Supporting Information

Selective Piperidine Synthesis Exploiting Iodine-Catalyzed C_{sp}^3-H Amination under Visible Light

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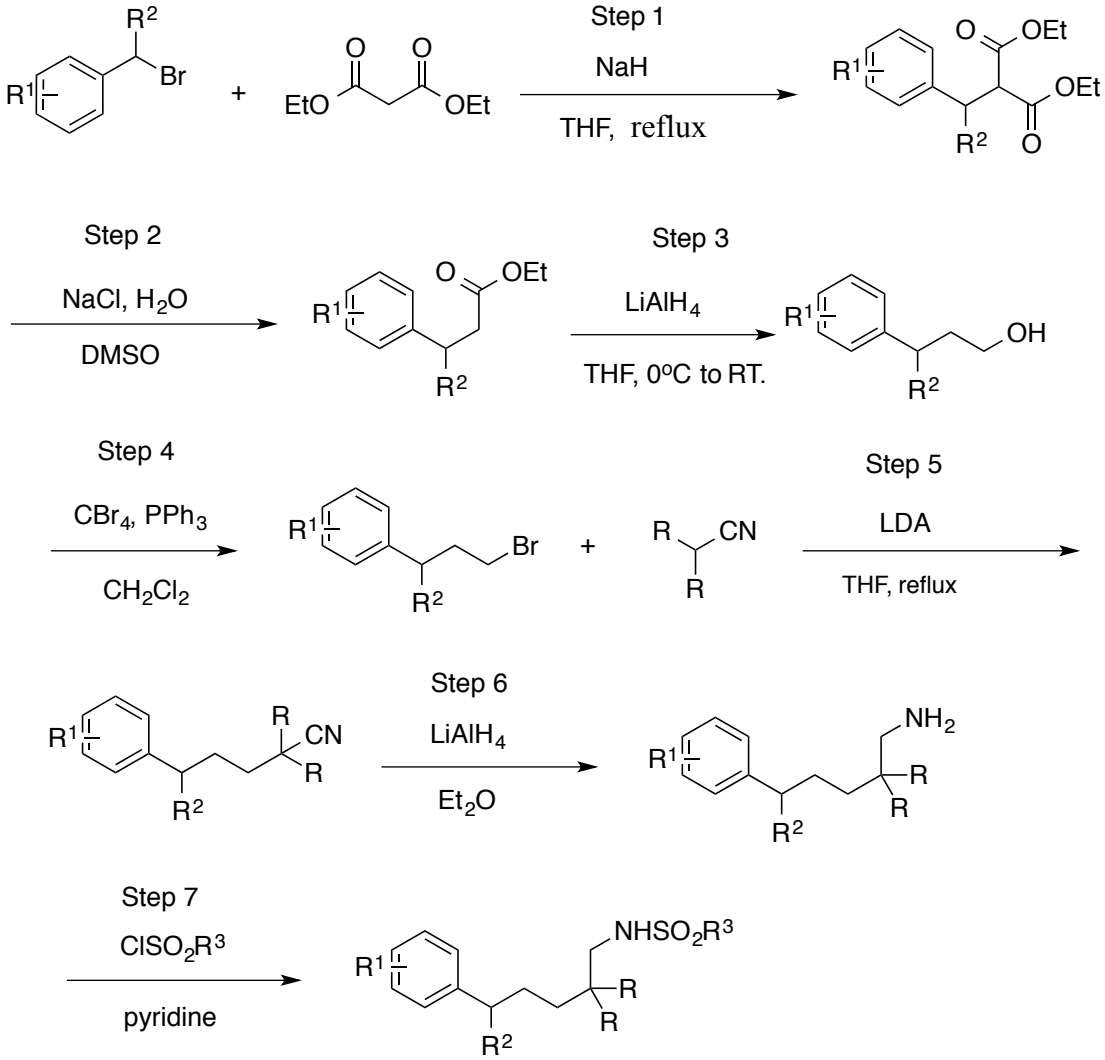
Table of contents

1- General remarks

If not otherwise stated, All solvents, reagents and all deuterated solvents were purchased from Aldrich and TCI commercial suppliers. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2 mm). NMR spectra were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer, respectively. All chemical shifts in NMR experiments were reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ δ = 7.26 and 77.0 ppm, CD_2Cl_2 δ = 5.32 and 54.00 ppm, $(CD_2Cl)_2$ δ = 5.32 ppm. MS (ESI-LCMS) experiments were performed using an Agilent 1100 HPLC with a Bruker micro-TOF instrument (ESI). A Supelco C8 (5 cm x 4.6 mm, 5 μm particles) column was used with a linear elution gradient from 100% H_2O (0.5% HCO_2H) to 100% MeCN in 13 min at a flow rate of 0.5 mL/min. MS (EI) and HRMS experiments were performed on a Kratos MS 50 within the service centres at ICIQ. IR spectra were taken in a Bruker Alpha instrument in the solid state.

2- General procedure for the synthesis of starting materials

Starting materials were synthesised according to procedures described previously in the literature.[1,2]



Scheme S1. synthesis of starting materials

Step 1

Diethyl malonate (1.05 equiv) was added drop-wise to a suspension of NaH (55%, 1.05 equiv) in THF at 0 °C and was stirred for 15 min. Benzyl bromide was then added in one portion and the resulting milky mixture was stirred at reflux for 1 h. The reaction was then cooled and quenched by the addition of H_2O. THF was removed under reduced pressure and the resulting crude was dissolved in Et_2O and washed with water. The aqueous layer was extracted with Et_2O (4 x), and the combined organics were washed with brine, dried over

$MgSO_4$ and filtered. The solvent was evaporated under reduced pressure. The crude product was directly used for the subsequent step.

Step 2

A solution of the diester (1.0 equiv), NaCl (2.1 equiv), and H_2O (2.1 equiv) in DMSO (30 mL) was heated at reflux for 8 h. The reaction was then cooled to 25 ºC, diluted with a solution 3N HCl and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with water (5 x 50 mL), then brine (1 x 100 mL) and dried over $MgSO_4$. The crude brown oil was then filtered through a pad of silica to obtain the desired ester in a quantitative yield.

Step 3

$LiAlH_4$ (2.0 equiv) was added slowly to the THF solution of ester (1.0 equiv) at 0 ºC and then the solution was stirred for two hour at room temperature. After that, a solution of NaOH (10% in water) was added carefully until a white solid precipitated. After filtration over $MgSO_4$ and evaporation of the solvent the crude amine was obtained in quantitative yields.

Step 4

A solution of the propanol (1.0 equiv) in CH_2Cl_2 at 0 ºC was treated with CBr_4 (1.05 equiv) followed by the portionwise addition of triphenylphosphine (1.05 equiv). The reaction was allowed to warm to 25 ºC, and monitored by TLC. No starting material remained after 3 h. The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, *n*-hexane) to give the pure product bromide.

Step 5

A Schlenk tube equipped with a stirrer bar was charged with the corresponding nitrile compound (1.2 equiv) and THF (20 mL). LDA (1.2 equiv) was added drop-wise at -78 ºC and the solution was stirred for 30 min. After that period, the corresponding bromide (1.0 equiv) was added in a single portion and the mixture was stirred at room temperature for 12 h. A saturated aqueous solution of NH_4Cl was added and the resulting mixture was extracted with CH_2Cl_2 (3x). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was directly used for the subsequent reduction step.

Step 6

A flame dried Schlenk equipped with a stirrer bar and a reflux condenser was charged with

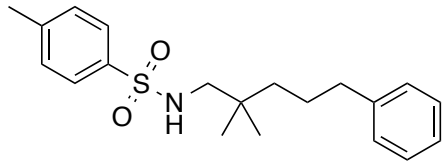
$LiAlH_4$ (3 equiv), Et_2O was added carefully and the mixture was cooled to 0 ºC with an external ice/water cooling bath. The crude nitrile (1 equiv) was dissolved in a small volume of Et_2O and added carefully to the $LiAlH_4$ suspension. The mixture was heated to reflux for 2 h and cooled to 0 ºC afterwards. A solution of NaOH (10% in water) was added carefully until a white solid precipitated. After filtration over $MgSO_4$ and evaporation of the solvent the crude amine was obtained in quantitative yields.

Step 7

The crude amine from step 6 (1 equiv) was dissolved in pyridine (20 mL) and the respective sulfonyl chloride (1.5 equiv) was added at 0 ^oC. The solution was stirred overnight at 25 ºC. CH_2Cl_2 was added, and the mixture was washed three times with a hydrochloride solution (10% HCl in water). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was purified by chromatography (silica gel, *n*-hexane/ethyl acetate) to give the pure product.

3- Data for starting materials

N-(2,2-Dimethyl-5-phenylpentyl)-4-methylbenzenesulfonamide 2a



White solid.

mp: 60-61 ^{o}C.

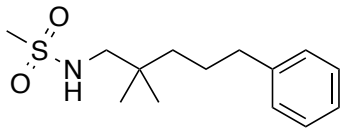
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74-7.71 (m, 2H), 7.31-7.25 (m, 4H), 7.20-7.16 (m, 1H), 7.15-7.13 (m, 2H), 4.42 (d, *J* = 7.1 Hz, 1H), 2.66 (d, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.42 (s, 3H), 1.52-1.44 (m, 2H), 1.25-1.20 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 142.3, 137.0, 129.7, 128.3, 128.3, 127.1, 125.8, 52.87, 39.0, 36.5, 33.7, 25.7, 24.9, 21.5.

IR *v* (cm^{-1}): 3273, 3024, 2959, 2933, 2865.

HRMS (m/z): calcd. for $C_{20}H_{27}NNaO_2S^+$, 368.1655; found, 368.1668.

N-(2,2-Dimethyl-5-phenylpentyl)methanesulfonamide 2b



Yellow oil.

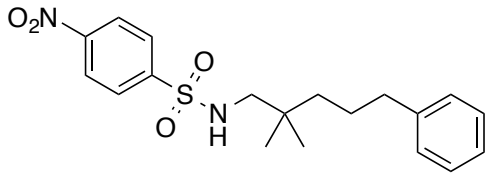
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.27 (m, 2H), 7.21-7.18 (m, 2H), 7.17 (d, *J* = 2.0 Hz, 1H), 4.26 (d, *J* = 7.0 Hz, 1H), 2.91 (s, 3H), 2.88 (d, *J* = 6.8 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.55-1.60 (m, 2H), 1.26-1.31(m, 2H), 0.90 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.3, 128.4, 128.4, 125.8, 53.1, 40.0, 40.0, 36.5, 33.9, 25.8, 24.8.

IR *v* (cm^{-1}): 3291, 3025, 2937, 2866.

HRMS (m/z): calcd. for $C_{14}H_{23}NNaO_2S^+$, 292.1342; found, 292.1348.

***N*-(2,2-Dimethyl-5-phenylpentyl)-4-nitrobenzenesulfonamide 2c**



White solid.

mp: 71-72 °C.

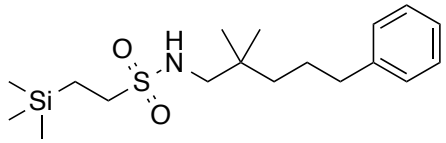
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.30-7.25 (m, 2H), 7.21-7.17 (m, 1H), 7.16-7.13 (m, 2H), 4.66 (d, *J* = 7.2 Hz, 1H), 2.74 (d, *J* = 6.7 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.55-1.47 (m, 2H), 1.20-1.21 (m, 2H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.0, 145.9, 142.1, 128.4, 128.3, 128.2, 125.9, 124.4, 53.1, 38.91, 38.9, 36.4, 33.9, 25.7, 24.8.

IR *v* (cm^{-1}): 3295, 3108, 3024, 2940, 2862.

HRMS (m/z): calcd. for $C_{19}H_{24}N_2NaO_4S^+$, 399.1349 ; found, 399.1352.

***N*-(2,2-Dimethyl-5-phenylpentyl)-2-(trimethylsilyl)ethane-1-sulfonamide 2d**



White solid.

mp: 65-66 °C

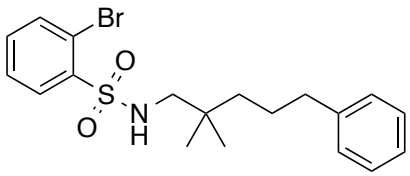
^{1}H NMR (**500 MHz**, **$CDCl_3$**): δ = 7.32–7.26 (m, 2H), 7.21–7.16 (m, 3H), 4.09 (d, *J* = 7.2 Hz, 1H), 2.95–2.88 (m, 2H), 2.85 (d, *J* = 6.8 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.62–1.55(m, 2H), 1.33–1.26 (m, 2H), 1.03–0.97 (m, 2H), 0.90 (s, 6H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.8, 128.7, 127.1 127.0, 55.7, 53.1, 49.6, 32.7, 30.4, 28.6, 26.31, 24.3, 10.5, -2.0.

IR *v* (cm^{-1}): 3276, 3065, 3024, 2951.

HRMS (m/z): calcd. for $C_{18}H_{33}NNaO_2SSi^+$, 378.1893; found, 378.1897.

2-Bromo-*N*-(2,2-dimethyl-5-phenylpentyl)benzenesulfonamide 2e



White solid.

mp: 59-60 °C.

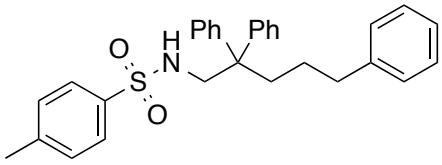
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.49 (td, *J* = 7.6, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.9 Hz, 1H), 7.32-7.28 (m, 2H), 7.23-7.16 (m, 3H), 5.10 (t, *J* = 6.7 Hz, 1H), 2.64 (d, *J* = 6.8 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.57-1.49 (m, 2H), 1.30-1.26 (m, 2H), 0.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.3, 138.7, 134.9, 133.7, 131.7, 128.4, 128.3, 127.9, 125.8, 119.5, 52.9, 39.1, 36.5, 33.7, 25.8, 25.0.

IR *v* (cm^{-1}): 3305, 3098, 3025, 2969, 2937, 2845.

HRMS (m/z): calcd. for $C_{19}H_{24}BrNNaO_2S^+$, 432.0603; found, 432.0615.

4-Methyl-*N*-(2,2,5-triphenylpentyl)benzenesulfonamide 2f



White solid.

mp: 135-136 °C.

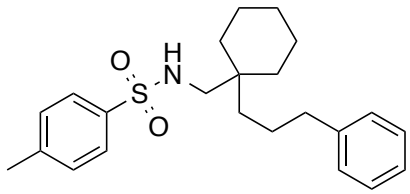
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.60 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.15-7.25 (m, 9H), 7.02 (ddd, *J* = 6.8, 3.6, 1.9 Hz, 6H), 3.85 (t, *J* = 6.5 Hz, 1H), 3.56 (dd, *J* = 6.6, 1.8 Hz, 2H), 2.49 (t, *J* = 7.7 Hz, 2H), 2.41 (s, 3H), 2.18-2.14 (m, 2H), 1.36-1.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0, 143.4, 142.0, 136.4, 129.7, 128.4, 128.3, 128.2, 127.7, 127.1, 126.6, 125.7, 49.7, 49.5, 36.2, 36.1, 25.4, 21.5.

IR *v* (cm^{-1}): 3255, 3087, 3060, 3024, 2941, 2921, 2859.

HRMS (m/z): calcd. for $C_{30}H_{31}NNaO_2S^+$, 492.1968; found, 492.1972.

4-Methyl-*N*-((1-(3-phenylpropyl)cyclohexyl)methyl)benzenesulfonamide 2g



White solid.

mp: 93-94 °C.

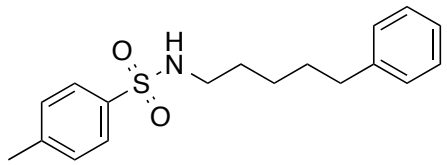
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30-7.28 (m, 3H), 7.26 (d, *J* = 1.5 Hz, 1H), 7.20-7.16 (m, 1H), 7.15-7.12 (m, 2H), 4.43 (t, *J* = 6.8 Hz, 1H), 2.73 (d, *J* = 6.8 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 1.42-1.26 (m, 11H), 1.22 (q, *J* = 6.8, 6.0 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 142.4, 137.0, 129.7, 128.3, 128.3, 127.1, 125.8, 49.0, 36.4, 35.7, 34.7, 33.5, 26.1, 24.6, 21.5, 21.3.

IR *v* (cm^{-1}): 3280, 3031, 2926, 2856.

HRMS (m/z): calcd. for $C_{23}H_{31}NNaO_2S^+$, 408.1968; found, 408.1977.

4-Methyl-*N*-(5-phenylpentyl)benzenesulfonamide 2h



White solid.

mp: 52-53 °C.

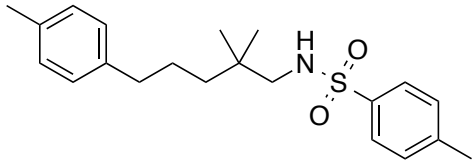
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.28-7.25 (m, 2H), 7.19-7.16 (m, 1H), 7.13-7.12 (m, 2H), 4.41 (t, *J* = 6.2 Hz, 1H), 2.92 (td, *J* = 7.1, 6.1 Hz, 2H), 2.58-2.52 (m, 2H), 2.42 (s, 3H), 1.59-1.45 (m, 6H), 1.32-1.26 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.4, 142.2, 137.0, 129.7, 128.3, 128.3, 127.1, 125.8, 43.1, 35.7, 30.8, 29.5, 26.1, 21.5.

IR *v* (cm^{-1}): 3288, 3270, 3027, 2928, 2862.

HRMS (m/z): calcd. for $C_{18}H_{23}NNaO_2S^+$, 340.1342; found, 340.1344.

***N*-(2,2-Dimethyl-5-(*p*-tolyl)pentyl)-4-methylbenzenesulfonamide 2i**



White solid.

mp: 80-81 ^{o}C.

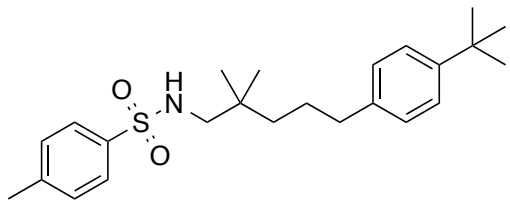
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 6.8 Hz, 1H), 2.66 (d, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 7.7 Hz, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 1.48-1.42 (m, 2H), 1.22-1.19 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.3, 139.2, 137.0, 135.2, 129.7, 129.0, 128.2, 127.1, 52.9, 39.0, 36.0, 33.7, 25.8, 24.9, 21.5, 21.0.

IR *v* (cm^{-1}): 3275, 2957, 2931, 2873.

HRMS (m/z): calcd. for $C_{21}H_{29}NNaO_2S^+$, 382.1811; found, 382.1811.

***N*-(5-(4-(*tert*-Butyl)phenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2j**



White solid.

mp: 120-121 ^{o}C.

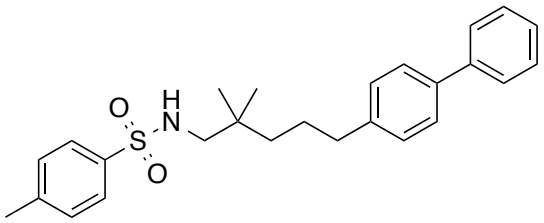
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 4H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.63 (t, *J* = 6.6 Hz, 1H), 2.67 (d, *J* = 6.8 Hz, 2H), 2.49 (t, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 1.51-1.44 (m, 2H), 1.32 (s, 9H), 1.26-1.23 (m, 2H), 0.84 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.5, 143.3, 139.3, 137.1, 129.7, 128.0, 127.1, 125.2, 52.9, 39.2, 36.0, 34.4, 33.8, 31.4, 25.8, 24.9, 21.5.

IR *v* (cm^{-1}): 3284, 2956, 2867.

HRMS (m/z): calcd. for $C_{24}H_{35}NNaO_2S^+$, 424.2281; found, 424.2282.

***N*-(5-([1,1'-Biphenyl]-4-yl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2k**



White solid.

mp: 97-98 °C.

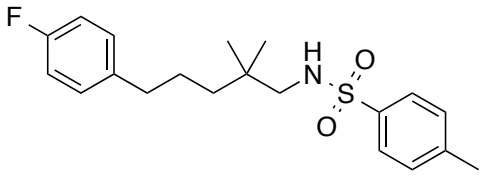
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.59 (dt, *J* = 7.7, 1.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35-7.31 (m, 1H), 7.32-7.29 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.50 (t, *J* = 6.8 Hz, 1H), 2.69 (d, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.41 (s, 3H), 1.55-1.50 (m, 2H), 1.29-1.25 (m, 2H), 0.85 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.3, 141.5, 141.1, 138.8, 137.1, 129.7, 128.8, 128.7, 127.1, 127.1, 127.0, 127.0, 52.9, 39.1, 36.1, 33.8, 25.7, 24.9, 21.5.

IR *v* (cm^{-1}): 3271, 3028, 2957, 2934, 2869.

HRMS (m/z): calcd. for $C_{26}H_{31}NNaO_2S^+$, 444.1968; found, 444.1963.

***N*-(5-(4-Fluorophenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2l**



White solid.

mp: 61-62 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.31-7.29 (m, 2H), 7.08 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 2.68-2.64 (m, 2H), 2.50 (t, *J* = 7.7 Hz, 2H), 2.42 (s, 3H), 1.49-1.43 (m, 2H), 1.26-1.20 (m, 2H), 0.82 (s, 6H).

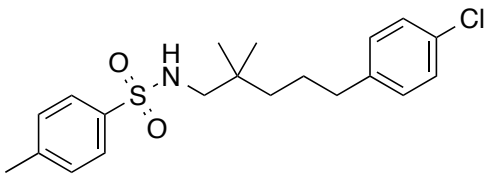
^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.0 (d, $J_{C\text{-}F}$ = 242.7 Hz), 143.3, 137.9, 137.1, 129.7, 129.7, 129.6, 127.1, 115.1 (d, $J_{C\text{-}F}$ = 21.1 Hz), 52.9, 38.9, 35.6, 33.7, 25.8, 24.9, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -117.94- -118.02 (m, 1F).

IR *v* (cm^{-1}): 3289, 2968, 2942, 2860.

HRMS (m/z): calcd. for $C_{20}H_{25}FNO_2S^-$, 362.1596; found, 362.1607.

***N*-(5-(4-Chlorophenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2m**



White solid.

mp: 62-63 °C.

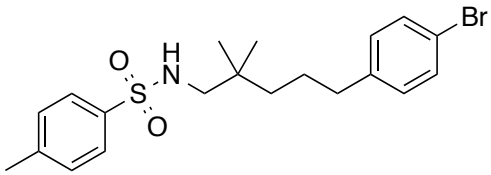
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30-7.28 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.73 (t, *J* = 6.8 Hz, 1H), 2.65 (d, *J* = 6.9 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.48-1.43 (m, 2H), 1.23-1.18 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 140.8, 137.0, 131.4, 129.7, 128.4, 127.1, 52.8, 38.85, 35.8, 33.7, 25.6, 24.9, 21.5.

IR *v* (cm^{-1}): 3266, 2964, 2937, 2857.

HRMS (m/z): calcd. for $C_{20}H_{26}ClNNaO_2S^+$, 402.1265; found, 402.1269.

***N*-(5-(4-Bromophenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2n**



White solid.

mp: 71-72 °C.

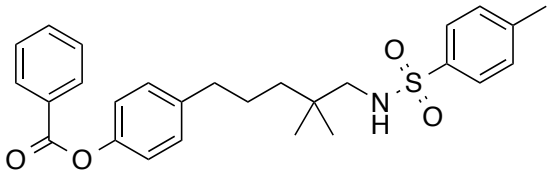
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 6.4, 1.8 Hz, 2H), 7.38 (dd, *J* = 6.4, 1.9 Hz, 2H), 7.29-7.30 (m, 2H), 7.01 (dd, *J* = 6.4, 2.0 Hz, 2H), 4.33 (s, 1H), 2.66 (d, *J* = 6.9 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.48-1.44 (m, 2H), 1.22-1.19 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.3, 141.3, 137.0, 131.3, 130.1, 129.7, 127.1, 119.5, 52.8, 38.9, 35.9, 33.8, 25.5, 24.9, 21.5.

IR *v* (cm^{-1}): 3302, 2930, 2863.

HRMS (m/z): calcd. for $C_{20}H_{26}BrNNaO_2S^+$, 446.0760; found, 446.0767.

4-(4,4-Dimethyl-5-((4-methylphenyl)sulfonamido)pentyl)phenyl benzoate 2o



White solid.

mp: 105-106 °C

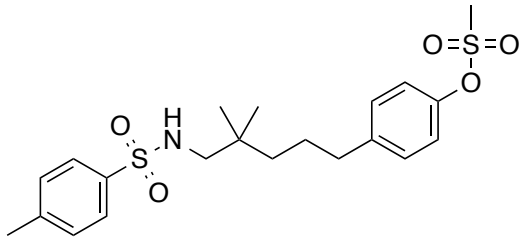
^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.21 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.80–7.72 (m, 2H), 7.67–7.58 (m, 1H), 7.56–7.49 (m, 2H), 7.34–7.28 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 4.74 (t, *J* = 6.8 Hz, 1H), 2.68 (d, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.42 (s, 3H), 1.58–1.43 (m, 2H), 1.35–1.17 (m, 2H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 149.0, 143.3, 140.0, 137.0, 133.7, 133.5, 130.2, 130.2, 129.7, 129.7, 129.3, 128.6, 128.5, 127.1, 121.4, 52.9, 39.0, 35.9, 33.8, 25.7, 24.9, 21.5.

IR *v* (cm^{-1}): 3327, 3282, 2971, 2932.

HRMS (m/z): calcd. for $C_{27}H_{30}NO_4S^-$, 464.1901; found, 464.1888.

4-(4,4-Dimethyl-5-((4-methylphenyl)sulfonamido)pentyl)phenyl methanesulfonate 2p



White solid.

mp: 99-100 °C

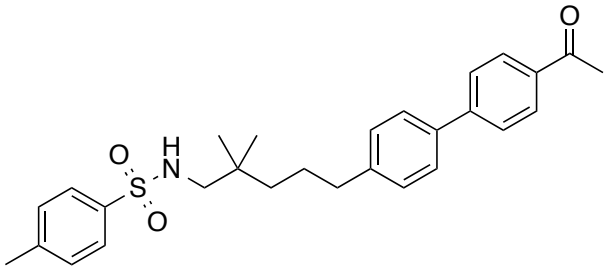
^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.37–7.30 (m, 2H), 7.21 (s, 4H), 4.50 (d, *J* = 7.6 Hz, 1H), 3.15 (s, 3H), 2.69 (d, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.50 (td, *J* = 11.6, 9.9, 6.1 Hz, 2H), 1.28-1.24 (m, 2H), 0.85 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.3, 143.4, 141.8, 137.0, 129.8, 129.7, 127.0, 121.8, 52.8, 38.9, 37.2, 35.9, 33.8, 25.6, 24.9, 21.5.

IR *v* (cm^{-1}): 3278, 2987, 2968, 2939, 2901.

HRMS (m/z): calcd. for $C_{21}H_{28}NO_5S_2^-$, 438.1414; found, 438.1408.

***N*-(5-(4'-Acetyl-[1,1'-biphenyl]-4-yl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2q**



White solid.

mp: 95-96 °C.

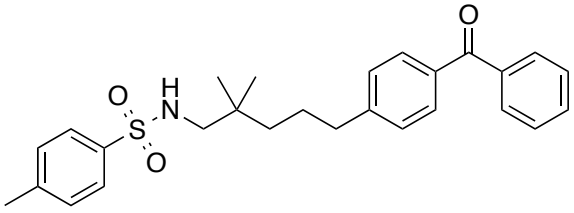
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.99 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.28-7.26 (m, 2H), 7.24-7.22 (m, 2H), 4.38 (t, *J* = 6.8 Hz, 1H), 2.66 (d, *J* = 6.9 Hz, 2H), 2.61 (s, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.39 (s, 3H), 1.56-1.41 (m, 2H), 1.26-1.22 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.8, 145.7, 143.3, 142.7, 137.4, 137.1, 135.7, 129.7, 129.0, 128.9, 127.2, 127.1, 127.0, 52.9, 39.0, 36.1, 33.8, 26.7, 25.6, 24.9, 21.5.

IR *v* (cm^{-1}): 3262, 3028, 2968, 2865.

HRMS (m/z): calcd. for $C_{28}H_{33}NNaO_3S^+$, 486.2073; found, 486.2067.

***N*-(5-(4-benzoylphenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2r**



Oil.

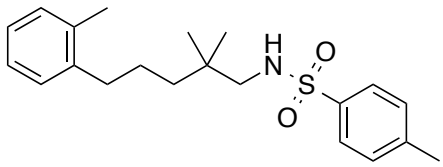
^{1}H NMR (**500 MHz**, **$CDCl_3$**): δ = 7.82 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.79–7.74 (m, 4H), 7.62-7.58 (m, 1H), 7.52–7.49 (m, 2H), 7.33 (dt, *J* = 7.9, 0.7 Hz, 2H), 7.28–7.26 (m, 2H), 4.40 (t, *J* = 6.9 Hz, 1H), 2.71 (d, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.60–1.54 (m, 2H), 1.31–1.26 (m, 2H), 0.86 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.5, 147.5, 143.4, 137.9, 137.0, 135.3, 132.2, 130.4, 130.0, 129.7, 128.3, 128.2, 127.1, 52.9, 38.9, 36.5, 33.8, 25.4, 24.9, 21.5.

IR *v* (cm^{-1}): 3291, 3059, 2953, 2866.

HRMS (m/z): calcd. for $C_{27}H_{31}NNaO_3S^+$, 472.1917; found, 472.1925.

***N*-(2,2-Dimethyl-5-(*o*-tolyl)pentyl)-4-methylbenzenesulfonamide 2s**



White solid.

mp: 94-95 °C.

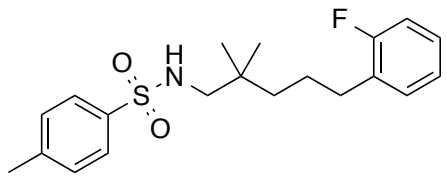
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.30 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.15-7.08 (m, 4H), 4.78 (s, 1H), 2.68 (d, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 1.49-1.41 (m, 2H), 1.31-1.27 (m, 2H), 0.85 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 140.6, 137.1, 135.8, 130.1, 129.7, 128.7, 127.1, 125.9, 52.9, 39.4, 33.8, 24.9, 24.5, 21.5, 19.3.

IR *v* (cm^{-1}): 3269, 2954, 2930, 2875.

HRMS (m/z): calcd. for $C_{21}H_{29}NNaO_2S^+$, 382.1811; found, 382.1809.

***N*-(5-(2-Fluorophenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2t**



White solid.

mp: 68-69 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.33-7.31 (m, 2H), 7.21-7.15 (m, 2H), 7.07 (td, *J* = 7.4, 1.3 Hz, 1H), 7.02 (ddd, *J* = 9.6, 8.1, 1.2 Hz, 1H), 4.44 (s, 1H), 2.69 (d, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.53-1.47 (m, 2H), 1.28-1.23 (m, 2H), 0.85 (s, 6H).

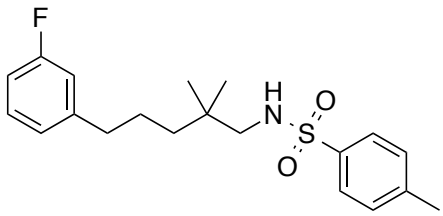
^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.0 (d, $J_{C\text{-}F}$ = 244.0 Hz), 160.1, 143.3, 137.0, 130.6, 130.5, 129.7, 129.1, 129.0, 128.3, 127.5, 127.5, 127.1, 123.9, 123.9, 115.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 52.9, 39.0, 33.8, 29.5, 29.5, 24.9, 24.4, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): -119.00 - -119.07 (m, 1F).

IR *v* (cm^{-1}): 3254, 2957, 2930.

HRMS (m/z): calcd. for $C_{20}H_{26}FNNaO_2S^+$, 386.1560; found, 386.1566.

***N*-(5-(3-Fluorophenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2u**



White solid.

mp: 64-65 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (dt, *J* = 8.0, 0.8 Hz, 2H), 7.22 (td, *J* = 7.9, 6.1 Hz, 1H), 6.91 (ddd, *J* = 7.6, 1.6, 0.9 Hz, 1H), 6.87-6.82 (m, 2H), 4.36 (t, *J* = 6.8 Hz, 1H), 2.67 (d, *J* = 6.7 Hz, 2H), 2.52 (t, *J* = 7.7 Hz, 2H), 2.42 (s, 3H), 1.54-1.44 (m, 2H), 1.23-1.20 (m, 2H), 0.83 (s, 6H).

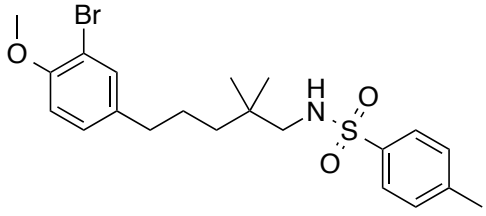
^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.0 (d, J_{C-F} = 234.0 Hz), 145, 143.3, 137.0, 129.7, 129.6, 127.1, 124.0, 124.0, 115.0 (d, J_{C-F} = 20.4 Hz), 112.0 (d, J_{C-F} = 22.0 Hz), 52.81, 38.9, 36.2, 36.2, 33.8, 25.4, 24.9, 24.9, 21.5.

IR *v* (cm^{-1}): 3293, 2965, 2929, 2864.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -113.95 - -114.01 (m, 1F).

HRMS (m/z): calcd. for $C_{20}H_{26}FNNaO_2S^+$, 386.1560; found, 386.1563.

***N*-(5-(3-Bromo-4-methoxyphenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide 2v**



White solid.

mp: 81-82 °C.

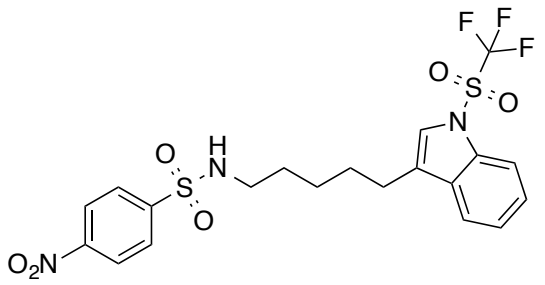
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.34-7.29 (m, 3H), 7.06 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.89 (s, 3H), 2.68 (d, *J* = 6.9 Hz, 2H), 2.46 (t, *J* = 7.7 Hz, 5H), 2.44 (s, 4H), 1.49-1.43 (m, 2H), 1.24-1.21 (m, 2H), 0.85 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.0, 143.3, 137.0, 136.1, 133.0, 129.7, 128.2, 127.1, 111.9, 111.4, 56.3, 52.8, 38.8, 35.2, 33.8, 25.7, 24.9, 21.5.

IR *v* (cm^{-1}): 3288, 3270, 3027, 2928, 2862.

HRMS (m/z): calcd. for $C_{21}H_{28}BrNNaO_3S^+$, 476.0865; found, 476.0865.

4-Nitro-*N*-(5-(1-((trifluoromethyl)sulfonyl)-1*H*-indol-3-yl)pentyl)benzenesulfonamide 2w



White solid.

mp: 91-92 °C

^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.36 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.92-7.85 (m, 1H), 7.58-7.51 (m, 1H), 7.45-7.32 (m, 2H), 7.09 (s, 1H), 4.60 (t, *J* = 6.2 Hz, 1H), 3.08-2.98 (m, 2H), 2.72-2.63 (m, 2H), 1.74-1.66 (m, 2H), 1.64-1.51 (m, 2H), 1.47-1.36 (m, 2H).

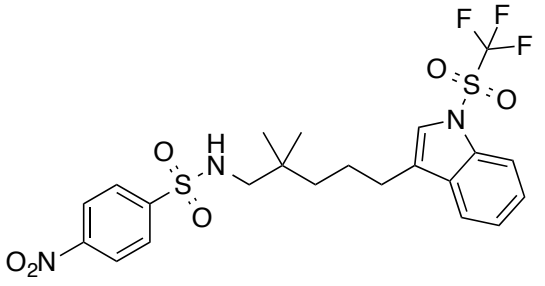
^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.1, 146.0, 135.7, 131.1, 128.3, 125.9, 125.3, 124.7, 124.4, 122.1, 121.2, 119.9, 118.0, 113.9, 43.3, 29.6, 28.0, 26.2, 24.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.42 (s, 3F).

IR *v* (cm^{-1}): 3274, 3120, 2943, 2860.

HRMS (m/z): calcd. for $C_{20}H_{20}F_3N_3NaO_6S_2^+$, 542.0638; found, 542.0649.

***N*-(2,2-Dimethyl-5-(1-((trifluoromethyl)sulfonyl)-1*H*-indol-3-yl)pentyl)-4-nitrobenzenesulfonamide 2x**



White solid.

mp: 88-89 °C

^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.36 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.91-7.87 (m, 1H), 7.59-7.55 (m, 1H), 7.39 (td, *J* = 7.4, 1.5 Hz, 2H), 7.11 (s, 1H), 4.64 (t, *J* = 6.8 Hz, 1H), 1.72-1.61 (m, 2H), 1.38-1.31 (m, 2H), 0.87 (s, 6H).

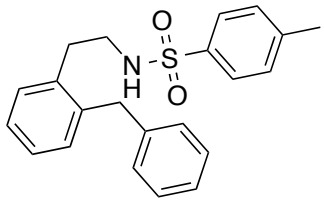
^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.1, 145.9, 135.7, 131.1, 128.2, 125.9, 125.4, 124.7, 124.4, 124.4, 122.2, 119.9, 113.9, 53.2, 39.1, 33.9, 25.4, 24.8, 22.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -75.29 (s, 3F).

IR *v* (cm^{-1}): 3850, 3742, 3267, 2943.

HRMS (m/z): calcd. for $C_{22}H_{24}F_3N_3NaO_6S_2^+$, 570.0951; found, 570.0961.

N-(2-Benzylphenethyl)-4-methylbenzenesulfonamide 2y



White solid.

mp: 89-90 °C.

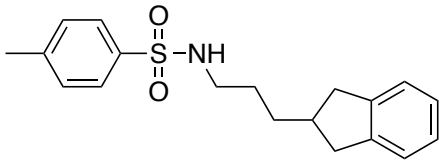
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.2 Hz, 2H), 7.24-7.27 (m, 2H), 7.24-7.21 (m, 2H), 7.19-7.15 (m, 3H), 7.12 (dt, *J* = 5.9, 3.0 Hz, 1H), 7.08-7.06 (m, 1H), 7.05-7.02 (m, 2H), 4.34 (s, 1H), 3.94 (s, 2H), 3.05-3.00 (m, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.4, 140.5, 138.8, 136.9, 136.2, 131.0, 129.7, 129.7, 128.6, 128.5, 127.1, 127.0, 126.9, 126.2, 43.4, 39.0, 32.9, 21.5.

IR *v* (cm^{-1}): 3334, 3278, 3061, 3024, 2958, 2870.

HRMS (m/z): calcd. for $C_{22}H_{23}NNaO_2S^+$, 388.1342; found, 388.1336.

N-(3-(2,3-Dihydro-1*H*-inden-2-yl)propyl)-4-methylbenzenesulfonamide 2z



White solid.

mp: 83-84 °C.

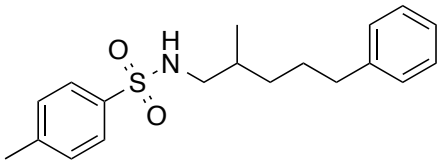
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.31 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.18-7.13 (m, 2H), 7.13-7.09 (m, 2H), 4.65 (s, 1H), 2.97 (ddt, *J* = 9.2, 6.4, 3.5 Hz, 4H), 2.50 (dd, *J* = 15.4, 8.1 Hz, 2H), 2.43 (s, 3H), 2.34 (ddd, *J* = 15.1, 8.2, 7.1 Hz, 1H), 1.50-1.56 (m, 2H), 1.42-1.48 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.4, 143.2, 137.0, 129.7, 127.1, 126.1, 124.4, 43.4, 39.6, 39.1, 32.5, 28.4, 21.5.

IR *v* (cm^{-1}): 3256, 3062, 3015, 2949, 2928, 2834.

HRMS (m/z): calcd. for $C_{19}H_{23}NNaO_2S^+$, 352.1342; found, 352.1330.

4-Methyl-*N*-(2-methyl-5-phenylpentyl)benzenesulfonamide 2aa



Yellow oil.

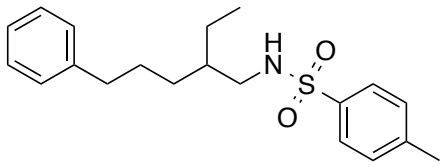
^{1}H NMR (**500 MHz**, **$CDCl_3$**): δ = 7.75–7.71 (m, 2H), 7.32–7.28 (m, 3H), 7.27–7.25 (m, 1H), 7.21–7.16 (m, 1H), 7.15–7.11 (m, 2H), 4.41 (t, *J* = 6.6 Hz, 1H), 2.84 (dt, *J* = 12.5, 6.2 Hz, 1H), 2.73 (dt, *J* = 12.5, 6.7 Hz, 1H), 2.53 (ddd, *J* = 8.6, 6.6, 5.1 Hz, 2H), 2.42 (s, 3H), 1.65–1.54 (m, 1H), 1.54–1.44 (m, 1H), 1.40–1.30 (m, 1H), 1.16–1.06 (m, 1H), 0.86 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 142.3, 137.1, 129.7, 128.3, 128.3, 127.1, 125.8, 49.0, 36.0, 33.5, 33.1, 28.5, 21.5, 17.4.

IR *v* (cm^{-1}): 3284, 3061, 3026, 2929, 2858.

HRMS (m/z): calcd. for $C_{19}H_{25}NNaO_2S^+$, 354.1498; found, 354.1511.

N-(2-Ethyl-5-phenylpentyl)-4-methylbenzenesulfonamide 2ab



White solid,

mp: 56-57 °C.

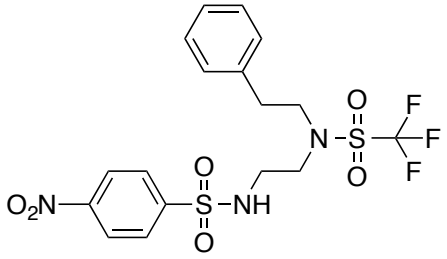
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.32 (dt, *J* = 8.8, 1.4 Hz, 2H), 7.30-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.16-7.14 (m, 2H), 4.46 (s, 1H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.56-1.50 (m, 2H), 1.42 (dt, *J* = 12.4, 6.2 Hz, 1H), 1.34-1.26 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ =143.3, 142.3, 137.0, 129.7, 128.3, 128.3, 127.1, 125.8, 45.7, 39.1, 36.0, 30.5, 28.3, 23.9, 21.5, 10.7.

IR *v* (cm^{-1}): 3277, 3024, 2963, 2932, 2859.

HRMS (m/z): calcd. for $C_{20}H_{27}NNaO_2S^+$, 368.1655; found, 368.1668.

4-Nitro-*N*-(2-((1,1,1-trifluoro-*N*-phenethylmethyl)sulfonamido)ethyl)benzenesulfonamide 2ac



White solid.

mp: 90-91 °C

^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.36 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.35-7.30 (m, 2H), 7.29-7.24 (m, 1H), 7.22-7.16 (m, 2H), 5.05 (t, *J* = 6.2 Hz, 1H), 3.58 (d, *J* = 8.3 Hz, 2H), 3.50 (s, 2H), 3.17 (q, *J* = 6.3 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H).

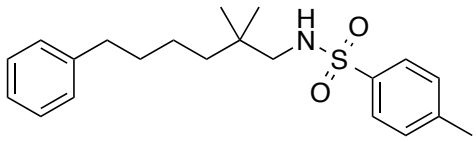
^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.3, 145.3, 136.6, 128.9, 128.7, 128.3, 127.3, 124.6, 121.5, 118.3, 51.5, 48.9, 41.7, 35.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -75.05 (s, 3F).

IR *v* (cm^{-1}): 3861, 3850, 3742, 3276, 3107, 2959.

HRMS (m/z): calcd. for $C_{17}H_{18}F_3N_3NaO_6S_2^+$, 504.0481; found, 504.0485.

N-(2,2-Dimethyl-6-phenylhexyl)-4-methylbenzenesulfonamide 4



White solid.

mp: 81-82 °C.

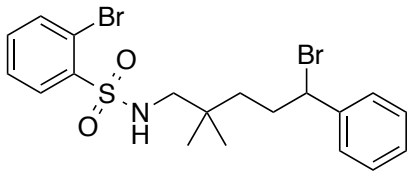
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.74 (m, 2H), 7.36–7.27 (m, 4H), 7.24–7.14 (m, 3H), 4.68 (s, 1H), 2.69 (d, *J* = 6.8 Hz, 2H), 2.64–2.54 (m, 2H), 2.44 (s, 3H), 1.63–1.50 (m, 2H), 1.22 (q, *J* = 2.8, 2.2 Hz, 4H), 0.85 (d, *J* = 1.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 142.6, 137.1, 129.7, 128.3, 128.3, 127.1, 125.6, 53.0, 39.3, 35.8, 33.8, 32.1, 24.9, 23.3, 21.5.

IR *v* (cm^{-1}): 3689, 3675, 3649, 3270, 2972, 2932, 2902.

HRMS (m/z): calcd. for $C_{21}H_{30}NO_2S^+$, 360.1992; found, 360.1998.

2-Bromo-*N*-(5-bromo-2,2-dimethyl-5-phenylpentyl)benzenesulfonamide 7



Oil.

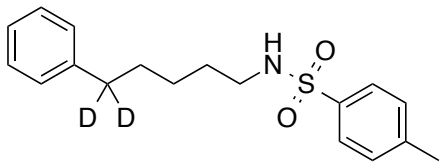
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.39-7.34 (m, 4H), 7.31-7.28 (m, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 4.83 (dd, *J* = 8.0, 6.8 Hz, 1H), 2.61 (dd, *J* = 6.9, 2.5 Hz, 2H), 2.21-2.01 (m, 2H), 1.46 (ddd, *J* = 13.6, 12.1, 4.4 Hz, 1H), 1.15 (ddd, *J* = 13.6, 12.4, 4.6 Hz, 1H), 0.88 (d, *J* = 2.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.9, 138.6, 135.0, 133.7, 131.7, 128.8, 128.4, 127.9, 127.2, 119.5, 55.9, 52.8, 37.7, 34.5, 33.7, 24.9.

IR *v* (cm^{-1}): 3307, 3063, 3029, 2958, 2866.

HRMS (m/z): calcd. for $C_{19}H_{23}Br_2NNaO_2S^+$, 509.9708; found, 509.9683.

4-Methyl-*N*-(5-phenylpentyl-5,5-*d*$_2$)benzenesulfonamide 2h-d$_2$



White solid.

mp: 52-53 °C.

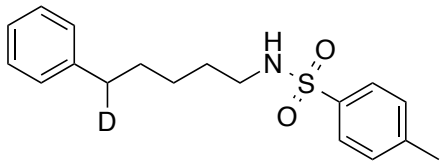
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75-7.72 (m, 2H), 7.32–7.24 (m, 4H), 7.20–7.15 (m, 1H), 7.14–7.10 (m, 2H), 4.33 (t, *J* = 6.2 Hz, 1H), 2.92 (td, *J* = 7.1, 6.2 Hz, 2H), 2.42 (s, 3H), 1.53 (q, *J* = 8.5, 8.1 Hz, 2H), 1.50–1.43 (m, 2H), 1.35–1.25 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.4, 142.1, 137.0, 129.7, 128.3, 128.3, 127.1, 125.8, 43.1, 30.9, 30.7, 29.5, 26.1, 21.5 (benzylic CD_2 not detected).

IR *v* (cm^{-1}): 3287, 3269, 3053, 3025, 2959, 2926, 2853.

HRMS (m/z): calcd. for $C_{18}H_{21}D_2NNaO_2S^+$, 342.1467; found, 342.1463.

4-Methyl-*N*-(5-phenylpentyl-5-*d*)benzenesulfonamide 2h-d$_1$



White solid.

mp: 52-53 ^{o}C.

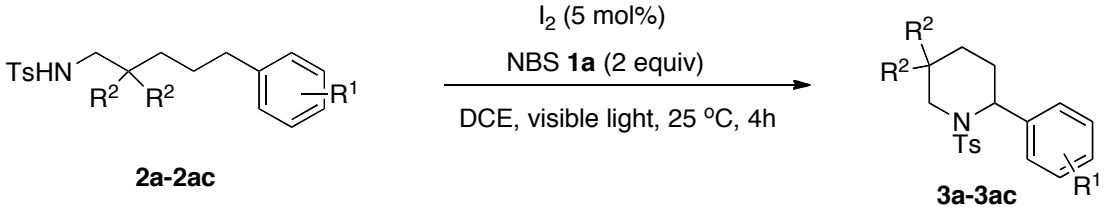
^{1}H NMR (400 MHz, CDCl$_3$): δ =7.76-7.71 (m, 2H), 7.34-7.23 (m, 4H), 7.20–7.15 (m, 1H), 7.14–7.10 (m, 2H), 4.34 (t, *J* = 6.2 Hz, 1H), 2.92 (td, *J* = 7.1, 6.2 Hz, 2H), 2.53 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.42 (s, 3H), 1.57–1.43 (m, 4H), 1.34–1.24 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ =143.4, 142.2, 137.0, 129.7, 128.3, 128.3, 127.1, 125.8, 43.1, 35.5 (t, *J* = 19.3 Hz), 35.3, 35.1, 30.7, 29.5, 26.1, 21.5.

IR *v* (cm^{-1}): 3287, 3270, 3056, 3027, 2924, 2854.

HRMS (m/z): calcd. for $C_{18}H_{22}DNNaO_2S^+$, 341.1404; found, 341.1405.

4- General procedure for the C-H amination reaction (GP2)

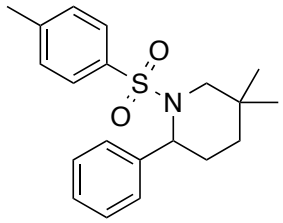


2a-2ac **3a-3ac**

A Schlenk tube equipped with a stirrer bar was charged with NBS **1a** (71.2mg, 0.4 mmol, 2.0 equiv), I_2 (2.6 mg, 0.01 mmol, 5%) and the sulfonamide **2** (0.2 mmol, 1.0 equiv), evacuated, and backfilled with argon, before 1.5 mL of absolute dichloroethane were added. The solution was stirred at 25 °C for 4 h under visible light. CH_2Cl_2 was added and the resulting solution was washed with saturated aqueous solutions of $Na_2S_2O_3$ and $NaHCO_3$ and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4 and solvents were evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, *n*-hexane/ethyl acetate) to give the pure product **3**.

5- Data for piperidine products

5,5-Dimethyl-2-phenyl-1-tosylpiperidine 3a



White solid, 80%.

mp: 80-81 °C.

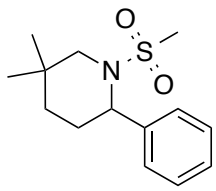
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.0 Hz, 2H), 7.24-7.20 (m, 4H), 7.17-7.14 (m, 2H), 5.23 (t, *J* = 4.0 Hz, 1H), 3.41 (d, *J* = 16.0 Hz, 1H), 2.86 (d, *J* = 16.0 Hz, 1H), 2.40 (s, 3H), 2.12-2.08 (m, 2H), 1.25-1.21 (m, 2H), 0.79 (d, *J* = 4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.7, 138.9, 138.6, 129.4, 128.4, 127.0, 126.9, 126.7, 55.3, 52.5, 32.5, 30.3, 28.6, 25.7, 24.1, 21.5.

IR *v* (cm^{-1}): 3054, 3023, 2956, 2932, 2868.

HRMS (m/z): calcd. for $C_{20}H_{25}NNaO_2S^+$, 366.1498; found, 366.1493.

5,5-Dimethyl-1-(methylsulfonyl)-2-phenylpiperidine 3b



White solid, 62%.

mp: 78-79 °C.

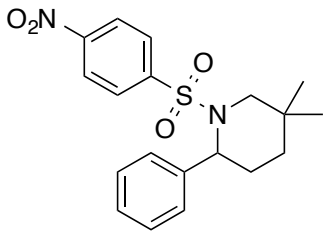
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 4.5 Hz, 4H), 7.30-7.26 (m, 1H), 5.12 (dd, *J* = 6.0, 2.7 Hz, 1H), 3.41 (dt, *J* = 13.4, 1.3 Hz, 1H), 2.93 (dd, *J* = 13.4, 0.8 Hz, 1H), 2.80 (s, 3H), 2.27-2.17 (m, 1H), 2.14-2.08 (m, 1H), 1.39-1.30 (m, 2H), 1.11 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 128.8, 127.2, 127.0, 55.2, 52.4, 40.4, 32.6, 30.3, 28.62, 26.0, 24.2.

IR *v* (cm^{-1}): 3020, 2951, 2924, 2866.

HRMS (m/z): calcd. for $C_{14}H_{21}NNaO_2S^+$, 290.1185; found, 290.1188.

5,5-Dimethyl-1-((4-nitrophenyl)sulfonyl)-2-phenylpiperidine 3c



White solid, 81%.

mp: 115-116 °C.

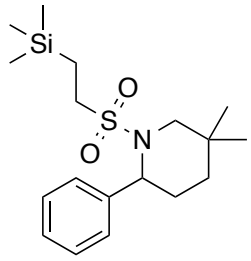
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24-8.21 (m, 2H), 7.88-7.84 (m, 2H), 7.23-7.19 (m, 3H), 7.10-7.07 (m, 2H), 5.24 (t, *J* = 4.0 Hz, 1H), 3.47 (d, *J* = 12.0 Hz, 1H), 2.95 (d, *J* = 12.0 Hz, 1H), 2.11-2.08 (m, 2H), 1.32-1.27 (m, 2H), 0.86 (d, *J* = 2.3 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.5, 147.0, 138.4, 128.6, 128.1, 127.2, 126.8, 124.0, 56.1, 53.1, 32.3, 30.6, 28.5, 26.2, 24.3.

IR *v* (cm^{-1}): 3026, 2969, 2928, 2866.

HRMS (m/z): calcd. for $C_{19}H_{22}N_2NaO_4S^+$, 397.1192; found, 397.1200.

5,5-Dimethyl-2-phenyl-1-((2-(trimethylsilyl)ethyl)sulfonyl)piperidine 3d



White solid, 47%.

mp: 54-55 °C.

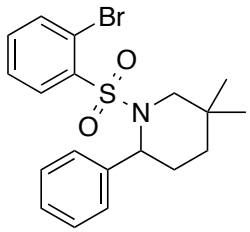
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.34 (m, 4H), 7.30–7.24 (m, 1H), 5.08 (dd, *J* = 5.9, 3.0 Hz, 1H), 3.38 (dt, *J* = 13.5, 1.3 Hz, 1H), 2.99 (d, *J* = 13.5 Hz, 1H), 2.84–2.74 (m, 2H), 2.27-2.18 (m, 1H), 2.15–2.06 (m, 1H), 1.38–1.29 (m, 2H), 1.10 (s, 3H), 1.07–1.00 (m, 1H), 0.99–0.91 (m, 1H), 0.87 (s, 3H), -0.03 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.8, 128.7, 127.1, 127.0, 55.7, 53.1, 49.6, 32.7, 30.4, 28.6, 26.3, 24.3, 10.5, -2.0.

IR *v* (cm^{-1}): 3061, 2952, 2868.

HRMS (m/z): calcd. for $C_{18}H_{31}NNaO_2SSi^+$, 376.1737; found, 376.1736

1-((2-Bromophenyl)sulfonyl)-5,5-dimethyl-2-phenylpiperidine 3e



White solid, 77%.

mp: 114-115 °C.

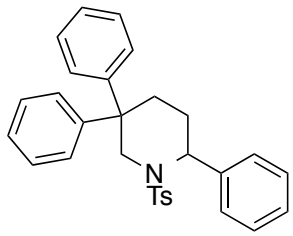
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.75 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.39-7.27 (m, 6H), 7.21-7.17 (m, 1H), 5.31 (t, *J* = 4.0 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.42-2.33 (m, 1H), 2.21-2.15 (m, 1H), 1.30 (dd, *J* = 9.3, 3.7 Hz, 2H), 0.79 (d, *J* = 18.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.8, 138.9, 135.3, 133.2, 132.3, 128.5, 127.4, 126.8, 126.8, 120.4, 56.3, 53.2, 32.7, 30.6, 28.5, 25.4, 23.8.

IR *v* (cm^{-1}): 3085, 3082, 2939, 2923, 2864.

HRMS (m/z): calcd. for $C_{19}H_{22}BrNNaO_2S^+$, 430.0447; found, 430.0448.

2,5,5-Triphenyl-1-tosylpiperidine 3f



White solid, 45%.

mp: 73-74 °C.

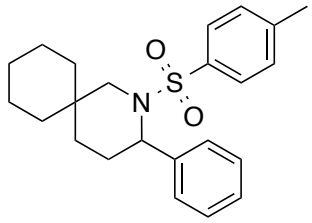
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.43 (m, 2H), 7.34-7.27 (m, 6H), 7.27-7.13 (m, 7H), 7.12-7.07 (m, 2H), 7.04-7.01 (m, 2H), 4.96 (dd, *J* = 5.6, 3.6 Hz, 1H), 4.57 (dd, *J* = 13.2, 1.6 Hz, 1H), 3.78 (d, *J* = 13.2 Hz, 1H), 2.36 (s, 3H), 2.39-2.28 (m, 2H), 2.06-1.98 (m, 1H), 1.95-1.88 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.1, 144.6, 142.7, 140.4, 136.2, 129.1, 128.5, 128.4, 128.2, 127.9, 127.4, 127.3, 126.8, 126.4, 126.1, 56.9, 51.6, 45.8, 29.5, 28.7, 21.4.

IR *v* (cm^{-1}): 3058, 3028, 2950, 2871.

HRMS (m/z): calcd. for $C_{30}H_{29}NNaO_2S^+$, 490.1811; found, 490.1820.

3-Phenyl-2-tosyl-2-azaspiro[5.5]undecane 3g



White solid, 78%.

mp: 79-80 °C.

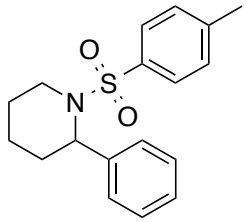
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.26-7.14 (m, 7H), 5.21 (t, *J* = 4.2 Hz, 1H), 3.73 (d, *J* = 13.6 Hz, 1H), 2.78 (d, *J* = 13.7 Hz, 1H), 2.40 (s, 3H), 2.28-2.03 (m, 2H), 1.48-1.25 (m, 8H), 1.20-1.03 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 139.0, 138.5, 129.3, 128.4 127.0, 126.9, 126.7, 56.0, 50.1, 37.8, 32.6, 31.8, 30.8, 26.5, 25.0, 21.6, 21.5, 21.4.

IR *v* (cm^{-1}): 3067, 3032, 2915, 2859.

HRMS (m/z): calcd. for $C_{23}H_{29}NNaO_2S^+$, 406.1811; found, 406.1813.

2-Phenyl-1-tosylpiperidine 3h



White solid, 73%.

mp: 126-127 °C.

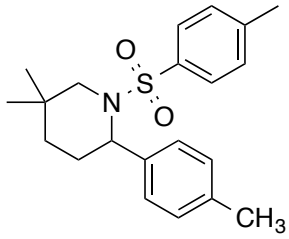
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.35-7.28 (m, 6H), 7.25-7.22 (m, 1H), 5.27 (d, *J* = 4.1 Hz, 1H), 3.87-3.81 (m, 1H), 3.01 (ddd, *J* = 14.3, 12.4, 3.1 Hz, 1H), 2.44 (s, 3H), 2.24-2.18 (m, 1H), 1.70-1.62 (m, 1H), 1.50 (dt, *J* = 8.4, 4.2 Hz, 1H), 1.43-1.27 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.9, 138.9, 138.7, 129.7, 128.6, 127.0, 127.0, 126.8, 55.3, 41.9, 27.3, 24.3, 21.5, 19.0.

IR *v* (cm^{-1}): 3050, 2955, 2927, 2868.

HRMS (m/z): calcd. for $C_{18}H_{21}NNaO_2S^+$, 338.1185; found, 338.1178.

5,5-Dimethyl-2-(*p*-tolyl)-1-tosylpiperidine 3i



White solid, 63%.

mp: 132-133 °C.

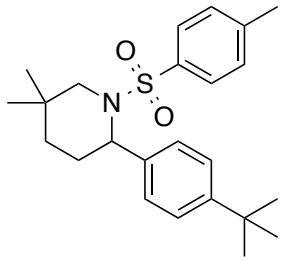
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.23-7.21 (m, 2H), 7.04 (s, 4H), 5.18 (t, *J* = 4.1 Hz, 1H), 3.39 (dt, *J* = 13.4, 1.4 Hz, 1H), 2.85 (d, *J* = 13.4 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.11-2.01 (m, 2H), 1.30-1.17 (m, 2H), 0.79 (d, *J* = 4.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.7, 138.6, 136.3, 135.8, 129.4, 129.1, 127.0, 126.9, 55.2, 52.45, 32.5, 30.3, 28.6, 25.7, 24.1, 21.5, 20.9.

IR *v* (cm^{-1}): 3025, 2953, 2916, 2860.

HRMS (m/z): calcd. for $C_{21}H_{27}NNaO_2S^+$, 380.1655; found, 380.1652.

2-(4-(*tert*-Butyl)phenyl)-5,5-dimethyl-1-tosylpiperidine 3j



Oil, 80%.

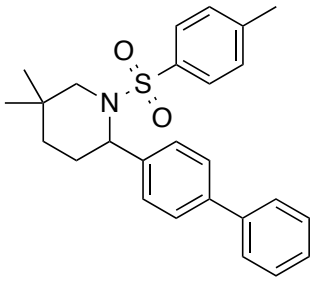
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.25-7.16 (m, 4H), 7.07 (dd, *J* = 8.8, 0.9 Hz, 2H), 5.18 (t, *J* = 4.2 Hz, 1H), 3.41 (ddd, *J* = 13.3, 1.9, 1.0 Hz, 1H), 2.88 (d, *J* = 13.4 Hz, 1H), 2.39 (s, 3H), 2.07 (dt, *J* = 7.7, 4.1 Hz, 2H), 1.31-1.19 (m, 11H), 0.81 (s, 6H).

^{13}C NMR (101 MHz, CDCl3): δ = 149.5, 142.5, 138.6, 135.9, 129.3, 127.0, 126.7, 125.3, 55.2, 52.53, 34.3, 32.5, 31.4, 30.4, 28.7, 25.8, 24.2, 21.5.

IR *v* (cm^{-1}): 2953, 2866, 1739.

HRMS (m/z): calcd. for $C_{24}H_{33}NNaO_2S^+$, 422.2124; found, 422.2129.

2-([1,1'-Biphenyl]-4-yl)-5,5-dimethyl-1-tosylpiperidine 3k



White solid, 78%.

mp: 65-66 °C.

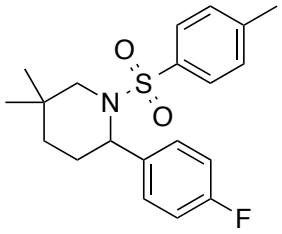
^{1}H NMR (500 MHz, $CDCl_3$): δ =7.68 (d, *J* = 13.5 Hz, 2H), 7.57-7.54 (m, 2H), 7.48-7.42 (m, 4H), 7.36-7.33 (m, 1H), 7.25-7.22 (m, 4H), 5.27 (t, *J* = 3.9 Hz, 1H), 3.45 (ddd, *J* = 13.5, 1.8, 1.0 Hz, 1H), 2.92 (d, *J* = 13.5 Hz, 1H), 2.40 (s, 3H), 2.14-2.11 (m, 2H), 1.31-1.25 (m, 2H), 0.83 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ =142.8, 140.7, 139.6, 138.6, 138.0, 129.4, 128.8, 127.4, 127.3, 127.11, 127.0, 127.0, 55.3, 52.6, 32.6, 30.4, 28.6, 25.8, 24.2, 21.5.

IR *v* (cm^{-1}): 3029, 2950, 2864.

HRMS (m/z): calcd. for $C_{26}H_{29}NNaO_2S^+$, 442.1811; found, 442.1824.

2-(4-Fluorophenyl)-5,5-dimethyl-1-tosylpiperidine 3l



White solid, 66%.

mp: 97-98 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94-6.90 (m, 2H), 5.18 (t, *J* = 3.9 Hz, 1H), 3.38 (dd, *J* = 13.7, 1.0 Hz, 1H), 2.82 (dd, *J* = 13.4, 0.9 Hz, 1H), 2.40 (s, 3H), 2.05 (ddd, *J* = 8.4, 5.7, 4.4 Hz, 2H), 1.24-1.20 (m, 2H), 0.78 (d, *J* = 10.9 Hz, 6H).

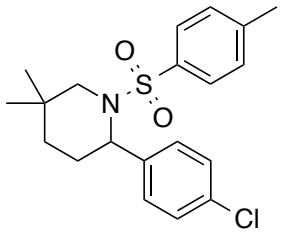
^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.0 (d, J_{C-F} = 244.0 Hz), 142.9, 138.4, 134.6, 129.4, 128.0 (d, J_{C-F} = 7.9 Hz), 127.0, 115.0 (d, J_{C-F} = 22.0 Hz), 54.9, 52.5, 32.5, 30.3, 28.5, 25.8, 24.1, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -116.51 - -116.55 (m, 1F).

IR *v* (cm^{-1}): 3022, 2953, 2867.

HRMS (m/z): calcd. for $C_{20}H_{24}FNNaO_2S^+$, 384.1404; found, 384.1406.

2-(4-Chlorophenyl)-5,5-dimethyl-1-tosylpiperidine 3m



White solid, 71%.

mp: 124-125 °C.

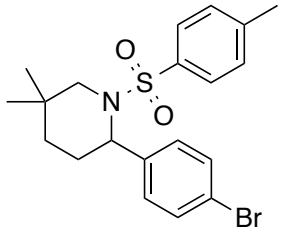
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.63 (m, 2H), 7.25-7.19 (m, 4H), 7.11-7.08 (m, 2H), 5.17 (t, *J* = 4.3 Hz, 1H), 3.39 (dt, *J* = 13.5, 1.1 Hz, 1H), 2.81 (d, *J* = 13.5 Hz, 1H), 2.41 (s, 3H), 2.08-2.03 (m, 2H), 1.18-1.22 (m, 2H), 0.78 (d, *J* = 8.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.0, 138.4, 137.5, 132.6, 129.5, 128.6, 128.4, 127.0, 55.0, 52.5, 32.5, 30.3, 28.5, 25.7, 24.1, 21.5.

IR *v* (cm^{-1}): 2951, 2860, 1739.

HRMS (m/z): calcd. for $C_{20}H_{24}ClNNaO_2S^+$, 400.1108; found, 400.1109.

2-(4-Bromophenyl)-5,5-dimethyl-1-tosylpiperidine 3n



White solid, 70%.

mp: 140-141 °C.

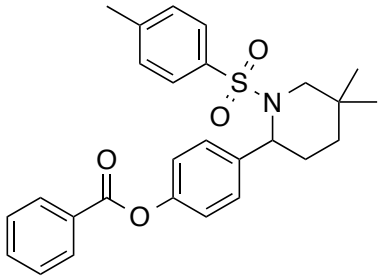
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 6.5, 1.8 Hz, 2H), 7.35 (dd, *J* = 6.5, 2.0 Hz, 2H), 7.22 (dd, *J* = 8.6, 0.8 Hz, 2H), 7.03 (dd, *J* = 8.7, 1.0 Hz, 2H), 5.14 (t, *J* = 4.2 Hz, 1H), 3.38 (dt, *J* = 13.5, 1.2 Hz, 1H), 2.80 (d, *J* = 13.4 Hz, 1H), 2.40 (s, 3H), 2.09-1.99 (m, 2H), 1.24-1.15 (m, 2H), 0.78 (d, *J* = 8.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.0, 138.3, 138.1, 131.5, 129.5, 128.8, 127.0, 120.7, 55.0, 52.6, 32.5, 30.3, 28.5, 25.7, 24.1, 21.5.

IR *v* (cm^{-1}): 3058, 3030, 2953, 2921, 2859.

HRMS (m/z): calcd. for $C_{20}H_{24}BrNNaO_2S^+$, 444.0603; found, 444.0610.

4-(5,5-Dimethyl-1-tosylpiperidin-2-yl)phenyl benzoate 3o



White solid, 72%.

mp: 134-135 °C.

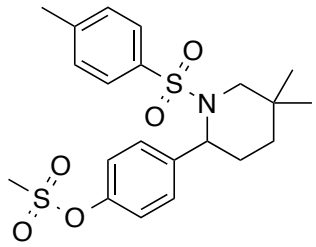
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.17 (m, 2H), 7.70–7.65 (m, 2H), 7.65–7.62 (m, 1H), 7.55–7.48 (m, 2H), 7.26–7.23 (m, 2H), 7.22–7.18 (m, 2H), 7.12–7.08 (m, 2H), 5.27–5.19 (t, *J* = 4.2 Hz, 1H), 3.43 (dt, *J* = 13.5, 1.3 Hz, 1H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.41 (s, 3H), 2.15-2.07 (m, 2H), 1.33–1.21 (m, 2H), 0.82 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.1, 149.7, 142.9, 138.5, 136.5, 133.6, 130.2, 129.5, 129.5, 128.6, 128.1, 127.0, 121.6, 55.0, 52.5, 32.5, 30.4, 28.6, 25.7, 24.1, 21.5.

IR *v* (cm^{-1}): 3689, 3675, 3649, 3372, 2971, 2932.

HRMS (m/z): calcd. for $C_{21}H_{29}NNaO_4S_2^+$, 486.1710; found, 486.1715.

4-(5,5-Dimethyl-1-tosylpiperidin-2-yl)phenyl methanesulfonate 3p



White solid, 71%.

mp: 109-110 °C.

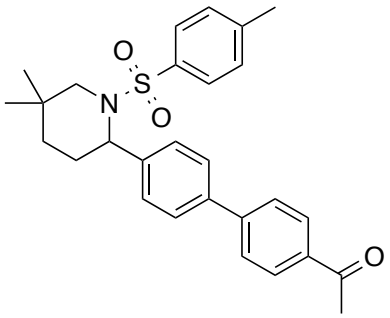
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.61 (m, 2H), 7.26–7.21 (m, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.21 (t, *J* = 4.1 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 3.14 (s, 3H), 2.82 (d, *J* = 13.5 Hz, 1H), 2.41 (s, 3H), 2.11–2.02 (m, 2H), 1.25–1.17 (m, 2H), 0.81 (s, 3H), 0.76 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 143.1, 138.6, 138.3, 129.5, 128.7, 127.0, 121.9, 55.0, 52.6, 37.4, 32.4, 30.3, 28.5, 25.8, 24.1, 21.5.

IR *v* (cm^{-1}): 3629, 3278, 2987, 2968, 2939, 2901.

HRMS (m/z): calcd. for $C_{19}H_{23}Br_2NNaO_2S^+$, 460.1223; found, 460.1226.

1-(4'-(5,5-Dimethyl-1-tosylpiperidin-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one 3q



White solid, 40%.

mp: 157-158 °C.

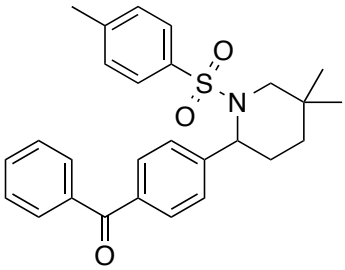
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (dd, *J* = 7.0, 1.9 Hz, 2H), 7.68-7.64 (m, 4H), 7.51 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.28-7.27 (m, 2H), 7.24-7.22 (m, 2H), 5.26 (t, *J* = 3.6 Hz, 1H), 3.43 (dt, *J* = 13.4, 1.3 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.64 (s, 3H), 2.40 (s, 3H), 2.16-2.07 (m, 2H), 1.31-1.24 (m, 2H), 0.81 (d, *J* = 10.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 197.6, 145.2, 142.8, 139.3, 138.5, 138.3, 135.9, 129.4, 128.9, 127.6, 127.3, 127.1, 127.0, 55.3, 52.7, 32.6, 30.4, 28.6, 26.6, 25.8, 24.1, 21.5.

IR *v* (cm^{-1}): 3031, 2970, 2953, 2865.

HRMS (m/z): calcd. for $C_{28}H_{31}NNaO_3S^+$, 484.1917; found, 484.1928.

(4-(5,5-Dimethyl-1-tosylpiperidin-2-yl)phenyl)(phenyl)methanone 3r



Oil, 56%.

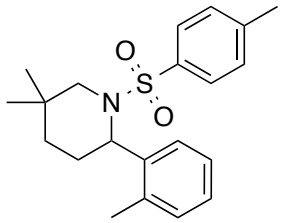
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.77 (m, 2H), 7.69 (t, *J* = 8.0 Hz, 4H), 7.63–7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.23 (m, 2H), 5.29 (t, *J* = 4.2 Hz, 1H), 3.47–3.40 (m, 1H), 2.87 (d, *J* = 13.5 Hz, 1H), 2.41 (s, 3H), 2.17–2.10 (m, 2H), 1.29–1.18 (m, 2H), 0.80 (d, *J* = 7.7 Hz, 6H).

^{13}C NMR (126 MHz, CDCl3): δ = 196.2, 144.1, 143.1, 138.3, 137.54, 136.1, 132.5, 130.3, 130.0, 129.5, 128.3, 127.0, 126.9, 55.4, 52.7, 32.6, 30.3, 28.6, 25.8, 24.0, 21.5.

IR *v* (cm^{-1}): 3501, 3059, 2952, 2866.

HRMS (m/z): calcd. for $C_{27}H_{29}NNaO_3S^+$, 470.1760; found, 470.1760.

5,5-Dimethyl-2-(*o*-tolyl)-1-tosylpiperidine 3s



White solid, 62%.

mp: 95-96 °C.

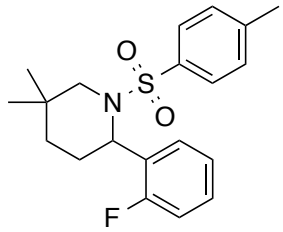
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 7.09-7.01 (m, 4H), 6.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.82-6.78 (m, 1H), 5.10 (t, *J* = 5.8 Hz, 1H), 3.39 (dd, *J* = 12.6, 1.0 Hz, 1H), 3.31 (d, *J* = 12.6 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.07-2.01 (m, 1H), 1.74-1.66 (m, 1H), 1.48-1.42 (m, 1H), 1.32-1.27 (m, 1H), 1.06 (d, *J* = 2.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.4, 140.0, 137.3, 134.8, 130.6, 128.9, 127.0, 126.8, 126.6, 125.29, 55.1, 53.9, 33.2, 30.6, 27.8, 27.8, 25.7, 21.4, 19.6.

IR *v* (cm^{-1}): 3013, 2945, 2864.

HRMS (m/z): calcd. for $C_{21}H_{27}NNaO_2S^+$, 380.1655; found, 380.1654

2-(2-Fluorophenyl)-5,5-dimethyl-1-tosylpiperidine 3t



White solid, 54%.

mp: 60-61 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 6.4, 1.9 Hz, 2H), 7.15-7.13 (m, 3H), 7.08-7.06 (m, 1H), 6.95-6.88 (m, 2H), 5.25 (t, *J* = 5.1 Hz, 1H), 3.37 (d, *J* = 12.9 Hz, 1H), 3.17 (d, *J* = 13.0 Hz, 1H), 2.37 (s, 3H), 2.02-1.98 (m, 2H), 1.26-1.23 (m, 2H), 0.94 (s, 3H), 0.88 (s, 3H).

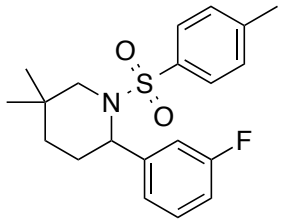
^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.8 (d, $J_{C\text{-}F}$ = 248.1 Hz), 158.9, 142.8, 137.5, 129.2, 129.0, 129.0, 128.5, 128.4, 128.0, 127.9, 127.1, 123.5 (d, $J_{C\text{-}F}$ = 5.0 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.4 Hz), 54.2, 52.0, 33.2, 30.3, 28.1, 27.2, 27.1, 24.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -115.08 – -115.35 (m, 1F).

IR *v* (cm^{-1}): 3062, 2983, 2949, 2921, 2862.

HRMS (m/z): calcd. for $C_{20}H_{24}FNNaO_2S^+$, 384.1404; found, 384.1410.

2-(3-Fluorophenyl)-5,5-dimethyl-1-tosylpiperidine 3u



Oil, 45%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.63 (m, 2H), 7.25-7.18 (m, 3H), 6.97-6.94 (m, 1H), 6.87 (dd, *J* = 1.7, 0.8 Hz, 1H), 6.79 (d, *J* = 10.6 Hz, 1H), 5.21 (d, *J* = 4.0 Hz, 1H), 3.42 (dd, *J* = 13.5, 1.3 Hz, 1H), 2.82 (dd, *J* = 13.5, 0.8 Hz, 1H), 2.40 (s, 3H), 2.08-2.04 (m, 2H), 1.27-1.17 (m, 2H), 0.79 (d, *J* = 3.1 Hz, 6H).

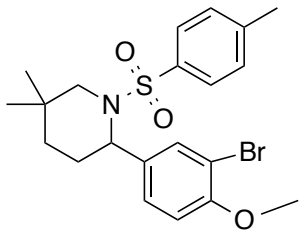
^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.3 (d, $J_{C\text{-}F}$ = 245.1 Hz), 143.0, 141.9, 141.9, 138.4, 130.0, 129.9, 129.5, 127.0, 122.6, 122.5, 113.0 (dd, $J_{C\text{-}F}$ = 44.5, 22.3 Hz), 55.0, 54.9, 52.5, 32.5, 30.3, 28.6, 25.7, 24.0, 21.5.

IR *v* (cm^{-1}): 3029, 2952, 2866.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -112.99 – -113.12 (m, 1F).

HRMS (m/z): calcd. for $C_{20}H_{24}FNNaO_2S^+$, 384.1404; found, 384.1408.

2-(3-Bromo-4-methoxyphenyl)-5,5-dimethyl-1-tosylpiperidine 3v



White solid, 77%.

mp: 131-132 °C.

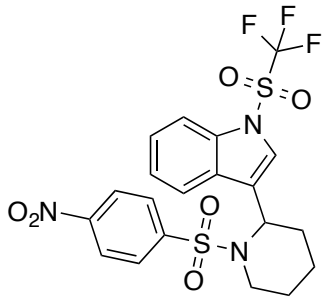
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.25-7.21 (m, 2H), 7.11 (dd, *J* = 2.4, 1.0 Hz, 1H), 7.06 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.12 (td, *J* = 3.7, 1.8 Hz, 1H), 3.86 (s, 3H), 3.41 (d, *J* = 13.4 Hz, 1H), 2.80 (d, *J* = 13.4 Hz, 1H), 2.41 (s, 3H), 2.12-1.97 (m, 2H), 1.27-1.21 (m, 2H), 0.83 (d, *J* = 11.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.6, 143.0, 138.4, 132.4, 131.8, 129.6, 127.3, 126.8, 111.8, 111.6, 56.2, 54.5, 52.5, 32.6, 30.4, 28.5, 25.8, 24.1, 21.5.

IR *v* (cm^{-1}): 2970, 2945, 2867.

HRMS (m/z): calcd. for $C_{21}H_{26}BrNNaO_3S^+$, 474.0709; found, 474.0708.

3-(1-((4-Nitrophenyl)sulfonyl)piperidin-2-yl)-1-((trifluoromethyl)sulfonyl)-1*H*-indole 3w



White solid, 51%.

mp: 167-168 °C

^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.27 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.92-7.87 (m, 2H), 7.50-7.41 (m, 2H), 7.07 (d, *J* = 1.4 Hz, 1H), 5.61 (d, *J* = 5.5 Hz, 1H), 3.96 (d, *J* = 13.8 Hz, 1H), 3.16 (ddd, *J* = 13.9, 12.5, 2.7 Hz, 1H), 2.15 (d, *J* = 14.1 Hz, 1H), 1.85 (ddt, *J* = 13.6, 9.8, 4.7 Hz, 1H), 1.74-1.53 (m, 4H).

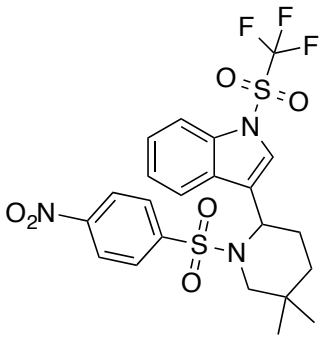
^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.9, 146.4, 135.4, 129.4, 128.2, 126.5, 125.2, 124.3, 123.7, 122.8, 121.1, 120.9, 117.9, 113.8, 50.1, 42.8, 28.1, 24.2, 19.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.95 (s, 3F).

IR *v* (cm^{-1}): 3861, 3732, 3120, 2956, 2874.

HRMS (m/z): calcd. for $C_{20}H_{18}F_3N_3NaO_6S_2^+$, 540.0481; found, 540.0484.

3-(5,5-Dimethyl-1-((4-nitrophenyl)sulfonyl)piperidin-2-yl)-1-((trifluoromethyl)sulfonyl)-1*H*-indole 3x



White solid, 63%.

mp: 162-163 °C

^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.17-8.07 (m, 2H), 7.83 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.78-7.72 (m, 2H), 7.70-7.65 (m, 1H), 7.50-7.35 (m, 2H), 6.75 (s, 1H), 5.60-5.51 (m, 1H), 3.61-3.48 (m, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.32-2.22 (m, 1H), 2.05-1.98 (m, 1H), 1.44-1.32 (m, 2H), 1.04 (s, 3H), 1.00 (s, 3H).

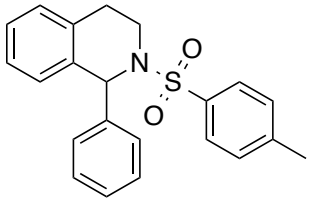
^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.8, 145.8, 135.1, 129.2, 127.9, 126.6, 125.1, 123.9, 122.9, 122.7, 120.3, 113.9, 53.4, 49.2, 32.4, 30.5, 28.7, 26.0, 23.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -75.44 (s, 3F).

IR *v* (cm^{-1}): 3850, 3742, 3170, 2969, 2353, 2337.

HRMS (m/z): calcd. for $C_{22}H_{22}F_3N_3NaO_6S_2^+$, 568.0794; found, 568.0820.

1-Phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinoline 3y



White solid, 51%.

mp: 155-156 °C.

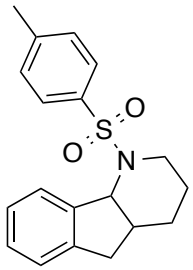
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 6.4, 1.8 Hz, 2H), 7.28-7.25 (m, 3H), 7.23-7.20 (m, 2H), 7.17-7.14 (m, 2H), 7.11-7.09 (m, 2H), 7.02-7.00 (m, 2H), 6.26 (s, 1H), 3.80 (dddd, *J* = 14.1, 6.5, 2.9, 1.2 Hz, 1H), 3.34 (ddd, *J* = 14.1, 11.0, 5.2 Hz, 1H), 2.77-2.65 (m, 1H), 2.59 (ddd, *J* = 16.7, 5.2, 2.8 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.0, 141.6, 137.7, 134.1, 133.8, 129.3, 128.9, 128.7, 128.4, 128.2, 127.6, 127.1, 127.0, 126.1, 59.2, 39.1, 26.7, 21.4.

IR *v* (cm^{-1}): 3061, 3029, 2982, 2970, 2928, 2872.

HRMS (m/z): calcd. for $C_{22}H_{21}NNaO_2S^+$, 386.1185; found, 386.1195.

1-Tosyl-2,3,4,4a,5,9b-hexahydro-1*H*-indeno[1,2-*b*]pyridine 3z



White solid, 63%.

mp: 93-94 °C.

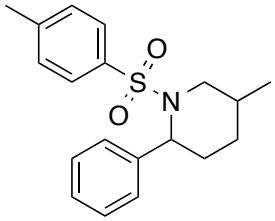
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.81 (m, 2H), 7.34-7.31 (m, 2H), 7.19 (s, 4H), 5.40 (d, *J* = 6.3 Hz, 1H), 3.87-3.82 (m, 1H), 2.97-2.92 (m, 1H), 2.80 (ddd, *J* = 14.1, 12.5, 2.6 Hz, 1H), 2.43-2.46 (m, 4H), 2.34 (dd, *J* = 11.9, 6.0 Hz, 1H), 1.61-1.55 (m, 1H), 1.30 (dt, *J* = 13.3, 3.1 Hz, 1H), 1.23-1.16 (m, 1H), 1.09-1.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.1, 141.1, 139.8, 138.8, 129.8, 127.5, 127.0, 126.8, 125.6, 123.9, 61.0, 41.3, 37.2, 37.0, 26.1, 23.2, 21.5.

IR *v* (cm^{-1}): 3028, 2926, 2855.

HRMS (m/z): calcd. for $C_{19}H_{21}NNaO_2S^+$, 350.1185; found, 350.1190.

5-Methyl-2-phenyl-1-tosylpiperidine *syn/anti*-3aa



Oil, 66%.

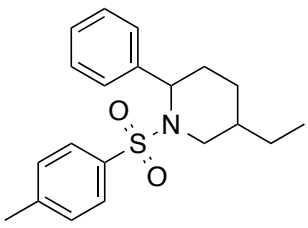
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.60–7.56 (m, 3H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.29 (dt, *J* = 8.0, 0.8 Hz, 2H), 7.25–7.17 (m, 12H), 5.27 (d, *J* = 5.4 Hz, 1H), 4.77 (t, *J* = 5.0 Hz, 1.5H), 3.84–3.71 (m, 1H), 3.52 (dd, *J* = 12.9, 3.8 Hz, 1.5H), 3.12 (ddt, *J* = 12.9, 5.1, 0.9 Hz, 1.5H), 2.58-2.52 (m, 1H), 2.43 (s, 3H), 2.40 (s, 4.5H), 2.24 (dd, *J* = 14.1, 2.1 Hz, 1H), 1.98 (dt, *J* = 7.2, 5.1 Hz, 3H), 1.82 (ddd, *J* = 11.3, 6.0, 2.7 Hz, 1.5H), 1.73 – 1.60 (m, 2.7H), 1.51–1.45 (m, 1H), 1.41 (dt, *J* = 7.2, 4.5 Hz, 1H), 1.16 (dd, *J* = 13.6, 5.5 Hz, 1.6H), 1.08–0.98 (m, 1H), 0.87 (d, *J* = 6.9 Hz, 4.5H), 0.70 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3): δ = 142.8, 140.0, 138.7, 137.3, 129.7, 129.3, 128.6, 128.2, 127.3, 127.2, 127.0, 126.9, 126.8, 126.8, 57.8, 54.4, 49.2, 48.3, 29.9, 28.3, 27.8, 27.4, 27.2, 26.9, 21.5, 21.5, 18.9, 18.0.

IR *v* (cm^{-1}): 3060, 3028, 2953, 2926, 2870.

HRMS (m/z): calcd. for $C_{19}H_{24}NO_2S^+$, 330.1522; found, 330.1524.

5-Ethyl-2-phenyl-1-tosylpiperidine *syn/anti*-3ab



Oil, 60%.

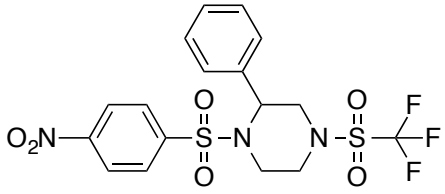
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.37-7.33 (m, 4H), 7.33-7.30 (m, 2H), 7.27-7.21 (m, 9H), 5.31 (dd, *J* = 5.3, 1.8 Hz, 1H), 4.84 (t, *J* = 5.0 Hz, 1H), 3.97-3.85 (m, 1H), 3.55-3.49 (m, 2H), 3.28 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.58 (dd, *J* = 14.3, 11.7 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 4H), 2.27 (dd, *J* = 14.1, 2.1 Hz, 1H), 2.00-1.95 (m, 2H), 1.50-1.71 (m, 6H), 1.34-1.18 (m, 6H), 1.07-1.00 (m, 3H), 0.88-0.80 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.9, 142.8, 140.0, 138.8, 138.7, 137.3, 129.7, 129.3, 128.6, 128.2, 127.3, 127.2, 127.0, 126.9, 126.8, 126.8, 57.8, 54.8, 46.9, 46.8, 36.5, 35.4, 27.6, 27.1, 26.6, 25.6, 24.8, 24.7, 21.5, 21.5, 11.8, 11.0.

IR *v* (cm^{-1}): 3059, 3028, 2928, 2873.

HRMS (m/z): calcd. for $C_{20}H_{25}NNaO_2S^+$,366.1498; found, 366.1496.

1-((4-Nitrophenyl)sulfonyl)-2-phenyl-4-((trifluoromethyl)sulfonyl)piperazine 3ac



White solid, 36%.

mp: 159-160 °C

^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.27 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 2H), 7.31-7.25 (m, 3H), 7.23-7.15 (m, 2H), 5.22 (s, 1H), 4.28 (s, 1H), 3.88 (dt, *J* = 13.1, 2.8 Hz, 1H), 3.82 (d, *J* = 12.0 Hz, 1H), 3.57 (dd, *J* = 13.4, 4.1 Hz, 1H), 3.47-3.26 (m, 2H).

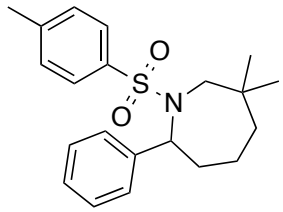
^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.1, 145.3, 134.7, 129.1, 128.7, 128.3, 127.2, 124.4, 121.5, 118.3, 49.1, 46.1, 41.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.12 (s, 3F).

IR *v* (cm^{-1}): 3850, 3742, 3644, 3116, 3028, 2870.

HRMS (m/z): calcd. for $C_{17}H_{16}F_3N_3NaO_6S_2^+$, 502.0325; found, 502.0349.

6,6-dimethyl-2-phenyl-1-tosylazepane 5



White solid, 31%.

mp: 93-94 °C.

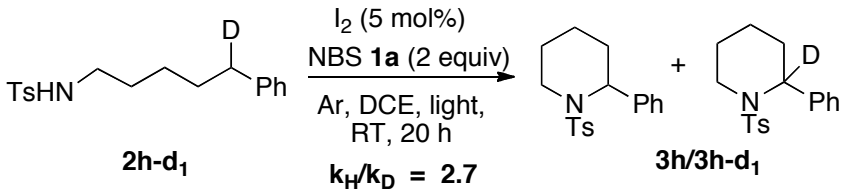
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.05 (m, 2H), 7.05–7.00 (m, 1H), 6.98–6.92 (m, 2H), 6.90–6.86 (m, 2H), 6.85–6.81 (m, 2H), 4.92 (dd, *J* = 11.6, 5.7 Hz, 1H), 3.67 (ddd, *J* = 14.9, 2.1, 0.8 Hz, 1H), 3.33 (d, *J* = 14.8 Hz, 1H), 2.25 (s, 3H), 2.17–2.03 (m, 1H), 1.79–1.68 (m, 2H), 1.60–1.53 (m, 2H), 1.25-1.17 (m, 4H), 0.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.2, 141.6, 138.5, 128.6, 128.0, 126.9, 126.6, 126.5, 63.0, 55.5, 44.7, 39.3, 35.8, 29.5, 24.9, 22.6, 21.3.

IR *v* (cm^{-1}): 3292, 3022, 2961, 2915.

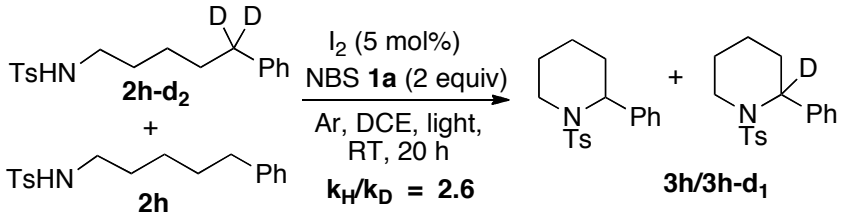
HRMS (m/z): calcd. for $C_{21}H_{28}NO_2S^+$, 358.1835; found, 358.1841.

6- Kinetic isotope (KIE) studies



Scheme S2. Intramolecular KIE effect

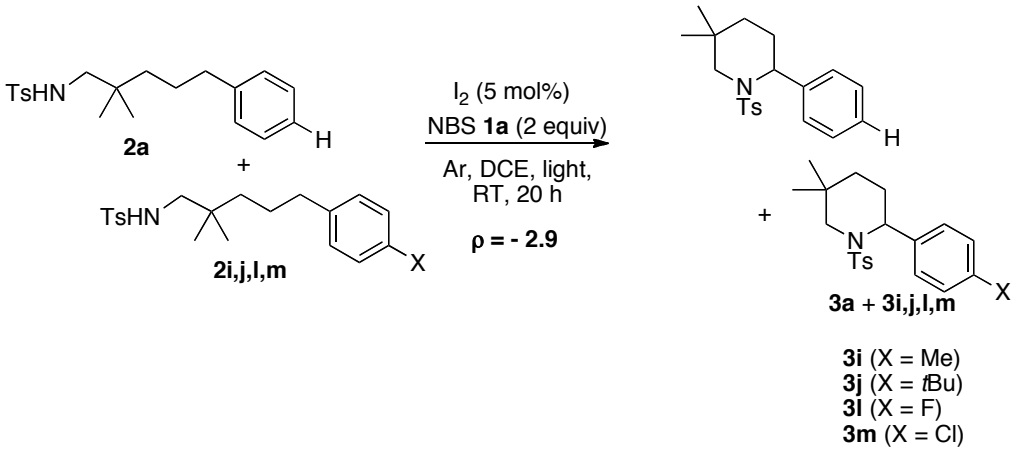
The experiment for the intramolecular KIE was carried out following the general procedure. Integration of the ^{1}H NMR spectrum of the crude reaction mixture revealed an isotope effect k_H/k_D = 2.7.



Scheme S3. Intermolecular KIE effect

KIE experiment for the intramolecular KIE was carried out following the general procedure with 2.5 equivalents of substrate **1h** and 2.5 equivalents of substrate **1h-d2**. The reaction was run to full conversion, which accounts for a 20% total conversion of the starting materials. Integration of the ^{1}H NMR spectrum of the crude reaction mixture revealed an isotope effect k_H/k_D = 2.6.

7- Hammett correlation studies



Scheme S4. Hammett correlation studies

General procedure. A Schlenk tube equipped with a stirrer bar is charged with 35.6 mg NBS (0.2 mmol, 1.0 equiv), 2.6 mg I_2 (0.01 mmol, 0.05 equiv), *N*- (2,2-dimethyl-4-phenylbutyl)-4-methylbenzenesulfonamidesulfonamide **2a** (0.5 mmol, 2.5 equiv) and the corresponding substituted sulfonamide **2i-m** (0.5 mmol, 2.5 equiv), evacuated, and backfilled with argon. At this point, 2.0 mL of absolute dichloroethane are added. The solution is stirred at 25 ^{o}C for 4h. CH_2Cl_2 is added and the residue is washed with saturated aqueous solutions of Na_2SO_3 and $NaHCO_3$ and extracted with CH_2Cl_2 (3x). The combined organic layers are dried over Na_2SO_4 and solvents evaporated under reduced pressure. For each independent run, the ratio of the two products (**2a** vs **2i, j, l, m**, respectively) was calculated within a 5% error from the resulting ^{1}H NMR spectra.

Table S1. Hammett constant.

Entry	X	k_X/k_H	$\log(k_X/k_H)$	Hammett constant $\sigma_{p\text{-}X}$
1	Cl	0.4	-0.39794	0.23
2	F	0.8	-0.09691	0.06
3	H	1	0	0
4	Me	4.16	0.61978	-0.17
5	^{t}Bu	7.69	0.88606	-0.20

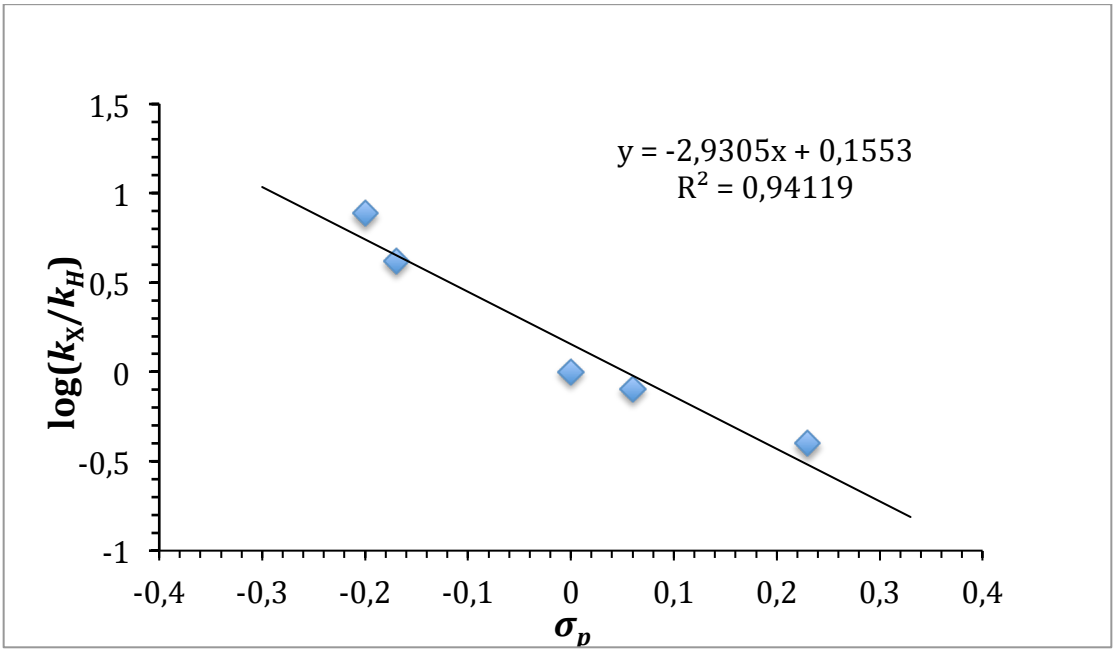
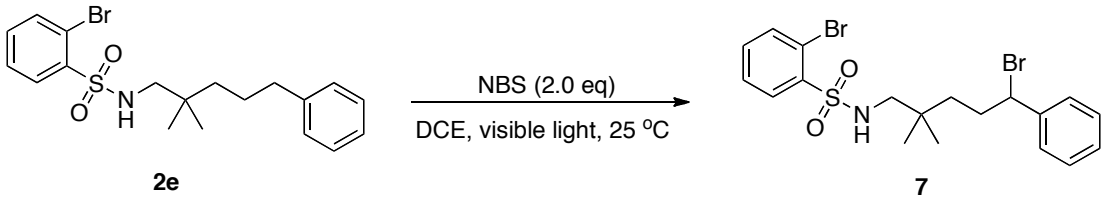


Figure S1. Hammett correlation study. Kinetic competition experiments between compound **2a** and compounds **2i**, **2j**, **2l** and **2m**, respectively.

8 - Investigation on potential intermediate 7

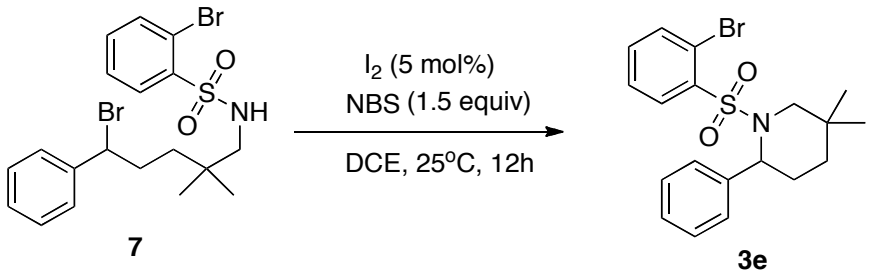
8.1 Procedure for the independent synthesis of brominated derivative 7



2e **7**

A Schlenk tube equipped with a stirrer bar was charged with NBS (71.2 mg, 0.4 mmol, 1.0 equiv), the sulfonamide **2e** (0.2 mmol, 1.0 equiv), evacuated, and backfilled with argon, before 1.5 mL of absolute dichloroethane was added. The solution was stirred at 25 °C for 12 h under visible light. CH_2Cl_2 was added and the resulting solution was washed with saturated aqueous solutions of $Na_2S_2O_3$ and $NaHCO_3$ and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4 and solvents were evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, *n*-hexane/ethyl acetate 6/1, v/v) to give the pure product **7** in 60% yield.

8.2 Reaction of 7 under GP2



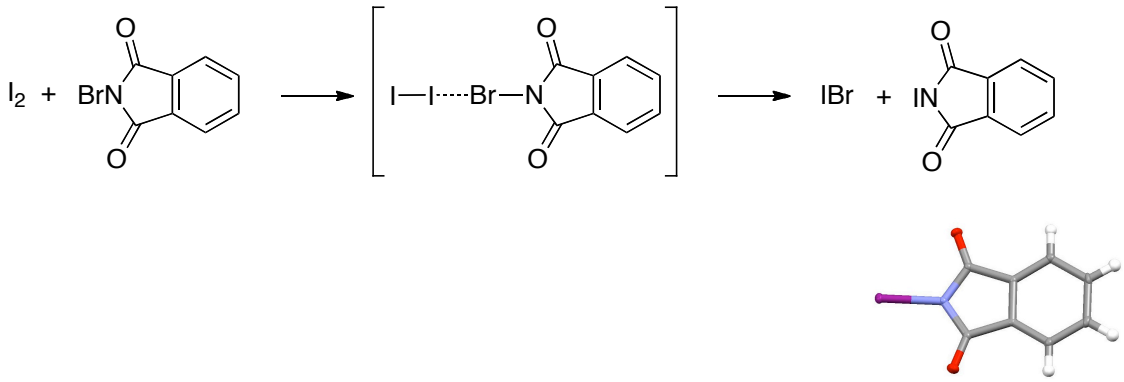
7 **3e**

A Schlenk tube equipped with a stirrer bar was charged with NBS (29.4 mg, 0.22 mmol, 1.5 equiv), I_2 (1.2 mg, 0.0055 mmol, 5 mol%) and the sulfonamide **7** (0.11 mmol, 1.0 equiv), evacuated, and backfilled with argon, before 1.0 mL of absolute dichloroethane was added. The solution was stirred at 25 °C for 12 h under visible light. CH_2Cl_2 was added and the resulting solution was washed with saturated aqueous solutions of $Na_2S_2O_3$ and $NaHCO_3$ and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4 and solvents were evaporated under reduced pressure. The NMR yield of **3e** is only 6% suggesting that benzylic bromine derivatives do not represent active intermediates.

9- Investigation on molecular iodine and *N*-bromo phthalimide 1d

To gain further evidence for the interaction between molecular iodine and N-brominated reagents **1a** and **1d**, their solution behavior was investigated.

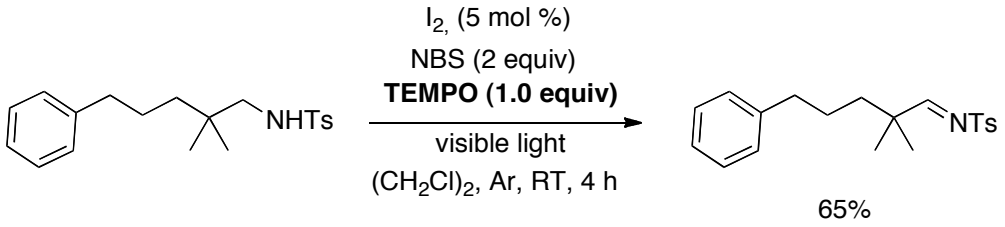
Upon mixing equimolar amounts of 1 mmol of molecular iodine and *N*-bromo phthalimide in 10 mL of dichloromethane, the reaction turned deep violet and gradually remained over the course of two days. At this point crystals appeared, which were separated and isolated. The solid residue was identified as N-iodo phthalimide by NMR and an unresolved X-ray analysis.



This reaction outcome likely proceeds through the involvement of the postulated halogen bonding, which in turn could not be isolated in structure. However, *N*-iodo phthalimide cannot be an active reagent in the present transformation, as it is known to promote Hofmann-Löffler pathway to pyrrolidines.[3]

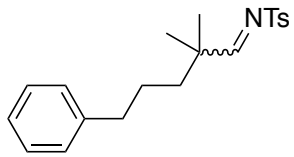
10- Investigation on TEMPO as additive

In order to demonstrate a possible interception of the radical pathway, a modified reaction under the general conditions GP2 was carried out adding 1 equivalent of TEMPO to the standard conditions.



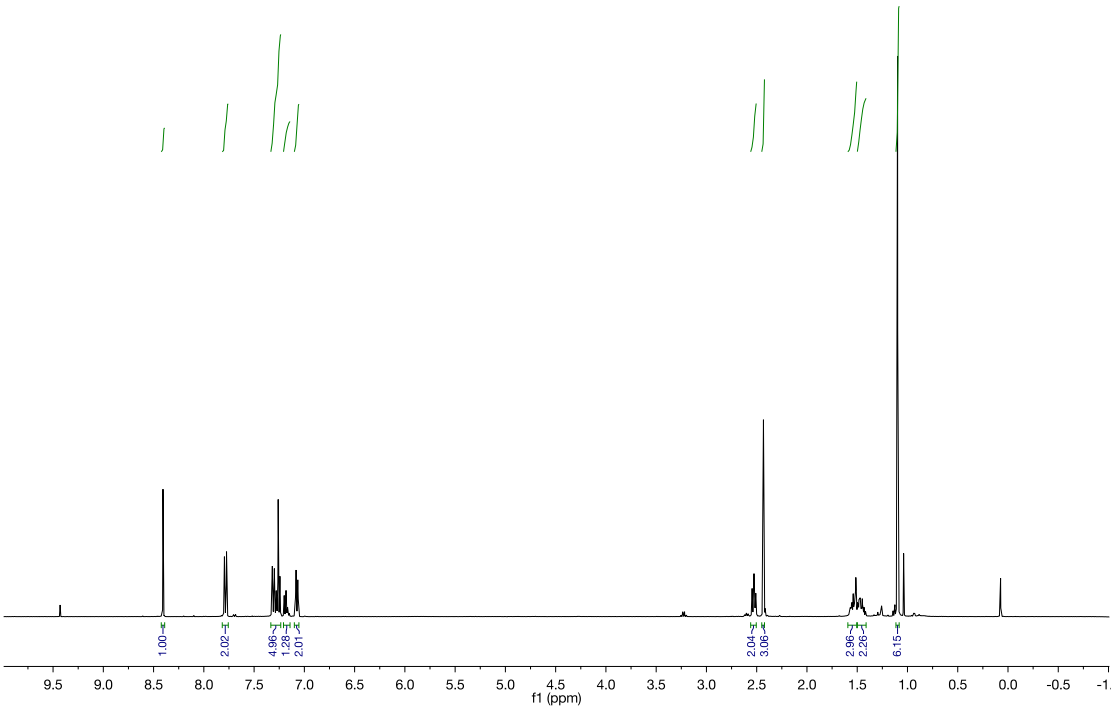
Under these conditions, the oxidation pathway is altered and leads to formation of the corresponding imine as the only identified product.

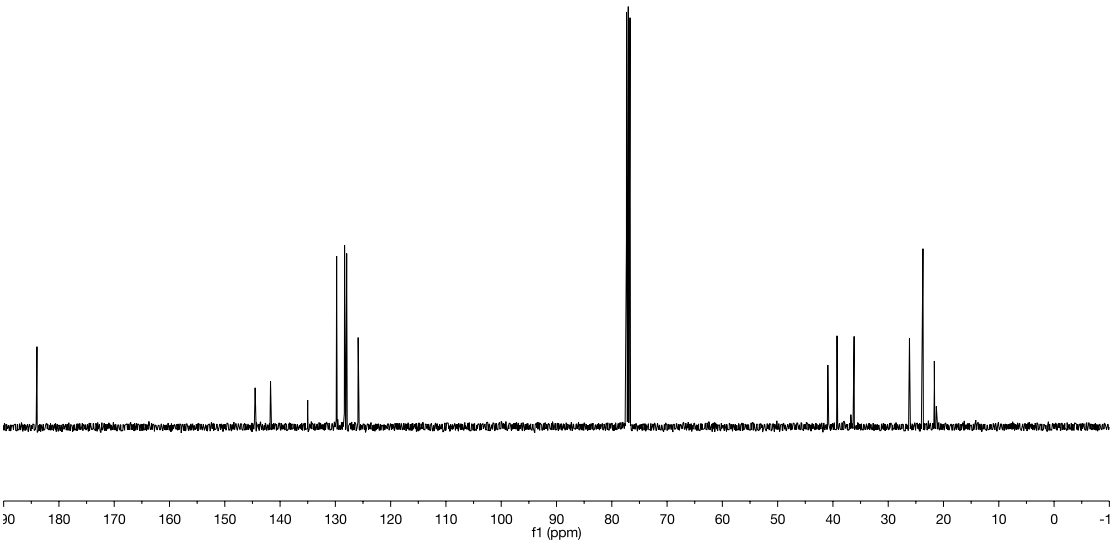
***N*-(2,2-Dimethyl-5-phenylpentylidene)-4-methylbenzenesulfonamide**



^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ = 8.41 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.33-7.23 (m, 5H), 7.21-7.14 (m, 1H), 7.10-7.05 (m, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.59-1.50 (m, 3H), 1.50-1.41 (m, 2H), 1.10 (s, 6H).

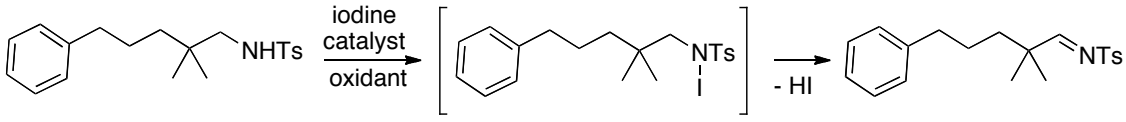
^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.9, 144.5, 141.7, 135.0, 129.8, 128.3, 128.3, 127.9, 125.9, 40.9, 39.3, 36.2, 26.2, 23.7, 21.7.


1.00
2.02
4.96
1.28
2.01
2.04
3.06
2.96
2.26
6.15
f1 (ppm)


f1 (ppm)

11- Investigation on alternative oxidants

In order to demonstrate the unique efficiency of the combined halide oxidants for catalytic C-H amination, the reaction was conducted under conditions that had previously been developed for intermolecular benzylic C-H amination.



Conditions

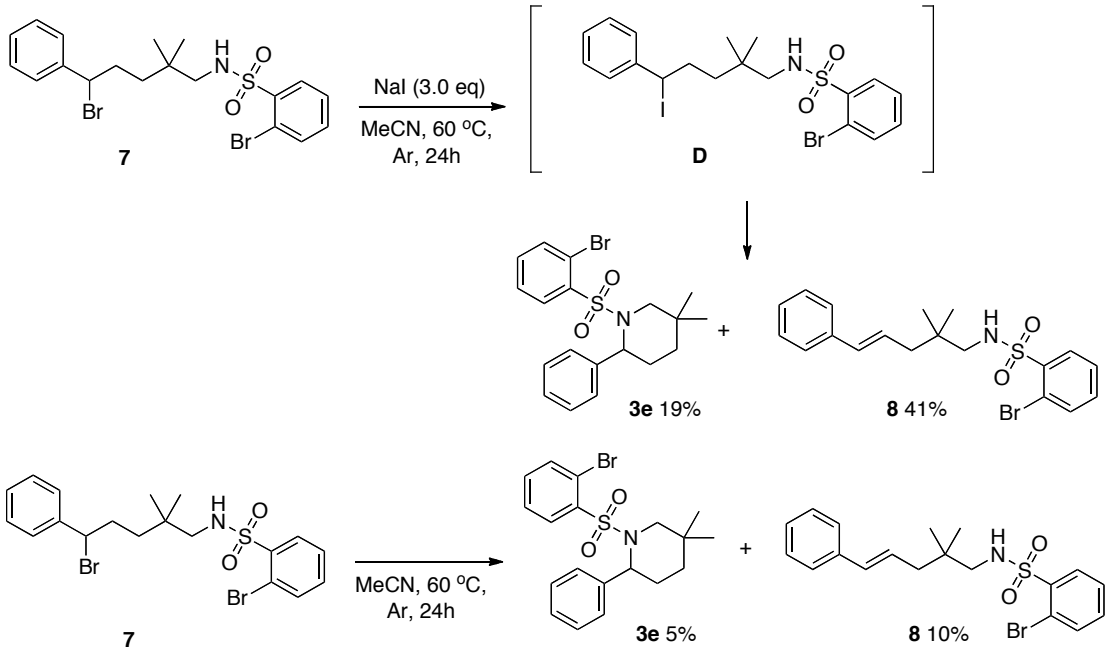
*t*BuOOH (5 equiv), Bu_4NI (20 mol%), $(CH_2Cl)_2$	76% conversion to imine
*t*BuOOH (5 equiv), Bu_4NI (20 mol%), CH_2Cl_2	62% conversion to imine
*t*BuOOH (5 equiv), Bu_4NI (20 mol%), CH_3CN	<5% conversion to imine

Scheme S5. Investigation on alternative oxidants

Under these conditions, the reaction provides exclusive access to the aldimine reported in section 10. Obviously, the intermediary N-iodinated derivative undergoes α-elimination as previously observed for some non-related cases.[4]

12- Investigation on the Intermediate D

The postulated intermediate **D** could not be isolated or synthesized independently due to its high reactivity. Its synthesis was therefore addressed by an indirect manner. Reaction of the benzyl bromide **7** with sodium iodide in acetonitrile proceeds sluggishly at 60 ºC. It provides a total of 60% conversion after 24 h and provides a mixture of the cyclized product **3e** and the elimination product **8**, which both stem from the putative intermediate **D**. The loss in chemoselectivity is the result of the high reaction temperature.



Scheme S6. Investigation on putative intermediate **D** from **7** and NaI.

In contrast, the direct transformation of **7** under these conditions provides less piperidine formation and elimination due to the lower reactivity of the benzyl bromide (compare section 8.2).

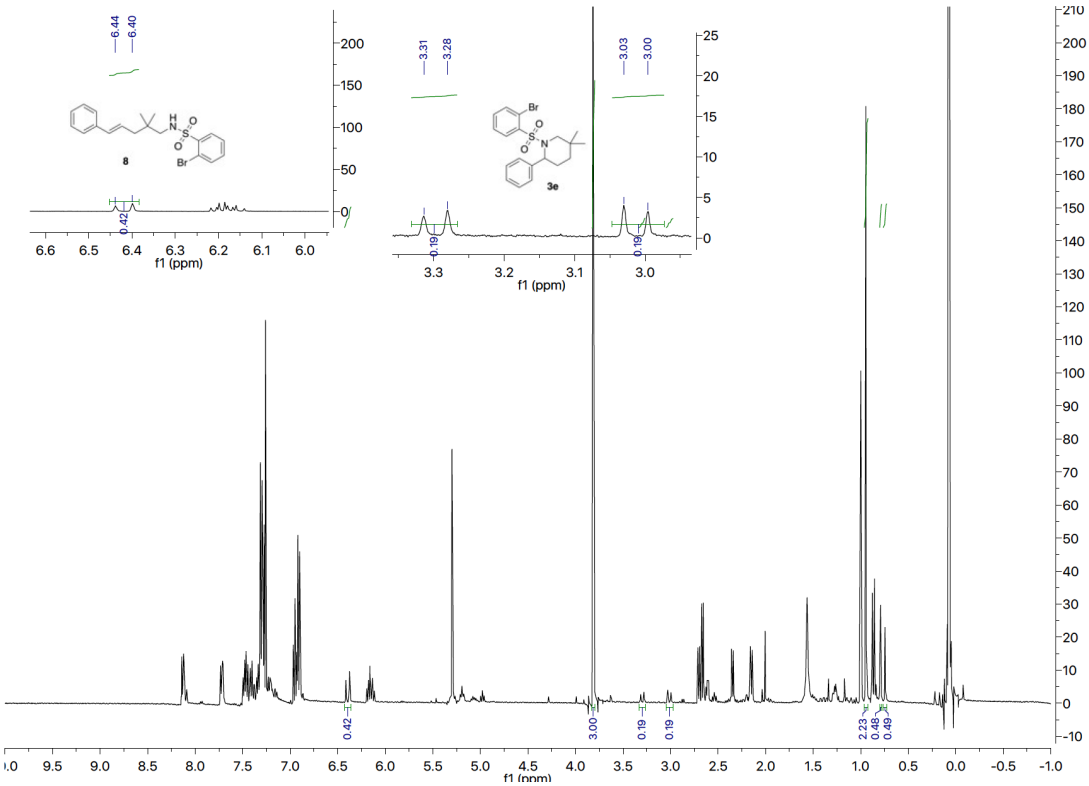
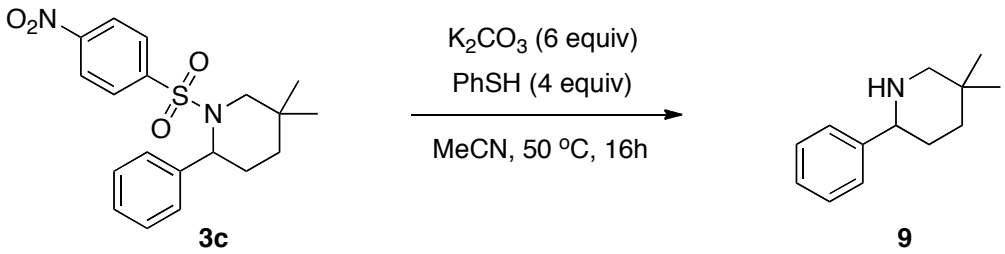


Figure S2. 1H NMR spectrum of the crude mixture of piperidine **3e** and elimination product **8**.

13- Deprotection of 3c to free piperidine 9



3c **9**

A flame-dried pressure tube equipped with a magnetic stir bar was charged **3c** (93.5 mg, 0.25 mmol, 100 mol%) and K_2CO_3 (207.3 mg, 1.5 mmol, 6 equiv). The reaction tube was placed under an atmosphere of argon, PhSH (0.102 mL, 1.0 mmol, 4 equiv) and MeCN (4 mL) was added by syringe. The tube was capped and the reaction mixture was allowed to stir at 50 °C for 16 h. CH_2Cl_2 was added and the resulting solution was washed with saturated aqueous solutions of $NaHCO_3$ and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4 and solvents were evaporated under reduced pressure. The crude product was purified by chromatography (silica gel, *n*-hexane/ethyl acetate 2/1, v/v) to give the pure product **9** as yellow oil in 90% yield (42.5 mg). Compound **9** was reported previously.[5]

Yellow oil, 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.37 (m, 2H), 7.35-7.29 (m, 2H), 7.26-7.21 (m, 1H), 3.52 (dd, *J* = 10.5, 3.8 Hz, 1H), 2.74 (dd, *J* = 11.6, 2.4 Hz, 1H), 2.62 (dd, *J* = 11.6, 0.8 Hz, 1H), 1.72-1.61 (m, 2H), 1.59-1.51 (m, 1H), 1.45-1.36 (m, 1H), 1.12 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.5, 128.3, 126.9, 126.7, 62.2, 59.2, 38.6, 31.2, 29.7, 29.6, 23.8.

14- X-Ray structure analyses of products 3c, 3m, 3z and 5

14.1 X-Ray Structure of 3c

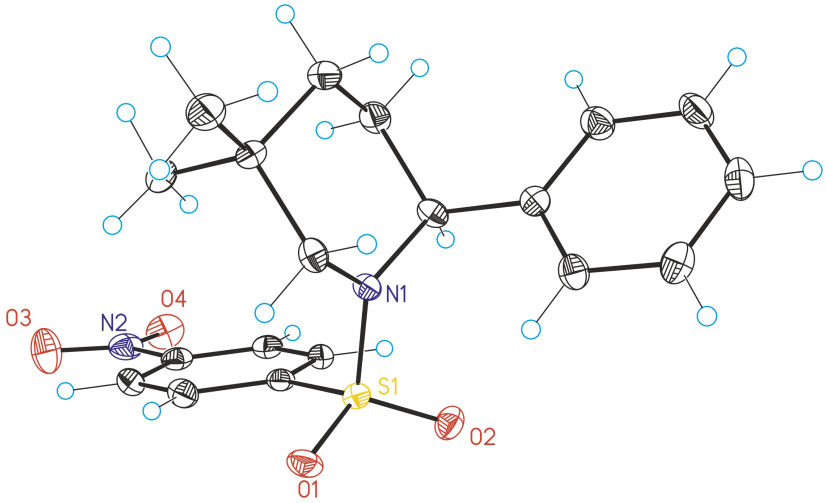


Table S2. Crystal data and structure refinement for compound **3c**.

Identification code	CCDC 1522790	
Empirical formula	C19 H22 N2 O4 S	
Formula weight	374.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 16.4786(7)Å	a= 90°.
	b = 7.7790(4)Å	b = 90°.
	c = 28.3488(15)Å	g = 90°.
Volume	3633.9(3) $Å^3$	
Z	8	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.205 mm^{-1}	
F(000)	1584	
Crystal size	0.20 x 0.08 x 0.04 mm^3	
Theta range for data collection	1.895 to 25.758°.	
Index ranges	-19<=h<=20,-9<=k<=7,-23<=l<=34	
Reflections collected	18028	
Independent reflections	3426[R(int) = 0.0672]	
Completeness to theta =25.758°	98.2%	
Absorption correction	Empirical	
Max. and min. transmission	0.992 and 0.892	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3426/ 0/ 237	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.0881	
R indices (all data)	R1 = 0.0673, wR2 = 0.0992	
Largest diff. peak and hole	0.277 and -0.380 e.$Å^{-3}$	

14.2 X-Ray Structure of 3m

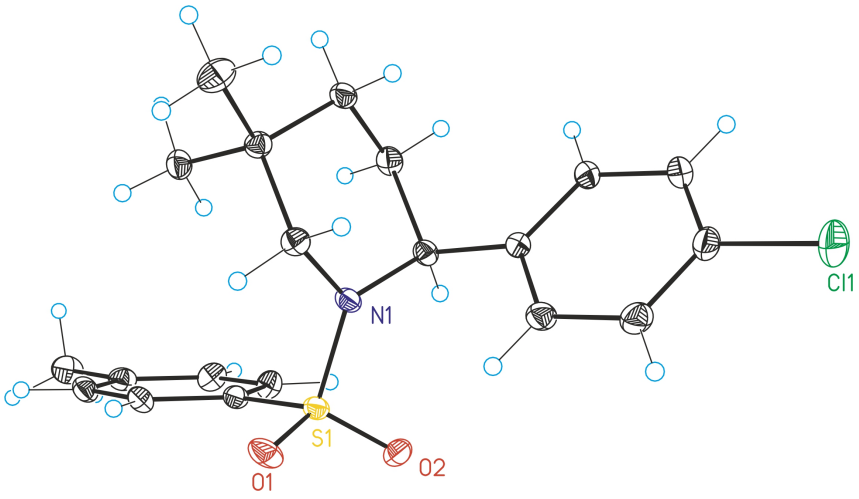


Table S3. Crystal data and structure refinement for compound **3m**.

Identification code	CCDC 1522791	
Empirical formula	C20 H24 Cl N O2 S	
Formula weight	377.91	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.59310(10)Å	⟨= 90°.
	b = 12.8055(2)Å	® =
102.1500(10)°.		
	c = 15.6673(2)Å	© = 90°.
Volume	1881.53(4) Å^3	
Z	4	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	0.327 mm^{-1}	
F(000)	800	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	2.172 to 40.097°.	
Index ranges	-17<=h<=17,-23<=k<=23,-28<=l<=28	
Reflections collected	54349	
Independent reflections	11469[R(int) = 0.0291]	
Completeness to theta =40.097°	97.799995%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.968 and 0.745	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11469/ 0/ 229	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.1001	
R indices (all data)	R1 = 0.0413, wR2 = 0.1042	
Largest diff. peak and hole	0.773 and -0.684 e.Å^{-3}	

14.3 X-Ray Structure of 3aa

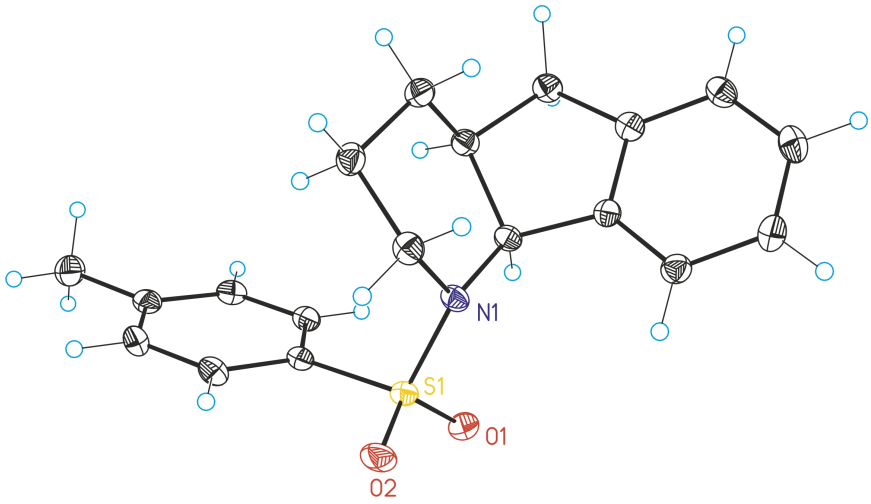


Table S4. Crystal data and structure refinement for compound **3z**.

Identification code	CCDC 1522793	
Empirical formula	C19 H21 N O2 S	
Formula weight	327.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.2375(2)Å	a= 90°.
	b = 9.4009(2)Å	b = 98.412(2)°.
	c = 16.6135(4)Å	g = 90°.
Volume	1581.71(7) $Å^3$	
Z	4	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	696	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	2.496 to 34.243°.	
Index ranges	-15<=h<=15,-14<=k<=14,-25<=l<=25	
Reflections collected	29572	
Independent reflections	6195[R(int) = 0.0501]	
Completeness to theta =34.243°	94.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.979 and 0.753	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6195/ 0/ 217	
Goodness-of-fit on F^2	0.963	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0916	
R indices (all data)	R1 = 0.0519, wR2 = 0.0930	
Largest diff. peak and hole	0.446 and -0.364 $e.Å^{-3}$	

14.4 X-Ray Structure of 5

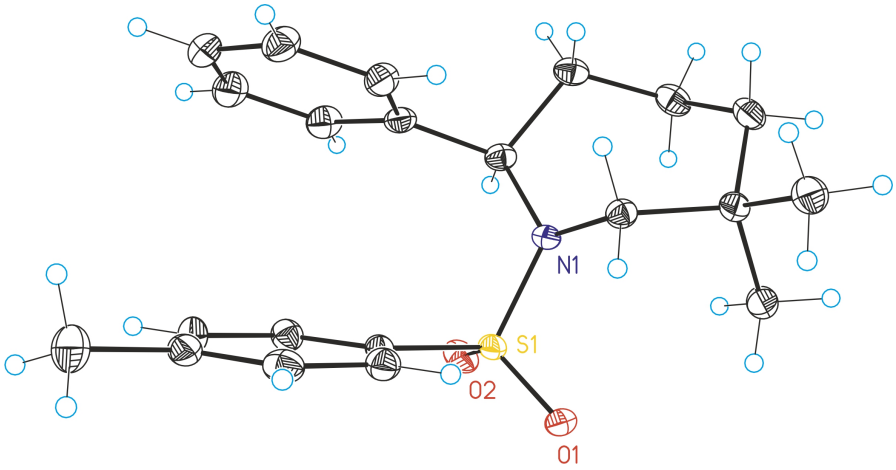


Table S5. Crystal data and structure refinement for compound **5**.

Identification code	CCDC 1522792	
Empirical formula	C10.50 H13.50 N0.50 O S0.50	
Formula weight	178.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.6983(3)Å	a= 90°.
	b = 13.0767(3)Å	b = 114.637(4)°.
	c = 13.6557(5)Å	g = 90°.
Volume	1898.81(11) $Å^3$	
Z	8	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	0.184 mm^{-1}	
F(000)	768	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.997 to 29.012°.	
Index ranges	-15<=h<=15,-16<=k<=17,-17<=l<=17	
Reflections collected	35085	
Independent reflections	4596[R(int) = 0.0302]	
Completeness to theta =29.012°	91.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.985 and 0.758	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4596/ 0/ 229	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0975	
R indices (all data)	R1 = 0.0416, wR2 = 0.1006	
Largest diff. peak and hole	0.671 and -0.394 e.$Å^{-3}$	

15. List of references

1) Martínez, C.; Muñiz, K. *Angew Chem. Int. Ed.* **2015**, *54*, 8287-8291.

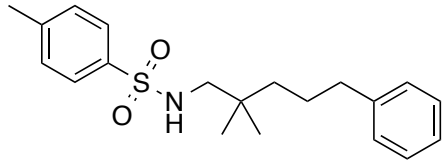
2) Fillion, E.; Trépanier, V. É.; Heikkinen, J. J.; Remorova, A. A.; Carson, R. J.; Goll, J. M.; Seed, A. *Organometallics* **2009**, *28*, 3518–3531.

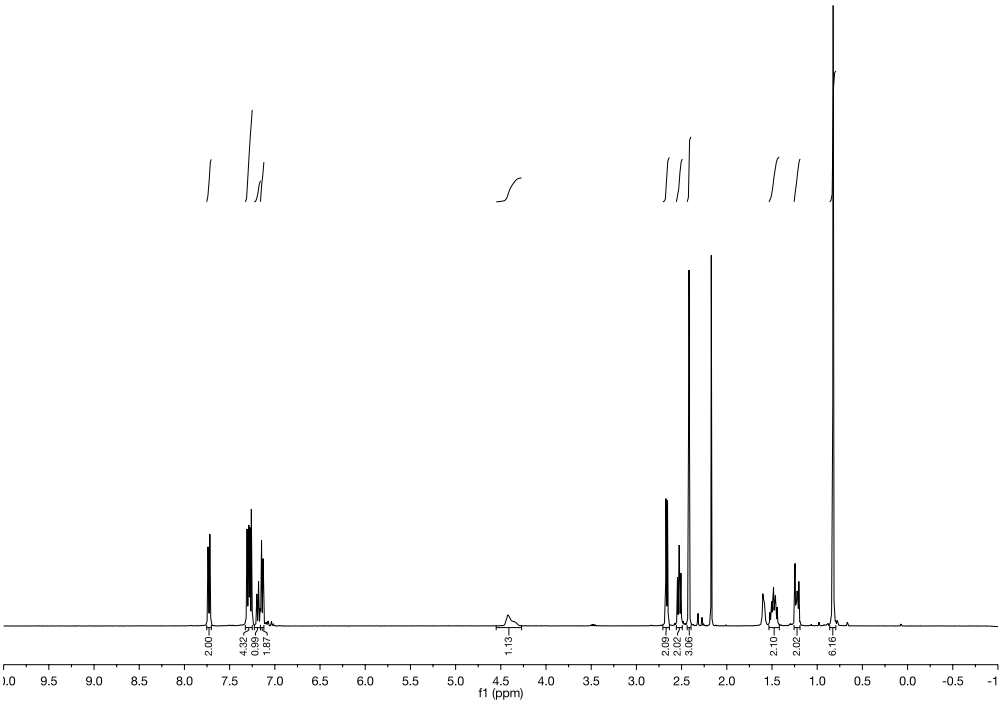
3) O'Broin, C. Q.; Fernández, P.; Martínez, C.; Muñiz, K. *Org. Lett*. **2016**, *18*, 436-439.

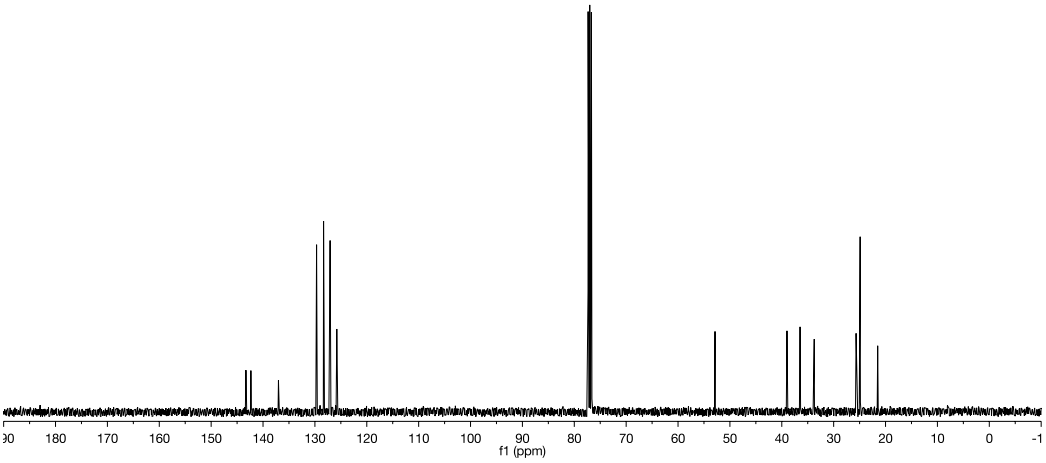
4) Fan, R.; Pu, D.; Wen, F.; Wu, J. *J. Org. Chem.* **2007**, *72*, 8994-8997.

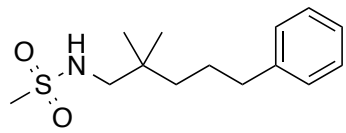
5) Healy, M. A. M.; Smith, S. A. M.; Stemp, G. *Synth. Commun.* **1995**, *25*, 3789-3797.

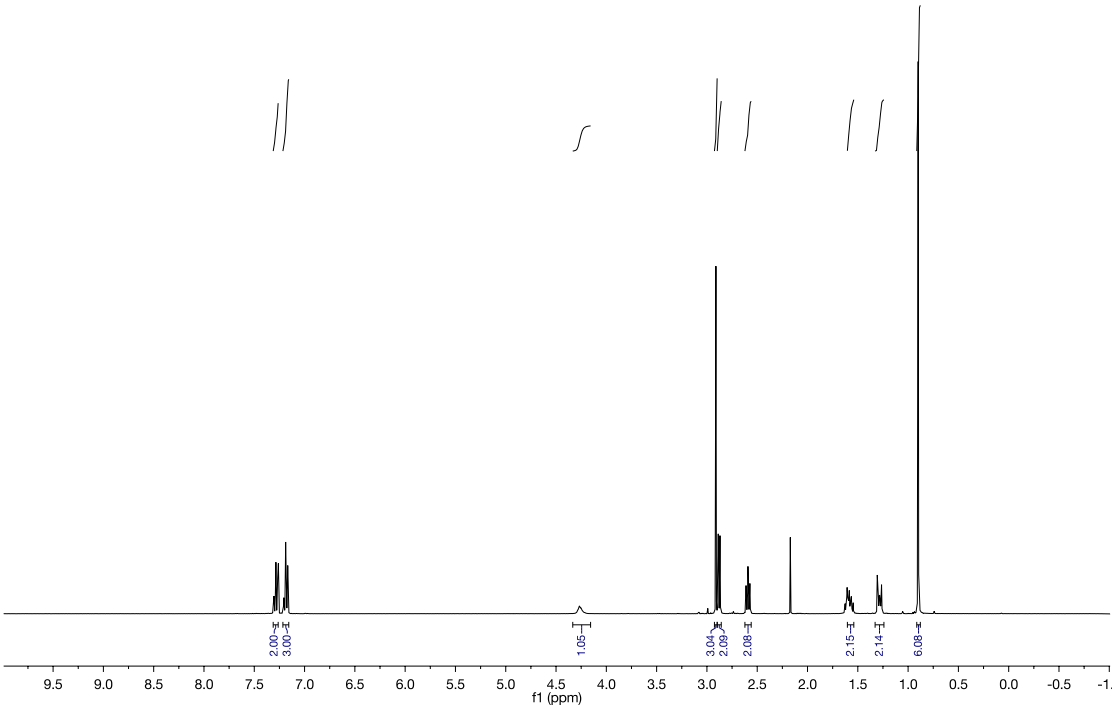
16- NMR Charts of starting materials








O
H
N
S
O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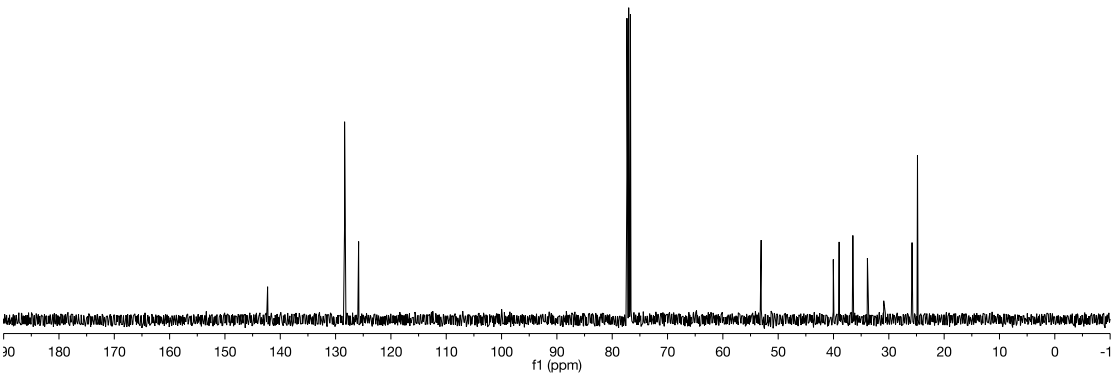
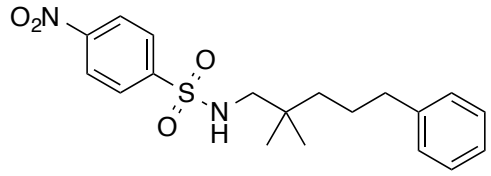
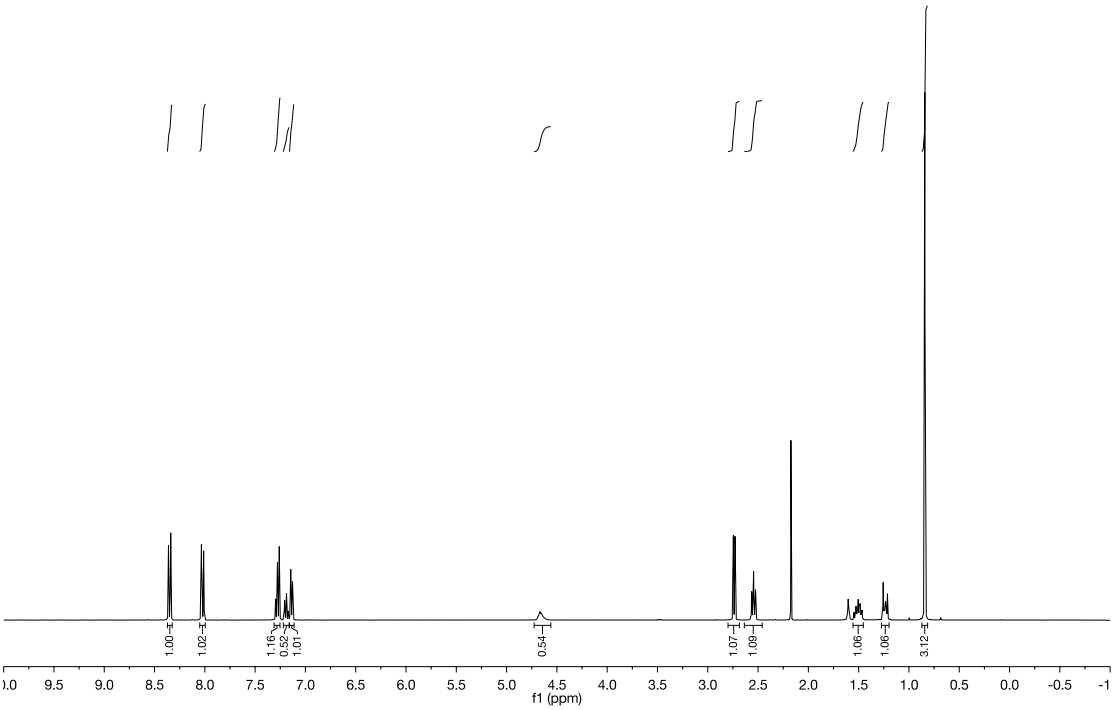
3.00
1.05
3.04
2.09
2.08
2.15
2.14
6.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2N
O
S
O
N
H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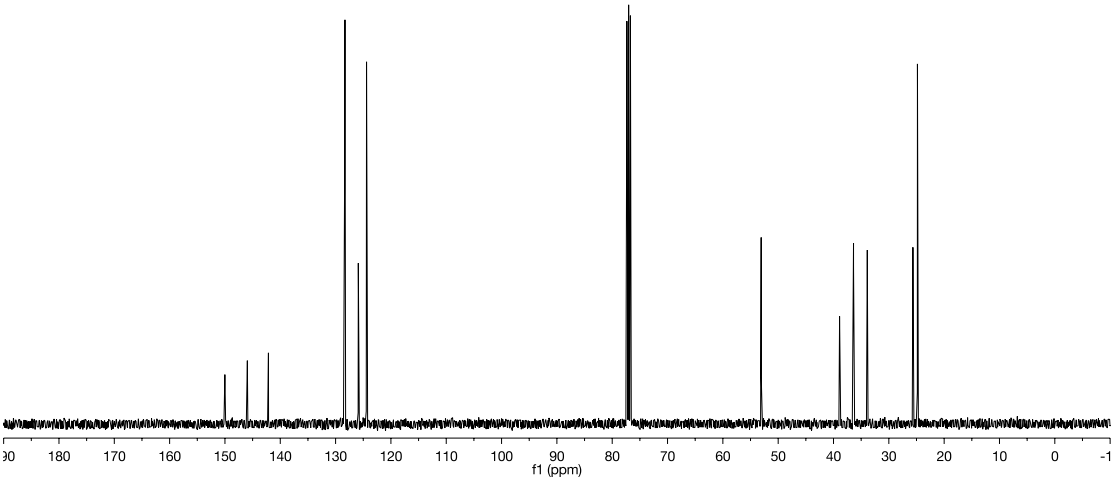
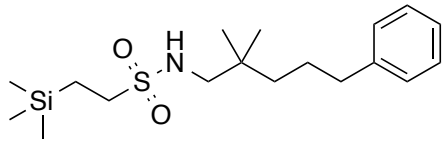
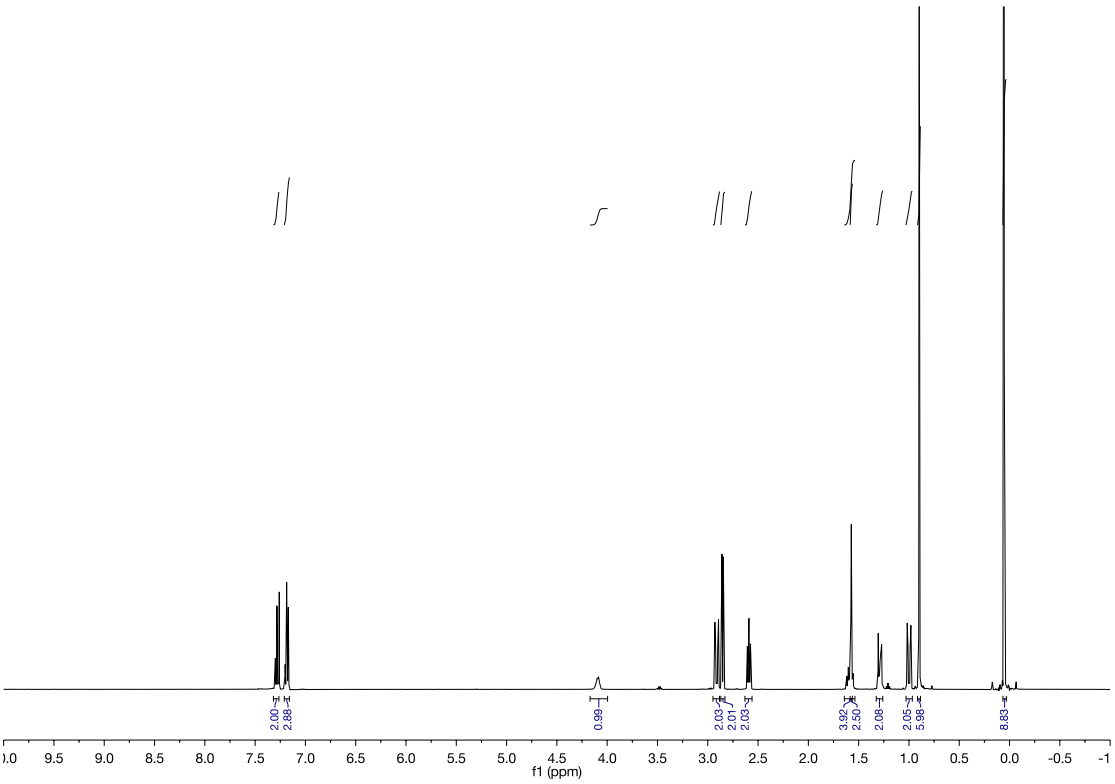
1.06
1.06
3.12
f1 (ppm)


f1 (ppm)


O
H
N
S
O
Si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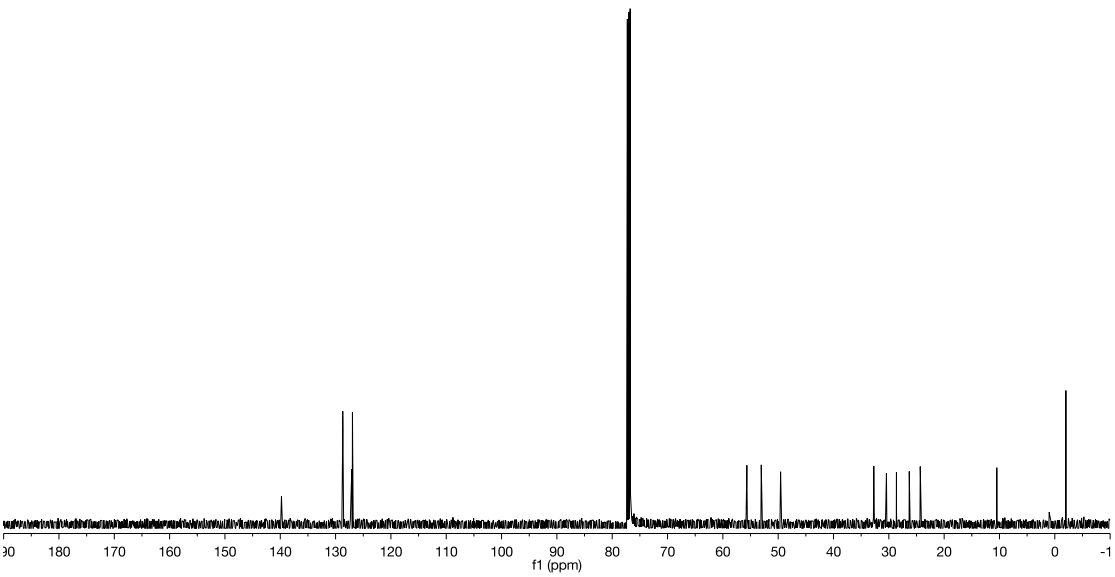
2.05
5.98
8.83
f1 (ppm)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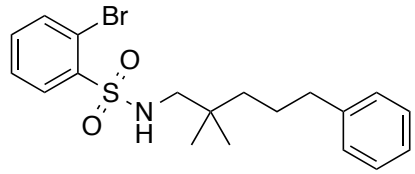
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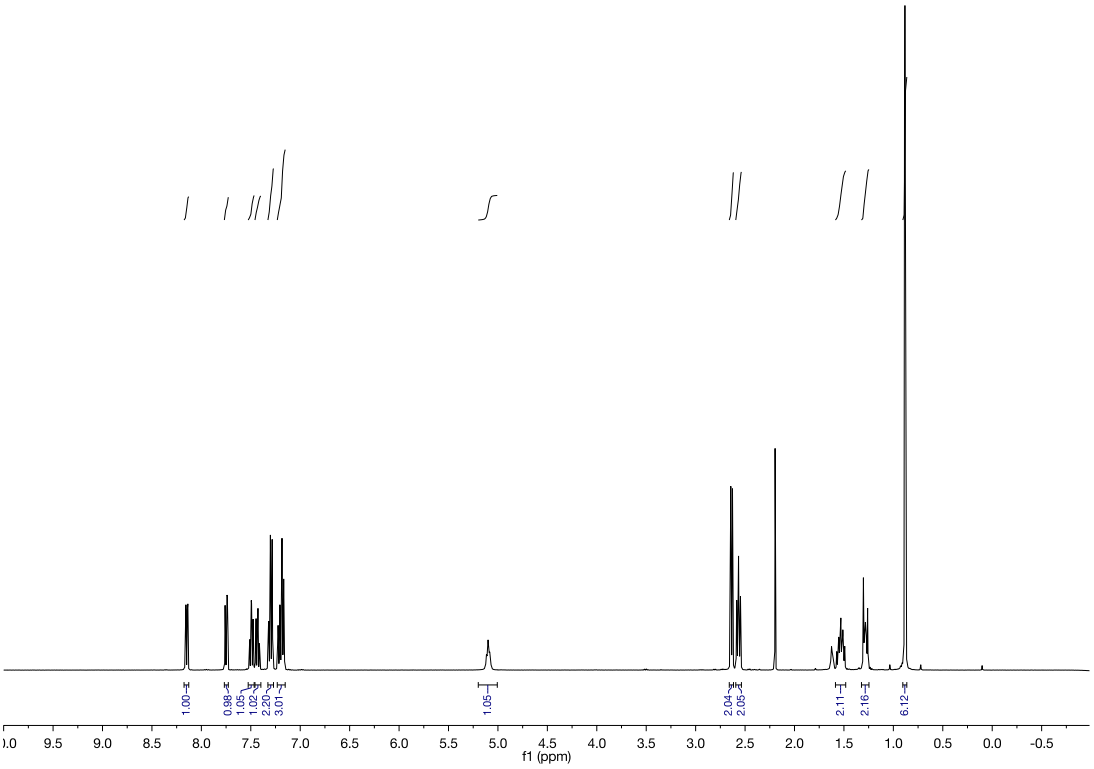
O
S
N
H
O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1.05
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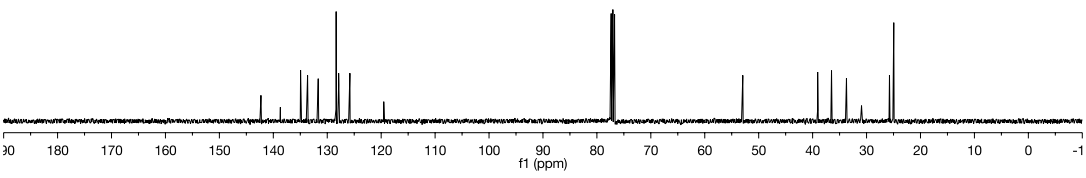
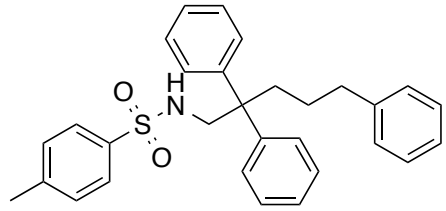
2.05
2.11
2.16
6.12
f1 (ppm)


f1 (ppm)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H
N
S
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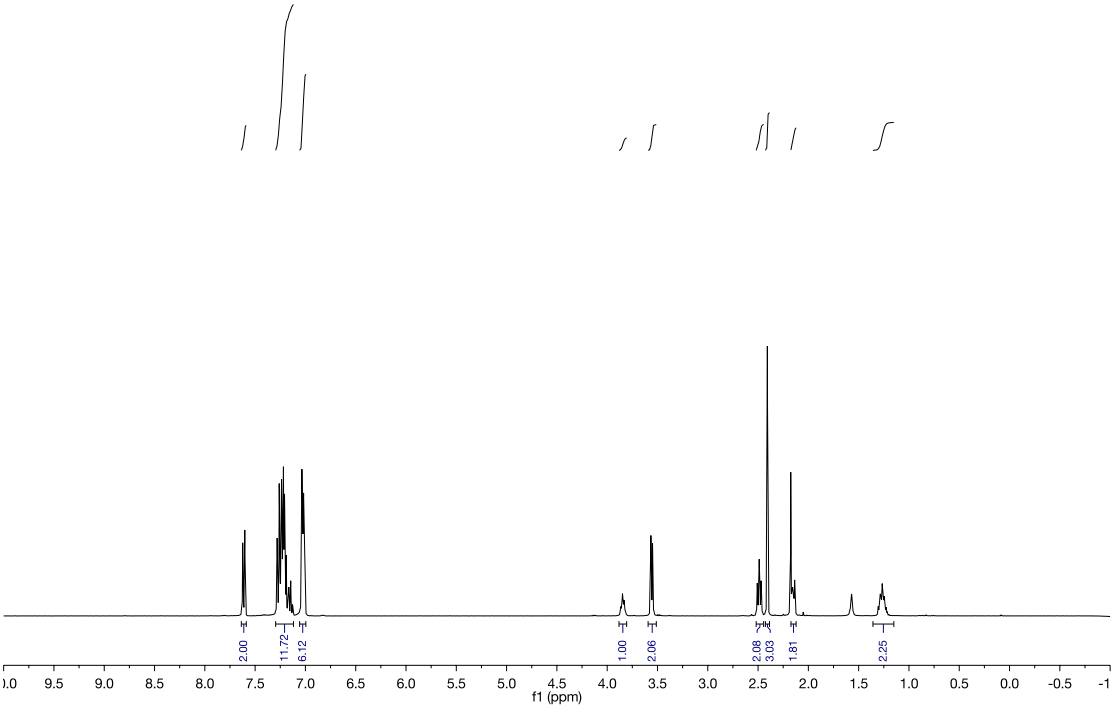
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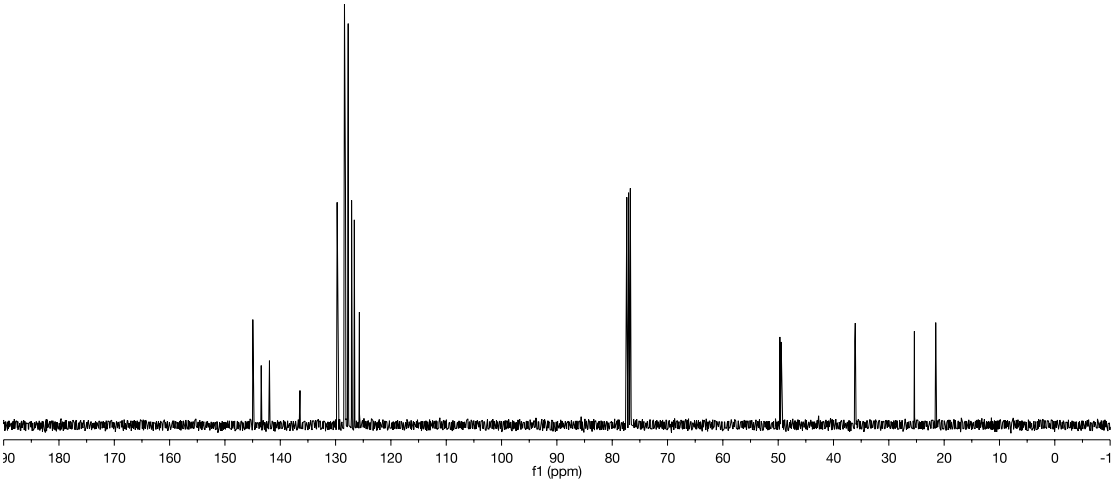
1.81
2.25
f1 (ppm)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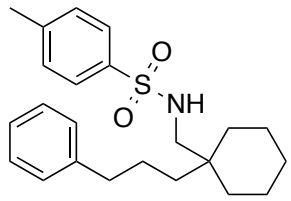
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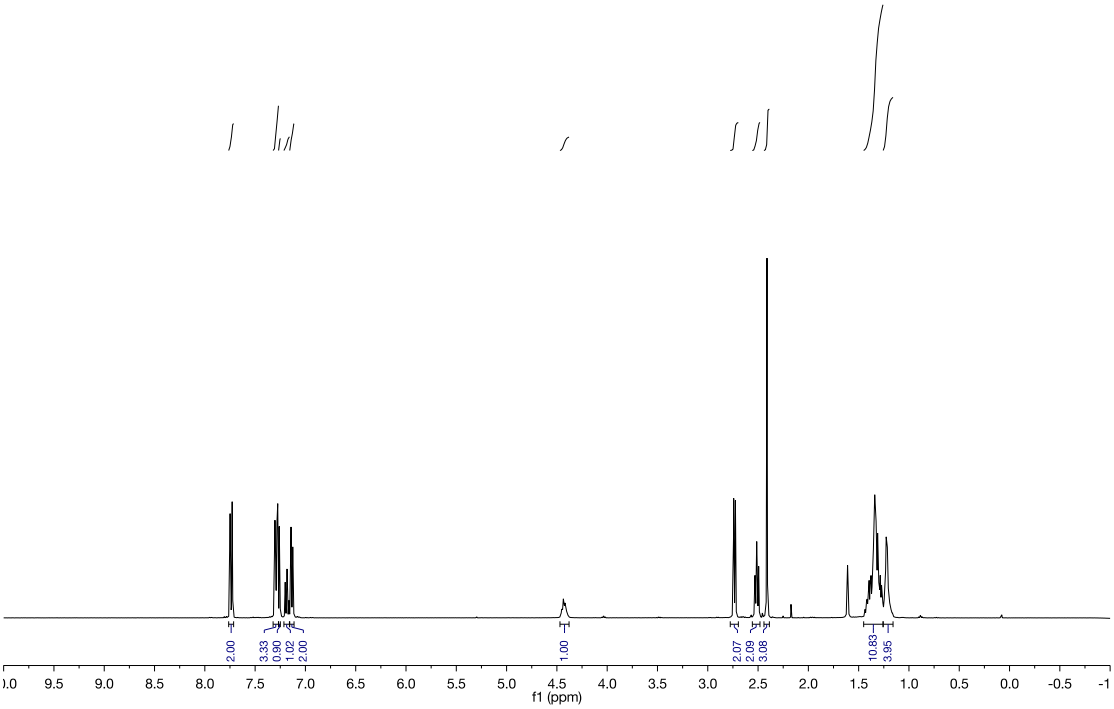
S
O
NH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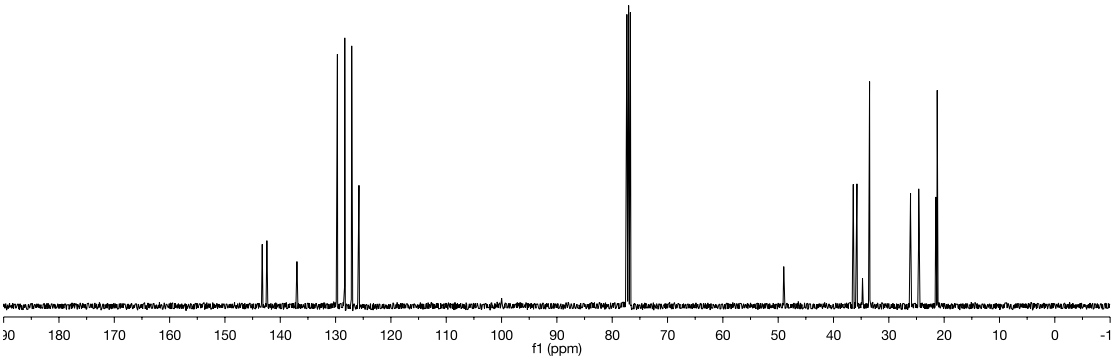
f1 (ppm)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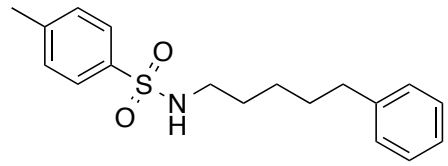
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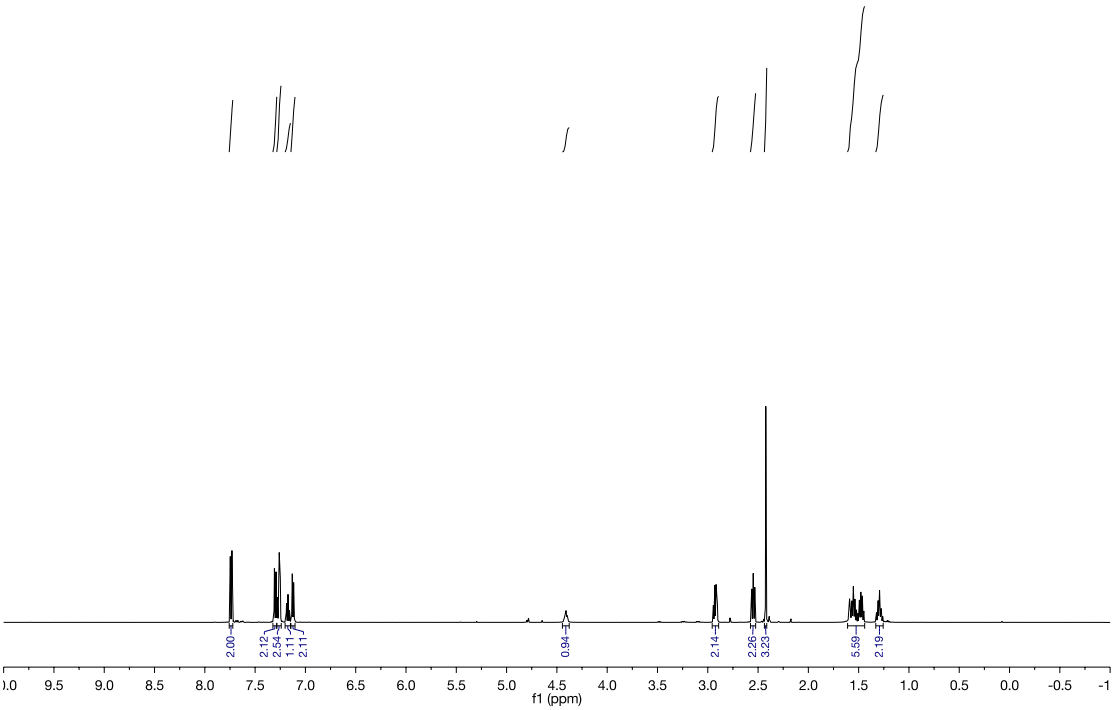
S
O
N
H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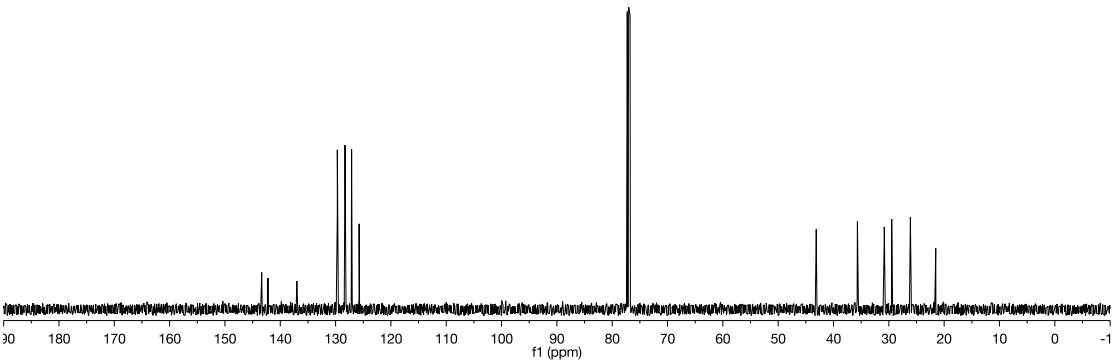
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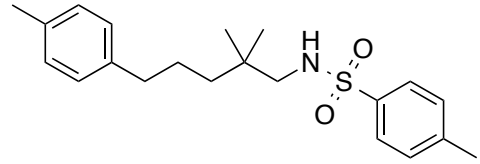
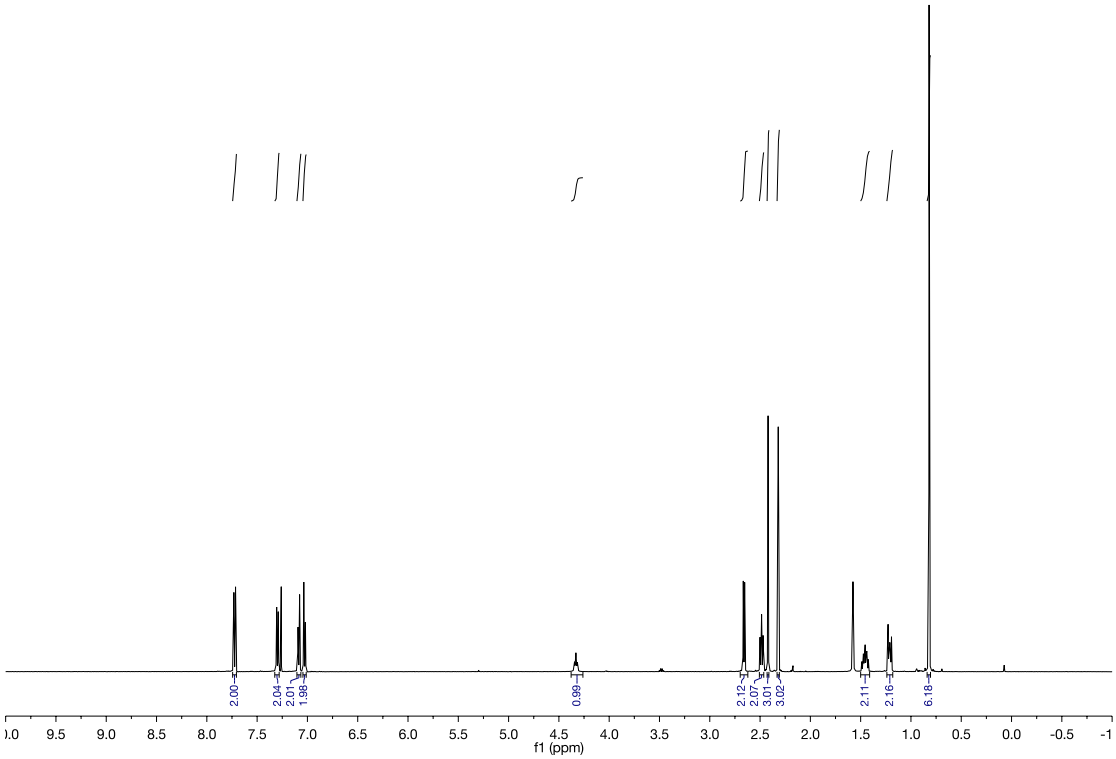

H
N
S
O
O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0.99
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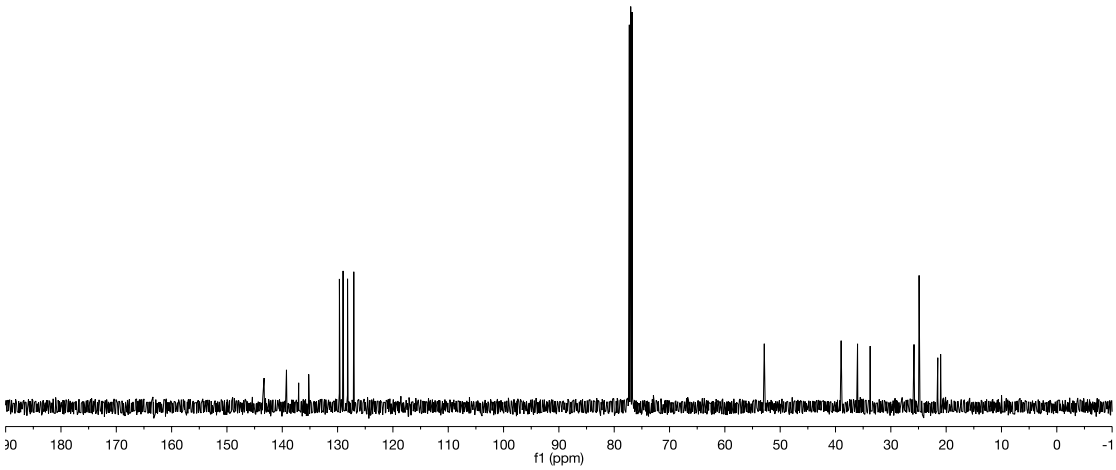
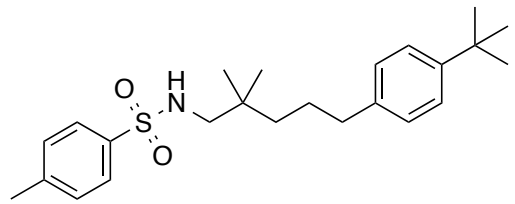
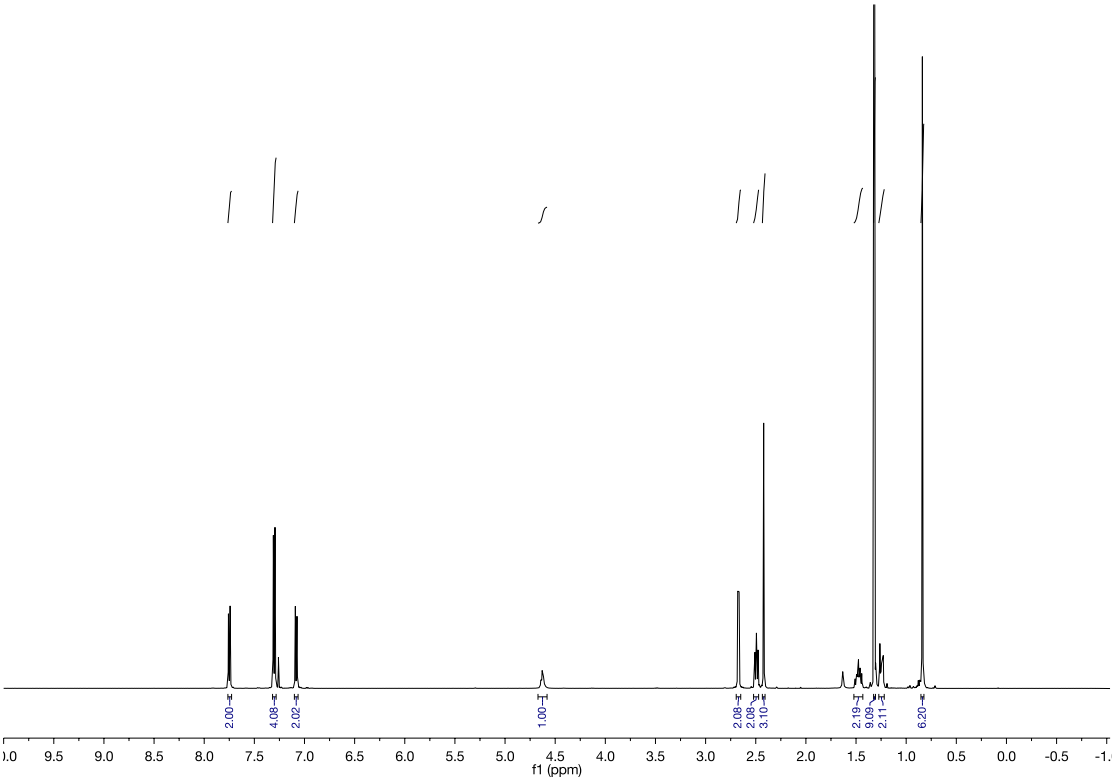
2.16
6.18
f1 (ppm)


f1 (ppm)


O
H
N
S
O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4.08
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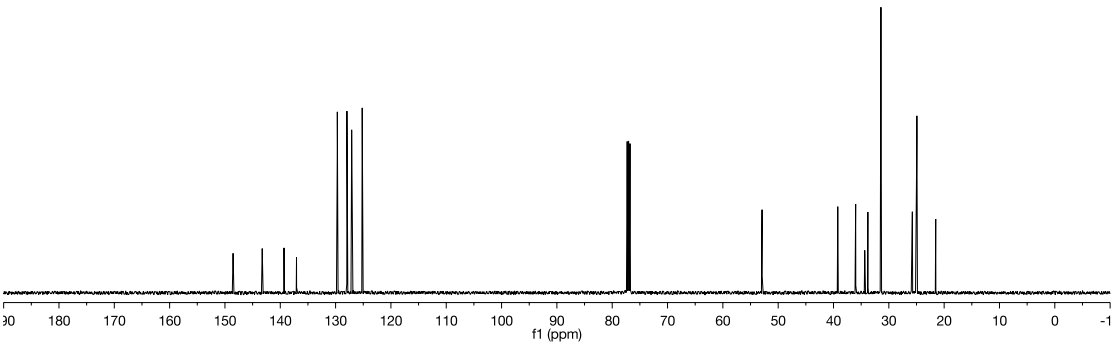
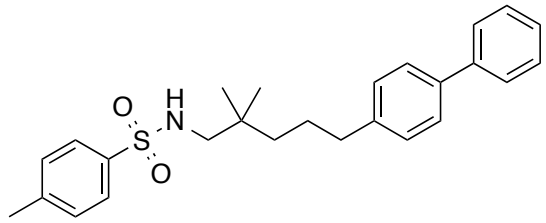
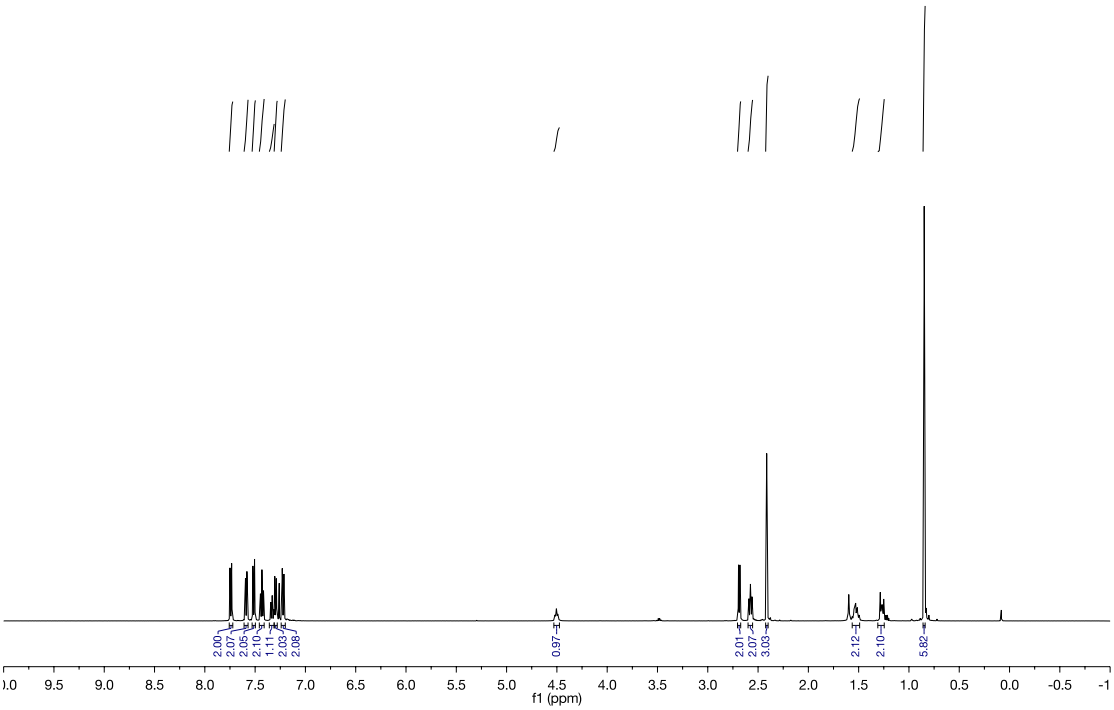
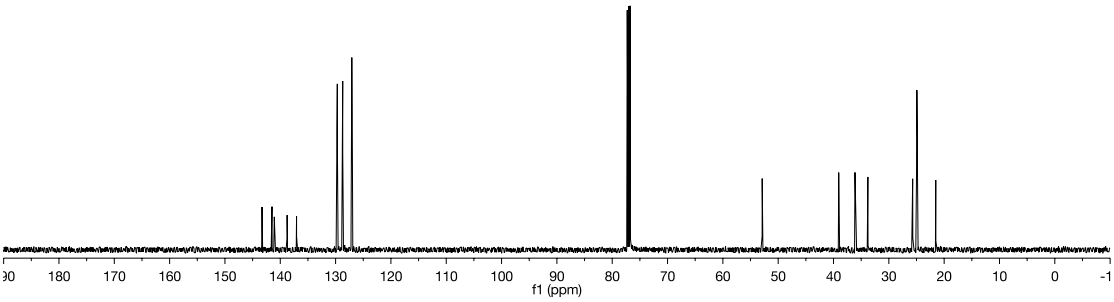
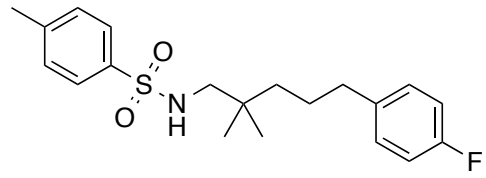
2.08
2.08
3.10
2.19
9.09
2.11
6.20
f1 (ppm)

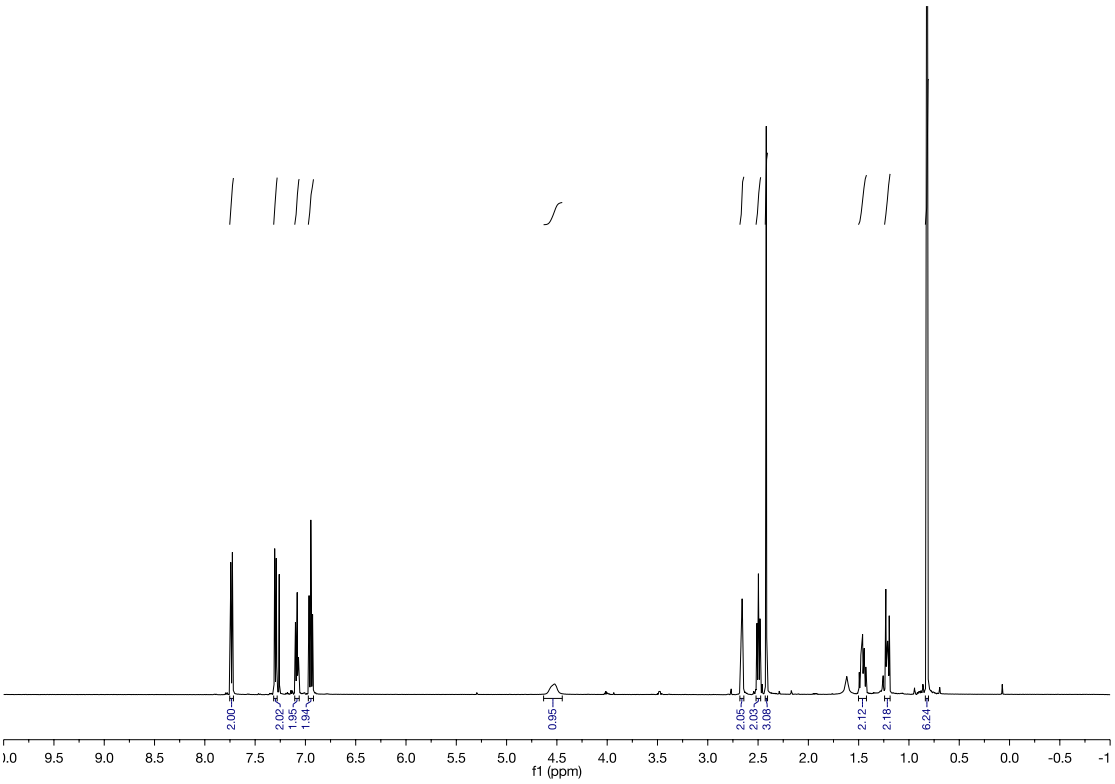

f1 (ppm)


O
H
N
S
O


2.00
2.07
2.05
2.10
1.11
2.03
2.08
0.97
2.01
2.07
3.03
2.12
2.10
5.82
f1 (ppm)


f1 (ppm)


O
S
O
N
H
F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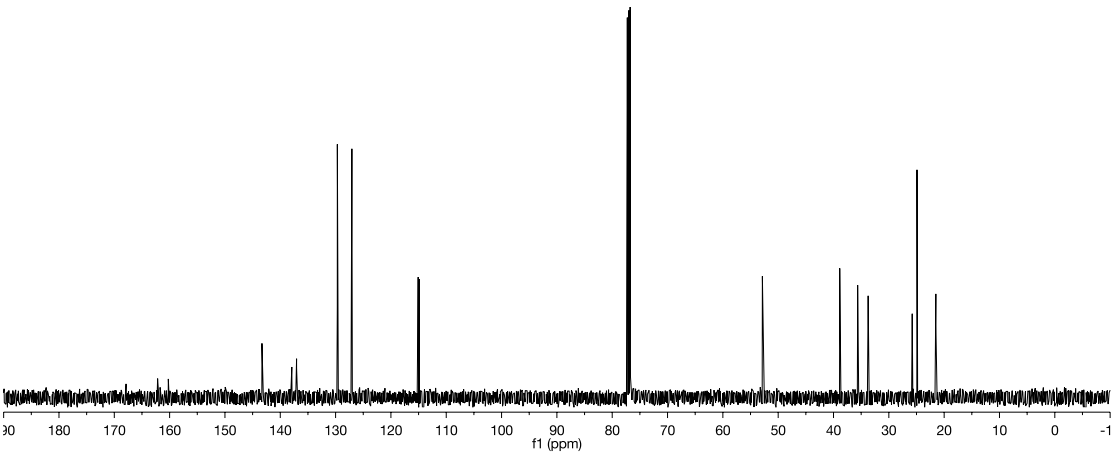
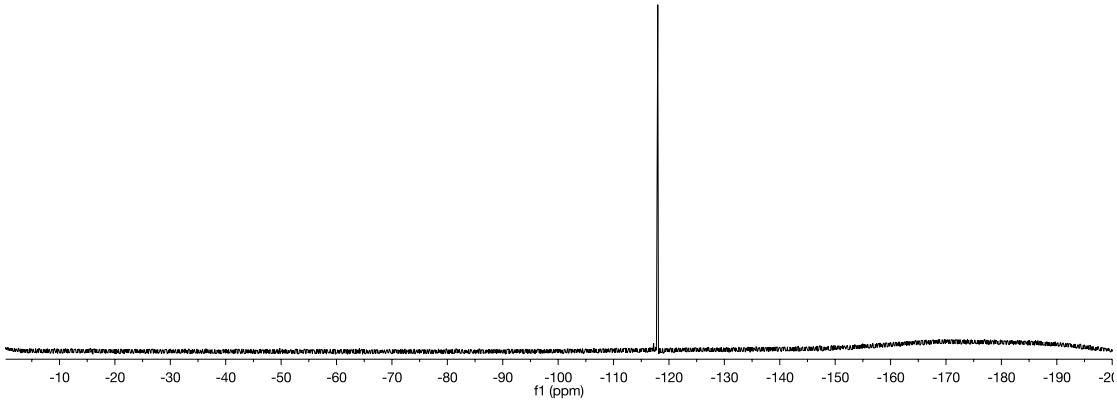
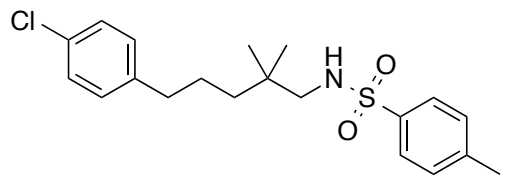
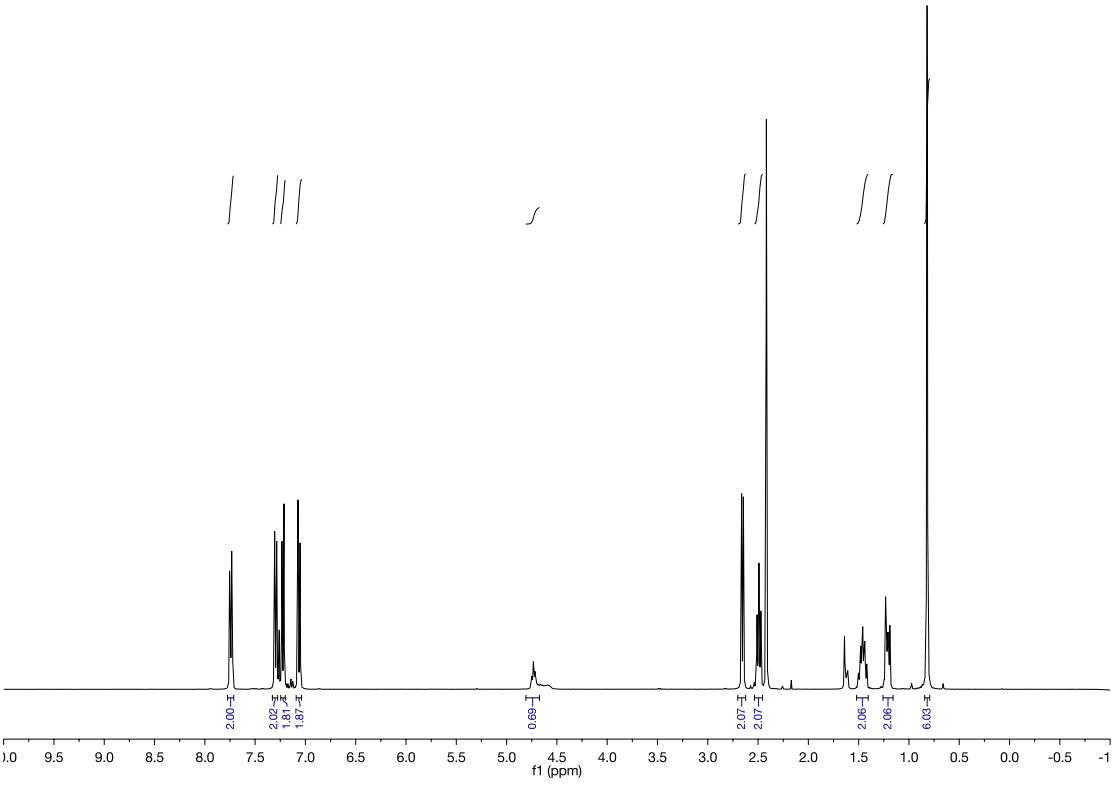
1.94
0.95
2.05
2.03
3.08
2.12
2.18
6.24
f1 (ppm)


f1 (ppm)


-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


Cl
H
N
S
O
O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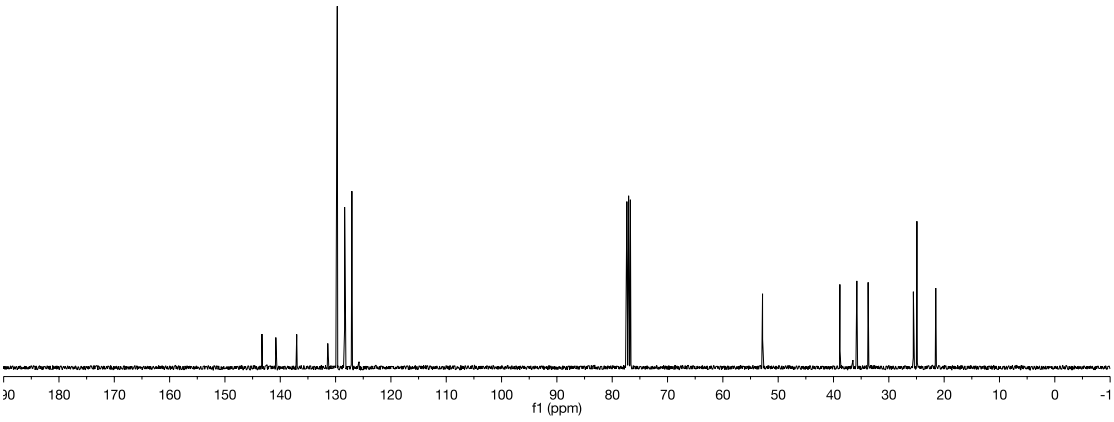
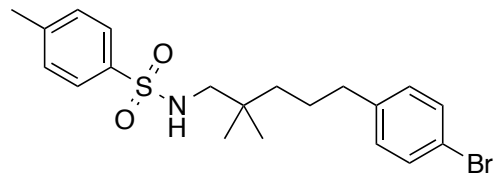
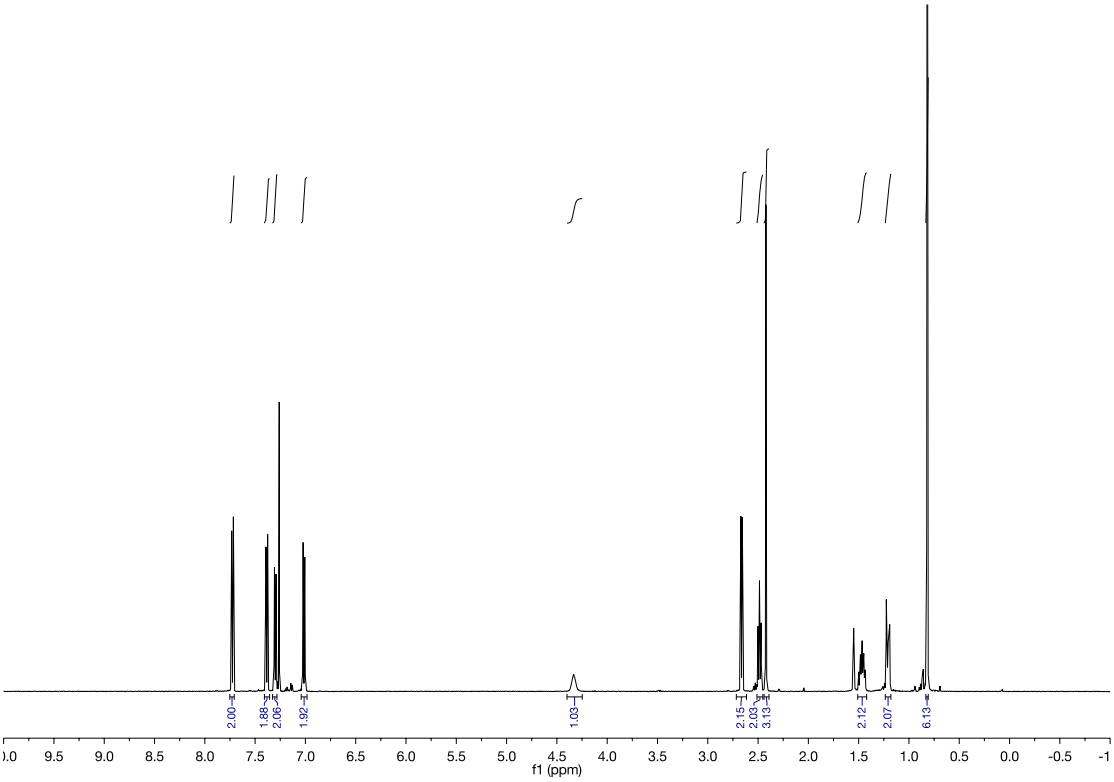
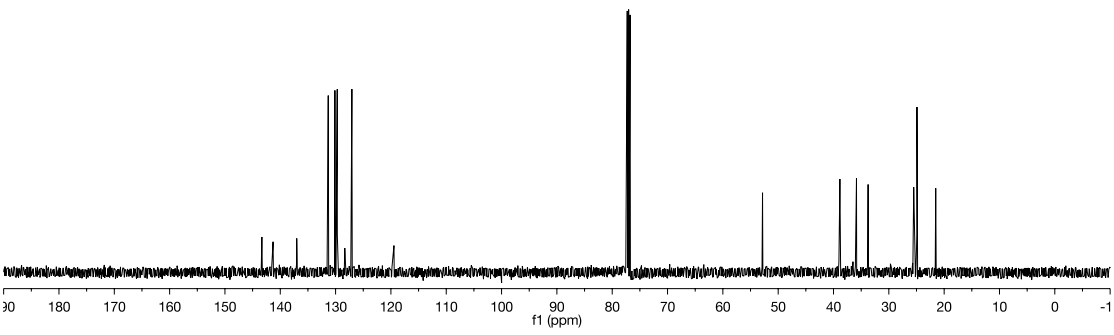
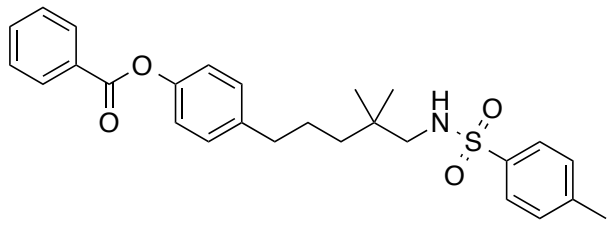
0.69
2.07
2.07
2.06
2.06
6.03
f1 (ppm)

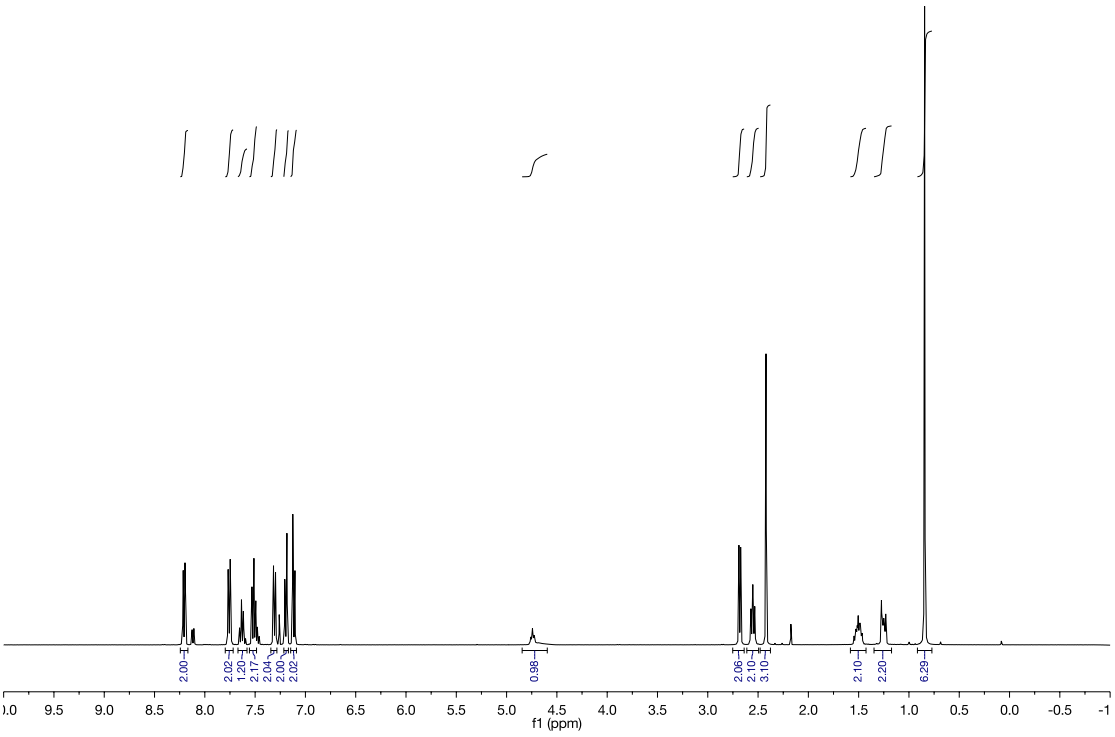

f1 (ppm)

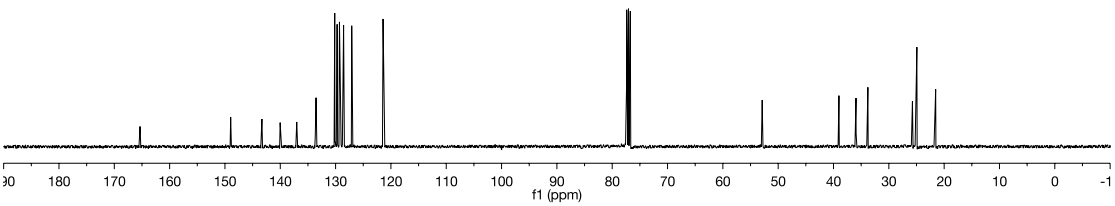

O
S
O
N
H
Br

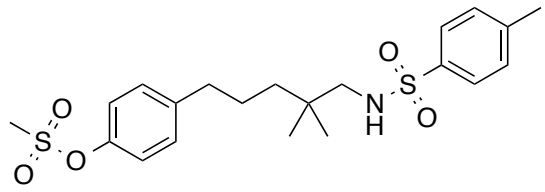

2.00
1.88
2.06
1.92
1.03
2.15
2.03
3.13
2.12
2.07
6.13
f1 (ppm)

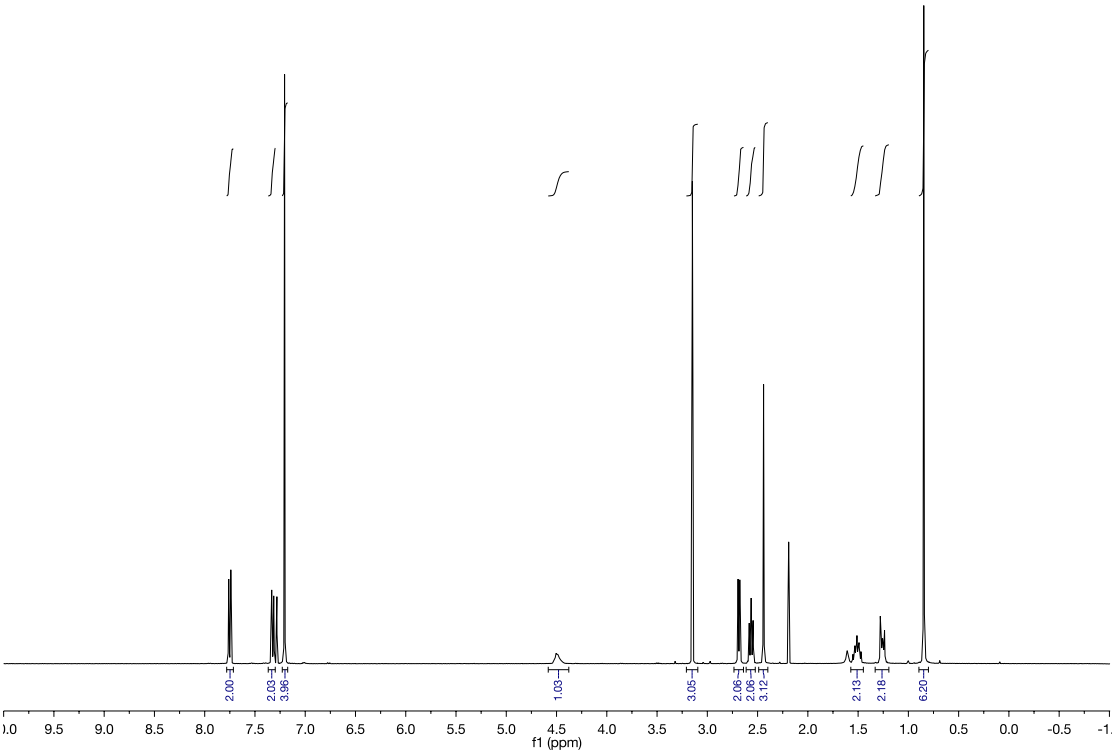

f1 (ppm)

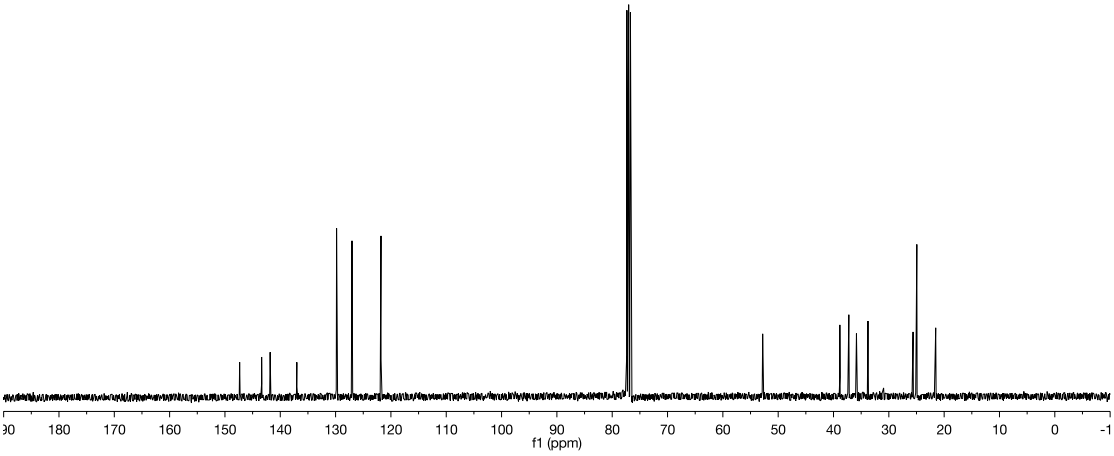

O
O
H
N
S
O
O

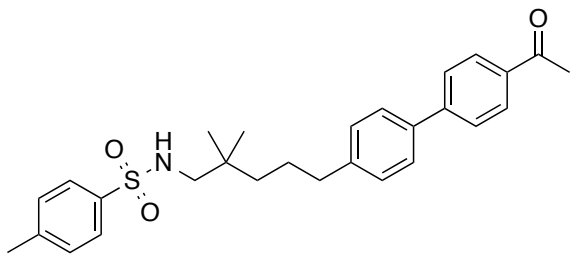

2.00
2.02
1.20
2.07
2.04
2.00
2.02
0.98
2.06
2.10
3.10
2.10
2.20
6.29
f1 (ppm)

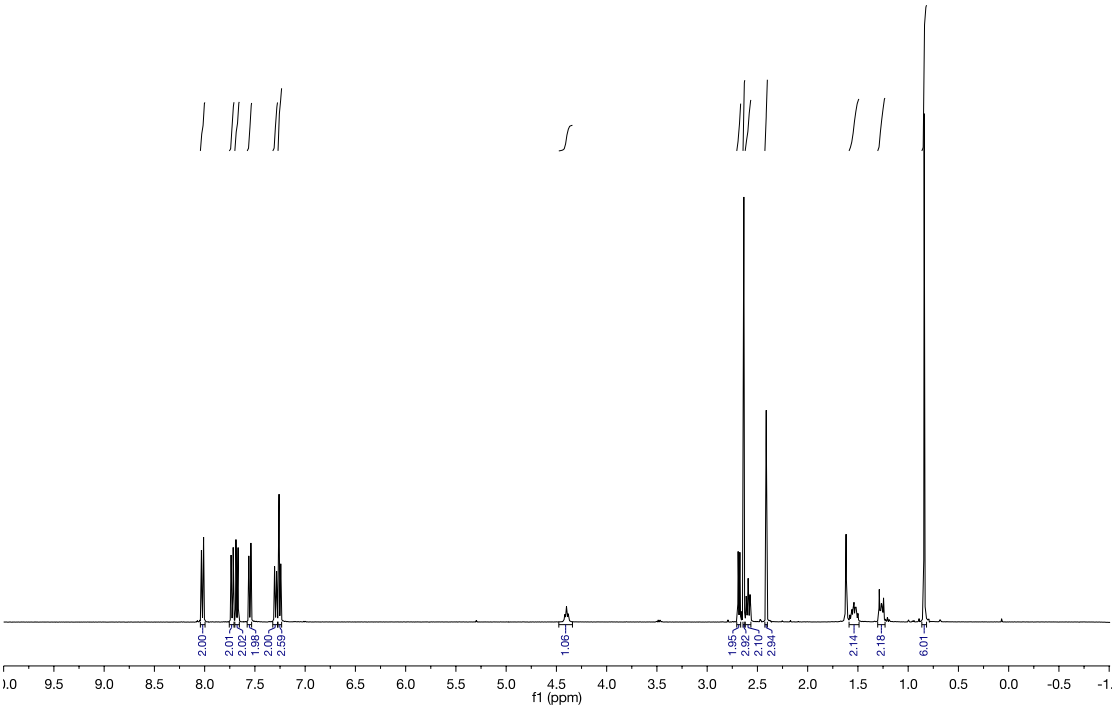

f1 (ppm)

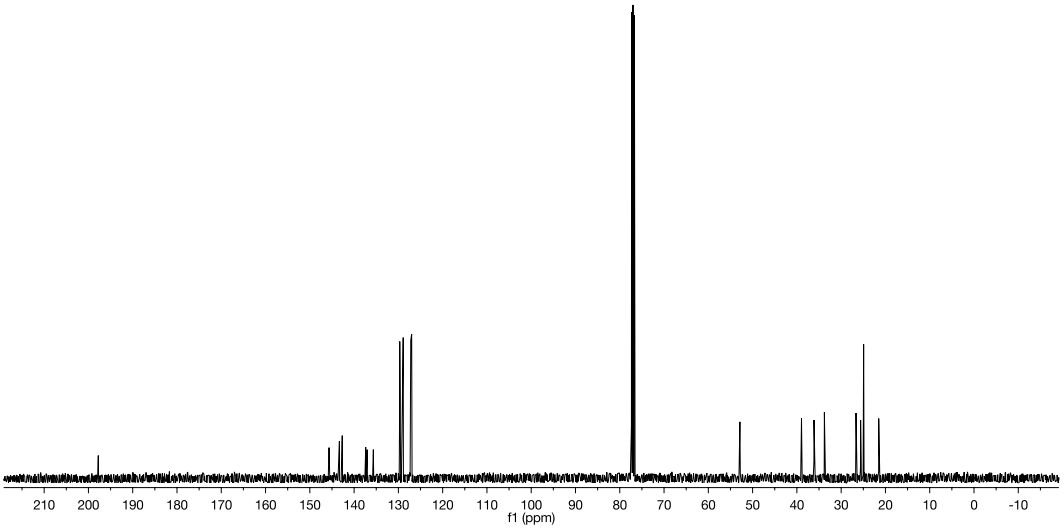

O
S
O
O
N
H
O
S
O
O

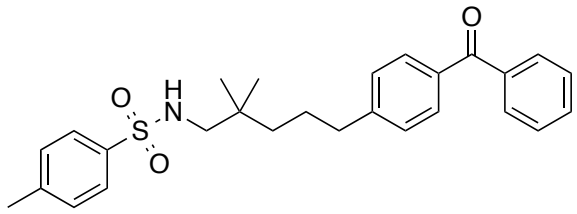

2.00
2.03
3.96
1.03
3.05
2.06
2.06
3.12
2.13
2.18
6.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

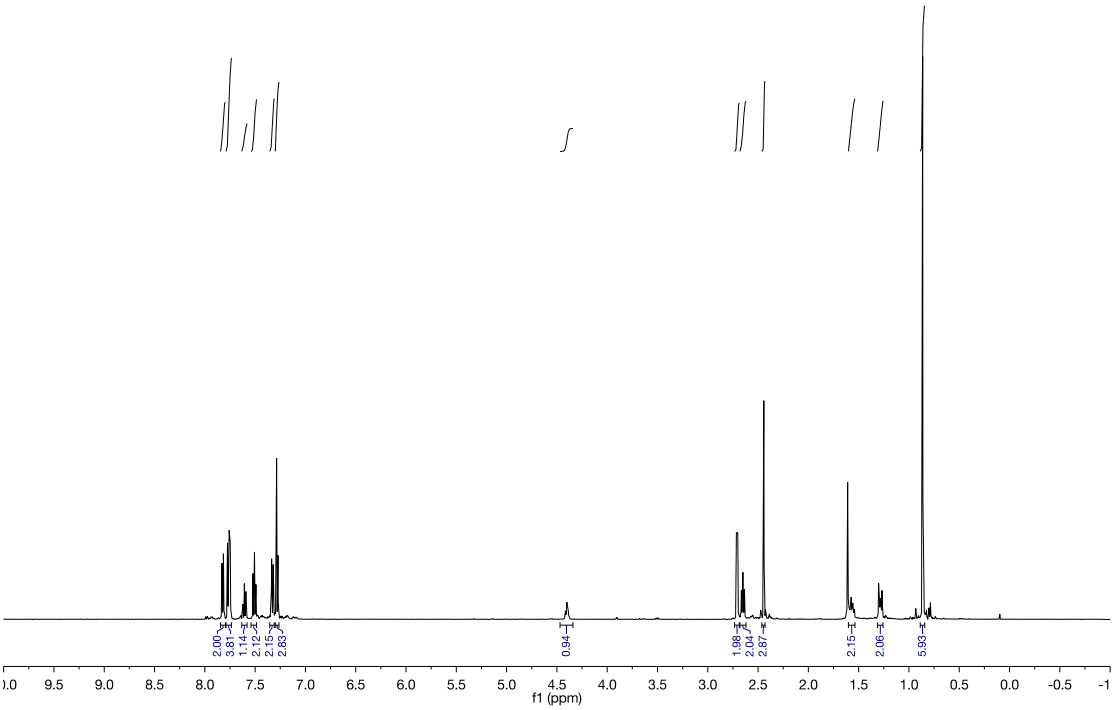

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H
N
O
S
O


2.00
2.01
2.02
1.98
2.00
2.59
1.06
1.95
2.92
2.10
2.94
2.14
2.18
6.01
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 -0.5
f1 (ppm)


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)


O
H
N
O
S
O


2.00
3.81
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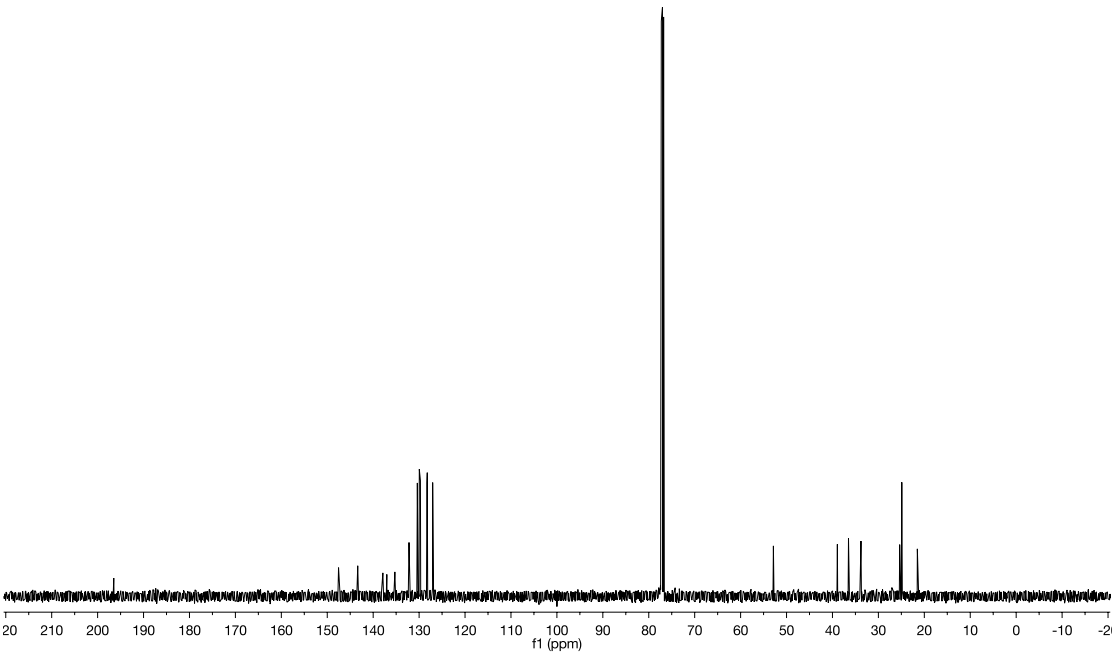
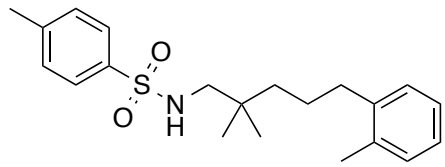
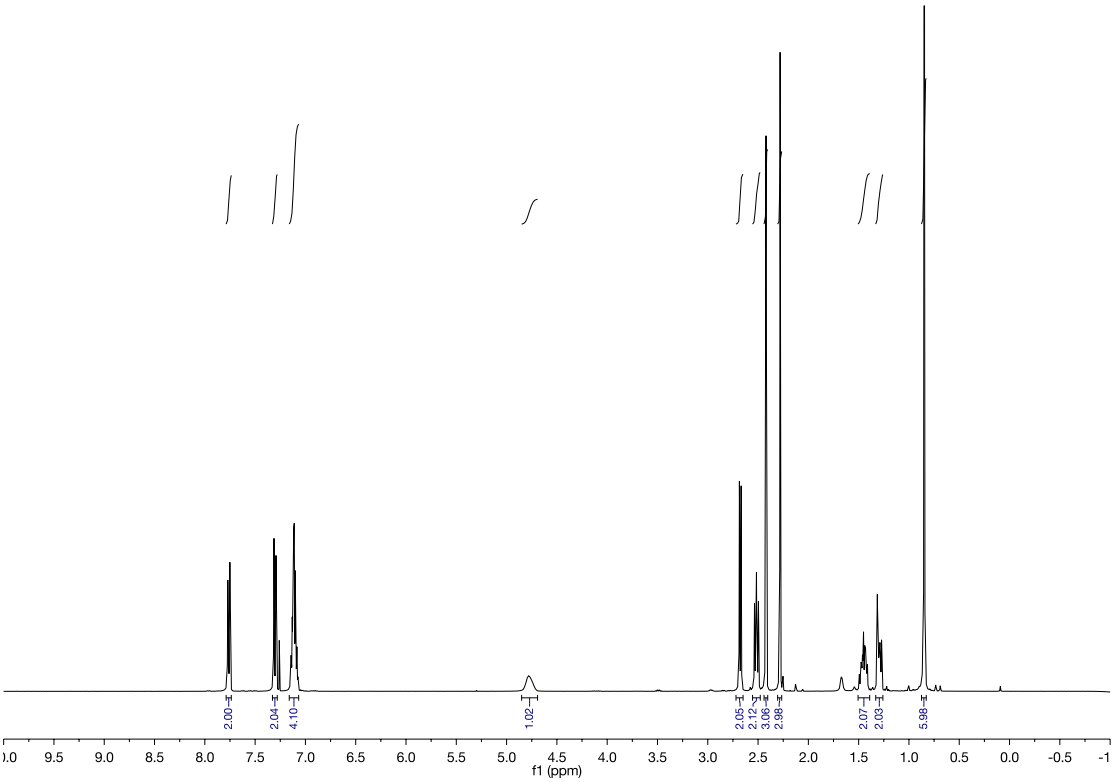
2.12
2.15
2.83
0.94
1.98
2.04
2.87
2.15
2.06
5.93
f1 (ppm)


f1 (ppm)


O
S
O
N
H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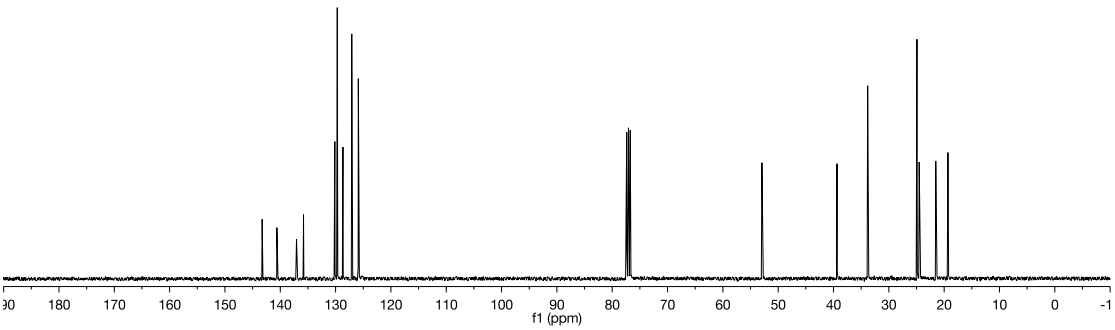
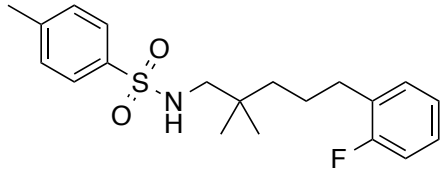
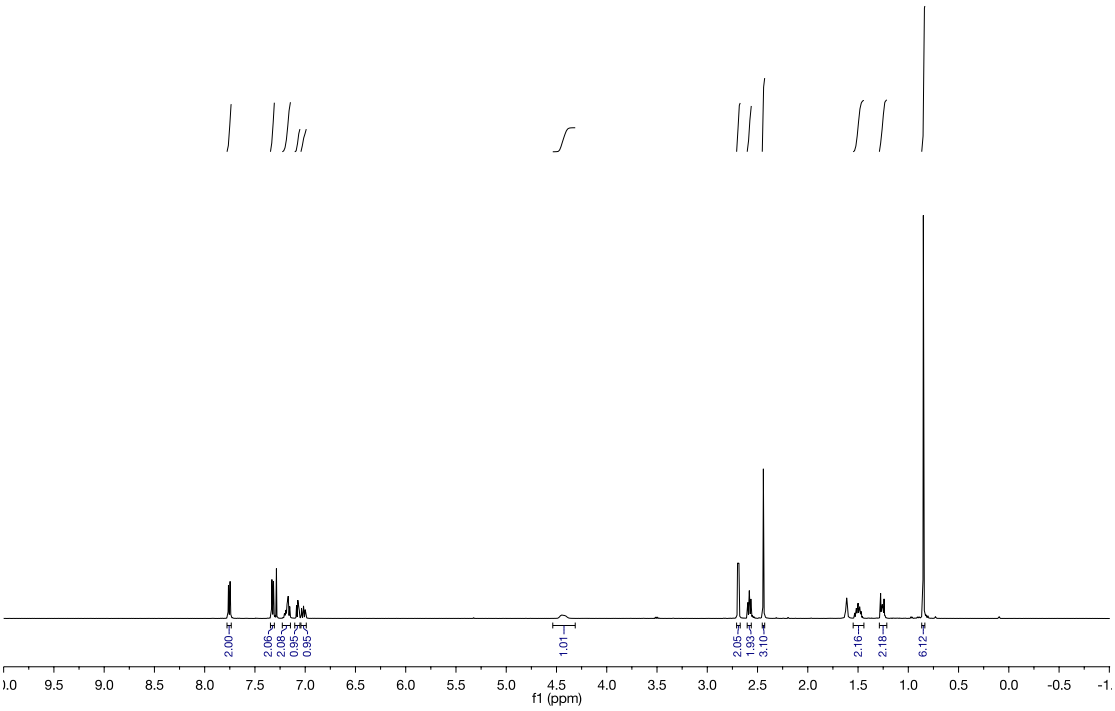
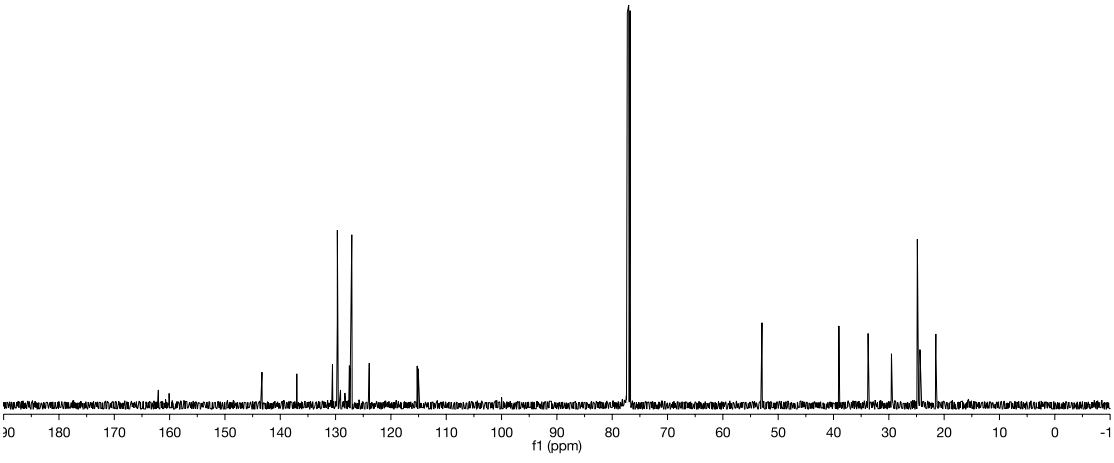
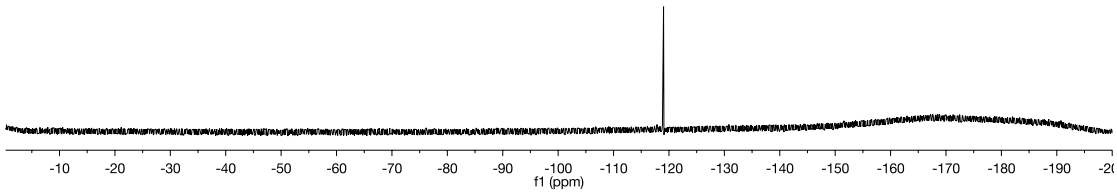
2.04
4.10
1.02
2.05
2.12
3.06
2.98
2.07
2.03
5.98
f1 (ppm)


f1 (ppm)


O
S
O
N
H
F


2.00
2.06
2.08
0.95
0.95
1.01
2.05
1.93
3.10
2.16
2.18
6.12
f1 (ppm)


f1 (ppm)


-10
-20
-30
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-80
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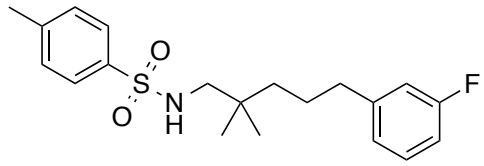
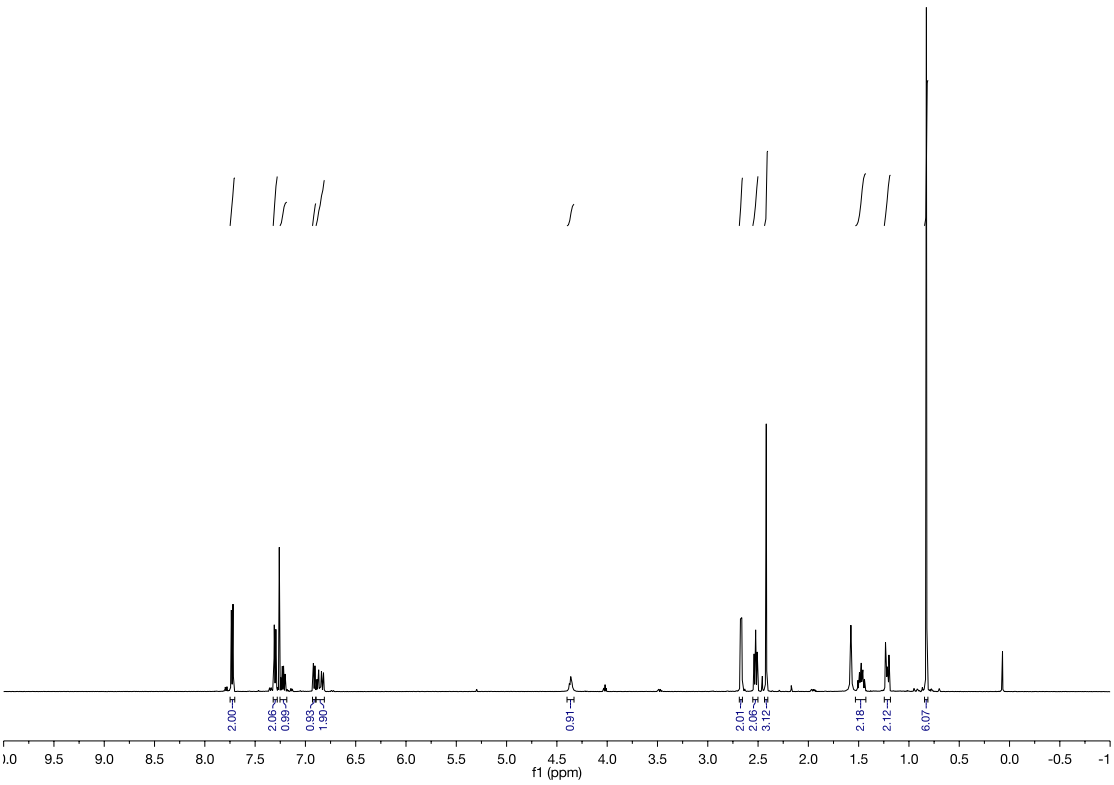
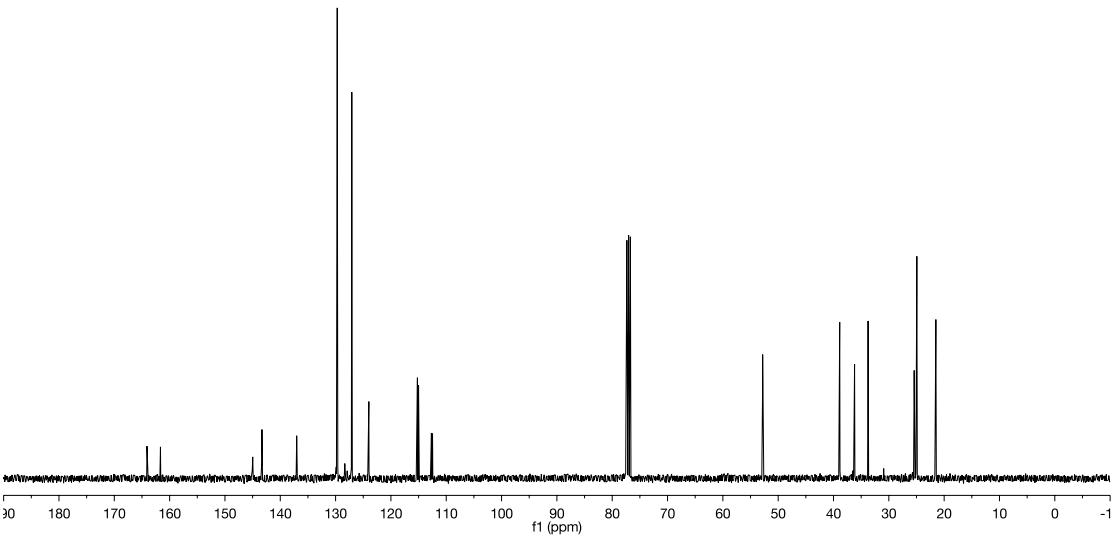
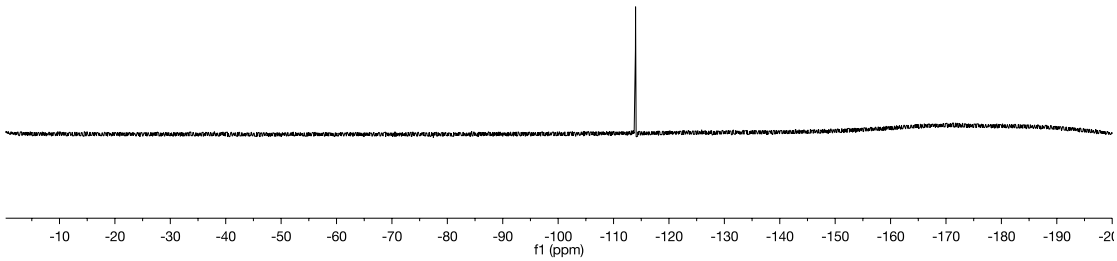
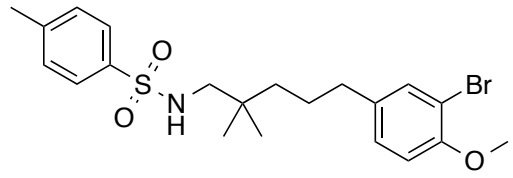
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

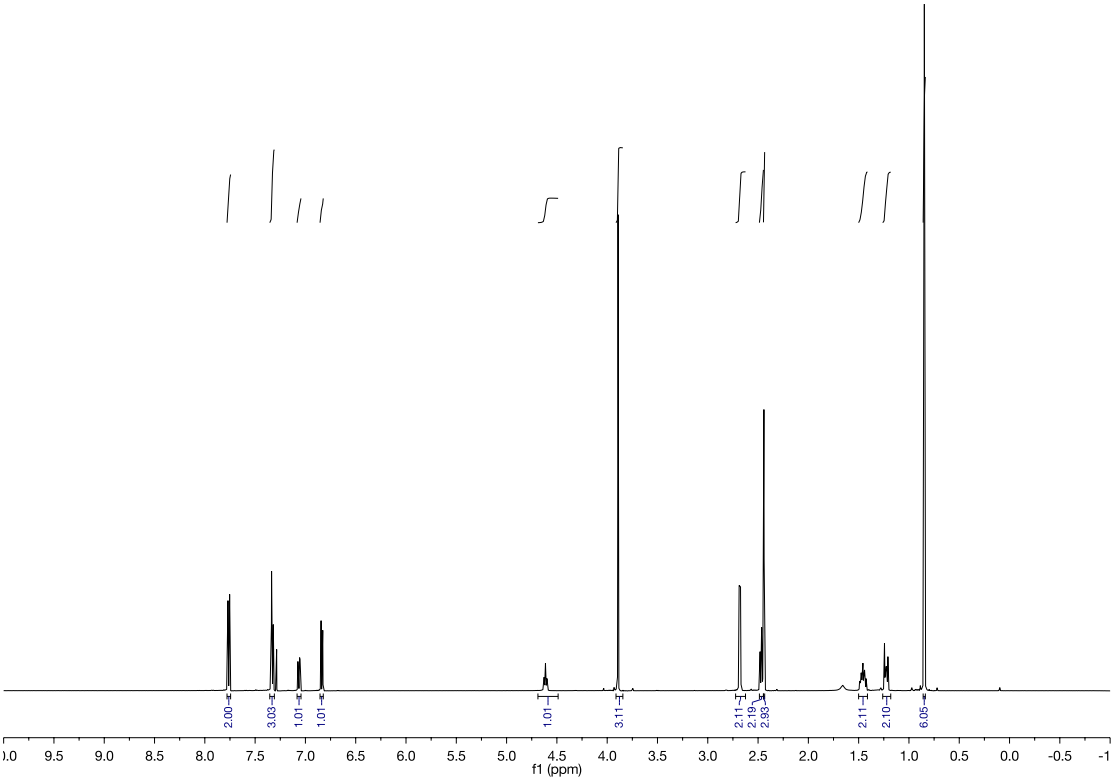

O
S
O
N
H
F

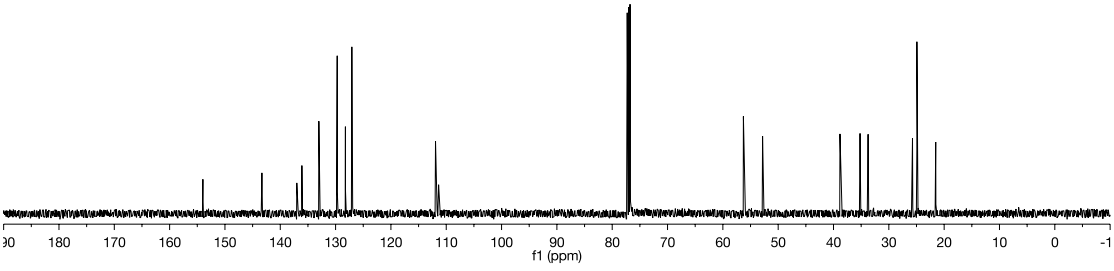

2.00
2.06
0.99
0.93
1.90
0.91
2.01
2.06
3.12
2.18
2.12
6.07
f1 (ppm)

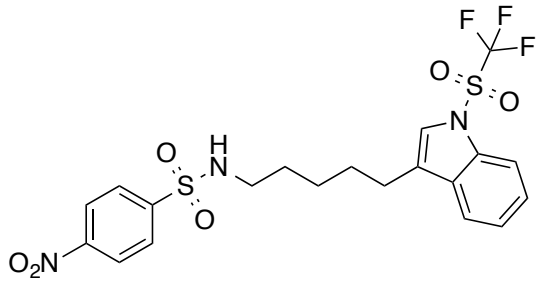

f1 (ppm)

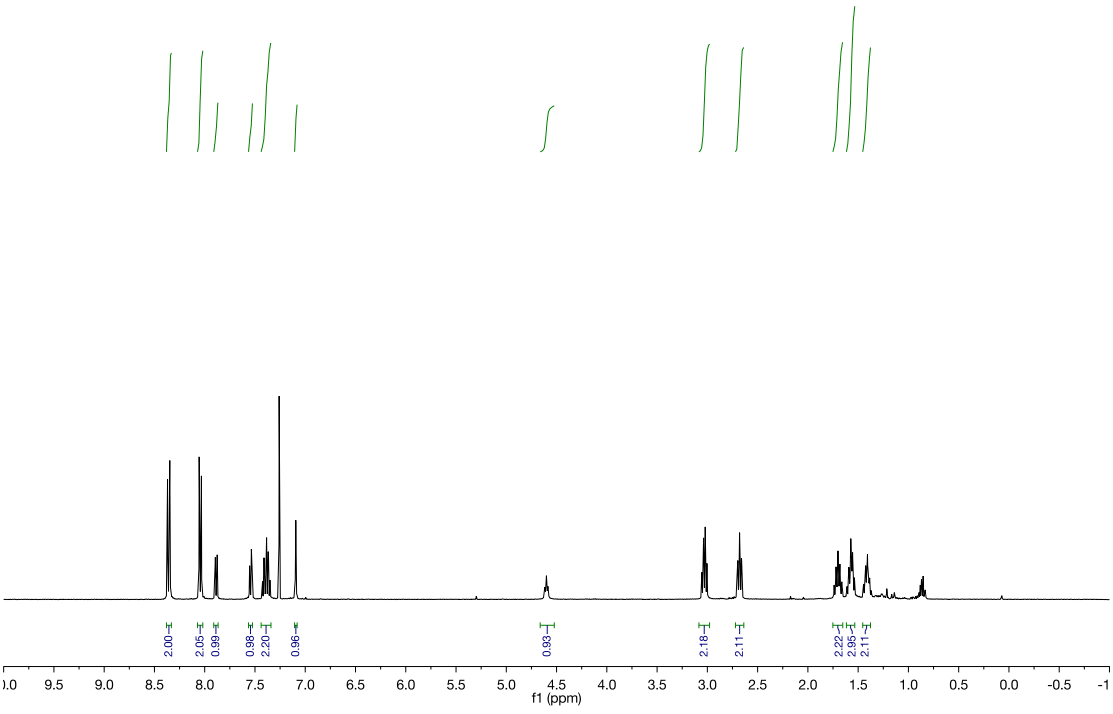

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

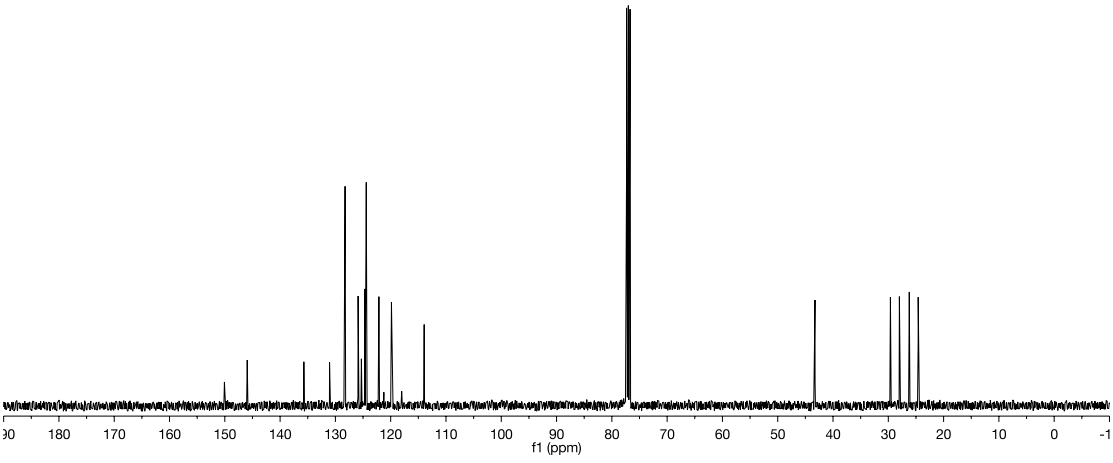

O
S
O
N
H
Br
O

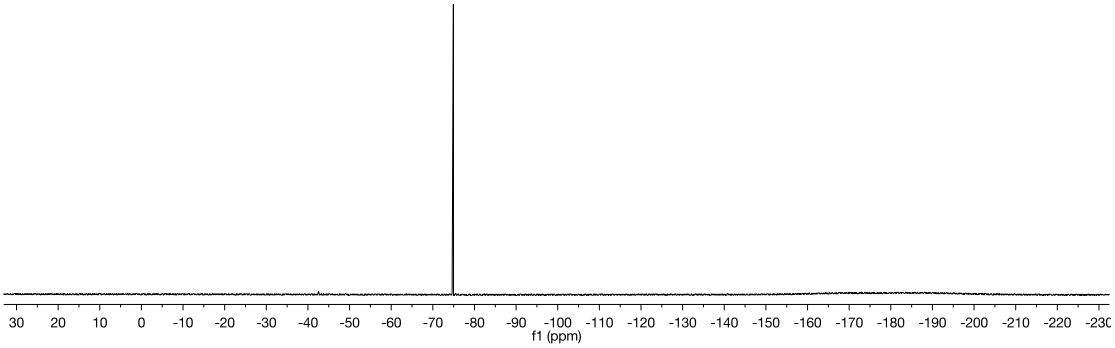

2.00
3.03
1.01
1.01
1.01
3.11
2.11
2.19
2.93
2.11
2.10
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

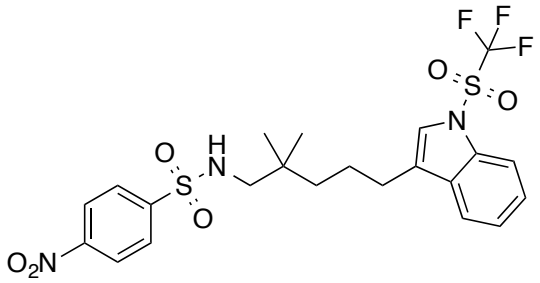

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

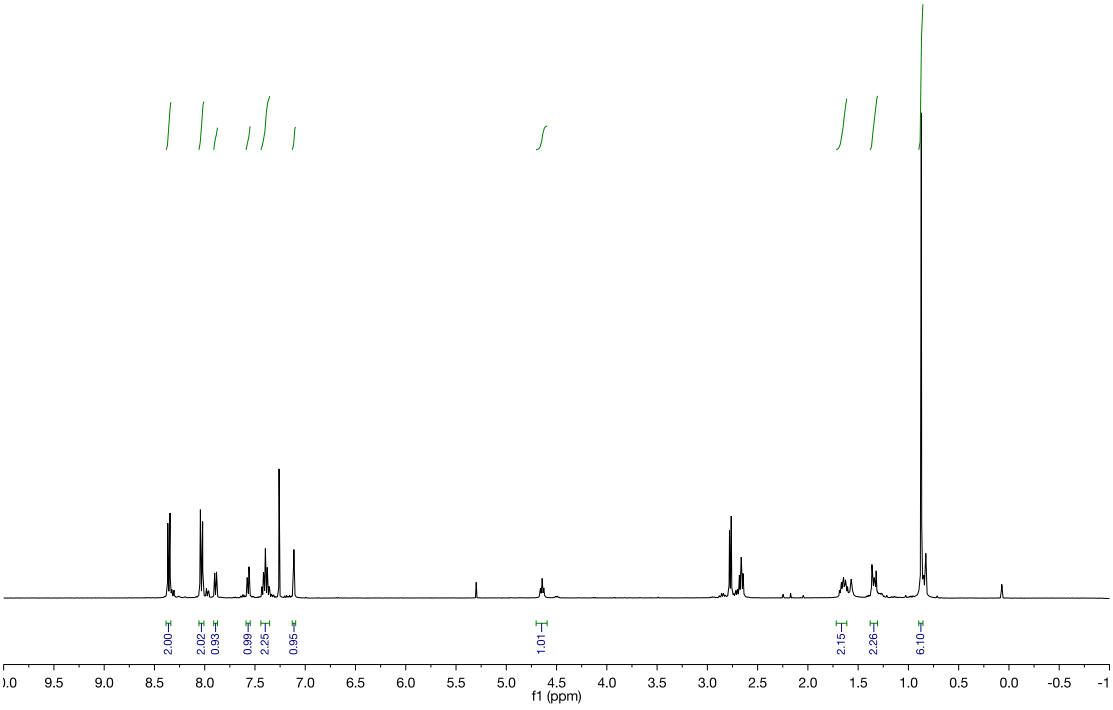

F
F
F
O
S
O
N
H
N
O
S
O
O2N

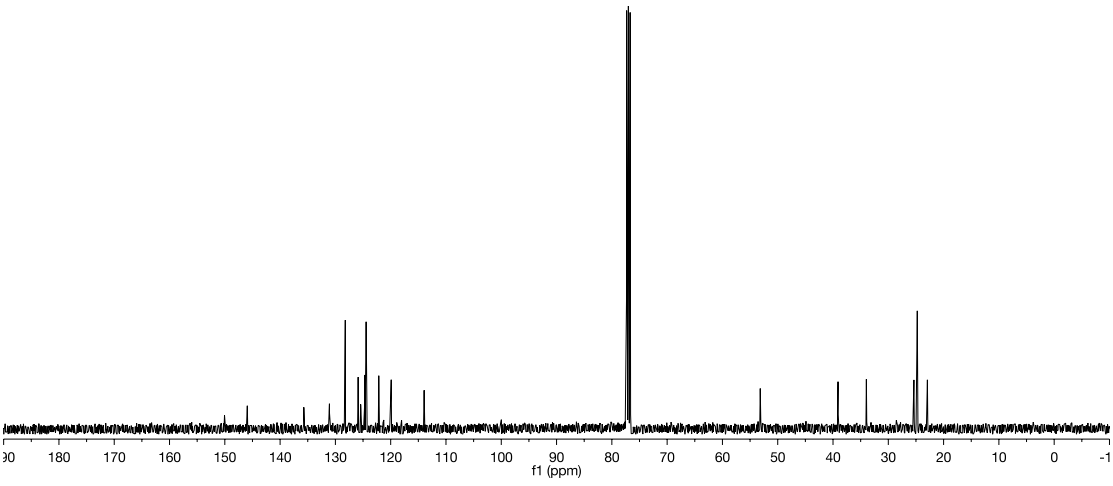

2.00
2.05
0.99
0.98
2.20
0.96
0.93
2.18
2.11
2.22
2.95
2.11
f1 (ppm)

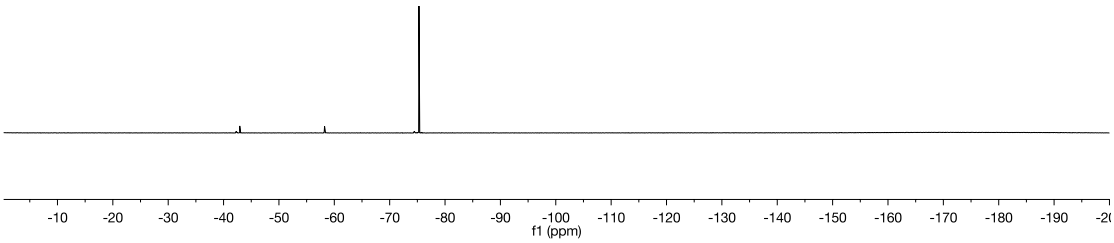

f1 (ppm)

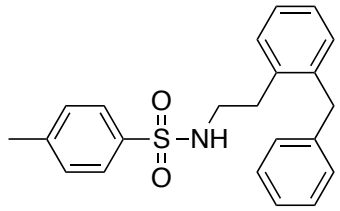

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

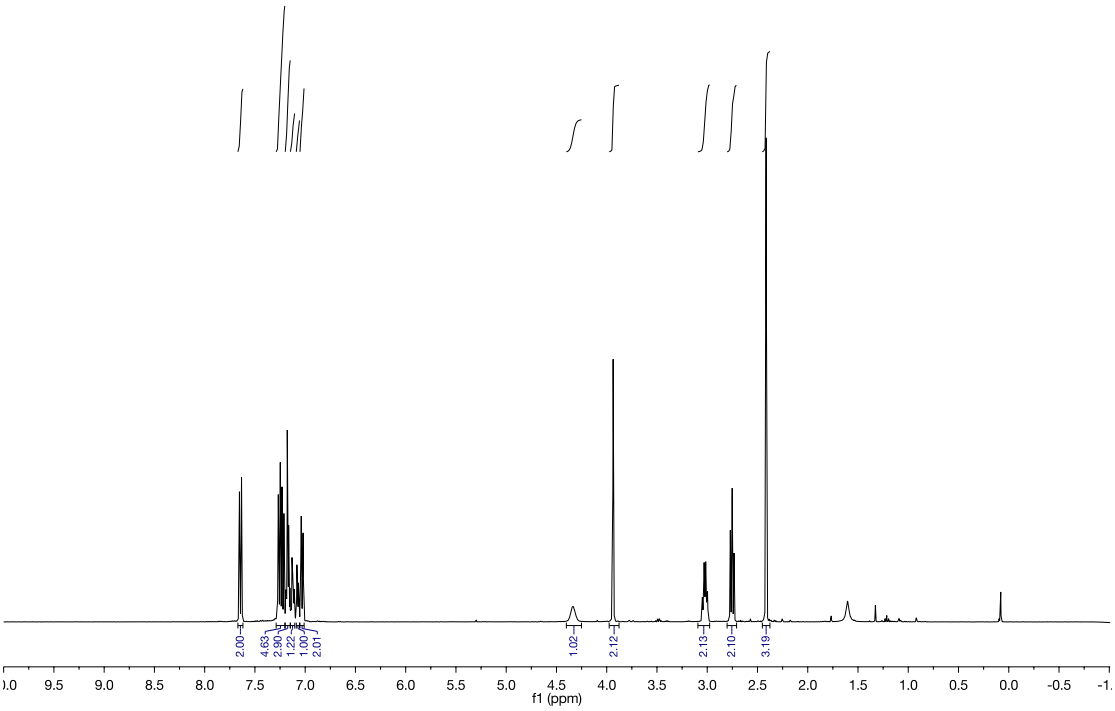

F
F
F
O
S
O
N
H
N
O
S
O
O2N

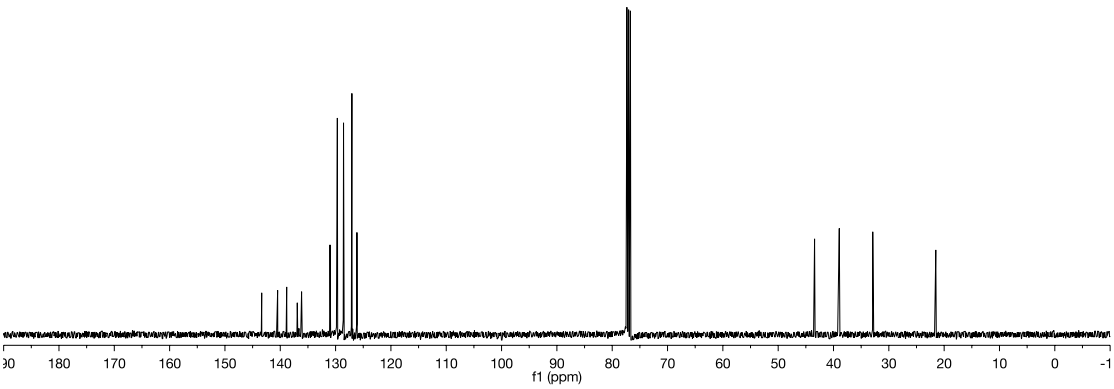

2.00
2.02
0.93
0.99
2.25
0.95
1.01
2.15
2.26
6.10
f1 (ppm)

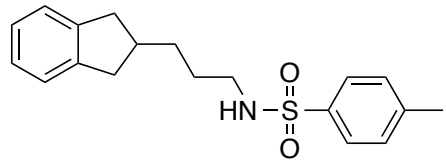

f1 (ppm)


-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

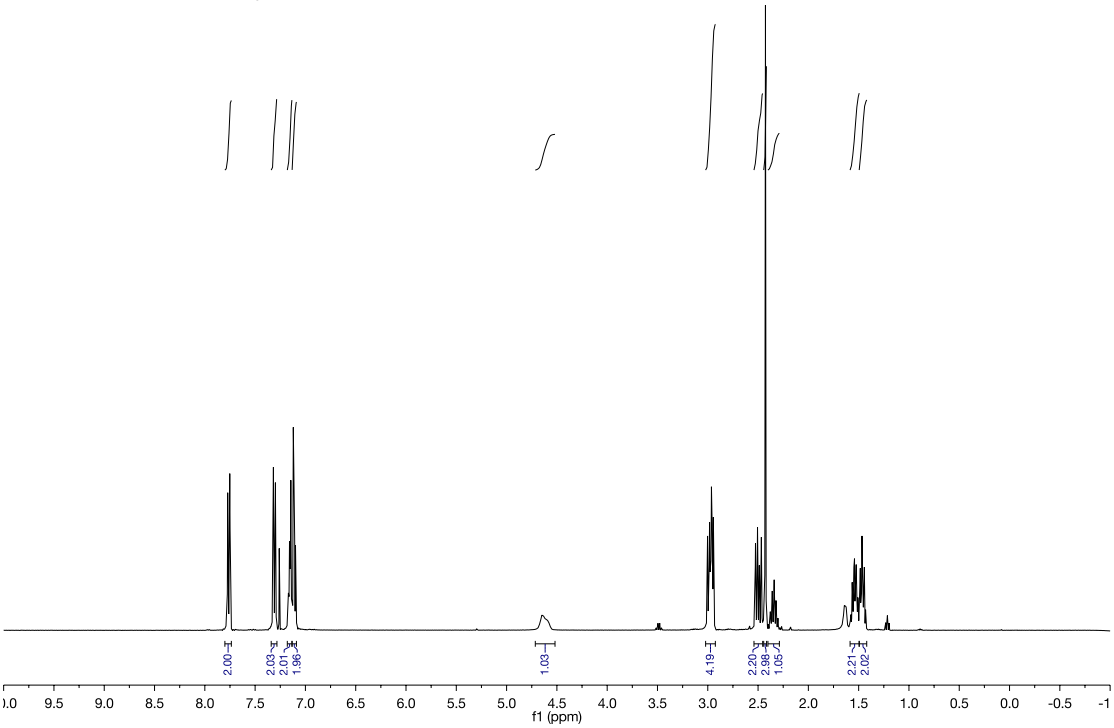

O
S
NH
O

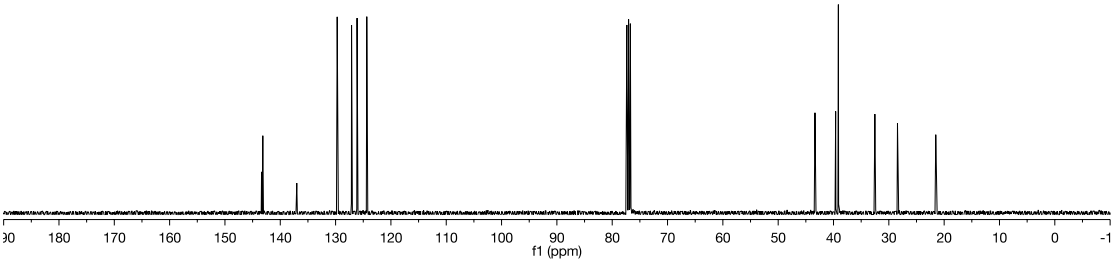

2.00
4.63
2.90
1.22
1.00
2.01
1.02
2.12
2.13
2.10
3.19
f1 (ppm)

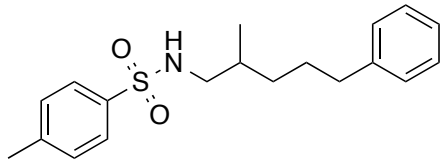

f1 (ppm)

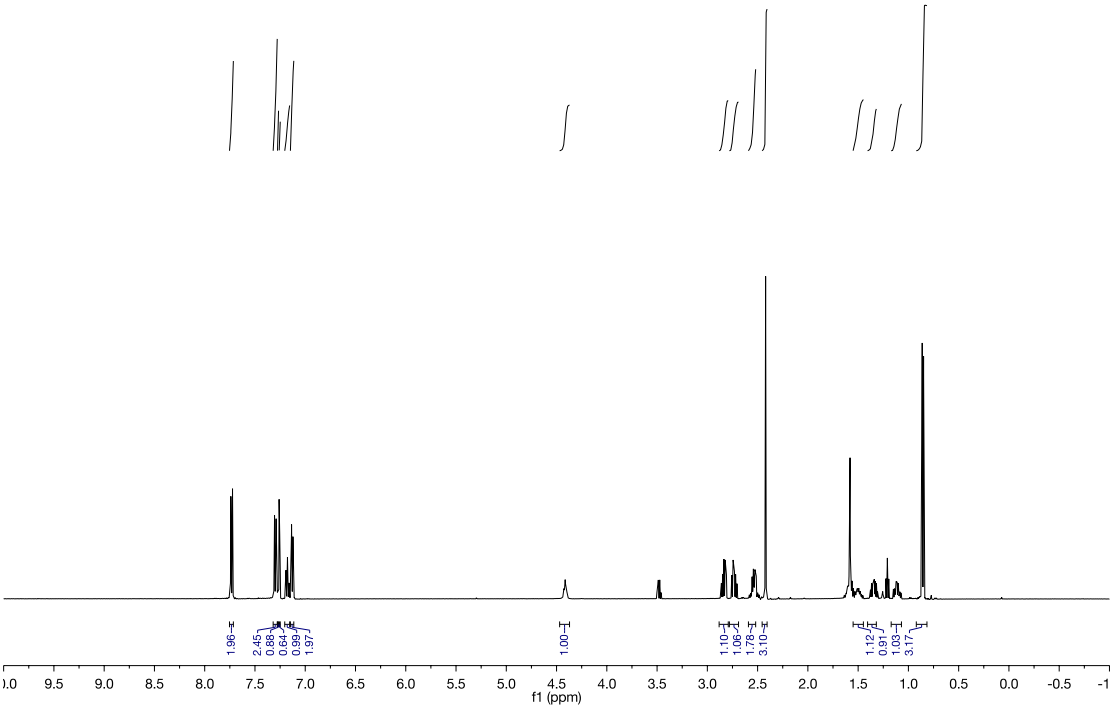


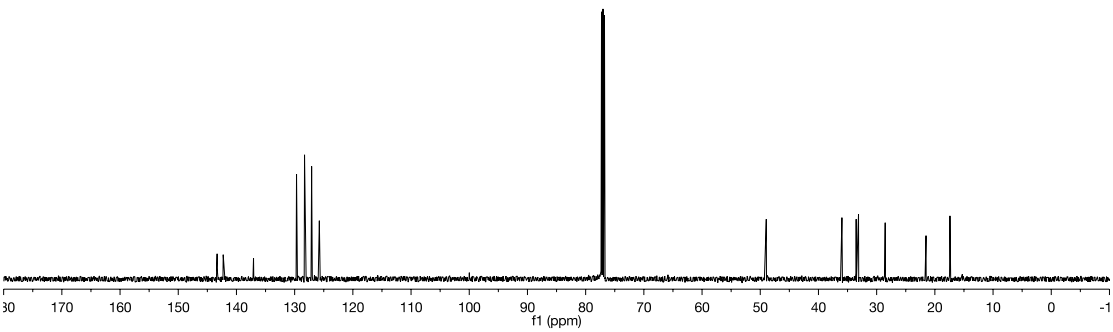
KMZHWd2p.10.fid
ResearchGroup Muniz
ICIQ_1H12p8s CDCl3 /opt/topspin hzhang 15

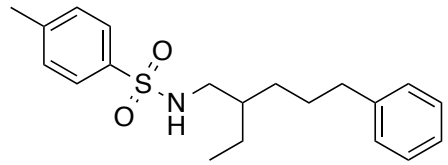


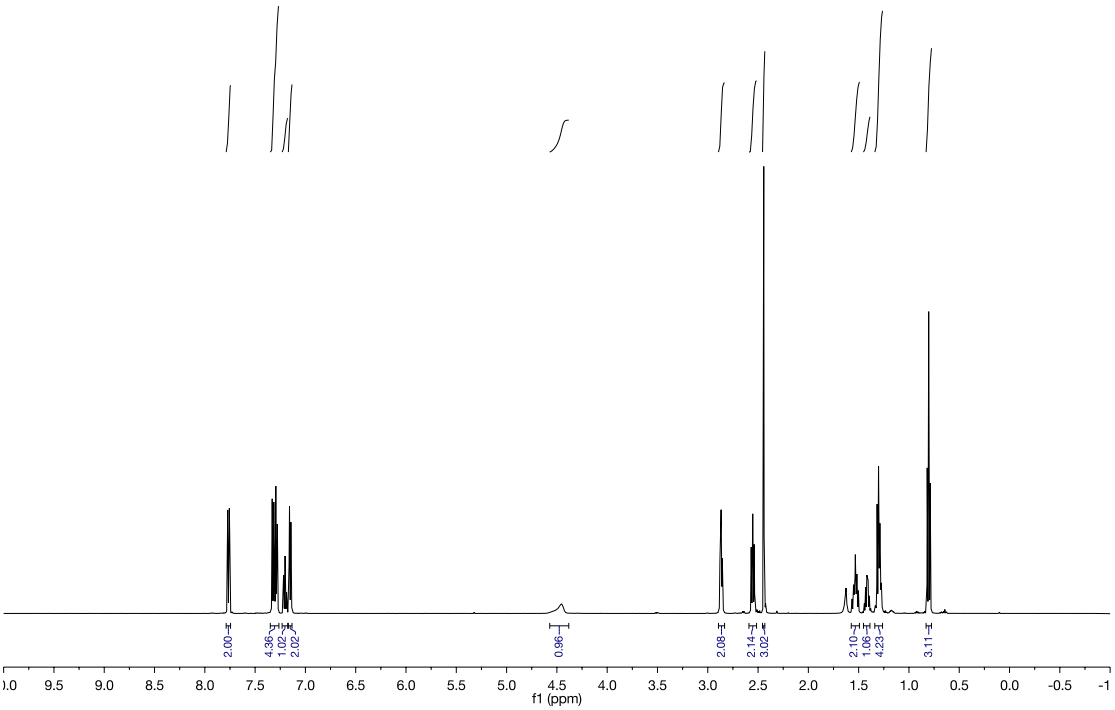


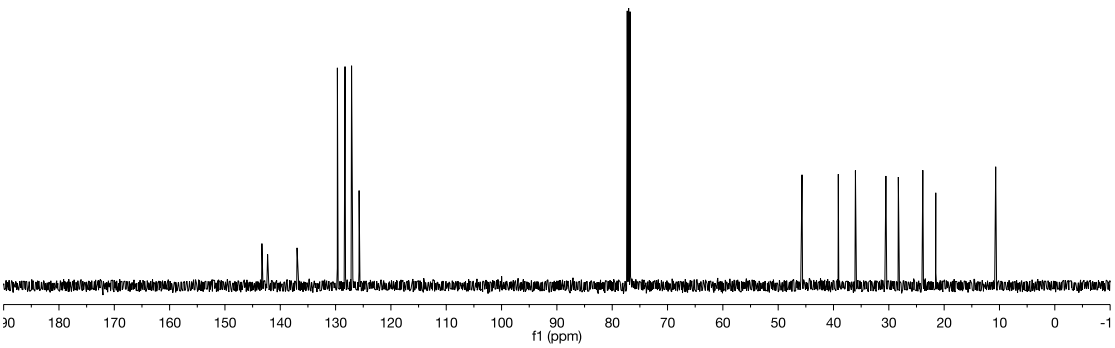

O
H
N
S
O

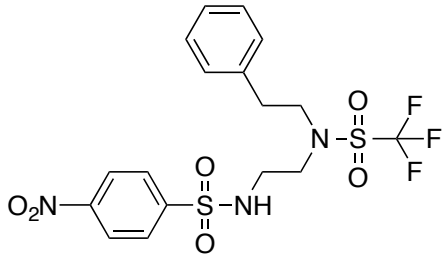

1.96
2.45
0.88
0.64
0.99
1.97
1.00
1.10
1.06
1.78
3.10
1.12
0.91
1.03
3.17
f1 (ppm)

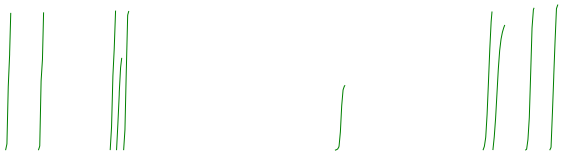

f1 (ppm)

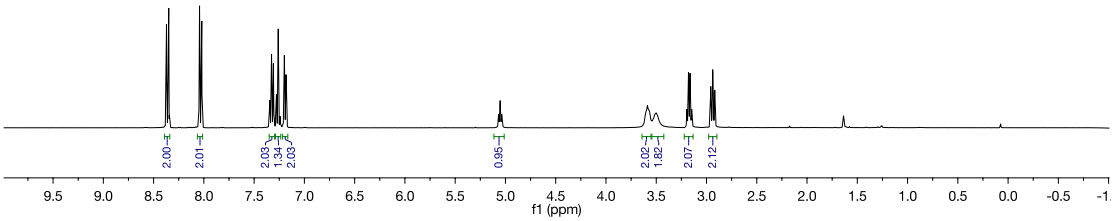

O
S
O
N
H

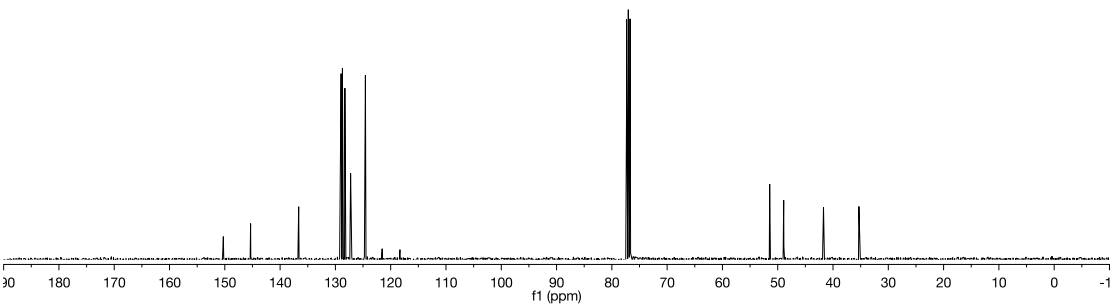

2.00
4.96
1.02
2.02
0.96
2.08
2.14
3.02
2.10
1.06
4.23
3.11
f1 (ppm)

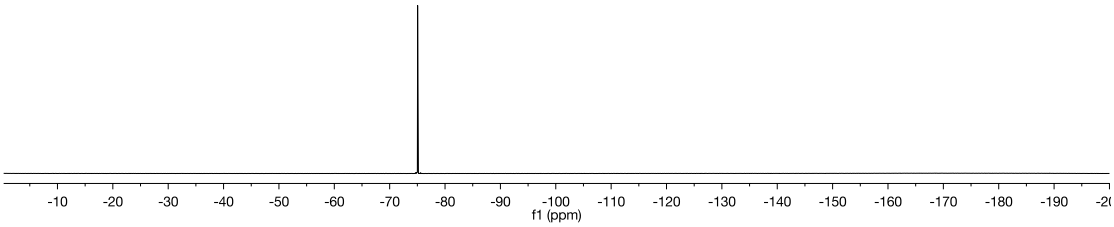

f1 (ppm)

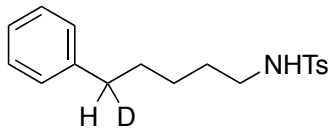

O
F
N
S
F
O
F
O
O2N
S
NH
O

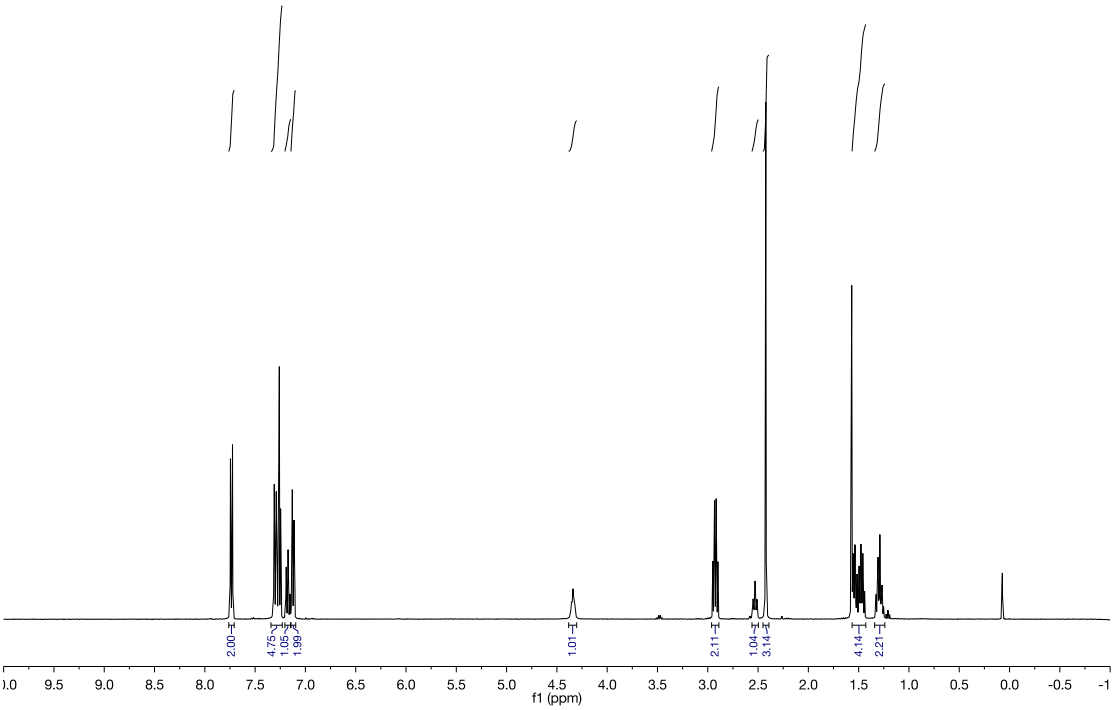


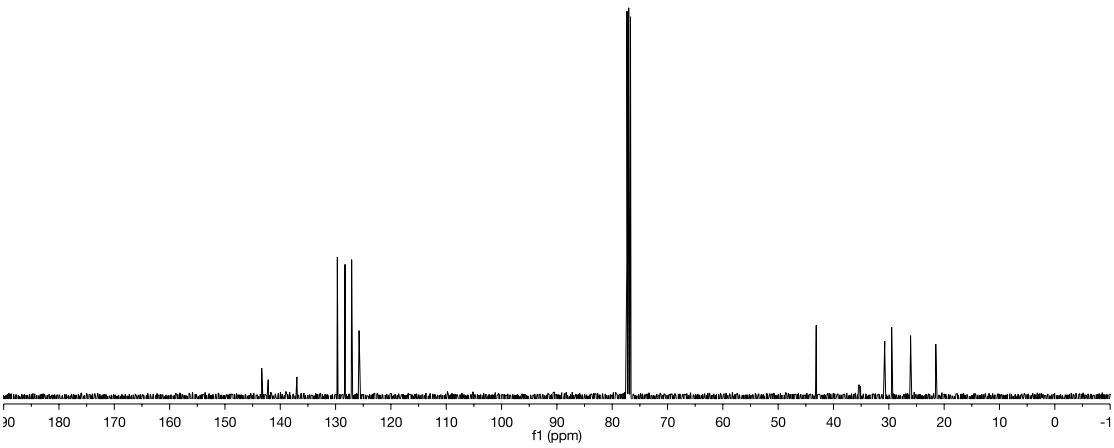

2.00
2.01
2.03
1.34
2.03
0.95
2.02
1.82
2.07
2.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

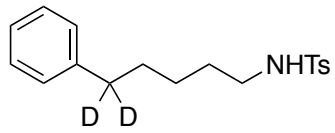

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

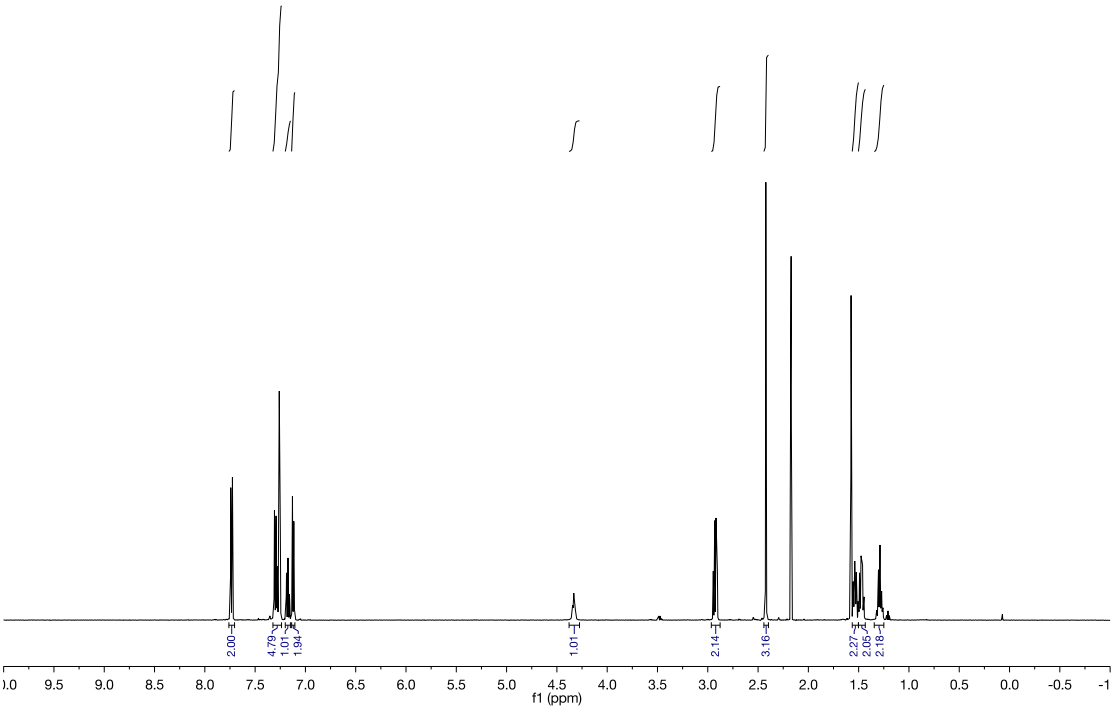

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

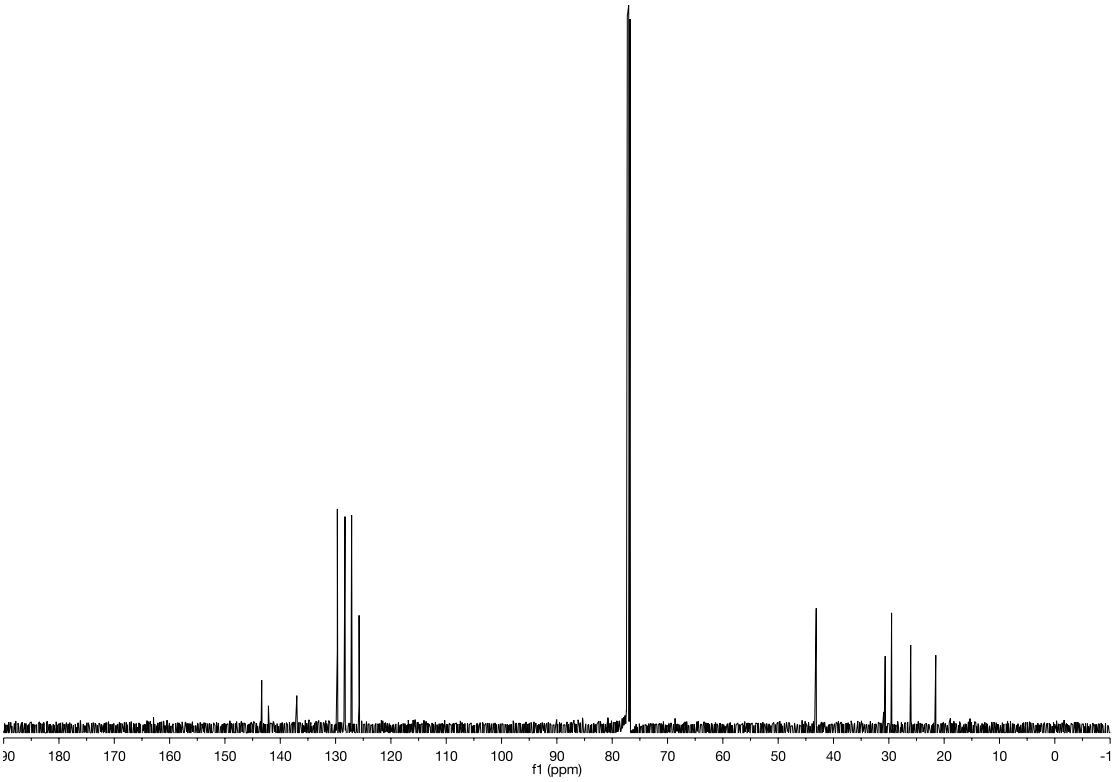

NHTs
H D

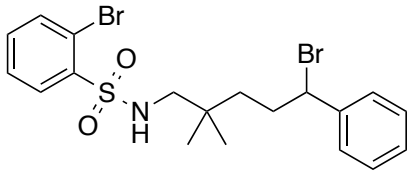

2.00
4.75
1.05
1.99
1.01
2.11
1.04
3.14
4.14
2.21
f1 (ppm)

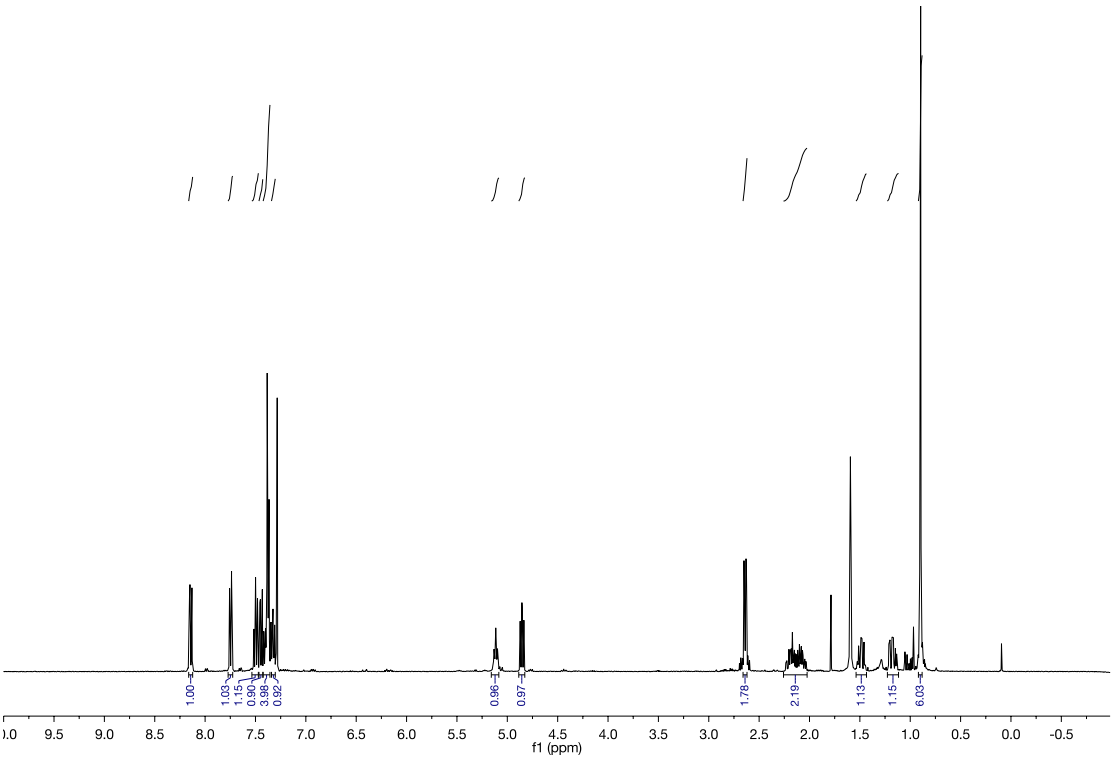

f1 (ppm)

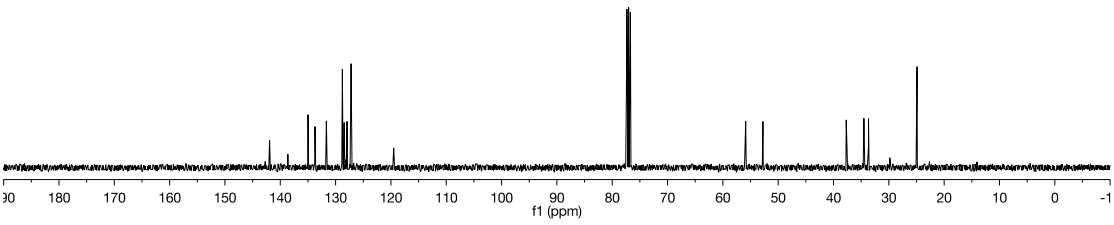

NHTs
D D

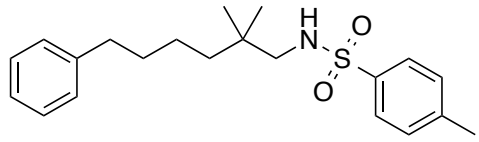

2.00
4.79
1.01
1.94
1.01
2.14
3.16
2.27
2.05
2.18
f1 (ppm)

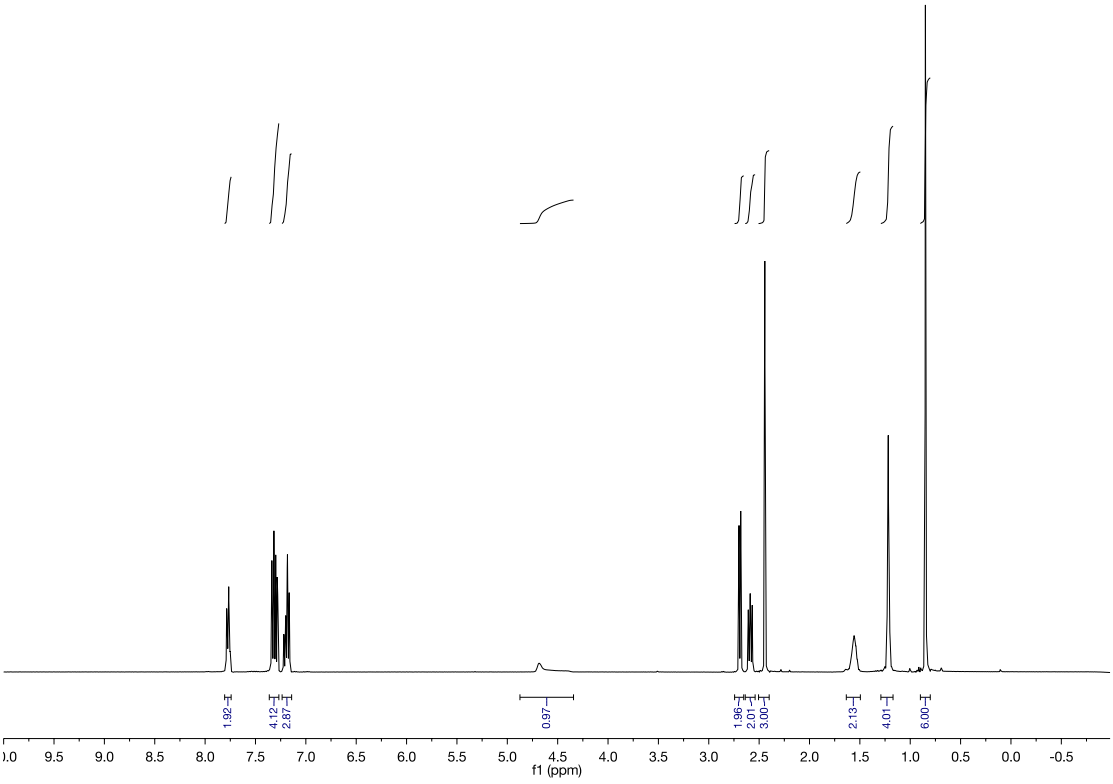

f1 (ppm)

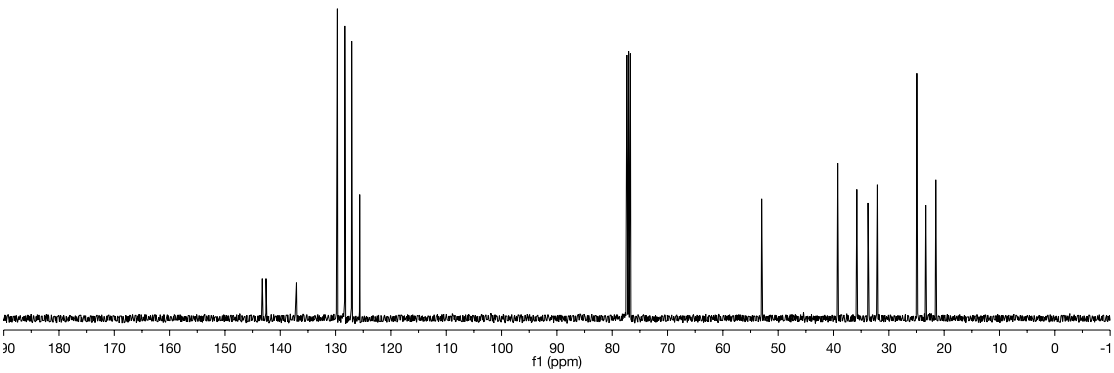

Br
O
S
N
H
O
Br


1.00
1.03
1.15
0.90
3.98
0.92
0.96
0.97
1.78
2.19
1.13
1.15
6.03
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 -0.5
f1 (ppm)

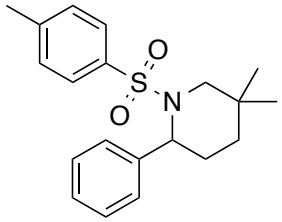

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

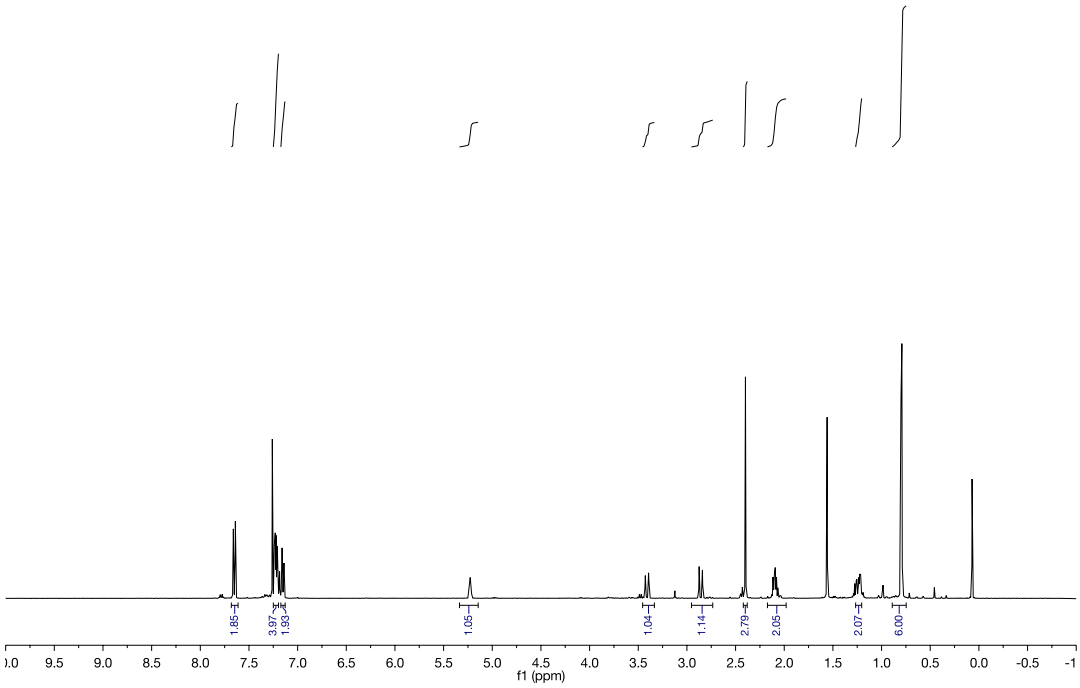

H
N
S
O
O

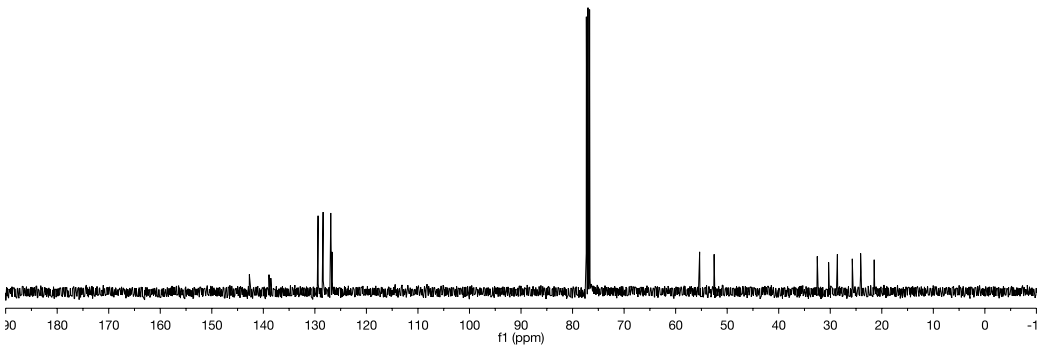

1.92
4.12
2.87
0.97
1.96
2.01
3.00
2.13
4.01
6.00
f1 (ppm)

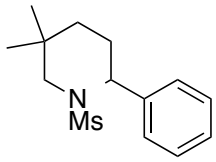

f1 (ppm)

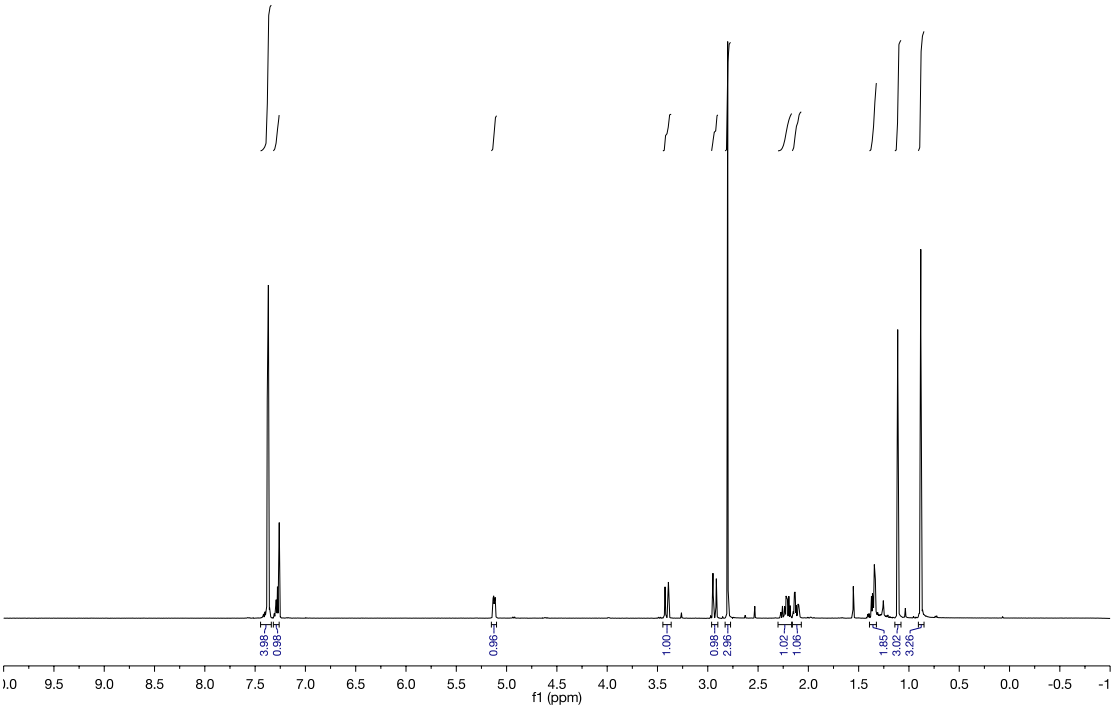
17- NMR Charts of amination products

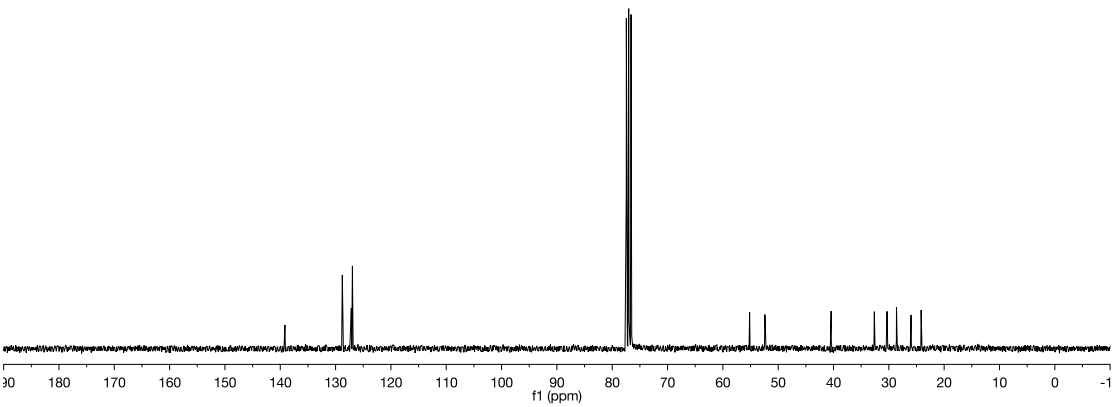


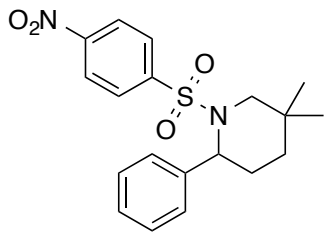


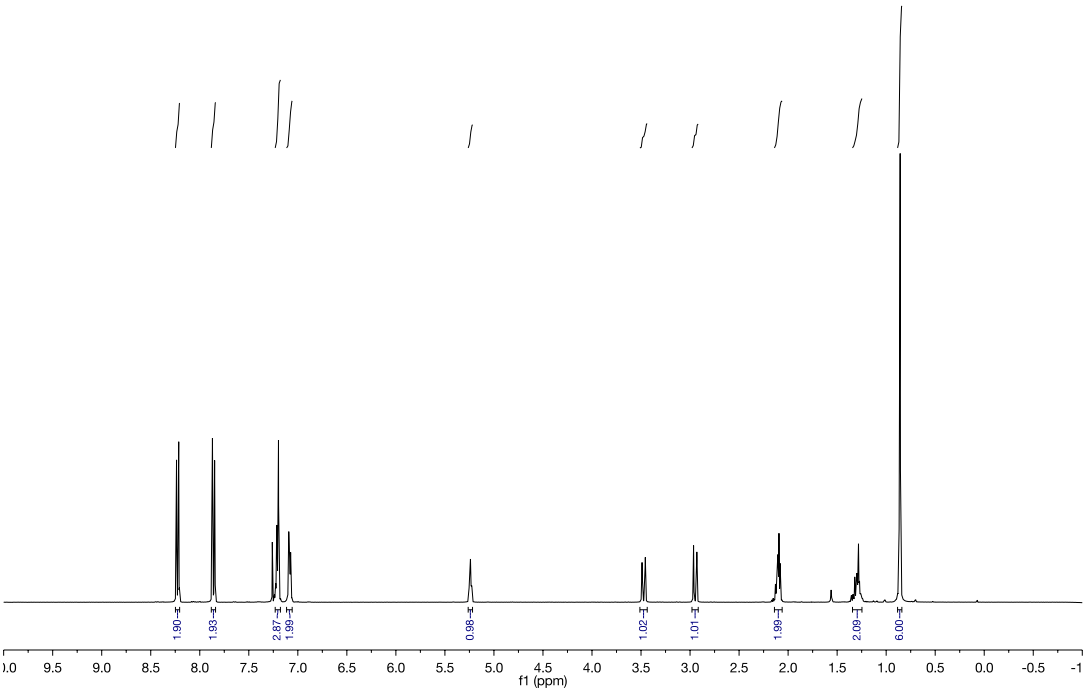


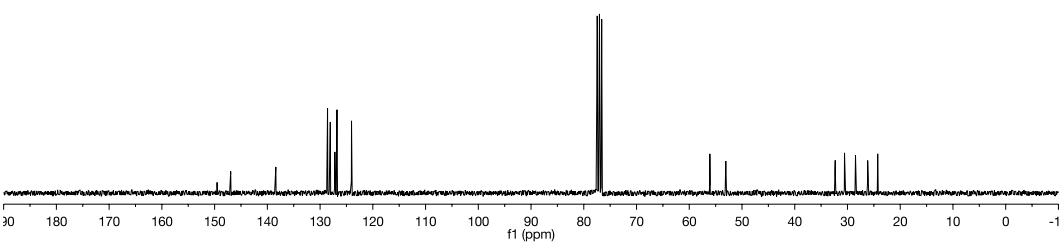

N
Ms

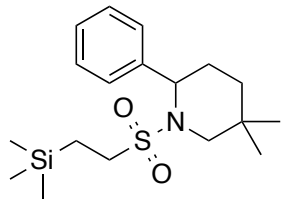

3.98
0.98
0.96
1.00
0.98
2.96
1.02
1.06
1.85
3.02
3.26
f1 (ppm)

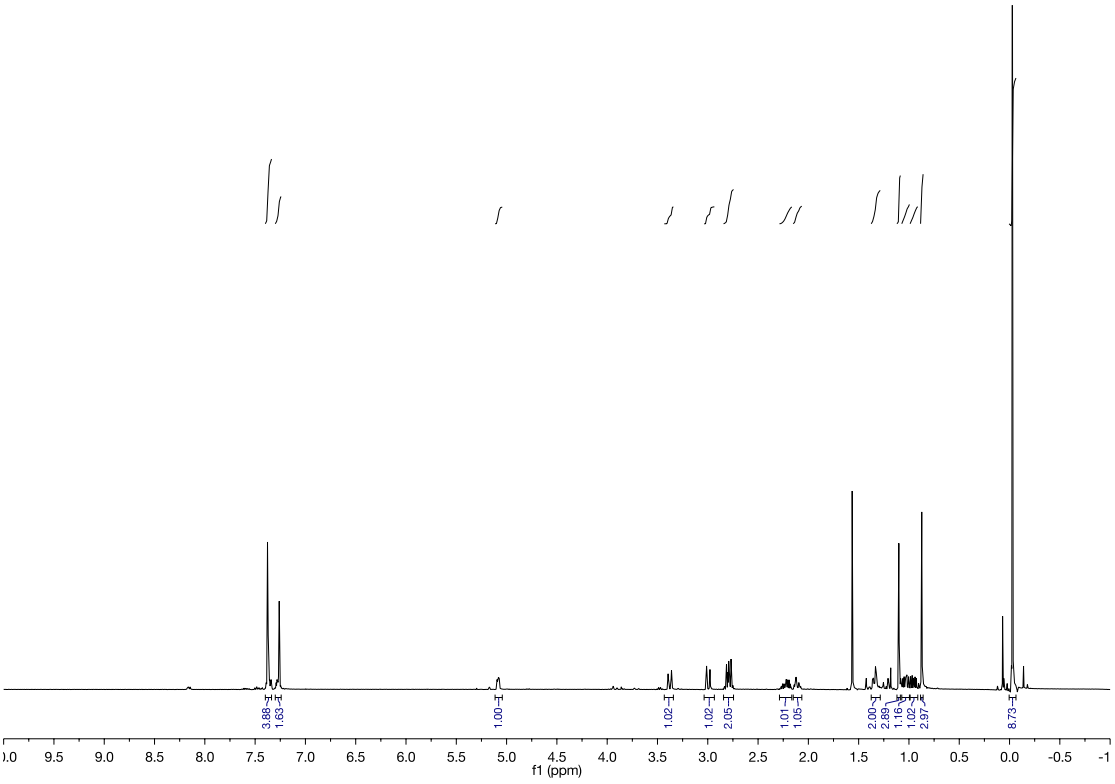

f1 (ppm)

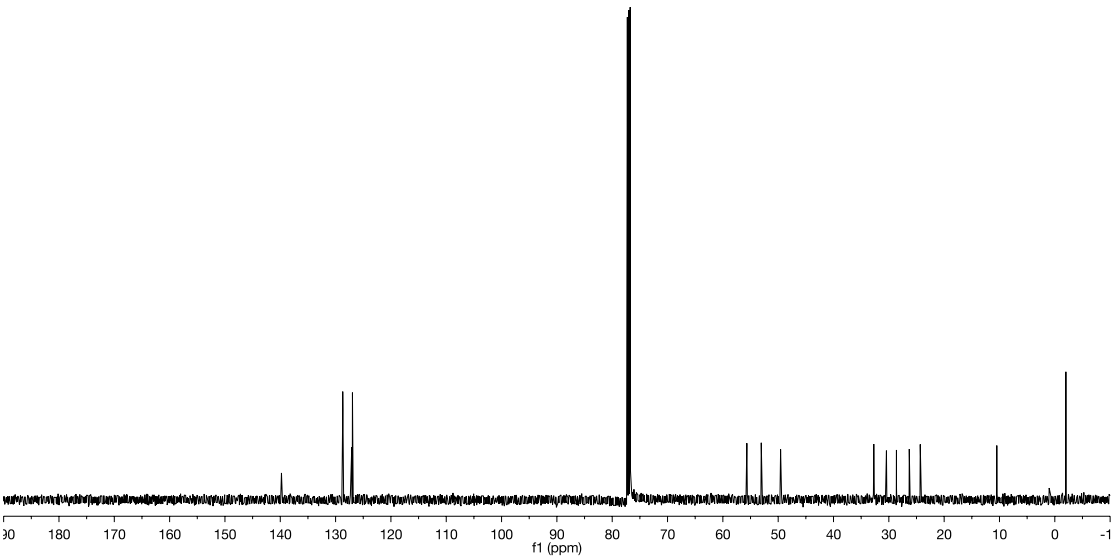

O2N
O
S
O
N

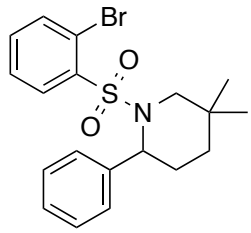

1.90
1.93
2.87
1.99
0.98
1.02
1.01
1.99
2.09
6.00
f1 (ppm)

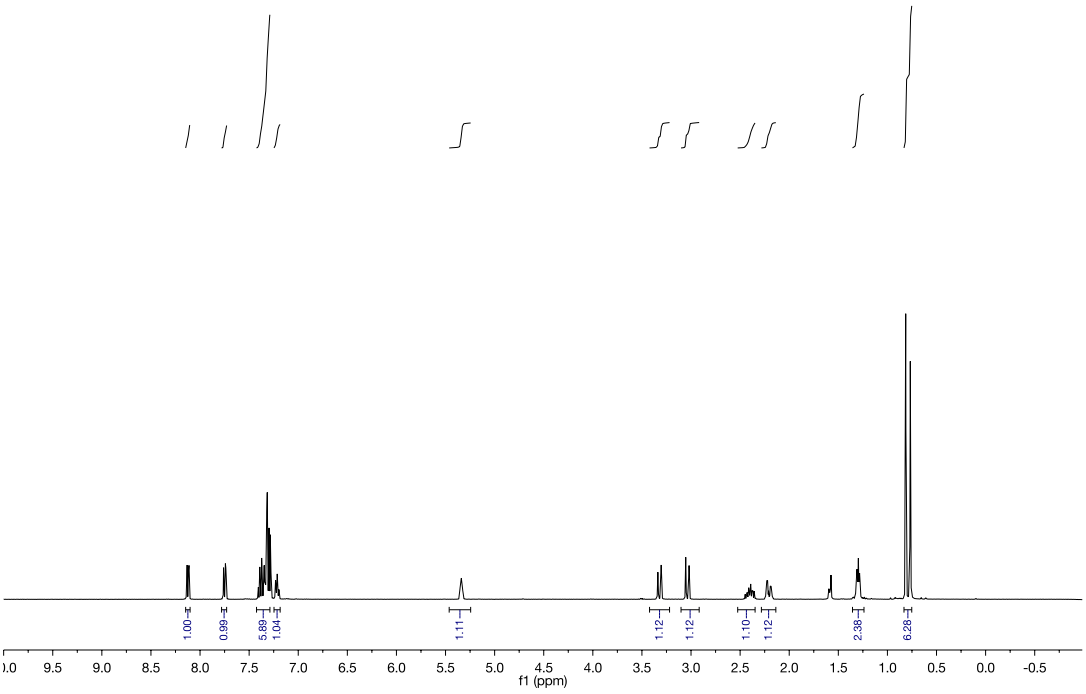

f1 (ppm)

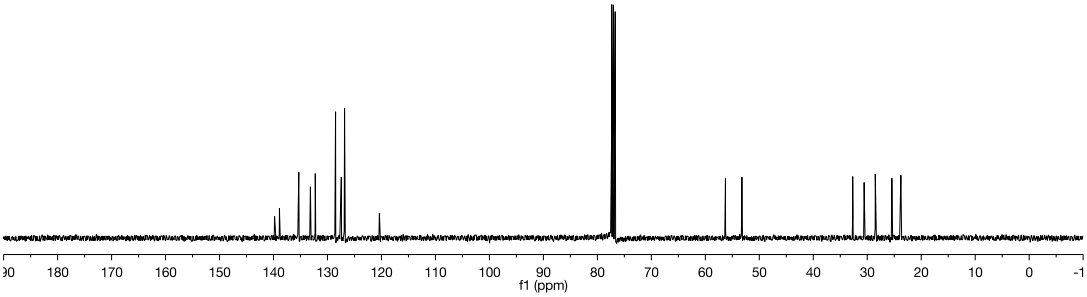

O
N
S
O
Si

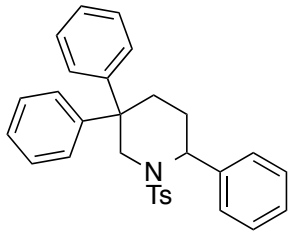

3.88
1.63
1.00
1.02
1.02
2.05
1.01
1.05
2.00
2.89
1.16
1.09
2.97
8.73
f1 (ppm)

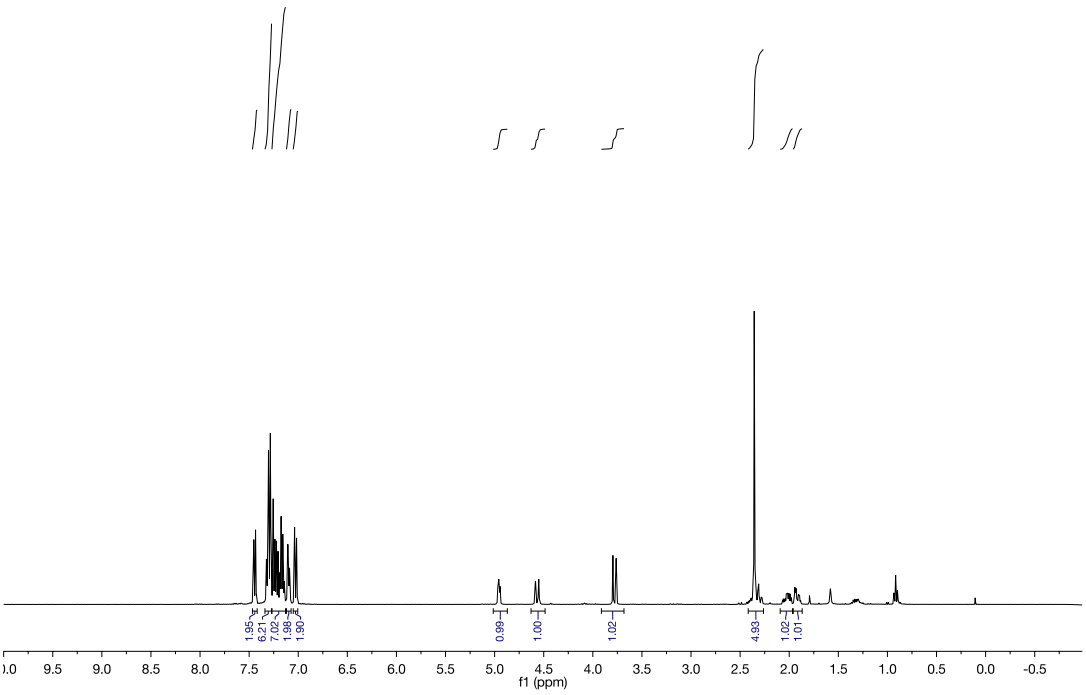

f1 (ppm)

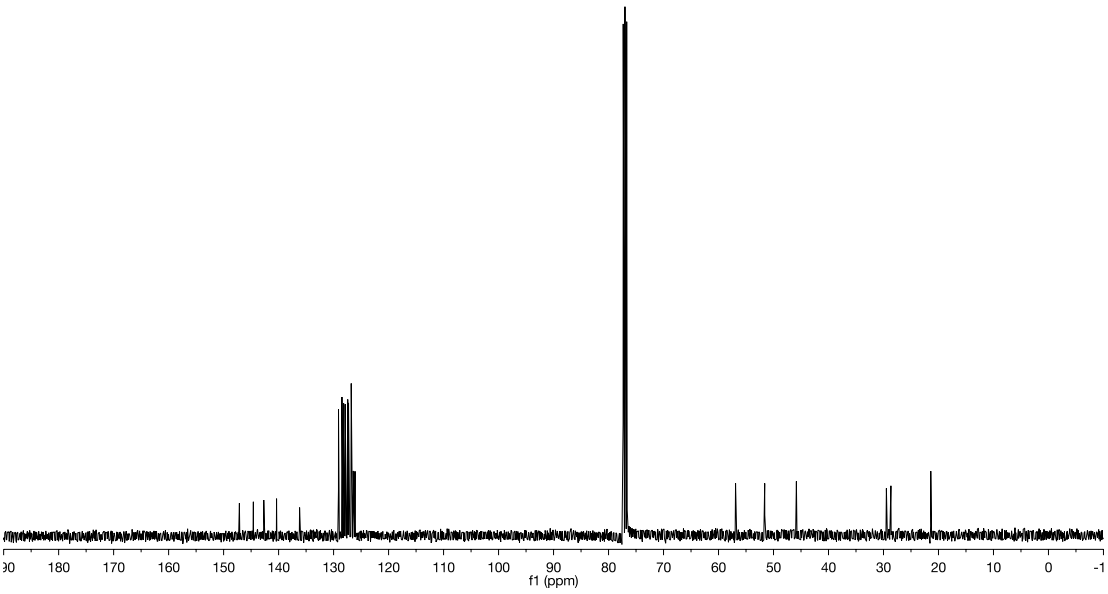

Br
O
S
O
N

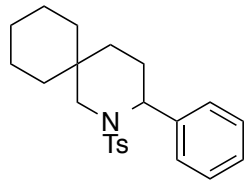

1.00
0.99
5.89
1.04
1.11
1.12
1.12
1.10
1.12
2.38
6.28
f1 (ppm)

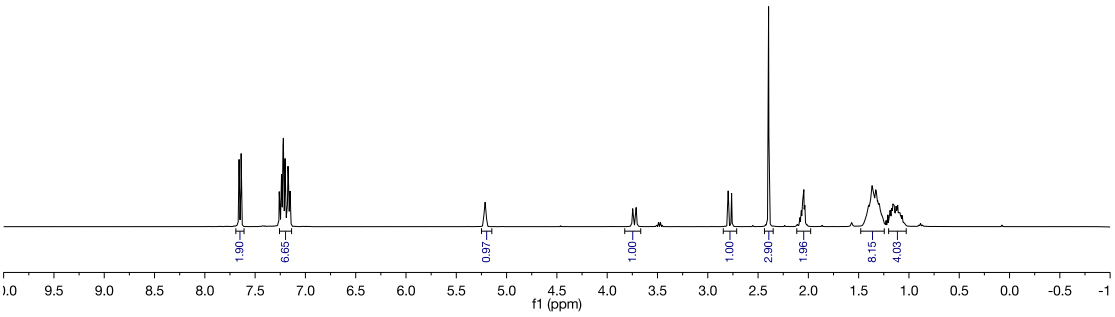

f1 (ppm)


N
Ts


1.95
6.21
7.02
1.98
1.90
0.99
1.00
1.02
4.93
1.02
1.01
f1 (ppm)


f1 (ppm)


N
Ts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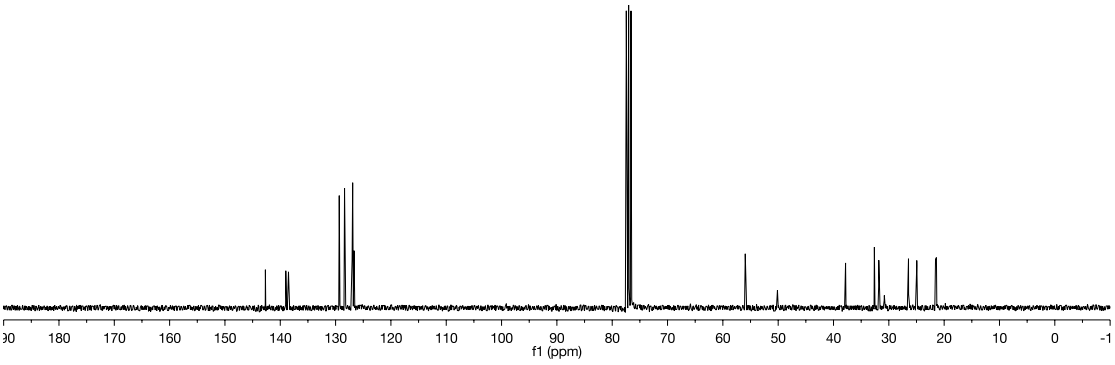
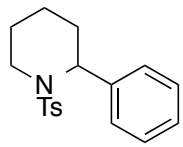
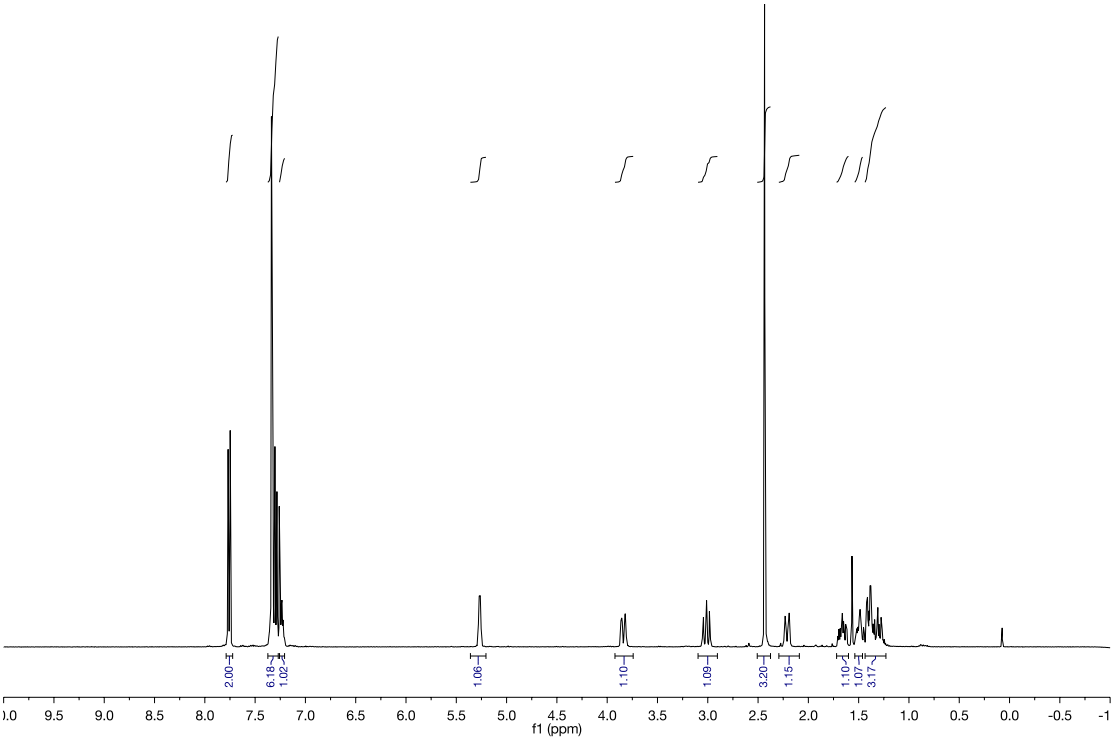
6.65
0.97
1.00
1.00
2.90
1.98
8.15
4.03
f1 (ppm)


f1 (ppm)


N
Ts


2.00
6.18
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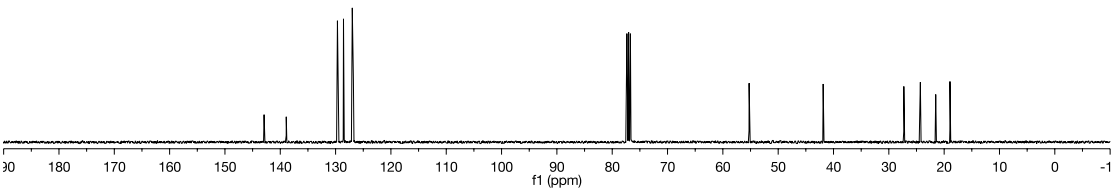
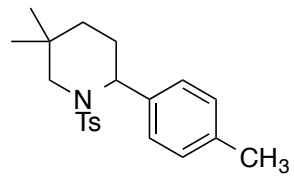
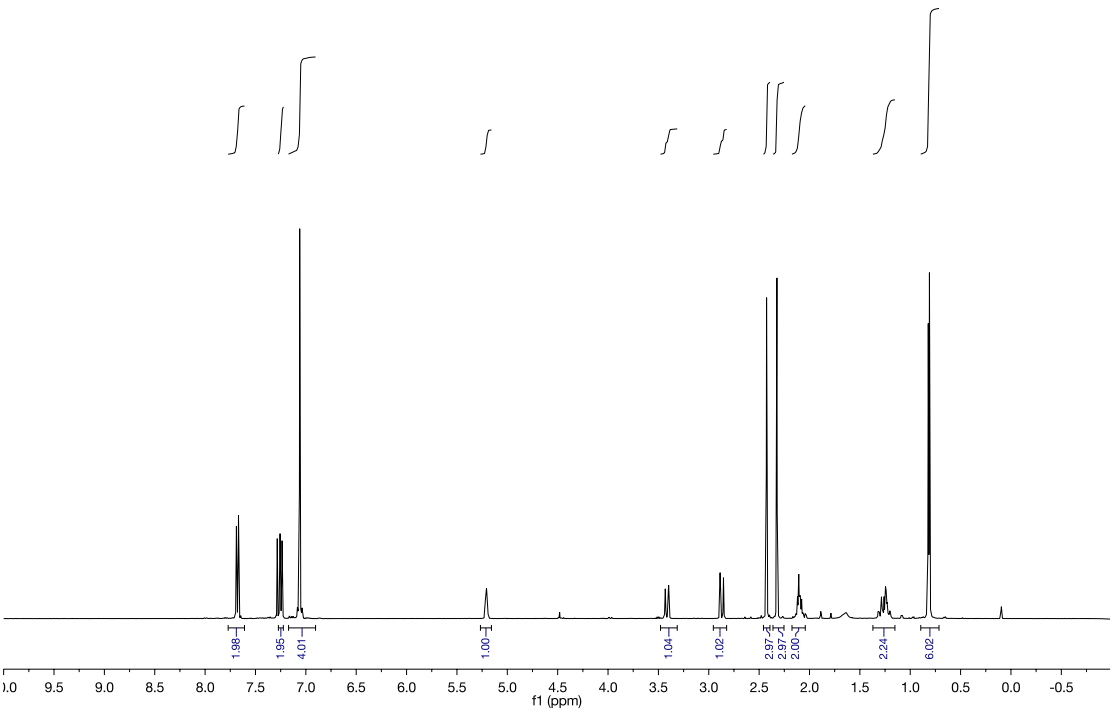
1.06
1.10
1.09
3.20
1.15
1.10
1.07
3.17
f1 (ppm)


f1 (ppm)


N
Ts
CH3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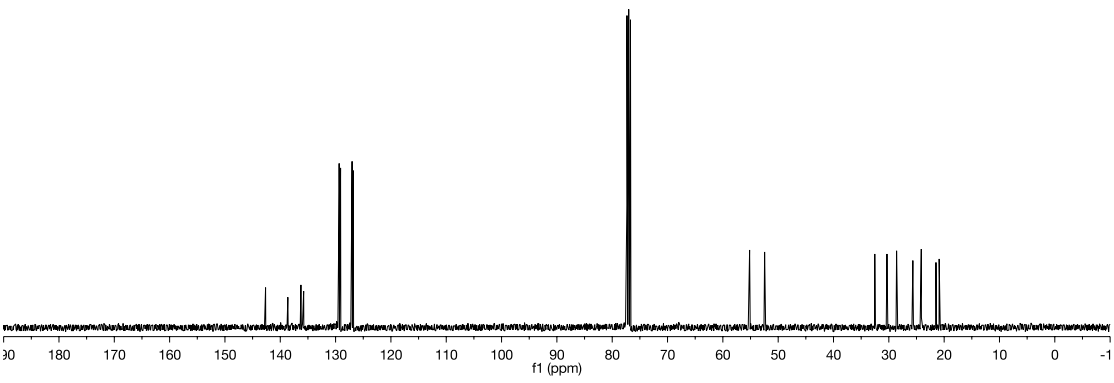
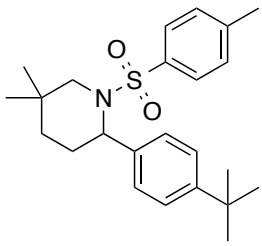
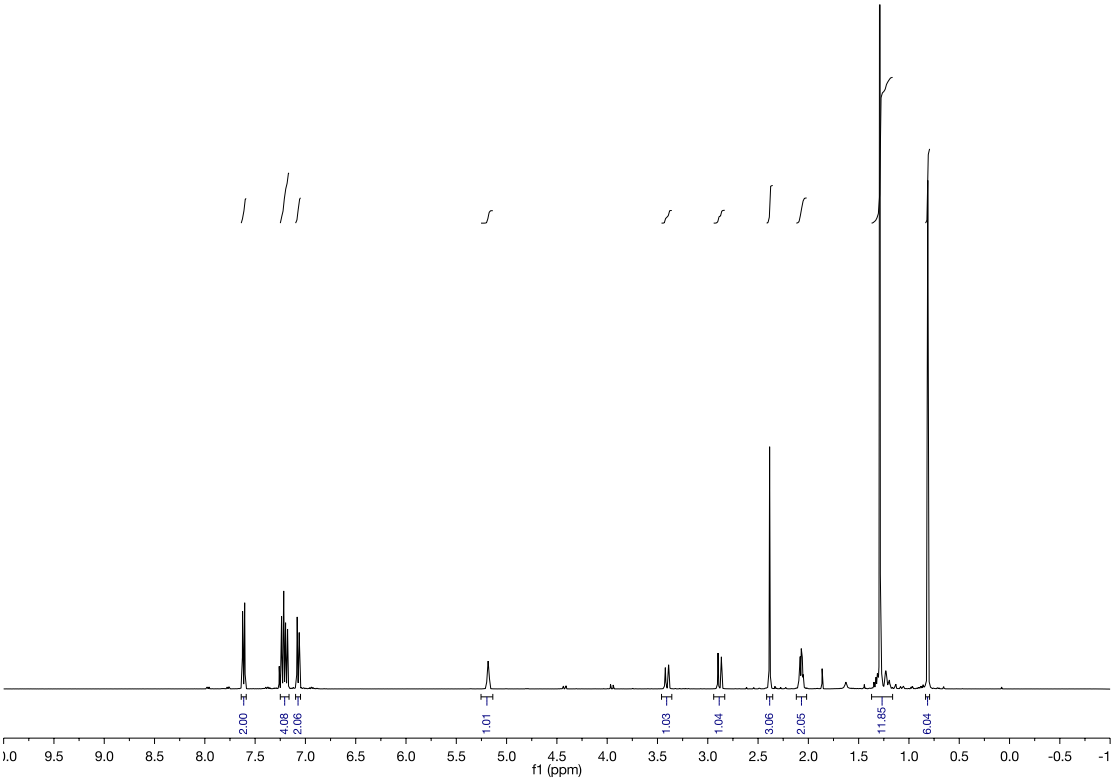
1.95
4.01
1.00
1.04
1.02
2.97
2.97
2.00
2.24
6.02
f1 (ppm)


f1 (ppm)


O
S
N
O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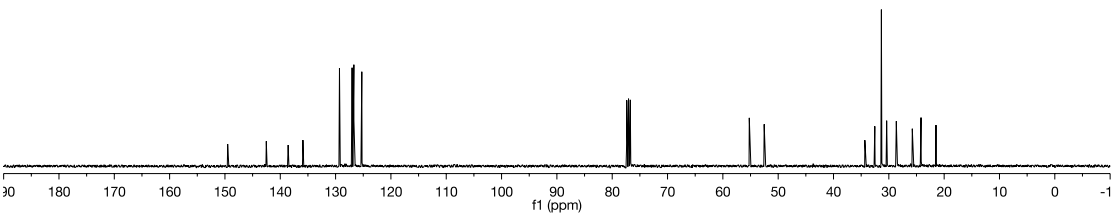
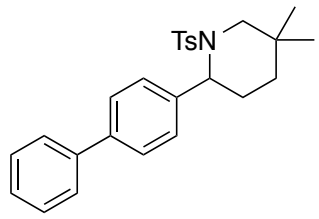
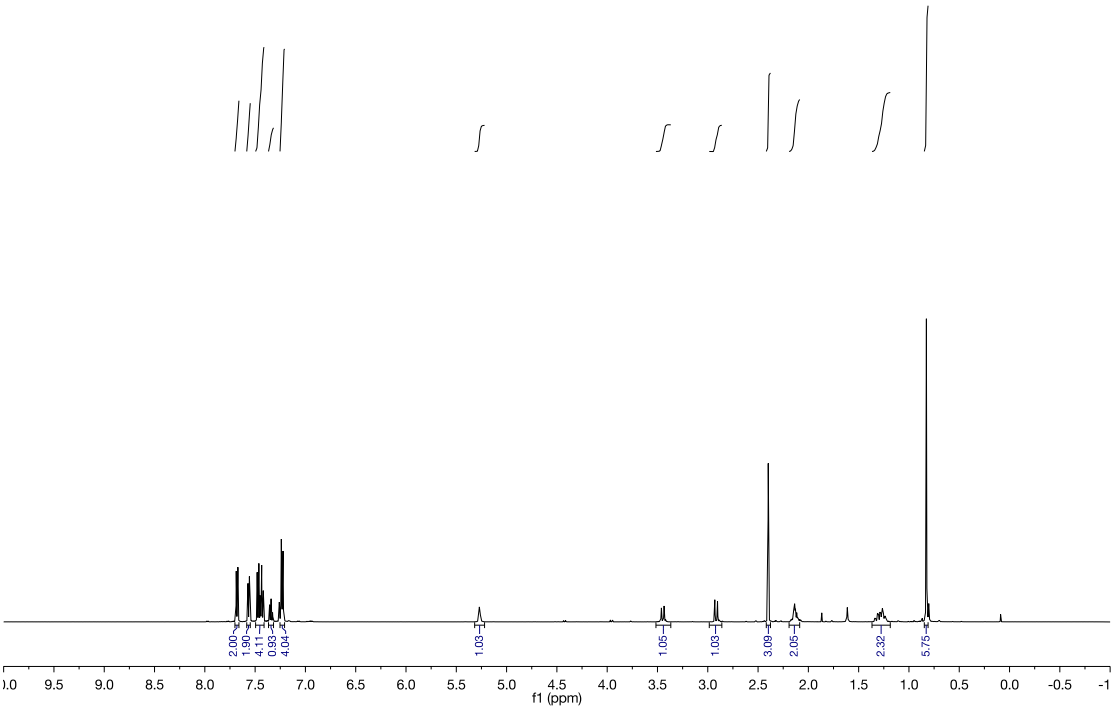
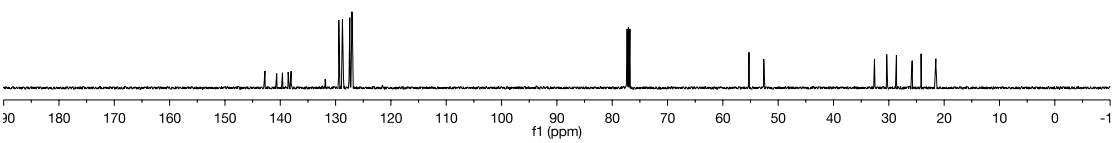
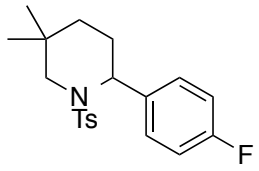
1.01
1.03
1.04
3.06
2.05
11.85
6.04
f1 (ppm)

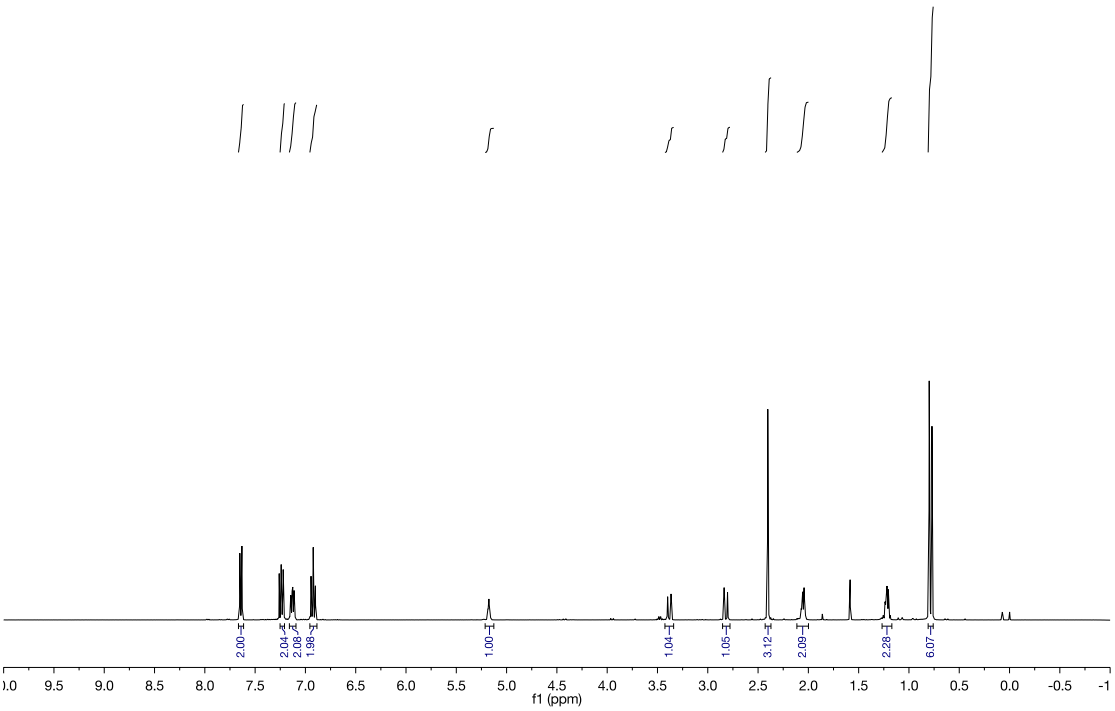

f1 (ppm)


TsN


2.00
1.90
4.11
0.93
4.04
1.03
1.05
1.03
3.09
2.05
2.32
5.75
f1 (ppm)


f1 (ppm)


N
Ts
F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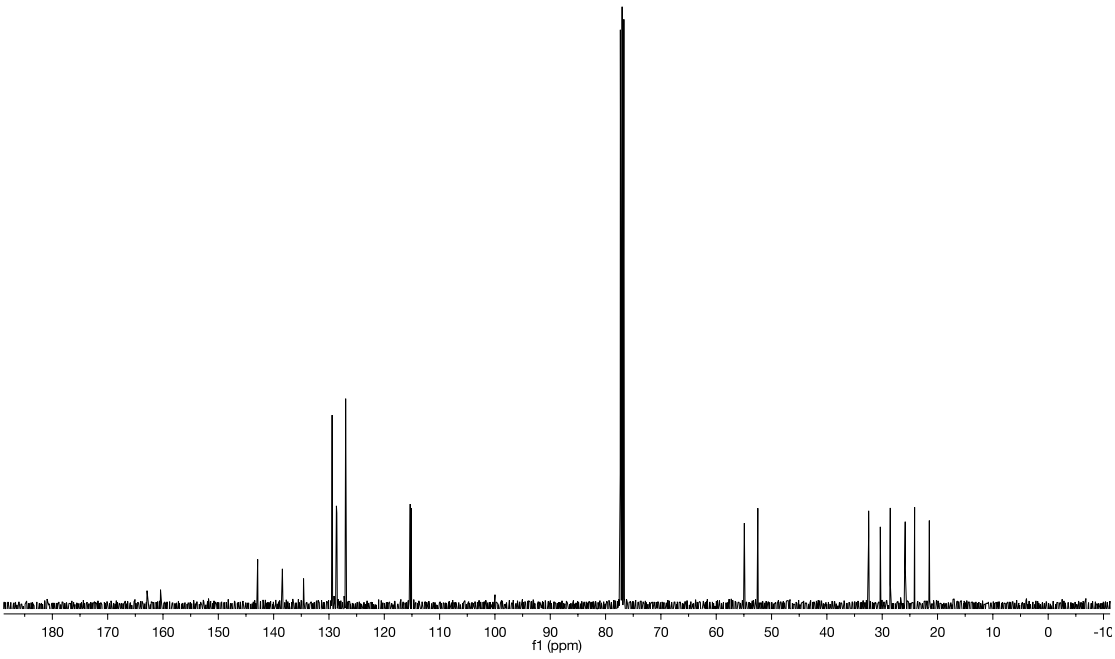
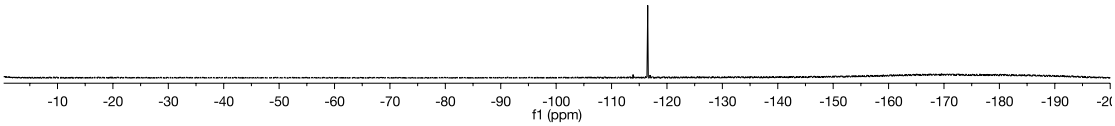
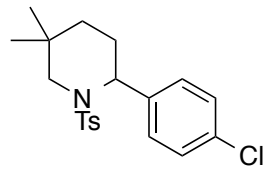
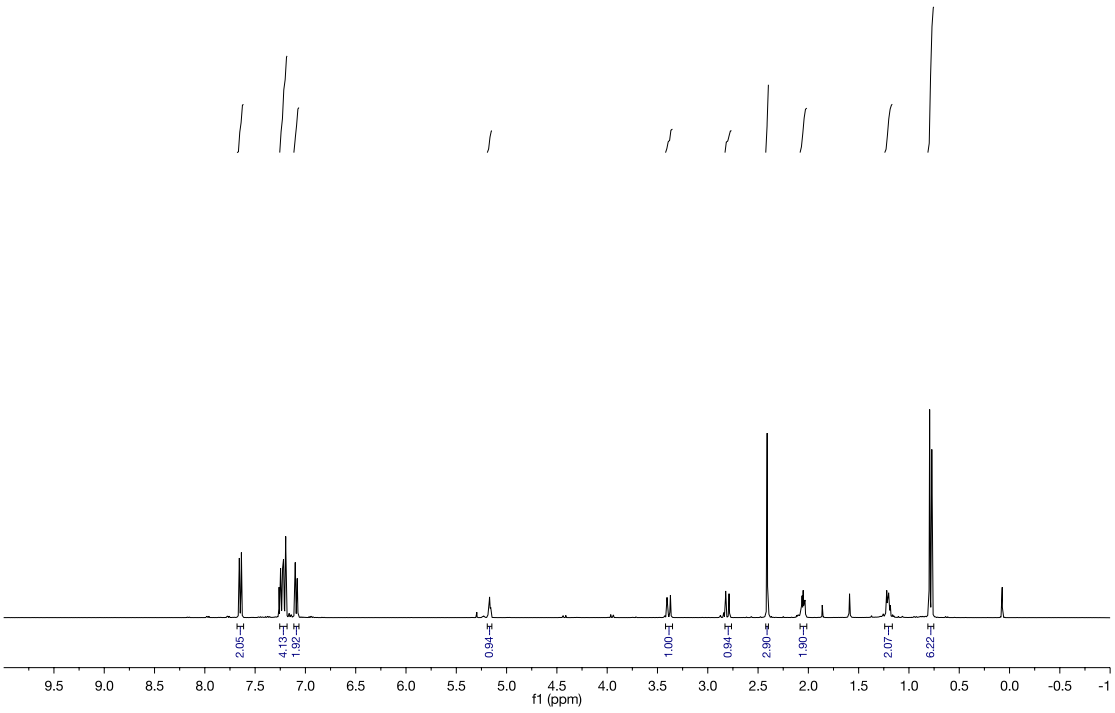
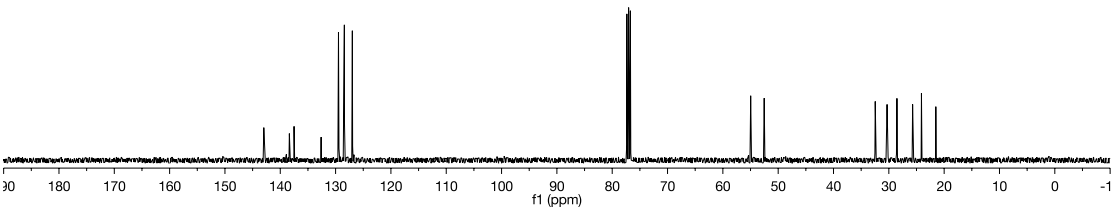
2.04
2.08
1.98
1.00
1.04
1.05
3.12
2.09
2.28
6.07
f1 (ppm)

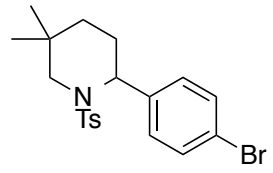

f1 (ppm)

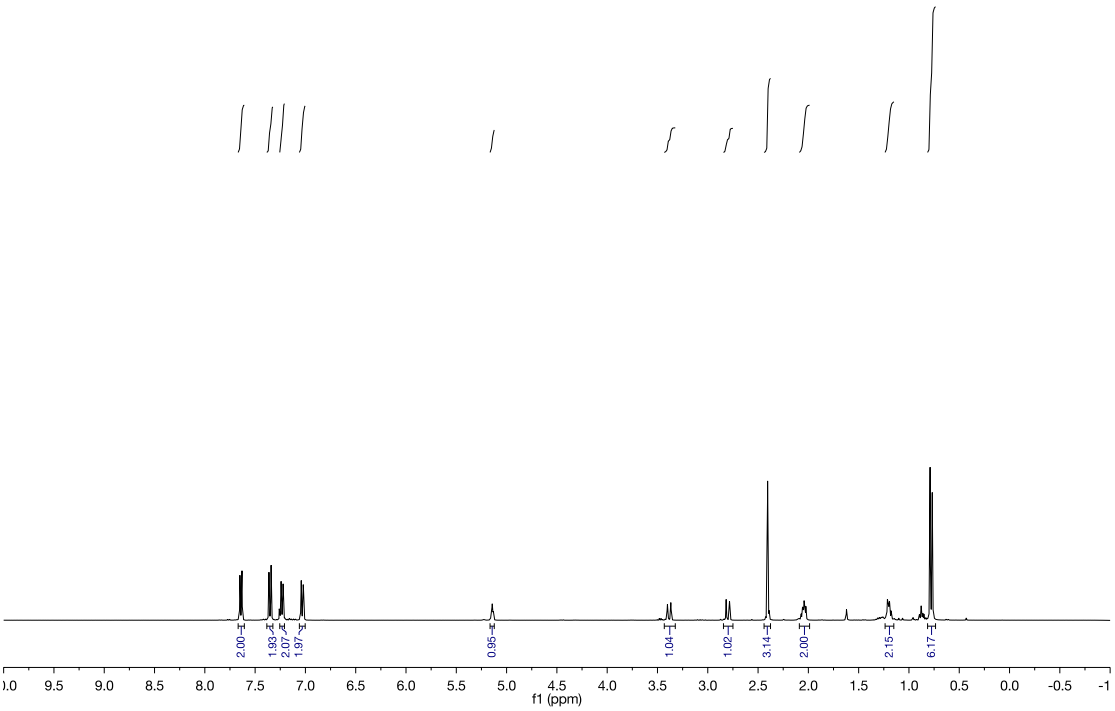

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

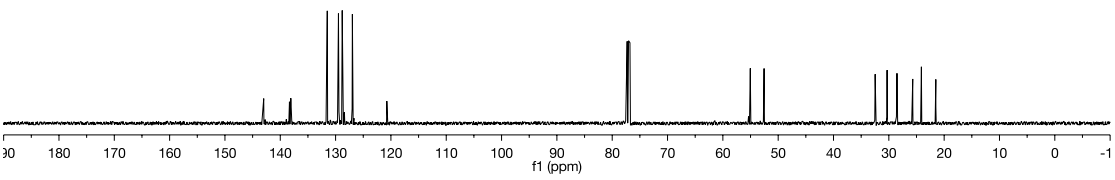

N
Ts
Cl

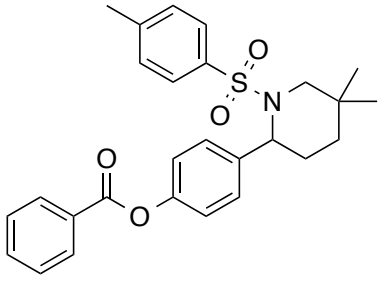

2.05
4.13
1.92
0.94
1.00
0.94
2.90
1.90
2.07
6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

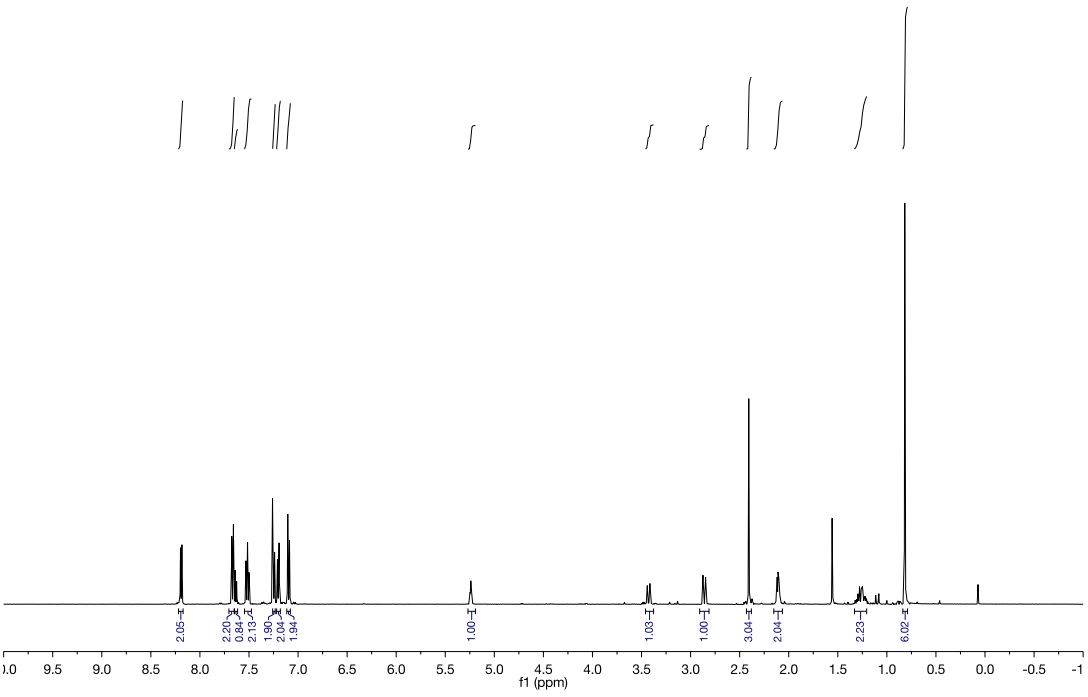

90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

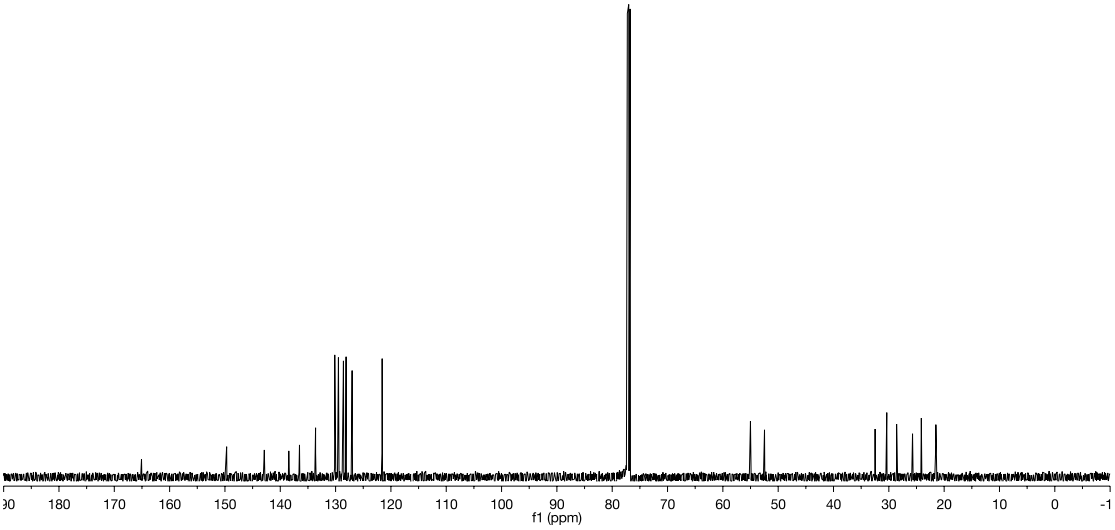

N
Ts
Br

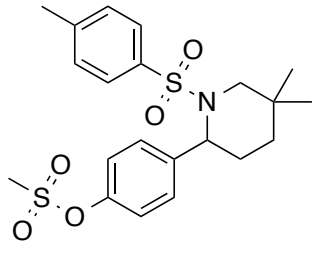

2.00
1.93
2.07
1.97
0.95
1.04
1.02
3.14
2.00
2.15
6.17
f1 (ppm)

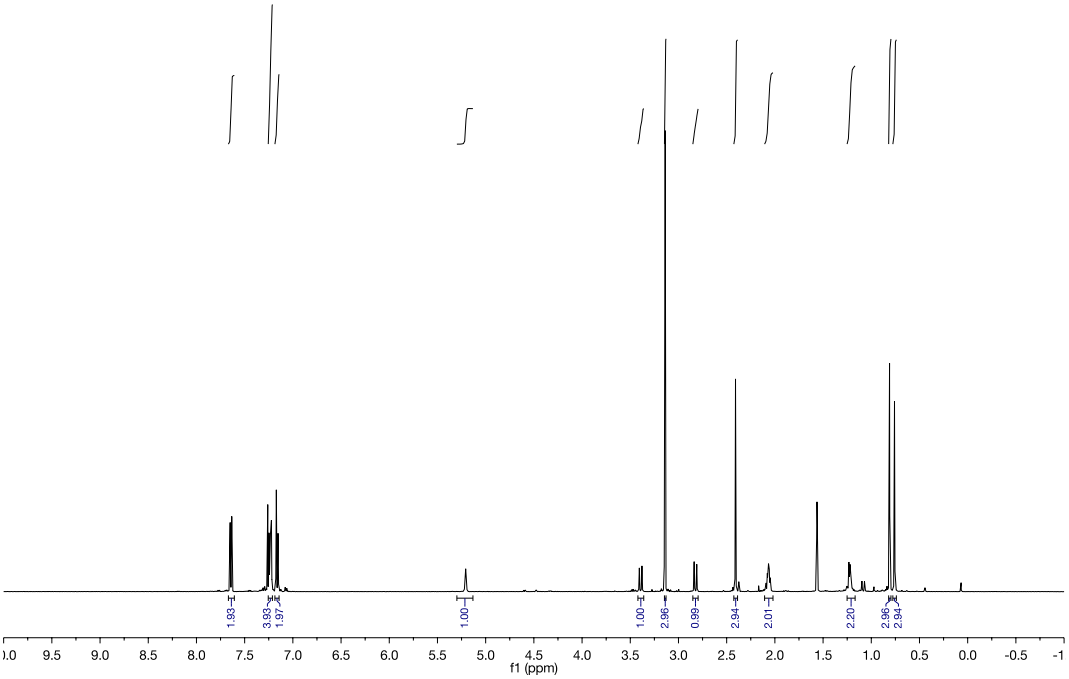

f1 (ppm)

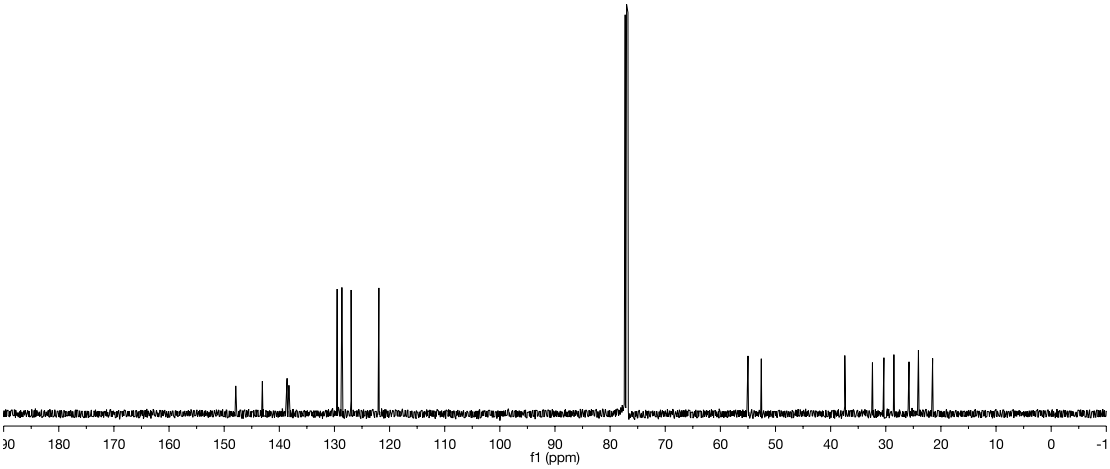

O
S
O
N
O
O

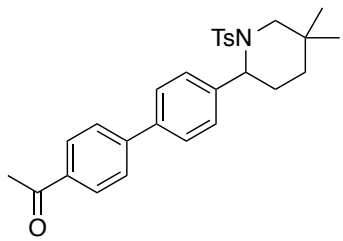

2.05
2.20
0.64
2.13
1.99
2.04
1.94
1.00
1.03
1.00
3.04
2.04
2.23
6.02
f1 (ppm)

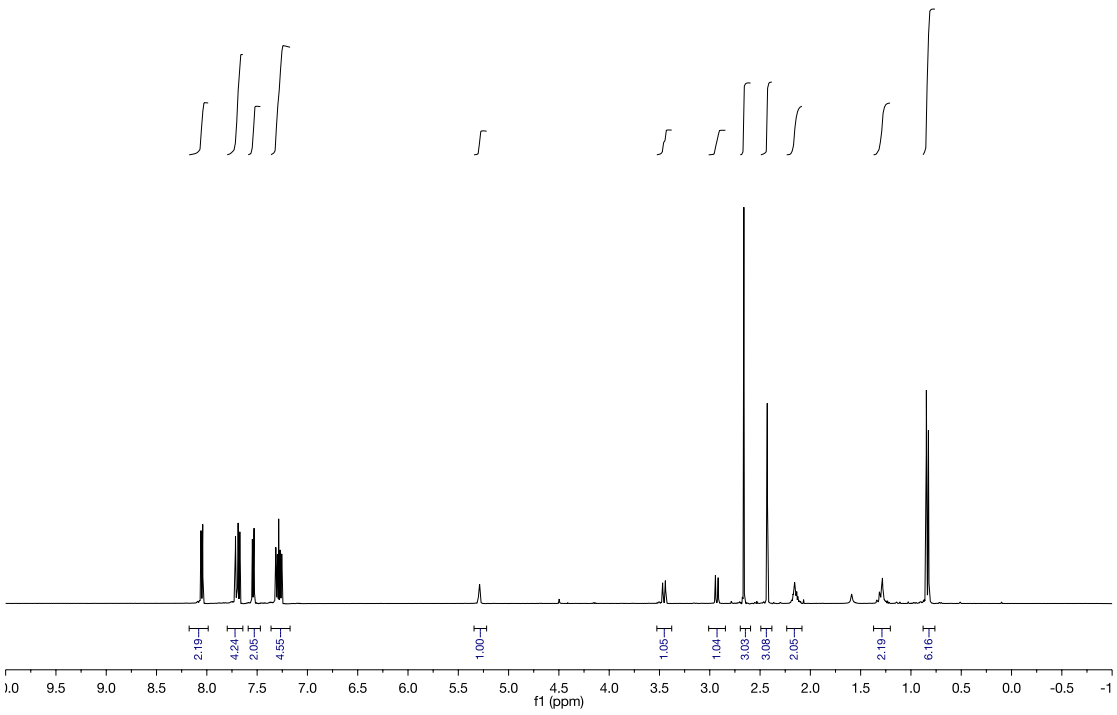

f1 (ppm)

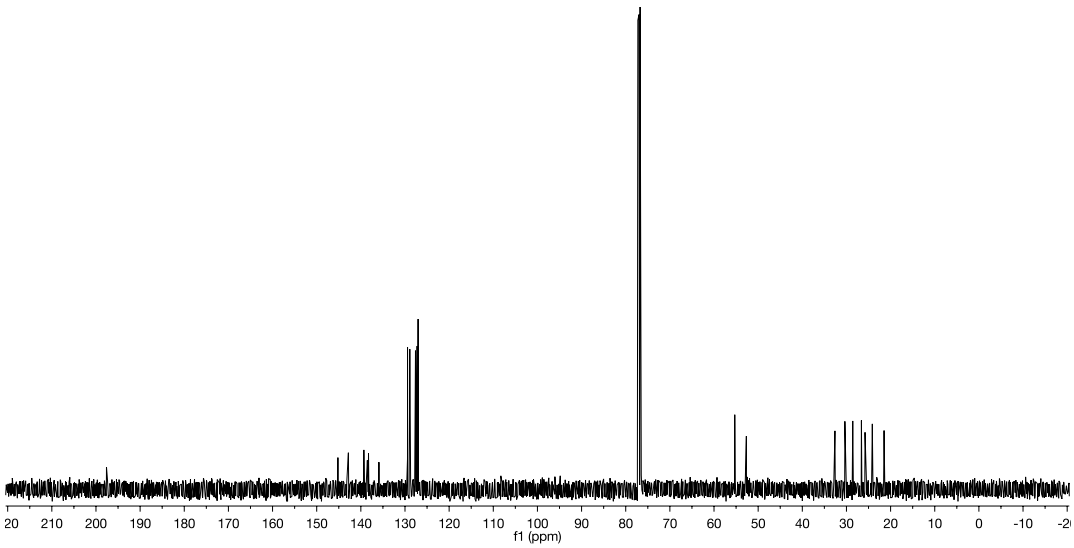

O
S
N
O
O
S
O
O

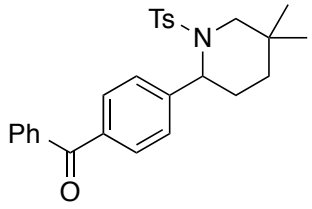

1.93
3.93
1.97
1.00
1.00
2.96
0.99
2.94
2.01
2.20
2.96
2.94
f1 (ppm)

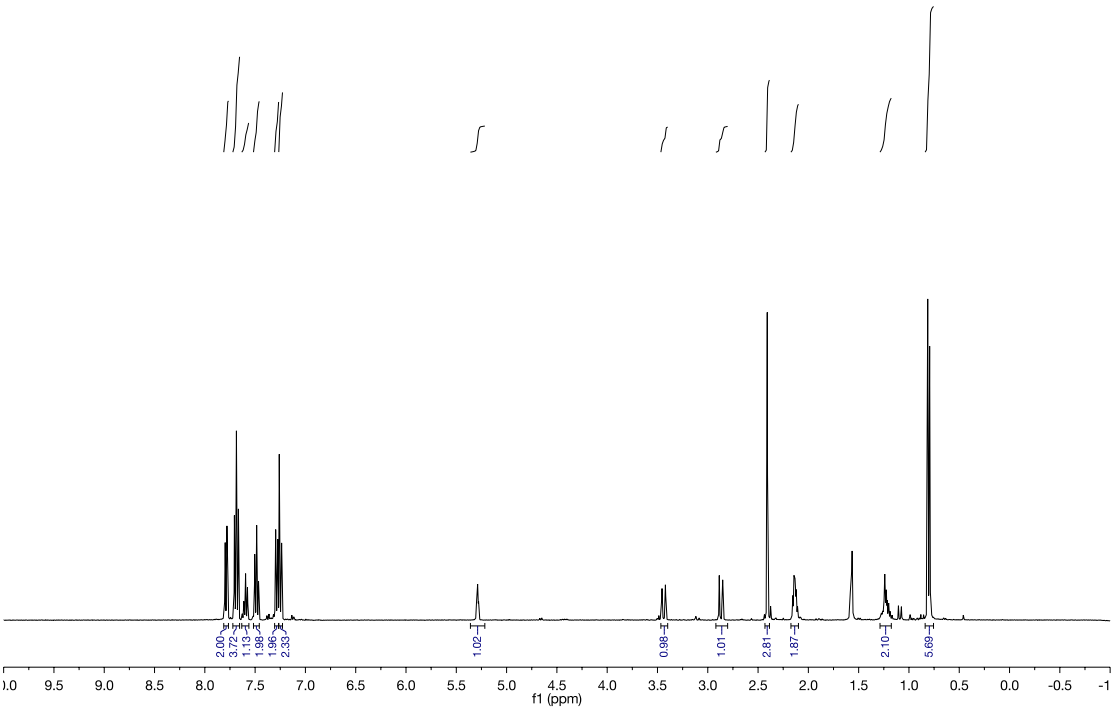

f1 (ppm)


TsN
O


2.19
4.24
2.05
4.55
1.00
1.05
1.04
3.03
3.08
2.05
2.19
6.16
f1 (ppm)


f1 (ppm)


Ts
N
Ph
O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3.72
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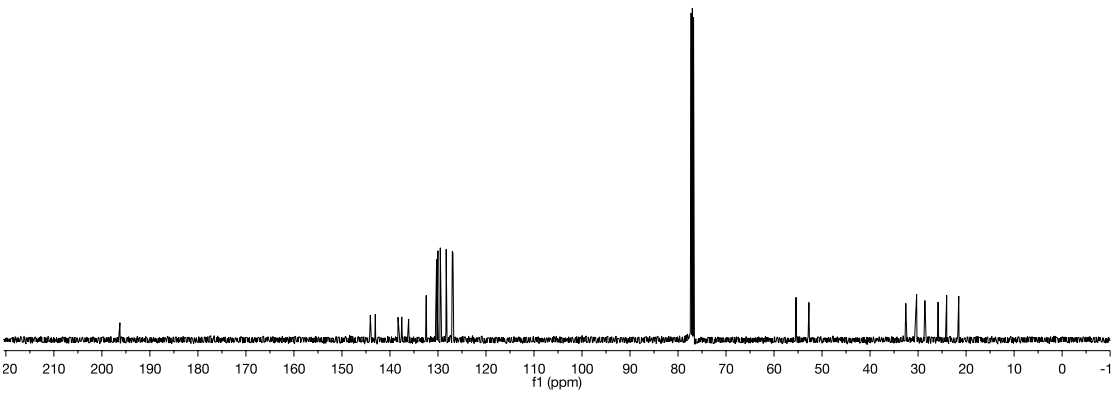
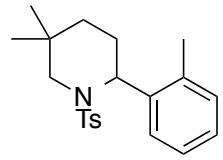
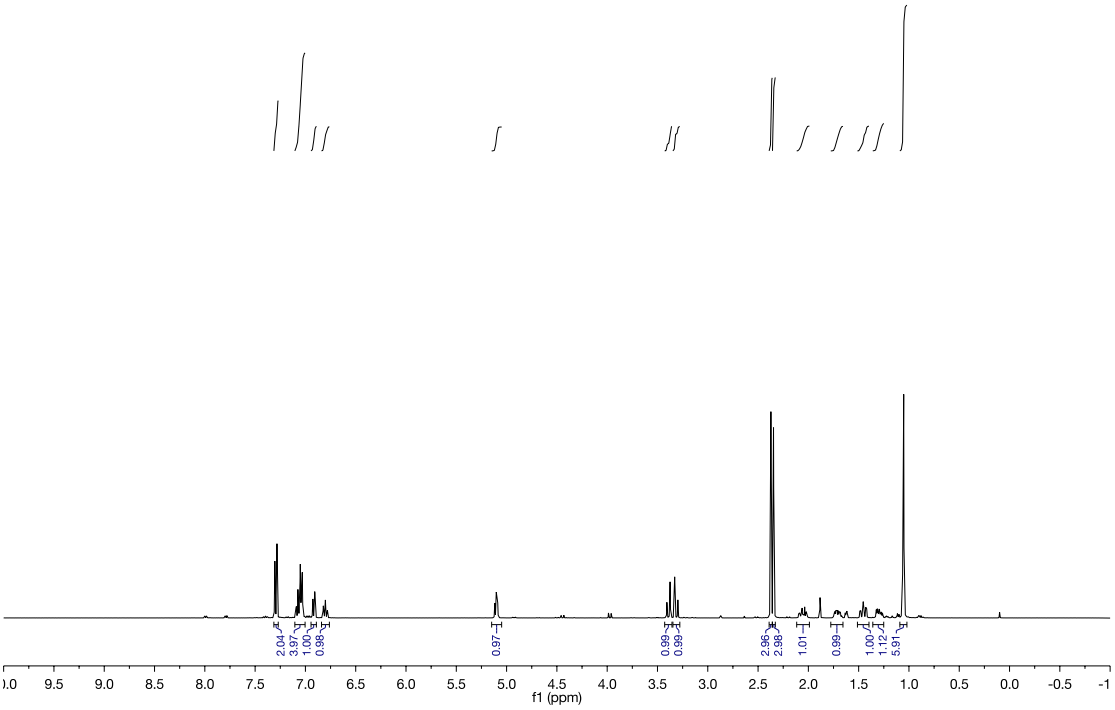
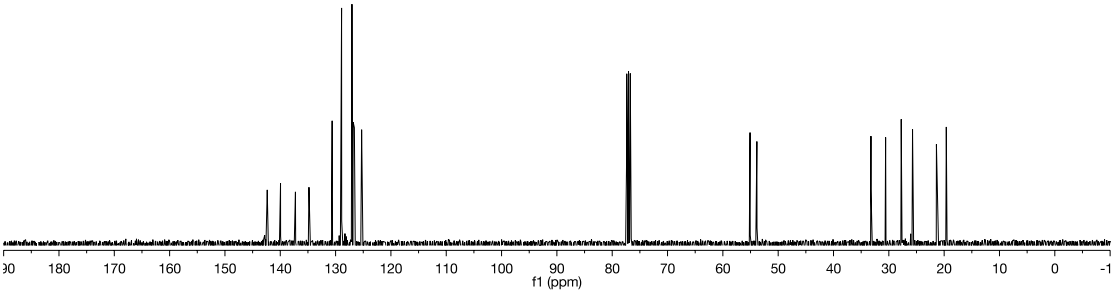
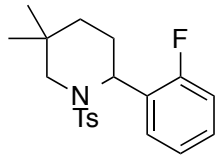
1.96
2.33
1.02
0.98
1.01
2.81
1.87
2.10
5.69
f1 (ppm)

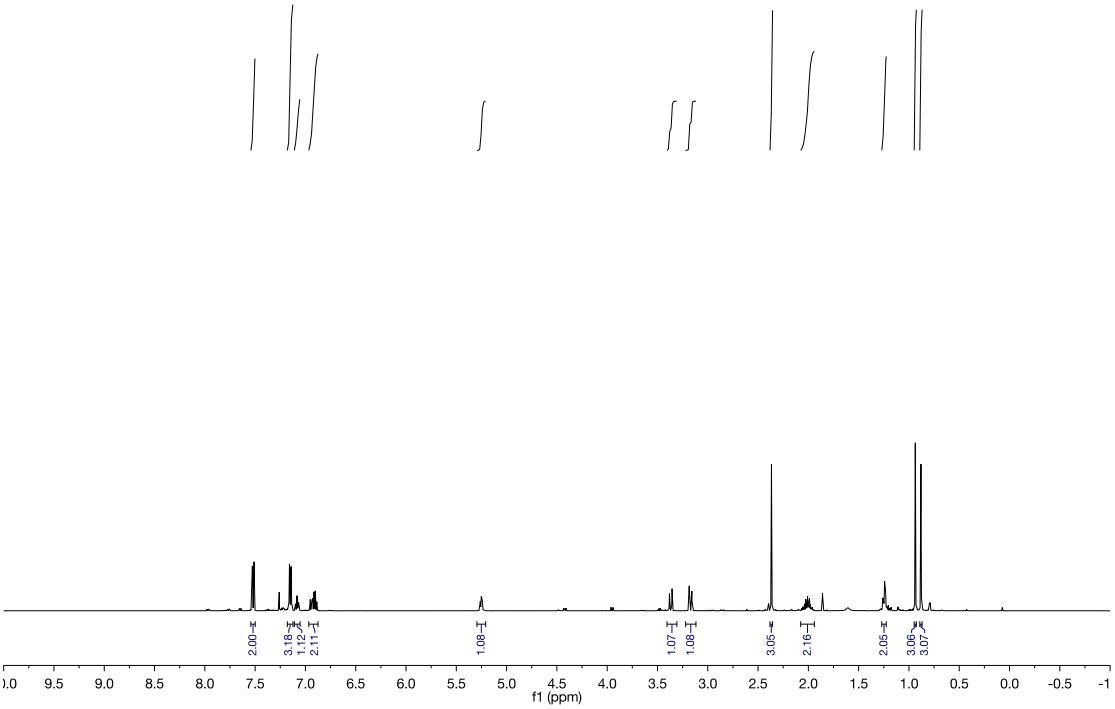

f1 (ppm)

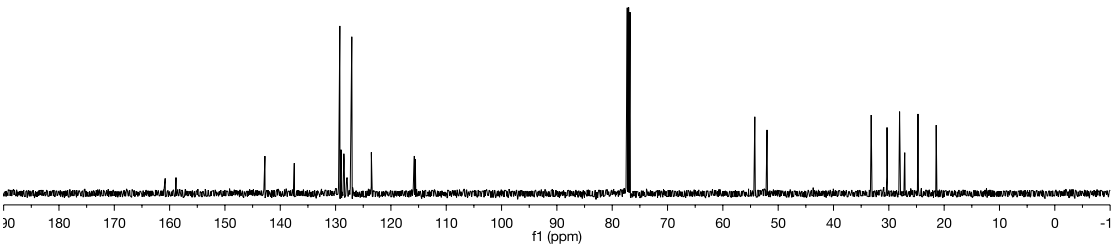

N
Ts

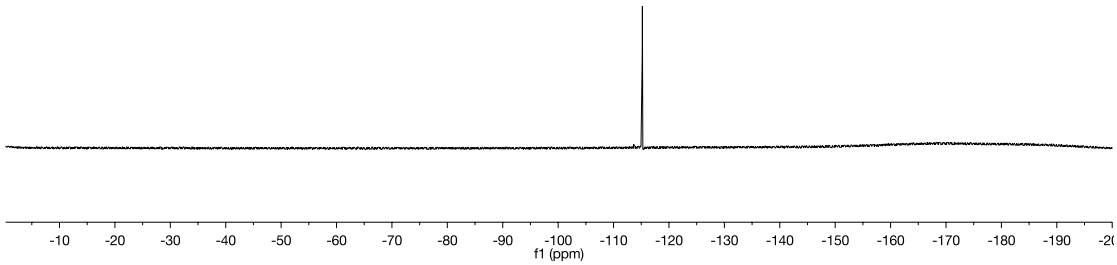

2.04
3.97
1.00
0.98
0.97
0.99
0.99
2.96
2.98
1.01
0.99
1.00
1.12
5.91
f1 (ppm)


f1 (ppm)


F
N
Ts


2.00
3.18
1.12
2.11
1.08
1.07
1.08
3.05
2.16
2.05
3.06
3.07
f1 (ppm)


f1 (ppm)


-10
-20
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-50
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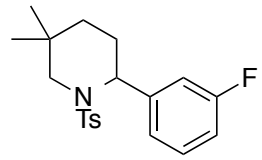
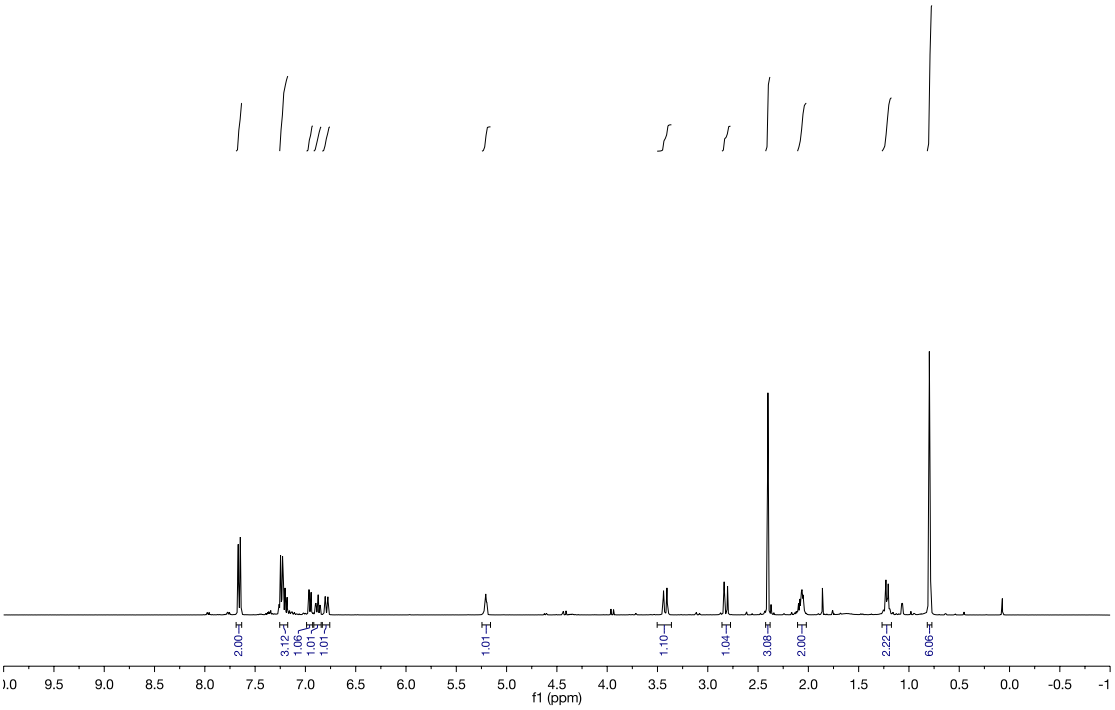
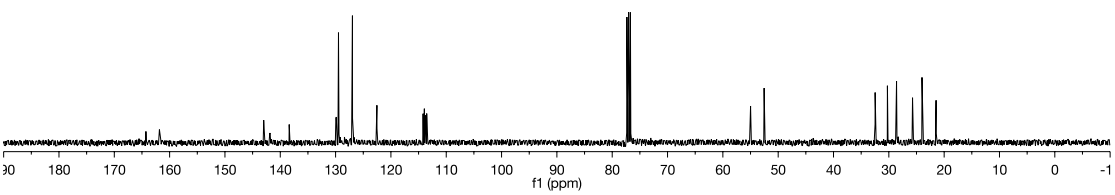
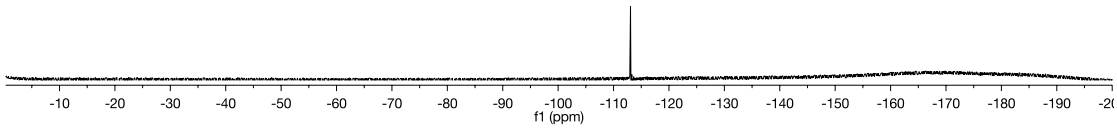
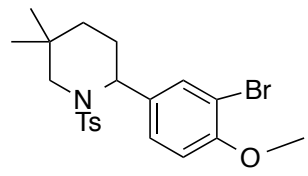
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

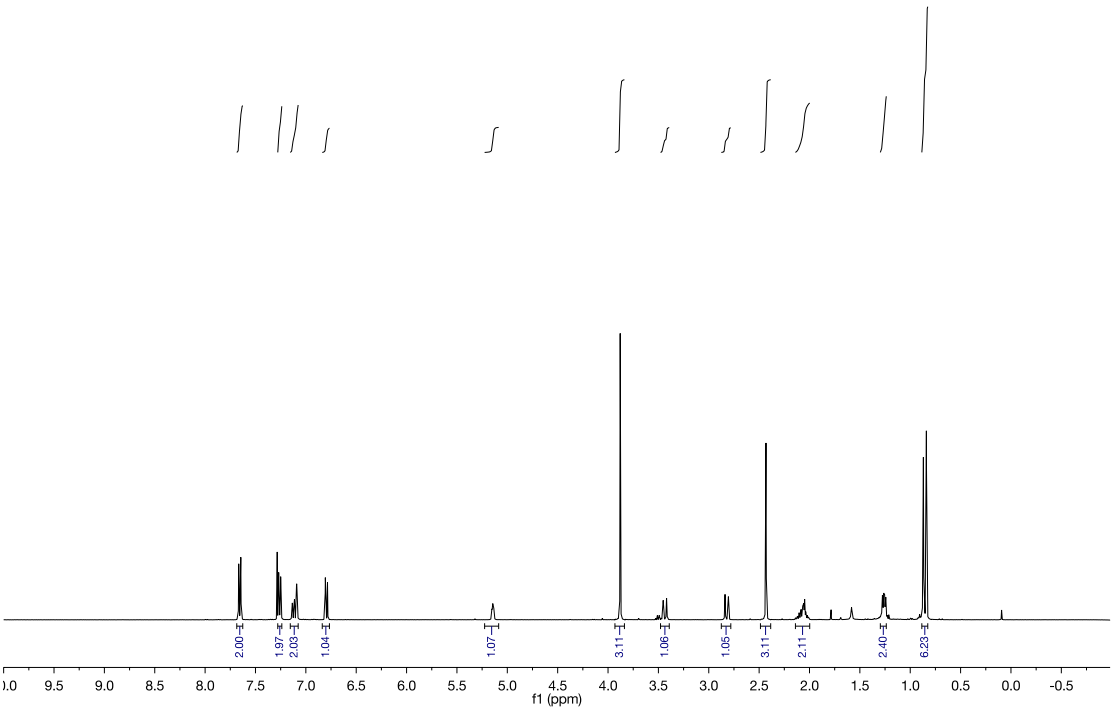

N
Ts
F

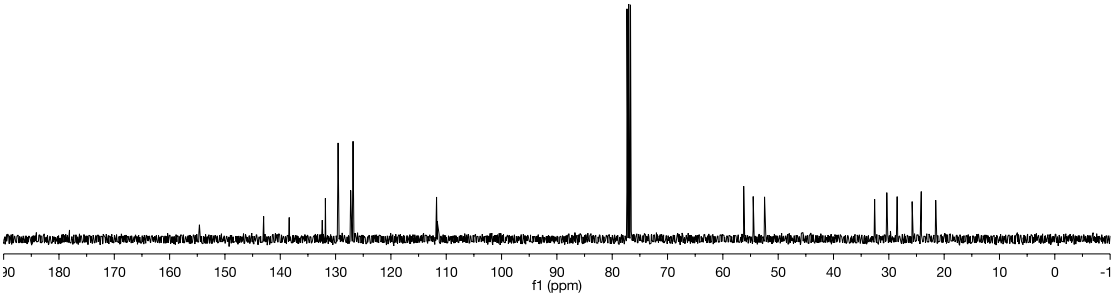

2.00
3.12
1.06
1.01
1.01
1.01
1.10
1.04
3.08
2.00
2.22
6.06
f1 (ppm)

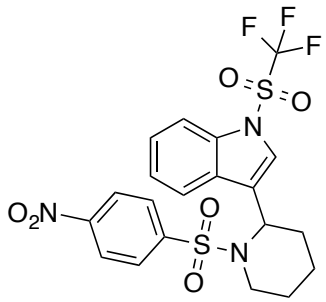

f1 (ppm)

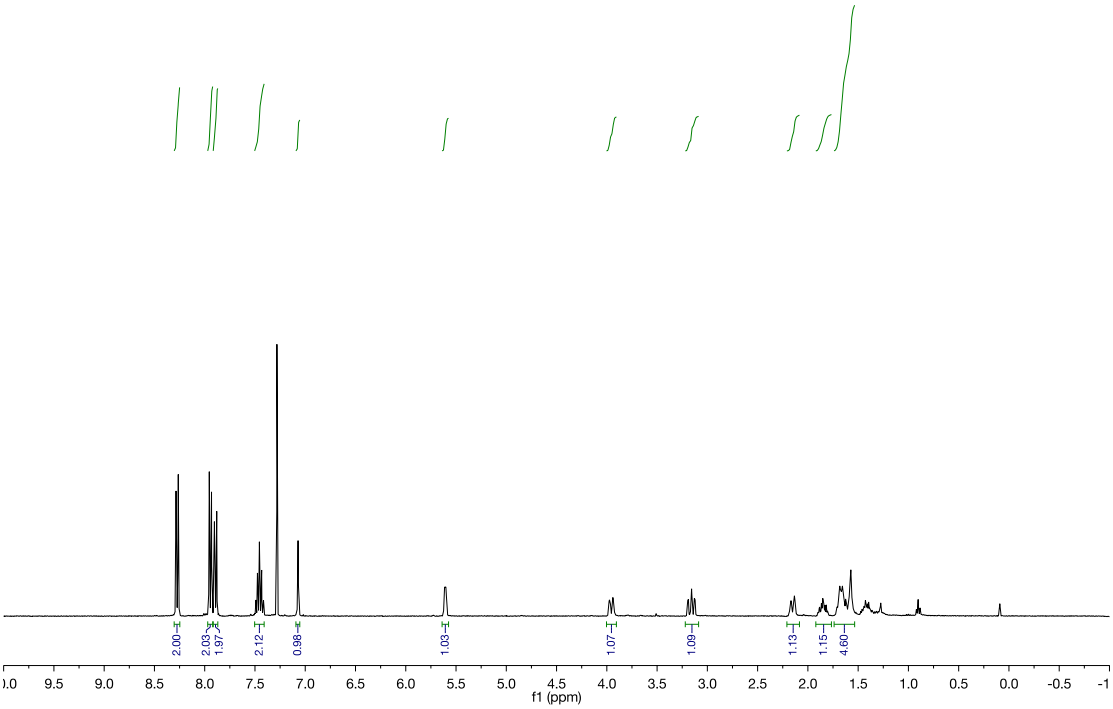

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

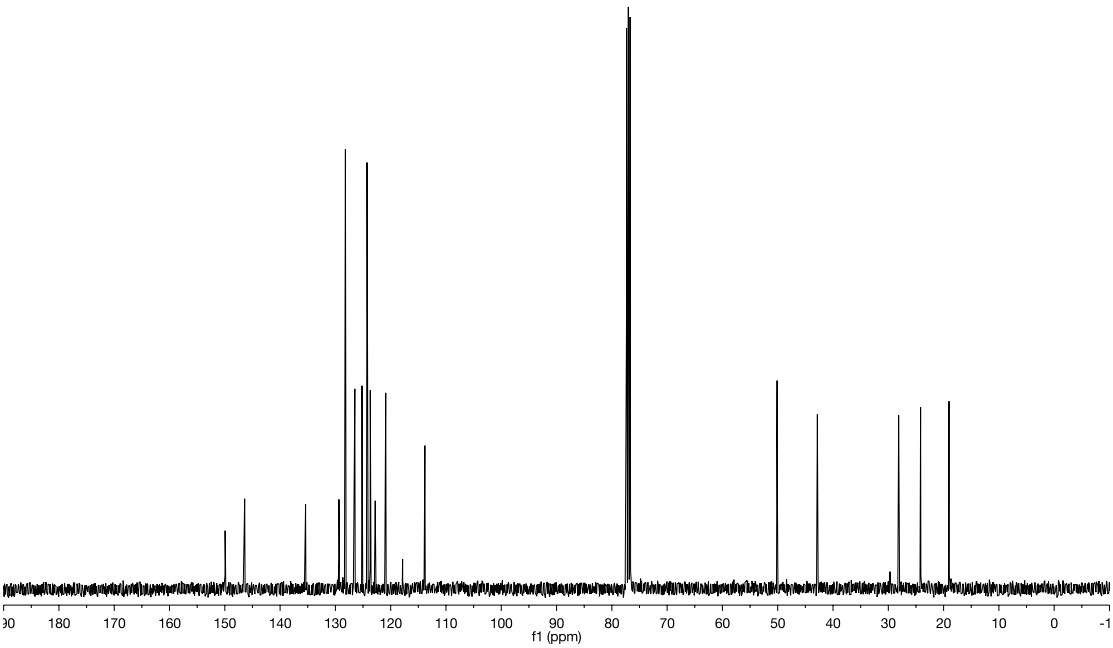

N
Ts
Br
O

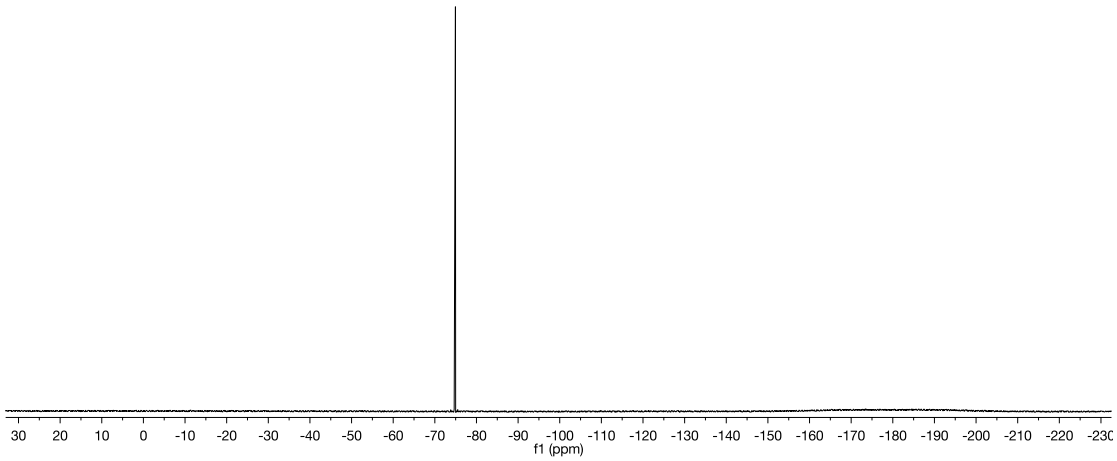

2.00
1.97
2.03
1.04
1.07
3.11
1.06
1.05
3.11
2.11
2.40
6.23
f1 (ppm)

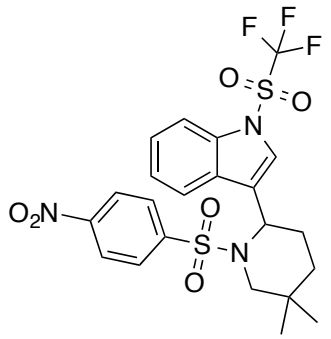

f1 (ppm)

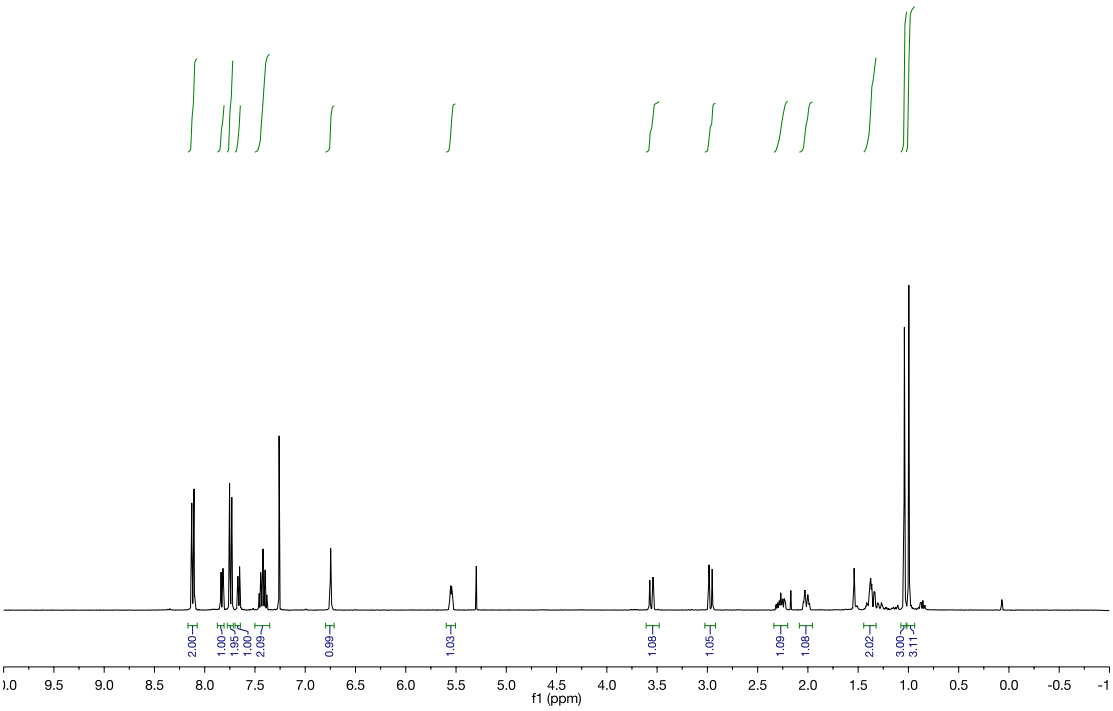

F
F
F
O
S
O
N
O2N
O
S
N
O

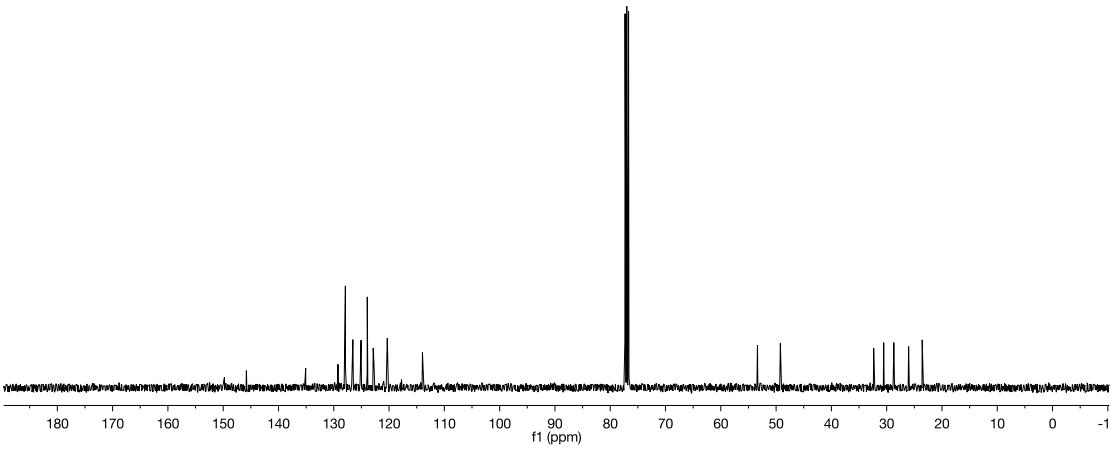

2.00
2.03
1.97
2.12
0.98
1.03
1.07
1.09
1.13
1.15
4.60
f1 (ppm)

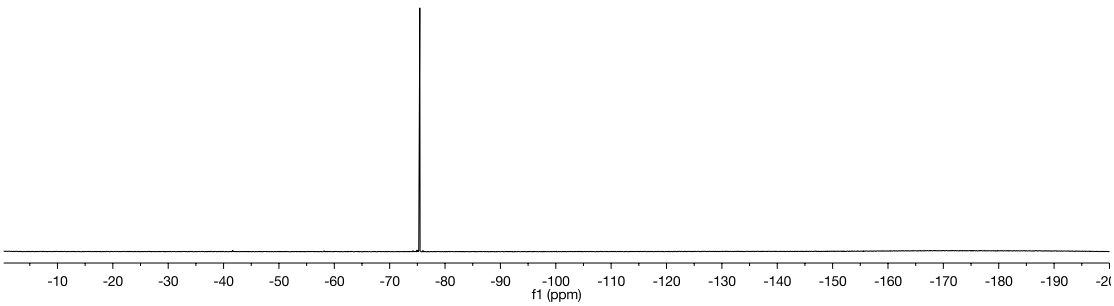

f1 (ppm)

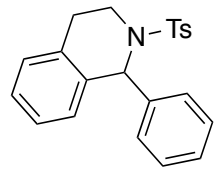

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

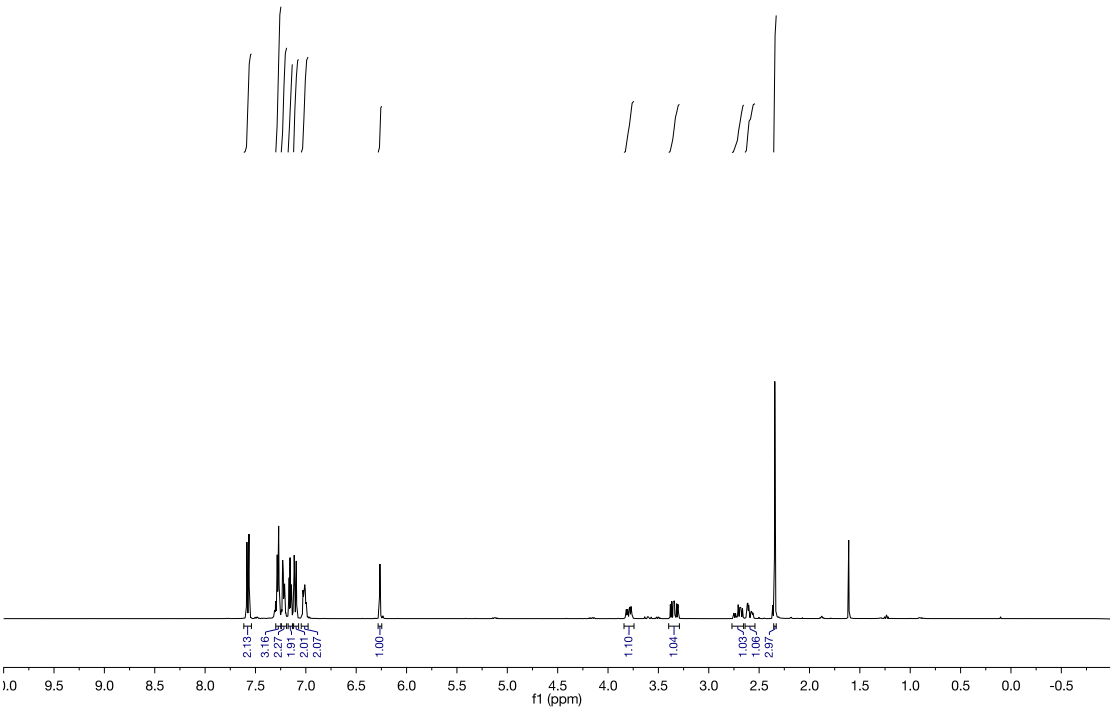

F
F
F
O
S
O
N
O2N
O
S
N
O

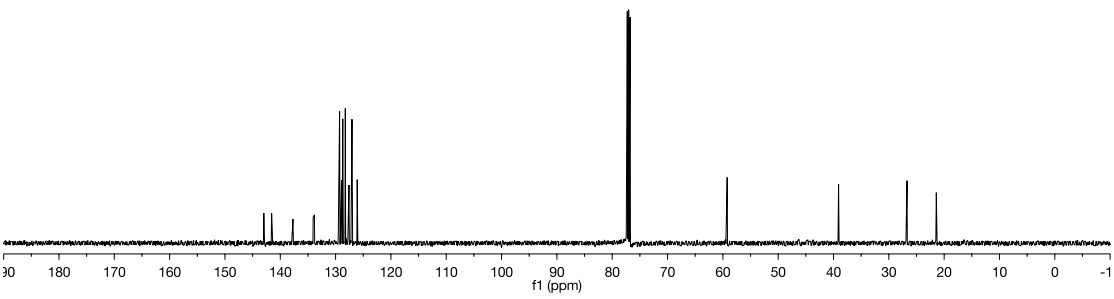

2.00
1.00
1.95
1.00
2.09
0.99
1.03
1.08
1.05
1.09
1.08
2.02
3.00
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

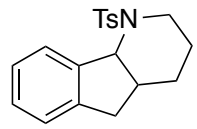

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

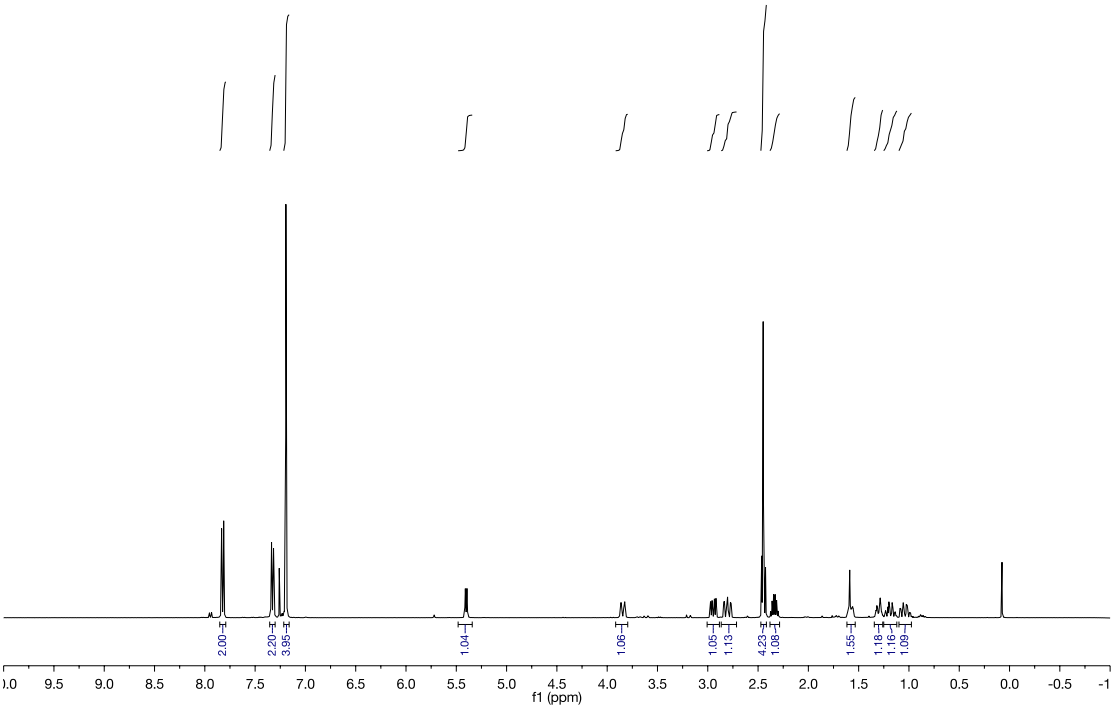

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

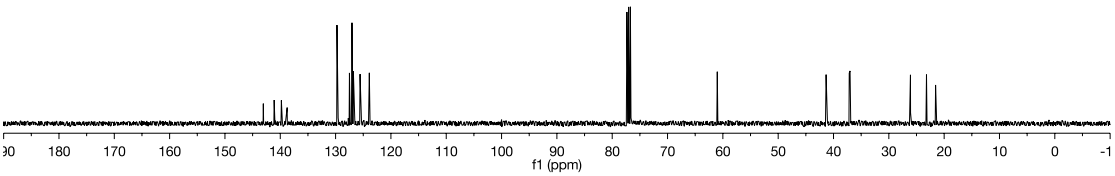

N
Ts

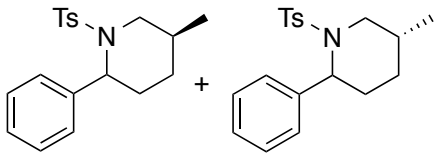

2.13
3.16
2.27
1.91
2.01
2.07
1.00
1.10
1.04
1.03
1.06
2.97
f1 (ppm)


f1 (ppm)

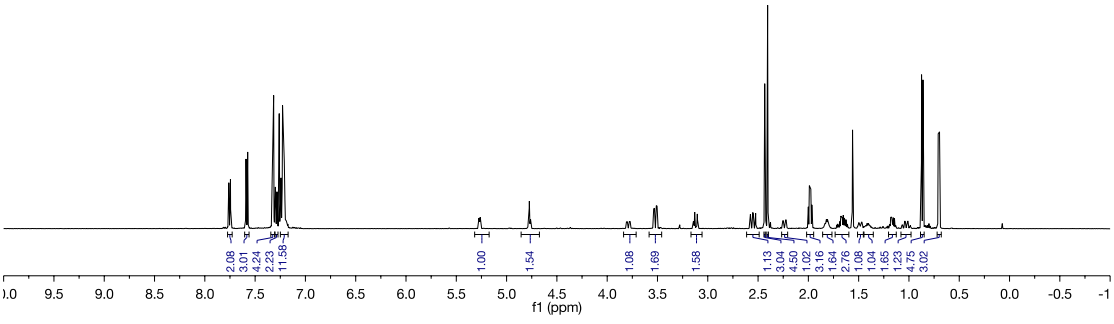

TsN


2.00
2.20
3.95
1.04
1.06
1.05
1.13
4.23
1.08
1.55
1.18
1.16
1.09
f1 (ppm)


f1 (ppm)


Ts
N
+
Ts
N

1.5 : 1


2.08
3.01
4.24
2.23
11.58
1.00
1.54
1.08
1.69
1.58
1.13
3.04
4.50
1.02
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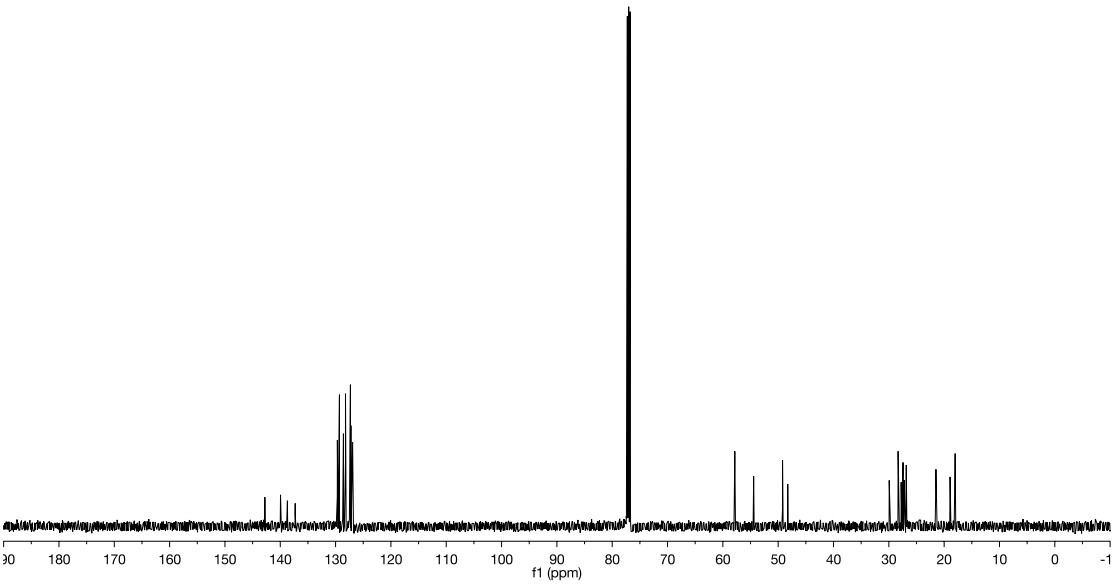
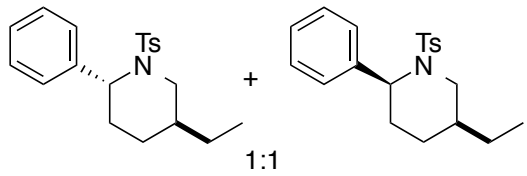
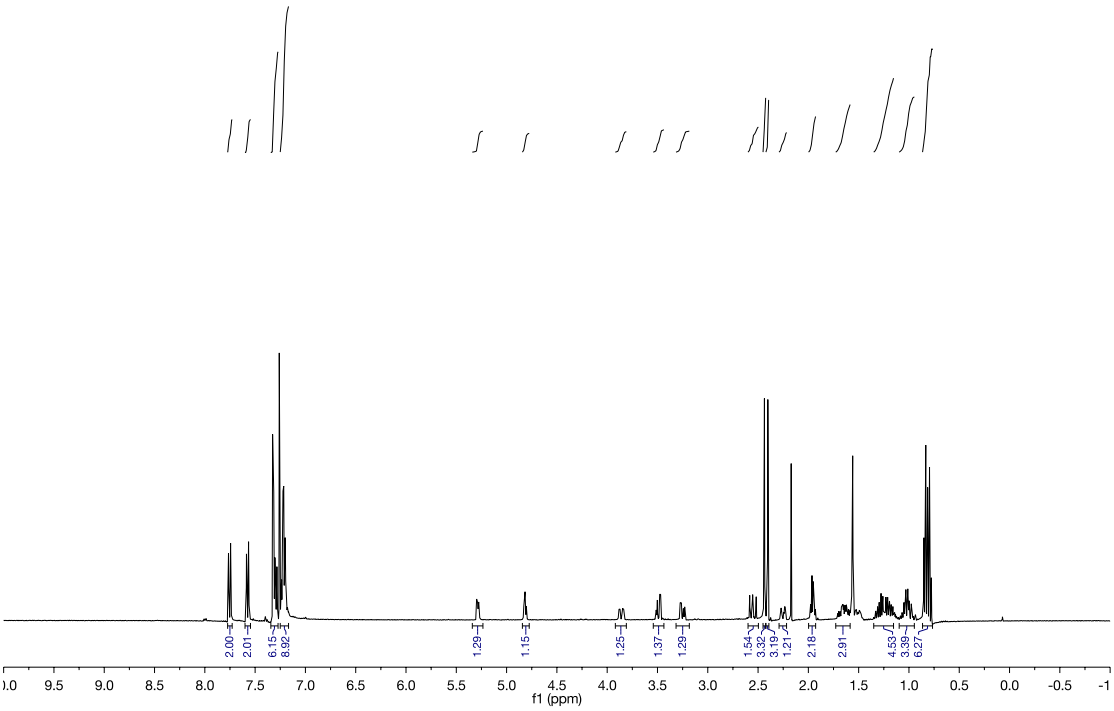
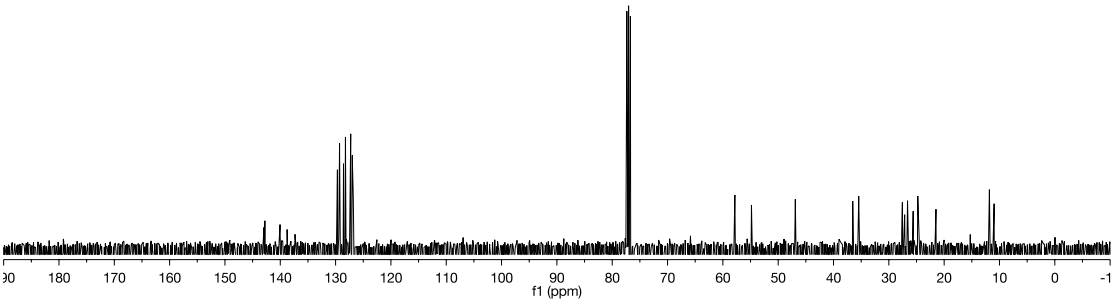
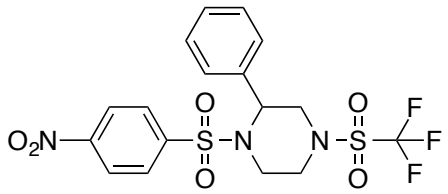
1.64
2.76
1.08
1.04
1.65
1.23
4.73
3.02
f1 (ppm)

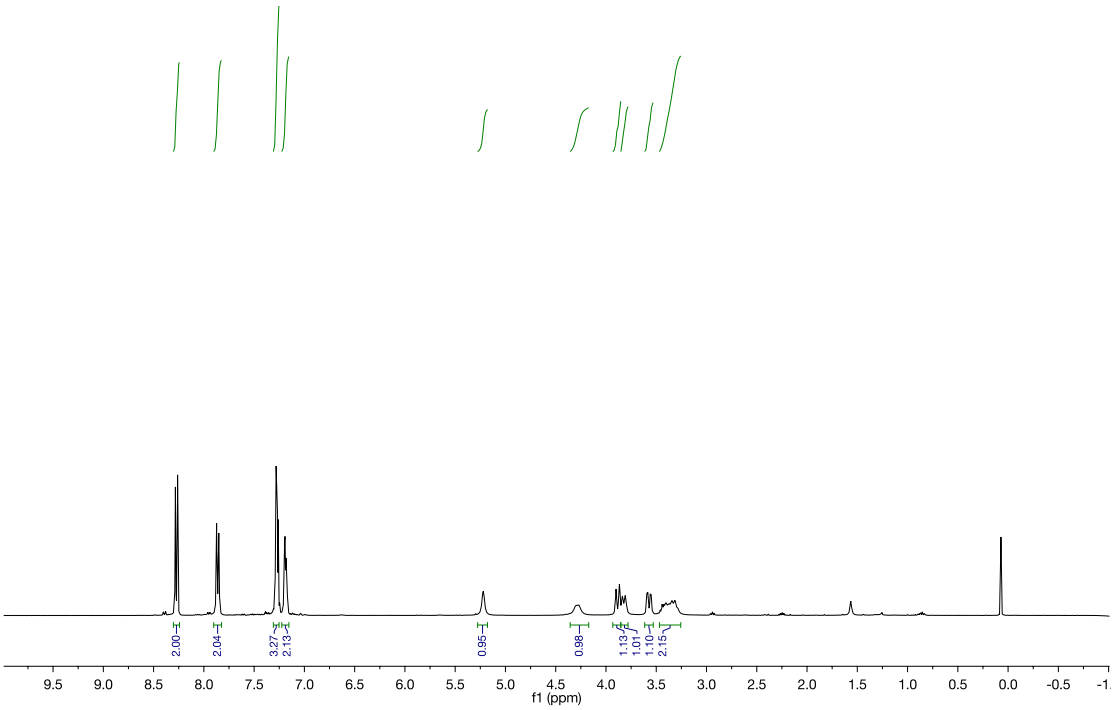

f1 (ppm)

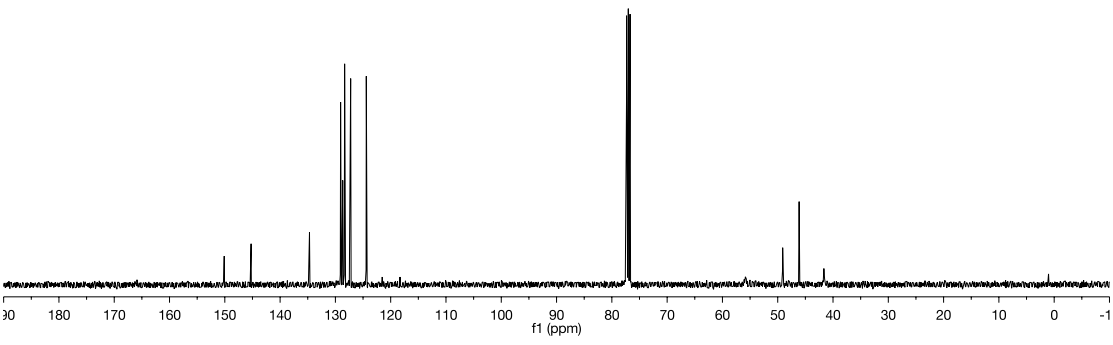

Ts
N
+
Ts
N
1:1

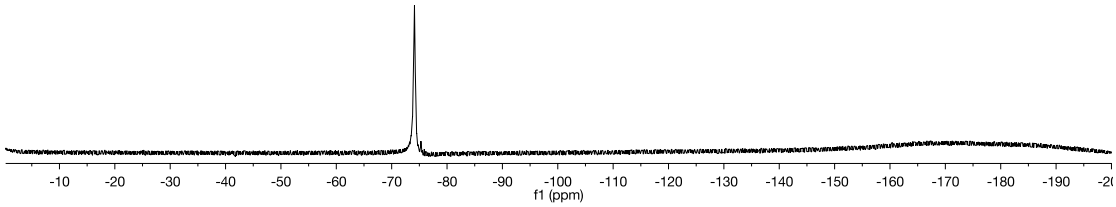

2.00
2.01
6.15
8.92
1.29
1.15
1.25
1.37
1.29
1.54
3.32
3.19
1.21
2.18
2.91
4.53
3.39
6.27
f1 (ppm)

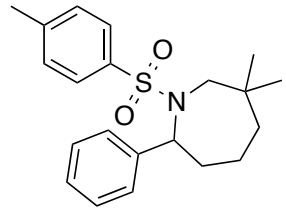

f1 (ppm)

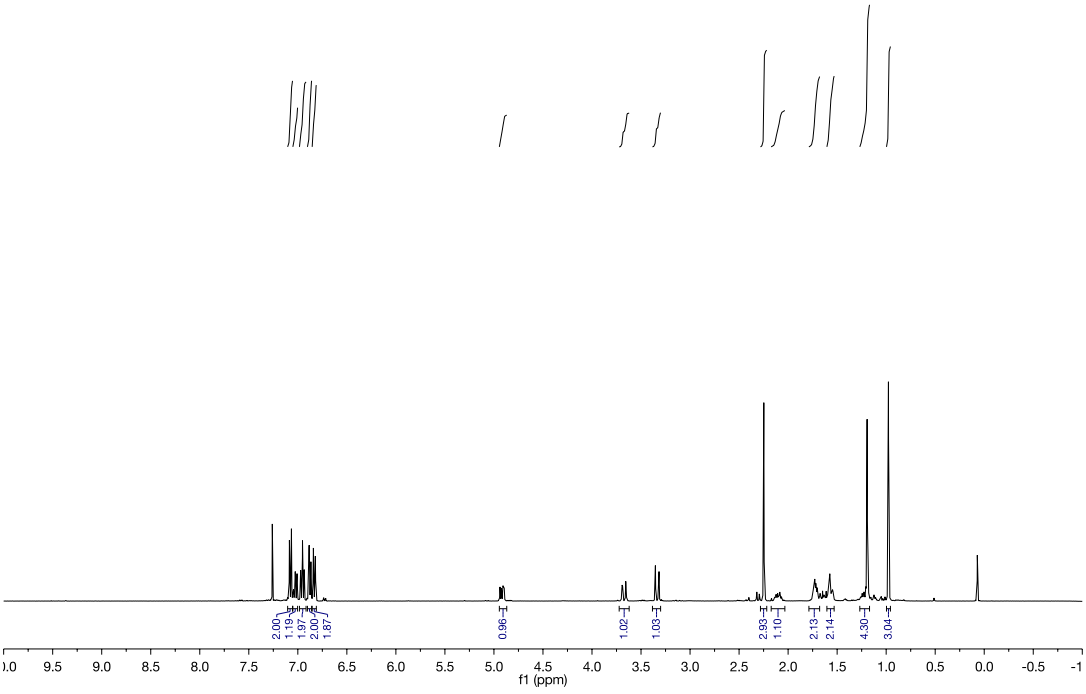


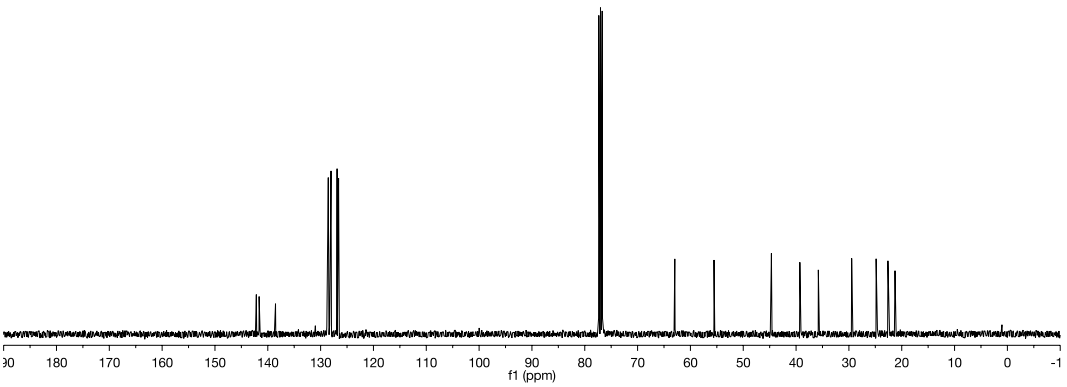

2.00
2.04
3.27
2.13
0.95
0.98
1.13
1.01
1.10
2.15
f1 (ppm)

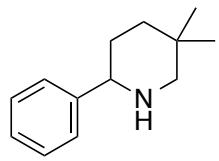

f1 (ppm)

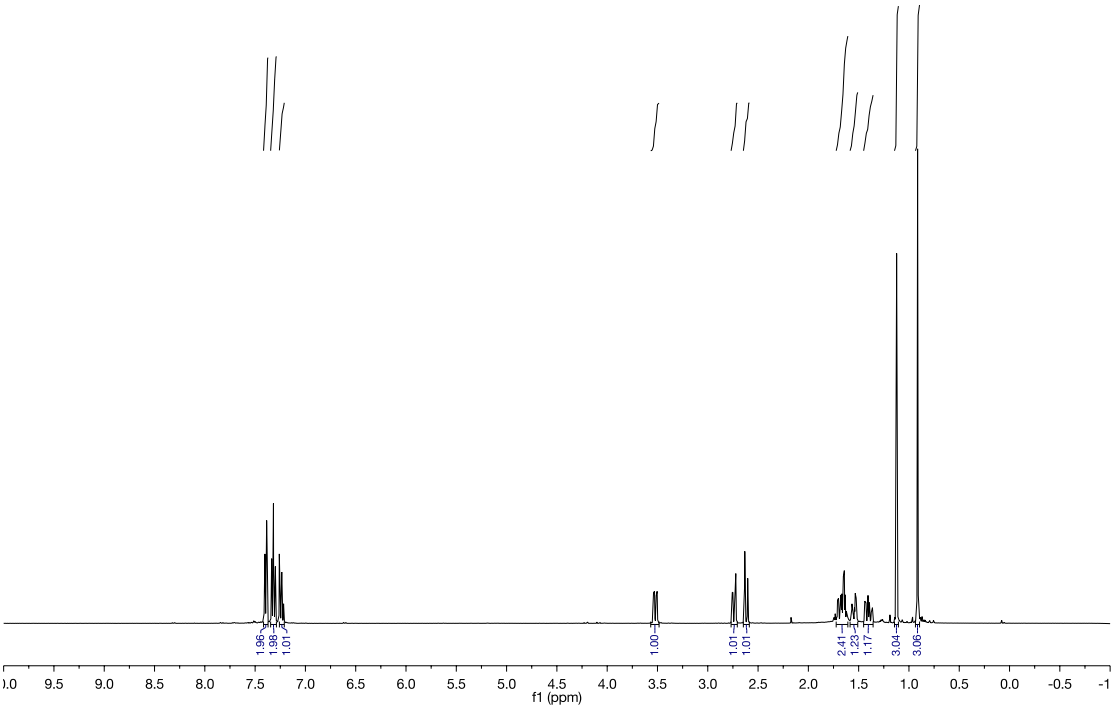

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

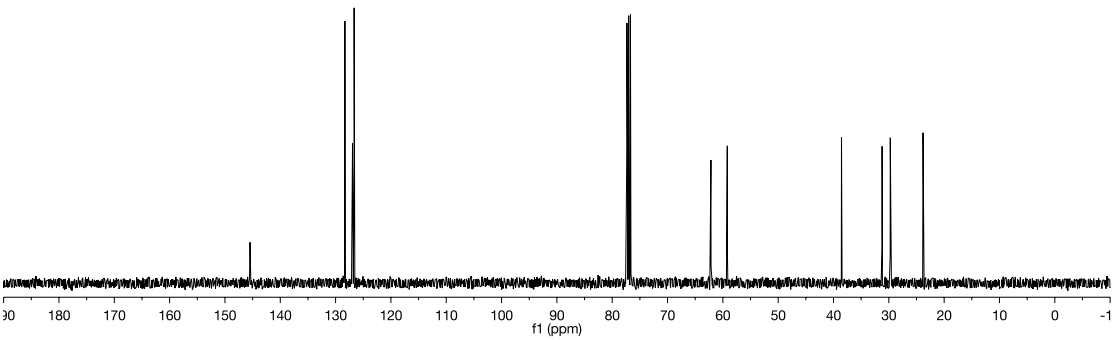

O
S
O
N


2.00
1.19
1.97
2.00
1.87
0.96
1.02
1.03
2.93
1.10
2.13
2.14
4.30
3.04
f1 (ppm)


f1 (ppm)


N
H


1.96
1.98
1.01
1.00
1.01
1.01
2.41
1.23
1.17
3.04
3.06
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 -0.5 -1
f1 (ppm)


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)