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Supporting Information

Ruthenium Catalyzed *α*-Methylation of Sulfones with Methanol as a Sustainable C1 Source

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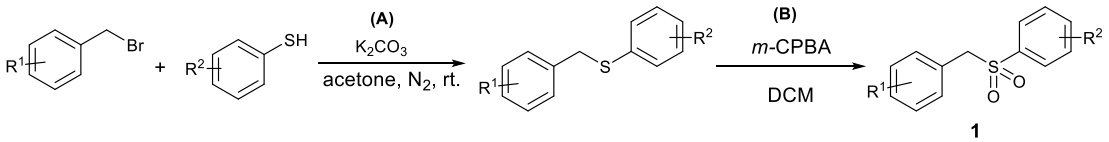
1. General Information.

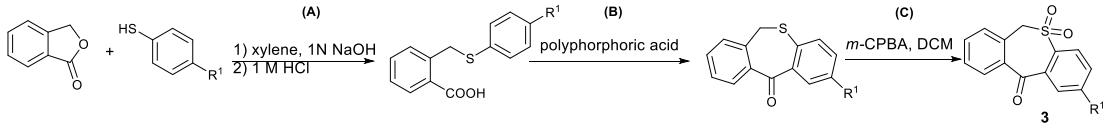
All commercial materials were used as received unless otherwise noted. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar, J&K. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded on Bruker AVANCE II instruments in $CDCl_3$ with TMS as internal standard. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). HRMS spectra were recorded on an Agilent 1200HPLC-6210TOFMS using ESI as ion source.

2. General Procedure A for the Synthesis of Starting Materials 1[1]



All the sulfones **1** were known compounds and prepared according to reference 1: **(A)**: To a 100 mL round-bottomed flask that equipped with a magnetic stir bar, was charged with benzyl bromides (4.0 mmol), thiophenols (4.0 mmol) and K_2CO_3 (4.4 mmol, 1520.0 mg) in acetone (60 mL) under N_2 at room temperature for 4 h. Then, water (60 mL) was added, and the mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed by brine, dried over anhydrous $MgSO_4$ and concentrated with a rotary evaporator under reduced pressure to yield the crude sulfide. which was used in the next step without purification. **(B)**: To a stirred solution of crude sulfide in DCM (40 mL), a solution of *m*-CPBA* (10 mmol) in DCM (15 mL) was added dropwise over 15 min. The reaction mixture was stirred for 16 h, washed with saturated $NaHCO_3$ solution (3 x 30 mL) and water (30 mL), dried with $MgSO_4$ and concentrated under reduced pressure to yield the crude product **1** as a white solid. The sulfone **1** was purified by column chromatography with hexane/ethyl acetate as eluent.

3. General Procedure B for the Synthesis of Starting Material 3[2]



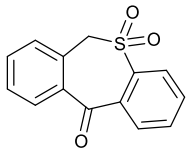
(A): Sodium hydroxide (1 N, 3.0 mmol) was added to a solution of thiophenol (3.0 mmol) in xylene (60 mL) and the mixture was refluxed. Upon addition of phthalide (3.0 mmol), the mixture was refluxed for another 8 h, then cooled, and the solidified mixture was dissolved in 10% potassium hydroxide and diluted with 100 mL water. The aqueous phase was separated and acidified by 1M hydrochloric acid (pH = 3), dried with $MgSO_4$ and concentrated under reduced pressure. The thioether product was purified by column chromatography with hexane/ethyl acetate (3:1) as eluent.

(B): Polyphosphoric acid (50.0 g) was heated to 80 °C and 2-((phenylthio)methyl)benzoic acid derivative (3.0 mmol) were slowly added, and the mixture was heated for one hour at 130 °C. After partial cooling (80 °C), ice and water were added, product was extracted with dichloromethane and washed with water and 5% aq. sodium hydroxide. The solvent was removed under vacuum and the residue was recrystallized from isopropanol and used in the next step without further characterization.

(C): To a stirred solution of crude sulfide in DCM (40 mL), a solution of *m*-CPBA* (7.5 mmol) in DCM (15 mL) was added, dropwise over 15 min. The reaction mixture was stirred for 16 h, washed with saturated $NaHCO_3$ solution (3 x 30 mL) and water (30 mL), dried with $MgSO_4$ and concentrated under reduced pressure to yield the crude product **3** as a white solid. The sulfone **3** was purified by column chromatography with hexane/ethyl acetate as eluent.

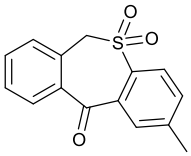
Analytic Data of sulfone 3

Dibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (3a)



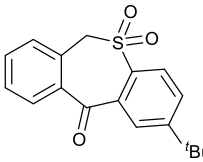
Compound **3a** was prepared following the general procedure B. m.p. 97-99 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (dd, *J* = 5.6, 3.6 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.97 – 7.95 (m, 1H), 7.76 – 7.73 (m, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 193.0, 138.4, 138.3, 136.7, 133.8, 133.4, 132.6, 131.4, 131.2, 131.2, 129.2, 127.9, 125.4, 60.7. HRMS (ESI-TOF) calcd for $C_{14}H_{10}O_3SNa$ $[M + Na]^+$: 281.0243; found: 281.0248.

2-Methyldibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (3b)



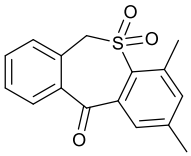
Compound **3b** was prepared following the general procedure B. m.p. 166-168 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.60 – 7.48 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 4.78 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 193.3, 144.9, 138.3, 136.7, 135.7, 133.3, 133.1, 131.5, 131.3, 131.2, 129.1, 128.1, 125.6, 60.8, 21.5. HRMS (ESI-TOF) calcd for $C_{15}H12O_3SNa$ [M + Na]$^{+}$: 295.0399; found: 295.0400.

2-(*tert*-Butyl)dibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (3c)



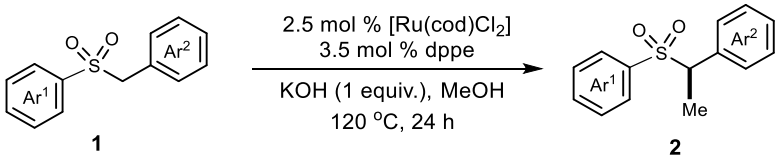
Compound **3a** was prepared following the general procedure B. m.p. 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 – 7.49 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.79 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 193.0, 138.4, 138.3, 136.7, 133.8, 133.4, 132.6, 131.4, 131.2, 131.2, 129.2, 127.8, 125.4, 60.7, 38.6, 29.7. HRMS (ESI-TOF) calcd for $C_{18}H_{18}O_3SNa$ [M + Na]$^{+}$: 337.0869; found: 337.0873.

2,4-Dimethyldibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (3d)



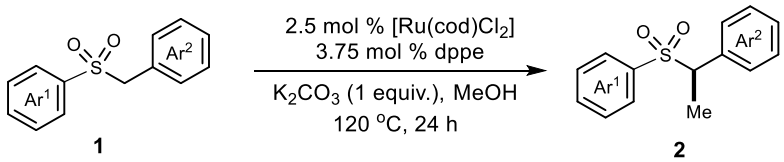
Compound **3a** was prepared following the general procedure B. m.p. 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 4.73 (s, 2H), 2.78 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.4, 143.2, 141.1, 138.2, 137.8, 137.6, 134.6, 132.3, 130.5, 129.3, 128.9, 128.4, 125.5, 60.6, 21.1, 20.6. HRMS (ESI-TOF) calcd for $C_{16}H_{14}O_3SNa$ [M + Na]$^{+}$: 309.0556; found: 309.0562.

4. General Procedure C for the Synthesis of Products 2 and 4



A mixture of [Ru(cod)Cl_2] (2.5 mol % mmol), dppe (3.5 mol % mmol), KOH (0.5 mmol), aryl sulfone **1** or **3** (0.5 mmol) and methanol (2.0 mL) was stirred at 120 °C for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1-10:1) to give the methylated products **2** and **4**.

5. General Procedure D for the Synthesis of Products 2f, 2g, compound B.



A mixture of [Ru(cod)Cl_2] (2.5 mol %), dppe (3.5 mol %), K_2CO_3 (0.5 mmol), aryl sulfone (0.5 mmol) and methanol (2.0 mL) was stirred at 120 °C for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1-10:1) to give the methylated products **2f, 2g,** and **compound B**.

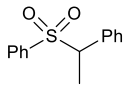
The synthesis of 2a on 5.0 mmol scale

A mixture of [Ru(cod)Cl_2] (2.5 mol % mmol), dppe (3.5 mol % mmol), KOH (5.0 mmol), sulfone **1a** (5.0 mmol) and methanol (10.0 mL) was stirred at 120 °C for 36 h under Ar in a pressure tube (ACE pressure tube, 120 mL). After cooling to room temperature, the reaction was diluted with ethyl acetate (50 mL) and water (80 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 mL) for three times. The combined organic layer was washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate =

10:1) to give **2a** in 1050.0 mg, 85% yield.

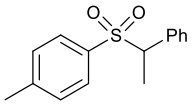
Analytic Data of product 2

((1-Phenylethyl)sulfonyl)benzene (2a)



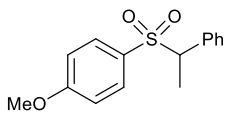
Compound **2a** was prepared following the general procedure C, starting from (benzylsulfonyl)benzene (**1a**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2a** was obtained as white solid (110.0 mg, 90% isolated yield). m.p. 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.58 – 7.53 (m, 3H), 7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 – 7.21 (m, 2H), 7.14 – 7.12 (m, 2H), 4.23 (q, *J* = 7.2 Hz, 1H), 1.78 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.9, 133.8, 133.5, 129.4, 129.2, 128.8, 128.6, 128.4, 66.1, 14.0. HRMS (ESI-TOF) calcd for $C_{14}H_{14}O_2SNa$ $[M + Na]^+$: 269.0607; found: 269.0615.

1-Methyl-4-(1-(phenylsulfonyl)ethyl)benzene (2b)



Compound **2b** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-4-methylbenzene (**1b**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2b** was obtained as white solid (108.0 mg, 83% isolated yield). m.p. 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H) 4.21 (q, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.5, 134.0, 133.9, 129.4, 129.3, 129.2, 128.7, 128.4, 66.1, 21.6, 14.1. HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_2SNa$ $[M + Na]^+$: 283.0763; found: 283.0751.

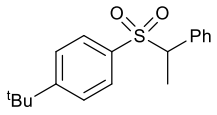
1-Methoxy-4-((1-phenylethyl)sulfonyl)benzene (2c)



Compound **2c** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-4-methoxybenzene (**1c**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2c** was obtained as white solid (124.0 mg, 80% isolated yield). m.p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.47 – 7.40 (m, 2H), 7.32 – 7.22 (m, 3H), 7.14 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.87 – 6.81 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz,

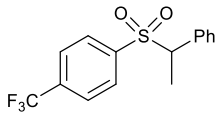
$CDCl_3$, ppm) δ 163.6, 134.1, 131.3, 129.4, 128.7, 128.3, 113.8, 66.2, 55.6, 14.1. HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_3SNa$ $[M + Na]^+$: 299.0712; found: 299.0725.

1-(*tert*-Butyl)-4-((1-phenylethyl)sulfonyl)benzene (2d)



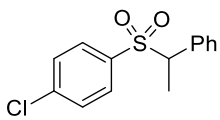
Compound **2d** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-4-(tert-butyl)benzene (**1d**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2d** was obtained as white solid (118.0 mg, 78% isolated yield). m.p. 95-97 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.24 (s, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 1.78 (d, *J* = 7.2 Hz, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.5, 134.0, 133.9, 129.5, 129.1, 128.7, 128.3, 125.6, 66.1, 35.2, 31.1, 14.2. HRMS (ESI-TOF) calcd for $C_{18}H_{22}O_2SNa$ $[M + Na]^+$: 325.1233; found: 325.1250.

1-((1-Phenylethyl)sulfonyl)-4-(trifluoromethyl)benzene (2e)



Compound **2e** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-4-(trifluoromethyl)benzene (**1e**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2e** was obtained as white solid (138.0 mg, 88% isolated yield). m.p. 158-160 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (s, 4H), 7.37 – 7.27 (m, 3H), 7.18 – 7.13 (m, 2H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.83 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.6, 135.2 (d, *J* = 32.8 Hz), 133.2, 129.8, 129.4, 129.1, 128.6, 125.7 (d, *J* = 3.7 Hz), 123.1 (d, *J* = 271.4 Hz), 66.3, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -63.2. HRMS (ESI-TOF) calcd for $C_{15}H_{13}F_3O_2SNa$ $[M + Na]^+$: 337.0480; found: 337.0499.

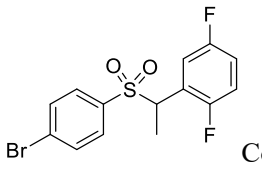
1-Chloro-4-((1-phenylethyl)sulfonyl)benzene (2f)



Compound **2f** was prepared following the general procedure D, starting from 1-(benzylsulfonyl)-4-chlorobenzene (**1f**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2f** was obtained as white solid (67.4 mg, 48% isolated yield). m.p. 142-144 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.33 –

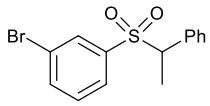
7.26 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 1H), 1.80 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.3, 135.3, 133.5, 130.7, 129.4, 129.0, 129.0, 128.6, 66.2, 13.9. HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClO_2SNa$ [M + Na]$^+$: 303.0217; found: 303.0221.

2-(1-((4-Bromophenyl)sulfonyl)ethyl)-1,4-difluorobenzene (2g)



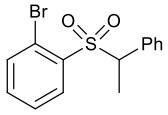
Compound **2g** was prepared following the general procedure D, starting from 2-(((4-bromophenyl)sulfonyl)methyl)-1,4-difluorobenzene (**1g**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2g** was obtained as white solid (93.6 mg, 52% isolated yield). m.p. 178-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.22 (ddd, *J* = 8.4, 5.6, 3.2 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.84 (td, *J* = 9.2, 4.2 Hz, 1H), 4.65 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.8 (dd, *J* = 216.5, 2.5 Hz), 156.4 (dd, *J* = 217.2, 2.5 Hz), 136.0, 132.2, 130.5, 129.4, 122.8 (dd, *J* = 16.1, 7.9 Hz), 117.4 (dd, *J* = 24.1, 8.9 Hz), 116.5 (dd, *J* = 25.7, 8.5 Hz), 116.1 (dd, *J* = 25.3, 2.9 Hz), 57.2, 13.3. ^{119}F NMR (376 MHz, Chloroform-*d*) δ -116.8 (d, *J* = 17.7 Hz), -122.7 (d, *J* = 17.6 Hz). HRMS (ESI-TOF) calcd for $C_{14}H_{11}BrF_2O_2SNa$ [M + Na]$^+$: 382.9523; found: 382.9529.

Bromo-3-((1-phenylethyl)sulfonyl)benzene (2h)



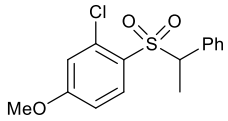
Compound **2h** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-3-bromobenzene (**1h**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2h** was obtained as white solid (133.0 mg, 82% isolated yield). m.p. 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 – 7.61 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 1.78 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.8, 136.6, 133.3, 132.1, 130.1, 129.4, 129.1, 128.5, 127.8, 122.7, 66.3, 13.9. HRMS (ESI-TOF) calcd for $C_{14}H_{13}BrO_2SNa$ [M + Na]$^+$: 346.9712; found: 346.9725.

1-Bromo-2-((1-phenylethyl)sulfonyl)benzene (2i)



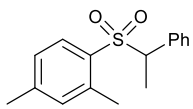
Compound **2i** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-2-bromobenzene (**1i**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2i** was obtained as white solid (67.0 mg, 41% isolated yield). m.p. 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.72 (ddd, *J* = 6.0, 4.4, 1.6 Hz, 2H), 7.35 (td, *J* = 7.2, 1.6 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.25 – 7.21 (m, 3H), 4.99 (q, *J* = 7.2 Hz, 1H), 1.80 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.0, 135.2, 134.4, 133.3, 133.0, 129.3, 128.9, 128.5, 127.6, 120.9, 62.8, 13.5. HRMS (ESI-TOF) calcd for $C_{14}H_{13}BrO_2SNa$ $[M + Na]^+$: 346.9712; found: 346.9722.

2-Chloro-4-methoxy-1-((1-phenylethyl)sulfonyl)benzene (2j)



Compound **2j** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-2-chloro-4-methoxybenzene (**1j**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2j** was obtained as white solid (116.0 mg, 75% isolated yield). m.p. 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.25 – 7.21 (m, 3H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.80 (q, *J* = 7.1 Hz, 1H), 3.82 (s, 3H), 1.79 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.7, 134.2, 134.1, 133.8, 129.2, 128.8, 128.5, 127.1, 117.1, 112.2, 63.7, 55.9, 13.6. HRMS (ESI-TOF) calcd for $C_{15}H_{15}ClO_3SNa$ $[M + Na]^+$: 333.0322; found: 333.0346.

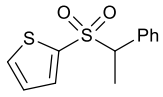
2,4-Dimethyl-1-((1-phenylethyl)sulfonyl)benzene (2k)



Compound **2k** was prepared following the general procedure C, starting from 1-(benzylsulfonyl)-2,4-dimethylbenzene (**1k**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2k** was obtained as white solid (114.0 mg, 83% isolated yield). m.p. 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 5.5 Hz, 2H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 6.8 Hz, 2H), 7.03 (d, *J* = 9.9 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.79 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ144.3, 138.9,

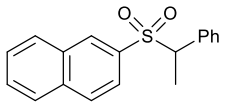
133.8, 133.1, 132.4, 131.6, 129.5, 128.7, 128.4, 126.9, 65.5, 21.3, 20.2, 13.8. HRMS (ESI-TOF) calcd for $C_{16}H_{18}O_2SNa$ $[M + Na]^+$:297.0920; found: 297.0906.

2-((1-Phenylethyl)sulfonyl)thiophene (2l)



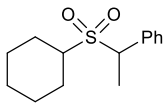
Compound **2l** was prepared following the general procedure, starting from 2-(benzylsulfonyl)thiophene (**1l**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2l** was obtained as white solid (107.0 mg, 85% isolated yield). m.p. 65-67 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 3.6 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.20 (d, *J* = 6.3 Hz, 2H), 7.01 (t, *J* = 4.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 1H), 1.83 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.2, 134.3, 133.9, 129.3, 129.0, 128.5, 127.5, 67.3, 29.7, 14.2. HRMS (ESI-TOF) calcd for $C_{12}H_{12}O_2S_2Na$ $[M + Na]^+$:275.0171; found: 275.0165.

2-((1-Phenylethyl)sulfonyl)naphthalene (2m)



Compound **2m** was prepared following the general procedure C, starting from 2-(benzylsulfonyl)naphthalene (**1m**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2m** was obtained as white solid (130.0 mg, 88% isolated yield). m.p. 140-142 °C.^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.13 (s, 1H), 7.89 – 7.81 (m, 3H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H),7.49 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 1H), 1.81 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.2, 133.9, 133.8, 131.9, 131.2, 129.5, 129.4, 129.2, 128.8, 128.7, 128.4, 127.9, 127.5, 123.9, 66.2, 14.1. HRMS (ESI-TOF) calcd for $C_{18}H_{16}O_2SNa$ $[M + Na]^+$: 319.0763; found: 319.0769.

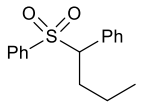
(1-(Cyclohexylsulfonyl)ethyl)benzene (2n)



Compound **2n** was prepared following the general procedure C, starting from ((cyclohexylsulfonyl)methyl)benzene (**1n**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2n** was obtained as white solid (65.0 mg, 52% isolated yield). m.p. 83-84 °C.^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 (d, *J* = 1.6 Hz, 2H), 7.38 (dd, *J* = 6.4, 1.2 Hz, 3H),

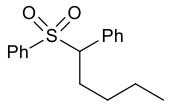
4.27 (q, *J* = 7.2 Hz, 1H), 2.59 (tt, *J* = 12.4, 3.2 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.85 – 1.84 (m, 2H), 1.76 (d, *J* = 6.8 Hz, 3H), 1.66 – 1.50 (m, 4H), 1.16 – 1.10 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 134.9, 129.0, 128.9, 59.9, 57.8, 26.1, 25.1, 25.0, 24.8, 23.6, 14.0. HRMS (ESI-TOF) calcd for $C_{14}H_{20}O_2SNa$ $[M + Na]^+$: 275.1076; found: 275.1078.

((1-Phenylbutyl)sulfonyl)benzene (2o)



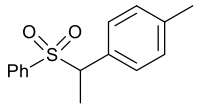
Compound **2o** was prepared following the general procedure C, starting from (benzylsulfonyl)benzene (**1a**, 0.5 mmol) and C_3H_7OH (2.0 mL). After purification by column chromatography, **2o** was obtained as Colorless oil (58.0 mg, 43% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.56 – 7.51 (m, 3H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 7.11 – 7.08 (m, 2H), 4.06 (dd, *J* = 11.6, 3.7 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.21 – 2.11 (m, 1H), 1.29 – 1.18 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.4, 133.4, 132.4, 129.9, 129.0, 128.7, 128.6, 128.4, 71.4, 29.3, 20.1, 13.6. HRMS (ESI-TOF) calcd for $C_{16}H_{18}O_2SNa$ $[M + Na]^+$: 297.0920; found: 297.0911.

((1-Phenylpentyl)sulfonyl)benzene (2p)



Compound **2p** was prepared following the general procedure C, starting from (benzylsulfonyl)benzene (**1a**, 0.5 mmol) and C_4H_9OH (2.0 mL). After purification by column chromatography, **2p** was obtained as Colorless oil (59.0 mg, 41% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 – 7.51 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.30 – 7.27 (m, *J* = 1.9 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.10 – 7.08 (m, 2H), 4.03 (dd, *J* = 11.6, 3.7 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.21 – 2.11 (m, 1H), 1.30 – 1.27 (m, 2H), 1.22 – 1.16 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}CNMR (100 MHz, $CDCl_3$, ppm) δ δ 137.5, 133.4, 132.4, 129.9, 129.0, 128.7, 128.6, 128.4, 71.7, 28.9, 27.0, 22.3, 13.7. HRMS (ESI-TOF) calcd for $C_{17}H_{20}O_2SNa$ $[M + Na]^+$: 311.1076; found: 311.1095.

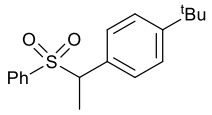
1-Methyl-4-((1-phenylethyl)sulfonyl)benzene (2q)



Compound **2q** was prepared following the general procedure C, starting from 1-methyl-4-((phenylsulfonyl)methyl)benzene (**1q**, 0.5 mmol) and CH_3OH (2.0 mL). After purification

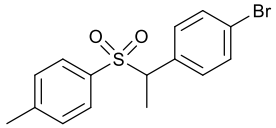
by column chromatography, **2q** was obtained as white solid (105.0 mg, 81% isolated yield). m.p. 136-138 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.56 (t, *J* = 7.6 Hz, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.03 (q, *J* = 8.4 Hz 4H), 4.20 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.73 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.7, 137.0, 133.5, 130.6, 129.3, 129.2, 129.1, 128.6, 65.8, 21.2, 14.1. HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_2SNa$ $[M + Na]^+$: 283.0763; found: 283.0779.

1-(*tert*-Butyl)-4-(1-(phenylsulfonyl)ethyl)benzene (2r)



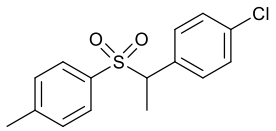
Compound **2r** was prepared following the general procedure C, starting from 1-(*tert*-butyl)-4-((phenylsulfonyl)methyl)benzene (**1r**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2r** was obtained as white solid (119.0 mg, 79% isolated yield). m.p. 145-147°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 – 7.55 (m, 3H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 152.0, 137.1, 133.5, 130.5, 129.2, 129.1, 128.6, 125.3, 65.8, 34.6, 31.3, 14.1. HRMS (ESI-TOF) calcd for $C_{18}H_{22}O_2SNa$ $[M + Na]^+$: 325.1233; found: 325.1250.

1-Bromo-4-(1-tosylethyl)benzene (2s)



Compound **2s** was prepared following the general procedure C, starting from 1-bromo-4-(tosylmethyl)benzene (**1s**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2s** was obtained as white solid (130.0 mg, 77% isolated yield). m.p. 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 8.8, 3.6 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 1H), 2.39 (s, 3H), 1.70 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.8, 134.8, 133.7, 132.5, 130.77, 129.5, 129.2, 128.6, 65.3, 21.6, 14.2. HRMS (ESI-TOF) calcd for $C_{15}H_{15}BrO_2SNa$ $[M + Na]^+$: 360.9868; found: 360.9878.

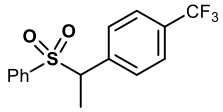
1-Chloro-4-(1-tosylethyl)benzene (2t)



Compound **2t** was prepared following the general procedure C, starting from 1-chloro-4-(tosylmethyl)benzene (**1t**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by

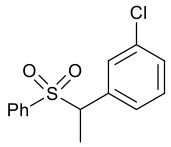
column chromatography, **2t** was obtained as white solid (115.0 mg, 78% isolated yield). m.p. 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 1H), 2.40 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.8, 133.7, 133.0, 131.5, 131.0, 129.5, 129.2, 123.0, 65.4, 21.7, 14.2. HRMS (ESI-TOF) calcd for $C_{15}H_{15}ClO_2SNa$ $[M + Na]^+$: 317.0373; found: 317.0366.

1-(1-(Phenylsulfonyl)ethyl)-4-(trifluoromethyl)benzene (2u)



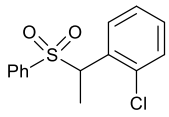
Compound **2u** was prepared following the general procedure C, starting from 1-((phenylsulfonyl)methyl)-4-(trifluoromethyl)benzene (**1u**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2u** was obtained as white solid (133.0 mg, 85% isolated yield). m.p. 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60 – 7.57 (m, 3H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 1.76 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.8, 136.6, 133.9, 131.0 (q, *J* = 33.2 Hz) 129.9, 129.1, 128.9, 125.3 (q, *J* = 3.8 Hz), 123.8 (d, *J* = 270.9 Hz), 65.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -62.790. HRMS (ESI-TOF) calcd for $C_{15}H_{13}F_3O_2SNa$ $[M + Na]^+$: 337.0480; found: 337.0496.

1-Chloro-3-(1-(phenylsulfonyl)ethyl)benzene (2v)



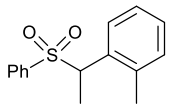
Compound **2v** was prepared following the general procedure C, starting from 1-chloro-3-((phenylsulfonyl)methyl)benzene (**1v**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2v** was obtained as white solid (120.0 mg, 86% isolated yield). m.p. 67-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61 – 7.57 (m, 3H), 7.47 – 7.40 (m, 2H), 7.30 – 7.26 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.6, 135.8, 134.3, 133.8, 129.6, 129.5, 129.2, 129.0, 128.8, 127.7, 65.5, 14.0. HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClO_2SNa$ $[M + Na]^+$:303.0217; found: 303.0226.

1-Chloro-2-(1-(phenylsulfonyl)ethyl)benzene (2w)



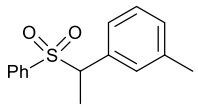
Compound **2w** was prepared following the general procedure C, starting from 1-chloro-2-((phenylsulfonyl)methyl)benzene (**1w**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2w** was obtained as white solid (118.0 mg, 84% isolated yield). m.p. 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, *J* = 6.8 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (td, *J* = 7.2, 1.6 Hz, 1H), 7.23 – 7.15 (m, 2H), 4.97 (q, *J* = 7.2 Hz, 1H), 1.77 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.5, 135.2, 133.7, 132.0, 129.9, 129.8, 129.4, 129.1, 128.7, 127.2, 60.6, 14.1. HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClO_2SNa$ $[M + Na]^+$: 303.0217; found: 303.0201.

1-Methyl-2-(1-(phenylsulfonyl)ethyl)benzene (2x)



Compound **2x** was prepared following the general procedure C, starting from 1-methyl-2-((phenylsulfonyl)methyl)benzene (**1x**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2x** was obtained as white solid (110.0 mg, 85% isolated yield). m.p. 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.58 – 7.54 (m, 3H), 7.42 – 7.38 (m, 3H), 7.21 – 7.18 (m, 2H), 7.04 – 7.01 (m, 1H), 4.56 (q, *J* = 7.2 Hz, 1H), 2.00 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.61, 137.49, 133.58, 132.36, 130.35, 129.22, 128.65, 128.59, 128.22, 126.31, 60.93, 19.42, 14.74. HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_2SNa$ $[M + Na]^+$: 283.0763; found: 283.0768.

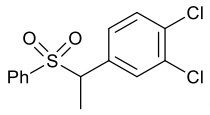
1-Methyl-3-(1-(phenylsulfonyl)ethyl)benzene (2y)



Compound **2y** was prepared following the general procedure, starting from 1-methyl-3-((phenylsulfonyl)methyl)benzene (**1y**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2y** was obtained as white solid (114.0 mg, 88% isolated yield). m.p. 134-136 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.58 – 7.55 (m, 3H), 7.42 – 7.38 (m, 2H), 7.14 – 7.08 (m, 2H), 6.93 – 6.90 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 2.26 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.1, 136.9, 133.6, 133.5, 130.2, 129.5, 129.3, 128.6, 128.2, 126.5, 66.1, 21.3, 14.0. HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_2SNa$ $[M + Na]^+$: 283.0763; found:

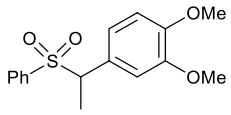
283.0769.

1,3-Dichloro-5-((1-phenylethyl)sulfonyl)benzene (2z)



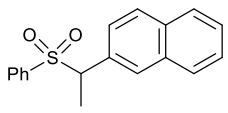
Compound **2z** was prepared following the general procedure C, starting from 1-methyl-3-((phenylsulfonyl)methyl)benzene (**1z**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2z** was obtained as white solid (129.0 mg, 82% isolated yield). m.p. 186-188°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.64 – 7.61 (m, 3H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.5, 134.0, 133.1, 132.6, 131.3, 130.3, 129.1, 129.0, 128.7, 64.9, 14.1. HRMS (ESI-TOF) calcd for $C_{14}H_{12}Cl_2O_2SNa$ $[M + Na]^+$: 336.9827; found: 336.9843.

1,3-Dimethoxy-5-(1-(phenylsulfonyl)ethyl)benzene (2aa)



Compound **2aa** was prepared following the general procedure, starting from 1,2-dimethoxy-4-((phenylsulfonyl)methyl)benzene (**1aa**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2aa** was obtained as white solid (127.0 mg, 83 % isolated yield). m.p. 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61 – 7.52 (m, 3H), 7.43 – 7.37 (m, 2H), 6.35 (t, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.65 (s, 6H), 1.72 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.5, 136.9, 135.9, 133.6, 129.2, 128.7, 107.4, 100.9, 66.2, 55.3, 14.1. HRMS (ESI-TOF) calcd for $C_{16}H_{18}O_4SNa$ $[M + Na]^+$: 329.0818; found: 329.0802.

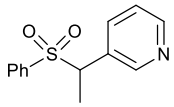
2-(1-(Phenylsulfonyl)ethyl)naphthalene (2ab)



Compound **2ab** was prepared following the general procedure C, starting from 2-((phenylsulfonyl)methyl)naphthalene (**1ab**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2ab** was obtained as white solid (112.0 mg, 76% isolated yield). m.p. 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (d, *J* = 6.8 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 2H), 7.56 – 7.45 (m, 6H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.41 (q, *J* = 7.2 Hz,

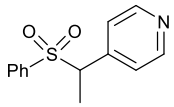
1H), 1.87 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.8, 133.6, 133.3, 132.9, 131.2, 129.2, 129.1, 128.7, 128.1, 128.0, 127.6, 126.7, 126.6, 126.4, 66.2, 14.7. HRMS (ESI-TOF) calcd for $C_{18}H_{16}O_2SNa$ $[M + Na]^+$: 319.0763; found: 319.0745.

3-((1-Phenylethyl)sulfonyl)pyridine (2ac)



Compound **2ac** was prepared following the general procedure C, starting from 3-((phenylsulfonyl)methyl)pyridine (**1ac**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2ac** was obtained as white solid (102.0 mg, 83% isolated yield). m.p. 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.53 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.18 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.26 – 7.23 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 1H), 1.77 (d, *J* = 7.2, Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.5, 150.0, 136.5, 136.4, 134.0, 129.9, 129.1, 129.0, 123.4, 63.5, 13.8. HRMS (ESI-TOF) calcd for $C_{13}H_{13}NO_2SNa$ $[M + Na]^+$: 270.0559; found: 270.0577.

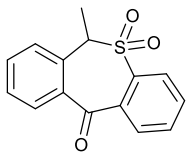
4-((1-Phenylethyl)sulfonyl)pyridine (2ad)



Compound **2ad** was prepared following the general procedure C, starting from 4-((phenylsulfonyl)methyl)pyridine (**1ad**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2ad** was obtained as white solid (106.0 mg, 86% isolated yield). m.p. 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.50 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.62 – 7.57 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.08 (dd, *J* = 4.4, 1.6 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.76 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.9, 142.9, 136.3, 134.1, 129.2, 129.0, 124.2, 65.2, 13.6. HRMS (ESI-TOF) calcd for $C_{13}H_{13}NO_2SNa$ $[M + Na]^+$: 270.0559; found: 270.0569.

Analytic Data of product 4

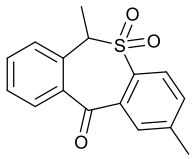
6-Methyldibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (4a)



Compound **4a** was prepared following the general procedure C, starting from 4-((phenylsulfonyl)methyl)pyridine (**3a**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by

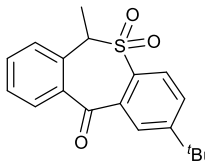
column chromatography, **2ab** was obtained as white solid (88.0 mg, 65% isolated yield). m.p. 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 – 8.04 (m, 2H), 7.91 (dd, *J* = 6.0, 3.6 Hz, 1H), 7.76 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.58 (td, *J* = 7.6, 1.2 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.69 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ δ 193.3, 137.6, 136.9, 134.7, 134.4, 134.0, 133.4, 132.4, 131.6, 130.8, 130.4, 128.8, 127.2, 65.4, 18.9. HRMS (ESI-TOF) calcd for $C_{15}H_{12}O_3SNa$ $[M + Na]^+$: 295.0399; found: 295.0400.

2,6-Dimethyldibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (4b)



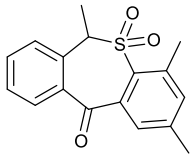
Compound **4b** was prepared following the general procedure C, starting from 4-((phenylsulfonyl)methyl)pyridine (**3b**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2ab** was obtained as white solid (89.0 mg, 62% isolated yield). m.p. 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.59 – 7.53 (m, 2H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 4.67 (q, *J* = 7.2 Hz, 1H), 2.49 (s, 3H), 1.56 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 193.6, 145.2, 137.6, 136.9, 134.9, 133.4, 132.9, 131.6, 131.5, 131.2, 130.5, 128.7, 127.4, 65.4, 21.6, 19.0. HRMS (ESI-TOF) calcd for $C_{16}H_{14}O_3SNa$ $[M + Na]^+$: 309.0556; found: 309.0561.

2-(*tert*-Butyl)-6-methyldibenzo[b,e]thiepin-11(6*H*)-one 5,5-dioxide (4c)



Compound **4c** was prepared following the general procedure C, starting from 4-((phenylsulfonyl)methyl)pyridine (**3c**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2ab** was obtained as white solid (95.0 mg, 58% isolated yield). m.p. 234-236 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.57 (td, *J* = 7.2, 1.2 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 4.67 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 193.9, 158.0, 137.4, 137.1, 134.6, 133.2, 131.8, 131.5, 130.4, 129.6, 128.7, 127.7, 127.3, 65.3, 35.5, 31.0, 18.7. HRMS (ESI-TOF) calcd for $C_{19}H_{20}O_3SNa$ $[M + Na]^+$: 351.1025; found: 351.1026.

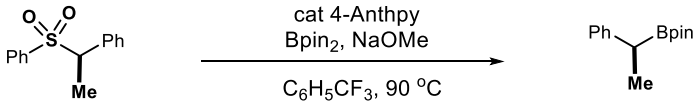
2,4,6-Trimethyldibenzo[*b,e*]thiepin-11(6*H*)-one (4d)



Compound **4d** was prepared following the general procedure C, starting from 4-((phenylsulfonyl)methyl)pyridine (**4d**, 0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, **2ab** was obtained as white solid (90.0 mg, 60% isolated yield). m.p. 200-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.54 (td, *J* = 7.2, 1.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.27 (s, 1H), 4.70 (q, *J* = 7.2 Hz, 1H), 2.77 (s, 3H), 2.40 (s, 3H), 1.72 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.3, 143.7, 139.3, 139.2, 139.0, 137.1, 132.9, 132.5, 131.1, 129.2, 129.1, 128.7, 128.5, 64.9, 21.2, 20.7, 16.0. HRMS (ESI-TOF) calcd for $C_{17}H_{16}O_3SNa$ $[M + Na]^+$: 323.0712; found: 323.0722.

5. Transformations

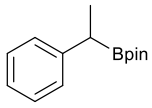
Desulfonative coupling for the synthesis of 5a[3]



2a **5a**, 65%

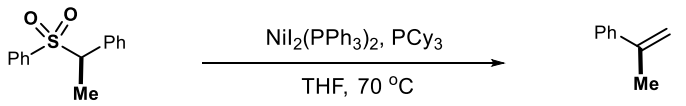
In a nitrogen-atmosphere glove box, 4-anthracenyl pyridine (5-10 mol%), NaOMe (1.3 equiv), B_2pin_2 (2.0 equiv), and sulfone **2a** (1.0 equiv) were weighed, followed by $C_6H_5CF_3$ (1 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 90 ºC for 24 h. The reaction mixture was cooled down to room temperature. The reaction was quenched with sat. NH_4Cl_{aq} and extracted with EtOAc three times. The collected organic phase was dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography to afford the **5a** in 95.0 mg, 65% yield.

4,4,5,5-*tetra*-Methyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (5a)[4]



^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.20 (s, 6H), 1.21 (s, 6H), 1.33 (d, *J* = 7.6 Hz, 3H), 2.43 (q, *J* = 7.6 Hz, 1H), 7.12 – 7.15 (m, 1H), 7.21 -7.28 (m, 4H). The product was characterized by comparison with previously reported ^{1}H and ^{13}C NMR data.

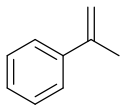
Desulfonative coupling for the synthesis of 6a[5]



2a **6a**, 71%

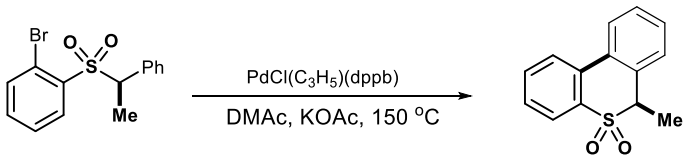
To a Schlenk tube were added sulfone **2a** (0.5 mmol) and methylmagnesium bromide (2.5 mmol), $NiI_2(PPh_3)_2$ (5.0 mol %), PCy_3 (10.0 mol %) and THF (2.0 mL). Then the tube was charged with argon, and stirred at 70 ºC overnight until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford the **6a** in 42.0 mg, 71% yield.

Prop-1-en-2-ylbenzene (6a)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ: 7.48 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.29-7.07 (m, 1H), 5.38 (s, 1H), 5.09 (s, 1H), 2.16 (s, 3H). The product was characterized by comparison with previously reported ^{1}H and ^{13}C NMR data.

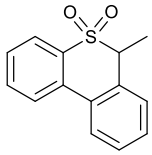
Pd-Catalyzed intramolecular coupling the synthesis of 7g[6]



2h **7h**, 35%

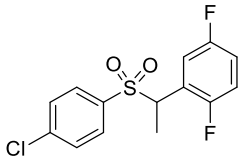
The reaction of 1-bromo-2-((1-phenylethyl)sulfonyl)benzene (**2g**, 0.4 mmol), Cs_2CO_3 (0.8 mmol), KOAc (0.8 mmol) at 150 °C during 16 h in DMAc (4.0 mL) in the presence of $PdCl(C_3H_5)(dppb)$ (5.0 mol %) under argon affords the coupling product after addition of water (20 mL), extraction with dichloromethane (20 mL), drying on $MgSO_4$, evaporation and purification on silica gel to give **7g** in 34.0 mg, 35% yield.

6-Methyl-6*H*-benzo[*c*]thiochromene 5,5-dioxide Prop-1-en-2-ylbenzene (7g)



White solid, m.p. 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 2H), 7.73 (td, *J* = 7.2, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.42 (td, *J* = 7.2, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.0, 134.2, 133.8, 132.9, 130.1, 129.7, 129.4, 129.1, 128.9, 126.7, 126.2, 125.2, 58.4, 14.7. HRMS (ESI-TOF) calcd for $C_{14}H_{12}O_2SNa$ $[M + Na]^+$: 267.0540; found: 267.0544.

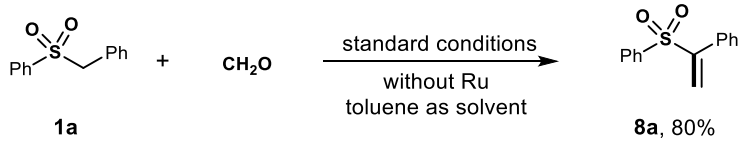
2-(1-((4-chlorophenyl)sulfonyl)ethyl)-1,4-difluorobenzene (compound B)



Compound **B** was prepared following the general procedure D, starting from 2-(((4-chlorophenyl)sulfonyl)methyl)-1,4-difluorobenzene (0.5 mmol) and CH_3OH (2.0 mL). After purification by column chromatography, Compound **B** was obtained as white solid (86.9 mg, 55% isolated yield). m.p. 192-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.20 (ddd, *J* = 8.8, 5.2, 3.2 Hz, 1H), 6.96 (ddd, *J* = 11.2, 6.4, 3.2 Hz, 1H), 6.83 (td, *J* = 9.2, 4.4 Hz, 1H), 4.65 (q, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.8 (dd, *J* = 214.7, 2.5 Hz), 156.4 (dd, *J* = 215.5, 2.5 Hz), 140.7, 135.4, 130.4, 129.2, 122.8 (dd, *J* = 16.1, 7.9 Hz), 117.4 (dd, *J* = 24.1, 8.8 Hz), 116.4 (dd, *J* = 25.6, 8.6 Hz), 116.1 (dd, *J* = 25.2, 2.9 Hz), 57.2, 13.3. ^{119}F NMR (376 MHz, Chloroform-*d*) δ -116.8 (d, *J* = 17.7 Hz), -122.7 (d, *J* = 17.6 Hz). HRMS (ESI-TOF) calcd for $C_{14}H_{11}ClF_2O_2SNa$ $[M + Na]^+$: 339.0028; found: 339.0030.

6. Mechanism Studies

Synthesis of 8a with paraformaldehyde

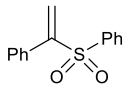


1a **8a**, 80%

A mixture of KOH (1.0 mmol), paraformaldehyde, sulfone **1a** (1.0 mmol) and toluene (5.0 mL)

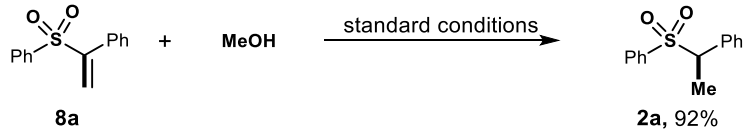
was stirred at 120 °C for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give **8a** in 195.0 mg, 80% yield.

(1-(Phenylsulfonyl)vinyl)benzene (8a)[7]



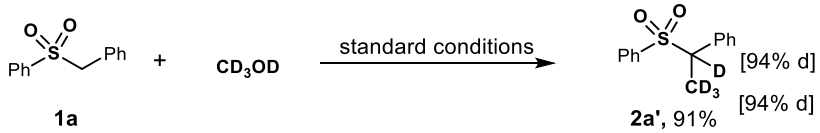
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 – 7.64 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.26 (m, 5H), 6.57 (s, 1H), 6.29 (s, 1H). The product was characterized by comparison with previously reported ^{1}H and ^{13}C NMR data.

Subjecting 8a to MeOH under standard conditions



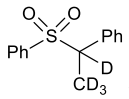
A mixture of [Ru(cod)Cl_2] (2.5 mol % mmol), dppe (3.5 mol % mmol), KOH (0.5 mmol), aryl sulfone **8a** (0.5 mmol) and methanol (2.0 mL) was stirred at 120 °C for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1-10:1) to give the methylated product **2a** in 113.0 mg, 92% yield.

Deuterium labeling reaction using methanol-*d*$_4$



A mixture of [Ru(cod)Cl_2] (2.5 mol % mmol), dppe (3.5 mol % mmol), KOH (0.5 mmol), aryl sulfone **8a** (0.5 mmol) and methanol-d_4 (2.0 mL) was stirred at 120 °C for 24 h under Ar in a pressure tube (ACE pressure tube, 15 mL). After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1-10:1) to give the methylated product **2a'** in 112.0 mg, 91% yield with 94% deuteration.

((1-Phenylethyl-1,2,2,2-d$_4$)sulfonyl)benzene (2a')



m.p. 134-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59 – 7.51 (m, 3H), 7.43 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 7.14 – 7.11 (m, 2H). HRMS (ESI-TOF) calcd for $C_{14}H_{10}D_4NaO_2S$ $[M + Na]^+$: 273.0858; found: 273.0870.

7. Reference

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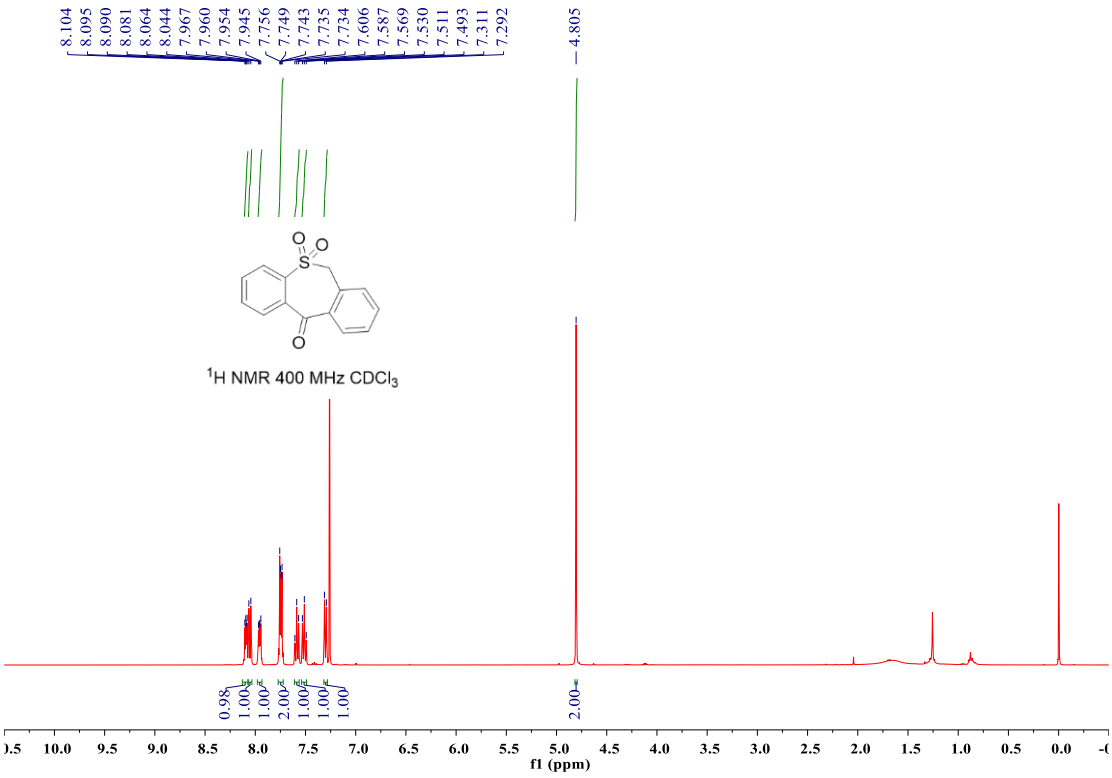
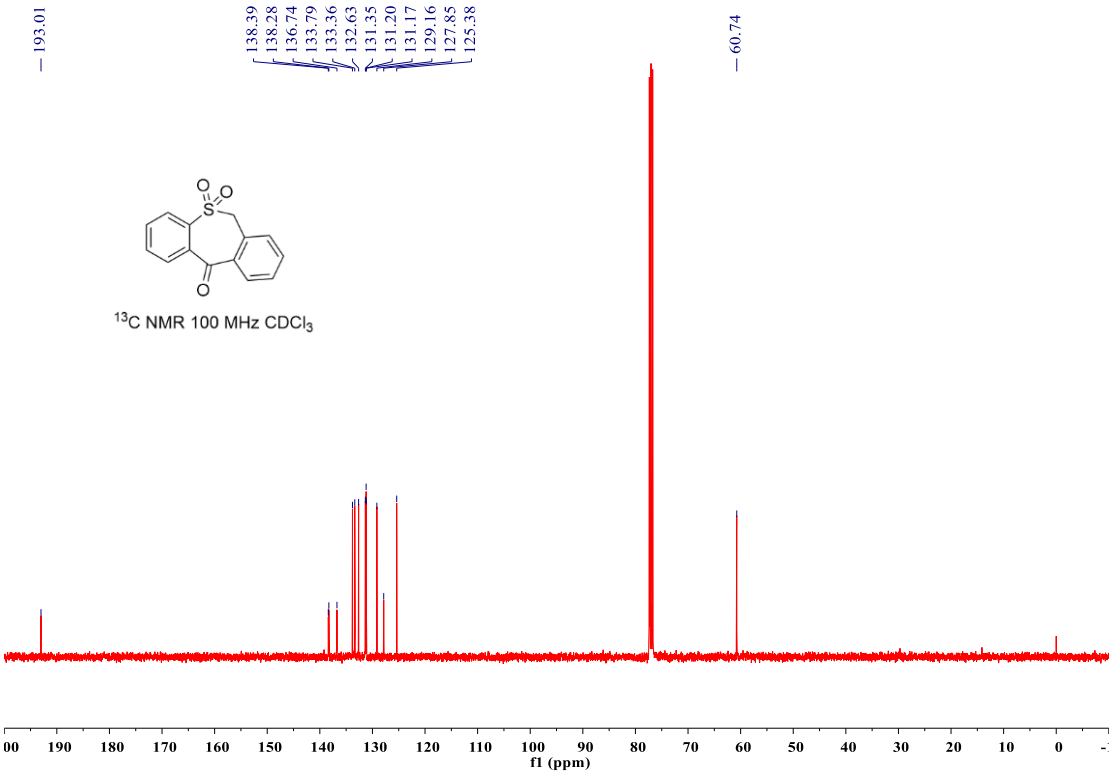
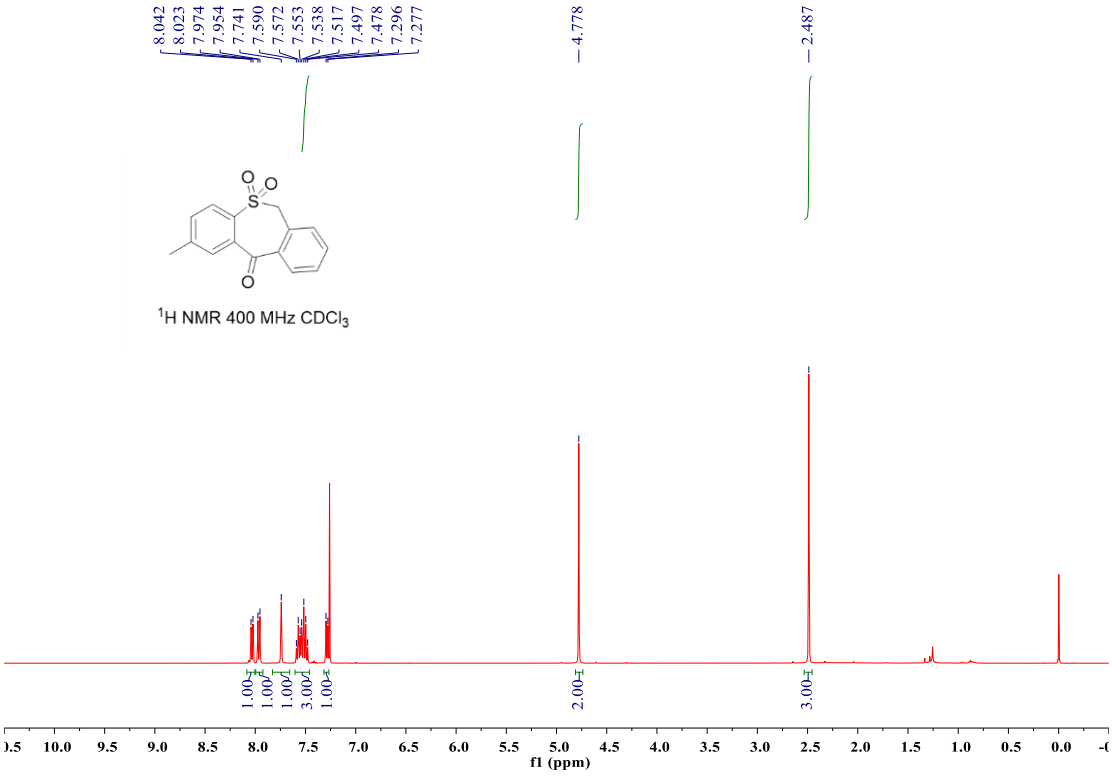
Copies of NMR Spectrum

Dibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (3a)

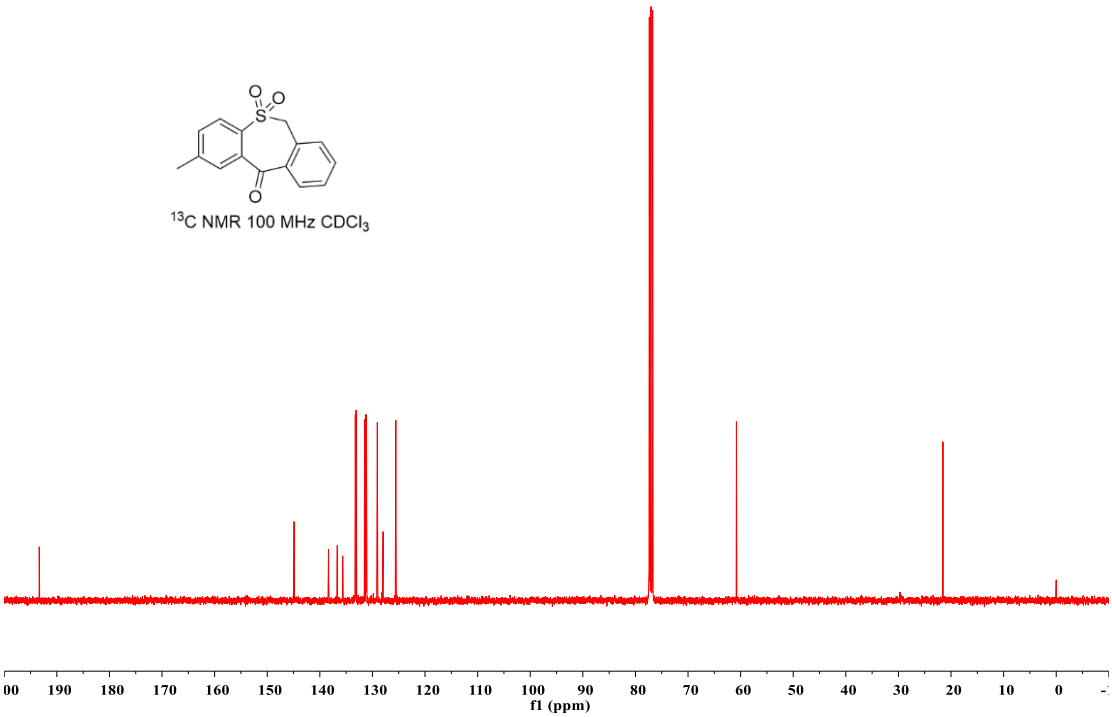




2-Methyldibenzo[*b*,*e*]thiepin-11(6H)-one 5,5-dioxide (3b)

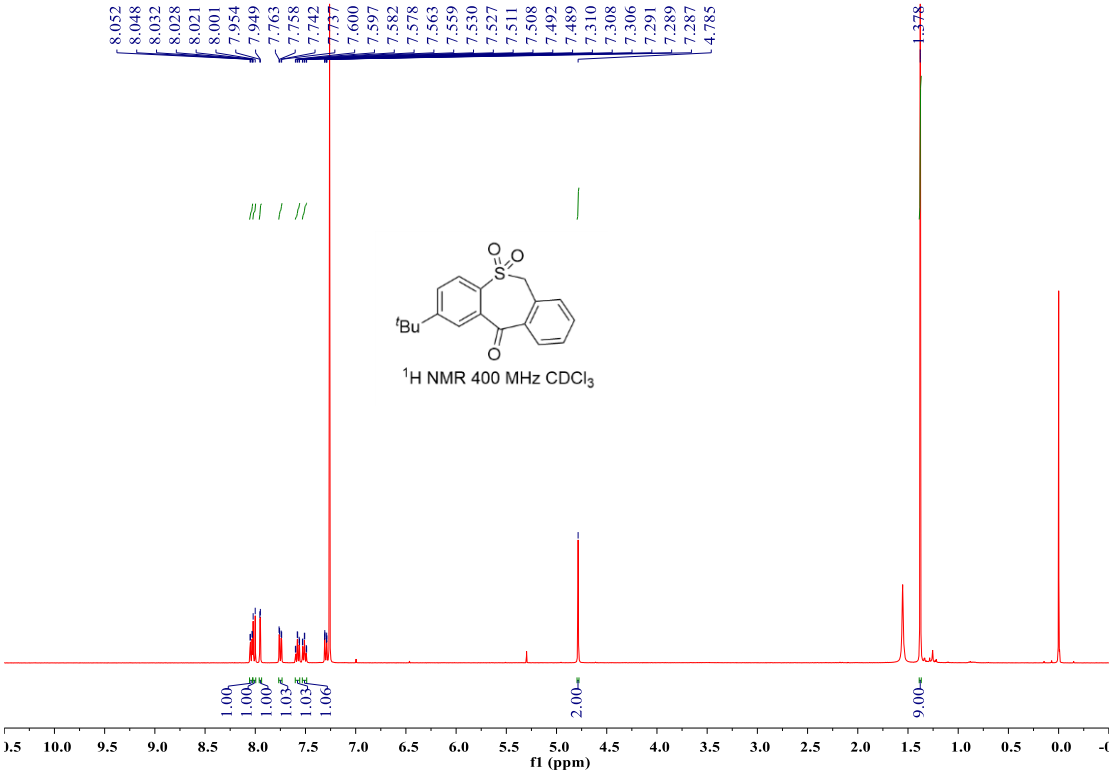


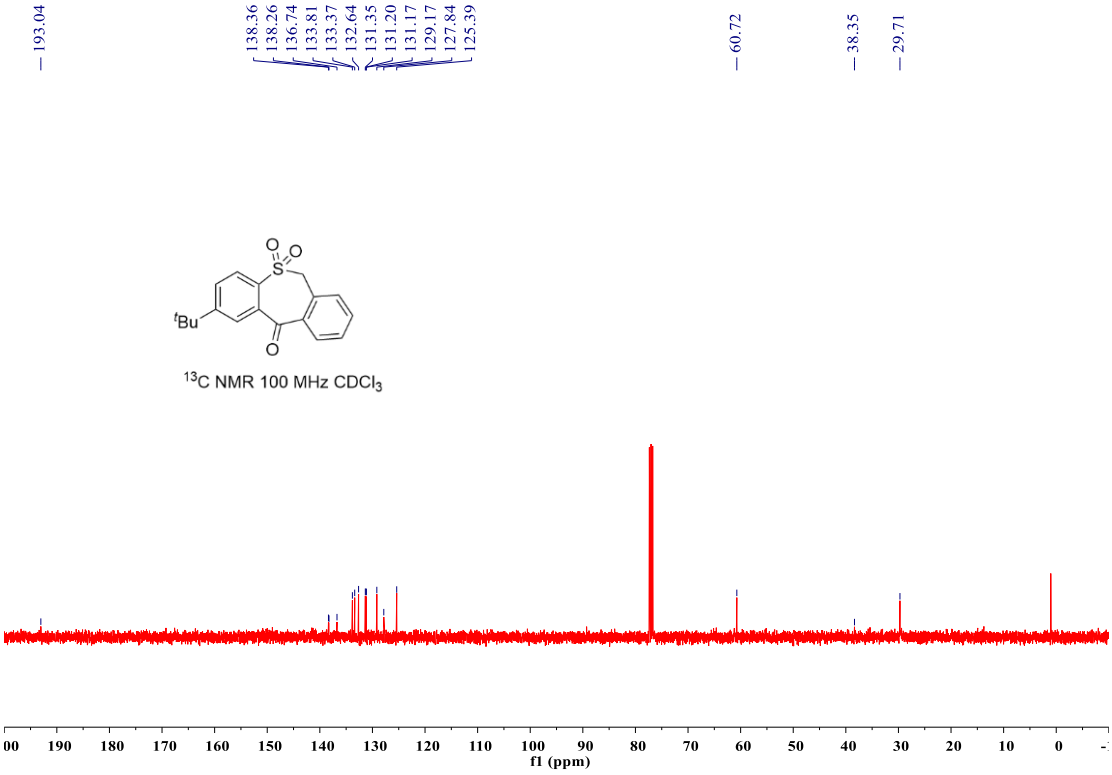
^{1}H NMR 400 MHz $CDCl_3$



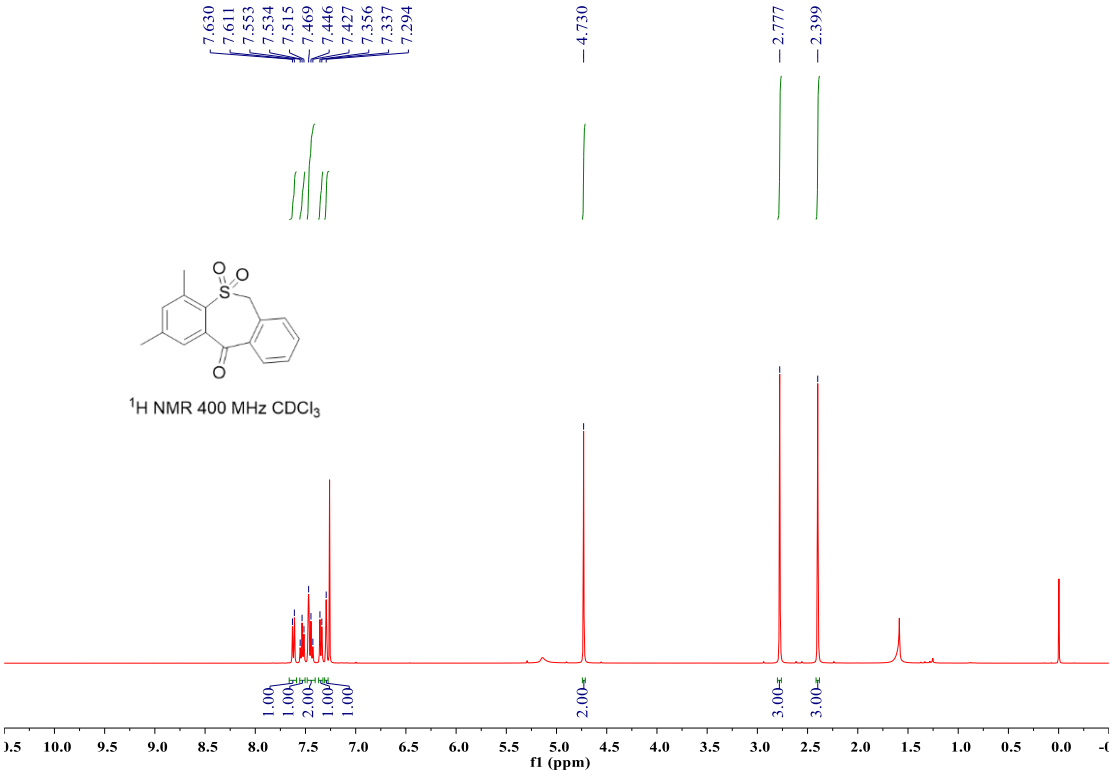
^{13}C NMR 100 MHz $CDCl_3$

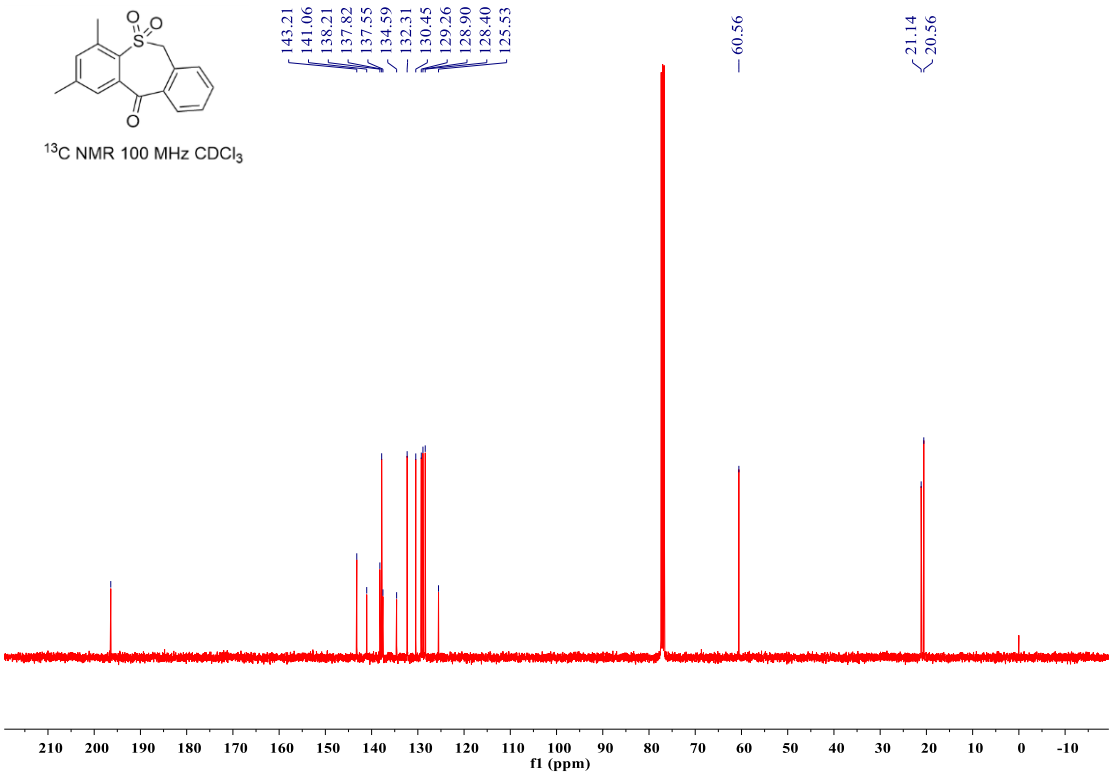
2-(*tert*-Butyl)dibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (3c)



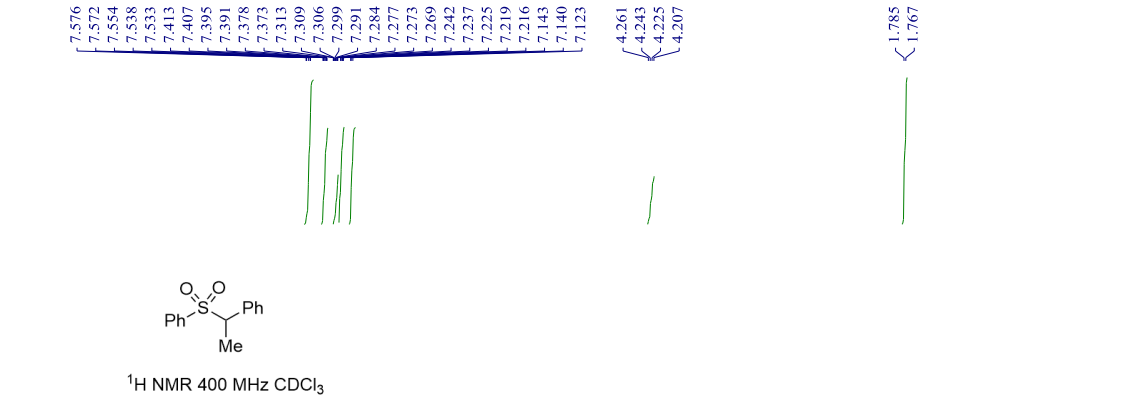


2,4-Dimethyldibenzo[*b,e*]thiepin-11(6*H*)-one 5,5-dioxide (4d)

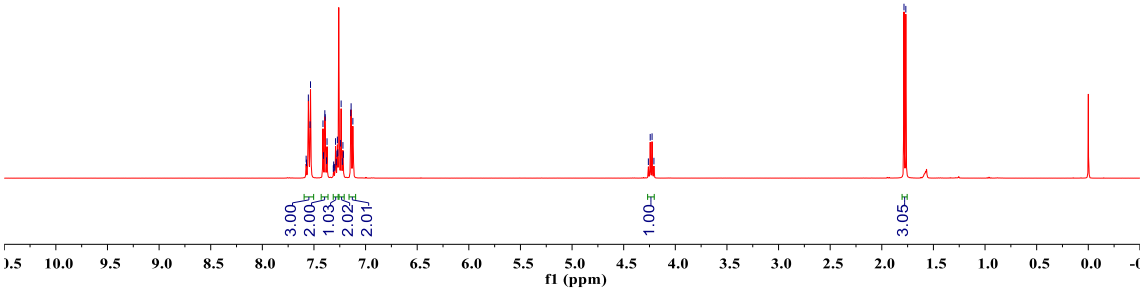


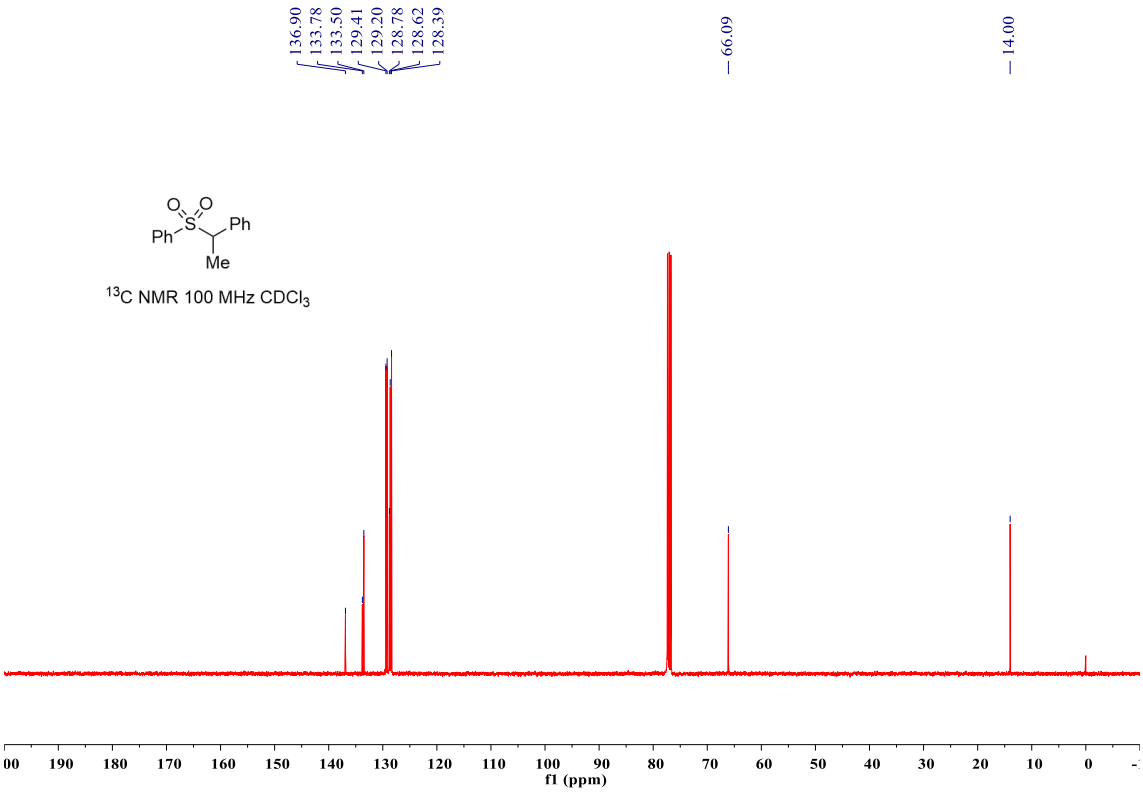


((1-Phenylethyl)sulfonyl)benzene (2a)



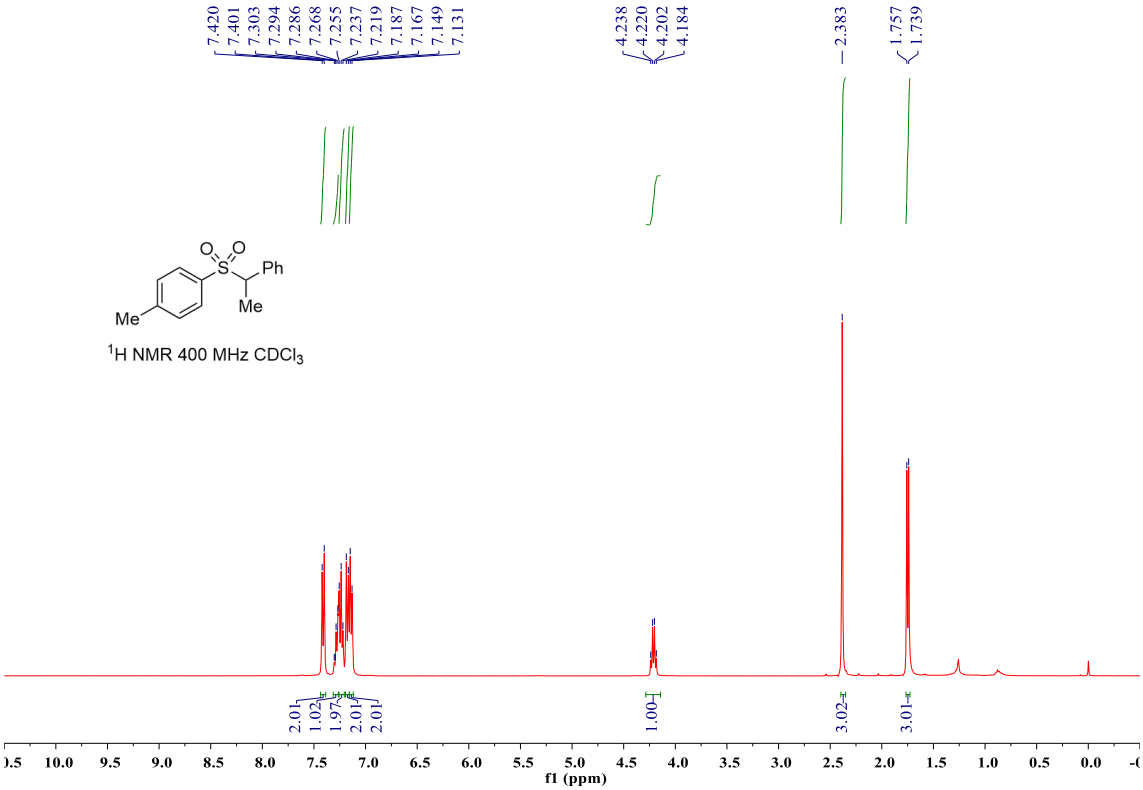
^{1}H NMR 400 MHz $CDCl_3$

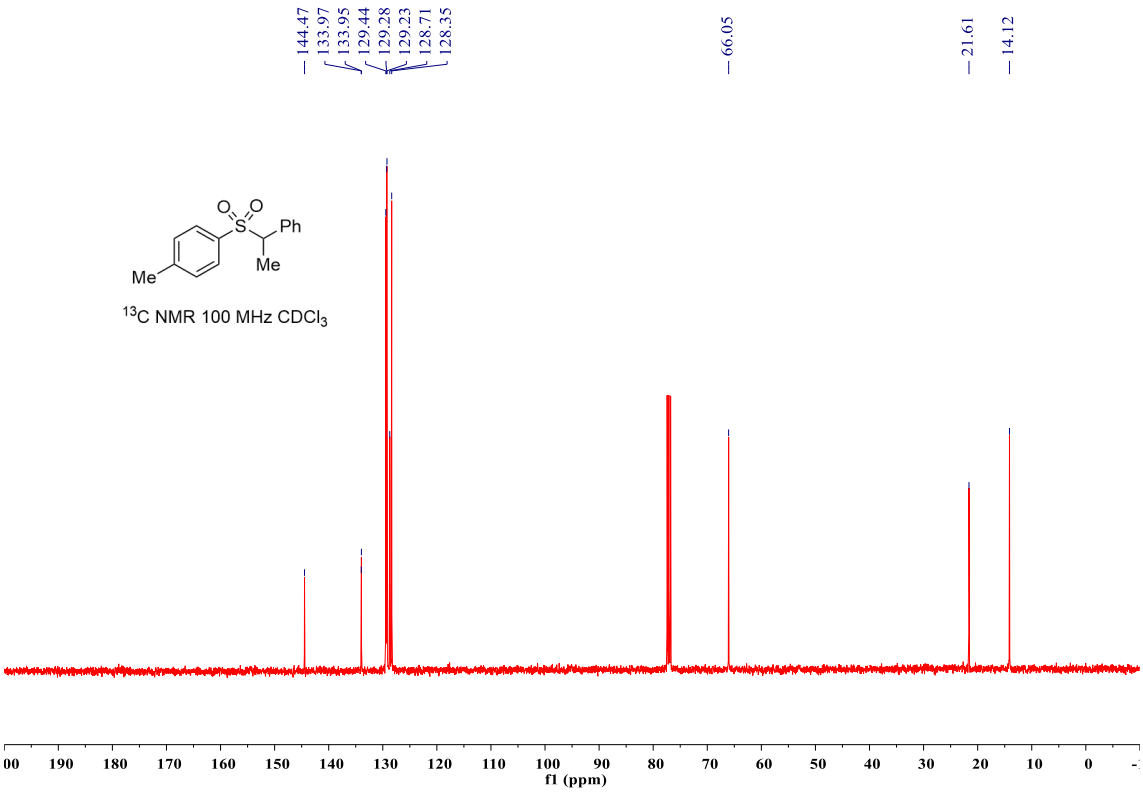




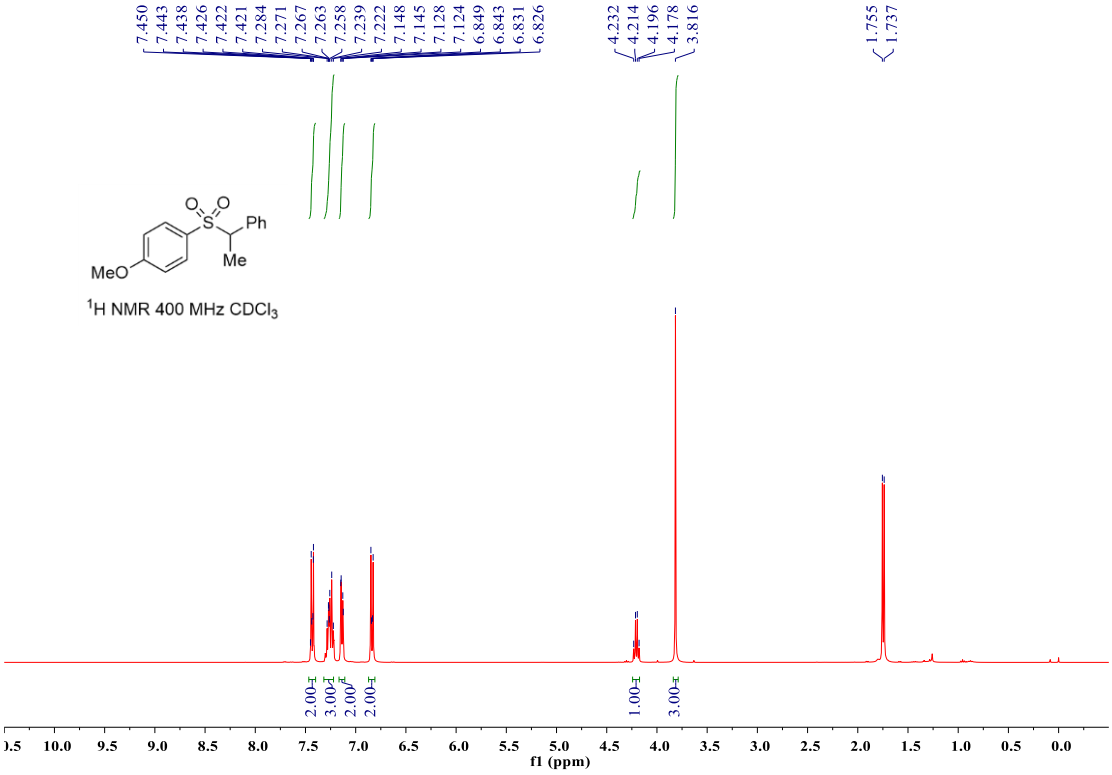
^{13}C NMR 100 MHz $CDCl_3$

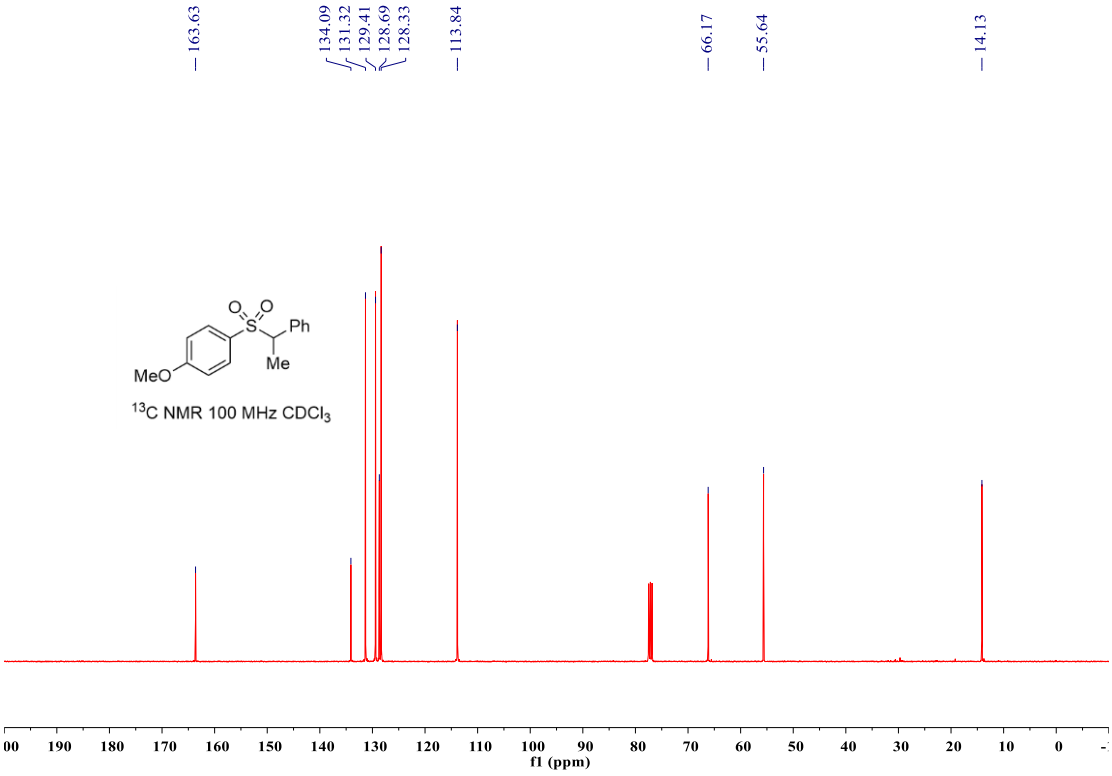
1-Methyl-4-(1-(phenylsulfonyl)ethyl)benzene (2b)



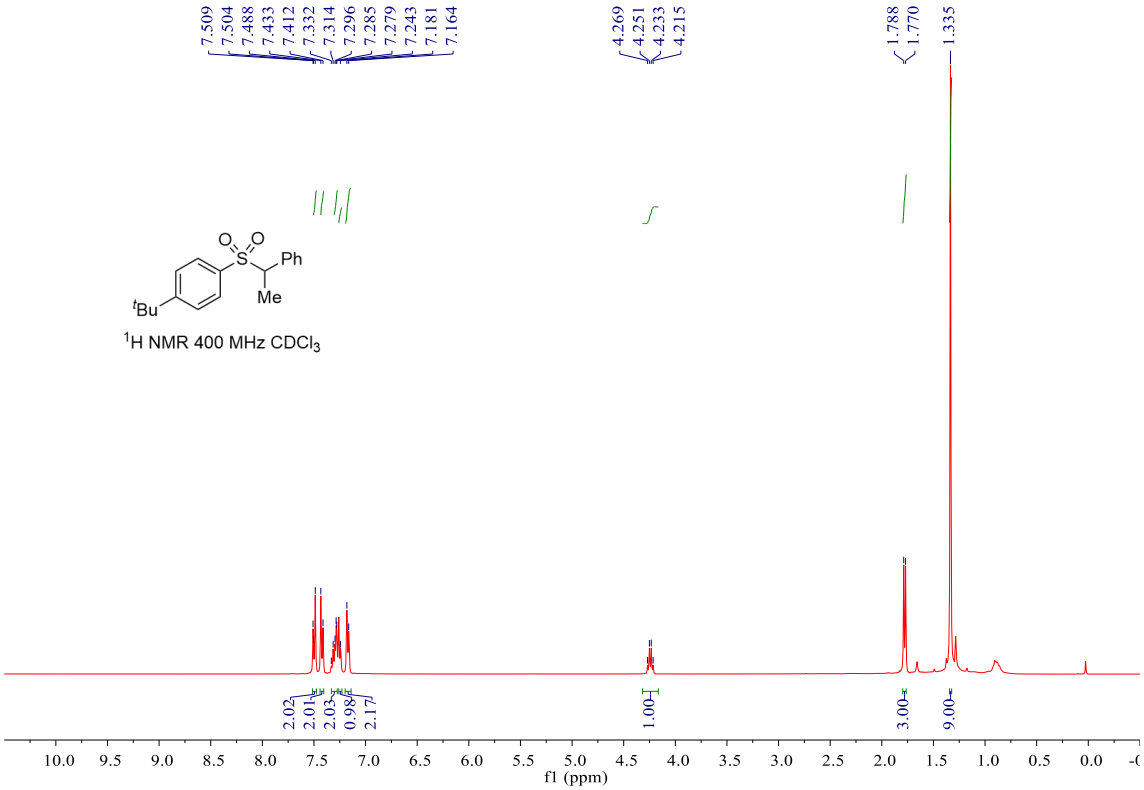


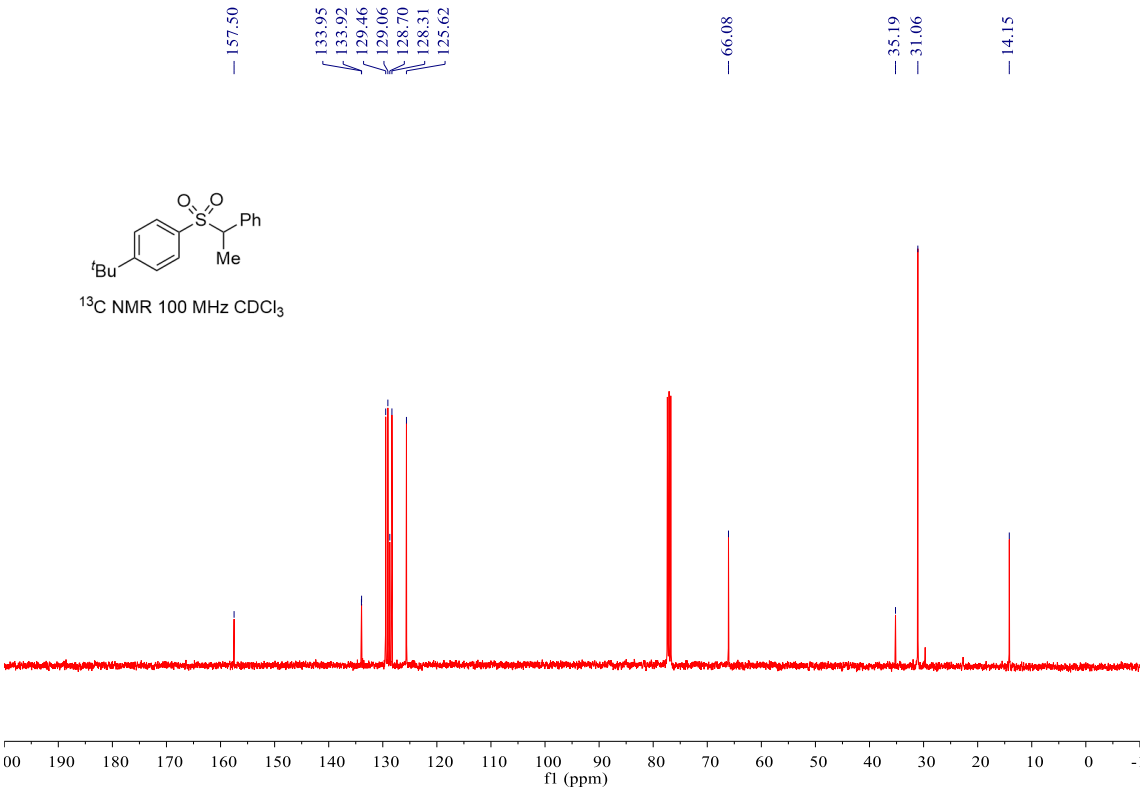
1-Methoxy-4-(1-(phenylsulfonyl)ethyl)benzene (2c)



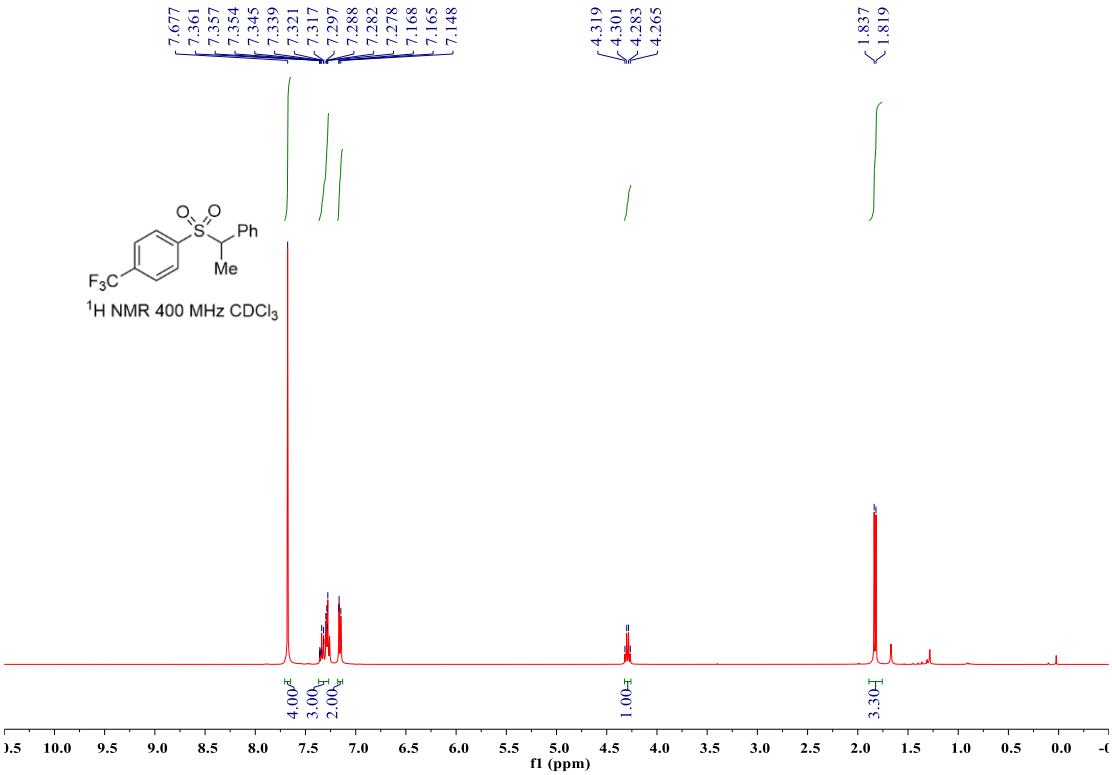


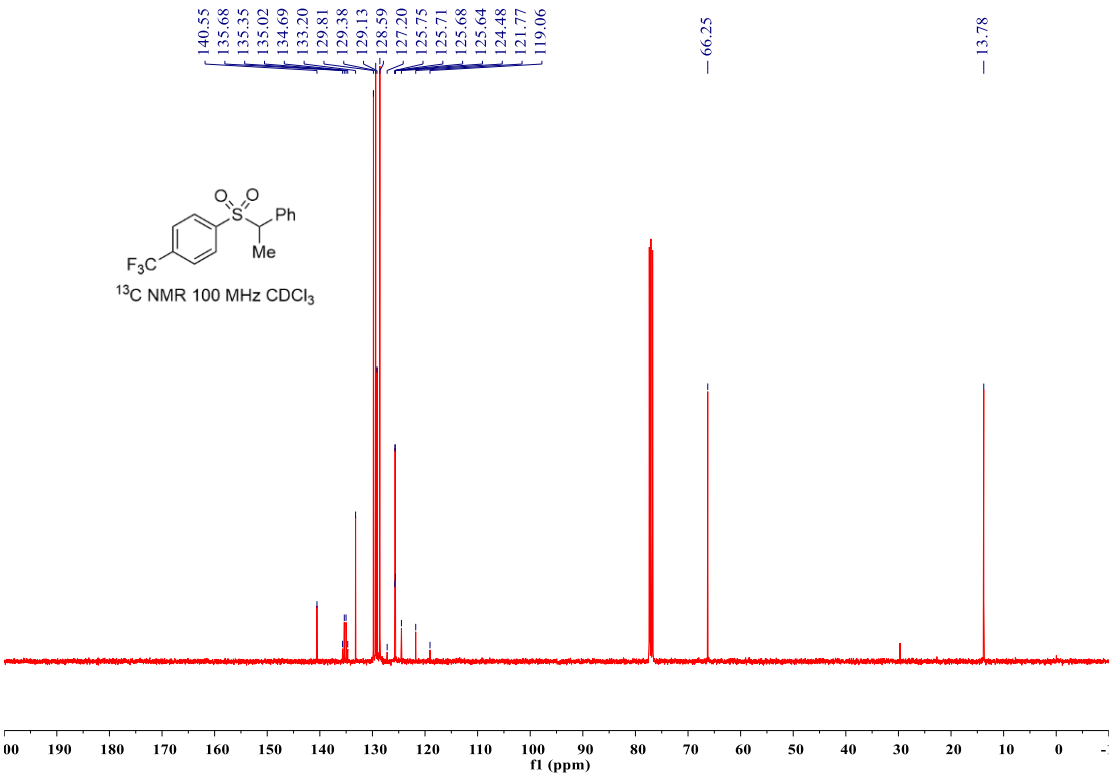
1-(*tert*-Butyl)-4-((1-phenylethyl)sulfonyl)benzene (2d)

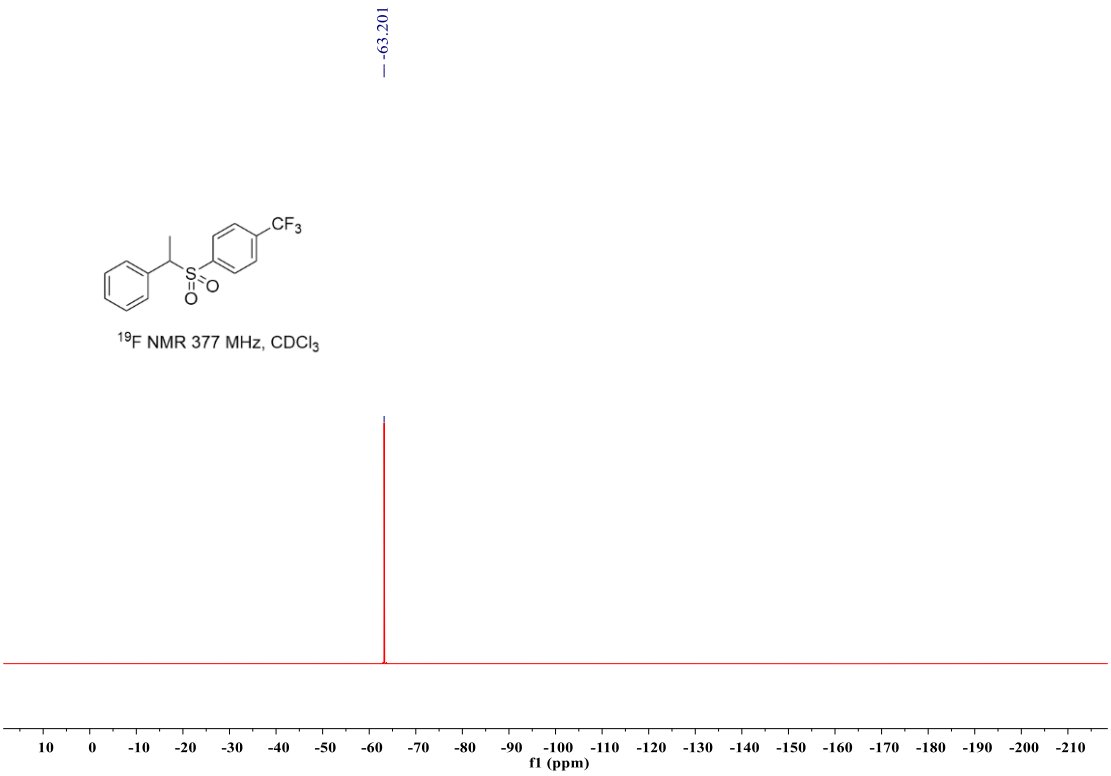




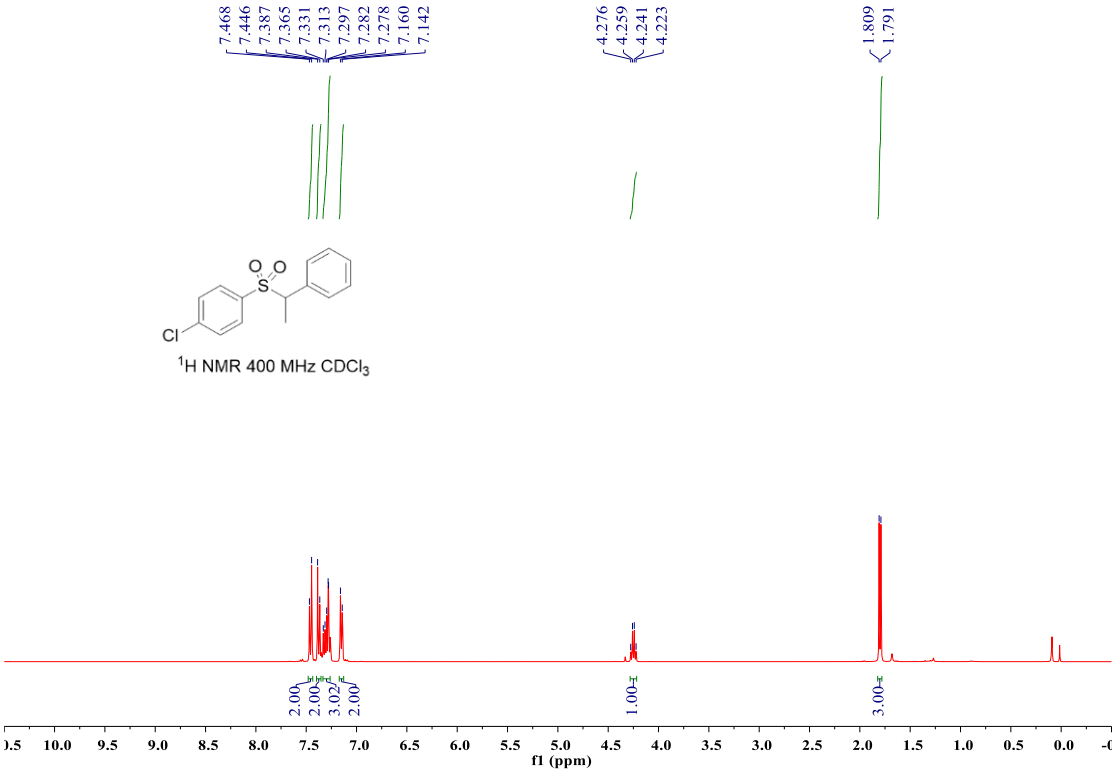
1-((1-Phenylethyl)sulfonyl)-4-(trifluoromethyl)benzene (2e)

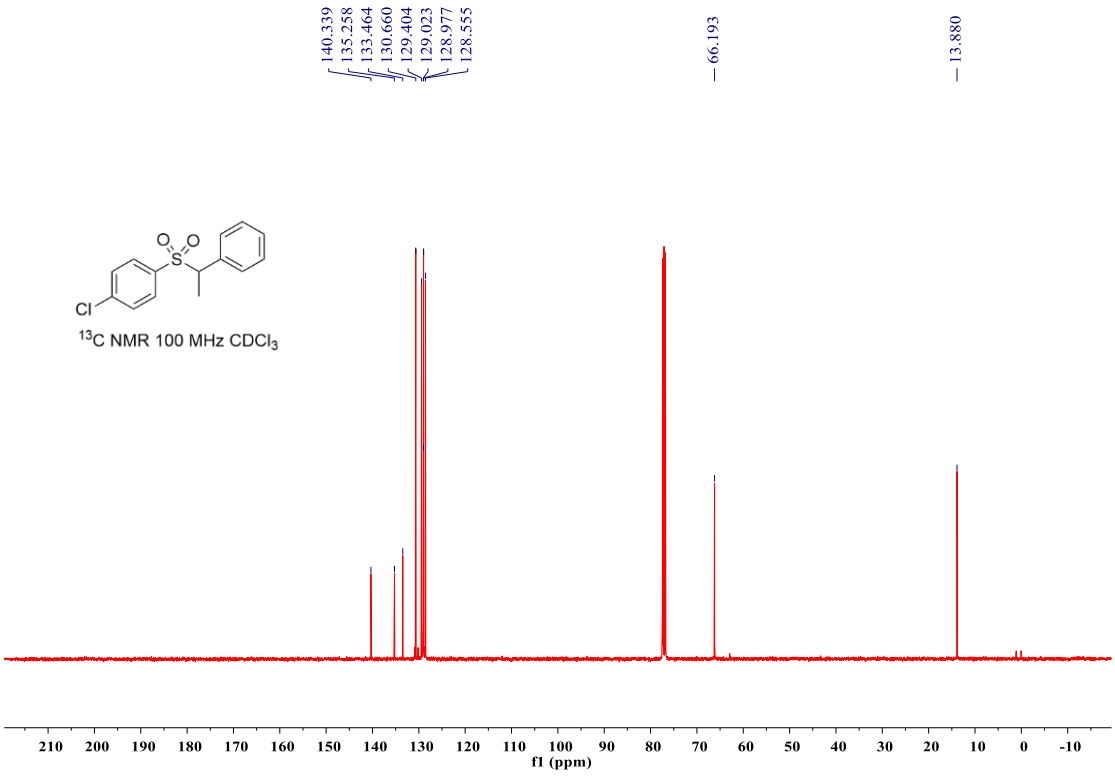




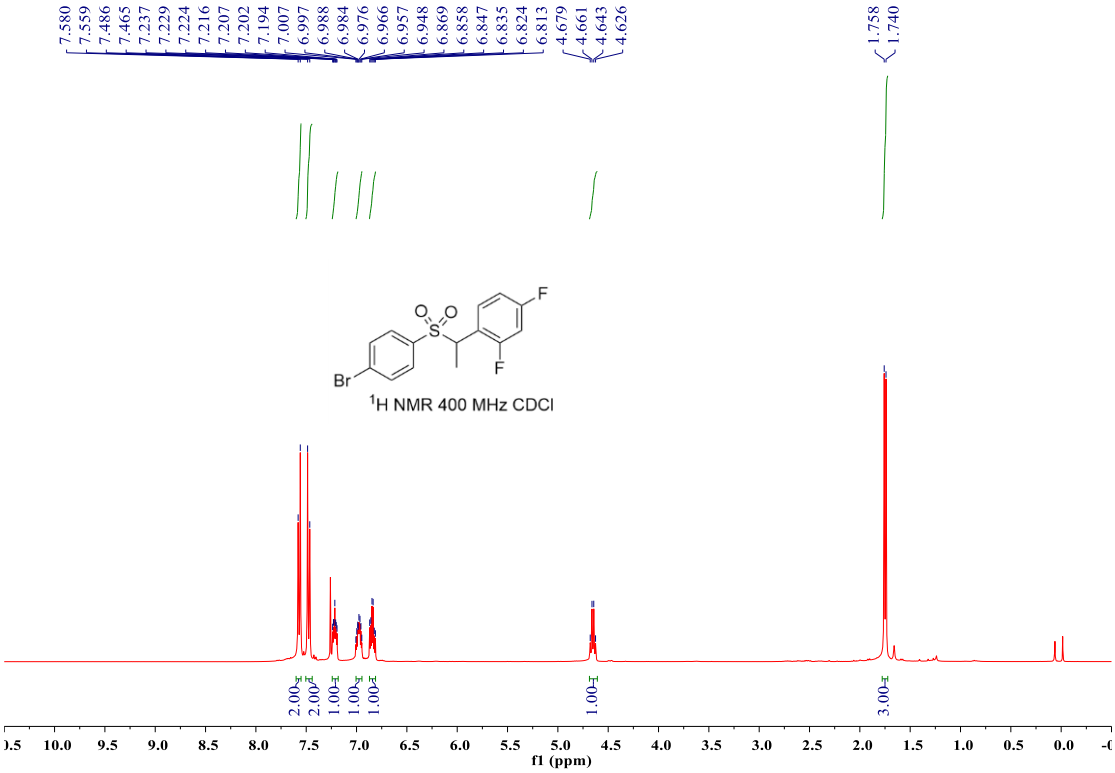

-63.201
CF3
S
O
O
19F NMR 377 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

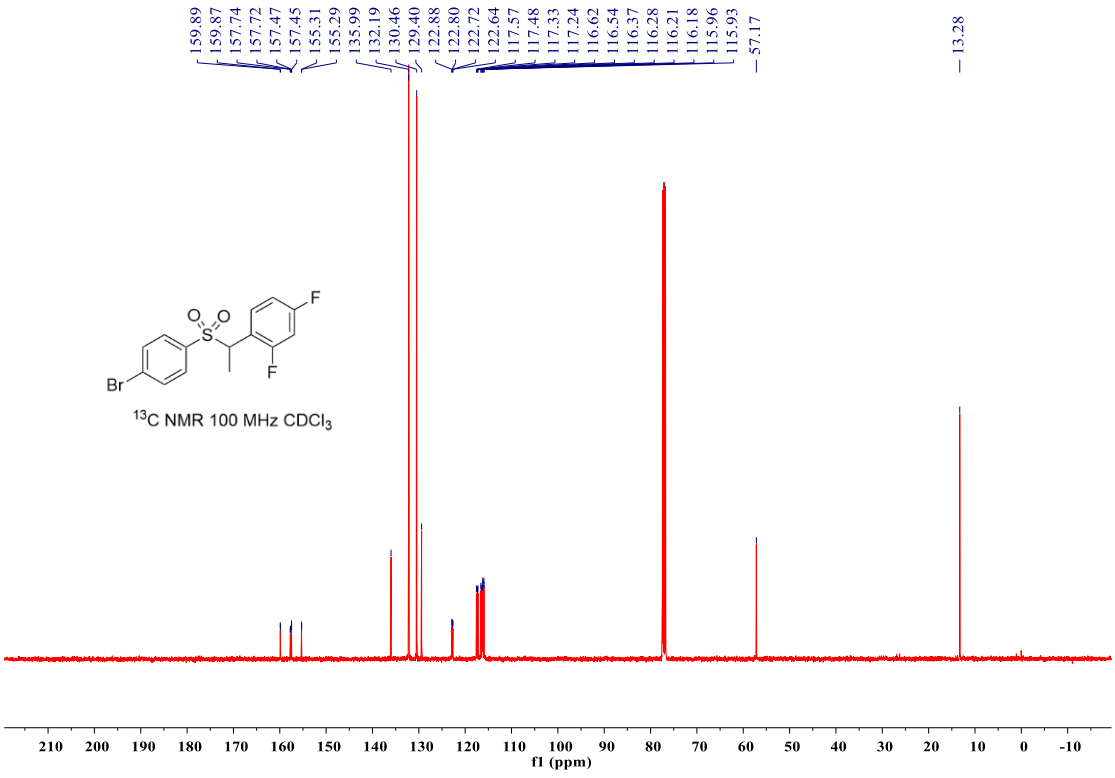
1-chloro-4-((1-phenylethyl)sulfonyl)benzene (2f)

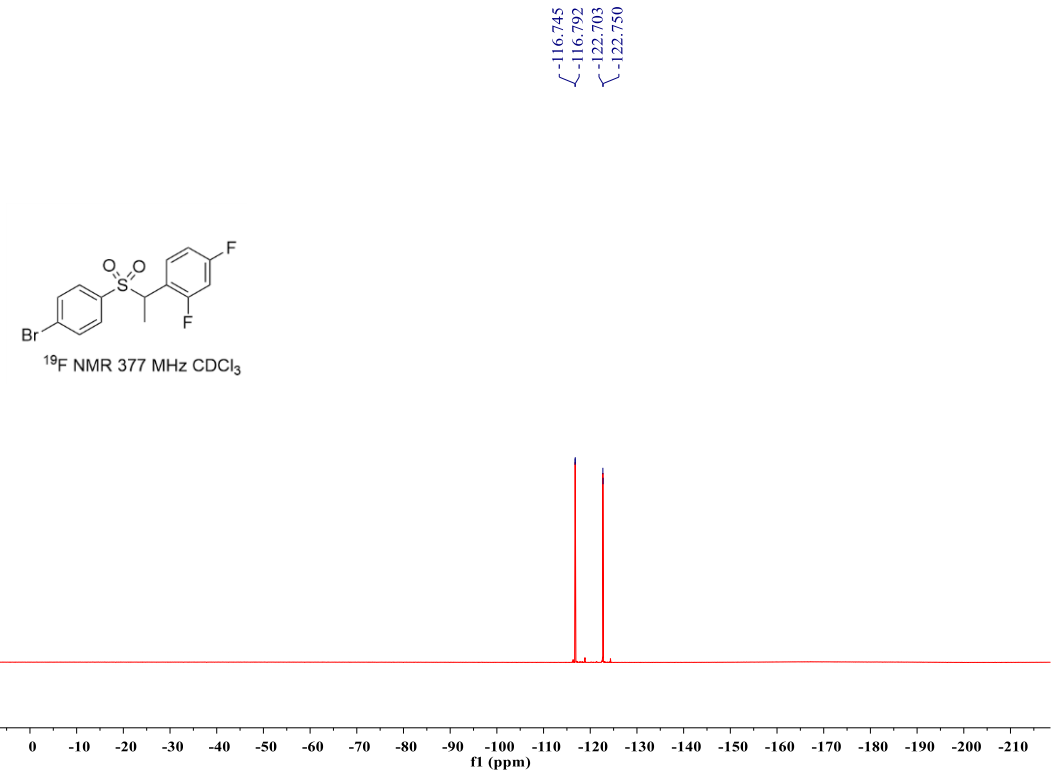




2-(1-((4-bromophenyl)sulfonyl)ethyl)-1,4-difluorobenzene (2g)

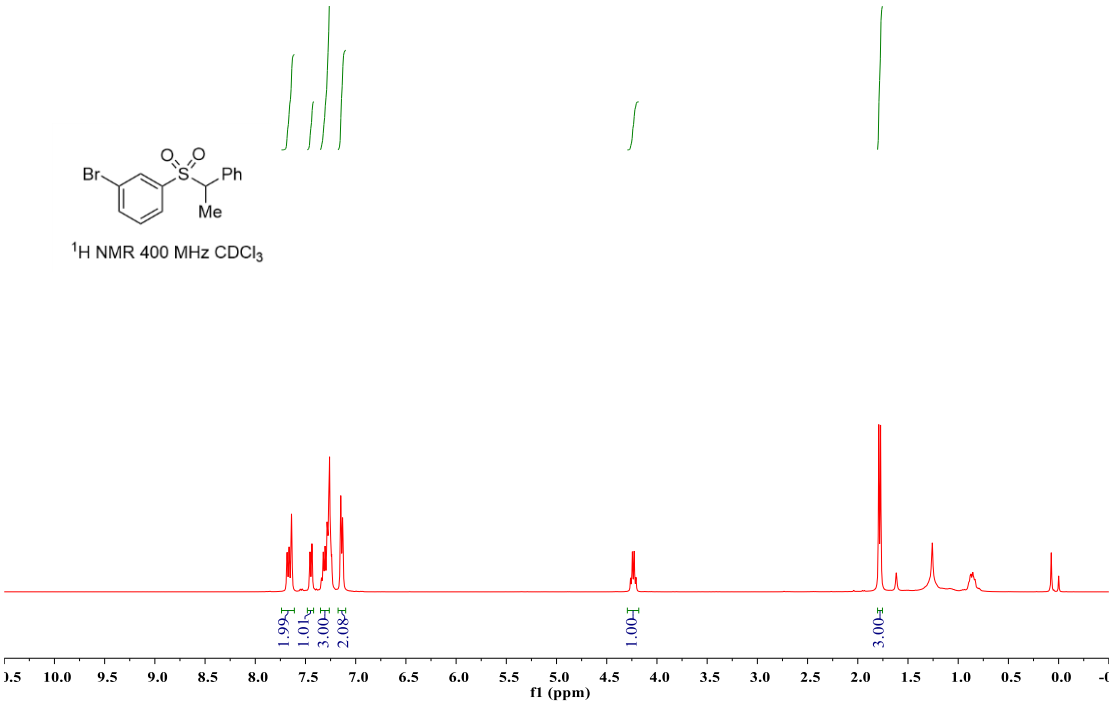


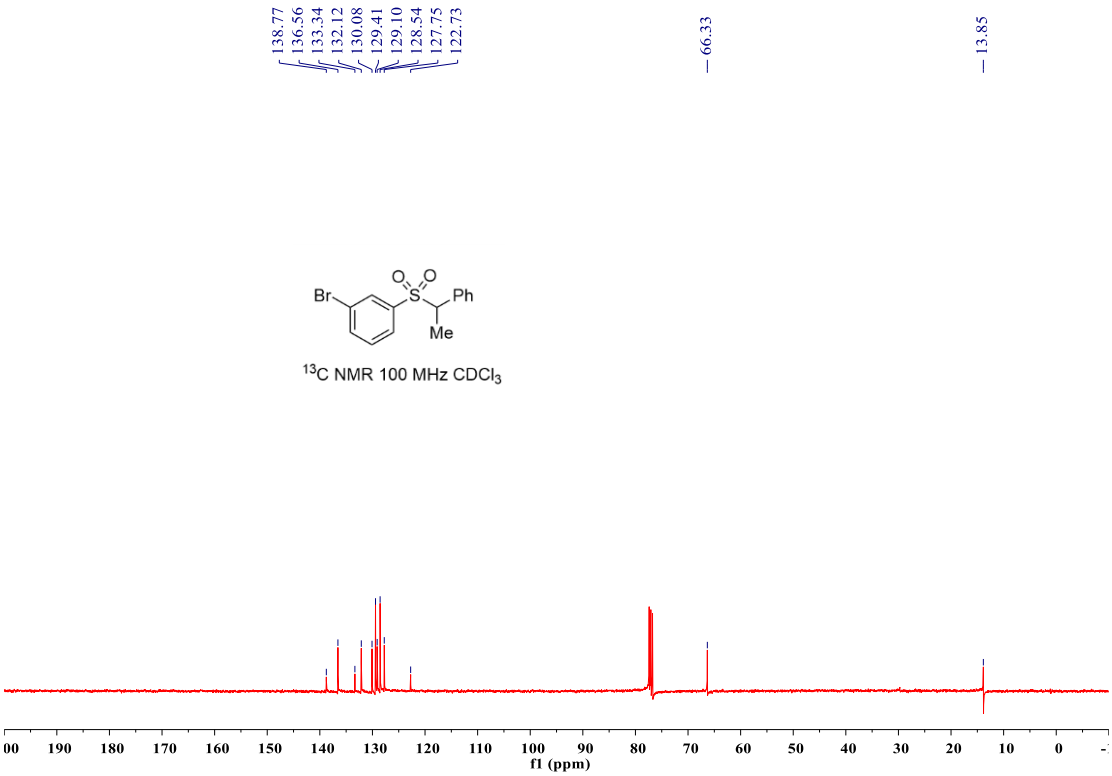




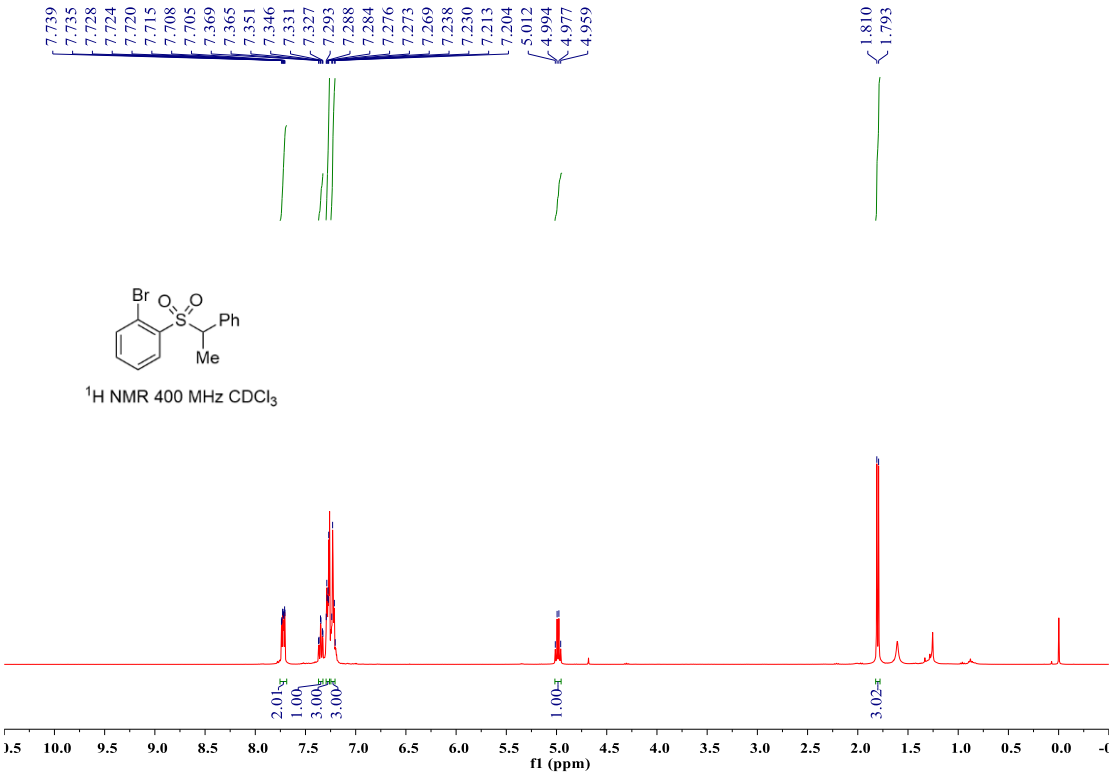
^{19}F NMR 377 MHz $CDCl_3$

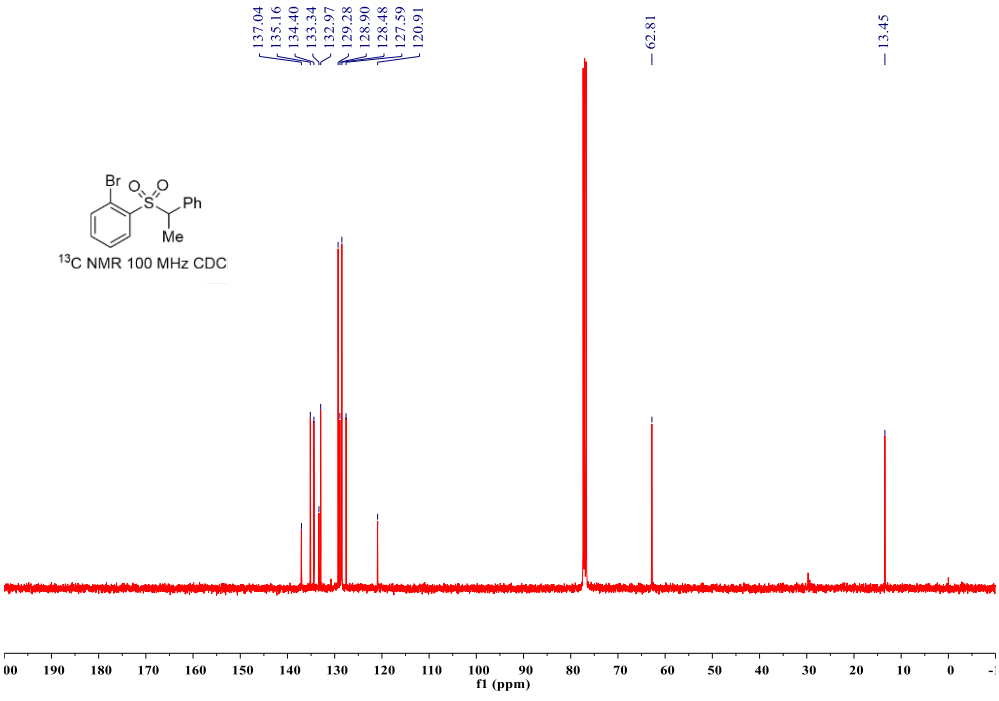
1-Bromo-3-((1-phenylethyl)sulfonyl)benzene (2h)



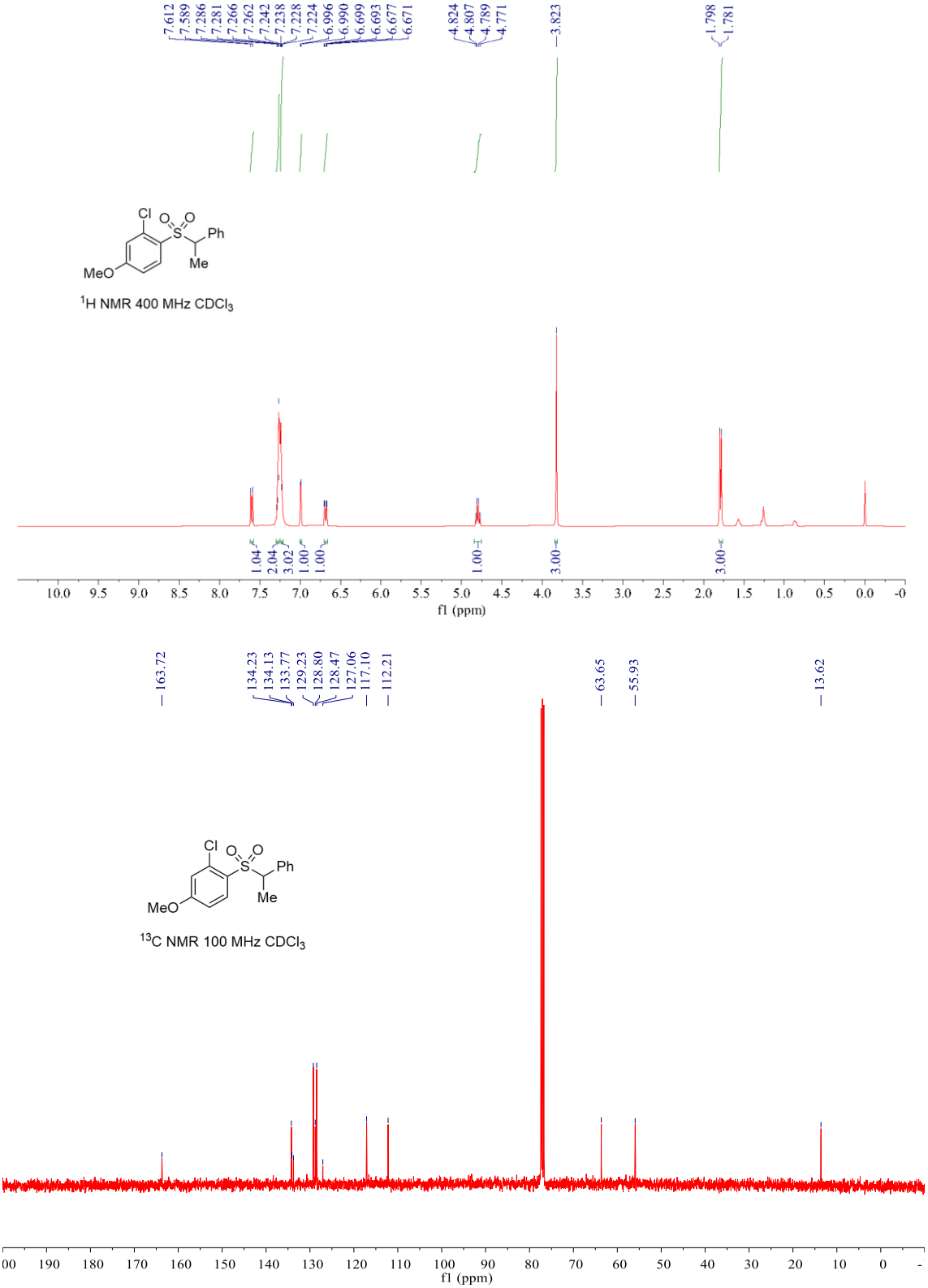


1-Bromo-2-((1-phenylethyl)sulfonyl)benzene (2i)

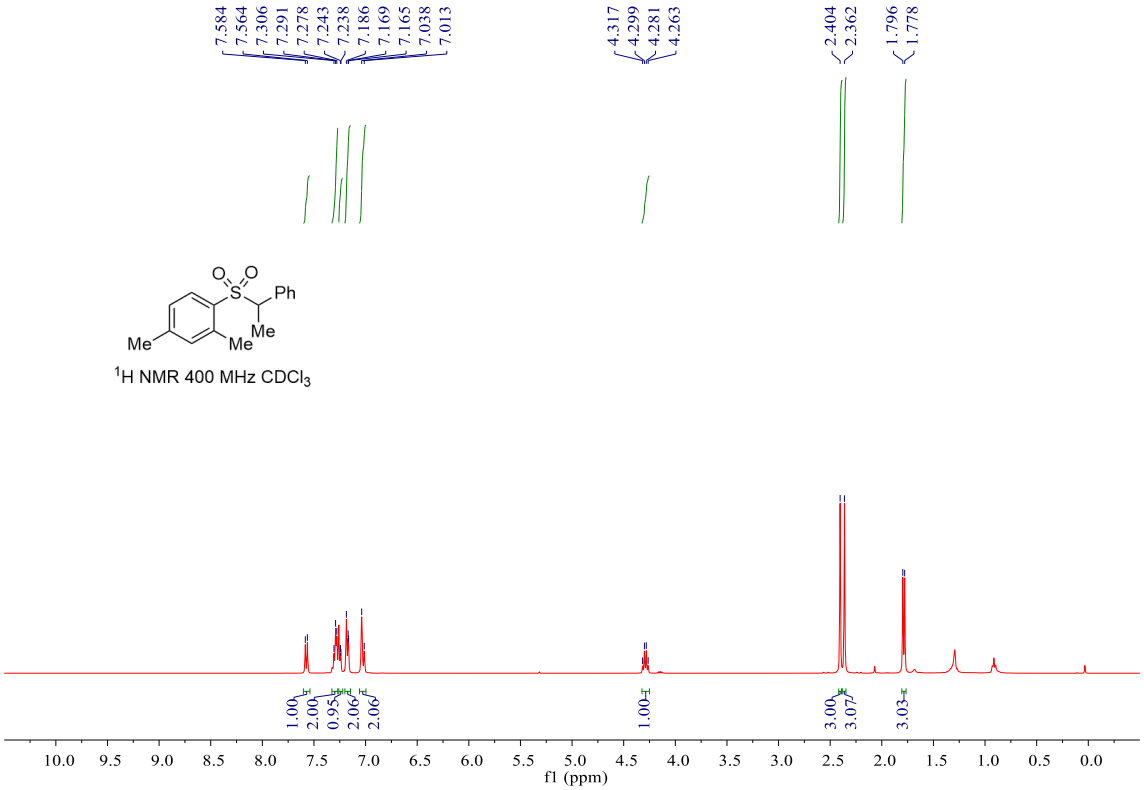


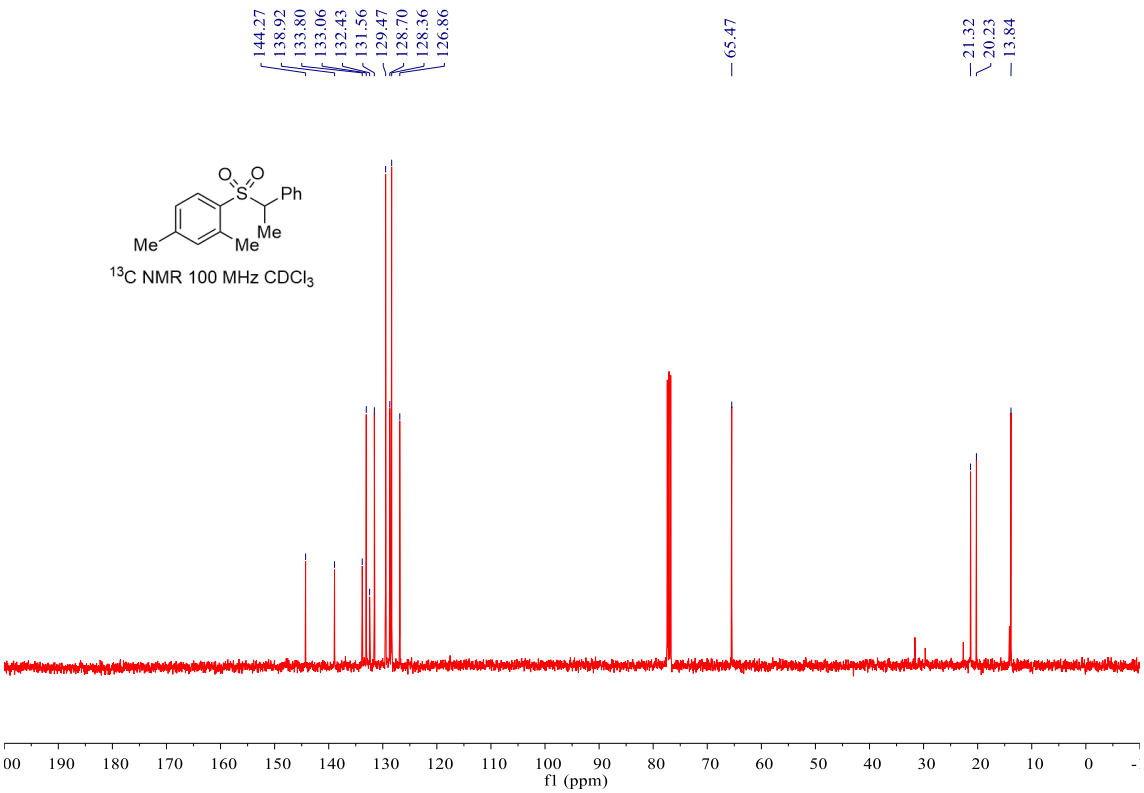


1-Chloro-4-methoxy-1-((1-phenylethyl)sulfonyl)benzene (2j)

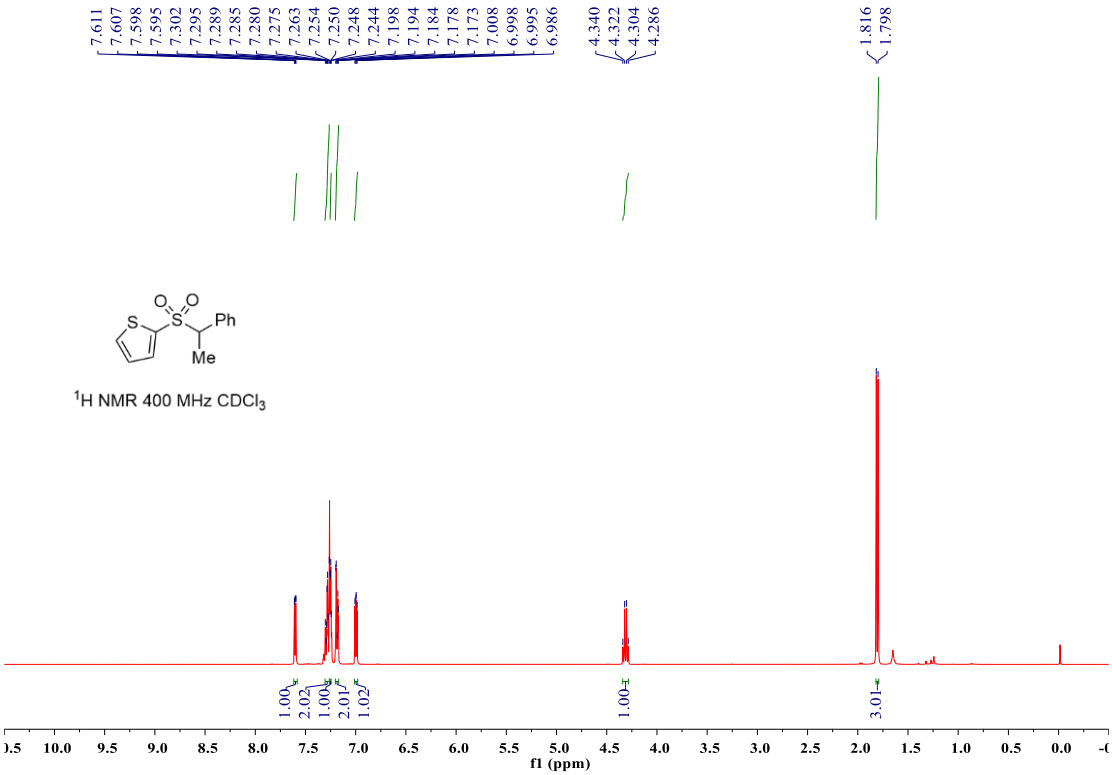


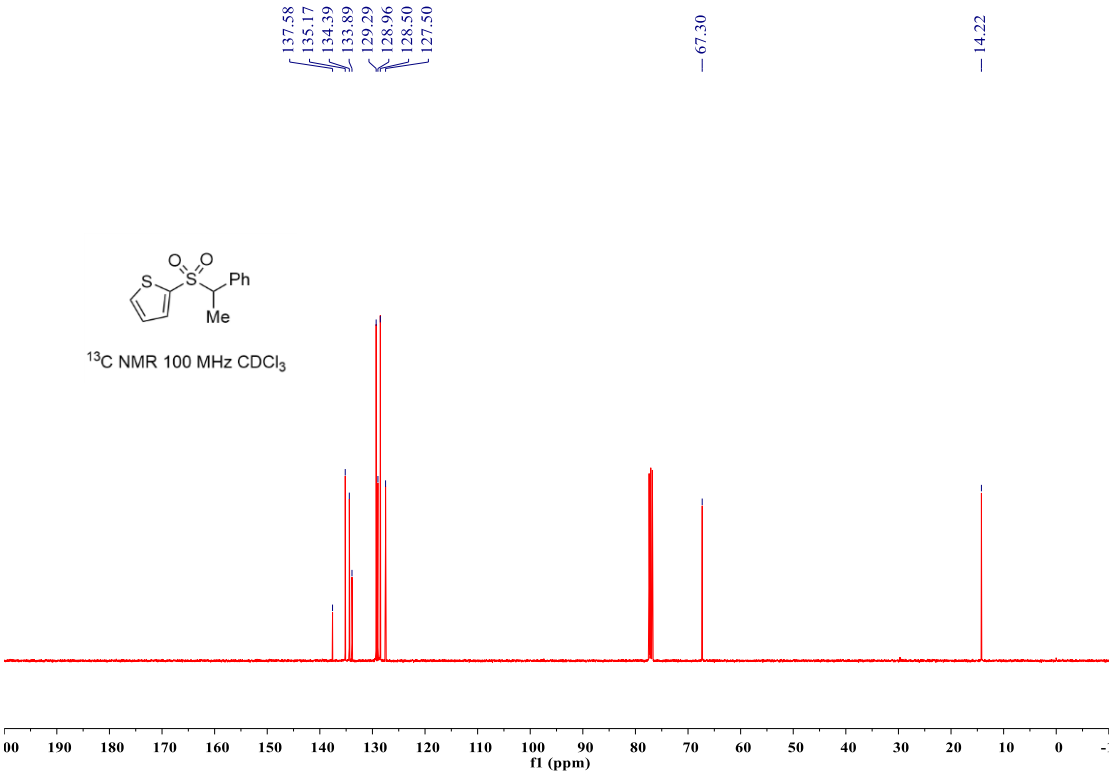
2,4-Dimethyl-1-((1-phenylethyl)sulfonyl)benzene (2k)



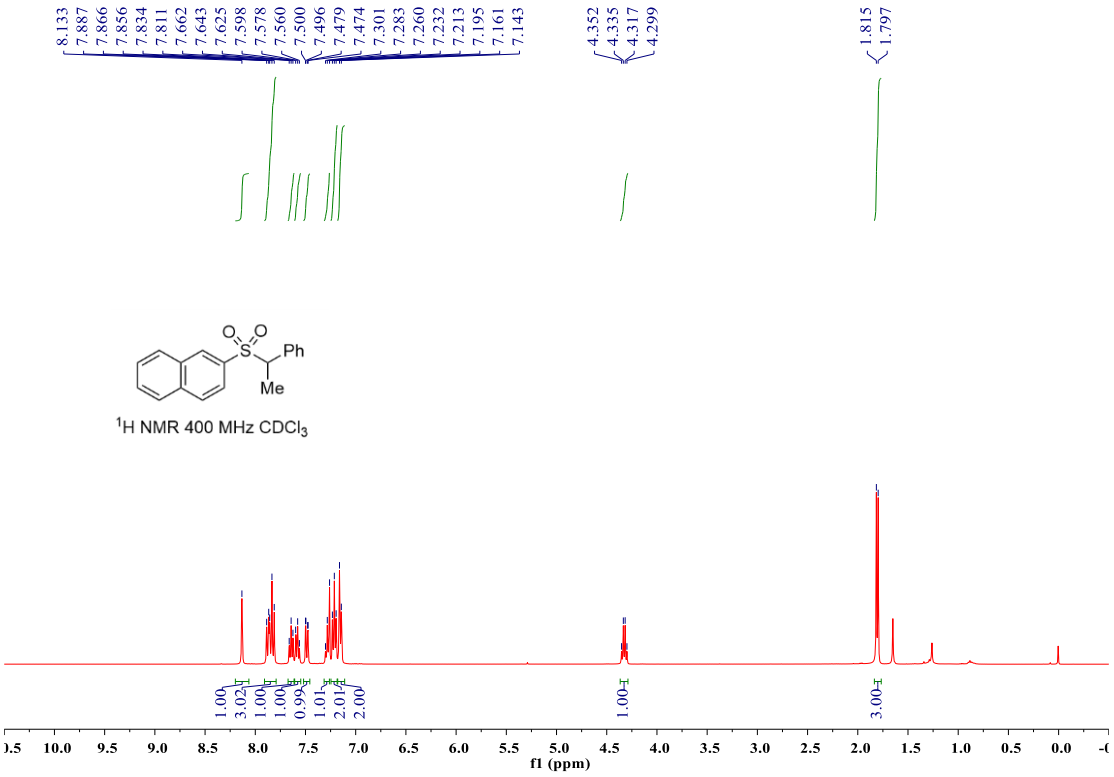


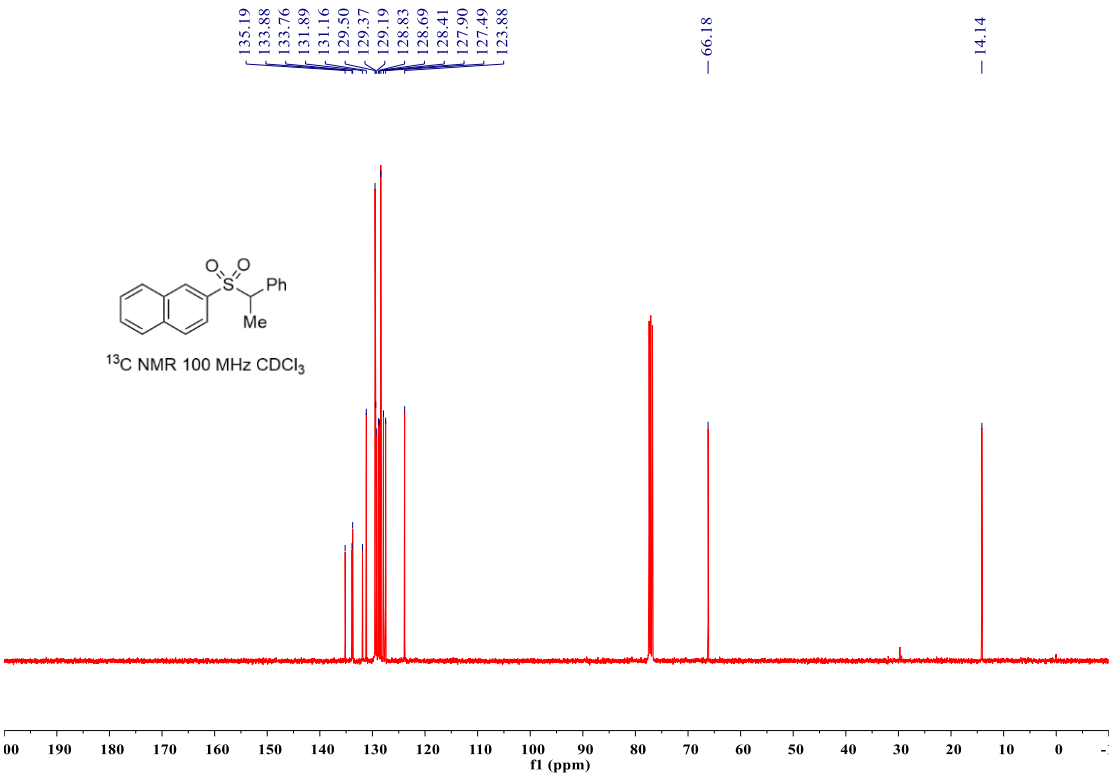
2-((1-Phenylethyl)sulfonyl)thiophene (2l)



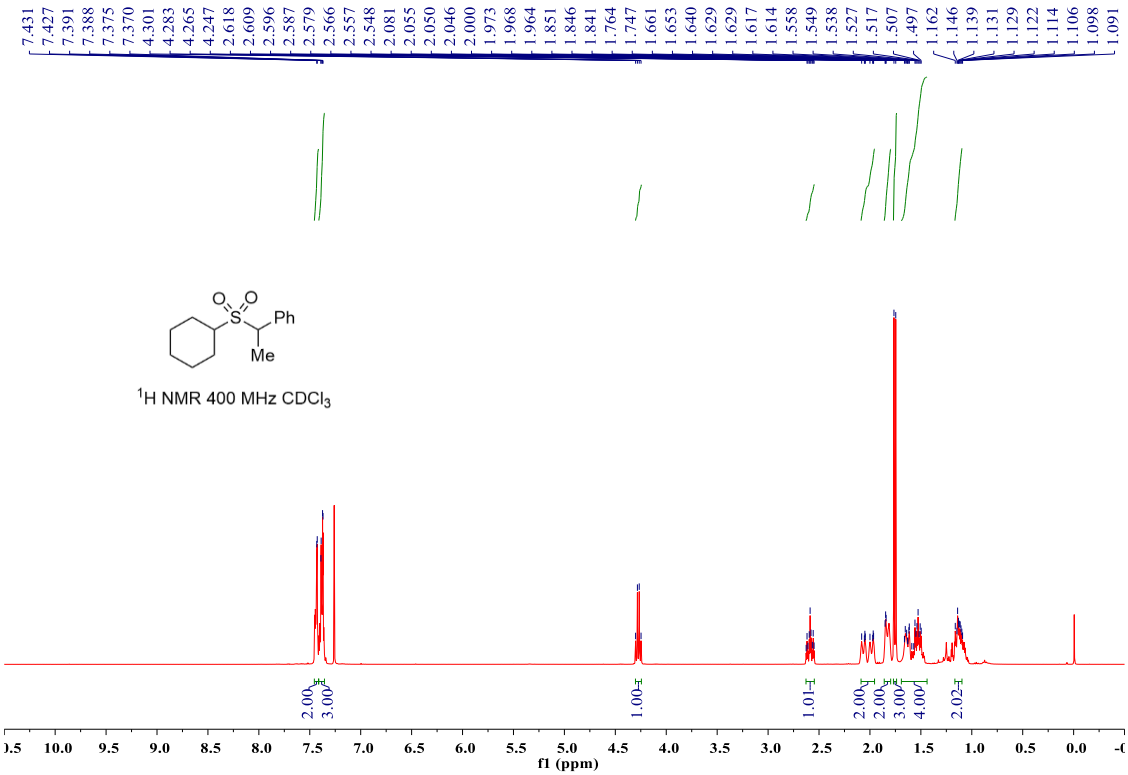


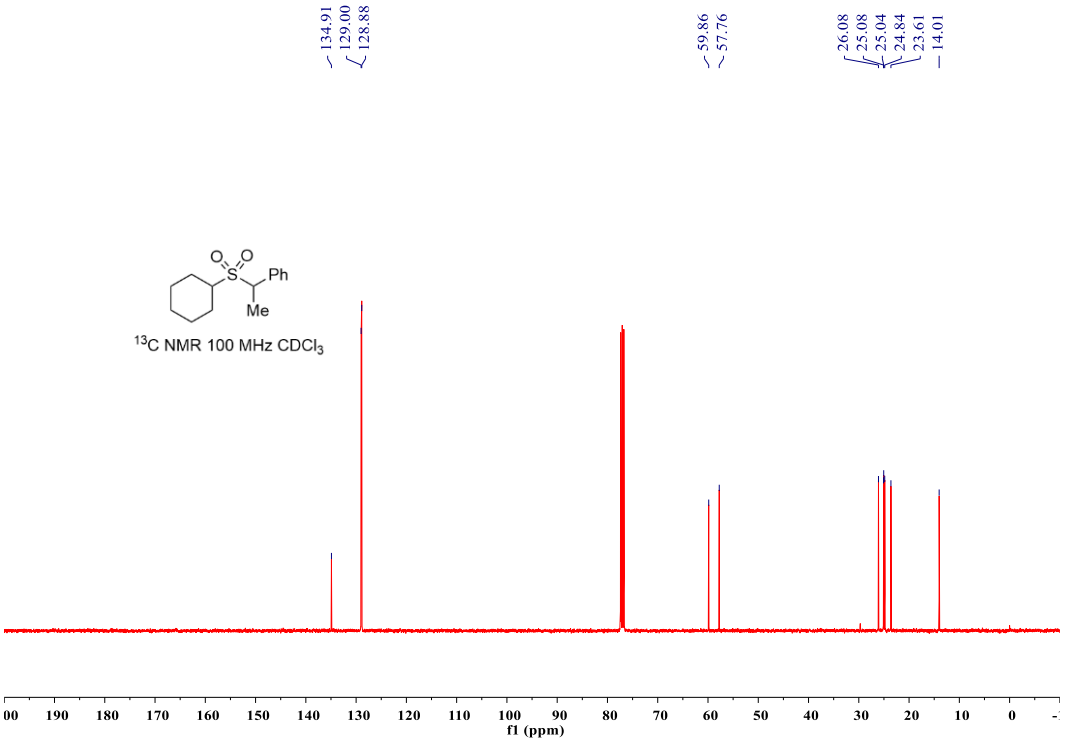
2-((1-Phenylethyl)sulfonyl)naphthalene (2m)



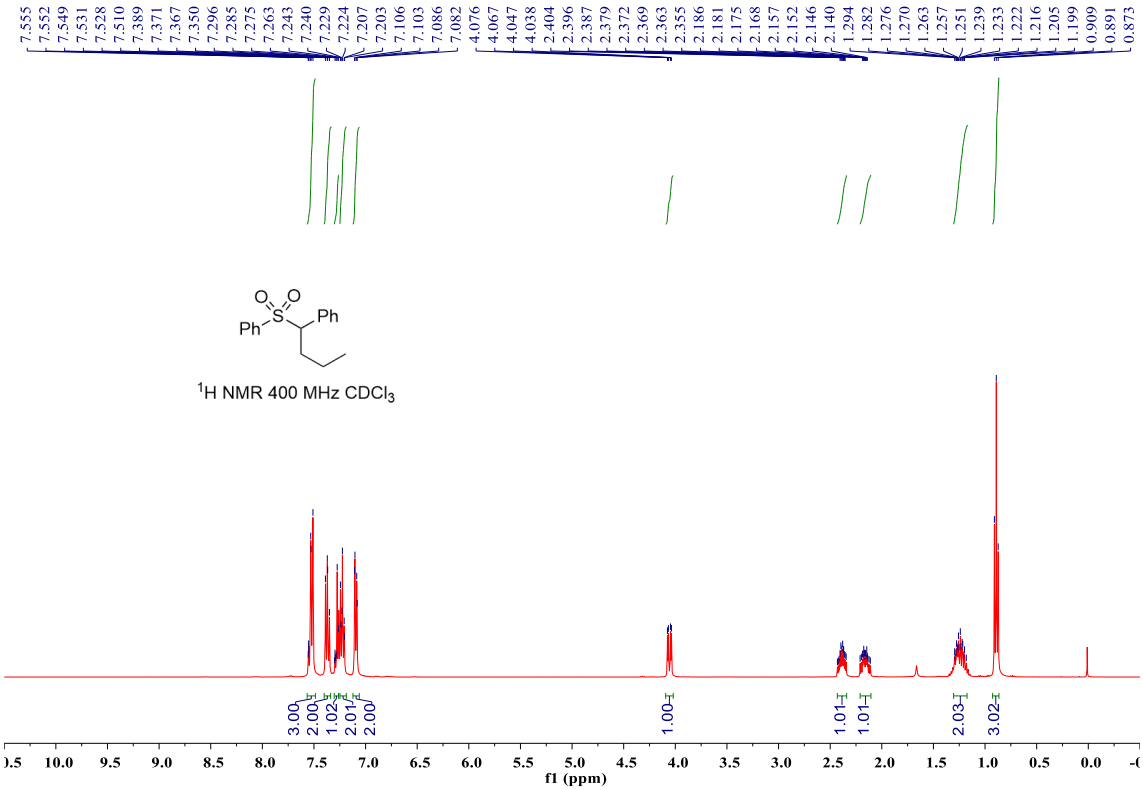


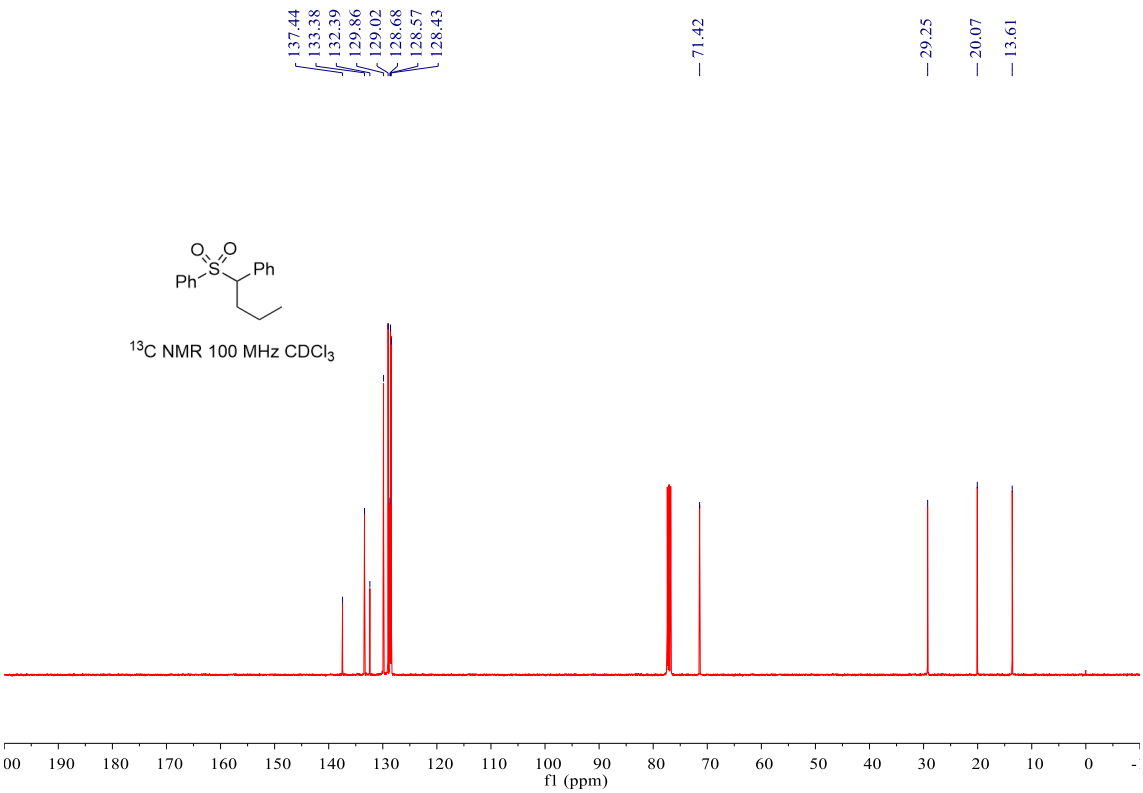
(1-(Cyclohexylsulfonyl)ethyl)benzene (2n)



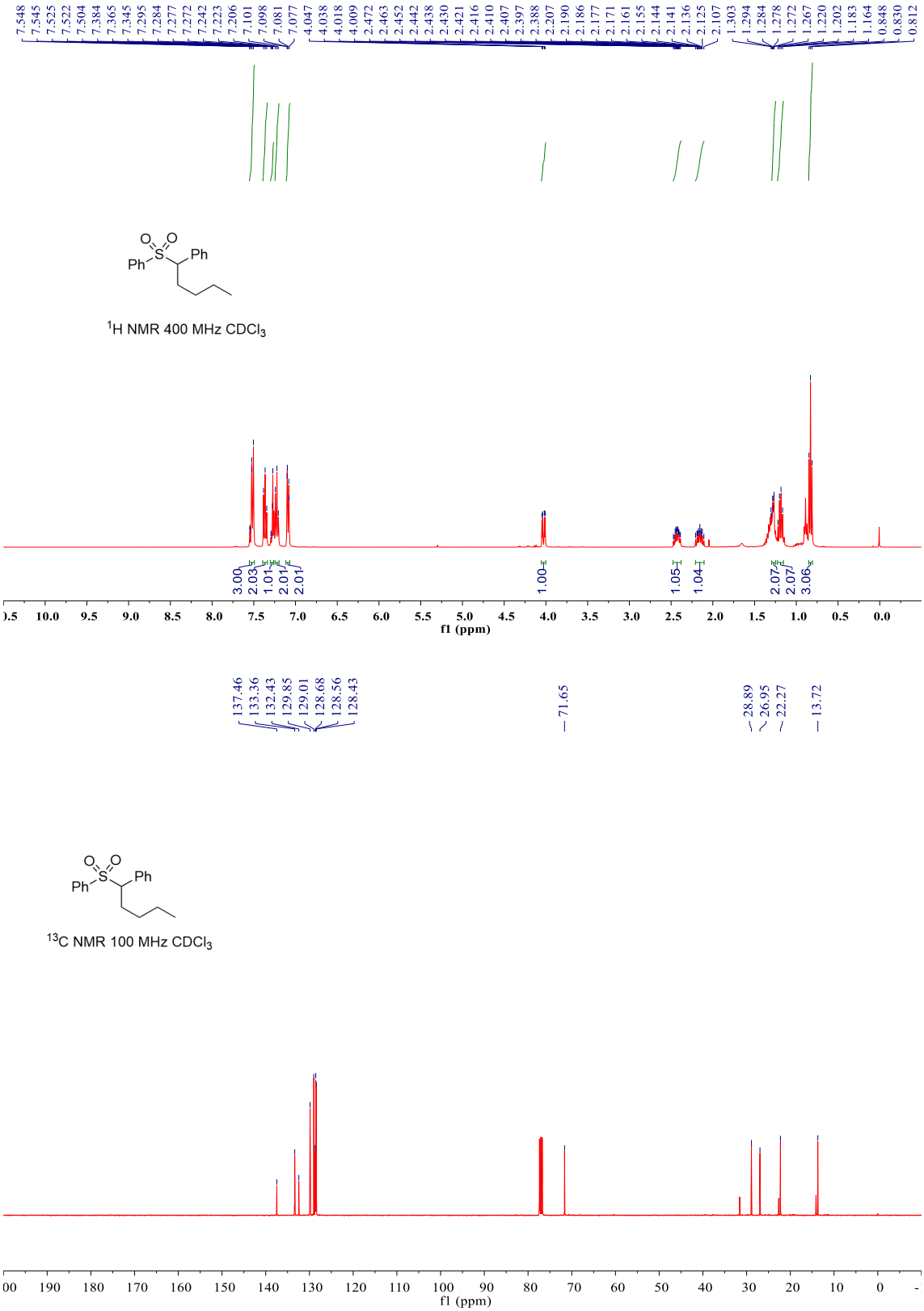


((1-Phenylbutyl)sulfonyl)benzene (2o)

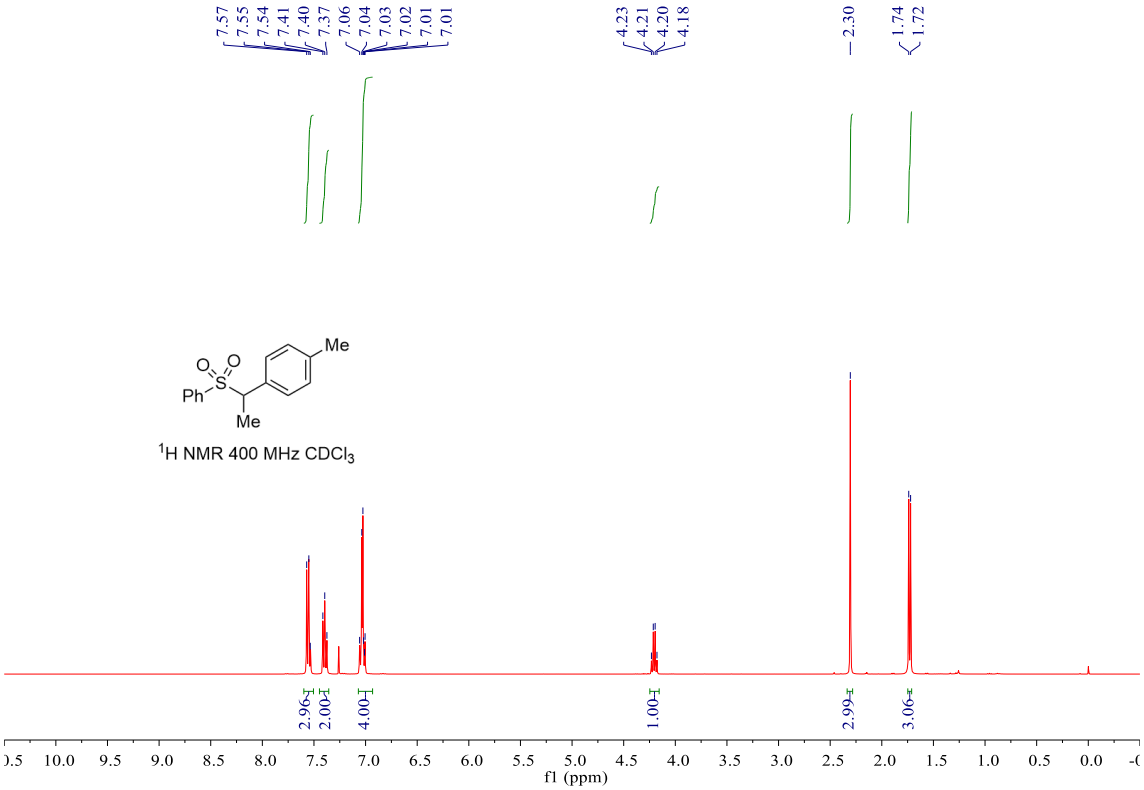


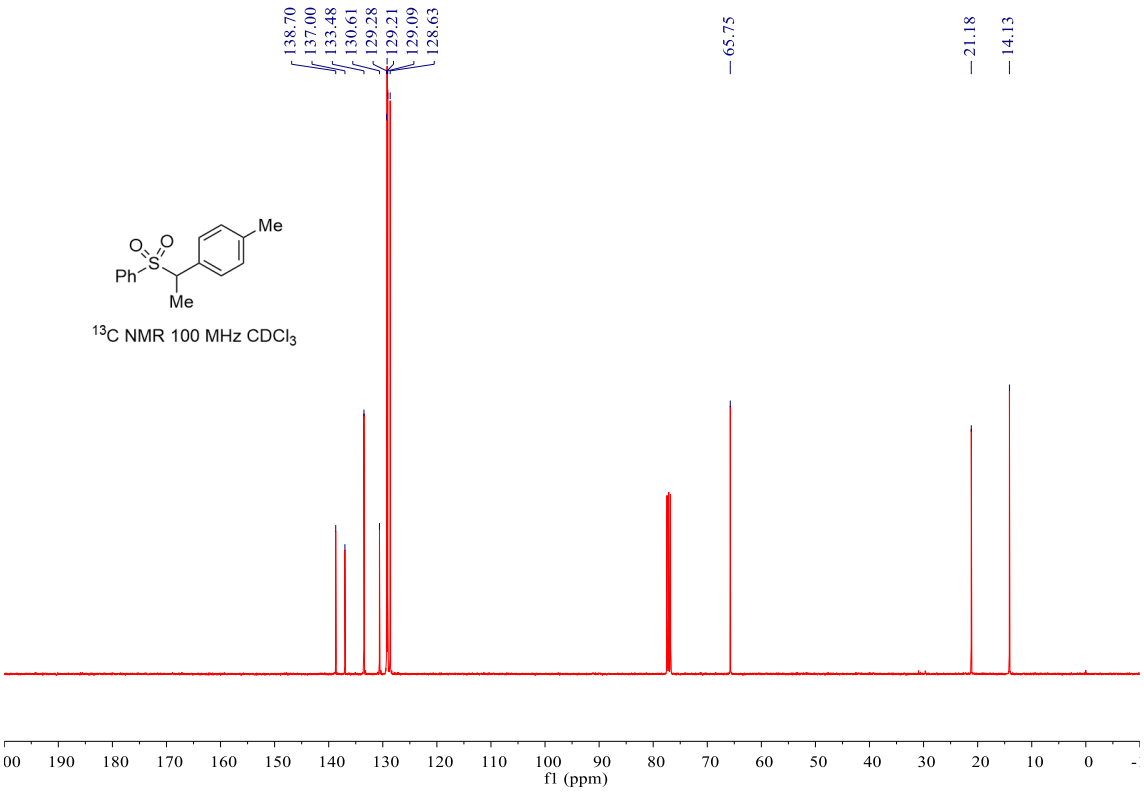


((1-Phenylpentyl)sulfonyl)benzene (2p)

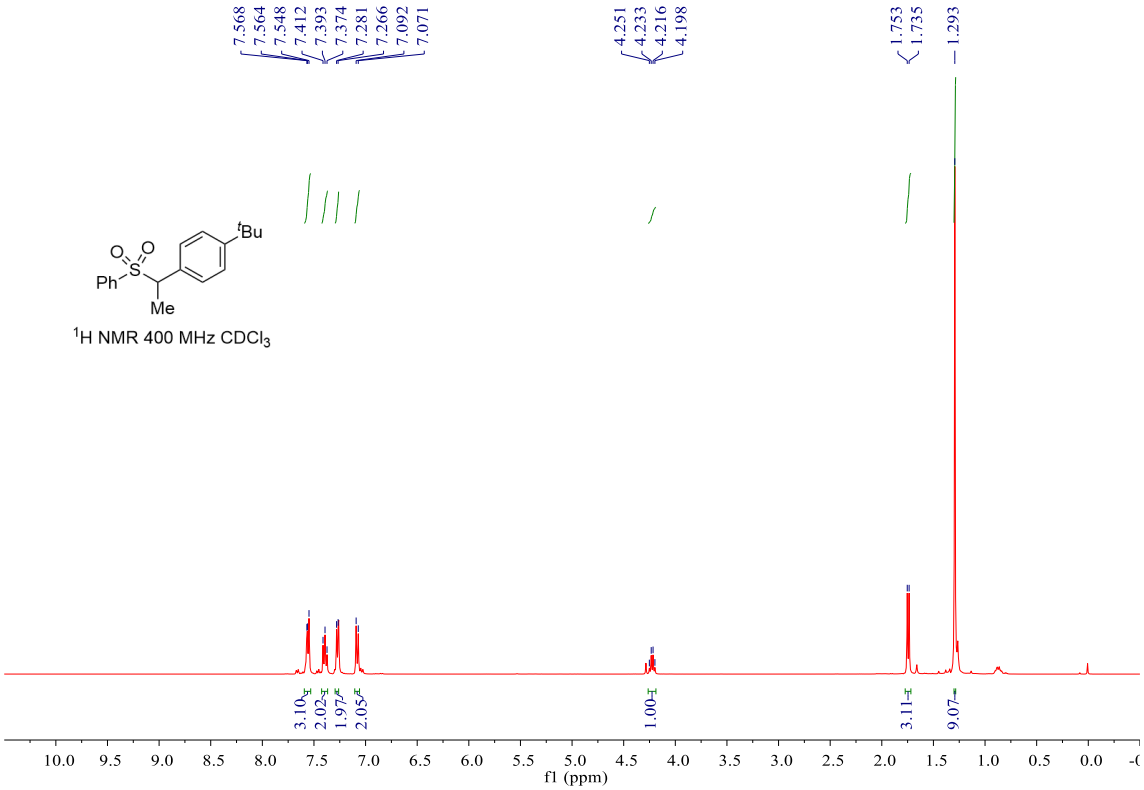


1-Methyl-4-(1-(phenylsulfonyl)ethyl)benzene (2q)

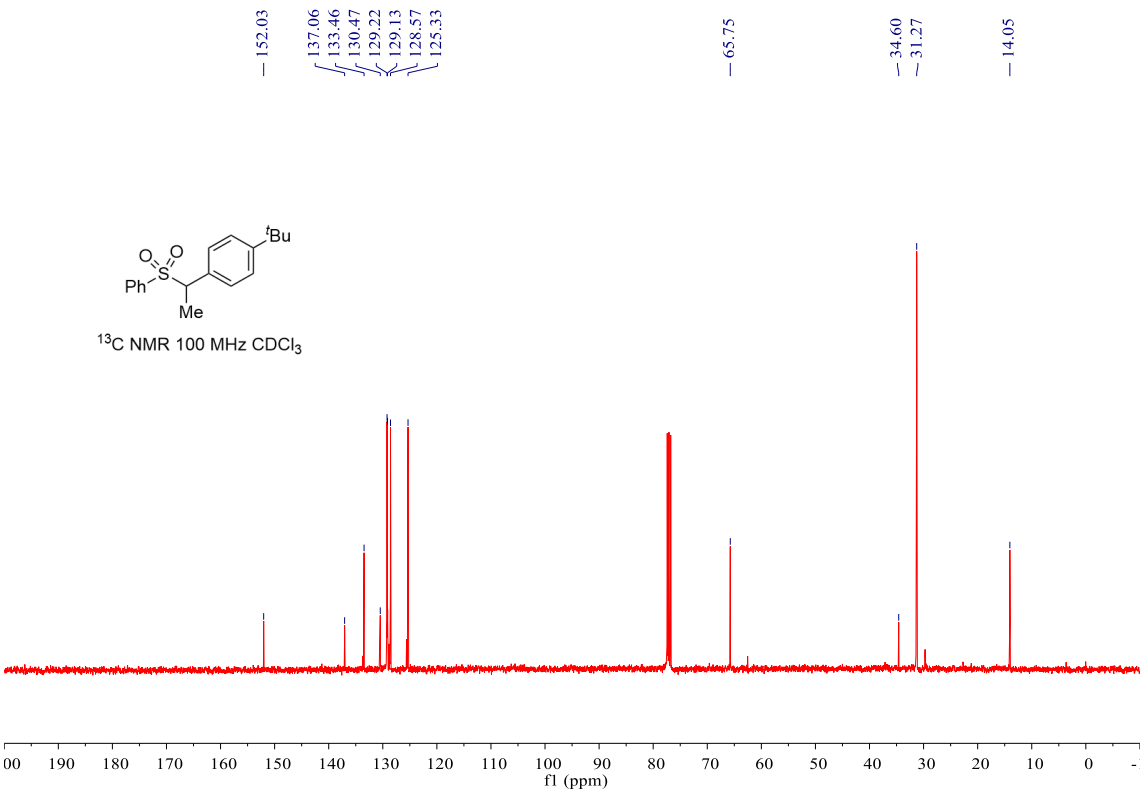




1-(*tert*-Butyl)-4-(1-(phenylsulfonyl)ethyl)benzene (2r)

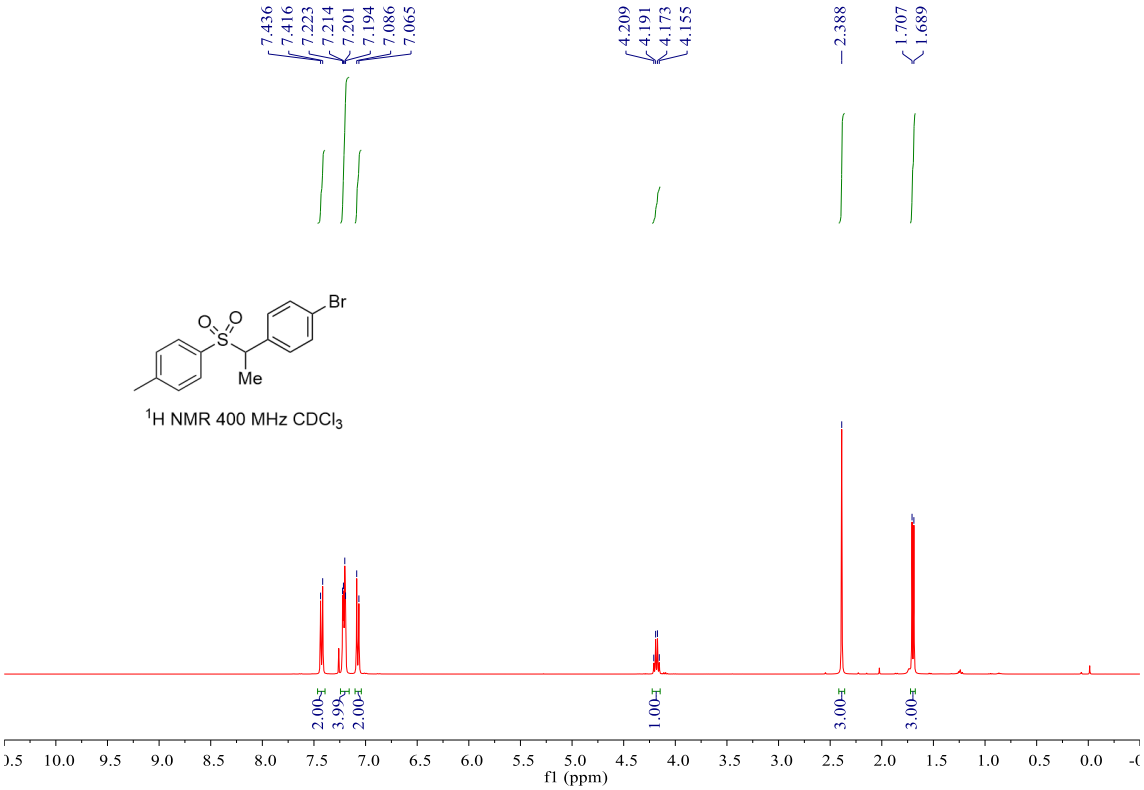


^{1}H NMR 400 MHz $CDCl_3$

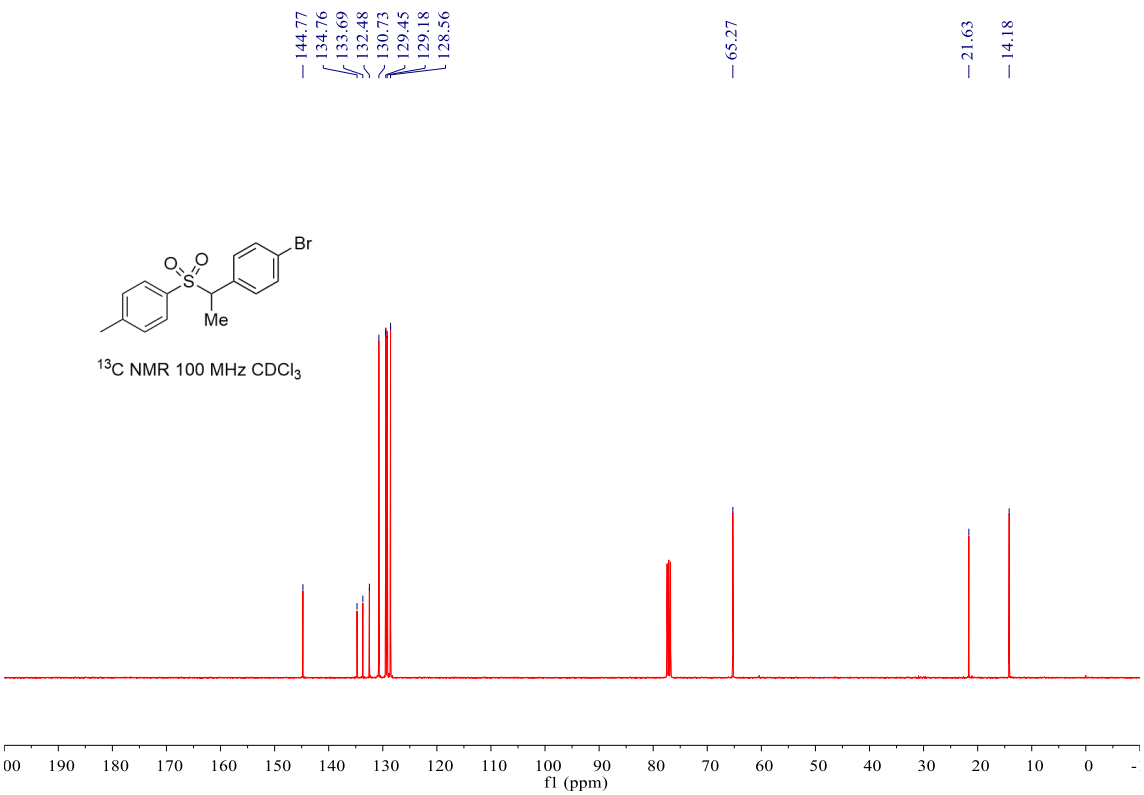


^{13}C NMR 100 MHz $CDCl_3$

1-Bromo-4-(1-tosylethyl)benzene (2s)

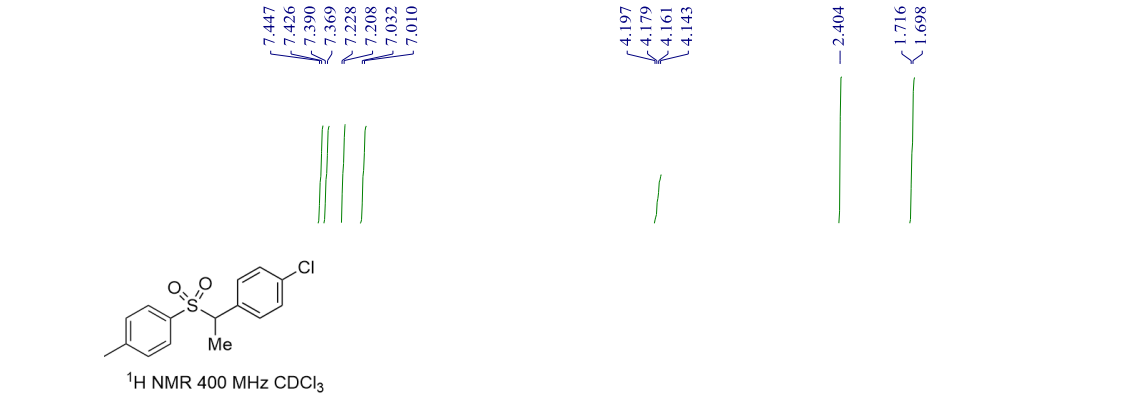


^{1}H NMR 400 MHz $CDCl_3$

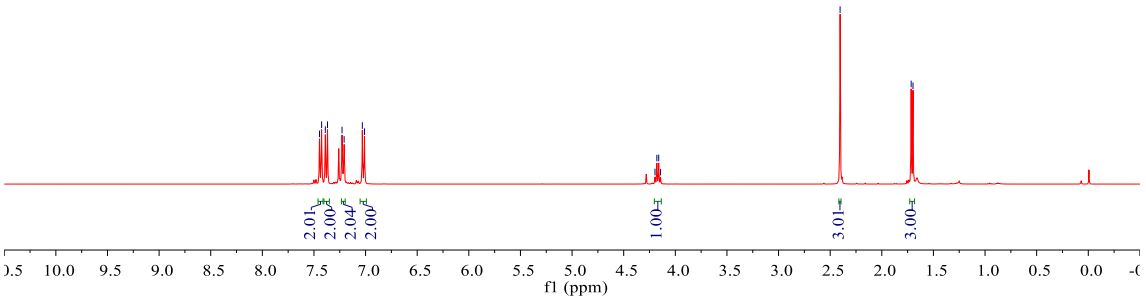


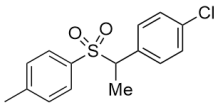
^{13}C NMR 100 MHz $CDCl_3$

1-Chloro-4-(1-tosylethyl)benzene (2t)

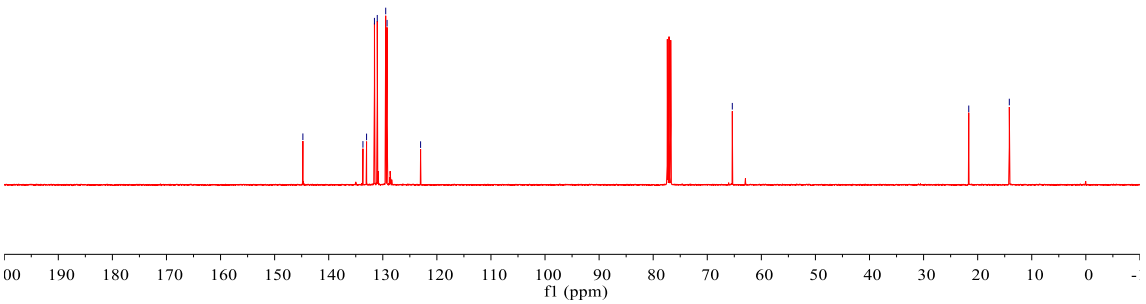


^{1}H NMR 400 MHz $CDCl_3$

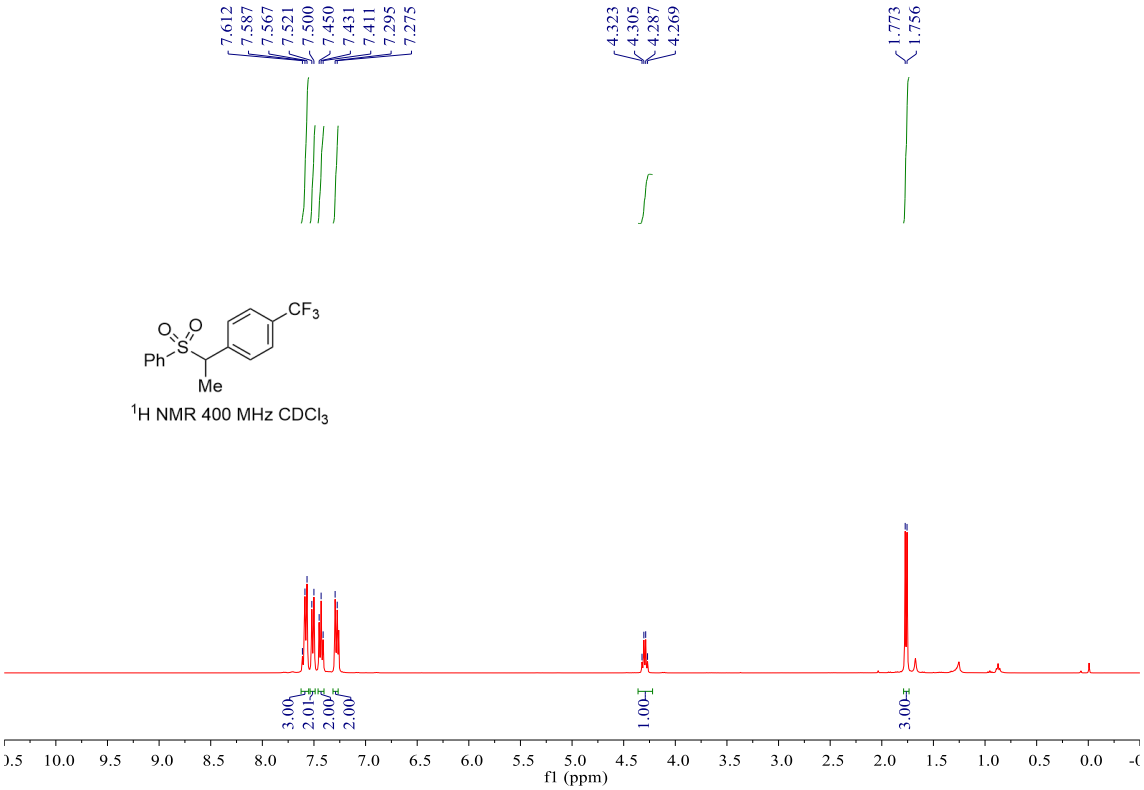


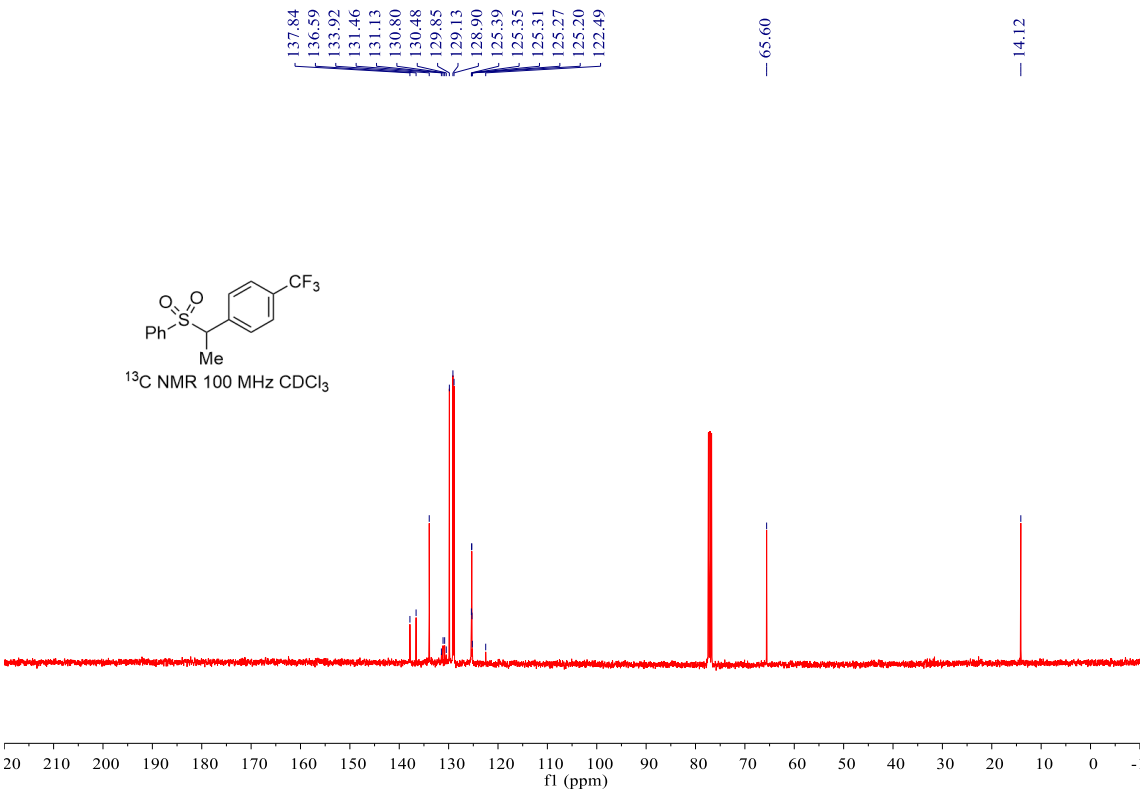


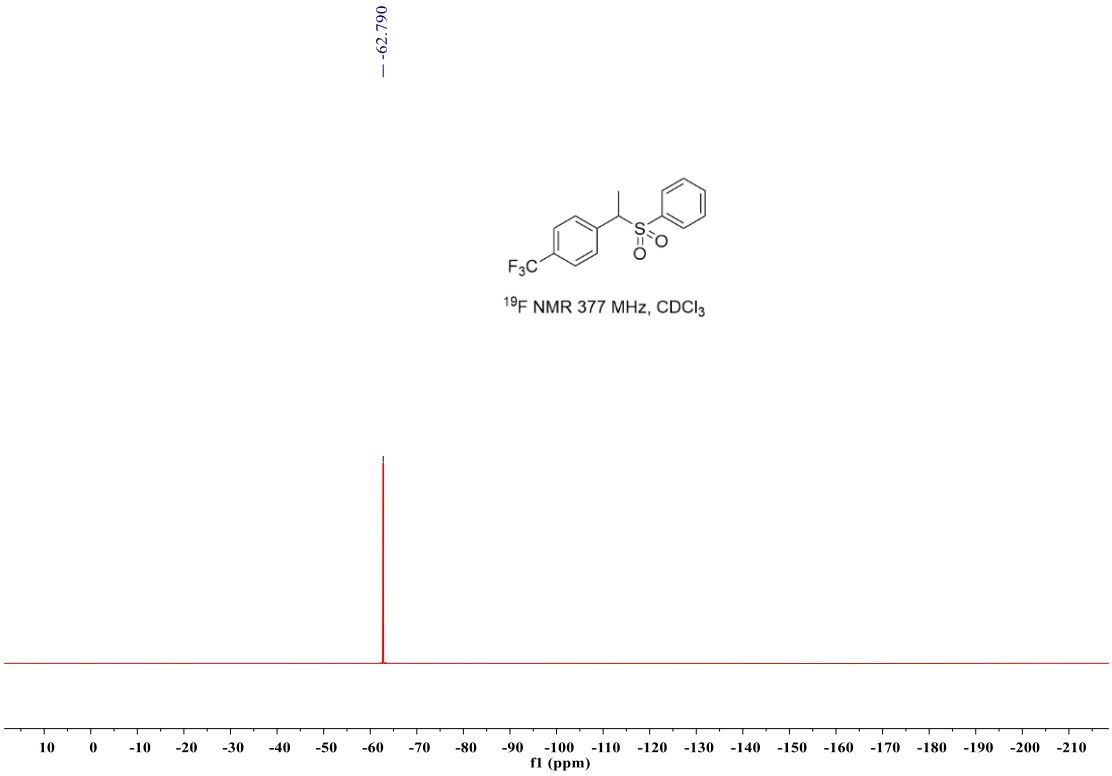
^{13}C NMR 100 MHz $CDCl_3$



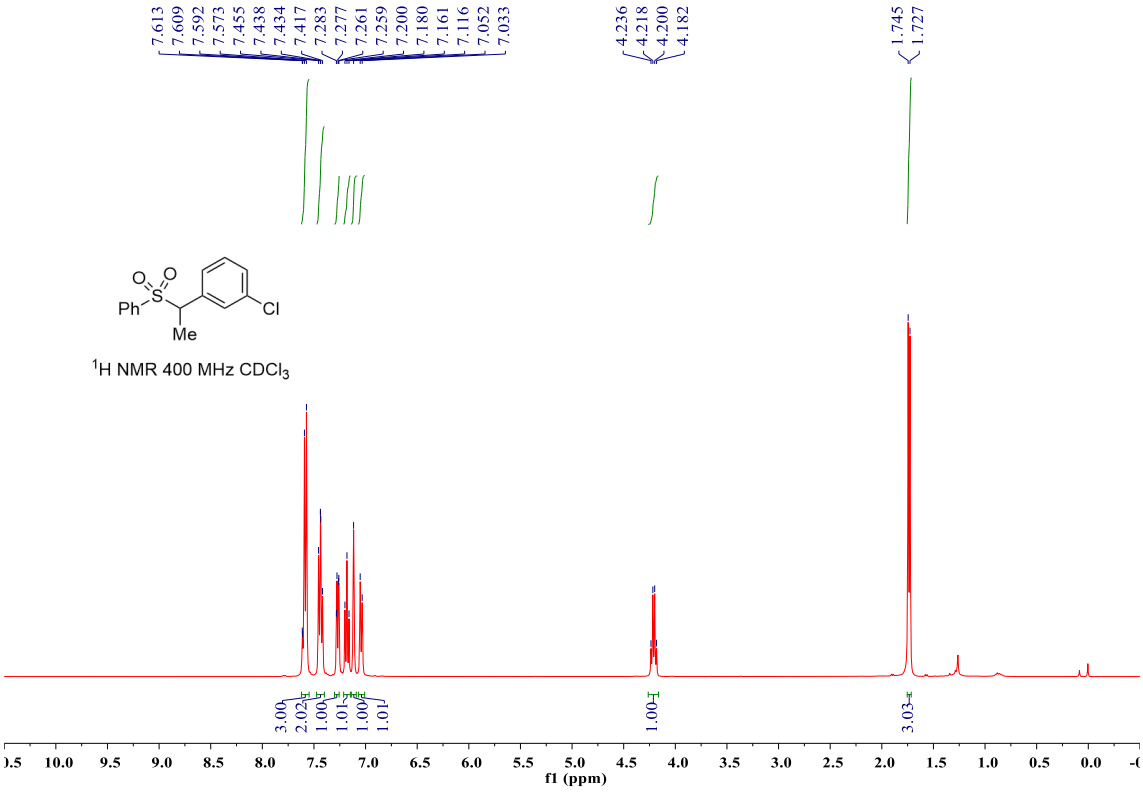
1-(1-(Phenylsulfonyl)ethyl)-4-(trifluoromethyl)benzene (2u)

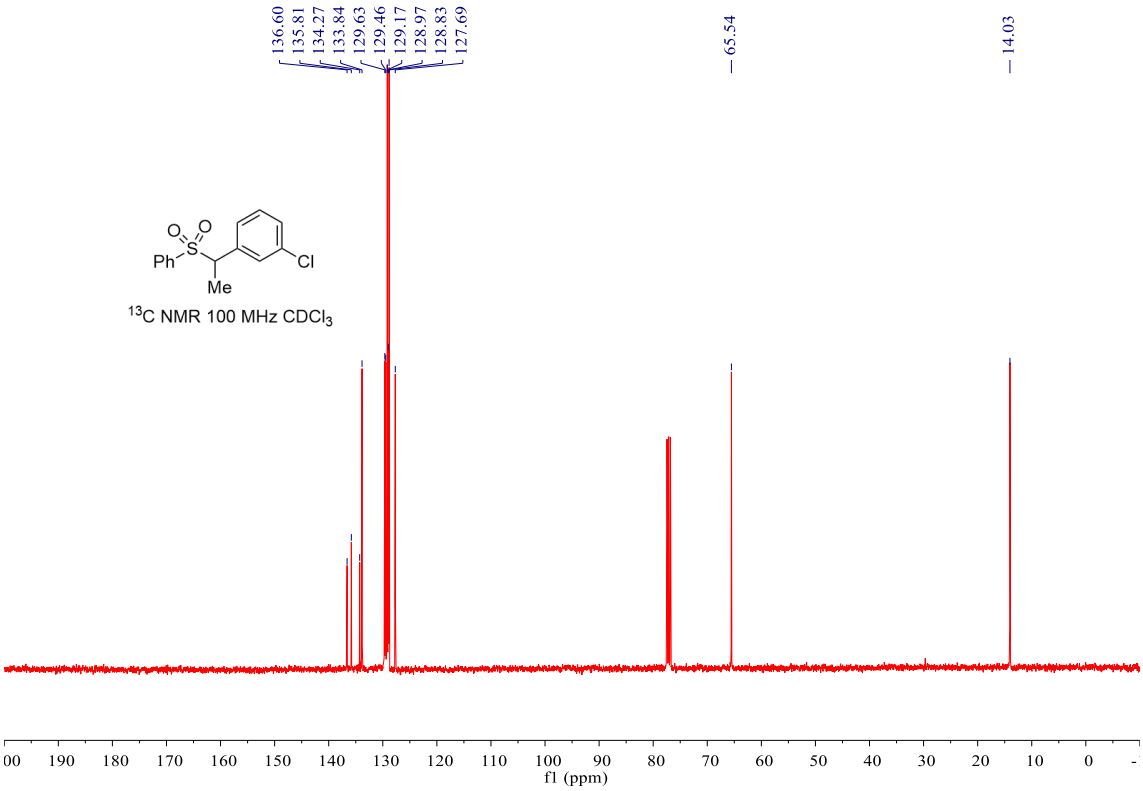




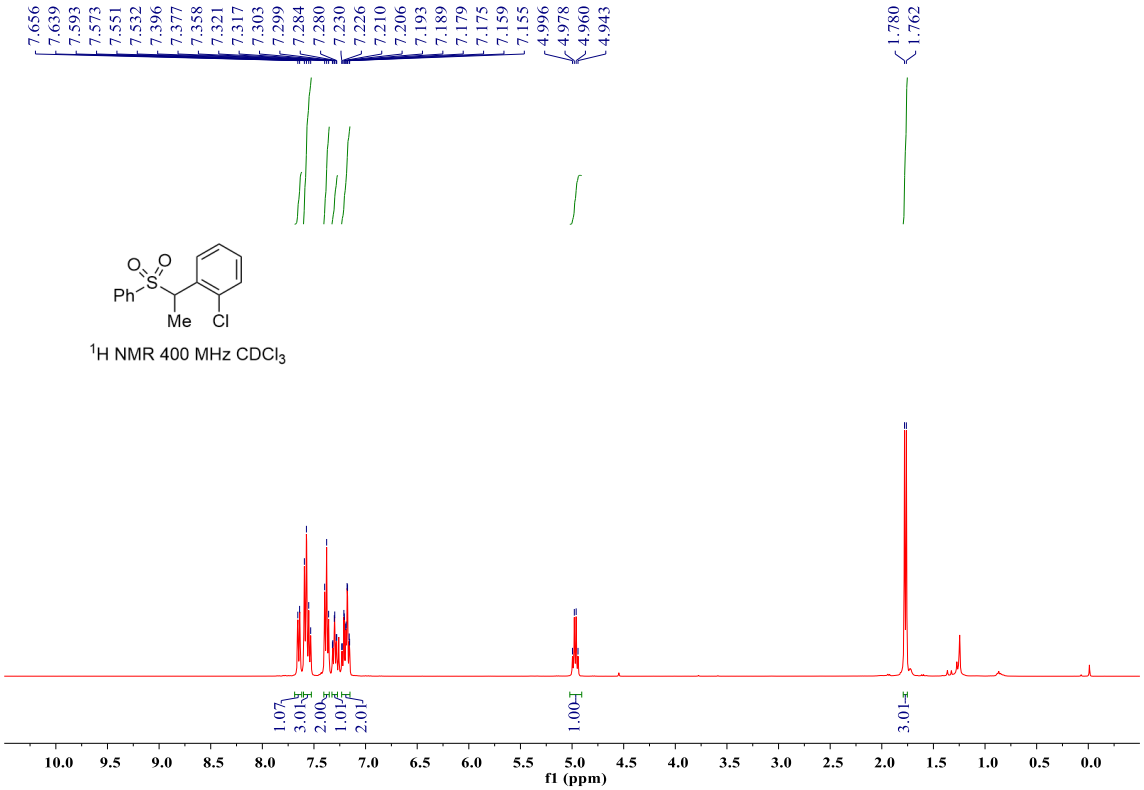

-62.790
F3C
S
O
O
19F NMR 377 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

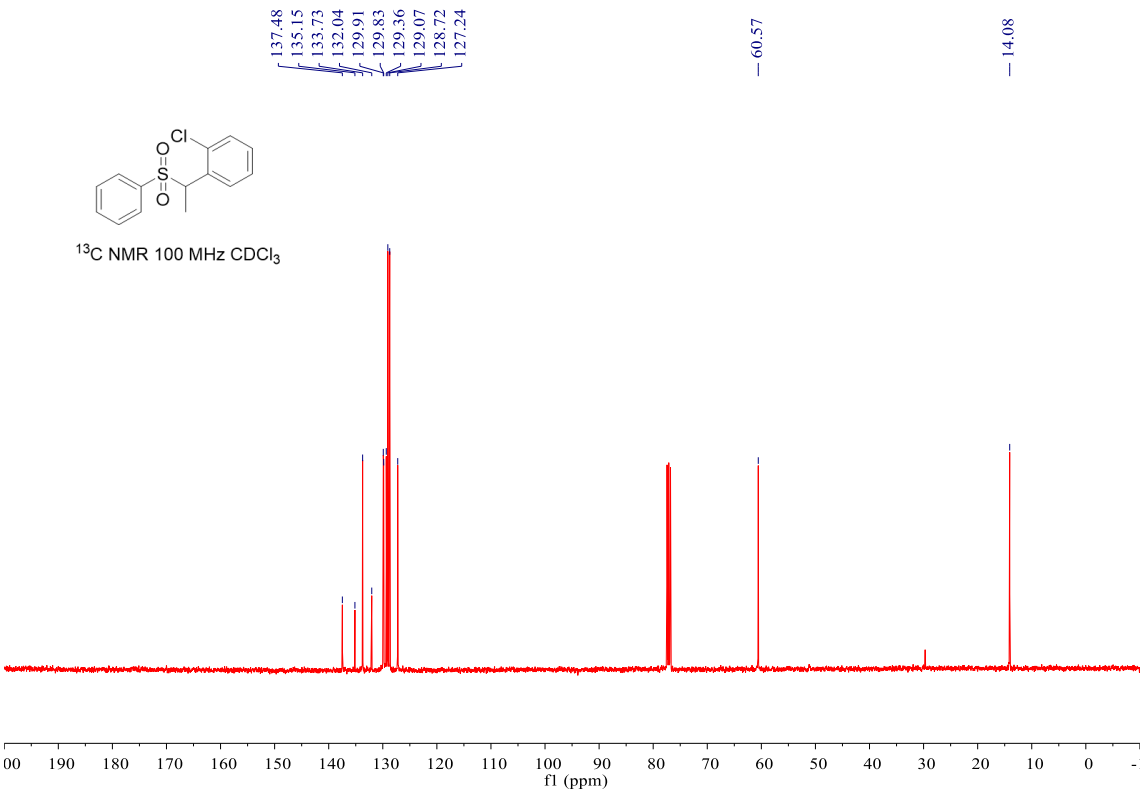
1-Chloro-3-(1-(phenylsulfonyl)ethyl)benzene (2v)



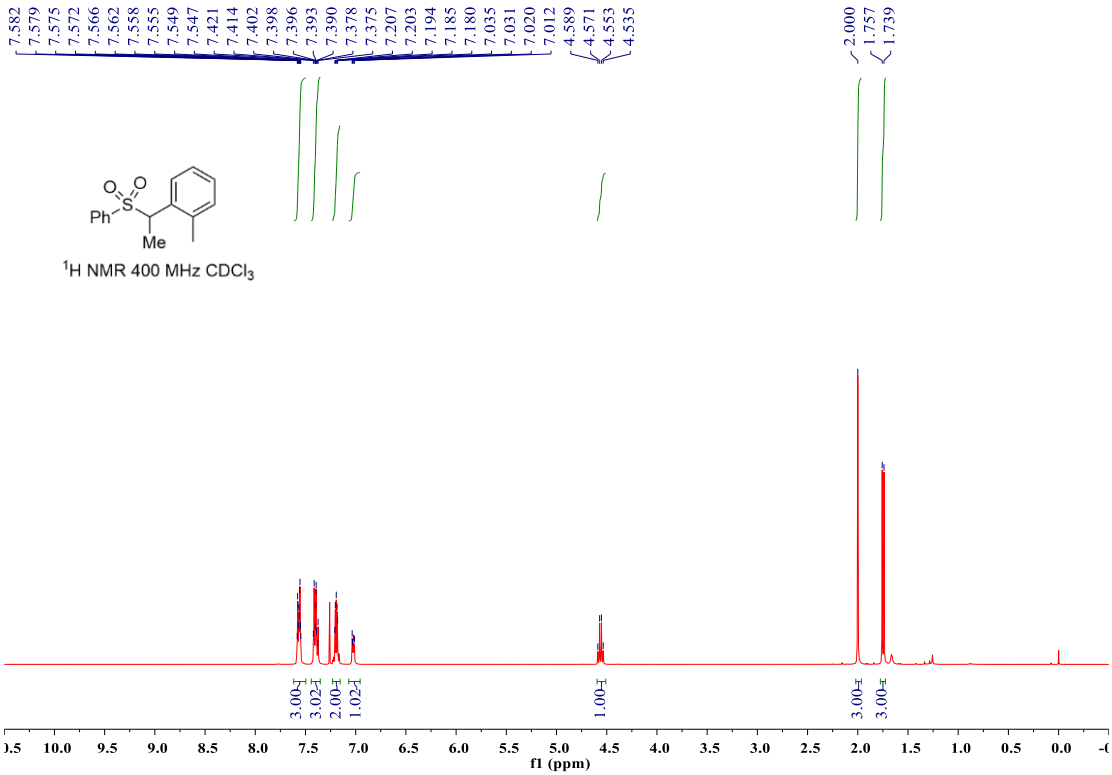


1-Chloro-2-(1-(phenylsulfonyl)ethyl)benzene (2w)

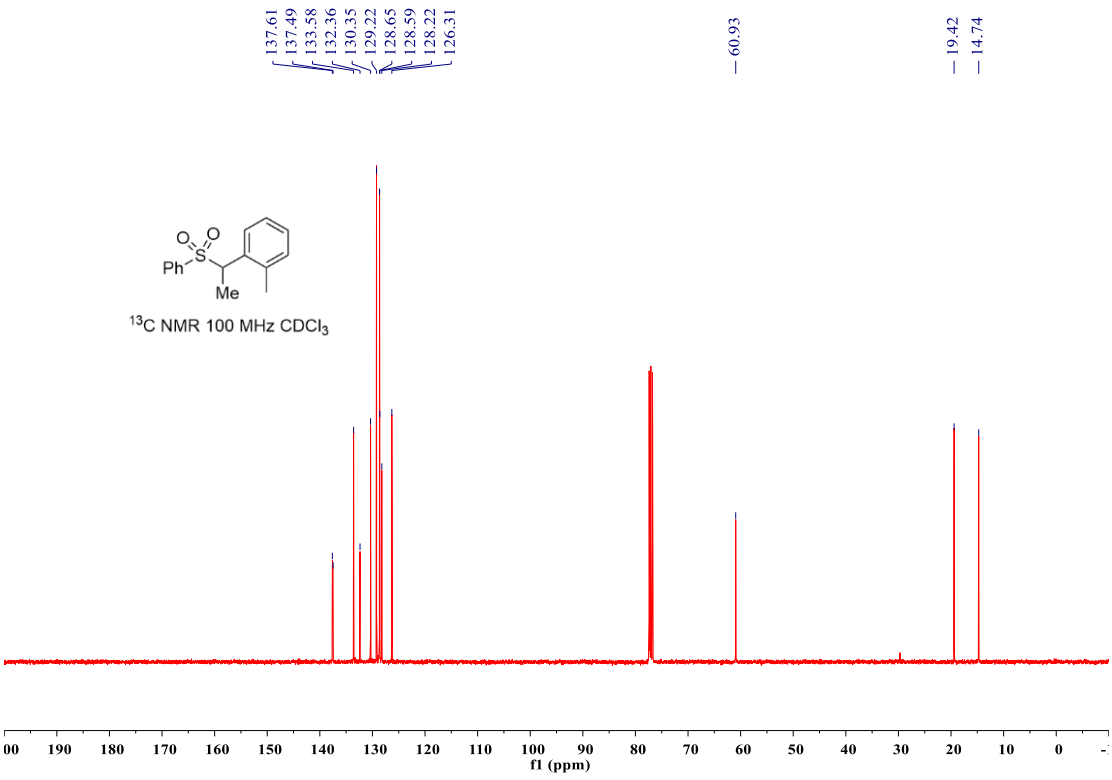




1-Methyl-2-(1-(phenylsulfonyl)ethyl)benzene (2x)

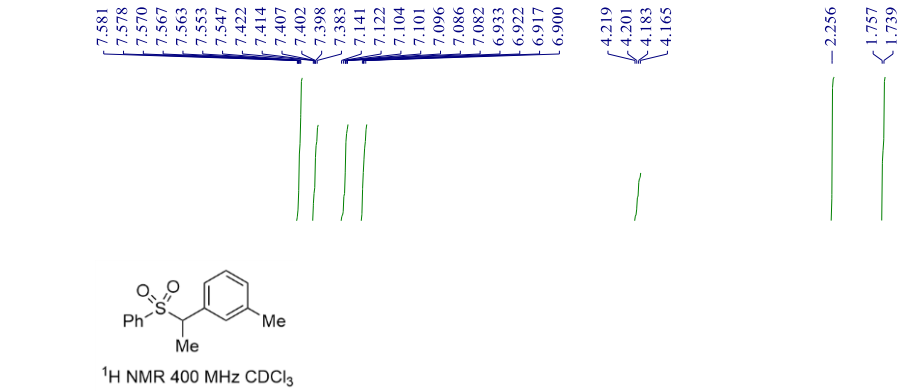


^{1}H NMR 400 MHz $CDCl_3$

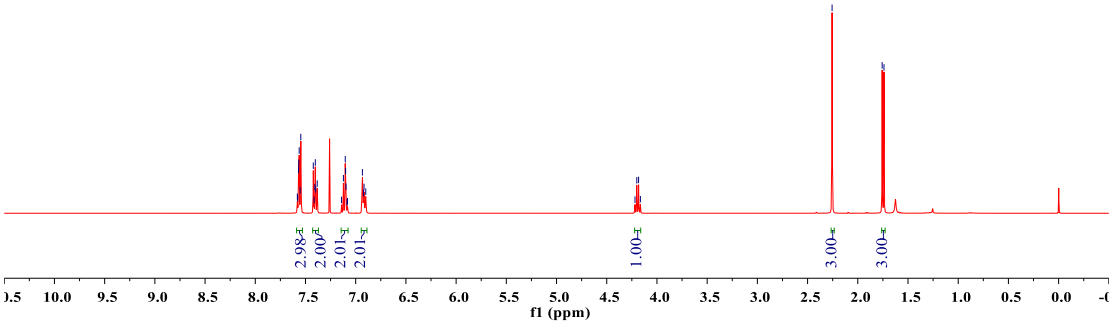


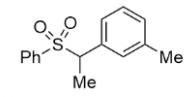
^{13}C NMR 100 MHz $CDCl_3$

1-Methyl-3-(1-(phenylsulfonyl)ethyl)benzene (2y)

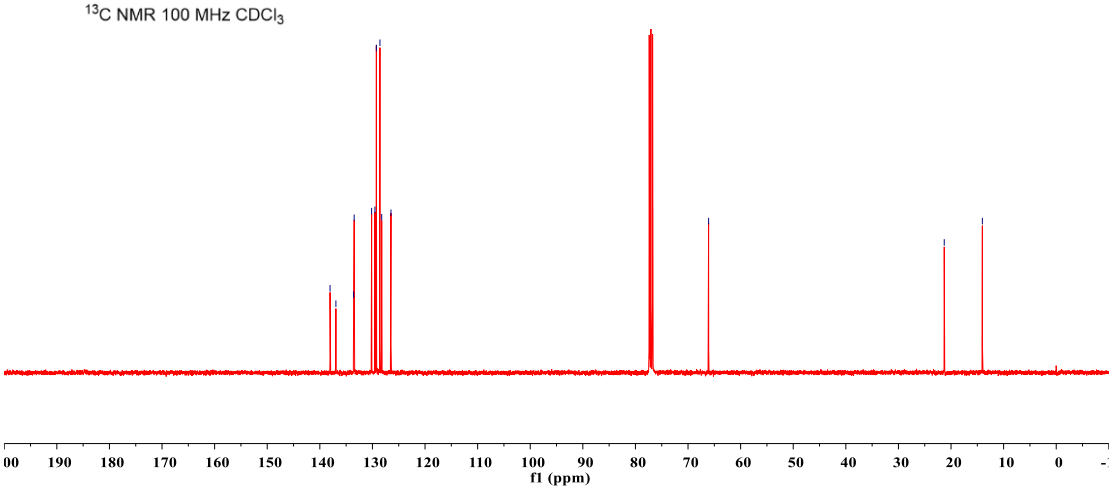


^{1}H NMR 400 MHz $CDCl_3$

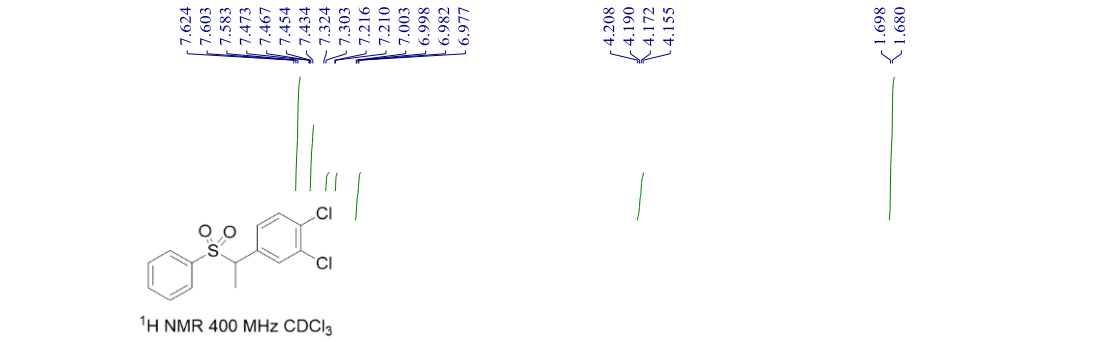




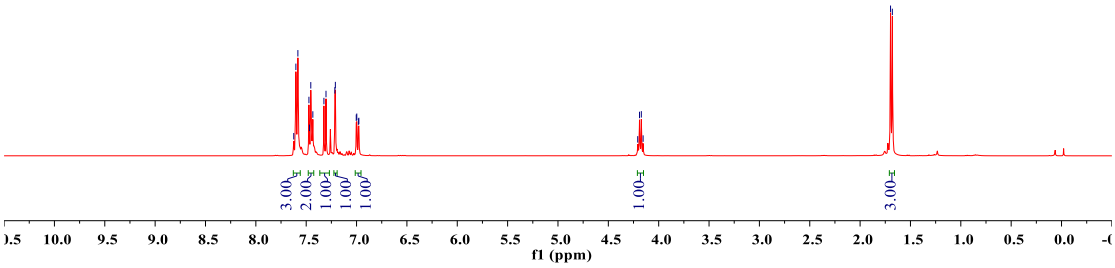
^{13}C NMR 100 MHz $CDCl_3$

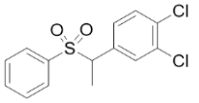


1,3-Dichloro-5-((1-phenylethyl)sulfonyl)benzene (2z)

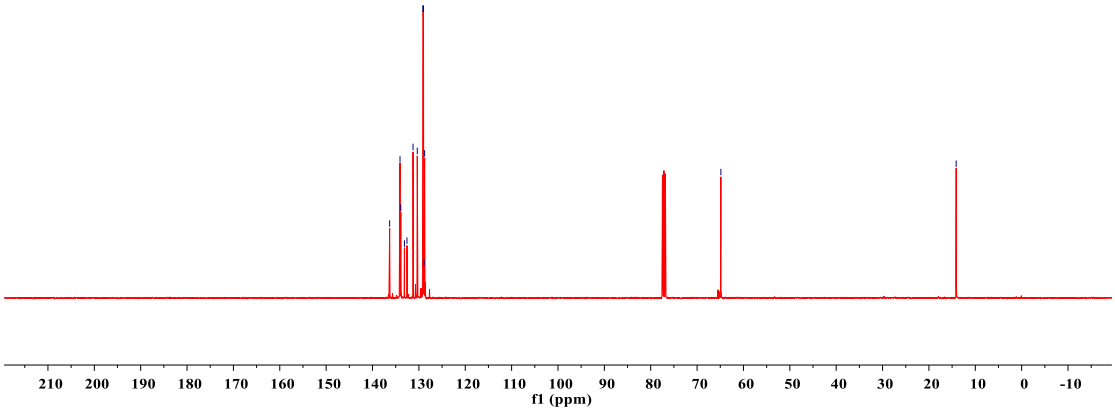


^{1}H NMR 400 MHz $CDCl_3$

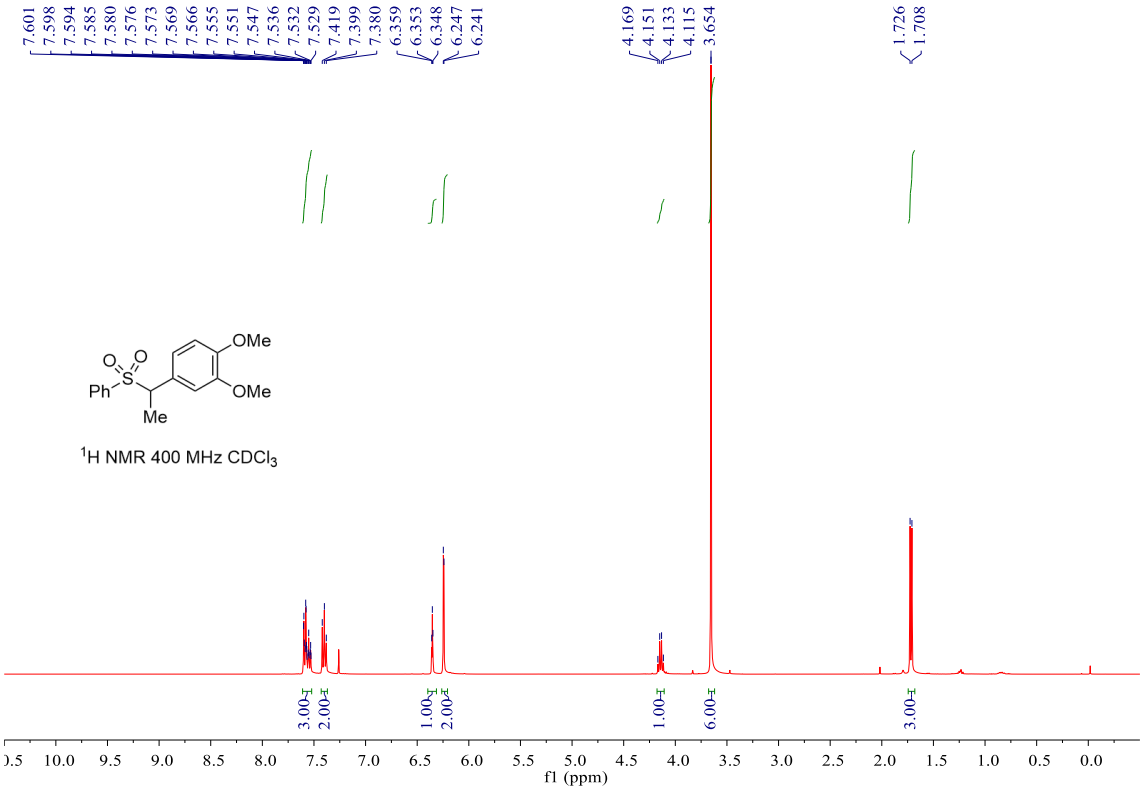


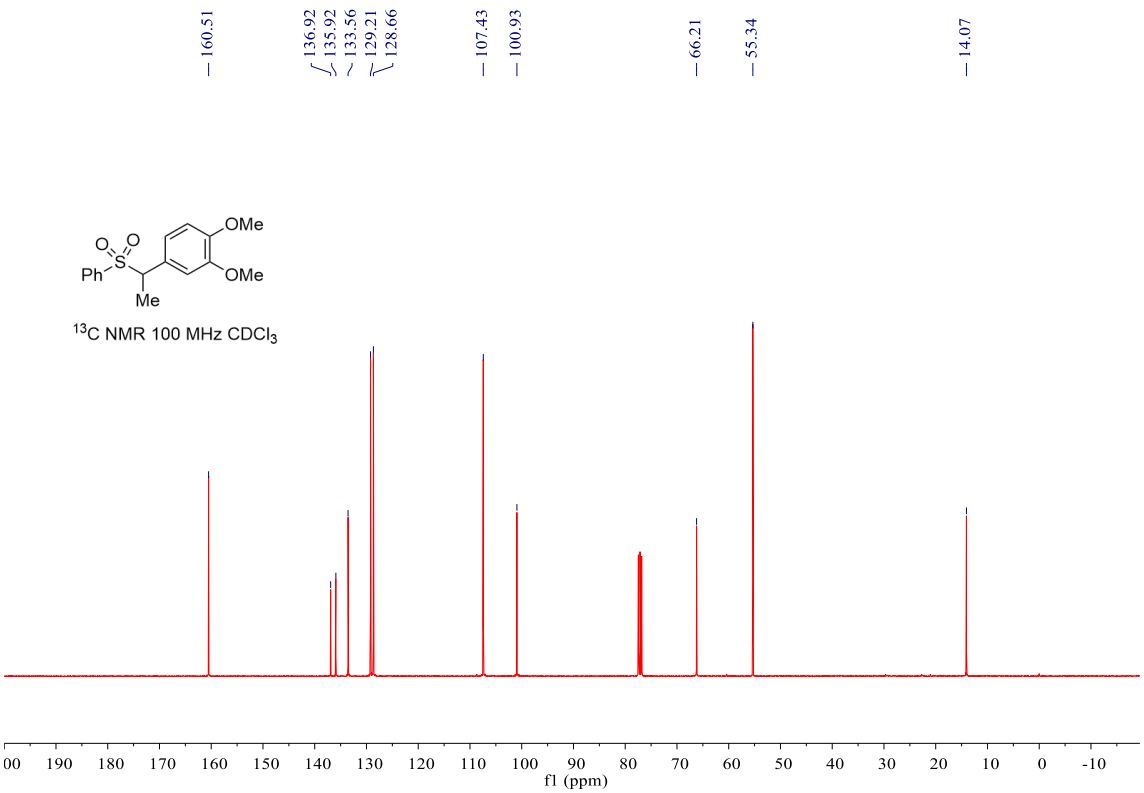


^{13}C NMR 100 MHz $CDCl_3$

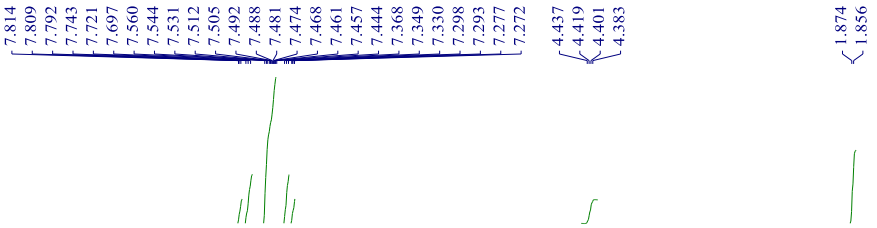


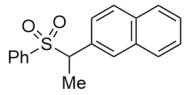
1,3-Dimethoxy-5-(1-(phenylsulfonyl)ethyl)benzene (2aa)



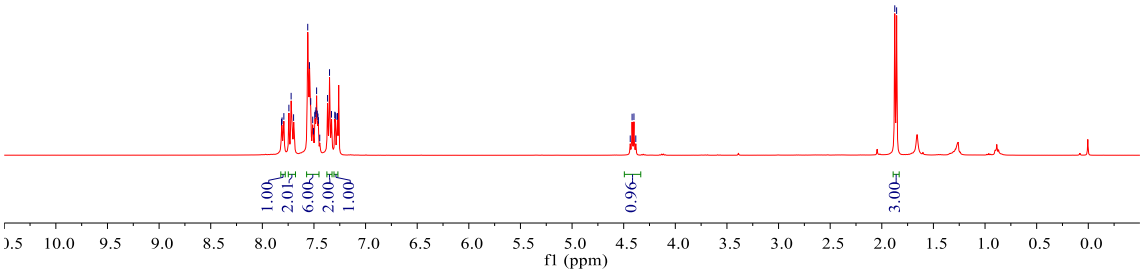


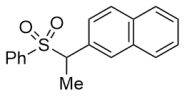
2-(1-(Phenylsulfonyl)ethyl)naphthalene (2ab)



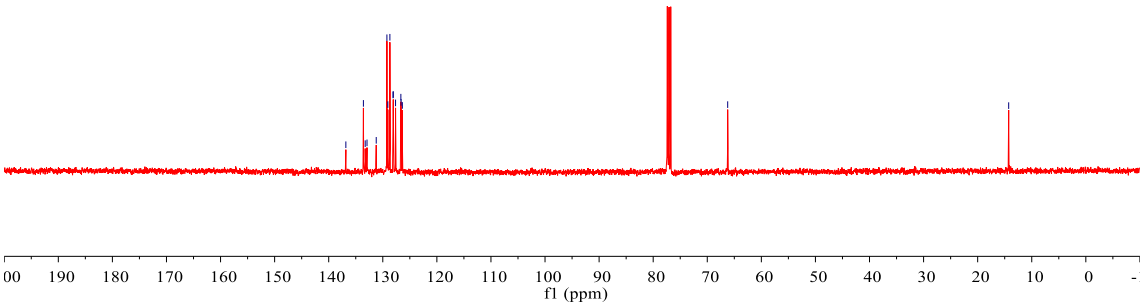


^{1}H NMR 400 MHz $CDCl_3$

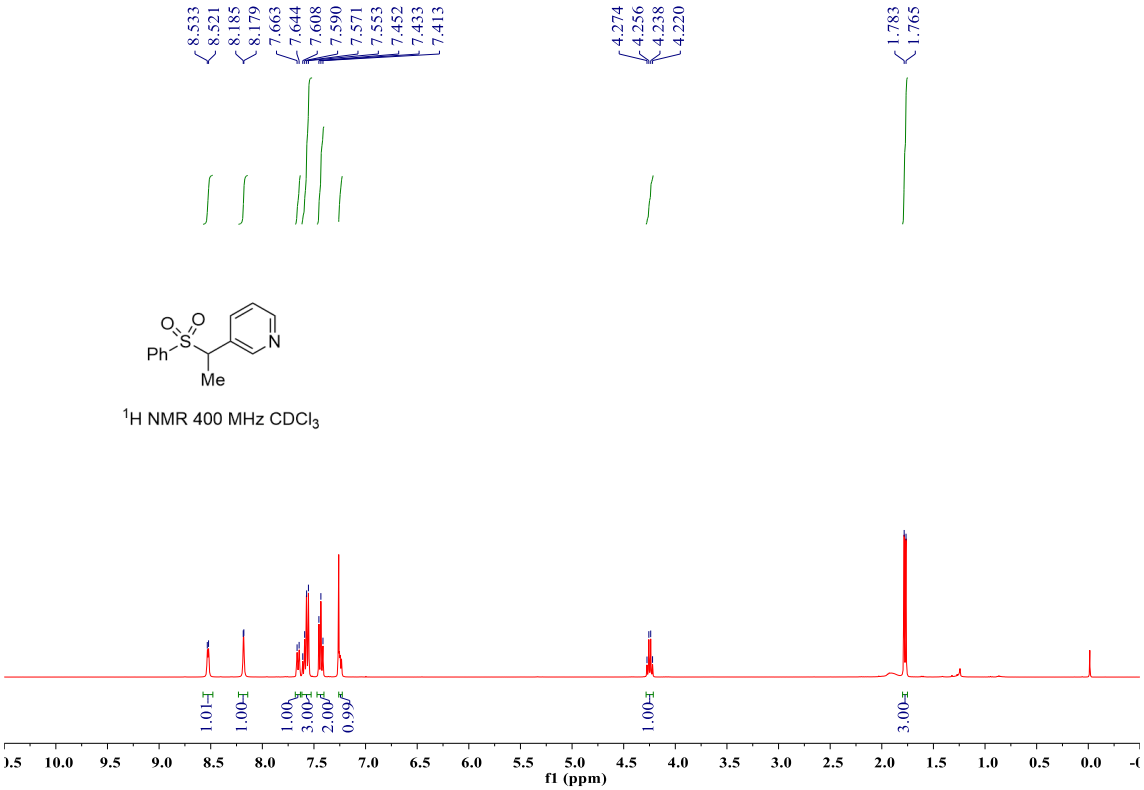




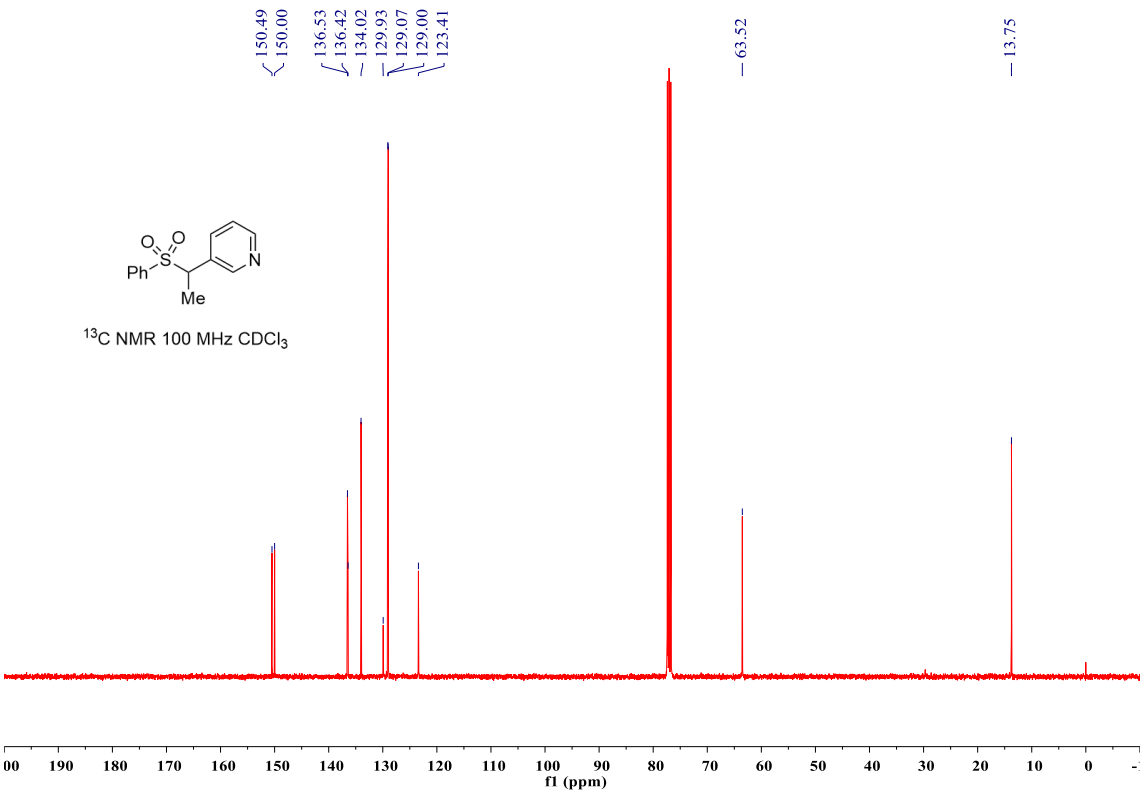
^{13}C NMR 100 MHz $CDCl_3$



3-((1-Phenylethyl)sulfonyl)pyridine (2ac)

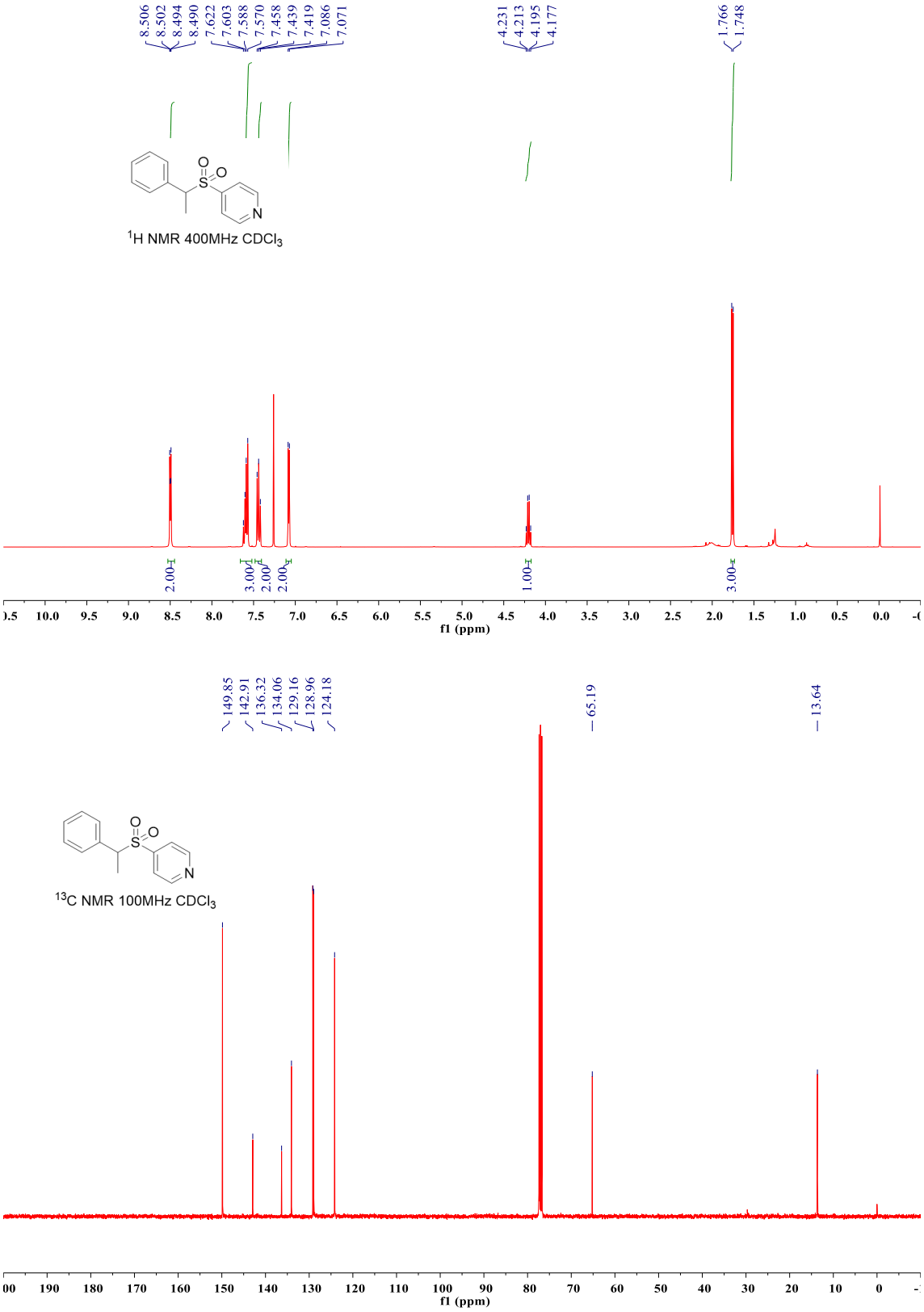


^{1}H NMR 400 MHz $CDCl_3$

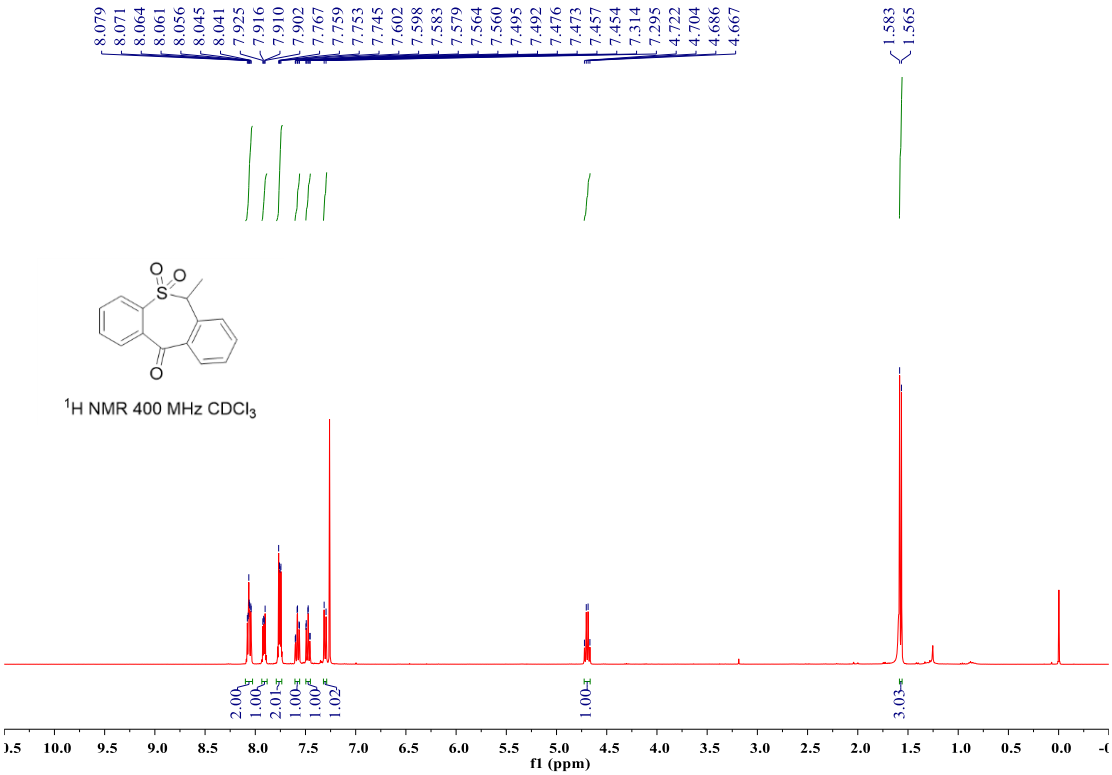


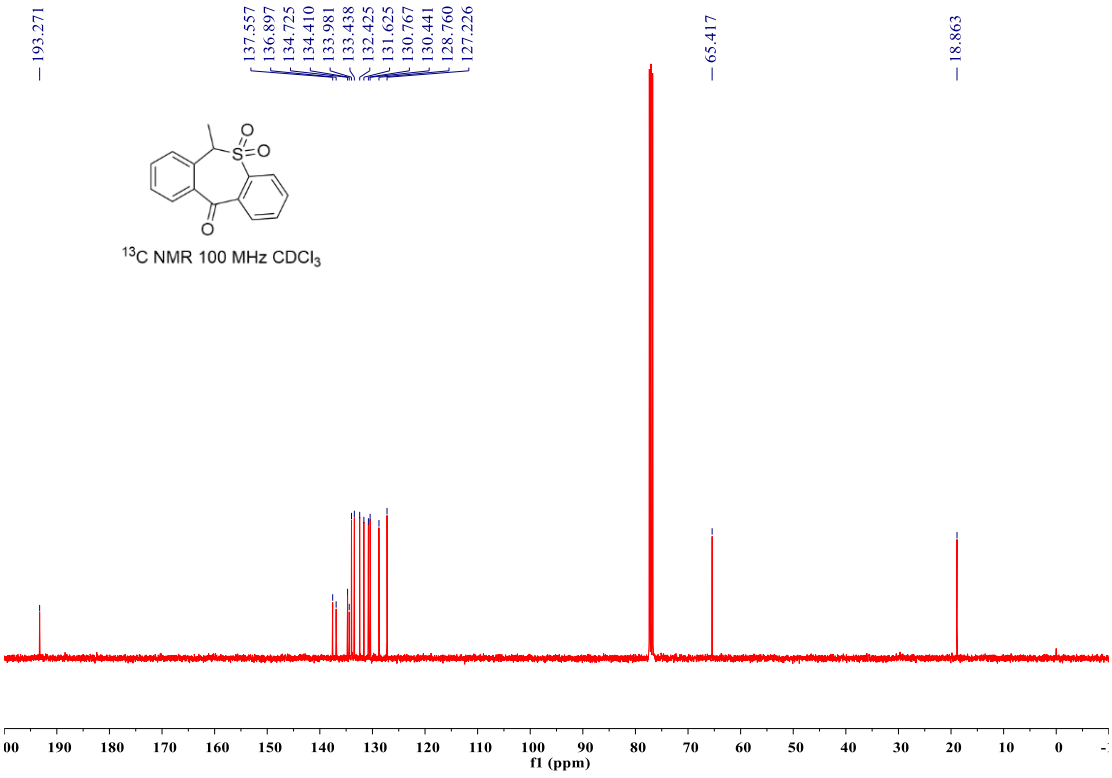
^{13}C NMR 100 MHz $CDCl_3$

4-((1-Phenylethyl)sulfonyl)pyridine (2ad)

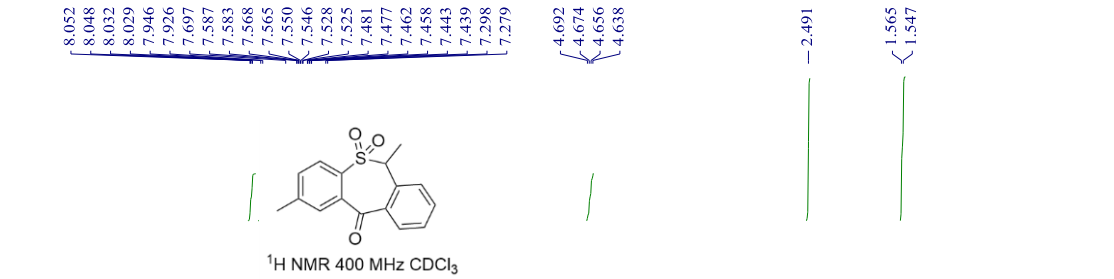


6-Mmethyldibenzo[*b*,*e*]thiepin-11(6*H*)-one 5,5-dioxide (4a)

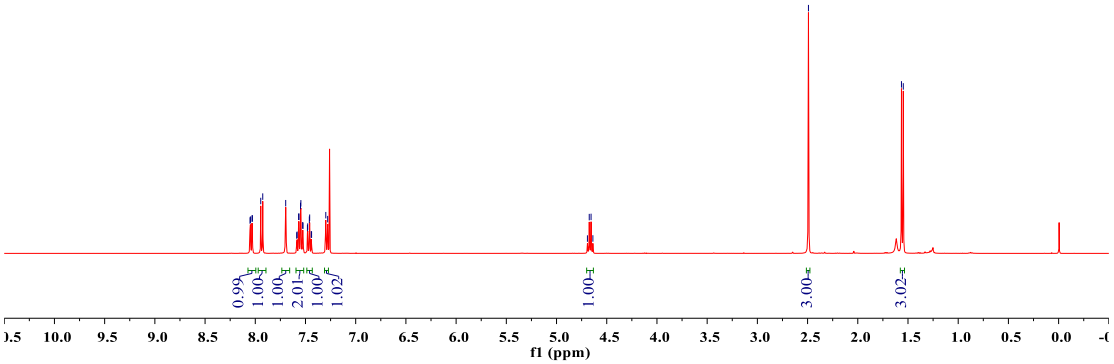


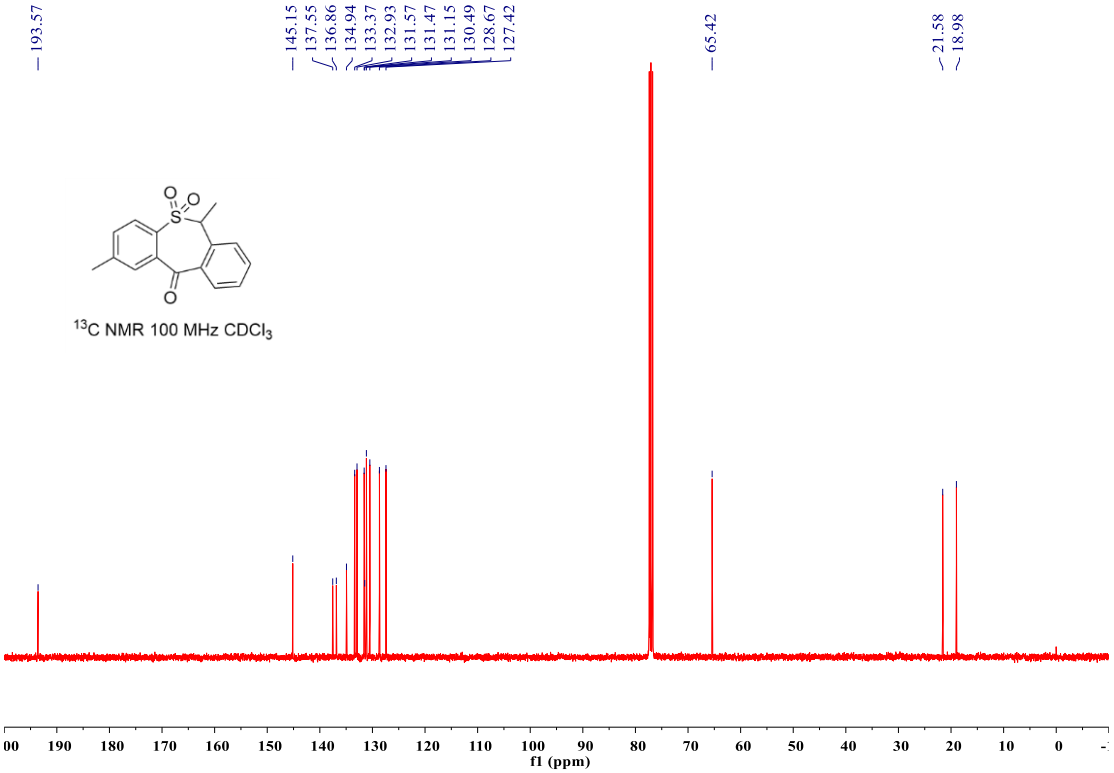


2,6-Dimethyldibenzo[*b*,*e*]thiepin-11(6*H*)-one 5,5-dioxide (4b)



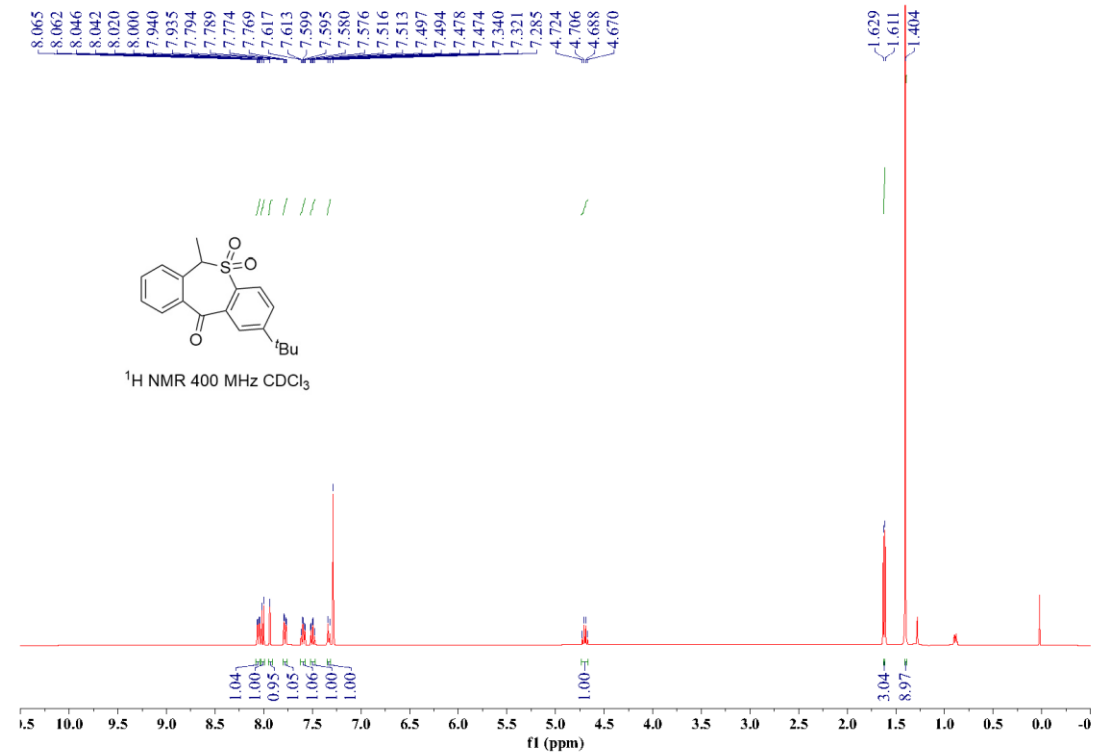
^{1}H NMR 400 MHz $CDCl_3$



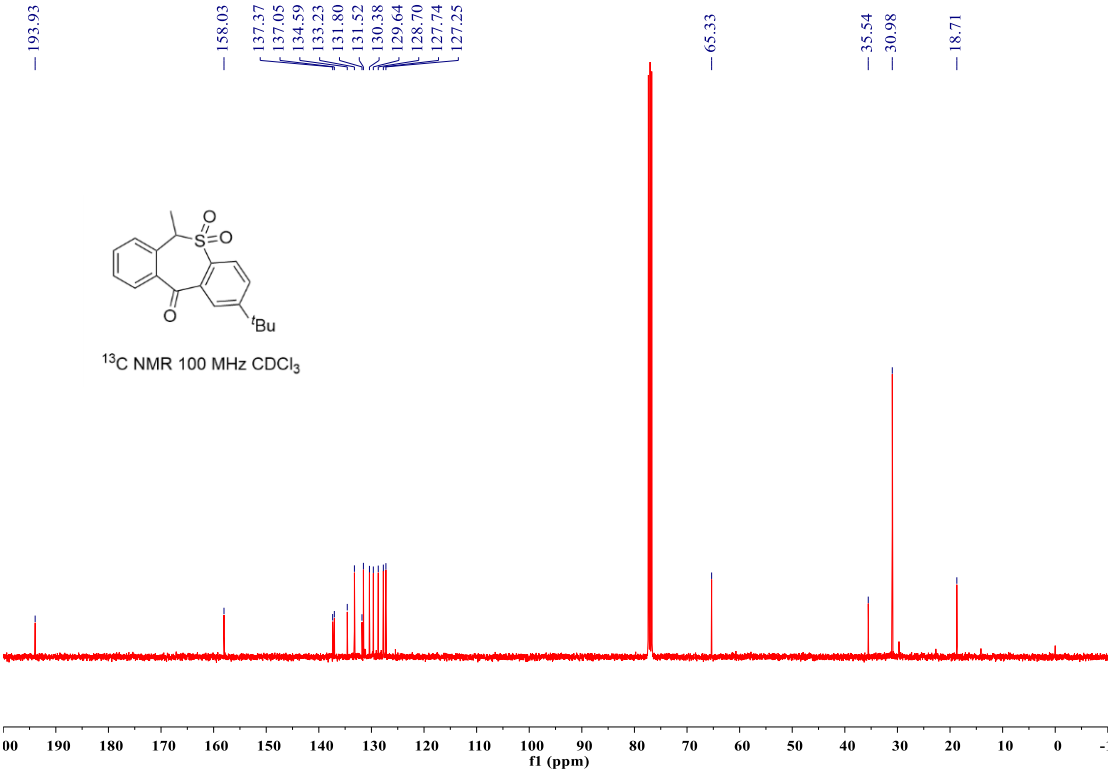


^{13}C NMR 100 MHz $CDCl_3$

2-(*tert*-Butyl)-6-methyldibenzo[*b*,*e*]thiepin-11(6*H*)-one 5,5-dioxide (4c)

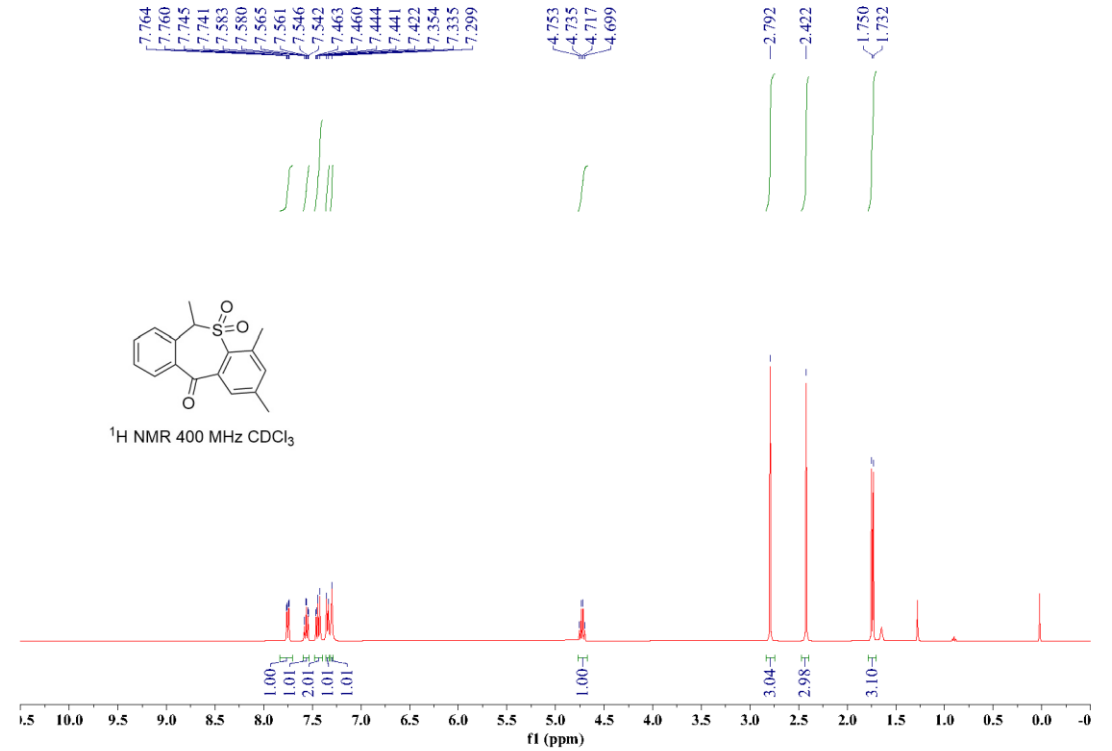


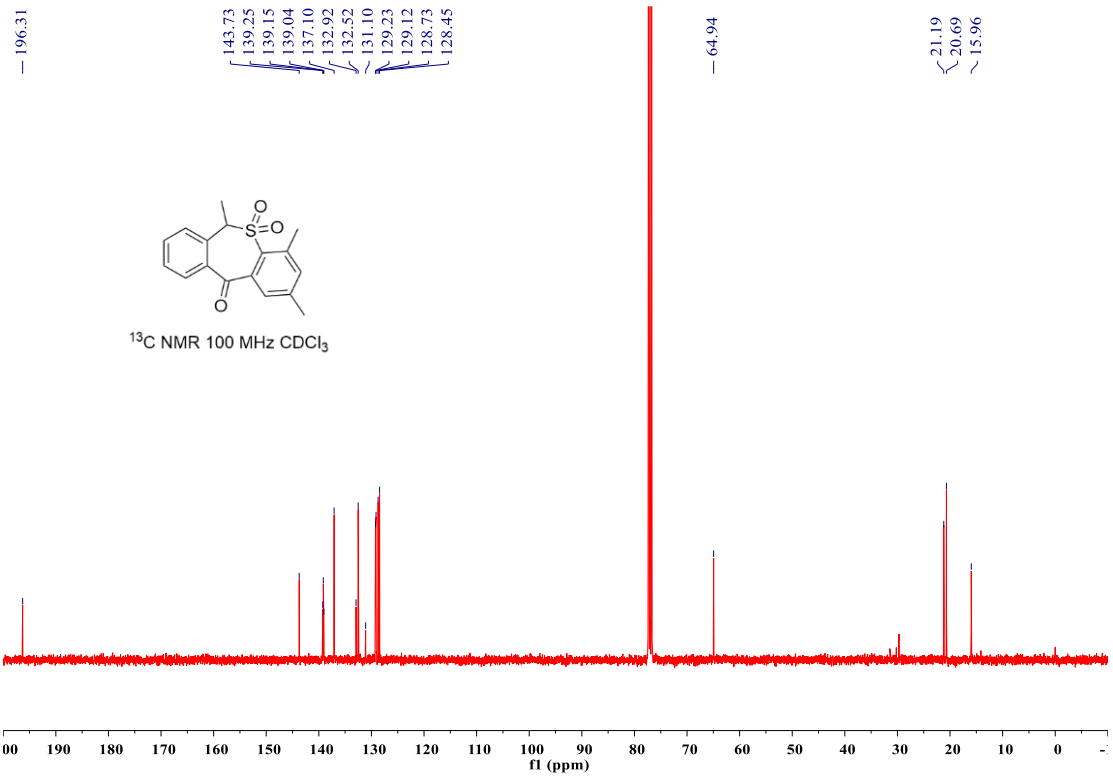
^{1}H NMR 400 MHz $CDCl_3$



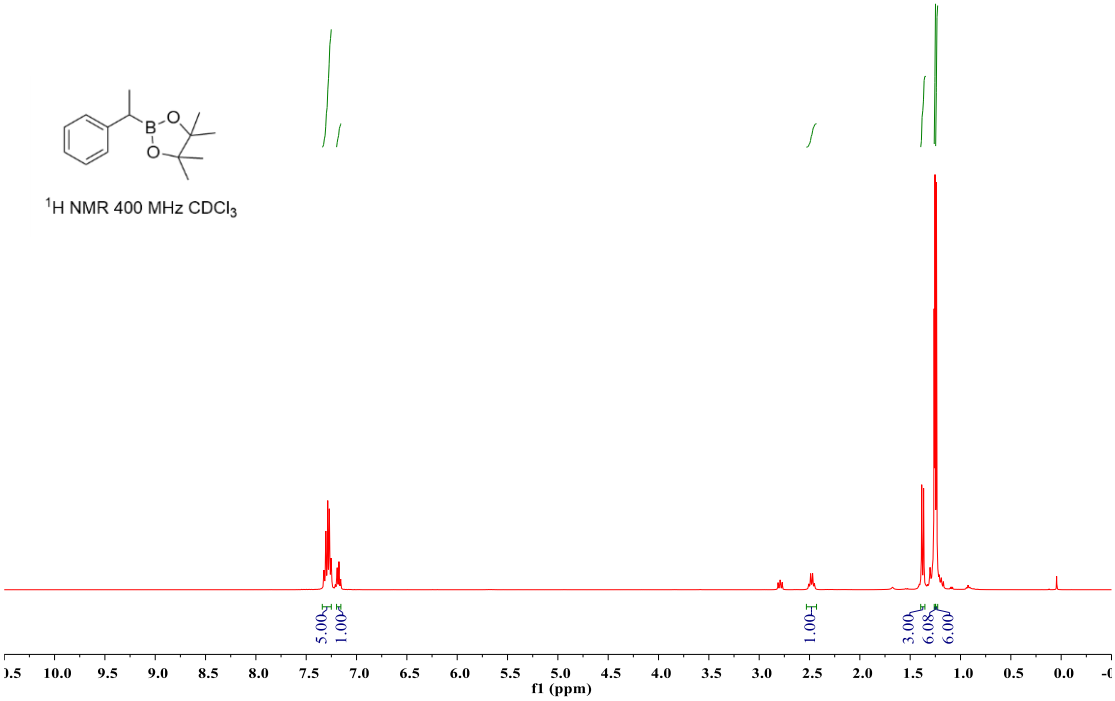
^{13}C NMR 100 MHz $CDCl_3$

2,4,6-Trimethyldibenzo[*b*,*e*]thiepin-11(6*H*)-one 5,5-dioxide (4d)

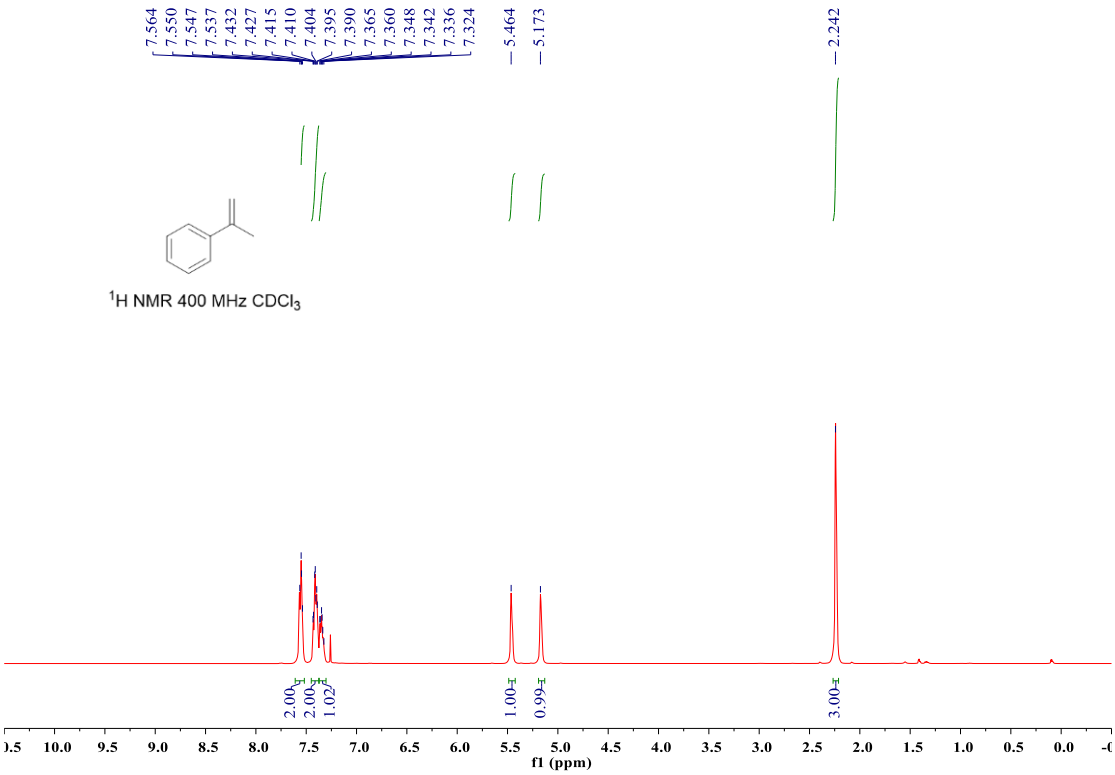




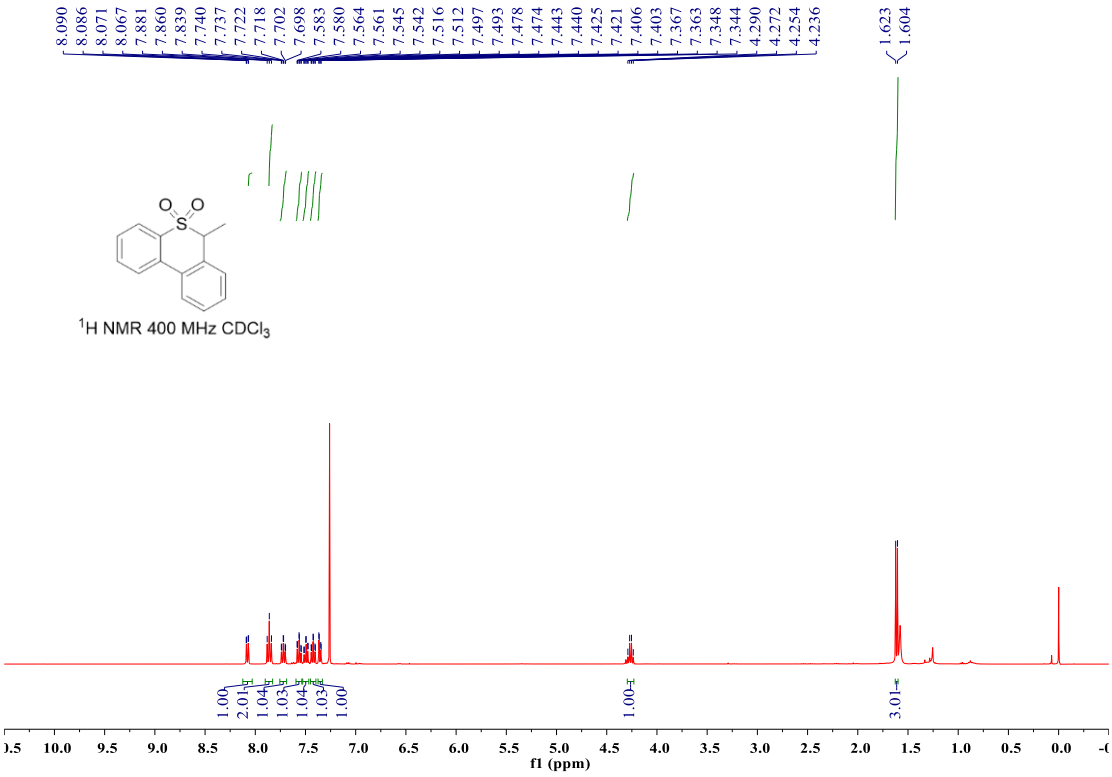
4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (5a)

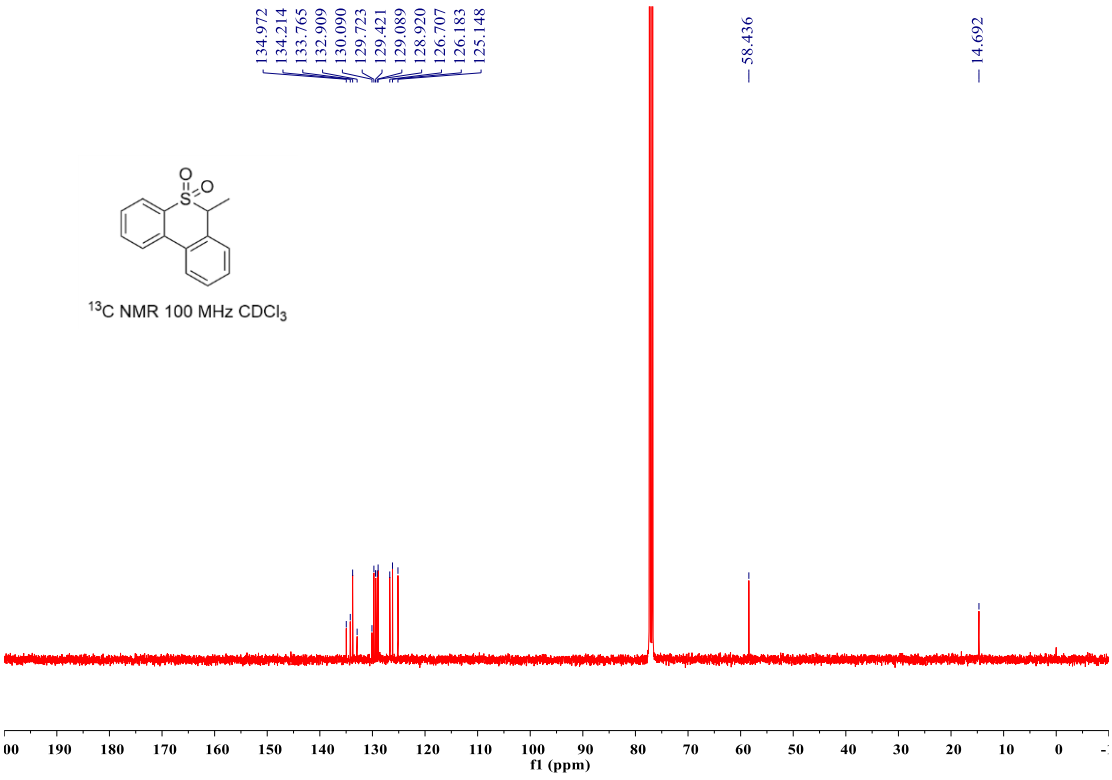


prop-1-en-2-ylbenzene (6a)

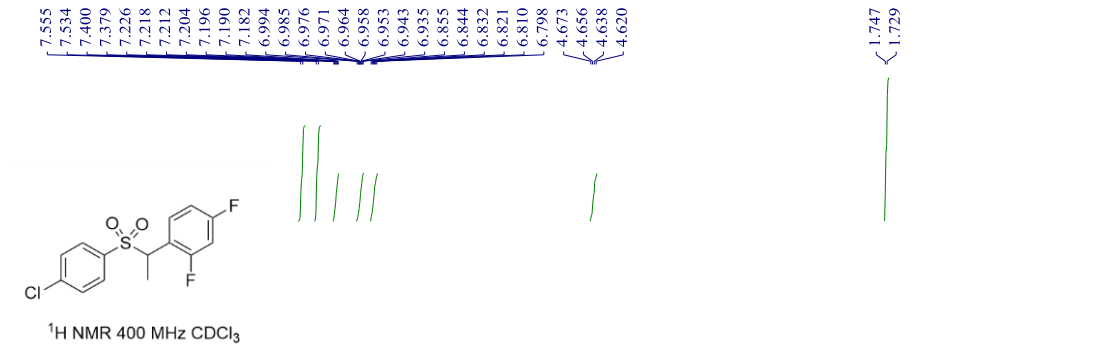


6-Methyl-6*H*-benzo[*c*]thiochromene 5,5-dioxide (7i)

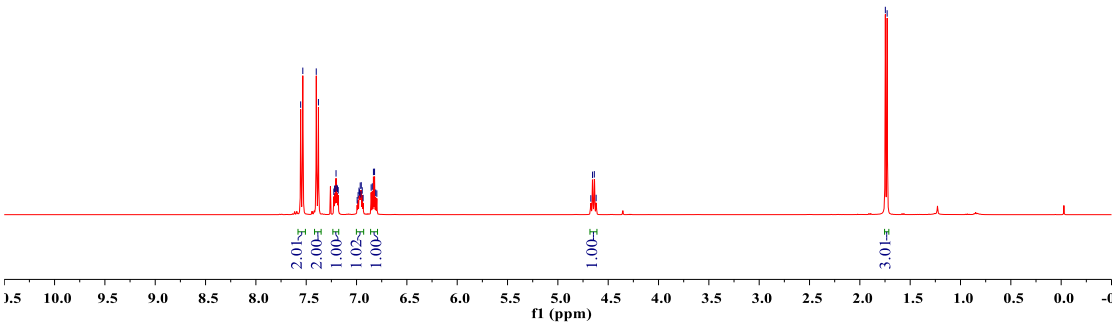


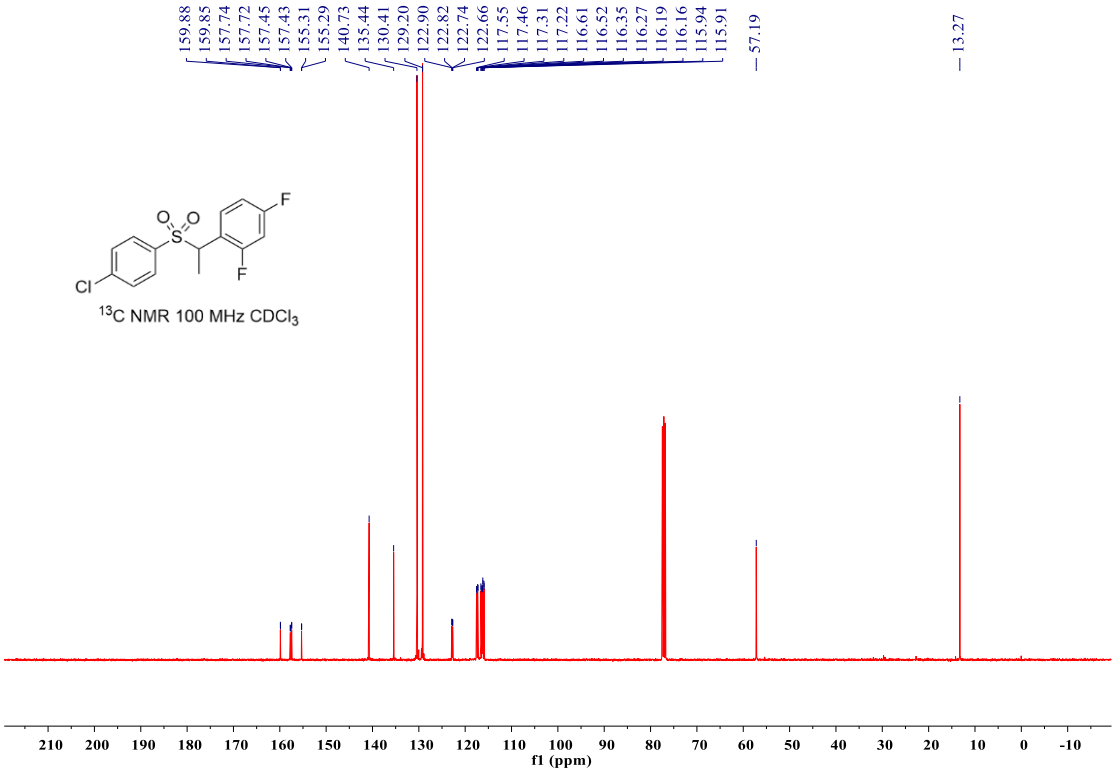


2-(1-((4-chlorophenyl)sulfonyl)ethyl)-1,4-difluorobenzene (compound B)

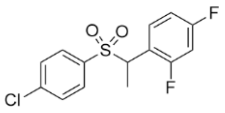


^{1}H NMR 400 MHz $CDCl_3$



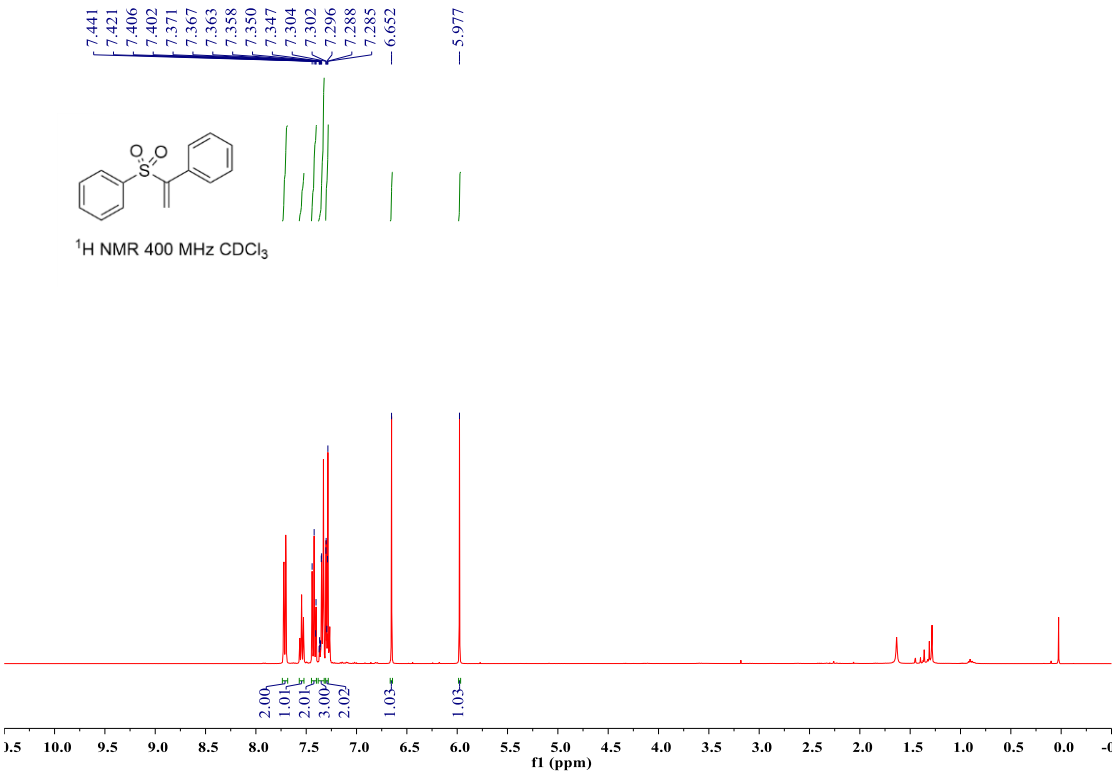


^{13}C NMR 100 MHz $CDCl_3$



^{19}F NMR 377 MHz $CDCl_3$

(1-(phenylsulfonyl)vinyl)benzene (8a)



((1-Phenylethyl-1,2,2,2-d$_4$)sulfonyl)benzene (2a')