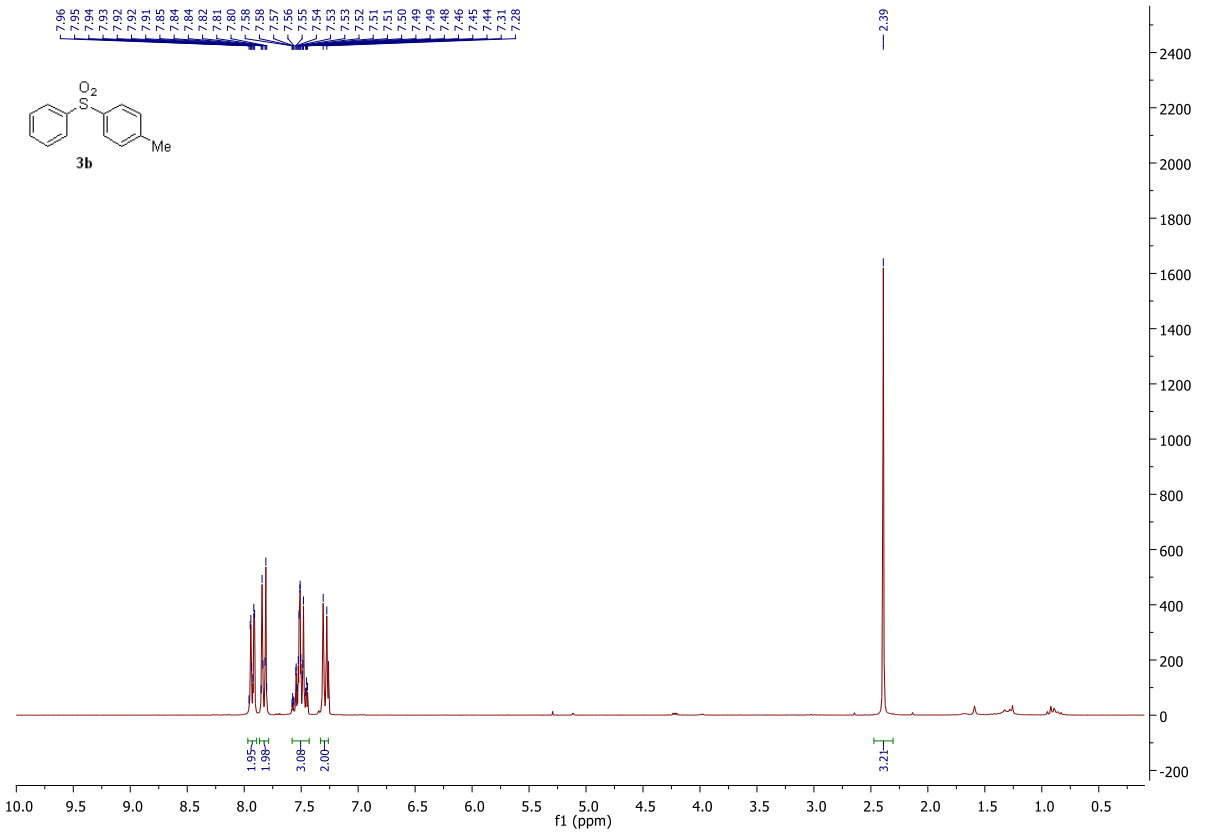
10 ^{1}H, ^{13}C, ^{19}F NMR Spectra



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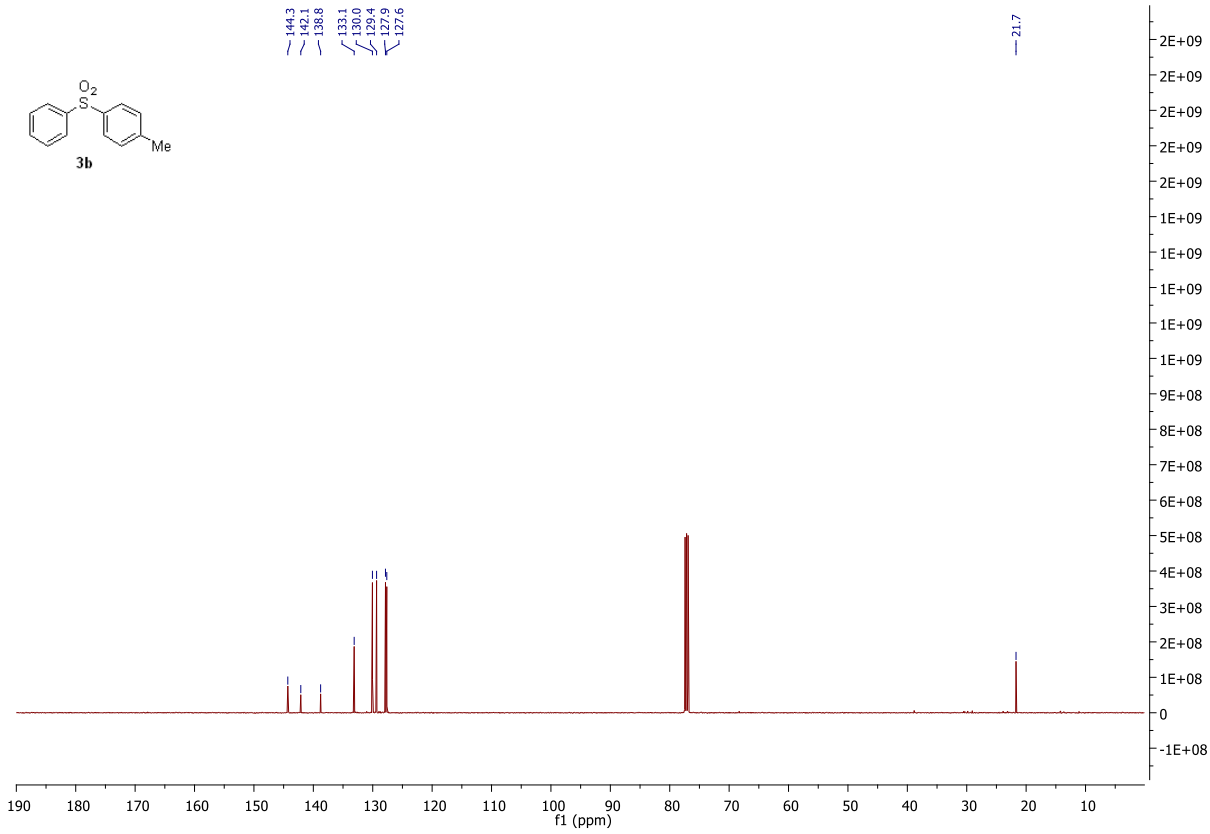
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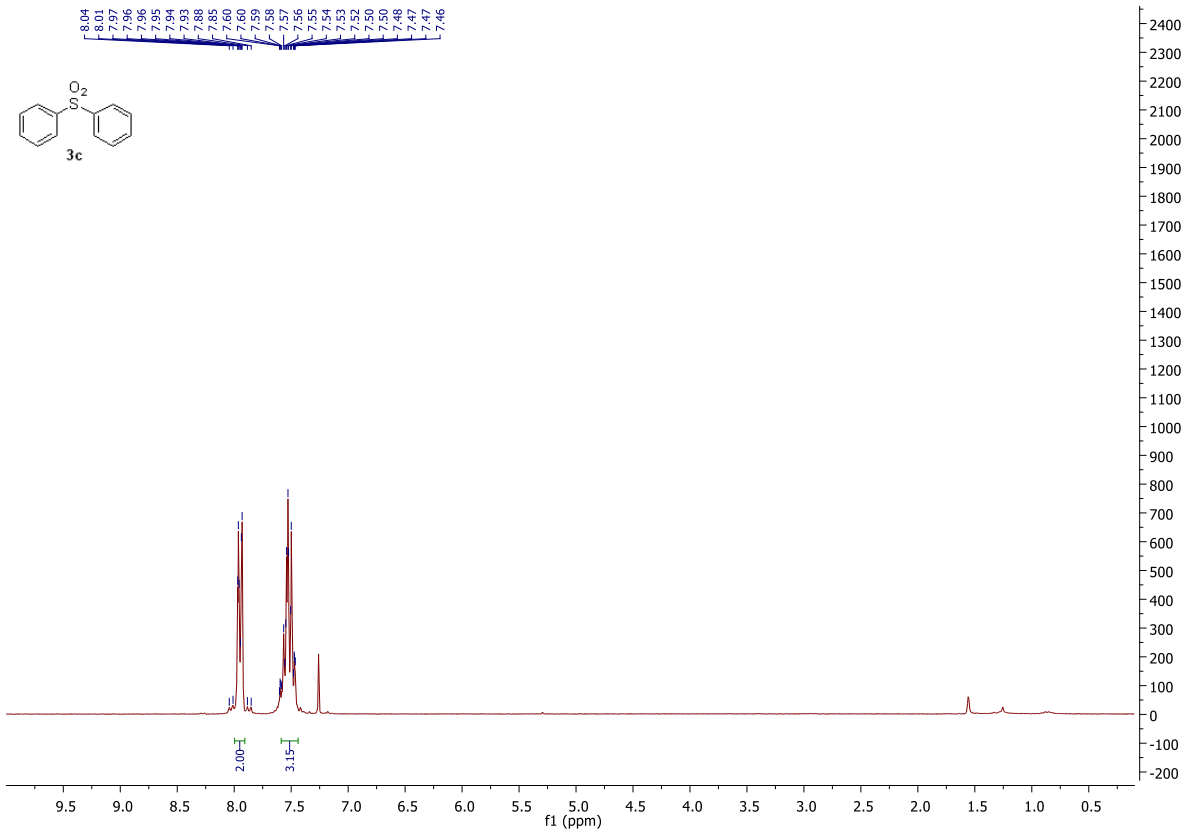
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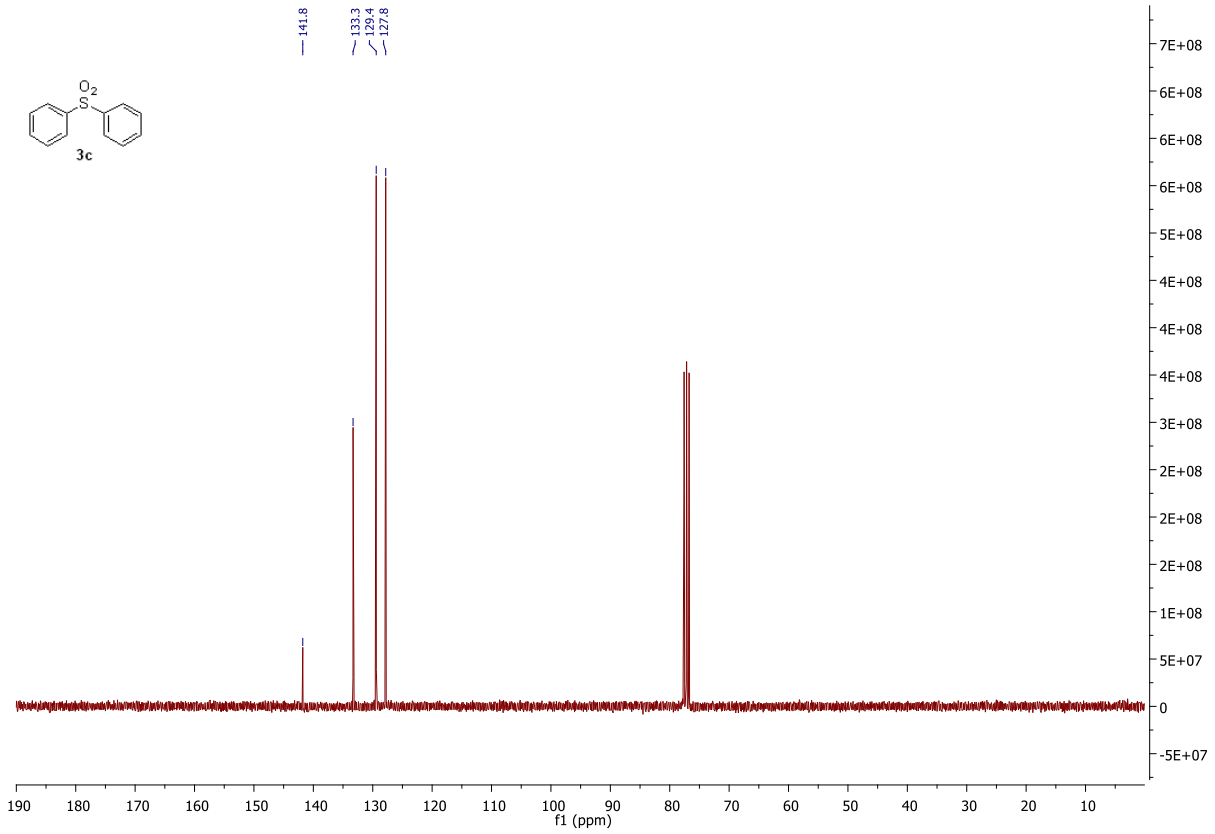
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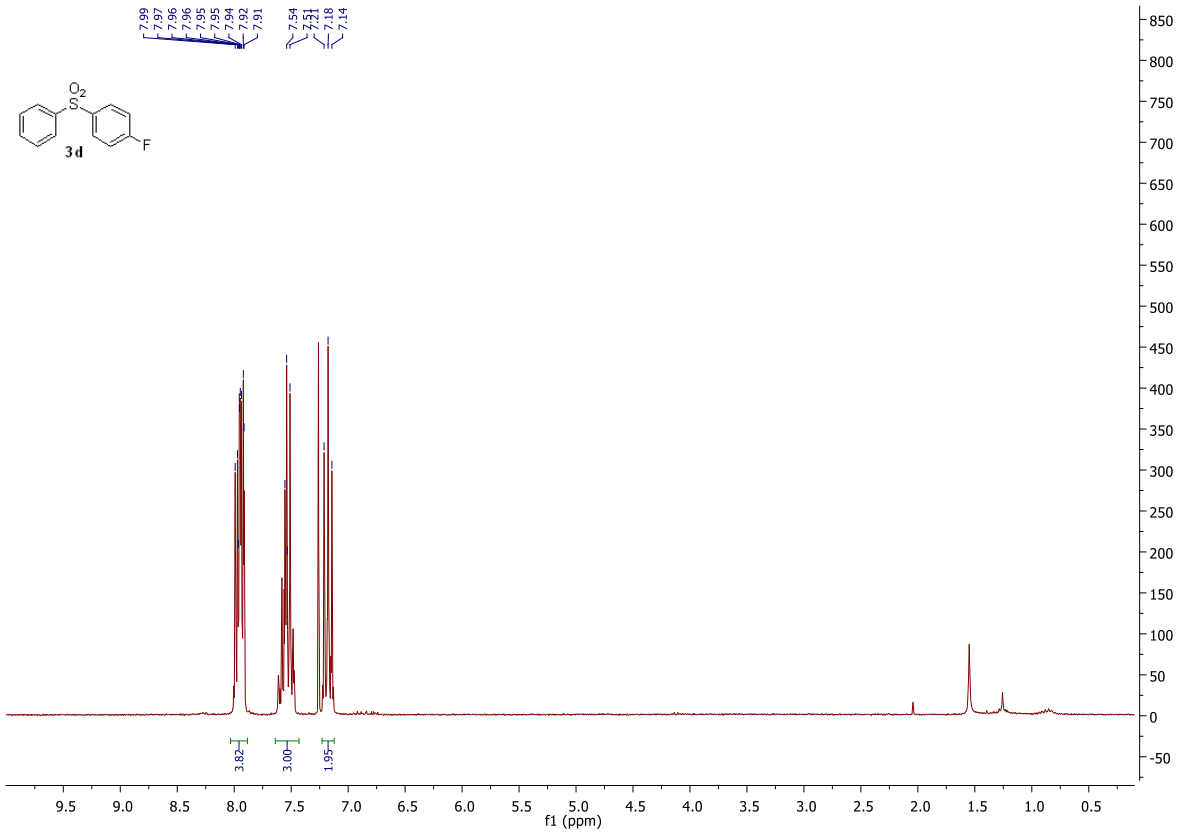
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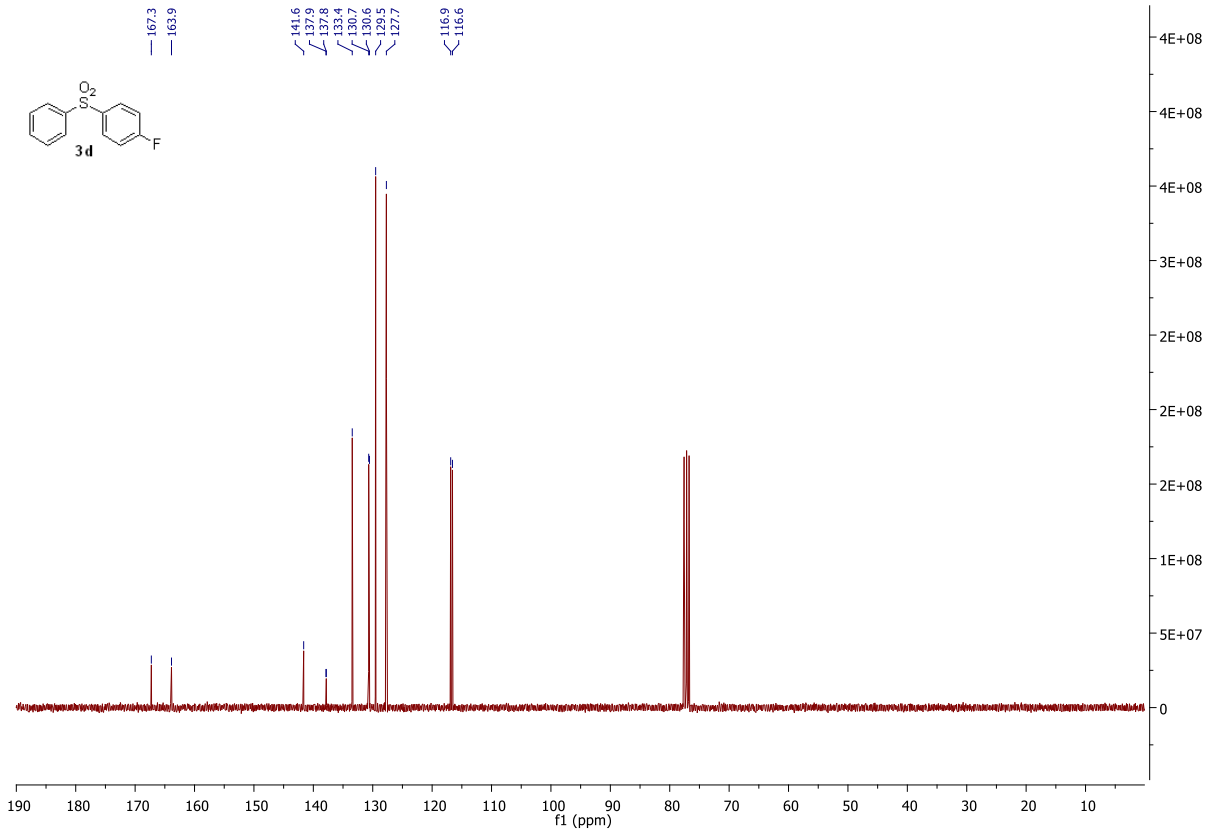
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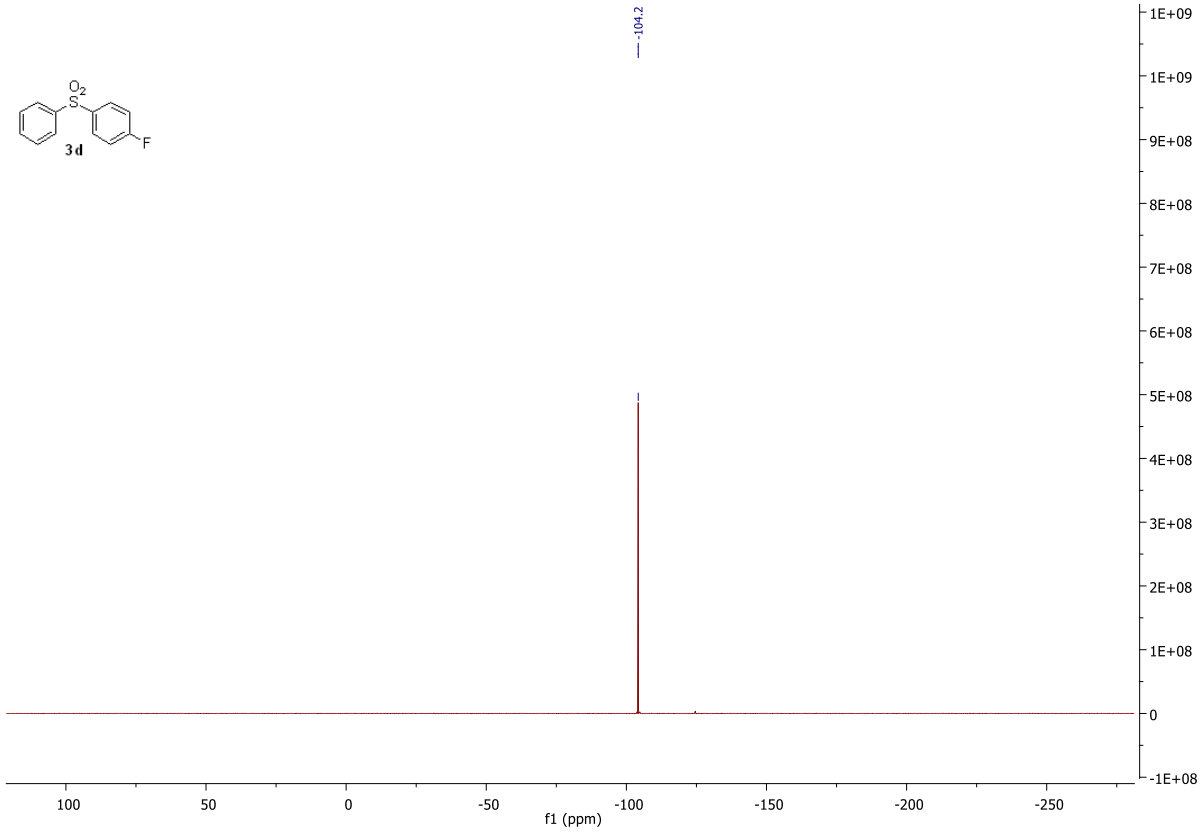
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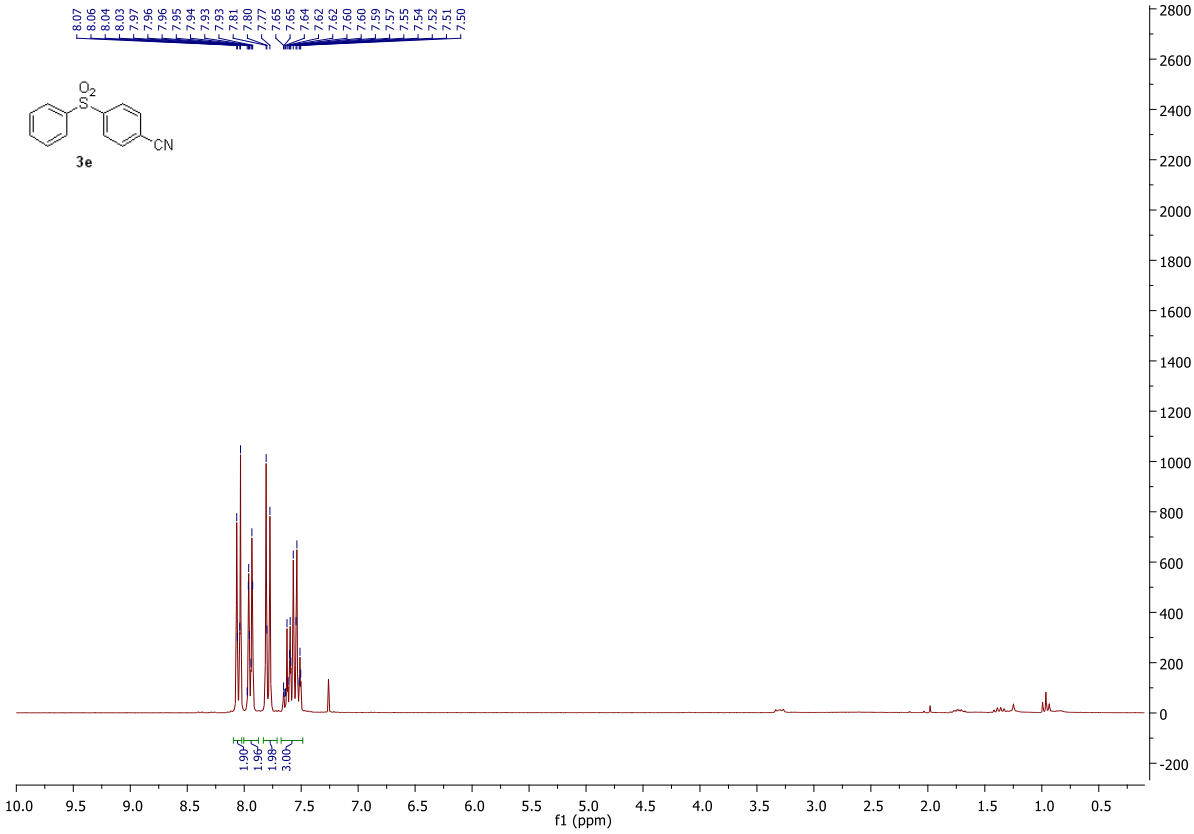
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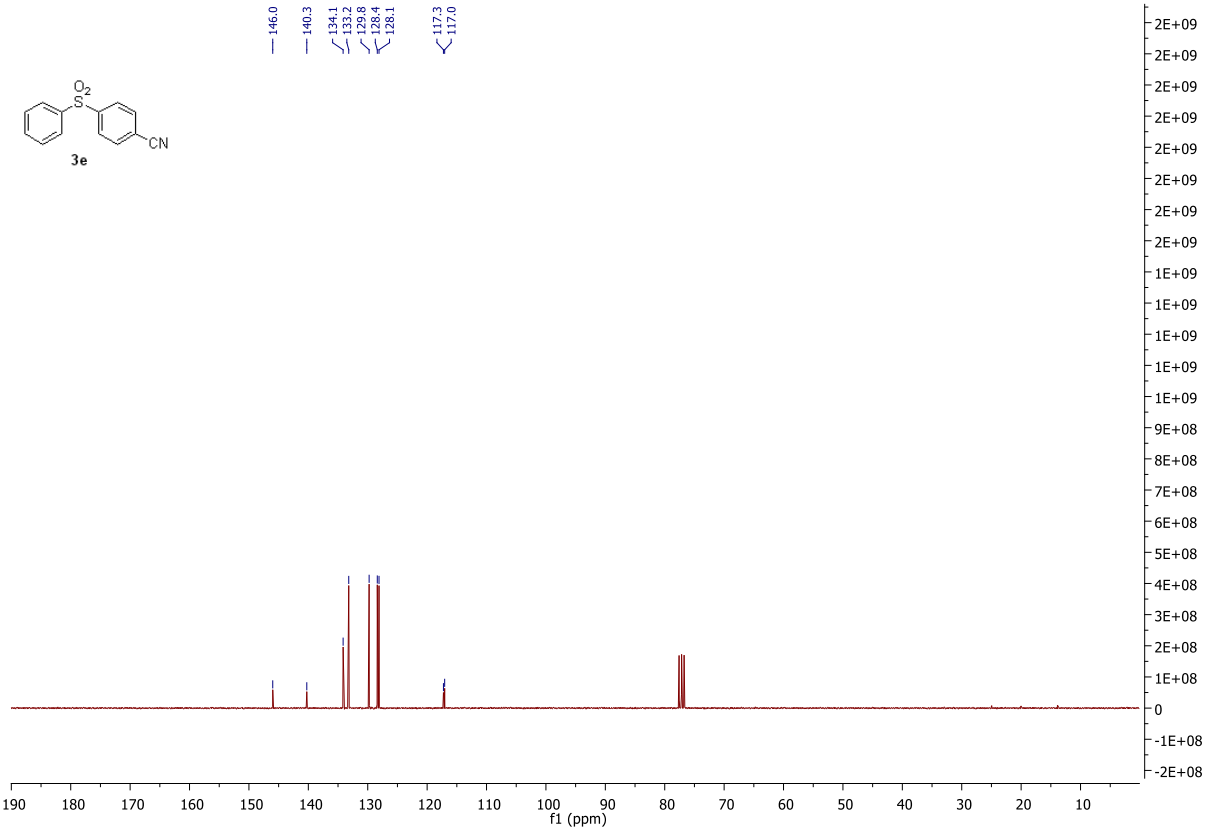
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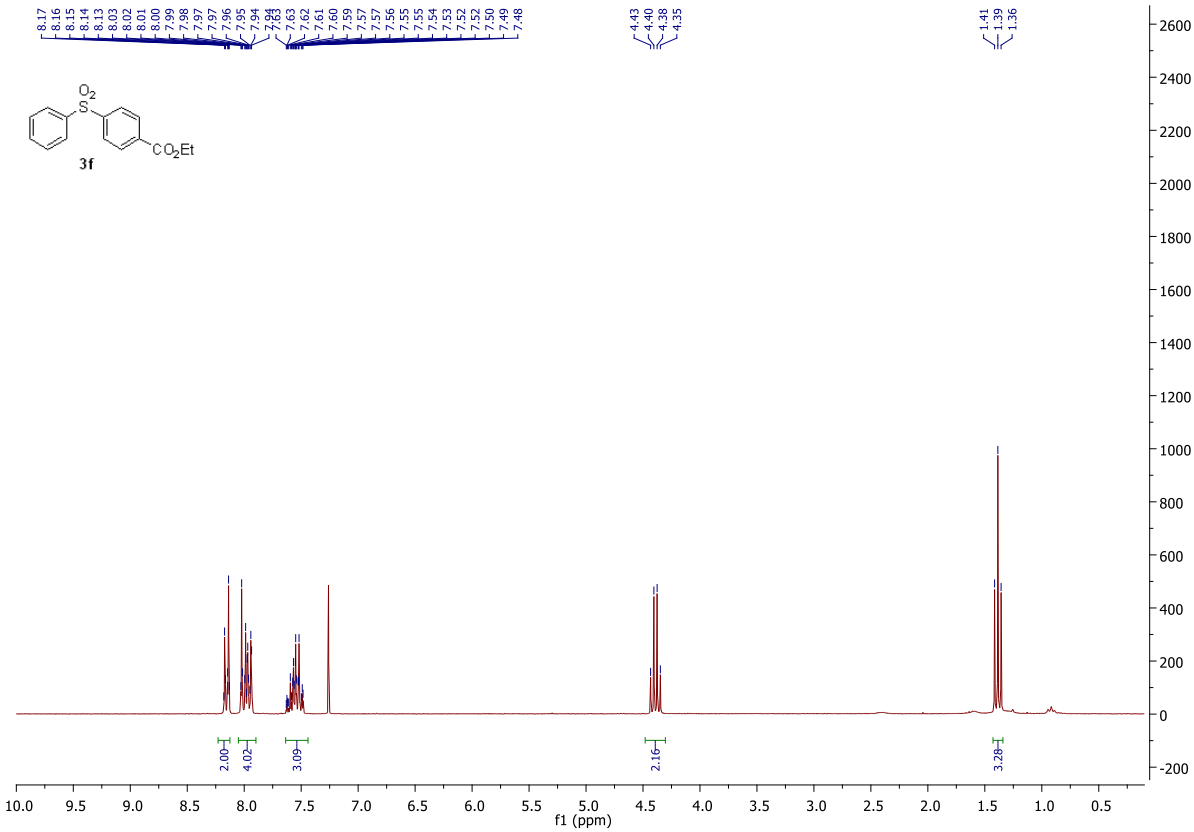
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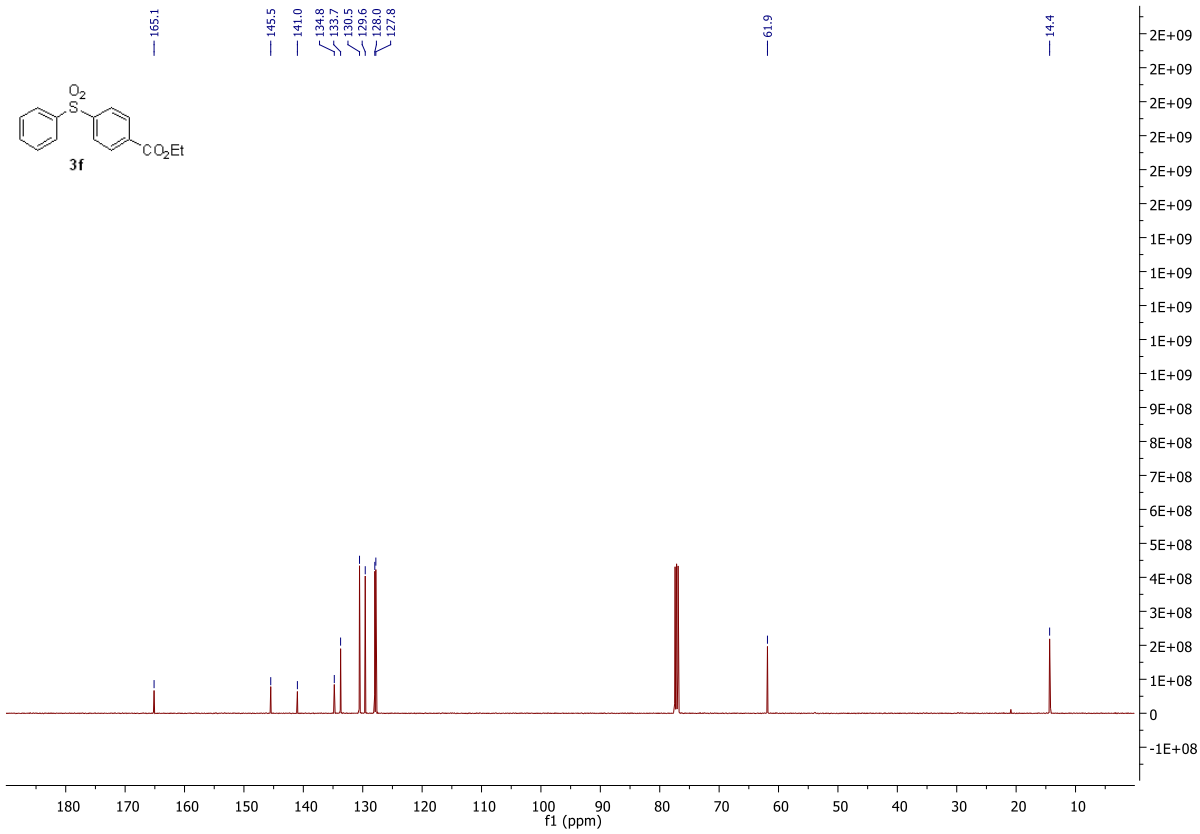
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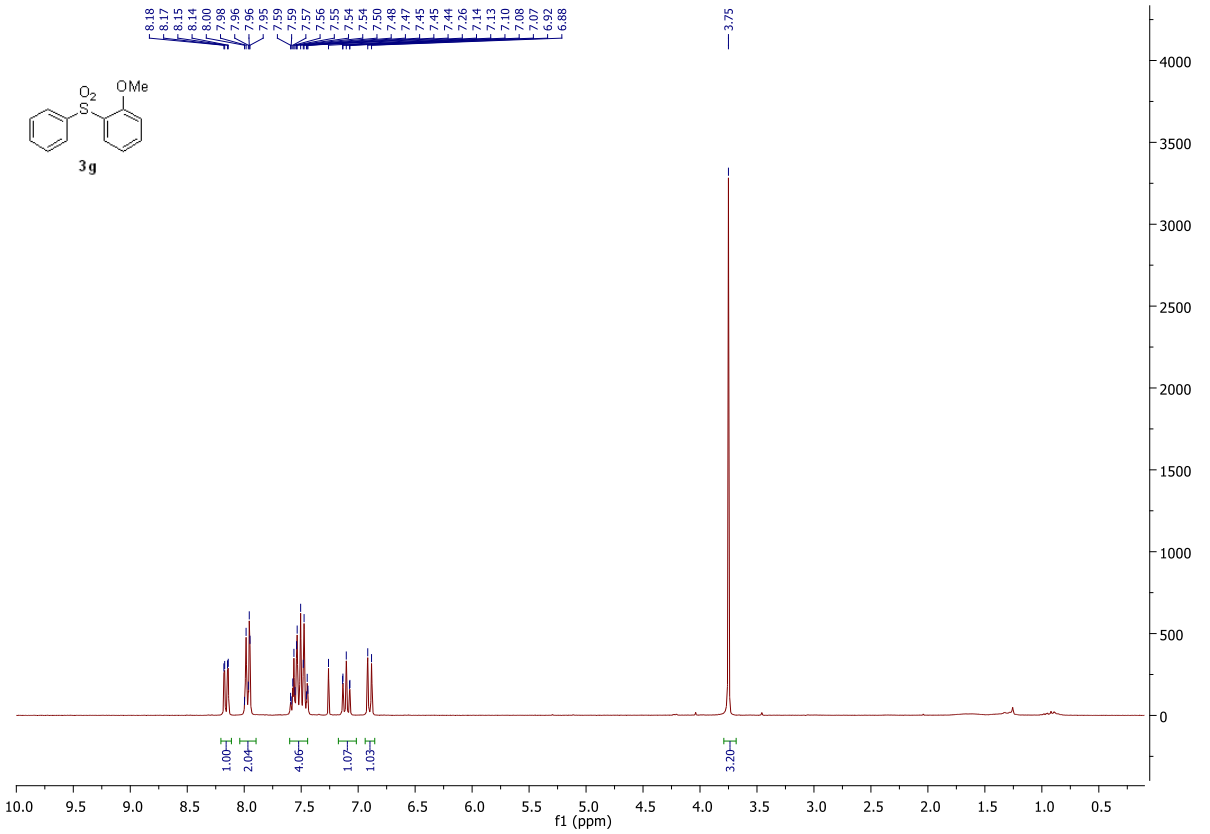
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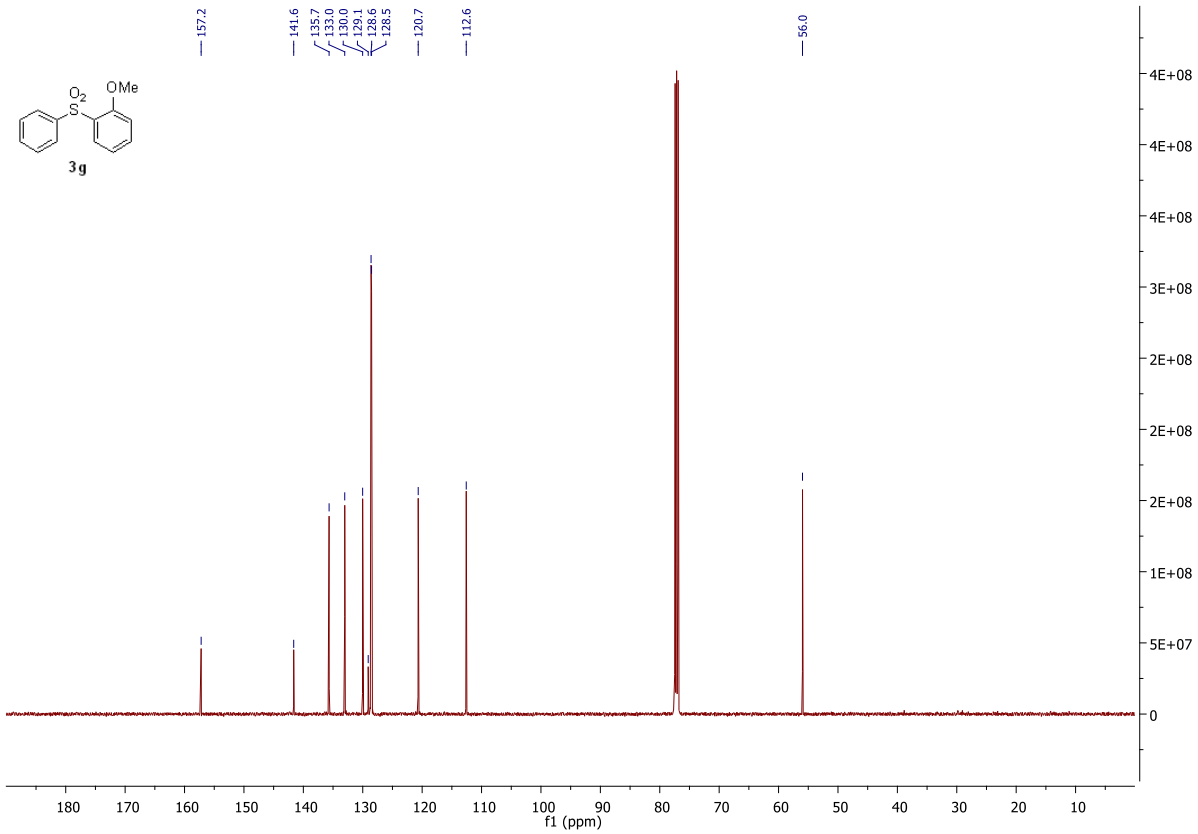
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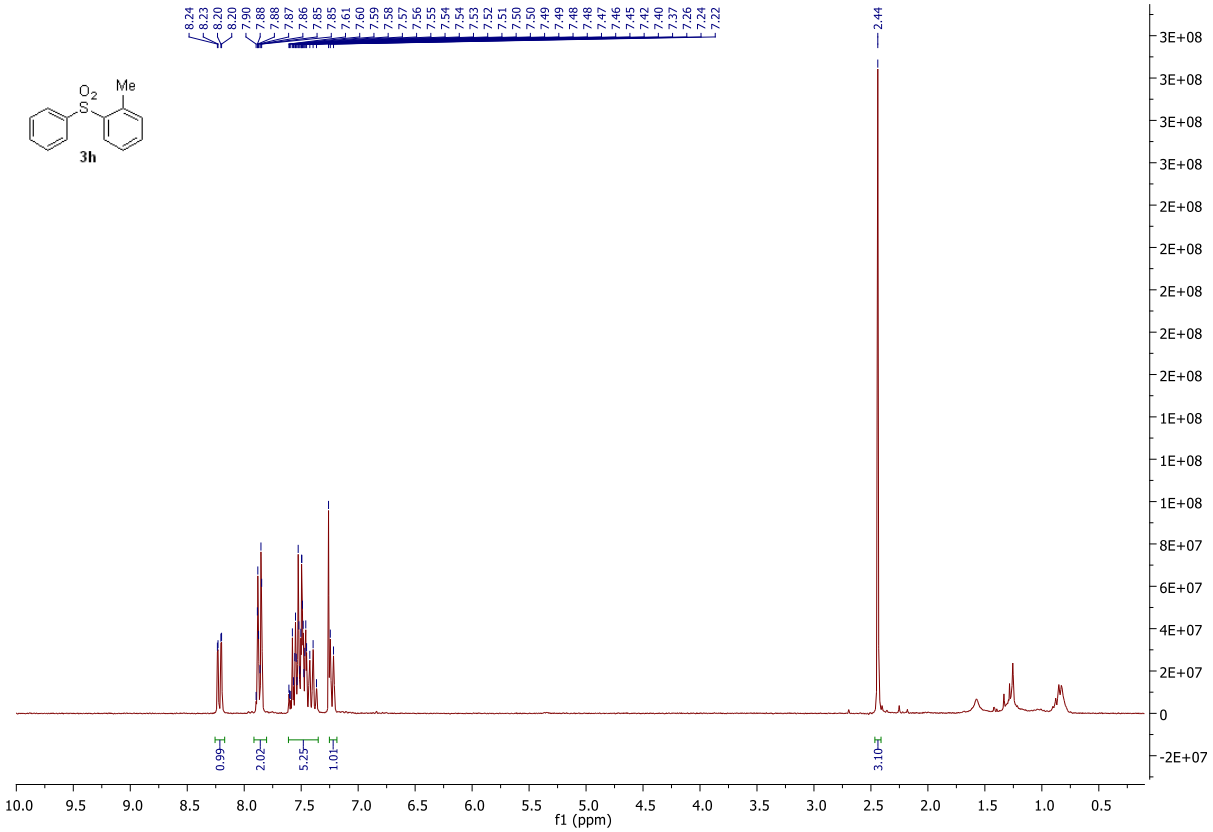
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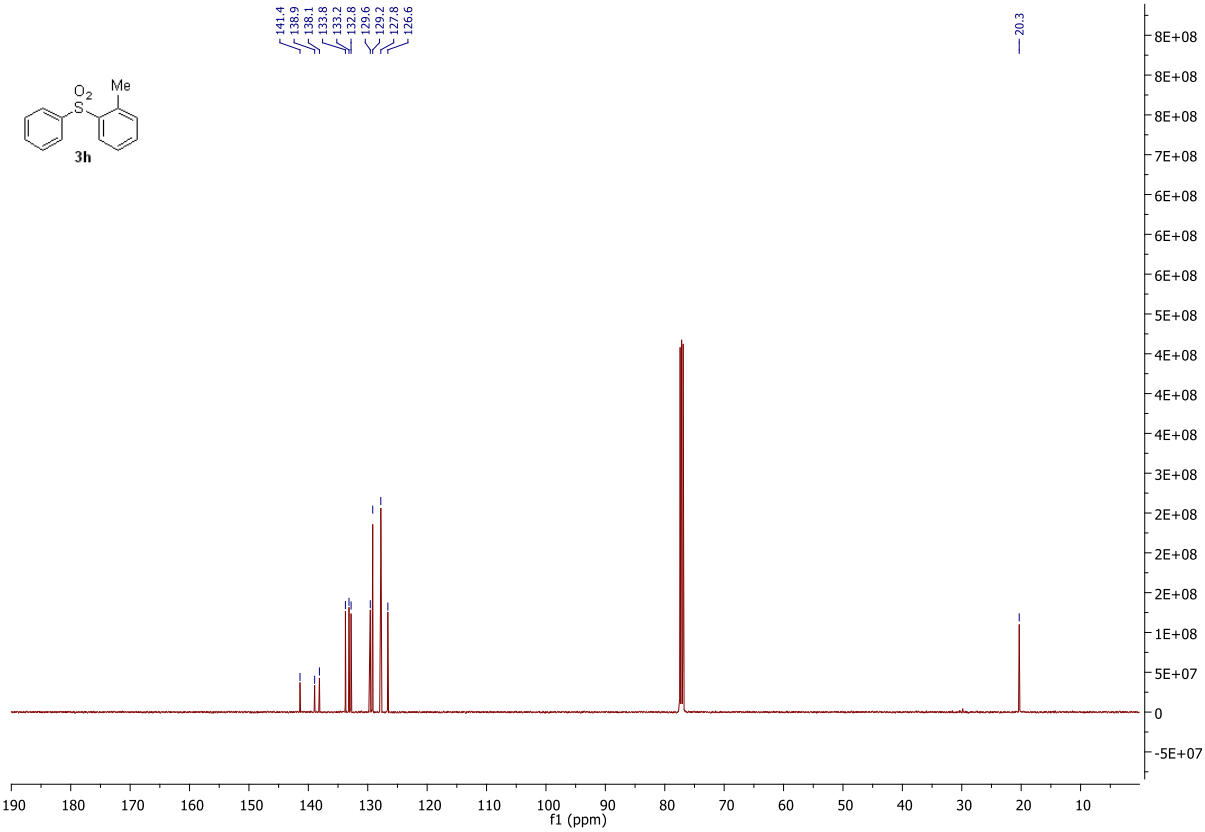
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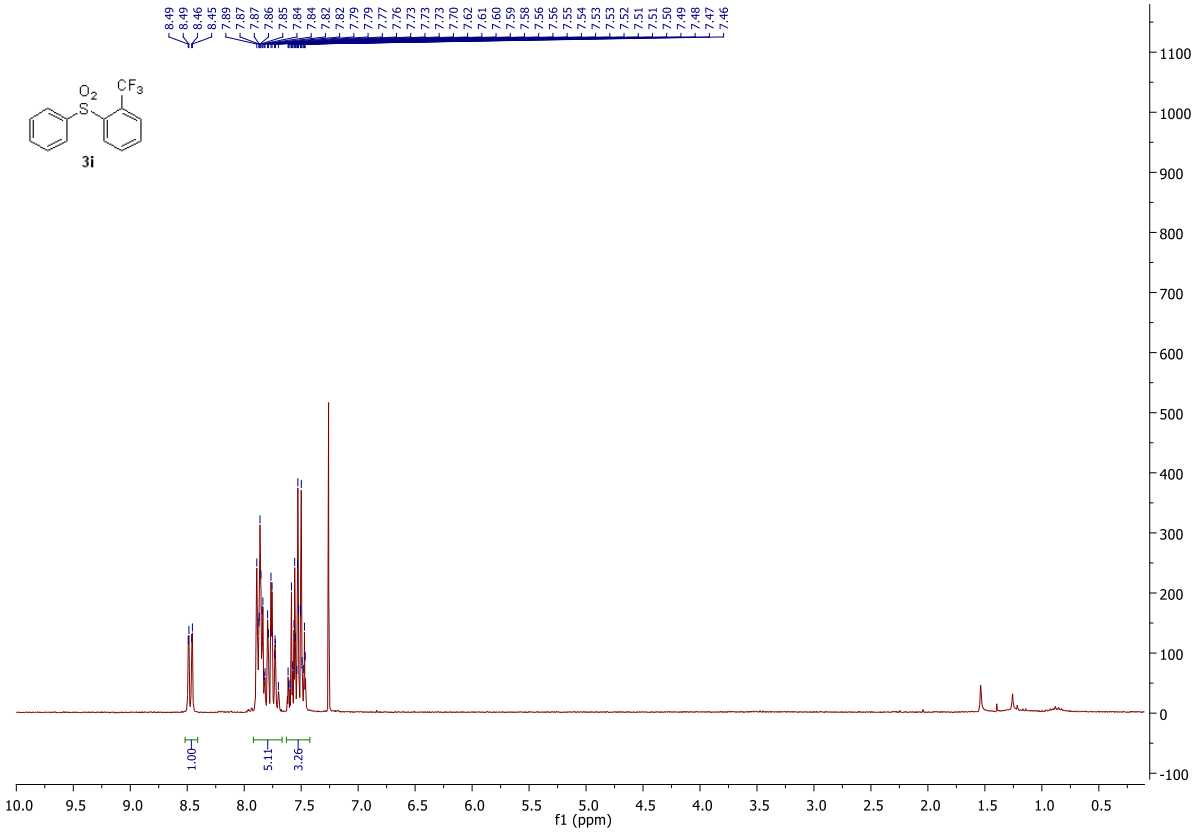
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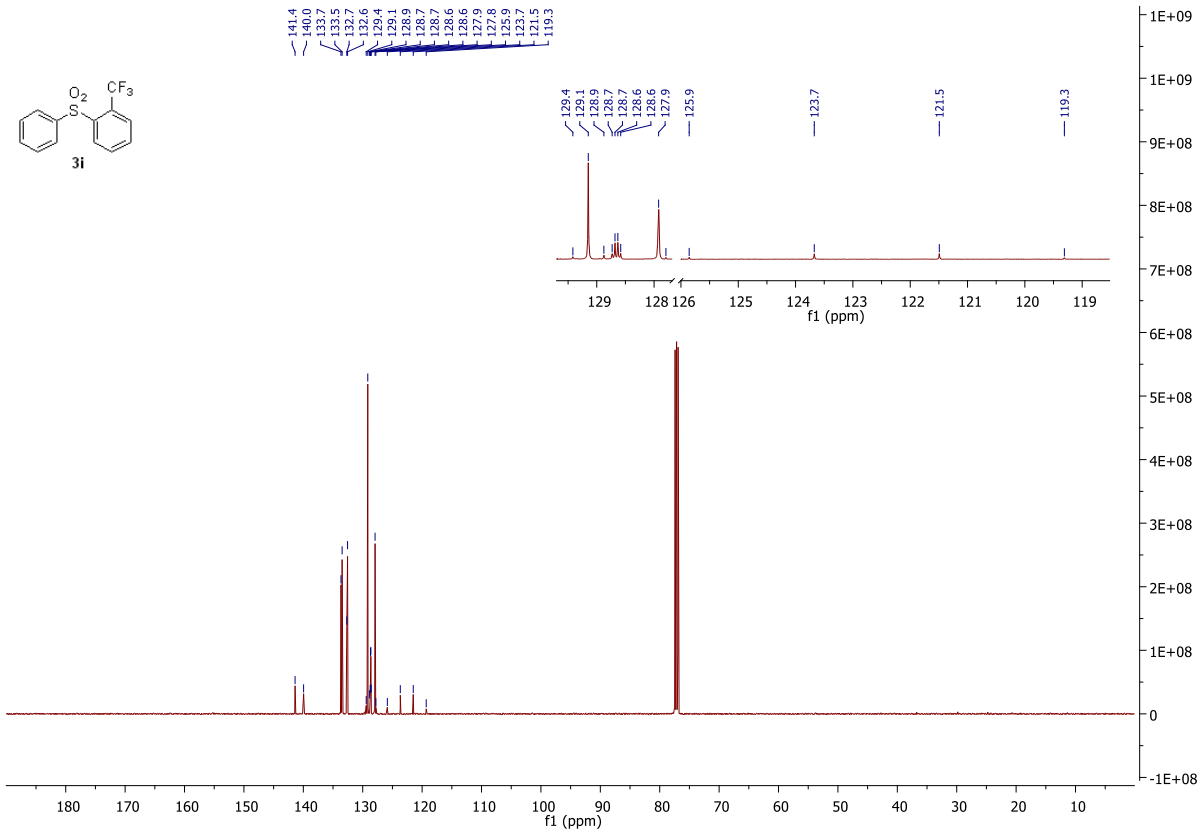
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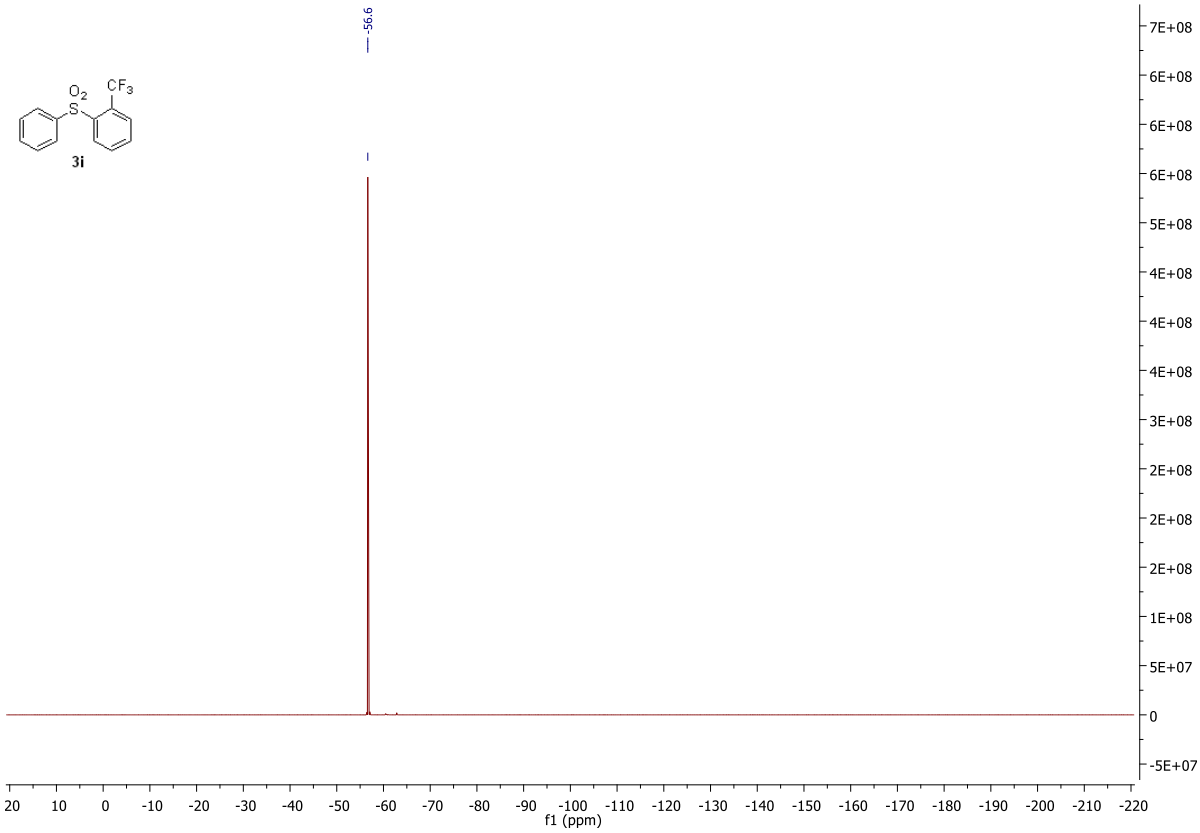
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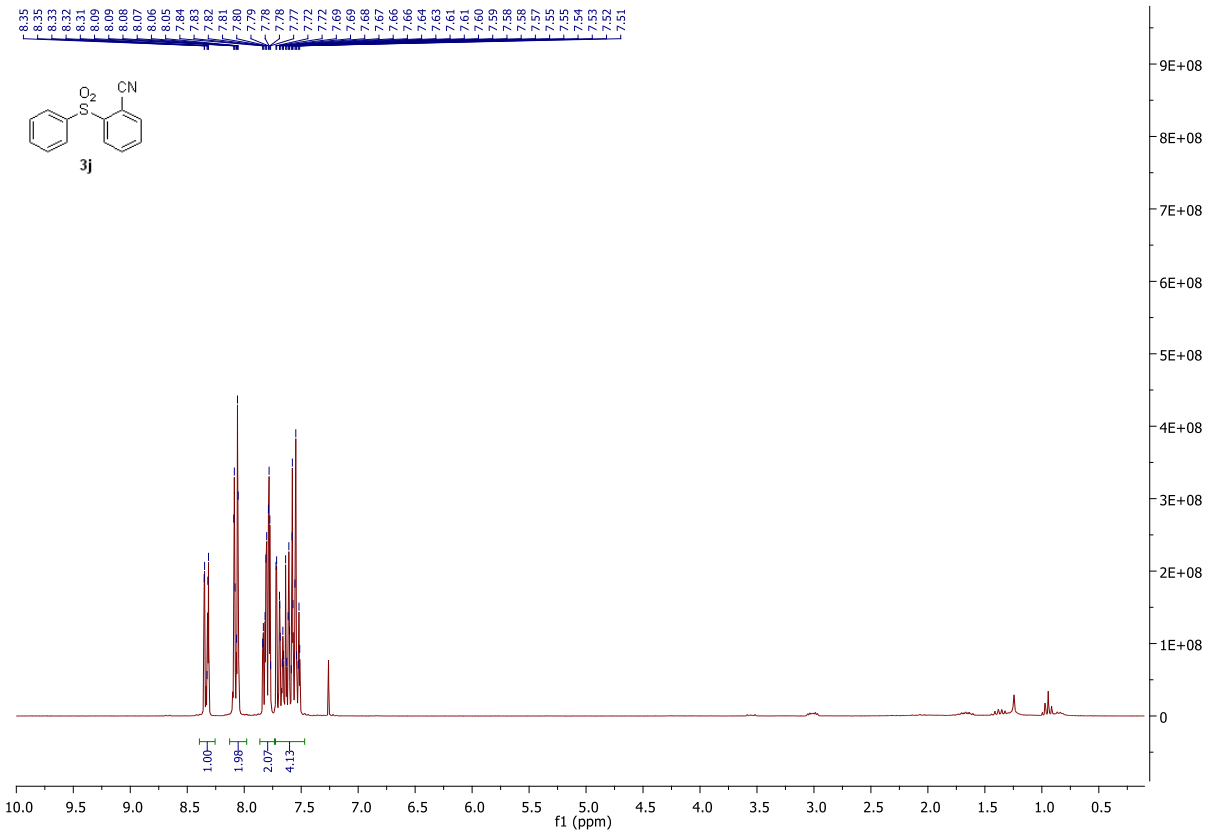
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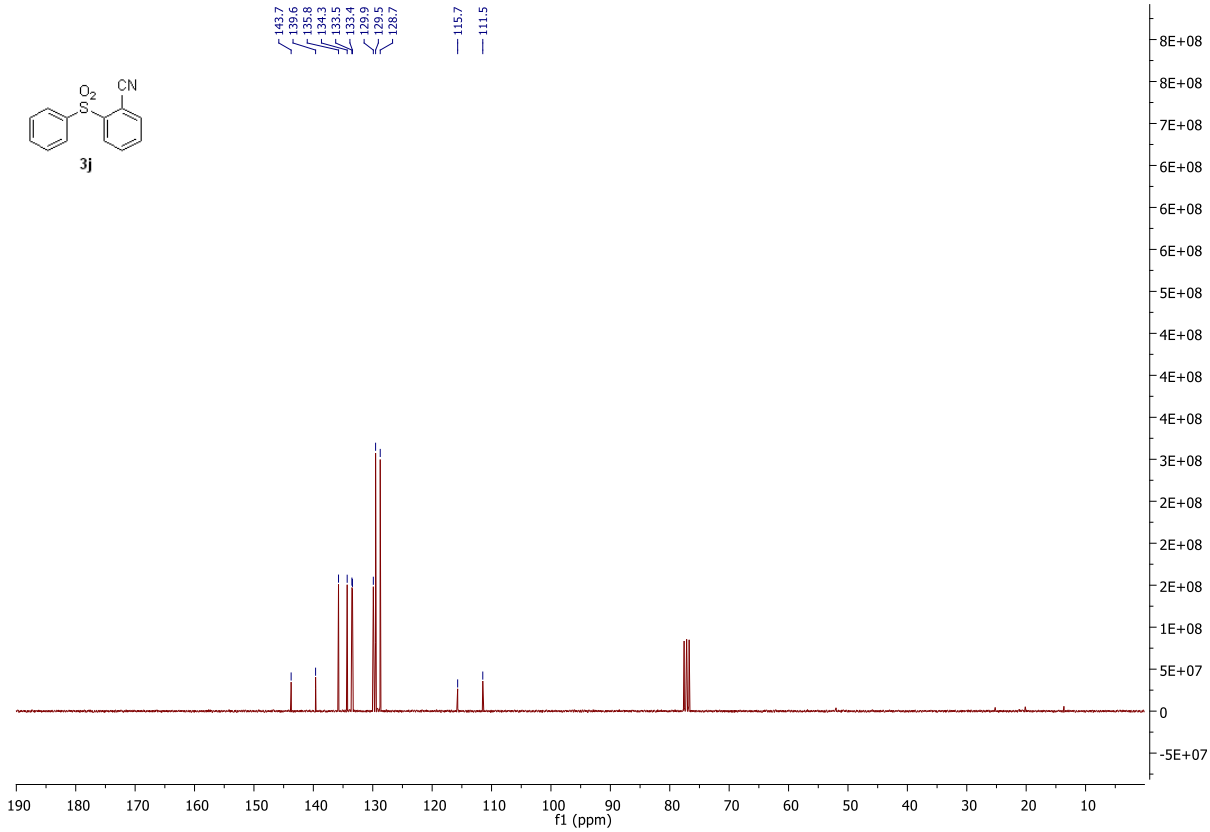
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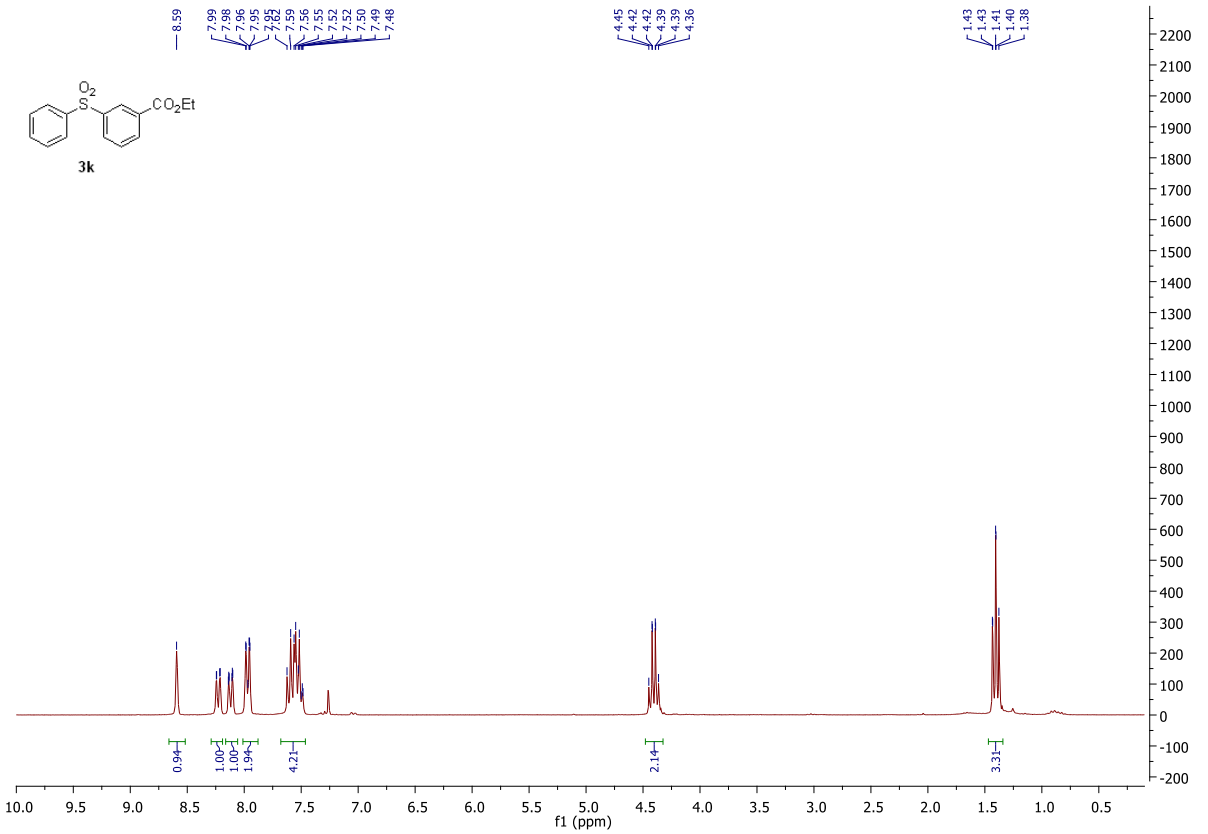
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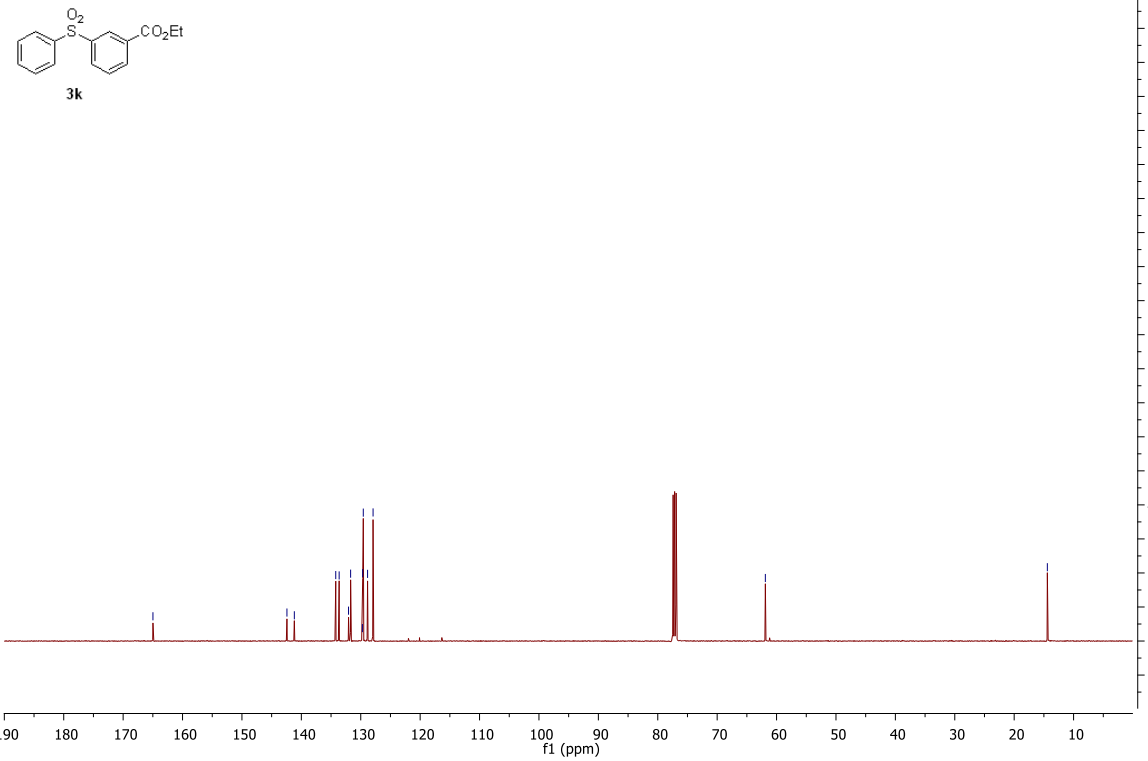
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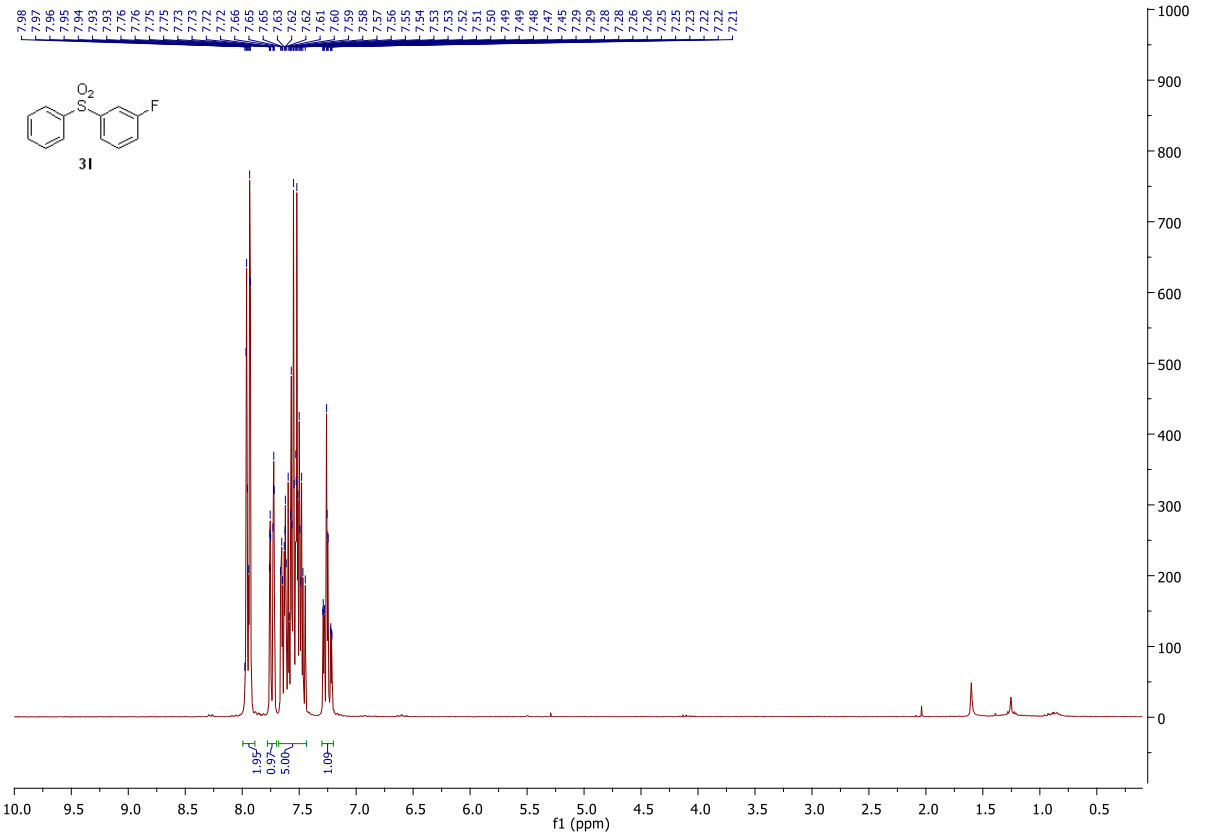
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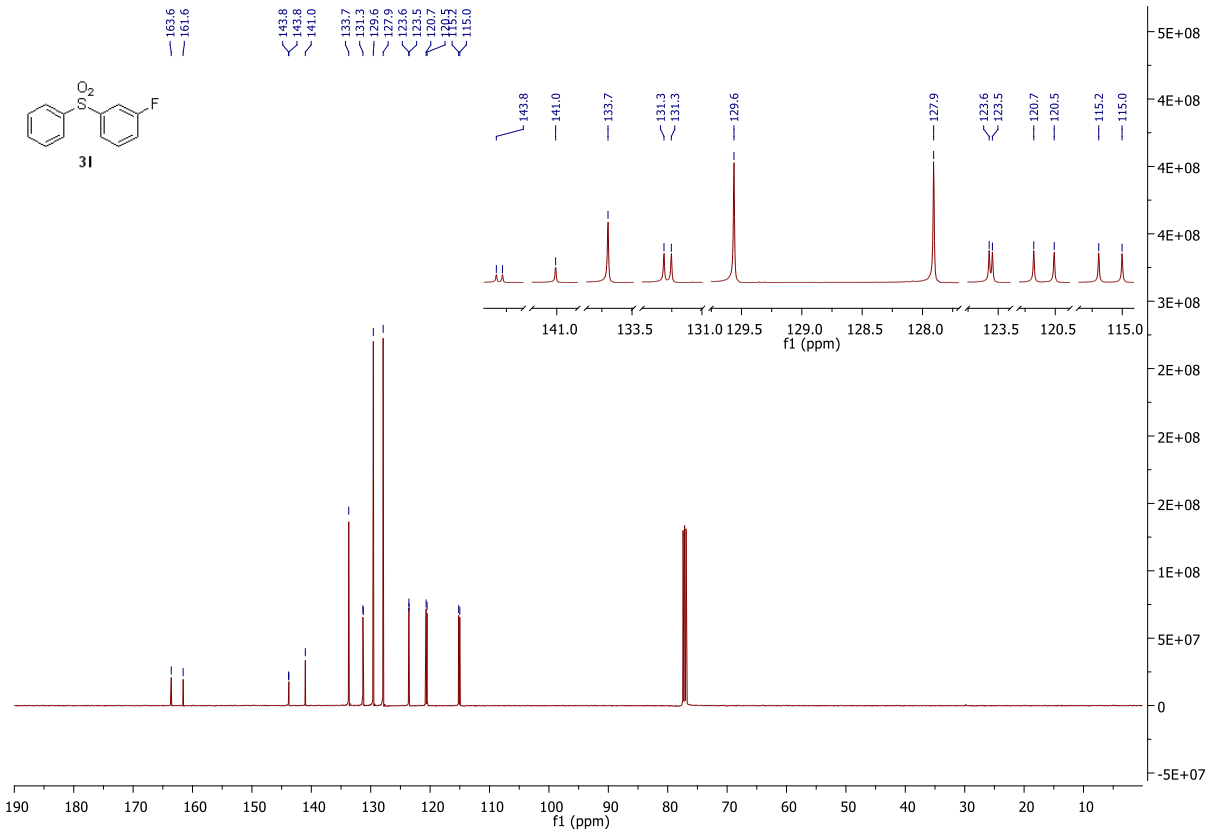
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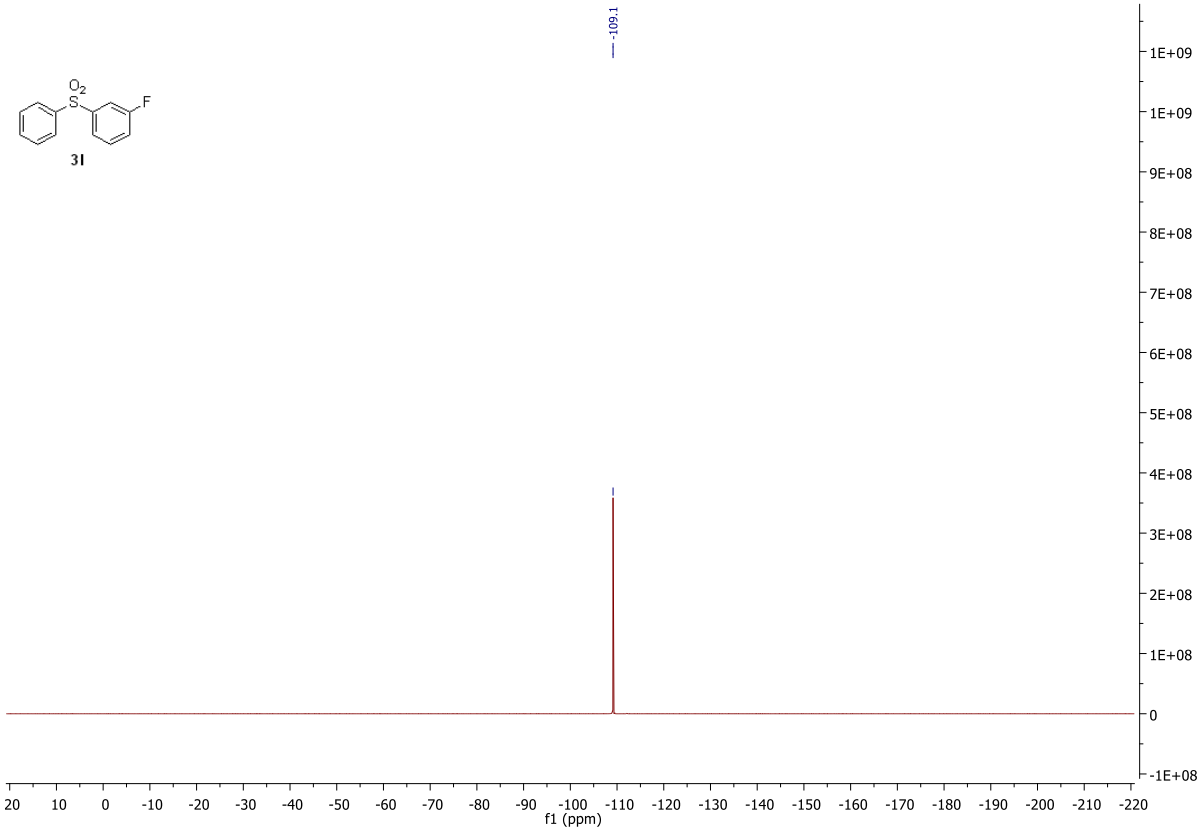
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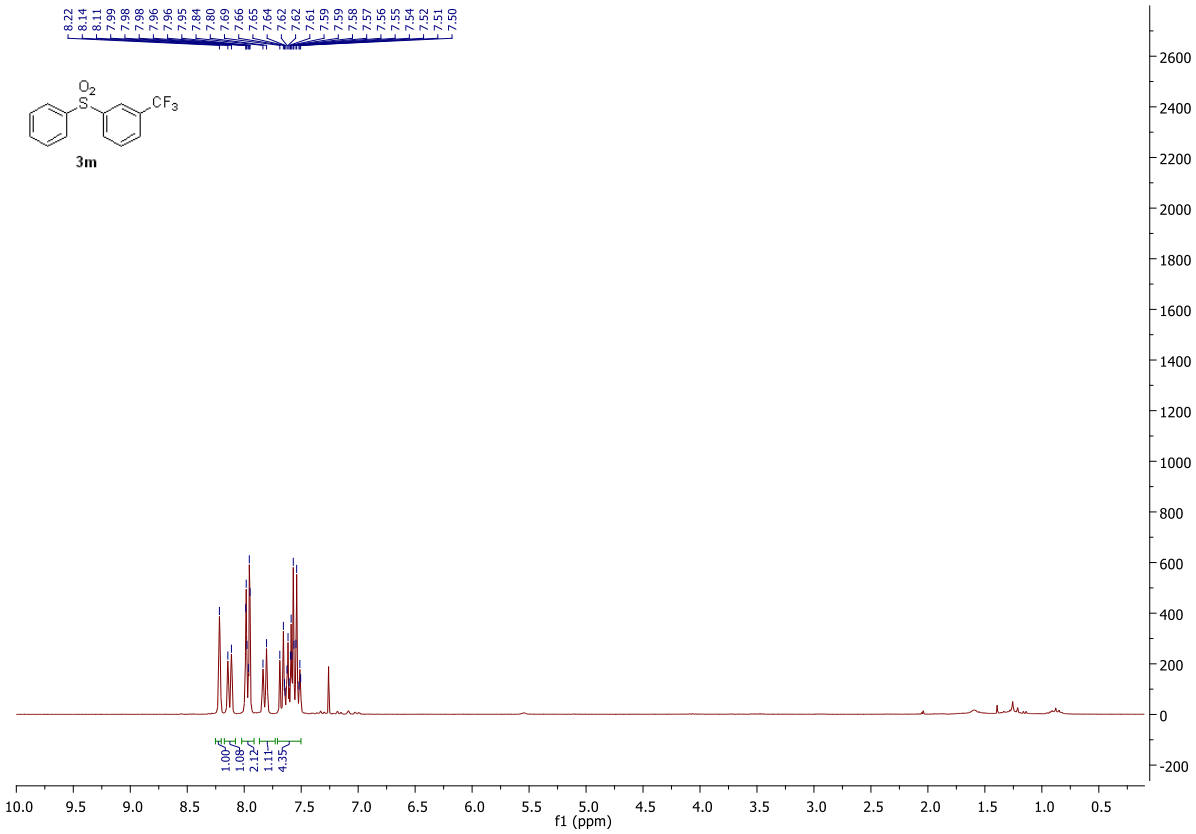
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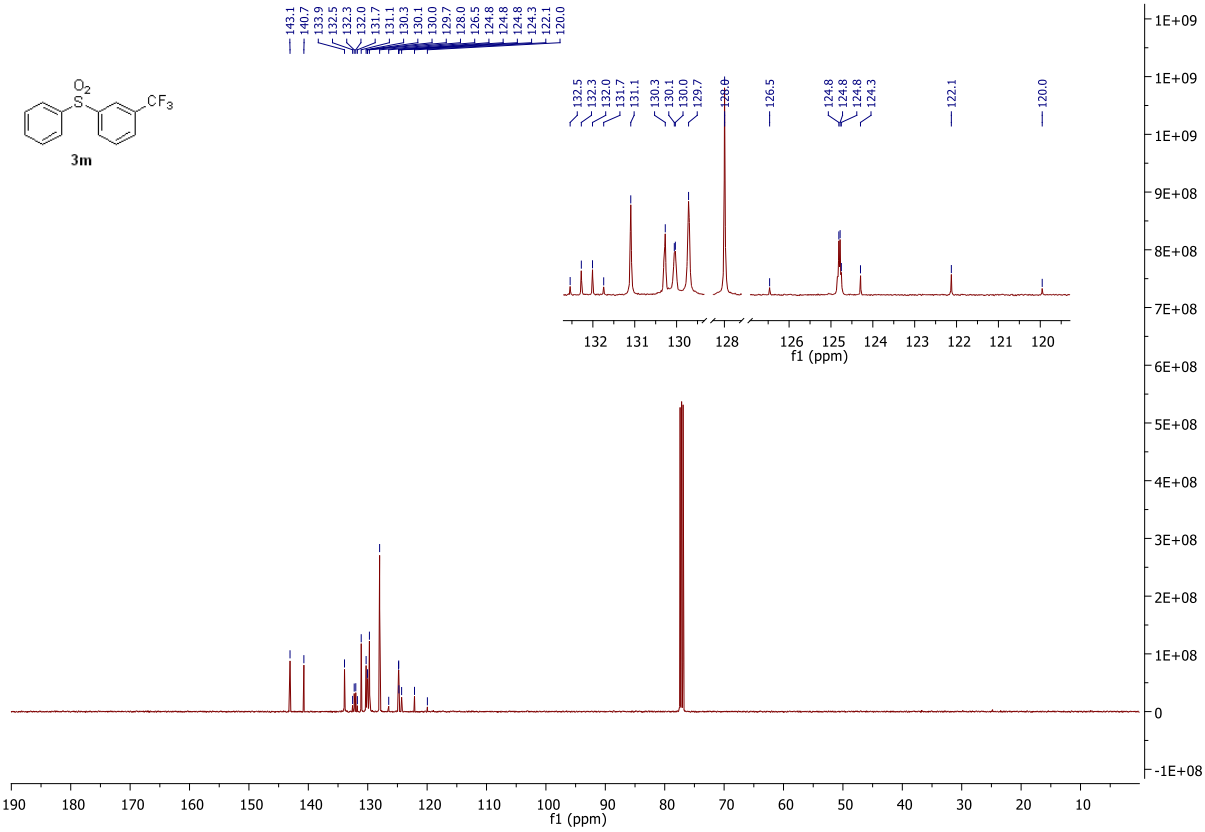
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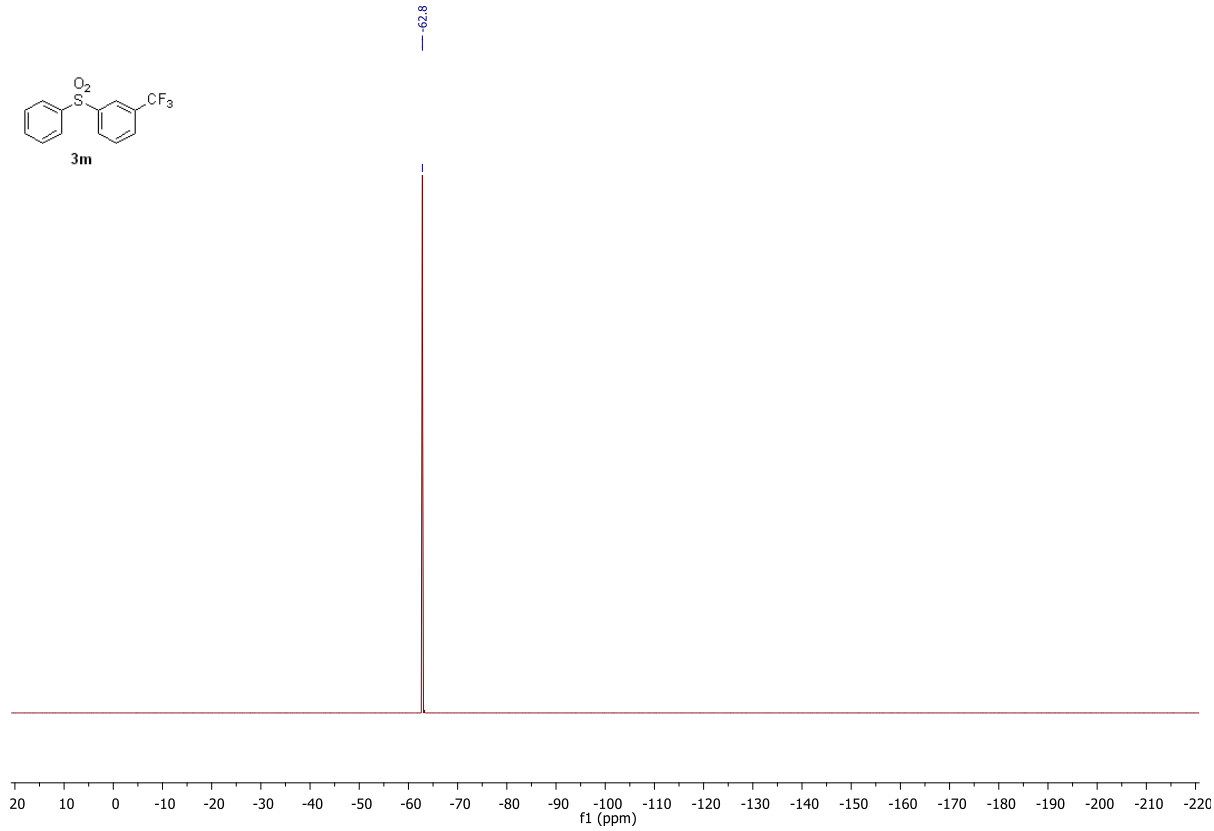
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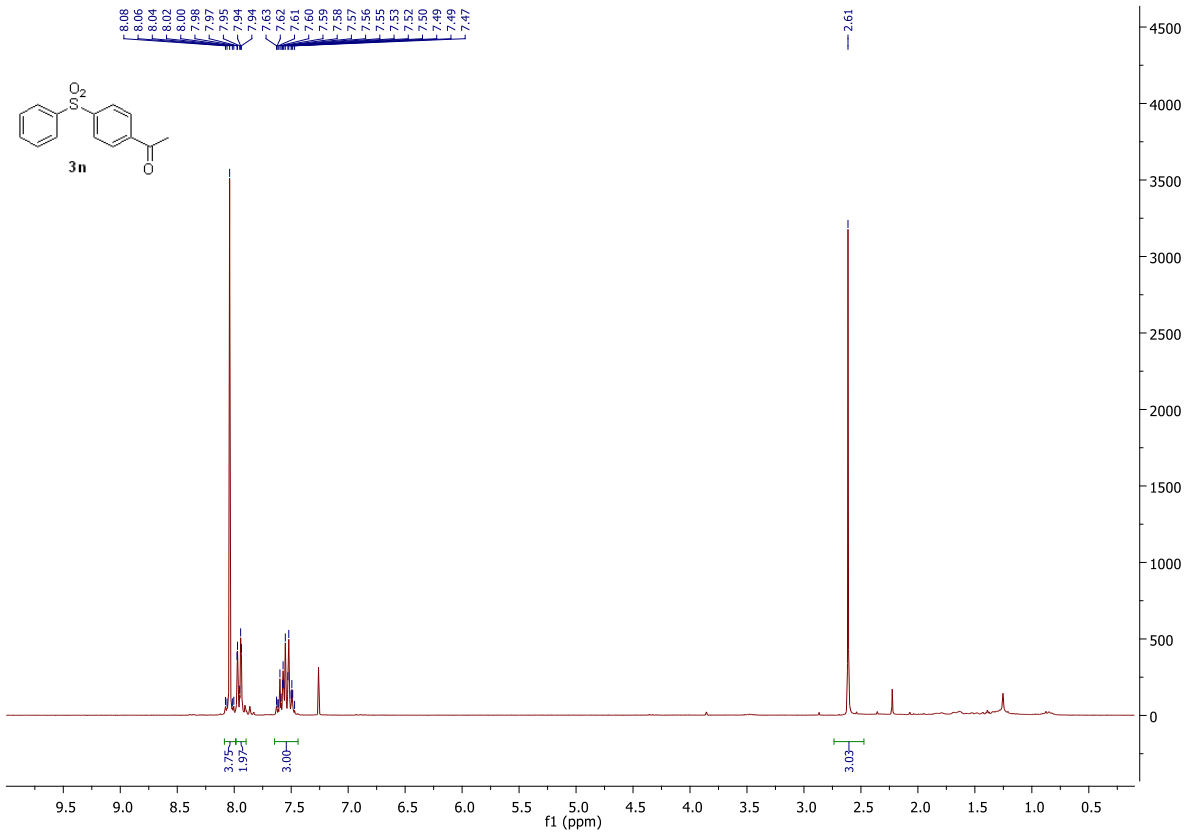
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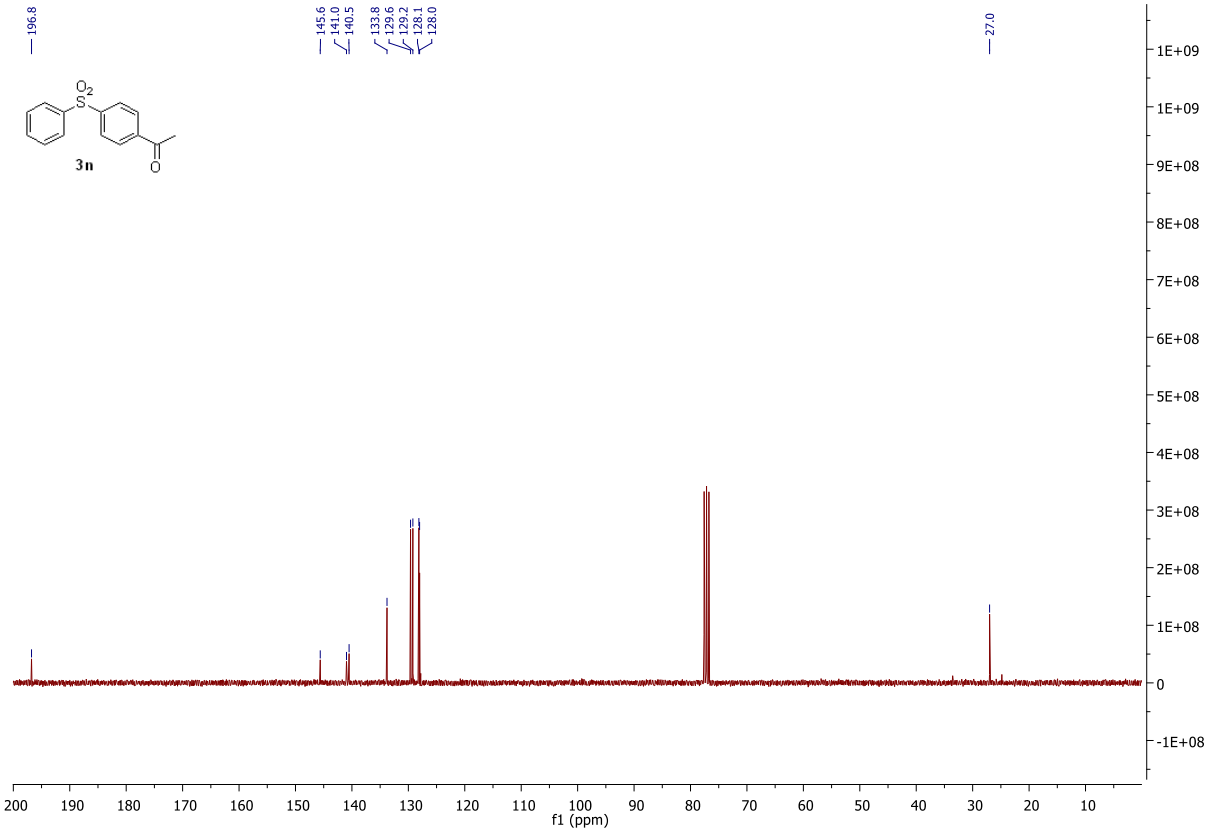
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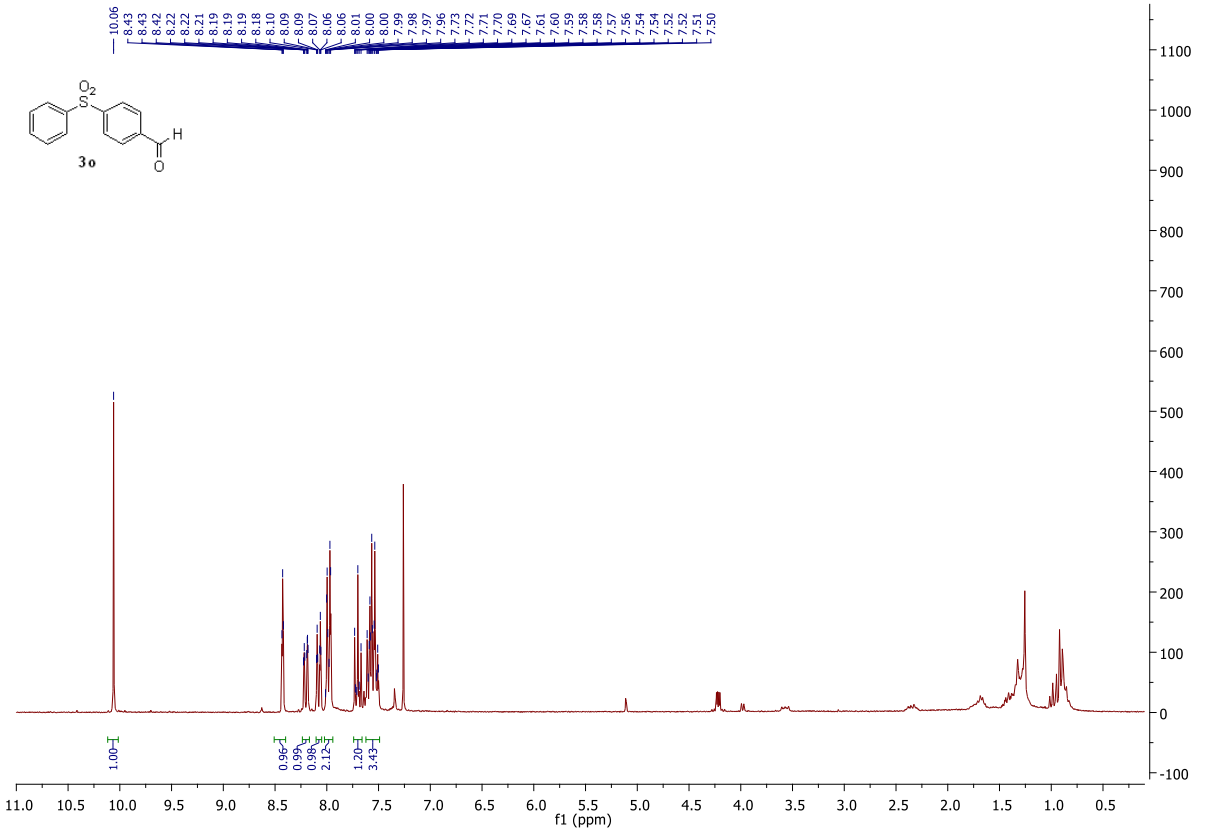
27.0
3n
f1 (ppm)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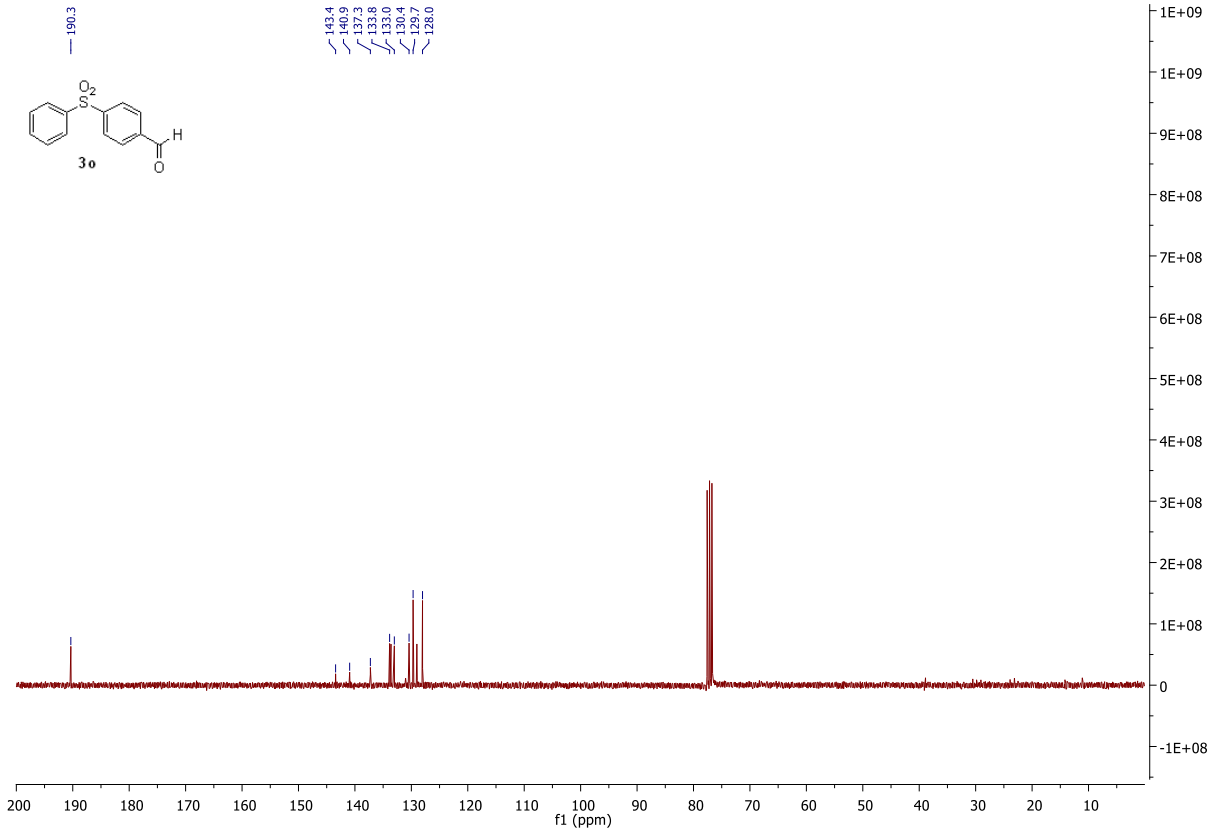
8.22
8.21
8.19
8.19
8.19
8.18
8.10
8.09
8.09
8.07
8.06
8.06
8.01
8.00
8.00
7.99
7.98
7.97
7.96
7.73
7.72
7.71
7.70
7.69
7.67
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.54
7.54
7.52
7.51
7.50
O2
S
H
O
3o
1.00
0.96
0.99
0.98
2.12
1.20
3.43
f1 (ppm)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143.4
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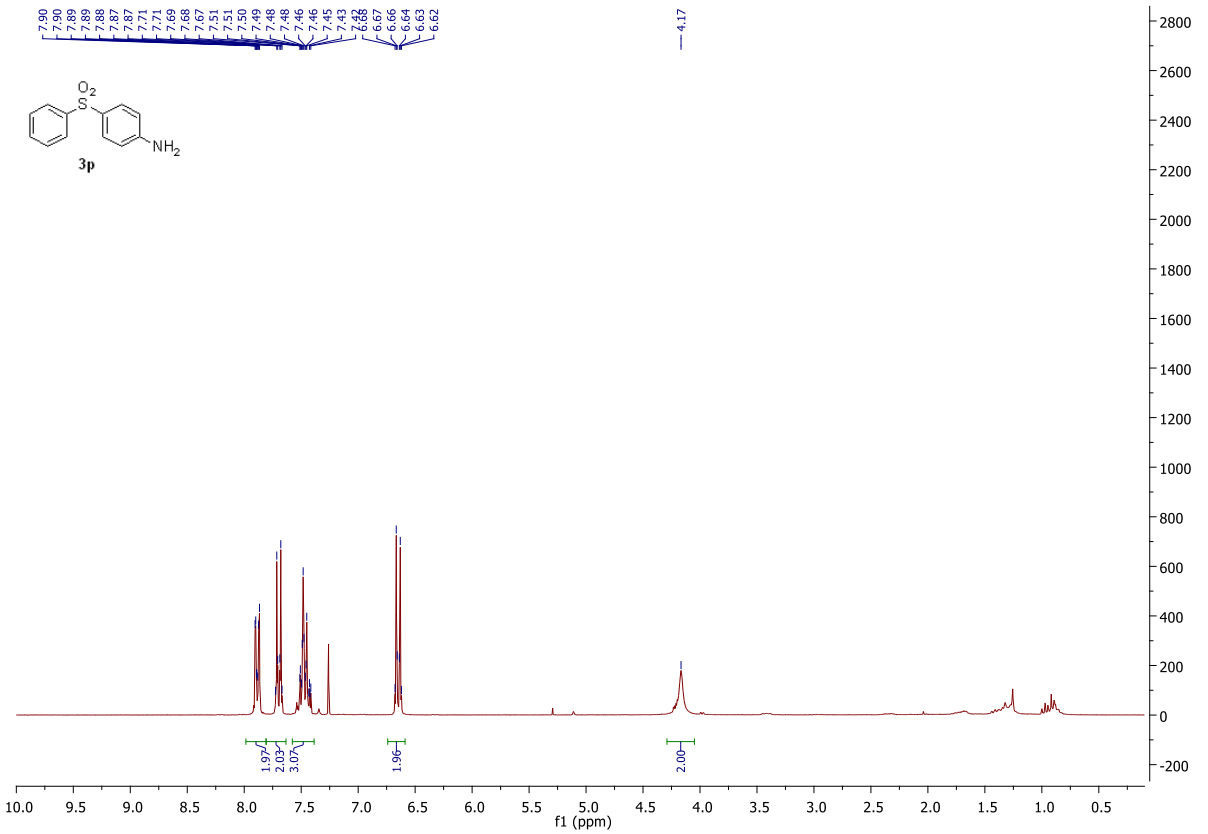
133.8
133.0
130.4
129.7
128.0
O2
S
H
O
3o
f1 (ppm)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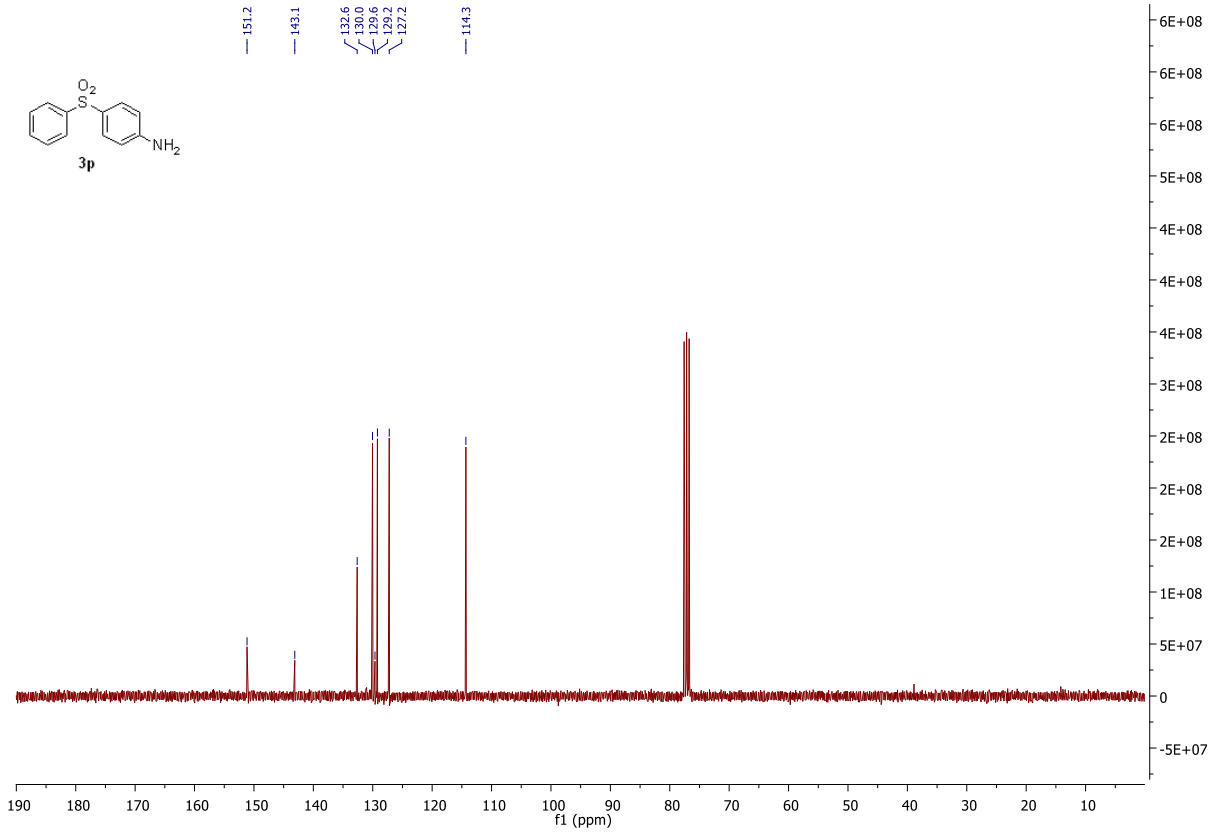
7.68
7.67
7.51
7.51
7.50
7.49
7.48
7.48
7.46
7.46
7.45
7.43
7.42
6.68
6.67
6.66
6.64
6.63
6.62
4.17
O2
S
NH2
3p
1.97
2.03
3.07
1.96
2.00
f1 (ppm)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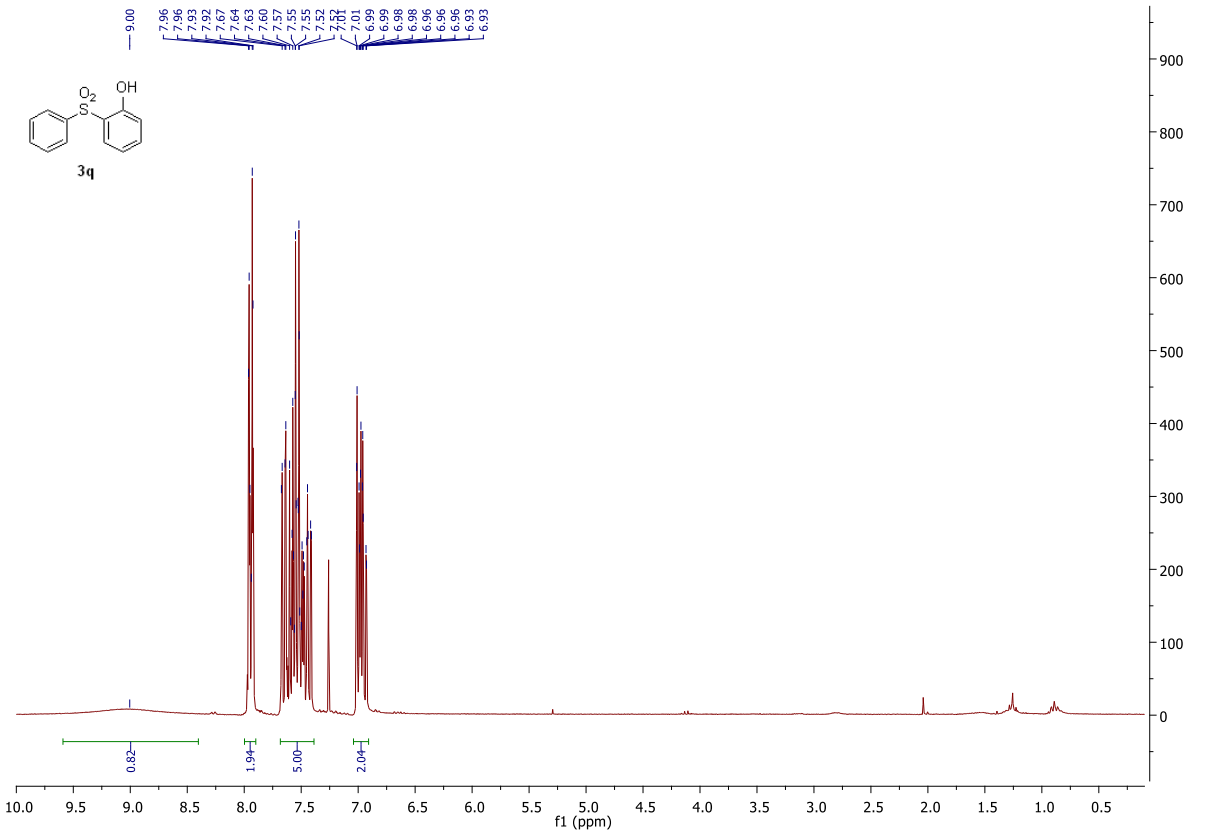
129.2
127.2
114.3
O2
S
NH2
3p
f1 (ppm)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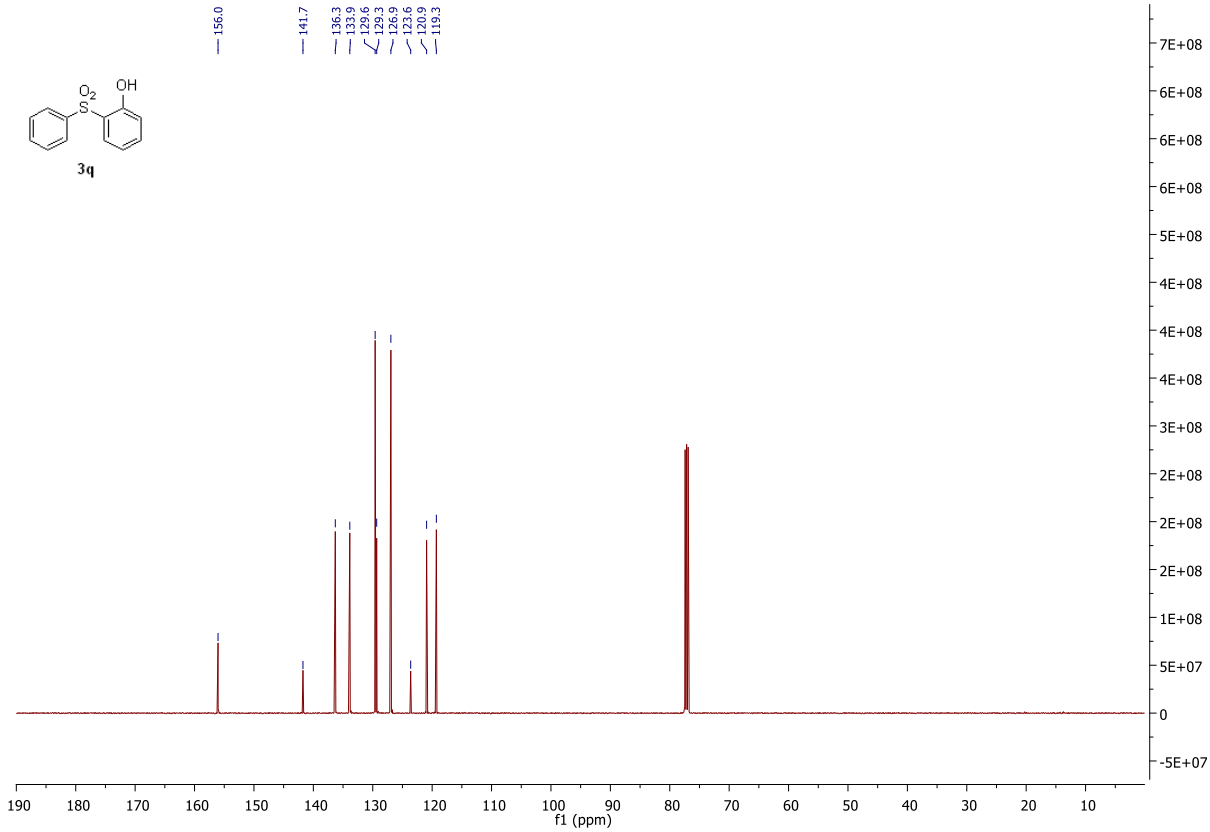
7.92
7.67
7.64
7.63
7.60
7.57
7.55
7.55
7.52
7.52
7.01
7.01
6.99
6.99
6.98
6.98
6.96
6.96
6.96
6.93
6.93
OH
3q
0.82
1.94
5.00
2.04
f1 (ppm)


156.0
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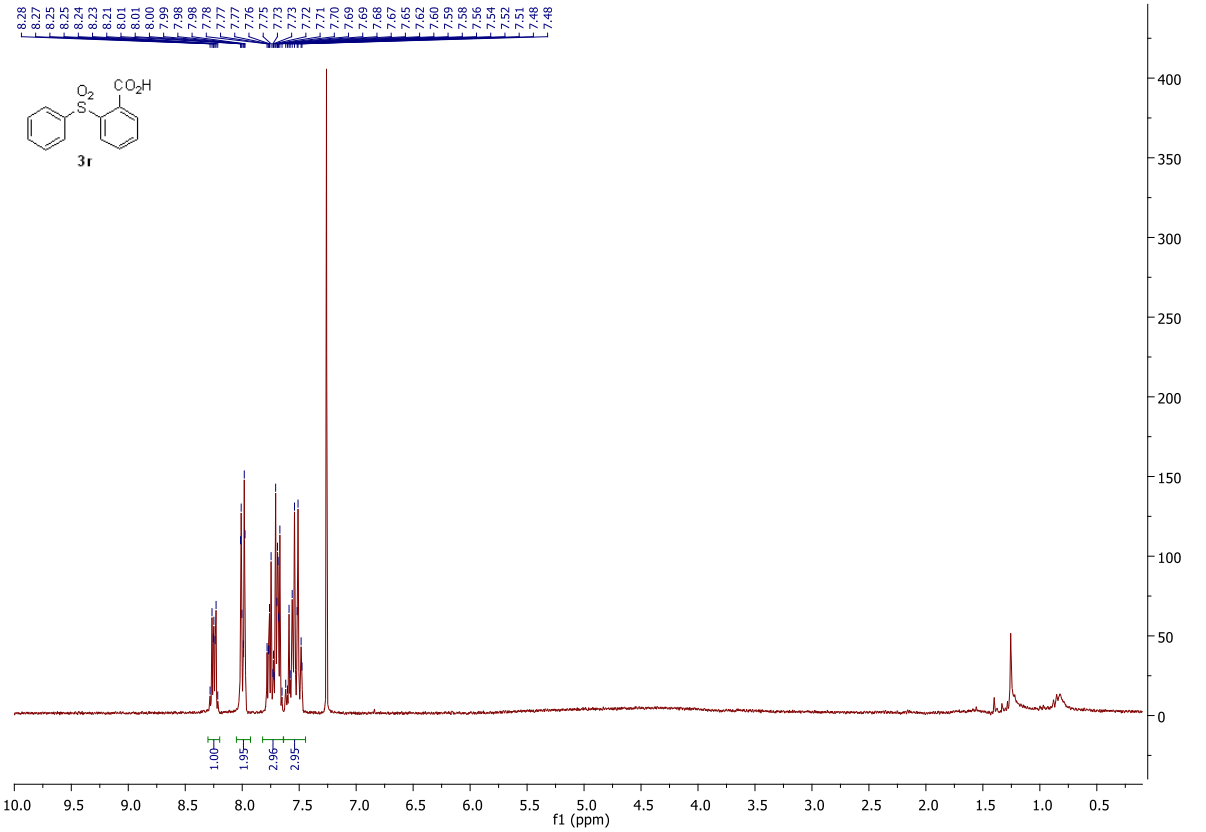
133.9
129.6
129.3
126.9
123.6
120.9
119.3
OH
3q
f1 (ppm)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7.99
7.99
7.98
7.98
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7.78
7.77
7.77
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7.76
7.75
7.75
7.73
7.73
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7.71
7.70
7.69
7.69
7.68
7.67
7.65
7.62
7.60
7.59
7.58
7.56
7.54
7.52
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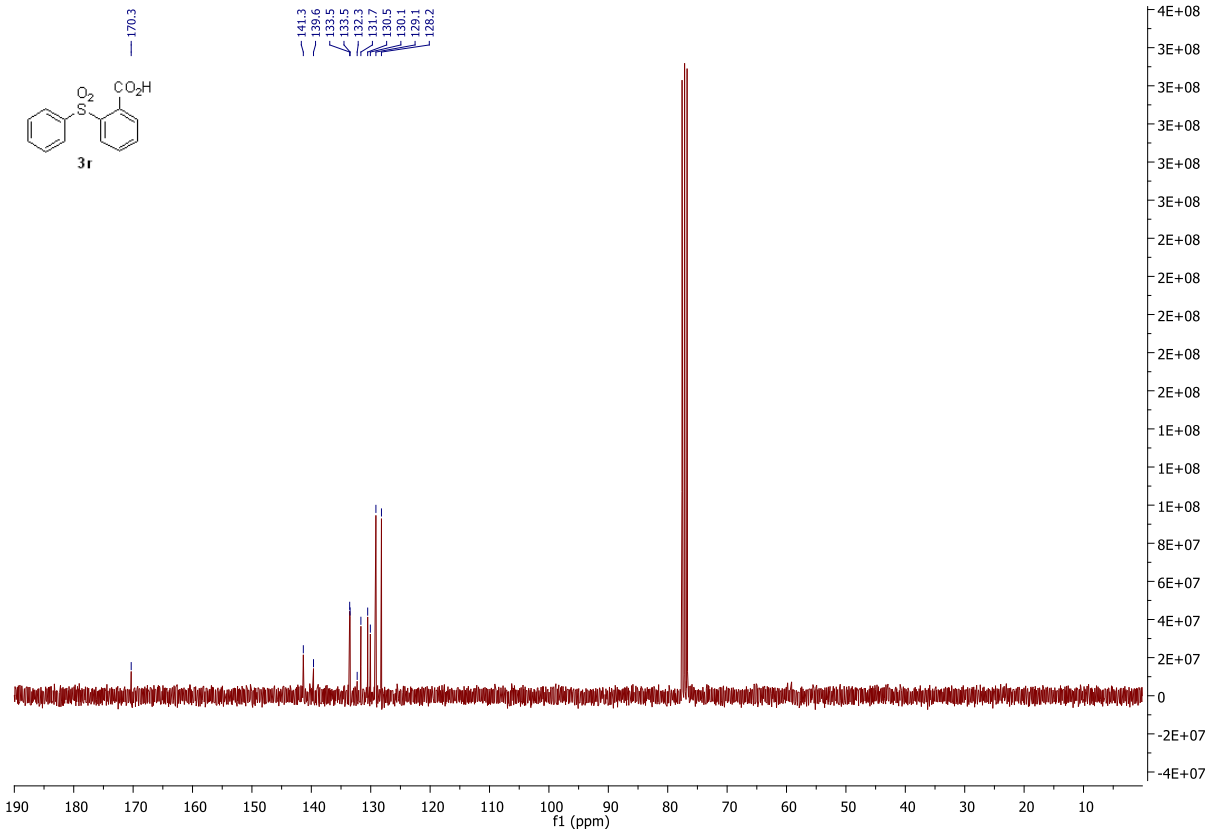
7.48
CO2H
O2
S
3r
1.00
1.95
2.96
2.95
f1 (ppm)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139.6
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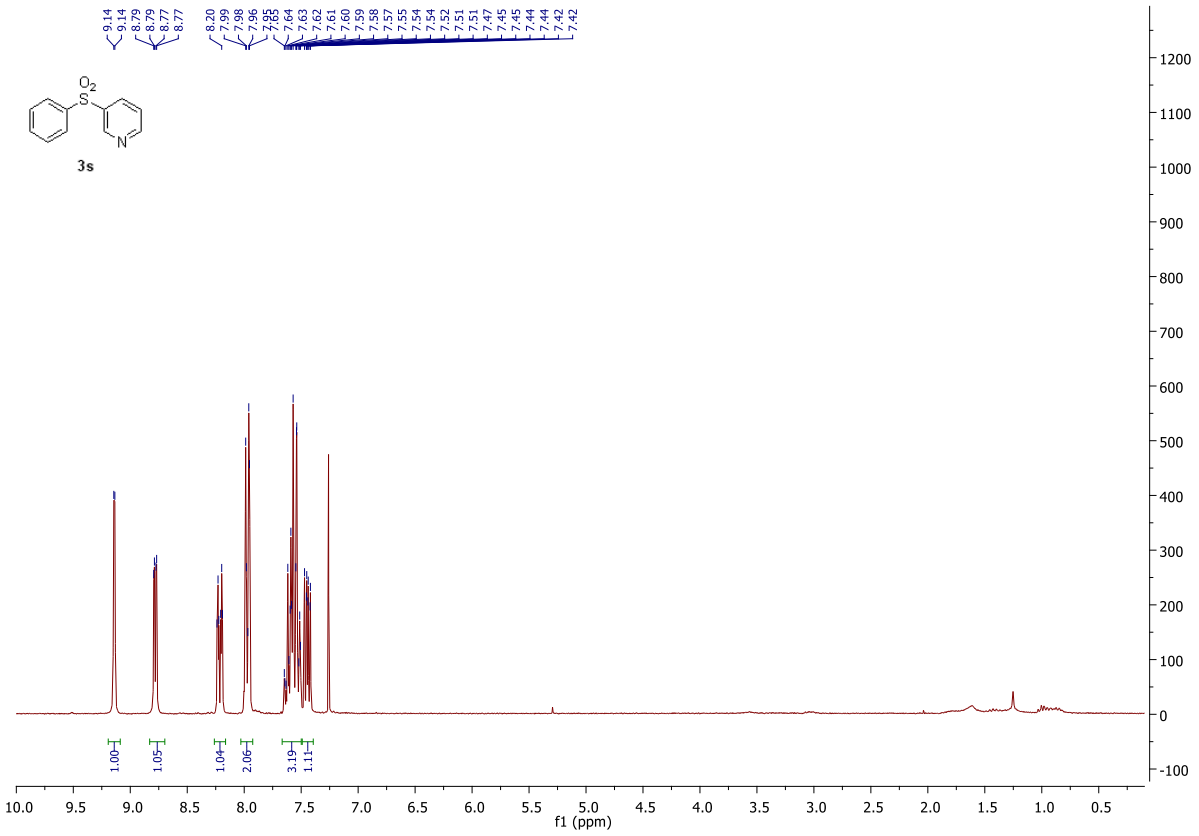
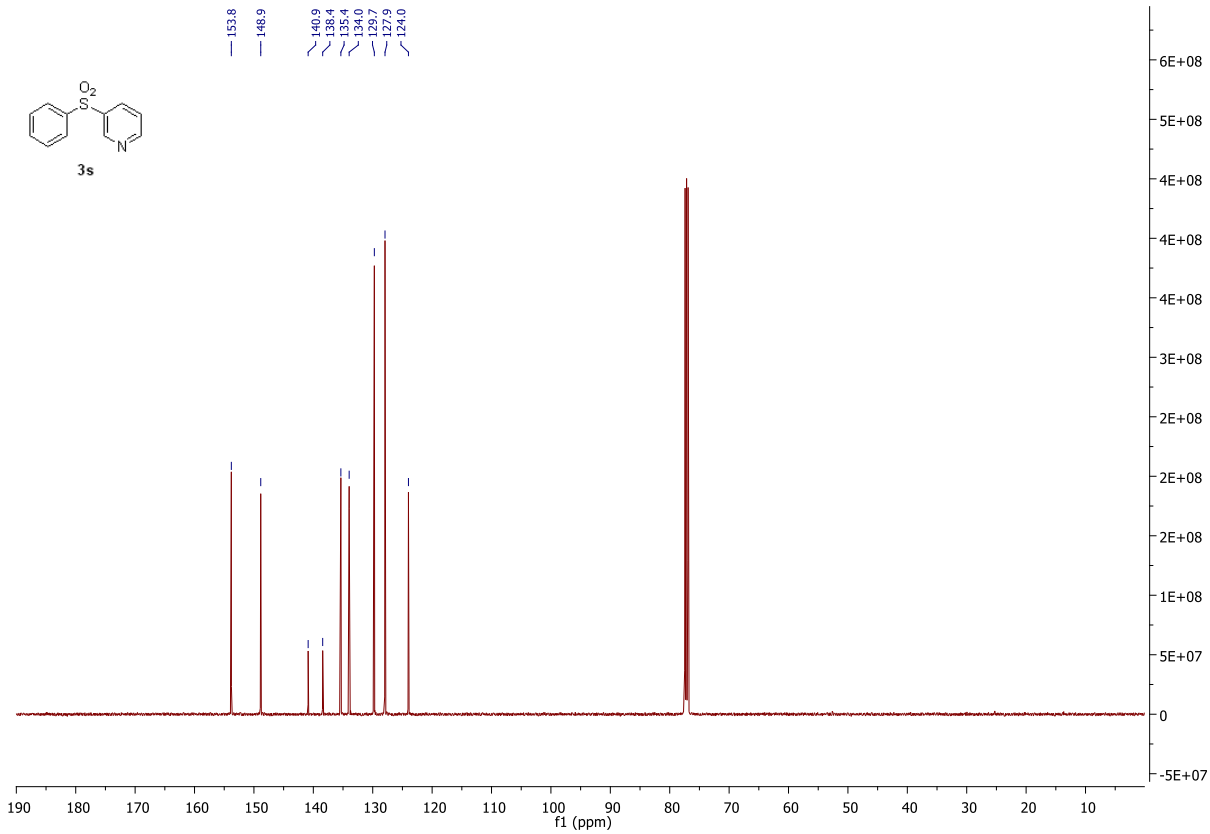
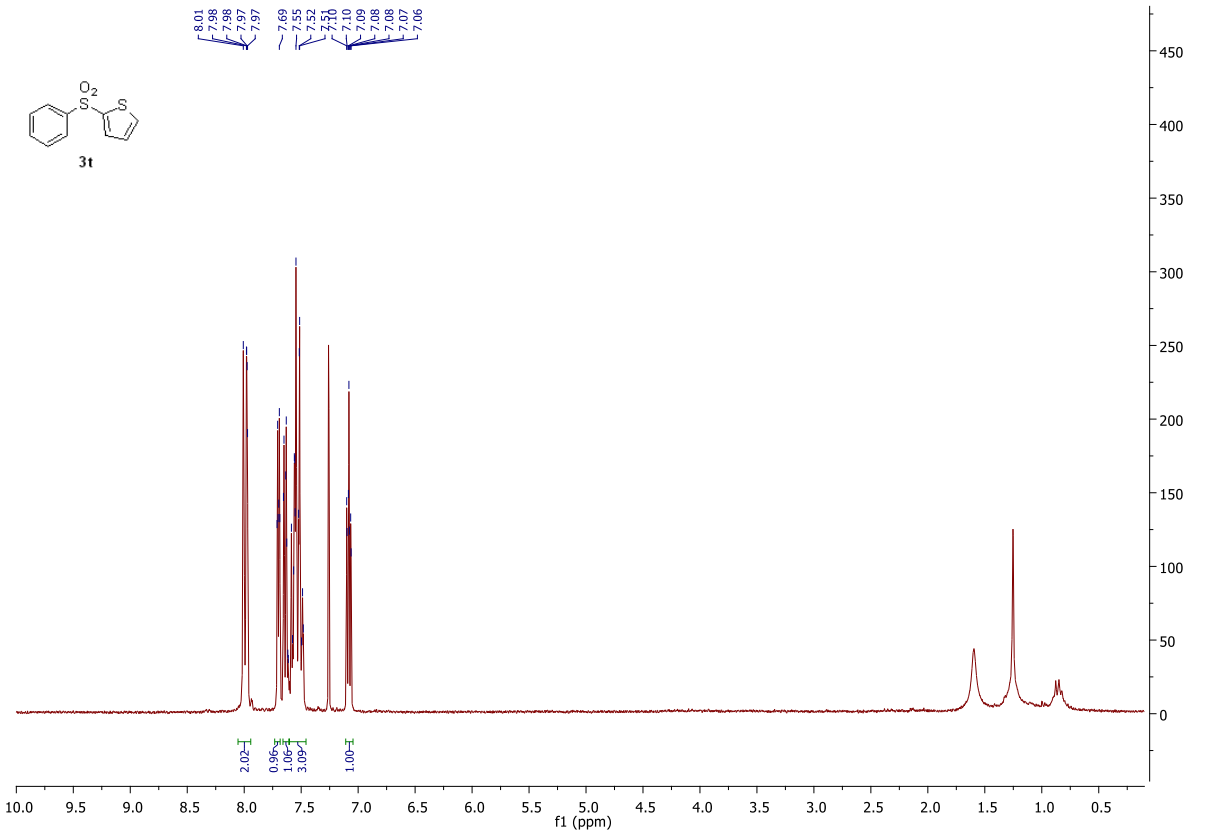
133.5
132.3
131.7
130.5
130.1
129.1
128.2
CO2H
O2
S
3r
f1 (ppm)


3s
f1 (ppm)


3s
f1 (ppm)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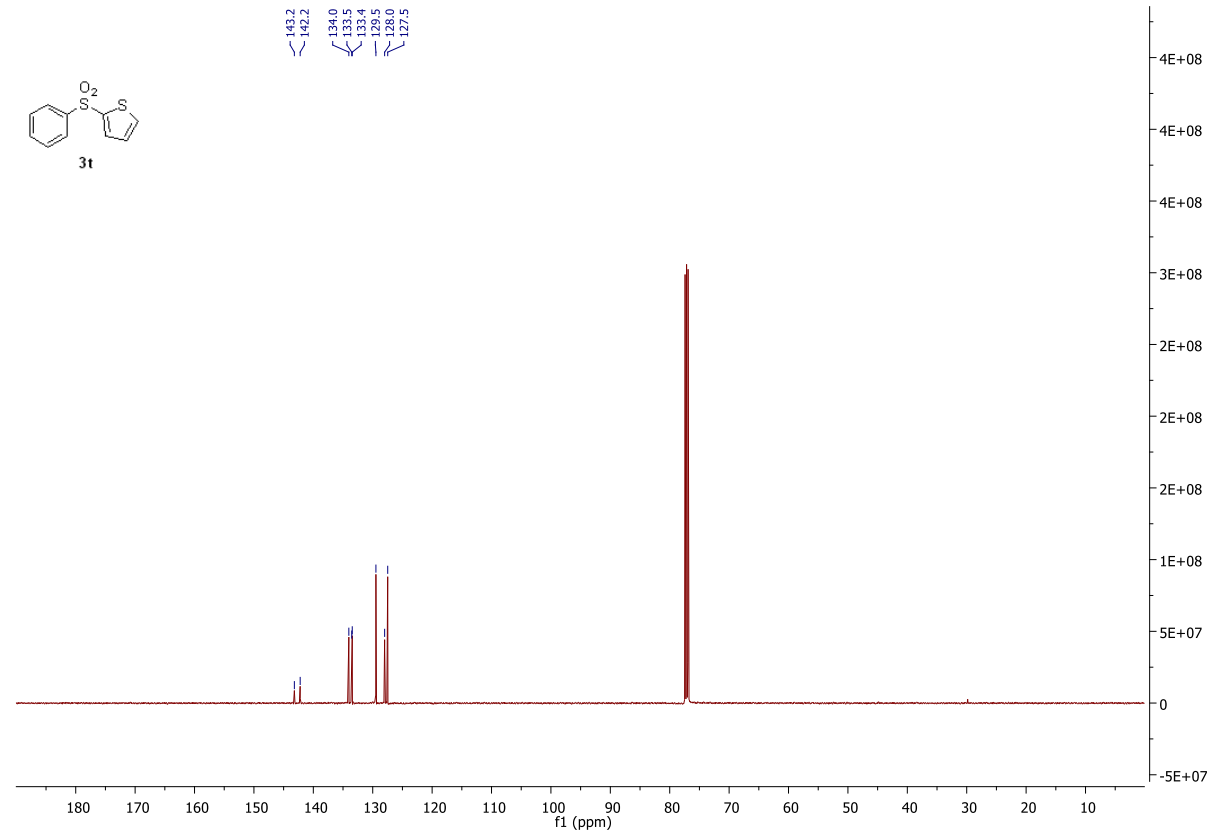
7.97
7.69
7.55
7.52
7.51
7.10
7.10
7.09
7.08
7.08
7.07
7.07
7.06
3t
2.02
0.96
1.06
3.09
1.00
f1 (ppm)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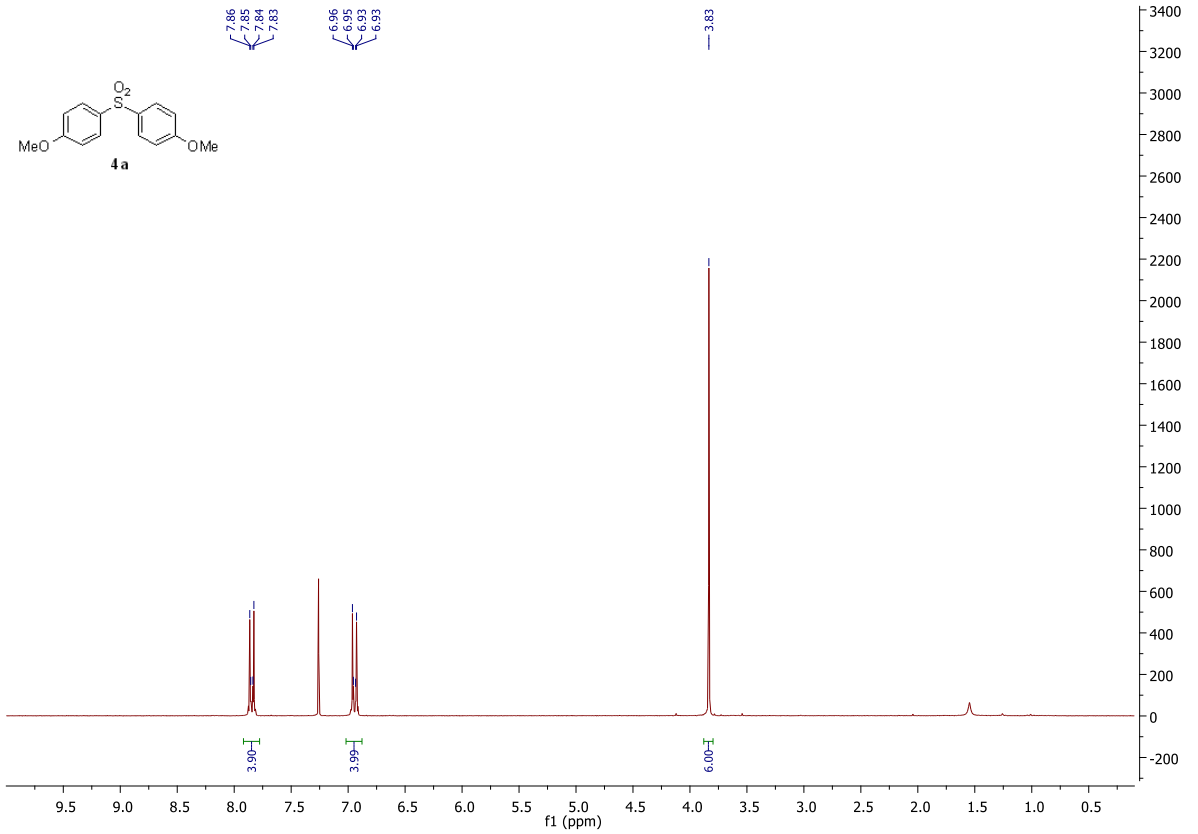
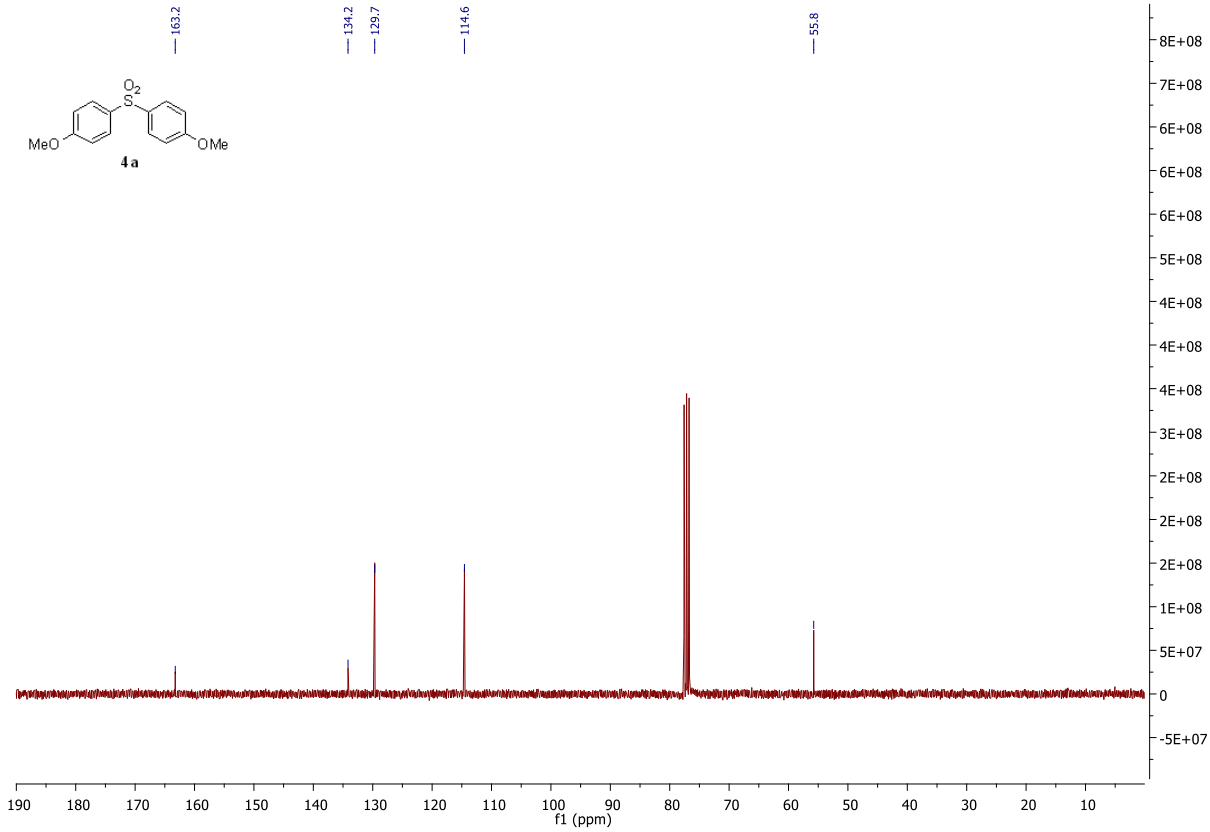
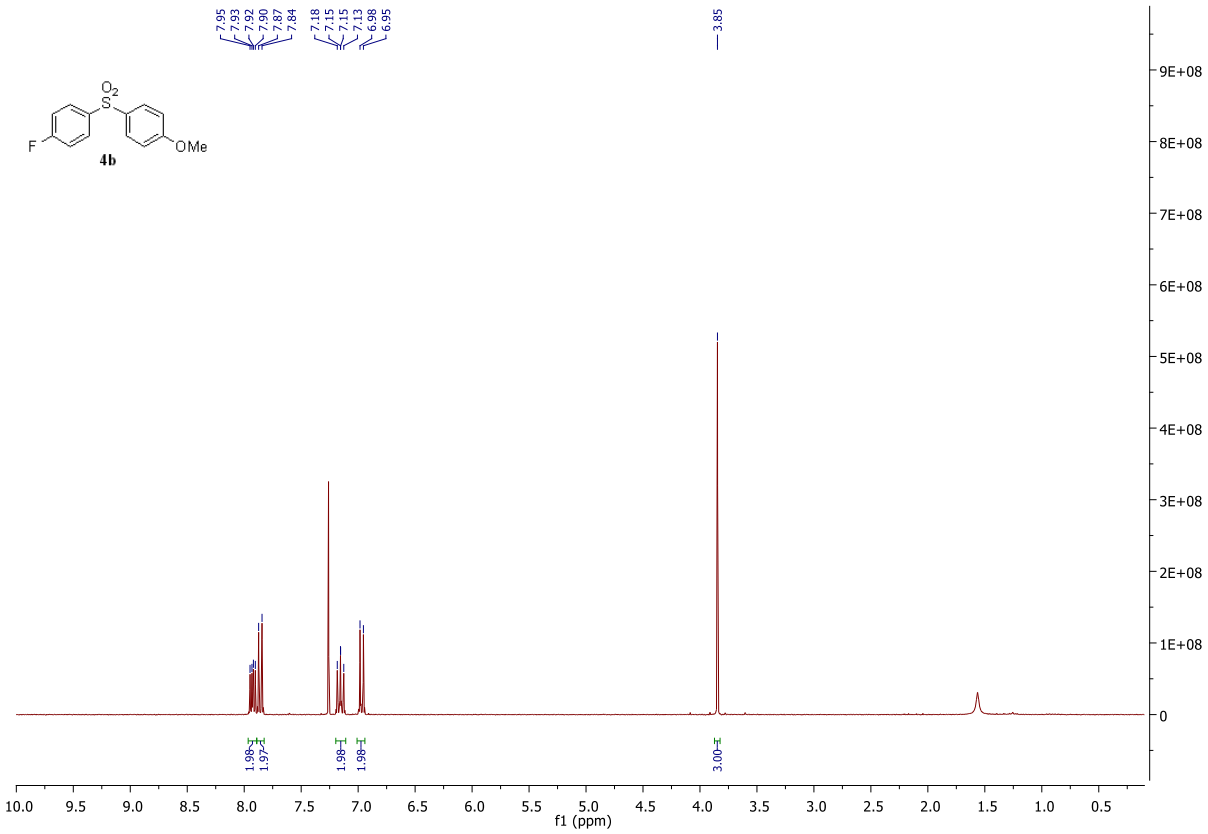
142.2
134.0
133.5
133.4
129.5
128.0
127.5
3t
f1 (ppm)


7.86
7.85
7.84
7.83
6.96
6.95
6.93
6.93
3.83
MeO
OMe
4a
3.90
3.99
6.00
f1 (ppm)


163.2
134.2
129.7
114.6
55.8
MeO
OMe
4a
f1 (ppm)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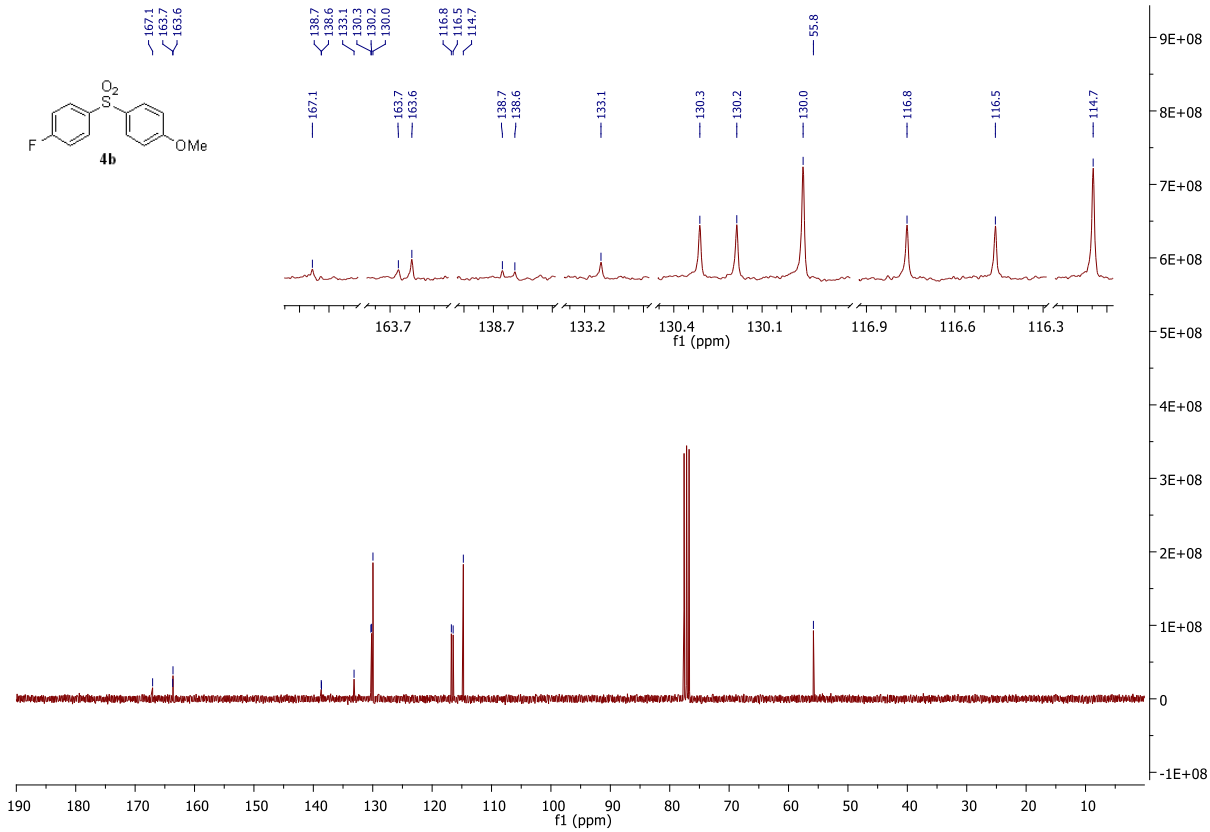
7.92
7.90
7.87
7.84
7.18
7.15
7.15
7.13
6.98
6.95
3.85
O2
S
F
OMe
4b
1.98
1.97
1.98
1.98
3.00
f1 (ppm)


167.1
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163.6
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138.6
133.1
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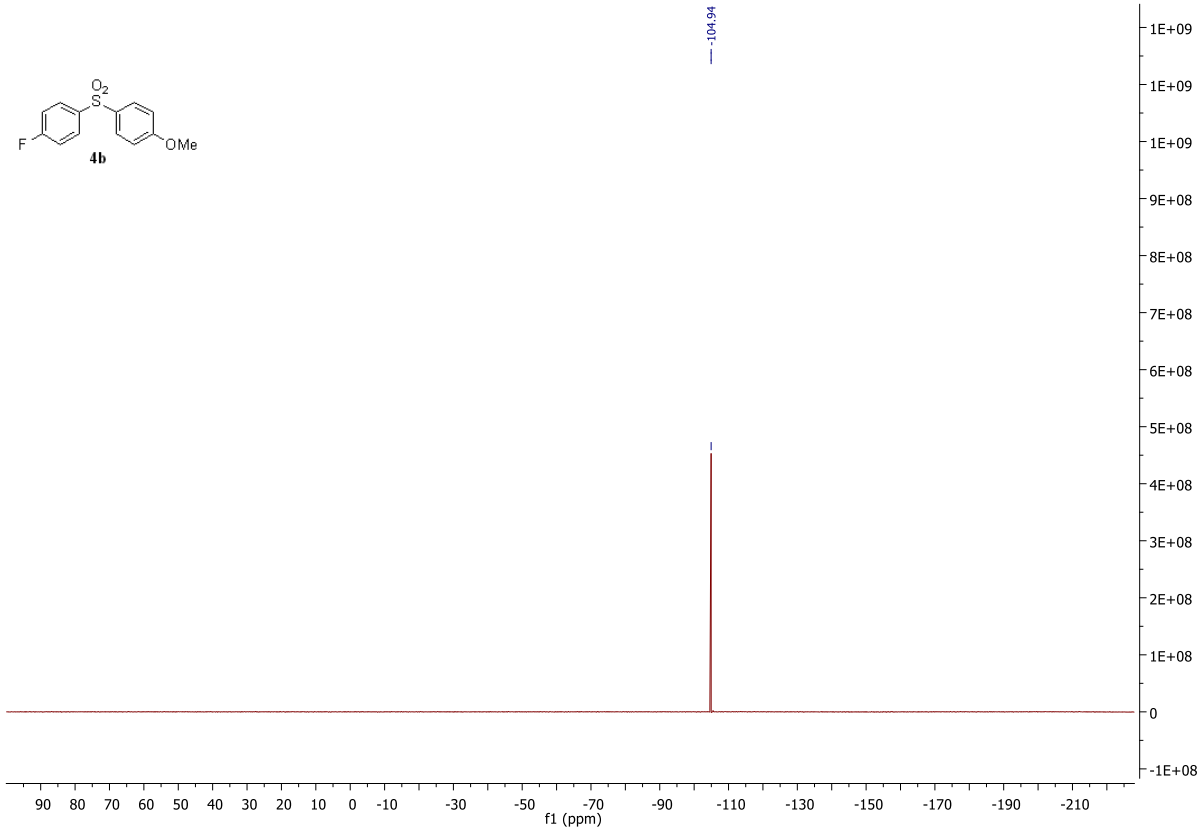
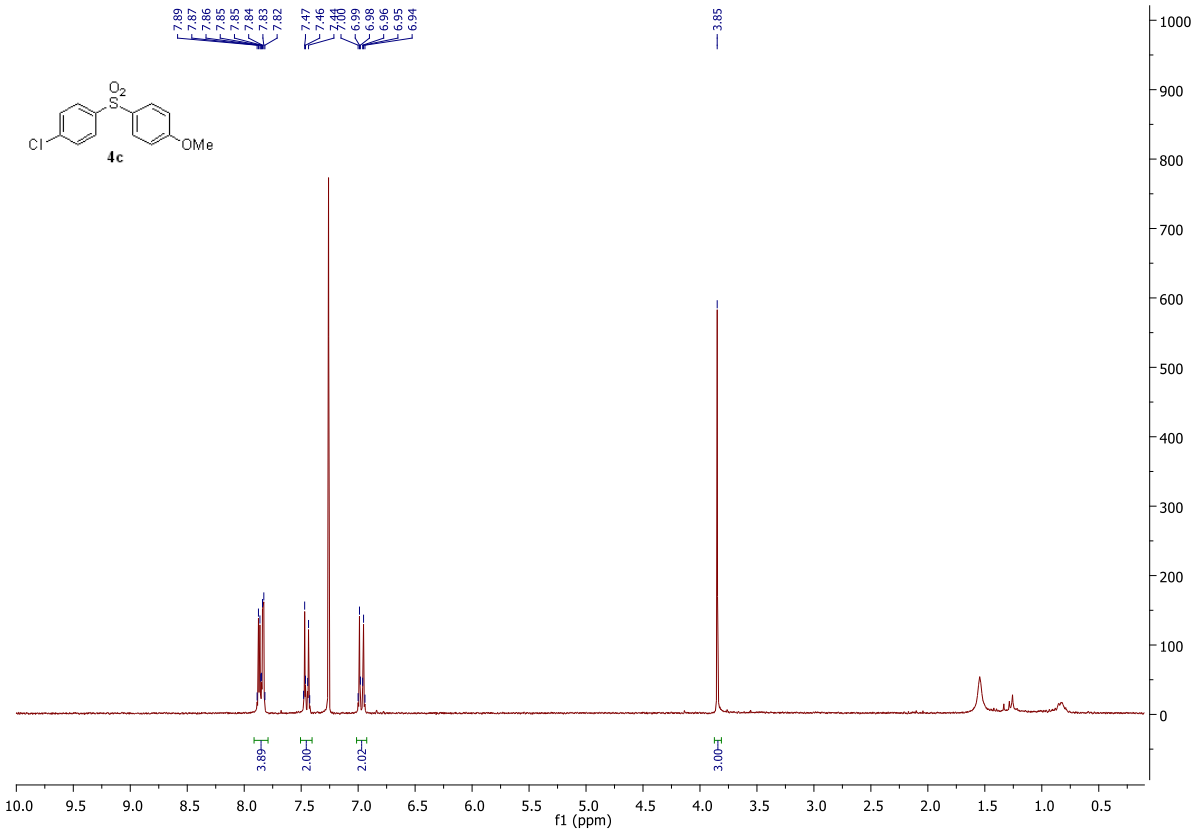
130.0
116.8
116.5
114.7
55.8
O2
S
F
OMe
4b
f1 (ppm)


-104.94
F
OMe
4b
f1 (ppm)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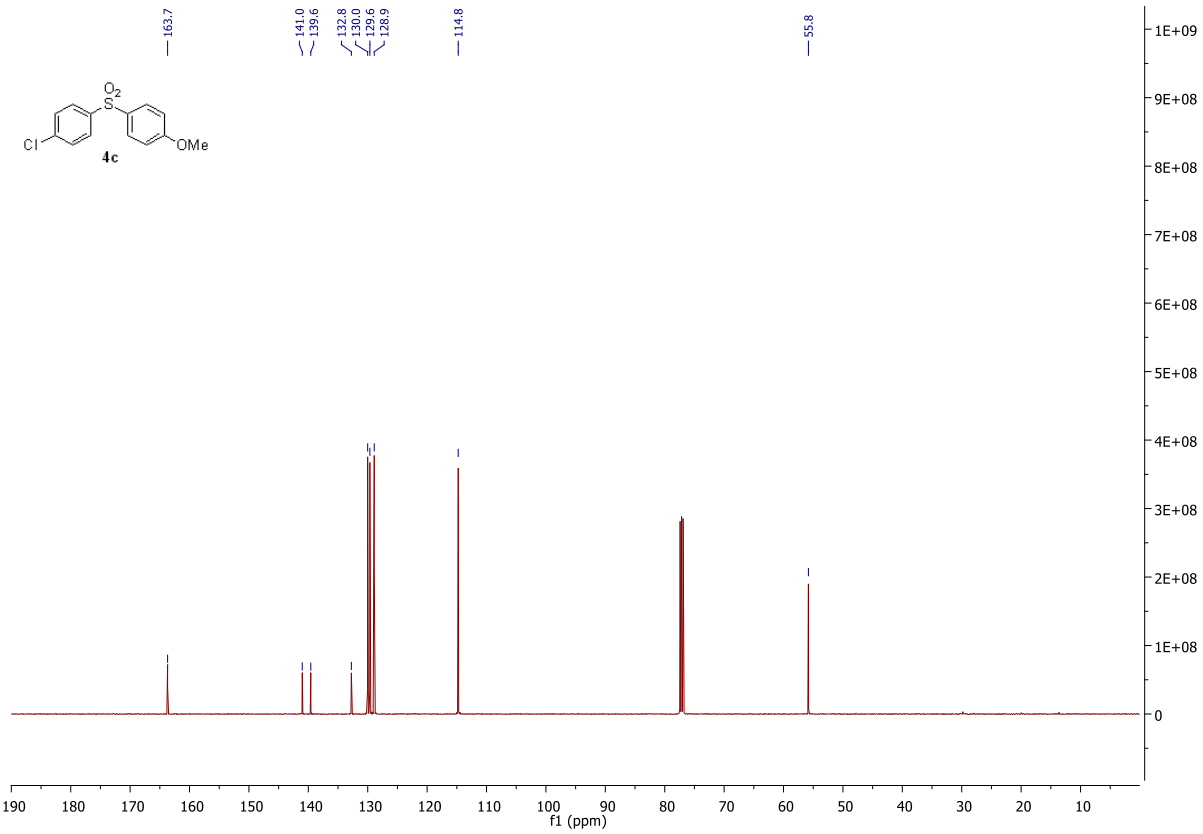
7.85
7.85
7.84
7.83
7.82
7.47
7.46
7.44
7.00
6.99
6.98
6.96
6.95
6.94
3.85
Cl
OMe
4c
3.89
2.00
2.02
3.00
f1 (ppm)


163.7
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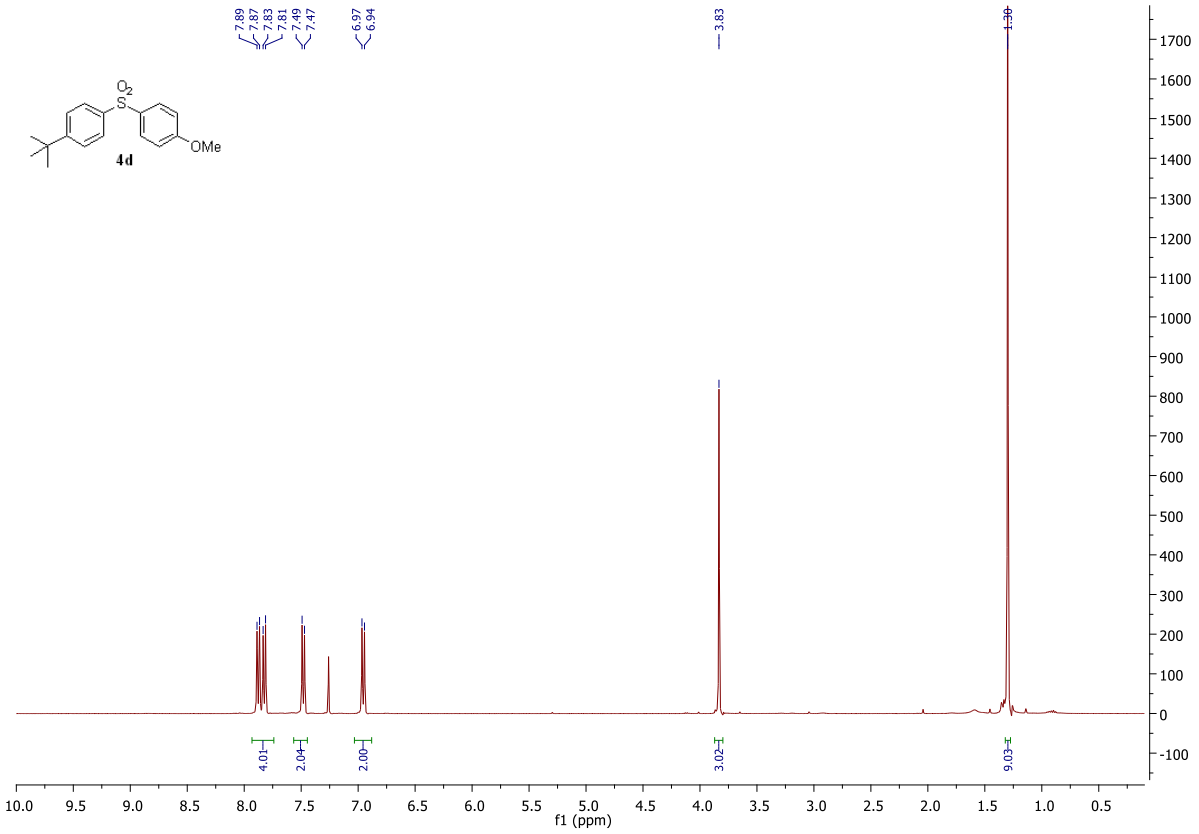
139.6
132.8
130.0
129.6
128.9
114.8
55.8
O2
S
Cl
OMe
4c
f1 (ppm)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7.49
7.47
6.97
6.94
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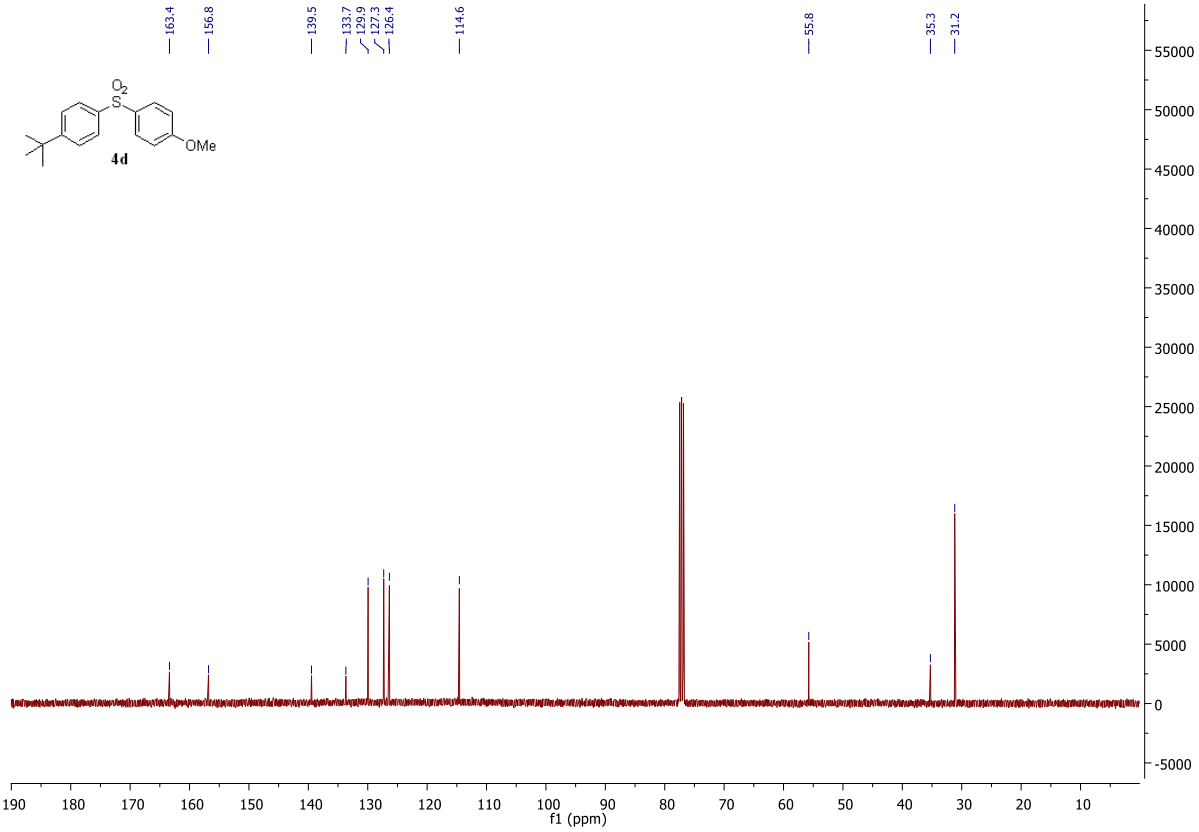
O2
S
OMe
4d
4.01
2.04
2.00
3.02
9.03
f1 (ppm)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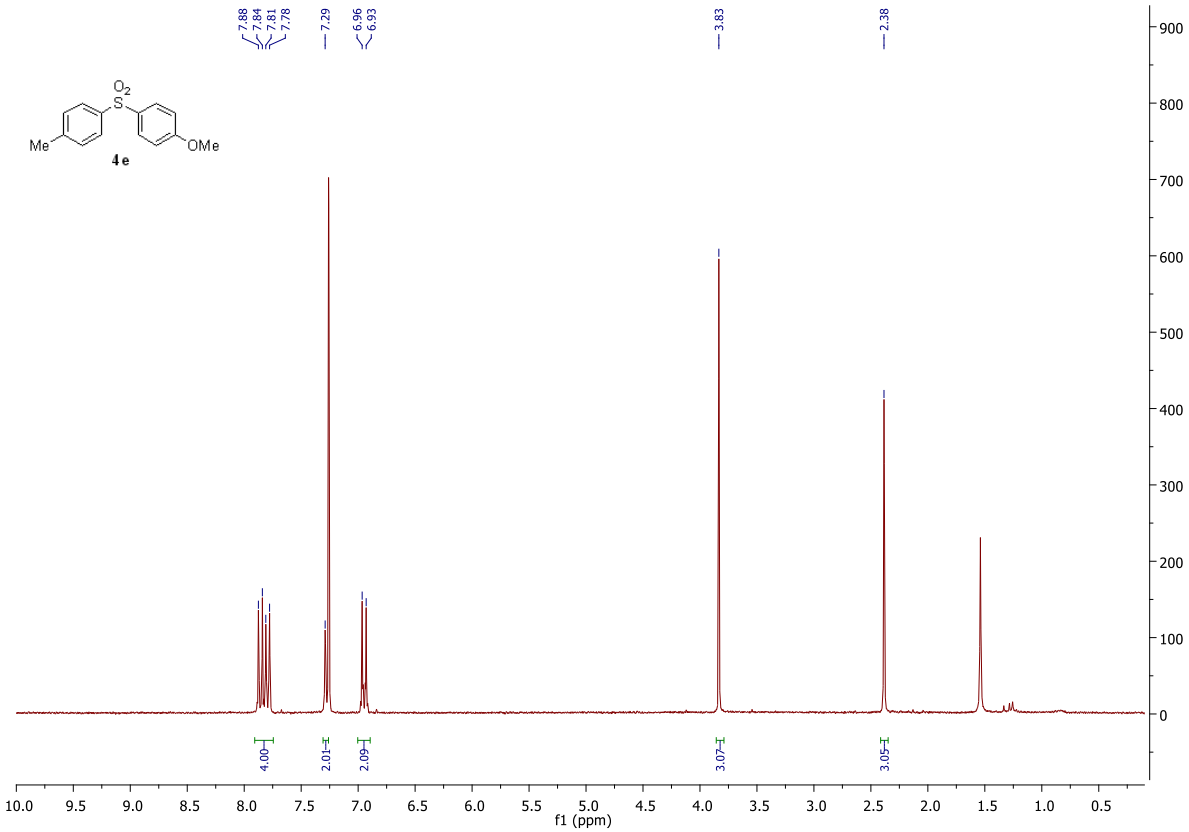
156.8
139.5
133.7
129.9
127.3
126.4
114.6
55.8
35.3
31.2
O2
S
OMe
4d
f1 (ppm)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7.84
7.81
7.78
7.29
6.96
6.93
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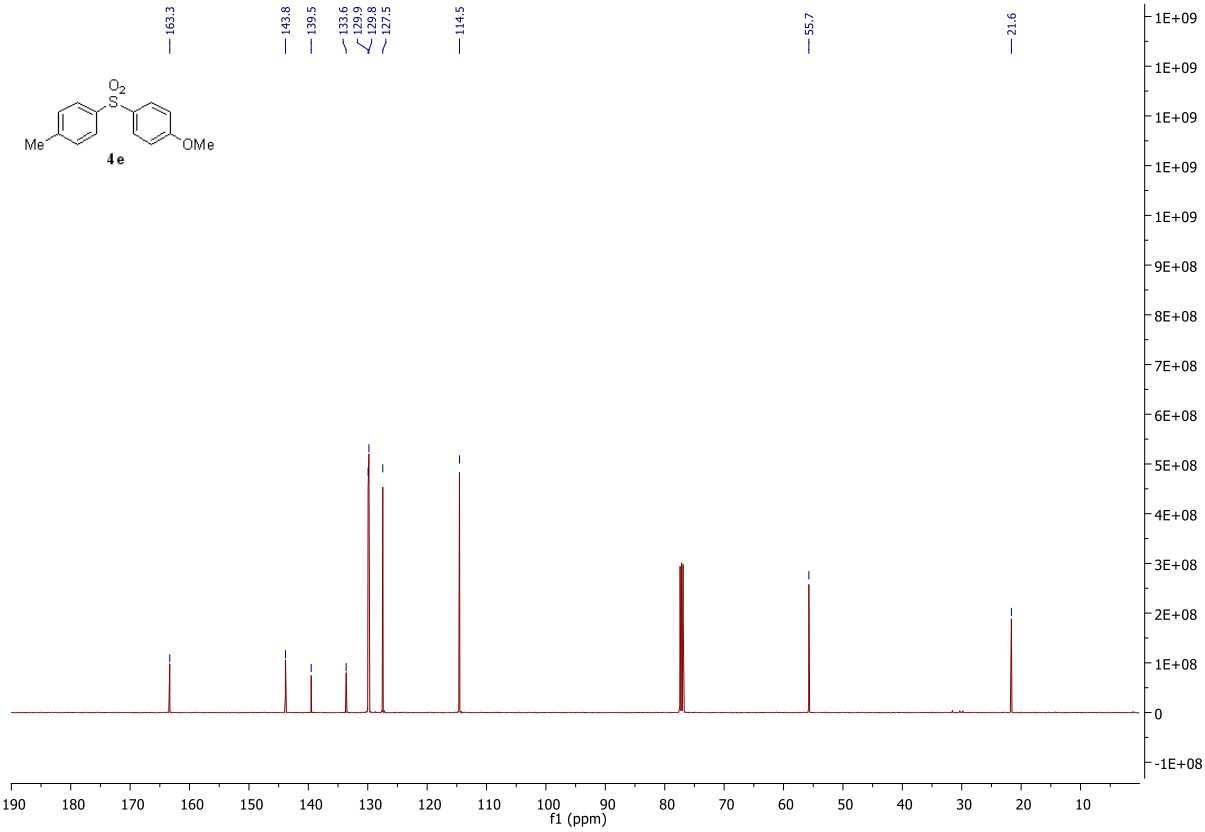
O2
S
Me
OMe
4e
4.00
2.01
2.09
3.07
3.05
f1 (ppm)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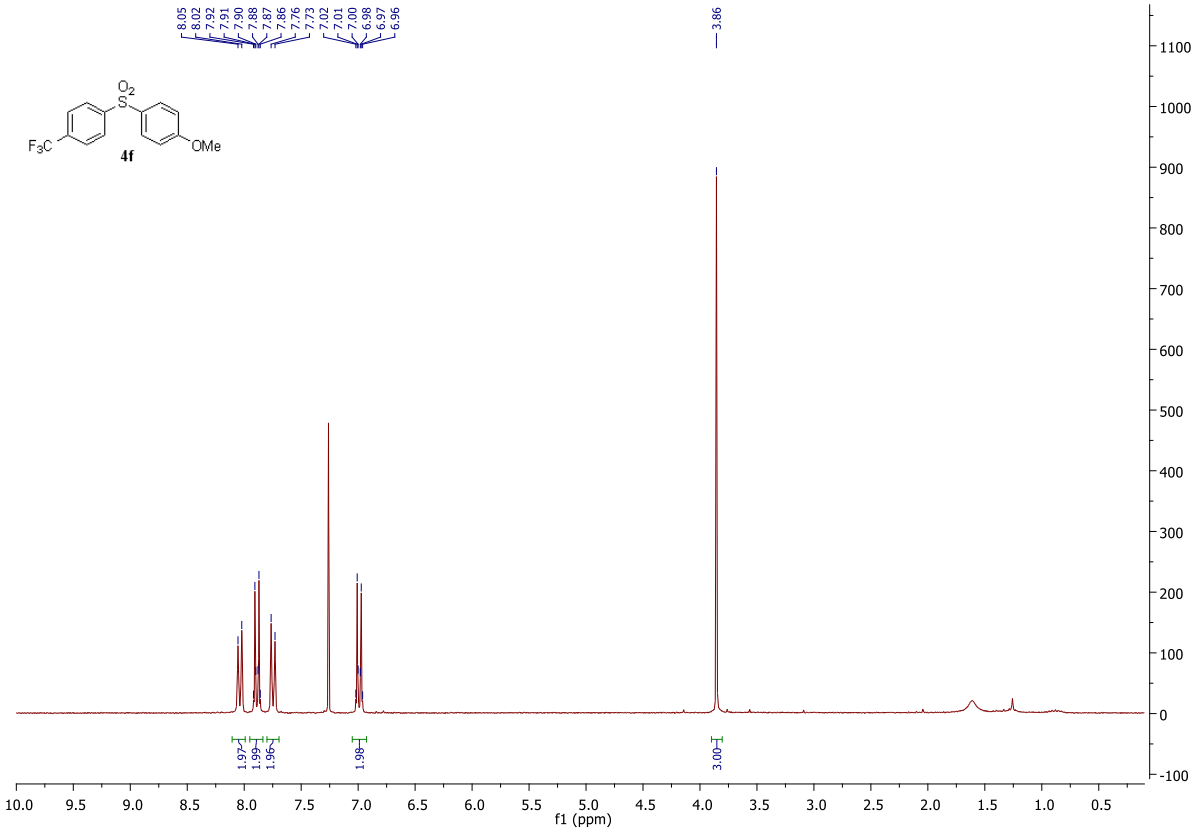
129.9
129.8
127.5
114.5
55.7
21.6
Me
OMe
4e
f1 (ppm)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7.01
7.00
6.98
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F3C
OMe
4f
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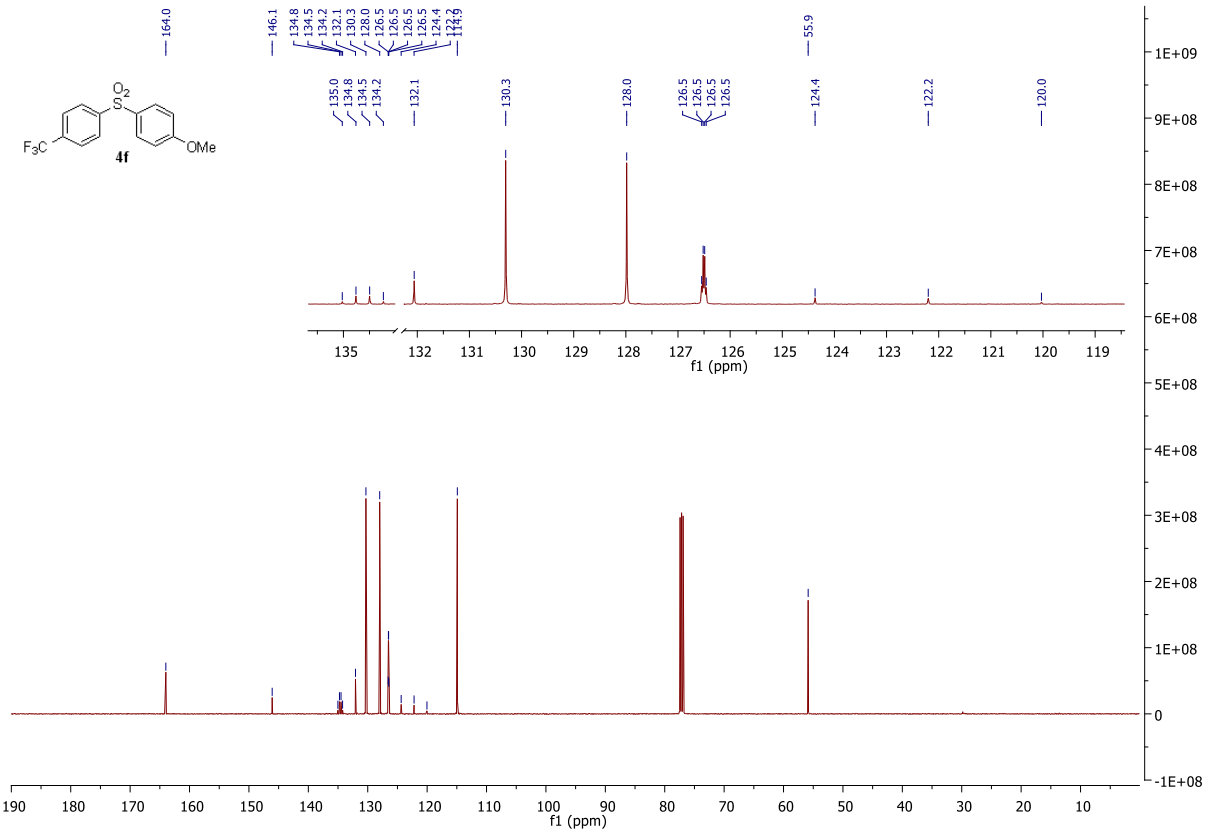
1.99
1.96
1.98
3.00
f1 (ppm)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132.1
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128.0
126.5
126.5
126.5
126.5
124.4
122.2
114.9
55.9
135.0
134.8
134.5
134.2
132.1
130.3
128.0
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126.5
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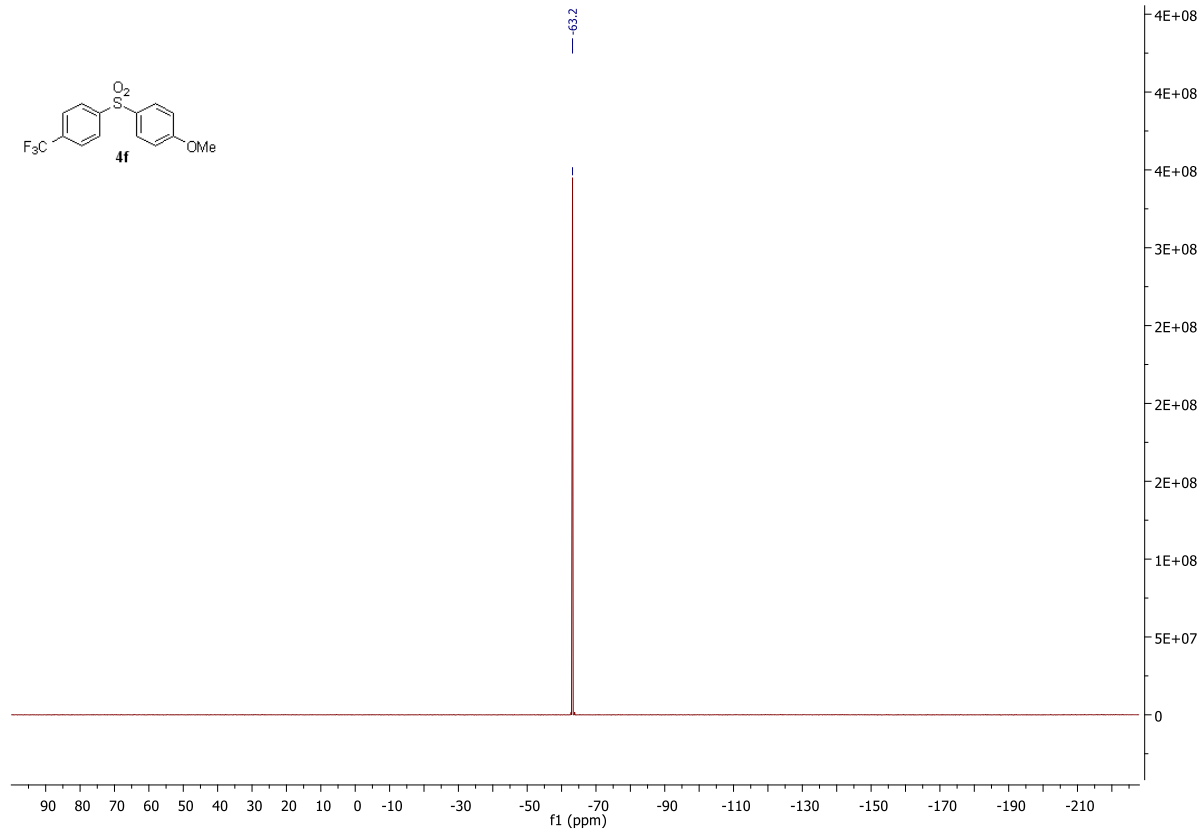
126.5
124.4
122.2
120.0
O2
S
F3C
OMe
4f
f1 (ppm)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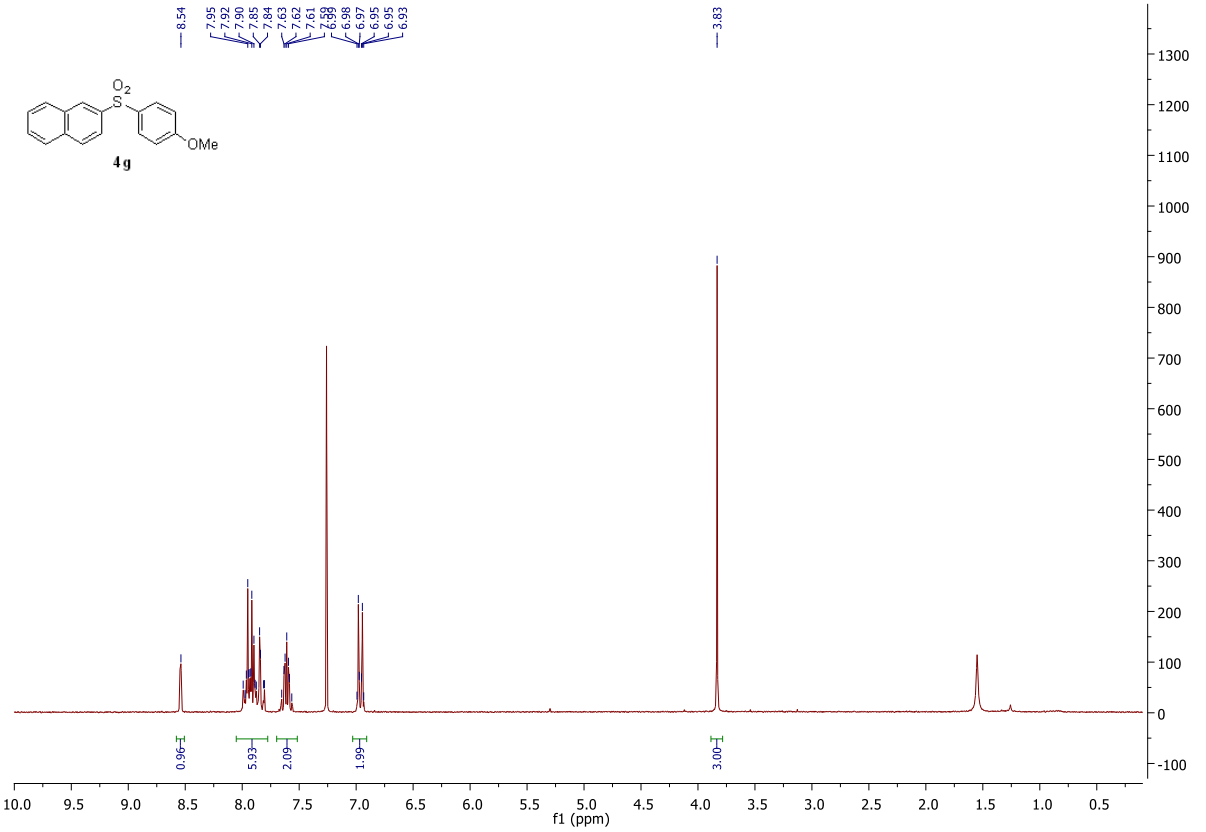
O2
S
F3C
OMe
4f
f1 (ppm)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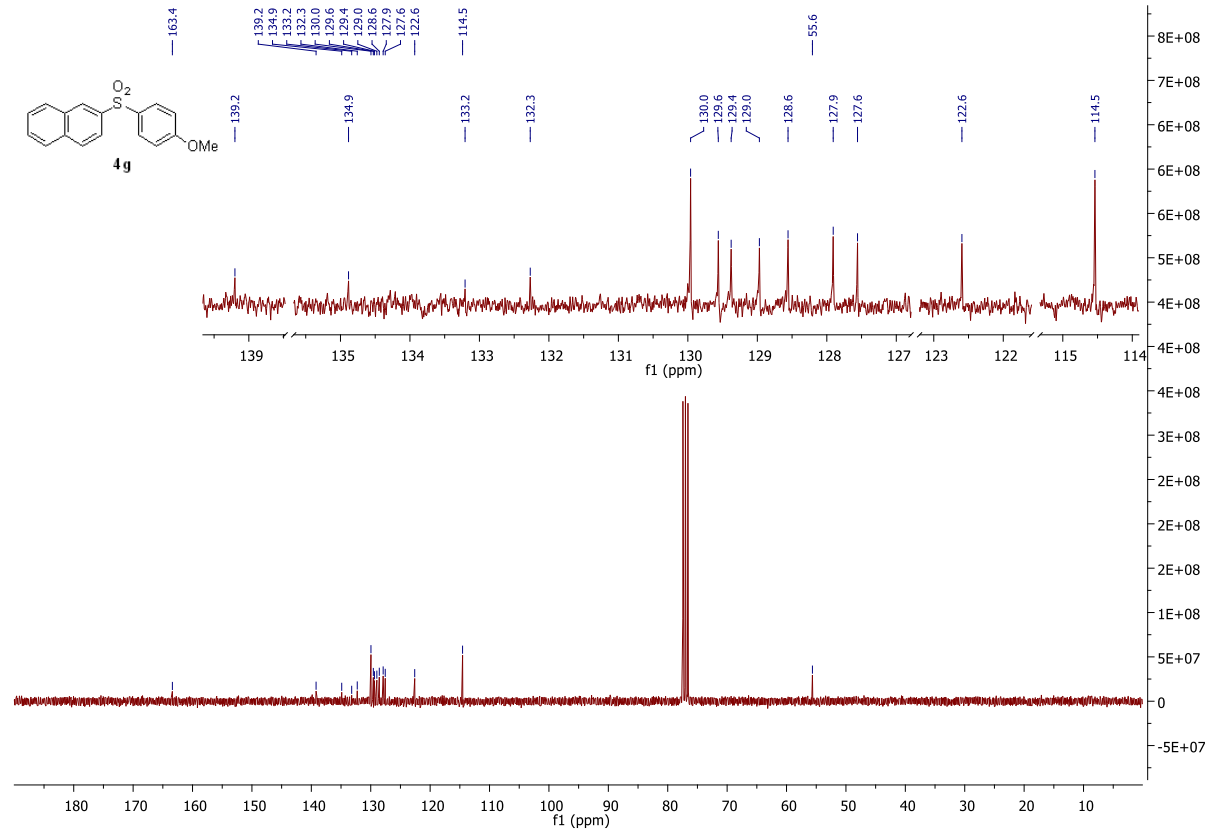
6.98
6.97
6.95
6.95
6.93
3.83
O2
S
OMe
4g
0.96
5.93
2.09
1.99
3.00
f1 (ppm)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133.2
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129.6
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129.0
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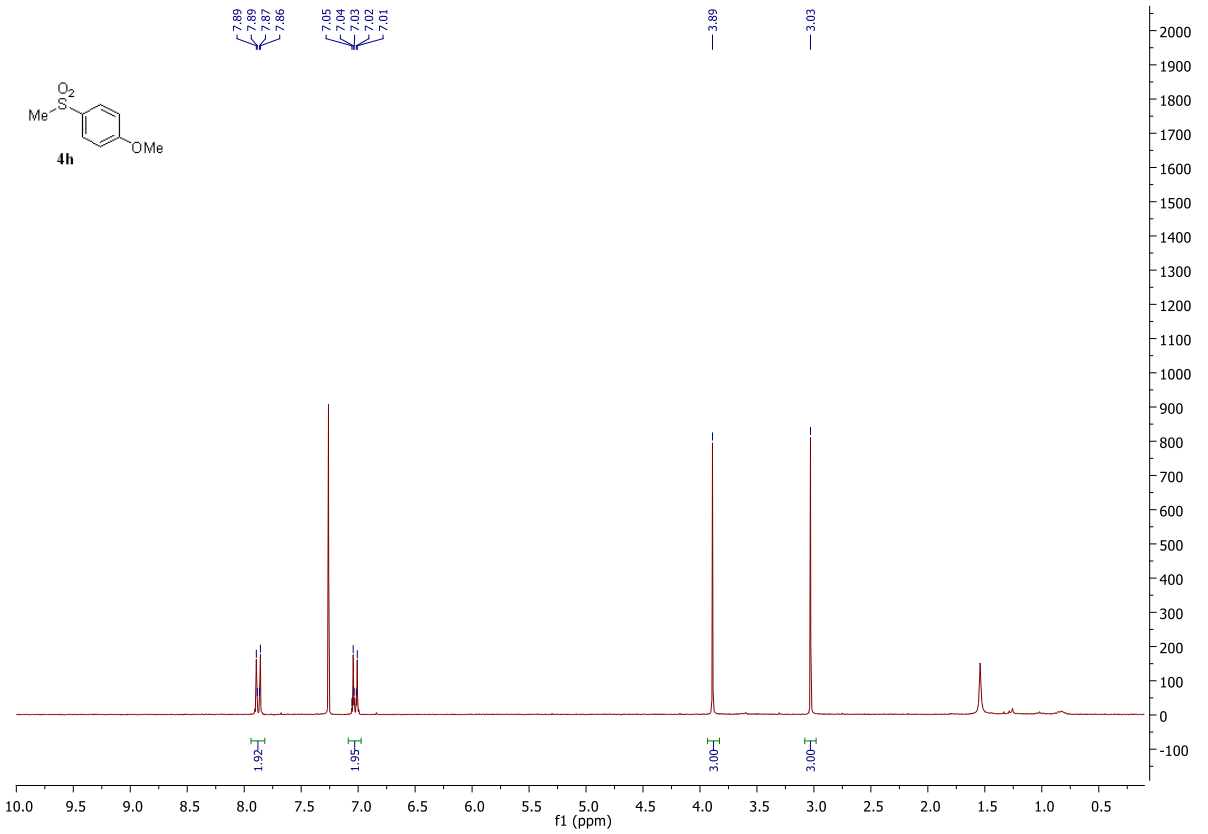
127.9
127.6
122.6
114.5
55.6
O2
S
OMe
4g
f1 (ppm)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7.02
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Me
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S
OMe
4h
1.92
1.95
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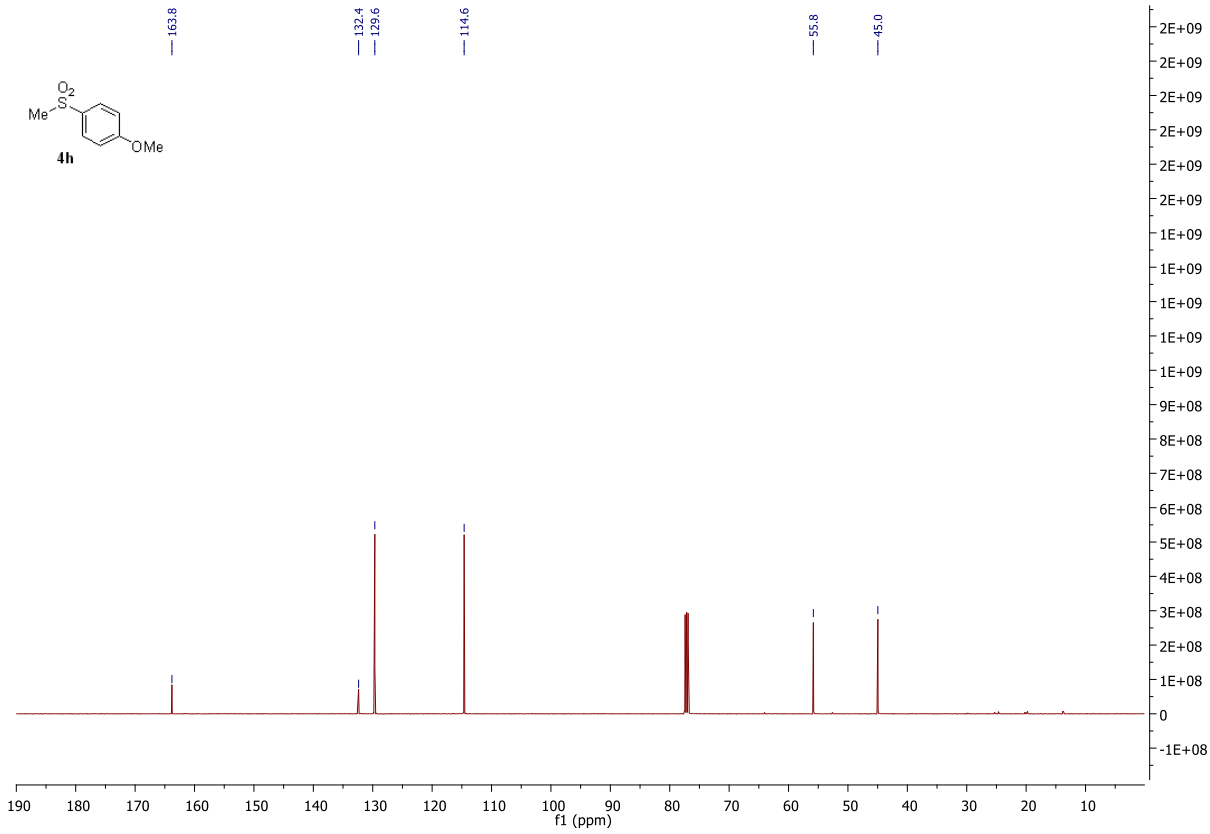
3.00
f1 (ppm)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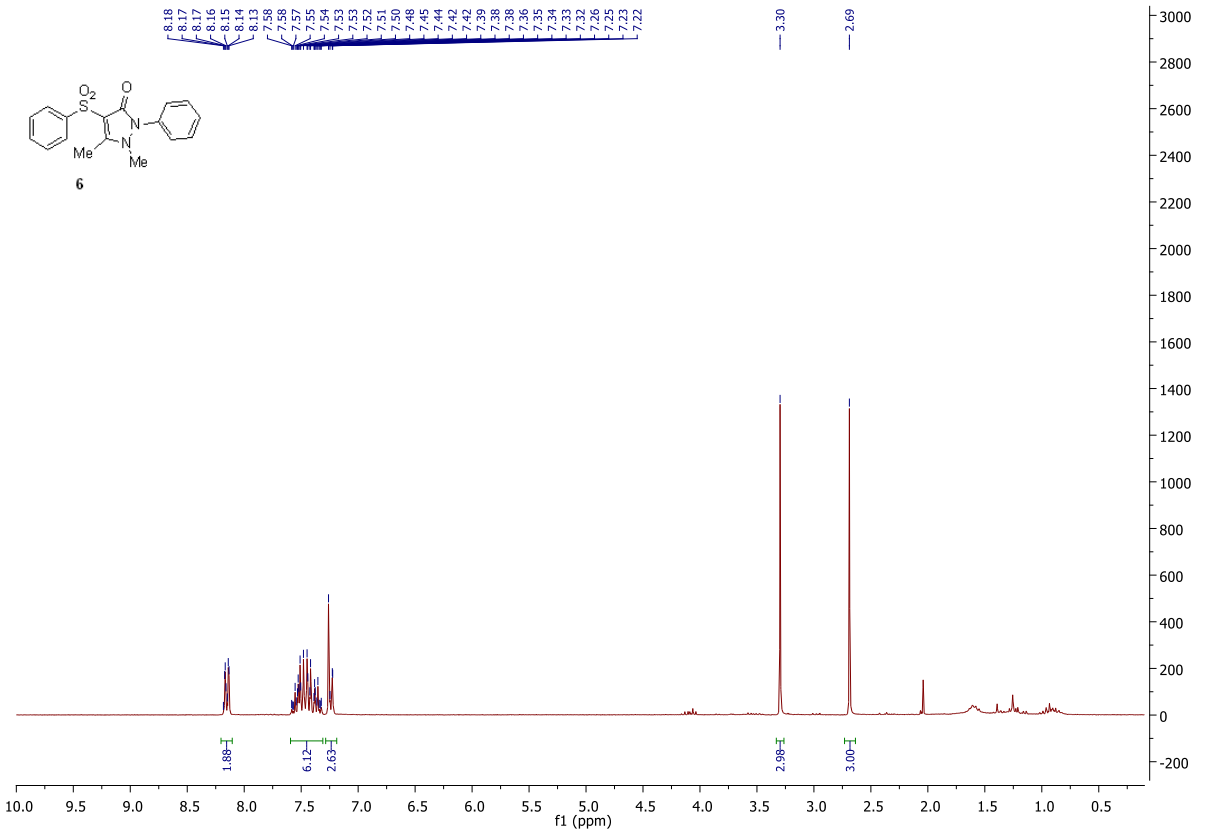
S
OMe
4h
f1 (ppm)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7.32
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6.12
2.63
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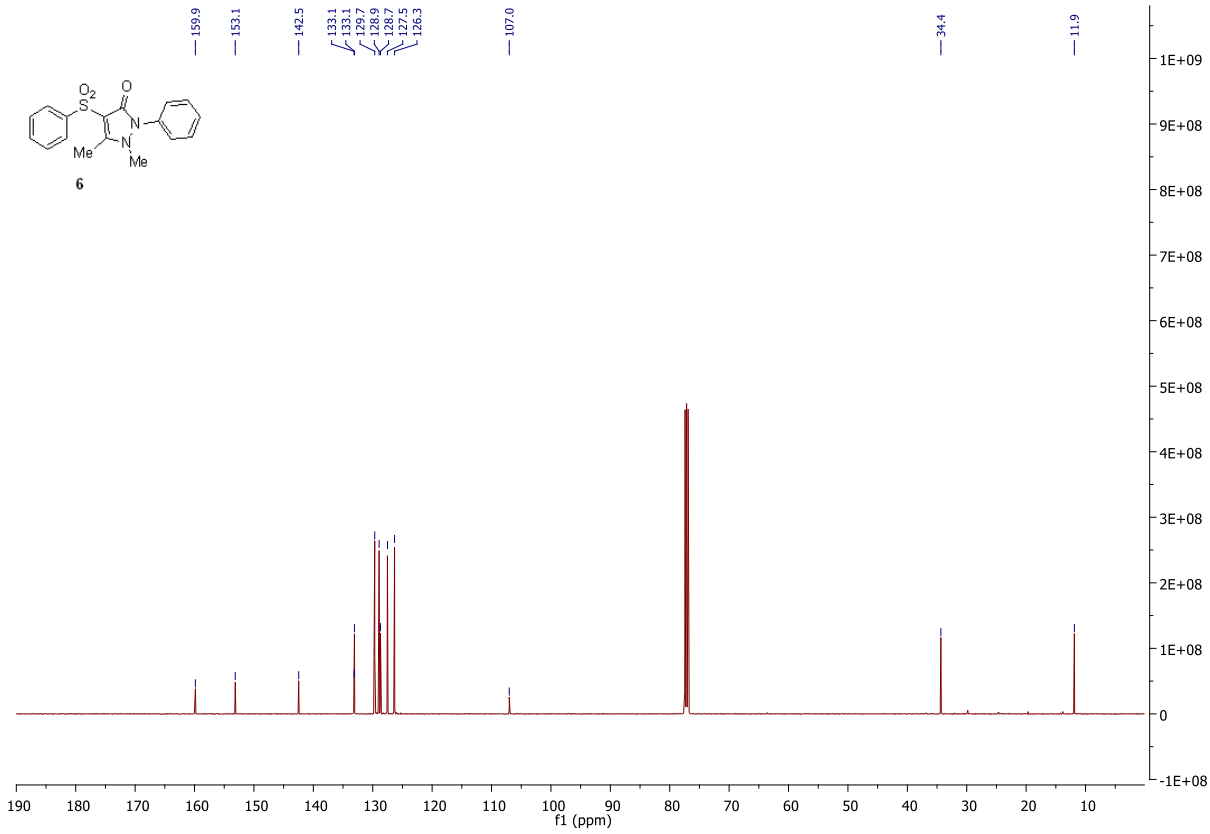
3.00
f1 (ppm)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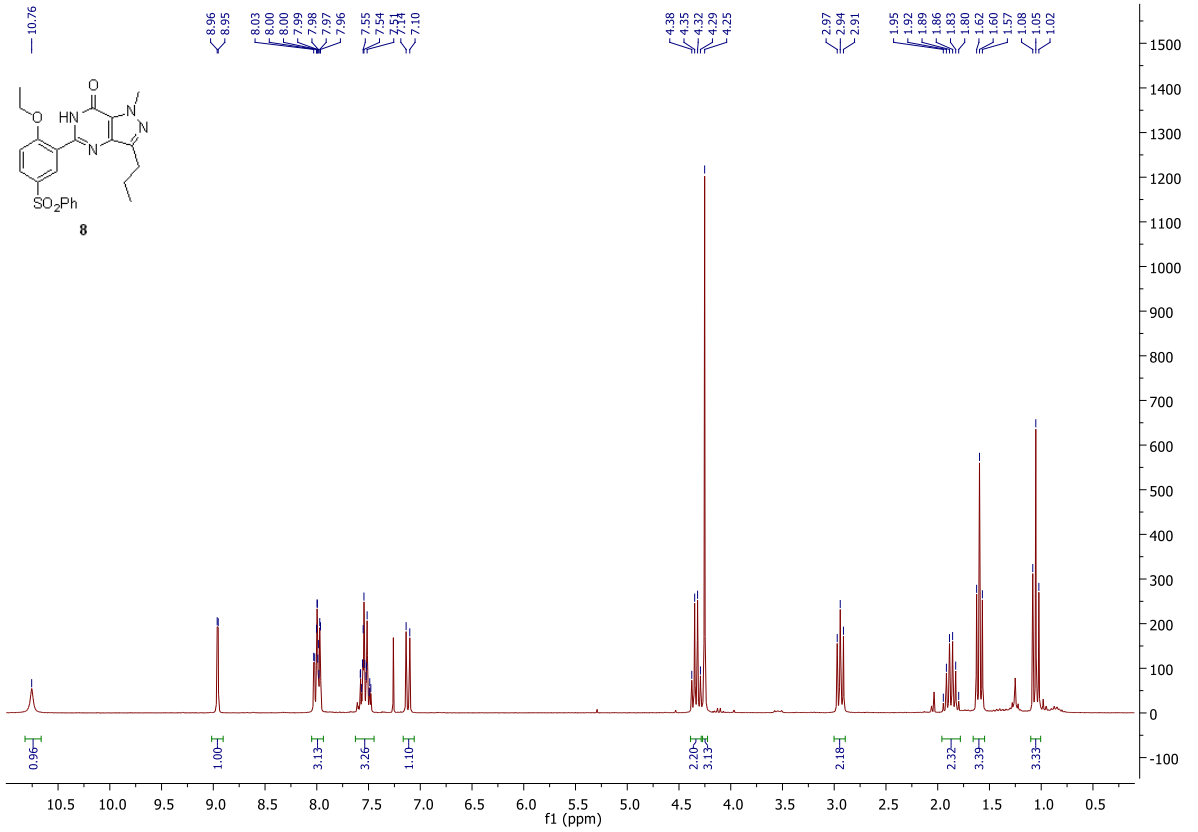
128.7
127.5
126.3
107.0
34.4
11.9
f1 (ppm)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7.14
7.11
7.10
4.38
4.35
4.32
4.29
4.25
2.97
2.94
2.91
1.95
1.92
1.89
1.86
1.83
1.80
1.62
1.60
1.57
1.08
1.05
1.02
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2.18
2.32
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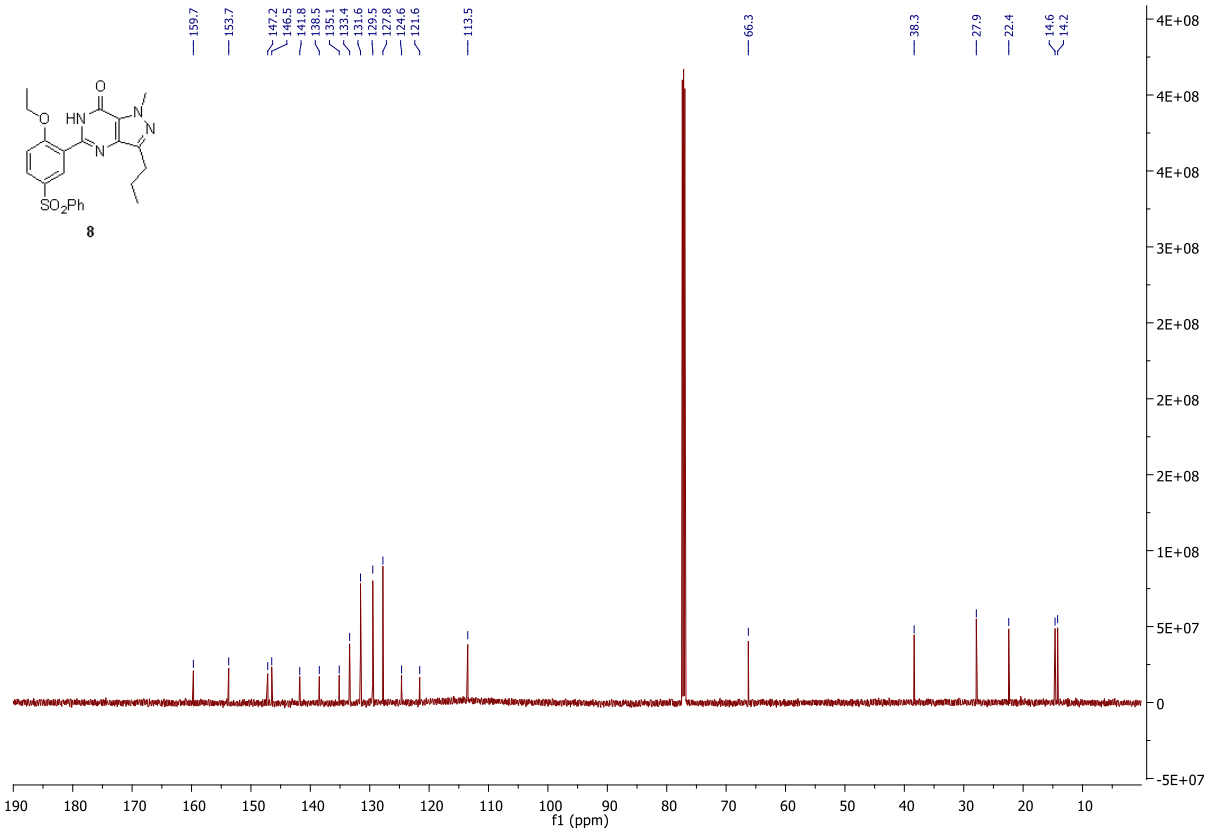
3.33
f1 (ppm)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27.9
22.4
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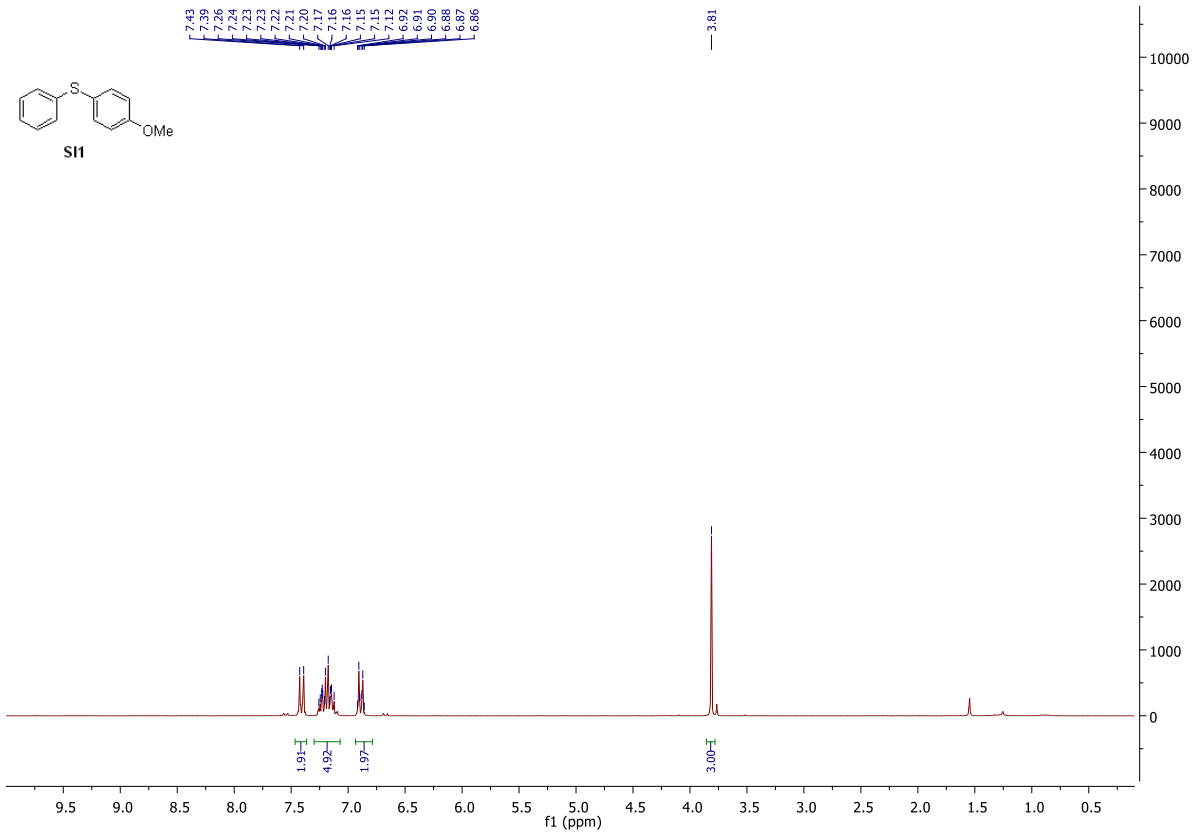
14.2
f1 (ppm)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7.15
7.12
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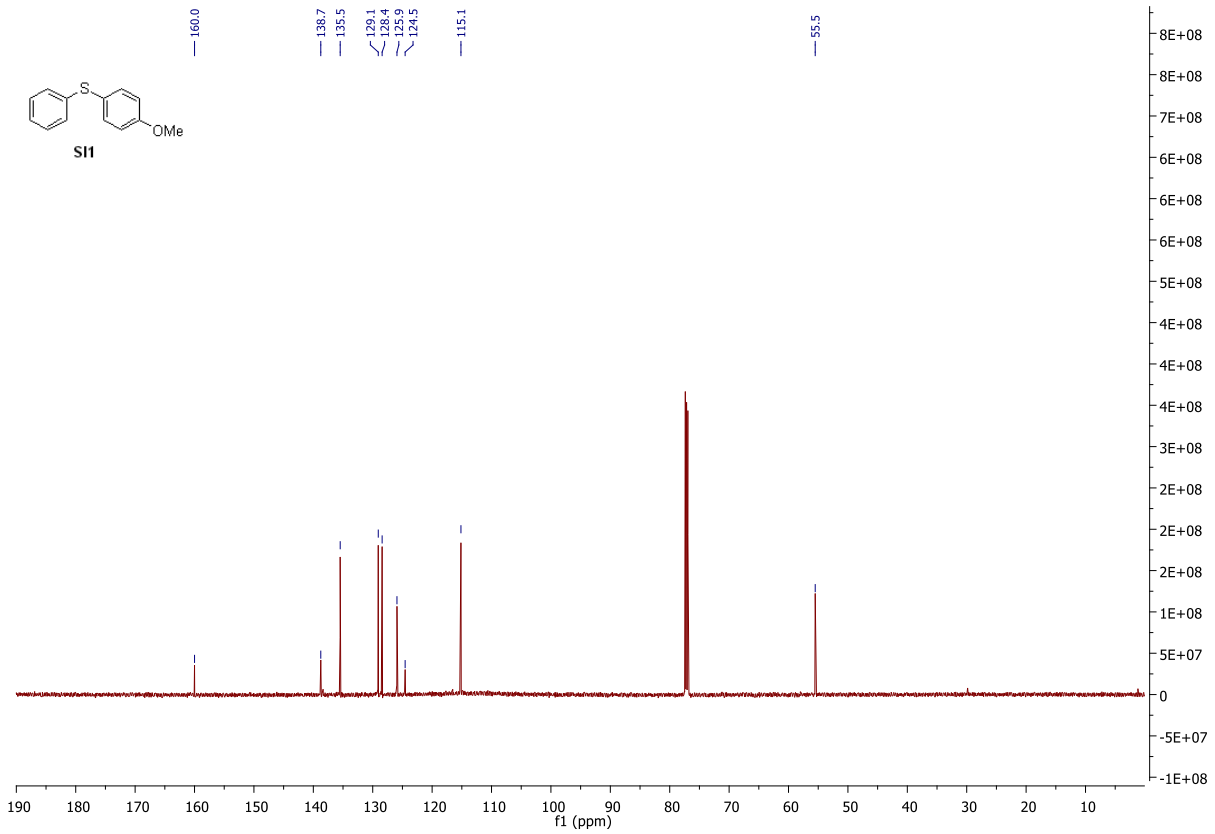
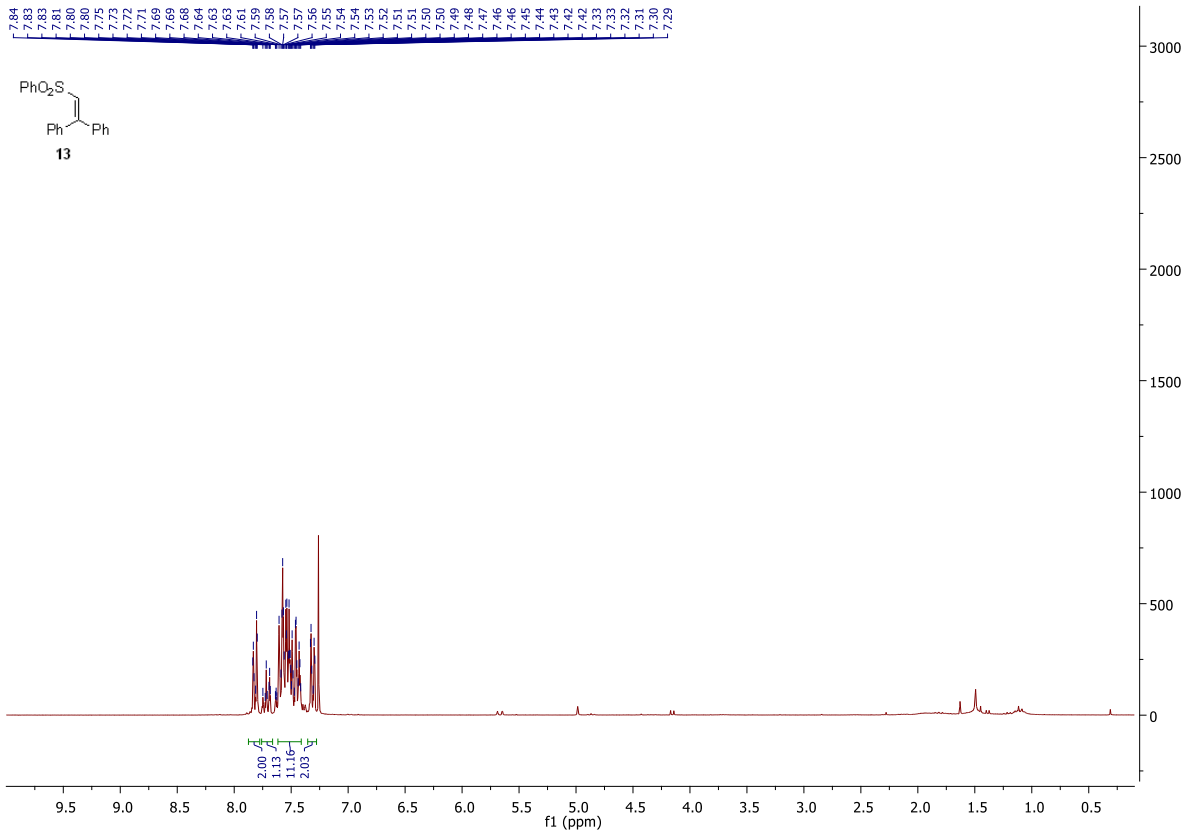
6.91
6.90
6.88
6.87
6.86
3.81
S
OMe
SI1
1.91
4.92
1.97
3.00
f1 (ppm)


160.0
138.7
135.5
129.1
128.4
125.9
124.5
115.1
55.5
S
OMe
SI1
f1 (ppm)


PhO2S
Ph
Ph
13
2.00
1.13
11.16
2.03
f1 (ppm)