SUPPLEMENTARY INFORMATION FOR:

Organocatalytic Nitrenoid Transfer: Metal-Free Selective Intermolecular C(sp^3)-H Amination Catalysed by an Iminium Salt

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CONTENTS

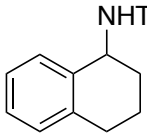
I. General Information

Unless otherwise noted, all substrates, reagents and solvents were obtained commercially in reagent grade or better quality and used without further purification. Anhydrous solvents were obtained from an aluminum oxide solvent purification system. Flash column chromatography was performed using silica gel (230 - 400 mesh) purchased from Fisher Scientific. Elution of compounds was monitored by UV or PMA stain. ^{1}H and ^{13}C NMR spectra were measured on a Varian Inova 600 (600 MHz) spectrometer and acquired at 300 K. Chemical shifts are reported in parts per million (ppm δ) referenced to the residual ^{1}H or ^{13}C resonance of the solvent. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet and br - broad. Gas chromatography yield analysis was performed using an Agilent 7820A GC with FID detector using *n*-dodecane as an internal standard. IR spectra were recorded on a Shimadzu IRAffinity-1S. HRMS data were obtained from the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign and are accurate to within 5 ppm.

II. Amination Reactions

Representative procedure:
Unless otherwise noted, amination reactions were performed on a 0.5 mmol scale. In a nitrogen glovebox at room temperature, the substrate (0.5 mmol, 1 equiv), [N-(p-tolylsulfonyl)imino]phenyliodinane (373 mg, 1 mmol, 2 equiv) and iminium **5a** (33 mg, 0.1 mmol, 0.2 equiv) were combined in a vial or Schlenk flask equipped with a stir bar. Anhydrous dichloromethane (2 mL) was then added and the reactions mixture was either left in the glovebox and stirred at room temperature for 20 hours or removed from the glovebox, place under positive pressure of nitrpogen, and stirred at room temperature for 20 hours. The reaction mixture was then filtered through a silica gel plug, eluting with EtOAc. After removal of the solvent under reduced pressure, the crude reaction mixture was then purified by flash chromatography using the conditions noted.

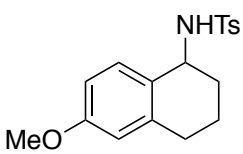
4-methyl-N-(1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide (4)



4

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes). Yield: 96 mg (0.32 mmol, 64%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.62 (d, *J* = 7.8 Hz, 1H), 4.45 (q, *J* = 5.7 Hz, 1H), 2.78 – 2.73 (m, 1H), 2.70 – 2.63 (m, 1H), 2.46 (s, 1H), 1.87 – 1.79 (m, 3H), 1.77 – 1.68 (m, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.38, 138.12, 137.53,135.57,129.75, 129.20, 128.75, 127.62, 127.12, 126.28, 51.89, 30.75, 28.86, 21.56, 19.09 ppm. NMR spectra are consistent with literature reports.[1]

N-(6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-4-methylbenzenesulfonamide (6)

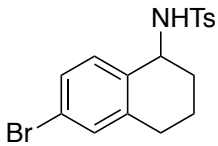


6

Purified by silica gel flash chromatography (5-20% ethyl acetate in hexanes). Yield: 96 mg (0.3 mmol, 58%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.60 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 4.60 (d, *J* = 7.5 Hz, 1H), 4.44 – 4.31 (m, 1H), 3.73 (s, 3H), 2.71

(dt, *J* = 17.2, 5.5 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.45 (s, 3H), 1.87 – 1.73 (m, 3H), 1.73 – 1.65 (m, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.83, 143.34, 138.96, 138.15, 130.03, 129.73, 127.76, 127.12, 113.39, 112.74, 55.18, 51.44, 30.85, 29.22, 21.55, 18.87 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{18}H_{21}NO_3S+Na]^+$: 354.1137; found: 354.1140.

N-(6-bromo-1,2,3,4-tetrahydronaphthalen-1-yl)-4-methylbenzenesulfonamide (7)

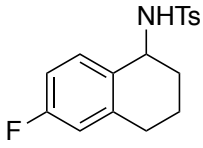


7

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes). Yield: 72 mg (0.19 mmol, 37%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.2, 6.3 Hz, 2H), 7.35 (dd, *J* = 17.2, 8.0 Hz, 2H), 7.23 – 7.04 (m, 2H), 6.90 – 6.80 (m, 1H), 4.54 (dd, *J* = 15.1, 8.2 Hz, 1H), 4.39 (q, *J* = 5.8, 4.7 Hz, 1H), 2.79 – 2.68 (m, 1H), 2.66 – 2.57 (m, 1H), 2.45 (s, 3H), 1.78 (ddt, *J* = 11.6, 8.9, 4.5 Hz, 3H), 1.70 (td, *J* = 8.9, 8.2, 3.5 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.56, 139.66, 134.66,131.84, 130.51, 129.81, 129.47, 127.07, 126.97, 121.51, 51.45, 30.61, 28.69, 21.56, 18.98 ppm.
HRMS (ESI): *m/z* calcd for $[C_{17}H_{18}NO_2SBr+Na]^+$: 402.0138; found: 402.0139.

N-(6-fluoro-1,2,3,4-tetrahydronaphthalen-1-yl)-4-methylbenzenesulfonamide (8)

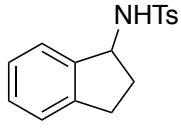


8

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes). Yield: 72 mg (0.20 mmol, 41%)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.33 (m, 2H), 6.96 – 6.92 (m, 1H), 6.79 – 6.74 (m, 1H), 6.73 (dd, *J* = 9.5, 2.7 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.43 (dd, *J* = 8.2, 4.7 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.68 – 2.61 (m, 1H), 2.46 (s, 3H), 1.84 – 1.76 (m, 3H), 1.74 – 1.68 (m, 1H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.05 (d, *J* = 246.8 Hz), 143.67, 139.96 (d, *J* = 7.8 Hz), 138.26, 131.52, 130.85 (d, *J* = 8.5 Hz), 129.97, 127.26, 115.36 (d, *J* = 20.7 Hz), 113.77 (d, *J* = 21.4 Hz), 51.52, 30.84, 29.20, 21.73, 19.02.
HRMS (ESI): *m/z* calcd for $[C_{17}H_{17}NO_2FS]^-$: 318.0964; found: 318.0966.

N-(2,3-dihydro-1H-inden-1-yl)-4-methylbenzenesulfonamide (10)

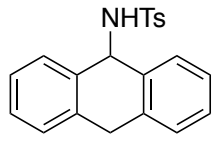


10

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes). Isolated as a inseparable 8:1 mixture with the corresponding imine. Yield: 66 mg (0.23 mmol, 46%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.23 – 7.15 (m, 2H), 7.13 (td, *J* = 7.2, 1.6 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 4.82 (q, *J* = 7.8 Hz, 1H), 4.67 (d, *J* = 9.0 Hz, 1H), 2.88 (ddd, *J* = 16.0, 8.7, 3.6 Hz, 1H), 2.73 (dt, *J* = 16.1, 8.2 Hz, 1H), 2.44 (s, 3H), 2.32 (dtd, *J* = 13.0, 7.8, 3.7 Hz, 1H), 1.74 (dtd, *J* = 13.1, 8.5, 7.3 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.46, 142.82, 141.93,138.18, 129.77, 128.30, 127.12, 126.86, 124.80, 124.03, 58.72, 34.78, 29.95, 21.54 ppm. Diagnostic imine chemical shifts: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 3.45 – 3.41 (m, 2H), 3.22 – 3.19 (m, 2H), 2.45 (s, 3H). NMR spectra are consistent with literature reports.[1]

N-(9,10-dihydroanthracen-9-yl)-4-methylbenzenesulfonamide (11)



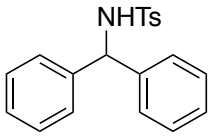
11

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes). Yield: 101 mg (0.29 mmol, 58%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.26 (s, 2H), 7.21 (td, *J* = 7.5, 1.5 Hz, 3H), 7.18 – 7.13 (m, 1H), 5.52

(d, *J* = 6.9 Hz, 1H), 4.79 (d, *J* = 6.9 Hz, 1H), 4.00 (d, *J* = 18.0 Hz, 1H), 3.83 (d, *J* = 18.0 Hz, 1H), 2.41 (s, 2H) ppm. **^{13}C NMR** (150 MHz, CDCl3) δ 143.16, 138.08, 136.76,135.83, 129.46, 127.67, 127.19, 126.97, 126.54, 56.23, 35.15, 21.49 ppm. NMR spectra are consistent with literature reports.[2]

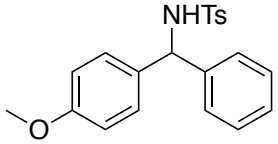
N-benzhydryl-4-methylbenzenesulfonamide (12)



12

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes).
Yield: 67 mg (0.2 mmol, 40%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 6.5 Hz, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.05 (m, 4H), 5.56 (d, *J* = 7.0 Hz, 1H), 5.07 (d, *J* = 7.1 Hz, 1H), 2.36 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.18, 140.47, 137.30,129.32,128.52, 127.56, 127.33, 127.17, 61.30, 21.45 ppm. NMR spectra are consistent with literature reports.[1]

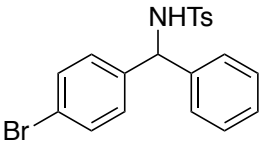
N-((4-methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (13)



13

Purified by silica gel flash chromatography (10-20% ethyl acetate in hexanes).
Yield: 73 mg (0.2 mmol, 40%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.17 (m, 3H), 7.16 – 7.11 (m, 2H), 7.11 – 7.06 (m, 2H), 7.02 – 6.95 (m, 2H), 6.76 – 6.68 (m, 2H), 5.51 (d, *J* = 6.8 Hz, 1H), 4.91 (d, *J* = 6.8 Hz, 1H), 3.75 (s, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.98, 143.12, 140.66, 137.35,132.69, 129.31, 128.58, 128.47, 127.47, 127.24, 127.19, 113.87, 60.79, 55.23, 21.45 ppm. NMR spectra are consistent with literature reports.[3]

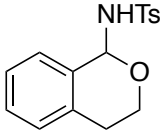
N-((4-bromophenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (14)



14

Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes).
Yield: 122 mg (0.3mmol, 59%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.35 – 7.31 (m, 2H), 7.23 (d, *J* = 5.1 Hz, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 5.2 Hz, 2H), 7.02 – 6.98 (m, 2H), 5.52 (d, *J* = 6.9 Hz, 1H), 4.96 (d, *J* = 6.8 Hz, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.48, 139.94, 139.39, 137.20,131.57,129.42, 129.09, 128.74, 127.92, 127.25, 127.17, 121.61, 60.80, 21.48 ppm. NMR spectra are consistent with literature reports.[3]

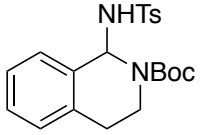
N-(isochroman-1-yl)-4-methylbenzenesulfonamide (15)



15

Purified by silica gel flash chromatography (2-15% acetone in hexanes).
Yield: 104 mg (0.34 mmol, 69%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 8.6 Hz, 1H), 5.41 (d, *J* = 8.6 Hz, 1H), 3.71 – 3.59 (m, 2H), 2.85 (ddd, *J* = 15.9, 9.7, 5.7 Hz, 1H), 2.61 (dt, *J* = 16.6, 3.8 Hz, 1H), 2.44 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.34, 138.73, 134.47, 132.77, 129.45, 128.80, 128.41, 127.19, 126.71, 126.44, 79.87, 58.73, 27.53, 21.55 ppm. NMR spectra are consistent with literature reports.[4]

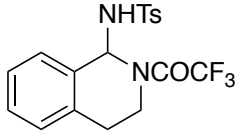
tert-butyl 1-((4-methylphenyl)sulfonamido)-3,4-dihydroisoquinoline-2(1H)-carboxylate (16)



16

Purified by silica gel flash chromatography (2-15% acetone in hexanes). Yield: 94 mg (.24 mmol, 47%)
Mixture of rotamers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 48.5, 7.9 Hz, 2H), 7.32 (dd, *J* = 10.8, 7.9 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.15 – 7.08 (m, 1H), 6.59 (t, *J* = 7.3 Hz, 1H), 5.22 (dd, *J* = 28.9, 7.0 Hz, 1H), 4.00 (ddd, *J* = 101.0, 13.5, 5.7 Hz, 1H), 3.24 – 2.95 (m, 1H), 2.94 – 2.78 (m, 1H), 2.68 – 2.62 (m, 1H), 2.45 (s, 3H), 1.41 (s, 9H) ppm. **^{13}C NMR** (201 MHz, $CDCl_3$) δ 153.67, 153.22, 143.69, 143.53, 143.23, 139.23, 138.72, 138.16, 135.35, 135.04, 134.44, 133.42, 129.83, 129.73, 129.54, 129.45, 129.10, 128.65, 128.45, 128.23, 127.55, 127.05, 126.95, 126.88, 126.80, 126.75, 126.58, 81.26, 80.48, 77.16, 63.32, 62.40, 37.42, 35.77, 28.60, 28.41, 28.29, 28.10, 27.63, 21.67 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{21}H_{26}N_2O_4S+H]^+$: 403.1692; found: 403.1682.

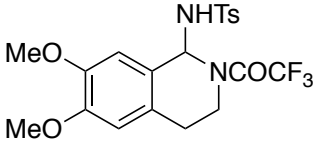
4-methyl-N-(2-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)benzenesulfonamide (17)



17

Purified by gradient elution on silica gel with acetone (8-20%) in hexanes. Yield: 159 mg (0.4 mmol, 80%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.13 – 7.04 (m, 2H), 6.75 (d, *J* = 6.6 Hz, 1H), 5.56 (d, *J* = 6.5 Hz, 1H), 3.97 – 3.81 (m, 1H), 3.65 (ddd, *J* = 14.4, 12.8, 4.2 Hz, 1H), 2.94 (ddd, *J* = 18.2, 12.9, 5.9 Hz, 1H), 2.80 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.44 (s, 3H) ppm. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -70.13 ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.75, 155.51, 144.27, 136.80, 133.56, 131.42, 129.78, 129.21, 129.19, 128.36, 127.57, 127.44, 116.99, 115.08, 77.16, 60.98, 38.50, 38.48, 28.70, 21.67 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{18}H_{17}F_3N_2O_3S+Na]^+$: 421.0810; found: 421.0818.

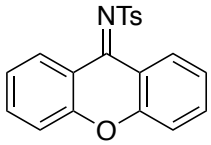
N-(6,7-dimethoxy-2-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-4-methylbenzenesulfonamide (19)



19

Purified by silca gel flash chromatography (1% methanol in dichloromethane). Yield: 178 mg (0.4 mmol, 80%)
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.41 – 7.38 (m, 1H), 6.80 – 6.76 (m, 1H), 6.59 (d, *J* = 6.1 Hz, 1H), 5.75 (d, *J* = 6.5 Hz, 1H), 3.93 (m, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.66 (ddd, *J* = 14.5, 12.9, 4.2 Hz, 1H), 2.95 (ddd, *J* = 16.4, 12.7, 5.8 Hz, 1H), 2.77 (ddd, *J* = 16.6, 4.6, 1.3 Hz, 1H), 2.52 (s, 3H) ppm. **^{13}C NMR** (201 MHz, $CDCl_3$) δ 155.54 (q, *J* = 37.5, 36.7 Hz), 149.81, 148.56, 144.30, 137.05, 129.77, 127.53, 125.90, 123.08, 116.03 (q, *J* = 288.3 Hz), 110.95, 110.07, 77.16, 60.86, 56.09, 56.08, 38.58, 38.56, 28.35, 21.66 ppm. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -70.06 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{20}H_{21}F_3N_2O_5S+H]^+$: 459.1202; found: 459.1193.

4-methyl-N-(9H-xanthen-9-ylidene)benzenesulfonamide (20)

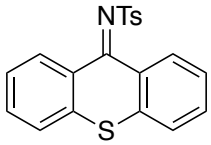


20

Purified by silica gel flash chromatography (20 % ethyl acetate in hexanes). Isolated as an inseparable 5.9:1 mixture with the corresponding amine. Yield: 132 mg (0.38 mmol, 76%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 8.3, 1.6 Hz, 2H), 8.02 – 7.98 (m, 2H), 7.74 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 2H), 7.50 (ddd, *J* = 8.4, 1.2, 0.4 Hz, 2H), 7.40 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 2H), 7.37 – 7.34 (m, 2H), 2.46 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.33, 154.79, 142.49, 141.02, 135.28, 129.57, 129.30, 126.36, 124.28, 119.31, 117.75, 21.35 ppm. Diagnostic amine chemical shifts: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.15 (ddt, *J* = 7.8, 1.7, 0.5 Hz, 2H), 7.08 (dd, *J* = 8.2, 1.2 Hz, 2H), 6.99 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 2H), 5.78 (d, *J* = 8.6 Hz, 1H), 4.92 (d, *J* = 8.6 Hz, 1H), 2.47 (s, 3H) ppm. NMR spectra are consistent with literature reports.[5,6]

4-methyl-N-(9H-thioxanthen-9-ylidene)benzenesulfonamide (21)



21

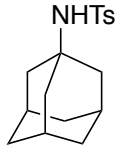
Purified by silica gel flash chromatography (20 % ethyl acetate in hexanes).
Yield: 158 mg (0.43 mmol, 87%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.53 (m, 4H), 7.46 (td, *J* = 7.5, 6.9, 1.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.53, 142.75, 140.24, 136.22, 131.81, 131.81, 131.35, 129.30, 129.12, 126.66, 126.36, 125.58, 21.50 ppm. NMR spectra are consistent with literature reports.[7]

N-((1R,2R,4S)-bicyclo[2.2.1]heptan-2-yl)-4-methylbenzenesulfonamide (22)

22

Purified by silica gel flash chromatography (5% ethyl acetate in hexanes).
Yield: 74 mg (0.28 mmol, 56%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.49 (d, *J* = 7.2 Hz, 1H), 3.15 – 3.07 (m, 1H), 2.41 (s, 3H), 2.17 (d, *J* = 4.4 Hz, 1H), 2.08 (d, *J* = 4.3 Hz, 1H), 1.60 – 1.56 (m, 1H), 1.44 – 1.34 (m, 2H), 1.30 (dp, *J* = 10.2, 2.0 Hz, 1H), 1.16 – 1.08 (m, 2H), 1.05 – 0.97 (m, 2H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.17, 137.89, 129.62,127.05, 56.63, 42.45, 40.76, 35.55, 35.14, 27.97, 26.29, 21.50 ppm. NMR spectra are consistent with literature reports.[7]

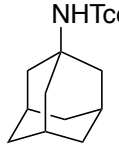
N-((3s,5s,7s)-adamantan-1-yl)-4-methylbenzenesulfonamide (23)



23

Purified by silica gel flash chromatography (5% EtOAc in hexanes).
Yield: 108 mg (0.36 mmol, 71%)
^{1}H NMR (600 MHz, CDCl3) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 4.38 (s, 1H), 2.41 (s, 3H), 2.02 – 1.96 (m, 3H), 1.77 (d, *J* = 2.9 Hz, 6H), 1.60 – 1.53 (m, 6H) ppm. **^{13}C NMR** (150 MHz, CDCl3) δ 142.68, 141.05, 129.39,126.89, 55.05, 43.06, 35.82, 29.45, 21.48 ppm. NMR spectra are consistent with literature reports.[8]

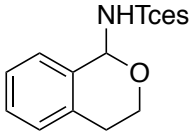
2,2,2-trichloroethyl ((3s,5s,7s)-adamantan-1-yl)sulfamate (24)



24

Purified on silica gel by gradient elution with 3-8% acetone in hexanes.
Yield: 20 mg (0.055 mmol, 55%) on 0.1 mmol scale.
^{1}H NMR (598 MHz, $CDCl_3$) δ 4.62 (s, 2H), 4.51 (br s, 1H), 2.14 (d, *J* = 3.3 Hz, 3H), 1.99 (d, *J* = 2.9 Hz, 6H), 1.69 – 1.65 (m, 6H) ppm. ^{13}C NMR (201 MHz, $CDCl_3$) δ 93.54, 78.15, 56.17, 42.54, 35.80, 29.56 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{12}H_{17}NO_3SCl_3]^-$: 359.9995; found: 359.9990.

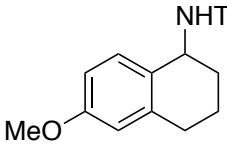
N-(isochroman-1-yl)-4-methylbenzenesulfonamide (25)



25

Purified on silica gel by gradient elution with 3-10% acetone in hexanes.
Yield: 17.3 mg (0.05 mmol, 50%) on 0.1 mmol scale.
^{1}H NMR (598 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 7.18 – 7.15 (m, 1H), 6.11 (s, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 10.9 Hz, 1H), 4.06 – 4.02 (m, 2H), 2.97 (ddd, *J* = 15.6, 8.9, 6.1 Hz, 1H), 2.77 (dt, *J* = 16.6, 3.9 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 134.77, 131.70, 129.16, 129.12, 127.20, 126.98, 93.66, 80.73, 78.69, 77.16, 59.83, 27.74 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{11}H_{11}NO_4SCl_3]^-$: 357.9474; found: 357.9481.

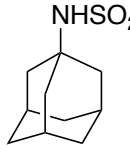
2,2,2-trichloroethyl (6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate (26)



26

Purified on silica gel by gradient elution with 10-20% ethyl acetate in hexanes.
Yield: 50 mg (0.13 mmol, 53%) on 0.25 mmol scale.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 4.74 (dd, *J* = 8.6, 4.1 Hz, 2H), 4.67 (d, *J* = 4.2 Hz, 2H), 3.77 (s, 3H), 2.85 – 2.63 (m, 2H), 2.17 – 1.98 (m, 2H), 1.92 – 1.78 (m, 2H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.22, 139.07, 130.54, 126.58, 113.60, 112.97, 93.59, 78.03, 55.25, 53.04, 30.30, 29.16, 18.73 ppm. NMR spectra are consistent with literature reports.[9]

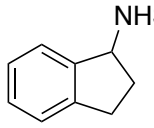
N-((3s,5s,7s)-adamantan-1-yl)-4-methylbenzenesulfonamide (27)



27

Purified on silica gel by gradient elution with 2-15% acetone in hexanes.
Yield: 16.7 mg (0.057 mmol, 57%) on 0.1 mmol scale.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.55 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 4.59 (br s, 1H), 2.00 (t, *J* = 3.4 Hz, 3H), 1.79 (d, *J* = 2.9 Hz, 6H), 1.63 – 1.53 (m, 6H) ppm. **^{13}C NMR** (201 MHz, CDCl3)) δ 144.11, 132.21, 128.96, 127.01, 126.96, 77.16, 55.33, 43.21, 35.96, 29.61 ppm. NMR spectra are consistent with literature reports.[10]

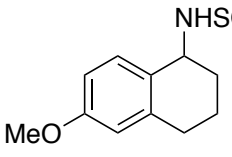
N-(2,3-dihydro-1H-inden-1-yl)benzenesulfonamide (28)



28

Purified on silica gel by gradient elution with 5-15% ethyl acetate in hexanes.
Isolated as an inseparable 8:1 mixture with the corresponding imine.Yield: 30 mg, (0.11 mmol, 44%) on 0.25 mmol scale.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.62 – 7.59 (m, 1H), 7.57 – 7.52 (m, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 4.85 (q, *J* = 7.7 Hz, 1H), 4.64 (d, *J* = 9.1 Hz, 1H), 2.90 (ddd, *J* = 15.9, 8.8, 3.7 Hz, 1H), 2.74 (dt, *J* = 16.1, 8.1 Hz, 1H), 2.34 (dtd, *J* = 13.0, 7.7, 3.8 Hz, 1H), 1.76 (dq, *J* = 13.1, 8.2 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.08, 141.06, 140.42, 131.93, 128.43, 127.60, 126.29, 126.13, 124.07, 123.23, 58.04, 34.01, 29.19 ppm. Diagnostic chemical shifts for the imine: **^{1}H NMR** (600 MHz, CDCl3) δ 8.08 – 8.05 (m, 2H), 3.48 – 3.44 (m, 2H), 3.24 – 3.21 (m, 2H) ppm. NMR spectra are consistent with literature reports.[10]

N-(6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide (29*)*



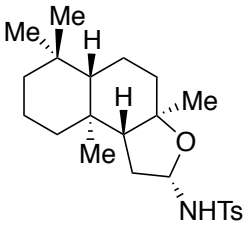
29

Purified on silica gel by gradient elution with 10-20% ethyl acetate in hexanes.

Yield: 43 mg, (0.13 mmol, 54%) on 0.25 mmol scale.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.62 – 7.58 (m, 1H), 7.56 – 7.53 (m, 2H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.59 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.54 (d, *J* = 2.7 Hz, 1H), 4.59 (d, *J* = 7.6 Hz, 1H), 4.43 – 4.40 (m, 1H), 3.73 (s, 3H), 2.71 (dt, *J* = 17.2, 5.3 Hz, 1H), 2.65 – 2.59 (m, 1H), 1.85 – 1.82 (m, 1H), 1.80 – 1.75 (m, 2H), 1.70 (ddd, *J* = 10.0, 4.9, 2.9 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.85, 141.15, 138.95, 132.60, 129.99, 129.15, 127.64, 127.05, 113.41, 112.74, 55.18, 51.52, 30.88, 29.20, 18.85 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{17}H_{18}NO_3S]^-$: 316.1007; found: 316.0999.

4-methyl-N-((3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan-2-yl)benzenesulfonamide (30)



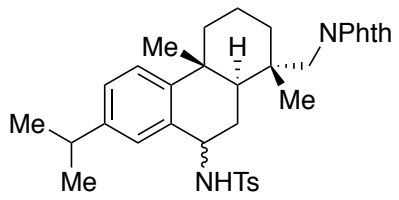
30
dr = 1.5:1

Purified on silica gel by gradient elution with acetone (2-15%) in hexanes.

Yield: 190.5 mg (0.469 mmol, 47%) as an inseparable 1.5:1 mixture of diastereomers (major diastereomer shown) on a 1.0 mmol scale.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 5.31 – 5.24 (m, 1H), 5.19 (d, *J* = 9.4 Hz, 1H), 2.41 (s, 3H), 1.76 (dt, *J* = 11.7, 3.2 Hz, 1H), 1.72 – 1.51 (m, 3H), 1.45 – 1.35 (m, 3H), 1.32 – 1.09 (m, 4H), 1.01 (s, 3H), 0.98 – 0.85 (m, 3H), 0.83 (s, 3H), 0.78 (s, 3H) ppm. **^{13}C NMR** (201 MHz, $CDCl_3$) δ 143.22, 143.17, 138.69, 138.61, 129.53, 129.46, 127.33, 127.23, 84.13, 83.09, 82.74, 81.76, 77.16, 60.11, 58.16, 57.20, 57.00, 42.42, 42.41, 39.98, 39.91, 39.84, 39.78, 36.12, 33.57, 33.54, 33.14, 31.44, 31.39, 23.91, 23.89, 22.16, 21.67, 21.65, 21.14, 20.65, 20.47, 18.38, 15.31, 15.14 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{23}H_{35}NO_3S+Na]^+$: 428.2235; found: 428.2240.

N-((1S,4aR,10aS)-1-((1,3-dioxoisoindolin-2-yl)methyl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-9-yl)-4-methylbenzenesulfonamide (31)



31
dr = 1:1

Purified on silica gel by gradient elution with 20% EtOAc in hexanes.

Yield: 105 mg, (0.18 mmol, 36%) as an inseparable 1:1 mixture of diastereomers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.83 (dddd, *J* = 14.7, 11.2, 8.8, 5.8 Hz, 5H), 7.71 (ddt, *J* = 8.9, 6.0, 3.6 Hz, 5H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 3H), 7.10 – 6.99 (m, 3H), 6.96 (d, *J* = 12.9 Hz, 1H), 6.80 (s, 1H), 5.81 (d, *J* = 7.9 Hz, 1H), 4.79 (q, *J* = 8.9 Hz, 1H), 4.65 (d, *J* = 8.8 Hz, 1H), 4.58 (t, *J* = 6.3 Hz, 1H), 3.55 (d, *J* = 13.9 Hz, 1H), 3.37 – 3.32 (m, 1H), 3.31 – 3.23 (m, 2H), 2.76 (p, *J* = 7.0 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.43 (d, *J* = 4.8 Hz, 3H), 2.37 (s, 3H), 2.30 (d, *J* = 7.8 Hz, 1H), 2.22 – 2.13 (m, 2H), 1.94 – 1.91 (m, 1H), 1.69 – 1.63 (m, 2H), 1.43 (q, *J* = 12.4, 11.1 Hz, 4H), 1.36 (d, *J* = 7.4 Hz, 2H), 1.24 (d, *J* = 2.6 Hz, 3H), 1.20 (s, 3H), 1.14 (dd, *J* = 7.0, 4.6 Hz, 6H), 1.09 – 1.04 (m, 6H), 0.95 (s, 3H), 0.92 – 0.89 (m, 3H), 0.82 (t, *J* = 3.8 Hz, 2H), 0.78 – 0.75 (m, 1H), 0.70 (dd, *J* = 6.5, 3.8 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.37, 169.15, 147.32, 146.49, 143.28, 143.15, 138.67, 138.38, 134.30, 134.07, 133.88, 133.36, 131.94,

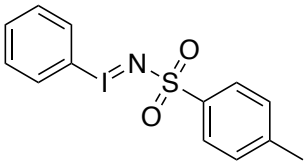
131.78, 129.70, 129.64, 129.49, 128.05, 127.51, 127.46, 126.14, 125.86, 125.82, 123.93, 123.58, 123.44, 123.37, 123.29, 53.97, 51.20, 48.37, 48.32, 44.16, 41.43, 39.00, 38.82, 37.88, 37.72, 37.59, 37.41, 36.09, 33.41, 33.40, 29.67, 29.55, 26.81, 26.24, 24.94, 23.90, 23.64, 23.52, 21.43, 19.20, 19.06, 18.19, 18.17 ppm. **HRMS** (ESI): *m/z* calcd for $[C_{35}H_{39}N_2O_2S]^-$: 583.2631; found: 583.2630.

III. Synthesis of Iminium Salts

Iminium salts **5a-5g** were synthesized according to previously reported methods.[11]

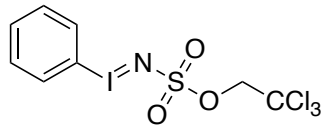
IV. Synthesis of Iminoiodinanes

[N-(p-tolenesulfonyl)imino]phenyliodinane: p-Toluenesulfonamide (2.8 g, 16.4 mmol) and potassium hydroxide (2.32 g, 41 mmol) were dissolved in 60 mL of methanol and cooled to -10 °C. To this mixture, (diacetoxy)iodosobenzene (5.3 g, 16.5 mmol) was added slowly. The resulting mixture was stirred 30 minutes at -10 °C then 3 hours at room temperature at which time 100 mL ice cold water was added and the mixture was cooled to 0 °C until a fine white precipitate had formed. The precipitate was collected by filtration, washed with cold methanol (20 mL) then ethyl acetate (100 mL) to yield the title compound as fine, pale, yellow crystals: 4.4 g (12.21 mmol, 74%).



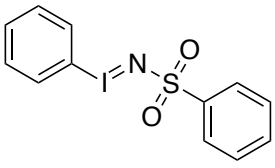
^{1}H NMR (598 MHz, DMSO-d_6) δ 7.69 (dd, J = 8.4, 1.1 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.29 (m, 2H), 7.06 (dd, J = 8.5, 0.7 Hz, 2H), 2.27 (s, 3H) ppm. NMR spectra are consistent with literature reports.[12]

[N-(2,2,2-trichloroethoxysulfonyl) imino]-phenyliodinane: 2,2,2-trichloroethylsulfamate (3.66 g, 16.5 mmol) and potassium hydroxide (2.32 g, 41 mmol) were dissolved in 60 mL of methanol and cooled to -10˚C. To this mixture, (diacetoxy)iodosobenzene (5.3 g, 16.5 mmol) was added slowly. The resulting mixture was stirred 30 minutes at -10˚C then 3 hours at room temperature at which time 100 mL cold water was added and the mixture was cooled to 0˚C. Stirring was continued until a fine white precipitate had formed. The precipitate was collected by filtration, washed with cold methanol (20 mL) then ethyl acetate (100 mL) to yield the title compound as fine, pale, yellow crystals: 4.1 g (9.6 mmol, 60%).



^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10 (dd, J = 8.3, 1.2 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H), 4.22 (s, 2H) ppm. NMR spectra are consistent with literature reports.[9]

[N-(benzenesulfonyl)imino]phenyliodinane: Benzenesulfonamide (2.6 g, 16.5 mmol) and potassium hydroxide (2.32 g, 41 mmol) were dissolved in 60 mL of methanol and cooled to -10˚C. To this mixture, (diacetoxy)iodosobenzene (5.3 g, 16.5 mmol) was added slowly. The resulting mixture was stirred 30 minutes at -10˚C then 3 hours at room temperature at which time 100 mL ice cold water was added and the mixture was cooled to 0˚C until a fine white precipitate had formed. The precipitate was



collected by filtration, washed with cold methanol (20 mL) then ethyl acetate (100 mL) to yield the title compound as fine, pale, yellow crystals: 3.0 g (8.4 mmol, 51%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 (dd, J = 8.3, 1.2 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.47 – 7.43 (m, 1H), 7.37 – 7.32 (m, 1H), 7.32 – 7.25 (m, 3H), 7.19 (dd, J = 8.2, 7.5 Hz, 1H) ppm. NMR spectra are consistent with literature reports.[13]

V. Mechanistic Experiments

V(a). Kinetic Isotope Effect Determination

Isochroman (13.6 µL, 0.11 mmol) and Isochroman-1,1-d_2 (13.6 µL, 0.11 mmol) were combined with N-(p-toleunesulfonyl)phenyliminoiodinane (37.3 mg, 0.1 mmol) and iminium **1a** (6.6 mg, 0.02 mmol) in anhydrous DCM under N_2. The reaction was stirred 24 hours at room temperature before being filtered through silica with EtOAc. Ratio of H:D was determined by ^{1}H NMR. Reactions were performed in triplicate.

V(b). LCMS Detection of Diaziridinium

In a nitrogen glovebox at room temperature, [N-(p-tolylsulfonyl)imino]phenyliodinane (373 mg, 1 mmol, 2 equiv) and iminium **5a** (33 mg, 0.1 mmol, 0.2 equiv) were combined in a vial. Anhydrous dichloromethane (2 mL) was then added and the reaction mixture was stirred at room temperature for 20 hours. The reaction mixture was then filtered through a silica gel plug, eluting with EtOAc. After removal of the solvent under reduced pressure, the crude reaction mixture was analyzed by reverse phase ESI-LCMS using positive ionization mode. The mass spectrum of the major peak was evaluated and a parent ion peak (m/z = 411) and major fragments [(M-CH_3+H)$^+$ and (M-CH_3-F)$^+$] consistent with the presence of diaziridinium **37** were observed (Figure S1).

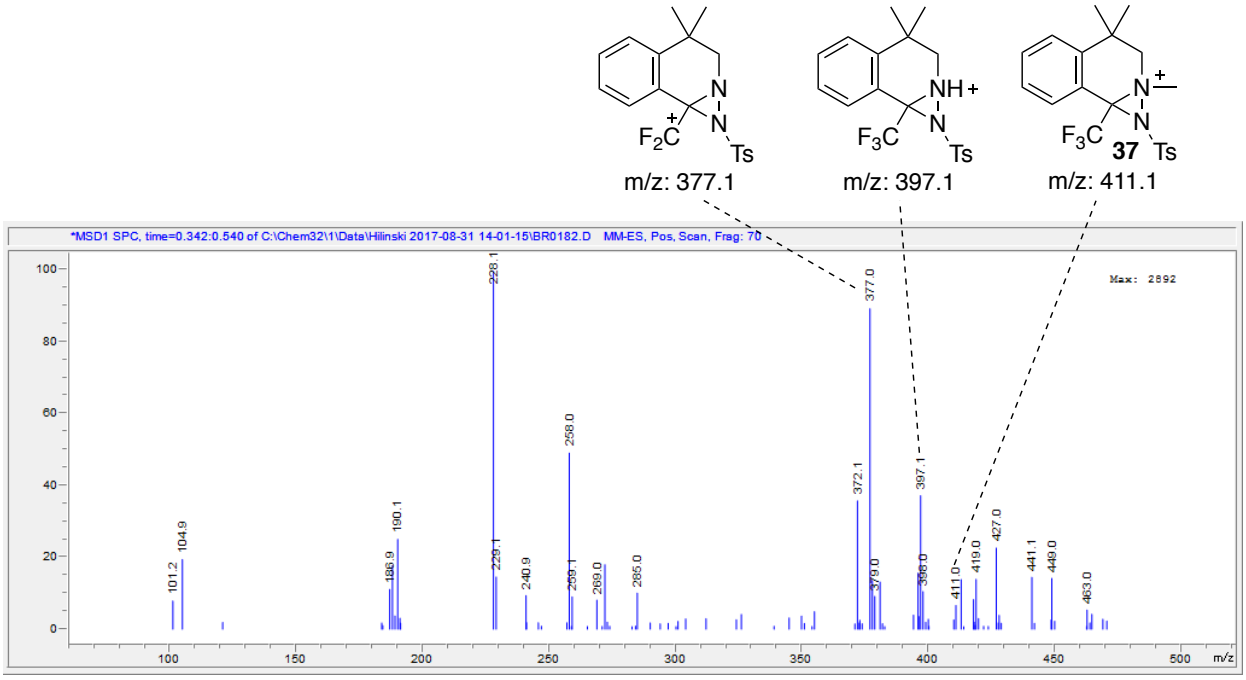


Figure S1. Mass spectrum of the mixture produced from the reaction of **5a** with PhINTs.

V(c). Representative procedure for Hammett Correlation Experienment

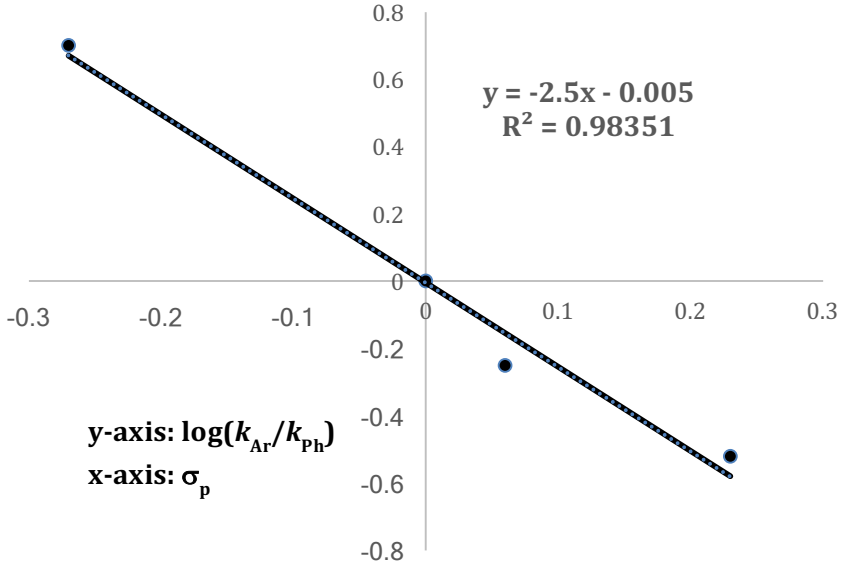
In a nitrogen glovebox at room temperature, the substrate 1,2,3,4-tetrahydronaphthalene (262 mg, 2 mmol, 10 equiv.) and 6-substituted 1,2,3,4-tetrahydronaphthalene (2 mmol, 10 equiv.), [N-(p-tolylsulfonyl)imino]phenyliodinane (75 mg, 0.2 mmol, 1 equiv.) and iminium **5a** (13 mg, 0.04 mmol, 0.2 equiv.) were combined in a 20 mL black cap vial equipped with a stir bar. Anhydrous dichloromethane (0.4 mL) was then added and the reactions mixture was stirred at room temperature in the glovebox under positive pressure of nitrogen, and stirred at room temperature for 20 hours. The reaction mixture was then filtered through a silica gel plug, eluting with EtOAc. After removal of the solvent under reduced pressure, the ratio of products in the crude reaction mixture was determined by gas chromatography compared to an authentic standard.

Hammett plots:

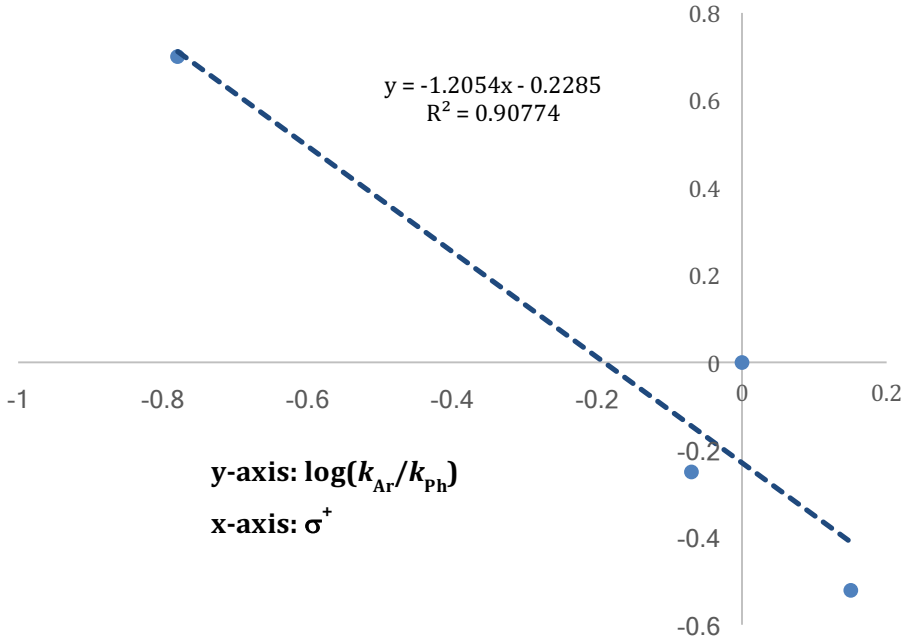
For Ar = 6-R-tetralin (*para* to site of amination)

R	σ_p	σ^+	$\sigma^\bullet$	product ratio Ar/tetralin
MeO	-0.27	-0.78	+0.23	5:1
F	+0.06	-0.07	-0.02	1:1.8
Br	+0.23	+0.15	-0.52	1:3.3

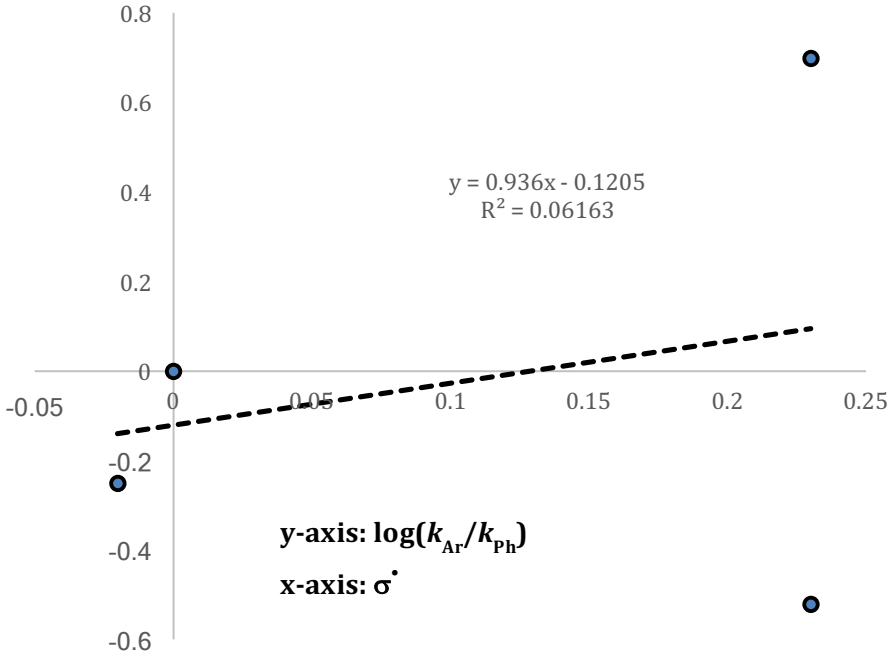
Hammett plot fit against σ_p values



Hammett plot fit against σ^+ values



Hammett plot fit against $\sigma^\cdot$ values



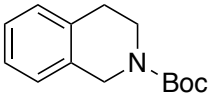
V(d). Experimental procedure for aziridination reaction of *trans*-stillbene

In a nitrogen glovebox at room temperature [N-(p-tolylsulfonyl)imino]phenyliodinane (75 mg, 0.2 mmol, 1 equiv.) and iminium **5a** (13 mg, 0.04 mmol, 0.2 equiv.) were combined in a 25 mL

schlenk flask equipped with a stir bar. Anhydrous dichloromethane (0.4 mL) was then added and the flask was removed from the glove box and the flask was transferred to the ice bath under positive pressure of nitrogen. The substrate *trans*-stillbene (36 mg, 0.2 mmol, 1 equiv.) was added to the schlenk flask using microliter syringe. The reaction mixture was stirred at 0 ^{o}C for 1 h and was transferred at -4 ^{o}C. The reaction was further stirred at -4 ^{o}C for 20 h. The reaction mixture was then filtered through a silica gel plug, eluting with EtOAc. After removal of the solvent under reduced pressure, the crude reaction mixture was then purified by flash chromatography using 20 % EtOAc/Hexane to provide aziridine **35** (36 mg, 51%) as a 10:1 mixture with the N-tosyl imine derived from 2,2-diphenylacetaldehyde. Spectral data matched literature values.

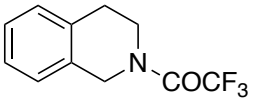
VI. Synthesis of Substrates

N-tert-butylcarbonyl-1,2,3,4-tetrahydro-5,6-dimethoxyisoquinoline



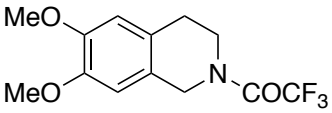
Prepared according to previously reported procedures. [14]

N-trifluoroacetyl-1,2,3,4-tetrahydroisoquinoline



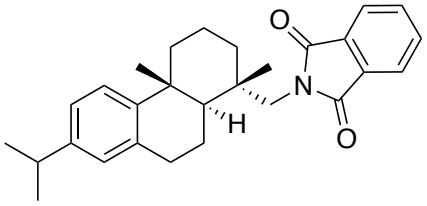
Prepared according to previously reported procedures. [15]

N-trifluoroacetyl-1,2,3,4-tetrahydro-5,6-dimethoxyisoquinoline



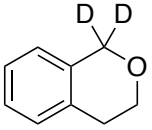
Prepared according to previously reported procedures.[16]

(+)-(N-phthaloyl)dehydroabietylamine



Prepared according to previously reported procedures. [17]

isochroman-1,1-d2 *– for KIE experiments*[18]



Prepared according to previously reported procedures.[18]

VII. References

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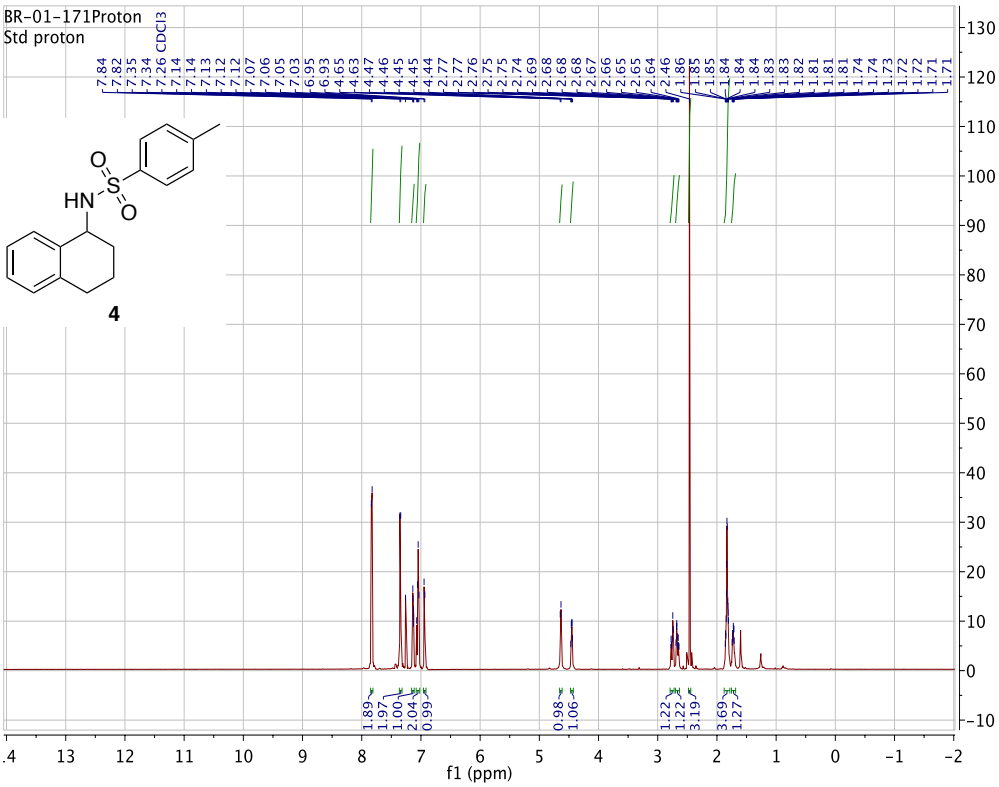
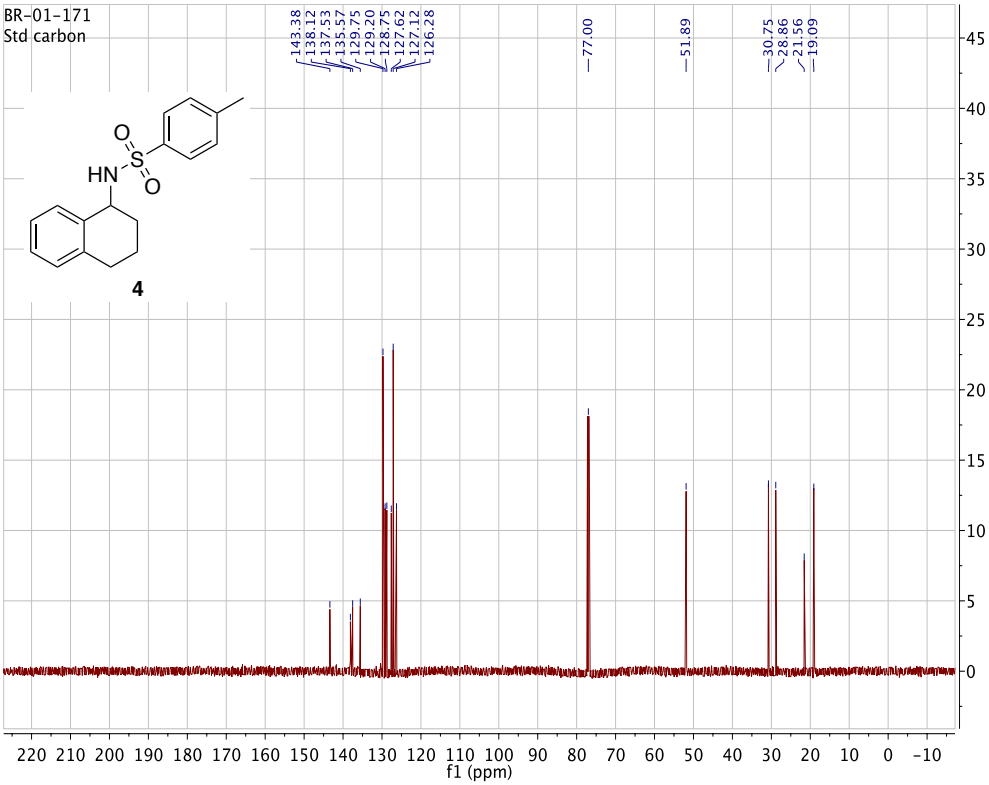
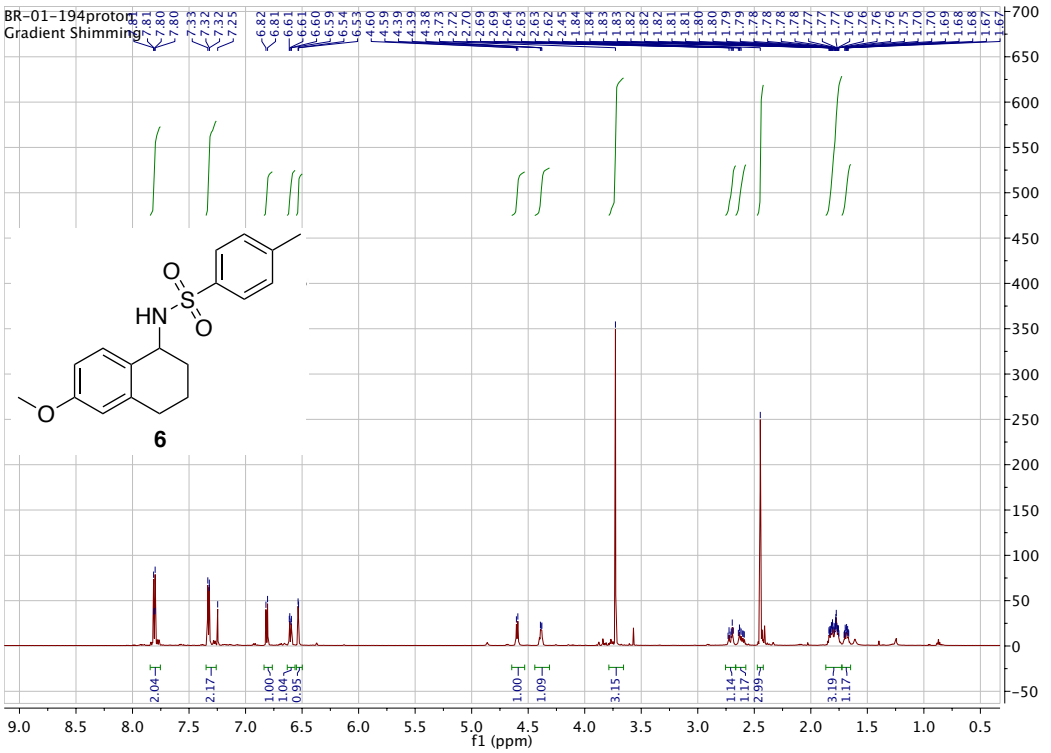
VIII. NMR Spectra



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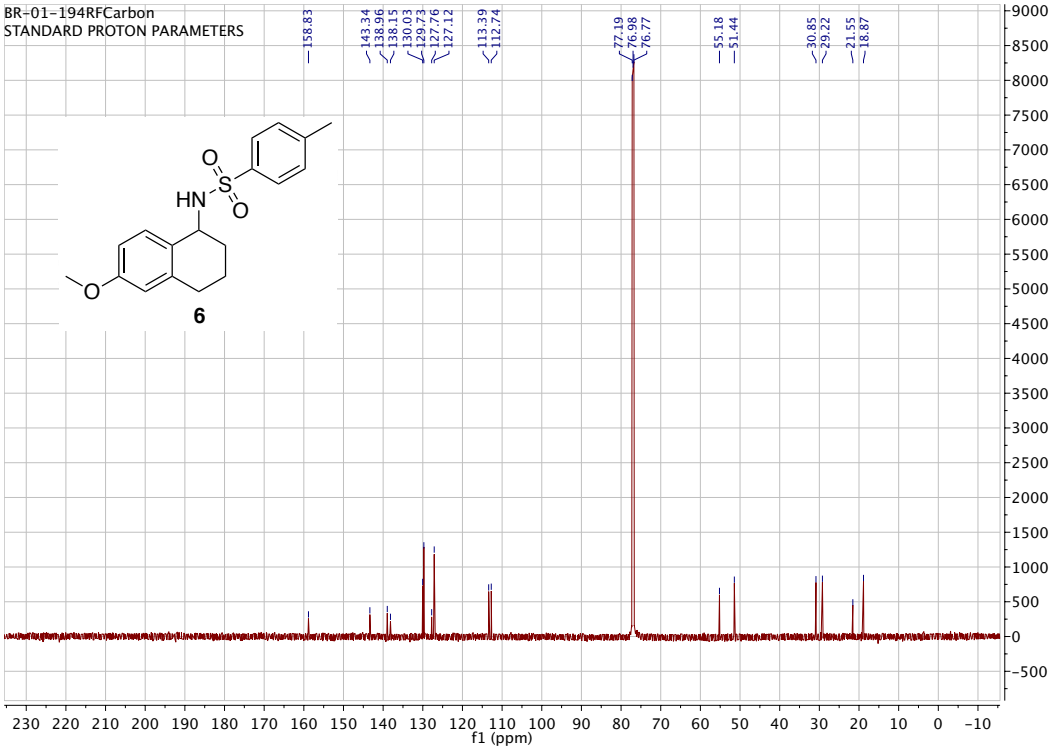
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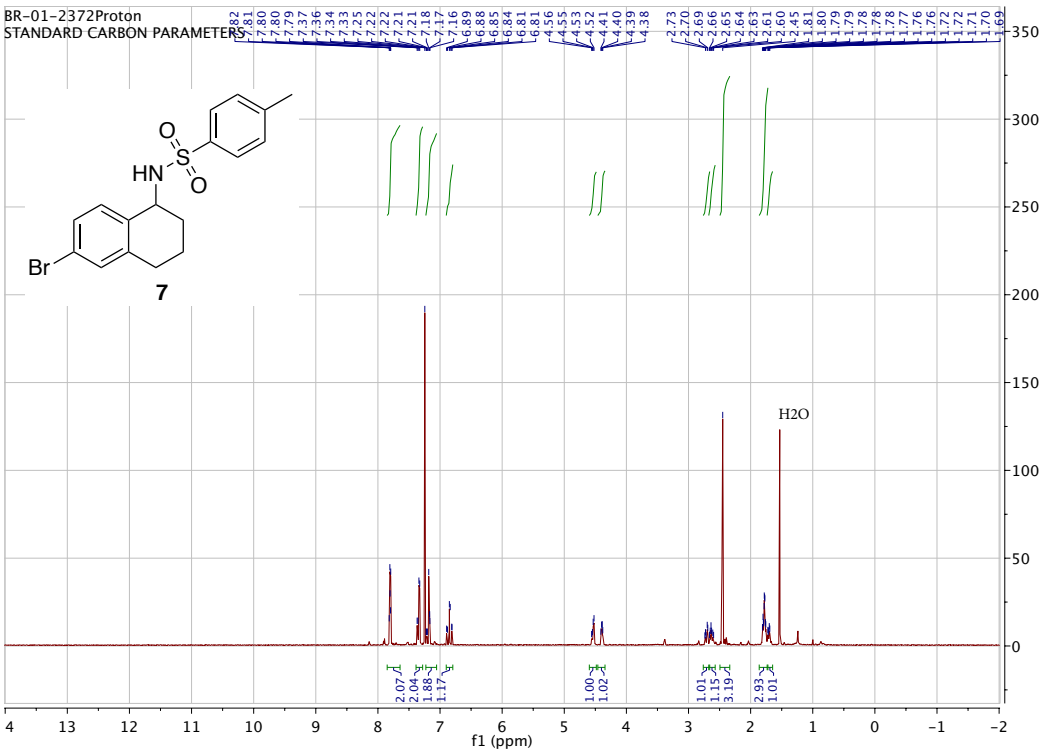
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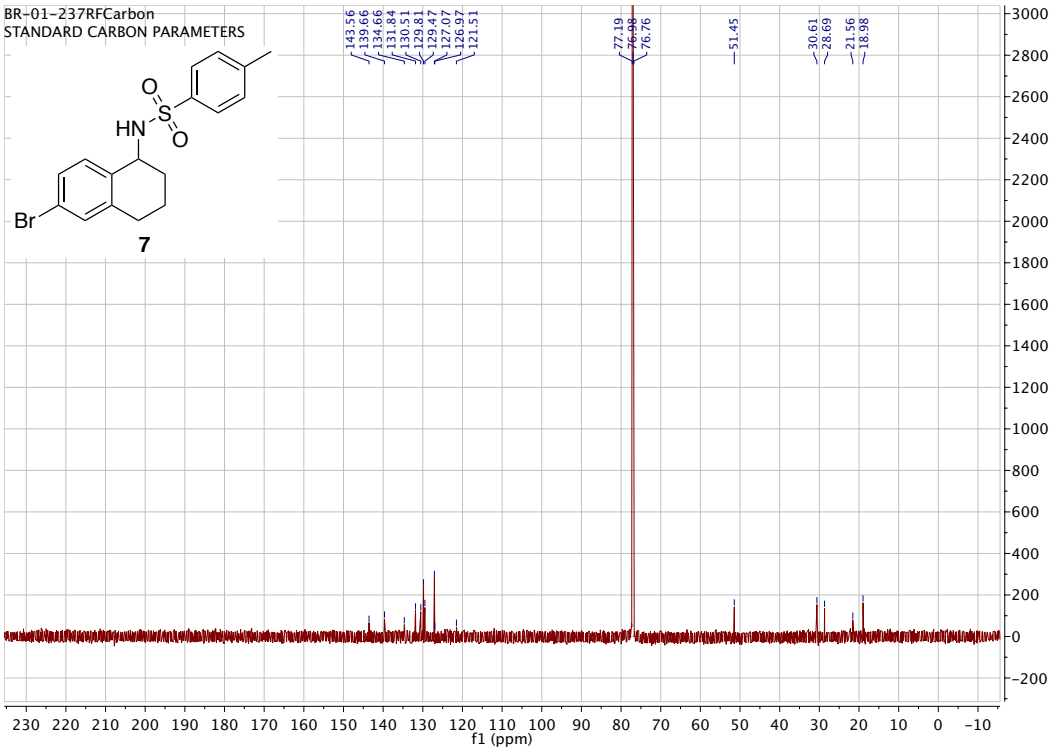
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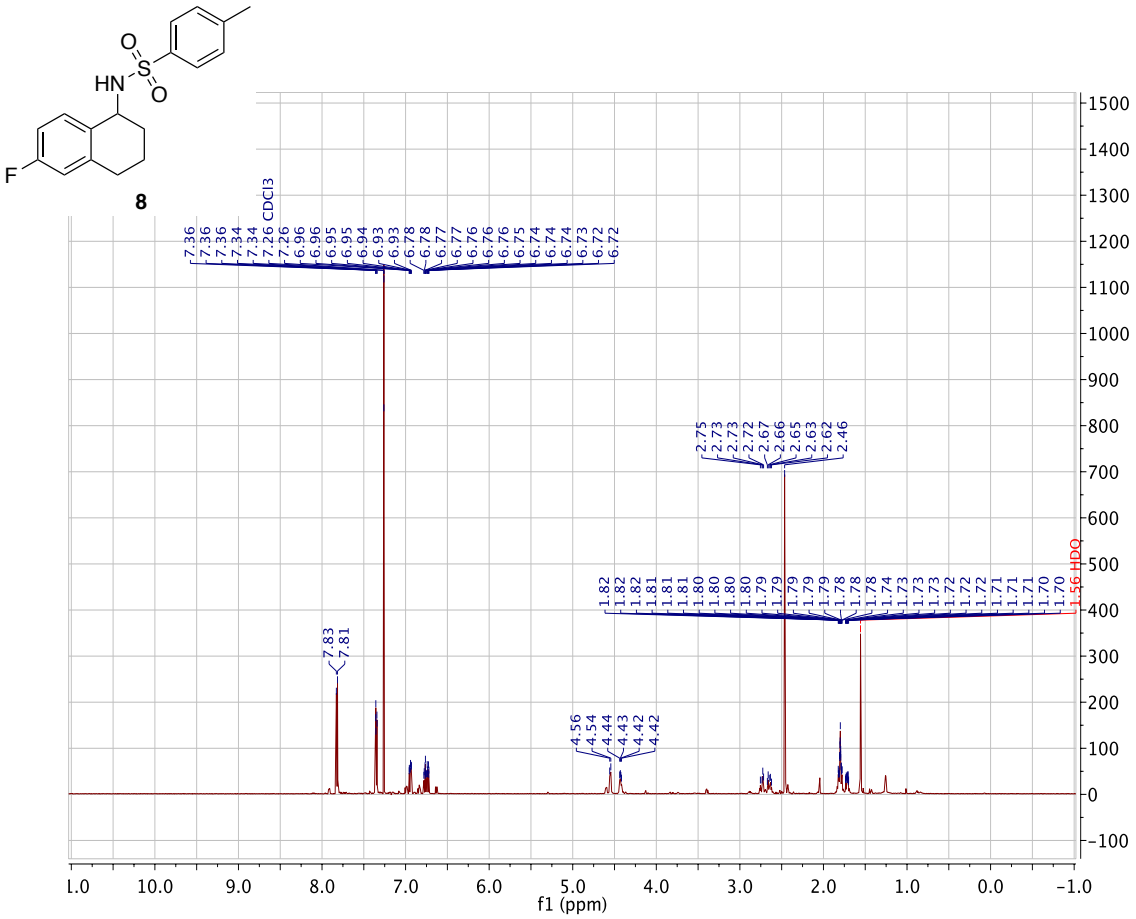
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6.75
6.74
6.74
6.74
6.73
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6.72
7.83
7.81
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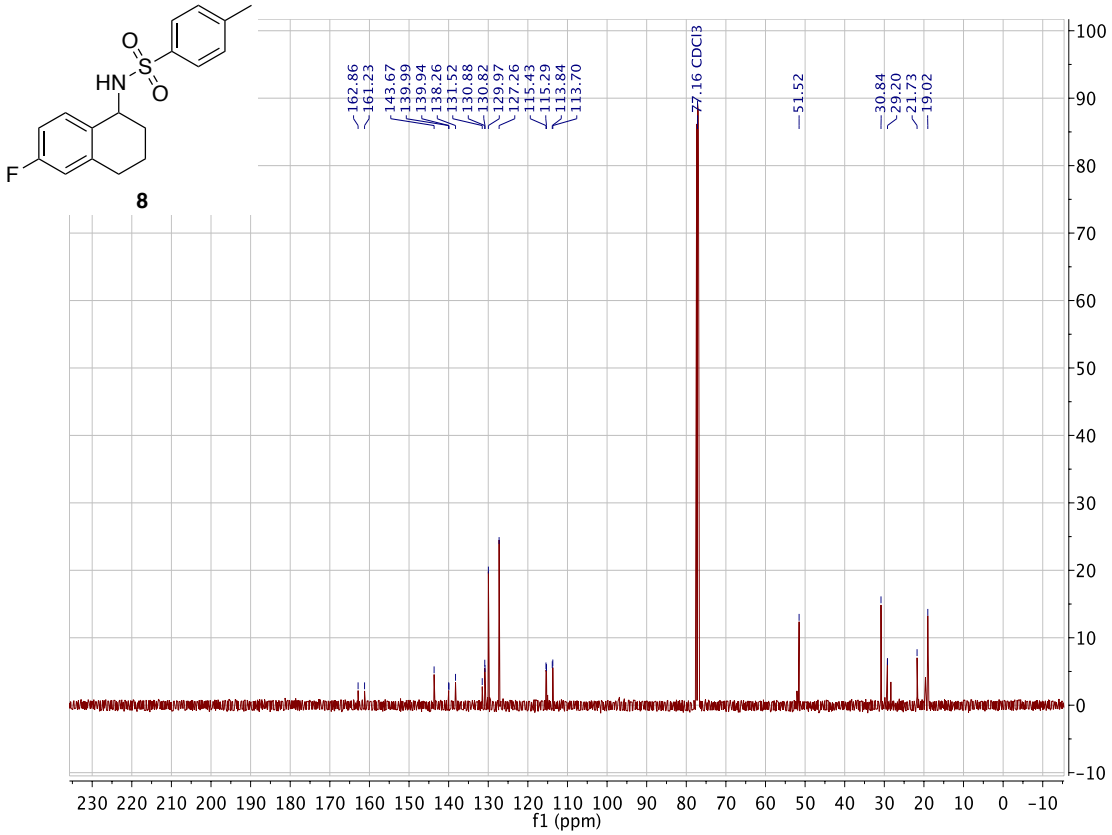
f1 (ppm)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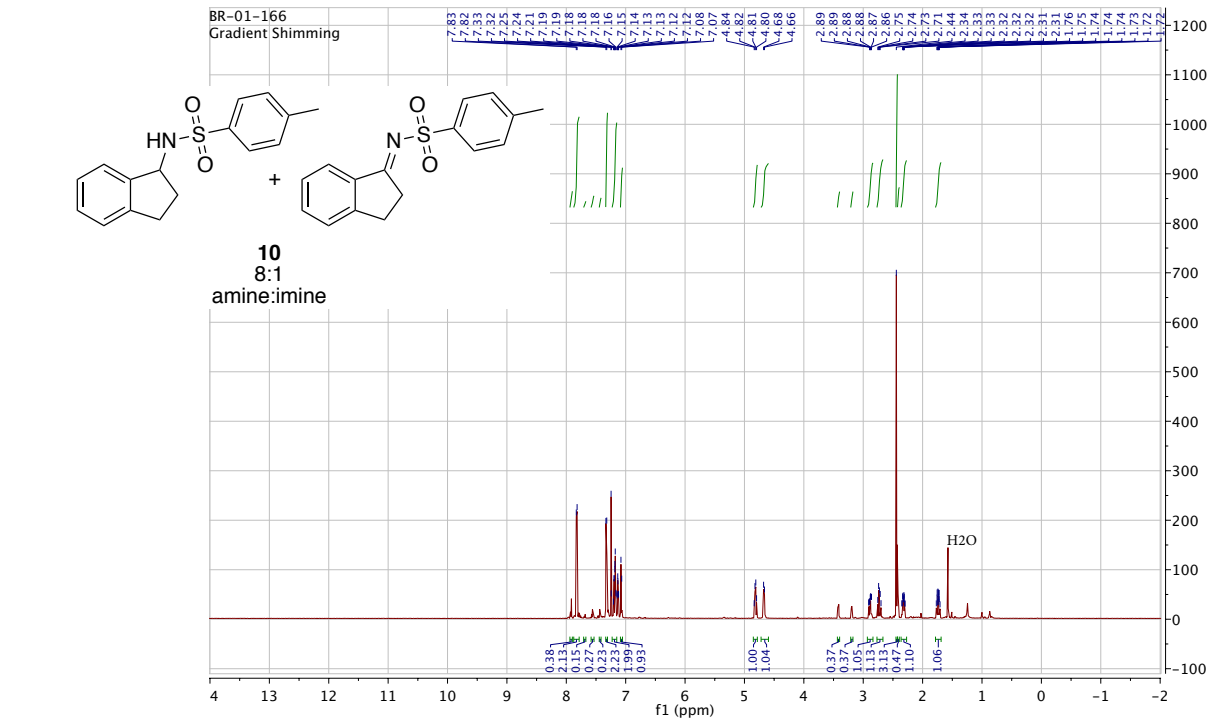
f1 (ppm)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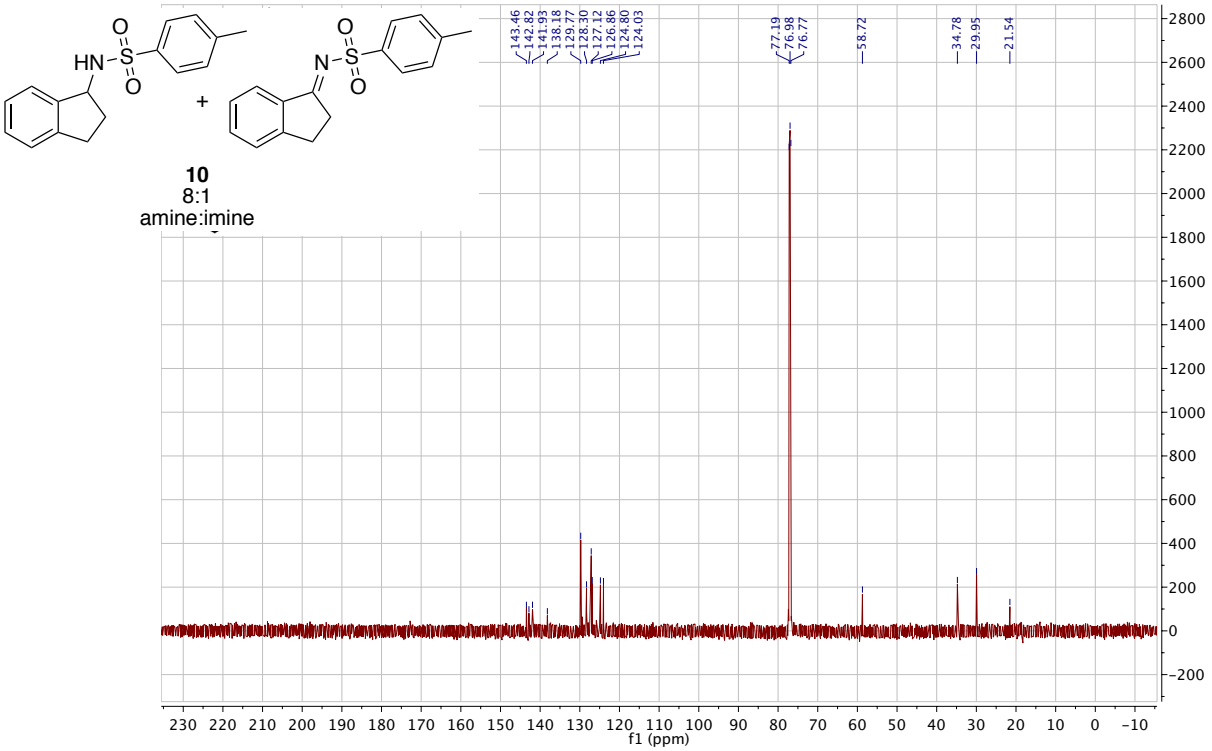
f1 (ppm)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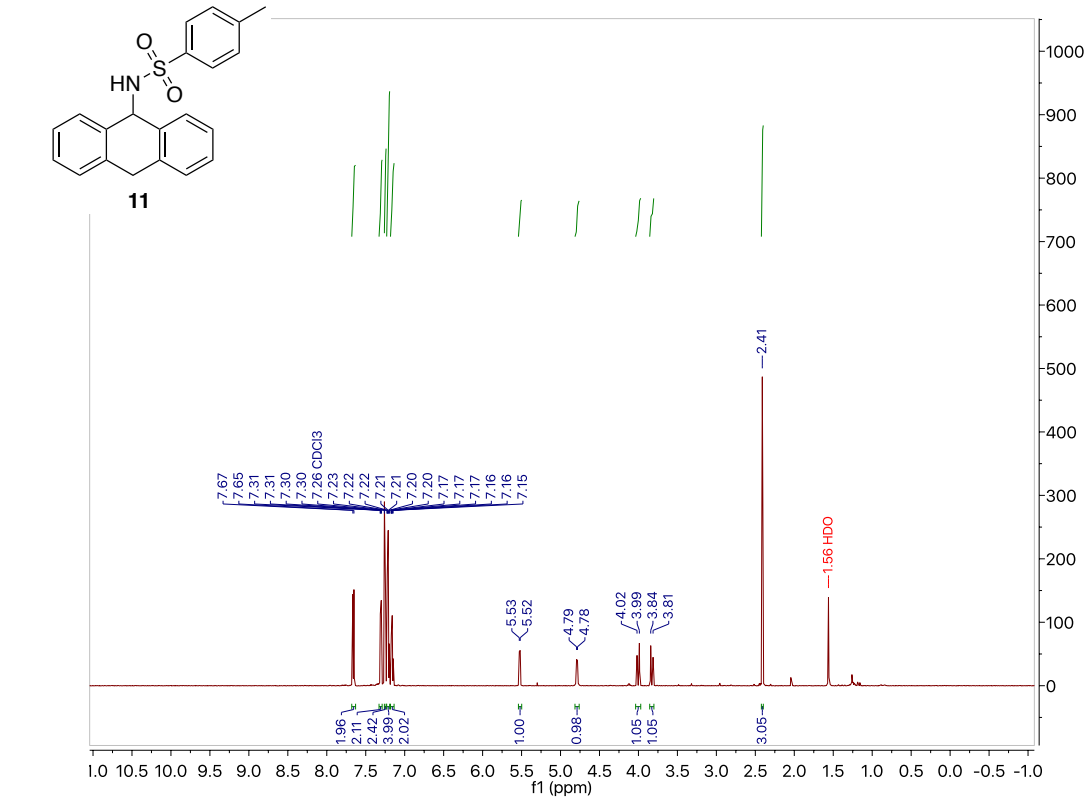
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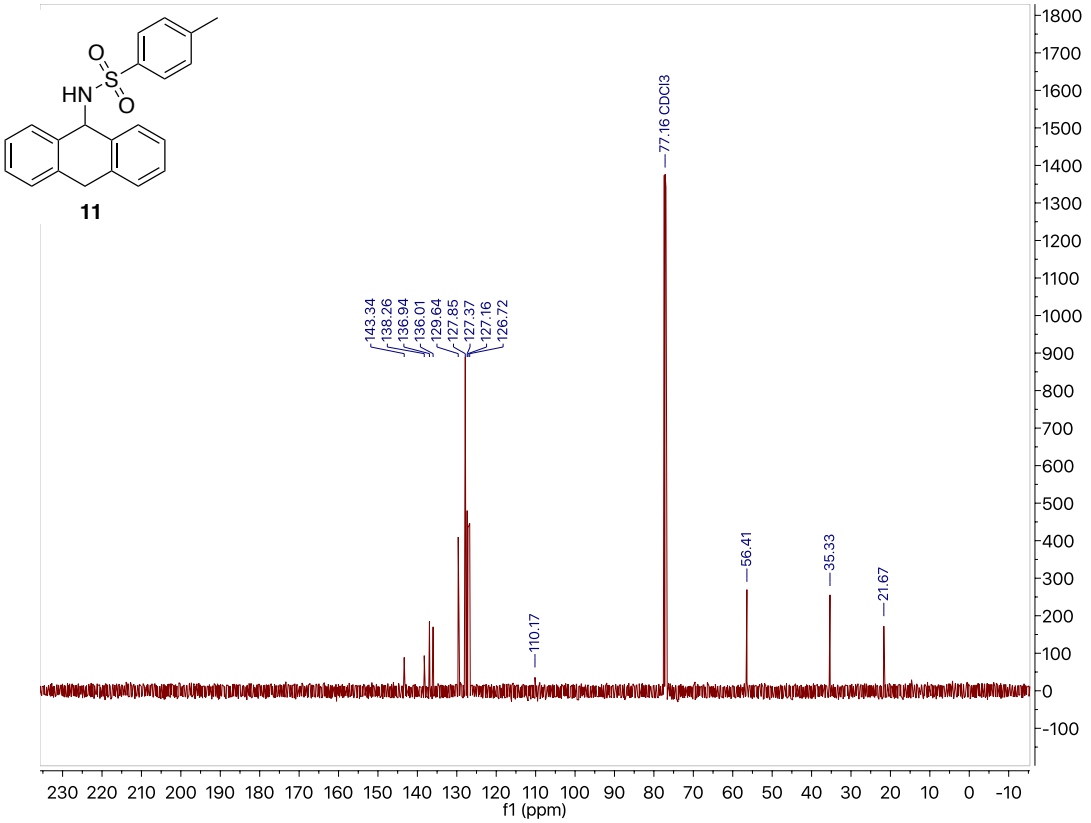
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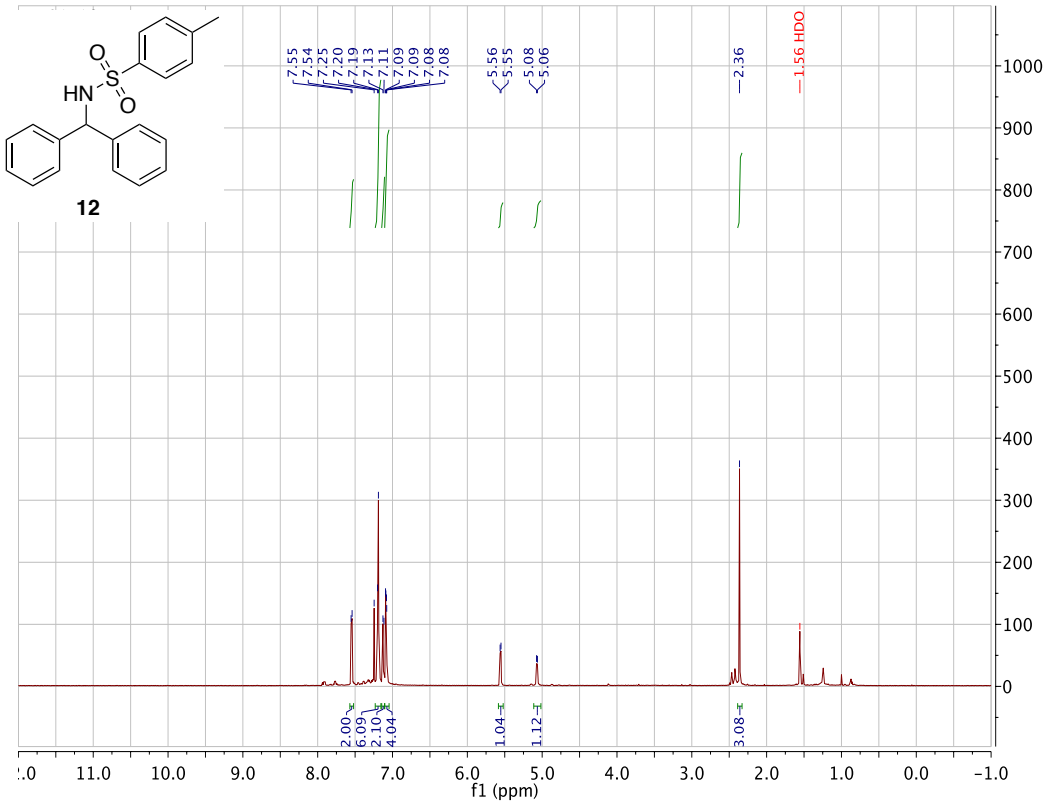
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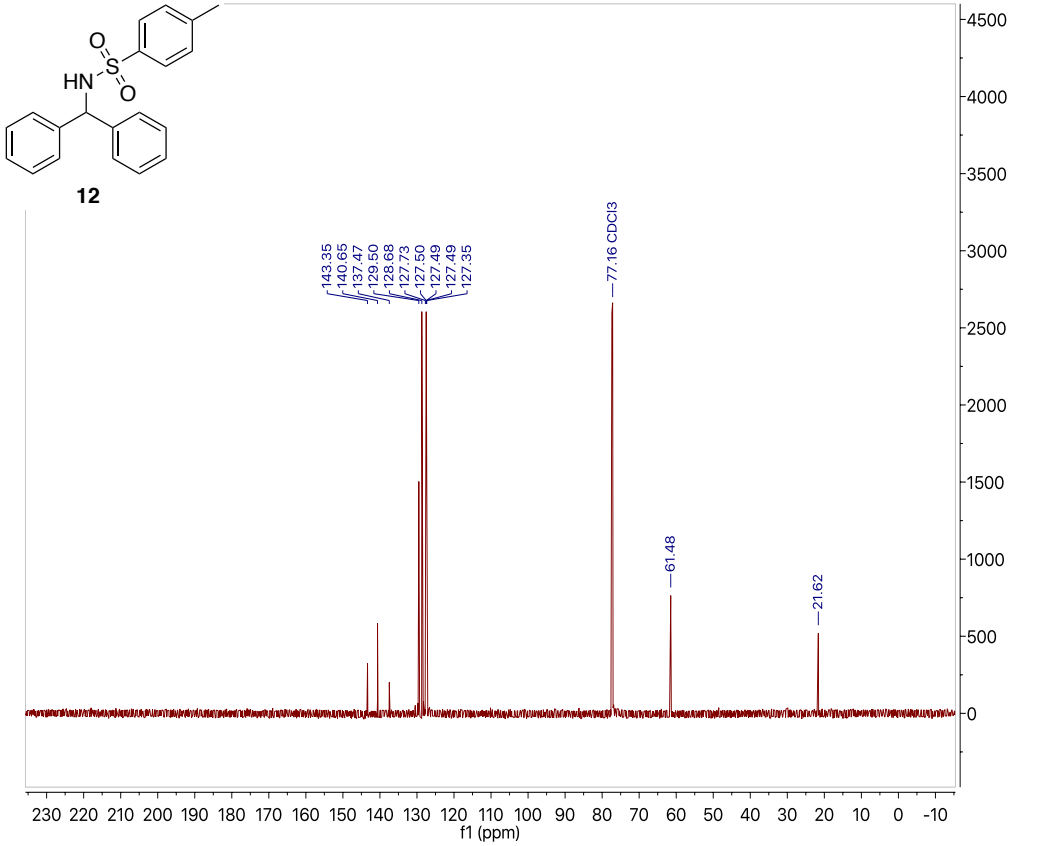
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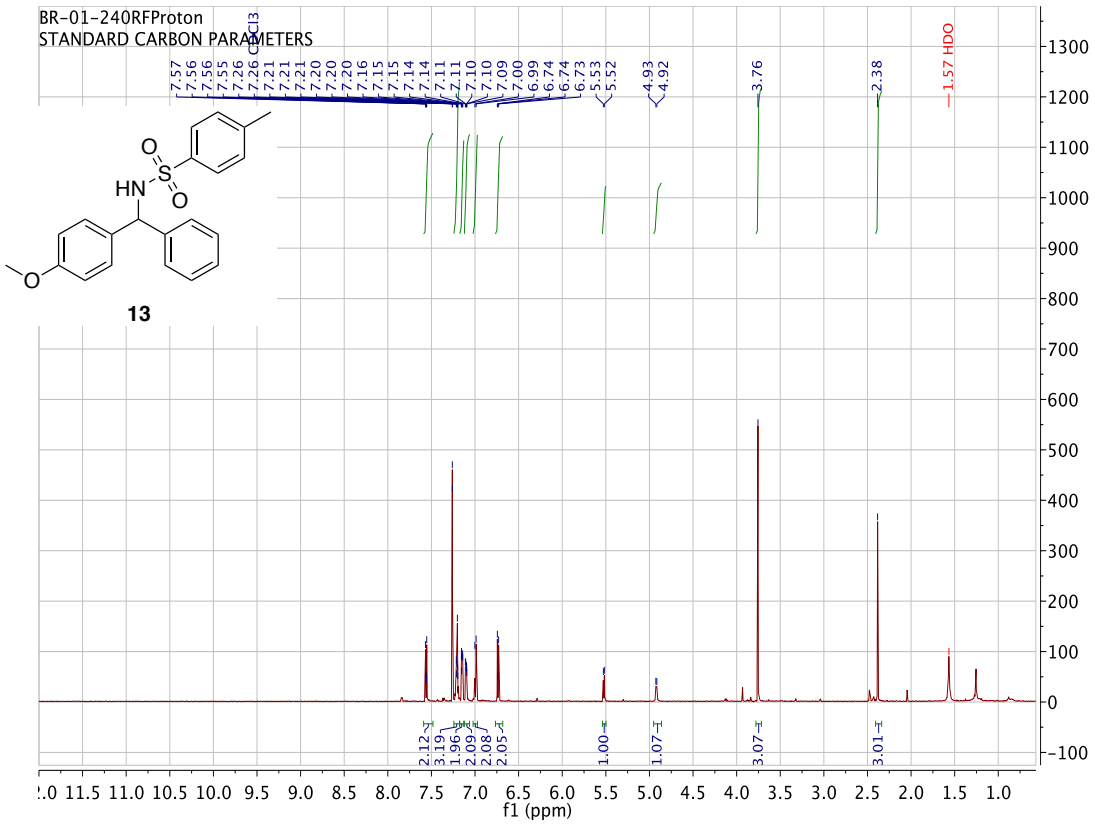
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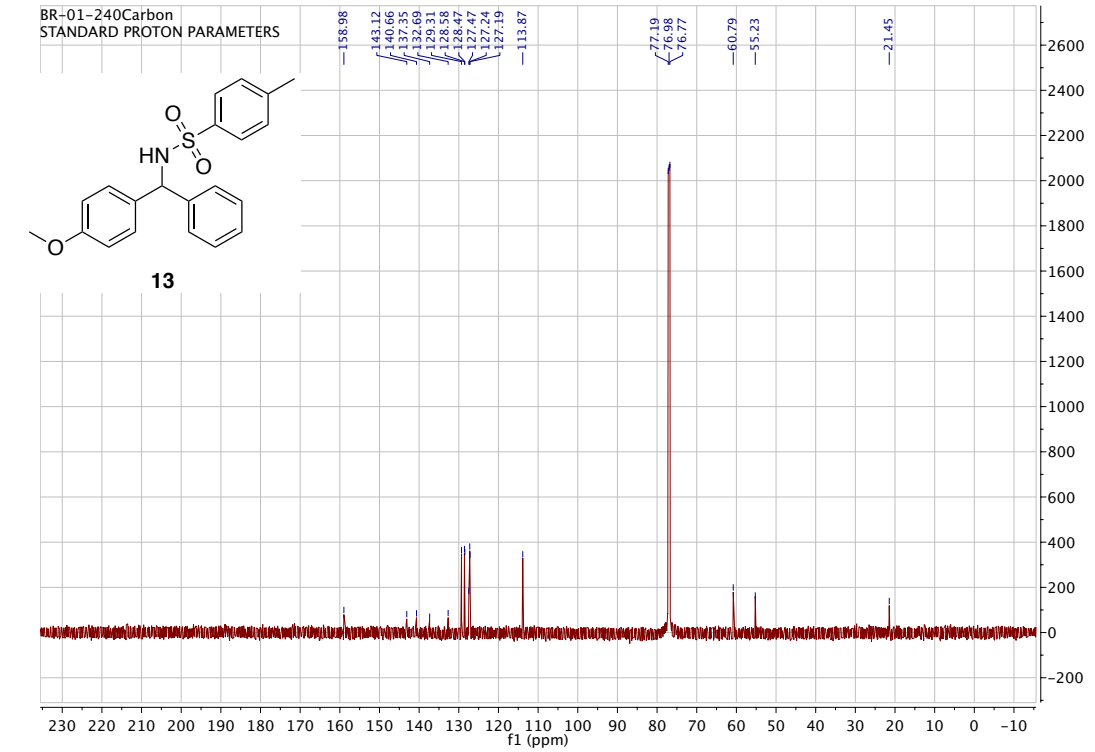
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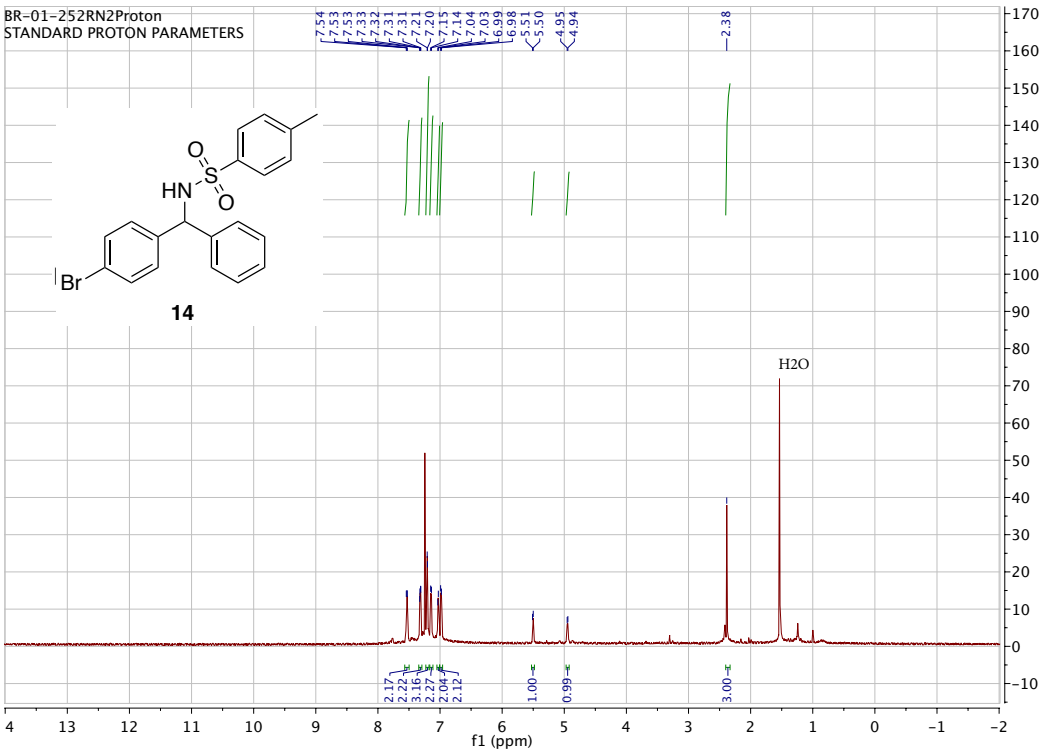
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HN
O
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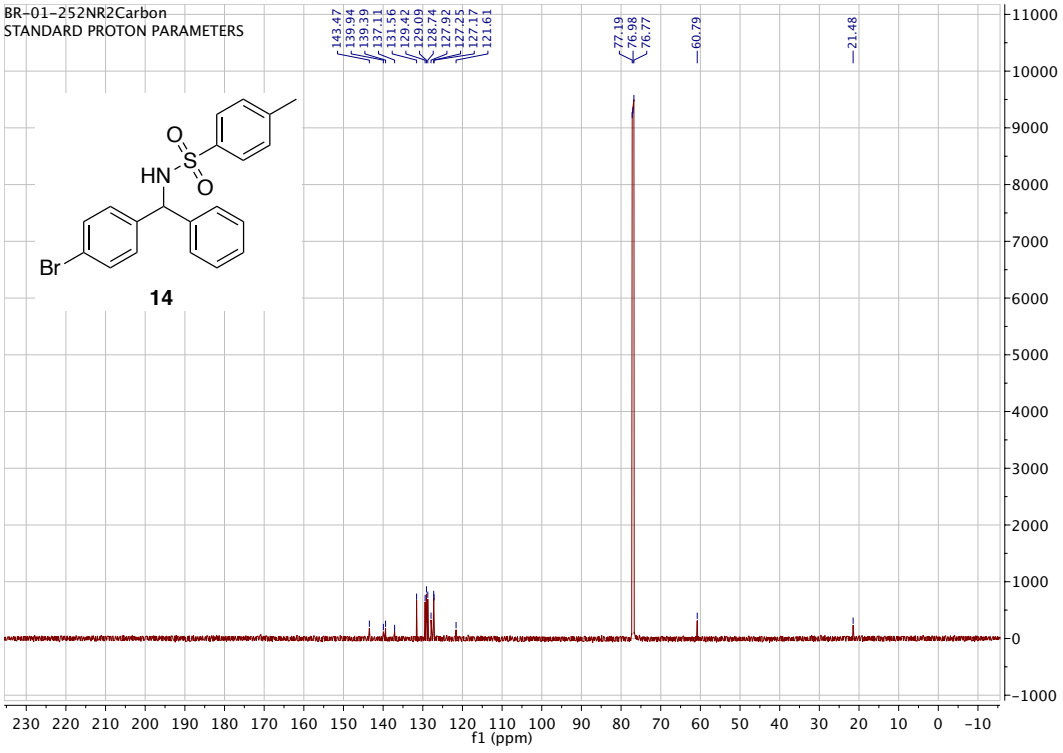
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S
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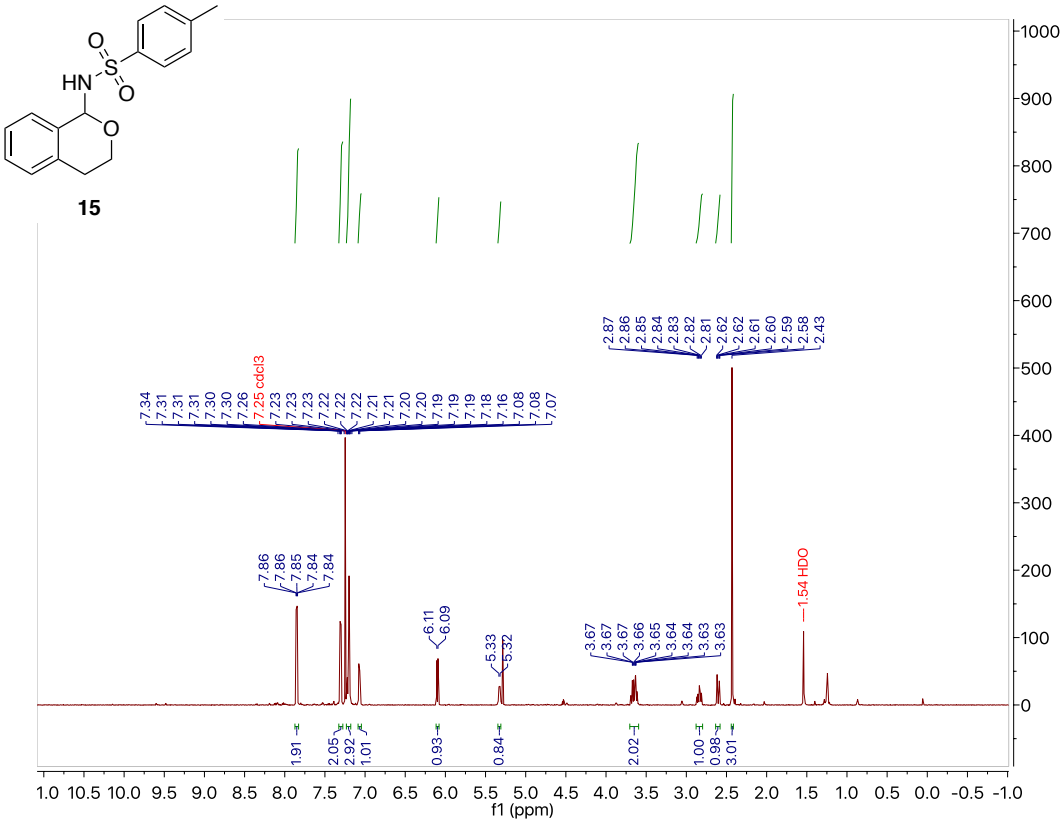
O
Br
14
f1 (ppm)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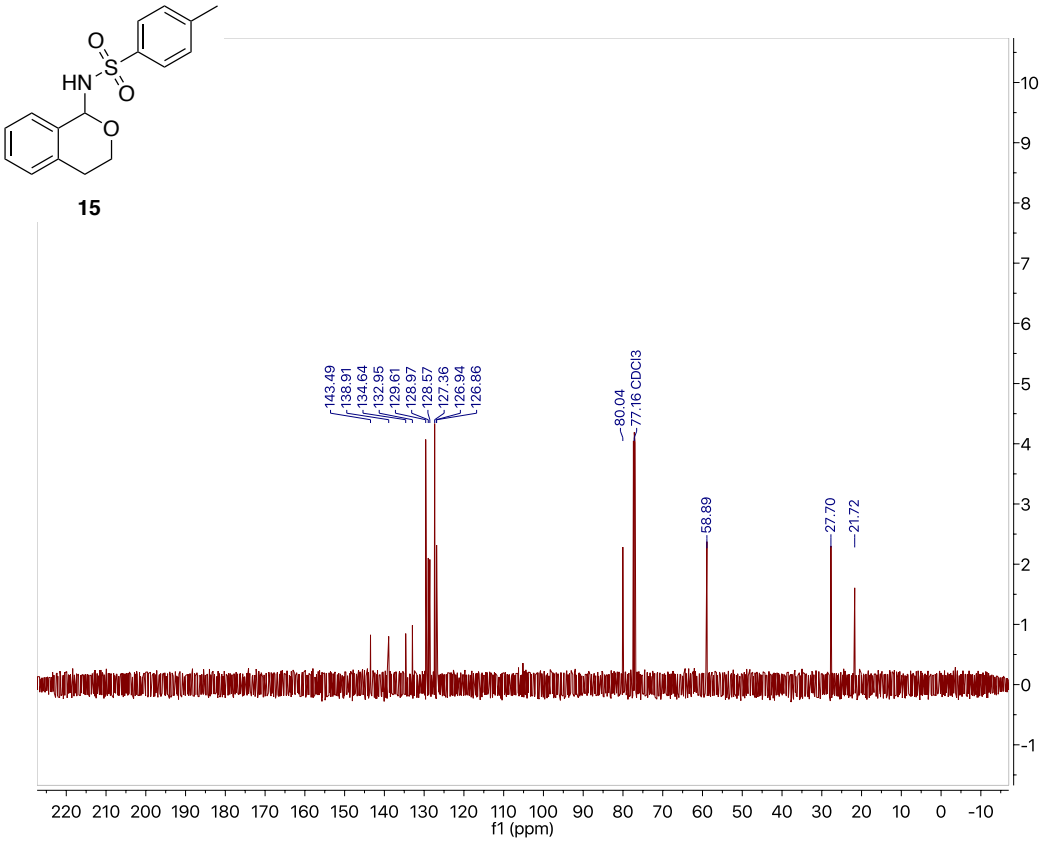
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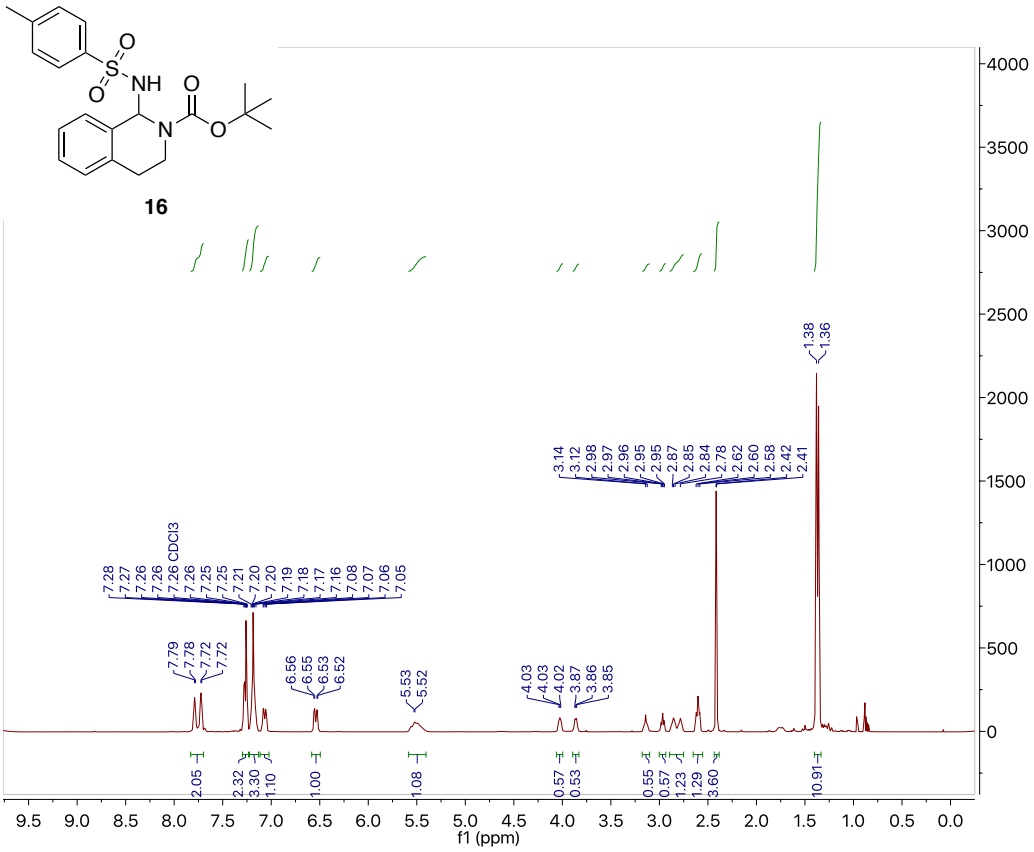
f1 (ppm)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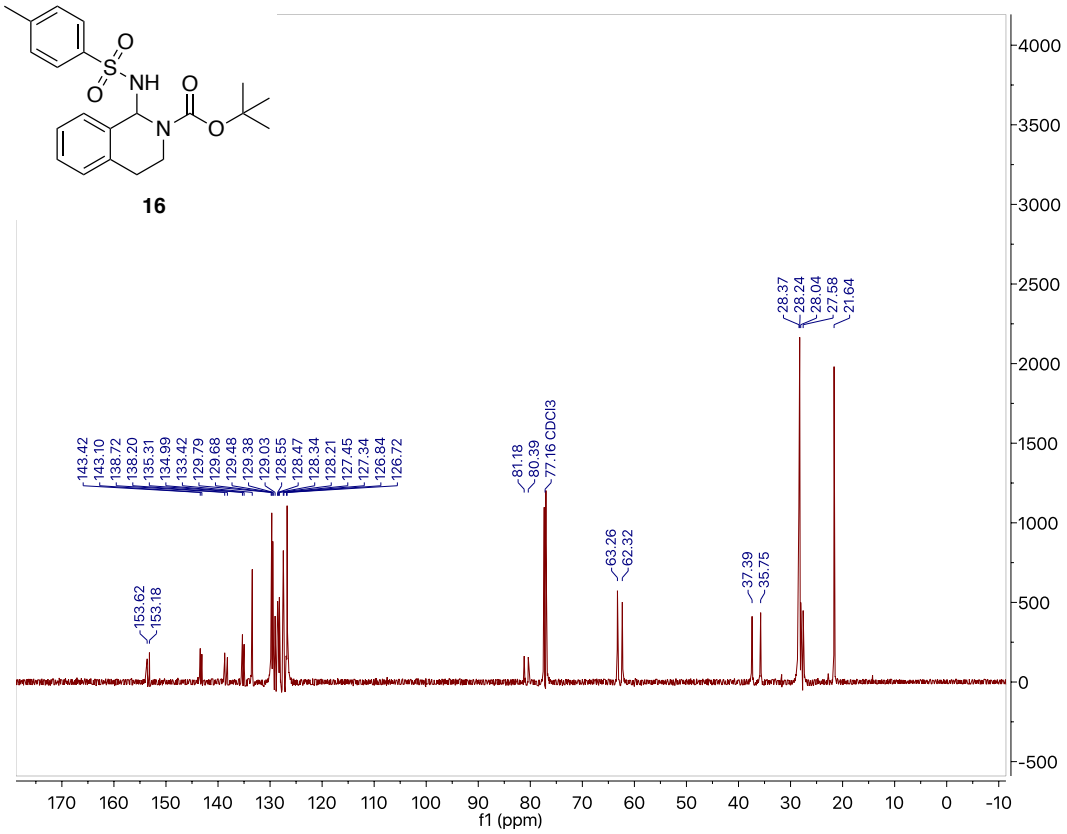
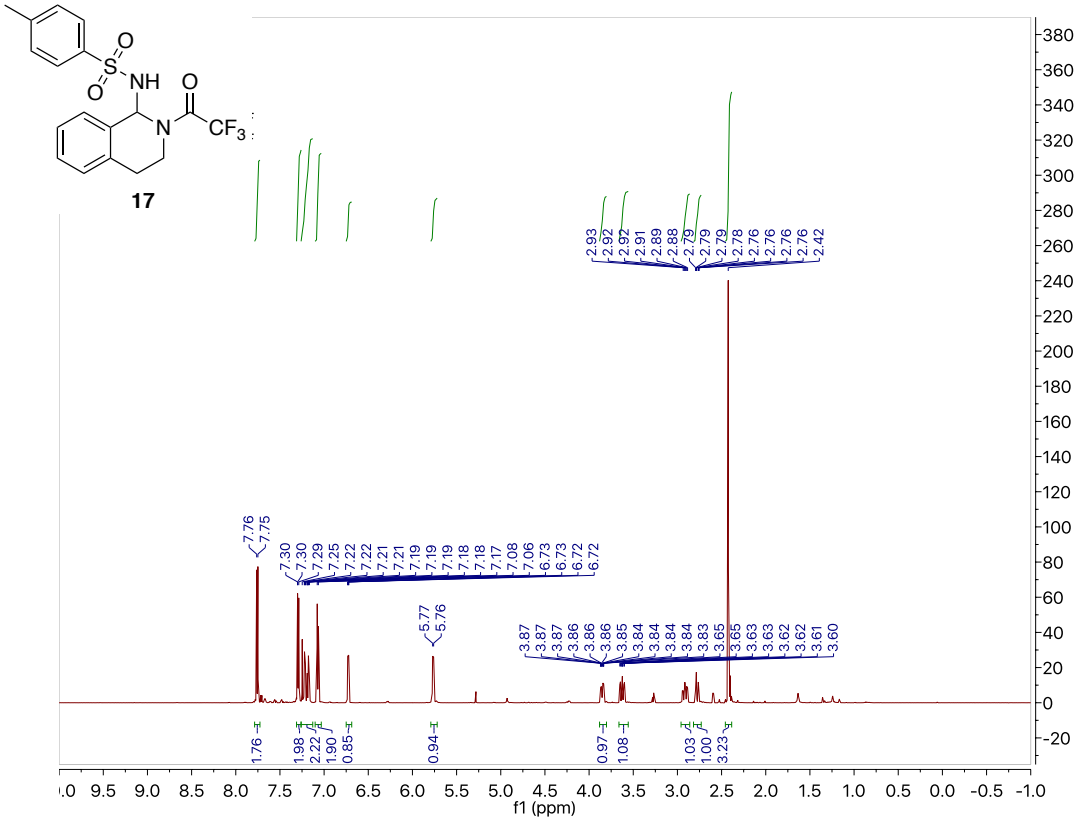
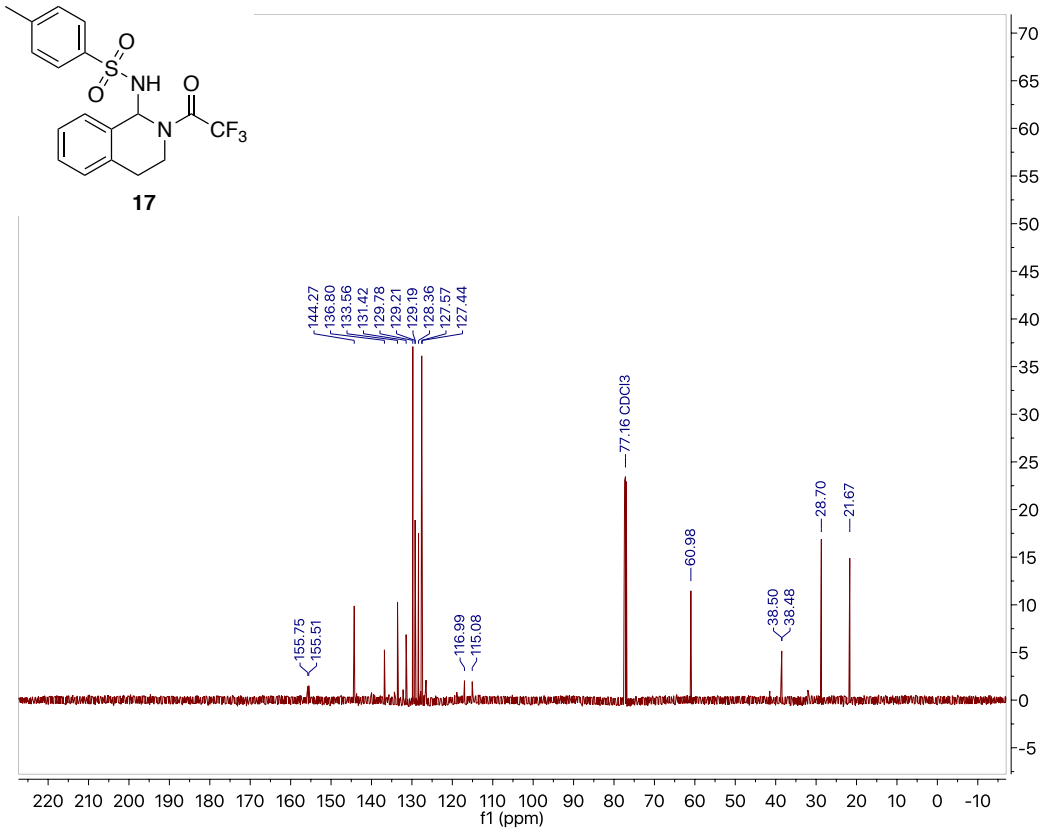
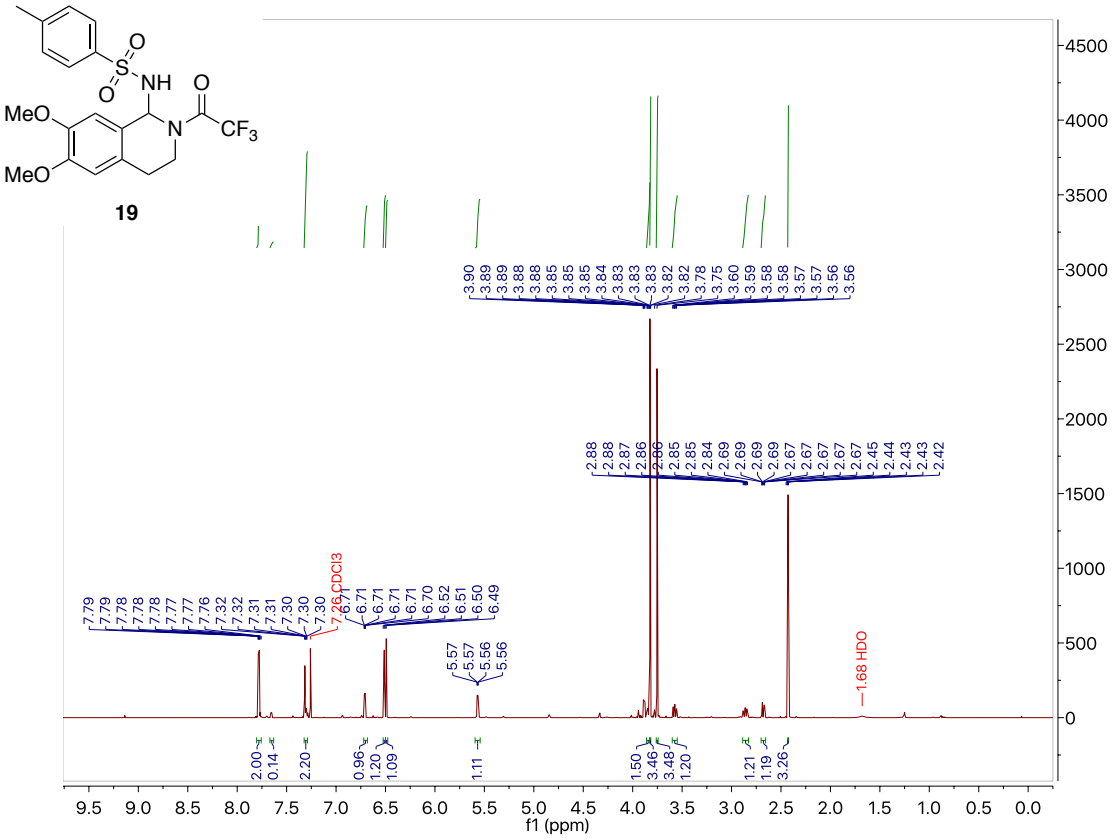
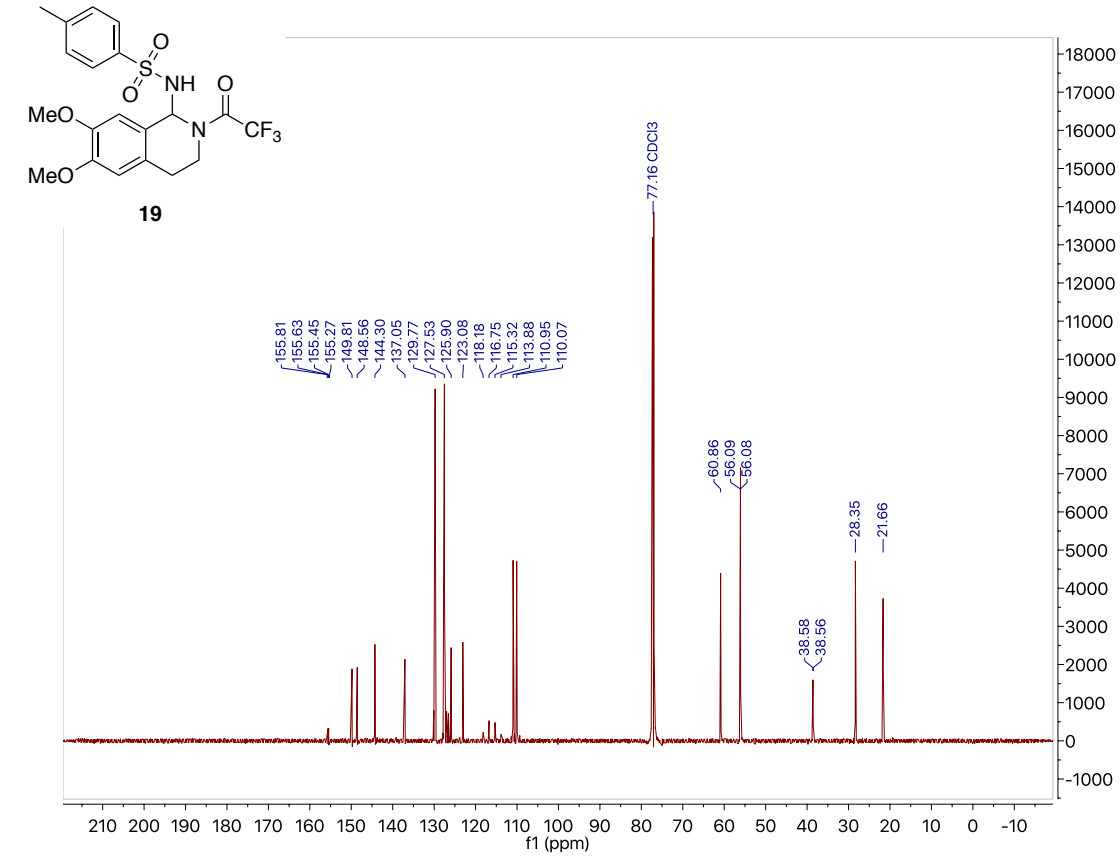
6.53
6.52
5.53
5.52
4.03
4.02
4.02
3.87
3.86
3.85
3.14
3.12
2.98
2.97
2.96
2.95
2.95
2.87
2.85
2.84
2.78
2.62
2.60
2.58
2.42
2.41
1.38
1.36
2.05
2.32
3.30
1.10
1.00
1.08
0.57
0.53
0.55
0.57
1.23
1.29
3.60
10.91
f1 (ppm)

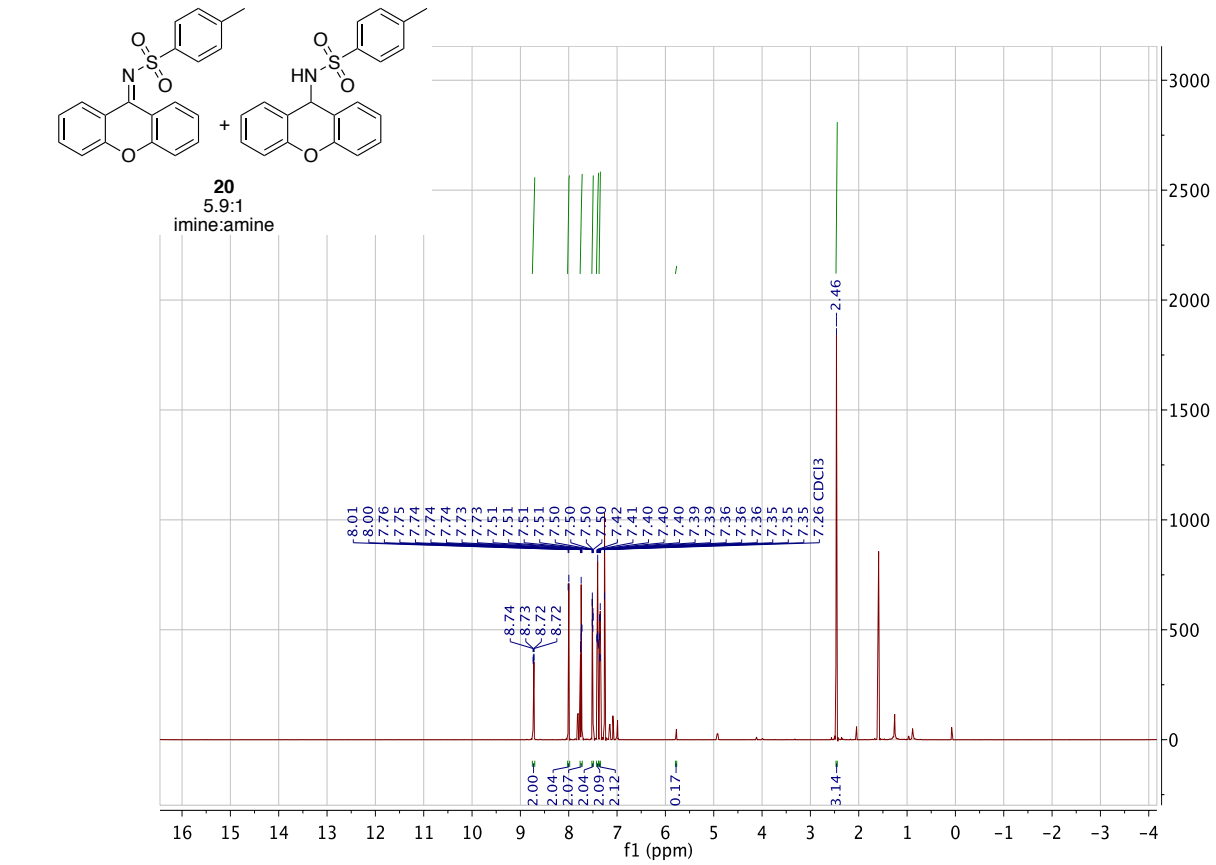

16
143.42
143.10
138.72
138.20
135.31
134.99
133.42
129.79
129.68
129.48
129.38
129.03
128.55
128.47
128.34
128.21
127.45
127.34
126.84
126.72
81.18
80.39
77.16 CDCl3
63.26
62.32
37.39
35.75
28.37
28.24
28.04
27.58
21.64
153.62
153.18
f1 (ppm)

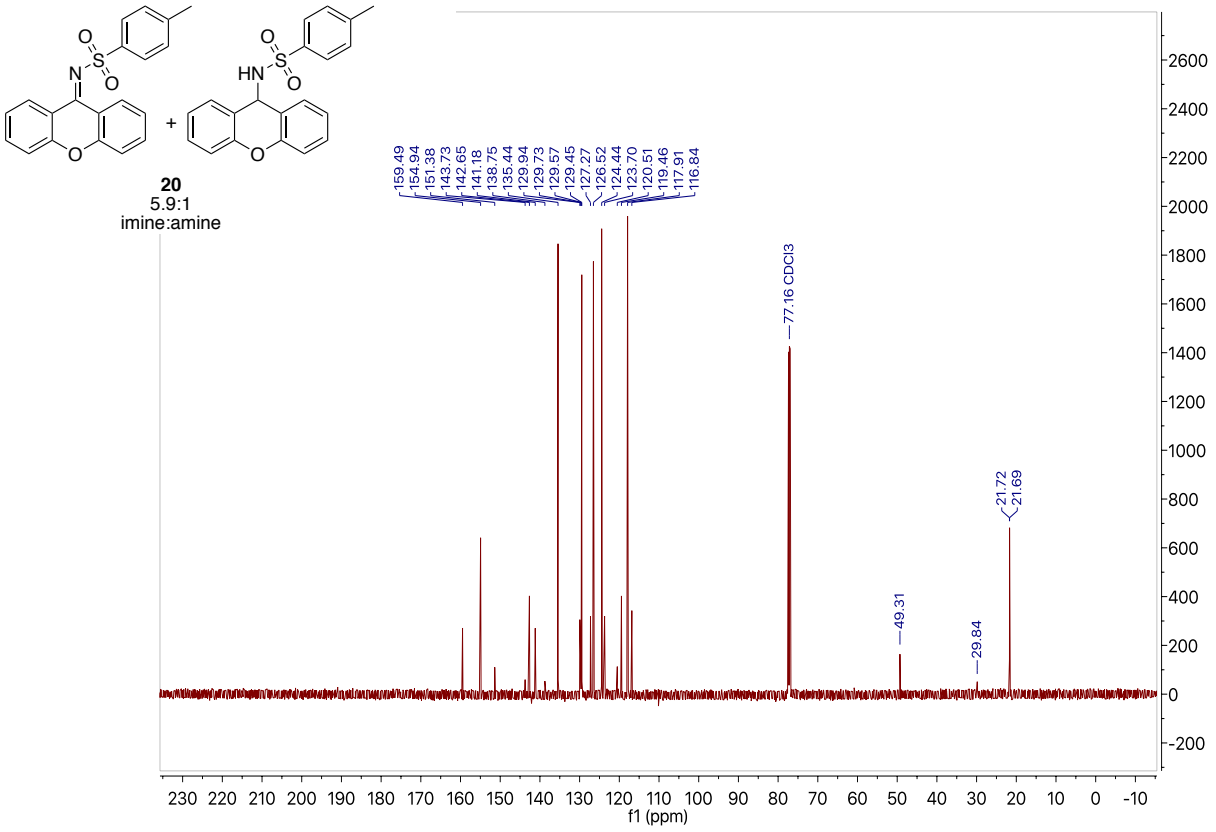

17
f1 (ppm)

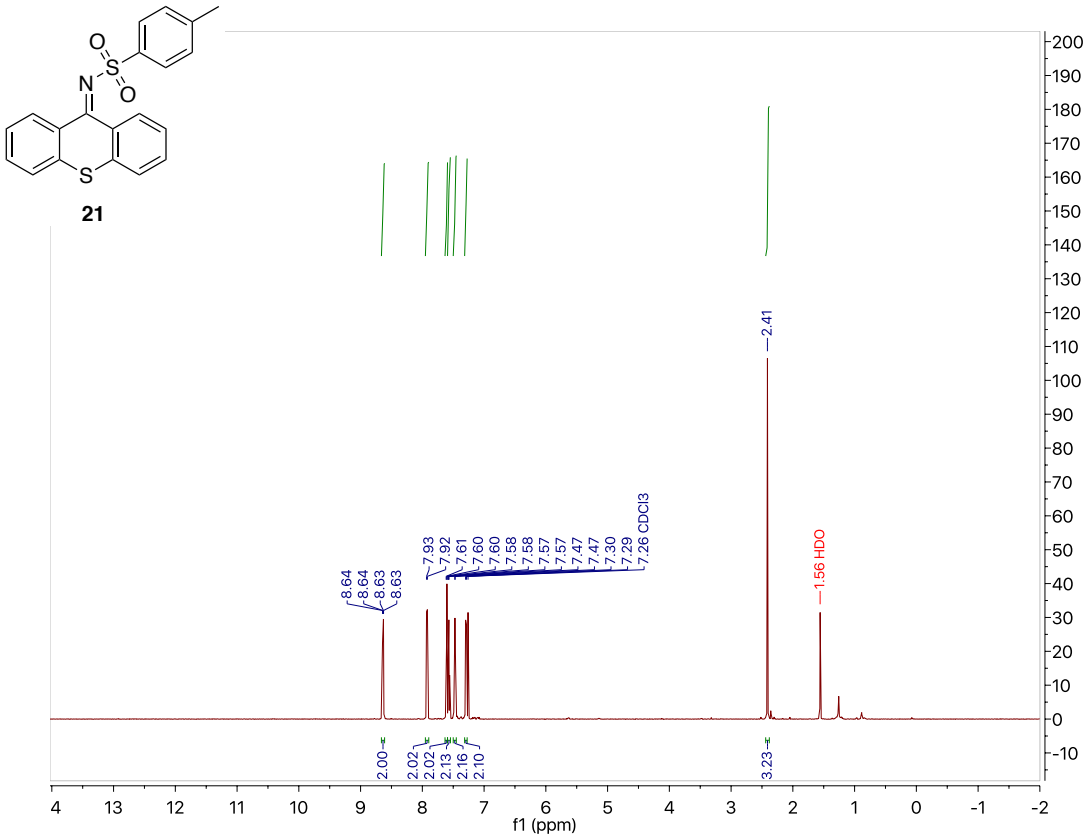

17
77.16 CDCl3
f1 (ppm)

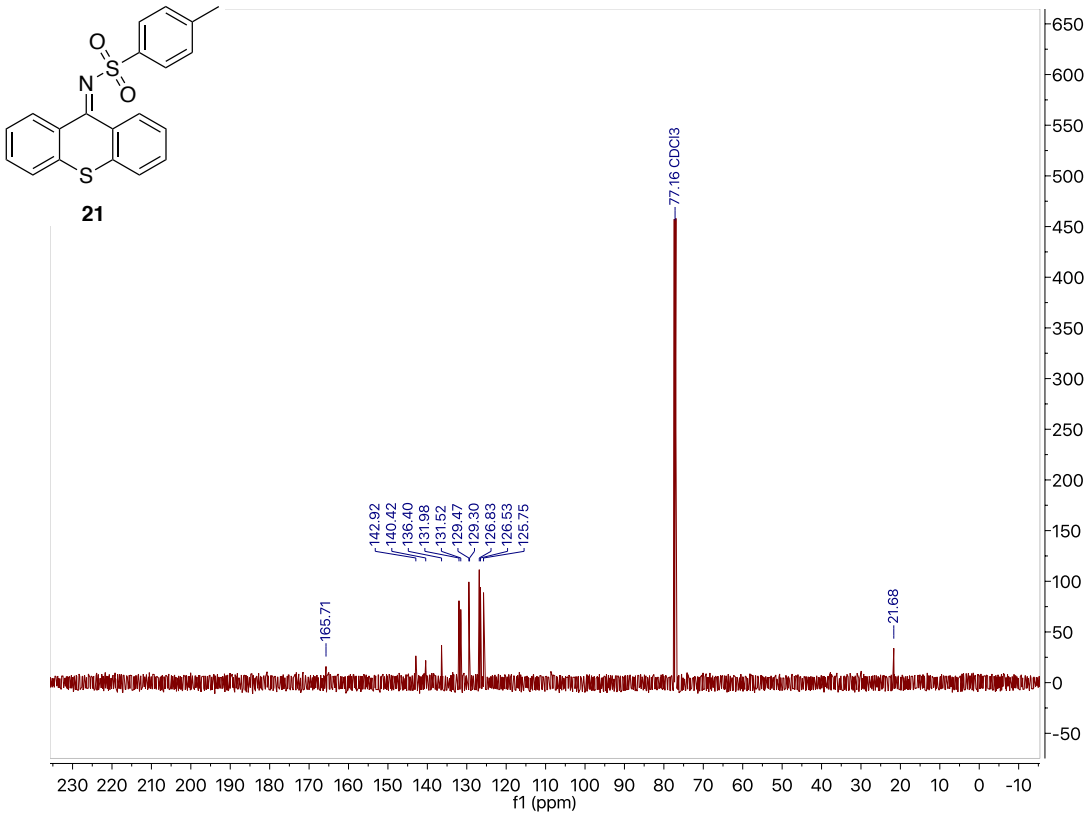

MeO
MeO
NH
O
O
S
O
N
O
CF3
19
7.79
7.78
7.77
7.76
7.32
7.31
7.30
7.26 CDCl3
6.71
6.70
6.52
6.51
6.50
6.49
5.57
5.56
3.90
3.89
3.88
3.85
3.84
3.83
3.82
3.78
3.75
3.60
3.59
3.58
3.57
3.56
2.88
2.87
2.86
2.85
2.84
2.69
2.67
2.45
2.44
2.43
2.42
1.68 HDO
2.00
0.14
2.20
0.96
1.20
1.09
1.11
1.50
3.46
3.48
1.20
1.21
1.19
3.26
f1 (ppm)

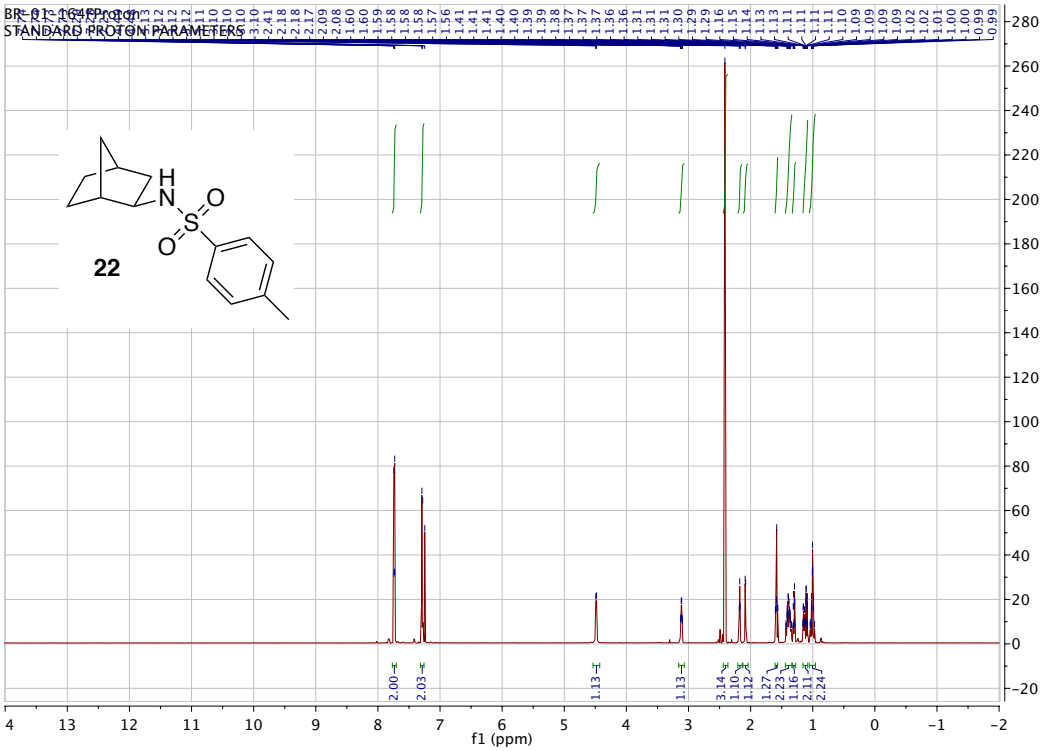

MeO
MeO
NH
O
O
S
O
N
O
CF3
19
155.81
155.63
155.45
155.27
149.81
148.56
144.30
137.05
129.77
127.53
125.90
123.08
118.18
116.75
115.32
113.88
110.95
110.07
77.16 CDCl3
60.86
56.09
56.08
38.58
38.56
28.35
21.66
f1 (ppm)

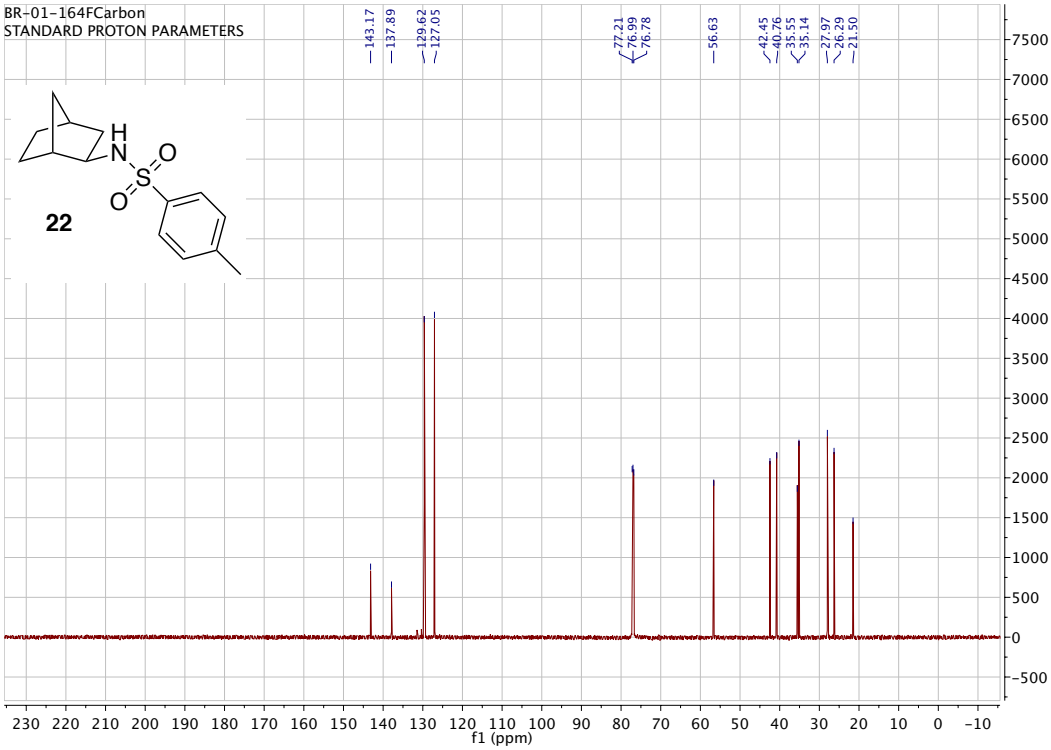

20
5.9:1
imine:amine
8.01
8.00
7.76
7.75
7.74
7.74
7.74
7.73
7.73
7.51
7.51
7.51
7.51
7.50
7.50
7.50
7.50
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.36
7.36
7.36
7.35
7.35
7.35
7.26 CDCl3
2.46
8.74
8.73
8.72
8.72
2.00
2.04
2.07
2.04
2.09
2.12
0.17
3.14
f1 (ppm)

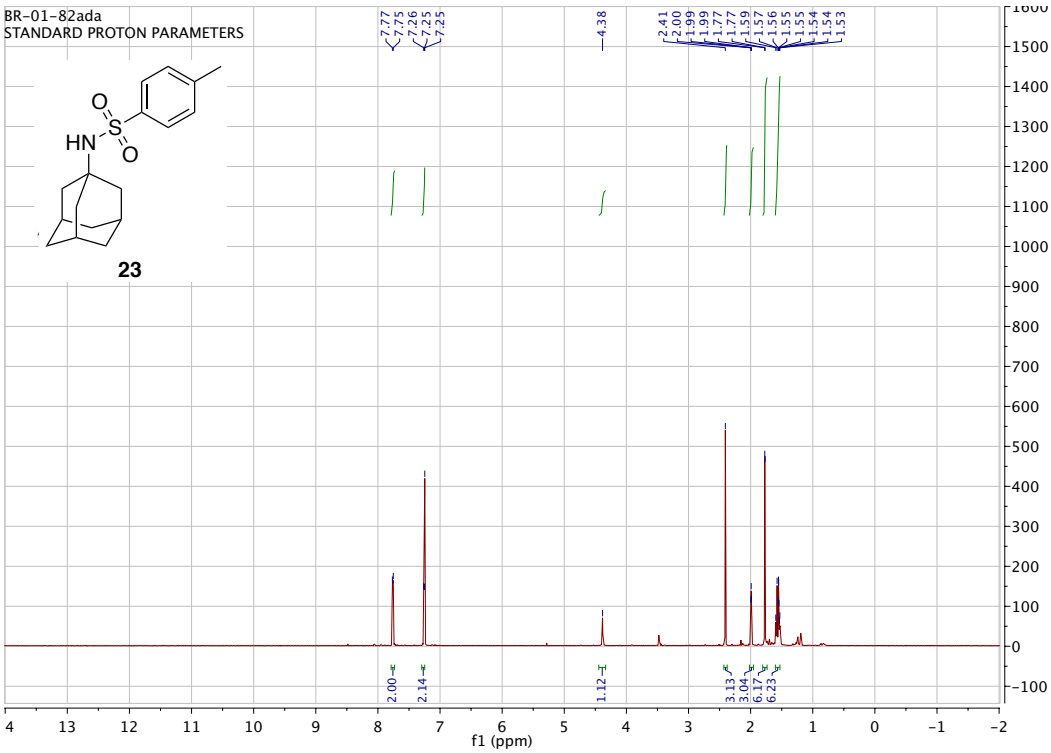

20
5.9:1
imine:amine
159.49
154.94
151.38
143.73
142.65
141.18
138.75
135.44
129.94
129.73
129.57
129.45
127.27
126.52
124.44
123.70
120.51
119.46
117.91
116.84
77.16 CDCl3
49.31
29.84
21.72
21.69
f1 (ppm)

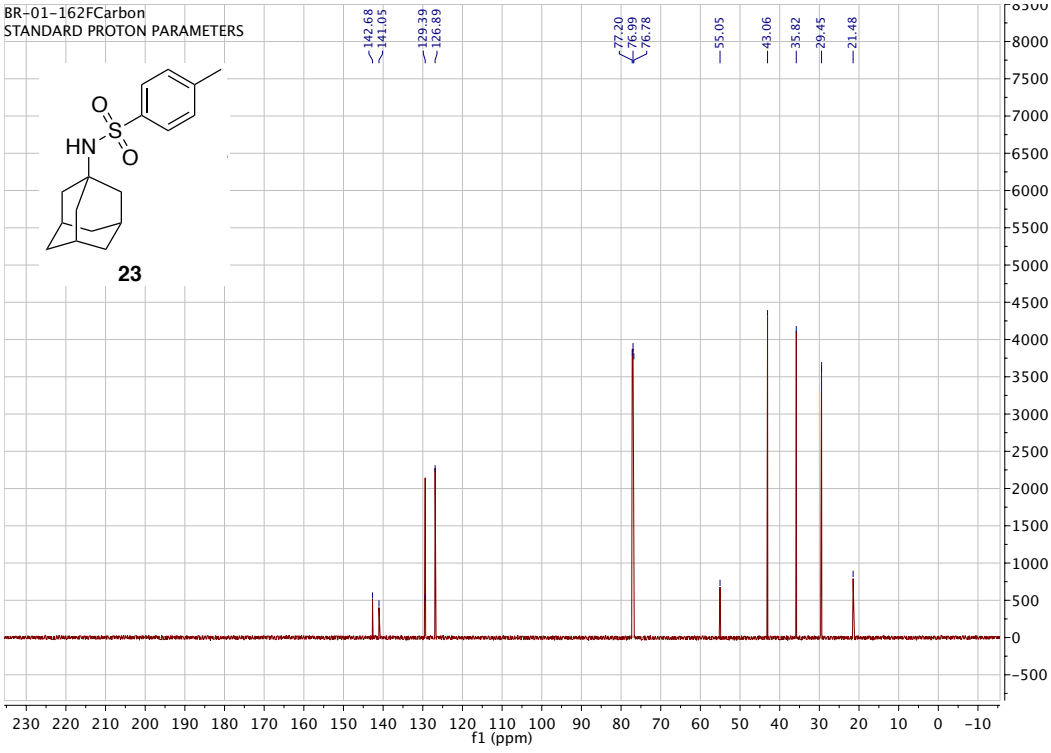

21
8.64
8.64
8.63
8.63
7.93
7.92
7.61
7.60
7.60
7.58
7.58
7.57
7.57
7.47
7.47
7.30
7.29
7.26 CDCl3
2.41
1.56 HDO
2.00
2.02
2.02
2.13
2.16
2.10
3.23
f1 (ppm)

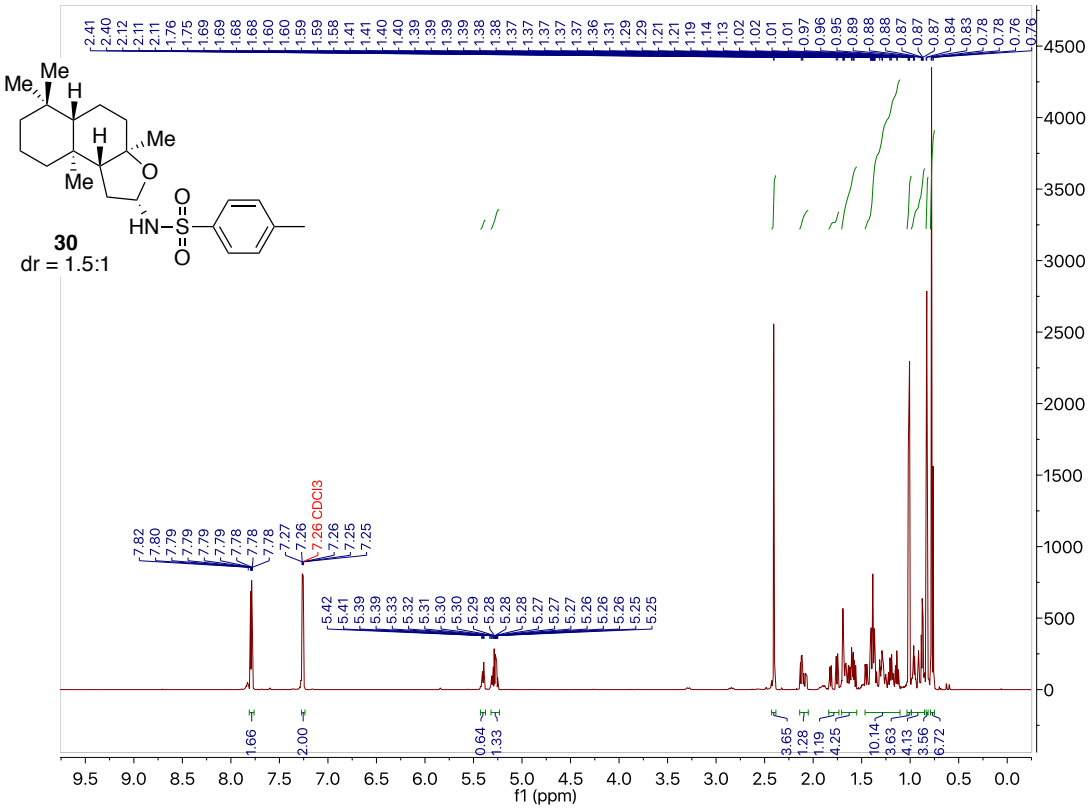

21
77.16 CDCl3
142.92
140.42
136.40
131.98
131.52
129.47
129.30
126.83
126.53
125.75
165.71
21.68
f1 (ppm)

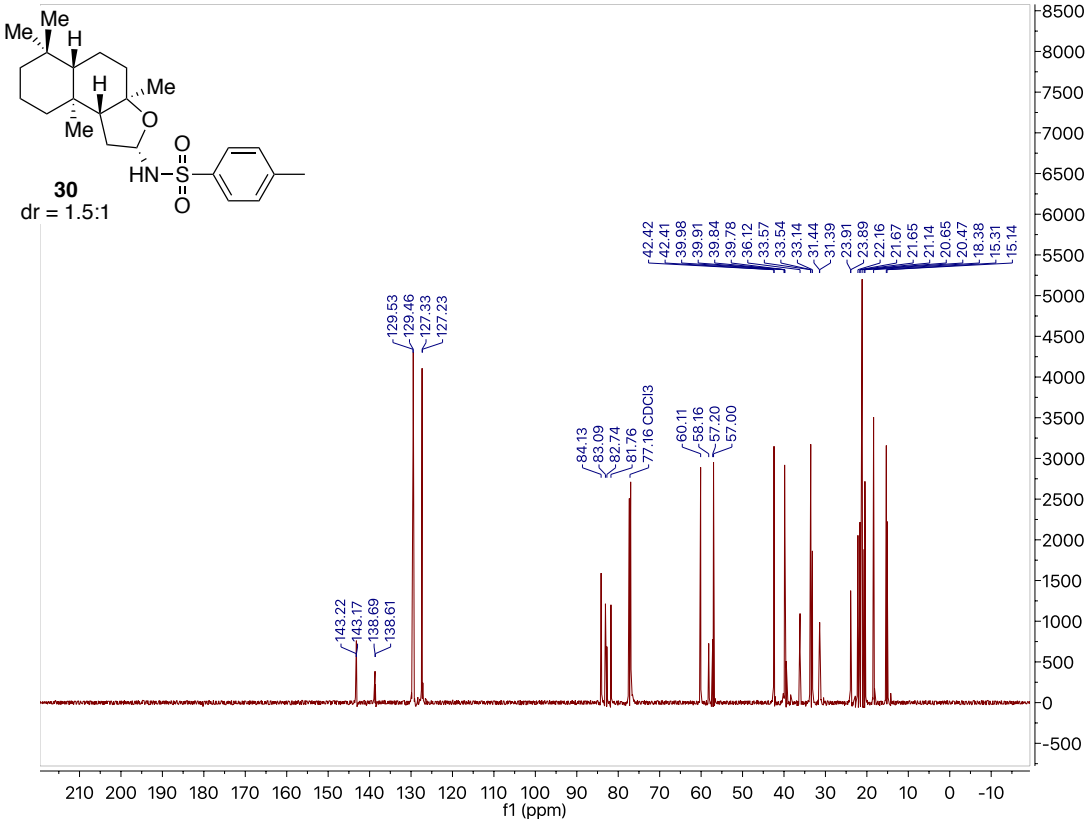

BR-01-164FProton
STANDARD PROTON PARAMETERS
22
f1 (ppm)


BR-01-164FCarbon
STANDARD PROTON PARAMETERS
143.17
137.89
129.62
127.05
77.21
76.99
76.78
56.63
42.45
40.76
35.55
35.14
27.97
26.29
21.50
22
f1 (ppm)

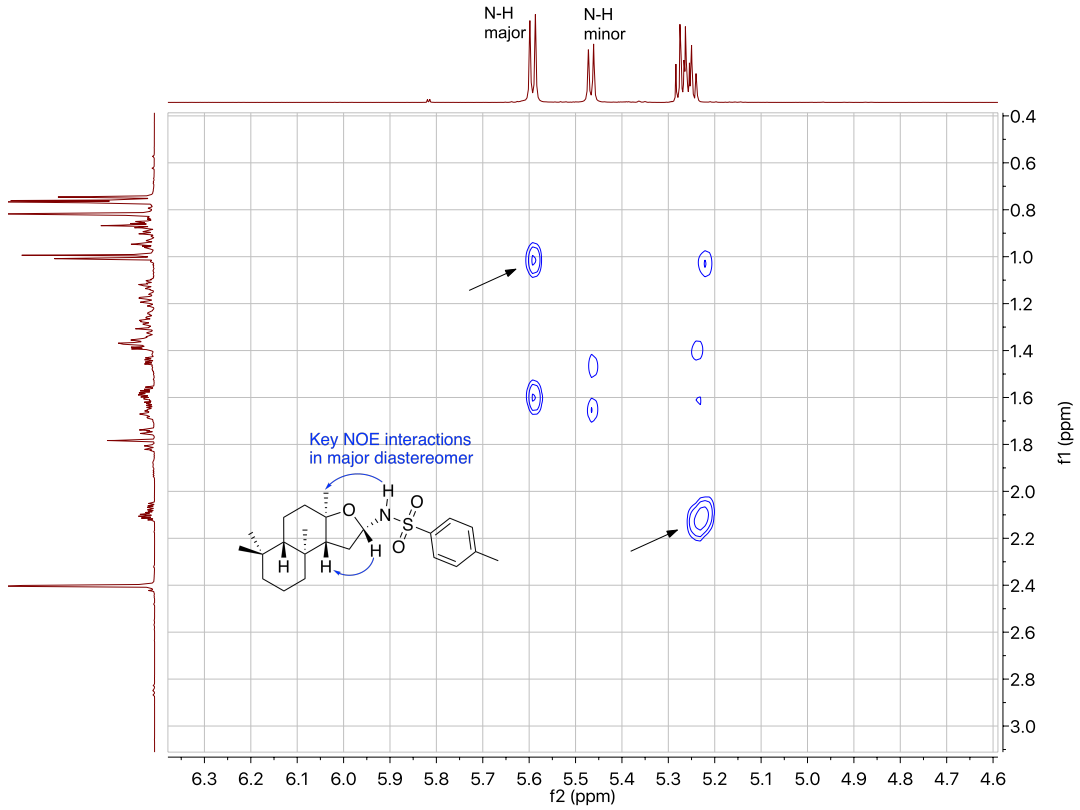

BR-01-82ada
STANDARD PROTON PARAMETERS
23
f1 (ppm)

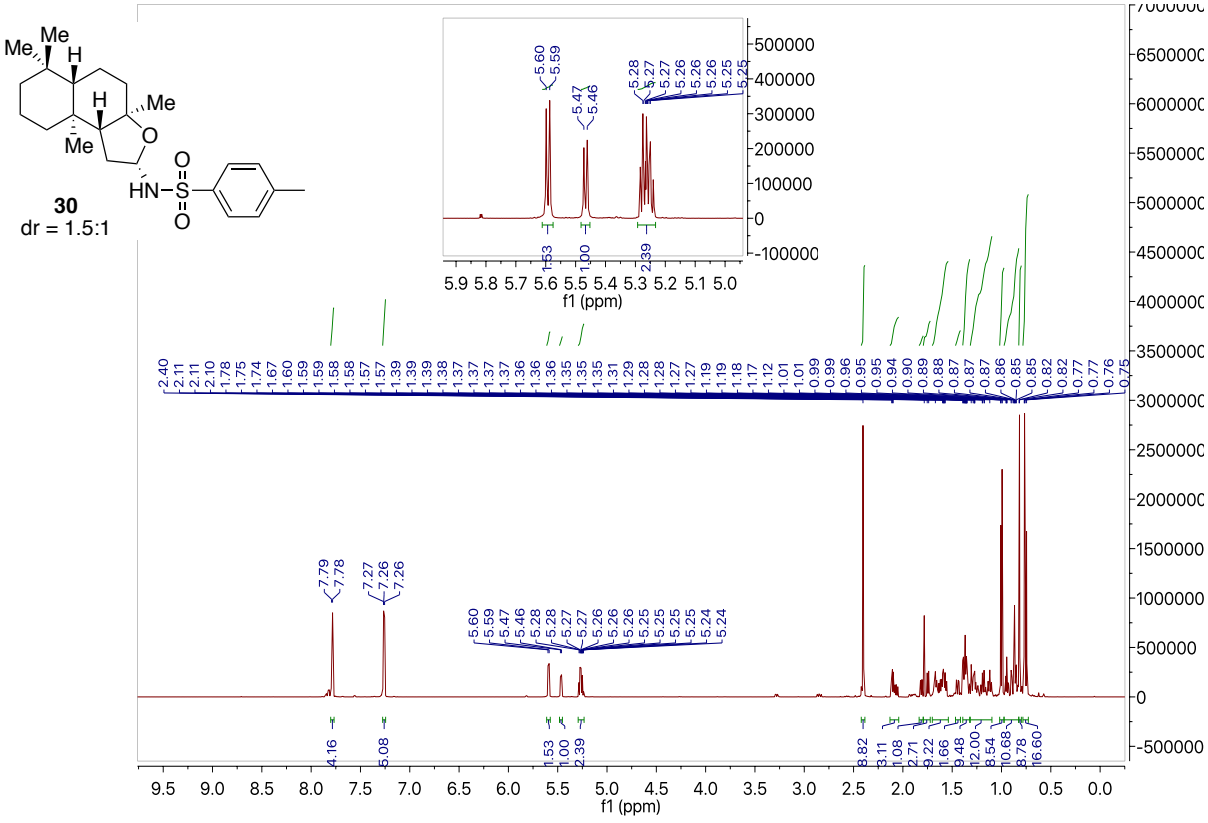

BR-01-162FCarbon
STANDARD PROTON PARAMETERS
23
f1 (ppm)

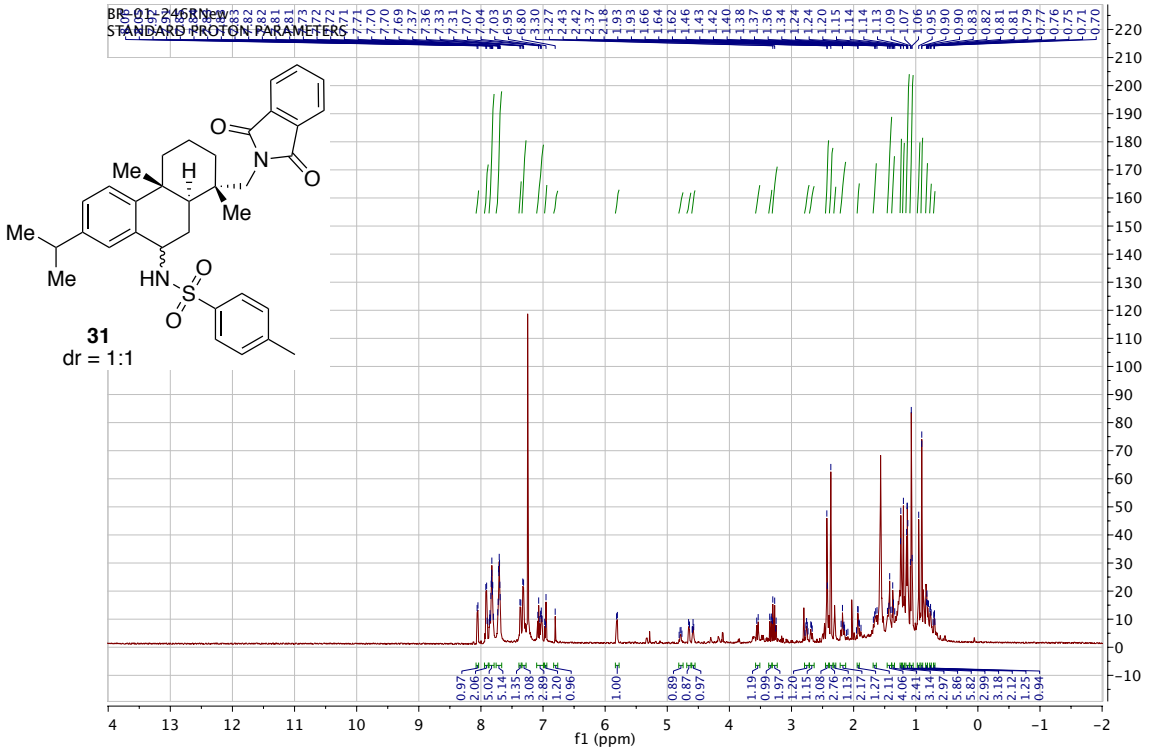

Me
Me
H
H
Me
O
Me
HN
S
O
O
30
dr = 1.5:1
CDCl3
f1 (ppm)

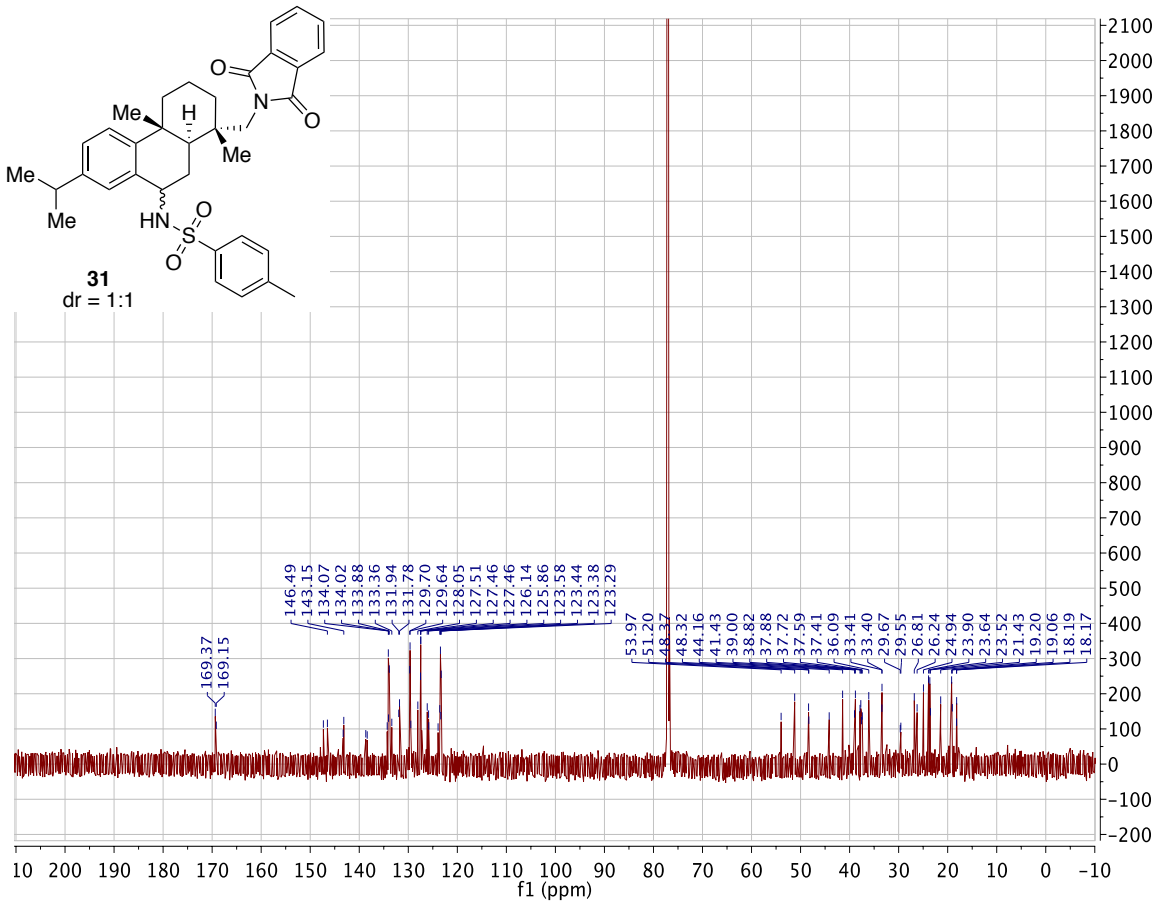

Me
Me
H
H
Me
O
Me
HN
S
O
O
30
dr = 1.5:1
CDCl3
f1 (ppm)

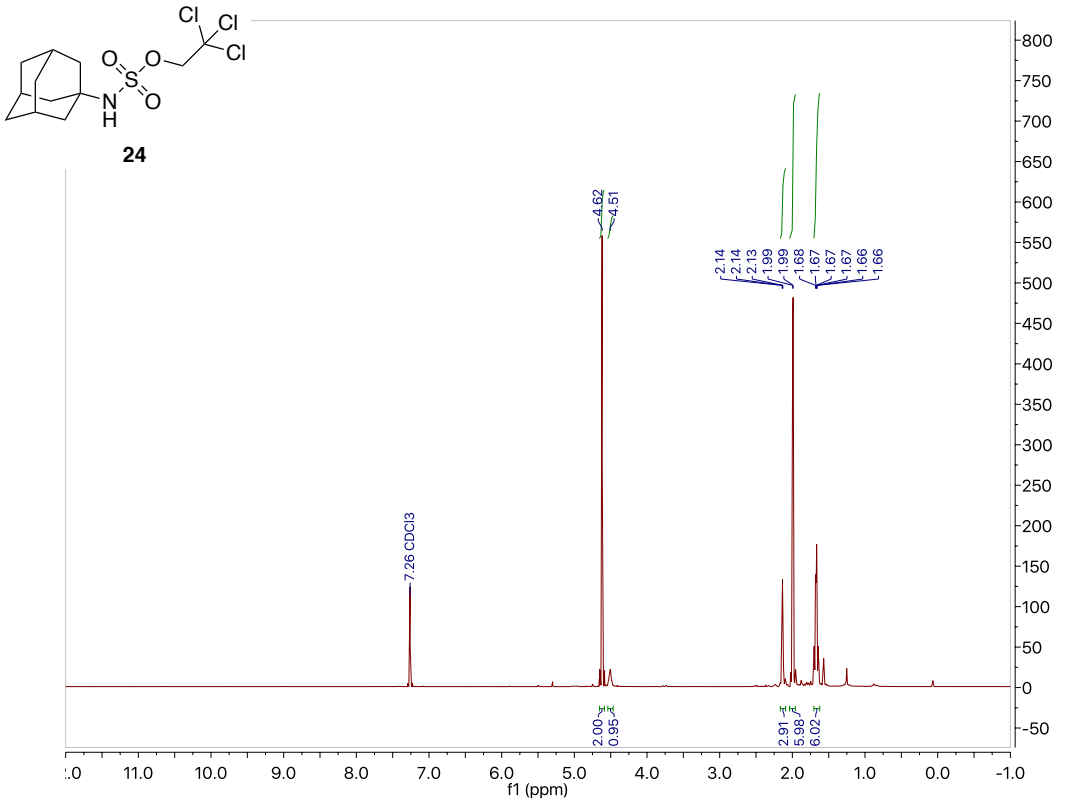
NOE and ^{1}HNMR obtained at 10˚C

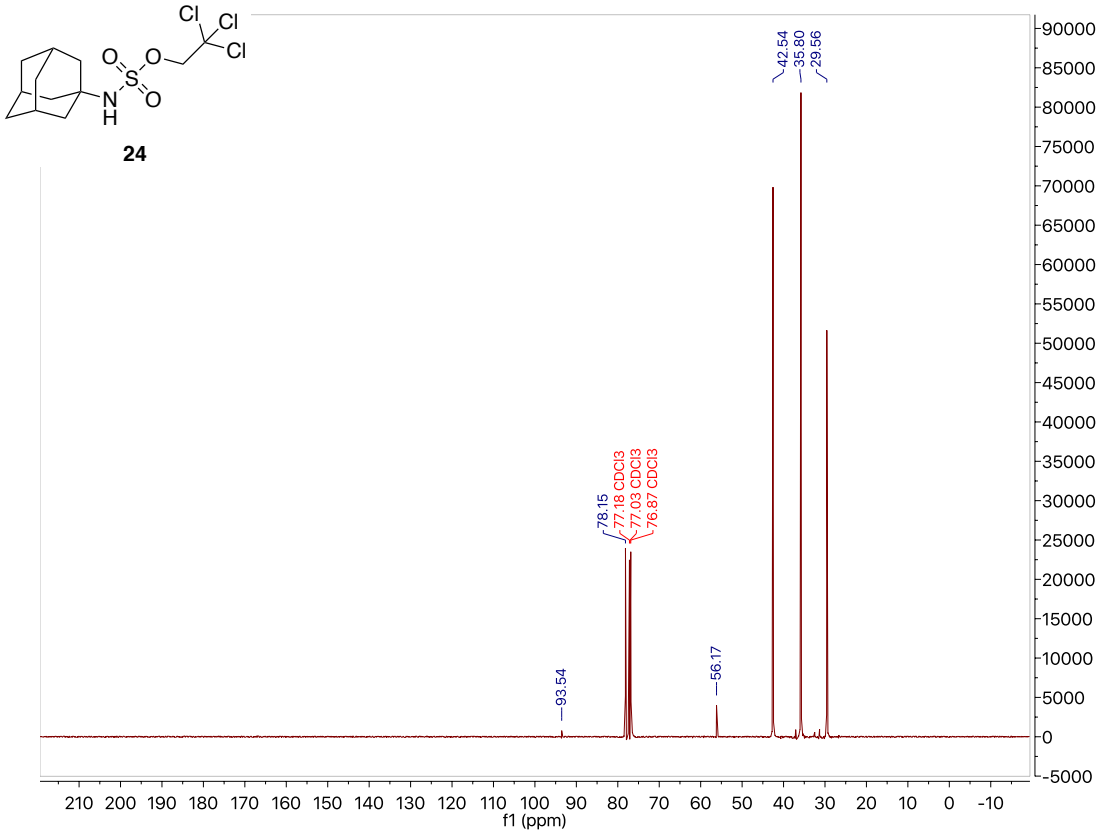


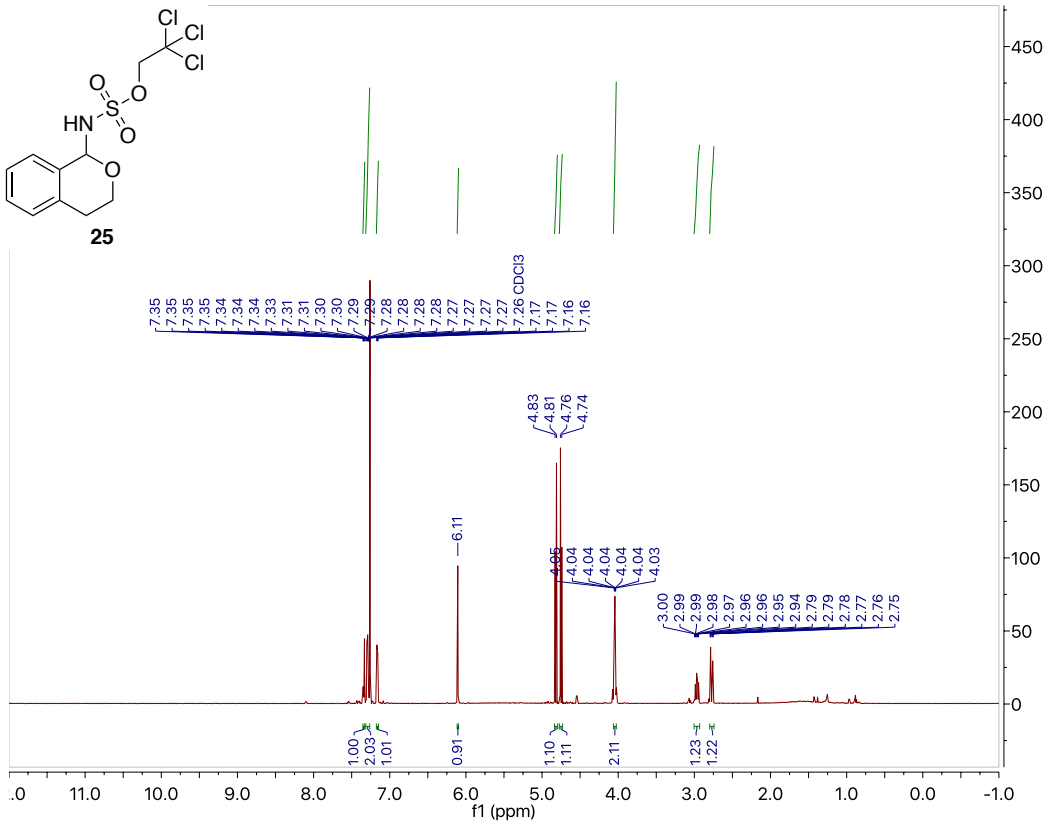


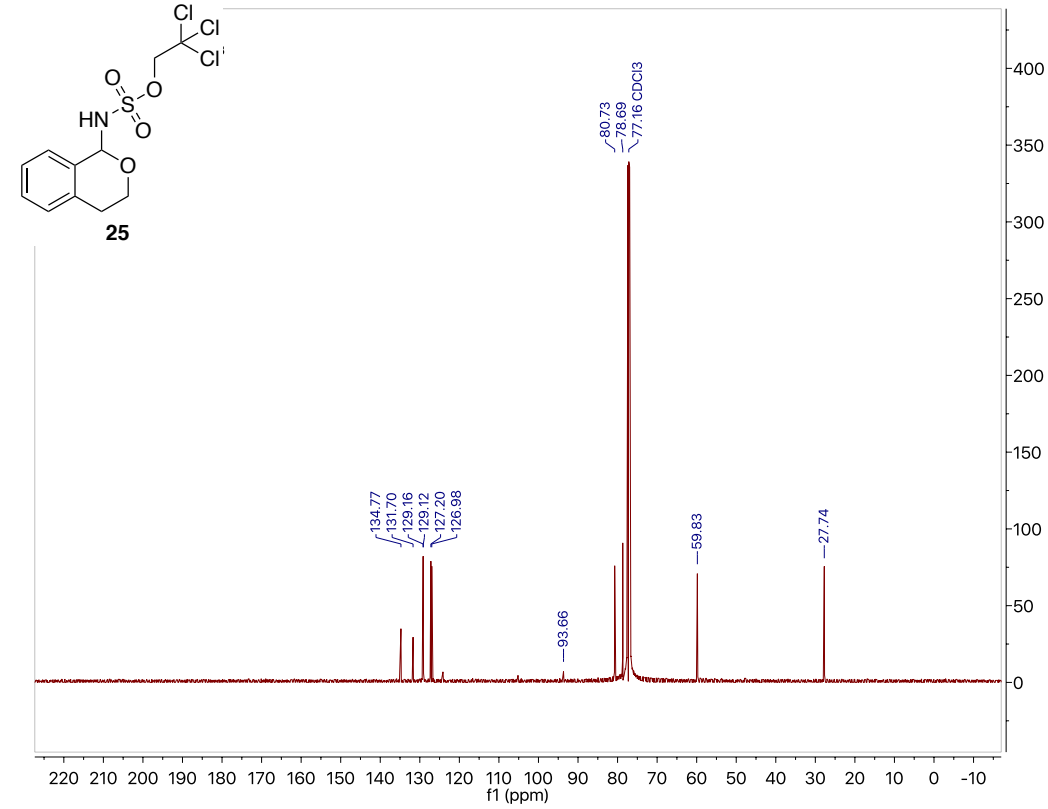

BR-01-246RNew
STANDARD PROTON PARAMETERS
31
dr = 1:1
f1 (ppm)

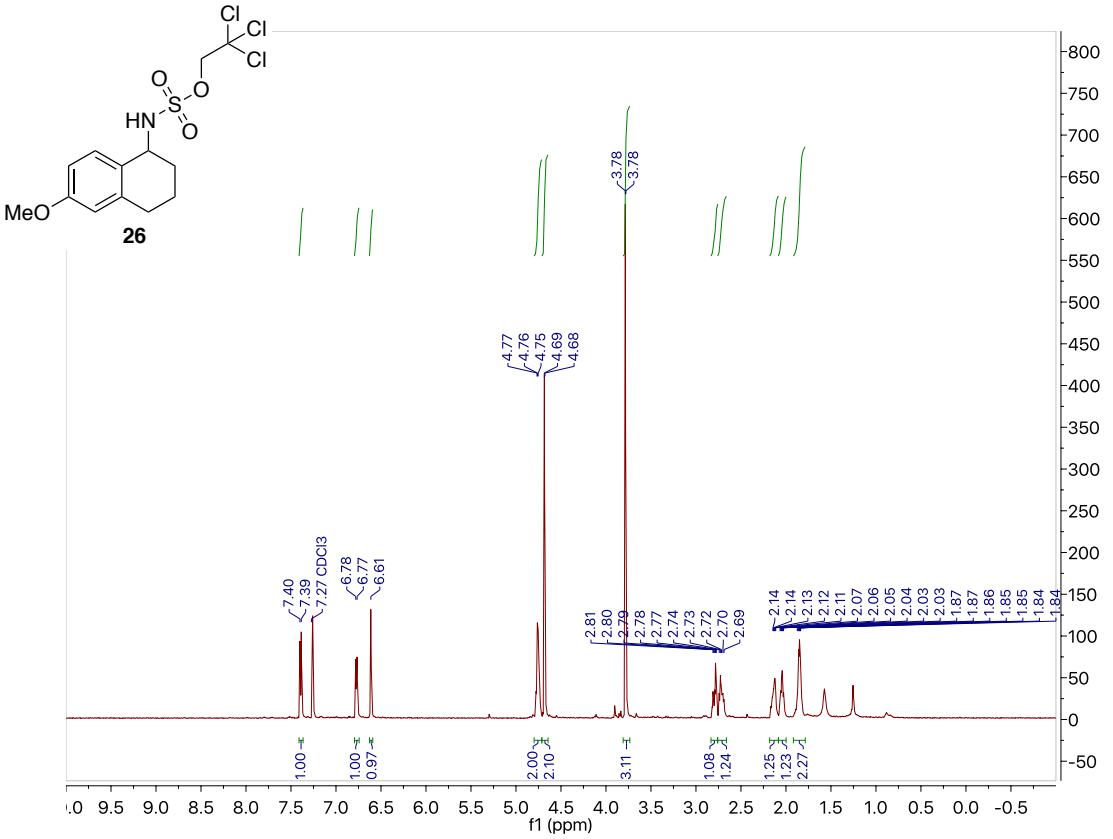

31
dr = 1:1
f1 (ppm)

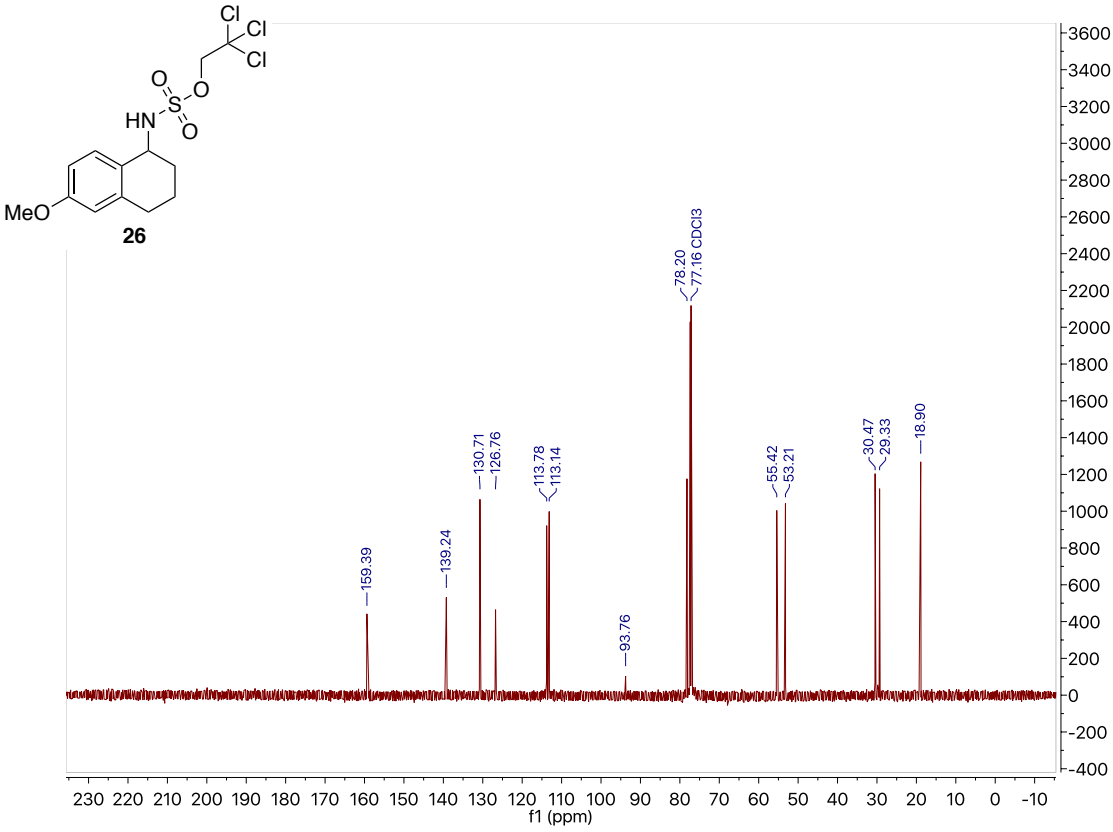

24
7.26 CDCl3
4.62
4.51
2.14
2.14
2.13
1.99
1.99
1.68
1.67
1.67
1.67
1.66
1.66
2.00
0.95
2.91
5.98
6.02
f1 (ppm)

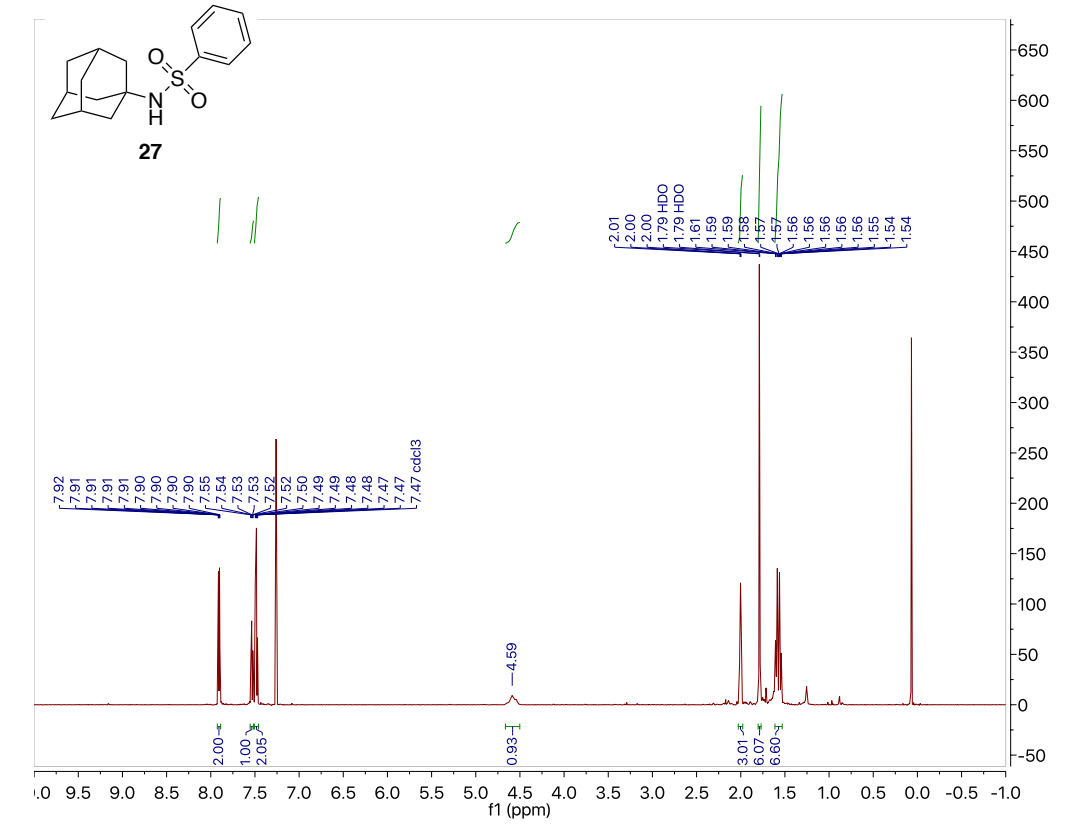

24
42.54
35.80
29.56
78.15
77.18 CDCl3
77.03 CDCl3
76.87 CDCl3
93.54
56.17
f1 (ppm)

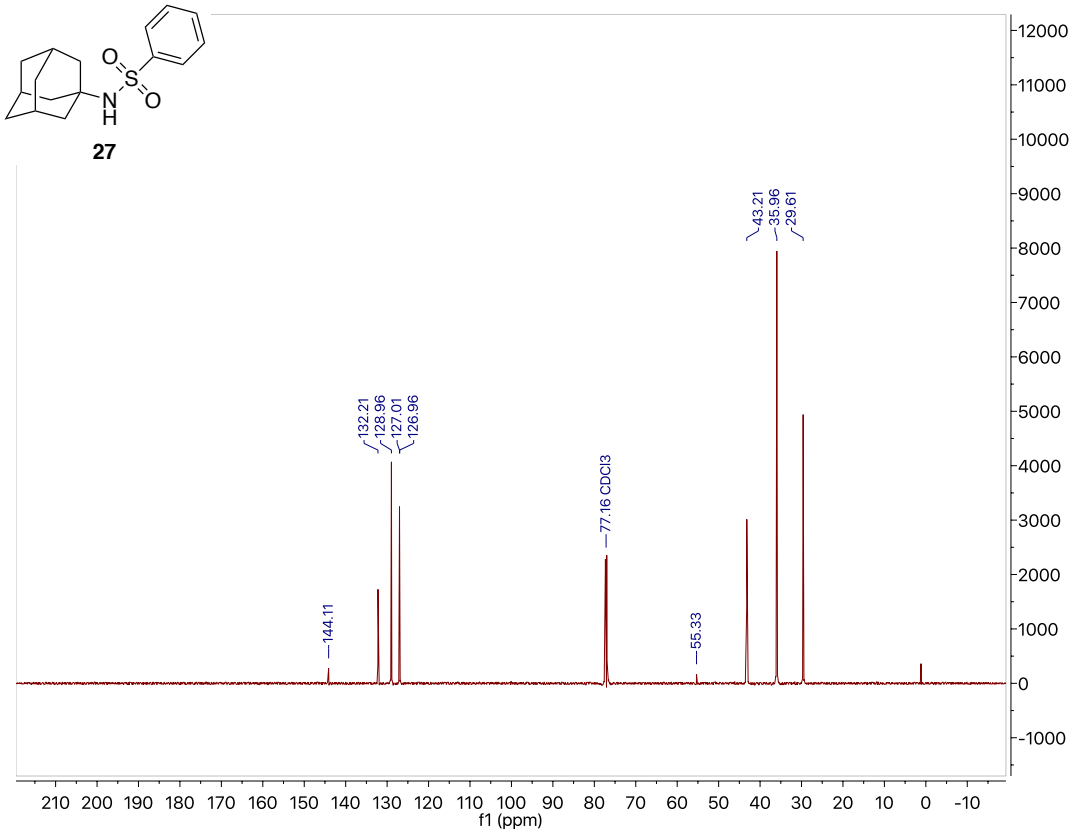

Cl
Cl
Cl
O
O
S
HN
O
O
25
7.35
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.28
7.27
7.27
7.27
7.27
7.26 CDCl3
7.17
7.17
7.16
7.16
4.83
4.81
4.76
4.74
6.11
4.05
4.04
4.04
4.04
4.04
4.03
3.00
2.99
2.99
2.98
2.97
2.96
2.96
2.95
2.94
2.79
2.79
2.78
2.77
2.76
2.75
1.00
2.03
1.01
0.91
1.10
1.11
2.11
1.23
1.22
f1 (ppm)

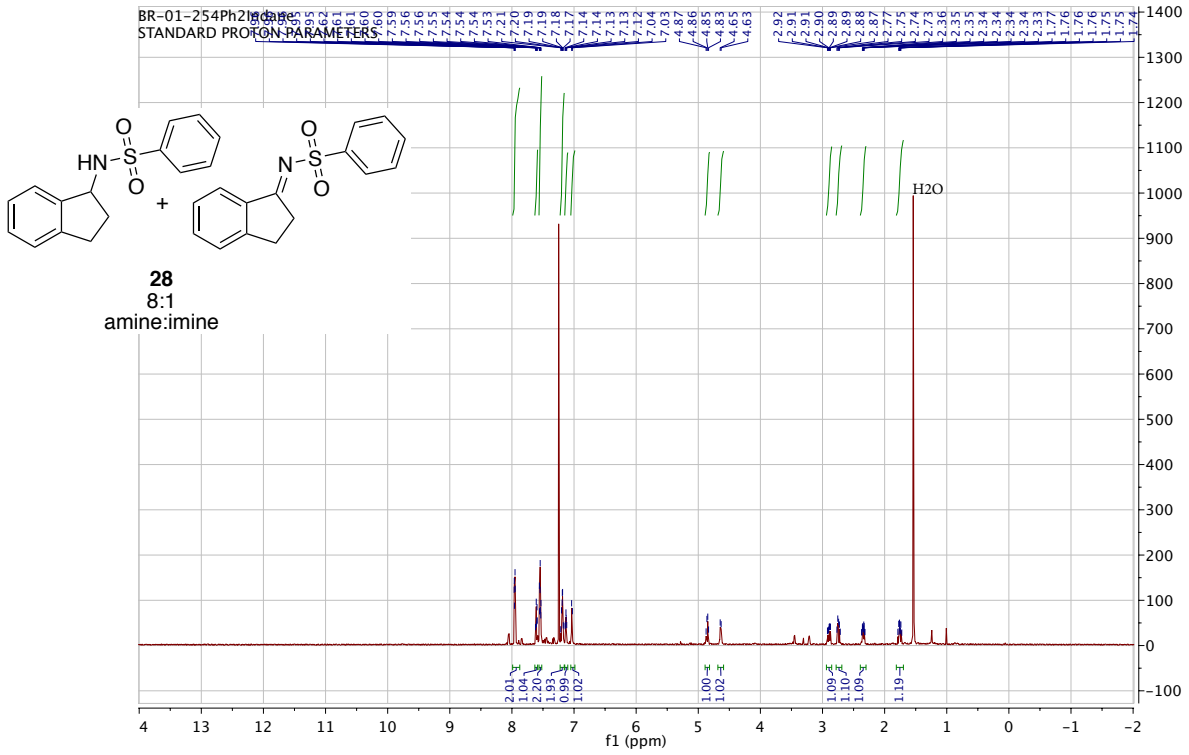

Cl
Cl
Cl
O
O
S
HN
O
O
25
80.73
78.69
77.16 CDCl3
134.77
131.70
129.16
129.12
127.20
126.98
93.66
59.83
27.74
f1 (ppm)

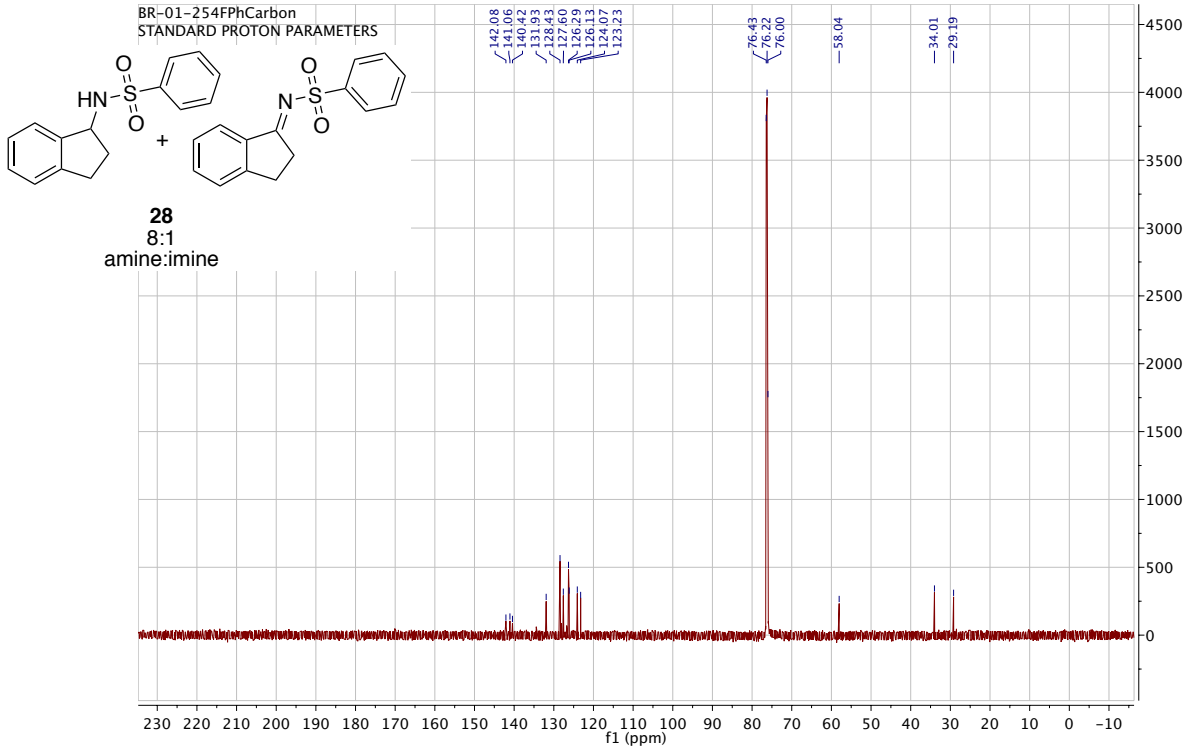

Cl
Cl
Cl
O
O
S
O
HN
MeO
26
7.40
7.39
7.27 CDCl3
6.78
6.77
6.61
4.77
4.76
4.75
4.69
4.68
3.78
3.78
2.81
2.80
2.79
2.78
2.77
2.74
2.73
2.72
2.70
2.69
2.14
2.14
2.13
2.12
2.11
2.07
2.06
2.05
2.04
2.03
2.03
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.00
1.00
0.97
2.00
2.10
3.11
1.08
1.24
1.25
1.23
2.27
f1 (ppm)

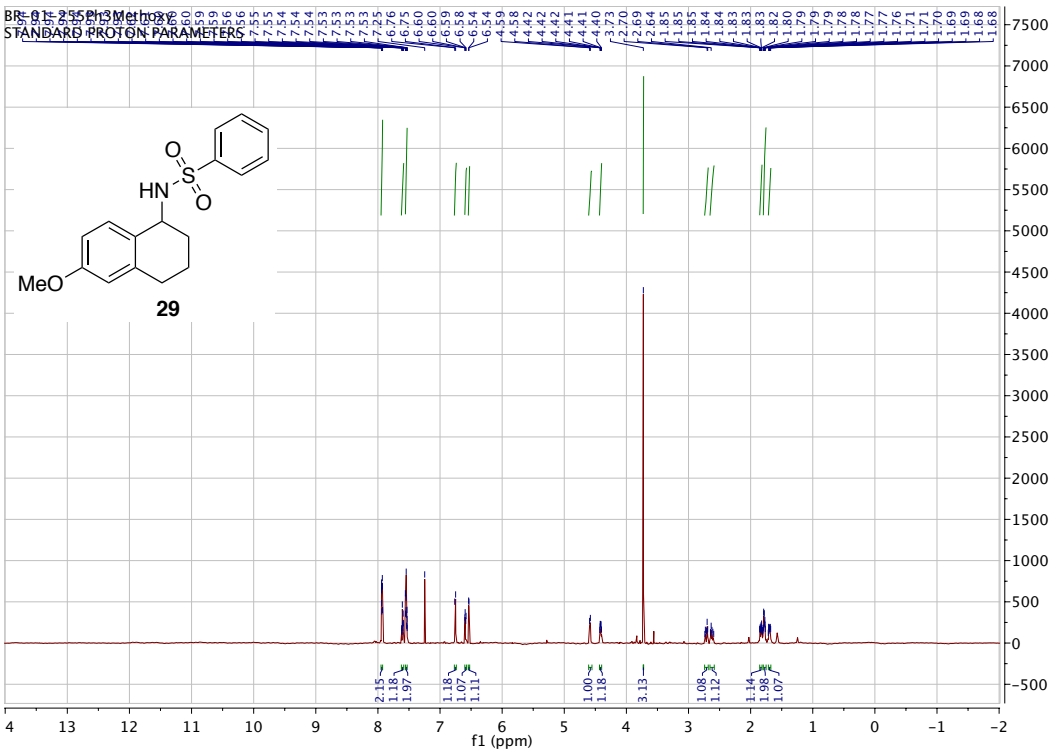

Cl
Cl
Cl
O
O
S
O
HN
MeO
26
159.39
139.24
130.71
126.76
113.78
113.14
93.76
78.20
77.16 CDCl3
55.42
53.21
30.47
29.33
18.90
f1 (ppm)

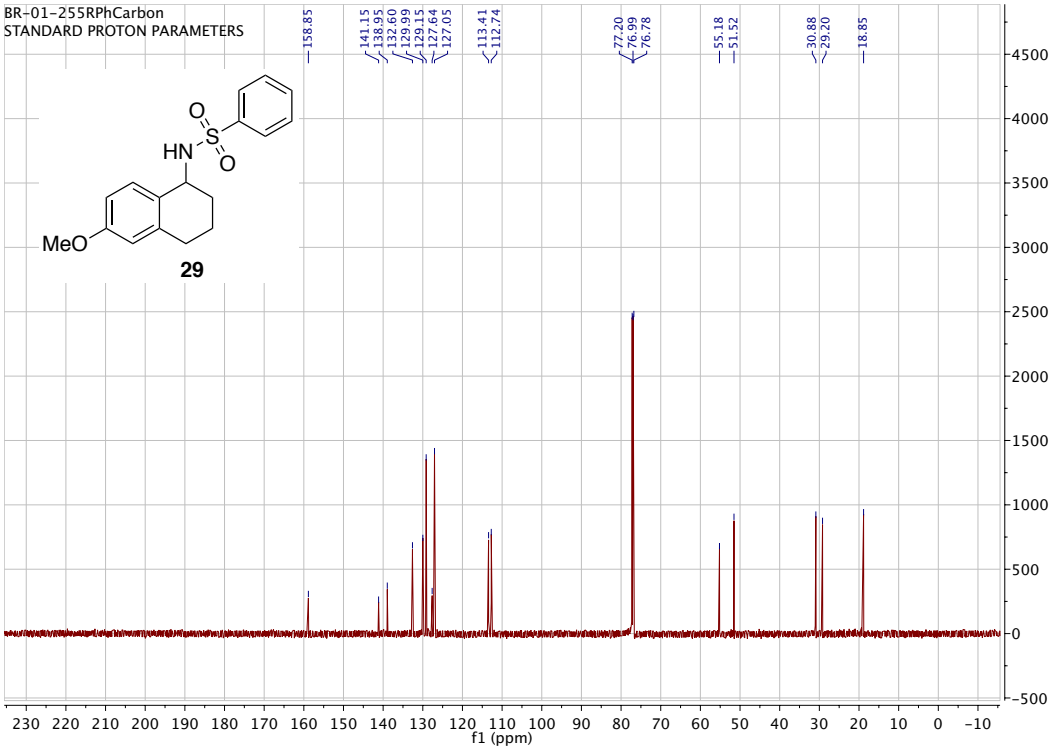

27
7.92
7.91
7.91
7.91
7.91
7.90
7.90
7.90
7.90
7.55
7.54
7.53
7.53
7.52
7.52
7.50
7.49
7.49
7.48
7.47
7.47
7.47 cdcl3
2.01
2.00
2.00
1.79 HDO
1.79 HDO
1.61
1.59
1.59
1.58
1.57
1.57
1.56
1.56
1.56
1.56
1.56
1.55
1.54
1.54
4.59
2.00
1.00
2.05
0.93
3.01
6.07
6.60
f1 (ppm)


27
144.11
132.21
128.96
127.01
126.96
77.16 CDCl3
55.33
43.21
35.96
29.61
f1 (ppm)


BR-01-254Ph2Indane
STANDARD PROTON PARAMETERS
HN
S
O
O
+
N
S
O
O
28
8:1
amine:imine
H2O
f1 (ppm)


BR-01-254FPhCarbon
STANDARD PROTON PARAMETERS
HN
S
O
O
+
N
S
O
O
28
8:1
amine:imine
142.08
141.06
140.42
131.93
128.43
127.60
126.29
126.13
124.07
123.23
76.43
76.22
76.00
58.04
34.01
29.19
f1 (ppm)


BR-01-255PhMethoxy
STANDARD PROTON PARAMETERS
MeO
29
f1 (ppm)


BR-01-255RPhCarbon
STANDARD PROTON PARAMETERS
158.85
141.15
138.95
132.60
129.99
129.15
127.64
127.05
113.41
112.74
77.20
76.99
76.78
55.18
51.52
30.88
29.20
18.85
MeO
29
f1 (ppm)