

**TRANSITION-METAL-FREE AND VISIBLE LIGHT MEDIATED
DESULFONYLATION AND DEHALOGENATION REACTIONS:
HANTZSCH ESTER ANION AS ELECTRON AND HYDROGEN ATOM
DONOR**

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Supporting Information

Table of Contents

1.1. General Methods.	S-1
1.2. Materials.	S-3
1.3. Typical Procedures for Synthesis of Sulfonamides.	S-3
1.4. Typical Procedures for Methylation of Sulfonamides	S-6
1.4.1. Methylation of Synthesized Sulfonamides	S-6
1.4.2. One-pot Synthesis of <i>N</i> -methyl- <i>N</i> -arylsulfonamides.	S-6
1.5 Characterization Data of Synthesized Sulfonamides.	S-7
1.6. Typical Procedures for Desulfonylation Reactions in Dark Conditions.....	S-14
1.7. Typical Procedures for Photodesulfonylation Reactions under Visible Light Irradiation.....	S-15
2. Spectroscopic Study	S-15
2.1. Spectroscopic measurements.	S-15
2.2. UV-Vis spectra in DMSO	S-15
3. NMR spectra of compounds 1	S-18
4. NMR spectra of products 2	S-101
5. References	S-117

1. General Procedures and Equipment

1.1. General Methods. Purification of desired compounds was made by column chromatography on silica gel. Gas chromatographic (GC) analysis were performed with a flame-ionization detector, on 30 m capillary column of a 0.32 mm x 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. Gas chromatography-mass spectroscopy (GC-MS) analysis were performed employing an electronic impact (EI) ionization method and a 25 m x 0.2 mm x 0.33 μm column with a 5% phenylpolysiloxane phase. ^1H NMR and ^{13}C NMR $\{^1\text{H}\}$ spectra were recorded on a 400 and 500 MHz in spectrometer CDCl_3 , Acetone- d_6 (CD_3COCD_3) or DMSO- d_6 ($\text{CD}_3\text{S}(\text{O})\text{CD}_3$) as solvents with TMS as internal standard. Additional ^{19}F NMR spectra was performed for fluorinated compounds and was recorded on 377 MHz in spectrometer CDCl_3 or Acetone- d_6 as solvents. Coupling constants are given in Hz and chemical shifts are reported in δ values in ppm. Data are reported as followed: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. All new products were further characterized by 2D NMR techniques ($^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HSQC and $^1\text{H}/^{13}\text{C}$ HMBC) and high resolution mass spectrometry (HRMS). HRMS analyses were carried out using a time-of-flight mass spectrometry (TOF-MS) instrument with an electrospray ionization (ESI) source. Photoinduced reactions were conducted with blue LED ($\lambda = (465 \pm 20)$ nm) lights performing at 3W of potency and 700 mV of current emission spectra (Figure S1) and HPIT 400W lamps ($\lambda \geq 350$ nm, Figure S2). Apparatus and irradiation setup is shown in Figure S3.

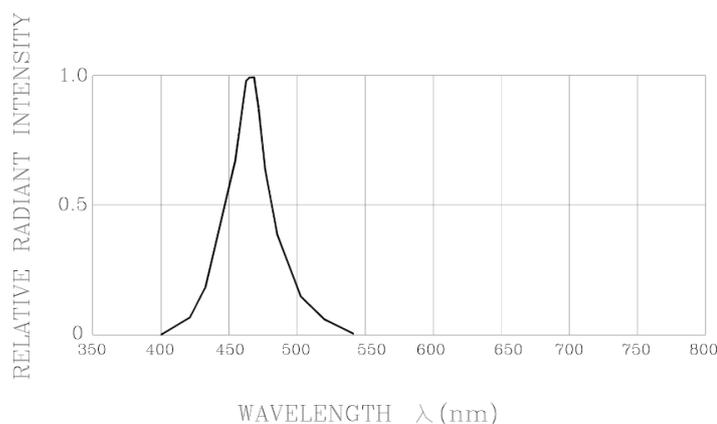


Figure S1. Emission Spectrum for Blue-LEDs as provided by the supplier.

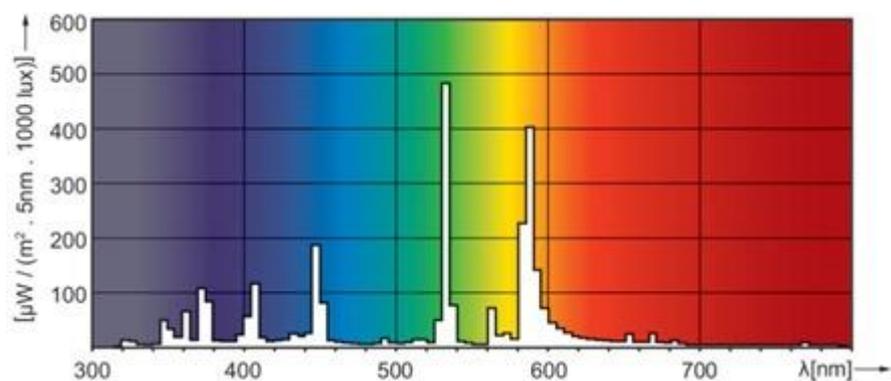


Figure S2. Emission Spectrum for HPIT 400W lamps ($\lambda \geq 350$ nm).



3 W Blue LED

HPI-T 400-W lamps

Figure S3. Apparatus and irradiation setup used.

Table S1. Details of light sources employed

	BLUE-LEDs	HPIT
Manufacturer and model	OSRAM Oslon	Philips HPIT
Potency	3 W	400 W
Wavelength of peak intensity	465 ± 20 nm	$\lambda \geq 350$ nm
Spectral distribution and intensity	See Figure S1	See Figure S2
Distance from the light source	1 cm	15 cm
Material of the irradiation vessel	borosilicate glass	borosilicate glass

1.2. Materials. *N*-indole (**2a**), 1*H*-pyrrolo[2,3-*b*]pyridine (**2b**), 1*H*-benzo[*d*][1,2,3]triazole (**2c**), 1*H*-pyrrole (**2d**), 9*H*-carbazole (**2e**), *N,N*-diphenylamine (**2i**), 4-methoxyphenol (**2n**), 4-hydroxybenzotrile (**2o**), 2-iodophenol (**2p**), aniline, benzyl bromide, 4-methoxyaniline, 4-methylaniline, 4-aminobenzotrile, 4-(*tert*-butyl)-aniline, [1,1'-biphenyl]-2-amine, 4-(trifluoromethoxy)aniline, 4-fluoroaniline, 4-iodoaniline, 4-aminophenol, 3-aminoacetophenone, benzenesulfonyl chloride, 2-chlorobenzenesulfonyl chloride, 2-nitrobenzenesulfonyl chloride, 2-iodonaphtalene (**10a**), 1-bromonaphtalene (**10b**), 1-chloronaphtalene (**10c**), 9-bromoanthracene (**10d**), 9-bromophenanthrene (**10e**), 4-bromo-1,1'-biphenyl (**10f**), 3-iodopyridine (**10g**), 2-chloropyridine (**10h**), 4-bromobenzotrile (**10i**), 4-chlorobenzotrile (**10j**), naphtalene (**11a**), anthracene (**11d**), phenanthrene (**11e**), biphenyl (**11f**), pyridine (**11g**), cyanobenzene (**11i**), KO^tBu, NaO^tBu, K₂CO₃, Cs₂CO₃, KOH, NaOH, NaH (60% in mineral oil), NH₄NO₃, NH₄Cl, tetrabutylammonium hydrogensulfate, Na₂SO₄, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), Hantzsch ester, NEt₃, DIPEA, 1,1-diphenyl ethene, pyridine were purchased from commercial suppliers and used without further purification.

DMSO, DMF, THF, CH₂Cl₂ and toluene were distilled and dried under molecular sieves (3 Å). All solvents were analytical grade. The silica used in column chromatography corresponds to silica gel 60 (0.063–0.200 mm).

1.3. Typical Procedures for Synthesis of Sulfonamides.

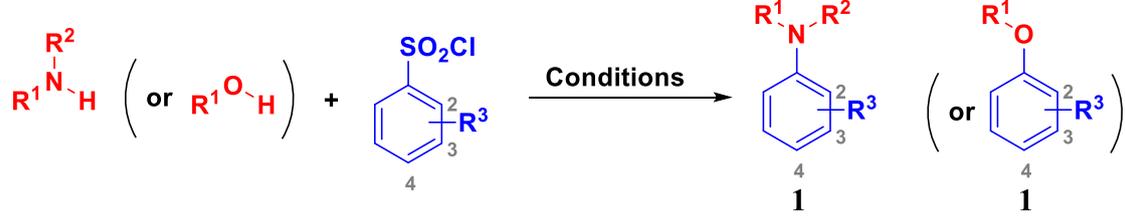
Method A. The reaction was carried out in a Schlenk tube equipped with an inert N₂ inlet and magnetic stirred at rt. In the Schlenk tube, DMSO (5 mL) was dried and deoxygenated, KO^tBu (1.0 equiv, 112 mg, 1 mmol) was added and the mixture was protected from light with aluminum foil. Then, the corresponding NH-heterocycle or aniline (1 equiv, 1 mmol) and benzenesulfonyl chloride (1.2 equiv, 1.2 mmol) were added and the reaction mixture was stirred overnight (18 hours). After the reaction was finished, it was quenched with NH₄NO₃ or NH₄Cl and water in excess and the residue was extracted with EtOAc or CH₂Cl₂ (3 x 30 mL), the organic layers extracted were combined, washed with water, dried with anhydrous Na₂SO₄ and concentrated under reduced pressure to leave the crude products. The reaction was analyzed with TLC, GC and isolated with column chromatography over silica gel.

Method B. Employing previously described conditions,¹ in a round-bottom flask equipped with a magnetic stirred, the corresponding NH-heterocycle or aniline (1 equiv, 1 mmol) in anhydrous CH₂Cl₂ was treated with 1.2 equiv. of NaOH and 1.5 equiv. of corresponding sulfonyl chloride at rt. The resulting mixture was stirred overnight (18 h) and then filtered. The solid was washed with CH₂Cl₂ (50 mL), obtaining the crude reaction. The reaction was analyzed with TLC, GC and isolated with column chromatography over silica gel.

Method C. Employing previously described conditions,² to a solution of the corresponding NH-heterocycle or aniline (1 equiv, 1 mmol) in toluene (2 mL), tetrabutylammonium hydrogensulfate (0.07 equiv, 7 mol%, 0.07 mmol), the sulfonyl chloride (1.2 equiv) and KOH (1.3 mL of 50% aqueous solution) were added. The mixture was stirred at rt for 4 h and then water was added and the layers were separated. The organic layer was washed with water (2 x 20 mL) and brine (1 x 20 mL), dried over Na₂SO₄ and concentrated under reduced pressure to afford the reaction crude which was analyzed with TLC, GC and isolated with column chromatography over silica gel.

Method D: Employing previously described conditions,^{3,4} the corresponding amine (1 equiv, 1 mmol) was dissolved in CHCl₃ (1 mL) in a one-necked flask. Pyridine (2 equiv, 2 mmol) was slowly added to the flask at 0 °C. The resultant solution was stirred at the same temperature for 30 min. Subsequently, sulfonyl chloride (1.2 equiv, 1.2 mmol) was added dropwise and the resulting solution was stirred for 4 h at rt. The reaction mixture was neutralized with 5% HCl and extracted with diethyl ether (3 x 30 mL), the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to afford the reaction crude. The crude was analyzed with TLC, GC and isolated with column chromatography over silica gel.

Method E: Employing previously described conditions,⁵ the corresponding amine (1 equiv, 1 mmol) was dissolved in dry CH₂Cl₂ (1.2 mL) and the solution was treated with sulfonyl chloride (1.2 equiv, 1.2 mmol) and pyridine (3 equiv, 3 mmol). The mixture was stirred at rt for 18 h, diluted with H₂O (15 mL) and extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layers were washed with 1M HCl, brine, dried over Na₂SO₄ and concentrated in vacuum. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel.

Table S2: Sulfonylation of NH-heterocycles, amines and phenols (compounds **1**)^a

Entry	NH-heterocycle/ amine/phenol	Cl-S(O) ₂ R	Conditions	
			(Method A, B, C, D or E)	1 , yield (%) ^b
1			A	1a , 31
2		R ³ =4-Me	B	1a , 87
3	Indole		C	1a , 45
4		R ³ =H	B	1f , 66
5 ^c		R ³ =2-Cl	B	1g , 71
6		R ³ =2-NO ₂	B	1h , 12
7	7-Aza-indole	R ³ =4-Me	A	1b , 67
8	1 <i>H</i> -benzo[<i>d</i>][1,2,3]triazole	R ³ =4-Me	B	1c , 61
9	Pyrrole		A	1d , 63
10		R ³ =4-Me	C	1d , 17
11	9 <i>H</i> -Carbazole	R ³ =4-Me	A	1e , 75
12		R ³ =4-Me	A	1i , 14
13	Diphenyl-amine		A	1j , 16
14		R ³ =H	D	1j , 23
15	Aniline		E	1k , 72
16		R ³ =H	E	1r-s , 97
17 ^d	4-Aminophenol	R ³ =4-Me	A, E	1m-s , 47
18	4-Cyanoaniline	R ³ =4-Me	E	1u-s , 41
19	4- <i>t</i> -Butylamine	R ³ =H	E	1v-s , 98
20	4-Methoxyphenol	R ³ =4-Me	A	1n , 58
21	4-Cyanophenol	R ³ =4-Me	A	1o , 60
22	2-Iodophenol	R ³ =4-Me	A	1p , 37
23	2-Iodophenol	R ³ =H	E	1q , 65
24	[1,1'-biphenyl]-2-amine	R ³ =H	E	1w-s , 86
25	4-(trifluoromethoxy)aniline	R ³ =H	E	1y-s , 99
26	4-iodoaniline	R ³ =H	E	1aa-s , 90

^a**Conditions:** **Method A:** Heterocycle, amine or phenol in DMSO with KO^tBu (1 equiv) is treated with sulfonyl chloride (1.2 equiv) under N₂ at rt for 18 h. **Method B¹:** Heterocycle or amine (1 equiv) in CH₂Cl₂ is treated with NaOH (1.2 equiv) and sulfonyl chloride (1.5 equiv) at rt for 18 h. **Method C²:** Heterocycle or amine in toluene is treated with sulfonyl chloride (1.2 equiv), 1.3 mL of KOH (50%) and

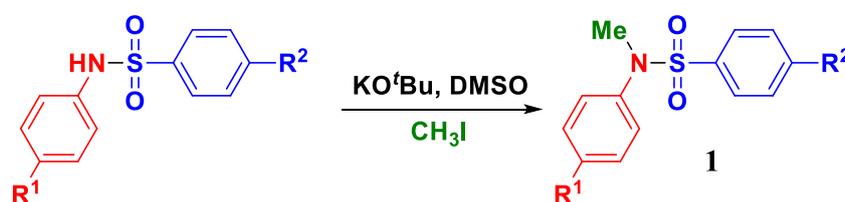
0.07 equiv of (*t*-Bu)₄NHSO₄ at rt for 4 h. **Method D**³⁻⁵: Amine (1 equiv) in CHCl₃ at 0°C is treated with pyridine (2 equiv) and stirred for 30 minutes. Then, sulfonyl chloride (1.2 equiv) was added at rt for 4 h. **Method E**^c: Amine or phenol in CH₂Cl₂ is treated with sulfonyl chloride (1.2 equiv) and pyridine (3 equiv) at rt for 18 h. ^b Isolated yield. ^c A second addition of NaOH and 2-chlorobenzenesulfonyl chloride is required to obtain full conversion. ^d First, 4-aminophenol was treated with *p*-toluenesulfonyl chloride (Method A) giving 4-Aminophenyl 4-methylbenzenesulfonate in 62% isolated yield. After, this product was treated with with *p*-toluenesulfonyl chloride (Method E) giving **1m-s** in 72% isolated yield (total yield 47%).

1.4. Typical Procedures for Methylation of Sulfonamides

1.4.1. Methylation of Synthetized Sulfonamides. Method F. The reaction was carried out in a round-bottom flask equipped with a magnetic stirred bar. KO^tBu was added (1.1 equiv) to a solution of sulfonamide (1 equiv) in DMSO (2 mL) and then iodomethane (3 equiv) was slowly added. The resulting mixture was stirred at rt overnight. Water was added, the crude was extracted with EtOAc (3 x 30 mL) and the layers were separated. The organic layers extracted were combined, washed with water, dried with anhydrous Na₂SO₄ and concentrated under reduced pressure to leave the crude products. The reaction was analyzed with TLC, GC and isolated with column chromatography over silica gel.

1.4.2. One-pot Synthesis of *N*-methyl-*N*-arylsulfonamides. 1s, 1t, 1x, 1z and 1ab were prepared by a one-pot synthesis starting from the corresponding anilines (2 mmol). First, the sulfonylation reaction was carried out according to Methods A to E and secondly, without purification, methylation reaction proceeded.

Table S3: Methylation of Sulfonamides (compounds 1)^a



Entry	Sulfonamide/ Amine	Cl-S(O) ₂ R ²	1, yield (%) ^b
1	1k	R ² = Me	1l , 69
2	1r-s	R ² = H	1r , 58
3	4-Methoxyaniline	R ² = Me	1s , 85 ^c
4	4-Methoxyaniline	R ² = H	1x , 90 ^c
5	4-Methylaniline	R ² = Me	1t , 70 ^c
6	1u-s	R ² = Me	1u , 78

7	1v-s	R ² = H	1v , 74
8	1w-s	R ² = H	1w , 80
9	1y-s	R ² = H	1y , 70
10	4-Fluoroaniline	R ² = H	1z , 79 ^c
11	1aa-s	R ² = H	1aa , 55
12	1m-s	R ² = Me	1m , 38
13	3-aminoacetophenone	R ² = H	1ab , 65 ^c

^aConditions: Sulfonamide (1 equiv.) in DMSO is treated with KO^tBu and iodomethane (3 equiv.) at rt overnight. ^bIsolated yield. ^cGlobal yield from the corresponding amine using Methods E and F (one-pot synthesis).

1.5 Characterization Data of Synthetized Sulfonamides.

1-[(4-Methylphenyl)sulfonyl]-1H-indole (1a).⁶ Titled compound was obtained according to Methods A, B and C, obtaining the best result with methodology B and was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 80:20). White solid was isolated in 87% yield (0.87 mmol, 236 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 3.7 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.34-7.28 (m, 1H), 7.24-7.21 (m, 3H), 6.66 (d, *J* = 3.7 Hz, 1H), 2.34 (s, 3H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 144.9, 135.3, 134.8, 130.8, 129.9, 126.8, 126.3, 124.6, 123.3, 121.4, 113.6, 109.0, 21.6. GC/MS EI *m/z* 272 (M⁺ +1, 7), 271 (M⁺, 44), 155 (50), 120 (21), 116 (34), 92 (11), 91 (100), 89 (23), 65 (21), 63 (12), 44 (12).

1-[(4-Methylphenyl)sulfonyl]-1H-pyrrolo[2,3-*b*]pyridine (1b).⁷ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc (90:10 → 70:30). White solid was isolated in 67% yield (0.67 mmol, 182 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.08-8.02 (m, 2H), 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.29-7.22 (m, 2H), 7.15 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.56 (d, *J* = 4.0 Hz, 1H), 2.34 (s, 3H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 147.2, 145.1, 144.8, 135.5, 129.6, 129.5, 128.0, 126.4, 122.8, 118.8, 105.2, 21.6. GC/MS EI *m/z* 273 (M⁺ +1, 1), 272 (M⁺, 3), 208 (43), 207 (38), 117 (30), 91 (100), 90 (30), 89 (13), 65 (46), 64 (19), 63 (47).

1-Tosyl-1H-benzo[*d*][1,2,3]triazole (1c).⁸ Titled compound was obtained according to Method B and was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 → 70:30). White solid was isolated in 61% yield (0.61 mmol, 168 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.3 Hz,

1H), 8.00 (d, $J = 8.4$ Hz, 2H), 7.76-7.63 (m, 1H), 7.49-7.45 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 146.7, 145.5, 134.1, 131.6, 130.3, 130.2, 128.0, 125.8, 120.6, 112.1, 21.7. GC/MS EI m/z 274 ($\text{M}^+ +1$, 3), 273 (M^+ , 9), 106 (23), 92 (12), 91 (100), 90 (410), 89 (14), 78 (17), 73 (14), 65 (59), 64 (30), 63 (40), 62 (12), 51 (12).

1-[(4-Methylphenyl)sulfonyl]-1H-pyrrole (1d).⁹ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 \rightarrow 95:5). Light yellow solid was isolated in 63% yield (0.63 mmol, 139 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.18-7.09 (m, 2H), 6.33-6.22 (m, 2H), 2.40 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 144.9, 136.2, 130.0, 126.8, 120.7, 113.5, 21.6. GC/MS EI m/z 222 ($\text{M}^+ +1$, 3), 221 (M^+ , 18), 155 (18), 91 (100), 66 (15), 65 (39), 63 (12).

9-[(4-Methylphenyl)sulfonyl]-9H-carbazole (1e).⁹ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 \rightarrow 90:10). White solid was isolated in 75% yield (0.75 mmol, 241 mg). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.26 (d, $J = 8.4$ Hz, 2H), 8.14 (d, $J = 7.7$ Hz, 2H), 7.73 (d, $J = 7.9$ Hz, 2H), 7.58 (ddd, $J = 8.4, 7.3, 1.3$ Hz, 2H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.30-7.20 (m, 2H), 2.21 (s, 3H). GC/MS EI m/z 322 ($\text{M}^+ +1$, 6), 321 (M^+ , 28), 167 (16), 166 (100), 140 (29), 139 (15), 91 (40), 89 (11), 65 (31), 63 (12).

1-(Phenylsulfonyl)-1H-indole (1f).⁹ Titled compound was obtained according to Method B and was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 \rightarrow 80:20). White solid was isolated in 66% yield (0.66 mmol, 170 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.3$ Hz, 1H), 7.88 (dd, $J = 8.5, 1.4$ Hz, 2H), 7.57 (d, $J = 3.7$ Hz, 1H), 7.55 - 7.49 (m, 2H), 7.43 (t, $J = 7.9$ Hz, 2H), 7.33 - 7.29 (m, 1H), 7.25 - 7.19 (m, 1H), 6.66 (d, $J = 3.7$ Hz, 1H). ^{13}C NMR {1H} (101 MHz, CDCl_3) δ 138.3, 134.9, 133.8, 130.8, 129.3, 126.8, 126.3, 124.7, 123.4, 121.4, 113.5, 109.3. GC/MS EI m/z 258 ($\text{M}^+ +1$, 6), 257 (M^+ , 36), 141 (13), 117 (13), 116 (82), 90 (12), 89 (54), 77 (100), 63 (30), 51 (55), 50 (16).

1-(2-Nitrophenylsulfonyl)-1H-indole (1h).¹⁰ Titled compound was obtained according to Method B and was purified by column chromatography on silica gel eluting with hexane/acetone (90:10 \rightarrow 80:20). Light yellow solid was isolated in 12 % yield (0.12 mmol, 36 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.89 – 7.84 (m, 1H), 7.78 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.75 – 7.68 (m, 2H), 7.66 – 7.56 (m, 3H), 7.34 – 7.27 (m, 2H), 6.75 (dd, $J =$

3.8, 0.8 Hz, 1H). ^{13}C NMR{1H} (126 MHz, CDCl_3) δ 148.1, 134.9, 134.8, 132.5, 132.1, 130.8, 129.9, 127.5, 125.1, 125.0, 124.0, 121.9, 113.5, 109.0.

4-Methyl-*N,N*-diphenylbenzenesulfonamide (1i).¹¹ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc 80:20. White solid was isolated in 14% yield (0.14 mmol, 45 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.1$ Hz, 2H), 7.33-7.26 (m, 12H), 2.43 (s, 3H). GC/MS EI m/z 324 ($\text{M}^+ +1$, 6), 323 (M^+ , 10), 169 (17), 168 (100), 167 (44), 51 (10), 47 (2).

***N,N*-Diphenylbenzenesulfonamide (1j).**¹¹ Titled compound was obtained according to Method D, and was purified by column chromatography on silica gel eluting with pentane/EtOAc 80:20. White solid was isolated in 23% yield (0.22 mmol, 69 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.8$ Hz, 2H), 7.59 (t, $J = 7.1$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.31-7.26 (m, 10H). GC/MS EI m/z 310 ($\text{M}^+ +1$, 2), 309 (M^+ , 17), 169 (15), 168 (100), 167 (75), 16(13), 51 (58), 50 (10).

4-Methyl-*N*-phenylbenzenesulfonamide (1k).¹² Titled compound was obtained according to Method E and was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 \rightarrow 80:20). White solid was isolated in 72% yield (0.72 mmol, 178 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.4$ Hz, 2H), 7.25-7.20 (m, 4H), 7.13-7.04 (m, 3H), 6.64 (s br, 1H), 2.37 (s, 3H). GC/MS EI m/z 248 ($\text{M}^+ +1$, 6), 247 (M^+ , 41), 182 (23), 168 (18), 155 (39), 92 (50), 91 (100), 65 (51), 41 (3).

4-[(4-Methylphenyl)sulfonyl]amino}phenyl 4-methylbenzenesulfonate (**1m-s**).^{13,14} 4-Aminophenyl 4-methylbenzenesulfonate¹⁵ was obtained according to Method A from 4-Aminophenol and was purified by column chromatography on silica gel eluting with pentane/EtOAc (80:20 \rightarrow 50:50) as a solid with 62% yield (0.62 mmol, 163 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.76-6.69 (m, 2H), 6.55-6.48 (m, 2H), 3.68 (s br, 2H), 2.44 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 145.4, 145.1, 141.6, 132.4, 129.6, 128.6, 123.2, 115.3, 21.7. GC/MS EI m/z 264 ($\text{M}^+ +1$, 1), 263 (M^+ , 5), 108 (100), 91 (17), 80 (42), 65 (23), 53 (23). After that, **1m-s** was obtained according to Method E from 4-aminophenyl 4-methylbenzenesulfonate and was purified by column chromatography on silica gel eluting with pentane/EtOAc (90:10 \rightarrow 50:50). Light yellow solid was isolated in 76% yield (0.47 mmol, 159 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.00-6.94

(m, 2H), 6.87-6.79 (m, 3H), 2.45 (s, 3H), 2.40 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 146.7, 145.6, 144.3, 135.7, 135.4, 132.1, 129.8, 129.8, 128.5, 127.2, 123.4, 122.5, 21.8, 21.6. GC/MS EI m/z 418 (M^+ +1, 1), 417 (M^+ , 5), 65 (30), 91 (100), 155 (47), 262 (20).

4-Methoxyphenyl 4-methylbenzenesulfonate (1n).¹⁶ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc 80:20. Brown solid was isolated in 58% yield (0.58 mmol, 161 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.89-6.86 (m, 2H), 6.78-6.75 (m, 2H), 3.76 (s, 3H), 2.44 (s, 3H). GC/MS EI m/z 279 (M^+ +1, 1), 278 (M^+ , 10), 123 (100), 95 (35), 91 (36), 65 (47), 63 (17), 54 (10), 52 (18), 51 (10).

4-Cyanophenyl 4-methylbenzenesulfonate (1o).¹⁷ Titled compound was obtained according to Method A, and was purified by column chromatography on silica gel eluting with pentane/EtOAc 80:20. Brown solid was isolated in 60% yield (0.60 mmol, 164 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.8, 2H), 7.34 (d, J = 8.1, 2H), 7.14 (d, J = 8.8 Hz, 2H), 2.46 (s, 3H). GC/MS EI m/z 274 (M^+ +1, 1), 273 (M^+ , 4), 155 (29), 91 (100), 90 (20), 65 (39), 64 (15), 63 (17).

2-Iodophenyl 4-methylbenzenesulfonate (1p).¹⁸ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc 80:20. Brown solid was isolated in 37% yield (0.37 mmol, 139 mg) after vacuum distillation. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 7.9 Hz, 1H), 7.33-7.32 (m, 4H), 7.03-6.92 (m, 1H), 2.46 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 150.0, 145.7, 140.1, 132.9, 129.8, 129.5, 128.8, 128.3, 123.0, 90.2, 21.7. GC/MS EI m/z 375 (M^+ +1, 2), 374 (M^+ , 18), 155 (33), 92 (25), 91 (100), 89 (11), 65 (45), 64 (28), 63 (44).

2-Iodophenyl benzenesulfonate (1q).¹⁸ Titled compound was obtained according to Method A and was purified by column chromatography on silica gel eluting with pentane/EtOAc 90:10. Yellow oil was isolated in 65% yield (0.65 mmol, 233 mg) after vacuum distillation. ^1H NMR (400 MHz, CDCl_3) δ 7.94-7.92 (m, 2H), 7.75 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.34-7.33 (m, 2H), 7.00-6.96 (m, 1H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 149.9, 140.1, 135.8, 134.5, 129.5, 129.2, 128.8, 128.4, 123.1, 90.1. GC/MS EI m/z 361 (M^+ +1, 3), 360 (M^+ , 24), 141 (54), 92 (19), 77 (100), 64 (19), 63 (14), 51 (20).

N-Phenylbenzenesulfonamide (**1r-s**)¹⁹ was obtained according to Method E and was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 80:20). White solid was isolated in 97% yield (0.97 mmol, 226 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.78 (m, 2H), 7.56-7.48 (m, 1H), 7.45-7.41 (m, 2H), 7.25-7.21 (m, 2H), 7.13-7.00 (m, 4H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 139.1, 136.4, 133.0, 129.3, 129.0, 127.2, 125.5, 121.8. GC/MS EI *m/z* 234 (M⁺ +1, 3), 233 (M⁺, 27), 168 (16), 141 (13), 93 (12), 92 (100), 77 (96), 66 (10), 65 (91), 64 (13), 63 (13), 51 (59), 50 (16).

N-(4-Cyanophenyl)-4-methylbenzenesulfonamide (**1u-s**)²⁰ was obtained according to Method E and was purified by column chromatography on silica gel eluting with pentane/EtOAc 80:20. White solid was isolated in 41% yield (0.41 mmol, 112 mg). ¹H NMR (400 MHz, Acetone-*d*₆) δ 9.57 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.71-7.62 (m, 2H), 7.45-7.34 (m, 4H), 2.39 (s, 3H). ¹³C NMR{1H} (101 MHz, Acetone-*d*₆) δ 144.3, 142.4, 136.8, 133.4, 129.8, 127.1, 119.1, 118.2, 106.8, 20.5. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 2.40 (s, 3H). ¹³C NMR{1H} (400 MHz, CDCl₃) δ 144.8, 141.0, 135.5, 133.6, 130.0, 127.2, 119.3, 118.4, 107.6, 21.6. GC/MS EI *m/z* 273 (M⁺ +1, 3), 272 (M⁺, 12), 155 (23), 117 (11), 91 (100), 90 (28), 89 (11), 65 (45), 65 (12), 63 (21).

N-(4-(*tert*-Butyl)phenyl)benzenesulfonamide (**1v-s**)²¹ was obtained according to Method E and was purified by column chromatography on silica gel eluting pentane/EtOAc 80:20. Yellow solid was isolated in 98% yield (0.98 mmol, 590 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.12 (s br, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 1.24 (s, 9H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 148.5, 139.3, 133.6, 132.8, 128.9, 127.2, 126.12, 121.6, 34.3, 31.2. GC/MS EI *m/z* 290 (M⁺ +1, 4), 289 (M⁺, 22), 275 (17), 274 (87), 148 (11), 133 (19), 132 (19), 118 (14), 106 (15), 105 (16), 91 (35), 79 (13), 78 (18), 77 (100), 65 (13), 51 (38).

N-([1,1'-Biphenyl]-2-yl)benzenesulfonamide (**1w-s**)²² was obtained according to Method E and was purified by column chromatography on silica gel eluting pentane/EtOAc (90:10→80:20). White solid was isolated in 86% yield (0.86 mmol, 266 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.57-7.52 (m, 3H), 7.41-

7.31 (m, 6H), 7.17-7.08 (m, 2H), 6.82-6.80 (m, 2H), 6.59 (s br, 1H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 139.1, 137.1, 134.2, 133.6, 132.9, 130.2, 129.1, 128.9, 128.8, 128.7, 128.1, 127.1, 125.1, 121.7. GC/MS EI *m/z* 310 (M⁺ +1, 3), 309 (M⁺, 11), 169 (11), 168 (100), 167 (82), 166 (21), 140 (11), 139 (14), 115 (11), 77 (67), 51 (36).

N-(4-(Trifluoromethoxy)phenyl)benzenesulfonamide (**1y-s**)²³ was obtained according to Method E and was purified by column chromatography on silica gel eluting with hexane/EtOAc: 80:20 → 60:40. Yellow liquid was isolated in 99% yield (0.99 mmol, 317 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.34 (s br, 1H), 7.13-7.07 (m, 4H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 146.5, 138.7, 135.0, 133.3, 129.2, 127.2, 122.9, 121.9, 120.3 (q, *J* = 257, 1C). GC/MS EI *m/z* 318 (M⁺ +1, 5), 317 (M⁺, 32), 176 (100), 149 (15), 83 (14), 78 (13), 77 (99), 69 (53), 53 (11), 52 (22), 51 (58), 50 (14).

N-(4-Iodophenyl)benzenesulfonamide (**1aa-s**)²⁴ was obtained according to Method E and was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20). Solid was isolated in 90% global yield (0.90 mmol, 323 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.58-7.53 (m, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 6.85-6.83 (m, 3H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 138.8, 138.4, 136.2, 133.3, 129.2, 127.2, 123.4, 89.5. GC/MS EI *m/z* 360 (M⁺ +1, 6), 359 (M⁺, 47), 218 (64), 91 (63), 90 (10), 78 (11), 77 (100), 65 (15), 64 (53), 63 (48), 62 (12), 52 (11), 51 (70), 50 (22).

***N*,4-Dimethyl-*N*-phenylbenzenesulfonamide (1l)**.^{25,26} Titled compound was obtained from **1j** and was purified by column chromatography on silica gel eluting with pentane/EtOAc (100:0 → 90:10). White solid was isolated in 69% yield (0.23 mmol, 60 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.31-7.22 (m, 5H), 7.10-7.08 (m, 2H), 3.16 (s, 3H), 2.41 (s, 3H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 143.5, 141.6, 133.5, 129.3, 128.8, 127.8, 127.2, 126.6, 38.0, 21.5. GC/MS EI *m/z* 262 (M⁺ +1, 2), 261 (M⁺, 14), 197 (16), 196 (12), 106 (98), 105 (12), 104 (19), 91 (63), 89 (13), 79 (41), 70 (21), 77 (100), 65 (51), 63 (19), 51 (26).

4-(*N*,4-Dimethylphenylsulfonamido)phenyl 4-methyl benzenesulfonate (1m).²⁷ Titled compound was obtained from **1m-s** and was purified by column chromatography on silica gel eluting with pentane/EtOAc (90:10 → 60:40). White solid was isolated in 38% yield (0.052 mmol, 22.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.2 Hz,

2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 3.11 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 148.1, 145.6, 143.8, 140.3, 133.1, 132.3, 129.8, 129.4, 128.5, 127.8, 127.6, 122.7, 37.9, 21.7, 21.5. GC/MS EI m/z 432 ($\text{M}^+ + 1$, 1), 431 (M^+ , 6), 65 (25), 91 (100), 92 (10), 155 (57), 276 (20).

***N*-Methyl-*N*-phenylbenzenesulfonamide (1r)**²⁸ was obtained from **1r-s** and was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 \rightarrow 80:20). White solid was isolated in 58% yield (0.72 mmol, 178 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.54 (m, 3H), 7.47-7.43 (m, 2H), 7.31-7.26 (m, 3H), 7.09 (d, $J = 6.8$ Hz, 2H), 3.18 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 141.5, 136.6, 132.7, 128.9, 128.7, 127.8, 127.3, 126.6, 38.1. GC/MS EI m/z 248 ($\text{M}^+ + 1$, 1), 247 (M^+ , 10), 106 (63), 104 (12), 79 (29), 78 (17), 77 (100), 51 (45), 50 (10).

***N*-(4-Cyanophenyl)-*N*,4-dimethylbenzenesulfonamide (1u)**²⁹ was obtained from **1u-s** and was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 \rightarrow 80:20). White solid was isolated in 78% yield (0.55 mmol, 158 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.61 (dd, $J = 8.8, 2.3$ Hz, 2H), 7.45-7.39 (m, 2H), 7.32-7.24 (m, 4H), 3.20 (s, 3H), 2.43 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 145.7, 144.3, 133.1, 132.8, 129.7, 127.6, 126.0, 118.3, 110.2, 37.4, 21.5. GC/MS EI m/z 286 (M^+ , 7), 222 (5), 155 (23), 131 (15), 129 (6), 104 (9), 103 (7), 102 (28), 92 (7), 91 (100), 90 (6), 89 (10), 77 (9), 76 (6), 75 (9), 65 (39), 64 (10), 63 (15), 51 (15).

***N*-(4-Iodophenyl)-*N*-methylbenzenesulfonamide (1aa)**²⁴ was obtained from **1aa-s** and was purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10 \rightarrow 80:20). Solid was isolated in 55% yield (0.55 mmol, 207 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.54 (m, 5H), 7.47 (t, $J = 7.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 3.14 (s, 3H). ^{13}C NMR{1H} (101 MHz, CDCl_3) δ 141.3, 138.0, 136.2, 133.0, 128.9, 128.3, 127.8, 92.4, 37.9. GC/MS EI m/z 374 ($\text{M}^+ + 1$, 2), 373 (M^+ , 30), 232 (41), 105 (81), 104 (28), 90 (25), 78 (23), 77 (100), 76 (40), 64 (14), 63 (29), 52 (10), 51 (66), 50 (23).

One-pot Synthesis of *N*-methyl-*N*-arylsulfonamides. 1s, 1t, 1x and 1z were prepared by a one-pot synthesis starting from the corresponding anilines (2 mmol). First, the sulfonylation reaction was carried out according to Methods A to E and secondly, without purification, methylation reaction proceeded.

***N*-(4-Methoxyphenyl)-*N*,4-dimethylbenzenesulfonamide (1s)**³⁰ was obtained from 4-methoxyaniline according to Methods E and methylation reaction and was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 → 80:20). Light brown solid was isolated in 85% global yield (1.7 mmol, 495 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.01-6.97 (m, 2H), 6.82-6.78 (m, 2H), 3.79 (s, 3H), 3.13 (s, 3H), 2.42 (s, 3H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 158.7, 143.4, 134.3, 133.7, 129.3, 128.1, 127.9, 114.0, 55.4, 38.4, 21.5. GC/MS EI *m/z* 292 (M⁺ +1, 1), 291 (M⁺, 11), 136 (100), 121 (14), 108 (17), 93 (14), 92 (13), 91 (27), 77 (13), 67 (14), 66 (15), 65 (33).

***N*,4-Dimethyl-*N*-(*p*-tolyl)benzenesulfonamide (1t)**³¹ was obtained from 4-methylaniline according to Methods E and methylation reaction and was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 80:20). Light brown solid was isolated in 70% global yield (1.4 mmol, 385 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.43 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.97-6.95 (m, 2H), 3.13 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H). GC/MS EI *m/z* 276 (M⁺ +1, 2), 275 (M⁺, 13), 120 (100), 118 (11), 93 (12), 92 (19), 91 (93), 89 (10), 77 (23), 65 (57), 63 (12), 51 (12).

***N*-(4-Methoxyphenyl)-*N*-methylbenzenesulfonamide (1x)**³² was obtained according from 4-methoxyaniline to Methods E and methylation reaction and was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5 → 80:20). Brown solid was isolated in 90% global yield (1.8 mmol, 476 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.55 (m, 3H), 7.47-7.43 (m, 2H), 6.99-6.95 (m, 2H), 6.82-6.78 (m, 2H), 3.79 (s, 3H), 3.15 (s, 3H). ¹³C NMR{1H} (101 MHz, CDCl₃) δ 158.7, 136.6, 134.1, 132.6, 128.6, 128.1, 127.9, 114.0, 55.4, 38.5. GC/MS EI *m/z* 277 (M⁺, 10), 137 (9), 136 (100), 121 (18), 120 (13), 108 (18), 93 (18), 92 (16), 78 (15), 77 (78), 67 (20), 66 (19), 65 (14), 51 (47), 50 (12).

1.6. Typical Procedures for Desulfonylation Reactions in Dark Conditions. The desulfonylation reaction was carried out in a Schlenk tube equipped with an inert N₂ inlet and magnetic stirred at rt. In the Schlenk tube, DMSO (1 mL) was dried and deoxygenated, then the corresponding sulfonamide (1 equiv, 0.1 mmol) and KO^tBu (3 equiv, 0.3 mmol) were added and the mixture was protected from light with aluminum

foil. After the reaction was finished, it was quenched with NH_4NO_3 or NH_4Cl and water in excess and the residue was extracted with EtOAc (3 x 30 mL). The organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to leave the crude products. Yields were quantified by GC employing internal method using biphenyl as internal standard.

1.7. Typical Procedures for Photodesulfonylation Reactions under Visible Light Irradiation. The photodesulfonylation reactions were carried out in a vial at rt and under N_2 atmosphere and irradiated with blue LED (3 W) using 1 equiv. (0.1 mmol) of sulfonamide, 2.2 equiv. of KO^tBu (0.22 mmol) and 2 equiv. of Hantzsch ester (0.2 mmol) in DMSO (1 mL previously dried and deoxygenated). After the reaction was finished, it was quenched with NH_4NO_3 or NH_4Cl and water in excess and the residue was extracted with EtOAc (3 x 30 mL). The organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to leave the crude products. Yields were quantified by GC using internal method employing 9H-carbazole as internal standard.

2. Spectroscopic Study

2.1. Spectroscopic measurements. The UV-vis and the spectrofluorimetric determinations were carried out in a Shimadzu UV-2101 PC and a Jasco FP-777, respectively. All measurements were carried out under an inert atmosphere of nitrogen, in quartz cuvettes, at room temperature. Solutions of KO^tBu were prepared at time of use. UV-vis spectra were recorded on UV-vis spectrophotometer.

2.2. UV-Vis spectra in DMSO

UV-vis spectra of HE, HE anion and compound **1r** are presented in Figure S3, S4 and S5.

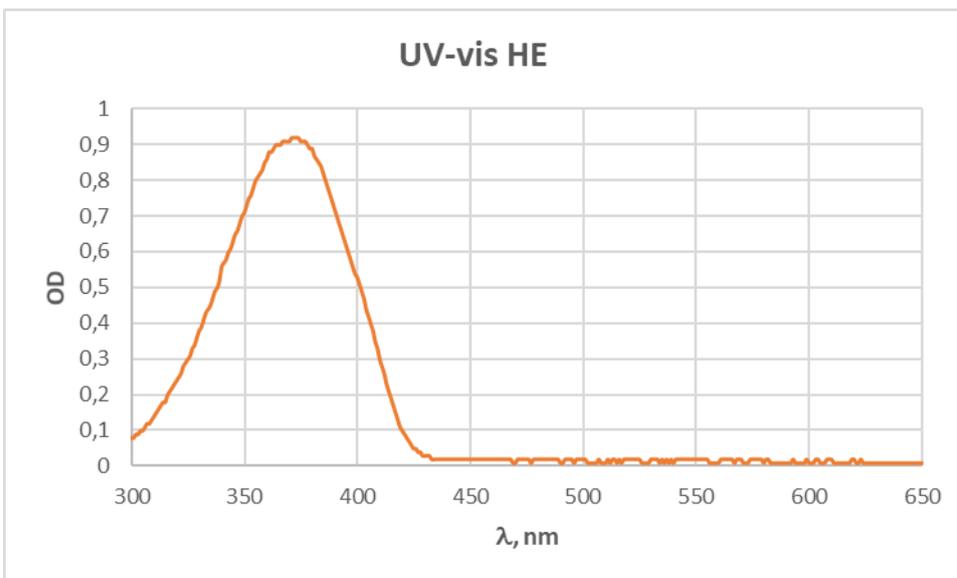


Figure S4. UV-vis spectrum for HE ($5 \cdot 10^{-5}$ M) in DMSO under N_2 atmosphere.

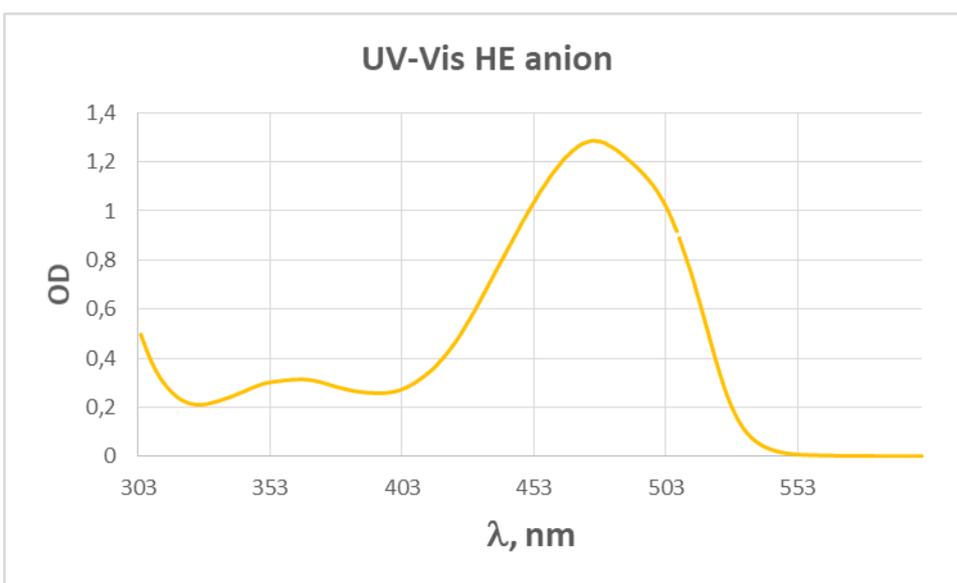


Figure S5. UV-vis spectrum for HE anion ($2,5 \times 10^{-4}$ M) in DMSO under N_2 atmosphere.

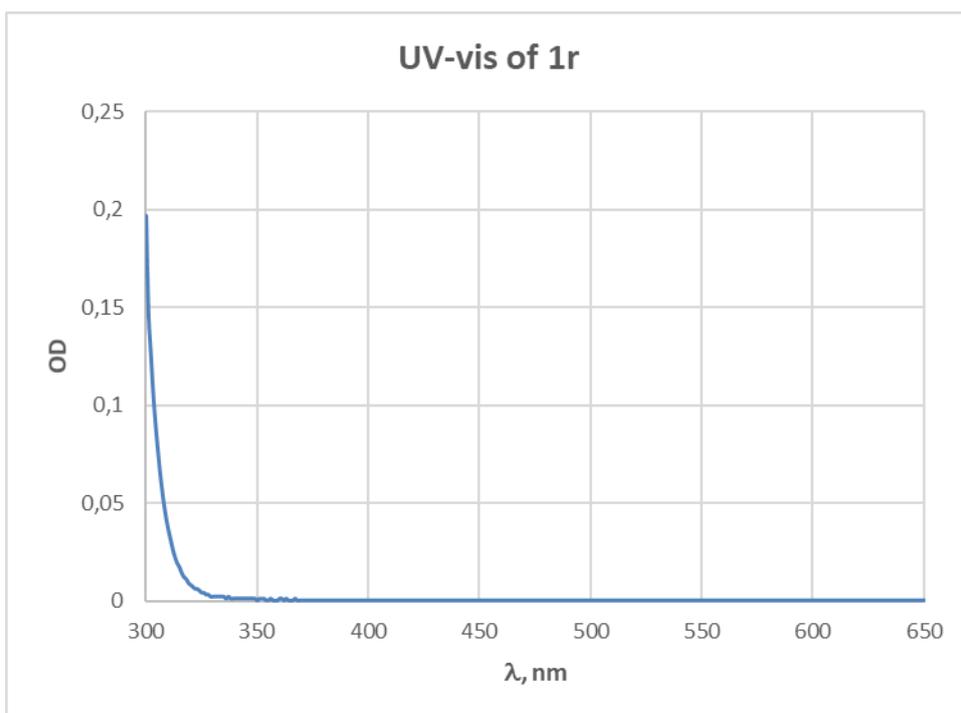
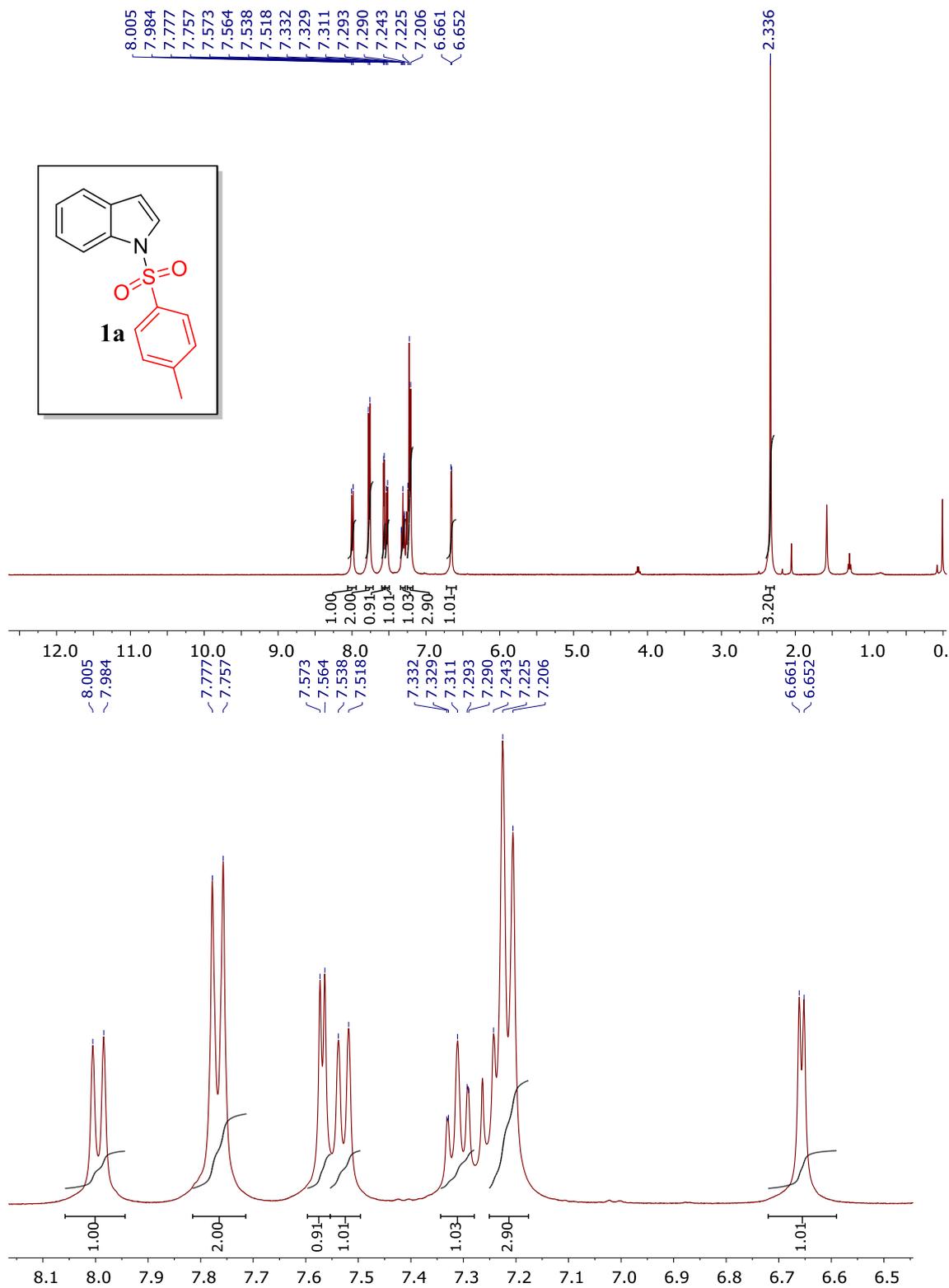


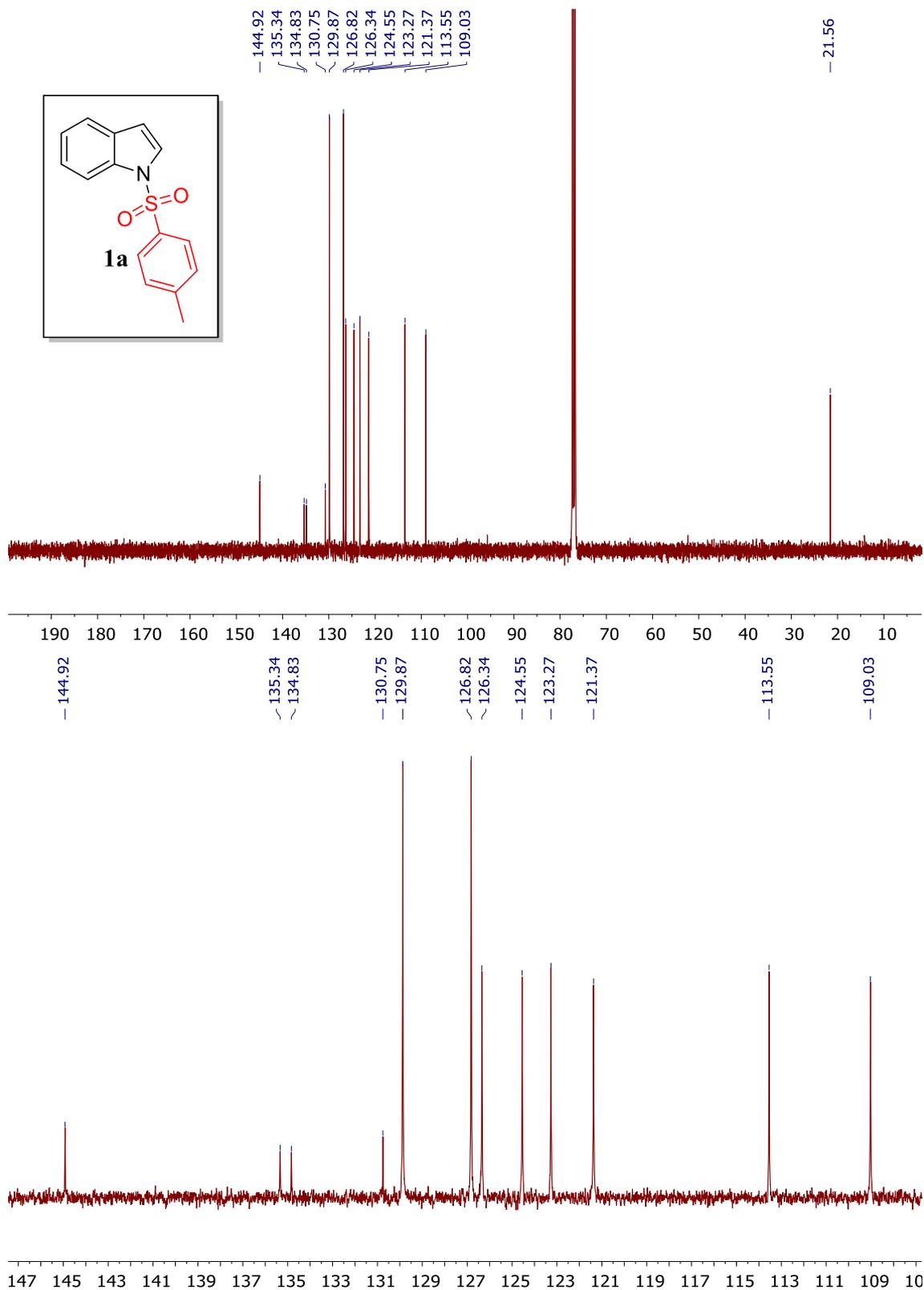
Figure S6. UV-vis spectrum for compound **1r** ($7 \cdot 10^{-5}$ M) in DMSO under N_2 atmosphere.

3. NMR spectra of compounds 1

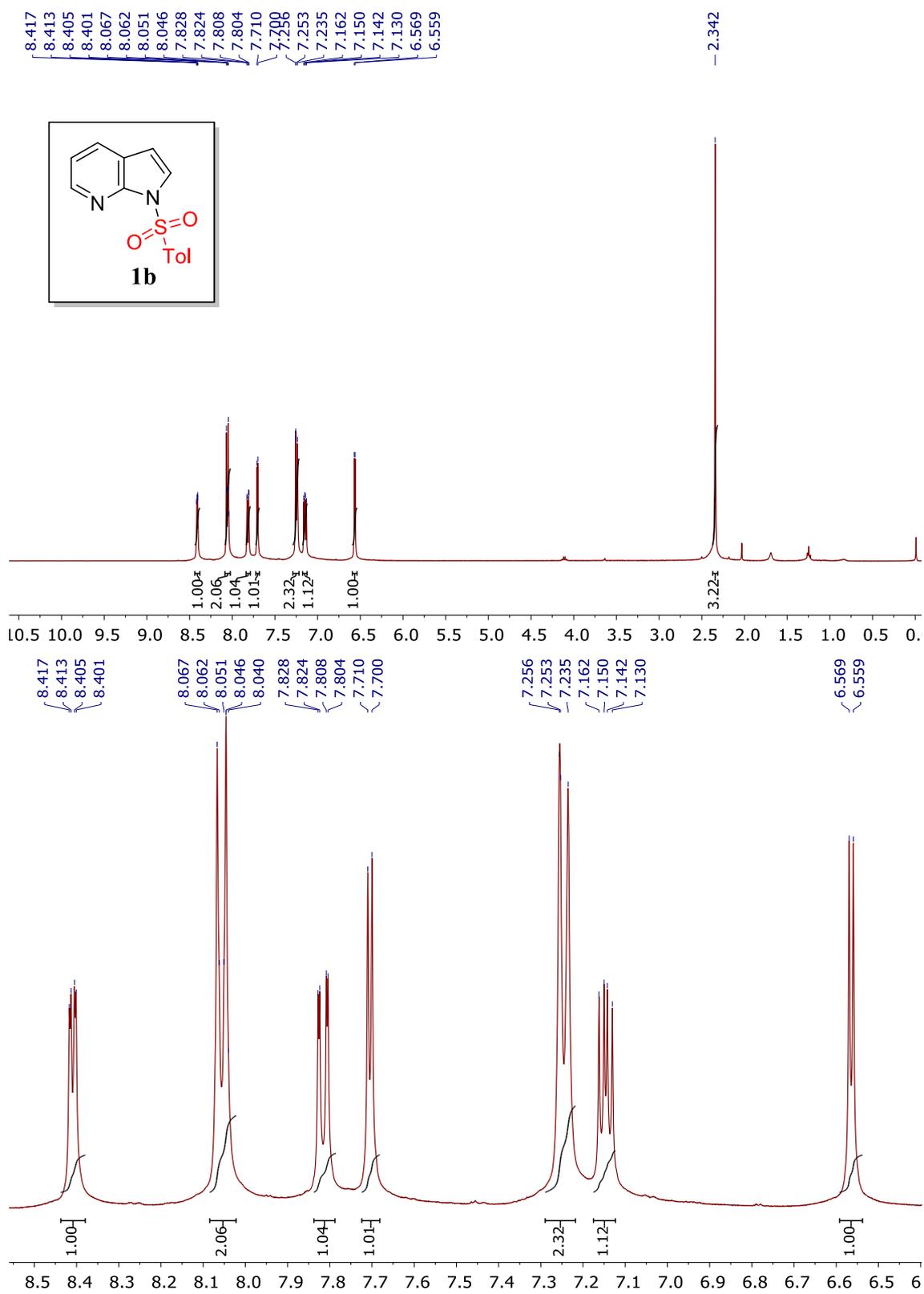
¹H-NMR (400 MHz, CDCl₃). 1-[(4-Methylphenyl)sulfonyl]-1*H*-indole (**1a**).



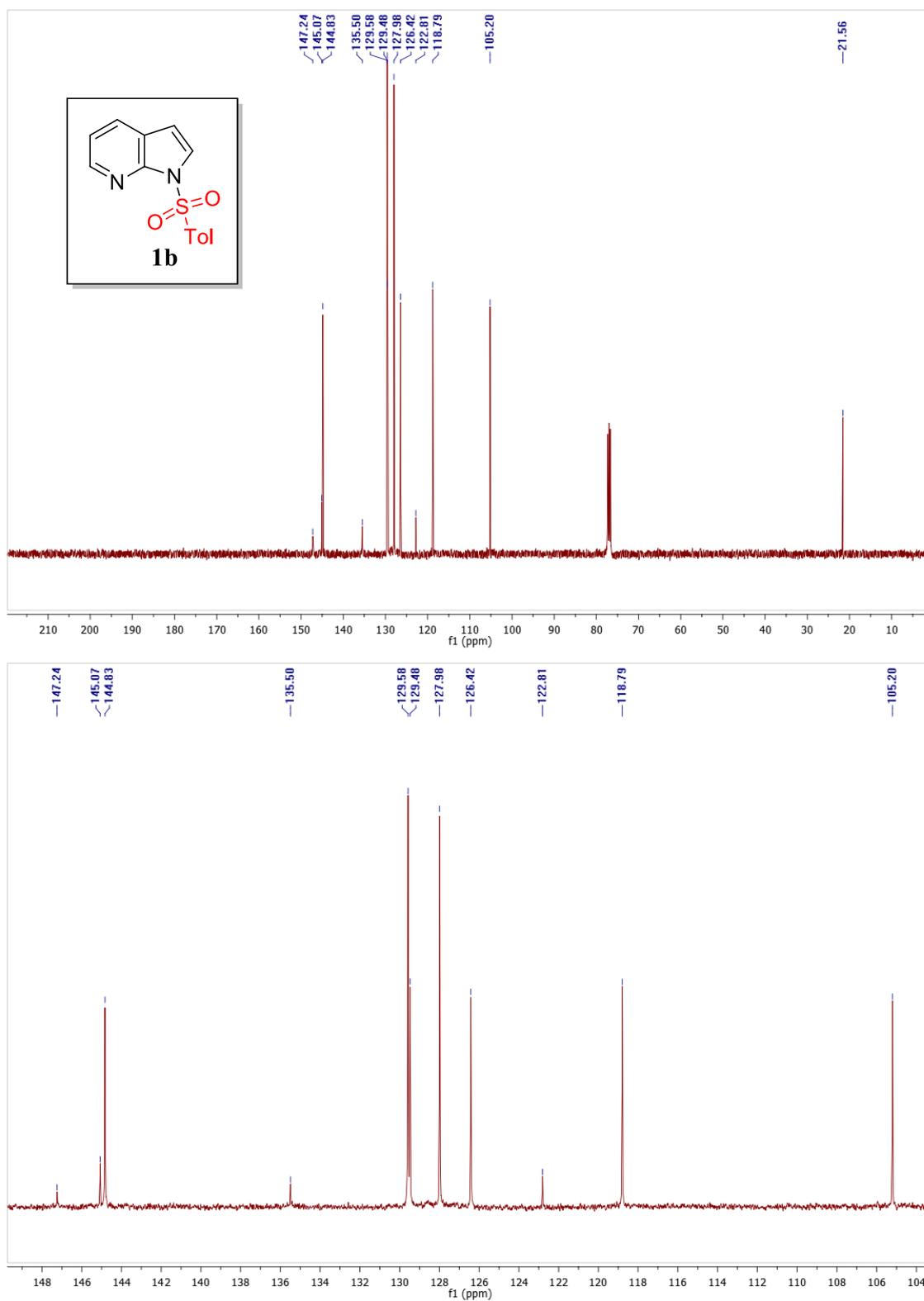
^{13}C -NMR {H} (101 MHz, CDCl_3). 1-[(4-Methylphenyl)sulfonyl]-1*H*-indole (**1a**).



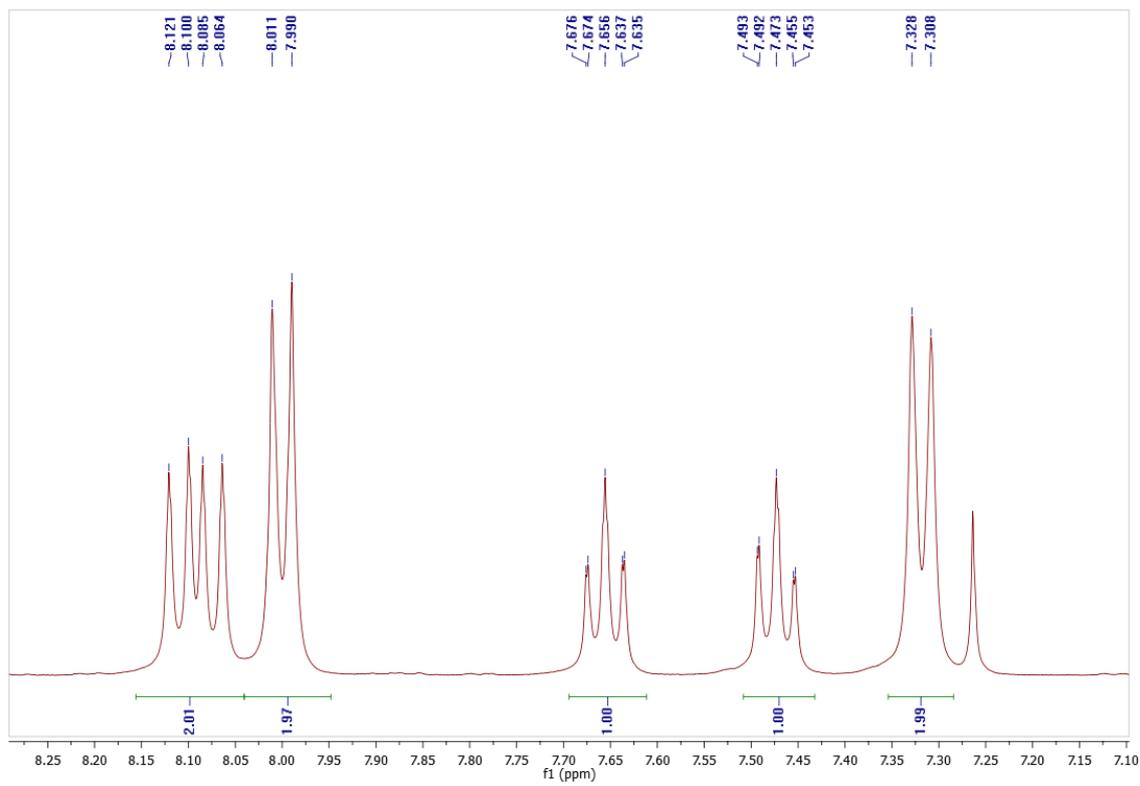
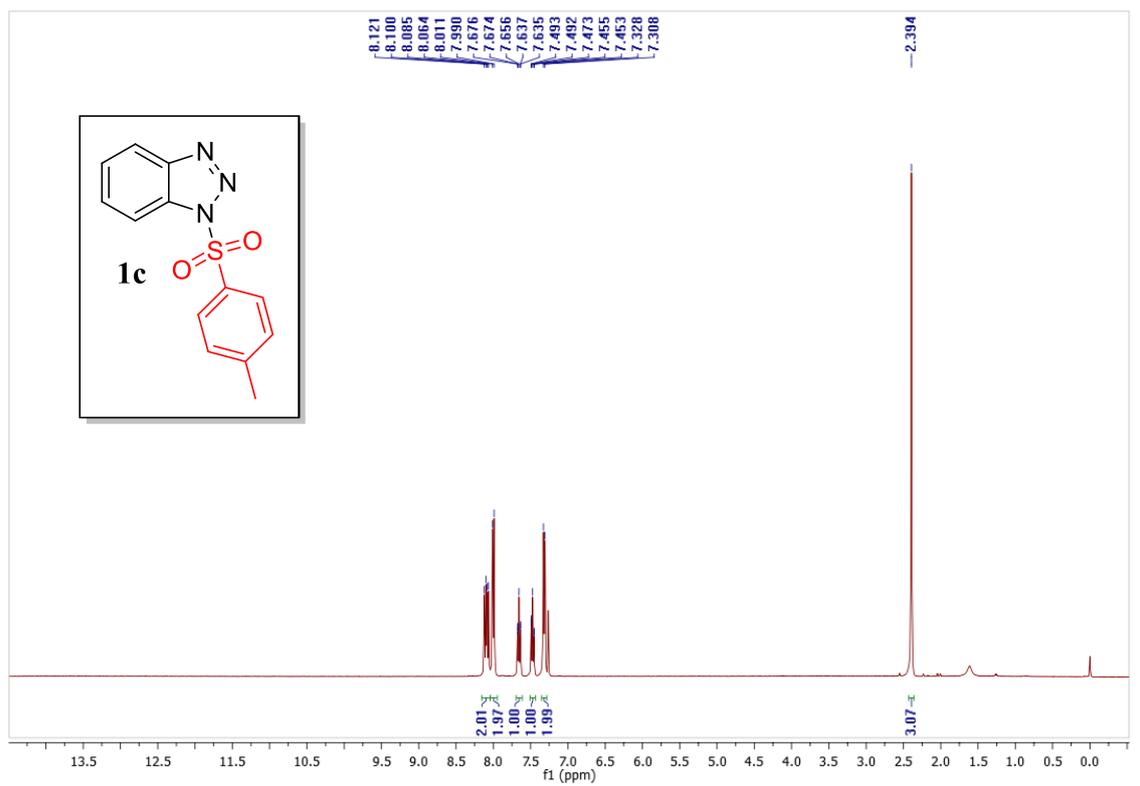
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 1-Tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (**1b**).



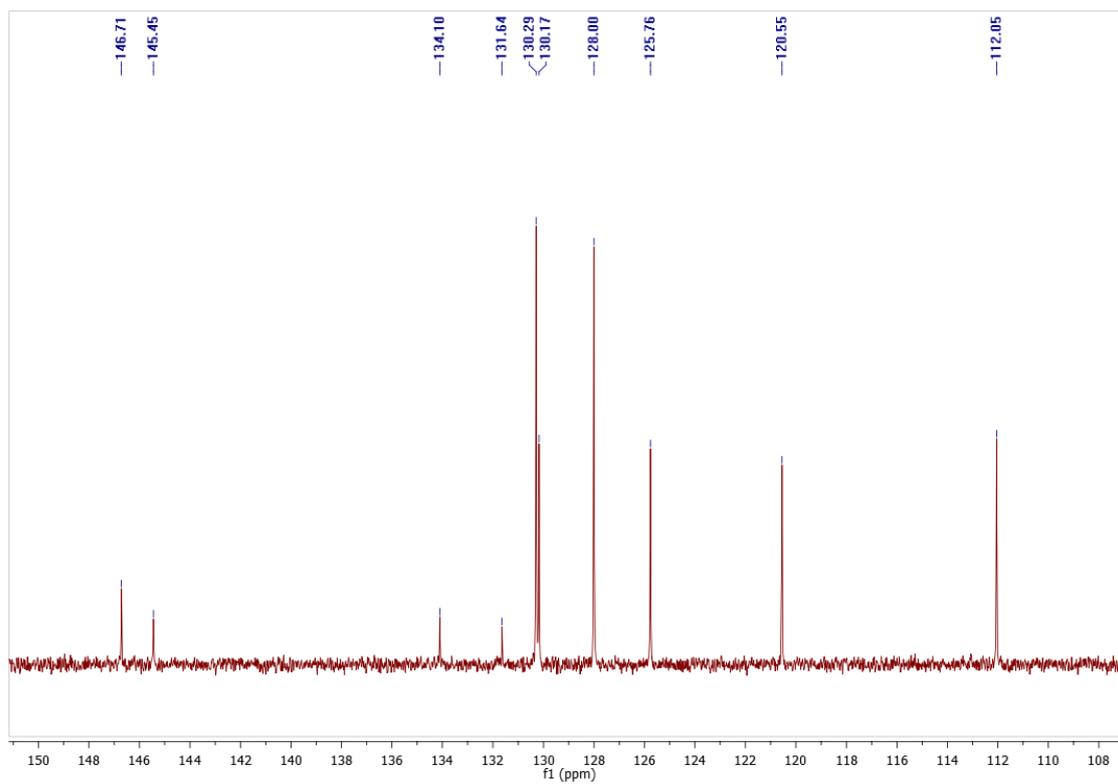
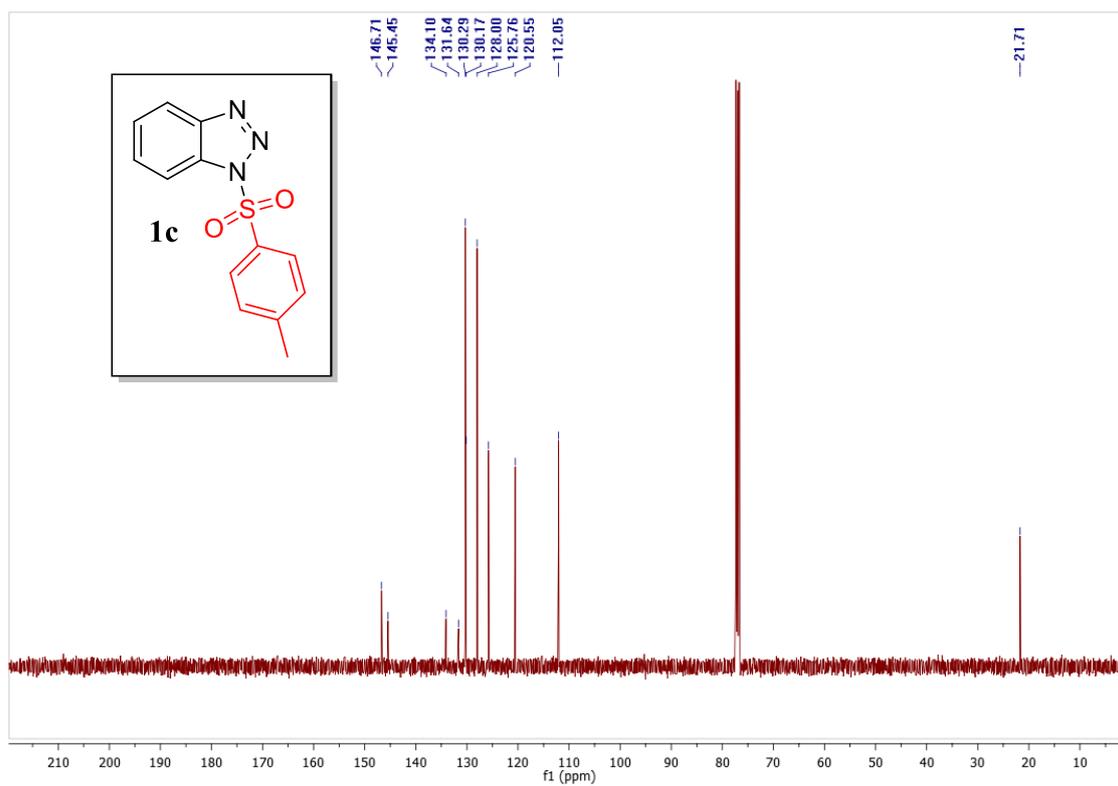
^{13}C -NMR {H} (101 MHz, CDCl_3). 1-Tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (**1b**).



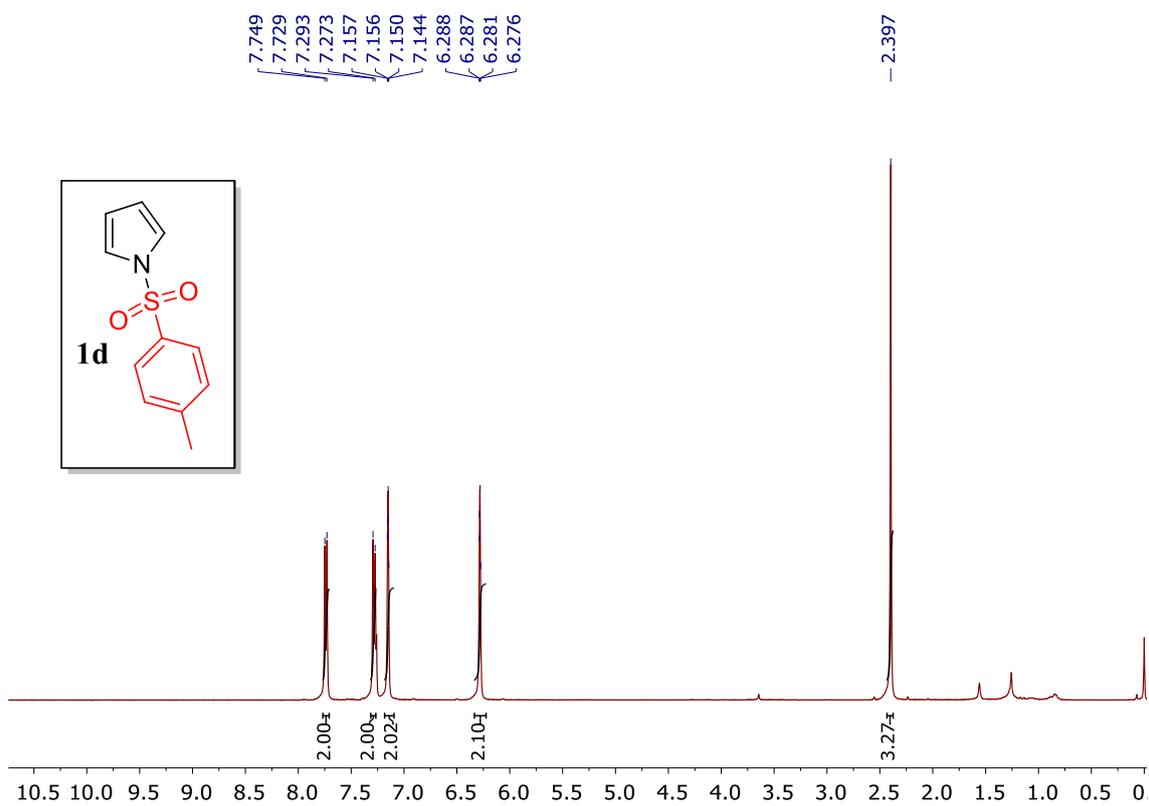
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 1-Tosyl-1*H*-benzo[*d*][1,2,3]triazole (**1c**).



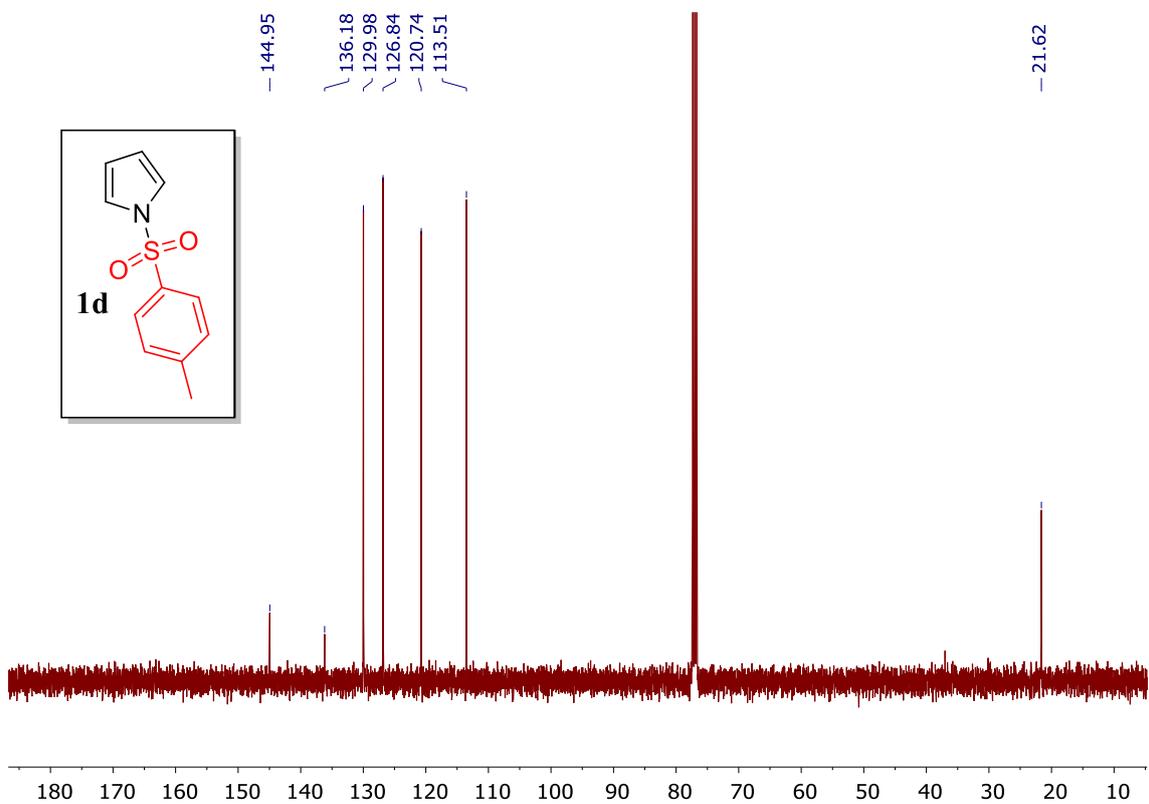
^{13}C -NMR {H} (101 MHz, CDCl_3). 1-Tosyl-1*H*-benzo[*d*][1,2,3]triazole (**1c**).



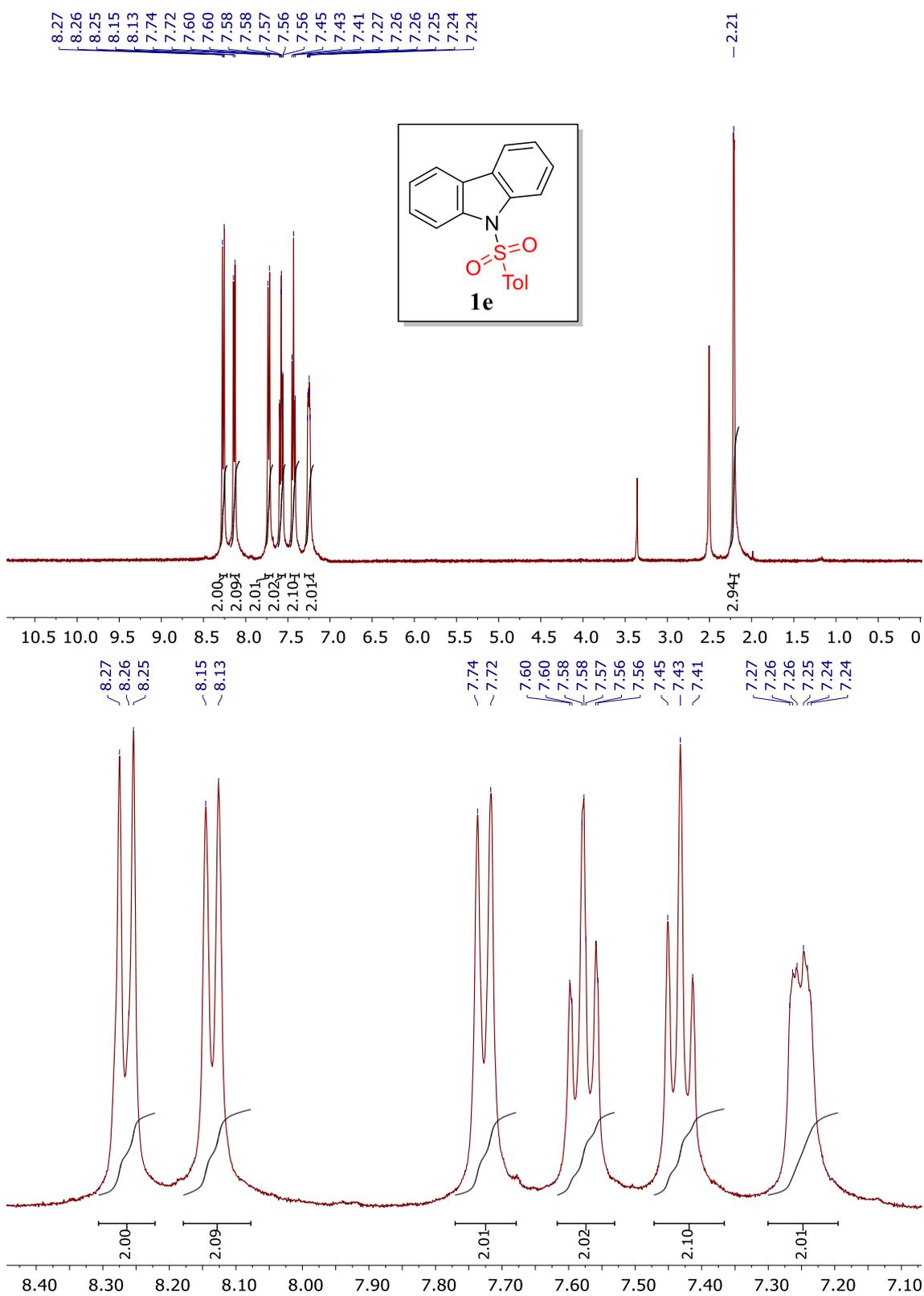
$^1\text{H-NMR}$ (101 MHz, CDCl_3). 1-Tosyl-1*H*-pyrrole (**1d**).



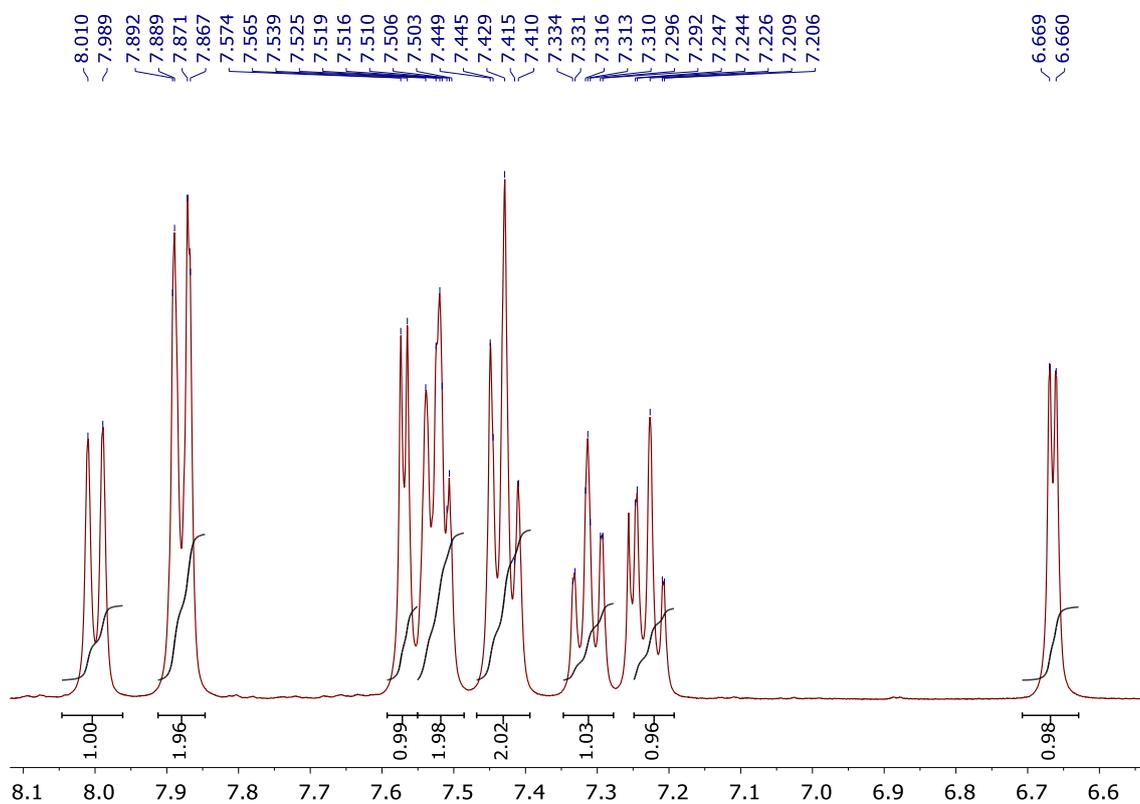
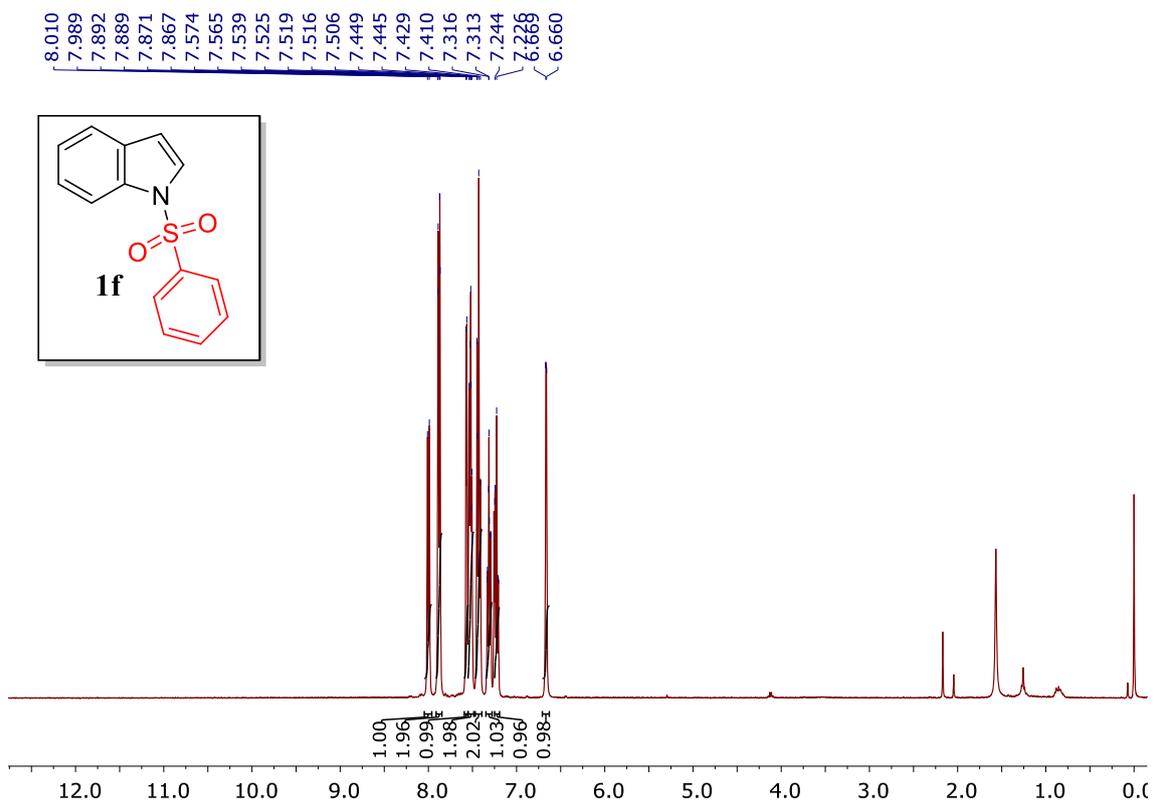
$^{13}\text{C-NMR}$ {H} (101 MHz, CDCl_3). 1-Tosyl-1*H*-pyrrole (**1d**).



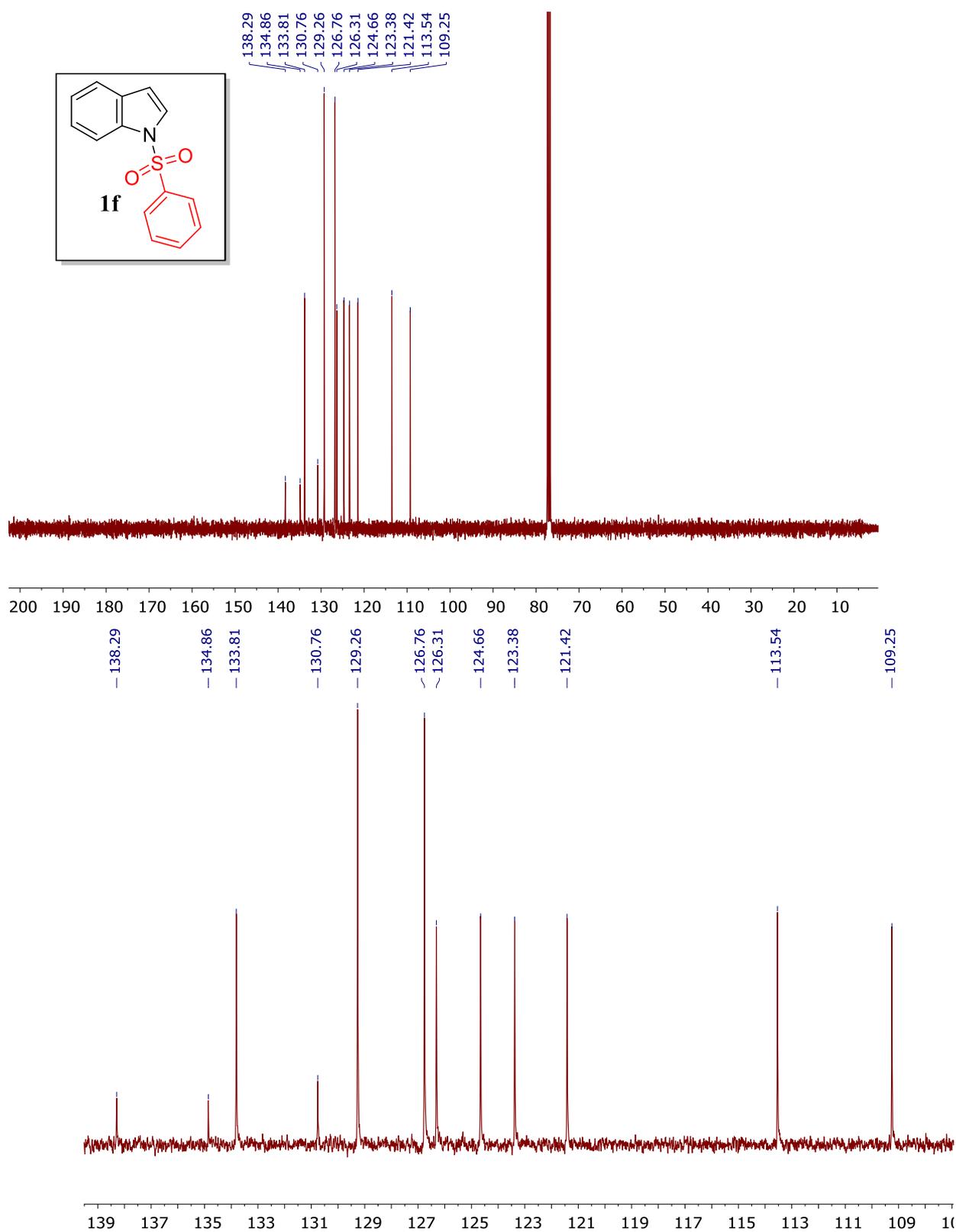
¹H-NMR (400 MHz, CDCl₃). 9-Tosyl-9H-carbazole (**1e**).



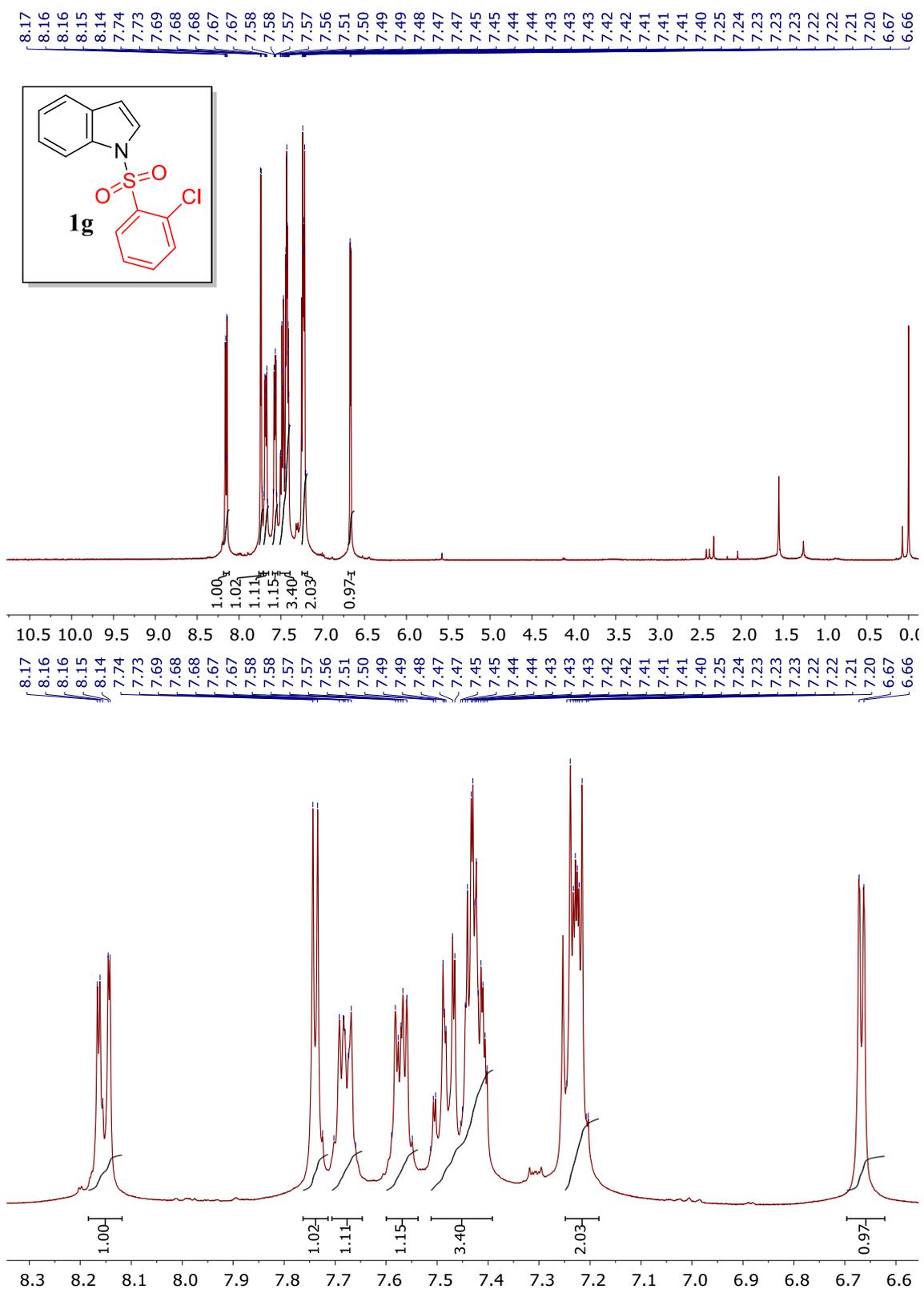
¹H-NMR (400 MHz, CDCl₃). 1-(Phenylsulfonyl)-1*H*-indole (**1f**).



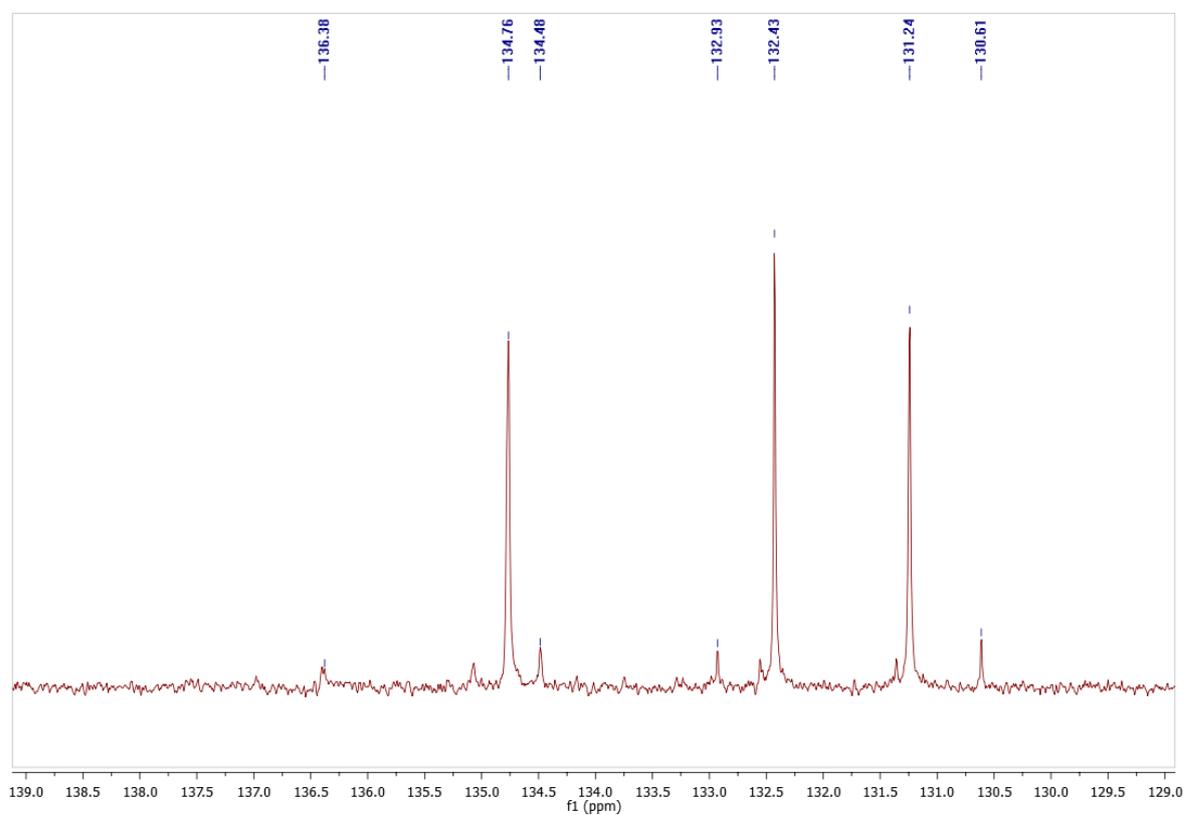
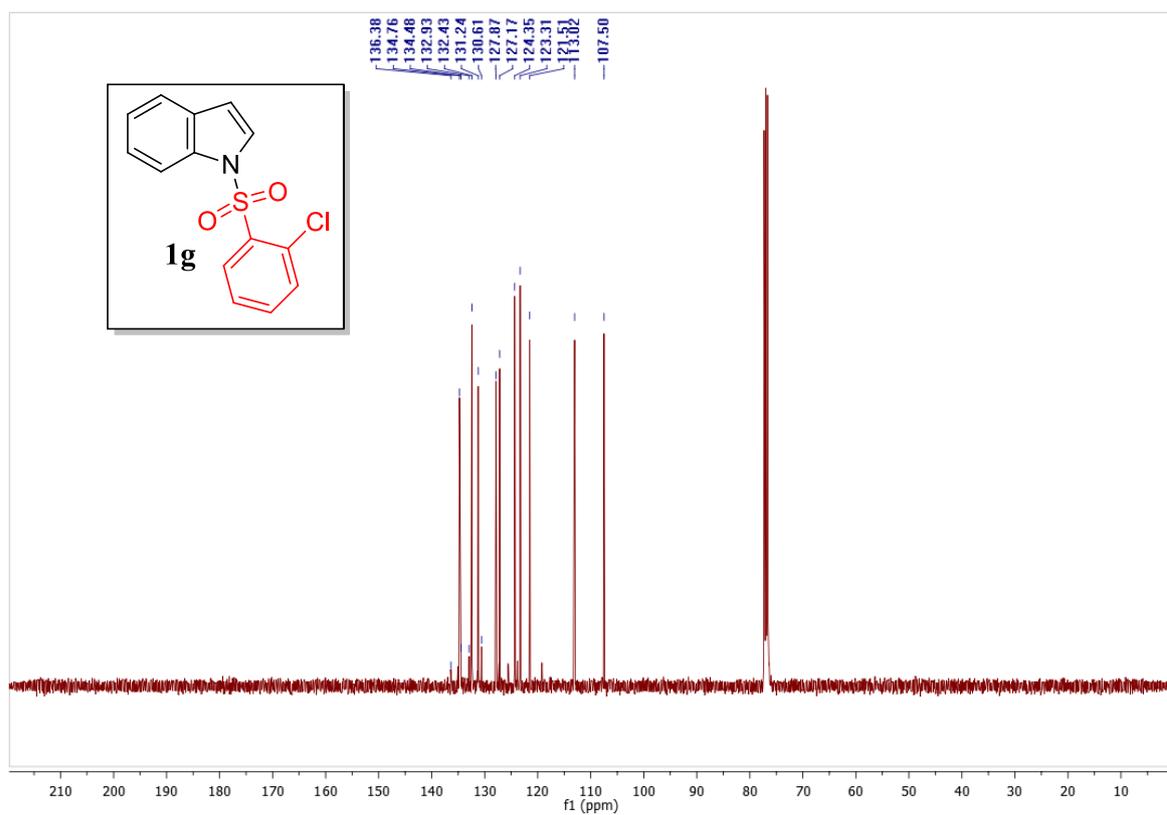
^{13}C -NMR {H} (101 MHz, CDCl_3). 1-(Phenylsulfonyl)-1*H*-indole (**1f**).



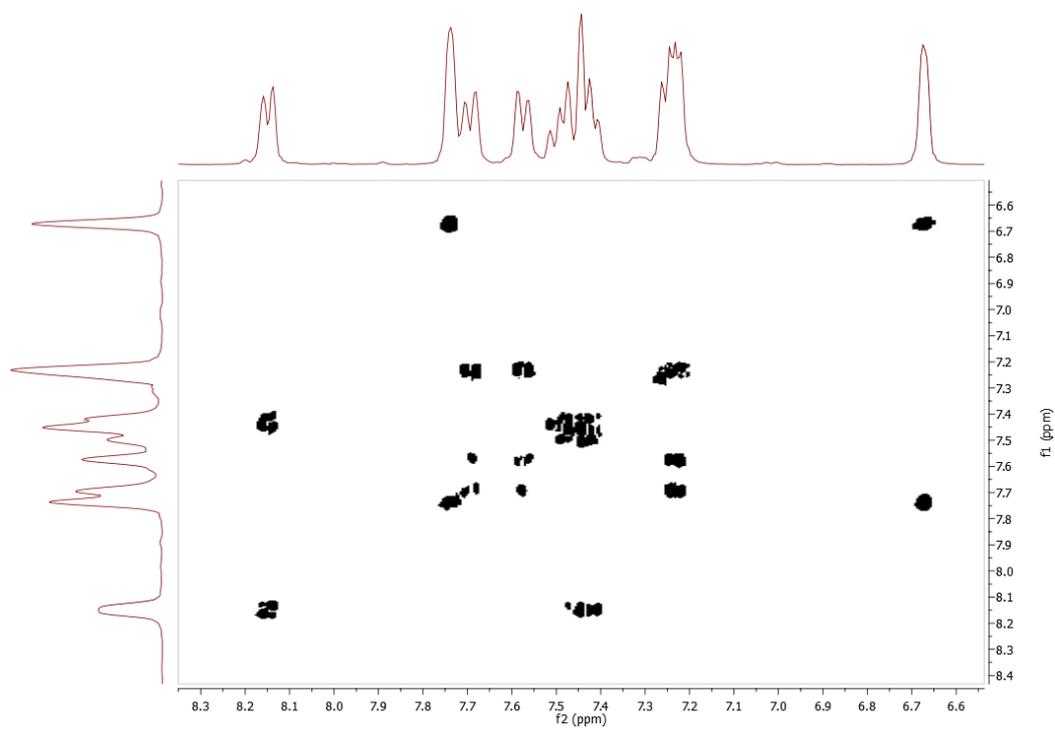
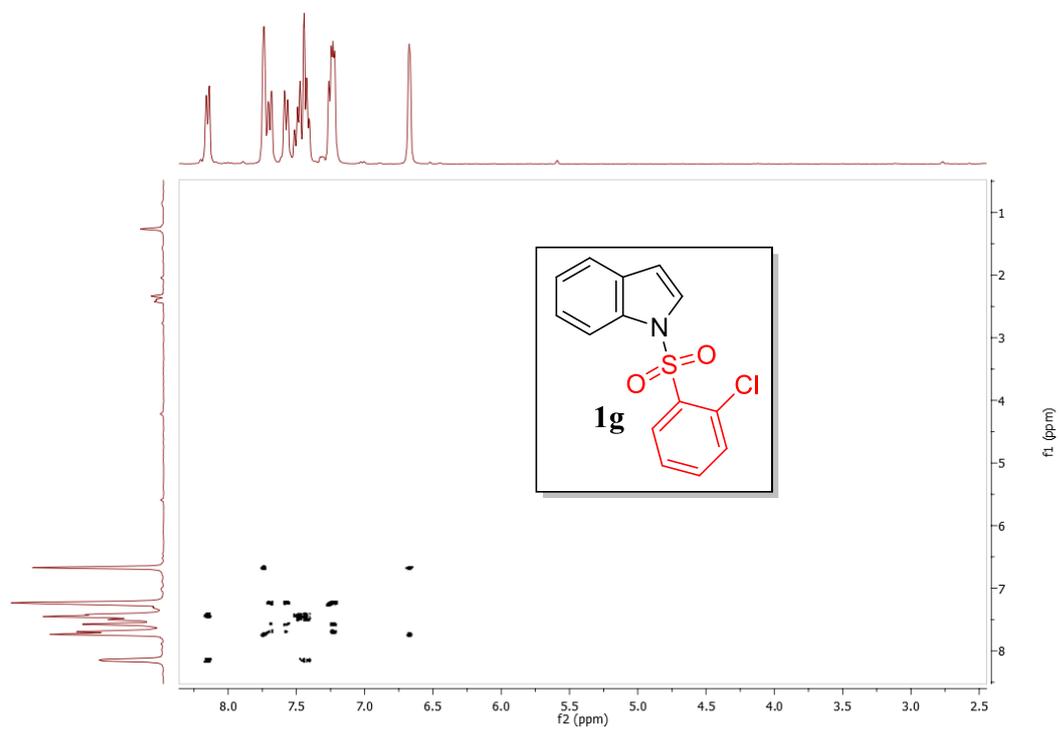
¹H-NMR (400 MHz, CDCl₃). 1-[(2-Chlorophenyl)sulfonyl]-1*H*-indole (**1g**).



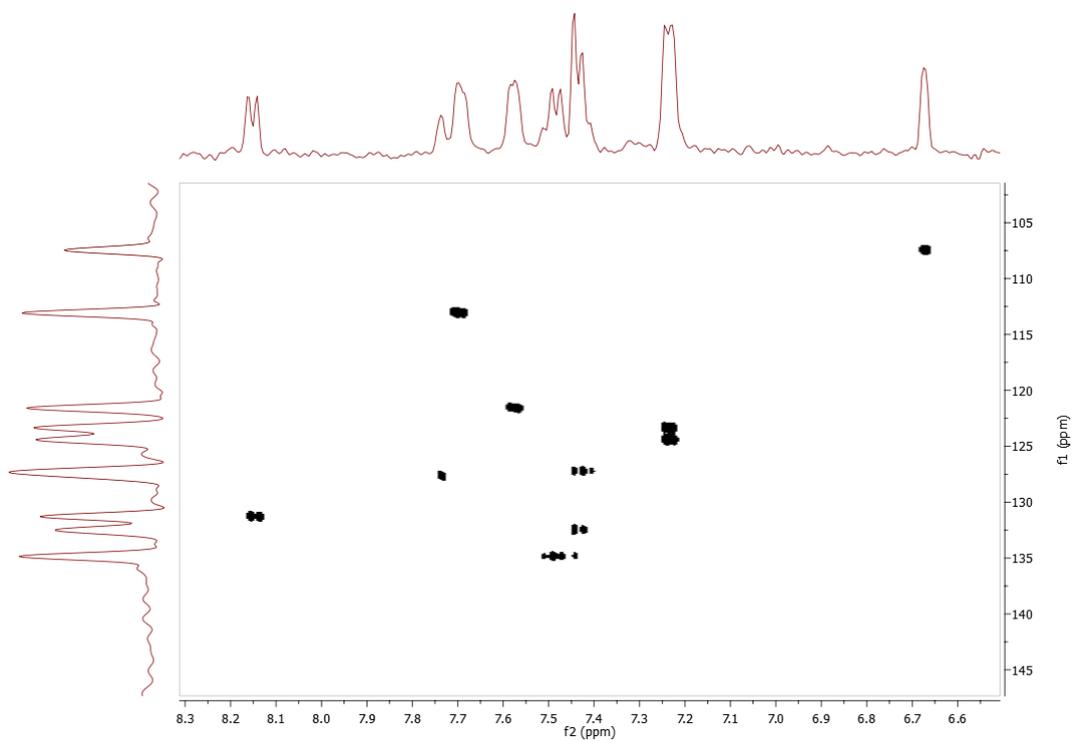
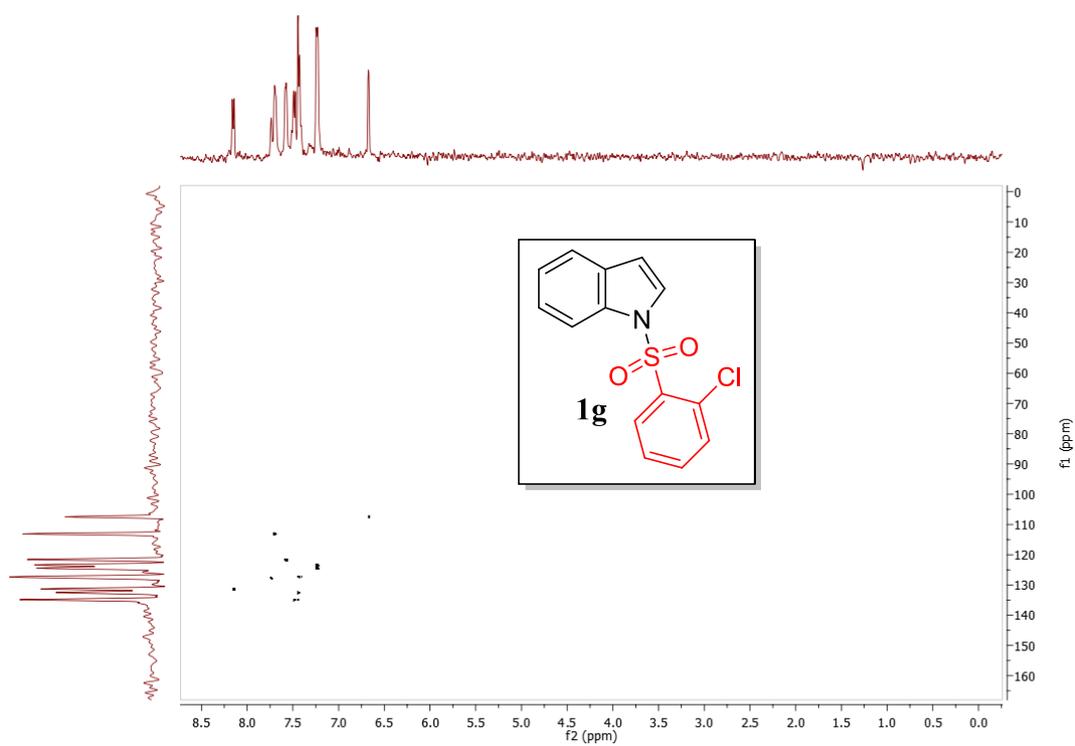
^{13}C -NMR {H} (101 MHz, CDCl_3). 1-[(2-Chlorophenyl)sulfonyl]-1*H*-indole (**1g**).



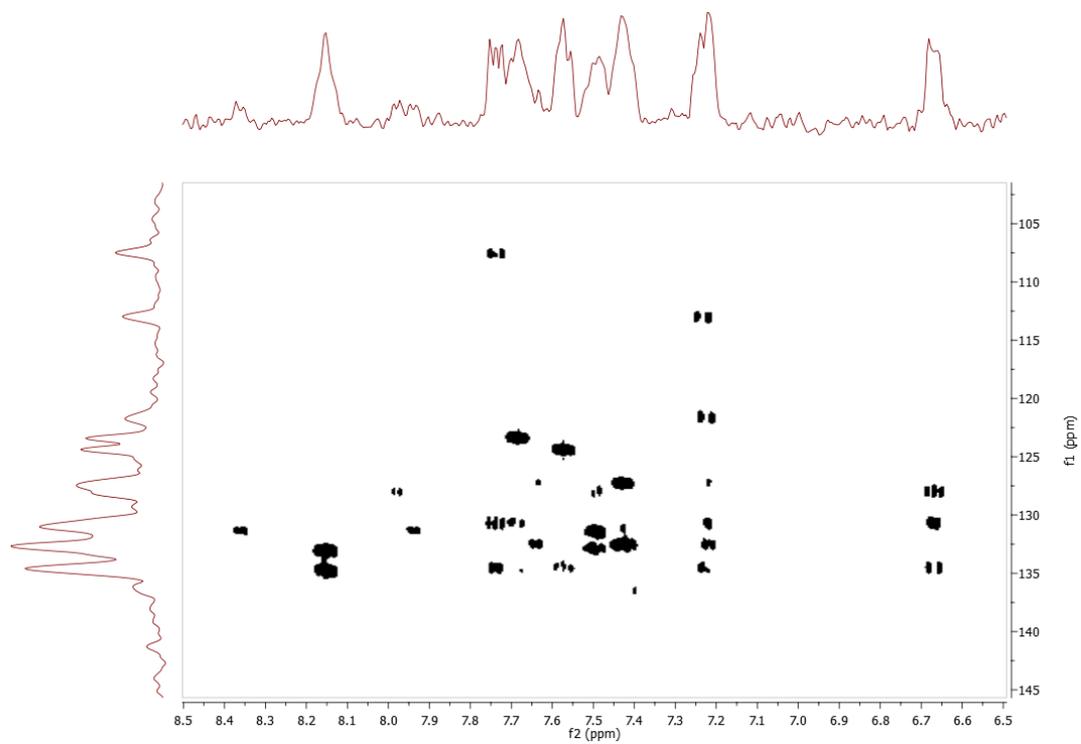
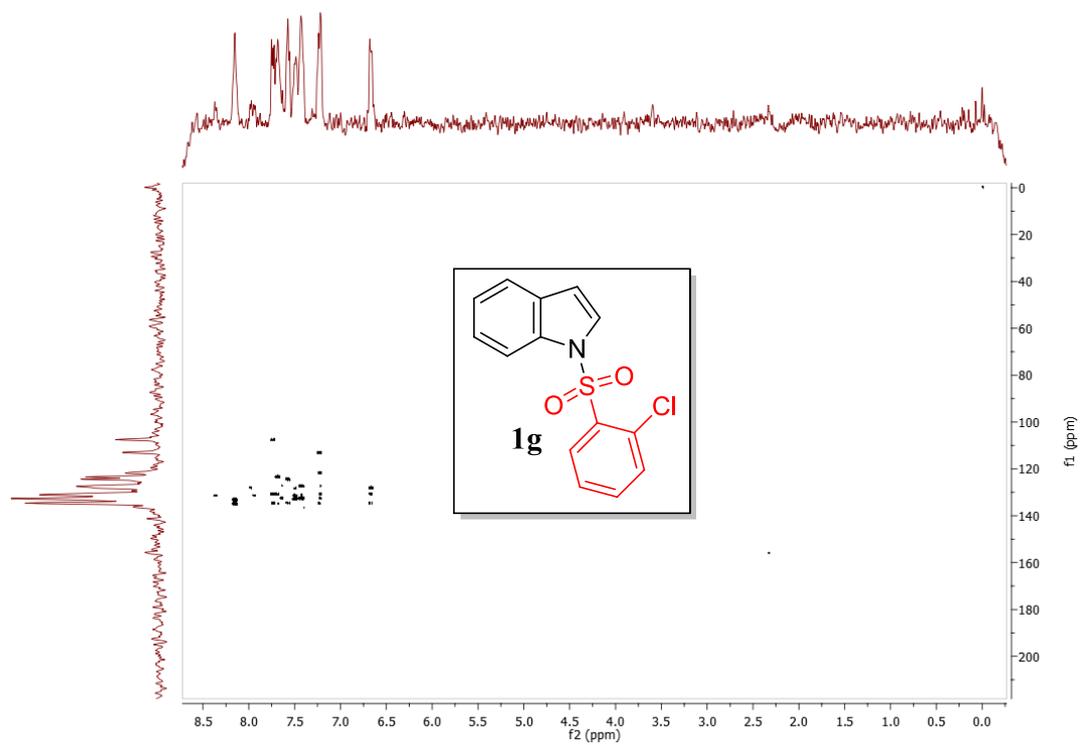
$^1\text{H}/^1\text{H}$ COSY NMR (400 MHz, CDCl_3). 1-[2-Chlorophenylsulfonyl]-1*H*-indole (**1g**).



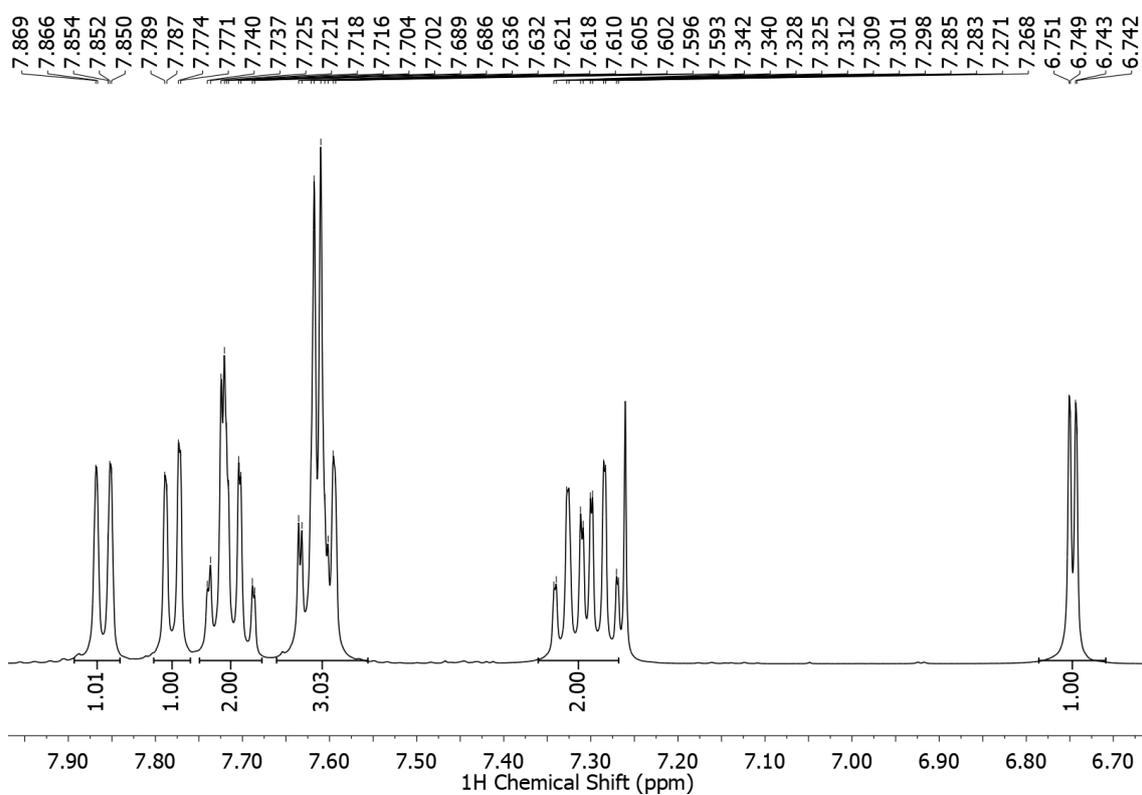
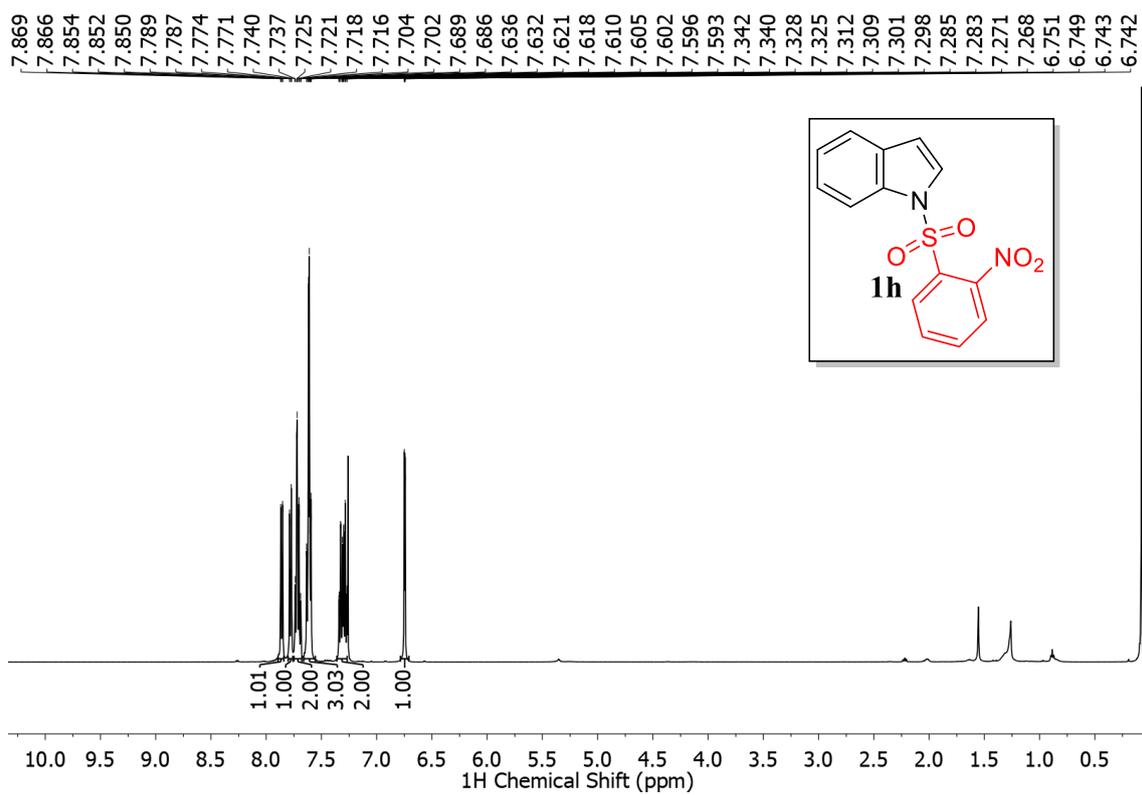
$^1\text{H}/^{13}\text{C}$ HSQC NMR (400 MHz, CDCl_3). 1-[(2-Chlorophenyl)sulfonyl]-1*H*-indole (**1g**).



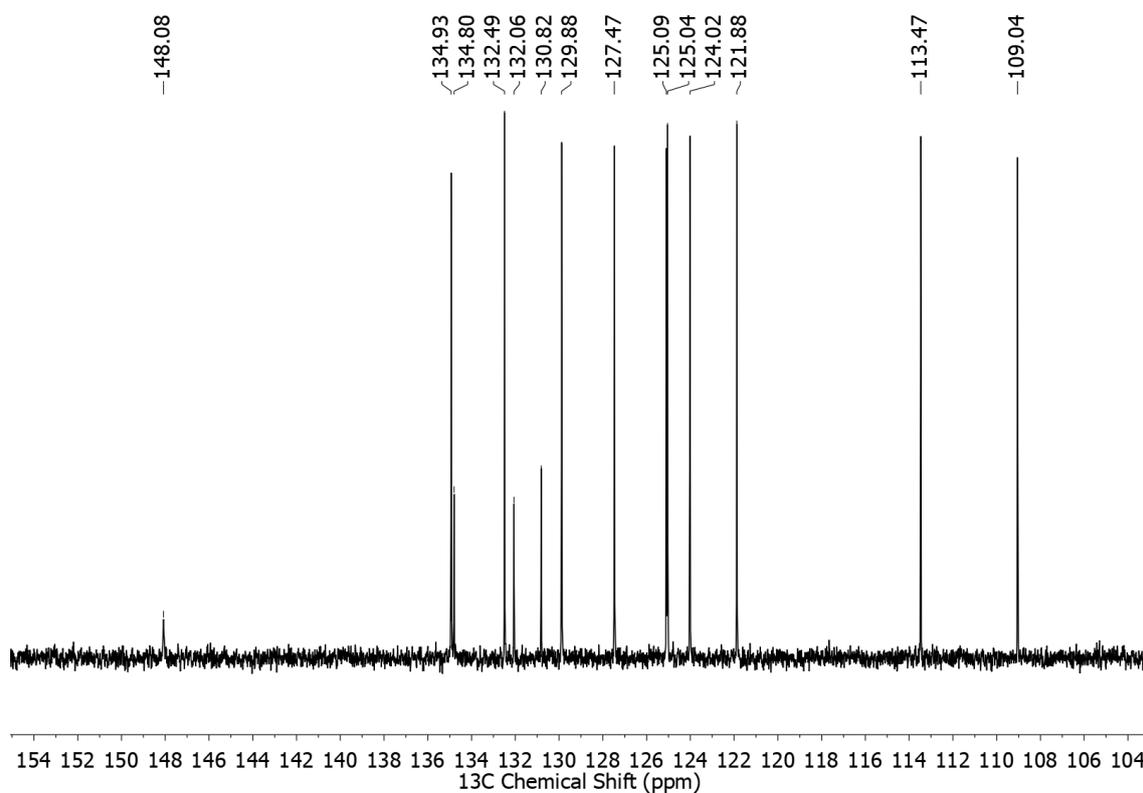
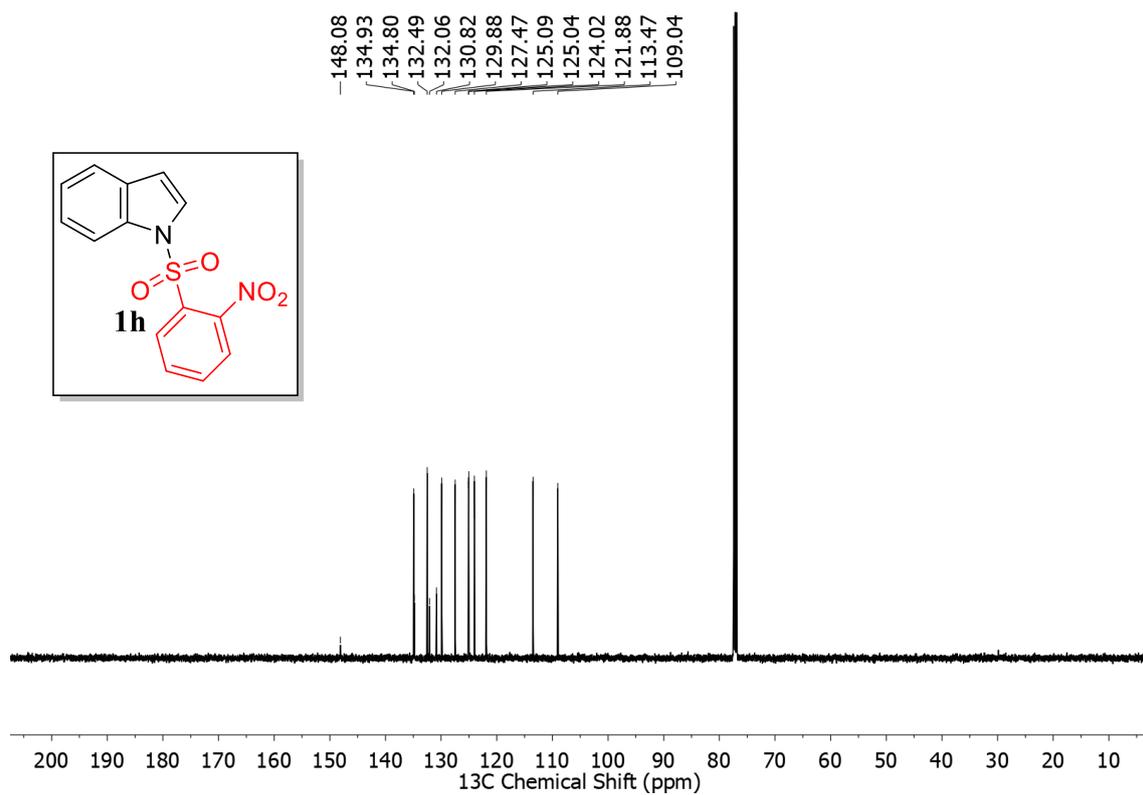
$^1\text{H}/^{13}\text{C}$ HMBC NMR (400 MHz, CDCl_3). 1-[(2-Chlorophenyl)sulfonyl]-1*H*-indole (**1g**)



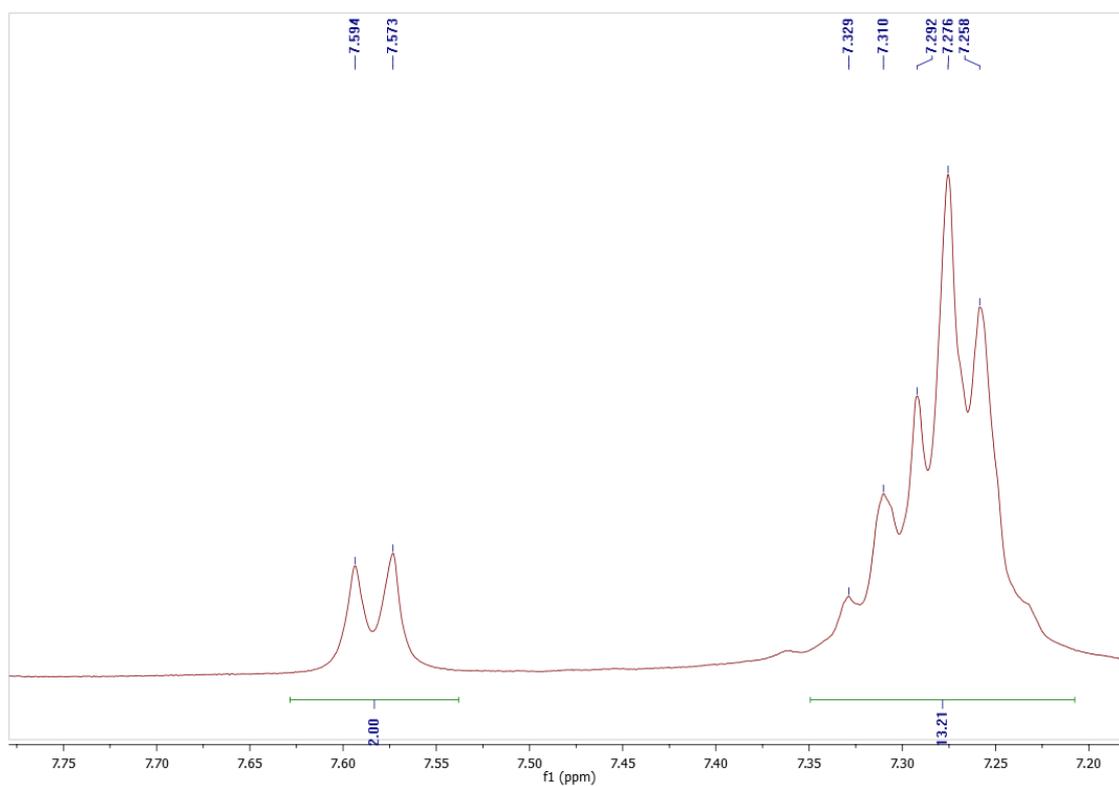
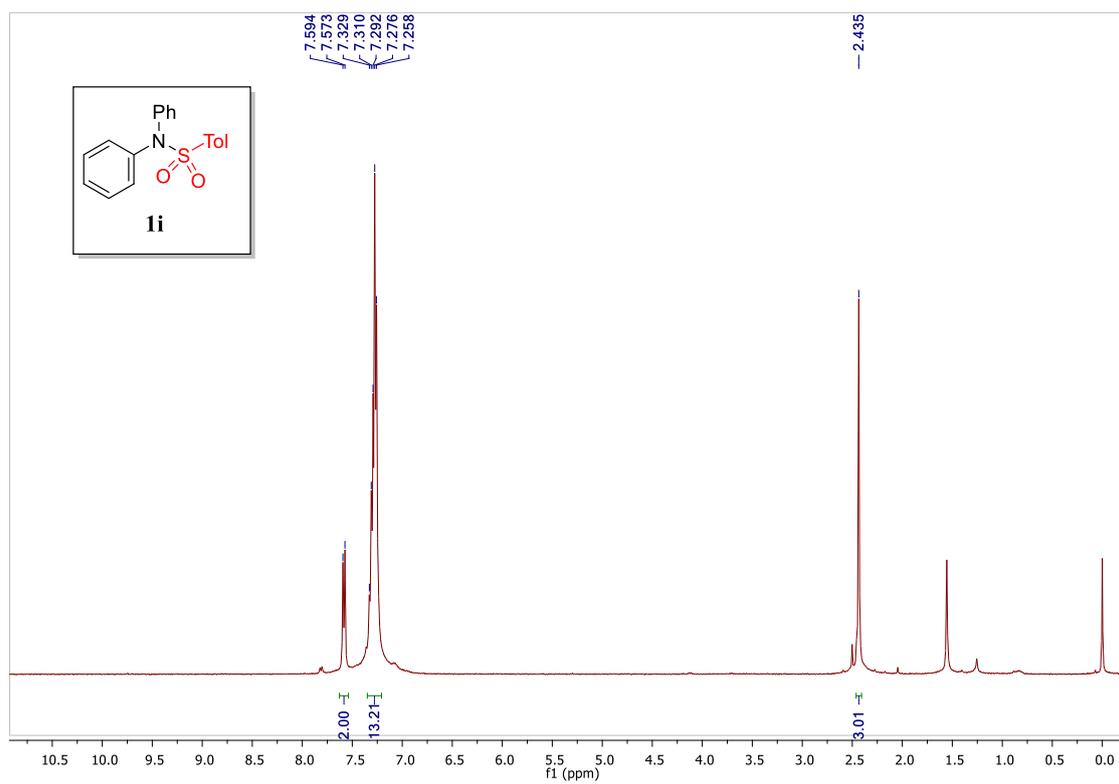
¹H-NMR (500 MHz, CDCl₃). 1-((2-Nitrophenyl)sulfonyl)-1H-indole (**1h**).



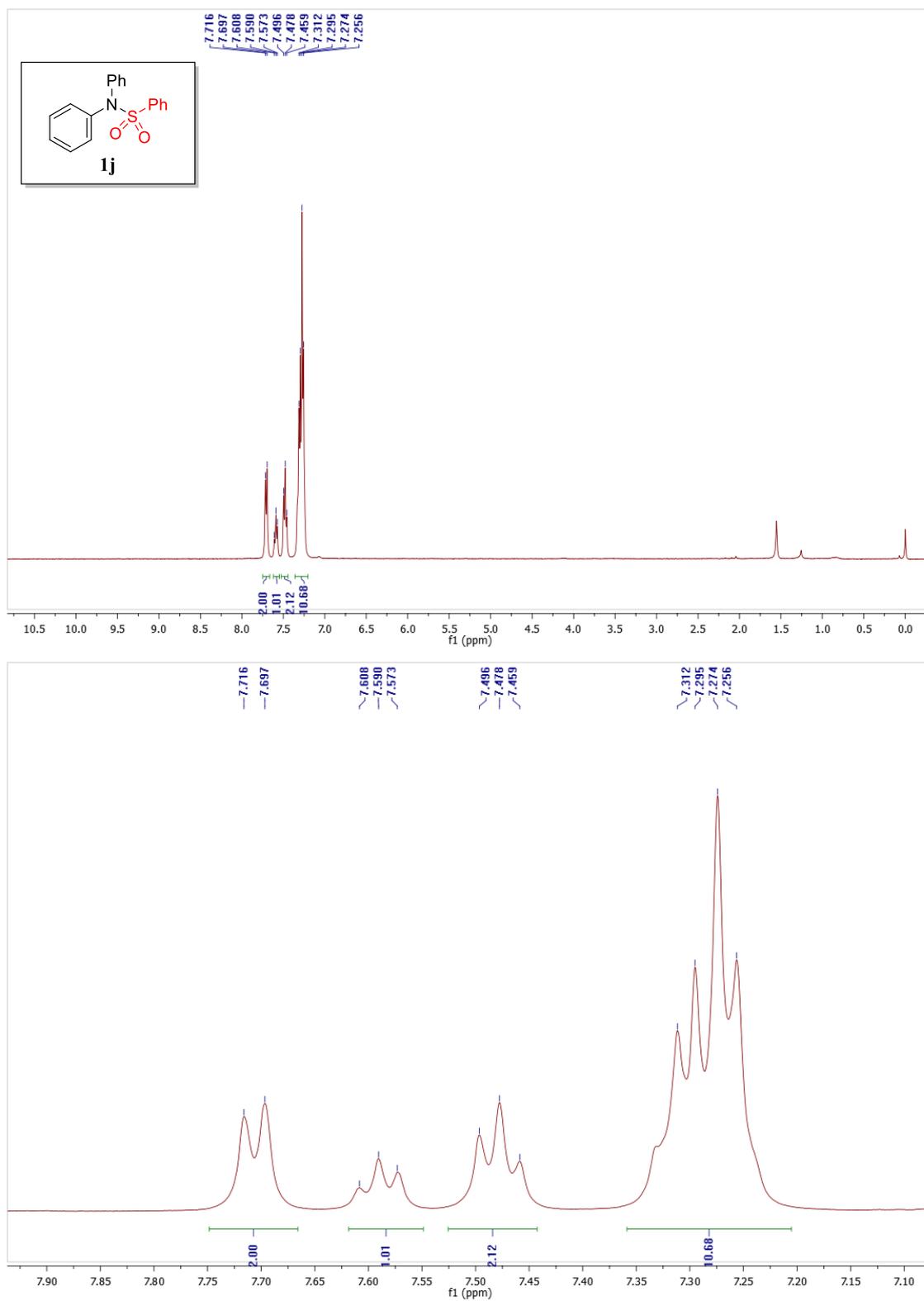
^{13}C -NMR {H} (126 MHz, CDCl_3). 1-((2-Nitrophenyl)sulfonyl)-1*H*-indole (**1h**).



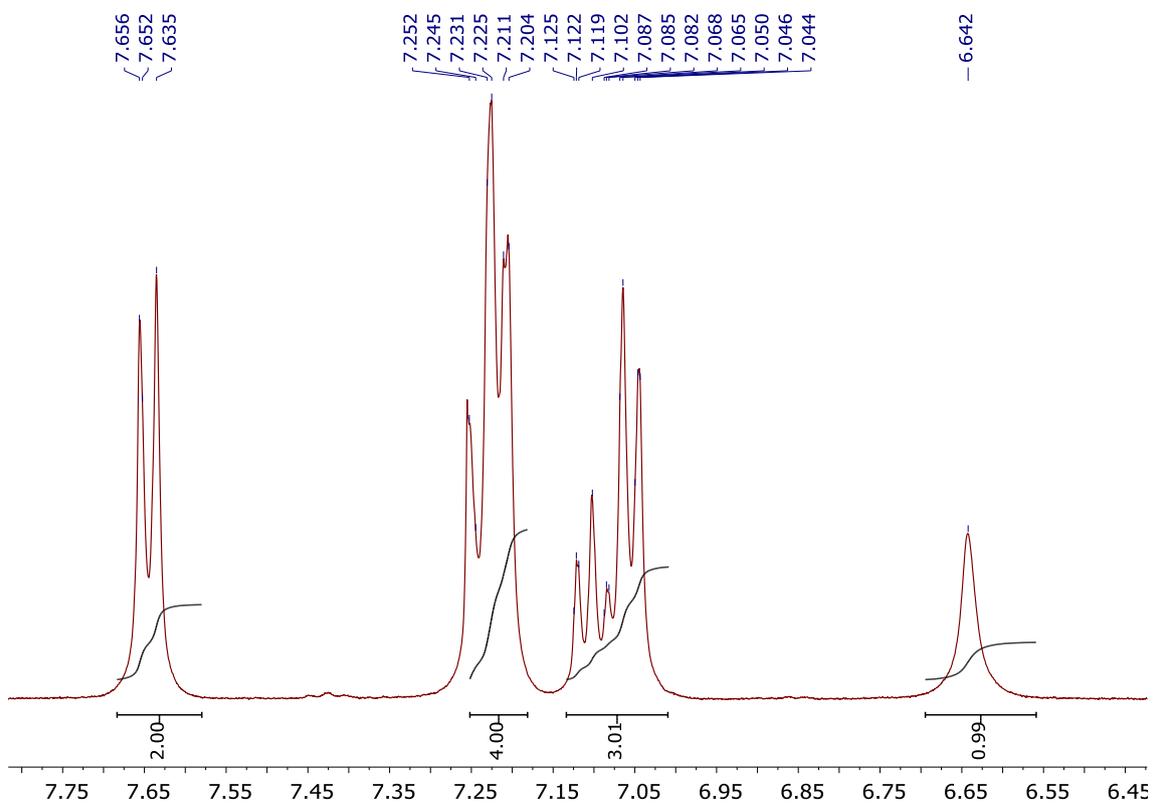
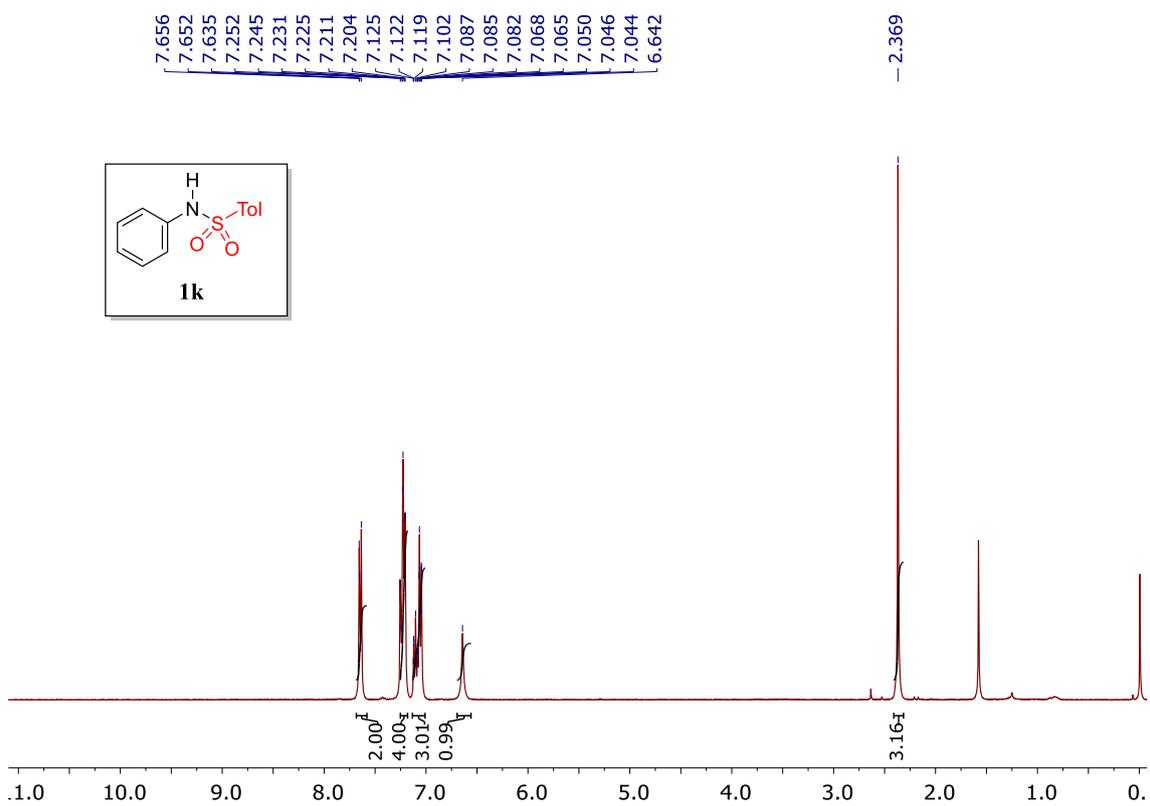
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Methyl-*N,N*-diphenylbenzenesulfonamide (**1i**).



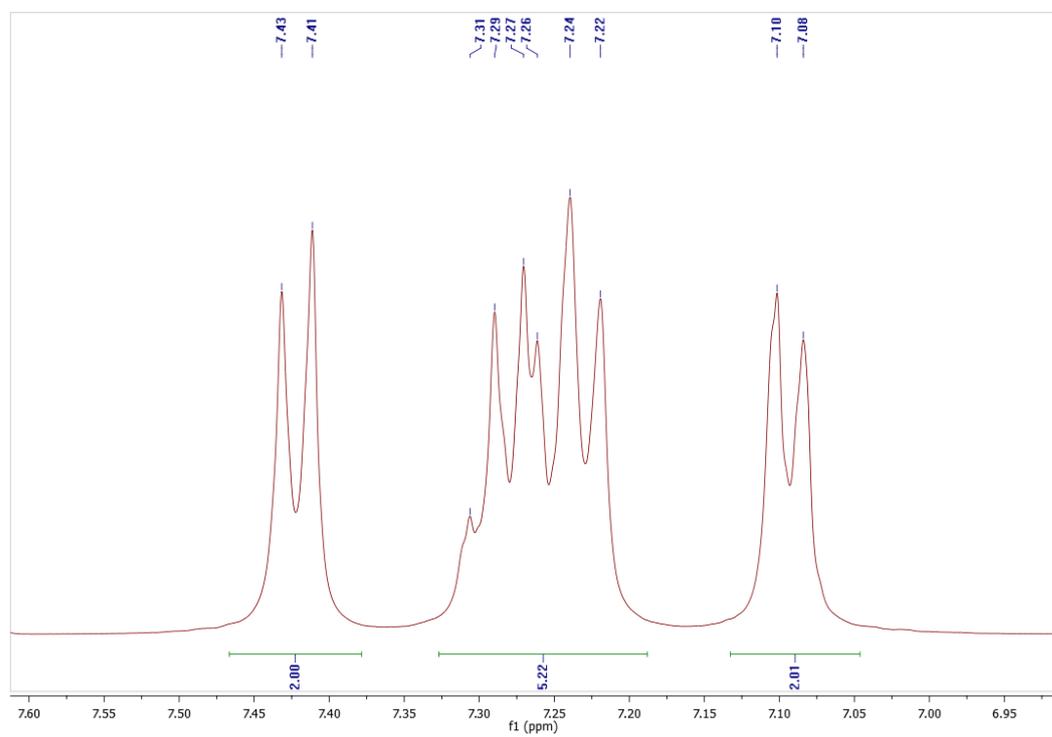
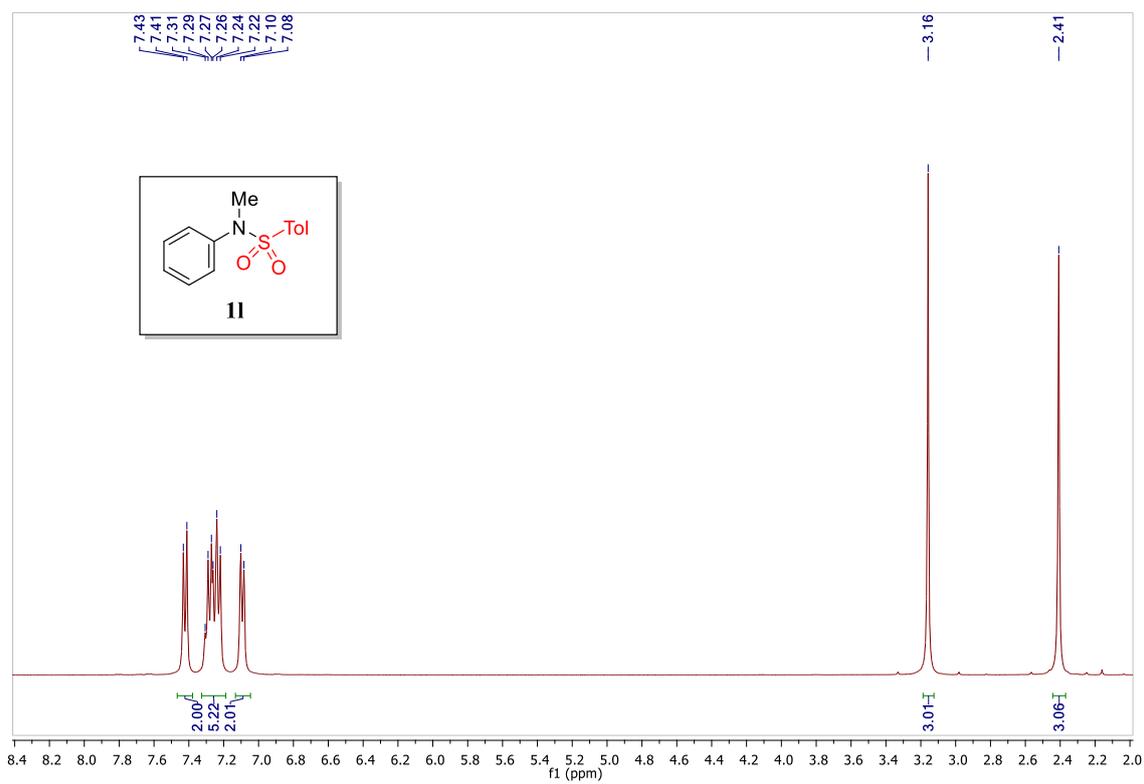
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N,N*-Diphenylbenzenesulfonamide (**1j**).



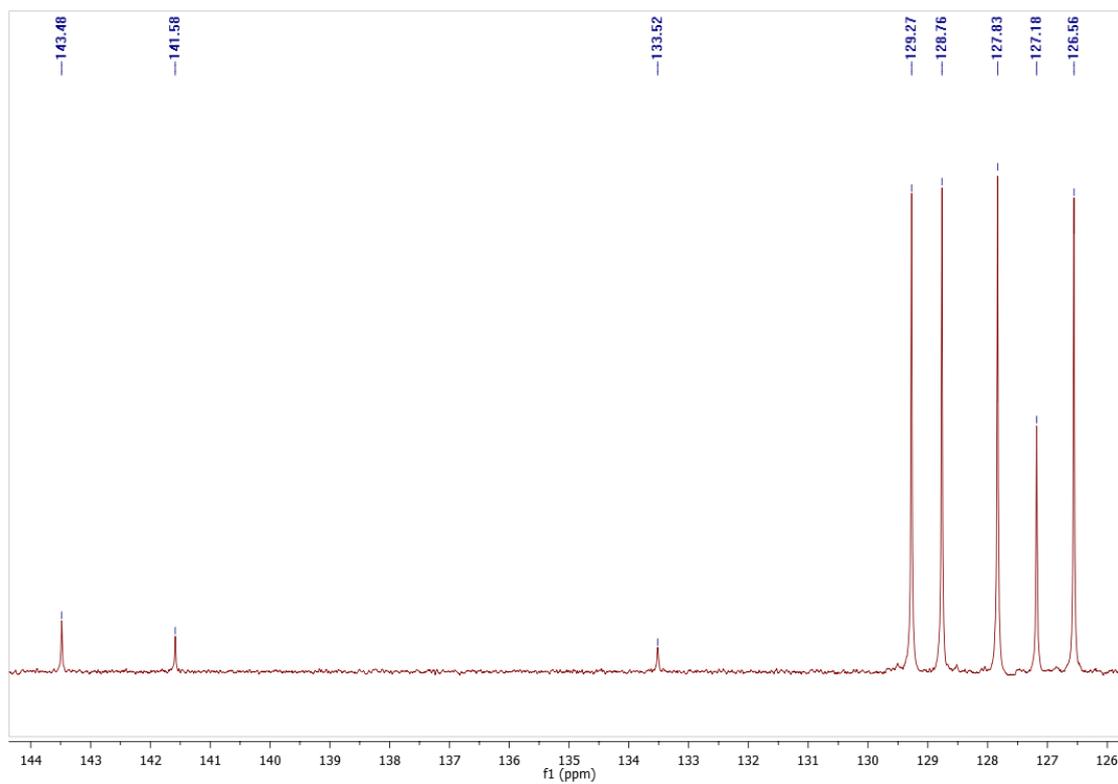
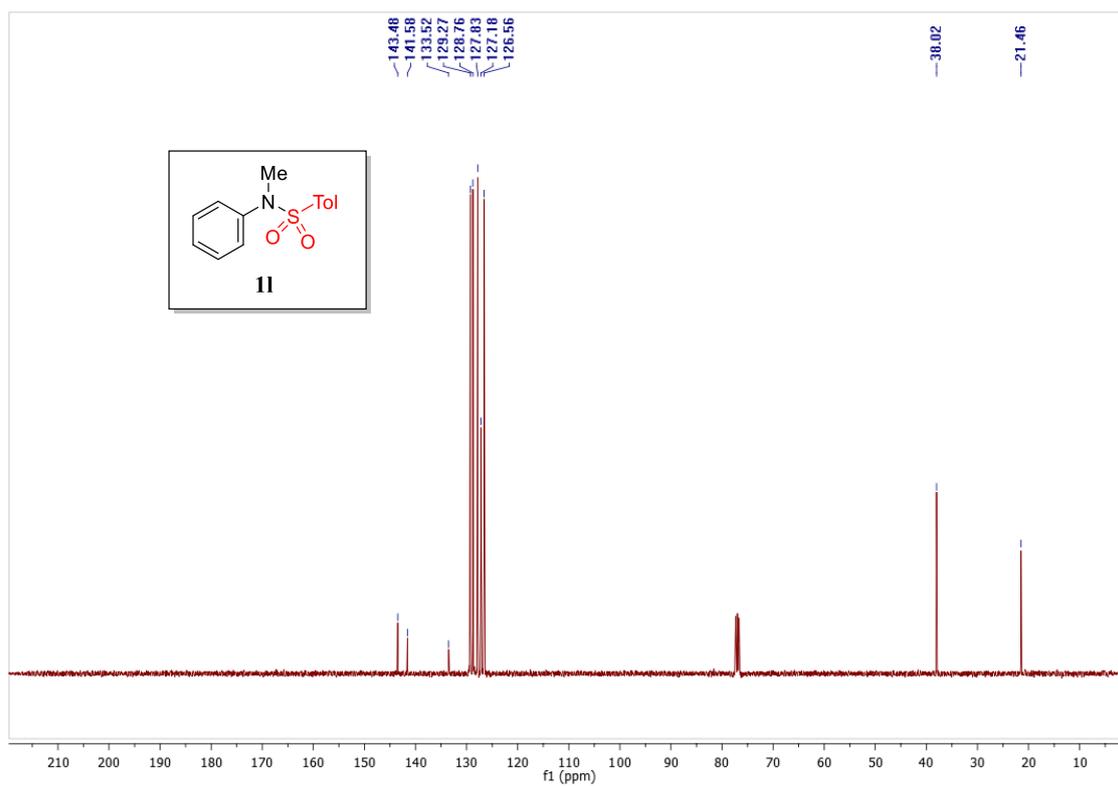
¹H-NMR (400 MHz, CDCl₃). 4-Methyl-*N*-phenylbenzenesulfonamide (**1k**).



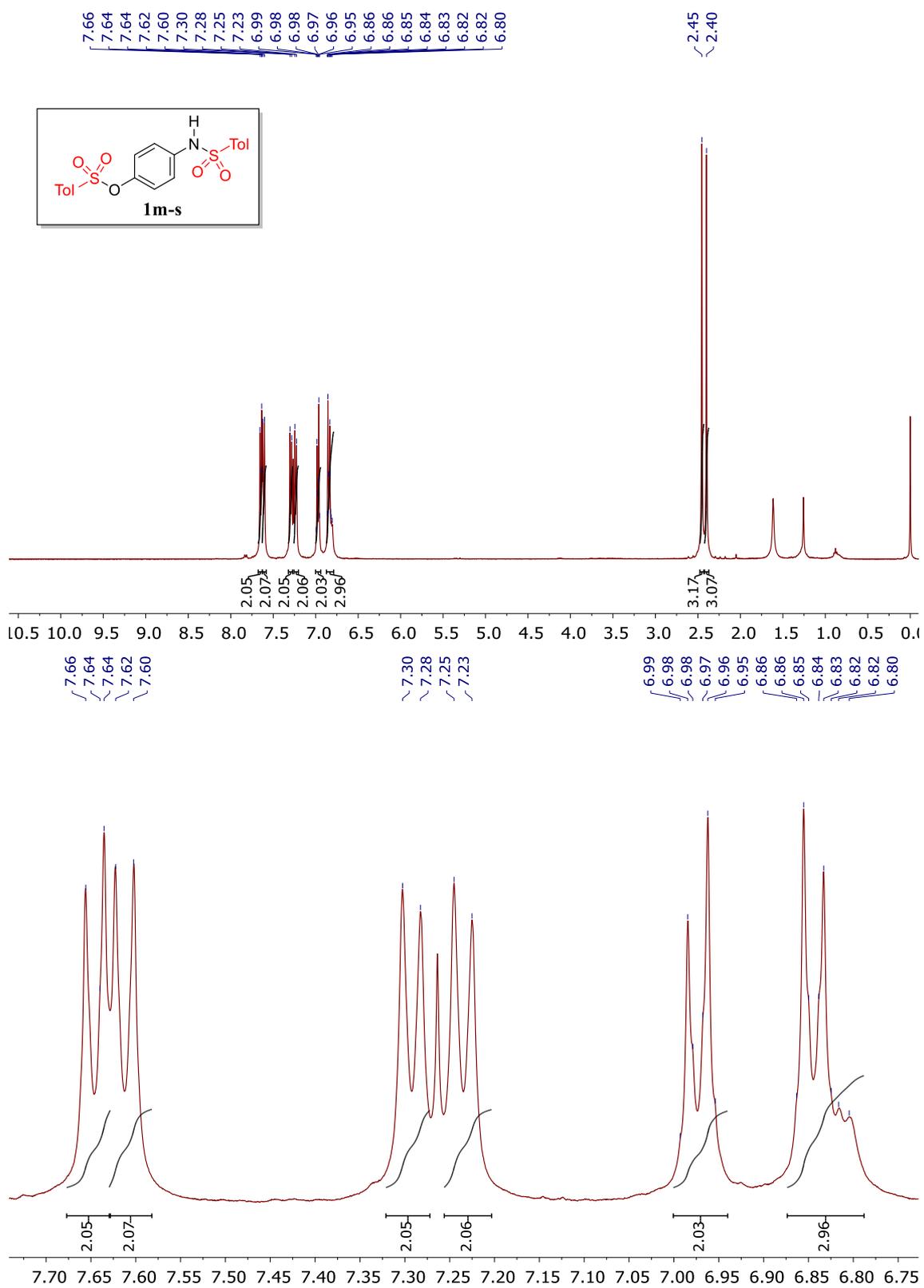
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*,4-dimethyl-*N*-phenylbenzenesulfonamide (**11**).



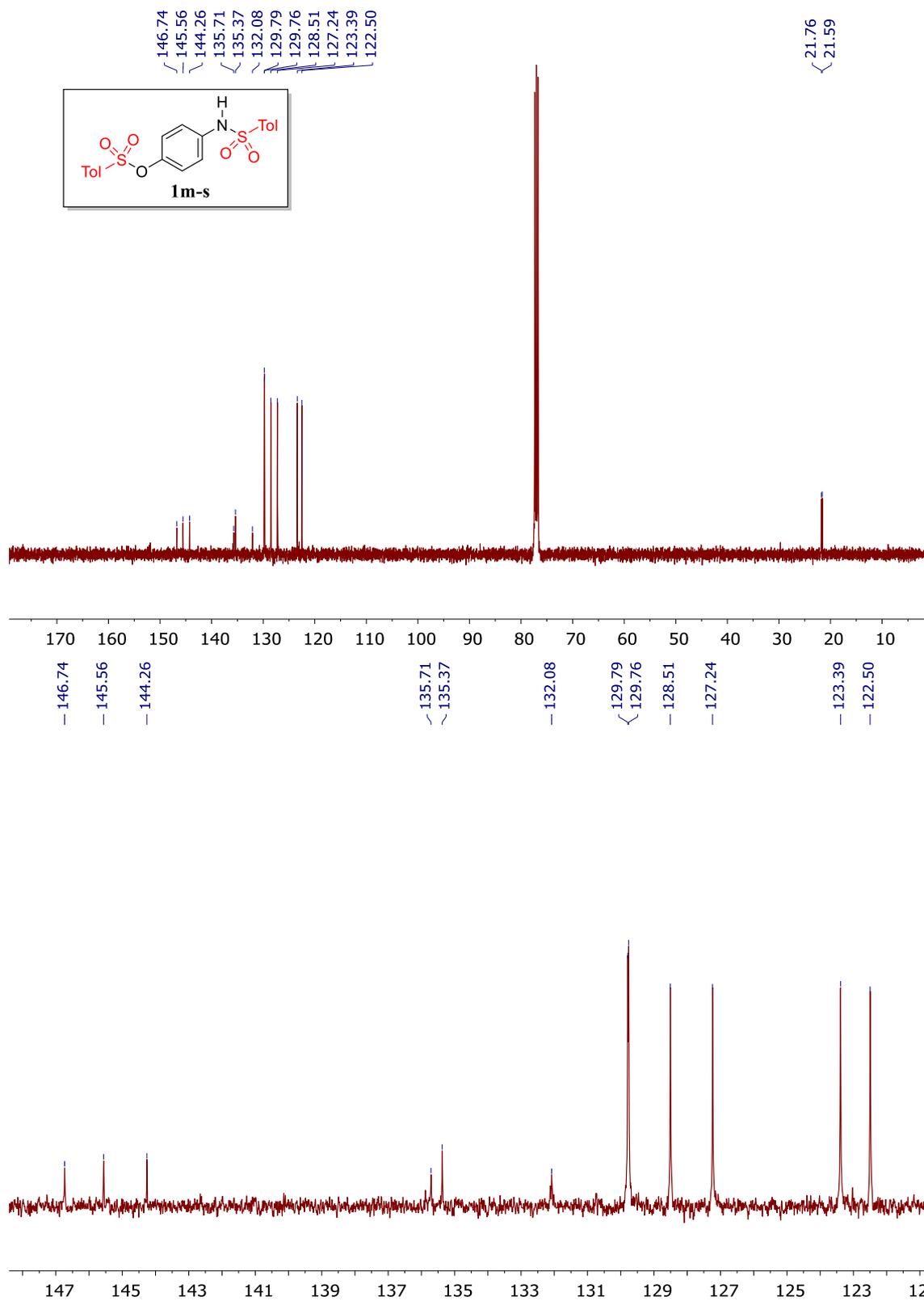
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*,4-dimethyl-*N*-phenylbenzenesulfonamide (**11**).



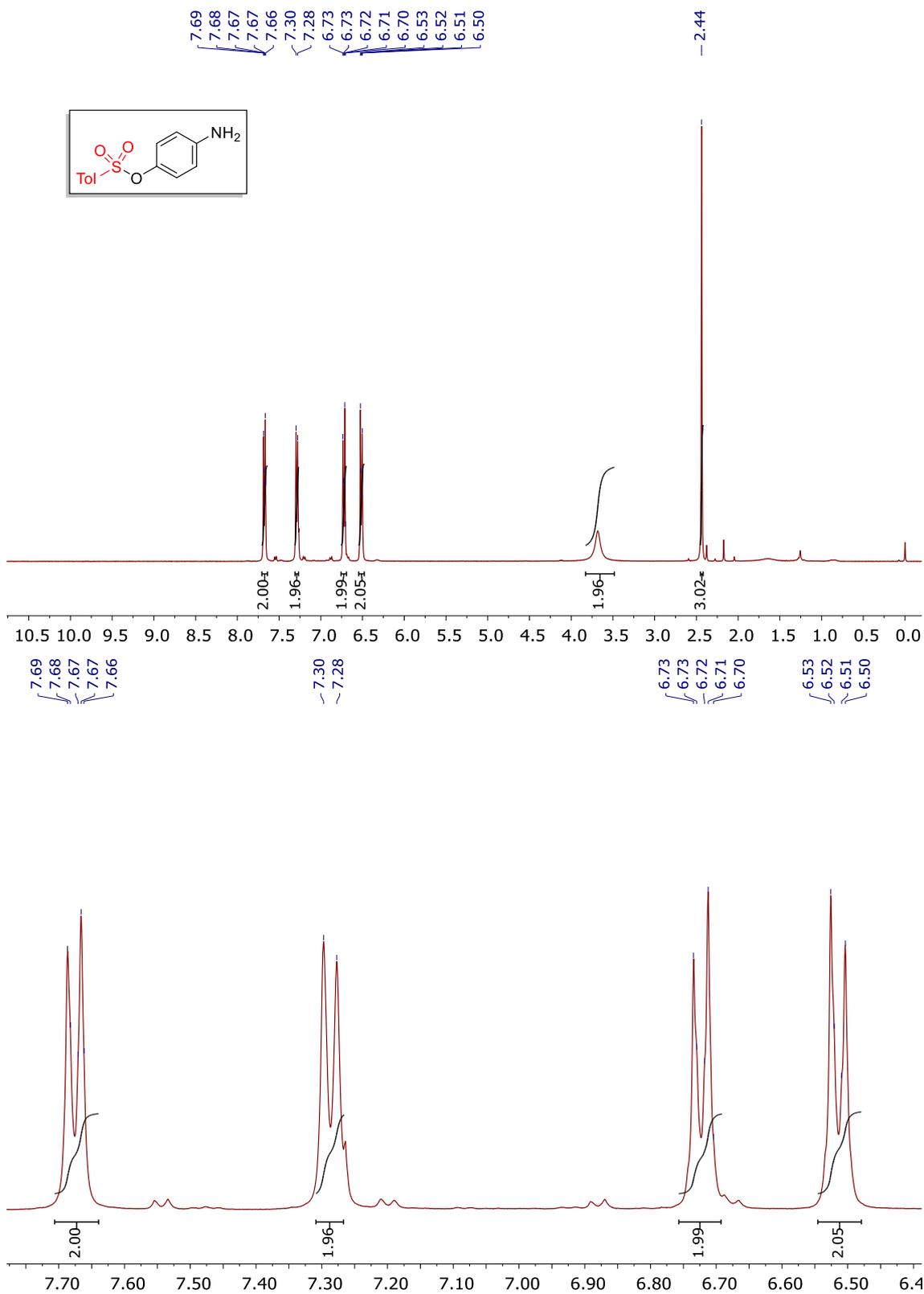
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-(4-Methylphenylsulfonamido) phenyl 4-methyl benzenesulfonate (**1m-s**).



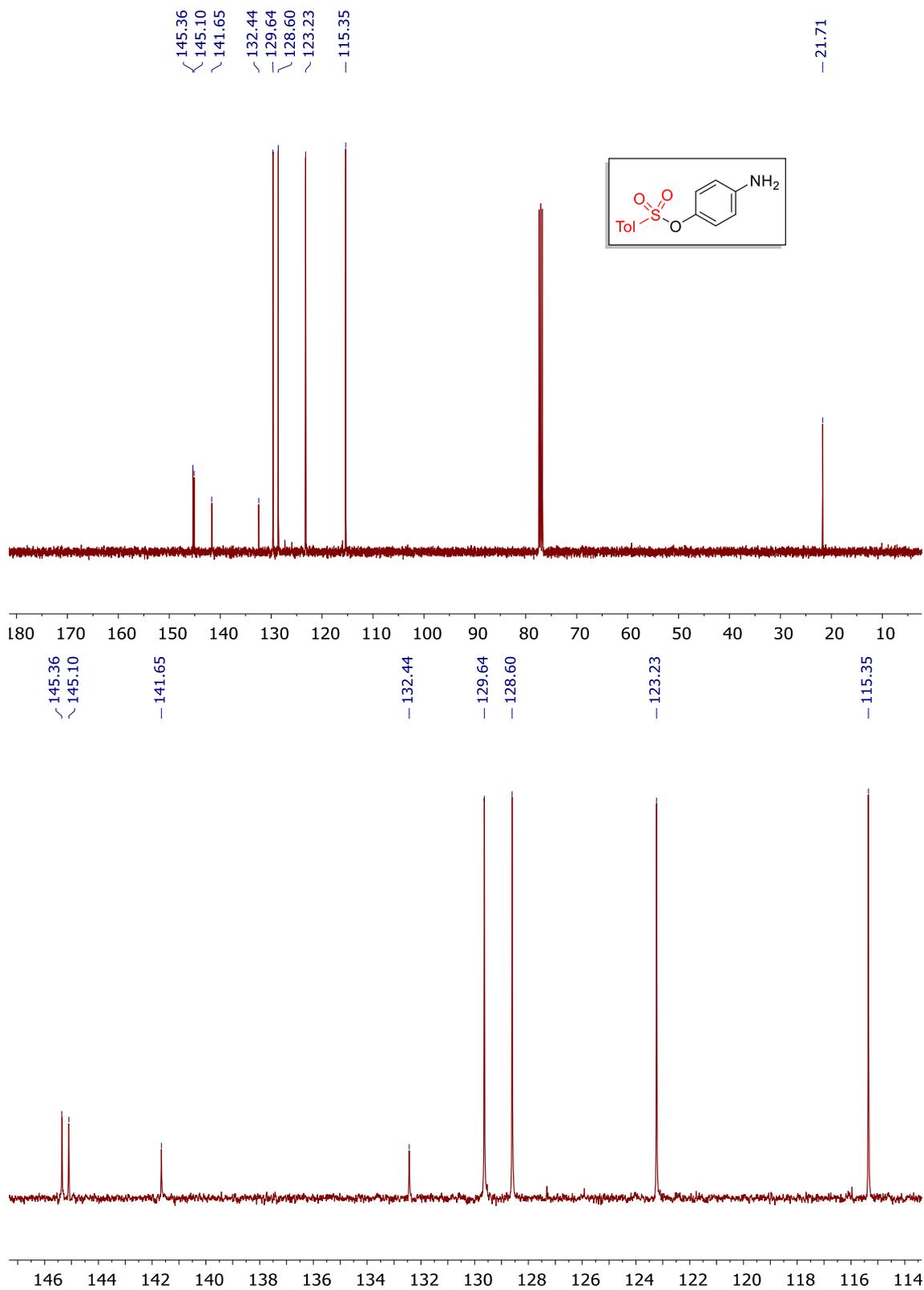
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-(4-Methylphenylsulfonamido) phenyl 4-methylbenzenesulfonate (**1m-s**)



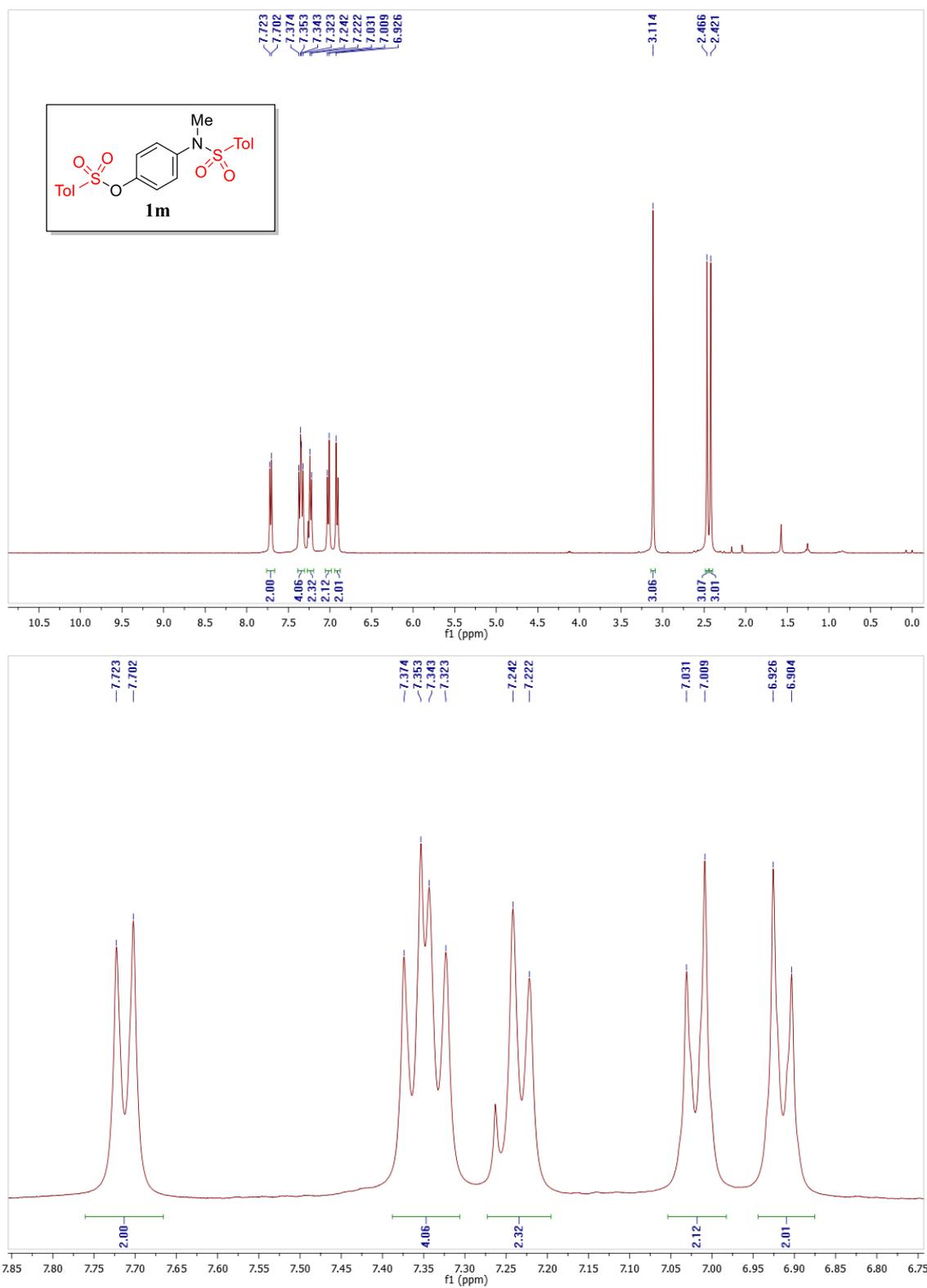
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Aminophenyl 4-methylbenzenesulfonate.



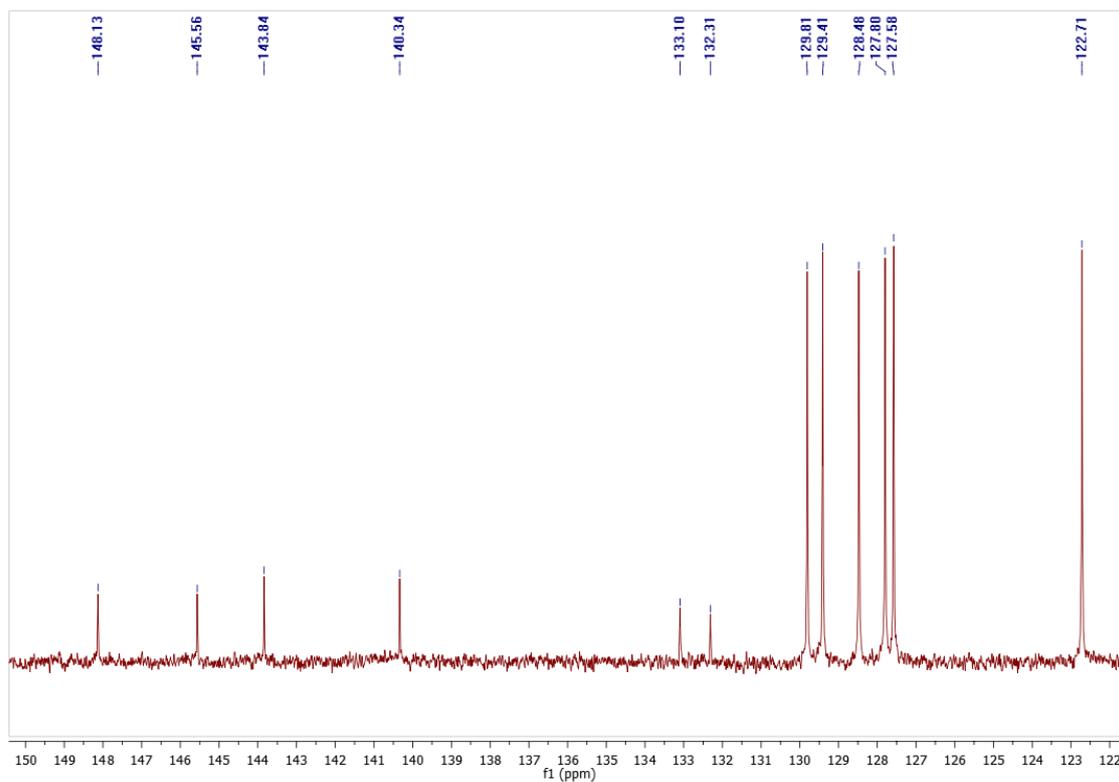
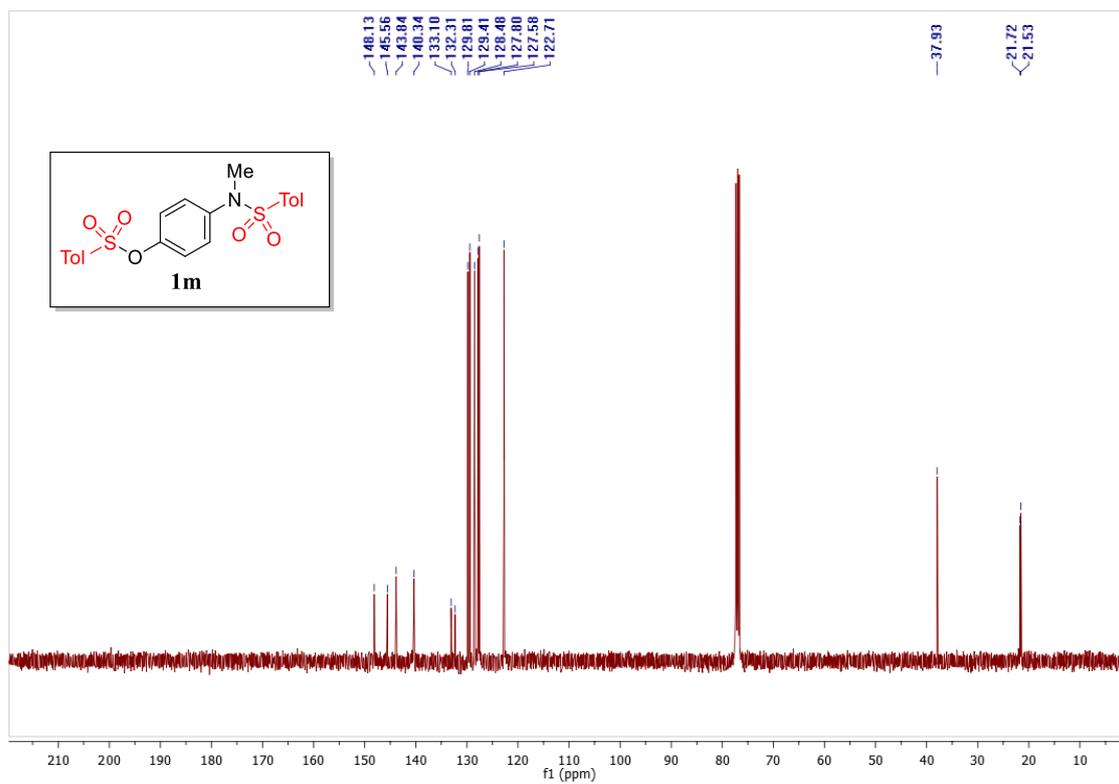
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-Aminophenyl 4-methylbenzenesulfonate.



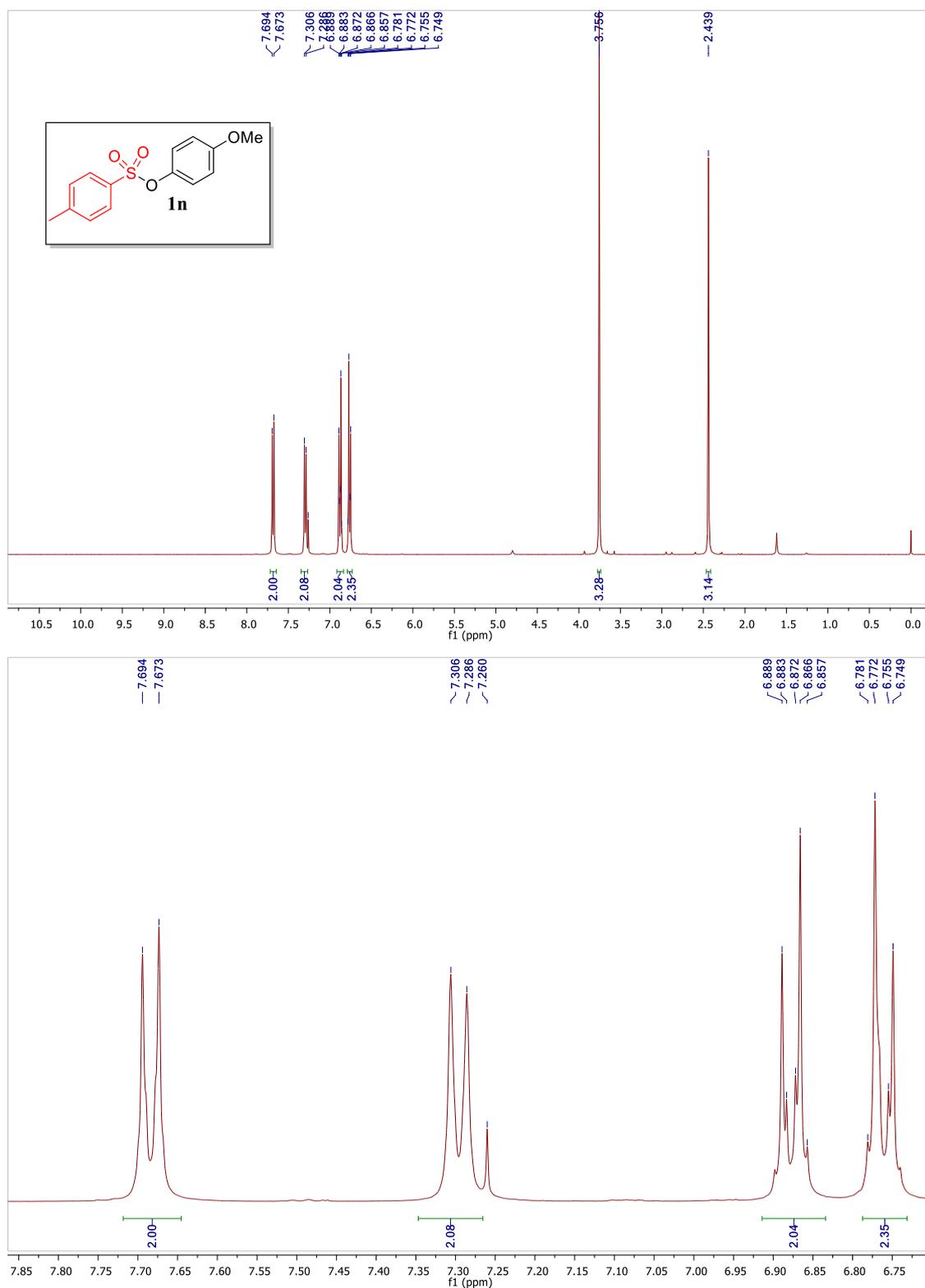
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-(*N*,4-Dimethylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (**1m**).



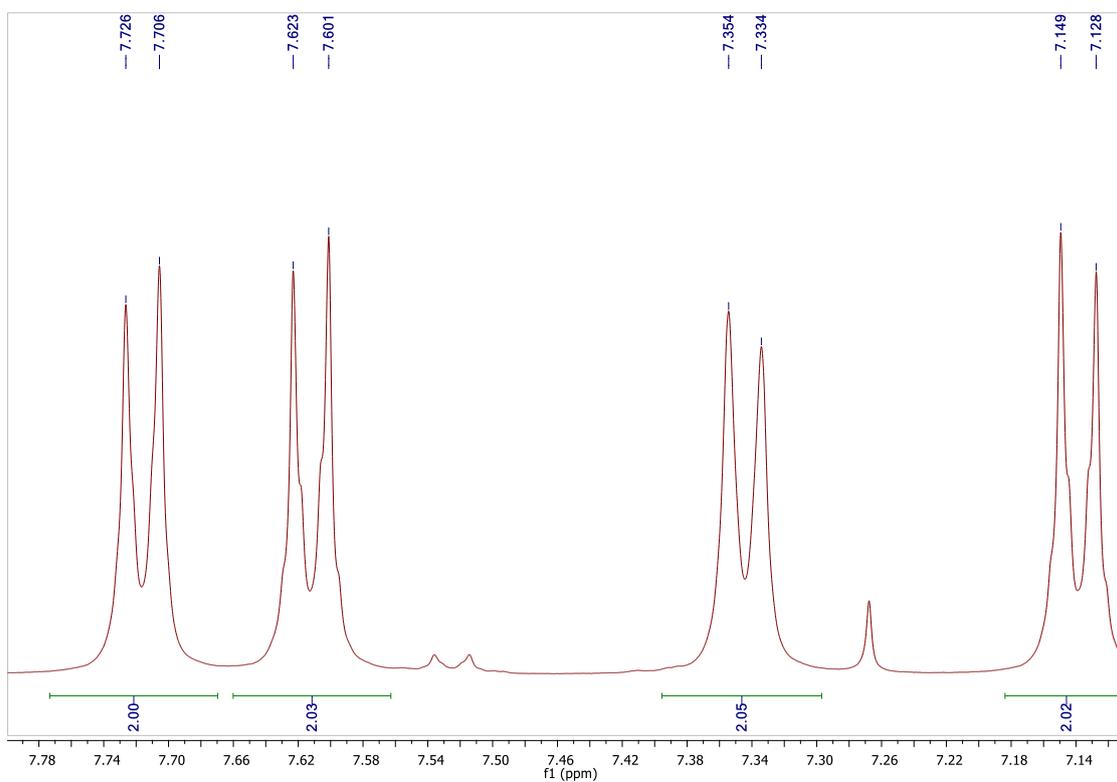
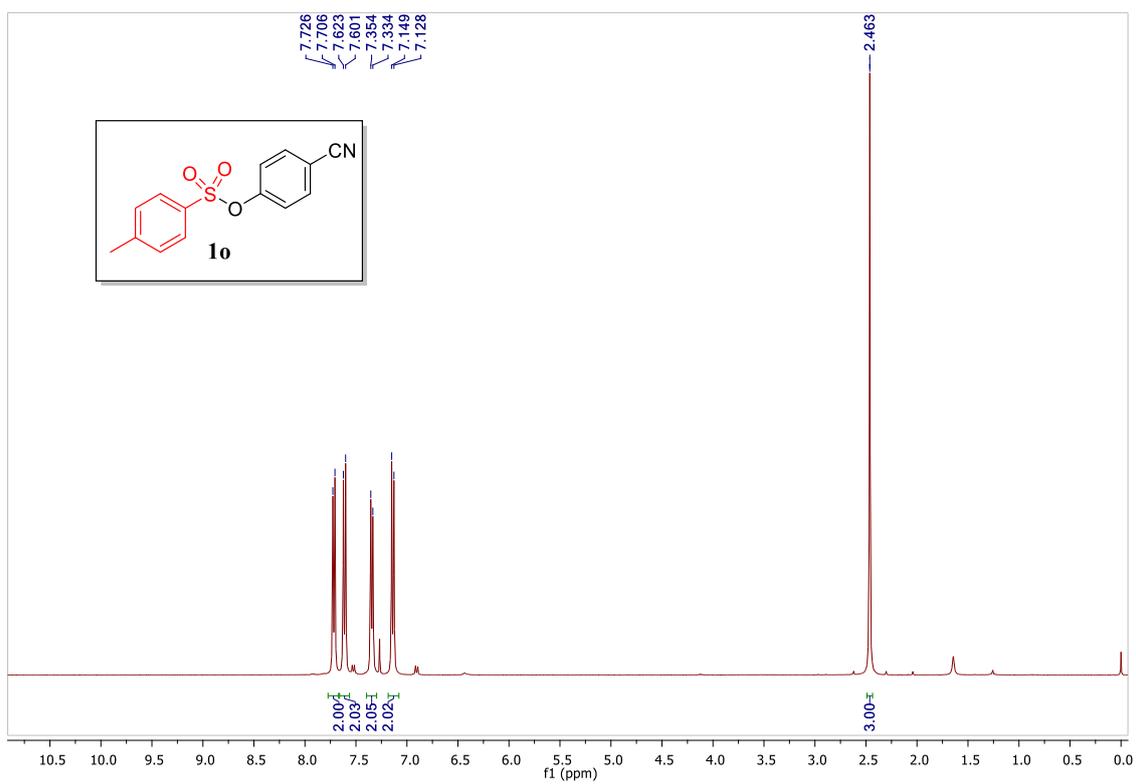
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-(*N*,4-Dimethylphenylsulfonamido)phenyl 4-methyl benzenesulfonate (**1m**).



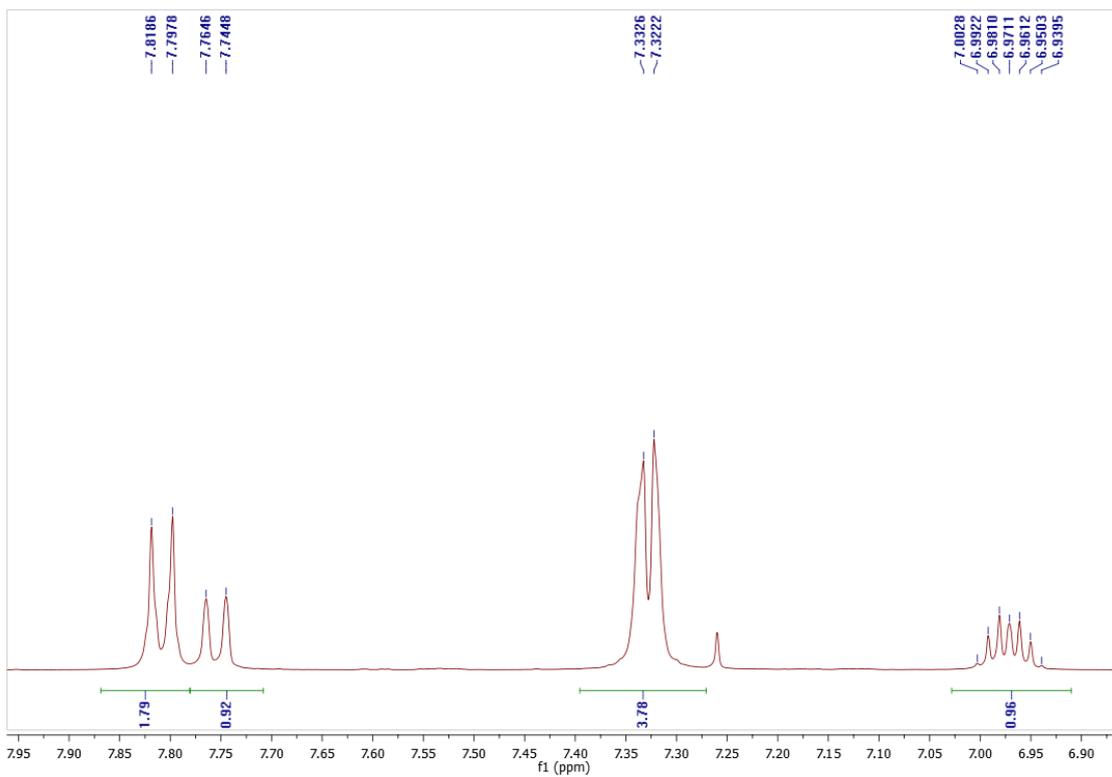
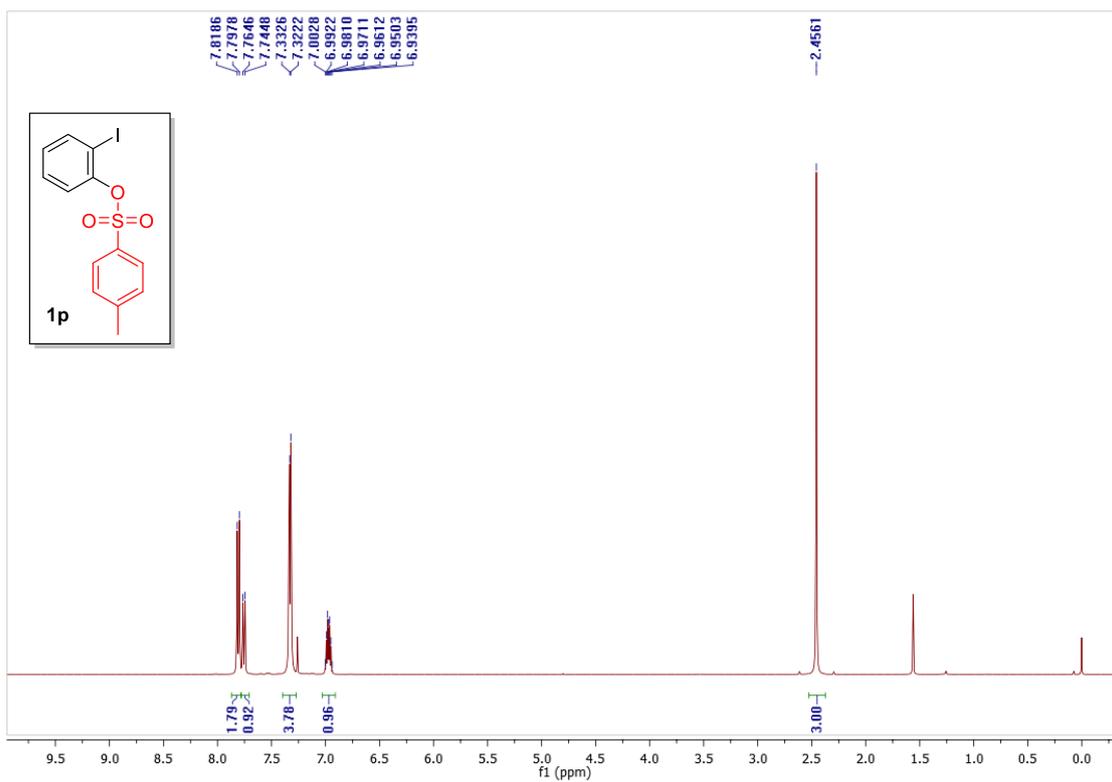
¹H-NMR (400 MHz, CDCl₃). 4-Methoxyphenyl 4-methylbenzenesulfonate (**1n**).



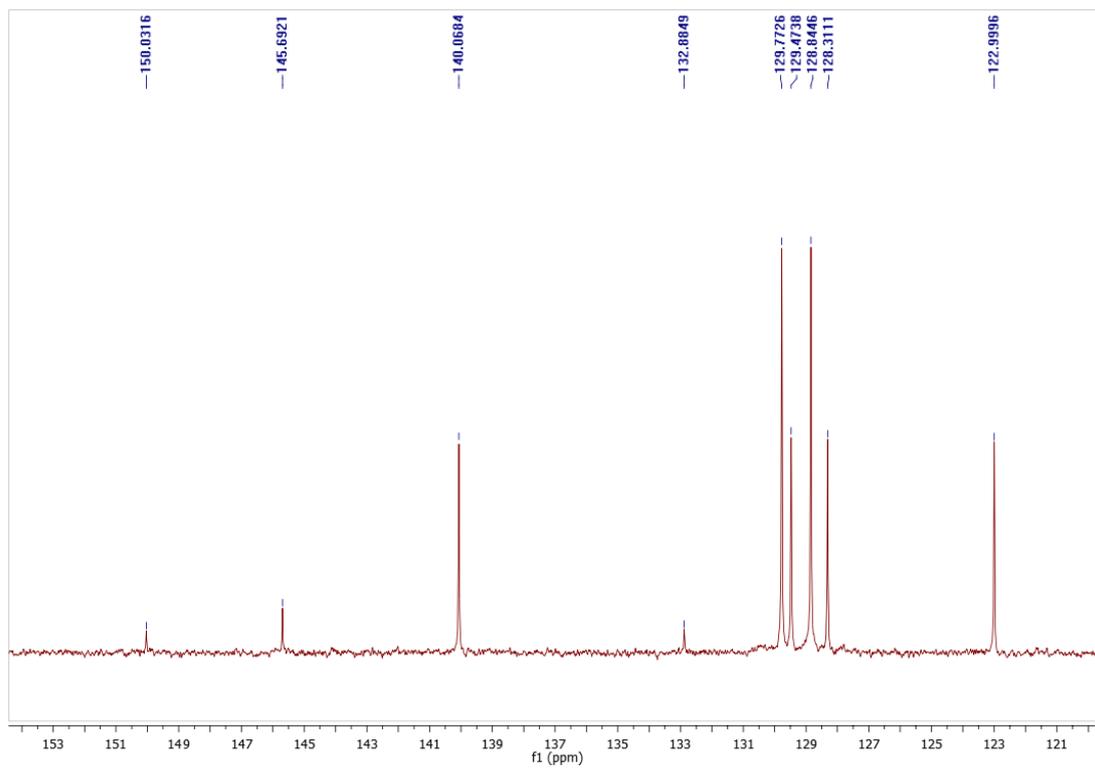
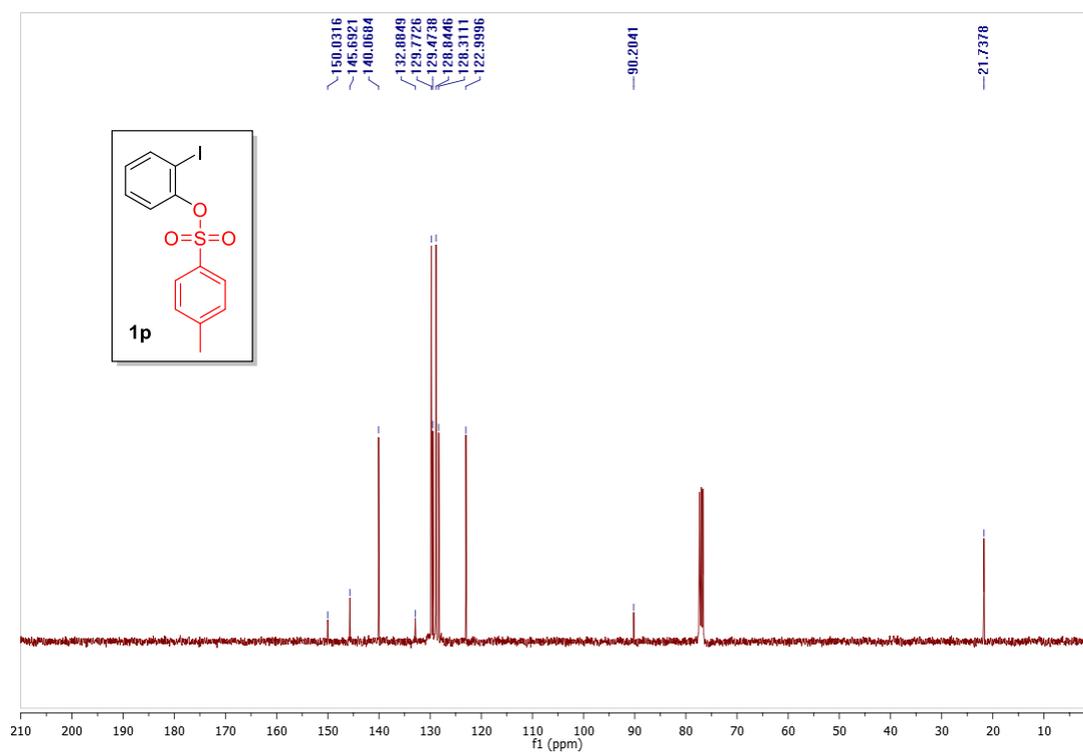
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Cyanophenyl 4-methylbenzenesulfonate (**1o**).



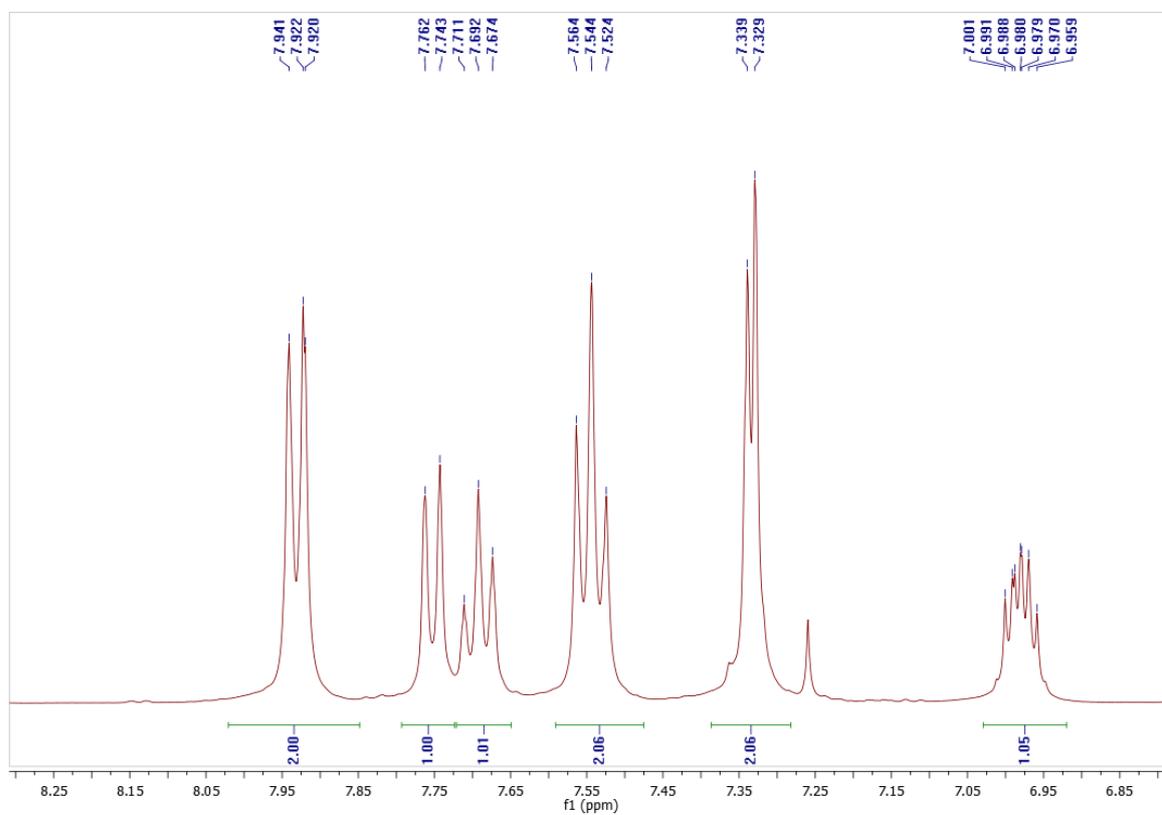
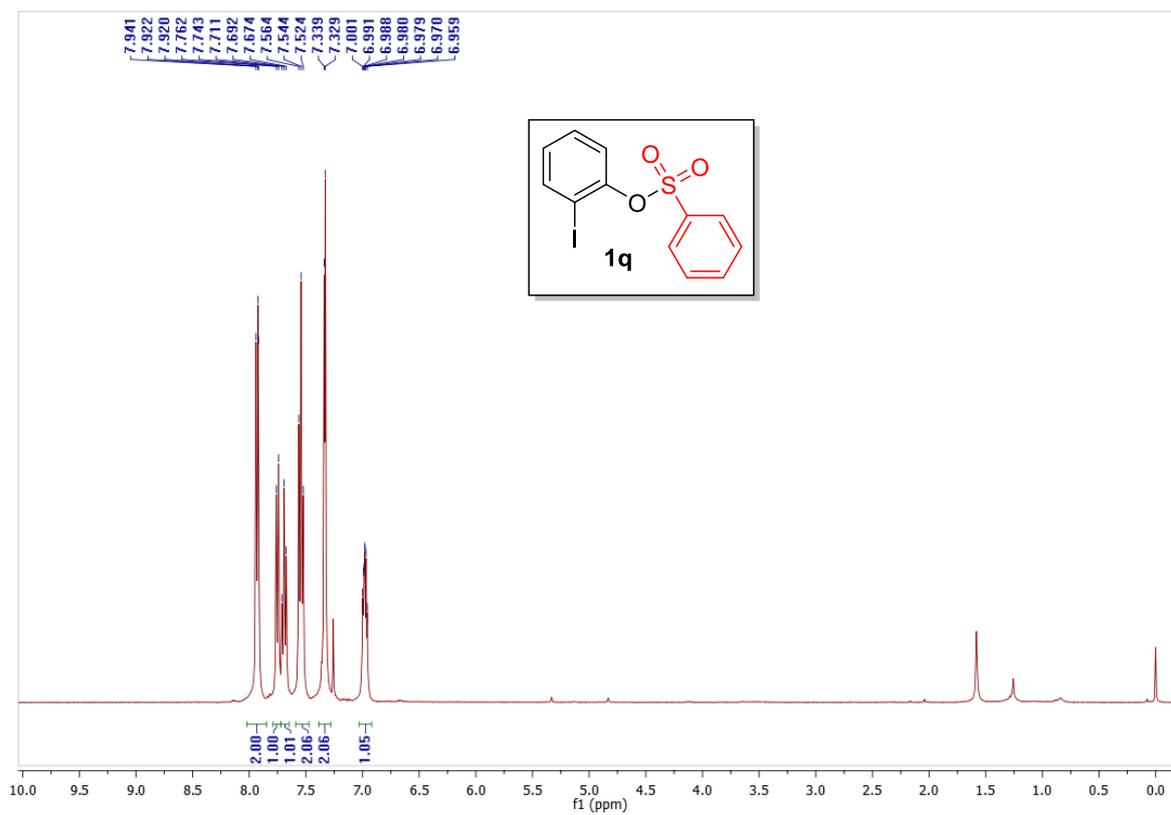
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 2-Iodophenyl 4-methylbenzenesulfonate (**1p**).



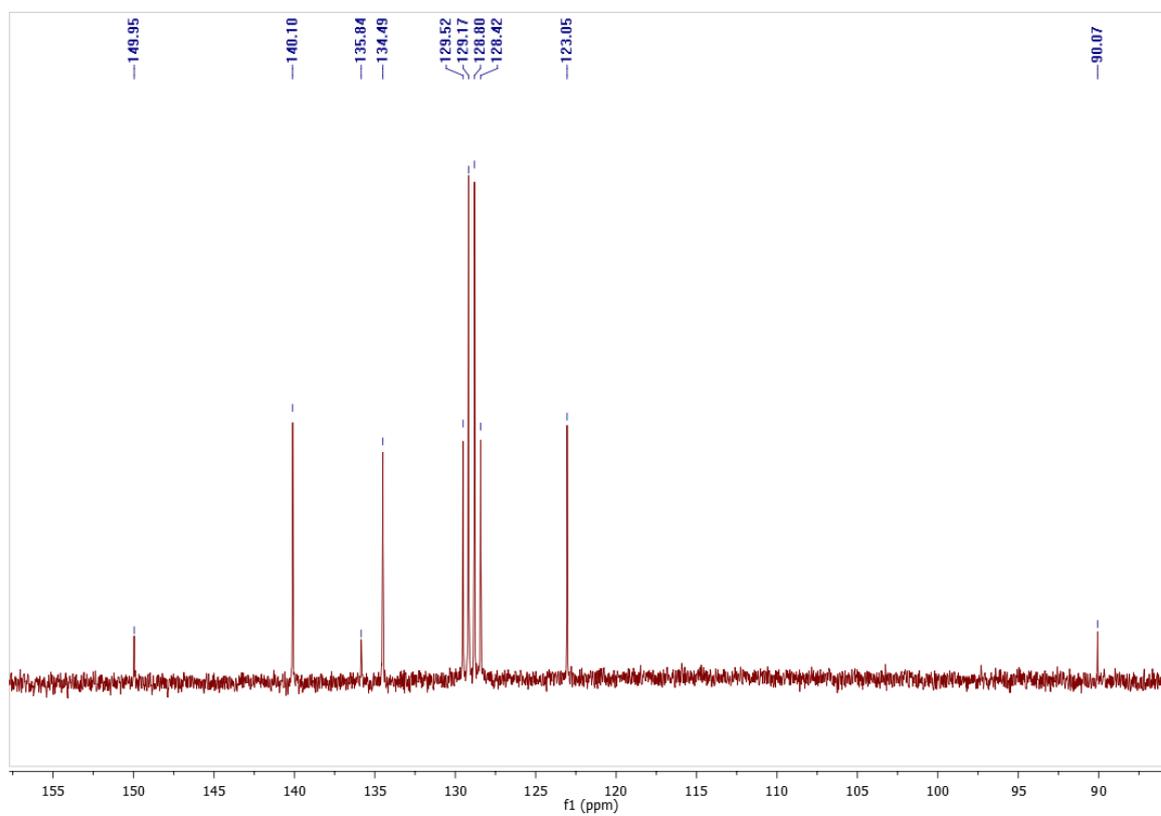
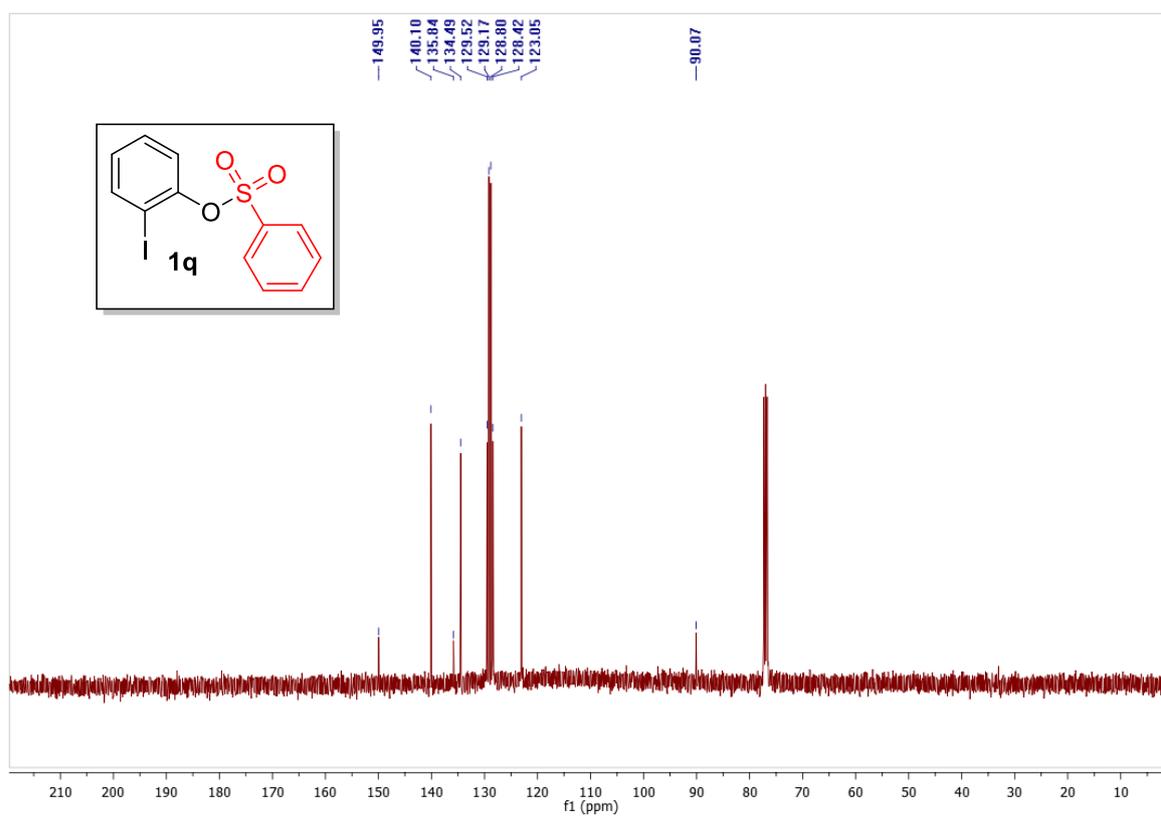
^{13}C -NMR {H} (101 MHz, CDCl_3). 2-Iodophenyl 4-methylbenzenesulfonate (**1p**).



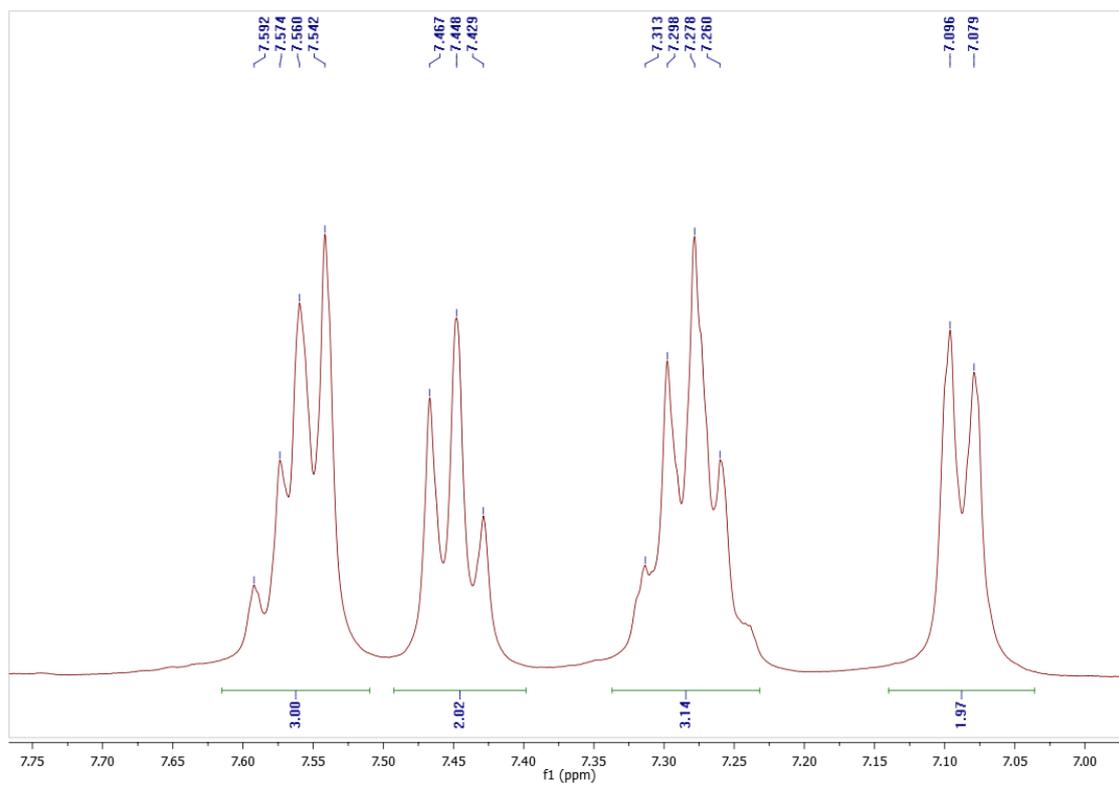
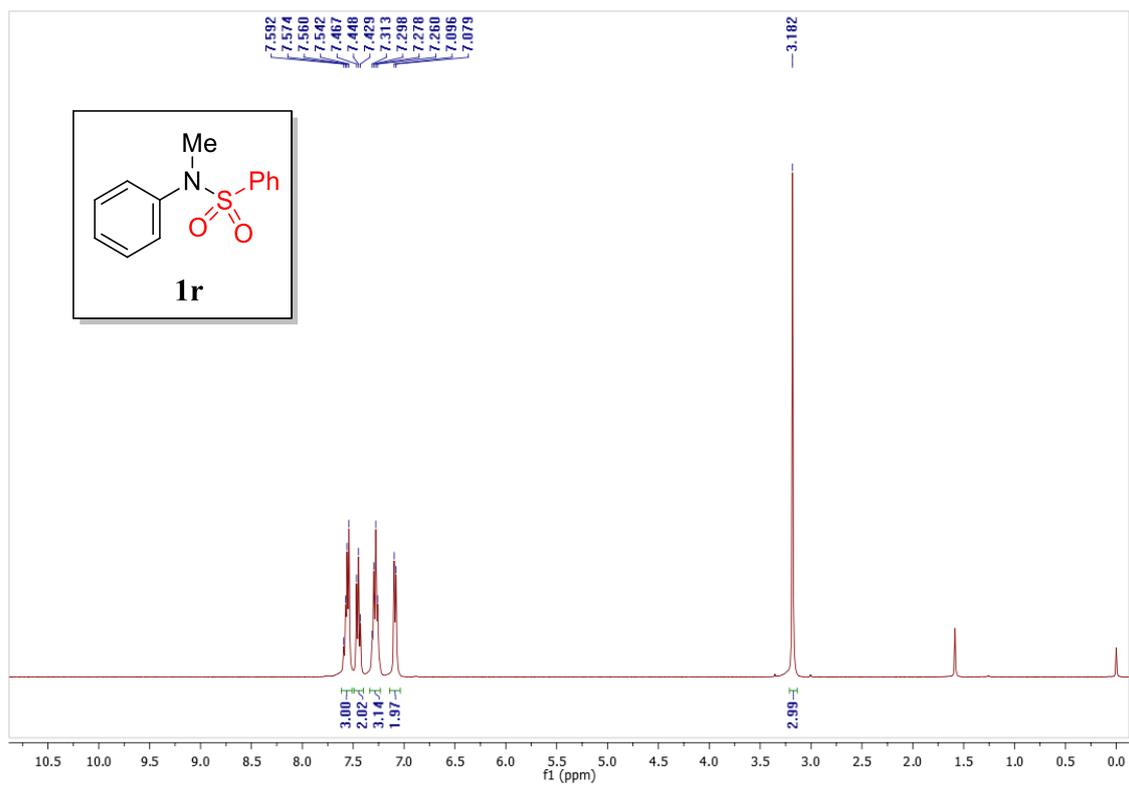
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 2-Iodophenyl benzenesulfonate (**1q**).



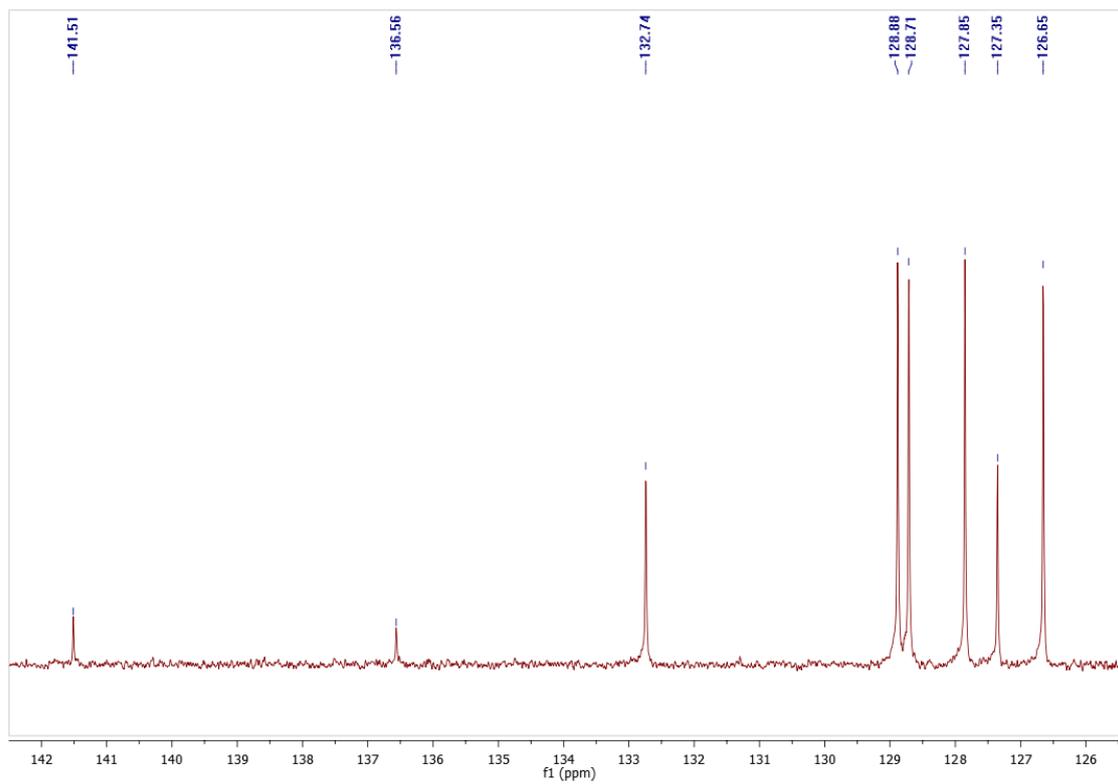
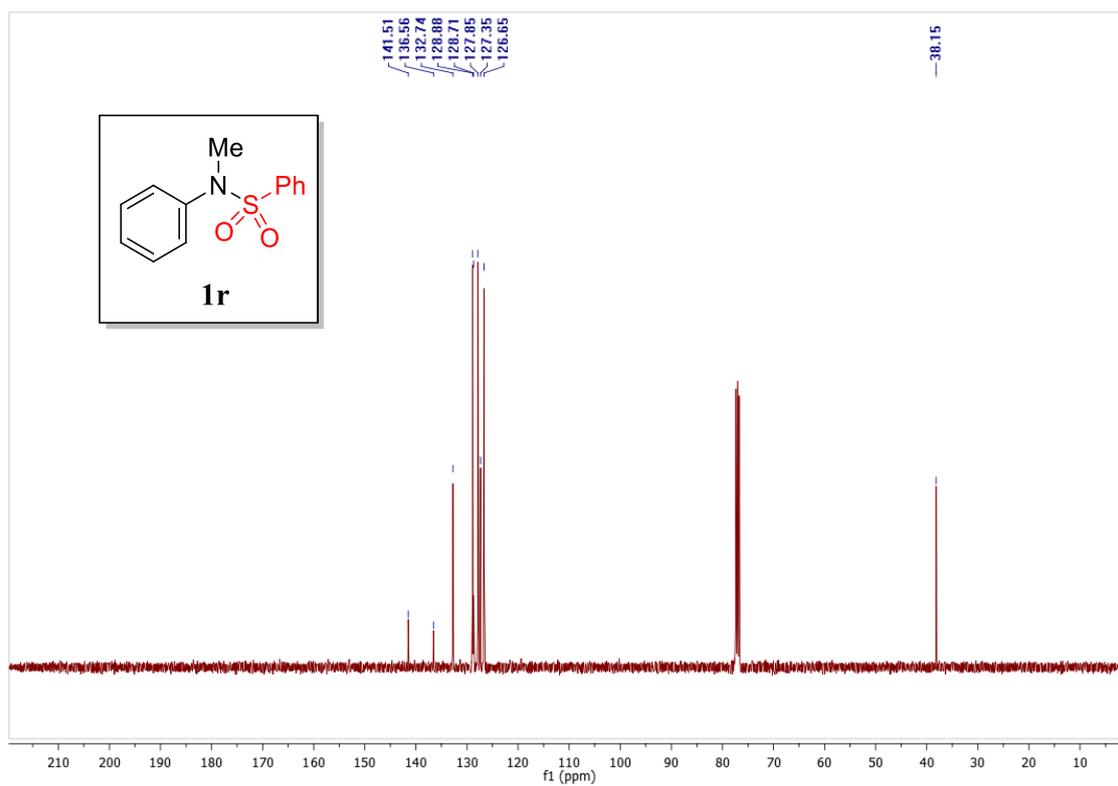
^{13}C -NMR {H} (101 MHz, CDCl_3). 2-Iodophenyl benzenesulfonate (**1q**).



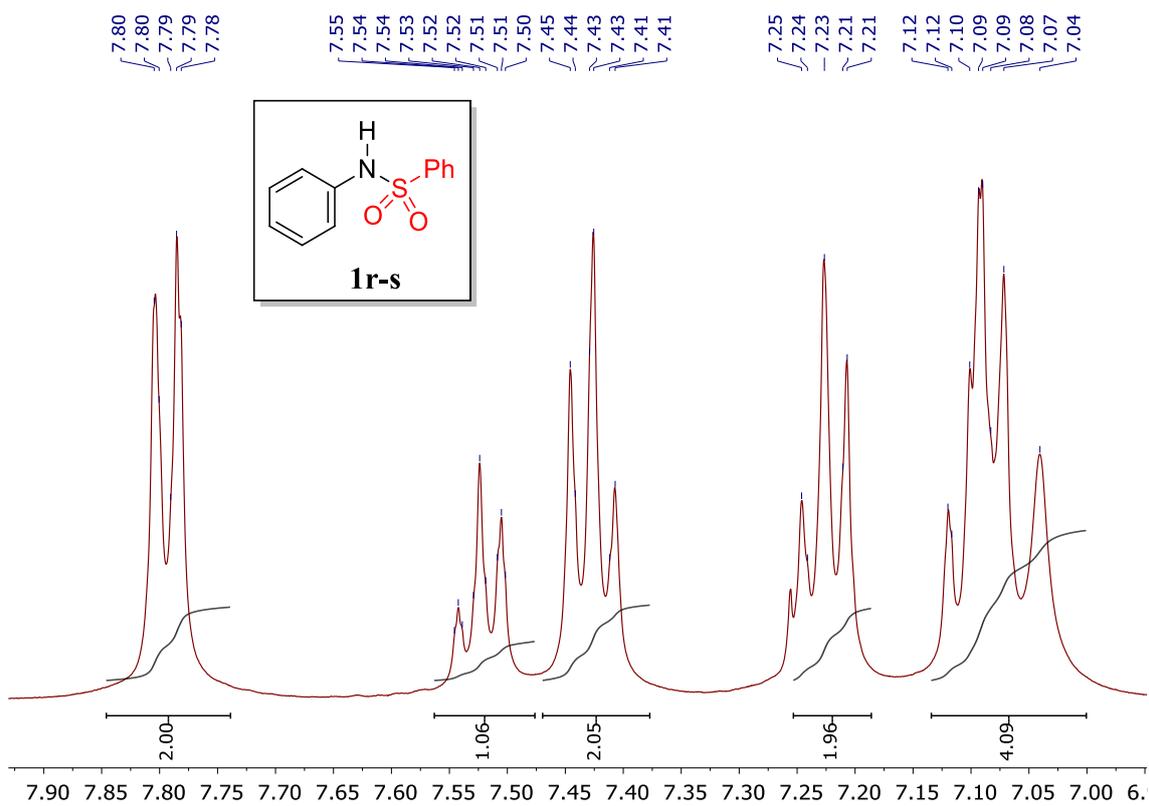
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-Methyl-*N*-phenylbenzenesulfonamide (**1r**).



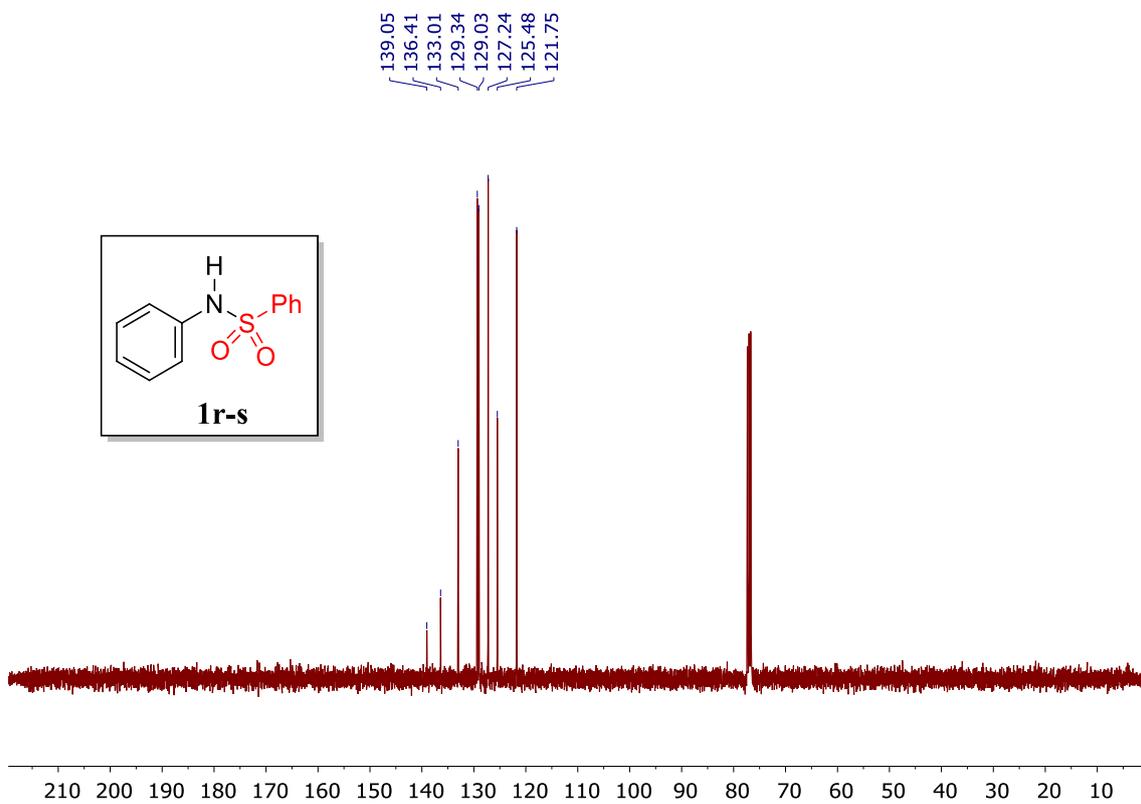
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-Methyl-*N*-phenylbenzenesulfonamide (**1r**).

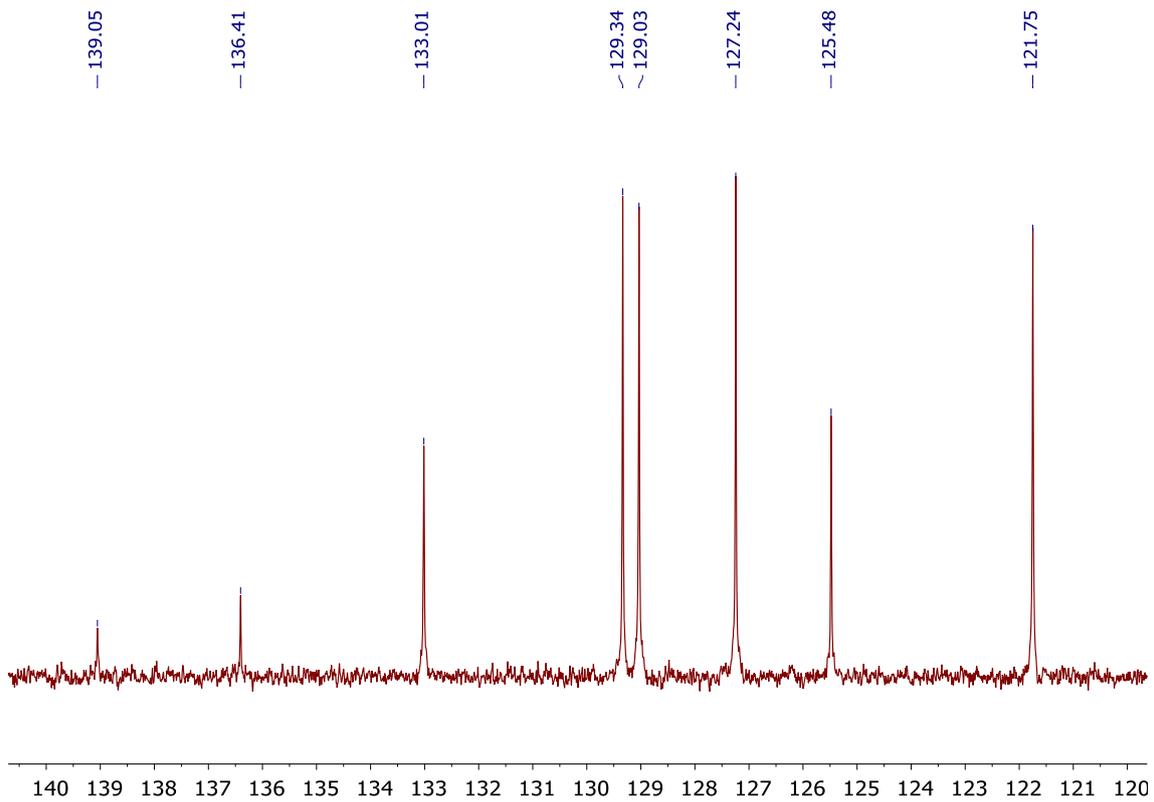


$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-Phenylbenzenesulfonamide (**1r-s**).

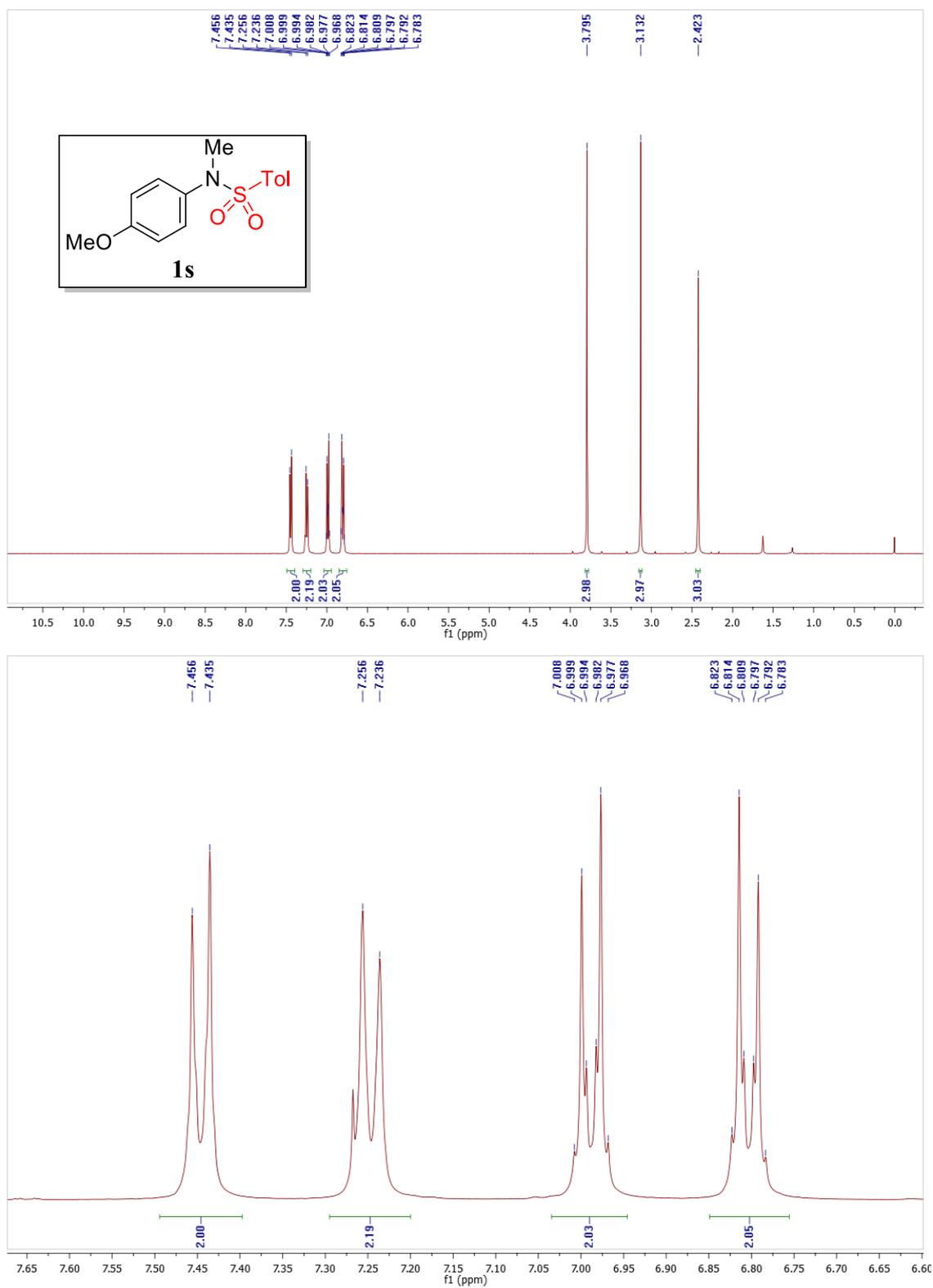


$^{13}\text{C-NMR}$ {H} (101 MHz, CDCl_3). *N*-Phenylbenzenesulfonamide (**1r-s**).

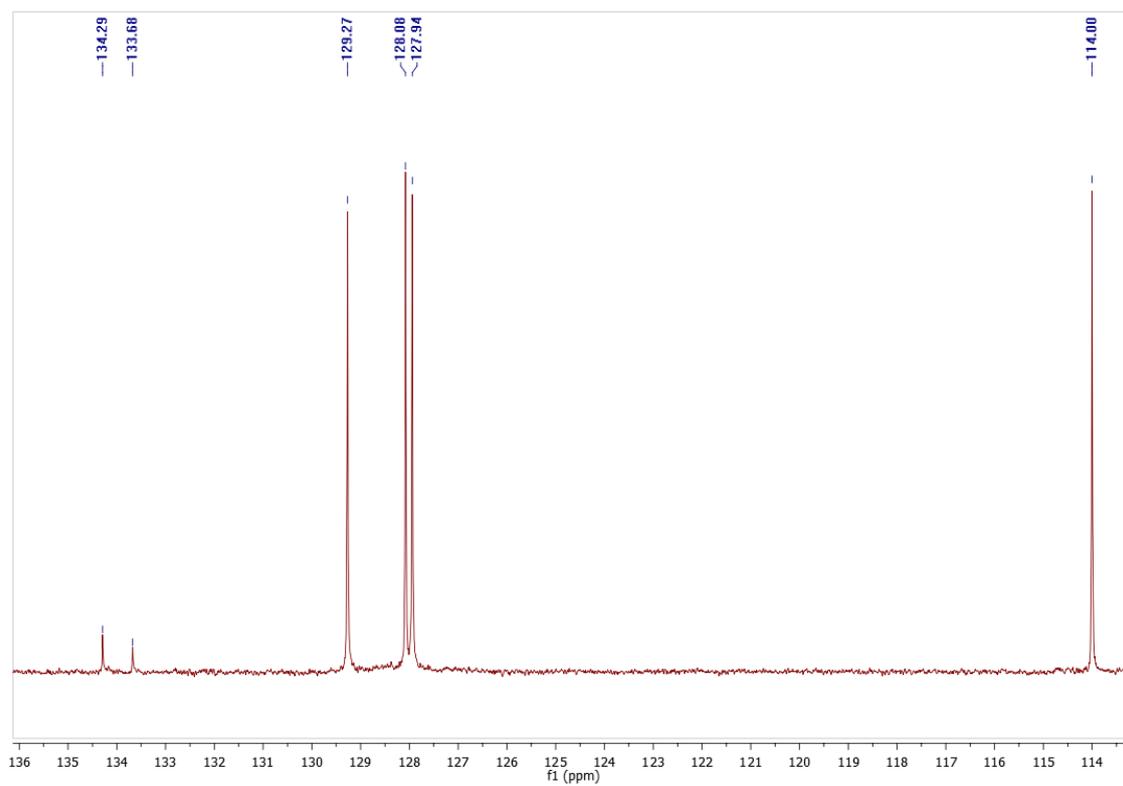
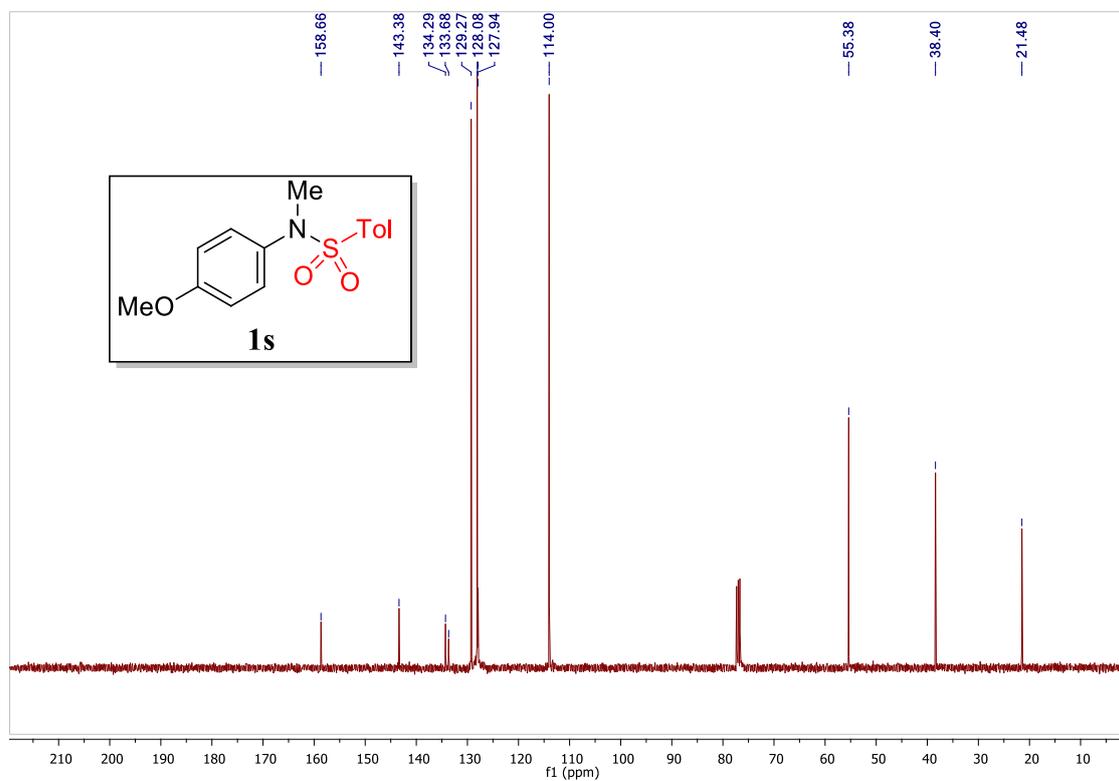




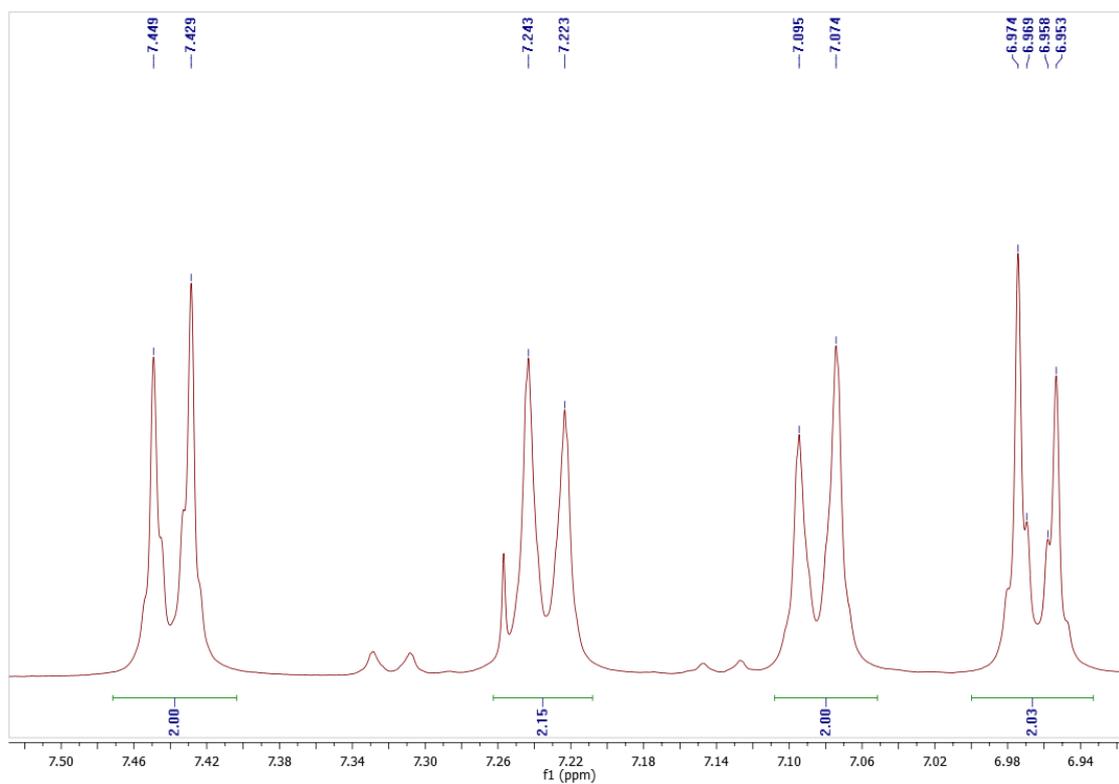
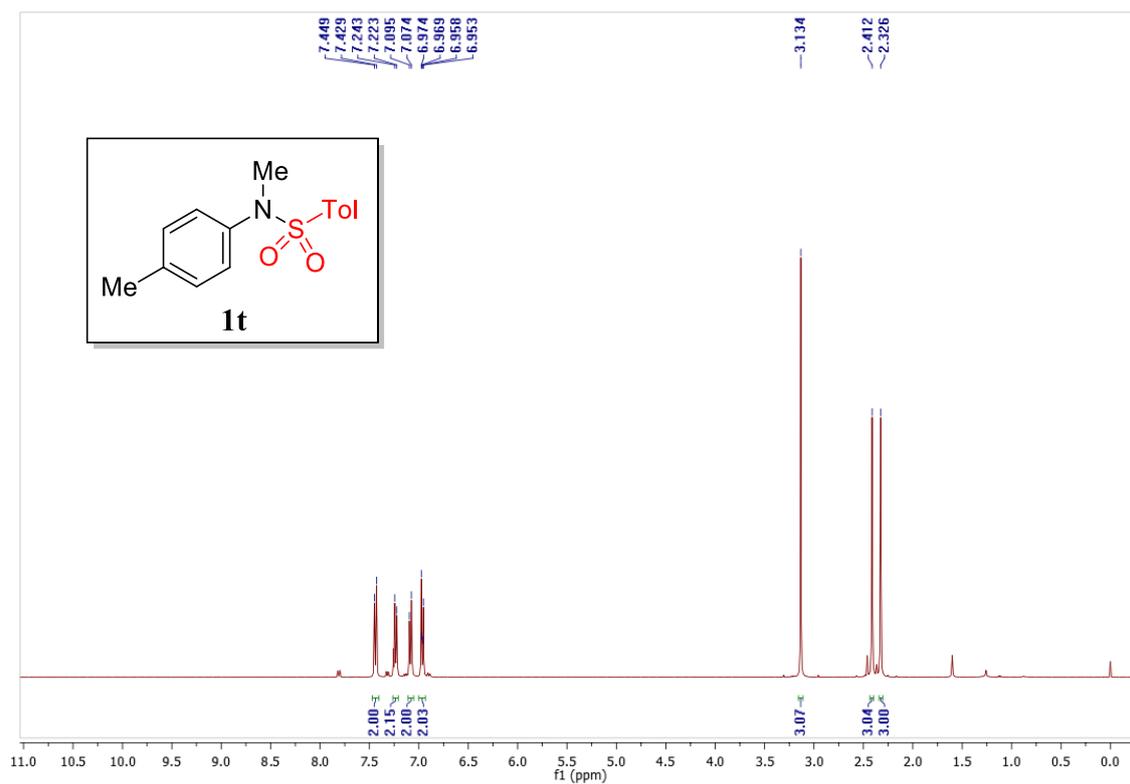
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Methoxyphenyl)-*N*,4-dimethylbenzenesulfonamide (**1s**).



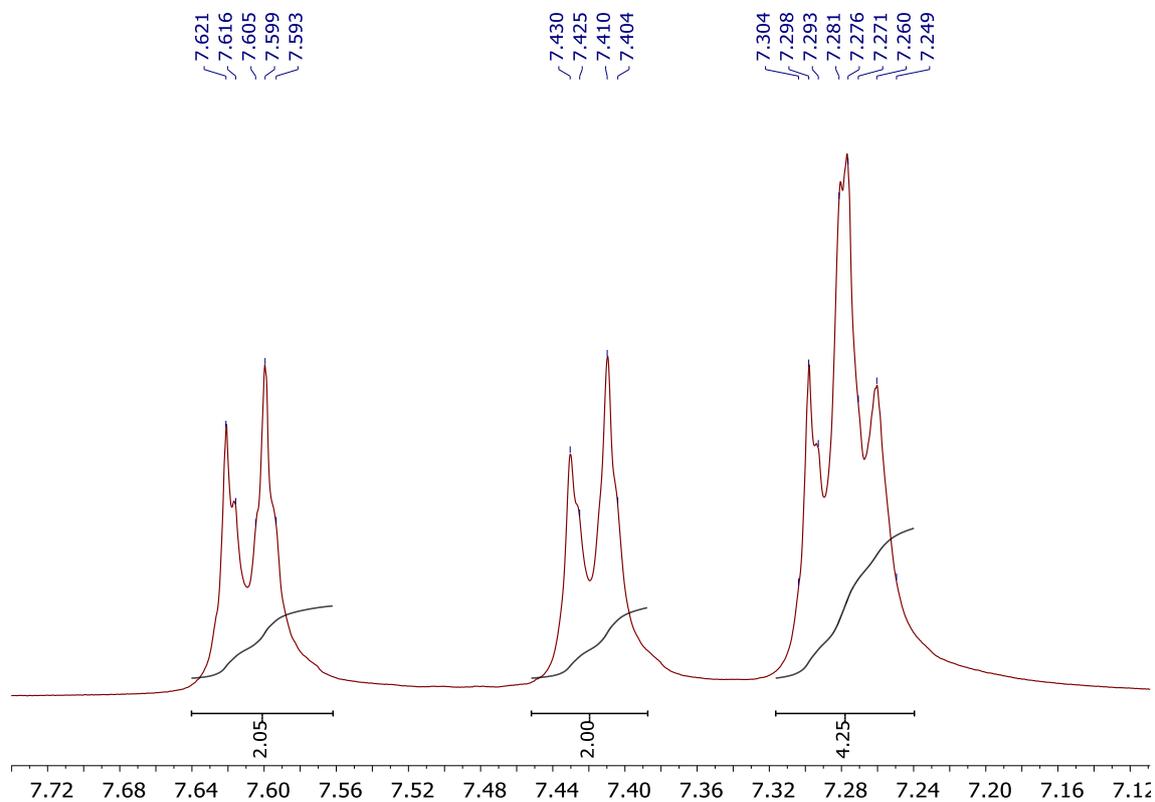
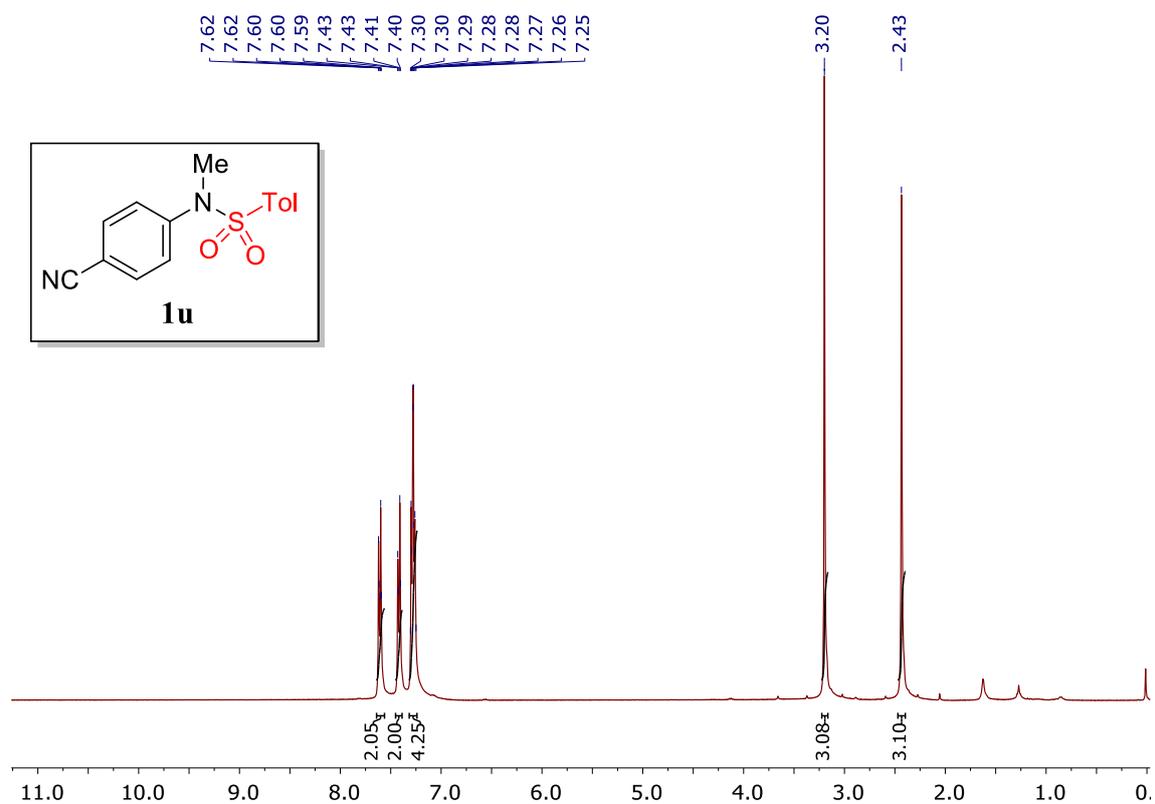
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Methoxyphenyl)-*N*,4-dimethylbenzenesulfonamide (**1s**).



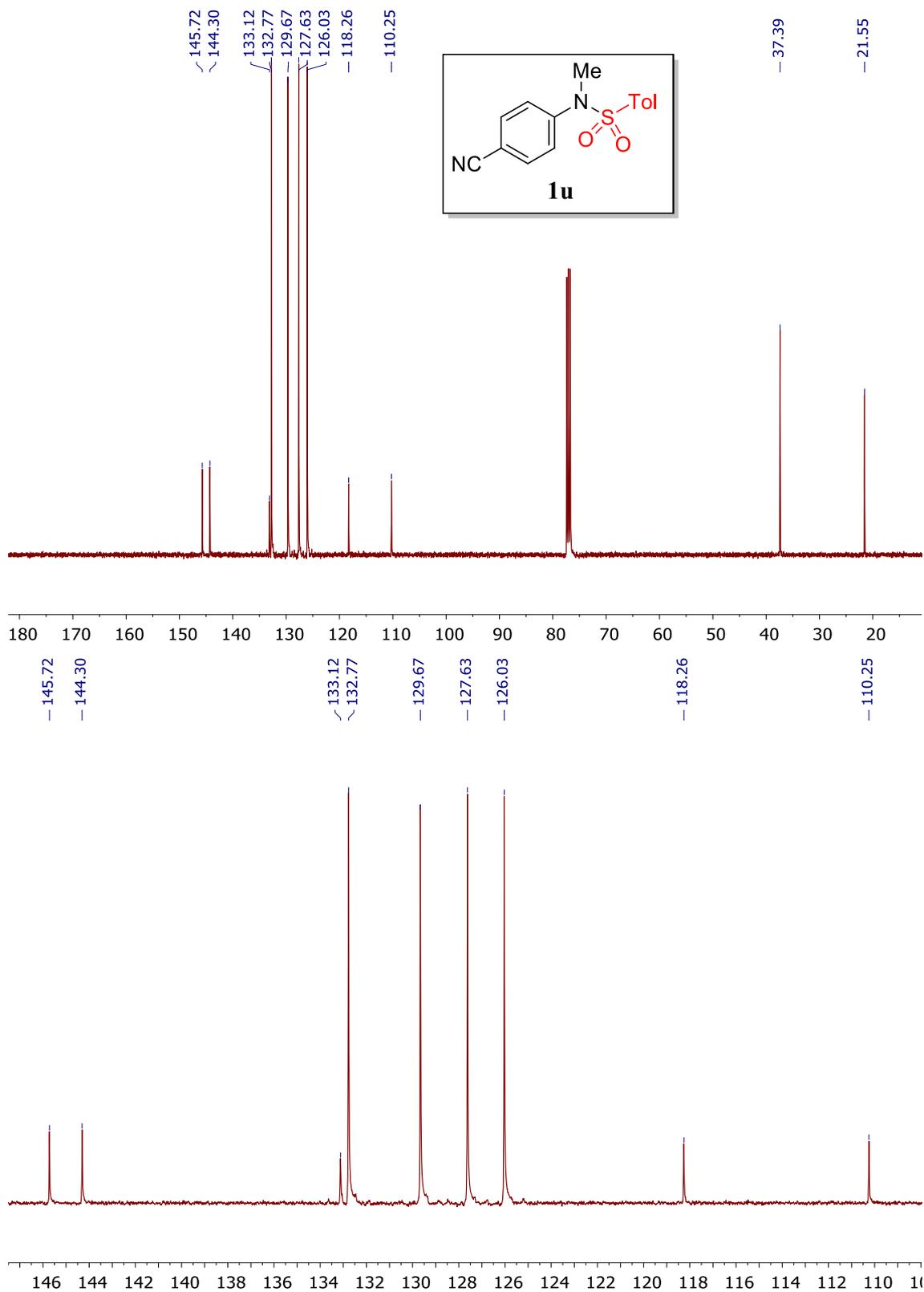
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*,4-Dimethyl-*N*-(*p*-tolyl)benzenesulfonamide (**1t**).



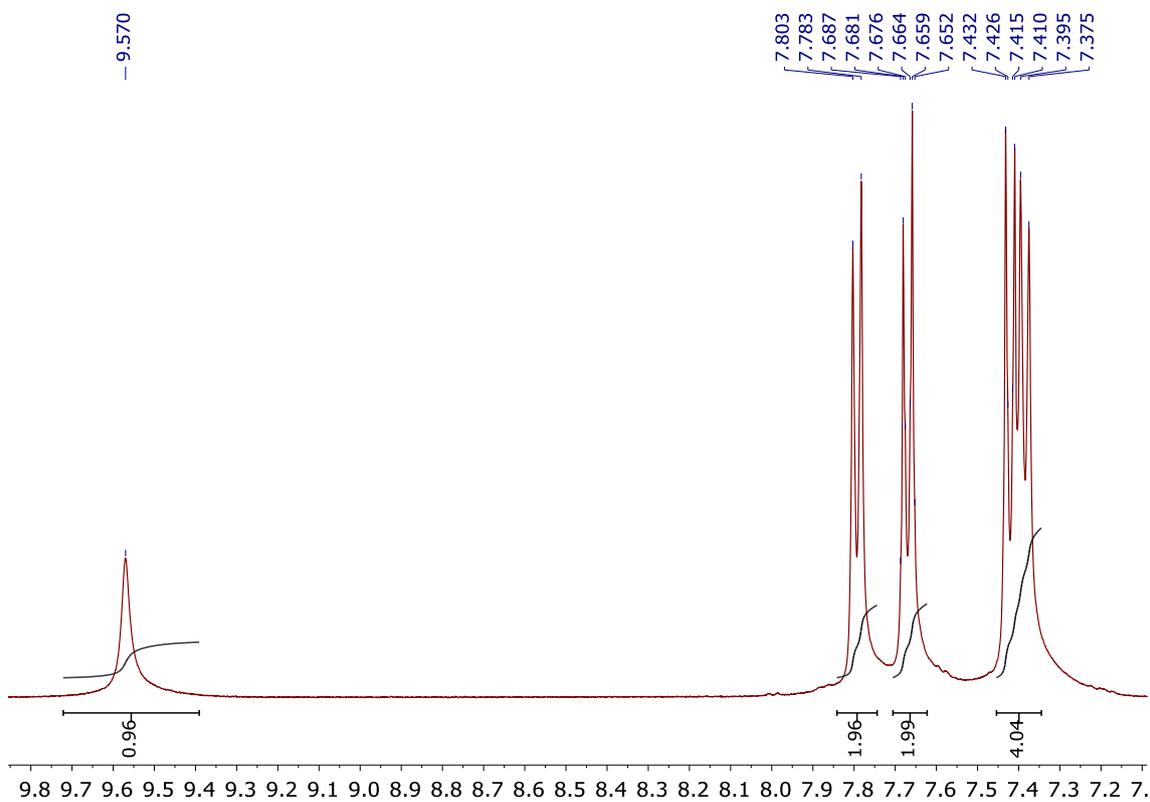
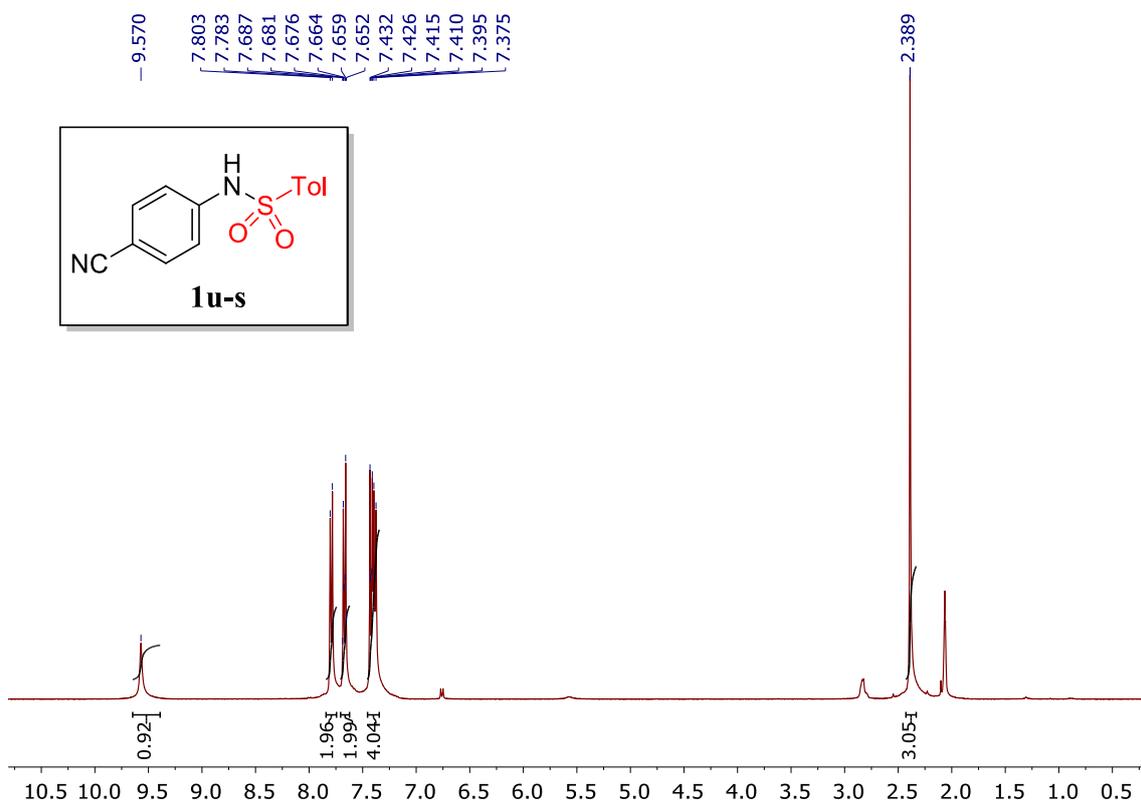
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Isocyanophenyl)-*N*,4-dimethylbenzenesulfonamide (**1u**).



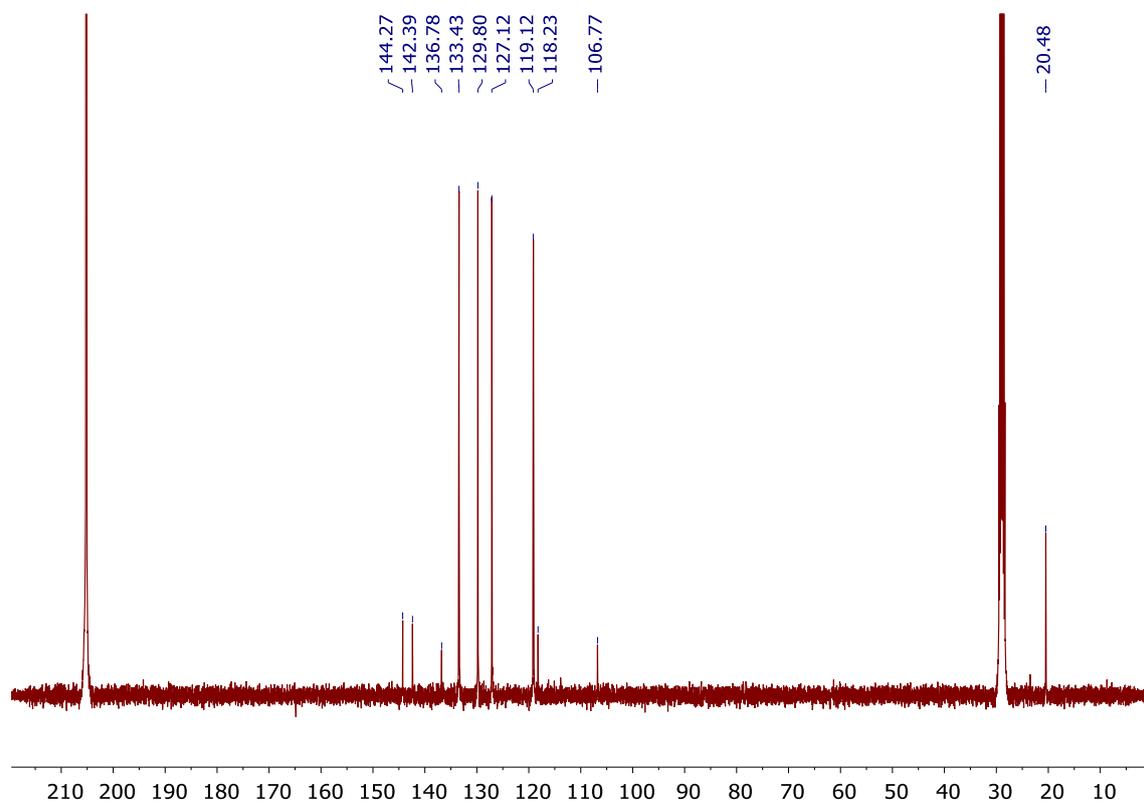
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Isocyanophenyl)-*N*,4-dimethylbenzenesulfonamide (**1u**).

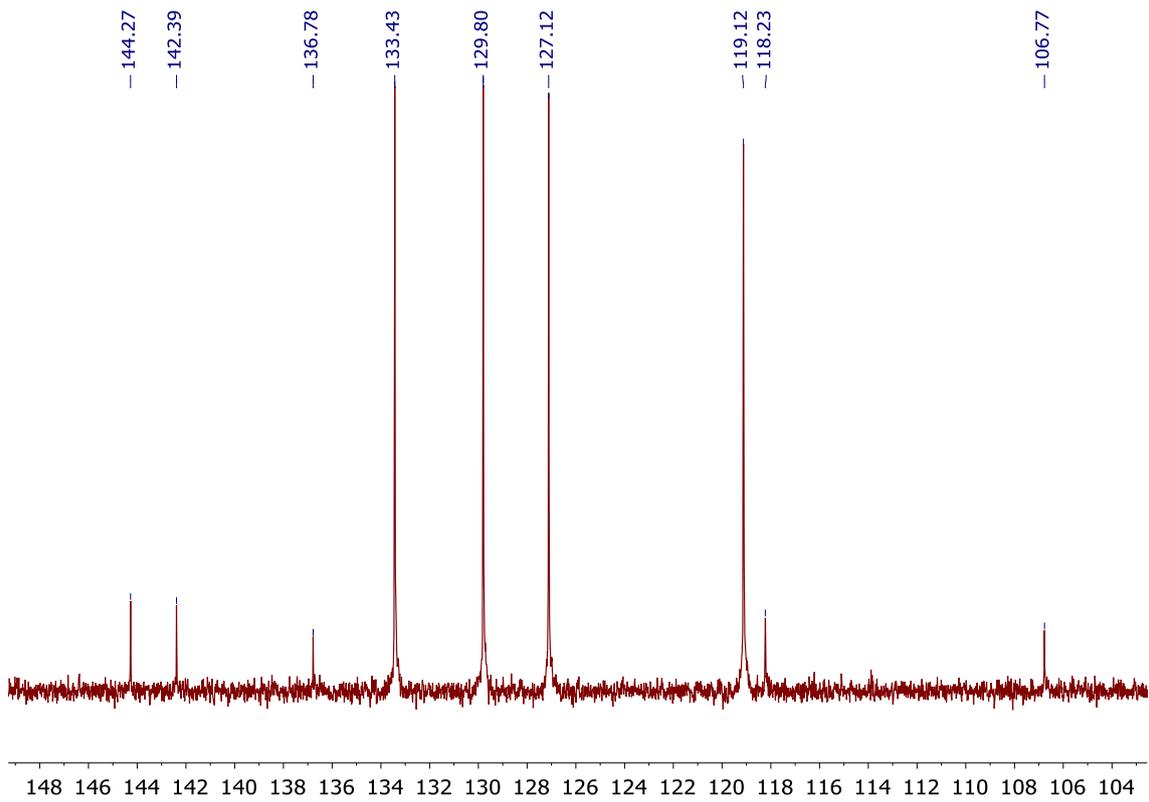


$^1\text{H-NMR}$ (400 MHz, CD_3COCD_3). *N*-(4-Isocyanophenyl)-4-methylbenzenesulfonamide (**1u-s**).

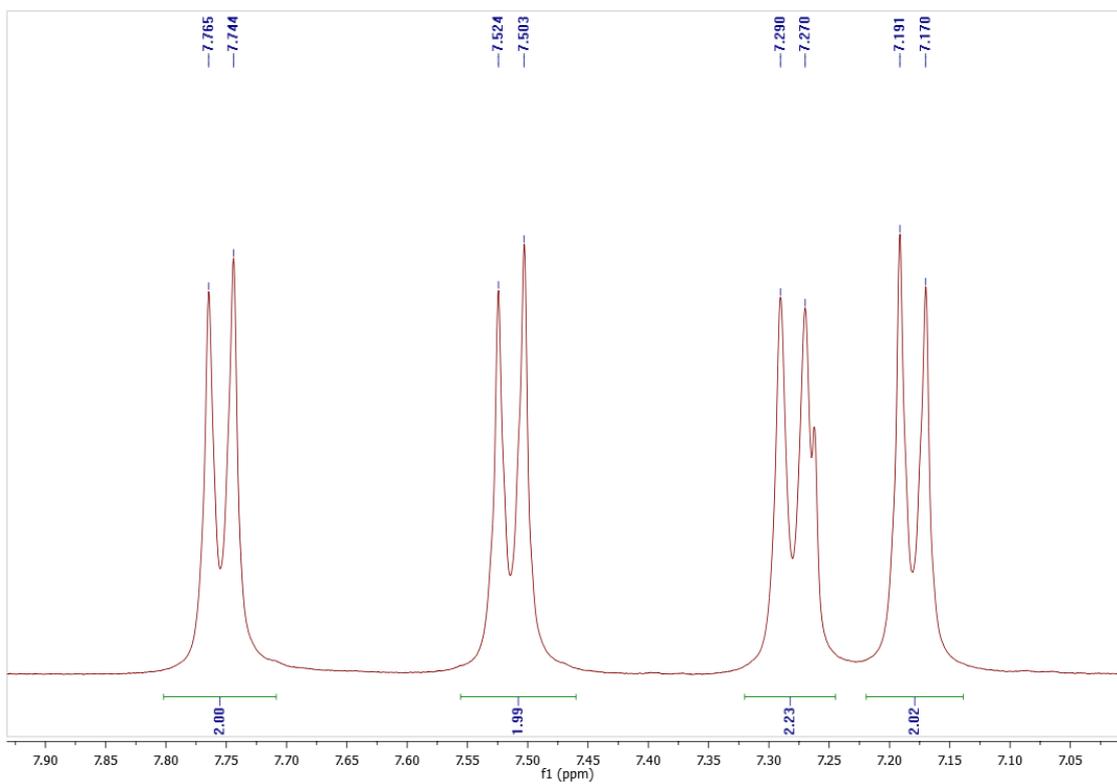
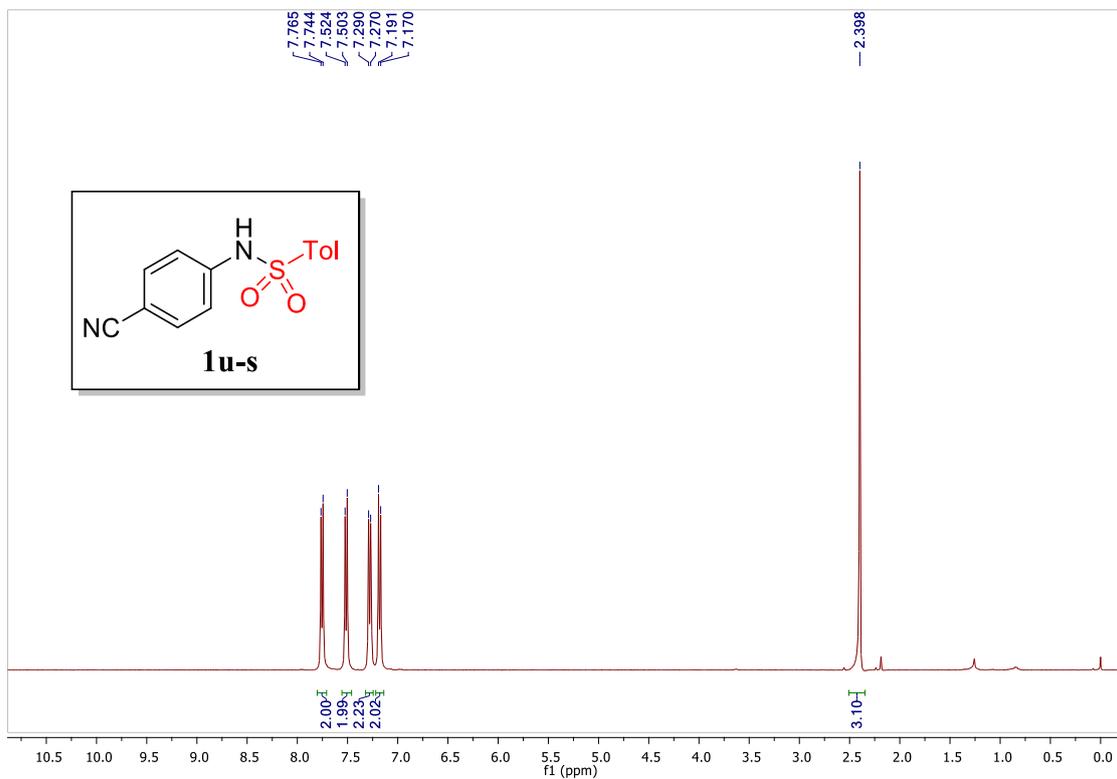


^{13}C -NMR {H} (101 MHz, CD_3COCD_3). *N*-(4-Isocyanophenyl)-4-methylbenzene sulfonamide (**1u-s**).

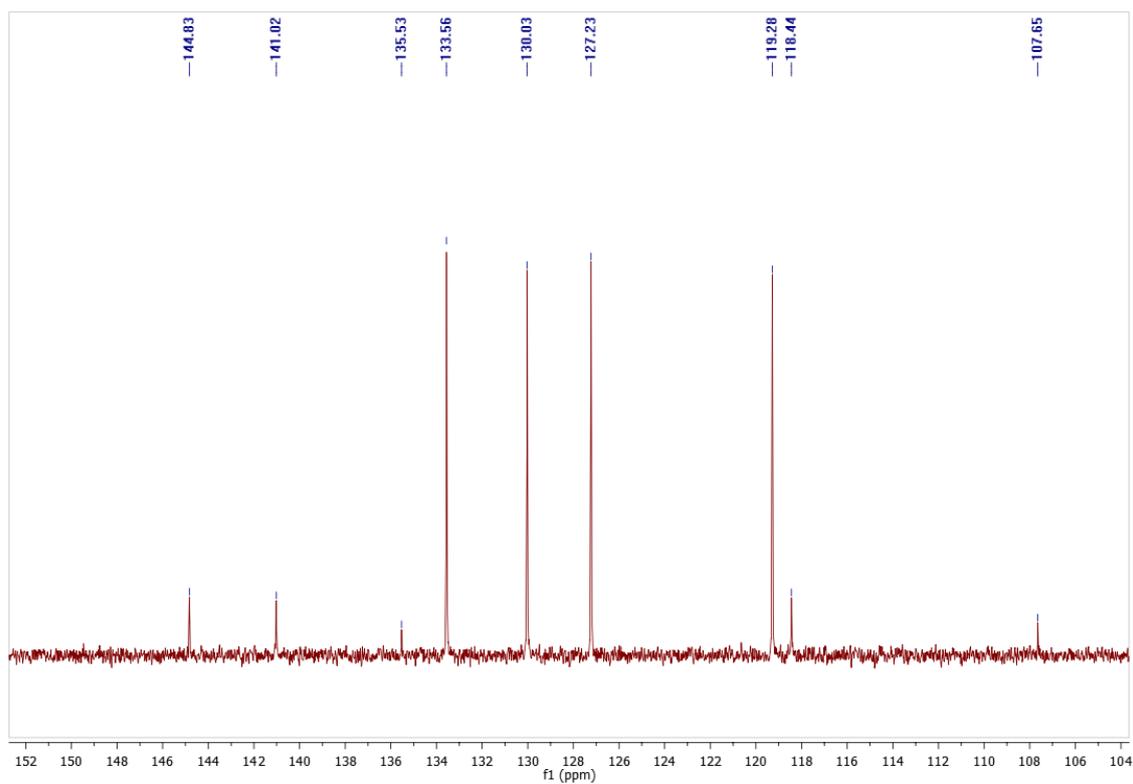
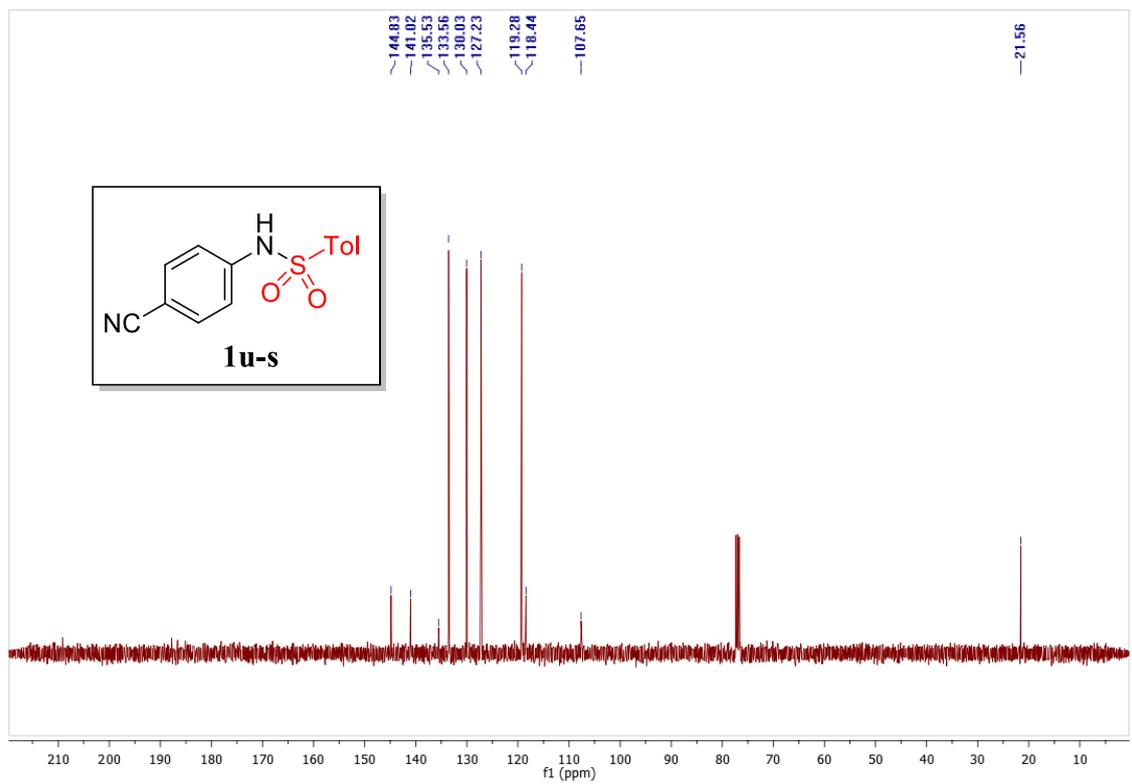




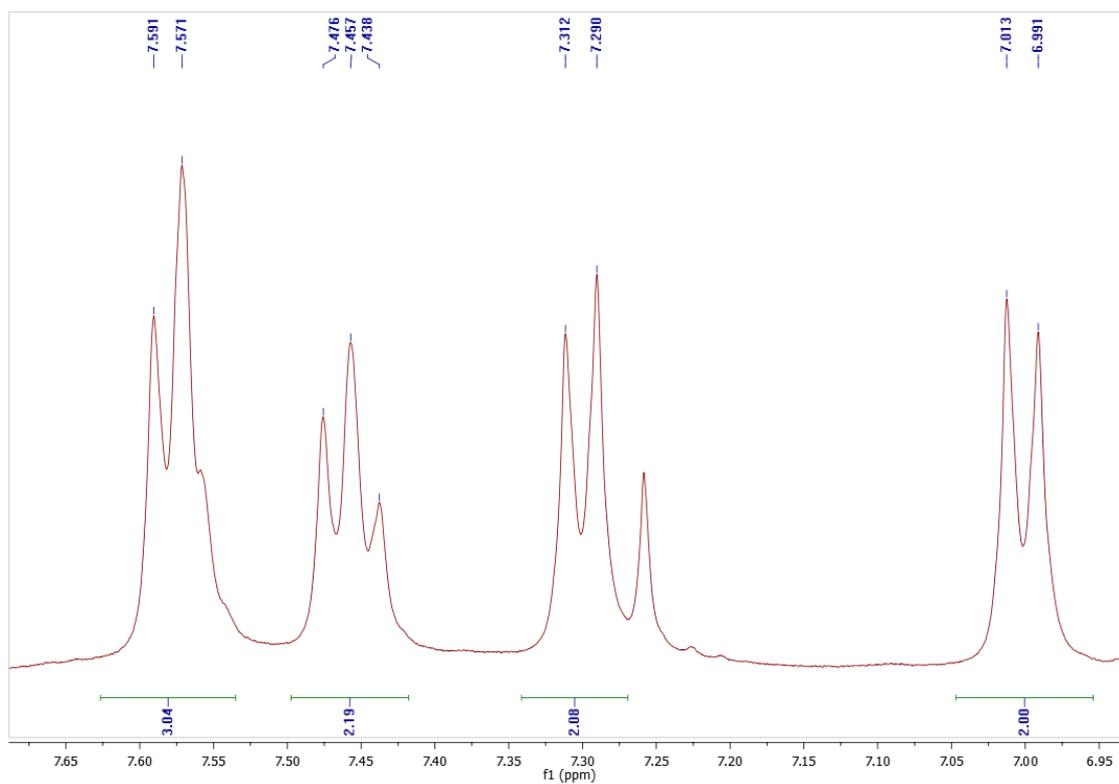
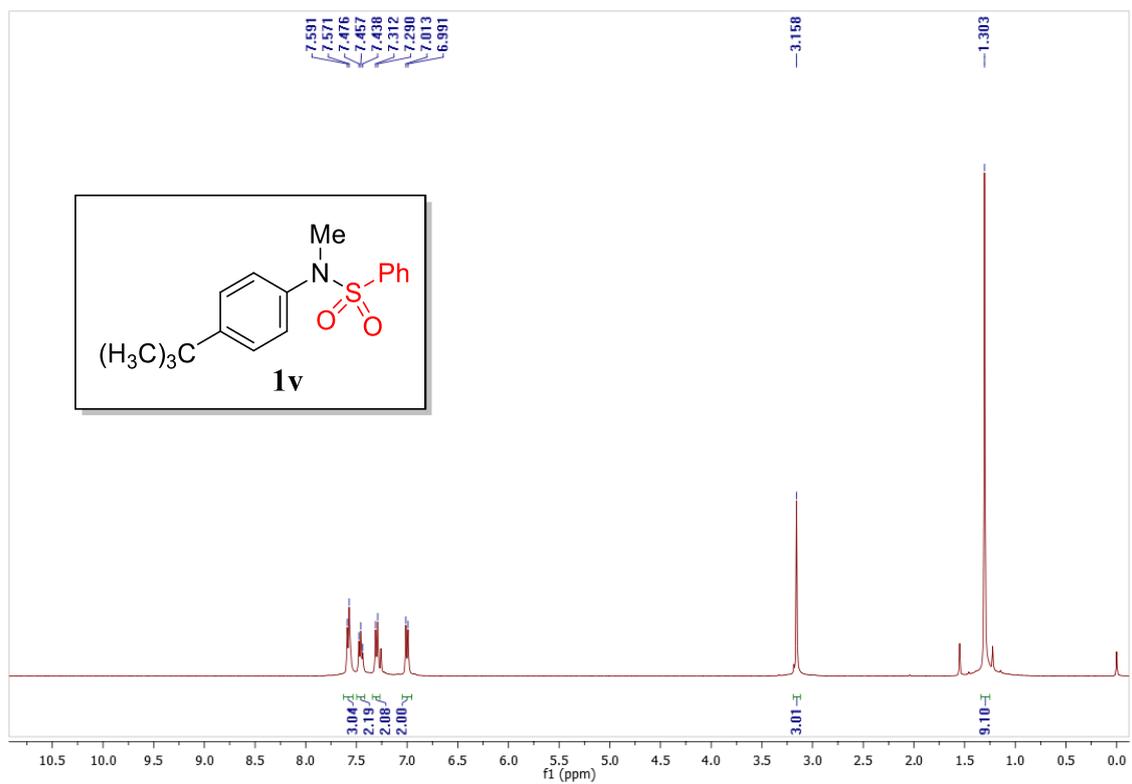
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Isocyanophenyl)-4-methylbenzenesulfonamide (**1u-s**).



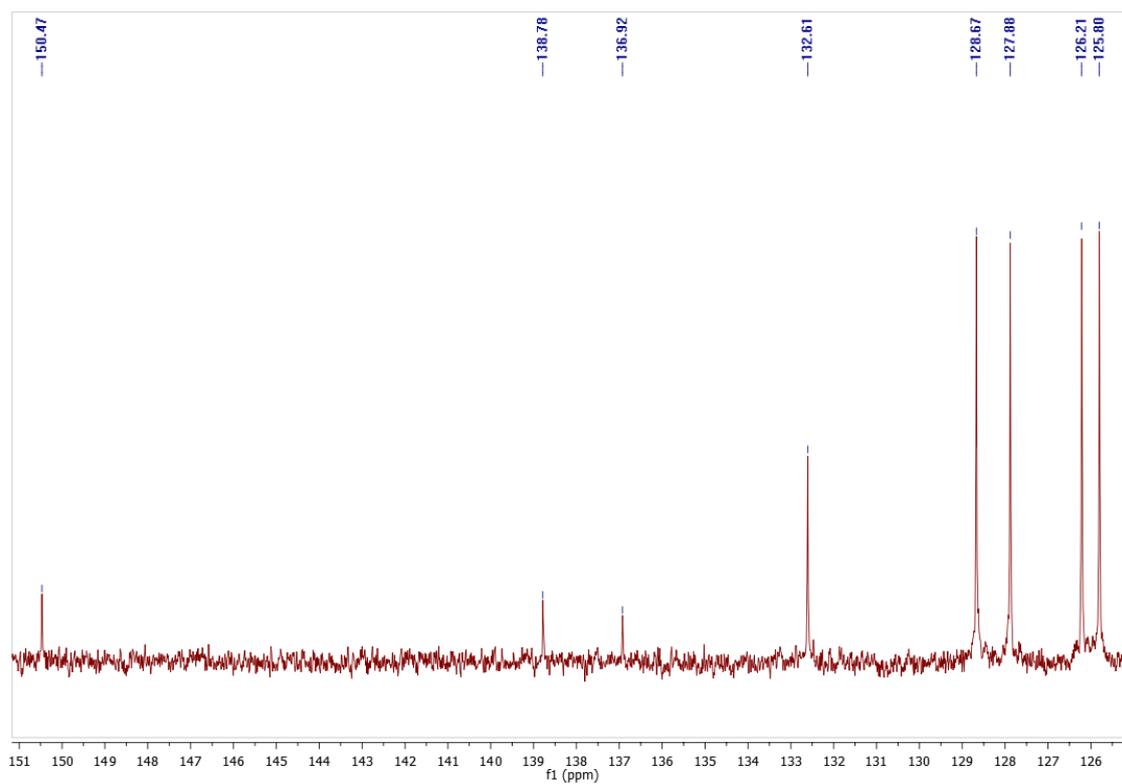
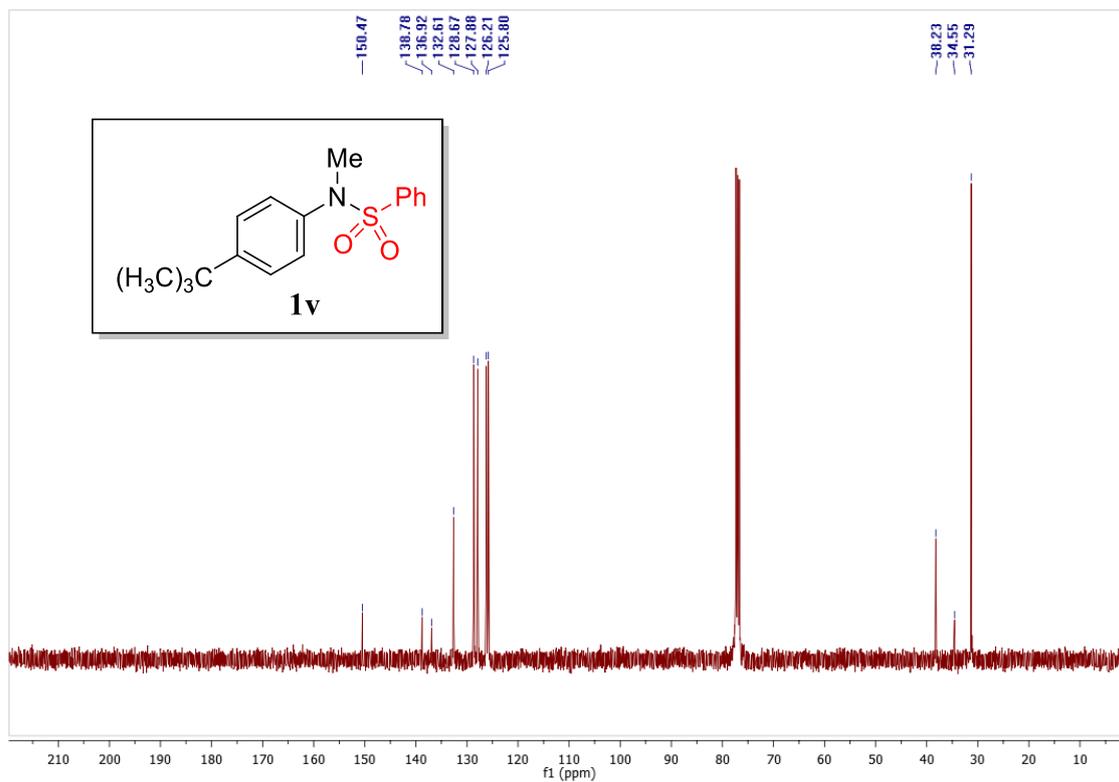
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Isocyanophenyl)-4-methylbenzenesulfonamide (**1u-s**).



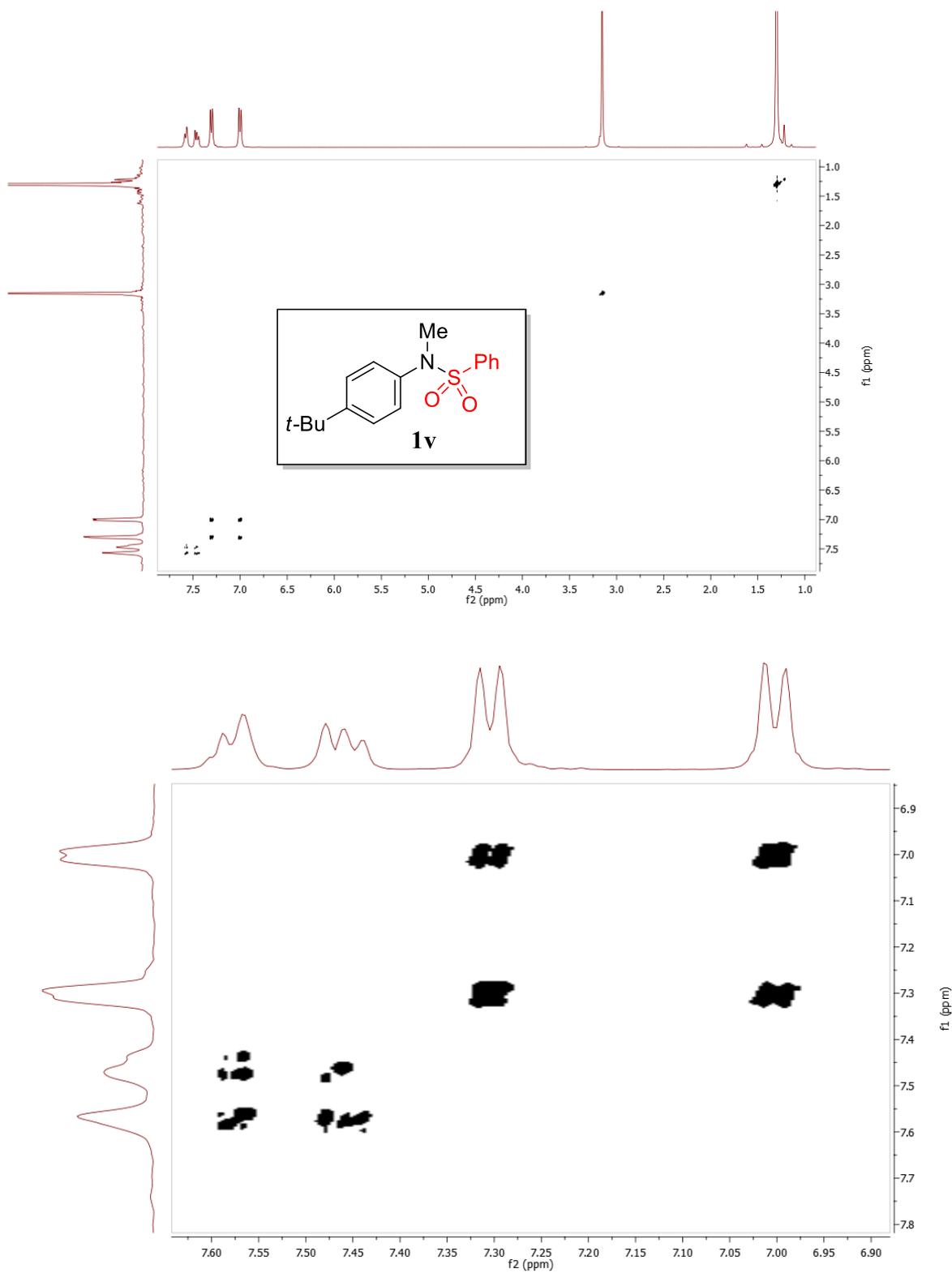
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-(*tert*-butyl)phenyl)-*N*-methylbenzenesulfonamide (**1v**).



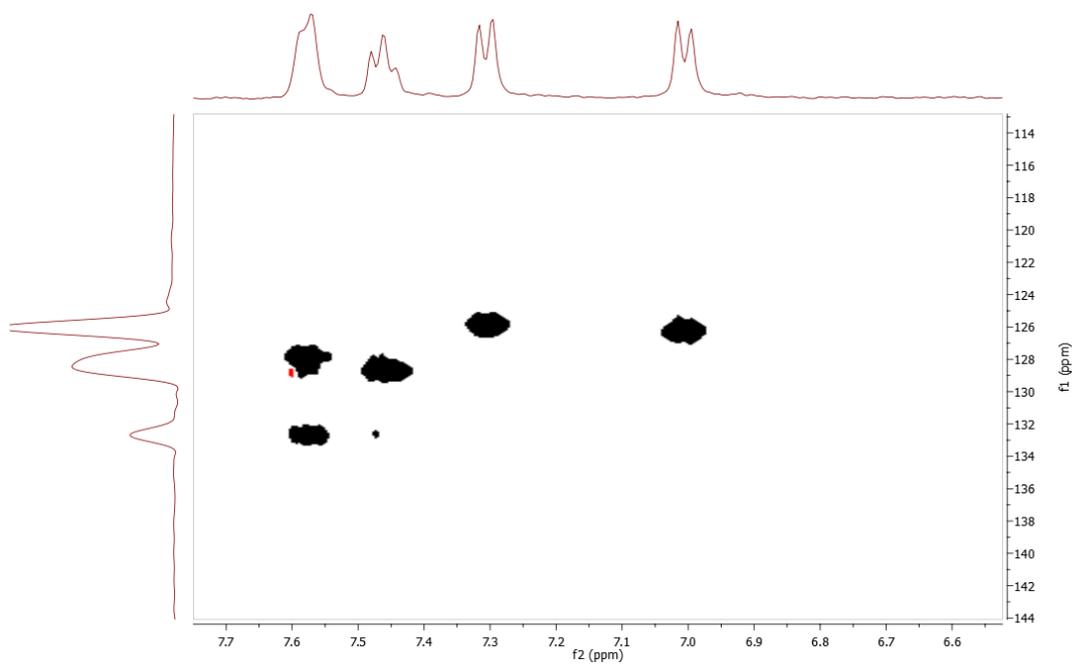
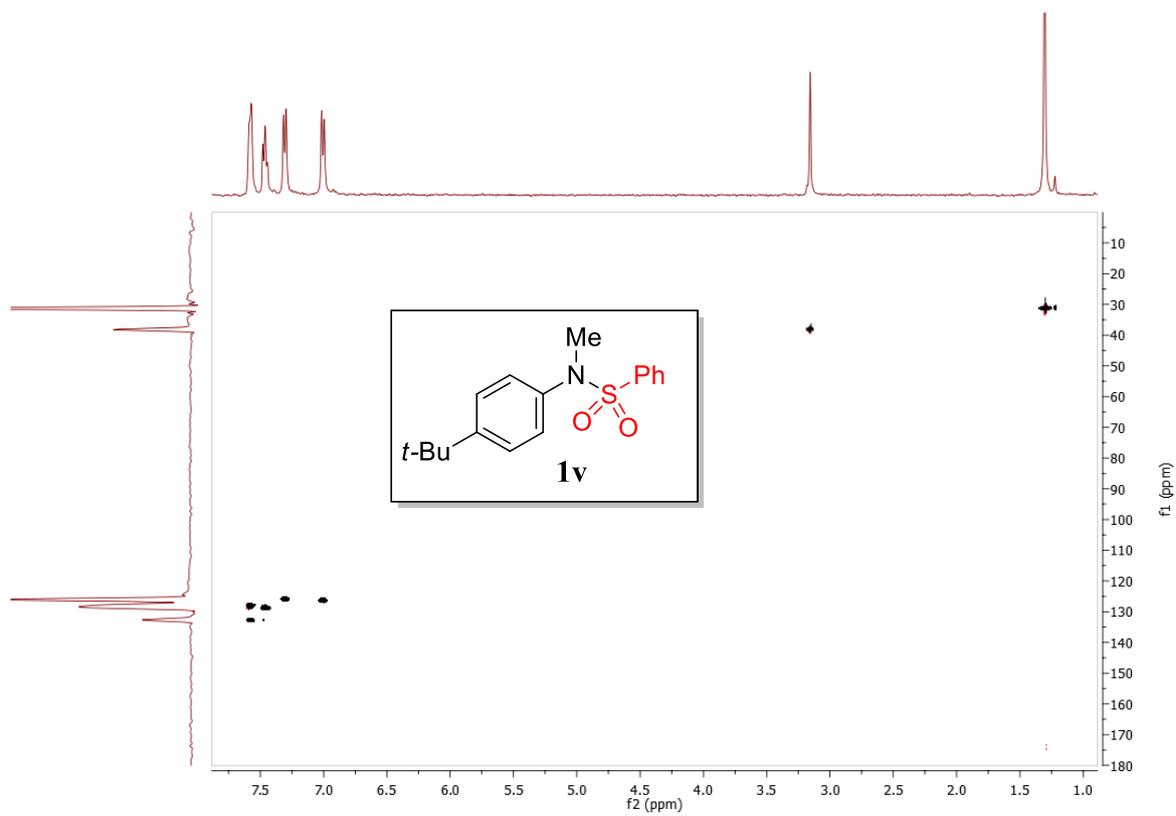
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-(*tert*-butyl)phenyl)-*N*-methylbenzene sulfonamide (**1v**).



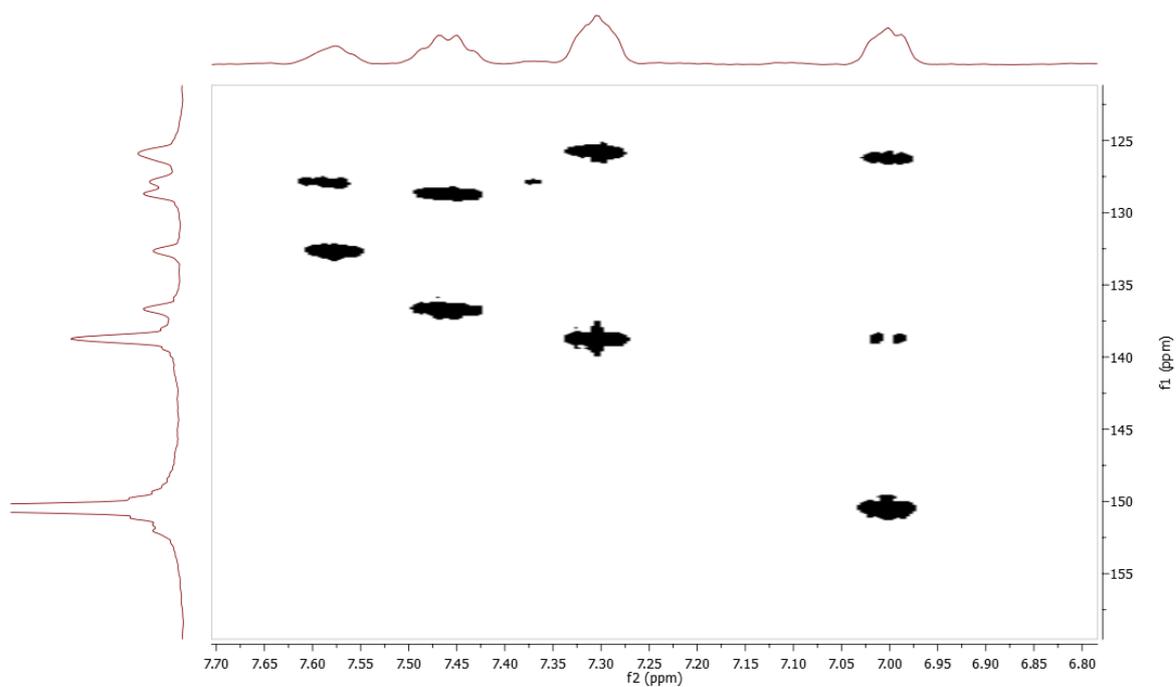
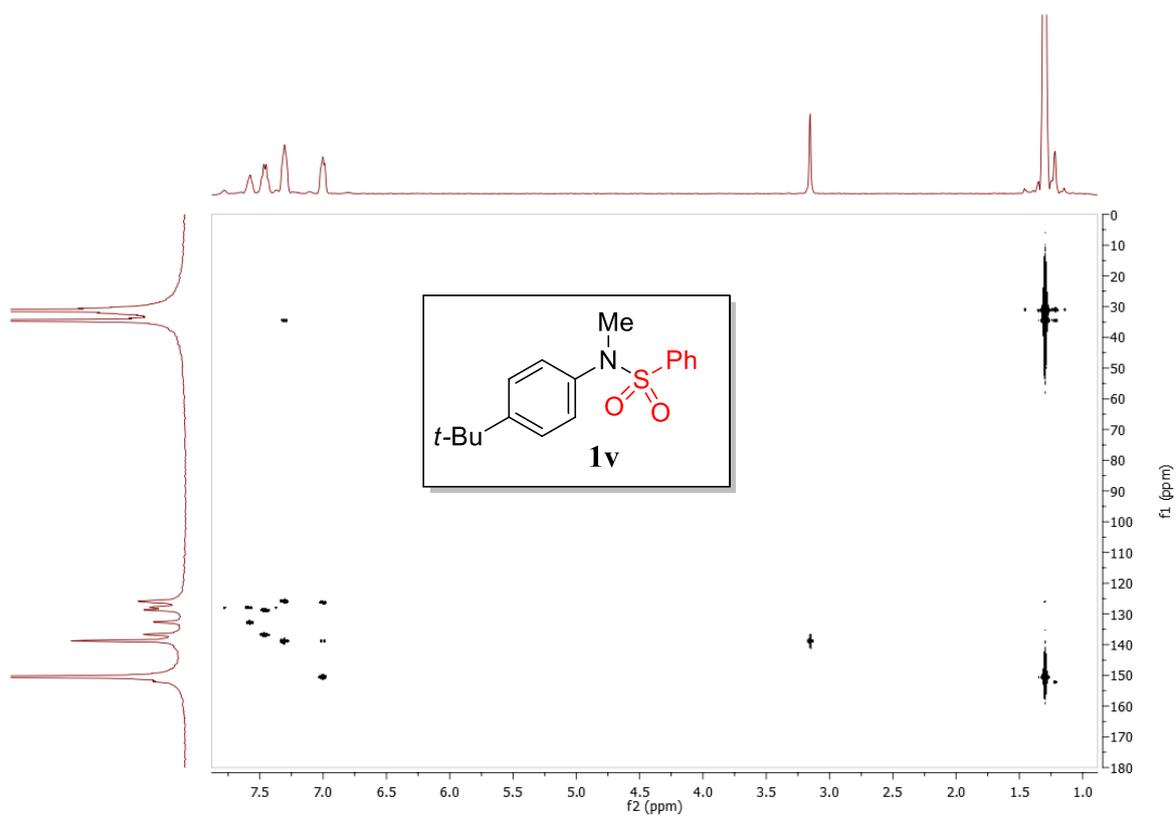
$^1\text{H}/^1\text{H}$ COSY NMR (400 MHz, CDCl_3). *N*-(4-(*tert*-butyl)phenyl)-*N*-methylbenzene sulfonamide (**1v**).



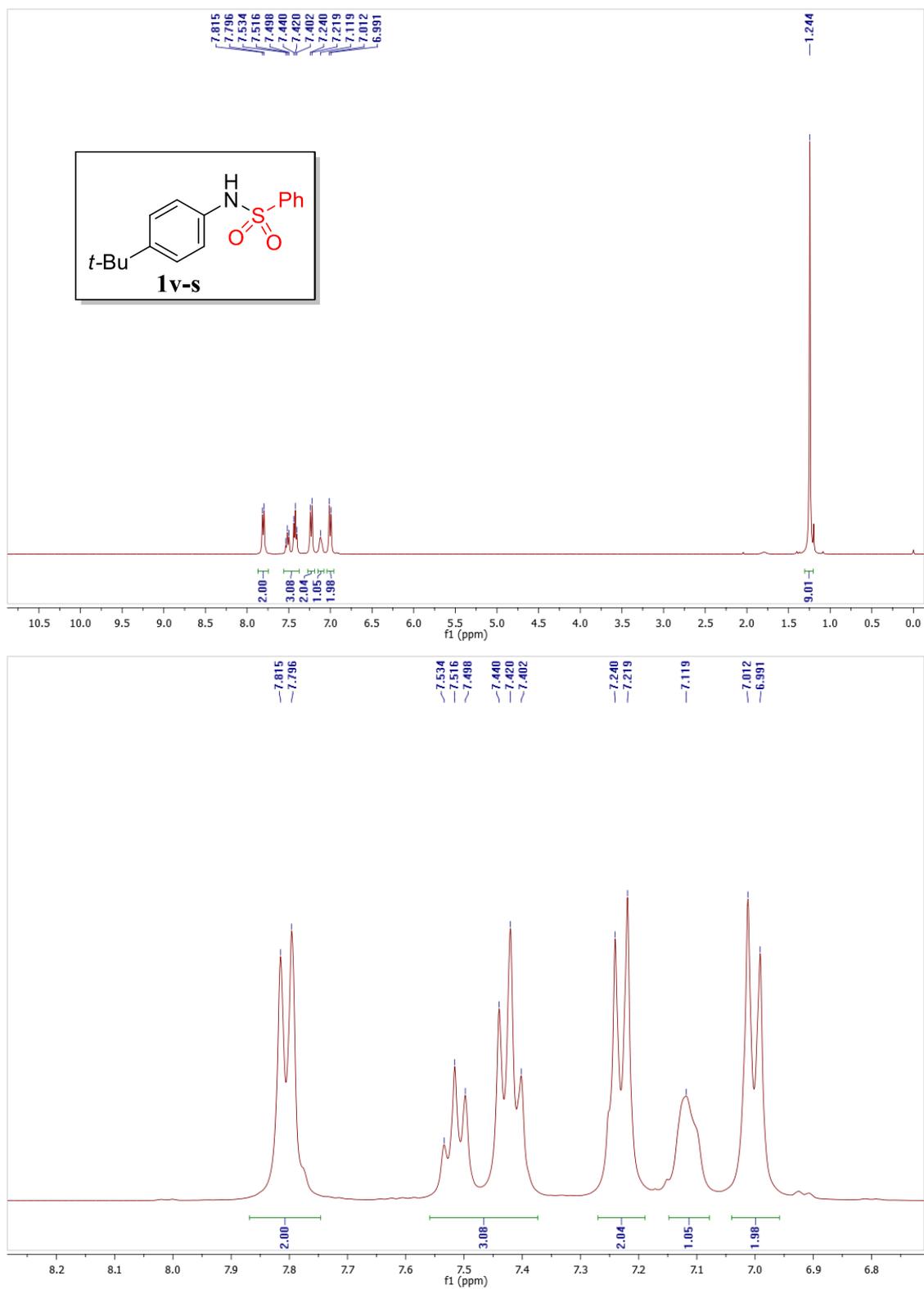
$^1\text{H}/^{13}\text{C}$ HSQC NMR (400 MHz, CDCl_3). *N*-(4-(*tert*-butyl)phenyl)-*N*-methylbenzene sulfonamide (**1v**).



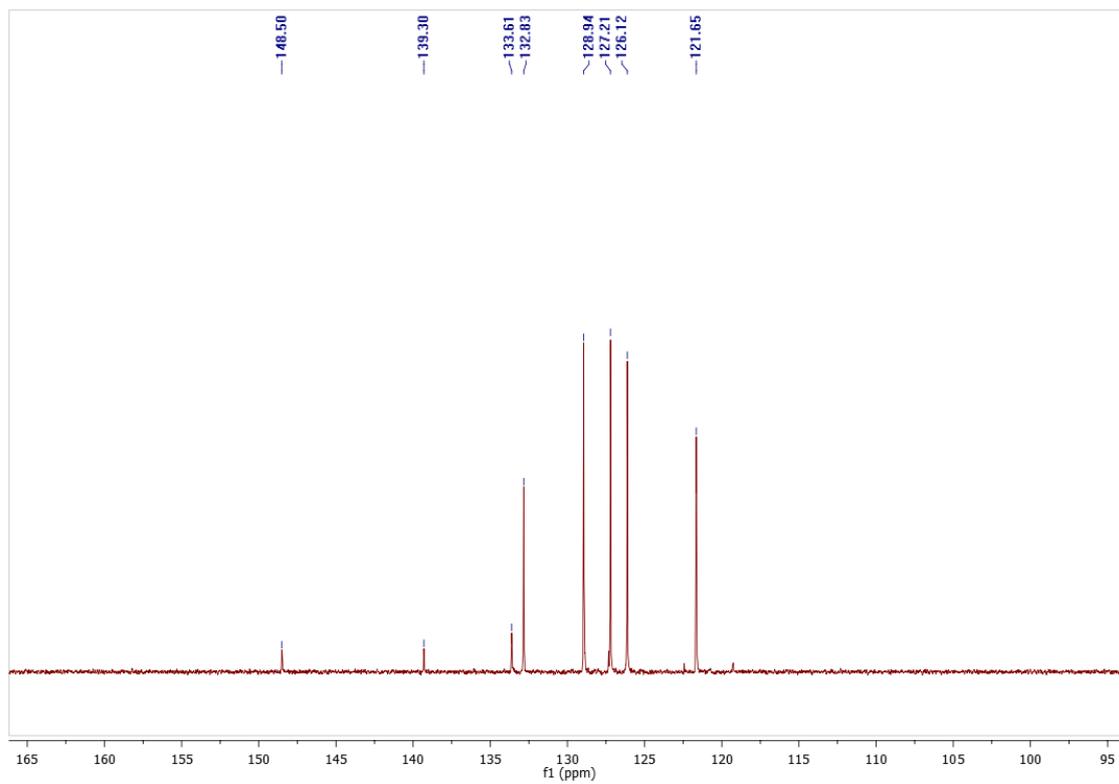
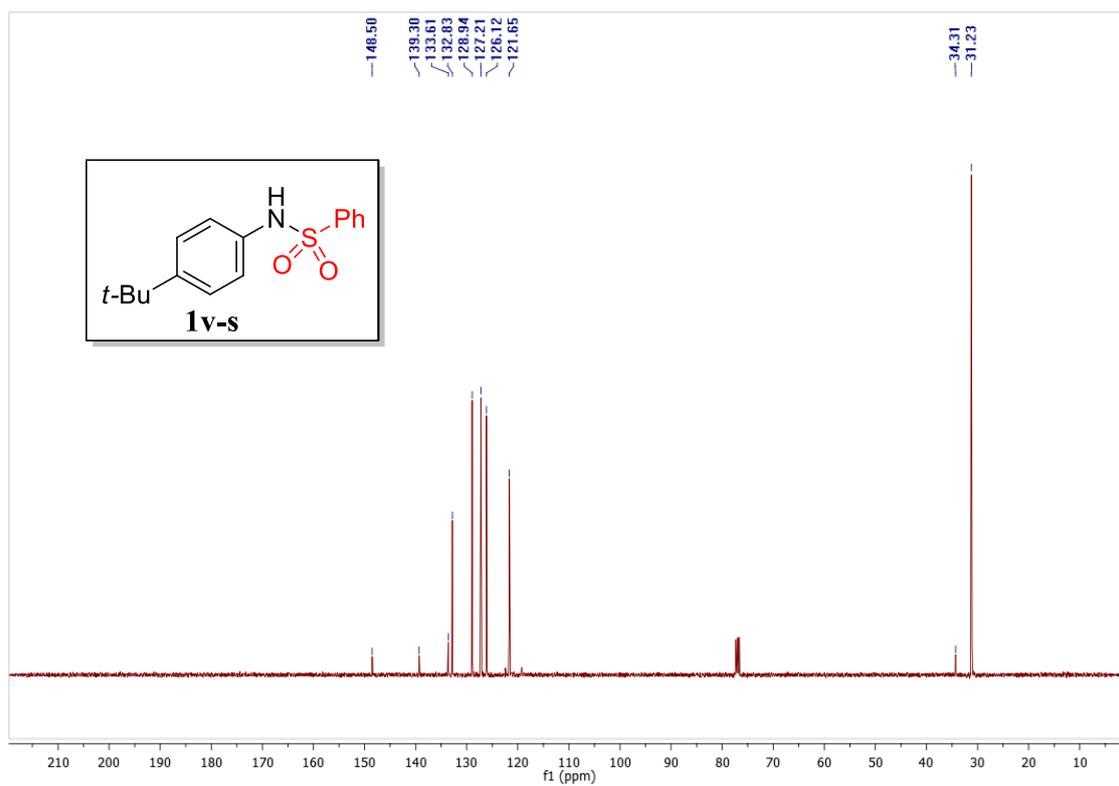
$^1\text{H}/^{13}\text{C}$ HMBC NMR (400 MHz, CDCl_3). *N*-(4-(*tert*-butyl)phenyl)-*N*-methylbenzene sulfonamide (**1v**).



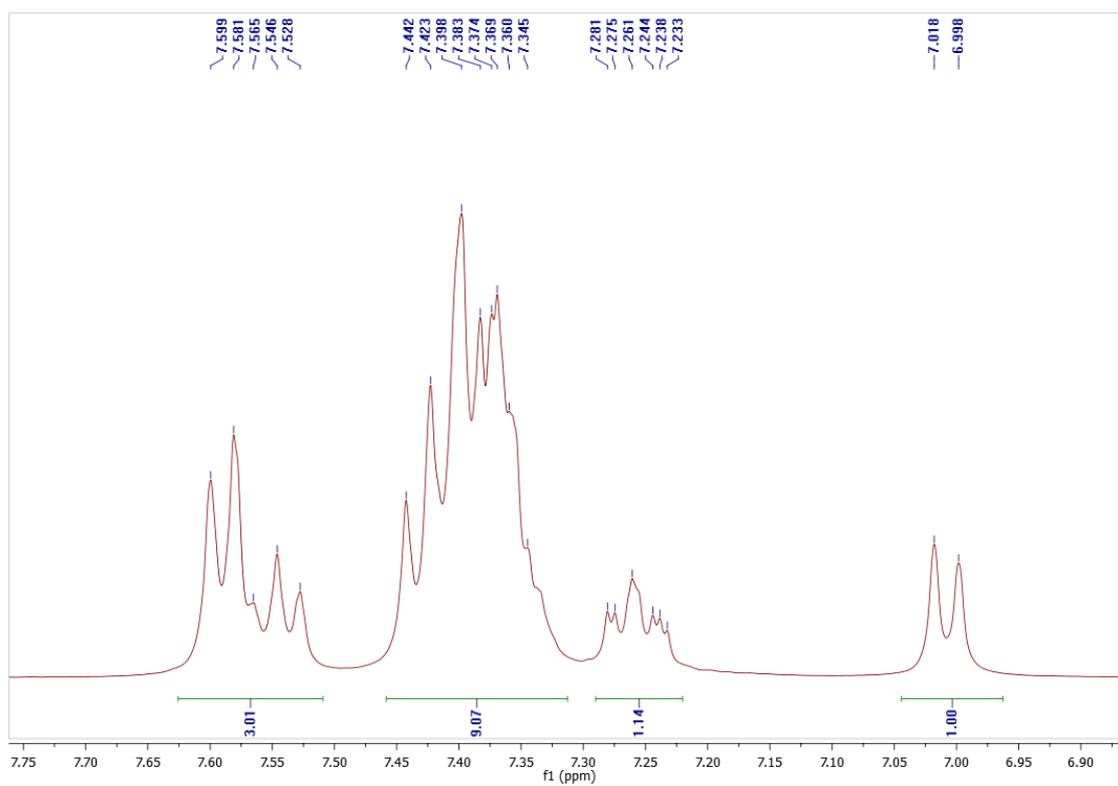
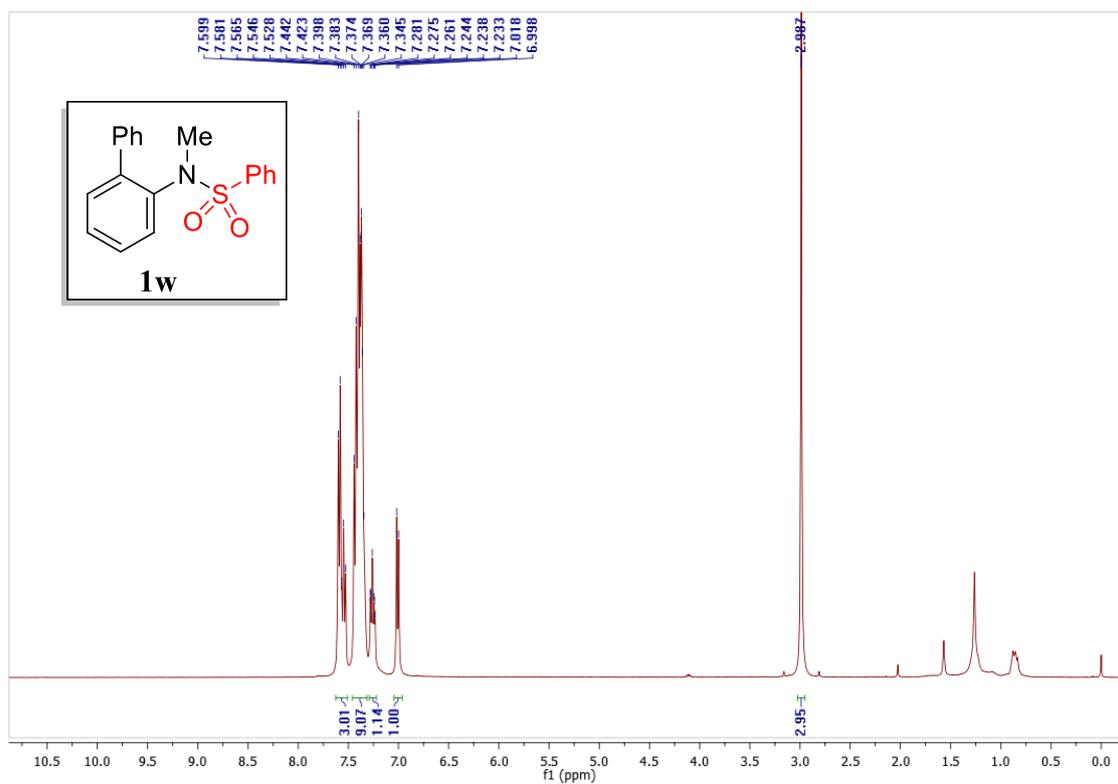
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-(*tert*-Butyl)phenyl)benzenesulfonamide (**1v-s**).



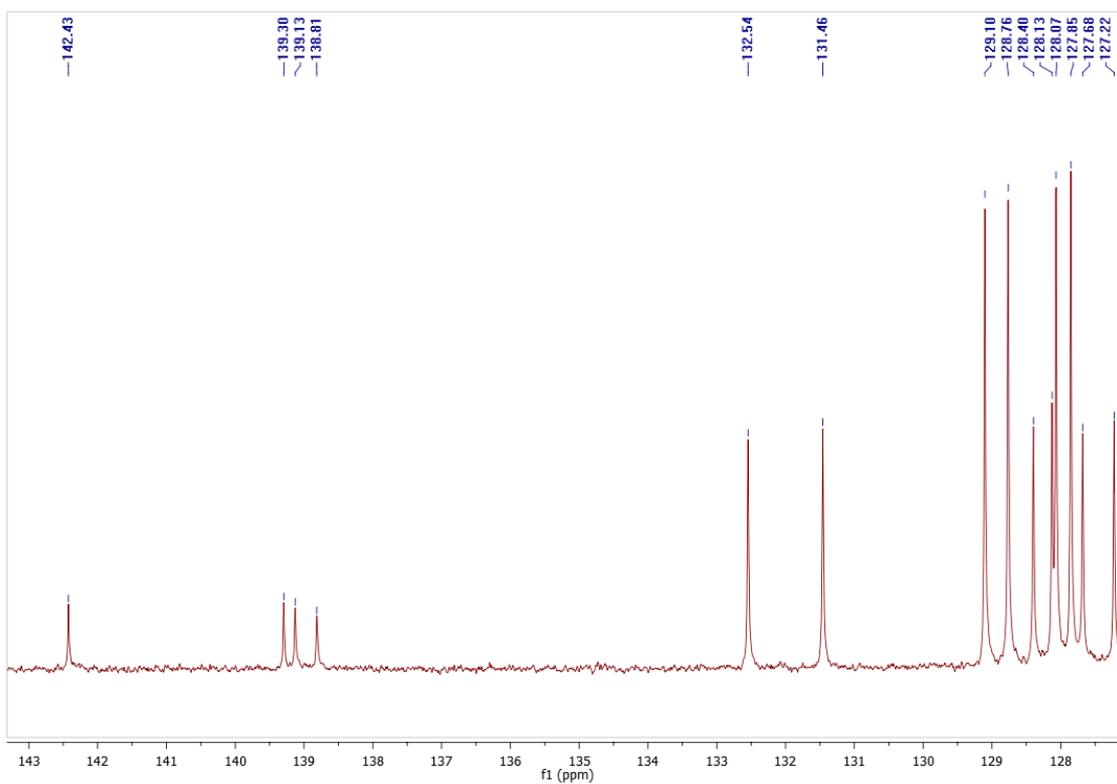
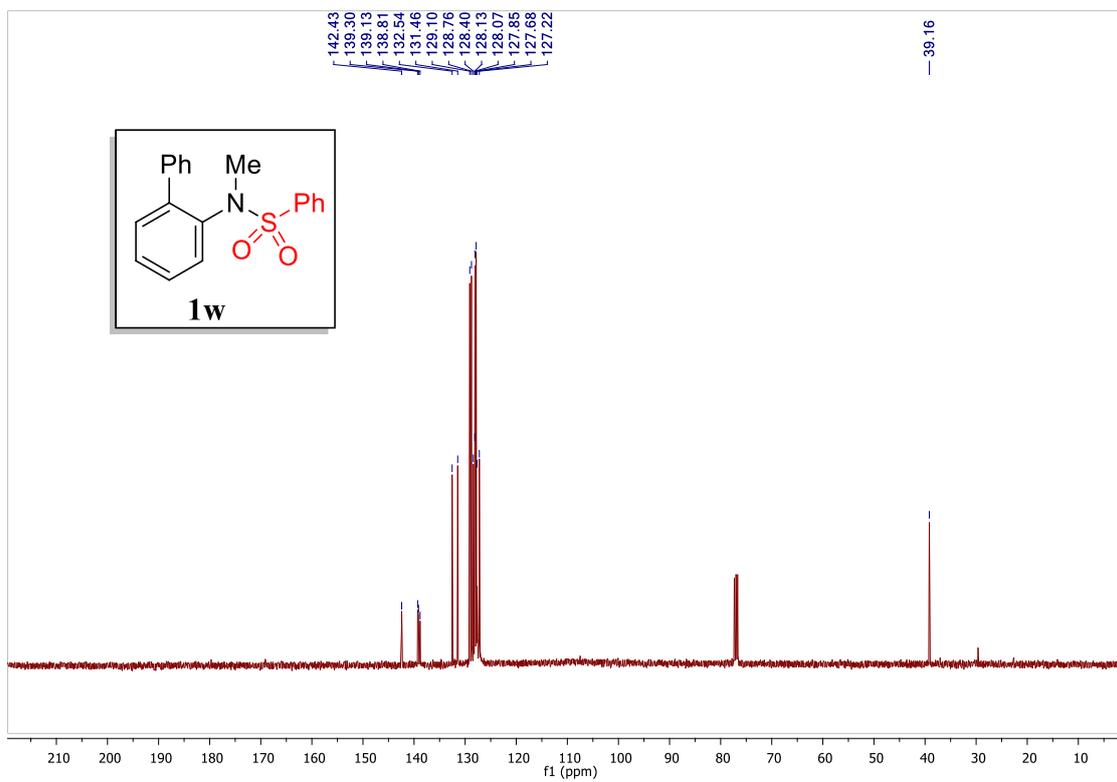
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-(*tert*-Butyl)phenyl)benzenesulfonamide (**1v-s**).



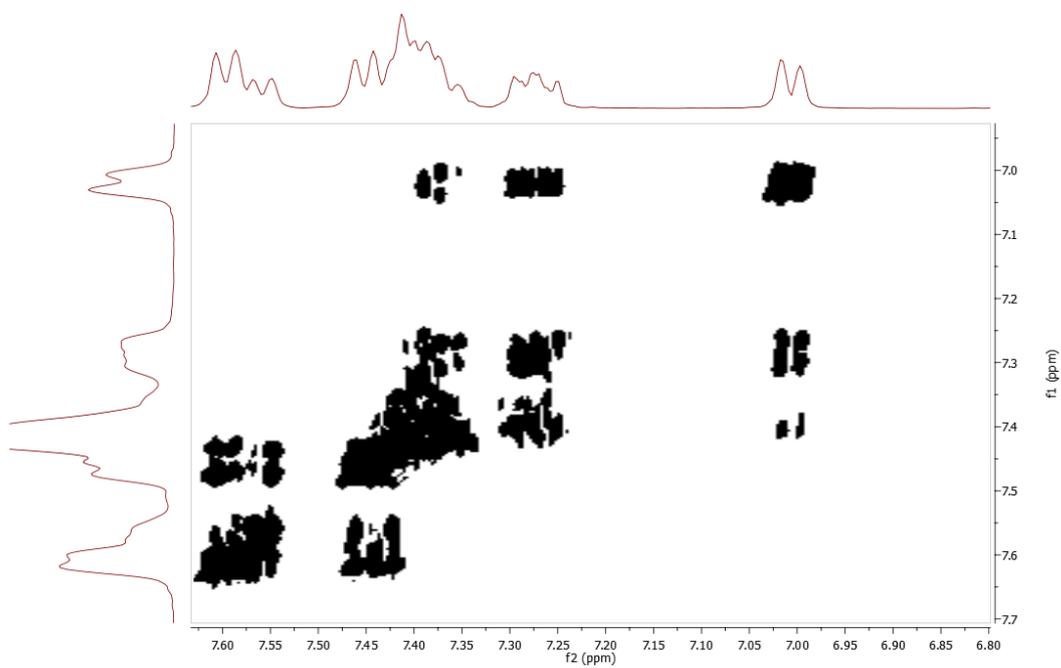
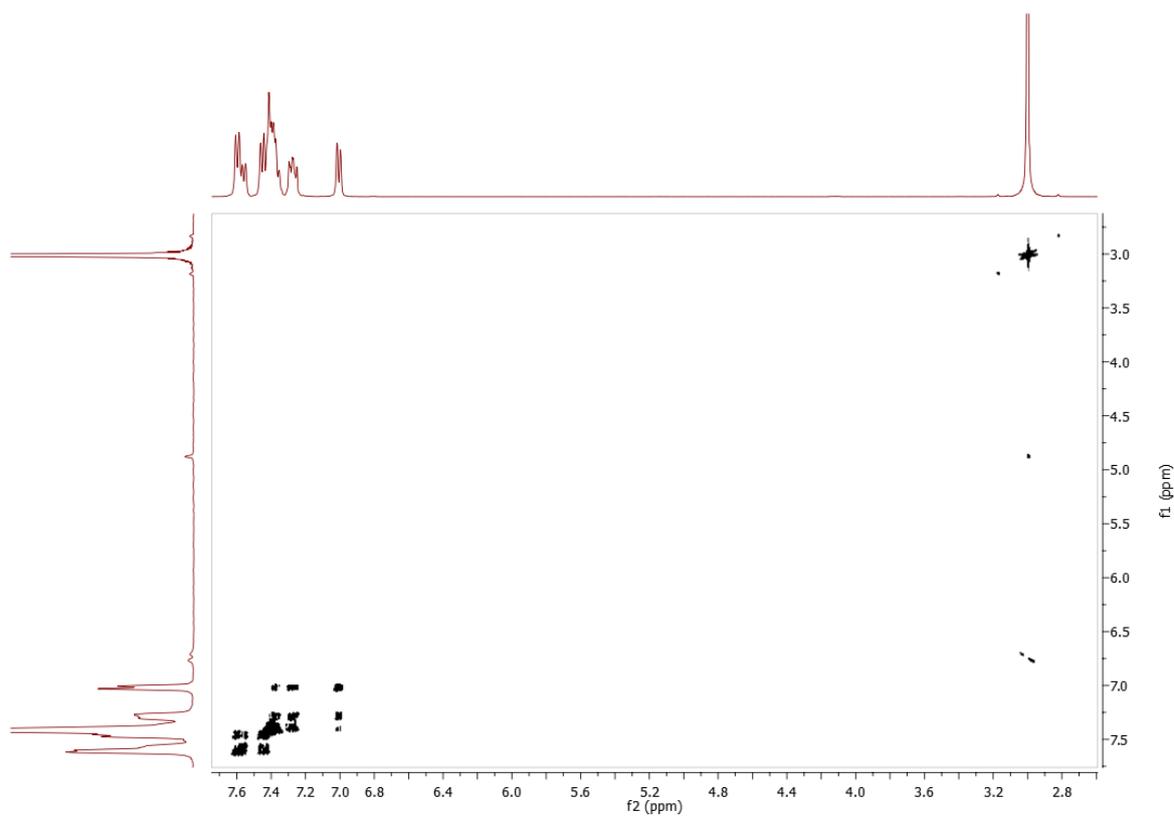
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-([1,1'-Biphenyl]-2-yl)-*N*-methylbenzenesulfonamide (**1w**).



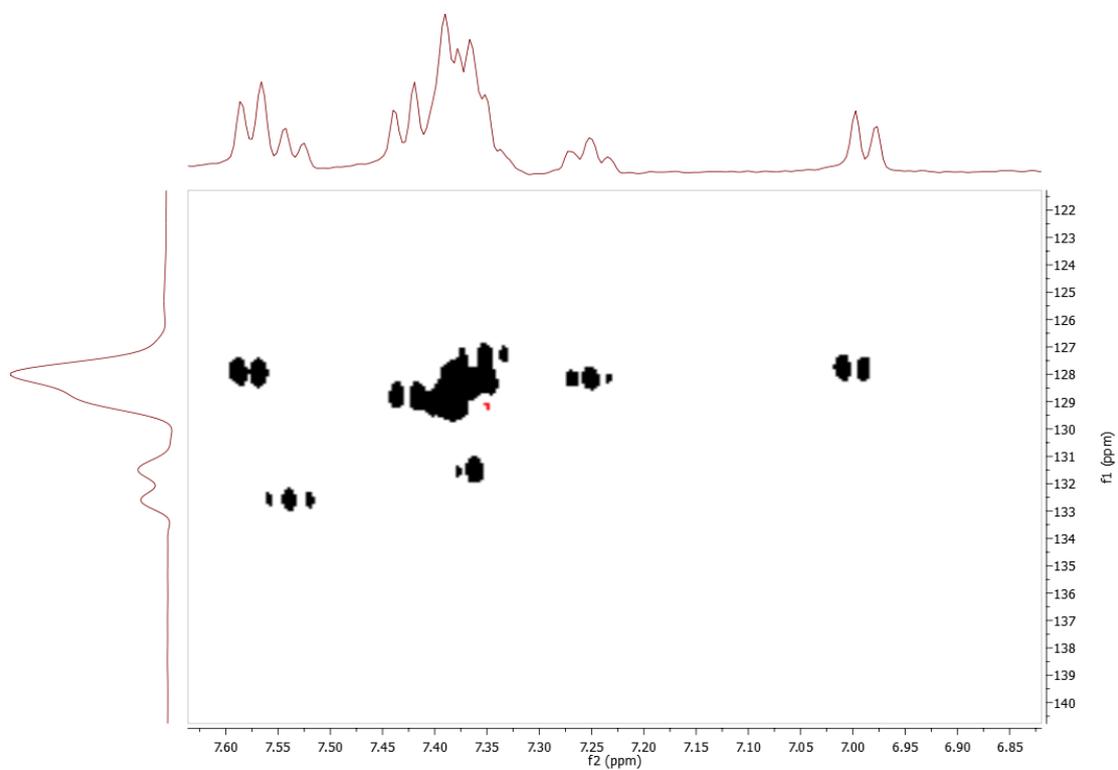
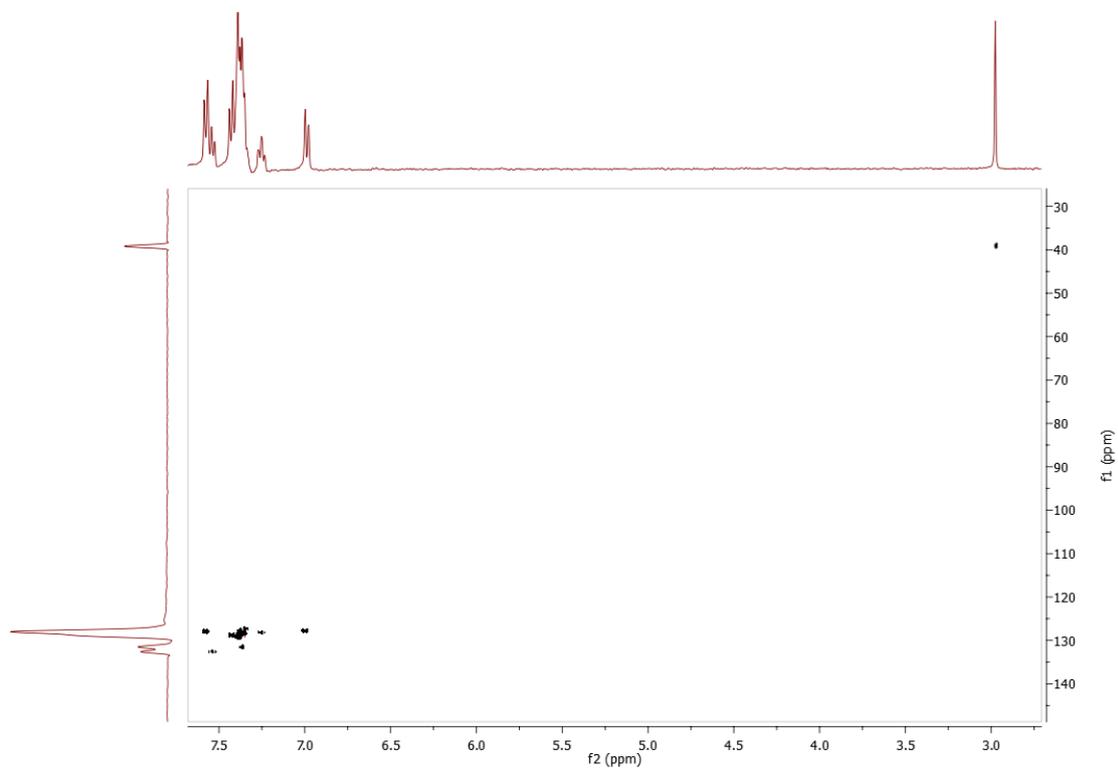
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-([1,1'-Biphenyl]-2-yl)-*N*-methylbenzene sulfonamide (**1w**).



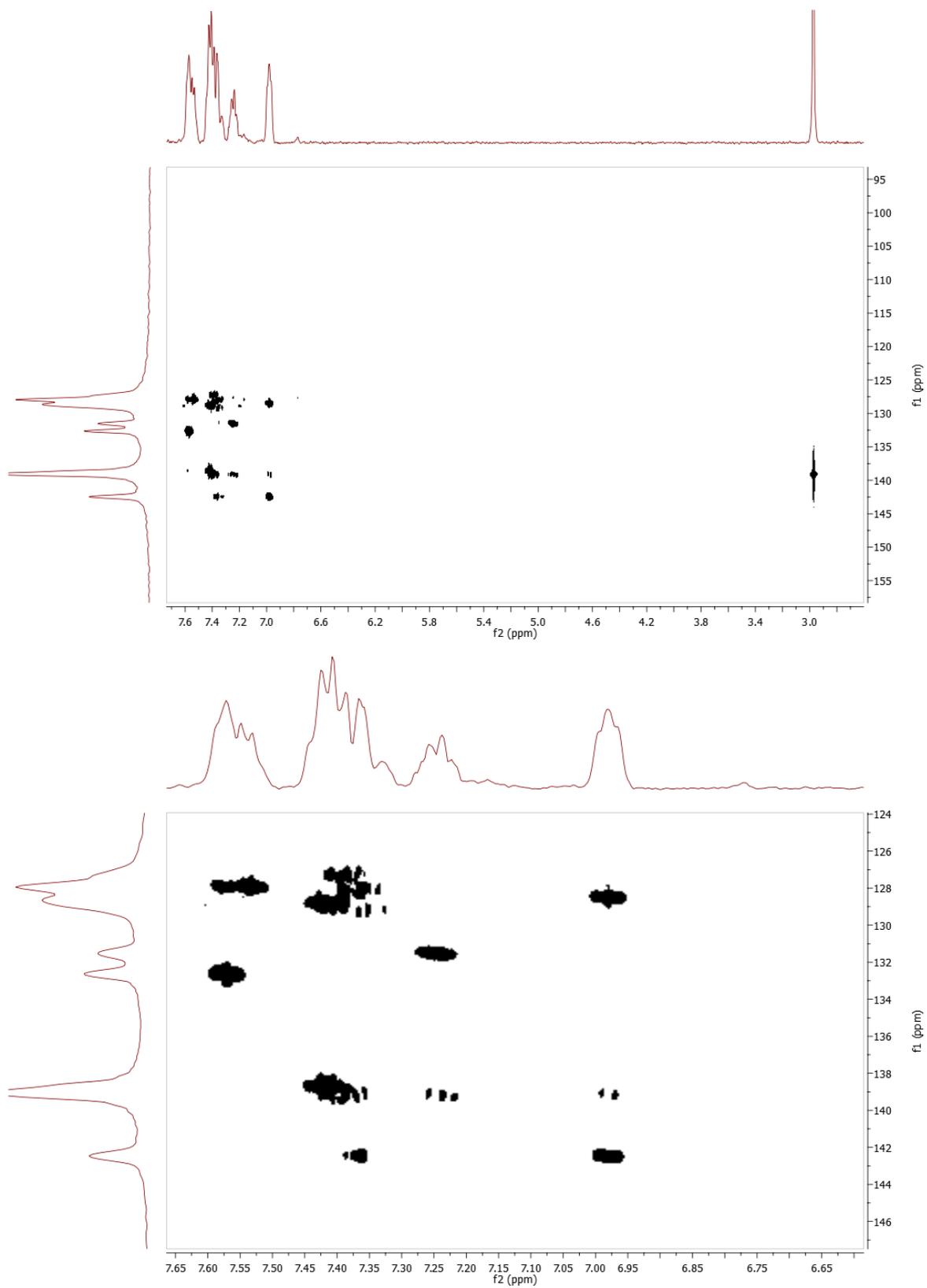
$^1\text{H}/^1\text{H}$ COSY NMR (400 MHz, CDCl_3). *N*-([1,1'-biphenyl]-2-yl)-*N*-methylbenzenesulfonamide (**1w**).



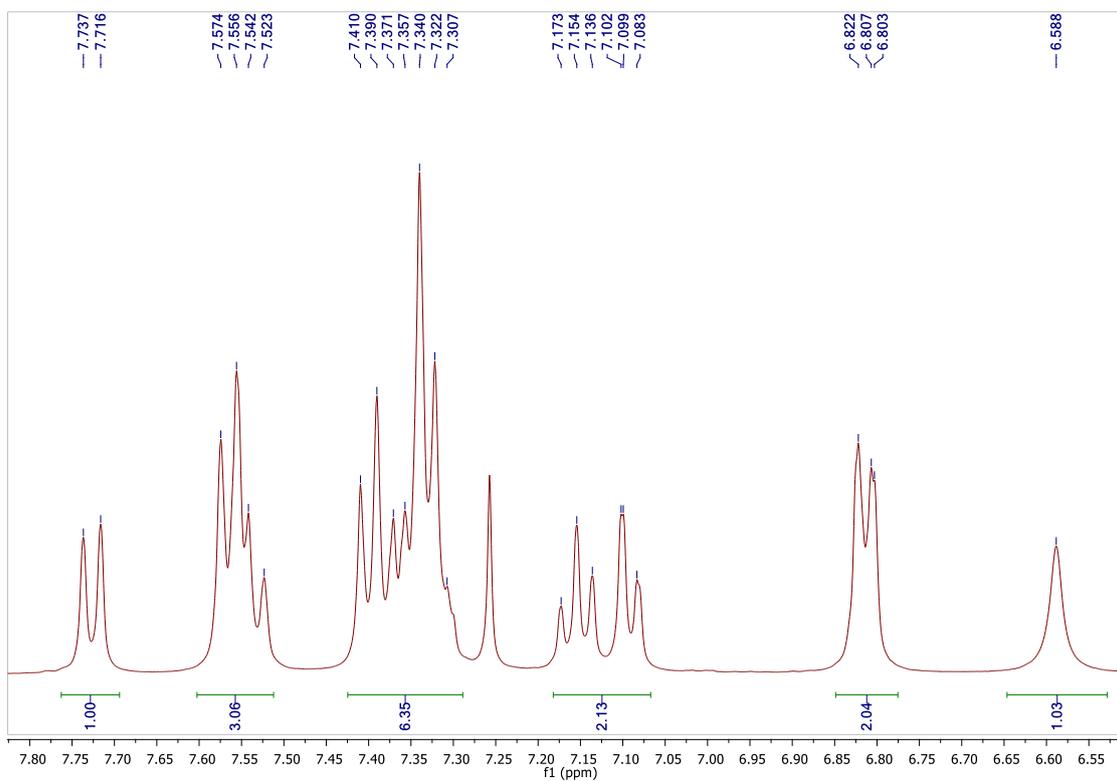
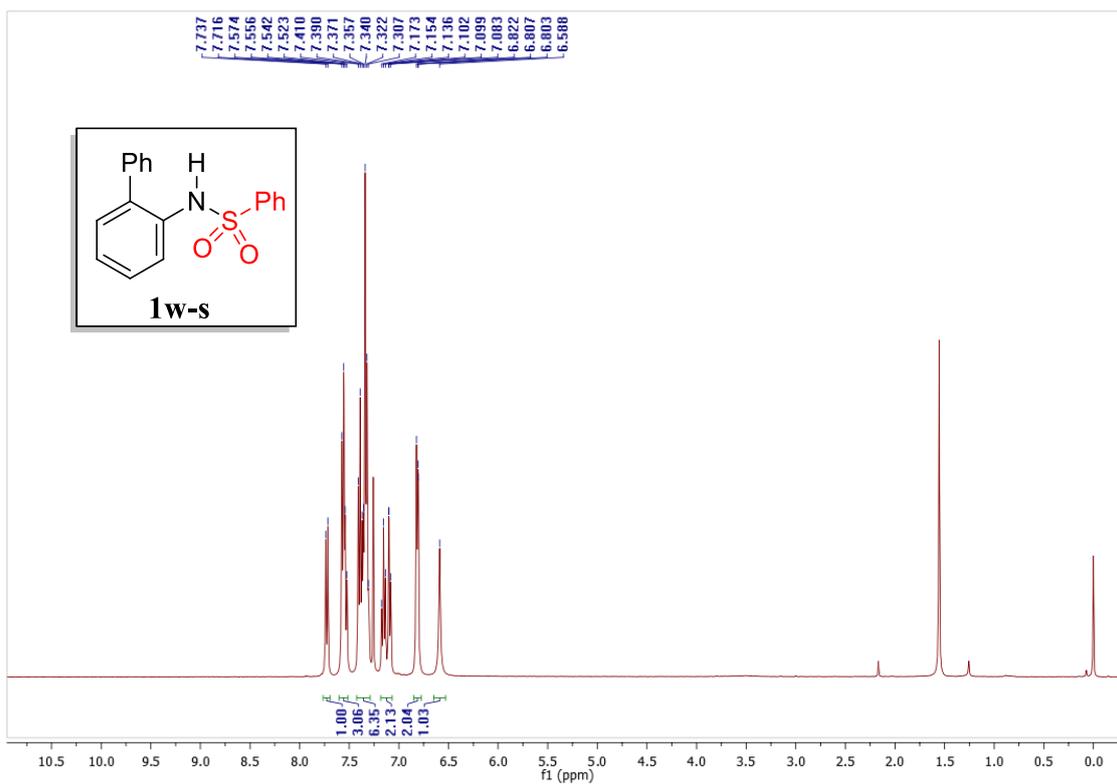
$^1\text{H}/^{13}\text{C}$ HSQC NMR (400 MHz, CDCl_3). *N*-([1,1'-biphenyl]-2-yl)-*N*-methylbenzene sulfonamide (**1w**).



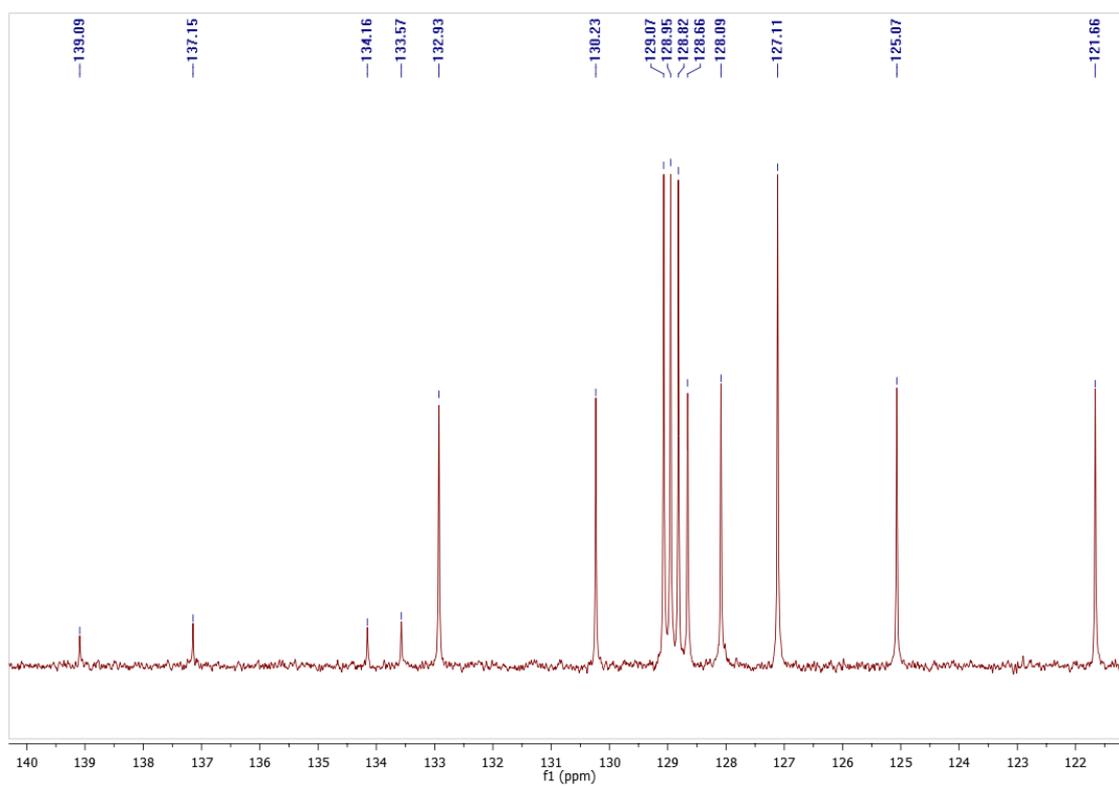
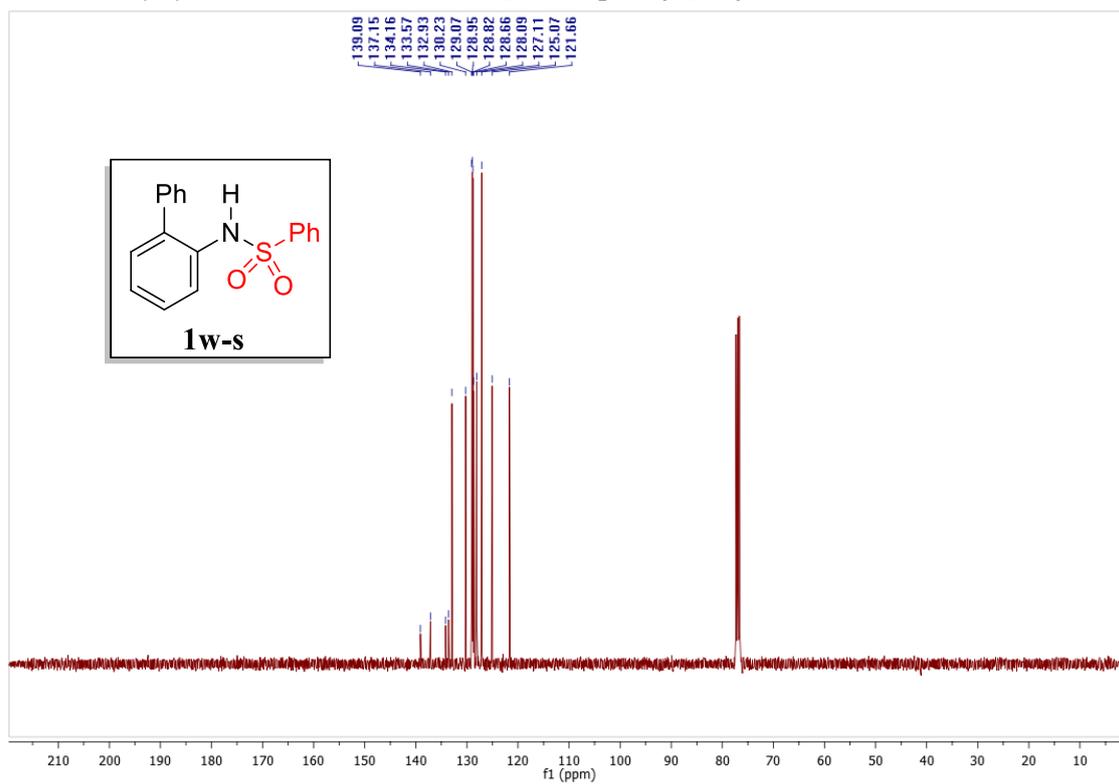
$^1\text{H}/^{13}\text{C}$ HMBC NMR (400 MHz, CDCl_3). *N*-([1,1'-biphenyl]-2-yl)-*N*-methylbenzene sulfonamide (**1w**).



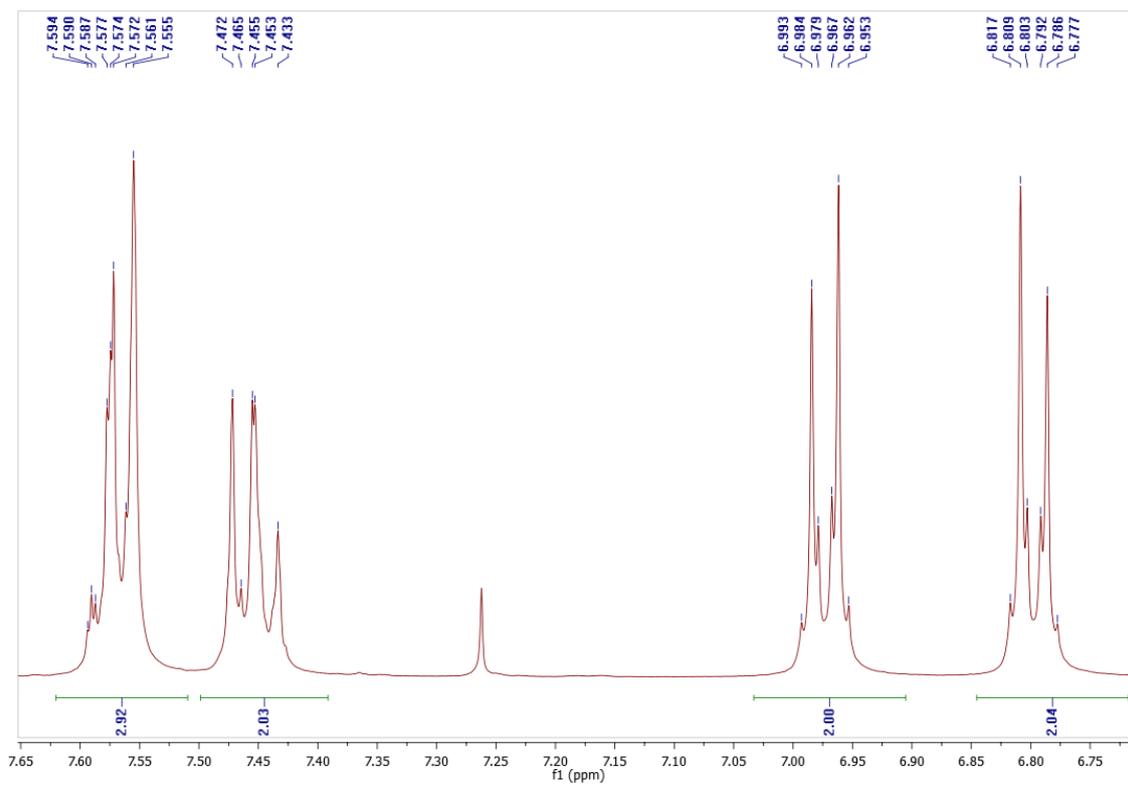
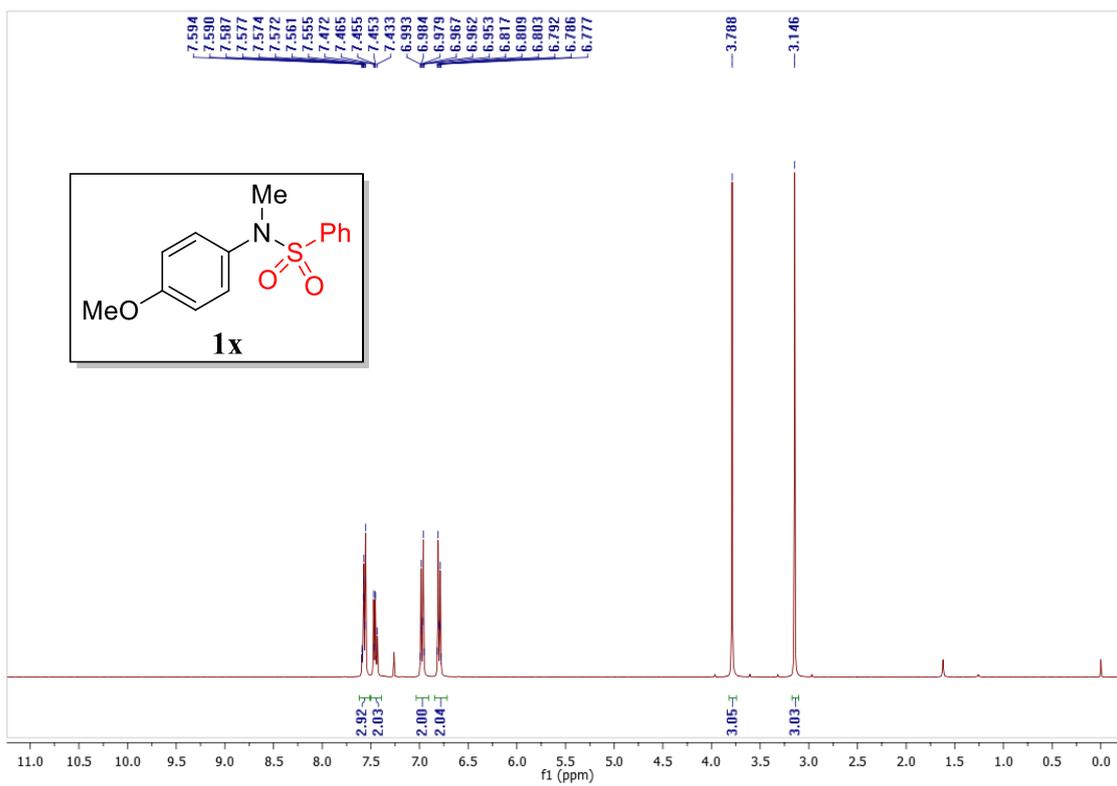
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-([1,1'-Biphenyl]-2-yl)benzenesulfonamide (**1w-s**).



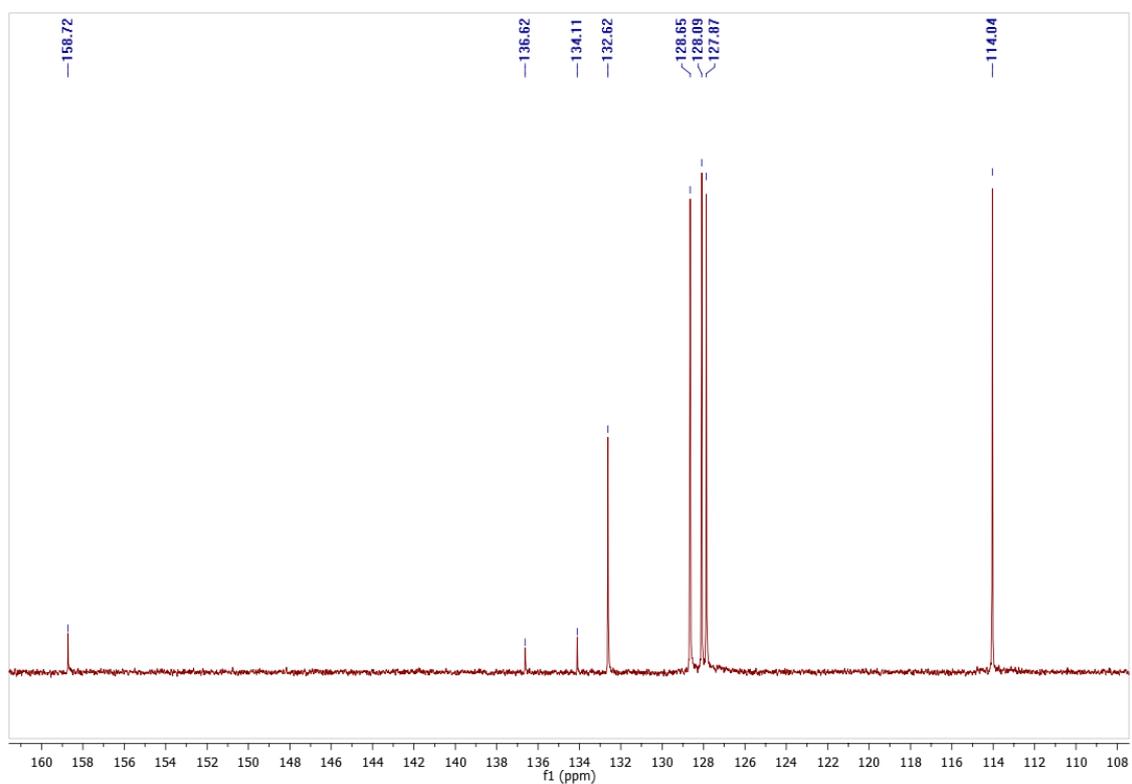
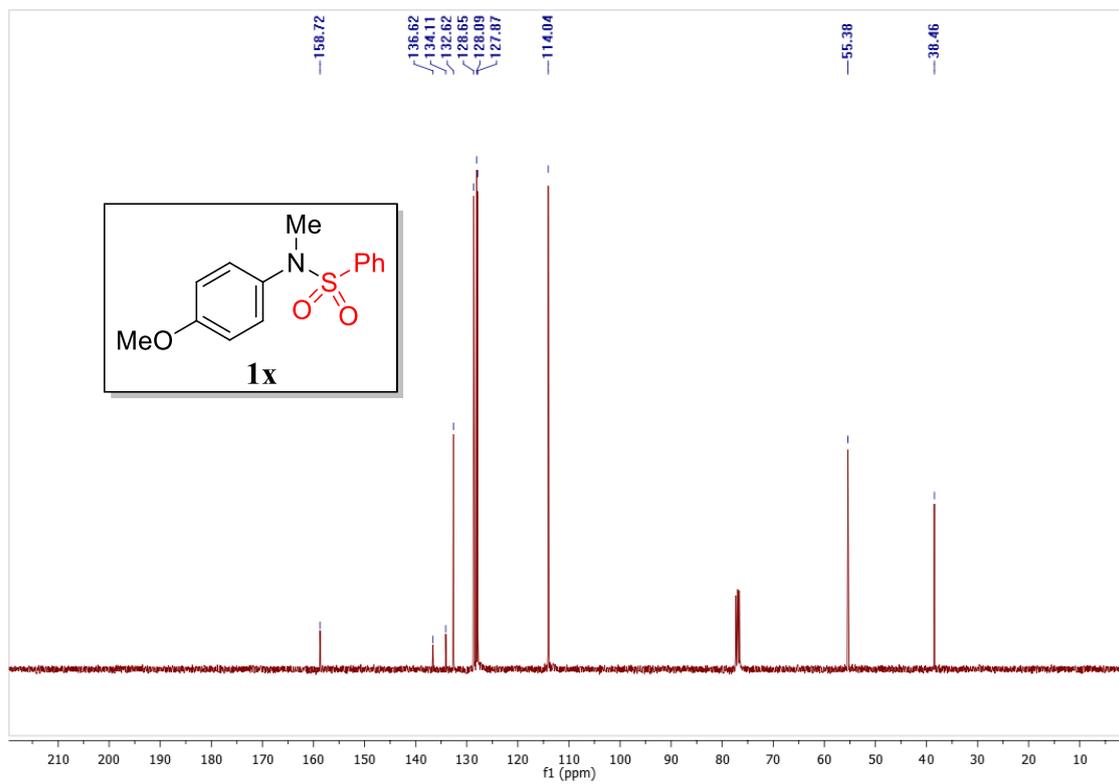
^{13}C -NMR {H} (400 MHz, CDCl_3). *N*-([1,1'-Biphenyl]-2-yl)benzenesulfonamide (**1w-s**).



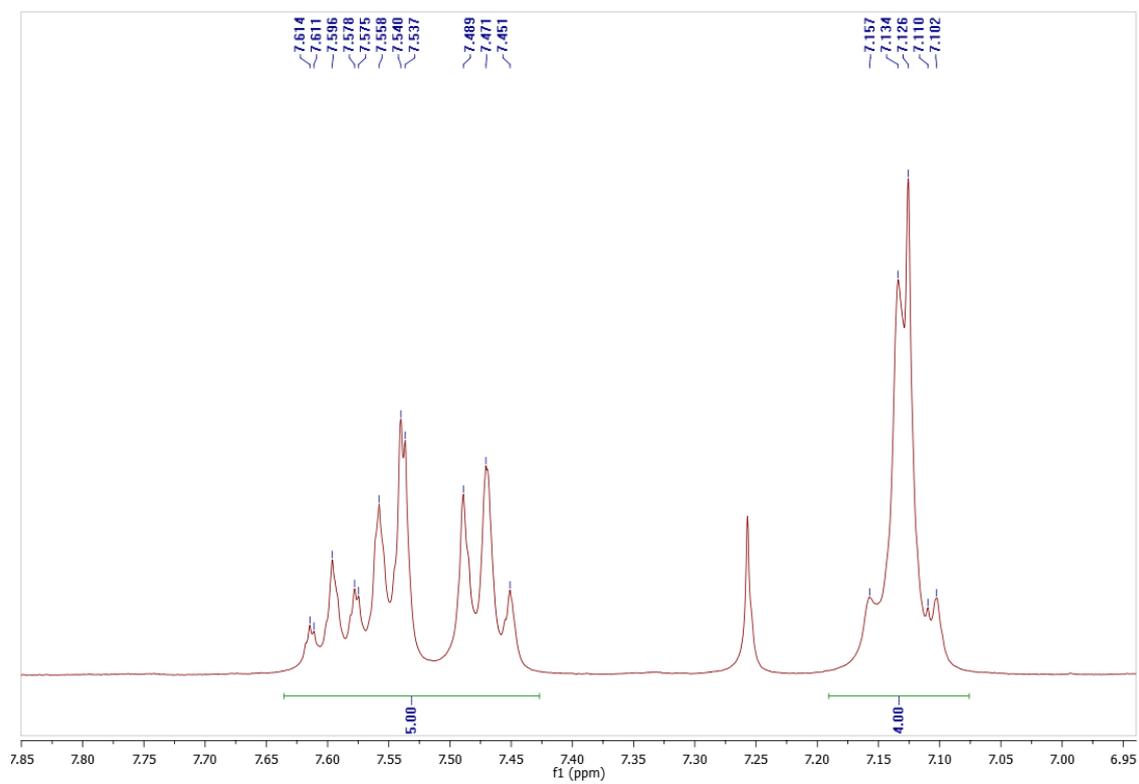
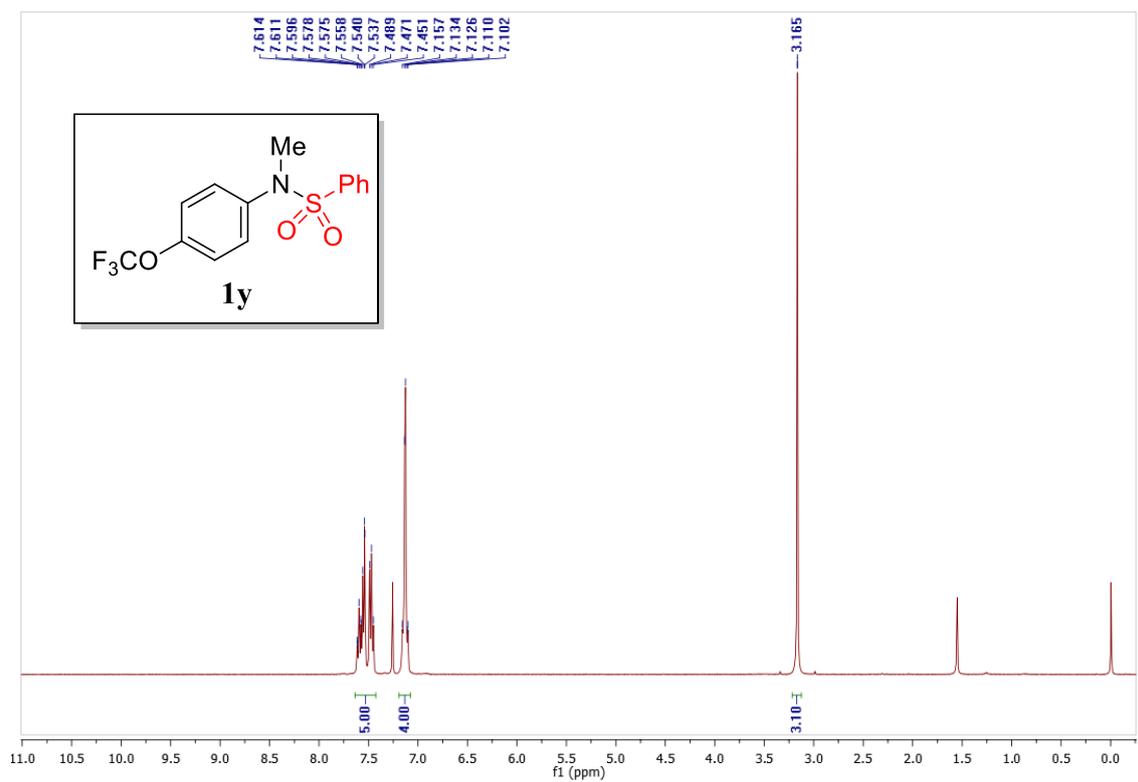
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Methoxyphenyl)-*N*-methylbenzenesulfonamide (**1x**).



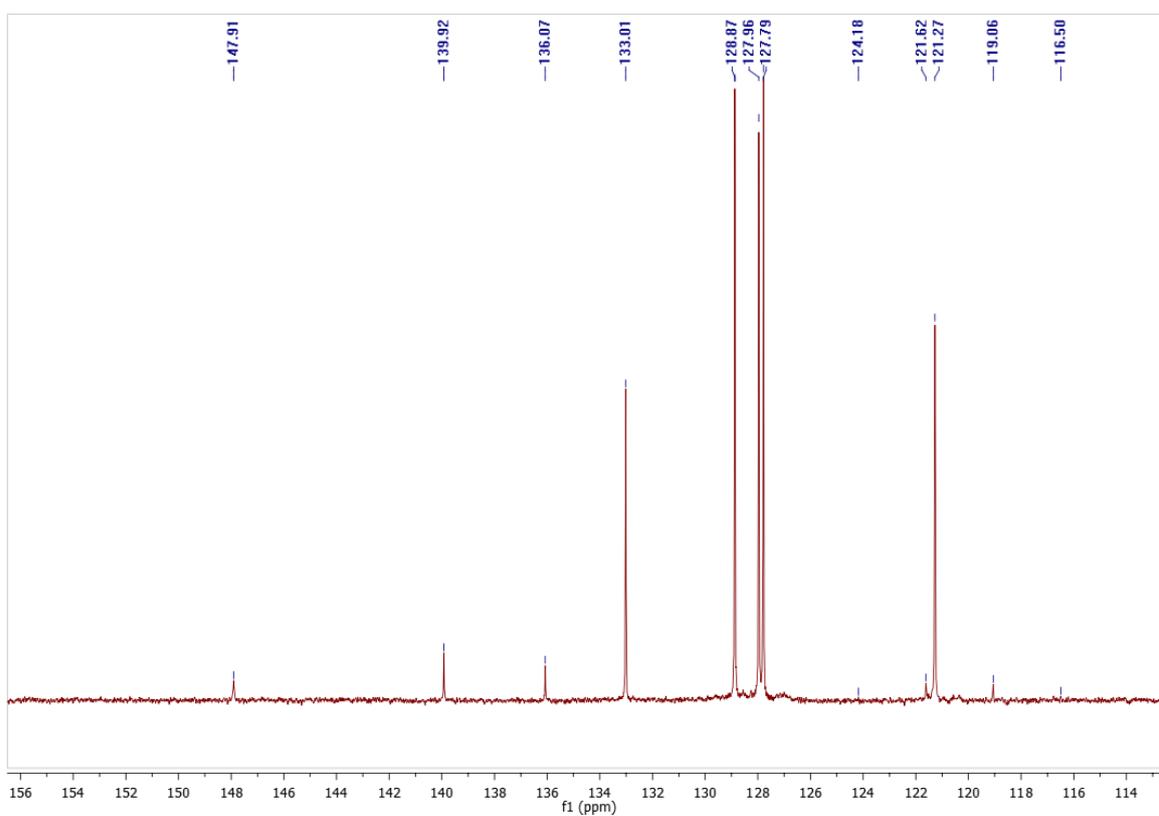
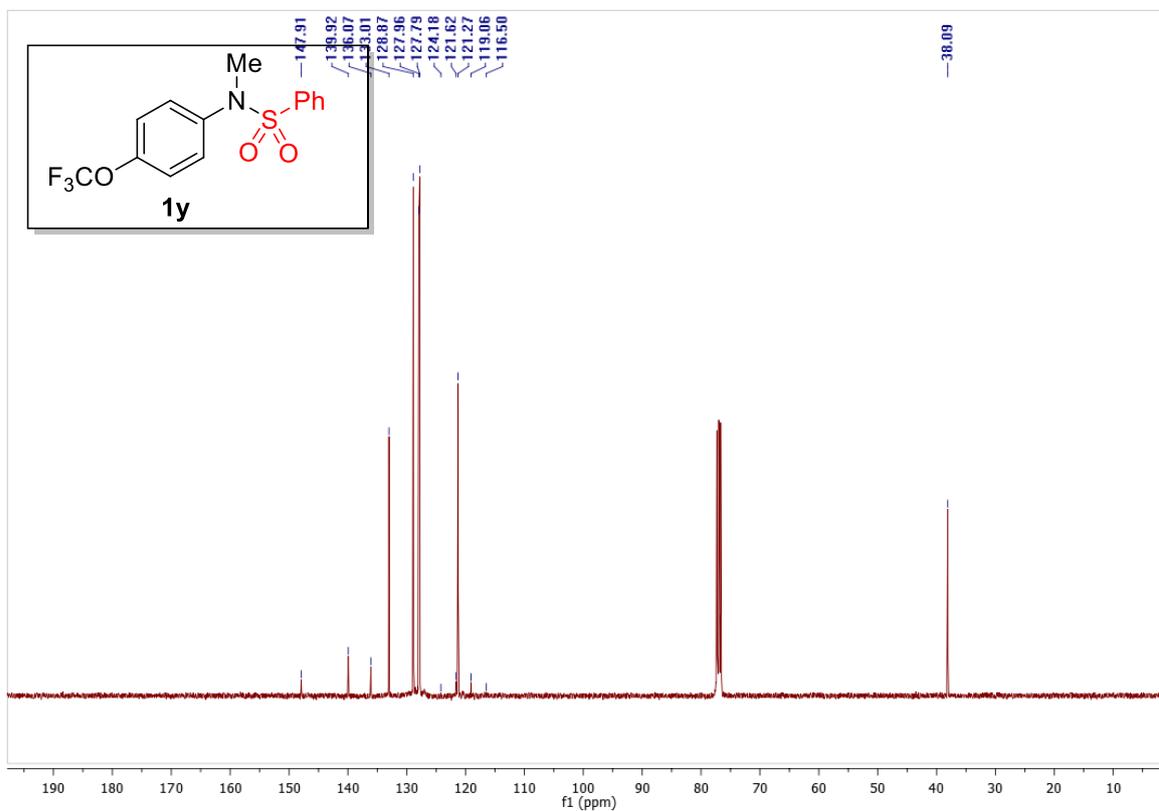
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Methoxyphenyl)-*N*-methylbenzenesulfonamide (**1x**).



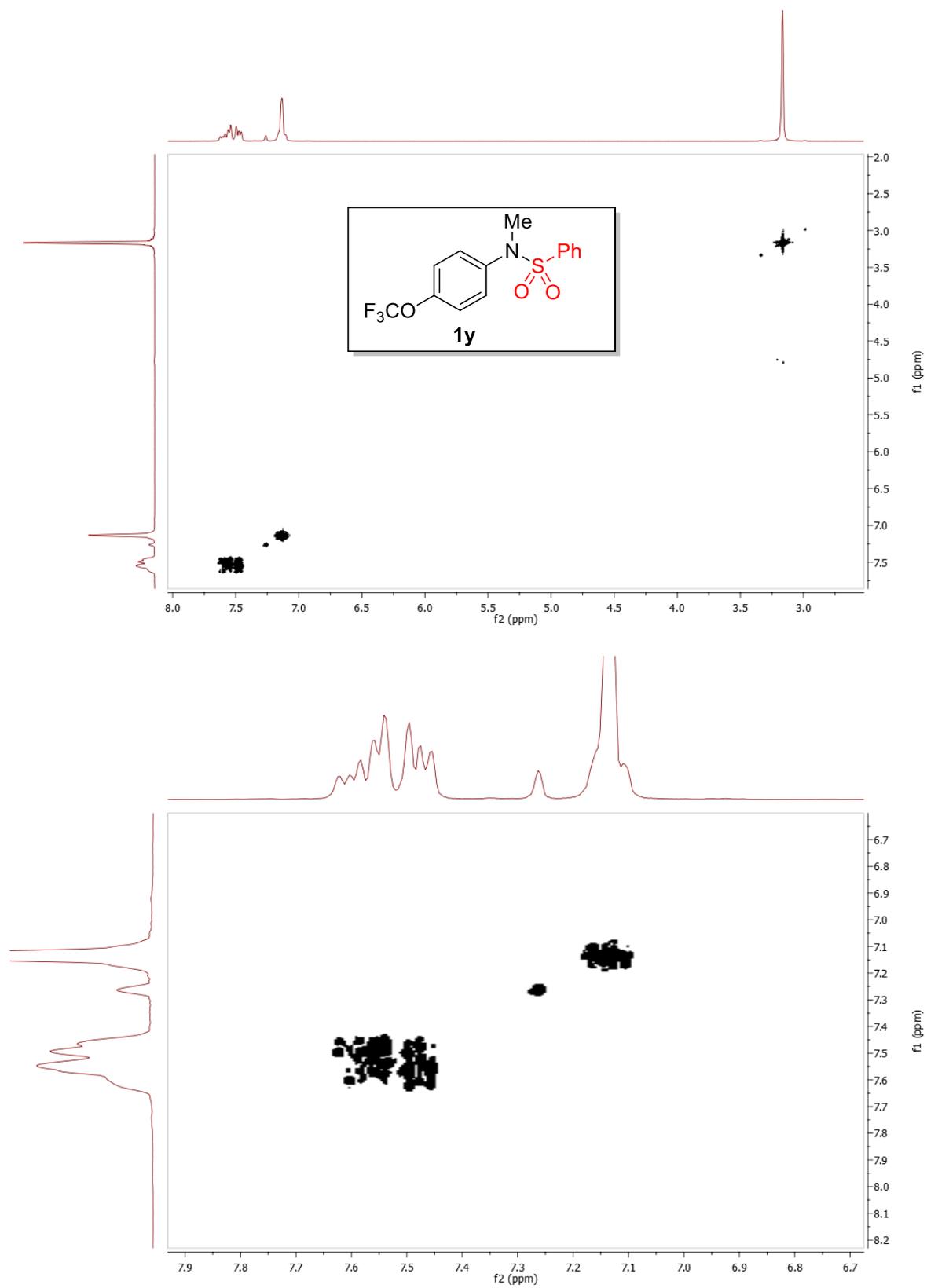
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-Methyl-*N*-(4-(trifluoromethoxy)phenyl) benzenesulfonamide (**1y**).



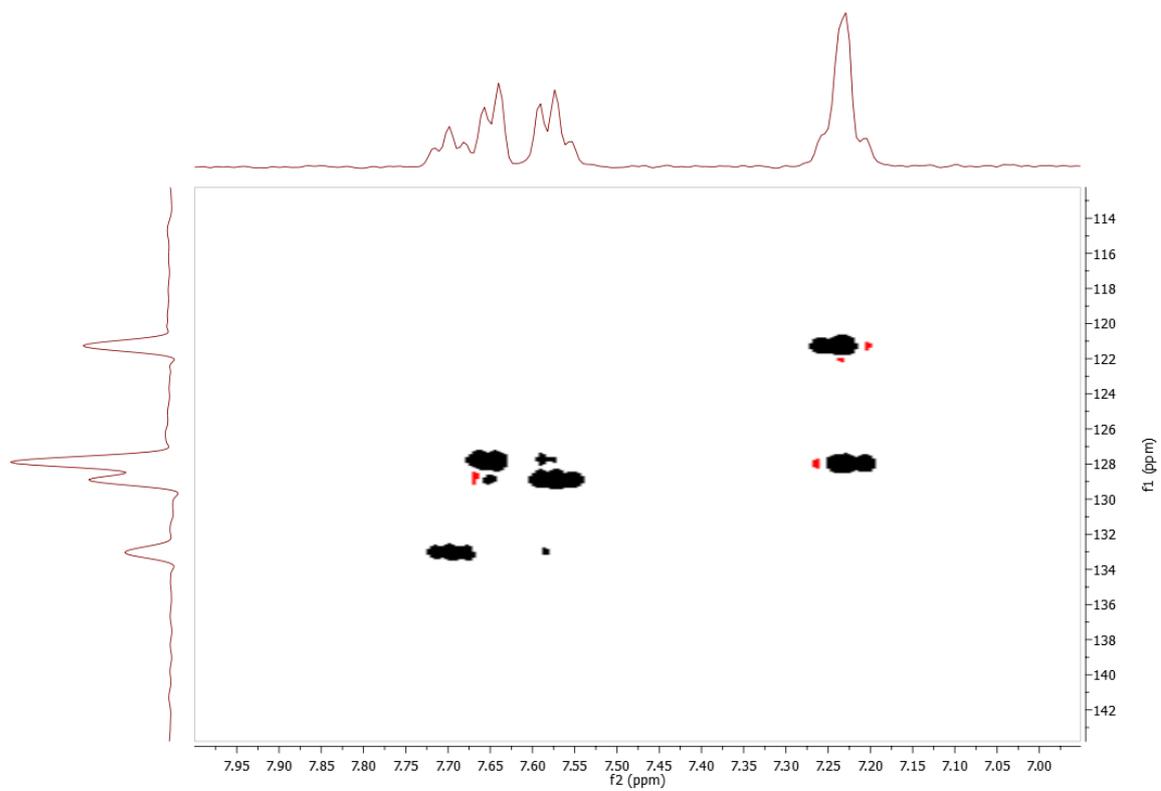
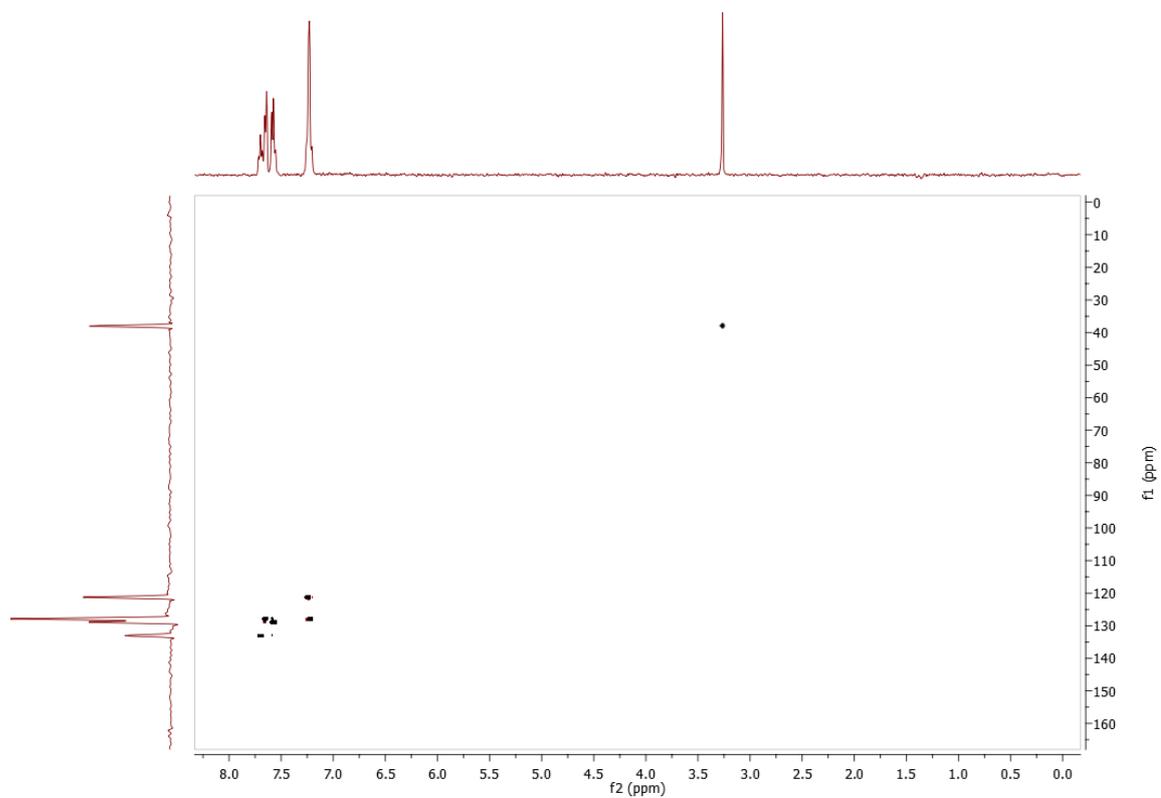
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-Methyl-*N*-(4-(trifluoromethoxy)phenyl)benzenesulfonamide (**1y**).



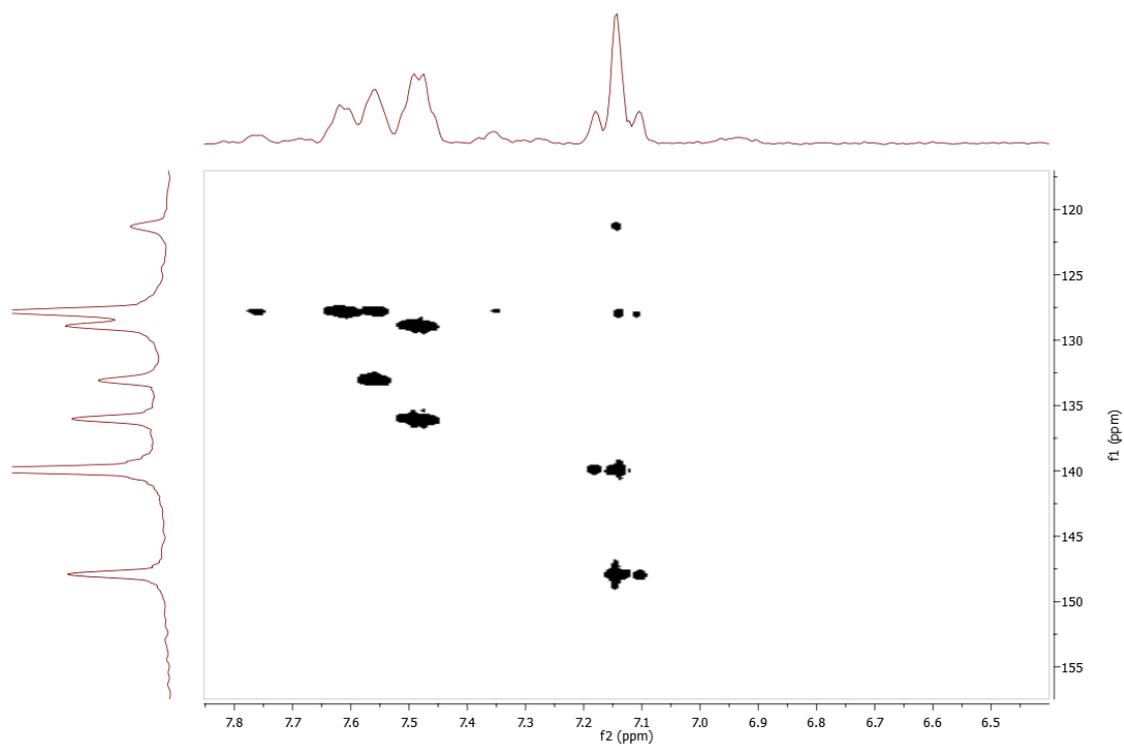
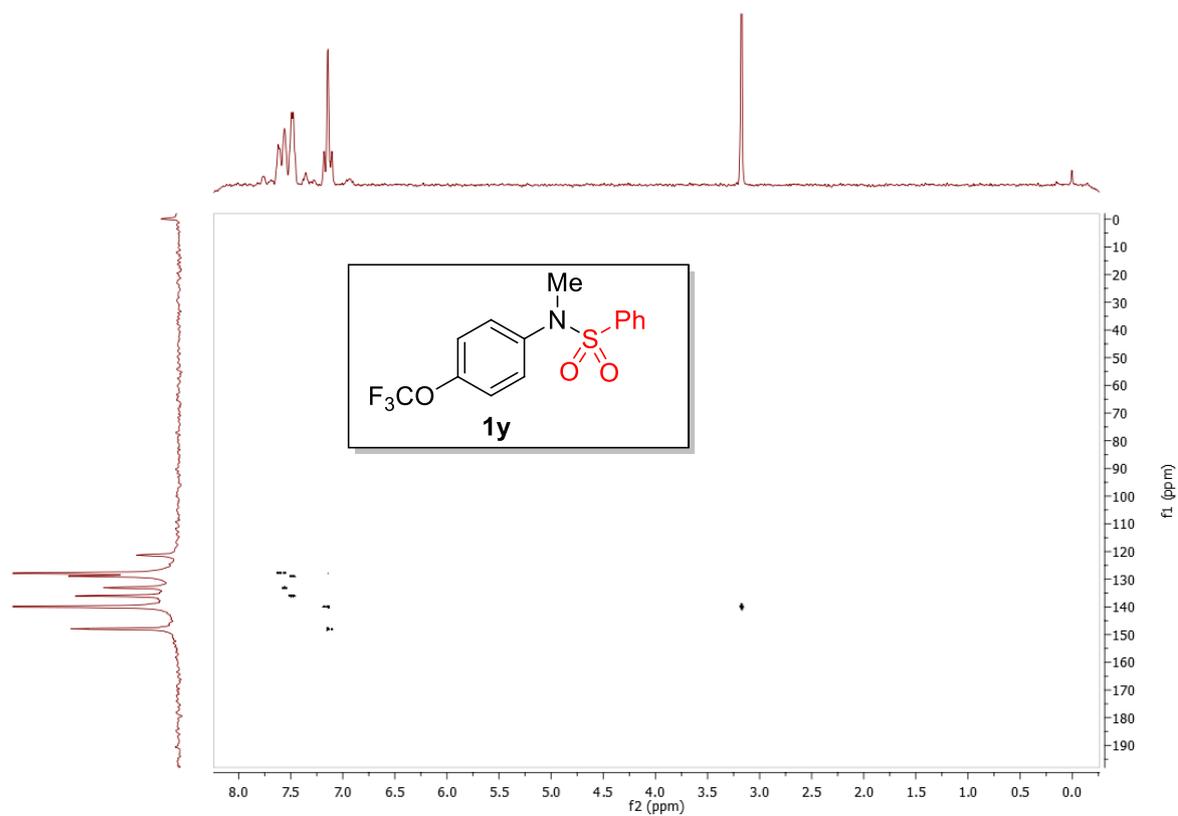
$^1\text{H}/^1\text{H}$ COSY NMR (400 MHz, CDCl_3). *N*-Methyl-*N*-(4-(trifluoromethoxy)phenyl)benzenesulfonamide (**1y**).



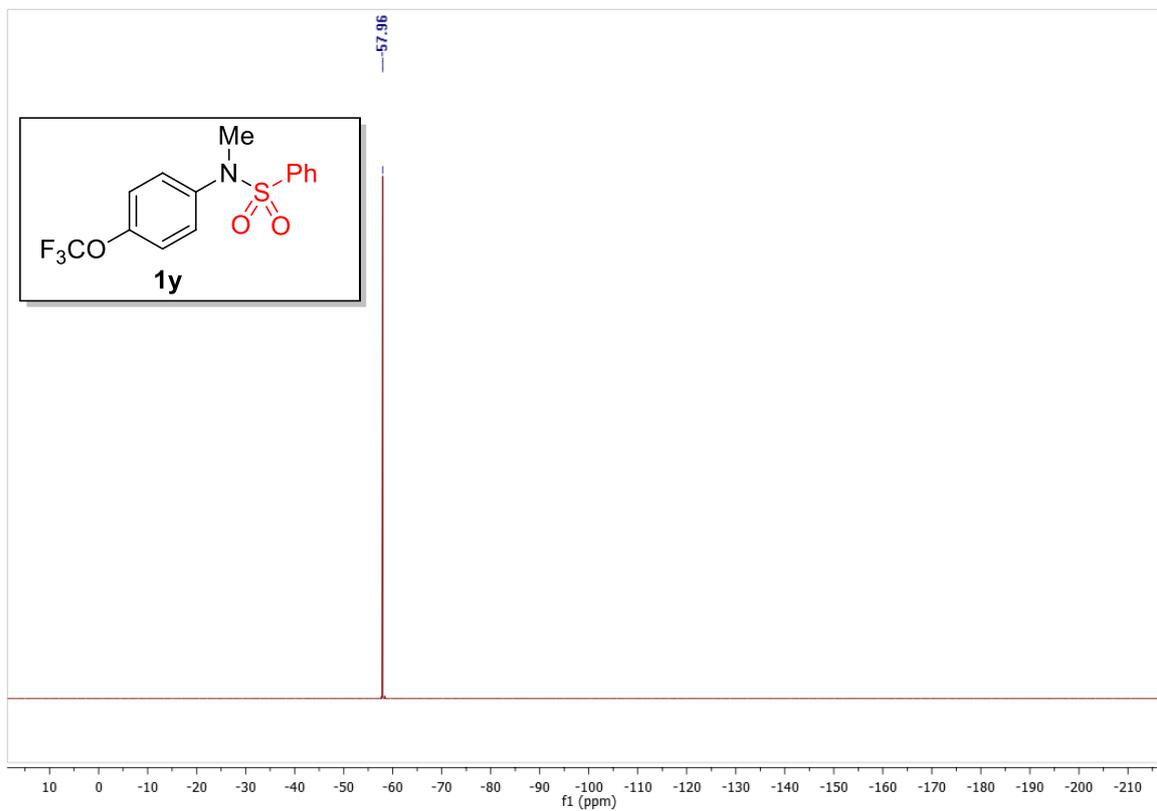
$^1\text{H}/^{13}\text{C}$ HSQC NMR (400 MHz, CDCl_3). *N*-Methyl-*N*-(4-(trifluoromethoxy)phenyl)benzenesulfonamide (**1y**).



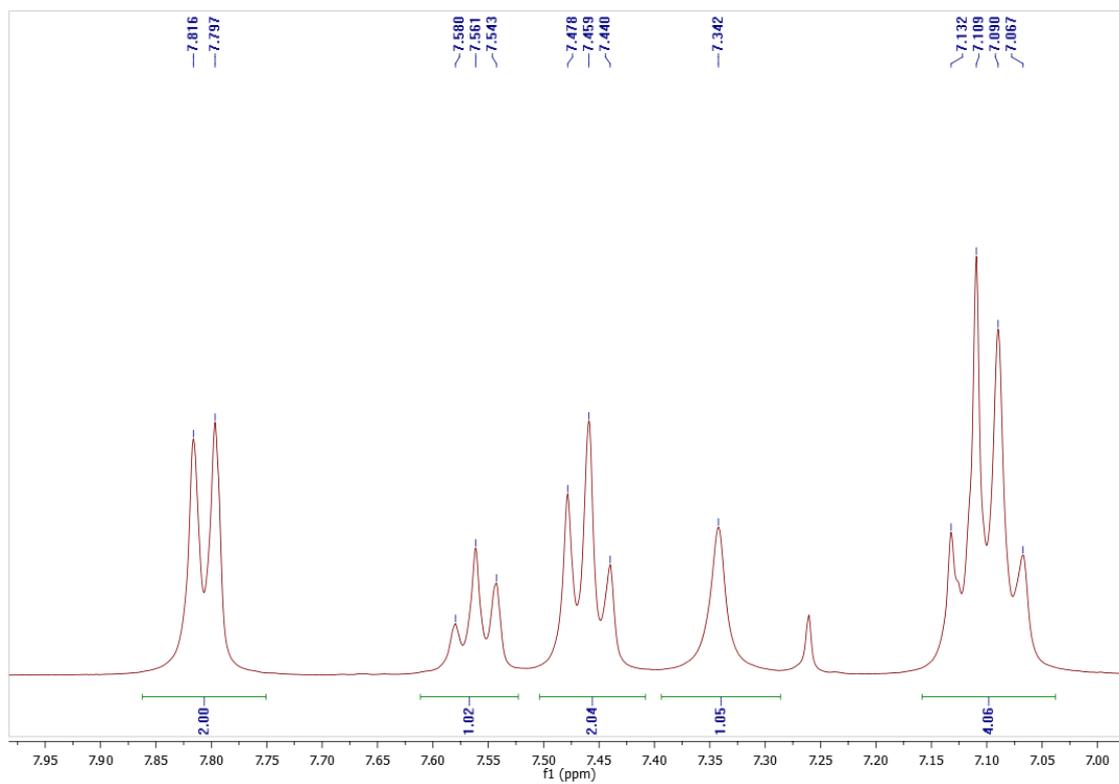
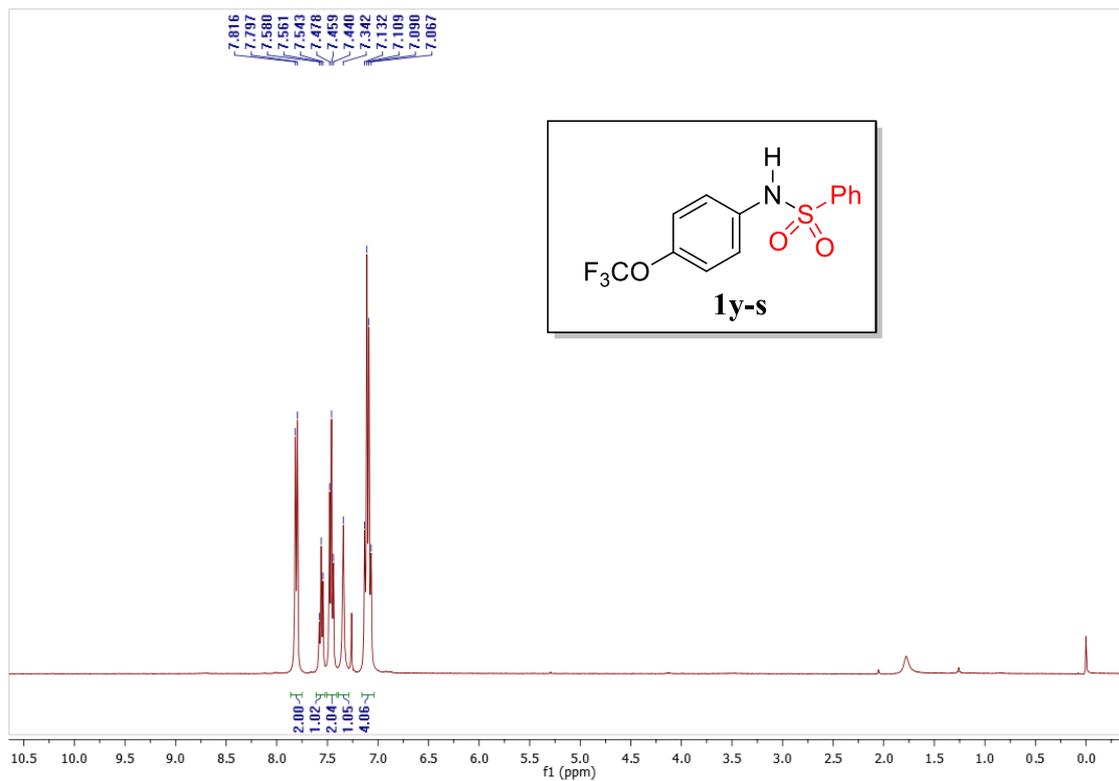
$^1\text{H}/^{13}\text{C}$ HMBC NMR (400 MHz, CDCl_3). *N*-Methyl-*N*-(4-(trifluoromethoxy)phenyl)benzenesulfonamide (**1y**).



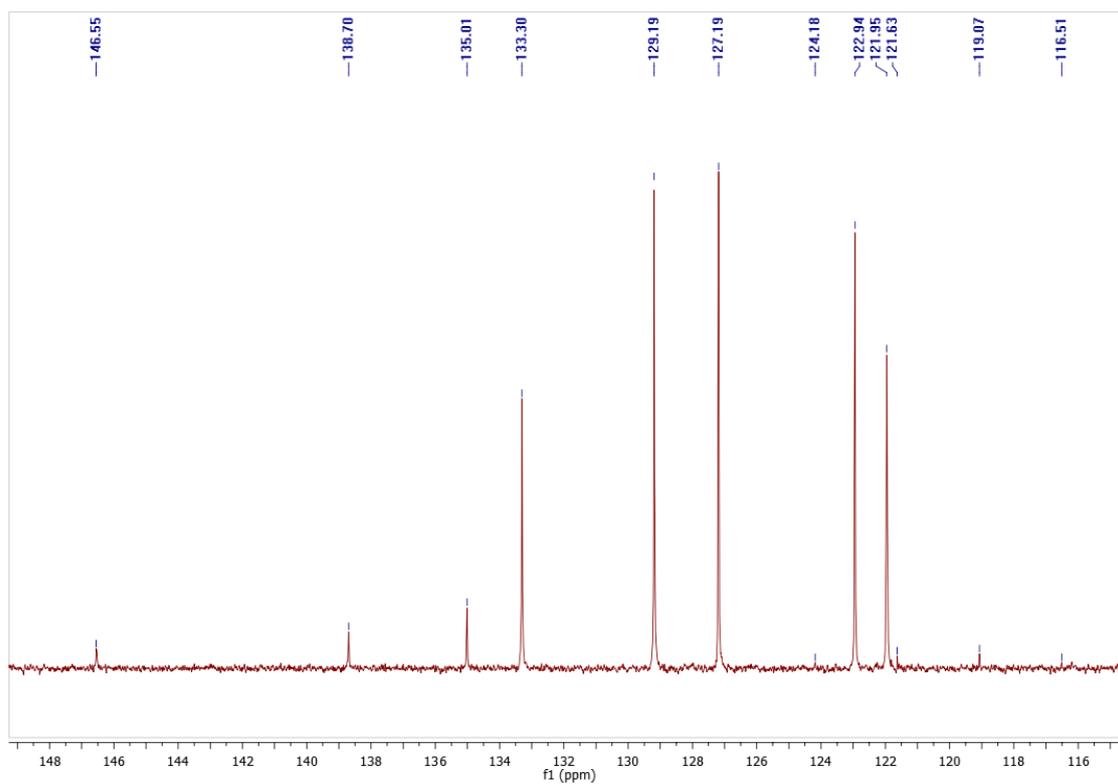
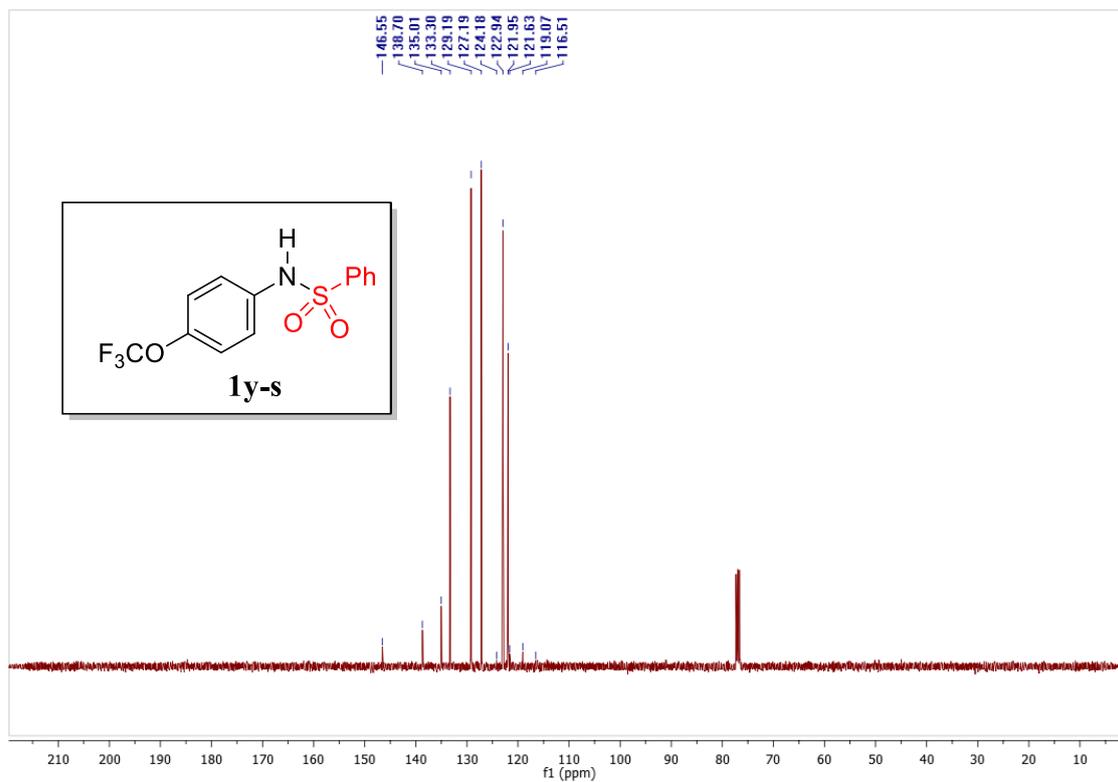
^{19}F -NMR (377 MHz, CDCl_3). *N*-Methyl-*N*-(4-(trifluoromethoxy)phenyl)benzene sulfonamide (**1y**).



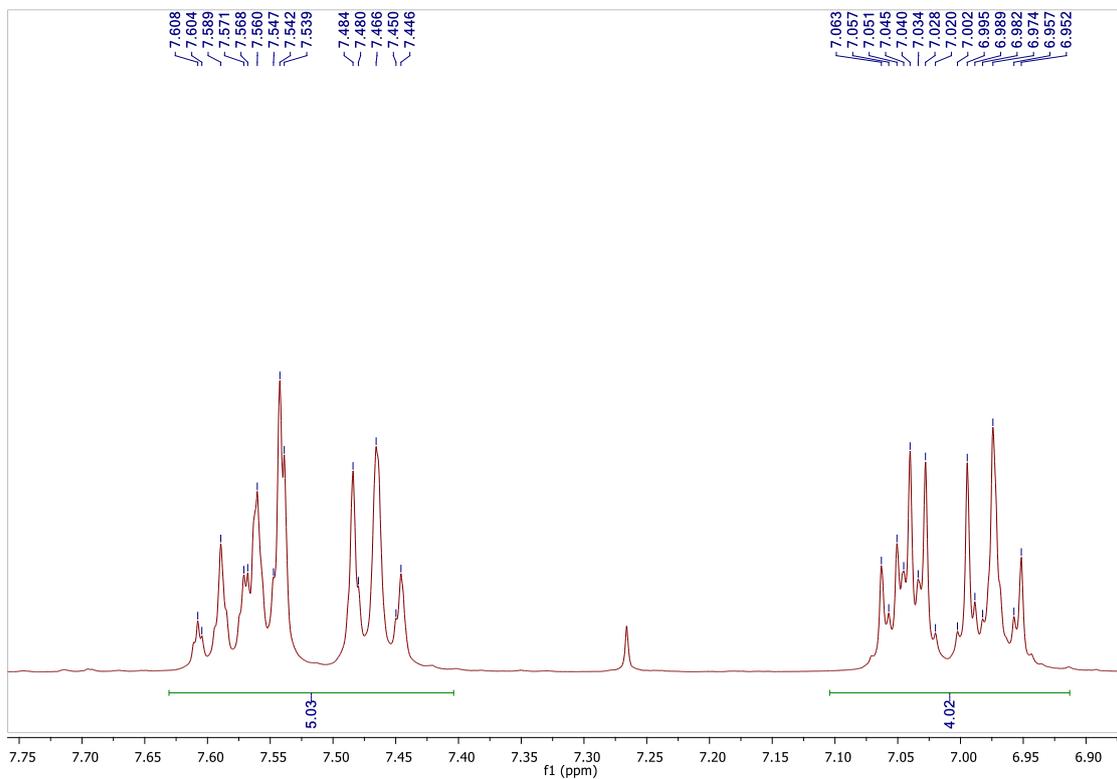
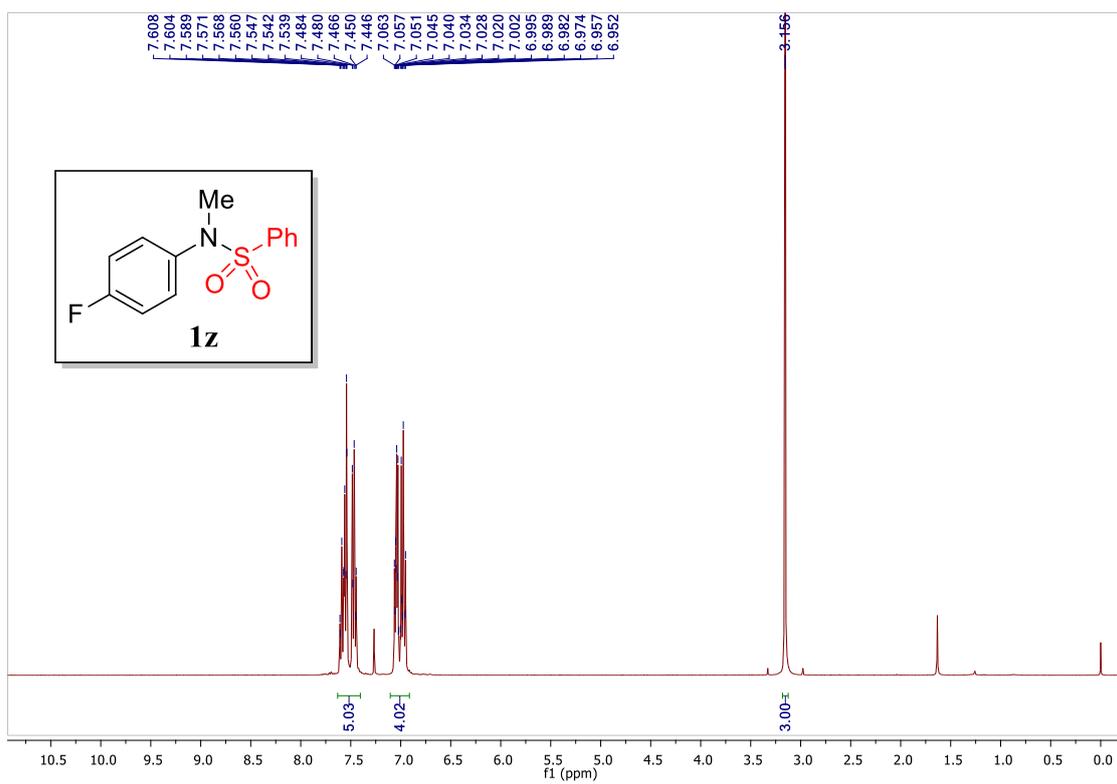
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-(Trifluoromethoxy)phenyl)benzenesulfonamide (**1y-s**).



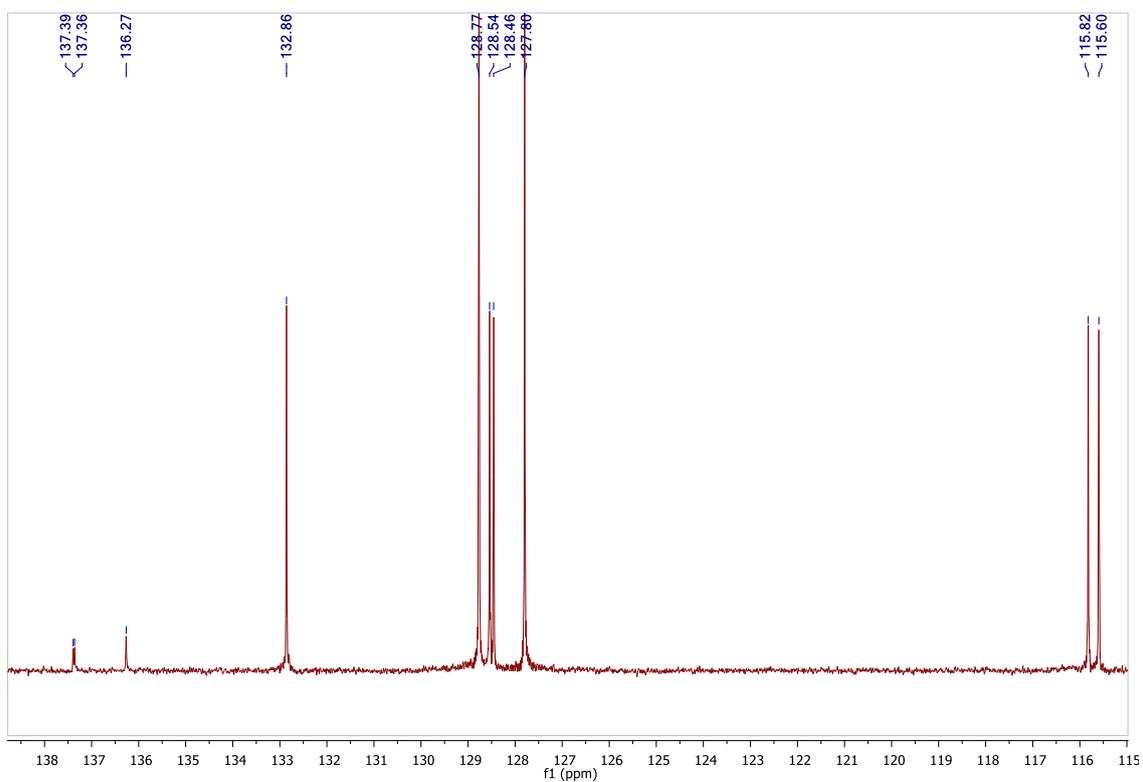
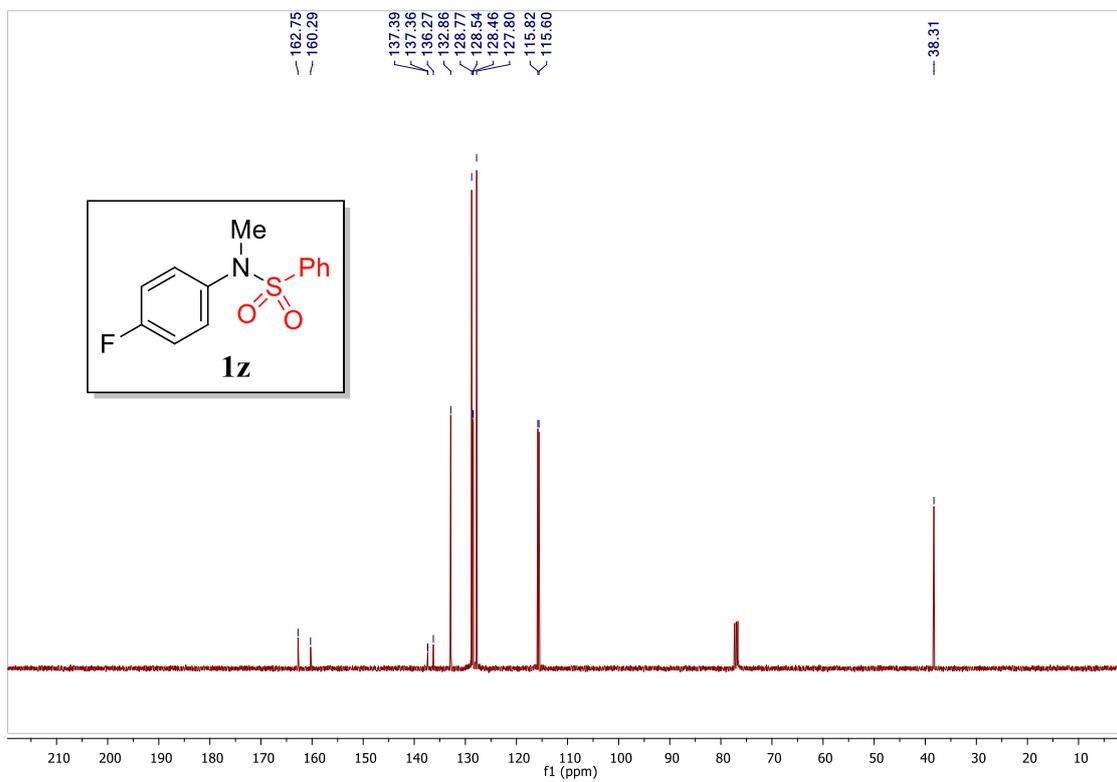
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-(Trifluoromethoxy)phenyl)benzene sulfonamide (**1y-s**).



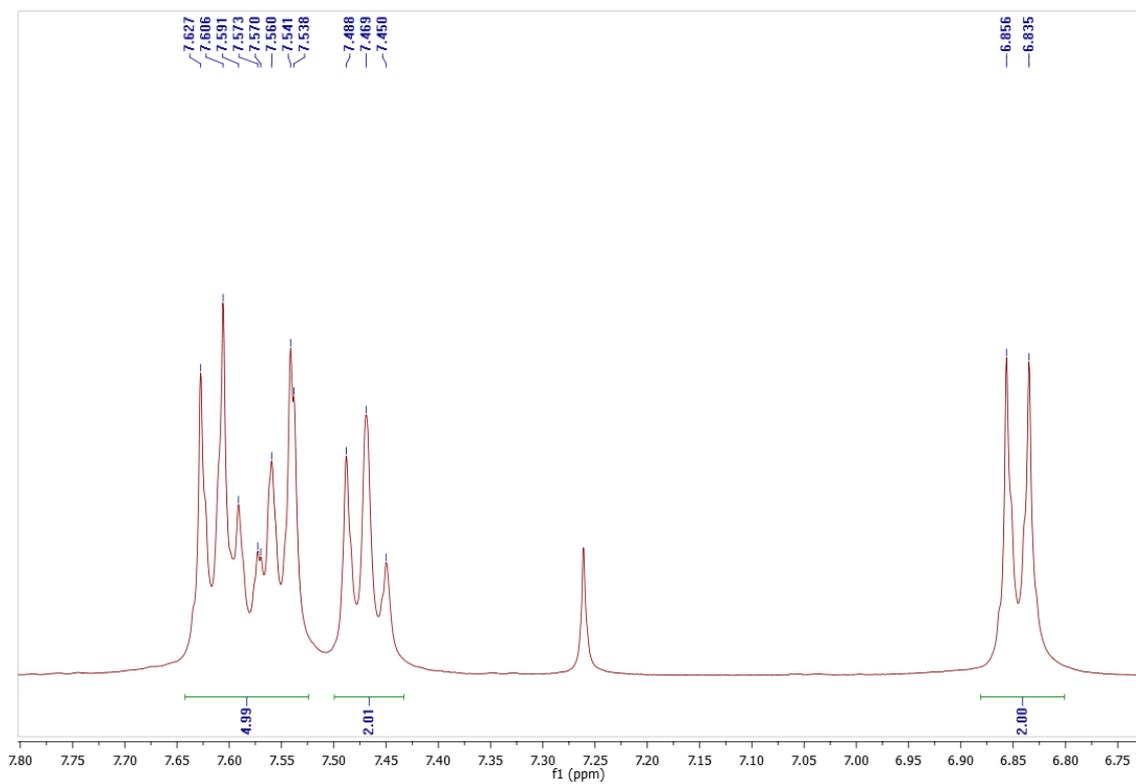
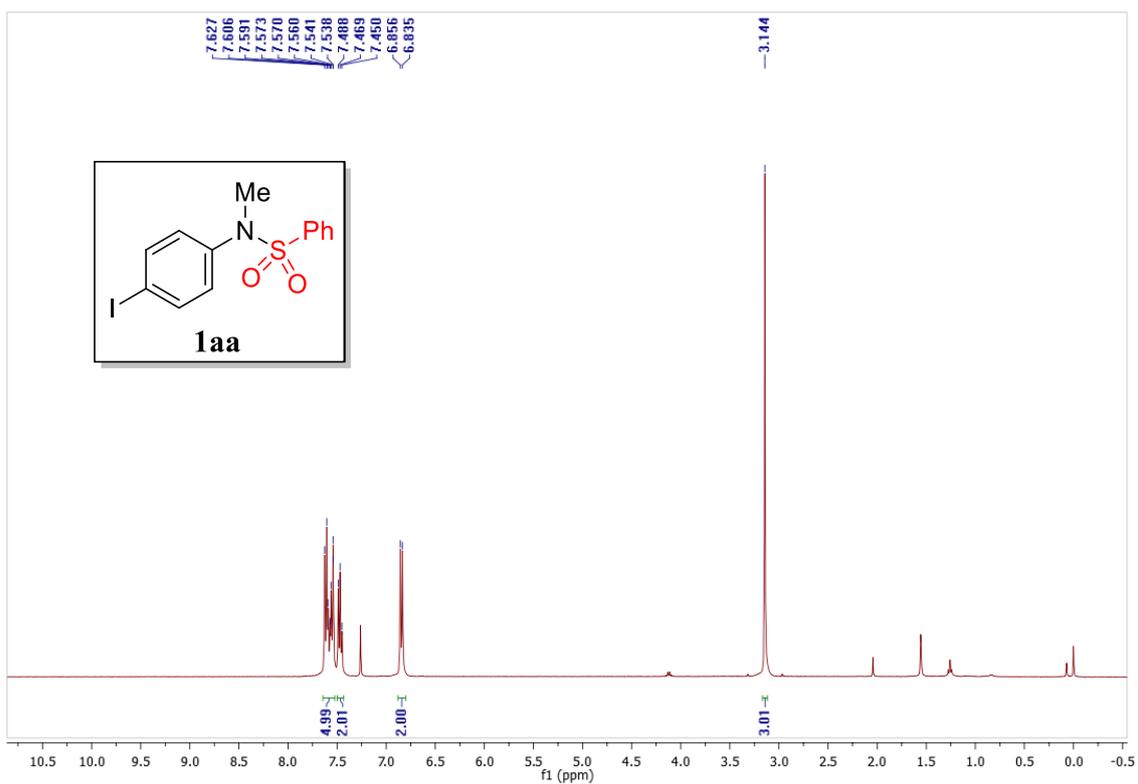
¹H-NMR (400 MHz, CDCl₃). *N*-(4-Fluorophenyl)-*N*-methylbenzenesulfonamide (**1z**).



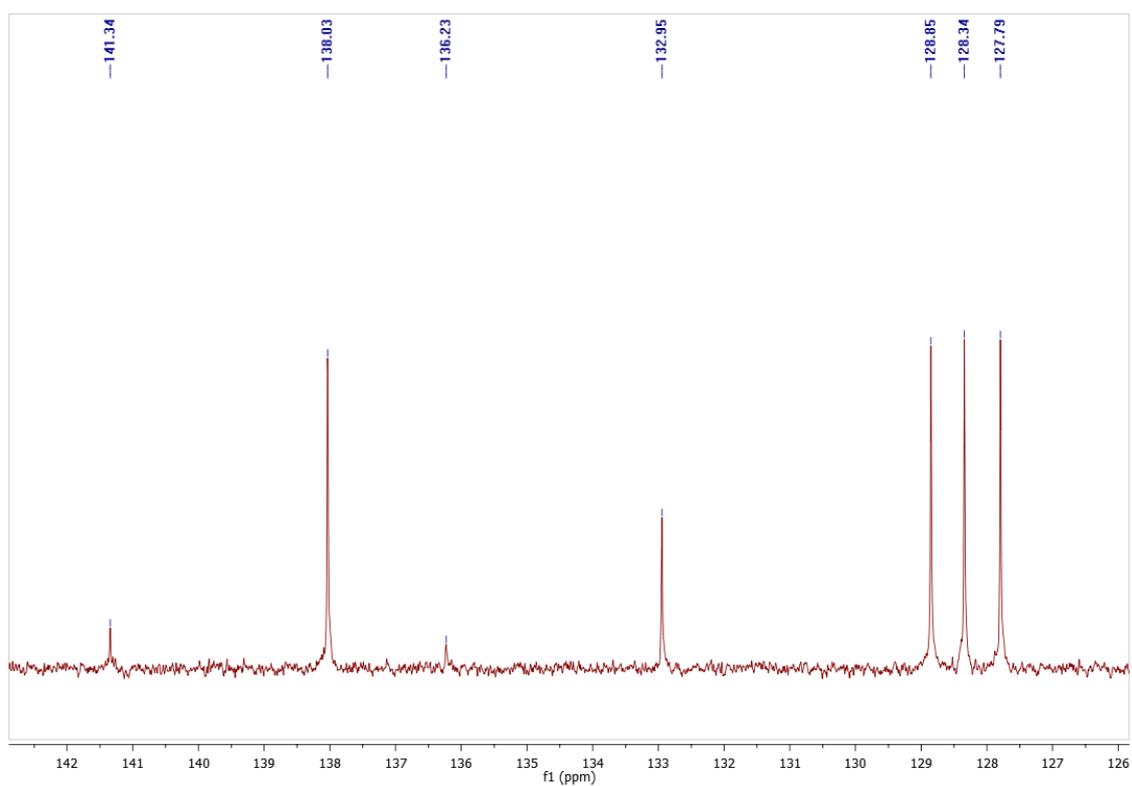
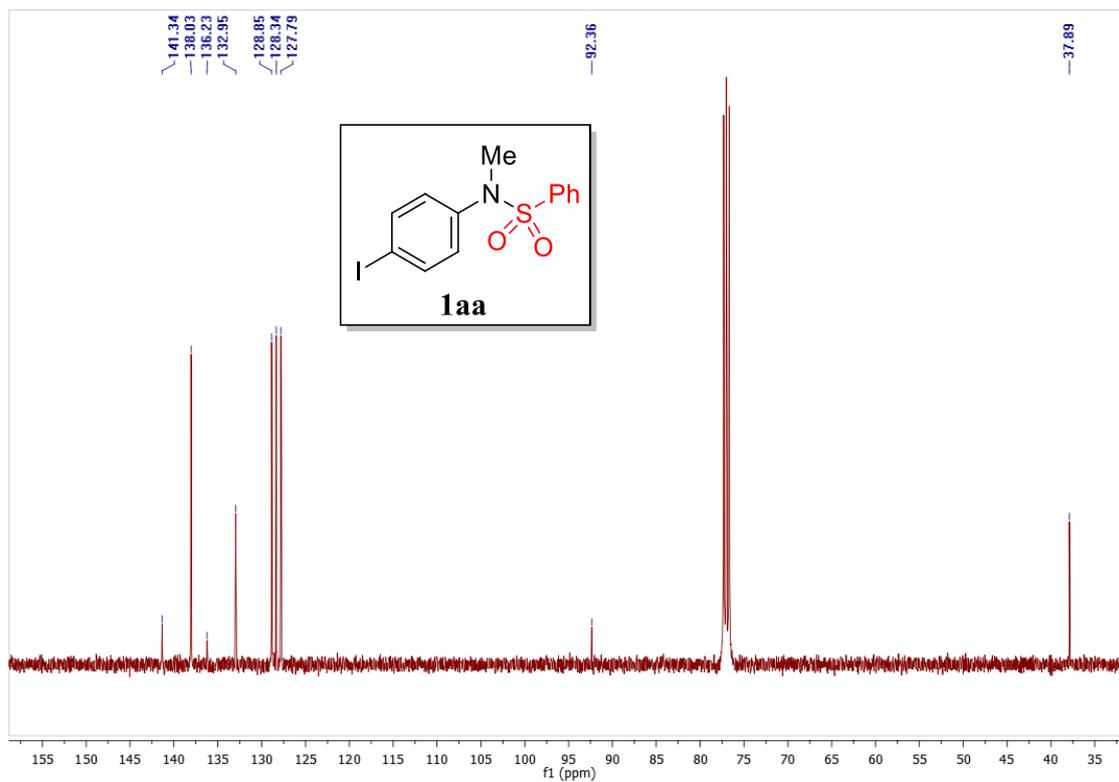
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Fluorophenyl)-*N*-methylbenzenesulfonamide (**1z**).



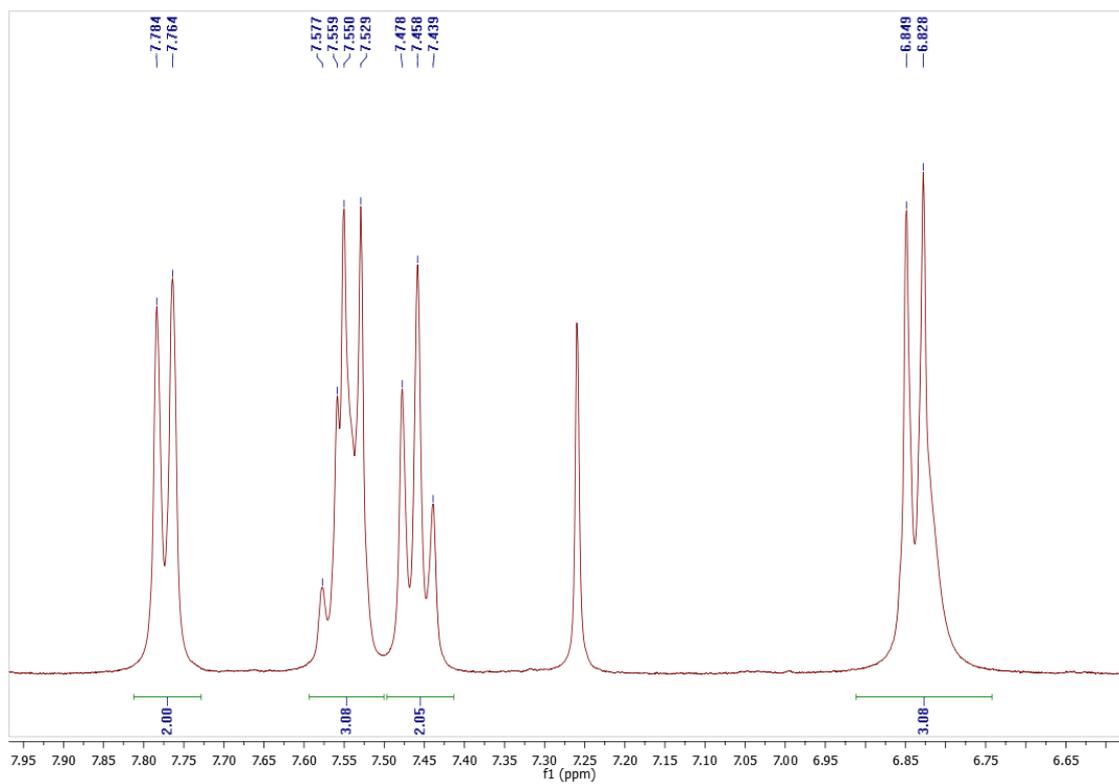
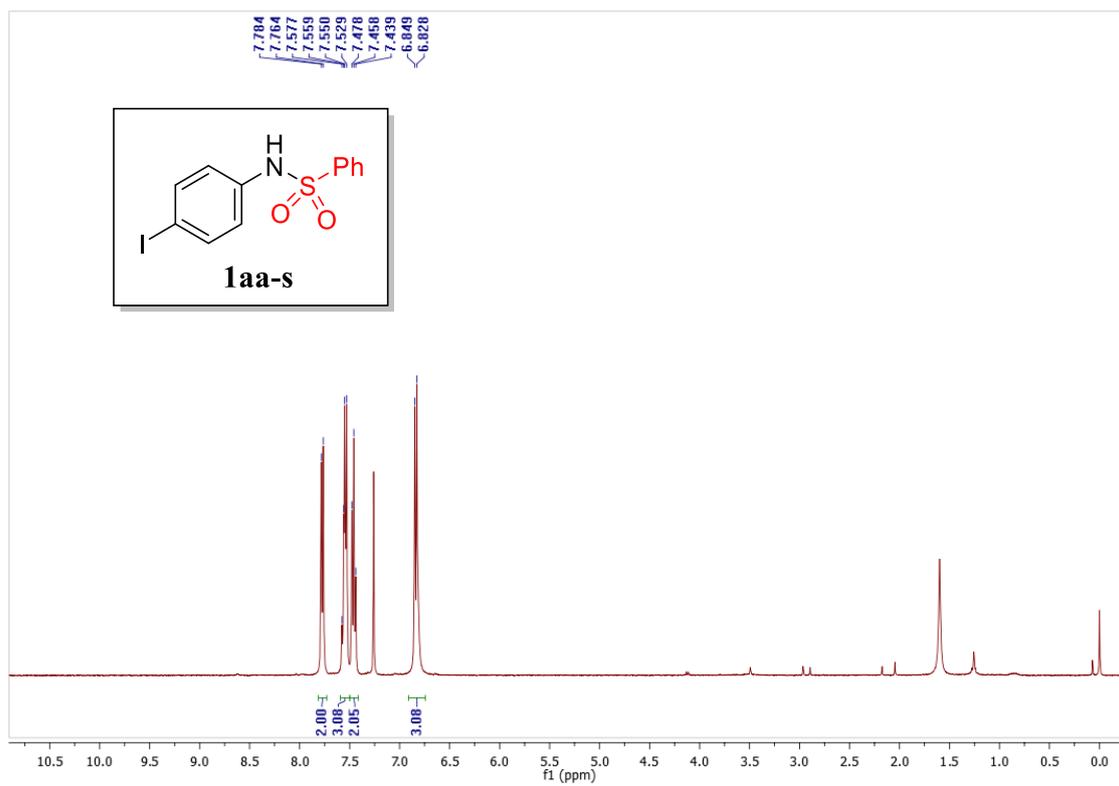
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Iodophenyl)-*N*-methylbenzenesulfonamide (**1aa**).



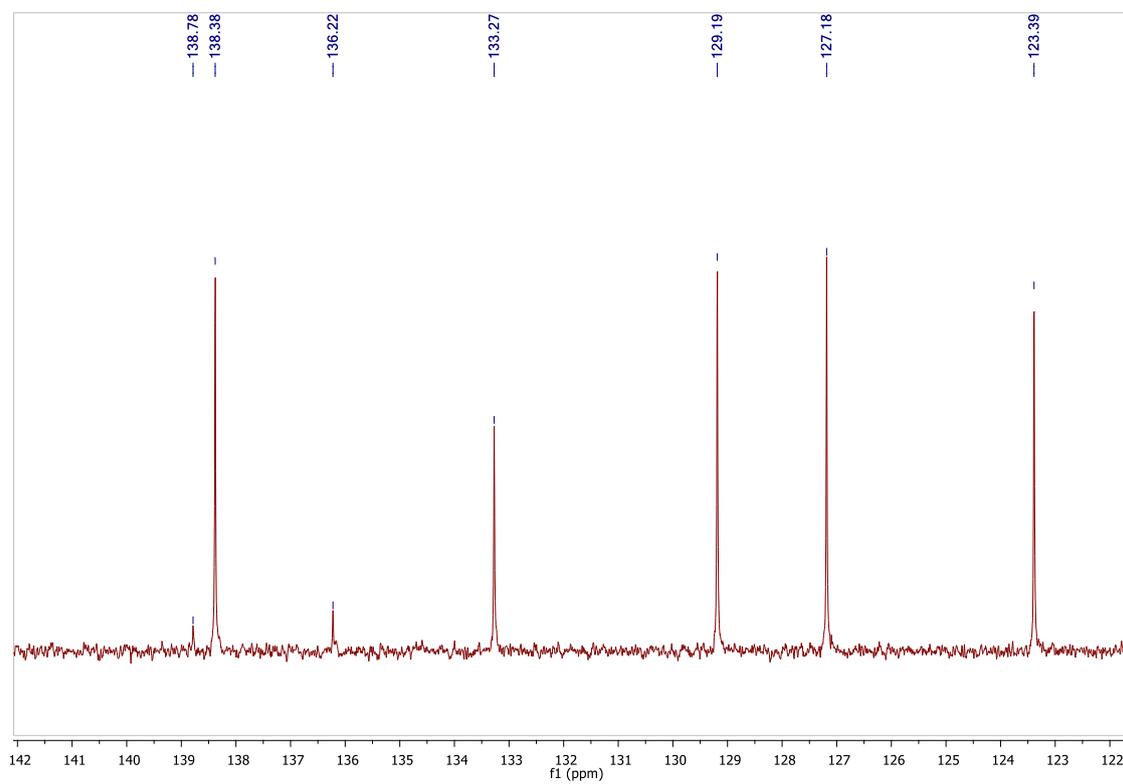
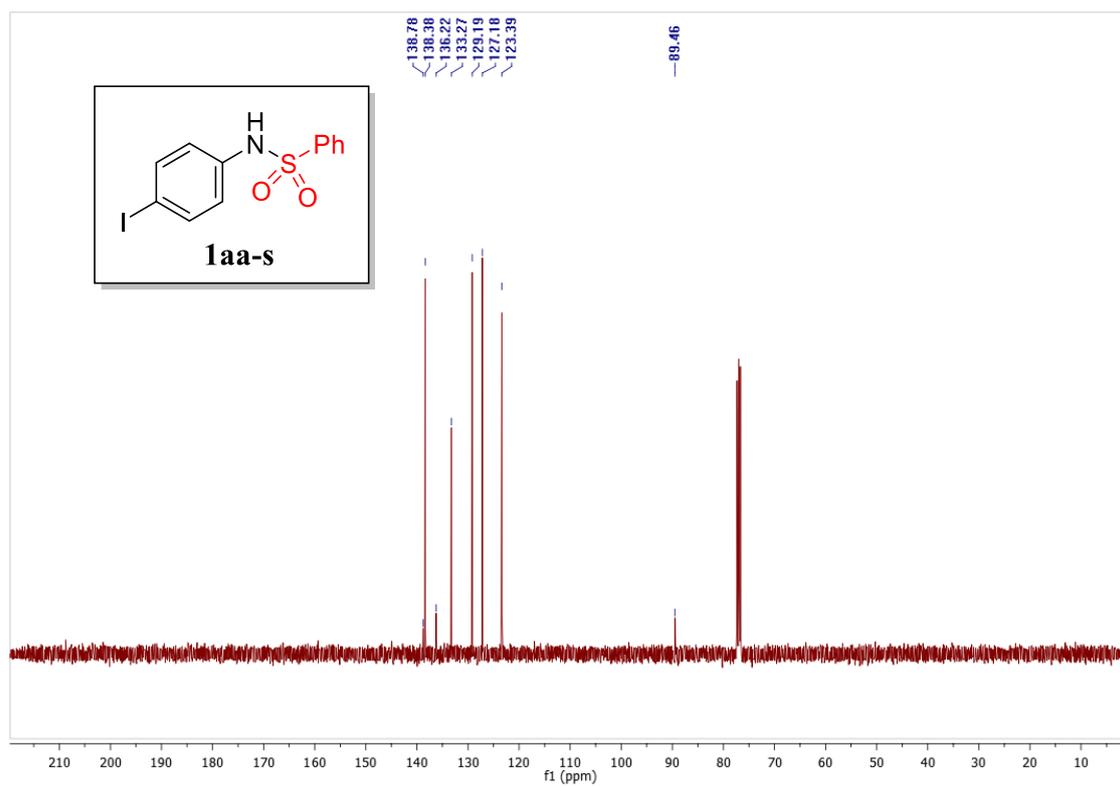
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Iodophenyl)-*N*-methylbenzenesulfonamide (**1aa**).



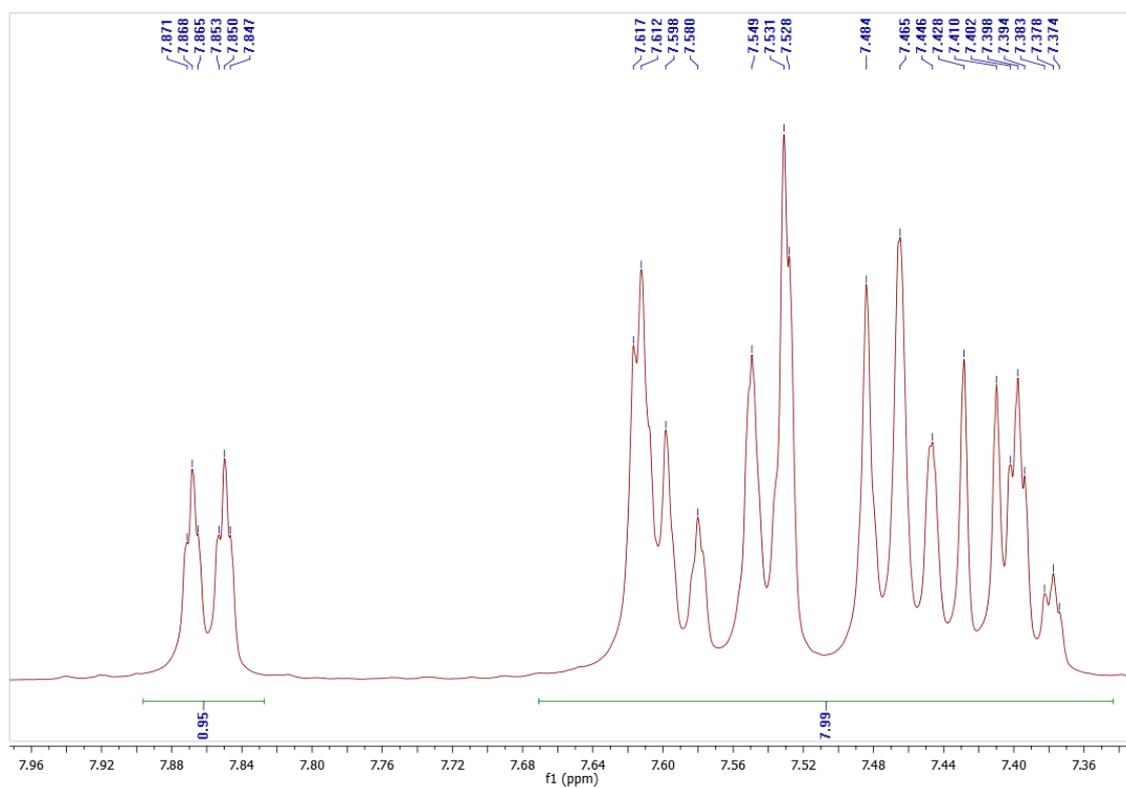
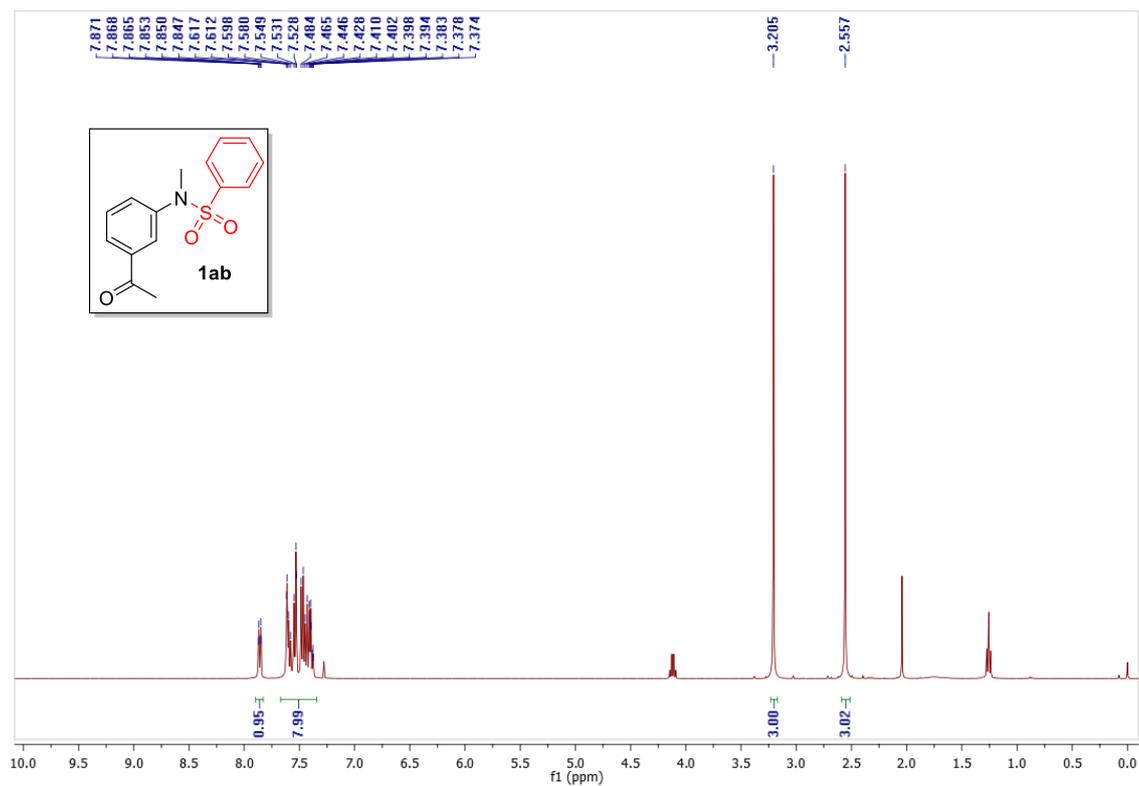
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Iodophenyl)benzenesulfonamide (**1aa-s**).



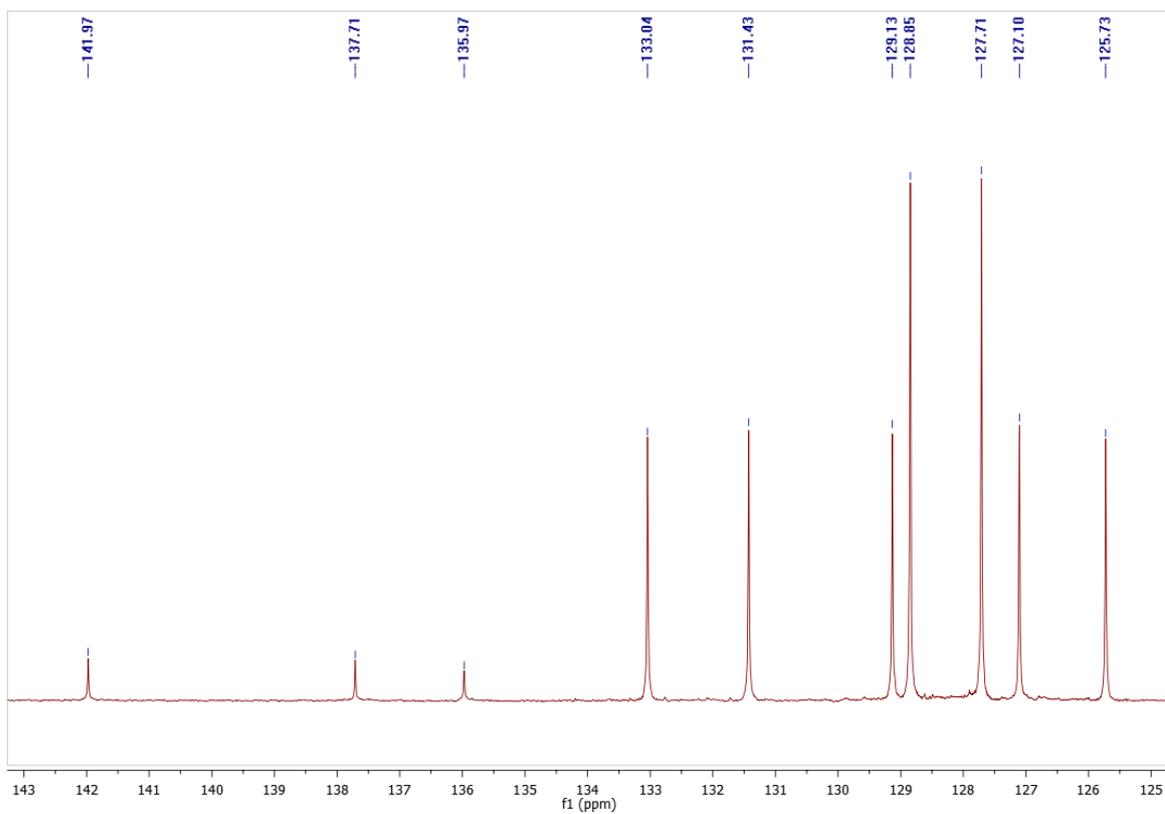
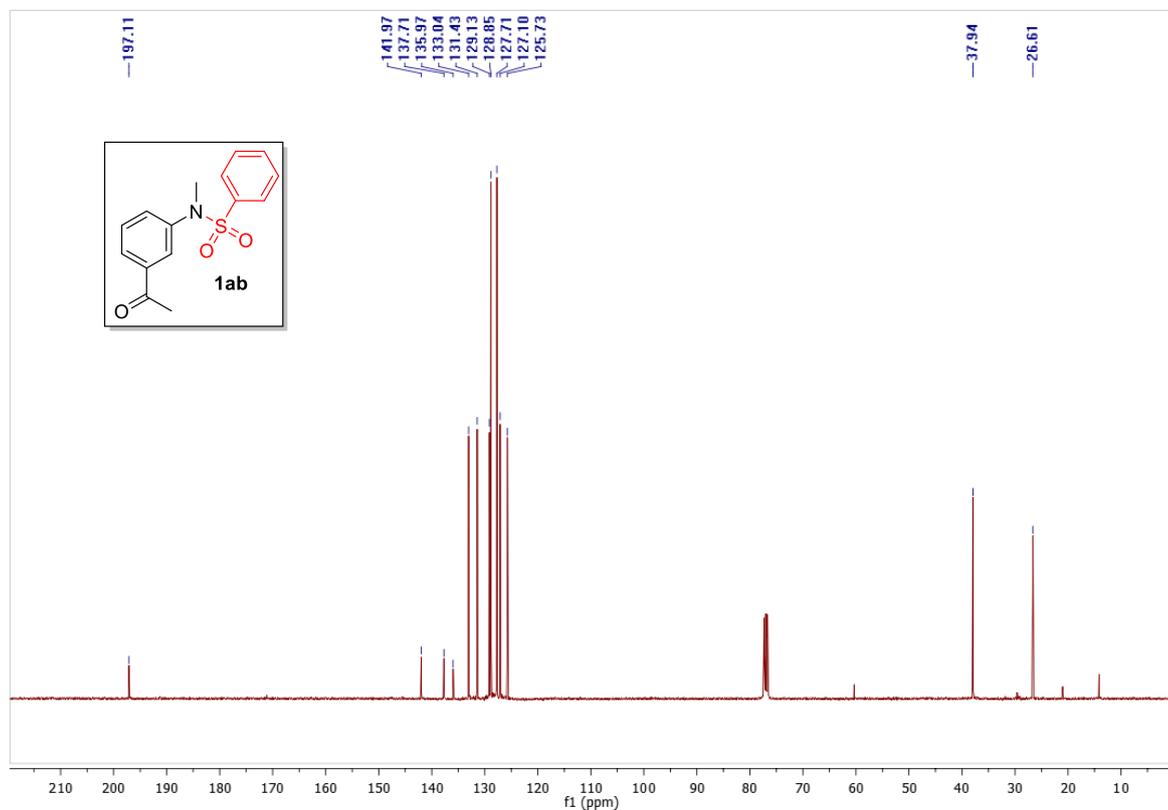
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Iodophenyl)benzenesulfonamide (**1aa-s**).



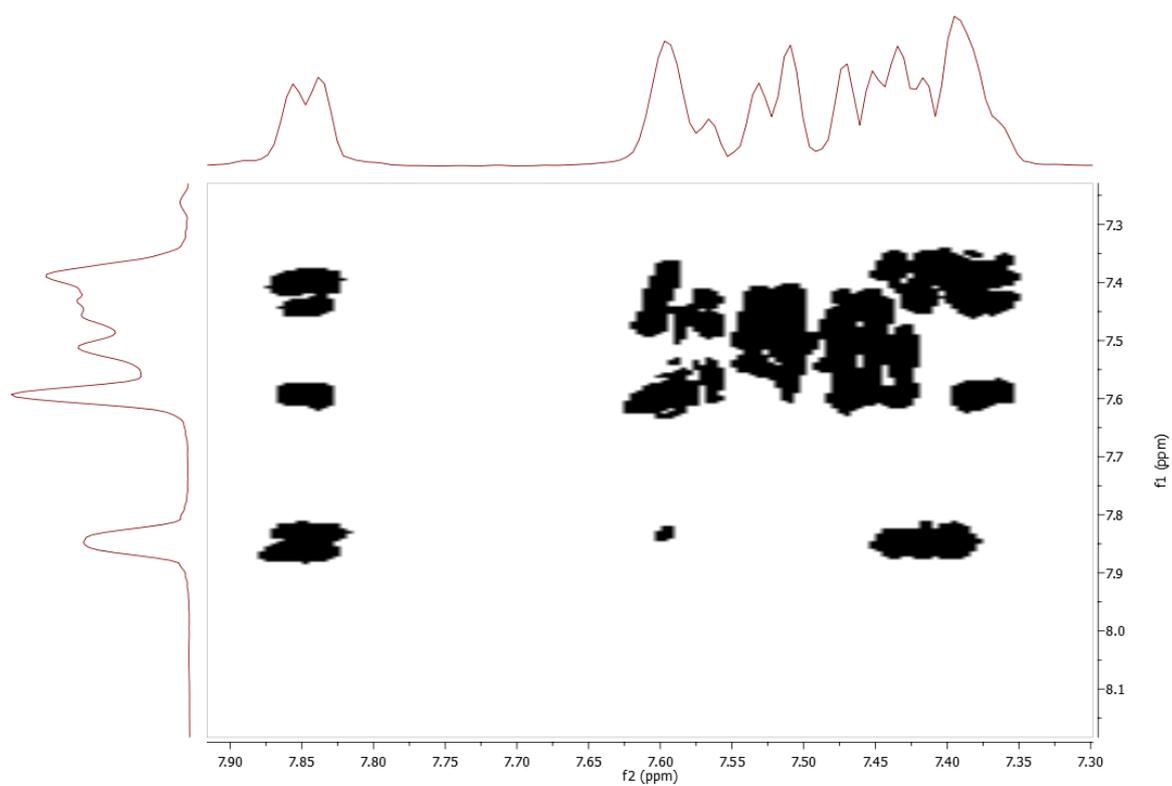
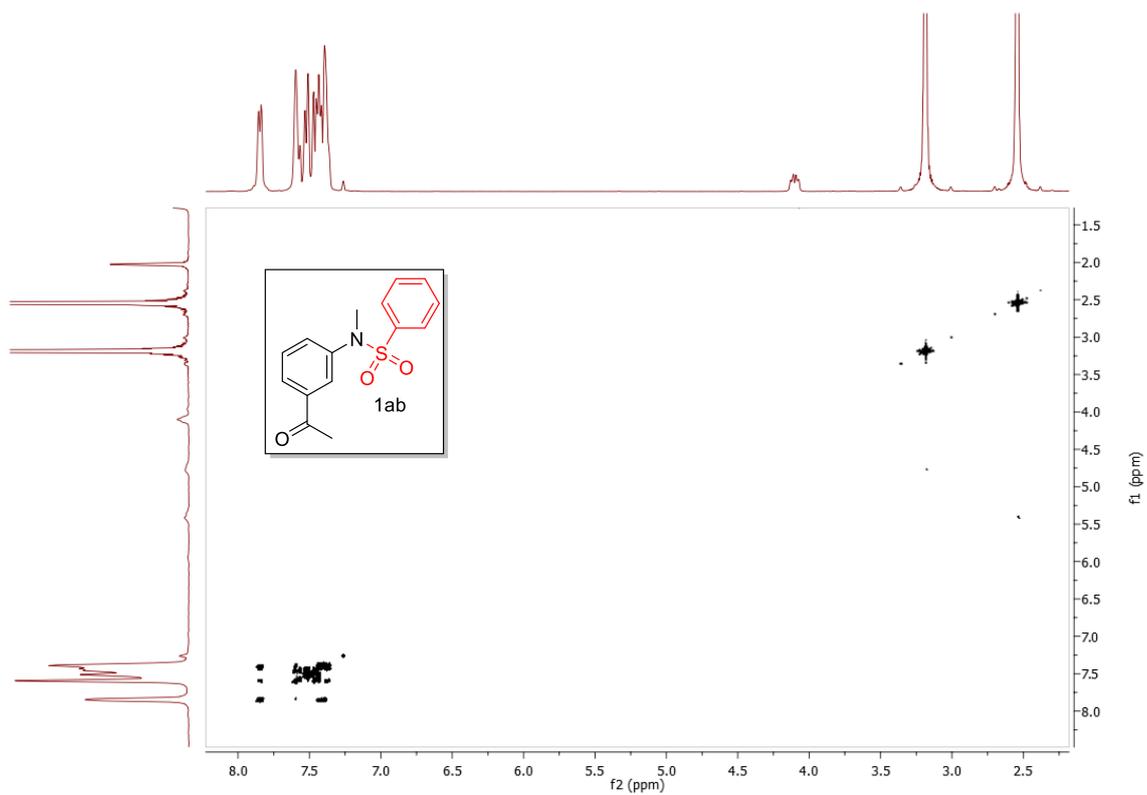
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(3-acetylphenyl)-*N*-methylbenzene sulfonamide (**1ab**).



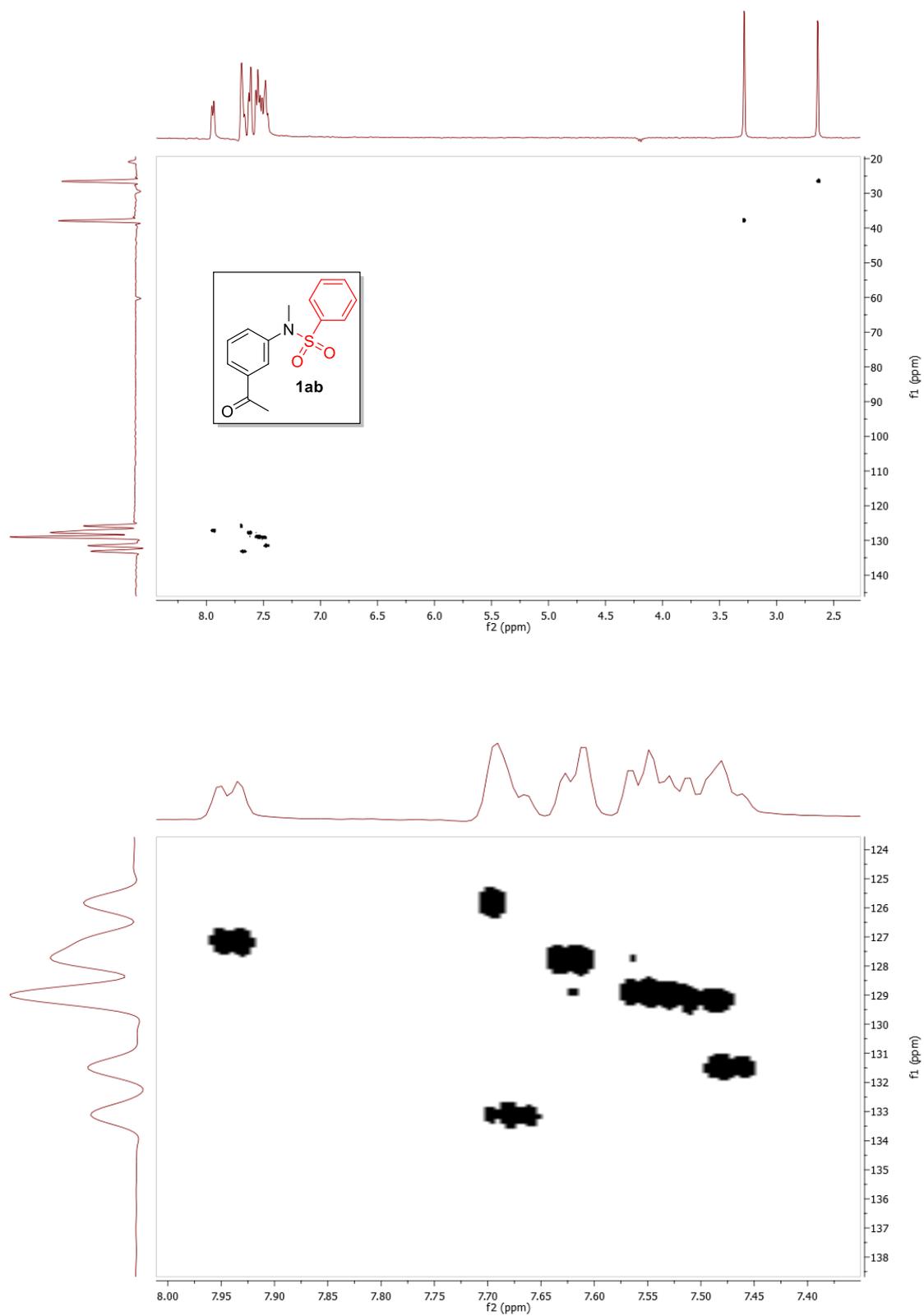
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(3-acetylphenyl)-*N*-methylbenzene sulfonamide (**1ab**).



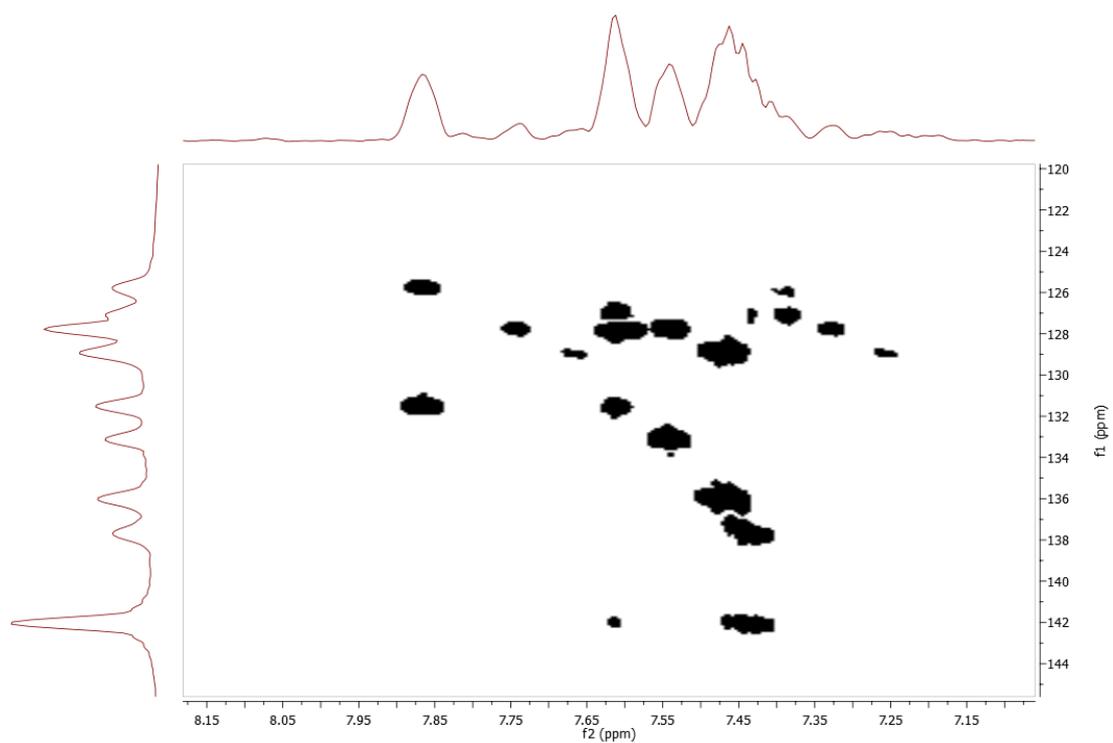
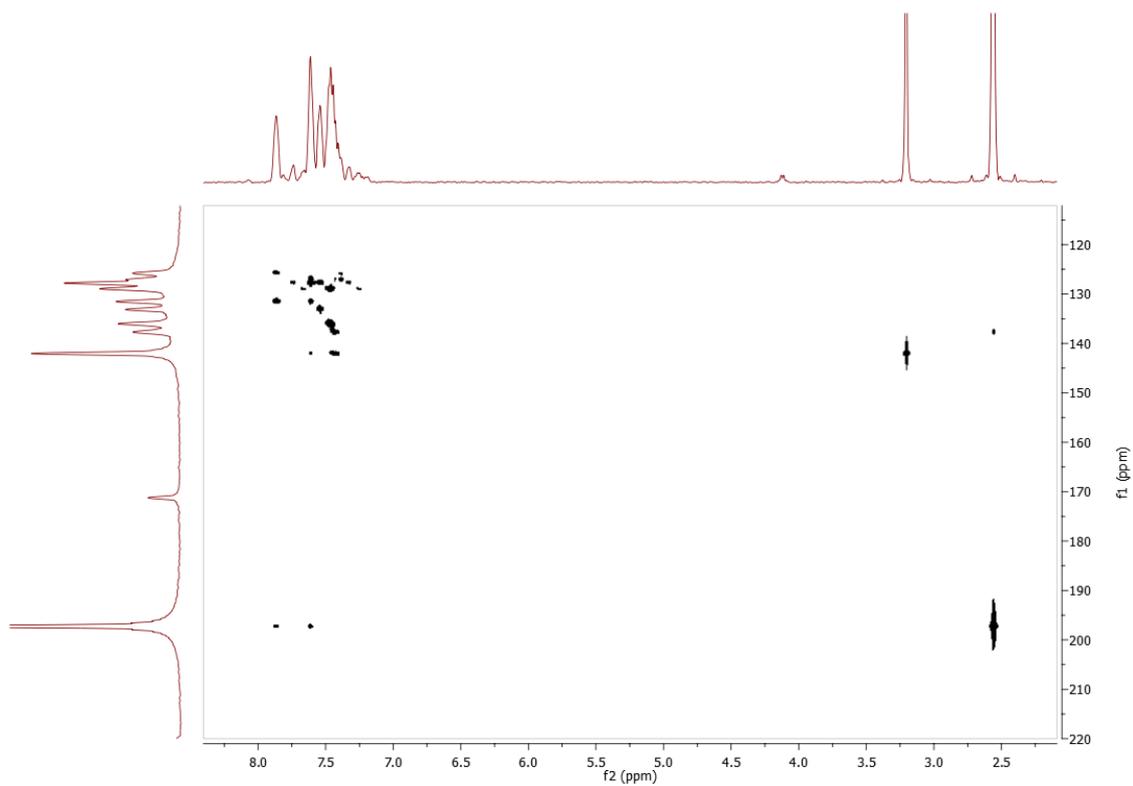
$^1\text{H}/^1\text{H}$ COSY NMR (400 MHz, CDCl_3). *N*-(3-acetylphenyl)-*N*-methylbenzene sulfonamide (**1ab**).



$^1\text{H}/^{13}\text{C}$ HSQC NMR (400 MHz, CDCl_3). *N*-(3-acetylphenyl)-*N*-methylbenzene sulfonamide (**1ab**).

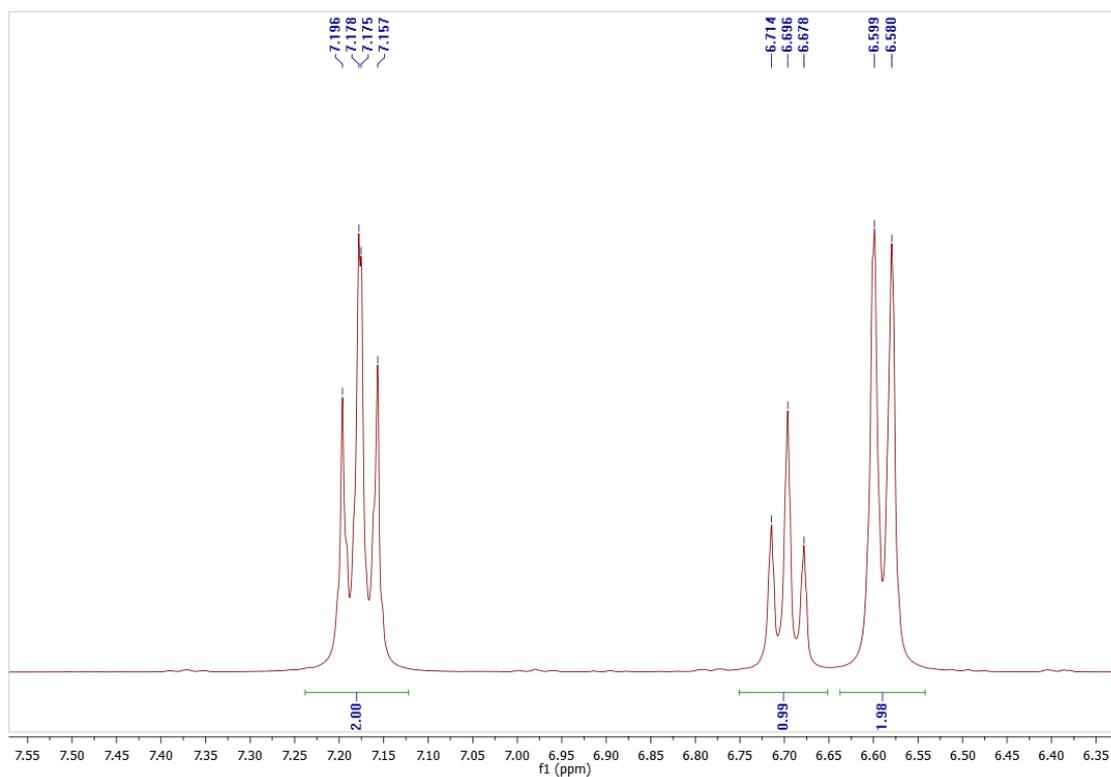
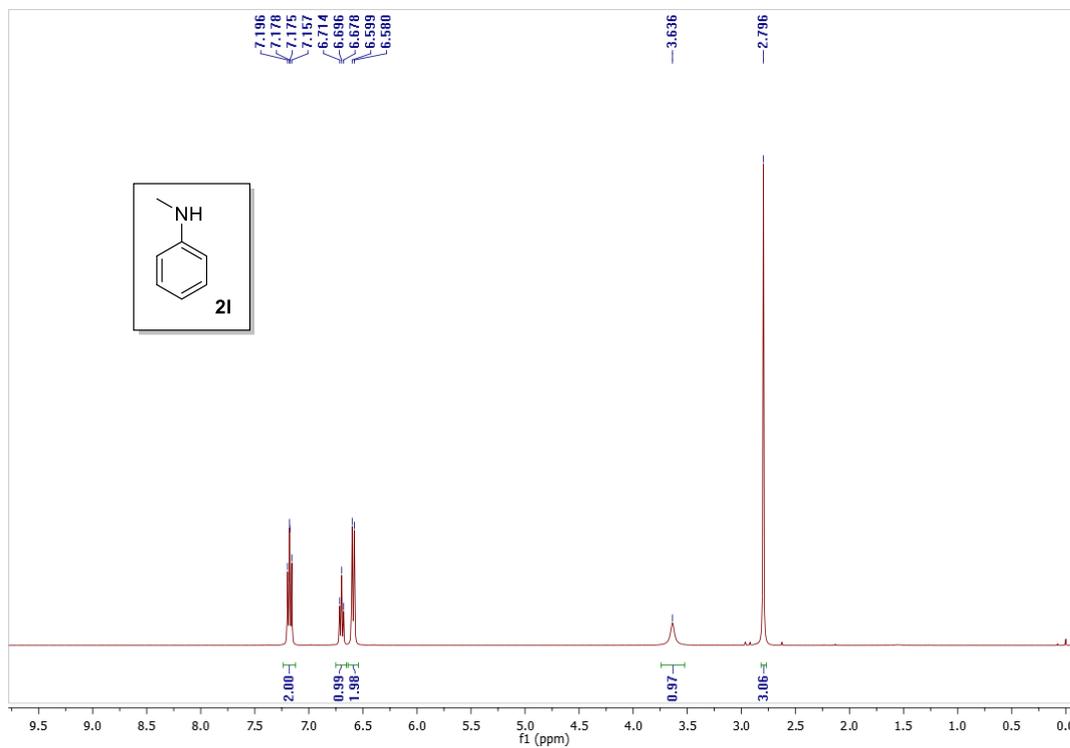


$^1\text{H}/^{13}\text{C}$ HMBC NMR (400 MHz, CDCl_3). *N*-(3-acetylphenyl)-*N*-methylbenzene sulfonamide (**1ab**).

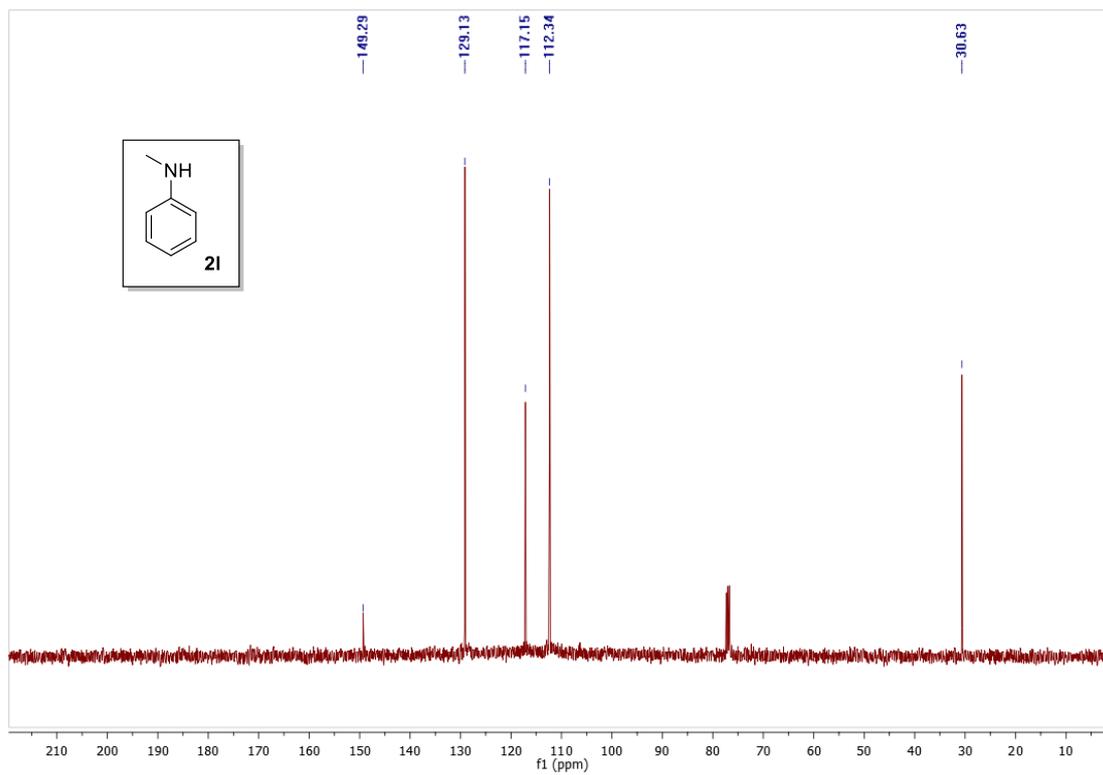


4. NMR spectra of products 2

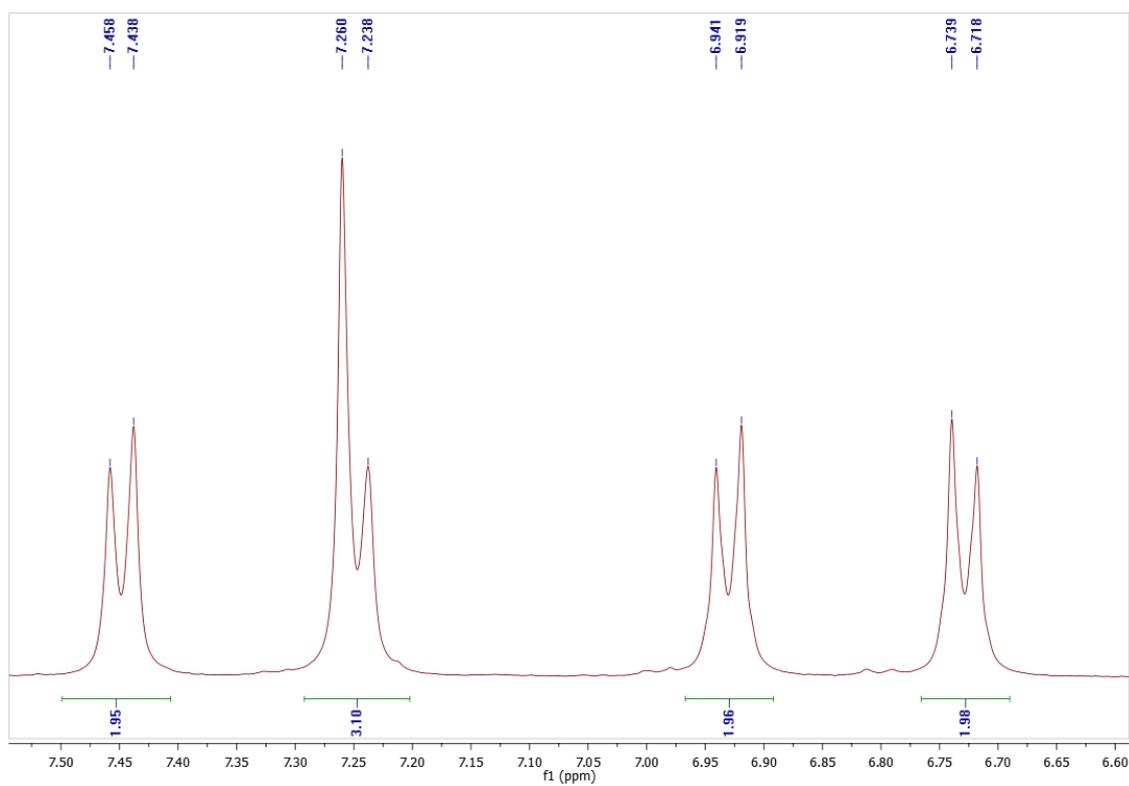
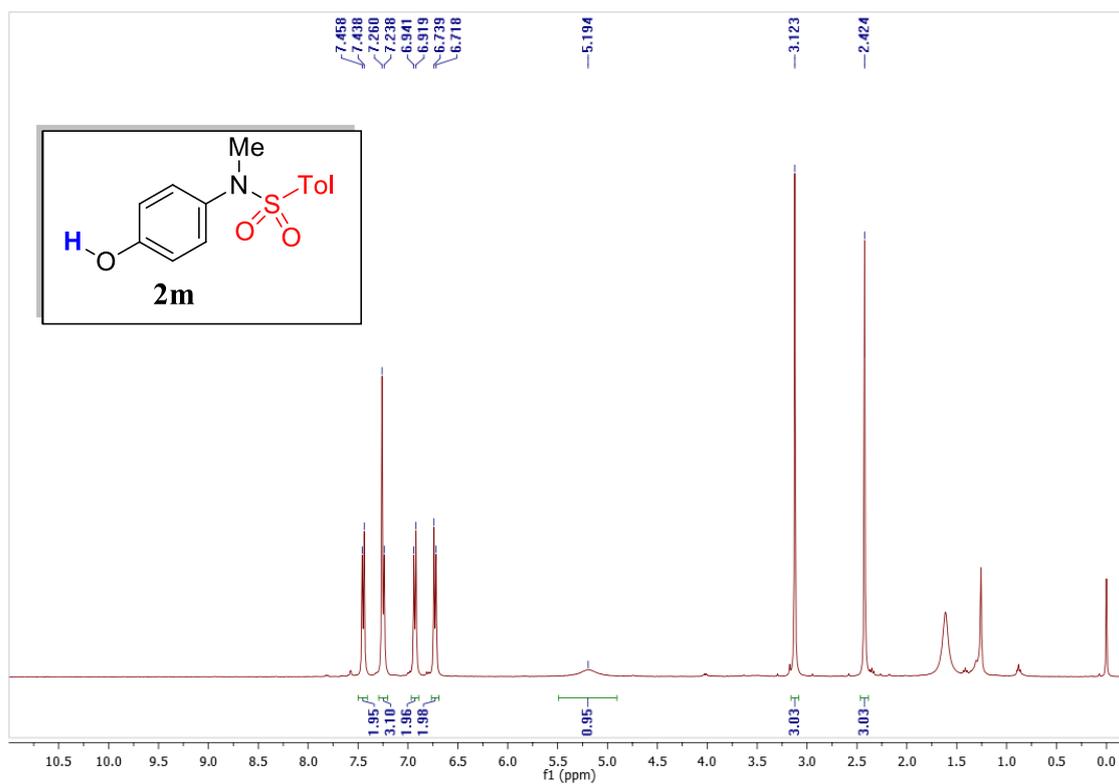
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-Methylaniline (**2I**).



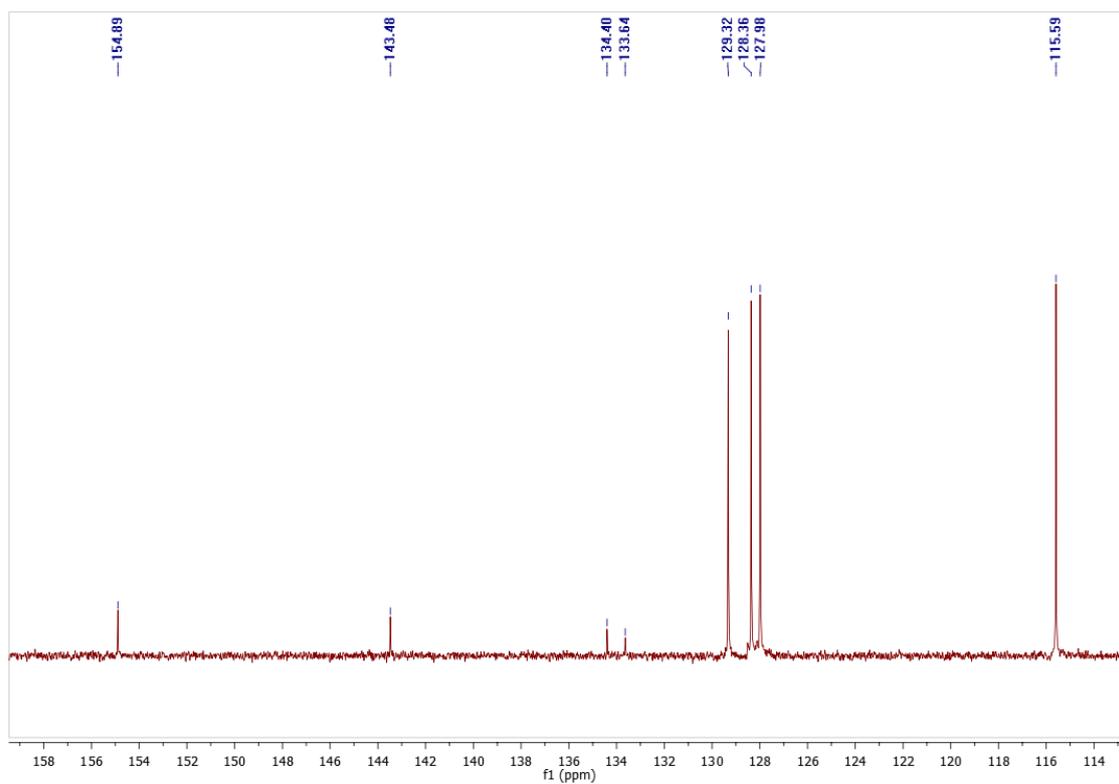
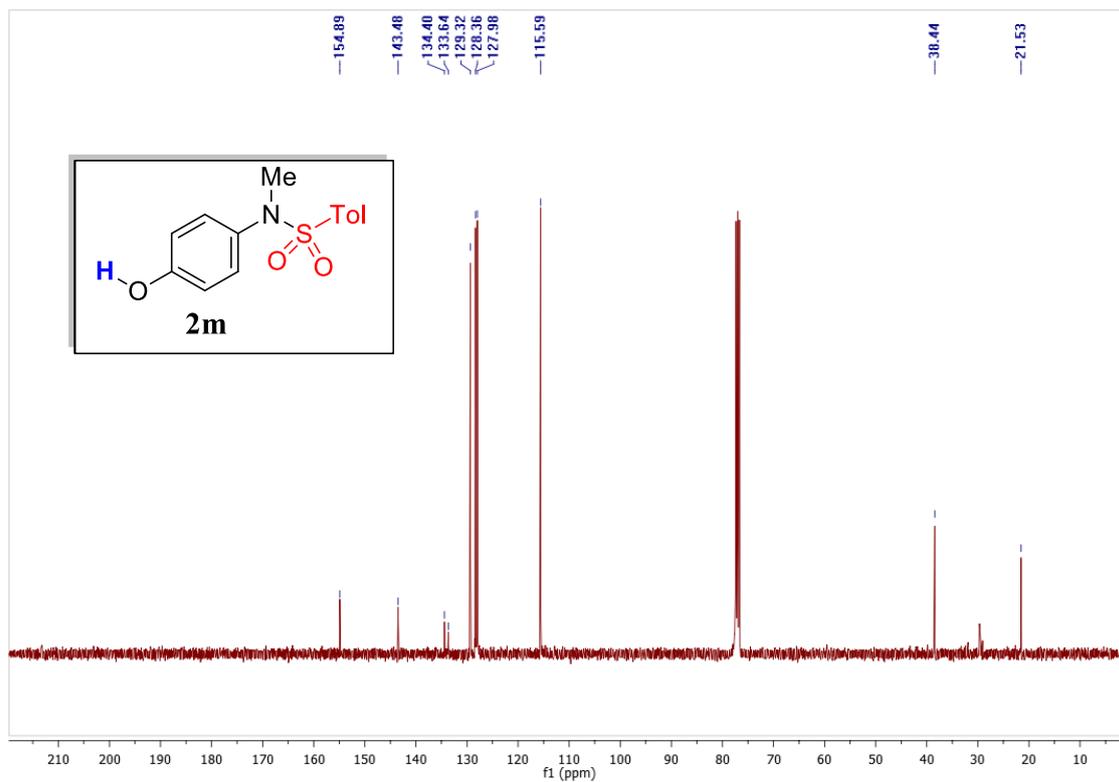
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-Methylaniline (**21**).



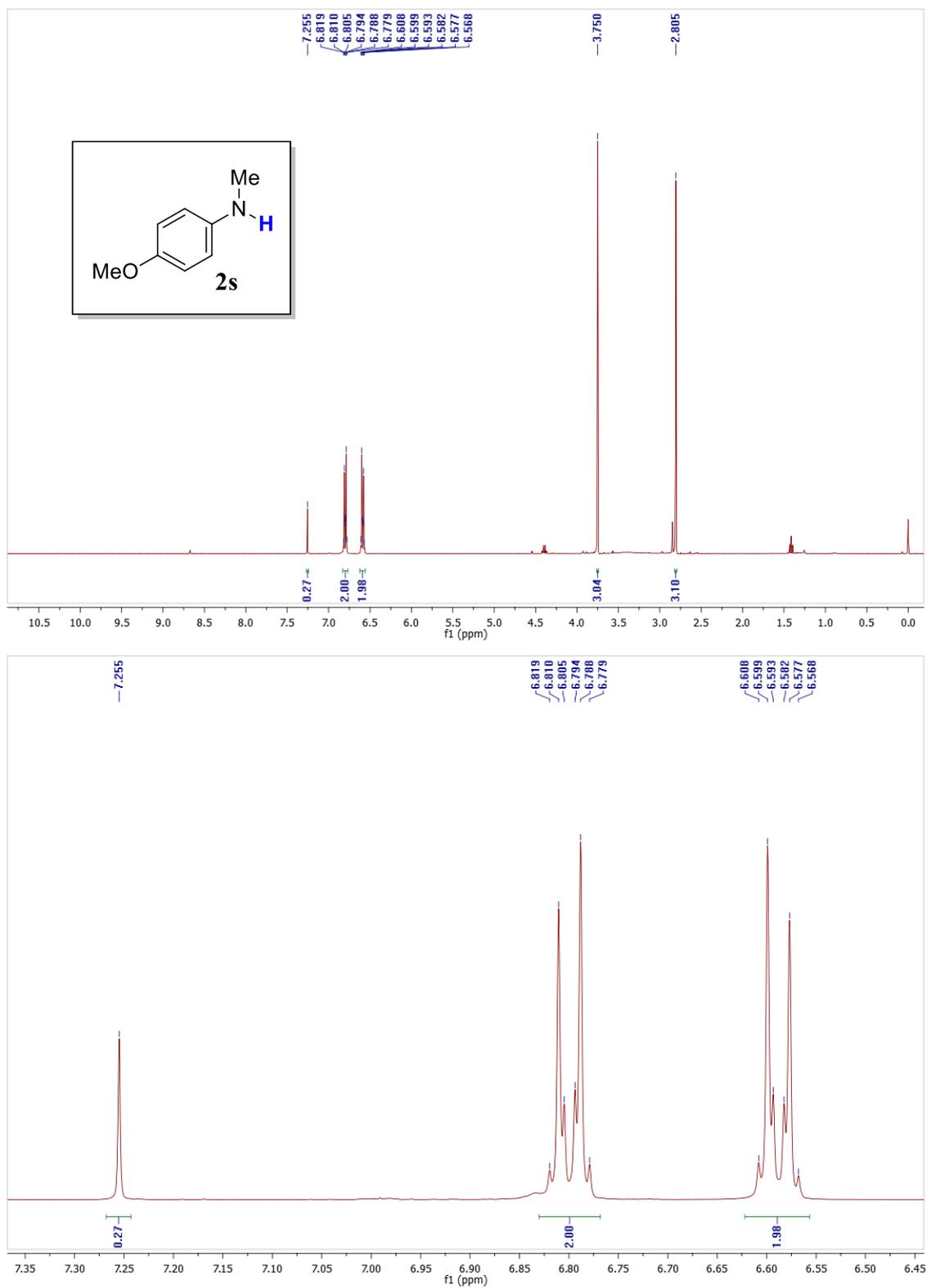
$^1\text{H-NMR}$ (400 MHz, CDCl_3). *N*-(4-Hydroxyphenyl)-*N*,4-dimethylbenzenesulfonamide (**2m**).



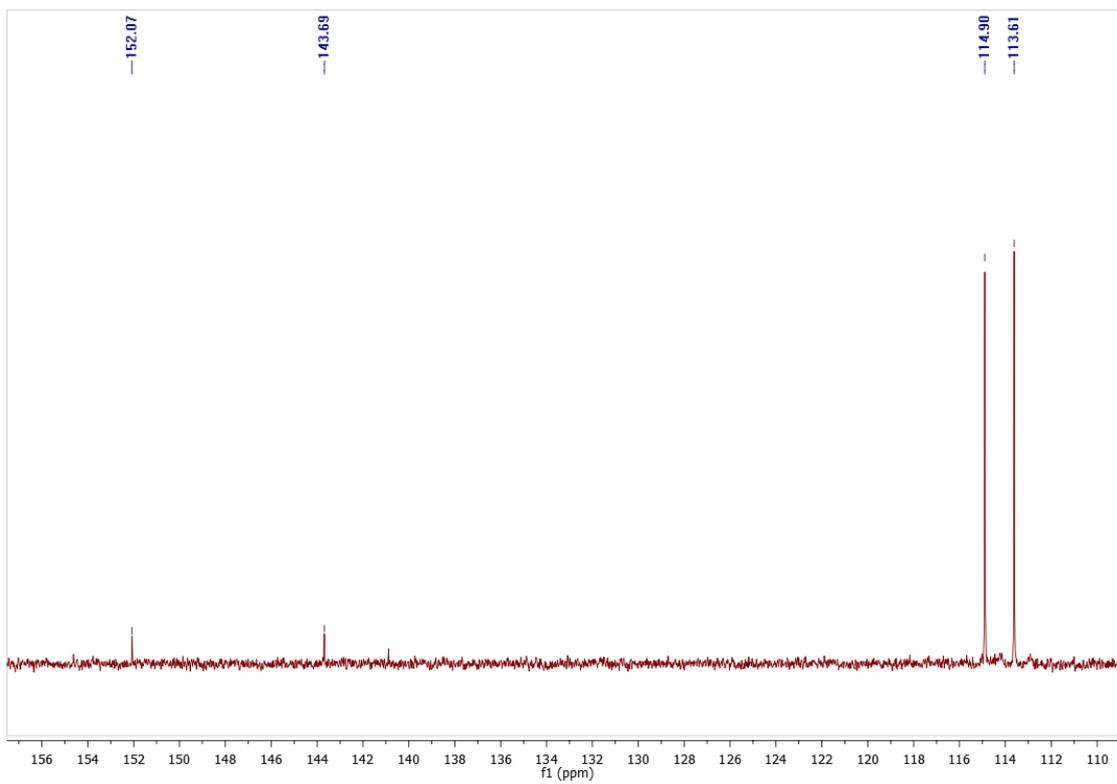
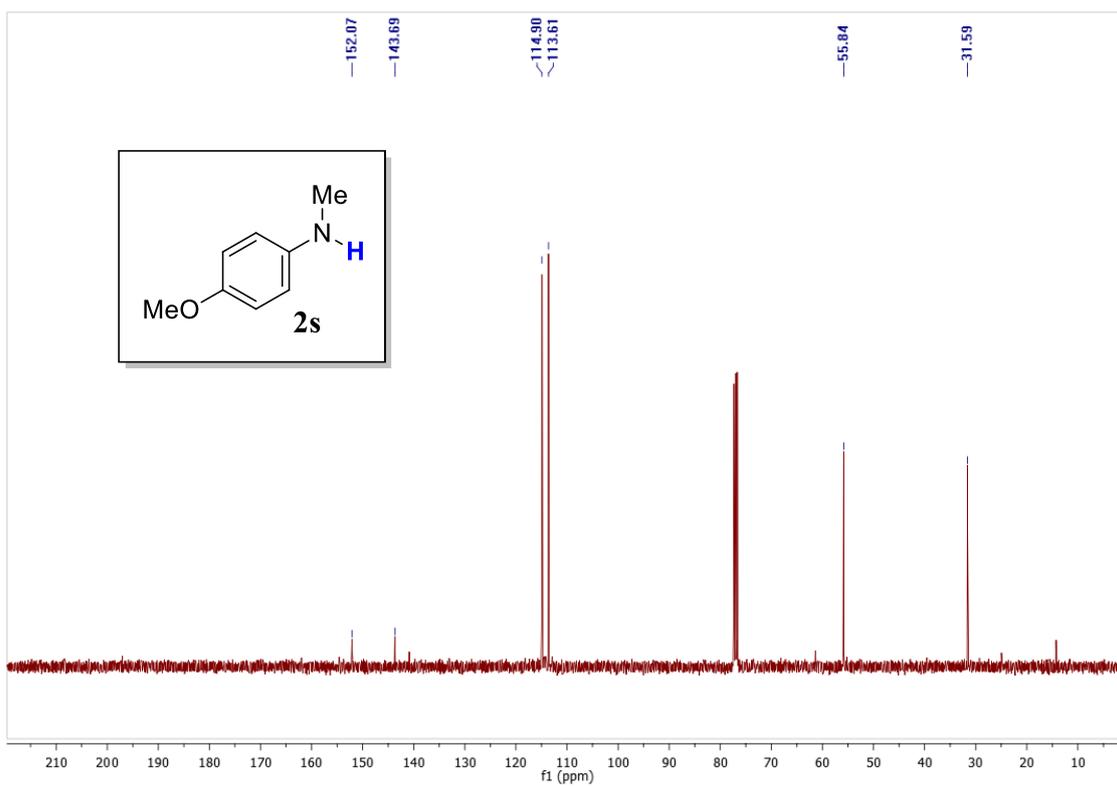
^{13}C -NMR {H} (101 MHz, CDCl_3). *N*-(4-Hydroxyphenyl)-*N*,4-dimethylbenzenesulfonamide (**2m**).



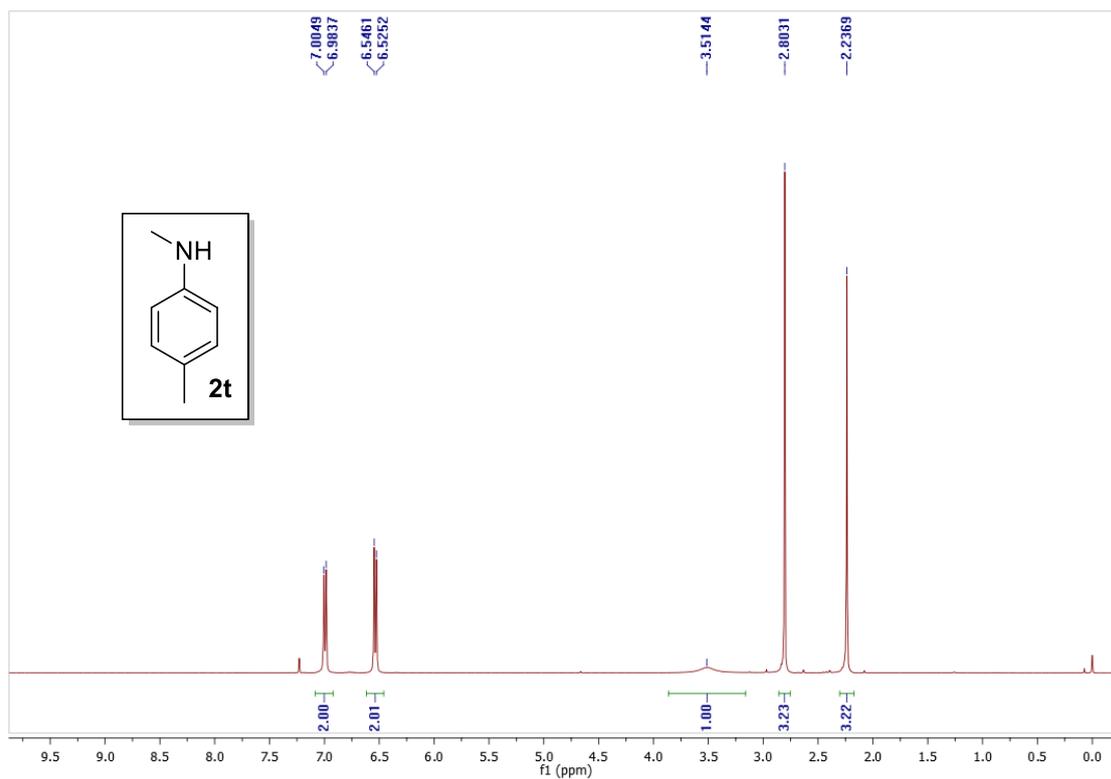
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Methoxy-*N*-methylaniline (**2s**).



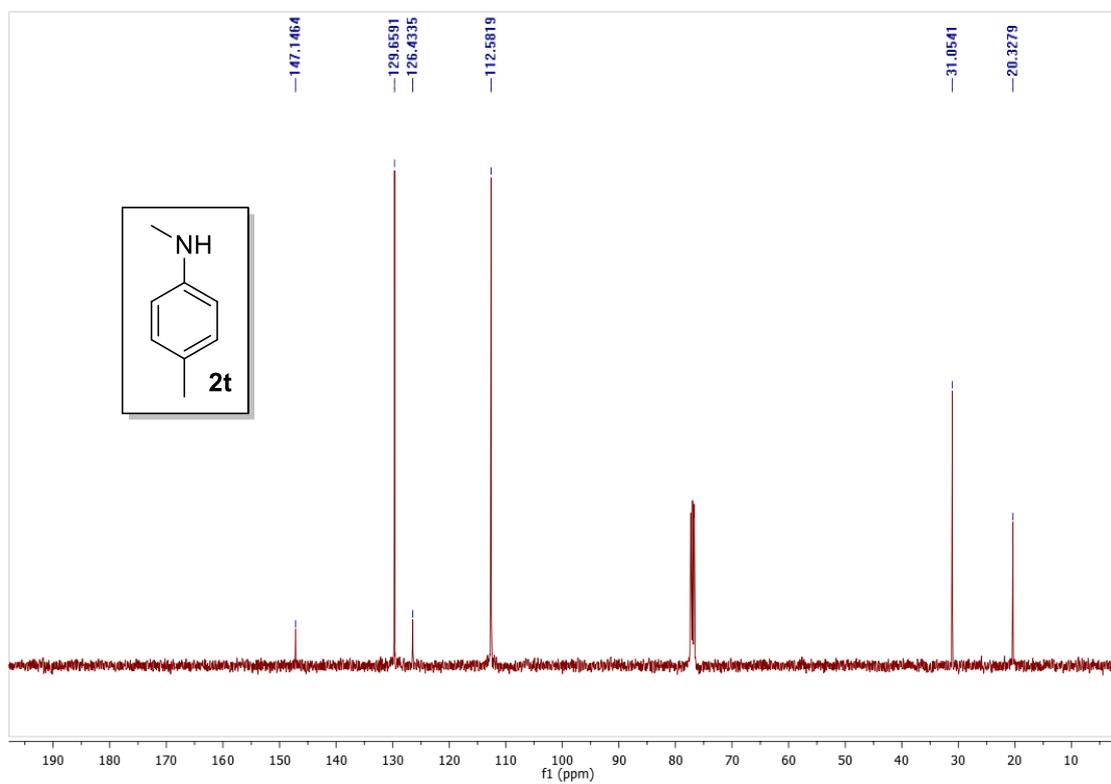
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-Methoxy-*N*-methylaniline (**2s**).



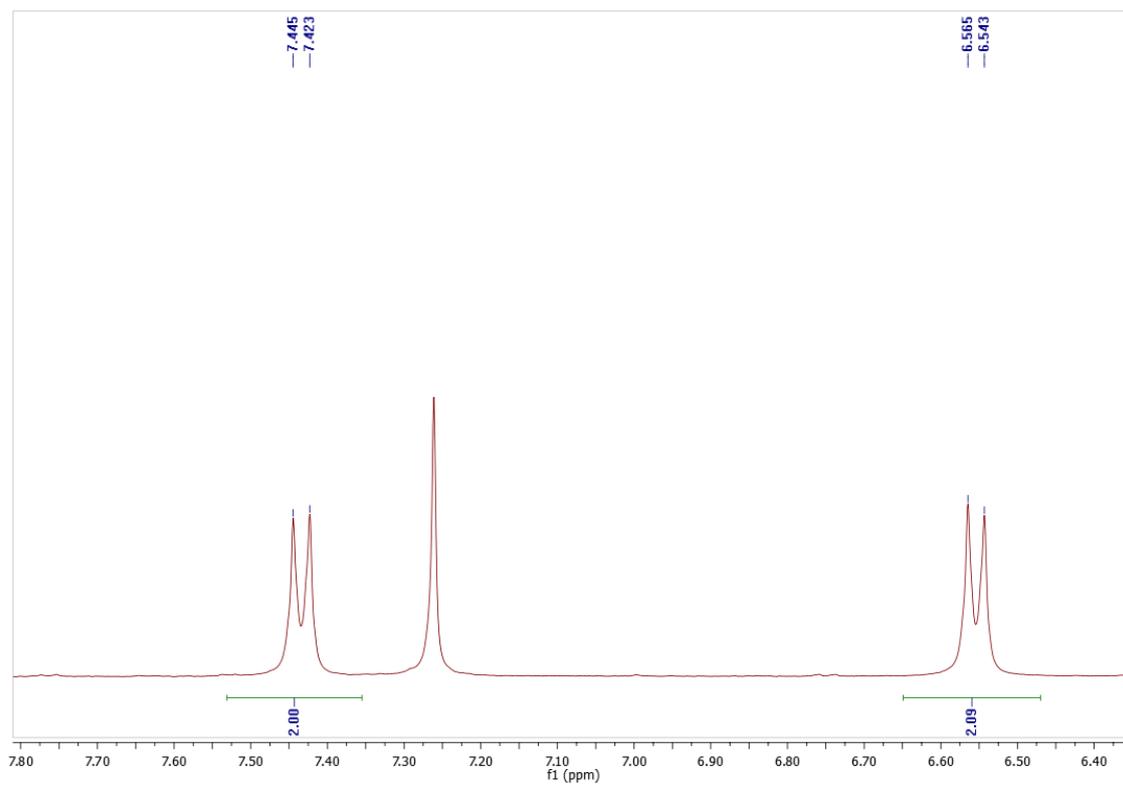
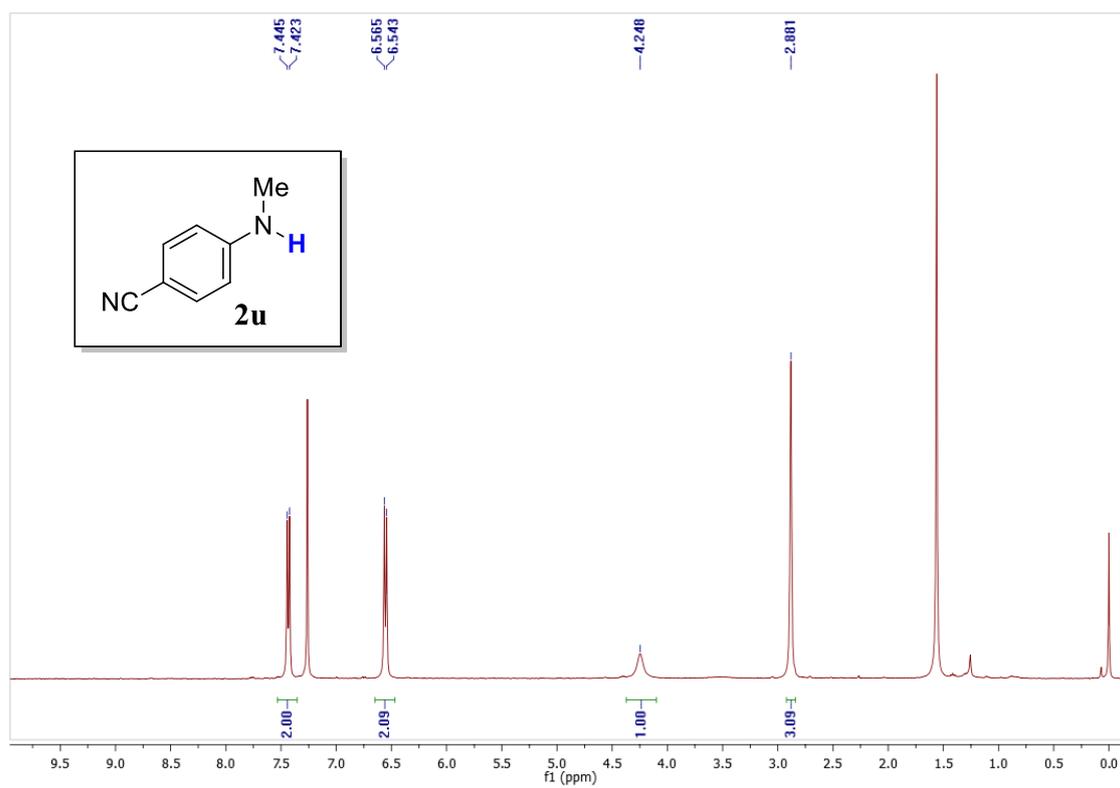
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Methyl-*N*-methylaniline (**2t**).



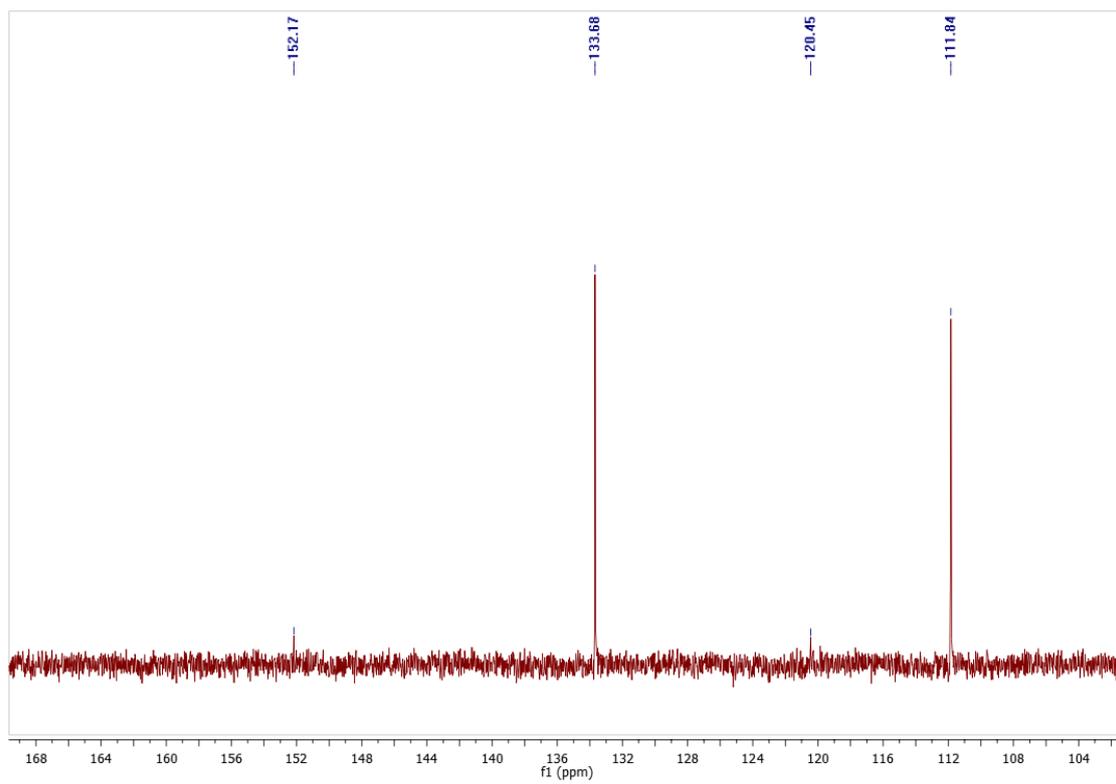
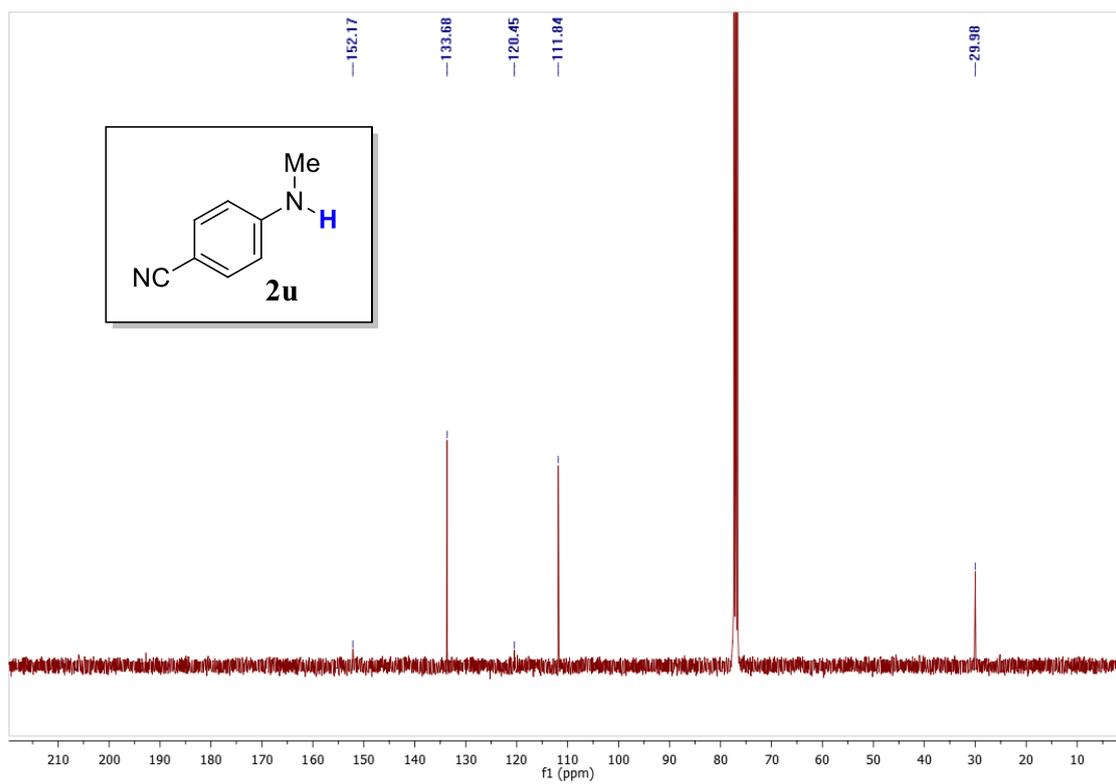
$^{13}\text{C-NMR}$ {H} (101 MHz, CDCl_3). 4-Methyl-*N*-methylaniline (**2t**).



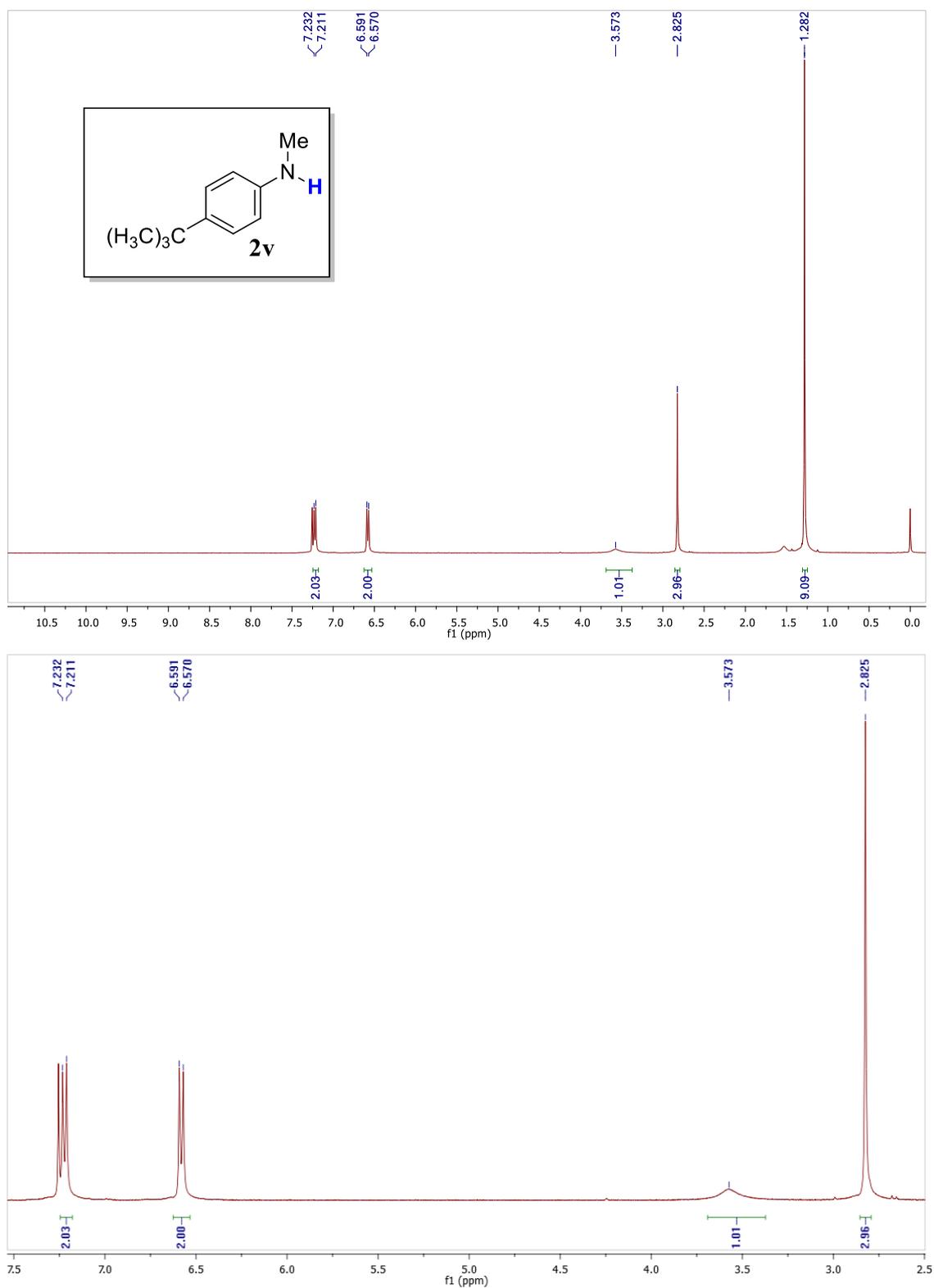
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Isocyano-*N*-methylaniline (**2u**).



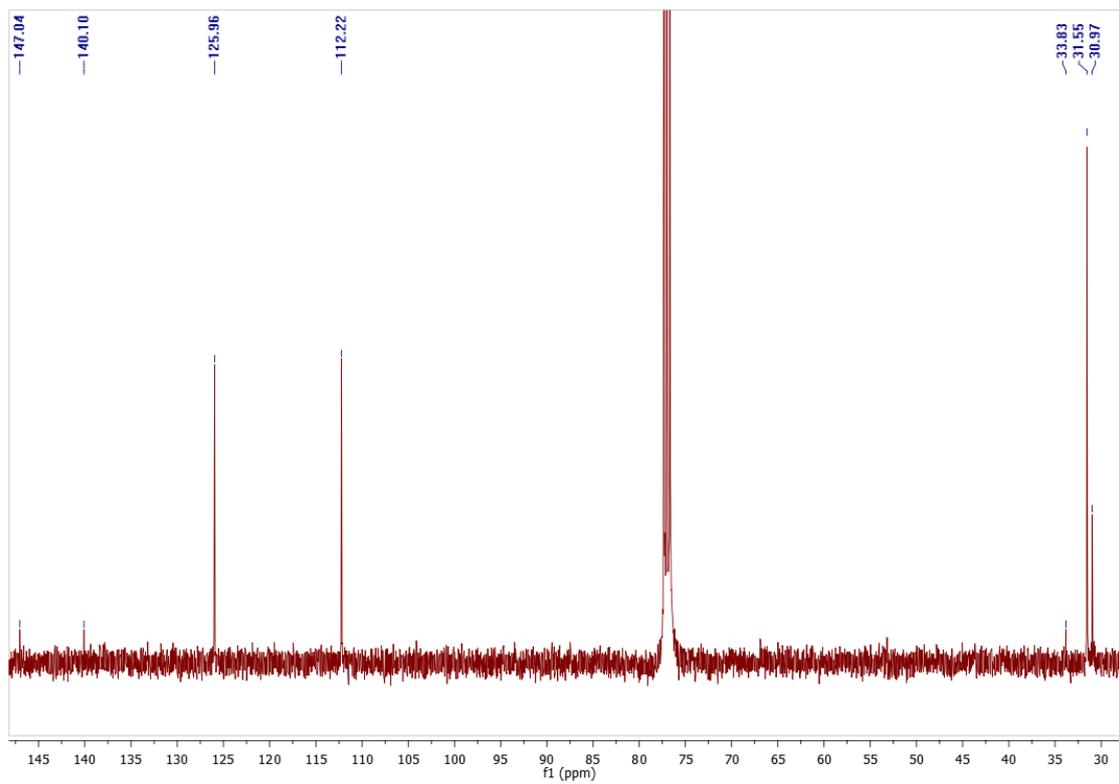
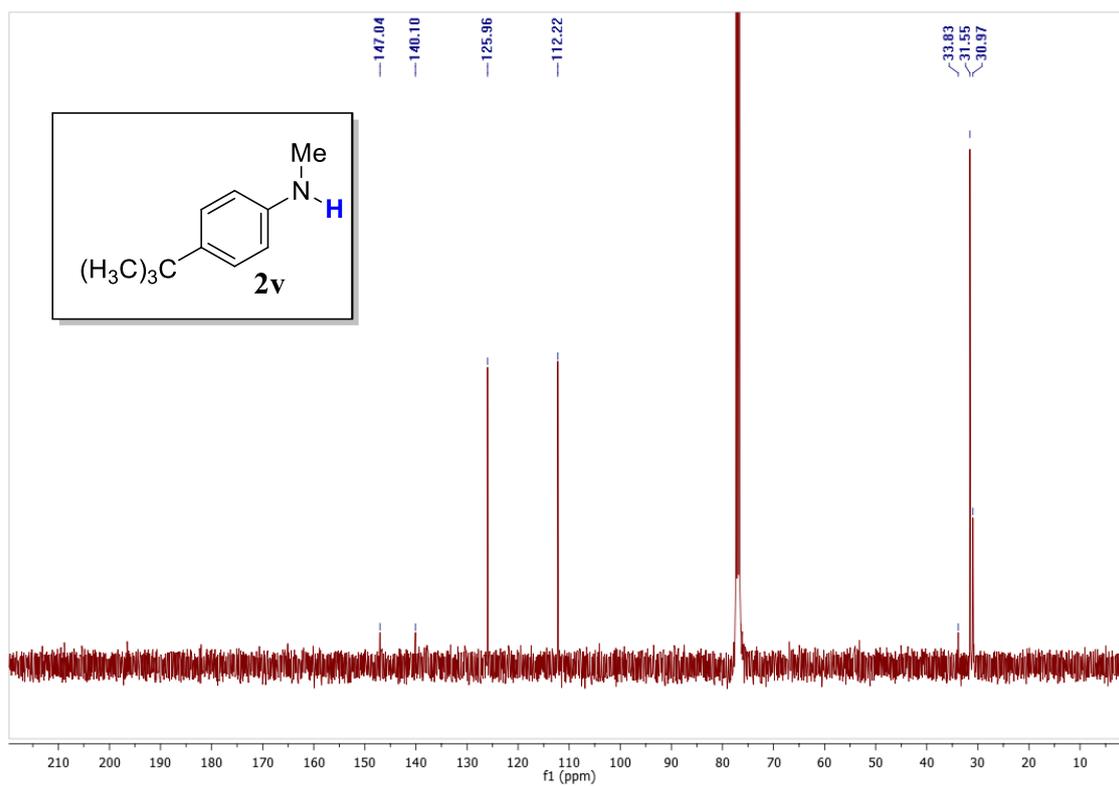
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-Isocyano-*N*-methylaniline (**2u**).



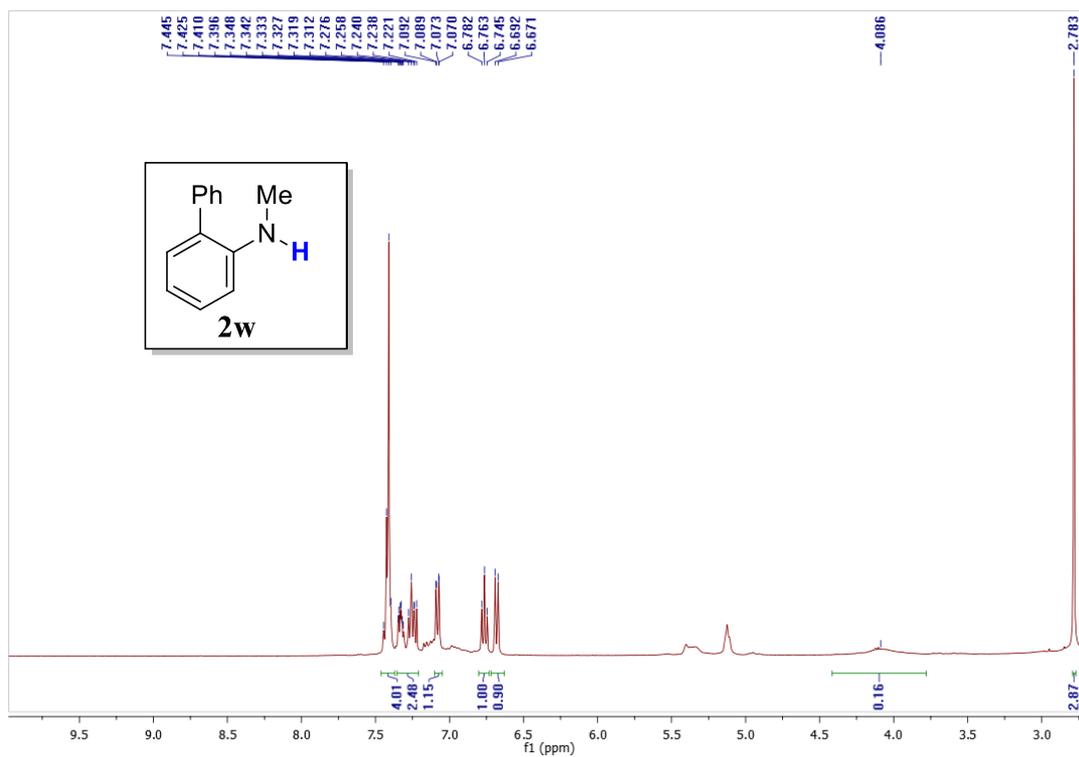
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-(*tert*-Butyl)-*N*-methylaniline (**2v**).



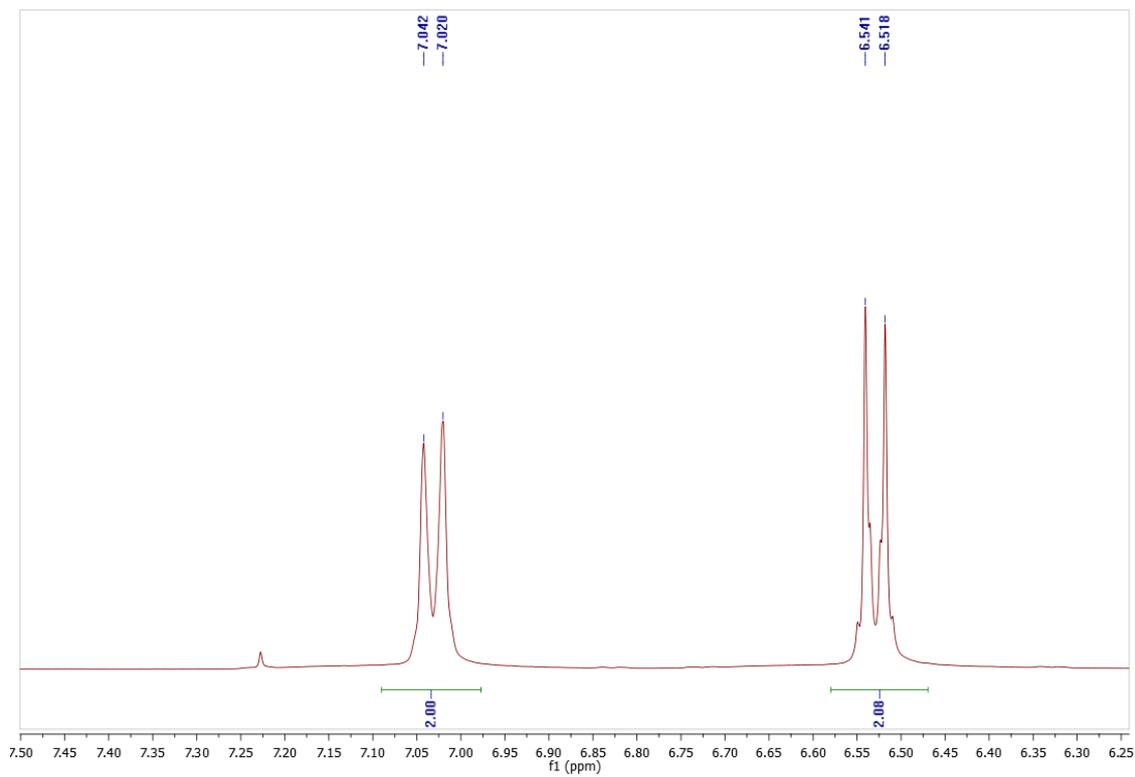
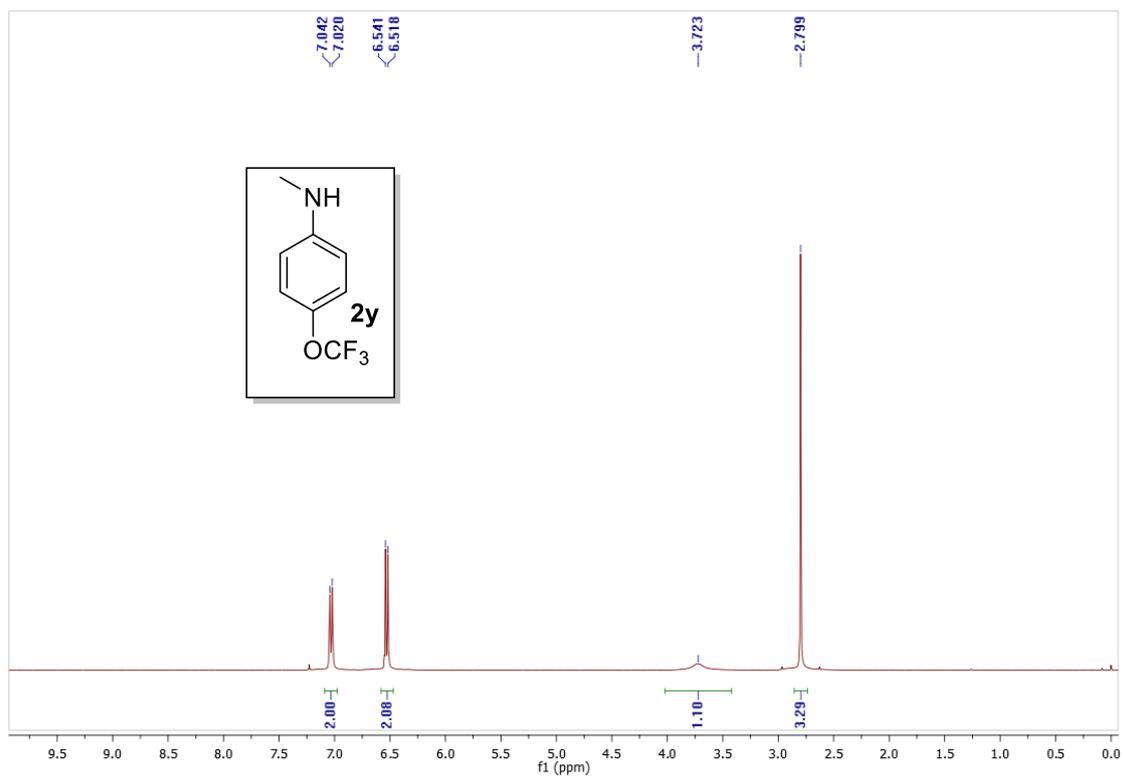
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-(*tert*-Butyl)-*N*-methylaniline (**2v**).



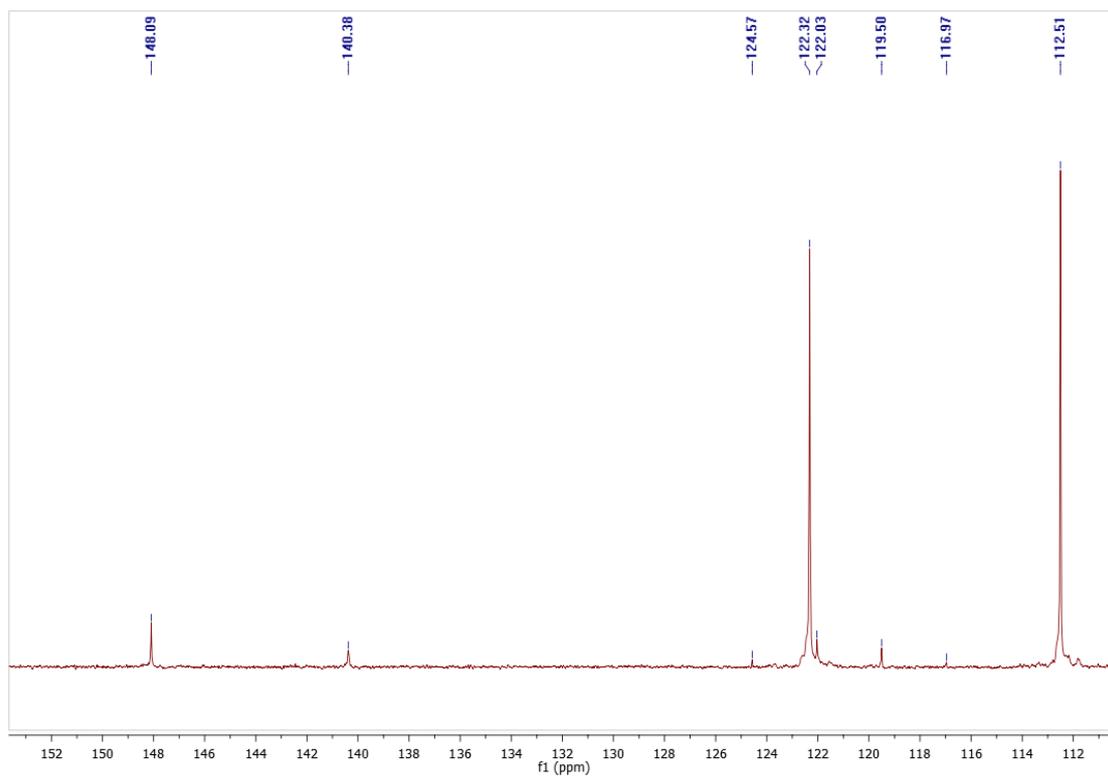
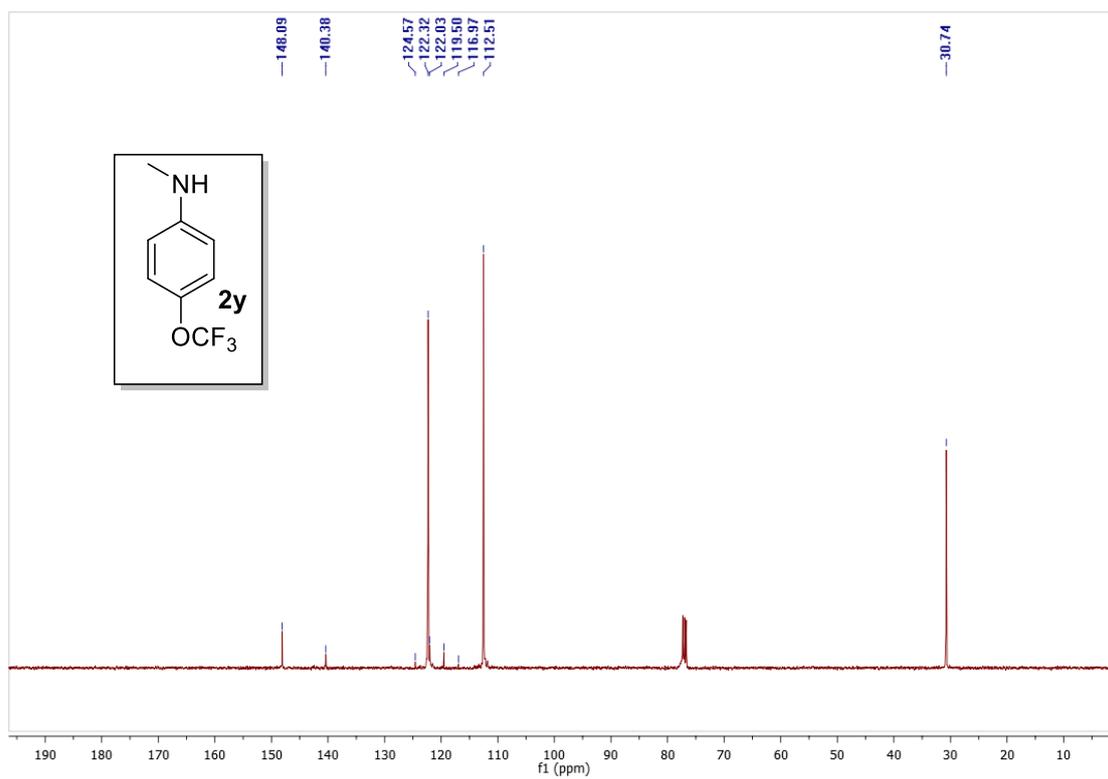
^1H NMR (400 MHz, CDCl_3). *N*-Methyl-[1,1'-biphenyl]-2-amine (**2w**).



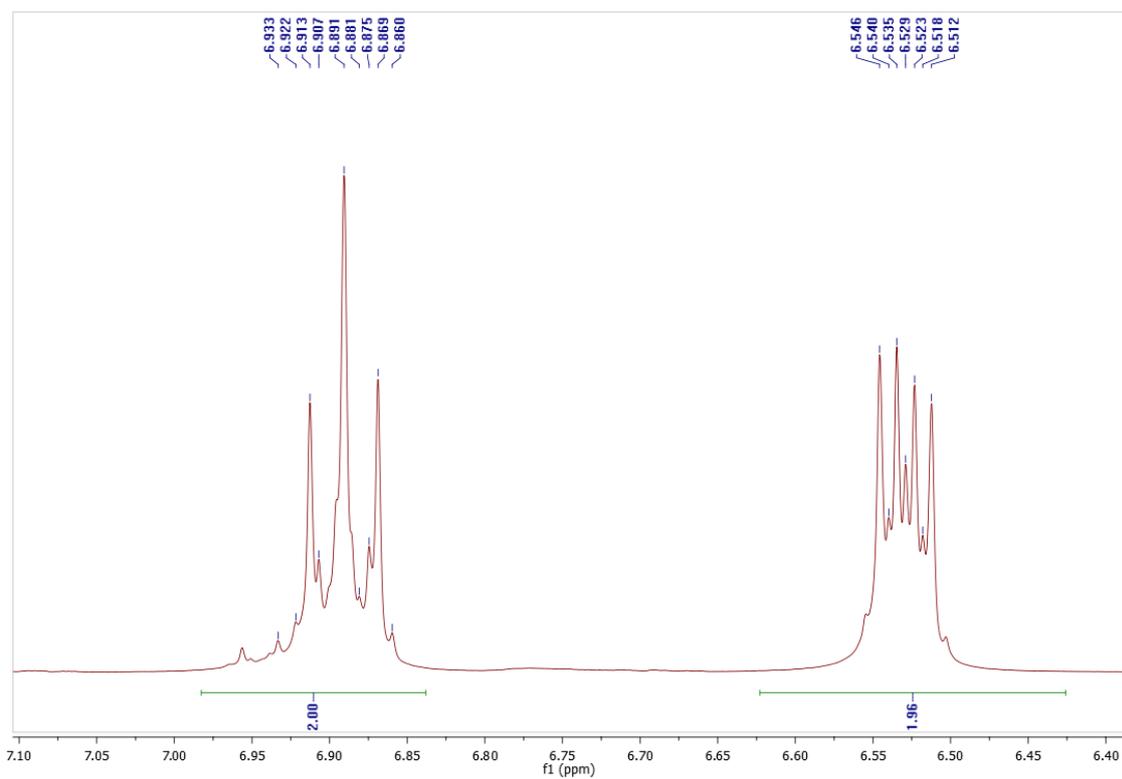
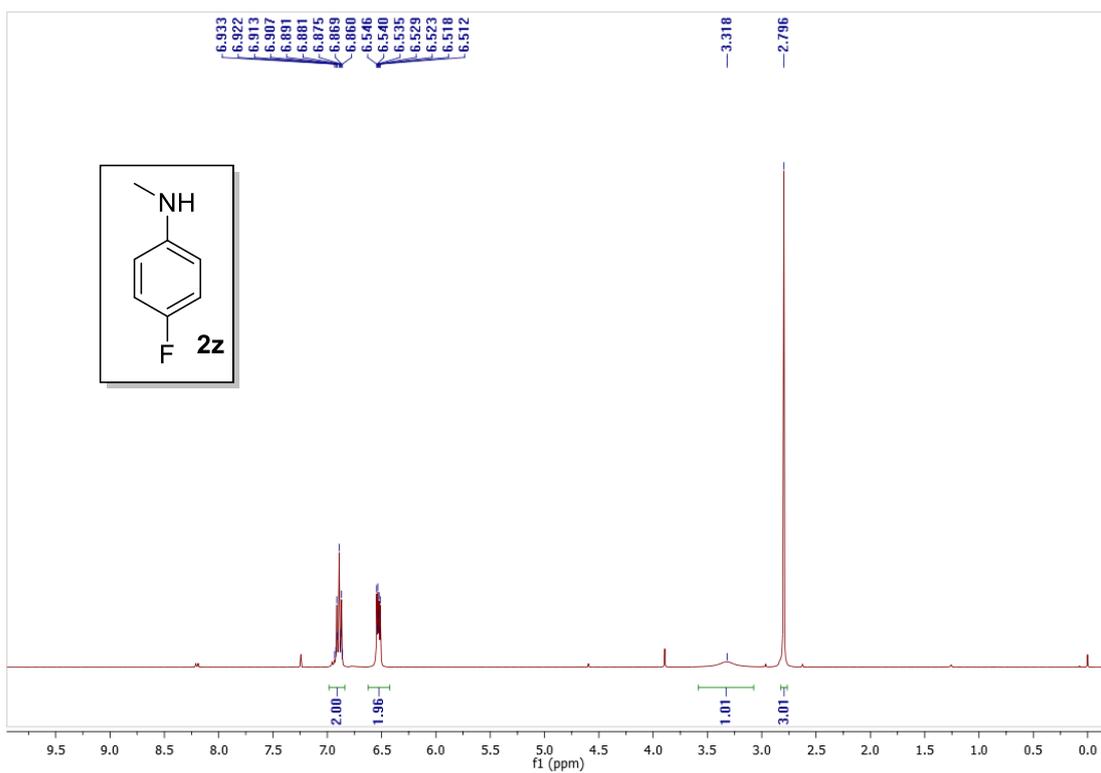
$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-(Trifluoromethoxy)-*N*-methylaniline (**2y**).



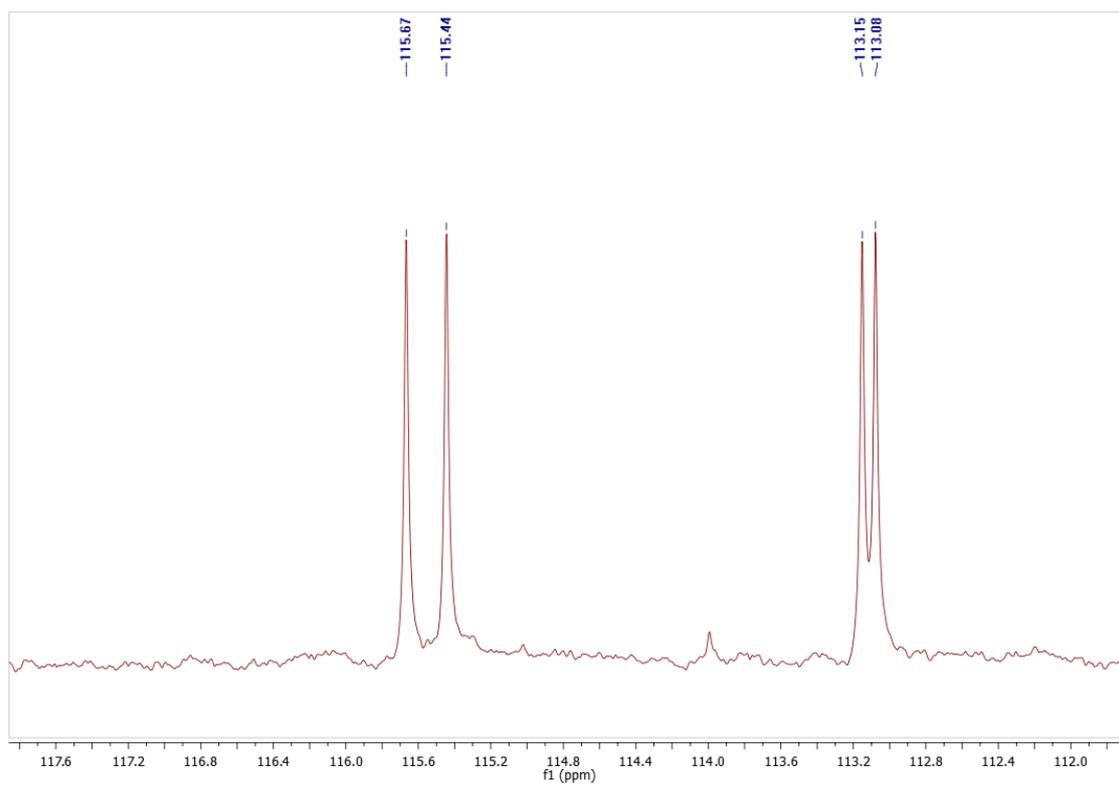
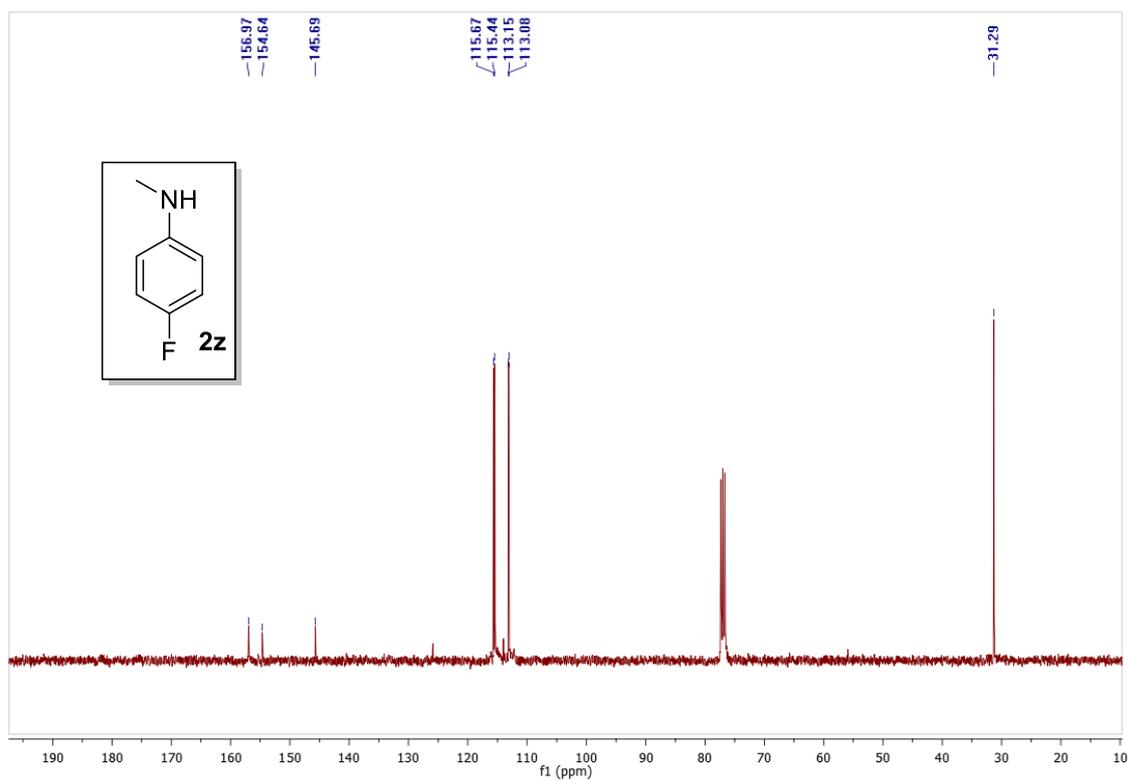
^{13}C -NMR {H} (101 MHz, CDCl_3). 4-(Trifluoromethoxy)-*N*-methylaniline (**2y**).



$^1\text{H-NMR}$ (400 MHz, CDCl_3). 4-Fluoro-*N*-methylaniline (**2z**)



^{13}C -NMR {H} (101 MHz, CDCl_3). 4-Fluoro-*N*-methylaniline (**2z**)



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