# Intermolecular Anti-Markovnikov Hydroamination of Unactivated Alkenes with Sulfonamides Enabled by Proton-Coupled Electron Transfer

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**Supporting Information**

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# I. Materials and Methods

## General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego[1]. All solvents were purified according to the method of Grubbs[2]. Nitromethane was bought from Sigma-Aldrich, and dried by 4A molecular sieve in a flame-dried Schlenk flask. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel according to the method of Still[3]. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, Seebach's stain and potassium permanganate stain.

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on a Bruker 500 (500, 125 and 470 MHz) instrument, and chemical shifts are calibrated by internal standard tetramethylsilane (TMS). Data for $^{1}H$ NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and assignment. Data for $^{13}C$ NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption ($cm^{-1}$). High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Gas chromatographymass spectrometry (GC-MS) was performed on an Agilent 6890 GC-5975C MSD.

## General procedures for hydrosulfonamidation reactions

Method A (reaction optimization):
An oven-dried 2-dram vial was charged with a magnetic stir bar, substrate (0.05 mmol, 1.0 equiv) and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)]PF_6$ (0.001 mmol, 2 mol%, 1.2 mg). The vial was brought into a glove box where tetrabutylammonium dibutyl phosphate (0.01 mmol, 20 mol%, 4.5 mg) was added. The vial was then sealed with a Teflon septa and removed from the glovebox. The vial was then evacuated and backfilled with Ar three times. 1 mL of anhydrous solvent was added, followed by 2,4,6-triisopropylbenzene thiol (0.015 mmol, 30 mol%, 3.6 mg). The reaction was stirred at room temperature and irradiated with one Kessil lamp for 18 h. The reaction was filtered through a pipette containing 0.75 inch of silica gel, and rinsed with ethyl acetate. The yields were determined on GC with 5μL diphenyl ether as an internal standard.

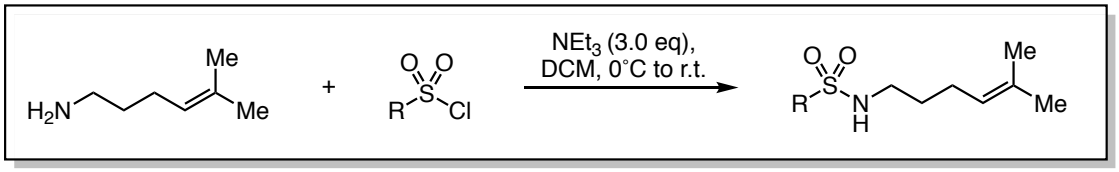
Method B (preparative scale for intramolecular hydrosulfonamidation):
An oven-dried 2-dram vial was charged with a magnetic stir bar, substrate (0.5 mmol, 1.0 equiv) and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)]PF_6$ (0.001 mmol, 2 mol%, 11.5 mg). The vial was brought into a glove box where tetrabutylammonium dibutyl phosphate (0.1 mmol, 20 mol%, 45.2 mg) was added. The vial was then sealed with a Teflon septa and removed from the glovebox. The vial was then evacuated and backfilled with Ar three times. 5.0 mL (0.1 mmol/mL) anhydrous trifluorotoluene was added, followed by 2,4,6-

triisopropylbenzene thiol (0.15 mmol, 30 mol%, 35.5 mg). The reaction was stirred at room temperature and irradiated with blue LED Kessil lamps for 36 h. Solvent was removed under vacuum, and the crude product was purified by silica gel (25 gram) flash column chromatography (eluted with hexane/ethylacetate) to afford the named products.

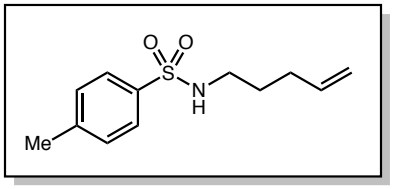
Method C (preparative scale for intermolecular hydrosulfonamidation):
An oven-dried 2-dram vial was charged with a magnetic stir bar, sulfonamides (0.5 mmol, 1.0 equiv) and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)]PF_6$ (0.001 mmol, 2 mol%, 11.5 mg). The vial was brought into a glove box where tetrabutylammonium dibutyl phosphate (0.1 mmol, 20 mol%, 45.2 mg) was added. The vial was then sealed with a Teflon septa and removed from the glovebox. The vial was then evacuated and backfilled with Ar three times. 5.0 mL (0.1 mmol/mL) degassed anhydrous trifluorotoluene was added, followed by 2,4,6-triisopropylbenzene thiol (0.15 mmol, 30 mol%, 35.5 mg) and the corresponding alkene acceptor (1.5 mmol, 3.0 eq). The reaction was stirred at room temperature and irradiated with blue LED Kessil lamps for 36 h (or otherwise indicated). Solvent was removed under vacuum, and the crude product was purified by silica gel (25 gram) flash column chromatography (eluted with hexane/ethylacetate) to afford the named products.

# II. Synthesis and Characterization of Substrates

**General procedure for synthesis of sulfonamides**



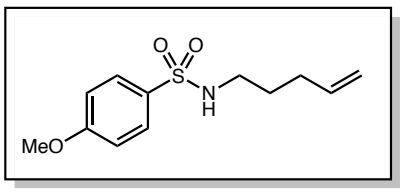

To a flame-dried round bottom flask was charged with magnetic stir bar, 5-methylhex-4-en-1-amine[4] (crude from LAH reduction, 10.0 mmol), dichloromethane (40 mL, 0.25 M) and triethylamine (4.18 mL, 30.0 mmol, 3.0 eq). The flask was cooled to 0°C. Corresponding sulfonyl chloride (1.1 eq, 11.0 mmol) was added dropwise or in small portions. After addition, reaction was warmed up to room temperature gradually and stirred at room temperature for two hours. Reaction was quenched by adding 100mL brine, and extract by 3×30 mL dichloromethane. Combined organic phase was washed by brine three times. Collect the organic phase and dried over $Na_2SO_4$. Crude product was purified by silica gel flash chromatography to obtain the sulfonamide products.




4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. Pent-4-en-1-amine was synthesized corresponding to a reported method[5] and was used in this reaction without further purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford a colorless liquid.

**IR** (Neat): 3282, 2934, 1426, 1324, 1158, 1094, 815, 664cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.33-7.29 (m, 2H), 5.74-5.66 (m, 1H), 4.99-4.93 (m, 2H), 4.78 (br, 1H), 2.94 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.06-2.01 (m, 2H), 1.59-1.53 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 143.37, 137.25, 136.93, 129.71, 127.09, 115.55, 42.63, 30.66, 28.67, 21.54;
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{17}NO_2S$) from $[M+H]^+$ requires m/z 239.09800, found m/z 239.09782, difference 0.73 ppm.

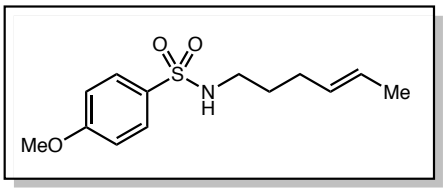



4-methoxy-*N*-(pent-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above and was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless liquid.

**IR** (Neat): 3281, 2939, 1597, 1498, 1323, 1302, 1259, 1152, 1095, 833cm$^{-1}$;

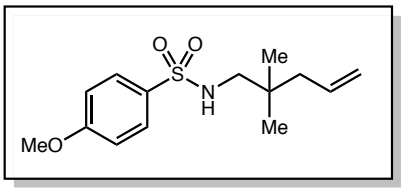
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.00-6.96 (m, 2H), 5.74-5.66 (m, 1H), 4.99-4.93 (m, 2H), 4.70 (br, 1H), 3.87 (s, 3H), 2.93 (q, *J* = 7.0 Hz, 2H), 2.07-2.02 (m, 2H), 1.59-1.53 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.83, 137.26, 131.51, 129.20, 115.56, 114.23, 55.63, 42.60, 30.68, 28.65;
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{17}NO_3S$) from $[M+H]^+$ requires m/z 255.09291, found m/z 255.09297, difference 0.21 ppm.




(*E*)-*N*-(hex-4-en-1-yl)-4-methoxybenzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. (E)-hex-4-en-1-amine was synthesized corresponding to a reported method[6] and used without further purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless liquid.

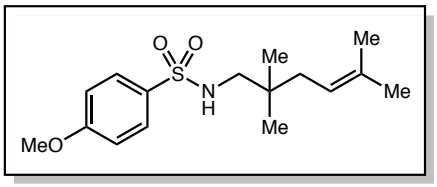
**IR** (Neat): 3281, 2936, 1597, 1498, 1259, 1153, 1096, 834$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.00-6.96 (m, 2H), 5.41-5.26 (m, 2H), 4.52 (br, 1H), 3.87 (s, 3H), 2.92 (q, *J* = 7.0 Hz, 2H), 1.98-1.93 (m, 2H), 1.60 (d, *J* = 6.5 Hz, 3H), 1.54-1.48 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.82, 131.55, 129.67, 129.22, 126.16, 114.21, 55.62, 42.62, 29.51, 29.22, 17.88;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_3S$) from $[M+H]^+$ requires m/z 269.10856, found m/z 269.10908, difference 1.93 ppm.




*N*-(2,2-dimethylpent-4-en-1-yl)-4-methoxybenzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. 2,2-dimethylpent-4-en-1-amine was synthesized corresponding to a reported method[7] and was used without further purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless liquid.

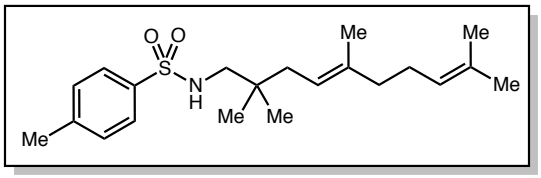
**IR** (Neat): 3280, 2961, 1597, 1498, 1259, 1152, 1096, 834$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.00-6.96 (m, 2H), 5.71-5.65 (m, 1H), 4.93-4.86 (m, 2H), 4.46 (br, 1H), 3.88 (s, 3H), 2.91-2.86 (m, 2H), 1.49-1.46 (m, 2H),0.94 (s, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.82, 147.12, 131.52, 129.20, 114.21, 111.53, 55.62, 41.86, 39.86, 35.86, 26.74;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12407, difference 0.5 ppm.




4-methoxy-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. 2,2,5-trimethylhex-4-en-1-amine was synthesized corresponding to an alteration of a reported method,[7] using 1-bromo-3-methylbut-2-ene instead of allylbromide, and carried on for use without in this reaction without purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a light-yellow liquid.

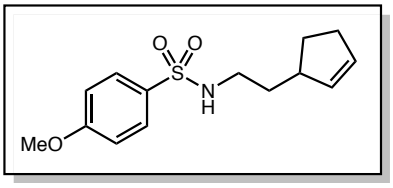
**IR** (Neat): 3287, 2965, 1597, 1498, 1326, 1259, 1155, 1096, 833cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.00-6.96 (m, 2H), 5.07-5.03 (m, 1H), 4.38 (br, 1H), 3.88 (s, 3H), 2.67 (d, J = 7.0 Hz, 2H), 1.86 (d, J = 8.0 Hz, 2H), 1.68 (s, 6H), 1.56 (s, 3H), 0.84 (s, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.77, 134.11, 131.54, 129.21, 119.71, 114.18, 55.61, 52.97, 37.85, 34.86, 26.04, 24.90, 17.91;
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_3S$) from $[M+H]^+$ requires m/z 311.15551, found m/z 311.15542, difference 0.29 ppm.




(*E*)-4-methyl-*N*-(2,2,5,9-tetramethyldeca-4,8-dien-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. (E)-2,2,5,9-tetramethyldeca-4,8-dien-1-amine was synthesized corresponding to an alteration of a reported method,[7] using (*E*)-1-bromo-3,7-dimethylocta-2,6-diene instead of allyl bromide and carried on for use in this reaction without purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a light-yellow liquid.

**IR** (Neat): 3284, 2964, 1598, 1498, 1326, 1259, 1155, 1096, 833, 669cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 6.99-6.95 (m, 2H), 5.06-5.02 (m, 2H), 4.44 (br, 1H), 3.88 (s, 3H), 2.67 (d, J = 7.0 Hz, 2H), 2.06-2.02 (m, 2H), 1.99-1.96 (m, 2H), 1.88 (d, *J* = 8.0 Hz, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.54 (s, 3H), 0.83 (s, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.76, 137.64, 131.55, 129.20, 124.20, 119.78, 114.18, 55.59, 53.02, 40.03, 37.67, 34.96, 26.60, 25.74, 24.83, 17.71, 16.17;
**HRMS** (ESI) exact mass calculated for [M] ($C_{21}H_{33}NO_3S$) from $[M+H]^+$ requires m/z 379.21811, found m/z 379.21884, difference 1.91 ppm.

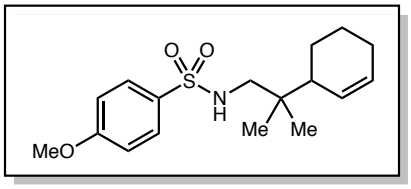



*N*-(2-(cyclopent-2-en-1-yl)ethyl)-4-methoxybenzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. 2-(cyclopent-2-en-1-

yl)ethan-1-amine was synthesized according to published procedure[8] and carried on for use in this reaction without purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a light-yellow liquid.

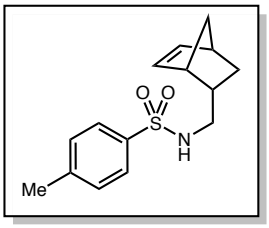
**IR** (Neat): 3281, 2939, 1597, 1498, 1323, 1260, 1152, 1096, 834, 671cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.00-6.96 (m, 2H), 5.72-5.69 (m, 1H), 5.57-5.54 (m, 1H), 4.62 (br, 1H), 3.88 (s, 3H), 2.99-2.92 (m, 2H), 2.68-2.61 (m, 1H), 2.33-2.20 (m, 2H), 2.01-1.94 (m, 1H), 1.60-1.54 (m, 1H), 1.48-1.41 (m, 1H), 1.34-1.28 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.82, 133.79, 131.47, 131.20, 129.22, 114.23, 55.63, 42.74, 41.87, 35.60, 31.89, 29.48;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{19}NO_3S$) from $[M+H]^+$ requires m/z 281.10856, found m/z 281.10849, difference 0.28 ppm.



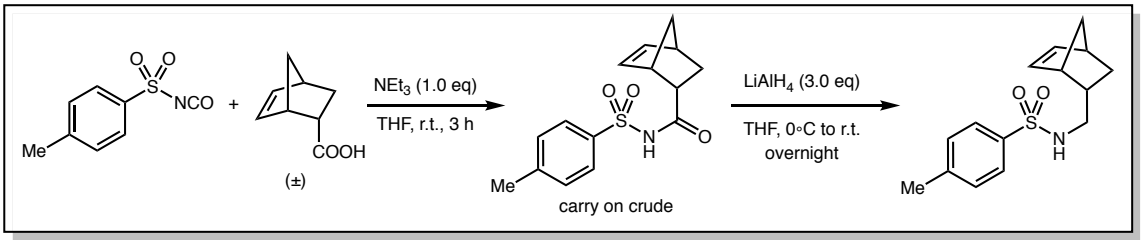

*N*-(2-(cyclohex-2-en-1-yl)-2-methylpropyl)-4-methoxybenzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. 2-(cyclohex-2-en-1-yl)-2-methylpropan-1-amine was synthesized corresponding to an alteration of a reported method,[7] using 3-bromocyclohex-1-ene instead of allyl bromide and carried on crude for use in this reaction without purification. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless liquid.

**IR** (Neat): 3283, 2932, 1597, 1498, 1325, 1259, 1153, 1096, 834, 671cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.00-6.96 (m, 2H), 5.77-5.71 (m, 1H), 5.57-5.53 (m, 1H), 4.46 (br, 1H), 3.88 (s, 3H), 2.65 (d, J = 7.0 Hz, 2H), 2.05-1.99 (m, 1H), 1.96-1.85 (m, 2H), 1.85-1.72 (m, 1H), 1.68-1.63 (m, 1H), 1.48-1.39 (m, 1H), 1.19-1.11 (m, 1H), 0.83 (d, J = 9.0 Hz, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.78, 131.49, 129.21, 127.57, 114.21, 55.62, 51.36, 41.98, 36.16, 25.10, 23.80, 23.26, 22.56, 22.52;
**HRMS** (ESI) exact mass calculated for [M] ($C_{17}H_{25}NO_3S$) from $[M+H]^+$ requires m/z 323.15551, found m/z 323.15593, difference 1.28 ppm.

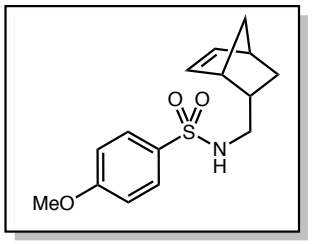



(±)-*N*-(((1*S*,2*S*,4*S*)-bicyclo[2.2.1]hept-5-en-2-yl)methyl)-4-methylbenzenesulfonamide

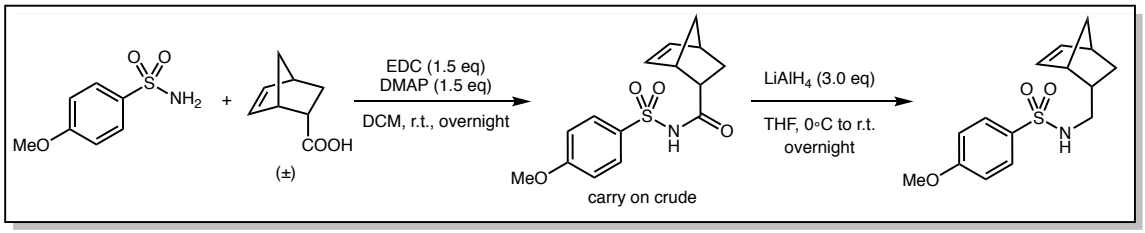



(±)-(1S,2S,4S)-N-tosylbicyclo[2.2.1]hept-5-ene-2-carboxamide was synthesized according to a reported procedure.[9] The crude intermediate was reduced by LAH in the same manner described before. The crude product (~3:1 exo:endo) was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford the exo-substrate as a light-yellow liquid (1.23 g, 29% yield over two steps).

**IR** (Neat): 3279, 2965, 1599, 1425, 1323, 1157, 1094, 815, 667cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.34-7.30 (m, 2H), 6.12-6.09 (m, 1H), 5.79-5.75 (m, 1H), 4.62 (br, 1H), 2.83-2.77 (m, 2H), 2.74-2.70 (m, 1H), 2.61-2.57 (m, 1H), 2.45 (s, 3H), 2.21-2.15 (m, 1H), 1.83-1.78 (m, 1H), 1.45-1.41 (m, 1H), 1.24-1.20 (m, 1H), 0.49-0.45 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 143.31, 137.90, 136.89, 131.64, 129.67, 127.10, 49.44, 47.14, 43.96, 42.33, 38.89, 30.04, 21.55;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 277.11365, found m/z 277.11420, difference 1.99 ppm.



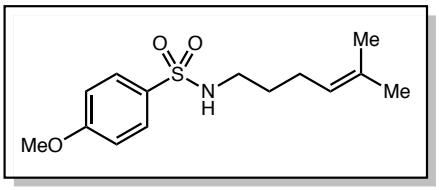

(±)-*N*-(((1*S*,2*S*,4*S*)-bicyclo[2.2.1]hept-5-en-2-yl)methyl)-4-methoxybenzenesulfonamide




(±)-(1S,2S,4S)-N-((4-methoxyphenyl)sulfonyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide was synthesized according to a reported procedure.[10] To an ice-cold THF solution of the crude intermediate (1.0 eq,15 mmol, 4.61g), $LiAlH_4$ (3.0 eq, 45 mmol, 1.71g) was added in small portions. After addition, the reaction was warmed up to room temperature and stirred overnight. The reaction was then cooled in an ice-bath. Next, 1.7mL water, 1.7 mL 15% NaOH(aq) solution and 5.1 mL water were sequentially added dropwise. This was followed by the addition of 2.0 gram of anhydrous magnesium sulfate and then the mixture was stirred for half an hour. The resulting mixture was filtered through a celite

plug to remove the white solid. The filtrate was concentrated under reduced pressure and purified the crude product (~3:1 exo:end), which was then purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford the sulfonamide as a white solid (1.12 g, 25% yield over two steps).

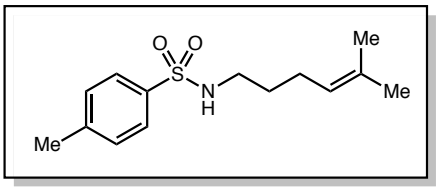
**IR** (Neat): 3278, 2965, 1597, 1498, 1322, 1259, 1152, 1096, 833, 671cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.00-6.96 (m, 2H), 6.11-6.07 (m, 1H), 5.78-5.74 (m, 1H), 4.58 (br, 1H), 3.85 (s, 3H), 2.80-2.73 (m, 2H), 2.70-2.65 (m, 1H), 2.56-2.50 (m, 1H), 2.17-2.10 (m, 1H), 1.79-1.73 (m, 1H), 1.41-1.36 (m, 1H), 1.19-1.16 (m, 1H), 0.45-0.40 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.78, 137.90, 131.64, 131.47, 129.21, 114.24, 55.62, 49.44, 47.11, 43.96, 42.33, 38.84, 30.05;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{19}NO_3S$) from $[M+H]^+$ requires m/z 293.10856, found m/z 293.10852, difference 0.14 ppm.




4-methoxy-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a light-yellow solid.

**IR** (Neat): 3281, 2928, 1710, 1597, 1259, 1154, 834 cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.00-6.97 (m, 2H), 5.02 – 4.98 (m, 1H), 4.32 (br, 1H), 3.88 (s, 3H), 2.93 (q, *J* = 6.5 Hz, 2H), 1.96 (q, *J* = 7.0 Hz, 2H), 1.66 (s, 3H), 1.55 (s, 3H), 1.52-1.46 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.82, 132.84, 131.55, 129.21, 122.92, 114.20, 55.62, 42.90, 29.56, 25.70, 25.08, 17.72.;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12448, difference 0.92 ppm.

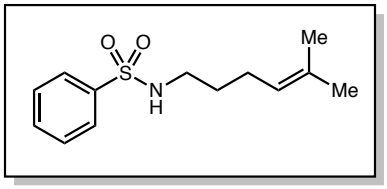



4-methyl-N-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford a light-yellow oil.

**IR** (Neat): 3281, 2926, 1439, 1325, 1158, 1095, 815, 664 cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.77-7.73 (m, 2H), 7.34-7.28 (m, 2H), 5.00 – 4.97 (m, 1H), 4.58 (br, 1H), 2.93 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.95 (q, *J* = 7.0 Hz, 2H), 1.65 (s, 3H), 1.54 (s, 3H), 1.51-1.46 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 143.33, 136.94, 132.77, 129.68, 127.11, 122.95, 42.92, 29.57, 25.69, 25.07, 21.54, 17.69.;

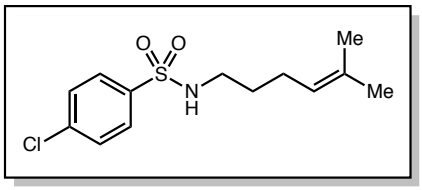
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.12930, found m/z 267.12910, difference 0.74 ppm.



*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford a light-yellow liquid.

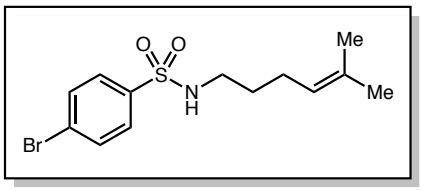
**IR** (Neat): 3283, 2928, 1447, 1325, 1159, 1095, 755, 690 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.60-7.57 (m, 1H), 7.55-7.51 (m, 2H), 5.01 – 4.95 (m, 1H), 4.57 (br, 1H), 2.95 (q, *J* = 7.0 Hz, 2H), 1.95 (q, *J* = 7.0 Hz, 2H), 1.65 (s, 3H), 1.54 (s, 3H), 1.52-1.47 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 139.94, 132.86, 132.59, 129.09, 127.04, 122.88, 42.96, 29.58, 25.69, 25.05, 17.70.;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 253.11365, found m/z 253.11331, difference 1.33 ppm.



4-chloro-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford a light-yellow solid.

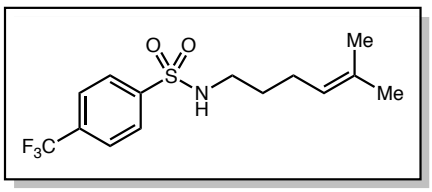
**IR** (Neat): 3283, 2928, 1477, 1328, 1161, 1095, 1085, 827, 753$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.67-7.63 (m, 2H), 5.01 – 4.96 (m, 1H), 4.70 (br, 1H), 2.95 (q, *J* = 7.0 Hz, 2H), 1.96 (q, *J* = 7.0 Hz, 2H), 1.66 (s, 3H), 1.54 (s, 3H), 1.53-1.47 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 139.05, 132.98, 132.38, 128.63, 127.54, 122.76, 42.95, 29.57, 25.70, 25.01, 17.72;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{18}ClNO_2S$) from $[M+H]^+$ requires m/z 287.07468, found m/z 287.07467, difference 0.03 ppm.



4-bromo-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford a light-yellow solid.
**IR** (Neat): 3282, 2926, 1576, 1327, 1160, 1092, 1069, 822, 739$cm^{-1}$;

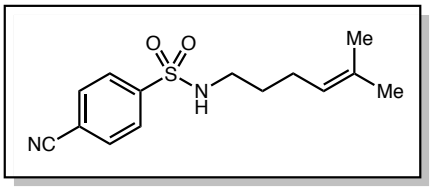
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.50-7.46 (m, 2H), 5.01 – 4.96 (m, 1H), 4.71 (br, 1H), 2.95 (q, *J* = 7.0 Hz, 2H), 1.96 (q, *J* = 7.0 Hz, 2H), 1.66 (s, 3H), 1.54 (s, 3H), 1.53-1.47 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 139.05, 132.98, 132.38, 128.63, 127.54, 122.76, 42.95, 29.58, 25.70, 25.01, 17.72;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{18}BrNO_2S$) from $[M+H]^+$ requires m/z 331.02416, found m/z 331.02450, difference 1.03 ppm.




*N*-(5-methylhex-4-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 15% EtOAc/hexane) to afford a light-yellow solid.

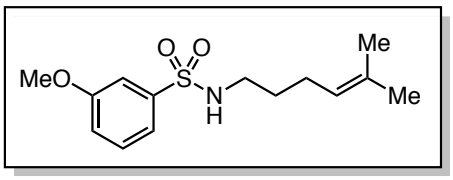
**IR** (Neat): 3287, 2929, 1405, 1323, 1165, 1134, 1063, 843, 711 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 5.01 – 4.95 (m, 1H), 4.70 (br, 1H), 2.99 (q, *J* = 7.0 Hz, 2H), 1.96 (q, *J* = 7.0 Hz, 2H), 1.65 (s, 3H), 1.54 (s, 3H), 1.53-1.48 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 143.66, 134.34 (q, *J* = 33.0 Hz), 133.08, 127.56, 126.30 (q, *J* = 3.7 Hz), 123.23 (q, *J* = 273.2 Hz), 122.65, 43.01, 29.61, 25.66, 24.97, 17.69;
**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ = -63.12;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{18}F_3NO_2S$) from $[M+H]^+$ requires m/z 321.10103, found m/z 321.10057, difference 1.45 ppm.




4-cyano-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a white solid.

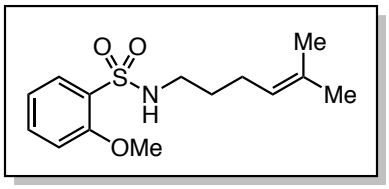
**IR** (Neat): 3264, 2915, 2239, 1434, 1323, 1153, 1089, 845, 675$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.85-7.82 (m, 2H), 5.01-4.97 (m, 1H), 4.72 (br, 1H), 3.01-2.97 (m, 2H), 1.99-1.94 (m, 2H), 1.66 (s, 3H), 1.55-1.48 (m, 5H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 144.43, 133.17, 132.96, 127.67, 122.58, 117.34, 116.34, 43.05, 29.64, 25.70, 24.96, 17.73;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{18}N_2O_2S$) from $[M+H]^+$ requires m/z 278.10890, found m/z 278.10904, difference 0.51 ppm.




3-methoxy-N-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a light-yellow oil.

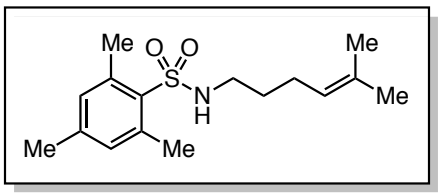
**IR** (Neat): 3282, 2929, 1598, 1478, 1431, 1316, 1245, 1154, 1038, 685cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.46-7.40 (m, 2H), 7.39-7.38 (m, 1H), 7.11-7.09 (m, 1H), 5.01-4.98 (m, 1H), 4.63 (br, 1H), 3.86 (s, 3H), 2.96 (q, *J* = 6.7 Hz, 2H), 1.96 (q, *J* = 7.3 Hz, 2H), 1.65 (s, 3H), 1.54 (s, 3H), 1.53-1.47 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 159.93, 141.05, 132.84, 130.14, 122.89, 119.19, 118.99, 111.71, 55.66, 43.01, 29.58, 25.68, 25.05, 17.69;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12387, difference 1.23 ppm.




2-methoxy-N-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a light-yellow oil.

**IR** (Neat): 3302, 2931, 1592, 1480, 1325, 1279, 1157, 1071, 1019, 758cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.55 (ddd, 1H), 7.08 (td, *J* = 7.6, 1.0 Hz, 1H), 7.04 (dd, *J* = 8.4, 0.9 Hz, 1H), 4.98 (tdt, *J* = 7.2, 2.8, 1.4 Hz, 1H), 4.90 (t, *J* = 6.3 Hz, 1H), 3.98 (s, 3H), 2.87 (q, *J* = 6.8 Hz, 2H), 1.95 (q, *J* = 7.3 Hz, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 1.51-1.45 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 156.09, 134.44, 132.68, 130.46, 127.32, 122.92, 120.73, 112.04, 56.35, 43.12, 29.59, 25.69, 25.02, 17.70;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12468, difference 1.66 ppm.

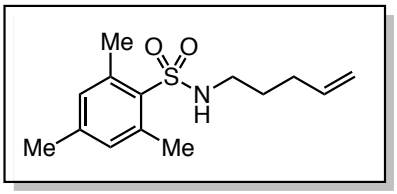



2,4,6-trimethyl-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 16% EtOAc/hexane) to afford a light-yellow oil.

**IR** (Neat): 3304, 2929, 1604, 1447, 1320, 1151, 1082, 851cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 6.96 (s, 2H), 5.01 – 4.93 (m, 1H), 4.53 (br, 1H), 2.89 (q, *J* = 6.8 Hz, 2H), 2.64 (s, 6H), 2.30 (s, 3H), 1.93 (q, *J* = 7.3 Hz, 2H), 1.65 (s, 3H), 1.54 (s, 3H), 1.52 – 1.42 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 142.09, 139.06, 133.65, 132.79, 131.94, 122.97, 42.29, 29.59, 25.68, 25.13, 22.98, 20.94, 17.68;

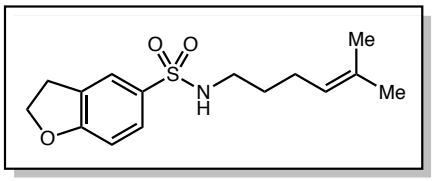
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 295.16060, found m/z 295.16046, difference 0.49 ppm.




2,4,6-trimethyl-N-(pent-4-en-1-yl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless oil.

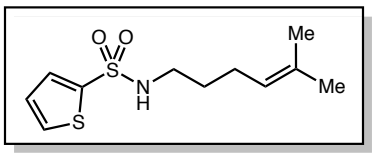
**IR** (Neat): 3306, 2938, 1604, 1452, 1320, 1153, 1083, 852, 654$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 6.96 (s, 2H), 5.78 – 5.62 (m, 1H), 5.03 – 4.90 (m, 2H), 4.47 (s, 1H), 2.91 (q, *J* = 6.8 Hz, 2H), 2.64 (s, 6H), 2.30 (s, 3H), 2.10 – 1.96 (m, 2H), 1.64 – 1.49 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 142.15, 139.05, 137.24, 133.62, 131.96, 115.61, 42.04, 30.77, 28.68, 22.98, 20.94;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.12930, found m/z 267.12893, difference 1.37 ppm.




*N*-(5-methylhex-4-en-1-yl)-2,3-dihydrobenzofuran-5-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a light-yellow oil.

**IR** (Neat): 3280, 2923, 1606, 1486, 1328, 1241, 1144, 1066, 899, 821$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.70-7.67 (m, 1H), 7.66-7.64 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.02-4.98 (m, 1H), 4.68 (t, *J* = 8.5 Hz, 2H), 4.49 (br, 1H), 3.27 (t, *J* = 8.5 Hz, 2H), 2.92 (q, *J* = 6.5 Hz, 2H), 1.99-1.93 (m, 2H), 1.66 (s, 3H), 1.55 (s, 3H), 1.53-1.47 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 163.70, 132.75, 131.43, 128.66, 128.29, 124.38, 122.99, 109.44, 72.26, 42.90, 29.58, 29.12, 25.70, 25.11, 17.70;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{20}NO_3S$) from $[M+H]^+$ requires m/z 295.12421, found m/z 295.12432, difference 0.37 ppm.

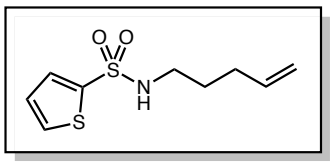



*N*-(5-methylhex-4-en-1-yl)thiophene-2-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 16% EtOAc/hexane) to afford a colorless liquid.

**IR** (Neat): 3284, 2967, 1406, 1328, 1154, 1092, 1017, 721, 667$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.58 (m, 2H), 7.11-7.08 (m, 1H), 5.03-5.00 (m, 1H), 4.71 (br, 1H), 3.06-3.01 (m, 2H), 2.01-1.97 (m, 2H), 1.66 (s, 3H), 1.56-1.51 (m, 5H);

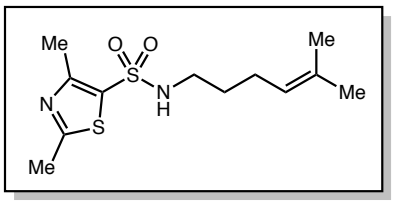
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 140.94, 132.93, 132.05, 131.73, 127.38, 122.87, 43.21, 29.45, 25.71, 25.08, 17.72;
**HRMS** (ESI) exact mass calculated for [M] ($C_{11}H_{17}NO_2S_2$) from $[M+H]^+$ requires m/z 259.07007, found m/z 259.07053, difference 1.78 ppm.



N-(pent-4-en-1-yl)thiophene-2-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless liquid.

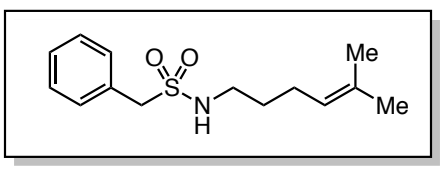
**IR** (Neat): 3284, 2936, 1406, 1326, 1154, 1017, 915, 721, 667cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.67 – 7.52 (m, 2H), 7.15 – 7.01 (m, 1H), 5.91 – 5.59 (m, 1H), 5.10 – 4.91 (m, 2H), 4.49 (s, 1H), 3.06 (d, *J* = 6.9 Hz, 2H), 2.16 – 1.98 (m, 2H), 1.71 – 1.56 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 140.94, 137.11, 132.12, 131.80, 127.38, 115.77, 42.95, 30.69, 28.58.
**HRMS** (ESI) exact mass calculated for [M] ($C_9H_{13}NO_2S_2$) from $[M+H]^+$ requires m/z 231.03877, found m/z 231.03838, difference 1.7 ppm.



2,4-dimethyl-*N*-(5-methylhex-4-en-1-yl)thiazole-5-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a light-yellow oil.

**IR** (Neat): 3290, 2926, 1440, 1332, 1157, 1083, 652cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.05-5.01 (m, 1H), 4.82 (br, 1H), 3.06-3.02 (m, 2H), 2.69 (s, 3H), 2.61 (s, 3H), 2.03-1.98 (m, 2H), 1.68 (s, 3H), 1.58-1.52 (m, 5H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 168.51, 155.73, 133.06, 129.66, 122.74, 42.99, 29.52, 25.70, 25.07, 19.42, 17.73, 16.36;
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{20}N_2O_3S_2$) from $[M+H]^+$ requires m/z 288.09662, found m/z 288.09646, difference 0.56 ppm.

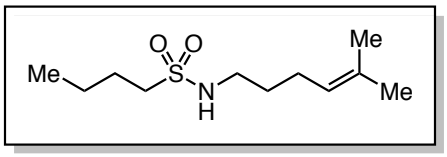


N-(5-methylhex-4-en-1-yl)-1-phenylmethanesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 16% EtOAc/hexane) to afford a white solid.

**IR** (Neat): 3230, 2919, 1456, 1305, 1133, 1068, 909, 781, 732, 694cm$^{-1}$;

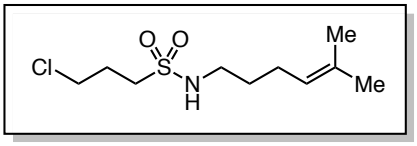
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.44 – 7.30 (m, 5H), 5.07 – 4.97 (m, 1H), 4.24 (br, 2H), 4.11 (s, 1H), 2.97 (q, *J* = 6.8 Hz, 2H), 1.97 (q, *J* = 7.3 Hz, 2H), 1.68 (s, 3H), 1.59 – 1.46 (m, 5H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 132.86, 130.58, 129.47, 128.85, 128.73, 122.87, 58.65, 43.42, 30.36, 25.72, 25.01, 17.75;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+Na]^+$ requires m/z 267.12930, found m/z 267.12883, difference 1.76 ppm.



N-(5-methylhex-4-en-1-yl)butane-1-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a colorless oil.

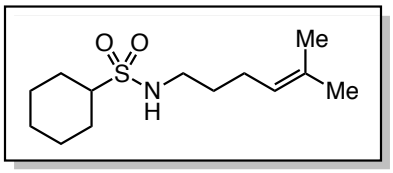
**IR** (Neat): 3285, 2932, 1440, 1319, 1142, 1080, 840$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 5.14 – 5.03 (m, 1H), 4.50 (br, 1H), 3.15 – 3.05 (m, 2H), 3.05 – 2.94 (m, 2H), 2.05 (q, *J* = 7.4 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.69 (s, 3H), 1.64 – 1.56 (m, 5H), 1.51 – 1.41 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 132.81, 122.96, 52.27, 42.92, 30.36, 25.72, 25.66, 25.08, 21.56, 17.75, 13.62
**HRMS** (ESI) exact mass calculated for [M] ($C_{11}H_{24}NO_2S$) from $[M+H]^+$ requires m/z 233.14495, found m/z 233.14482, difference 0.56 ppm.



3-chloro-N-(5-methylhex-4-en-1-yl)propane-1-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a light-yellow solid.

**IR** (Neat): 3269, 2967, 1432, 1311, 1138, 1121, 1064, 915, 794, 719$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 5.15 – 5.02 (m, 1H), 4.50 – 4.35 (m, 1H), 3.69 (t, *J* = 6.2 Hz, 2H), 3.19 (d, *J* = 6.3 Hz, 2H), 3.12 (q, *J* = 6.7 Hz, 2H), 2.34 – 2.23 (m, 2H), 2.06 (q, *J* = 7.2 Hz, 2H), 1.70 (d, *J* = 1.4 Hz, 3H), 1.66 – 1.54 (m, 5H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 133.02, 122.82, 49.77, 43.00, 42.87, 30.31, 26.92, 25.73, 25.07, 17.79.
**HRMS** (ESI) exact mass calculated for [M] ($C_{10}H_{20}NO_2SCl$) from $[M+H]^+$ requires m/z 253.09033, found m/z 253.08983, difference 1.96 ppm.

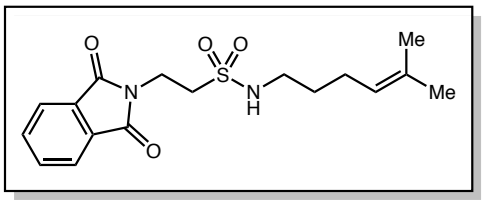


N-(5-methylhex-4-en-1-yl)cyclohexanesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient

from 0% to 15% EtOAc/hexane) to afford a colorless oil.

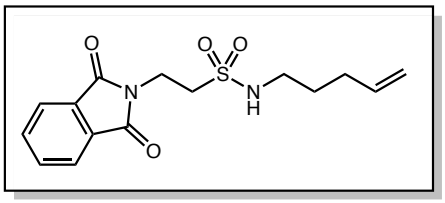
**IR** (Neat): 3286, 2931, 2857, 1450, 1312, 1141, 1082, 894cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 5.16 – 5.00 (m, 1H), 4.25 (br, 1H), 3.10 (t, *J* = 6.7 Hz, 2H), 2.91 – 2.81 (m, 1H), 2.18 – 2.12 (m, 2H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.64 – 1.56 (m, 5H), 1.56 – 1.44 (m, 2H), 1.33 – 1.15 (m, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 132.76, 123.03, 61.16, 43.26, 30.70, 26.47, 25.72, 25.21, 25.16, 25.12, 17.76;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 259.16060, found m/z 259.16056, difference 0.14 ppm.




2-(1,3-dioxoisoindolin-2-yl)-*N*-(5-methylhex-4-en-1-yl)ethane-1-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 10% to 40% EtOAc/hexane) to afford a white solid.

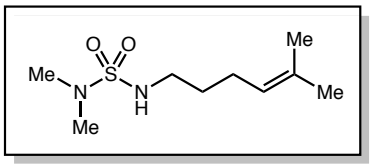
**IR** (Neat): 3296, 2930, 1709, 1397, 1322, 1143, 1084, 867, 718cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.76-7.72 (m, 2H), 5.09-5.05 (m, 1H), 4.78 (br, 1H), 4.13 (t, *J* = 6.0 Hz, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 3.13 (q, *J* = 6.5 Hz, 2H), 2.09-2.04 (m, 2H), 1.69-1.60 (m, 8H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 168.10, 134.32, 132.98, 131.81, 123.63, 122.81, 49.02, 42.96, 32.85, 30.39, 25.74, 25.06, 17.79;
**HRMS** (ESI) exact mass calculated for [M] ($C_{17}H_{21}N_2O_4S$) from $[M+H]^+$ requires m/z 350.13003, found m/z 350.12988, difference 0.42 ppm.




2-(1,3-dioxoisoindolin-2-yl)-N-(pent-4-en-1-yl)ethane-1-sulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 10% to 40% EtOAc/hexane) to afford a colorless liquid.

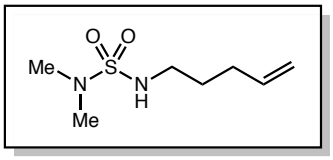
**IR** (Neat): 3298, 2939, 1710, 1397, 1323, 1144, 1085, 718cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.89 – 7.84 (m, 2H), 7.77 – 7.71 (m, 2H), 5.85 – 5.70 (m, 1H), 5.10 – 4.98 (m, 2H), 4.86 (s, 1H), 4.16 – 4.08 (m, 2H), 3.41 – 3.35 (m, 2H), 3.19 – 3.12 (m, 2H), 2.22 – 2.10 (m, 2H), 1.74 – 1.65 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 168.13, 137.10, 134.35, 131.80, 123.65, 115.83, 49.03, 42.68, 32.85, 30.65, 29.41
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{18}N_2O_4S$) from $[M+H]^+$ requires m/z 322.09873, found m/z 322.09805, difference 2.1 ppm.



*N'*-(5-methylhex-4-en-1-yl)-N,N-dimethylsulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 20% EtOAc/hexane) to afford a light-yellow liquid.

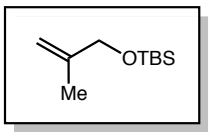
**IR** (Neat): 3297, 2929, 1447, 1323, 1146, 952, 703cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 5.11 – 5.06 (m, 1H), 4.30 (br, 1H), 3.05 (q, *J* = 7.0 Hz, 2H), 2.80 (s, 3H), 2.04 (q, *J* = 7.0 Hz, 2H), 1.69 (s, 3H), 1.61-1.56 (m, 5H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 132.74, 123.07, 43.34, 38.05, 29.91, 25.72, 25.19, 17.75.;
**HRMS** (ESI) exact mass calculated for [M] ($C_9H_{20}N_2O_2S$) from $[M+H]^+$ requires m/z 220.12455, found m/z 220.12490, difference 1.60 ppm.



*N'*-(4-hexen-1-yl)-N,N-dimethylsulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a colorless liquid.

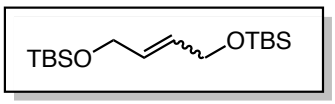
**IR** (Neat): 3302, 2934, 1457, 1324, 1147, 953, 704cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 5.87 – 5.72 (m, 1H), 5.12 – 4.95 (m, 2H), 4.05 (s, 1H), 3.14 – 3.01 (m, 2H), 2.81 (s, 6H), 2.16 – 2.10 (m, 2H), 1.70 – 1.62 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 137.31, 115.67, 43.14, 38.07, 30.83, 28.99;
**HRMS** (ESI) exact mass calculated for [M] ($C_7H_{17}N_2O_2S$) from $[M+H]^+$ requires m/z 192.09325, found m/z 192.09313, difference 0.63 ppm.



*tert*-butyldimethyl((2-methylallyl)oxy)silane

The title compound was synthesized according to a published procedure[11].

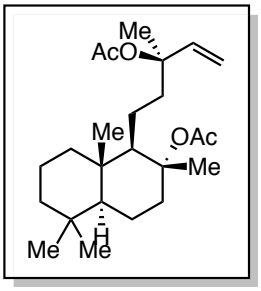
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 4.98 (s, 1H), 4.80 (s, 1H), 4.03 (s, 2H), 1.70 (s, 3H), 0.92 (s, 9H), 0.07 (s, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 145.03, 109.54, 67.20, 26.32, 19.36, 18.81, -4.97.;



2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodec-6-ene

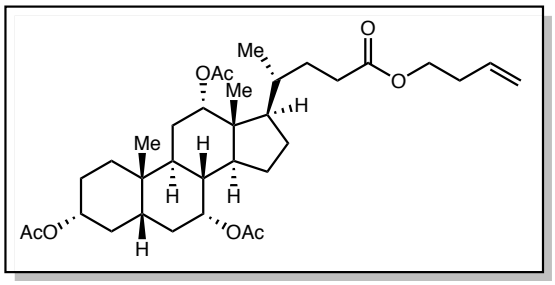
The title compound was synthesized according to a published procedure[12]. Used as a mixture of 3:1 of E:Z ratio.

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 5.61-5.52 (m, 1.5 H), 5.12-5.21 (m, 0.5 H), 4.15-4.25 (m, 1H), 3.52-3.65 (m, 3H), 0.89 (s, 4.5 H), 0.81 (s, 13.5 H), 0.07 (3 H), 0.01 (s, 9H)

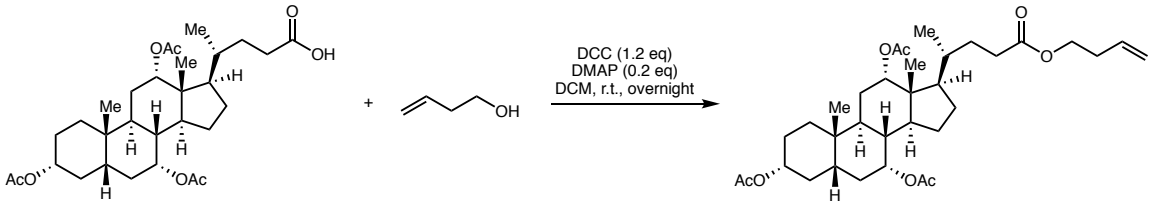


(*R*)-5-((1*R*,2*R*,4a*S*,8a*S*)-2-acetoxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)-3-methylpent-1-en-3-yl acetate

The title compound was synthesized according to a published procedure[13] with minor alteration. The solution of (-)-Sclareol (3.00 g, 10 mmol) and *N*,*N*-dimethylaniline (5 mL) in $CH_2Cl_2$ (10 mL) was added acetyl chloride (4.2 mL, 60 mmol) at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred overnight. The product was then extracted with diethyl ether three times. The combined organic phase was washed with 1.0 M HCl twice followed by a brine wash. The organic phase was then dried over $Na_2SO_4$ and filtered. Evaporation of the organic solvent gave a crude product, which was purified on silica gel to give a white solid (3.52 g, 90%). All characterization data are consistent with reported data.



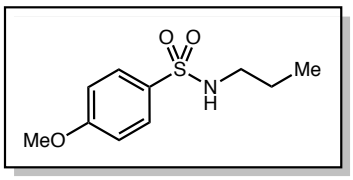
(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((R)-5-(but-3-en-1-yloxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate




To a round bottle flask charged with a stir bar, (R)-4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-triacetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoic acid (5.0 mmol, 2.74 g),[15] DCM (25 mL), 3-buten-1-ol (6.0 mmol, 0.433 g), and DMAP (1.0 mmol, 0.122 g) were added in sequence. The flask was cooled in an ice-bath, and DCC (6.0 mmol, 1.24 g) was added. The reaction was warmed to room temperature and stirred overnight. The reaction was quenched by 1M HCl (*aq*) (50 mL) and filtered through celite. The water phase was extracted with 50 mL DCM three times. The combined organic phase was dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the product was purified by silica gel chromatography (gradient from 10% to 35% EtOAc/hexane) to afford a white solid (1.2 g, 40%).

**IR** (Neat): 2944, 1731, 1377, 1239, 1023, 731 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 5.82-5.74 (m, 1H), 5.13-5.06 (m, 3H), 4.91 (d, *J* = 3.5 Hz, 1H), 4.61-4.54 (m, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.40-2.31 (m, 3H), 2.23-2.17 (m, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.05-2.01 (m, 5H), 1.98-1.22 (m, 20H), 0.92 (s, 3H), 0.81 (d, *J* = 6.5 Hz, 3H), 0.73 (s, 3H);

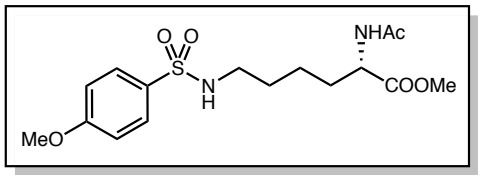
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 174.07, 170.54, 170.39, 134.03, 117.20, 75.40, 74.10, 70.70, 63.36, 47.42, 45.06, 43.40, 40.94, 37.74, 34.70, 34.62, 34.59, 34.34, 33.09, 31.25, 31.12, 30.79, 28.90, 27.19, 26.90, 25.59, 22.81, 22.58, 21.65, 21.52, 21.47, 17.50, 12.25;
**HRMS** (ESI) exact mass calculated for [M] ($C_{34}H_{52}O_8$) from $[M+Na]^+$ requires m/z 588.36622, found m/z 588.36500, difference 2.07 ppm.




4-methoxyl-*N*-propylbenzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a white solid.

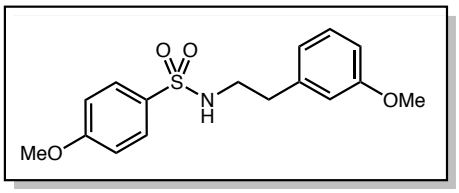
**IR** (Neat): 3282, 2967, 1597, 1498, 1322, 1259, 1153, 1095, 834 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.00-6.96 (m, 2H), 4.57 (br, 1H), 3.87 (s, 3H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.52-1.45 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.80, 131.58, 129.20, 114.21, 55.62, 44.93, 22.90, 11.15;
**HRMS** (ESI) exact mass calculated for [M] ($C_{10}H_{15}NO_3S$) from $[M+H]^+$ requires m/z 229.07726, found m/z 229.07689, difference 1.64 ppm.




methyl N2-acetyl-N6-tosyl-L-lysinate

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 20% EtOAc/hexane to 70% EtOAc/hexane) to afford a light-yellow liquid.

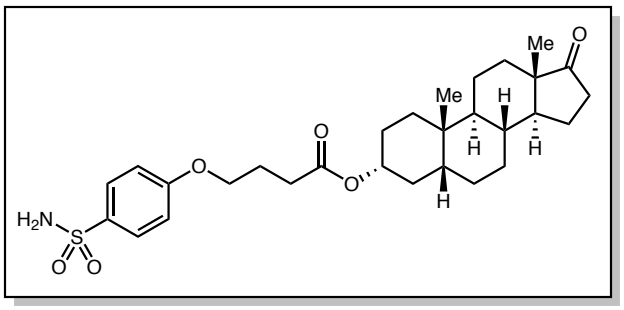
**IR** (Neat): 3281, 2949, 1739, 1656, 1597, 1498, 1301, 1258, 1150, 1095, 1024, 835 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.00-6.97 (m, 2H), 6.26 (br, 1H), 4.93 (br, 1H), 4.58-4.54 (m, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 2.93-2.87 (m, 2H), 2.03 (s, 3H), 1.82-1.75 (m, 1H), 1.67-1.60 (m, 1H), 1.56-1.45 (m, 2H), 1.40-1.31 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 172.99, 170.21, 162.82, 131.46, 129.13, 114.25, 55.63, 52.47, 51.81, 42.58, 31.82, 28.78, 23.16, 22.03;
**LC-MS** (ESI) exact mass calculated for [M] ($C_{16}H_{24}N_2O_6S$) from $[M+H]^+$ requires m/z 372.1, found m/z 372.1.



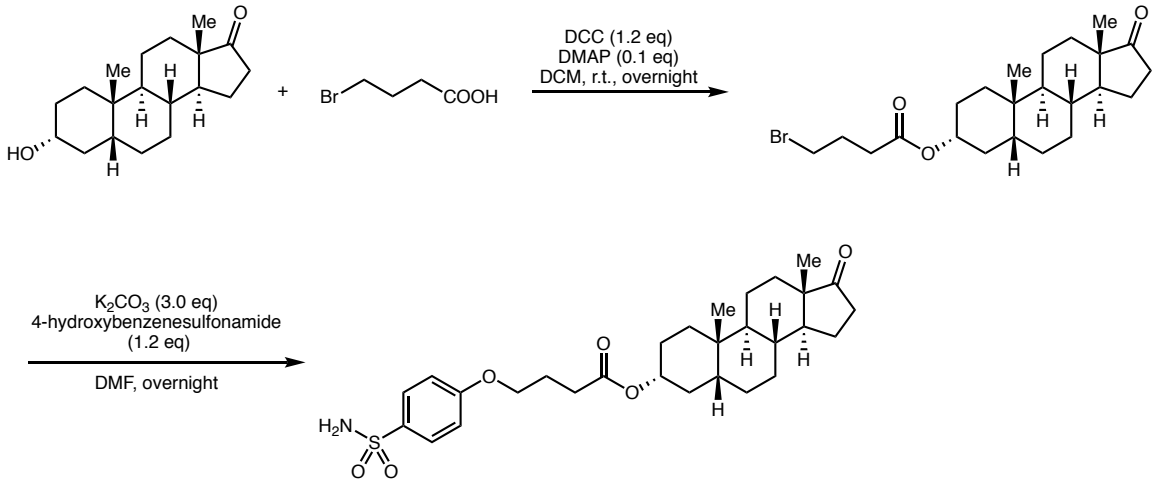

4-methoxy-N-(3-methoxyphenethyl)benzenesulfonamide

The title sulfonamide was synthesized following the general procedure found above. The title sulfonamide was purified by silica gel chromatography (gradient from 0% to 25% EtOAc/hexane) to afford a light-yellow liquid.

**IR** (Neat): 3279, 2943, 1596, 1497, 1322, 1257, 1150, 1095, 834 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.97-6.93 (m, 2H), 6.77-6.74 (m, 1H), 6.68-6.65 (m, 1H), 6.61-6.60 (m, 1H), 4.49 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.19 (q, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.0 Hz, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.84, 159.84, 139.27, 131.37, 129.76, 129.20, 121.00, 114.41, 114.23, 112.12, 55.62, 55.15, 44.08, 35.74;
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{19}NO_4S$) from $[M+H]^+$ requires m/z 321.10348, found m/z 321.10333, difference 0.47 ppm.



(3R,5R,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4-sulfamoylphenoxy)butanoate




To a round bottle flask charged with a stir bar, (3*R*,5*R*,8*R*,9*S*,10*S*,13*S*,14*S*)-3-hydroxy-10,13-dimethylhexadecahydro-17*H*-cyclopenta[a]phenanthren-17-one (10.0 mmol, 2.76 g), DCM (50 mL), 4-bromobutanoic acid (12.0 mmol, 2.00 g) and DMAP (1.0 mmol, 0.122 g) were added in sequence. The flask was cooled in an ice-bath, and DCC (12.0 mmol, 2.48 g) was added. The reaction was warmed to room temperature and stirred overnight. The reaction was quenched with 1M HCl (aq.) (50 mL) and filtered through celite. The aqueous phase was extracted with 50 mL DCM three times. The combined organic phase was dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the crude product was carried on without further purification.

To a flame-dried round bottle flask charged with a stir bar, 4-hydroxybenzenesulfonamide (12 mmol, 2.08 g) and dry DMF (40 mL) were added in sequence. After the reaction was cooled in an ice-bath, $K_2CO_3$ (30 mmol, 4.14 g) was

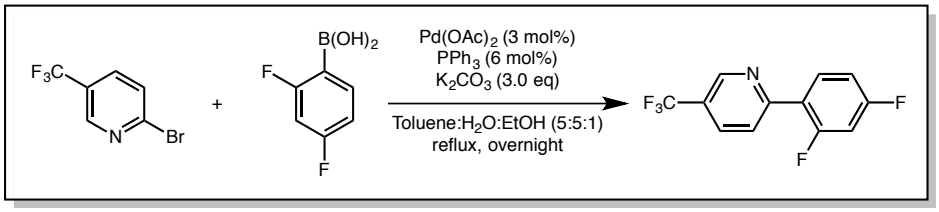
added in small portions and the reaction was stirred for 30 min at 0°C. Then the solution of crude (3*R*,5*R*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-bromobutanoate in 10 mL of DMF was added slowly, using another 2 mL of DMF to transfer completely. The reaction was warmed gradually to room temperature and stirred over night. The reaction was quenched by adding 250 mL of water and extract by 50 mL ether four times. The combined organic phase was washed with brine three times and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum to afford the crude product, which was further purified by silica gel chromatography (gradient from 0 to 50% EtOAc/hexane) to afford a white solid (1.8 g, 34% yield over two steps).

**IR** (Neat): 3259, 2936, 1727, 1597, 1335, 1255, 1158, 833, 731 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.87-7.84 (m, 2H), 6.97-6.94 (m, 2H), 4.84 (br, 2H), 4.75-4.69 (m, 1H), 4.07 (t, *J* = 6.0 Hz, 2H), 2.50-2.41 (m, 3H), 2.15-2.03 (m, 3H), 1.96-1.90 (m, 1H), 1.83-1.73 (m, 4H), 1.68-1.45 (m, 5H), 1.41-1.17 (m, 7H), 1.07-0.94 (m, 2H), 0.86 (s, 3H), 0.85 (s, 3H), 0.74-0.69 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 221.36, 172.50, 162.22, 133.67, 128.62, 114.69, 73.76, 67.24, 54.28, 51.35, 47.80, 44.64, 36.68, 35.86, 35.65, 35.02, 33.98, 31.51, 30.93, 30.80, 28.27, 27.44, 24.44, 21.78, 20.47, 13.83, 12.23;
**HRMS** (ESI) exact mass calculated for [M] ($C_{29}H_{41}NO_6S$) from $[M+Na]^+$ requires m/z 531.26546, found m/z 531.26509, difference 0.29 ppm.

# III. Synthesis and Characterization of Photocatalyst

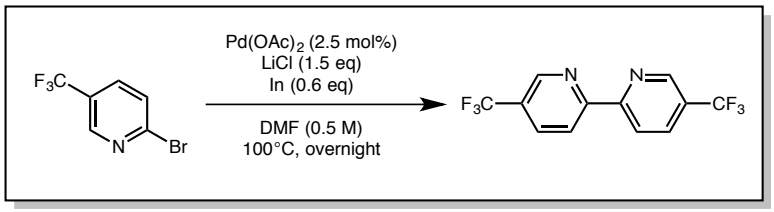
## Synthesis of ligand

2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyridine




To a flame-dried 250 three-neck round bottom flask charged with a magnetic stir bar was added *2-bromo-5-(trifluoromethyl)pyridine* (6.78 g, 30 mmol, 1.0 eq), *(2,4-difluorophenyl)boronic acid* (5.68 g, 36 mmol, 1.2 eq), $Pd(OAc)_2$ (202 mg, 0.90 mmol, 3 mol %), $PPh_3$ (472 mg, 1.80 mmol, 6 mol %), and $K_2CO_3$ (12.44 g, 90 mmol, 3.0 eq). The flask was evacuated and backfilled with Ar three times. Toluene (40 mL), water (40 mL) and Ethanol (8.0 mL) were added and reaction was heated to reflux under severe stirring overnight. The reaction was cooled to room temperature and 100 mL water was added to quench the reaction. The organic phase was separated and saved while the aqueous phase was extracted with 40 mL of ether three times. The combined organic phase was washed with brine three times. The organic phase was collect and dried over $Na_2SO_4$ and the solvent was removed under vacuum. The crude product was purified by silica gel flash chromatography (gradient from 0% to 12% EtOAc/hexane) to afford a light-yellow solid in 86% yield. Characterization data are consistent with a prior report.[16]

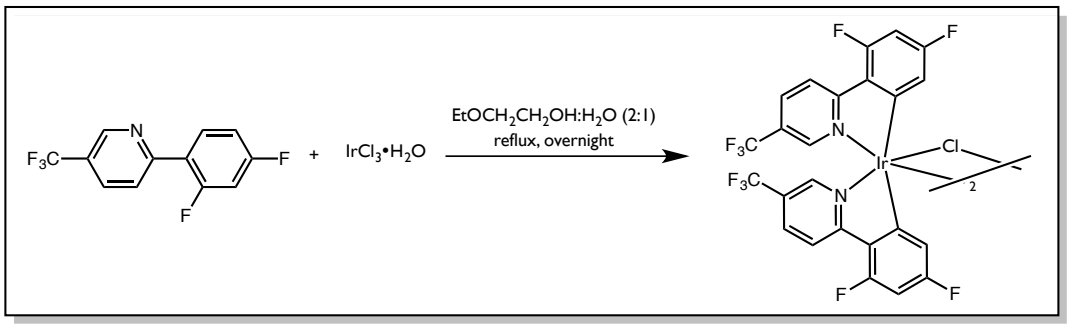
5,5'-bis(trifluoromethyl)-2,2'-bipyridine




The title compound was synthesize according to a prior report with which all characterization data are consistent.[17] In an oven-dried 250-mL round-bottomed flask, 2-bromo-5-(trifluoromethyl)pyridine (30.0 mmol, 6.78 g), $Pd(OAc)_2$ (2.5 mol%, 168 mg, 0.75 mmol), and indium powder (0.6 eq., 2.07 g, 18.0 mmol) were added under normal atmosphere. Next, this was followed by addition of LiCl (1.5 eq., 1.91 g, 45 mmol) in a glove box. DMF (60 mL) was added under argon, and the reaction was heated at 100°C overnight. After completion, the reaction was cooled to room temperature. 180 mL of water and 60 mL of ether were added and the mixture was filtered through a celite pad with three rinses using 40 mL ether. The filtrate was transferred to a separatory funnel and the aqueous layer was extracted with 40 mL ether three times. The organic layers were combined and washed with 50 mL brine three times and dried over $Na_2SO_4$. The

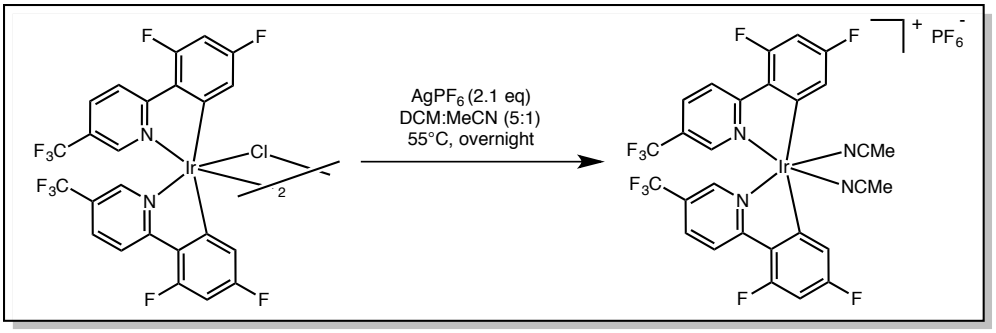
solvent was removed and the crude product was purified by silica flash chromatography to afford the product as a white solid (1.5 g, 34% yield).

**Synthesize [Ir(dF-CF$_3$-ppy)$_2$Cl]$_2$-dimer**




To a flame-dried 250 mL three necked round bottom flask with reflux condenser a magnetic stir bar was added $IrCl_3$•$H_2O$ (1.90 g, 6.0 mmol, 1.0 eq.) and 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyridine (3.19 g, 12.3 mmol, 2.05 eq.). The flask was evacuated and backfilled with Ar three times. 2-ethoxyethanol (80 mL) and water (40 mL) were added and degassed for half an hour. The reaction was heated to 135 °C and the reaction was stirred overnight. Upon completion, the reaction was cooled to room temperature and precipitation was observed. The precipitate was filtered and washed with 100 mL water three times. The powder was dried under air flow and carried on without further purification (3.60 g, 81% yield).

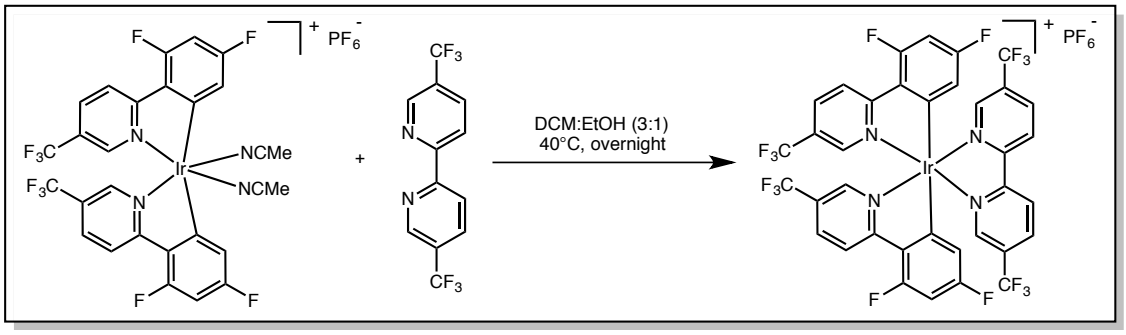
**Synthesize cationic [Ir(dF-CF$_3$-ppy)$_2$(NCMe)$_2$]$^+$PF$_6$**




To a 250mL three-necked round bottom flask charged with stir bar and fitted with a condenser, [Ir(dF-CF$_3$-ppy)$_2$Cl]$_2$-dimer (3.60 g, 2.42 mmol, 1.0 eq) and $AgPF_6$ (super hydroscopic, handle in a glove box or weight very fast in air, 1.25 g, 4.96 mmol, 2.05 eq) were added. The reaction vessel was placed under vacuum and refilled with Argon three times. Dry dichloromethane (60 mL) and acetonitrile (20 mL) were added to the reaction, which was heated to reflux overnight in a 55 °C oil bath. Upon completion. the reaction was cooled to room temperature. The reaction was filtered through a celite pad to remove the AgCl precipitate. The solution was concentrated to give a yellow solid, which was then partially dissolve in 20 mL warm 1:1 DCM:acetone. The mixture was allowed to

cool at which point pentane was added to afford a light yellow precipitate which was obtained via filtration and used without further purification (4.29 g, quant.).

**Synthesize $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)_2]^+PF_6$**

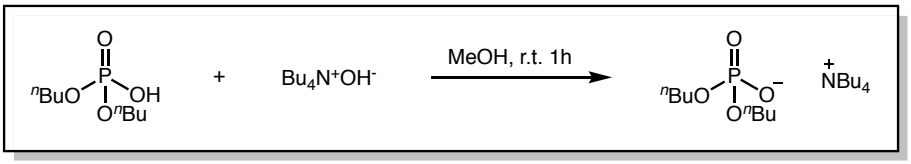



In a 100 mL three-necked round bottom flask charged with stir bar and affixed with a condenser, $[Ir(dF\text{-}CF_3\text{-}ppy)_2(NCMe)_2]PF_6$ (4.29 g, 5.03 mmol, 1 eq) and 5,5'-bis(trifluoromethyl)-2,2'-bipyridine (1.62 g, 5.53 mmol, 1.1 eq) were added, followed by dichloromethane (60 mL) and ethanol (20 mL). The reaction was heated to 40 °C and stirred overnight. Upon completion, the reaction was cooled to room temperature and the reaction was filtered through celite using acetone to wash away the iridium complex from the solid. The filtrate was then concentrated under vacuum and the crude product was purified by silica gel flash chromatography gradient with 0 to 25% Acetone/DCM to afford a yellow solid. The product was recrystallized from acetone and pentane to afford a yellow crystal as the pure photocatalyst (5.76 g, 64% yield).

**$^1$H NMR** (500 MHz, $d_6$-Acetone) δ = 9.29 (d, $J$ = 8 Hz, 1H), 8.83 (d, J = 8.5 Hz, 1H), 8.61 (dd, $J^1$ = 9 Hz, $J^2$ = 2.5 Hz, 1H), 8.55 (s, 1H), 8.41 (dd, $J^1$ = 8.5 Hz, $J^2$ = 2 Hz, 1H), 8.19 (s, 1H), 6.91 (t, $J$ = 11 Hz, 1H), 5.98 (dd, $J^1$ = 8.5 Hz, $J^2$ = 2.5 Hz, 1H).
**$^{13}$C NMR** (126 MHz, $d_6$-Acetone) δ = 168.20 (d, $J$ = 6.6 Hz), 166.19 (d, $J$ = 12.6 Hz), 164.14 (d, $J$ = 12.6 Hz), 162.10 (d, $J$ = 13.4 Hz), 159.27, 153.58 (d, $J$ = 7.1 Hz), 149.65, 148.21 (q, $J$ = 4.7 Hz), 139.31 (d, $J$ = 3.4 Hz), 138.50 (d, $J$ = 3.4 Hz), 131.58 (q, $J$ = 34.8 Hz), 128.01, 126.37 (q, $J$ = 34.3 Hz), 124.92 (d, $J$ = 21.0 Hz), 124.04, 121.86, 115.91 (d, $J$ = 18.1 Hz), 100.69 (t, $J$ = 27.1 Hz).
**$^{19}$F NMR** (282 MHz, $d_6$-Acetone) δ = -63.57 (d, $J$ = 107.2 Hz, 12F), -72.58 (d, $J$ = 705 Hz, 6F), -104.47 (m, 2F), -107.88 (t, $J$ = 14.1 Hz, 2F).
**$^{31}$P NMR** (121 MHz, $d_6$-Acetone) δ = -144.25 (hept, $J$ = 704.2 Hz).
**HRMS (ESI)** exact mass calculated for $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)_2]^+$ ($C_{36}H_{16}F_{16}IrN_4$) requires m/z 1001.07432, found m/z 1001.07398, difference 0.66 ppm.

# IV. Synthesis and Characterization of Phosphate and TRIP Thiol

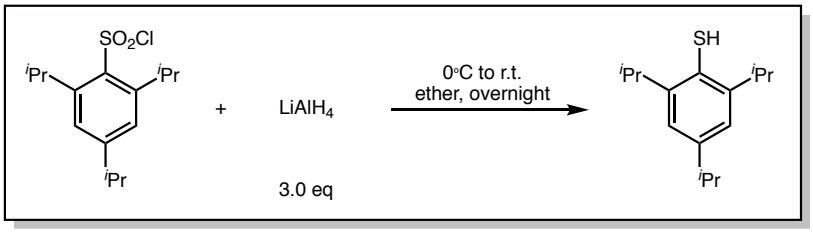
Synthesis of phosphate:




In a 100 mL flame-dried round bottom flask charged with a stir bar, dibutyl phosphoric acid (1.0 eq, 20 mmol, 4.20 g) was added, followed by the addition of 10 mL dry MeOH. The reaction was cooled to 0°C in an ice bath and 20 mL 1M tetrabutylammonium hydroxide methanol solution was added slowly. After addition, the reaction was warmed to room temperature and was stirred for an hour. After the reaction was completed, solvent was removed under vacuum. The reaction mixture was keep under vacuum and heat up in a 60°C oil bath for three days with constant agitation to remove the rest of water as much as possible. After the product forms a white solid, the flask was stored in a glove box under nitrogen (yield: 98%).

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 3.85-3.80 (m, 4.2H), 3.42-3.35 (m, 8H), 1.70-1.60 (m, 12.4H), 1.49-1.35 (m, 12.4 H), 0.99 (t, *J* = 7.4 Hz, 12H), 0.89 (t, *J* = 7.4 Hz, 6.5H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 64.58, 58.85, 33.15, 24.19, 19.79, 19.17, 13.96, 13.73.
**$^{31}$P NMR** (121 MHz, $CDCl_3$) δ = 0.75 (s)

Synthesis of 2,4,6-triisopropylbenzene thiol:

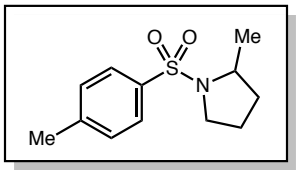



Synthesis of TRIP thiol is following a published procedure and the characterization data is consistent.[18] To a dry 100-mL round bottom flask, lithium aluminum hydride (LiAlH4) (1.52 g, 40.0 mmol) was added. Dry $Et_2O$ (13 mL) was then added to form a suspension and it was cooled to 0 °C. To this mixture, a solution of 2,4,6-triisopropylbenzene-1-sulfonyl chloride (6.06 g, 20 mmol) in $Et_2O$ (20 ml) was added slowly. After completion of addition, an additional load of $LiAlH_4$ (760 mg, 20 mmol) was added. The reaction was allowed to warm to room temperature as it was stirred overnight. Upon completion, the reaction is cooled to 0°C and dilute with 40 mL $Et_2O$. The reaction was quenched with water (1 mL per gram of LiAlH4), 15% w:w NaOH solution (1 mL per gram of LiAlH4) and water (3 mL per gram of LiAlH4). The reaction was stirred for 10 min at 0 °C before MgSO4 was added. The resulting white slurry was allowed to stir for 30min at room temperature. The while solids were then removed via filtration, with $Et_2O$ rinsing.

The solution was then concentrated and the product was distilled (95–105°C) at reduced pressure (0.5 torr) to provide 4.08 g (17 mmol, 86 % yield) of the title compound. Notably, it is critical to keep the reaction temperature as low as possible when adding the substrate and reagents and during the quenching process. Warming may result in reductive desulfurization, forming a mixture of the desired compound and 1,3,5-triisopropylbenzene that is difficult to separate.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ =7.02 (s, 2H), 3.60 – 3.46 (m, 2H), 3.09 (s, 1H), 2.95 – 2.82 (m, 1H), 1.33 – 1.24 (m, 18H).

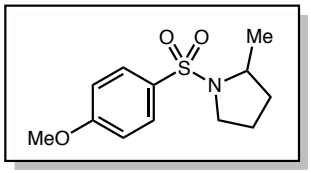
# V. Characterization of Products




2-methyl-1-tosylpyrrolidine

The reaction was set up following general procedure B with 4-methyl-N-(pent-4-en-1-yl)benzenesulfonamide (120 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 103.3 mg (86% yield) of the title compound as a white solid.

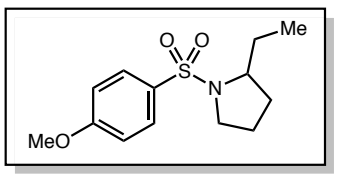
**IR** (Neat): 2970, 1342, 1158, 1093, 817, 718, 662 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.33-7.29 (m, 2H), 3.74-3.68 (m, 1H), 3.46-3.41 (m, 1H), 3.17-3.12 (m, 1H), 2.43 (s, 3H), 1.87-1.78 (m, 1H), 1.73-1.66 (m, 1H), 1.57-1.45 (m, 2H), 1.31 (d, $J$ = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 143.17, 134.85, 129.58, 127.45, 56.10, 49.08, 33.48, 23.91, 22.89, 21.52;
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{17}NO_2S$) from $[M+H]^+$ requires m/z 239.09800, found m/z 239.09813, difference 0.55 ppm.




1-((4-methoxyphenyl)sulfonyl)-2-methylpyrrolidine

The reaction was set up following general procedure B with 4-methoxy-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (128 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 118.0 mg (92% yield) of the title compound as a white solid.

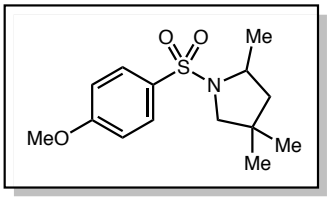
**IR** (Neat): 2969, 1596, 1497, 1341, 1333, 1258, 1153, 1093, 1024, 804, 666 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.00-6.97 (m, 2H), 3.87 (s, 3H), 3.72-3.65 (m, 1H), 3.45-3.41 (m, 1H), 3.16-3.11 (m, 1H), 1.87-1.78 (m, 1H), 1.73-1.66 (m, 1H), 1.57-1.46 (m, 2H), 1.31 (d, $J$ = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.73, 129.61, 129.48, 114.10, 56.07, 55.58, 49.09, 33.49, 23.93, 22.89;
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{17}NO_3S$) from $[M+H]^+$ requires m/z 255.09291, found m/z 255.09333, difference 1.65 ppm.




2-ethyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine

The reaction was set up following general procedure B with (E)-N-(hex-4-en-1-yl)-4-methoxybenzenesulfonamide (135 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 123.3 mg (91% yield) of the title compound as a colorless oil.

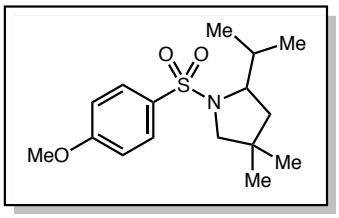
**IR** (Neat): 2968, 1596, 1497, 1339, 1258, 1154, 1093, 668 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.00-6.96 (m, 2H), 3.87 (s, 3H), 3.55-3.50 (m, 1H), 3.39-3.35 (m, 1H), 3.21-3.16 (m, 1H), 1.89-1.73 (m, 2H), 1.62-1.43 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.73, 129.72, 129.49, 114.10, 61.81, 55.58, 49.02, 30.15, 29.21, 24.13, 10.38;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_3S$) from $[M+H]^+$ requires m/z 269.10856, found m/z 269.10896, difference 1.46 ppm.




1-((4-methoxyphenyl)sulfonyl)-2,4,4-trimethylpyrrolidine

The reaction was set up following general procedure B with N-(2,2-dimethylpent-4-en-1-yl)-4-methoxybenzenesulfonamide (142 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 128.3 mg (90% yield) of the title compound as a white solid.

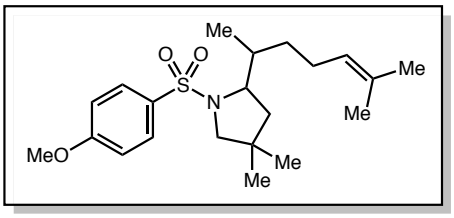
**IR** (Neat): 2965, 1596, 1497, 1338, 1258, 1154, 1095, 1025, 804, 665 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.00-6.96 (m, 2H), 3.87 (s, 3H), 3.46-3.42 (m, 1H), 3.17-3.11 (m, 2H), 1.71-1.66 (m, 1H), 1.36-1.31 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.91 (s, 3H), 0.53 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.71, 129.49, 129.40, 114.00, 64.85, 55.57, 46.41, 41.12, 37.17, 26.39, 22.59, 18.63;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12389, difference 1.13 ppm.




2-isopropyl-1-((4-methoxyphenyl)sulfonyl)-4,4-dimethylpyrrolidine

The reaction was set up following general procedure B with 4-methoxy-N-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide (156 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 142.9 mg (92% yield) of the title compound as a colorless oil.

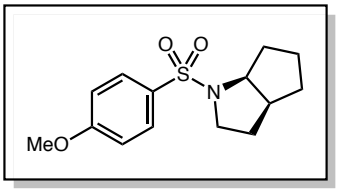
**IR** (Neat): 2960, 1597, 1497, 1337, 1258, 1153, 1094, 665 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 6.99-6.95 (m, 2H), 3.86 (s, 3H), 3.68-3.64 (m, 1H), 3.26-3.23 (m, 1H), 3.04-3.00 (m, 1H), 2.55-2.48 (m, 1H), 1.53-1.41 (m, 2H), 1.00 (s, 3H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.50 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.62, 131.08, 129.25, 113.97, 64.84, 61.85, 55.57, 39.21, 37.10, 30.25, 26.17, 25.84, 19.31, 14.52;
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_3S$) from $[M+H]^+$requires m/z 311.15551, found m/z 311.15524, difference 0.89 ppm.




1-((4-methoxyphenyl)sulfonyl)-4,4-dimethyl-2-(6-methylhept-5-en-2-yl)pyrrolidine

The reaction was set up following general procedure B with (E)-4-methyl-N-(2,2,5,9-tetramethyldeca-4,8-dien-1-yl)benzenesulfonamide (190 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 153.2 mg (81% yield) of the title compound as a colorless oil.

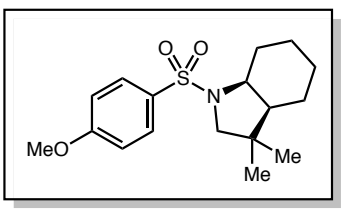
**IR** (Neat): 2959, 1197, 1497, 1338, 1258, 1153, 1094, 834, 666 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 6.98-6.94 (m, 2H), 5.12-5.06 (m, 1H), 3.86 (s, 3H), 3.72-3.67 (m, 1H), 3.30 (d, *J* = 11.0 Hz, 0.5H), 3.26-3.23 (m, 0.5H), 3.02-2.99 (m, 1H), 2.42-2.34 (m, 0.5H), 2.28-2.21 (m, 0.5H), 2.09-2.00 (m, 1H), 1.99-1.92 (m, 0.5H), 1.84-1.77 (0.5H), 1.71-1.67 (s, 3H), 1.62-1.59 (m, 3H), 1.54-1.48 (m, 2H), 1.43-1.39 (m, 0.5H), 1.22-1.09 (m, 4H), 0.85-0.81 (m, 3H), 0.53-0.49 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.59, 131.50, 131.15, 131.01, 129.27, 129.18, 124.92, 124.48, 113.96, 113.94, 109.91, 109.48, 65.16, 63.77, 61.96, 61.90, 55.56, 55.55, 40.20, 39.43, 37.15, 37.03, 35.54, 35.08, 34.30, 29.29, 26.25, 26.13, 26.07, 26.07, 25.80, 25.75, 25.73, 25.70, 17.72, 17.68, 16.67, 12.41;
**HRMS** (ESI) exact mass calculated for [M] ($C_{21}H_{33}NO_3S$) from $[M+H]^+$ requires m/z 379.21811, found m/z 379.21827, difference 0.42 ppm.




(±)-(3a*S*,6a*S*)-1-((4-methoxyphenyl)sulfonyl)octahydrocyclopenta[*b*]pyrrole

The reaction was set up following general procedure B with N-(2-(cyclopent-2-en-1-yl)ethyl)-4-methoxybenzenesulfonamide (141 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 121.6 mg (85% yield) of the title compound as a colorless oil.

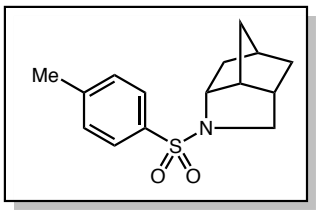
**IR** (Neat): 2949, 1596, 1497, 1341, 1258, 1154, 1093, 1023, 826, 804 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.00-6.96 (m, 2H), 3.87 (s, 3H), 3.76-3.73 (m, 1H), 3.45-3.41 (m, 1H), 3.01-2.96 (m, 1H), 2.52-2.45 (m, 1H), 2.07-2.00 (m, 1H),1.77-1.39 (m, 7H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.81, 129.79, 128.72, 114.06, 64.96, 55.60, 49.77, 43.37, 34.66, 31.98, 31.00, 24.47;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{19}NO_3S$) from $[M+H]^+$requires m/z 281.10856, found m/z 281.10856, difference 0.03 ppm.




(±)- (3a*S*,7a*S*)-1-((4-methoxyphenyl)sulfonyl)-3,3-dimethyloctahydro-1*H*-indole

The reaction was set up following general procedure B with N-(2-(cyclohex-2-en-1-yl)-2-methylpropyl)-4-methoxybenzenesulfonamide (162 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 144.2 mg (89% yield) of the major diastereomer as a colorless oil.

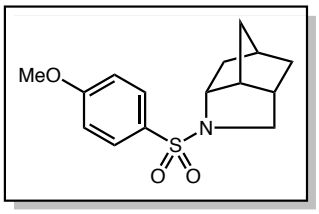
**IR** (Neat): 2932, 1596, 1497, 1258, 1154, 1093, 1024, 836, 804, 745, 670 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.00-6.96 (m, 2H), 3.87 (s, 3H), 3.56-3.52 (m, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 3.04 (d, *J* = 10.5 Hz, 1H), 2.53-2.49 (m, 1H), 1.69-1.40 (m, 6H), 1.26-1.12 (m, 2H), 0.90 (s, 3H), 0.49 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.74, 129.55, 128.97, 113.96, 60.43, 58.88, 55.58, 47.80, 38.96, 28.90, 27.12, 24.70, 24.40, 21.89, 20.34;
**HRMS** (ESI) exact mass calculated for [M] ($C_{17}H_{25}NO_3S$) from $[M+H]^+$ requires m/z 323.15551, found m/z 323.15491, difference 1.87 ppm.




1-tosyloctahydro-3,5-methanocyclopenta[*b*]pyrrole

The reaction was set up following general procedure B with (±)-*N*-(((1*S*,2*S*,4*S*)-bicyclo[2.2.1]hept-5-en-2-yl)methyl)-4-methylbenzenesulfonamide (139 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 119.3 mg (86% yield) of the title compound as a colorless oil.

**IR** (Neat): 2957, 1598, 1341, 1155, 1095, 816, 665 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.73-7.69 (m, 2H), 7.31-7.27 (m, 2H), 3.97 (dd, $J_1$ = 8.5 Hz, $J_2$ = 5.0 Hz, 1H), 3.28 (d, *J* = 9.5 Hz, 1H), 3.17 (dd, $J_1$ = 9.5 Hz, $J_2$ = 5.0 Hz, 1H), 2.42 (s, 3H), 2.30-2.26 (m, 1H), 2.19-2.15 (m, 2H), 1.92-1.86 (m, 1H), 1.74-1.69 (m, 1H), 1.41-1.36 (m, 2H), 1.30-1.27 (m, 1H), 1.10-1.06 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 142.97, 136.04, 129.57, 127.13, 60.31, 53.68, 45.95, 40.41, 38.10, 38.01, 37.18, 34.72;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 277.11365, found m/z 277.11388, difference 0.83 ppm.

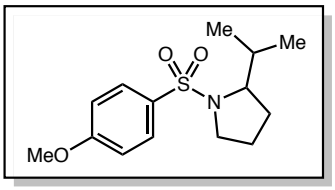



1-((4-methoxyphenyl)sulfonyl)octahydro-3,5-methanocyclopenta[*b*]pyrrole

The reaction was set up following general procedure B with (±)-N-(((1S,2S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)methyl)-4-methoxybenzenesulfonamide (147 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using solica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 128.8 mg (88% yield) of the title compound as a colorless oil.

**IR** (Neat): 2957, 1596, 1497, 1341, 1258, 1253, 1096, 1025, 804, 670 $cm^{-1}$;

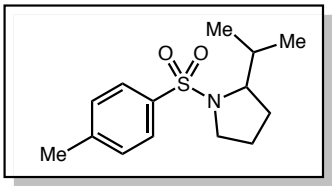
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 6.99-6.95 (m, 2H), 3.96-3.93 (m, 1H), 3.87 (s, 3H), 3.25 (d, *J* = 9.5 Hz, 1H), 3.17-3.13 (m, 1H), 2.29-2.26 (m, 1H), 2.18-2.13 (m, 2H), 1.90-1.84 (m, 1H), 1.73-1.67 (m, 1H), 1.40-1.33 (m, 2H), 1.29-1.26 (m, 1H), 1.09-1.05 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.60, 130.77, 129.15, 114.09, 60.28, 55.58, 53.68, 45.94, 40.37, 38.10, 38.01, 37.18, 34.72;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{19}NO_3S$) from $[M+H]^+$requires m/z 293.10856, found m/z 293.10805, difference 1.75 ppm.




2-isopropyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine

The reaction was set up following general procedure B with 4-methoxy-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (142 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 135.0 mg (96% yield) of the title compound as a white solid.

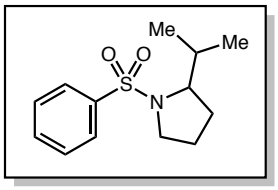
**IR** (Neat): 2964, 2875, 1597, 1498, 1340, 1259, 1156, 1093, 671 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.00-6.97 (m, 2H), 3.87 (s, 3H), 3.52-3.48 (m, 1H), 3.32-3.26 (m, 2H), 2.18-2.10 (m, 1H), 1.73-1.60 (m, 2H), 1.50-1.43 (m, 1H), 1.39-1.32 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.74, 129.81, 129.51, 114.11, 65.58, 55.58, 49.47, 32.05, 26.15, 24.59, 19.83, 16.53;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12449, difference 0.97 ppm.




2-isopropyl-1-tosylpyrrolidine

The reaction was set up following general procedure B with 4-methyl-N-(5-methylhex-4-en-1-yl)benzenesulfonamide (134 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 98.7 mg (74% yield) of the title compound as a colorless oil.

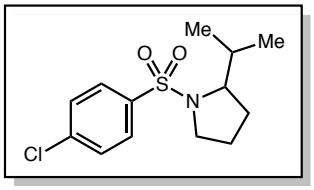
**IR** (Neat): 2962, 2874, 1468, 1341, 1158, 1092, 1001, 816, 659 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.33-7.28 (m, 2H), 3.53-3.49 (m, 1H), 3.34-3.26 (m, 2H), 2.43 (s, 3H), 2.21-2.11 (m, 1H), 1.73-1.60 (m, 2H), 1.49-1.42 (m, 1H), 1.38-1.30 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 143.18, 135.06, 129.59, 127.51, 65.61, 49.47, 32.05, 26.13, 24.56, 21.52, 19.82, 16.52.;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.12930, found m/z 267.12927, difference 0.12 ppm.



2-isopropyl-1-(phenylsulfonyl)pyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)benzenesulfonamide (127 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 83.5 mg (66% yield) of the title compound as a colorless oil.

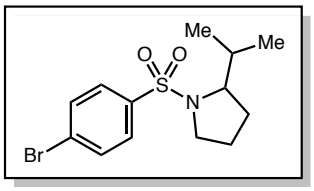
**IR** (Neat): 2963, 1446, 1340, 1160, 1092, 996, 719, 693cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.61-7.56 (m, 1H), 7.54-7.49 (m, 2H), 3.56-3.52 (m, 1H), 3.36-3.28 (m, 2H), 2.22-2.12 (m, 1H), 1.73-1.60 (m, 2H), 1.51-1.43 (m, 1H), 1.38-1.28 (m, 1H), 0.94 (d, $J$ = 7.0 Hz, 3H), 0.89 (d, $J$ = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 138.04, 132.49, 128.99, 127.46, 65.68, 49.47, 32.04, 26.14, 24.57, 19.81, 16.51.;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 253.11365, found m/z 253.11370, difference 0.21 ppm.



1-((4-chlorophenyl)sulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with 4-chloro-N-(5-methylhex-4-en-1-yl)benzenesulfonamide (144 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 98.7 mg (69% yield) of the title compound as a white solid.

**IR** (Neat): 2963, 2874, 1585, 1475, 1343, 1160, 1090, 1002, 827, 755cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.51-7.48 (m, 2H), 3.53-3.49 (m, 1H), 3.35-3.27 (m, 2H), 2.21-2.11 (m, 1H), 1.76-1.63 (m, 2H), 1.53-1.46 (m, 1H), 1.43-1.35 (m, 1H), 0.93 (d, $J$ = 7.0 Hz, 3H), 0.88 (d, $J$ = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 138.96, 136.64, 129.30, 128.88, 65.80, 49.50, 32.00, 26.16, 24.60, 19.78, 16.47.;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{18}ClNO_2S$) from $[M+H]^+$ requires m/z 287.07468, found m/z 287.07417, difference 1.76 ppm.

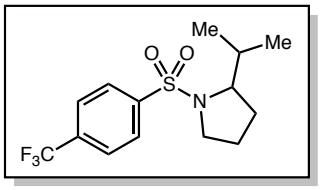


1-((4-bromophenyl)sulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with 4-bromo-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (166 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 108.8 mg (66% yield) of the title compound as a white solid.

**IR** (Neat): 2963, 2874, 1574, 1469, 1344, 1161, 1090, 1002, 824, 738cm$^{-1}$;

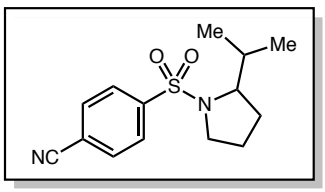
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2H), 7.67-7.64 (m, 2H), 3.52-3.49 (m, 1H), 3.35-3.27 (m, 2H), 2.21-2.11 (m, 1H), 1.76-1.63 (m, 2H), 1.54-1.46 (m, 1H), 1.43-1.35 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 137.15, 132.28, 128.99, 127.43, 65.81, 49.51, 31.99, 26.16, 24.60, 19.78, 16.47;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{18}BrNO_2S$) from $[M+H]^+$ requires m/z 331.02416, found m/z 331.02485, difference 2.09 ppm.




2-isopropyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (161 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 105.2 mg (65% yield) of the title compound as a white solid.

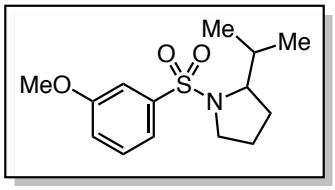
**IR** (Neat): 2966, 1404, 1321, 1163, 1131, 1062, 1005, 845, 711cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 3.57-3.53 (m, 1H), 3.38-3.30 (m, 2H), 2.23-2.14 (m, 1H), 1.79-1.65 (m, 2H), 1.54-1.47 (m, 1H), 1.44-1.36 (m, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 141.73, 134.15 (q, *J* = 33.1 Hz), 127.94, 126.15, 123.29 (q, *J* = 273.2 Hz), 65.91, 49.52, 31.98, 26.16, 24.61, 19.75, 16.41;
**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ = -63.05;
**HRMS** (ESI) exact mass calculated for $[M]^+$ ($C_{14}H_{18}F_3NO_2S$) from $[M+H]^+$ requires m/z 321.10103, found m/z 321.10062, difference 1.27 ppm.




4-((2-isopropylpyrrolidin-1-yl)sulfonyl)benzonitrile

The reaction was set up following general procedure B with 4-cyano-N-(5-methylhex-4-en-1-yl)benzenesulfonamide (139 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 79.0 mg (57% yield) of the title compound as a white solid.

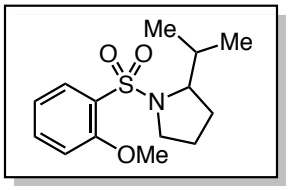
**IR** (Neat): 2964, 2233, 1468, 1345, 1159, 1090, 1005, 841 cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H), 7.85-7.82 (m, 1H), 3.57-3.53 (m, 1H), 3.37-3.30 (m, 2H), 2.21-2.12 (m, 1H), 1.80-1.66 (m, 2H), 1.55-1.37 (m, 2H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 142.49, 132.85, 128.01, 117.38, 116.21, 66.02, 49.53, 31.94, 26.18, 24.63, 19.73, 16.40;




2-isopropyl-1-((3-methoxyphenyl)sulfonyl)pyrrolidine

The reaction was set up following general procedure B with 3-methoxy-N-(5-methylhex-4-en-1-yl)benzenesulfonamide (142 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 122.0 mg (86% yield) of the title compound as a colorless liquid.

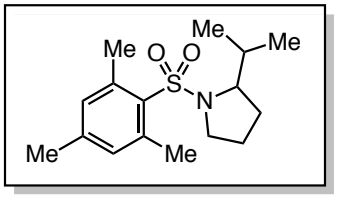
**IR** (Neat): 2963, 1596, 1478, 1342, 1240, 1156, 1040, 1005, 691cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.45-7.39 (m, 2H), 7.36-7.33 (m, 1H), 7.13-7.08 (m, 1H), 3.86 (s, 3H), 3.58-3.52 (m, 1H), 3.38-3.27 (m, 2H), 2.21-2.12 (m, 1H), 1.75-1.61 (m, 2H), 1.53-1.44 (m, 1H), 1.43-1.34 (m, 1H), 0.93 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H).;
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 159.82, 139.19, 130.05, 119.62, 118.51, 112.55, 65.69, 55.67, 49.48, 32.03, 26.15, 24.58, 19.81, 16.51;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12391, difference 1.08 ppm.




2-isopropyl-1-((2-methoxyphenyl)sulfonyl)pyrrolidine

The reaction was set up following general procedure B with 3-methoxy-N-(5-methylhex-4-en-1-yl)benzenesulfonamide (142 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 66.2 mg (47% yield) of the title compound as a colorless liquid.

**IR** (Neat): 2962, 1590, 1480, 1331, 1279, 1154, 1072, 1015, 759cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.95 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.06 – 6.97 (m, 2H), 3.93 (s, 3H), 3.80 (q, *J* = 6.3 Hz, 1H), 3.58 – 3.51 (m, 1H), 3.30 – 3.24 (m, 1H), 2.11 – 2.02 (m, 1H), 1.82 – 1.73 (m, 1H), 1.70 (q, *J* = 6.8 Hz, 2H), 1.62 – 1.52 (m, 1H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 156.64, 134.13, 132.18, 127.57, 120.28, 111.99, 65.47, 55.81, 49.13, 31.72, 26.42, 24.88, 19.70, 16.44;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12381, difference 1.41 ppm.

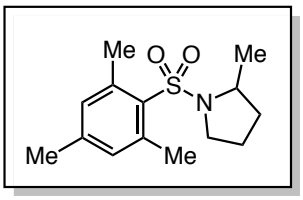



2-isopropyl-1-(mesitylsulfonyl)pyrrolidine

The reaction was set up following general procedure B with 2,4,6-trimethyl-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (148 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 123.1 mg (83% yield) of the title compound as a colorless liquid.

**IR** (Neat): 2962, 1604, 1473, 1311, 1150, 1058, 978, 667cm$^{-1}$;

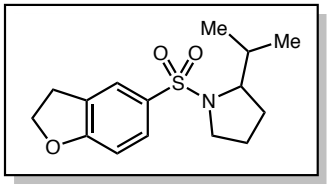
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 6.93 (s, 2H), 3.88 – 3.81 (m, 1H), 3.56 – 3.47 (m, 1H), 3.09 – 2.99 (m, 1H), 2.65 (s, 6H), 2.29 (s, 3H), 1.96 – 1.68 (m, 5H), 0.79 – 0.71 (m, 6H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 142.30, 140.01, 133.51, 131.83, 64.34, 48.61, 31.12, 26.21, 25.22, 22.89, 20.96, 19.77, 16.17;
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 295.16060, found m/z 295.16006, difference 1.83 ppm.




1-(mesitylsulfonyl)-2-methylpyrrolidine

The reaction was set up following general procedure B with 2,4,6-trimethyl-N-(pent-4-en-1-yl)benzenesulfonamide (134 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 109.2 mg (82% yield) of the title compound as a white solid.

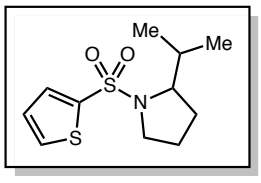
**IR** (Neat): 2970, 1604, 1454, 1308, 1149, 1059, 852, 667cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 6.94 (s, 2H), 4.06 – 3.94 (m, 1H), 3.39 – 3.29 (m, 1H), 3.20 – 3.10 (m, 1H), 2.65 (s, 6H), 2.29 (s, 3H), 2.13 – 2.00 (m, 1H), 1.93 – 1.80 (m, 2H), 1.62 – 1.53 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 142.33, 140.10, 133.43, 131.81, 54.81, 47.45, 33.97, 24.11, 22.84, 21.31, 20.97.
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.12930, found m/z 267.12912, difference 0.68 ppm.




1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)-2,3-dihydrobenzofuran-5-sulfonamide (148 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 132.8 mg (90% yield) of the title compound as a white solid.

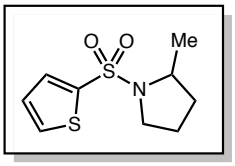
**IR** (Neat): 2962, 1605, 1485, 1472, 1339, 1240, 1144, 1065, 981, 891, 696cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.65 (m, 1H), 7.63-7.61 (m, 1H), 6.85-6.83 (m, 1H), 4.70-4.66 (m, 2H), 3.52-3.48 (m, 1H), 3.30-3.26 (m, 4H), 2.20-2.10 (m, 1H), 1.74-1.61 (m, 2H), 1.53-1.46 (m, 1H), 1.43-1.35 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 169.43, 146.45, 132.46, 132.03, 128.00, 123.89, 116.56, 65.62, 49.49, 49.13, 32.06, 27.65, 26.17, 24.61, 24.30, 19.83, 16.53;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 295.12421, found m/z 295.12444, difference 0.76 ppm.




2-isopropyl-1-(thiophen-2-ylsulfonyl)pyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)thiophene-2-sulfonamide (130 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 16% EtOAc/hexanes) to give 116.2 mg (89% yield) of the title compound as a white solid.

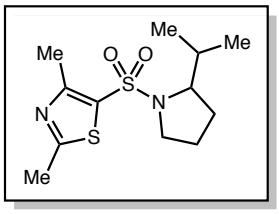
**IR** (Neat): 3114, 1964, 1334, 1150, 1017, 854, 742, 672 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.14-7.12 (m, 1H), 3.56-3.52 (m, 1H), 3.39-3.36 (m, 2H), 2.22-2.13 (m, 1H), 1.78-1.64 (m, 2H), 1.53-1.46 (m, 1H), 1.43-1.35 (m, 1H), 0.96-0.91 (m, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 137.87, 132.00, 131.47, 127.34, 66.05, 49.72, 32.06, 26.12, 24.54, 19.80, 16.58;
**HRMS** (ESI) exact mass calculated for [M] ($C_{11}H_{17}NO_2S_2$) from $[M+H]^+$ requires m/z 259.07007, found m/z 259.06997, difference 0.39 ppm.




2-methyl-1-(thiophen-2-ylsulfonyl)pyrrolidine

The reaction was set up following general procedure B with N-(pent-4-en-1-yl)thiophene-2-sulfonamide (116 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 16% EtOAc/hexanes) to give 91.0 mg (79% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3114, 1964, 1334, 1150, 1017, 854, 742, 672 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.16 – 7.11 (m, 1H), 3.79 – 3.71 (m, 1H), 3.53 – 3.46 (m, 1H), 3.24 – 3.17 (m, 1H), 1.93 – 1.83 (m, 1H), 1.76 – 1.70 (m, 1H), 1.61 – 1.50 (m, 2H), 1.35 (d, $J$ = 6.3 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ =137.70, 131.95, 131.41, 127.33, 56.63, 49.32, 33.40, 23.97, 22.83.
**HRMS** (ESI) exact mass calculated for [M] ($C_9H_{13}NO_2S_2$) from $[M+H]^+$ requires m/z 231.03877, found m/z 231.03832, difference 1.93 ppm.

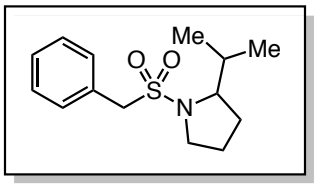



5-((2-isopropylpyrrolidin-1-yl)sulfonyl)-2,4-dimethylthiazole

The reaction was set up following general procedure B with 2,4-dimethyl-N-(5-methylhex-4-en-1-yl)thiazole-5-sulfonamide (144 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 116.6 mg (81% yield) of the title compound as a white solid.

**IR** (Neat): 2962, 1465, 1344, 1287, 1157, 1076, 1004, 737$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.59-3.55 (m, 1H), 3.41-3.32 (m, 2H), 2.70 (s, 3H), 2.67 (s, 3H), 2.22-2.15 (m, 1H), 1.84-1.71 (m, 2H), 1.68-1.52 (m, 2H), 0.93 (d, $J$ = 7.0 Hz, 3H), 0.90 (d, $J$ = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 168.40, 156.05, 127.30, 65.91, 49.63, 31.87, 26.17, 24.70, 19.79, 19.41, 16.82, 16.37;

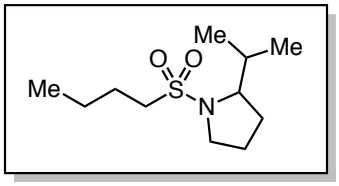
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{20}N_2O_2S_2$) from $[M+H]^+$ requires m/z 288.09662, found m/z 288.09702, difference 1.39 ppm.



1-(benzylsulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)-1-phenylmethanesulfonamide (134 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 108.7 mg (81% yield) of the title compound as a white solid.

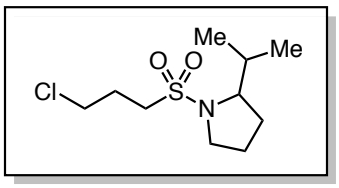
**IR** (Neat): 2962, 1456, 1334, 1150, 1126, 1007, 779, 597$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.49 – 7.40 (m, 2H), 7.40 – 7.32 (m, 3H), 4.27 – 4.17 (m, 2H), 3.68 – 3.60 (m, 1H), 3.37 – 3.28 (m, 1H), 3.15 – 3.04 (m, 1H), 2.09 – 1.97 (m, 1H), 1.82 – 1.63 (m, 4H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 130.74, 129.30, 128.66, 128.55, 65.43, 56.60, 49.62, 31.86, 26.05, 25.41, 19.62, 16.19.
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.12930, found m/z 267.12894, difference 1.33 ppm.



1-(butylsulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)butane-1-sulfonamide (117 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 80.1 mg (69% yield) of the title compound as a colorless oil.

**IR** (Neat): 2960, 2874, 1468, 1332, 1142, 1053, 1003, 772$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 3.77 – 3.71 (m, 1H), 3.55 – 3.47 (m, 1H), 3.26 – 3.19 (m, 1H), 2.95 – 2.89 (m, 2H), 2.12 – 2.04 (m, 1H), 1.90 – 1.73 (m, 6H), 1.51 – 1.41 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 65.03, 49.81, 49.22, 31.86, 26.31, 25.51, 25.26, 21.79, 19.65, 16.28, 13.65.
**HRMS** (ESI) exact mass calculated for [M] ($C_{11}H_{23}NO_2S$) from $[M+H]^+$ requires m/z 233.14495, found m/z 233.14517, difference 0.93 ppm.

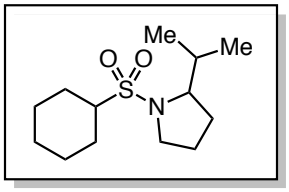


1-((3-chloropropyl)sulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with 3-chloro-N-(5-methylhex-4-en-1-yl)propane-1-sulfonamide (127 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column

chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 89.1 mg (70% yield) of the title compound as a colorless oil.

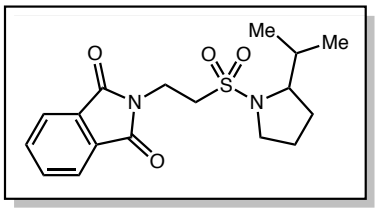
**IR** (Neat): 2963, 1468, 1331, 1307, 1145, 1006, 750cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 3.79 – 3.67 (m, 3H), 3.58 – 3.47 (m, 1H), 3.30 – 3.20 (m, 1H), 3.09 (d, *J* = 7.5 Hz, 2H), 2.38 – 2.26 (m, 2H), 2.15 – 2.03 (m, 1H), 1.95 – 1.75 (m, 4H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 65.22, 49.28, 47.00, 43.22, 31.84, 26.55, 26.32, 25.48, 19.65, 16.30.
**HRMS** (ESI) exact mass calculated for [M] ($C_{10}H_{20}NO_2SCl$) from $[M+H]^+$ requires m/z 253.09033, found m/z 253.09030, difference 0.12 ppm.




1-(cyclohexylsulfonyl)-2-isopropylpyrrolidine

The reaction was set up following general procedure B with N-(5-methylhex-4-en-1-yl)cyclohexanesulfonamide (130 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 15% EtOAc/hexanes) to give 86.8 mg (67% yield) of the title compound as a colorless oil.

**IR** (Neat): 2935, 2869, 1453, 1320, 1138, 994cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 3.93 (dt, *J* = 7.9, 5.1 Hz, 1H), 3.63 – 3.56 (m, 1H), 3.15 – 3.08 (m, 1H), 2.93 – 2.84 (m, 1H), 2.21 – 2.03 (m, 3H), 1.92 – 1.78 (m, 5H), 1.75 – 1.68 (m, 2H), 1.62 – 1.51 (m, 2H), 1.31 – 1.17 (m, 3H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 64.85, 61.69, 49.67, 31.70, 26.55, 26.42, 25.95, 25.86, 25.31, 25.31, 25.24, 19.63, 16.09.
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 259.16060, found m/z 259.16049, difference 0.43 ppm.

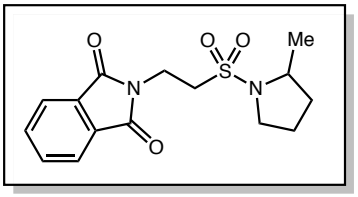



2-(2-((2-isopropylpyrrolidin-1-yl)sulfonyl)ethyl)isoindoline-1,3-dione

The reaction was set up following general procedure B with 2-(1,3-dioxoisoindolin-2-yl)-N-(5-methylhex-4-en-1-yl)ethanesulfonamide (175 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 5% to 40% EtOAc/hexanes) to give 134.8 mg (77% yield) of the title compound as a white solid.

**IR** (Neat): 2962, 1710, 1396, 1334, 1144, 717cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.76-7.72 (m, 1H), 4.23-4.12 (m, 2H), 3.79-3.75 (m, 1H), 3.58-3.53 (m, 1H), 3.40-3.26 (m, 3H), 2.12-2.04 (m, 1H), 1.93-1.76 (m, 4H), 0.92-0.89 (m, 6H);

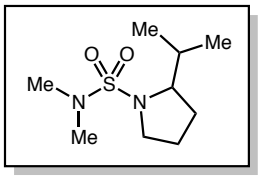
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 167.67, 134.23, 131.89, 123.49, 65.32, 49.29, 47.09, 32.52, 31.77, 26.30, 25.43, 19.62, 16.26;
**HRMS** (ESI) exact mass calculated for [M] ($C_{17}H_{21}N_2O_4S$) from $[M+H]^+$ requires m/z 350.13003, found m/z 350.12988, difference 0.42 ppm.



2-(2-((2-methylpyrrolidin-1-yl)sulfonyl)ethyl)isoindoline-1,3-dione

The reaction was set up following general procedure B with 2-(1,3-dioxoisoindolin-2-yl)-N-(pent-4-en-1-yl)ethanesulfonamide (161 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 5% to 40% EtOAc/hexanes) to give 122.4 mg (76% yield) of the title compound as a white solid.

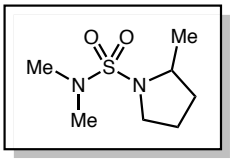
**IR** (Neat): 2971, 1709, 1396, 1328, 1145, 1084, 977, 866, 717$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.77 – 7.72 (m, 2H), 4.22 – 4.10 (m, 2H), 4.00 – 3.94 (m, 1H), 3.47 – 3.39 (m, 2H), 3.39 – 3.31 (m, 2H), 2.14 – 2.05 (m, 1H), 2.04 – 1.85 (m, 2H), 1.67 – 1.58 (m, 1H), 1.28 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 167.67, 134.23, 131.88, 123.48, 56.01, 48.55, 47.47, 33.85, 32.55, 24.51, 22.34.
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{18}N_2O_4S$) from $[M+H]^+$ requires m/z 322.09873, found m/z 322.09828, difference 1.4 ppm.



2-isopropyl-*N*,*N*-dimethylpyrrolidine-1-sulfonamide

The reaction was set up following general procedure B with N'-(5-methylhex-4-en-1-yl)-N,N-dimethylsulfonamide (110 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 100.3 mg (91% yield) of the title compound as a colorless oil.

**IR** (Neat): 2960, 2875, 1465, 1326, 1143, 959, 707$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.77-3.73 (m, 1H), 3.48-3.42 (m, 1H), 3.12-3.07 (m, 1H), 2.82 (s, 6H), 2.14-2.08 (m, 1H), 1.91-1.81 (m, 3H), 1.87-1.70 (m, 1H), 0.90-0.87 (m, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 65.54, 49.54, 38.02, 31.26, 25.89, 25.43, 19.70, 16.18;
**HRMS** (ESI) exact mass calculated for [M] ($C_9H_{20}N_2O_2S$) from $[M+H]^+$ requires m/z 220.12455, found m/z 220.12440, difference 0.69 ppm.

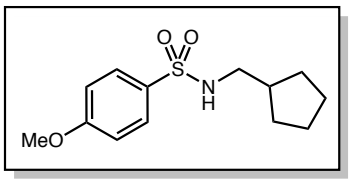


2-isopropyl-*N*,*N*-dimethylpyrrolidine-1-sulfonamide

The reaction was set up following general procedure B with N'-( pent-4-en-1-yl)-N,N-dimethylsulfonamide (96 mg, 0.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica

column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 76.6 mg (80% yield) of the title compound as a light-yellow oil.

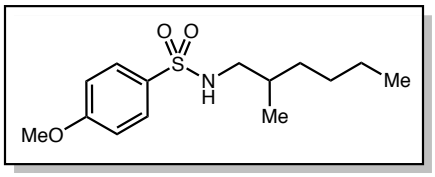
**IR** (Neat): 2966, 1460, 1321, 1143, 956, 714cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 3.98 – 3.88 (m, 1H), 3.41 – 3.33 (m, 1H), 3.29 – 3.21 (m, 1H), 2.80 (s, 6H), 2.13 – 2.01 (m, 1H), 1.97 – 1.84 (m, 2H), 1.63 – 1.53 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 56.27, 48.83, 37.91, 33.60, 24.46, 21.87.
**HRMS** (ESI) exact mass calculated for [M] ($C_7H_{16}N_2O_2S$) from $[M+H]^+$ requires m/z 192.09325, found m/z 192.09321, difference 0.18 ppm.




<u>*N*-(cyclopentylmethyl)-4-methoxybenzenesulfonamide</u>

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and methylenecyclopentene (82 mg, 1.0 mmol, 2.0 eq) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 85.8 mg (64% yield) of the title compound as a colorless oil.

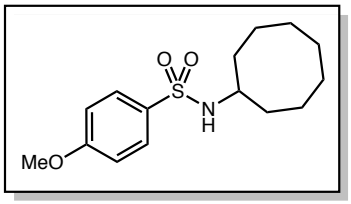
**IR** (Neat): 3281, 2952, 1597, 1498, 1324, 1259, 1153, 1095, 834, 670 cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.00-6.97 (m, 2H), 4.53 (br, 1H), 3.88 (s, 3H), 2.86-2.82 (m, 2H), 2.01-1.92 (m, 1H), 1.73-1.67 (m, 2H), 1.57-1.48 (m, 4H), 1.14-1.07 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.78, 131.53, 129.21, 114.20, 55.62, 48.19, 39.47, 30.19, 25.17;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_3S$) from $[M+H]^+$ requires m/z 269.10856, found m/z 269.10835, difference 0.81 ppm.




<u>4-methoxy-*N*-(2-methylhexyl)benzenesulfonamide</u>

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and 2-methylhex-1-ene (147 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using solica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 118.0 mg (82% yield) of the title compound as a colorless liquid.

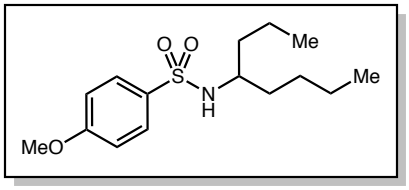
**IR** (Neat): 3284, 2928, 1597, 1499, 1324, 1259, 1154, 1096, 1027, 834, 669 cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 6.99-6.96 (m, 2H), 4.70 (br, 1H), 3.87 (s, 3H), 2.85-2.80 (m, 1H), 2.73-2.68 (m, 1H), 1.57-1.51 (m, 1H), 1.31-1.02 (m, 6H), 0.86-0.83 (m, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.76, 131.61, 129.19, 114.19, 55.61, 49.04, 33.68, 33.10, 28.88, 22.80, 17.49, 14.03;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{23}NO_3S$) from $[M+H]^+$ requires m/z 285.13986, found m/z 285.13988, difference 0.06 ppm.




*N*-cyclooctyl-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and (Z)-cyclooctene (165 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 111.7 mg (75% yield) of the title compound as a white solid.

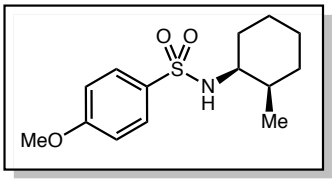
**IR** (Neat): 3277, 2921, 1597, 1498, 1300, 1257, 1152, 1096, 1023, 833, 669 $cm^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 6.99-6.96 (m, 2H), 4.73 (br, 1H), 3.87 (s, 3H), 3.37-3.04 (m, 1H), 1.72-1.66 (m, 2H), 1.59-1.33 (m, 12H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.62, 132.82, 129.09, 114.13, 55.60, 53.80, 32.56, 27.21, 25.23, 23.15;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{23}NO_3S$) from $[M+H]^+$ requires m/z 297.13986, found m/z 297.13972, difference 0.50 ppm.




4-methoxy-*N*-(octan-4-yl)benzenesulfonamide

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and (Z/E)-oct-4-ene (168 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 129.6 mg (86% yield) of the title compound as a white solid. And 118.4 mg (79% yield) from (E)-oct-4-ene.

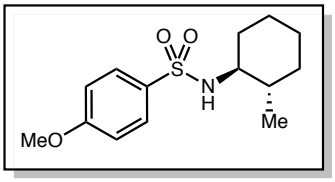
**IR** (Neat): 3281, 2957, 1597, 1498, 1322, 1258, 1154, 1096, 1027, 834, 670 $cm^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 6.99-6.95 (m, 2H), 4.60 (br, 1H), 3.87 (s, 3H), 3.22-3.15 (m, 1H), 1.41-1.07 (m, 10H), 0.80-0.77 (m, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.63, 133.13, 129.09, 114.02, 55.61, 53.79, 37.17, 34.65, 27.35, 22.46, 18.46, 13.87;
**HRMS** (ESI) exact mass calculated for [M] ($C_{15}H_{25}NO_3S$) from $[M+H]^+$ requires m/z 299.15551, found m/z 299.15579, difference 0.92 ppm.




(±)-4-methoxy-*N*-((1*S*,2*R*)-2-methylcyclohexyl)benzenesulfonamide

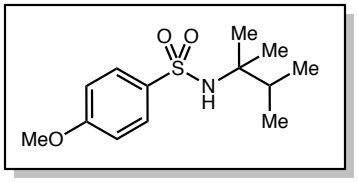
The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and 1-methylcyclohex-1-ene (144 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 85.5 mg (60% yield) of the title compound as a white solid (cis:trans ratio is determined by HNMR of crude reaction to be 1:2).

**IR** (Neat): 3290, 2930, 1597, 1499, 1326, 1259, 1158, 1147, 1096, 1022, 834, 672 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 6.98-6.94 (m, 2H), 4.71 (br, 1H), 3.87 (s, 3H), 3.33-3.29 (m, 1H), 1.70-1.62 (m, 1H), 1.54-1.48 (m, 2H), 1.45-1.30 (m, 4H), 1.26-1.11 (m, 2H), 0.75 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.64, 132.85, 129.14, 114.08, 55.59, 54.35, 34.36, 30.32, 29.88, 23.43, 21.59, 16.46;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 284.13204, found m/z 284.13187, difference 0.59 ppm.




(±)-4-methoxy-*N*-((1*S*,2*S*)-2-methylcyclohexyl)benzenesulfonamide

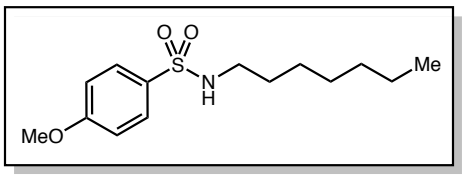
**IR** (Neat): 3279, 2928, 1597, 1498, 1324, 1258, 1151, 1091, 1027, 834, 670$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 6.99-6.95 (m, 2H), 4.47 (br, 1H), 3.87 (s, 3H), 2.73-2.67 (m, 1H), 1.78-1.55 (m, 4H), 1.25-0.92 (m, 5H), 0.81 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.58, 133.23, 129.07, 114.05, 59.08, 55.58, 38.40, 34.70, 34.42, 25.48, 25.35, 19.13;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 284.13204, found m/z 284.13148, difference 1.97 ppm.




*N*-(2,3-dimethylbutan-2-yl)-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and 2,3-dimethl-2-butene (126 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 121.7 mg (89% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3279, 2974, 1598, 1499, 1313, 1257, 1142, 1095, 1025, 834, 667 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 6.97-6.93 (m, 2H), 4.74 (br, 1H), 3.87 (s, 3H), 1.81-1.73 (m, 1H), 1.12 (s, 6H), 0.86 (d, *J* = 7.0 Hz, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.35, 135.38, 129.04, 113.93, 59.83, 55.56, 38.11, 24.31, 17.23;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{21}NO_3S$) from $[M+Na]^+$ requires m/z 271.12421, found m/z 271.12432, difference 0.39 ppm.

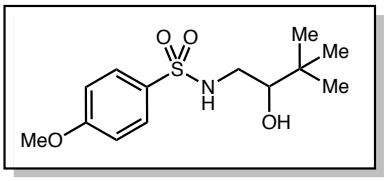



*N*-heptyl-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and hept-1-ene (147 mg, 1.5 mmol) for 36 hours. Upon completion, the crude

product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 86.5 mg (60% yield) of the title compound as a colorless liquid.

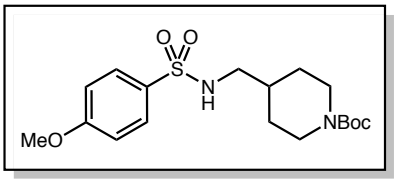
**IR** (Neat): 3281, 2928, 1597, 1499, 1323, 1259, 1153, 1096, 1027, 834, 670 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.00-6.96 (m, 2H), 4.55 (br, 1H), 3.87 (s, 3H), 2.91 (q, *J* = 6.5 Hz, 2H), 1.47-1.41 (m, 2H), 1.27-1.20 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.80, 131.55, 129.22, 114.20, 55.61, 43.19, 31.63, 29.51, 28.74, 26.49, 22.53, 14.05;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{23}NO_3S$) from $[M+H]^+$ requires m/z 285.13986, found m/z 285.13983, difference 0.11 ppm.




*N*-(2-hydroxy-3,3-dimethylbutyl)-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and ((3,3-dimethylbut-1-en-2-yl)oxy)trimethylsilane (259 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 40% EtOAc/hexanes) to give 84.8 mg (59% yield) of the title compound as a white solid.

**IR** (Neat): 3516, 3280, 2958, 1597, 1499, 1323, 1260, 1152, 1081, 833, 558 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.00-6.96 (m, 2H), 3.88 (s, 3H), 3.35-3.32 (m, 1H), 3.19-3.16 (m, 1H), 2.76-2.71 (m, 1H), 0.86 (s, 9H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.91, 131.30, 129.21, 114.32, 78.05, 55.64, 44.70, 34.07, 25.56;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{21}NO_4S$) from $[M+H]^+$ requires m/z 287.11913, found m/z 287.11895, difference 0.63 ppm.

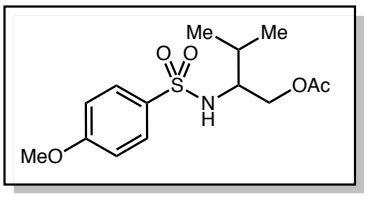



*tert*-butyl 4-(((4-methoxyphenyl)sulfonamido)methyl)piperidine-1-carboxylate

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and tert-butyl 4-methylenepiperidine-1-carboxylate (296 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 25% EtOAc/hexanes) to give 163.0 mg (85% yield) of the title compound as a colorless oil.

**IR** (Neat): 3293, 2927, 1665, 1597, 1423, 1256, 1150, 1094, 1024, 833, 668 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.00-6.96 (m, 2H), 4.94 (br, 1H), 4.06 (d, *J* = 15 Hz, 2H), 3.88 (s, 3H), 2.80-2.77 (m, 2H), 2.65-2.59 (m, 2H), 1.66-1.55 (m, 3H), 1.43 (s, 9H), 1.08-0.99 (m, 2H);

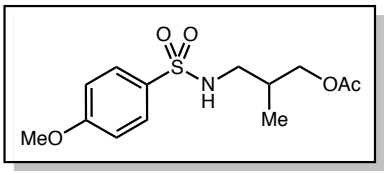
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.87, 154.73, 131.45, 129.15, 114.27, 79.47, 55.64, 48.51, 43.42, 36.37, 29.57, 28.43;
**HRMS** (ESI) exact mass calculated for [M-$C_4H_8$] ($C_{14}H_{20}N_2O_5S$) from [M-$C_4H_8$+H]$^+$ requires m/z 328.10929, found m/z 328.10956, difference 0.81 ppm.




2-((4-methoxyphenyl)sulfonamido)-3-methylbutyl acetate

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and 3-methylbut-2-en-1-yl acetate (192 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 40% EtOAc/hexanes) to give 70.8 mg (45% yield) of the title compound as a colorless oil.

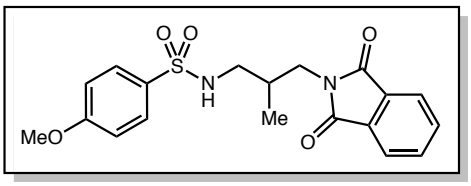
**IR** (Neat): 3283, 2966, 1735, 1597, 1498, 1325, 1255, 1152, 1093, 1025, 834, 671 cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 6.99-6.95 (m, 2H), 4.83 (br, 1H), 4.05-4.02 (m, 1H), 3.93-3.90 (m, 1H), 3.88 (s, 3H), 3.31-3.26 (m, 1H), 1.93 (s, 3H), 1.85-1.78 (m, 1H), 0.88-0.84 (m, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 170.91, 162.79, 132.73, 129.14, 114.15, 64.07, 57.86, 55.62, 29.94, 20.74, 18.87, 18.22;
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_5S$) from [M+H]$^+$ requires m/z 315.11404, found m/z 315.11379, difference 0.80 ppm.




3-((4-methoxyphenyl)sulfonamido)-2-methylpropyl acetate

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and 2-methylallyl acetate (171 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 40% EtOAc/hexanes) to give 101 mg (67% yield) of the title compound as a colorless oil.

**IR** (Neat): 3280, 2967, 1726, 1597, 1498, 1324, 1251, 1150, 1094, 1025, 833, 668 cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.00-6.96 (m, 2H), 5.07 (br, 1H), 4.03-3.98 (m, 1H), 3.92-3.87 (m, 4H), 2.87-2.83 (m, 2H), 2.02-1.94 (m, 4H), 0.92 (d, *J* = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 171.22, 162.84, 131.44, 129.17, 114.25, 66.29, 55.63, 45.69, 33.09, 20.84, 14.60;
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_5S$) from [M+H]$^+$ requires m/z 301.09839, found m/z 301/09830, difference 0.31 ppm.

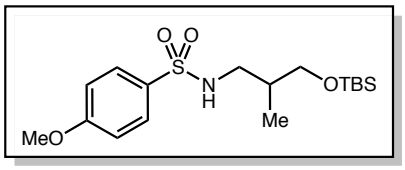



*N*-(3-(1,3-dioxoisoindolin-2-yl)-2-methylpropyl)-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide

(94 mg, 0.5 mmol) and 2-(2-methylallyl)isoindoline-1,3-dione (302 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 150.5 mg (78% yield) of the title compound as a colorless oil.

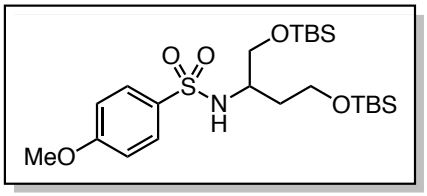
**IR** (Neat): 3284, 2937, 1703, 1596, 1399, 1326, 1257, 1151, 1049, 911, 833, 723 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.78 (m, 4H), 7.75-7.71 (m, 2H), 6.96-6.93 (m, 2H), 5.52 (br, 1H), 3.84 (s, 3H), 3.66-3.57 (m, 2H), 2.82-2.72 (m, 2H), 2.12-2.07 (m, 1H), 0.96 (d, $J$ = 7.0 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 168.94, 162.68, 134.24, 131.72, 129.12, 123.42, 114.16, 55.59, 45.71, 40.35, 33.57, 15.63;
**HRMS** (ESI) exact mass calculated for [M] ($C_{19}H_{20}N_2O_5S$) from $[M+H]^+$ requires m/z 388.10929, found m/z 388.10941, difference 0.29 ppm.




<u>*N*-(3-((*tert*-butyldimethylsilyl)oxy)-2-methylpropyl)-4-methoxybenzenesulfonamide</u>

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and tert-butyldimethyl((2-methylallyl)oxy)silane (280 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 148.8 mg (80% yield) of the title compound as a colorless oil.

**IR** (Neat): 3286, 2930, 2857, 1598, 1498, 1256, 1153, 1094, 832, 776, 667 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4H), 6.99-6.95 (m, 2H), 5.34 (br, 1H), 3.87 (s, 3H), 3.59-3.56 (m, 1H), 3.37-3.33 (m, 1H), 3.00-2.95 (m, 1H), 2.89-2.83 (m, 1H), 1.87-1.78 (m, 1H), 0.88 (s, 9H), 0.82 (d, $J$ = 6.5 Hz, 3H), 0.03-0.02 (m, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.68, 131.66, 129.16, 114.13, 67.98, 55.59, 48.20, 34.77, 25.85, 18.13, 14.52, -5.61;
**HRMS** (ESI) exact mass calculated for [M] ($C_{17}H_{31}NO_4SSi$) from $[M+H]^+$ requires m/z 373.17431, found m/z 373.17470, difference 1.05 ppm.

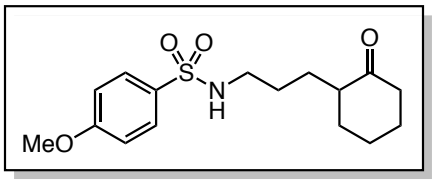



<u>4-methoxy-N-(2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodecan-6-yl)benzenesulfonamide</u>

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and 2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodec-6-ene (475 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 120.4 mg (48% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3282, 2954, 2929, 2884, 1598, 1499, 1302, 1256, 1157, 1088, 832, 776$cm^{-1}$;

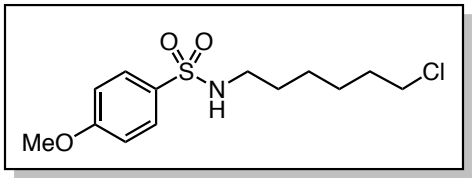
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.81-7.78 (m, 2H), 6.97-6.94 (m, 2H), 5.37 (d, *J* = 7.0 Hz, 1H), 3.87 (s, 3H), 3.69-3.64 (m, 1H), 3.61-3.59 (m, 1H), 3.56-3.52 (m, 1H), 3.48-3.45 (m, 1H), 3.38-3.32 (m, 1H), 1.67-1.63 (m, 2H), 0.88 (s, 9H), 0.84 (s, 9H), 0.02 (s, 6H), -0.01 (s, 3H), -0.02 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.68, 132.54, 129.19, 114.10, 64.28, 60.10, 55.58, 53.36, 33.59, 25.84, 18.15, -5.4;
**HRMS** (ESI) exact mass calculated for [M] ($C_{23}H_{45}NO_5SSi$) from $[M+H]^+$ requires m/z 503.25570, found m/z 503.25469, difference 2.00 ppm.




4-methoxy-N-(3-(2-oxocyclohexyl)propyl)benzenesulfonamide

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and 2-allylcyclohexanone (207 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 40% EtOAc/hexanes) to give 84.6 mg (52% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3275, 2935, 1701, 1596, 1498, 1324, 1257, 1151, 1094, 1024, 833, 729$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.82 – 7.76 (m, 2H), 7.00 – 6.94 (m, 2H), 4.78 (br, 1H), 3.87 (s, 3H), 2.96 – 2.82 (m, 2H), 2.39 – 2.32 (m, 1H), 2.30 – 2.17 (m, 2H), 2.08 – 2.00 (m, 2H), 1.85 – 1.60 (m, 4H), 1.50 – 1.42 (m, 2H), 1.36 – 1.28 (m, 1H), 1.22 – 1.14 (m, 1H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 213.22, 162.78, 131.49, 129.21, 114.20, 55.63, 50.19, 43.16, 42.10, 34.17, 28.03, 27.20, 26.32, 25.02.;
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{23}NO_4S$) from $[M+H]^+$ requires m/z 325.13478, found m/z 325.13504, difference 0.79 ppm.

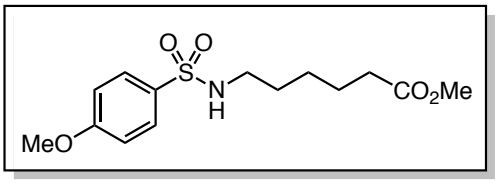



N-(6-chlorohexyl)-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and 6-chlorohex-1-ene (178 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 76.2 mg (50% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3281, 2937, 1597, 1498, 1322, 1259, 1151, 1094, 1025, 834$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.85 – 7.77 (m, 2H), 7.01 – 6.96 (m, 2H), 4.66 (s, 1H), 3.88 (s, 3H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.92 (q, *J* = 6.8 Hz, 2H), 1.74 – 1.68 (m, 2H), 1.51 – 1.43 (m, 2H), 1.40 – 1.34 (m, 2H), 1.32 – 1.26 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.84, 131.46, 129.20, 114.25, 55.64, 44.91, 43.00, 32.32, 29.37, 26.30, 25.78.

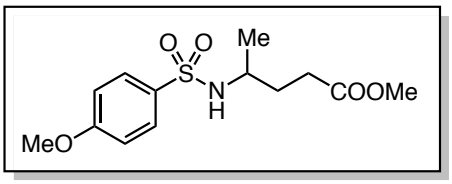
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{20}ClNO_3S$) from $[M+H]^+$ requires m/z 305.08524, found m/z 305.08501, difference 0.76 ppm.




methyl 6-((4-methoxyphenyl)sulfonamido)hexanoate

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and methyl hex-5-enoate (192 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 80.2 mg (51% yield) of the title compound as a light-yellow liquid.

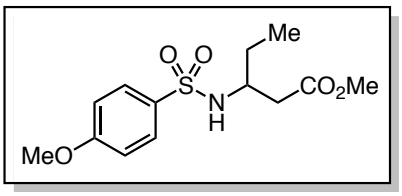
**IR** (Neat): 3293, 2950, 1729, 1597, 1258, 1151, 1067, 834cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ =7.84 – 7.79 (m, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 4.51 (s, 1H), 3.89 (s, 3H), 3.68 (s, 3H), 2.94 (q, *J* = 6.8 Hz, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.54 – 1.45 (m, 2H), 1.35 – 1.28 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ =173.95, 162.84, 131.50, 129.20, 114.24, 55.62, 51.57, 42.90, 33.74, 29.20, 25.98, 24.23.
**HRMS** (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_5S$) from $[M+H]^+$ requires m/z 315.11404, found m/z 315.11359, difference 1.45 ppm.




methyl 4-((4-methoxyphenyl)sulfonamido)pentanoate

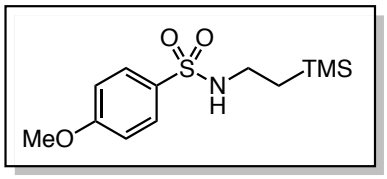
The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and (E)-methyl pent-3-enoate (171 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 66.4 mg (44% yield) of the mixture of the title compound (major) and the other regioisomer (minor) shown below as a colorless liquid. The ratio of the regioisomers was determined by crude HNMR.

**IR** (Neat): 3286, 2962, 1732, 1597, 1499, 1328, 1259, 1153, 1094, 1022, 836cm$^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ =7.85 – 7.78 (m, 2H), 7.01 – 6.96 (m, 2H), 4.55 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 3.66 (s, 3H), 3.41 – 3.30 (m, 1H), 2.38 – 2.32 (m, 2H), 1.80 – 1.73 (m, 1H), 1.70 – 1.64 (m, 2H), 1.04 (d, *J* = 6.5 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ =173.93, 162.76, 132.60, 129.11, 114.20, 55.61, 51.72, 49.56, 32.07, 30.22, 21.89.
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_5S$) from $[M+H]^+$ requires m/z 301.09839, found m/z 301.09784, difference 1.85 ppm.




methyl 3-((4-methoxyphenyl)sulfonamido)pentanoate

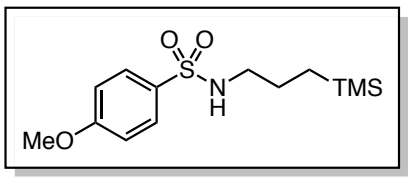
**IR** (Neat): 3278, 2957, 1733, 1597, 1499, 1323, 1259, 1154, 836cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ =7.83 – 7.79 (m, 2H), 6.99 – 6.95 (m, 2H), 5.13 (d, *J* = 9.9 Hz, 1H), 3.87 (s, 3H), 3.62 (s, 3H), 3.46 – 3.39 (m, 1H), 2.49 – 2.36 (m, 2H), 1.55 – 1.46 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ =171.81, 162.78, 132.61, 129.16, 114.17, 55.61, 52.12, 51.76, 38.19, 27.76, 10.36.
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_5S$) from $[M+H]^+$ requires m/z 301.09839, found m/z 301.09780, difference 1.97 ppm.




4-methoxy-N-(2-(trimethylsilyl)ethyl)benzenesulfonamide

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and trimethyl(vinyl)silane (150 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 60.2 mg (42% yield) of the title compound as a colorless liquid.

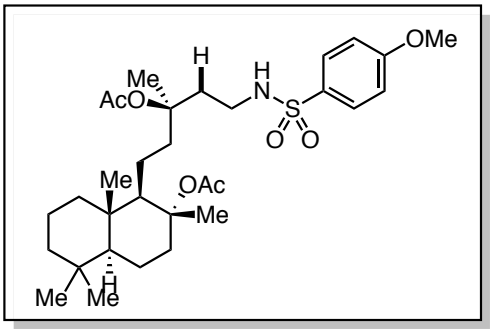
**IR** (Neat): 3280, 2953, 1597, 1498, 1255, 1151, 1096, 832cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.84 – 7.80 (m, 2H), 7.03 – 6.97 (m, 2H), 4.46 (s, 1H), 3.89 (s, 3H), 3.03 – 2.96 (m, 2H), 0.79 – 0.73 (m, 2H), -0.02 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ =164.49, 133.24, 130.88, 115.90, 57.30, 41.58, 19.59, -0.00.
**HRMS** (ESI) exact mass calculated for [M] ($C_{12}H_{21}NO_3SSi$) from $[M+H]^+$ requires m/z 287.10114, found m/z 287.10115, difference 0.03 ppm.




4-methoxy-N-(3-(trimethylsilyl)propyl)benzenesulfonamide

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and allyltrimethylsilane (171 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 74.4 mg (49% yield) of the title compound as a colorless liquid.

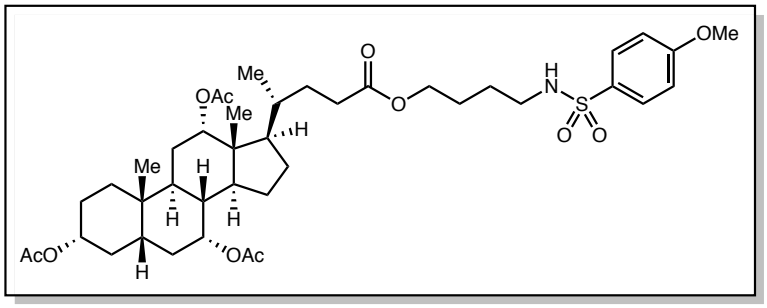
**IR** (Neat): 3281, 2952, 1597, 1498, 1324, 1254, 1151, 1096, 832cm$^{-1}$;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ =7.88 – 7.81 (m, 2H), 7.08 – 6.97 (m, 2H), 4.66 (s, 1H), 3.91 (s, 3H), 2.94 (q, *J* = 6.8 Hz, 2H), 1.51 – 1.41 (m, 2H), 0.48 – 0.37 (m, 2H), -0.03 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ =164.65, 133.59, 131.04, 116.06, 57.47, 48.12, 26.12, 15.39, -0.00.
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{24}NO_3SSi$) from $[M+H]^+$ requires m/z 301.11679, found m/z 301.11634, difference 1.5 ppm.



(*R*)-1-((1*R*,2*R*,4a*S*,8a*S*)-2-acetoxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)-5-((4-methoxyphenyl)sulfonamido)-3-methylpentan-3-yl acetate

The reaction was set up following general procedure C with 4-methoxylbenzenesulfonamide (94 mg, 0.5 mmol) and (*R*)-5-((1*R*,2*R*,4a*S*,8a*S*)-2-acetoxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)-3-methylpent-1-en-3-yl acetate (393 mg, 1.0 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 35% EtOAc/hexanes) to give 144.8 mg (50% yield) of the title compound as a colorless oil.

**IR** (Neat): 3276, 2937, 2874, 1722, 1598, 1367, 1252, 1154, 1021, 834, 732 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.81-7.78 (m, 2H), 7.00-6.97 (m, 2H), 4.73 (br, 1H), 3.88 (s, 3H), 3.04-2.95 (m, 2H), 2.66-2.62 (m, 1H), 2.07-1.99 (m, 2H), 1.94-1.81 (m, 7H), 1.71-1.62 (m, 3H), 1.59-1.50 (m, 2H), 1.43-1.36 (m, 9H), 1.30-1.10 (m, 4H), 0.96-0.88 (m, 2H), 0.86 (s, 3H), 0.80 (s, 3H), 0.77 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 170.28, 170.08, 162.87, 131.42, 129.18, 114.26, 87.86, 83.61, 58.79, 55.63, 55.60, 41.82, 41.16, 39.40, 39.34, 38.76, 38.74, 38.01, 33.30, 33.08, 23.64, 22.87, 22.32, 21.38, 20.37, 19.93, 19.55, 18.31, 15.76;
**HRMS** (ESI) exact mass calculated for [M] ($C_{31}H_{49}NO_7S$) from $[M+H]^+$ requires m/z 579.32379, found m/z 579.32297, difference 1.42 ppm.

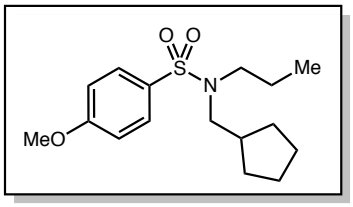


(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((R)-5-(4-((4-methoxyphenyl)sulfonamido)butoxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and (3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((R)-5-(but-3-en-1-yloxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate (589 mg, 1.0 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 45% EtOAc/hexanes) to give 181.8 mg (47% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3281, 2946, 1726, 1597, 1377, 1243, 1155, 1024, 915, 731 $cm^{-1}$;

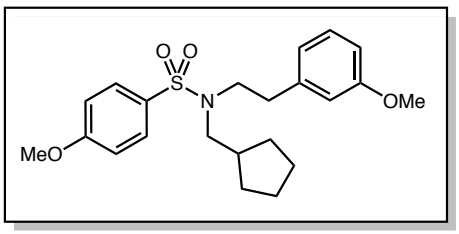
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.82-7.78 (m, 2H), 6.99-6.96 (m, 2H), 5.09 (t, *J* = 3.0 Hz, 1H), 4.91 (d, *J* = 3.0 Hz, 1H), 4.73-4.69 (m, 1H), 4.61-4.55 (m, 1H), 4.01 (t, *J* = 6.5 Hz, 1H), 3.88 (s, 3H), 2.95 (q, *J* = 6.5 Hz, 2H), 2.34-2.27 (m, 1H), 2.21-2.14 (m, 4H), 2.09-1.84 (m, 11H), 1.80-1.49 (m, 14H), 1.45-1.23 (m, 5H), 1.15-1.04 (m, 2H), 0.92 (s, 3H), 0.81 (d, *J* = 6.5 Hz, 3H), 0.73 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 174.10, 170.61, 170.43, 162.86, 131.42, 129.16, 75.37, 74.10, 70.71, 63.61, 55.64, 47.38, 45.08, 43.38, 42.74, 40.93, 37.72, 34.69, 34.61, 34.57, 34.34, 31.25, 31.10, 30.71, 28.90, 27.13, 26.90, 26.26, 25.75, 25.60, 22.81, 22.58, 21.66, 21.53, 21.49, 17.55, 12.26;
**HRMS** (ESI) exact mass calculated for [M] ($C_{41}H_{61}NO_{11}S$) from $[M+Na]^+$ requires m/z 775.39653, found m/z 775.39572, difference 1.04 ppm.




*N*-(cyclopentylmethyl)-4-methoxyl-*N*-propylbenzenesulfonamide

The reaction was set up following general procedure C with 4-methyl-N-propylbenzenesulfonamide (115 mg, 0.5 mmol) and methylenecyclopentene (123 mg, 1.5 mmol) for 36 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 88.5 mg (57% yield) of the title compound as a colorless oil.

**IR** (Neat): 2957, 1596, 1497, 1341, 1258, 1253, 1096, 1025, 804, 670 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 6.98-6.95 (m, 2H), 3.86 (s, 3H), 3.05-3.02 (m, 2H), 2.99 (d, *J* = 7.5 Hz, 2H), 2.18-2.09 (m, 1H), 1.74-1.64 (m, 2H), 1.68-1.49 (m, 6H), 1.26-1.19 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.50, 131.74, 129.18, 114.03, 55.57, 53.32, 50.30, 38.58, 30.39, 25.04, 22.02, 11.31;
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_3S$) from $[M+H]^+$ requires m/z 311.15551, found m/z 311.15563, difference 0.37 ppm.

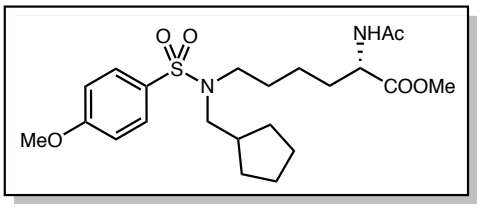



N-(cyclopentylmethyl)-4-methoxy-N-(3-methoxyphenethyl)benzenesulfonamide

The reaction was set up following general procedure C with 4-methoxy-N-(3-methoxyphenethyl)benzenesulfonamide (161 mg, 0.5 mmol) and methylenecyclopentane (123 mg, 1.5 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 35% EtOAc/hexanes) to give 106.8 mg (53% yield) of the title compound as a colorless oil.

**IR** (Neat): 2948, 1597, 1495, 1336, 1258, 1151, 1093, 807 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.75-7.72 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.97-6.94 (m, 2H), 6.76-6.74 (m, 2H), 6.70-6.69 (m, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.31-3.27 (m, 2H), 3.04 (d, *J* = 7.5 Hz, 2H), 2.84-2.80 (m, 2H), 2.19-2.10 (m, 1H), 1.74-1.50 (m, 6H), 1.28-1.21 (m, 2H);

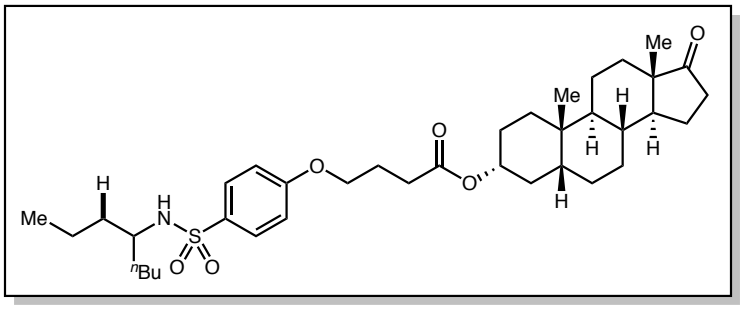
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.63, 159.73, 140.31, 131.48, 129.57, 129.22, 121.08, 114.57, 114.15, 111.70, 55.59, 55.21, 53.53, 50.05, 38.53, 35.76, 30.40, 25.06;
**HRMS** (ESI) exact mass calculated for [M] ($C_{22}H_{30}NO_4S$) from $[M+H]^+$ requires m/z 403.18173, found m/z 403.18159, difference 0.33 ppm.




methyl N2-acetyl-N6-(cyclopentylmethyl)-N6-((4-methoxyphenyl)sulfonyl)-L-lysinate

The reaction was set up following general procedure C with methyl N2-acetyl-N6-tosyl-L-lysinate (186 mg, 0.5 mmol) and methylenecyclopentane (123 mg, 1.5 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient 10% EtOAc/hexanes to 70% EtOAc/hexanes) to give 104.2 mg (46% yield) of the title compound as a colorless oil.

**IR** (Neat): 3297, 2950, 1743, 1659, 1597, 1497, 1334, 1258, 1152, 1093, 806 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.73-7.70 (m, 2H), 6.98-6.95 (m, 2H), 6.24 (d, *J* = 7.5 Hz, 1H), 4.57-4.53 (m, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 3.13-2.91 (m, 4H), 2.14-2.08 (m, 1H), 2.03 (s, 3H), 1.86-1.79 (m, 1H), 1.73-11.65 (m, 3H), 1.62-1.50 (m, 6H), 1.38-1.31 (m, 2H), 1.25-1.14 (m, 2H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 172.95, 170.06, 162.64, 131.23, 129.18, 114.13, 55.60, 53.76, 52.41, 52.13, 48.13, 38.60, 31.64, 30.40, 28.27, 25.02, 23.14, 22.18;
**HRMS** (ESI) exact mass calculated for [M] ($C_{22}H_{34}N_2O_6S$) from $[M+H]^+$ requires m/z 454.21376, found m/z 454.12287, difference 1.95 ppm.

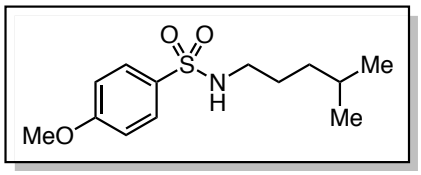



(3R,5R,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4-(N-(octan-4-yl)sulfamoyl)phenoxy)butanoate

The reaction was set up following general procedure C with (3R,5R,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4-sulfamoylphenoxy)butanoate (266 mg, 0.5 mmol) and *cis*-4-octene (168 mg, 1.5 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 45% EtOAc/hexanes) to give 182.1 mg (57% yield) of the title compound as a colorless liquid.

**IR** (Neat): 3283, 2932, 2859, 1731, 1596, 1498, 1324, 1255, 1154, 1096, 1014, 732 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.80-7.77 (m, 2H), 6.96-6.93 (m, 2H), 4.75-4.69 (m, 1H), 4.39 (br, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.22-3.15 (m, 1H), 2.51-2.41 (m, 3H), 2.15-

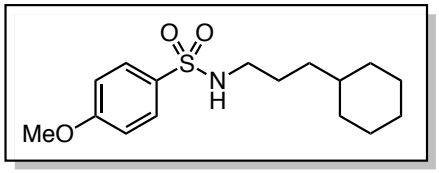
2.03 (m, 3H), 1.96-1.90 (m, 1H), 1.83-1.73 (m, 4H), 1.67-1.46 (m, 5H), 1.41-0.98 (m, 19H), 0.86 (s, 3H), 0.85 (s, 3H), 0.80-0.77 (m, 6H), 0.74-0.69 (m, 1H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 221.34, 172.51, 161.90, 133.11, 129.08, 114.47, 73.72, 67.17, 54.27, 53.78, 51.34, 47.79, 44.63, 37.21, 36.67, 35.86, 35.64, 35.01, 34.68, 33.97, 31.51, 30.95, 30.79, 28.26, 27.43, 27.35, 24.46, 22.46, 21.78, 20.46, 18.46, 13.95, 13.89, 13.82, 12.22;
**HRMS** (ESI) exact mass calculated for [M] ($C_{37}H_{57}NO_6S$) from $[M+Na]^+$ requires m/z 643.39066, found m/z 643.39002, difference 1.00 ppm.




4-methoxy-N-(4-methylpentyl)benzenesulfonamide

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and 4-methylpent-1-ene (210 mg, 2.5 mmol, 5.0 eq) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 100.8 mg (74% yield) of the title compound as a colorless liquid.

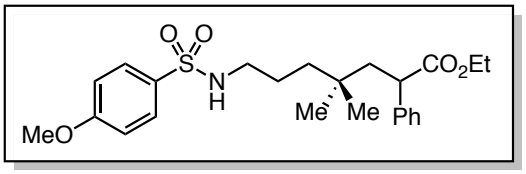
**IR** (Neat): 3280, 2954, 1597, 1498, 1322, 1258, 1152, 1095, 1025, 833$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.85 – 7.77 (m, 2H), 7.01 – 6.94 (m, 2H), 4.62 (br, 1H), 3.87 (s, 3H), 2.95 – 2.85 (m, 2H), 1.53 – 1.38 (m, 3H), 1.18 – 1.06 (m, 2H), 0.82 (s, 3H), 0.81 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.80, 131.60, 129.21, 114.21, 55.62, 43.48, 35.67, 27.58, 27.42, 22.42.
**HRMS** (ESI) exact mass calculated for [M] ($C_{13}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 271.12421, found m/z 271.12397, difference 0.88 ppm.




N-(3-cyclohexylpropyl)-4-methoxybenzenesulfonamide

The reaction was set up following general procedure C with 4-methoxybenzenesulfonamide (94 mg, 0.5 mmol) and allylcyclohexane (311 mg, 2.5 mmol) for 48 hours. Upon completion, the crude product was purified using solica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 116.7 mg (75% yield) of the title compound as a colorless liquid.

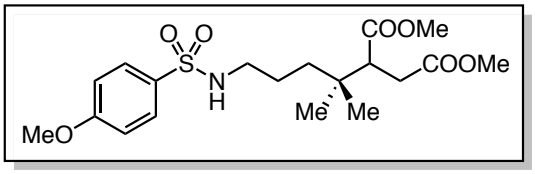
**IR** (Neat): 3279, 2921, 1597, 1498, 1322, 1258, 1151, 1095, 1026, 833$cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.89 – 7.75 (m, 2H), 6.98 (dd, J = 8.9, 1.8 Hz, 2H), 4.58 (br, 1H), 3.87 (s, 3H), 3.00 – 2.79 (m, 2H), 1.69 – 1.54 (m, 5H), 1.50 – 1.39 (m, 2H), 1.22 – 1.04 (m, 6H), 0.88 – 0.73 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 162.80, 131.59, 129.22, 114.21, 55.61, 43.51, 37.14, 34.19, 33.19, 26.87, 26.56, 26.26.
**HRMS** (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_3S$) from $[M+H]^+$ requires m/z 311.15551, found m/z 311.15568, difference 0.52 ppm.




ethyl 7-((4-methoxyphenyl)sulfonamido)-4,4-dimethyl-2-phenylheptanoate

The reaction was set up following general procedure reported in our previous paper[19] with 4-methoxy-N-(4-methylpentyl)benzenesulfonamide (136 mg, 0.5 mmol) and ethyl 2-phenylacrylate (176 mg, 1.0 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 185.5 mg (83% yield) of the title compound as a colorless liquid.

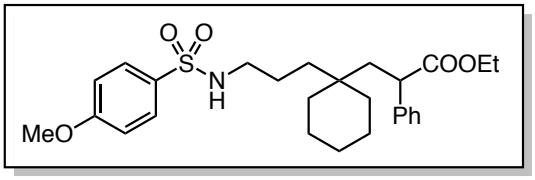
**IR** (Neat): $cm^{-1}$ 3282, 2956, 1729, 1597, 1498, 1326, 1259, 1153, 1096, 1025, 834;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.83 – 7.74 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.00 – 6.94 (m, 2H), 4.52 (br, 1H), 4.15 – 4.01 (m, 2H), 3.86 (s, 3H), 3.57 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.83 (q, *J* = 6.8 Hz, 2H), 2.22 (dd, *J* = 14.2, 9.0 Hz, 1H), 1.49 (dd, *J* = 14.2, 3.9 Hz, 1H), 1.44 – 1.27 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.15 – 1.05 (m, 2H), 0.81 (s, 3H), 0.80 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 174.73, 162.81, 140.84, 131.53, 129.22, 128.64, 127.76, 127.07, 114.21, 60.92, 55.62, 47.71, 44.88, 43.82, 38.76, 33.24, 27.08, 24.20, 14.05.
**HRMS** (ESI) exact mass calculated for [M] ($C_{24}H_{33}NO_5S$) from $[M+Na]^+$ requires m/z 447.20794, found m/z 447.20785, difference 0.21 ppm.




dimethyl 2-(5-((4-methoxyphenyl)sulfonamido)-2-methylpentan-2-yl)succinate

The reaction was set up following general procedure reported in our previous paper[19] with 4-methoxy-N-(4-methylpentyl)benzenesulfonamide (136 mg, 0.5 mmol) and dimethyl fumarate (144 mg, 1.0 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 50% EtOAc/hexanes) to give 146.2 mg (70% yield) of the title compound as a colorless liquid.

**IR** (Neat): $cm^{-1}$ 3285, 2955, 1731, 1597, 1499, 1437, 1258, 1152, 1095, 835;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.84 – 7.74 (m, 2H), 7.03 – 6.94 (m, 2H), 4.61 (br, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 2.90 (q, *J* = 6.7 Hz, 2H), 2.81 – 2.63 (m, 2H), 2.39 (dd, *J* = 16.3, 2.6 Hz, 1H), 1.58 – 1.47 (m, 1H), 1.45 – 1.36 (m, 1H), 1.27 – 1.14 (m, 2H), 0.87 (s, 3H), 0.86 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 174.41, 173.04, 162.85, 131.48, 129.21, 114.25, 55.63, 51.87, 51.55, 49.29, 43.68, 37.45, 34.86, 32.15, 25.01, 24.81, 24.00.
**HRMS** (ESI) exact mass calculated for [M] ($C_{19}H_{29}NO_7S$) from $[M+Na]^+$ requires m/z 415.16647, found m/z 415.16661, difference 0.34 ppm.




ethyl 3-(1-(3-((4-methoxyphenyl)sulfonamido)propyl)cyclohexyl)-2-phenylpropanoate

The reaction was set up following general procedure reported in our previous paper[19] with N-(3-cyclohexylpropyl)-4-methoxybenzenesulfonamide (156 mg, 0.5 mmol) and ethyl 2-phenylacrylate (176 mg, 1.0 mmol) for 48 hours. Upon completion, the crude product was purified using silica column chromatography (gradient hexanes to 25% EtOAc/hexanes) to give 189.2 mg (78% yield) of the title compound as a colorless liquid.

**IR** (Neat): $cm^{-1}$ 3281, 2927, 1729, 1597, 1498, 1326, 1258, 1153, 1096, 1027, 834;
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 7.83 – 7.75 (m, 2H), 7.32 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.01 – 6.93 (m, 2H), 4.41 (t, *J* = 6.0 Hz, 1H), 4.15 – 4.01 (m, 2H), 3.87 (s, 3H), 3.54 (dd, *J* = 8.6, 4.0 Hz, 1H), 2.89 – 2.70 (m, 2H), 2.24 (dd, *J* = 14.6, 8.6 Hz, 1H), 1.54 (dd, *J* = 14.6, 4.0 Hz, 1H), 1.43 – 1.11 (m, 17H).f
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 174.92, 162.78, 140.99, 131.52, 129.23, 128.64, 127.84, 127.08, 114.18, 61.02, 55.62, 46.73, 43.77, 35.80, 35.79, 35.49, 26.19, 22.91, 21.41, 14.05.
**HRMS** (ESI) exact mass calculated for [M] ($C_{27}H_{37}NO_5S$) from $[M+Na]^+$ requires m/z 487.23924, found m/z 487.23842, difference 1.69 ppm.

# VI. Mechanistic Studies

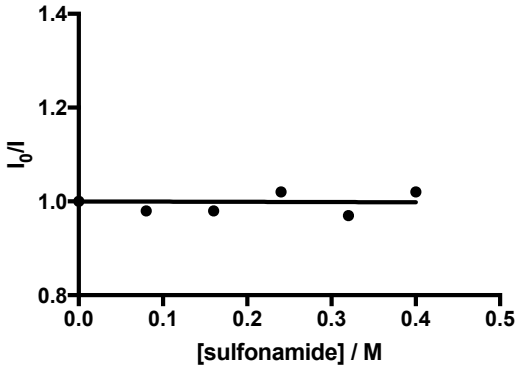
**Stern-Volmer Experiments**

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously degassed (with argon) solutions of each component were prepared prior to each set of experiments. Because the photocatalyst is poorly soluble in trifluorotoluene, luminescence quenching experiments were run with dichloromethane as the solvent. The solutions were irradiated at 420 nm and luminescence was measured at 593 nm. All the experiments are run in duplicate. $I^0/I$ values per run are generated from the average of all three scans per data point. For determination of $K_{sv}$, the value for $I^0/I$ from each run is averaged to yield an $I^0/I$ value for the experiment. Linear regression of $I^0/I$ against concentration to yield $K_{sv}$ is done in Microsoft Excel. *N*-propyl-4-methoxybenzenesulfonamide was used as the model amide to study the N-H bond activation step by joint action of the base and photocatalyst.

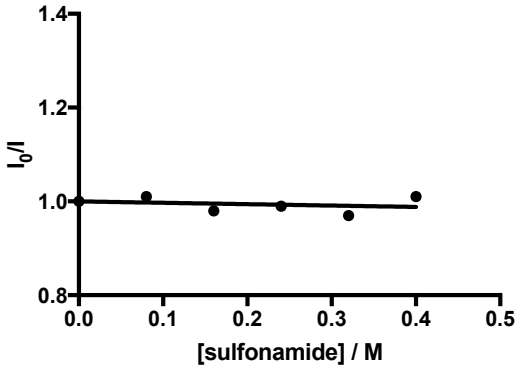
Experiment 1: Constant photocatalyst; Varied sulfonamide

| Species | Concentration |
|---|---|
| $[Ir(dFCF_3ppy)_2(dCF_3bpy)]PF_6$ | 0.2 mM |
| Sulfonamide | Varied |

| Run | [Amide] M | Scan 1 | Scan 2 | Scan 3 | Average | $I_0/I$ |
|---|---|---|---|---|---|---|
| **#1** | 0.000 | 757.1 | 761.3 | 754.7 | 757.7 | 1.00 |
| | 0.008 | 772.4 | 768.8 | 769.6 | 770.3 | 0.98 |
| | 0.016 | 765.4 | 767.8 | 776.3 | 769.8 | 0.98 |
| | 0.024 | 746.3 | 750.8 | 740.8 | 746.0 | 1.02 |
| | 0.032 | 778.3 | 782.0 | 787.4 | 782.6 | 0.97 |
| | 0.040 | 742.1 | 742.6 | 741.2 | 742.0 | 1.02 |
| **#2** | 0.000 | 759.2 | 756.7 | 760.4 | 758.8 | 1.00 |
| | 0.008 | 752.2 | 752.8 | 749.1 | 751.4 | 1.01 |
| | 0.016 | 770.9 | 769.2 | 776.5 | 772.2 | 0.98 |
| | 0.024 | 768.0 | 765.4 | 769.6 | 767.7 | 0.99 |
| | 0.032 | 758.3 | 756.5 | 760.5 | 758.4 | 1.00 |
| | 0.040 | 754.8 | 747.8 | 753.0 | 751.8 | 1.01 |




**y = −0.005 x +1**
**$r^2$ = -0.05**

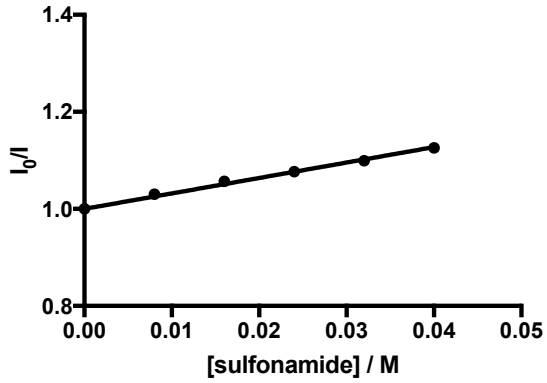



**y = −0.027 x +1**
**$r^2$ = -0.02**

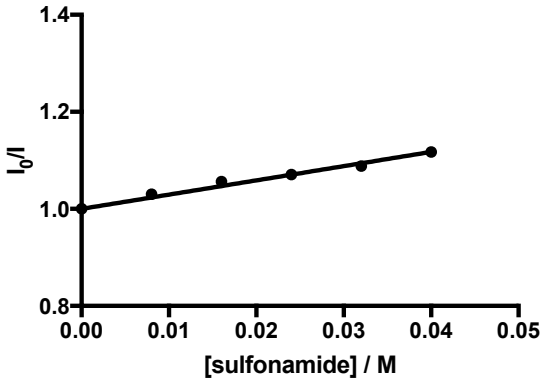
Experiment 2: Constant photocatalyst; Constant phosphate; Varied sulfonamide

| Species | Concentration |
|---|---|
| $[Ir(dFCF_3ppy)_2(dCF_3bpy)]PF_6$ | 0.15 mM |
| $(BuO)_2POONBu_4$ | 1.20 mM |
| Sulfonamide | Varied |

| Run | Conc. (M) | I(1st) | I(2nd) | I(3rd) | I(average) | $I_0/I$ |
|---|---|---|---|---|---|---|
| **#1** | 0.000 | 393.5 | 388.4 | 388.9 | 390.3 | 1.00 |
| | 0.008 | 379.1 | 378.7 | 378.8 | 378.9 | 1.03 |
| | 0.016 | 370.5 | 369.6 | 368.0 | 369.4 | 1.06 |
| | 0.024 | 364.6 | 362.1 | 360.7 | 362.5 | 1.08 |
| | 0.032 | 356.1 | 355.4 | 353.7 | 355.1 | 1.10 |
| | 0.040 | 348.8 | 345.7 | 345.0 | 346.5 | 1.13 |
| **#2** | 0.000 | 392.6 | 388.3 | 389.2 | 390.0 | 1.00 |
| | 0.008 | 381.2 | 377.9 | 377.0 | 378.7 | 1.03 |
| | 0.016 | 371.2 | 369.8 | 367.4 | 369.5 | 1.06 |
| | 0.024 | 365.9 | 364.3 | 362.4 | 364.2 | 1.07 |
| | 0.032 | 360.2 | 358.5 | 356.4 | 358.4 | 1.09 |
| | 0.040 | 350.3 | 349.9 | 347.7 | 349.3 | 1.12 |




**y = 3.19 x +1**
**$r^2$ = 0.99**

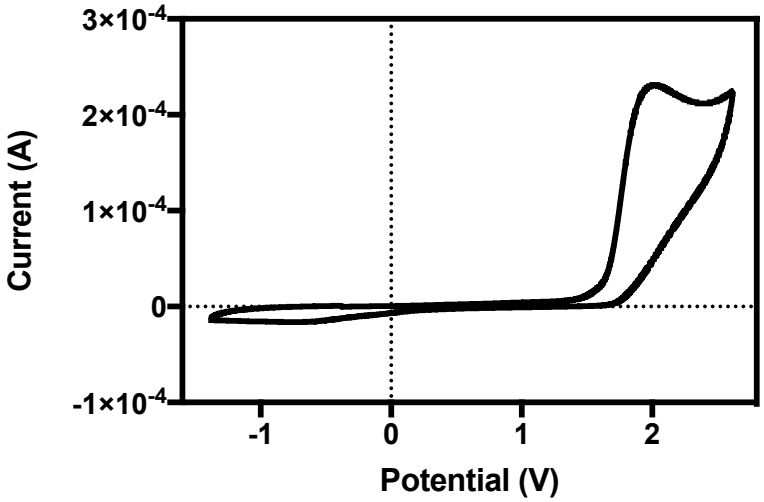



**y = 2.83 x +1**
**$r^2$ = 0.98**

**Cyclic voltammetry details and results**

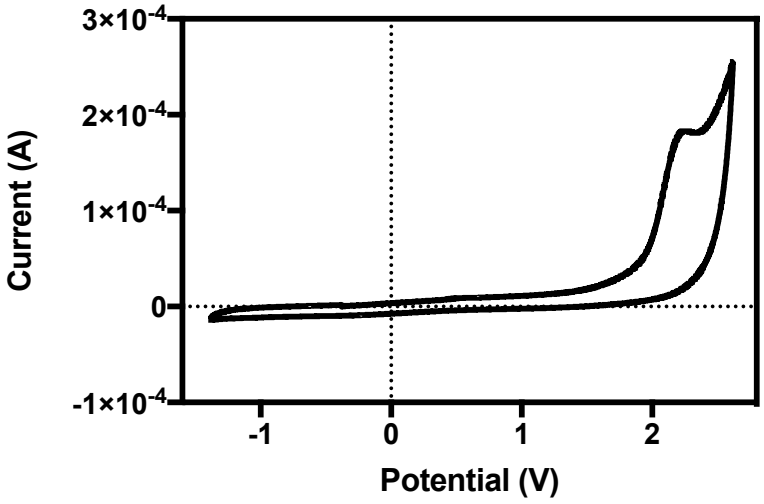
Cyclic voltammetry experiments were carried out with 0.1 M $NBu_4PF_6$ as electrolyte in acetonitrile. Experiments were run using a 0.002 M substrate, glassy carbon as working electrode, platinum mesh as counter electrode and SEC as reference electrode with a scan rate of 0.1 V/s.

1. 4-methoxyl-*N*-propylbenzenesulfonamide



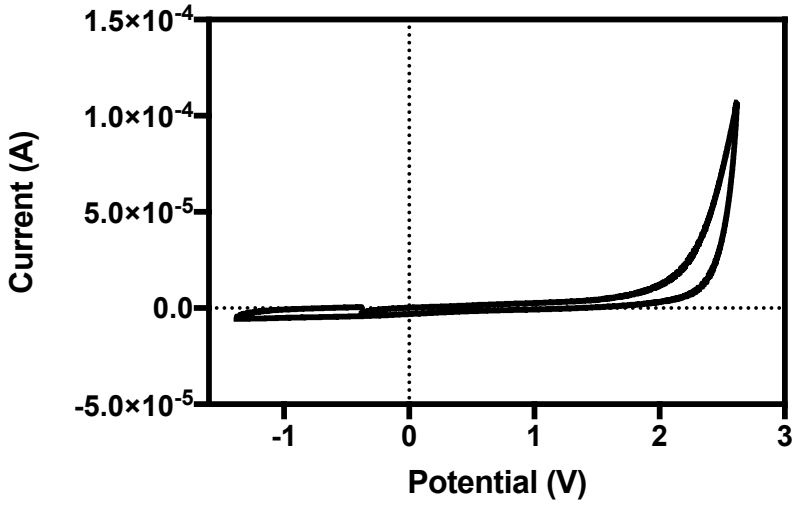

**$E_p$ = 2.08 V vs. $Fc^+$/Fc**
**$E_{p/2}$ = 1.77 V vs. $Fc^+$/Fc**

2. 4-methyl-*N*-propylbenzenesulfonamide



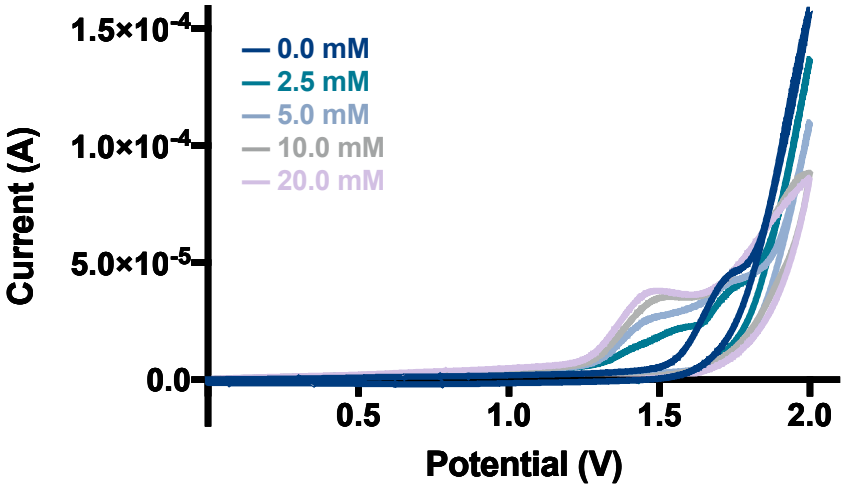

**$E_p$ = 2.31 V vs. $Fc^+$/Fc**
**$E_{p/2}$ = 2.07 V vs. $Fc^+$/Fc**

3. 4-cyano-*N*-propylbenzenesulfonamide




4. 4-methoxybenzenesulfonamide with different loading of phosphate base

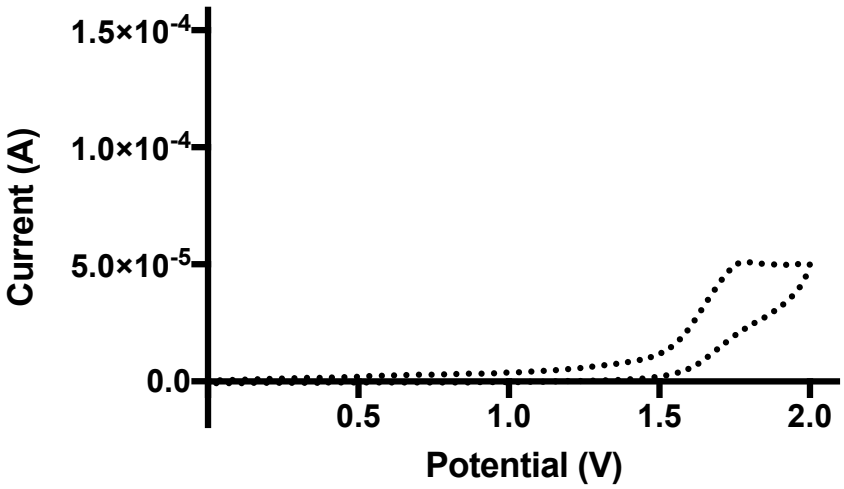
Cyclic voltammetry experiments were carried out with 0.1 M $NBu_4PF_6$ as electrolyte in dichloromethane. Experiments were run using a 0.0025 M substrate and various concentration of tetrabutylammonium dibutylphosphate, glassy carbon were used as working electrode, platinum mesh were used as counter electrode and $Ag^+/Ag$ (in acetonitrile) were used as reference electrode with a scan rate of 0.1 V/s.




4. tetrabutylammonium dibutylphosphate base

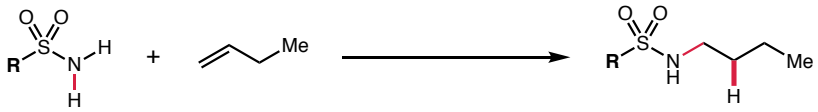
Cyclic voltammetry experiments were carried out with 0.1 M $NBu_4PF_6$ as electrolyte in dichloromethane. Experiments were run using a 0.005 M tetrabutylammonium dibutylphosphate, glassy carbon were used as working electrode, platinum mesh were

used as counter electrode and $Ag^{+}/Ag$ (in acetonitrile) were used as reference electrode with a scan rate of 0.1 V/s.

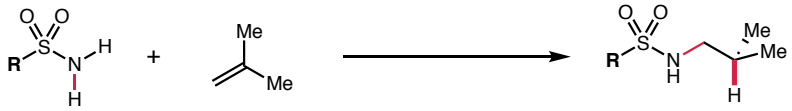


## DFT computational details and results

All calculations used DFT methodology as implemented in the Gaussian 09 series of computer programs. The absolute values were benchmarked with experimental bond strength of benzenesulfonamide (105.0 kcal/mol).[20] All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis. BDFE were calculated using the conversion factor 627.51 kcal $mol^{-1}$ per hartree and are rounded off after the third decimal place.

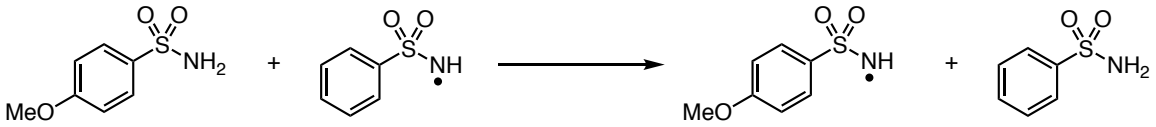


**ΔG°** (R = Me): – **4.7** kcal/mol
**ΔG°** (R = Ph): – **5.0** kcal/mol



**ΔG°** (R = Me): – **4.7** kcal/mol
**ΔG°** (R = Ph): – **5.7** kcal/mol

**Calculation 1:**
We employed the unrestricted B3LYP functional with basis set 6-31G+(d,p) in gas phase.



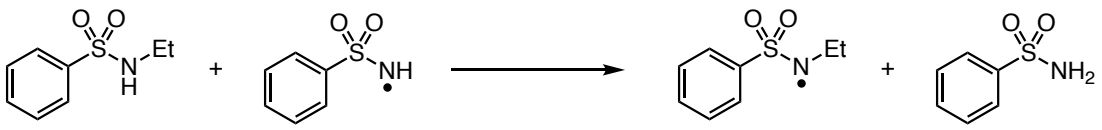
| Entry | Job name | E+ZPE | G | H | S |
|---|---|---|---|---|---|
| 1 | 4-methoxy-benzenesulfonamide | -950.577854 | -950.616903 | -950.565039 | 109.158161 |
| 2 | benzenesulfonamidyl radical | -835.419574 | -835.455010 | -835.409614 | 95.544961 |
| 3 | 4-methoxy-benzenesulfonamidyl radical | -949.918338 | -949.957344 | -949.905731 | 108.629881 |
| 4 | benzenesulfonamide | -836.079698 | -836.114941 | -836.069526 | 95.584951 |

ΔBDFE = (-949.957344 – 836.114941 + 950.616903 + 835.455010) * 627.51 = -0.233 kcal/mol

In 4- methoxy-benzenesulfonamide, BDFE(N-H) = 104.8 kcal/mol

**Calculation 2:**

We employed the unrestricted B3LYP functional with basis set 6-31G+(d,p) in gas phase.



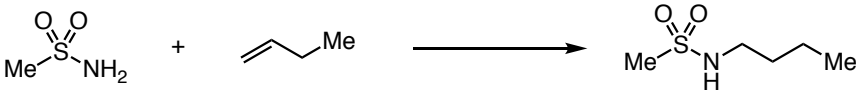
| Entry | Job name | E+ZPE | G | H | S |
|---|---|---|---|---|---|
| 5 | *N*-ethyl-benzenesulfonamide | -914.651680 | -914.691609 | -914.638843 | 111.056600 |
| 2 | benzenesulfonamidyl radical | -835.419574 | -835.455010 | -835.409614 | 95.544961 |
| 6 | N-ethyl-benzenesulfonamidyl radical | -914.003977 | -914.044624 | -913.990993 | 112.877166 |
| 4 | benzenesulfonamide | -836.079698 | -836.114941 | -836.069526 | 95.584951 |

$\Delta$BDFE = (-914.044624 – 836.114941 + 914.651680+ 835.455010) * 627.51 = -8.124 kcal/mol

In *N*-ethyl-benzenesulfonamide, BDFE(N-H) = 96.9 kcal/mol

**Calculation 3:**

We employed the CBS-QB3 functional in gas phase.

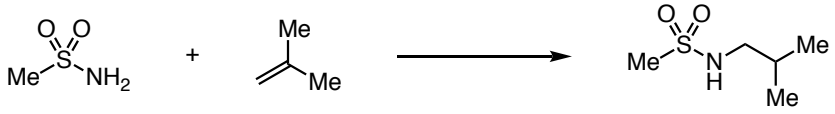


| Entry | Job name | CBS-QB3 (0K) | G | H | S |
|---|---|---|---|---|---|
| 7 | methanesulfonamide | -643.721196 | -643.750311 | -643.714204 | 75.994403 |
| 8 | 1-butene | -156.871268 | -156.898797 | -156.865019 | 71.092557 |
| 9 | N-butyl-methanesulfonamide | -800.618010 | -800.656505 | -800.605468 | 107.417574 |

$\Delta G^0$ = (- 800.656505 + 156.898797 + 643.750311) * 627.51 = -4.6 kcal/mol

**Calculation 4:**

We employed the CBS-QB3 functional in gas phase.

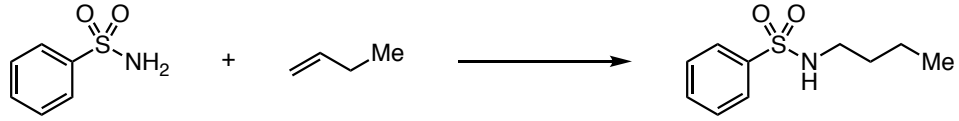


| Entry | Job name | CBS-QB3 (0K) | G | H | S |
|---|---|---|---|---|---|
| 7 | methanesulfonamide | -643.721196 | -643.750311 | -643.714204 | 75.994403 |
| 10 | 2-methylpropene | -156.874796 | -156.901566 | -156.869121 | 68.286992 |
| 11 | *N*-isobutyl-methanesulfonamide | -800.621303 | -800.659322 | -800.608846 | 106.236837 |

$\Delta G^0$ = (- 800.659322 + 156.901566 + 643.750311) * 627.51 = -4.7 kcal/mol

**Calculation 5:**

We employed the CBS-QB3 functional in gas phase.

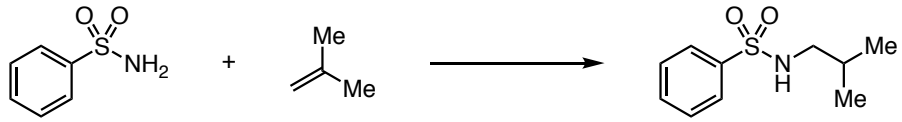


| Entry | Job name | CBS-QB3 (0K) | G | H | S |
|---|---|---|---|---|---|
| 12 | benzenesulfonamide | -835.107164 | -835.142191 | -835.097063 | 94.980902 |
| 8 | 1-butene | -156.871268 | -156.898797 | -156.865019 | 71.092557 |
| 13 | N-butyl-benzenesulfonamide | -992.006035 | -992.050118 | -991.990394 | 107.417574 |

$\Delta G^0$ = (- 992.050118+ 156.898797 + 835.142191) * 627.51 = -5.7 kcal/mol

**Calculation 6:**

We employed the CBS-QB3 functional in gas phase.



| Entry | Job name | CBS-QB3 (0K) | G | H | S |
|---|---|---|---|---|---|
| 12 | benzenesulfonamide | -835.107164 | -835.142191 | -835.097063 | 94.980902 |
| 10 | 2-methylpropene | -156.874796 | -156.901566 | -156.869121 | 68.286992 |
| 14 | N-butyl-benzenesulfonamide | -992.009120 | -992.053084 | -991.993463 | 125.484319 |

$\Delta G^0$ = (- 992.053084 + 156.901566 + 835.142191) * 627.51 = -5.9 kcal/mol

**Optimized Geometries**

Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points.

1. 4-methoxy-benzenesulfonamide

E(UB3LYP) = -950.737356
Zero-point correction= 0.159503 (Hartree/Particle)
Thermal correction to Energy= 0.171373
Thermal correction to Enthalpy= 0.172317
Thermal correction to Gibbs Free Energy= 0.120454
Sum of electronic and zero-point Energies= -950.577854
Sum of electronic and thermal Energies= -950.565983
Sum of electronic and thermal Enthalpies= -950.565039
Sum of electronic and thermal Free Energies= -950.616903

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | -1.68258480 | -0.98601197 | -0.02403387 |
| C | -0.29059138 | -1.09699140 | -0.07020642 |
| C | 0.49706338 | 0.05155635 | -0.08002149 |
| C | -0.08918859 | 1.32396093 | -0.05317409 |
| C | -1.47056760 | 1.43819203 | -0.00568135 |
| C | -2.27532307 | 0.28448729 | 0.01163235 |
| H | -2.28425184 | -1.88648063 | -0.02438082 |
| H | 0.17872709 | -2.07370821 | -0.11523259 |
| H | 0.53493304 | 2.21035601 | -0.08550759 |
| H | -1.95322466 | 2.40953360 | 0.00994720 |
| O | -3.61626816 | 0.50577543 | 0.05627734 |
| C | -4.49905356 | -0.61331539 | 0.06833927 |
| H | -5.50487222 | -0.19459024 | 0.10632461 |
| H | -4.38841029 | -1.21606686 | -0.84097242 |
| H | -4.33129758 | -1.24189459 | 0.95108663 |
| S | 2.27687084 | -0.10019159 | -0.13731789 |
| O | 2.81463272 | 1.08744984 | -0.81418815 |

| | | | |
|---|---|---|---|
| O | 2.59158430 | -1.46593184 | -0.57935834 |
| N | 2.75640069 | 0.03579865 | 1.48803082 |
| H | 3.11157840 | -0.85558041 | 1.82499962 |
| H | 3.45396269 | 0.77129181 | 1.57163267 |

2. benzenesulfonamidyl radical

E(UB3LYP) = -835.521969
Zero-point correction= 0.113111 (Hartree/Particle)
Thermal correction to Energy= 0.122126
Thermal correction to Enthalpy= 0.123071
Thermal correction to Gibbs Free Energy= 0.077674
Sum of electronic and zero-point Energies= -835.419574
Sum of electronic and thermal Energies= -835.410558
Sum of electronic and thermal Enthalpies= -835.409614
Sum of electronic and thermal Free Energies= -835.455010

Charge = 0; multiplicity = 2;

| | | | |
|---|---|---|---|
| C | 2.37295858 | 1.21326389 | 0.02396927 |
| C | 0.97803177 | 1.22150605 | -0.02794255 |
| C | 0.30131907 | 0.00000808 | -0.04995650 |
| C | 0.97800027 | -1.22149684 | -0.02786790 |
| C | 2.37292869 | -1.21328236 | 0.02406644 |
| H | 2.91543120 | 2.15343441 | 0.03772157 |
| H | 0.42241691 | 2.15211929 | -0.06381333 |
| H | 0.42241545 | -2.15213069 | -0.06371577 |
| H | 2.91538361 | -2.15346245 | 0.03790325 |
| S | -1.48638313 | 0.00002642 | -0.10060079 |
| O | -1.94955008 | -1.27856451 | -0.66553311 |
| O | -1.94957845 | 1.27923752 | -0.66415462 |
| N | -1.90534938 | -0.00068863 | 1.53192843 |
| H | -2.93913834 | -0.00080774 | 1.51918881 |
| C | 3.06734523 | -0.00002018 | 0.05204756 |
| H | 4.15259361 | -0.00001097 | 0.09043313 |

3. 4-methoxy-benzenesulfonamidyl radical

E(UB3LYP) = -950.059398
Zero-point correction= 0.145568 (Hartree/Particle)
Thermal correction to Energy= 0.157232
Thermal correction to Enthalpy= 0.158176
Thermal correction to Gibbs Free Energy= 0.106563
Sum of electronic and zero-point Energies= -949.918338
Sum of electronic and thermal Energies= -949.906675
Sum of electronic and thermal Enthalpies= -949.905731
Sum of electronic and thermal Free Energies= -949.957344

Charge = 0; multiplicity = 2;

| | | | |
|---|---|---|---|
| C | -1.64733710 | -0.98768801 | -0.02652585 |
| C | -0.25634358 | -1.09482819 | -0.06082751 |
| C | 0.52586277 | 0.05897041 | -0.06522126 |
| C | -0.06207671 | 1.33092046 | -0.03941422 |
| C | -1.44405743 | 1.43949404 | -0.00476513 |
| C | -2.24430542 | 0.28233717 | 0.00462155 |
| H | -2.24668414 | -1.88953114 | -0.02936805 |
| H | 0.21581469 | -2.07057238 | -0.09664991 |
| H | 0.56117344 | 2.21815581 | -0.05981558 |
| H | -1.93048750 | 2.40880886 | 0.01017900 |
| O | -3.58421022 | 0.49800309 | 0.03869596 |
| C | -4.46560125 | -0.62360083 | 0.05018547 |
| H | -5.47190580 | -0.20588047 | 0.08125329 |
| H | -4.34870098 | -1.22869215 | -0.85652997 |
| H | -4.30092236 | -1.24762515 | 0.93642072 |
| S | 2.29700185 | -0.08754923 | -0.09011322 |
| O | 2.87335296 | 1.14069514 | -0.66503231 |
| O | 2.66268002 | -1.40916209 | -0.62919538 |
| N | 2.71105234 | -0.09541242 | 1.54544990 |
| H | 3.74088684 | -0.18590826 | 1.53410839 |

4. benzenesulfonamide

E(UB3LYP) = -836.204312

Zero-point correction= 0.127034 (Hartree/Particle)

Thermal correction to Energy= 0.136262

Thermal correction to Enthalpy= 0.137206

Thermal correction to Gibbs Free Energy= 0.091791

Sum of electronic and zero-point Energies= -836.079698

Sum of electronic and thermal Energies= -836.070470

Sum of electronic and thermal Enthalpies= -836.069526

Sum of electronic and thermal Free Energies= -836.114941

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | 2.39947584 | 1.21233084 | 0.04211556 |
| C | 1.00527223 | 1.21944441 | -0.03371405 |
| C | 0.32597452 | -0.00005026 | -0.06417670 |
| C | 1.00533237 | -1.21945933 | -0.03366858 |
| C | 2.39957881 | -1.21225057 | 0.04214940 |
| H | 2.94107830 | 2.15312018 | 0.06165634 |
| H | 0.45122473 | 2.15028666 | -0.08609612 |
| H | 0.45137306 | -2.15035728 | -0.08596537 |
| H | 2.94122402 | -2.15301638 | 0.06171501 |
| S | -1.46920420 | -0.00008914 | -0.15268156 |

| | | | |
|---|---|---|---|
| O | -1.88846466 | -1.28758460 | -0.72067840 |
| O | -1.88845678 | 1.28681073 | -0.72203625 |
| N | -1.95130223 | 0.00074961 | 1.47410755 |
| H | -2.48237532 | 0.84312455 | 1.67974442 |
| H | -2.48264195 | -0.84126490 | 1.68053899 |
| C | 3.09479131 | 0.00004174 | 0.08318062 |
| H | 4.17932109 | 0.00013614 | 0.13895855 |

5. *N*-ethyl-benzenesulfonamide

E(UB3LYP) = -914.835419
Zero-point correction= 0.183740 (Hartree/Particle)
Thermal correction to Energy= 0.195632
Thermal correction to Enthalpy= 0.196577
Thermal correction to Gibbs Free Energy= 0.143811
Sum of electronic and zero-point Energies= -914.651680
Sum of electronic and thermal Energies= -914.639787
Sum of electronic and thermal Enthalpies= -914.638843
Sum of electronic and thermal Free Energies= -914.691609

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | 2.99492798 | 0.42123746 | 1.02491630 |
| C | 1.68475407 | 0.84292591 | 0.80143355 |
| C | 0.90803423 | 0.16645083 | -0.14377327 |
| C | 1.41643559 | -0.90981801 | -0.87186572 |
| C | 2.73152571 | -1.32370638 | -0.63800449 |
| H | 3.61023130 | 0.94010555 | 1.75368179 |
| H | 1.27077067 | 1.68730451 | 1.34201746 |
| H | 0.79471647 | -1.39748654 | -1.61453541 |
| H | 3.13971522 | -2.15793343 | -1.20045804 |
| S | -0.77899064 | 0.71735188 | -0.44646224 |
| O | -1.26338567 | -0.02573383 | -1.61974233 |
| O | -0.81261653 | 2.18583093 | -0.40570076 |
| N | -1.59343968 | 0.23600511 | 0.94922224 |
| H | -2.18809404 | 1.00546155 | 1.24893942 |
| C | 3.51703988 | -0.66216365 | 0.30833191 |
| H | 4.53878060 | -0.98498834 | 0.48527856 |
| C | -2.20941423 | -1.10103173 | 1.02284465 |
| H | -2.24966216 | -1.36433493 | 2.08596967 |
| H | -1.51755933 | -1.80627880 | 0.55295194 |
| C | -3.59751228 | -1.20494670 | 0.38766514 |
| H | -3.55355705 | -0.97962067 | -0.68060793 |
| H | -3.99592787 | -2.21762688 | 0.51640180 |
| H | -4.29821387 | -0.50873109 | 0.86345727 |

6. N-ethyl-benzenesulfonamidyl radical
E(UB3LYP) = -914.173473
Zero-point correction= 0.169496 (Hartree/Particle)
Thermal correction to Energy= 0.181536
Thermal correction to Enthalpy= 0.182480
Thermal correction to Gibbs Free Energy= 0.128849
Sum of electronic and zero-point Energies= -914.003977
Sum of electronic and thermal Energies= -913.991938
Sum of electronic and thermal Enthalpies= -913.990993
Sum of electronic and thermal Free Energies= -914.044624

Charge = 0; multiplicity = 2;

| | | | |
|---|---|---|---|
| C | 2.93814639 | 0.54486780 | -1.21348712 |
| C | 1.63224172 | 0.05147486 | -1.22077491 |
| C | 0.99657787 | -0.18335124 | 0.00010096 |
| C | 1.63208794 | 0.05344186 | 1.22068030 |
| C | 2.93798821 | 0.54681172 | 1.21277186 |
| H | 3.44827447 | 0.72935485 | -2.15389513 |
| H | 1.11617354 | -0.16087802 | -2.15062289 |
| H | 1.11589635 | -0.15741750 | 2.15079979 |
| H | 3.44802094 | 0.73278030 | 2.15294016 |
| S | -0.68368095 | -0.80349525 | 0.00050090 |
| O | -0.93374546 | -1.48829218 | 1.28028785 |
| O | -0.93390517 | -1.48932490 | -1.27864058 |
| N | -1.58032785 | 0.64924217 | 0.00038100 |
| C | 3.58759211 | 0.79403633 | -0.00051793 |
| H | 4.60423668 | 1.17593394 | -0.00075288 |
| C | -3.01667028 | 0.42495706 | -0.00031823 |
| H | -3.28522747 | -0.18448677 | 0.87784756 |
| H | -3.28437270 | -0.18538415 | -0.87811857 |
| C | -3.76594443 | 1.75441592 | -0.00133248 |
| H | -3.51280575 | 2.34306183 | -0.88789167 |
| H | -4.84601829 | 1.57541931 | -0.00191507 |
| H | -3.51389984 | 2.34385587 | 0.88501443 |

7. methanesulfonamide

Total energy: -643.613144
E(ZPE)= 0.073542
E(Thermal)= 0.079590
E(SCF)= -642.562648
DE(MP2)= -1.050496
DE(CBS)= -0.109972
DE(MP34)= -0.030512
DE(CCSD)= -0.024685
DE(Int)= 0.035015

DE(Empirical)= -0.051440
CBS-QB3 (0 K)= -643.721196
CBS-QB3 Energy= -643.715148
CBS-QB3 Enthalpy= -643.714204
CBS-QB3 Free Energy= -643.750311

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | -1.54842225 | 0.64158152 | 0.00049240 |
| H | -1.62910284 | 1.25179187 | -0.89735983 |
| H | -1.62902059 | 1.25068412 | 0.89910123 |
| H | -2.30158929 | -0.14635603 | 0.00002224 |
| S | 0.04434696 | -0.17045559 | -0.00008200 |
| O | 0.19288432 | -0.85186443 | -1.26401485 |
| O | 0.19333172 | -0.85294090 | 1.26321582 |
| N | 1.10115947 | 1.13400065 | 0.00040815 |
| H | 1.67190011 | 1.11031401 | 0.83879086 |
| H | 1.67095005 | 1.11180442 | -0.83866175 |

8. 1-butene

Total energy: -156.830191
E(ZPE)= 0.106896
E(Thermal)= 0.112200
E(SCF)= -156.159726
DE(MP2)= -0.670465
DE(CBS)= -0.064311
DE(MP34)= -0.051655
DE(CCSD)= -0.020173
DE(Int)= 0.023407
DE(Empirical)= -0.035240
CBS-QB3 (0 K)= -156.871268
CBS-QB3 Energy= -156.865964
CBS-QB3 Enthalpy= -156.865019
CBS-QB3 Free Energy= -156.898797

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | 1.85790274 | 0.01723232 | -0.28063846 |
| H | 1.95202164 | 0.92452634 | -0.87048695 |
| H | 2.73420582 | -0.61865800 | -0.22178390 |
| C | 0.72412363 | -0.29416259 | 0.34029145 |
| H | 0.67642907 | -1.21693392 | 0.91831420 |
| C | -0.53898363 | 0.51999234 | 0.30799349 |
| H | -0.36536248 | 1.44205099 | -0.25613937 |
| H | -0.79644153 | 0.82229414 | 1.33138510 |
| C | -1.72774405 | -0.24675452 | -0.29414868 |
| H | -1.92876147 | -1.16625588 | 0.26389827 |

| | | | |
|---|---|---|---|
| H | -2.63690288 | 0.36019756 | -0.27414455 |
| H | -1.52698033 | -0.52506655 | -1.33202959 |

9. N-butyl-methanesulfonamide

Total energy: -800.475480
E(ZPE)= 0.185531
E(Thermal)= 0.197128
E(SCF)= -798.741668
DE(MP2)= -1.733812
DE(CBS)= -0.174223
DE(MP34)= -0.080132
DE(CCSD)= -0.044902
DE(Int)= 0.057991
DE(Empirical)= -0.086794
CBS-QB3 (0 K)= -800.618010
CBS-QB3 Energy= -800.606412
CBS-QB3 Enthalpy= -800.605468
CBS-QB3 Free Energy= -800.656505

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | -2.41171216 | -1.04401473 | -1.16626670 |
| H | -1.73569929 | -1.89836122 | -1.16147894 |
| H | -2.38157052 | -0.52317523 | -2.12106099 |
| H | -3.42573711 | -1.36593301 | -0.92849538 |
| S | -1.91680518 | 0.09551096 | 0.12148836 |
| O | -1.89984215 | -0.64346488 | 1.36357982 |
| O | -2.68903706 | 1.30808236 | -0.02732013 |
| N | -0.35592866 | 0.49115999 | -0.33242880 |
| H | -0.28305473 | 1.50365654 | -0.32692460 |
| C | 0.77694706 | -0.19709054 | 0.31384489 |
| H | 0.67157956 | -1.26907839 | 0.12719116 |
| H | 0.76302081 | -0.05849701 | 1.40030457 |
| C | 2.09423009 | 0.30483053 | -0.27622671 |
| H | 2.07930137 | 0.15770182 | -1.36164568 |
| H | 2.17475155 | 1.38703641 | -0.10893884 |
| C | 3.31714542 | -0.39114516 | 0.33205136 |
| H | 3.23816775 | -1.47166357 | 0.16373107 |
| H | 3.31146244 | -0.25035701 | 1.41905968 |
| C | 4.64147446 | 0.11910716 | -0.24245449 |
| H | 5.49359149 | -0.39622358 | 0.20796403 |
| H | 4.69100224 | -0.03898150 | -1.32407911 |
| H | 4.76609241 | 1.19051698 | -0.05820666 |

10. 2-methylpropene

Total energy: -156.833026
E(ZPE)= 0.105912
E(Thermal)= 0.110642
E(SCF)= -156.160516
DE(MP2)= -0.672510
DE(CBS)= -0.064408
DE(MP34)= -0.051147
DE(CCSD)= -0.020313
DE(Int)= 0.023410
DE(Empirical)= -0.035224
CBS-QB3 (0 K)= -156.874796
CBS-QB3 Energy= -156.870065
CBS-QB3 Enthalpy= -156.869121
CBS-QB3 Free Energy= -156.901566

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | -0.02760245 | 1.45285707 | -0.00001074 |
| H | 0.88759065 | 2.03648441 | -0.00010924 |
| H | -0.96000885 | 2.00686567 | 0.00002369 |
| C | -0.00728634 | 0.12033853 | 0.00002090 |
| C | 1.29691214 | -0.65727766 | -0.00003251 |
| H | 1.12253164 | -1.73553245 | -0.00073755 |
| H | 1.90012281 | -0.42025575 | -0.88109956 |
| H | 1.89952225 | -0.42132803 | 0.88173712 |
| C | -1.27217374 | -0.69796549 | 0.00003535 |
| H | -1.31253091 | -1.35257750 | -0.87865895 |
| H | -1.31232485 | -1.35285061 | 0.87853142 |
| H | -2.16400047 | -0.06852041 | 0.00023509 |

11. *N*-isobutyl-methanesulfonamide

Total energy: -800.478827
E(ZPE)= 0.185086
E(Thermal)= 0.196599
E(SCF)= -798.741298
DE(MP2)= -1.737529
DE(CBS)= -0.174262
DE(MP34)= -0.079241
DE(CCSD)= -0.045297
DE(Int)= 0.057995
DE(Empirical)= -0.086756
CBS-QB3 (0 K)= -800.621303
CBS-QB3 Energy= -800.609790
CBS-QB3 Enthalpy= -800.608846

CBS-QB3 Free Energy= -800.659322

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | -1.99184646 | 1.32030689 | -0.90153555 |
| H | -1.26571547 | 1.38182154 | -1.71123818 |
| H | -1.91884237 | 2.18181957 | -0.24097464 |
| H | -2.99942436 | 1.22290722 | -1.30616219 |
| S | -1.67482347 | -0.15967185 | 0.05306295 |
| O | -1.72090853 | -1.27652037 | -0.86295035 |
| O | -2.50111743 | -0.11605765 | 1.23808720 |
| N | -0.10788944 | 0.08083420 | 0.58455144 |
| H | -0.09976074 | -0.05469937 | 1.59041094 |
| C | 1.00744683 | -0.57266438 | -0.12337798 |
| H | 0.89071688 | -0.37304282 | -1.19205526 |
| H | 0.97237985 | -1.66027844 | 0.00187548 |
| C | 2.35969273 | -0.02587377 | 0.35874834 |
| H | 2.40666438 | -0.17434950 | 1.44685914 |
| C | 3.49997820 | -0.83479583 | -0.27327900 |
| H | 3.49198583 | -0.73519195 | -1.36386738 |
| H | 4.47097047 | -0.48224241 | 0.08374874 |
| H | 3.42085532 | -1.89883379 | -0.03383228 |
| C | 2.50924908 | 1.47298444 | 0.07275689 |
| H | 2.50522356 | 1.66164623 | -1.00653572 |
| H | 1.69365324 | 2.04591898 | 0.51767116 |
| H | 3.45278034 | 1.85431500 | 0.47226198 |

12. benzenesulfonamide

Total energy: -834.927290
E(ZPE)= 0.126002
E(Thermal)= 0.135158
E(SCF)= -833.119155
DE(MP2)= -1.808135
DE(CBS)= -0.180544
DE(MP34)= -0.040913
DE(CCSD)= -0.061028
DE(Int)= 0.059017
DE(Empirical)= -0.082406
CBS-QB3 (0 K)= -835.107164
CBS-QB3 Energy= -835.098007
CBS-QB3 Enthalpy= -835.097063
CBS-QB3 Free Energy= -835.142191

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | -0.31788366 | 0.00001392 | -0.05547863 |
| C | -0.99941585 | -1.21498079 | -0.03020399 |

| | | | |
|---|---|---|---|
| C | -2.38966922 | -1.20864447 | 0.04053841 |
| C | -3.08340414 | -0.00002632 | 0.07933825 |
| C | -2.38969731 | 1.20861169 | 0.04068738 |
| C | -0.99944304 | 1.21498951 | -0.03005424 |
| H | -0.44588683 | -2.14350977 | -0.08311370 |
| H | -2.93050052 | -2.14769144 | 0.05687653 |
| H | -4.16622303 | -0.00004133 | 0.13041432 |
| H | -2.93055153 | 2.14764346 | 0.05714193 |
| H | -0.44593074 | 2.14353476 | -0.08285064 |
| S | 1.46733477 | 0.00003300 | -0.15343636 |
| O | 1.87538993 | 1.26753464 | -0.71244646 |
| O | 1.87541404 | -1.26728370 | -0.71284719 |
| N | 1.94074221 | -0.00026072 | 1.45372924 |
| H | 2.46375737 | -0.84210048 | 1.66668313 |
| H | 2.46343109 | 0.84167301 | 1.66711154 |

13. N-butyl-benzenesulfonamide

Total energy: -991.792269
E(ZPE)= 0.237991
E(Thermal)= 0.252687
E(SCF)= -989.299363
DE(MP2)= -2.492907
DE(CBS)= -0.244595
DE(MP34)= -0.089974
DE(CCSD)= -0.081411
DE(Int)= 0.081963
DE(Empirical)= -0.117739
CBS-QB3 (0 K)= -992.006035
CBS-QB3 Energy= -991.991339
CBS-QB3 Enthalpy= -991.990394
CBS-QB3 Free Energy= -992.050118

Charge = 0; multiplicity = 1;

| | | | |
|---|---|---|---|
| C | 1.65835017 | 0.03997367 | 0.00849492 |
| C | 2.04082577 | -0.55676613 | 1.20668505 |
| C | 2.87774498 | -1.67155431 | 1.17152932 |
| C | 3.32419395 | -2.17152058 | -0.04877844 |
| C | 2.93990754 | -1.55849432 | -1.24297058 |
| C | 2.10513984 | -0.44748023 | -1.22019107 |
| H | 1.69554453 | -0.14026024 | 2.14393313 |
| H | 3.18351719 | -2.14269891 | 2.09843896 |
| H | 3.97718858 | -3.03656559 | -0.07245433 |
| H | 3.29614396 | -1.94424714 | -2.19112399 |
| H | 1.80822189 | 0.04631137 | -2.13653775 |
| S | 0.60912944 | 1.48872739 | 0.04159406 |

| | | | |
|---|---|---|---|
| N | -0.83288254 | 0.90182999 | -0.56100350 |
| H | -1.22333151 | 1.60725924 | -1.17831221 |
| O | 1.07227031 | 2.42402836 | -0.95830693 |
| O | 0.46492081 | 1.87588839 | 1.42792578 |
| C | -1.80020143 | 0.28979664 | 0.36472808 |
| H | -2.12199177 | 0.99970508 | 1.13512322 |
| H | -1.29497554 | -0.53546865 | 0.87448790 |
| C | -3.00178934 | -0.24414633 | -0.41427318 |
| H | -3.48338063 | 0.58515635 | -0.94907429 |
| H | -2.64688749 | -0.94397643 | -1.17851705 |
| C | -4.03457869 | -0.92955859 | 0.48704961 |
| H | -4.37289774 | -0.22398583 | 1.25478074 |
| H | -3.55297056 | -1.75607958 | 1.02264026 |
| C | -5.24416242 | -1.45980272 | -0.28763588 |
| H | -5.96040107 | -1.94605186 | 0.37958629 |
| H | -5.76885240 | -0.65066734 | -0.80492518 |
| H | -4.94093163 | -2.19289511 | -1.04130398 |

14. N-butyl-benzenesulfonamide
Total energy: -991.795401
E(ZPE)= 0.237427
E(Thermal)= 0.252140
E(SCF)= -989.298559
DE(MP2)= -2.496841
DE(CBS)= -0.244529
DE(MP34)= -0.089020
DE(CCSD)= -0.081850
DE(Int)= 0.081946
DE(Empirical)= -0.117694
CBS-QB3 (0 K)= -992.009120
CBS-QB3 Energy= -991.994407
CBS-QB3 Enthalpy= -991.993463
CBS-QB3 Free Energy= -992.053084

Charge = 0; multiplicity = 1;

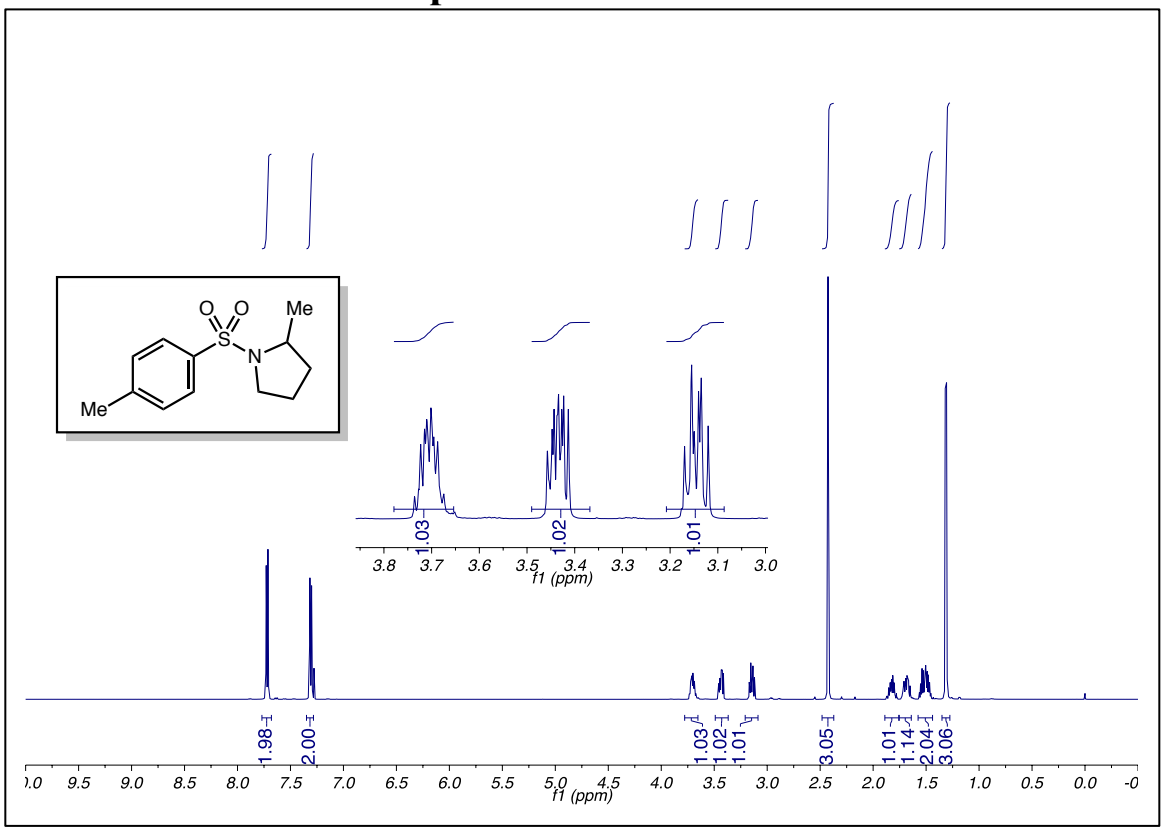
| | | | |
|---|---|---|---|
| C | 1.51541629 | 0.17779228 | 0.00620568 |
| C | 2.08518143 | -0.37672664 | 1.14878613 |
| C | 3.09268616 | -1.33083003 | 1.00893395 |
| C | 3.51895002 | -1.71569830 | -0.25924986 |
| C | 2.94387657 | -1.14669819 | -1.39736648 |
| C | 1.93920305 | -0.19489042 | -1.27008458 |
| H | 1.74800020 | -0.05148667 | 2.12435125 |
| H | 3.54507386 | -1.76710199 | 1.89188145 |
| H | 4.30388200 | -2.45601094 | -0.36446943 |
| H | 3.28303714 | -1.44224514 | -2.38342982 |
| H | 1.49114513 | 0.26267593 | -2.14278678 |

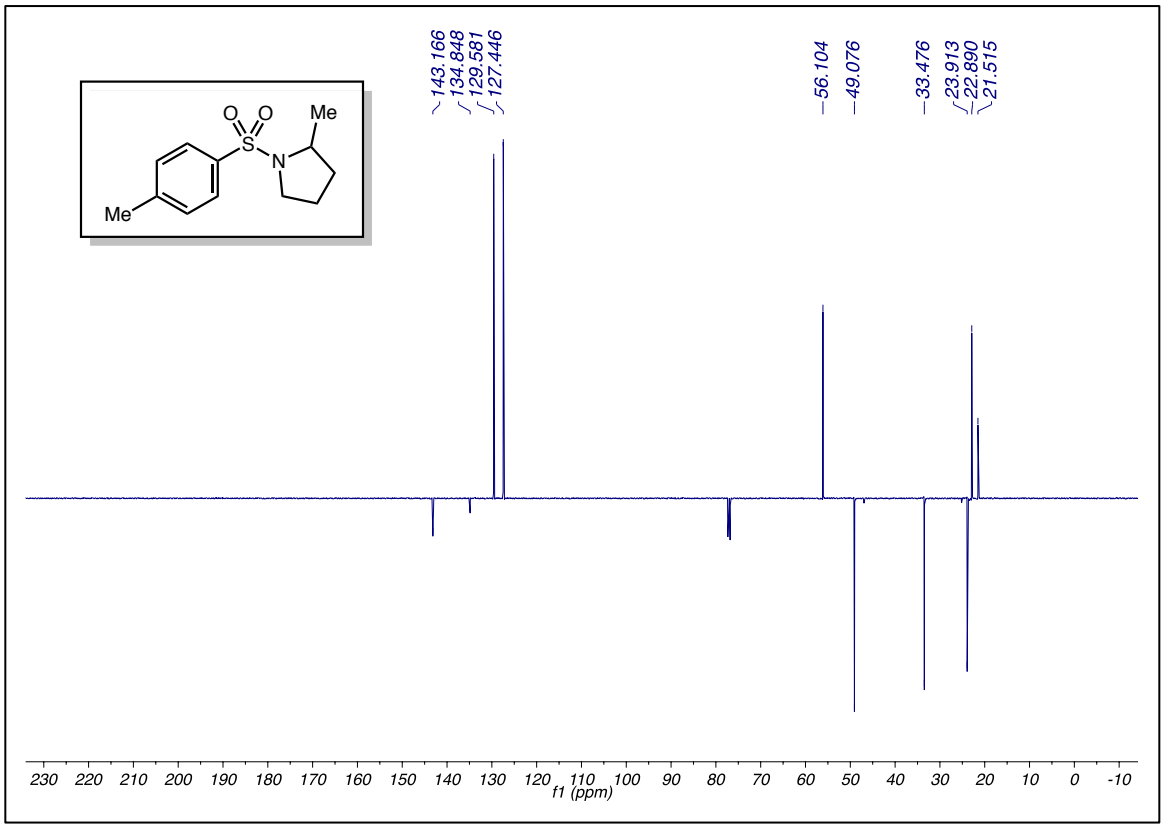
| | | | |
|---|---|---|---|
| S | 0.24678333 | 1.42867349 | 0.17407199 |
| N | -1.10612914 | 0.64870194 | -0.41520554 |
| H | -1.63148169 | 1.32101513 | -0.96415284 |
| O | 0.50253273 | 2.48635387 | -0.77733746 |
| O | 0.10792515 | 1.70400330 | 1.58724602 |
| C | -1.90903429 | -0.17640537 | 0.50166931 |
| H | -2.42623595 | 0.44037561 | 1.24767900 |
| H | -1.21728199 | -0.82478261 | 1.04462021 |
| C | -2.91968077 | -1.04449809 | -0.26179889 |
| H | -2.35133492 | -1.63993714 | -0.98596823 |
| C | -3.61722696 | -2.00047654 | 0.71540811 |
| H | -4.19273769 | -1.44802412 | 1.46549034 |
| H | -4.31047269 | -2.65951235 | 0.18637472 |
| H | -2.89545992 | -2.62968236 | 1.24408877 |
| C | -3.94651097 | -0.20142723 | -1.03090089 |
| H | -4.50307567 | 0.45466995 | -0.35294105 |
| H | -3.47902723 | 0.42059456 | -1.79948453 |
| H | -4.67048617 | -0.84394353 | -1.53884959 |

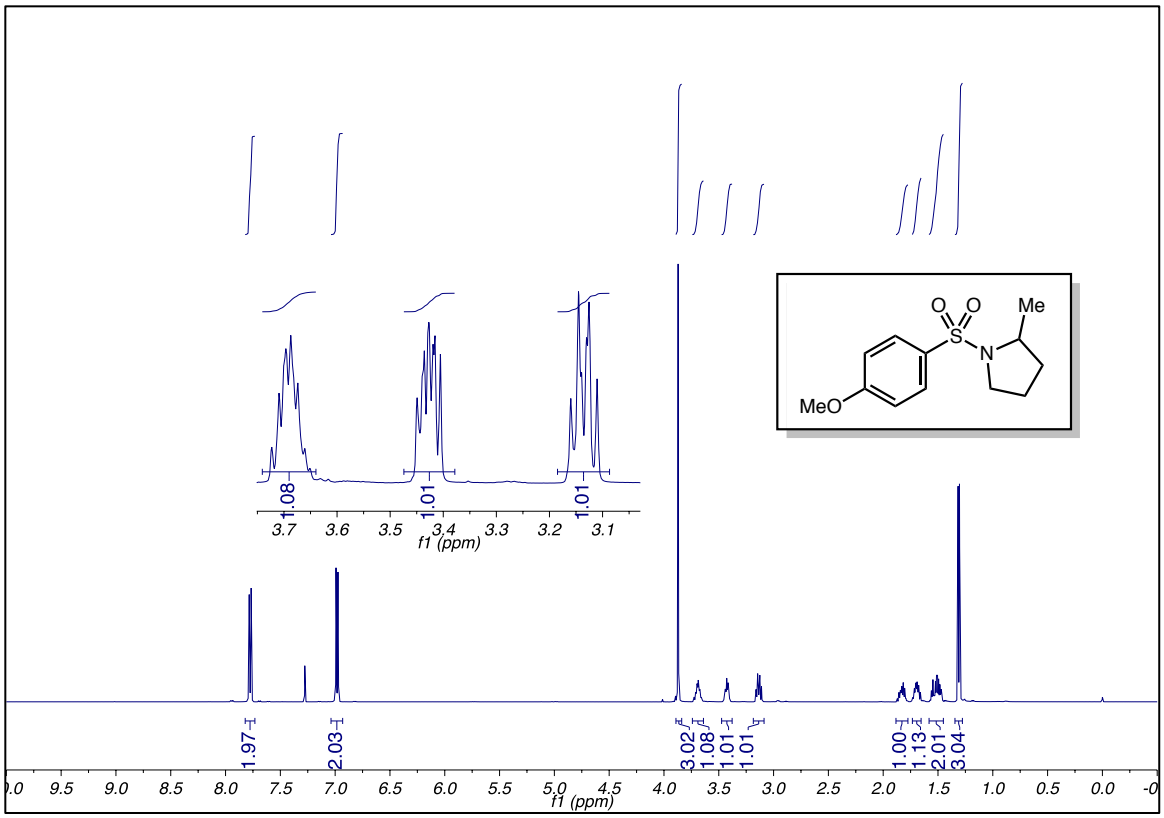
**Reference:**

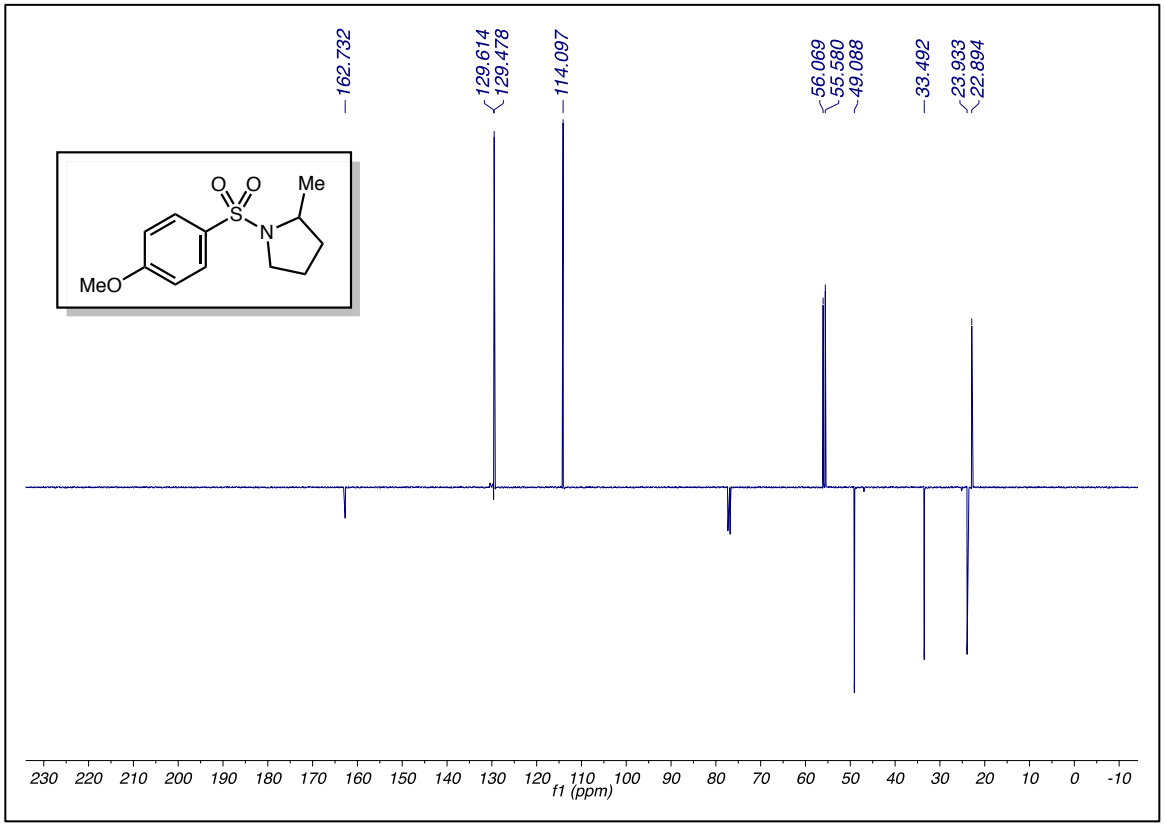

1. D. D. Perrin, W. L. F. Amarego, *Purification of Laboratory Chemicals* (Pergamon, Press, Oxford, ed. 3, 1988).
2. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15* , 1518.
3. Still, W. C.; Khan, M.; Mitra, A.; *J. Org. Chem.* **1978** , *43* , 2923.
4. Bondalapati, S., Indukuri, K., Ghosh, P. and Saikia, A. K., *Eur. J. Org. Chem.*, **2013**, 952.
5. Kim, J. Y. and Livinghouse, T., *Org. Lett*., **2005**, *7*, 1737.
6. Ryu, J.-S., Marks, T. J., McDonald, F. E., *Org. Lett*., **2001**, *3*, 3091.
7. Bender, C. F., Widenhoefer, R. A., *J. Am. Chem. Soc*, **2005**, *127*, 1070.
8. Nicolai, S. and Waser, J., *Org. Lett.*, **2011**, *13*, 6324.
9. Nagamoto, M., Yanagi, T., Nishimura, T. and Yorimitsu, H., *Org. Lett*., **2016**, *18*, 4474.
10. Nguyen, T. and Nicewicz, D. A. *J. Am. Chem. Soc.*, **2013**, *135*, 9588.
11. Su, C.-C., Williard, P. G., *Org. Lett.*, **2010**, *12*, 5378.
12. Abraham, E., Cooke, J. W. B., Davies, S. G., Naylor, A., Nicholson, R. L., Price, P. D., Smith, A. D., *Tetrahedron*, **2007**, *63*, 5855.
13. Wang, P., Li, J., Yu, C.-L, Xiao, X., Wu, P.-Y., Zeng, B.-B., *Tetrahedron*, **2015**, *71*, 4647.
14. Mao, S.-W., Shuai, L., He, H.-B., Pan, N., Gao, L.-X., Yu, L.-F., Li, J., Li, J.-Y., Yang, F., *RSC Adv.*, **2015**, *5*, 106511.
15. Gargiulo, D., Blizzard, T. A., Nakanishi, K., *Tetrahedron*, **1989**, *45*, 5423.
16. A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, J. D. Weaver, *J. Organomet. Chem.* **2015**, *776*, 51.
17. L. Li, M. Zeng, and S. B. Herzon, *Angew. Chem. Int. Ed.* **2014**, *53*, 7892.
18. Musacchio, A. J.; Lainhart, B. C.; Zhang, X.; Naguib, S. G.; Sherwood, T. C.; Knowles, R. R. *Science*, **2017**, *355*, 727.
19. Choi, G. J., Zhu, Q., Miller, D. C., Gu, C. J., Knowles, R. R., *Nature*, **2016**, *539*, 268.
20. Zhao, Y.; Bordwell, F. G.; Cheng, J.; Wang, D. *J. Am. Chem. Soc.* **1997**, *119*, 9125.

# VII. $^{1}$H and $^{13}$C NMR Spectra of Products




O
O
Me
S
N
MeO
1.08
1.01
1.01
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f1 (ppm)
1.97
2.03
3.02
1.08
1.01
1.01
1.00
1.13
2.01
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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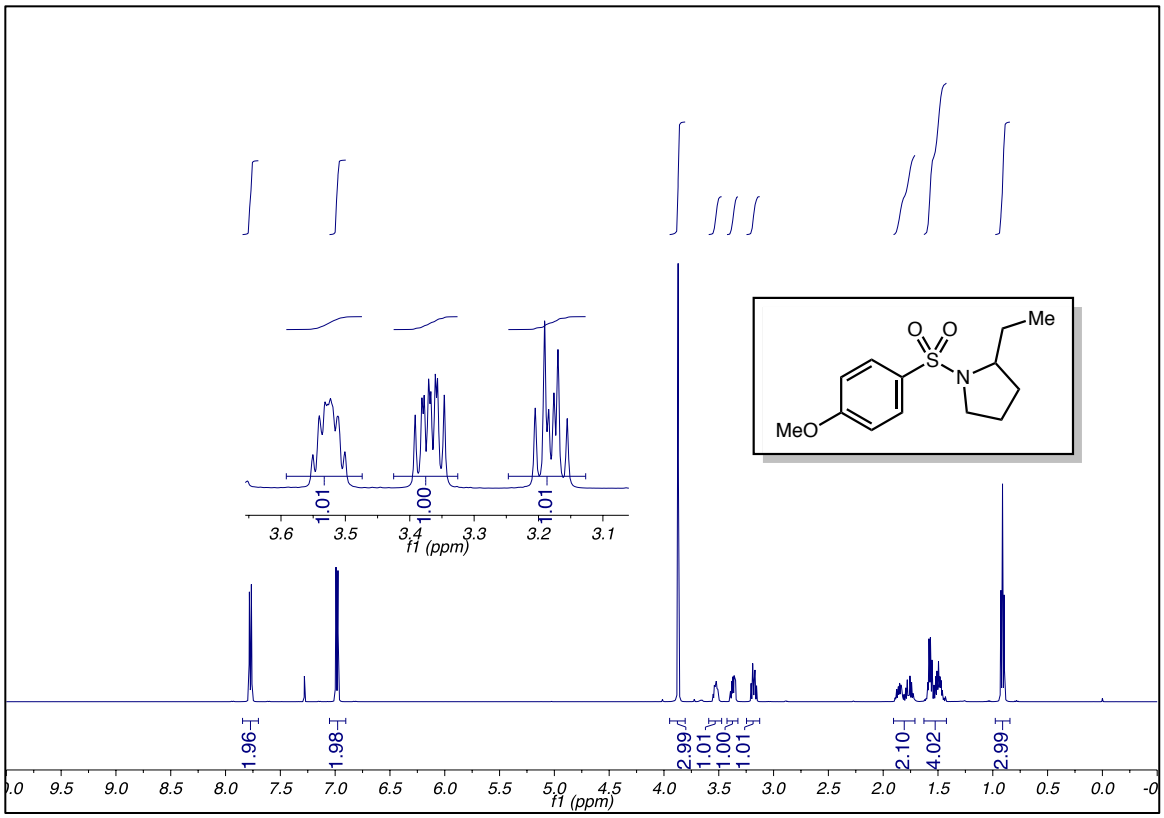
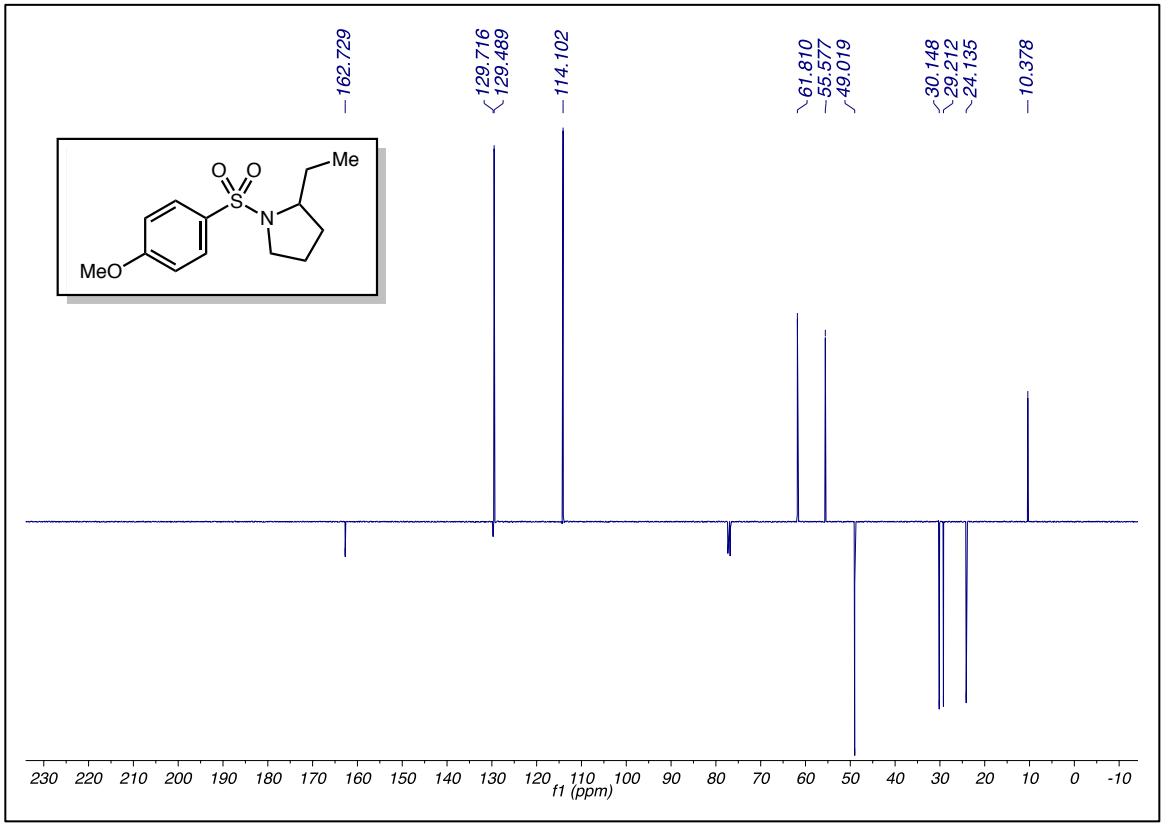
129.614
129.478
114.097
56.069
55.580
49.088
33.492
23.933
22.894
O
O
Me
S
N
MeO
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
O
O
S
N
MeO
1.01
1.00
1.01
3.6
3.5
3.4
3.3
3.2
3.1
f1 (ppm)
1.96
1.98
2.99
1.01
1.00
1.01
2.10
4.02
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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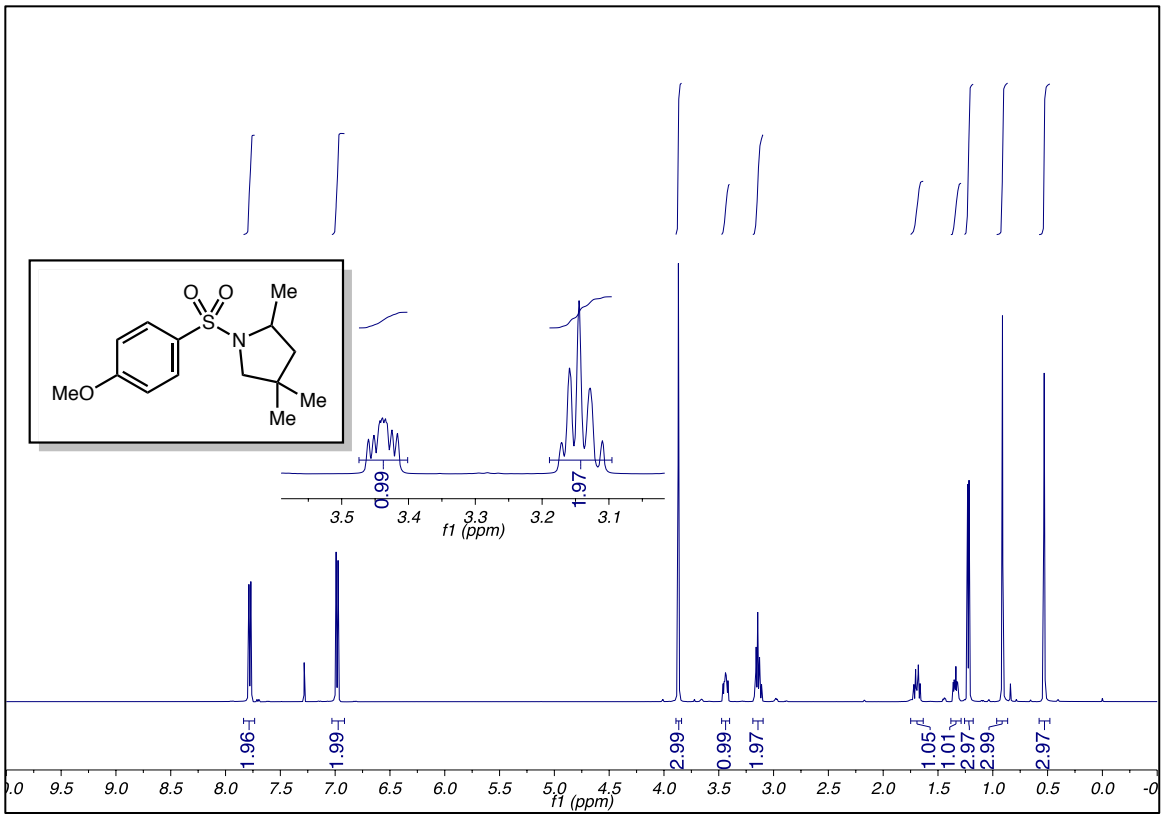
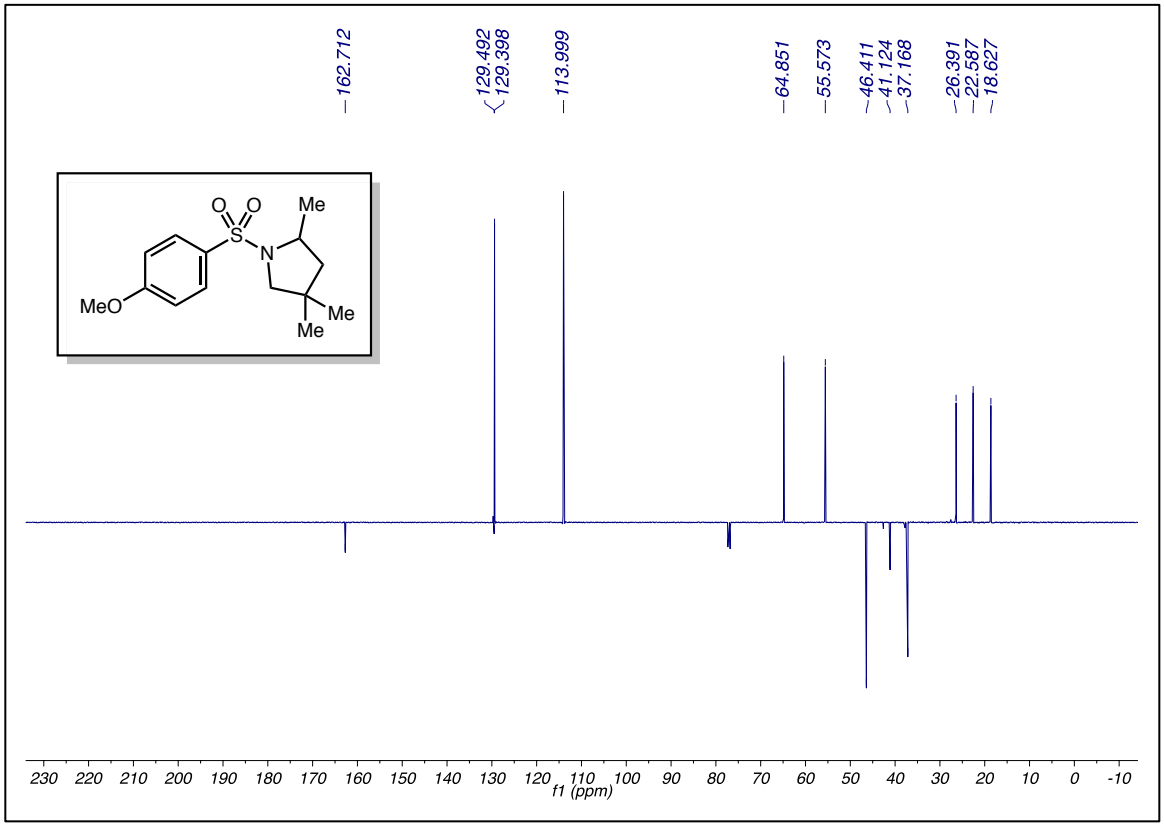
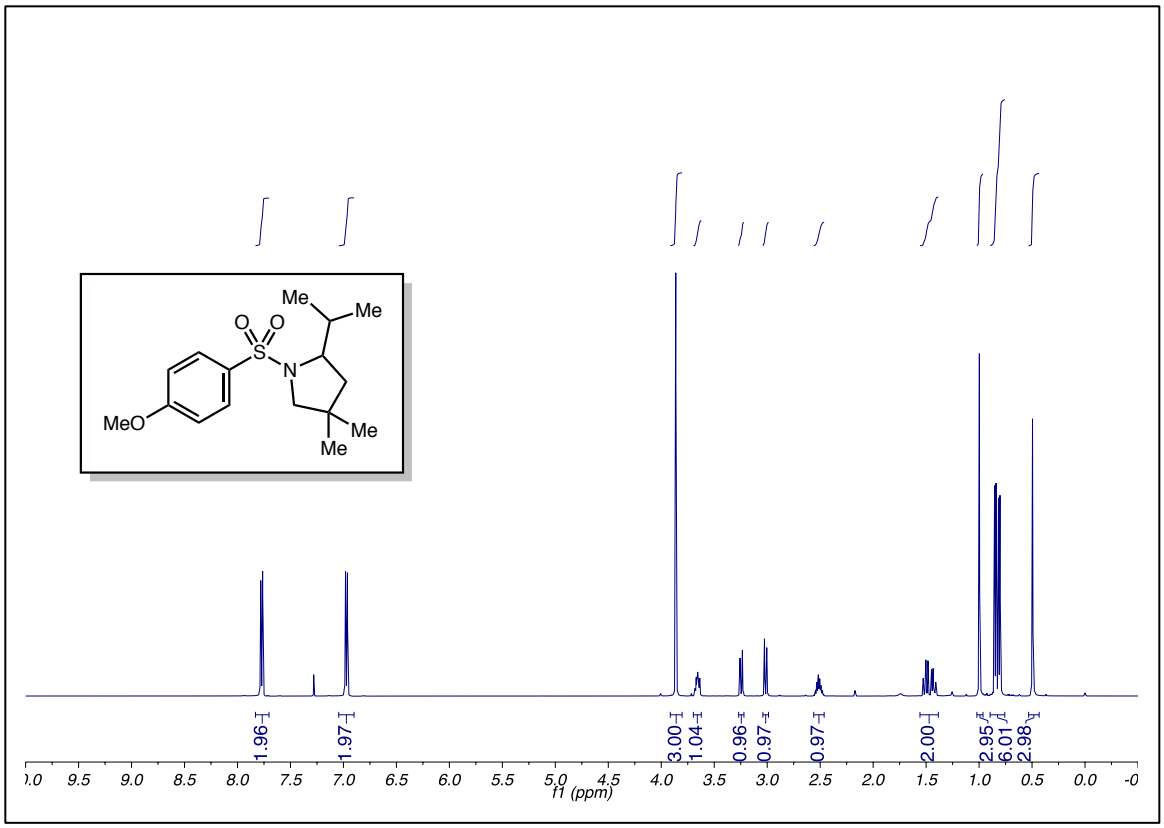
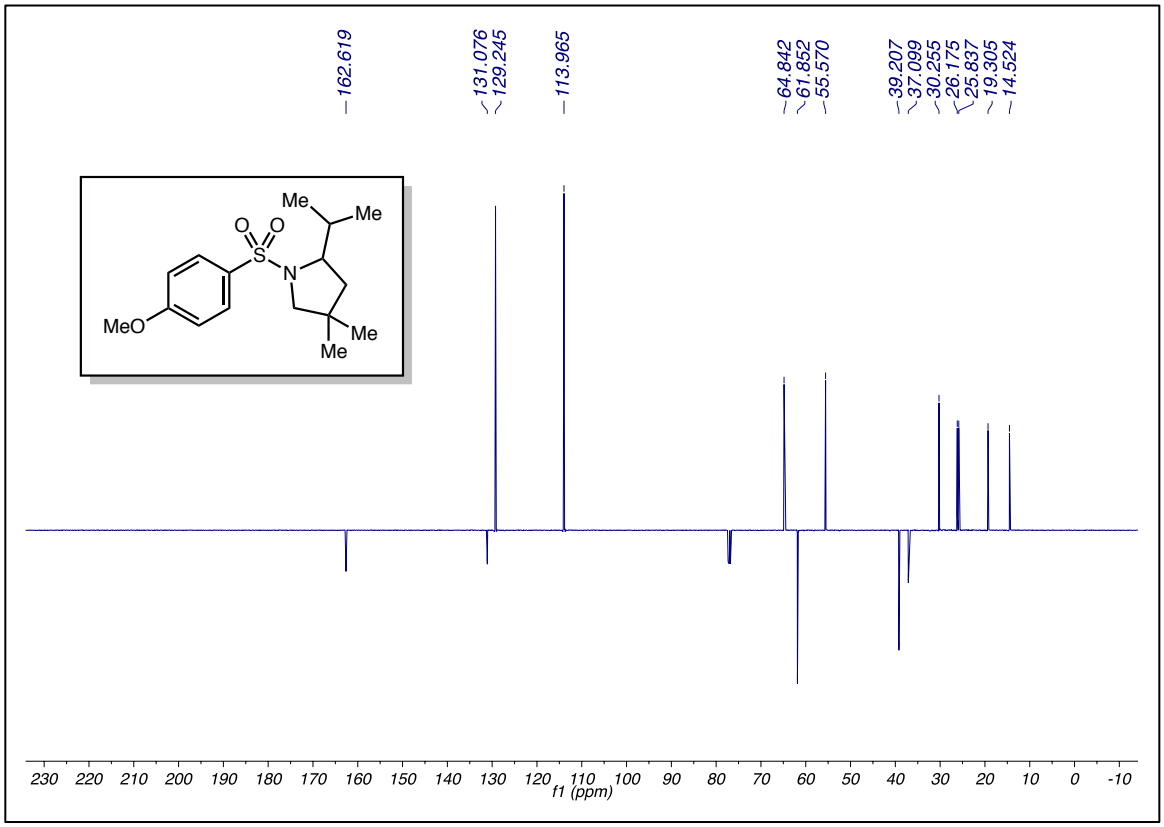
129.716
129.489
114.102
61.810
55.577
49.019
30.148
29.212
24.135
10.378
Me
O
O
S
N
MeO
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
Me
Me
Me
1.96
1.99
2.99
0.99
1.97
1.05
1.01
2.97
2.99
2.97
f1 (ppm)


162.712
129.492
129.398
113.999
64.851
55.573
46.411
41.124
37.168
26.391
22.587
18.627
MeO
Me
Me
Me
f1 (ppm)


Me
Me
O
O
S
N
MeO
Me
Me
1.96
1.97
3.00
1.04
0.96
0.97
0.97
2.00
2.95
6.01
2.98
f1 (ppm)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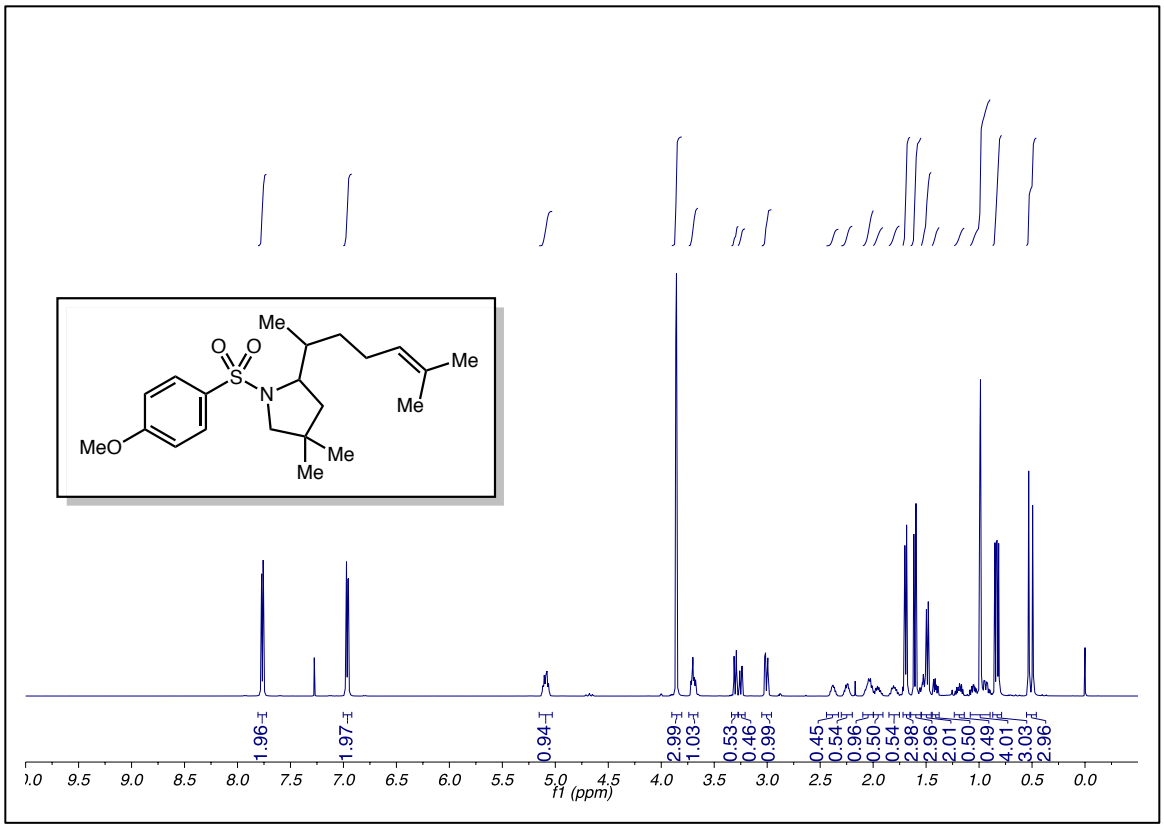
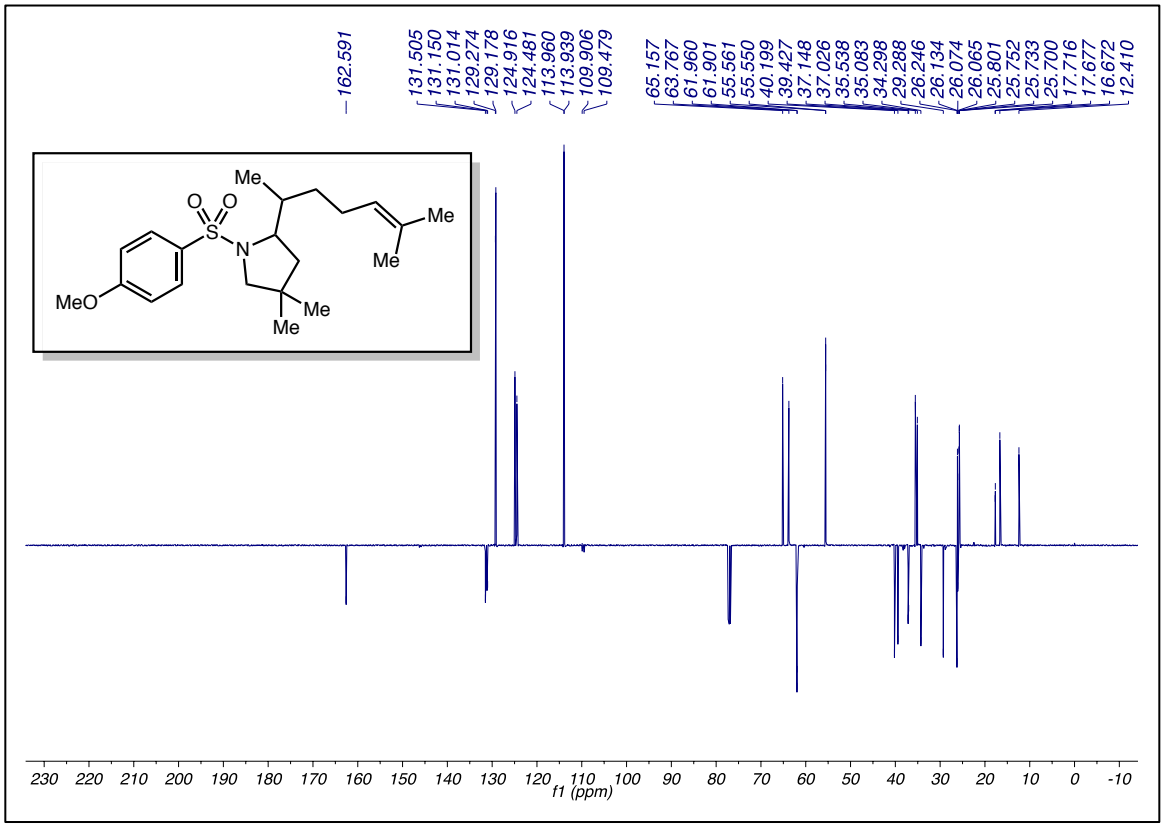
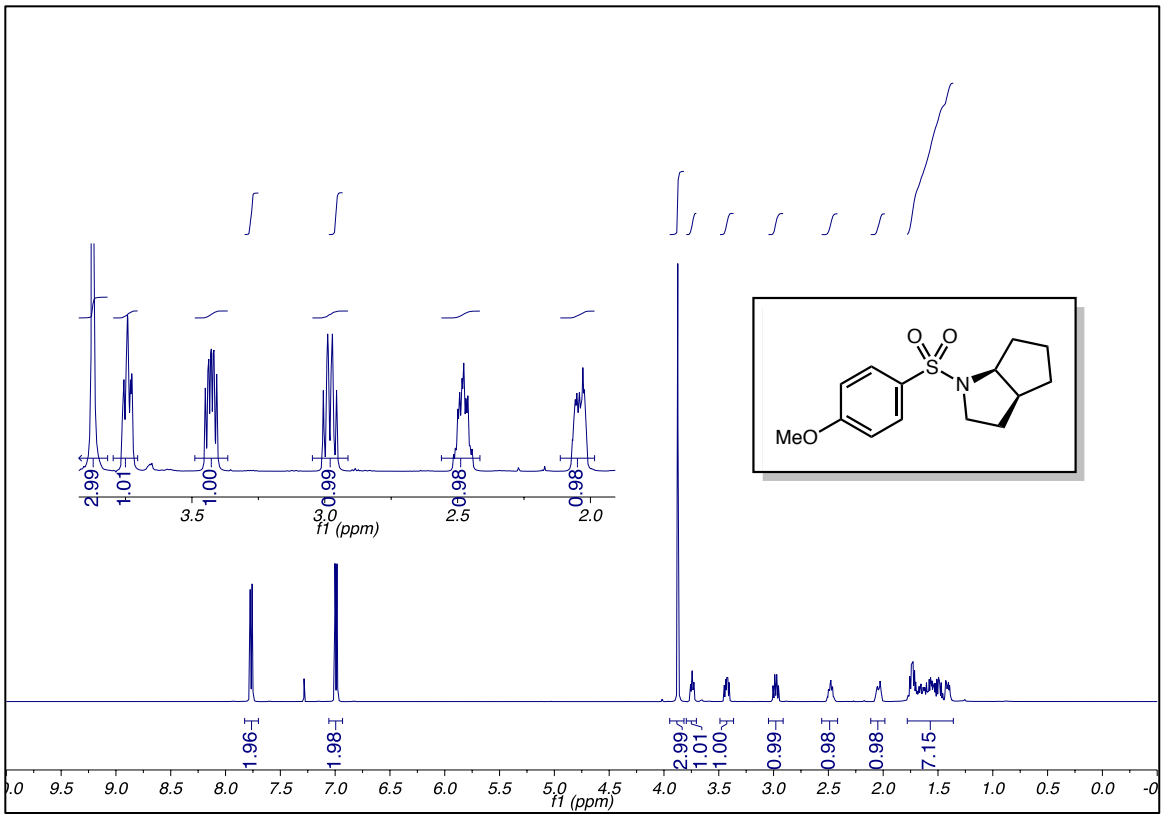
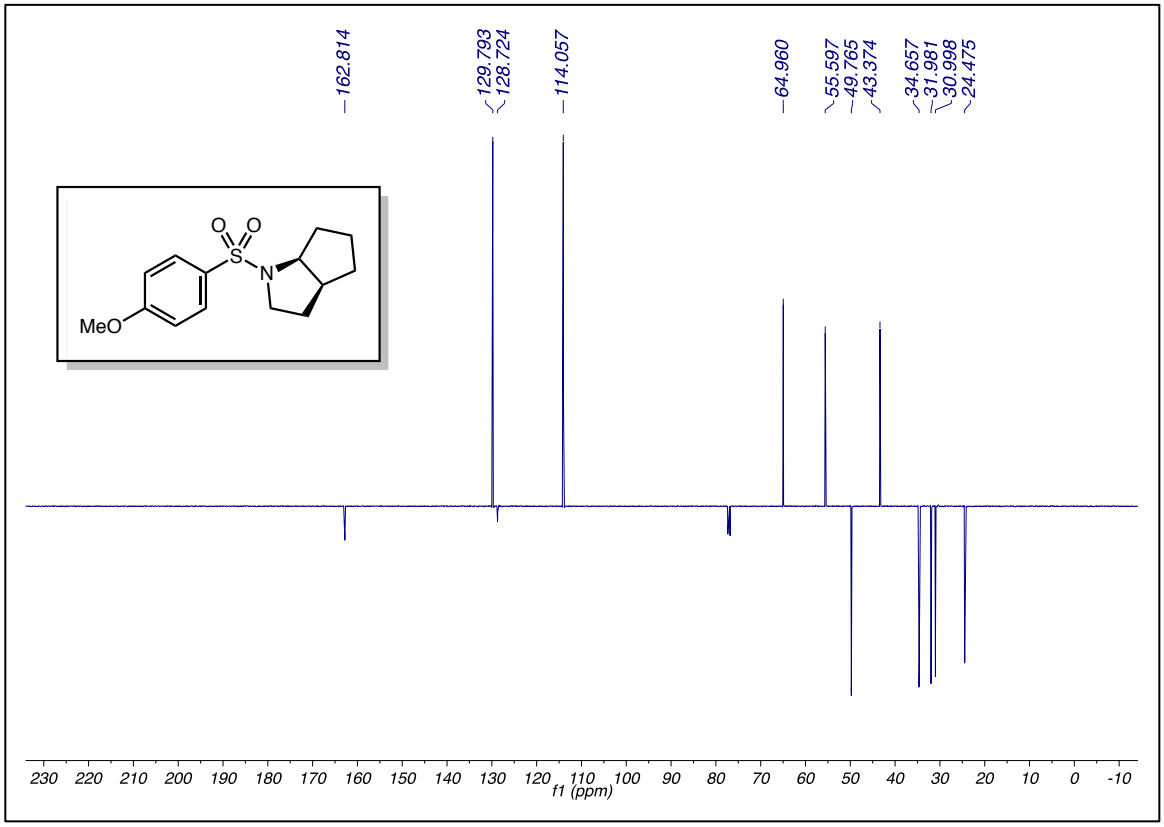
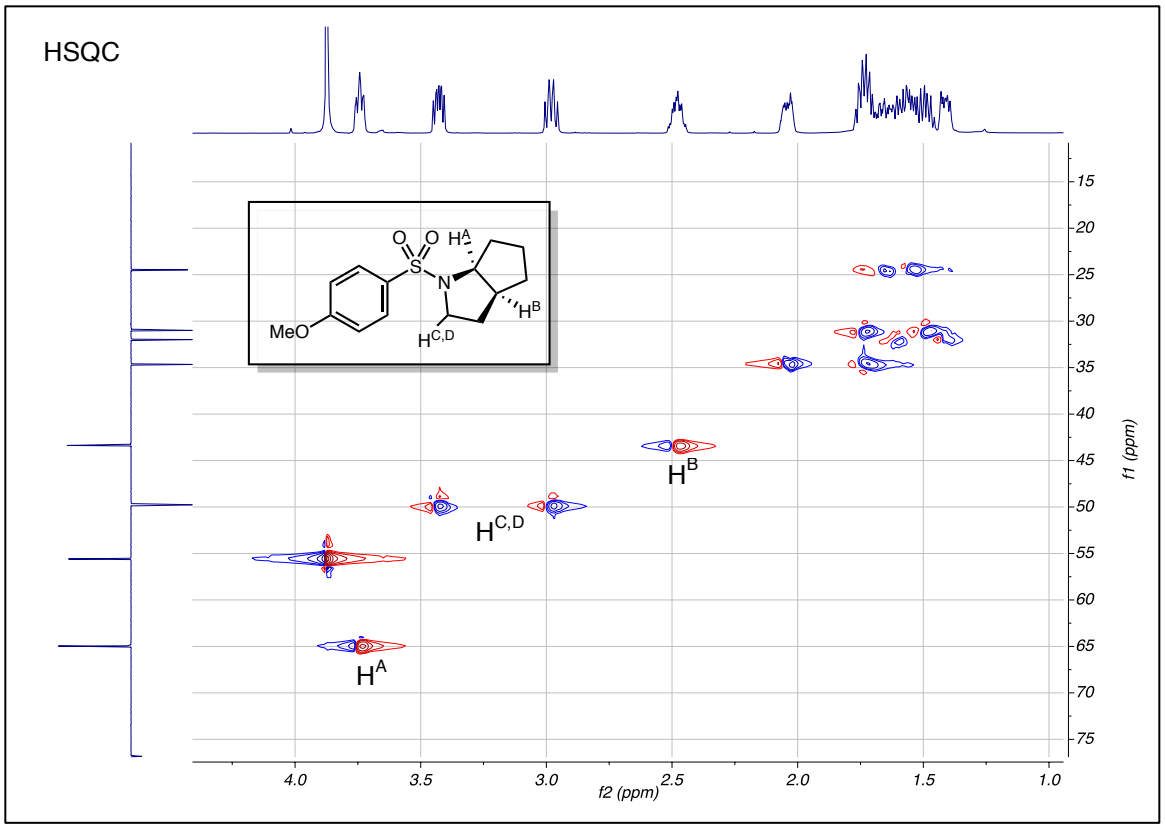
64.842
61.852
55.570
39.207
37.099
30.255
26.175
25.837
19.305
14.524
Me
Me
O
O
S
N
MeO
Me
Me
f1 (ppm)

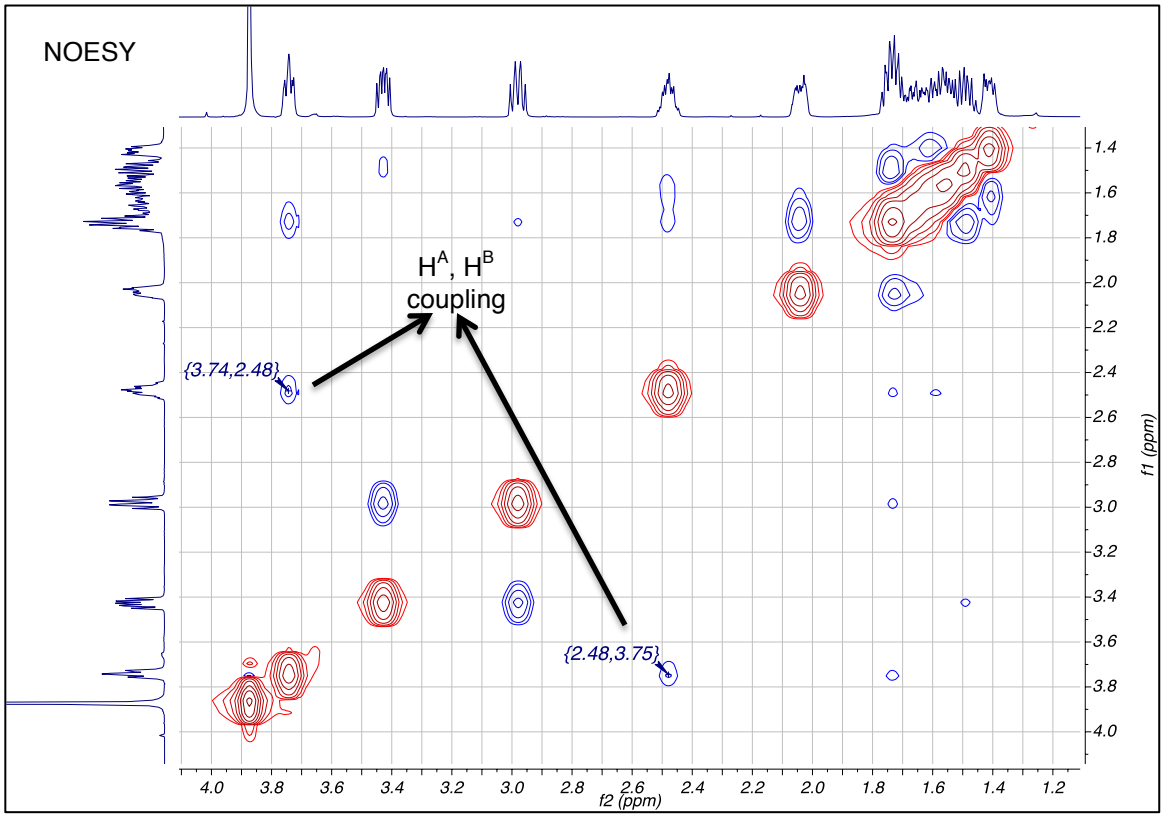

Me
O
O
S
N
Me
Me
MeO
Me
Me
1.96
1.97
0.94
2.99
1.03
0.53
0.46
0.99
0.45
0.54
0.96
0.50
0.54
2.98
2.96
2.01
0.50
0.49
4.01
3.03
2.96
f1 (ppm)

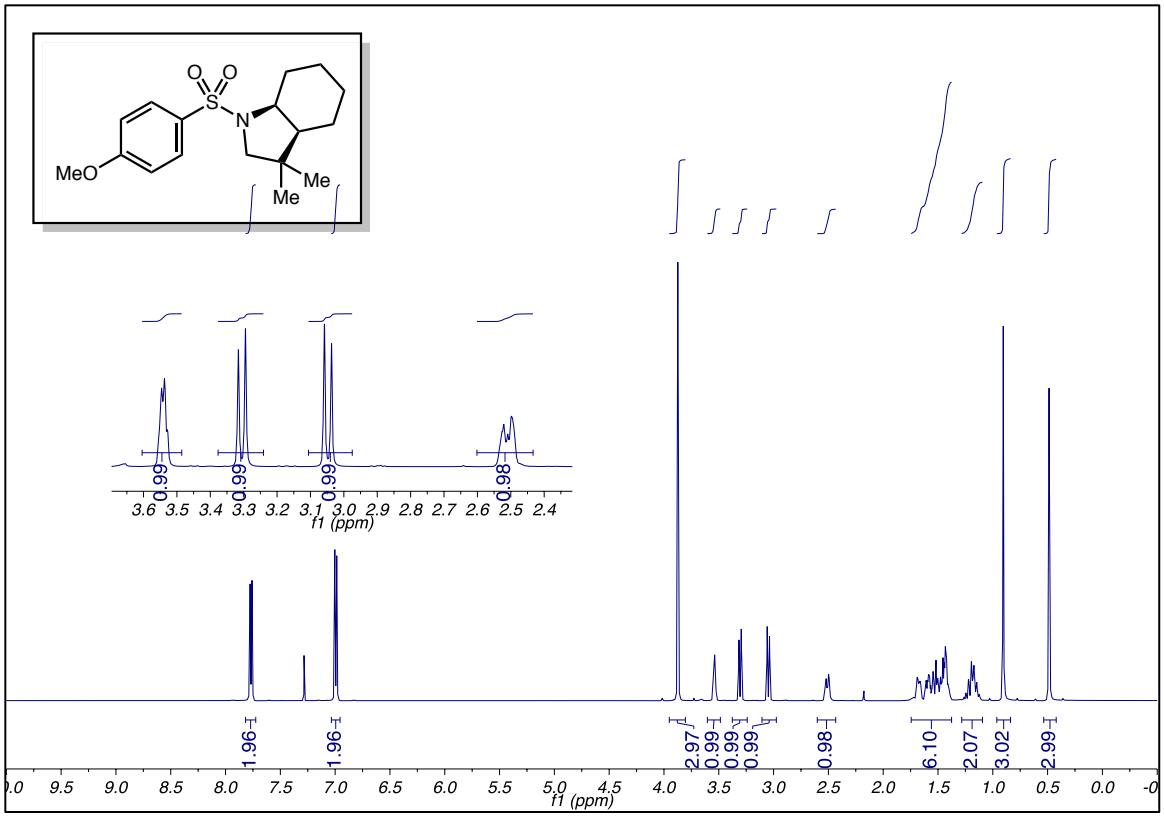

162.591
131.505
131.150
131.014
129.274
129.178
124.916
124.481
113.960
113.939
109.906
109.479
65.157
63.767
61.960
61.901
55.561
55.550
40.199
39.427
37.148
37.026
35.538
35.083
34.298
29.288
26.246
26.134
26.074
26.065
25.801
25.752
25.733
25.700
17.716
17.677
16.672
12.410
Me
O
O
S
N
Me
Me
MeO
Me
Me
f1 (ppm)

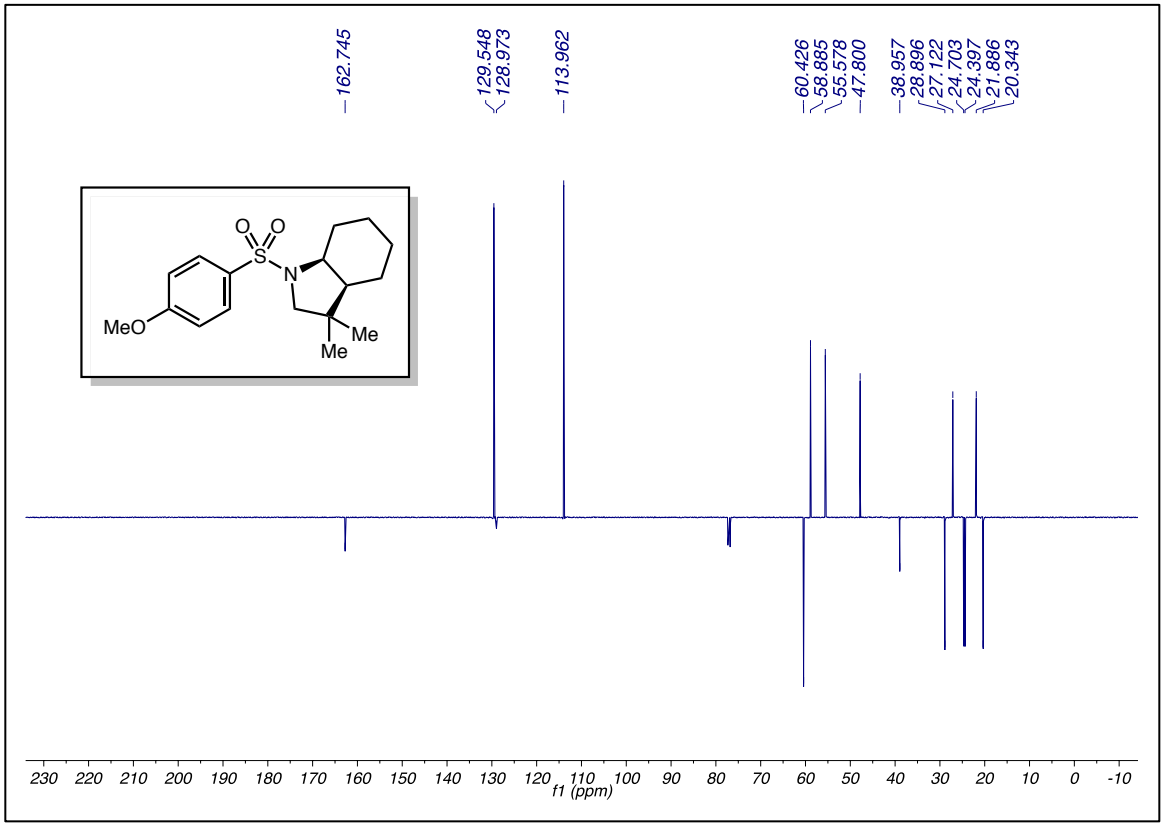

MeO
1.96
1.98
2.99
1.01
1.00
0.99
0.98
0.98
7.15
f1 (ppm)

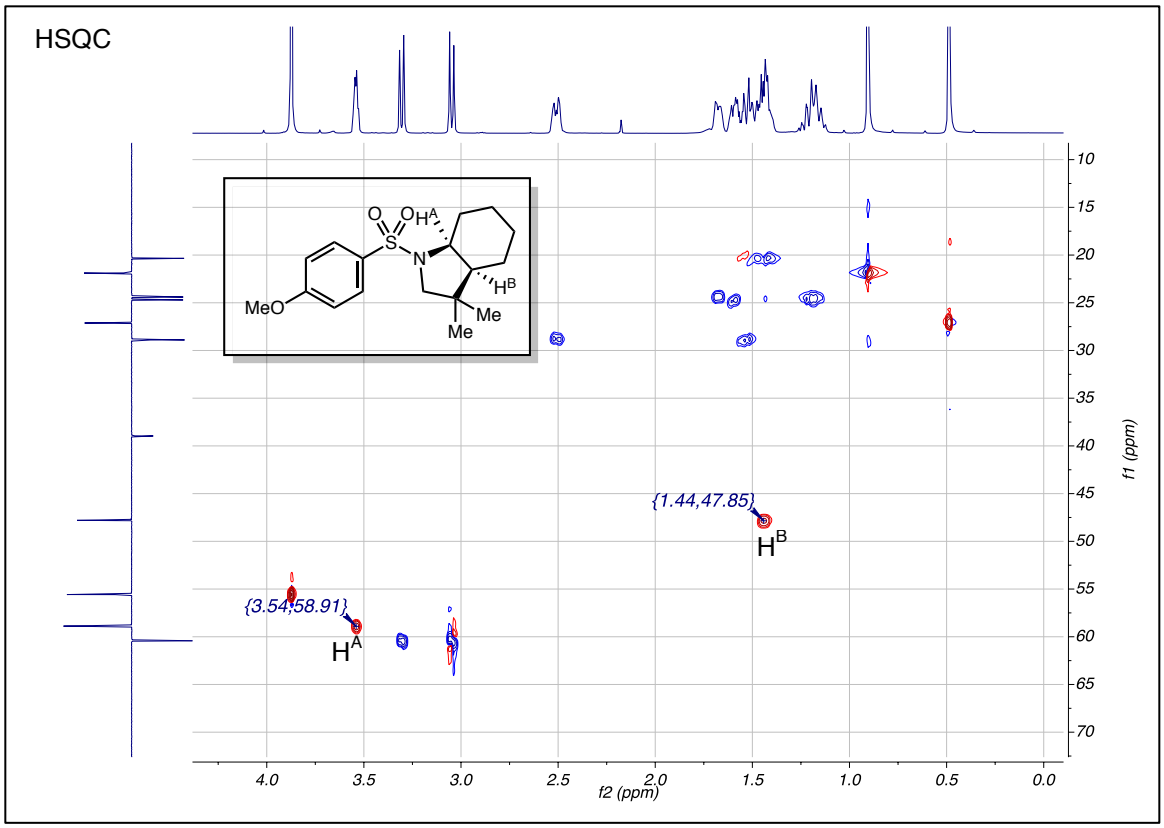

162.814
129.793
128.724
114.057
64.960
55.597
49.765
43.374
34.657
31.981
30.998
24.475
MeO
f1 (ppm)

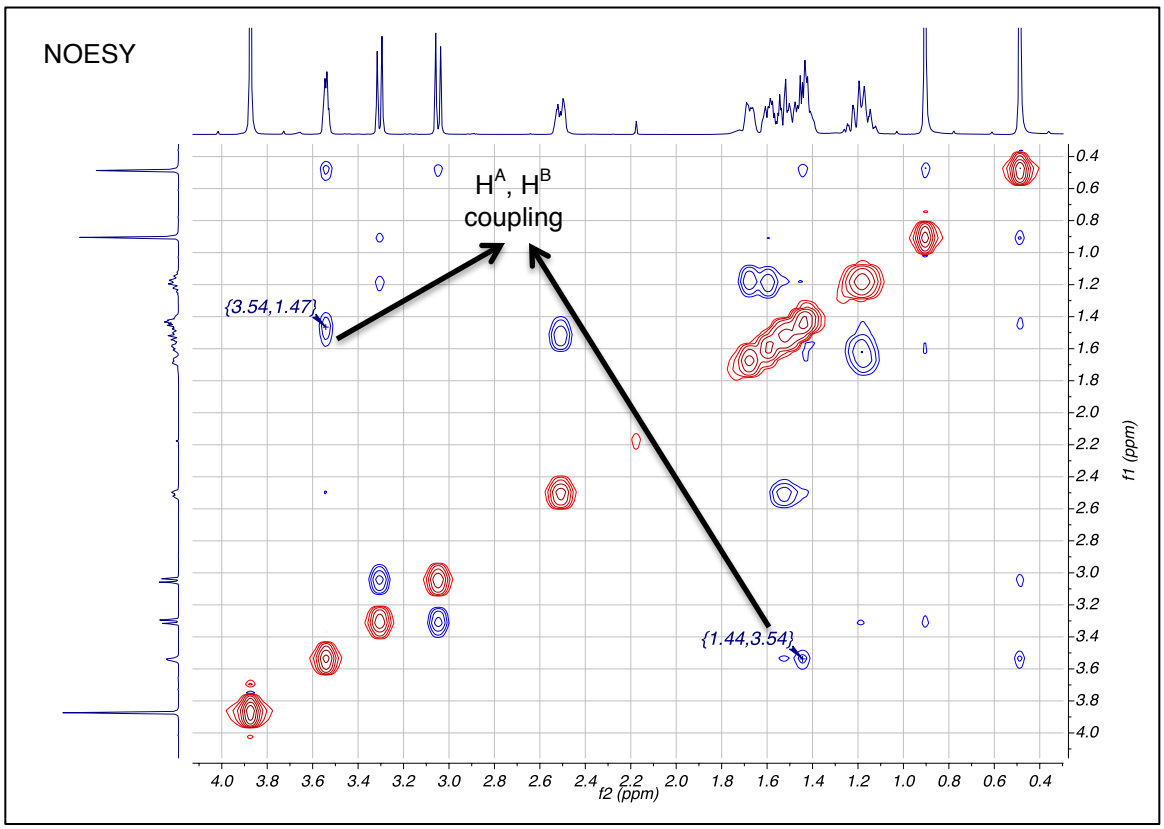

HSQC
MeO
$H^{C,D}$
$H^{B}$
$H^{A}$
f2 (ppm)
f1 (ppm)

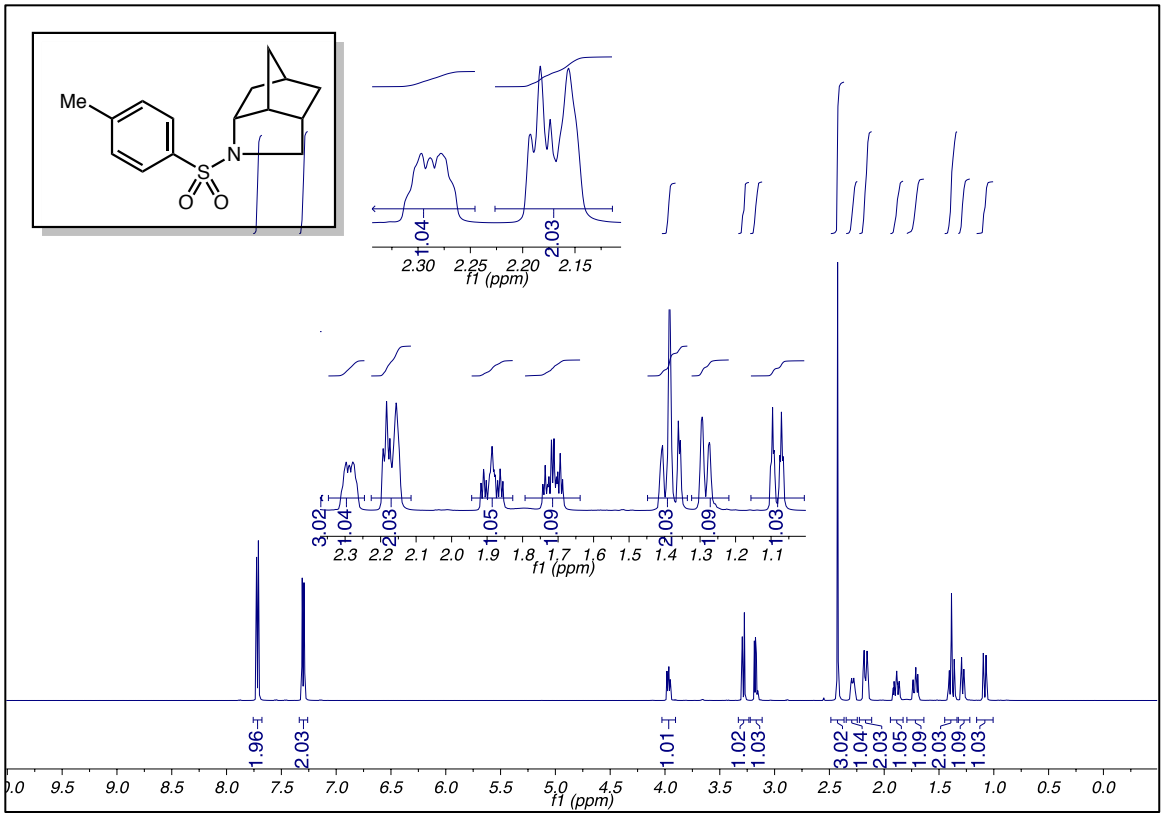

NOESY
$H^{A}$, $H^{B}$
coupling
{3.74,2.48}
{2.48,3.75}
f2 (ppm)
f1 (ppm)

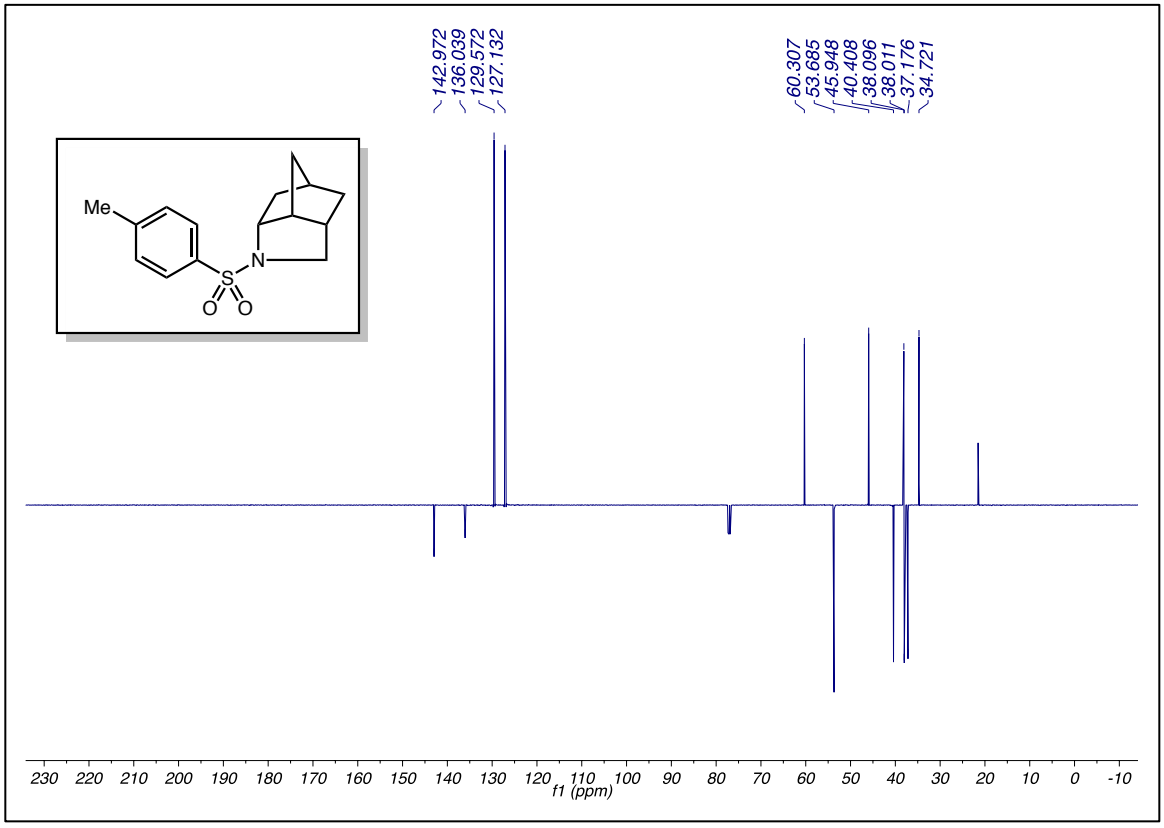

MeO
Me
Me
f1 (ppm)

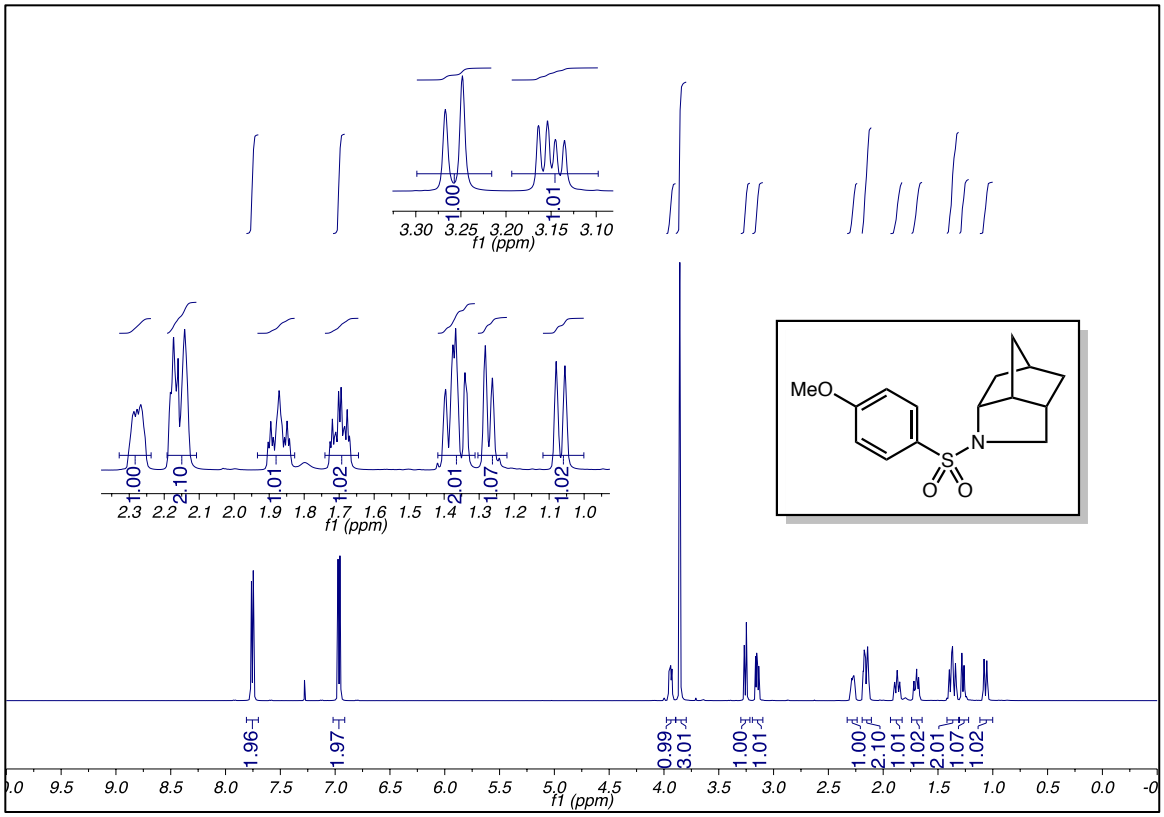

162.745
129.548
128.973
113.962
60.426
58.885
55.578
47.800
38.957
28.896
27.122
24.703
24.397
21.886
20.343
MeO
Me
Me
f1 (ppm)

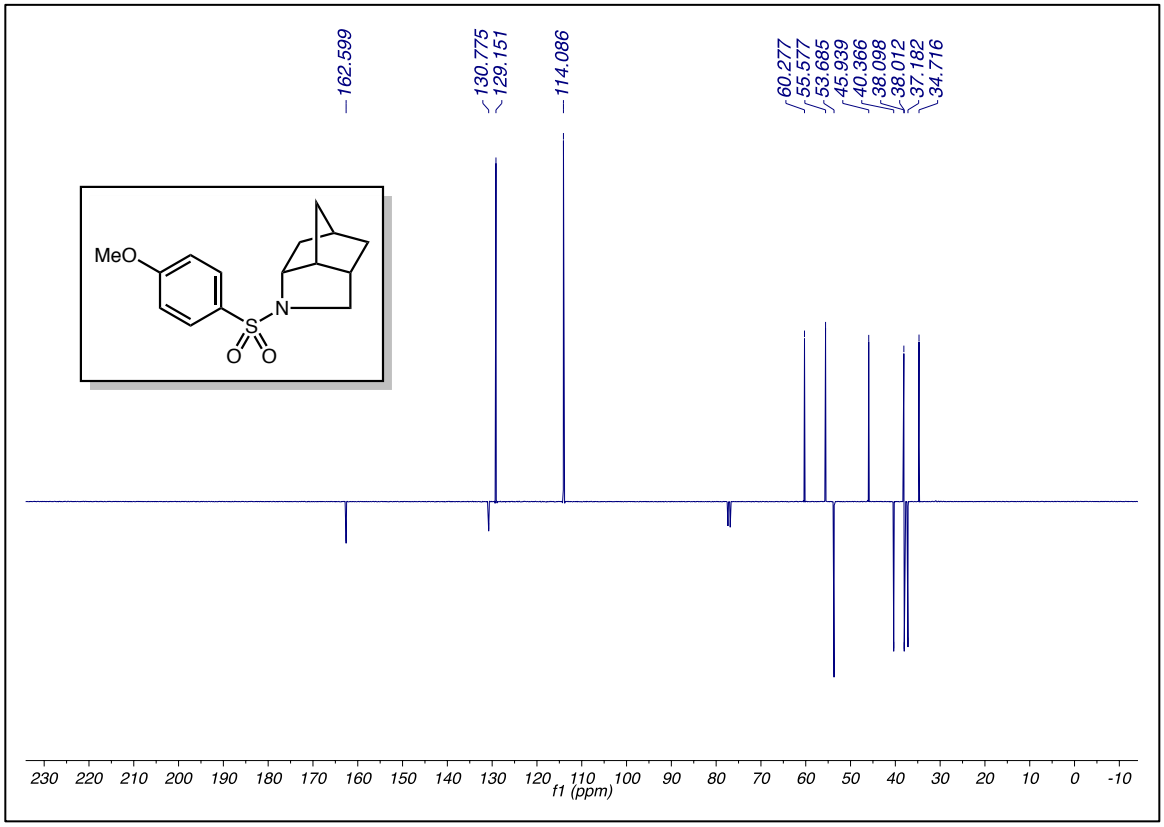

HSQC
O
O
H^A
S
N
H^B
MeO
Me
Me
{1.44,47.85}
H^B
{3.54,58.91}
H^A
f2 (ppm)
f1 (ppm)

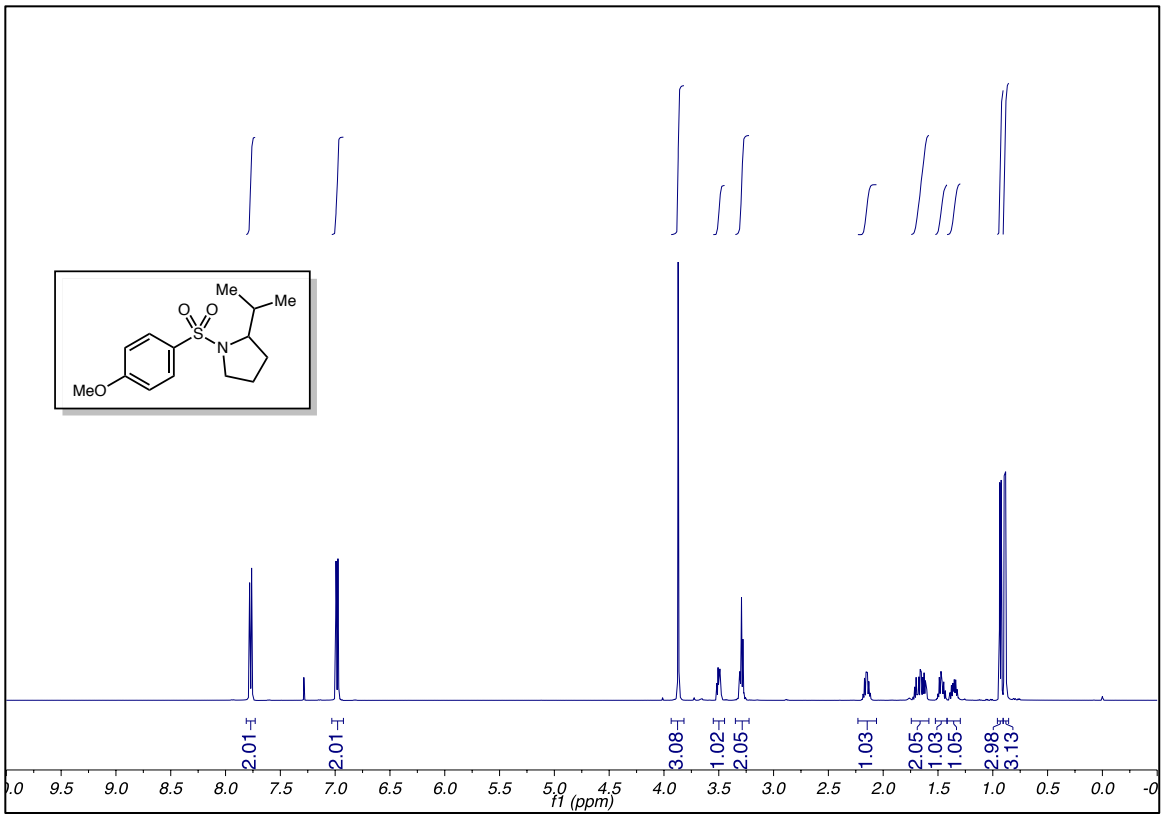

NOESY
H^A, H^B
coupling
{3.54,1.47}
{1.44,3.54}
f2 (ppm)
f1 (ppm)

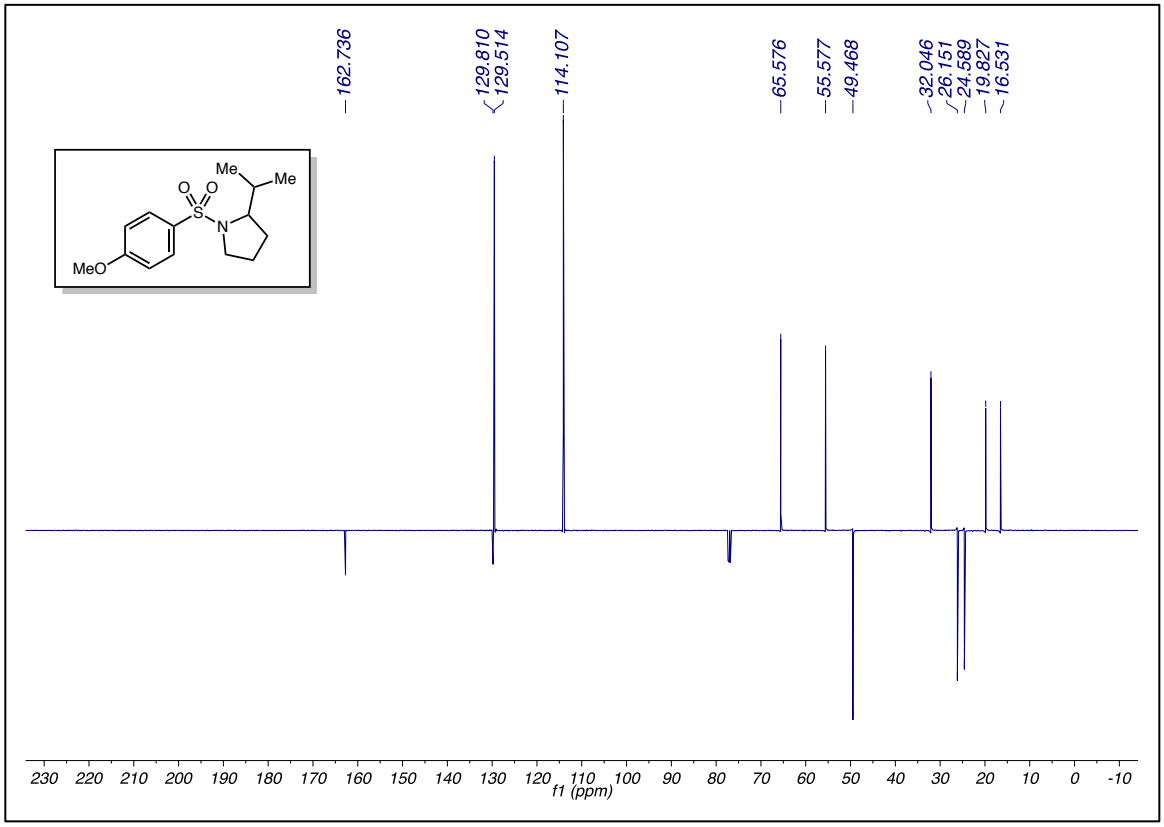

Me
S
N
O
O
1.04
2.03
2.30 2.25 2.20 2.15
f1 (ppm)
3.02
1.04
2.03
1.05
1.09
2.03
1.09
1.03
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1
f1 (ppm)
1.96
2.03
1.01
1.02
1.03
3.02
1.04
2.03
1.05
1.09
2.03
1.09
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

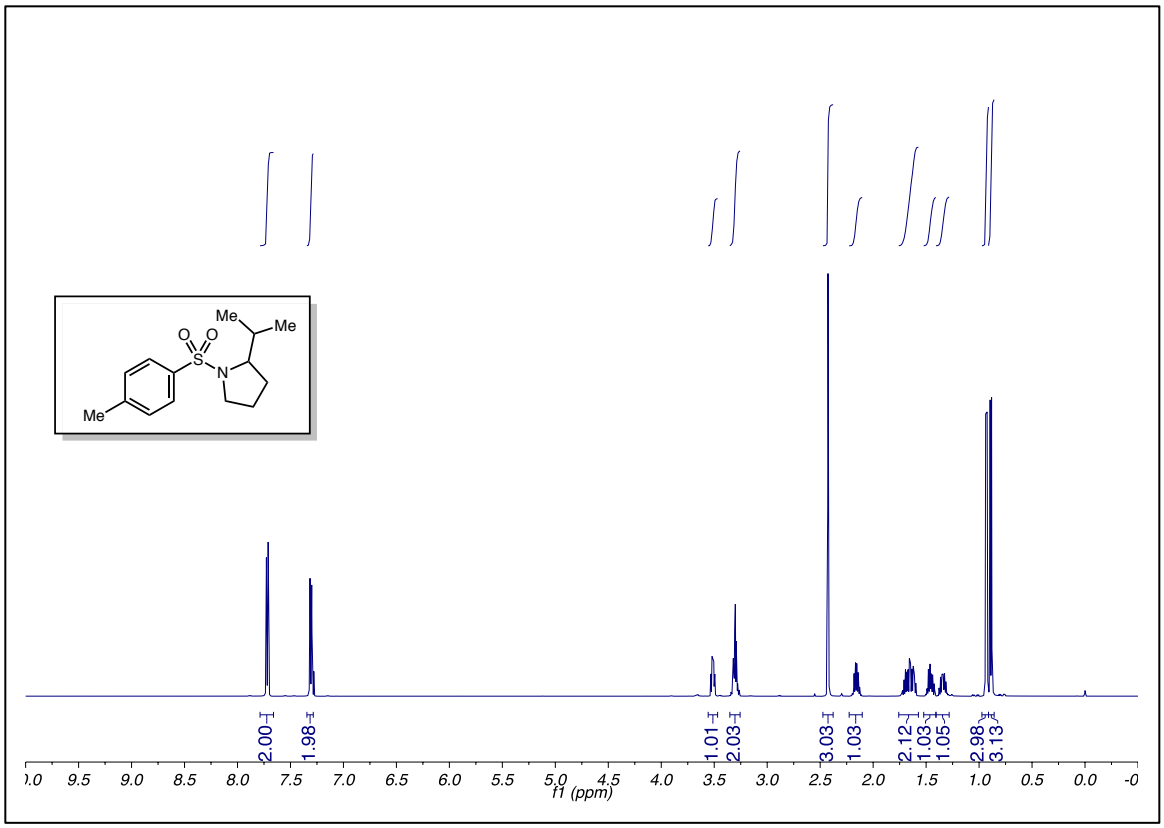

142.972
136.039
129.572
127.132
60.307
53.685
45.948
40.408
38.096
38.011
37.176
34.721
Me
S
N
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

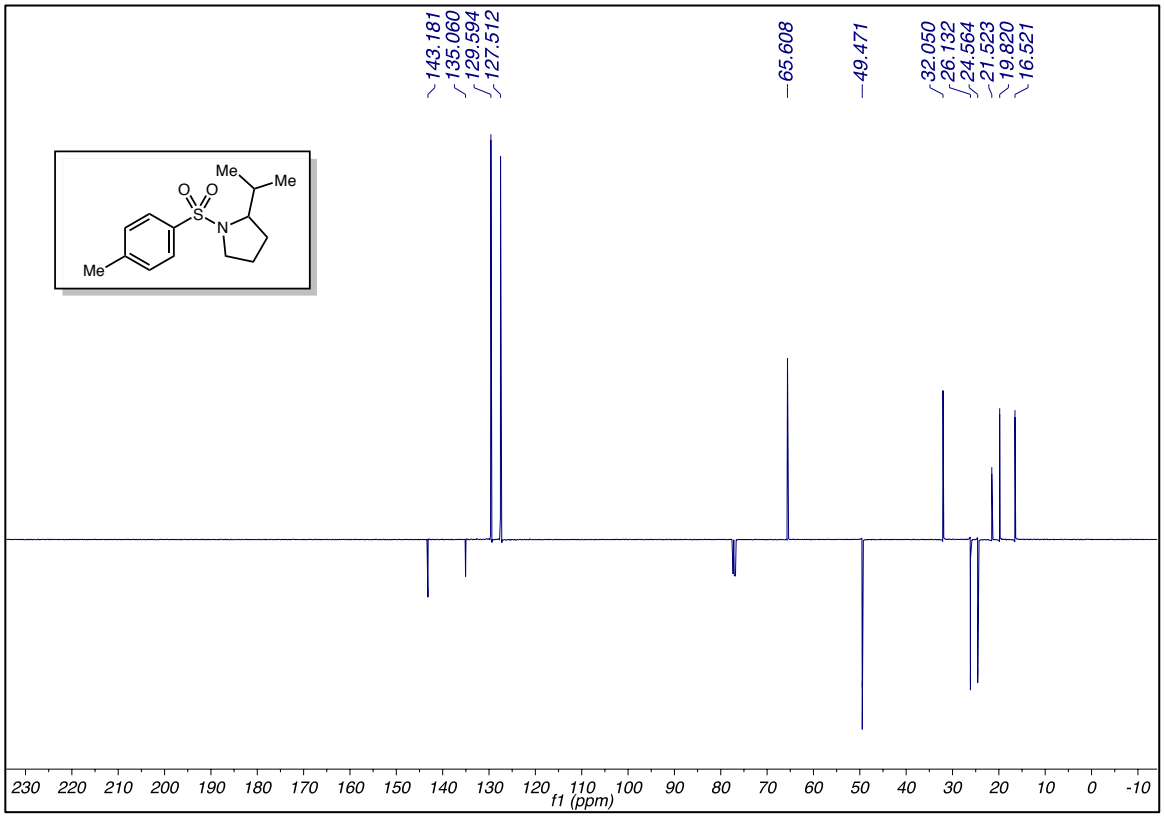

MeO
N
S
O
O
f1 (ppm)

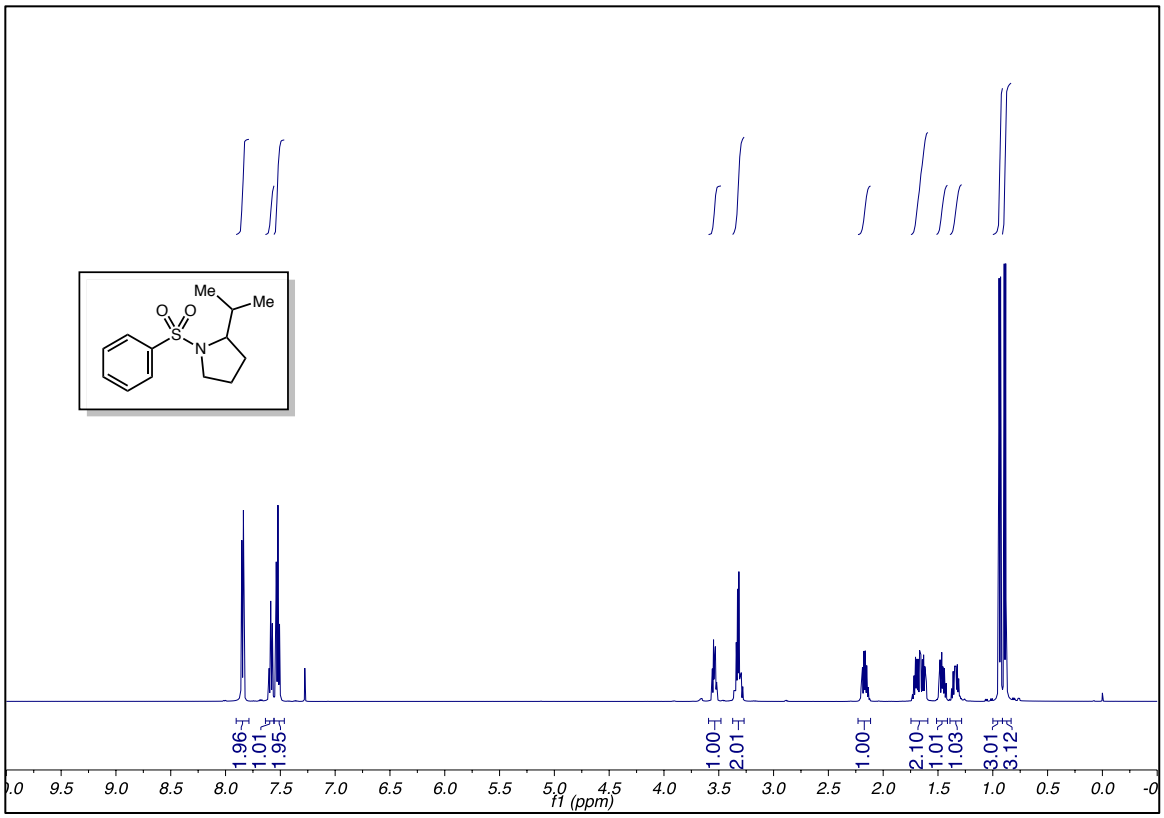

162.599
130.775
129.151
114.086
60.277
55.577
53.685
45.939
40.366
38.098
38.012
37.182
34.716
MeO
N
S
O
O
f1 (ppm)

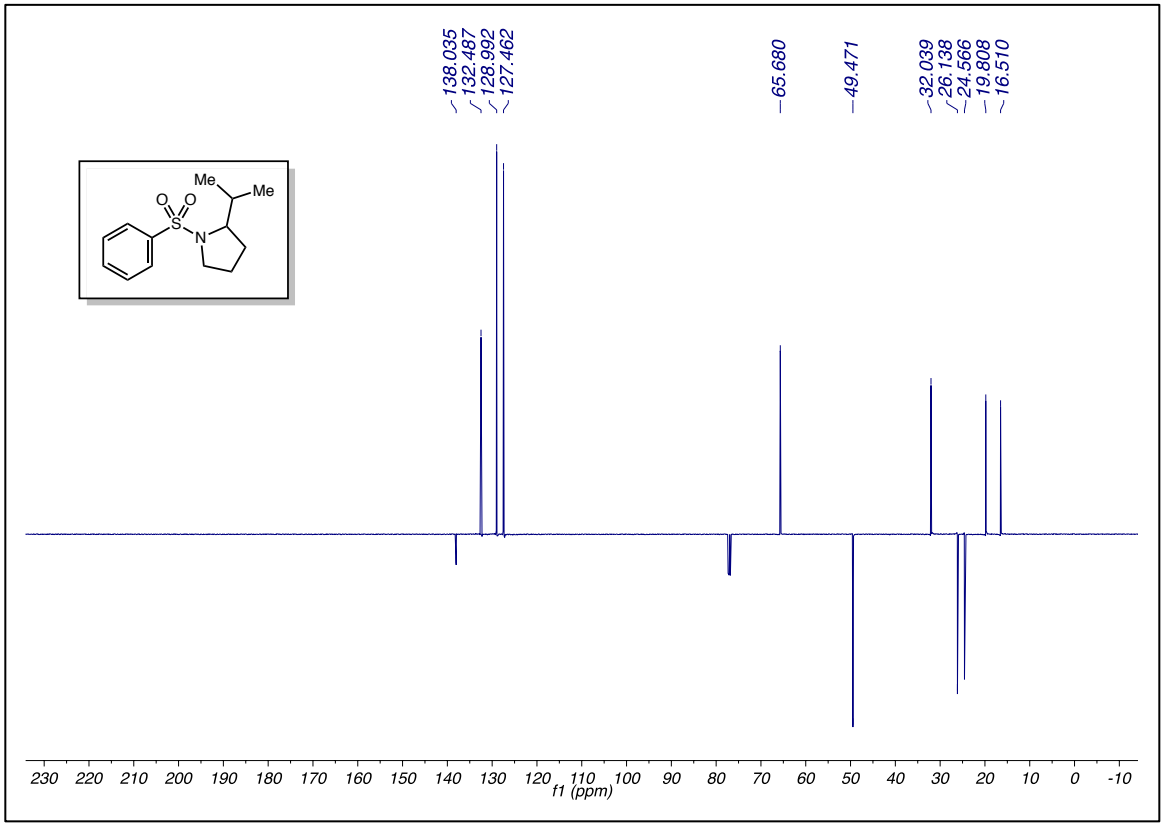

Me
Me
O
O
S
N
MeO
2.01
2.01
3.08
1.02
2.05
1.03
2.05
1.03
1.05
2.98
3.13
f1 (ppm)

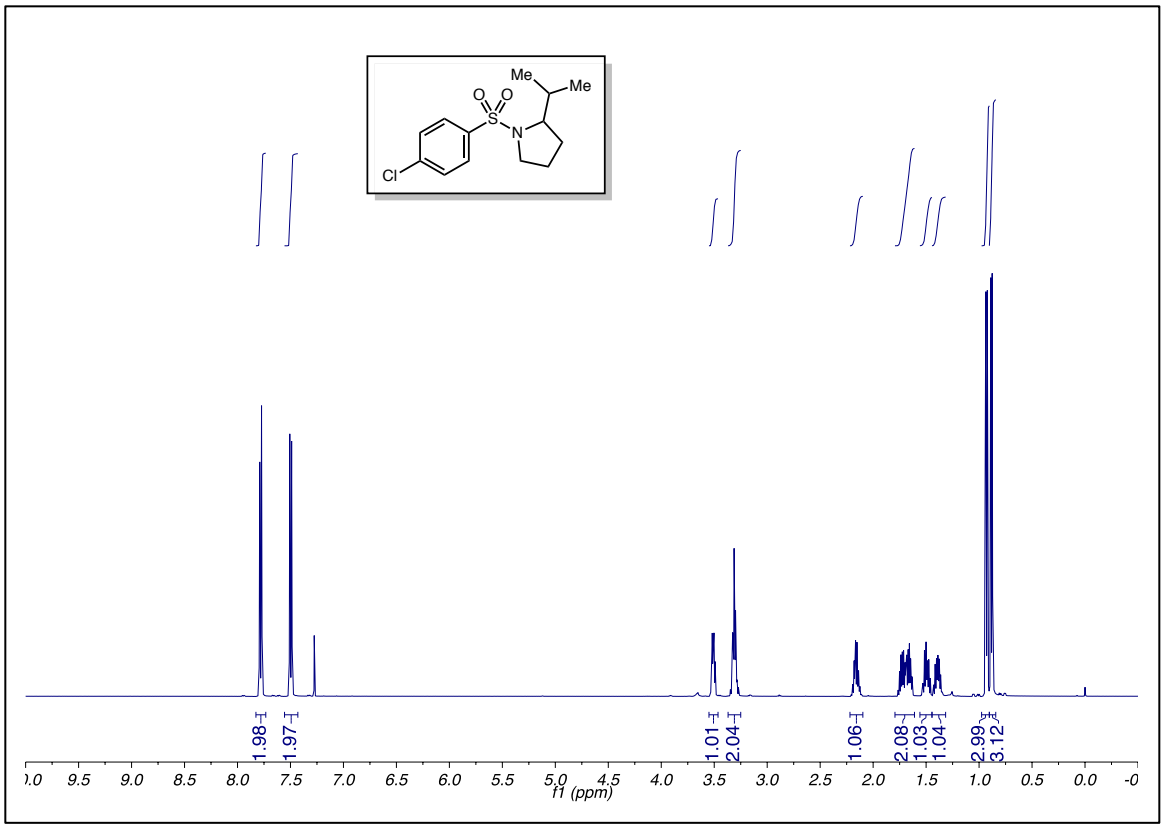

162.736
129.810
129.514
114.107
65.576
55.577
49.468
32.046
26.151
24.589
19.827
16.531
Me
Me
O
O
S
N
MeO
f1 (ppm)

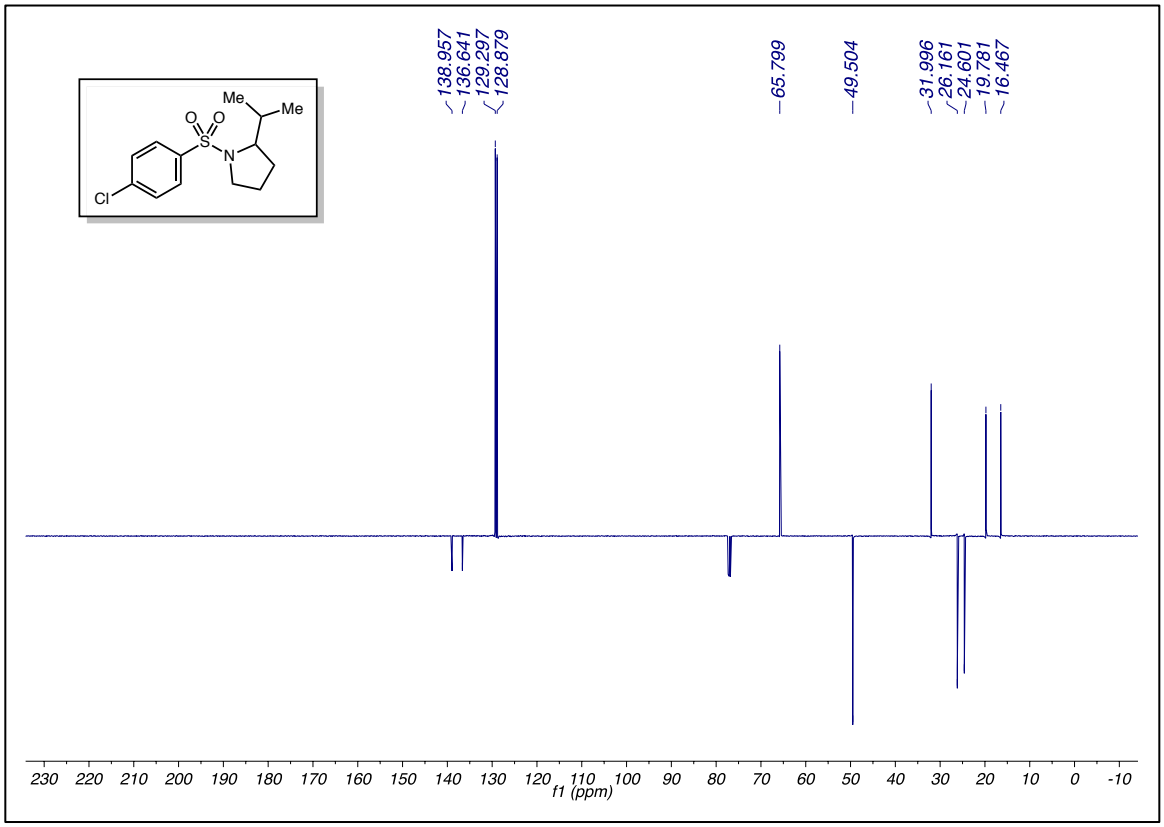

Me
Me
O
O
S
N
Me
2.00
1.98
1.01
2.03
3.03
1.03
2.12
1.03
1.05
2.98
3.13
f1 (ppm)

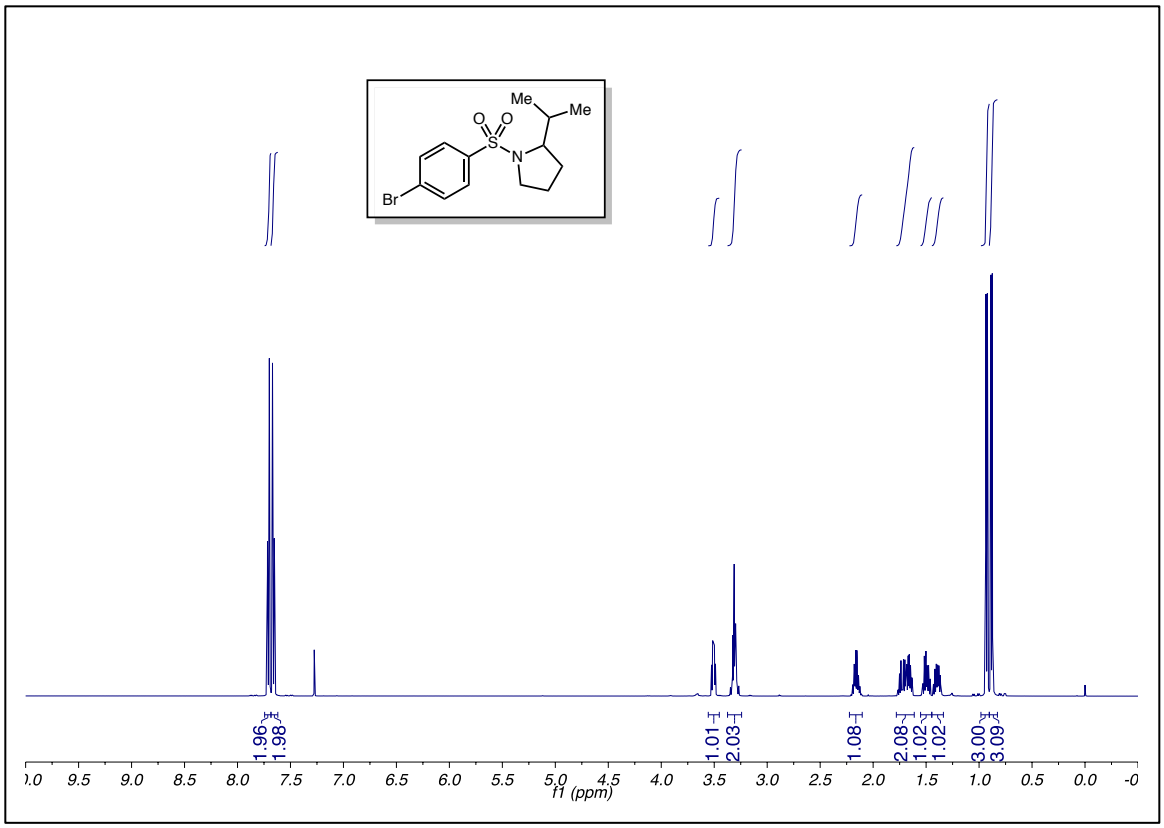

143.181
135.060
129.594
127.512
65.608
49.471
32.050
26.132
24.564
21.523
19.820
16.521
Me
Me
O
O
S
N
Me
f1 (ppm)

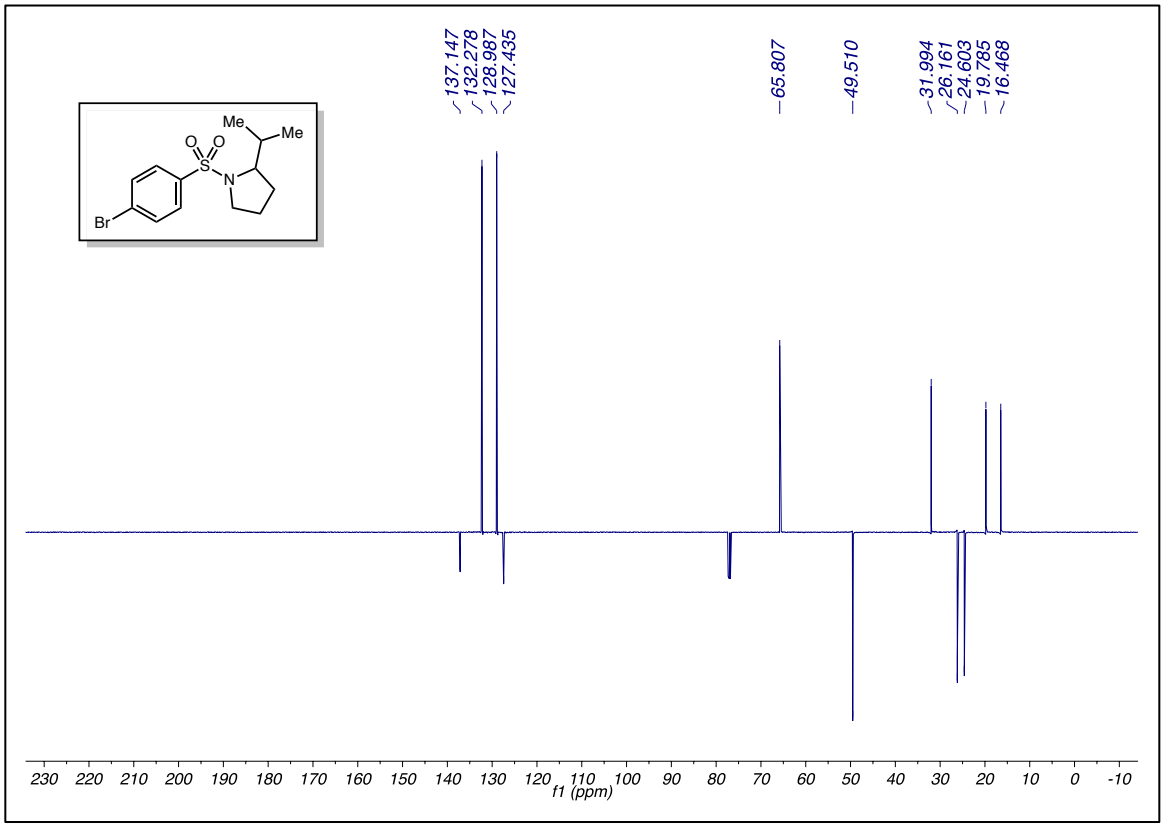

Me
Me
O
O
S
N
1.96
1.01
1.95
1.00
2.01
1.00
2.10
1.01
1.03
3.01
3.12
f1 (ppm)

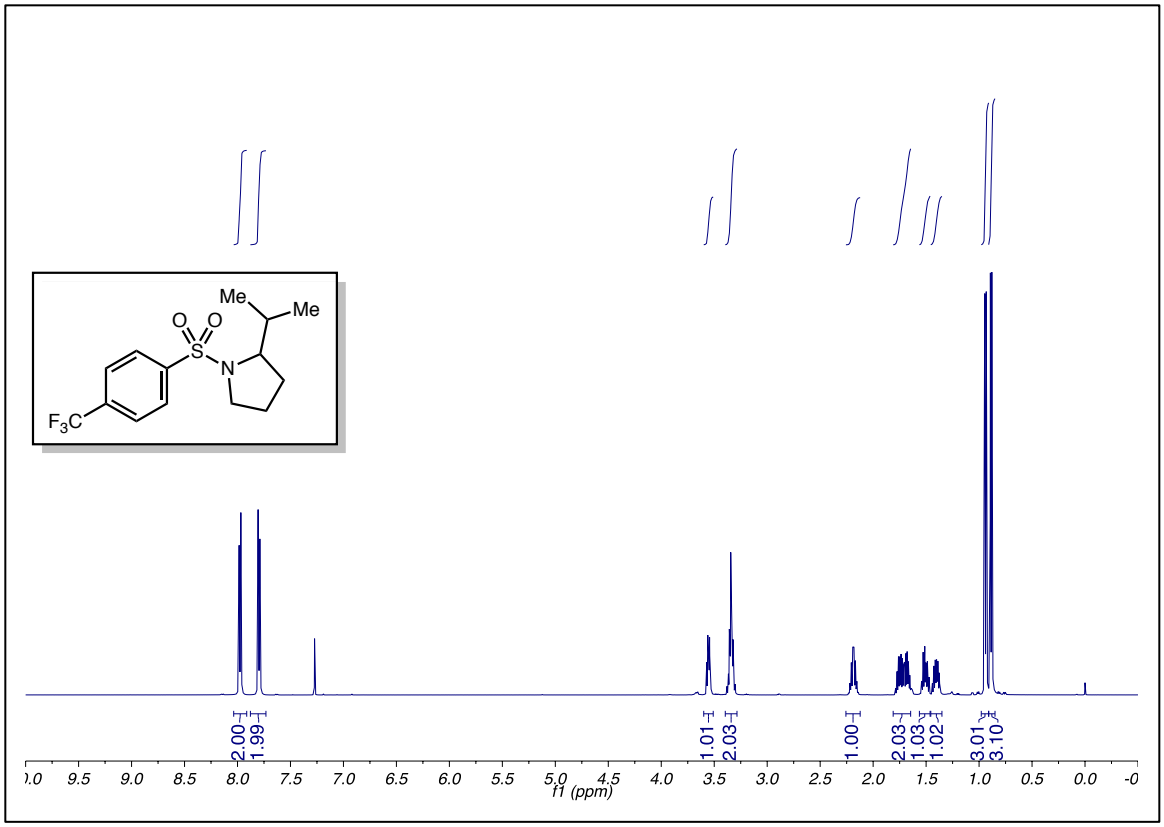

138.035
132.487
128.992
127.462
65.680
49.471
32.039
26.138
24.566
19.808
16.510
Me
Me
O
O
S
N
f1 (ppm)

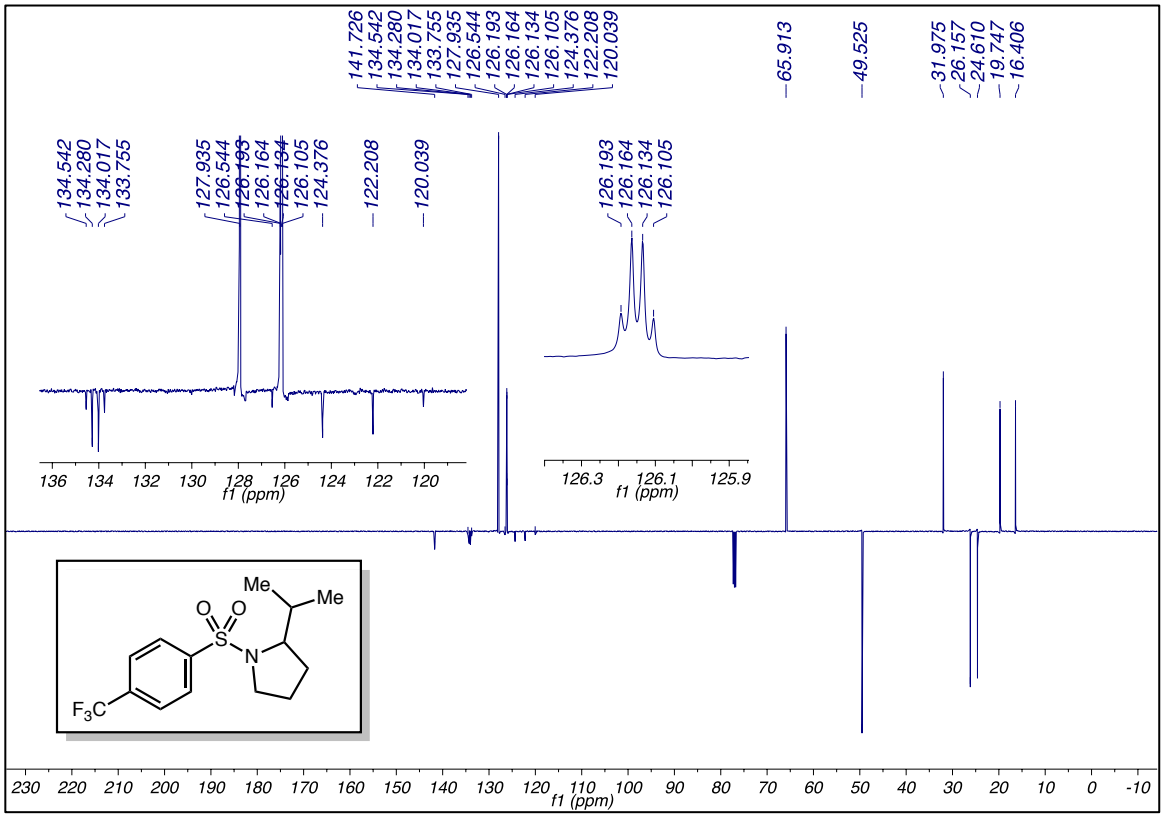

Me
Me
O
O
S
N
Cl
1.98
1.97
1.01
2.04
1.06
2.08
1.03
1.04
2.99
3.12
f1 (ppm)

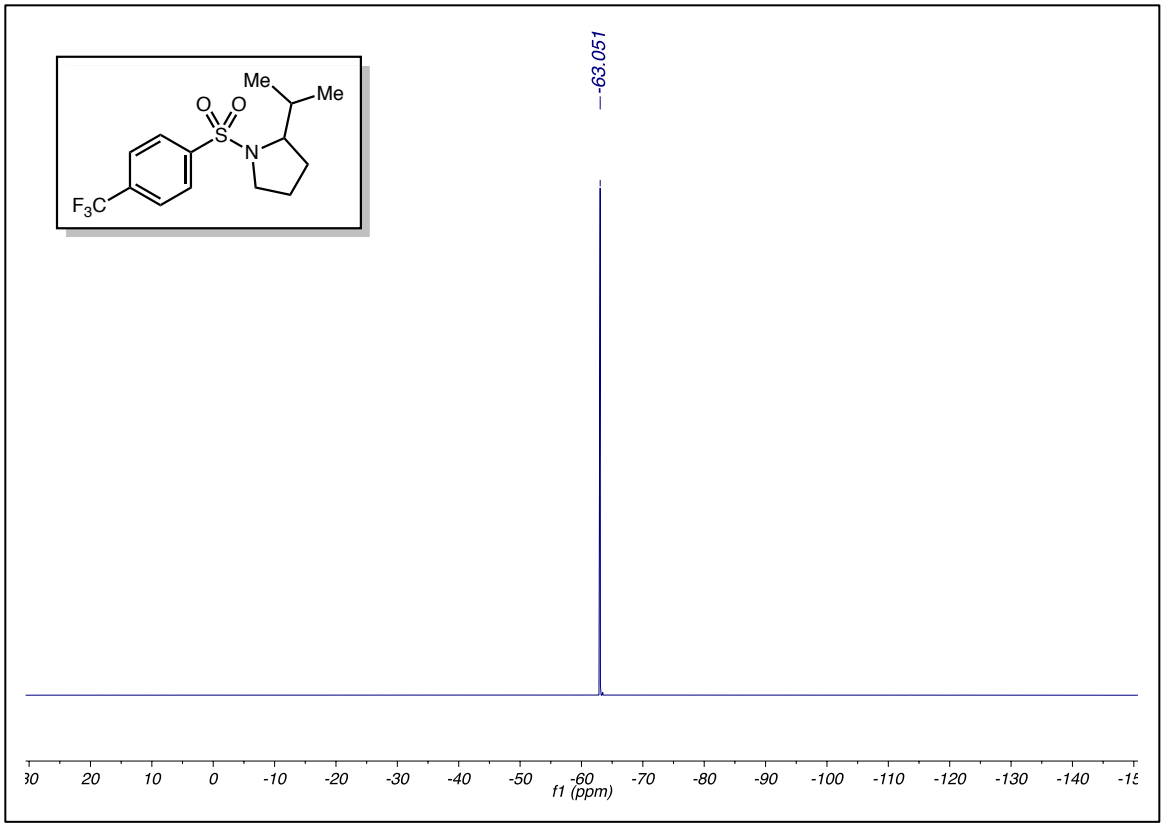

138.957
136.641
129.297
128.879
65.799
49.504
31.996
26.161
24.601
19.781
16.467
Me
Me
O
O
S
N
Cl
f1 (ppm)

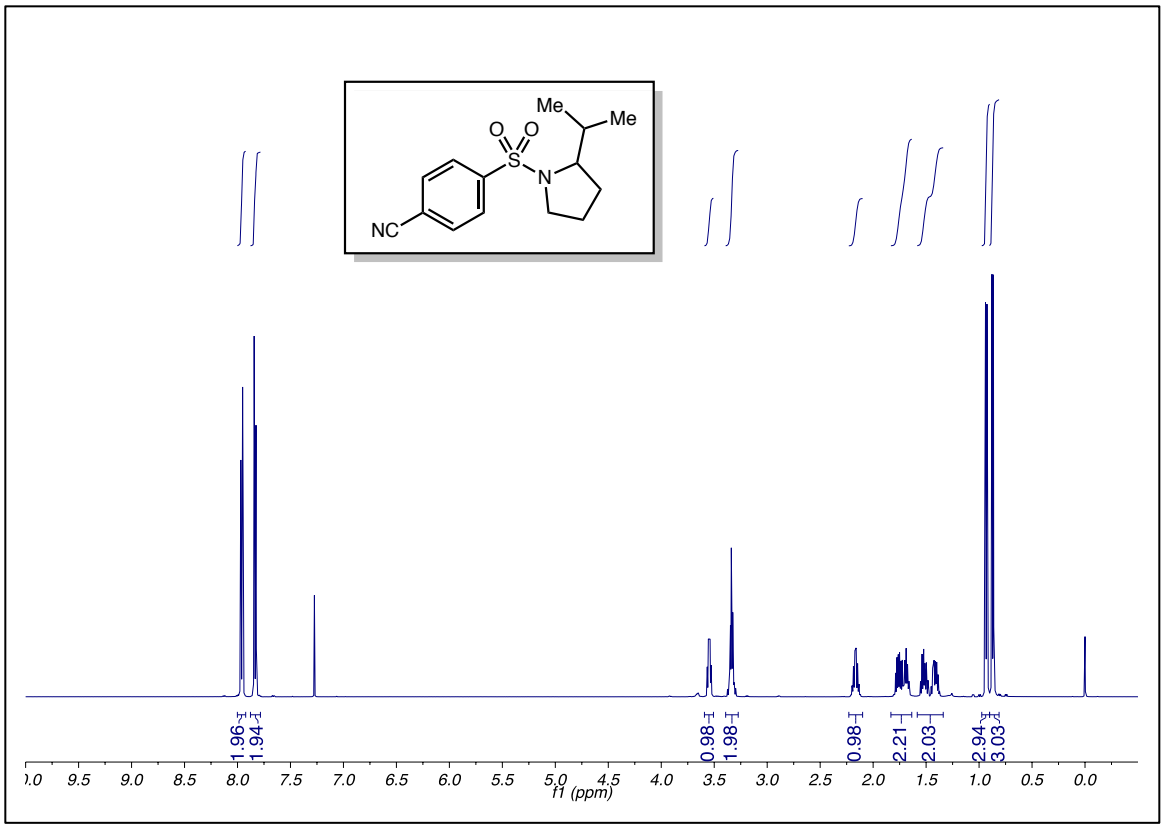

Me
Me
O
O
S
N
Br
1.96
1.98
1.01
2.03
1.08
2.08
1.02
1.02
3.00
3.09
f1 (ppm)

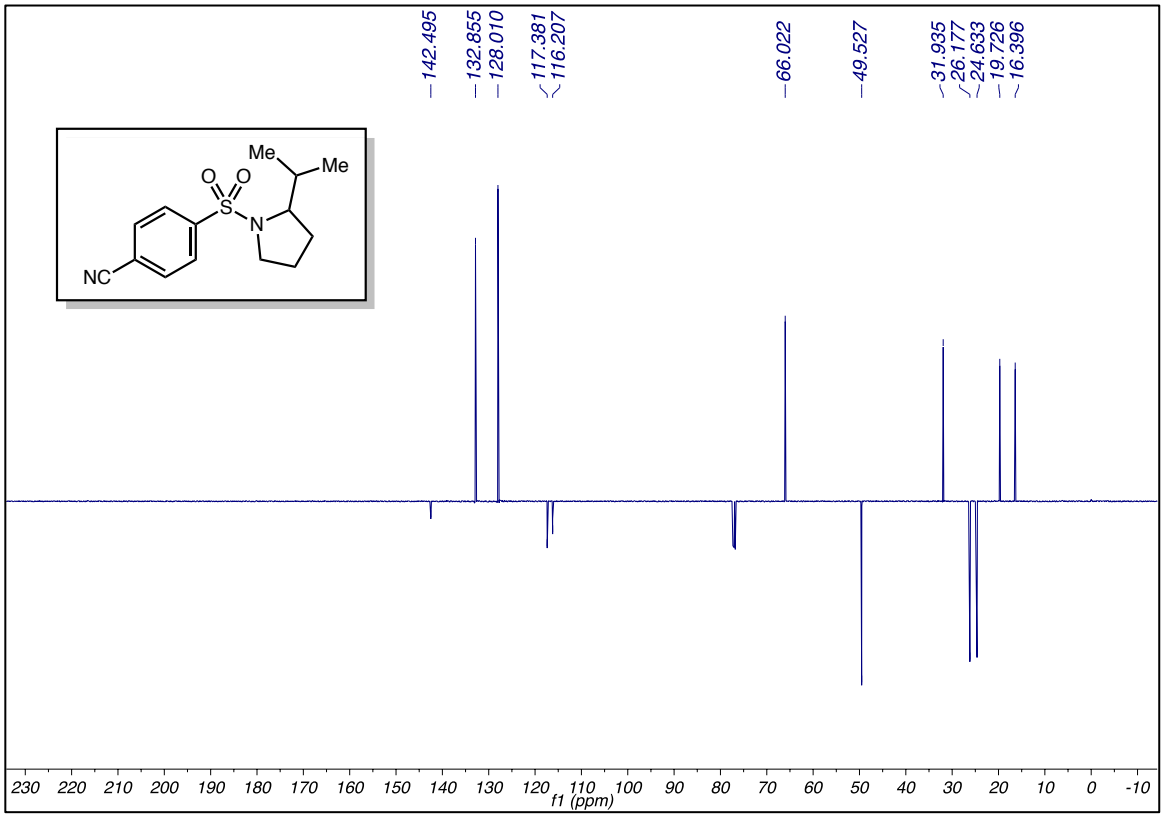

137.147
132.278
128.987
127.435
65.807
49.510
31.994
26.161
24.603
19.785
16.468
Me
Me
O
O
S
N
Br
f1 (ppm)

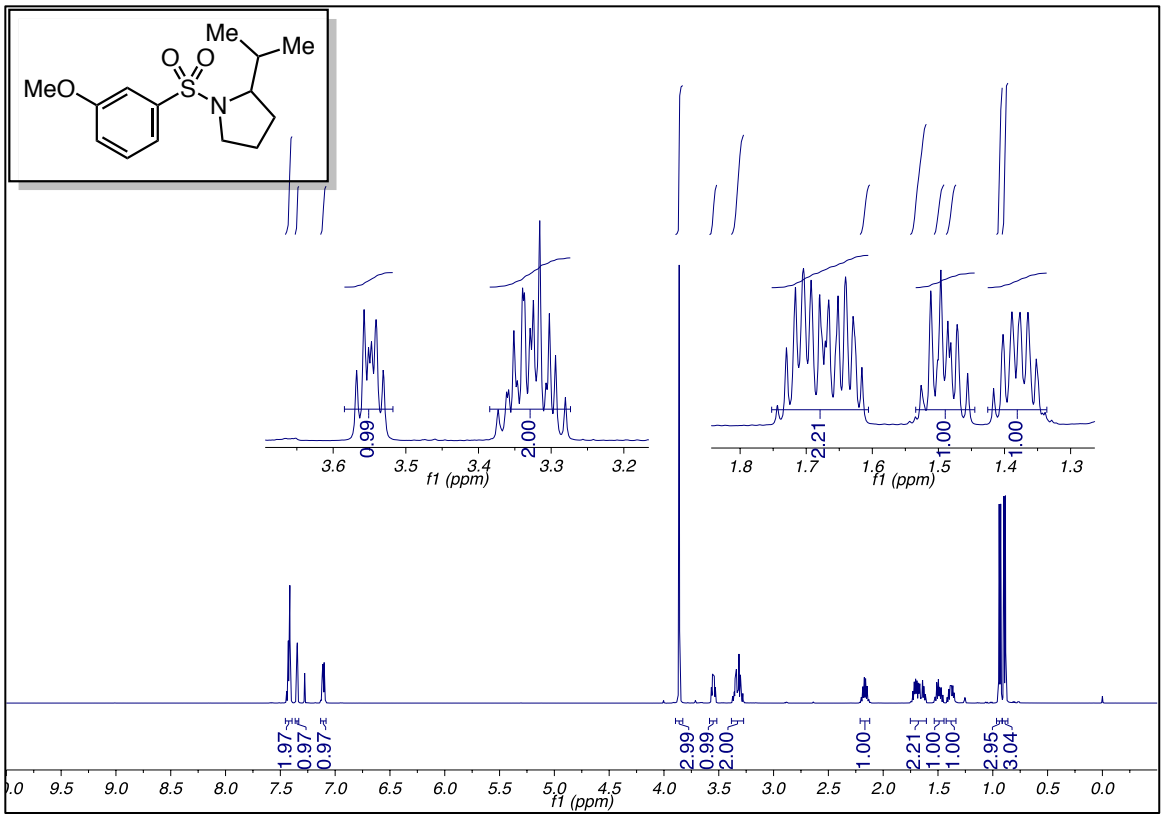

Me
Me
O
O
S
N
F3C
2.00
1.99
1.01
2.03
1.00
2.03
1.03
1.02
3.01
3.10
f1 (ppm)

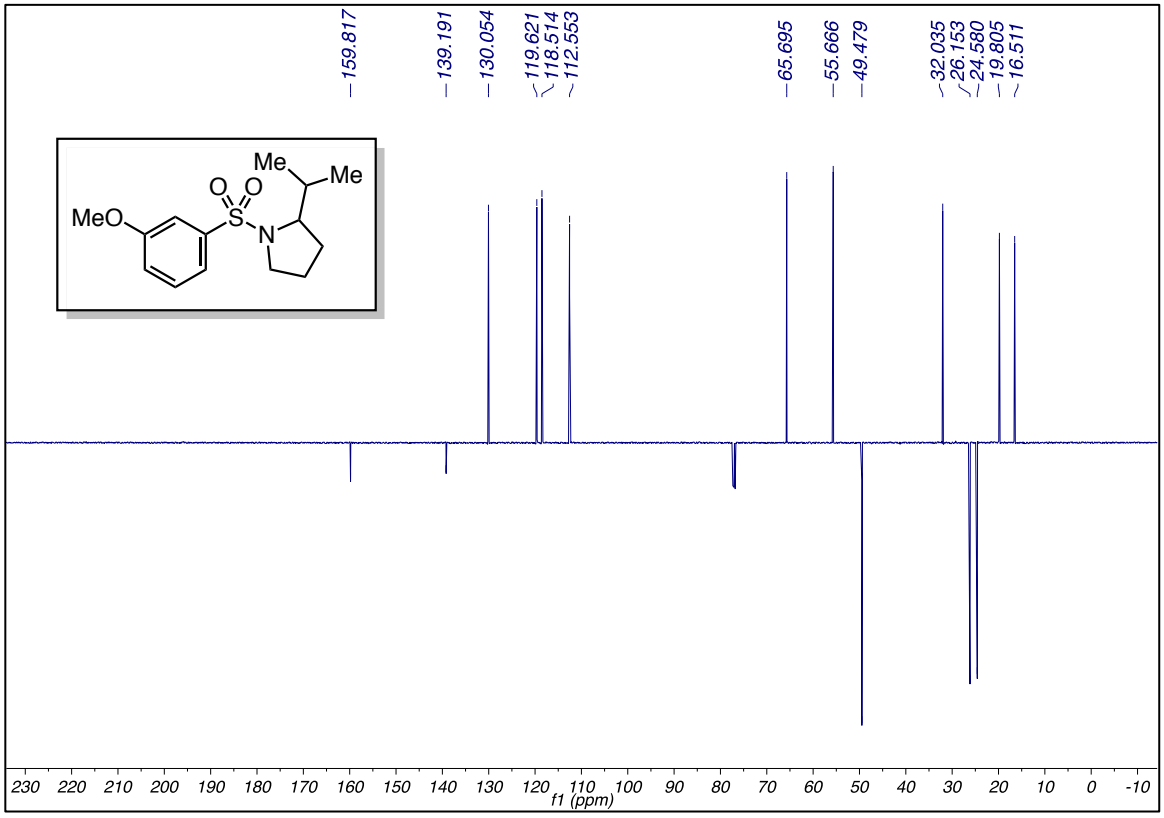

141.726
134.542
134.280
134.017
133.755
127.935
126.544
126.193
126.164
126.134
126.105
124.376
122.208
120.039
65.913
49.525
31.975
26.157
24.610
19.747
16.406
f1 (ppm)
Me
Me
O
O
S
N
F3C

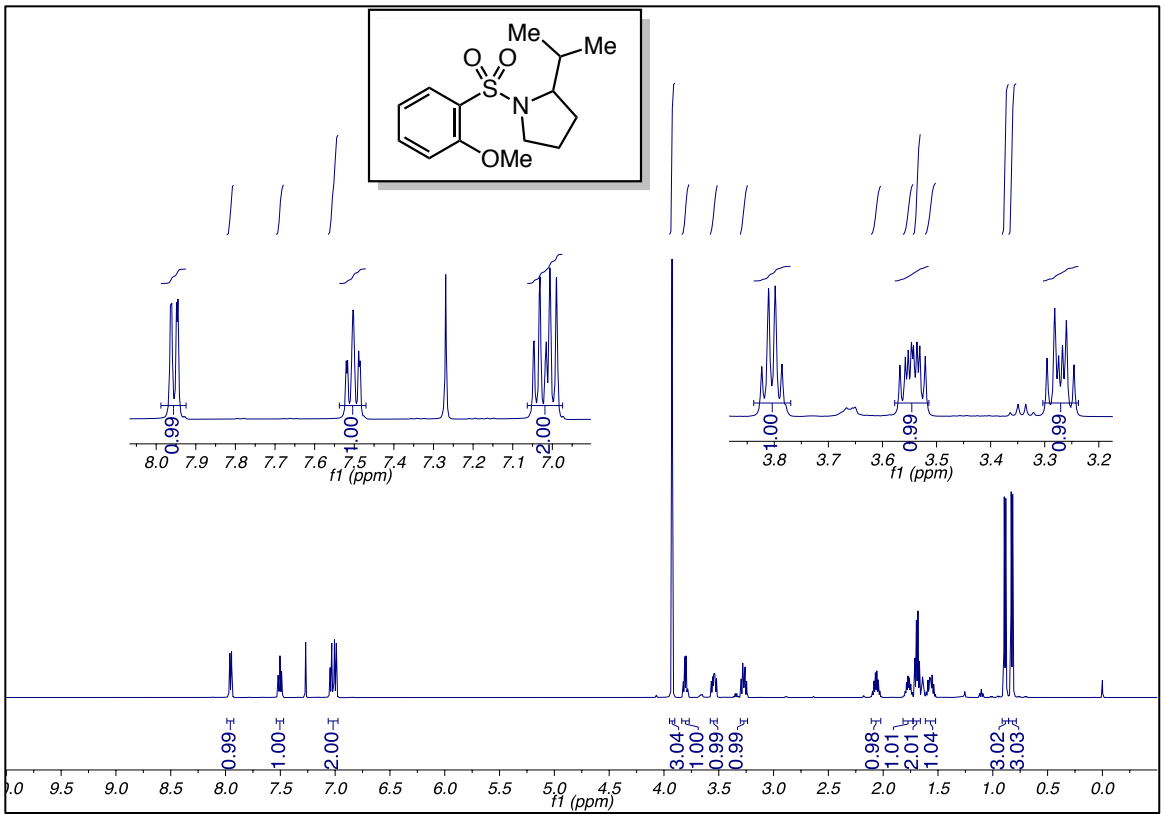

Me
Me
O
O
S
N
F3C
-63.051
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

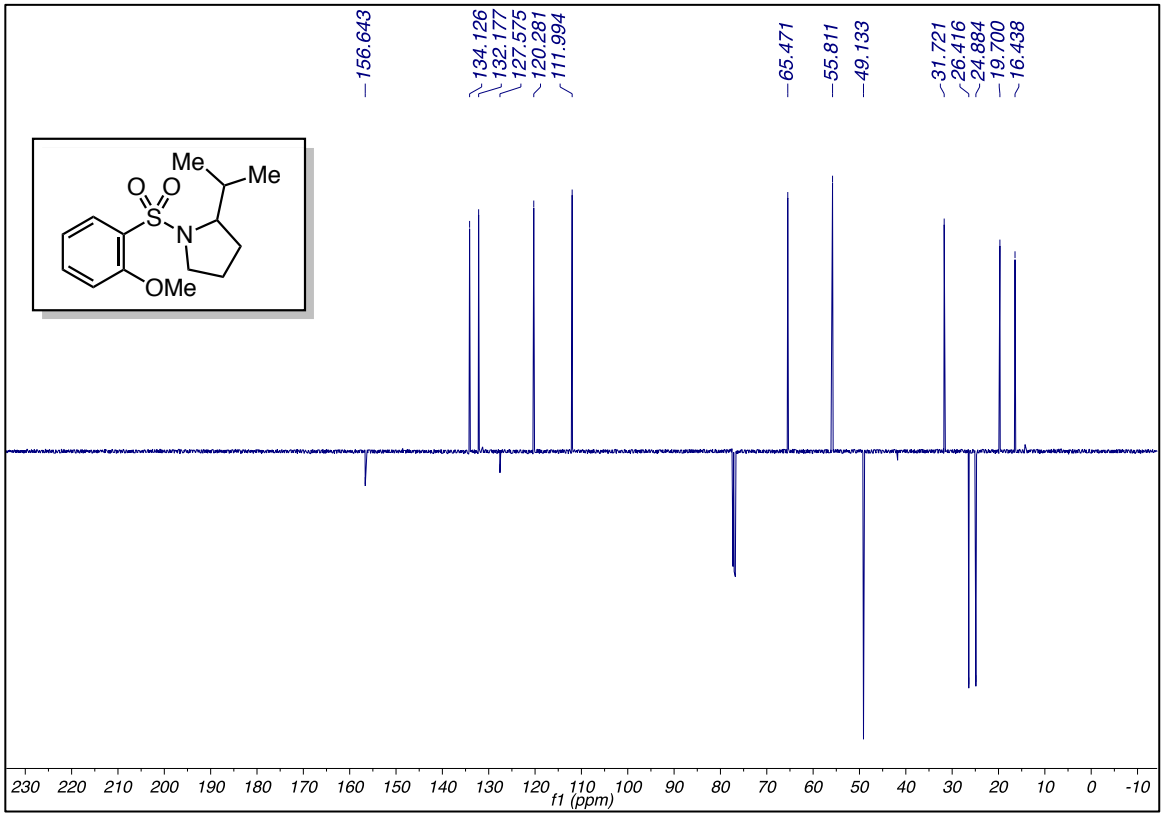

Me
Me
O
O
S
N
NC
1.96
1.94
0.98
1.98
0.98
2.21
2.03
2.94
3.03
f1 (ppm)

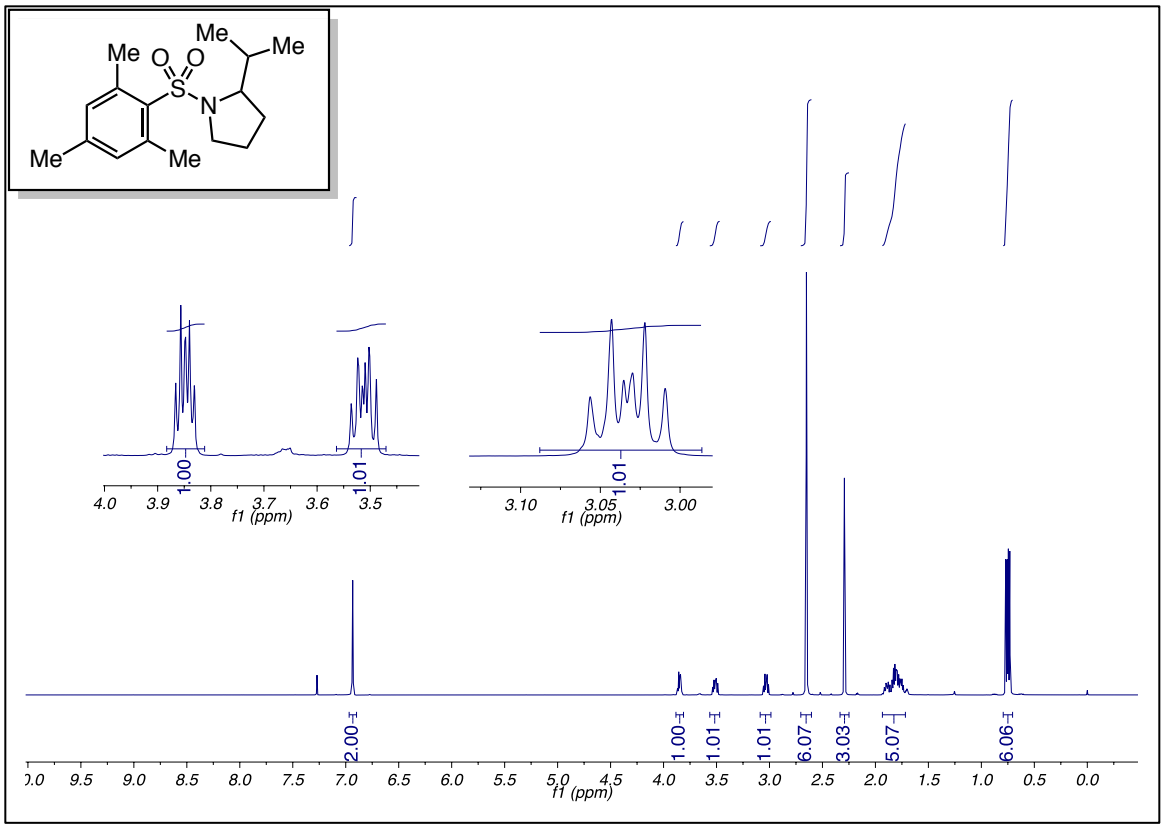

142.495
132.855
128.010
117.381
116.207
66.022
49.527
31.935
26.177
24.633
19.726
16.396
Me
Me
O
O
S
N
NC
f1 (ppm)

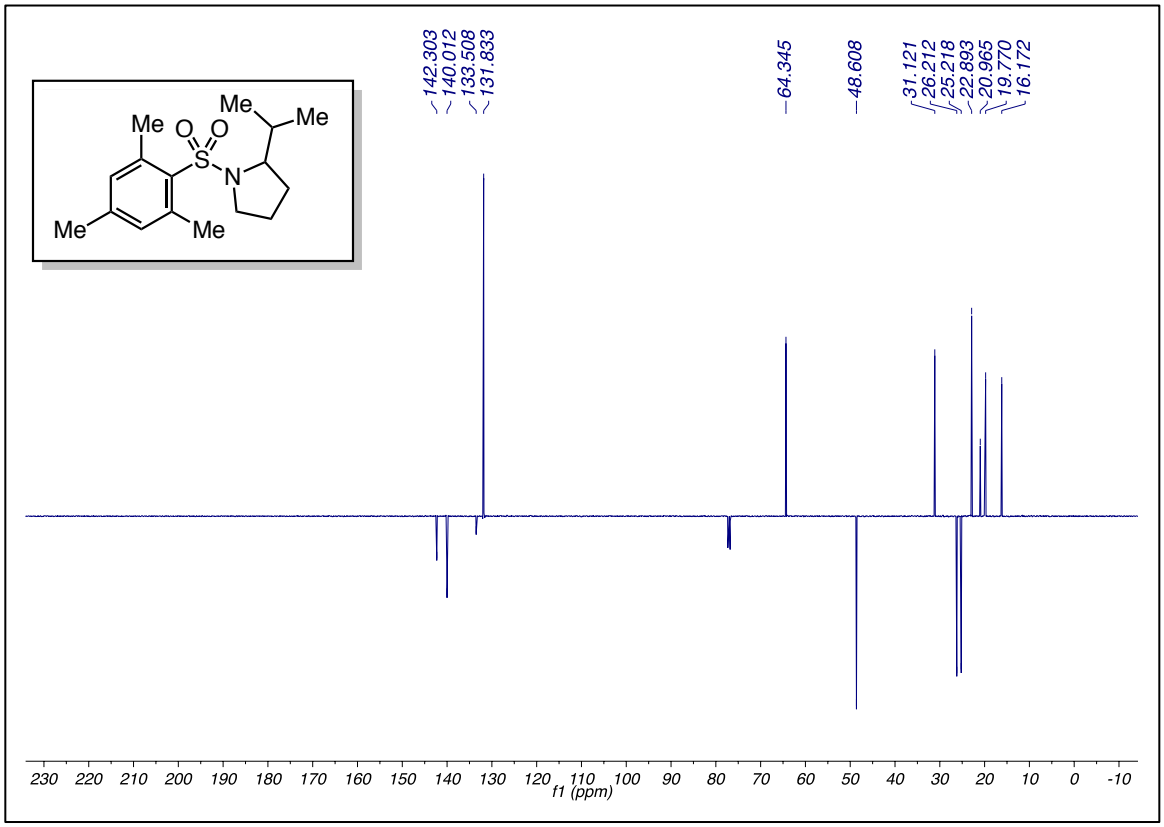

Me
Me
O
O
MeO
S
N
0.99
2.00
2.21
1.00
1.00
f1 (ppm)
1.97
0.97
0.97
2.99
0.99
2.00
1.00
2.21
1.00
1.00
2.95
3.04
f1 (ppm)

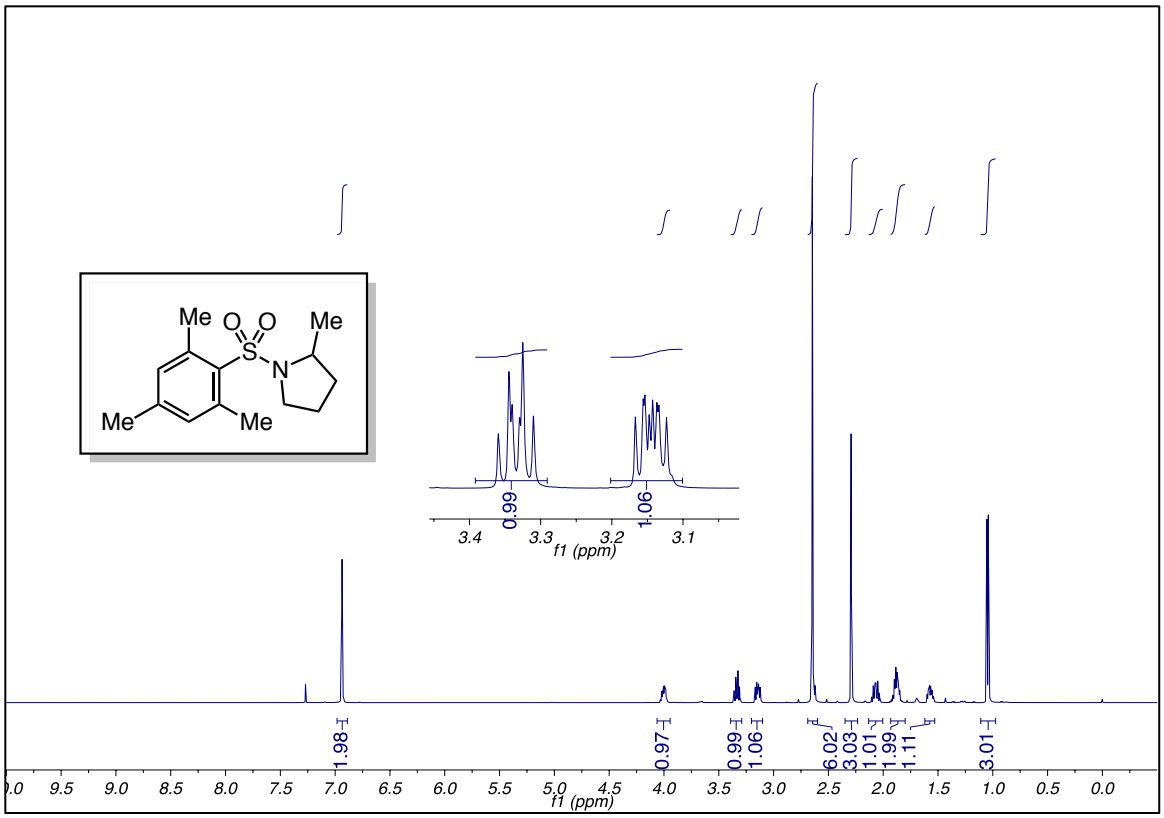

159.817
139.191
130.054
119.621
118.514
112.553
65.695
55.666
49.479
32.035
26.153
24.580
19.805
16.511
Me
Me
O
O
MeO
S
N
f1 (ppm)

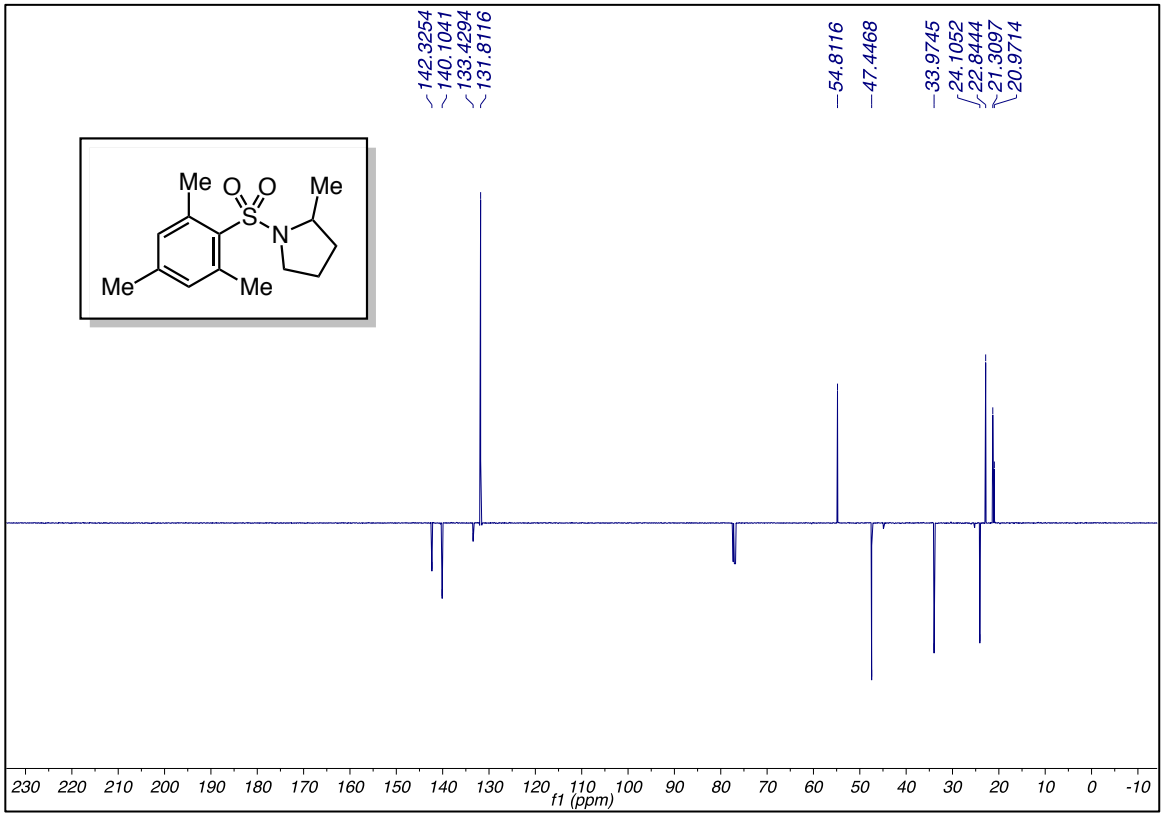

Me
Me
O
O
S
N
OMe
0.99
1.00
2.00
1.00
0.99
0.99
f1 (ppm)
0.99
1.00
2.00
3.04
1.00
0.99
0.99
0.98
1.01
2.01
1.04
3.02
3.03
f1 (ppm)

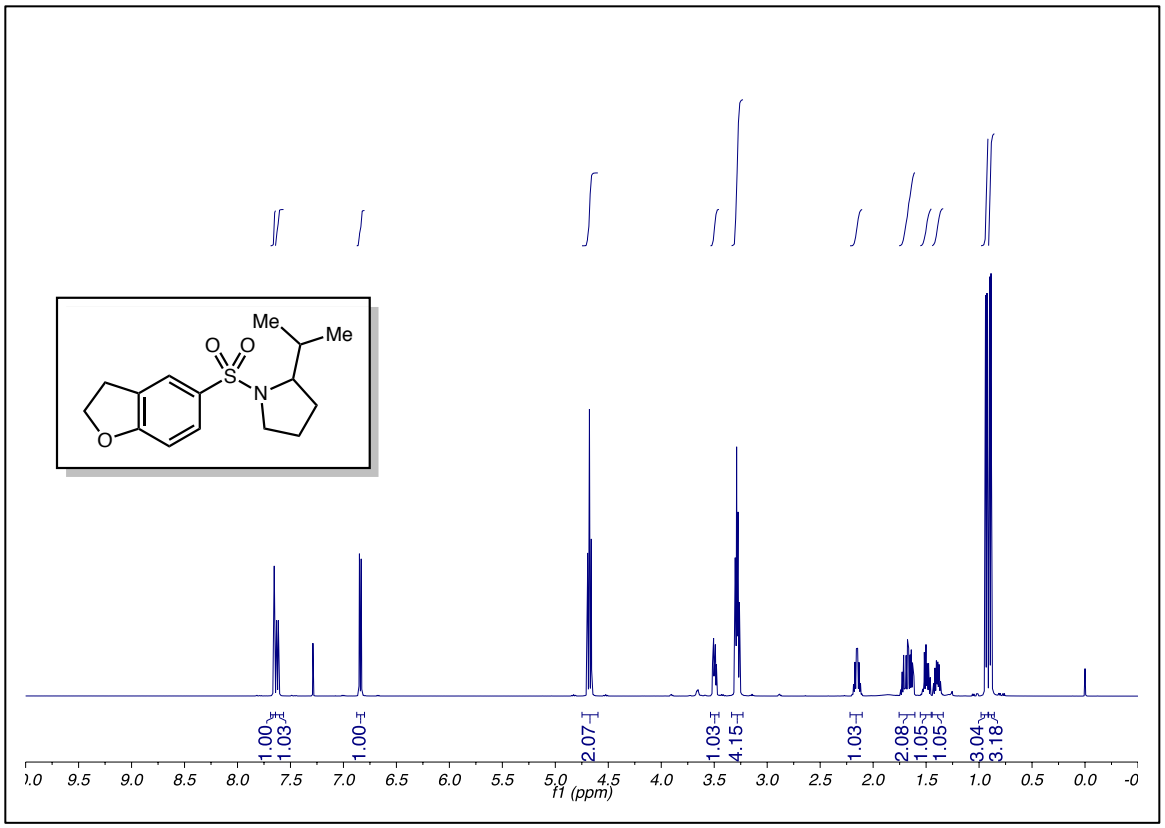

156.643
134.126
132.177
127.575
120.281
111.994
65.471
55.811
49.133
31.721
26.416
24.884
19.700
16.438
Me
Me
O
O
S
N
OMe
f1 (ppm)

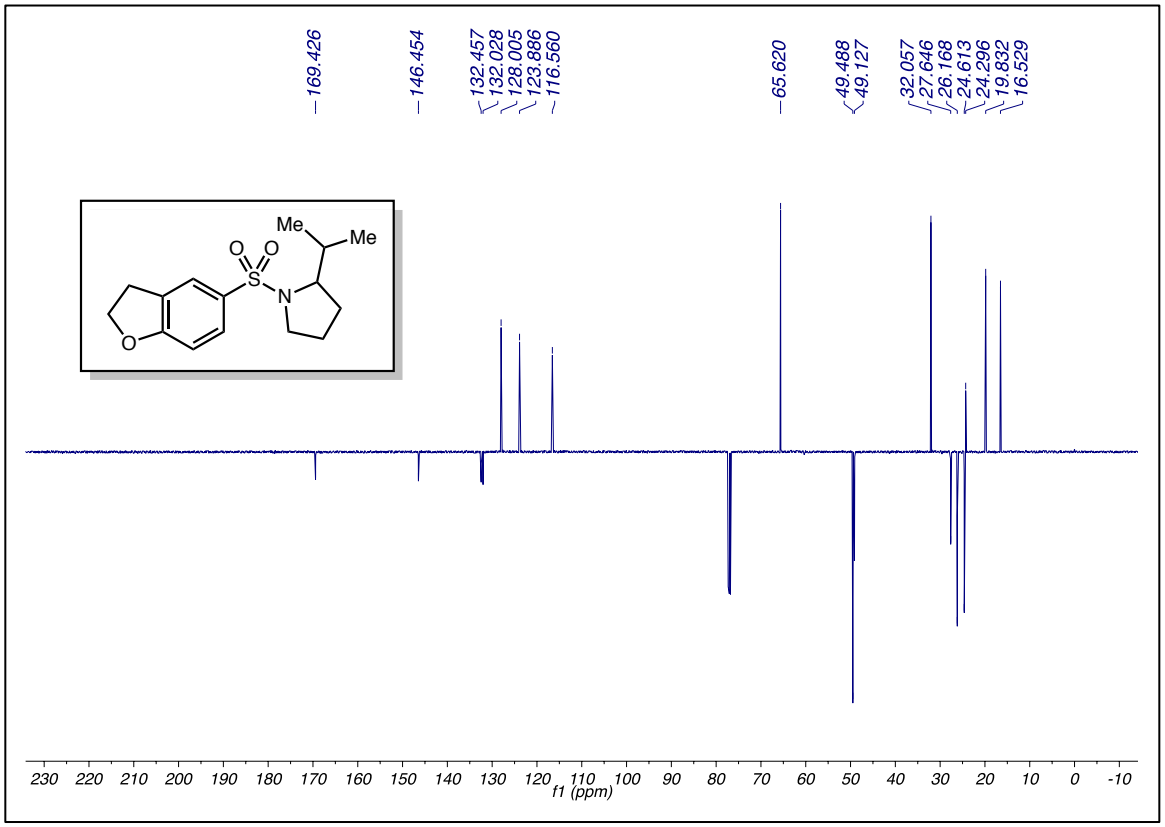

Me
Me
O
O
S
N
Me
Me
Me
1.00
1.01
f1 (ppm)
2.00
1.00
1.01
1.01
6.07
3.03
5.07
6.06
f1 (ppm)

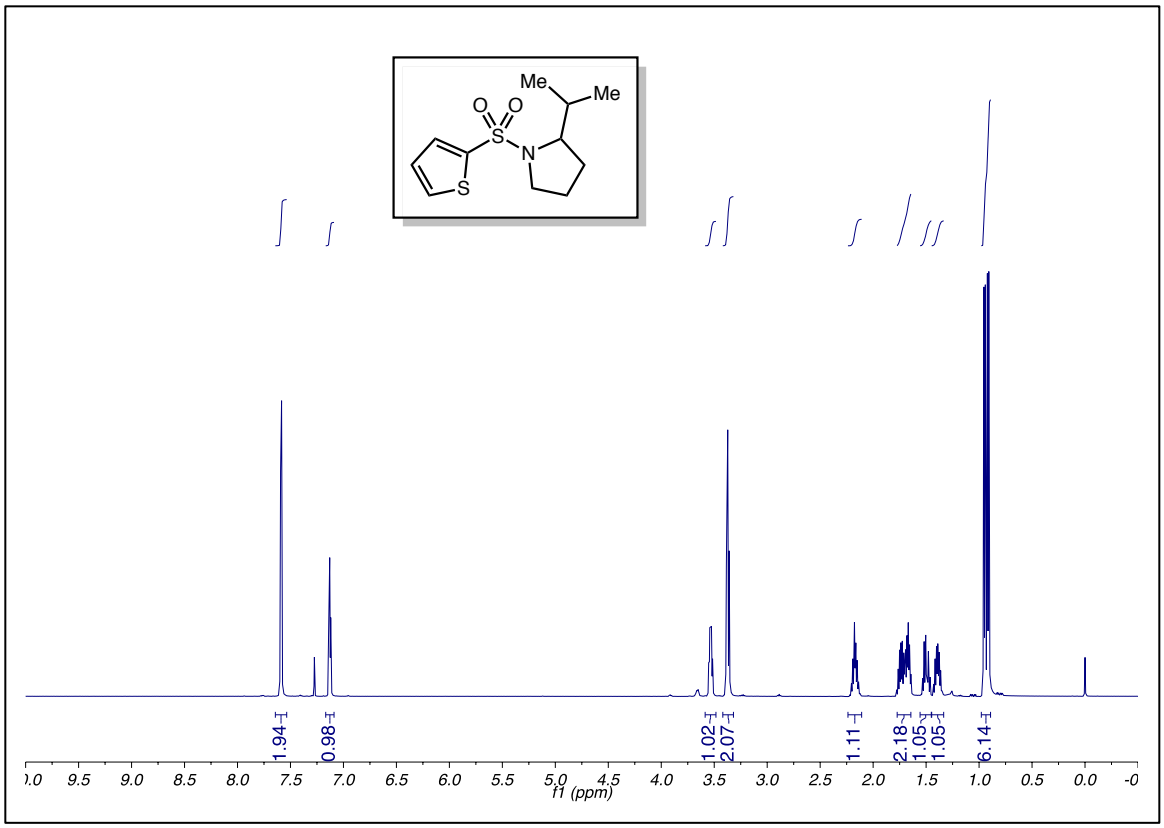

Me
Me
O
O
S
N
Me
Me
142.303
140.012
133.508
131.833
64.345
48.608
31.121
26.212
25.218
22.893
20.965
19.770
16.172
f1 (ppm)

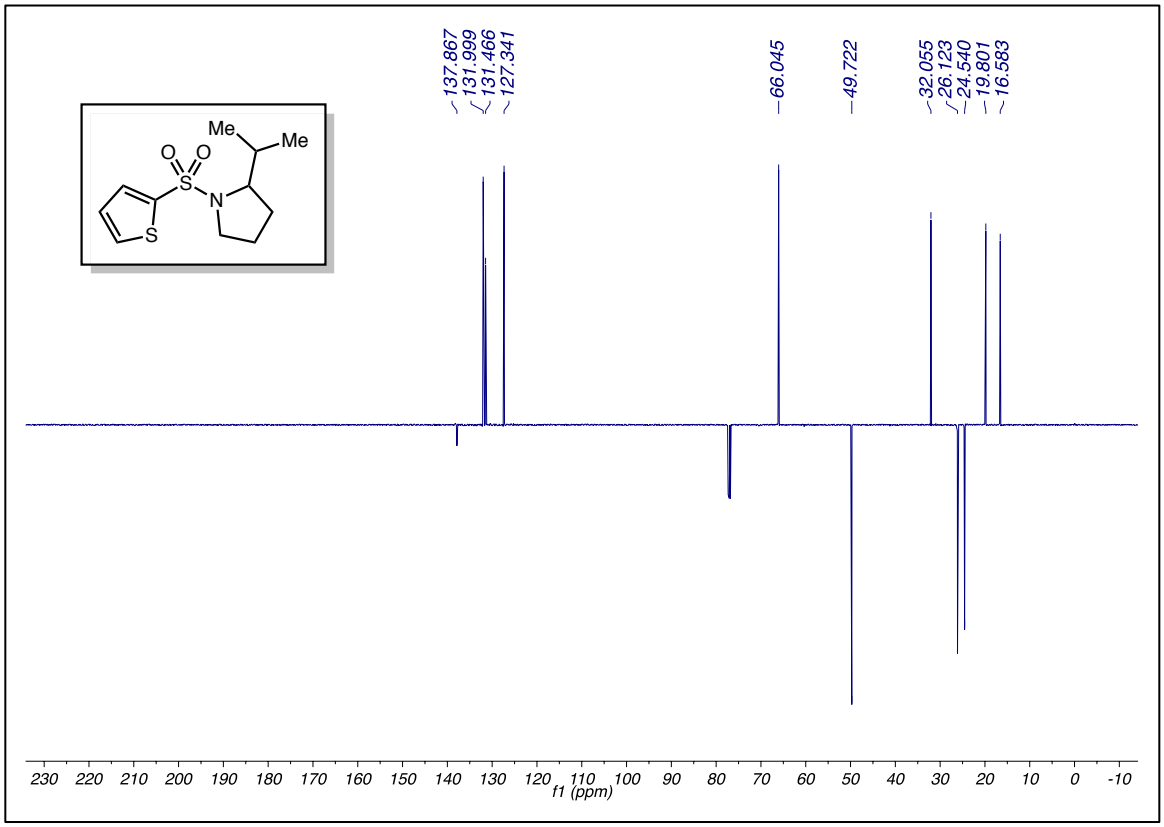

Me
O
O
Me
S
N
Me
Me
0.99
1.06
3.4
3.3
3.2
3.1
f1 (ppm)
1.98
0.97
0.99
1.06
6.02
3.03
1.01
1.99
1.11
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

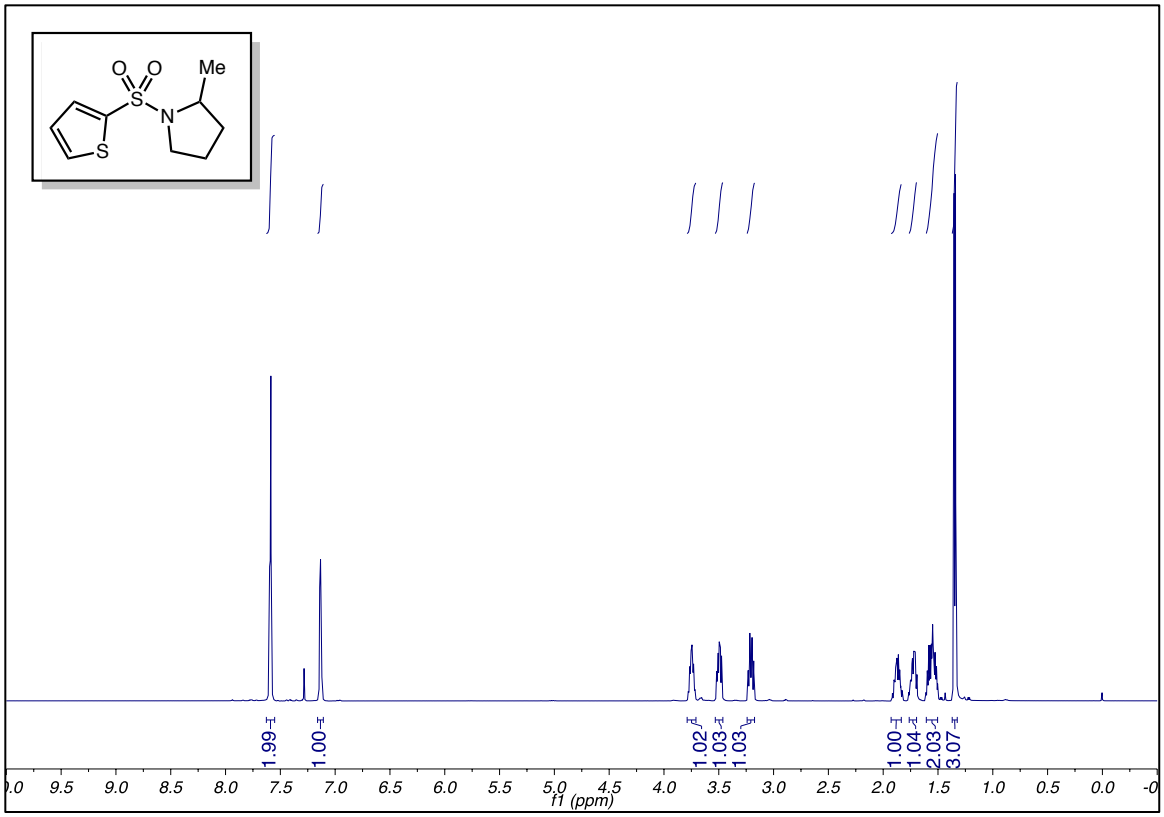

142.3254
140.1041
133.4294
131.8116
54.8116
47.4468
33.9745
24.1052
22.8444
21.3097
20.9714
Me
O
O
Me
S
N
Me
Me
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

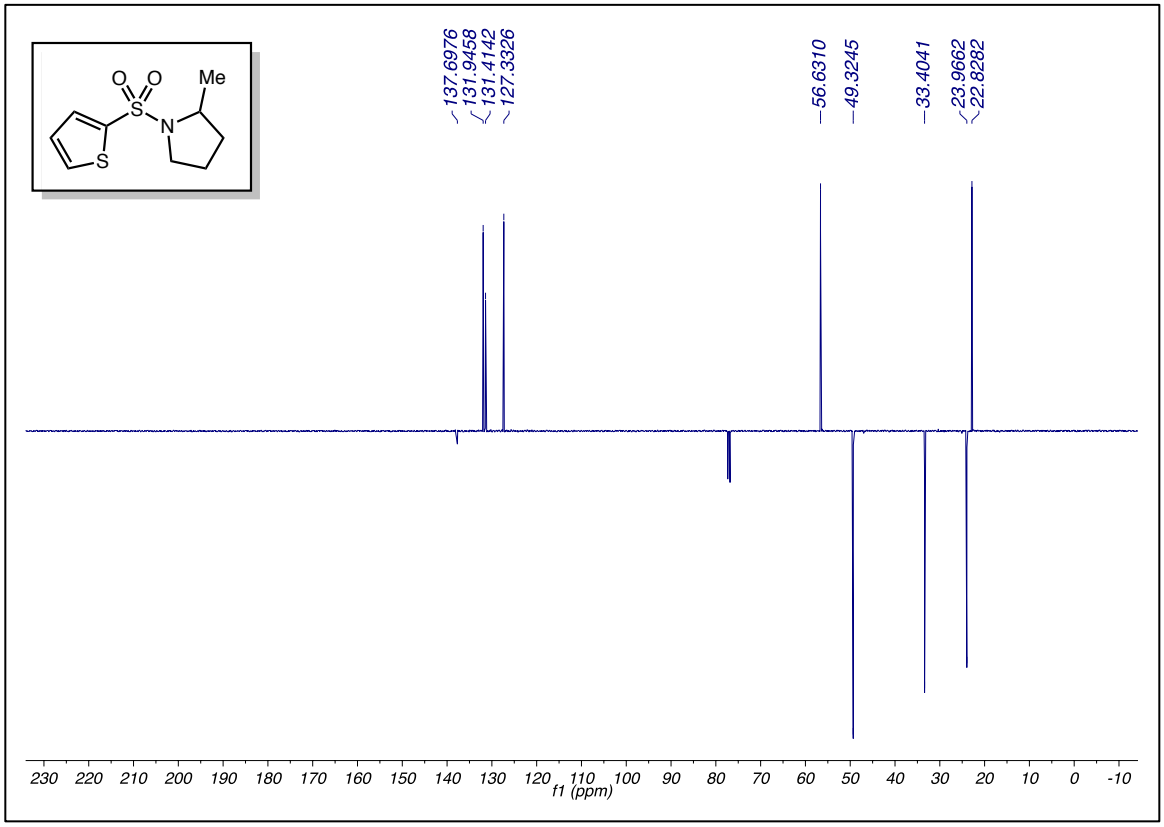

Me
Me
O
O
S
N
O
1.00
1.03
1.00
2.07
1.03
4.15
1.03
2.08
1.05
1.05
3.04
3.18
f1 (ppm)

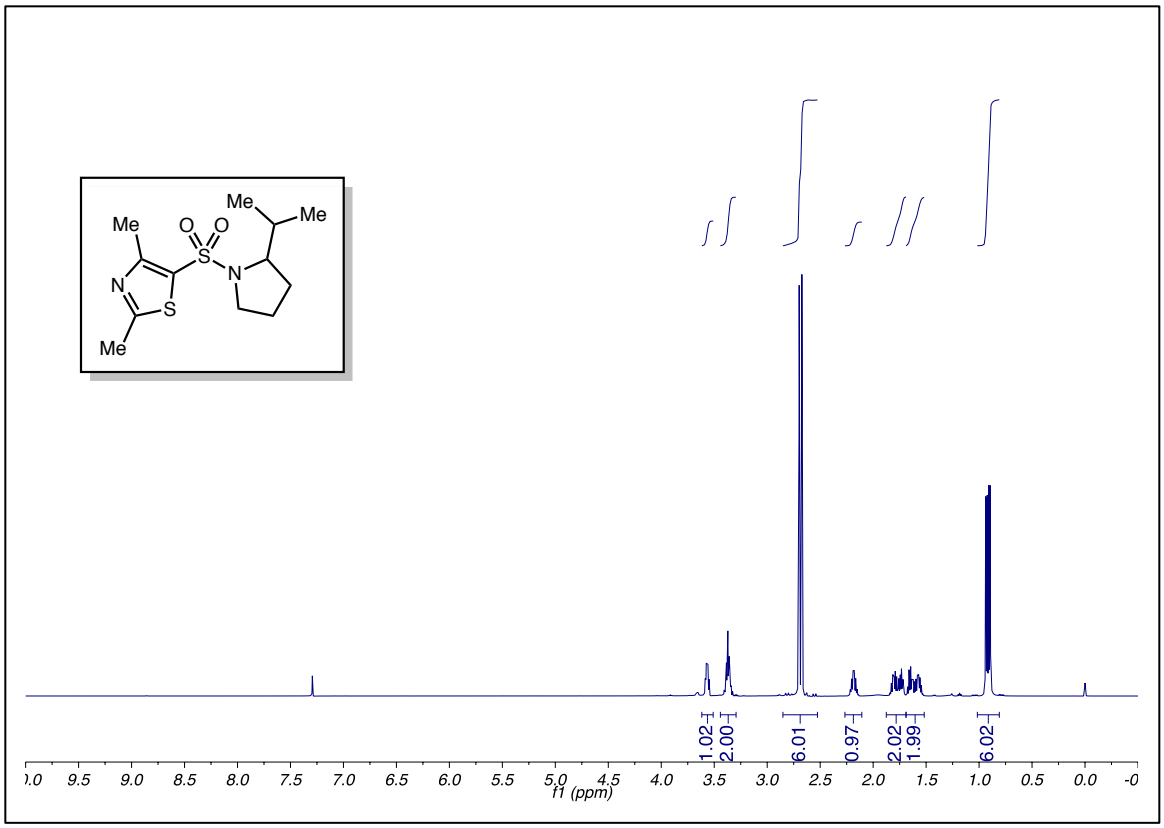

169.426
146.454
132.457
132.028
128.005
123.886
116.560
65.620
49.488
49.127
32.057
27.646
26.168
24.613
24.296
19.832
16.529
Me
Me
O
O
S
N
O
f1 (ppm)

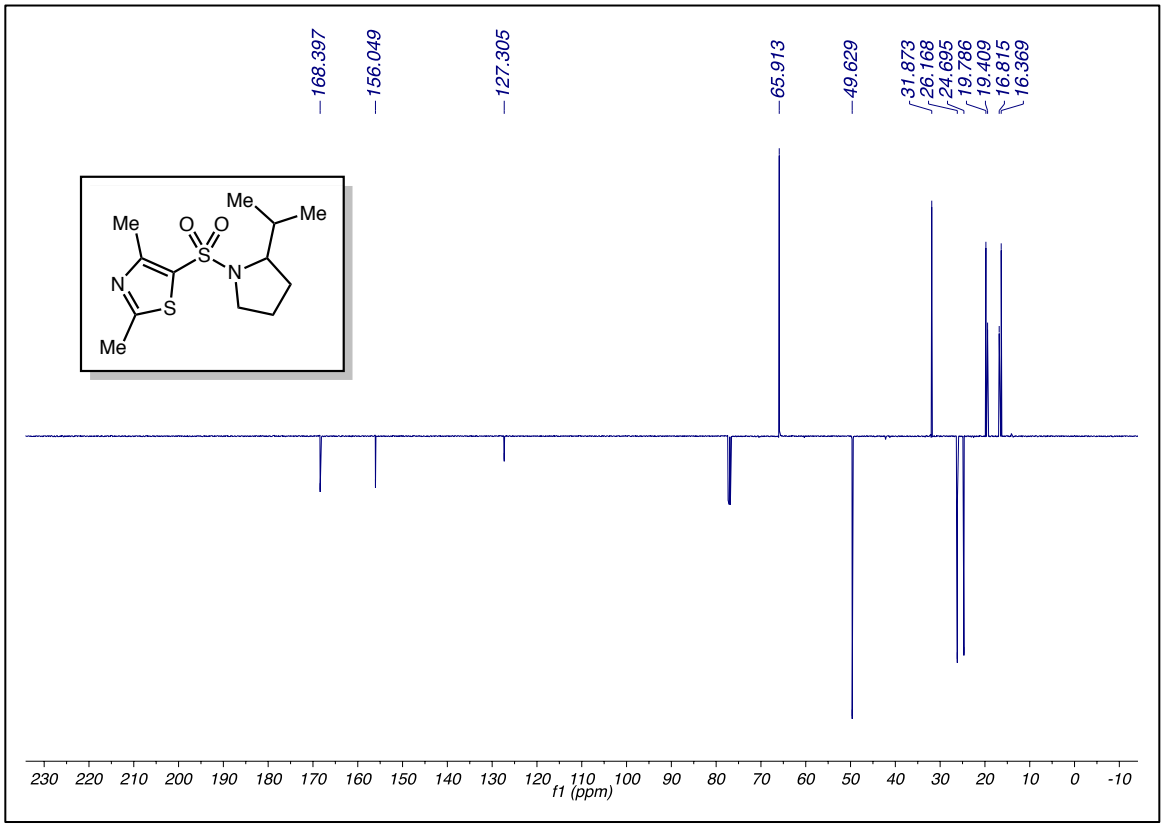

Me
Me
O
O
S
N
S
1.94
0.98
1.02
2.07
1.11
2.18
1.05
1.05
6.14
f1 (ppm)

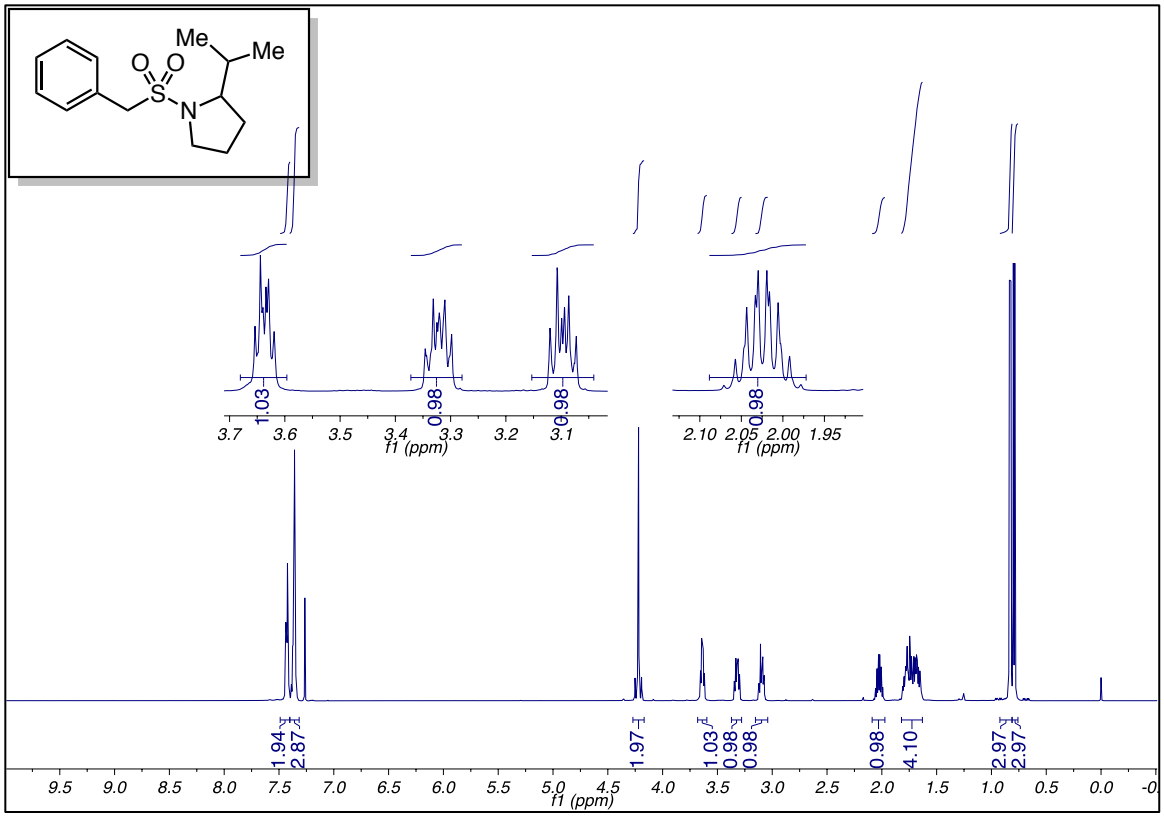

137.867
131.999
131.466
127.341
66.045
49.722
32.055
26.123
24.540
19.801
16.583
Me
Me
O
O
S
N
S
f1 (ppm)

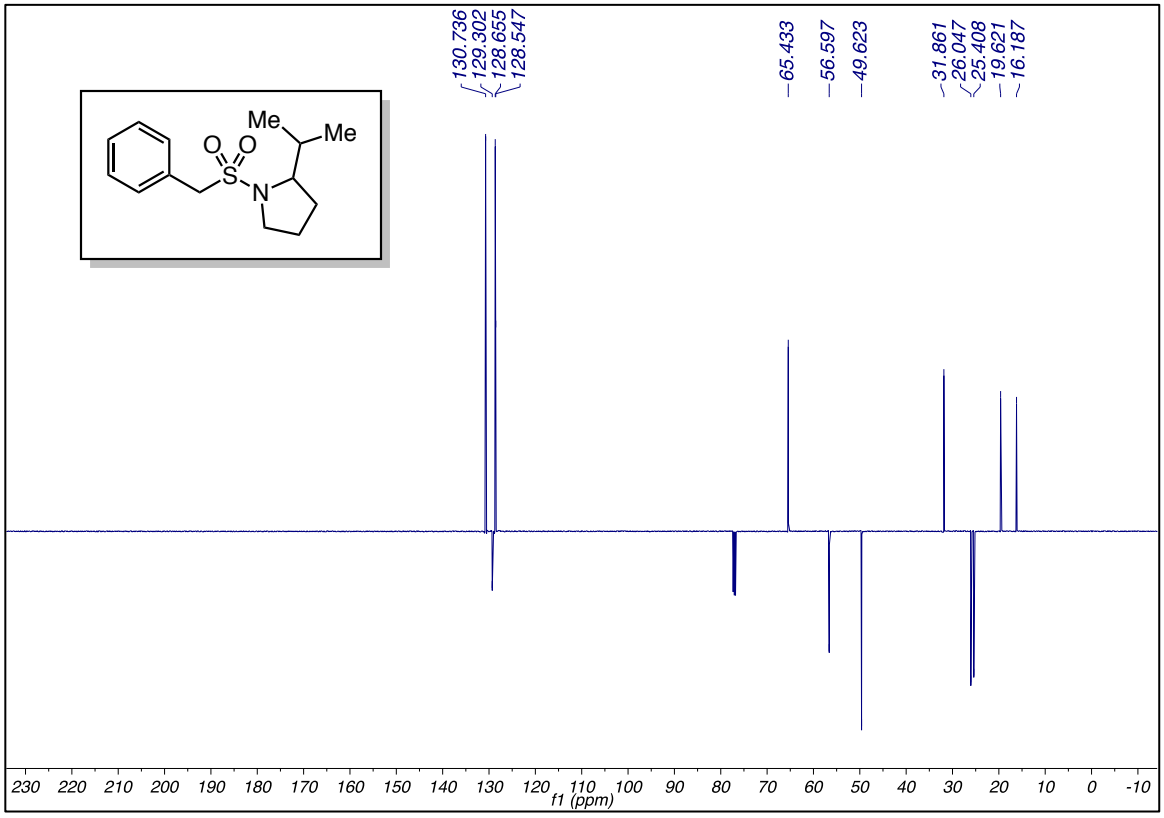

O
O
Me
S
N
S
1.99
1.00
1.02
1.03
1.03
1.00
1.04
2.03
3.07
f1 (ppm)

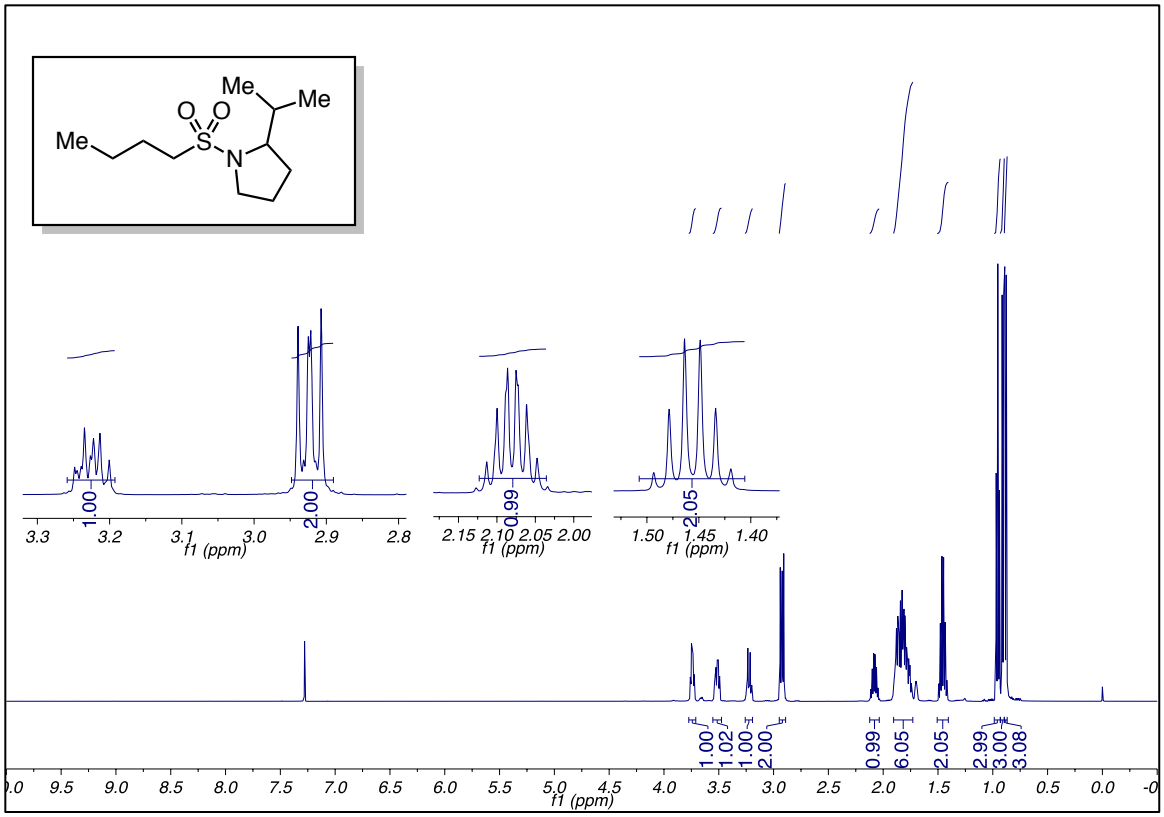

O
O
Me
S
N
S
137.6976
131.9458
131.4142
127.3326
56.6310
49.3245
33.4041
23.9662
22.8282
f1 (ppm)

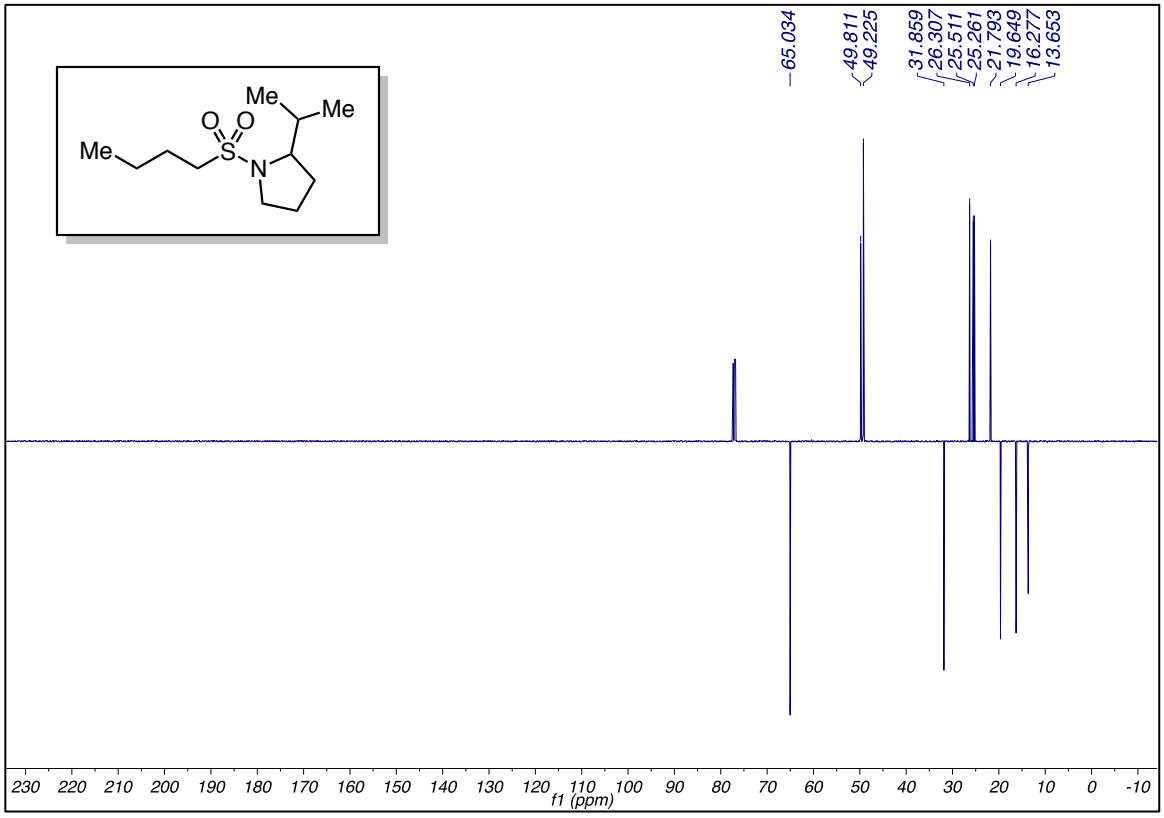

Me
Me
O
O
S
N
N
S
Me
Me
1.02
2.00
6.01
0.97
2.02
1.99
6.02
f1 (ppm)

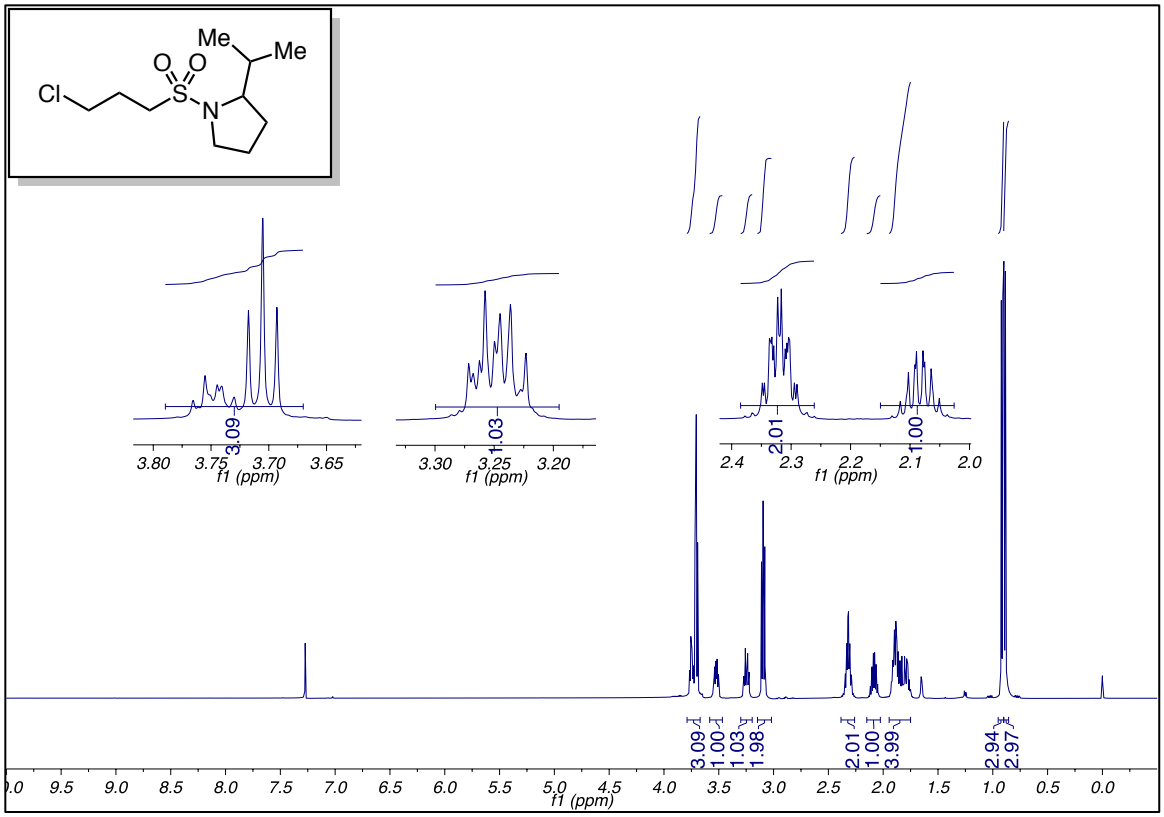

168.397
156.049
127.305
65.913
49.629
31.873
26.168
24.695
19.786
19.409
16.815
16.369
Me
Me
O
O
S
N
N
S
Me
Me
f1 (ppm)

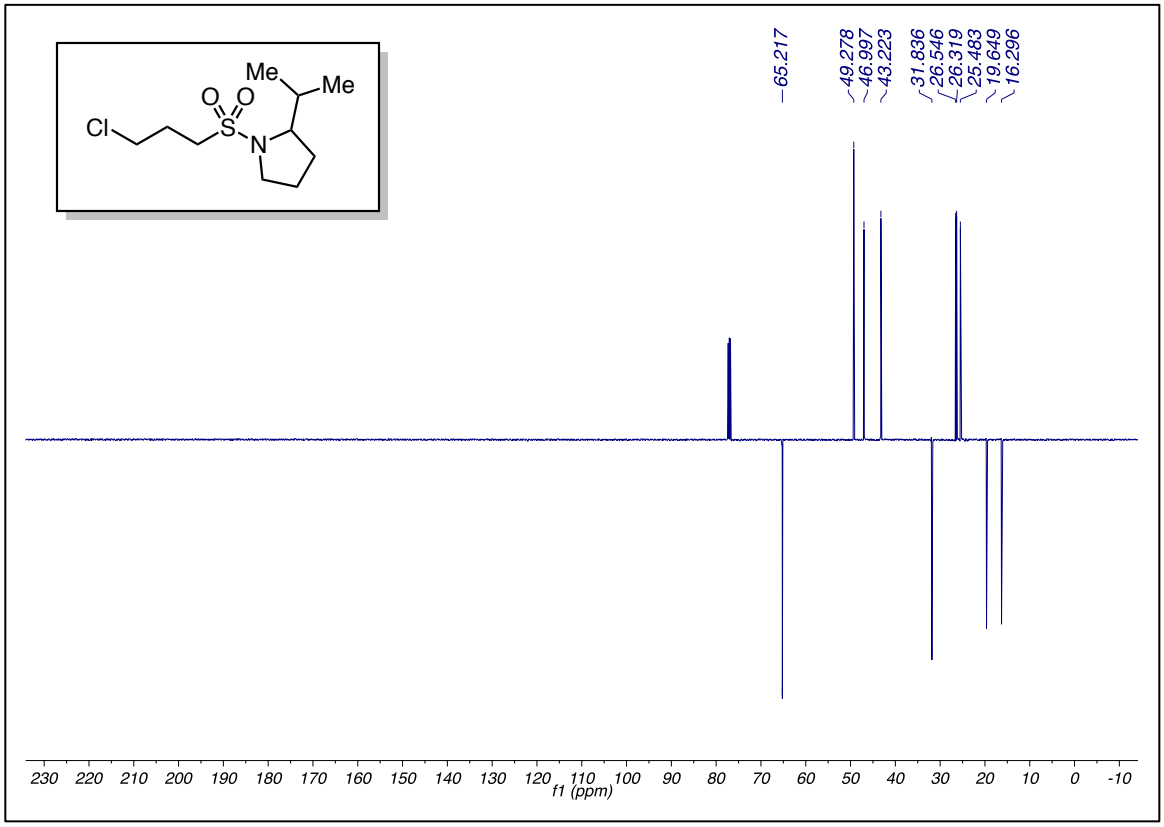

Me
Me
O
O
S
N
1.03
0.98
0.98
0.98
3.7 3.6 3.5 3.4 3.3 3.2 3.1
f1 (ppm)
2.10 2.05 2.00 1.95
f1 (ppm)
1.94
2.87
1.97
1.03
0.98
0.98
0.98
4.10
2.97
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

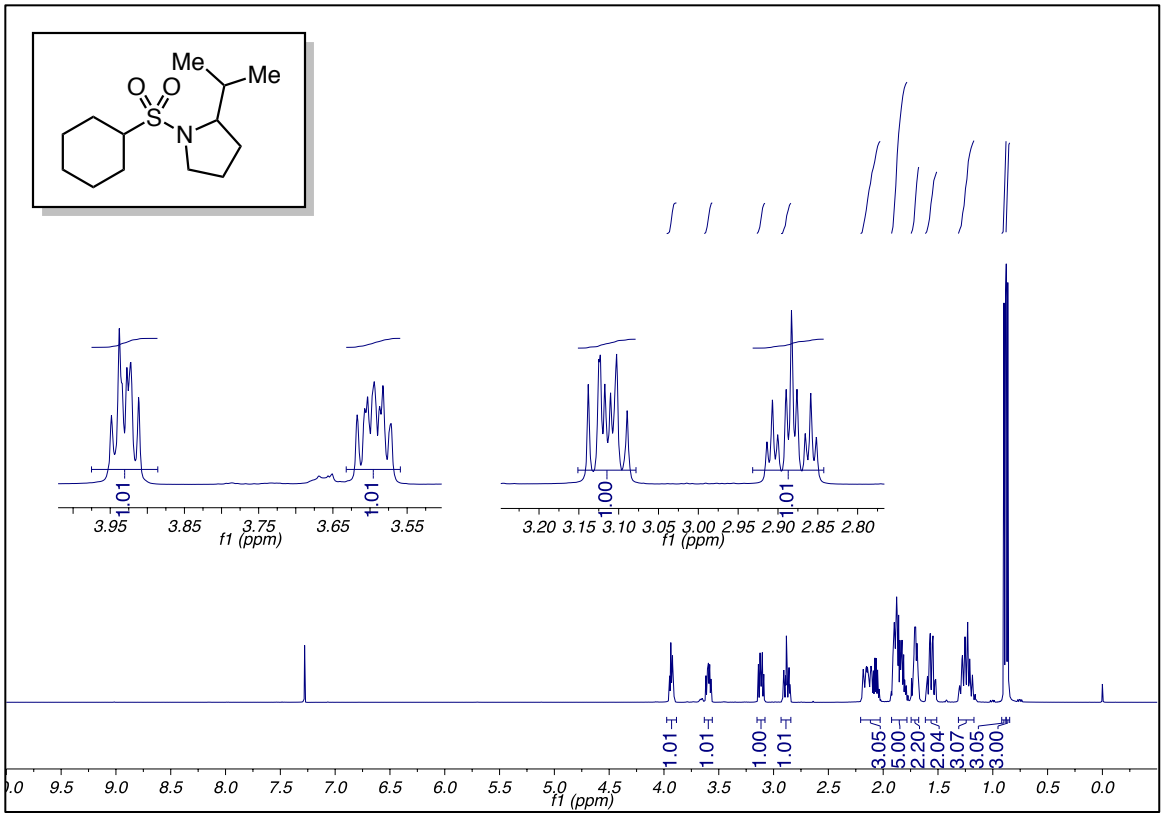

130.736
129.302
128.655
128.547
65.433
56.597
49.623
31.861
26.047
25.408
19.621
16.187
Me
Me
O
O
S
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

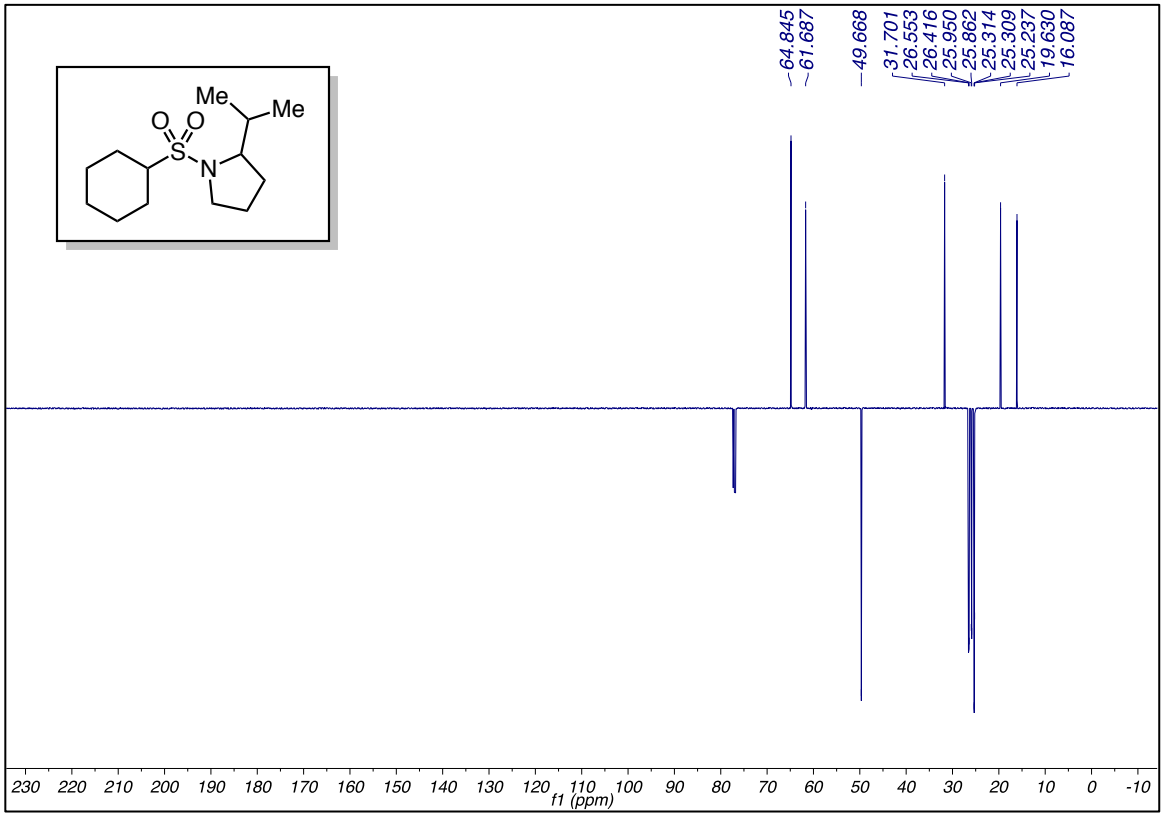

Me
Me
Me
O
O
S
N
1.00
2.00
0.99
2.05
f1 (ppm)
1.00
1.02
1.00
2.00
0.99
6.05
2.05
2.99
3.00
3.08

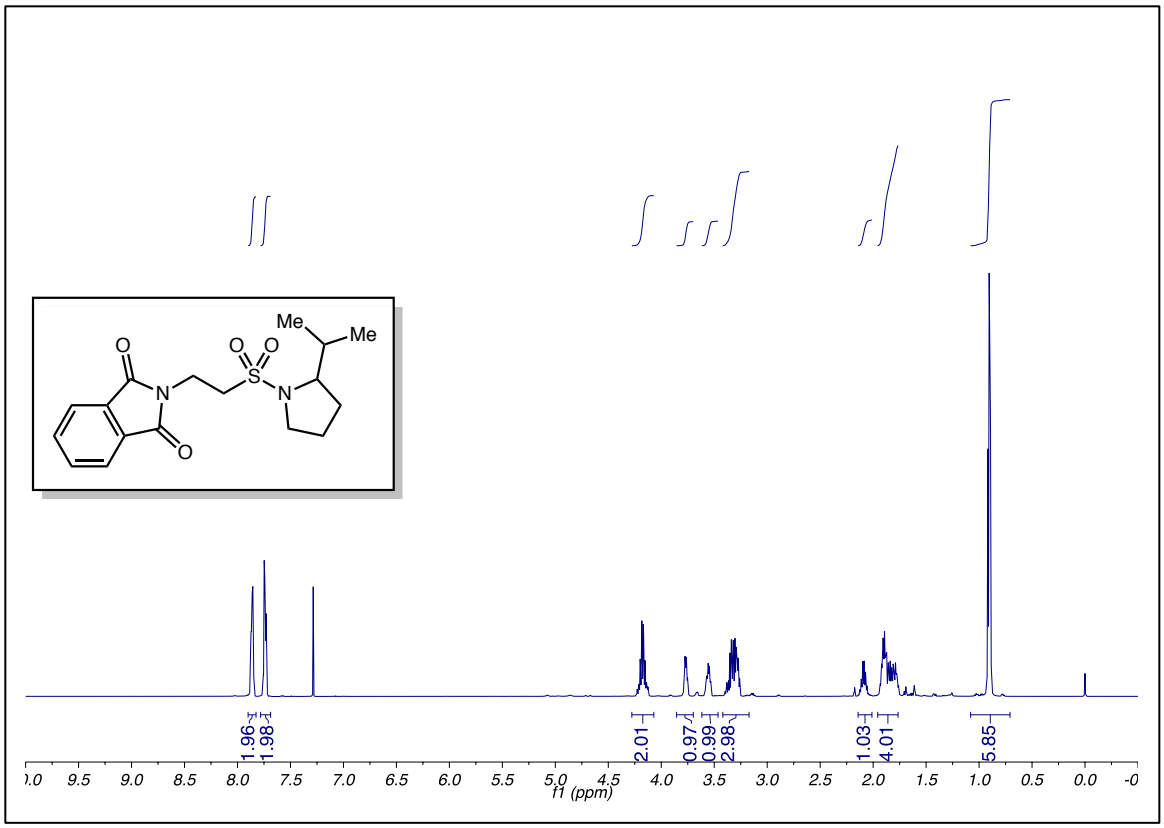

Me
Me
Me
O
O
S
N
65.034
49.811
49.225
31.859
26.307
25.511
25.261
21.793
19.649
16.277
13.653
f1 (ppm)

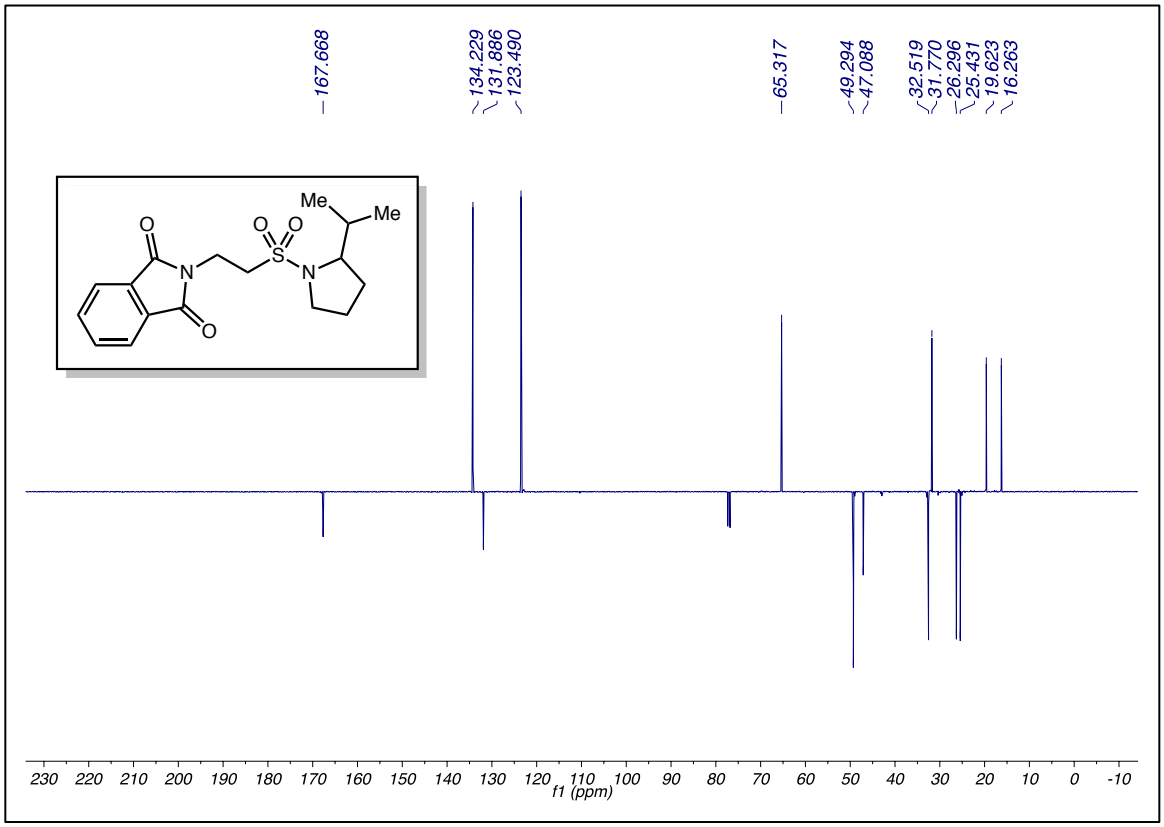

Me
Me
O
O
S
N
Cl
3.09
1.03
2.01
1.00
f1 (ppm)
3.09
1.00
1.03
1.98
2.01
1.00
3.99
2.94
2.97
f1 (ppm)

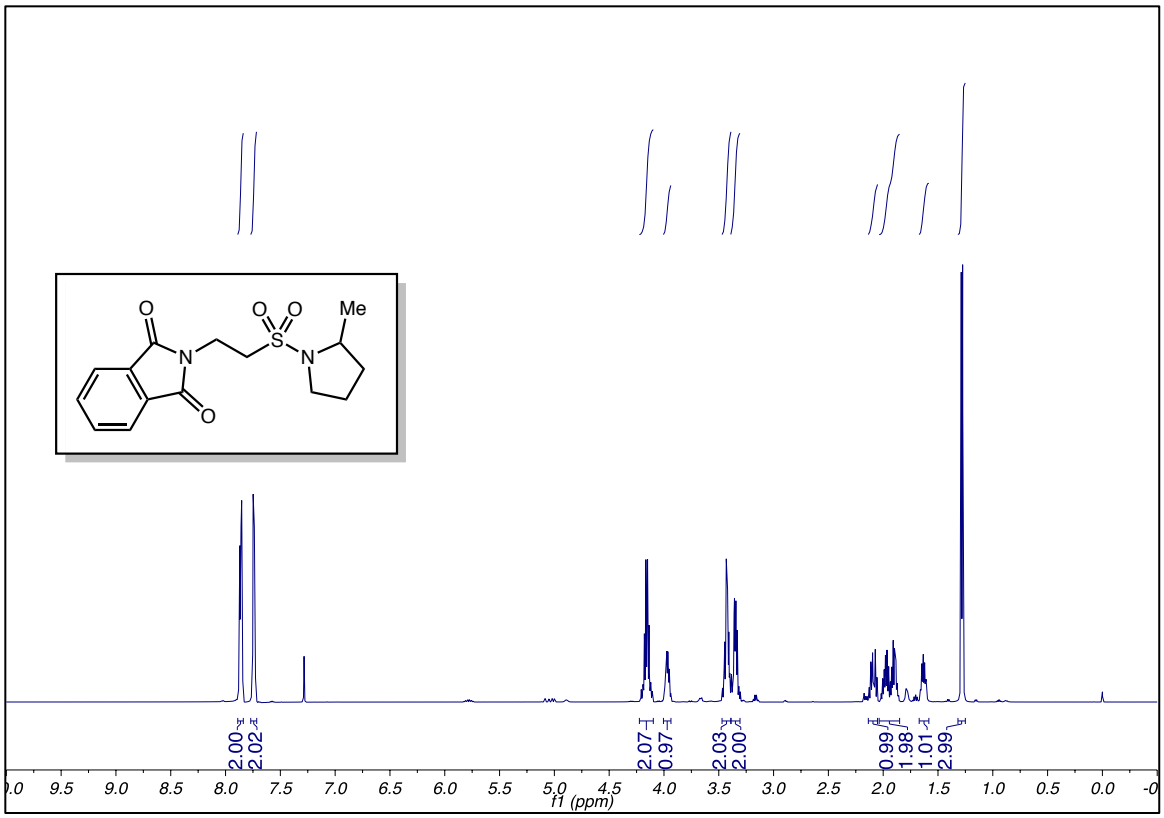

Me
Me
O
O
S
N
Cl
65.217
49.278
46.997
43.223
31.836
26.546
26.319
25.483
19.649
16.296
f1 (ppm)

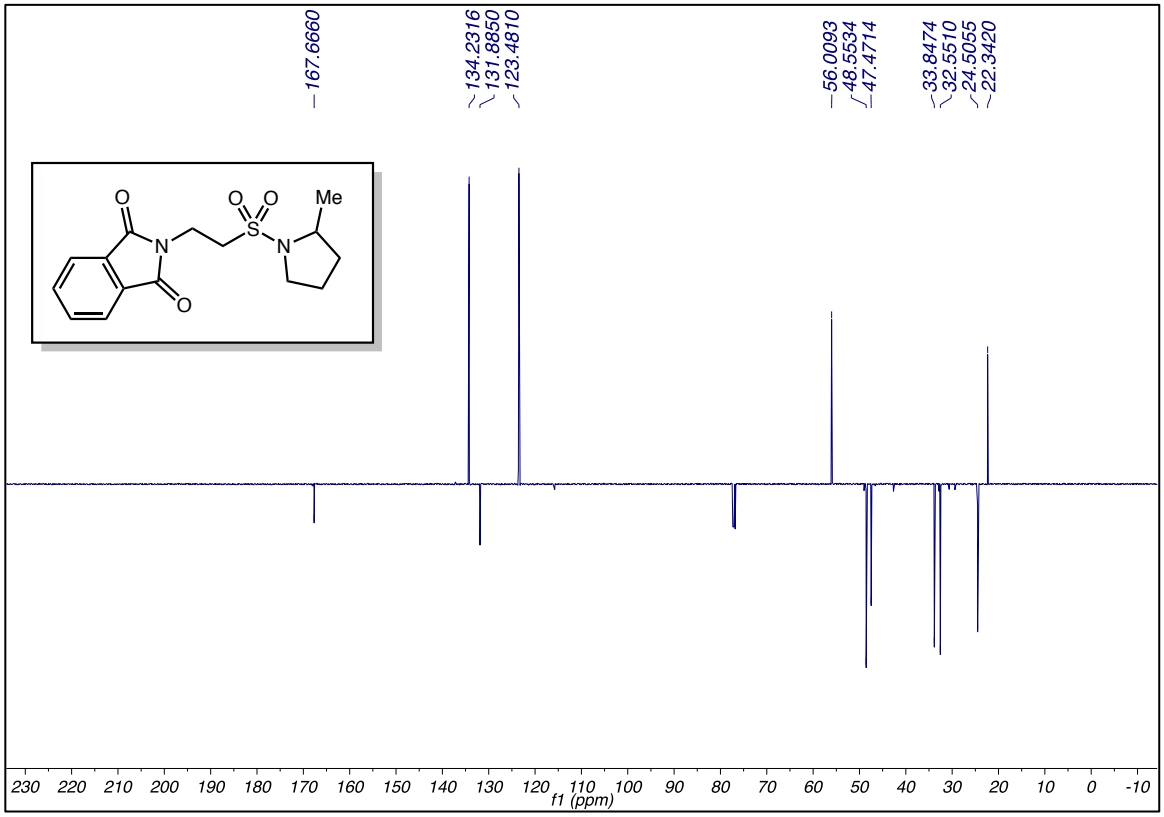

Me
Me
O
O
S
N
1.01
1.01
1.00
1.01
3.95 3.85 3.75 3.65 3.55
f1 (ppm)
3.20 3.15 3.10 3.05 3.00 2.95 2.90 2.85 2.80
f1 (ppm)
1.01
1.01
1.00
1.01
3.05
5.00
2.20
2.04
3.07
3.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

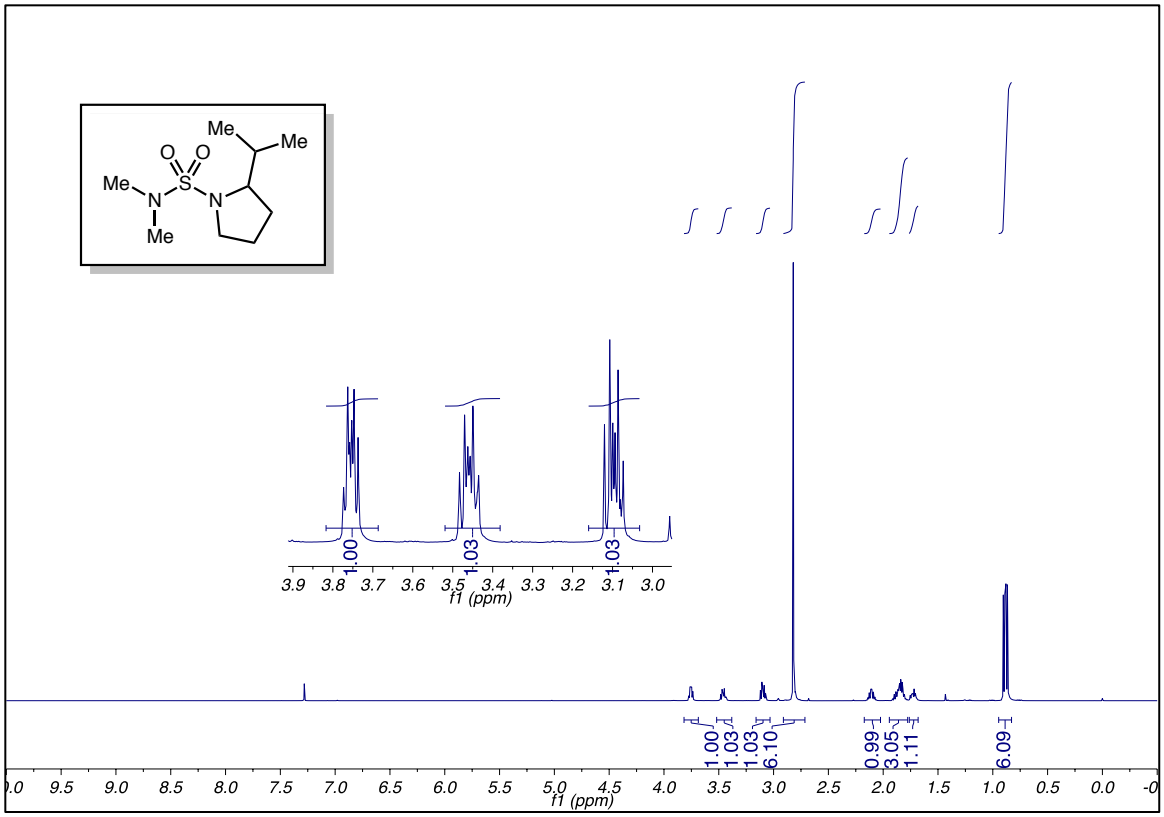

64.845
61.687
49.668
31.701
26.553
26.416
25.950
25.862
25.314
25.309
25.237
19.630
16.087
Me
Me
O
O
S
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

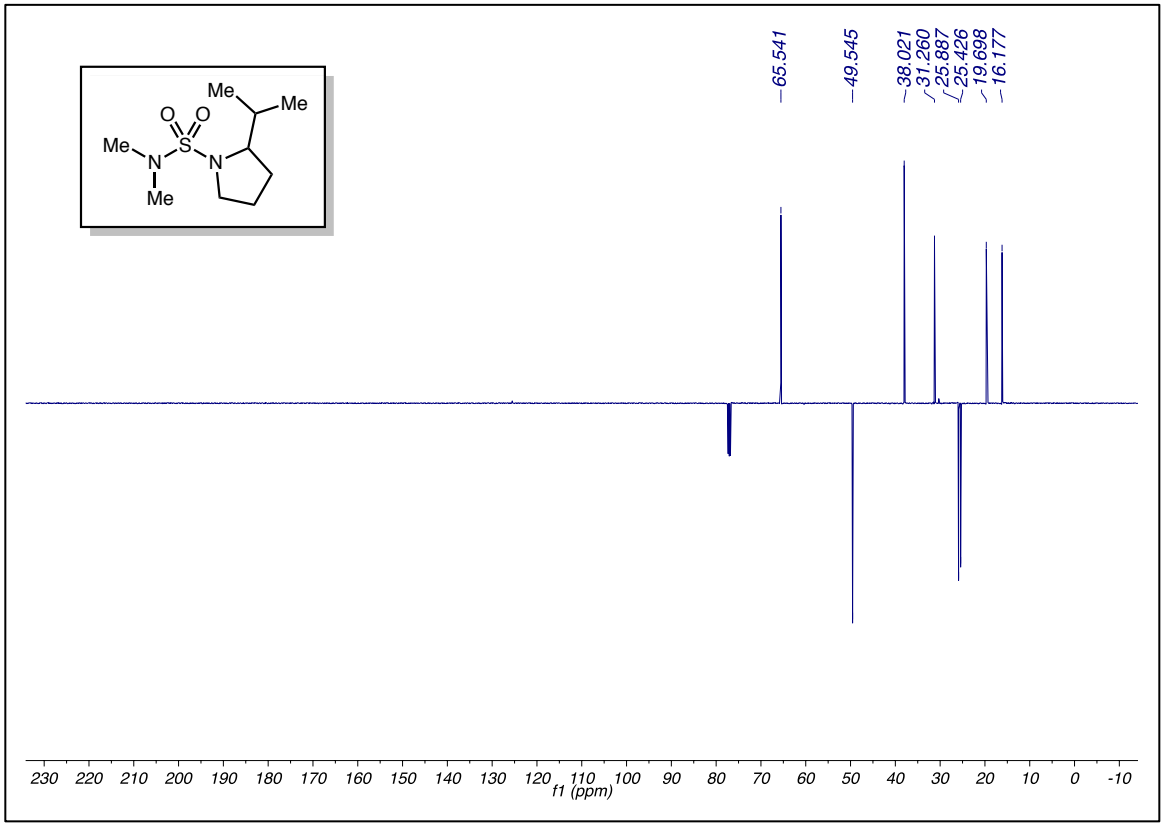

Me
Me
O
O
O
N
S
N
O
1.96
1.98
2.01
0.97
0.99
2.98
1.03
4.01
5.85
f1 (ppm)

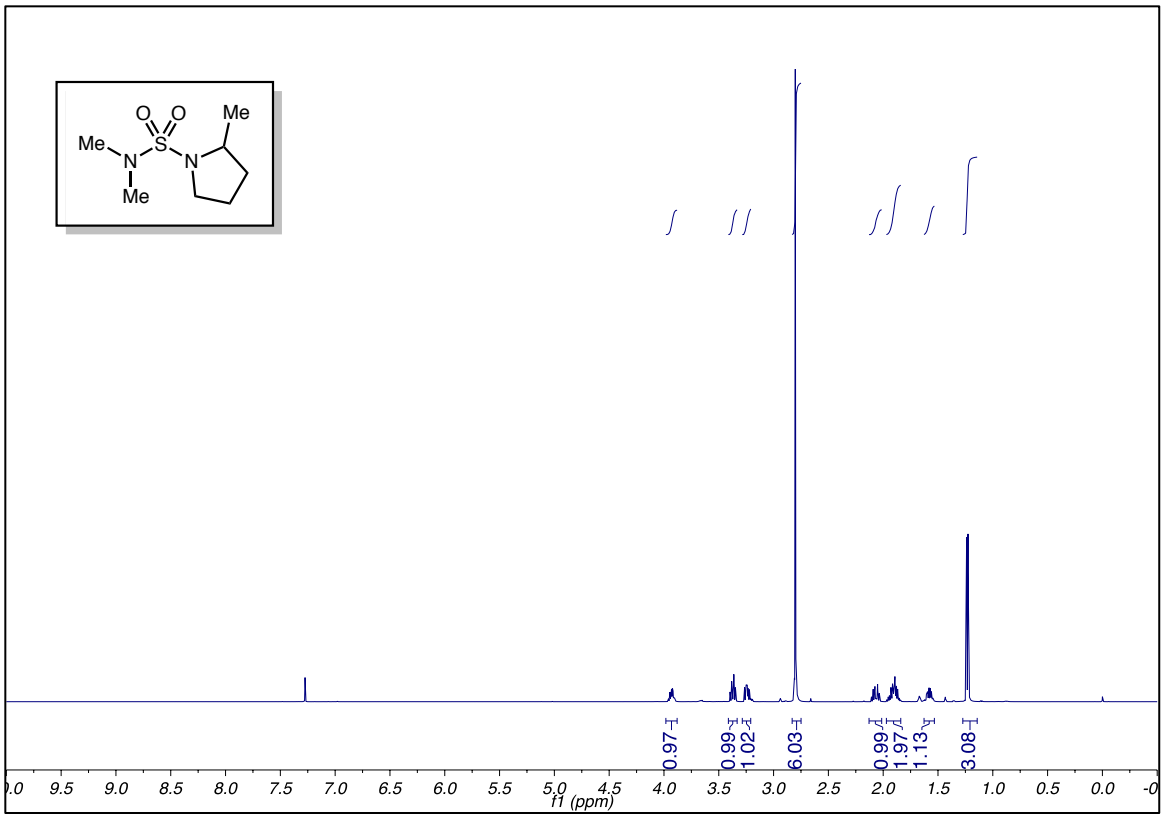

167.668
134.229
131.886
123.490
65.317
49.294
47.088
32.519
31.770
26.296
25.431
19.623
16.263
Me
Me
O
O
O
N
S
N
O
f1 (ppm)

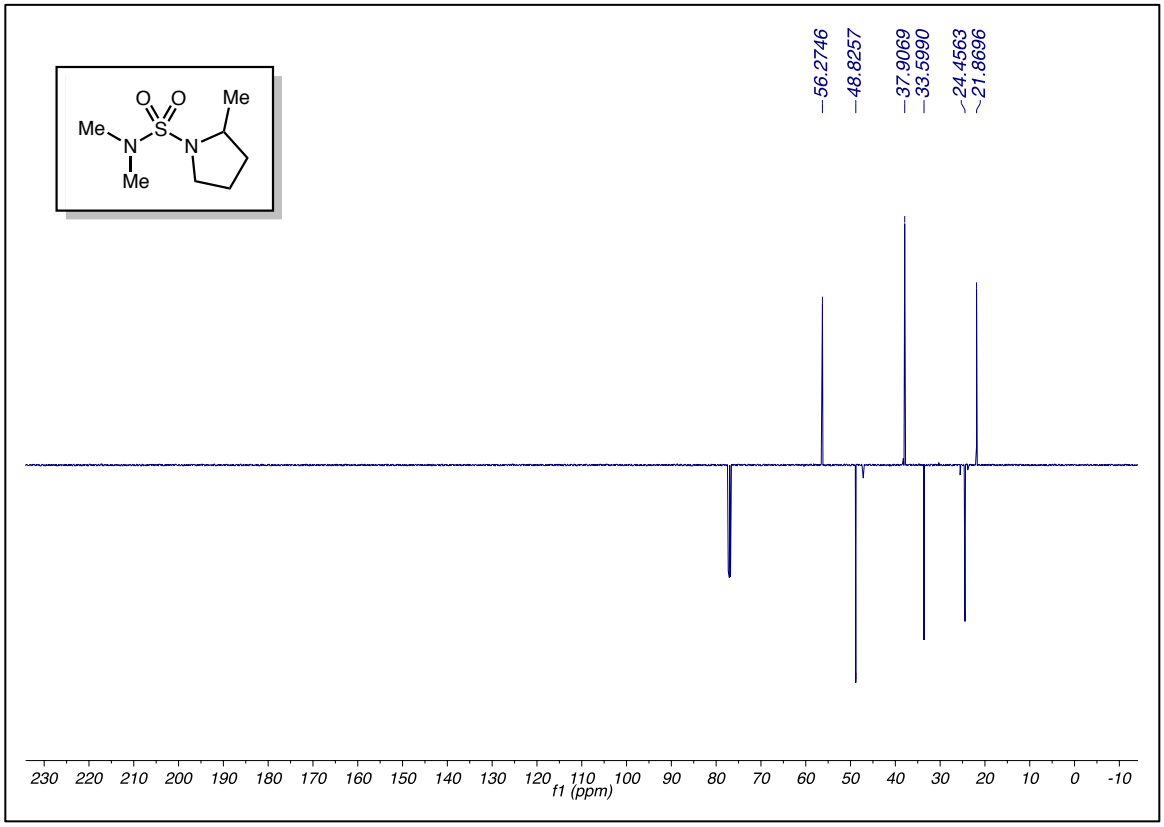

O
O
O
S
N
N
Me
O
2.00
2.02
2.07
0.97
2.03
2.00
0.99
1.98
1.01
2.99
f1 (ppm)

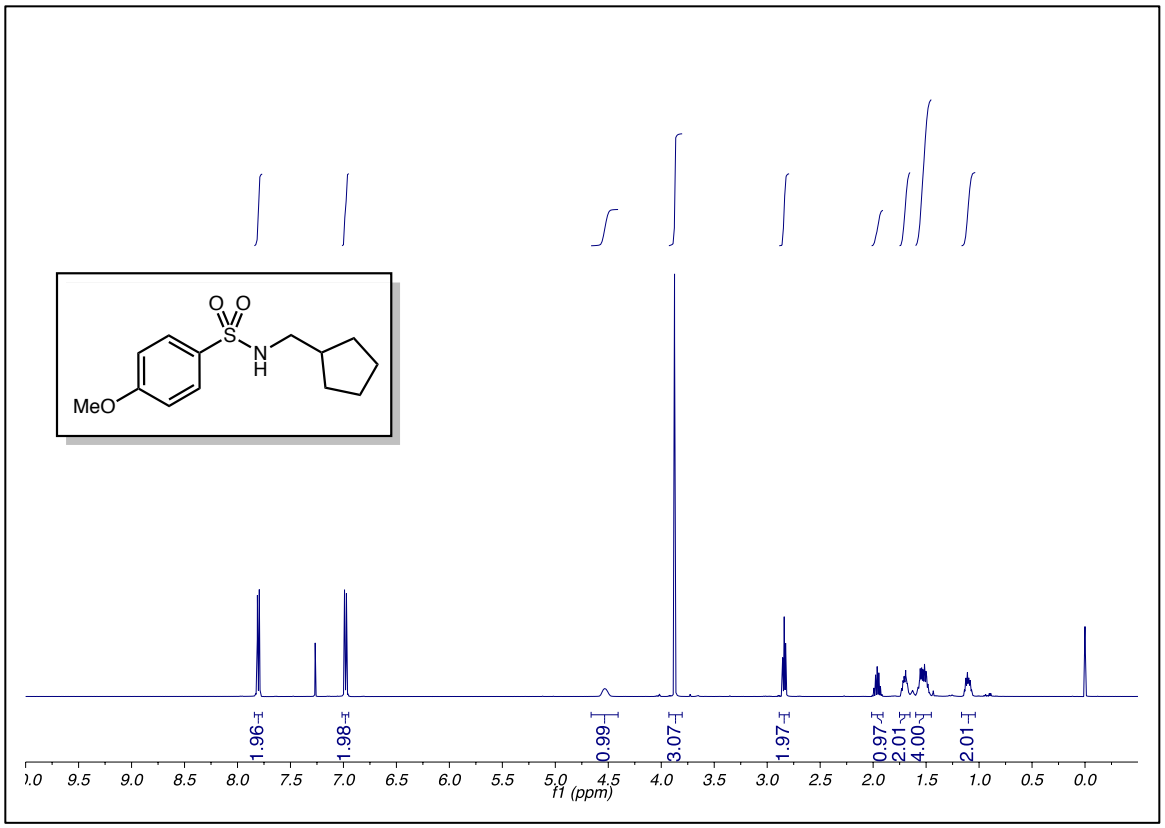

167.6660
134.2316
131.8850
123.4810
56.0093
48.5534
47.4714
33.8474
32.5510
24.5055
22.3420
O
O
O
S
N
N
Me
O
f1 (ppm)

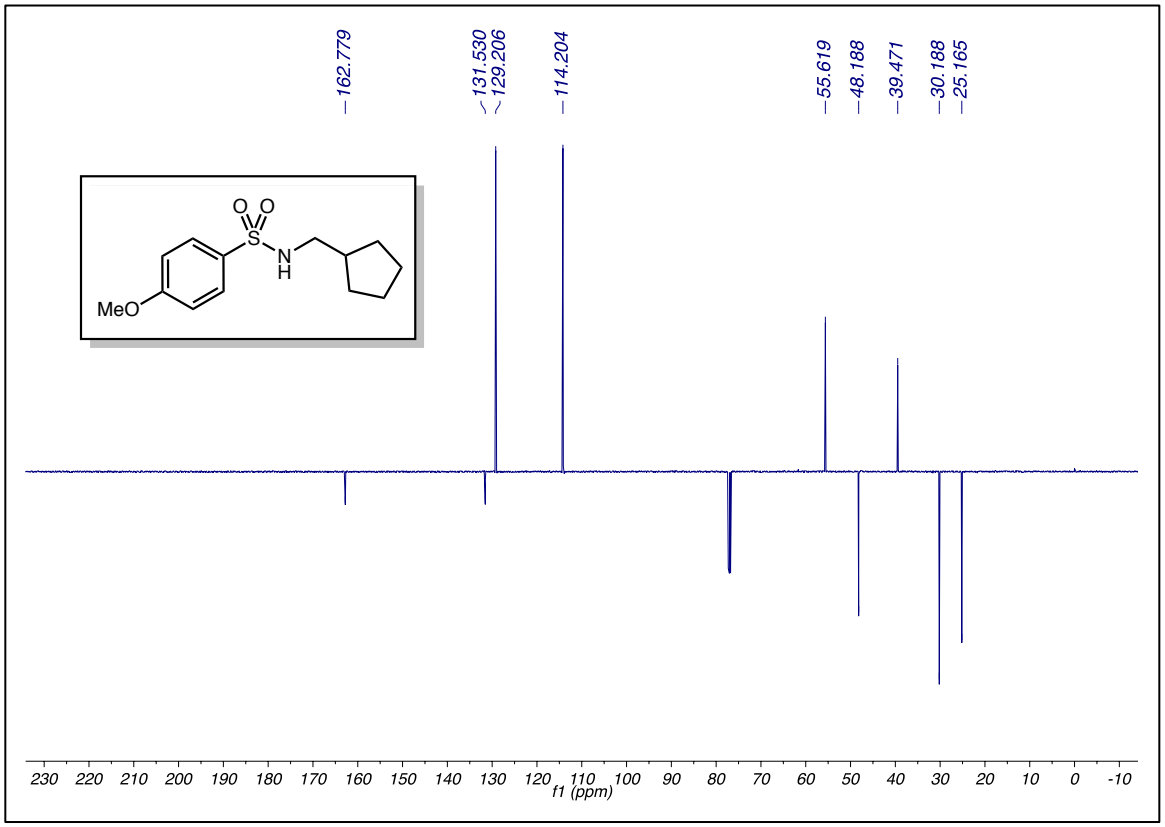

Me
Me
O
O
Me
N
S
N
Me
1.00
1.03
1.03
3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
f1 (ppm)
1.00
1.03
6.10
0.99
3.05
1.11
6.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

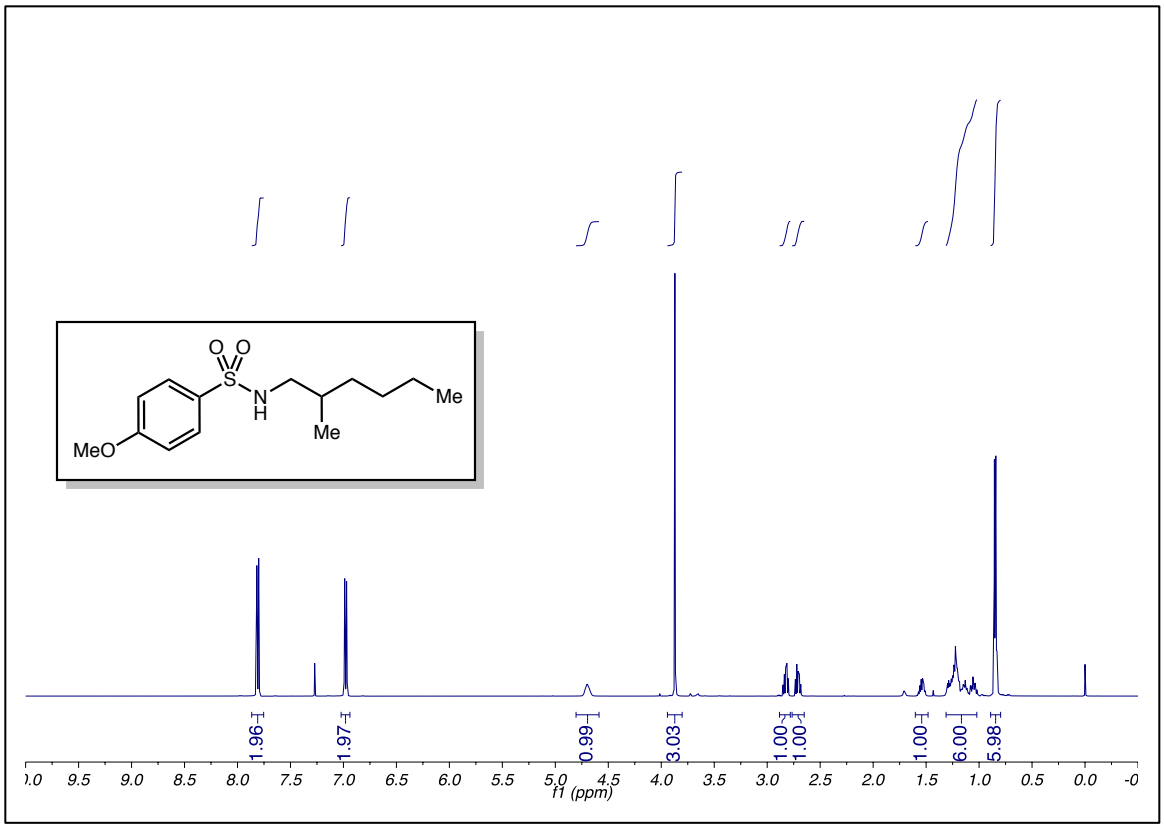

Me
Me
O
O
Me
N
S
N
Me
65.541
49.545
38.021
31.260
25.887
25.426
19.698
16.177
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

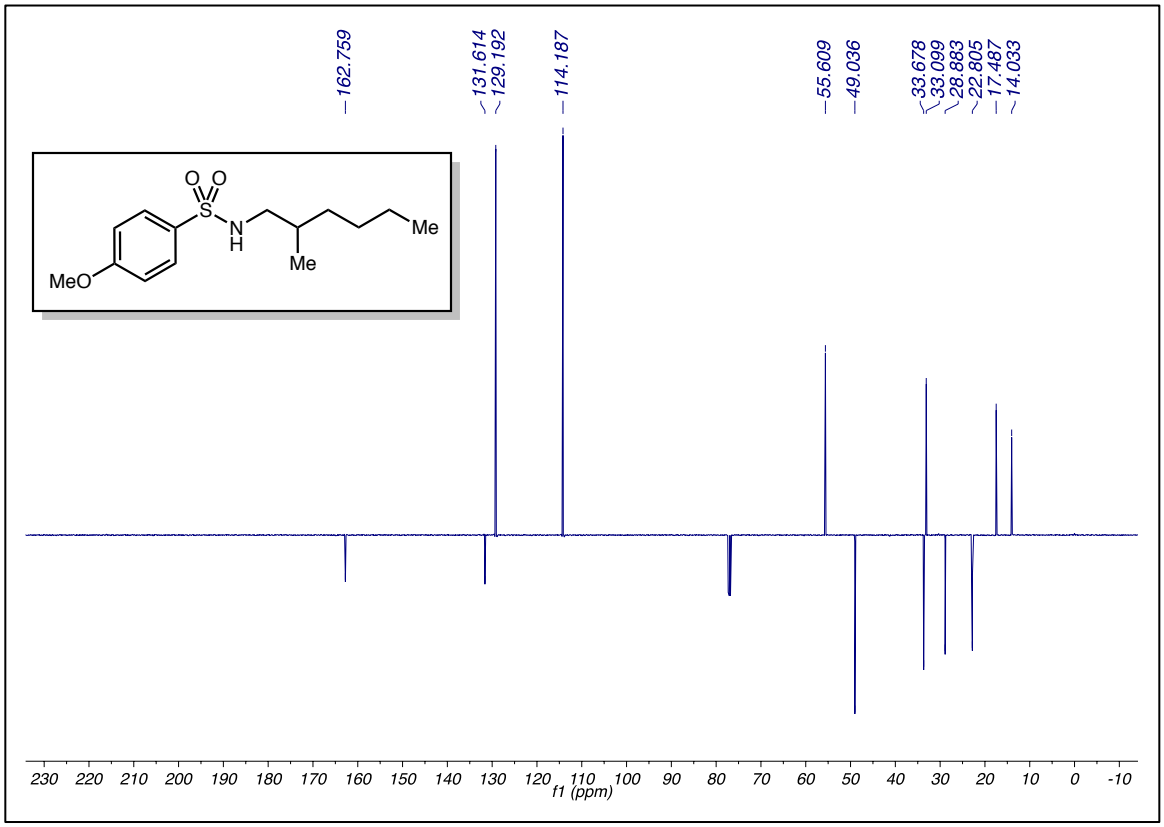

Me
O
O
Me
N
S
N
Me
0.97
0.99
1.02
6.03
0.99
1.97
1.13
3.08
f1 (ppm)

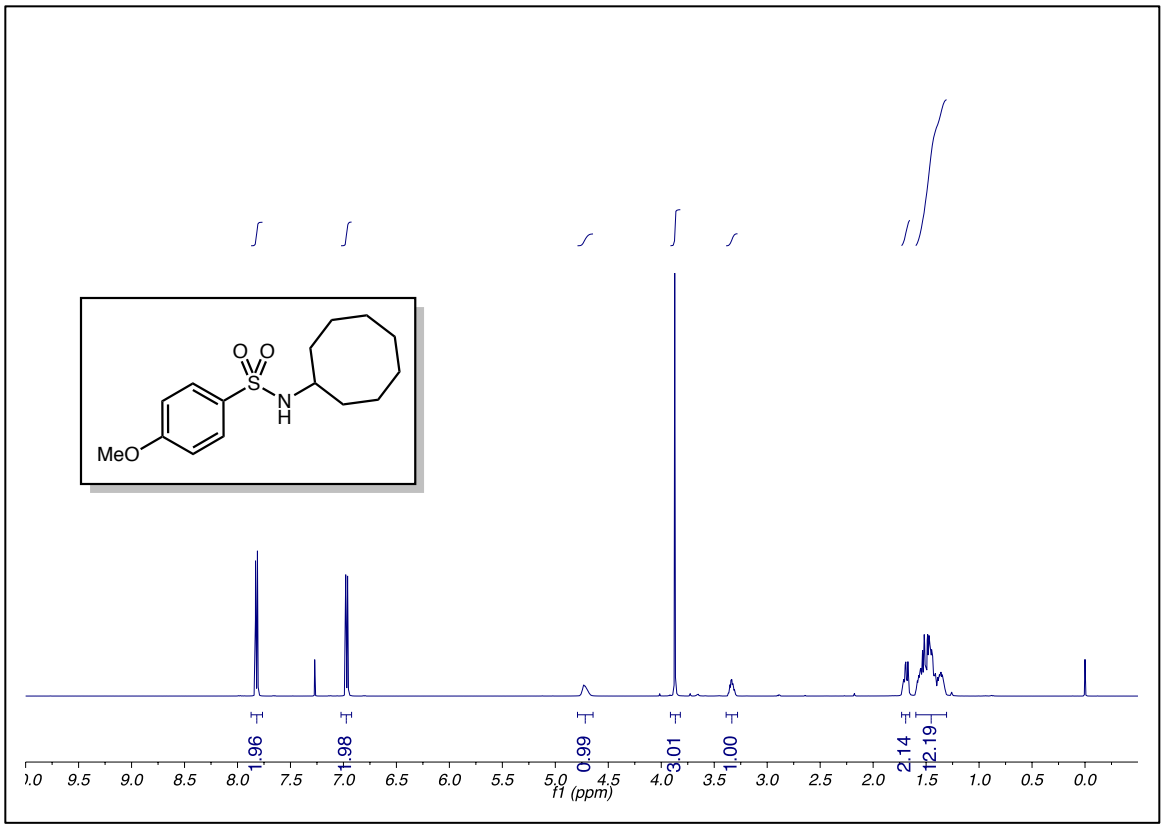

Me
O
O
Me
N
S
N
Me
56.2746
48.8257
37.9069
33.5990
24.4563
21.8696
f1 (ppm)

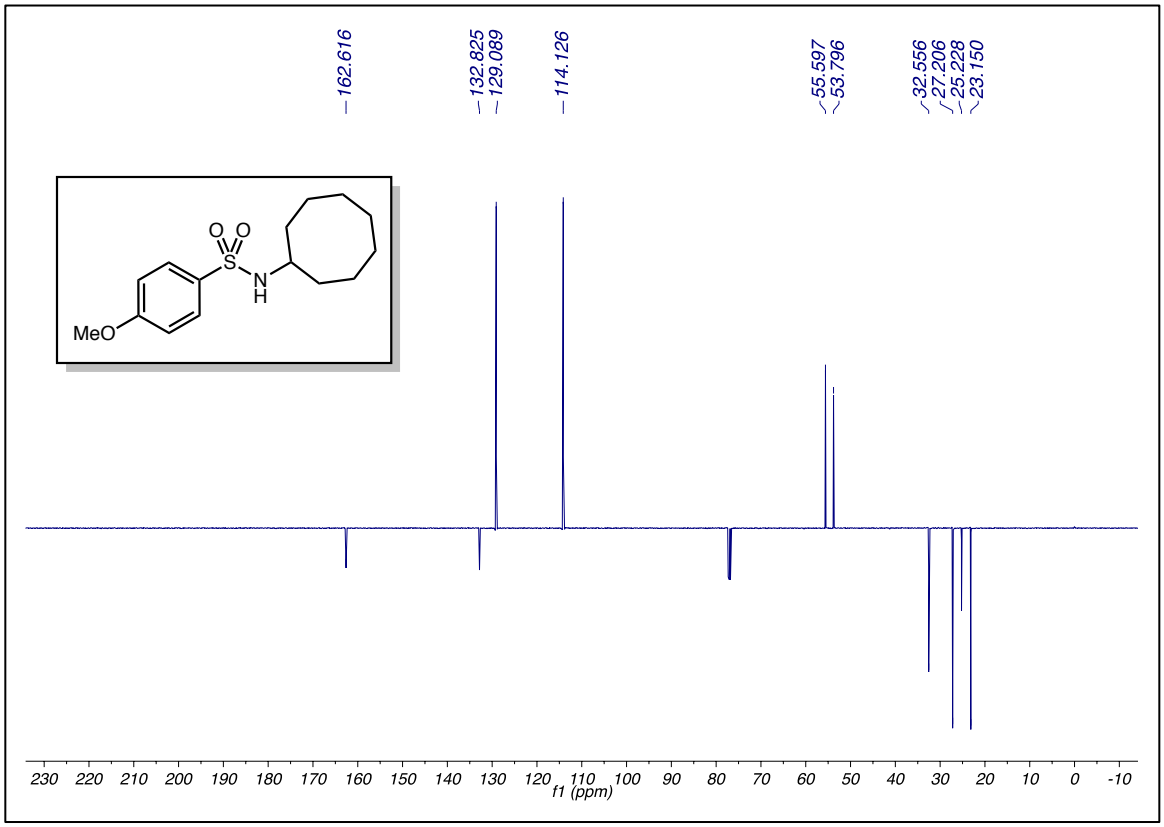

MeO
1.96
1.98
0.99
3.07
1.97
0.97
2.01
4.00
2.01
f1 (ppm)

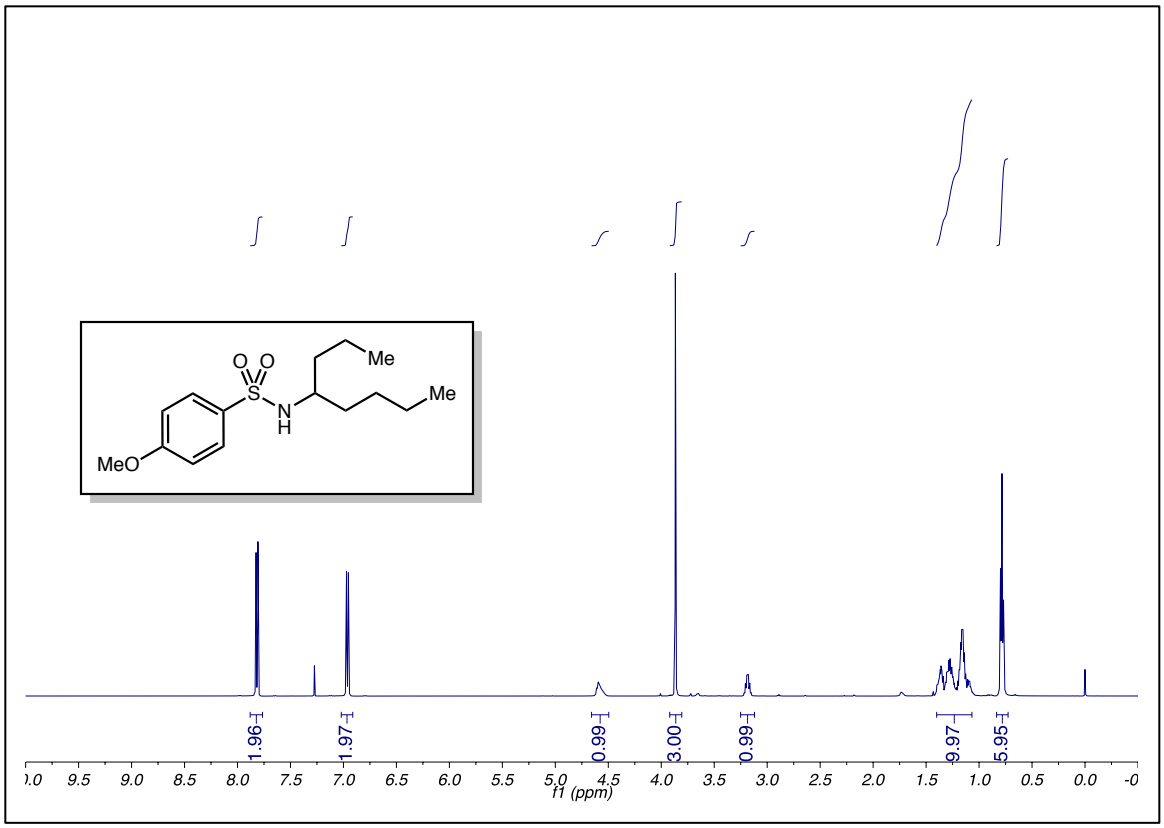

162.779
131.530
129.206
114.204
55.619
48.188
39.471
30.188
25.165
MeO
f1 (ppm)

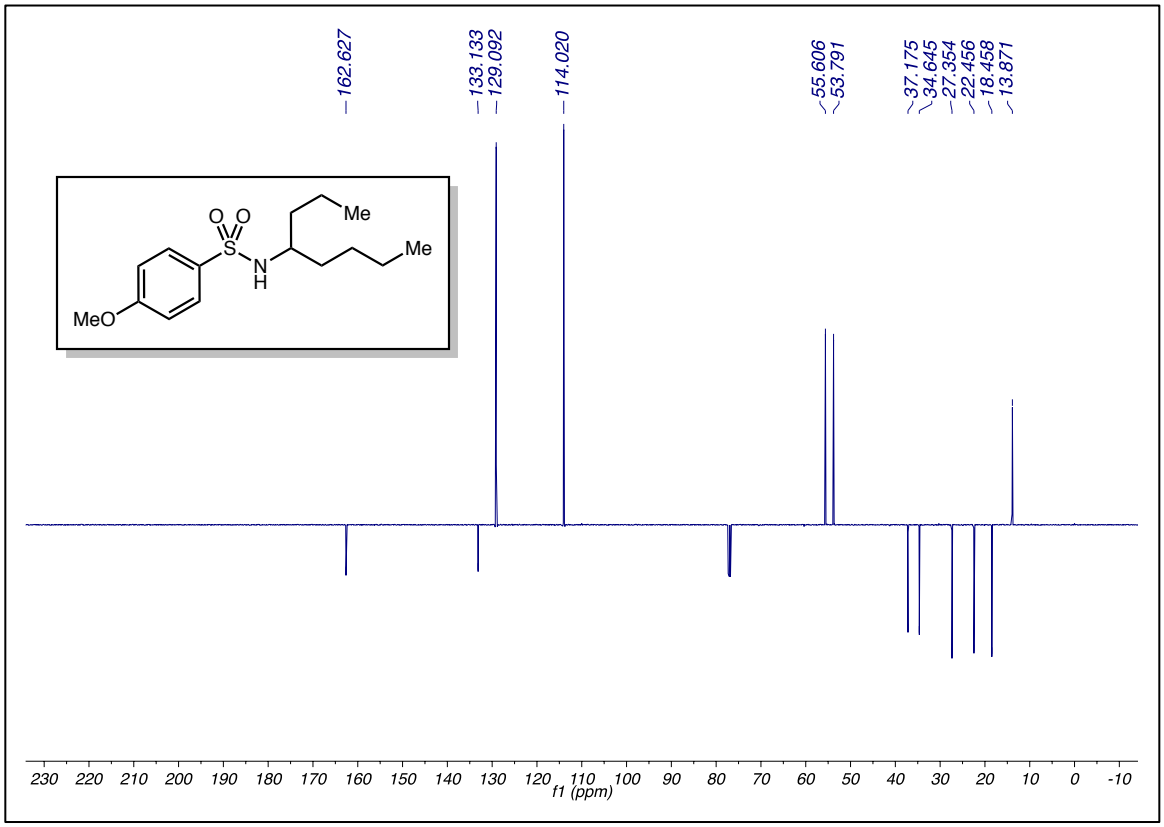

MeO
Me
Me
1.96
1.97
0.99
3.03
1.00
1.00
1.00
6.00
5.98
f1 (ppm)

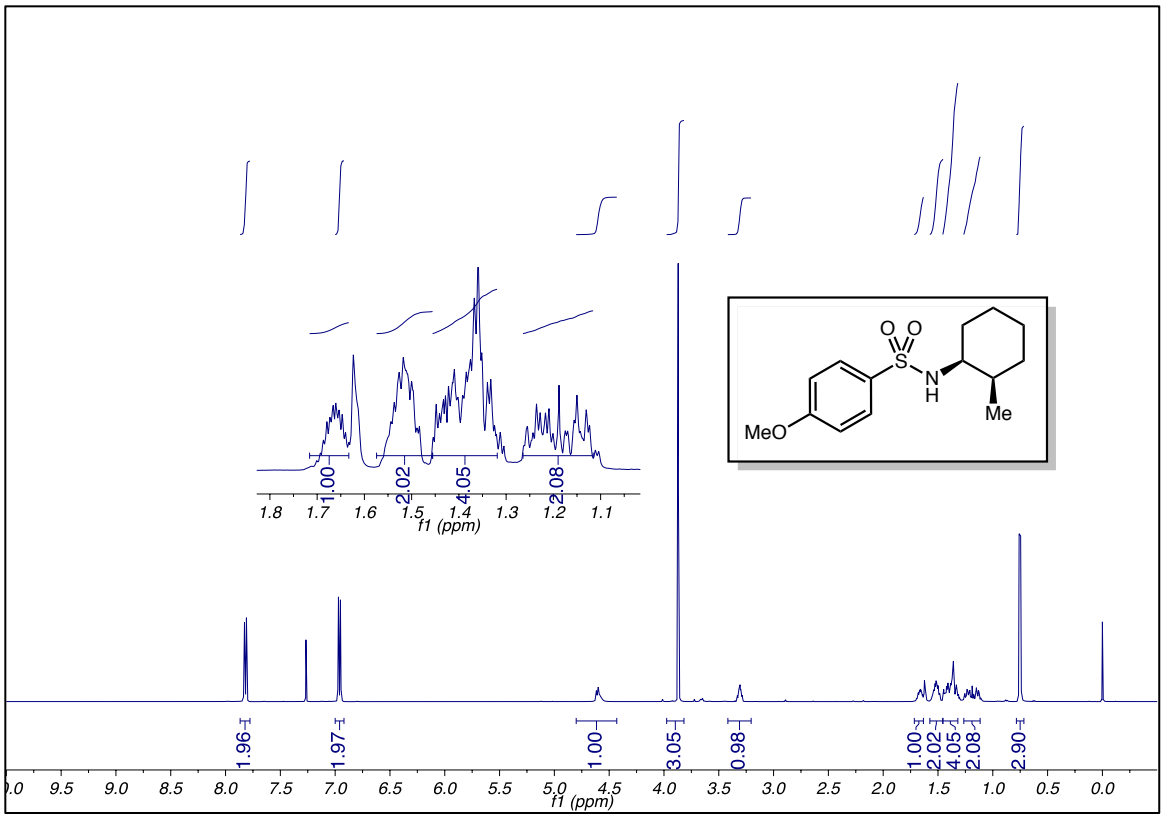

162.759
131.614
129.192
114.187
55.609
49.036
33.678
33.099
28.883
22.805
17.487
14.033
MeO
Me
Me
f1 (ppm)

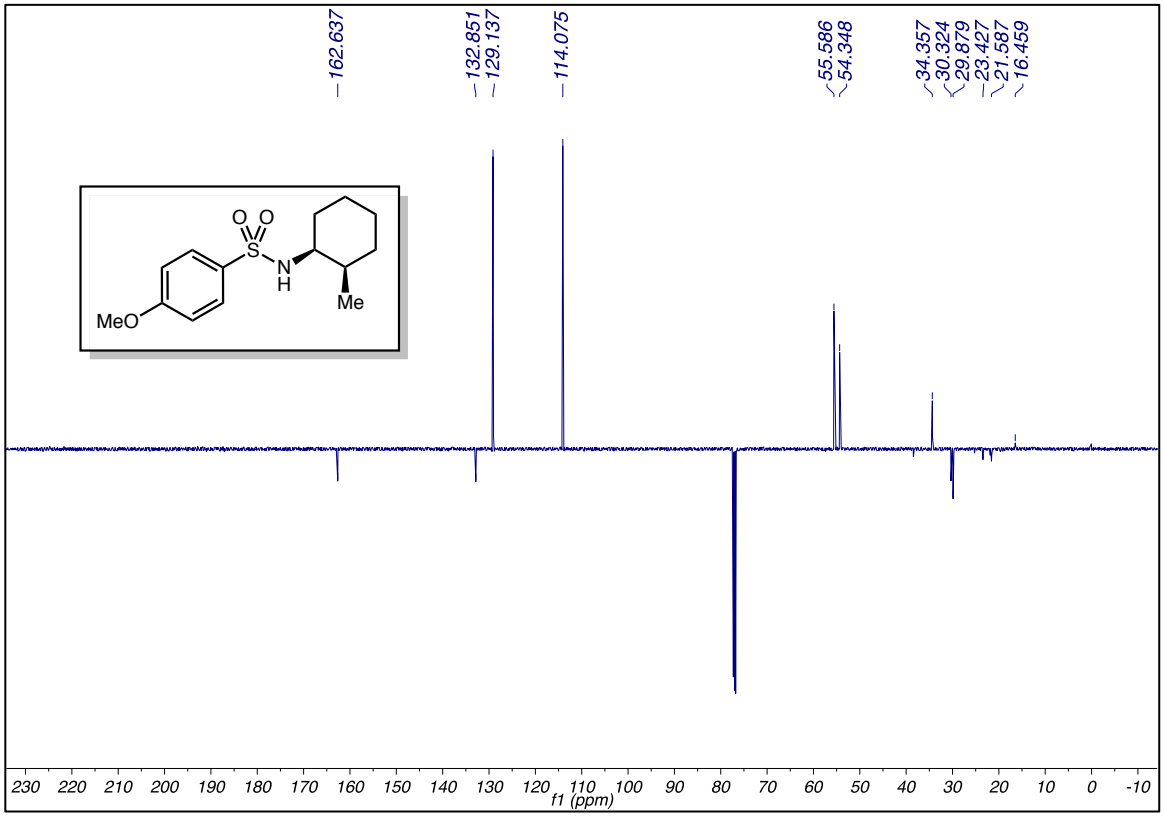

MeO
1.96
1.98
0.99
3.01
1.00
2.14
2.19
f1 (ppm)

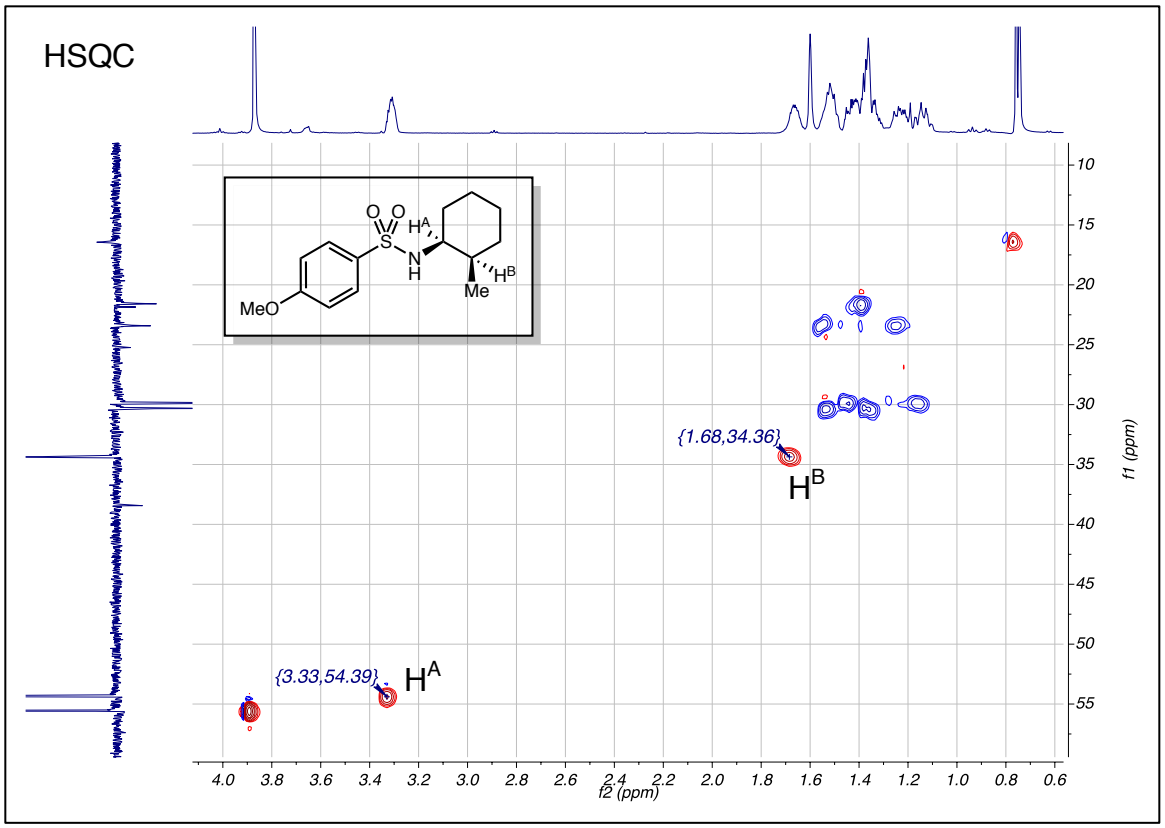

162.616
132.825
129.089
114.126
55.597
53.796
32.556
27.206
25.228
23.150
MeO
f1 (ppm)

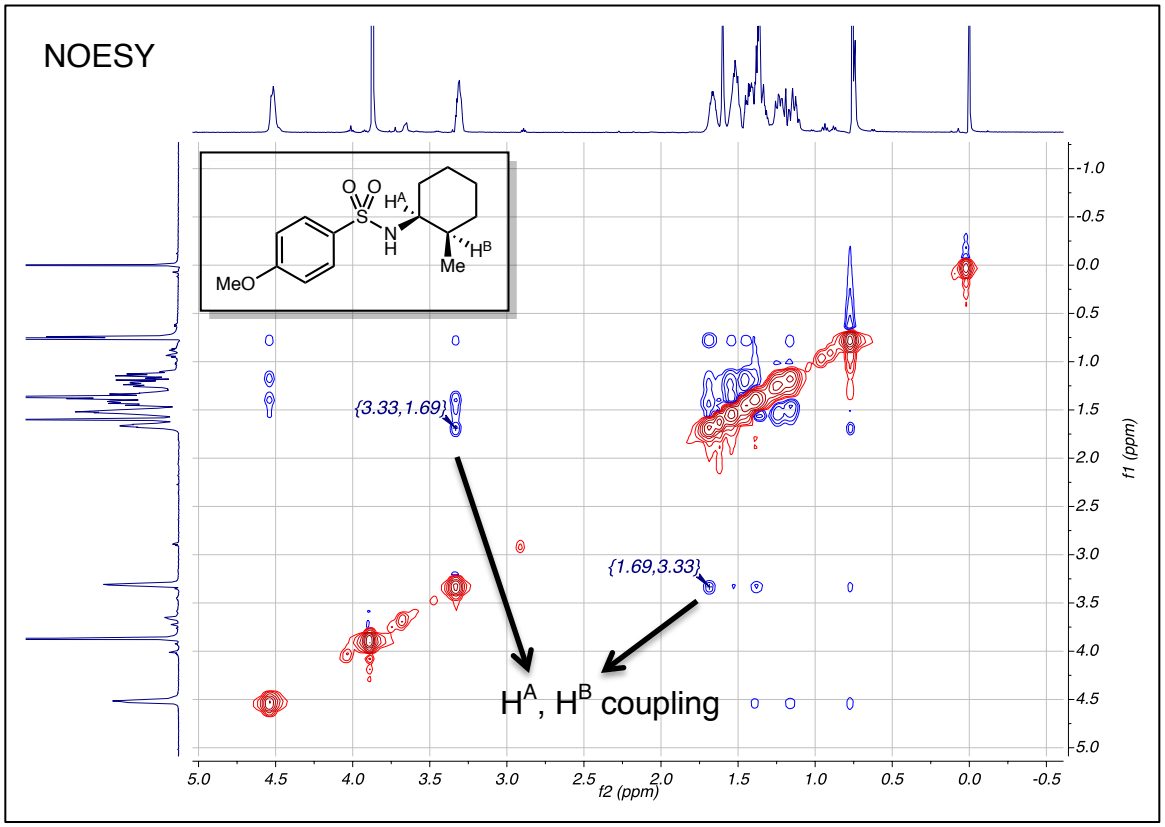

Me
Me
MeO
1.96
1.97
0.99
3.00
0.99
9.97
5.95
f1 (ppm)

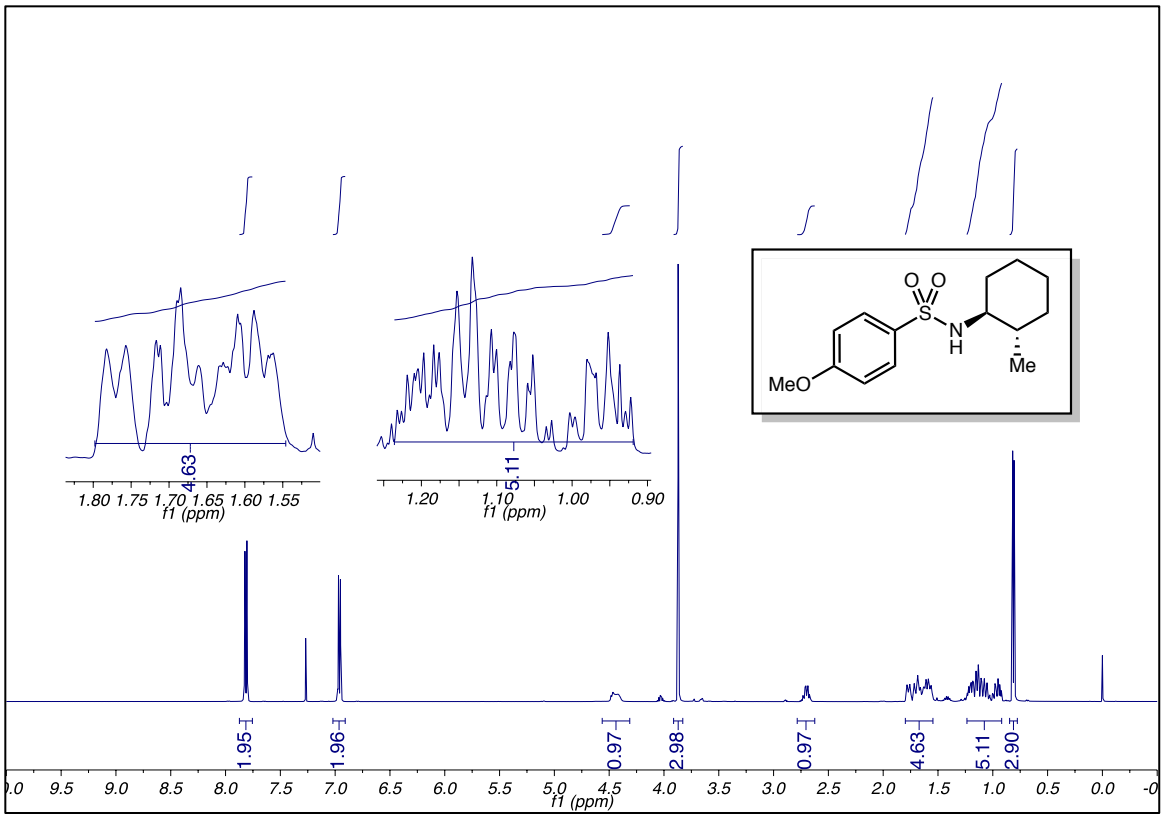

162.627
133.133
129.092
114.020
55.606
53.791
37.175
34.645
27.354
22.456
18.458
13.871
Me
Me
MeO
f1 (ppm)

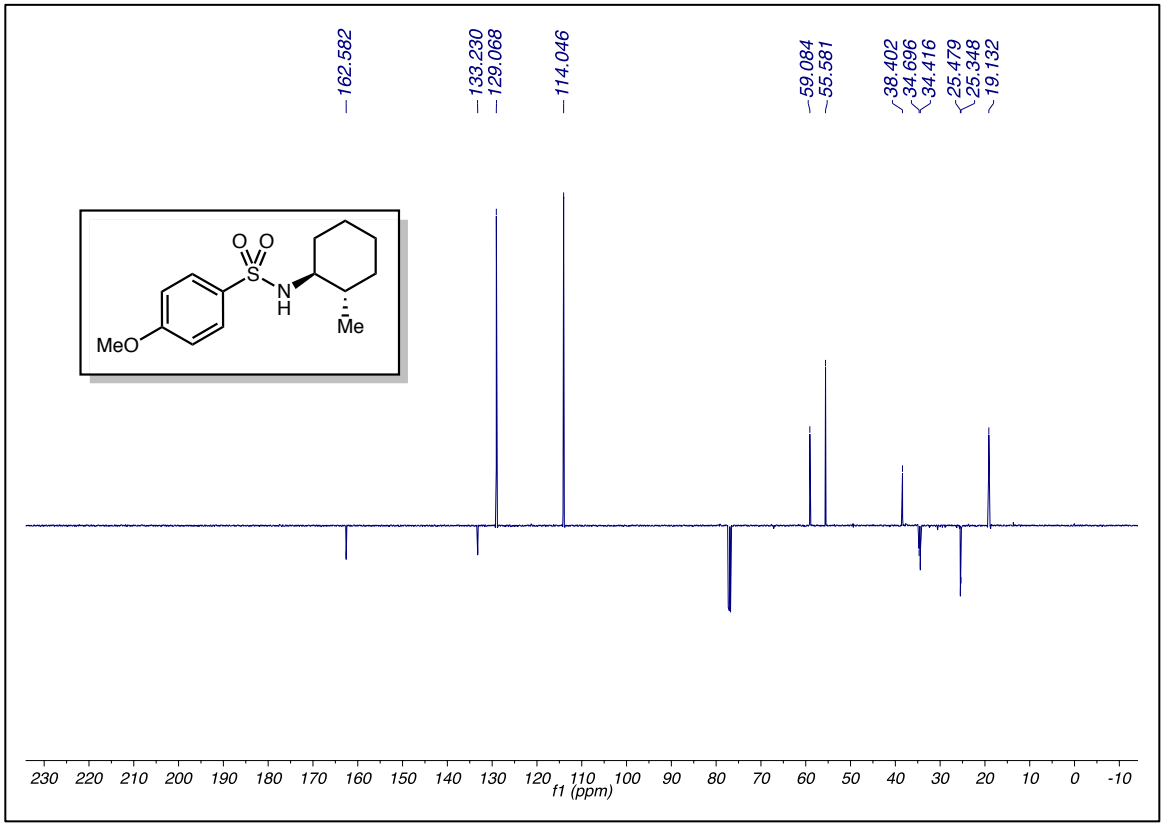

1.96
1.97
1.00
3.05
0.98
1.00
2.02
4.05
2.08
2.90
f1 (ppm)
MeO
Me

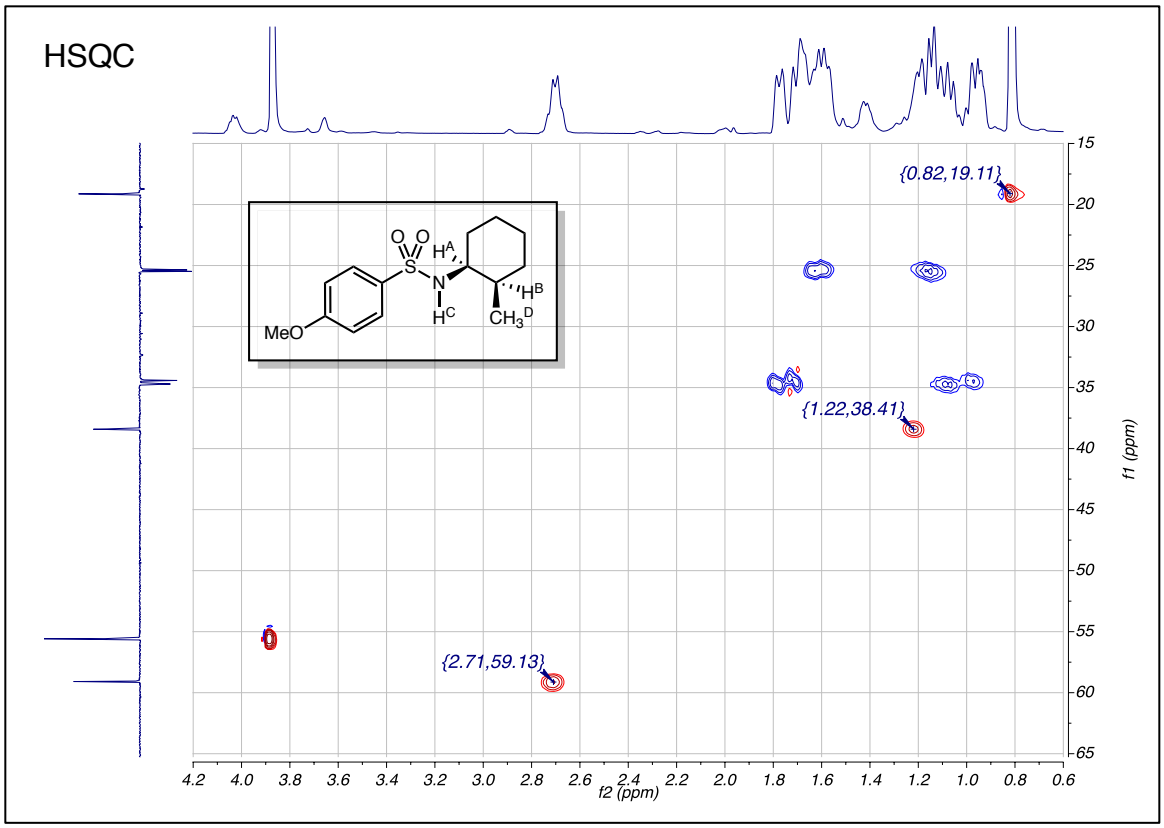

162.637
132.851
129.137
114.075
55.586
54.348
34.357
30.324
29.879
23.427
21.587
16.459
f1 (ppm)
MeO
Me

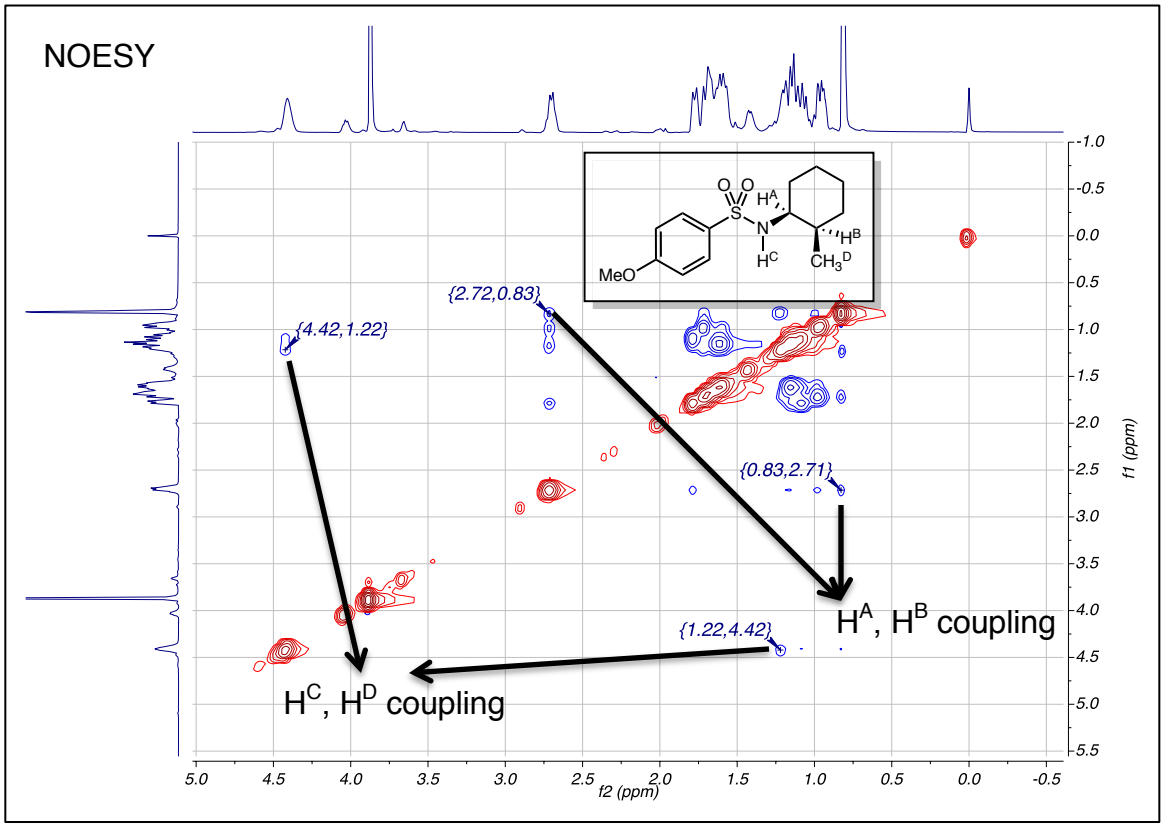

HSQC
MeO
Me
{1.68,34.36}
H^B
{3.33,54.39}
H^A
f2 (ppm)
f1 (ppm)

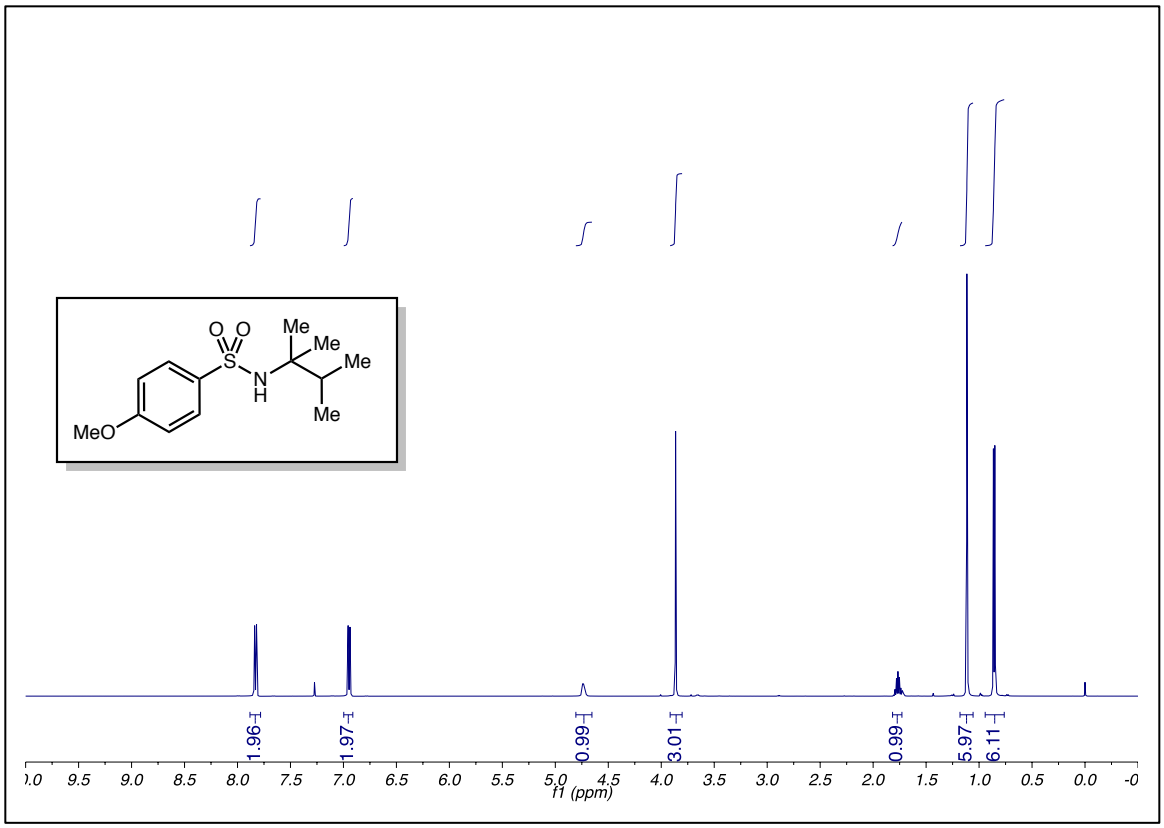

NOESY
MeO
Me
{3.33,1.69}
{1.69,3.33}
H^A, H^B coupling
f2 (ppm)
f1 (ppm)

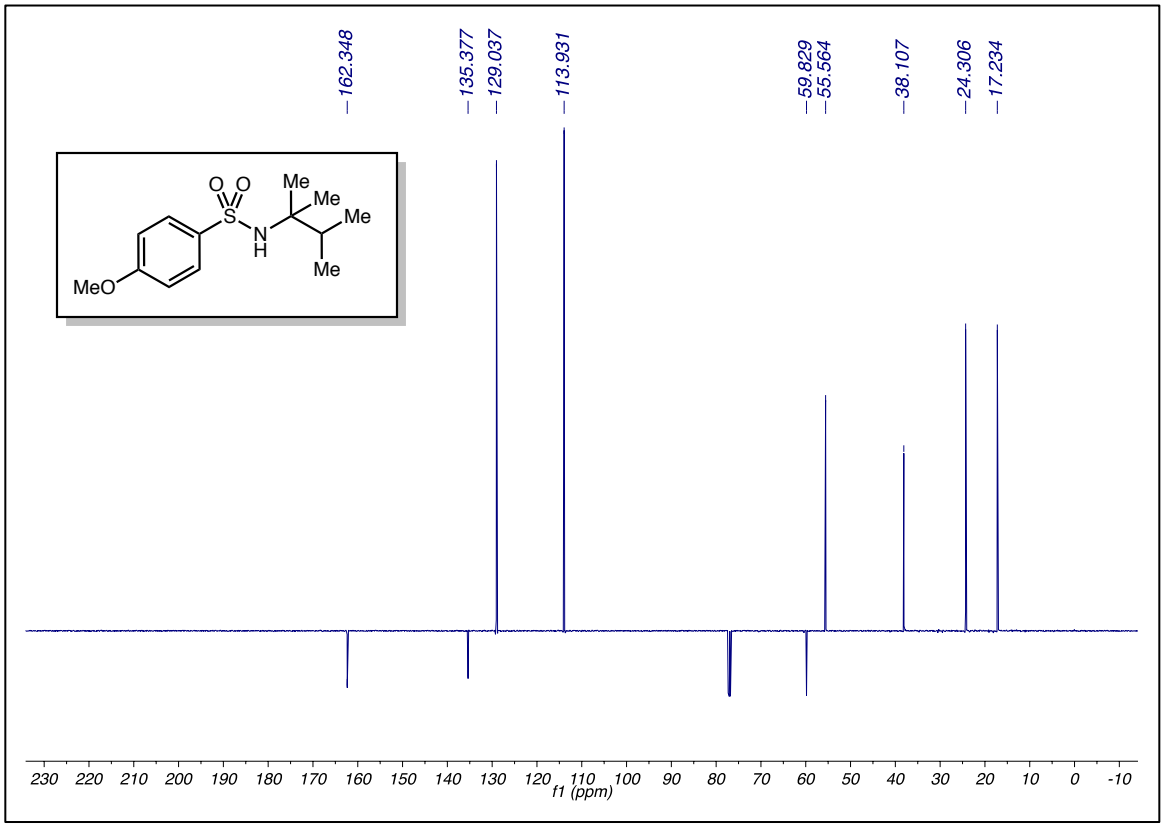

4.63
1.80 1.75 1.70 1.65 1.60 1.55
f1 (ppm)
5.11
1.20 1.10 1.00 0.90
f1 (ppm)
O O
S
N
H
Me
MeO
1.95
1.96
0.97
2.98
0.97
4.63
5.11
2.90
f1 (ppm)

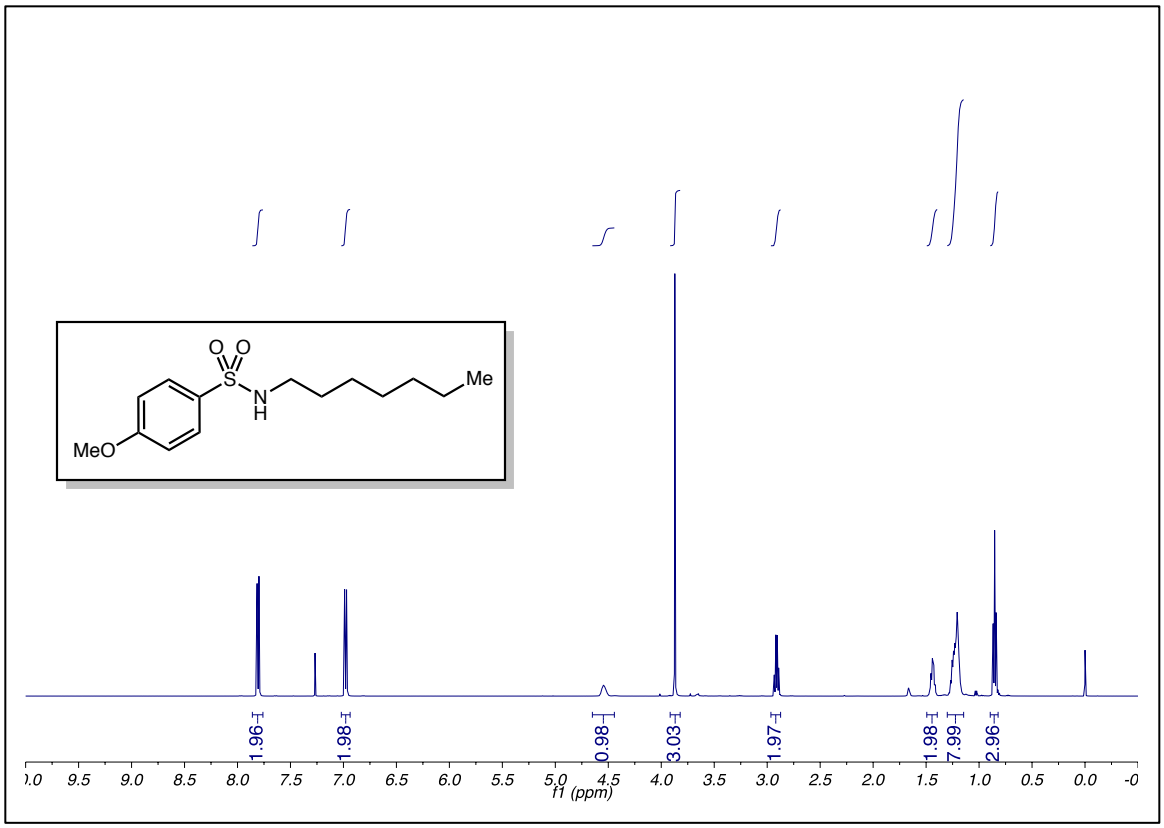

162.582
133.230
129.068
114.046
59.084
55.581
38.402
34.696
34.416
25.479
25.348
19.132
O O
S
N
H
Me
MeO
f1 (ppm)

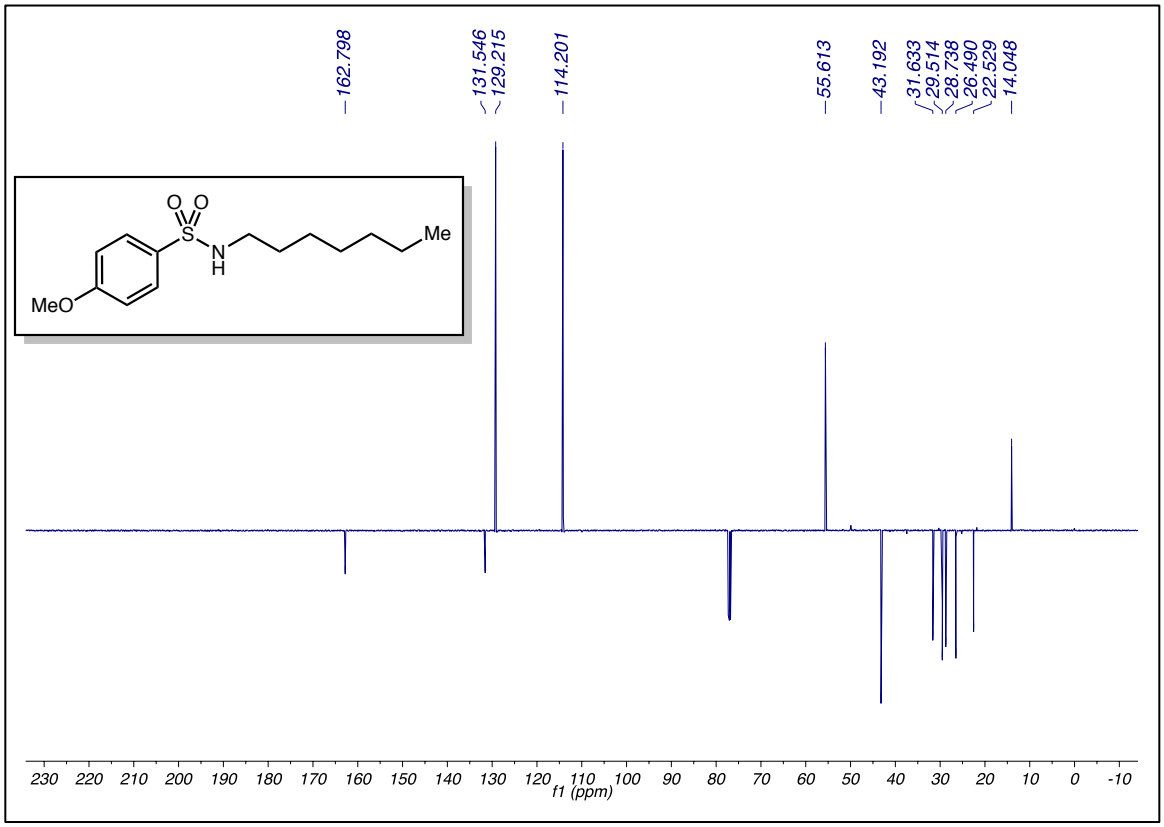

HSQC
{0.82,19.11}
{1.22,38.41}
{2.71,59.13}
MeO
f2 (ppm)
f1 (ppm)

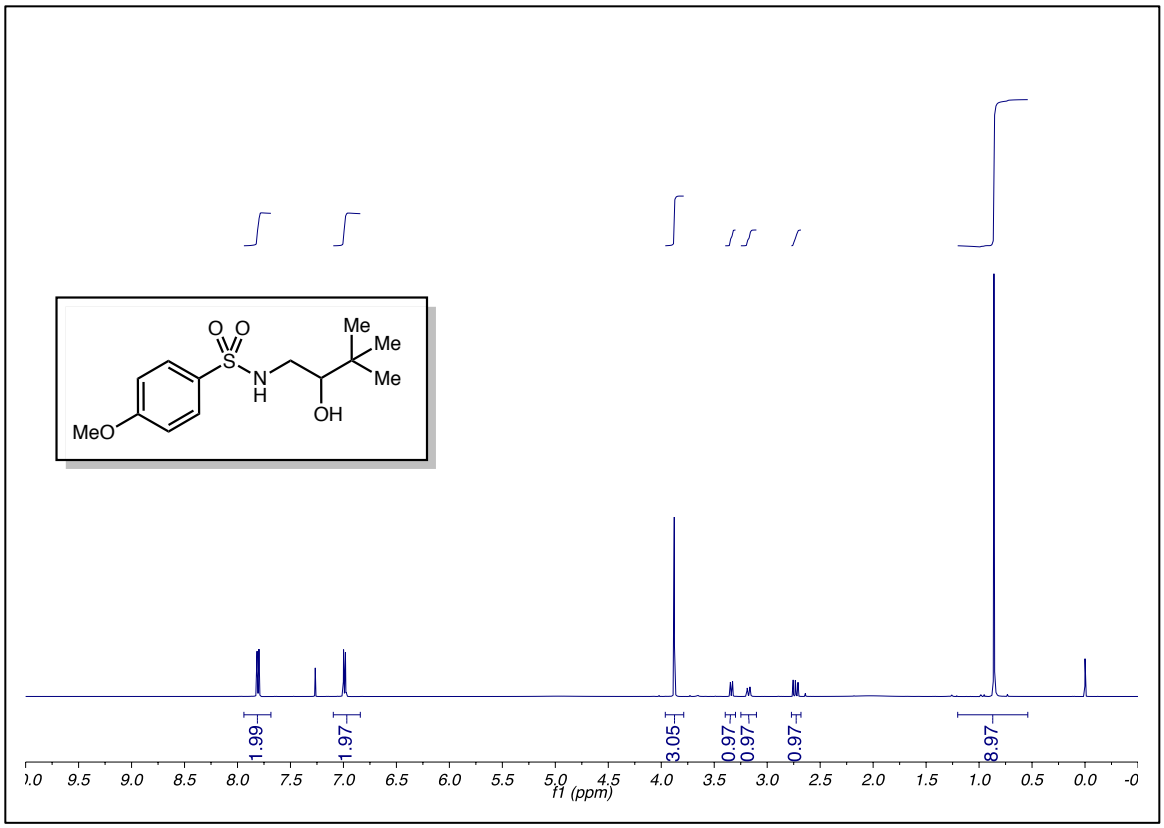

NOESY
{2.72,0.83}
{4.42,1.22}
{0.83,2.71}
{1.22,4.42}
H^A, H^B coupling
H^C, H^D coupling
MeO
f2 (ppm)
f1 (ppm)

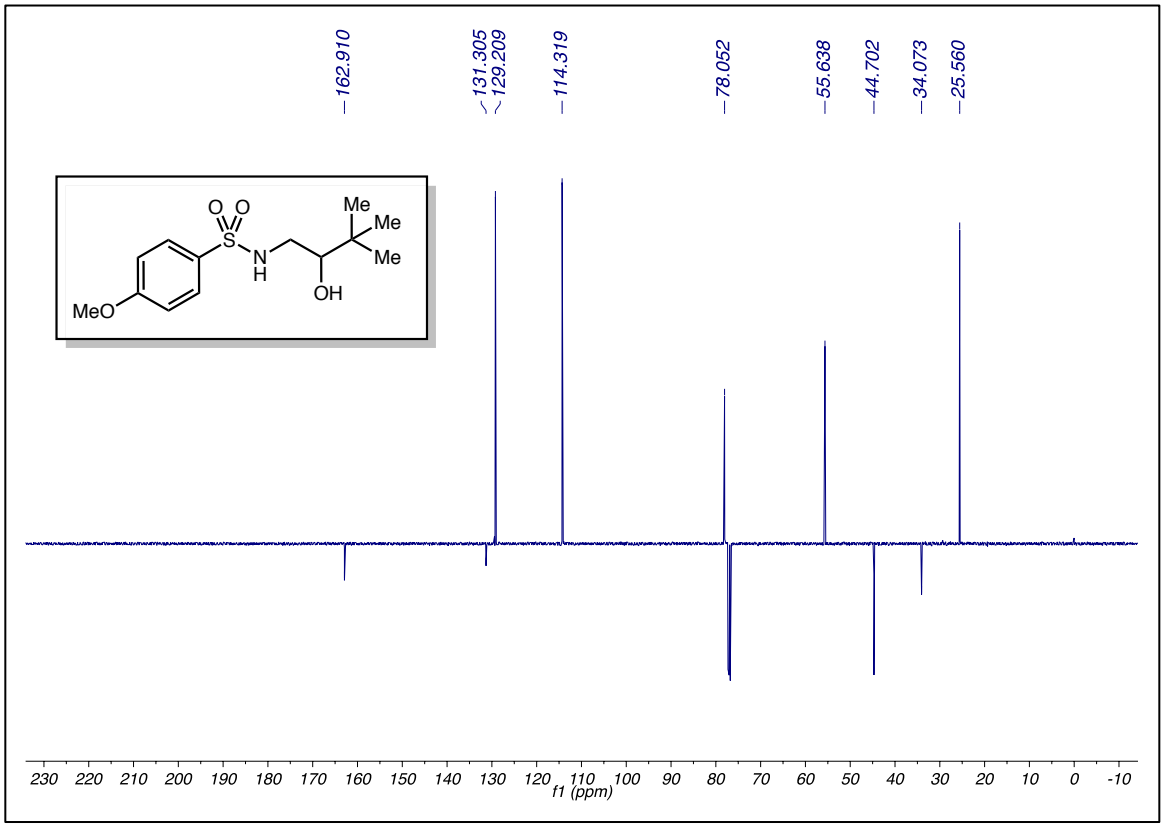

MeO
Me
Me
Me
Me
1.96
1.97
0.99
3.01
0.99
5.97
6.11
f1 (ppm)

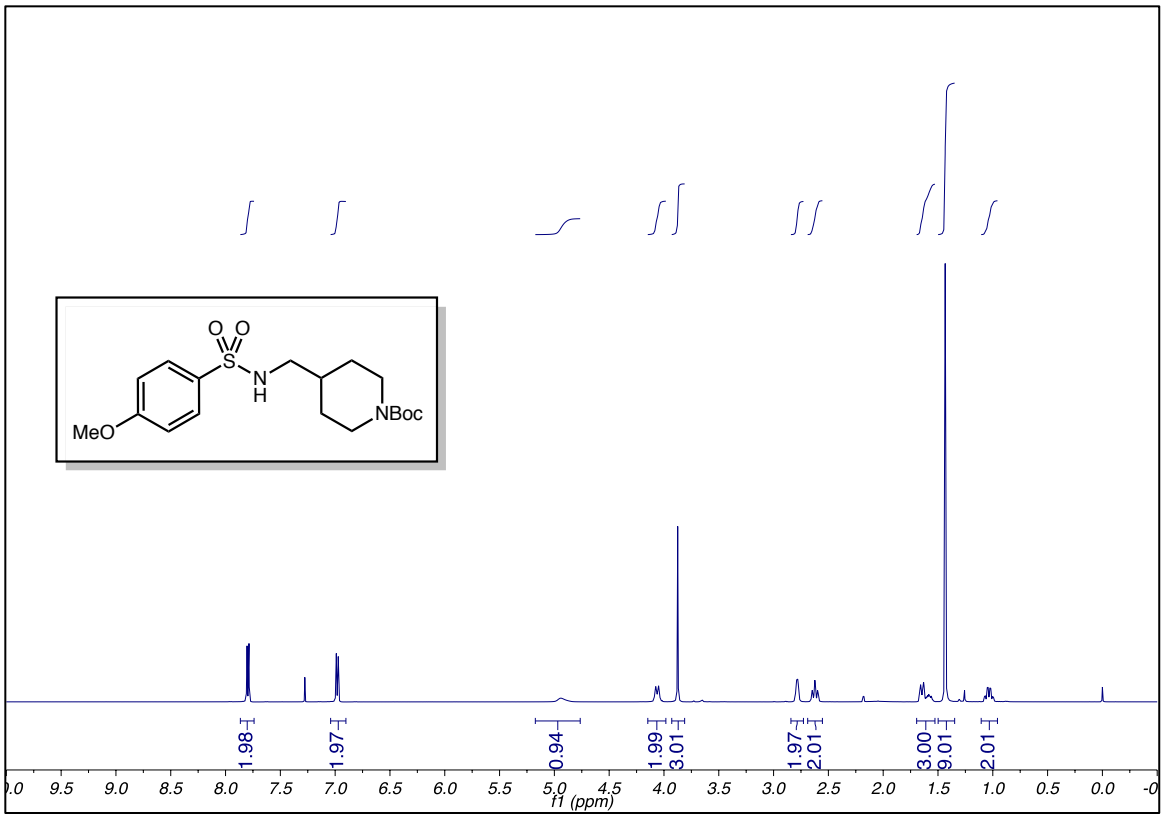

162.348
135.377
129.037
113.931
59.829
55.564
38.107
24.306
17.234
MeO
Me
Me
Me
Me
f1 (ppm)

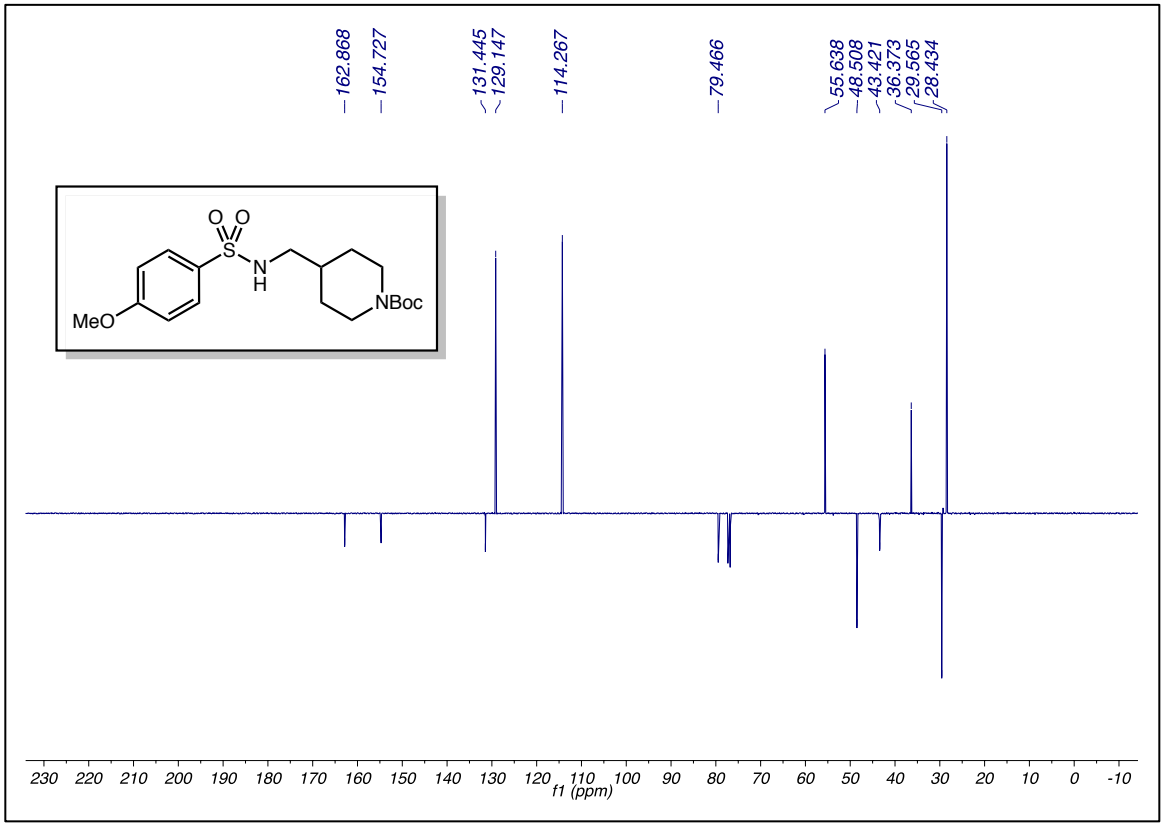

O
O
S
N
H
Me
MeO
1.96
1.98
0.98
3.03
1.97
1.98
7.99
2.96
f1 (ppm)

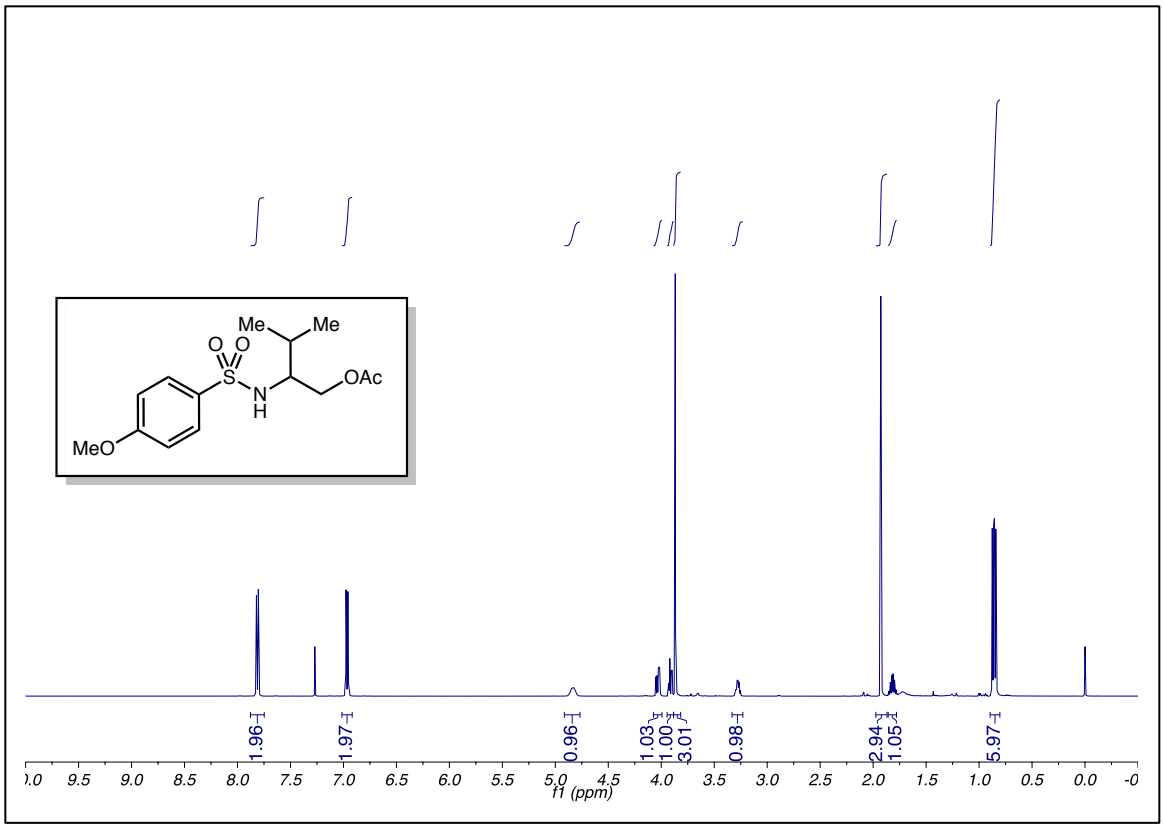

162.798
131.546
129.215
114.201
55.613
43.192
31.633
29.514
28.738
26.490
22.529
14.048
O
O
S
N
H
Me
MeO
f1 (ppm)

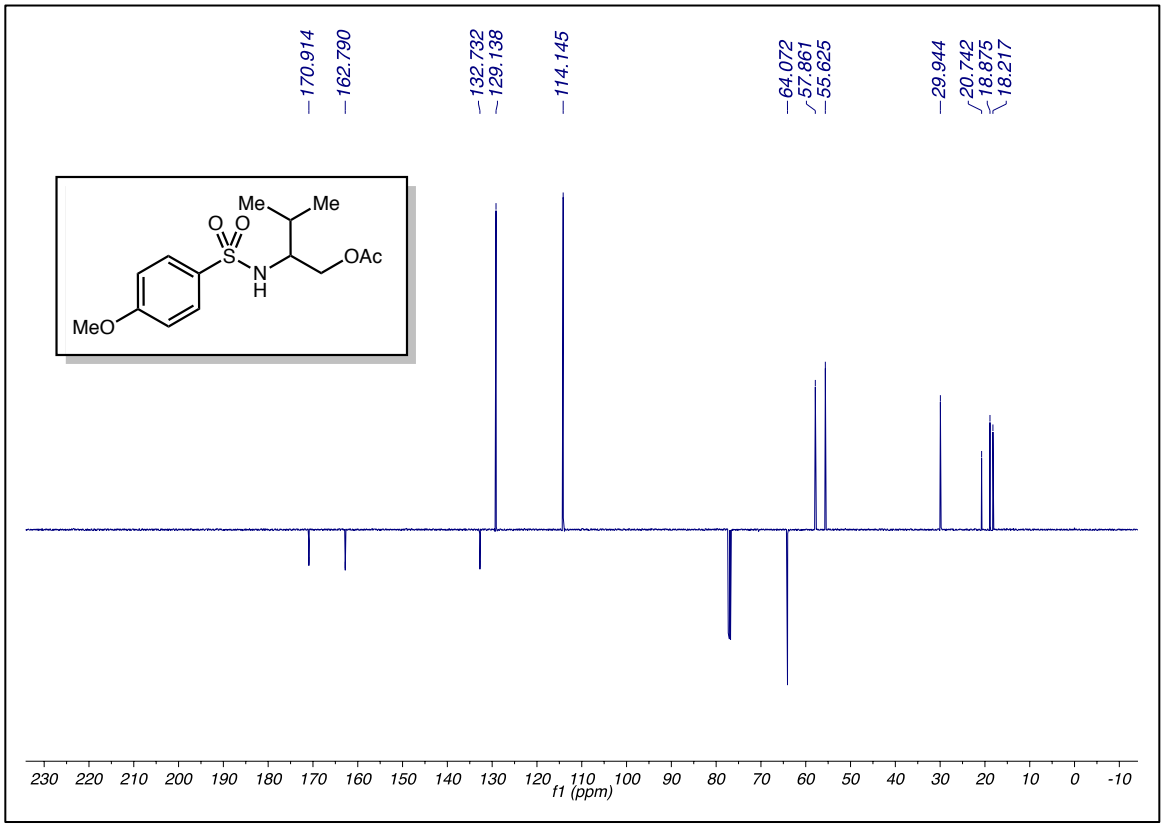

O
O
S
N
H
Me
Me
Me
OH
MeO
1.99
1.97
3.05
0.97
0.97
0.97
8.97
f1 (ppm)

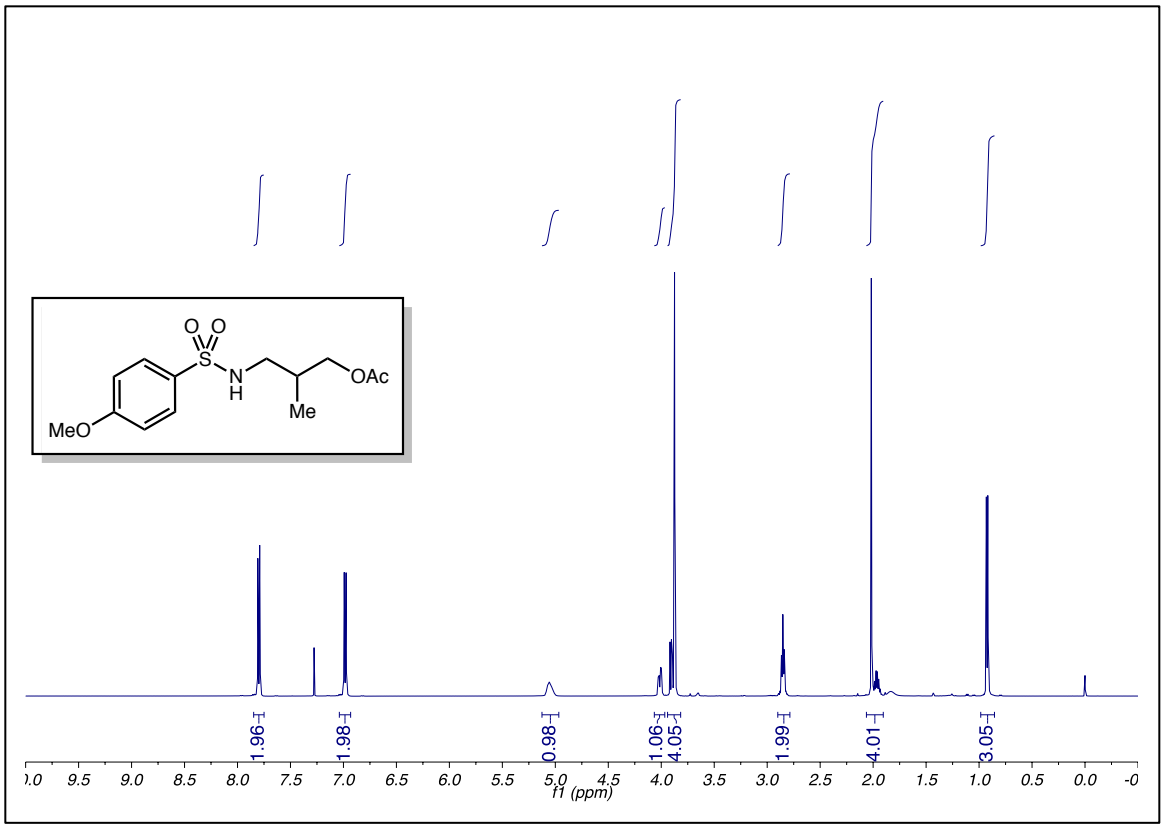

162.910
131.305
129.209
114.319
78.052
55.638
44.702
34.073
25.560
O
O
S
N
H
Me
Me
Me
OH
MeO
f1 (ppm)

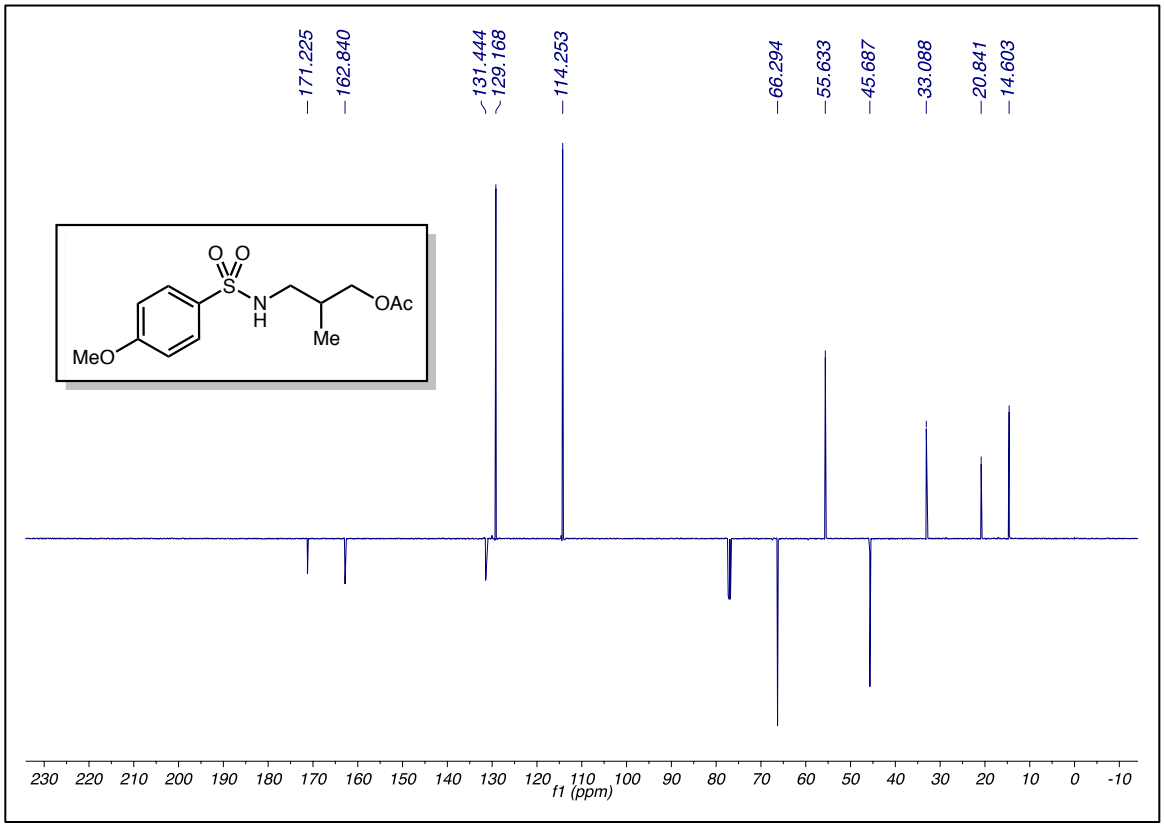

MeO
NBoc
1.98
1.97
0.94
1.99
3.01
1.97
2.01
3.00
9.01
2.01
f1 (ppm)

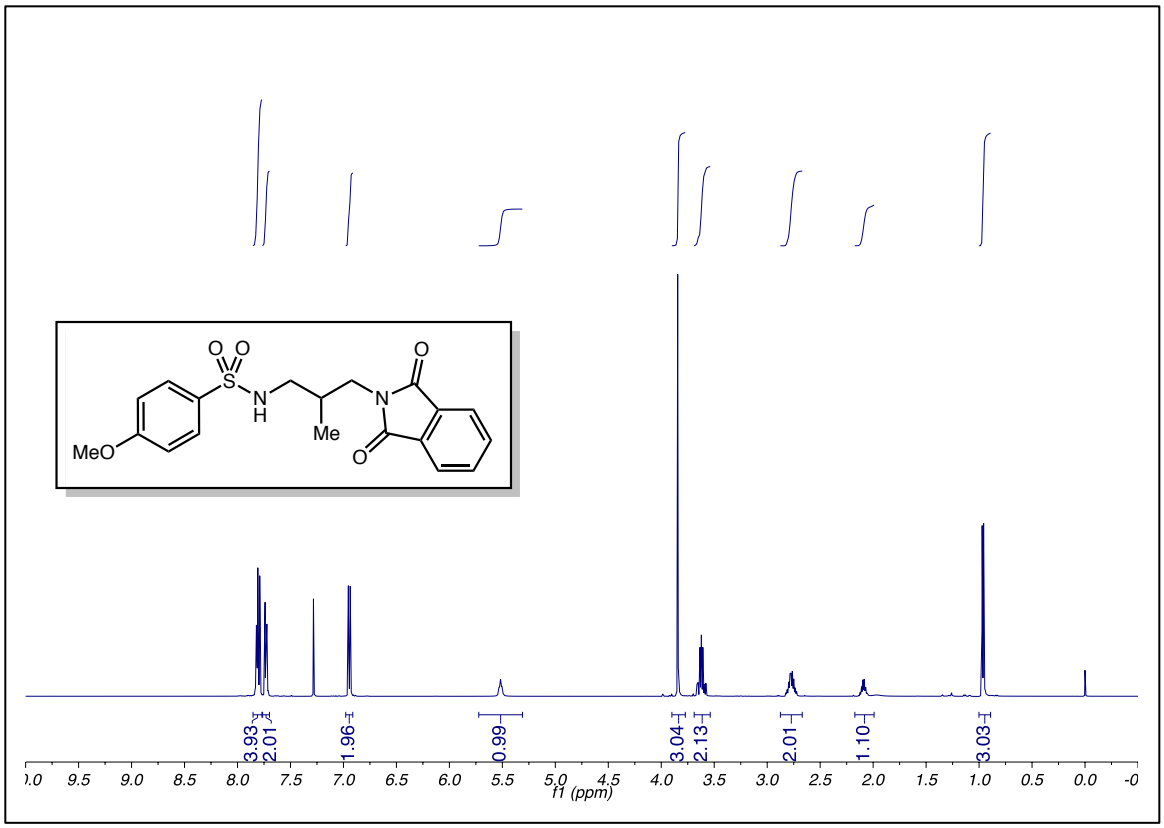

162.868
154.727
131.445
129.147
114.267
79.466
55.638
48.508
43.421
36.373
29.565
28.434
MeO
NBoc
f1 (ppm)

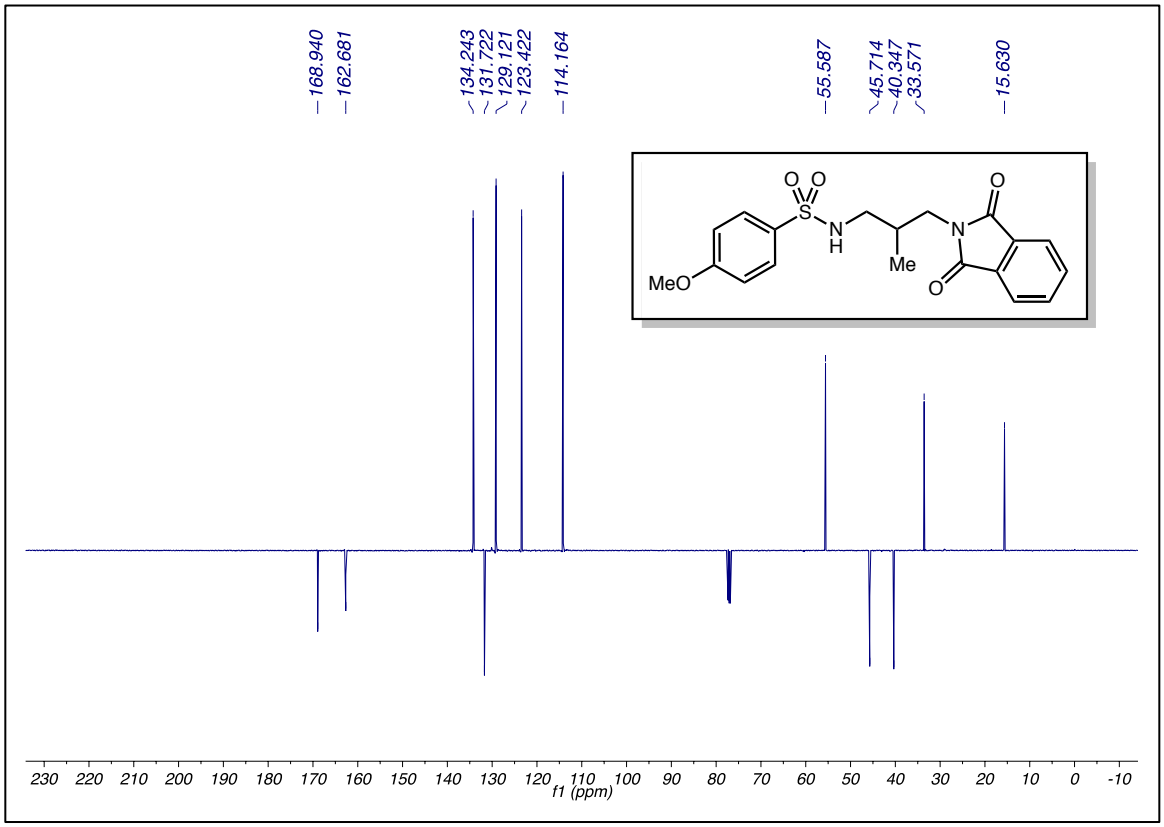

Me
Me
O
O
S
N
H
OAc
MeO
1.96
1.97
0.96
1.03
1.00
3.01
0.98
2.94
1.05
5.97
f1 (ppm)

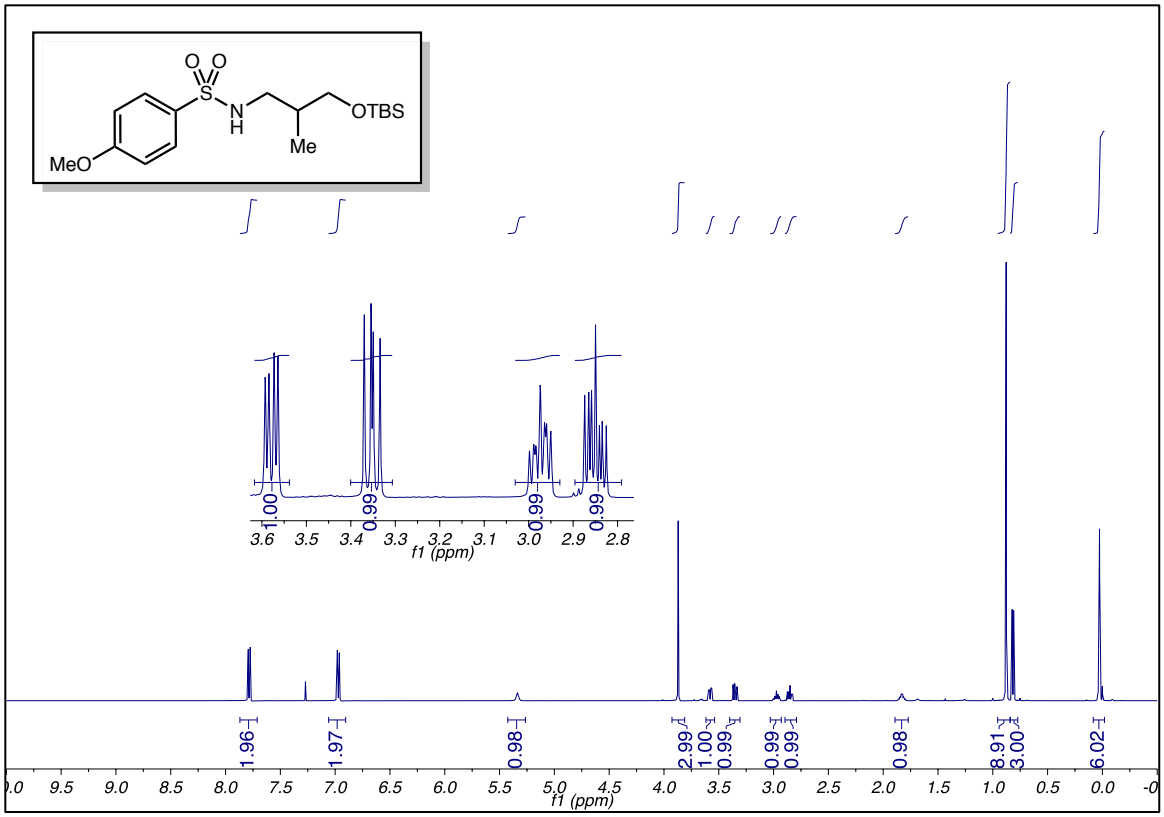

170.914
162.790
132.732
129.138
114.145
64.072
57.861
55.625
29.944
20.742
18.875
18.217
Me
Me
O
O
S
N
H
OAc
MeO
f1 (ppm)

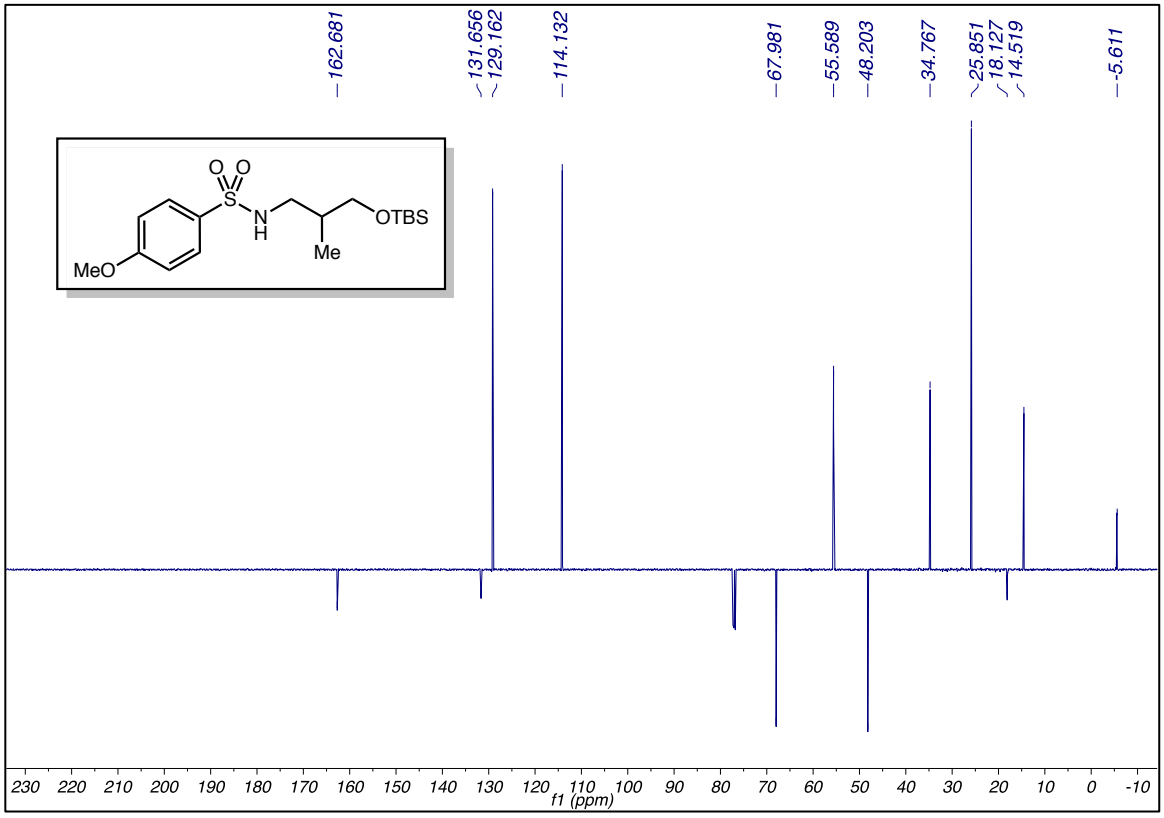

O
O
S
N
H
OAc
Me
MeO
1.96
1.98
0.98
1.06
4.05
1.99
4.01
3.05
f1 (ppm)

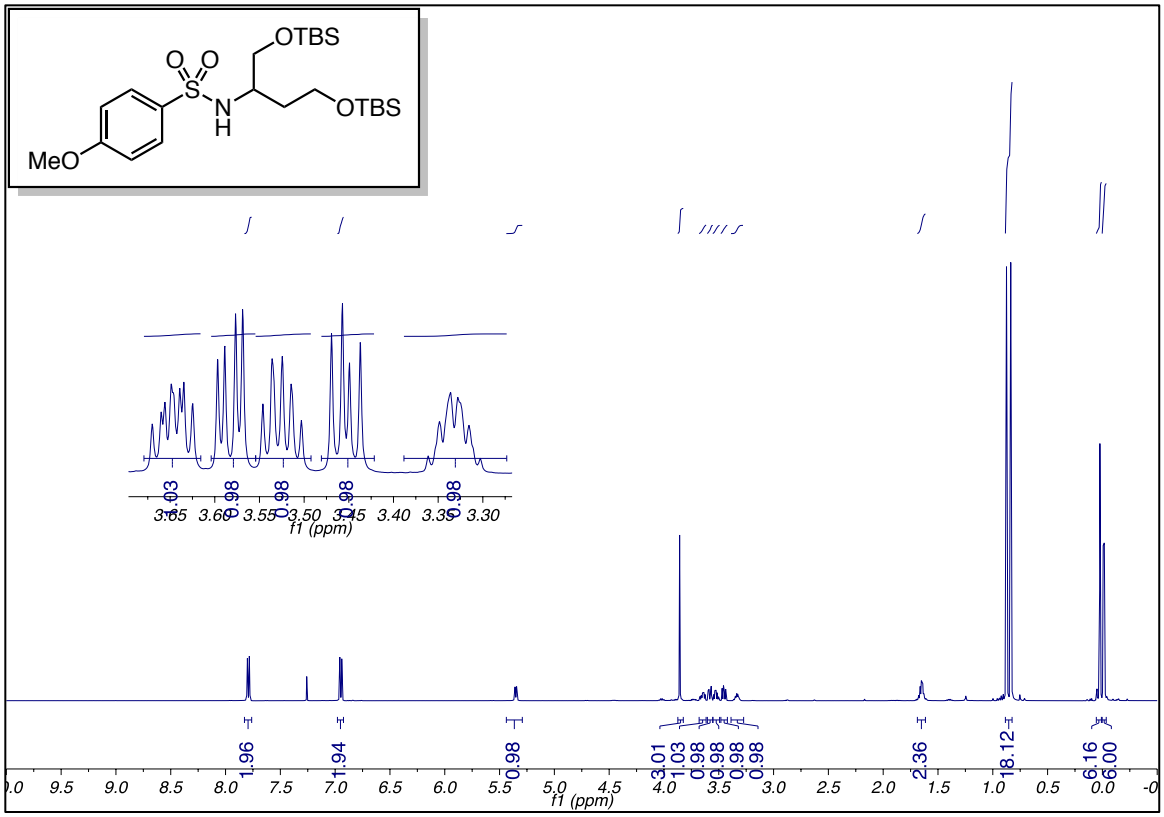

171.225
162.840
131.444
129.168
114.253
66.294
55.633
45.687
33.088
20.841
14.603
O
O
S
N
H
OAc
Me
MeO
f1 (ppm)

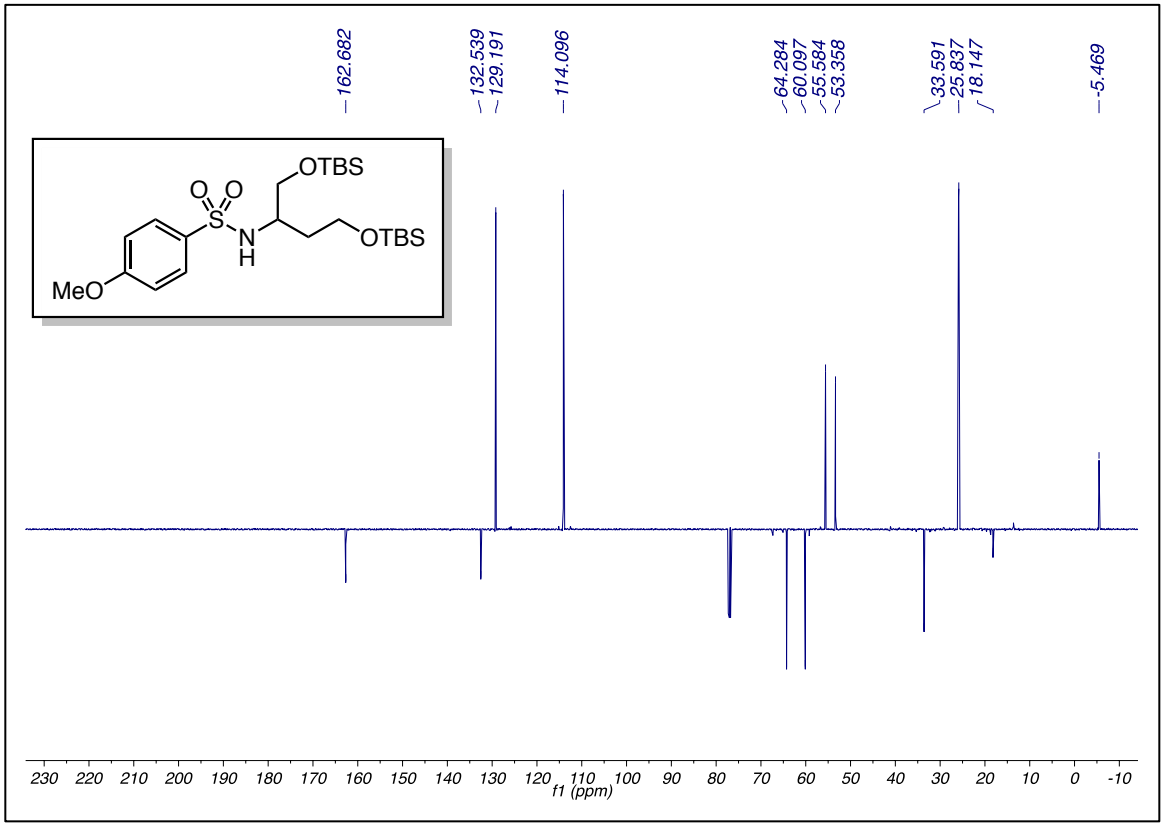

MeO
Me
3.93
2.01
1.96
0.99
3.04
2.13
2.01
1.10
3.03
f1 (ppm)

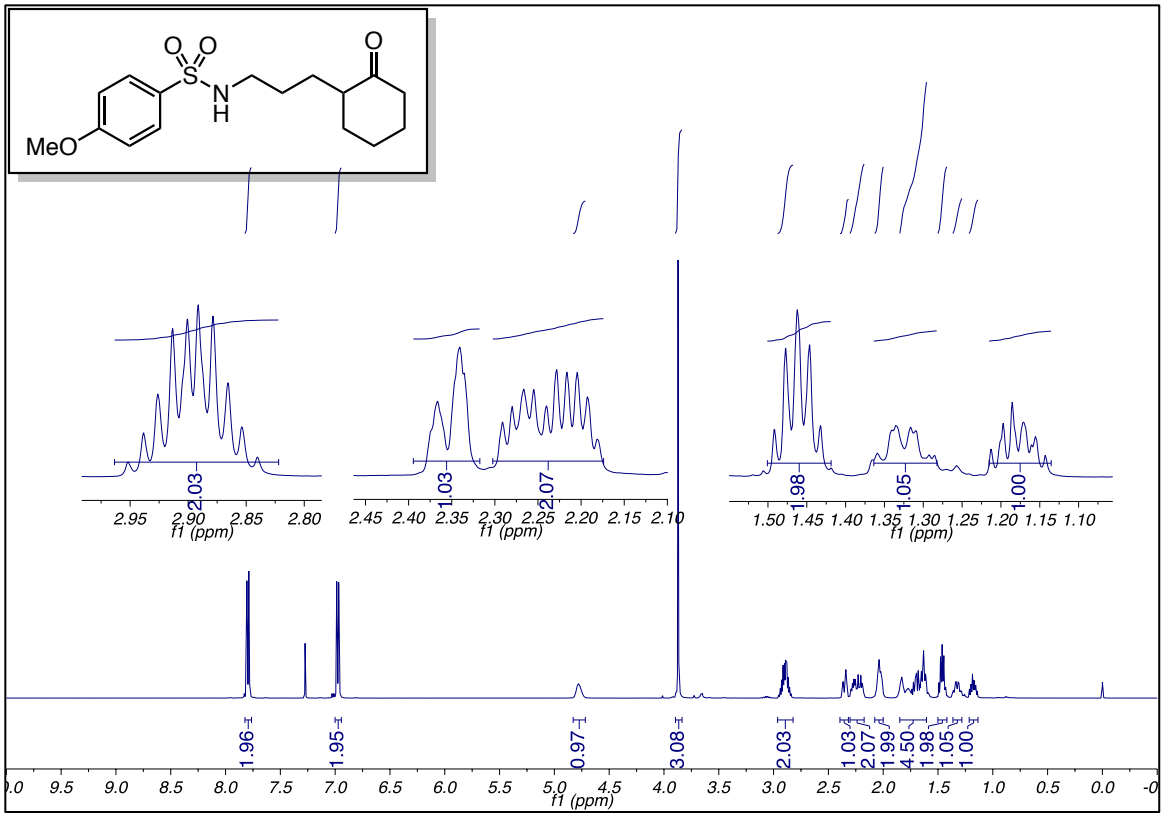

168.940
162.681
134.243
131.722
129.121
123.422
114.164
55.587
45.714
40.347
33.571
15.630
MeO
Me
f1 (ppm)

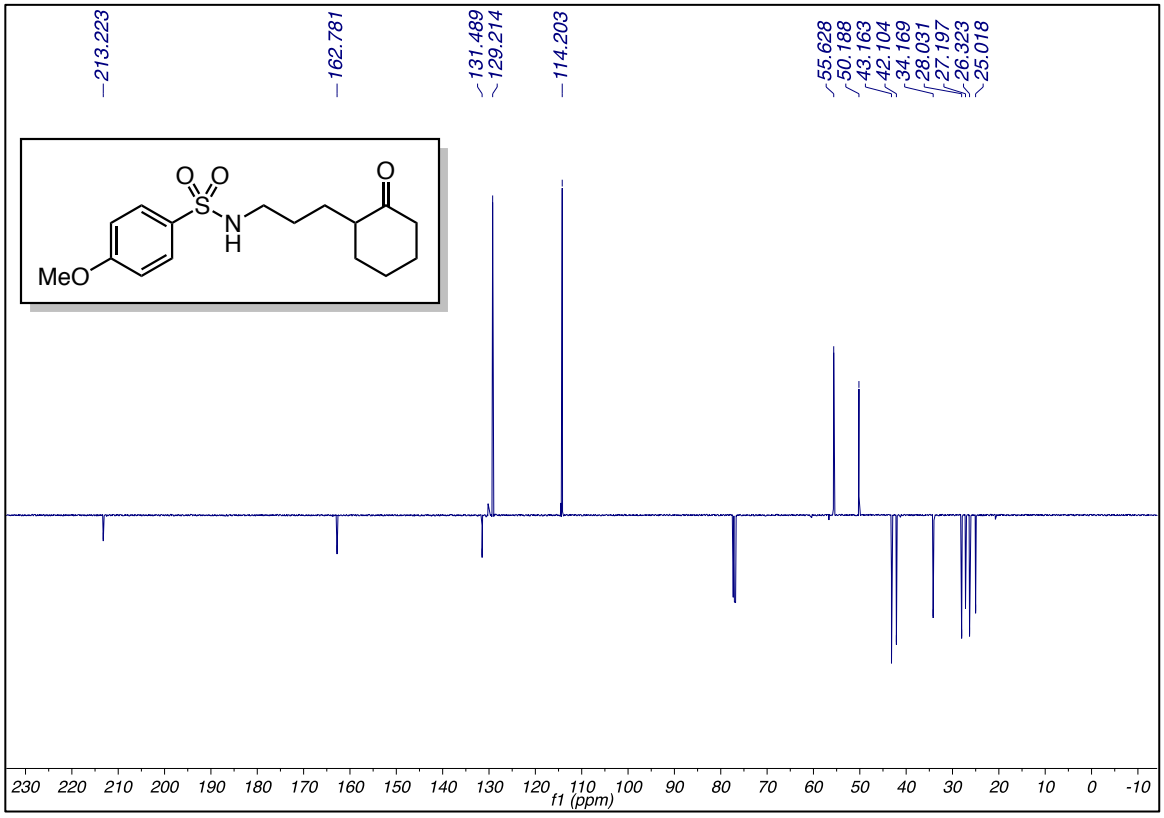

O
O
S
N
H
OTBS
Me
MeO
1.00
0.99
0.99
0.99
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8
f1 (ppm)
1.96
1.97
0.98
2.99
1.00
0.99
0.99
0.99
0.98
8.91
3.00
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

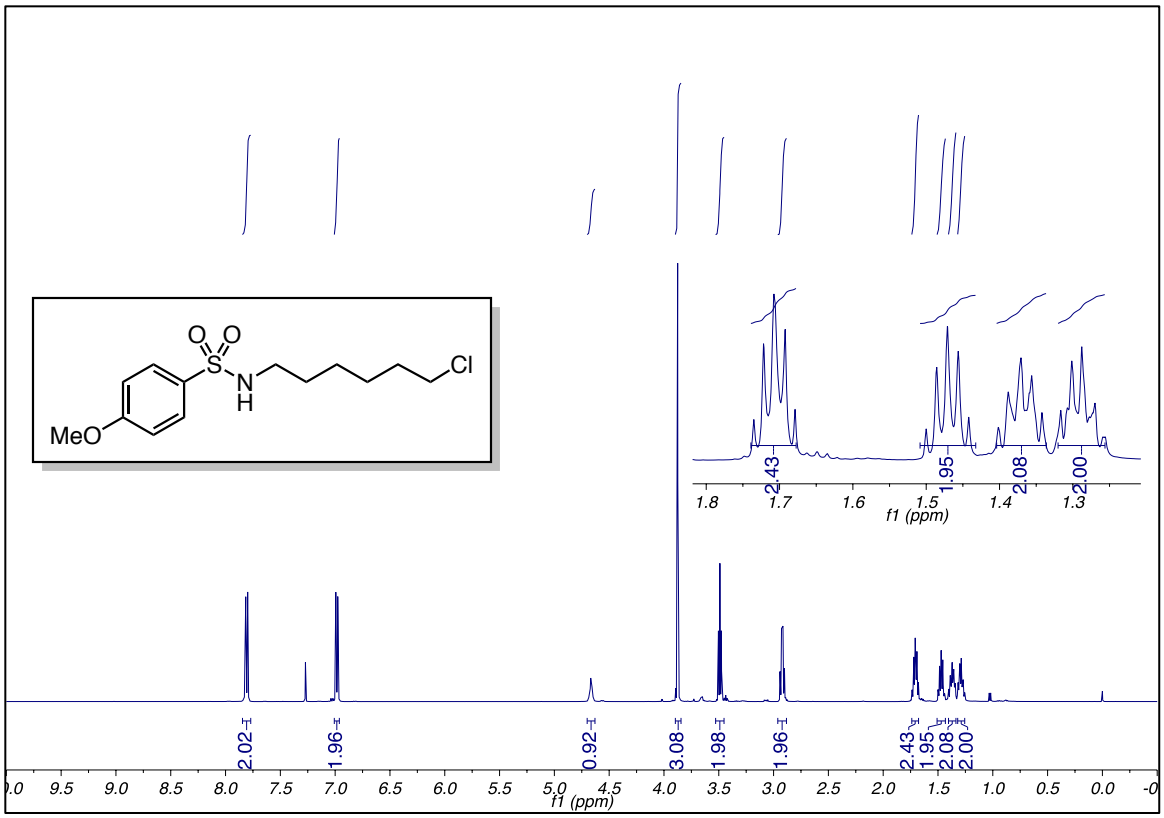

162.681
131.656
129.162
114.132
67.981
55.589
48.203
34.767
25.851
18.127
14.519
-5.611
O
O
S
N
H
OTBS
Me
MeO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

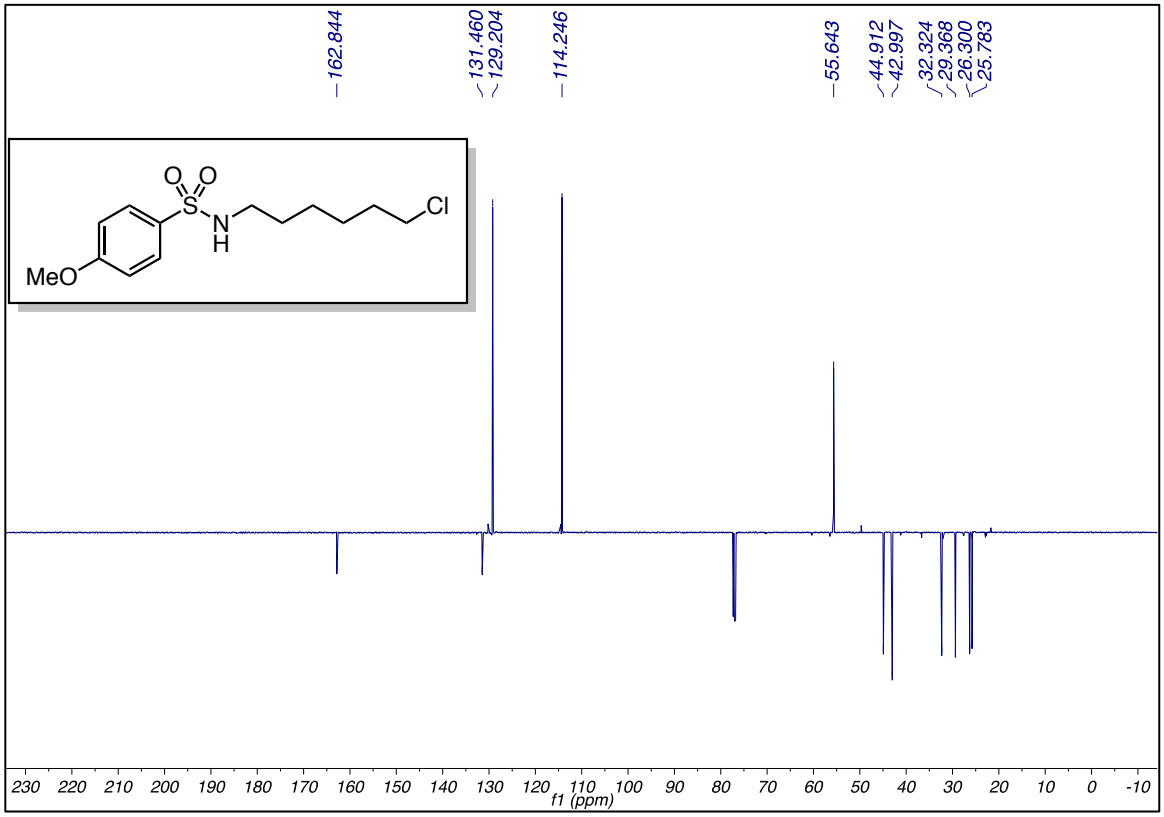

OTBS
OTBS
MeO
f1 (ppm)

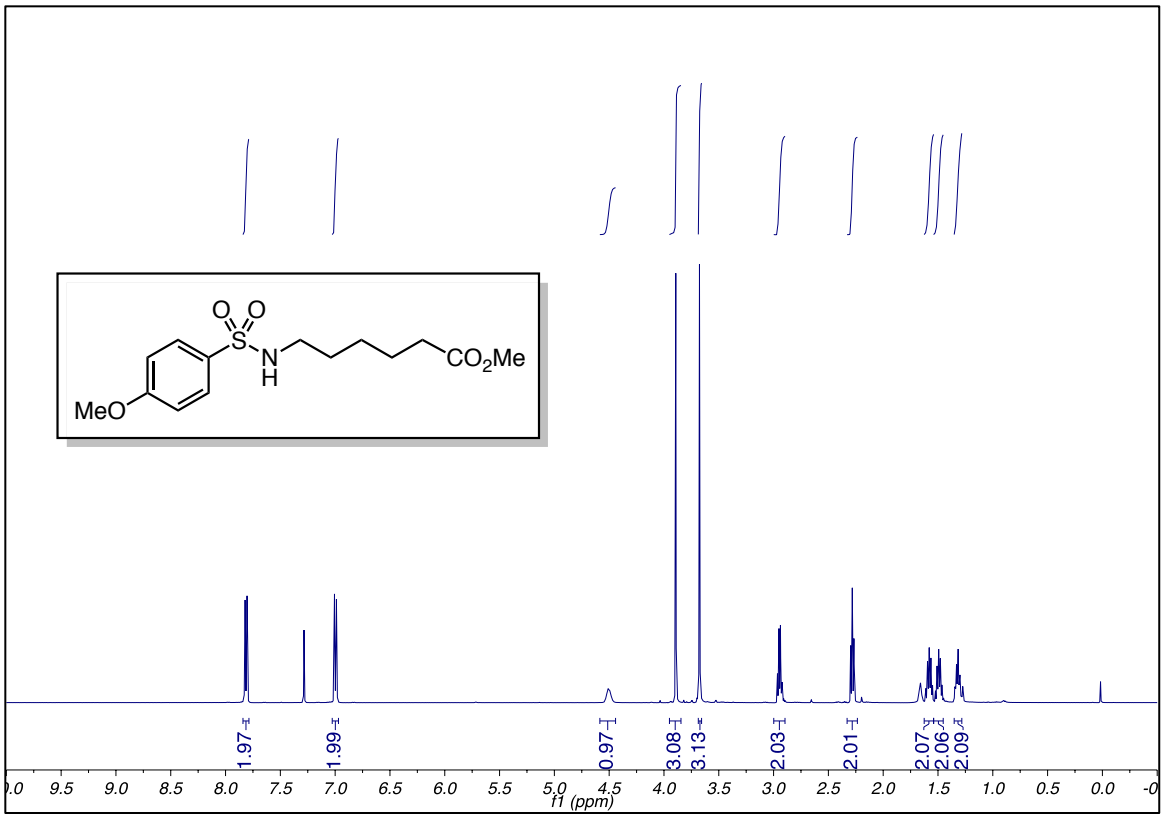

162.682
132.539
129.191
114.096
64.284
60.097
55.584
53.358
33.591
25.837
18.147
-5.469
OTBS
OTBS
MeO
f1 (ppm)

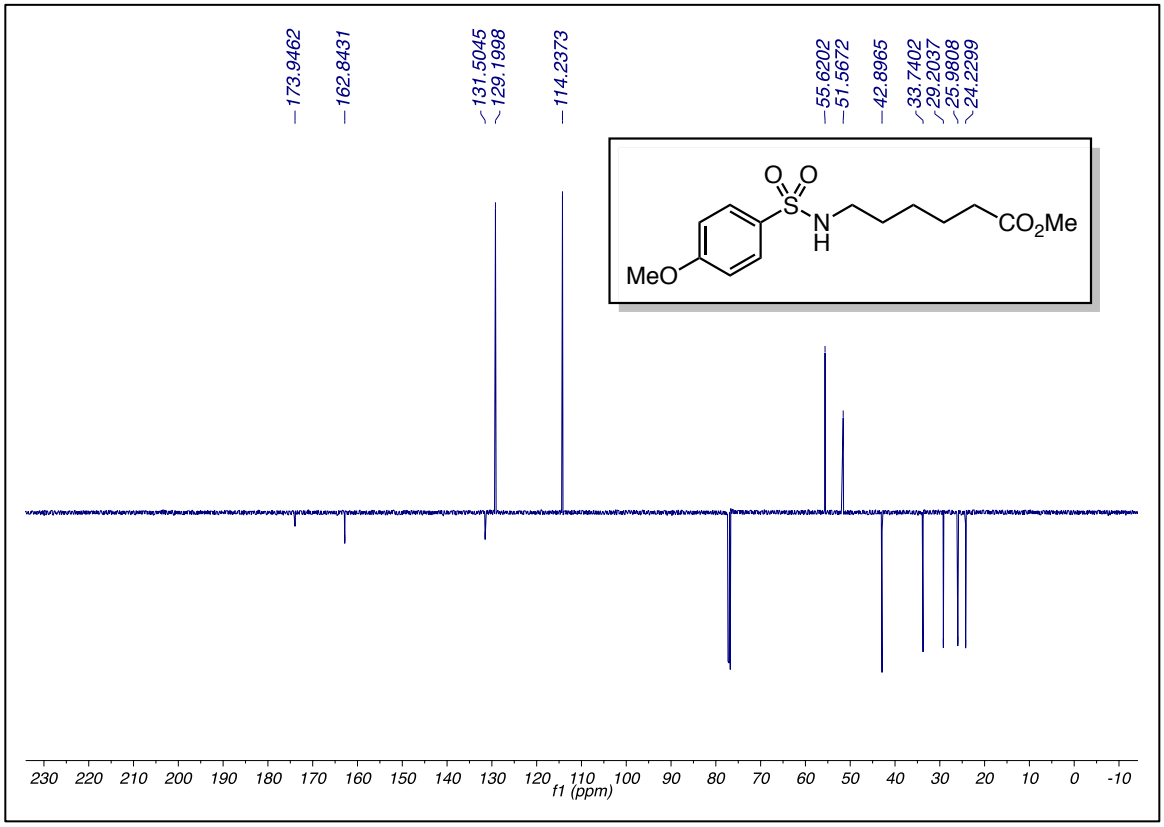

MeO
f1 (ppm)

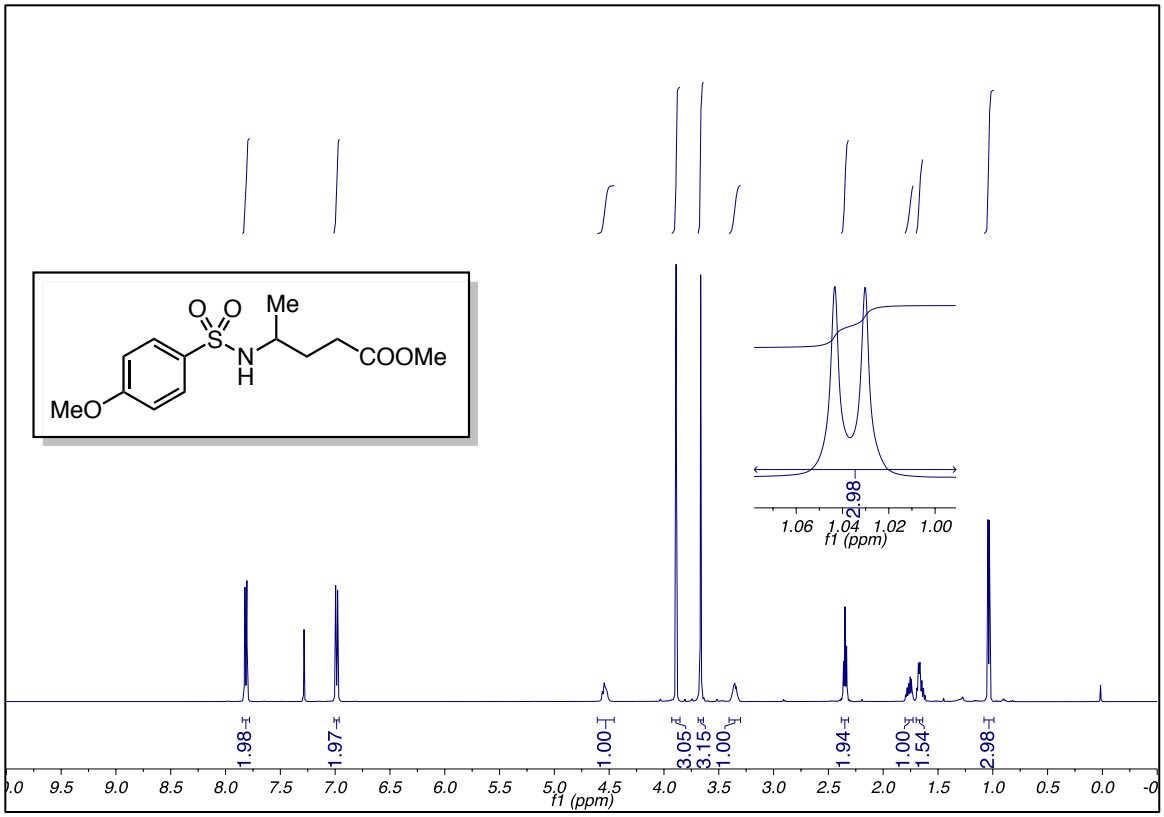

213.223
162.781
131.489
129.214
114.203
55.628
50.188
43.163
42.104
34.169
28.031
27.197
26.323
25.018
MeO
f1 (ppm)

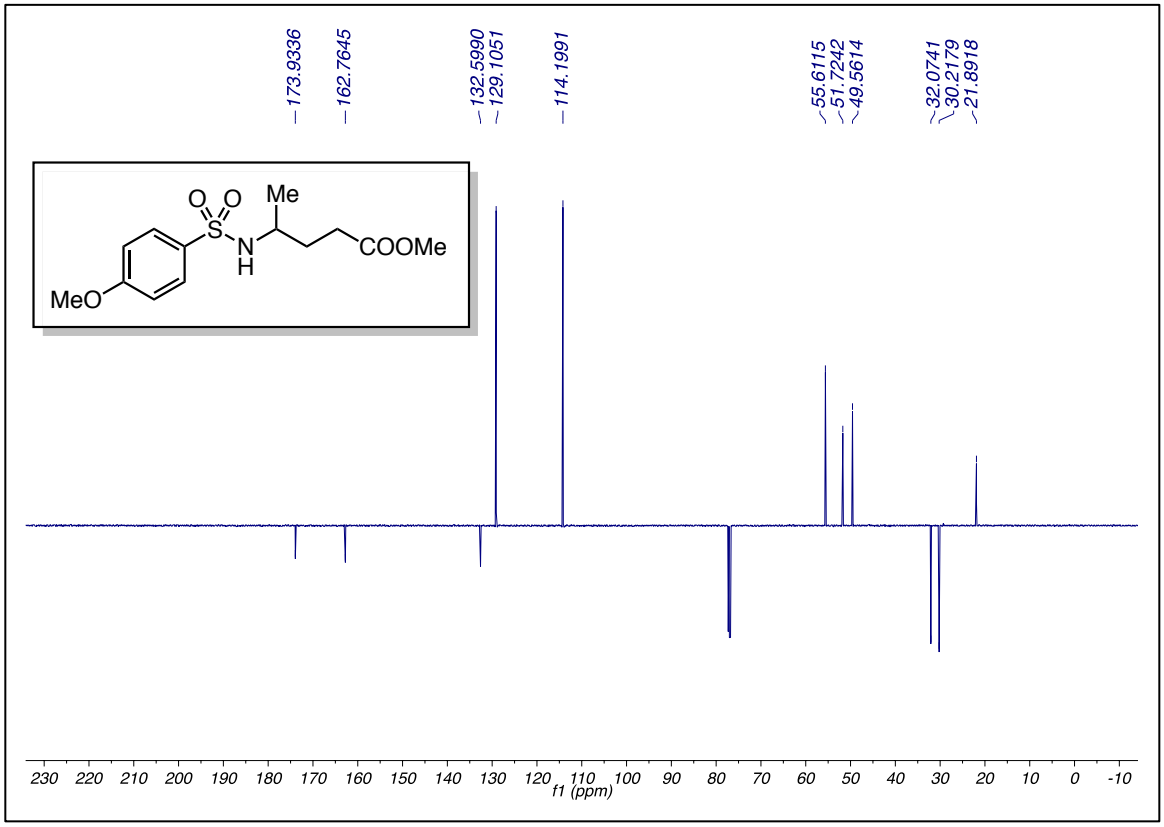

MeO
Cl
2.02
1.96
0.92
3.08
1.98
1.96
2.43
1.95
2.08
2.00
f1 (ppm)

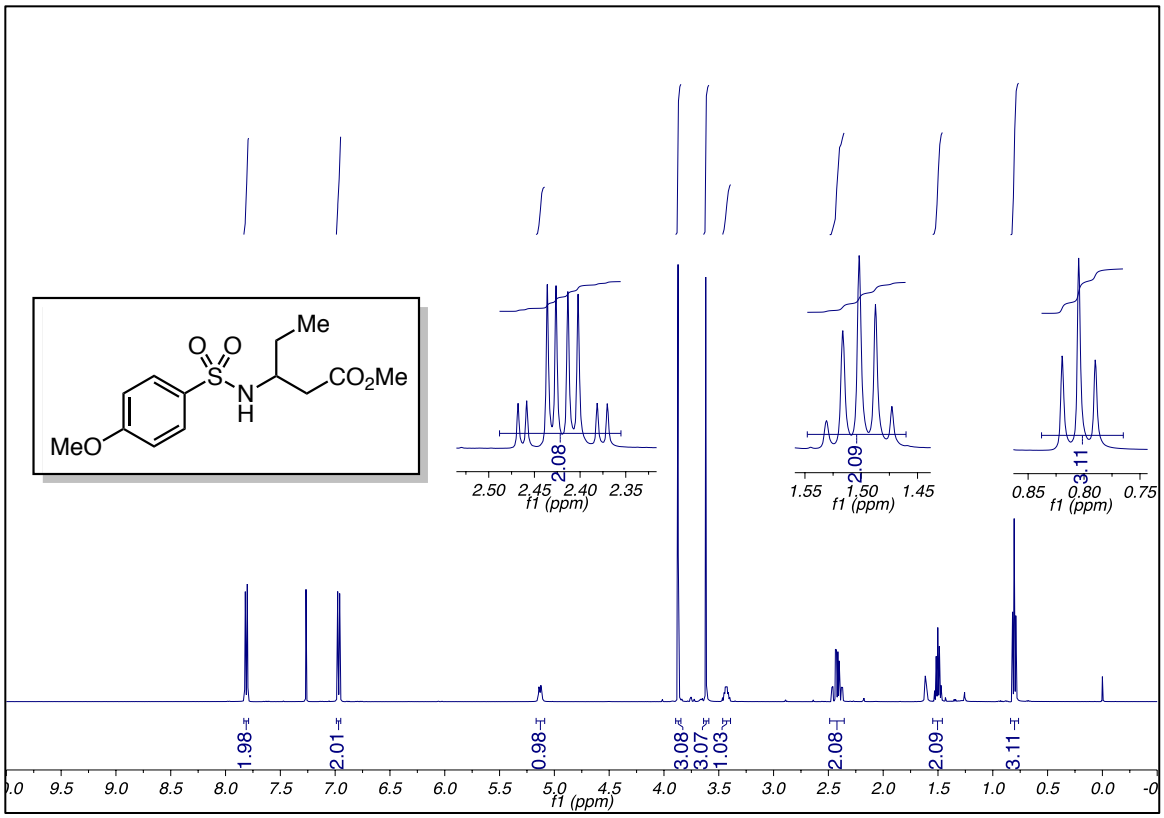

162.844
131.460
129.204
114.246
55.643
44.912
42.997
32.324
29.368
26.300
25.783
MeO
Cl
f1 (ppm)

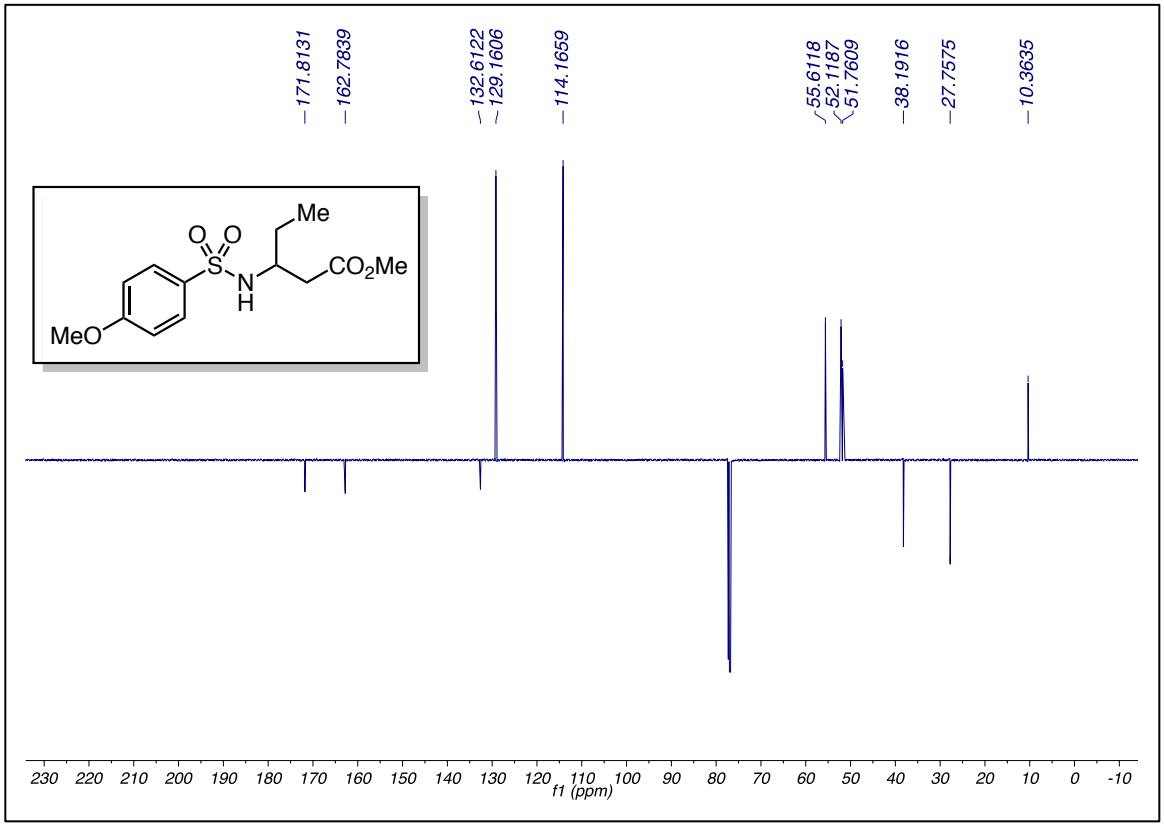

O
O
S
N
H
CO2Me
MeO
1.97
1.99
0.97
3.08
3.13
2.03
2.01
2.07
2.06
2.09
f1 (ppm)

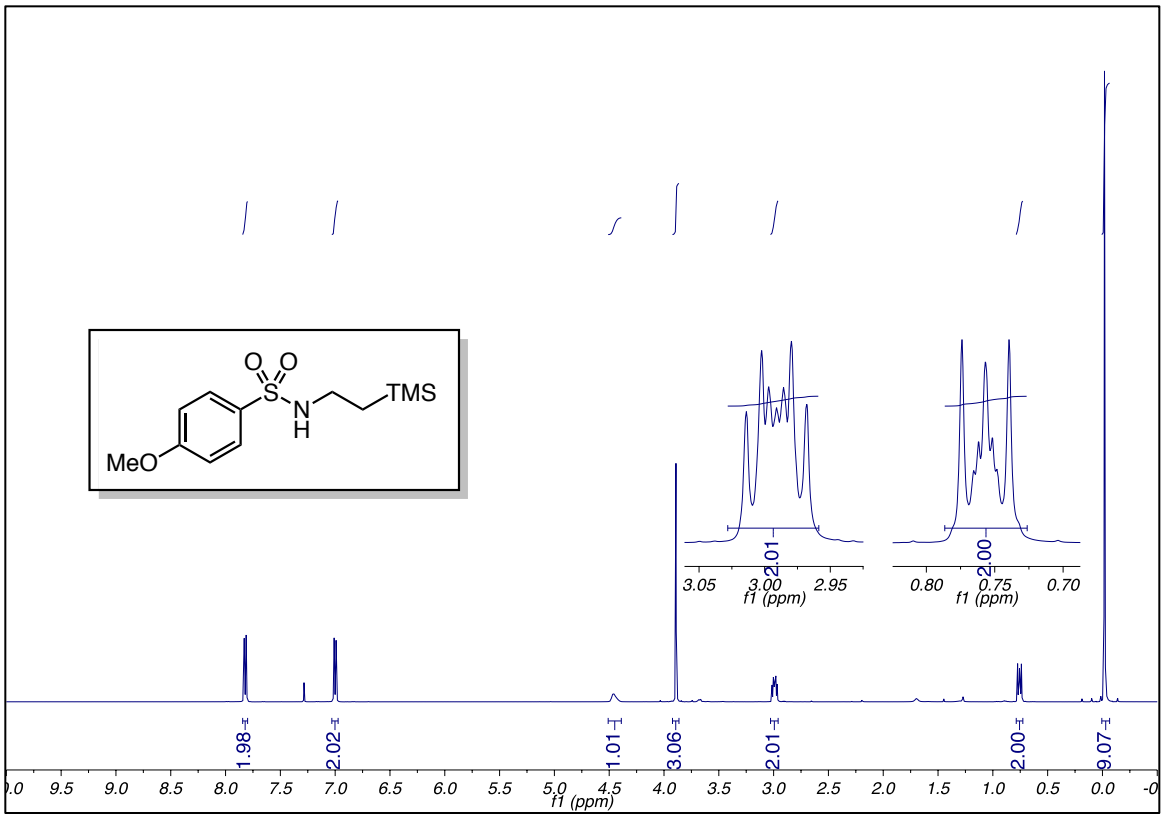

173.9462
162.8431
131.5045
129.1998
114.2373
55.6202
51.5672
42.8965
33.7402
29.2037
25.9808
24.2299
O
O
S
N
H
CO2Me
MeO
f1 (ppm)

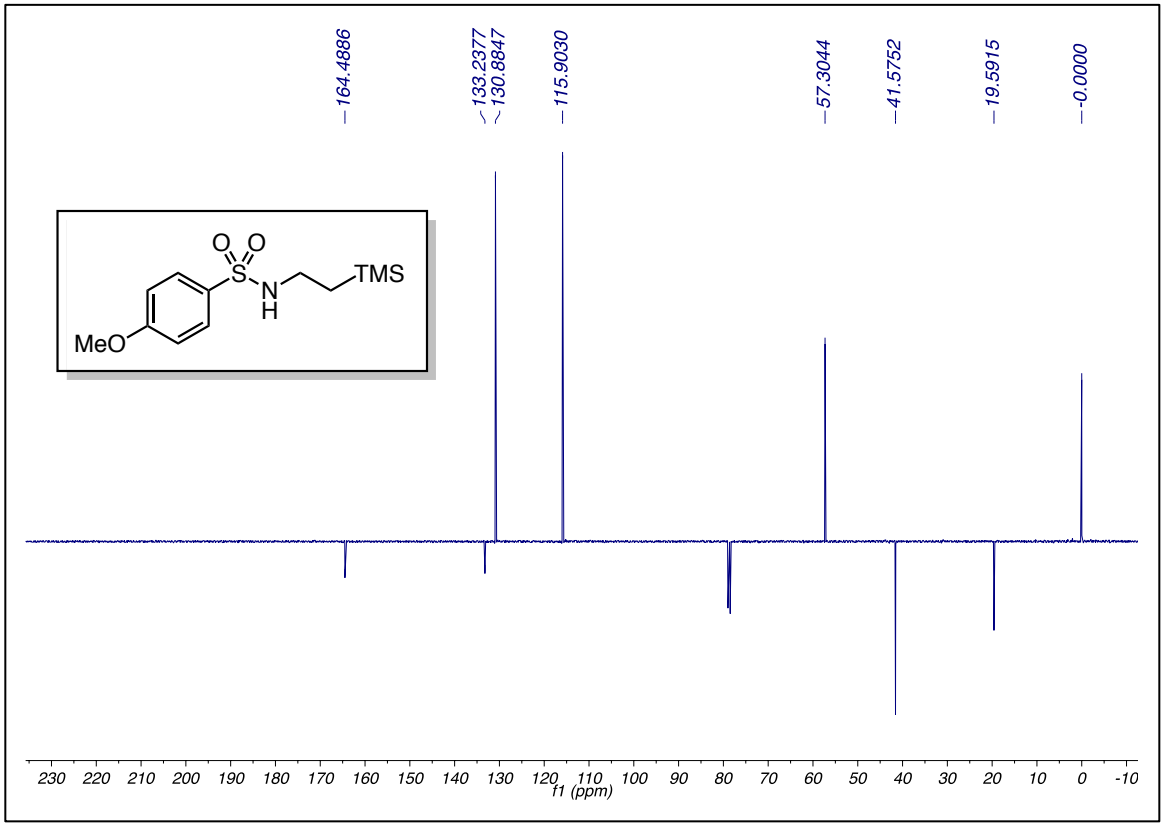

Me
O
O
S
N
H
COOMe
MeO
1.98
1.97
1.00
3.05
3.15
1.00
1.94
1.00
1.54
2.98
f1 (ppm)

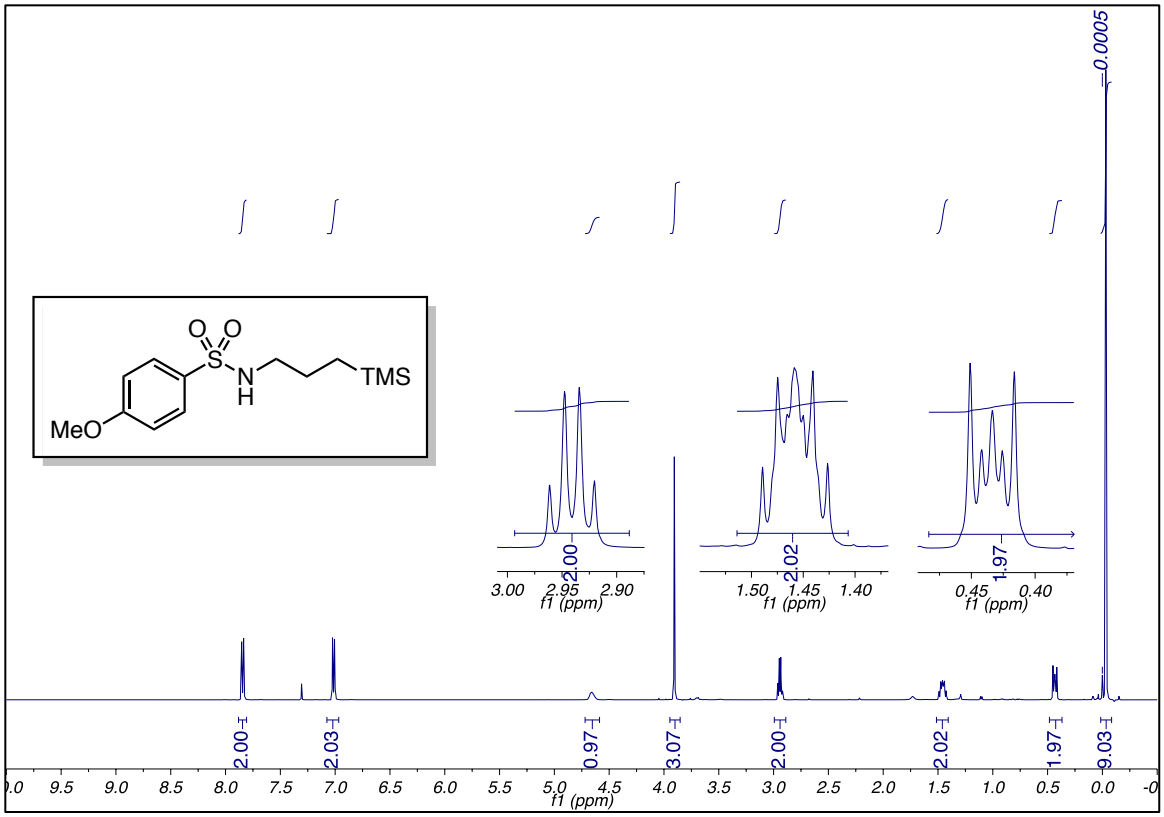

173.9336
162.7645
132.5990
129.1051
114.1991
55.6115
51.7242
49.5614
32.0741
30.2179
21.8918
Me
O
O
S
N
H
COOMe
MeO
f1 (ppm)

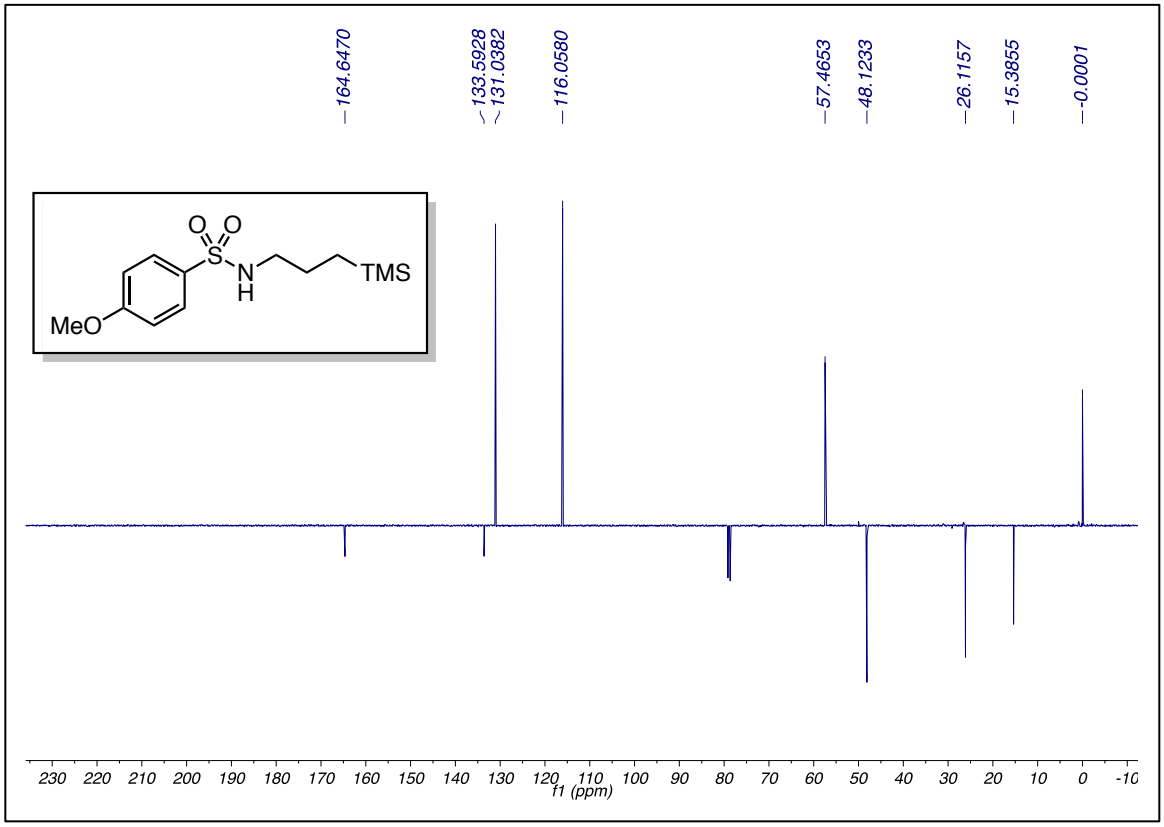

Me
O
O
S
N
H
CO2Me
MeO
2.08
2.09
3.11
f1 (ppm)
1.98
2.01
0.98
3.08
3.07
1.03
2.08
2.09
3.11
f1 (ppm)

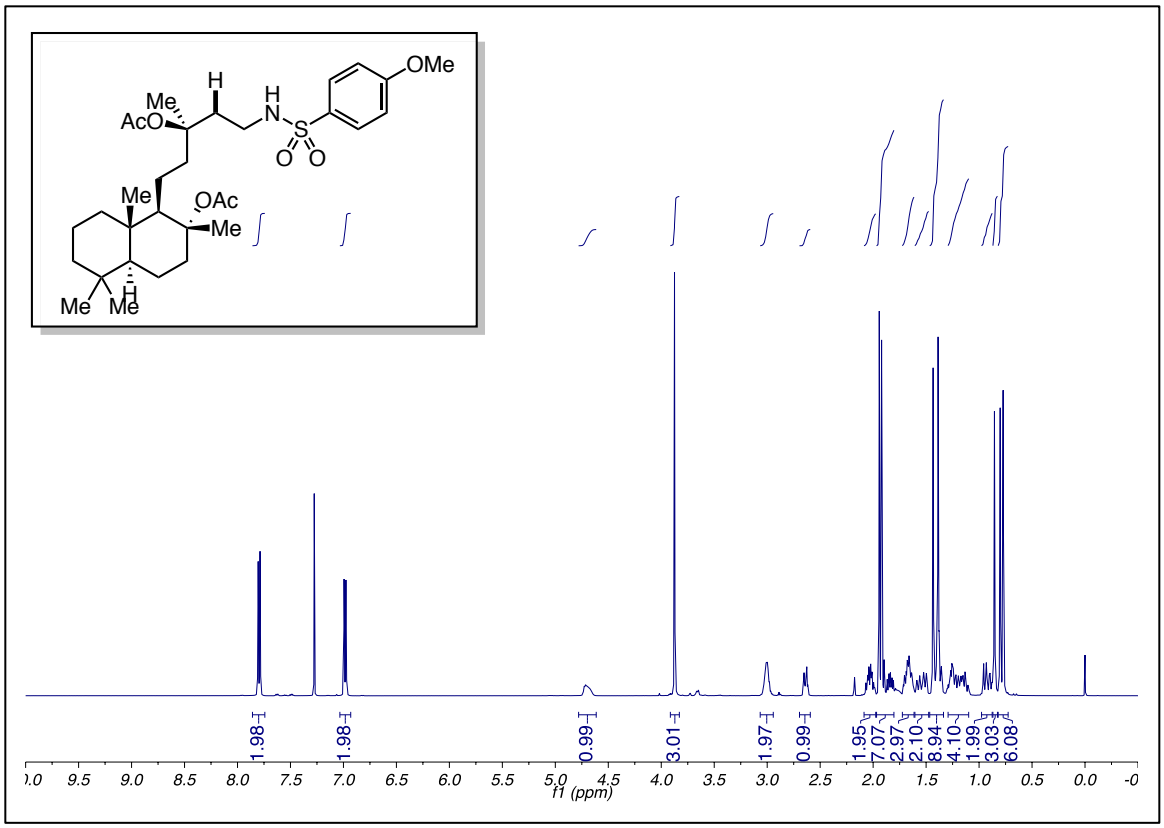

171.8131
162.7839
132.6122
129.1606
114.1659
55.6118
52.1187
51.7609
38.1916
27.7575
10.3635
Me
O
O
S
N
H
CO2Me
MeO
f1 (ppm)

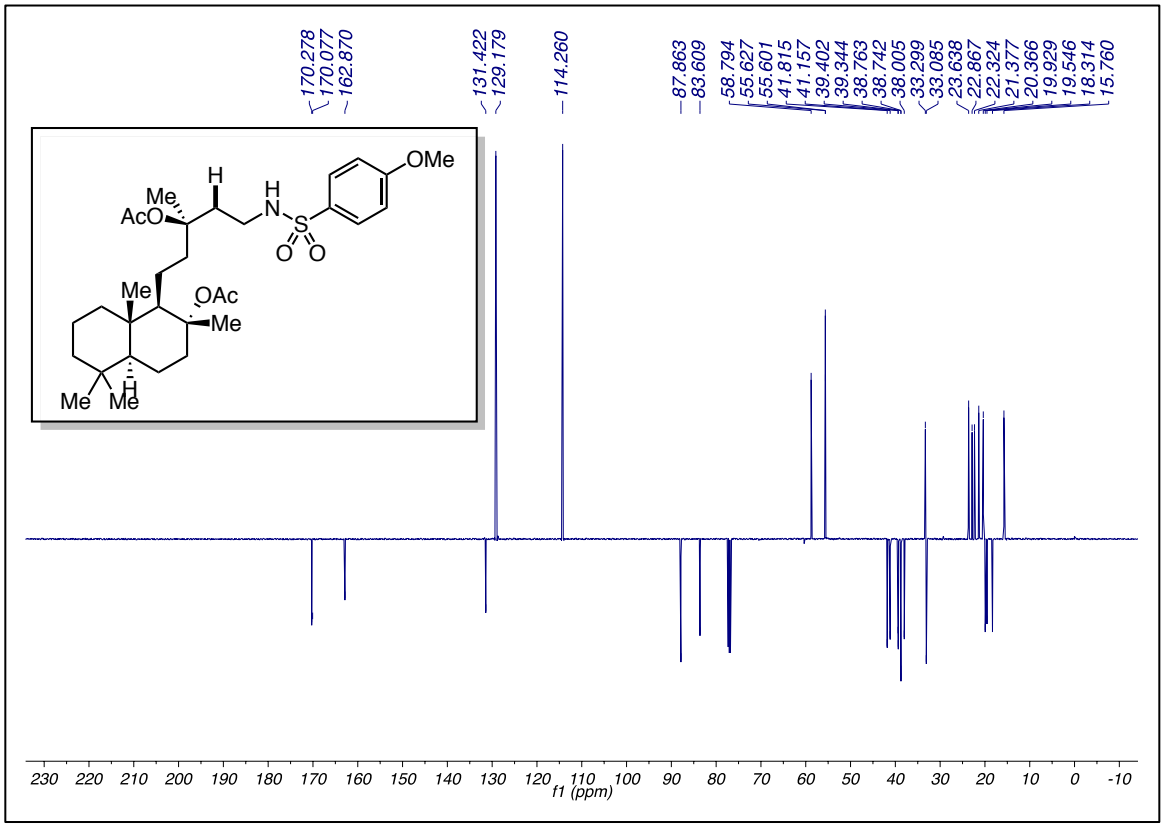

MeO
TMS
1.98
2.02
1.01
3.06
2.01
2.00
9.07
f1 (ppm)

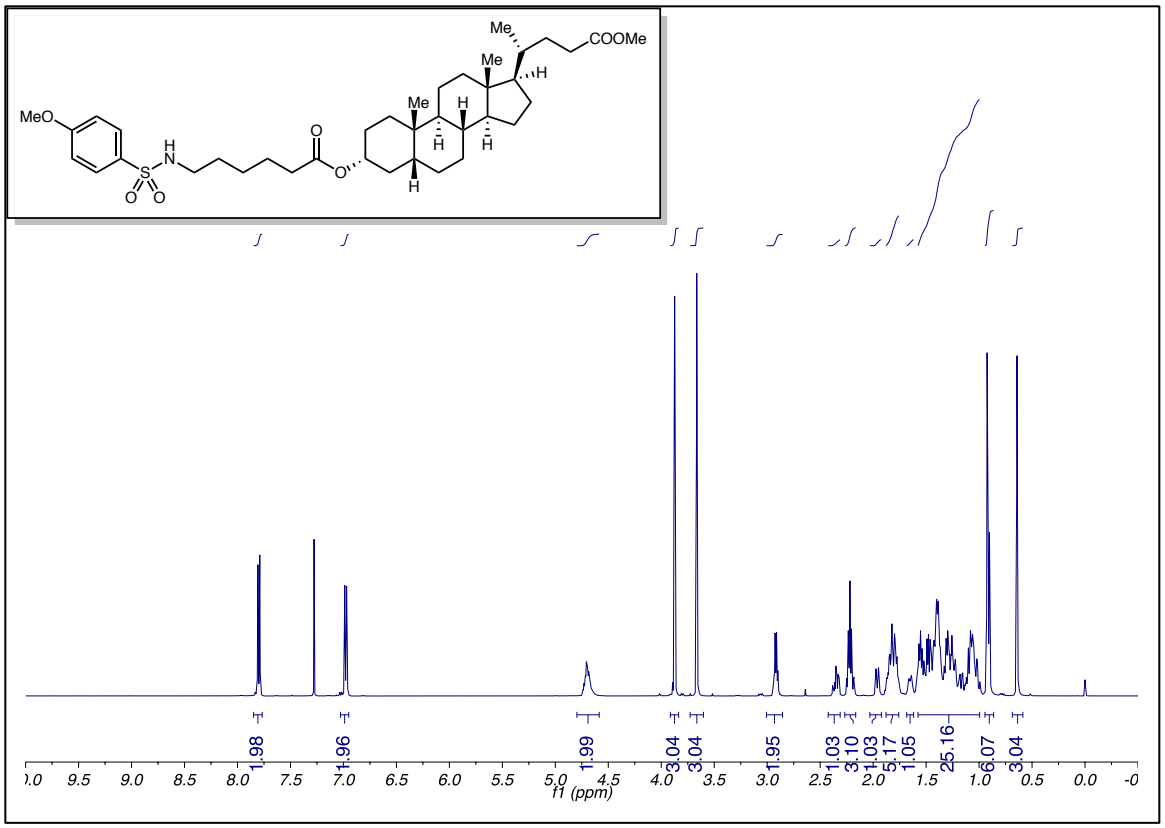

164.4886
133.2377
130.8847
115.9030
57.3044
41.5752
19.5915
-0.0000
MeO
TMS
f1 (ppm)

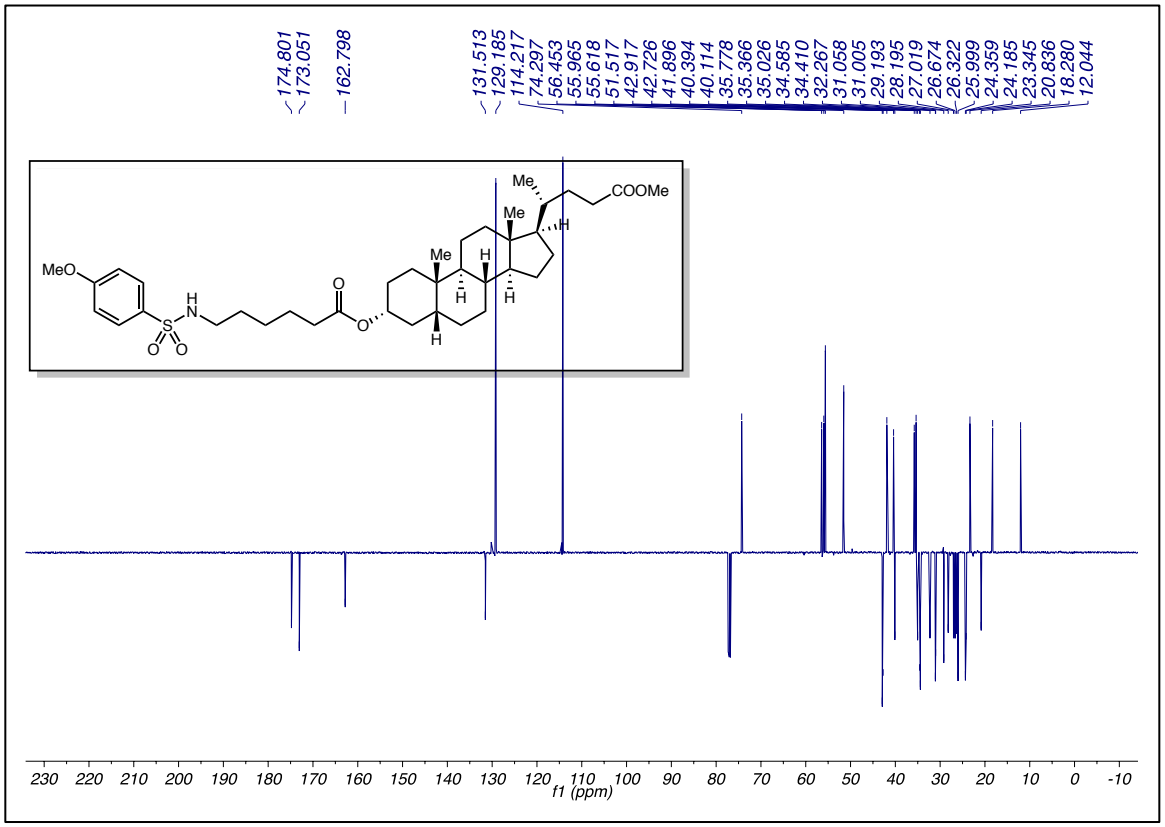

0.0005
MeO
TMS
2.00
2.03
0.97
3.07
2.00
2.02
1.97
9.03
f1 (ppm)


164.6470
133.5928
131.0382
116.0580
57.4653
48.1233
26.1157
15.3855
-0.0001
MeO
TMS
f1 (ppm)


OMe
H
H
N
S
O
O
Me
AcO
Me
OAc
Me
Me
Me
H
1.98
1.98
0.99
3.01
1.97
0.99
1.95
7.07
2.97
2.10
8.94
4.10
1.99
3.03
6.08
f1 (ppm)


170.278
170.077
162.870
131.422
129.179
114.260
87.863
83.609
58.794
55.627
55.601
41.815
41.157
39.402
39.344
38.763
38.742
38.005
33.299
33.085
23.638
22.867
22.324
21.377
20.366
19.929
19.546
18.314
15.760
OMe
H
H
N
S
O
O
Me
AcO
Me
OAc
Me
Me
Me
H
f1 (ppm)


MeO
COOMe
Me
H
O
S
N
1.98
1.96
1.99
3.04
3.04
1.95
1.03
3.10
1.03
5.17
1.05
25.16
6.07
3.04
f1 (ppm)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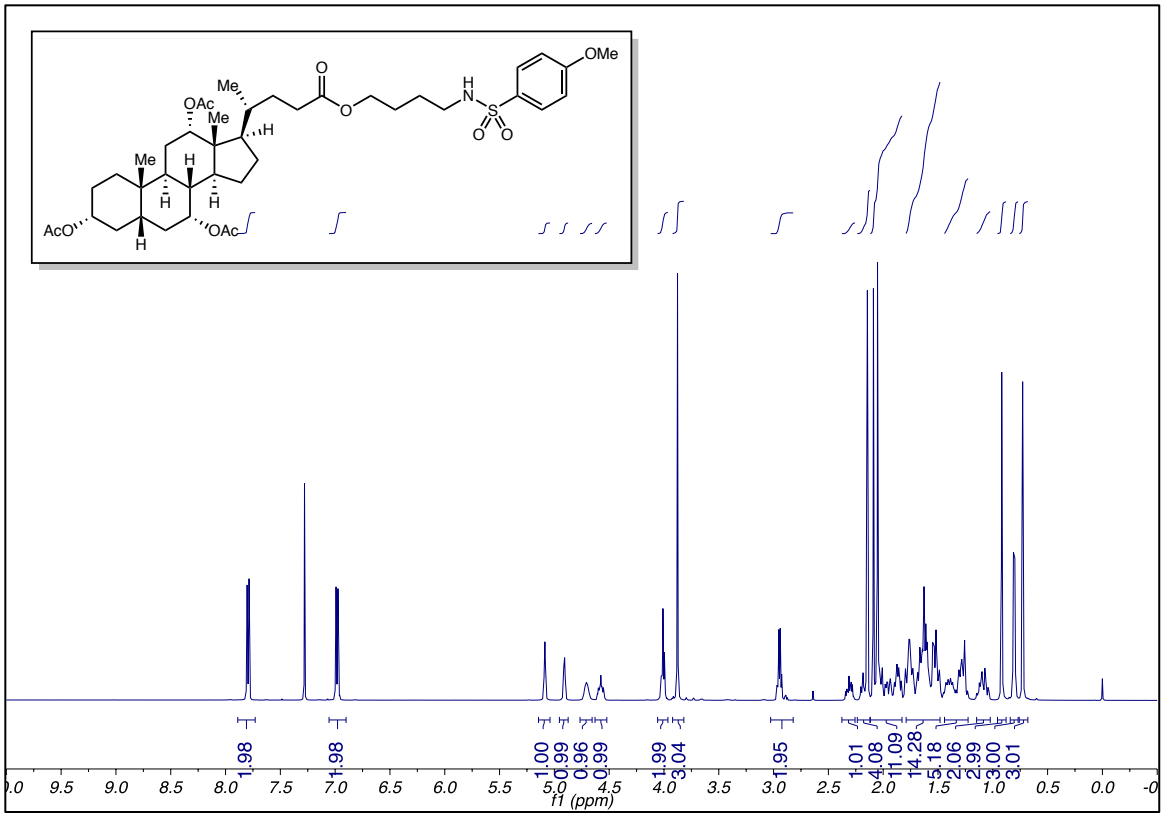
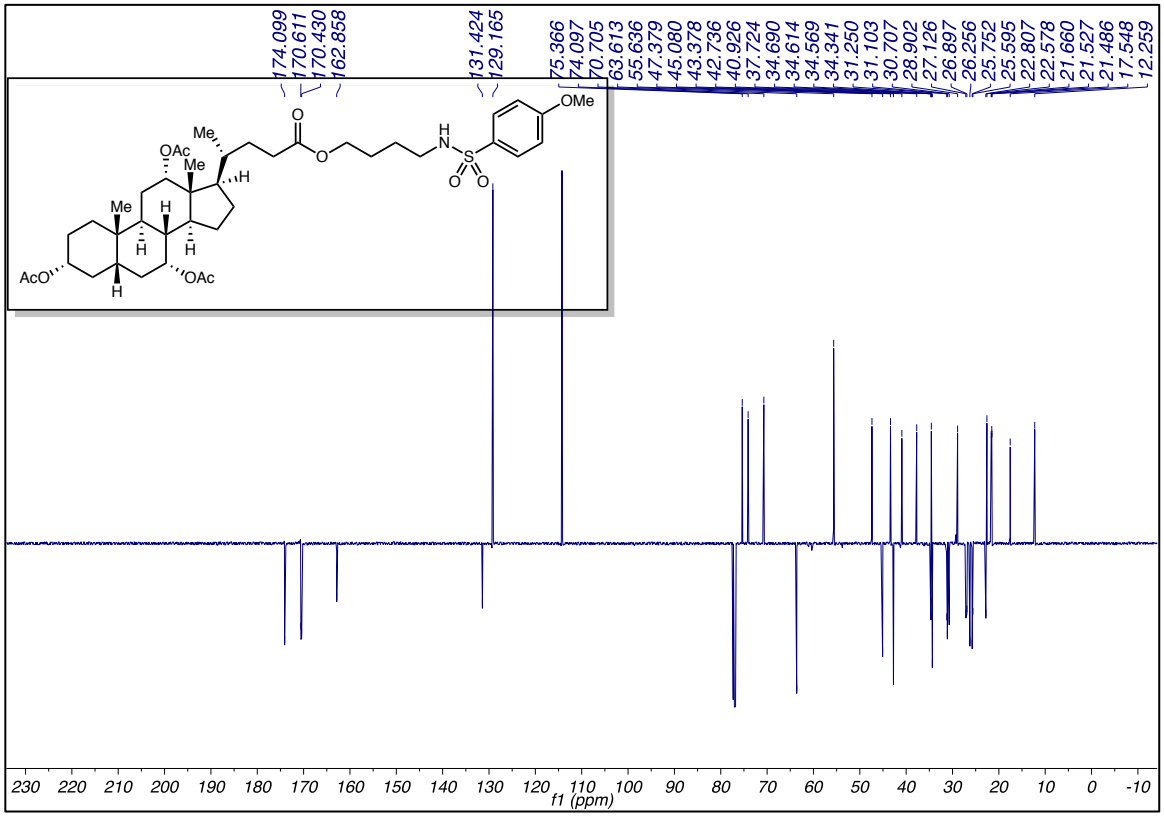
173.051
162.798
131.513
129.185
114.217
74.297
56.453
55.965
55.618
51.517
42.917
42.726
41.896
40.394
40.114
35.778
35.366
35.026
34.585
34.410
32.267
31.058
31.005
29.193
28.195
27.019
26.674
26.322
25.999
24.359
24.185
23.345
20.836
18.280
12.044
MeO
COOMe
Me
H
O
S
N
f1 (ppm)


OMe
Me
OAc
Me
H
Me
H
H
H
AcO
OAc
H
O
O
H
N
S
O
O
1.98
1.98
1.00
0.99
0.96
0.99
1.99
3.04
1.95
1.01
4.08
11.09
14.28
5.18
2.06
2.99
3.00
3.01
f1 (ppm)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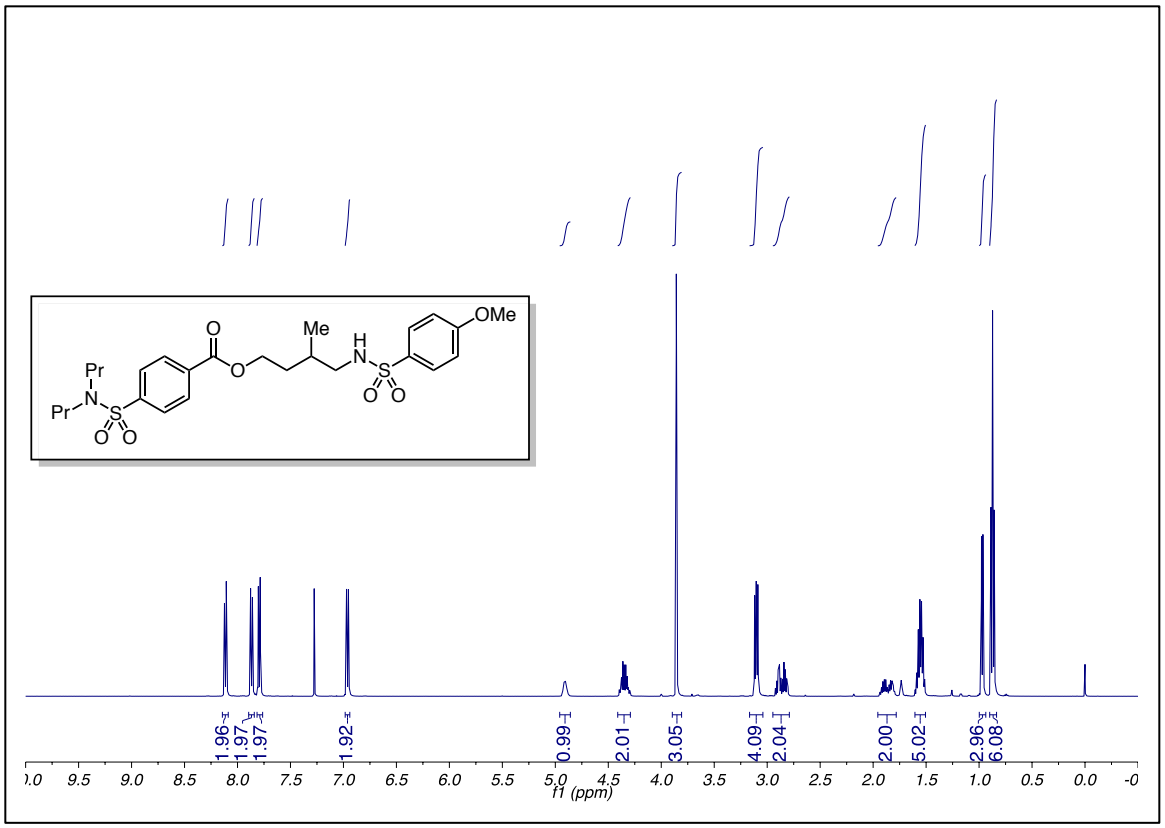
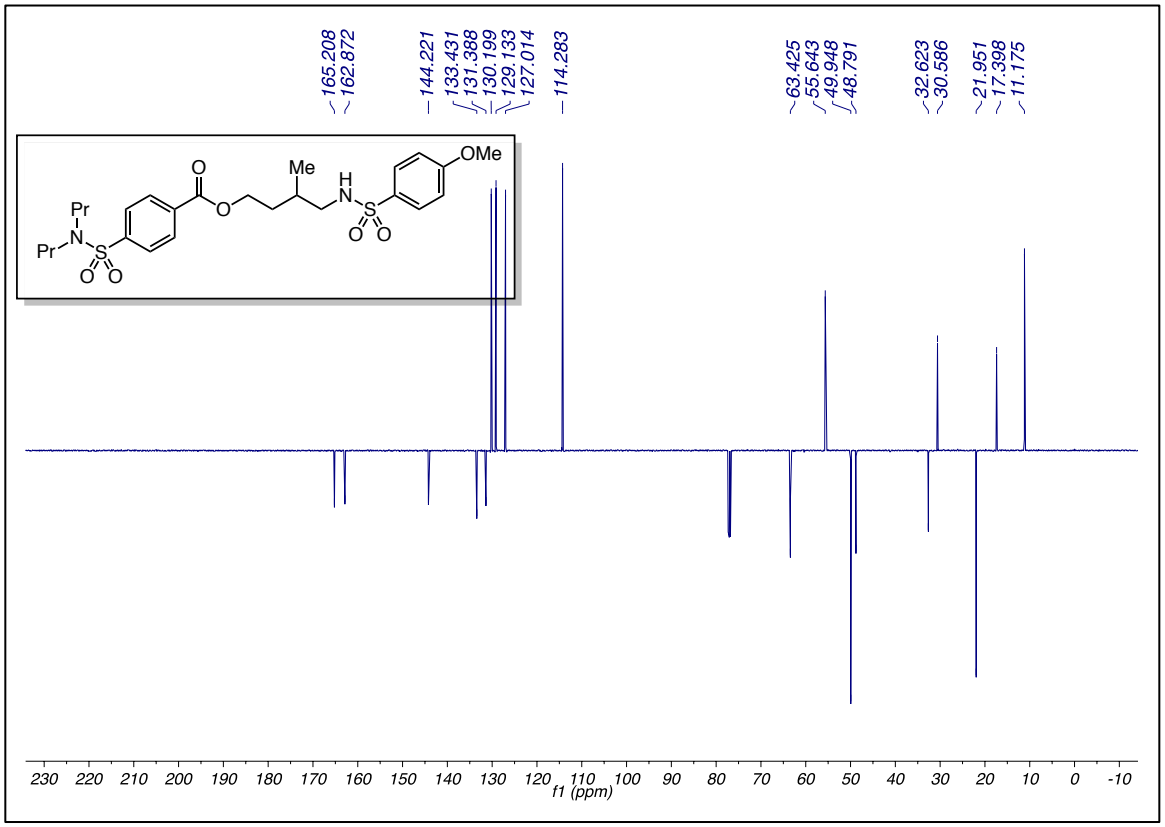
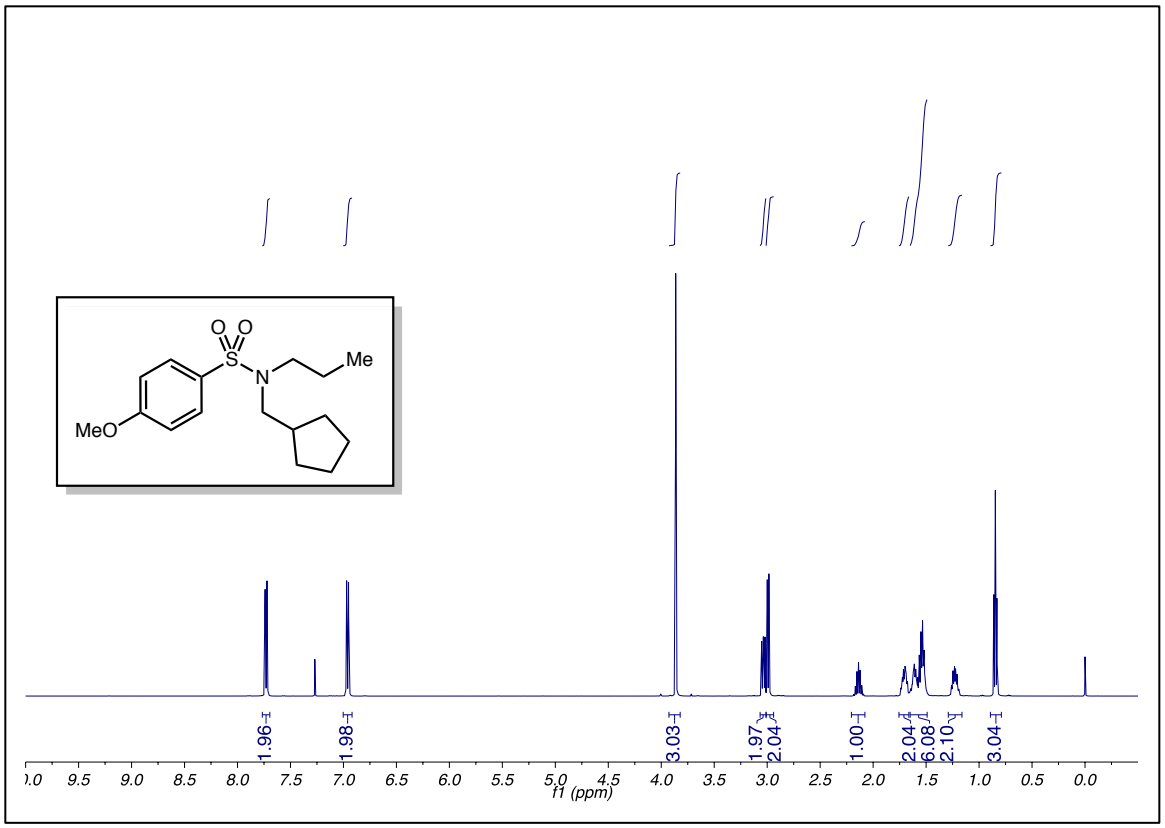
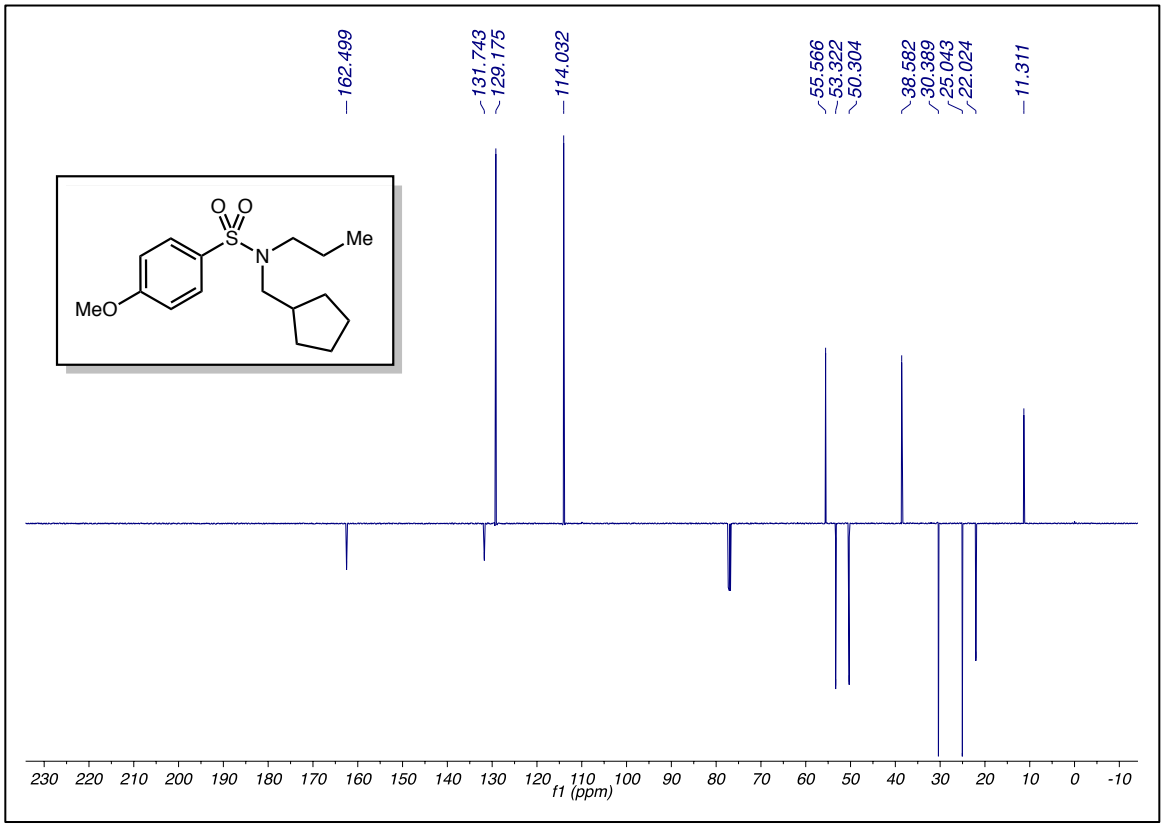
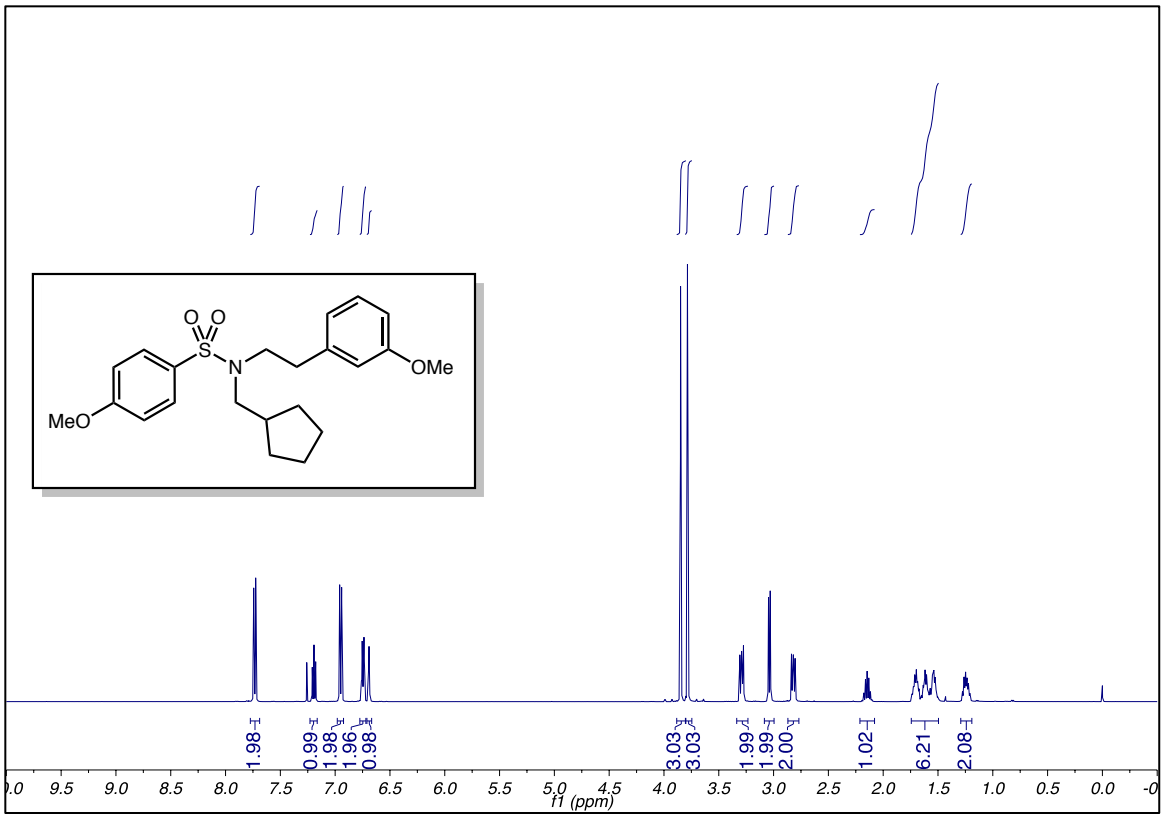
170.611
170.430
162.858
131.424
129.165
75.366
74.097
70.705
63.613
55.636
47.379
45.080
43.378
42.736
40.926
37.724
34.690
34.614
34.569
34.341
31.250
31.103
30.707
28.902
27.126
26.897
26.256
25.752
25.595
22.807
22.578
21.660
21.527
21.486
17.548
12.259
OMe
Me
OAc
Me
H
Me
H
H
H
AcO
OAc
H
O
O
H
N
S
O
O
f1 (ppm)

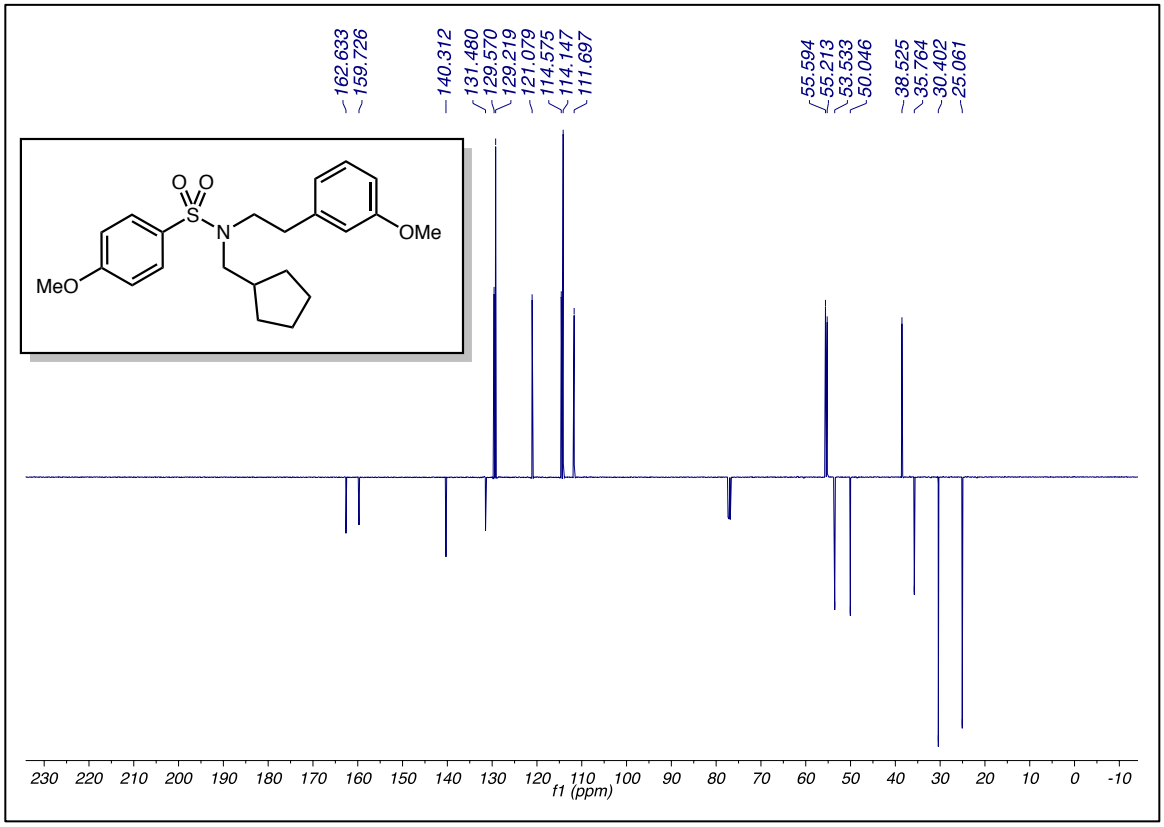

OMe
Me
H
N
O
S
Pr
N
Pr
1.96
1.97
1.97
1.92
0.99
2.01
3.05
4.09
2.04
2.00
5.02
2.96
6.08
f1 (ppm)

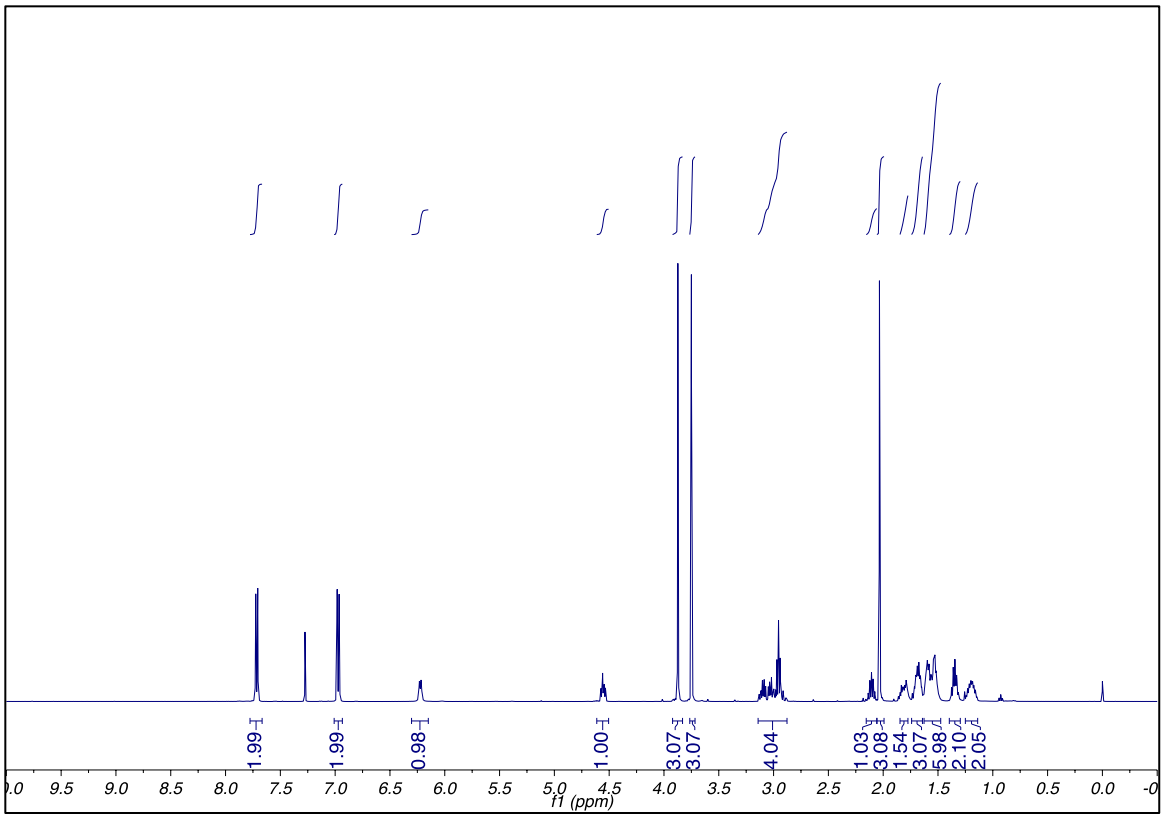

165.208
162.872
144.221
133.431
131.388
130.199
129.133
127.014
114.283
63.425
55.643
49.948
48.791
32.623
30.586
21.951
17.398
11.175
OMe
Me
H
N
O
S
Pr
N
Pr
f1 (ppm)

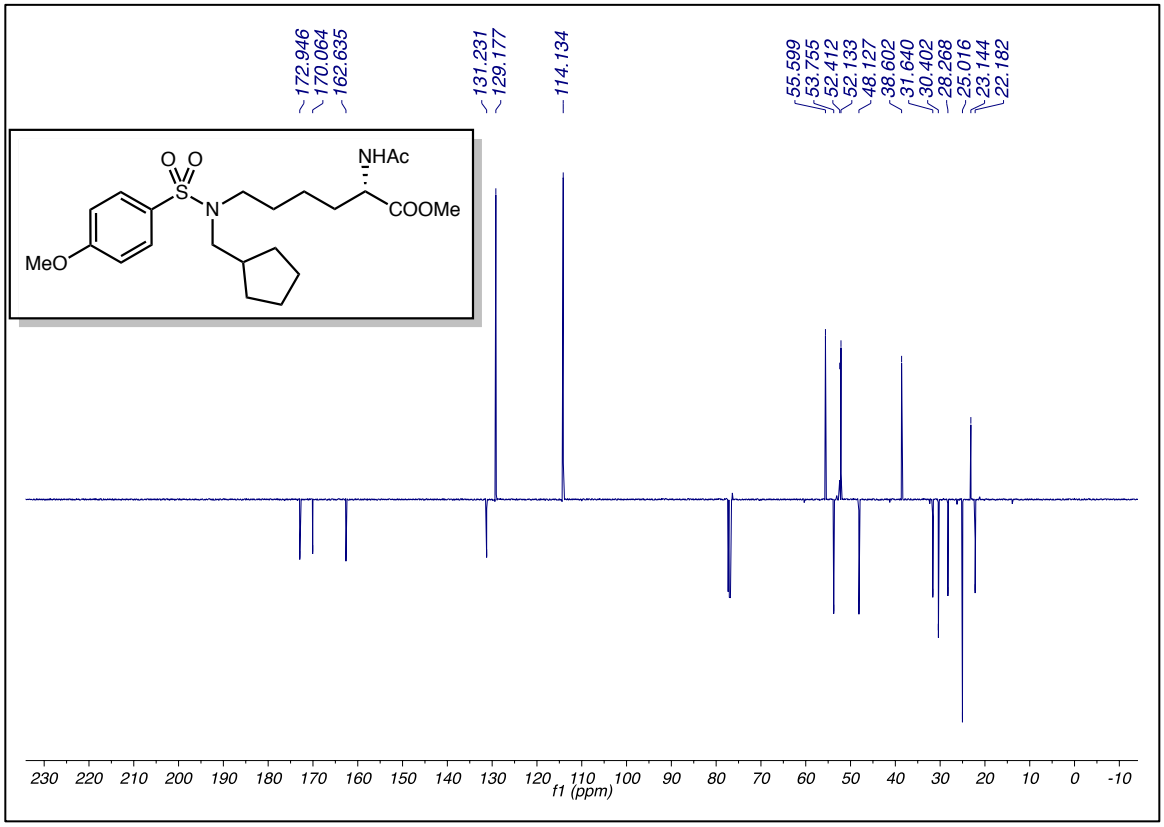

O
O
S
N
Me
MeO
1.96
1.98
3.03
1.97
2.04
1.00
2.04
6.08
2.10
3.04
f1 (ppm)

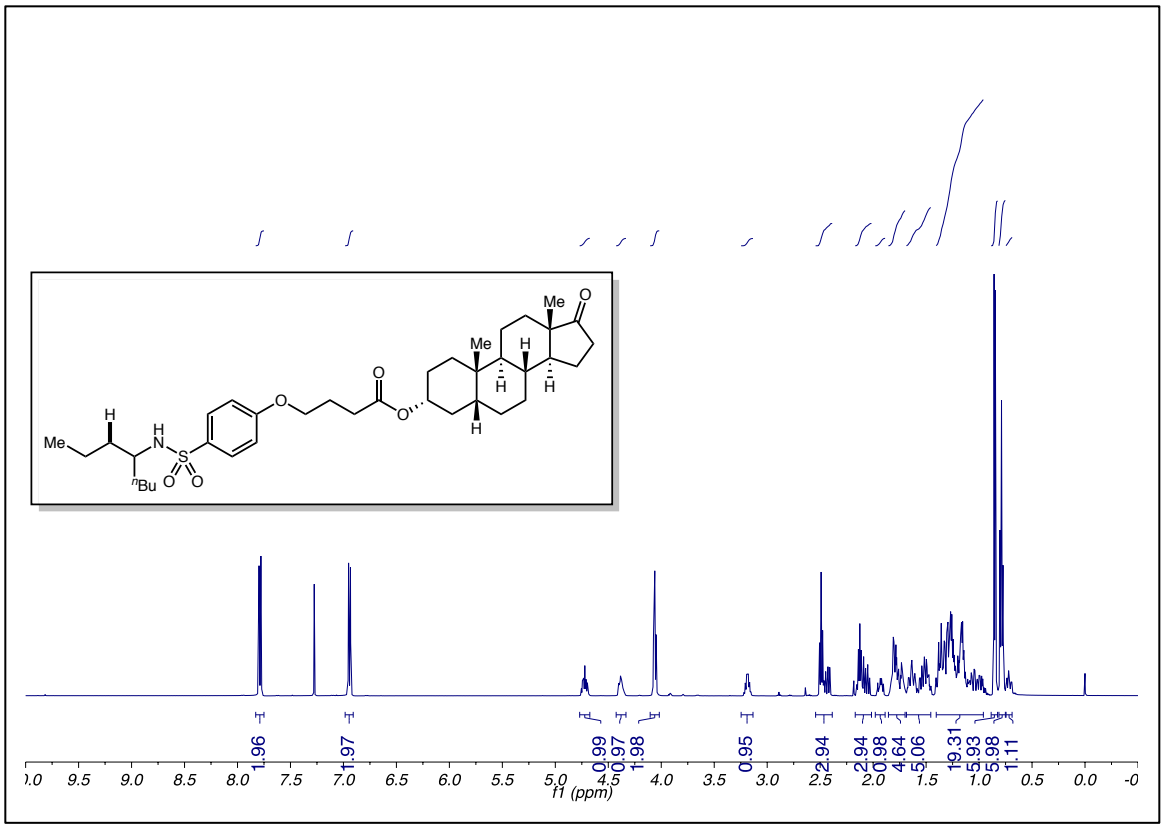

162.499
131.743
129.175
114.032
55.566
53.322
50.304
38.582
30.389
25.043
22.024
11.311
O
O
S
N
Me
MeO
f1 (ppm)

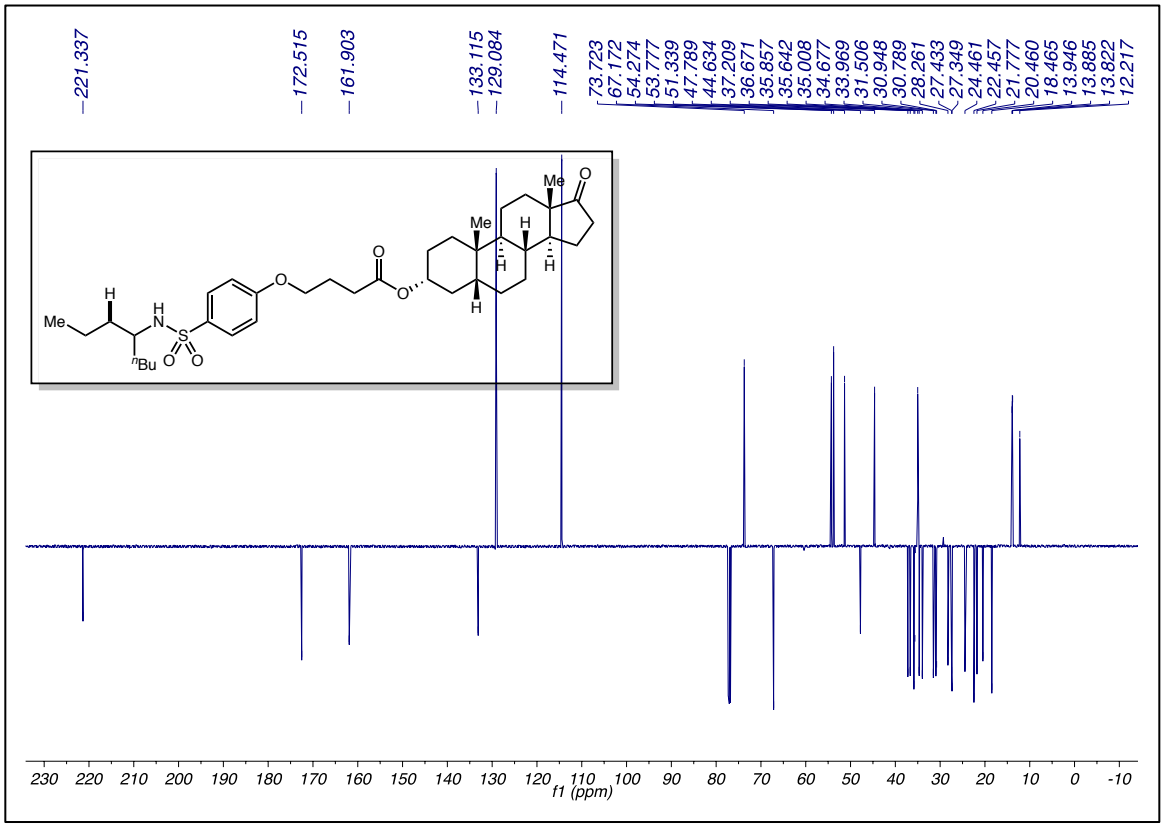

O
O
S
N
OMe
MeO
1.98
0.99
1.98
1.96
0.98
3.03
3.03
1.99
1.99
2.00
1.02
6.21
2.08
f1 (ppm)


162.633
159.726
140.312
131.480
129.570
129.219
121.079
114.575
114.147
111.697
55.594
55.213
53.533
50.046
38.525
35.764
30.402
25.061
O
O
S
N
OMe
MeO
f1 (ppm)

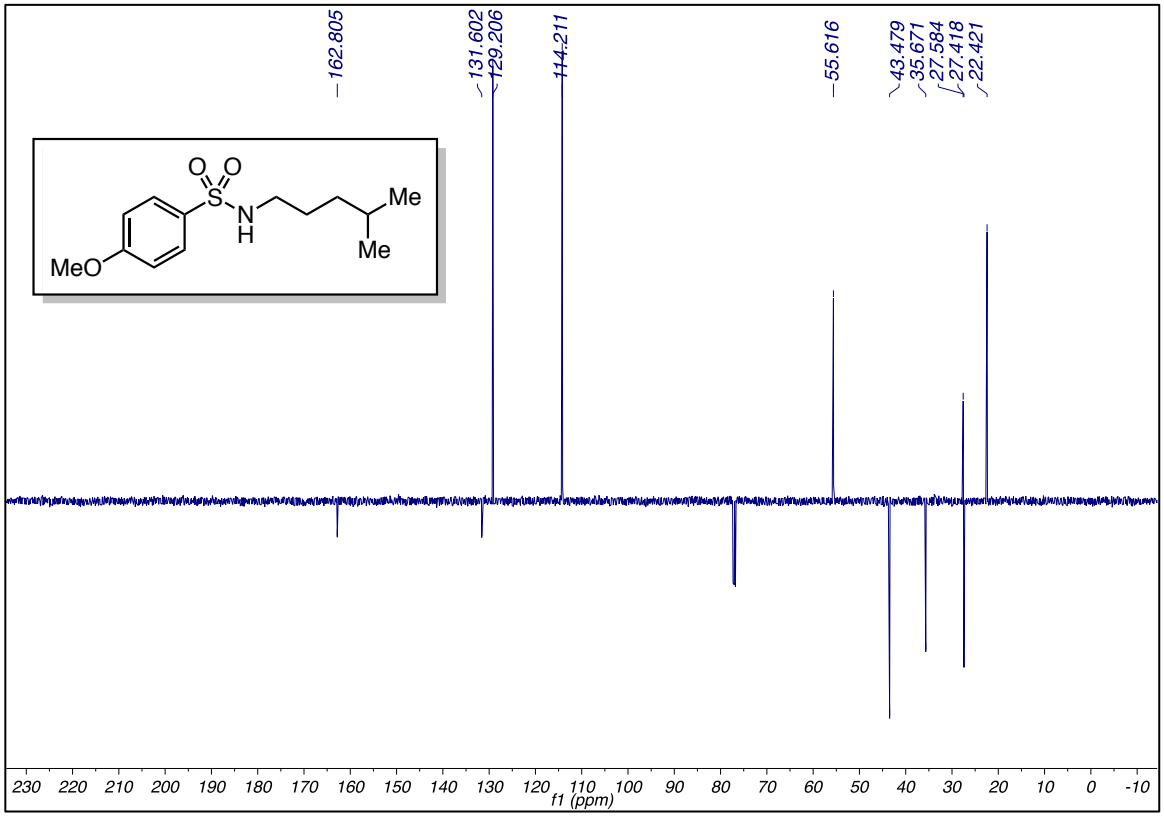

1.99
1.99
0.98
1.00
3.07
3.07
4.04
1.03
3.08
1.54
3.07
5.98
2.10
2.05
f1 (ppm)

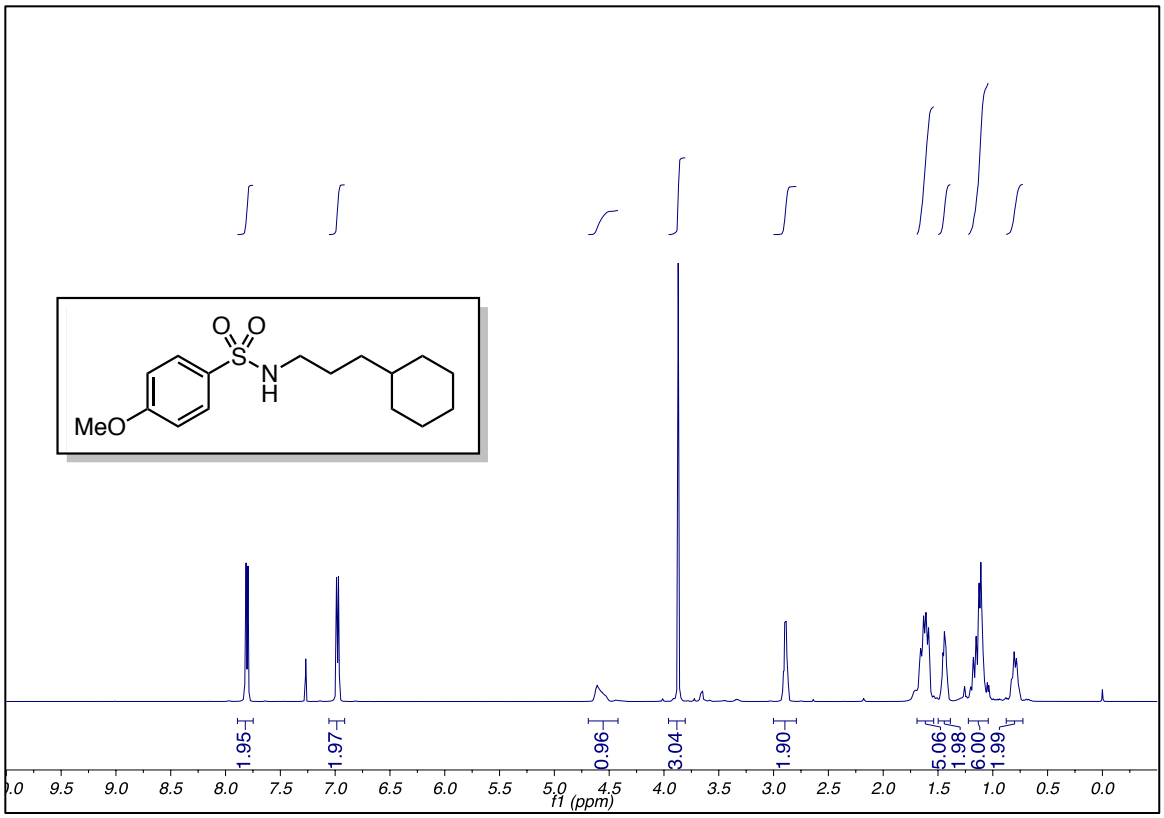

172.946
170.064
162.635
131.231
129.177
114.134
55.599
53.755
52.412
52.133
48.127
38.602
31.640
30.402
28.268
25.016
23.144
22.182
NHAc
COOMe
MeO
f1 (ppm)

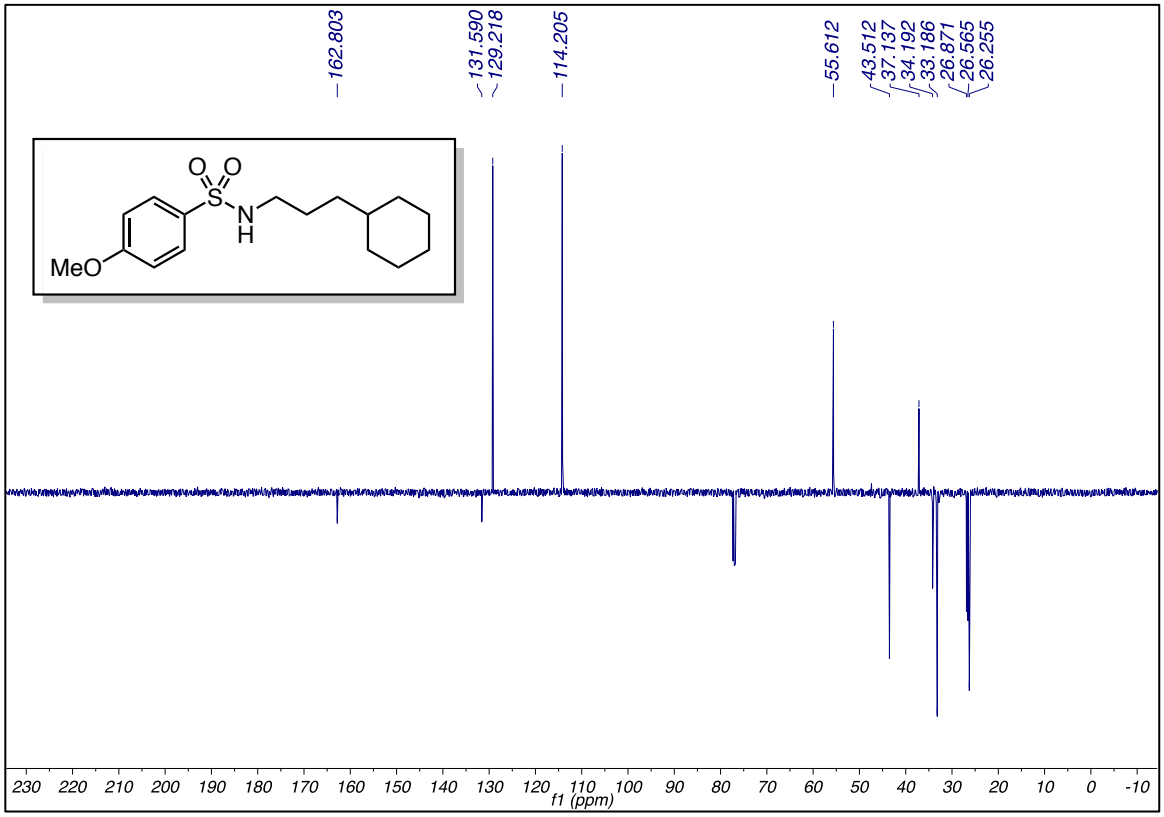

1.96
1.97
0.99
0.97
1.98
0.95
2.94
2.94
0.98
4.64
5.06
19.31
5.93
5.98
1.11
f1 (ppm)

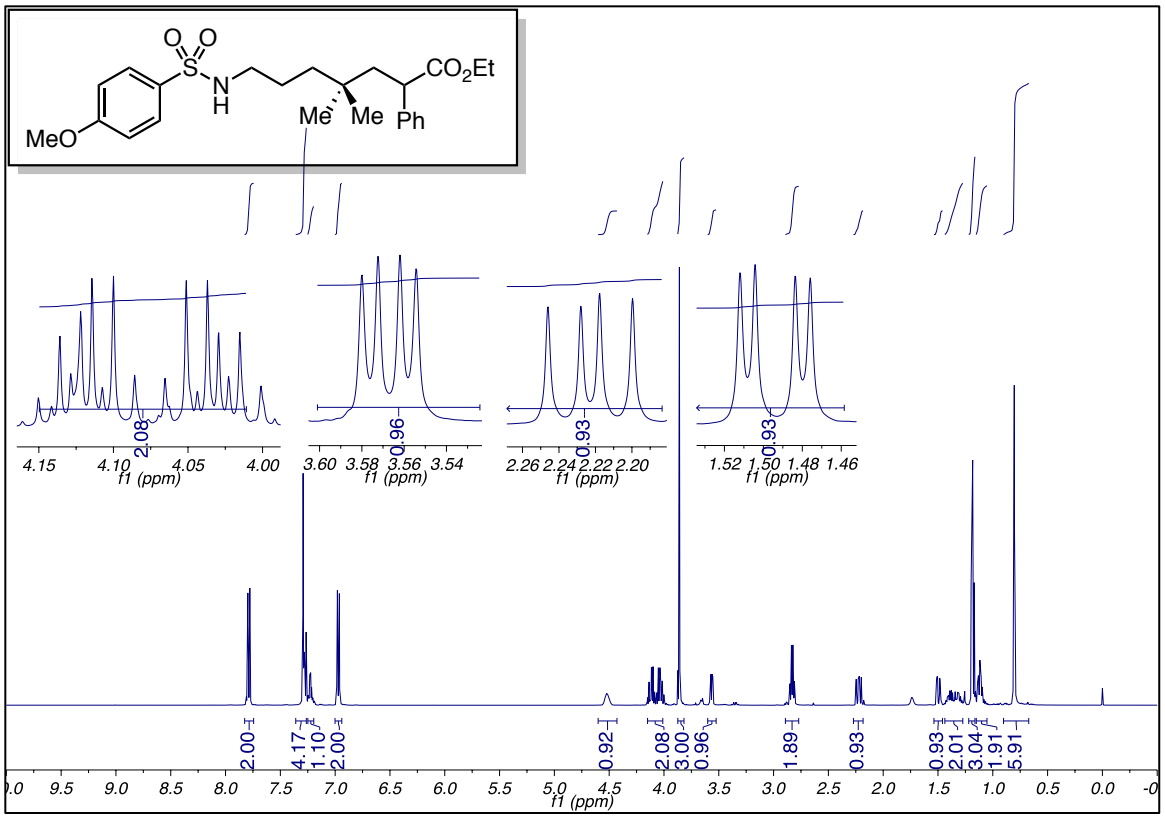

221.337
172.515
161.903
133.115
129.084
114.471
73.723
67.172
54.274
53.777
51.339
47.789
44.634
37.209
36.671
35.857
35.642
35.008
34.677
33.969
31.506
30.948
30.789
28.261
27.433
27.349
24.461
22.457
21.777
20.460
18.465
13.946
13.885
13.822
12.217
f1 (ppm)

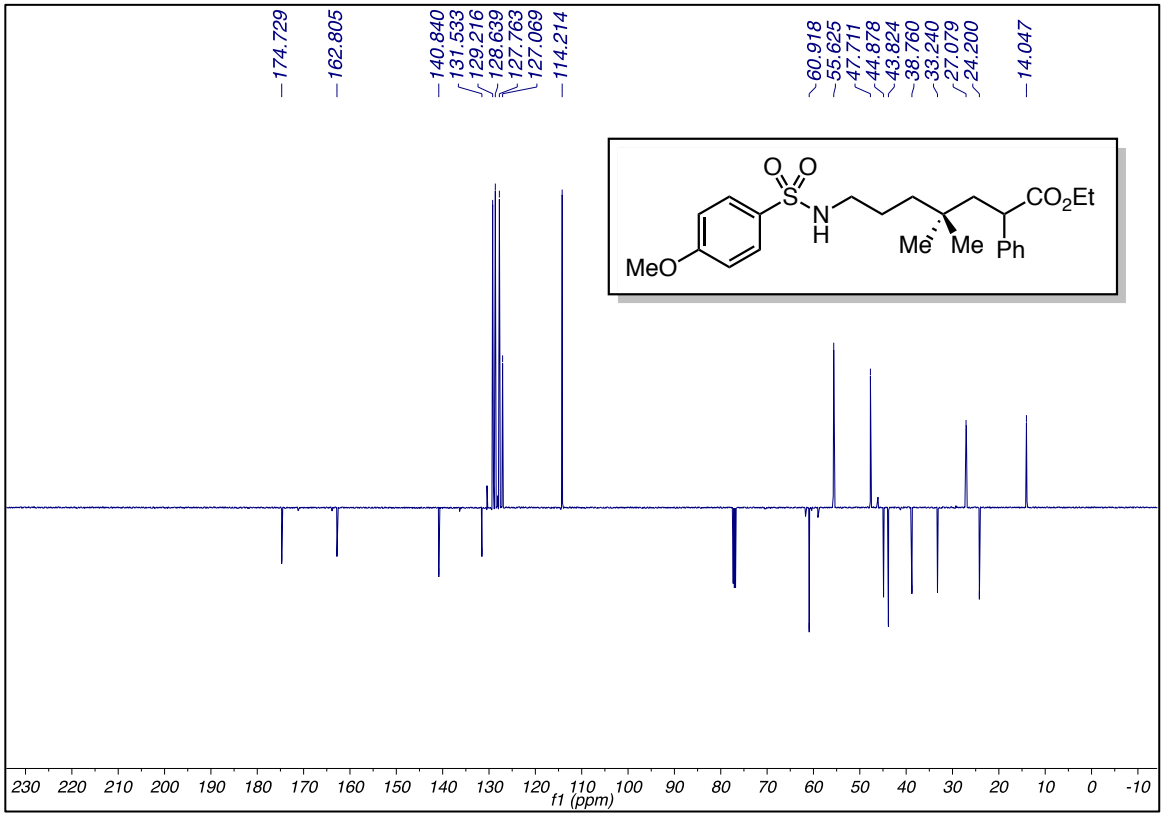

O
O
S
N
H
Me
Me
MeO
1.95
1.96
0.96
3.04
1.99
2.96
1.98
2.92
3.04
f1 (ppm)

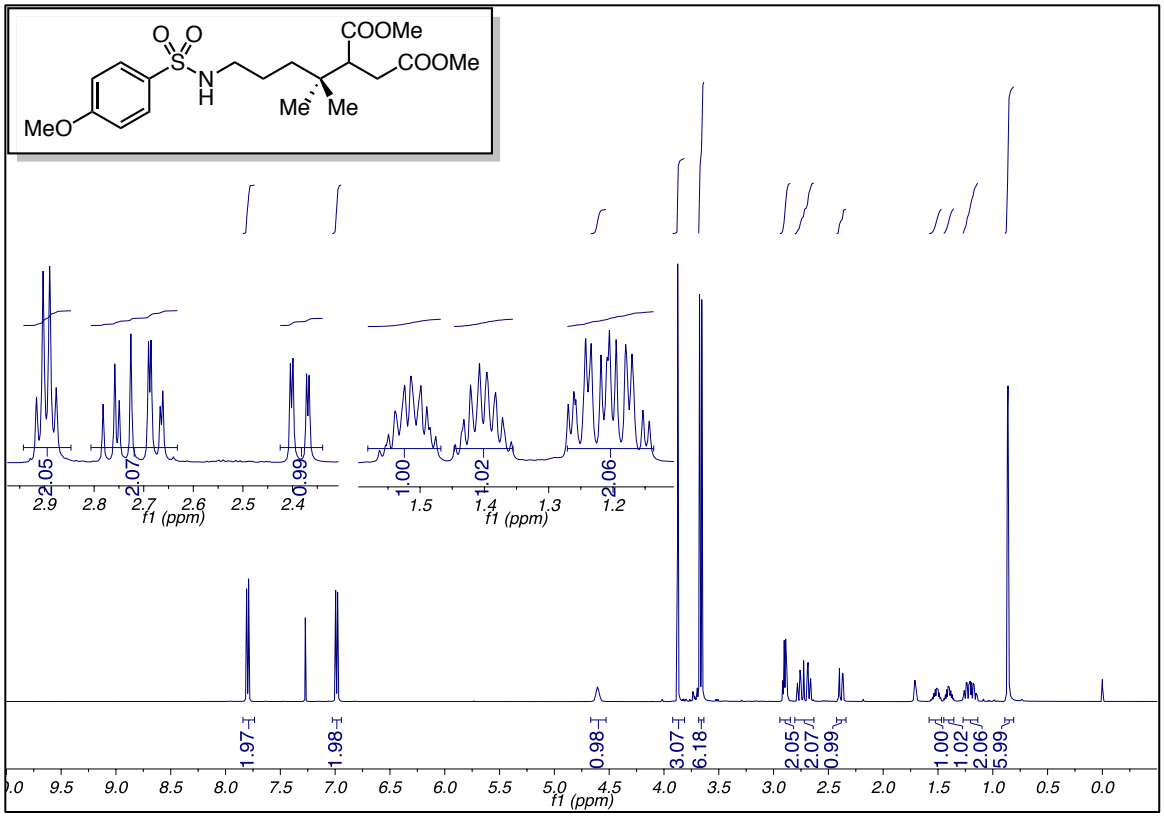

162.805
131.602
129.206
114.211
55.616
43.479
35.671
27.584
27.418
22.421
O
O
S
N
H
Me
Me
MeO
f1 (ppm)

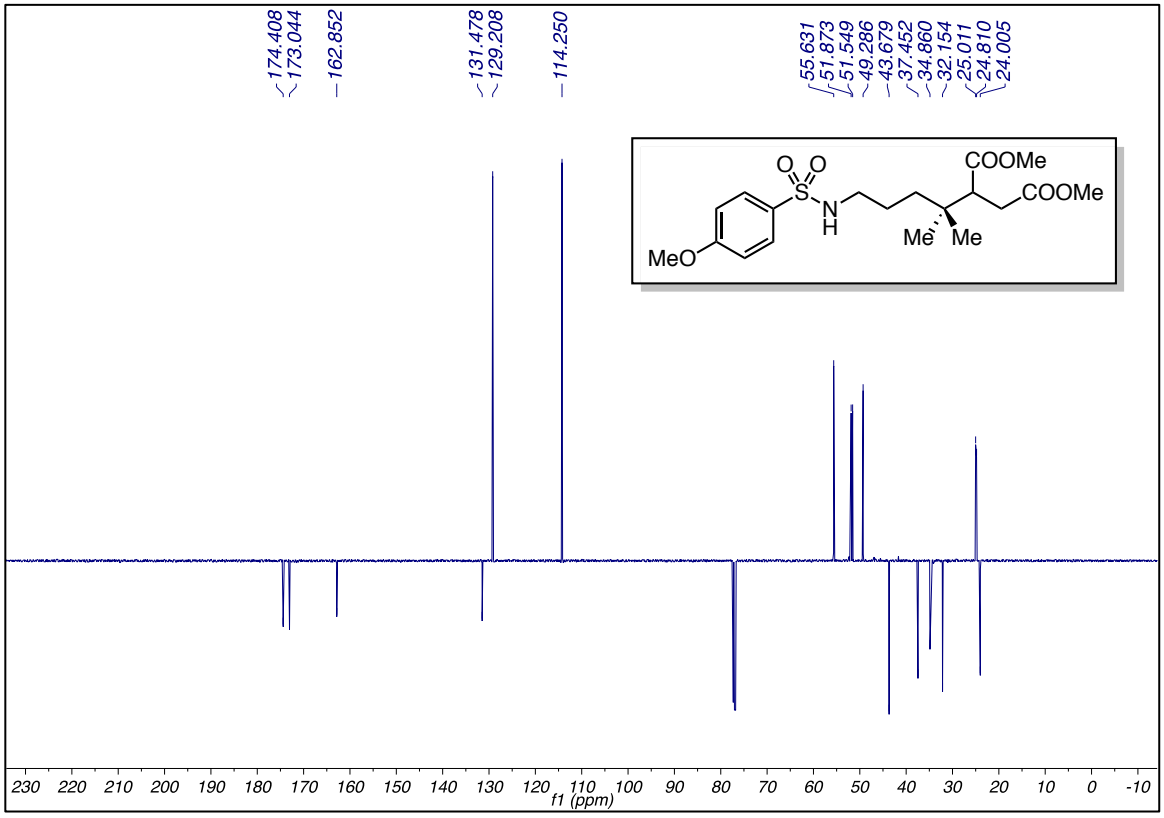

MeO
1.95
1.97
0.96
3.04
1.90
5.06
1.98
6.00
1.99
f1 (ppm)

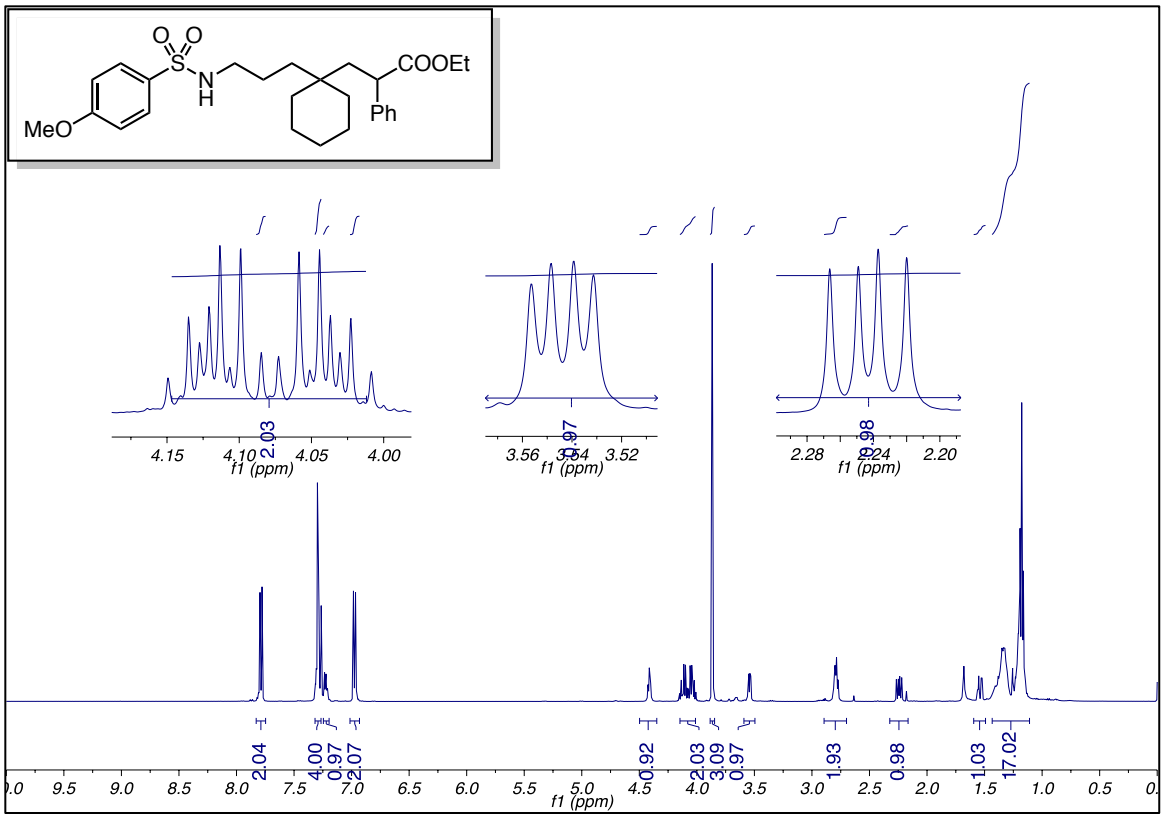

162.803
131.590
129.218
114.205
55.612
43.512
37.137
34.192
33.186
26.871
26.565
26.255
MeO
f1 (ppm)

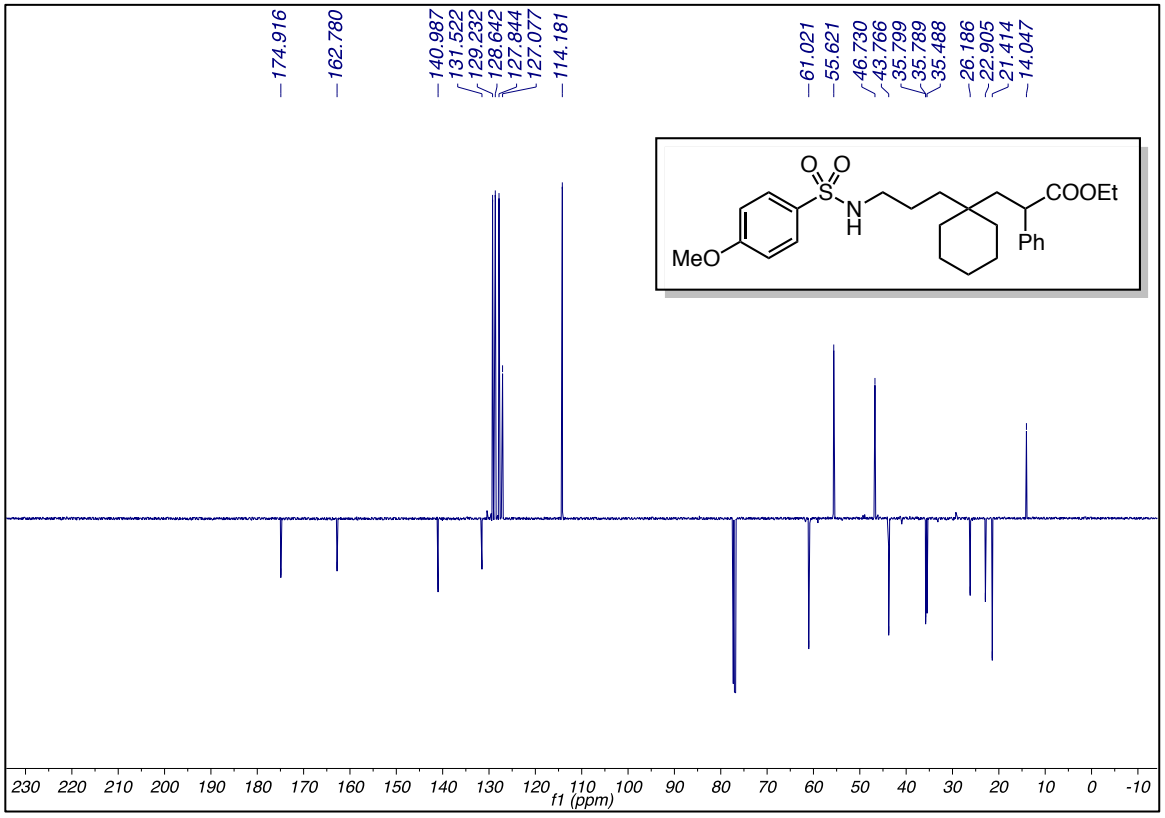

MeO
Me
Me
Ph
CO2Et
f1 (ppm)


174.729
162.805
140.840
131.533
129.216
128.639
127.763
127.069
114.214
60.918
55.625
47.711
44.878
43.824
38.760
33.240
27.079
24.200
14.047
MeO
Me
Me
Ph
CO2Et
f1 (ppm)


COOMe
COOMe
Me Me
MeO
1.97
1.98
0.98
3.07
6.18
2.05
2.07
0.99
1.00
1.02
2.06
5.99
f1 (ppm)


174.408
173.044
162.852
131.478
129.208
114.250
55.631
51.873
51.549
49.286
43.679
37.452
34.860
32.154
25.011
24.810
24.005
COOMe
COOMe
Me Me
MeO
f1 (ppm)


MeO
Ph
COOEt
f1 (ppm)


MeO
Ph
COOEt
f1 (ppm)