Electronic Supplementary Material (ESI) for ChemComm.

Copper-catalyzed synthesis of sulfonamides from nitroarenes with the insertion of sulfur dioxide

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Supporting Information

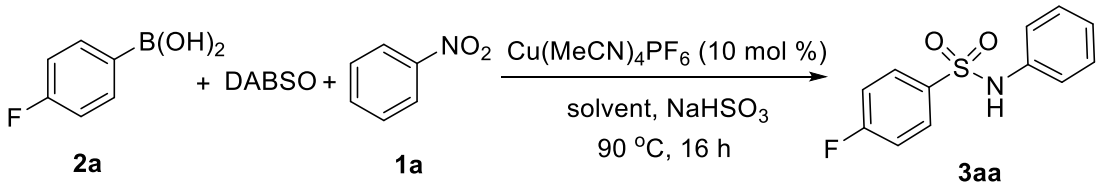
1. General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. $Cu(MeCN)_4PF_6$, 1,10-phenanthroline, *N*-methyl-2-pyrrolidinone (NMP, 99.5%, Extra Dry, with molecular sieves, Water≤50 ppm) and isopropanol (99.5%, Extra Dry, with molecular sieves, Water≤50 ppm) were purchased from *Energy Chemicals* and used as received. Cilnidipine, Flutamide, arylboronic acids and most of nitro compounds were purchased from *Bidepharm* and used as received. Flash column chromatography was performed using silica gel (300-400 mesh, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to 254 nm ultraviolet light or iodine stain. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 30–50°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million(ppm) from solvent residual peak on the δ scale. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in chloroform-*d* or acetone-d_6 on a Bruker DRX-400 spectrometer operating at 400 MHz, 101 MHz and 376 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. Melting points are tested automatically on a Melting Point Apparatus produced by *Shanghai JINGMI Scientific Instruments Co., Ltd.* High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker McriOTOF11 Instrument.

2. Optimization of "standard conditions"

Yields were determined by ^{19}F NMR using 4-fluoroanisole as internal standard.

2.1 Solvent

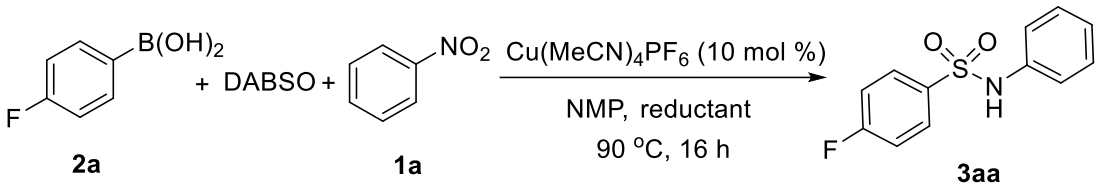


2a 2.5 equiv　　**1a** 2.0 equiv　　0.2 mmol　　**3aa**

entry	solvent	yield (%)
1	DMF	trace
2	NMP	14

3	DMSO	trace
4	DMAc	trace
5	HFIP	n.d.

2.2 Reductant

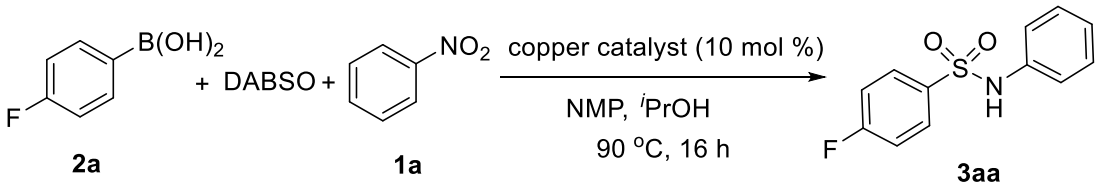


2a **1a** **3aa**

2.5 equiv 2.0 equiv 0.2 mmol

entry	reductant (amount)	yield (%)
1	$NaHSO_3$ (2.0 equiv)	13
2	Na_2SO_3 (2.0 equiv)	15
3	$Na_2S_2O_5$(2.0 equiv)	12
4	1,4-Cyclohexadiene (2.0 equiv)	n.d.
5	Hantzsch ester (2.0 equiv)	n.d.
6	HFIP (0.2 mL)	14
7	^{i}PrOH (0.2 mL)	20
8	none	n.d.

2.3 Cu catalyst



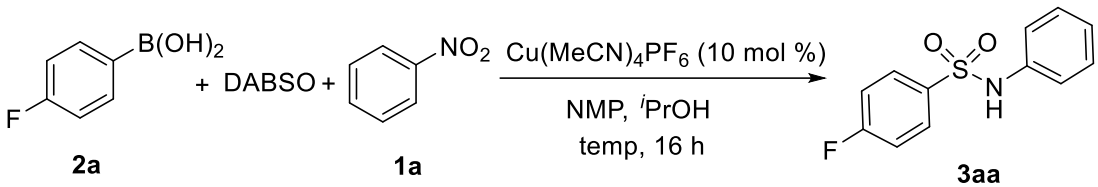
2a **1a** **3aa**

2.5 equiv 2.0 equiv 0.2 mmol

entry	catalyst	yield (%)
1	$Cu(MeCN)_4PF_6$	18
2	CuOAc	n.d.
3	CuI	n.d.
4	CuOTf	n.d.
5	$CuCl_2$	n.d.

6	$Cu(OTf)_2$	14
7	$Cu(acac)_2$	n.d.
8	$FeCl_2$	n.d.
9	$CuSO_4$	16
10	$Cu(TFA)_2$	13

2.4 Temperature

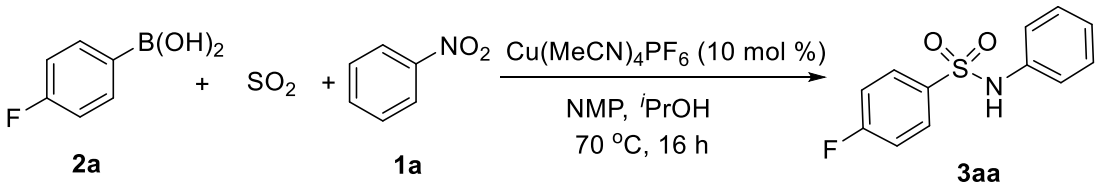


2a **1a** **3aa**

2.5 equiv 2.0 equiv 0.2 mmol

entry	temperature (°C)	yield (%)
1	70	18
2	90	11
3	110	4

2.5 SO_2 sources

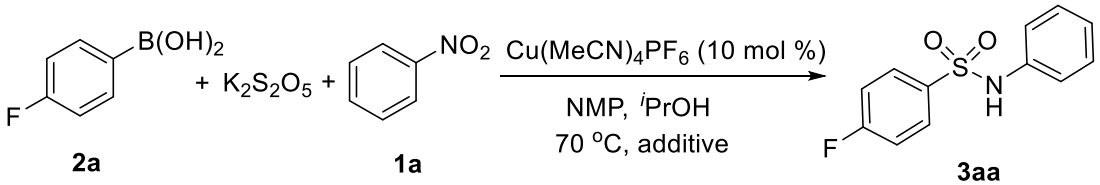


2a **1a** **3aa**

2.5 equiv 2.0 equiv 0.2 mmol

entry	SO_2 source	yield (%)
1	DABSO	18
2	$K_2S_2O_5$	38
3	$Na_2S_2O_5$	29
4	$Na_2S_2O_4$	n.d.
5	Na_2SO_3	n.d.
6	Formamidinesulfinic acid	n.d.

2.6 Additives

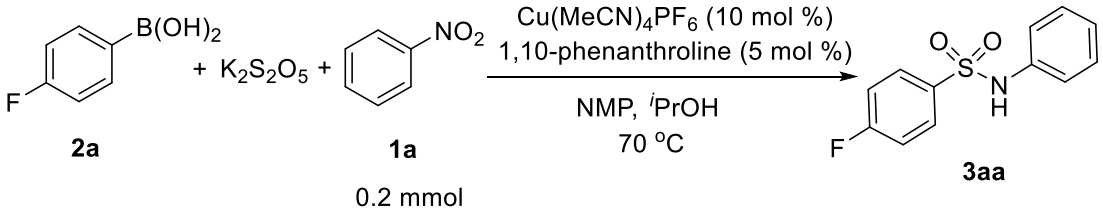


2a **1a** **3aa**

2.5 equiv 2.0 equiv 0.2 mmol

entry	additive (equiv)	time (h)	yield (%)
1	none	16	34
2	1,10-phenanthroline (0.1)	16	trace
3	1,10-phenanthroline (0.05)	16	46
4	PPh_3 (0.05)	16	24
5	none	48	70
6	1,10-phenanthroline (0.05)	48	72

2.7 More optimizations



2a **1a** **3aa**

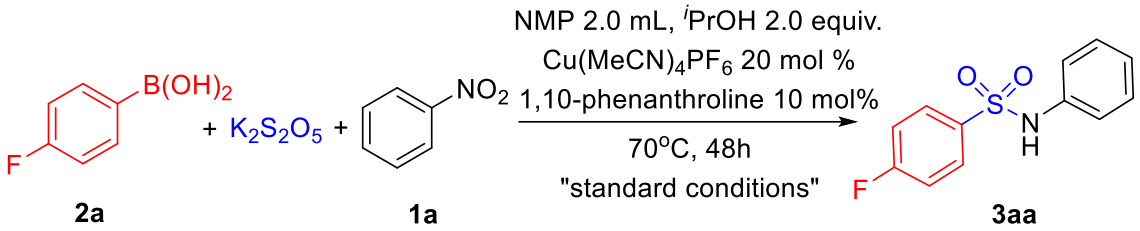
0.2 mmol

entry	variation	yield (%)
1	3.0 equiv $ArB(OH)_2$ instead of 2.5 equiv	77
2	3.0 equiv $K_2S_2O_5$ instead of 2.0 equiv	78
3	2.0 equiv ^{i}PrOH instead of 0.2 mL	77
3	20% [Cu], 10% L instead of 10% [Cu], 5% L	83
4	20% [Cu], 10% L, 2.0 equiv ^{i}PrOH 3.0 equiv $ArB(OH)_2$ and 3.0 equiv $K_2S_2O_5$	87

3. General experimental procedure:

3.1 Procedure of copper-catalyzed coupling reaction

*General experimental procedure for the reaction of benznenboronic acid **2**, $K_2S_2O_5$ and nitrobenzene **1**. Procedure to product **3aa** is shown below as an example.*



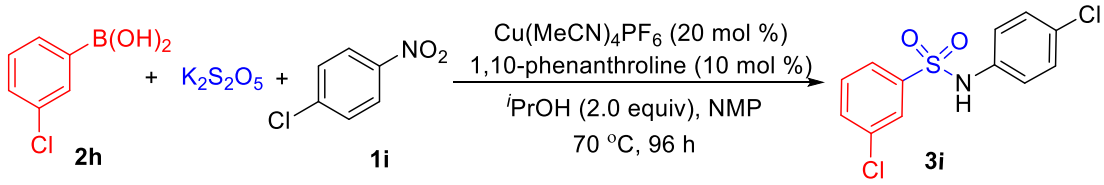
2a **1a** **3aa**

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-fluorobenzeneboronic acid **2a** (84.0 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3aa** (77% yield).

3.2 Procedure of the gram-scale synthesis

*General experimental procedure for the gram-scale synthesis of product **3i**.*

Entry 1: 20 mol % Cu catalyst and 10 mol % ligand were used.

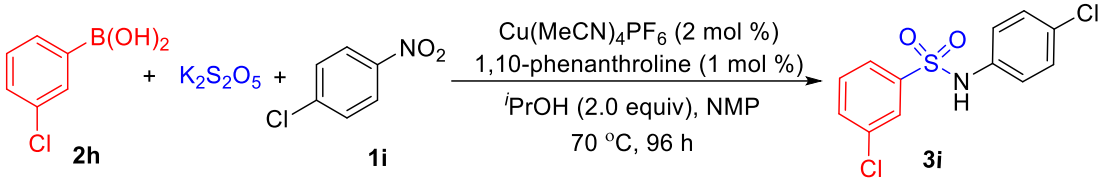


2h **1i** **3i**

NMP (10.0 mL) and isopropanol (465 µL, 2.0 equiv) were added to a rubber-septa-sealed 25ml round-bottom flask containing 3-chlorobenzeneboronic acid **2h** (936 mg, 6 mmol, 2.0 equiv), $K_2S_2O_5$ (1.998 g, 9 mmol, 3.0 equiv), 1-chloro-4-nitrobenzene **1i** (471mg, 3.0 mmol, 1.0 equiv), $Cu(MeCN)_4PF_6$ (223.8 mg, 0.6 mmol, 20 mol %) and 1,10-phenanthroline (54.0 mg, 0.3 mmol, 10 mol %) under Ar atmosphere via syringes.

The mixture was then stirred vigorously at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with with 0.03 M HCl (200 mL) and extracted with EtOAc (100 mL × 3). The organic phases were combined and washed with saturated brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3i** (0.722 g, 80% yield).

Entry 2: 2 mol % Cu catalyst and 1 mol % ligand were used. ***1i*** *was not consumed totally, but less byproducts were observed than entry 1.*



NMP (10.0 mL) and isopropanol (465 µL, 2.0 equiv) were added to a rubber-septa-sealed 25ml round-bottom flask containing 3-chlorobenzeneboronic acid **2h** (936 mg, 6 mmol, 2.0 equiv), $K_2S_2O_5$ (1.998 g, 9 mmol, 3.0 equiv), 1-chloro-4-nitrobenzene **1i** (471mg, 3.0 mmol), $Cu(MeCN)_4PF_6$ (22.4 mg, 0.06 mmol, 2 mol %) and 1,10-phenanthroline (5.4 mg, 0.03 mmol, 1 mol %) under Ar atmosphere via syringes. The mixture was then stirred vigorously at 70 °C for 96 h. After the scheduled time, the reaction mixture was diluted with with 0.03 M HCl (200 mL) and extracted with EtOAc (100 mL × 3). The organic phases were combined and washed with saturated brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3i** (0.660 g, 73% yield).

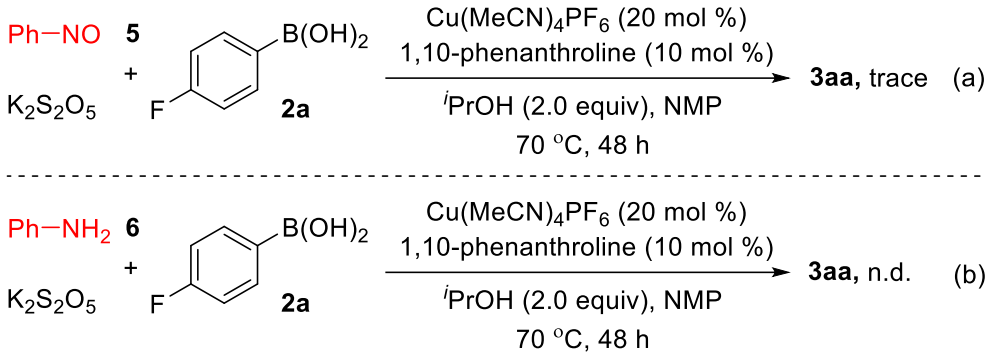
3.3 Procedure of the detection of sulfuric species

A standard reaction was quenched by 30 mL of 0.1 M HCl, and the mixture was extracted by CH_2Cl_2 (30 mL × 3). The aqueous phase was further acidized by concentrated HCl (10 mL) and refluxed under N_2 for 15 minutes to ensure complete decomposition of metabisulfites. After cooling down to room temperature, 0.1 M $BaCl_2$ (10 mL, 1.0 mmol) was added. The precipitates were filtered, washed by 1.0 M HCl, dried and weighed to give 17.1 mg white solid, indicating the generation of

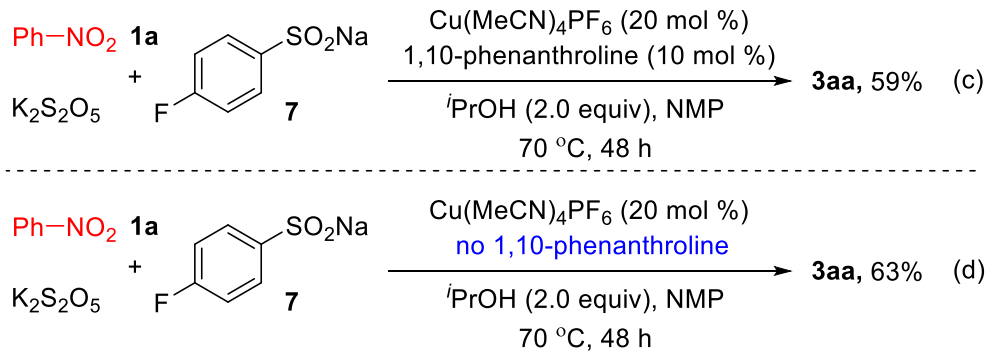
sulfuric species ($ArSO_3^-$, HSO_4^- or SO_4^{2-}) in the reaction.

3.4 Procedure of control experiments

Experimental procedure for the control experiments shown in Scheme 2 is described.

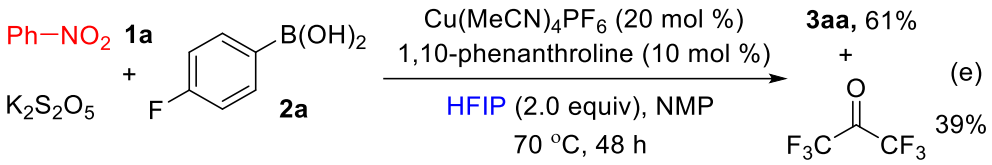


NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrosobenzene **5** (21.4 mg, 0.2 mmol, eq a) or aniline **6** (18.6 mg, 0.2 mmol, eq. b) were added to a rubber-septa-sealed tube containing 4-fluorobenzeneboronic acid **2a** (84.0 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was monitored directly by TLC.



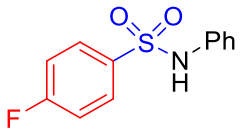
NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol) were added to a rubber-septa-sealed tube containing sodium 4-fluorobenzenesulfinate **7** (109.2 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10- phenanthroline (in eq. c, 3.6 mg, 0.02 mmol, 10 mol %, while in eq. d, no phenanthroline was added) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After

the scheduled time, the yield of product **3aa** was determined by ^{19}F NMR.



NMP (2.0 mL), HFIP (67.2 mg, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol) were added to a rubber-septa-sealed tube containing 4-fluorobenzeneboronic acid **2a** (84.0 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the yield of product **3aa** and hexafluoropropan-2-one was determined by ^{19}F NMR.

4. Characterization data:

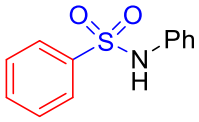


4-Fluoro-*N*-phenylbenzenesulfonamide (**3aa**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-fluorobenzeneboronic acid **2a** (84.0 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3aa**.

40.1 mg, 77% yield. White solid. M. p. 111.2 – 111.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.28 – 7.24 (m, 3H), 7.18 – 7.04 (m, 5H), 6.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 136.20, 130.13 (d, J_F = 9.5 Hz), 129.60, 125.99, 122.18, 116.45 (d, J_F = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.41.



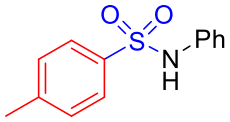
N-Phenylbenzenesulfonamide (**3ab**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing benzeneboronic acid **2b** (73.2 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous

Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3ab**.

33.5 mg, 72% yield. White solid. M. p. 105.5 – 107.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.13 – 7.07 (m, 3H), 6.49 (broad, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.10, 136.46, 133.16, 129.47, 129.17, 127.35, 125.65, 121.90.

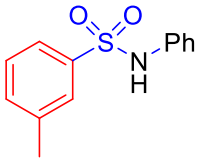


4-Methyl-*N*-phenylbenzenesulfonamide (**3ac**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing *p*-tolylboronic acid **2c** (81.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3ac**.

31.0 mg, 63% yield. White solid. M. p. 97.7 – 99.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.11 – 7.07 (m, 3H), 6.97 (broad, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.01, 136.66, 136.16, 129.78, 129.43, 127.40, 125.41, 121.65, 21.67.



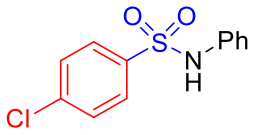
3-Methyl-*N*-phenylbenzenesulfonamide (**3ad**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing *m*-tolylboronic

acid **2d** (81.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3ad**.

27.5 mg, 56% yield. White solid. M. p. 96.2 – 97.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.13 - 7.06 (m, 3H), 6.87 (broad, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.40, 138.99, 136.57, 133.96, 129.44, 128.99, 127.69, 125.54, 124.50, 121.79, 21.41.



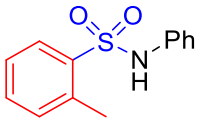
4-Chloro-*N*-phenylbenzenesulfonamide (**3ae**)[1]

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3ae**.

43.6 mg, 82% yield. White solid. M. p. 105.5 – 105.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.82 (broad, 1H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 139.76, 137.57, 136.08, 129.63, 129.50, 128.81, 126.04, 122.16.

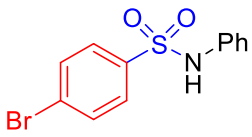


2-Methyl-*N*-phenylbenzenesulfonamide (**3af**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing *o*-tolylboronic acid **2f** (81.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3af**.

39.6 mg, 80% yield. White solid. M. p. 139.7 – 140.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.95 (broad, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.48, 137.31, 136.53, 133.29, 132.74, 130.14, 129.48, 126.43, 125.11, 120.71, 20.55.



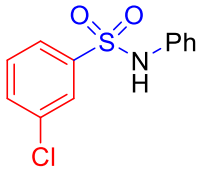
4-Bromo-*N*-phenylbenzenesulfonamide (**3ag**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-bromobenzeneboronic acid **2g** (120 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction

mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 15% EtOAc/*n*-hexane) to afford the corresponding product **3ag**.

49.8 mg, 80% yield. White solid. M. p. 118.5 – 119.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.00 (broad, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.05, 136.09, 132.48, 129.61, 128.88, 128.28, 125.98, 122.05.

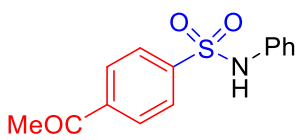


3-Chloro-*N*-phenylbenzenesulfonamide (**3ah**)[2]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3ah**.

44.3 mg, 83% yield. White solid. M. p. 91.0 – 92.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.78, 136.01, 135.40, 133.33, 130.46, 129.62, 127.45, 126.04, 125.47, 122.10.

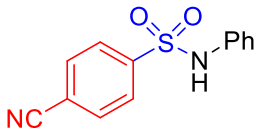


4-Acetyl-*N*-phenylbenzenesulfonamide (**3ai**)[3]

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-acetylbenzeneboronic acid **2i** (98.4 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 30% EtOAc/*n*-hexane) to afford the corresponding product **3ai**.

42.3 mg, 77% yield. White solid. M. p. 103.6 – 104.9 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.16 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.20 (m, 4H), 7.14 – 7.02 (m, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 197.23, 144.36, 141.07, 138.33, 130.10, 129.64, 128.22, 125.70, 121.85, 26.94.

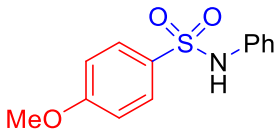


4-Cyano-*N*-phenylbenzenesulfonamide (**3aj**)[1]

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-cyanobenzeneboronic acid **2j** (88.2 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/*n*-hexane) to afford the corresponding product **3aj**.

38.6 mg, 75% yield. White solid. M. p. 111.0 – 111.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.17 (t, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.73 (broad, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.17, 135.56, 132.99, 129.75, 127.98, 126.46, 122.36, 117.32, 116.84.

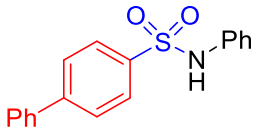


4-Methoxy-*N*-phenylbenzenesulfonamide (**3ak**)[1]

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-methoxybenzeneboronic acid **2k** (88.2 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/*n*-hexane) to afford the corresponding product **3ak**.

37.3 mg, 71% yield. White solid. M. p. 107.1 – 109.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 6.8 Hz, 3H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.33 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.21, 136.78, 130.68, 129.55, 129.41, 125.34, 121.63, 114.29, 55.68.



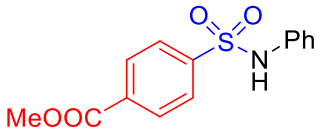
N-Phenyl-[1,1'-biphenyl]-4-sulfonamide (**3al**)[1]

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 4-phenylbenzeneboronic acid **2l** (88.2 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-

phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3al**.

41.9 mg, 68% yield. White solid. M. p. 126.4 – 127.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.28 – 7.24 (m, 2H), 7.15 – 7.13 (m, 3H), 6.79 (broad, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.02, 139.23, 137.69, 136.59, 129.54, 129.17, 128.68, 127.91, 127.76, 127.43, 125.58, 121.76.

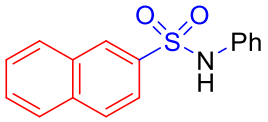


Methyl 4-(*N*-phenylsulfamoyl)benzoate (**3am**)

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing (4-(methoxycarbonyl)phenyl)boronic acid **2m** (108 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/*n*-hexane) to afford the corresponding product **3am**.

43.5 mg, 75% yield. White solid. M. p. 125.2 – 127.0 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.13 (broad, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.17 (m, 4H), 7.10 (t, *J* = 6.8 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 166.11, 144.77, 138.39, 134.90, 130.91, 130.20, 128.32, 125.93, 122.24, 52.96. HRMS (ESI) Calc. for $C_{14}H_{13}NNaO_4S^+$: 314.0457, found: 314.0456.

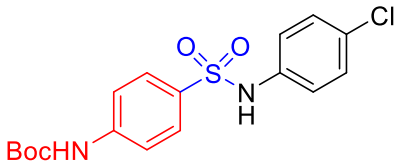


N-Phenylnaphthalene-2-sulfonamide (**3an**)[1]

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and nitrobenzene **1a** (24.6 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing naphthalen-2-ylboronic acid **2n** (103.2 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/*n*-hexane) to afford the corresponding product **3an**.

38.3 mg, 68% yield. White solid. M. p. 131.7 – 132.1 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.12 (s, 1H), 8.42 (s, 1H), 8.04 (t, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.82 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.69 – 7.56 (m, 2H), 7.28 – 7.15 (m, 4H), 7.04 – 6.98 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 138.74, 137.91, 135.71, 132.97, 130.15, 130.06, 129.98, 129.72, 129.27, 128.77, 128.47, 125.38, 123.28, 121.70.



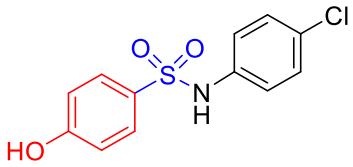
tert-Butyl (4-(*N*-(4-chlorophenyl)sulfamoyl)phenyl)carbamate (**3b**)

NMP (2.0 mL) and isopropanol (31 μL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-chloro-4-nitrobenzene **1i** (31.4 mg, 0.2 mmol, 1.0 equiv), (4-((tert-butoxycarbonyl)amino)phenyl)boronic acid **2bb** (142 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL ×

3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/*n*-hexane) to afford the corresponding product **3b**.

45.8 mg, 61% yield. White solid. M. p. 166.7 – 167.7 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 8.98 (broad, 1H), 8.84 (s, 1H), 7.73 – 7.65 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 153.38, 137.96, 133.32, 132.45, 129.99, 129.22, 123.14, 121.34, 118.44, 80.99, 28.41. HRMS (ESI) Calc. for $C_{17}H_{20}ClN_2O_4S^+$: 383.0827, found: 383.0821.

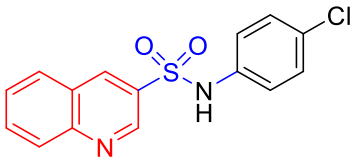


N-(4-Chlorophenyl)-4-hydroxybenzenesulfonamide (**3c**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-chloro-4-nitrobenzene **1i** (31.4 mg, 0.2 mmol, 1.0 equiv), 4-hydroxybenzeneboronic acid **2bc** (82.8 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 30% EtOAc/*n*-hexane) to afford the corresponding product **3c**.

34.5 mg, 61% yield. White solid. M. p. 155.1 – 156.4 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.12 (broad, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 162.28, 138.09, 131.15, 130.38, 129.94, 123.06, 116.44. HRMS (ESI) Calc. for $C_{12}H_{10}ClNNaO_3S^+$: 305.9962, found: 305.9966.

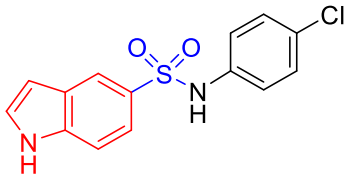


N-(4-Chlorophenyl)quinoline-3-sulfonamide (**3d**)

NMP (2.0 mL) and isopropanol (31 μL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-chloro-4-nitrobenzene **1i** (31.4 mg, 0.2 mmol, 1.0 equiv), quinolin-3-ylboronic acid **2bd** (104 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 30% EtOAc/*n*-hexane) to afford the corresponding product **3d**.

27.6 mg, 44% yield. Off-white solid. M. p. 192.5 – 193.9 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.43 (broad, 1H), 9.13 (s, 1H), 8.78 (s, 1H), 8.13 (t, *J* = 9.3 Hz, 2H), 7.94 (t, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 4H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 150.24, 147.80, 147.50, 137.45, 137.21, 133.52, 131.02, 130.43, 130.35, 129.35, 127.30, 123.91. HRMS (ESI) Calc. for $C_{15}H_{12}ClN_2O_2S^+$: 319.0303, found: 319.0306.



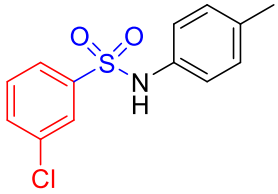
N-(4-Chlorophenyl)-1*H*-indole-5-sulfonamide (**3e**)

NMP (2.0 mL) and isopropanol (31 μL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-chloro-4-nitrobenzene **1i** (31.4 mg, 0.2 mmol, 1.0 equiv), (1*H*-indol-5-yl)boronic acid **2be** (96.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction

mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 30% EtOAc/*n*-hexane) to afford the corresponding product **3e**.

54.4 mg, 90% yield. White solid. M. p. 180.0 – 182.1 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 10.71 (broad, 1H), 8.95 (broad, 1H), 8.13 (s, 1H), 7.54 (s, 2H), 7.49 (s, 1H), 7.23 (s, 4H), 6.63 (s, 1H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 139.02, 138.43, 131.27, 129.85, 129.62, 128.42, 128.26, 122.77, 121.87, 120.64, 112.67, 103.93. HRMS (ESI) Calc. for $C_{14}H_{11}ClN_2NaO_2S^+$: 329.0122, found: 329.0128.

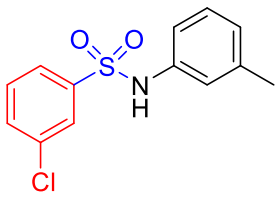


3-Chloro-*N*-(*p*-tolyl)benzenesulfonamide (**3f**)[4]

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-methyl-4-nitrobenzene **1f** (27.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3f**.

44.4 mg, 80% yield. White solid. M. p. 93.6 – 95.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.75 (broad, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.85, 136.25, 135.33, 133.20, 130.38, 130.16, 127.46, 125.52, 122.91, 21.01.

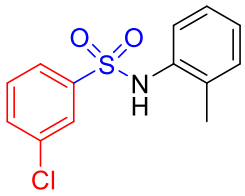


3-Chloro-*N*-(*m*-tolyl)benzenesulfonamide (**3g**)

NMP (2.0 mL) and isopropanol (31 μL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-methyl-3-nitrobenzene **1g** (27.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3g**.

36.6 mg, 66% yield. White solid. M. p. 119.9 – 121.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.96 – 6.87 (m, 3H), 6.22 (broad, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.83, 139.67, 135.91, 135.33, 133.25, 130.41, 129.35, 127.46, 126.78, 125.46, 122.67, 118.93, 21.45. HRMS (ESI) Calc. for $C_{13}H_{12}ClNNaO_2S^+$: 304.0169, found: 304.0150.



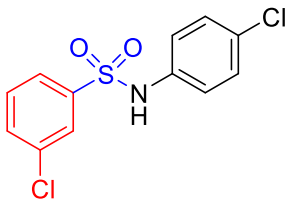
3-Chloro-*N*-(*o*-tolyl)benzenesulfonamide (**3h**)

NMP (2.0 mL), isopropanol (31 μL, 2.0 equiv) and 1-methyl-2-nitrobenzene **1h** (27.4 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The

mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3h**.

31.6 mg, 56% yield. White solid. M. p. 116.4 – 117.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.19 – 7.10 (m, 3H), 6.38 (broad, 1H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.36, 133.97, 133.23, 131.94, 131.11, 130.42, 127.35, 127.26, 126.97, 125.38, 124.88, 17.72. HRMS (ESI) Calc. for $C_{13}H_{12}ClNNaO_2S^+$: 304.0169, found: 304.0162.



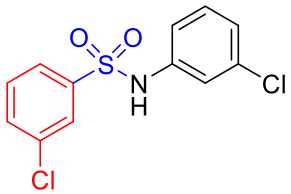
3-Chloro-*N*-(4-chlorophenyl)benzenesulfonamide (**3i**)[4]

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-chloro-4-nitrobenzene **1i** (31.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3i**.

55.5 mg, 92% yield. White solid. M. p. 102.6 – 103.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.93

(broad, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.47, 135.59, 134.51, 133.58, 131.80, 130.58, 129.77, 127.39, 125.45, 123.57.

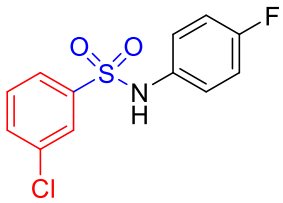


3-Chloro-*N*-(3-chlorophenyl)benzenesulfonamide (**3j**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-chloro-3-nitrobenzene **1j** (31.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3j**.

53.7 mg, 89% yield. White solid. M. p. 115.5 – 119.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.52, 137.30, 135.65, 135.26, 133.66, 130.63, 127.42, 126.03, 125.44, 121.65, 119.55. HRMS (ESI) Calc. for $C_{12}H_9Cl_2NNaO_2S^+$: 323.9623, found: 323.9611.



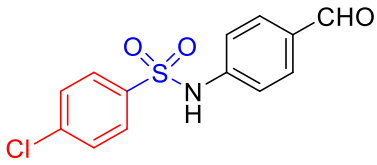
3-Chloro-*N*-(4-Fluorophenyl)benzenesulfonamide (**3k**)

NMP (2.0 mL), isopropanol (31 µL, 2.0 equiv) and 1-fluoro-4-nitrobenzene **1k** (28.2 mg, 0.2 mmol, 1.0 equiv) were added to a rubber-septa-sealed tube containing 3-chlorobenzeneboronic acid **2h** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6

mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3k**.

49.4 mg, 87% yield. White solid. M. p. 98.0 – 98.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.05 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 2H), 6.60 (broad, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, J_F = 247.1 Hz), 140.39, 135.48, 133.44, 131.75 (d, J_F = 3.0 Hz), 130.50, 127.42, 125.48, 125.15 (d, J_F = 8.5 Hz), 116.44 (d, J_F = 22.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.34. HRMS (ESI) Calc. for $C_{12}H_9ClFNNaO_2S^+$: 307.9919, found: 307.9901.

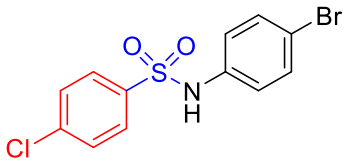


4-Chloro-*N*-(4-formylphenyl)benzenesulfonamide (**3l**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 4-nitrobenzaldehyde **1l** (30.2 mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 25% EtOAc/*n*-hexane) to afford the corresponding product **3l**.

44.3 mg, 76% yield. White solid. M. p. 161.1 – 163.1 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.90 (s, 1H), 9.68 (s, 1H), 7.91 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 191.58, 144.05, 139.42, 136.81, 133.70, 131.94, 130.49, 129.91, 120.05. HRMS (ESI) Calc. for $C_{13}H_{11}ClNO_3S^+$: 296.0143, found: 296.0130.

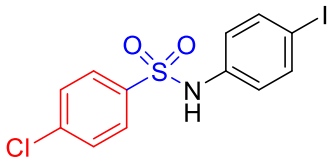


N-(4-Bromophenyl)-4-chlorobenzenesulfonamide (**3m**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-bromo-4-nitrobenzene **1m** (40.2 mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3m**.

59.7 mg, 87% yield. Off-white solid. M. p. 122.0 – 122.2 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.20 (broad, 1H), 7.80 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 139.57, 139.24, 137.78, 133.09, 130.22, 129.74, 123.75, 118.27. HRMS (ESI) Calc. for $C_{12}H_9BrClNNaO_2S^+$: 367.9118, found: 367.9114.



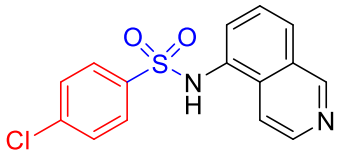
4-Chloro-*N*-(4-iodophenyl)benzenesulfonamide (**3n**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-iodo-4-nitrobenzene **1n** (49.8 mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6

mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with 0.03 M HCl (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3n**.

66.8 mg, 86% yield. Off-white solid. M. p. 130.1 – 131.5 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.15 (broad, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.64 – 7.58 (m, 4H), 7.05 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 139.69, 139.42, 139.25, 138.57, 130.36, 129.86, 123.92, 89.01. HRMS (ESI) Calc. for $C_{12}H_9ClINNaO_2S^+$: 415.8979, found: 415.8975.



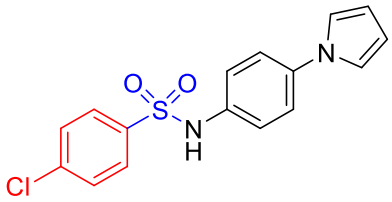
4-Chloro-*N*-(isoquinolin-5-yl)benzenesulfonamide (**3o**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 5-nitroisoquinoline **1o** (34.8 mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 40% EtOAc/*n*-hexane) to afford the corresponding product **3o**.

38.7 mg, 61% yield. White solid. M. p. 202.0 – 204.2 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.27 (s, 1H), 9.09 (broad, 1H), 8.44 (d, *J* = 5.6 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 1H), 7.90 (d, *J* = 5.6 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.58 (q, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ

153.55, 144.30, 139.77, 139.53, 133.12, 132.62, 130.36, 130.21, 129.91, 128.41, 128.03, 127.60, 116.30. HRMS (ESI) Calc. for $C_{15}H_{12}ClN_2O_2S^+$: 319.0303, found: 319.0319.

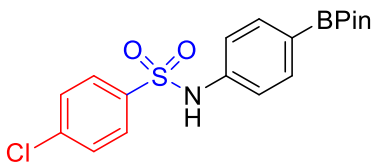


N-(4-(1*H*-Pyrrol-1-yl)phenyl)-4-chlorobenzenesulfonamide (**3p**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 1-(4-nitrophenyl)-1*H*-pyrrole **1p** (37.6 mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3p**.

47.0 mg, 71% yield. Light yellow solid. M. p. 191.6 – 191.9 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.10 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.18 (s, 2H), 6.25 (s, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 139.60, 139.53, 138.85, 135.62, 130.28, 129.89, 123.94, 121.38, 119.80, 111.41. HRMS (ESI) Calc. for $C_{16}H_{14}ClN_2O_2S^+$: 333.0459, found: 333.0458.



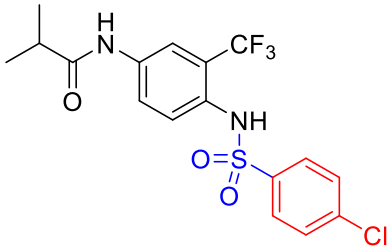
4-chloro-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzenesulfonamide (**3q**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane **1q** (49.8

mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10-phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 20% EtOAc/*n*-hexane) to afford the corresponding product **3q**.

34.6 mg, 45% yield. White solid. M. p. 191.6 – 193.1 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.21 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 1.30 (s, 12H). ^{13}C NMR (101 MHz, Acetone-d_6) δ141.37, 139.77, 139.63, 136.79, 130.33, 129.91, 120.23, 84.65, 25.31. HRMS (ESI) Calc. for $C_{18}H_{22}BClNO_4S^+$: 394.1046, found: 394.1048.



N-(4-((4-Chlorophenyl)sulfonamido)-3-(trifluoromethyl)phenyl)isobutyramide (**4a**)

NMP (2.0 mL) and isopropanol (31 µL, 2.0 equiv) were added to a rubber-septa-sealed tube containing Flutamide **1r** (55.2 mg, 0.2 mmol, 1.0 equiv), 4-chlorobenzeneboronic acid **2e** (93.6 mg, 0.6 mmol, 3.0 equiv), $K_2S_2O_5$ (132 mg, 0.6 mmol, 3.0 equiv), $Cu(MeCN)_4PF_6$ (14.8 mg, 0.04 mmol, 20 mol %) and 1,10- phenanthroline (3.6 mg, 0.02 mmol, 10 mol %) under Ar atmosphere via syringes. The mixture was then stirred at 70 °C for 48 h. After the scheduled time, the reaction mixture was diluted with water (60 mL) and extracted with EtOAc (20 mL × 3). The organic phases were combined and washed with brine twice before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (Eluent: 35% EtOAc/*n*-hexane) to afford the corresponding product **4a**.

62.5 mg, 75% yield. White solid. M. p. 149.3 – 149.6 °C.

^{1}H NMR (400 MHz, acetone-d_6) δ 9.39 (s, 1H), 8.57 (s, 1H), 8.14 (s, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.7 Hz, 2H), 7.39 (d, J = 8.7 Hz, 1H), 2.63 (dt, J = 13.3, 6.6 Hz, 1H), 1.16 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, Acetone-d_6) δ176.53, 140.52, 139.54 (d, J_F = 18.8 Hz), 130.16, 130.09, 129.79, 129.04, 126.67 (q, J_F = 29.9 Hz), 125.55, 123.76, 122.83, 117.94 (q, J_F = 5.5 Hz), 36.70, 19.72. ^{19}F NMR (376 MHz, Acetone-d_6) δ -60.24. HRMS (ESI) Calc. for $C_{17}H_{17}ClF_3N_2O_3S^+$: 421.0595, found: 421.0601.

References of Analytical Data:

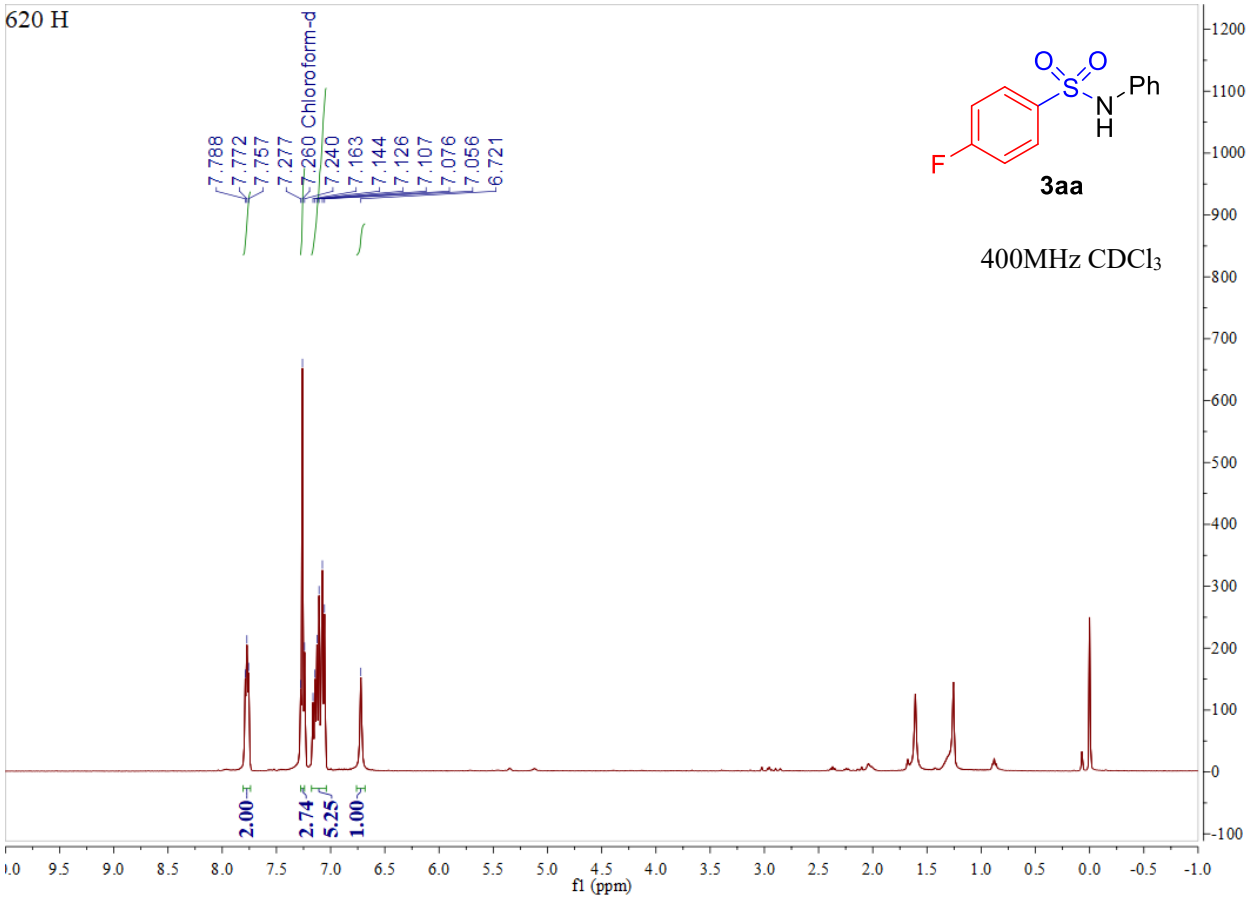
1. *Org. Biomol. Chem.*, **2018**, 16, 5016 – 5020.

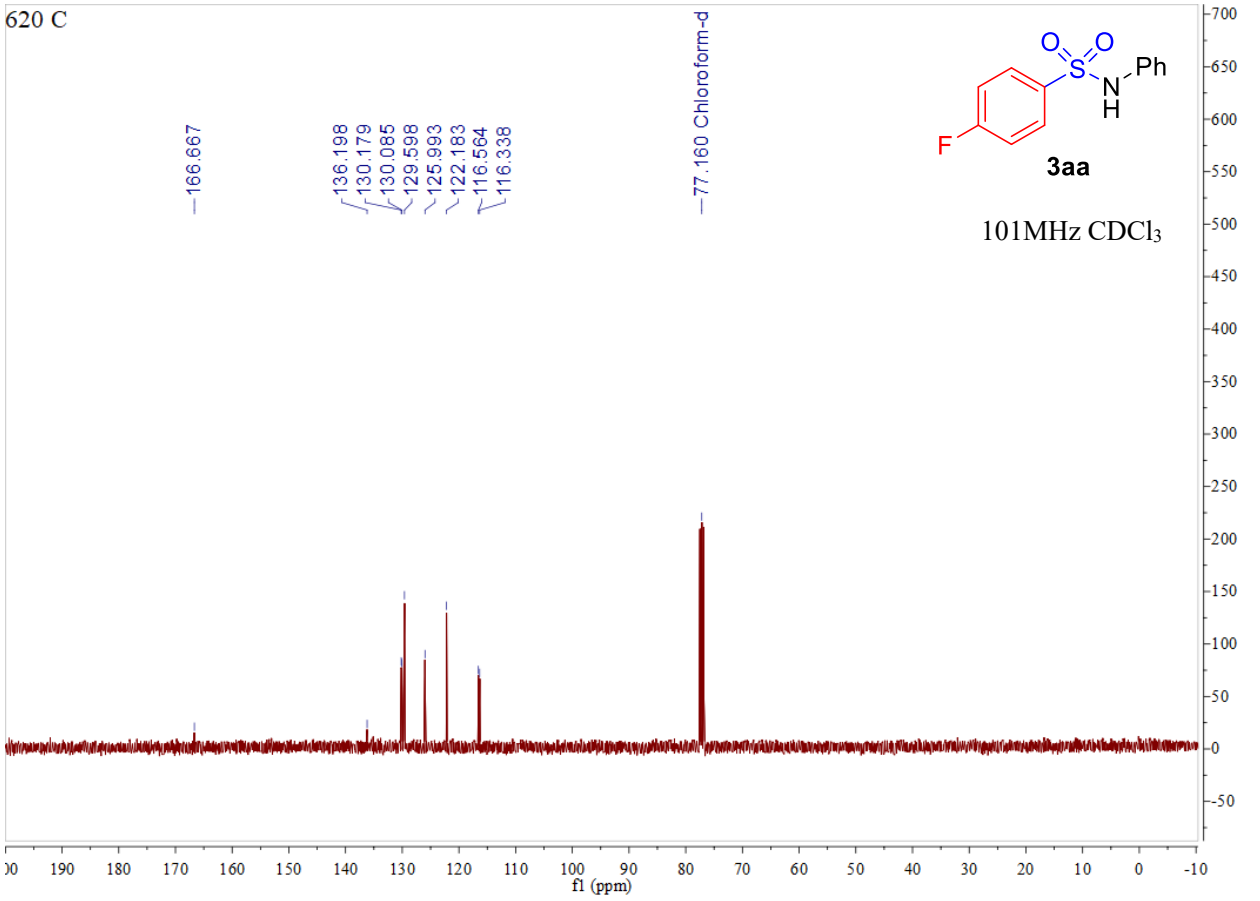
2. *ACS Med. Chem. Lett.*, **2016**, *7*, 1028 – 1033.

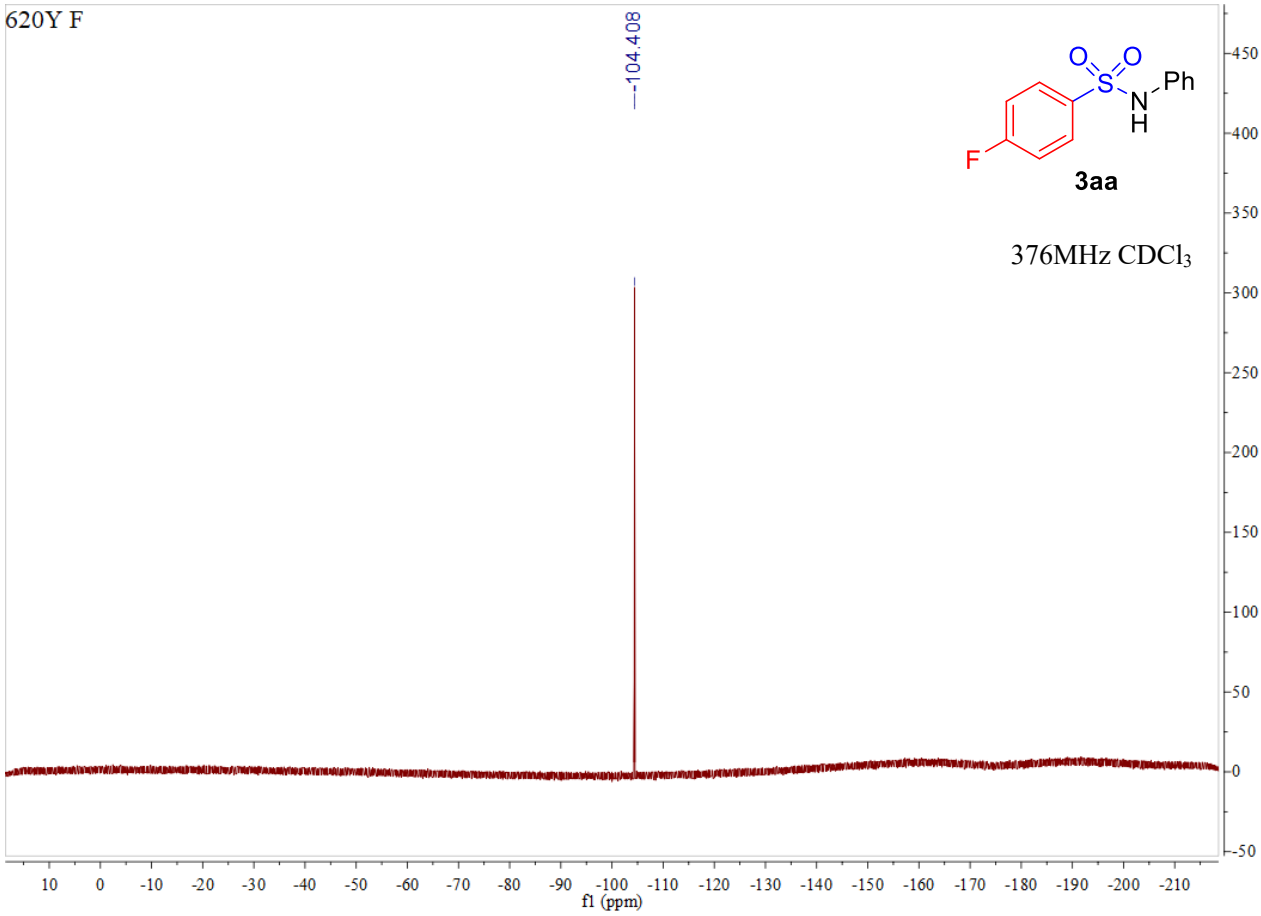
3. *Angew. Chem. Int. Ed.*, **2016**, *55*, 2450 – 2453.

4. *Crystal Growth and Design*, **2010**, *10*, 4550 – 4564.

5. ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds 3 and 4.




620 C
166.667
136.198
130.179
130.085
129.598
125.993
122.183
116.564
116.338
77.160 Chloroform-d
O
O
S
N
H
Ph
F
3aa
101MHz CDCl3
f1 (ppm)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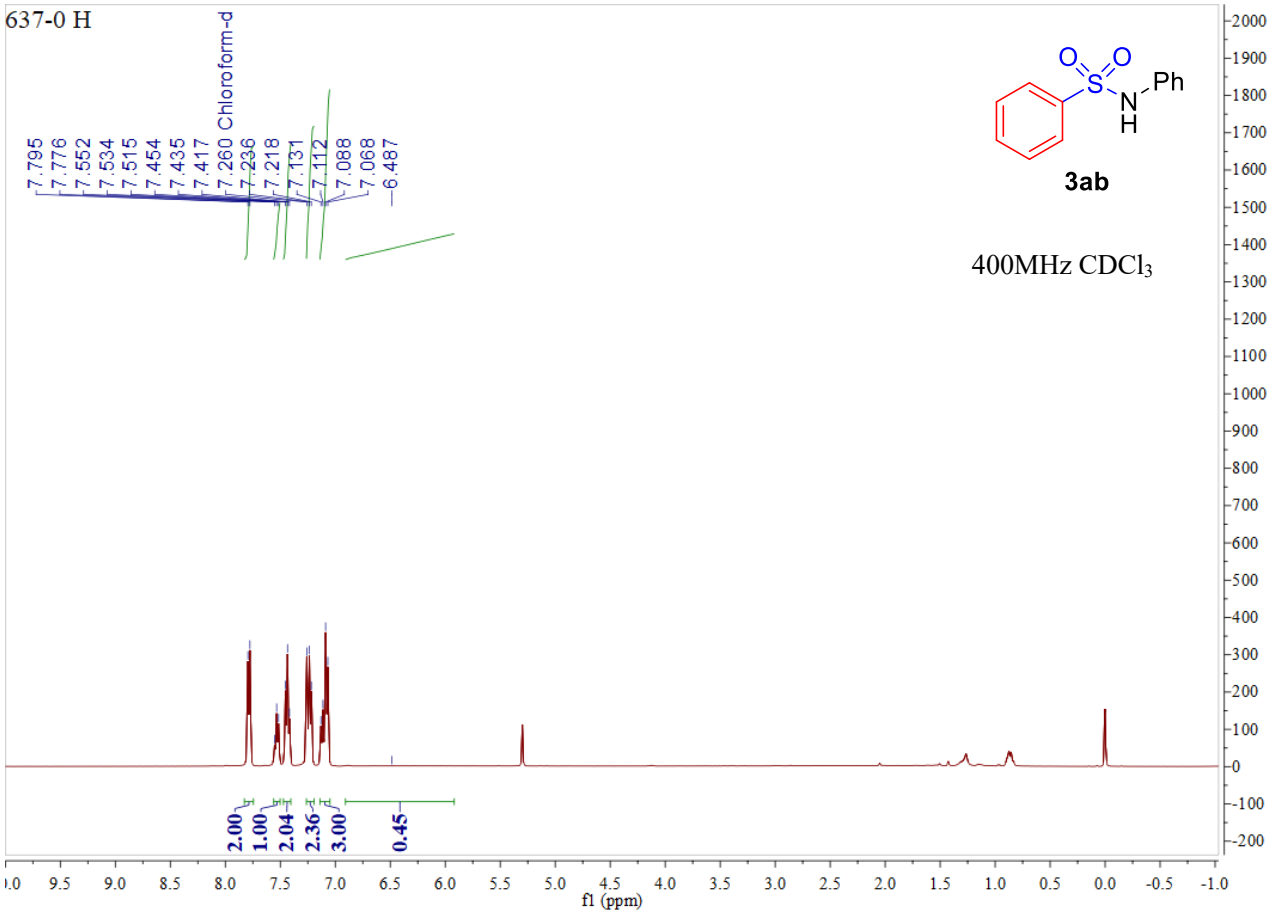
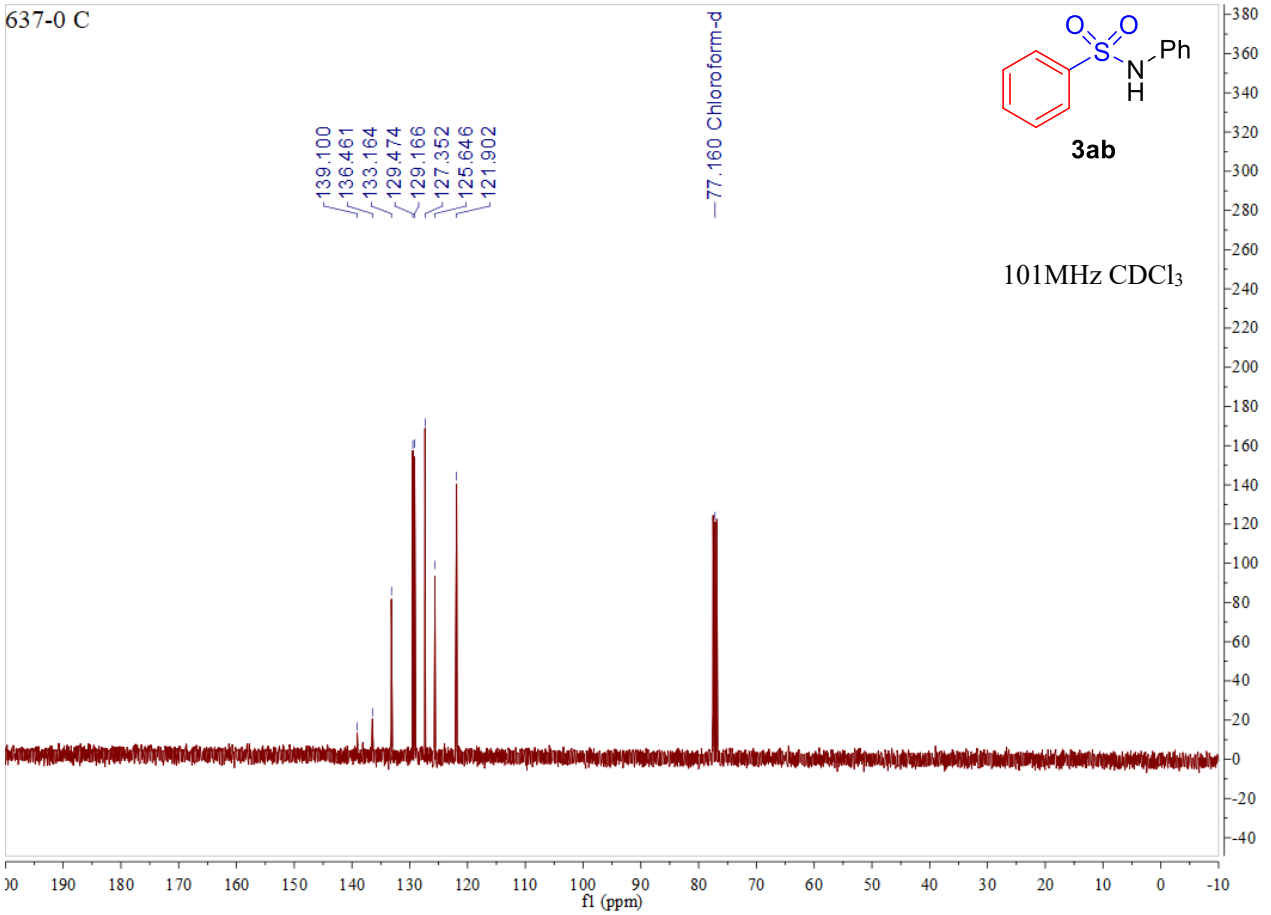
O
O
S
N
H
Ph
F
3aa
376MHz CDCl3
f1 (ppm)


637-0 H
7.795
7.776
7.552
7.534
7.515
7.454
7.435
7.417
7.260 Chloroform-d
7.236
7.218
7.131
7.112
7.088
7.068
6.487
2.00
1.00
2.04
2.36
3.00
0.45
f1 (ppm)
3ab
400MHz CDCl3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129.166
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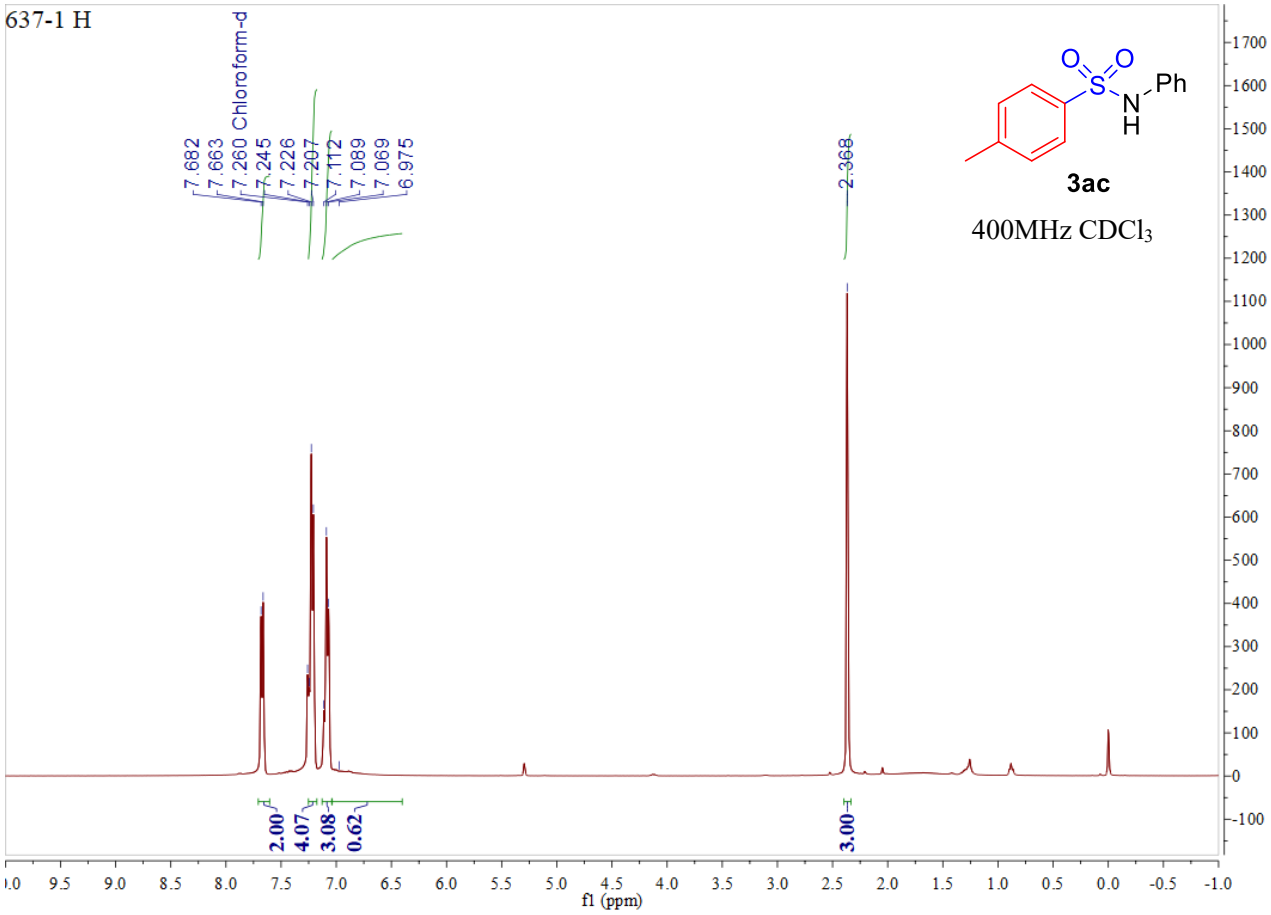
f1 (ppm)
3ab
101MHz CDCl3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7.663
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7.226
7.207
7.112
7.089
7.069
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2.368
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3.08
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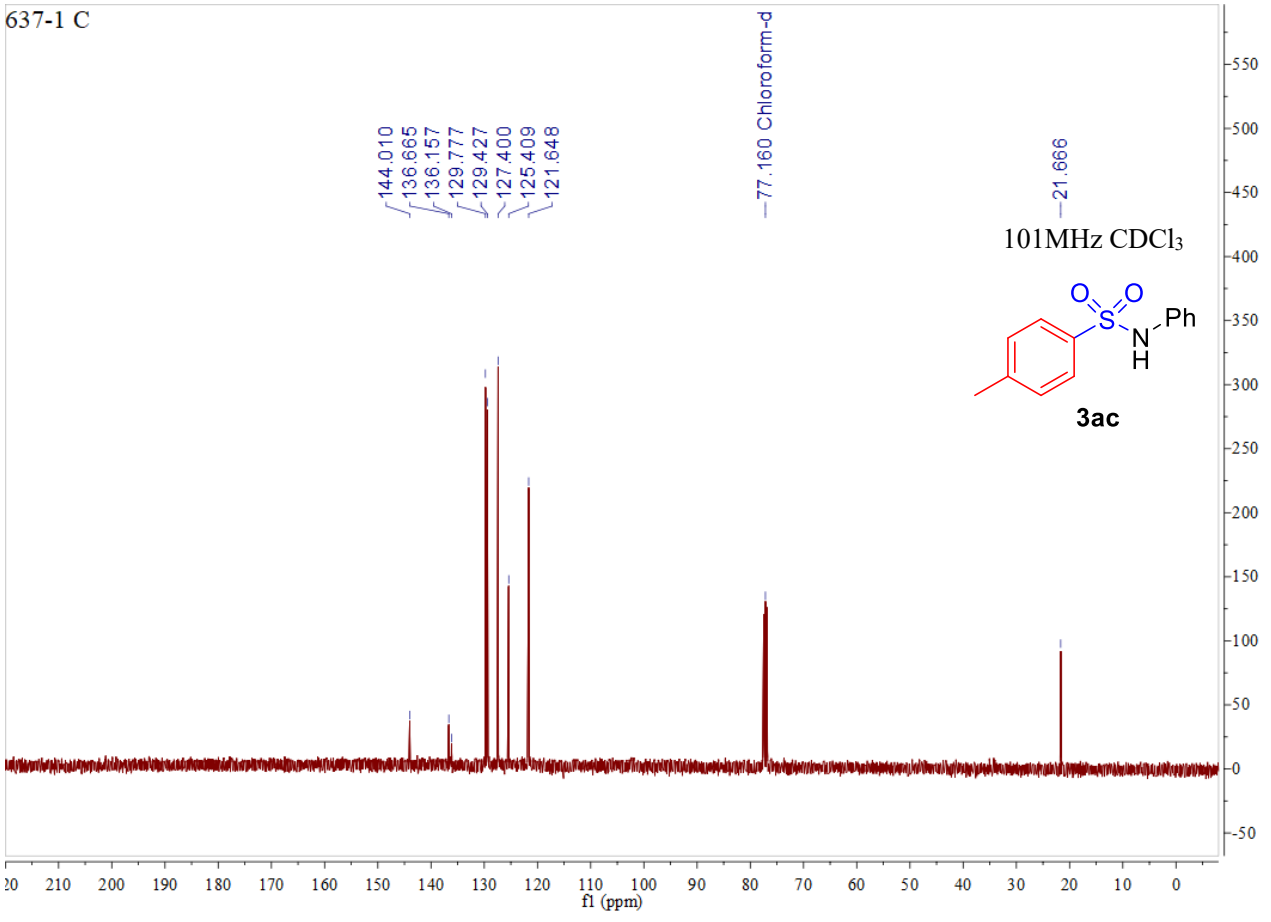
3.00
f1 (ppm)
3ac
400MHz CDCl3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136.665
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125.409
121.648
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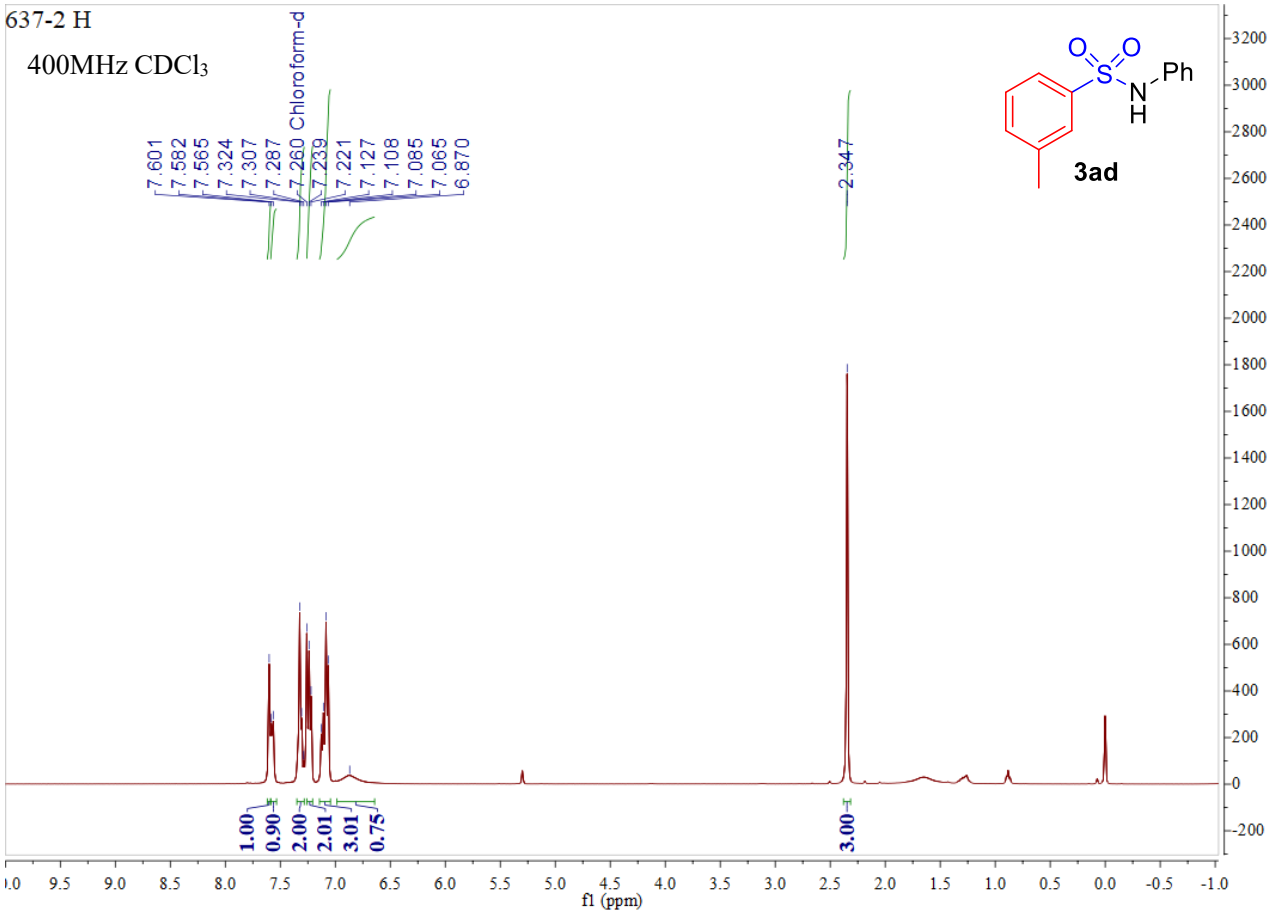
21.666
f1 (ppm)
101MHz CDCl3
3ac


637-2 H
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7.565
7.324
7.307
7.287
7.260 Chloroform-d
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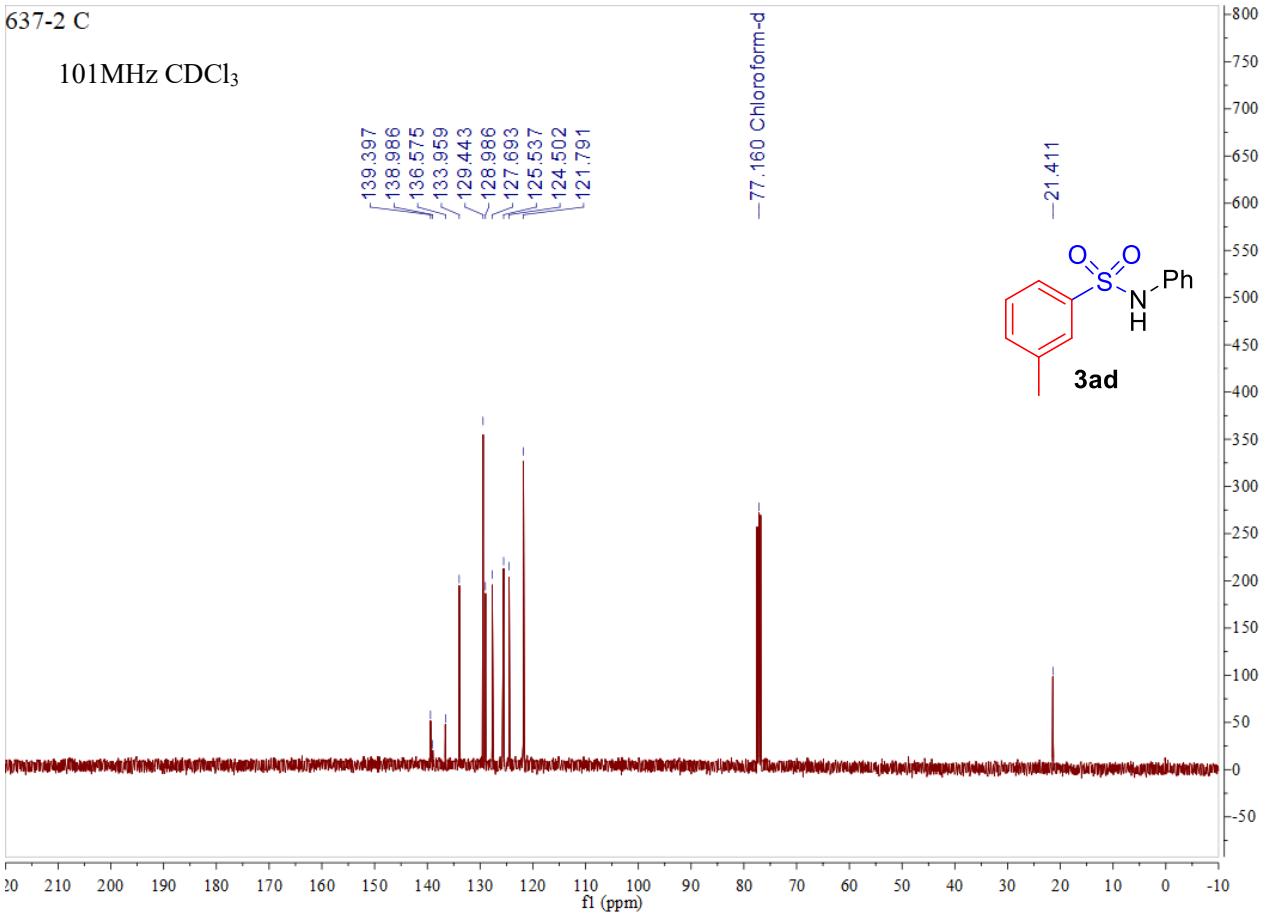
7.221
7.127
7.108
7.085
7.065
6.870
2.347
1.00
0.90
2.00
2.01
3.01
0.75
3.00
f1 (ppm)
Ph
N
H
O
S
3ad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136.575
133.959
129.443
128.986
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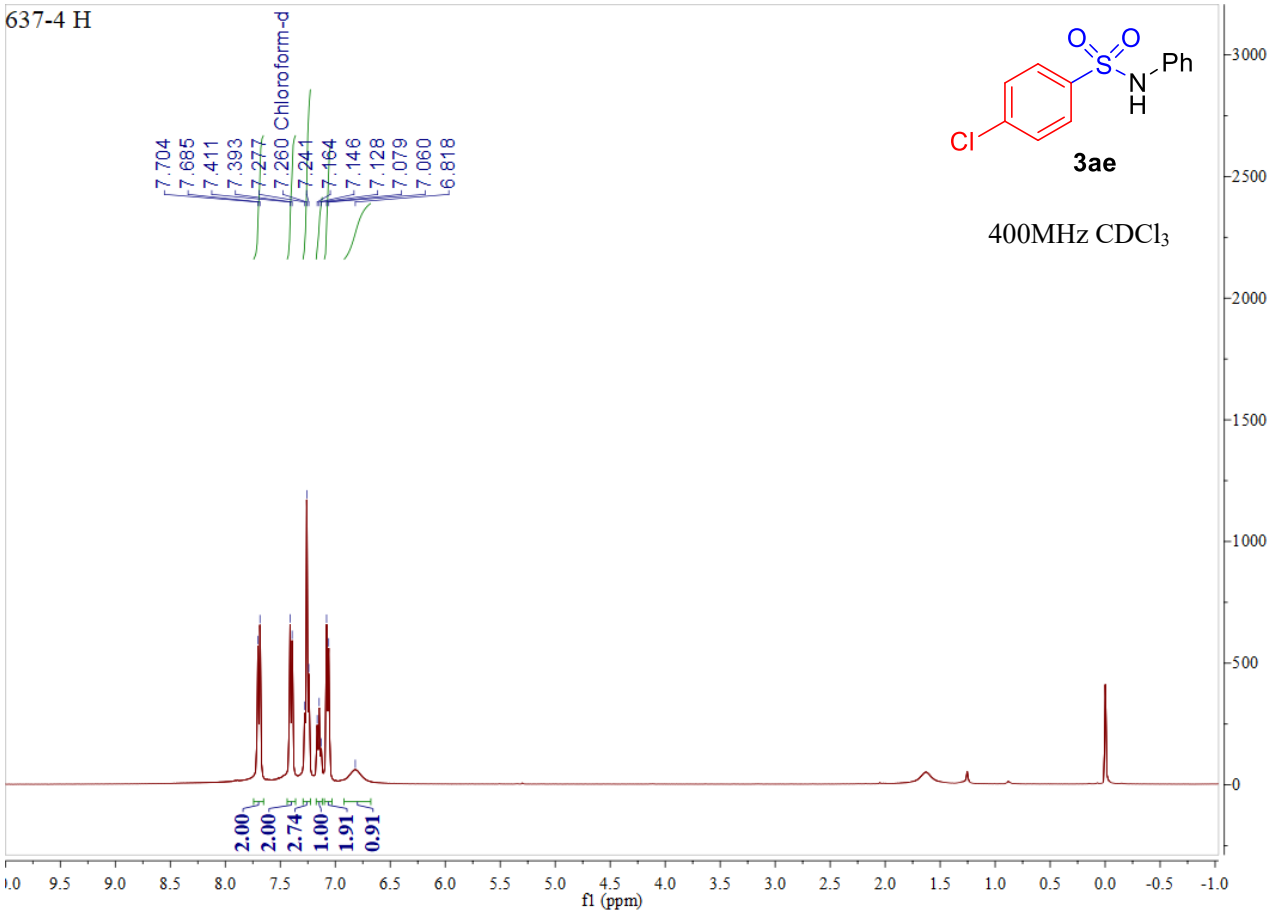
121.791
77.160 Chloroform-d
21.411
f1 (ppm)
Ph
N
H
O
S
3ad


637-4 H
7.704
7.685
7.411
7.393
7.277
7.260 Chloroform-d
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7.164
7.146
7.128
7.079
7.060
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2.00
2.00
2.74
1.00
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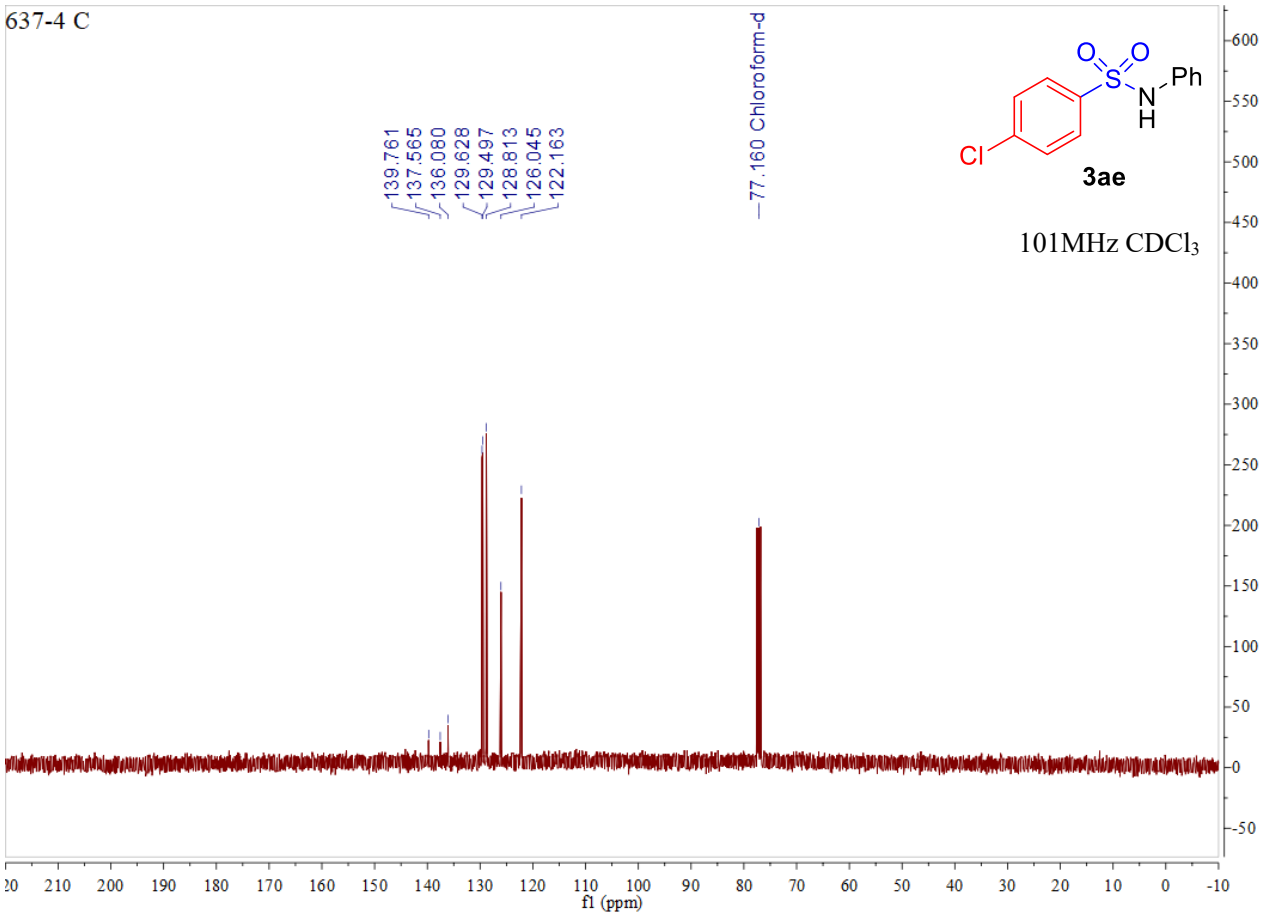
0.91
f1 (ppm)
3ae
400MHz CDCl3


637-4 C
139.761
137.565
136.080
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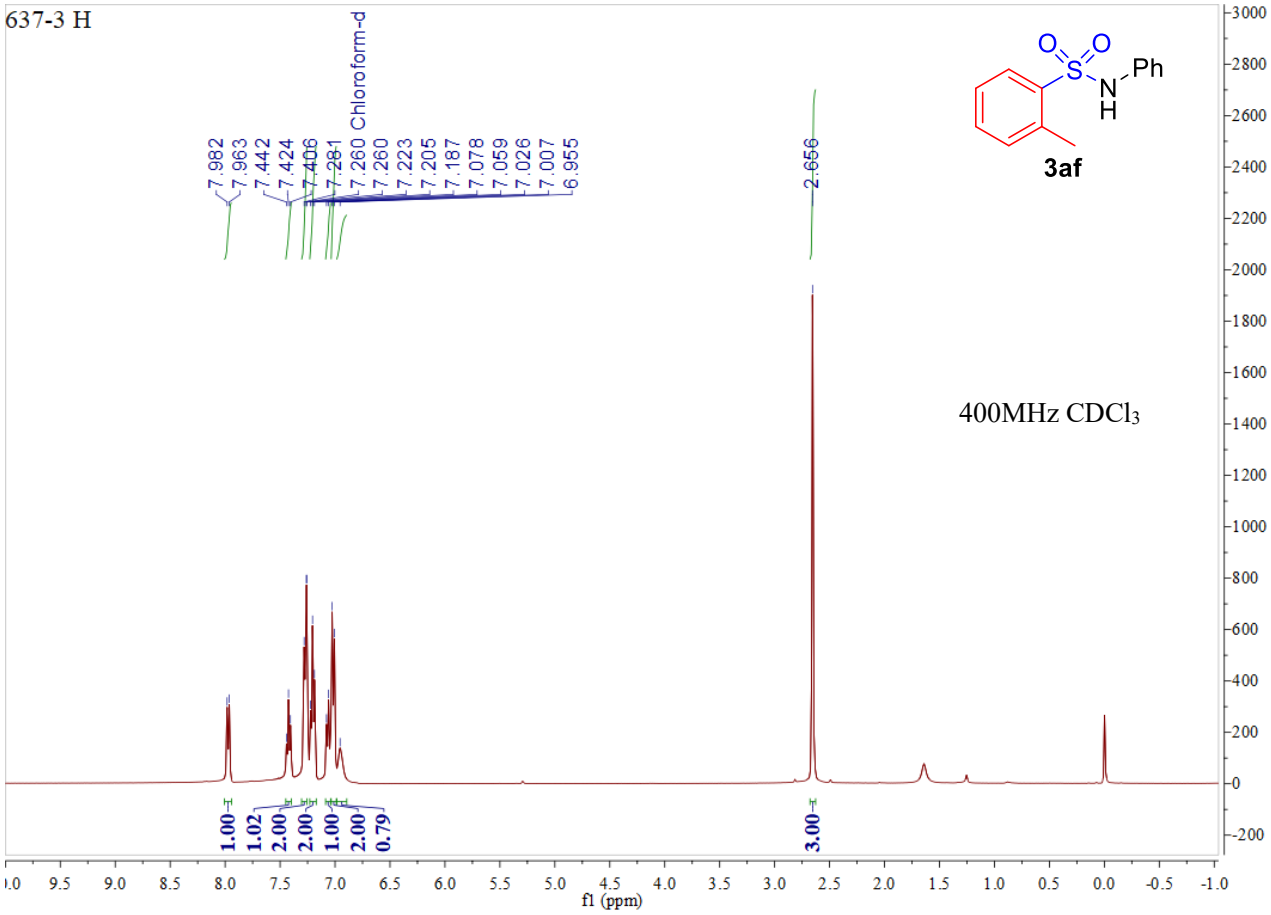
129.497
128.813
126.045
122.163
77.160 Chloroform-d
f1 (ppm)
3ae
101MHz CDCl3


637-3 H
7.982
7.963
7.442
7.424
7.406
7.281
Chloroform-d
7.260
7.260
7.223
7.205
7.187
7.078
7.059
7.026
7.007
6.955
2.656
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400MHz CDCl3
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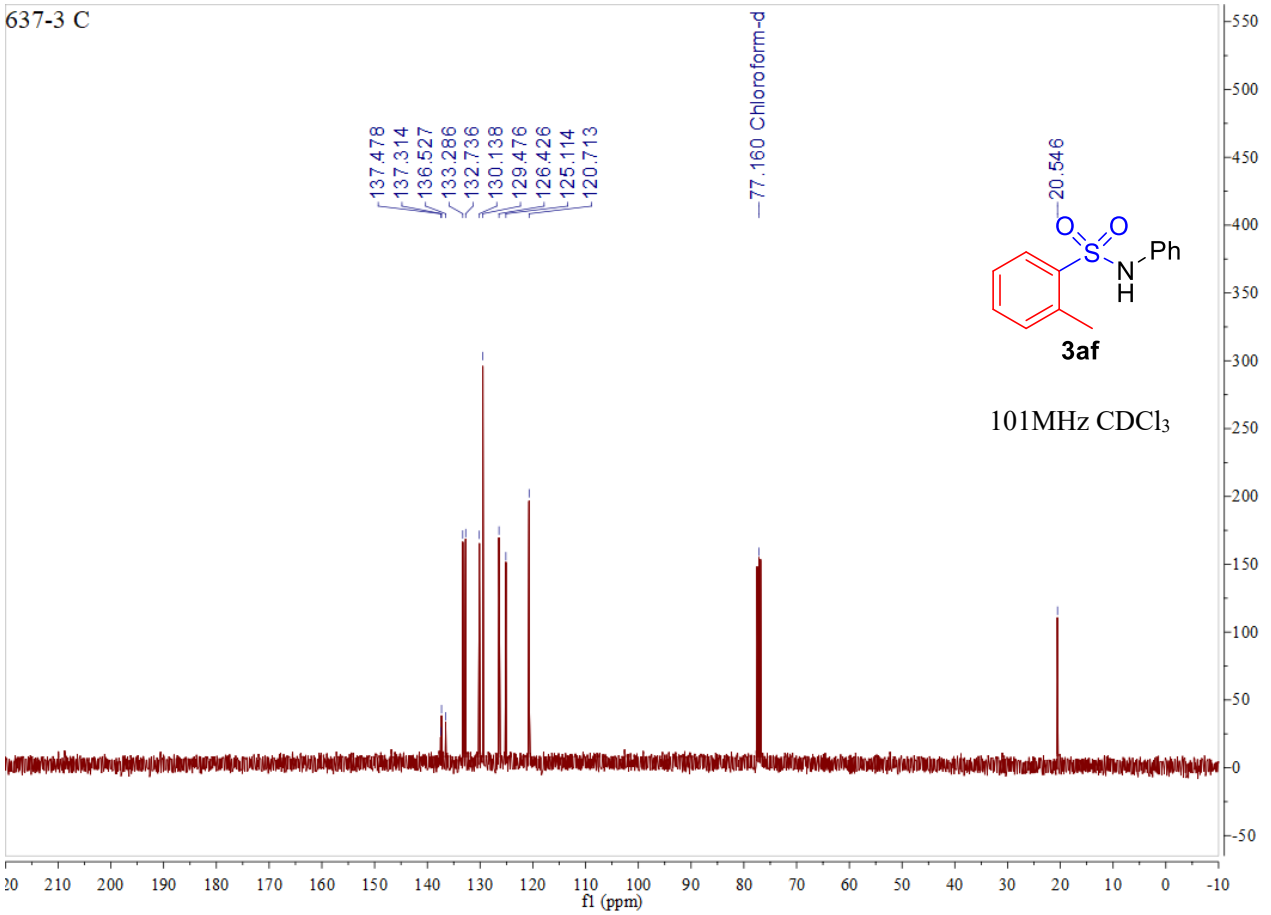
1.02
2.00
2.00
1.00
2.00
0.79
3.00
f1 (ppm)


637-3 C
137.478
137.314
136.527
133.286
132.736
130.138
129.476
126.426
125.114
120.713
77.160 Chloroform-d
20.546
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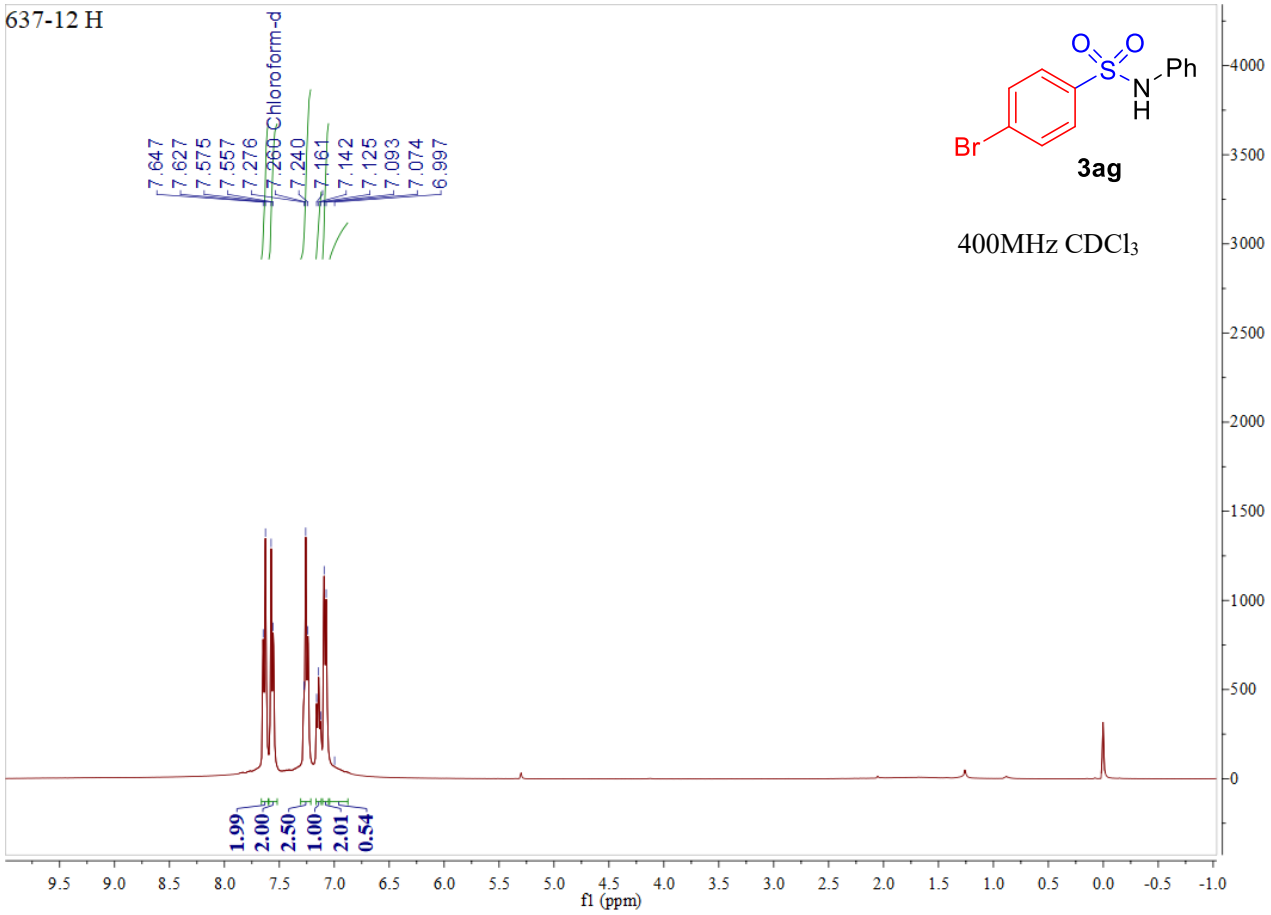
101MHz CDCl3
f1 (ppm)


637-12 H
7.647
7.627
7.575
7.557
7.276
7.260 Chloroform-d
7.240
7.161
7.142
7.125
7.093
7.074
6.997
Br
Ph
N
H
3ag
400MHz CDCl3
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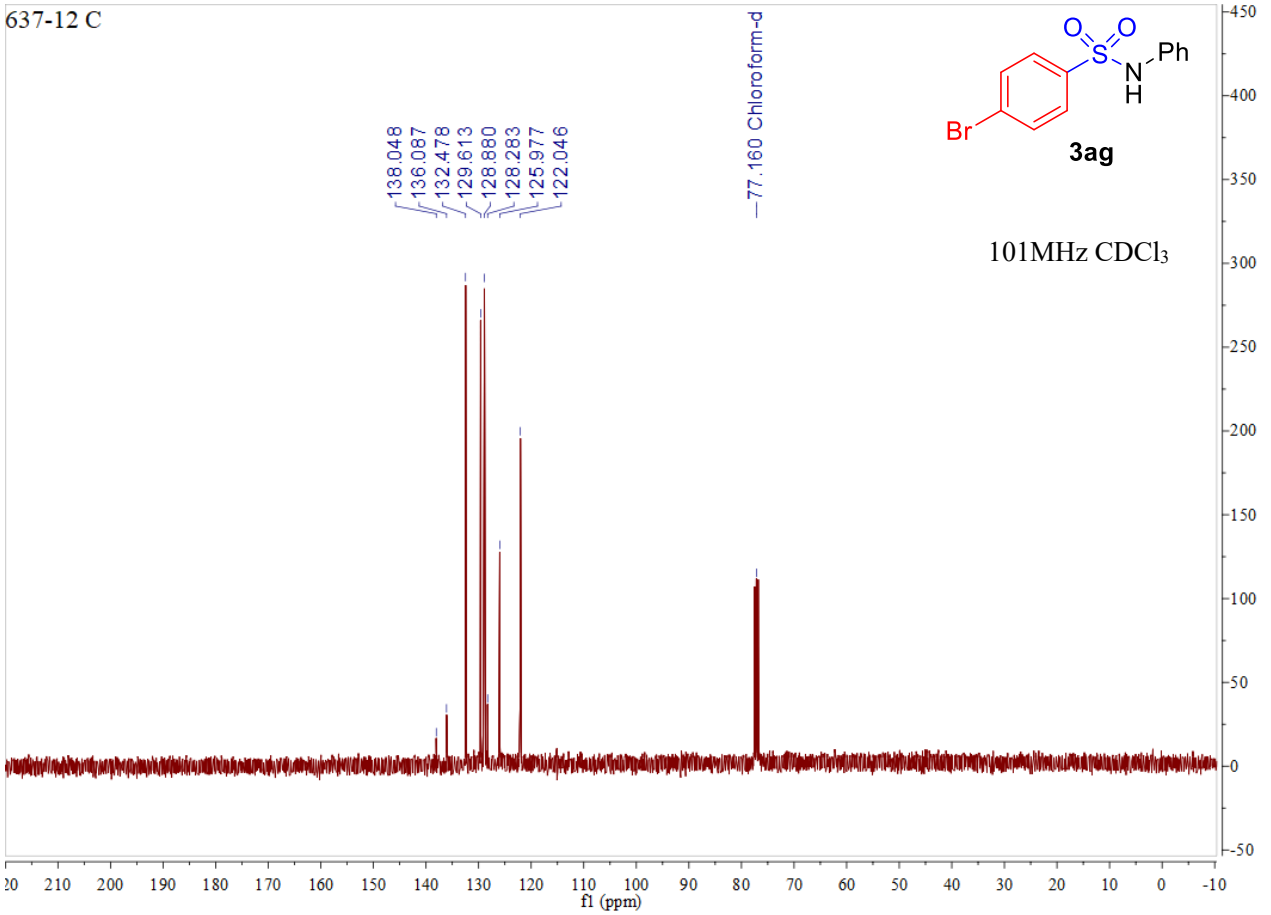
2.00
2.50
1.00
2.01
0.54
f1 (ppm)


637-12 C
138.048
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129.613
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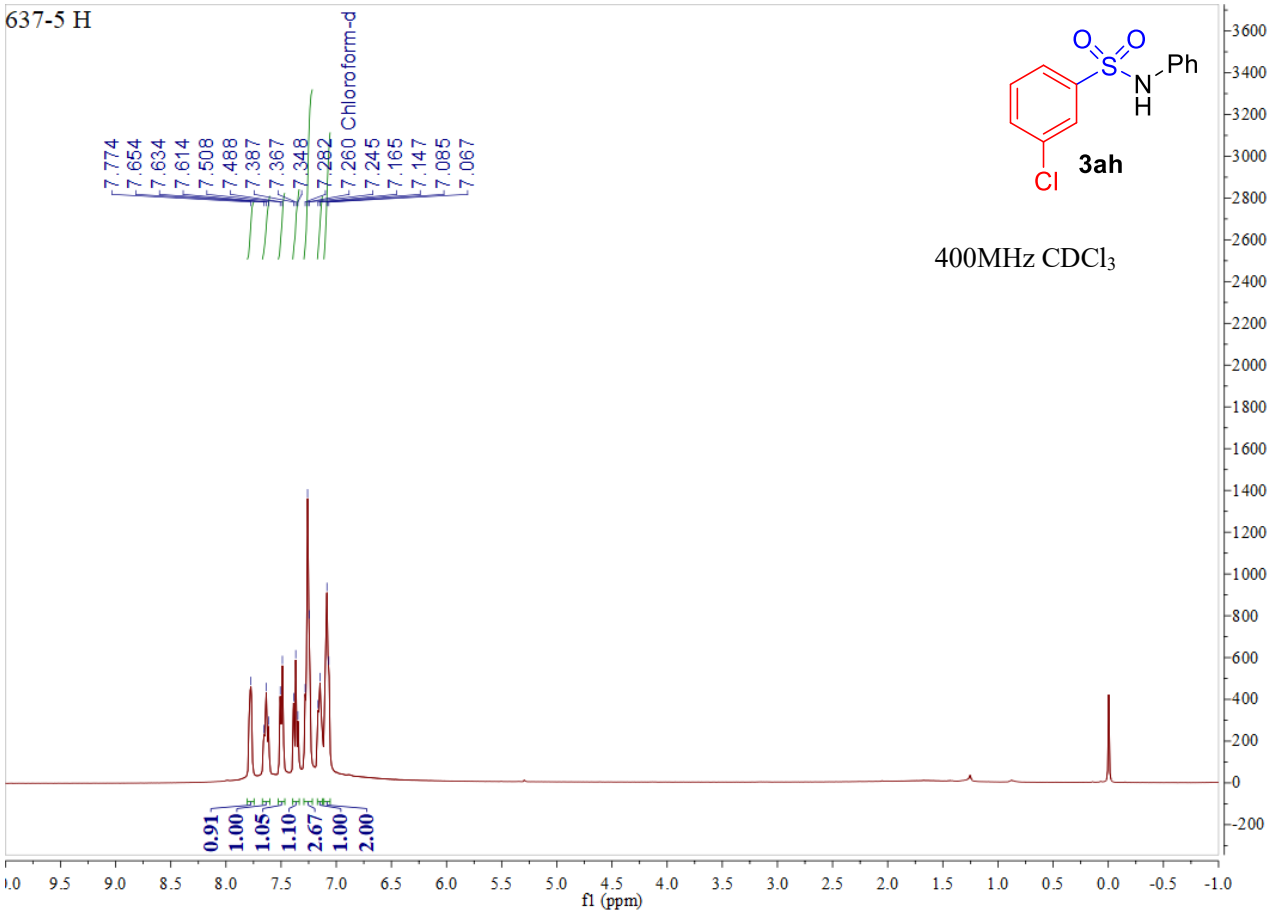
Ph
N
H
3ag
101MHz CDCl3
f1 (ppm)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7.614
7.508
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7.387
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7.348
7.282
7.260 Chloroform-d
7.245
7.165
7.147
7.085
7.067
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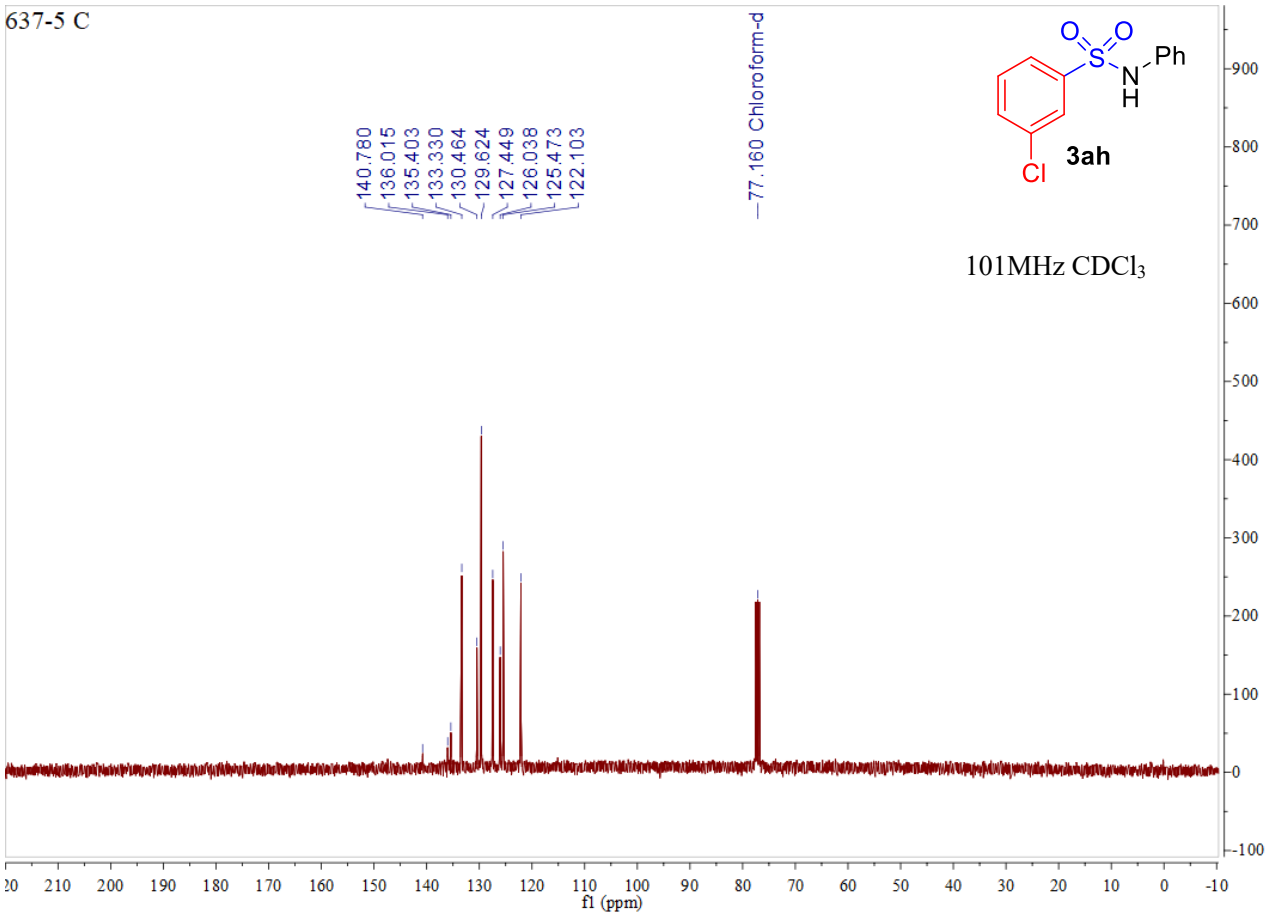
1.00
2.00
f1 (ppm)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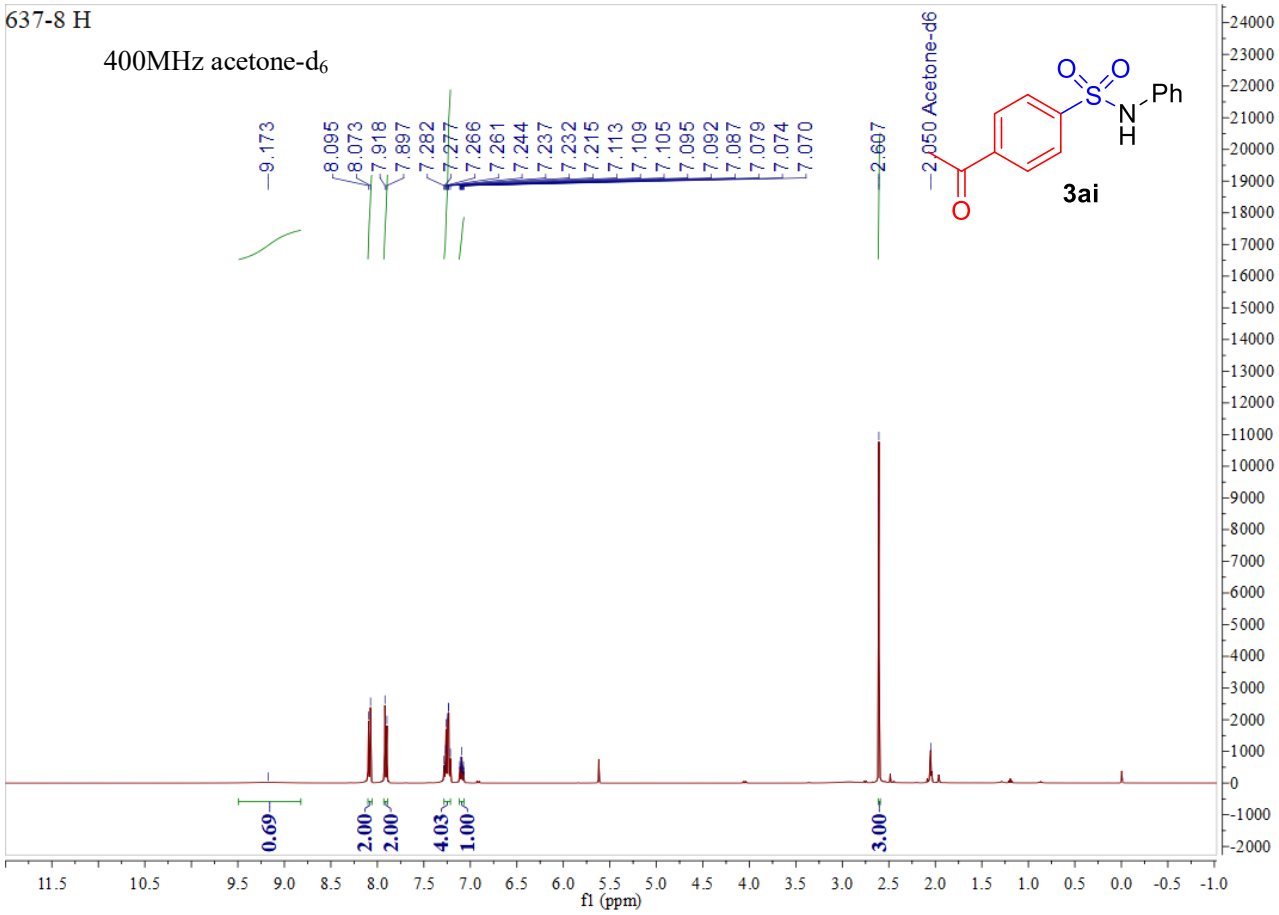
101MHz CDCl3
f1 (ppm)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7.897
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7.277
7.266
7.261
7.244
7.237
7.232
7.215
7.113
7.109
7.105
7.095
7.092
7.087
7.079
7.074
7.070
2.697
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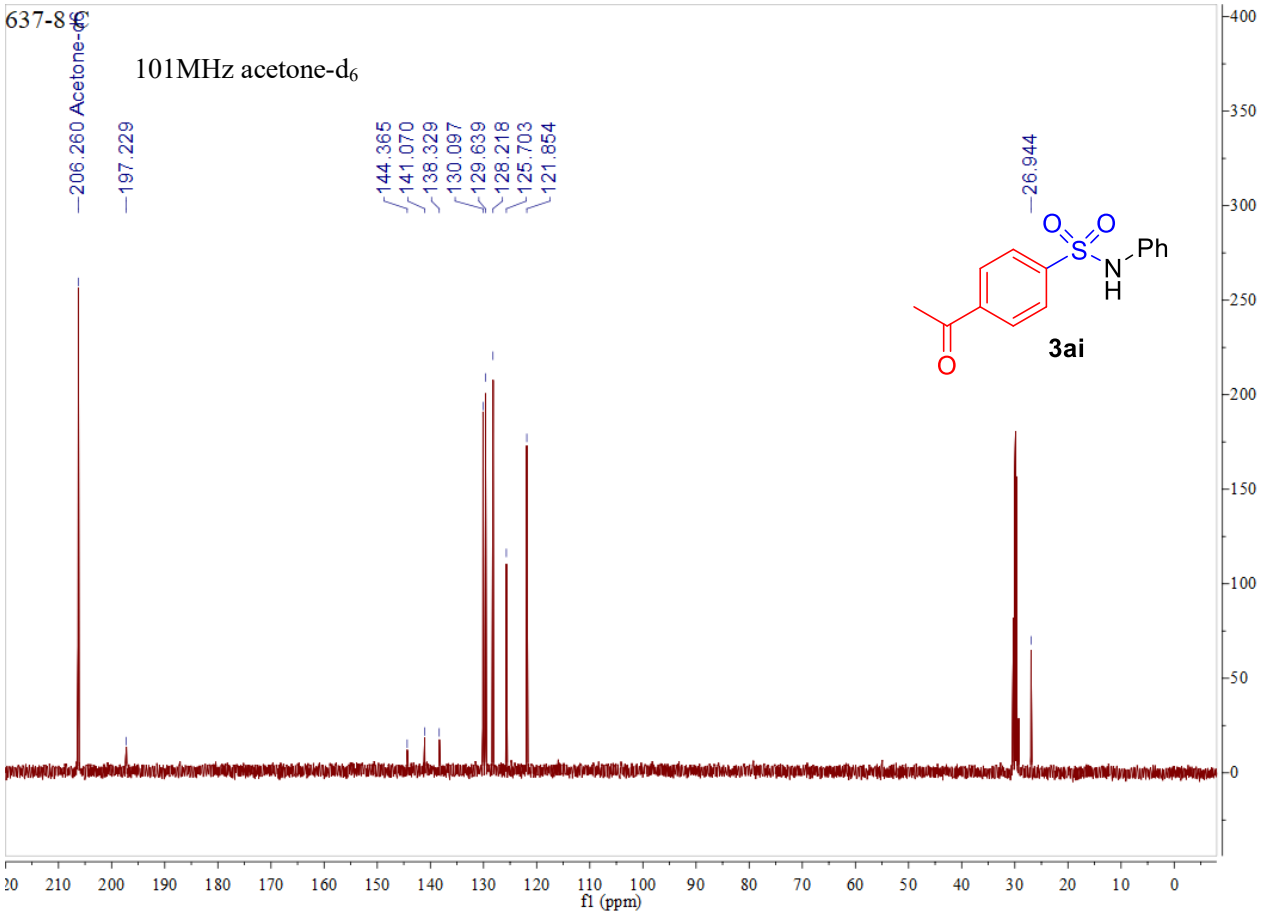
1.00
3.00
f1 (ppm)
3ai


637-8 C
101MHz acetone-d6
206.260 Acetone-d6
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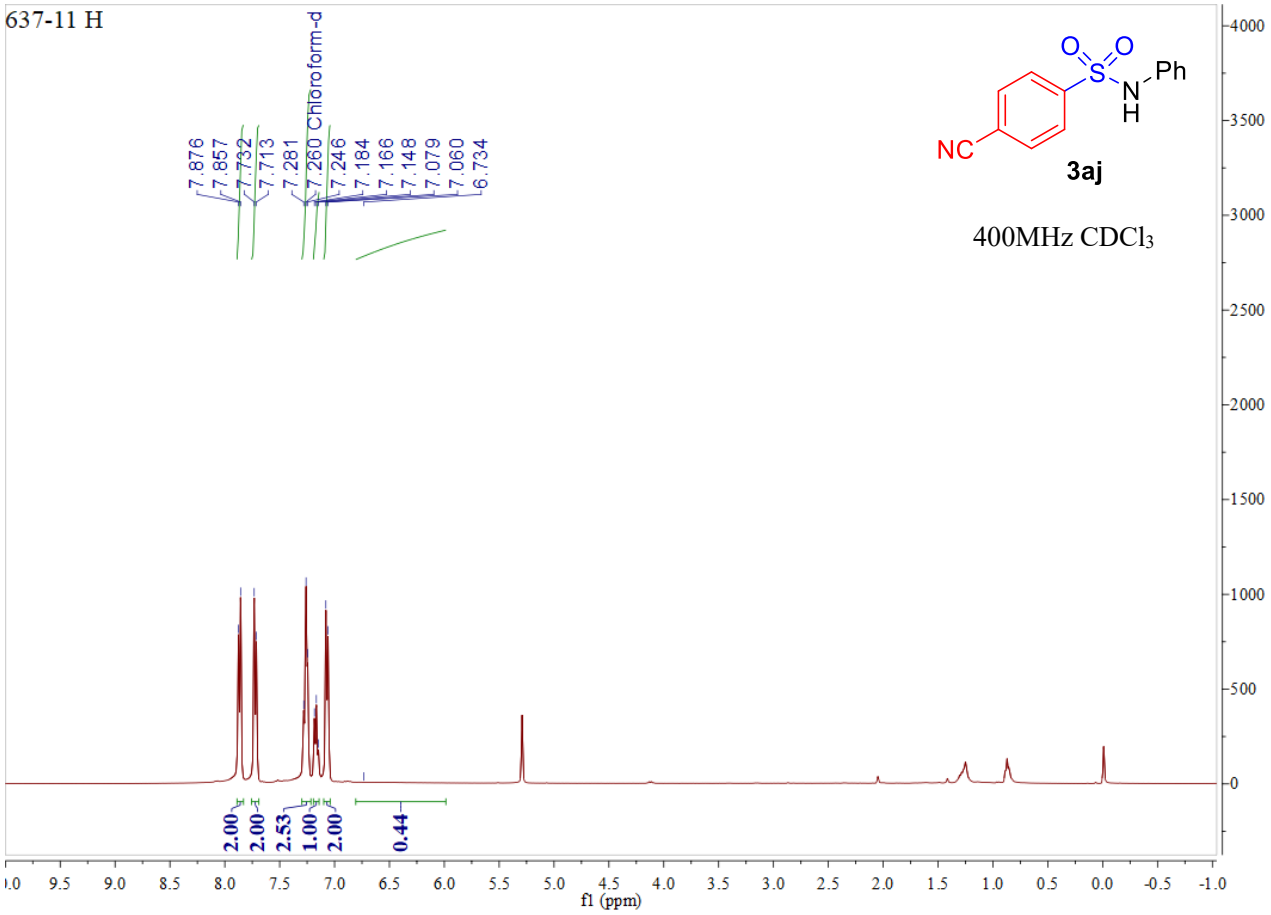
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7.260 Chloroform-d
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7.184
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7.060
6.734
NC
Ph
N
H
O
S
3aj
400MHz CDCl3
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2.53
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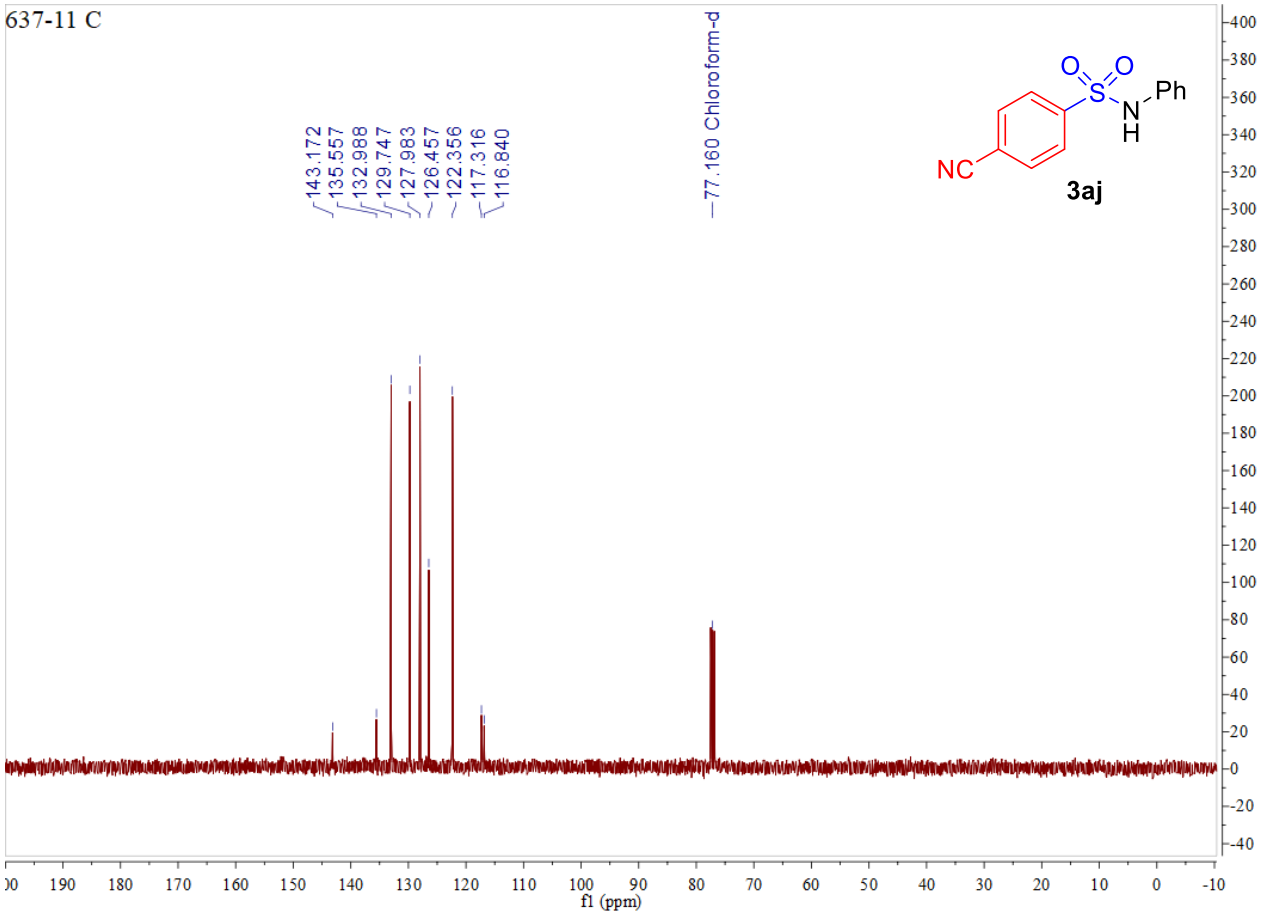
0.44
f1 (ppm)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117.316
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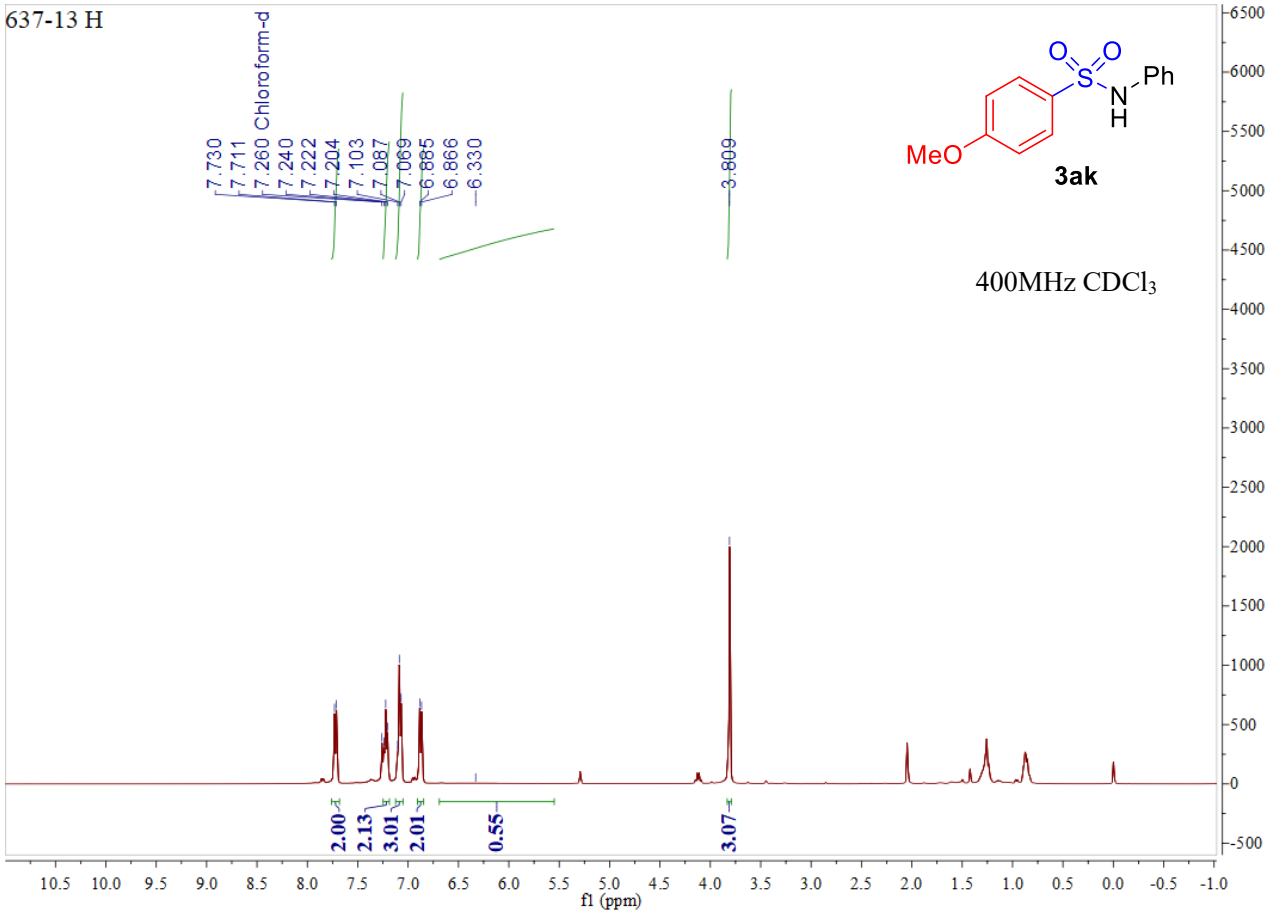
NC
Ph
N
H
O
S
3aj
f1 (ppm)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7.204
7.103
7.087
7.069
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6.866
6.330
3.809
MeO
Ph
N
H
O
S
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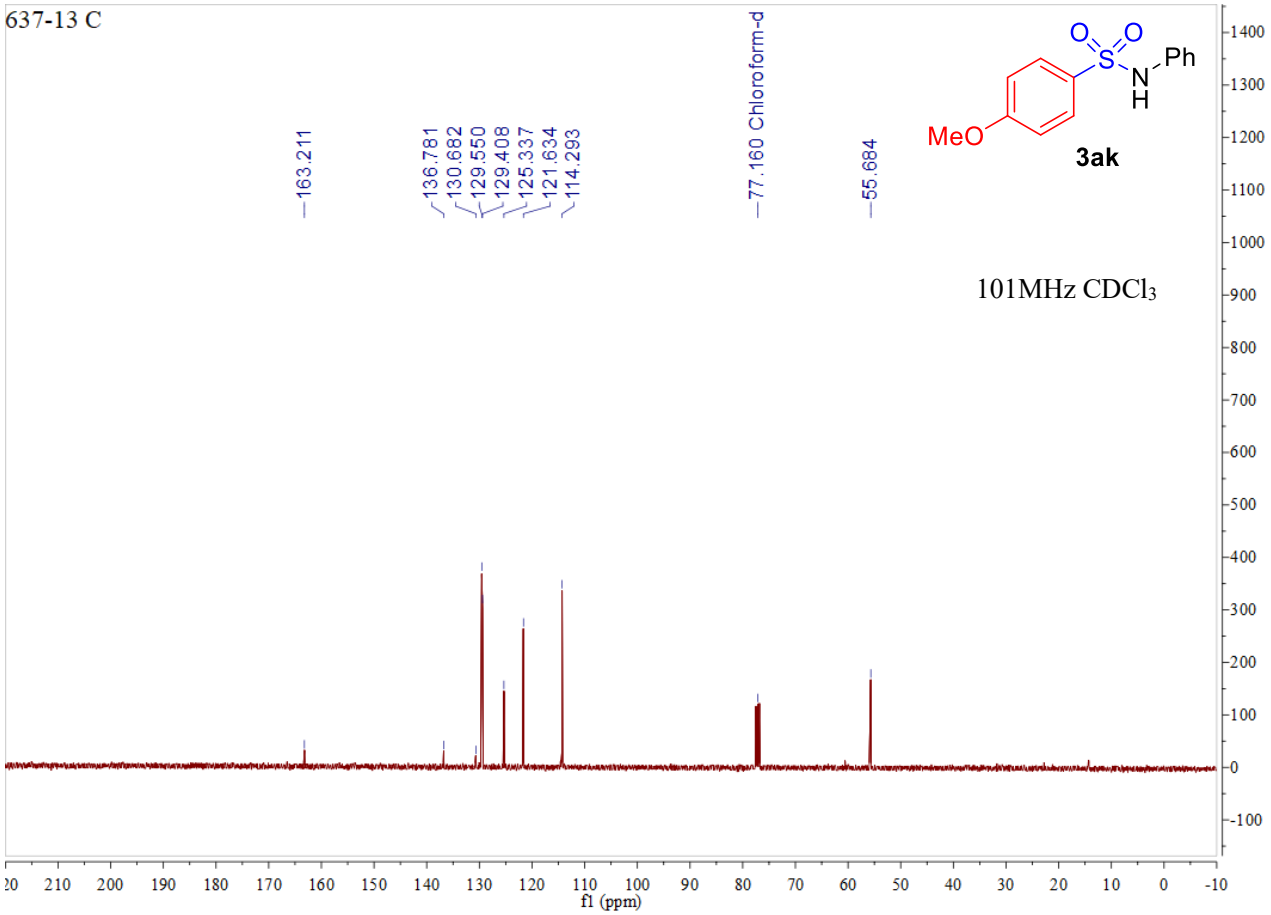
f1 (ppm)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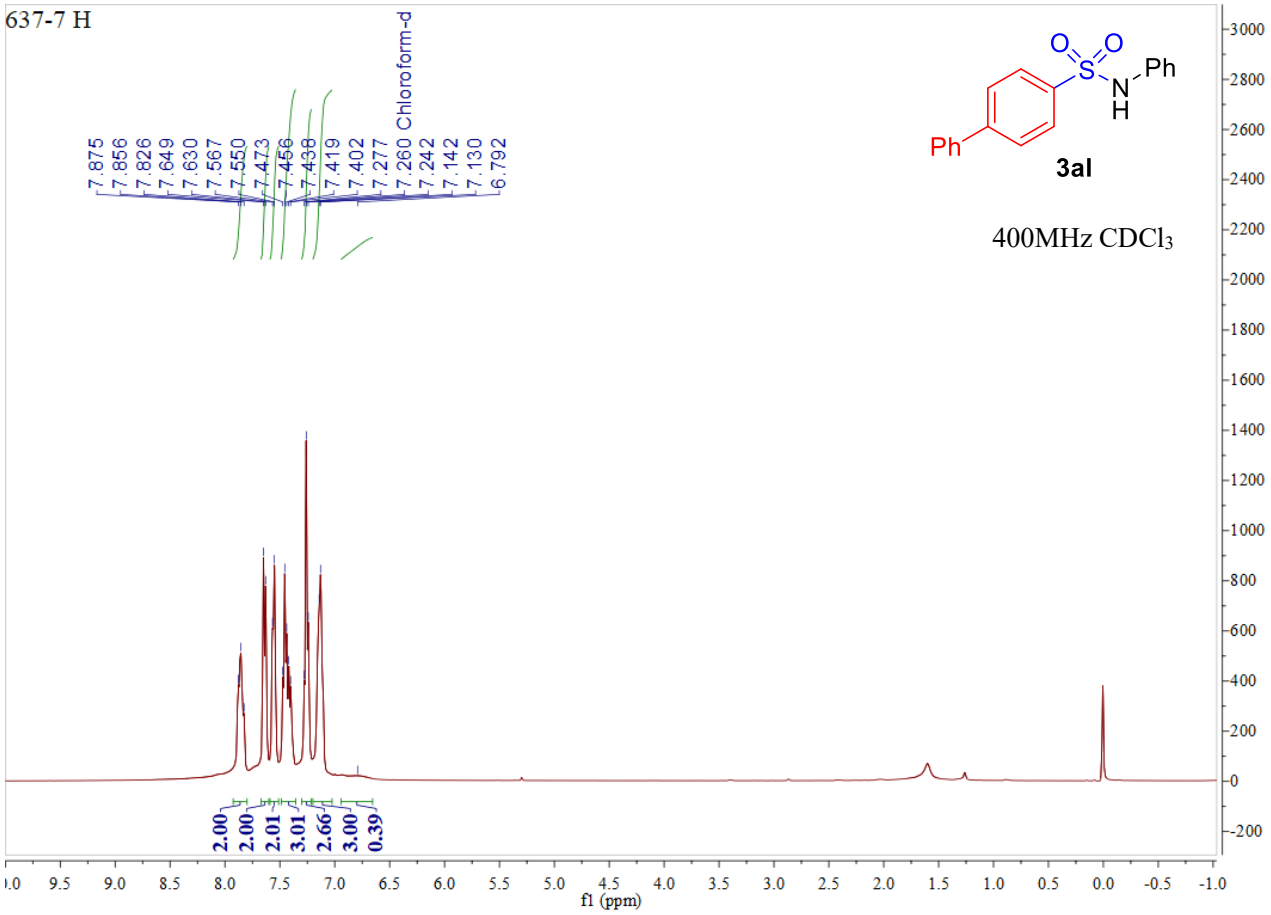
Ph
N
H
O
S
3ak
101MHz CDCl3
f1 (ppm)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7.277
7.260 Chloroform-d
7.242
7.142
7.130
6.792
2.00
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2.01
3.01
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3.00
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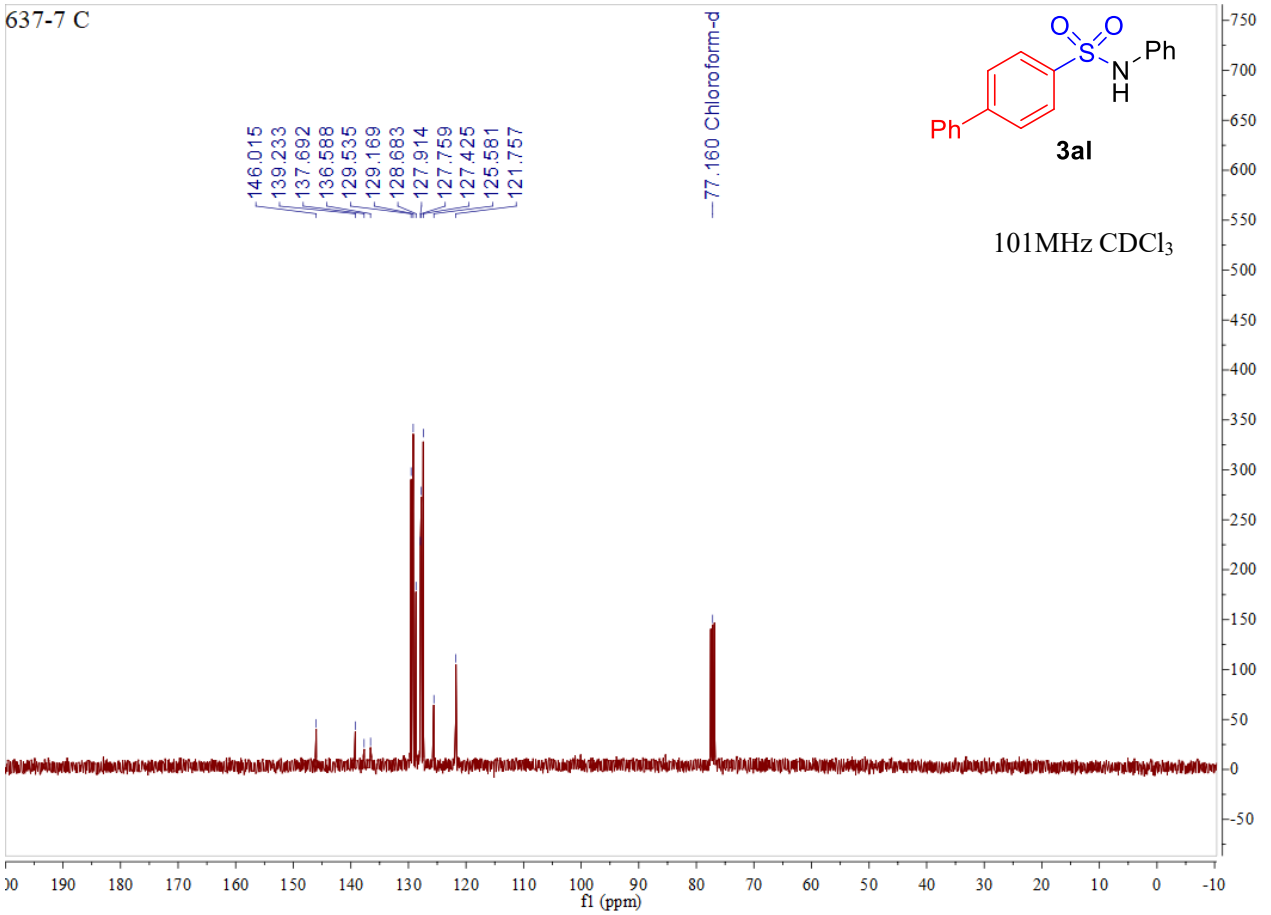
f1 (ppm)
Ph
Ph
3al
400MHz CDCl3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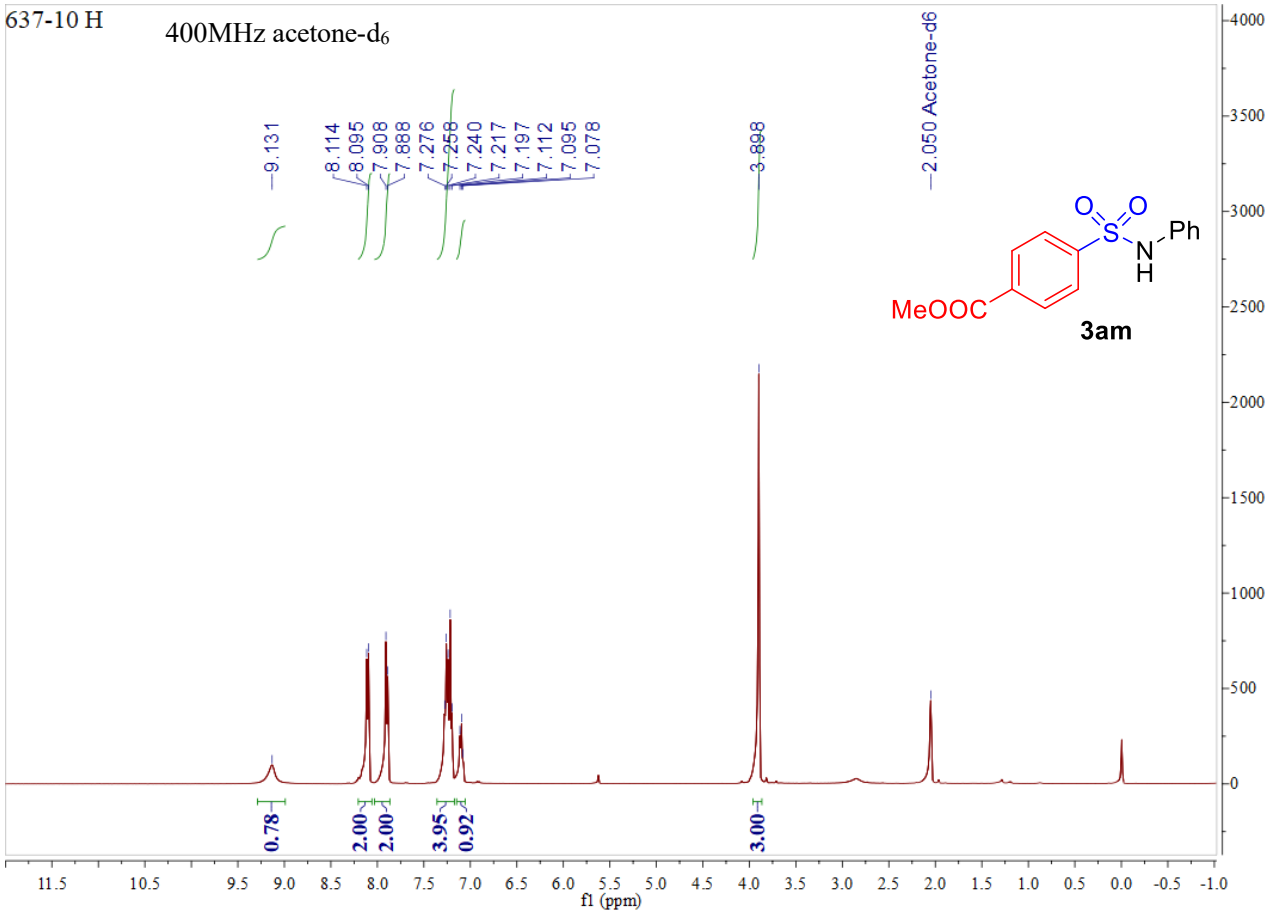
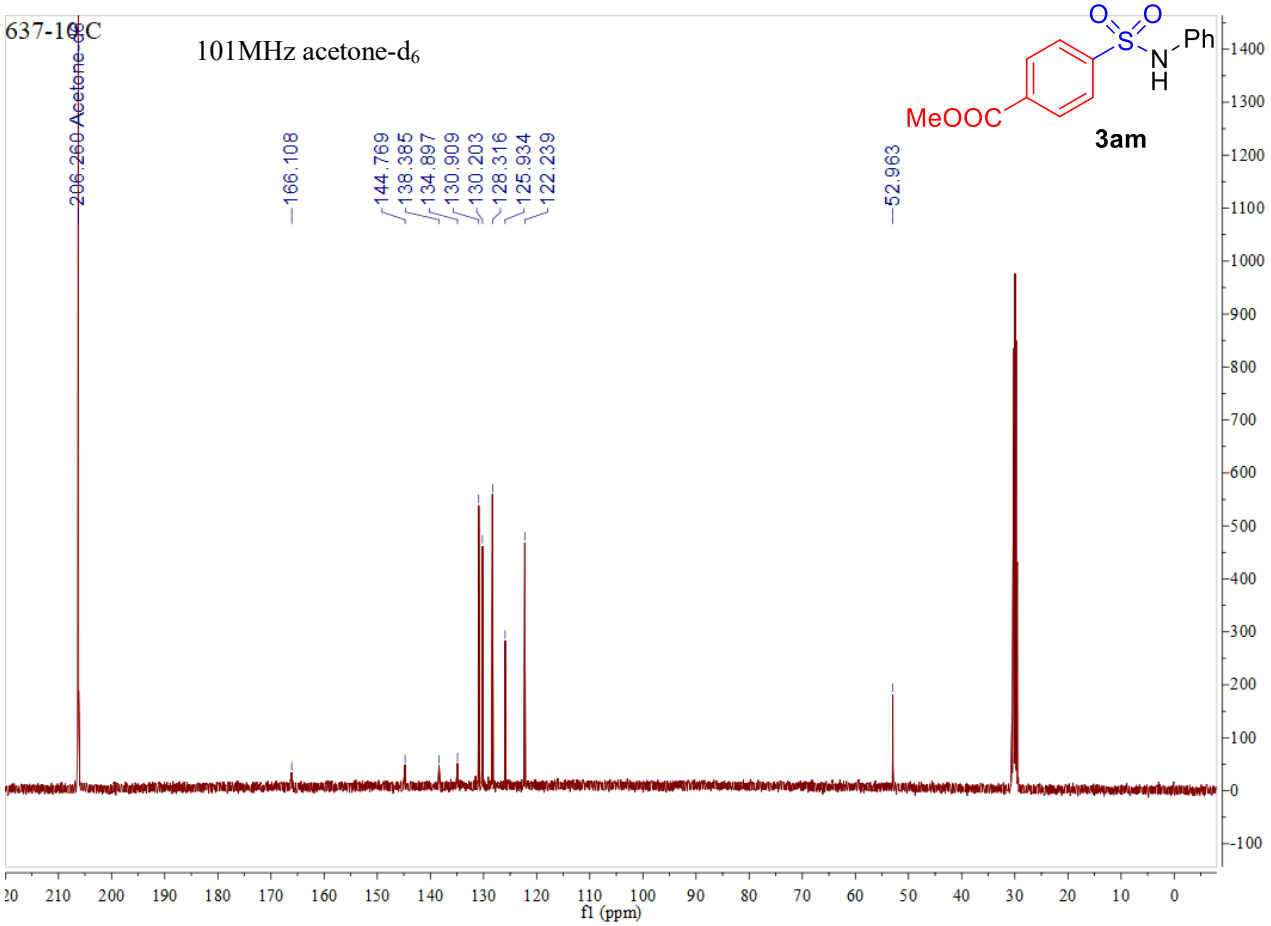
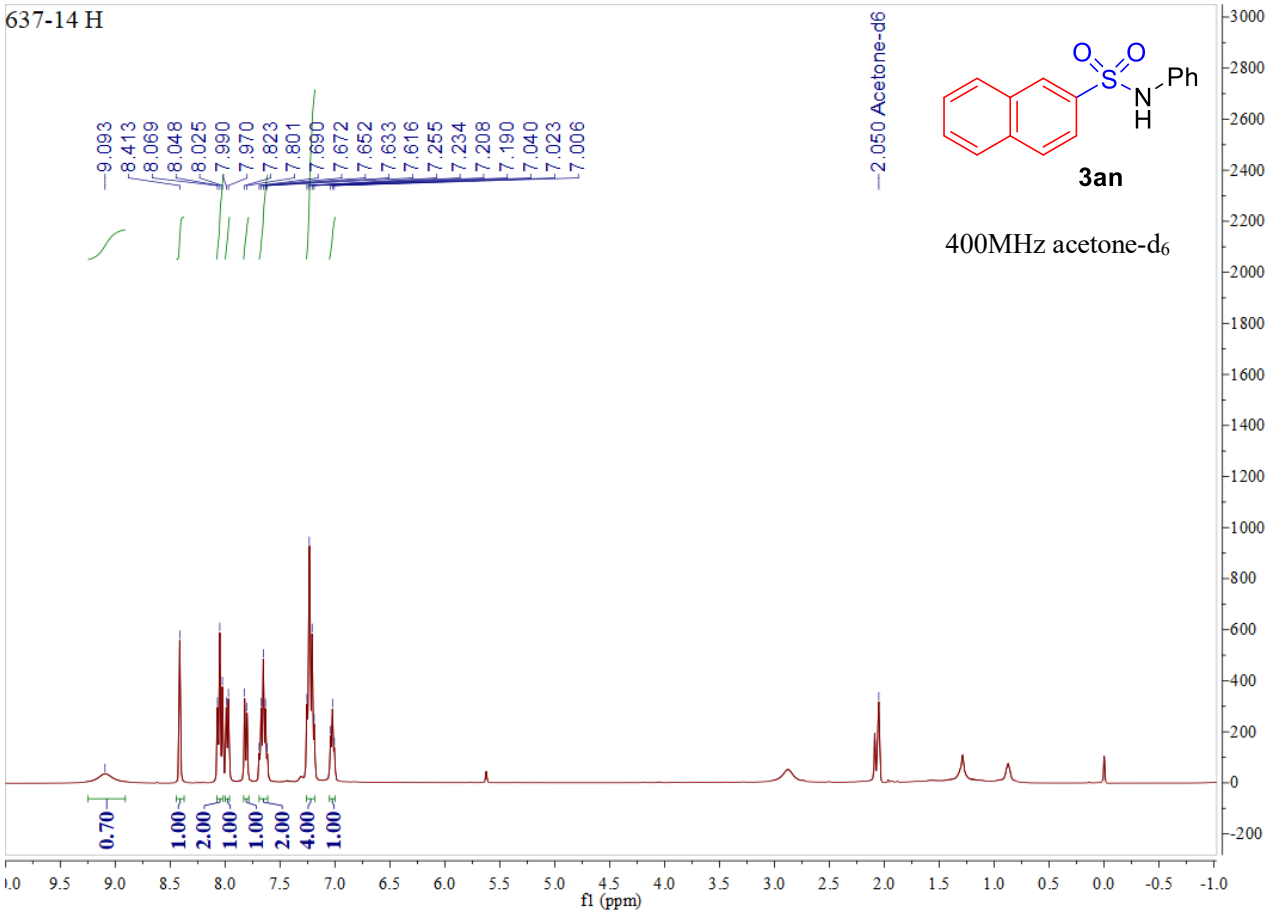
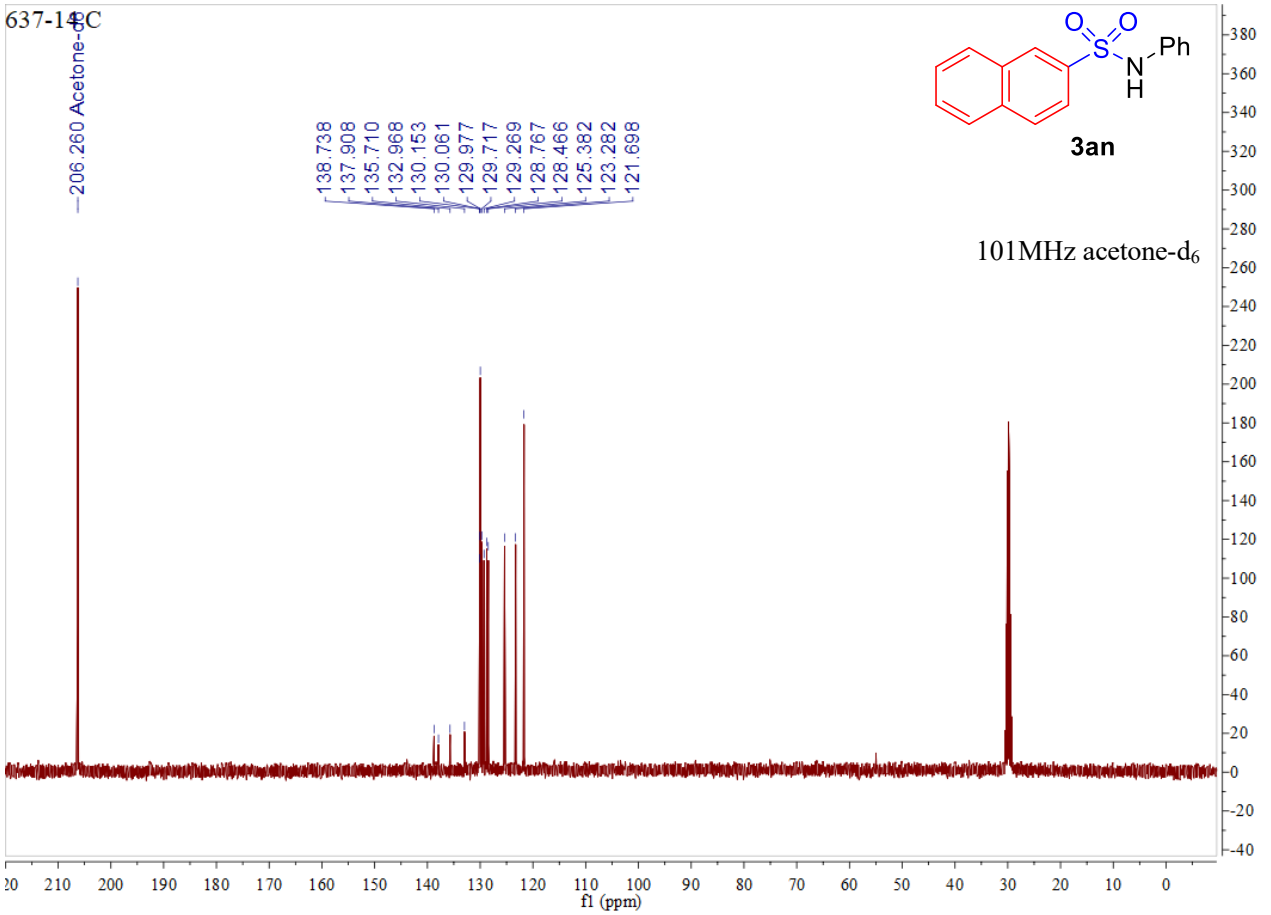
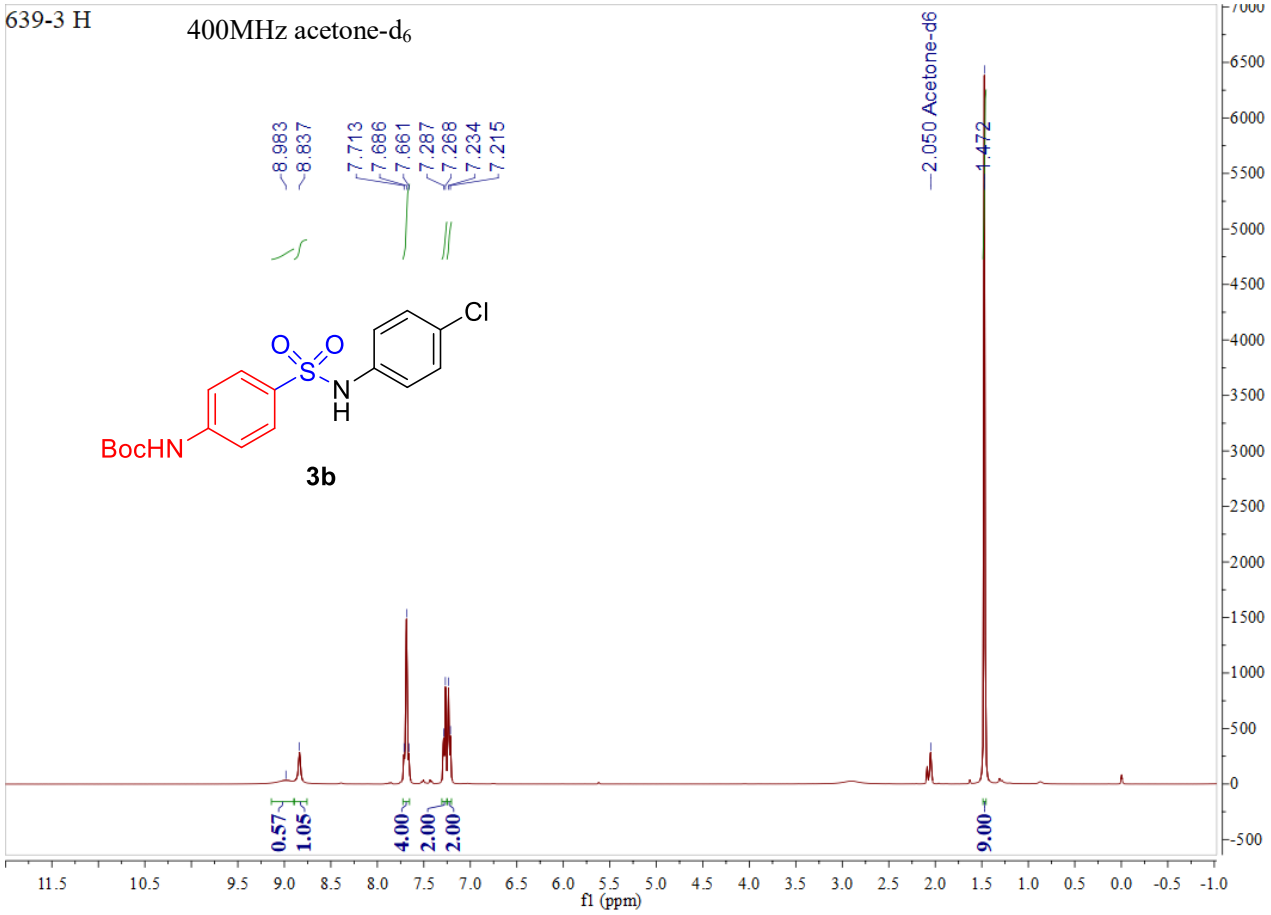
125.581
121.757
77.160 Chloroform-d
f1 (ppm)
Ph
Ph
3al
101MHz CDCl3

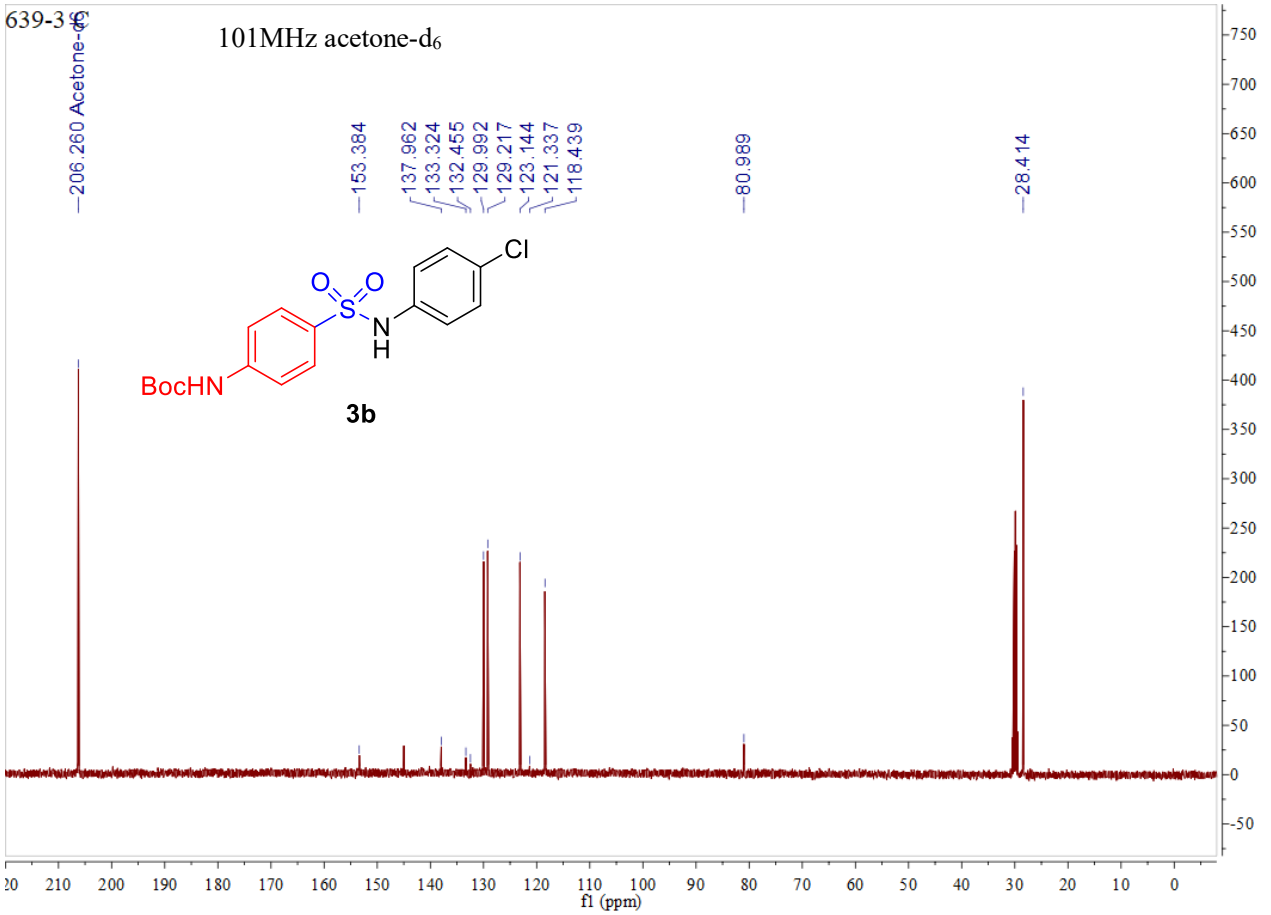

637-10 H
400MHz acetone-d6
9.131
8.114
8.095
7.908
7.888
7.276
7.258
7.240
7.217
7.197
7.112
7.095
7.078
3.898
2.050 Acetone-d6
0.78
2.00
2.00
3.95
0.92
3.00
f1 (ppm)
MeOOC
Ph
N
H
3am

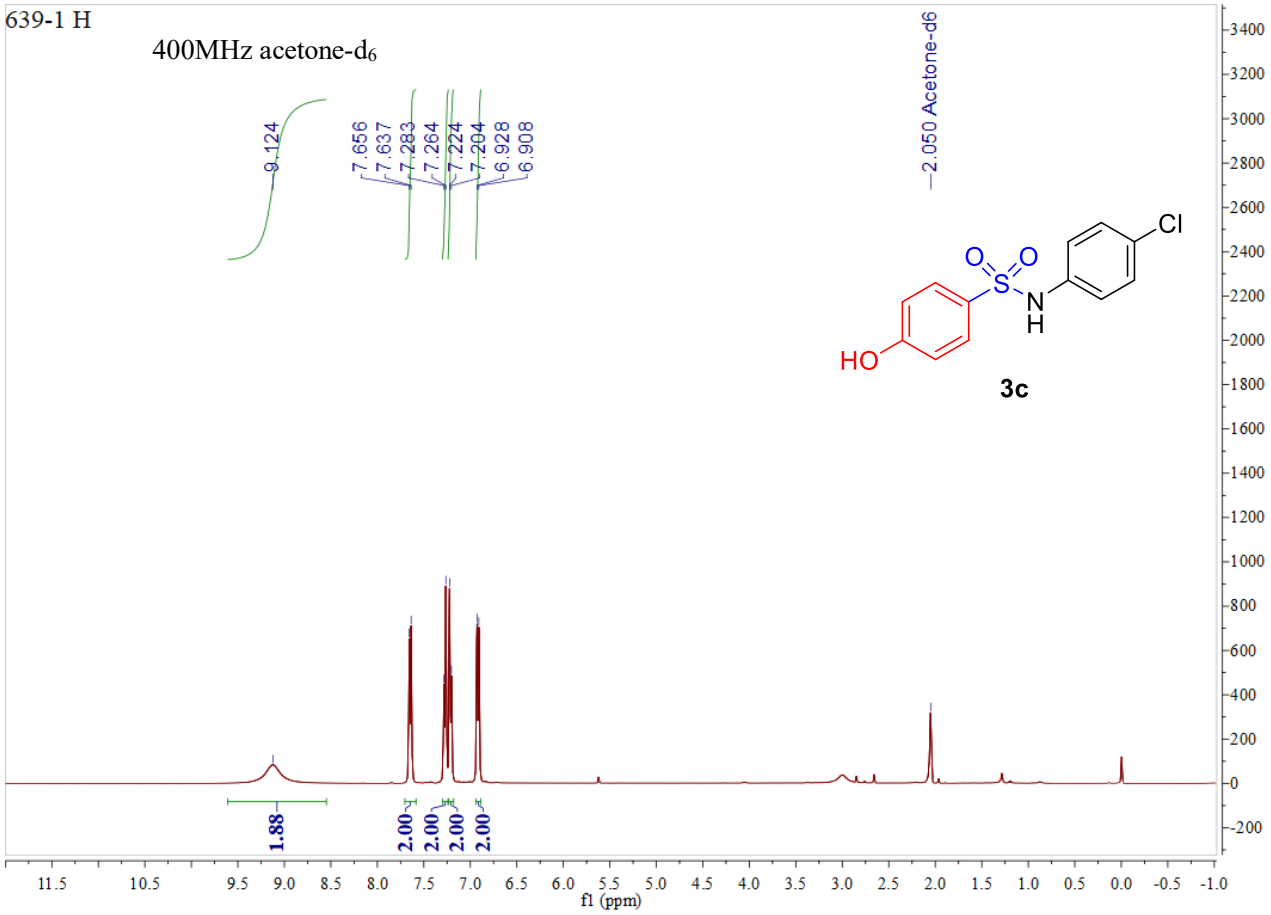

637-10 C
101MHz acetone-d6
206.260 Acetone-d6
166.108
144.769
138.385
134.897
130.909
130.203
128.316
125.934
122.239
52.963
f1 (ppm)
MeOOC
Ph
N
H
3am

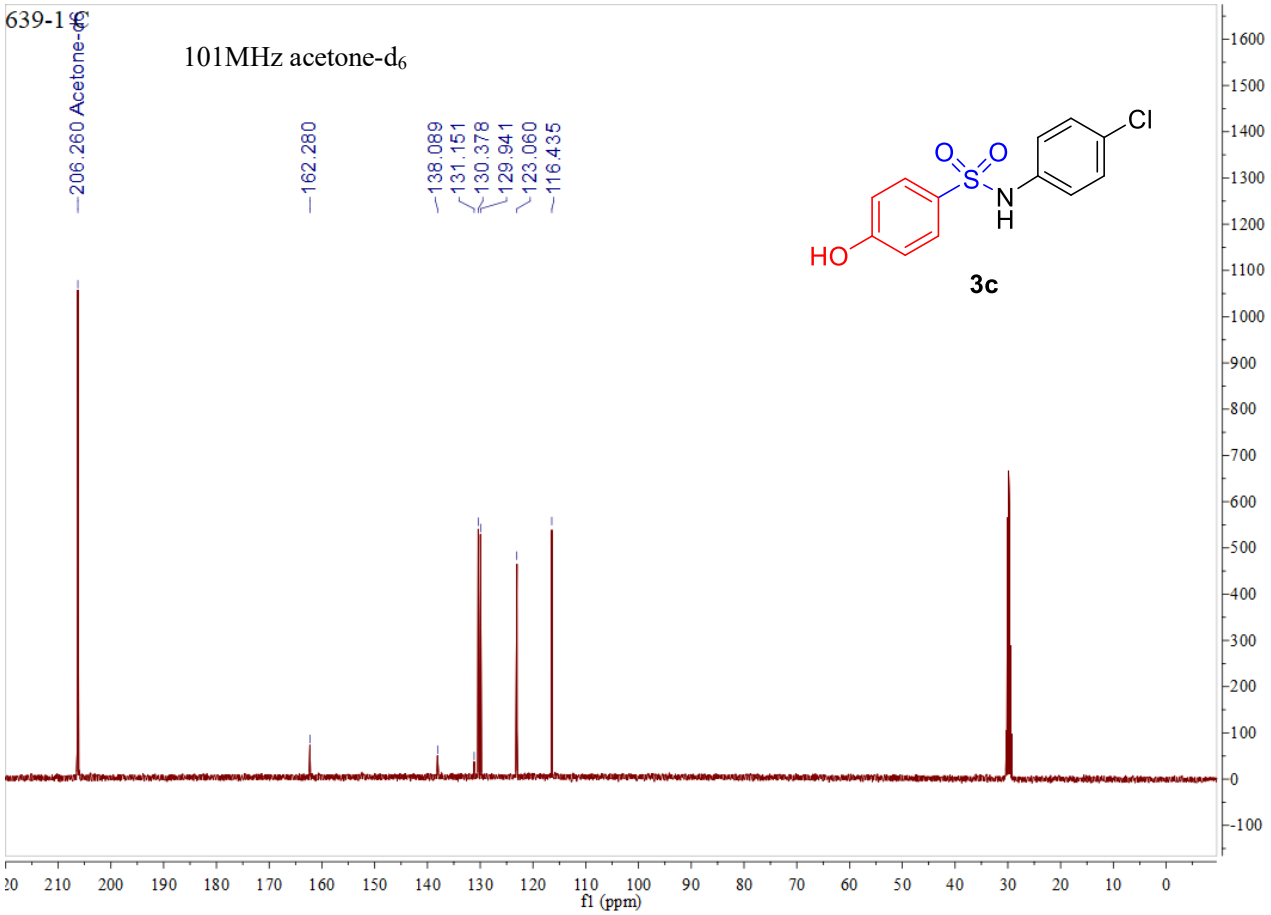

637-14 H
9.093
8.413
8.069
8.048
8.025
7.990
7.970
7.823
7.801
7.690
7.672
7.652
7.633
7.616
7.255
7.234
7.208
7.190
7.040
7.023
7.006
2.050 Acetone-d6
3an
400MHz acetone-d6
0.70
1.00
2.00
1.00
1.00
2.00
4.00
1.00
f1 (ppm)

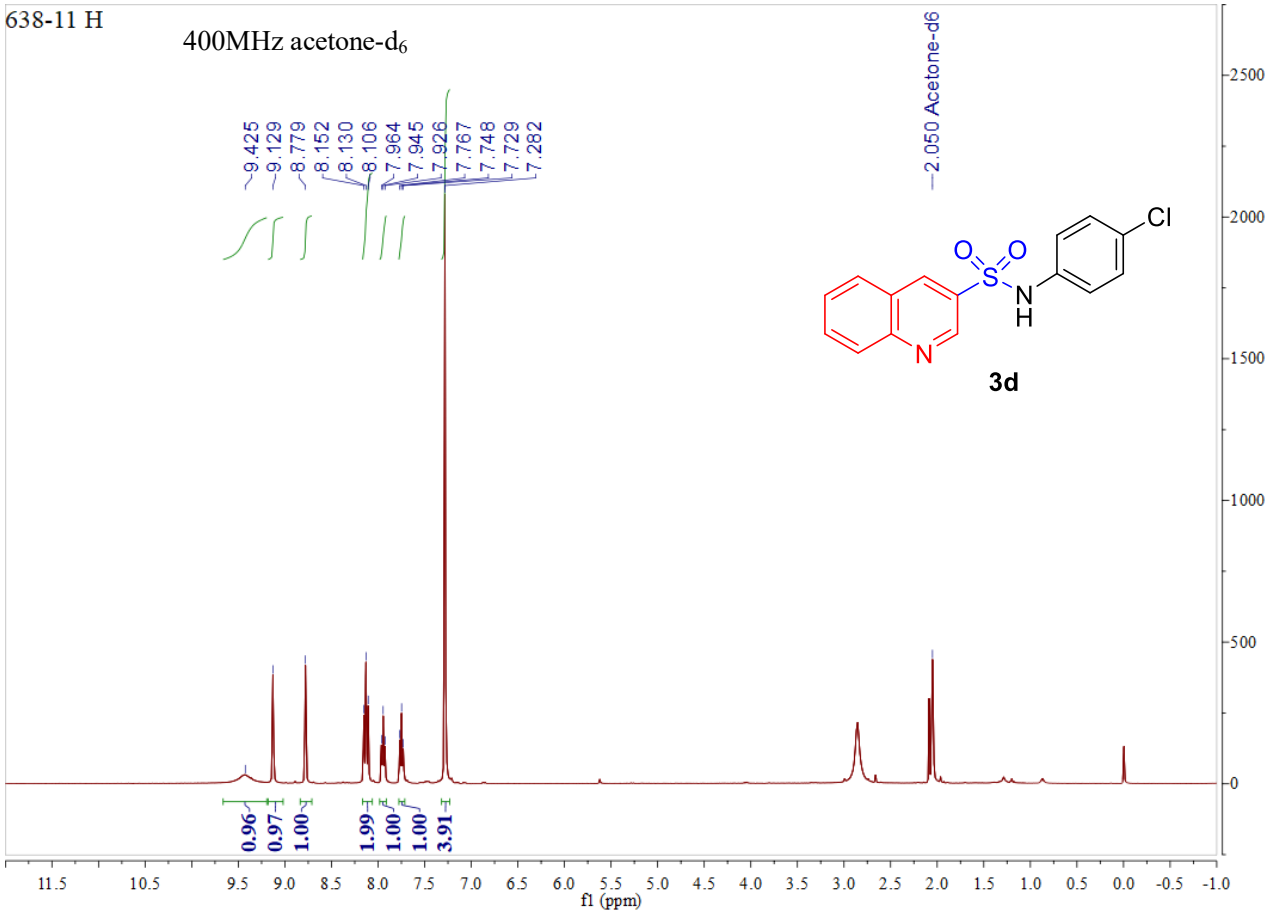

637-14 C
206.260 Acetone-d6
138.738
137.908
135.710
132.968
130.153
130.061
129.977
129.717
129.269
128.767
128.466
125.382
123.282
121.698
3an
101MHz acetone-d6
f1 (ppm)

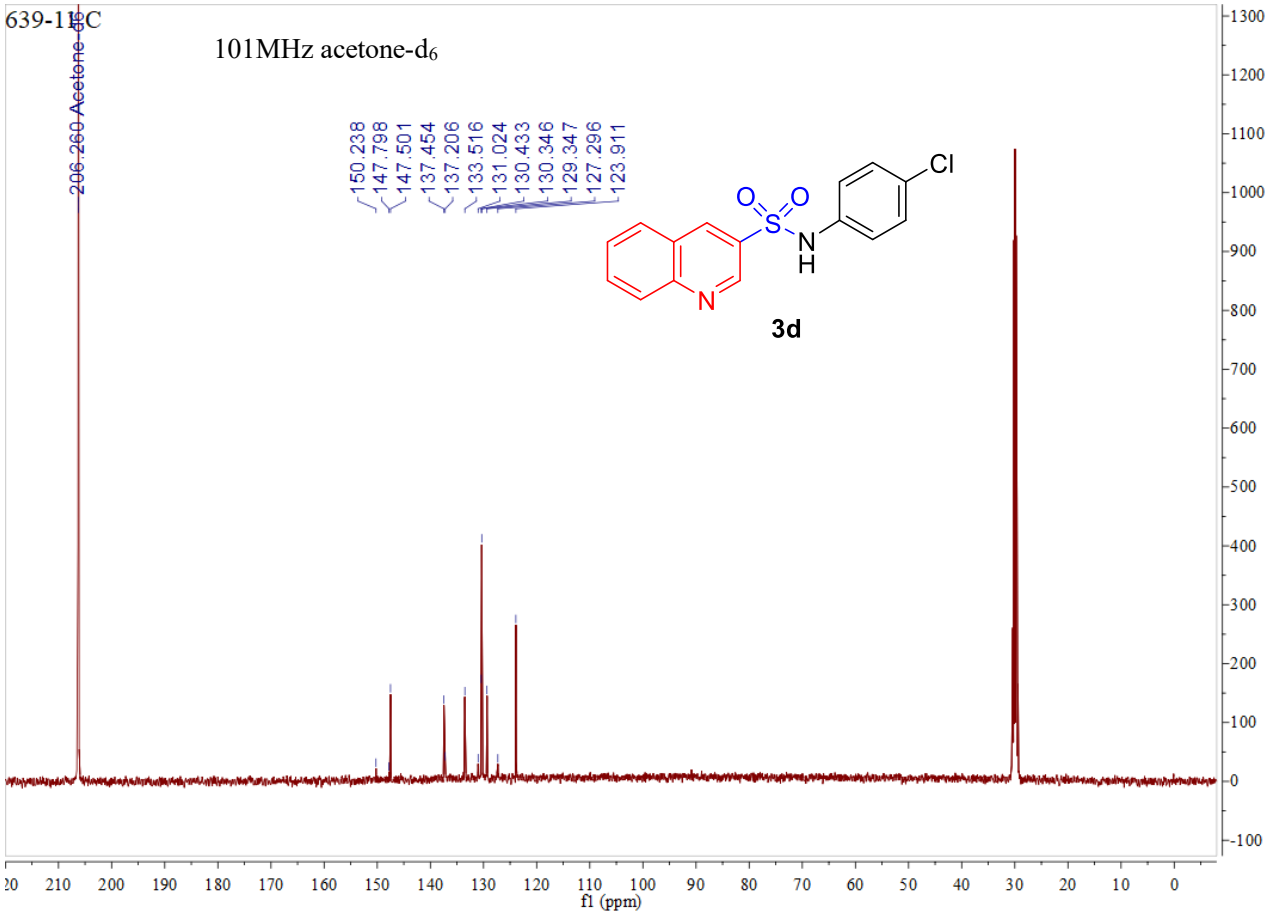

639-3 H
400MHz acetone-d6
8.983
8.837
7.713
7.686
7.661
7.287
7.268
7.234
7.215
2.050 Acetone-d6
1.472
Cl
O
S
O
N
H
BocHN
3b
0.57
1.05
4.00
2.00
2.00
9.00
f1 (ppm)

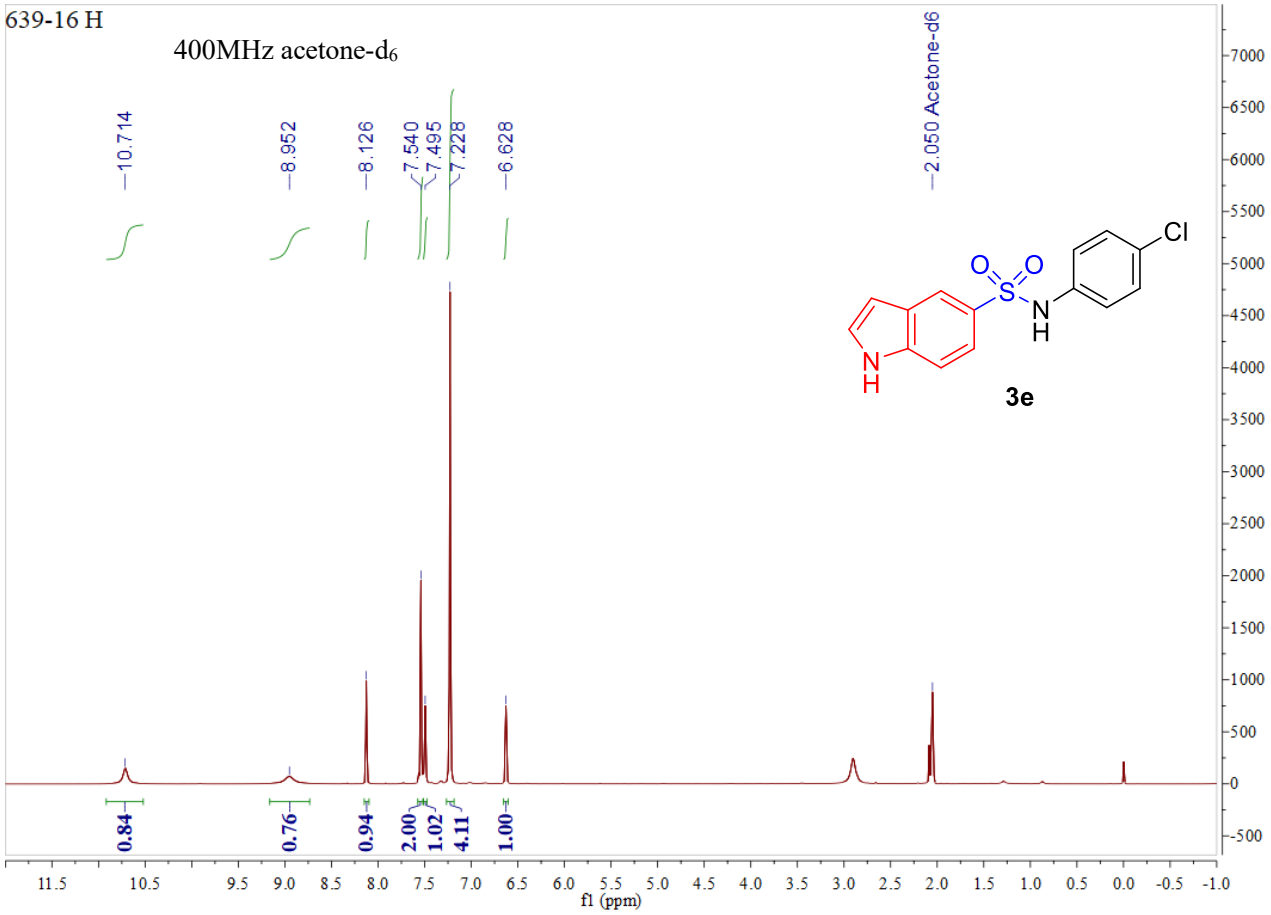

639-3 C
101MHz acetone-d6
206.260 Acetone-d6
153.384
137.962
133.324
132.455
129.992
129.217
123.144
121.337
118.439
80.989
28.414
Cl
O
S
O
N
H
BocHN
3b
f1 (ppm)

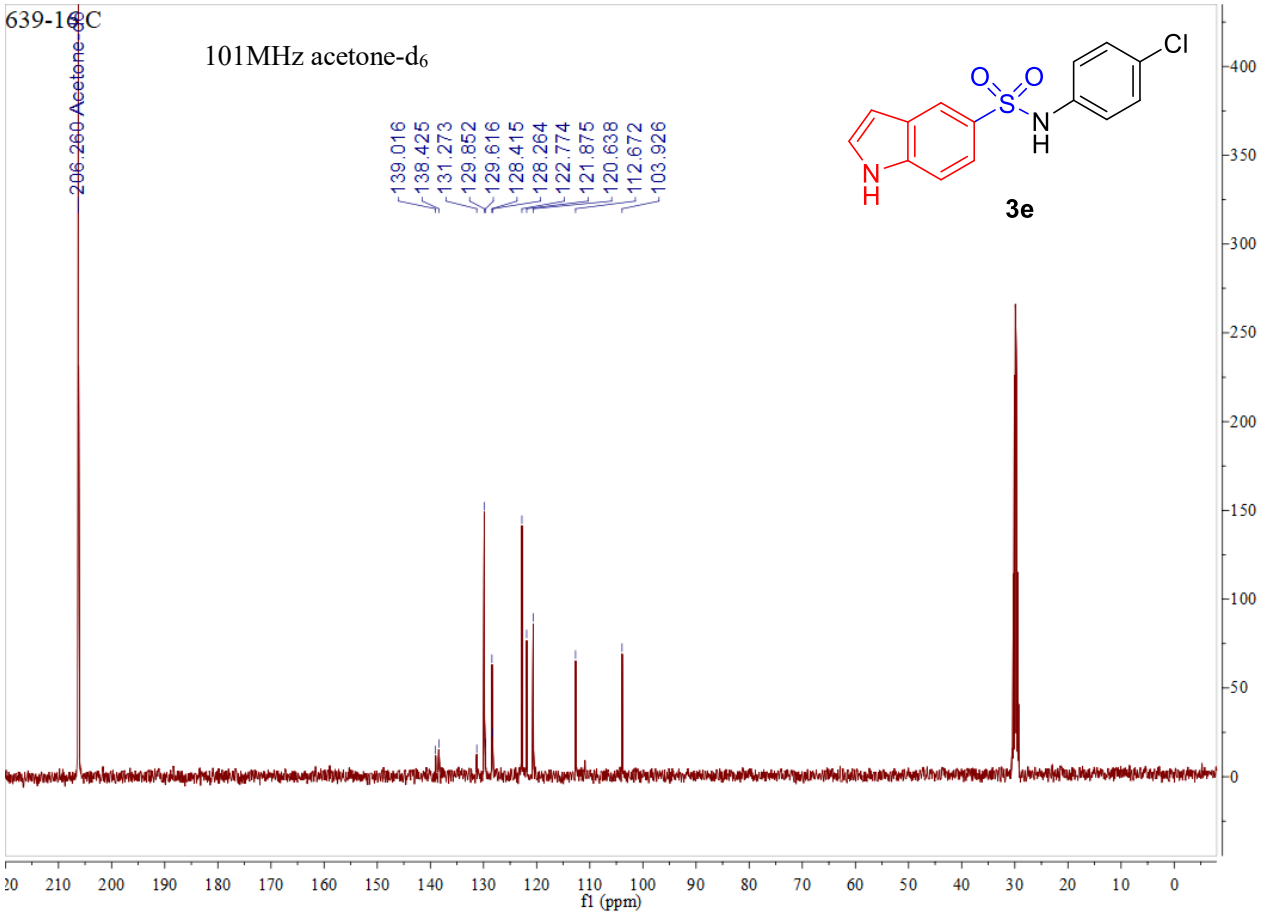

639-1 H
400MHz acetone-d6
9.124
7.656
7.637
7.283
7.264
7.224
7.204
6.928
6.908
2.050 Acetone-d6
Cl
O
S
O
N
H
HO
3c
1.88
2.00
2.00
2.00
2.00
f1 (ppm)

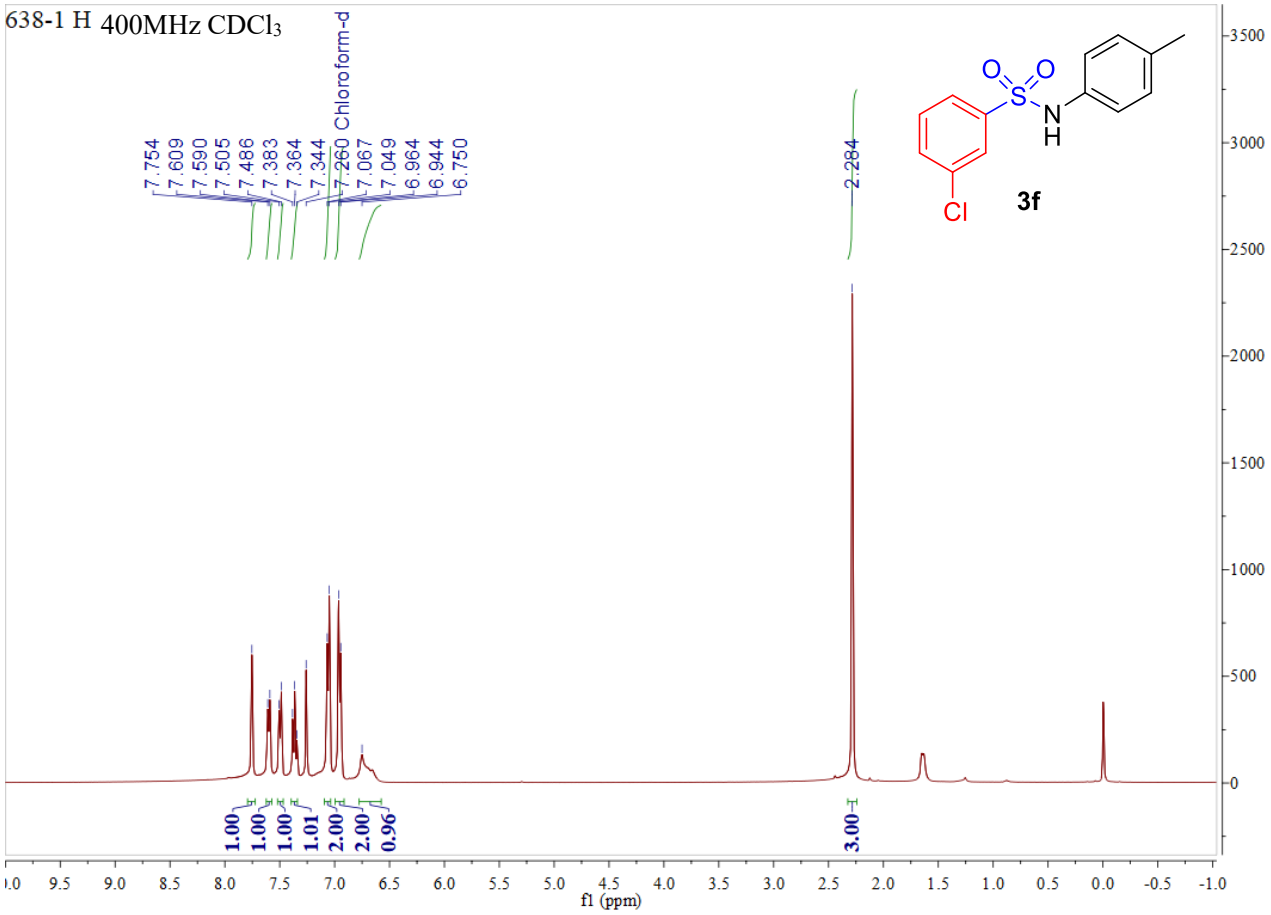

639-1 C
101MHz acetone-d6
206.260 Acetone-d6
162.280
138.089
131.151
130.378
129.941
123.060
116.435
Cl
O
S
O
N
H
HO
3c
f1 (ppm)

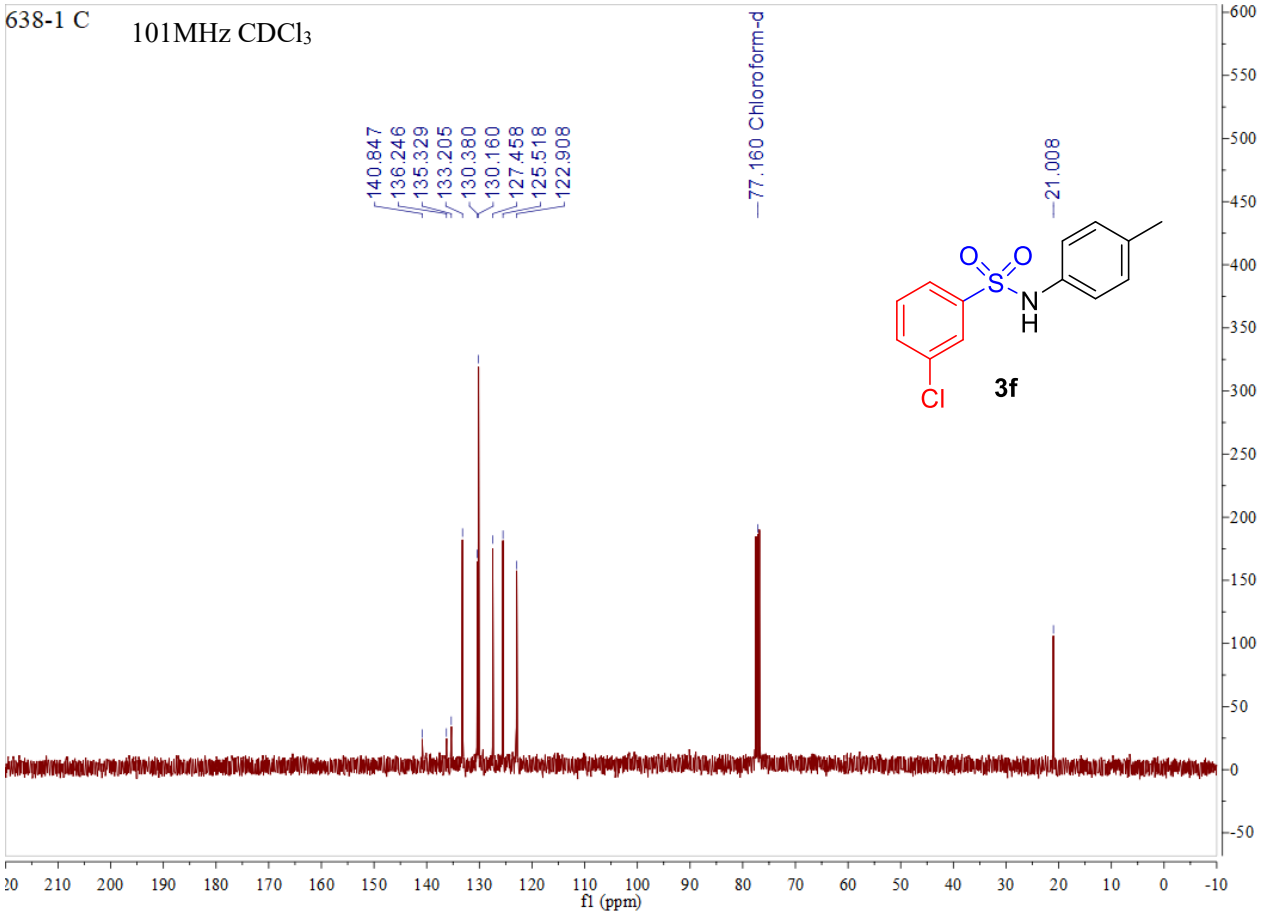

638-11 H
400MHz acetone-d6
9.425
9.129
8.779
8.152
8.130
8.106
7.964
7.945
7.926
7.767
7.748
7.729
7.282
2.050 Acetone-d6
Cl
O
S
O
N
H
N
3d
0.96
0.97
1.00
1.99
1.00
1.00
3.91
f1 (ppm)

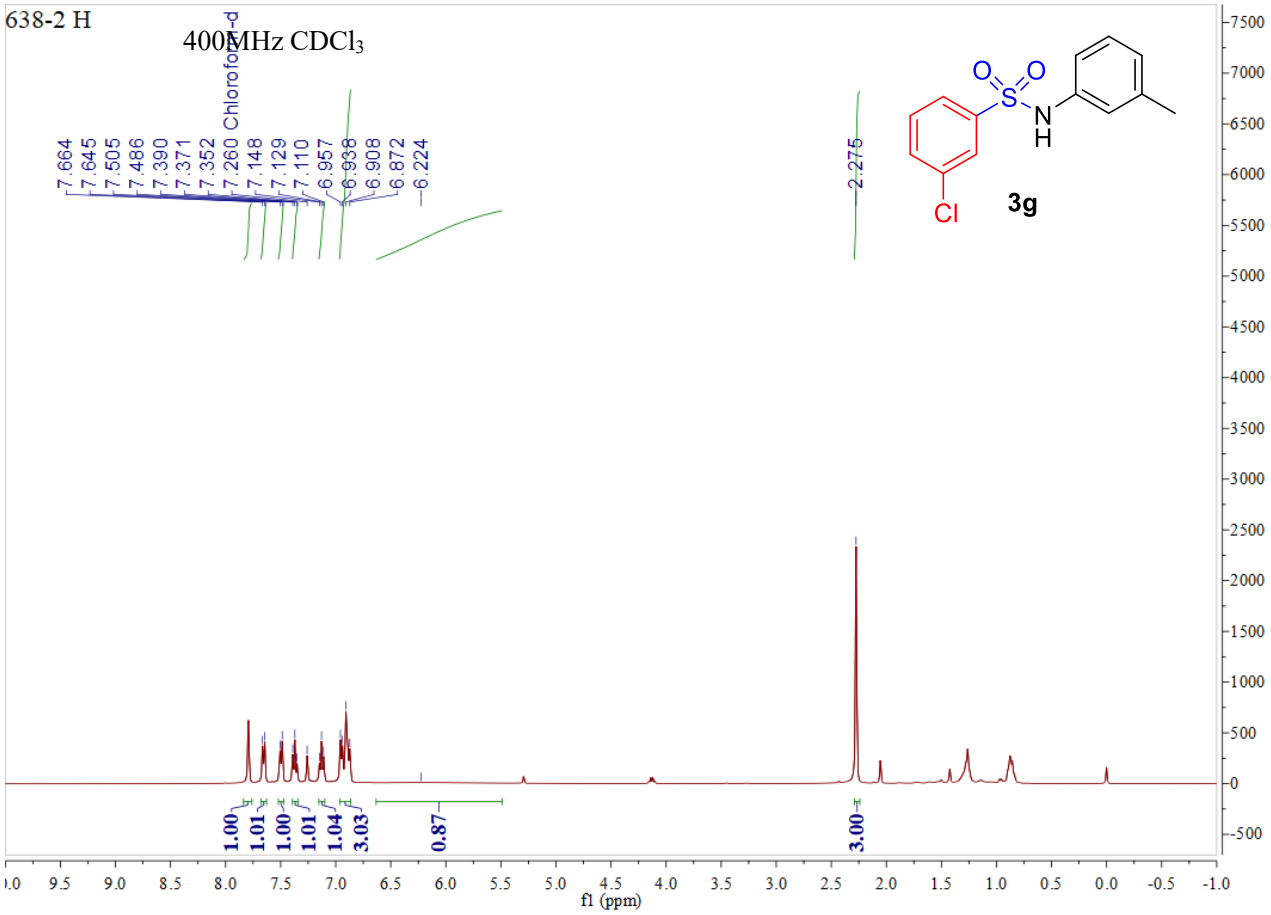

639-11C
101MHz acetone-d6
206.260 Acetone-d6
150.238
147.798
147.501
137.454
137.206
133.516
131.024
130.433
130.346
129.347
127.296
123.911
Cl
O
S
O
N
H
N
3d
f1 (ppm)

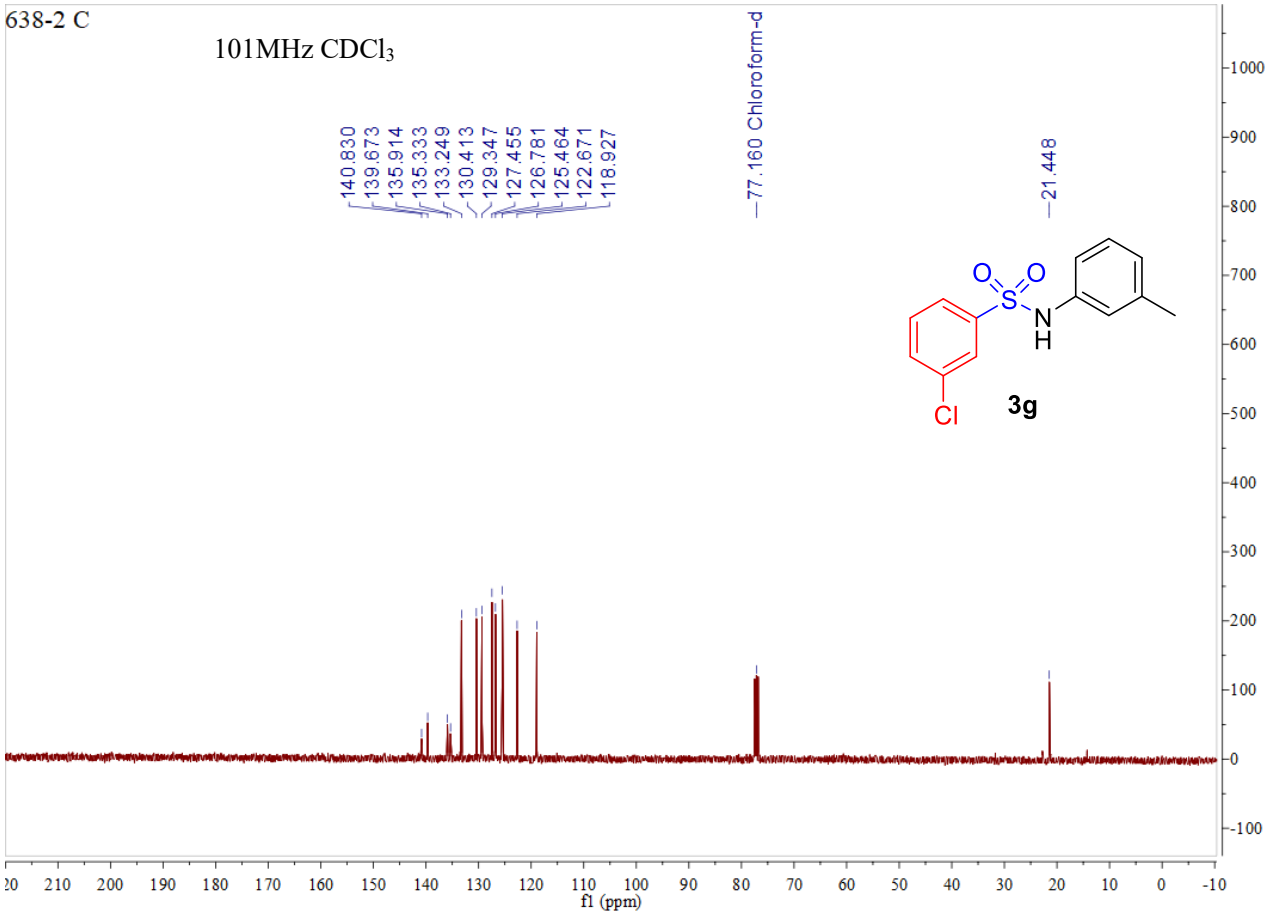

639-16 H
400MHz acetone-d6
10.714
8.952
8.126
7.540
7.495
7.228
6.628
2.050 Acetone-d6
0.84
0.76
0.94
2.00
1.02
4.11
1.00
f1 (ppm)
3e

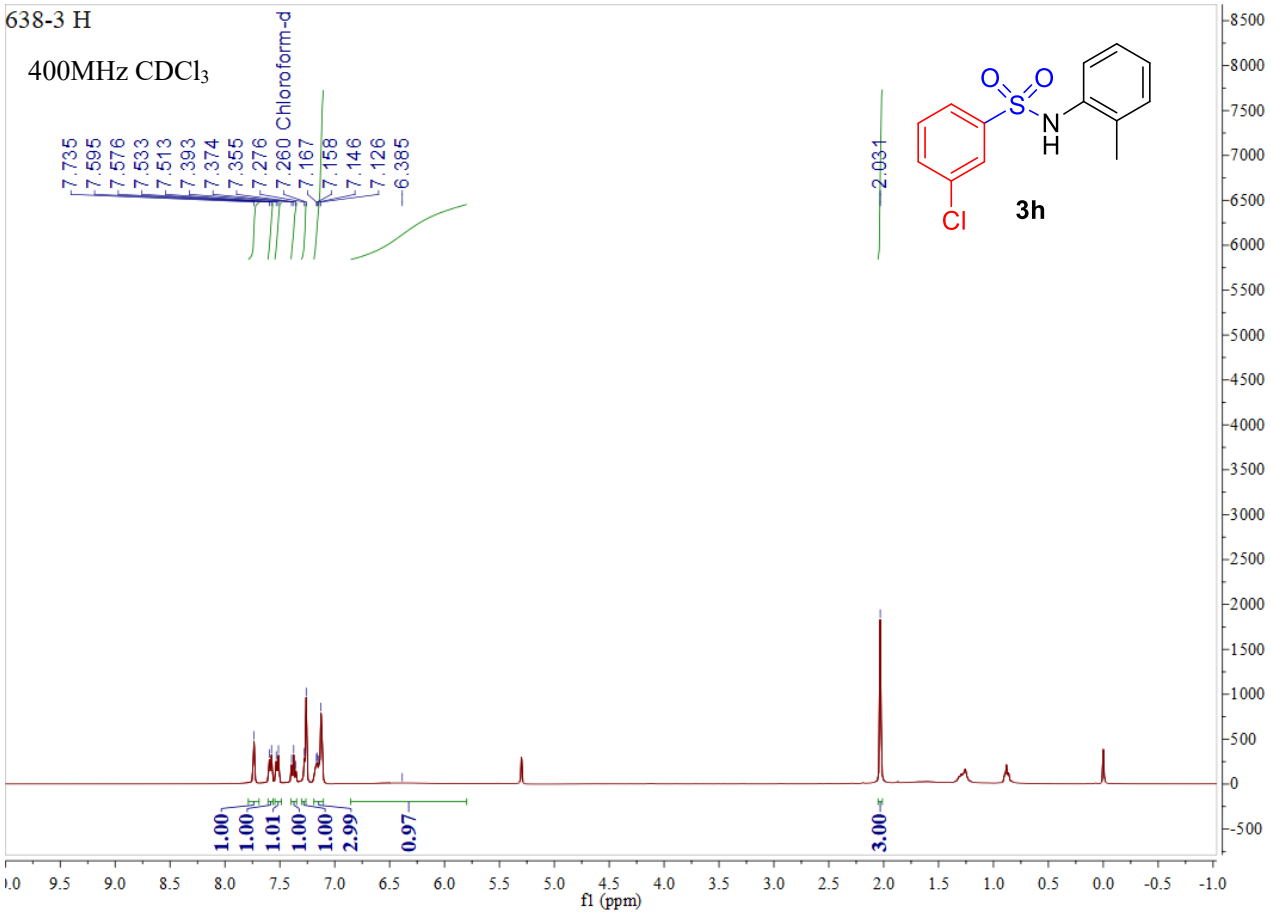

639-16C
101MHz acetone-d6
206.260 Acetone-d6
139.016
138.425
131.273
129.852
129.616
128.415
128.264
122.774
121.875
120.638
112.672
103.926
f1 (ppm)
3e

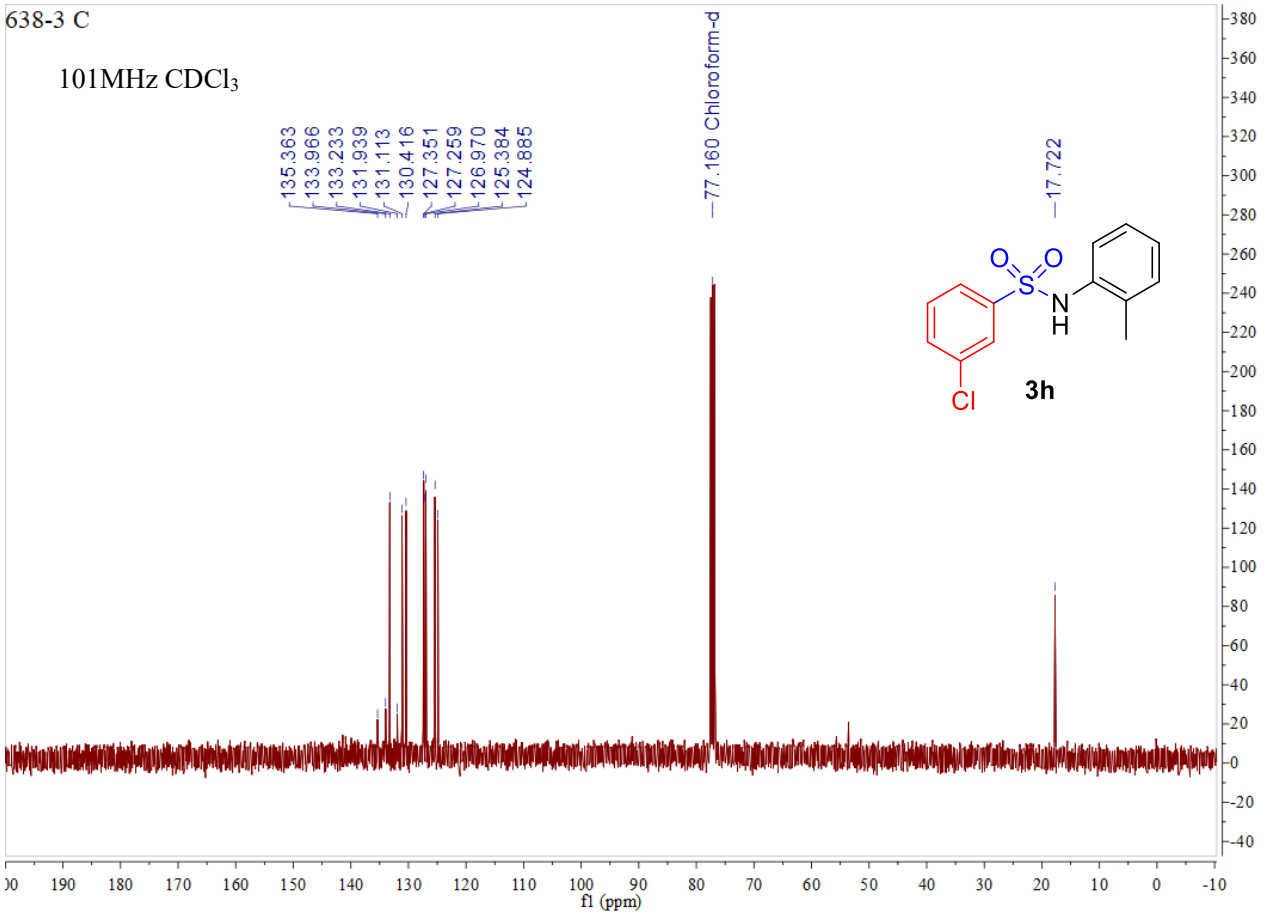

638-1 H 400MHz CDCl3
7.754
7.609
7.590
7.505
7.486
7.383
7.364
7.344
7.260 Chloroform-d
7.067
7.049
6.964
6.944
6.750
2.284
1.00
1.00
1.00
1.01
2.00
2.00
0.96
3.00
f1 (ppm)
3f

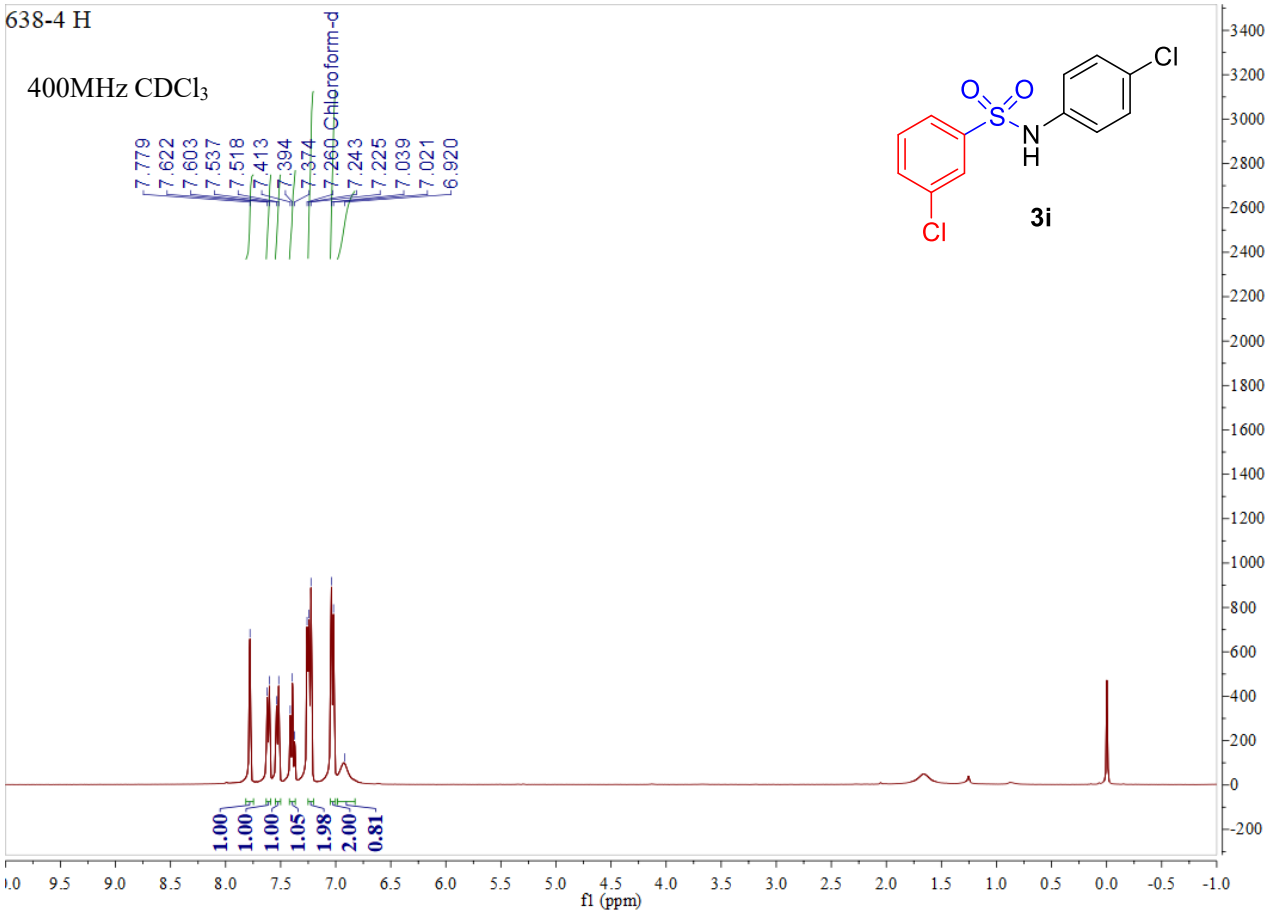

638-1 C 101MHz CDCl3
140.847
136.246
135.329
133.205
130.380
130.160
127.458
125.518
122.908
77.160 Chloroform-d
21.008
f1 (ppm)
3f

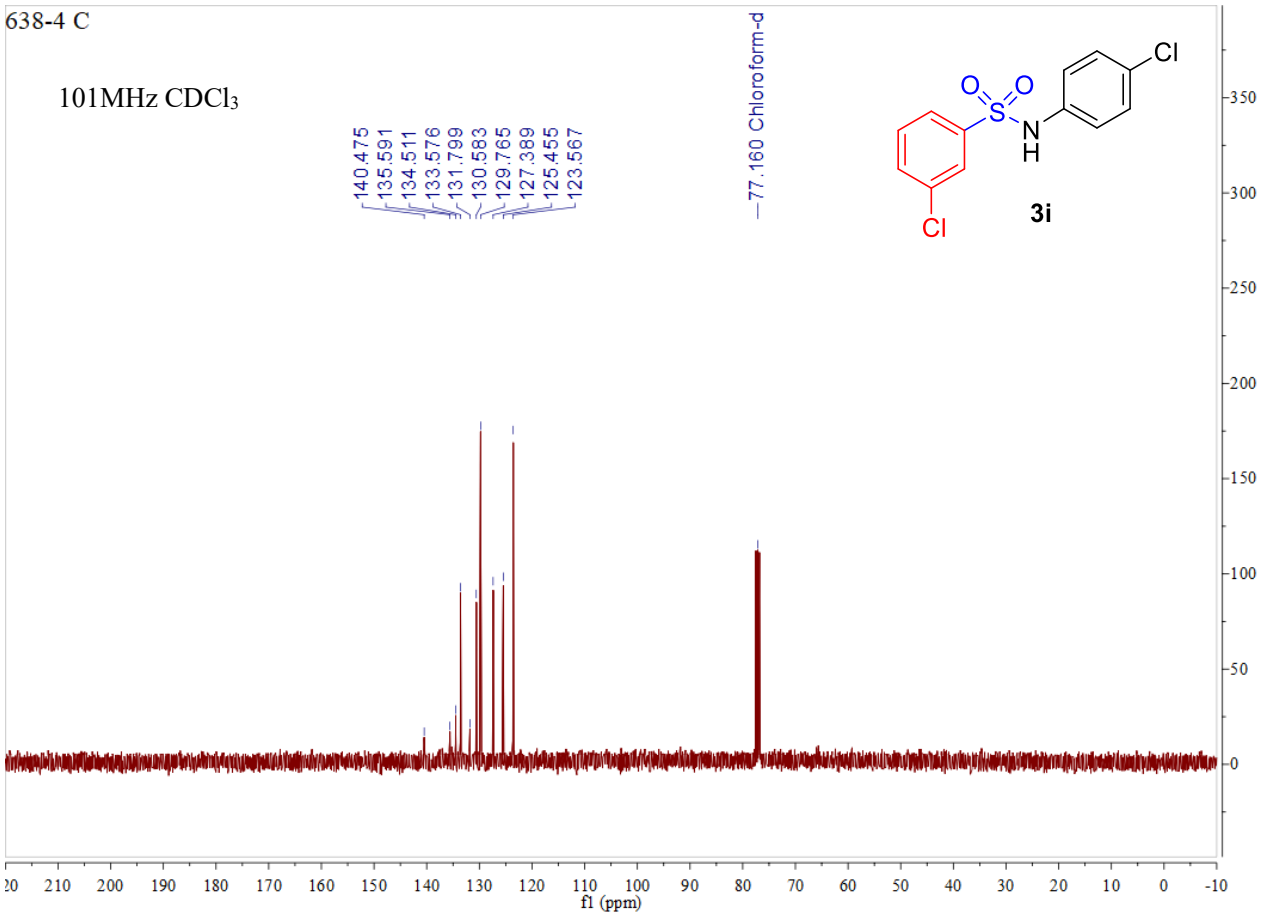

638-2 H
400MHz CDCl3
7.664
7.645
7.505
7.486
7.390
7.371
7.352
7.260 Chloroform-d
7.148
7.129
7.110
6.957
6.938
6.908
6.872
6.224
2.275
1.00
1.01
1.00
1.01
1.04
3.03
0.87
3.00
f1 (ppm)
3g

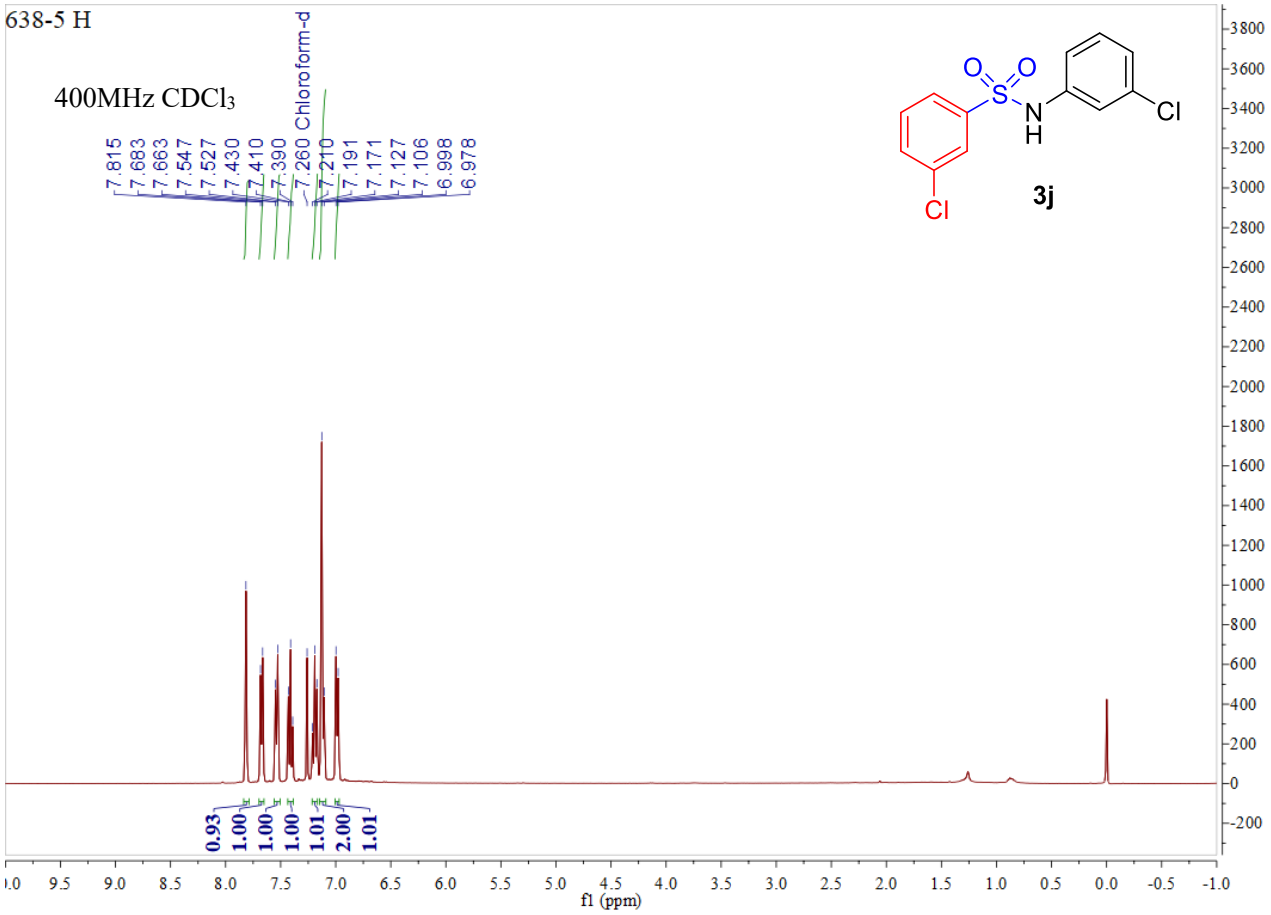

638-2 C
101MHz CDCl3
140.830
139.673
135.914
135.333
133.249
130.413
129.347
127.455
126.781
125.464
122.671
118.927
77.160 Chloroform-d
21.448
f1 (ppm)
3g

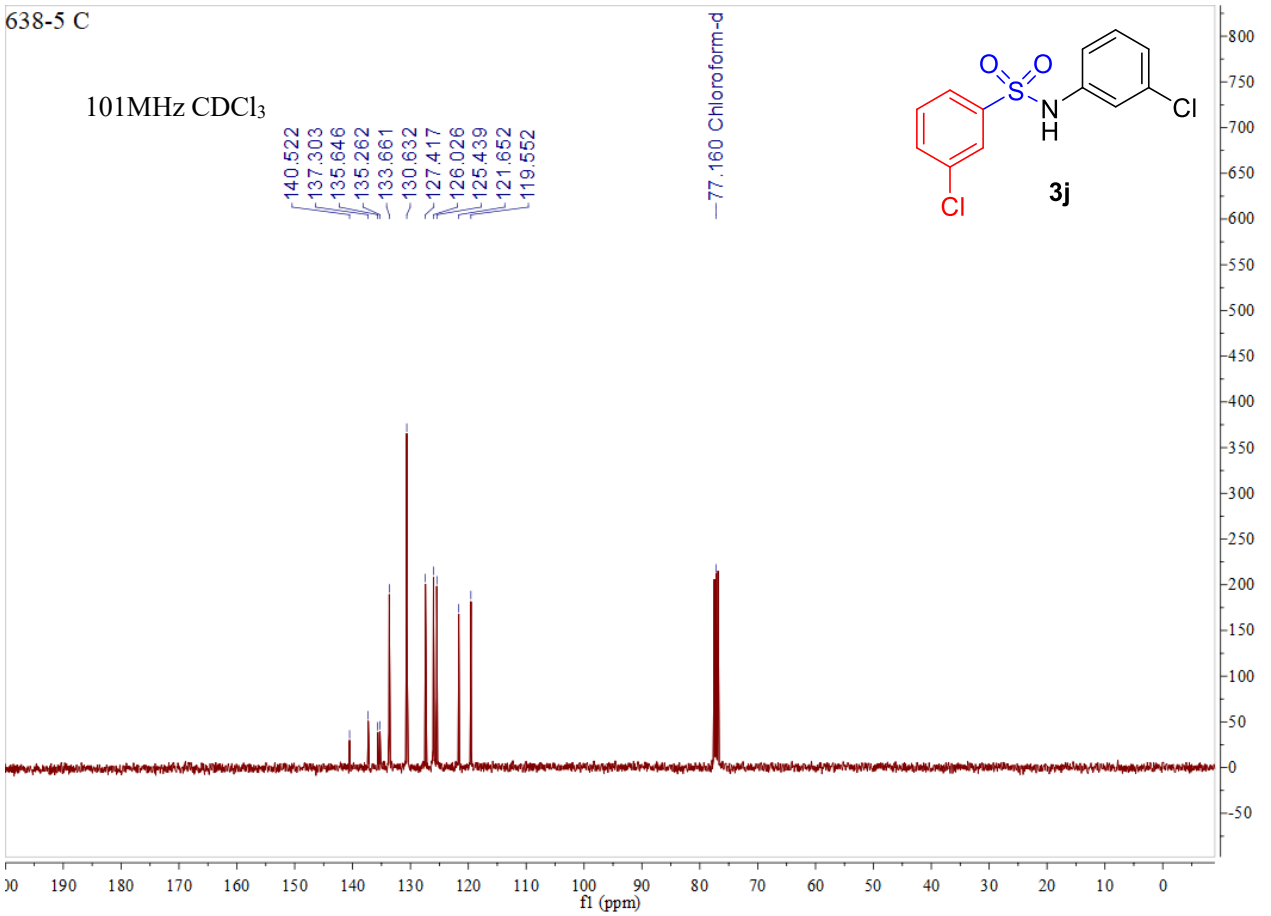

638-3 H
400MHz CDCl3
7.735
7.595
7.576
7.533
7.513
7.393
7.374
7.355
7.276
Chloroform-d
7.260
7.167
7.158
7.146
7.126
6.385
2.031
3h
1.00
1.00
1.01
1.00
1.00
2.99
0.97
3.00
f1 (ppm)

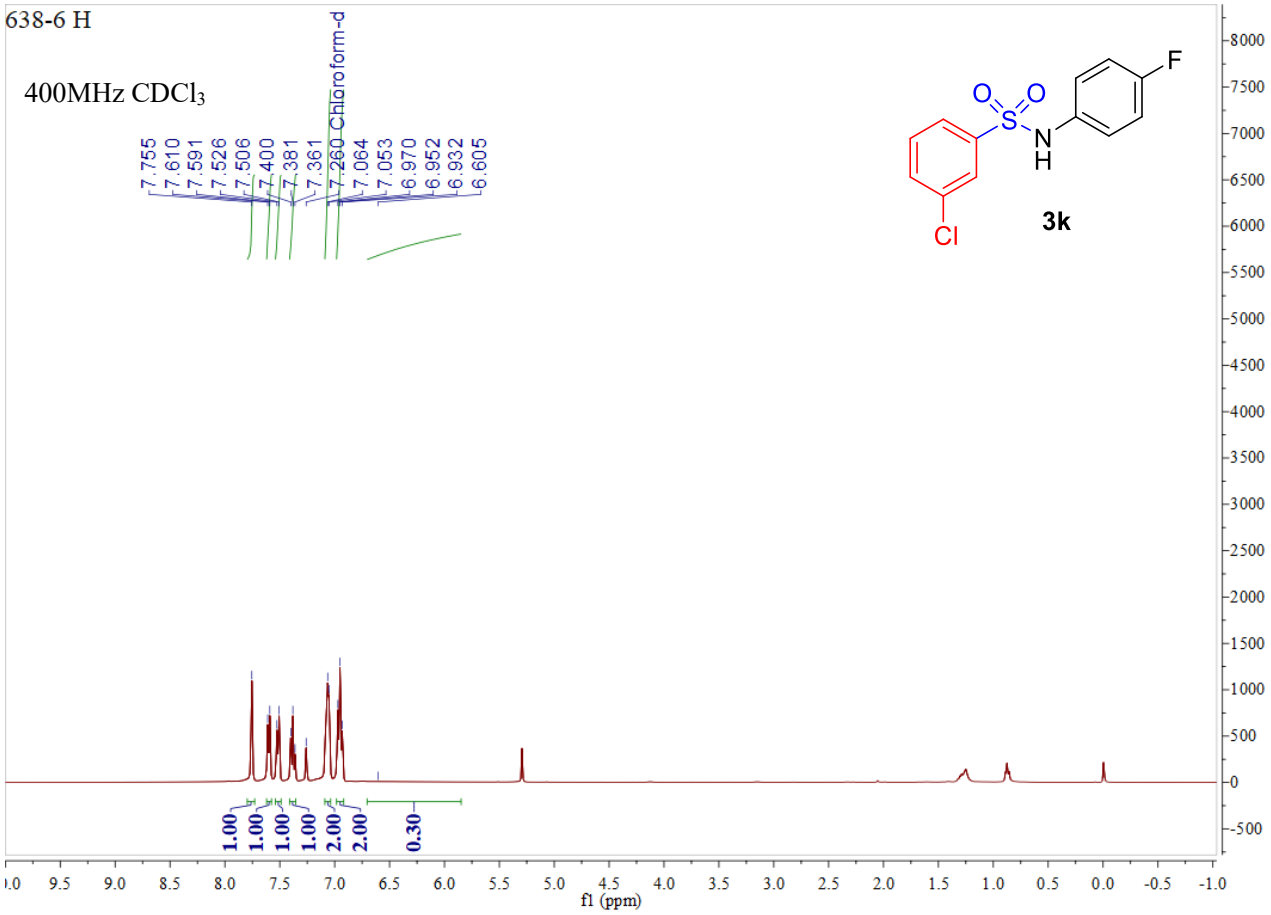

638-3 C
101MHz CDCl3
135.363
133.966
133.233
131.939
131.113
130.416
127.351
127.259
126.970
125.384
124.885
77.160
Chloroform-d
17.722
3h
f1 (ppm)

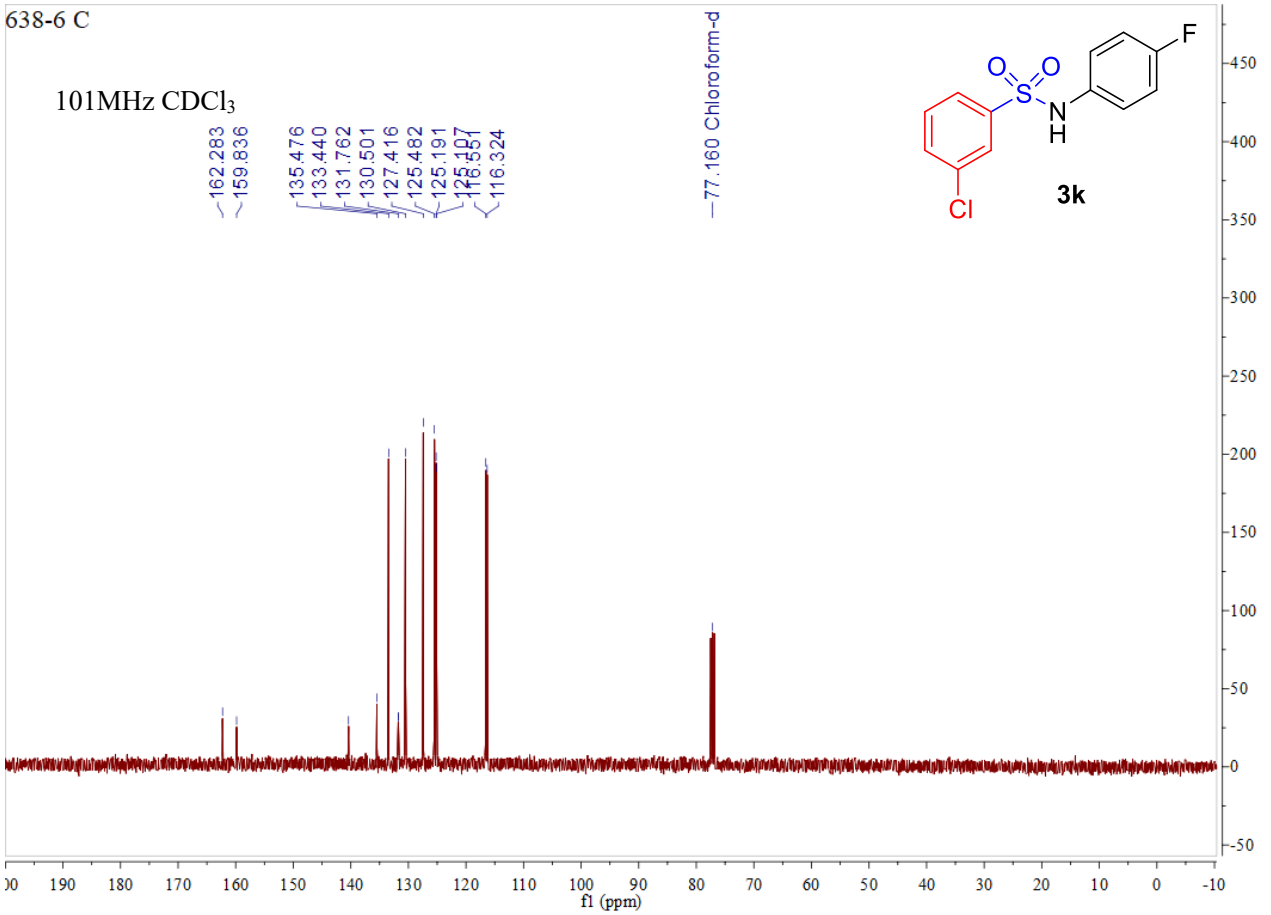

638-4 H
400MHz CDCl3
7.779
7.622
7.603
7.537
7.518
7.413
7.394
7.374
7.260 Chloroform-d
7.243
7.225
7.039
7.021
6.920
Cl
O
S
O
N
H
Cl
3i
1.00
1.00
1.00
1.05
1.98
2.00
0.81
f1 (ppm)

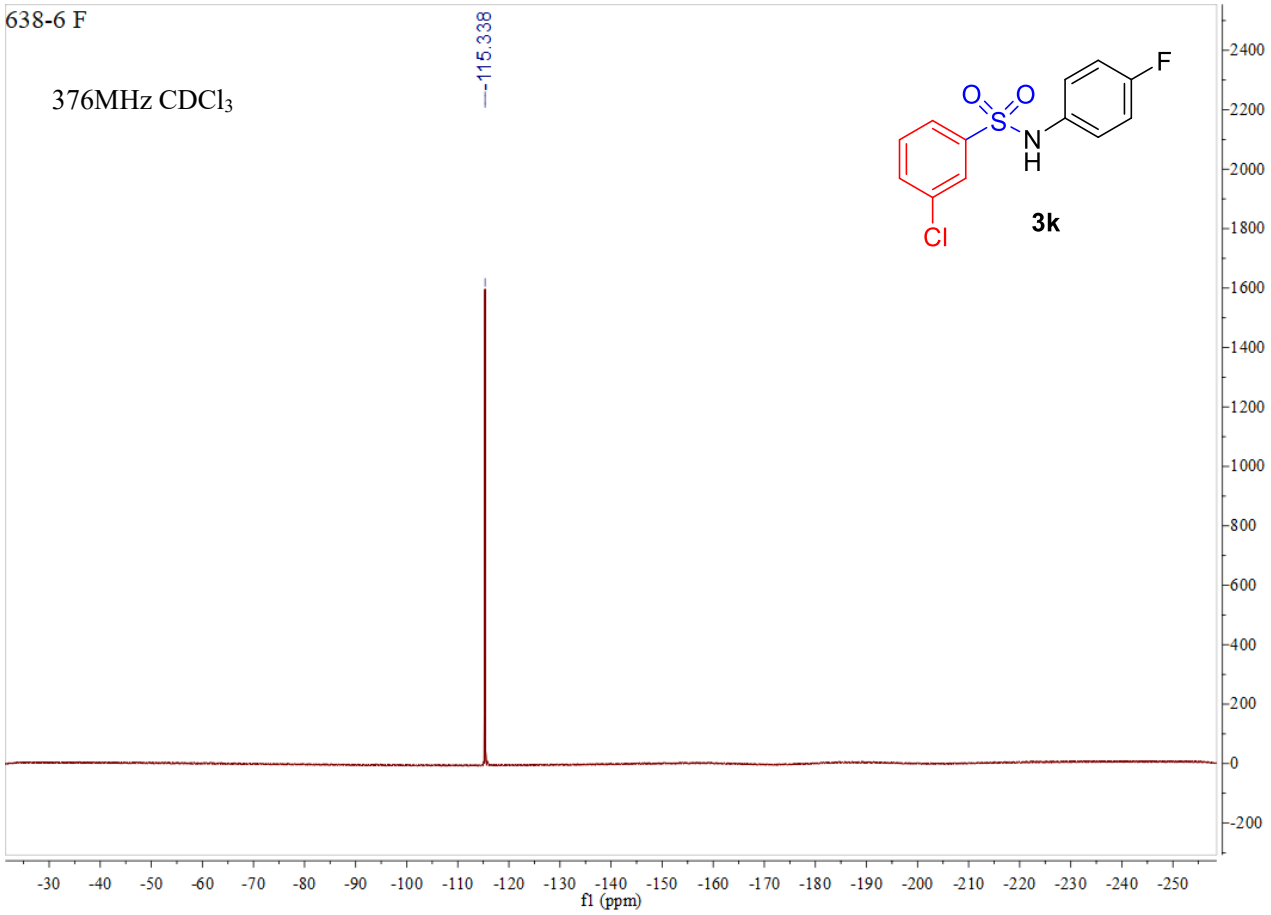

638-4 C
101MHz CDCl3
140.475
135.591
134.511
133.576
131.799
130.583
129.765
127.389
125.455
123.567
77.160 Chloroform-d
Cl
O
S
O
N
H
Cl
3i
f1 (ppm)

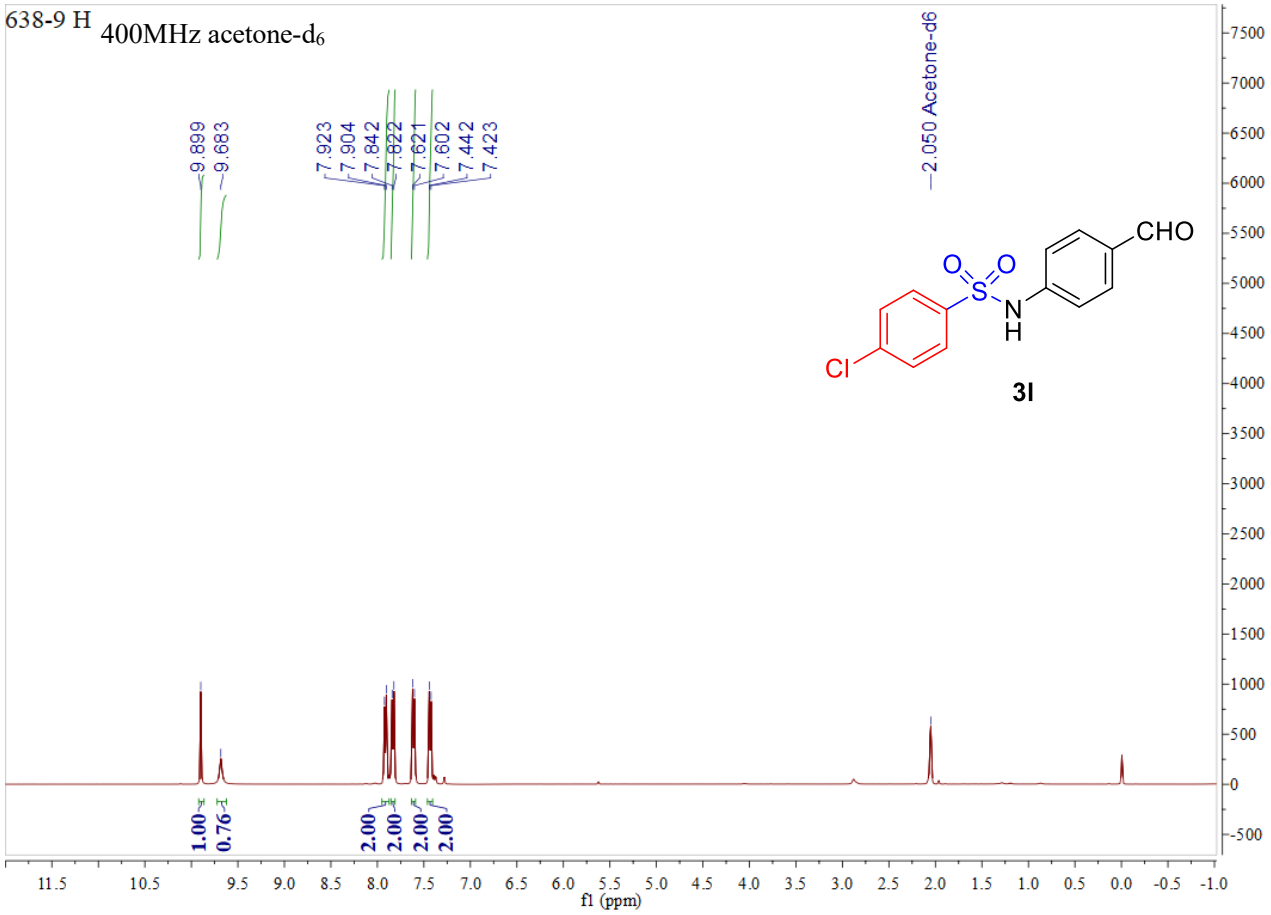

638-5 H
400MHz CDCl3
7.815
7.683
7.663
7.547
7.527
7.430
7.410
7.390
7.260 Chloroform-d
7.210
7.191
7.171
7.127
7.106
6.998
6.978
0.93
1.00
1.00
1.00
1.01
2.00
1.01
f1 (ppm)
3j

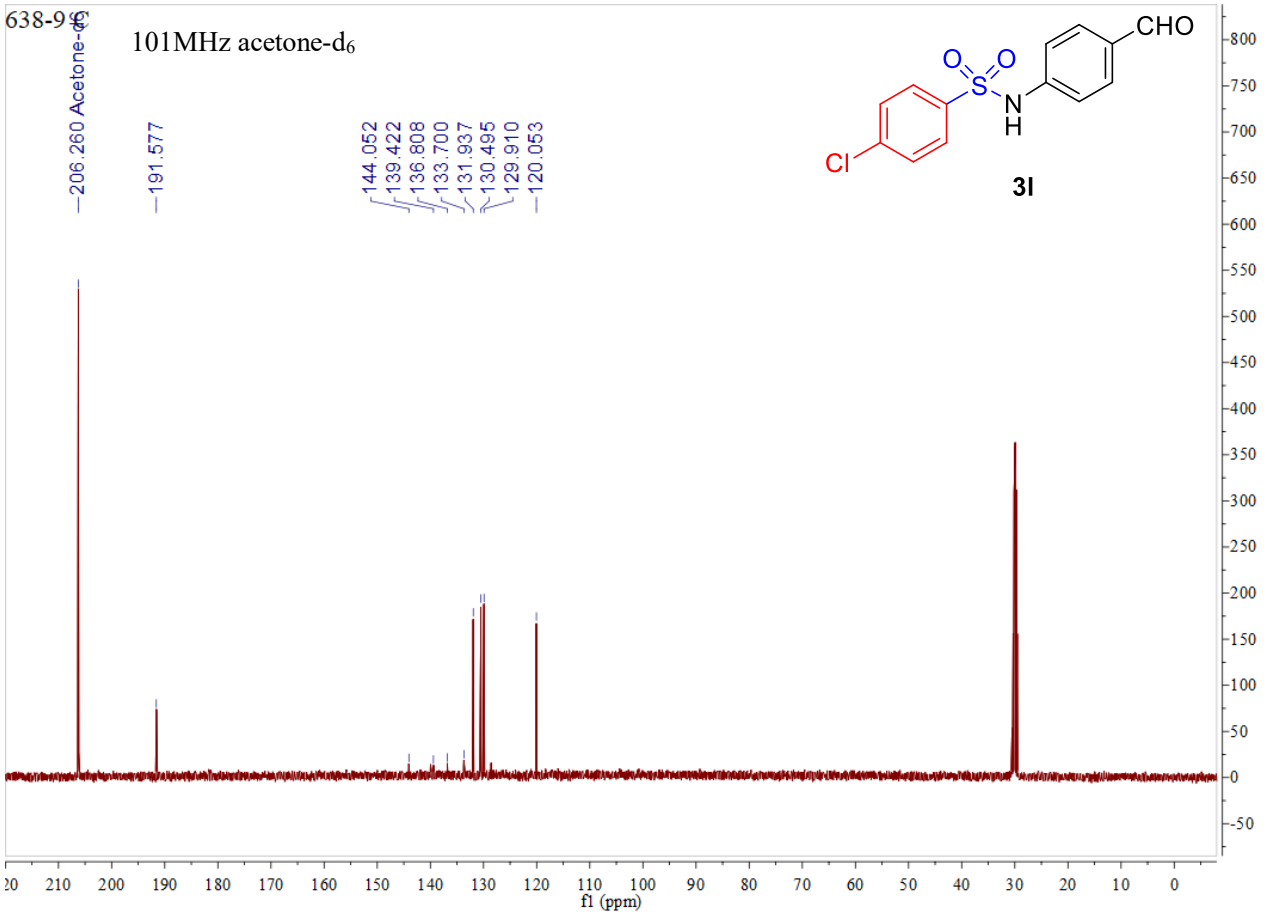

638-5 C
101MHz CDCl3
140.522
137.303
135.646
135.262
133.661
130.632
127.417
126.026
125.439
121.652
119.552
77.160 Chloroform-d
f1 (ppm)
3j

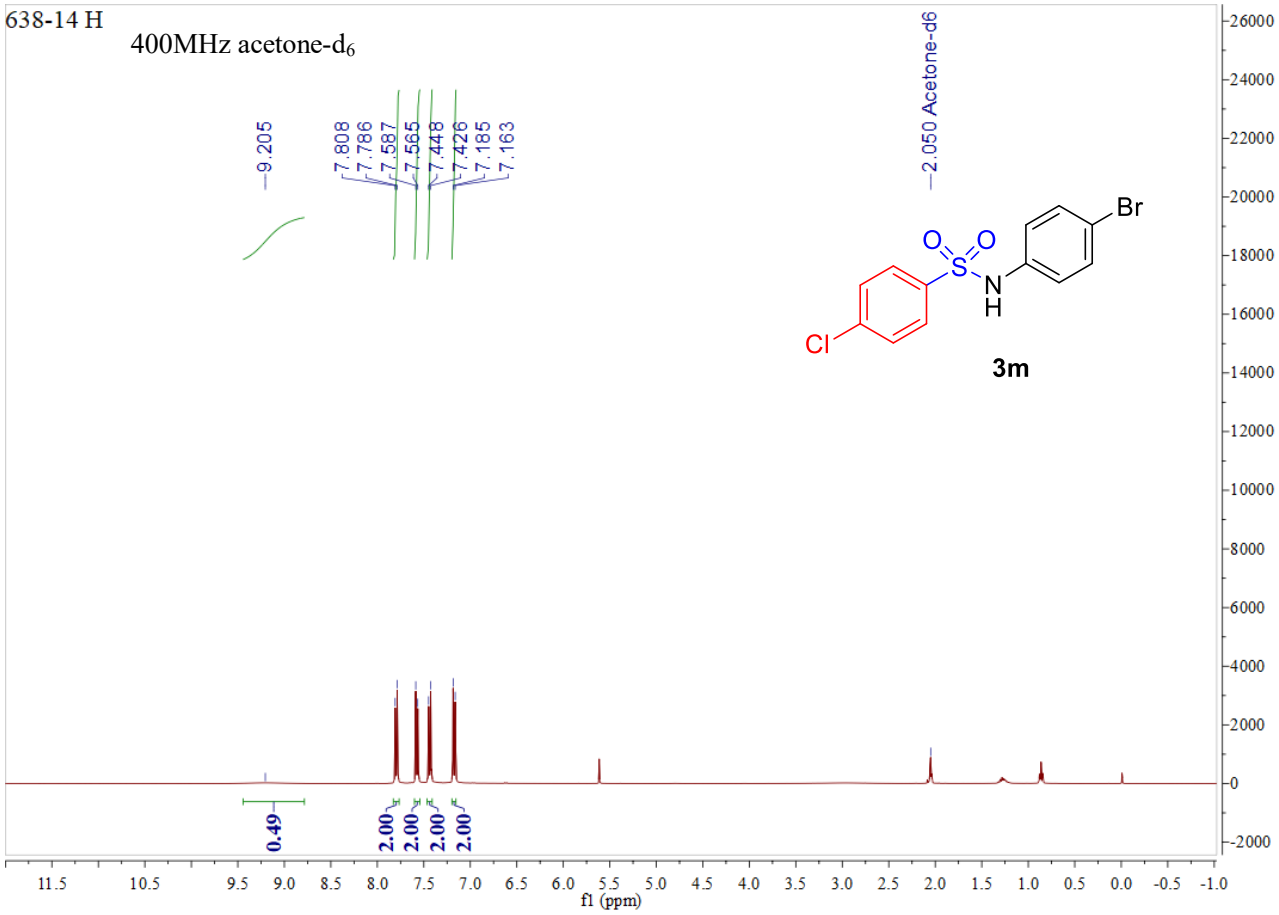

638-6 H
400MHz CDCl3
7.755
7.610
7.591
7.526
7.506
7.400
7.381
7.361
7.260 Chloroform-d
7.064
7.053
6.970
6.952
6.932
6.605
F
O
S
O
N
H
Cl
3k
1.00
1.00
1.00
1.00
2.00
2.00
0.30
f1 (ppm)

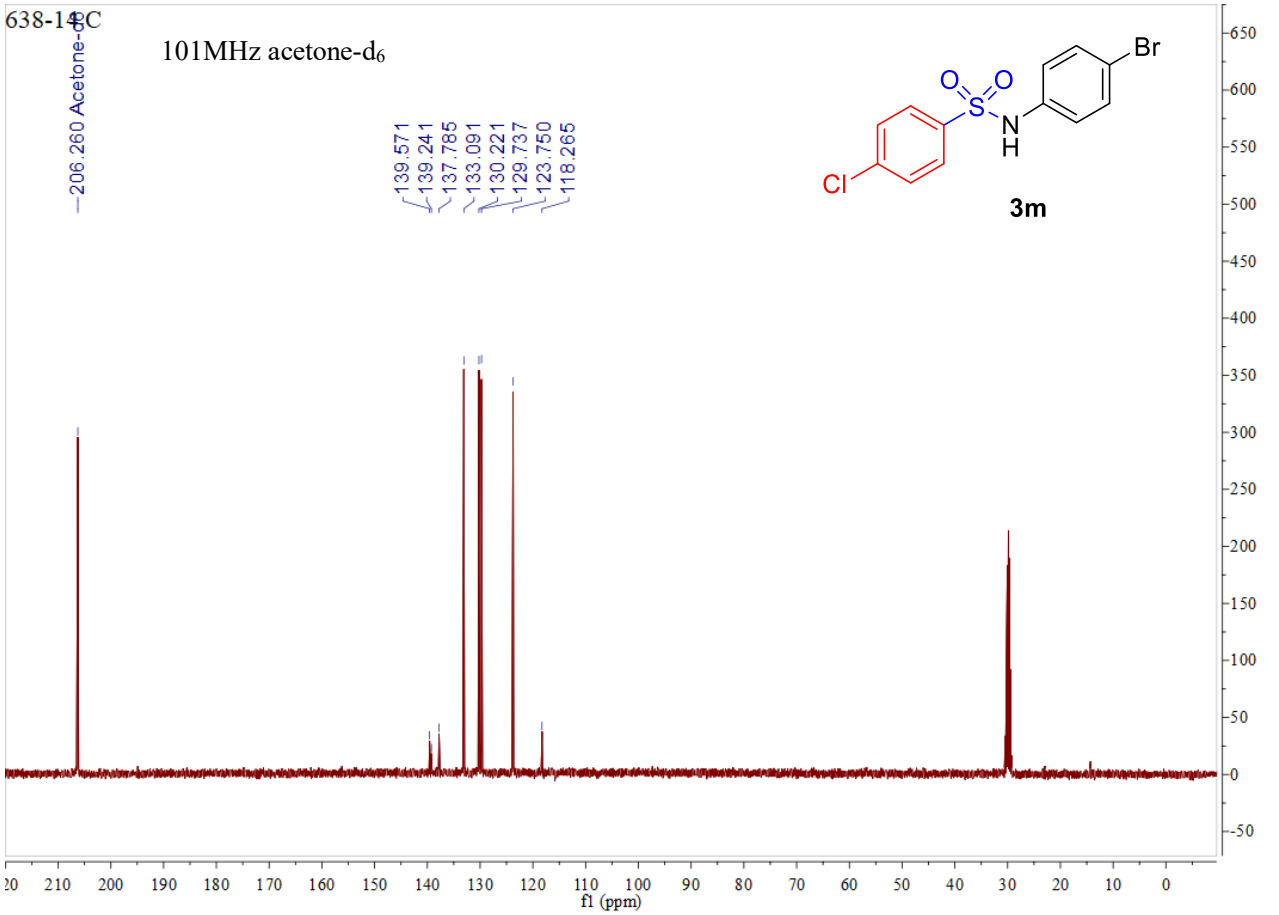

638-6 C
101MHz CDCl3
162.283
159.836
135.476
133.440
131.762
130.501
127.416
125.482
125.191
116.324
77.160 Chloroform-d
F
O
S
O
N
H
Cl
3k
f1 (ppm)

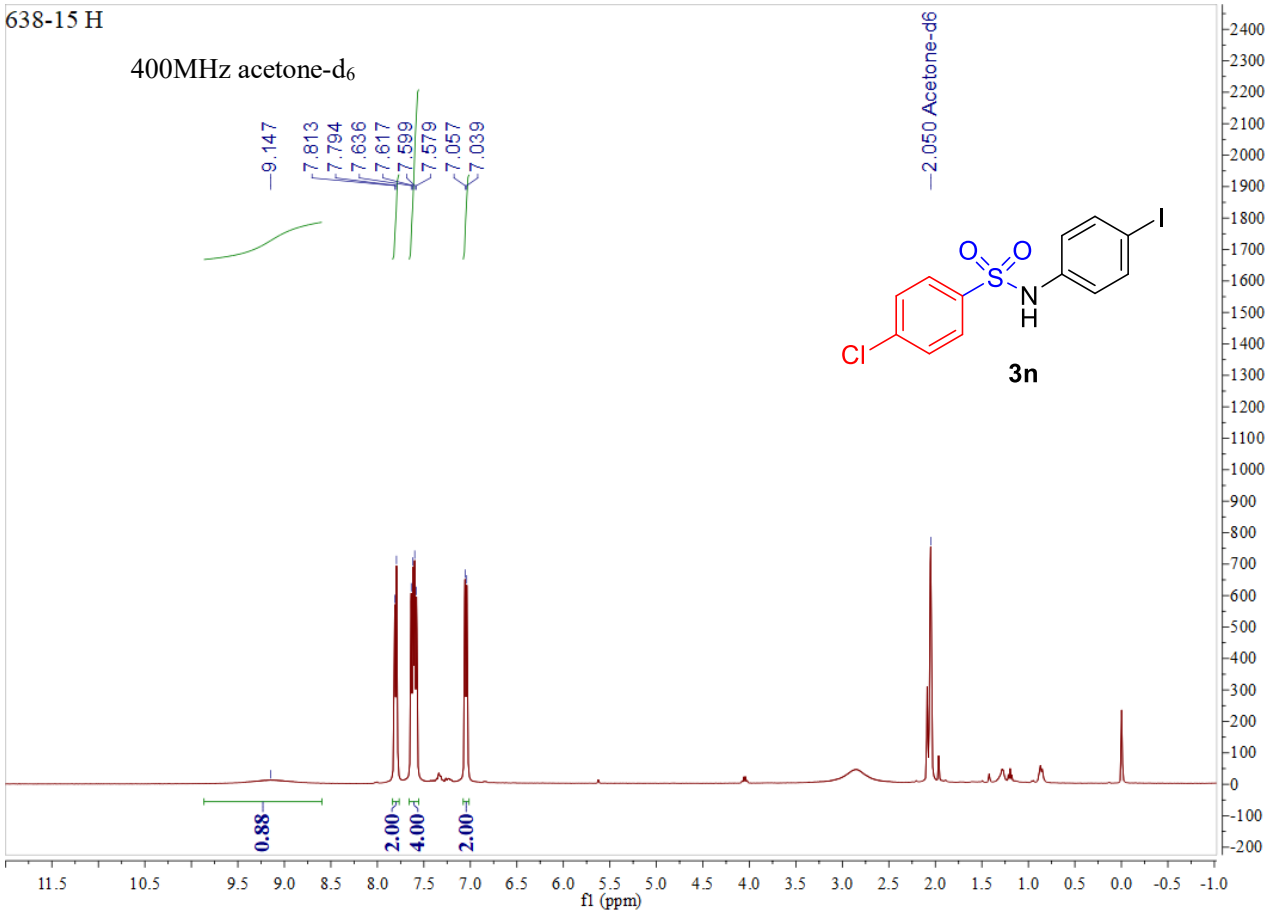

638-6 F
376MHz CDCl3
-115.338
F
O
O
S
N
H
Cl
3k
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

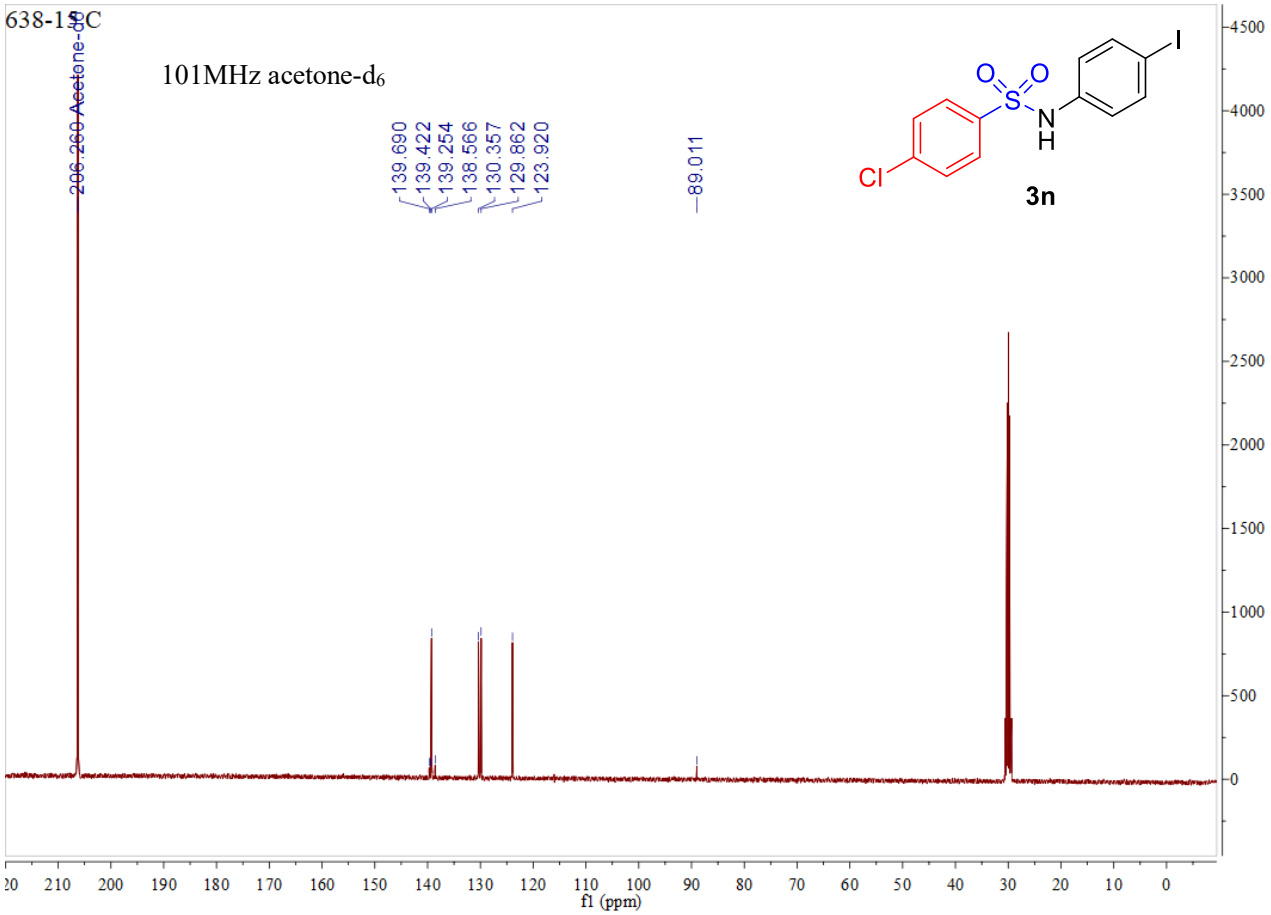

638-9 H
400MHz acetone-d6
9.899
9.683
7.923
7.904
7.842
7.822
7.621
7.602
7.442
7.423
2.050 Acetone-d6
CHO
O
S
O
N
H
Cl
3l
1.00
0.76
2.00
2.00
2.00
2.00
f1 (ppm)

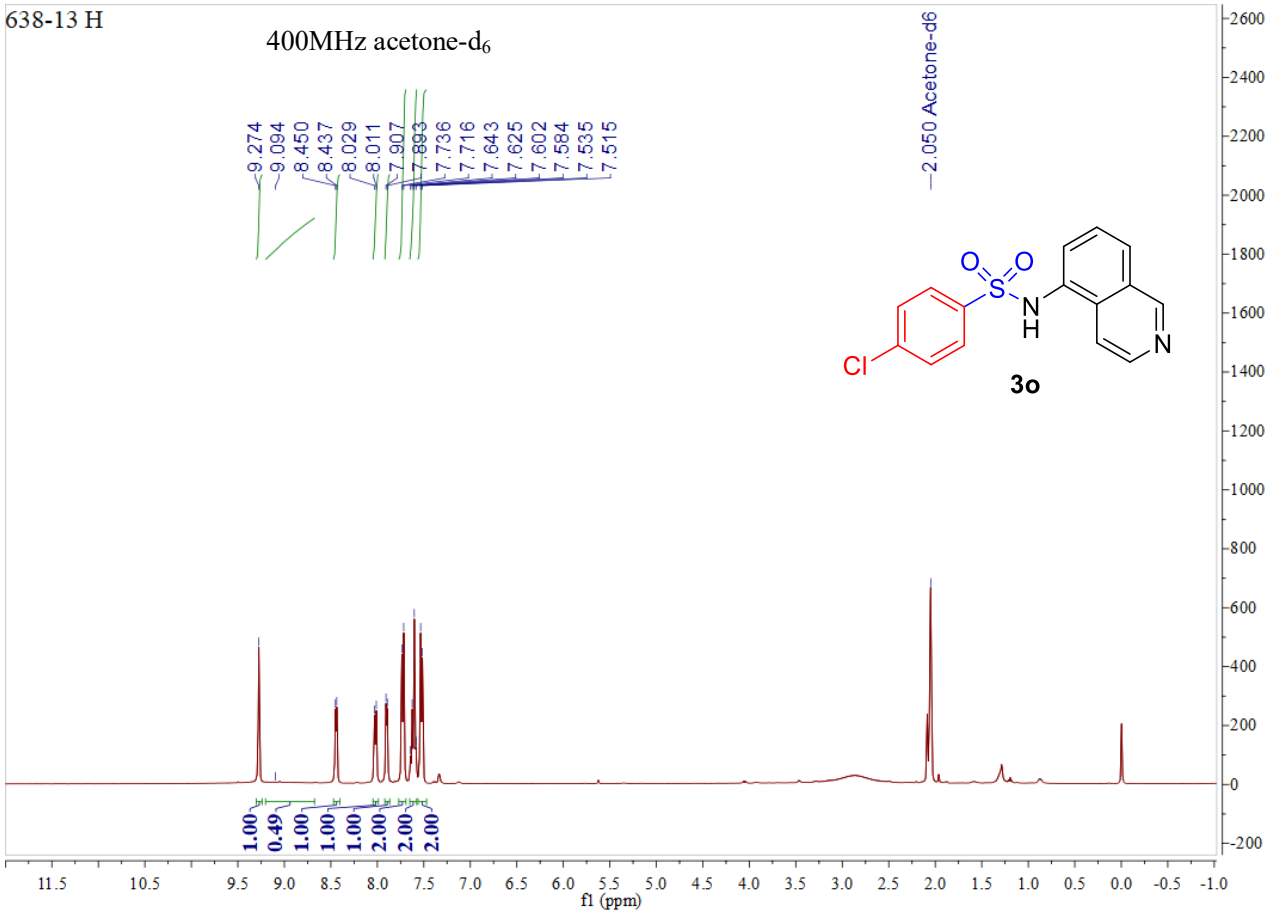

638-9 C
101MHz acetone-d6
206.260 Acetone-d6
191.577
144.052
139.422
136.808
133.700
131.937
130.495
129.910
120.053
CHO
O
S
O
N
H
Cl
3l
f1 (ppm)

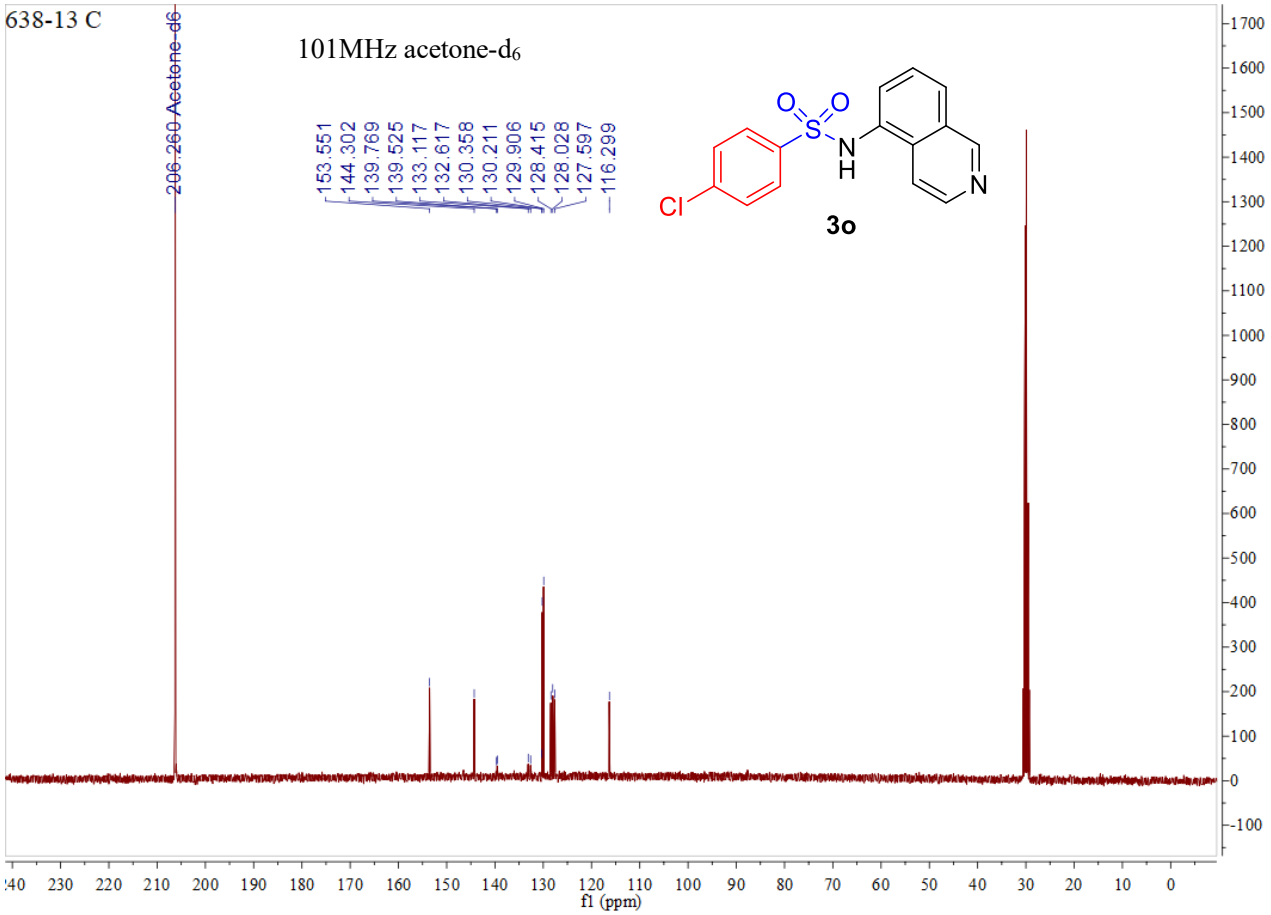

638-14 H
400MHz acetone-d6
9.205
7.808
7.786
7.587
7.565
7.448
7.426
7.185
7.163
2.050 Acetone-d6
Br
O
S
O
N
H
Cl
3m
0.49
2.00
2.00
2.00
2.00
f1 (ppm)

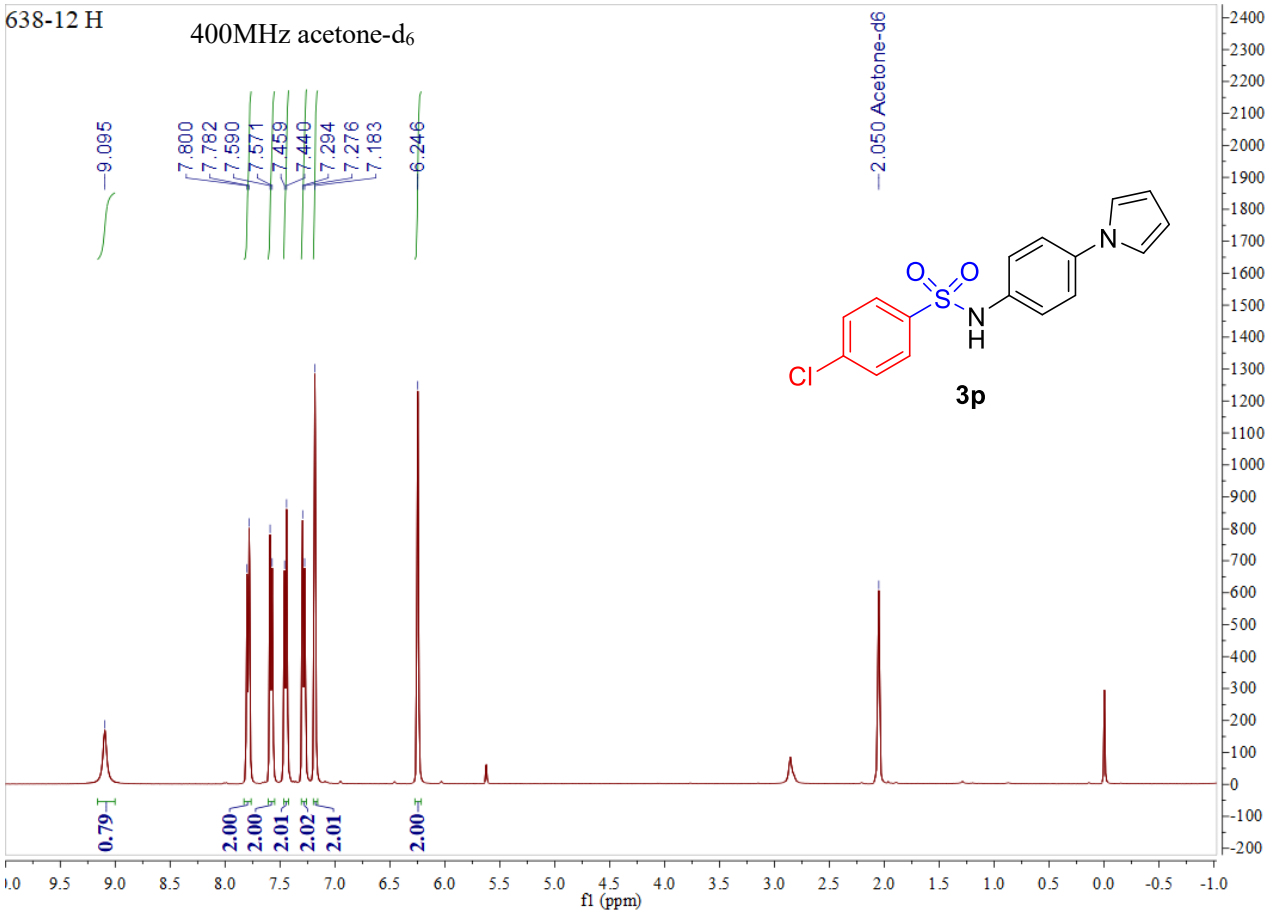

638-14 C
101MHz acetone-d6
206.260 Acetone-d6
139.571
139.241
137.785
133.091
130.221
129.737
123.750
118.265
Br
O
S
O
N
H
Cl
3m
f1 (ppm)

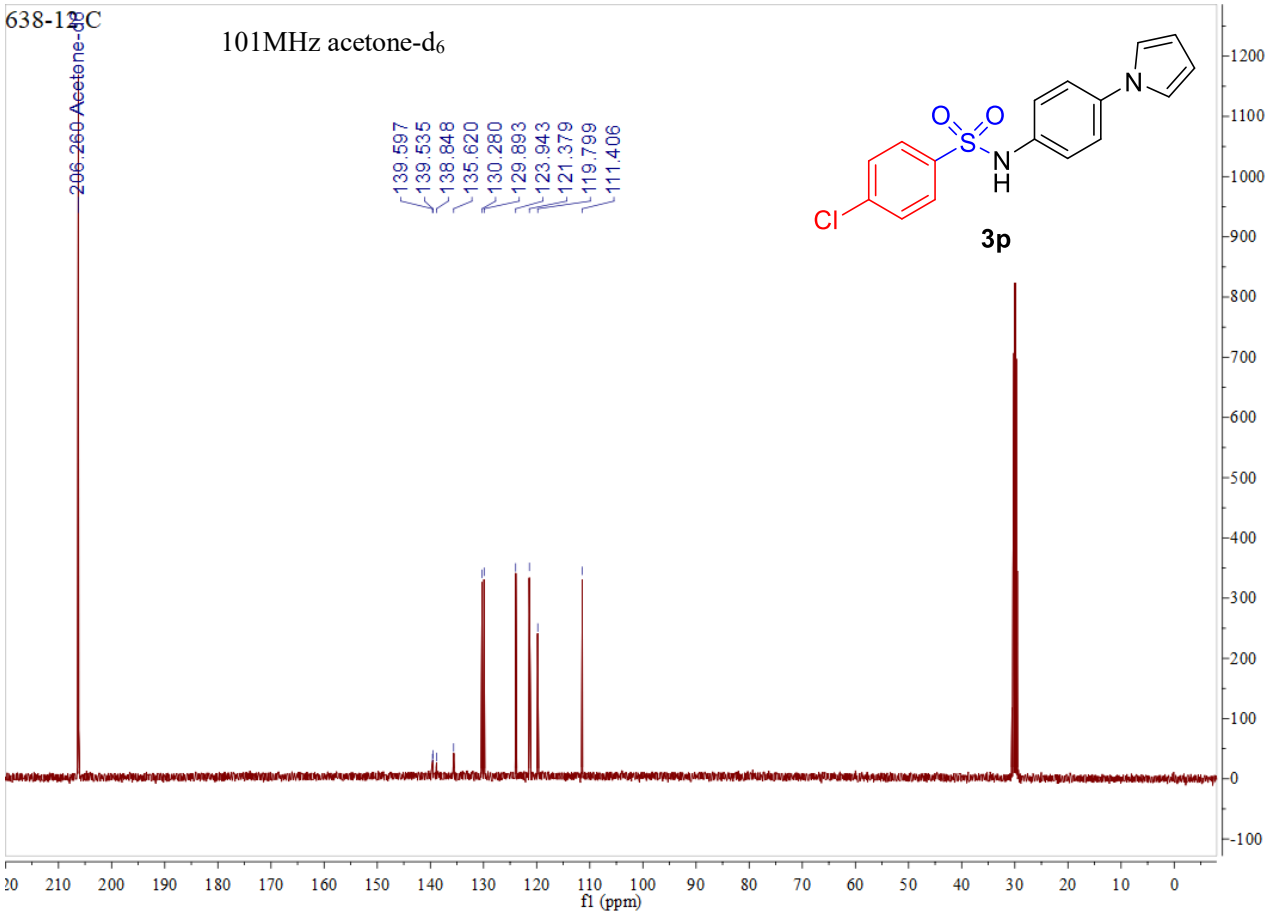

638-15 H
400MHz acetone-d6
9.147
7.813
7.794
7.636
7.617
7.599
7.579
7.057
7.039
2.050 Acetone-d6
3n
0.88
2.00
4.00
2.00
f1 (ppm)

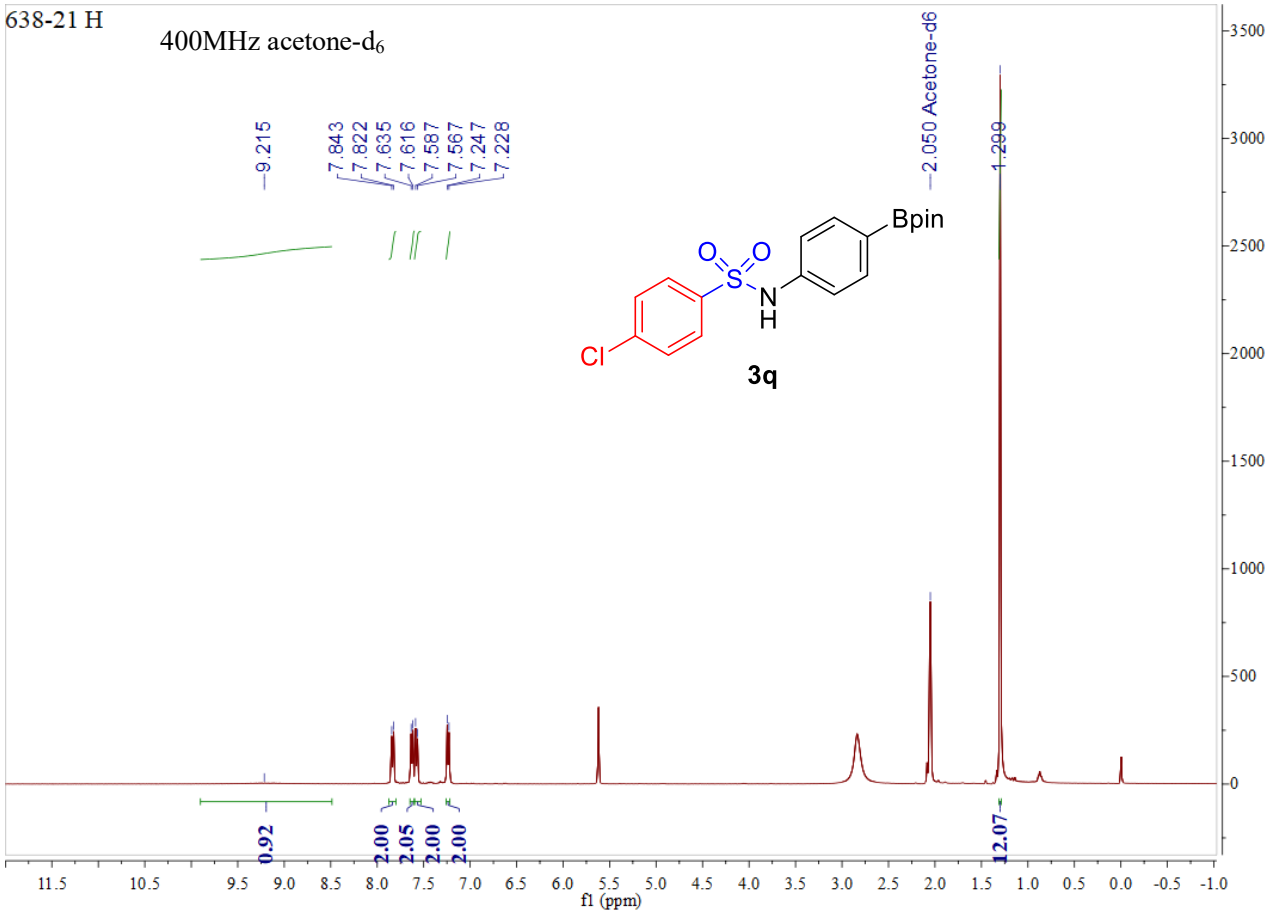

638-15 C
101MHz acetone-d6
206.260 Acetone-d6
139.690
139.422
139.254
138.566
130.357
129.862
123.920
89.011
3n
f1 (ppm)

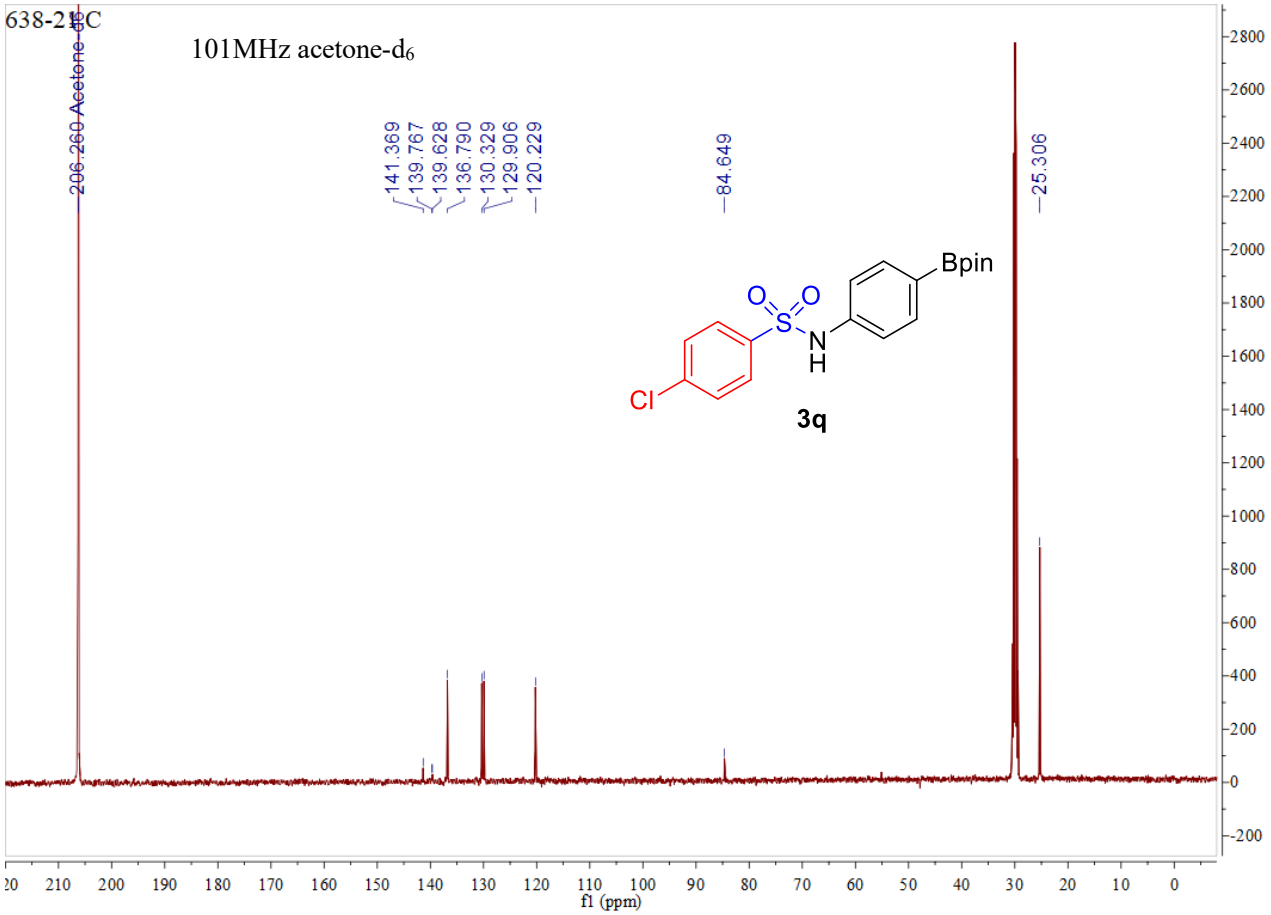

638-13 H
400MHz acetone-d6
9.274
9.094
8.450
8.437
8.029
8.011
7.907
7.893
7.736
7.716
7.643
7.625
7.602
7.584
7.535
7.515
2.050 Acetone-d6
3o
1.00
0.49
1.00
1.00
1.00
2.00
2.00
2.00
f1 (ppm)

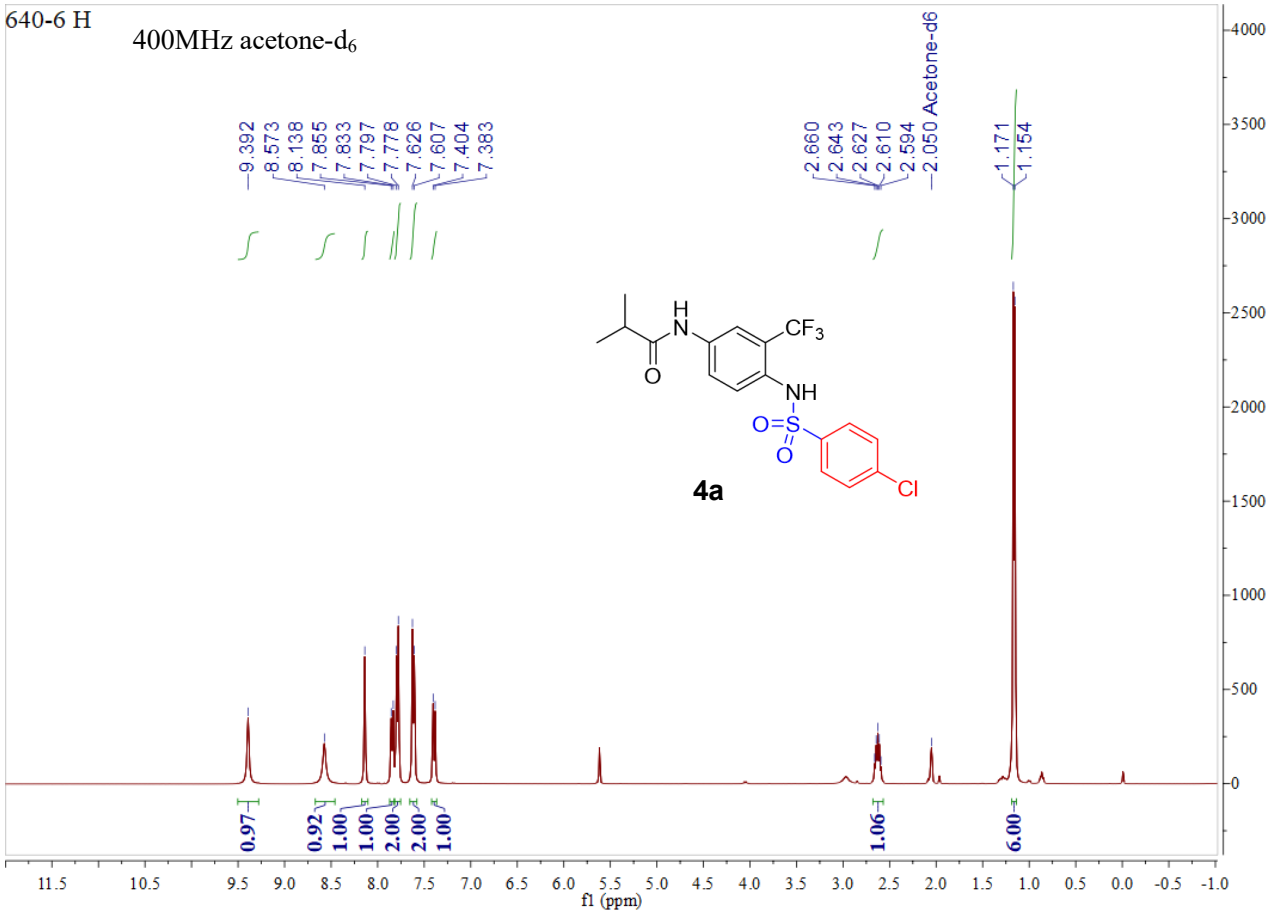

638-13 C
101MHz acetone-d6
206.260 Acetone-d6
153.551
144.302
139.769
139.525
133.117
132.617
130.358
130.211
129.906
128.415
128.028
127.597
116.299
3o
f1 (ppm)

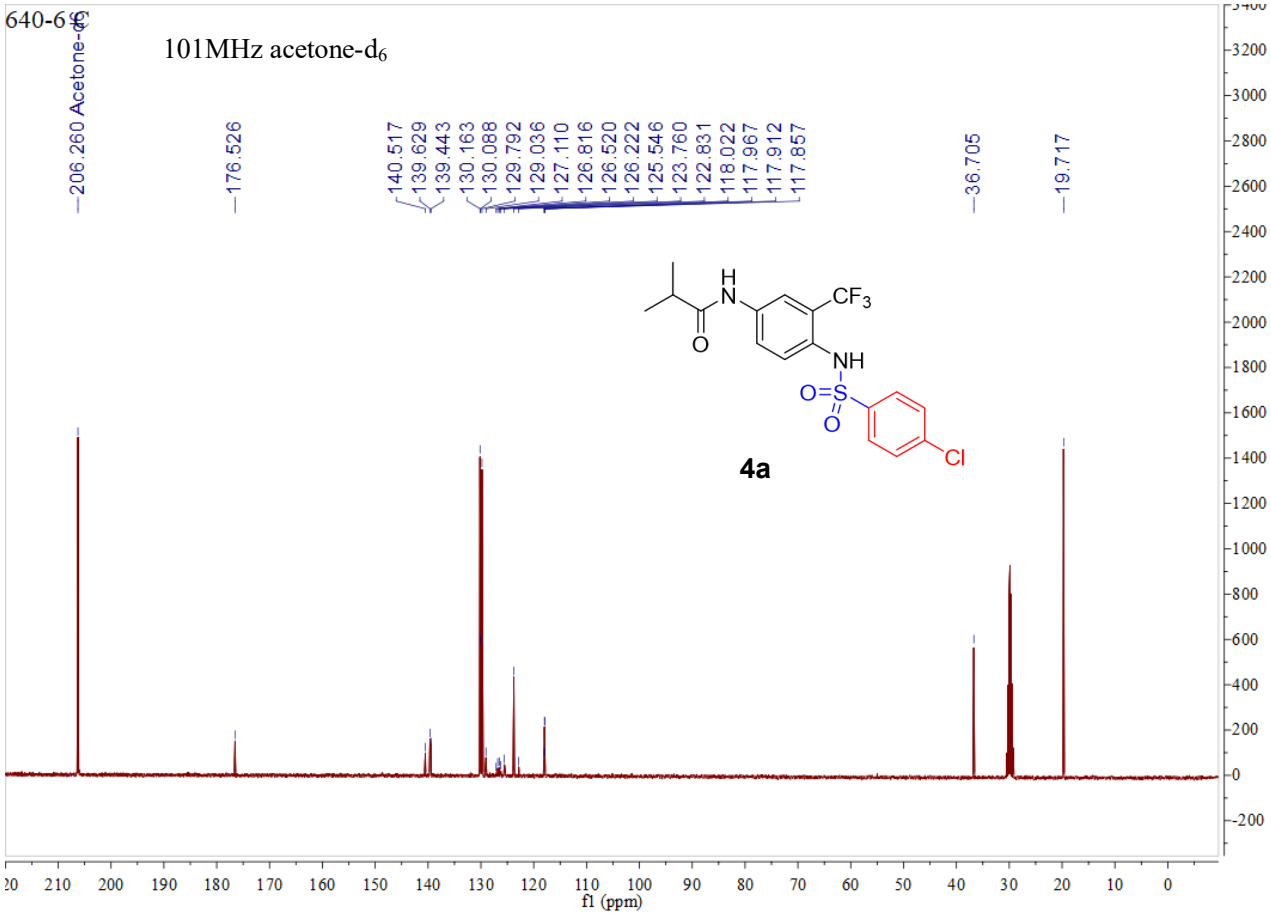

638-12 H
400MHz acetone-d6
9.095
7.800
7.782
7.590
7.571
7.459
7.440
7.294
7.276
7.183
6.246
2.050 Acetone-d6
0.79
2.00
2.00
2.01
2.02
2.01
2.00
f1 (ppm)
3p

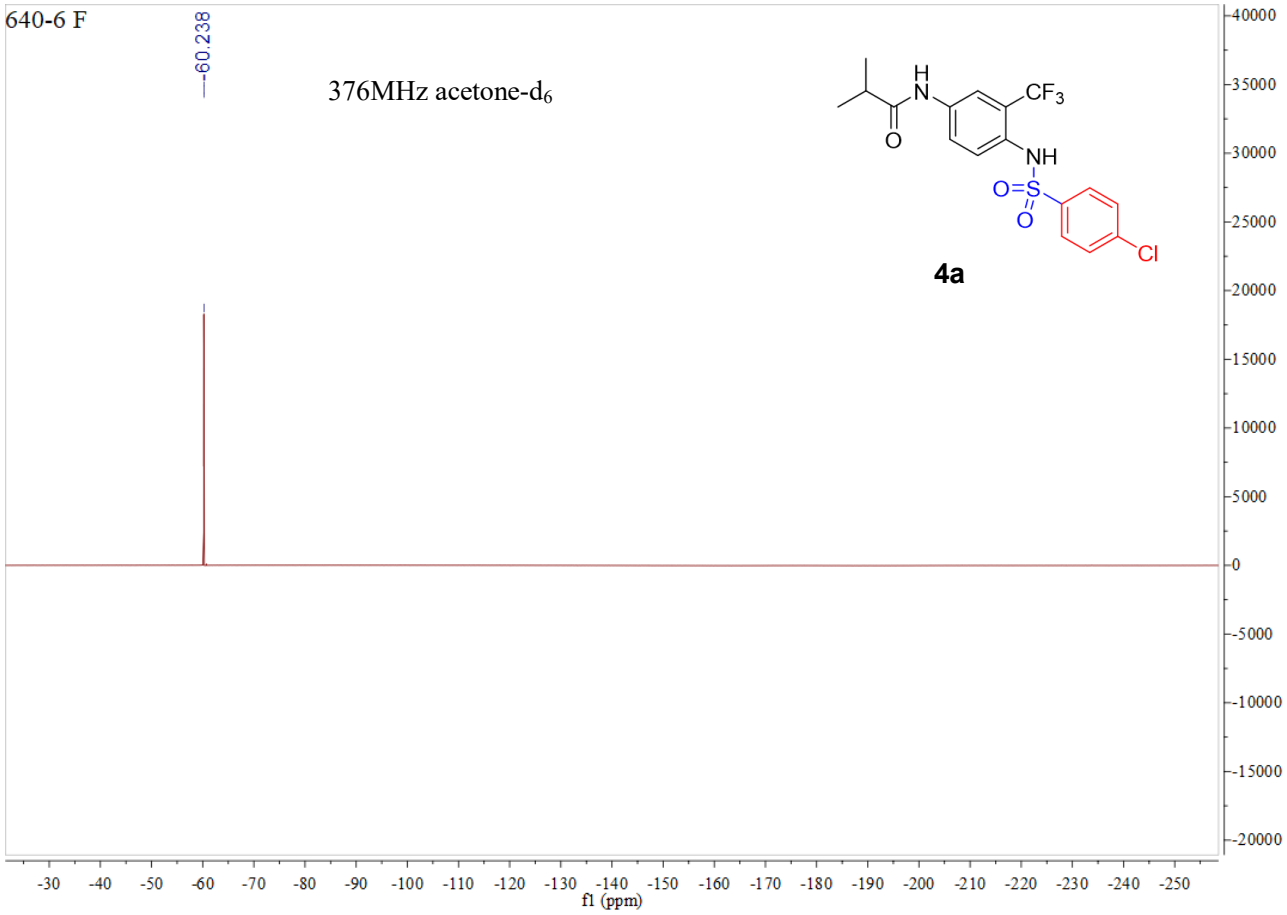

638-12C
101MHz acetone-d6
206.260 Acetone-d6
139.597
139.535
138.848
135.620
130.280
129.893
123.943
121.379
119.799
111.406
f1 (ppm)
3p


638-21 H
400MHz acetone-d6
9.215
7.843
7.822
7.635
7.616
7.587
7.567
7.247
7.228
2.050 Acetone-d6
1.290
Bpin
O
S
O
N
H
Cl
3q
0.92
2.00
2.05
2.00
2.00
12.07
f1 (ppm)


638-21 C
101MHz acetone-d6
206.260 Acetone-d6
141.369
139.767
139.628
136.790
130.329
129.906
120.229
84.649
25.306
Bpin
O
S
O
N
H
Cl
3q
f1 (ppm)


640-6 H
400MHz acetone-d6
9.392
8.573
8.138
7.855
7.833
7.797
7.778
7.626
7.607
7.404
7.383
2.660
2.643
2.627
2.610
2.594
2.050 Acetone-d6
1.171
1.154
4a
0.97
0.92
1.00
1.00
2.00
2.00
1.00
1.06
6.00
f1 (ppm)


640-6 C
101MHz acetone-d6
206.260 Acetone-d6
176.526
140.517
139.629
139.443
130.163
130.088
129.792
129.036
127.110
126.816
126.520
126.222
125.546
123.760
122.831
118.022
117.967
117.912
117.857
36.705
19.717
4a
f1 (ppm)


640-6 F
-60.238
376MHz acetone-d6
H
N
O
CF3
NH
O=S
O
Cl
4a
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)