# Metal-Free Synthesis of Diaryl Sulfones from Arylsulfinic Acid Salts and Diaryliododnium Salts

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## Supporting Information

**General**

**Solvents** All anhydrous solvents were purchased from commercial suppliers and stored over MS4A under an atmosphere of Argon. Solvents for column chromatography were technical standard.

**Regents** All starting materials which were purchased from commercial sources were used without further purification.
Sulfinic acid sodium salts were purchased. Non-commercially available sulfinic acid sodium salts were prepared from the corresponding sulphonyl chlorides according to Deng et. al.[1]
Commercially available diphenyliodonium salts were purchased. Following diaryliodonium salts were synthesized according to literature: Bis(4-methylphenyl)iodonium triflate (**2f**), bis(2,4,6-trimethylphenyl)iodonium triflate (**2g**), bis(2,4-dimethylphenyl)iodonium triflate (**2h**), bis(4-bromophenyl)iodonium triflate (**2j**), bis(4-fluorophenyl)iodonium triflate (**2k**), bis(4-chlorophenyl)iodonium triflate (**2l**), (2,4,6-trimethylphenyl)(phenyl)iodonium triflate (**2m**), (2-methylphenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2p**),[2] (2,4,6-triisopropylphenyl)(phenyl) iodonium triflate (**2n**),[3] bis(4-methoxyphenyl)iodonium tosylate (**2i**),[4] (3-trifluoromethylphenyl) (4-methoxyphenyl)iodonium tosylate (**2o**),[5] (2-methylphenyl)(2,4,6-triisopropylphenyl)iodonium triflate (**2q**).[6]

**Chromatography** Column chromatography was performed with Silica 0.04-0.063 mm/ 230-400 mesh. Thin layer chromatography was done using aluminium plates coated with $SiO_2$. The spots were visualized by ultraviolet light.

**NMR spectroscopy** $^{1}H$ and $^{13}C$ NMR spectra were recorded at 250 or 400 MHz and 63 or 101 MHz, respectively. Chemical shifts are reported as δ - values relative to the residual $CDCl_3$-peak (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; sp = septet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets.

**Mass Spectrometry** Mass spectra (MS) were measured on a *VG Plattform II* - spectrometer using ESI (electrospray ionisation) techniques at the Department of Chemistry.

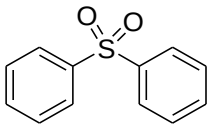
**Melting points** are reported uncorrected.

**Reactions** All reactions were carried out under an inert atmosphere in dried glassware unless otherwise noted. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by $^{1}$H-NMR.

**TP 1: Typical Procedure for Sulfones**

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with diaryiodonium salt **2** (1.1 equiv), arylsulfinic acid sodium salt **1** (1.0 equiv) and DMF (2.0 mL/mmol sodium salt, 0.5 M). The reaction mixture was heated to 90 °C and stirred at this temperature for 24 h. After cooling to room temperature, 10 mL sat. aqueous $NH_4Cl$-solution was added and the aqueous layers were extracted three times with 15 mL $CH_2Cl_2$. The combined organic layers were washed with 15 mL dest. $H_2O$, dried over $Na_2SO_4$ and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc) afforded the analytically pure product.

**1-(Phenylsulfonyl)benzene (3a)**



1-(Phenylsulfonyl)benzene **(3a**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless solid (104.2 mg, 96 %).

**m.p.:** 122-124 °C.

**$^{1}$H-NMR** (400 MHz, $CDCl_3$): δ = 7.96-7.93 (m, 4H), 7.58-7.47 (m, 6H).

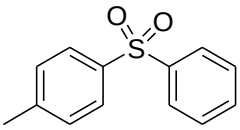
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 141.73, 133.30, 129.40, 127.77.

**MS:** m/z: calc. for $C_{12}H_{10}O_2S+Na^+$ 241.03, found 241.08.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.18.

Analytical data are consistent with literature.[7]

**1-Methyl-4-(phenylsulfonyl)benzene (3b)**



1-Methyl-4-(phenylsulfonyl)benzene (**3b**) was prepared according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and *p*-toluenebenzenesulfinic acid sodium salt (**1b**) (0.5 mmol, 93.8 mg) in 1.0 mL DMF.

Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (111.4 mg, 96 %).

1-Methyl-4-(phenylsulfonyl)benzene **(3b**) was also synthesized according to TP 1 from bis(4-methylphenyl)iodonium triflate **2f** (0.55 mmol, 252.0 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (107.0 mg, 92 %).

**m.p.:** 127-129 °C.

**$^{1}$H-NMR** (250 MHz, $CDCl_3$): δ = 7.98 – 7.89 (m, 2H), 7.86 – 7.79 (m, 2H), 7.58 – 7.44 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H).

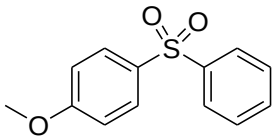
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 144.27, 142.19, 138.85, 133.09, 130.03, 129.33, 127.86, 127.63, 21.67.

**MS:** m/z: calc. for $C_{13}H_{12}O_2S+Na^+$ 255.05, found 255.09.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.27.

Analytical data are consistent with literature.[7]

**1-(4-Methoxyphenylsulfonyl)benzene (3c)**




1-(4-Methoxyphenylsulfonyl)benzene (**3c**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 4-methoxybenzenesulfinic acid sodium salt (**1c**) (0.5 mmol, 102.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless solid (111.7 mg, 90 %).

1-(4-Methoxyphenylsulfonyl)benzene (**3c**) was also prepared according to TP 1 from bis(4-methoxy-phenyl)iodonium tosylate (**2i**) (0.55 mmol, 248.8 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless solid (108.0 mg, 87 %).

**m.p.:** 92-93 °C.

**$^{1}$H-NMR** (400 MHz, $CDCl_3$): δ = 7.97 – 7.79 (m, 4H), 7.59 – 7.40 (m, 3H), 7.04 – 6.86 (m, 2H), 3.83 (s, 3H).

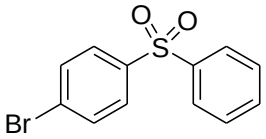
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 163.50, 142.50, 133.24, 132.95, 130.00, 129.31, 127.42, 114.63, 55.76.

**MS:** m/z: calc. for $C_{13}H_{12}O_3S+Na^+$ 271.04, found 271.08.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.13.

Analytical data are consistent with literature.[7]

**1-Bromo-4-(phenylsulfonyl)benzene (3d)**




1-Bromo-4-(phenylsulfonyl)benzene (**3d**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 4-bromobenzenesulfinic acid sodium salt (**1d**) (0.5 mmol, 135.3 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as yellow solid (133.0 mg, 90 %).

1-Bromo-4-(phenylsulfonyl)benzene (**3d**) was also prepared according to TP 1 from bis(4-bromophenyl) iodonium triflate (**2j**) (0.55 mmol, 323.4 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL NMP. Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as yellow solid (90.6 mg, 61 %).

**m.p.:** 98-99 °C.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.98 – 7.87 (m, 2H), 7.84 – 7.76 (m, 2H), 7.68 – 7.61 (m, 2H), 7.61 – 7.54 (m, 1H), 7.55 – 7.46 (m, 2H).

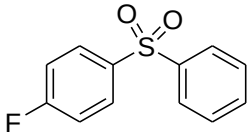
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 141.30, 140.83, 133.59, 132.74, 129.55, 129.33, 128.59, 127.79.

**MS:** m/z: calc. for $C_{12}H_9BrO_2S+Na^+$ 318.94, found 318.99.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.29.

Analytical data are consistent with literature.[7]

**1-(4-Fluorophenylsulfonyl)benzene (3e)**




1-(4-Fluorophenylsulfonyl)benzene (**3e**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 4-fluorobenzenesulfinic acid sodium salt (**1e**) (0.5 mmol, 96.1 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless solid (97.8 mg, 83 %).

1-(4-Fluorophenylsulfonyl)benzene (**3e**) was also prepared according to TP 1 from bis(4-fluorophenyl)iodonium triflate (**2k**) (0.55 mmol, 256.4 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL NMP. Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless solid (55.0 mg, 47 %).

**m.p.:** 112-113 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.15 – 7.74 (m, 4H), 7.65 – 7.42 (m, 3H), 7.18 (t, *J* = 8.4 Hz, 2H).

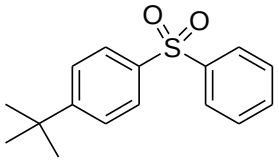
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 165.58 (d, *J* = 255.9 Hz), 141.63, 137.85 (d, *J* = 3.3 Hz), 133.45, 130.62 (d, *J* = 9.6 Hz), 129.51, 127.71, 116.73 (d, *J* = 22.7 Hz).

**MS:** m/z: calc. for $C_{12}H_9FO_2S+Na^+$ 259.02, found 259.06.

**$R_f$** (Cyclohexane:EtOAc 9:1): = 0.23.

Analytical data are consistent with literature. [7]

**1-(4-*tert*-Butylphenylsulfonyl)benzene (3f)**



1-(4-*tert*-Butylphenylsulfonyl)benzene (**3f**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.50 mmol, 215.1 mg) and 4-*tert*-butylbenzenesulfinic acid sodium salt (**1f**) (0.55 mmol, 165.3 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as white solid (73.4 mg, 54 %).

**m.p.:** 127-128 °C.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.97 - 7.94 (m, 2H), 7.87 - 7.84 (m, 2H), 7.57 – 7.47 (m, 5H), 1.30 (s, 9H).

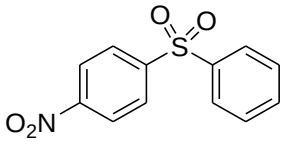
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 157.21, 142.10, 138.69, 133.12, 129.34, 127.74, 127.66, 126.44, 35.31, 31.16.

**MS:** m/z: calc. for $C_{16}H_{18}O_2S+Na^+$ 297.09, found 297.19.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.31.

Analytical data are consistent with literature.[8]

**1-(4-Nitrophenylsulfonyl)benzene (3g)**



1-(4-Nitrophenylsulfonyl)benzene (**3g**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 4-nitrobenzenesulfinic acid sodium salt (**1g**) (0.50 mmol, 139.5 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as yellowish powder (104.6 mg, 81 %).

**m.p.:** 143-145 °C.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 8.37 – 8.28 (m, 2H), 8.17 – 8.08 (m, 2H), 8.02 – 7.91 (m, 2H), 7.67 – 7.59 (m, 1H), 7.60 – 7.51 (m, 2H).

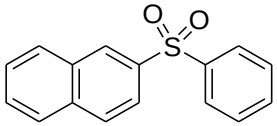
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 150.48, 147.50, 140.16, 134.25, 129.82, 129.10, 128.16, 124.65.

**MS:** m/z: calc. for $C_{12}H_9NO_4S+H^+$ 264.03, found 263.95.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.30.

Analytical data are consistent with literature.[9]

**2-(Phenylsulfonyl)naphthalene (3h)**



2-(Phenylsulfonyl)naphthalene (**3h**) was prepared according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 2-naphtalenesulfinic acid sodium salt (**1h**) (0.5 mmol, 107.1 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (84.4 mg, 63 %).

**m.p.:** 119-121 °C.

**$^{1}$H-NMR** (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 8.05 – 7.96 (m, 3H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.68 – 7.47 (m, 5H).

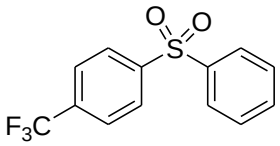
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 141.66, 138.42, 135.01, 133.15, 132.22, 129.63, 129.40, 129.27, 129.14, 129.09, 127.91, 127.71, 127.62, 122.69.

**MS:** m/z: calc. for $C_{16}H_{12}O_2S+Na^+$ 291.05, found 291.09.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.20.

Analytical data are consistent with literature.[10]

**1-(Trifluoromethyl)-4-(phenylsulfonyl)benzene (3i)**



1-(Trifluoromethyl)-4-(phenylsulfonyl)benzene (**3i**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 4-triflouromethylbenzenesulfinic acid sodium salt (**1i**) (0.5 mmol, 122.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (118.4 mg, 83 %).

**m.p.:** 90-91 °C.

**$^{1}$H-NMR** (250 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.2 Hz, 2H), 8.02 – 7.89 (m, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.67 – 7.49 (m, 3H).

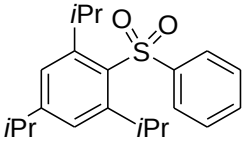
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 145.38, 140.71, 134.97 (d, *J* = 33.1 Hz), 133.91, 129.67, 128.34, 128.03, 126.57 (q, *J* = 3.7 Hz), 123.23 (d, *J* = 273.1 Hz).

**MS:** m/z: calc. for $C_{13}H_9F_3O_2S+Na^+$ 309.02, found 309.07.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.26.

Analytical data are consistent with literature.[11]

**1,3,5-Triisopropyl-2-(phenylsulfonyl)benzene (3j)**




1,3,5-Triisopropyl-2-(phenylsulfonyl)benzene (**3j**) was prepared according to TP 1 from (2,4,6-triisopropylphenyl)(phenyl)iodonium triflate (**2n**) (0.55 mmol, 311.5 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1) yielded the product as colorless solid (162.0 mg, 94 %).

1,3,5-Triisopropyl-2-(phenylsulfonyl)benzene (**3j**) was also synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 1,3,5-triisopropylbenzenesulfinic acid sodium salt (**1j**) (0.45 mmol, 161.3 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless solid (84.5 mg, 61 %).

**m.p.:** 122- 123 °C.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.81 – 7.69 (m, 2H), 7.58 – 7.42 (m, 3H), 7.16 (s, 2H), 4.18 (hept, *J* = 6.7 Hz, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.8 Hz, 12H).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 153.99, 151.45, 145.46, 132.37, 132.33, 129.07, 125.76, 124.15, 34.35, 29.54, 24.72, 23.69.

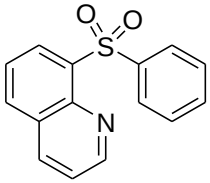
**MS:** m/z: calc. for $C_{21}H_{28}O_2S+Na^+$ 367.17, found 367.22.

| | | | | |
|---|---|---|---|---|
| **EA:** | calc.: | C 73.21 | H 8.19 | S 9.31 |
| | found: | C 73.09 | H 8.18 | S 9.28 |

**IR** ($cm^{-1}$): 2960, 1597, 1444, 1292, 1147, 1090, 1057, 886, 760, 691, 556, 573.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.50.

**8-(Phenylsulfonyl)quinoline (3k)**




8-(Phenylsulfonyl)quinoline (**3k**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 8-quinolinesulfinic acid sodium salt (**1k**) (0.55 mmol, 120.0 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded the product as colorless solid (120.4 mg, 90 %).

**m.p.:** 188-190 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.96 (dd, *J* = 4.0, 1.3 Hz, 1H), 8.73 (d, *J* = 7.3 Hz, 1H), 8.22 (dd, *J* = 7.5, 6.1 Hz, 2H), 8.19 – 8.02 (m, 2H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.56 – 7.38 (m, 4H).

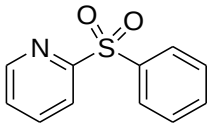
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 151.25, 143.89, 142.04, 138.09, 136.36, 134.68, 132.97, 131.90, 129.31, 129.06, 128.39, 125.61, 122.1.

**MS:** m/z: calc. for $C_{15}H_{11}NO_2S+H^+$ 270.05, found 270.11.

**$R_f$** (Cyclohexane:EtOAc 4:1): 0.11.

Analytical data are consistent with literature.[12]

**2-(Phenylsulfonyl)pyridine (3l)**



2-(Phenylsulfonyl)pyridine (**3l**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.55 mmol, 236.6 mg) and 2-pyridinesulfinic acid sodium salt (**1l**) (0.5 mmol, 87.0 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 1:1) yielded the product as colorless solid (44.0 mg, 40 %).

**m.p.:** 92-93 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.72 – 8.63 (m, 1H), 8.25 – 8.17 (m, *J* = 7.9, 0.9 Hz, 1H), 8.12 – 8.03 (m, 2H), 7.93 (td, *J* = 7.8, 1.7 Hz, 1H), 7.67 – 7.49 (m, 3H), 7.46 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H).

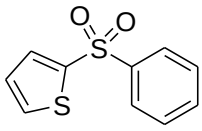
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 159.10, 150.62, 139.16, 138.20, 133.87, 129.25, 129.11, 127.00, 122.33.

**MS:** m/z: calc. for $C_{11}H_9NO_2S+Na^+$ 242.02, found 242.09.

**$R_f$** (Cyclohexane:EtOAc 4:1): 0.11.

Analytical data are consistent with literature.[9]

**2-(Phenylsulfonyl)thiophene (3m)**



2-(Phenylsulfonyl)thiophene (**3m**) was synthesized according to TP 1 from diphenyliodonium triflate (**2a**) (0.50 mmol, 215.1 mg) and 2-thiophenesulfinic acid sodium salt (**1m**) (0.55 mmol, 98.5 mg) in 1.0 mL DMSO. Purification by chromatography (Cyclohexane:EtOAc 9:1 → 4:1) yielded the product as colorless solid (93.6 mg, 83 %).

**m.p.:** 123-125 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.08 – 7.89 (m, 2H), 7.73 – 7.62 (m, 2H), 7.62 – 7.44 (m, 3H), 7.08 (dd, *J* = 4.9, 3.8 Hz, 1H).

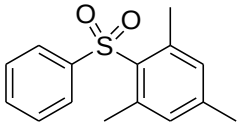
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 143.27, 142.29, 133.98, 133.51, 133.43, 129.45, 127.97, 127.47.

**MS:** m/z: calc. for $C_{10}H_8O_2S_2+Na^+$ 246.99, found 247.03.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.18.

Analytical data are consistent with literature.[9]

**1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (3n)**



1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (**3n**) was prepared according to TP 1 from bis(2,4,6-trimethylphenyl)iodonium triflate (**2g**) (0.55 mmol, 297.0 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 9:1) yielded the product as white solid (118.4 mg, 91 %).

1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (**3n**) was also synthesized according to TP 1 from (2,4,6-trimethylphenyl)(phenyl)iodonium triflate (**2m**) (0.55 mmol, 259.7 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as white solid (114.0 mg, 88 %).

**m.p.:** 87-89 °C.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.83 – 7.72 (m, 2H), 7.54 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 6.94 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H).

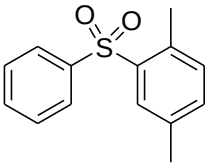
**$^{13}$C-NMR** (101 MHz, $CDCl_3$): δ = 143.70, 143.51, 140.25, 133.94, 132.69, 132.34, 129.02, 126.35, 22.94, 21.15.

**MS:** m/z: calc. for $C_{15}H_{16}O_2S+Na^+$ 283.08, found 283.13.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.34.

Analytical data are consistent with literature.[7]

**1,4-Dimethyl-2-(phenylsulfonyl)benzene (3o)**



1,4-Dimethyl-2-(phenylsulfonyl)benzene (**3o**) was prepared according to TP 1 from bis(2,5-dimethylphenyl)iodonium triflate (**2h**) (0.55 mmol, 297.2 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as white solid (103.9 mg, 84 %).

**m.p.:** 112-114 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.90 – 7.82 (m, 2H), 7.60 – 7.44 (m, 3H), 7.32 – 7.26 (m, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 2.39 (d, *J* = 10.6 Hz, 6H).

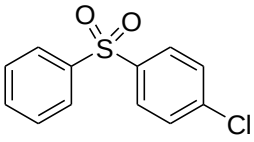
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 141.68, 138.56, 136.59, 134.95, 134.46, 133.03, 132.74, 129.89, 129.10, 127.70, 21.01, 19.81.

**MS:** m/z: calc. for $C_{14}H_{14}O_2S+Na^+$ 269.06, found 269.10.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.29.

Analytical data are consistent with literature.[7]

**1-(4-Chlorophenylsulfonyl)benzene (3p)**



1-(4-Chlorophenylsulfonyl)benzene (**3p**) was prepared according to TP 1 from bis(4-chlorophenyl)iodonium triflate (**2l**) (0.55 mmol, 274.5 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as white solid (120.9 mg, 96 %).

**m.p.:** 96-97 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.02 – 7.79 (m, 4H), 7.63 – 7.43 (m, 5H).

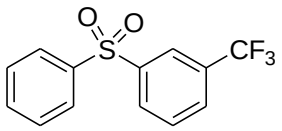
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 141.40, 140.34, 140.03, 133.55, 129.74, 129.54, 129.26, 127.78.

**MS:** m/z: calc. for $C_{12}H_9ClO_2S+Na^+$ 274.99, found 275.04.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.29.

Analytical data are consistent with literature.[7]

**1-(Trifluoromethyl)-3-(phenylsulfonyl)benzene (3q)**



1-(Trifluoromethyl)-3-(phenylsulfonyl)benzene (**3q**) was prepared according to TP 1 from (4-methoxyphenyl) (3-trifluoromethylphenyl)iodonium tosylate (**2o**) (0.55 mmol, 302.7 mg) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg) in 1.0 mL DMF. Purification by chromatography (Cyclohexane:EtOAc 20:1 → 9:1) yielded the product as colorless needles (111.7 mg, 78 %).

**m.p.:** 83-84 °C.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.02 – 7.92 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.49 (m, 4H).

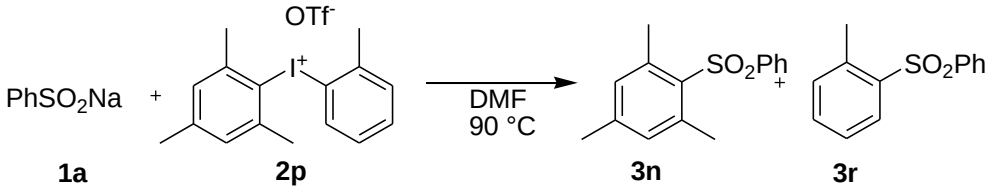
**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 142.02 (d, *J* = 147.0 Hz), 133.89, 132.19 (d, *J* = 33.6 Hz), 131.10 (d, *J* = 1.2 Hz), 130.27, 130.02 (q, *J* = 3.6 Hz), 129.71, 128.02, 124.82 (q, *J* = 3.9 Hz), 123.24 (d, *J* = 273.4 Hz).

**MS:** m/z: calc. for $C_{13}H_9FO_2S+Na^+$ 309.02, found 309.06.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.20.

Analytical data are consistent with literature.[13]

## Selectivity Studies

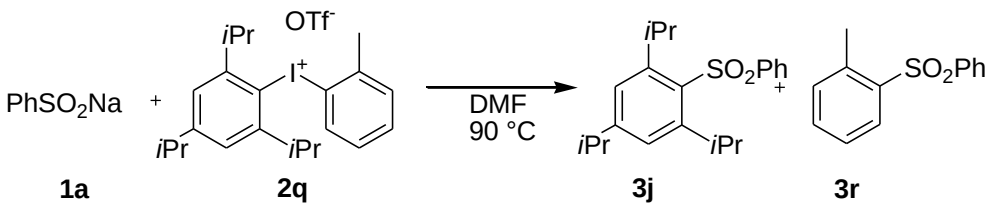



*Metall-free*

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with (2-methylphenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2p**) (0.55 mmol, 267.5 mg, 1.1 equiv) and benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg, 1.0 equiv) in 1.0 mL DMF. After heating to 90 °C, the reaction mixture was stirred at this temperature for 24 h. After cooling to room temperature, 10 mL sat. aq. $NH_4Cl$-solution was added and the aqueous layers were extracted three times with 15 mL $CH_2Cl_2$. The combined organic layers were washed with 15 mL dest. $H_2O$, dreid over $Na_2SO_4$ and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexan:EtOAc 20:1 → 9:1) yielded two products, **3n** (94.8 mg, 73 %) and **3r** (23.1 mg, 20 %), as colorless solids.

*Cu(I)-catalyzed*

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with (2-methylphenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2p**) (0.55 mmol, 267.5 mg, 1.1 equiv), benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg, 1.0 equiv) and CuI (0.05 mmol, 9.5 mg, 10 mol-%) in 1.0 mL DMF. After stirring at 90 °C for 24 h, the reaction was cooled to room temperature and 10 mL mL sat. aq. $NH_4Cl$-solution was added and the aqueous layers were extracted three times with 15 mL $CH_2Cl_2$. The combined organic layers were washed with 15 mL dest. $H_2O$, dried over $Na_2SO_4$ and the solvents were removed under reduced pressure. Isolation by column chromatography (Cyclohexan:EtOAc 100:1 → 9:1) afforded also two products, **3n** (22.5 mg, 17 %) and **3r** (65.9 mg, 57 %), as colorless solids.




*Metall-free*

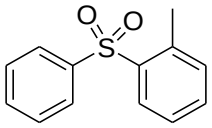
A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with (2-methylphenyl)(2,4,6-triisopropylphenyl)iodonium triflate (**2q**) (0.55 mmol, 313.17 mg, 1.1 equiv) and

benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg, 1.0 equiv) in 1.0 mL DMF. After heating to 90 °C, the reaction mixture was stirred at this temperature for 24 h. After cooling to room temperature, 10 mL sat. aq. $NH_4Cl$-solution was added and the aqueous layers were extracted three times with 15 mL $CH_2Cl_2$. The combined organic layers were washed with 15 mL dest. $H_2O$, dried over $Na_2SO_4$ and the solvents were removed under reduced pressure. Purification by column chromatography (Cyclohexane:EtOAc 20:1 → 4:1) yielded only product **3j** (173.8 mg, 96 %) as colorless solid.

*Cu(I)-catalyzed*

A dry, Ar-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with (2-methylphenyl)(2,4,6-triisopropylphenyl)iodonium triflate (**2q**) (0.55 mmol, 313.17 mg, 1.1 equiv), benzenesulfinic acid sodium salt (**1a**) (0.5 mmol, 82.2 mg, 1.0 equiv) and CuI (0.05 mmol, 9.5 mg, 10 mol-%) in 1.0 mL DMF. After stirring at 90 °C for 24 h, the reaction was cooled to room temperature and 10 mL mL sat. aq. $NH_4Cl$-solution was added and the aqueous layers were extracted three times with 15 mL $CH_2Cl_2$. The combined organic layers were washed with 15 mL dest. $H_2O$, dried over $Na_2SO_4$ and the solvents were removed under reduced pressure. Isolation by column chromatography (Cyclohexan:EtOAc 20:1 → 9:1) afforded the other sulfone **3r** (74.0 mg, 64 %) as colorless solids.

**1-methyl-2-(phenylsulfonyl)benzene (3r)**



**m.p.:** 73-73 °C.

**$^1$H-NMR** (250 MHz, $CDCl_3$): δ = 8.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.90 – 7.81 (m, *J* = 3.7, 2.7 Hz, 2H), 7.62 – 7.44 (m, 4H), 7.44 – 7.34 (m, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 2.44 (s, 3H).

**$^{13}$C-NMR** (63 MHz, $CDCl_3$): δ = 141.49, 139.00, 138.13, 133.72, 133.13, 132.80, 129.56, 129.14, 127.77, 126.59, 20.29.

**MS:** m/z: calc. for $C_{13}H_{12}O_2S+Na^+$ 255.05, found 255.08.

**$R_f$** (Cyclohexane:EtOAc 9:1): 0.24.

Analytical data are consistent with literature.[14]

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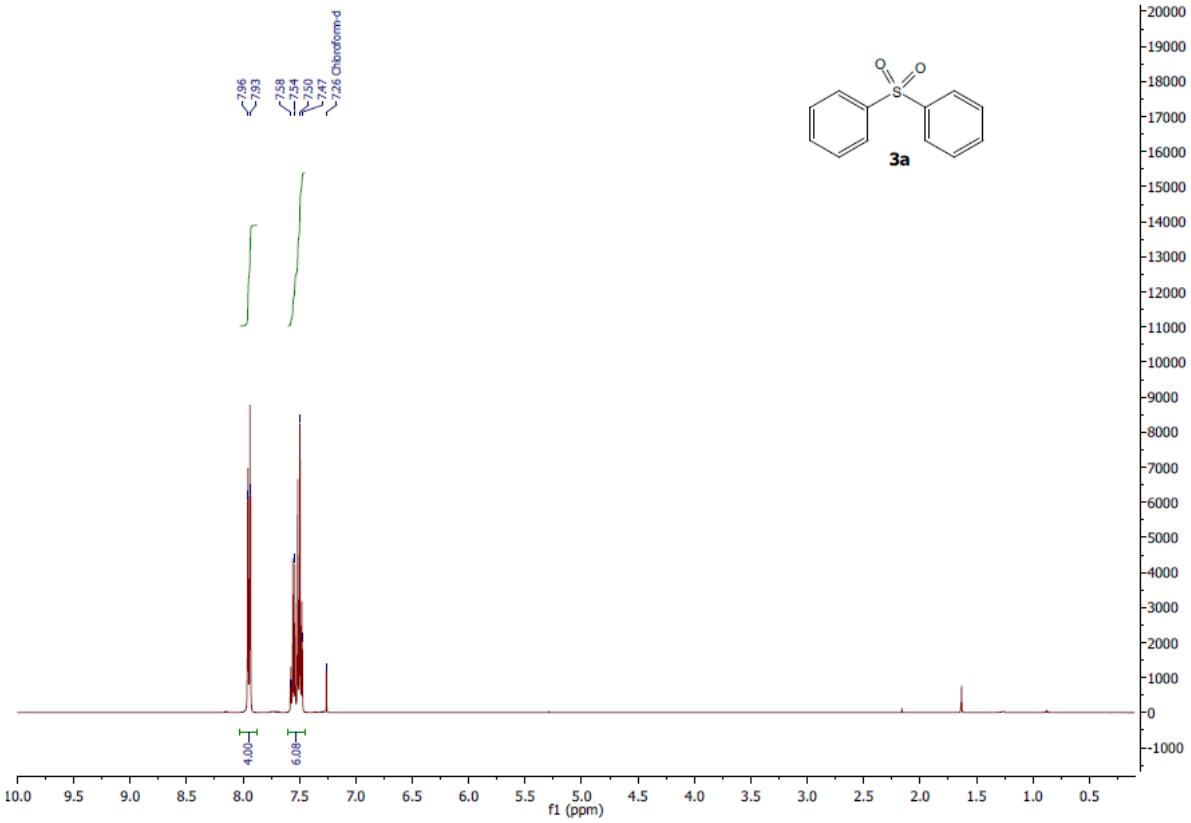
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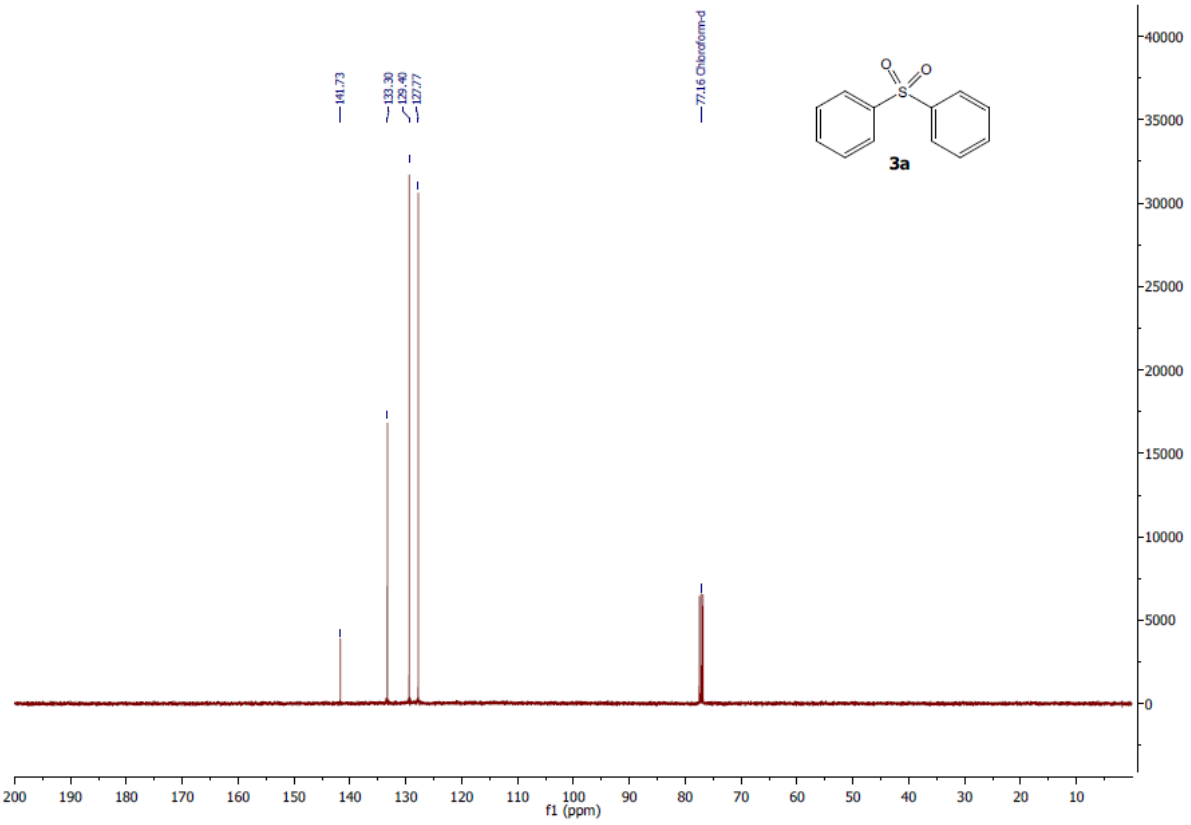
7.93
7.58
7.54
7.50
7.47
7.26 Chloroform-d
3a
4.00
6.08
f1 (ppm)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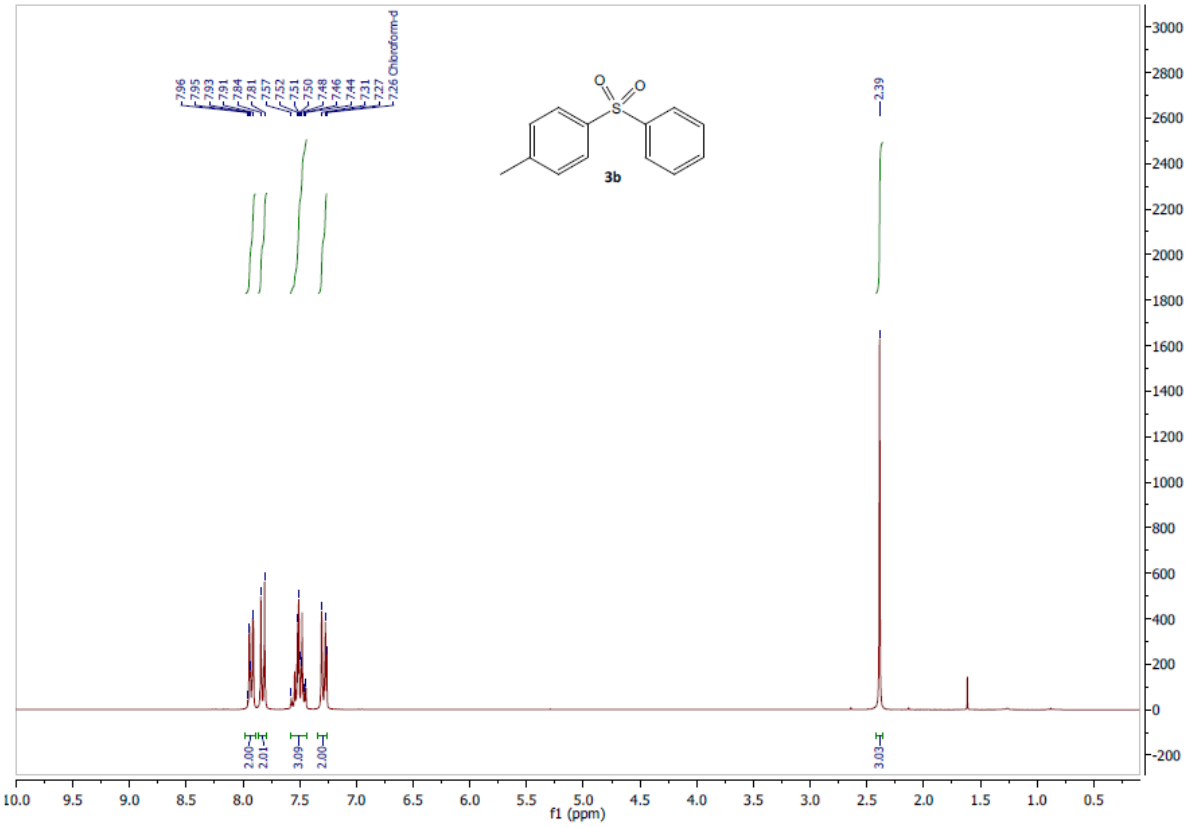
133.30
129.40
127.77
77.16 Chloroform-d
3a
f1 (ppm)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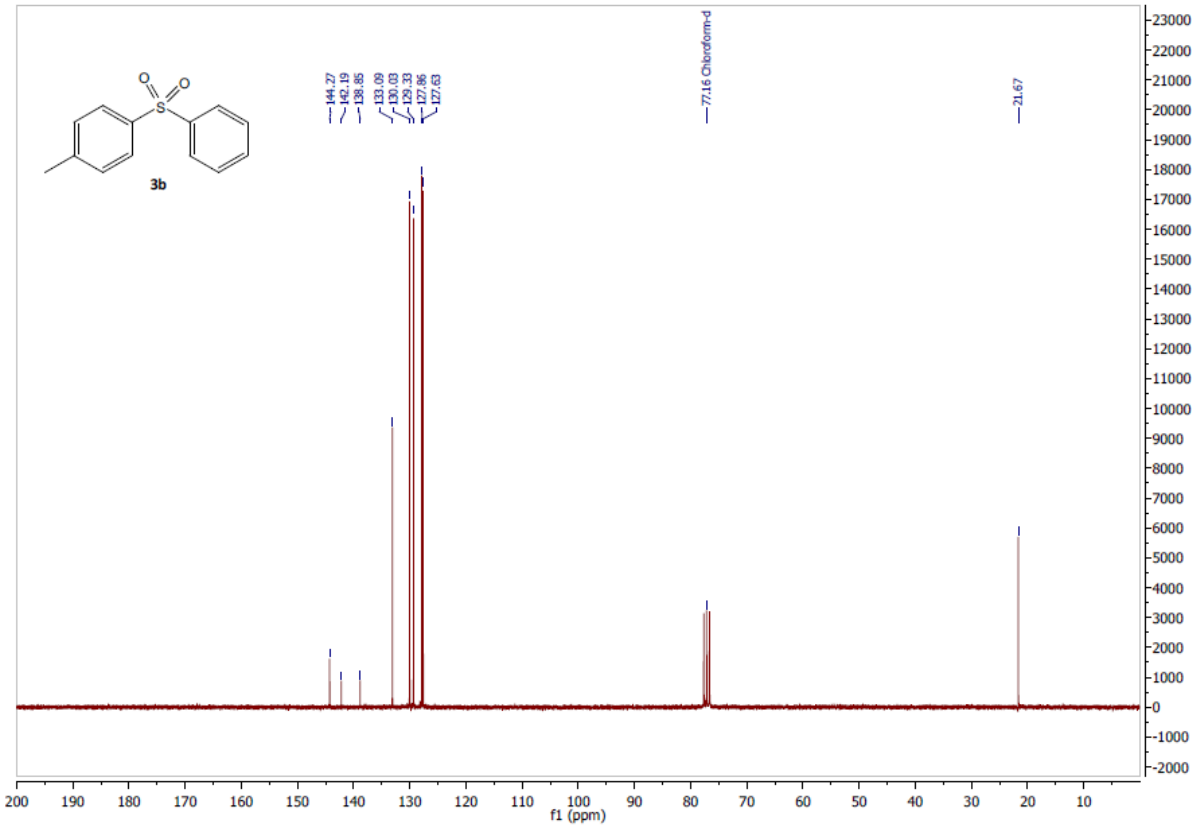
7.95
7.93
7.91
7.84
7.81
7.57
7.52
7.51
7.50
7.48
7.46
7.44
7.31
7.27
7.26 Chloroform-d
2.39
3b
2.00
2.01
3.09
2.00
3.03
f1 (ppm)


144.27
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129.33
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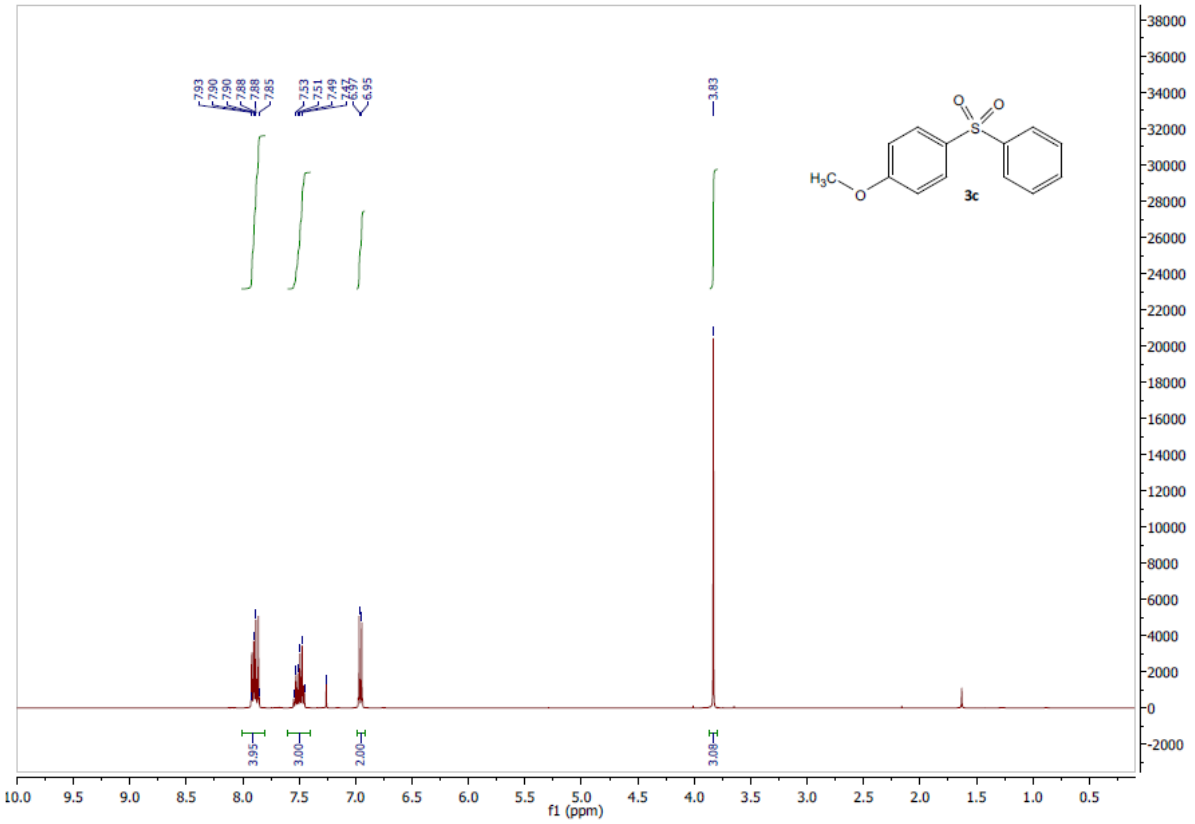
21.67
3b
f1 (ppm)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7.90
7.90
7.88
7.88
7.85
7.53
7.51
7.49
7.47
7.47
6.95
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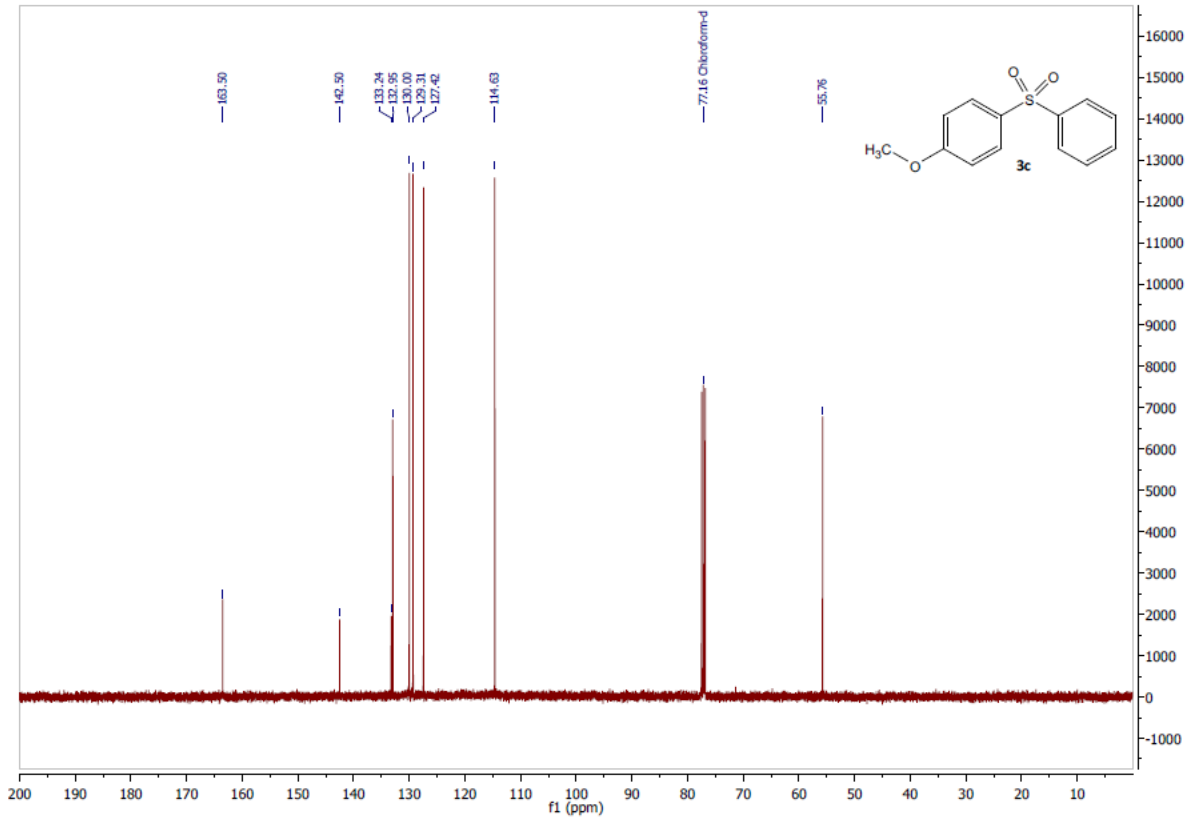
3c
3.95
3.00
2.00
3.08
f1 (ppm)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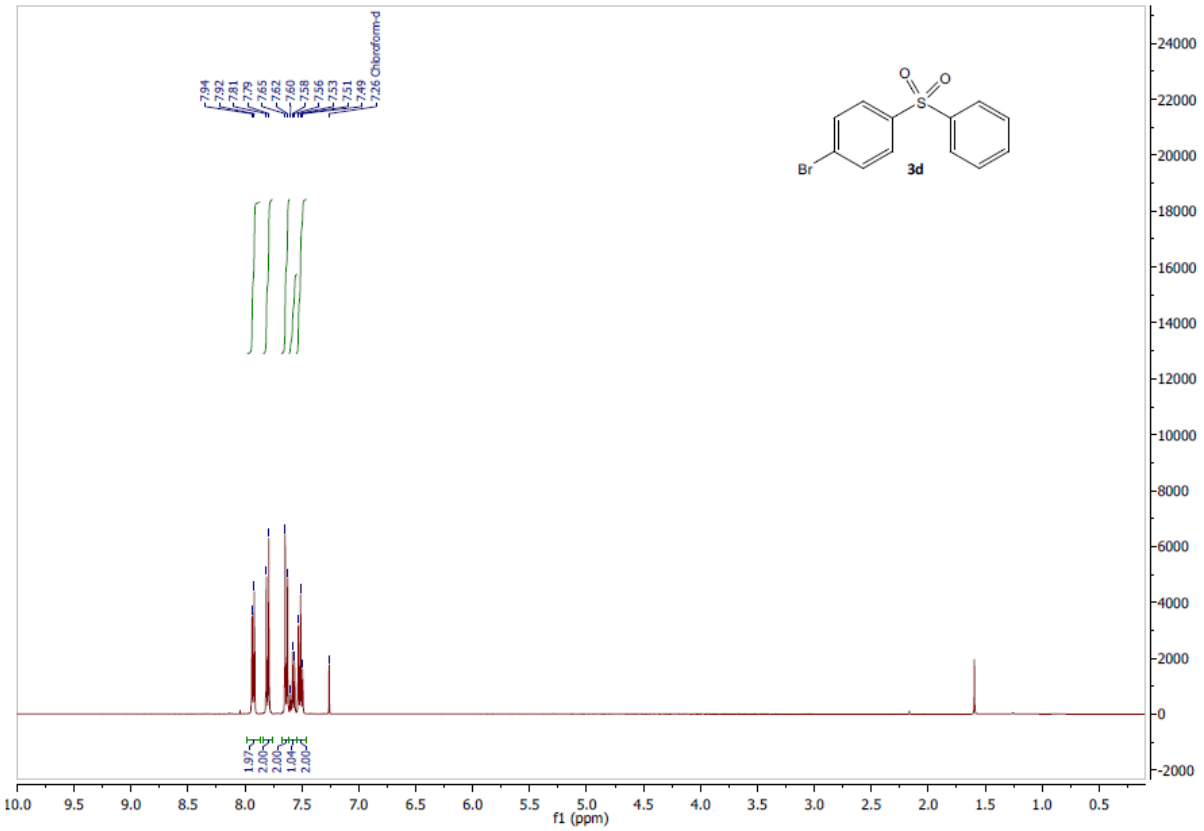
3c
f1 (ppm)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7.65
7.62
7.60
7.58
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7.53
7.51
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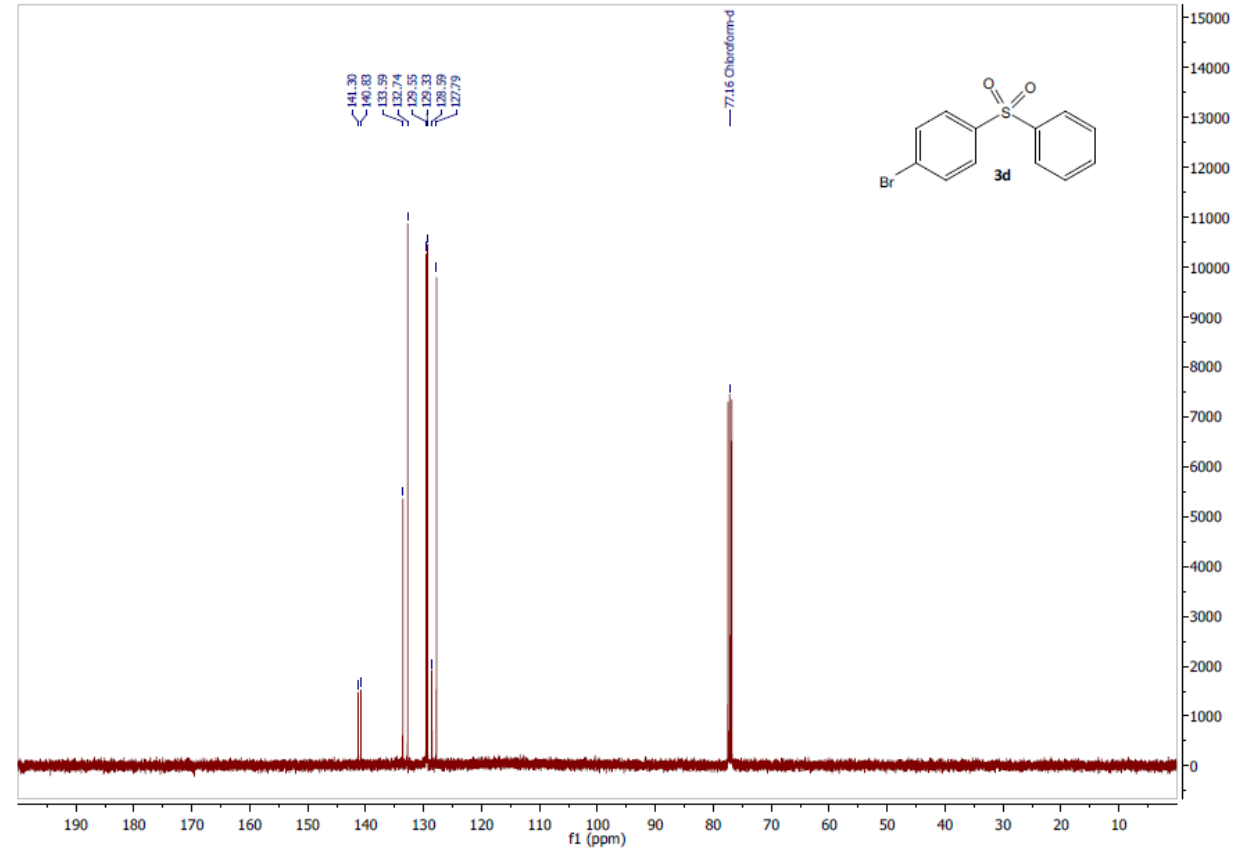
Br
3d
1.97
2.00
2.00
1.04
2.00
f1 (ppm)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129.33
128.59
127.79
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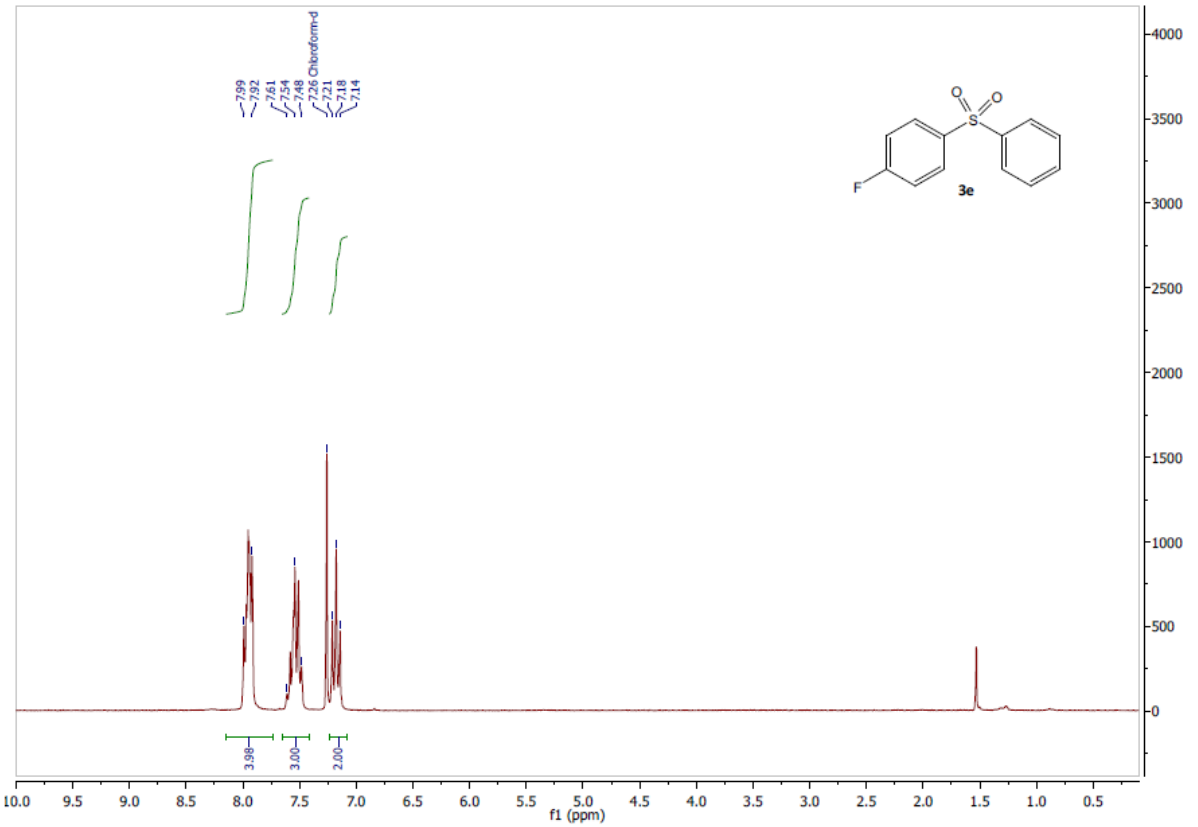
Br
3d
f1 (ppm)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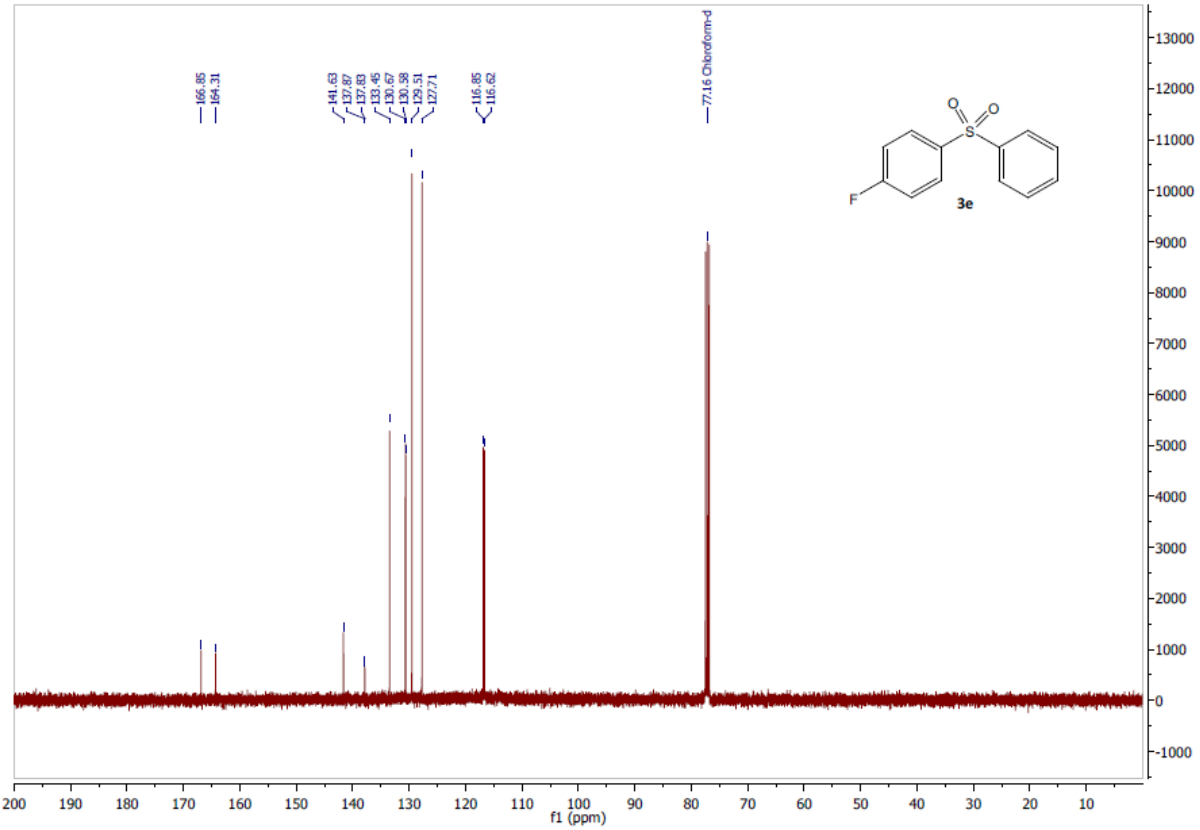
3.98
3.00
2.00
f1 (ppm)
3e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164.31
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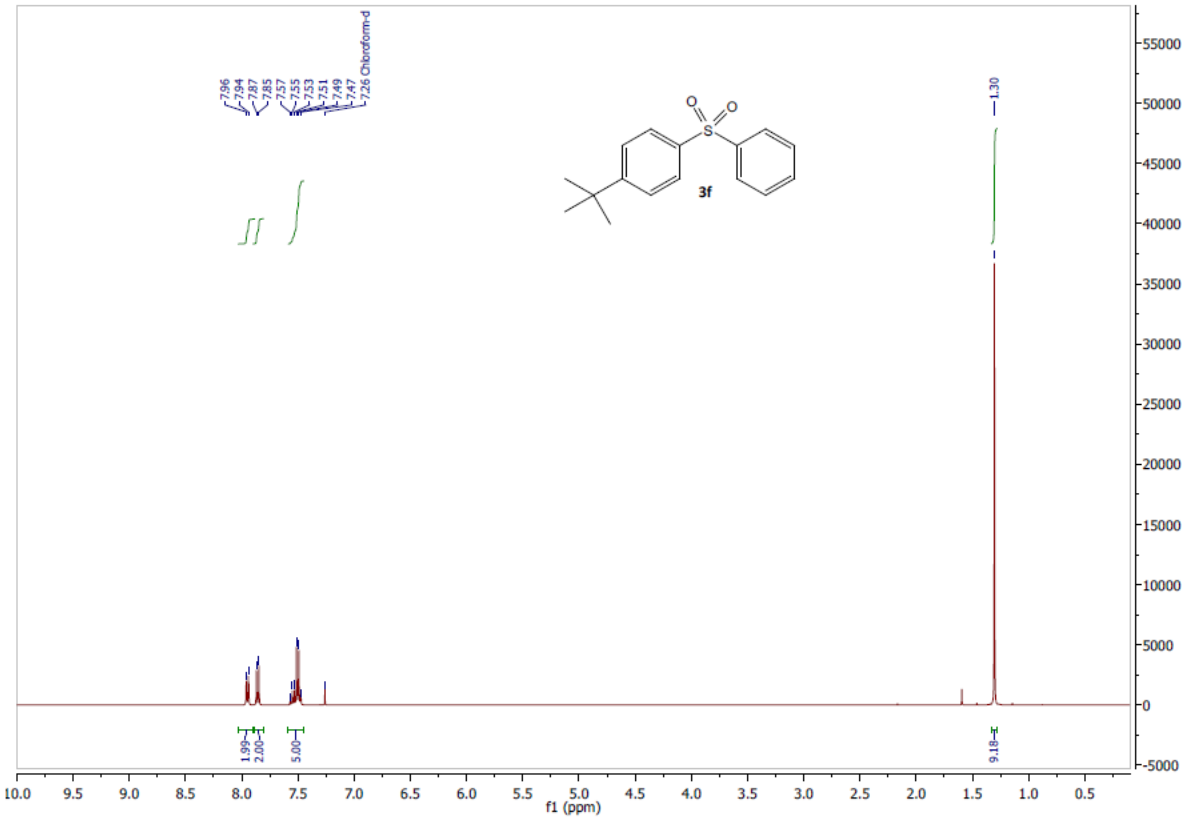
127.71
116.85
116.62
77.16 Chloroform-d
f1 (ppm)
3e


7.96
7.94
7.87
7.85
7.57
7.55
7.53
7.51
7.49
7.47
7.26 Chloroform-d
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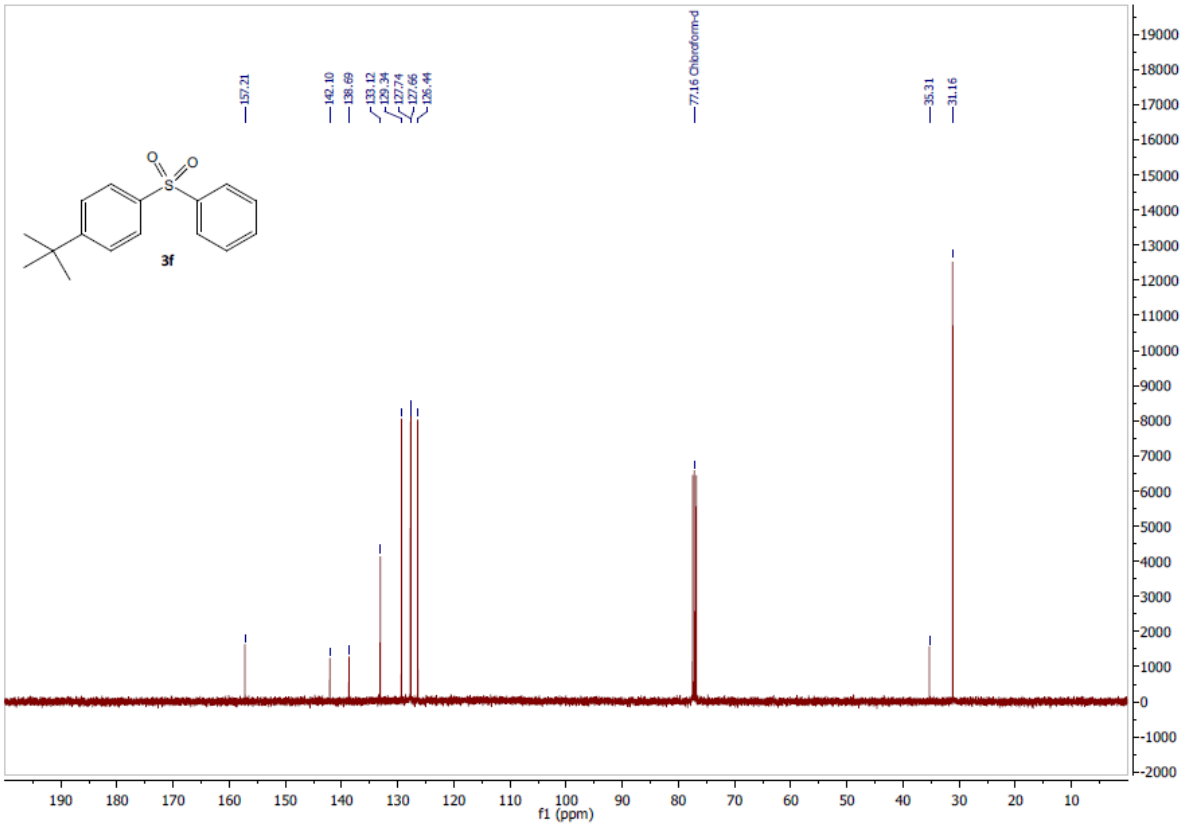
1.99
2.00
5.00
9.18
f1 (ppm)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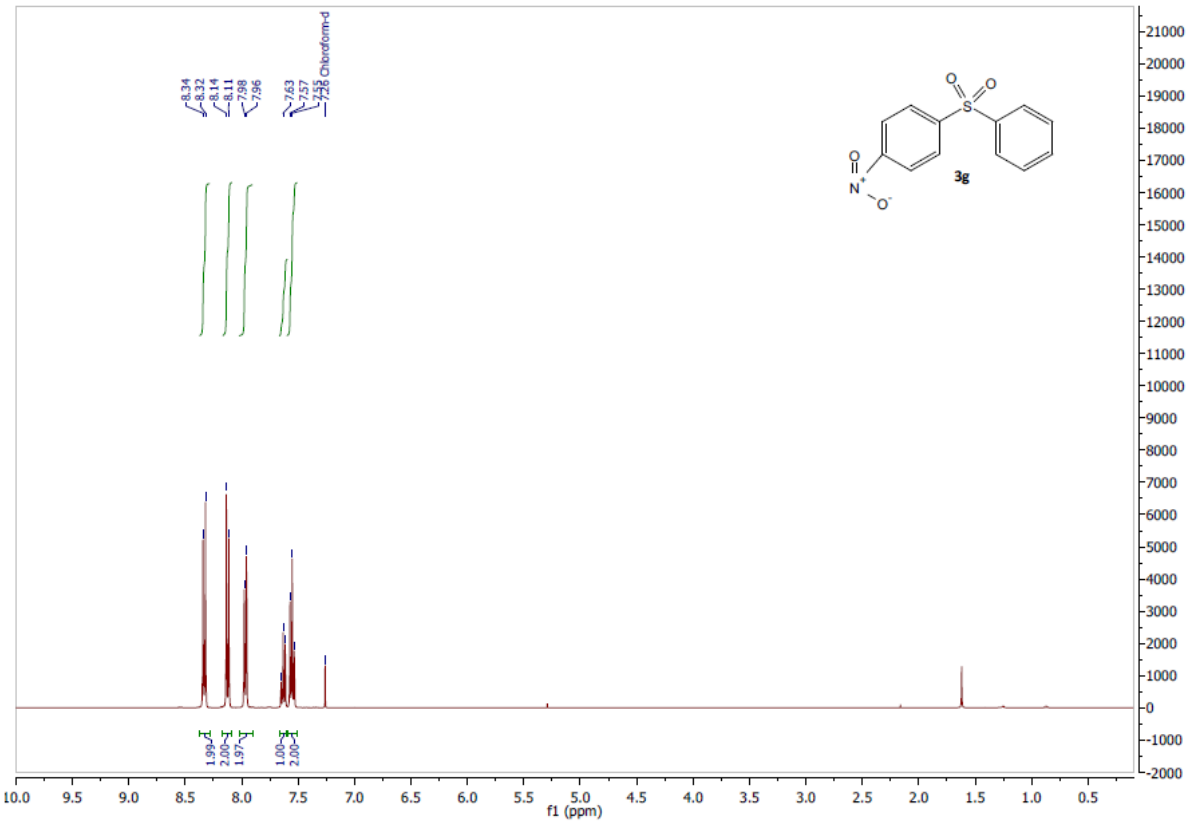
31.16
3f
f1 (ppm)


8.34
8.32
8.14
8.11
7.98
7.96
7.63
7.57
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1.99
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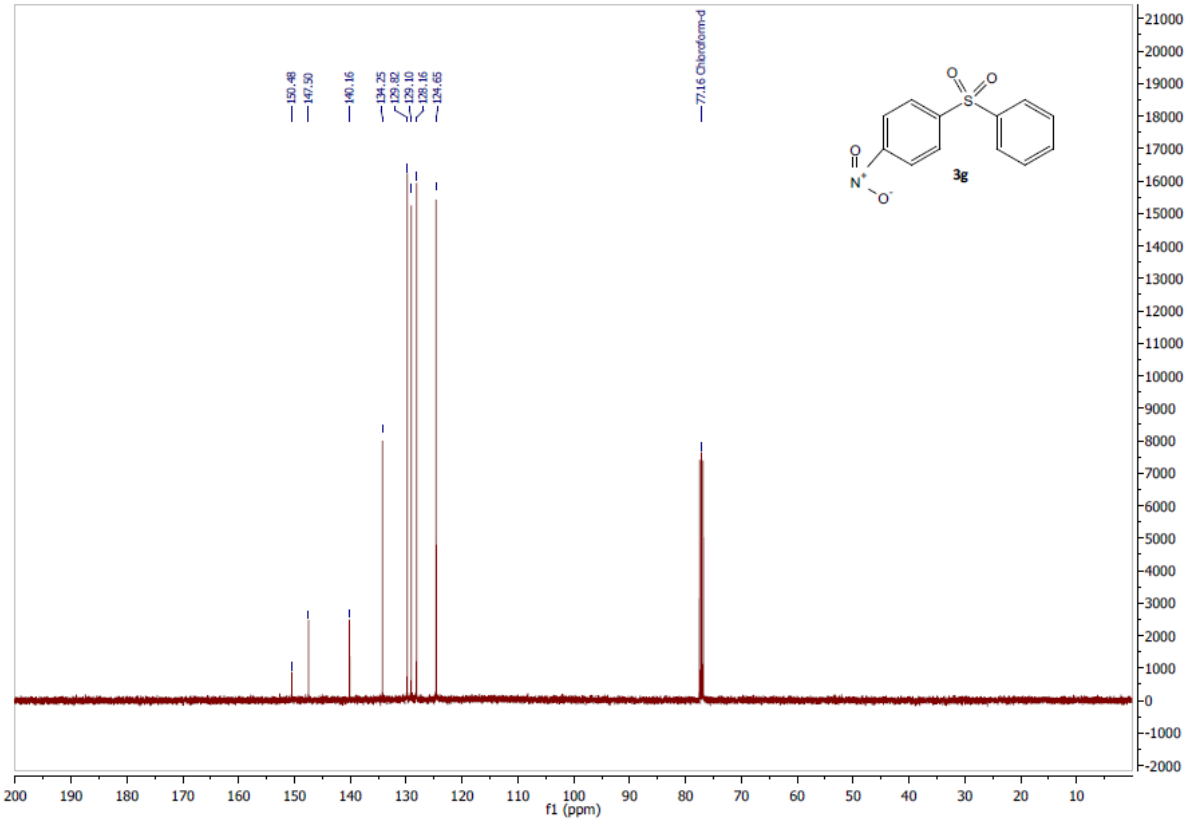
1.97
1.00
2.00
3g
f1 (ppm)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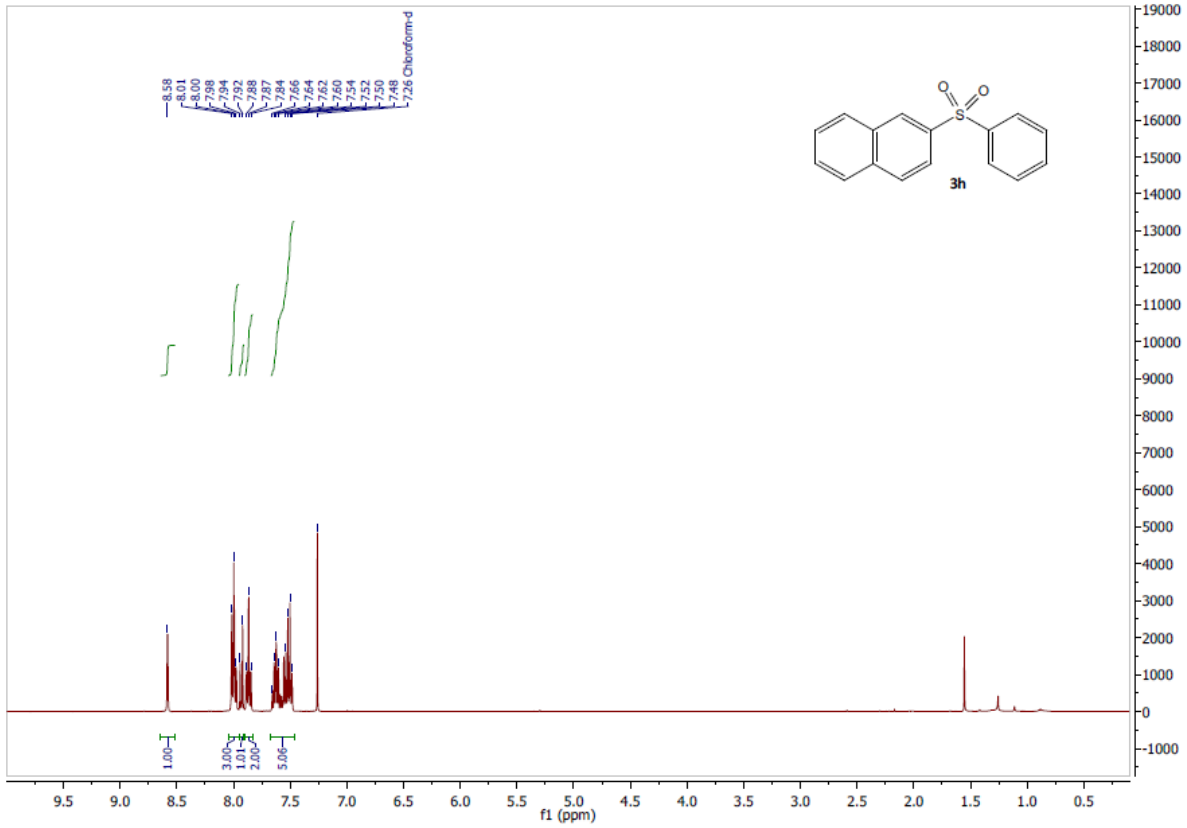
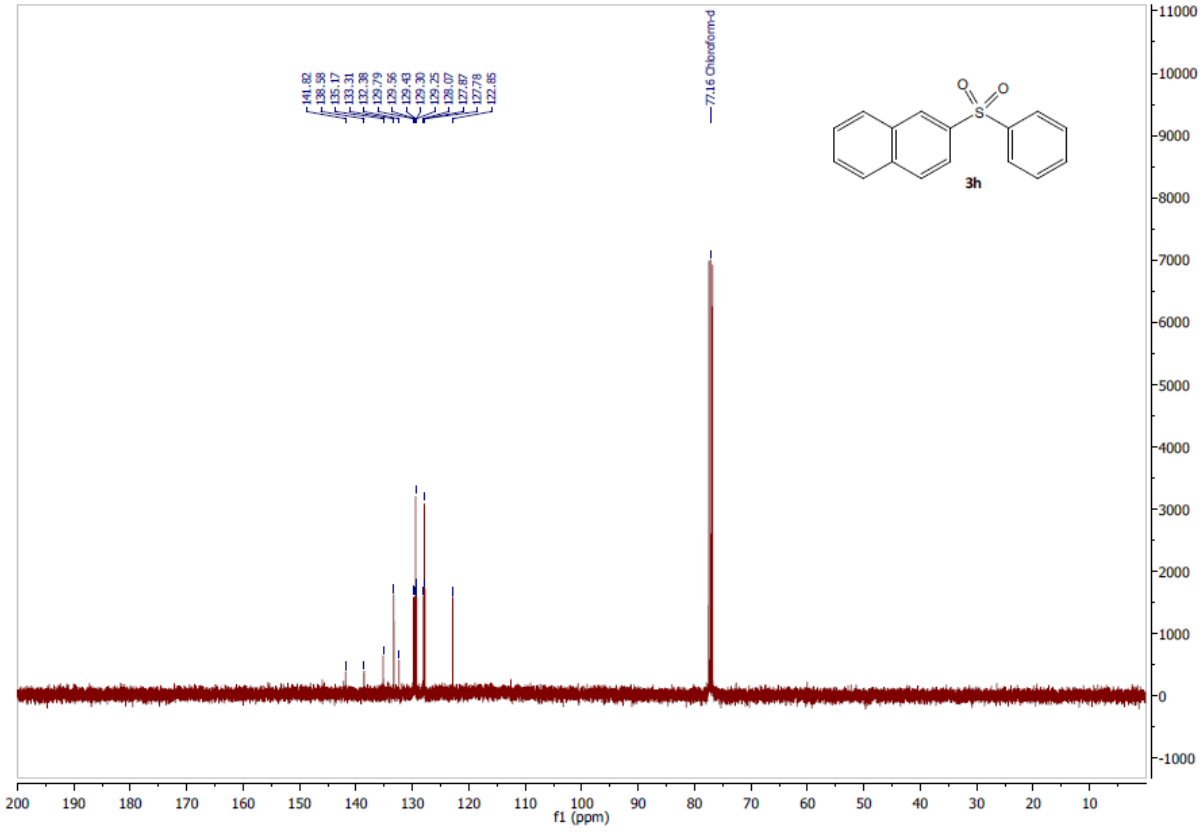
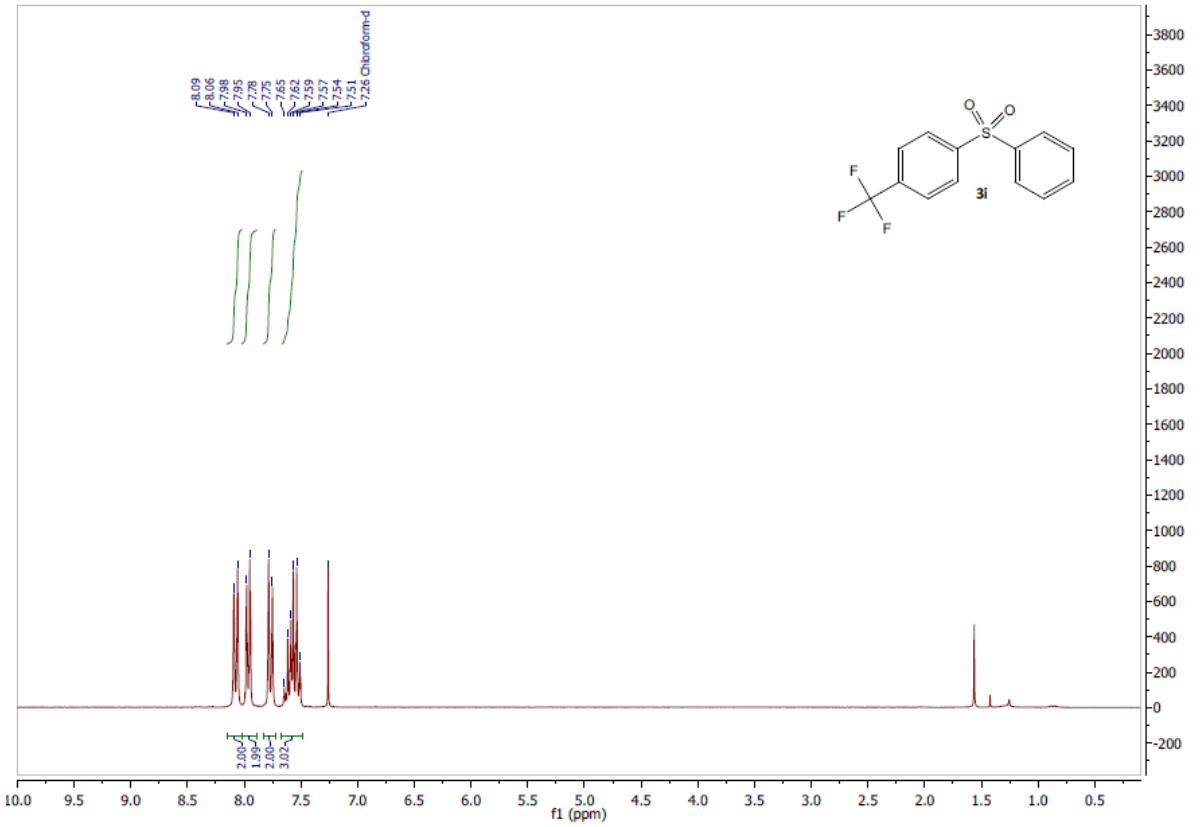
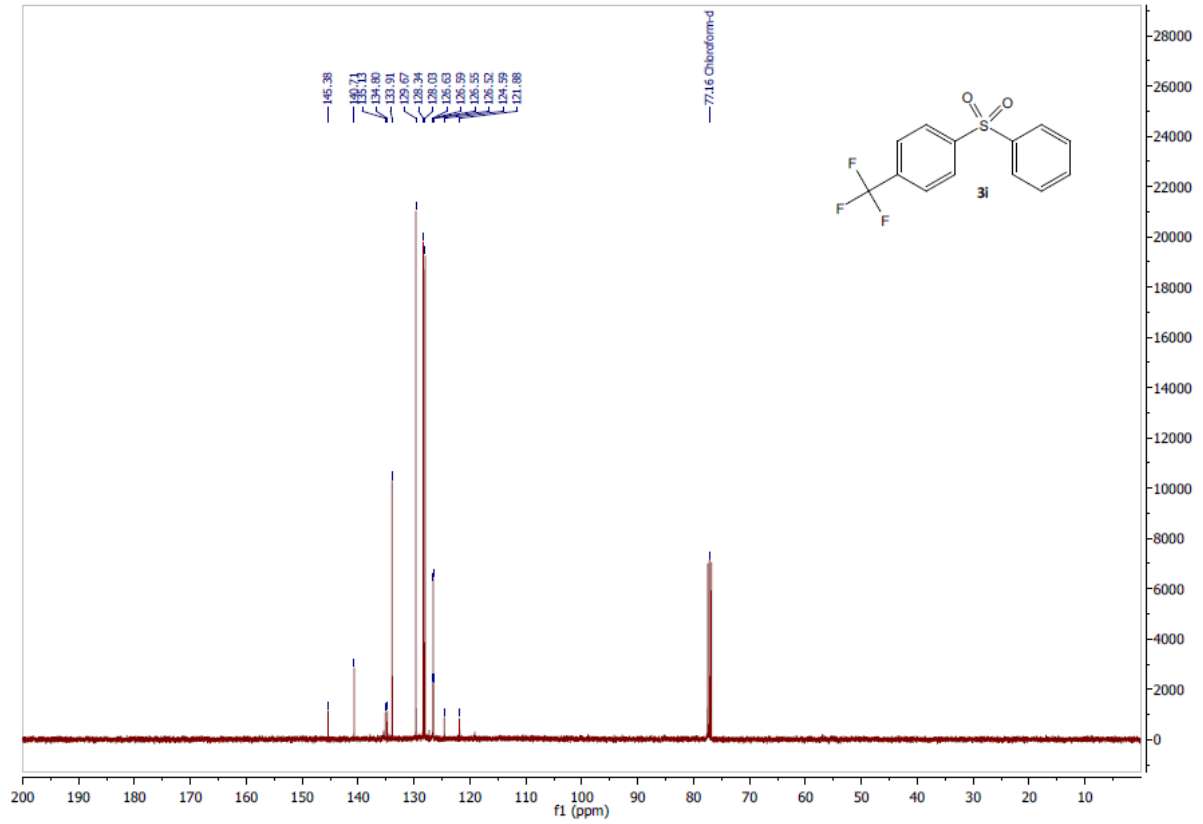
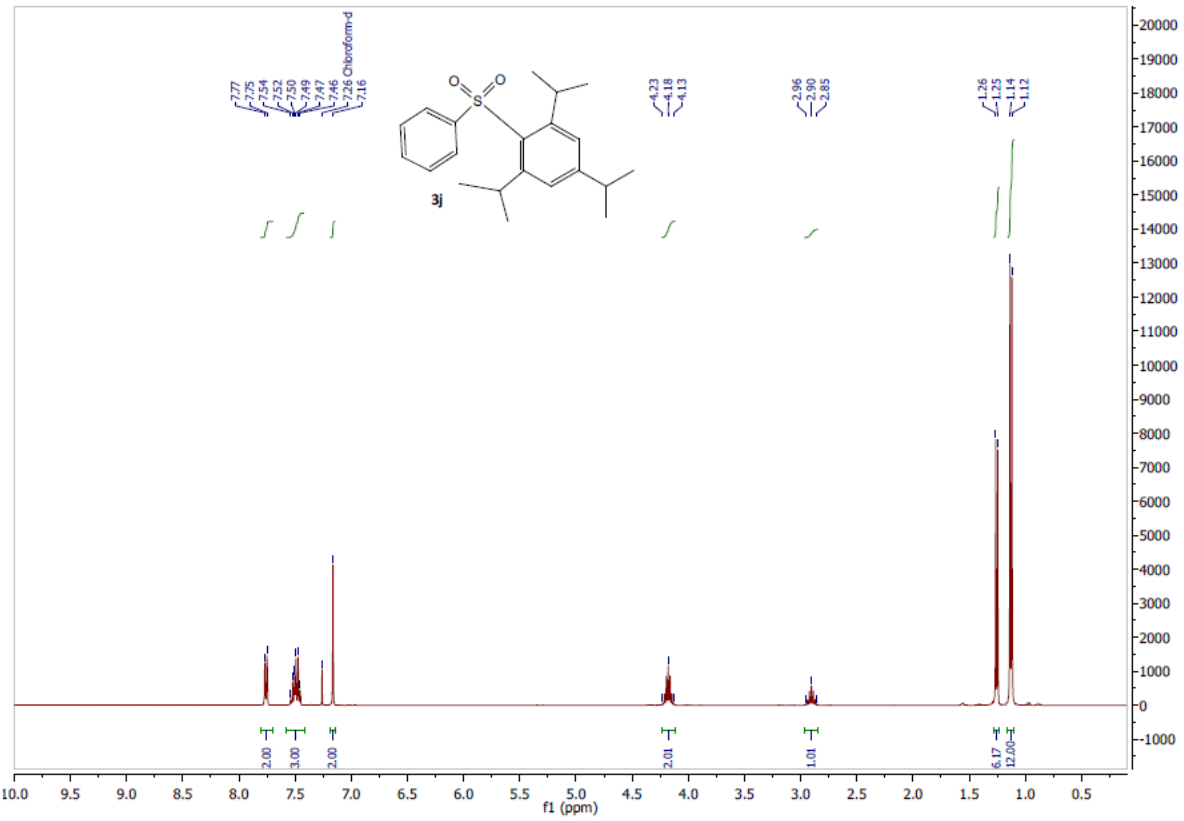
3g
f1 (ppm)

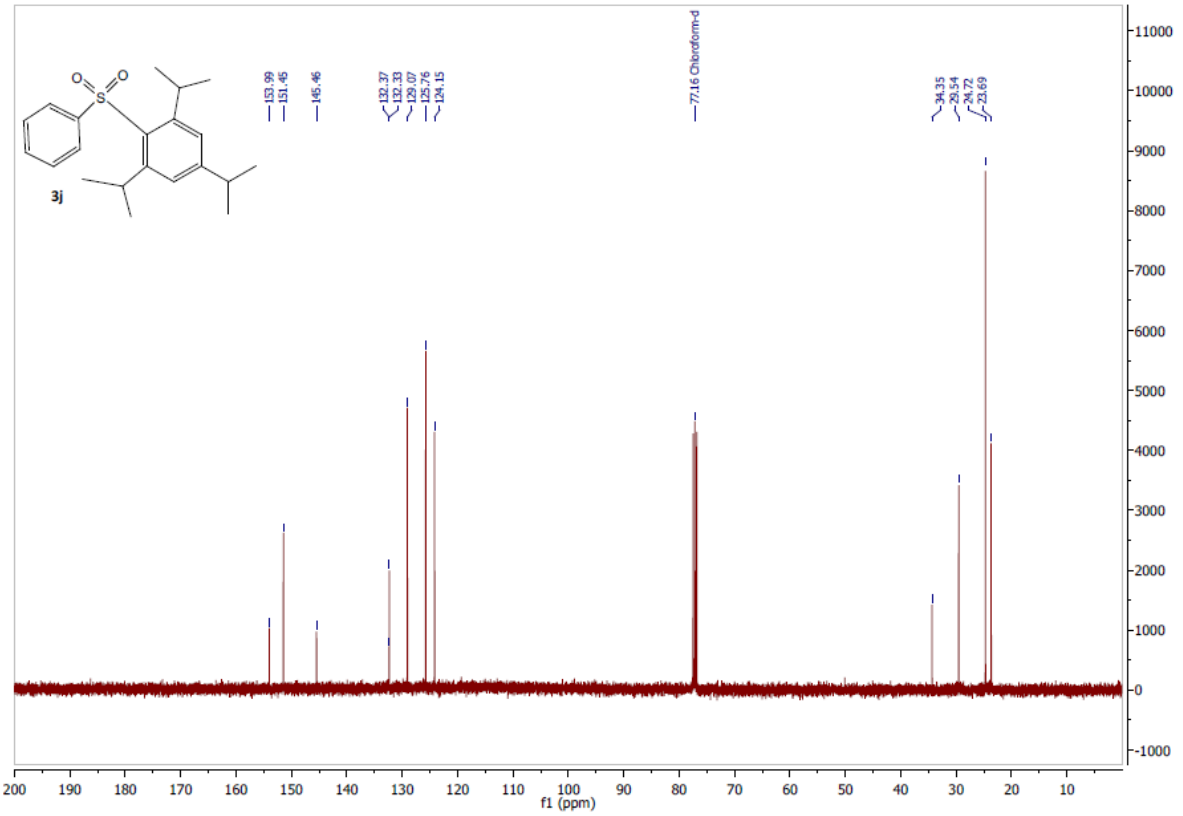

8.58
8.01
8.00
7.98
7.94
7.92
7.88
7.87
7.84
7.66
7.64
7.62
7.60
7.54
7.52
7.50
7.48
7.26 Chloroform-d
3h
1.00
3.00
1.01
2.00
5.06
f1 (ppm)

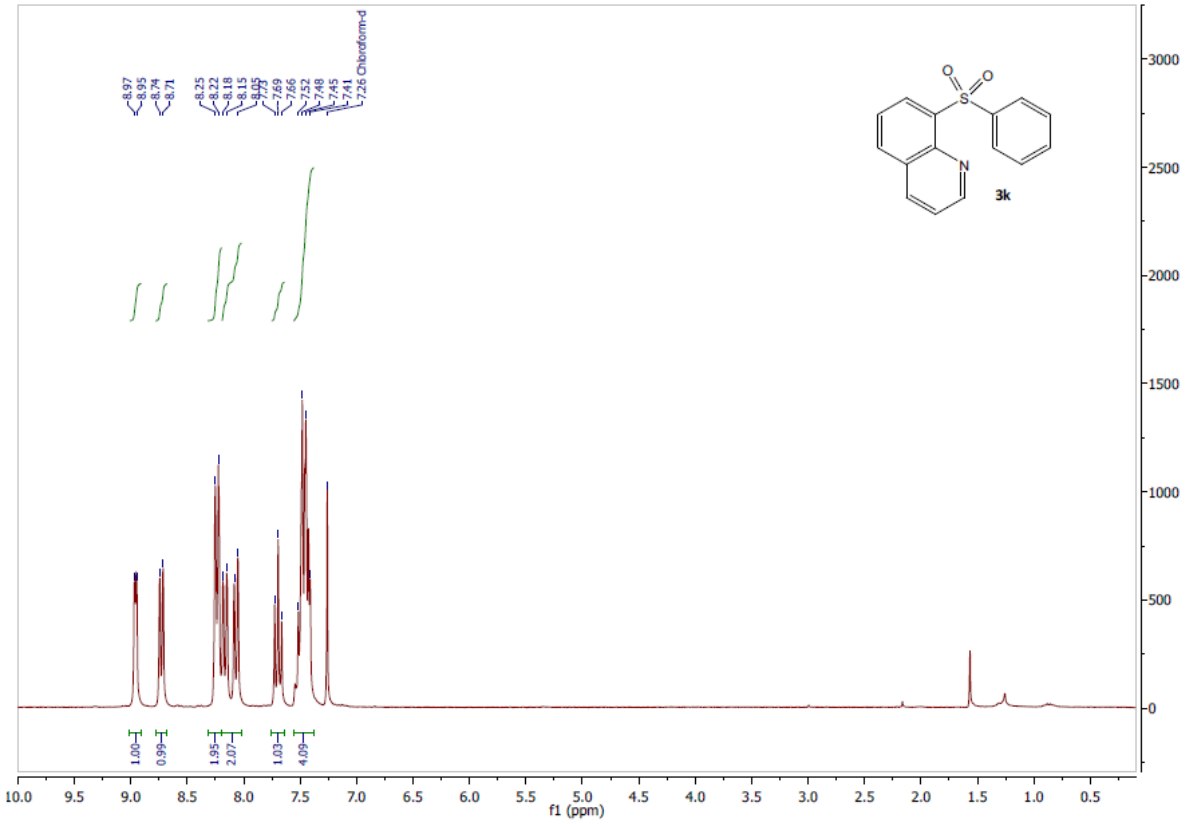

141.82
138.58
135.17
133.31
132.38
129.79
129.56
129.43
129.30
129.25
128.07
127.87
127.78
122.85
77.16 Chloroform-d
3h
f1 (ppm)

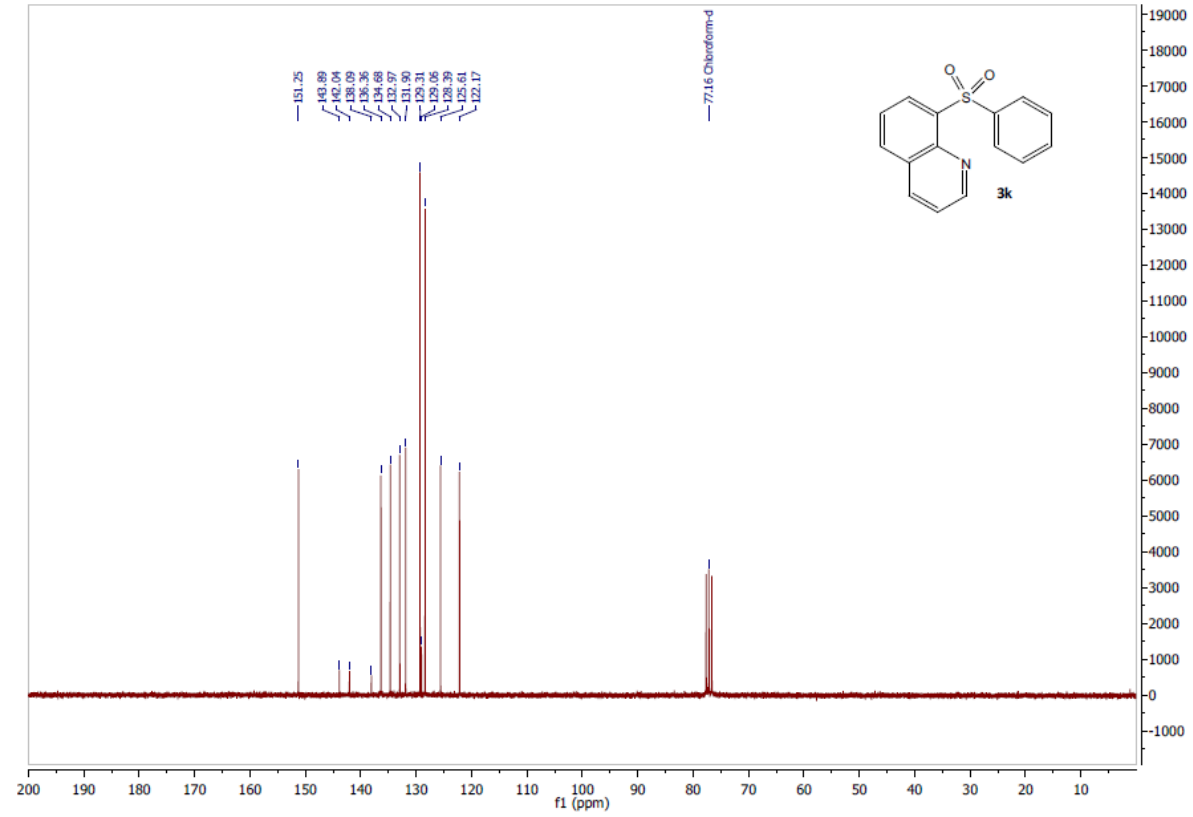

8.09
8.06
7.98
7.95
7.78
7.75
7.65
7.62
7.59
7.57
7.54
7.51
7.26 Chloroform-d
2.00
1.99
2.00
3.02
3i
f1 (ppm)

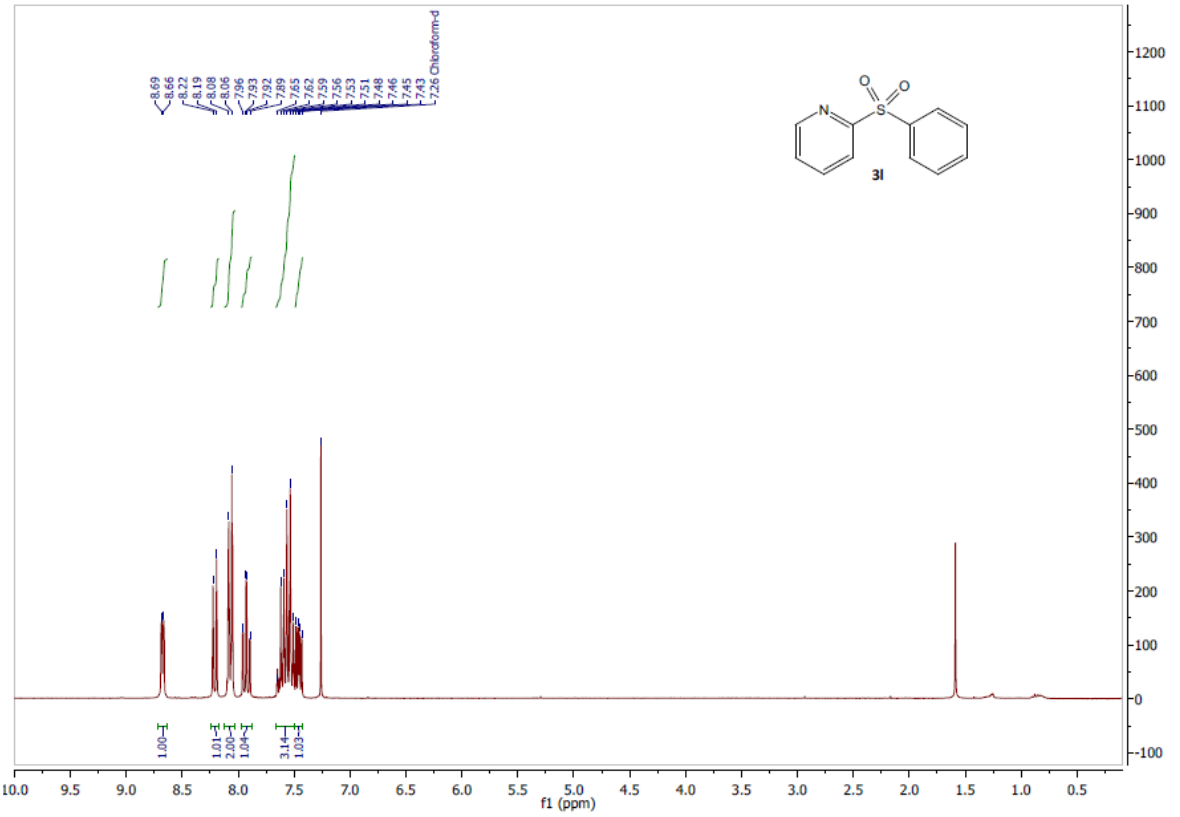

145.38
140.71
135.13
134.80
133.91
129.67
128.34
128.03
126.63
126.59
126.55
126.52
124.59
121.88
77.16 Chloroform-d
3i
f1 (ppm)

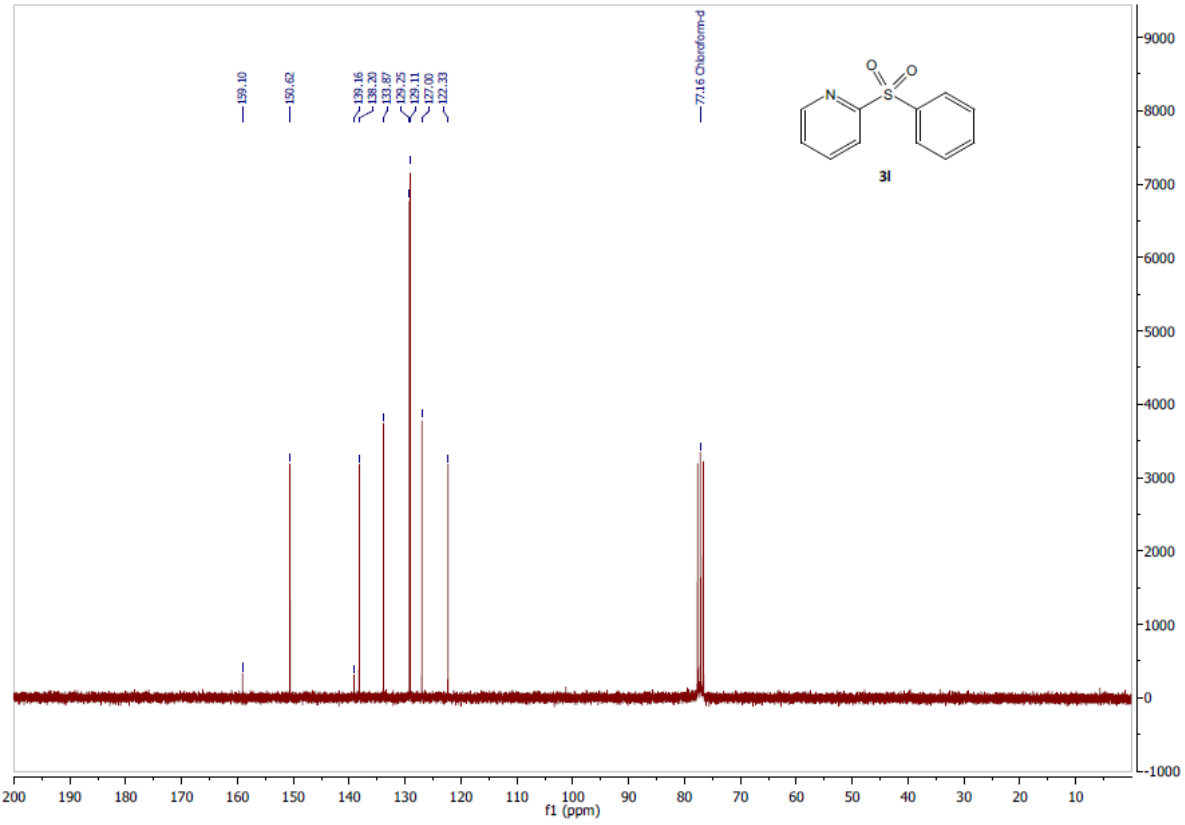

7.77
7.75
7.54
7.52
7.50
7.49
7.47
7.46
7.26 Chloroform-d
7.16
4.23
4.18
4.13
2.96
2.90
2.85
1.26
1.25
1.14
1.12
3j
2.00
3.00
2.00
2.01
1.01
6.17
12.00
f1 (ppm)

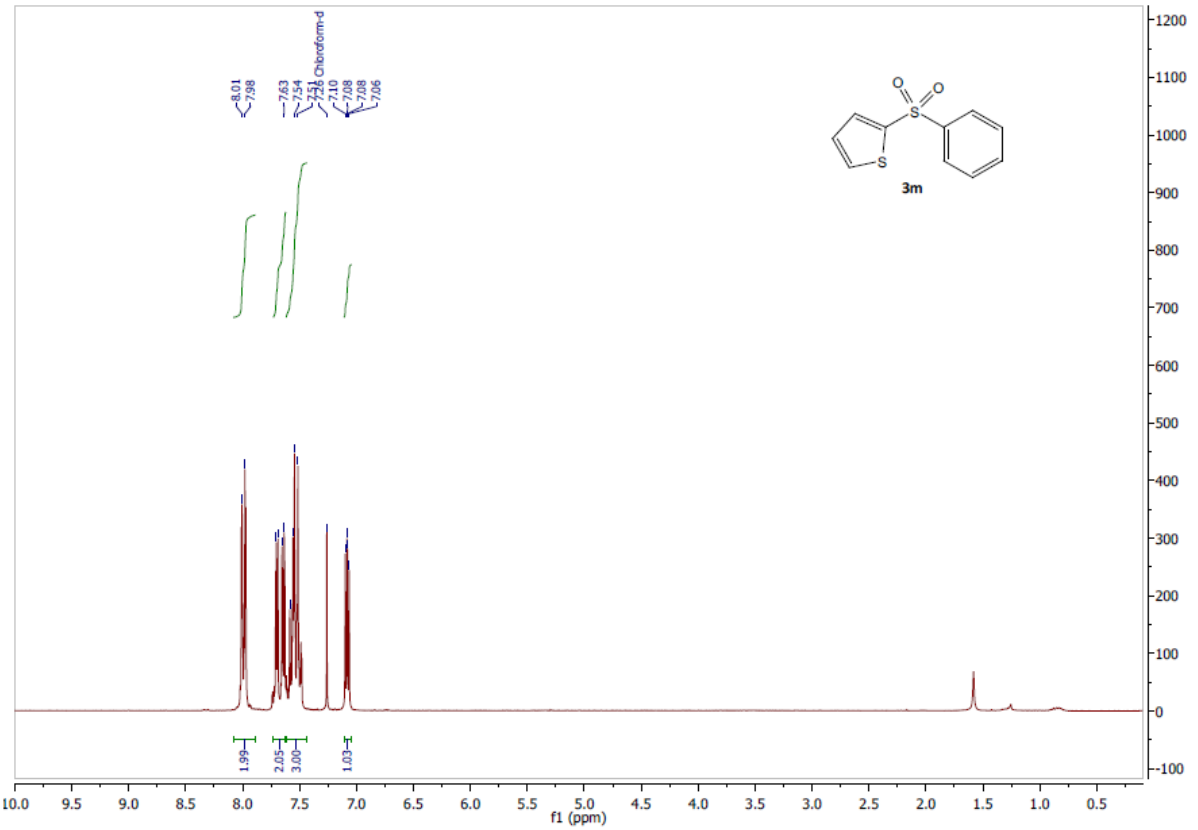

153.99
151.45
145.46
132.37
132.33
129.07
125.76
124.15
77.16 Chloroform-d
34.35
29.54
24.72
23.69
3j
f1 (ppm)

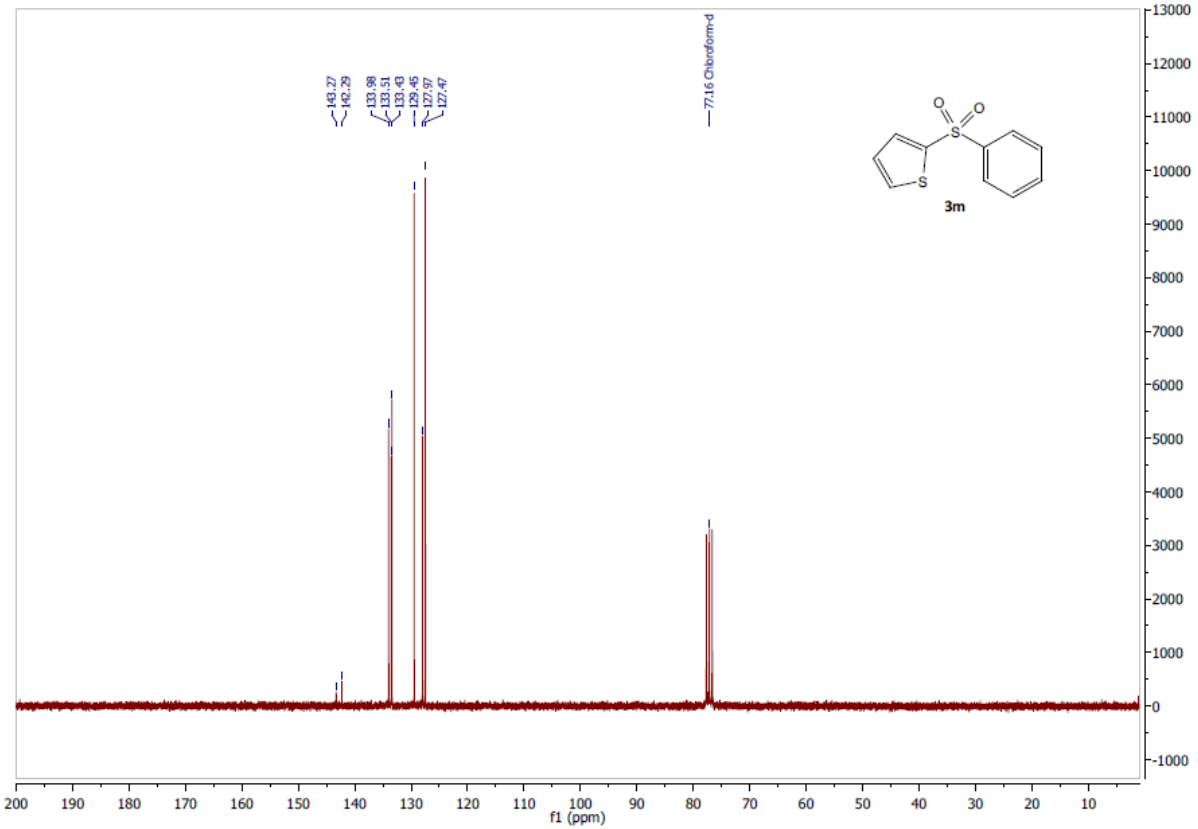

8.97
8.95
8.74
8.71
8.25
8.22
8.18
8.15
8.05
7.93
7.89
7.66
7.52
7.48
7.45
7.41
7.26 Chloroform-d
1.00
0.99
1.95
2.07
1.03
4.09
3k
f1 (ppm)

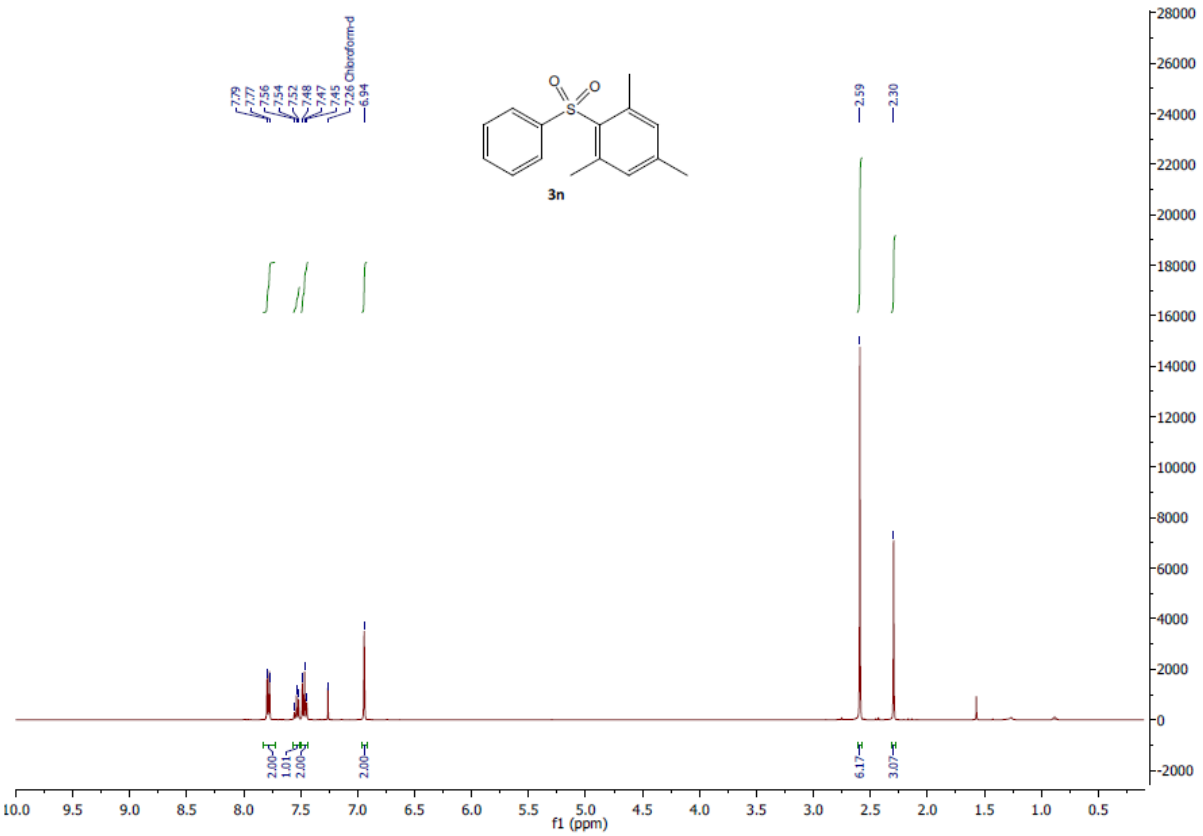

151.25
143.89
142.04
138.09
136.36
134.68
132.97
131.90
129.31
129.06
128.39
125.61
122.17
77.16 Chloroform-d
3k
f1 (ppm)

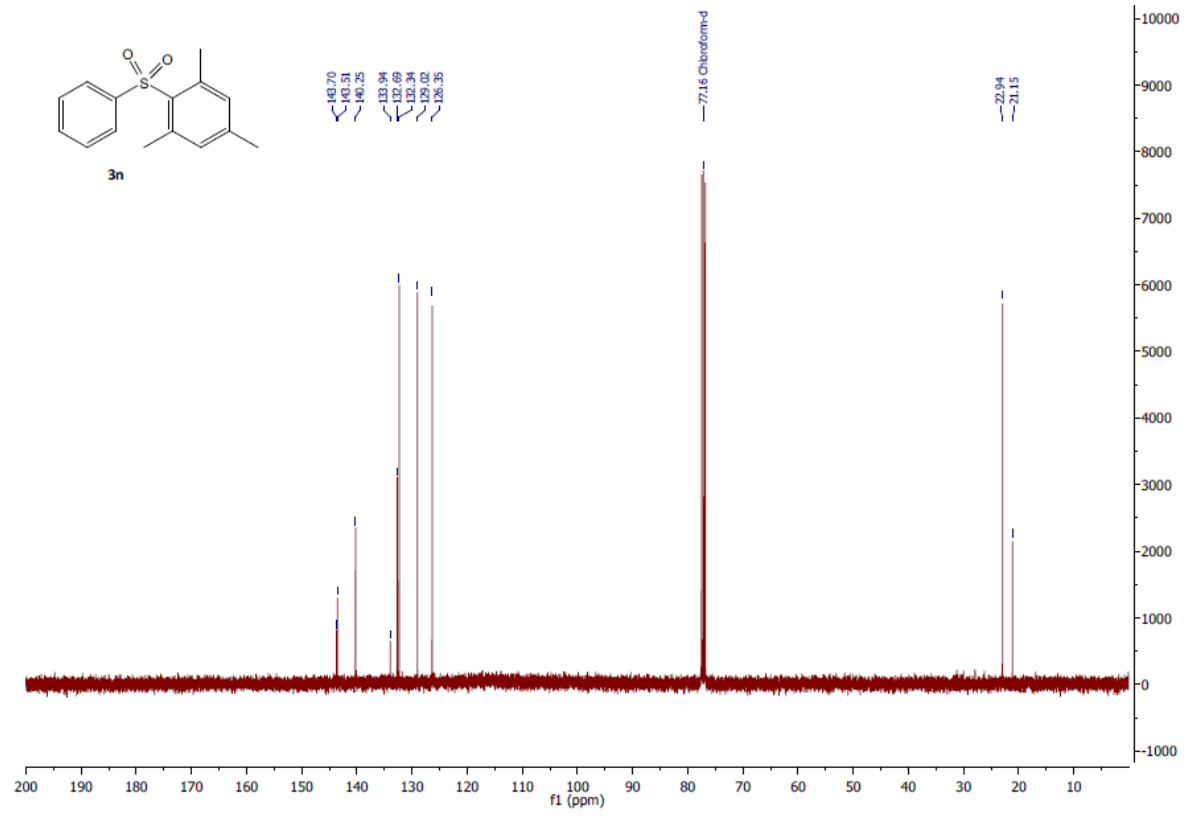

8.69
8.66
8.22
8.19
8.08
8.06
7.96
7.93
7.92
7.89
7.65
7.62
7.59
7.56
7.53
7.51
7.48
7.46
7.45
7.43
7.26 Chloroform-d
O
O
N
S
3l
1.00
1.01
2.00
1.04
3.14
1.03
f1 (ppm)

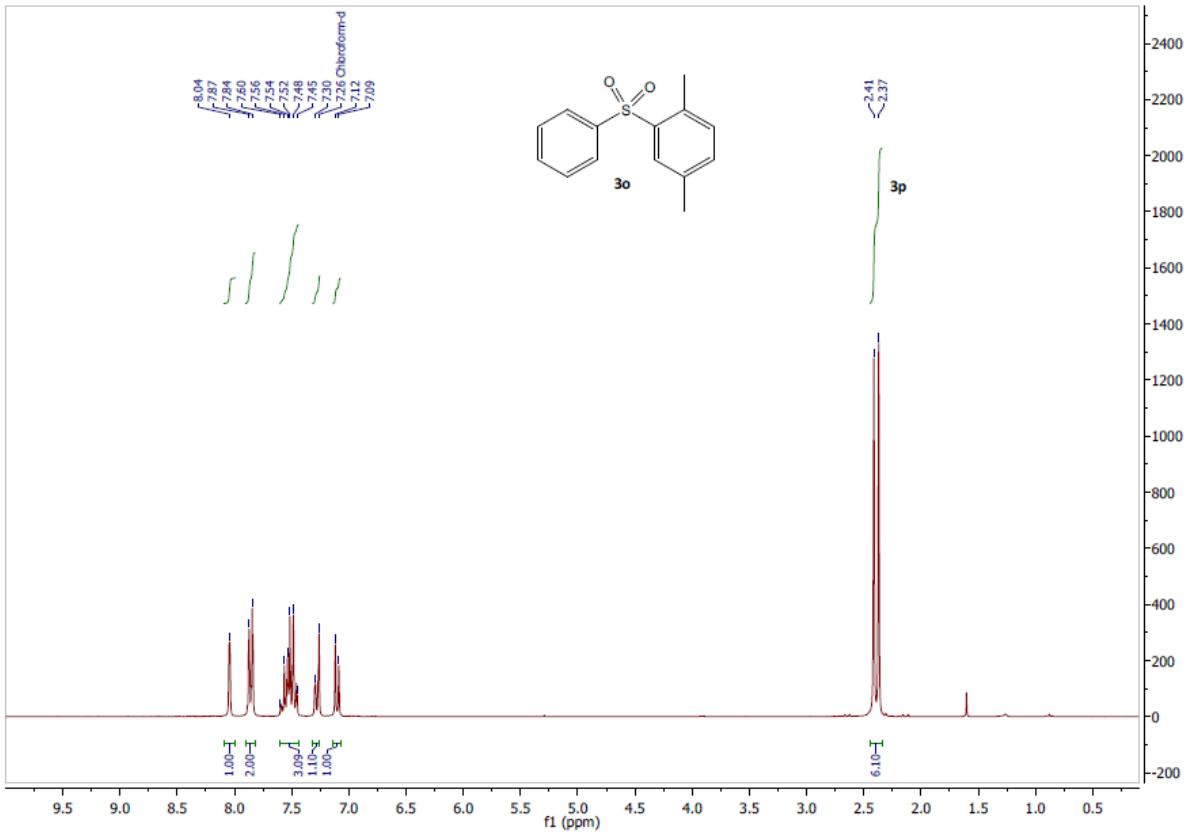

159.10
150.62
139.16
138.20
133.87
129.25
129.11
127.00
122.33
77.16 Chloroform-d
O
O
N
S
3l
f1 (ppm)

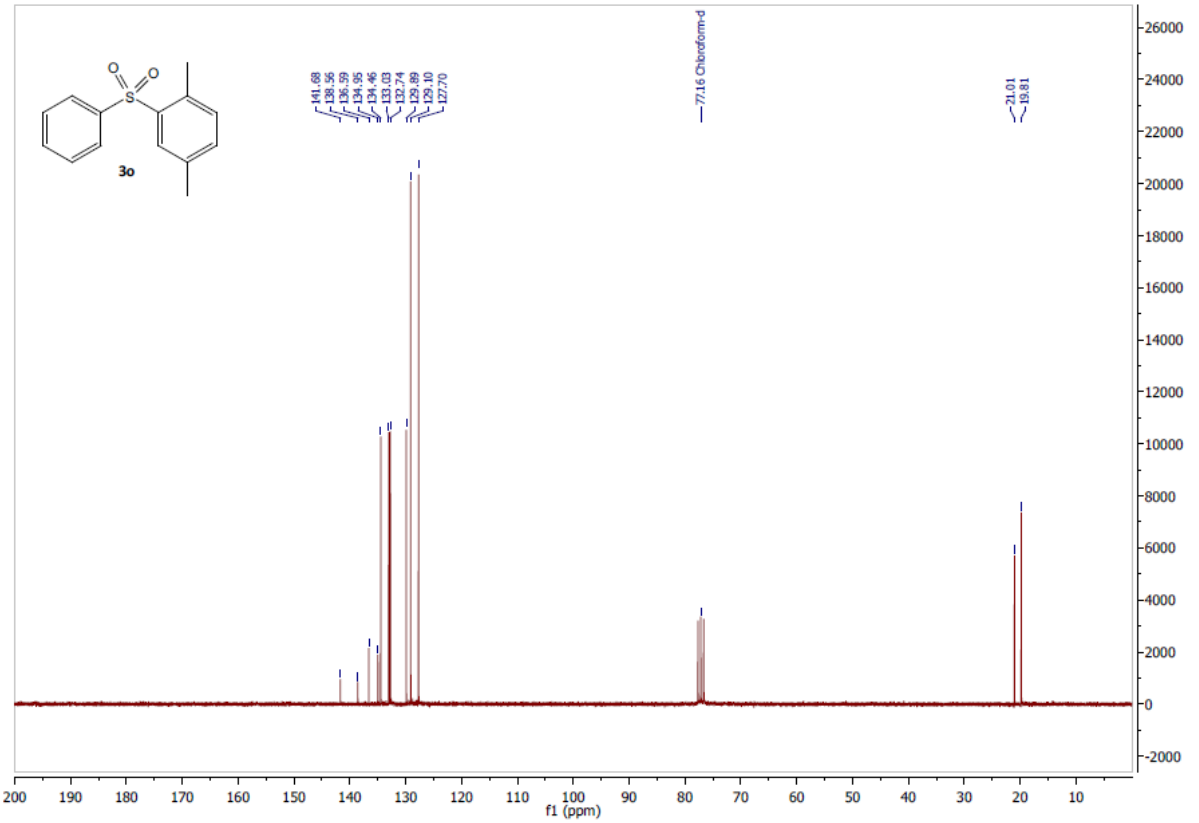

8.01
7.98
7.63
7.54
7.51
7.26 Chloroform-d
7.10
7.08
7.08
7.06
1.99
2.05
3.00
1.03
3m
f1 (ppm)

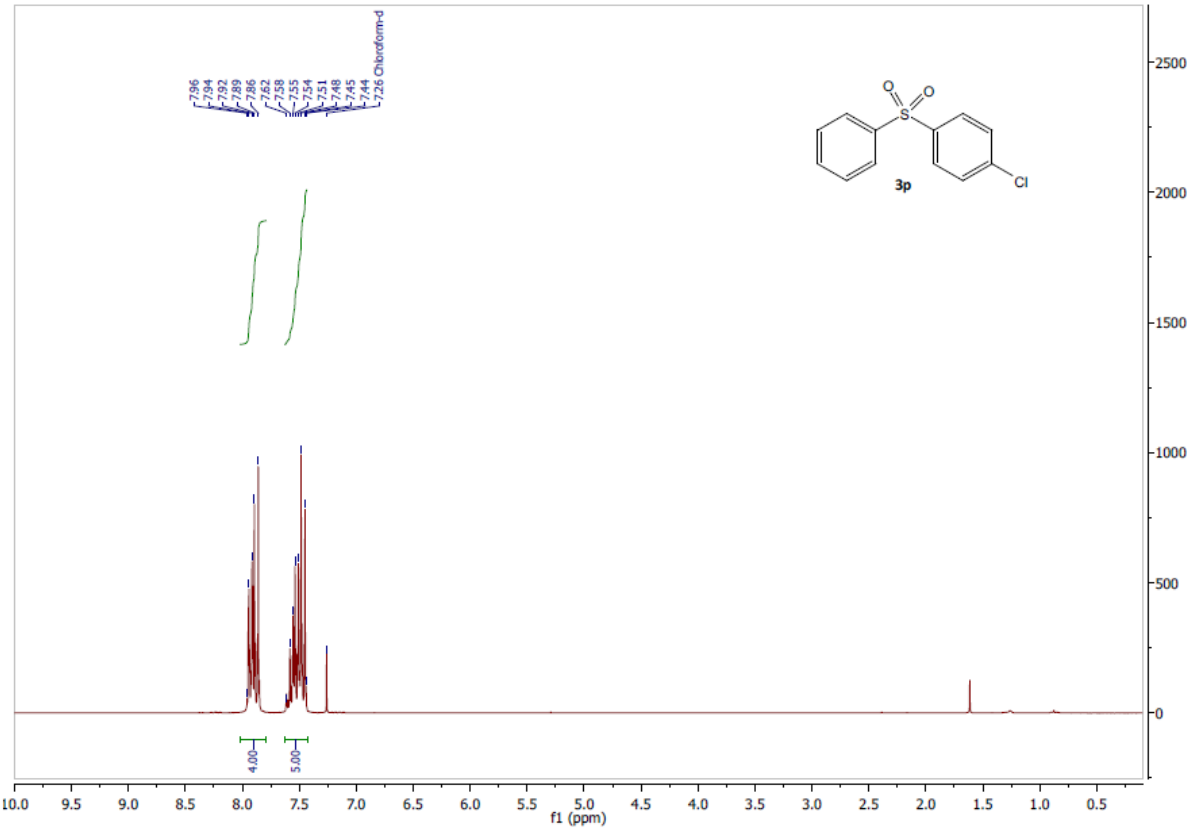

143.27
142.29
133.98
133.51
133.43
129.45
127.97
127.47
77.16 Chloroform-d
3m
f1 (ppm)

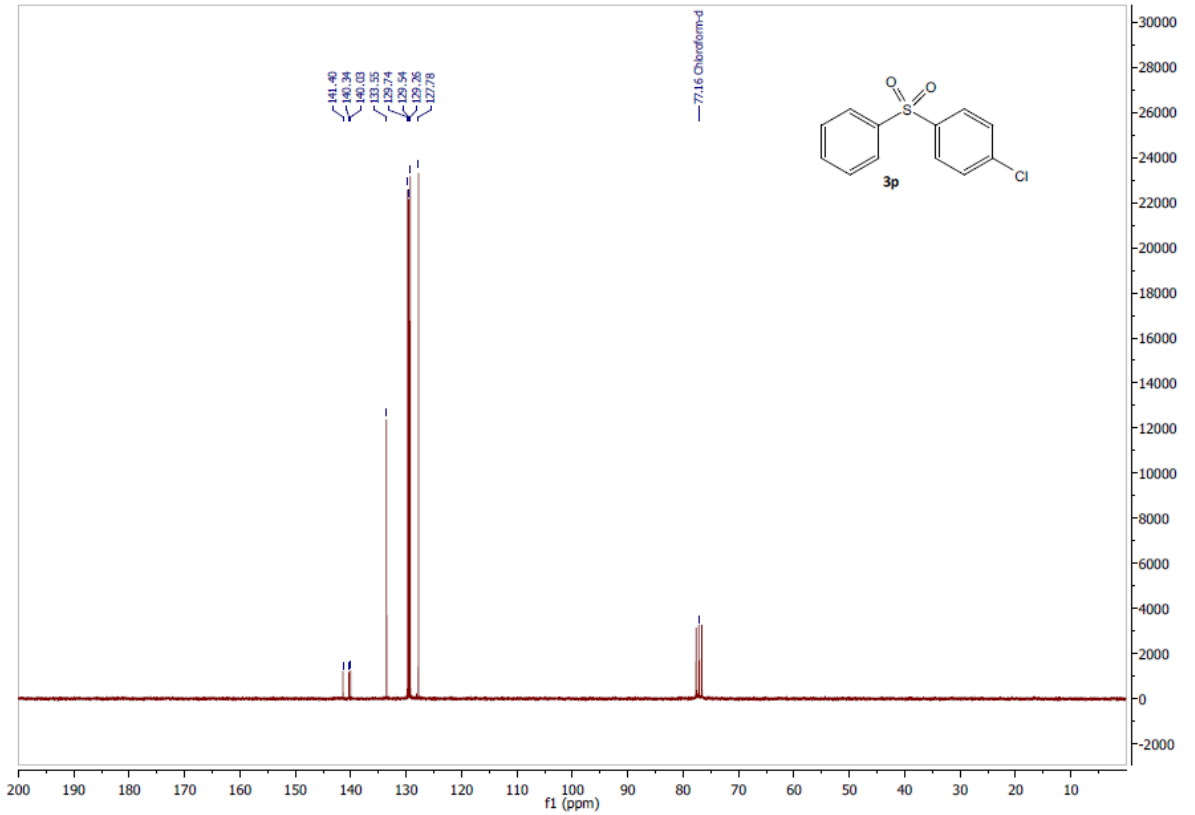

7.79
7.77
7.56
7.54
7.52
7.48
7.47
7.45
7.26 Chloroform-d
6.94
2.59
2.30
3n
2.00
1.01
2.00
2.00
6.17
3.07
f1 (ppm)


143.70
143.51
140.25
133.94
132.69
132.34
129.02
126.35
77.16 Chloroform-d
22.94
21.15
3n
f1 (ppm)


8.04
7.87
7.84
7.60
7.56
7.54
7.52
7.48
7.45
7.30
7.26 Chloroform-d
7.12
7.09
2.41
2.37
3o
3p
1.00
2.00
3.09
1.10
1.00
6.10
f1 (ppm)


3o
141.68
138.56
136.59
134.95
134.46
133.03
132.74
129.89
129.10
127.70
77.16 Chloroform-d
21.01
19.81
f1 (ppm)


7.96
7.94
7.92
7.89
7.86
7.62
7.58
7.55
7.54
7.51
7.48
7.45
7.44
7.26 Chloroform-d
3p
Cl
4.00
5.00
f1 (ppm)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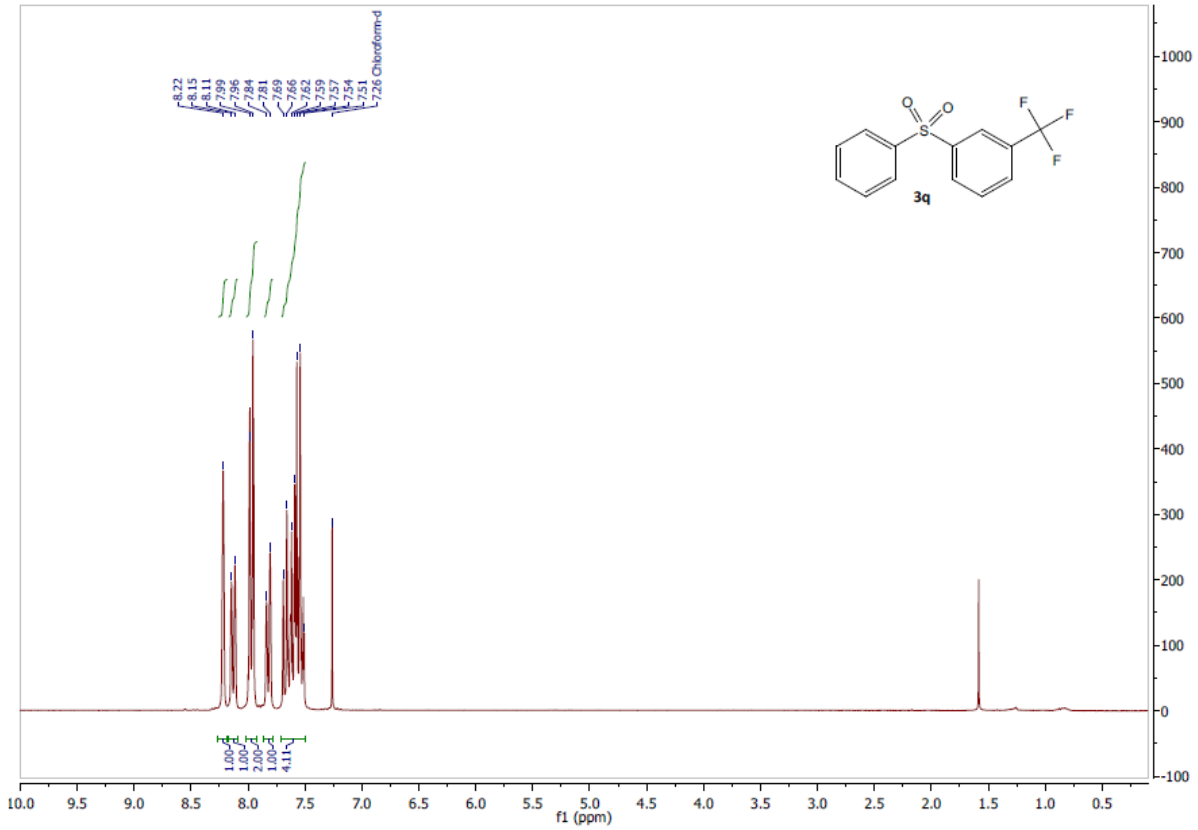
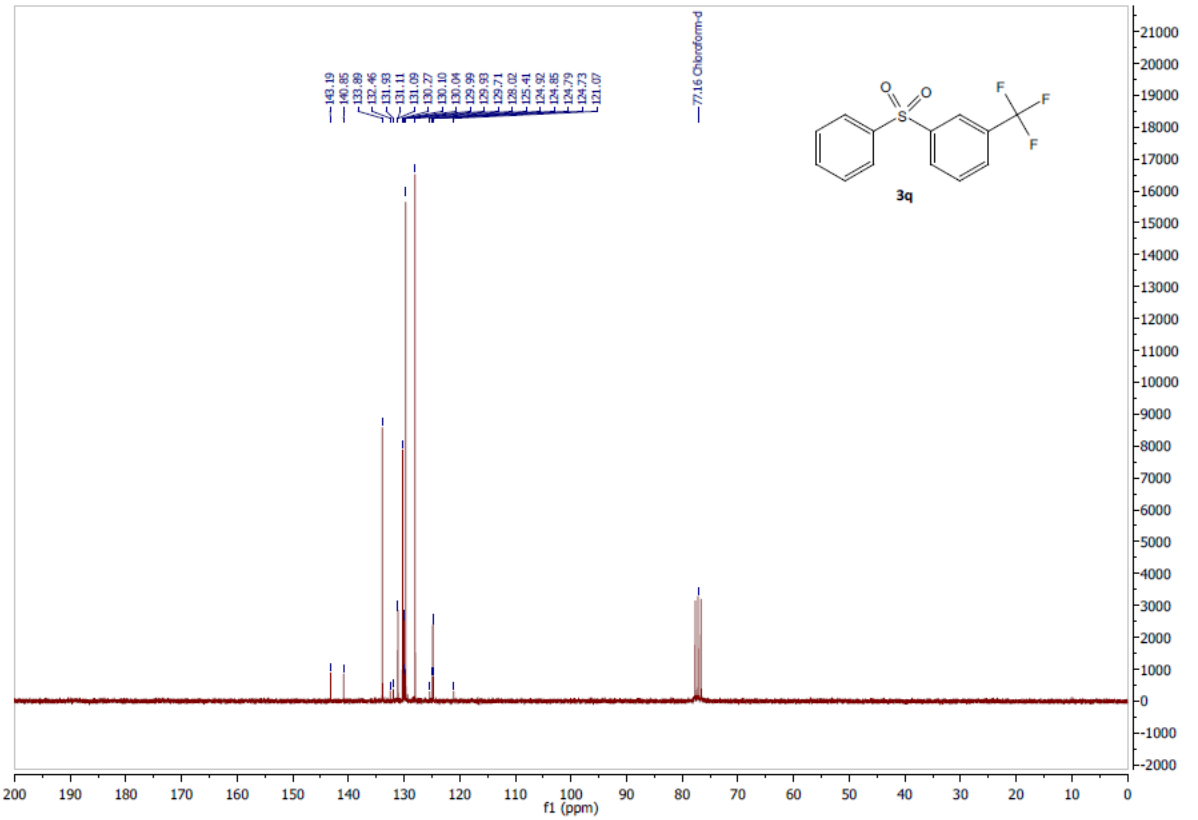
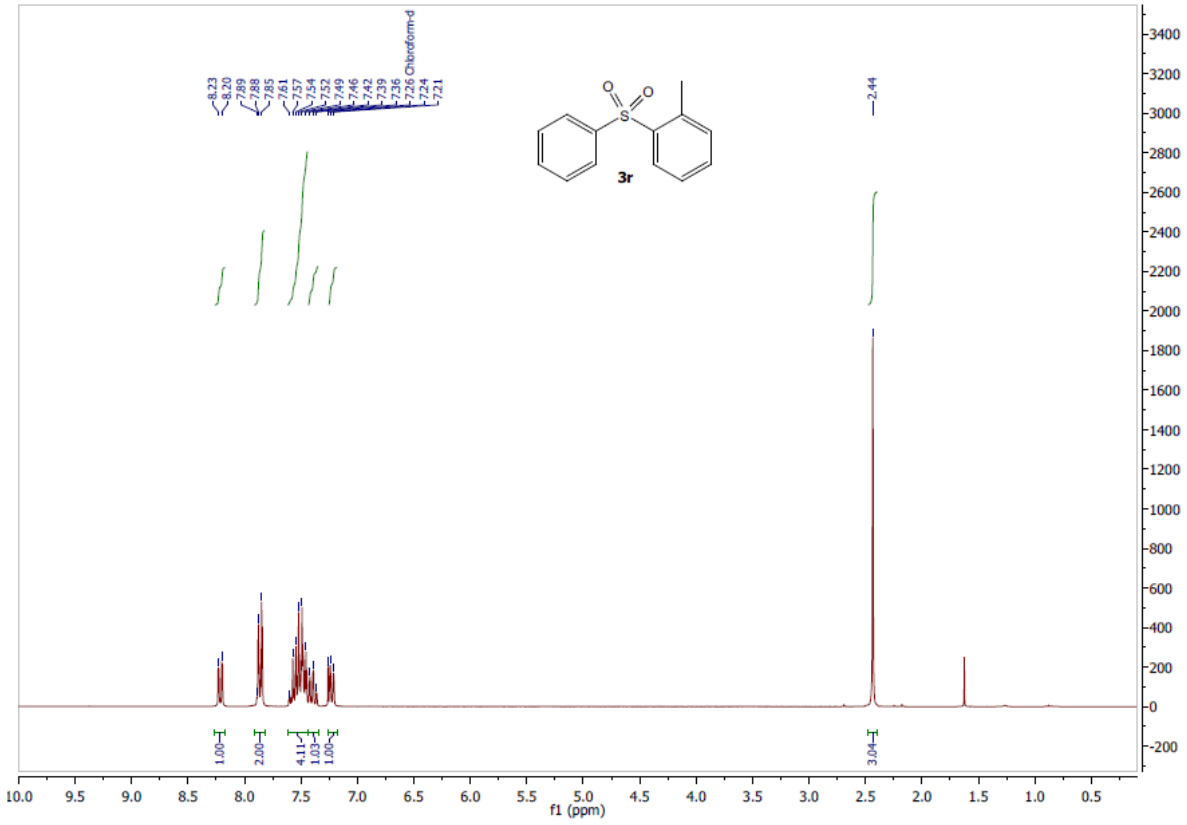
140.34
140.03
133.55
129.74
129.54
129.26
127.78
77.16 Chloroform-d
3p
Cl
f1 (ppm)


8.22
8.15
8.11
7.99
7.96
7.84
7.81
7.69
7.66
7.62
7.59
7.57
7.54
7.51
7.26 Chloroform-d
3q
1.00
1.00
2.00
1.00
4.11
f1 (ppm)


143.19
140.85
133.89
132.46
131.93
131.11
131.09
130.27
130.10
130.04
129.99
129.93
129.71
128.02
125.41
124.92
124.85
124.79
124.73
121.07
77.16 Chloroform-d
3q
f1 (ppm)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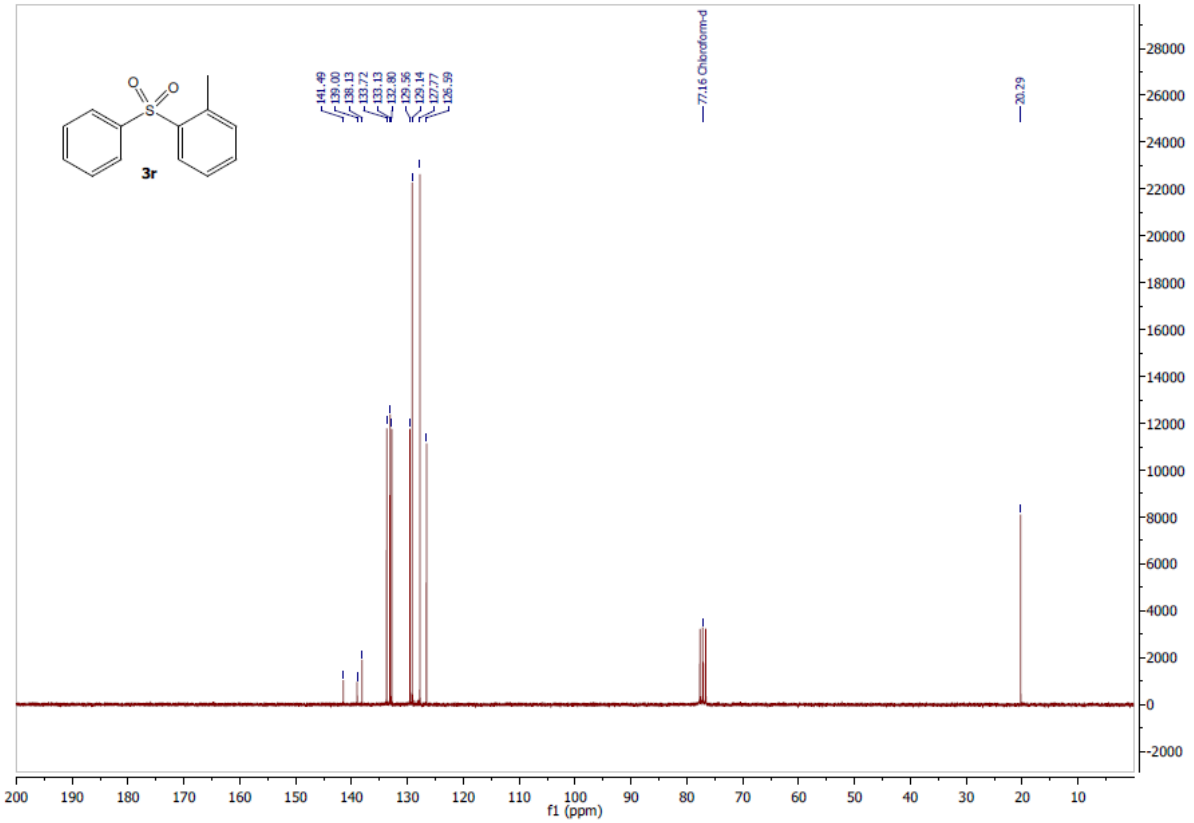
8.20
7.89
7.88
7.85
7.61
7.57
7.54
7.52
7.49
7.46
7.42
7.39
7.36
Chloroform-d
7.26
7.24
7.21
2.44
3r
1.00
2.00
4.11
1.03
1.00
3.04
f1 (ppm)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139.00
138.13
133.72
133.13
132.80
129.56
129.14
127.77
126.59
77.16
Chloroform-d
20.29
3r
f1 (ppm)