

Supplementary Information

Copper-Catalyzed Fluoroamide-Directed Remote Benzylic C-H Olefination: Facile Access to Internal Alkenes

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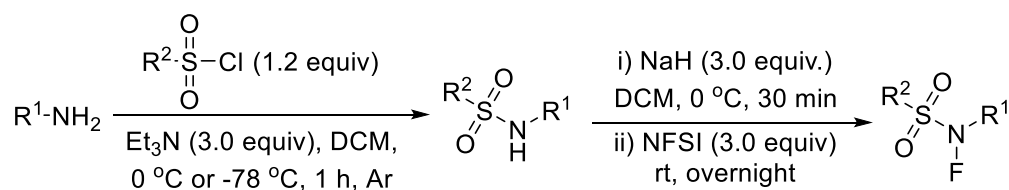
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(A) General Experimental Procedures

(a) General information

^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 MHz advance spectrometer at room temperature in CDCl_3 using TMS as internal standard. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting Points were recorded on Hanon MP100 Apparatus. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE) / ethyl acetate (EA). All *N*-Fluorosulfonamides **1** were synthesized according to the known procedures.¹⁻³

(b) General procedure for the synthesis *N*-Fluorosulfonamides.^{1,2}

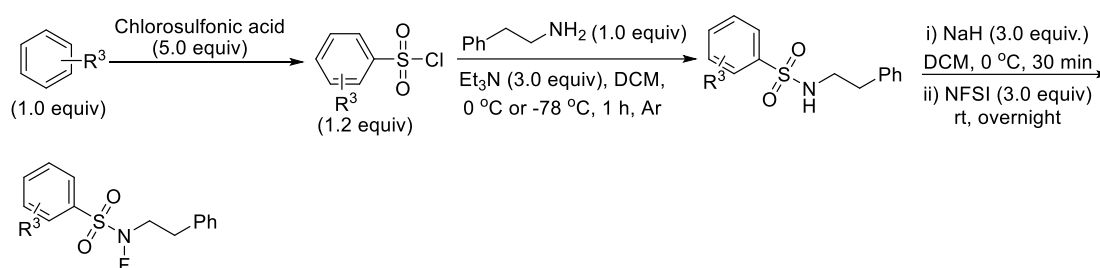


The sulfonamides were synthesized according to procedures described previously in the literature.¹ To a solution of amine (10 mmol; 1equiv) and Et_3N (15 mmol; 1.5 equiv) in dichloromethane (30mL) was added sulfonyl chloride (12 mmol; 1.2 equiv) under argon at 0°C . The mixture was then stirred for 30 min under 0°C . Then, the mixture was stirred for overnight at room temperature. A water (30 mL) was added to the reaction and the aqueous layer was extracted DCM (3×20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The crude material was purified by silica gel chromatography.

Starting materials **1a-1g**, **1i** and **1l-1q** were synthesized according to procedures described previously in the literature with 32-68% yields.^{1,2} To a clean, dry round bottom flask was added a magnetic stir bar, and NaH (15 mmol; 3 equiv) was dissolved in dry DCM (30 mL), followed by slow addition of sulfonamide (5 mmol; 1

equiv) in DCM (15 mL) under 0 °C. The mixture was then stirred for 30 min under nitrogen. Then, NFSI (15 mmol; 3 equiv) was added to the mixture and the resulting slurry was stirred for overnight at room temperature. Upon completion, the reaction was quenched by the addition of water. The mixture was extracted with DCM (3 × 30 mL) and the organic layers were combined, washed with brine, and dried over anhydrous Na₂SO₄. The crude mixture was filtered through celite and concentrated. The resulting residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate.

(c) General procedure for the synthesis of Substrates 1j-1k.^{1,3}



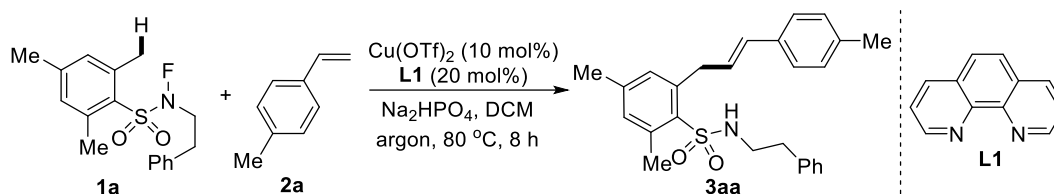
The benzenesulfonyl chlorides were synthesized according to procedures described previously in the literatures.^{1,3} Chlorosulfonic acid (5 mL; 5.0 equiv) was added to a solution of alkyl benzene (15 mmol) in chloroform (20 mL) dropwise at 0 °C. The resulting solution was stirred at room temperature for 1 h. The reaction mixture was poured onto ice, and the aqueous phase was extracted with chloroform twice. Upon reaction completion, the mixture was carefully poured over crushed ice and the aqueous layer was extracted with chloroform (3 × 5 mL). The combined organic layers were then washed with brine (10 mL), dried over sodium sulfate, and concentrated by rotary evaporation to give the crude product. The resulting oil was then purified by flash column chromatography (hexanes/ethyl acetate = 20:1).

The sulfonamides were synthesized according to procedures described previously in the literature.¹ To a solution of amine (10 mmol, 1 equiv) and Et₃N (15 mmol; 1.5 equiv) in dichloromethane (30 mL) was added sulfonyl chloride (12 mmol; 1.2 equiv) under argon at 0 °C. The mixture was then stirred for 30 min under 0 °C. Then, the mixture was stirred for overnight at room temperature. A water (30 mL) was added to the reaction and the aqueous layer was extracted DCM (3 × 20 mL). The combined

organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by silica gel chromatography.

To a clean, dry round bottom flask was added a magnetic stir bar, and NaH (15 mmol; 3equiv) was dissolved in dry DCM (30 mL), followed by slow addition of sulfonamide (5 mmol; 1 equiv) in DCM (15 mL) under 0 °C. The mixture was then stirred for 30 min under nitrogen. Then, NFSI (15 mmol; 3 equiv) was added to the mixture and the resulting slurry was stirred for overnight at room temperature. Upon completion, the reaction was quenched by the addition of water. The mixture was extracted with DCM (3 × 30 mL) and the organic layers were combined, washed with brine, and dried over anhydrous Na₂SO₄. The crude mixture was filtered through celite and concentrated. The resulting residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to give product **1j-k**.^{1,3}

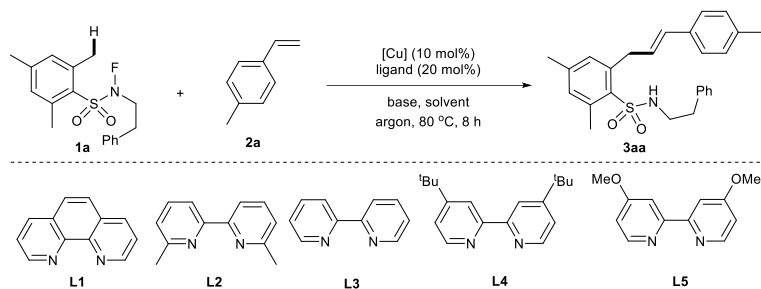
(d) Typical Experimental Procedure for Copper-Catalyzed Fluoroamide-Directed Remote Benzylic C-H Olefination:



To a Schlenk tube were added Cu(OTf)₂ (7.24 mg; 0.02 mmol; 10 mol%), 1,10-phenanthroline (7.20 mg; 0.04 mmol, 20 mol%), N-fluoro-2,4,6-trimethyl-N-phenethylbenzenesulfonamide **1a** (64.2 mg, 0.2 mmol, 1.0 equiv), 4-methylstyrene **2a** (47.2 mg, 0.4 mmol, 2.0 equiv), Na₂HPO₄ (56.8 mg; 0.4mmol; 2.0 equiv), and DCM (2 mL). Then the tube was charged with argon three times, and was stirred at 80 °C for 8 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1; R_f = 0.2) to provide **3aa** in 67% isolated yield (56.1 mg).

(e) Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions.^a

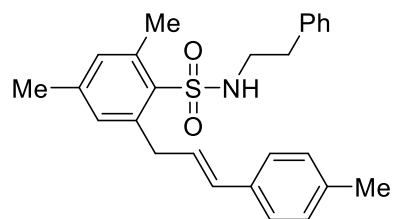


Entry	[Cu] [mol%]	Ligand	Base	Solvent	Yield [%] ^b
1	Cu(CH ₃ CN) ₄ PF ₆ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	23
2	Cu(CH ₃ CN) ₄ BF ₄ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	18
3	CuBr (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	<5
4 ^c	Cu(OAc) ₂ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	<5
5	Cu(OTf) ₂ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	67
6	Cu(OTf) ₂ (10)	L2	Na ₂ HPO ₄	CH ₂ Cl ₂	40
7	Cu(OTf) ₂ (10)	L3	Na ₂ HPO ₄	CH ₂ Cl ₂	61
8	Cu(OTf) ₂ (10)	L4	Na ₂ HPO ₄	CH ₂ Cl ₂	45
9	Cu(OTf) ₂ (10)	L5	Na ₂ HPO ₄	CH ₂ Cl ₂	35
10	Cu(OTf) ₂ (10)	—	Na ₂ HPO ₄	CH ₂ Cl ₂	trace
11	Cu(OTf) ₂ (10)	L1	Na ₂ HPO ₄	ClCH ₂ CH ₂ Cl	30
12	Cu(OTf) ₂ (10)	L1	Na ₂ HPO ₄	CH ₃ CN	15
13	Cu(OTf) ₂ (10)	L1	K ₂ HPO ₄	CH ₂ Cl ₂	18
14	Cu(OTf) ₂ (10)	L1	K ₃ PO ₄	CH ₂ Cl ₂	32
15	Cu(OTf) ₂ (10)	L1	—	CH ₂ Cl ₂	28
16	—	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	0
17	Cu(OTf) ₂ (5)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	38
18	Cu(OTf) ₂ (15)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	68
19 ^d	Cu(OTf) ₂ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	21
20 ^e	Cu(OTf) ₂ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	67
21 ^f	Cu(OTf) ₂ (10)	L1	Na ₂ HPO ₄	CH ₂ Cl ₂	61

^a Standard conditions: **1a** (0.2 mmol), **2a** (2 equiv), [Cu] (10 mol%), ligand (20 mol%), base (2 equiv), solvent (2 mL), argon, 80 °C and 8 h. ^b Yield of isolated product. ^c Some by products, including 7,9-dimethyl-2-phenethyl-3-(*p*-tolyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]-thiazepine 1,1-dioxide **8aa** (18% yield) via [5+2] annulation and substrate **1a** defluorination product **9a** (about 5% yield). ^d At 70 °C. ^e At 90 °C. ^f **1a** (1 mmol) for 20 h.

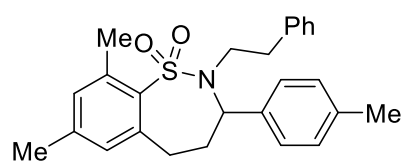
(B) Analytical data

(E)-2,4-dimethyl-N-phenethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3aa) (E/Z> 99:1).



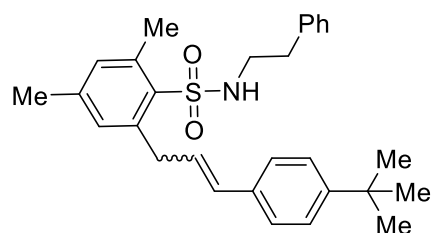
56.1 mg, 67% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.26 - 7.21 (m, 5H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.05 (s, 1H), 7.01 - 6.97 (m, 3H), 6.41 - 6.33 (m, 2H), 4.53 (t, $J = 6.0$ Hz, 1H), 3.95 (d, $J = 5.5$ Hz, 2H), 3.17 - 3.12 (m, 2H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.56 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 142.4, 141.2, 139.2, 137.7, 137.0, 134.4, 133.4, 132.4, 131.5, 131.0, 129.2, 128.7, 128.6, 128.4, 126.7, 126.0, 43.7, 37.8, 35.6, 23.0, 21.1, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 420.1992, found 420.1996.

7,9-dimethyl-2-phenethyl-3-(p-tolyl)-2,3,4,5-tetrahydrobenzo[f][1,2]thiazepine 1,1-dioxide (8aa).



15.1 mg, 18% yield; $R_f = 0.2$ (PE/EA = 20: 1); white solid; m.p. 163.2 - 164.5 °C (uncorrected); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.38 (d, $J = 7.5$ Hz, 2H), 7.24 (d, $J = 7.5$ Hz, 2H), 7.13 (t, $J = 7.0$ Hz, 2H), 7.10 - 7.06 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 2H), 6.69 (d, $J = 7.0$ Hz, 2H), 5.51 (d, $J = 10.5$ Hz, 1H), 3.72 (t, $J = 12.5$ Hz, 1H), 2.96 - 2.88 (m, 1H), 2.79 - 2.73 (m, 1H), 2.69 (s, 3H), 2.67 - 2.59 (m, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 2.18 - 2.07 (m, 2H), 1.84 - 1.75 (m, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 142.0, 140.02, 139.96, 139.0, 138.0, 135.9, 135.5, 132.0, 131.2, 129.2, 128.64, 128.57, 128.3, 126.1, 62.2, 46.4, 37.4, 35.3, 27.0, 23.0, 21.2, 20.9; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 420.1992, found 420.1996.

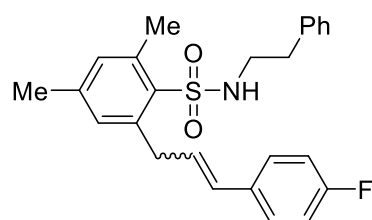
2-(3-(4-(tert-butyl)phenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3ab) (E/Z = 5:1).



53.5 mg, 58% yield; $R_f = 0.1$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.39 (d, $J = 8.0$ Hz, 0.4H), 7.33 (d, $J = 8.0$

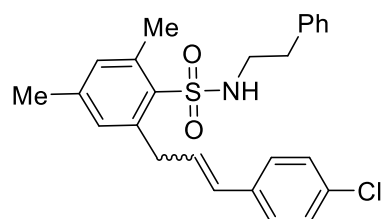
Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2.4H), 7.26 - 7.24 (m, 1.2H), 7.24 - 7.17 (m, 3.6H), 7.06 (s, 0.2H), 7.04 (s, 1H), 6.98 (d, $J = 8.0$ Hz, 2.4H), 6.41 - 6.31 (m, 2H), 4.55 (t, $J = 6.0$ Hz, 1H), 4.47 (t, $J = 6.0$ Hz, 0.2H), 3.95 (d, $J = 5.5$ Hz, 2H), 3.18 - 3.12 (m, 2.8H), 2.76 (t, $J = 7.0$ Hz, 0.4H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.56 (s, 3H), 2.49 (s, 0.6H), 2.31 (s, 3.6H), 1.31 (s, 10.8H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 150.3, 142.3, 141.2, 139.2, 137.7, 134.4, 133.3, 132.4, 131.4, 131.0, 128.65, 128.61, 128.59, 126.7, 125.8, 125.4, 43.7, 37.8, 35.6, 34.5, 31.2, 23.0, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{29}\text{H}_{36}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 462.2461, found 462.2466.

2-(3-(4-fluorophenyl)allyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide (3ac)
($E/Z = 4:1$).



63.4 mg, 75% yield; $R_f = 0.2$ (PE/EA = 10 : 1); white solid; m.p. 110.2 - 110.9 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.30 - 7.27 (m, 2H), 7.25 - 7.21 (m, 3H), 7.04 - 7.00 (m, 3H), 6.99 - 6.95 (m, 3H), 6.39 - 6.27 (m, 2H), 4.56 (t, $J = 6.0$ Hz, 0.8H), 4.49 (t, $J = 6.0$ Hz, 0.2H), 3.94 (d, $J = 6.0$ Hz, 2H), 3.18 - 3.15 (m, 2H), 2.76 (t, $J = 7.0$ Hz, 0.4H), 2.70 (t, $J = 7.0$ Hz, 1.6H), 2.55 (s, 2.4H), 2.49 (s, 0.6H), 2.33 (s, 2.4H), 2.32 (s, 0.6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 162.0 (d, $J_{\text{C-F}} = 244.6$ Hz), 142.7, 142.42, 142.38, 141.0, 139.1, 139.0, 137.63, 137.59, 133.3, 132.5, 132.4, 131.5, 129.8, 129.40, 129.39, 128.74, 128.67, 128.59, 128.56, 127.5 (d, $J_{\text{C-F}} = 8.0$ Hz), 126.8, 126.7, 115.4 (d, $J_{\text{C-F}} = 21.5$ Hz), 115.4 (d, $J_{\text{C-F}} = 21.5$ Hz), 43.7, 43.6, 37.9, 35.6, 35.5, 22.9, 22.6, 21.0, 20.9; ^{19}F NMR (471 MHz, CDCl_3) δ (ppm) -113.8 (s, 0.25F), -115.1 (s, 1.0F); LRMS (EI, 70 eV) m/z (%): 423(M^+ , 1), 303(5), 238(100), 223(62), 135(8), 109(22), 91(16); HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{FNO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 424.1741, found 424.1749.

2-(3-(4-chlorophenyl)allyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide (3ad)
($E/Z = 4:1$).

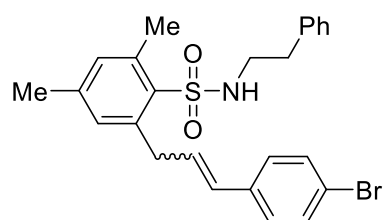


63.2 mg, 72% yield; $R_f = 0.2$ (PE/EA = 10 : 1); white solid; m.p. 118.7 - 119.5 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.25 - 7.20 (m, 7H), 7.04 -

6.97 (m, 4H), 6.42 - 6.31 (m, 2H), 4.47 (t, $J = 6.0$ Hz, 0.8H), 4.42 (t, $J = 6.0$ Hz, 0.2H), 3.93 (d, $J = 5.5$ Hz, 2H), 3.17 - 3.13 (m, 2H), 2.75 (d, $J = 7.0$ Hz, 0.40H), 2.70 (d, $J = 6.9$ Hz, 1.60H), 2.54 (s, 2.4H), 2.47 (s, 0.6H), 2.33 (s, 2.4H), 2.31 (s, 0.6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.5, 140.9, 139.1, 137.6, 135.7, 133.3, 132.7, 132.6, 131.5, 130.4, 129.8, 128.8, 128.7, 128.61, 128.58, 128.55, 127.3, 126.8, 43.7, 43.6, 38.0, 35.6, 35.5, 22.9, 22.6, 21.0, 20.9; LRMS (EI, 70 eV) m/z (%): 439(M^+ , 2), 319(4), 255(40), 254(100), 239(52), 220(18), 219(77), 205(9), 204(22), 125(24), 91(31); HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{ClNO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$ 440.1446, found440.1452.

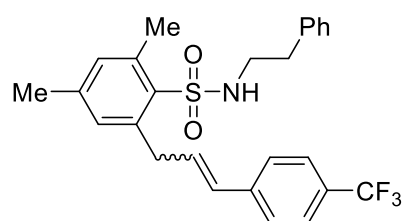
2-(3-(4-bromophenyl)allyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide

(3ae)($E/Z = 3:1$).



65.7 mg, 68% yield; $R_f = 0.2$ (PE/EA = 10 : 1); white solid; m.p. 126.7 - 127.5 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.48 (d, $J = 8.5$ Hz, 0.5H), 7.39 (d, $J = 8.5$ Hz, 1.5H), 7.24 - 7.21 (m, 3H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.03 - 6.98 (m, 4H), 6.40 (dt, $J = 16.0, 6.5$ Hz, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 4.56 (t, $J = 6.0$ Hz, 0.75H), 4.50 (t, $J = 6.0$ Hz, 0.25H), 3.93 (d, $J = 6.0$ Hz, 2H), 3.15 (q, $J = 6.5$ Hz, 2H), 2.76 (t, $J = 7.0$ Hz, 0.5H), 2.70 (t, $J = 7.0$ Hz, 1.5H), 2.55 (s, 2.25H), 2.49 (s, 0.75H), 2.33 (s, 2.25H), 2.31 (s, 0.75H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.4, 140.8, 139.1, 137.6, 136.2, 133.3, 132.6, 132.4, 131.51, 131.46, 130.6, 129.8, 128.73, 128.71, 128.67, 128.6, 128.5, 127.6, 126.8, 126.7, 120.8, 43.7, 43.6, 38.0, 35.6, 35.5, 22.8, 22.6, 21.0, 20.9; HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{BrNO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$ 484.0940, found484.0948.

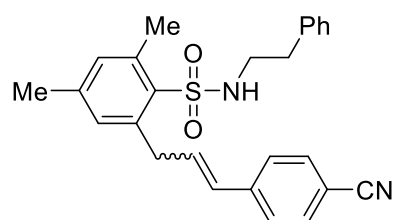
2,4-dimethyl-*N*-phenethyl-6-(3-(4-(trifluoromethyl)phenyl)allyl)benzenesulfonamide (3af)($E/Z = 2:1$).



61.5 mg, 65% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.61 (d, $J = 8.5$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1.33H), 7.48 - 7.43 (m, 1H), 7.40 (d, $J = 8.0$ Hz, 1.67H), 7.25 - 7.20 (m, 3H), 7.03 - 6.98 (m, 3H), 6.92 (d, $J = 11.0$ Hz, 0.33H), 6.65 - 6.44 (m, 1H), 6.41 (d, $J = 16.0$ Hz, 0.66H), 4.50 (t, $J = 6.0$ Hz, 0.66H), 4.46 (t, $J = 6.0$ Hz,

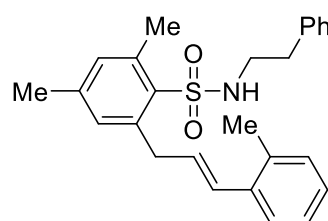
0.33H), 3.97 (d, $J = 6.5$ Hz, 1.34H), 3.19 - 3.13 (m, 2.67H), 2.77 - 2.71 (m, 2H), 2.54 (s, 2H), 2.48 (s, 1H), 2.33 (s, 2H), 2.31 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.6, 142.5, 140.8, 140.7, 139.2, 139.0, 137.56, 137.54, 133.4, 132.7, 132.6, 132.5, 131.5, 129.7, 128.8, 128.7, 128.61, 128.57, 126.9, 126.8, 126.2, 125.4 (q, $J_{\text{C-F}} = 3.5$ Hz), 43.69, 43.65, 38.1, 35.6, 35.5, 22.8, 22.6, 21.0, 20.9; ^{19}F NMR (471 MHz, CDCl_3) δ (ppm) -62.4 (s, 2F), -62.5 (s, 1F); LRMS (EI, 70 eV) m/z (%): 473(M^+ , 2), 353(12), 288(100), 274(15), 159(13), 120(21), 91(31); HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{F}_3\text{NO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$ 474.1709, found 474.1715.

2-(3-(4-cyanophenyl)allyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide (3ag)(*E/Z* = 1.5:1).



54.2 mg, 63% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.63 (d, $J = 8.0$ Hz, 0.8H), 7.53 (d, $J = 8.0$ Hz, 1.2H), 7.44 (d, $J = 8.0$ Hz, 0.8H), 7.37 (d, $J = 8.0$ Hz, 1.2H), 7.25 - 7.19 (m, 3H), 7.18 - 7.13 (m, 0.4H), 7.09 - 7.06 (m, 0.4H), 7.05 (d, $J = 7.0$ Hz, 0.8H), 7.02 (d, $J = 6.5$ Hz, 1.2H), 6.99 (s, 1.2H), 6.95 (s, 0.8H), 6.59 - 6.52 (m, 0.6H), 6.38 (d, $J = 16.0$ Hz, 0.6H), 4.52 (t, $J = 6.0$ Hz, 0.6H), 4.47 (t, $J = 6.0$ Hz, 0.4H), 3.96 (d, $J = 6.5$ Hz, 1.2H), 3.19 - 3.12 (m, 2.8H), 2.77 - 2.71 (m 2H), 2.53 (s, 1.8H), 2.47 (s, 1.2H), 2.33 (s, 1.8H), 2.31 (s, 1.2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.6, 142.5, 142.4, 141.8, 140.4, 139.2, 139.0, 137.5, 134.1, 133.4, 132.7, 132.6, 132.3, 132.2, 131.5, 129.3, 128.8, 128.7, 128.58, 128.55, 126.9, 126.8, 126.5, 125.85, 125.79, 110.2, 43.7, 43.6, 38.3, 35.6, 35.5, 22.7, 22.5, 21.0, 20.9; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$ [$\text{M}+\text{H}$] $^+$ 431.1788, found 431.1793.

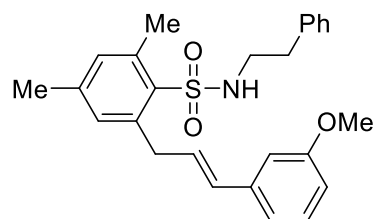
(*E*)-2,4-dimethyl-*N*-phenethyl-6-(3-(*o*-tolyl)allyl)benzenesulfonamide (3ah)(*E/Z* > 99:1).



52.8 mg, 63% yield; $R_f = 0.1$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.44 - 7.39 (m, 1H), 7.22 (t, $J = 8.5$ Hz, 3H), 7.17 - 7.13 (m, 3H), 7.07 (s, 1H), 7.01 (d, $J = 7.0$ Hz, 2H), 6.98 (s, 1H), 6.66 (d, $J = 16.0$ Hz, 1H), 6.28 - 6.20 (m, 1H), 4.54 (t, $J = 6.0$ Hz, 1H), 3.98 (d, $J = 6.5$ Hz, 2H),

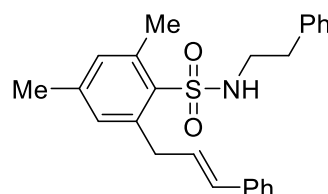
3.17 (q, $J = 6.5$ Hz, 2H), 2.72 (t, $J = 7.0$ Hz, 2H), 2.56 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.3, 141.3, 139.1, 137.6, 136.3, 135.1, 133.3, 132.4, 131.25, 130.6, 130.2, 129.1, 128.68, 128.6, 127.1, 126.7, 126.0, 125.4, 43.7, 38.2, 35.6, 23.0, 21.0, 19.8; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 420.1992, found 420.1999.

(E)-2-(3-(3-methoxyphenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3ai)(E/Z>99:1).



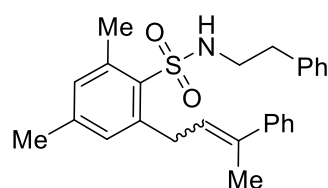
36.5 mg, 42% yield; $R_f = 0.1$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.25 - 7.18 (m, 4H), 7.04 (s, 1H), 7.02 - 6.96 (m, 3H), 6.94 (d, $J = 7.5$ Hz, 1H), 6.88 (s, 1H), 6.77 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.46 - 6.32 (m, 2H), 4.49 (t, $J = 6.0$ Hz, 1H), 3.95 (d, $J = 5.0$ Hz, 2H), 3.79 (s, 3H), 3.15 (q, $J = 7.0$ Hz, 2H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.55 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 159.8, 142.4, 141.0, 139.2, 138.7, 137.6, 133.4, 132.5, 131.5, 131.0, 129.9, 129.5, 128.7, 128.6, 126.8, 118.9, 112.9, 111.4, 55.2, 43.7, 37.8, 35.6, 23.0, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 436.1941, found 436.1945.

2-cinnamyl-4,6-dimethyl-N-phenethylbenzenesulfonamide (3aj)(E/Z > 99:1).



59.1 mg, 73% yield; $R_f = 0.1$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.34 (d, $J = 8.5$ Hz, 2H), 7.32 - 7.28 (m, 3H), 7.24 - 7.22 (m, 3H), 7.05 (s, 1H), 7.01 - 6.98 (m, 3H), 6.40 (s, 2H), 4.55 - 4.48 (m, 1H), 3.96 (s, 2H), 3.16 - 3.12 (m, 2H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.55 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.4, 141.0, 139.2, 137.6, 137.2, 133.3, 132.5, 131.5, 131.1, 129.5, 128.7, 128.6, 128.5, 127.2, 126.7, 126.1, 43.7, 37.9, 35.6, 23.0, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 406.1835, found 406.1842.

2,4-dimethyl-N-phenethyl-6-(3-phenylbut-2-en-1-yl)benzenesulfonamide (3al) (E/Z = 1:1).

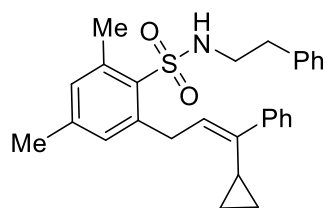


63.7 mg, 76% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.48 (d, $J = 7.5$ Hz, 2H), 7.40 (d, $J = 7.5$ Hz, 2H), 7.37 - 7.28 (m, 6H),

7.24 - 7.19 (m, 6H), 7.05 (d, $J = 6.0$ Hz, 3H), 7.00 (d, $J = 7.0$ Hz, 2H), 6.96 (s, 1H), 6.93 (s, 1H), 6.89 (s, 1H), 5.86 (t, $J = 6.5$ Hz, 1H), 5.31 (s, 1H), 5.11 (s, 1H), 4.52 (t, $J = 6.5$ Hz, 1H), 4.36 (t, $J = 6.5$ Hz, 1H), 3.97 (d, $J = 6.5$ Hz, 2H), 3.17 - 3.09 (m, 6H), 2.86 - 2.83 (m, 2H), 2.74 (t, $J = 7.0$ Hz, 2H), 2.68 (t, $J = 7.0$ Hz, 2H), 2.56 (s, 3H), 2.49 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 148.0, 143.5, 143.2, 142.4, 142.1, 142.0, 141.0, 139.2, 138.8, 137.65, 137.62, 136.0, 133.4, 133.1, 132.3, 132.2, 131.5, 131.0, 128.8, 128.7, 128.64, 128.60, 128.3, 128.2, 127.4, 127.0, 126.9, 126.8, 126.7, 126.2, 125.6, 112.8, 43.8, 43.6, 38.0, 35.63, 35.55, 34.5, 33.9, 23.1, 22.7, 21.0, 20.9, 16.2; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 420.1992, found 420.1997.

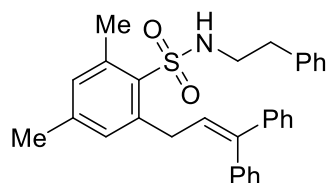
2-(3-cyclopropyl-3-phenylallyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide

(3am) (*E/Z* = 2:1).



65.0 mg, 73% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.34 - 7.30 (m, 3H), 7.25 - 7.21 (m, 5H), 7.21 - 7.16 (m, 4H), 7.05 - 6.98 (m, 3.5H), 6.95 (s, 0.5H), 6.90 (s, 1H), 6.82 (s, 1H), 5.80 - 5.74 (m, 0.5H), 5.67 - 5.57 (m, 1H), 4.72 - 4.61 (m, 0.5H), 4.48 - 4.37 (m, 1H), 4.15 (t, $J = 7.0$ Hz, 1H), 3.61 (t, $J = 7.5$ Hz, 2H), 3.15 - 3.10 (m, 1H), 3.09 - 3.02 (m, 2H), 2.70 - 2.66 (m, 3H), 2.56 (s, 1.5H), 2.51 (s, 3H), 2.31 (s, 1.5H), 2.28 (s, 3H), 1.89 - 1.83 (m, 0.5H), 1.64 - 1.60 (m, 1H), 0.87 - 0.83 (m, 1H), 0.66 - 0.58 (m, 2H), 0.45 - 0.39 (m, 2H), 0.39 - 0.36 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 143.0, 142.4, 142.3, 142.1, 141.6, 139.5, 139.1, 139.0, 137.7, 132.2, 132.0, 131.0, 130.7, 128.8, 128.7, 128.62, 128.59, 128.0, 127.7, 127.2, 126.8, 126.7, 126.6, 126.5, 123.84, 123.81, 43.8, 43.6, 35.7, 35.6, 33.8, 33.6, 23.1, 23.0, 21.0, 18.5, 11.6, 6.6, 5.1; HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{32}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 446.2148, found 446.2156.

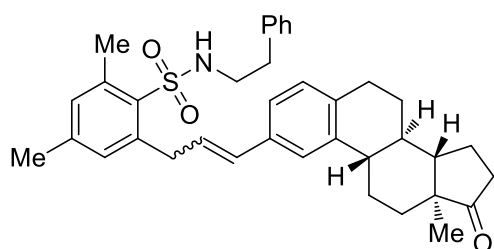
2-(3,3-diphenylallyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide (3an).



78.9 mg, 82% yield; $R_f = 0.2$ (PE/EA = 10 : 1); white solid; m.p. 121.4 - 122.4 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.37 (t, $J = 7.5$ Hz, 2H), 7.33 - 7.30 (m, 1H),

7.25 - 7.19 (m, 10H), 7.00 (d, $J = 7.0$ Hz, 2H), 6.93 (d, $J = 5.5$ Hz, 2H), 6.25 (t, $J = 7.0$ Hz, 1H), 4.42 - 4.34 (m, 1H), 3.85 (d, $J = 7.0$ Hz, 2H), 3.10 - 3.05 (m, 2H), 2.67 (t, $J = 7.0$ Hz, 2H), 2.52 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.4, 142.3, 142.2, 141.9, 139.6, 139.1, 137.6, 133.1, 132.3, 130.7, 129.8, 128.7, 128.6, 128.3, 128.1, 127.8, 127.3, 127.2, 127.1, 126.7, 43.6, 35.6, 34.7, 23.0, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{31}\text{H}_{32}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 482.2148, found 482.2161.

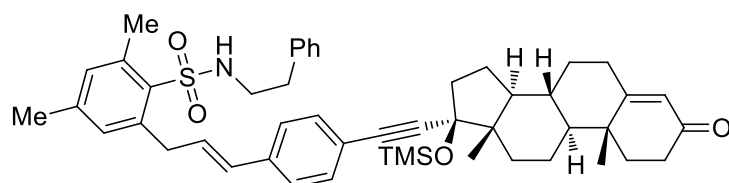
2,4-dimethyl-6-(3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)allyl)-*N*-phenethylbenzenesulfonamide (3ap) (*E/Z* = 5:1).



65.0 mg, 56% yield; $R_f = 0.2$ (PE/EA = 5 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.25 - 7.20 (m, 4.8H), 7.14 (d, $J = 8.0$ Hz, 1.2H), 7.08 (s, 1H), 7.07 (s, 0.2H), 7.05 (s, 0.2H), 7.03 (s, 1H), 7.00 (d, $J = 7.5$ Hz,

2.4H), 6.97 (s, 1H), 6.94 (s, 0.2H), 6.36 - 6.33 (m, 2H), 4.53 (t, $J = 6.0$ Hz, 1H), 4.46 (t, $J = 6.0$ Hz, 0.2H), 4.15-4.10 (m, 0.4H), 3.95-3.91 (m, 2H), 3.16 - 3.12 (m, 2.4H), 2.94 - 2.91 (m, 0.4H), 2.90 - 2.86 (m, 2H), 2.76 (t, $J = 7.0$ Hz, 0.4H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.55 (s, 3H), 2.49 (s, 0.2H), 2.48 (s, 1H), 2.44 - 2.40 (m, 1.2H), 2.31 (s, 3.6H), 2.27 (d, $J = 10.5$ Hz, 1.2H), 2.19 - 2.06 (m, 2.4H), 2.03 - 1.95 (m, 2.4H), 1.63 - 1.53 (m, 3.6H), 1.51 - 1.37 (m, 3.6H), 0.90 (s, 3.6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 220.9, 142.3, 141.2, 139.2, 138.9, 137.7, 136.6, 134.8, 133.3, 132.4, 131.4, 130.9, 128.8, 128.7, 128.6, 126.71, 126.69, 125.5, 123.6, 50.4, 47.9, 44.4, 43.7, 38.1, 37.8, 35.8, 35.6, 31.5, 29.3, 26.4, 25.7, 23.0, 21.5, 21.0, 13.8; HRMS m/z (ESI) calcd for $\text{C}_{37}\text{H}_{44}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 582.3036, found 582.3048.

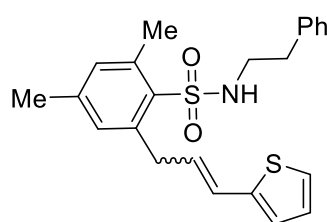
2-((E)-3-(4-(((8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-17-((trimethylsilyl)oxy)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethynyl)phenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3aq) (E/Z > 99:1).



70.8 mg, 45% yield; R_f = 0.2 (PE/EA = 5 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ

(ppm) 7.31 (d, J = 8.0 Hz, 2H), 7.26 - 7.19 (m, 5H), 7.02 - 6.96 (m, 4H), 6.44 - 6.33 (m, 2H), 5.72 (s, 1H), 4.51 (t, J = 6.0 Hz, 1H), 4.12 (q, J = 7.0 Hz, 1H), 3.94 (d, J = 5.5 Hz, 2H), 3.16 - 3.12 (m, 2H), 2.70 (t, J = 7.0 Hz, 2H), 2.53 (s, 3H), 2.43 - 2.34 (m, 4H), 2.32 (s, 3H), 2.30 - 2.24 (m, 3H), 2.04 - 1.97 (m, 3H), 1.76 - 1.68 (m, 4H), 1.65 - 1.59 (m, 2H), 1.26 (t, J = 7.0 Hz, 2H), 1.20 (s, 3H), 0.86 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 199.6, 171.4, 142.4, 140.9, 139.2, 137.6, 137.1, 133.4, 132.6, 131.52, 131.47, 130.7, 130.4, 128.7, 128.6, 126.7, 126.0, 123.8, 121.8, 93.8, 86.6, 80.9, 53.6, 49.1, 47.8, 43.7, 40.5, 38.6, 38.0, 36.4, 35.6, 33.9, 32.8, 32.7, 31.5, 23.3, 22.9, 21.0, 20.8, 17.4, 14.2, 12.9, 1.8; HRMS m/z (ESI) calcd for $\text{C}_{49}\text{H}_{62}\text{NO}_4\text{SSi}$ $[\text{M}+\text{H}]^+$ 788.4163, found 788.4173.

2,4-dimethyl-N-phenethyl-6-(3-(thiophen-2-yl)allyl)benzenesulfonamide (3ar) (E/Z = 2:1).

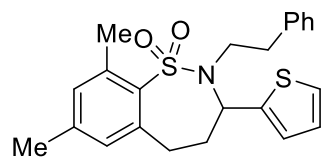


12.3 mg, 15% yield; R_f = 0.1 (PE/EA = 2 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.24 (d, J = 7.0 Hz, 3H), 7.11 (d, J = 5.5 Hz, 1.5H), 7.03 (t, J = 7.3 Hz, 4.5H), 6.98 (s, 1H), 6.95 - 6.90 (m, 4H), 6.88 (s, 1H), 6.60

(d, J = 16.0 Hz, 0.5H), 6.52 (d, J = 16.0 Hz, 1H), 6.37 - 6.07 (m, 1.5H), 4.50 (t, J = 6.5 Hz, 1H), 4.35 (t, J = 5.5 Hz, 0.5H), 3.92 (d, J = 6.5 Hz, 2H), 3.19 - 3.10 (m, 4H), 2.79 - 2.68 (m, 4.5H), 2.54 (s, 3H), 2.49 (s, 1.5H), 2.33 (s, 3H), 2.30 (s, 1.5H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 147.7, 143.6, 142.45, 142.37, 142.2, 140.8, 139.2, 138.9, 137.7, 133.3, 132.9, 132.6, 132.2, 131.9, 131.6, 131.3, 129.4, 128.73, 128.69, 128.67, 128.65, 128.6, 127.3, 126.8, 126.7, 125.2, 124.9, 124.4, 123.8, 123.6, 123.5, 123.4, 44.4, 43.7,

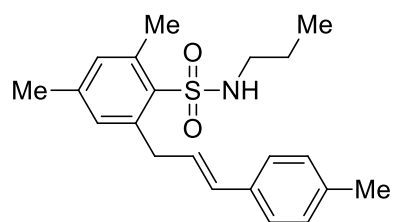
39.5, 37.7, 35.6, 33.5, 22.9, 22.7, 21.0, 20.9; HRMS m/z (ESI) calcd for $C_{23}H_{26}NO_2S_2$ $[M+H]^+$ 412.1399, found 412.1408.

7,9-dimethyl-2-phenethyl-3-(thiophen-2-yl)-2,3,4,5-tetrahydrobenzo[f][1,2]thiazepine 1,1-dioxide (8ar).



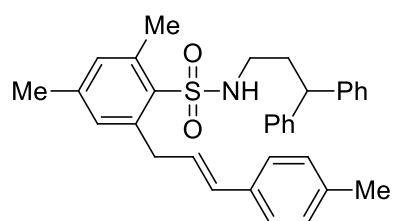
42.7 mg, 52% yield; R_f = 0.2 (PE/EA = 20 : 1); colorless viscous liquid; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.39 (d, J = 4.5 Hz, 1H), 7.22 - 7.10 (m, 4H), 7.10 - 7.06 (m, 1H), 6.95 (s, 1H), 6.91 (s, 1H), 6.81 (d, J = 7.0 Hz, 2H), 5.74 (d, J = 12.0 Hz, 1H), 3.72 (t, J = 13.2 Hz, 1H), 2.95 - 2.84 (m, 2H), 2.82 - 2.75 (m, 1H), 2.74 - 2.65 (m, 4H), 2.29 (s, 3H), 2.28 - 2.23 (m, 1H), 2.18 - 2.07 (m, 1H), 2.07 - 2.00 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 142.7, 142.2, 140.0, 139.6, 138.9, 135.3, 132.1, 131.3, 128.6, 128.3, 126.8, 126.7, 126.2, 125.9, 58.5, 46.7, 37.6, 35.2, 29.0, 23.0, 20.9; HRMS m/z (ESI) calcd for $C_{23}H_{26}NO_2S_2$ $[M+H]^+$ 412.1399, found 412.1408.

(E)-2,4-dimethyl-N-propyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ba) (E/Z > 99:1).



52.1 mg, 73% yield; R_f = 0.2 (PE/EA = 10 : 1); colorless viscous liquid; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.24 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H), 7.06 (s, 1H), 7.00 (s, 1H), 6.42 - 6.36 (m, 2H), 4.58 (t, J = 6.0 Hz, 1H), 4.02 (d, J = 5.0 Hz, 2H), 2.85 - 2.81 (m, 2H), 2.67 (s, 3H), 2.32 (s, 6H), 1.40 - 1.36 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 142.2, 141.0, 139.2, 137.0, 134.3, 133.5, 132.4, 131.6, 131.0, 129.2, 128.5, 125.9, 44.4, 37.9, 23.2, 22.8, 21.1, 21.0, 11.1; HRMS m/z (ESI) calcd for $C_{21}H_{28}NO_2S$ $[M+H]^+$ 358.1835, found 358.1839.

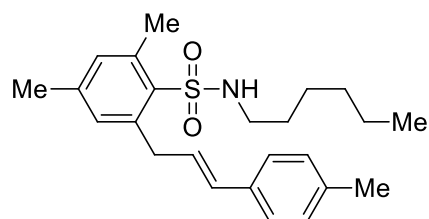
(E)-N-(3,3-diphenylpropyl)-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ca) (E/Z > 99:1).



65.2 mg, 64% yield; R_f = 0.1 (PE/EA = 10 : 1); colorless viscous liquid; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.23 (d, J = 6.5 Hz, 6H), 7.16 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.06 - 7.02 (m, 5H), 6.99 (s, 1H), 6.40 (d, J = 16.0 Hz, 1H), 6.32 (dd, J = 16.0, 8.0 Hz, 1H), 4.66 - 4.55 (m, 1H), 3.97 (d, J = 6.0

Hz, 2H), 3.81 (t, $J = 7.5$ Hz, 1H), 2.86 - 2.82 (m, 2H), 2.59 (s, 3H), 2.33 (s, 6H), 2.11 - 2.07 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 143.6, 142.3, 141.0, 139.3, 137.0, 134.2, 132.5, 131.6, 131.0, 129.2, 128.53, 128.50, 128.47, 127.6, 126.3, 126.0, 48.1, 41.1, 37.9, 35.3, 23.2, 21.1, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{33}\text{H}_{36}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 510.2461, found 510.2467.

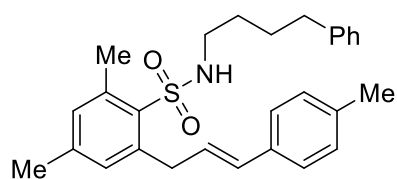
(E)-N-hexyl-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3da) (E/Z > 99:1).



53.5 mg, 67% yield; $R_f = 0.1$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.23 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.06 (s, 1H), 7.00 (s, 1H), 6.41 - 6.35 (m, 2H),

4.50 (t, $J = 5.5$ Hz, 1H), 4.02 (d, $J = 4.9$ Hz, 2H), 2.86 - 2.81 (m, 2H), 2.67 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 1.33 - 1.28 (m, 2H), 1.18 - 1.08 (m, 6H), 0.81 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.3, 140.9, 139.3, 137.0, 134.2, 133.5, 132.4, 131.7, 131.0, 129.2, 128.5, 126.0, 42.7, 37.9, 31.2, 29.4, 26.2, 23.3, 22.4, 21.1, 21.0, 13.9; LRMS (EI, 70 eV) m/z (%): 399(M^+ , 2), 335(3), 234(100), 219(52), 105(11); HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{34}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 448.2305, found 448.2318.

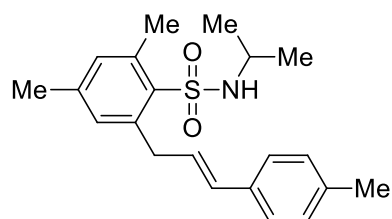
(E)-2,4-dimethyl-N-(4-phenylbutyl)-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ea) (E/Z > 99:1).



55.4 mg, 62% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.25 - 7.21 (m, 4H), 7.18 (d, $J = 7.0$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.06 (s, 1H), 7.03 (d, $J = 7.5$

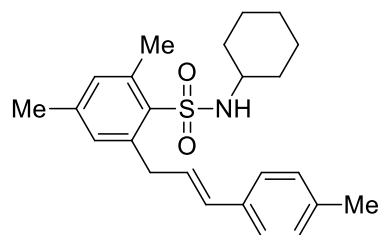
Hz, 2H), 7.00 (s, 1H), 6.41 - 6.35 (m, 2H), 4.58 (t, $J = 6.5$ Hz, 1H), 4.02 (d, $J = 4.5$ Hz, 2H), 2.89 - 2.84 (m, 2H), 2.66 (s, 3H), 2.43 (t, $J = 7.5$ Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.49 - 1.43 (m, 2H), 1.39 - 1.34 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.3, 141.7, 140.9, 139.2, 137.0, 134.2, 132.5, 131.7, 131.0, 129.2, 128.5, 128.25, 128.22, 126.0, 125.7, 42.4, 37.9, 35.1, 29.0, 28.2, 23.2, 21.1, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{34}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 400.2305, found 400.2312.

(E)-N-isopropyl-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3fa) (E/Z > 99:1).



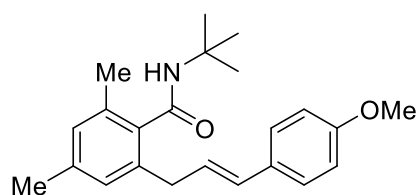
28.6 mg, 40% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.25 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.05 (s, 1H), 6.99 (s, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.38 - 6.32 (m, 1H), 4.41 (d, $J = 7.5$ Hz, 1H), 4.02 (d, $J = 6.5$ Hz, 2H), 3.51 - 3.44 (m, 1H), 2.68 (s, 3H), 2.32 (s, 6H), 1.01 (d, $J = 6.5$ Hz, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 142.1, 141.0, 138.8, 136.9, 134.8, 134.4, 132.4, 131.5, 131.1, 129.2, 128.8, 126.0, 45.7, 38.0, 23.7, 23.2, 21.1, 21.0; LRMS (EI, 70 eV) m/z (%): 357(M^+ , 1), 293(3), 234(100), 219(69), 203(9), 105(10); HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$ 358.1835, found 358.1838.

(E)-N-cyclohexyl-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ga) (E/Z > 99:1).



54.0 mg, 68% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.25 (d, $J = 6.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.05 (s, 1H), 6.99 (s, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.36 (dt, $J = 16.0$, 6.5 Hz, 1H), 4.55 (d, $J = 7.5$ Hz, 1H), 4.02 (d, $J = 6.5$ Hz, 2H), 3.20 - 3.12 (m, 1H), 2.68 (s, 3H), 2.32 (s, 6H), 1.75 - 1.70 (m, 2H), 1.58 - 1.53 (m, 2H), 1.48 - 1.43 (m, 1H), 1.16 - 1.04 (m, 5H); LRMS (EI, 70 eV) m/z (%): 397(M^+ , 1), 333(3), 234(100), 219(52), 204(7), 105(11), 98(8); HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{32}\text{NO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$ 398.2148, found 398.2153.

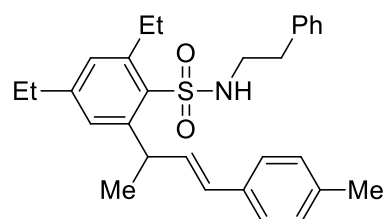
(E)-N-(tert-butyl)-2-(3-(4-methoxyphenyl)allyl)-4,6-dimethylbenzamide (3ho) (E/Z > 99:1).



29.5 mg, 42% yield; $R_f = 0.3$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.28 (d, $J = 11.0$ Hz, 2H), 6.88 (d, $J = 12.0$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 2H), 6.34 (d, $J = 16.0$ Hz, 1H), 6.24 - 6.18 (m, 1H), 5.49 (s, 1H), 3.79 (s, 3H), 3.51 (d, $J = 6.5$ Hz, 2H), 2.32 (s, 3H),

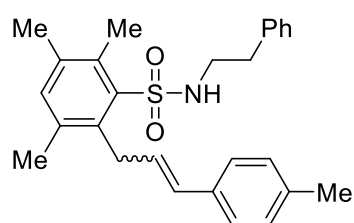
2.28 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 169.4, 158.8, 138.4, 136.3, 135.6, 134.3, 130.3, 130.1, 128.8, 127.5, 127.4, 127.2, 113.9, 55.2, 51.8, 36.4, 28.8, 21.1, 19.0; HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{30}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 352.2271, found 352.2279.

(E)-2,4-diethyl-N-phenethyl-6-(4-(p-tolyl)but-3-en-2-yl)benzenesulfonamide (3ia) (E/Z >99:1).



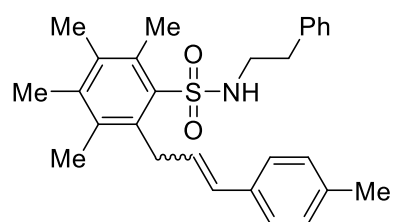
33.2 mg, 36% yield; R_f = 0.2 (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.23 (d, J = 7.5 Hz, 4H), 7.20 (d, J = 7.0 Hz, 1H), 7.13 - 7.09 (m, 3H), 7.04 (d, J = 7.0 Hz, 2H), 7.00 (s, 1H), 6.37 (d, J = 16.0 Hz, 1H), 6.31 (dd, J = 16.0, 5.0 Hz, 1H), 4.94 - 4.78 (m, 1H), 4.44 (t, J = 6.0 Hz, 1H), 3.25 - 3.20 (m, 1H), 3.17 - 3.13 (m, 1H), 3.12 - 3.07 (m, 1H), 3.02 - 2.98 (m, 1H), 2.80 - 2.73 (m, 2H), 2.62 (q, J = 7.5 Hz, 2H), 2.33 (s, 3H), 1.42 (d, J = 7.0 Hz, 3H), 1.27 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 148.5, 147.1, 145.8, 137.7, 137.0, 134.5, 134.0, 132.6, 129.6, 129.2, 128.70, 128.68, 128.5, 127.6, 126.8, 126.0, 43.9, 37.5, 35.8, 28.8, 28.5, 22.2, 21.1, 17.0, 14.9; HRMS m/z (ESI) calcd for $\text{C}_{29}\text{H}_{36}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 462.2461, found 462.2467.

2,3,5-trimethyl-N-phenethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ja) (E/Z = 5:1).



51.1 mg, 59% yield; R_f = 0.2 (PE/EA = 10 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.22 - 7.19 (m, 5H), 7.18 (s, 1H), 7.12 (dd, J = 13.0, 6.5 Hz, 1.2H), 7.08 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 6.0 Hz, 0.8H), 6.97 - 6.93 (m, 2H), 6.44 (d, J = 16.0 Hz, 0.2H), 6.39 - 6.31 (m, 1.2H), 6.18 (d, J = 16.0 Hz, 1H), 4.57 (t, J = 6.0 Hz, 1H), 4.39 (t, J = 6.0 Hz, 0.2H), 4.05 (d, J = 4.5 Hz, 2H), 3.12 (q, J = 6.8 Hz, 2.4H), 2.73 (t, J = 7.0, 0.4H), 2.67 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 2.33 (s, 0.6H), 2.32 (s, 3H), 2.27 (s, 3.6H), 2.21 (s, 0.6H), 2.20 (s, 0.6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 137.7, 137.0, 136.8, 136.7, 136.3, 136.1, 135.1, 134.5, 130.1, 129.2, 129.1, 128.61, 128.60, 127.6, 126.7, 125.9, 44.0, 35.6, 33.3, 21.2, 21.1, 20.4, 17.7; HRMS m/z (ESI) calcd for $\text{C}_{27}\text{H}_{32}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 434.2148, found 434.2152.

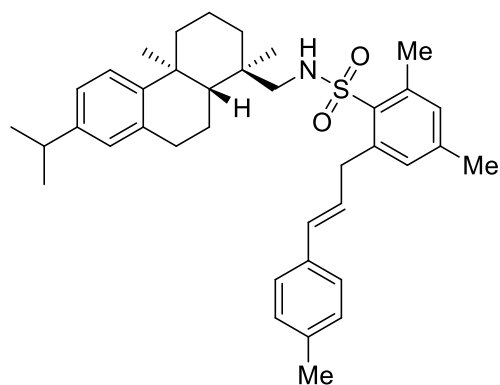
2,3,4,5-tetramethyl-*N*-phenethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (3ka)(*E/Z* = 5:1).



60.8 mg, 48% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.23 - 7.16 (m, 6H), 7.08 (d, $J = 8.0$ Hz, 2.4H), 7.02 (d, $J = 6.5$ Hz, 0.4H), 6.98 - 6.94 (m, 2H), 6.44 (d, $J = 16.0$

Hz, 0.2H), 6.36 (dt, $J = 16.0, 5.5$ Hz, 1.2H), 6.19 (d, $J = 16.0$ Hz, 1H), 4.58 (t, $J = 6.5$ Hz, 1H), 4.39 (t, $J = 6.5$ Hz, 0.2H), 4.20 - 4.05 (m, 2.4H), 3.12 - 3.07 (m, 2H), 2.72 (t, $J = 7.0$ Hz, 0.4H), 2.68 (t, $J = 7.0$ Hz, 2H), 2.45 (s, 3H), 2.33 (s, 1.2H), 2.32 (s, 3.6H), 2.30 - 2.28 (m, 6H), 2.24 (s, 3.6H), 2.10 (s, 0.6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 140.2, 137.8, 136.8, 135.9, 135.7, 135.6, 135.2, 134.6, 134.4, 130.2, 129.1, 128.64, 128.57, 128.1, 126.6, 125.9, 44.0, 35.6, 33.8, 21.1, 18.8, 17.8, 17.2, 16.8; HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{34}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 448.2305, found 448.2314.

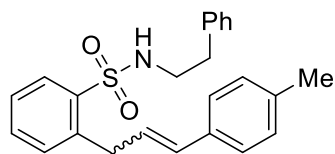
***N*-(((1*R*,4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)-2,4-dimethyl-6-((*E*)-3-(*p*-tolyl)allyl)benzenesulfonamide (3la) (*E/Z* > 99:1).**



46.6 mg, 40% yield; $R_f = 0.3$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.22 (d, $J = 8.0$ Hz, 2H), 7.12 (s, 1H), 7.06 (d, $J = 7.5$ Hz, 3H), 7.00 (s, 1H), 6.97 (d, $J = 9.0$ Hz, 1H), 6.84 (s, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.34 (dt, $J = 16.0, 7.5$ Hz, 1H), 4.48 (t, $J = 7.0$ Hz, 1H), 4.07 - 3.95 (m, 2H),

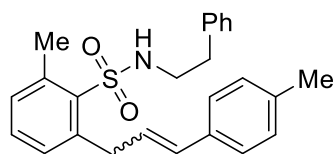
2.85 - 2.78 (m, 2H), 2.76 (s, 1H), 2.73 - 2.67 (m, 2H), 2.66 (s, 3H), 2.64 - 2.56 (m, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 1.30 - 1.25 (m, 6H), 1.23 (s, 3H), 1.21 (s, 3H), 1.13 (s, 3H), 0.78 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 146.9, 145.6, 142.2, 140.8, 138.9, 137.1, 134.6, 134.2, 133.8, 132.5, 131.8, 131.2, 129.2, 128.3, 126.8, 126.0, 124.1, 123.8, 53.2, 45.0, 37.9, 37.2, 36.7, 35.7, 33.4, 29.72, 29.68, 25.0, 24.0, 23.9, 23.4, 21.1, 21.0, 18.7, 18.4, 18.3; HRMS m/z (ESI) calcd for $\text{C}_{38}\text{H}_{50}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 584.3557, found 584.3566.

***N*-phenethyl-2-(3-(*p*-tolyl)allyl)benzenesulfonamide (3na) (*E/Z* = 5:1).**



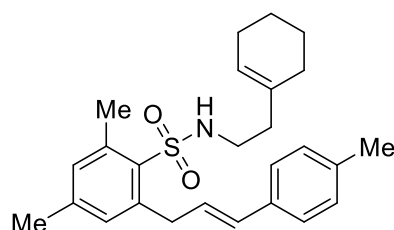
18.0 mg, 23% yield;; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.99 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 0.2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.46 (d, $J = 6.5$ Hz, 0.2H), 7.40 (d, $J = 7.5$ Hz, 1.2H), 7.36 (t, $J = 7.5$ Hz, 1.2H), 7.25 - 7.20 (m, 6H), 7.12 (d, $J = 8.0$ Hz, 2.4H), 6.96 (d, $J = 7.0$ Hz, 2.4H), 6.48 (d, $J = 7.5$ Hz, 0.2H), 6.40 - 6.35 (m, 1H), 6.32 (d, $J = 8.0$ Hz, 0.2H), 6.30 - 6.23 (m, 1H), 4.57 - 4.45 (m, 1H), 4.43 - 4.37 (m, 0.2H), 3.87 (d, $J = 6.5$ Hz, 2H), 3.23 - 3.20 (m, 0.4H), 3.16 - 3.11 (m, 2H), 2.77 (t, $J = 6.5$ Hz, 0.4H), 2.65 (t, $J = 7.0$ Hz, 2.4H), 2.33 (s, 3.6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 139.0, 137.6, 137.5, 137.4, 134.0, 132.9, 132.1, 131.9, 129.9, 129.3, 128.7, 128.6, 126.9, 126.7, 126.6, 126.0, 44.2, 36.0, 35.7, 21.2; HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 392.1679, found 392.1685.

2-methyl-*N*-phenethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (3oa) (*E/Z* = 1:1).



27.5 mg, 34% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.87 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.31 - 7.26 (m, 3H), 7.25 - 7.16 (m, 10H), 7.16 - 7.10 (m, 5H), 7.08 (d, $J = 6.2$ Hz, 4H), 6.97 (d, $J = 6.9$ Hz, 2H), 6.40 - 6.36 (m, 1H), 6.30 - 6.24 (m, 1H), 4.52 - 4.45 (m, 1H), 4.44 - 4.37 (m, 1H), 3.83 (d, $J = 6.5$ Hz, 2H), 3.21 - 3.16 (m, 2H), 3.13 - 3.09 (m, 2H), 2.76 (t, $J = 7.0$ Hz, 2H), 2.64 (t, $J = 7.0$ Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H), 2.33 - 2.30 (m, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 143.6, 143.4, 138.8, 137.7, 137.4, 136.8, 134.5, 134.0, 133.2, 132.7, 131.7, 130.1, 129.8, 129.3, 128.8, 128.7, 128.63, 128.61, 127.2, 127.1, 126.8, 126.7, 126.1, 44.1, 43.9, 35.9, 35.7, 35.7, 21.3, 21.2, 21.2, 19.9; HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 406.1835, found 406.1846.

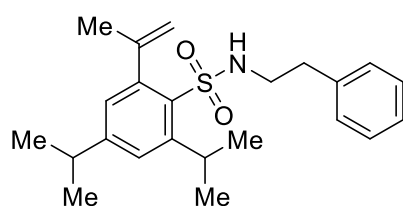
(*E*)-*N*-(2-(cyclohex-1-en-1-yl)ethyl)-2,4-dimethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (3qa) (*E/Z* > 99:1).



34.7 mg, 41% yield; $R_f = 0.2$ (PE/EA = 10 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.24 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 7.5$ Hz, 2H),

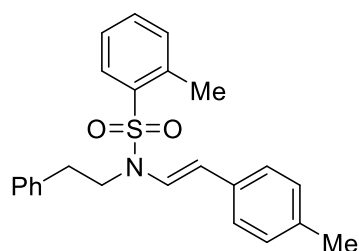
7.05 (s, 1H), 6.99 (s, 1H), 6.40 - 6.31 (m, 2H), 5.33 (s, 1H), 4.44 (t, $J = 5.5$ Hz, 1H), 3.98 (d, $J = 5.5$ Hz, 2H), 2.97 - 2.92 (m, 2H), 2.65 (s, 3H), 2.31 (s, 6H), 2.00 (t, $J = 6.0$ Hz, 2H), 1.95 - 1.91 (m, 2H), 1.68 (t, $J = 6.0$ Hz, 2H), 1.53 - 1.48 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.3, 141.4, 139.1, 136.9, 134.5, 133.6, 133.3, 132.4, 131.4, 131.0, 129.2, 128.5, 126.0, 124.5, 40.0, 38.0, 37.3, 27.5, 25.1, 23.1, 22.6, 22.2, 21.1, 21.0; HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{34}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 424.2305, found 424.2309.

2,4-diisopropyl-*N*-phenethyl-6-(prop-1-en-2-yl)benzenesulfonamide (4m).



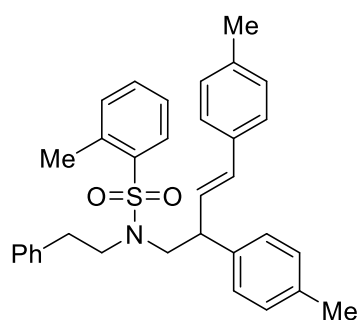
58.5 mg, 76% yield; $R_f = 0.2$ (PE/EA = 20 : 1); white solid; m.p. 111.0 - 112.1 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.28 (t, $J = 7.5$ Hz, 2H), 7.23 (d, $J = 10.0$ Hz, 2H), 7.13 (d, $J = 7.5$ Hz, 2H), 6.84 (s, 1H), 4.94 (s, 1H), 4.64 (t, $J = 6.0$ Hz, 1H), 4.51 (s, 1H), 4.15 - 4.07 (m, 1H), 3.32 - 3.20 (m, 1H), 3.19 - 3.11 (m, 1H), 2.92 - 2.87 (m, 1H), 2.86 - 2.77 (m, 2H), 2.13 (s, 3H), 1.25 (d, $J = 7.0$ Hz, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 152.4, 150.1, 148.9, 144.5, 137.9, 132.5, 128.8, 128.7, 126.7, 126.3, 124.9, 113.0, 44.1, 35.9, 33.8, 29.3, 26.0, 23.5; LRMS (EI, 70 eV) m/z (%): 385(M^+ , 24), 294(26), 265(100), 230(36), 134(34), 105(60), 91(35); HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{32}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 386.2148, found 386.2154.

(*E*)-2-methyl-*N*-(4-methylstyryl)-*N*-phenethylbenzenesulfonamide (5na).



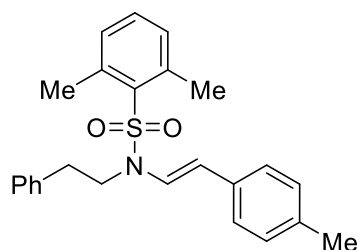
27.4 mg, 35% yield; $R_f = 0.6$ (PE/EA = 20 : 1); colorless viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.92 (d, $J = 8.0$ Hz, 1H), 7.49 - 7.43 (m, 2H), 7.35 - 7.29 (m, 4H), 7.26 (s, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 7.5$ Hz, 2H), 7.14 (d, $J = 7.5$ Hz, 2H), 5.88 (d, $J = 14.5$ Hz, 1H), 3.73 - 3.65 (m, 2H), 3.01 - 2.93 (m, 2H), 2.62 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 138.0, 137.6, 137.5, 136.1, 133.4, 133.1, 132.9, 129.4, 129.2, 128.7, 128.6, 126.7, 126.3, 125.7, 125.3, 109.0, 47.0, 33.4, 21.0, 20.6; HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 392.1679, found 392.1688.

(*E*)-*N*-(2,4-di-*p*-tolylbut-3-en-1-yl)-2-methyl-*N*-phenethylbenzenesulfonamide (6na).



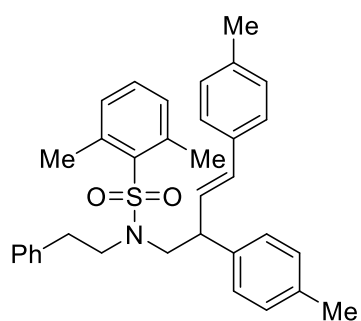
23.4 mg, 23% yield; $R_f = 0.5$ (PE/EA = 20 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.99 - 7.93 (m, 1H), 7.46 - 7.42 (m, 1H), 7.33 - 7.28 (m, 2H), 7.22 (d, $J = 5.5$ Hz, 1H), 7.17 - 7.13 (m, 3H), 7.12 - 7.06 (m, 7H), 7.01 - 6.97 (m, 2H), 6.34 - 6.24 (m, 1H), 6.10 - 5.97 (m, 1H), 3.69 - 3.60 (m, 2H), 3.57 - 3.49 (m, 2H), 3.45 - 3.38 (m, 1H), 2.92 - 2.85 (m, 1H), 2.83 - 2.78 (m, 1H), 2.36 (s, 3H), 2.33 (s, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 138.5, 138.2, 138.1, 137.8, 137.2, 136.5, 134.1, 132.8, 132.6, 131.4, 129.9, 129.4, 129.2, 129.1, 128.7, 128.6, 127.5, 126.5, 126.2, 125.9, 51.9, 48.6, 47.6, 34.6, 21.2, 21.0, 20.2; HRMS m/z (ESI) calcd for $\text{C}_{33}\text{H}_{36}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 510.2461, found 510.2475.

(E)-2,6-dimethyl-N-(4-methylstyryl)-N-phenethylbenzenesulfonamide (50a).



19.4 mg, 24% yield; $R_f = 0.6$ (PE/EA = 20 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.80 (d, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 14.5$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.24 - 7.19 (m, 3H), 7.17 (d, $J = 7.5$ Hz, 2H), 7.14 - 7.07 (m, 4H), 5.83 (d, $J = 14.5$ Hz, 1H), 3.71 - 3.60 (m, 2H), 2.98 - 2.90 (m, 2H), 2.54 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ (ppm) 143.9, 138.2, 137.5, 136.0, 134.5, 133.7, 133.6, 129.6, 129.4, 128.7, 126.8, 126.7, 125.9, 125.2, 108.6, 46.9, 33.3, 21.3, 21.1, 20.5; HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 406.1835, found 406.1843.

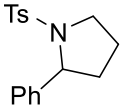
(E)-N-(2,4-di-p-tolylbut-3-en-1-yl)-2,6-dimethyl-N-phenethylbenzenesulfonamide (60a).



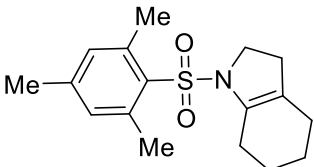
15.7 mg, 15% yield; $R_f = 0.5$ (PE/EA = 20 : 1); colorless viscous liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) 7.86 (d, $J = 8.0$ Hz, 1H), 7.25 - 7.19 (m, 2H), 7.16 - 7.12 (m, 4H), 7.11 - 7.07 (m, 6H), 7.00 (d, $J = 7.5$ Hz, 2H), 6.92 (s, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 5.99 (dd, $J = 16.0, 7.5$ Hz, 1H), 3.67 - 3.60 (m, 2H), 3.57 - 3.49 (m, 2H), 3.43 - 3.37 (m, 1H), 2.91 - 2.86 (m, 1H), 2.85 - 2.80 (m, 1H), 2.38 (s, 3H), 2.33 (s, 6H), 2.32 (s, 3H);

^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 143.1, 138.6, 138.3, 137.9, 137.1, 136.5, 134.8, 134.1, 133.5, 131.3, 130.1, 129.4, 129.3, 129.0, 128.7, 128.5, 127.5, 126.42, 126.38, 126.1, 51.8, 48.5, 47.5, 34.5, 21.2, 21.13, 20.99, 20.1; HRMS m/z (ESI) calcd for $\text{C}_{34}\text{H}_{38}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 524.2618, found : 524.2630.

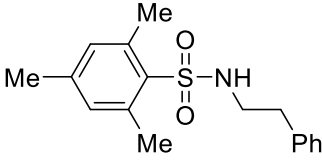
2-phenyl-1-tosylpyrrolidine (7p).

 51.2 mg, 85% yield; $R_f = 0.2$ (PE/EA = 20 : 1); white solid; m.p. 132.5 - 133.4 $^\circ\text{C}$ (uncorrected) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.67 (d, $J = 8.0$ Hz, 2H), 7.32 - 7.26 (m, 6H), 7.25 - 7.20 (m, 1H), 4.81 - 4.76 (m, 1H), 3.64 - 3.59 (m, 1H), 3.45 - 3.39 (m, 1H), 2.42 (s, 3H), 2.02 - 1.94 (m, 1H), 1.88 - 1.77 (m, 2H), 1.70 - 1.63 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 143.2, 143.0, 135.1, 129.5, 128.2, 127.4, 126.9, 126.1, 63.2, 49.3, 35.7, 23.9, 21.5. The analytical data are in accordance with those reported in the literature.⁴

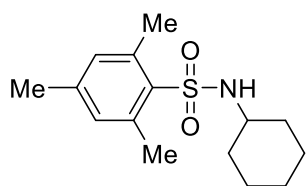
1-(mesitylsulfonyl)-2,3,4,5,6,7-hexahydro-1H-indole (7q).

 25.6 mg, 42% yield; $R_f = 0.4$ (PE/EA = 20 : 1); white solid; m.p. 110.1 - 110.9 $^\circ\text{C}$ (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 6.92 (s, 2H), 5.52 (s, 1H), 3.98 (d, $J = 4.5$ Hz, 1H), 3.58 - 3.52 (m, 1H), 3.05 - 2.99 (m, 1H), 2.64 (s, 6H), 2.56 - 2.49 (m, 1H), 2.36 - 2.31 (m, 1H), 2.28 (s, 3H), 2.04 - 1.94 (m, 3H), 1.71 (d, $J = 7.5$ Hz, 1H), 1.47 - 1.39 (m, 1H), 1.08 - 0.99 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.4, 140.0, 138.2, 133.6, 131.8, 120.6, 57.6, 46.1, 30.2, 28.7, 24.2, 22.7, 20.9, 20.3; LRMS (EI, 70 eV) m/z (%): 305(M^+ , 25), 277(39), 122(100), 94(76), 91(26); HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 306.1522, found 306.1526.

2,4,6-trimethyl-N-phenethylbenzenesulfonamide (9a).

 39.4 mg, 65% yield; $R_f = 0.5$ (PE/EA = 5 : 1); white solid; m.p. 96.7 - 97.5 $^\circ\text{C}$ (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.24 (d, $J = 5.5$ Hz, 2H), 7.22 - 7.18 (m, 1H), 7.05 (d, $J = 7.5$ Hz, 2H), 6.91 (s, 2H), 4.53 (s, 1H), 3.14 (q, $J = 6.5$ Hz, 2H), 2.74 (t, $J = 6.5$ Hz, 2H), 2.51 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 142.1, 139.0, 137.7, 133.4, 131.9, 128.7, 128.6, 126.8, 43.6, 35.5, 22.7, 20.8. The analytical data are in accordance with those reported in the literature.⁵

***N*-cyclohexyl-2,4,6-trimethylbenzenesulfonamide (9g).**

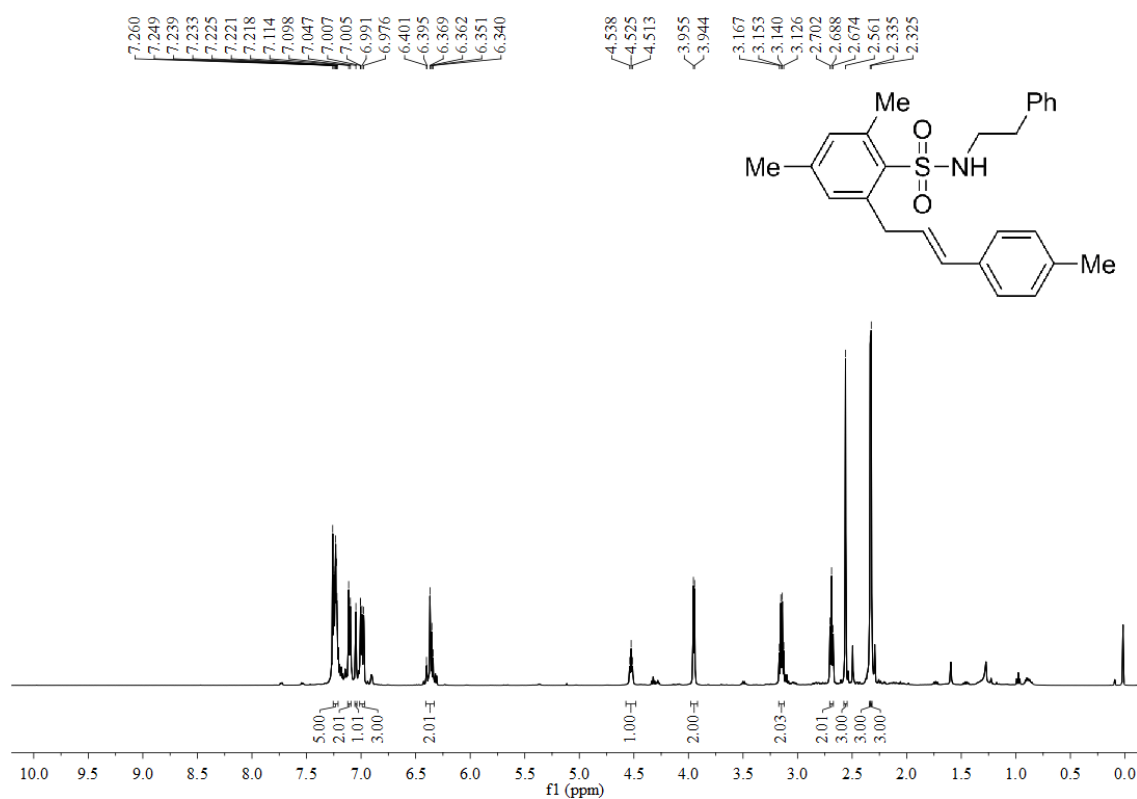


51.7 mg, 92% yield; $R_f = 0.5$ (PE/EA = 5 : 1); white solid; m.p. 87.7 - 88.5 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 6.94 (s, 2H), 4.59 - 4.40 (m, 1H), 3.17 - 3.02 (m, 1H), 2.64 (s, 6H), 2.30 (s, 3H), 1.74 (d, $J = 11.5$ Hz, 2H), 1.65 - 1.58 (m, 3H), 1.51 (d, $J = 11.5$ Hz, 1H), 1.26 - 1.09 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) 141.8, 138.7, 135.1, 131.9, 52.3, 33.8, 25.2, 24.6, 23.0, 20.9; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{24}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 282.1522, found 282.1528.

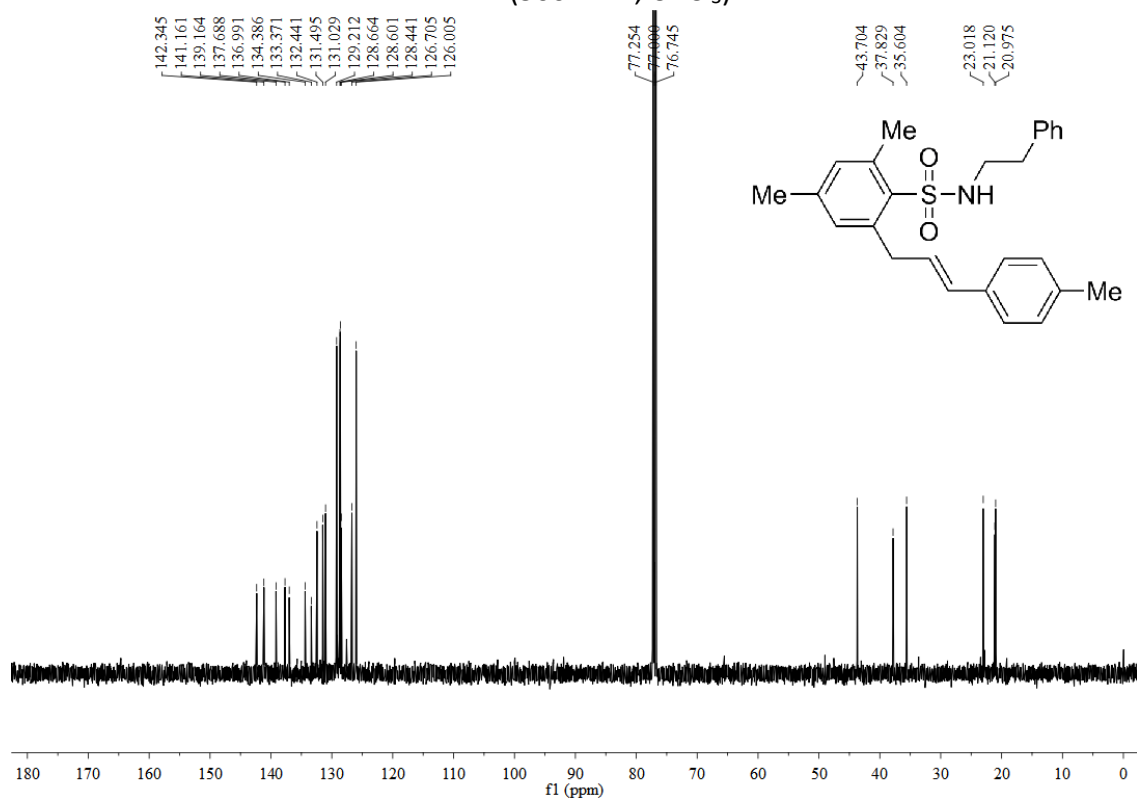
(C) Spectra

(*E*)-2,4-dimethyl-*N*-phenethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (3aa) (*E/Z*>

99:1).

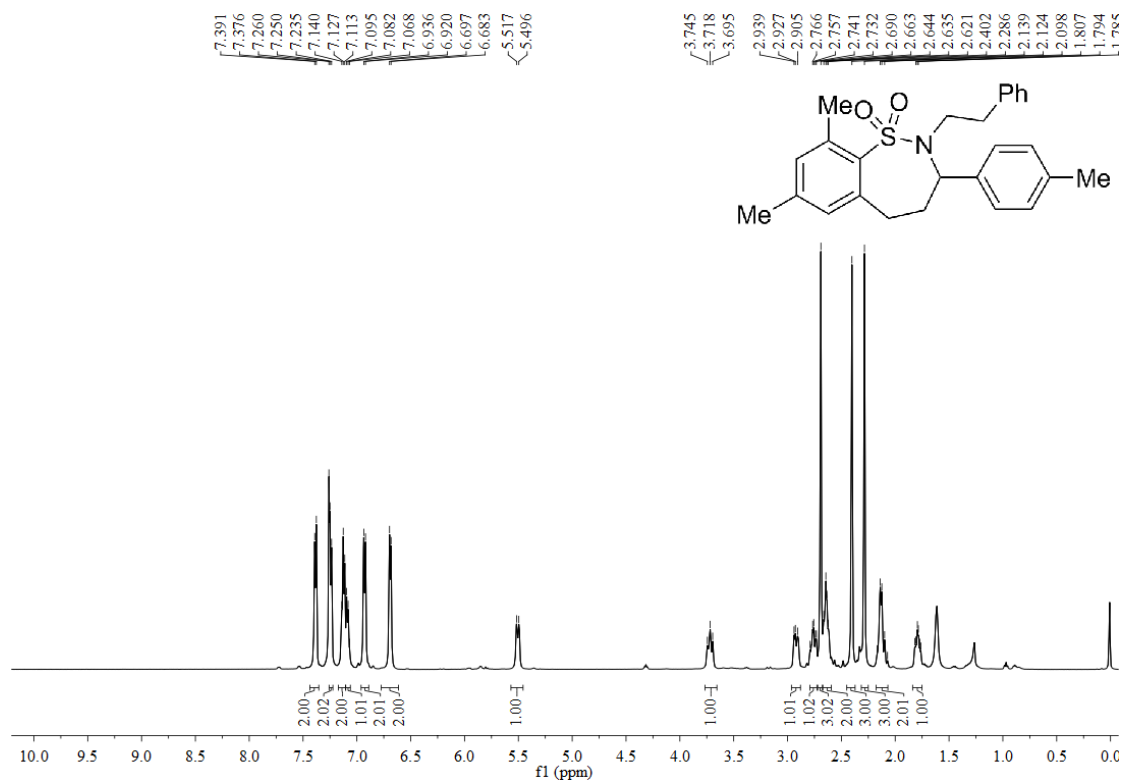


¹H NMR (500 MHz, CDCl₃)

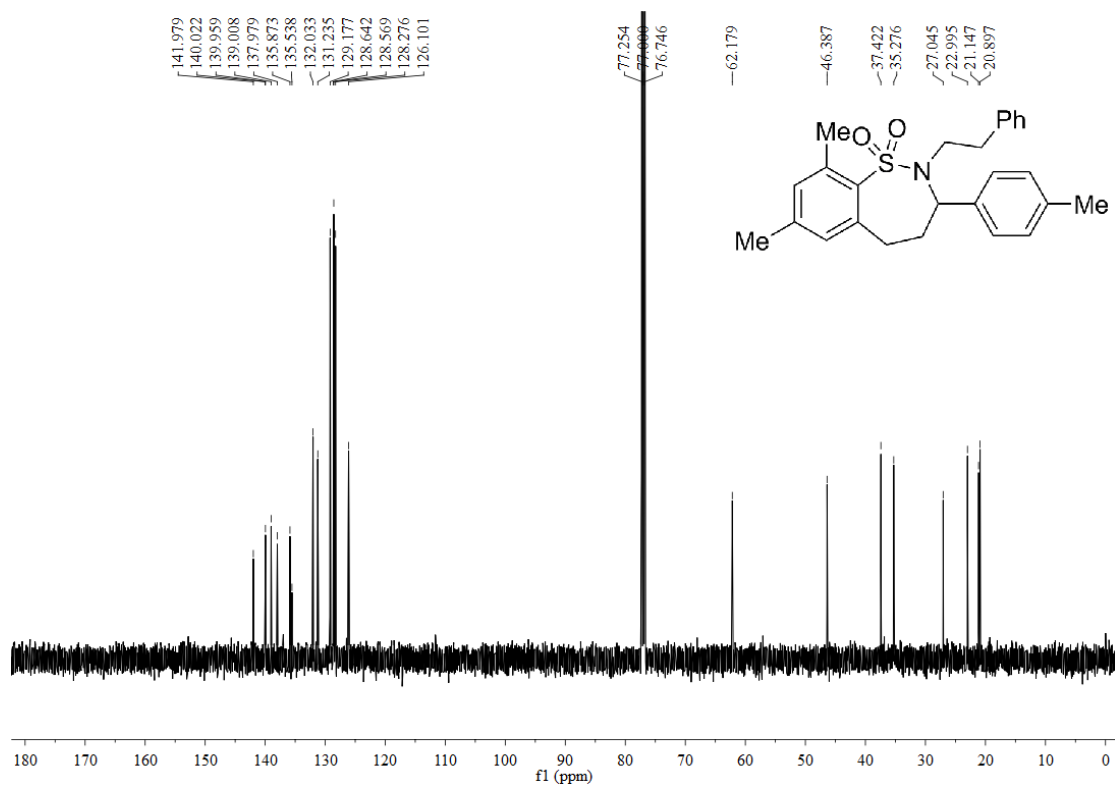


¹³C NMR (125 MHz, CDCl₃)

2-(3-(4-(*tert*-butyl)phenyl)allyl)-4,6-dimethyl-N-7,9-dimethyl-2-phenethyl-3-(*p*-tolyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]thiazepine 1,1-dioxide (4aa).



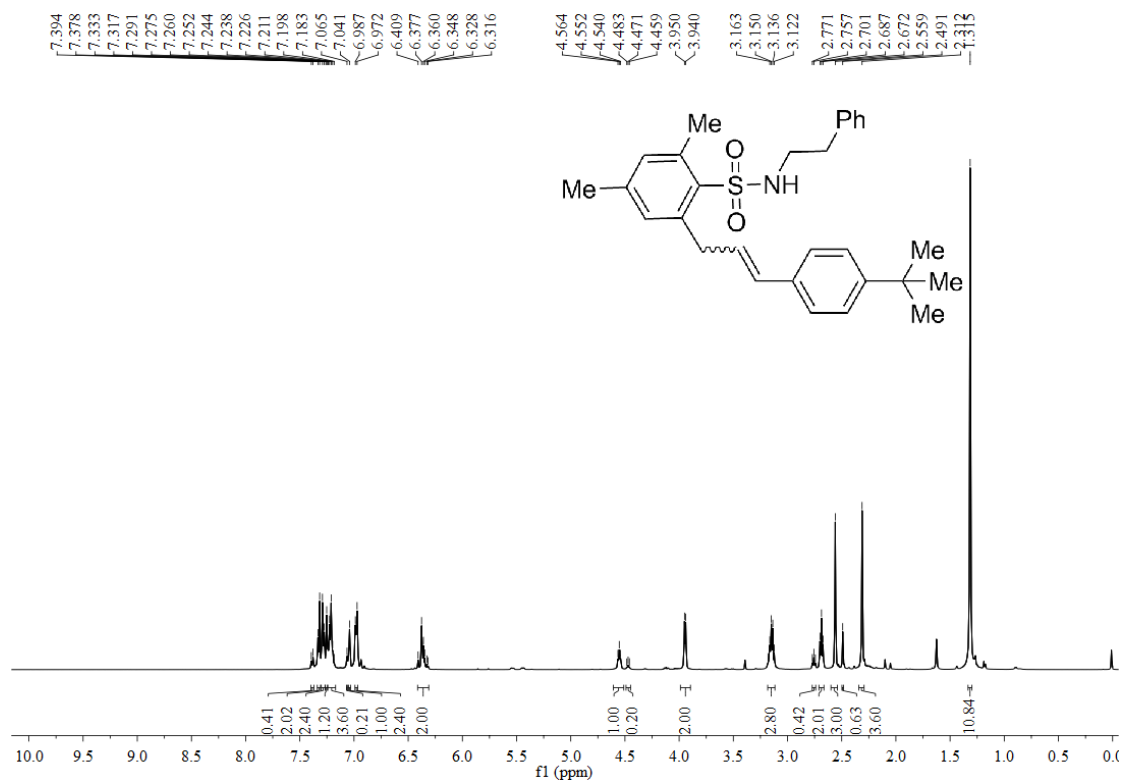
¹H NMR (500 MHz, CDCl₃)



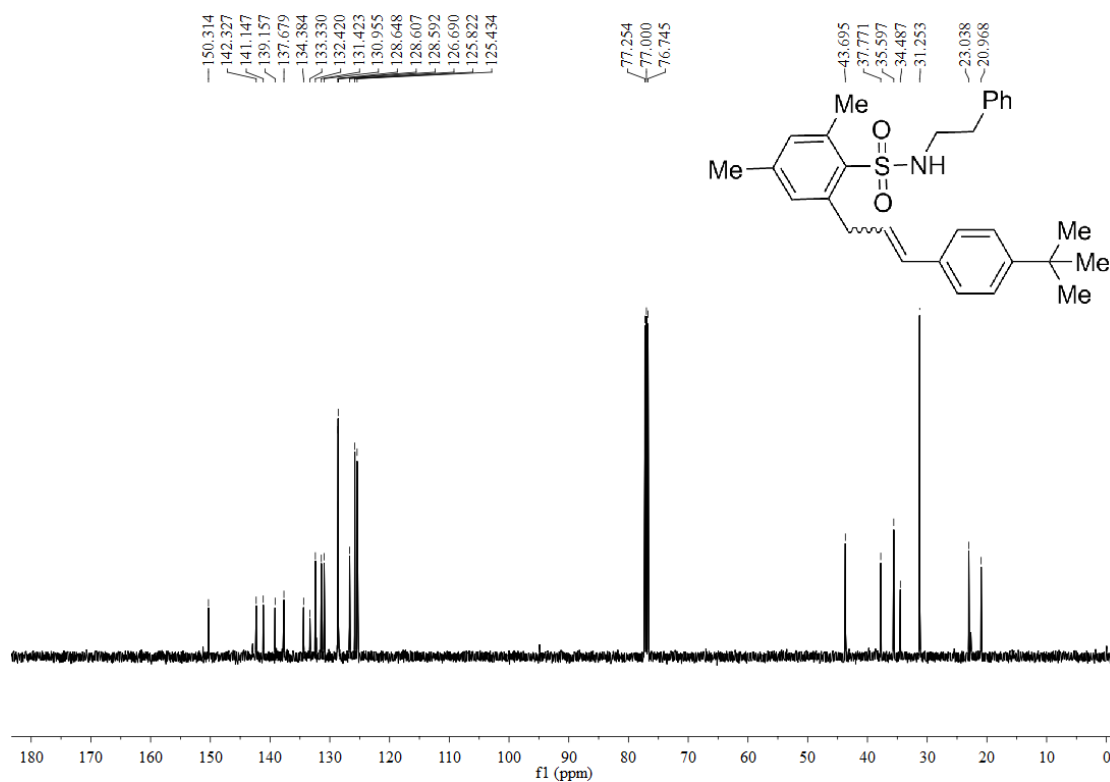
¹³C NMR (125 MHz, CDCl₃)

2-(3-(4-(*tert*-butyl)phenyl)allyl)-4,6-dimethyl-*N*-phenethylbenzenesulfonamide

(3ab) (*E/Z* = 5:1).



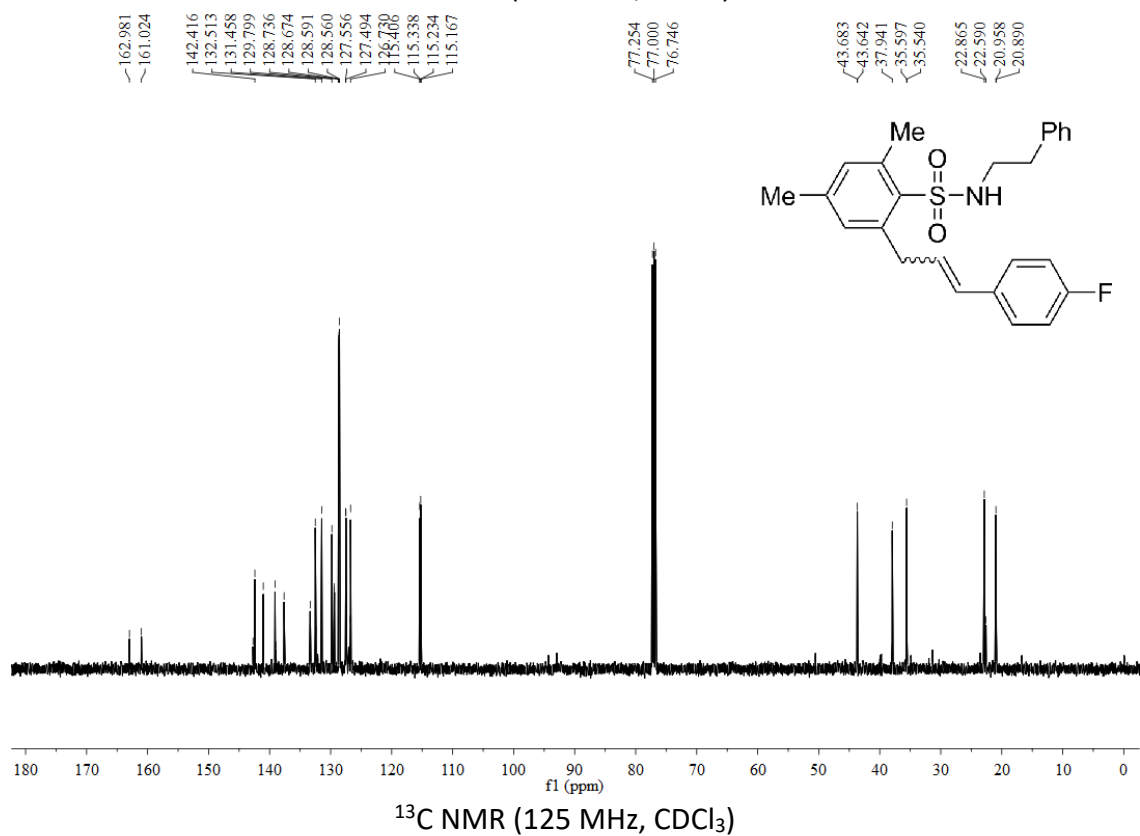
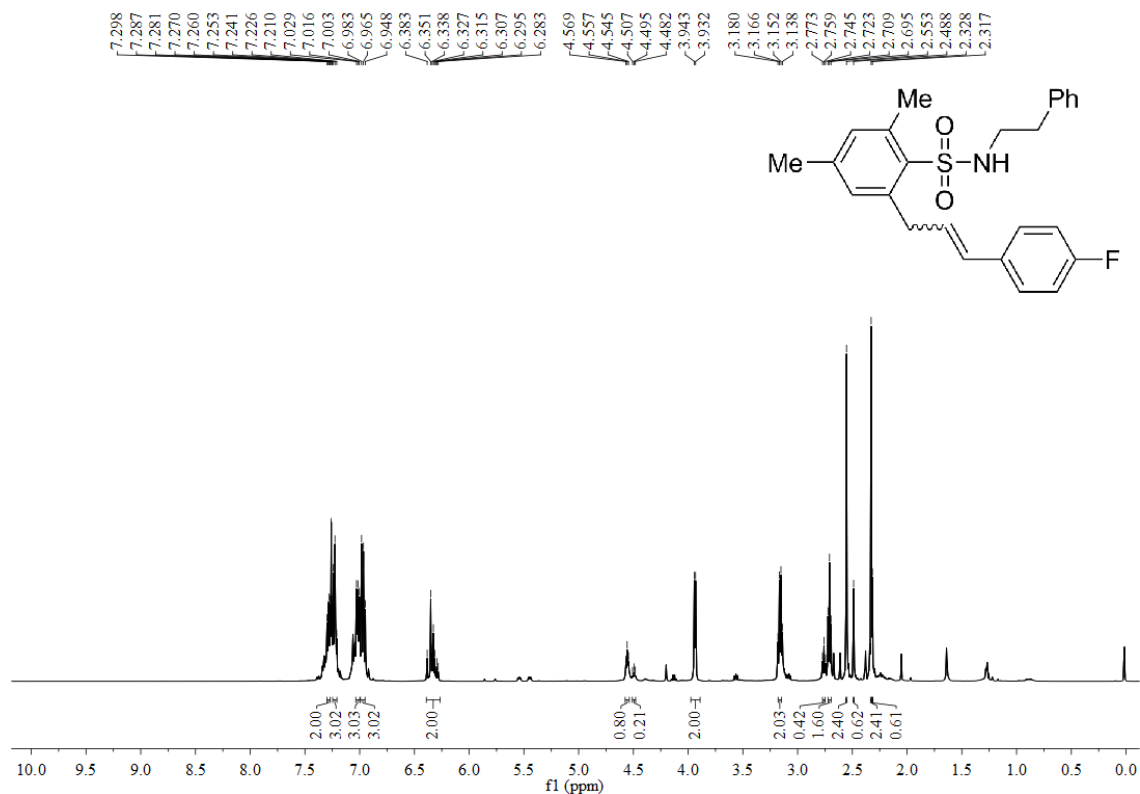
¹H NMR (500 MHz, CDCl₃)

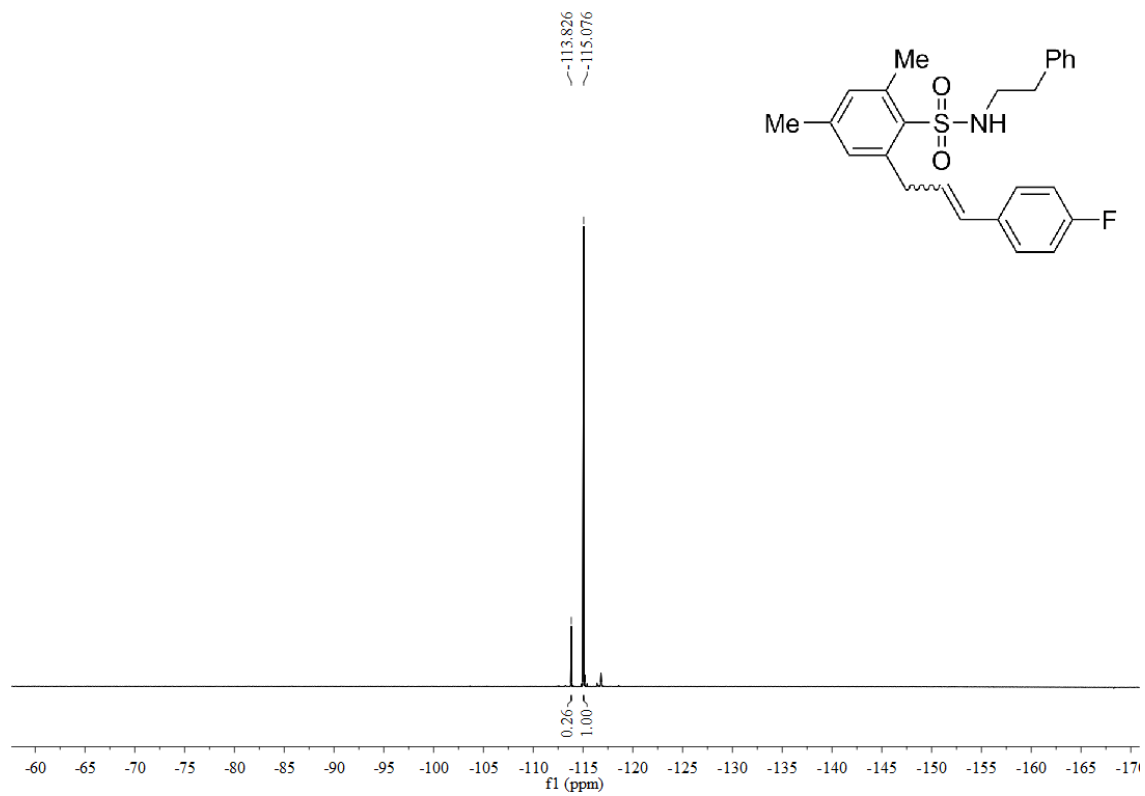


¹³C NMR (125 MHz, CDCl₃)

2-(3-(4-fluorophenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3ac)

(E/Z = 4:1).

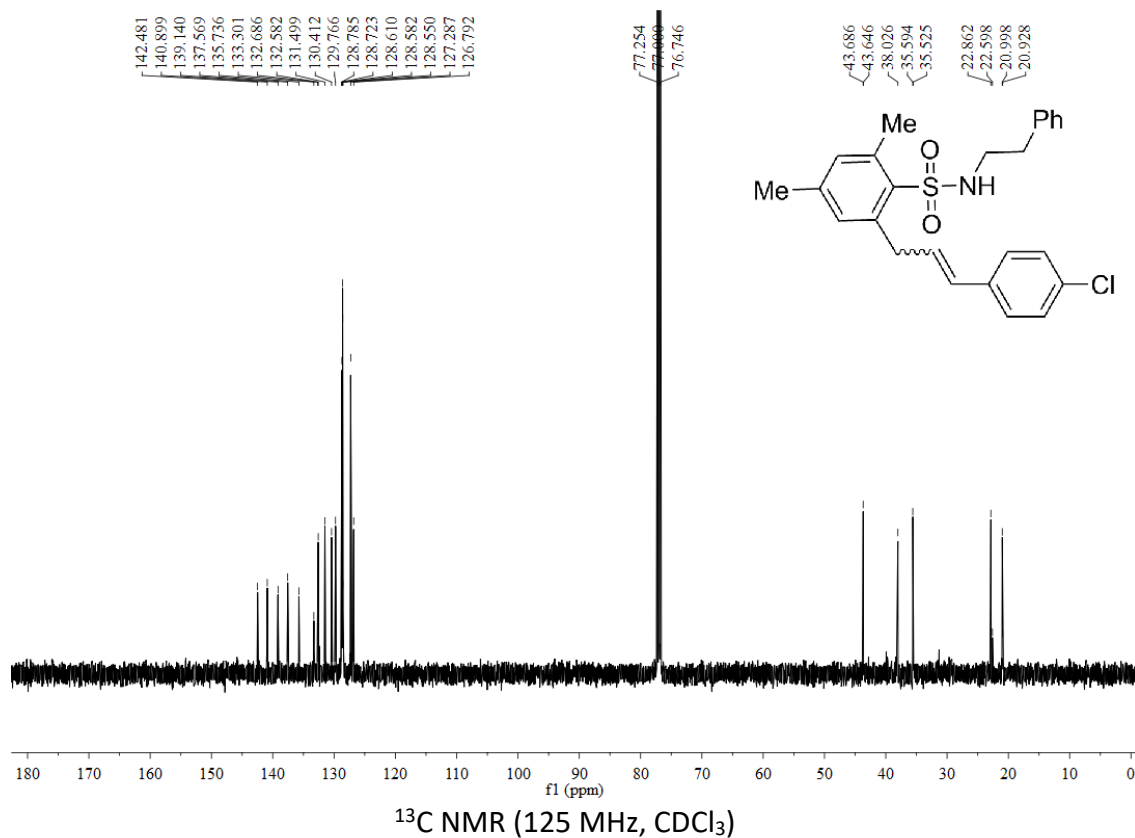
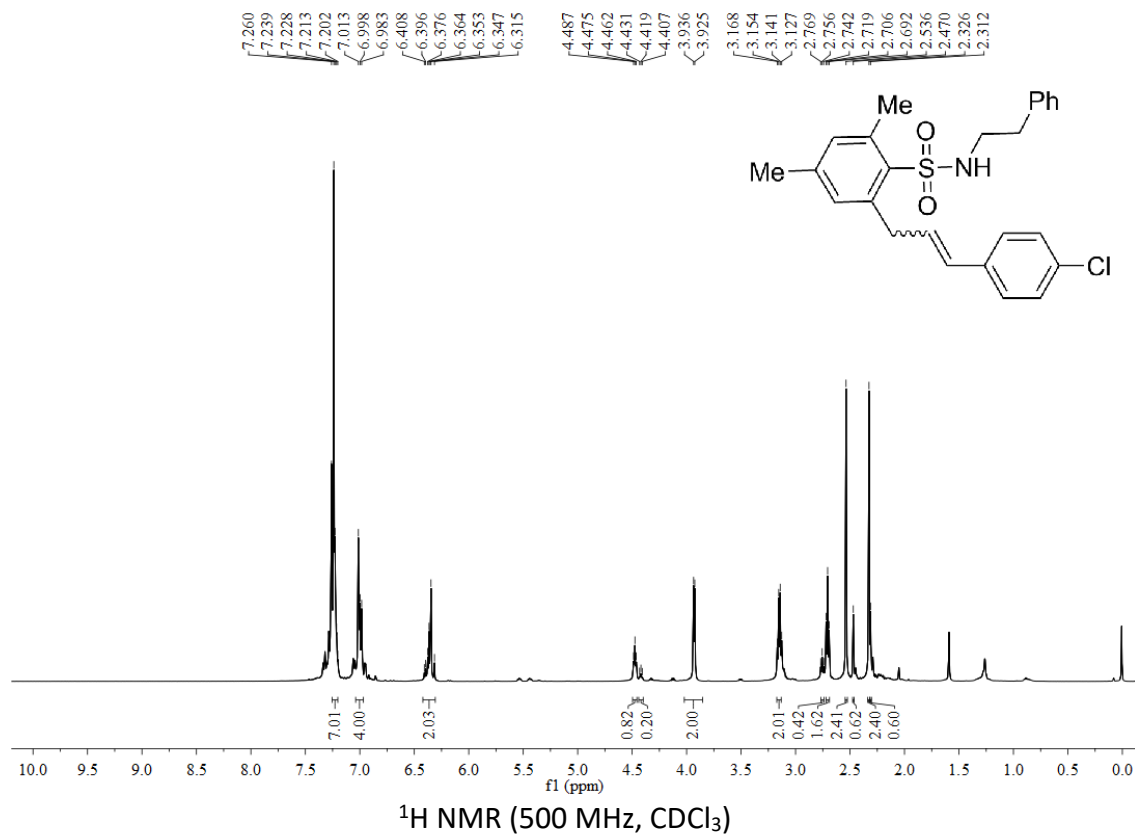




^{19}F NMR (471 MHz, CDCl_3)

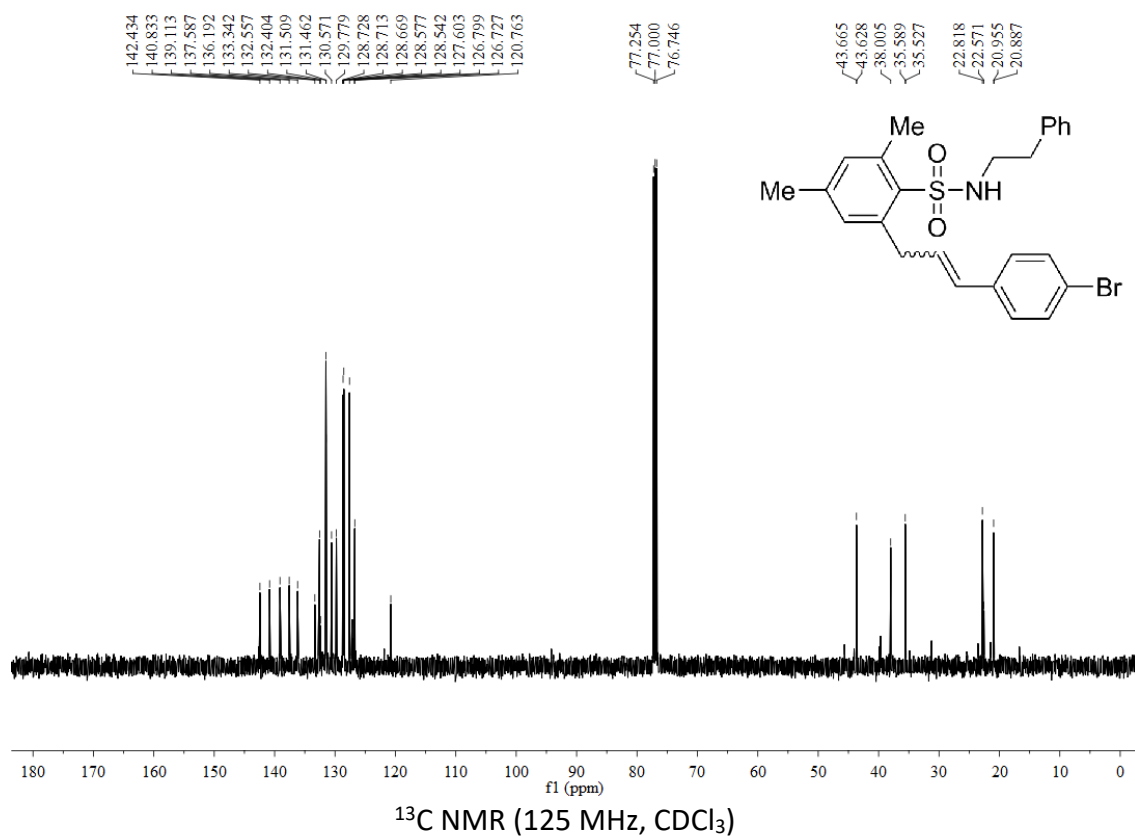
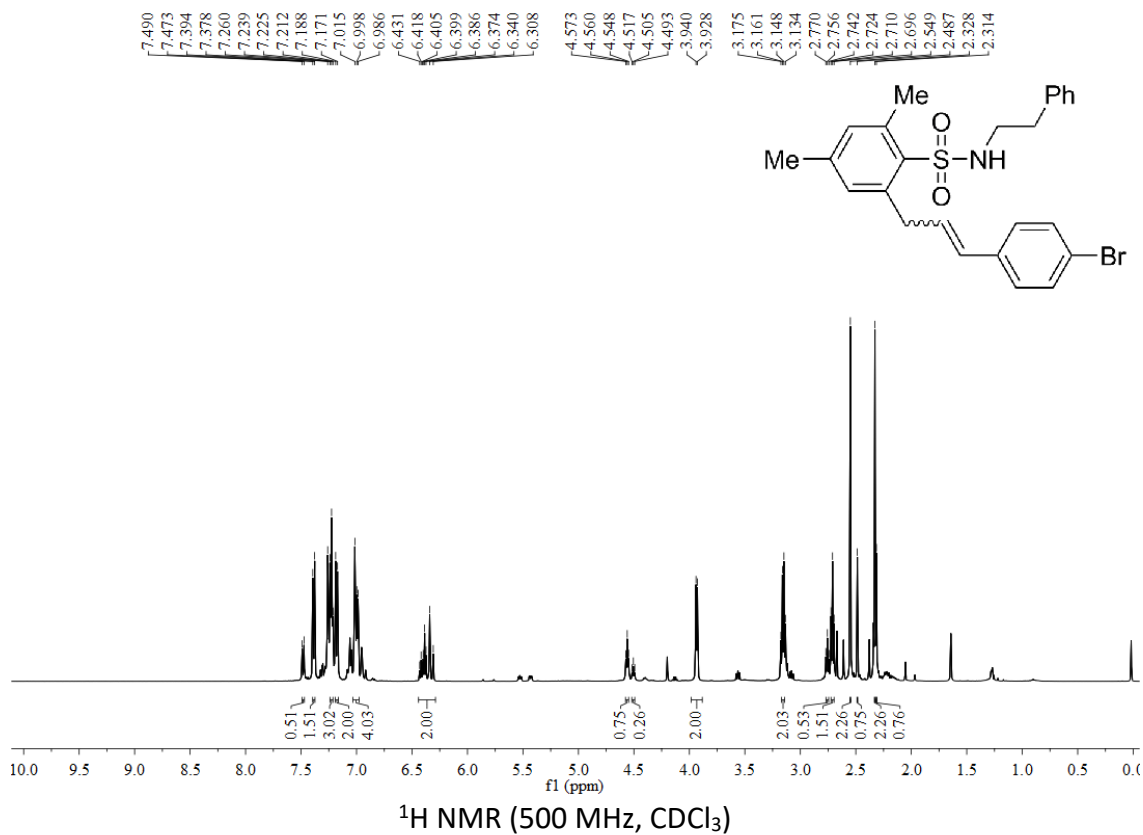
2-(3-(4-chlorophenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3ad)

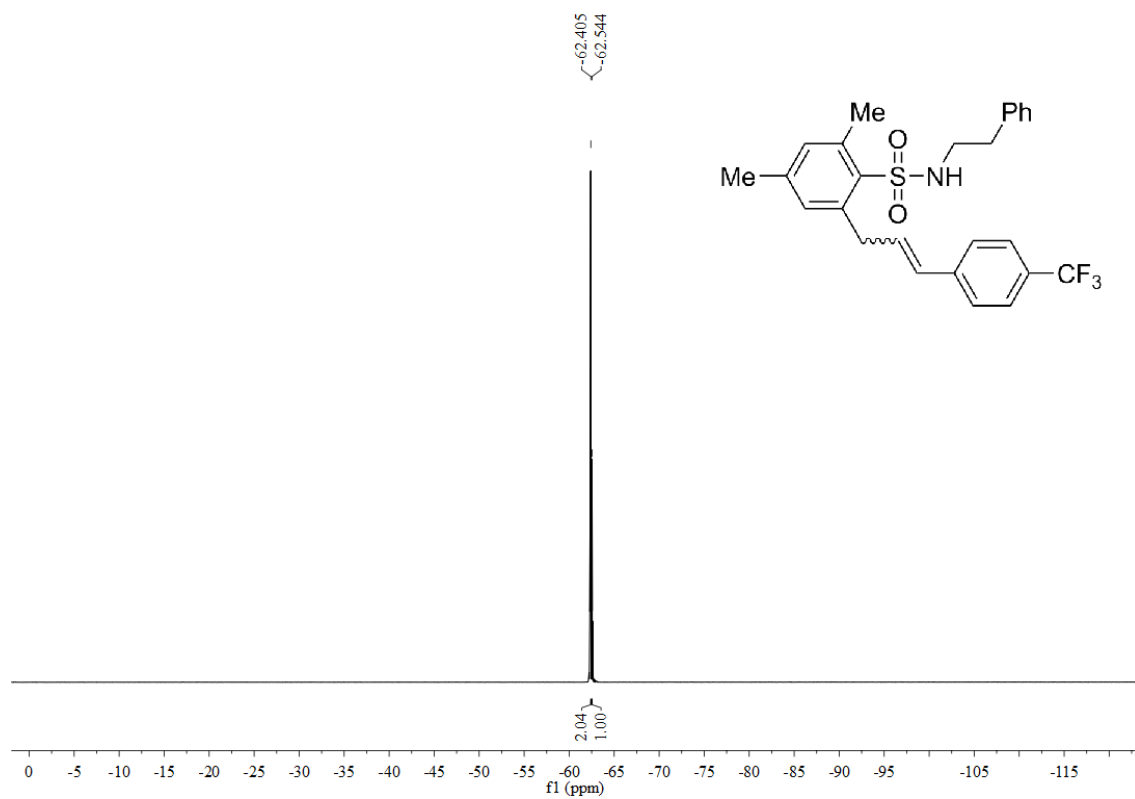
(E/Z = 4:1).



2-(3-(4-bromophenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide

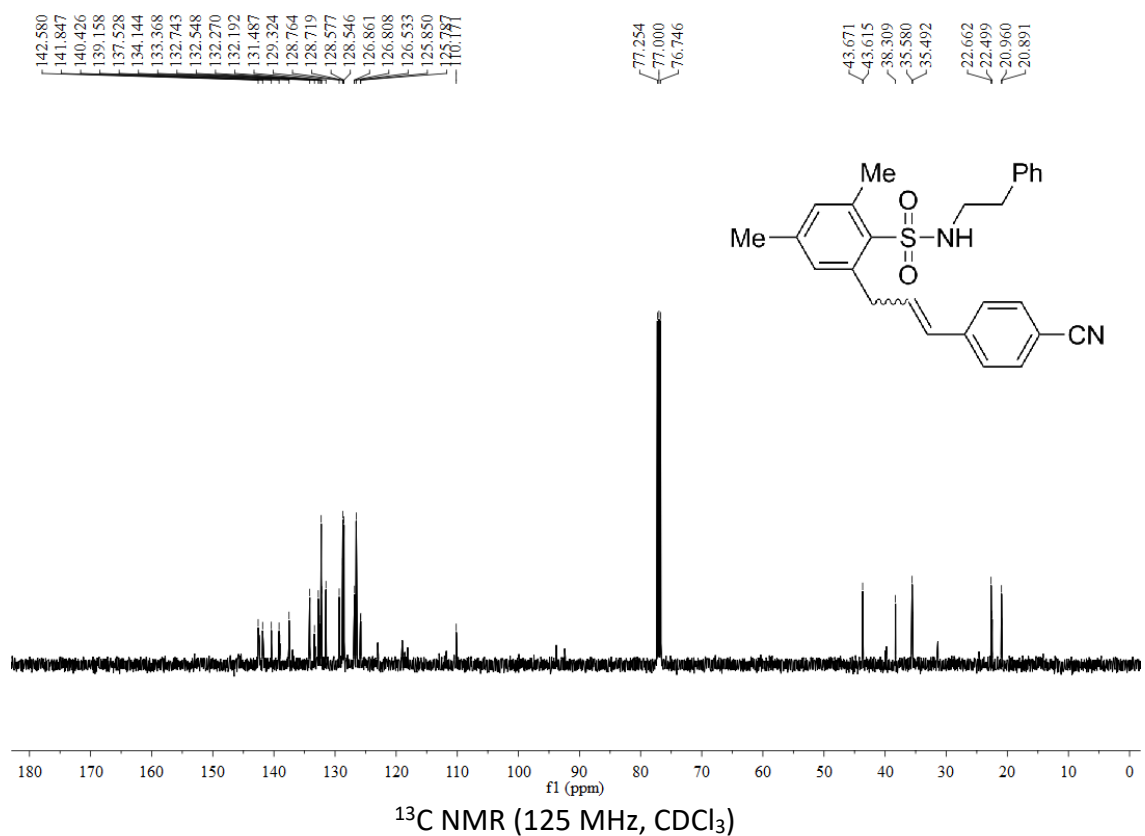
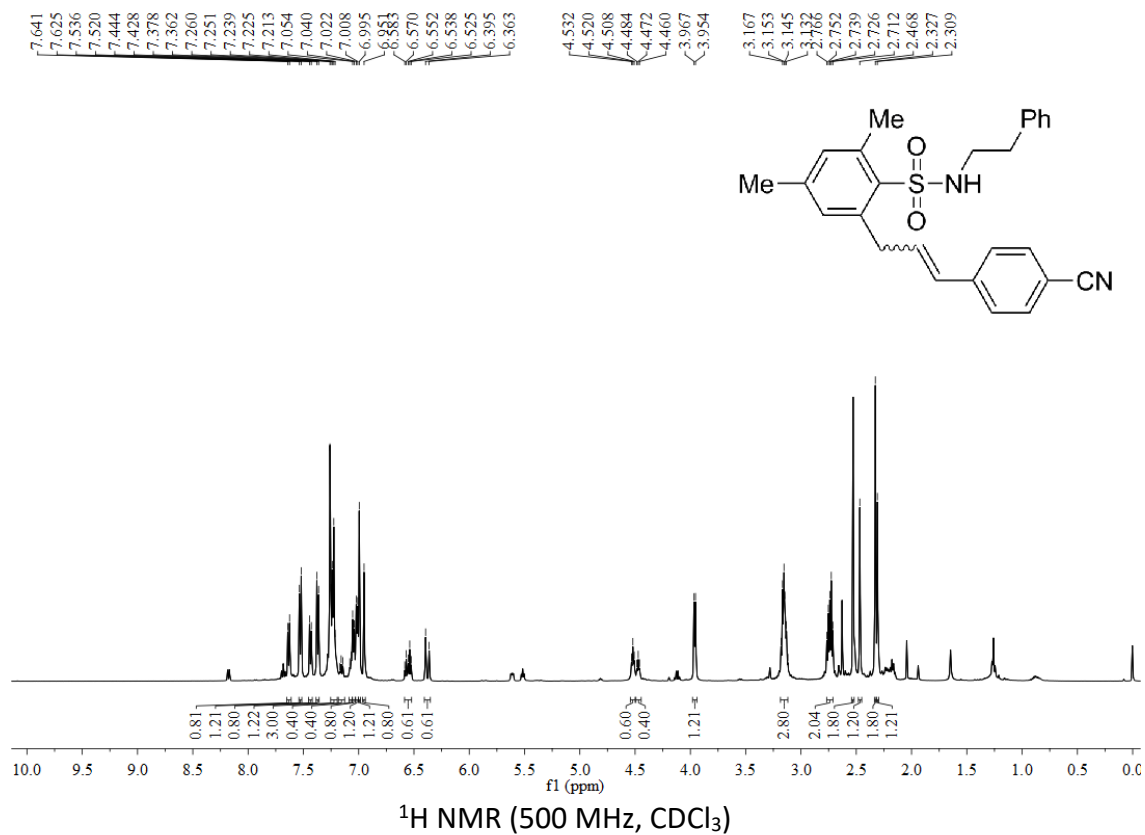
(3ae)(E/Z = 3:1).



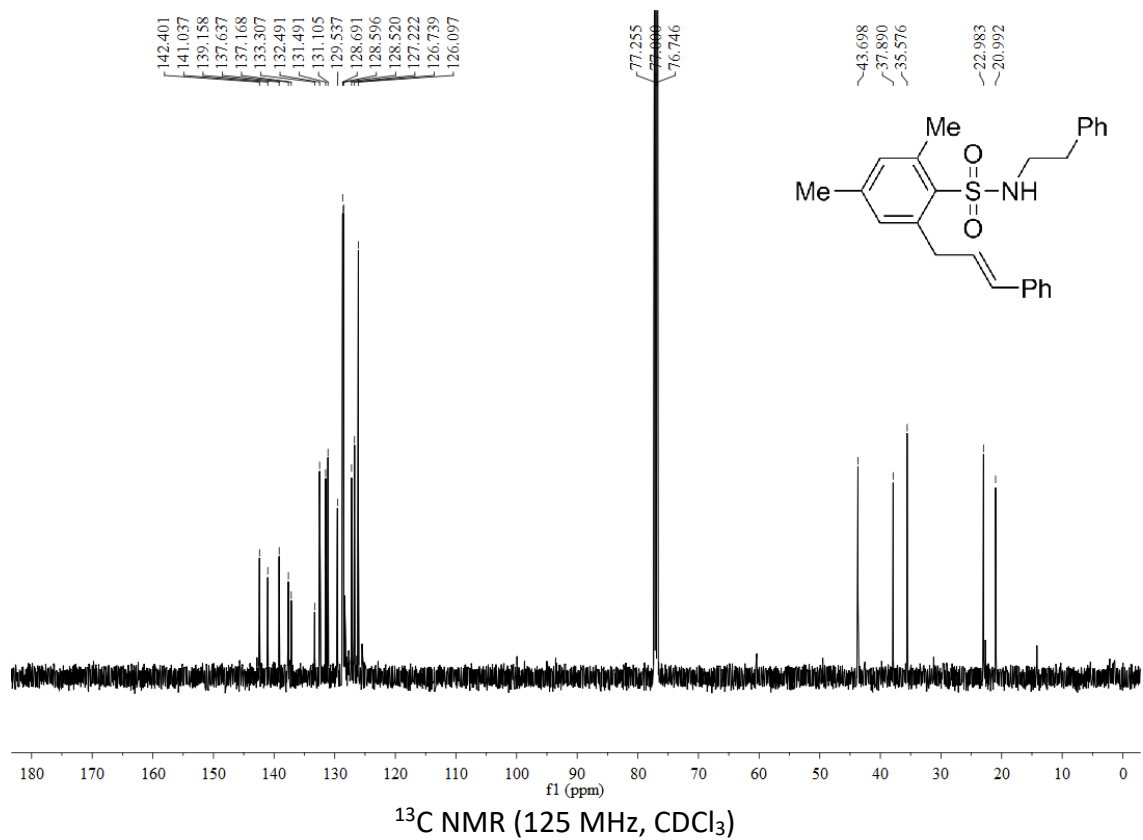
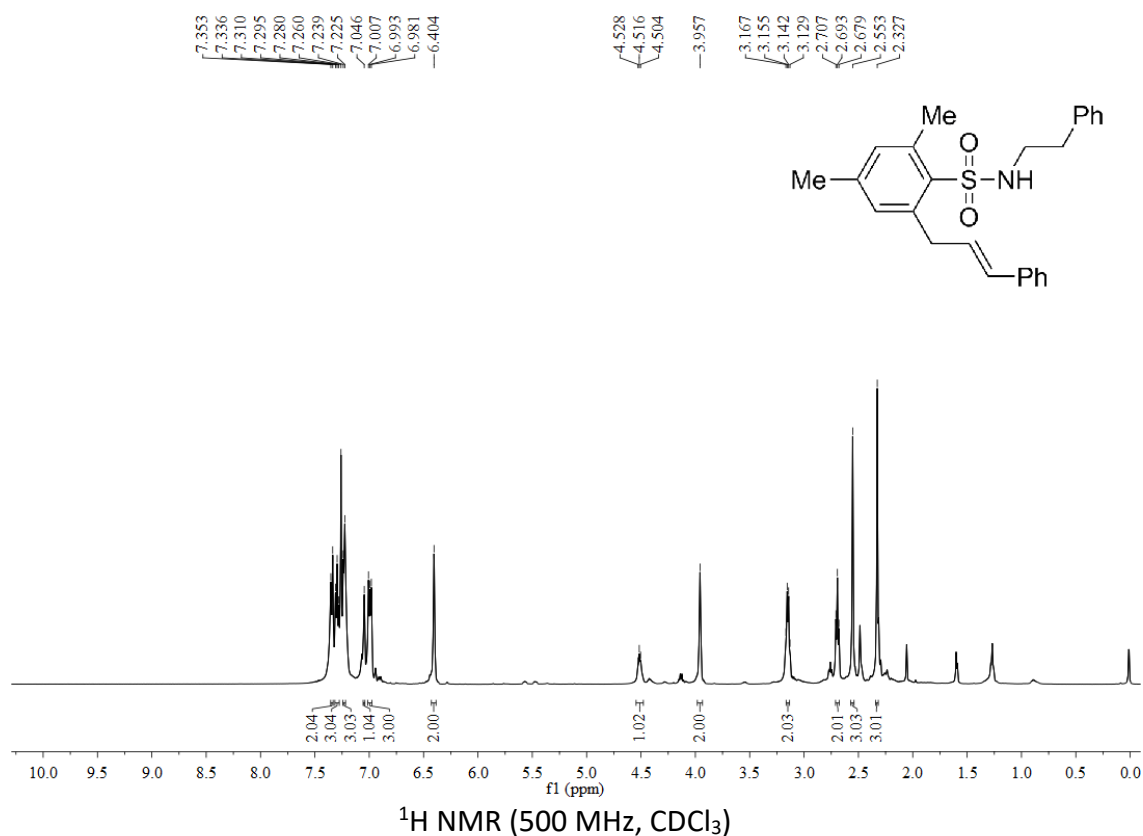


^{19}F NMR (471 MHz, CDCl_3)

2-(3-(4-cyanophenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3ag)(E/Z = 1.5:1).

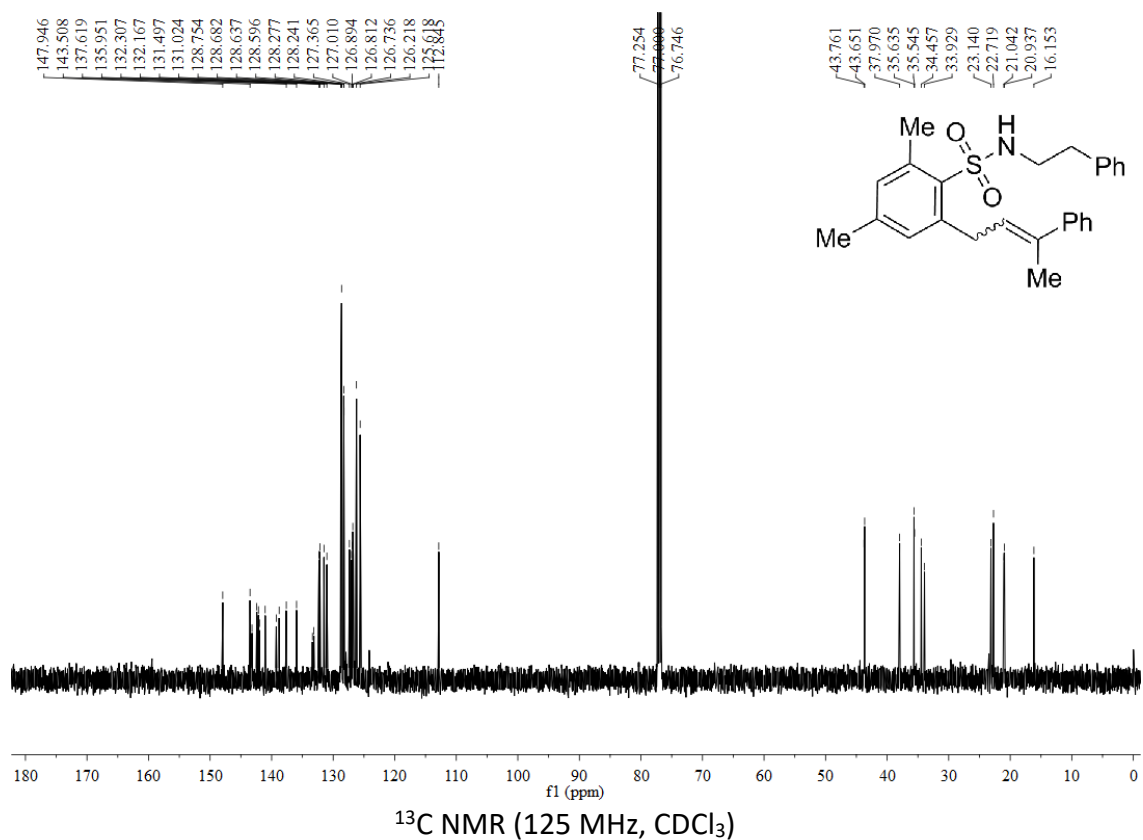
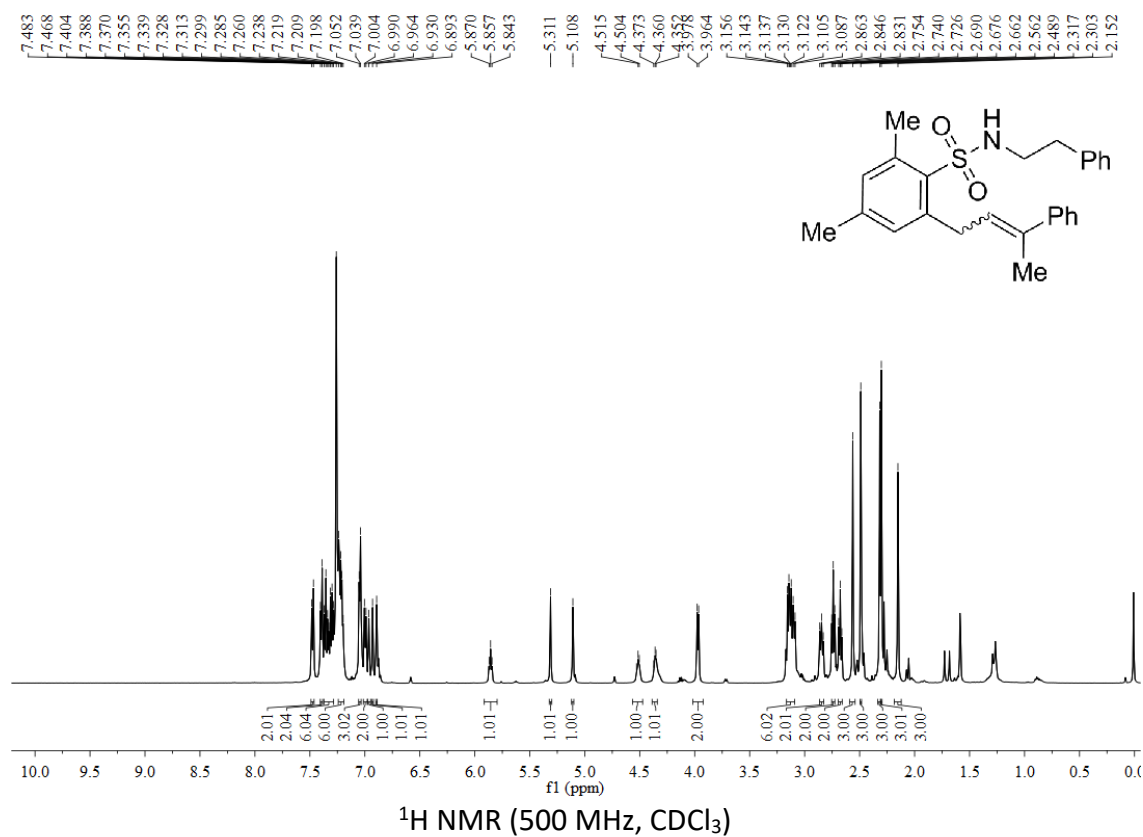


2-cinnamyl-4,6-dimethyl-N-phenethylbenzenesulfonamide (3aj) (E/Z>99:1).



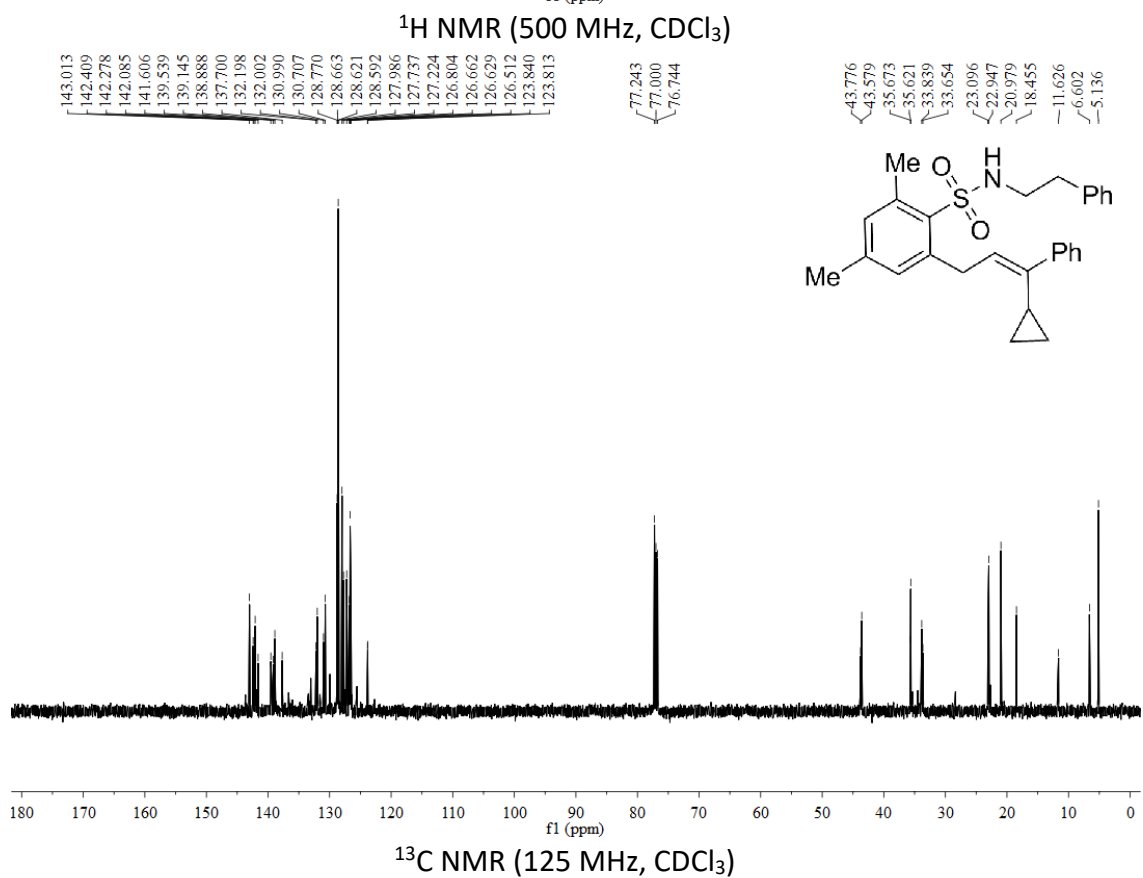
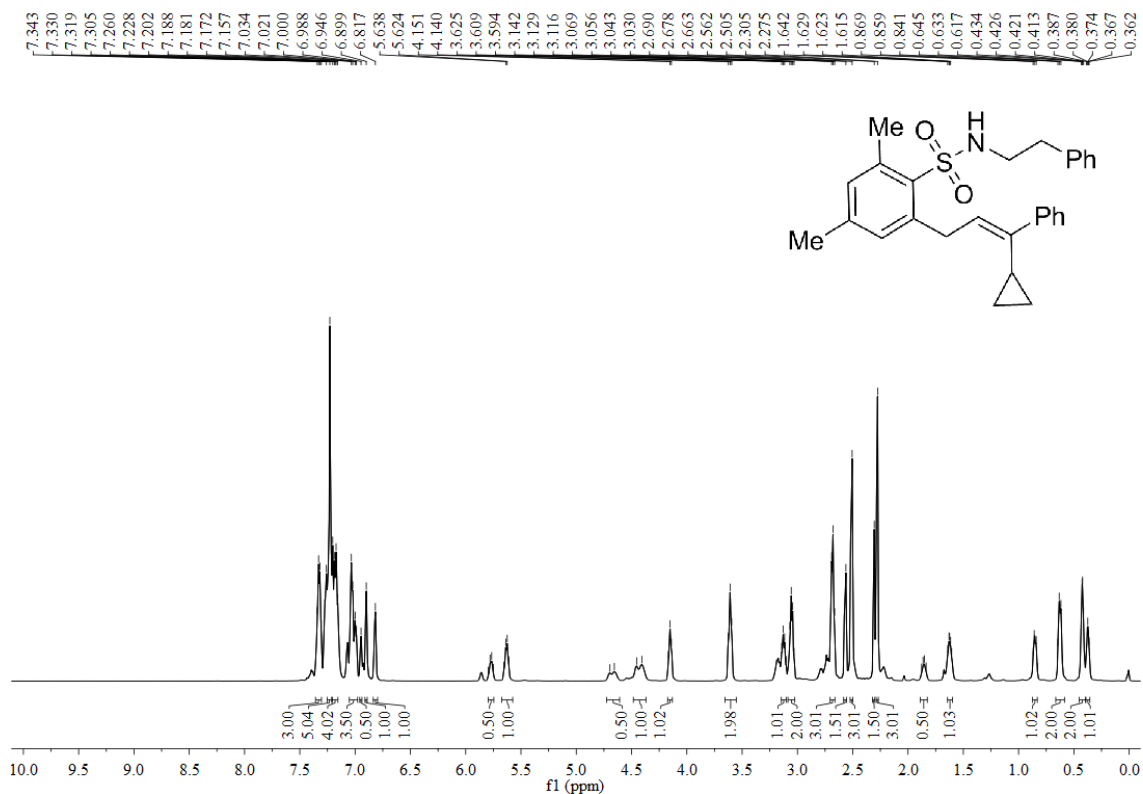
2,4-dimethyl-N-phenethyl-6-(3-phenylbut-2-en-1-yl)benzenesulfonamide (3a)

(E/Z=1:1).

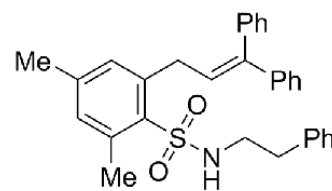
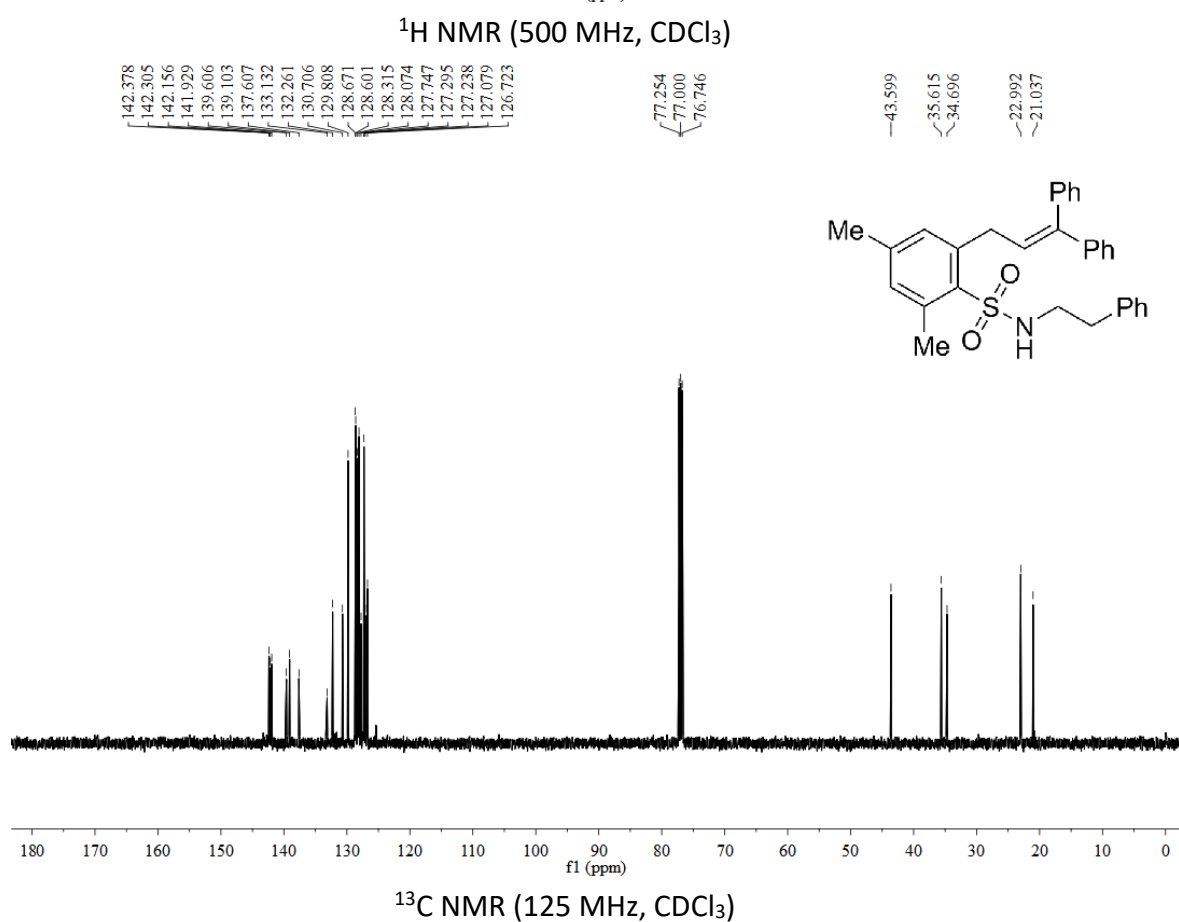
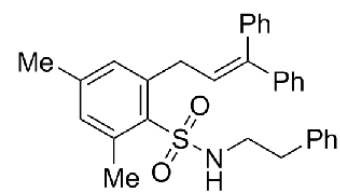
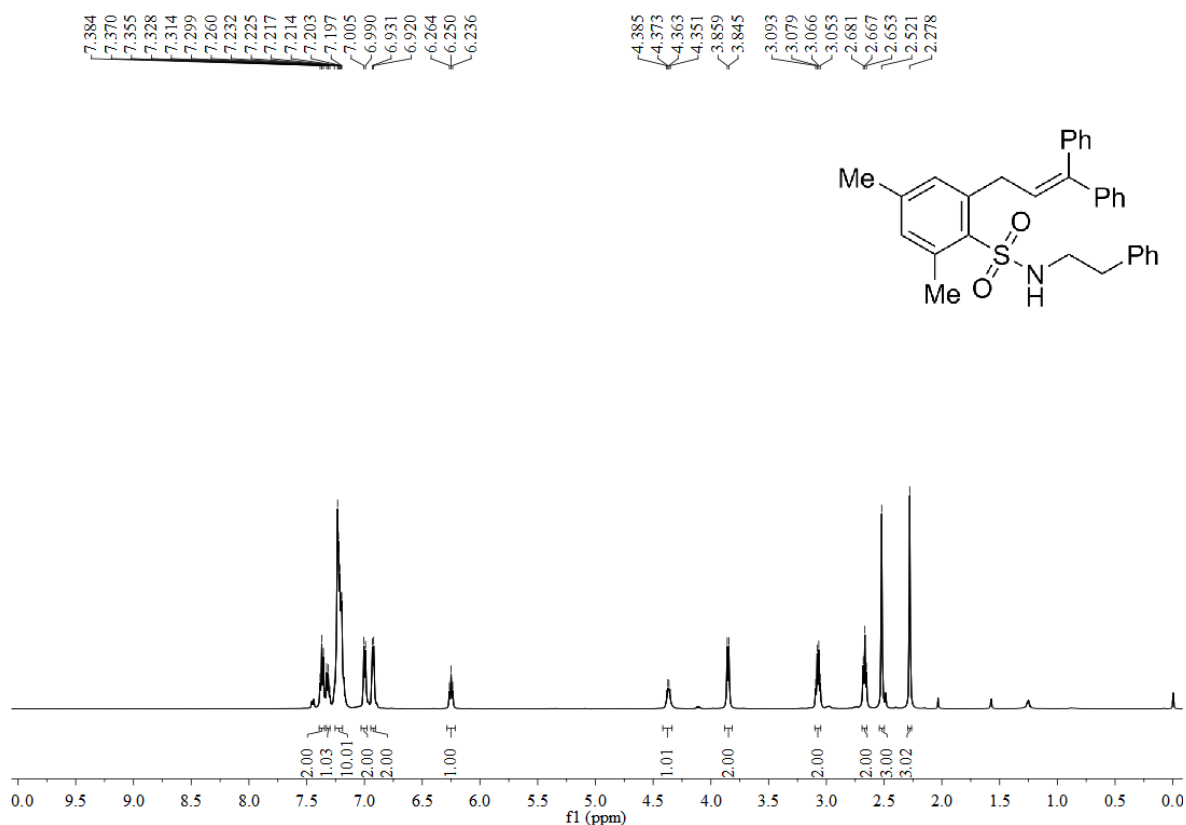


2-(3-cyclopropyl-3-phenylallyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide

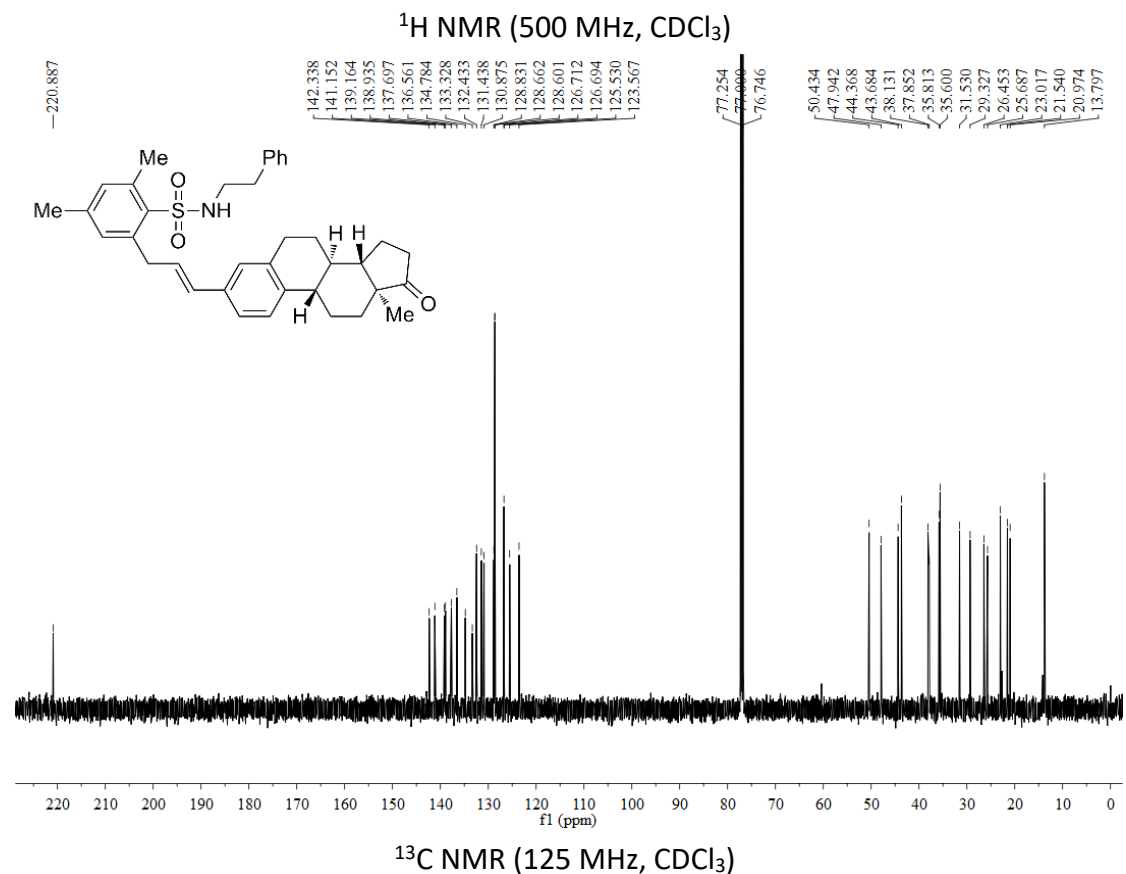
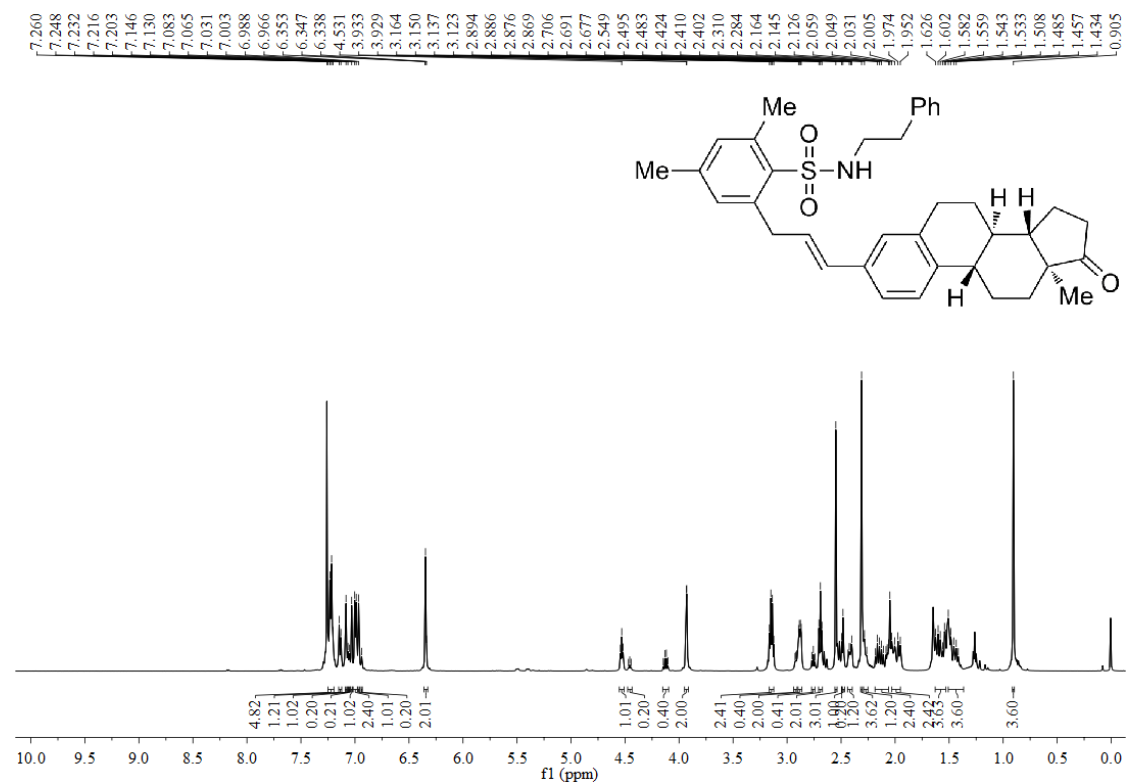
(3am) (*E/Z* = 2:1).



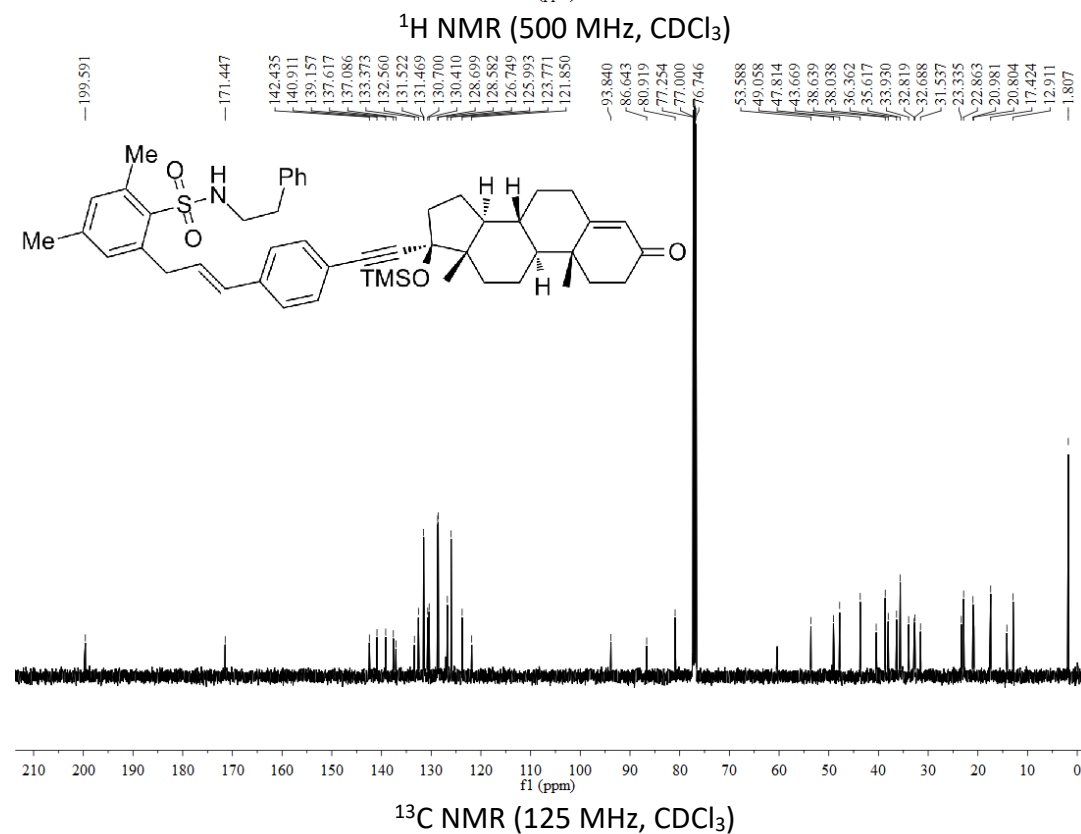
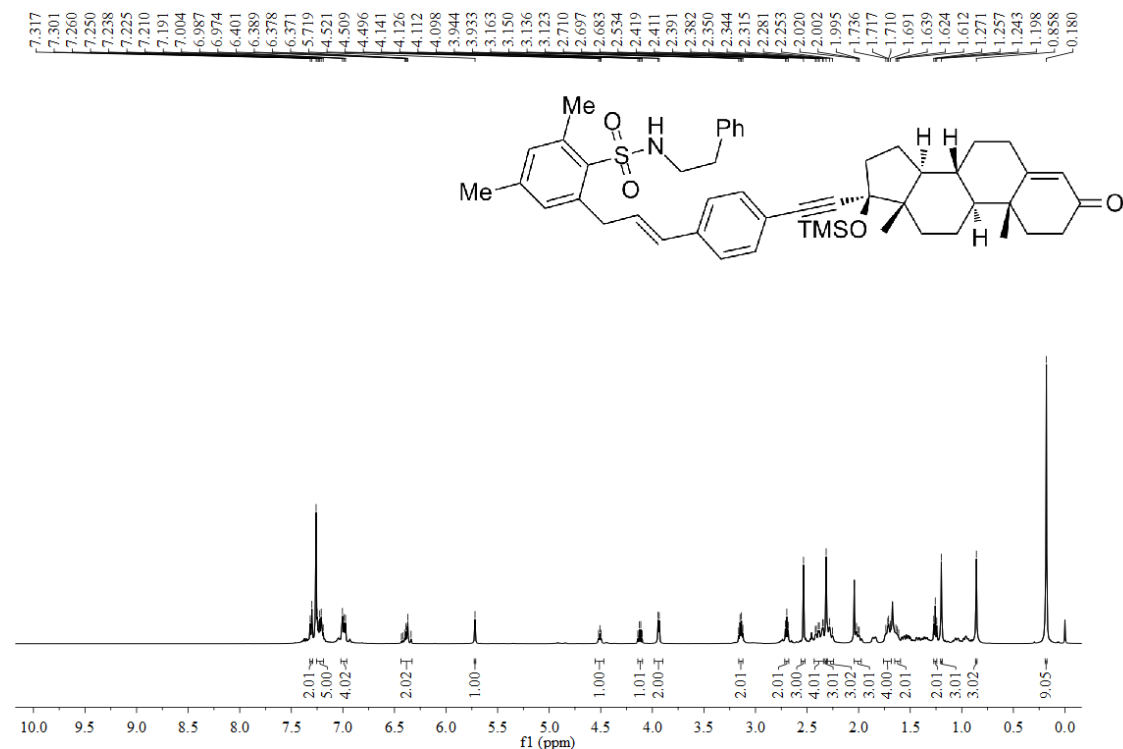
2-(3,3-diphenylallyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (3an).



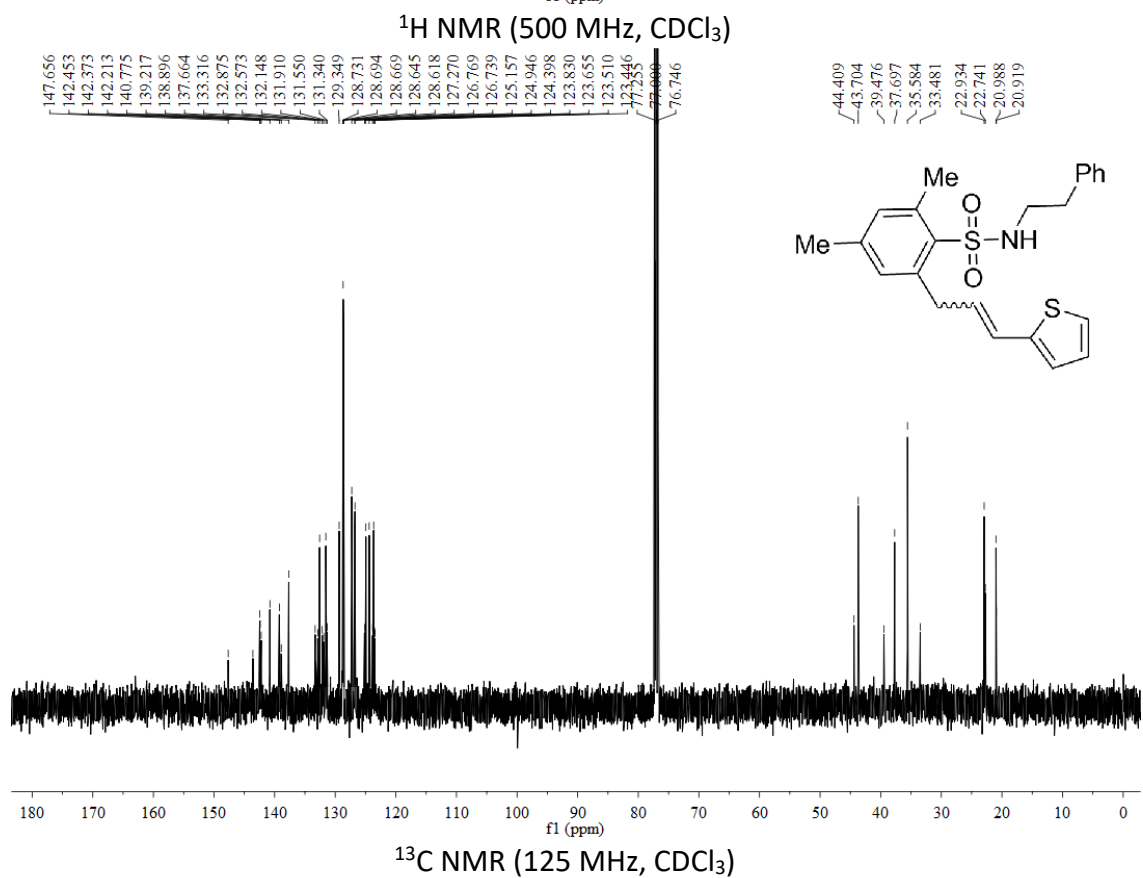
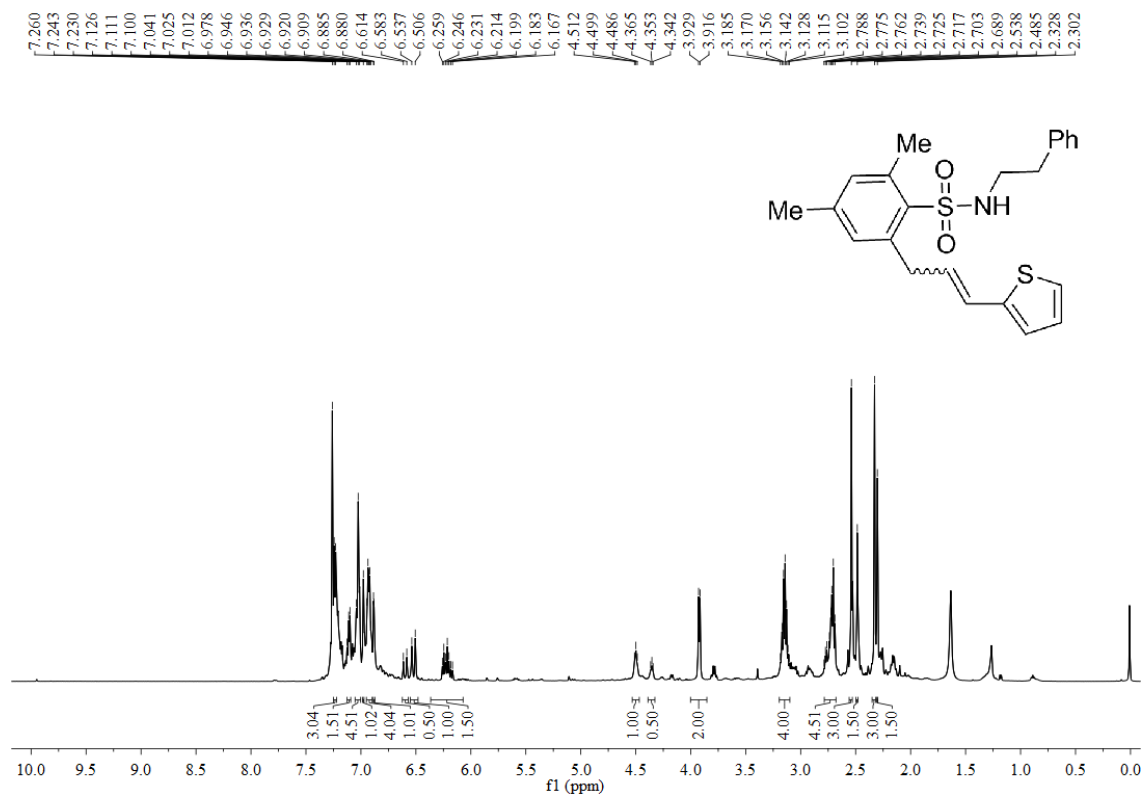
2,4-dimethyl-6-(3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)allyl)-*N*-phenethylbenzenesulfonamide (3ap) (*E/Z*=5:1).



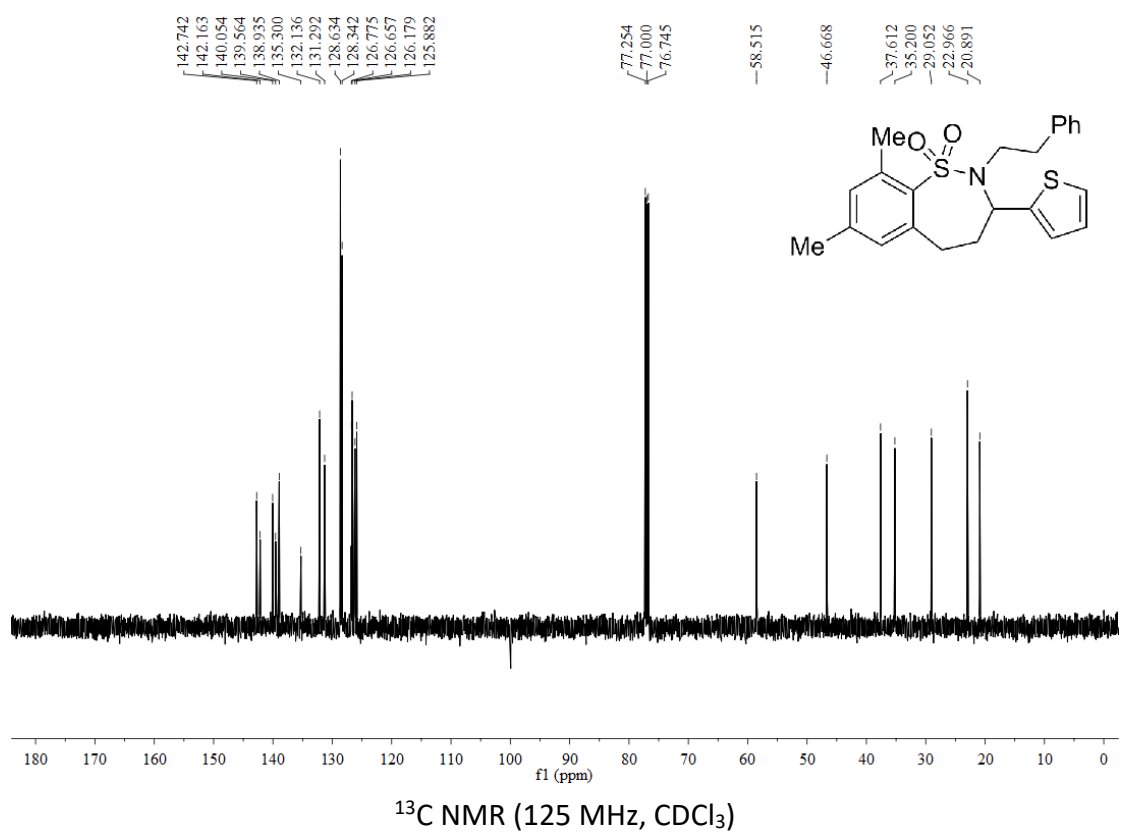
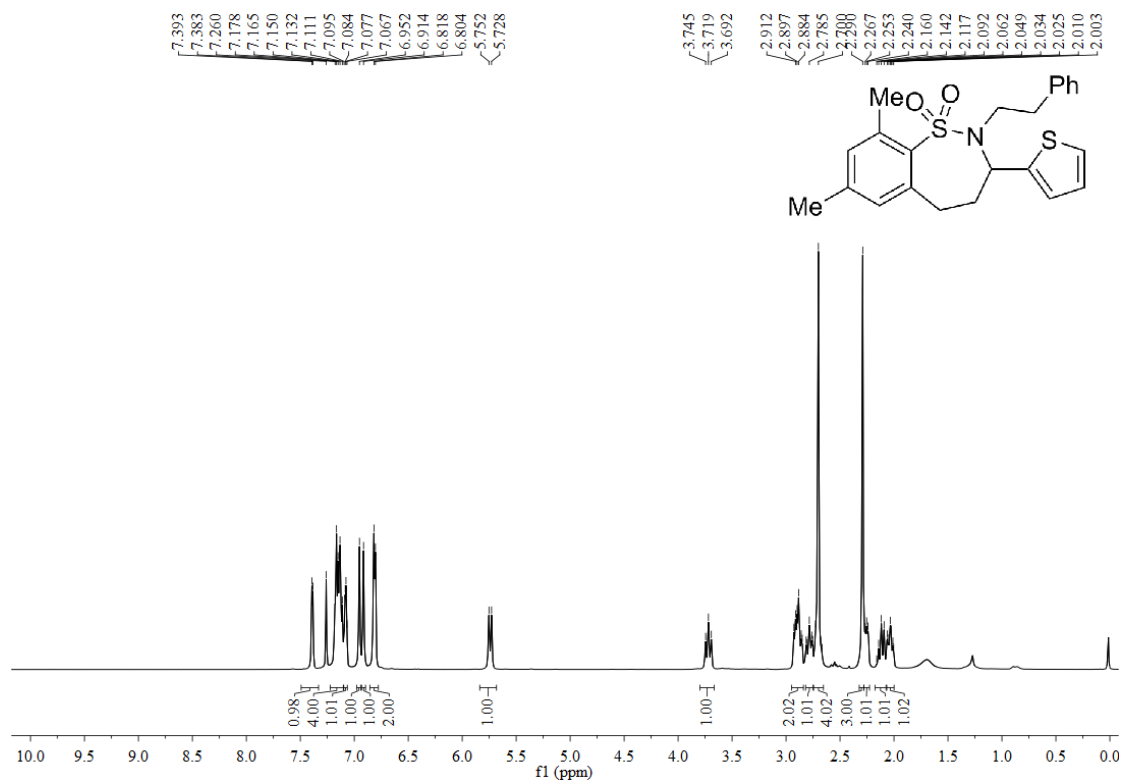
2-((*E*)-3-(4-(((*8R,9S,10R,13S,14S,17S*)-10,13-dimethyl-3-oxo-17-((trimethylsilyl)oxy)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-17-yl)ethynyl)phenyl)allyl)-4,6-dimethyl-N-phenethylbenzenesulfonamide (**3aq**) (*E/Z* >99:1).



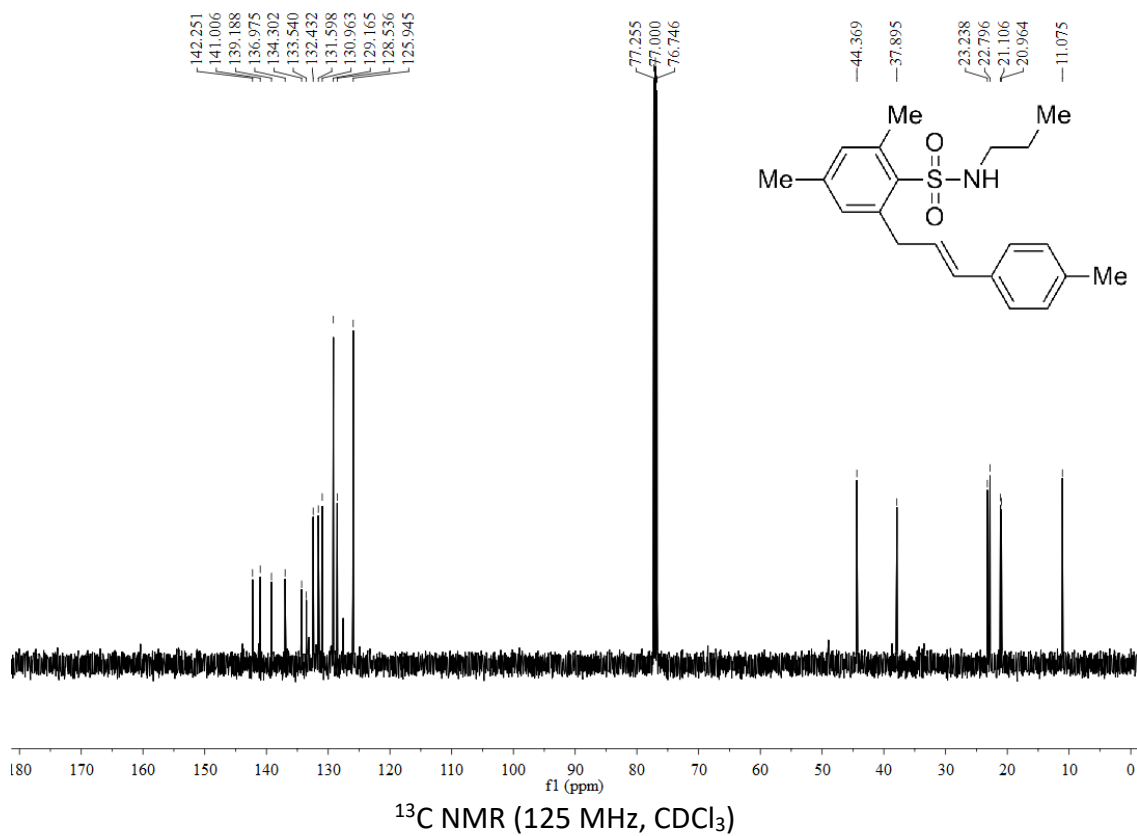
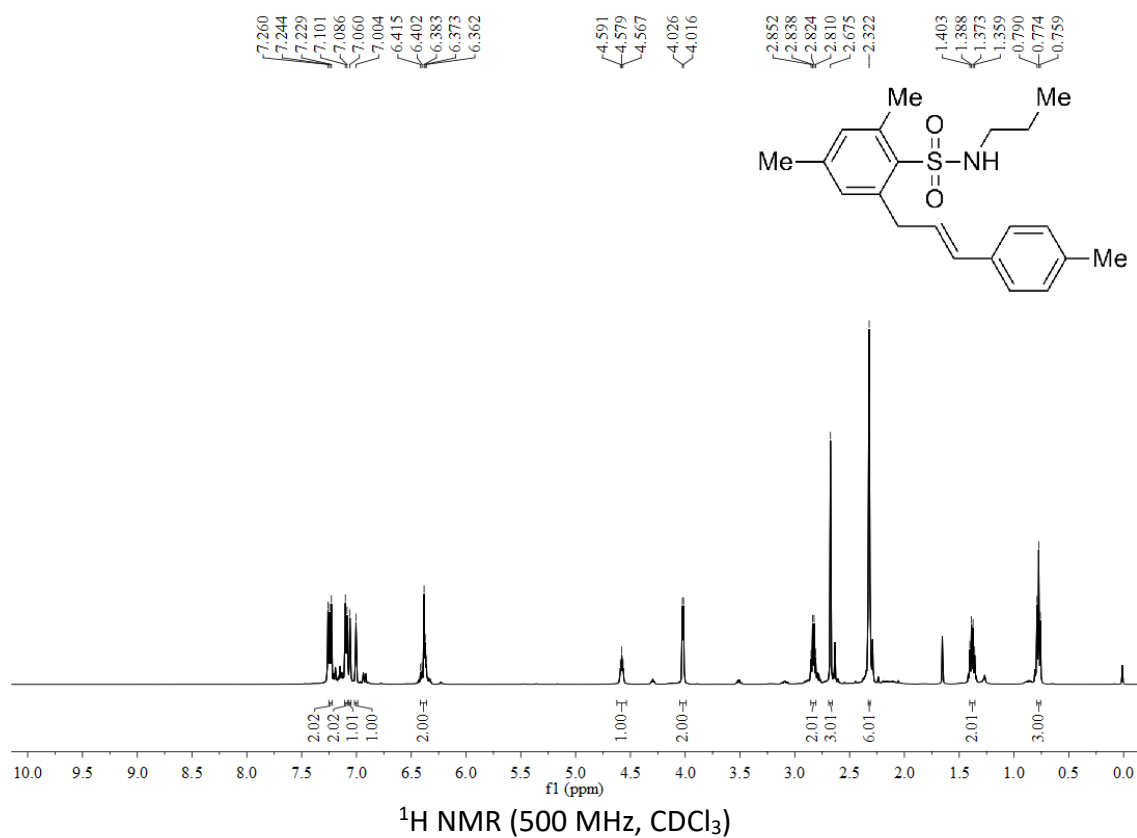
2,4-dimethyl-N-phenethyl-6-(3-(thiophen-2-yl)allyl)benzenesulfonamide (3ar)(E/Z = 2:1).



7,9-dimethyl-2-phenethyl-3-(thiophen-2-yl)-2,3,4,5-tetrahydrobenzo[f][1,2]thiazepine 1,1-dioxide (8ar).

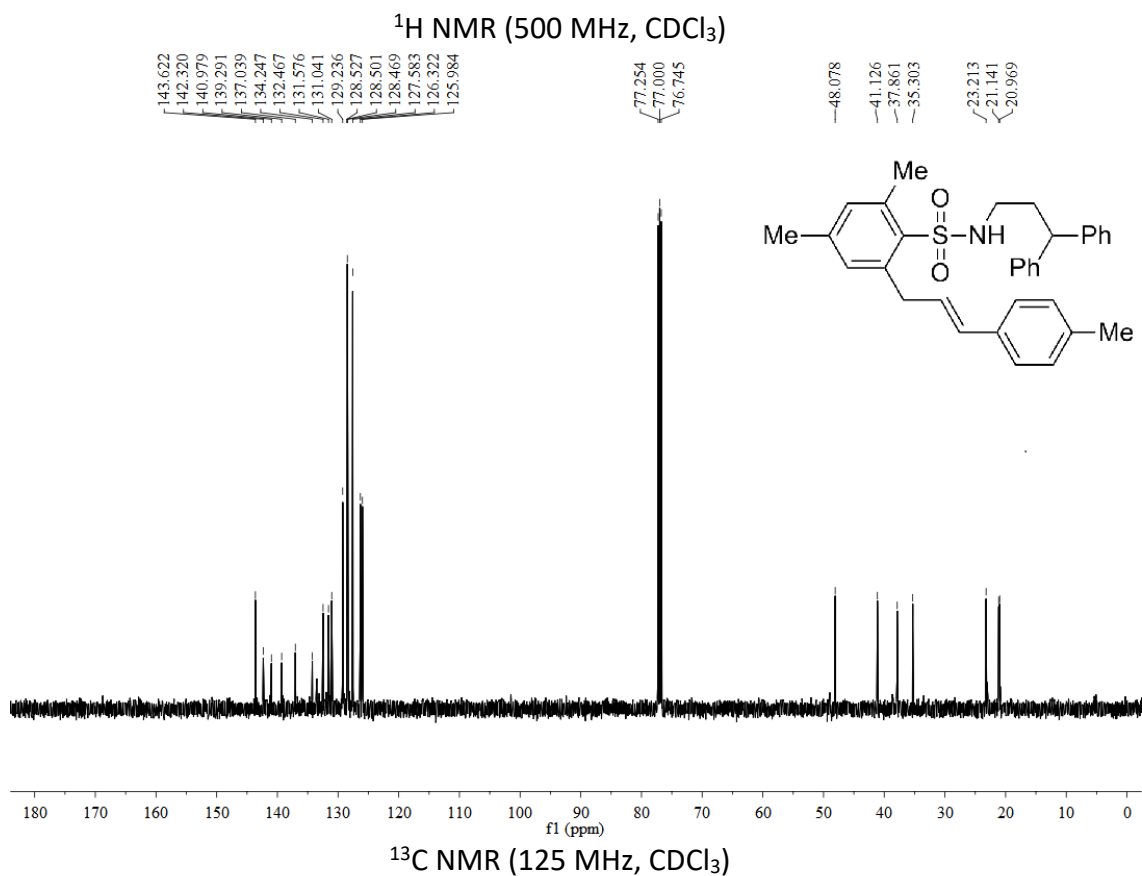
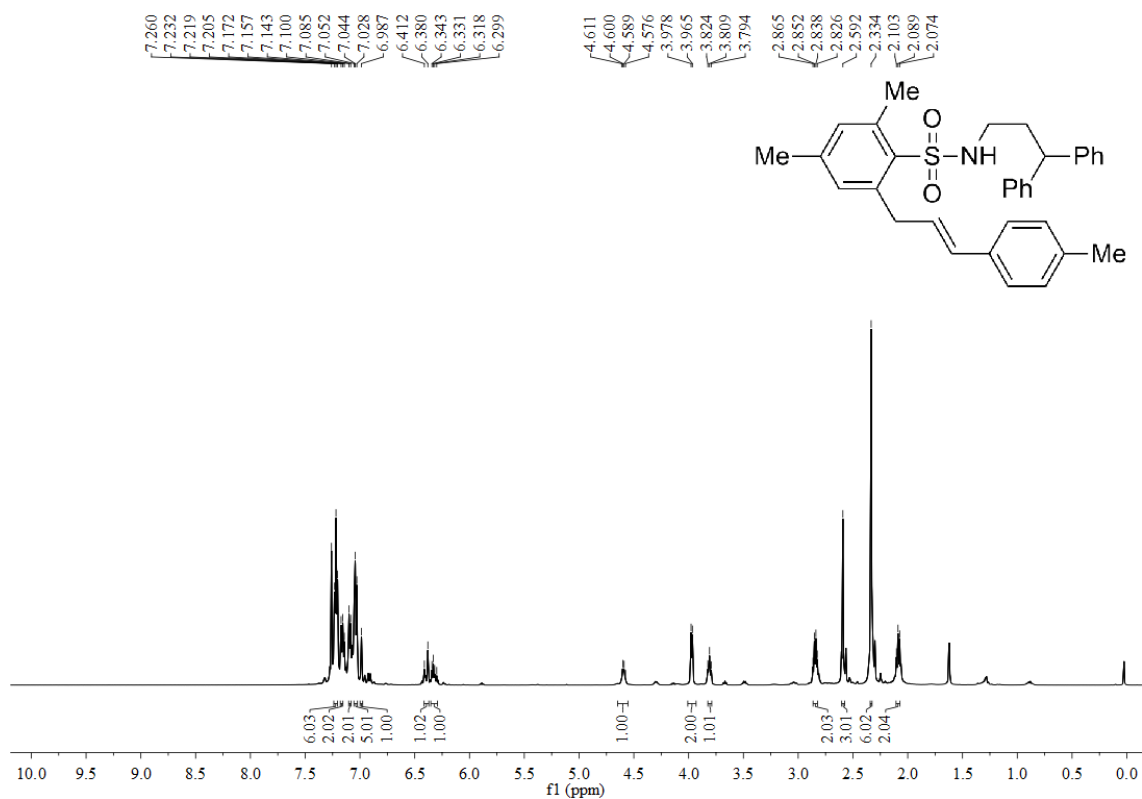


(E)-2,4-dimethyl-N-propyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ba) (E/Z > 99:1).

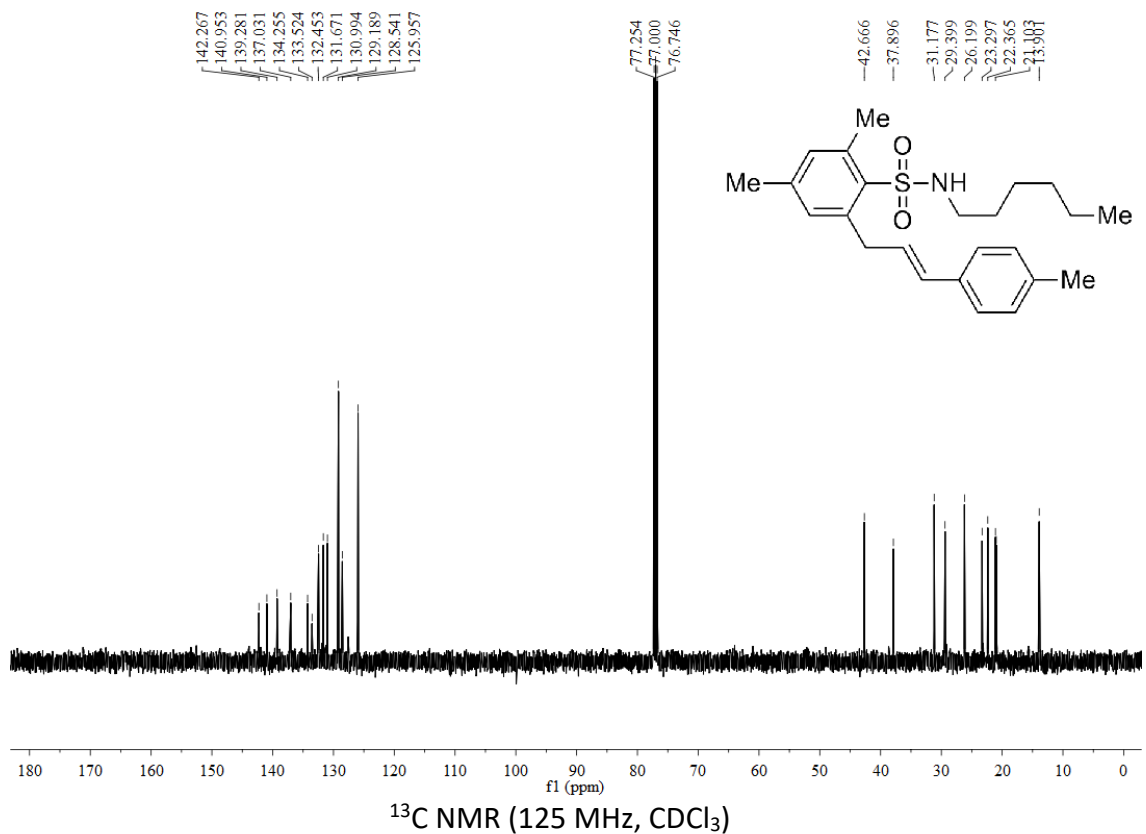
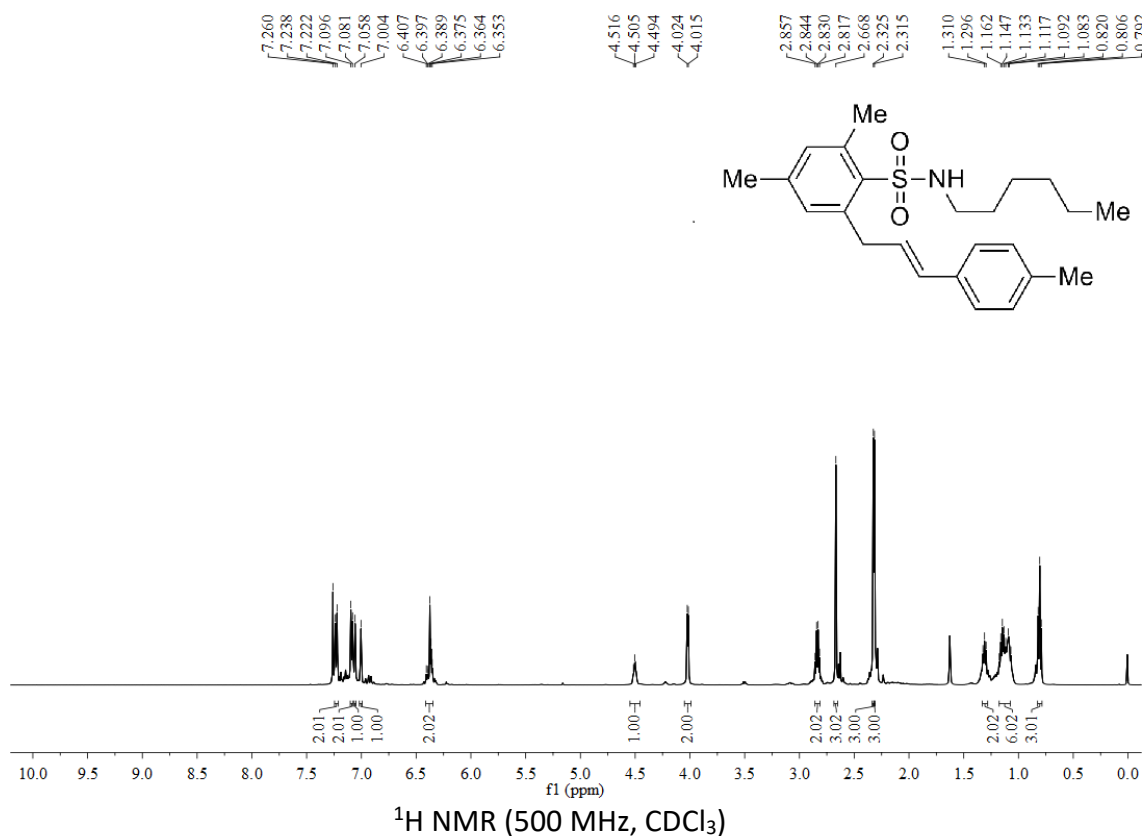


(E)-N-(3,3-diphenylpropyl)-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide

(3ca) (E/Z > 99:1).

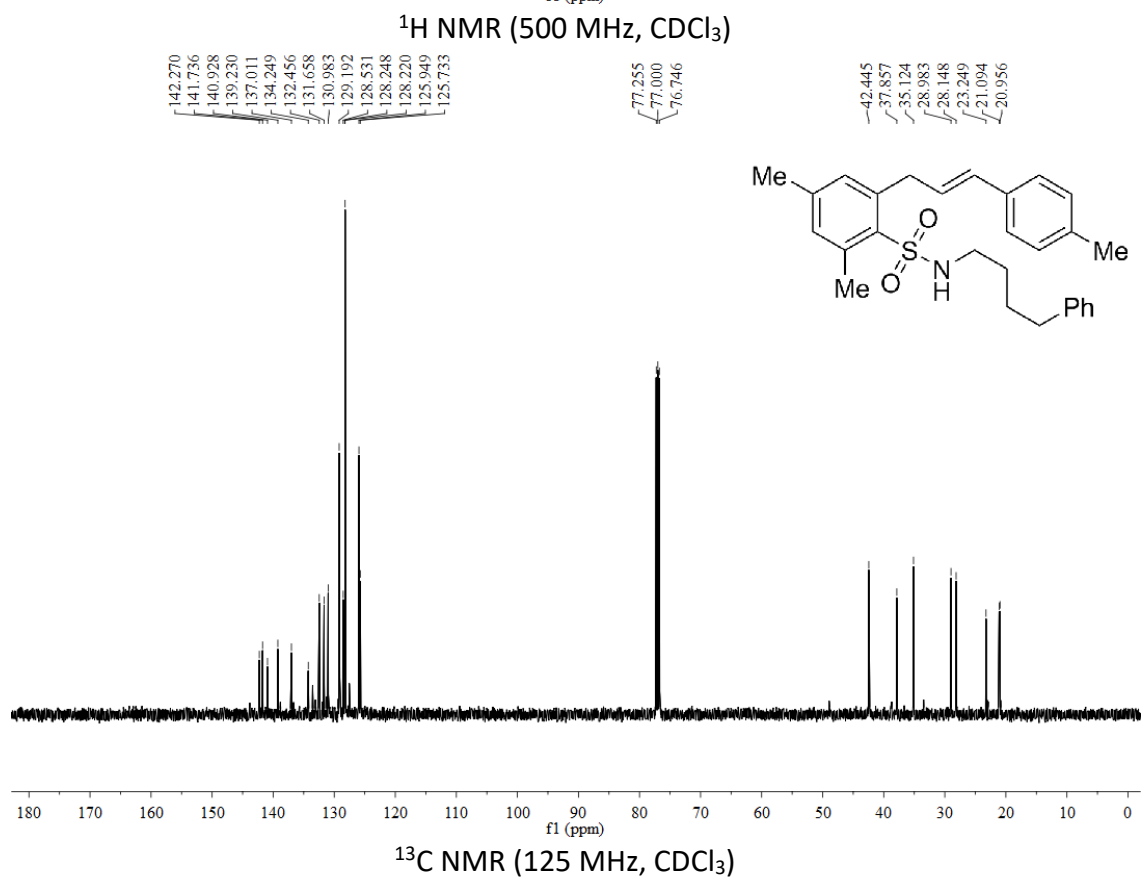
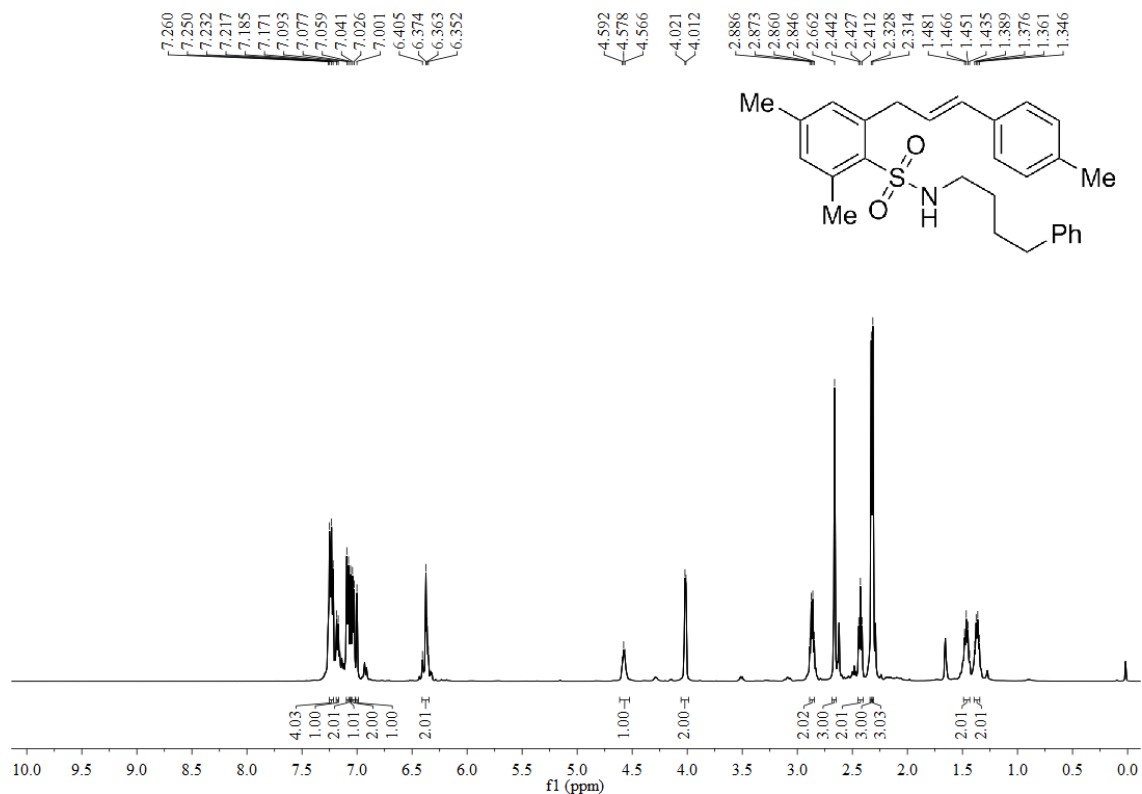


(E)-N-hexyl-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3da) (E/Z > 99:1).

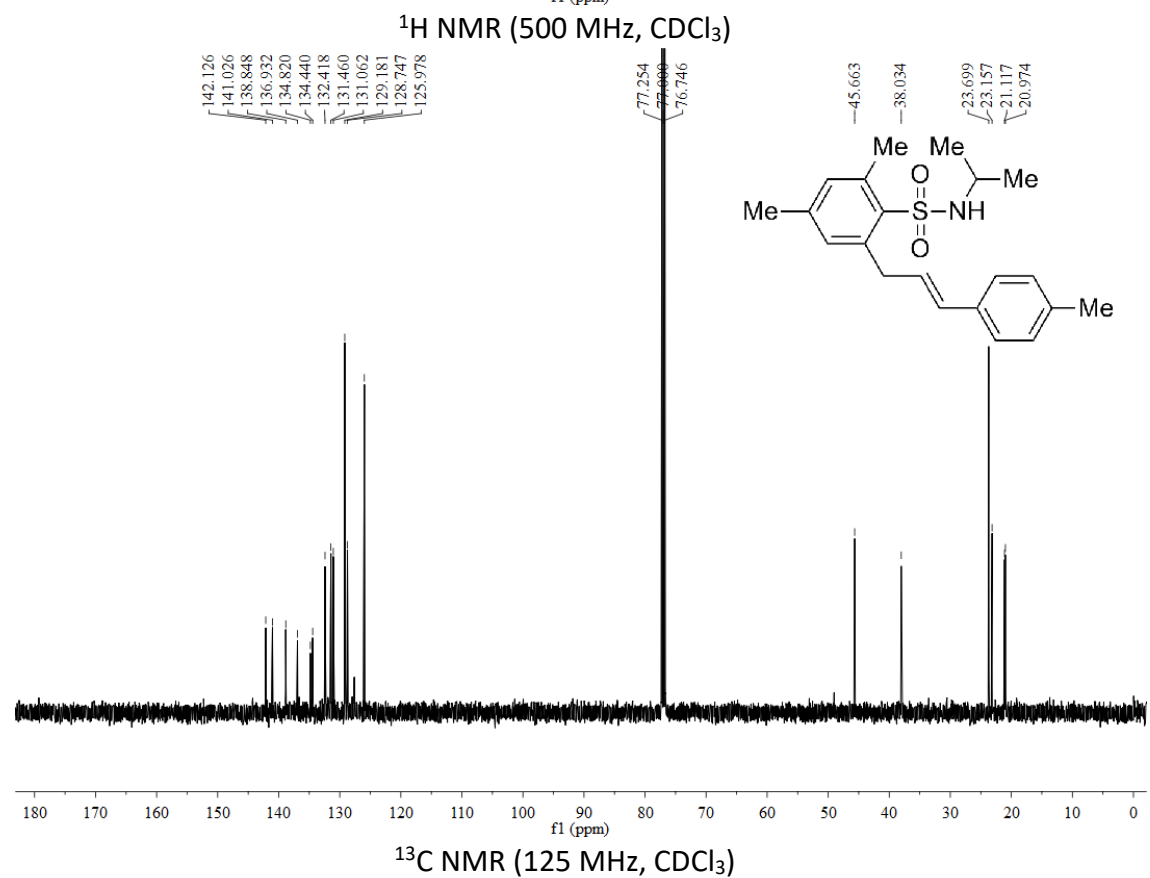
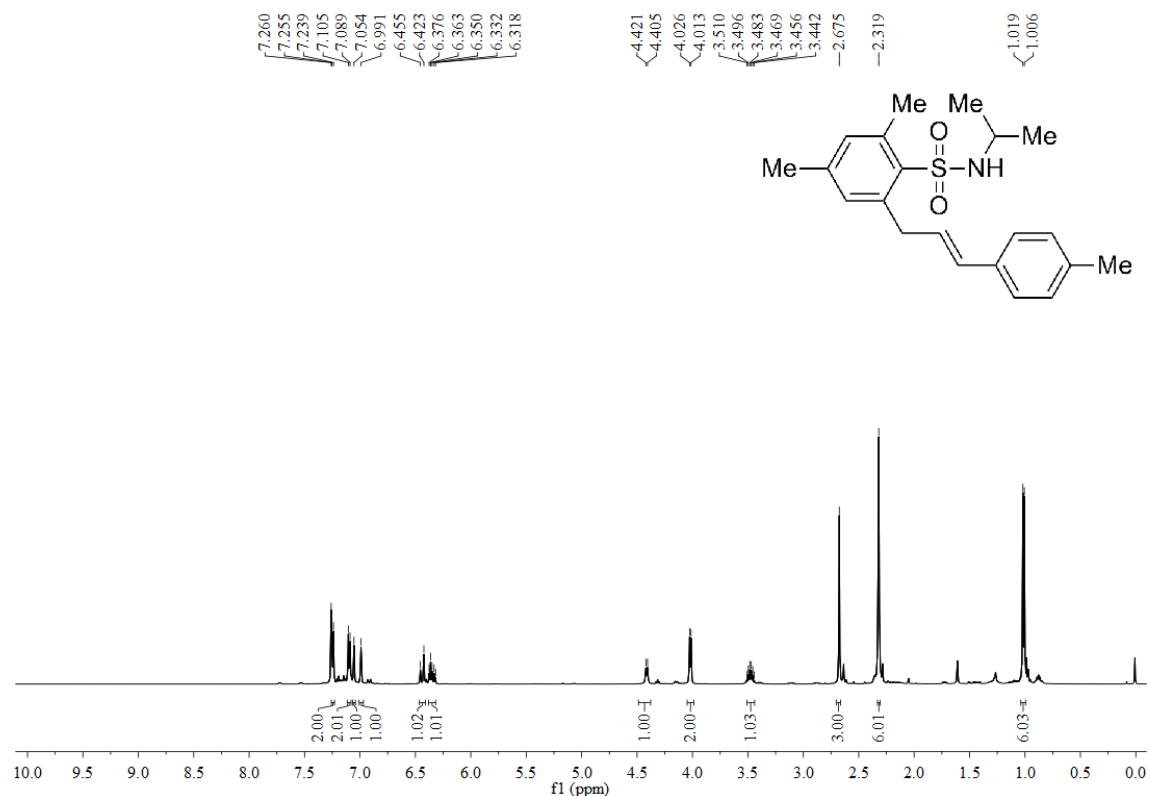


(E)-2,4-dimethyl-N-(4-phenylbutyl)-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ea)

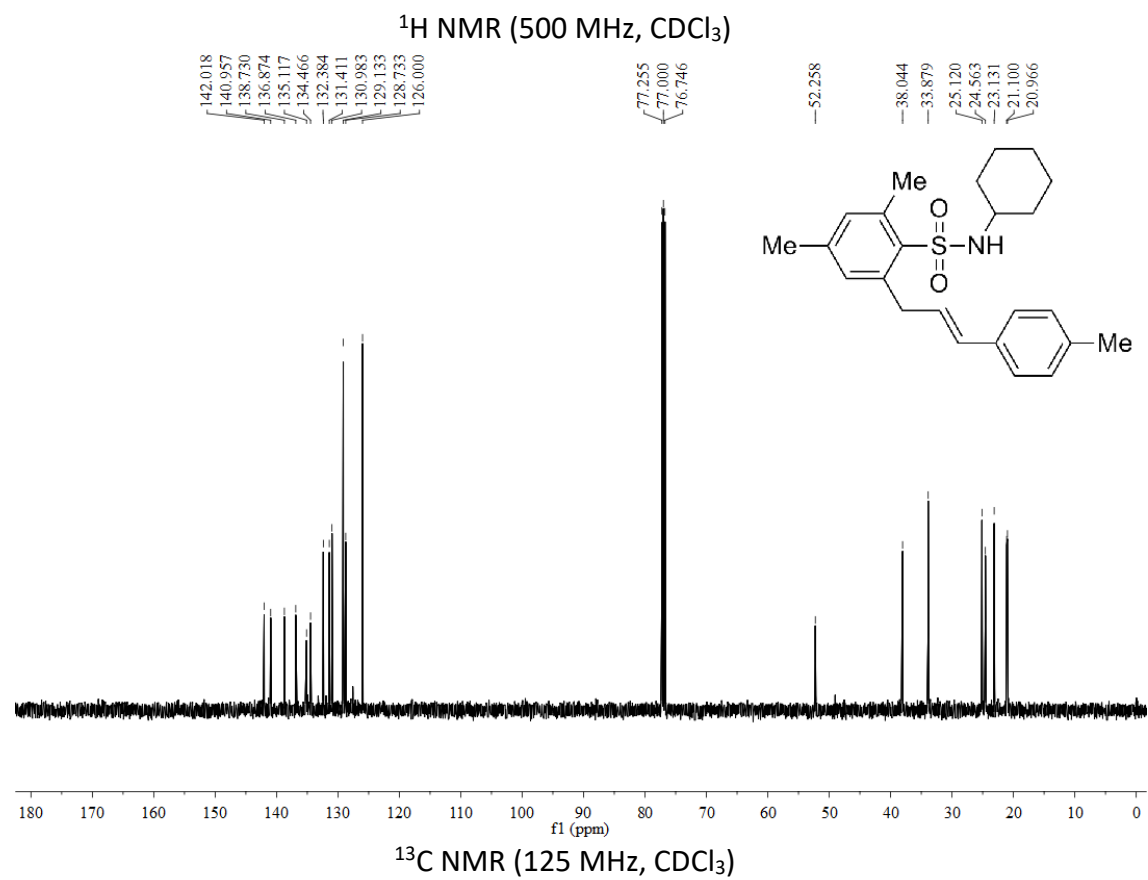
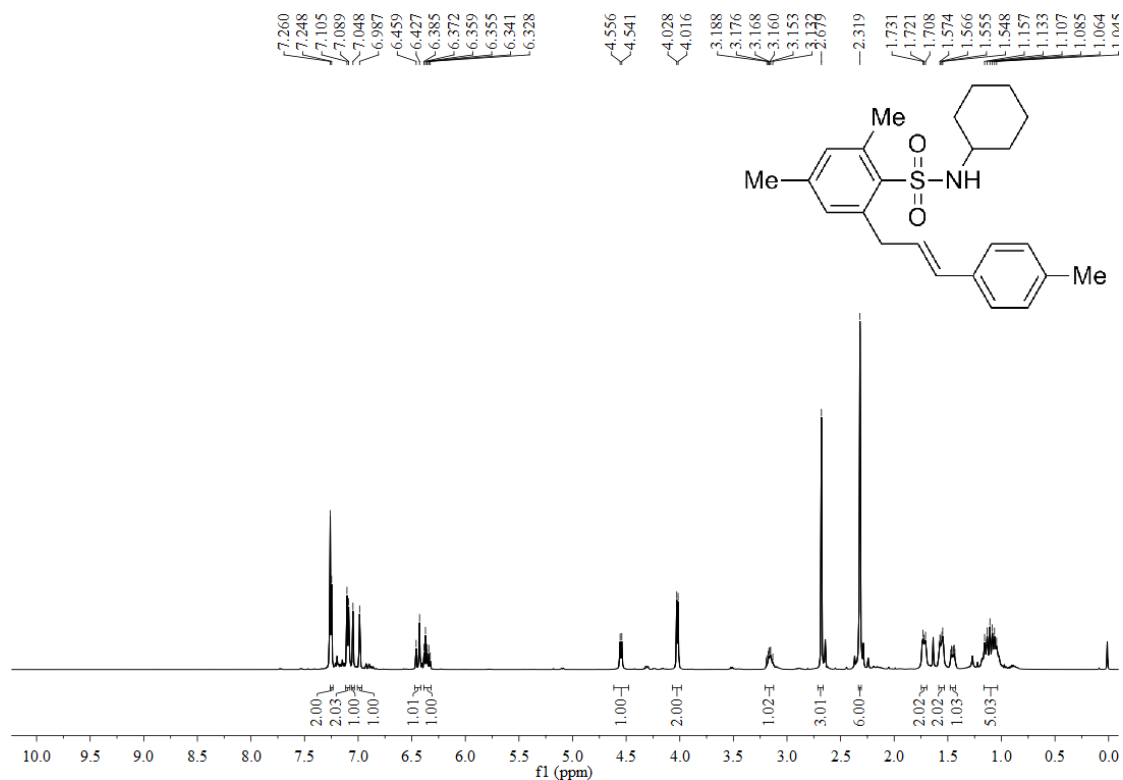
(E/Z > 99:1).



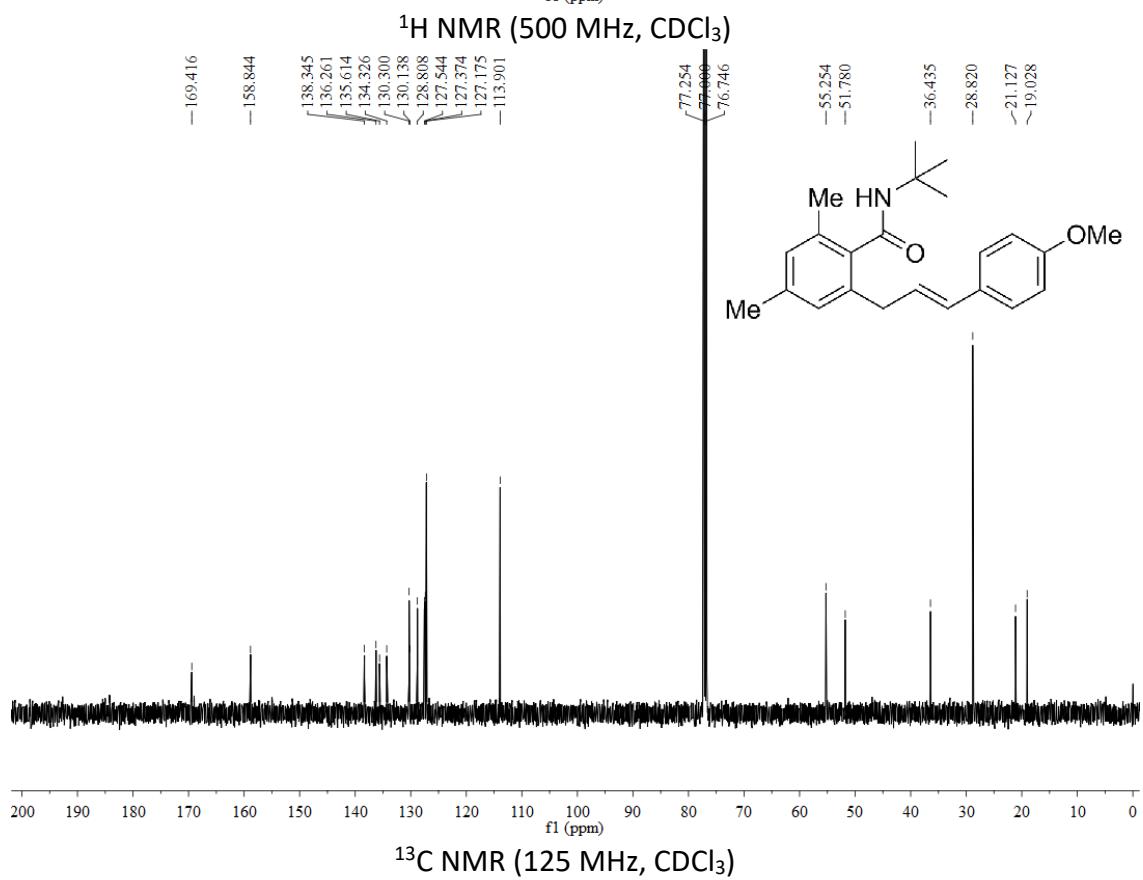
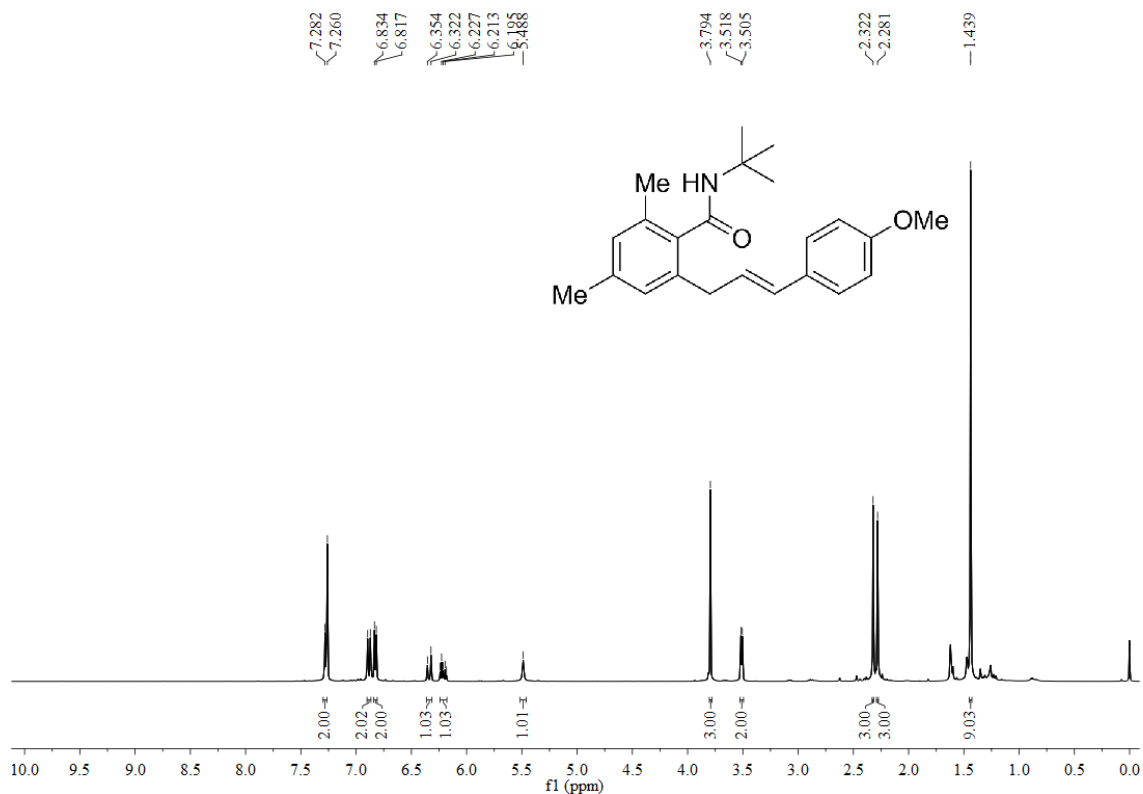
(E)-N-isopropyl-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3fa) (E/Z > 99:1).



(E)-N-cyclohexyl-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3ga) (E/Z > 99:1).

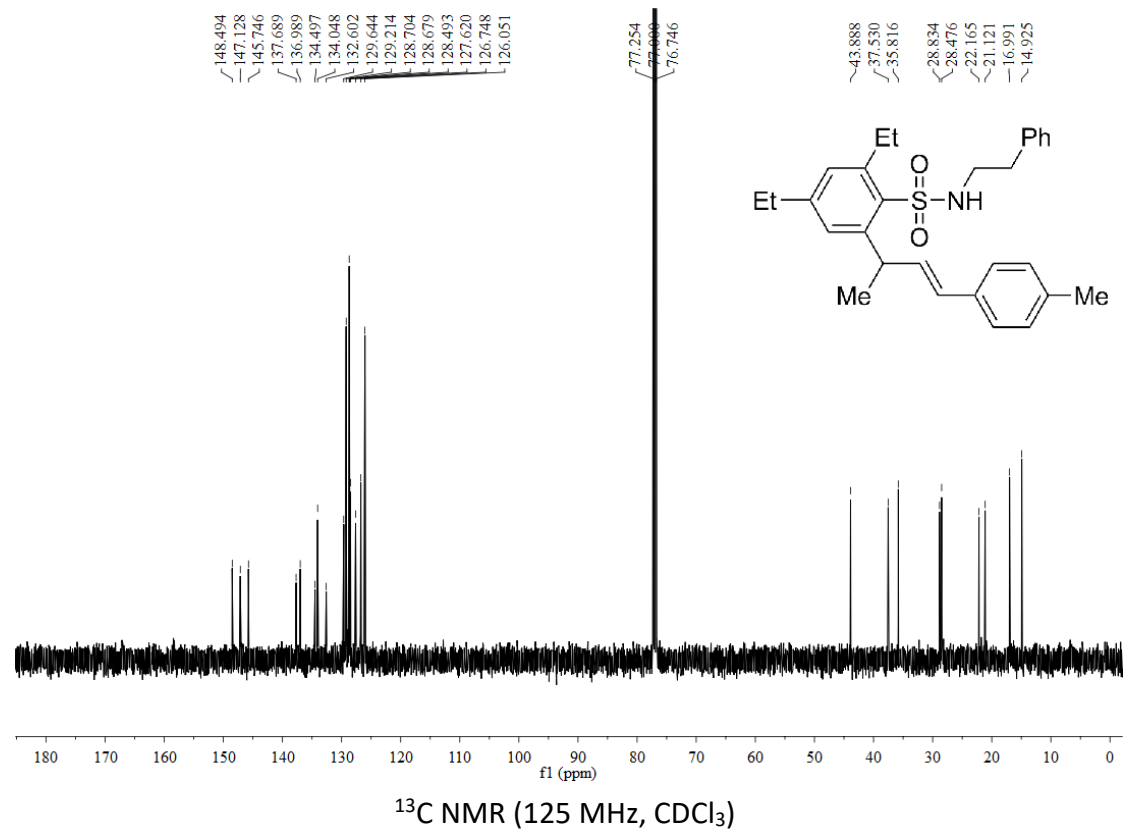
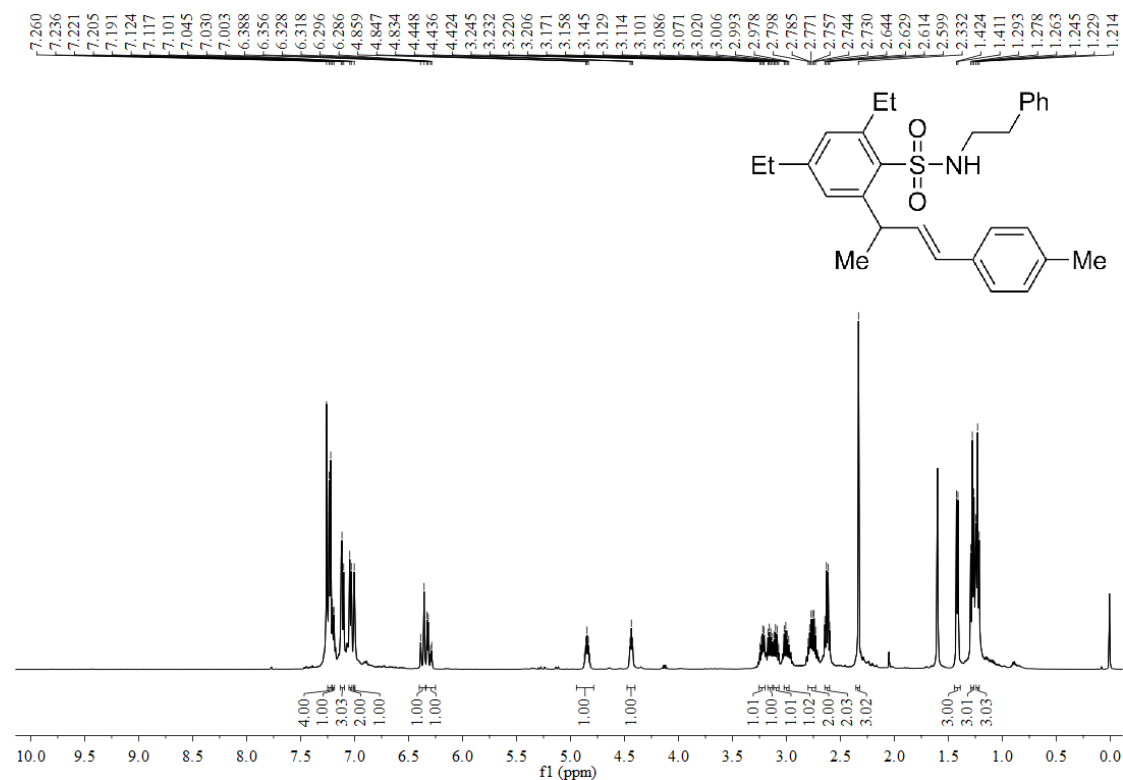


(E)-N-(tert-butyl)-2-(3-(4-methoxyphenyl)allyl)-4,6-dimethylbenzamide (3ho) (E/Z > 99:1).

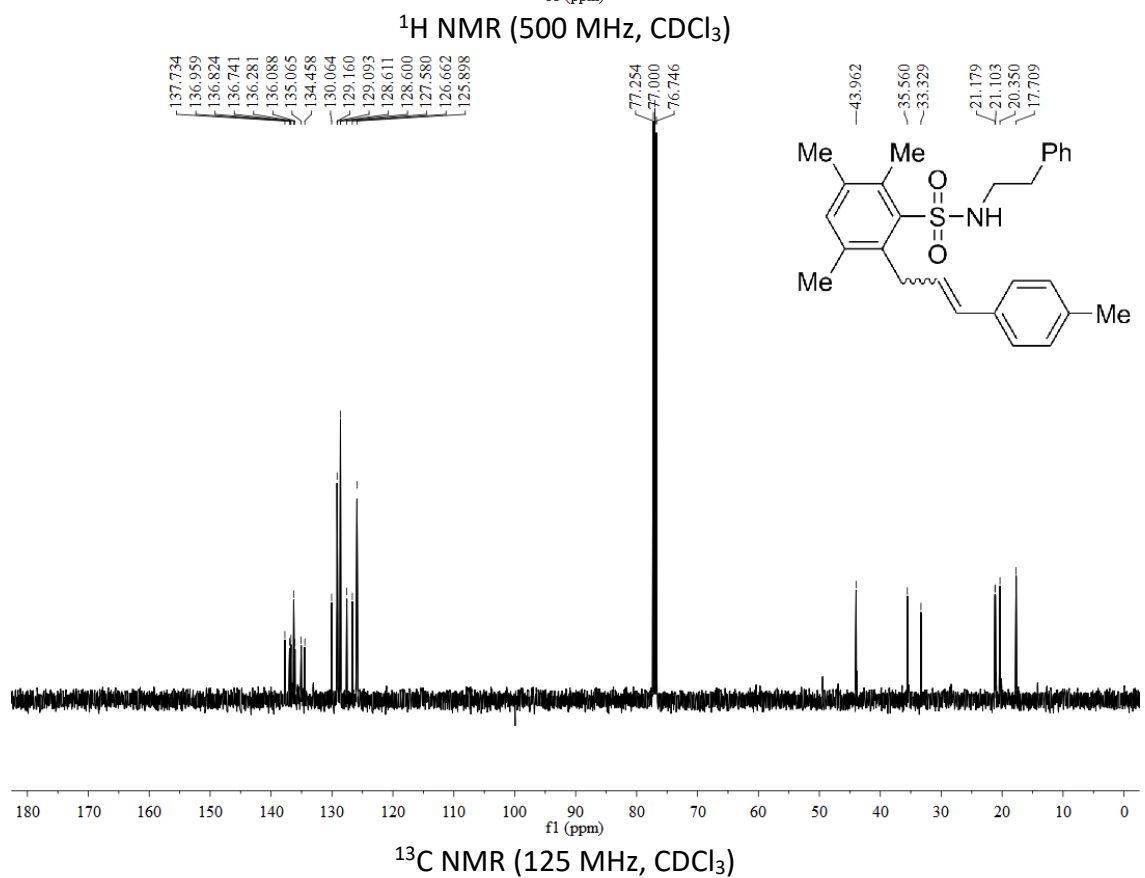
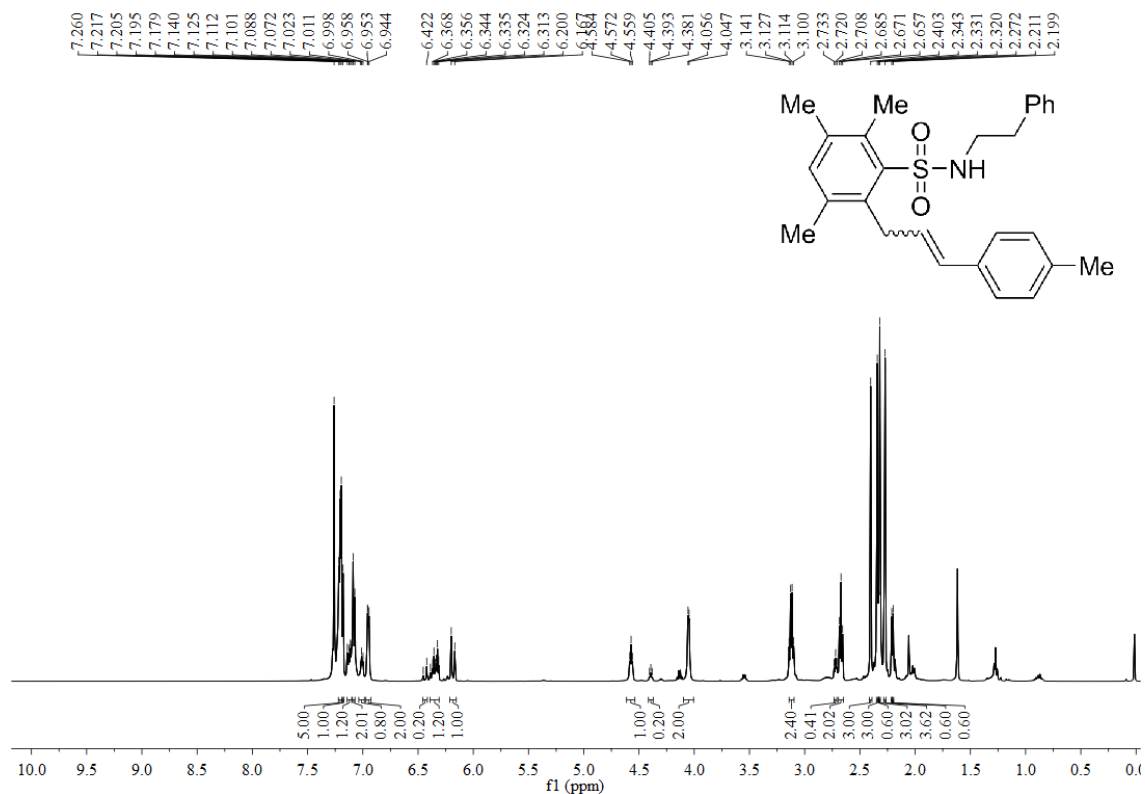


(E)-2,4-diethyl-N-phenethyl-6-(4-(p-tolyl)but-3-en-2-yl)benzenesulfonamide (3ia)

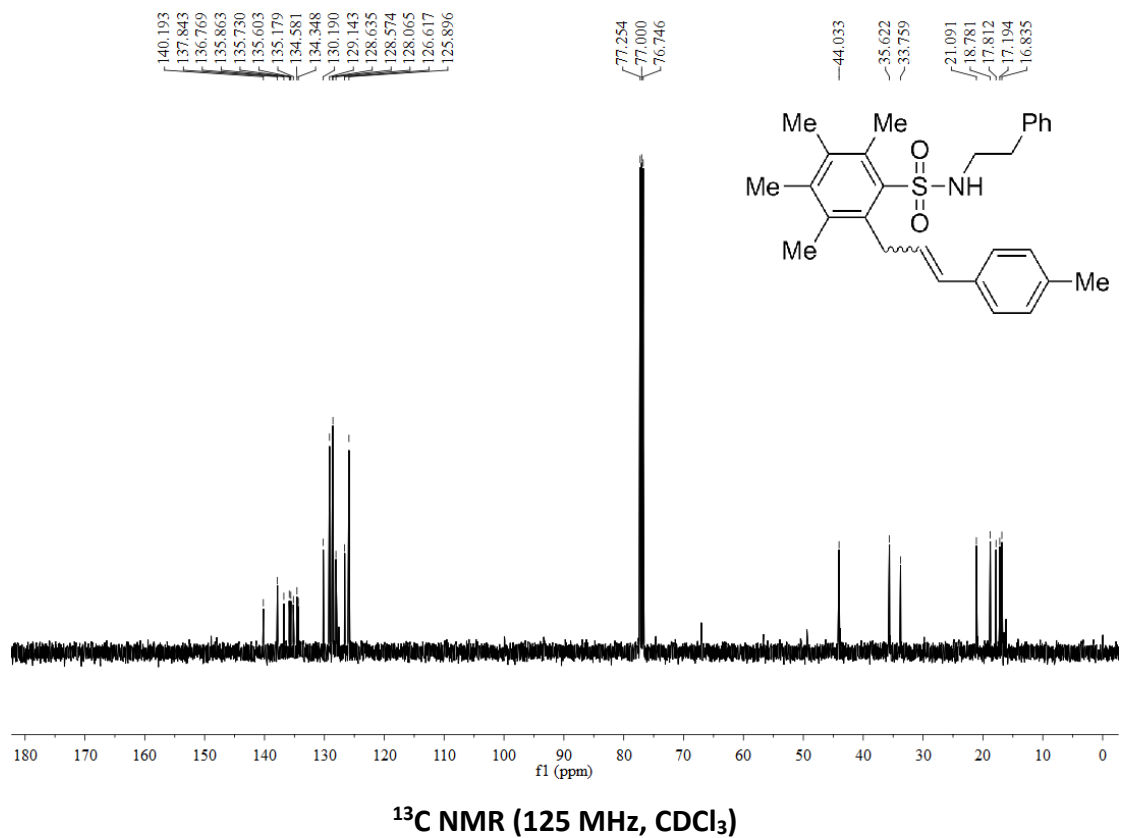
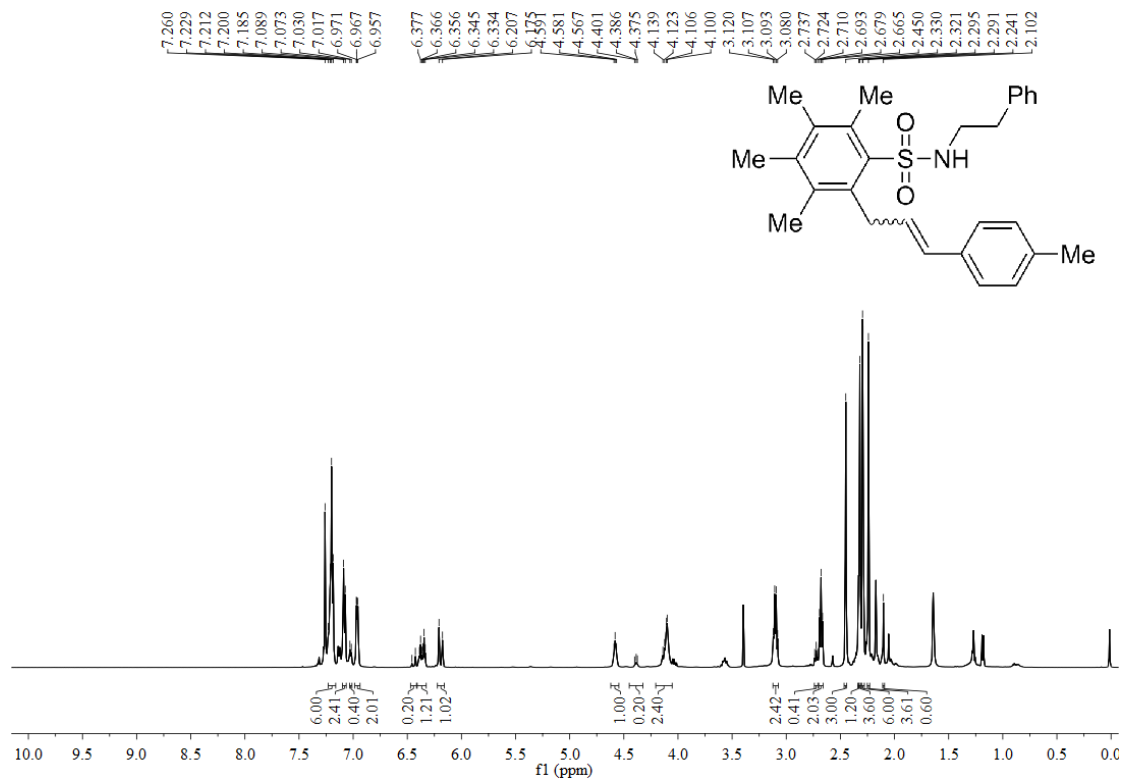
(E/Z >99:1).



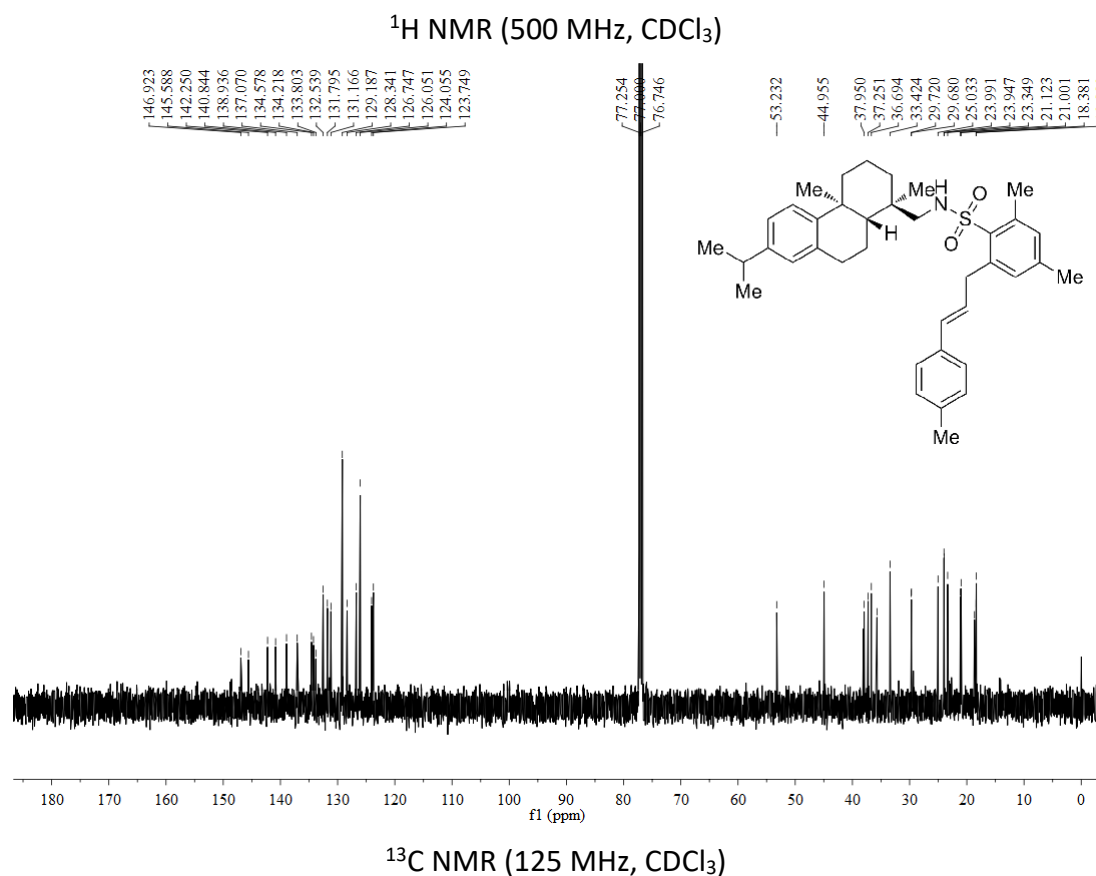
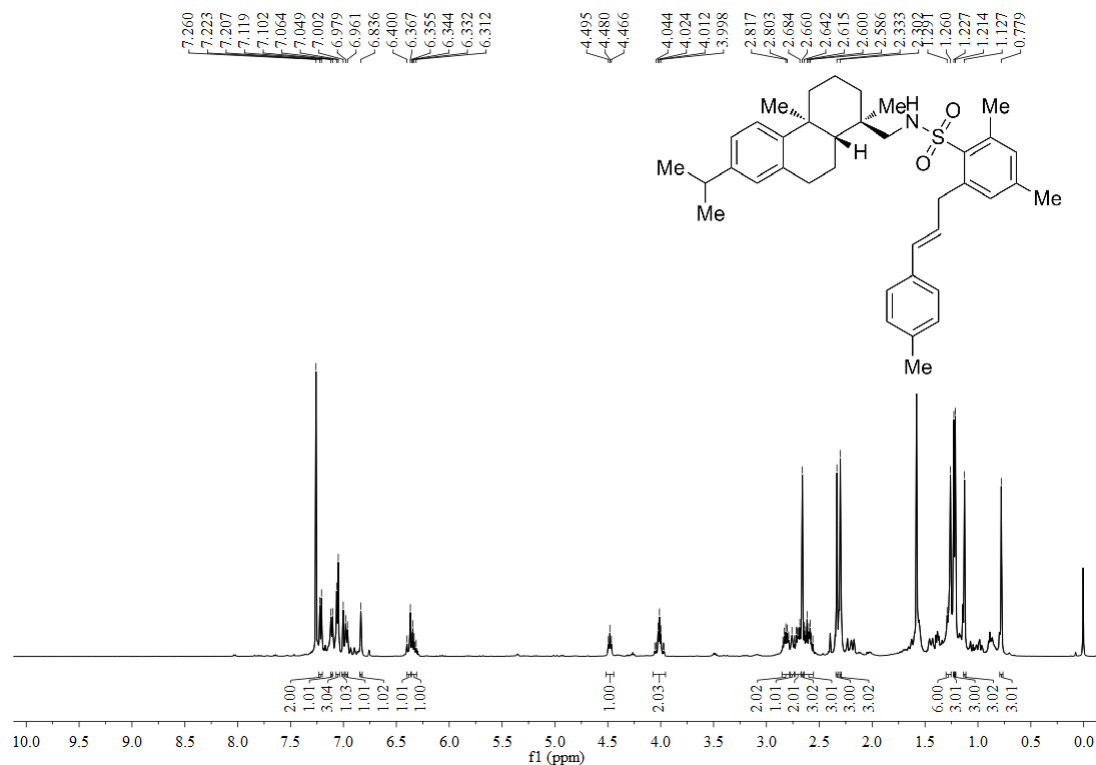
2,3,5-trimethyl-N-phenethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (3ja) (*E/Z* = 5:1).



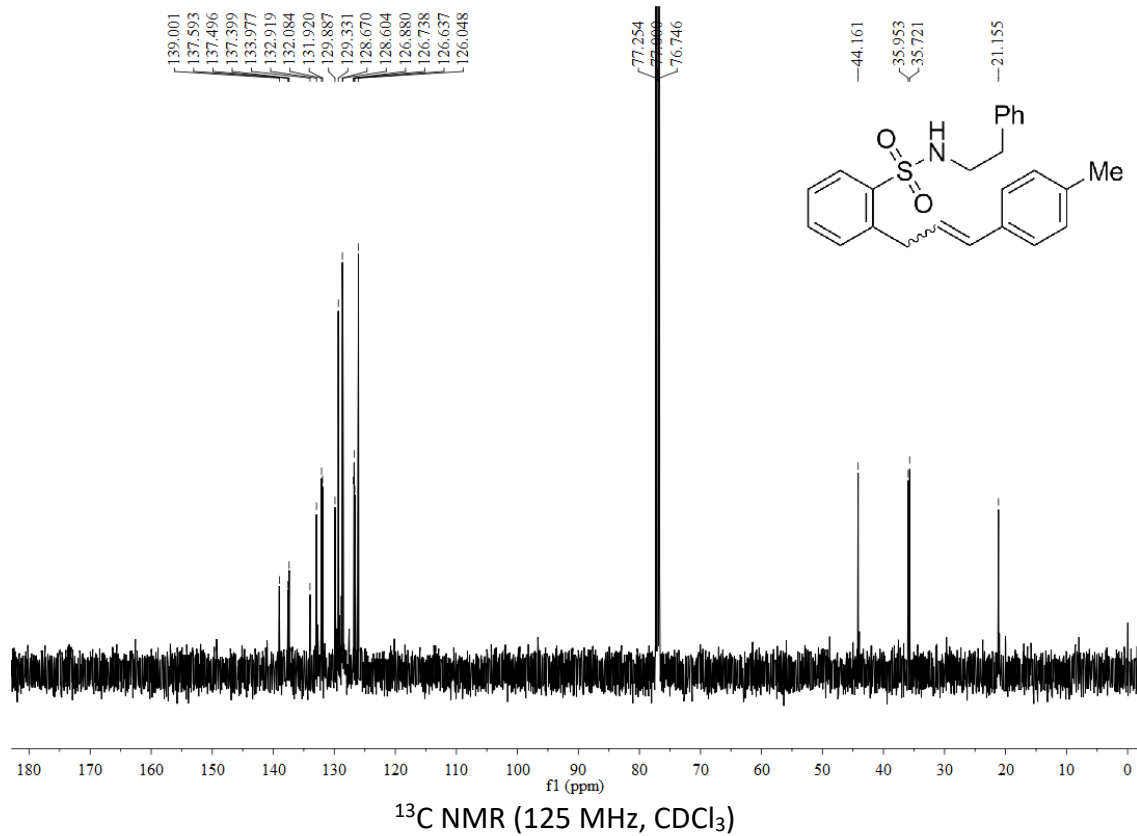
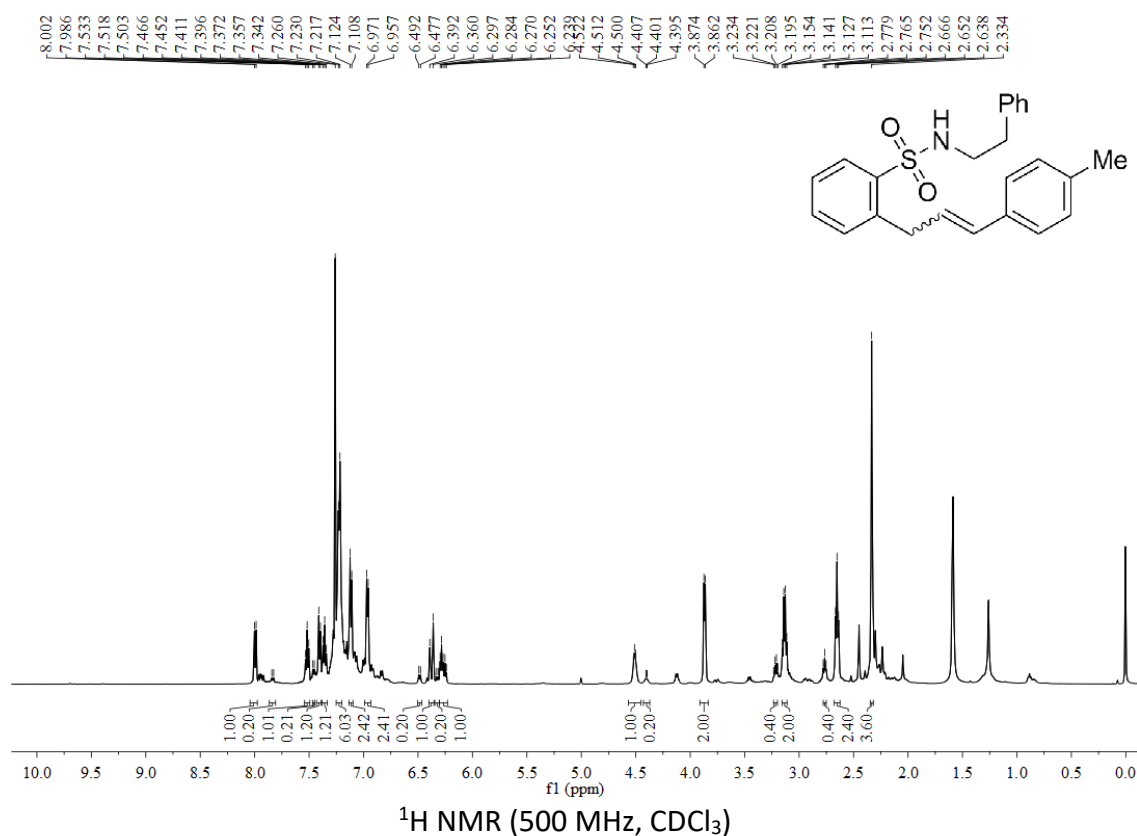
2,3,4,5-tetramethyl-N-phenethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (3ka) (*E/Z* = 5:1).



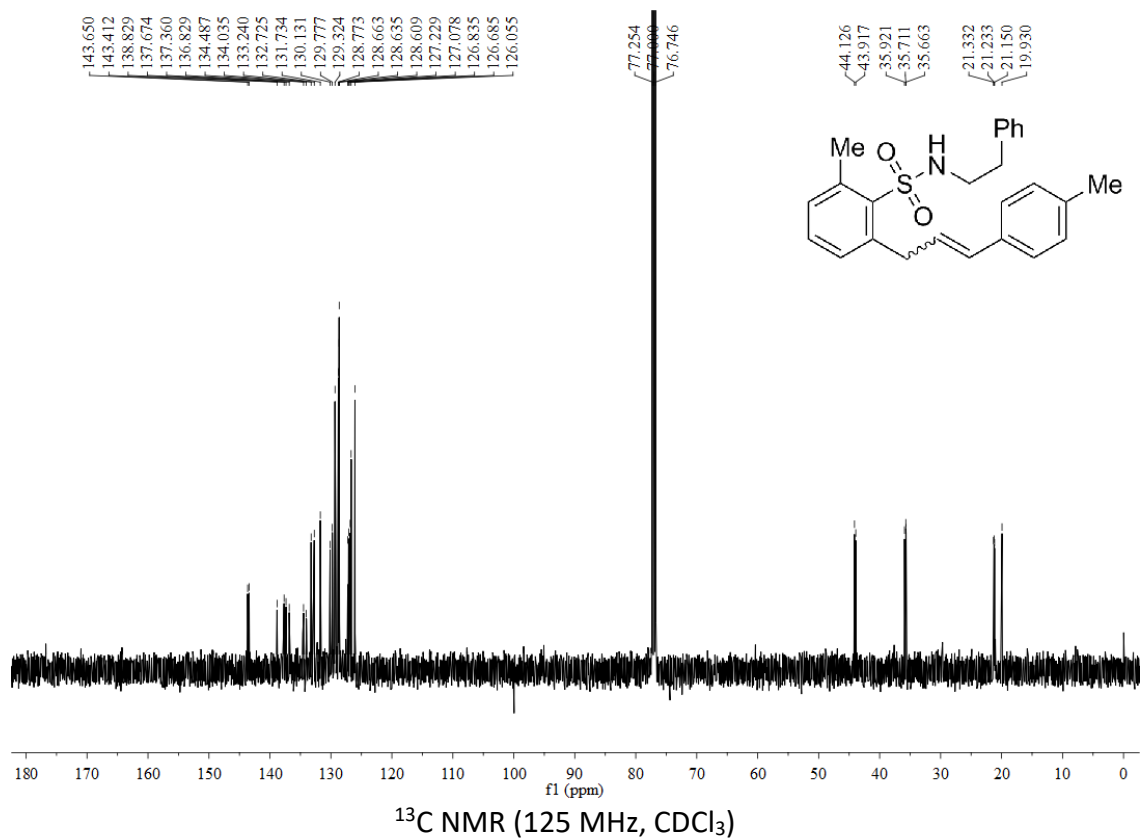
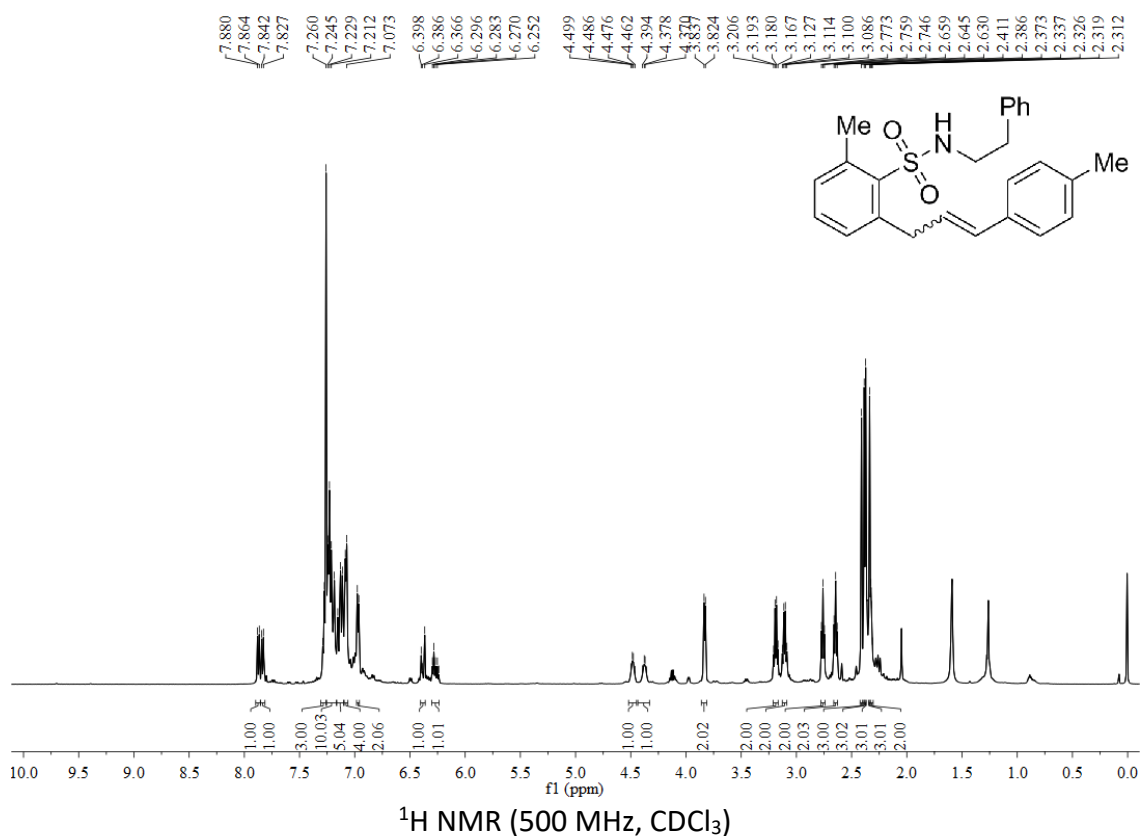
***N*-(((1*R*,4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)-2,4-dimethyl-6-((*E*)-3-(*p*-tolyl)allyl)benzenesulfonamide (31a)**
(*E*/*Z* > 99:1).



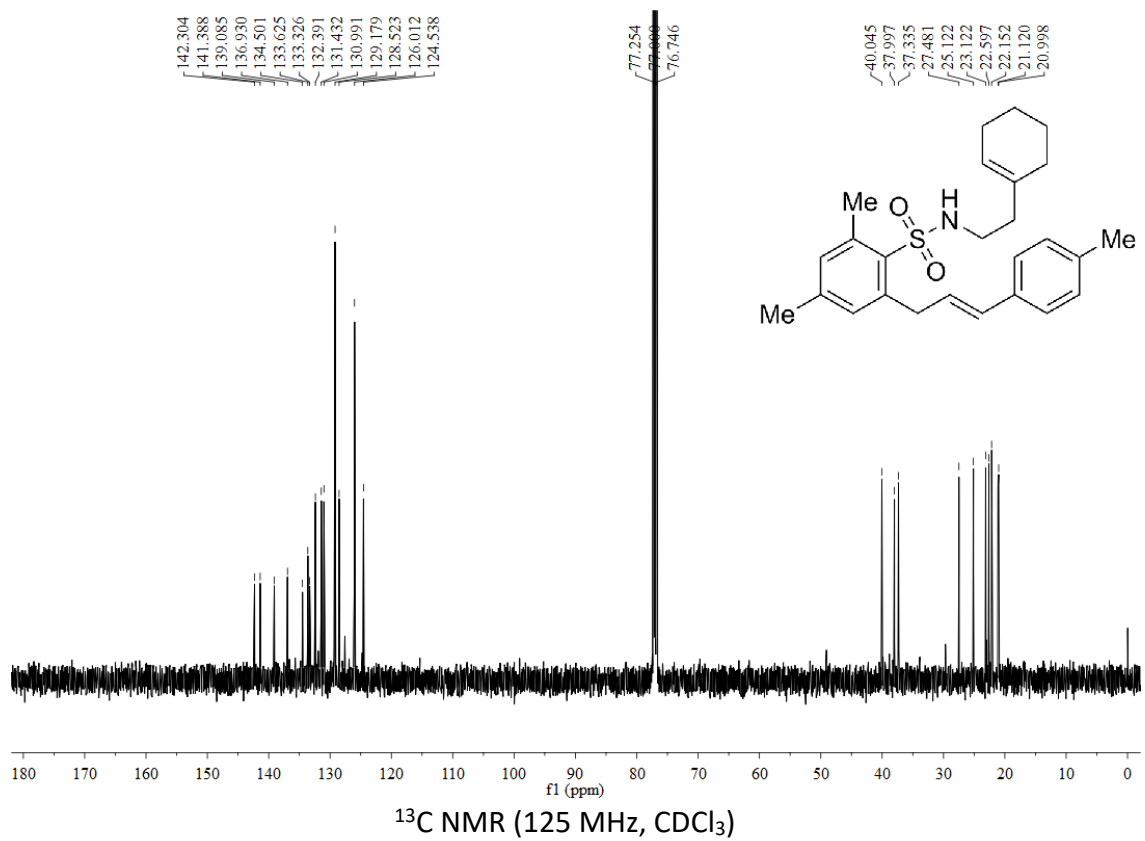
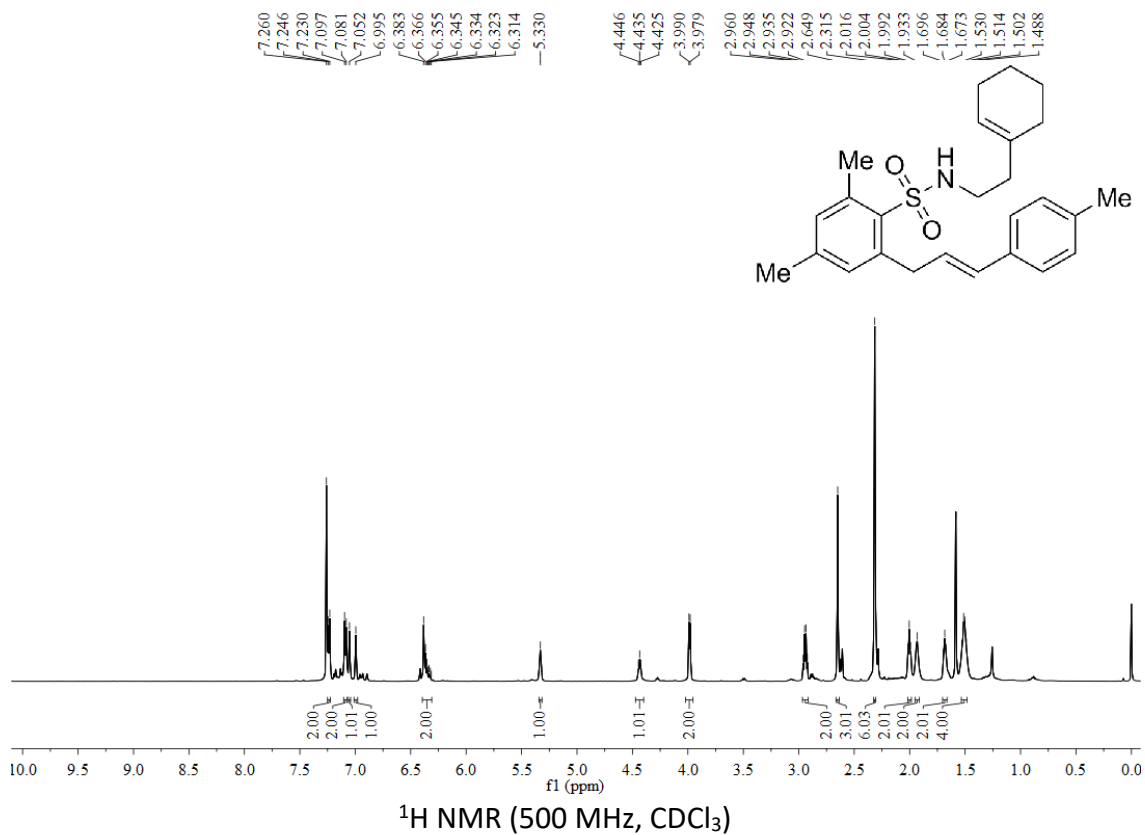
***N*-phenethyl-2-(3-(*p*-tolyl)allyl)benzenesulfonamide (3na) (*E/Z* = 5:1).**



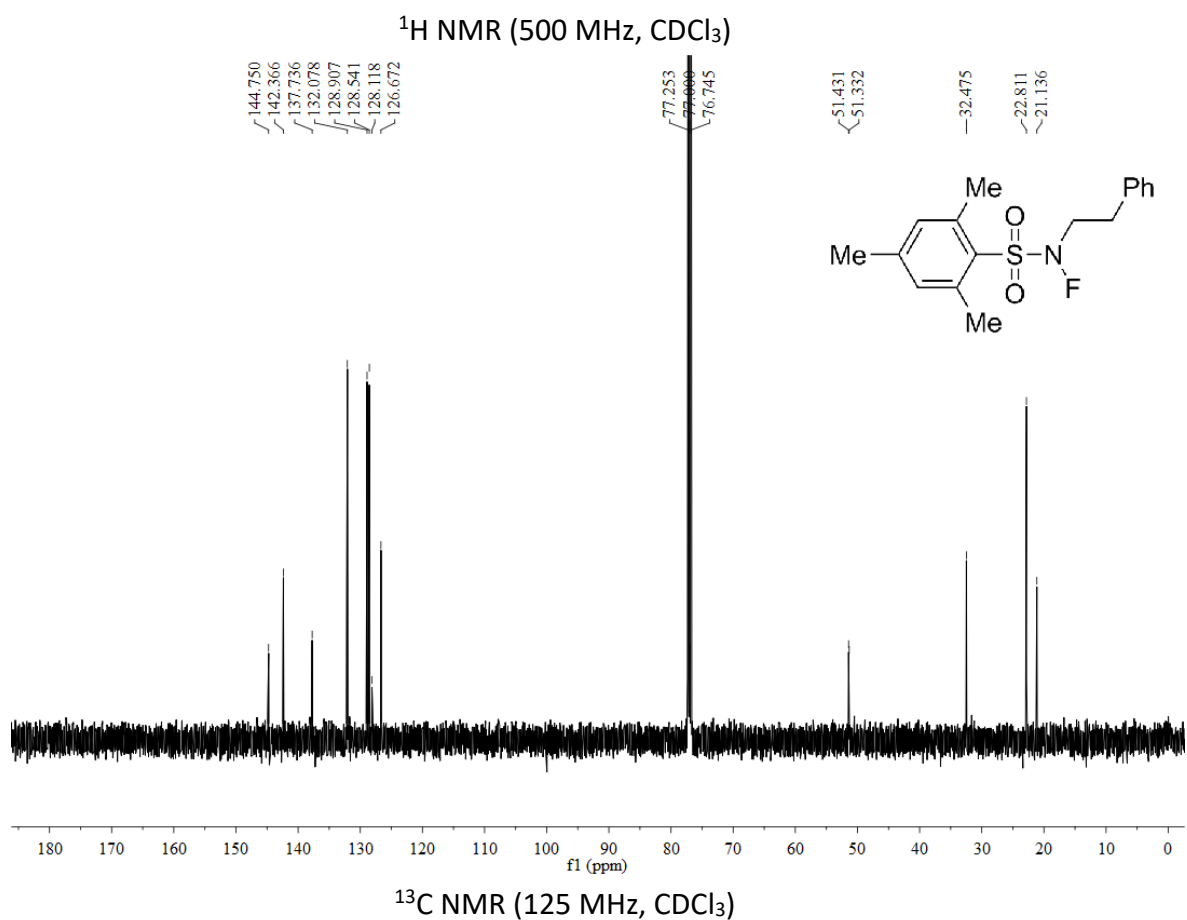
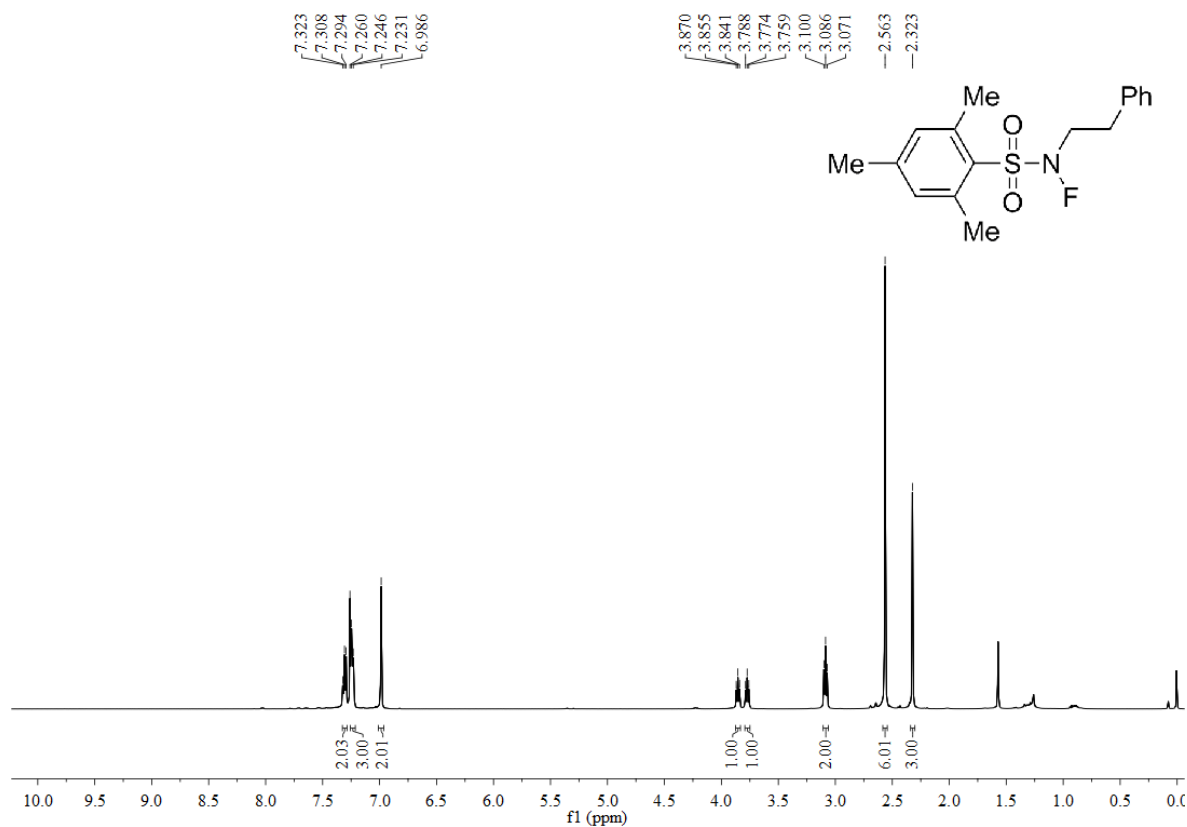
2-methyl-N-phenethyl-6-(3-(*p*-tolyl)allyl)benzenesulfonamide (30a) (*E/Z* = 1:1).

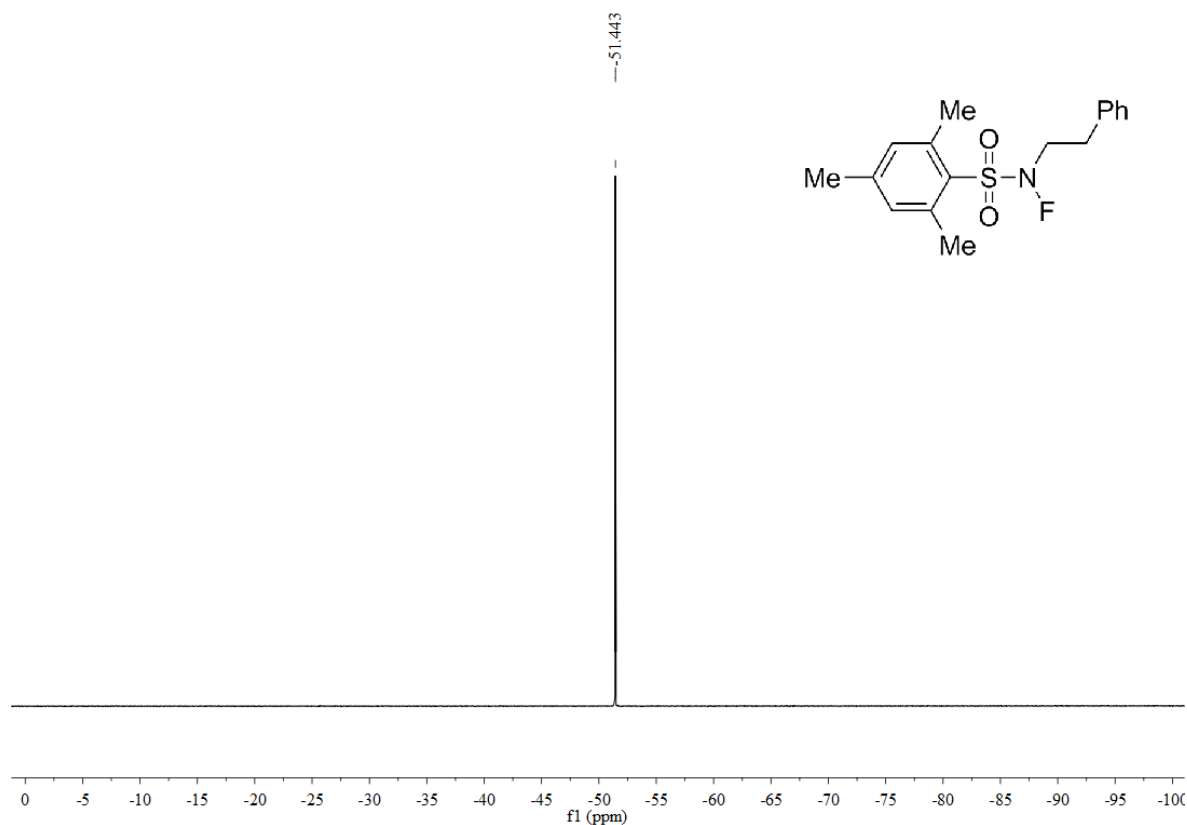


(E)-N-(2-(cyclohex-1-en-1-yl)ethyl)-2,4-dimethyl-6-(3-(p-tolyl)allyl)benzenesulfonamide (3qa) (E/Z > 99:1).



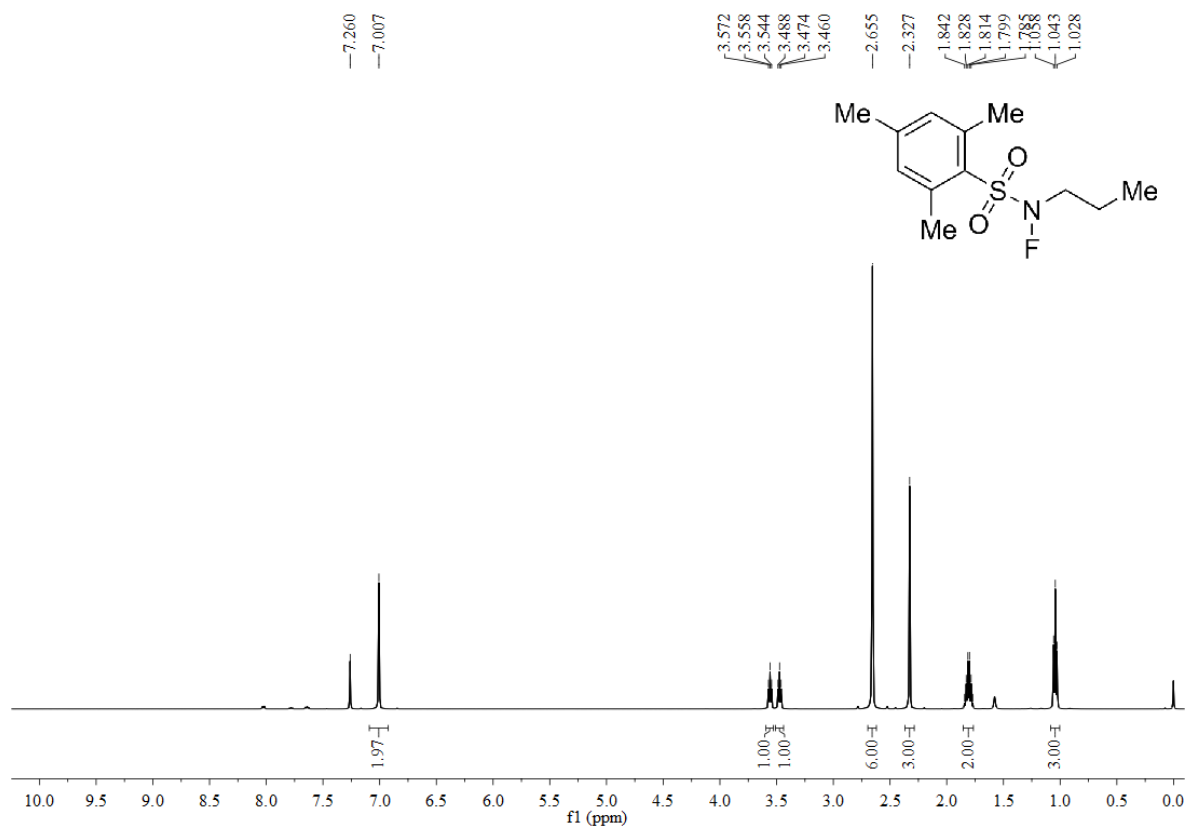
***N*-fluoro-2,4,6-trimethyl-*N*-phenethylbenzenesulfonamide (1a).**



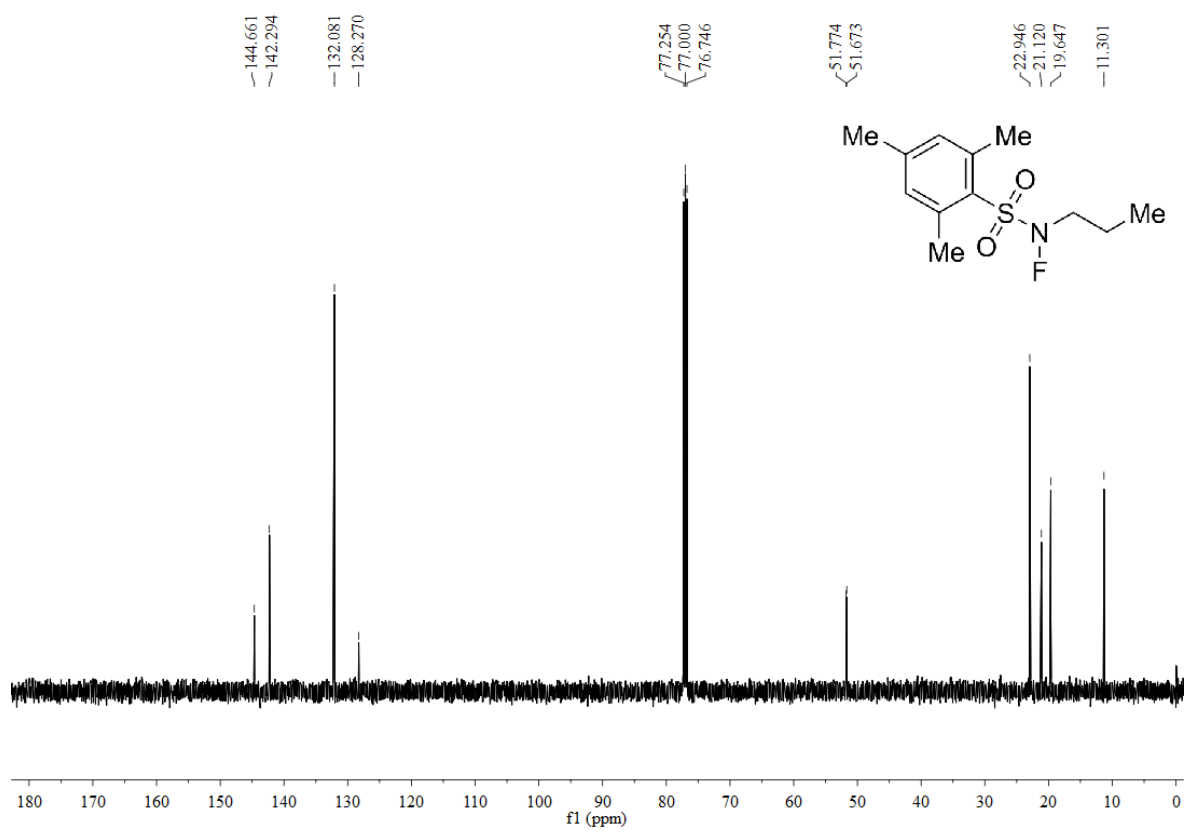


^{19}F NMR (471 MHz, CDCl_3)

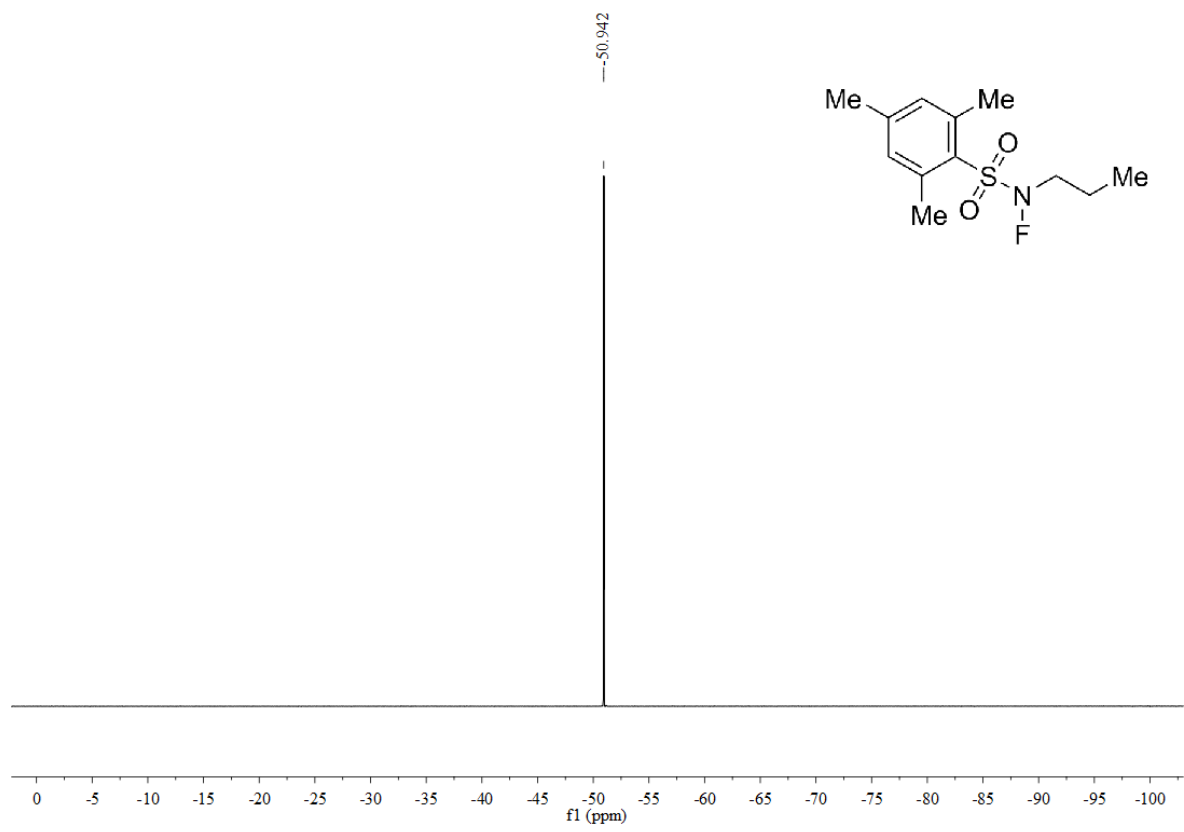
***N*-fluoro-2,4,6-trimethyl-*N*-propylbenzenesulfonamide (1b).**



^1H NMR (500 MHz, CDCl_3)

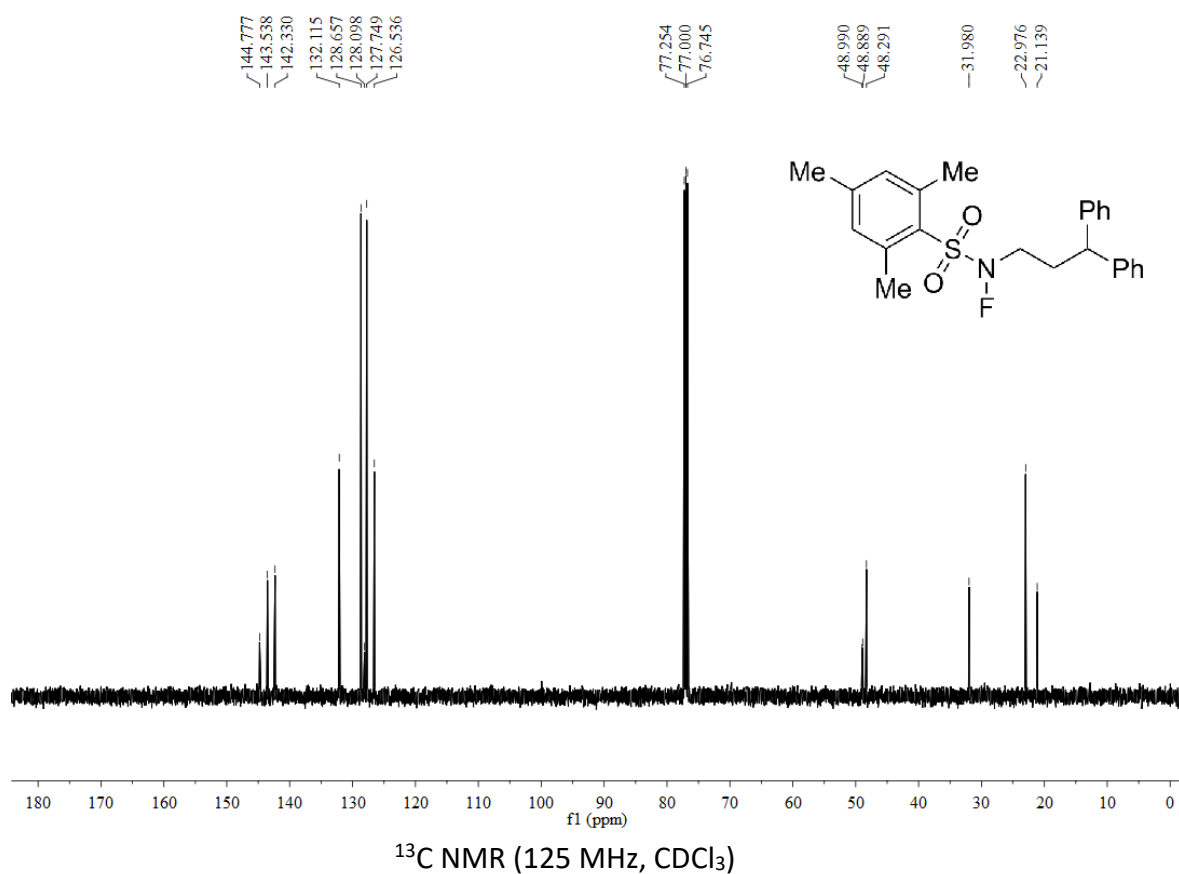
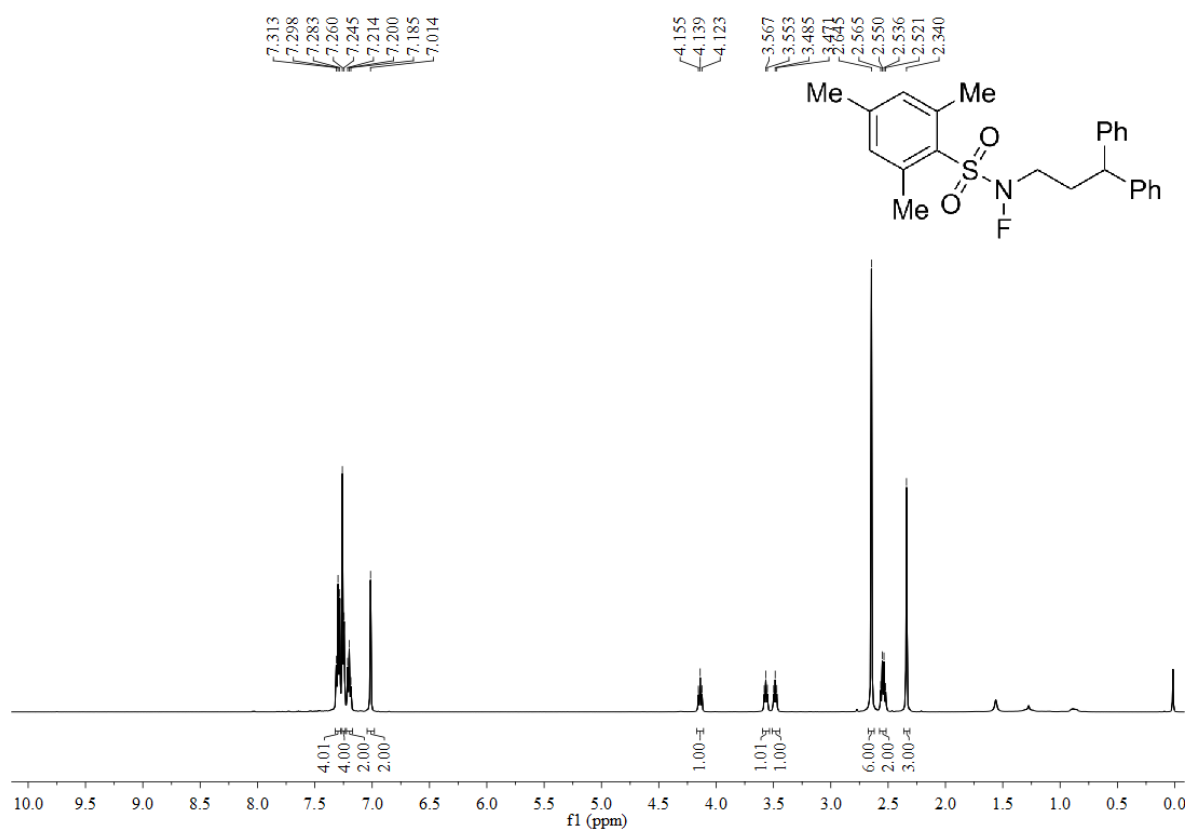


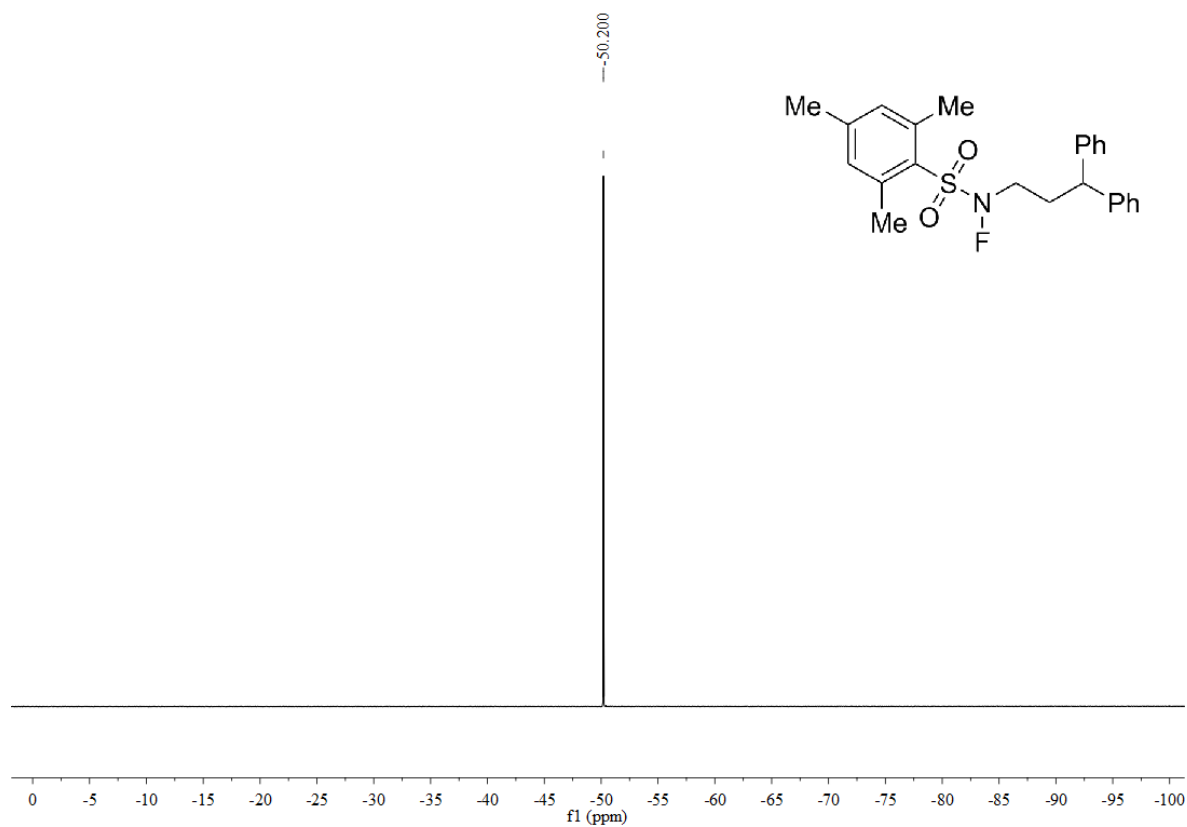
¹³C NMR (125 MHz, CDCl₃)



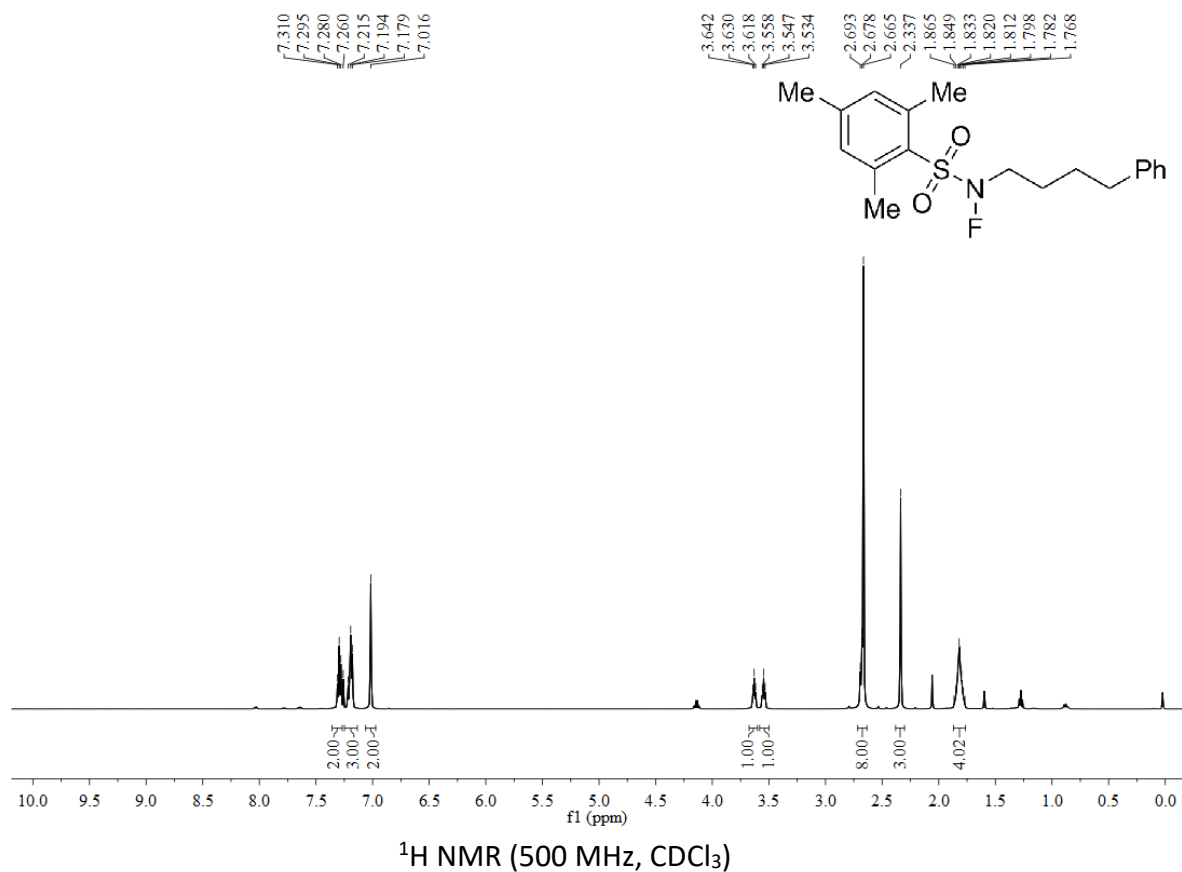
¹⁹F NMR (471 MHz, CDCl₃)

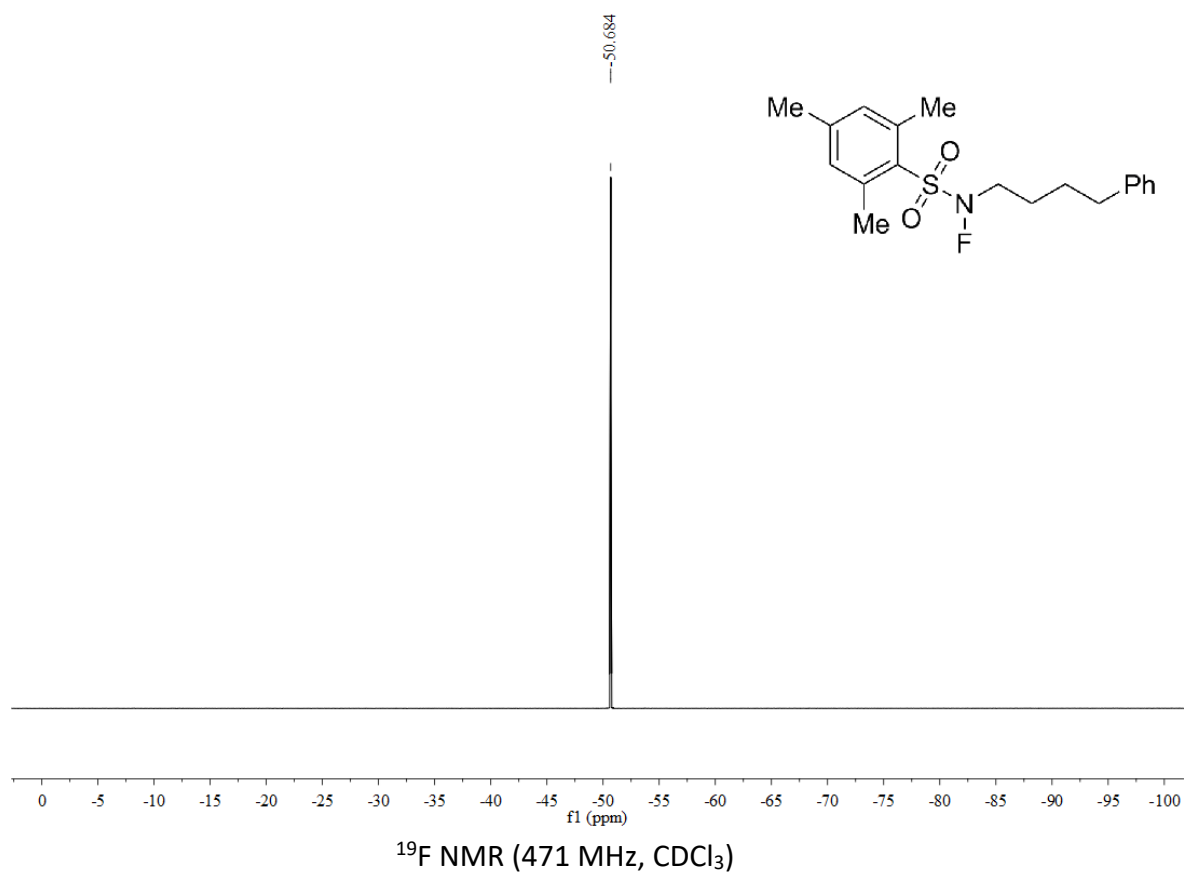
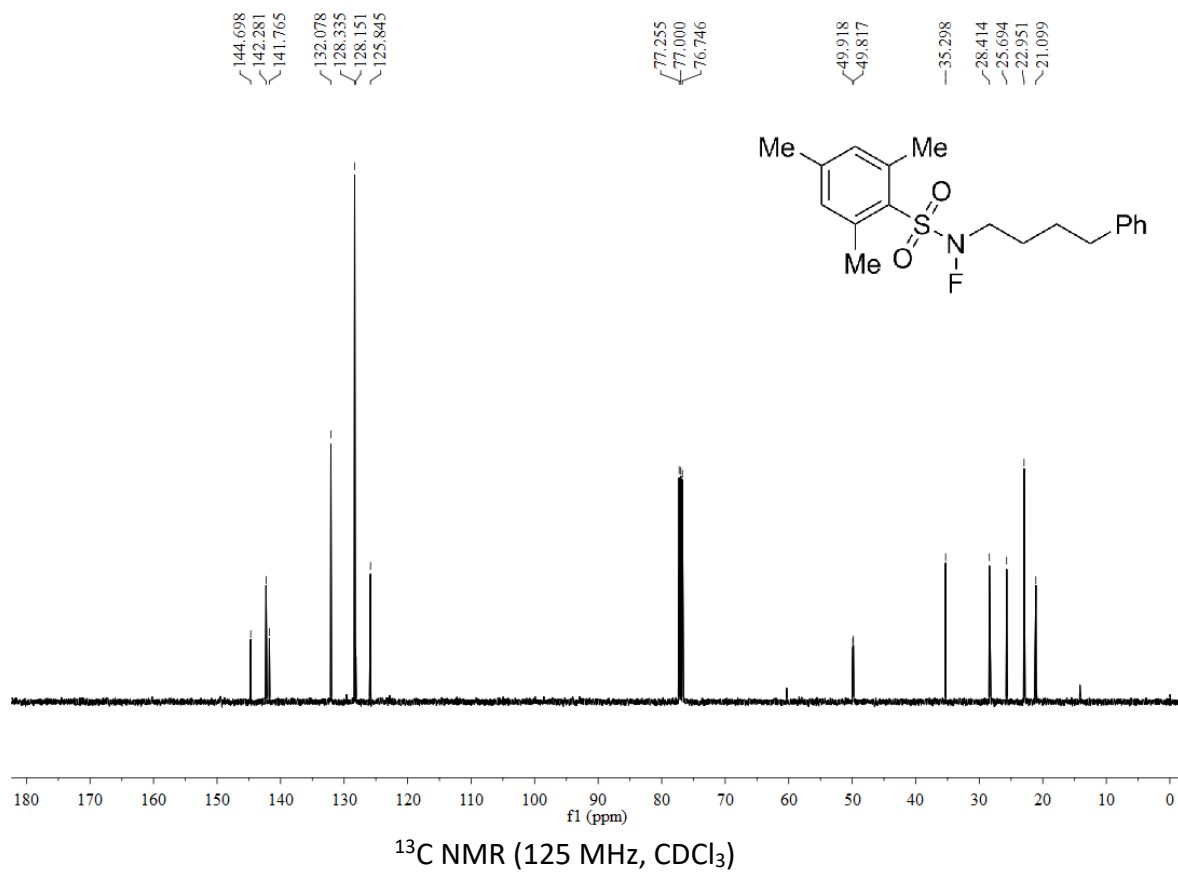
***N*-(3,3-diphenylpropyl)-*N*-fluoro-2,4,6-trimethylbenzenesulfonamide (1c).**



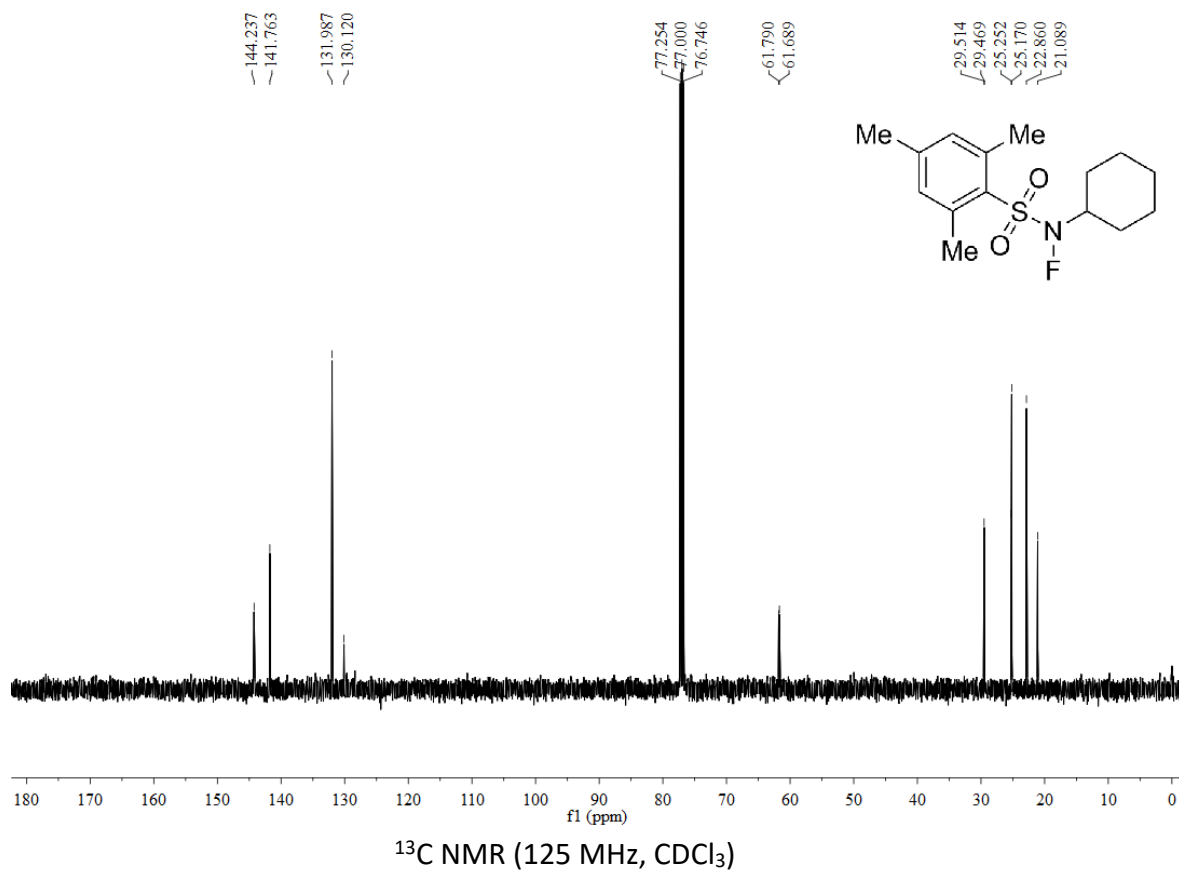
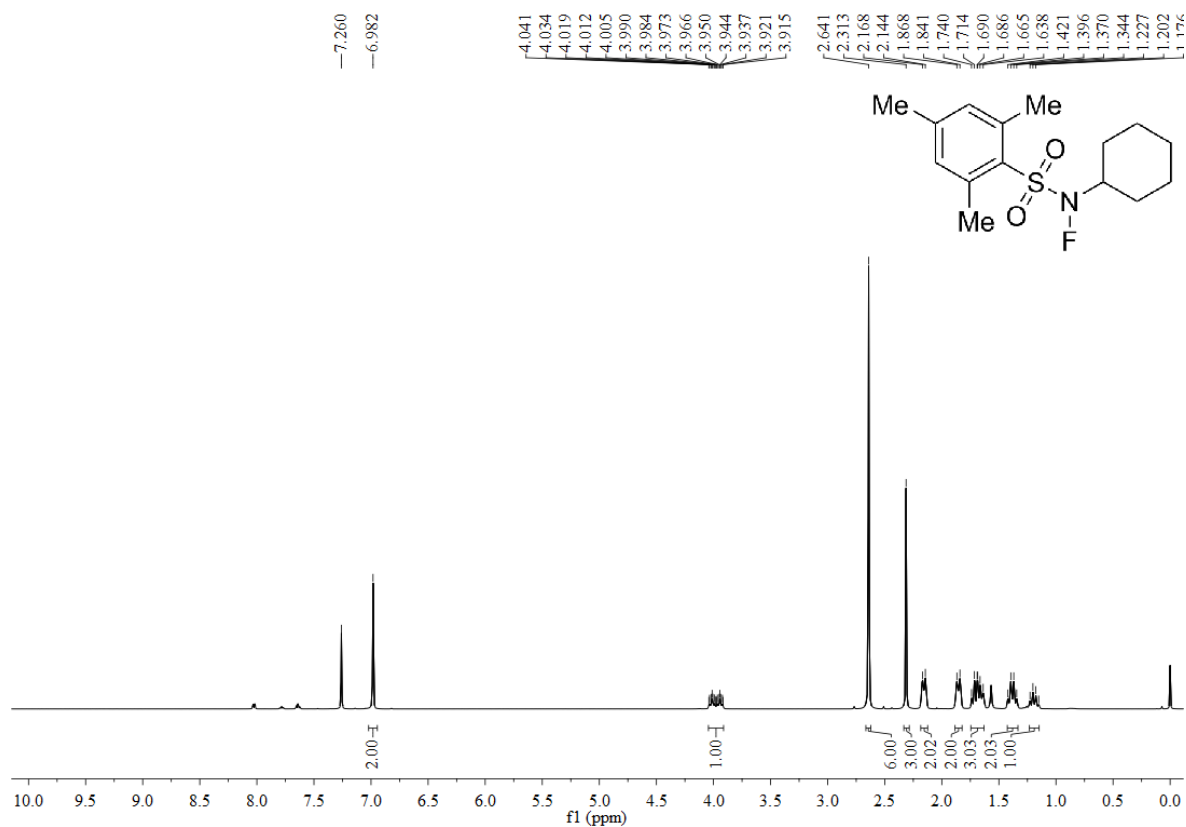


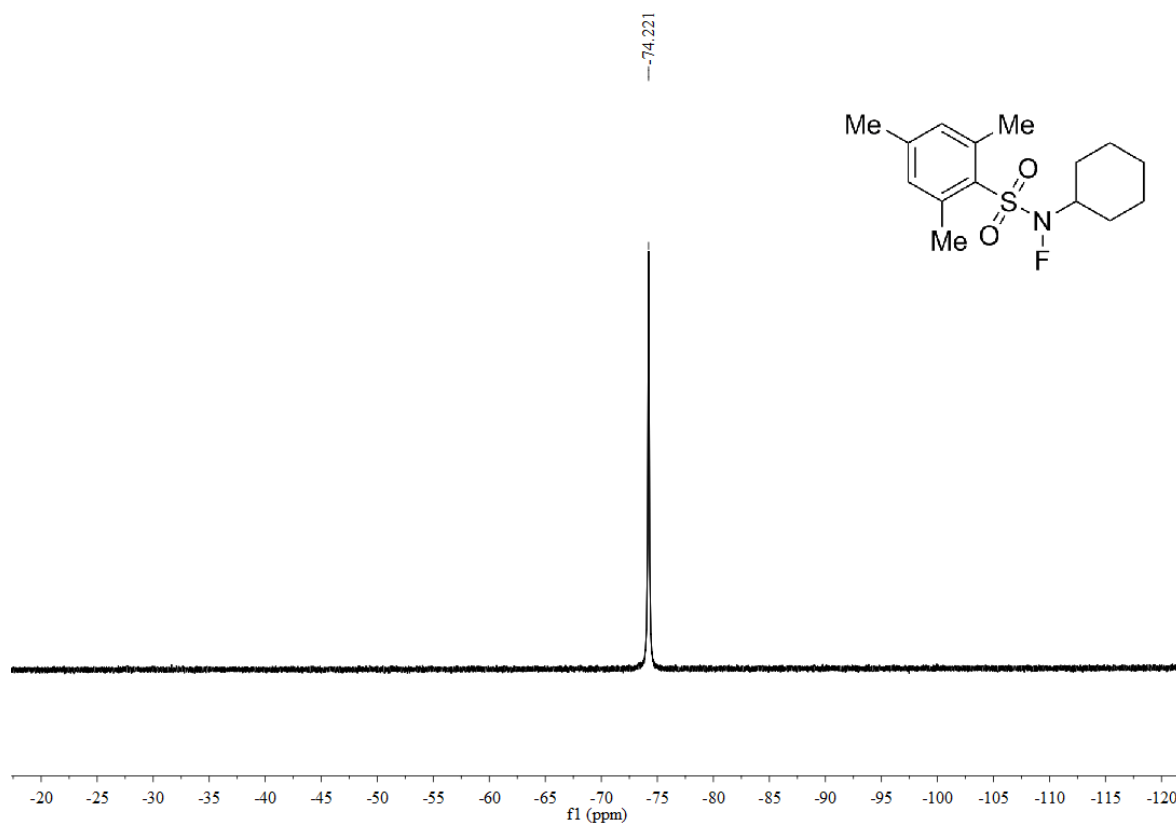
***N*-fluoro-2,4,6-trimethyl-*N*-(4-phenylbutyl)benzenesulfonamide (1e).**



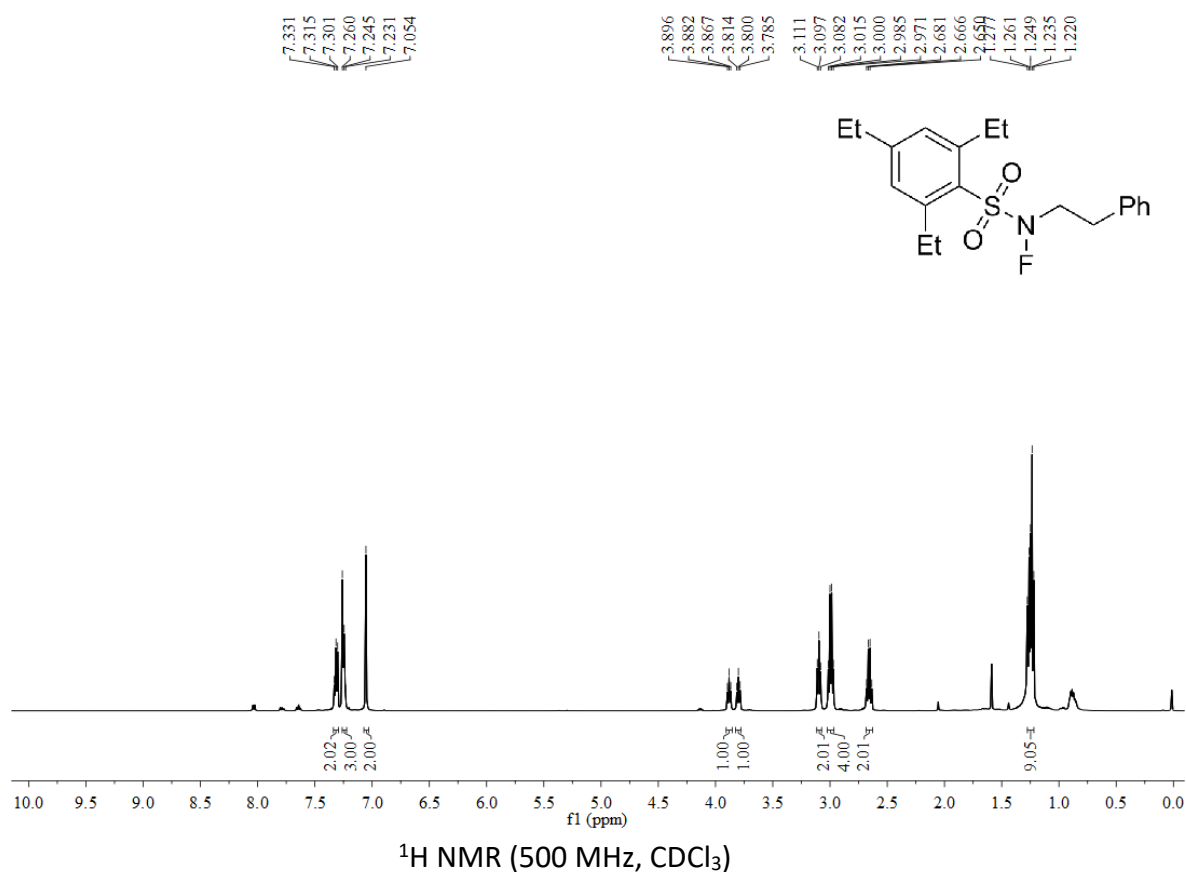


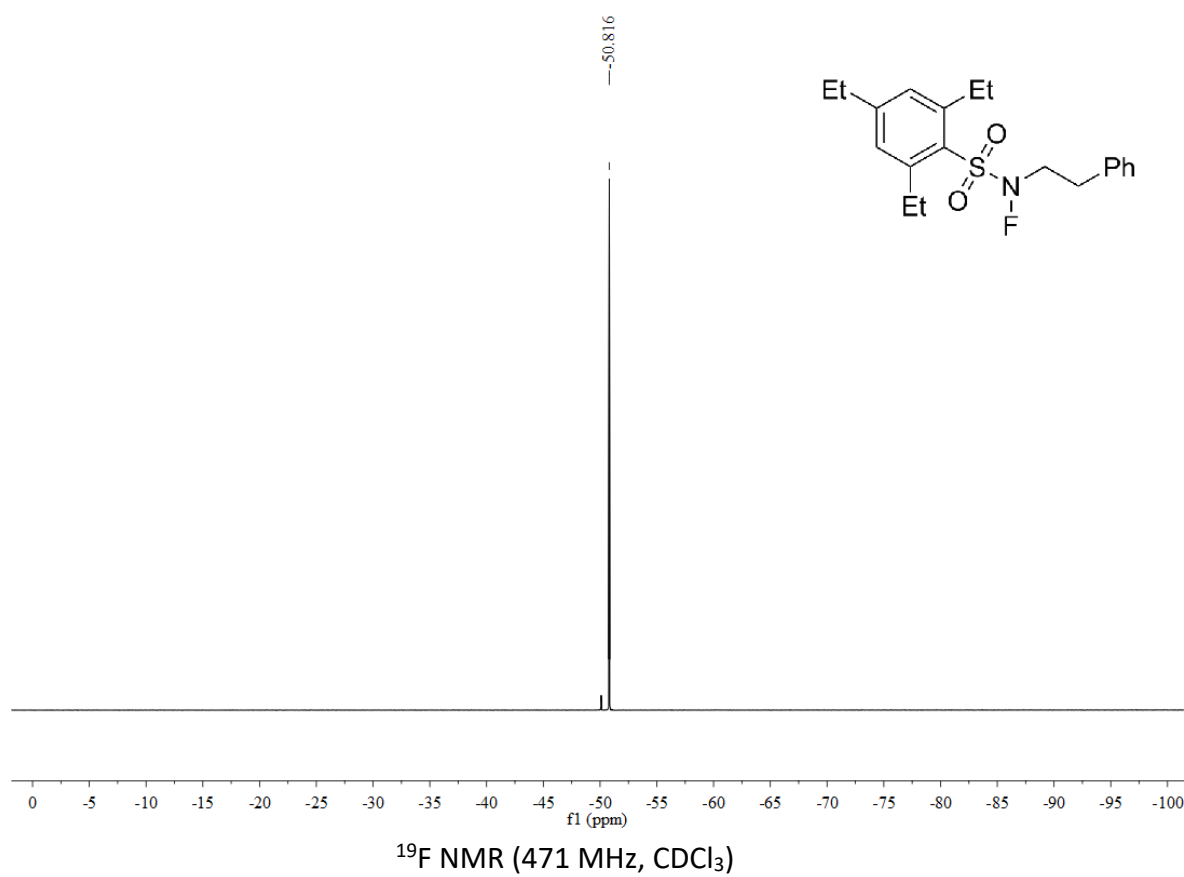
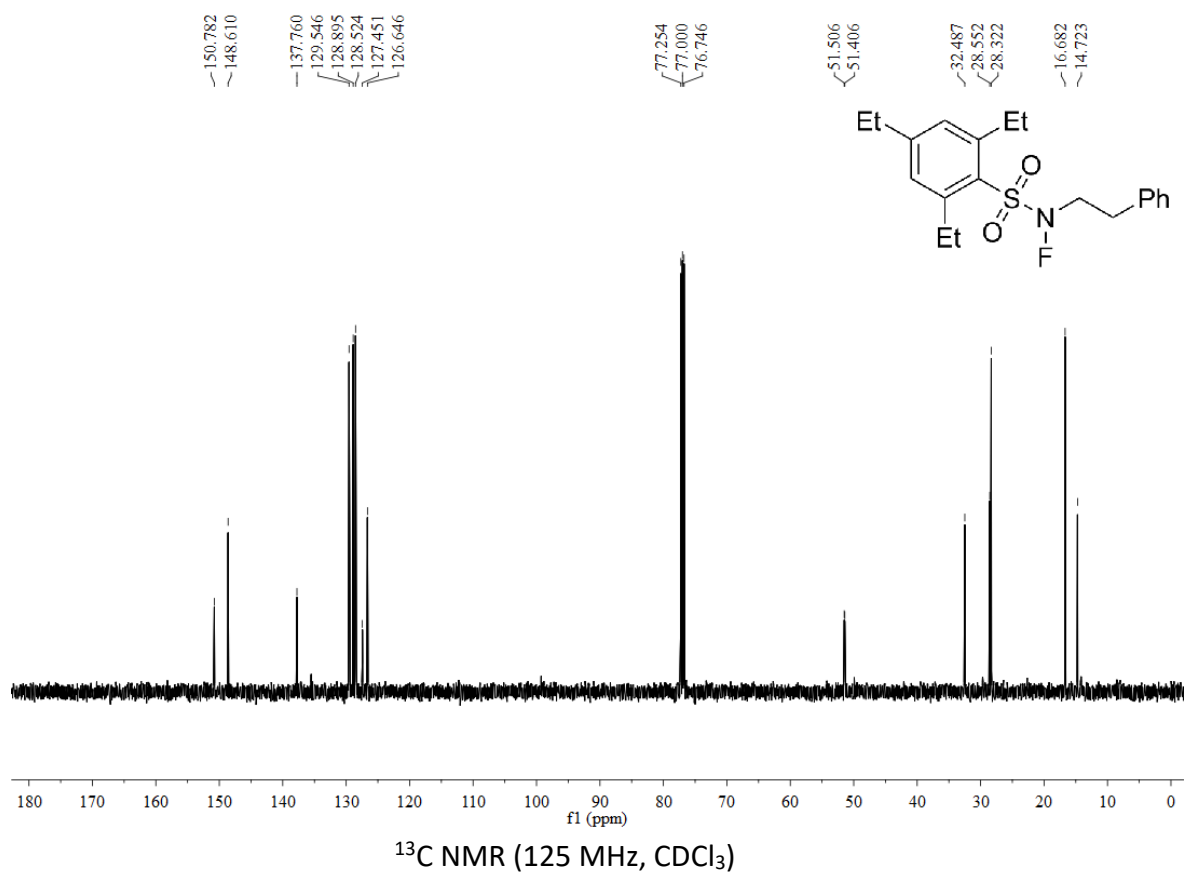
***N*-cyclohexyl-*N*-fluoro-2,4,6-trimethylbenzenesulfonamide (1g).**



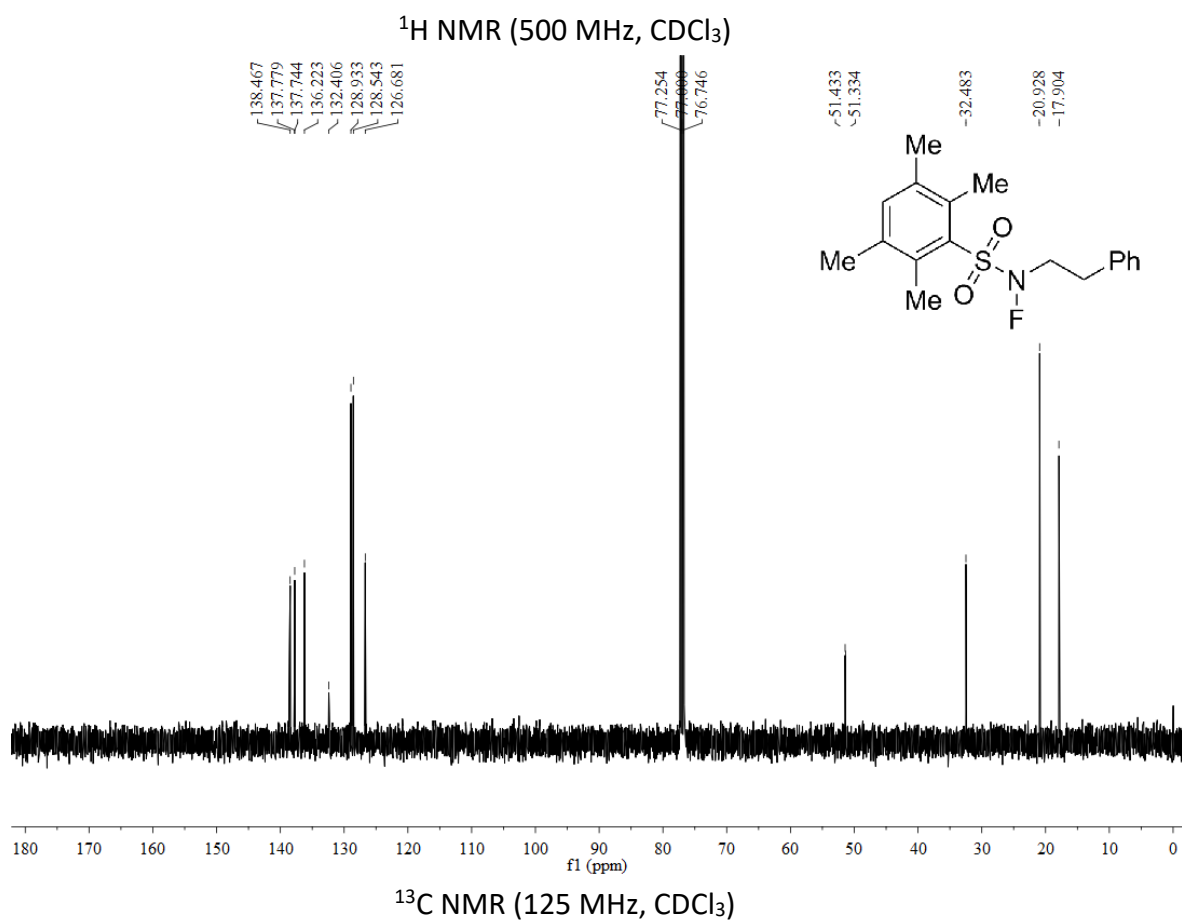
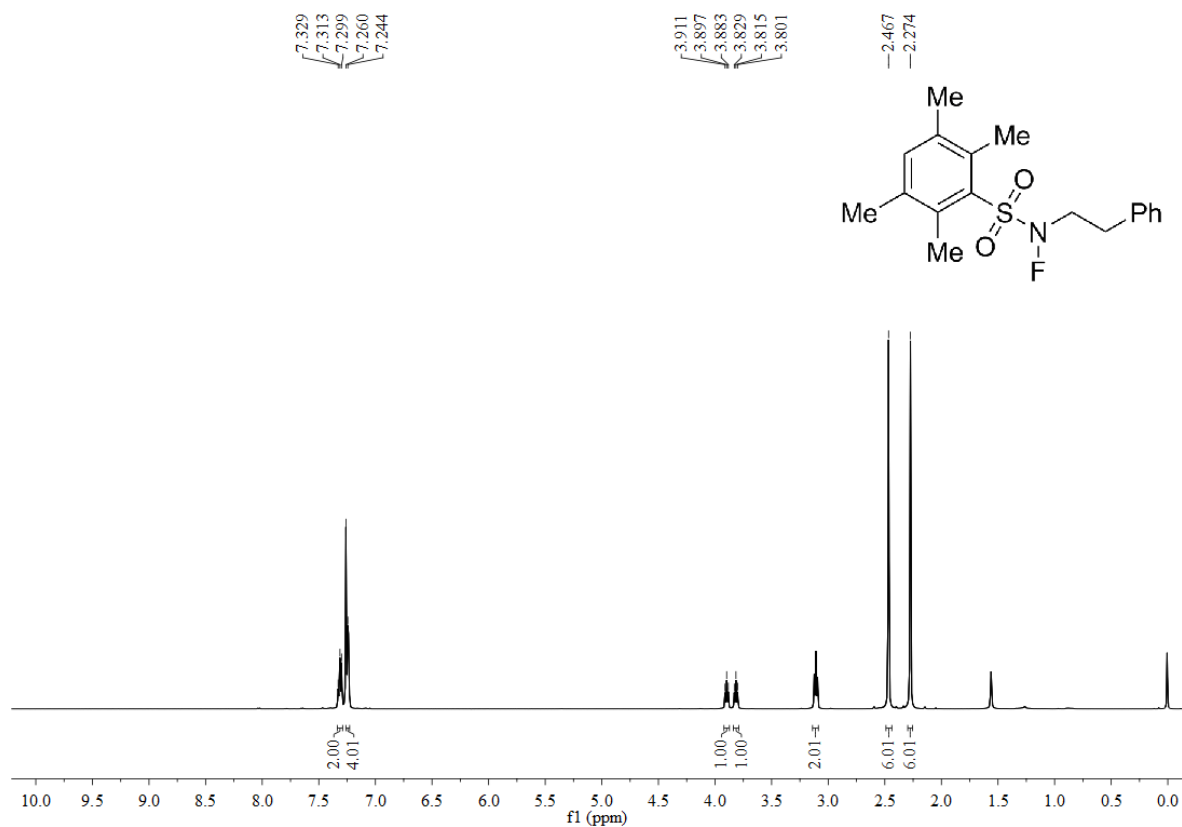


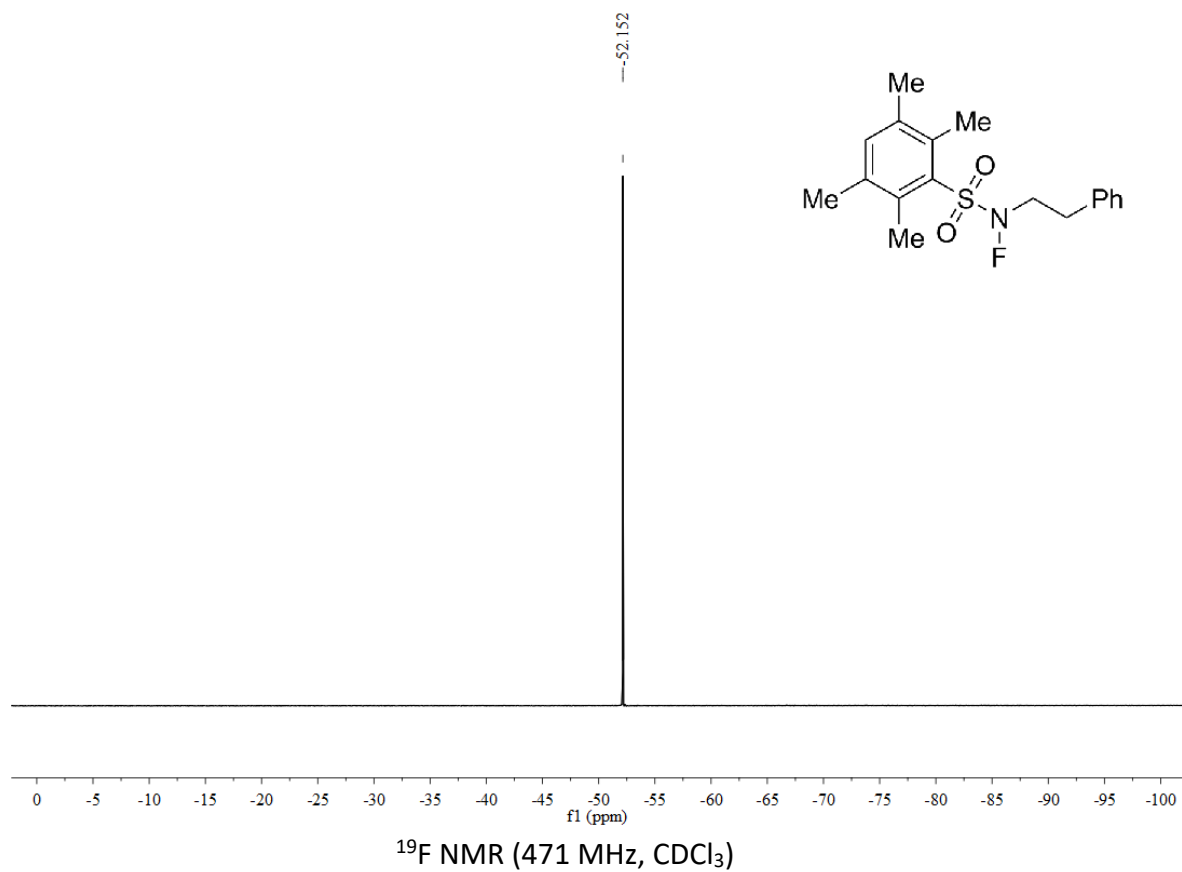
2,4,6-triethyl-N-fluoro-N-phenethylbenzenesulfonamide (1i).



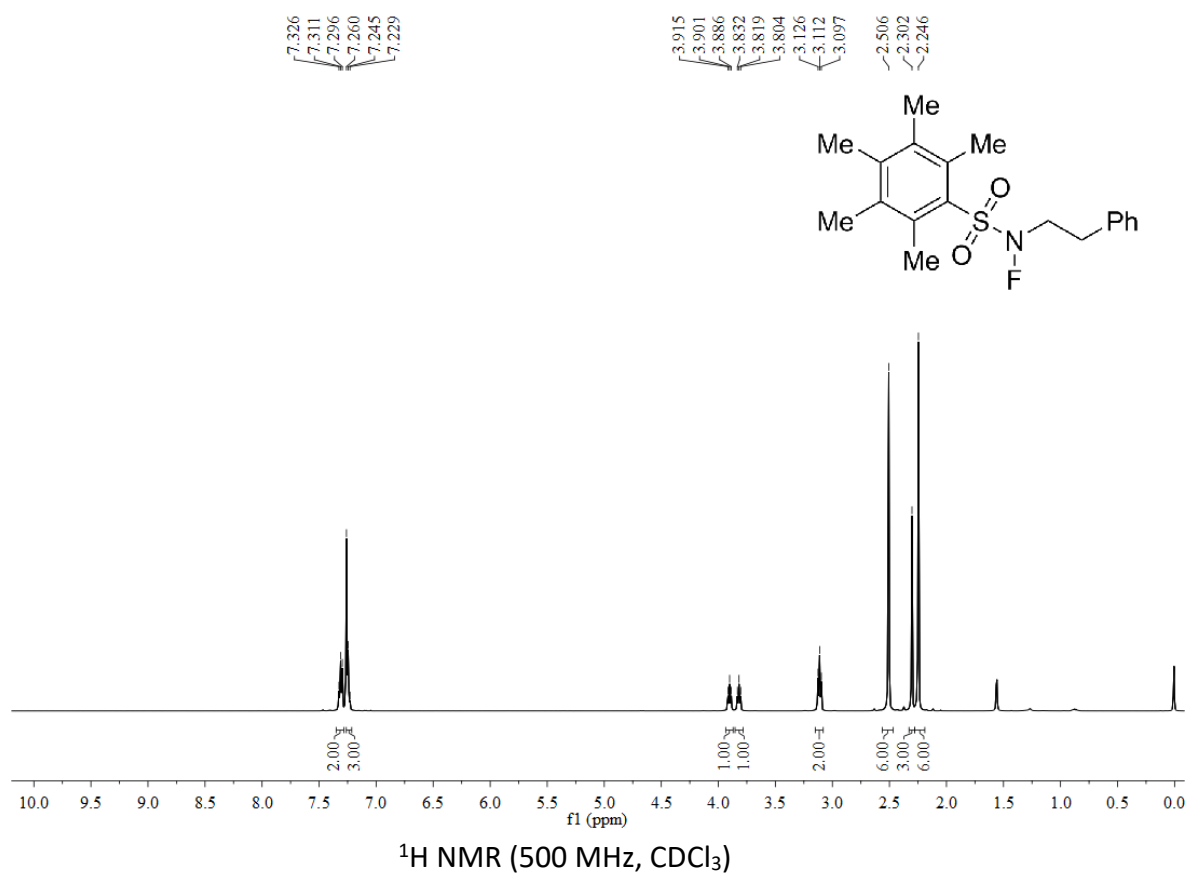


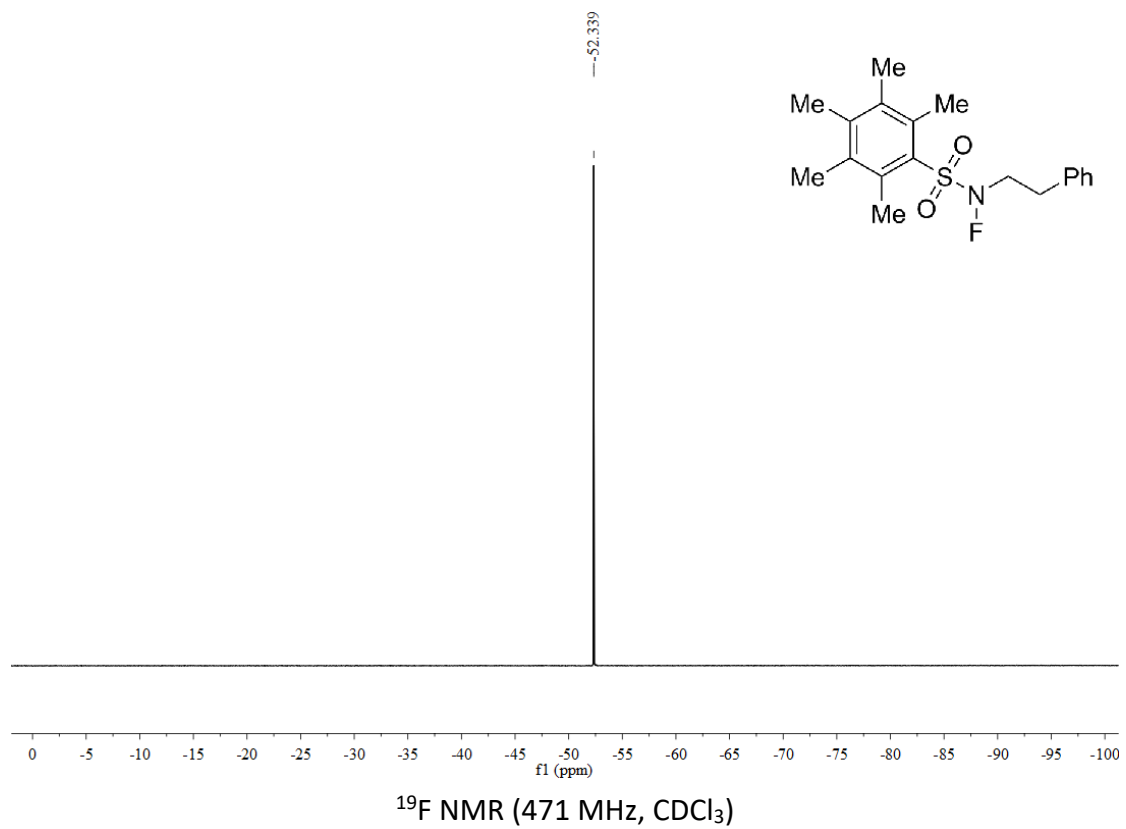
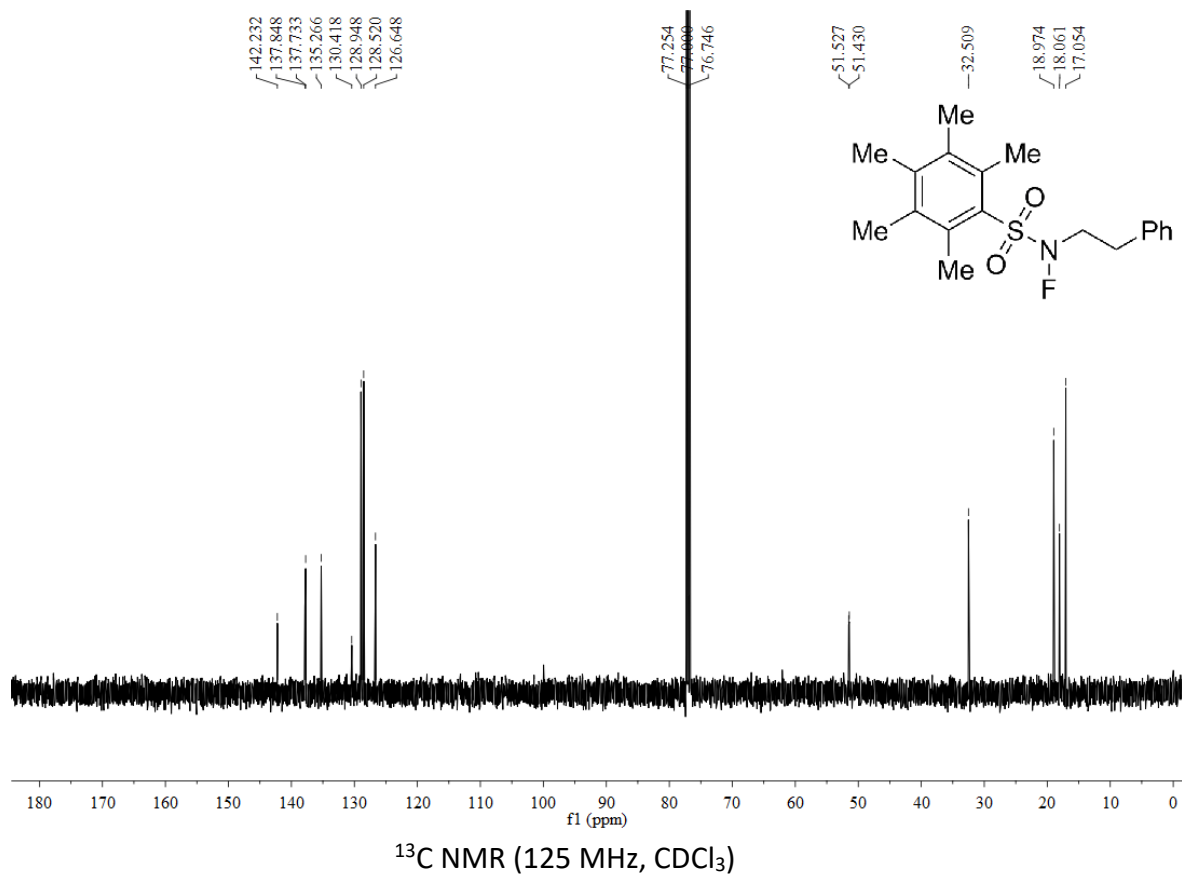
***N*-fluoro-2,3,5,6-tetramethyl-*N*-phenethylbenzenesulfonamide (1j).**



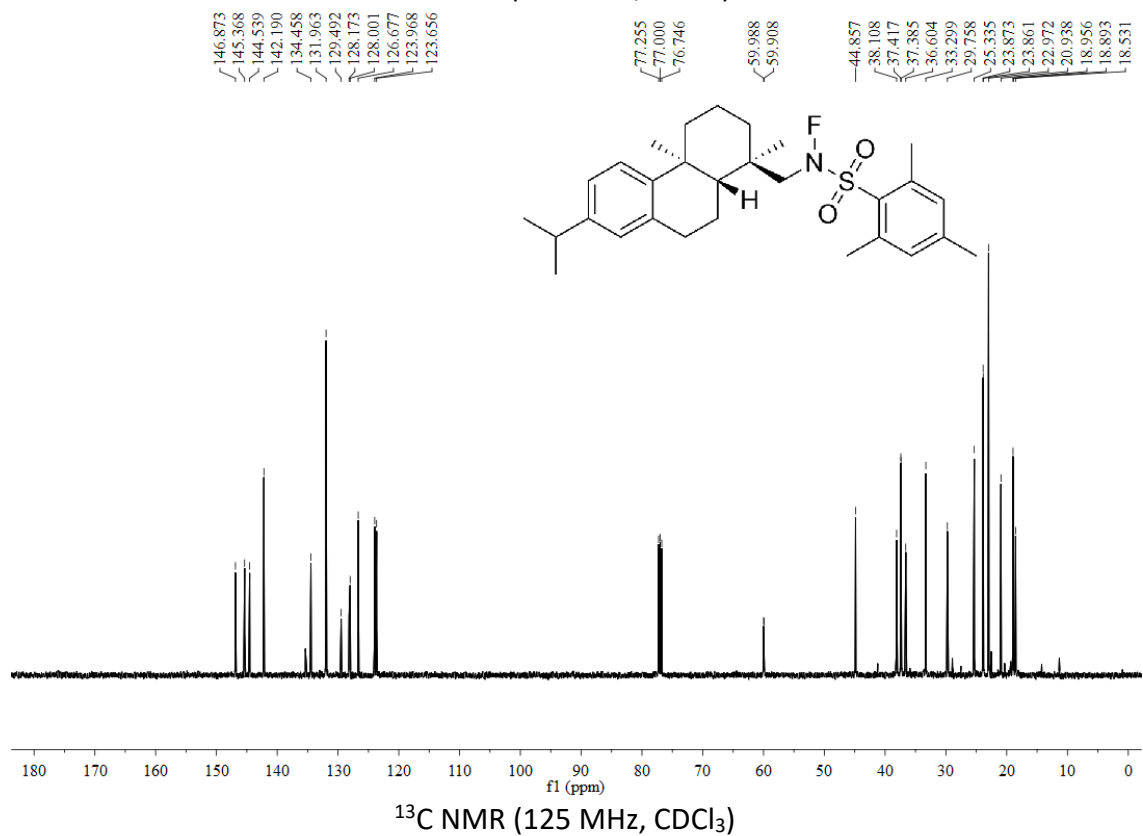
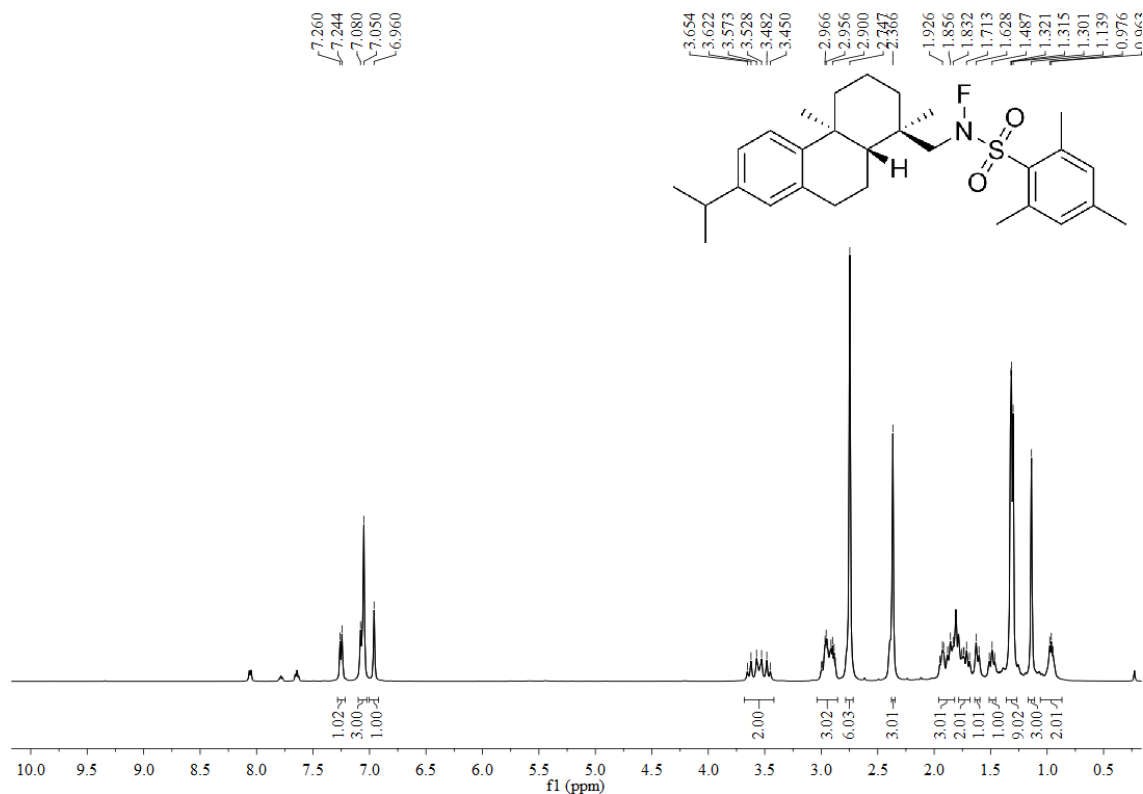


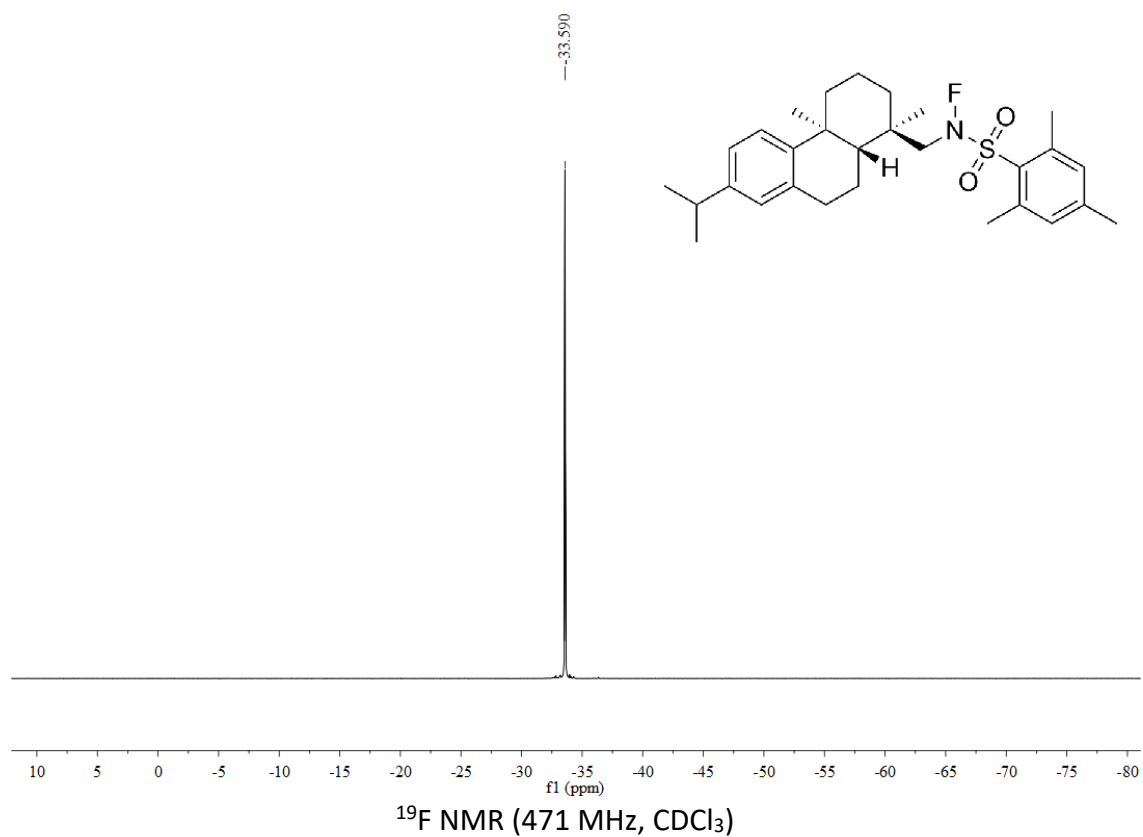
***N*-fluoro-2,3,4,5,6-pentamethyl-*N*-phenethylbenzenesulfonamide (1k).**



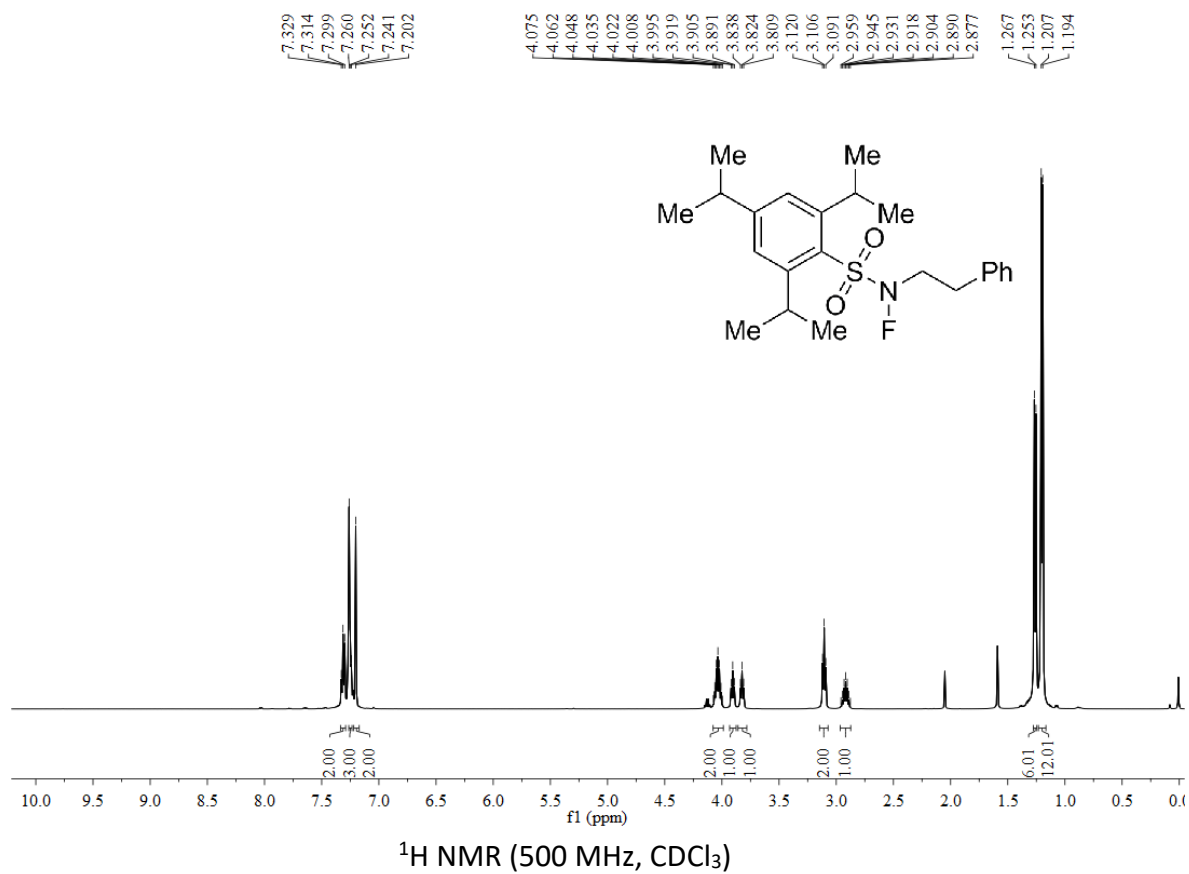


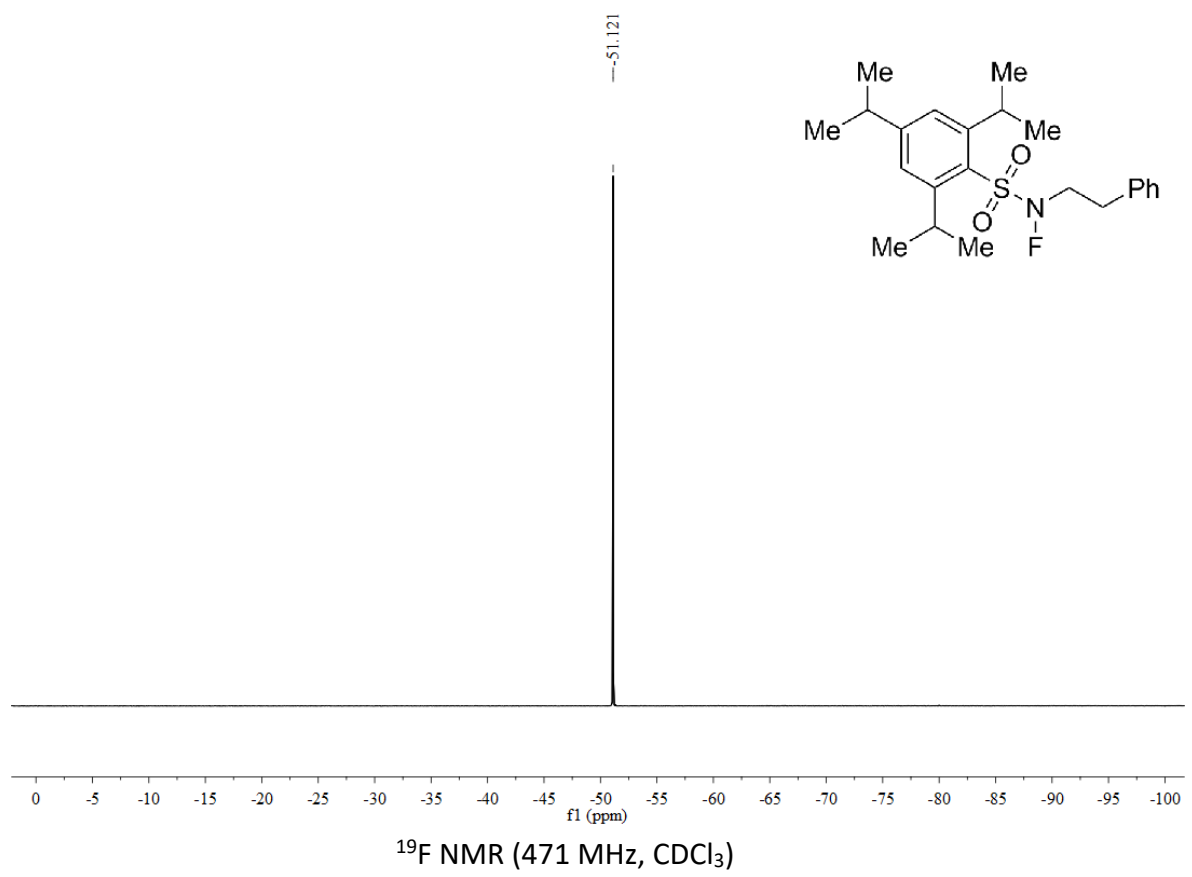
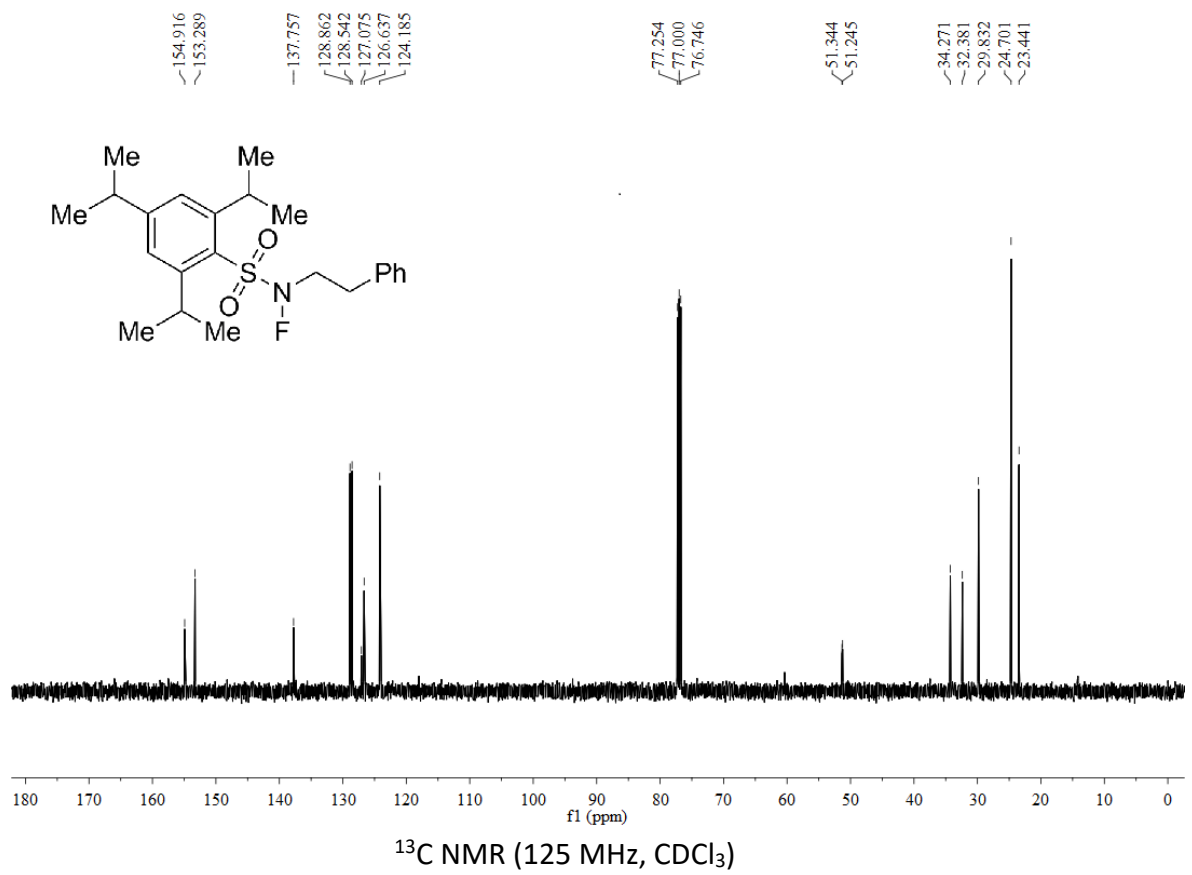
***N*-fluoro-*N*-(((1*R*,4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)-2,4,6-trimethylbenzenesulfonamide (1).**



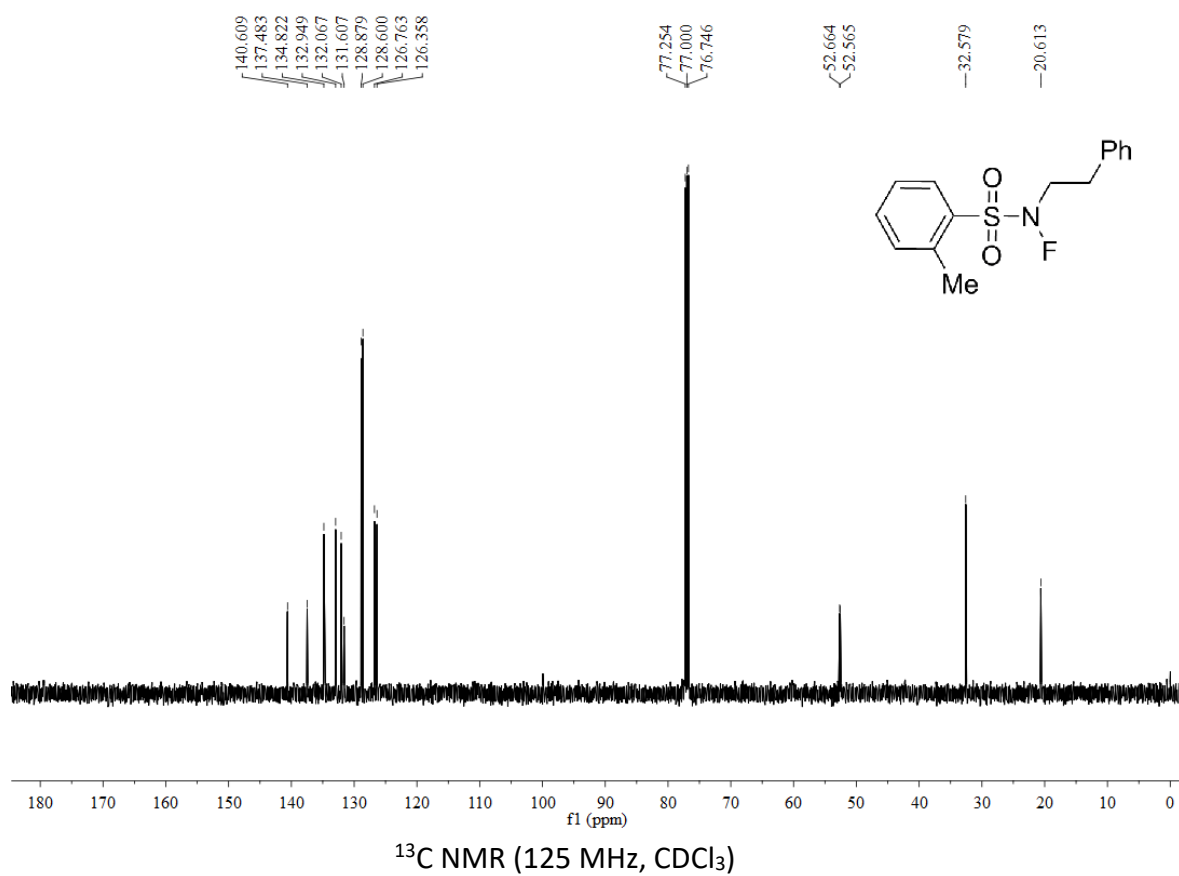
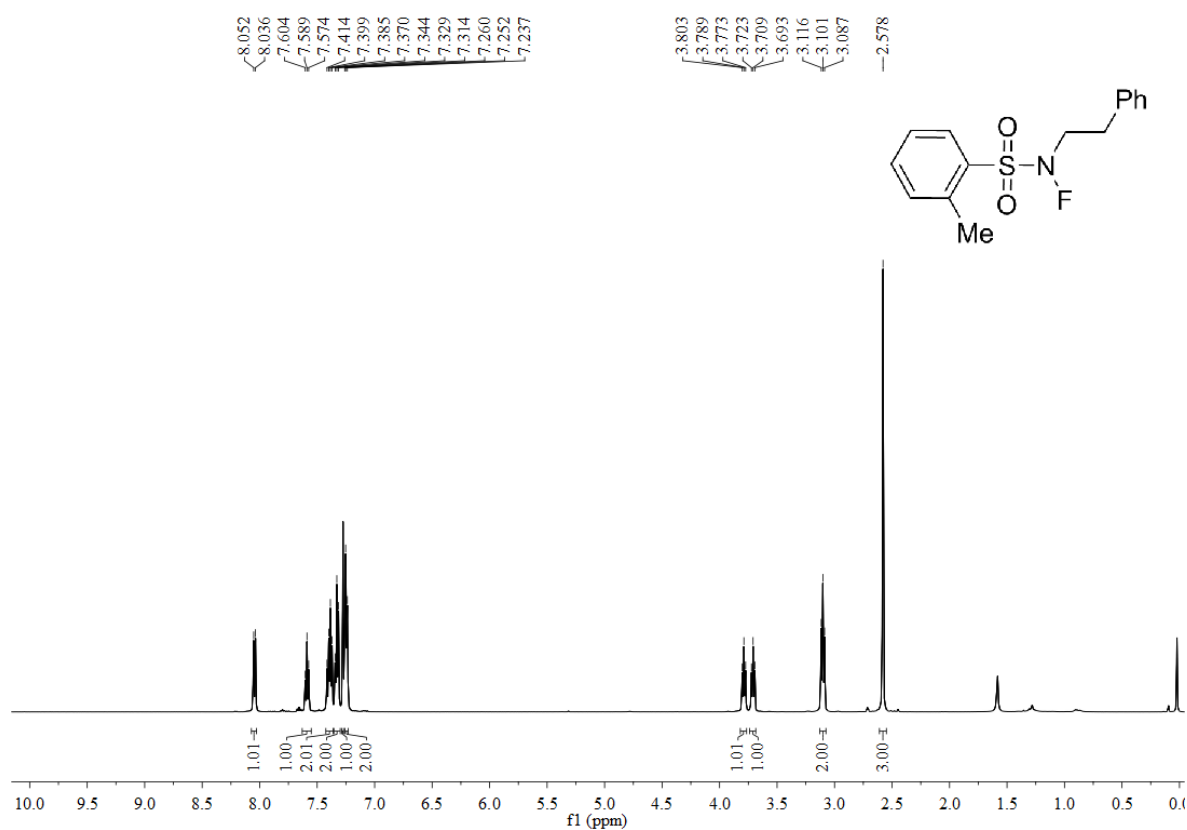


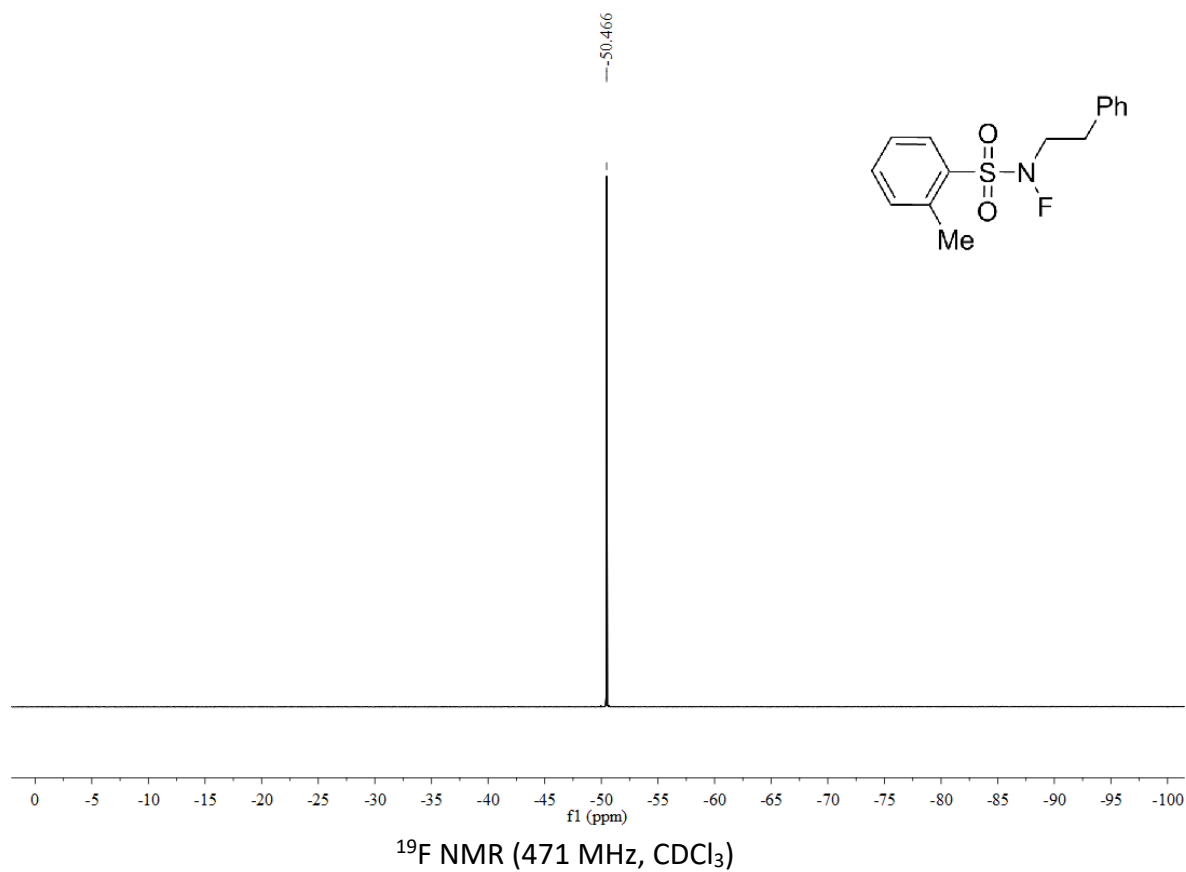
***N*-fluoro-2,4,6-triisopropyl-*N*-phenethylbenzenesulfonamide (1m).**



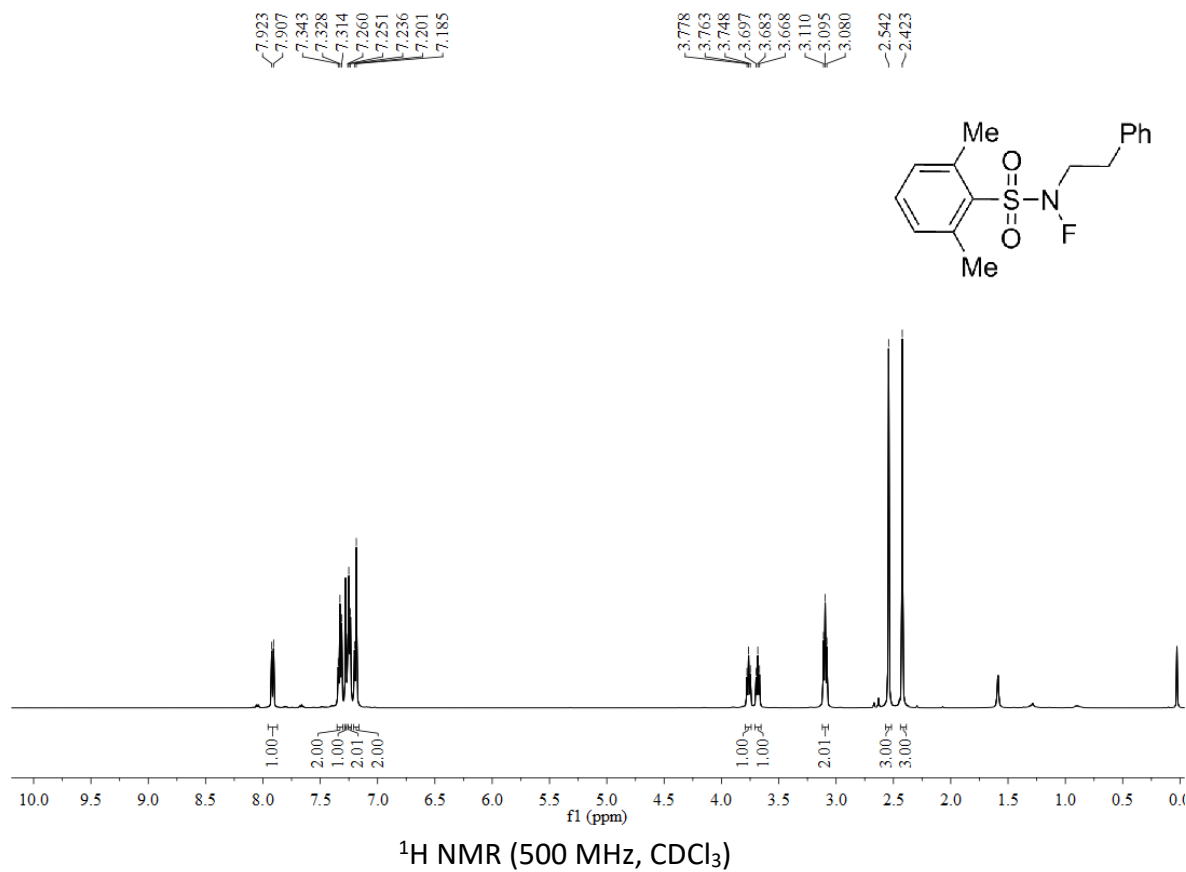


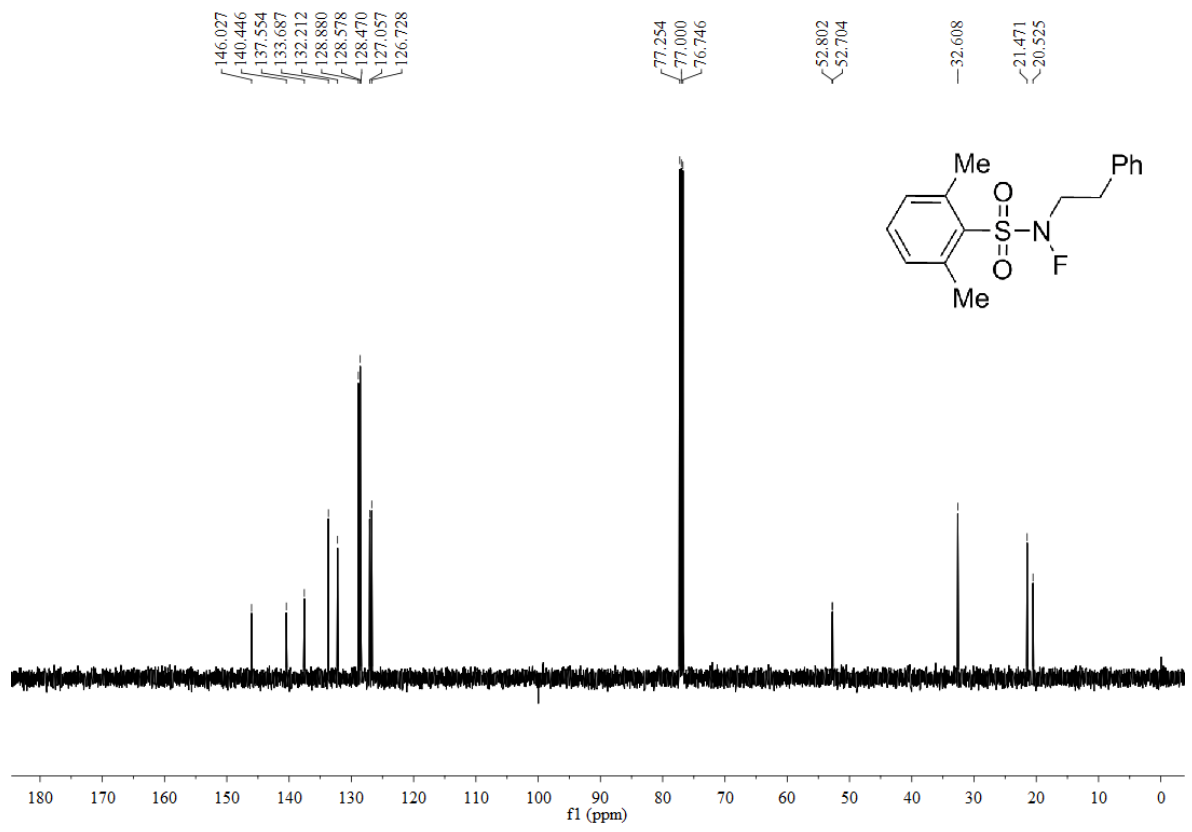
***N*-fluoro-2-methyl-*N*-phenethylbenzenesulfonamide (1n).**



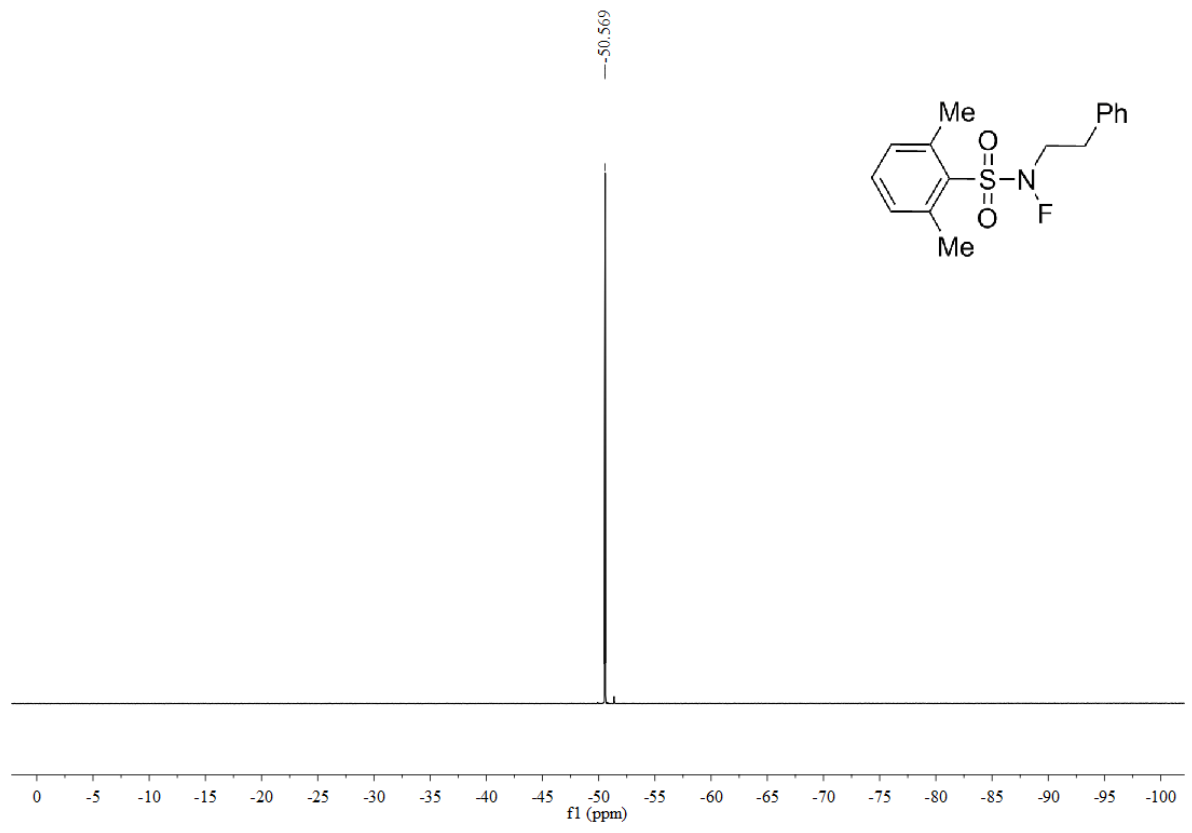


***N*-fluoro-2,6-dimethyl-*N*-phenethylbenzenesulfonamide(1o).**



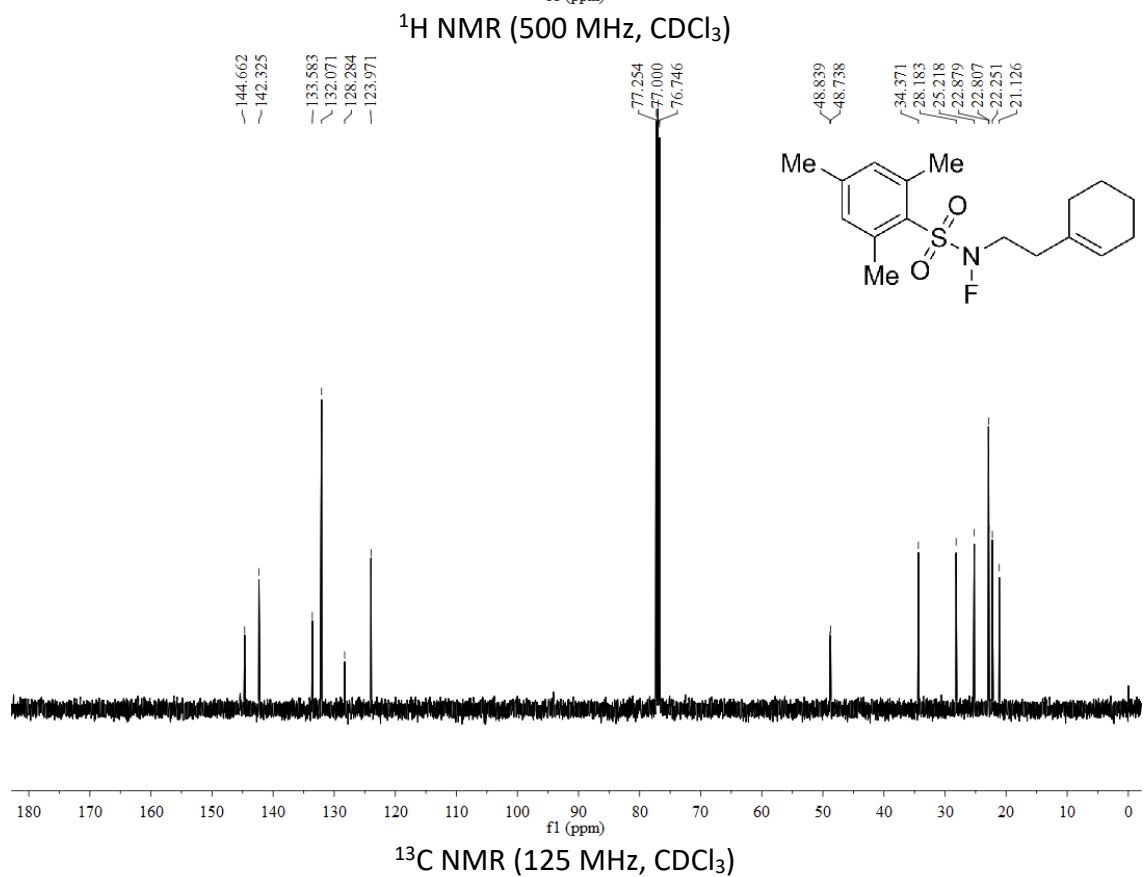
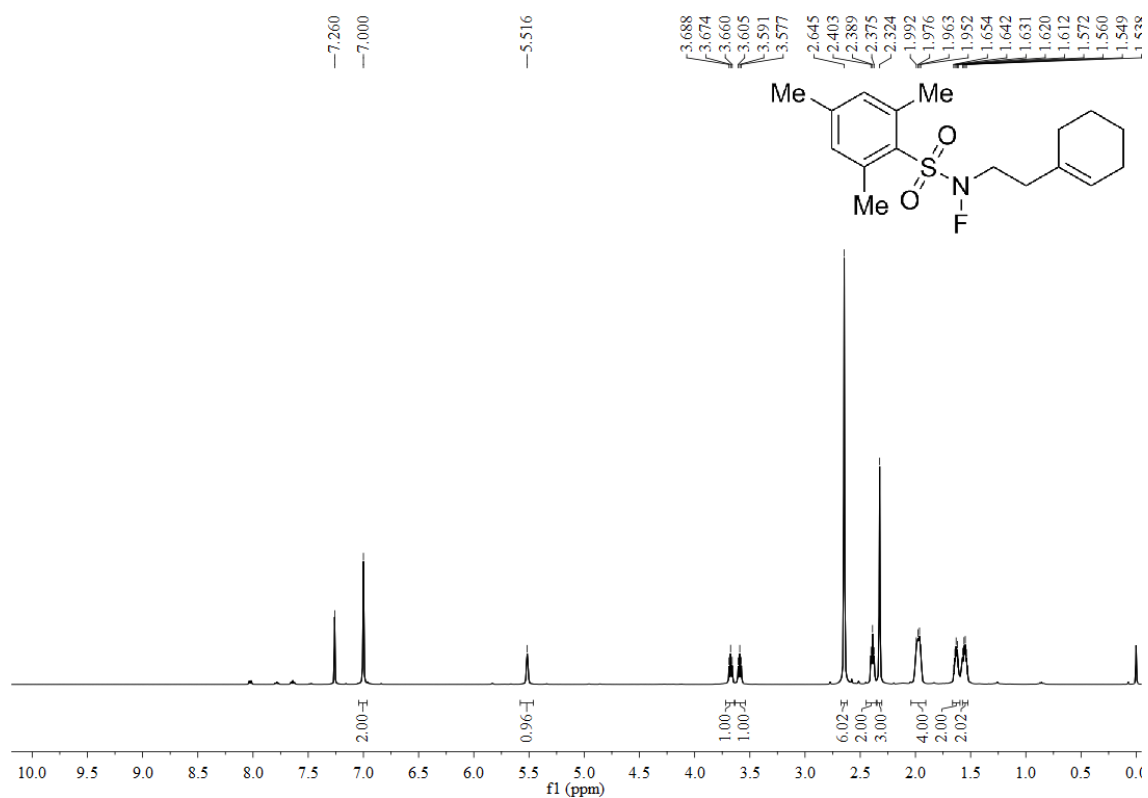


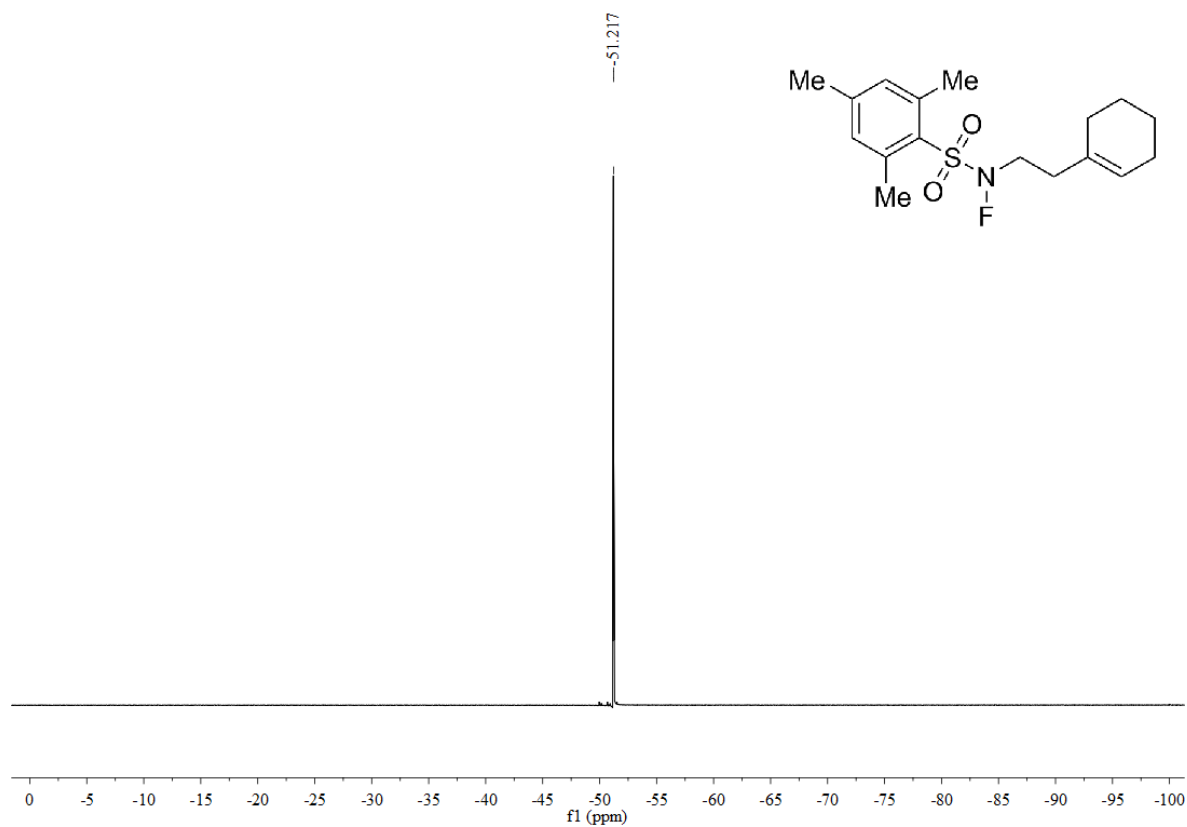
¹³C NMR (125 MHz, CDCl₃)



¹⁹F NMR (471 MHz, CDCl₃)

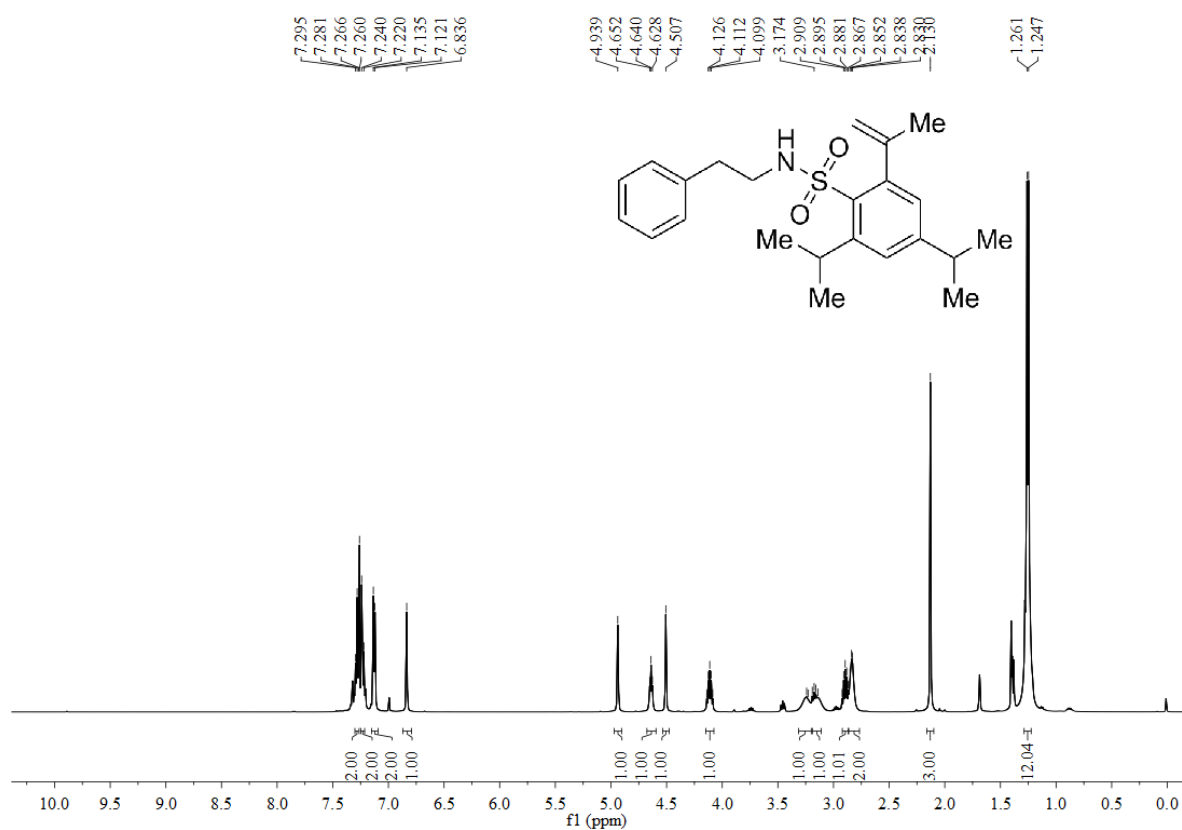
***N*-(2-(cyclohex-1-en-1-yl)ethyl)-*N*-fluoro-2,4,6-trimethylbenzenesulfonamide (1q).**



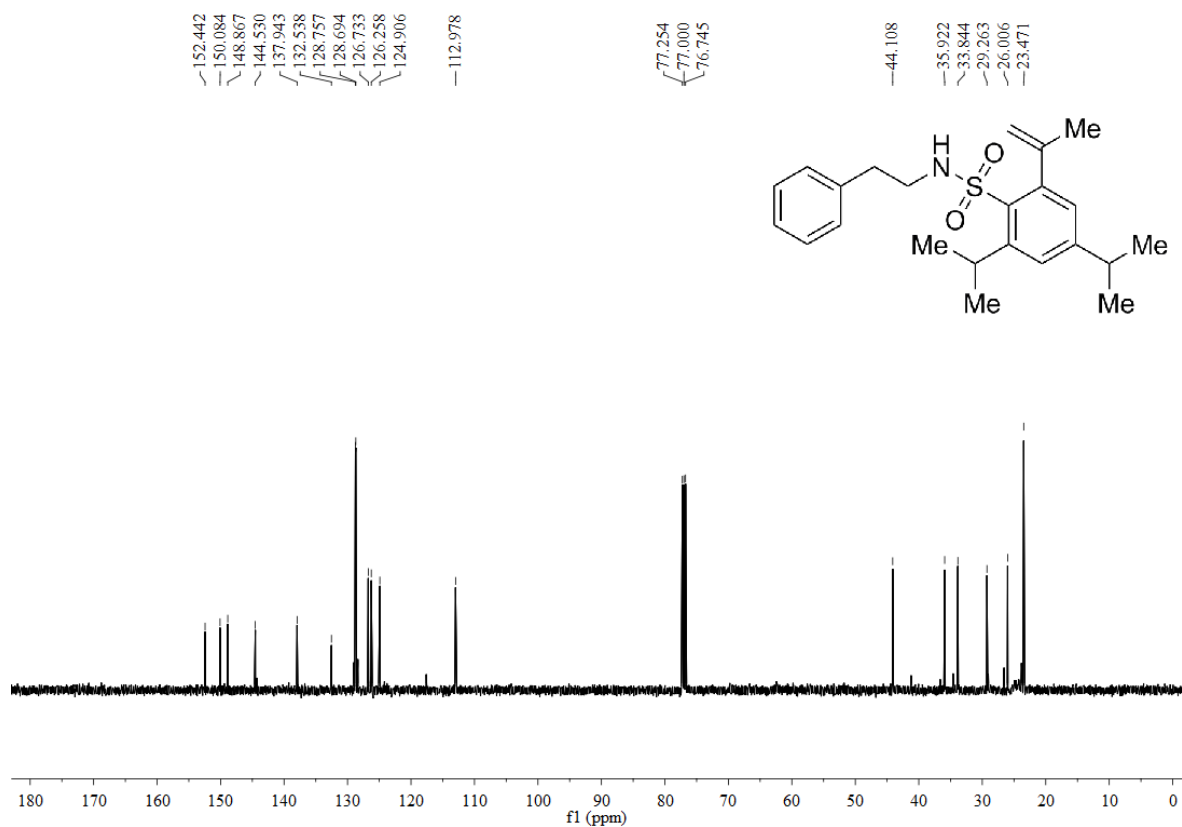


^{19}F NMR (471 MHz, CDCl_3)

2,4-diisopropyl-N-phenethyl-6-(prop-1-en-2-yl)benzenesulfonamide (4m).

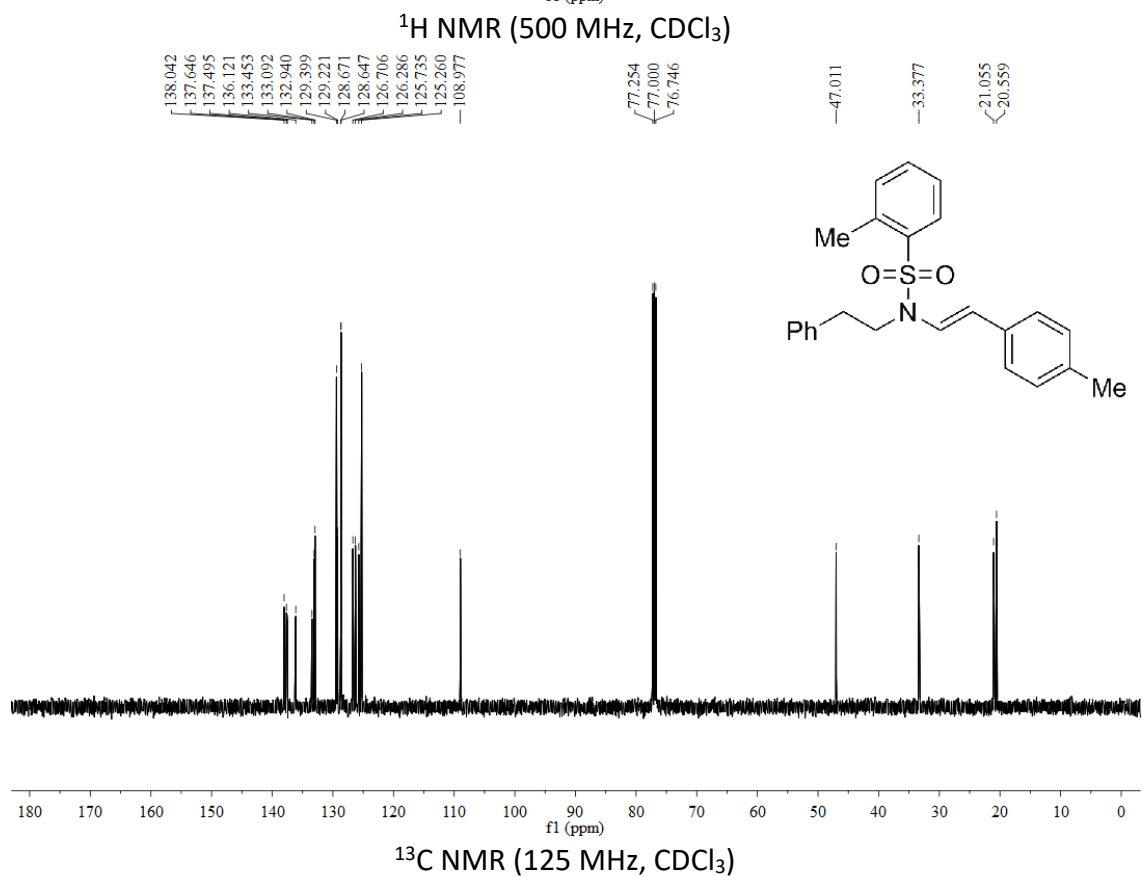
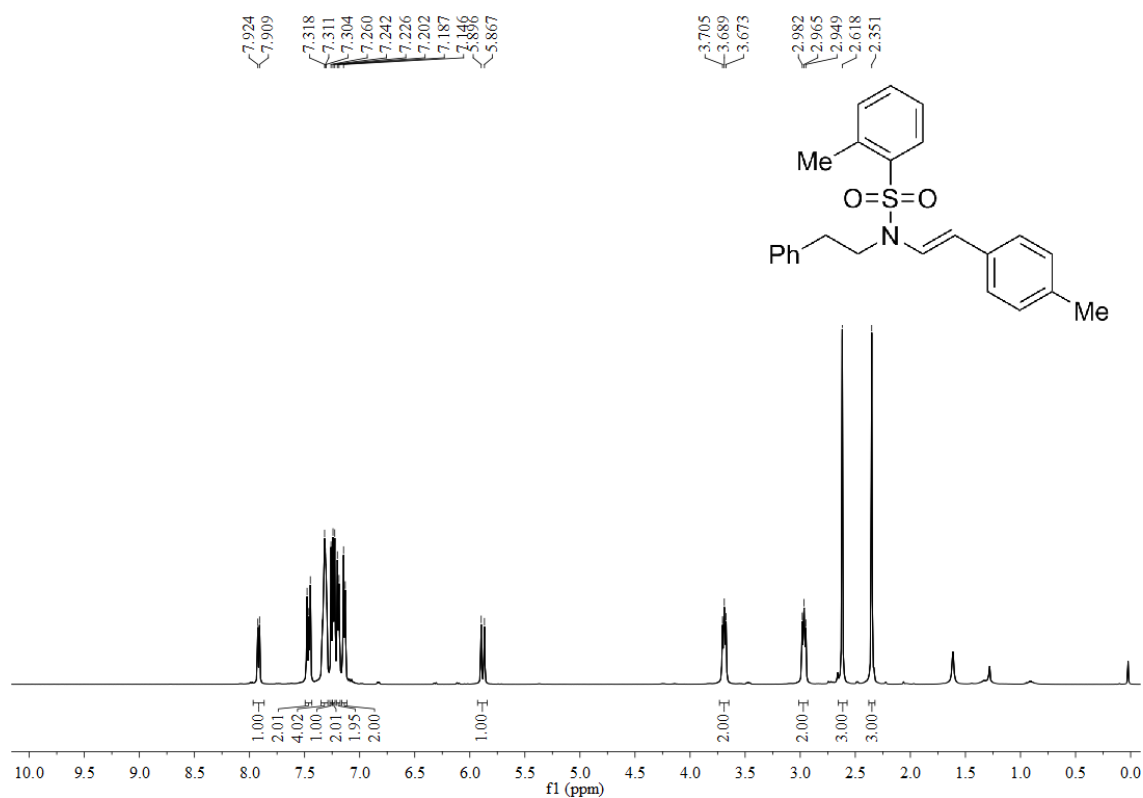


¹H NMR (500 MHz, CDCl₃)

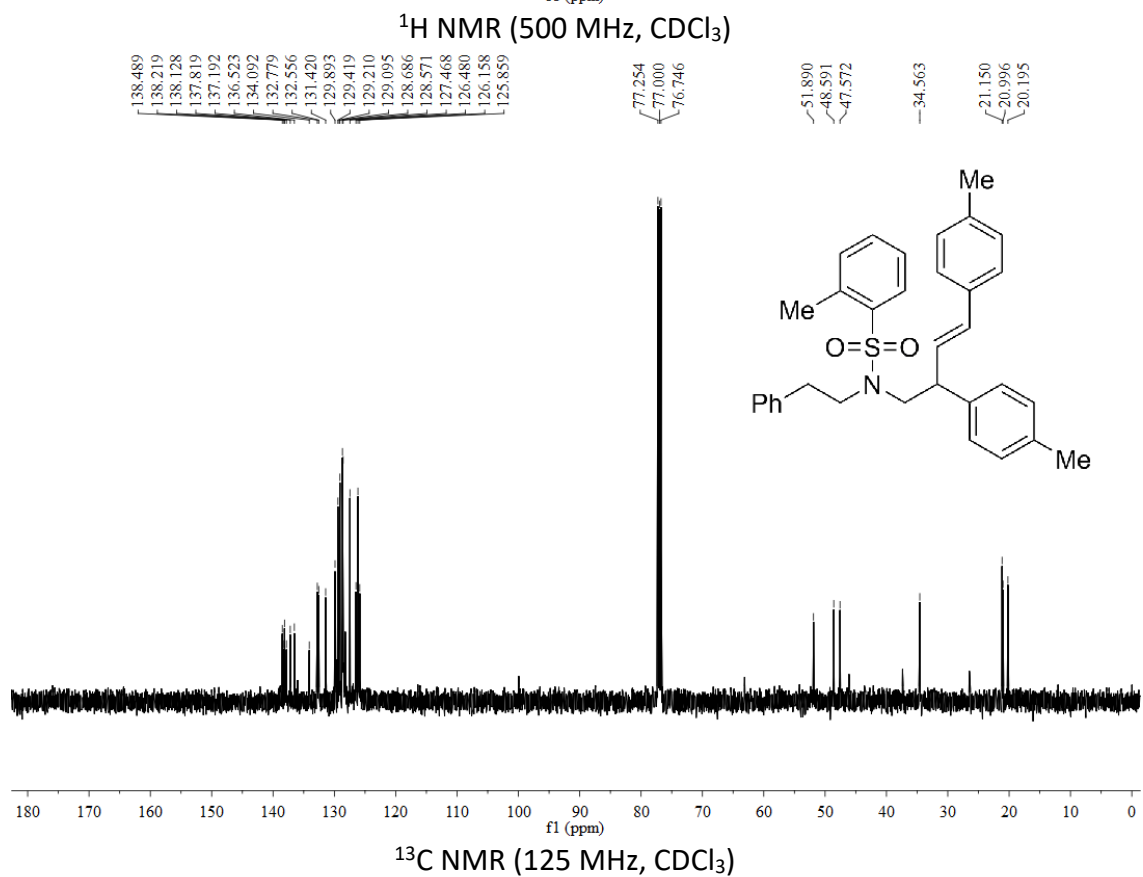
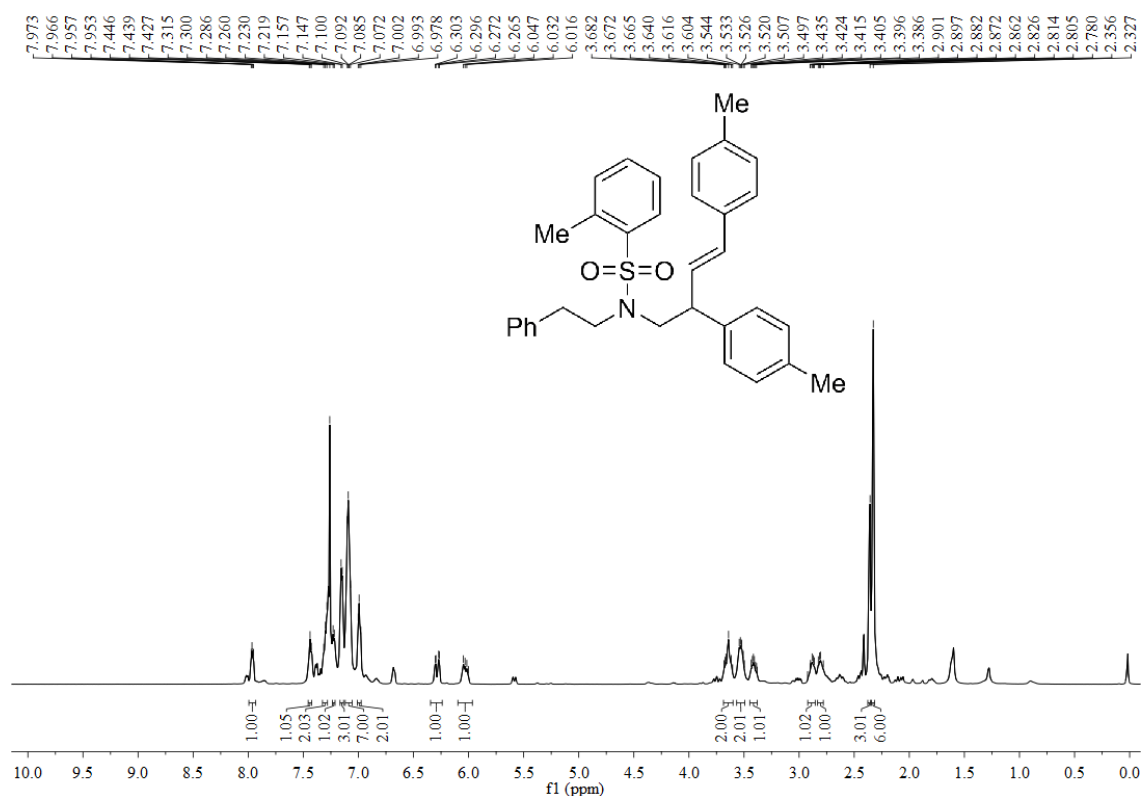


¹³C NMR (125 MHz, CDCl₃)

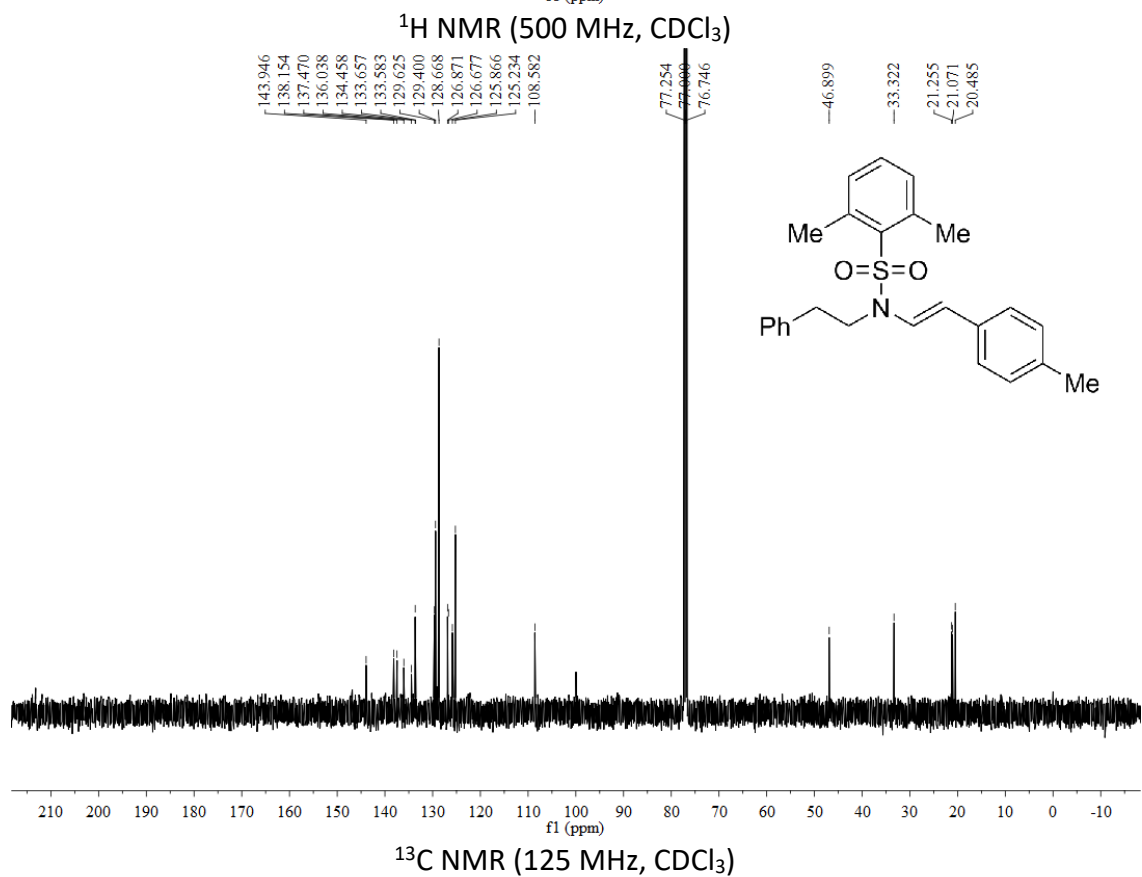
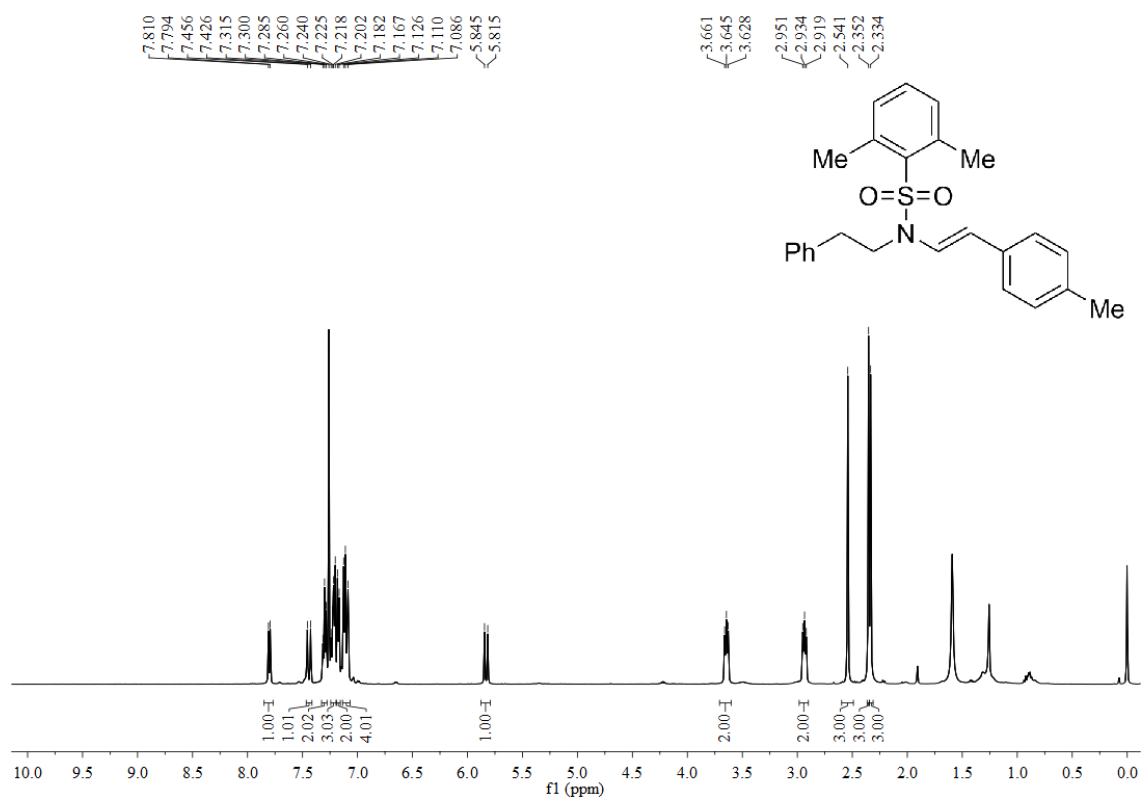
(E)-2-methyl-N-(4-methylstyryl)-N-phenethylbenzenesulfonamide (5na).



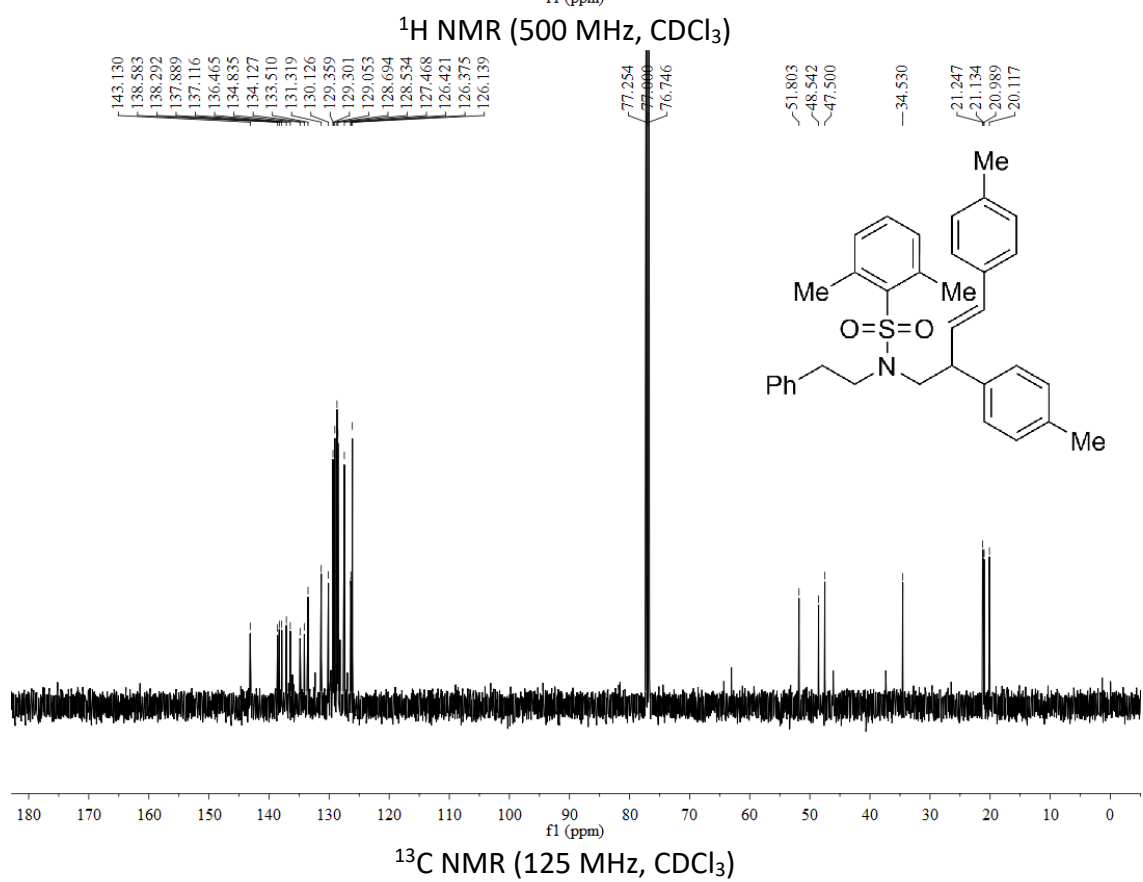
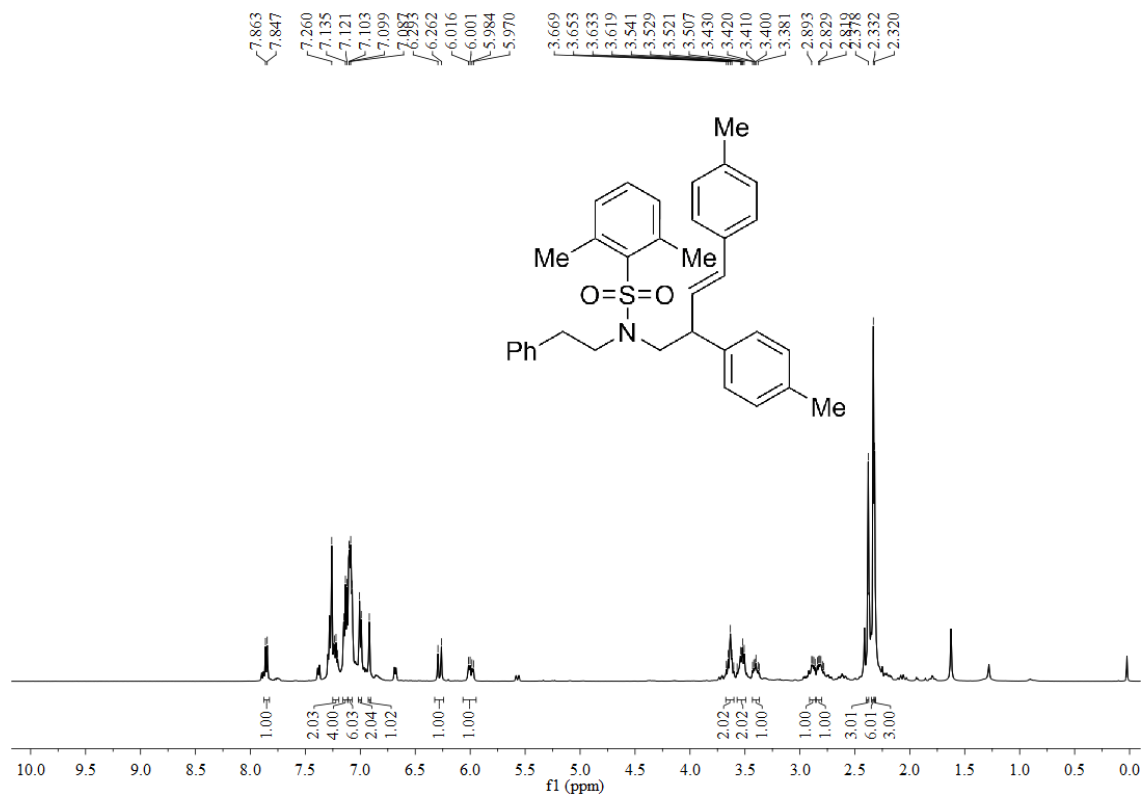
(E)-N-(2,4-di-p-tolylbut-3-en-1-yl)-2-methyl-N-phenethylbenzenesulfonamide (6na).



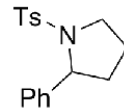
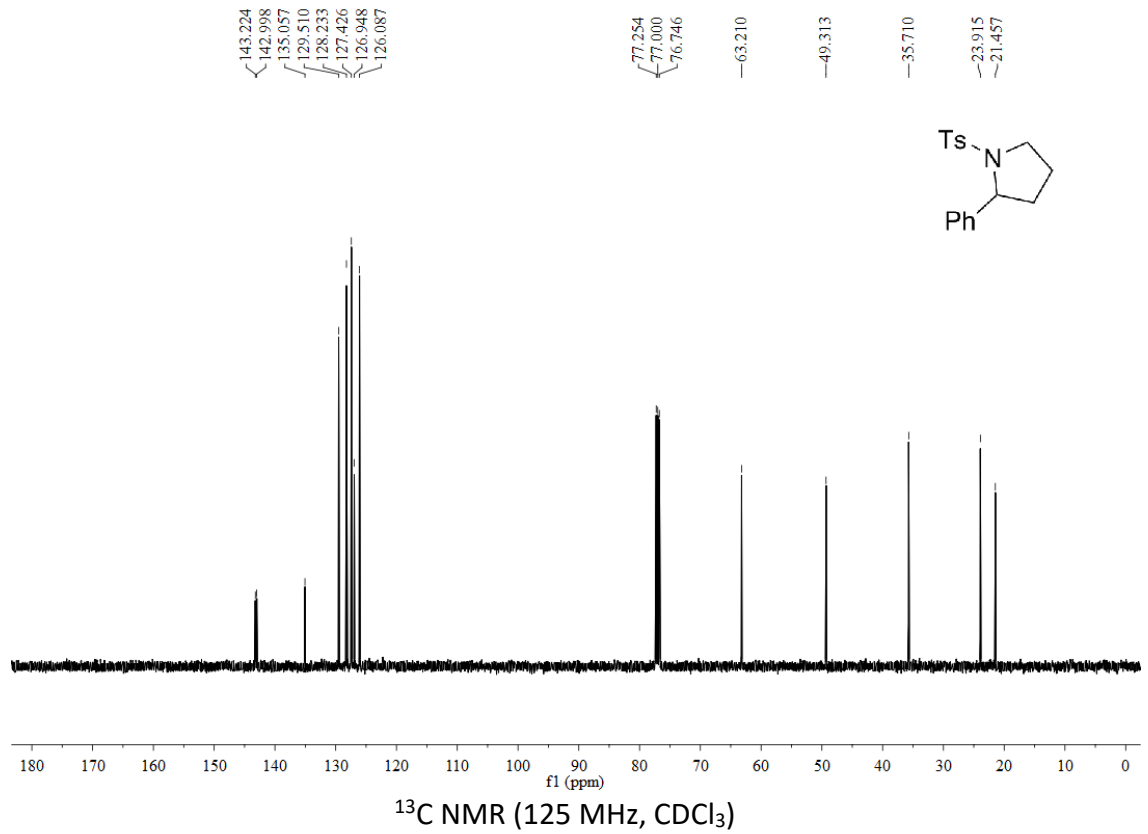
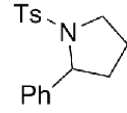
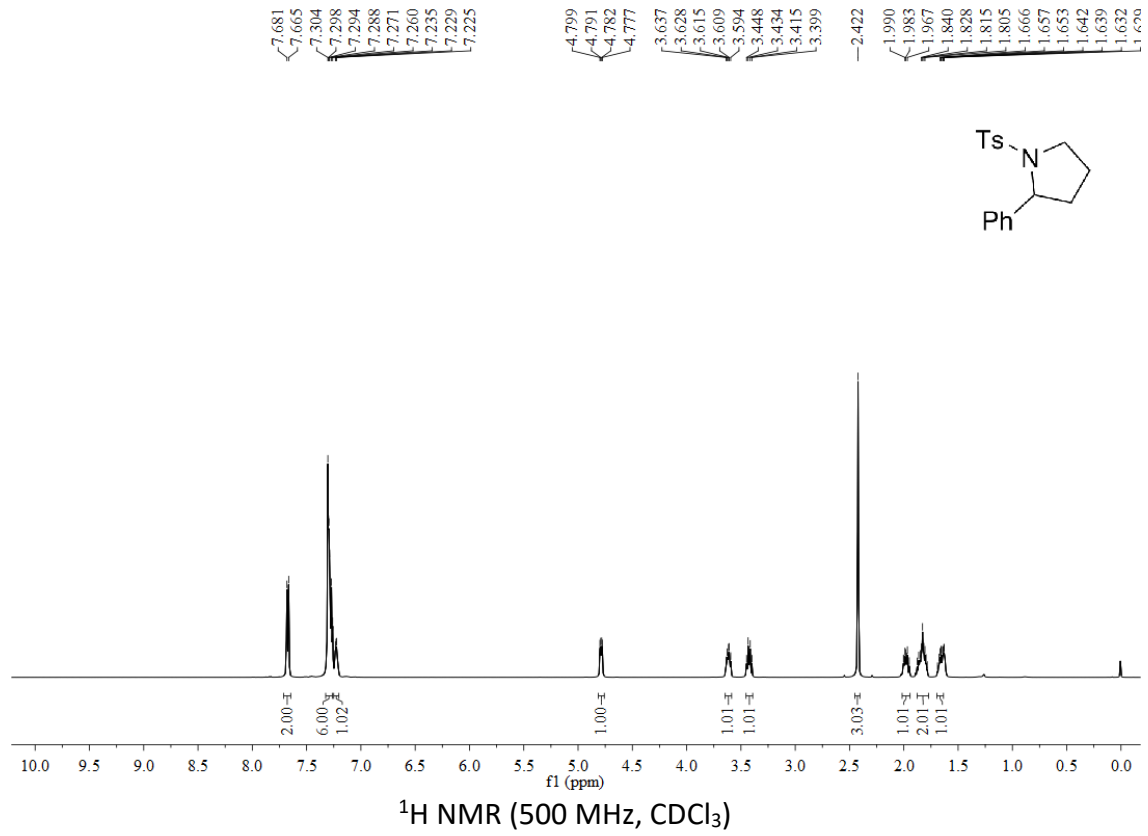
(E)-2,6-dimethyl-N-(4-methylstyryl)-N-phenethylbenzenesulfonamide (50a).



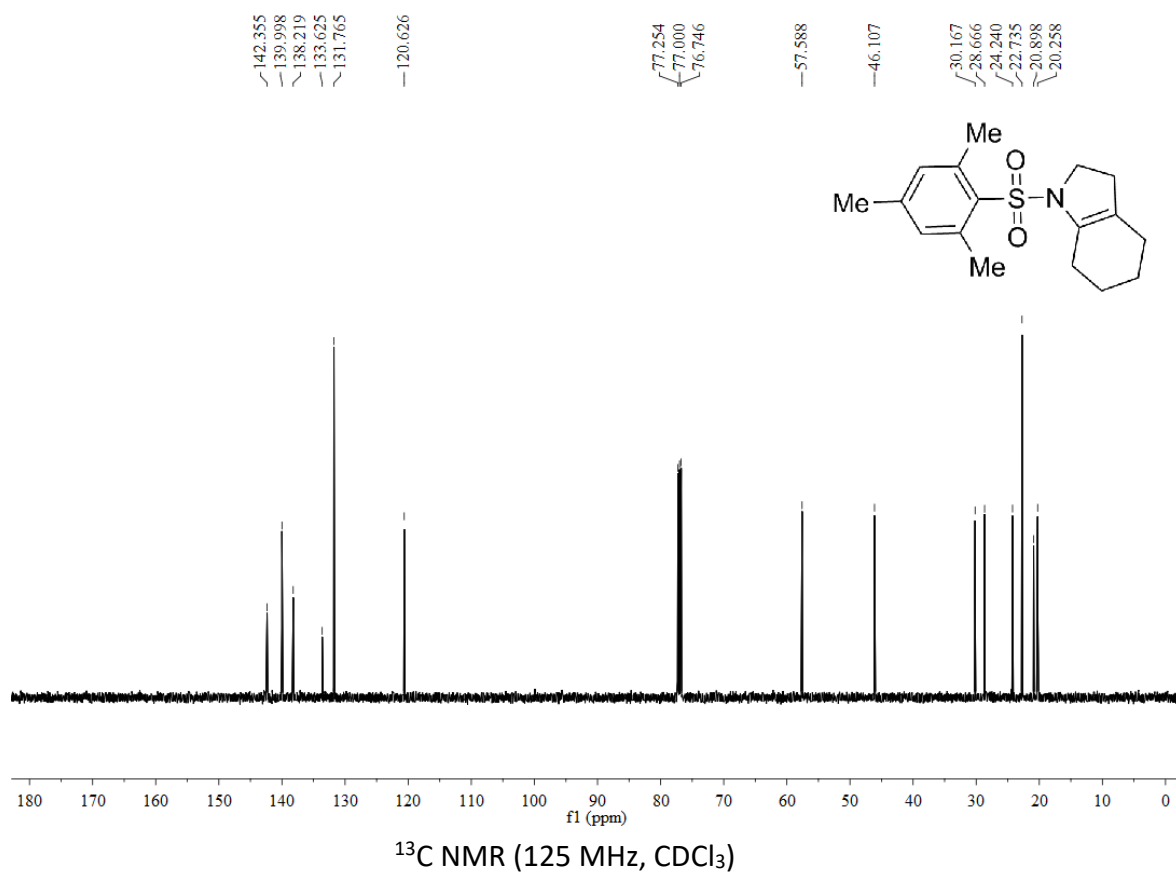
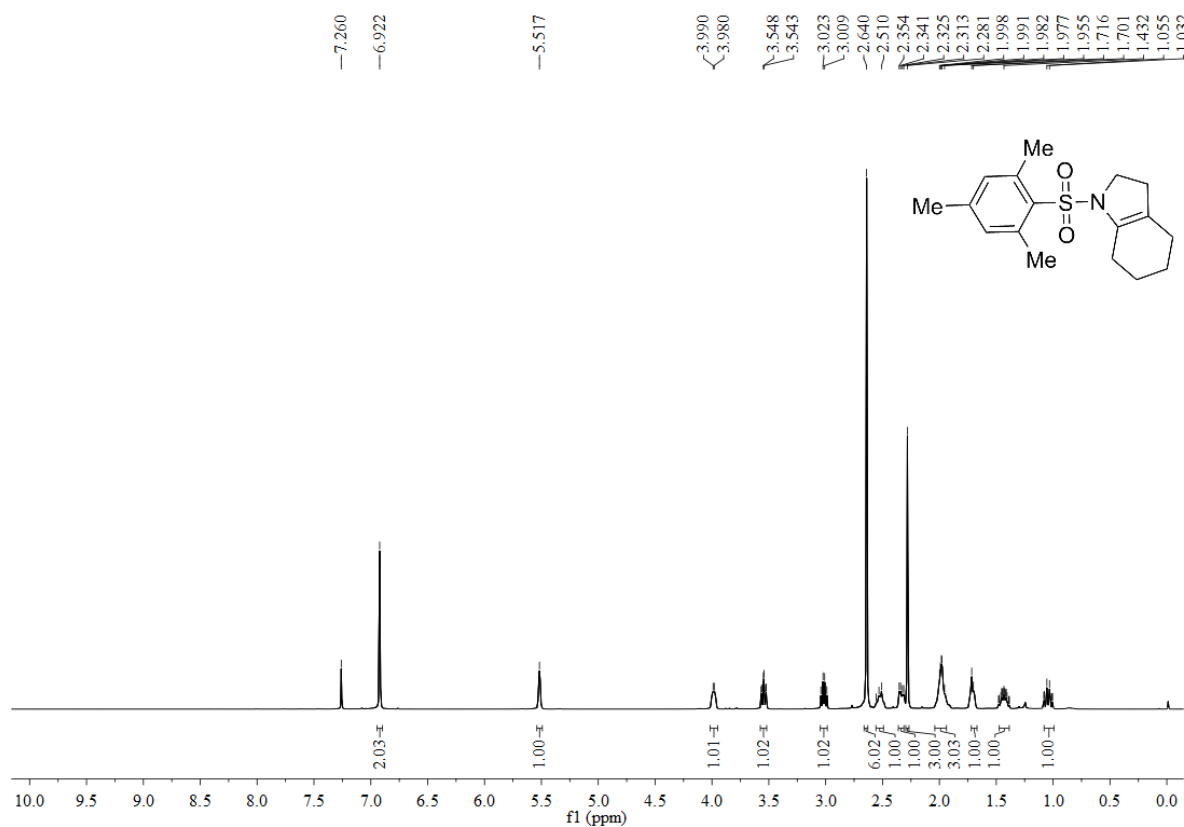
**(E)-N-(2,4-di-p-tolylbut-3-en-1-yl)-2,6-dimethyl-N-phenethylbenzenesulfonamide
(60a).**



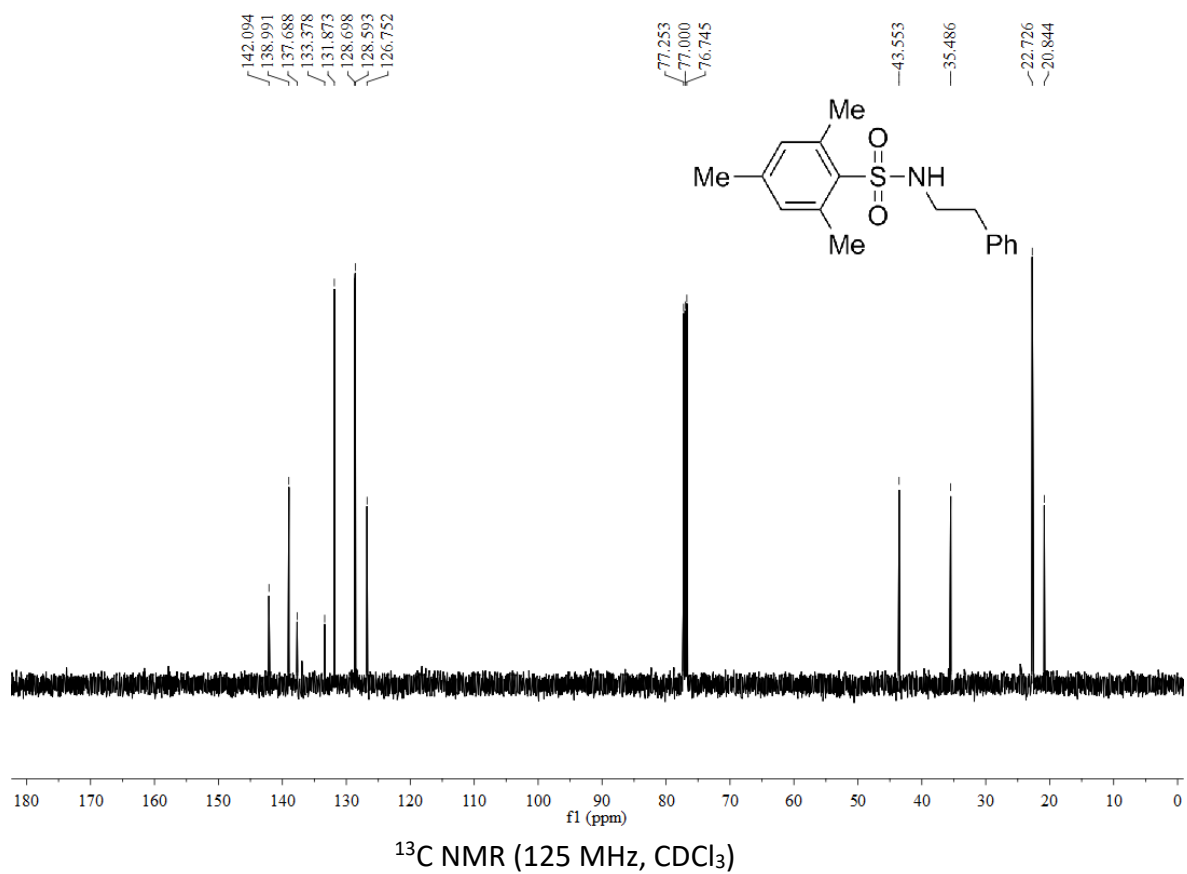
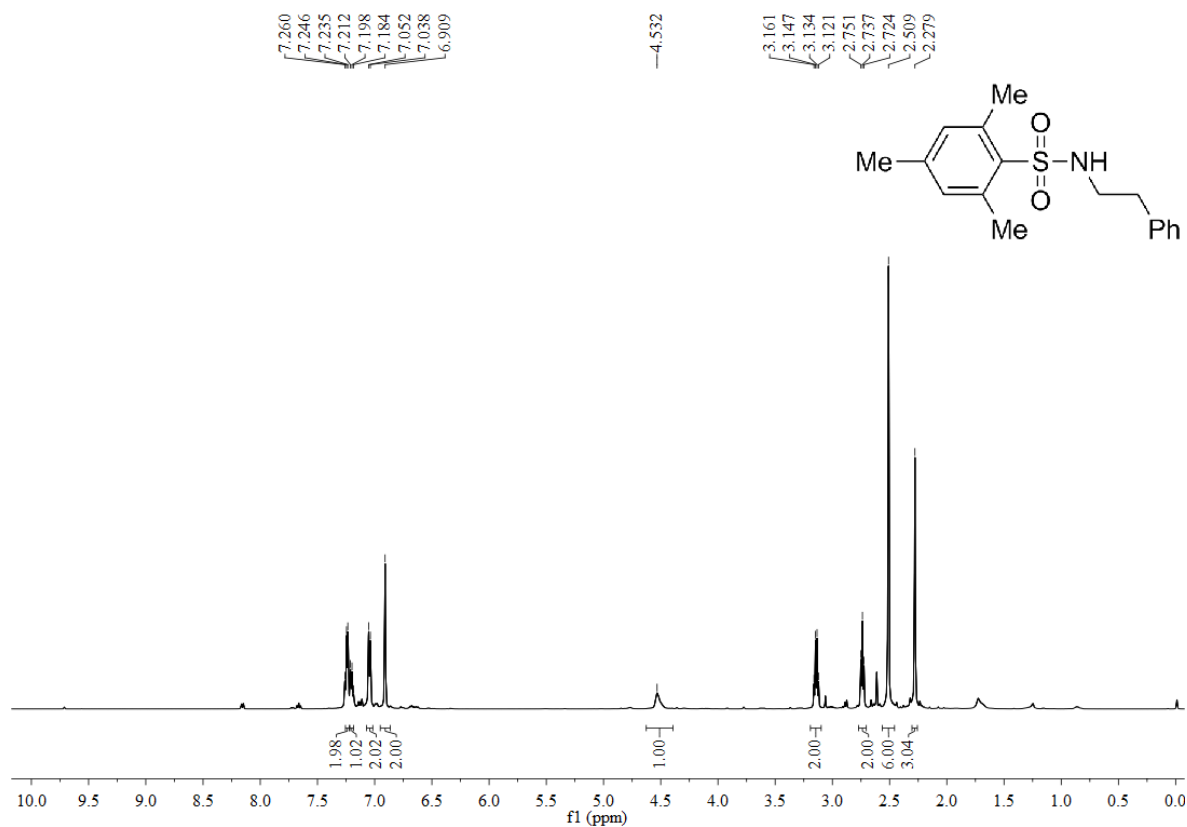
2-phenyl-1-tosylpyrrolidine (7p).



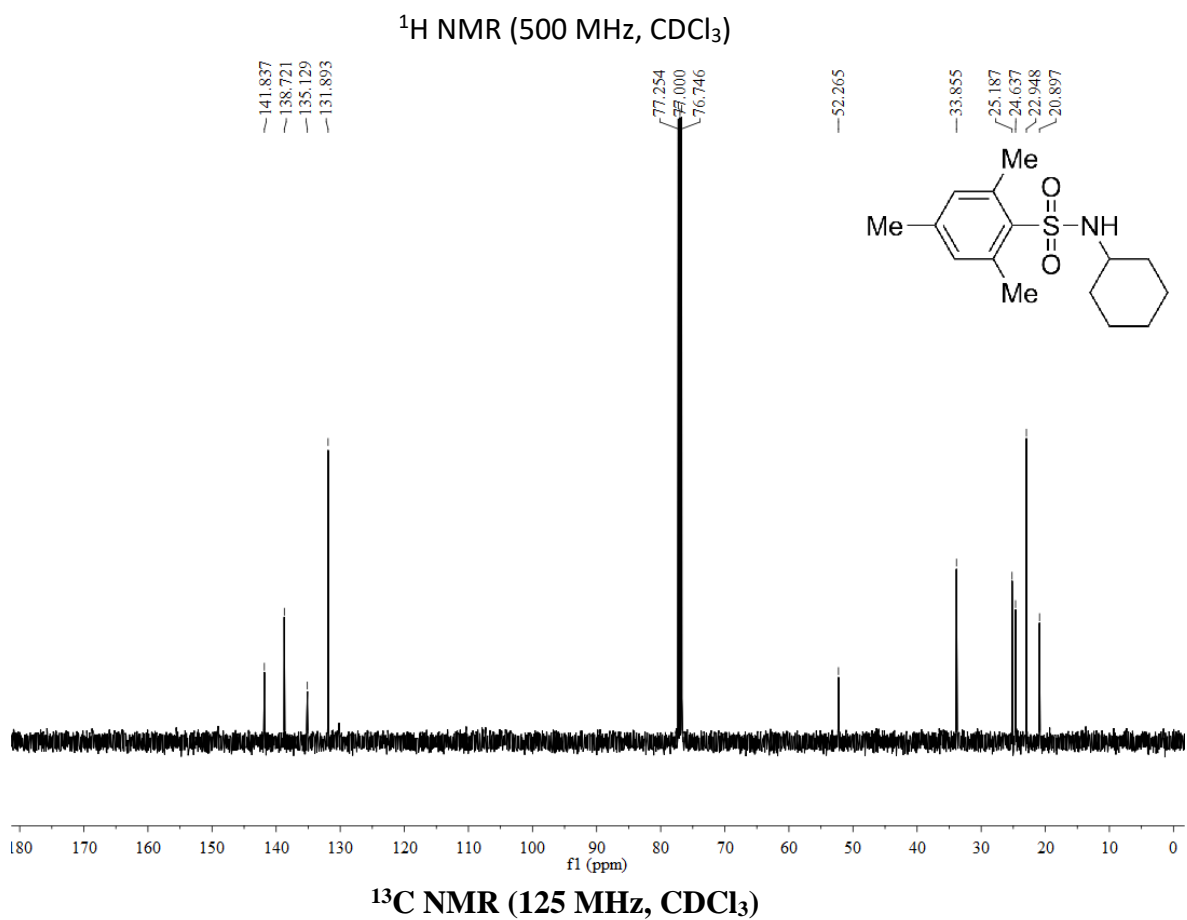
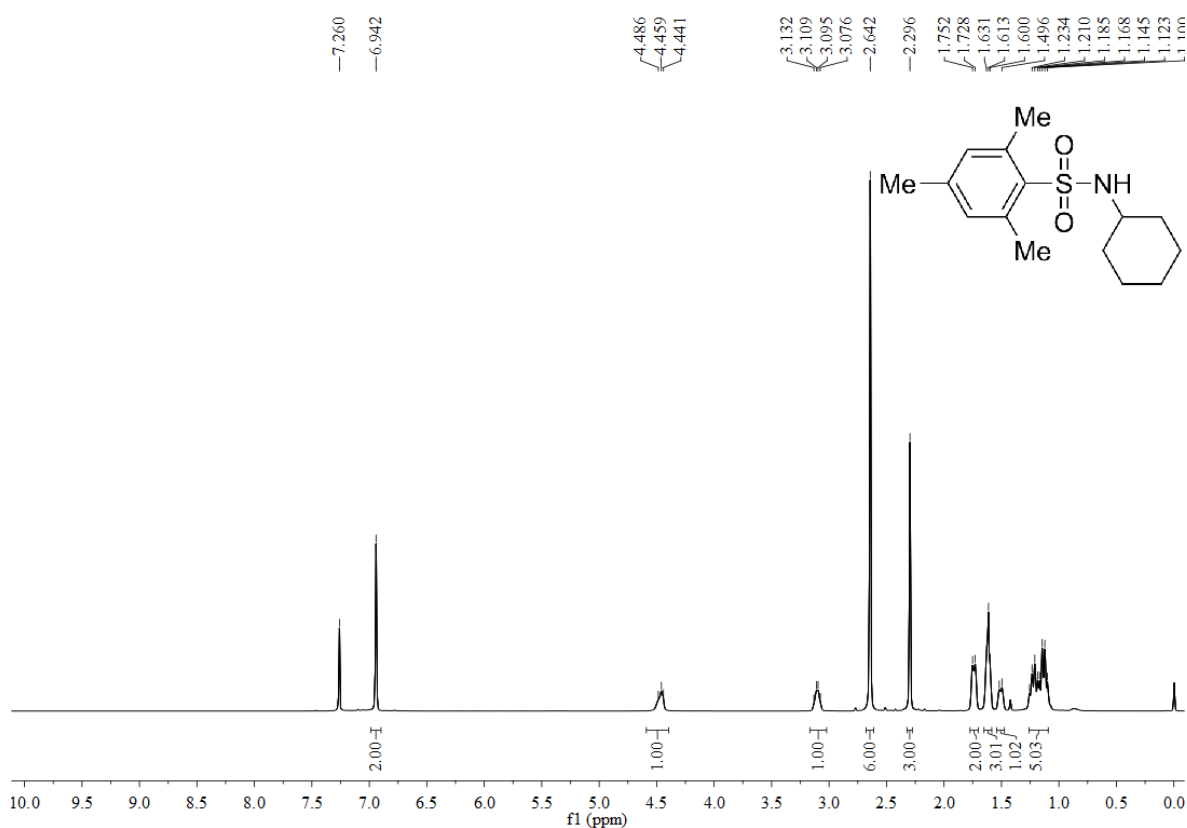
1-(mesitylsulfonyl)-2,3,4,5,6,7-hexahydro-1H-indole (7q).



2,4,6-trimethyl-N-phenethylbenzenesulfonamide (9a).



***N*-cyclohexyl-2,4,6-trimethylbenzenesulfonamide (9g).**



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