Supporting Information

Multicomponent Synthesis of Sulfonamides from Triarylbismuthines, Nitro Compounds and Sodium Metabisulfite in Deep Eutectic Solvents

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1. Procedures.

General

Melting points were obtained with a Reichert Thermovar apparatus. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as a solvent and TMS as internal standard for ^{1}H and ^{13}C; chemical shifts are given in δ (parts per million) and coupling constants (*J*) in Hertz. FT-IR spectra were obtained on a JASCO 4100LE (Pike Miracle ATR) spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Himazdu QP-5000 spectrometer, giving fragment ions in *m/z* with relative intensities (%) in parentheses The mass spectrometry analyses of high resolution (HRMS) were performed in the Mass Spectrometry Unit of the Technical Services Research at the University of Alicante with a spectrometer *Finnigan MAT95-S.* DIP analyses were performed using an Agilent mass spectrometer, model Network 5973 Mass Selective with direct sample introduction to the ion source through the SIS (Scientific Instrument Services) probe Direct Insertion Probe (73DIP-1) The chromatographic analyses (GLC) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and 12 m HP-1 capillary column (0.2 mm diam, 0.33 mm film thickness, OV-1 stationary phase), using nitrogen (2 mL/min) as a carrier gas, $T_{injector}$ = 275 ºC, $T_{detector}$ = 300ºC, T_{column} = 60ºC (3 min) and 60-270 ºC (15 ºC/min), *P* = 40 kPa. Thin layer chromatography (TLC) was carried out on Schleicher&Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light. DSC analysis were carried out on a *METTLER TOLEDO* equipment, model *TGA/SDTA851e/LF/16*00, and EM analysis on a *PFEIFFER VACUUM*, model *THERMOSTAR GSD301T*. pH measurements were performed using a *Mettler Toledo SevenEasy S20* pH-meter. Reactions carried out under microwave irradiation were performed on a *MW CEM Discovery 908010* apparatus. Column chromatography was performed using silica gel 60 of 40-63 mesh. All reagents were commercially available (Acros, Aldrich, Fluorochem) and were used as received.

Deep Eutectic Solvents preparation.

DESs were prepared by mixing the corresponding components in the appropriate molar ratio and heating the mixture at 80 ºC under Ar atmosphere until a clear solution was obtained. Since some of the components of DESs are very hygroscopic, they were always stored under Ar atmosphere, although the reactions employing DESs as solvents were carried out in opened to air reaction vessels.

Synthesis of Ar_3Bi.

For commercially available organomagnesium reagents: a solution of the $BiCl_3$ in dry THF (1M) was added dropwise over a solution of ArMgBr in THF or Et_2O (1M) under argon atmosphere with magnetic stirring. Once the addition was completed, the solution was heated to reflux for 12h. Then, the reaction was allowed to reach room temperature and poured slowly over a cold solution of NH_4Cl (sat. aq.). Product was extracted 3 times with Et_2O. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure.[1]

For non-commercially available organomagnesium reagents: the corresponding aryl iodide (6.2 mmol) was dissolved in dry THF and cooled to -78 ºC in an acetone bath. A *n*-butyllithium solution (2.5 M, 6.2 mmol) was added dropwise and the mixture was stirred at that temperature for 1h. Then, a solution of $BiCl_3$ (2 mmol) in dry THF was added dropwise and the mixture was slowly allowed to reach room temperature. The corresponding mixture was stirred overnight at rt and then quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with EtOAc (15 x 3 mL) and the combined organic layers washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered and reduced under reduced pressure.

Ar_3Bi were usually purified by recrystallization from hot EtOH or by flash chromatography using a mixture of EtOAc and hexanes.[2]

Synthesis of sulfonamides.

A solution of Ar_3Bi (0.2 mmol), sodium metabisulfite (1.32 mmol), CuCl (0.006 mmol) and the corresponding nitro compound (1.2 mmol) in 1.5 mL of DES was stirred for 24 h at 80 °C in a reaction vessel opened to air. Once the reaction was completed, water was added to dissolve the DES phase. That aqueous suspension was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Products were usually purified by chromatography on silica gel (hexane/ethyl acetate) and/or distillation to give the corresponding products **4/5**.

Alternatively, product could be retrieved by quenching the reaction mixture with $NaHCO_3$ and filtering the suspension. The filtrate was rinsed with distilled water to afford products **4** in high purity, although with lower yields than in the previous method due to the slight solubility of sulfonamides in water (Fig S1).

Microbial strain, culture media and incubation conditions.

The microorganism used in this study to test the toxicity, tolerance and the potential assimilation of the DESs here described was *Escherichia coli* BL21 (DE3) (Novagen). The incubation experiments were conducted in 250 mL Erlenmeyer with 50 mL of Luria-Bertani medium (LB). In all cases, the cells were grown at 37 °C with constant shaking (180 rpm). The growth of the bacterium was monitored by measuring the absorbance at 600 nm. All the physiological studies were done in triplicate. In order to test the toxicity/tolerance of the DES, the media were supplemented with it at final concentrations between 0 (control) and 750 mM.

2. Gram-Scale Reaction.

a)

Ph_3Bi	+	$Na_2S_2O_5$	+	$PhNO_2$	+	CuCl	AcChCl:Acetamide (1:2)	$PhSO_2NHPh$
2 mmol 880 mg		13.2 mmol 2.5 g		12 mmol 1.24 mL		0.06 5.9 mg	80°C	85% Yield 1.19 g

b)

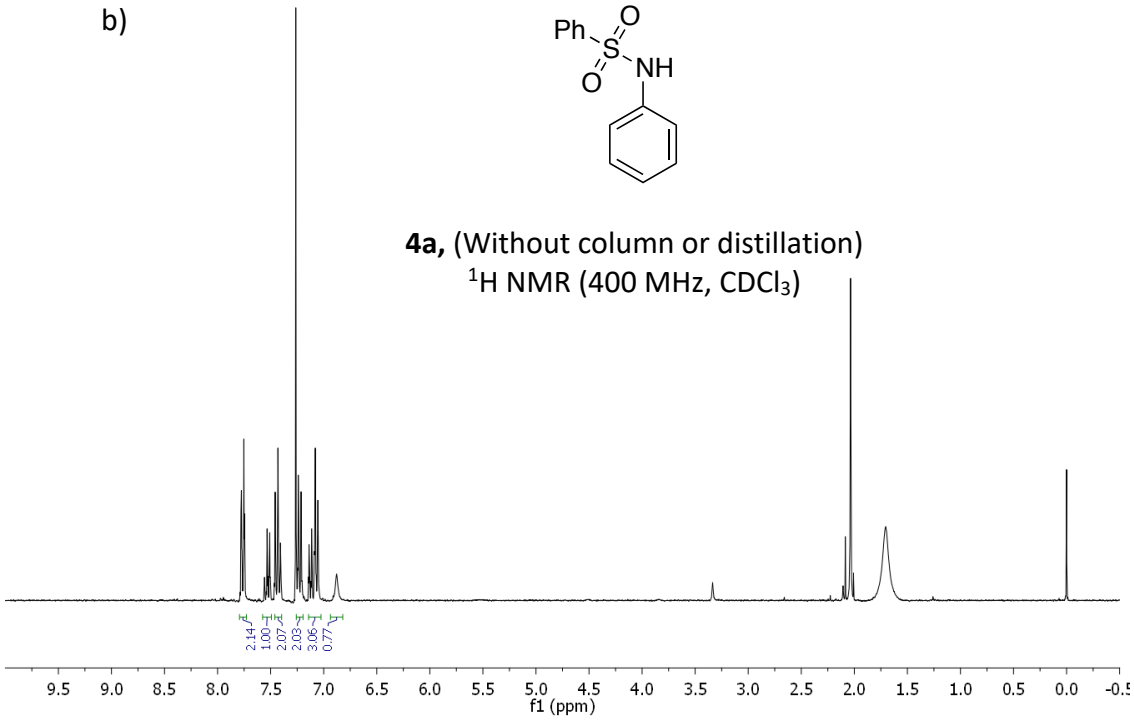
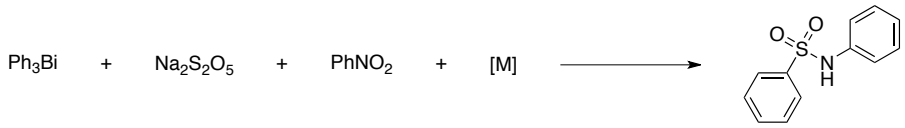


Fig. S1. a) Gram-scale reaction. b)^{1}H NMR spectra of compound **4a** directly filtered from the reaction media without any purification step.

3. Optimisation Studies.

Table S1. Optimisation of reaction conditions.[a]



Entry	DES (molar ratio)	[M] (1 mol%)	Ligand (mol%)	T (ºC)	t (h)	Yield (%)[b]
1	ChCl:Acetamide (1:2)	$CuCl_2$	-	50	15	-
2	ChCl:Acetamide (1:2)	$CuCl_2$	-	80	15	21%
3	ChCl:Acetamide (1:2)	$CuCl_2$	-	80	1	35[c]
4	ChCl:Acetamide (1:2)	$CuCl_2$	**L1** (1)	80	24	18
5	ChCl:Acetamide (1:2)	$CuCl_2$	**L2** (2)	80	24	31
6	ChCl:Acetamide (1:2)	$CuCl_2$	**L3** (2)	80	24	61
7	ChCl:Acetamide (1:2)	CuCl	-	80	24	43
8	ChCl:Acetamide (1:2)	CuI	-	80	24	29
9	ChCl:Acetamide (1:2)	CuO	-	80	24	20
10	ChCl:Acetamide (1:2)	Cu_2O	-	80	24	47
11	ChCl:Acetamide (1:2)	CuBr	-	80	24	27
12	ChCl:Acetamide (1:2)	Cu	-	80	24	8
13	ChCl:Acetamide (1:2)	CuCl	**L3** (2)	80	24	26
14	ChCl:Glycerol (1.2)	CuCl	-	80	24	5
15	Ph_3PMeBr:Glycerol (1:2)	CuCl	-	80	24	12
16	ChCl:$(HOCH_2)_2$ (1:2)	CuCl	-	80	24	18
17	ChCl:Urea (1:2)	CuCl	-	80	24	2
18	ChCl:Glucose (2:1)	CuCl	-	80	24	1
19	ChCl:Formic Ac (1:2)	CuCl	-	80	24	0
20	ChCl:Sorbitol (1:1)	CuCl	-	80	24	0
21	DecA:Menthol (1:2)	CuCl	-	80	24	0
22	Urea:Acetamide (1:2)	CuCl	-	80	24	19
23	Betaine:$PhCO_2H$ (2:3)	CuCl	-	80	24	43
24	Betaine:Acetamide (1:2)	CuCl	-	80	24	28
25	AcChCl:Acetamide (1:2)	CuCl	-	80	24	66
26	AcChCl:Acetamide (1:2)	CuCl	-	80	24	72[d]
27	AcChCl:Acetamide (1:2)	CuCl	-	80	24	99[e]
28	ChCl:Acetamide (1:2)	CuCl	-	80	24	49[e]
29	AcChCl:Urea (1:2)	CuCl	-	80	24	52[e]
30	AcChCl:Acetamide (1:2)	$FeCl_2$	-	80	24	43[e]
31	AcChCl:Acetamide (1:2)	$NiCl_2$	-	80	24	6[e]
32	AcChCl:Acetamide (1:2)	CuCl	-	80	24	22[e,f]
33	AcChCl:Acetamide (1:2)	CuCl	-	80	24	40[e,g]
34	AcChCl:Acetamide (1:2)	CuCl	-	60	24	49[e]
35	AcChCl:Acetamide (1:2)	CuCl	-	100	24	99[e]
36	H_2O	CuCl	-	80	24	0[e]
37	PhMe	CuCl	-	80	24	0[e]
38	MeOH	CuCl	-	80	24	3[e]

[a] Conditions: Ph_3Bi (0.2 mmol), $Na_2S_2O_5$ (1.32 mmol), $PhNO_2$ (0.6 mmol) in 1.5 ml of DES. [b] Yields determined by GC using tridecane as standard. [c] Reaction carried out under MW irradiation. [d] Reaction carried out using 1.5 eq of $PhNO_2$ [e] Reaction carried out using 2.0 eq of $PhNO_2$ [f] Reaction carried out using 1.0 eq of $Na_2S_2O_5$ [g] Reaction carried out using 1.6 eq of $Na_2S_2O_5$.

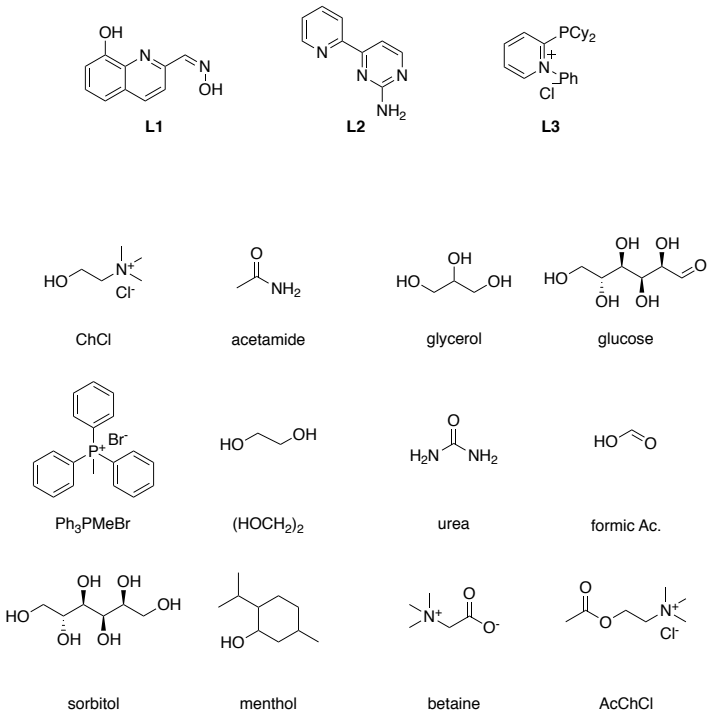


Fig S2. Ligands and DESs components.

Table S2. Study of SO_2 surrogates.[a]

Entry	SO_2 source	Yield (%)[b]
1	$Na_2S_2O_5$	99
2	$K_2S_2O_5$	95
3	DABSO	63
4	$Na_2S_2O_4$	15
5	S_8	0
6	NaO_2SCH_2OH	0

[a] Reaction carried out using compounds 1**a** (0.2 mmol), sulphur source (1.32 mmol) and **3a** (1.2 mmol) in 1.5 mL of DES. [b] Yield determined by GC using tridecane as internal standard.

Table S3. Study of aryl sources.[a]

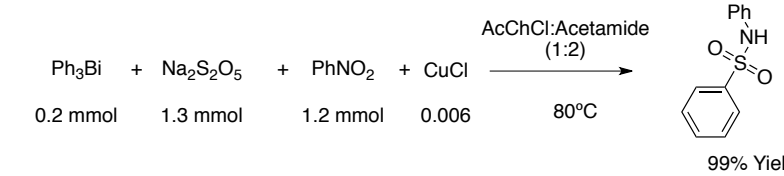
Entry	Aryl source	Yield (%)[b]
1	Ph_3Bi	99
2	$PhB(OH)_2$	16
3	PhMgBr	0
4	Ph_3Al	0
5	PhZnBr	0

[a] Reaction carried out using compounds **1** (1 eq mmol), $Na_2S_2O_5$ (2.2 equivalents) and **3a** (2 equivalents) in DES (0.4 M). [b] Yield determined by GC using tridecane as internal standard.

4. Control Experiments

A series of control experiments were carried out in order to shed some light about the reaction mechanism. Scheme a) shows the optimised reaction conditions, with the subsequent schemes showing modified conditions.

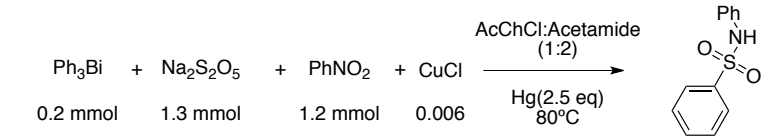
a)



99% Yield

The reaction was not catalysed by copper nanoparticles, since adding in 2.5 eq of Hg did not affect the reaction outcome (scheme b).

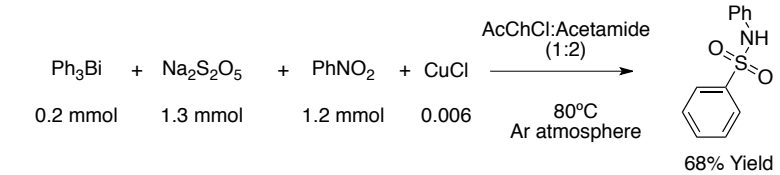
b)



99% Yield

When the reaction was run under argon atmosphere, a slightly decrease on the product yield was observed. Therefore, a role for molecular oxygen and/or moisture can be expected (scheme c). Oxygen can be involved in copper oxidation or in the oxidation of bismuth by-product to form Bi_2O_3, while moisture can interact with the DES (very hygroscopic) and act as a source of protons in the reduction step.

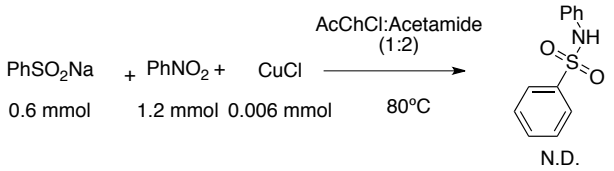
c)



68% Yield

Since Ar_3Bi and SO_2 produce sodium phenylsulfinate, several reactions were tested with this reagent. Running the reaction with sodium benzenesulfinate without sodium metabisulfite did not yield the final product, confirming the dual role of sodium metabisulfite as SO_2 source and reductant (scheme d).

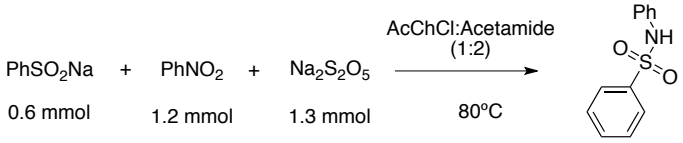
d)



N.D.

Surprisingly, reaction worked without adding the copper catalyst, although a very low yield was obtained (scheme e).

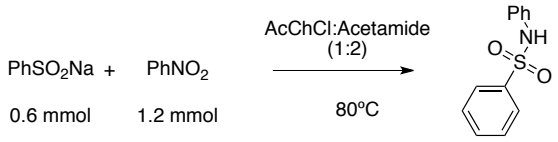
e)



16% Yield

As in scheme d, the absence of the reductant prevented the product formation (scheme f).

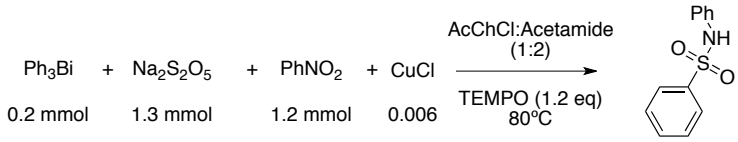
f)



N.D.

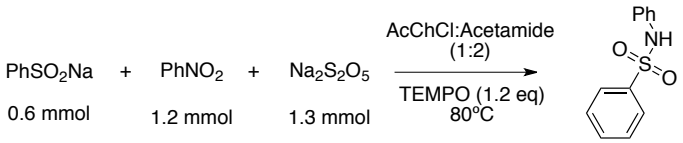
The reaction was inhibited by the use of a radical scavenger (TEMPO), involving a possible radical mechanism (schemes g and h).

g)



N.D.

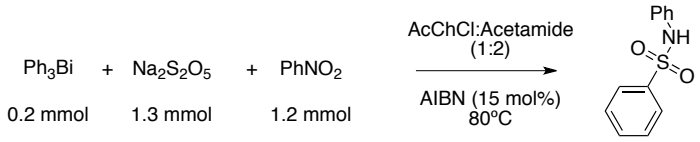
h)



N.D.

Using a catalytic amount of a radical initiator (AIBN) without using copper, product **4a** was obtained with 38% yield.

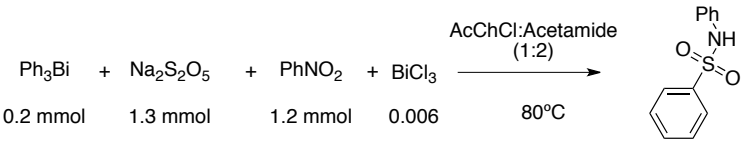
i)



38% Yield

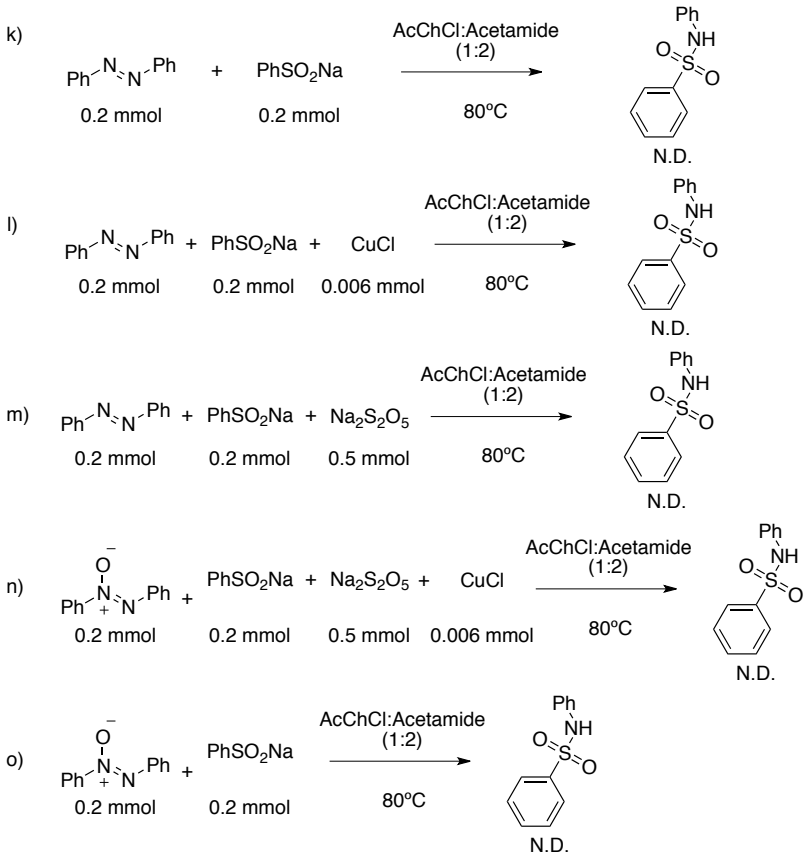
The possibility the actual catalyst was the $BiCl_3$ released during the reaction course was contemplated. Nevertheless, the same range of yield that in the absence of CuCl was obtained (scheme j).

j)



18% Yield

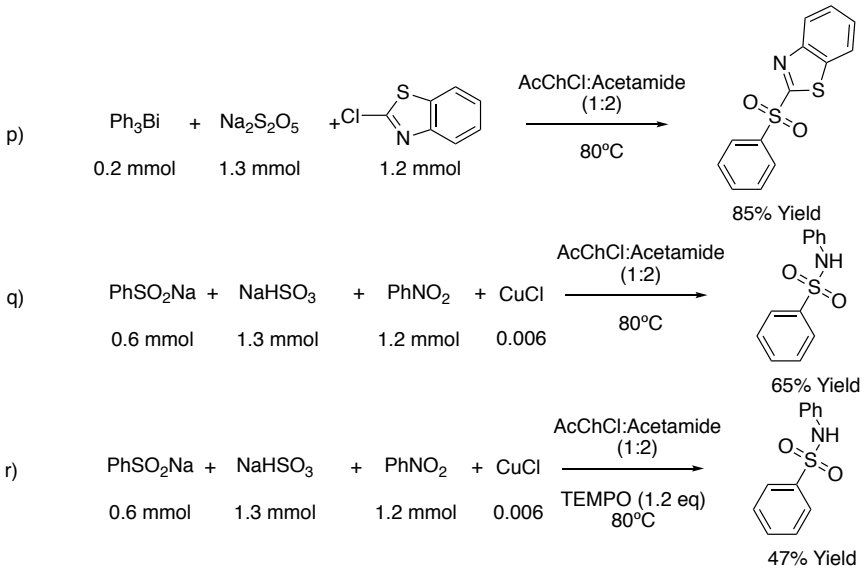
The reduction of nitro compounds usually takes place *via* a dimer. Therefore, several reactions were tested with some dimeric nitrogen species, but no product was obtained in any of them (schemes k-o).



The reaction of triphenylbismuthine with sodium metabisulfite to yield sodium benzenesulfinate and its subsequent reaction with an electrophile took place smoothly without the need of a copper catalyst. This result suggested that CuCl was only involved in the reduction step (scheme p).

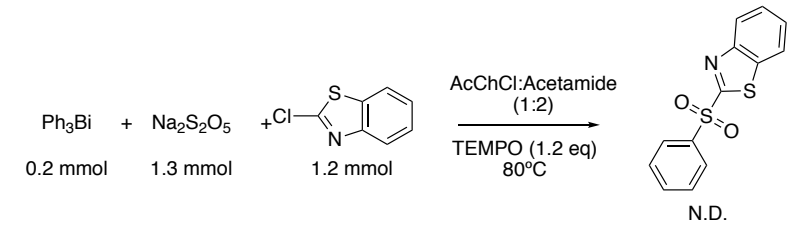
To further prove the role of CuCl as catalyst for the reduction step, the sodium benzenesulfinate was mixed with nitrobenzene and sodium bisulfite in the presence of CuCl, obtaining the corresponding sulphonamide in 65% yield (scheme q). However, the reaction took place with very low yield without copper (scheme e).

Performing the same reaction in the presence of a radical scavenger also afford the product, although a slight drop in yield was observed (scheme r). The reaction did take place with the sodium sulfinate, but not when Ph_3Bi was used as reagent (scheme g), confirming that the radical species are present in the sulfinate formation from $Na_2S_2O_5$ and Ph_3Bi.



The synthesis of sulfones under optimal conditions but in the presence of TEMPO did not afford the product, confirming that there are radical species involved in the sulfinate formation (scheme q).

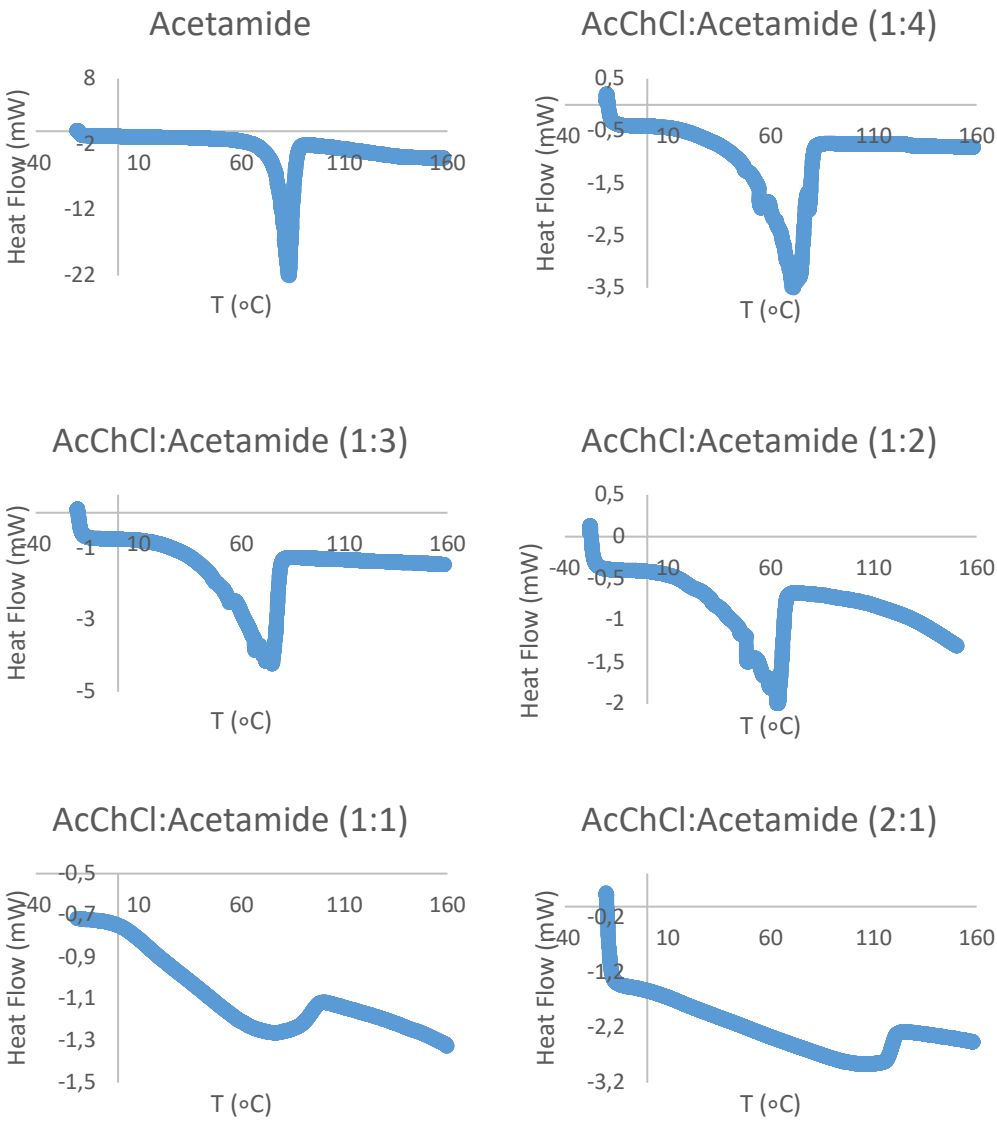
s)



5. DES Characterization

5.1. DSC

Samples were prepared by mixing the two components (AcChCl and acetamide) and grinding them together until an intimate mixture was obtained.



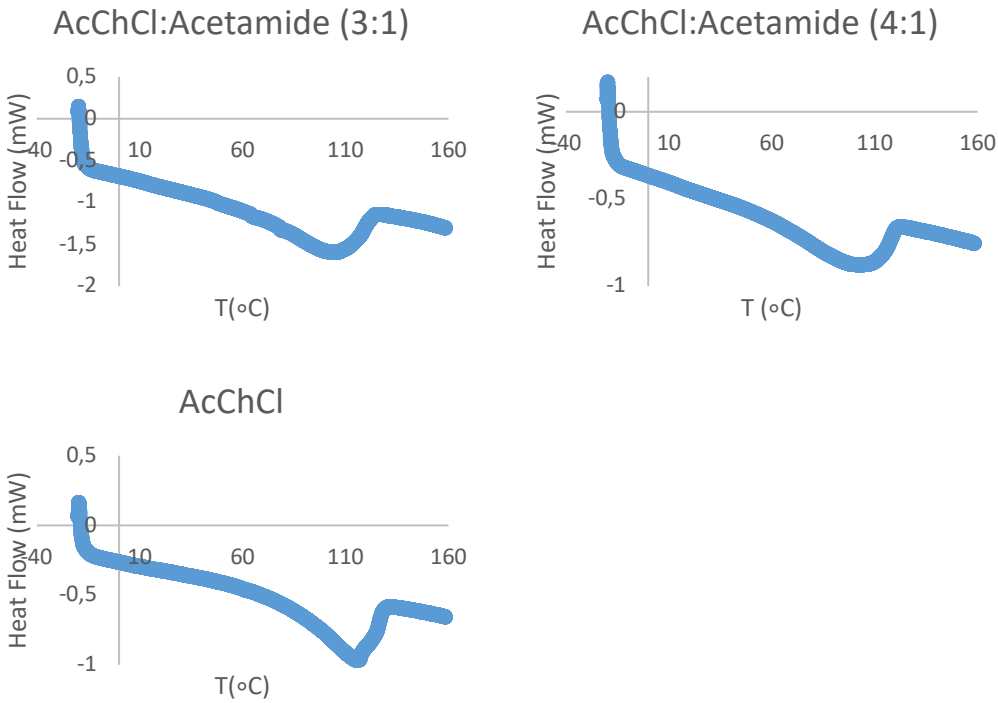


Fig S3. DSC analyses of different mixtures of AcChCl:Acetamide.

Despite of having a melting point around 60°C, the mixture did not return to solid state when cooled to room temperature.[3] Nevertheless, this eutectic mixture was very viscous at rt, making the nucleation and crystal growth process more difficult to happen. [4]

A second cycle in the DSC measurement was performed by cooling the sample to -90°C and heating it up again to 160 °C. In this second cycle, no melting point was observed. Instead, a glass transition temperature can be observed, confirming the glass nature of the mixture (Fig. S5).

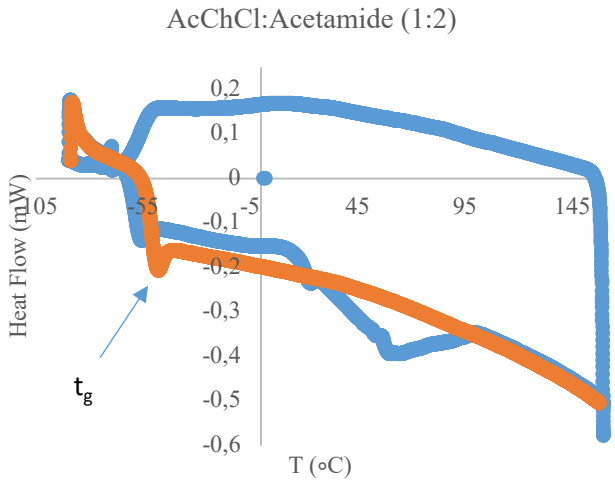


Fig. S4. DSC of the mixture AcChCl:acetamide (1:2) with 2 consecutive cycles of heating/cooling.

6. Characterization data.

***N*-phenylbenzenesulfonamide (4a)**:[5] Cream solid; m.p. 101-103 °C; R_f = 0.63 (hexane/ethyl acetate: 1/1); t_r = 15.00 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.80 (m, 2H, ArH), 7.55-7.50 (m, 1H, NH), 7.45-7.40 (m, 2H, ArH), 7.30-7.20 (m, 3H, ArH), 7.15-7.05 (m, 3H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.0, 136.5, 133.1, 129.4 (2C), 129.2 (2C), 127.3 (2C), 125.5, 121.8 (2C); IR (ATR): ν = 3204, 1302, 1151, 723 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 234 (M^++1, 12%), 233 (M^+, 86), 168 (40), 141 (24), 93 (12), 92 (100), 77 (51), 65 (33).

***N*-(p-tolyl)benzenesulfonamide (4b)**:[5] White solid; m.p. 101-103 °C; R_f = 0.23 (hexane/ethyl acetate: 4/1); t_r = 15.77 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.75 (m, 2H, ArH), 7.55-7.45 (m, 1H, ArH), 7.45-7.35 (m, 2H, ArH), 7.24 (br s, 1H, NH), 7.05-6.95 (m, 4H, ArH), 2.25 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.1, 135.5, 133.8, 133.0, 129.9 (2C), 129.1 (2C), 127.4 (2C), 122.4 (2C), 20.9; IR (ATR): ν = 3256, 1328, 1159, 687cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 247 (M^+, 57 %), 106 (100), 79 /18), 77 (36), 51 (10).

***N*-(4-methoxyphenyl)benzenesulfonamide (4c)**:[6] Brown solid; m.p. 87-89 °C; R_f = 0.63 (hexane/ethyl acetate: 1/1); t_r = 16.86 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75-7.70 (m, 2H, ArH), 7.60-7.50 (m, 1H, ArH), 7.45-7.40 (m, 2H, ArH), 7.05-6.95 (m, 2H, ArH), 6.86 (s, 1H, NH), 6.80-6.70 (m, 2H, ArH), 3.74 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.1, 139.0, 133.0, 129.1 (2C), 128.9, 127.4 (2C), 125.6 (2C), 114.5 (2C), 55.5; IR (ATR): ν = 3259, 1508, 1326, 1155 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 263 (M^+, 22%), 122 (100).

***N*-(4-aminophenyl)benzenesulfonamide (4d)**:[7] White solid; m.p. 168-170 °C; R_f = 0.30 (hexane/ethyl acetate: 1/1); t_r = 13.41 min; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.48 (s, 1H, NH), 7.65-7.60 (m, 2H, ArH), 7.60-7.50 (m, 3H, ArH), 6.70-6.65 (m, 2H, ArH), 6.45-6.35 (m, 2H, ArH), 5.15 (br s, 2H, NH_2); ^{13}C NMR (101 MHz, DMSO-d_6): δ = 146.1, 139.7, 132.4, 128.9 (2C), 126.7 (2C), 125.5, 124.6 (2C), 114.2 (2C); IR (ATR): ν = 3395, 1653, 1260, 1160 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 248 (M^+, 15%), 107 (100), 80 (13).

***N*-(4-hydroxyphenyl)benzenesulfonamide (4e)**:[8] White solid; m.p. 156-158 °C; R_f = 0.40 (hexane/ethyl acetate: 1/1); t_r = 17.95 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.73 (br s, 1H, NH), 9.31 (br s, 1H, OH), 7.70-7.65 (m, 2H, ArH), 7.60-7.45 (m, 3H, ArH), 6.85-6.75 (m, 2H, ArH), 6.65-6.55 (m, 2H, ArH); ^{13}C NMR (101 MHz, DMSO-d_6): δ = 154.9, 139.5, 132.6, 129.0 (2C), 128.4, 126.7 (2C), 124.1 (2C), 115.5 (2C); IR (ATR): ν = 3243, 1320, 1190, 686 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 249 (M^+, 36%), 108 (100), 81 (15), 77 (14).

***N*-(4-chlorophenyl)benzenesulfonamide (4f)**:[9] White solid; m.p. 116-118 °C; R_f = 0.57 (hexane/ethyl acetate: 1/1); t_r = 16.36 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (ddd, *J* = 7.1, 3.1, 1.8 Hz, 2H, ArH), 7.60-7.50 (m, 2H, ArH + NH), 7.50-7.40 (m, 2H, ArH), 7.20-7.15 (M, 2H, ArH), 7.10-7.00 (M, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 135.1, 133.4, 131.1, 129.5 (2C), 129.3 (2C), 127.3 (2C), 123.1 (2C); IR (ATR): ν = 3241, 1374, 1160, 688 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 269 (M^+ Cl^{37}, 27%), 267 (M^+ Cl^{35}, 71), 141 (15), 128 (33), 126 (100), 101 (10), 99 (28), 77 (40), 51 (16).

***N*-(4-acetylphenyl)benzenesulfonamide (4g)**:[10] Brown solid; m.p. 125-127 °C; R_f = 0.43 (hexane/ethyl acetate: 1/1); t_r = 18.17 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90-7.80 (m, 4H, ArH), 7.63 (s, 1H, NH), 7.60-7.55 (m, 1H, ArH), 7.50-7.45 (m, 2H, ArH), 7.25-7.15 (m, 2H, ArH), 2.53 (s, 3H, CH_3CO); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.1, 141.2, 138.9, 133.6, 133.5, 130.1 (2C), 129.4 (2C), 127.3 (2C), 119.2 (2C), 26.6; IR (ATR): ν = 3347, 1429, 1129, 695 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 275 (M^+, 53%), 261 (15), 260 (100), 119 (12), 77 (38).

***N*-(3-chlorophenyl)benzenesulfonamide (4h)**:[9] White solid; m.p. 114-116 °C; R_f = 0.67 (hexane/ethyl acetate: 1/1); t_r = 16.22 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.85 (m, 2H, ArH), 7.74 (s, 1H, NH), 7.60-7.55 (m, 1H, ArH), 7.50-7.45 (m, 2H, ArH), 7.20-7.10 (m, 2H, ArH), 7.10-7.00 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 137.9, 135.0, 133.5, 130.4, 129.3 (2C), 127.3 (2C), 125.4, 121.1, 119.1; IR (ATR): ν = 3195, 1312, 1152, 683 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 269 (M^+ Cl^{37}, 21%), 267 (M^+ Cl^{35}, 57), 203 (12), 202 (17), 168 (25), 167 (11), 141 (59), 126 (25), 99 (24), 91 (11), 78 (11), 77 (100).

***N*-*N*-(1,3-phenylene)dibenzenesulfonamide (4i)**: White solid; m.p. 162-165 °C; R_f = 0.37 (hexane/ethyl acetate: 1/1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.30 (s, 2H, 2xNH), 7.70-7.65 (m, 4H, ArH), 7.60 (*ap* t, *J* = 7.4 Hz, 2H, ArH), 7.51 (*ap* t, *J* = 7.6 Hz, 4H, ArH), 7.11 (t, *J* = 1.0 Hz, 1H, ArH), 7.02 (t, *J* = 8.1 Hz, 1H, ArH), 6.69 (dd, *J* = 8.1, 1.9 Hz, 2H, ArH); ^{13}C NMR (101 MHz, DMSO-d_6): δ = 139.3 (2C), 138.5 (2C), 132.9 (2C), 129.8, 129.2 (4C), 126.6 (4C), 115.2 (2C), 110.8; IR (ATR): ν = 3404, 1324, 1152, 688 cm^{-1}; MS (DIP): *m*/*z* (%): 388 (M^+, 43%), 183 (100), 182 (35), 181 (11), 167 (19), 166 (39), 156 (26), 141 (13), 125 (13), 105 (15), 79 (14), 78 (17), 77 (83), 51 (18); HRMS calcd. (%) for $C_{18}H_{16}N_2O_4S_2$: 388.0551; found: 388.0549.

***N*-(2-chlorophenyl)benzenesulfonamide (4j)**:[9] White solid; m.p. 146-148 °C; R_f = 0.63 (hexane/ethyl acetate: 1/1); t_r = 15.16 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.75 (m, 2H, ArH), 7.67 (dd, *J* = 8.5, 1.5 Hz, 1H, ArH), 7.60-7.50 (m, 1H, ArH), 7.45-7.40 (m, 2H, ArH), 7.30-7.20 (m, 2H, ArH), 7.10-7.05 (m, 1H, ArH), 7.00 (s, 1H, NH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.0, 133.4, 129.5, 129.2 (2C), 128.1 (2C), 127.4 (2C), 126.2, 125.4, 122.8; IR (ATR): ν = 3247, 1332, 1157 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 269 (M^+ Cl^{37}, 32%), 267 (M^+ Cl^{35}, 96), 168 (13), 167 (18), 141 (54), 128 (33), 126 (100), 102 (15), 99 (45), 90 (11), 77 (87), 63 (12).

***N*-(2-bromophenyl)benzenesulfonamide (4k)**:[11] White solid; m.p. 113-115 °C; R_f = 0.43 (hexane/ethyl acetate: 7/3); t_r = 16.08 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.75 (m, 2H, ArH), 7.68 (dd, *J* = 8.2, 1.5 Hz, 1H, ArH), 7.60-7.50 (m, 1H, ArH), 7.45-7.35 (m, 3H, ArH), 7.28 (ddd, *J* = 8.2, 7.5, 1.5 Hz, 1H, ArH), 6.99 (br s, 1H, NH), 6.98 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 134.7, 133.4, 132.7, 129.2 (2C), 128.7, 127.4 (2C), 126.6, 123.1, 116.1; IR (ATR): ν = 1333, 1159, 722 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 314 (M^+ Br^{81}+1 , 14%), 313 (M^+ Br^{81}, 98), 312 (M^+ Br^{79}+1,

13), 311 (M^+Br^{79}, 95), 172 (98), 170 (100), 145 (13), 143 (17), 141 (58), 125 (29), 91 (86), 90 (13), 77 (96), 65 (10), 64 (19), 63 (22), 51 (31).

***N*-(naphtalen-2-yl)benzenesulfonamide (4l):**[9] White solid; m.p. 96-98 °C; R_f = 0.63 (hexane/ethyl acetate: 1/1); t_r = 18.82 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90-7.80 (m, 2H, ArH), 7.75-7.65 (m, 3H, ArH), 7.58 (br s, 1H, NH), 7.56 (d, J = 2.2 Hz, 1H, ArH), 7.50-7.35 (m, 5H, ArH), 7.25 (dd, J = 8.9, 2.2 Hz, 1H, ArH);^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.0, 134.1, 133.7, 133.2, 131.2, 129.5, 129.2 (2C), 127.7, 127.6, 127.4 (2C), 126.8, 125.6, 121.2, 118.6; IR (ATR): ν = 3189, 1321, 1148, 648 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 283 (M^+, 51%), 142 (72), 115 (100), 110 (11), 77 (16).

***N*-cyclohexylbenzenesulfonamide (4m)**:[12] White solid; m.p. 81-83 °C; R_f= 0.67 (hexane/ethyl acetate: 1/1); t_r = 14.83 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95-7.85 (m, 2H, ArH), 7.60-7.50 (m, 3H, ArH), 4.46 (d, J = 6.3 Hz, 1H, C*H*NH), 3.17 (br s, 1H, NH), 1.80-1.75 (m, 2H, CH_2NH), 1.70-1.60 (m, 2H, CH_2Cy), 1.55-1.50 (m, 1H, CH_2Cy), 1.30-1.10 (m, 5H, CH_2Cy); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.6, 132.6, 129.2 (2C), 127.0 (2C), 52.8, 34.1 (2C), 25.3, 24.8; IR (ATR): ν = 3278, 2929, 1707, 1322, 1159 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 239 (M^+, 32%), 197 (12), 196 (100), 141 (44), 98 (15), 77 (46).

4-methyl-*N*-phenylbenzenesulfonamide (5a):[9] White solid; m.p. 98-100 °C; R_f= 0.37 (hexane/ethyl acetate: 1/1); t_r = 15.99 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70-7.60 (m, 2H, ArH), 7.30-7.20 (m, 5H, ArH + NH), 7.15-7.05 (m, 3H, ArH), 2.37 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.0, 136.7, 136.3, 129.8 (2C), 129.4 (2C), 127.4 (2C), 125.5, 121.7 (2C), 21.7; IR (ATR): ν = 3236, 1335, 1153, 753 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 248 (M^+1, 11%), 247 (M^+, 69), 182 (22), 168 (14), 155 (47), 92 (55), 91 (100), 65 (41).

***N*-phenylnaphtalene-1-sulfonamide (5b)**:[13] White solid; m.p. 149-151 °C; R_f= 0.43 (hexane/ethyl acetate: 7/3); t_r = 20.62 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (dd, J = 8.7, 0.7 Hz, 1H, ArH), 8.04 (d, J = 8.3 Hz, 1H, ArH), 7.94 (d, J = 8.1 Hz, 1H, ArH), 7.68 (ddd, J = 8.6, 7.0, 1.1 Hz, 1H, ArH), 7.61 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H, ArH), 7.46 (dd, J = 8.1, 7.5 Hz, 1H, ArH), 7.22 (s, 1H, NH), 7.15-7.10 (m, 2H, ArH), 7.05-7.00 (m, 1H, ArH), 7.00-6.95 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.4, 134.8, 134.3, 134.1, 130.5, 129.3 (3C), 128.7, 128.3, 127.0, 125.4, 124.3, 124.2, 121.7 (2C); IR (ATR): ν = 3234, 1322, 1160, 692 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 283 (M^+, 29%), 219 (16), 218 (56), 217 (15), 128 (20), 127 (100), 92 (14).

4-methoxy-*N*-phenylbenzenesulfonamide (5c):[9] White solid; m.p. 105-107 °C; R_f= 0.60 (hexane/ethyl acetate: 1/1); t_r = 17.32 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.6 Hz, 2H, ArH), 7.22 (ap t, J = 7.6 Hz, 2H, ArH), 7.15-7.05 (m, 3H, ArH), 6.87 (d, J = 8.6 Hz, 2H, ArH), 3.81 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.2, 136.8, 130.7, 129.6 (2C), 129.4 (2C), 125.3, 121.7 (2C), 114.3 (2C), 55.7; IR (ATR): ν = 3255, 1336, 1152, 695 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 263 (M^+, 61%), 171 (100), 123 (21), 107 (50), 92 (35), 77 (32), 65 (20), 64 (12).

3,4,5-trimethoxy-*N*-phenylbenzenesulfonamide (5d): White solid; m.p. 121-123 °C; R_f= 0.50 (hexane/ethyl acetate: 1/1); t_r = 20.43 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H, NH), 7.30-7.20 (m, 2H, ArH), 7.15-7.10 (m, 3H, ArH), 7.01 (s, 2H, ArH), 3.84 (s, 3H, OCH_3), 3.74 (s, 6H, 2xOCH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.2 (2C), 141.8, 136.7, 133.4, 129.4 (2C), 125.7, 122.1 (2C), 104.6 (2C), 61.0, 56.4 (2C);IR (ATR): ν = 3259, 1312, 1148, 1125 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 324 (M^++1, 14%), 323 (M^+, 81), 244 (11), 231 (19), 183 (25), 168 (14), 167 (100), 137 (13), 109 (11), 92 (15), 81 (11), 77 (12), 66 (12), 65 (14). HRMS calcd. (%) for $C_{15}H_{17}NO_5S$: 323.0827; found: 323.0824.

4-(dimethylamino)-*N*-phenylbenzenesulfonamide (5e): White solid; m.p. 172-174 °C; R_f= 0.27 (hexane/ethyl acetate: 7/1); t_r = 20.49 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.55 (m, 2H, ArH), 7.25-7.20 (m, 2H, ArH), 7.10-7.00 (m, 3H, ArH), 6.72 (s, 1H, NH), 6.60-6.55 (m, 2H, ArH), 3.00 (s, 6H, 2xCH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0, 137.3, 129.3 (2C), 129.2 (2C), 124.9, 124.5, 121.3 (2C), 111.0 (2C), 40.2 (2C); IR (ATR): ν = 3253, 1315, 1137, 1090 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 277 (M^++1, 13%), 276 (M^+, 70), 184 (67), 136 (100), 120 (69), 119 (11), 105 (16), 104 (16), 91 (11), 77 (20), 65 (14), 64 (18); HRMS calcd. (%) for $C_{14}H_{16}N_2O_2S$: 276.9032; found: 276.0942.

4-fluoro-*N*-phenylbenzenesulfonamide (5f):[9] White solid; m.p. 106-108 °C; R_f = 0.47 (hexane/ethyl acetate: 7/1); t_r = 15.99 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85-7.75 (m, 2H, ArH), 7.30-7.20 (m, 3H, ArH + NH), 7.25-7.05 (m, 5H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4 (d, J = 255.4 Hz), 136.3, 135.0 (d, J = 3.3 Hz), 130.1 (d, J = 9.5 Hz, 2C), 129.5 (2C), 125.8, 122.0 (2C), 116.4 (d, J = 22.6 Hz, 2C); IR (ATR): ν = 1334, 1149, 840 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 251 (M^+, 64%), 186 (21), 159 (18), 95 (33), 92 (100), 75 (12), 65 (33).

4-bromo-*N*-phenylbenzenesulfonamide (5g):[9] White solid; m.p. 106-109 °C; R_f= 0.57 (hexane/ethyl acetate: 1/1); t_r = 16.85 min; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70-7.60 (m, 2H, ArH), 7.55-7.50 (m, 2H, ArH), 7.40 (s, 1H, NH), 7.30-7.20 (m, 2H, ArH), 7.15-7.05 (m, 3H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.0, 136.2, 132.5 (2C), 129.6 (2C), 128.9 (2C), 128.2, 125.9, 121.9 (2C); IR (ATR): ν = 3250, 1335, 1155, 741 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 313 (M^+Br^{81}, 32%), 311 (M^+Br^{79}, 31%), 220 (12), 218 (11), 168 (21), 157 (19), 155 (19), 92 (100), 76 (11), 75 (11), 65 (32).

***N*-phenyl-2-(trifluoromethyl)benzenesulfonamide (5h)**: White solid; m.p. 97-99 °C; R_f= 0.37 (hexane/ethyl acetate: 7/3); t_r = 15.95 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.9 Hz, 1H, ArH), 7.87 (d, J = 7.6 Hz, 1H, ArH), 7.64 (t, J = 7.6 Hz, 1H, ArH), 7.56 (td, J = 7.9, 0.8 Hz, 1H, ArH), 7.25-7.20 (m, 2H, ArH), 7.15-7.10 (m, 1H, ArH), 7.10-7.00 (m, 2H, ArH), 6.75 (s, 1H, NH);^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.3, 125.7, 133.2, 132.6, 132.3, 129.5 (2C), 128.6 (q, J = 6.3 Hz), 127.8 (q, J = 32.9 Hz), 126.1, 123.1 (q, J = 273.8 Hz), 122.32 (2C); IR (ATR): ν = 3278, 1497, 1352, 1160 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 301 (M^+, 53%), 207 (15), 145 (31), 92 (100), 65 (37); HRMS calcd. (%) for $C_{13}H_{10}F_3NO_2S$: 301.0384; found: 301.0381.

***N*-phenyl-3-(trifluoromethyl)benzenesulfonamide (5i)**: White solid; m.p. 79-81 °C; R_f = 0.43 (hexane/ethyl acetate: 7/3); t_r = 15.56 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1H, NH), 7.96 (d, J = 7.9 Hz, 1H, ArH), 7.78 (d, J = 7.9 Hz, 1H, ArH), 7.58 (t, J = 7.9 Hz, 1H, ArH), 7.30-7.25 (m, 3H, ArH), 7.20-7.15 (m, 1H, ArH), 7.10-7.05 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.2, 135.8, 131.8 (q, J =33.5 Hz), 130.5, 130.0, 129.8 (q, J = 6.6 Hz), 129.6 (2C), 126.2, 124.2 (q, J = 7.2 Hz),

122.3 (2C), 120.45 (q, J = 272.9 Hz); IR (ATR): ν = 3231, 1322, 1165, 1155 cm^{-1}; MS (70 eV, EI): m/z (%): 301 (M^+, 52%), 145 (22), 92 (100), 65 (28); HRMS calcd. (%) for $C_{13}H_{10}F_3NO_2S$: 301.0384; found: 301.0382.

***N*-(2-benzoyl-4-chlorophenyl)-4-methylbenzenesulfonamide (5j)**:[14] Yellow solid; m.p. 114-116 °C; R_f = 0.53 (hexane/ethyl acetate: 7/1); t_r = 28.14 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1H, NH), 7.76 (d, J = 8.8 Hz, 1H, ArH), 7.65-7.55 (m, 1H, ArH), 7.53 (d, J = 8.3 Hz, 2H, ArH), 7.48 (dd, J = 8.8, 2.5 Hz, 1H, ArH), 7.45-7.40 (m, 2H), 7.40-7.35 (m, 2H), 7.32 (d, J = 2.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H, ArH), 2.22 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.1, 144.1, 137.4, 136.9, 135.6, 133.6, 133.3, 132.3, 130.0 (2C), 129.8 (2C), 129.4, 128.4 (2C), 128.0, 127.3 (2C), 125.2, 21.5; IR (ATR): ν = 3265, 1636, 1379, 1183 cm^{-1}; MS (70 eV, EI): m/z (%): 387 (M^+ Cl^{37}, 29%), 385 (M^+ Cl^{35}, 29%), 232 (33), 230 (100), 195 (54), 167 (24), 166 (14), 155 (15), 139 (12), 91 (66), 77 (21).

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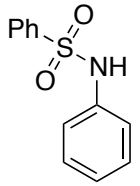
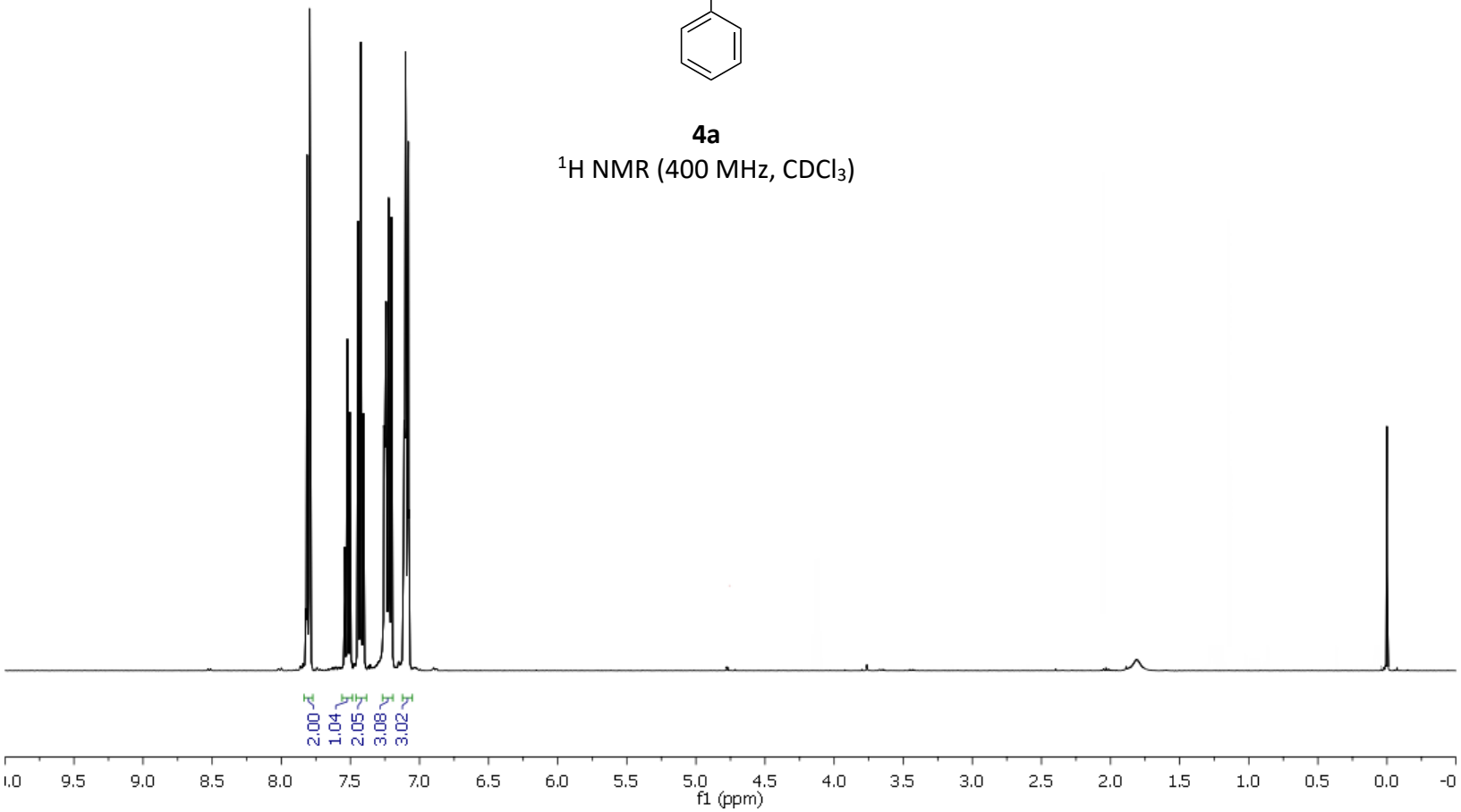
7. NMR Spectra



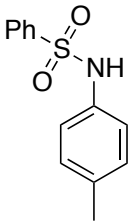
4a

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



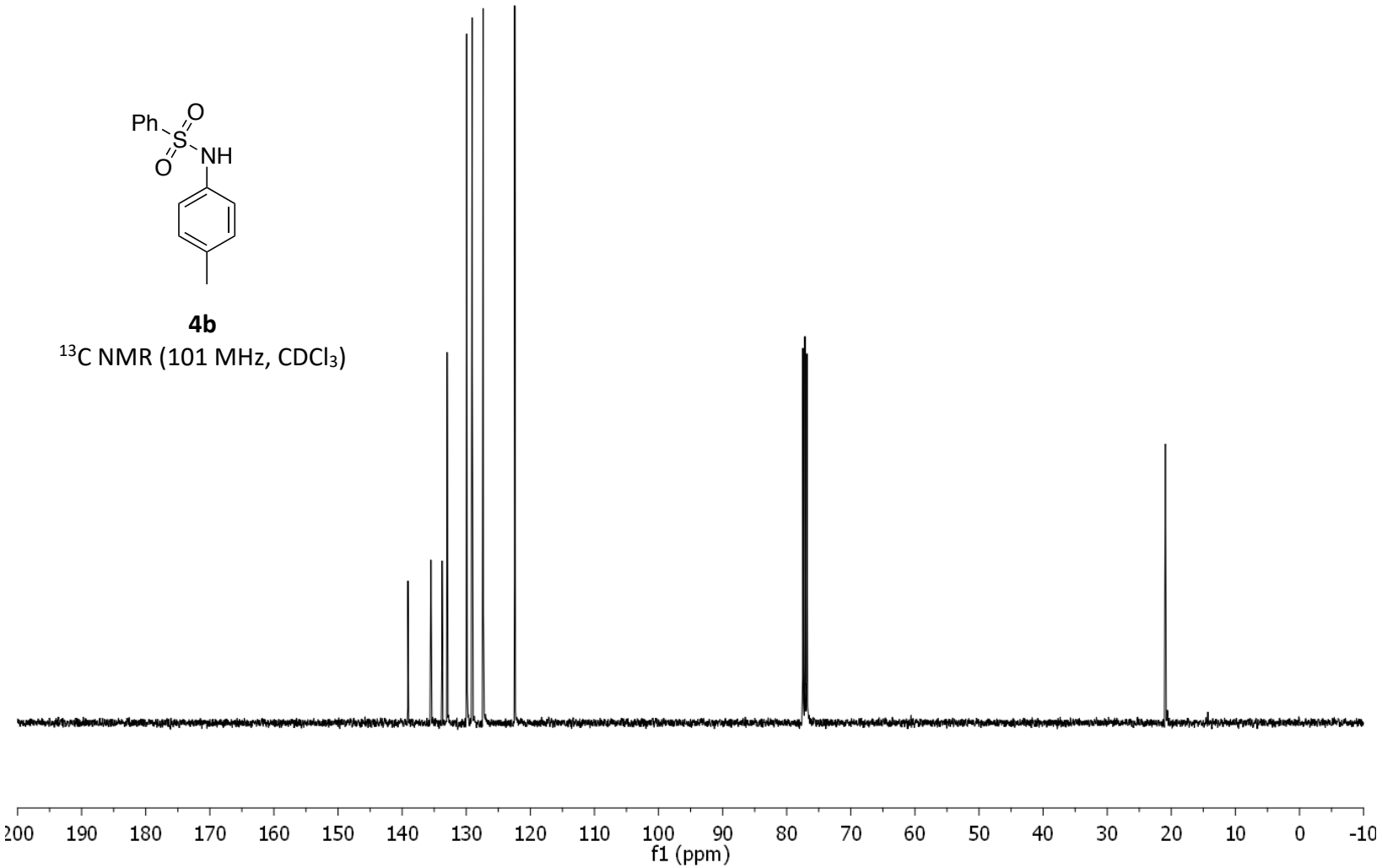
4a

^{13}C NMR (101 MHz, $CDCl_3$)



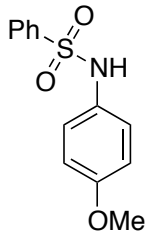
4b

^{1}H NMR (300 MHz, $CDCl_3$)



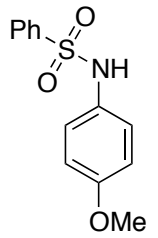
4b

^{13}C NMR (101 MHz, $CDCl_3$)



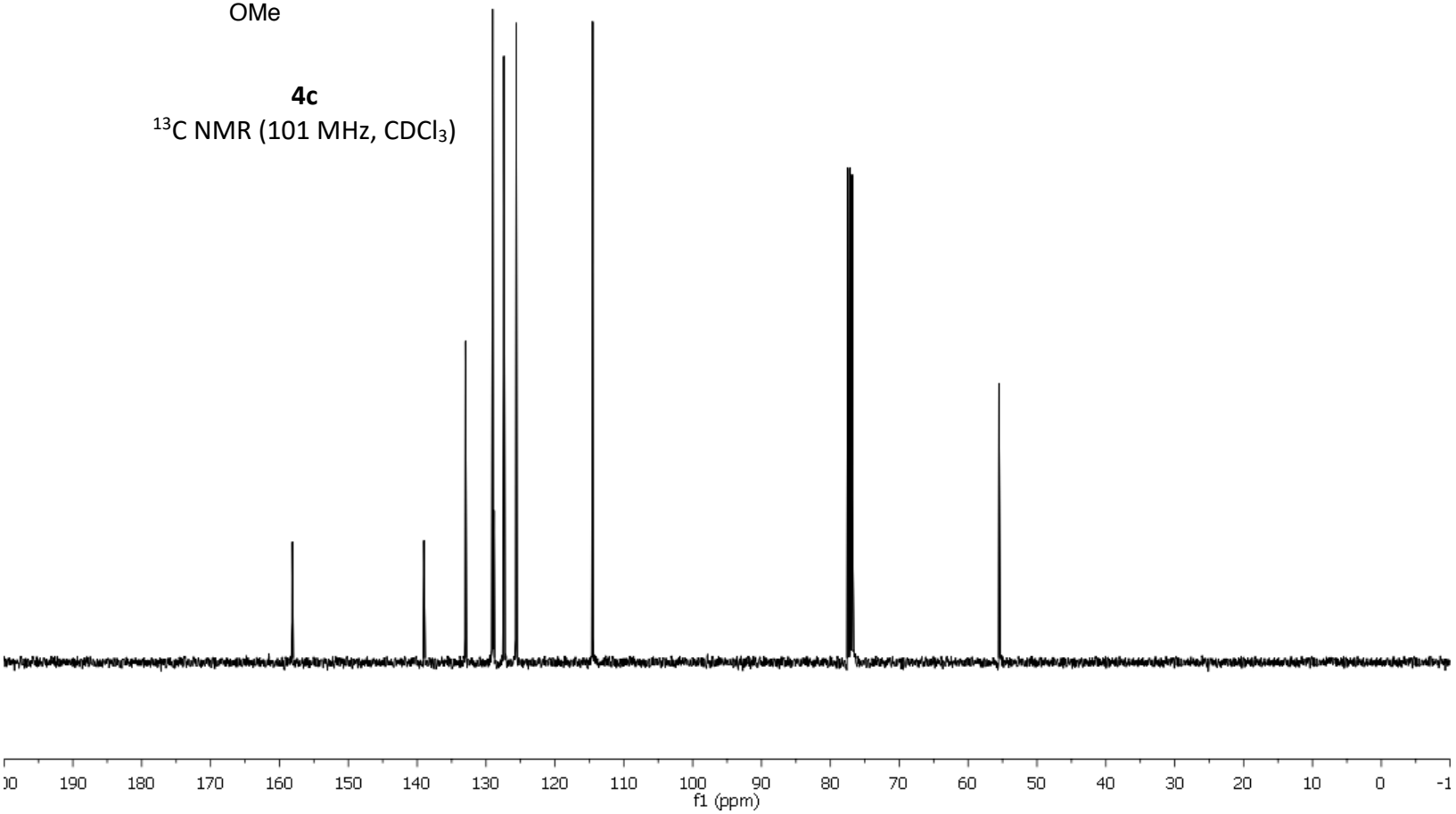
4c

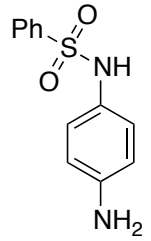
^{1}H NMR (300 MHz, $CDCl_3$)



4c

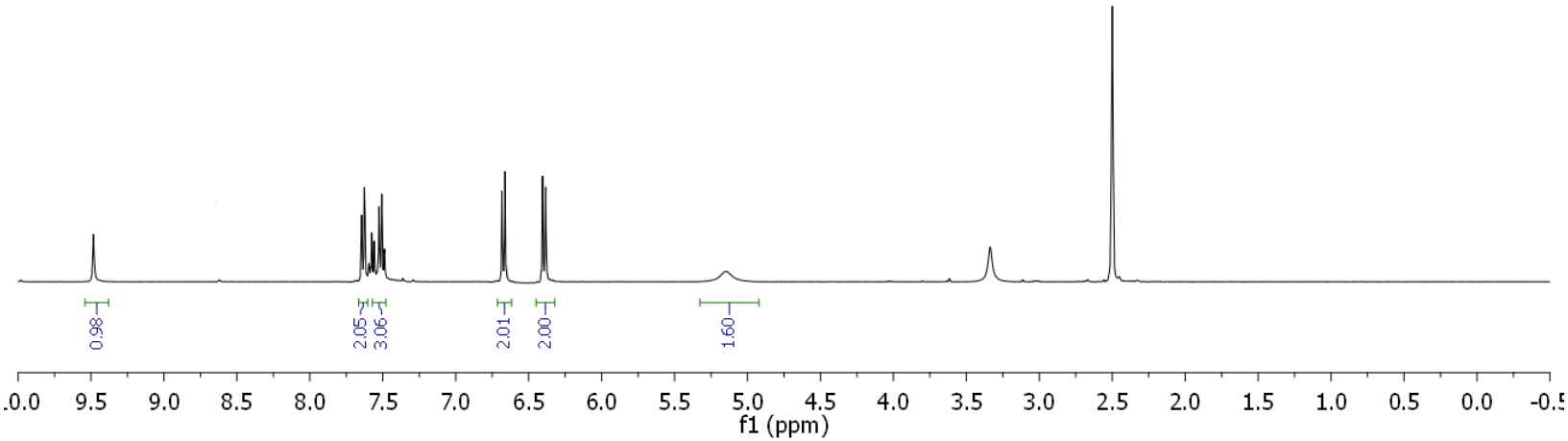
^{13}C NMR (101 MHz, $CDCl_3$)

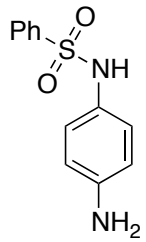




4d

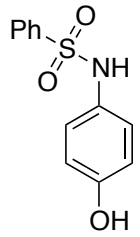
^{1}H NMR (400 MHz, DMSO-d_6)





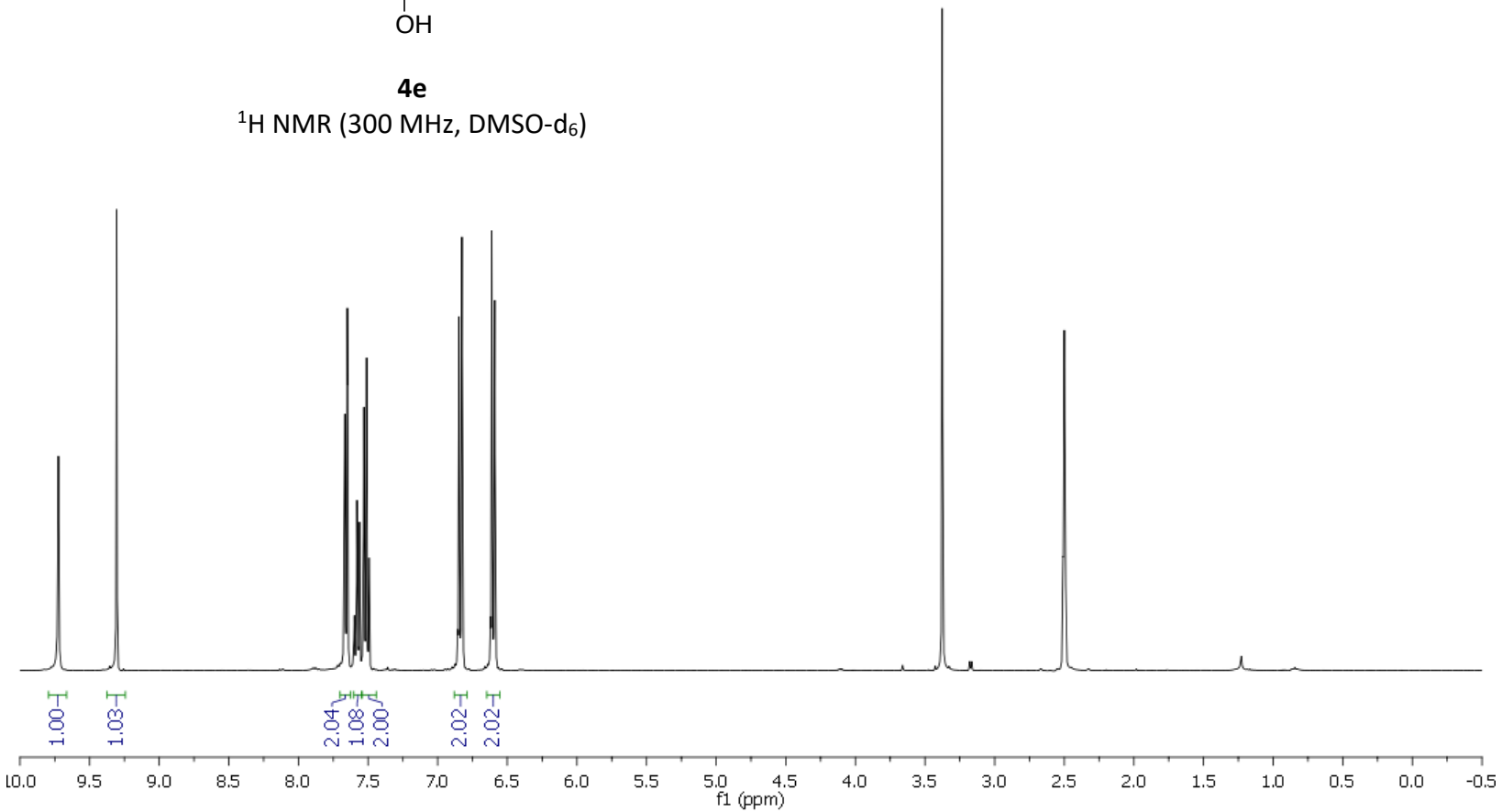
4d

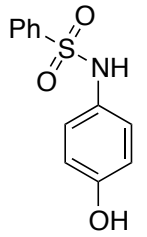
^{13}C NMR (101 MHz, DMSO-d_6)



4e

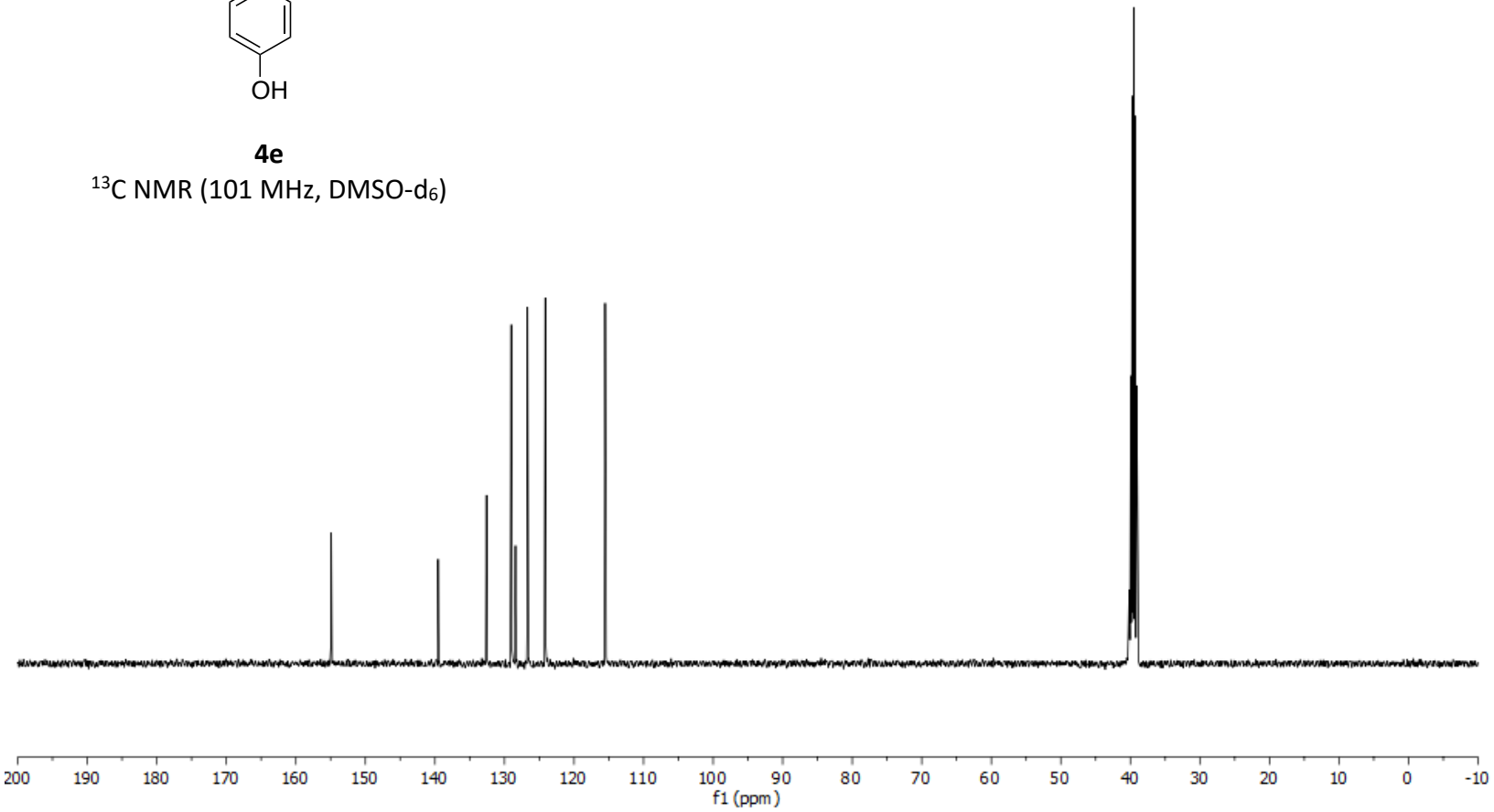
^{1}H NMR (300 MHz, DMSO-d_6)

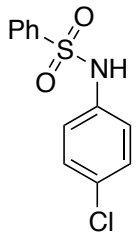




4e

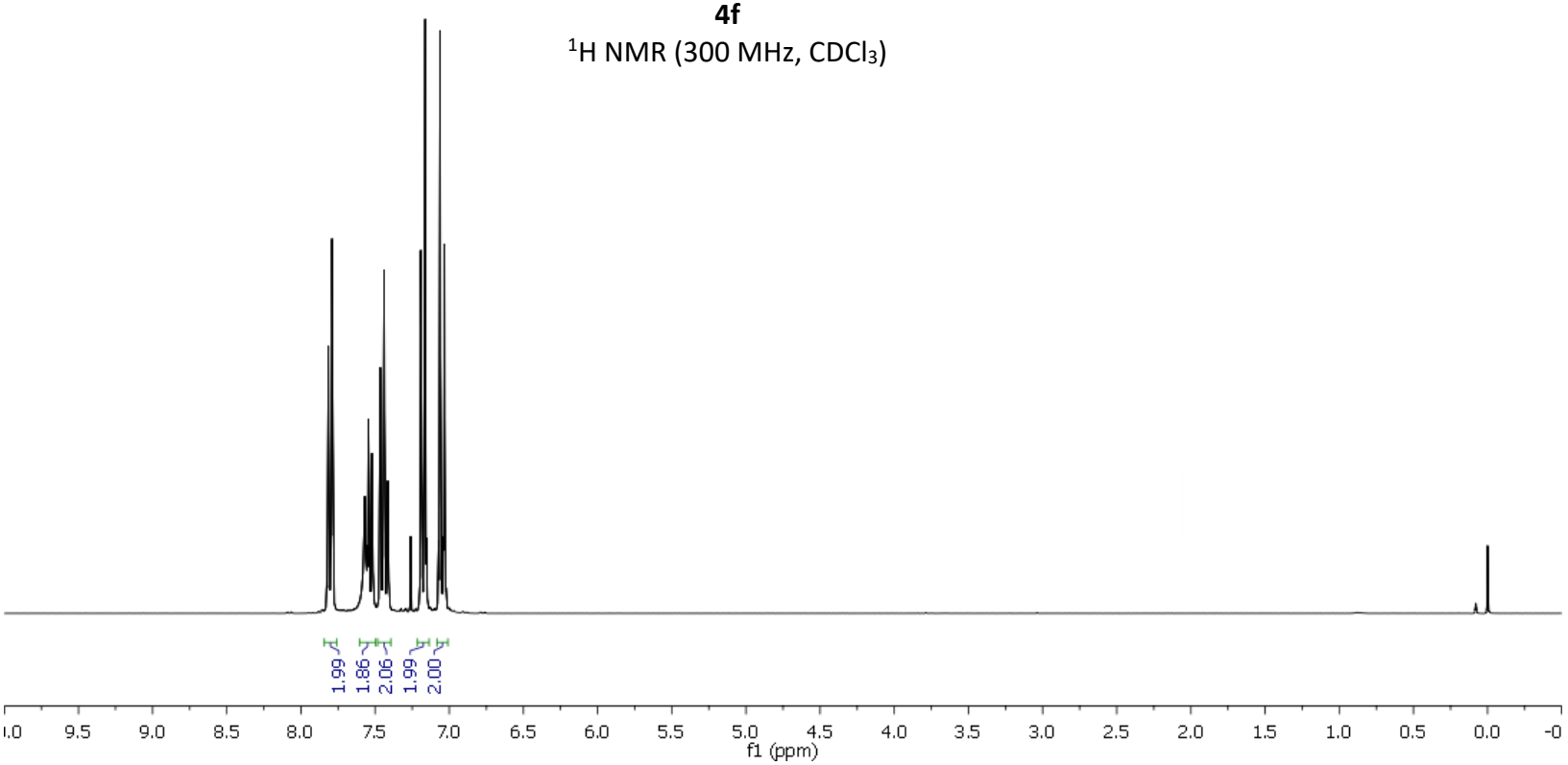
^{13}C NMR (101 MHz, DMSO-d_6)





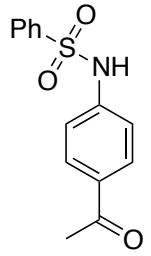
4f

^{1}H NMR (300 MHz, $CDCl_3$)



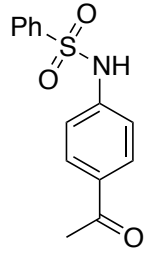
4f

^{13}C NMR (75 MHz, $CDCl_3$)



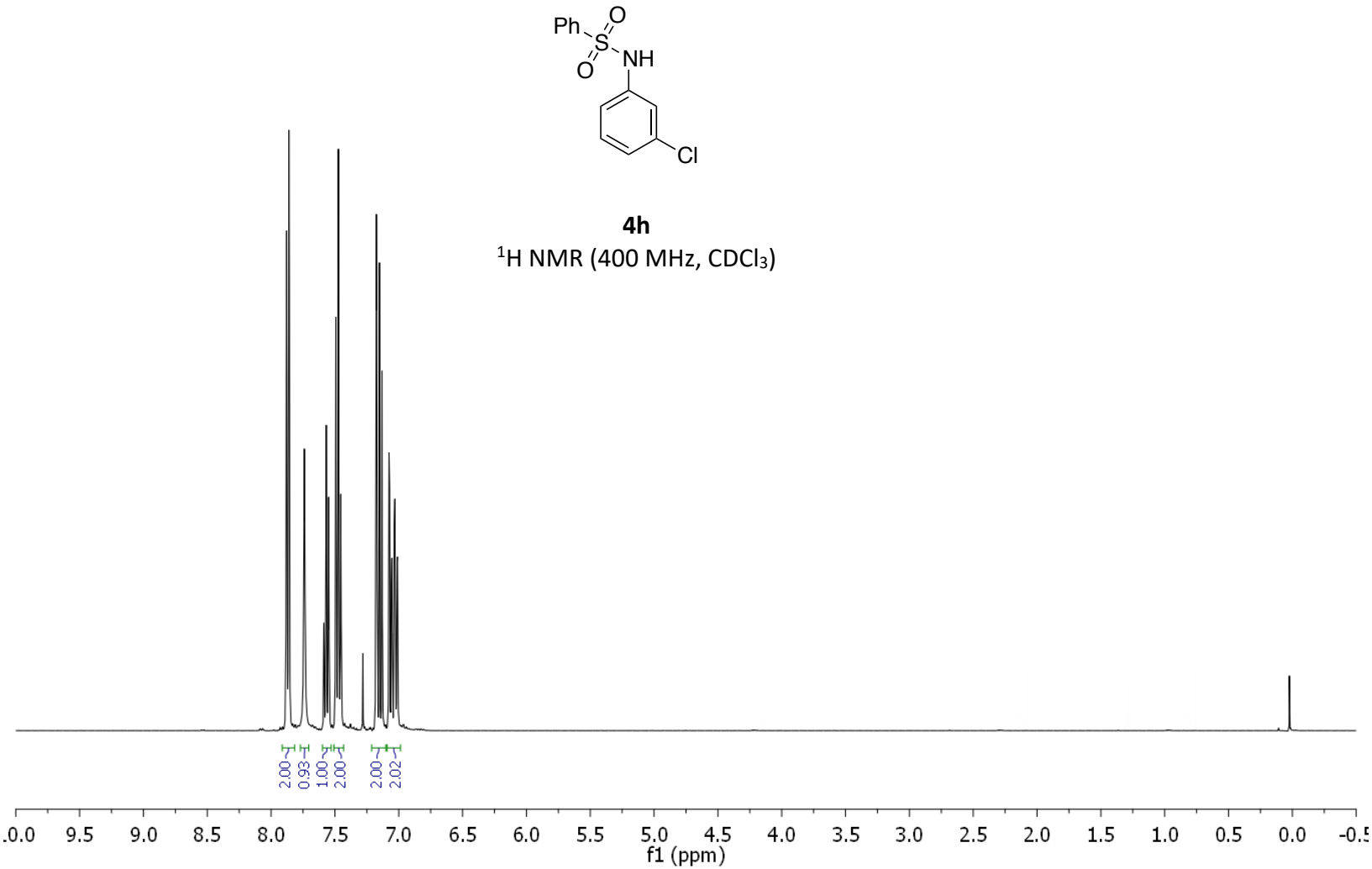
4g

^{1}H NMR (300 MHz, $CDCl_3$)



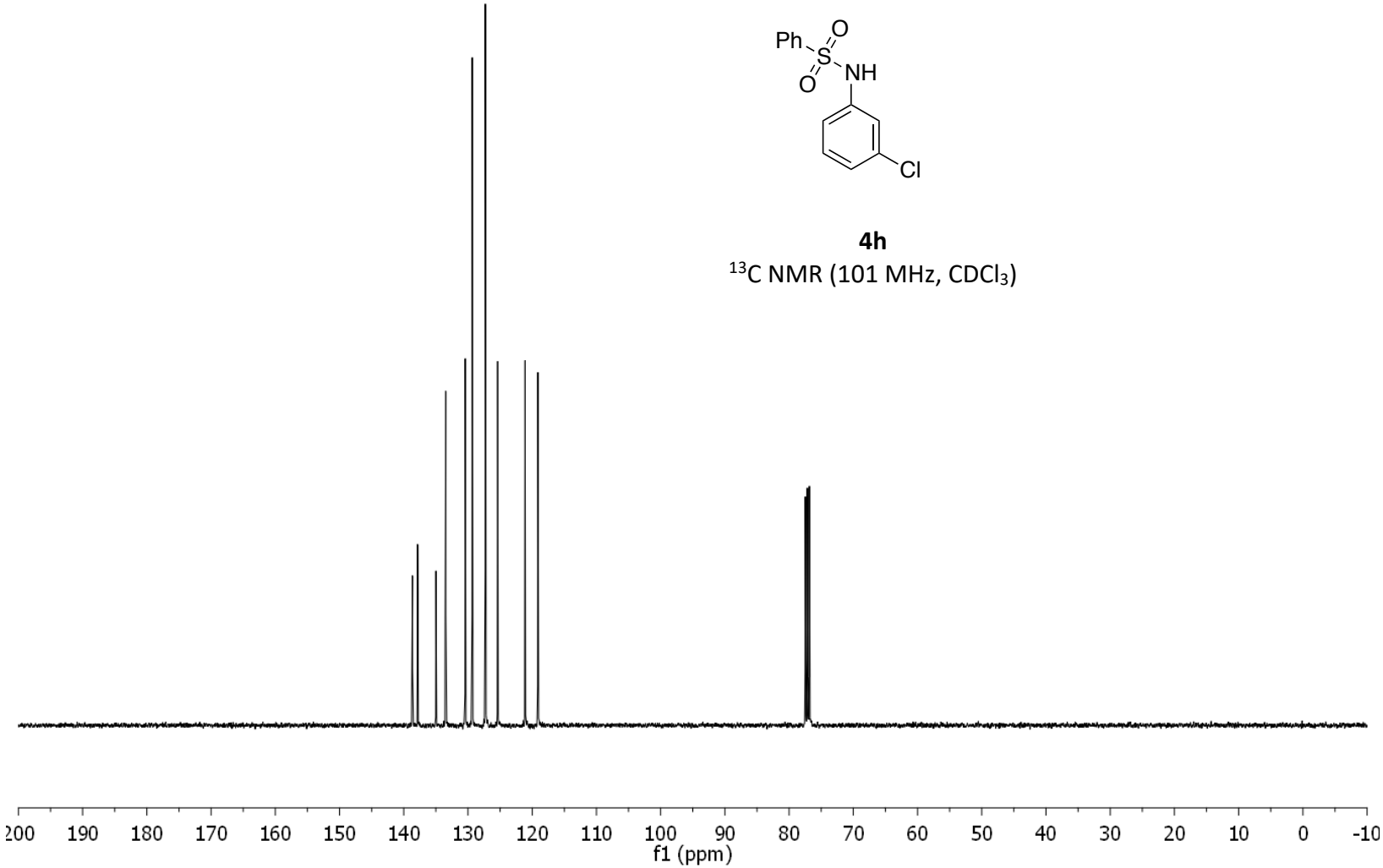
4g

^{13}C NMR (101 MHz, $CDCl_3$)



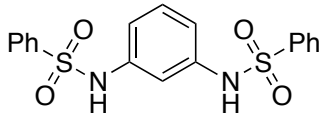
4h

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



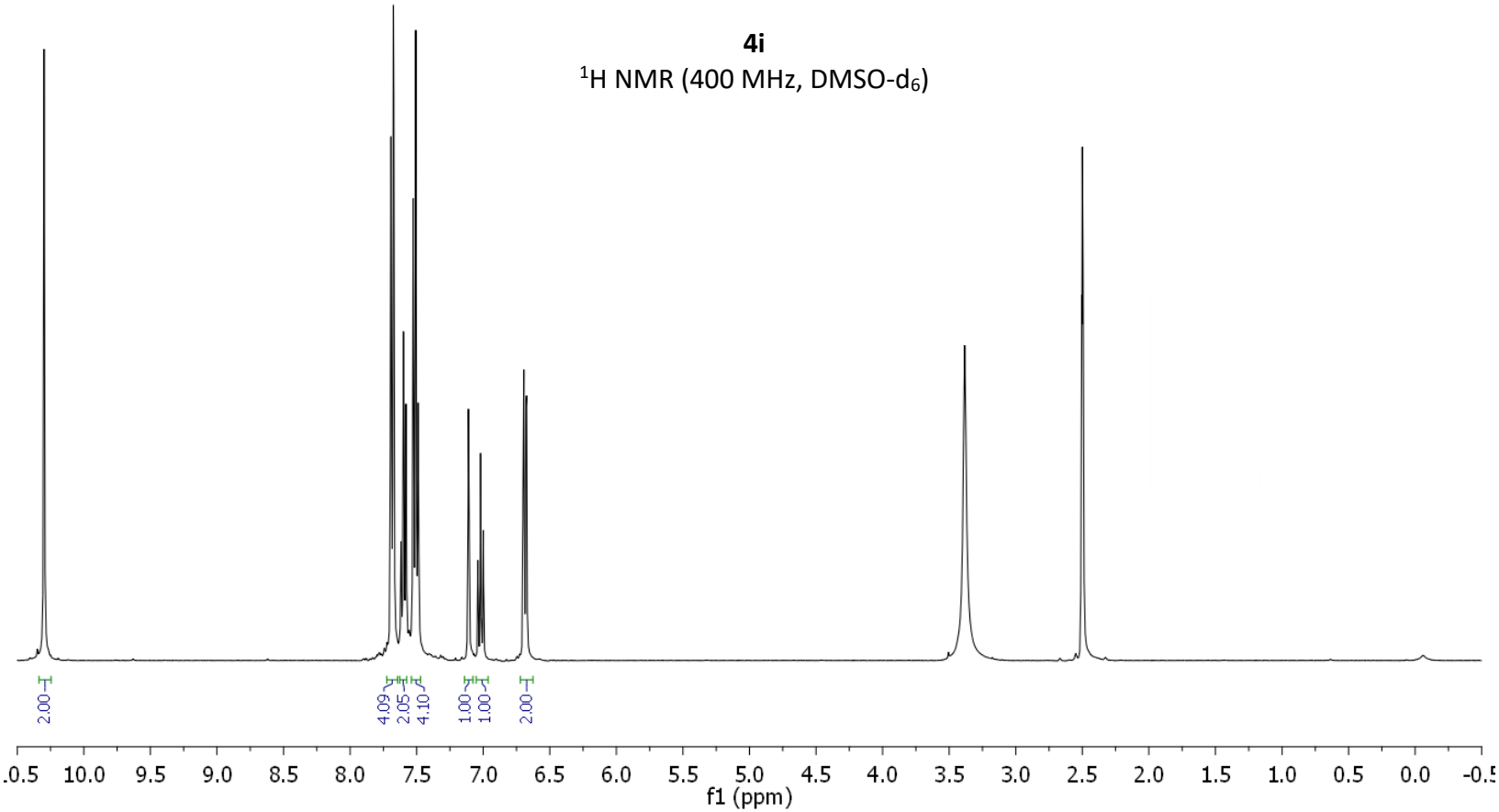
4h

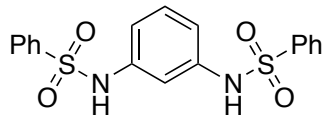
^{13}C NMR (101 MHz, $CDCl_3$)



4i

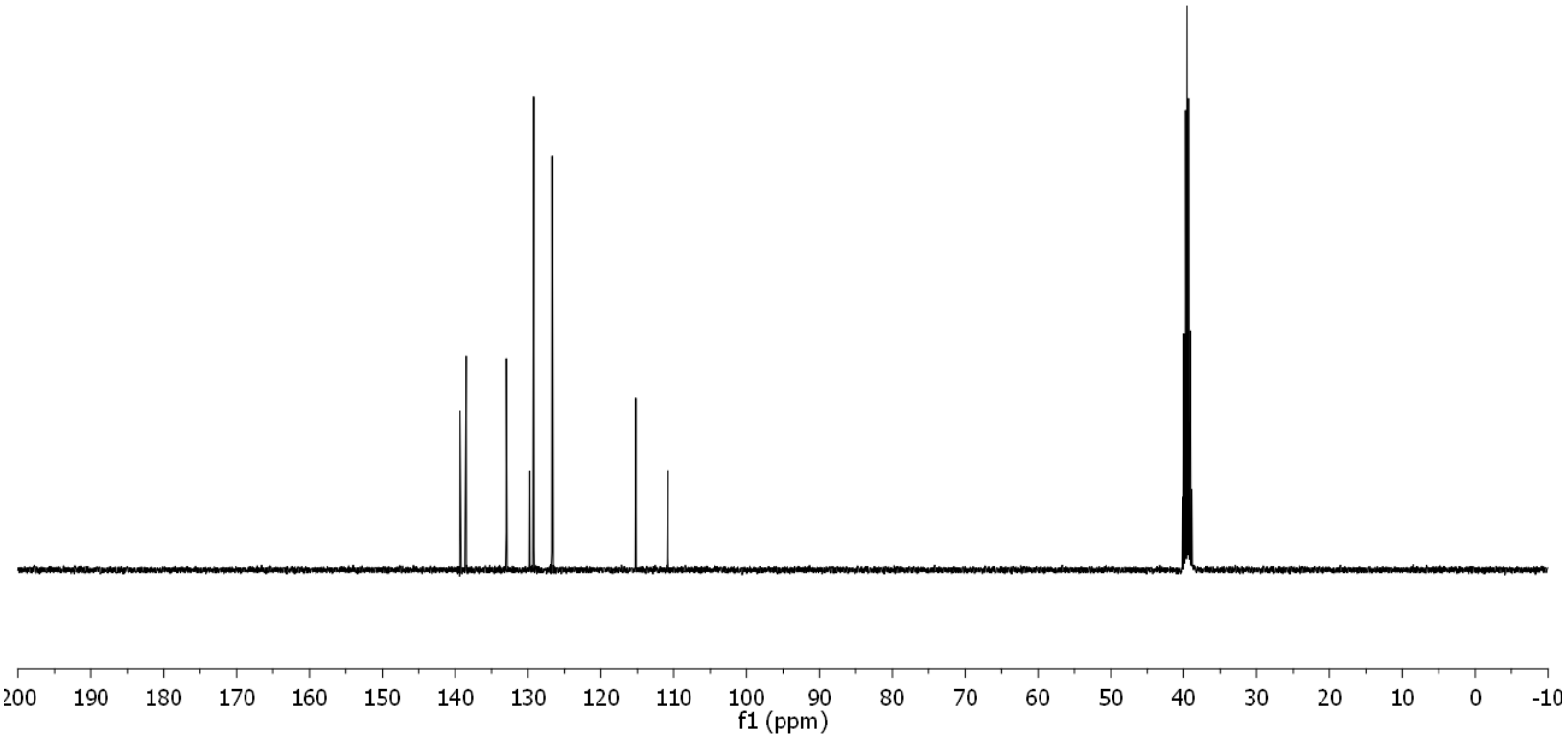
^{1}H NMR (400 MHz, DMSO-d_6)

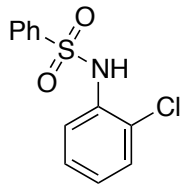




4i

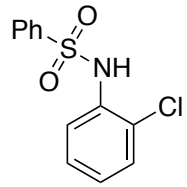
^{13}C NMR (101 MHz, DMSO-d_6)





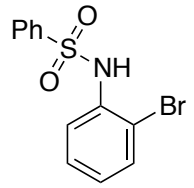
4j

^{1}H NMR (300 MHz, $CDCl_3$)



4j

^{13}C NMR (101 MHz, $CDCl_3$)



4k

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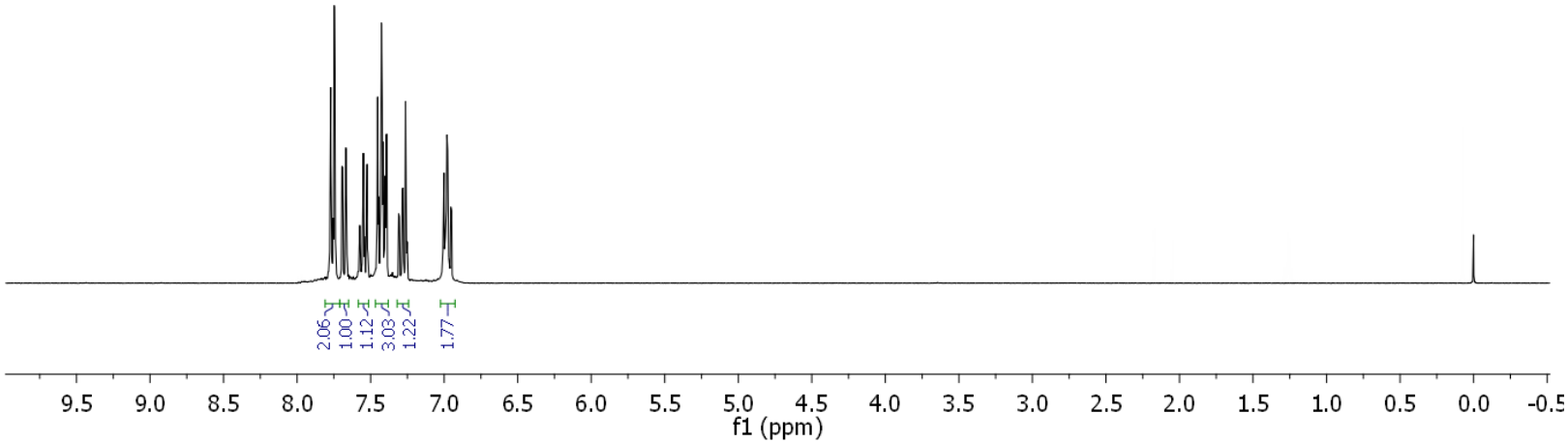

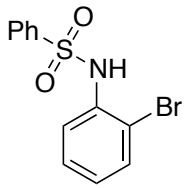

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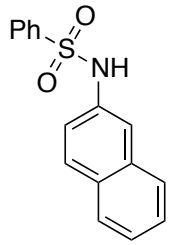

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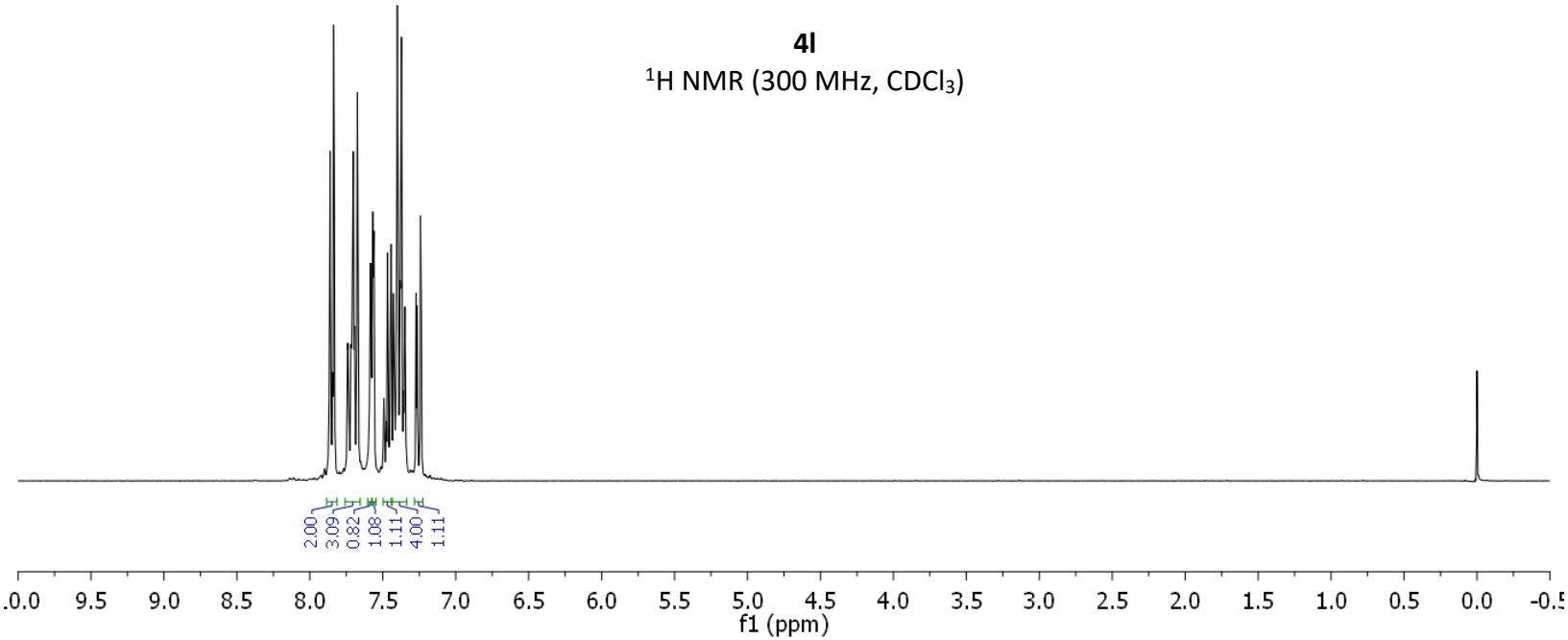
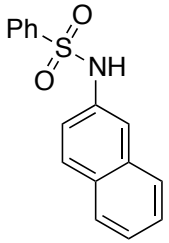
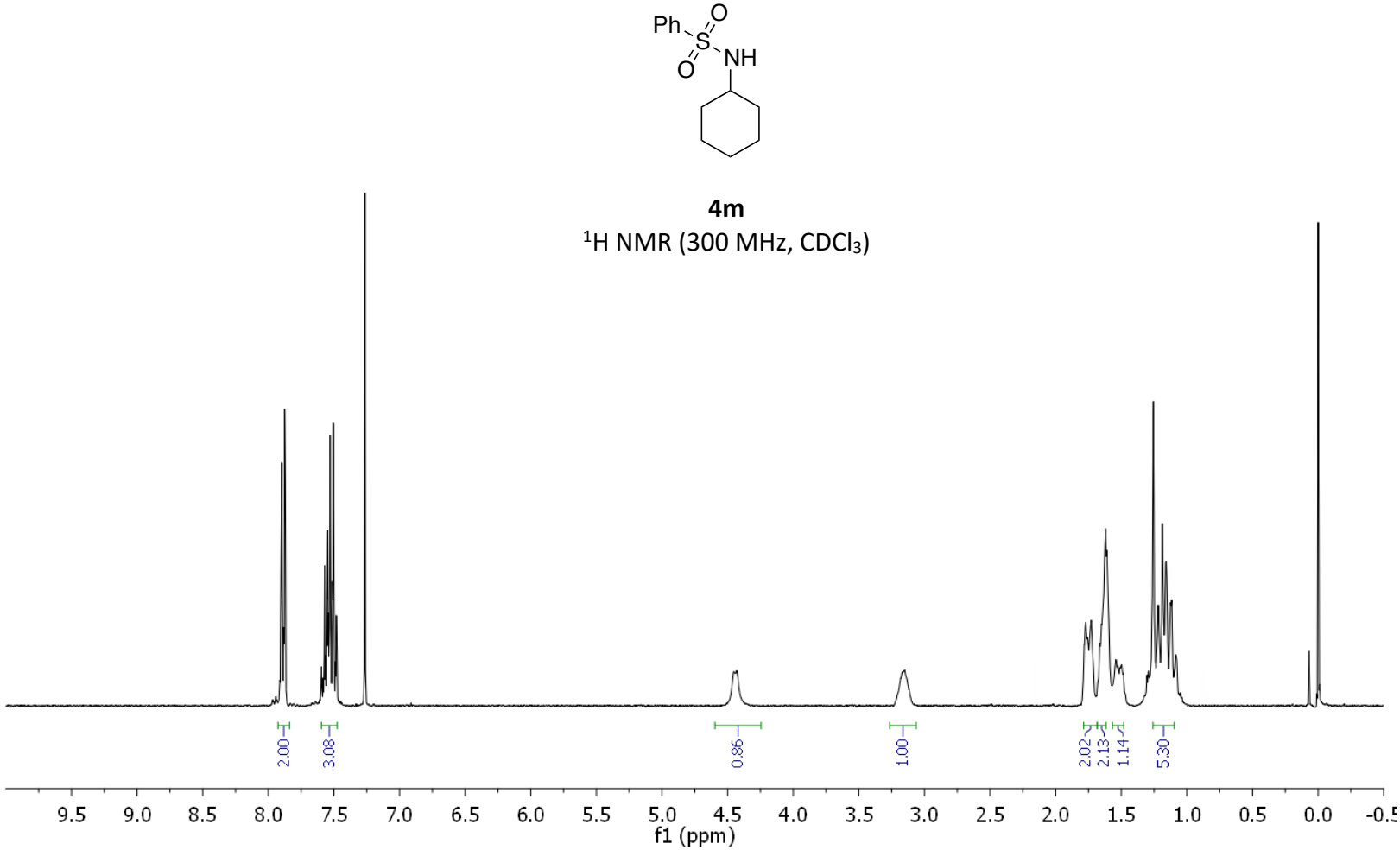
^{1}H NMR (300 MHz, $CDCl_3$)





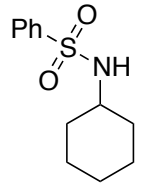
4l

^{13}C NMR (101 MHz, $CDCl_3$)



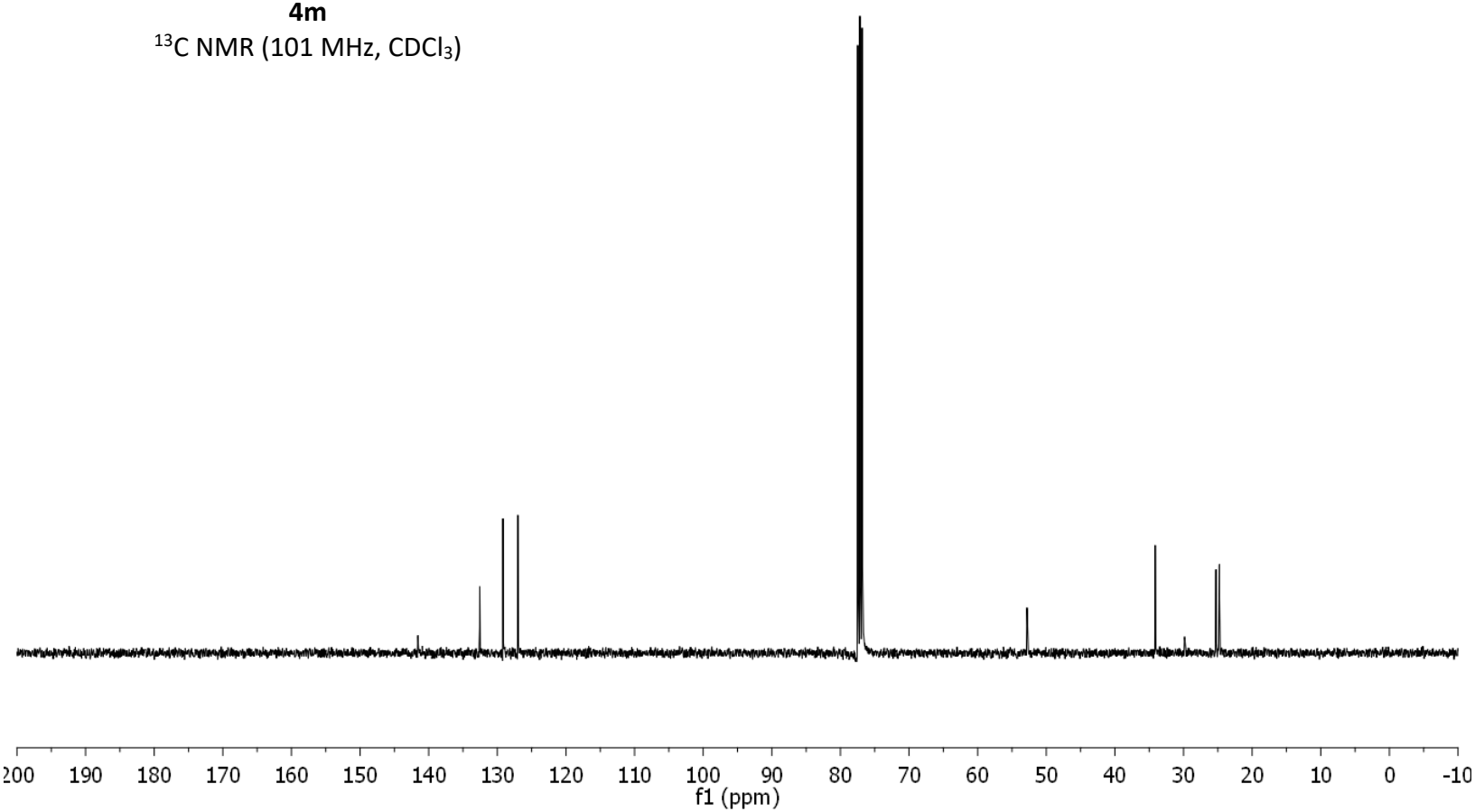
4m

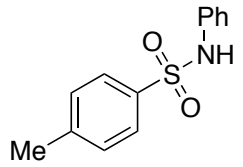
^{1}H NMR (300 MHz, $CDCl_3$)



4m

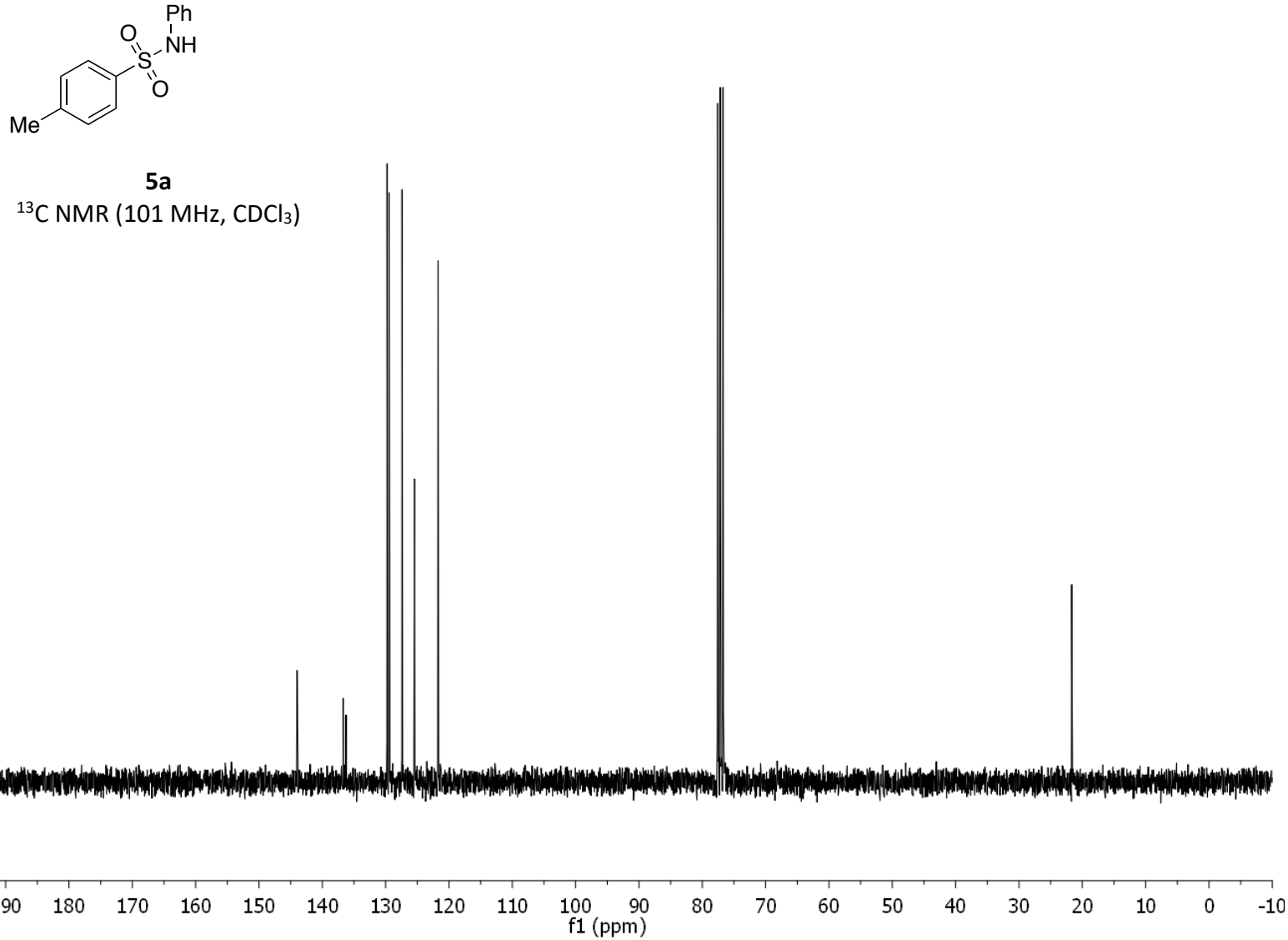
^{13}C NMR (101 MHz, $CDCl_3$)





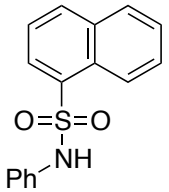
5a

^{1}H NMR (300 MHz, $CDCl_3$)



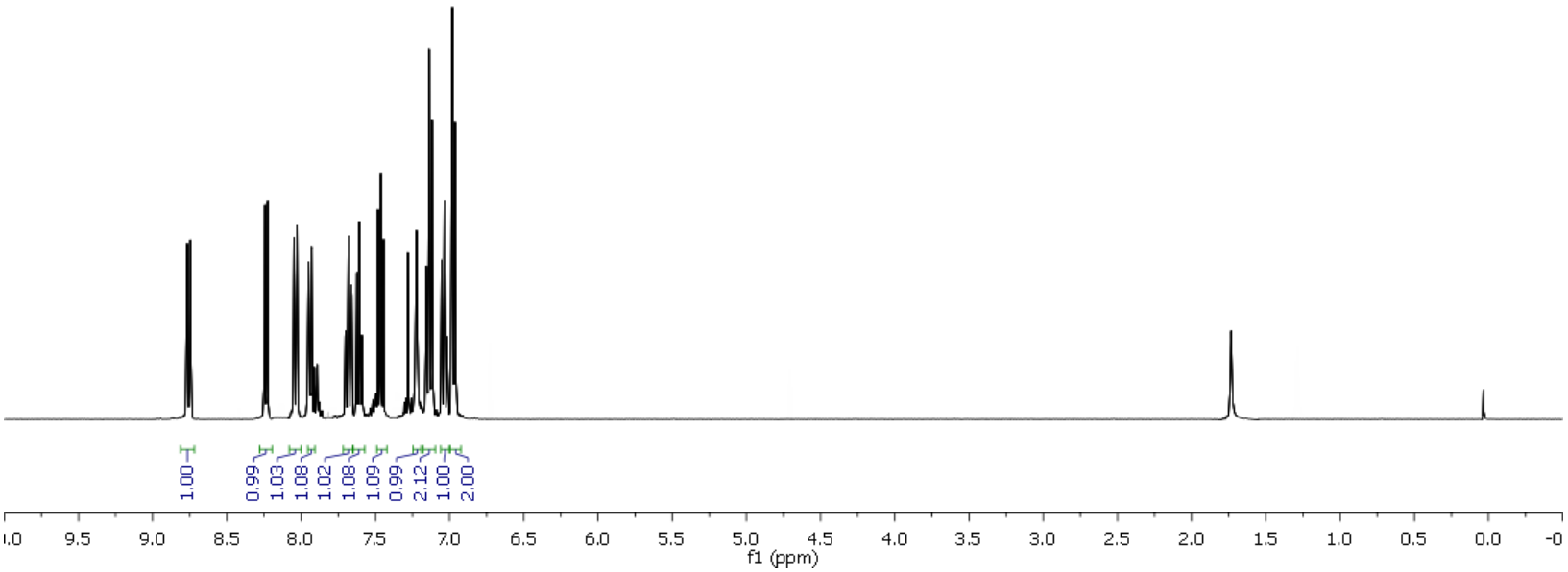
5a

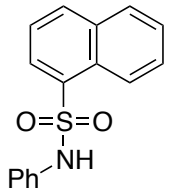
^{13}C NMR (101 MHz, $CDCl_3$)



5b

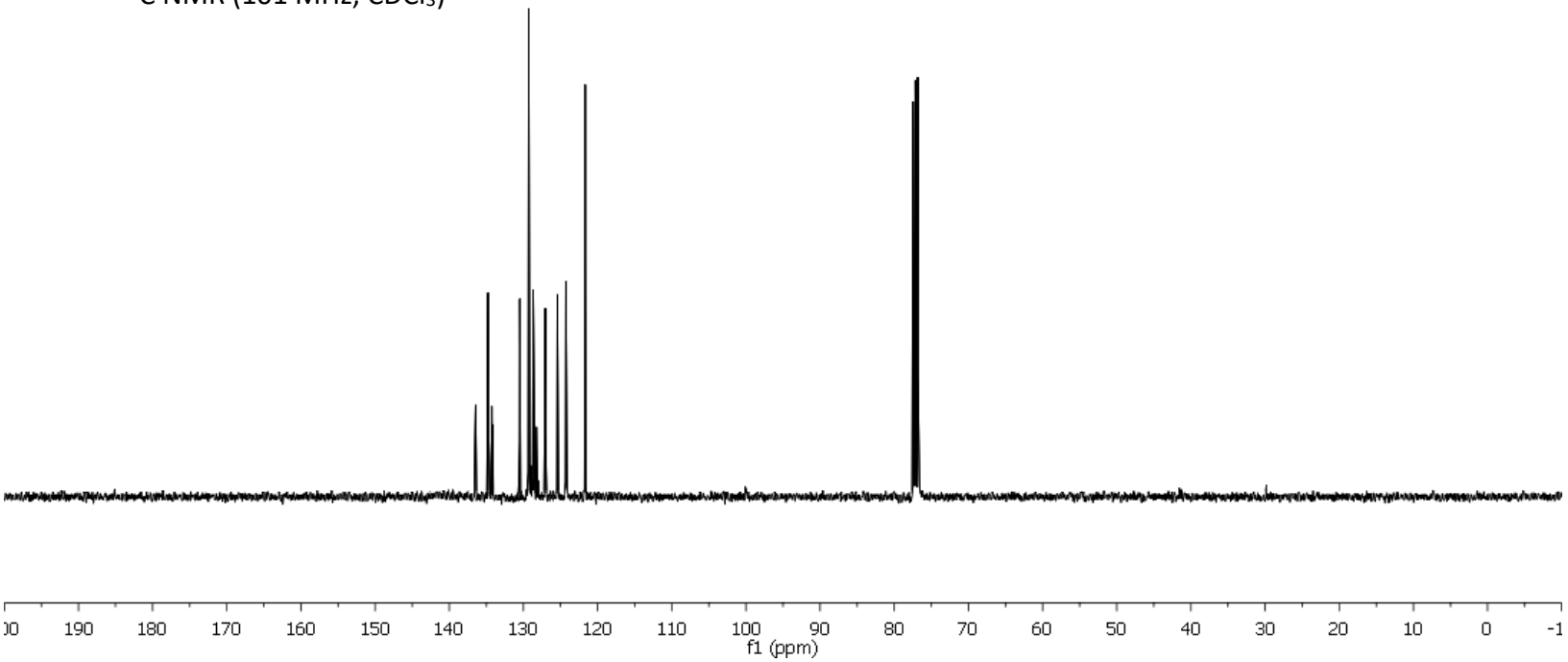
^{1}H NMR (300 MHz, $CDCl_3$)

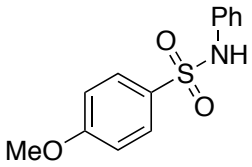




5b

^{13}C NMR (101 MHz, $CDCl_3$)





5c

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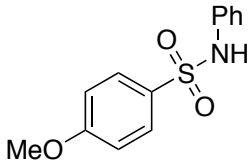
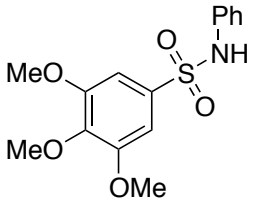


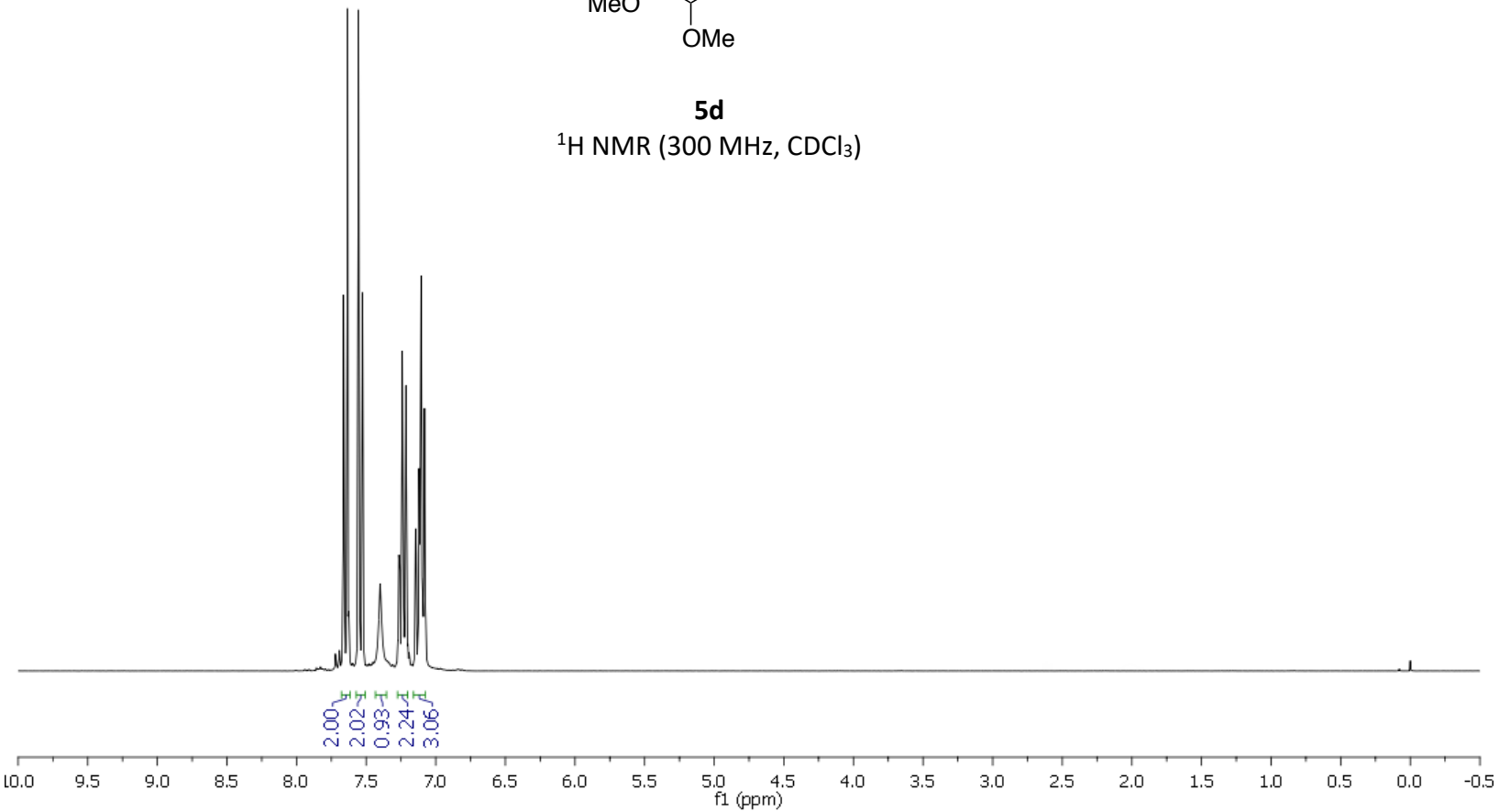
5c

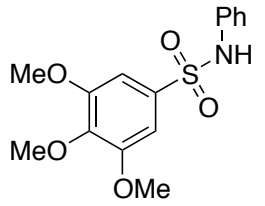
^{13}C NMR (101 MHz, $CDCl_3$)



5d

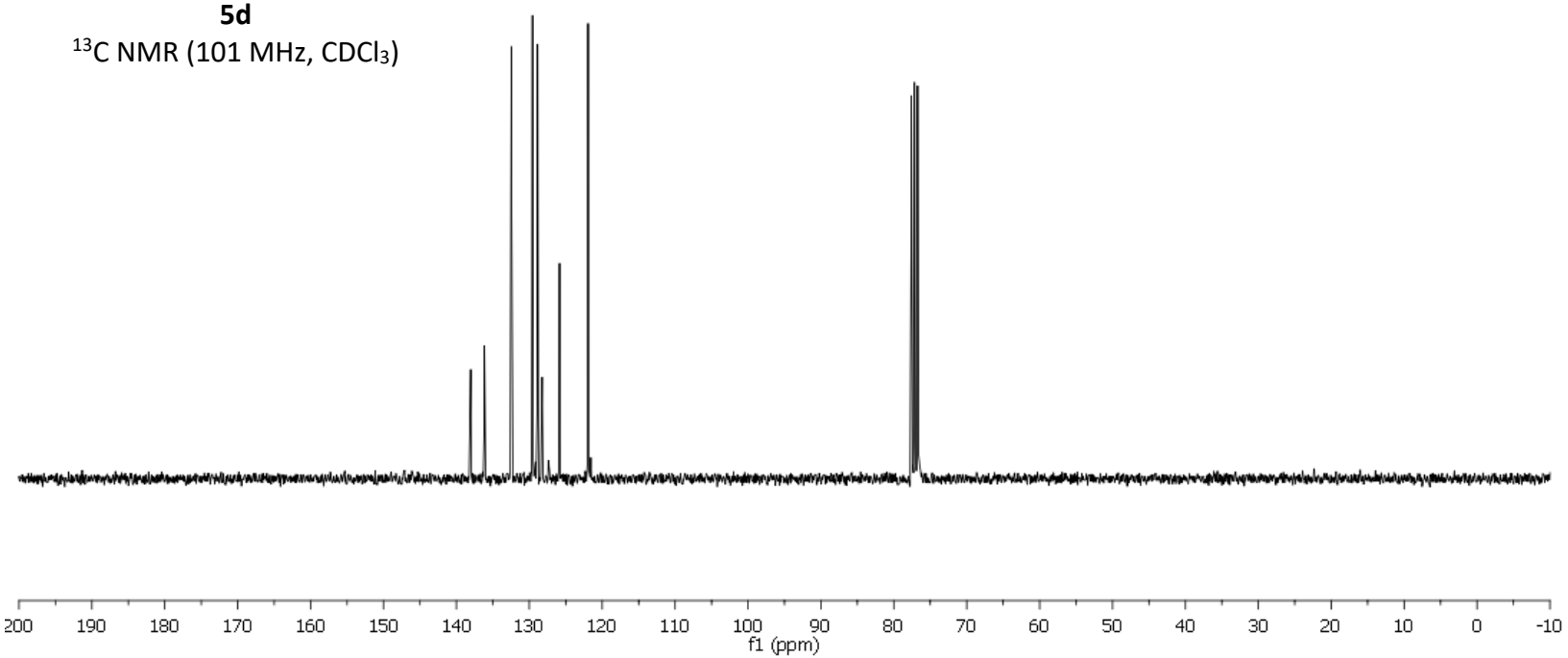
^{1}H NMR (300 MHz, $CDCl_3$)

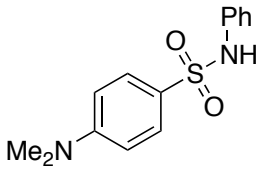




5d

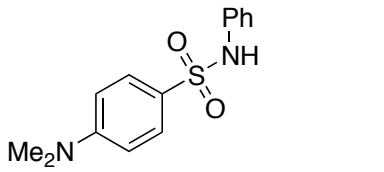
^{13}C NMR (101 MHz, $CDCl_3$)





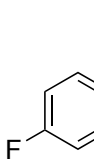
5e

^{1}H NMR (300 MHz, $CDCl_3$)



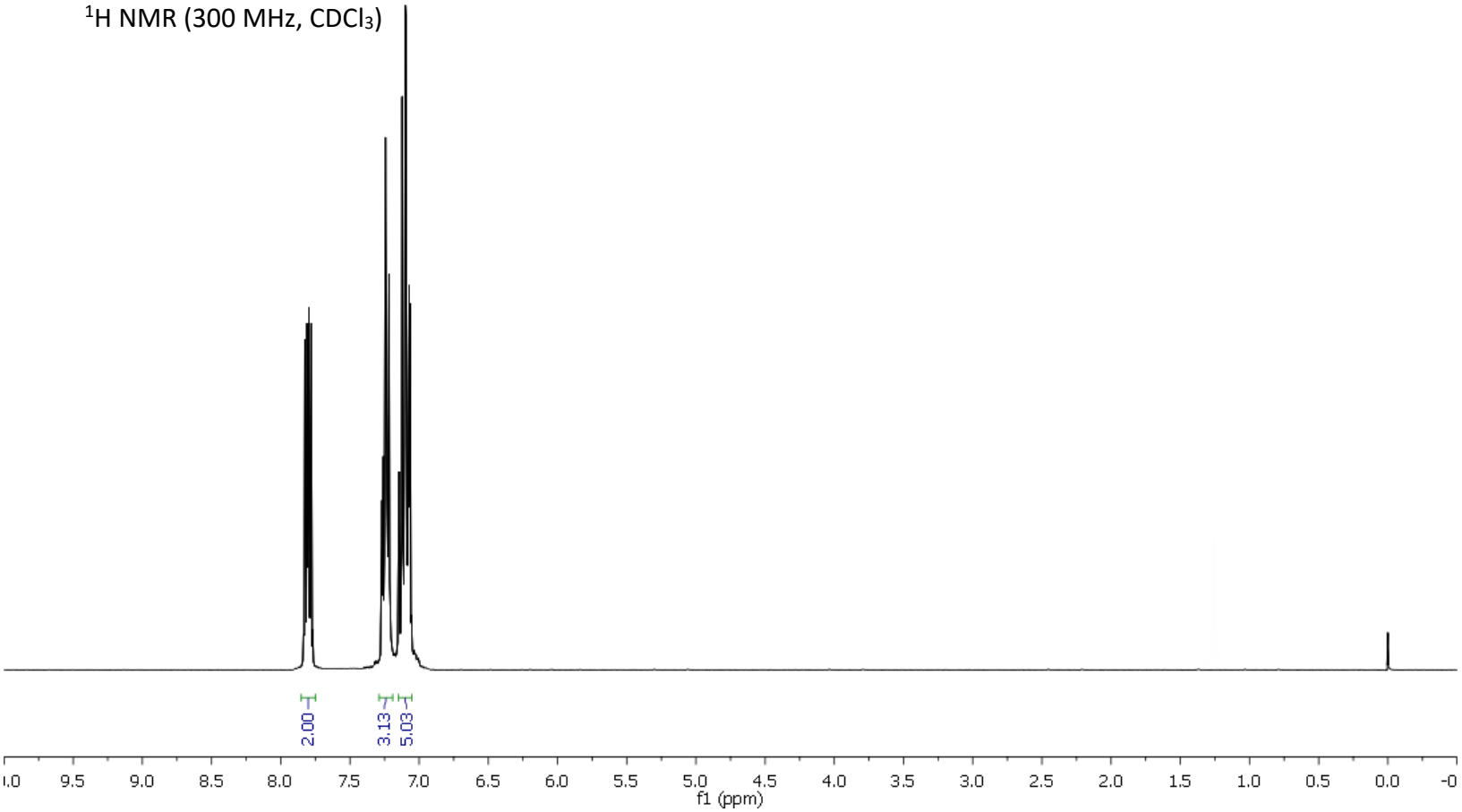
5e

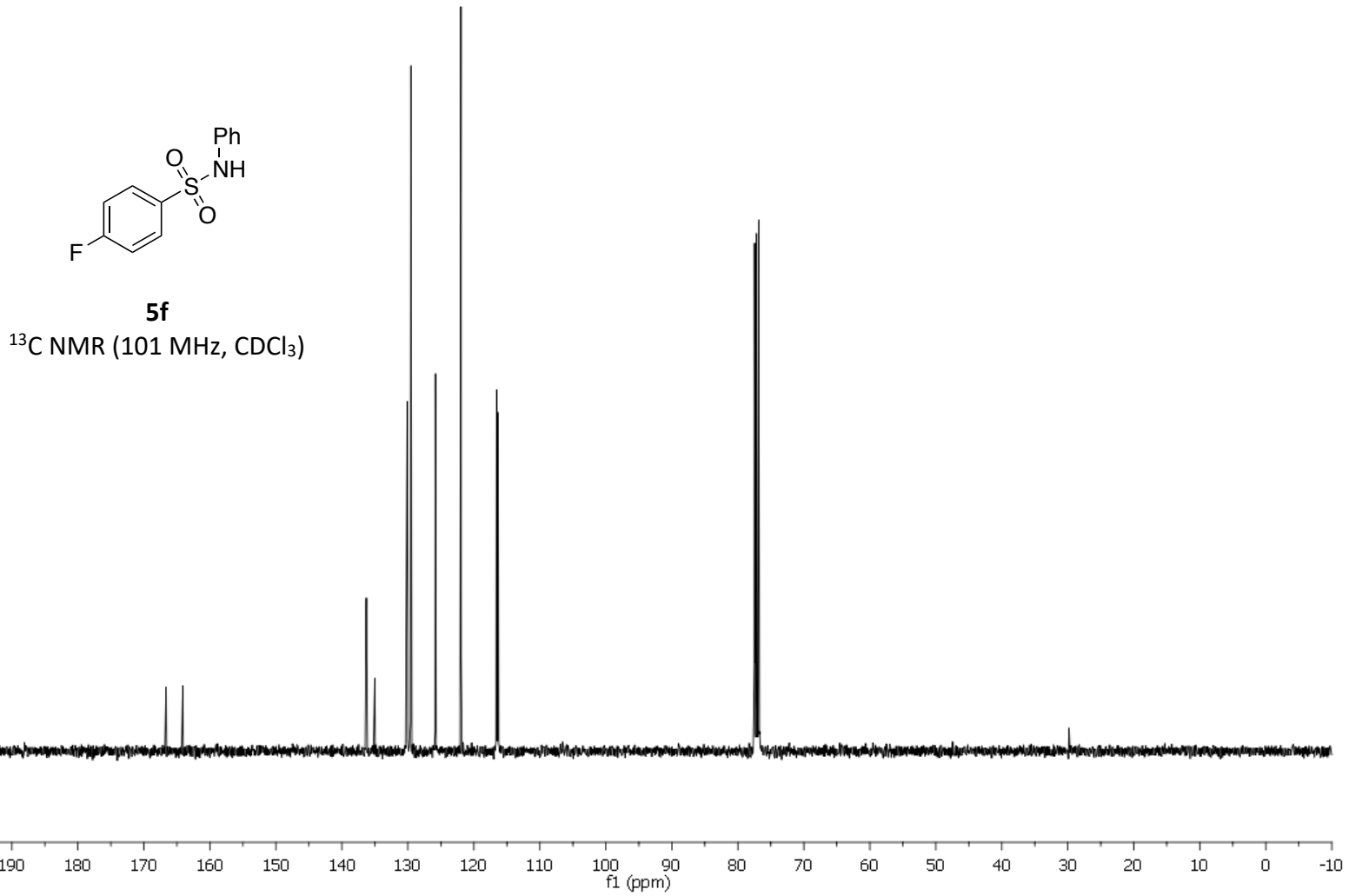
^{13}C NMR (101 MHz, $CDCl_3$)



5f

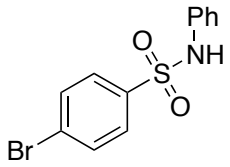
^{1}H NMR (300 MHz, $CDCl_3$)





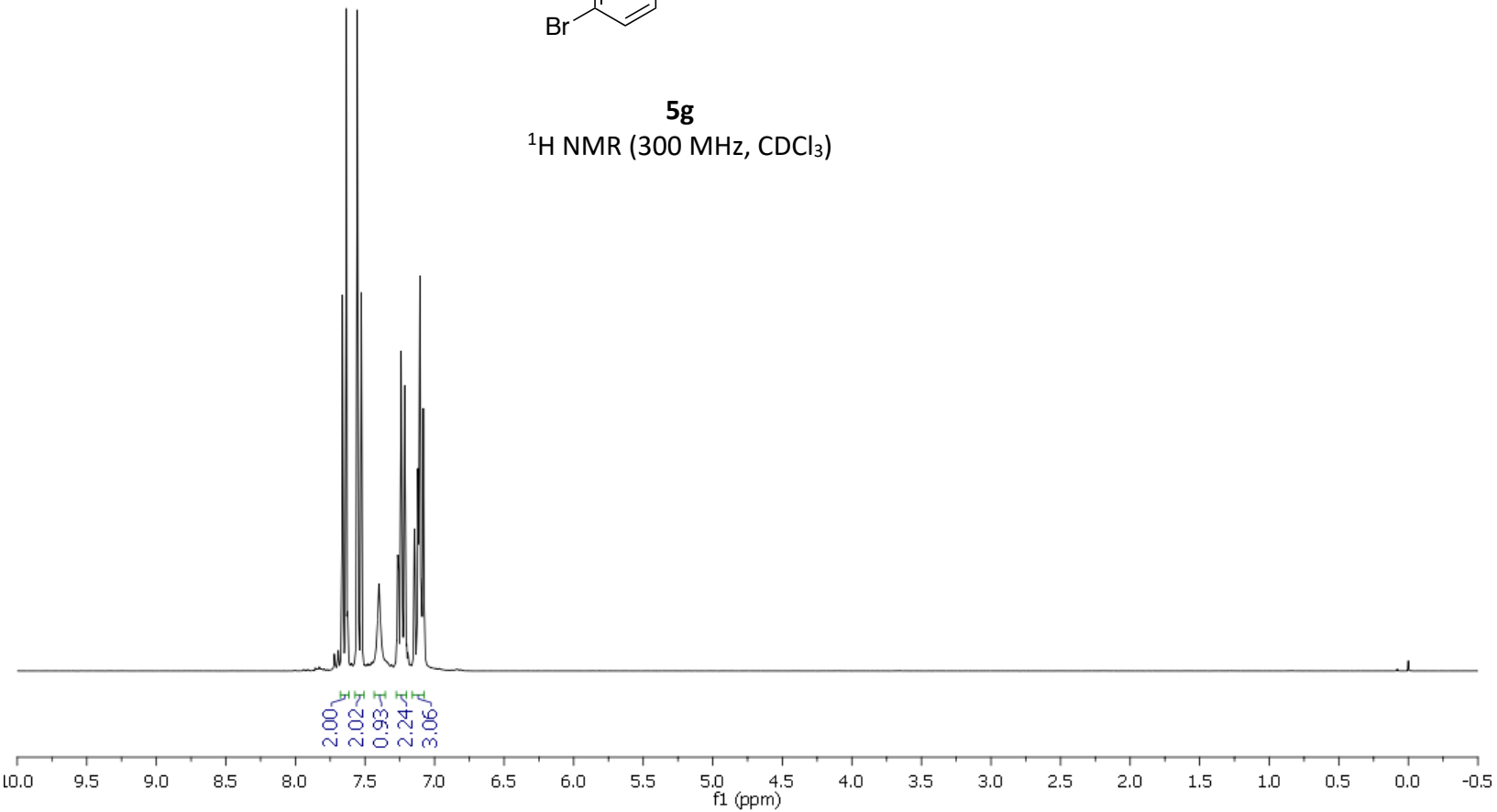
5f

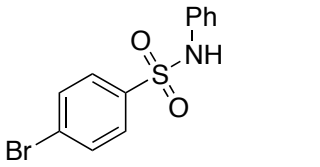
^{13}C NMR (101 MHz, $CDCl_3$)



5g

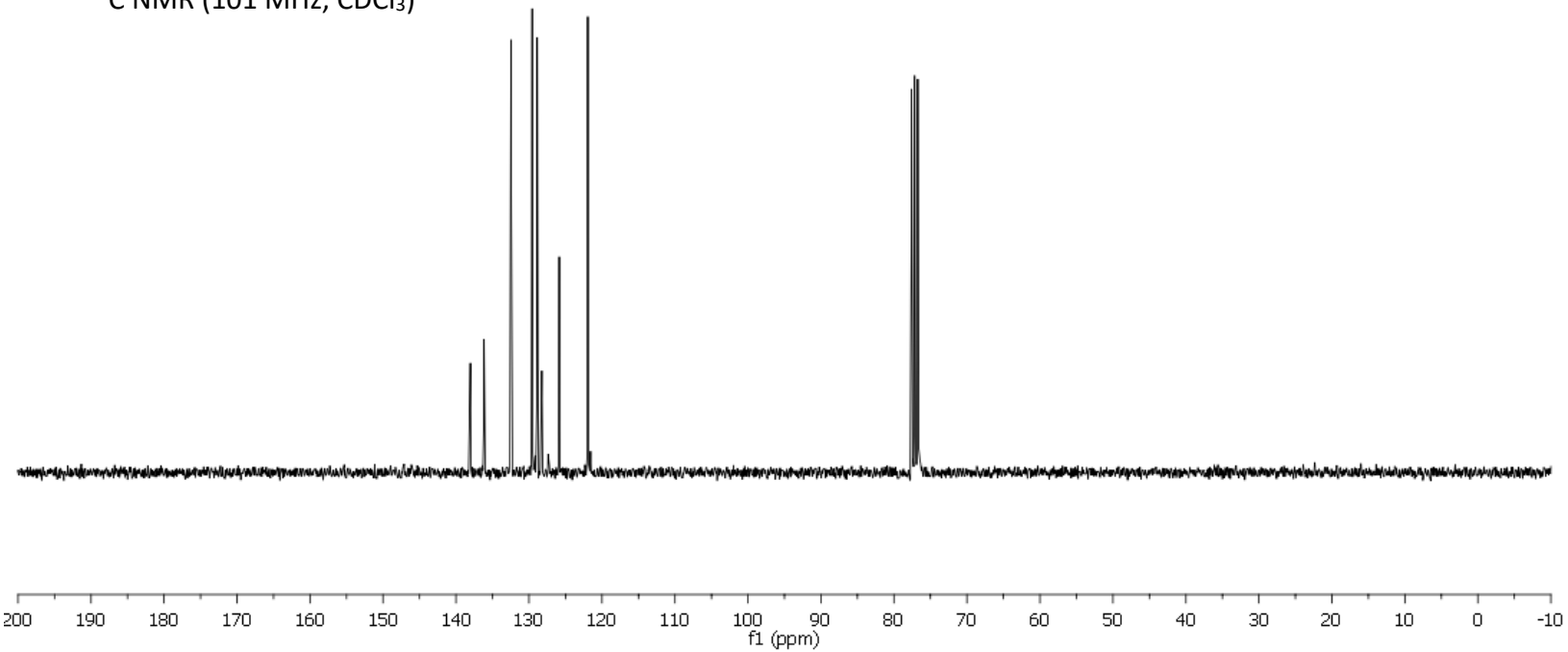
^{1}H NMR (300 MHz, $CDCl_3$)

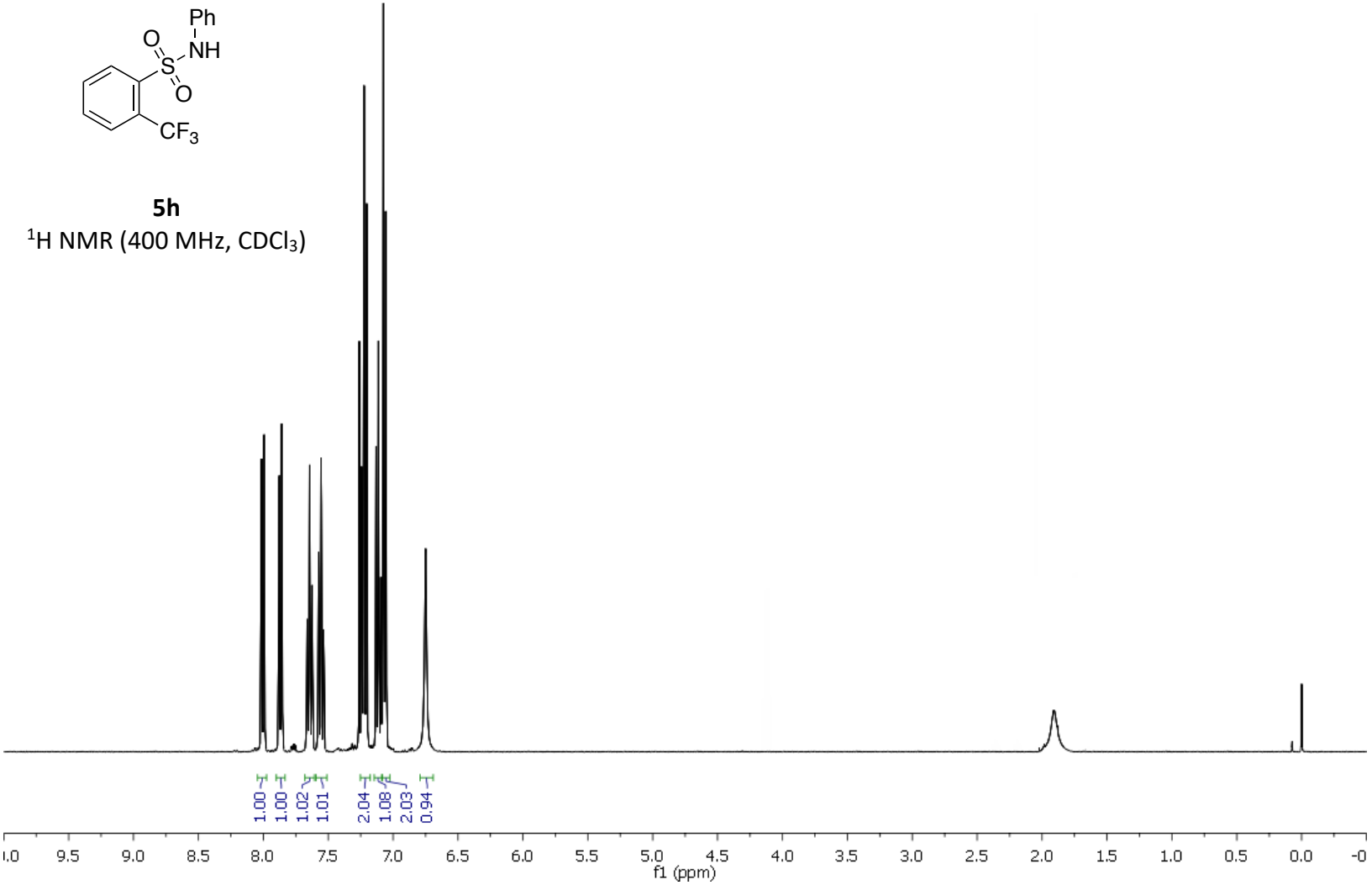




5g

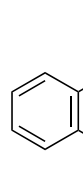
^{13}C NMR (101 MHz, $CDCl_3$)





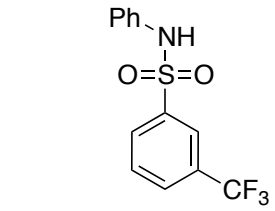
5h

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



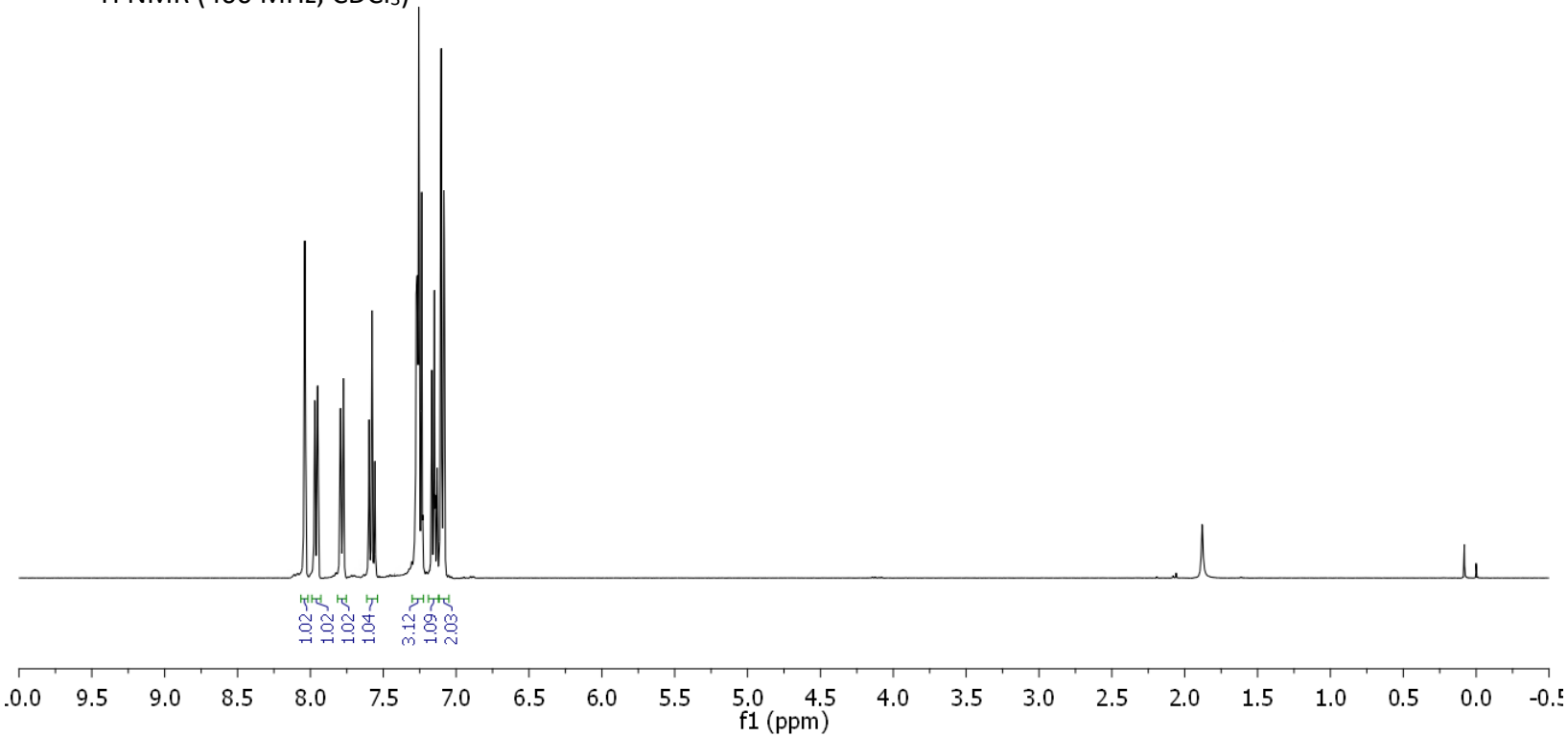
5h

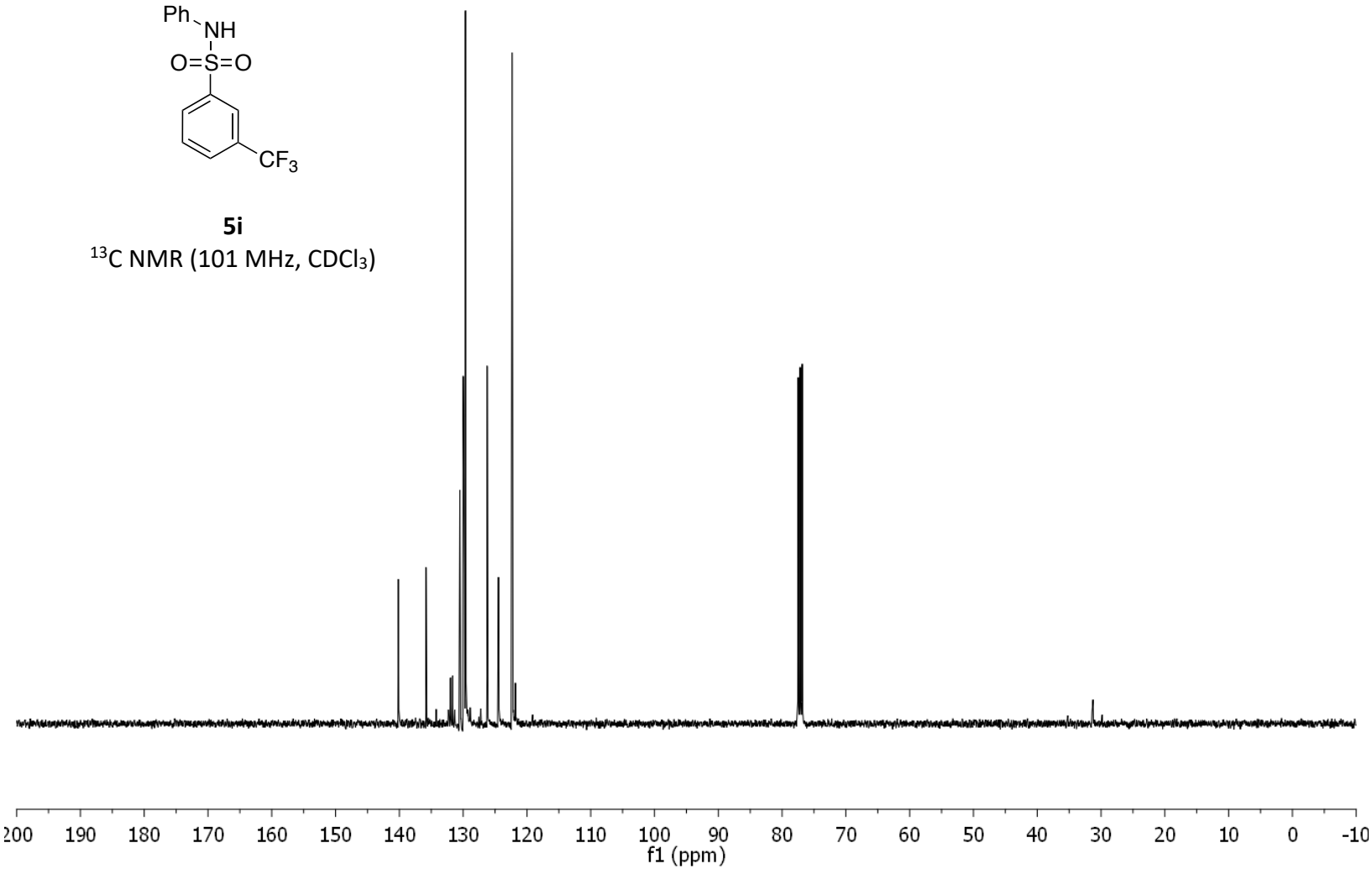
^{13}C NMR (101 MHz, $CDCl_3$)



5i

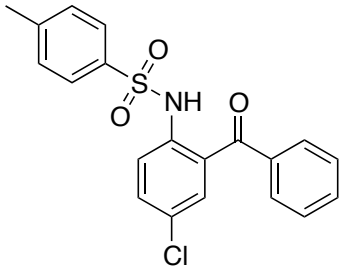
^{1}H NMR (400 MHz, $CDCl_3$)





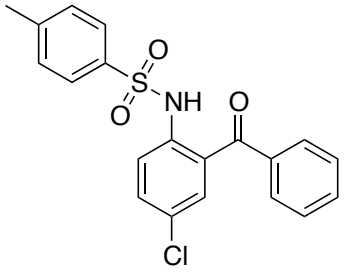
5i

^{13}C NMR (101 MHz, $CDCl_3$)



5j

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



5j

^{13}C NMR (101 MHz, $CDCl_3$)