Electronic Supplementary Material (ESI) for Chemical Communications

On the Utility of *S*-Mesitylsulfinimines for the Stereoselective Synthesis of Chiral Amines and Aziridines

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Supplementary Information

Experimental

General Information

All reactions were carried out under an environment of nitrogen. Dry solvents were purchased from Sigma-Aldrich. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. All reactions were stirred with a magnetic stirrer bar. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer: points of maximum absorption (ν_{max}) were recorded in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker 400 MHz spectrometers. Chemical shifts are quoted with the deuterated solvent as the reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (integration, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, oct = octet, m = multiplet or unresolved, coupling constant(s) in Hz). Melting points were measured using a Stuart SMP40 apparatus in open capillary tubes and are uncorrected. The (*S*)-mesitylsulfinimine starting materials were prepared by the reported method with enantiomeric excesses in the range of 98-100%.[1] Diastereomeric ratios (dr's) of the mesitylsulfinamides were determined by the crude 1H NMR spectra in acetone-d_6 (where possible) and confirmed by the purified 1H NMR spectra in acetone-d_6 and in some cases by chiral HPLC analysis in comparison with the authentic racemates. The absolute configuration of the asymmetric carbon atom of the major diastereomer of a range of the mesitylsulfinamides was determined by treatment of the mesitylsulfinamide with 2M aqueous hydrochloric acid in methanol (general procedure B) and comparison of the sign of specific rotation of the obtained free amine (or amine hydrochloride) with the reported data.[2-9]

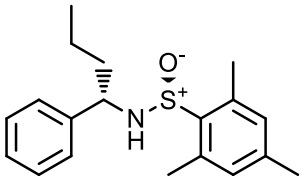
General Procedure A

A Grignard solution was added dropwise to a solution of (*S*)-mesitylsulfinimine in dry 2-methyltetrahydrofuran (1 mL) at -78 °C and stirred overnight (16-24 hr) whilst warming to room temperature. The cooled reaction mixture (0 °C) was quenched with saturated sodium bicarbonate solution and extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the crude mesitylsulfinamide, which was purified by flash chromatography.

General Procedure B

To a solution of mesitylsulfinamide (0.050-0.080 mmol) in methanol (1.5 mL), 2M aqueous hydrochloric acid (1.00 mL, 2.000 mmol) was added and it was stirred at room temperature for 1-3 hr. Then, the solvent was evaporated, a 2M aqueous hydrochloric acid solution (5 mL) was added and the mixture was extracted with three times with DCM. The organic layers were discarded. The aqueous layer was basified with solid sodium hydroxide and extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and then, either the solvent was evaporated to give the amine or 2M hydrochloric acid in ether (0.5 mL) was added and then the solvent was evaporated to give the amine hydrochloride, as required.

(*S*)-2,4,6-trimethyl-*N*-((*S*)-1-phenylbutyl)benzenesulfinamide 3a (Entry 5, Table 1)



The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (56 mg, 92.4:7.6 dr). Purification by flash chromatography on silica gel (elution with 0-50% ethyl acetate/cyclohexane) gave the *title compound* **3a** (38 mg, 0.120 mmol, 82%, 91.2:8.8 dr) as a colourless oil. Diastereomeric ratio: 90.7:9.3, determined by HPLC [Chiralcel OJ (heptane/ethanol 98:2, flow rate: 1.0 mL/min, l=215 nm, retention time: 11.039 (major), 13.184 (minor)]; $[\alpha]_D^{21}$ +177 (*c* 1.0, $CHCl_3$)]; IR (ATR) 3215, 2958, 2929, 2871, 1602, 1454, 1379, 1070, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereoisomer 7.15-7.34 (5H, m), 6.81 (2H, s), 5.70 (1H, d, *J* 6.8), 4.38 (1H, q, *J* 7.2), 2.50 (6H, s), 2.23 (3H, s), 1.89-2.00 (1H, m), 1.69-1.81 (1H, m), 1.21-1.44 (2H, m), 0.90 (3H, t, *J* 7.4); minor diastereomer 7.15-7.43 (5H, m), 6.85 (2H, s), 5.54 (1H, d, *J* 4.3), 4.34-4.44 (1H, m), 2.41 (6H, s), 2.25 (3H, s), 1.89-2.00 (1H, m), 1.70-1.81 (1H, m), 1.16-1.45 (2H, m), 0.83-0.94 (3H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereoisomer 144.9, 140.7, 139.6, 137.5, 131.4, 129.0, 127.8, 127.7, 60.3, 40.7, 21.0, 20.3, 19.7, 14.2; m/z (ES+) 338 ($[M+Na]^+$, 43%), 316 ($[M+H]^+$, 36), 299 (35), 149 (48); HRMS: Found: 316.1726 $C_{19}H_{26}NOS$ 316.1735.

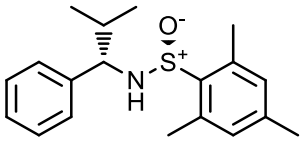
Alternative procedure for 3a (Entry 1, Table 1)

n-Propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) was added dropwise to a solution of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide (40 mg, 0.147 mmol) in dry DCM (1 mL) at -78 °C and stirred overnight (18 hr) whilst warming to room temperature. The cooled reaction mixture (0 °C) was quenched with saturated sodium bicarbonate solution and extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the crude product (48 mg, 52.6:47.4 dr). Purification by flash chromatography on silica gel (elution with 0-50% ethyl acetate/cyclohexane) gave the *title compound* **3a** (25 mg, 0.079 mmol, 54%, 50.6:49.4 dr) as a colourless oil. Spectral properties identical to previous compound **3a**.

Alternative procedure for 3a (Entry 3, Table 1)

n-Propylmagnesium chloride (2M in diethyl ether) (0.14 mL, 0.280 mmol) was added dropwise to a solution of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide (19 mg, 0.070 mmol) in dry THF (1 mL) at -78 °C and stirred for 3 hr whilst warming to room temperature. The cooled reaction mixture (0 °C) was quenched with saturated sodium bicarbonate solution and extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the crude product (25 mg, 85.8:14.2 dr). Purification by flash chromatography on silica gel (elution with 0-50% ethyl acetate/cyclohexane) gave the *title compound* **3a** (20 mg, 0.063 mmol, 90%, 84.7:15.3 dr) as a colourless oil. Spectral properties identical to previous compound **3a**.

(*S*)-2,4,6-trimethyl-*N*-((*S*)-2-methyl-1-phenylpropyl)benzenesulfinamide 3b (Entry 6, Table 1)



The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.15 mL, 0.295 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (56 mg, 98.3:1.7 dr). Purification by flash chromatography on silica gel (elution with 0-50% ethyl acetate/cyclohexane) gave the *title compound* **3b** (32 mg, 0.101 mmol, 69%, 98.2:1.8 dr) as a white solid. M.p. 98-100 °C; diastereomeric ratio: 98.2:1.8, determined by HPLC [Chiralcel OJ (heptane/ethanol 90:10, flow rate: 1.0 mL/min, l=215 nm, retention time: 7.453 min (major), 10.413 min (minor)]; $[\alpha]_D^{21}$ +224 (*c* 1.0, $CHCl_3$); IR (ATR) 3258, 2974, 2949, 2919, 2866, 1602, 1455, 1383, 1064, 1045; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.12-7.28 (5H, m), 6.76 (2H, s), 5.71 (1H, d, *J* 8.1), 4.04 (1H, t, *J* 7.9), 2.44 (6H, s), 2.20 (3H, s), 1.99-2.08 (1H, m), 0.96 (3H, d, *J* 6.5), 0.75 (3H, d, *J* 6.8); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 143.9, 140.7, 139.7, 137.5, 131.3, 128.8, 128.2, 127.6, 67.1, 35.1, 20.9, 20.0, 20.0, 19.7; m/z (ES+) 338 ($[M+Na]^+$, 50%), 316 ($[M+H]^+$, 40), 299 (50), 149 (29); HRMS: Found: 316.1745 $C_{19}H_{26}NOS$ 316.1735.

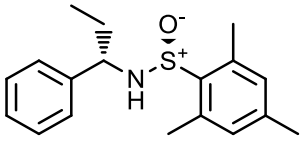
Alternative procedure for 3b (Entry 2, Table 1)

Iso-propylmagnesium chloride (2M in diethyl ether) (0.15 mL, 0.295 mmol) was added dropwise to a solution of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide (40 mg, 0.147 mmol) in dry DCM (1 mL) at -78 °C and stirred overnight (23 hr) whilst warming to room temperature. The cooled reaction mixture (0 °C) was quenched with saturated sodium bicarbonate solution and extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the crude product (46 mg, 69.0:31.0 dr). Purification by flash chromatography on silica gel (elution with 0-50% ethyl acetate/cyclohexane) gave the *title compound* **3b** (24 mg, 0.076 mmol, 52%, 67.5:32.5 dr) as a colourless oil. Spectral properties identical to previous compound **3b**.

Alternative procedure for 3b (Entry 4, Table 1)

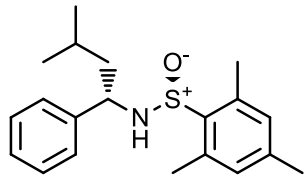
Trimethylaluminum (2M in toluene) (0.15 mL, 0.295 mmol) was added dropwise to a solution of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide (40 mg, 0.147 mmol) in dry THF (2 mL) at -78 °C and stirred for 17 min. Then, *iso*-propyllithium (0.7M in pentane) (0.84 mL, 0.590 mmol) was added dropwise and the mixture was left to warm to room temperature overnight (16 hr). The cooled reaction mixture (0 °C) was quenched with saturated sodium bicarbonate solution, filtered through a frit and extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the crude product (52 mg, 87.0:13.0 dr). Purification by flash chromatography on silica gel (elution with 0-50% ethyl acetate/cyclohexane) gave the *title compound* **3b** (37 mg, 0.117 mmol, 80%, 88.8:11.2 dr) as a pale yellow oil. Spectral properties identical to previous compound **3b**.

(*S*)-2,4,6-trimethyl-*N*-((*S*)-1-phenylpropyl)benzenesulfinamide 3c



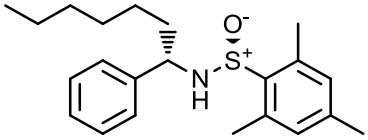
The general procedure A was followed using ethylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (49 mg, 90.6:9.4 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3c** (41 mg, 0.136 mmol, 92%, 90.8:9.2 dr) as a colourless oil. Diastereomeric ratio: 90.1:9.9, determined by HPLC [Chiralcel OJ (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 12.310 min (minor), 14.592 min (major)]; $[\alpha]_D^{20}$ +190 (*c* 1.0, $CHCl_3$)]; IR (ATR) 3213, 2964, 2928, 1602, 1453, 1378, 1071, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereoisomer 7.17-7.34 (5H, m), 6.82 (2H, s), 5.71 (1H, d, *J* 6.6), 4.29 (1H, q, *J* 7.1), 2.50 (6H, s), 2.23 (3H, s), 1.90-2.03 (1H, m), 1.74-1.90 (1H, m), 0.87 (3H, t, *J* 7.5); minor diastereoisomer 7.17-7.42 (5H, m), 6.85 (2H, s), 5.57 (1H, d, *J* 4.3), 4.24-4.34 (1H, m), 2.42 (6H, s), 2.25 (3H, s), 1.90-2.03 (1H, m), 1.74-1.90 (1H, m), 0.83-0.90 (3H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereoisomer 144.6, 140.7, 139.6, 137.5, 131.4, 129.0, 127.8, 127.8, 62.1, 31.3, 21.0, 19.7, 11.3; m/z (ES+) 324 ($[M+Na]^+$, 100%), 302 ($[M+H]^+$, 16), 237 (8), 167 (9); HRMS: Found: 324.1386 $C_{18}H_{23}NONaS$ 324.1398.

(*S*)-2,4,6-trimethyl-*N*-((*S*)-3-methyl-1-phenylbutyl)benzenesulfinamide 3d



The general procedure A was followed using *iso*-butylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (52 mg, 95.3:4.7 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3d** (38 mg, 0.115 mmol, 78%, 94.6:5.4 dr) as a colourless oil. Diastereomeric ratio: 93.6:6.4, determined by HPLC [Chiralpak IA (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 7.631 min (major), 9.215 min (minor)]; $[\alpha]_D^{20}$ +178 (*c* 1.0, $CHCl_3$); IR (ATR) 3212, 2955, 2926, 2868, 1602, 1454, 1382, 1070, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.15-7.35 (5H, m), 6.80 (2H, s), 5.74 (1H, d, *J* 7.3), 4.46 (1H, q, *J* 7.3), 2.50 (6H, s), 2.22 (3H, s), 1.79-1.89 (1H, m), 1.55-1.66 (2H, m), 0.94 (3H, d, *J* 6.3), 0.90 (3H, d, *J* 6.6); minor diastereomer 7.14-7.44 (5H, m), 6.84 (2H, s), 5.55 (1H, d, *J* 4.8), 4.39-4.52 (1H, m), 2.40 (6H, s), 2.25 (3H, s), 1.73-1.90 (1H, m), 1.53-1.68 (2H, m), 0.89-0.98 (3H, m), 0.87 (3H, d, *J* 6.3); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 145.3, 140.7, 139.6, 137.5, 131.4, 129.0, 127.7, 127.6, 58.8, 48.1, 25.6, 23.0, 22.7, 21.0, 19.6; m/z (ES+) 352 ($[M+Na]^+$, 100%), 330 ($[M+H]^+$, 12), 313 (12), 167 (12), 164 (13); HRMS: Found: 352.1699 $C_{20}H_{27}NONaS$ 352.1711.

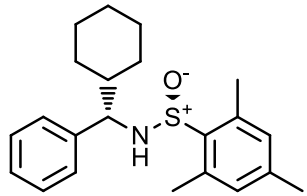
(*S*)-2,4,6-trimethyl-*N*-((*S*)-1-phenylheptyl)benzenesulfinamide 3e



The general procedure A was followed using *n*-hexylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (58 mg, 74.2:25.8 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3e** (39 mg, 0.109 mmol, 74%, 73.6:26.4 dr) as a colourless oil.

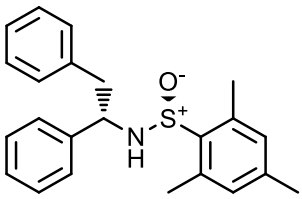
Diastereomeric ratio: 72.1:27.9, determined by HPLC [Chiralpak IA (heptane/ethanol 98:2, flow rate: 1.0 mL/min, l=215 nm, retention time: 13.888 min (major), 18.538 (minor)]; $[\alpha]_D^{21}$ +150 (*c* 1.0, $CHCl_3$); IR (ATR) 3209, 2926, 2856, 1602, 1454, 1378, 1071, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.15-7.44 (5H, m), 6.81 (2H, s), 5.79 (1H, d, *J* 7.1), 4.36 (1H, q, *J* 7.2), 2.50 (6H, s), 2.23 (3H, s), 1.83-2.00 (1H, m), 1.68-1.83 (1H, m), 1.14-1.42 (8H, m), 0.85 (3H, t, *J* 6.8); minor diastereomer 7.14-7.44 (5H, m), 6.85 (2H, s), 5.64 (1H, d, *J* 4.5), 4.31-4.42 (1H, m), 2.41 (6H, s), 2.25 (3H, s), 1.83-2.00 (1H, m), 1.68-1.83 (1H, m), 1.13-1.42 (8H, m), 0.80-0.89 (3H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 145.0, 140.6, 139.5, 137.4, 131.3, 129.0, 127.7, 127.7, 60.6, 38.5, 32.6, 29.8, 27.1, 23.3, 20.9, 19.7, 14.4; m/z (ES+) 380 ($[M+Na]^+$, 100%), 358 (15), 341 (22), 192 (13), 166 (6); HRMS: Found: 380.2024 $C_{22}H_{31}NONaS$ 380.2024.

(*S*)-*N*-((*S*)-cyclohexyl(phenyl)methyl)-2,4,6-trimethylbenzenesulfinamide 3f



The general procedure A was followed using cyclohexylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (61 mg, 98.9:1.1 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3f** (46 mg, 0.129 mmol, 88%, 99.3:0.7 dr) as a white solid. M.p. 120-122 °C; diastereomeric ratio: 98.5:1.5, determined by HPLC [Whelk-o 1 (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 15.371 min (minor), 22.016 min (major)]; $[\alpha]_D^{21}$ +171 (*c* 1.0, $CHCl_3$); IR (ATR) 3272, 2934, 2853, 1600, 1448, 1421, 1070, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.21-7.29 (4H, m), 7.13-7.20 (1H, m), 6.79 (2H, s), 5.82 (1H, d, *J* 8.6), 4.06 (1H, t, *J* 8.3), 2.46 (6H, s), 2.22 (3H, s), 1.97-2.07 (1H, m), 1.53-1.76 (4H, m), 1.31-1.40 (1H, m), 0.81-1.23 (5H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 144.1, 140.5, 139.6, 137.3, 131.3, 128.8, 128.1, 127.5, 66.6, 44.7, 30.9, 30.8, 27.1, 26.8, 26.8, 20.9, 19.7; m/z (ES+) 378 ($[M+Na]^+$, 100%), 339 (15), 190 (7), 167 (6); HRMS: Found: 378.1857 $C_{22}H_{29}NONaS$ 378.1868.

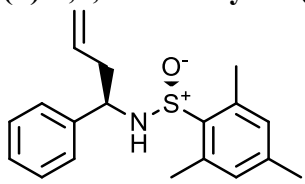
(*S*)-*N*-((*S*)-1,2-diphenylethyl)-2,4,6-trimethylbenzenesulfinamide 3g



The general procedure A was followed using benzylmagnesium chloride (1M in diethyl ether) (044 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (74 mg, 70.0:30.0 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3g** (50 mg, 0.137 mmol, 93%, 69.9:30.1 dr) as a white solid. M.p. 103-105 °C; diastereomeric ratio: 77.1:22.9, determined by HPLC [Chiralcel OD-H (heptane/ethanol 98:2, flow rate: 1.0 mL/min, l=215 nm, retention time: 10.103 min (minor), 15.578 min (major)]; $[\alpha]_D^{21}$ +185 (*c* 1.0, $CHCl_3$); IR (ATR) 3257, 3028, 2926, 1602, 1495, 1454, 1066, 1045; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.10-7.50 (10H, m), 6.78 (2H, s), 5.76 (1H, d, *J* 7.3), 4.65 (1H, ddd, *J* 8.2, 7.3, 6.6), 3.21 (1H, dd, *J* 13.6, 8.2), 3.11 (1H, dd, *J* 13.6, 6.6),

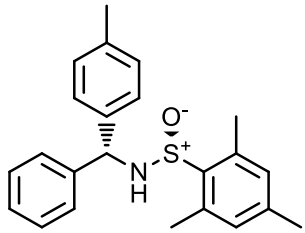
2.32 (6H, s), 2.22 (3H, s); minor diastereomer 7.11-7.48 (10H, m), 6.83 (2H, s), 5.23 (1H, d, *J* 3.5), 4.71 (1H, ddd, *J* 8.3, 6.6, 3.5), 3.13 (1H, dd, *J* 13.6, 6.6), 3.06 (1H, dd, *J* 13.6, 8.3), 2.27 (6H, s), 2.25 (3H, s); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 144.3, 140.7, 139.7, 139.7, 137.5, 131.3, 130.4, 129.0, 129.0, 128.0, 127.9, 127.1, 62.8, 45.1, 21.0, 19.5; minor diastereomer 143.0, 141.2, 139.5, 138.8, 137.6, 131.4, 130.3, 129.4, 129.2, 128.7, 128.5, 127.5, 60.3, 45.5, 21.0, 19.1; m/z (ES+) 386 ([M+Na]$^+$, 100%), 364 ([M+H]$^+$, 19); HRMS: Found: 364.1724 $C_{23}H_{26}NOS$ 364.1730.

(*S*)-2,4,6-trimethyl-*N*-((*R*)-1-phenylbut-3-en-1-yl)benzenesulfinamide 3h



The general procedure A was followed using allylmagnesium bromide (1M in diethyl ether) (044 mL, 0.442 mmol) and (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) and gave the crude product (55 mg, 83.4:16.6 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3h** (41 mg, 0.131 mmol, 89%, 83.2:16.8 dr) as a colourless oil. Diastereomeric ratio: 84.0:16.0, determined by HPLC [Chiralcel OJ (heptane/ethanol 98:2, flow rate: 1.0 mL/min, l=215 nm, retention time: 10.342 min (major), 16.032 min (minor)]; $[\alpha]_D^{21}$ +157 (*c* 1.0, $CHCl_3$); IR (ATR) 3212, 3029, 2922, 1601, 1454, 1380, 1071, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.25-7.46 (5H, m), 6.87 (2H, s), 5.77 (1H, m), 5.41 (1H, d, *J* 4.3), 5.03-5.13 (2H, m), 4.50 (1H, td, *J* 7.1, 4.3), 2.59 (2H, dd, *J* 7.1, 6.5), 2.43 (6H, s), 2.26 (3H, s); minor diastereomer 7.16-7.46 (5H, m), 6.82 (2H, s), 5.69-5.83 (2H, m), 4.95-5.03 (2H, m), 4.43-4.53 (1H, m), 2.56-2.63 (2H, m), 2.50 (6H, s), 2.23 (3H, s); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 143.3, 141.1, 139.7, 137.6, 135.9, 131.4, 129.2, 128.5, 128.4, 118.5, 58.8, 43.5, 21.0, 19.4; m/z (ES+) 336 ([M+Na]$^+$, 93%), 314 ([M+H]$^+$, 100), 287 (53), 261 (39), 217 (27), 167 (17); HRMS: Found: 314.1569 $C_{19}H_{24}NOS$ 314.1579.

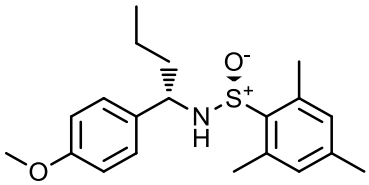
(*S*)-2,4,6-trimethyl-*N*-((*R*)-phenyl(*p*-tolyl)methyl)benzenesulfinamide 3i



p-Tolylmagnesium bromide (0.5M in diethyl ether) (1.77 mL, 0.884 mmol) was added to copper(I) iodide (84 mg, 0.442 mmol) in dry tetrahydrofuran (1 mL) at -30 °C and stirred for 35 min. The reaction mixture was cooled to -60 °C and a solution of (*S*,*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfinamide **2a** (40 mg, 0.147 mmol) in dry tetrahydrofuran (1 mL) was added slowly to the reaction mixture, and it was allowed to warm to room temperature overnight (16 hr). The cooled reaction mixture (0 °C) was quenched with saturated sodium bicarbonate solution, filtered through a frit and flushed and extracted three times with DCM. The combined organic layers were dried using a hydrophobic frit and concentrated to give the crude mesitylsulfinamide (79 mg). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **3i** (34 mg, 0.094 mmol, 64%, 82.6:17.4 dr) as a cream solid. M.p. 125-127 °C; diastereomeric ratio: 83.3:16.7, determined by HPLC [Chiralpak AD-H (heptane/isopropanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 23.927 min (major), 32.610 min (minor)]; $[\alpha]_D^{21}$ +140 (*c*

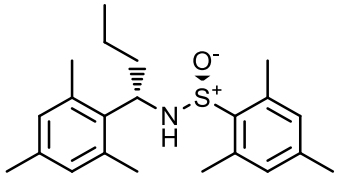
1.0, $CHCl_3$); IR (ATR) 3210, 3021, 2920, 1601, 1509, 1453, 1072, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.36 (4H, d, *J* 7.8), 7.26 (3H, t, *J* 7.4), 7.15 (2H, d, *J* 7.8), 6.85 (2H, s), 5.88 (1H, d, *J* 4.5), 5.66 (1H, d, *J* 4.8), 2.49 (6H, s), 2.30 (3H, s), 2.25 (3H, s); minor diastereomer 7.48 (2H, d, *J* 7.3), 7.13-7.39 (5H, m), 7.08 (2H, d, *J* 7.8), 6.85 (2H, s), 5.83-5.91 (1H, m), 5.64-5.68 (1H, m), 2.49 (6H, s), 2.26 (3H, s), 2.25 (3H, s); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 144.2, 141.0, 140.3, 139.3, 137.9, 137.8, 131.5, 129.9, 129.2, 128.9, 128.3, 128.0, 63.0, 21.2, 21.0, 19.6; m/z (ES+) 386 ($[M+Na]^+$, 100%), 364 ($[M+H]^+$, 19); HRMS: Found: 364.1724 $C_{23}H_{26}NOS$ 364.1730.

(*S*)-*N*-((*S*)-1-(4-methoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide 4b



The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(4-methoxybenzylidene)-2,4,6-trimethylbenzenesulfinamide **2b** (45 mg, 0.150 mmol) and gave the crude product (53 mg, 85.4:14.6 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4b** (42 mg, 0.120 mmol, 80%, 85.3:14.7 dr) as a white solid. M.p. 50-52 °C; diastereomeric ratio: 84.5:15.5, determined by HPLC [Chiralpak IA (heptane/ethanol 96:4, flow rate: 1.0 mL/min, l=215 nm, retention time: 13.942 min (major), 17.372 min (minor)]; $[\alpha]_D^{21}$ +169 (*c* 1.0, $CHCl_3$); IR (ATR) 3214, 2959, 2934, 2872, 1613, 1516, 1459, 1254, 1179, 1024; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.23 (2H, d, *J* 8.6), 6.82 (2H, d, *J* 8.6), 6.82 (2H, s), 5.54 (1H, d, *J* 6.3), 4.33 (1H, q, *J* 7.0), 3.76 (3H, s), 2.50 (6H, s), 2.23 (3H, s), 1.89-2.00 (1H, m), 1.69-1.79 (1H, m), 1.16-1.41 (2H, m), 0.89 (3H, t, *J* 7.3); minor diastereomer 7.32 (2H, d, *J* 8.7), 6.90 (2H, d, *J* 8.7), 6.84 (2H, s), 5.43 (1H, d, *J* 4.0), 4.28-4.39 (1H, m), 3.79 (3H, s), 2.42 (6H, s), 2.25 (3H, s), 1.65-2.01 (2H, m), 1.16-1.41 (2H, m), 0.86 (3H, t, *J* 7.4); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 159.8, 140.7, 139.7, 137.5, 136.7, 131.4, 128.9, 114.4, 59.7, 55.5, 40.6, 21.0, 20.3, 19.7, 14.2; m/z (ES+) 368 ($[M+Na]^+$, 100%), 346 ($[M+H]^+$, 68), 329 (46), 217 (25); HRMS: Found: 346.1840 $C_{20}H_{28}NO_2S$ 346.1841.

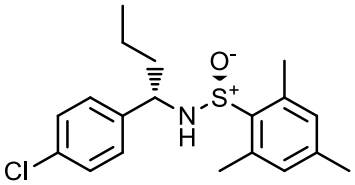
(*S*)-*N*-((*S*)-1-mesitylbutyl)-2,4,6-trimethylbenzenesulfinamide 4c



The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-2,4,6-trimethyl-*N*-(2,4,6-trimethylbenzylidene]benzenesulfinamide **2c** (47 mg, 0.150 mmol) and gave the crude product (59 mg, 93.9:6.1 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4c** (51 mg, 0.141 mmol, 94%, 94.5:5.5 dr) as a white solid. M.p. 66-68 °C; $[\alpha]_D^{21}$ +188 (*c* 1.0, $CHCl_3$); IR (ATR) 3248, 2957, 2927, 2870, 1605, 1454, 1377, 1071, 1050; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.85 (2H, s), 6.76 (2H, s), 5.30 (1H, d, *J* 5.1), 4.88 (1H, td, *J* 7.6, 5.1), 2.51 (6H, s), 2.44 (3H, br. s.), 2.27 (3H, br. s.), 2.24 (3H, s), 2.18 (3H, s), 2.07-2.17 (1H, m), 1.83-1.94 (1H, m), 1.33-1.48 (1H, m), 1.11-1.27 (1H, m), 0.91 (3H, t, *J* 7.3); minor diastereomer 6.85 (2H, s), 6.82 (2H, s), 5.22 (1H, d, *J* 2.5), 4.95 (1H, td, *J* 7.6, 2.5), 2.16-2.55 (18H, m), 2.07-

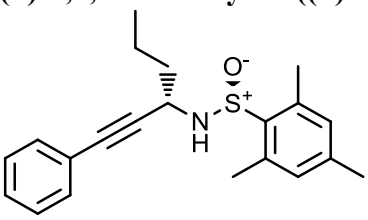
2.17 (1H, m), 1.83-1.94 (1H, m), 1.33-1.48 (1H, m), 1.11-1.27 (1H, m), 0.90 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 140.8, 139.4, 137.6, 137.2, 137.1, 136.9, 136.6, 132.0, 131.5, 129.9, 55.7, 37.5, 21.5, 21.3, 21.0, 20.9, 20.8, 19.6, 14.5; m/z (ES+) 380 ($[M+Na]^+$, 68%), 358 ($[M+H]^+$, 82), 341 (19), 238 (19), 217 (24); HRMS: Found: 358.2208 $C_{22}H_{32}NOS$ 358.2205.

(*S*)-*N*-((*S*)-1-(4-chlorophenyl)butyl)-2,4,6-trimethylbenzenesulfinamide 4d



The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(4-(chlorobenzylidene)-2,4,6-trimethylbenzenesulfinamide **2d** (46 mg, 0.150 mmol) and gave the crude product (57 mg, 88.4:11.6 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4d** (48 mg, 0.138 mmol, 92%, 86.7:13.3 dr) as a white solid. M.p. 75-77 °C; diastereomeric ratio: 86.3:13.7, determined by HPLC [Chiralpak IA (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 8.909 min (major), 11.568 min (minor)]; $[\alpha]_D^{21}$ +164 (*c* 1.0, $CHCl_3$); IR (ATR) 3204, 2959, 2929, 2872, 1601, 1460, 1408, 1065, 1032; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.32 (2H, d, *J* 8.6), 7.26 (2H, d, *J* 8.6), 6.79 (2H, s), 5.81 (1H, d, *J* 7.1), 4.41 (1H, q, *J* 7.1), 2.49 (6H, s), 2.22 (3H, s), 1.83-1.95 (1H, m), 1.67-1.78 (1H, m), 1.22-1.43 (2H, m), 0.90 (3H, t, *J* 7.4); minor diastereomer 7.43 (2H, d, *J* 8.6), 7.37 (2H, d, *J* 8.6), 6.85 (2H, s), 5.62 (1H, d, *J* 4.0), 4.36-4.45 (1H, m), 2.42 (6H, s), 2.25 (3H, s), 1.83-1.95 (1H, m), 1.67-1.78 (1H, m), 1.22-1.43 (2H, m), 0.88 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 144.1, 140.8, 139.3, 137.6, 132.9, 131.4, 129.5, 129.0, 59.5, 40.7, 21.0, 20.2, 19.7, 14.1; m/z (ES+) 372 ($[M+Na]^+$, 69%), 350 ($[M+H]^+$, 100), 333 (21), 217 (36); HRMS: Found: 350.1335 $C_{19}H_{25}NOSCl$ 350.1345.

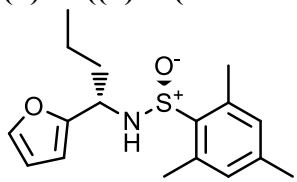
(*S*)-2,4,6-trimethyl-*N*-((*S*)-1-phenylhex-1-yn-3-yl)benzenesulfinamide 4e



The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-2,4,6-trimethyl-*N*-(3-phenylpropyn-2-yn-1-ylidene]benzenesulfinamide **2e** (44 mg, 0.150 mmol) and gave the crude product (50 mg, 88.0:12.0 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4e** (41 mg, 0.121 mmol, 81%, 88.0:12.0 dr) as a colourless oil. Diastereomeric ratio: 87.1:12.9, determined by HPLC [Chiralpak IA (heptane/isopropanol 97:3, flow rate: 1.0 mL/min, l=215 nm, retention time: 15.924 min (major), 17.239 min (minor)]; $[\alpha]_D^{21}$ +115 (*c* 1.0, $CHCl_3$); IR (ATR) 3200, 2959, 2927, 2871, 1600, 1490, 1443, 1379, 1070, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.29-7.40 (5H, m), 6.87 (2H, s), 5.77 (1H, d, *J* 6.8), 4.33 (1H, q, *J* 7.1), 2.58 (6H, s), 2.25 (3H, s), 1.76-1.95 (2H, m), 1.51-1.65 (2H, s), 0.97 (3H, t, *J* 7.4); minor diastereomer 7.29-7.46 (5H, m), 6.87 (2H, s), 5.65 (1H, d, *J* 6.3), 4.31-4.39 (1H, m), 2.58 (6H, s), 2.26 (3H, s), 1.76-1.95 (2H, m), 1.51-1.65 (2H, s), 0.93 (3H, t, *J* 7.6); ^{13}C NMR (101 MHz, acetone-d_6)

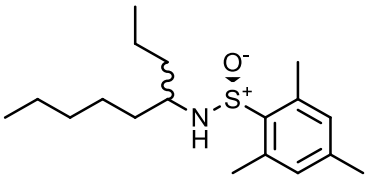
major diastereomer 141.0, 139.4, 137.7, 132.4, 131.5, 129.3, 129.1, 124.2, 90.9, 84.5, 48.3, 40.4, 21.0, 20.0, 19.6, 14.0; m/z (ES+) 362 ([M+Na]$^+$, 100%), 340 ([M+H]$^+$, 62), 217 (27); HRMS: Found: 340.1738 $C_{21}H_{26}NOS$ 340.1735.

(*S*)-*N*-((*S*)-1-(furan-2-yl)butyl)-2,4,6-trimethylbenzenesulfinamide 4f



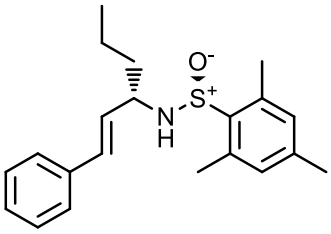
The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(furan-2-ylmethylene]-2,4,6-trimethylbenzenesulfinamide **2f** (39 mg, 0.150 mmol) and gave the crude product (50 mg, 86.8:13.2 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4f** (42 mg, 0.138 mmol, 92%, 87.6:12.4 dr) as a white solid. M.p. 48-50 °C; diastereomeric ratio: 86.4:13.6, determined by HPLC [Chiralpak IA (heptane/isopropanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 10.691 min (minor), 12.045 min (major)]; $[\alpha]_D^{21}$ +161 (*c* 1.0, $CHCl_3$); IR (ATR) 3170, 2956, 2929, 2871, 1602, 1453, 1377, 1150, 1069, 1045; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.43 (1H, dd, *J* 1.8, 0.8), 6.85 (2H, s), 6.32 (1H, dd, *J* 3.3, 1.8), 6.26 (1H, dd, *J* 3.3, 0.8), 5.69 (1H, d, *J* 7.3), 4.44 (1H, q, *J* 7.1), 2.51 (6H, s), 2.25 (3H, s), 1.86-1.95 (2H, m), 1.28-1.49 (2H, m), 0.92 (3H, t, *J* 7.4); minor diastereomer 7.47 (1H, dd, *J* 1.8, 0.8), 6.85 (2H, s), 6.36 (1H, dd, *J* 3.1, 1.8), 6.30-6.33 (1H, m), 5.57 (1H, d, *J* 6.3), 4.40-4.49 (1H, m), 2.47 (6H, s), 2.25 (3H, s), 1.82-1.98 (2H, m), 1.28-1.49 (2H, m), 0.88 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 157.2, 142.6, 140.8, 139.8, 137.5, 131.4, 111.0, 107.3, 54.5, 38.2, 21.0, 20.0, 19.6, 14.1; m/z (ES+) 328 ([M+Na]$^+$, 100%), 306 ([M+H]$^+$, 29), 289 (25), 217 (12); HRMS: Found: 306.1525 $C_{17}H_{24}NO_2S$ 306.1528.

(*S*)-2,4,6-trimethyl-*N*-(nonan-4-yl)benzenesulfinamide 4g



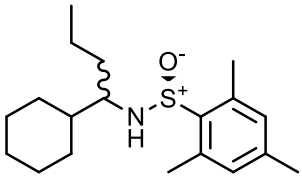
The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-hexylidene-2,4,6-trimethylbenzenesulfinamide **2g** (40 mg, 0.150 mmol) and gave the crude product (46 mg). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4g** (25 mg, 0.081 mmol, 54%) as a colourless oil. Diastereomeric ratio: 57.1:42.9, determined by HPLC [Chiralpak AY-H (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 24.387 min (major), 29.656 min (minor)]; $[\alpha]_D^{20}$ +169 (*c* 1.0, $CHCl_3$); IR (ATR) 3211, 2956, 2928, 2859, 1602, 1458, 1378, 1069, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major and minor diastereomers 6.86 (2H, s), 5.07-5.16 (1H, m), 3.18-3.29 (1H, m), 2.55 (6H, s), 2.25 (3H, s), 1.15-1.65 (12H, m), 0.82-0.94 (6H, m); ^{13}C NMR (101 MHz, acetone-d_6) major and minor diastereomers 140.5, 140.4, 137.2, 137.2, 131.4, 131.3, 57.3, 57.1, 39.5, 39.3, 37.2, 37.0, 32.7, 32.6, 26.5, 26.2, 23.4, 23.4, 21.0, 19.9, 19.7, 19.7, 19.7, 14.4; m/z (ES+) 332 ([M+Na]$^+$, 32%), 310 ([M+H]$^+$, 43), 293 (24); HRMS: Found: 310.2198 $C_{18}H_{32}NOS$ 310.2205.

(*S*)-2,4,6-trimethyl-*N*-((*S*,*E*)-1-phenylhex-1-en-3-yl)benzenesulfinamide 4h



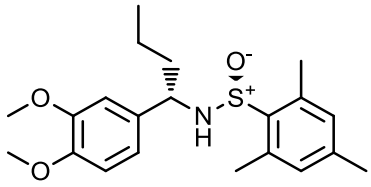
The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-2,4,6-trimethyl-*N*-((*E*)-3-phenylallylidene)benzenesulfinamide **2h** (45 mg, 0.150 mmol) and gave the crude product (51 mg, 91.2:8.8 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the impure product (45 mg) which was further purified by purification by flash chromatography on silica gel (elution with 0-13% ethyl acetate/DCM) to give the *title compound* **4h** (37 mg, 0.108 mmol, 72%, 91.8:8.2 dr) as a colourless oil. Diastereomeric ratio: 91.7:8.3, determined by HPLC [Chiralpak IA (heptane/ethanol 97:3, flow rate: 1.0 mL/min, l=215 nm, retention time: 13.066 min (major), 18.097 min (minor)]; $[\alpha]_D^{21}$ +166 (*c* 1.0, $CHCl_3$); IR (ATR) 3209, 2958, 2929, 2870, 1601, 1450, 1379, 1071, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.36 (2H, d, *J* 7.3), 7.30 (2H, t, *J* 7.3), 7.21 (1H, t, *J* 7.3), 6.85 (2H, s), 6.52 (1H, d, *J* 16.1), 6.26 (1H, dd, *J* 16.1, 7.1), 5.45 (1H, d, *J* 6.8), 4.01 (1H, qn, *J* 7.0), 2.59 (6H, s), 2.23 (3H, s), 1.58-1.81 (2H, m), 1.39-1.52 (2H, m), 0.94 (3H, t, *J* 7.4); minor diastereomer 7.14-7.47 (5H, m), 6.87 (2H, s), 6.65 (1H, d, *J* 15.9), 6.21-6.31 (1H, m), 5.35 (1H, d, *J* 5.0), 3.94-4.08 (1H, m), 2.53 (6H, s), 2.26 (3H, s), 1.58-1.81 (2H, m), 1.39-1.52 (2H, m), 0.85-0.97 (3H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 140.7, 139.8, 138.2, 137.5, 133.2, 131.4, 131.1, 129.4, 128.2, 127.3, 58.6, 39.1, 21.0, 19.9, 19.7, 14.2; m/z (ES+) 364 ($[M+Na]^+$, 98%), 342 ($[M+H]^+$, 100), 325 (20); HRMS: Found: 342.1898 $C_{21}H_{28}NOS$ 342.1892.

(*S*)-*N*-(1-cyclohexylbutyl)-2,4,6-trimethylbenzenesulfinamide 4i



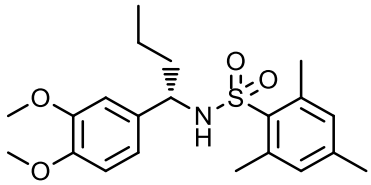
The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(cyclohexylmethylene)-2,4,6-trimethylbenzenesulfinamide **2i** (42 mg, 0.150 mmol) and gave the crude product (56 mg, 58.8:41.2 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4i** (35 mg, 0.109 mmol, 73%, 58.2:41.8 dr) as a white solid. M.p. 71-73 °C; $[\alpha]_D^{21}$ +159 (*c* 1.0, $CHCl_3$); IR (ATR) 3220, 2923, 2852, 1602, 1448, 1378, 1068, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.87 (2H, s), 4.98 (1H, d, *J* 8.1), 3.03-3.13 (1H, m), 2.55 (6H, s), 2.25 (3H, s), 0.92-1.81 (15H, m), 0.88 (3H, t, *J* 6.8); minor diastereomer 6.87 (2H, s), 5.13 (1H, d, *J* 8.6), 3.03-3.13 (1H, m), 2.55 (6H, s), 2.25 (3H, s), 0.92-1.81 (15H, m), 0.84-0.91 (3H, m); ^{13}C NMR (101 MHz, acetone-d_6) major and minor diastereomers 140.9, 140.7, 140.6, 140.5, 137.2, 137.1, 131.4, 131.3, 62.5, 62.0, 44.0, 43.6, 35.9, 35.7, 29.8, 29.3, 27.5, 27.4, 27.3, 27.3, 27.2, 21.0, 20.3, 19.9, 19.8, 19.7, 14.4, 14.4; m/z (ES+) 344 ($[M+Na]^+$, 34%), 322 ($[M+H]^+$, 100), 305 (19); HRMS: Found: 322.2199 $C_{19}H_{32}NOS$ 322.2205.

(*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide 4j



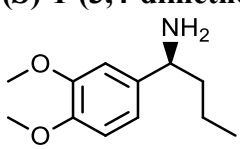
The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(3,4-dimethoxybenzylidene)-2,4,6-trimethylbenzenesulfinamide **2j** (50 mg, 0.150 mmol) and gave the crude product (64 mg, 79.4:20.6 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4j** (50 mg, 0.133 mmol, 89%, 82.0:18.0 dr) as a white solid. M.p. 123-125 °C; $[\alpha]_D^{21}$ +153 (*c* 1.0, $CHCl_3$); IR (ATR) 3247, 2955, 2915, 2871, 1595, 1516, 1456, 1260, 1023; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.94 (1H, s), 6.82 (4H, s), 5.60 (1H, d, *J* 6.8), 4.32 (1H, q, *J* 7.2), 3.76 (3H, s), 3.76 (3H, s), 2.51 (6H, s), 2.23 (3H, s), 1.83-1.98 (1H, m), 1.67-1.83 (1H, m), 1.20-1.44 (2H, m), 0.90 (3H, t, *J* 7.3); minor diastereomer 7.03 (1H, s), 6.90 (2H, s), 6.85 (2H, s), 5.42 (1H, d, *J* 4.3), 4.28-4.38 (1H, m), 3.80 (3H, s), 3.77 (3H, s), 2.44 (6H, s), 2.25 (3H, s), 1.83-1.98 (1H, m), 1.67-1.83 (1H, m), 1.20-1.44 (2H, m), 0.87 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 150.3, 149.5, 140.7, 139.7, 137.6, 137.5, 131.4, 119.8, 112.6, 112.0, 59.9, 56.2, 56.1, 40.8, 21.0, 20.4, 19.7, 14.2; m/z (ES+) 398 ($[M+Na]^+$, 100%), 376 ($[M+H]^+$, 97), 235 (18); HRMS: Found: 376.1939 $C_{21}H_{30}NO_3S$ 376.1946.

(*S*)-*N*-(1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfonamide



3-Chloroperbenzoic acid (22 mg, 0.089 mmol) (70% purity) was added to a solution of (*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide **4j** (30 mg, 0.080 mmol) in DCM (1 mL) at room temperature and was stirred for 2.5 hr. A saturated sodium bicarbonate solution (3 mL) was added and the mixture was extracted three times with DCM. The combined organic phase was washed with a saturated sodium bicarbonate solution, dried using a hydrophobic frit and the solvent evaporated to give the *title compound* (29 mg, 0.075 mmol, 94%) as a yellow oil. $[\alpha]_D^{21}$ -19 (*c* 1.1, $CHCl_3$); IR (ATR) 3296, 2958, 2936, 2872, 1603, 1514, 1454, 1319, 1261, 1147; ^{1}H NMR (400 MHz, acetone-d_6) 6.81 (2H, s), 6.68 (1H, d, *J* 1.9 Hz), 6.64 (1H, d, *J* 8.2), 6.62-6.66 (1H, m), 6.59 (1H, dd, *J* 8.2, 1.9), 4.17 (1H, q, *J* 7.8), 3.71 (3H, s), 3.66 (3H, s), 2.50 (6H, s), 2.19 (3H, s), 1.74-1.85 (1H, m), 1.59-1.70 (1H, m), 1.14-1.39 (2H, m), 0.83 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, acetone-d_6) 150.1, 149.5, 142.1, 139.3, 136.9, 135.5, 132.4, 119.6, 112.5, 111.1, 58.4, 56.3, 55.9, 40.5, 23.3, 20.8, 20.1, 13.9; m/z (ES+) 414 ($[M+Na]^+$, 14%), 392 ($[M+H]^+$, 12), 193 (18), 151 (100); HRMS: Found: 392.1875 $C_{21}H_{30}NO_4S$ 392.1890.

(*S*)-1-(3,4-dimethoxyphenyl)butan-1-amine



Trifluoroacetic acid (0.01 mL, 0.130 mmol) was added to a solution of (*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide **4j** (20 mg, 0.053 mmol,

82.0:18.0 dr) in dry methanol (2 mL) and stirred for 3 hr. The solvent was evaporated to give the crude product, to which DCM (5 mL) and 2M hydrochloric acid (5 mL) were added. The organic phase was discarded. The acid phase was basified with solid sodium hydroxide and then extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the *title compound* (9.4 mg, 0.045 mmol, 85%, 64% ee) as a colourless oil. $[\alpha]_D^{20}$ -5 (*c* 0.8, $CHCl_3$, 64% ee); IR (ATR) 3368, 3305, 2955, 2931, 1592, 1511, 1461, 1258, 1231, 1138; ^{1}H NMR (400 MHz, $CDCl_3$) 6.89 (1H, s), 6.83 (2H, s), 3.90 (3H, s), 3.88 (3H, s), 3.86 (1H, t, *J* 7.0), 1.55-1.70 (2H, m), 1.17-1.43 (2H, m), 0.92 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, $CDCl_3$) 149.1, 147.9, 139.6, 118.4, 111.1, 109.6, 56.0, 55.9, 55.8, 42.0, 19.8, 14.0.

Alternative procedure for (*S*)-1-(3,4-dimethoxyphenyl)butan-1-amine

Boron trifluoride diethyl etherate (0.014 mL, 0.107 mmol) was added to a solution of (*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide **4j** (20 mg, 0.053 mmol, 82.0:18.0 dr) in dry methanol (2 mL) and stirred for 3 hr. The solvent was evaporated to give the crude product, to which DCM (5 mL) and 2M hydrochloric acid (5 mL) were added. The organic phase was discarded. The acid phase was basified with solid sodium hydroxide and then extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the *title compound* (9.1 mg, 0.043 mmol, 82%, 64% ee) as a colourless oil. Spectral properties identical to previous compound.

Alternative procedure for (*S*)-1-(3,4-dimethoxyphenyl)butan-1-amine

The general procedure B was followed using (*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide **4j** (20 mg, 0.053 mmol, 82.0:18.0 dr) and gave the *title compound* (8.6 mg, 0.041 mmol, 77%, 64% ee) as a colourless oil. Spectral properties identical to previous compound.

Alternative procedure for (*S*)-1-(3,4-dimethoxyphenyl)butan-1-amine

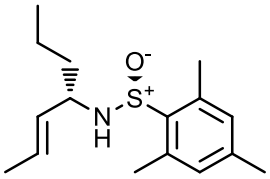
Methylmagnesium bromide (3M in diethyl ether) (0.053 mL, 0.160 mmol) was added dropwise to a solution of (*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)butyl)-2,4,6-trimethylbenzenesulfinamide **4j** (20 mg, 0.053 mmol, 82.0:18.0 dr) in dry THF (1 mL) at -78 °C and stirred for 40 min and then the dry ice bath was removed and it was stirred for 1 hr whilst warming to room temperature. DCM (5 mL) and 2M hydrochloric acid (5 mL) were added to the mixture and the aqueous phase was further extracted two times with DCM. The organic phase was discarded. The acid phase was basified with solid sodium hydroxide and then extracted three times with DCM. The combined organic phase was dried using a hydrophobic frit and the solvent evaporated to give the *title compound* (9.0 mg, 0.043 mmol, 81%, 64% ee) as a colourless oil. Spectral properties identical to previous compound.

Determination of the enantiomeric excess of (*S*)-1-(3,4-dimethoxyphenyl)butan-1-amine

(*S*)-1-(3,4-dimethoxyphenyl)butan-1-amine (8.8 mg, 0.042 mmol), 2-formylphenylboronic acid (6.3 mg, 0.042 mmol) and (S)-binol (13.3 mg, 0.046 mmol) were dissolved in chloroform-*d* (4 mL) in the presence of 4Å molecular sieves and the 1H NMR spectra of an aliquot was acquired after 5 min. The 1H NMR spectrum (400 MHz) of the diastereoisomeric imino-boronate esters had characteristic peaks for the imine proton (8.36 (1H, s) (R), 8.11 (1H, s) (S)), the α-methine proton (4.84 (1H, dd, *J* 10.5, 3.8) (S), 4.70 (1H,

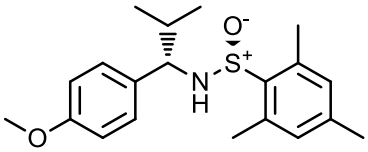
dd, *J* 10.8, 4.0) (R)) and the two methoxy groups (3.97 (3H, s) (S), 3.90 (3H, s) (S), 3.82 (3H, s) (R), 3.48 (3H, s) (R)) and the resonances were all well resolved. The relative intensities of these four sets of protons confirmed the enantiopurity of the amine, according to the reported procedure used for similar amines.[10]

(*S*)-*N*-((*S*,*E*)-hept-2-en-4-yl)-2,4,6-trimethylbenzenesulfinamide 4k



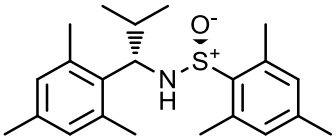
The general procedure A was followed using *n*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-((*E*)-but-2-en-1-ylidene)-2,4,6-trimethylbenzenesulfinamide **2k** (35 mg, 0.150 mmol) and gave the crude product (49 mg, 76.9:23.1 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **4k** (28 mg, 0.100 mmol, 67%, 77.5:22.5 dr) as a colourless oil. $[\alpha]_D^{20}$ +189 (*c* 1.0, $CHCl_3$); IR (ATR) 3208, 2958, 2929, 2871, 1602, 1451, 1378, 1071, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.86 (2H, s), 5.59 (1H, dd, *J* 15.7, 6.7), 5.47 (1H, ddd, *J* 15.7, 6.5, 1.5), 5.16 (1H, d, *J* 6.6), 3.76 (1H, qn, *J* 6.8), 2.53 (6H, s), 2.25 (3H, s), 1.62 (3H, d, *J* 6.5), 1.44-1.68 (2H, m), 1.31-1.44 (2H, m), 0.90 (3H, t, *J* 7.3); minor diastereomer 6.86 (2H, s), 5.58-5.74 (1H, m), 5.36-5.47 (1H, m), 5.10 (1H, d, *J* 4.0), 3.72-3.81 (1H, m), 2.51 (6H, s), 2.25 (3H, s), 1.70 (3H, dd, *J* 6.3, 1.5), 1.44-1.68 (2H, m), 1.31-1.44 (2H, m), 0.87 (3H, t, *J* 7.3); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 140.6, 140.1, 137.3, 134.6, 131.4, 126.7, 58.6, 39.1, 21.0, 19.9, 19.7, 18.0, 14.2; m/z (ES+) 302 ($[M+Na]^+$, 71%), 280 ($[M+H]^+$, 82), 263 (29); HRMS: Found: 280.1732 $C_{16}H_{26}NOS$ 280.1735.

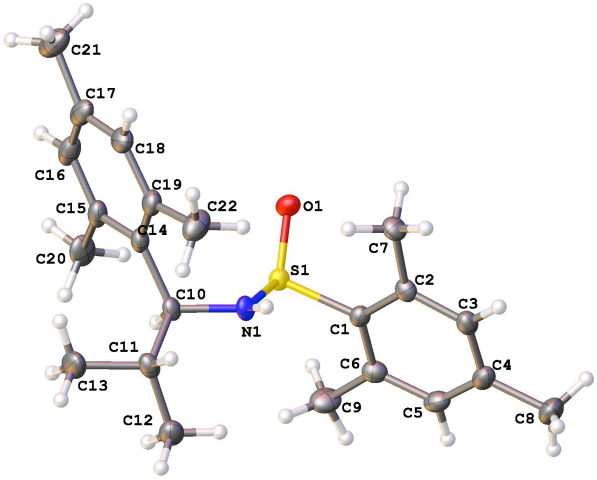
(*S*)-*N*-((*S*)-1-(4-methoxyphenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide 5b



The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(4-methoxybenzylidene)-2,4,6-trimethylbenzenesulfinamide **2b** (45 mg, 0.150 mmol) and gave the crude product (53 mg, 99.1:0.9 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5b** (41 mg, 0.119 mmol, 79%, 99.2:0.8 dr) as a white solid. M.p. 100-102 °C; diastereomeric ratio: 99.6:0.4, determined by HPLC [Chiralpak (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 9.884 min (minor), 11.277 min (major)]; $[\alpha]_D^{20}$ +197 (*c* 1.0, $CHCl_3$); IR (ATR) 3236, 2949, 2917, 2866, 1614, 1517, 1460, 1383, 1064, 1024; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.20 (2H, d, *J* 8.6), 6.81 (2H, d, *J* 8.6), 6.80 (2H, s), 5.64 (1H, d, *J* 7.8), 4.02 (1H, t, *J* 7.7), 3.76 (3H, s), 2.47 (6H, s), 2.23 (3H, s), 2.05 (1H, oct, *J* 6.8), 0.98 (3H, d, *J* 6.6), 0.77 (3H, d, *J* 6.8); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 159.6, 140.6, 139.8, 137.4, 135.8, 131.3, 129.2, 114.1, 66.6, 55.5, 35.0, 21.0, 20.1, 19.9, 19.7; m/z (ES+) 368 ($[M+Na]^+$, 100%), 346 ($[M+H]^+$, 8), 329 (13), 163 (15); HRMS: Found: 368.1646 $C_{20}H_{27}NO_2NaS$ 368.1660.

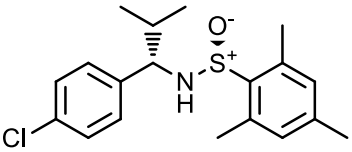
(*S*)-*N*-((*S*)-1-mesityl-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide 5c





The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-2,4,6-trimethyl-*N*-(2,4,6-trimethylbenzylidene]benzenesulfinamide **2c** (47 mg, 0.150 mmol) and gave the crude product (53 mg, 99.0:1.0 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5c** (44 mg, 0.123 mmol, 82%, 99.2:0.8 dr) as a white solid. M.p. 124-126 °C; diastereomeric ratio: 99.9:0.1, determined by HPLC [Chiralpak IA (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 4.661 min (minor), 8.220 min (major)]; $[\alpha]_D^{20}$ +237 (*c* 1.0, $CHCl_3$); IR (ATR) 3252, 2959, 2865, 1605, 1464, 1378, 1071, 1050; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.85 (2H, s), 6.81 (1H, s), 6.79 (1H, s), 5.24 (1H, d, *J* 7.8), 4.40 (1H, dd, *J* 10.4, 7.8), 2.47 (6H, s), 2.43 (3H, s), 2.34 (3H, s), 2.25 (3H, s), 2.23-2.37 (1H, m), 2.20 (3H, s), 1.18 (3H, d, *J* 6.6), 0.67 (3H, d, *J* 6.8); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 140.9, 140.5, 137.3, 137.2, 137.1, 136.7, 136.0, 131.9, 131.4, 130.0, 64.2, 33.8, 21.9, 21.8, 21.6, 21.0, 20.9, 20.1, 19.6; m/z (ES+) 380 ($[M+Na]^+$, 100%), 358 ($[M+H]^+$, 12), 341 (5); HRMS: Found: 380.2017 $C_{22}H_{31}NONaS$ 380.2024.

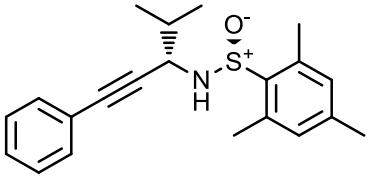
(*S*)-*N*-((*S*)-1-(4-chlorophenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide 5d



The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(4-(chlorobenzylidene)-2,4,6-trimethylbenzenesulfinamide **2d** (46 mg, 0.150 mmol) and gave the crude product (59 mg, 95.9:4.1 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5d** (47 mg, 0.134 mmol, 90%, 95.5:4.5 dr) as a white solid. M.p. 111-113 °C; diastereomeric ratio: 95.0:5.0, determined by HPLC [Chiralpak IA (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 9.290 min (major), 12.046 min (minor)]; $[\alpha]_D^{21}$ +184 (*c* 1.0, $CHCl_3$); IR (ATR) 3188, 2965, 2927, 2868, 1599, 1493, 1441, 1381, 1064, 1044; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.20-7.31 (4H, m), 6.77 (2H, s), 5.84 (1H, d, *J* 8.1), 4.10 (1H, t, *J* 7.9), 2.46 (6H, s), 2.22 (3H, s), 1.97-2.08 (1H, m), 0.98 (3H, d, *J* 6.8), 0.77 (3H, d, *J* 6.8); minor diastereomer 7.33-7.42 (4H, m), 6.85 (2H, s), 5.61 (1H, d, *J* 4.8), 4.16 (1H, dd, *J* 7.9, 4.8), 2.41 (6H, s), 2.25 (3H, s), 1.97-2.08 (1H, m), 0.95-1.02 (3H, m), 0.74-0.80 (3H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 143.0, 140.8, 139.3, 137.5, 132.7, 131.4,

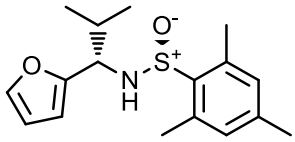
129.9, 128.7, 66.1, 35.1, 21.0, 20.0, 19.9, 19.7; m/z (ES+) 372 ($[M+Na]^+$, 100%), 350 ($[M+H]^+$, 10), 151 (12); HRMS: Found: 372.1176 $C_{19}H_{24}NONaSCl$ 372.1165.

(*S*)-2,4,6-trimethyl-*N*-((*S*)-4-methyl-1-phenylpent-1-yn-3-yl)benzenesulfinamide 5e



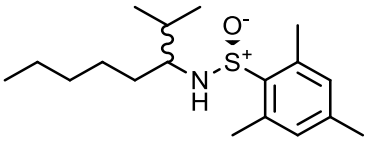
The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-2,4,6-trimethyl-*N*-(3-phenylpropyn-2-yn-1-ylidene]benzenesulfinamide **2e** (44 mg, 0.150 mmol) and gave the crude product (53 mg, 82.9:17.1 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5e** (31 mg, 0.091 mmol, 61%, 82.4:17.6 dr) as a colourless oil. Diastereomeric ratio: 83.3:16.7, determined by HPLC [Chiralpak AY-H (heptane/ethanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 26.606 min (minor), 30.466 min (major)]; $[\alpha]_D^{20}$ +160 (*c* 1.0, $CHCl_3$); IR (ATR) 3206, 2961, 2926, 2870, 1600, 1465, 1443, 1382, 1072, 1048; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.32-7.42 (5H, m), 6.88 (2H, s), 5.78 (1H, d, *J* 7.2), 4.12 (1H, dd, *J* 7.2, 6.3), 2.57 (6H, s), 2.25 (3H, s), 2.09 (1H, qqd, *J* 6.8, 6.6, 6.3), 1.11 (3H, d, *J* 6.8), 1.09 (3H, d, *J* 6.6); minor diastereomer 7.13-7.47 (5H, m), 6.90 (2H, s), 5.69 (1H, d, *J* 6.6), 4.23 (1H, dd, *J* 6.6, 5.3), 2.58 (6H, s), 2.26 (3H, s), 1.95-2.07 (1H, m), 1.02-1.09 (6H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 141.0, 139.3, 137.7, 132.4, 131.5, 129.3, 129.1, 124.1, 89.5, 85.4, 54.7, 35.2, 21.0, 19.7, 19.7, 18.7; m/z (ES+) 362 ($[M+Na]^+$, 100%), 340 ($[M+H]^+$, 29); HRMS: Found: 362.1542 $C_{21}H_{25}NONaS$ 362.1549.

(*S*)-*N*-((*S*)-1-(furan-2-yl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide 5f



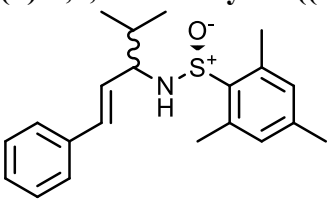
The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(furan-2-ylmethylene]-2,4,6-trimethylbenzenesulfinamide **2f** (39 mg, 0.150 mmol) and gave the crude product (53 mg, 96.8:3.2 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5f** (43 mg, 0.140 mmol, 93%, 97.8:2.2 dr) as a white solid. M.p. 73-75 °C; diastereomeric ratio: 97.1:2.9, determined by HPLC [Chiralpak AD (heptane/isopropanol 95:5, flow rate: 1.0 mL/min, l=215 nm, retention time: 11.233 min (minor), 13.365 min (major)]; $[\alpha]_D^{20}$ +202 (*c* 1.0, $CHCl_3$); IR (ATR) 3198, 2952, 2925, 2865, 1602, 1441, 1380, 1068, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.43 (1H, dd, *J* 1.8, 0.8), 6.85 (2H, s), 6.32 (1H, dd, *J* 3.3, 1.8), 6.23 (1H, d, *J* 3.3), 5.61 (1H, d, *J* 8.5), 4.19 (1H, dd, *J* 8.5, 6.8), 2.51 (6H, s), 2.25 (3H, s), 2.19 (1H, oct, *J* 6.8), 0.94 (3H, d, *J* 6.8), 0.88 (3H, d, *J* 6.8); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 156.6, 142.3, 140.8, 139.7, 137.4, 131.4, 110.9, 107.6, 60.9, 33.7, 21.0, 19.6, 19.2; m/z (ES+) 328 ($[M+Na]^+$, 100%), 306 ($[M+H]^+$, 38), 167 (16); HRMS: Found: 328.1335 $C_{17}H_{23}NO_2NaS$ 328.1347.

(*S*)-2,4,6-trimethyl-*N*-(2-methyloctan-3-yl)benzenesulfinamide 5g



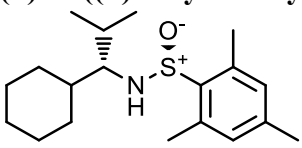
The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-hexylidene-2,4,6-trimethylbenzenesulfinamide **2g** (40 mg, 0.150 mmol) and gave the crude product (49 mg). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the impure product (30 mg) which was further purified by mass directed autopreparation (Xbridge column using acetonitrile/water with an ammonium carbonate modifier) to give the *title compound* **5g** (18 mg, 0.058 mmol, 39%, 51.0:49.0 dr) as a colourless oil. $[\alpha]_D^{21}$ +180 (*c* 1.0, $CHCl_3$); IR (ATR) 3217, 2956, 2928, 2870, 1602, 1462, 1379, 1069, 1046; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.87 (2H, s), 5.13 (1H, d, *J* 8.8), 3.03-3.15 (1H, m), 2.56 (6H, s), 2.26 (3H, s), 1.84-1.96 (1H, m), 1.17-1.58 (8H, m), 0.84-0.96 (9H, m); minor diastereomer 6.87 (2H, s), 5.02 (1H, d, *J* 7.8), 3.03-3.15 (1H, m), 2.56 (6H, s), 2.26 (3H, s), 1.84-1.96 (1H, m), 1.17-1.58 (8H, m), 0.84-0.96 (9H, m); ^{13}C NMR (101 MHz, acetone-d_6) major and minor diastereomers 140.9, 140.9, 140.6, 140.5, 137.3, 137.2, 131.4, 131.4, 63.3, 62.4, 33.5, 33.4, 33.3, 33.1, 32.6, 32.6, 27.0, 26.4, 23.4, 23.4, 21.0, 19.8, 19.3, 18.8, 18.8, 18.3, 14.4, 14.4; m/z (ES+) 332 ($[M+Na]^+$, 31%), 310 ($[M+H]^+$, 83); HRMS: Found: 310.2201 $C_{18}H_{32}NOS$ 310.2205.

(*S*)-2,4,6-trimethyl-*N*-((*E*)-4-methyl-1-phenylpent-1-en-3-yl)benzenesulfinamide 5h



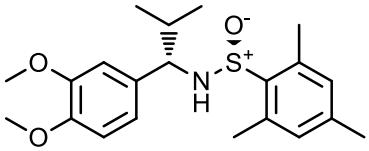
The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.15 mL, 0.300 mmol) and (*S*,*E*)-2,4,6-trimethyl-*N*-((*E*)-3-phenylallylidene)benzenesulfinamide **2h** (45 mg, 0.150 mmol) and gave the crude product (64 mg, 50.0:50.0 dr). Purification by flash chromatography on silica gel (elution with 0-13% ethyl acetate/DCM) gave the *title compound* **5h** (18 mg, 0.052 mmol, 34%, 51.5:48.5 dr) as a colourless oil. $[\alpha]_D^{21}$ +137 (*c* 1.0, $CHCl_3$); IR (ATR) 3211, 2958, 2926, 2870, 1601, 1450, 1380, 1071, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 7.12-7.49 (5H, m), 6.87 (2H, s), 6.65 (1H, d, *J* 15.9), 6.29 (1H, dd, *J* 15.9, 8.1), 5.31 (1H, d, *J* 5.6), 3.76-3.87 (1H, m), 2.54 (6H, s), 2.26 (3H, s), 1.90-2.03 (1H, m), 1.00 (3H, d, *J* 6.8), 0.95 (3H, d, *J* 6.8); minor diastereomer 7.12-7.49 (5H, m), 6.85 (2H, s), 6.49 (1H, d, *J* 15.9), 6.27 (1H, dd, *J* 15.9, 7.6), 5.41 (1H, d, *J* 7.1), 3.76-3.87 (1H, m), 2.56 (6H, s), 2.23 (3H, s), 1.90-2.03 (1H, m), 0.97 (6H, d, *J* 6.8); ^{13}C NMR (101 MHz, acetone-d_6) major and minor diastereomers 140.8, 140.7, 139.9, 139.8, 138.3, 138.1, 137.7, 137.5, 133.3, 132.2, 131.5, 131.4, 131.0, 130.1, 129.5, 129.4, 128.4, 128.2, 127.3, 127.3, 64.6, 64.2, 34.2, 21.0, 21.0, 19.8, 19.6, 19.6, 19.4, 19.1, 18.6; m/z (ES+) 364 ($[M+Na]^+$, 64%), 342 ($[M+H]^+$, 100); HRMS: Found: 342.1894 $C_{21}H_{28}NOS$ 342.1892.

(*S*)-*N*-((*S*)-1-cyclohexyl-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide 5i



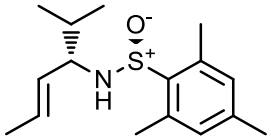
The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.15 mL, 0.300 mmol) and (*S*,*E*)-*N*-(cyclohexylmethylene)-2,4,6-trimethylbenzenesulfinamide **2i** (42 mg, 0.150 mmol) and gave the crude product (50 mg, 75.2:24.8 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5i** (27 mg, 0.085 mmol, 57%, 75.8:24.2 dr) as a white solid. M.p. 74-76 °C; $[\alpha]_D^{21}$ +143 (*c* 1.0, $CHCl_3$); IR (ATR) 3233, 2922, 2851, 1602, 1447, 1381, 1068, 1047; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.88 (2H, s), 4.87 (1H, d, *J* 8.8), 2.74-2.84 (1H, m), 2.59 (6H, s), 2.26 (3H, s), 1.04-2.03 (12H, m), 0.94 (3H, d, *J* 6.6), 0.79 (3H, d, *J* 6.8); minor diastereomer 6.88 (2H, s), 4.85-4.93 (1H, m), 2.74-2.84 (1H, m), 2.59 (6H, s), 2.26 (3H, s), 1.04-2.03 (12H, m), 1.01 (3H, d, *J* 6.8), 0.97 (3H, d, *J* 6.8); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 142.0, 140.5, 136.7, 131.4, 68.9, 41.2, 32.0, 30.8, 30.0, 27.4, 27.4, 27.2, 21.4, 21.0, 19.9, 18.0; m/z (ES+) 344 ($[M+Na]^+$, 14%), 322 ($[M+H]^+$, 88), 318 (28); HRMS: Found: 322.2206 $C_{19}H_{32}NOS$ 322.2205.

(*S*)-*N*-((*S*)-1-(3,4-dimethoxyphenyl)-2-methylpropyl)-2,4,6-trimethylbenzenesulfinamide 5j



The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.22 mL, 0.442 mmol) and (*S*,*E*)-*N*-(3,4-dimethoxybenzylidene)-2,4,6-trimethylbenzenesulfinamide **2j** (50 mg, 0.150 mmol) and gave the crude product (58 mg, 98.9:1.1 dr). Purification by flash chromatography on silica gel (elution with 0-25% ethyl acetate/cyclohexane) gave the *title compound* **5j** (52 mg, 0.138 mmol, 92%, 99.5:0.5 dr) as a white solid. M.p. 137-138 °C; $[\alpha]_D^{21}$ +179 (*c* 1.0, $CHCl_3$); IR (ATR) 3241, 2949, 2918, 2866, 1593, 1521, 1466, 1261, 1022; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.93 (1H, d, *J* 1.8), 6.81 (1H, d, *J* 8.3), 6.80 (2H, s), 6.77 (1H, dd, *J* 8.3, 1.8), 5.66 (1H, d, *J* 8.3), 4.00 (1H, t, *J* 8.0), 3.77 (6H, s), 2.48 (6H, s), 2.23 (3H, s), 2.04 (1H, oct, *J* 6.8), 0.99 (3H, d, *J* 6.6), 0.79 (3H, d, *J* 6.6); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 150.1, 149.3, 140.6, 139.8, 137.5, 136.7, 131.4, 120.3, 112.4, 112.3, 66.9, 56.2, 56.1, 35.2, 21.0, 20.2, 20.0, 19.7; m/z (ES+) 398 ($[M+Na]^+$, 89%), 376 ($[M+H]^+$, 100), 359 (17), 193 (20); HRMS: Found: 376.1939 $C_{21}H_{30}NO_3S$ 376.1946.

(*S*)-2,4,6-trimethyl-*N*-((*S*,*E*)-2-methylhex-4-en-3-yl)benzenesulfinamide 5k



The general procedure A was followed using *iso*-propylmagnesium chloride (2M in diethyl ether) (0.15 mL, 0.300 mmol) and (*S*,*E*)-*N*-((*E*)-but-2-en-1-ylidene)-2,4,6-trimethylbenzenesulfinamide **2k** (35 mg, 0.150 mmol) and gave the crude product (50 mg, 92.1:7.9 dr). Purification by flash chromatography on silica gel (elution with 0-13% ethyl acetate/DCM) gave the *title compound* **5k** (25 mg, 0.090 mmol, 60%, 93.0:7.0 dr) as a white solid. M.p. 67-69 °C; $[\alpha]_D^{20}$ +256 (*c* 1.0, $CHCl_3$); IR (ATR) 3175, 2951, 2921, 2866, 1602, 1438, 1379, 1068, 1044; ^{1}H NMR (400 MHz, acetone-d_6) major diastereomer 6.86 (2H, s), 5.58 (1H, dq, *J* 15.3, 6.5), 5.47 (1H, ddd, *J* 15.3, 7.1, 1.4), 5.12 (1H, d, *J* 6.6), 3.57 (1H, ddd, *J* 7.1, 6.8, 6.6), 2.54 (6H, s), 2.25 (3H, s), 1.86 (1H, oct, *J* 6.8), 1.64 (3H, d, *J* 6.5), 0.89 (6H, d, *J* 6.8); minor diastereomer 6.86 (2H, s), 5.39-5.75 (2H, m), 5.04-5.15 (1H, m), 3.51-3.63 (1H, m), 2.52 (6H, s), 2.25 (3H, s), 1.80-1.92 (1H, m), 1.72 (3H, dd, *J* 6.4, 1.4), 0.85-0.93

(6H, m); ^{13}C NMR (101 MHz, acetone-d_6) major diastereomer 140.6, 140.1, 137.4, 132.1, 131.4, 127.9, 64.6, 33.8, 21.0, 19.7, 19.4, 18.8, 18.1; m/z (ES+) 302 ([M+Na]$^+$, 57%), 280 ([M+H]$^+$, 71), 263 (28), 220 (13); HRMS: Found: 280.1735 $C_{16}H_{26}NOS$ 280.1735.

General procedures for the aziridine synthesis

Method A

NaH (60% in mineral oil, 1.860-5.720 mmol) was washed with pentane (2 x 5 mL) under argon and the pentane was removed by use of a syringe after the NaH had settled. To the pre-washed NaH was added DMSO (5 mL) and trimethysulfonium iodide (1.860-5.720 mmol) was added in small portions. The slurry was stirred at room temperature under argon until the solution became clear after which the mesitylsulfinimine (0.620-1.910 mmol) was added dropwise as a solution in DMSO (3 mL). The reaction was stirred at room temperature and monitored for completion by TLC. After completion, ice-cold saturated brine was added on completion and then filtered through a short pad of celite. The filtrate was extracted with ethyl acetate (3 x 20 mL) and concentrated in vacuo. The residue was dissolved in hexane-diethyl ether solution (1:1, 20 mL) and washed with water (20 mL) and the organic layer dried over Na2SO4 and concentrated *in vacuo*. The residue was purified by column chromatography using activity 4 alumina to give the sulfiny aziridines.

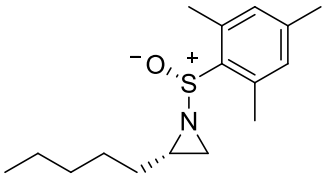
Method B

A solution of the *S*-allyltetrahydrothiophenium bromide, (1.500 mmol), in anhydrous tetrahydrofuran, (5 mL), was stirred at room temperature under an atmosphere of argon. After 10 minutes, a solution of mesitylsulfinyl imine (1.000 mmol), in anhydrous tetrahydrofuran, (5 mL), was added to the reaction mixture. The cloudy dispersion was then stirred for a further 20 minutes. At this stage the lithium *tert*-butoxide, (1.500 mmol), was added, portion-wise, to the reaction mixture, resulting in a significant colour change. Once the reaction was complete, ice-cold brine, (15 mL), was added, and the biphasic reaction was stirred rapidly for 10 minutes. The resulting cloudy mixture was then filtered through a pad of celite, the product extracted into diethyl ether, washed with brine and dried over sodium sulfate. The organic fraction was concentrated *in vacuo* to yield a crude mixture containing the aziridine which was isolated by column chromatography.

Method C

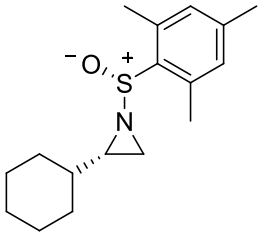
To a solution of ethyl α-bromoacetate (0.28-1.84 mmol) in anhydrous tetrahydrofuran (2.8-18.4 mL) at -78 °C was added lithium bis-(trimethyl-silyl)amide (0.28-1.84 mmol). The mixture was stirred for 30 minutes. At this stage a solution of (*R*,*E*) *N*-mesityl-sulfinylimine (0.14-0.92 mmol) in anhydrous tetrahydrofuran was added and the reaction was stirred at -78 ºC. Once the reaction was deemed complete by TLC, water (3-10mL) was added to the mixture. After 10 minutes the product was extracted with ethyl acetate (5-15mL), washed with brine (5-10 mL) and dried over sodium sulfate. The organic fractions were concentrated *in vacuo* to yield a crude mixture containing the aziridine.

2-Pentyl-1-(2,4,6-trimethylbenzene-(*R*)-sulfinyl)aziridine 6a



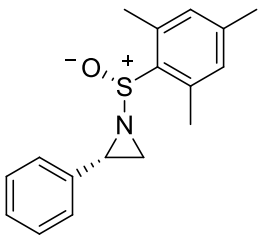
Method A was followed using (*R,E*)-*N*-(Hexylidene)-2,4,6-trimethylbenzenesulfinamide (0.45 g, 1.70 mmol) to give the product as a colourless oil (0.44 g, 93%) as an inseperable 4:1 mixture of diastereomers (major diastereomer shown). Major diastereomer: IR (neat) 3691, 2959, 2254, 1602, 1086; ^{1}H NMR (400 MHz, $CDCl_3$) 6.86 (2H, s), 2.68-2.73 (1H, m), 2.62 (6H, s), 2.31 (3H, s), 2.20 (1H, d, *J* 6.8), 1.90 (1H, d, *J* 4.4), 1.12 – 1.59 (8H, m), 0.83 (3H, m); ^{13}C NMR (101 MHz, $CDCl_3$) 138.2, 130.4, 130.0, 128.2, 38.1, 21.5, 32.5, 32.4, 25.1, 29.8, 23.1, 14.0, 14.1; m/z (EI/CI) 302 ($[M+H]^+$, 100%); HRMS: Found: 302.1546 $C_{16}H_{25}NNaOS$ 302.1549.

2-Cyclohexyl-1-(2,4,6-trimethylbenzene-(*R*)-sulfinyl)aziridine 6b



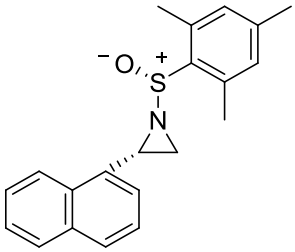
Method A was followed using (*R,E*)-*N*-(Cyclohexylmethylene)-2,4,6-trimethylbenzenesulfinamide (0.53 g, 1.91 mmol) to give the product as a colourless oil (0.37 g, 66%) as an inseperable 5:1 mixture of diastereomers (major diastereomer shown). Major diastereomer: IR (neat) 3691, 2929, 2254, 1602, 1084; ^{1}H NMR (400 MHz, $CDCl_3$) 6.86 (2H, s), 2.63 (6H, s), 2.49-2.52 (1H, m), 2.31 (3H, s), 2.16 (1H, d, *J* 6.8), 1.90 (1H, d, *J* 5.2), 1.60-1.66 (1H, m), 1.05-1.26 (6H, m), 0.81-0.96 (4H, m); ^{13}C NMR (101 MHz, $CDCl_3$) 136.3, 130.2, 129.5, 128.4, 38.1, 21.5, 32.9, 32.7, 31.4, 29.8, 23.1, 22.6; m/z (EI/CI) 314 ($[M+Na]^+$, 100%), 291 ($[M+H]^+$, 23); HRMS: Found: 314.1535 $C_{17}H_{25}NNaOS$ 314.1549.

2-Phenyl-1-(2,4,6-trimethylbenzene-(*R*)-sulfinyl)aziridine 6c



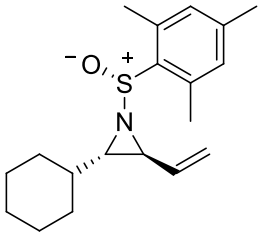
Method A was followed using (*R,E*)-*N*-(benzylidene)-2,4,6-trimethylbenzenesulfinamide (0.35 g, 1.29 mmol) to give the product as a colourless oil (0.35 g, 95%) as an inseperable 9:2 mixture of diastereomers (major diastereomer shown. Major diastereomer: IR (neat) 2926, 1498, 1087, 908; ^{1}H NMR (400 MHz, $CDCl_3$) 7.12-7.30 (5H, m), 6.83 (2H, s), 3.86 (1H, dd, *J* 4.8, 6.8), 2.62 (1H, d, *J* 4.8), 2.60 (6H, s), 2.30 (1H, d, *J* 6.8), 2.28 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) 136.8, 130.1, 130.0, 128.1, 127.5, 127.3, 125.9, 125.6, 32.7, 31.4, 28.9, 18.0; m/z (EI/CI) 286 ($[M+H]^+$, 54%); HRMS: Found: 286.1262 $C_{17}H_{20}NOS$ 286.1260.

2-Naphthalen-1-yl-1-(2,4,6-trimethylbenzene-(*R*)-sulfinyl)aziridine 6d



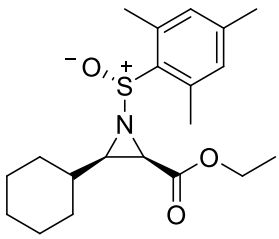
Method A was followed using (*R,E*)-*N*-(Naphthalen-1-ylmethylene)-2,4,6-trimethylbenzenesulfiamide (0.20 g, 0.62 mmol) to give the product as a colourless oil (0.10 g, 50%) as an inseperable 8:1 mixture of diastereomers (major diastereomer shown). Major diastereomer: IR (neat) 3979, 1596, 1089; ^{1}H NMR (400 MHz, $CDCl_3$) 8.22 (1H, d), 7.85 (1H, d), 7.72 (1H, d), 7.51 (2H, m), 7.23 (1H, m), 7.12 (1H, d), 6.83 (2H, s), 4.38 (1H, dd, *J* 4.0, 4.0), 2.75 (1H, d, *J* 4.0), 2.61 (6H, s), 2.27 (3H, s), 2.21 (1H, d, *J* 4.0); ^{13}C NMR (101 MHz, $CDCl_3$) 136.8, 133.3, 133.1, 132.6, 130.1, 130.0, 128.1, 127.5, 127.3, 125.9, 125.6, 128.5, 127.8, 126.4, 32.7, 31.4, 28.9, 18.0; m/z (EI/CI) 358 ($[M+Na]^+$, 100%); HRMS: Found: 358.1222 $C_{21}H_{21}NNaOS$ 358.1236.

Cyclohexyl-1-(2,4,6-trimethylbenzene-(*R*)-sulfinyl)-3-vinylaziridine 6e



Method B was followed using (*R,E*)-*N*-(Cyclohexylmethylene)-2,4,6-trimethylbenzenesulfinamide (0.28 g, 1.000 mmol) to give the product as a colourless oil (0.23 g, 73%) as an inseperable 5:1 mixture of diastereomers (major diastereomer shown). ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer 6.81 (2H, s), 5.91 (1H, ddd, *J* 16.0, 8.0, 4.0), 5.45 (1H, d, *J* 16.0), 5.35 (1H, d, *J* 8.0), 2.93 (1H, dd, *J* 4.0), 2.64 (6H, s), 2.25 (3H, s), 2.08 (1H, dd, *J* 8.0, 4.0); 1.53 (4H, m), 1.05 (4H, m), 0.83 (2H, m), 0.56 (1H, m); minor diastereomer 6.79 (2H, s), 5.78 (1H, ddd, *J* 12.0, 8.0, 4.0), 5.41 (1H, d, *J* 12.0), 5.24 (1H, d, *J* 8.0), 2.97 (1H, dd, *J* 4.0), 2.58 (1H, dd, *J* 4.0), 2.54 (6H, s), 2.24 (3H, s), 1.66 (4H, m), 1.17 (7H, m), 0.83 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer 141.7, 138.8, 137.2, 132.7, 130.6, 121.3, 60.3, 49.1, 47.6, 39.2, 29.8, 25.9, 21.0, 19.5; m/z (EI/CI) 318 ($[M+H]^+$, 32%); HRMS: Found: 318.1884 $C_{19}H_{28}NOS$ 318.1886.

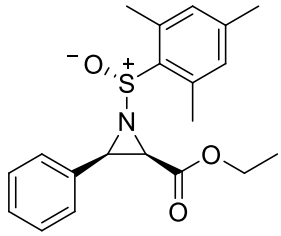
(2*R*,3*R*)-Ethyl *N*-[2,4,6-trimethylbenzene-(*R*)-sulfinyl]-3-cyclohexylaziridine 2-carboxylate 6f



Method C was followed using (*R,E*)-*N*-(Cyclohexylmethylene)-2,4,6-trimethylbenzenesulfinamide (105 mg, 0.38 mmol) at room temperature and gave the crude product (125 mg , 96:4 dr, 65:35 cis/trans) as a colourless oil. Purification by column chromatography over silica gel (eluting with 20:1 petroleum ether/ethyl acetate (1% Et_3N))

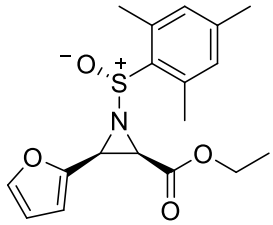
gave the *title compound* **6f** (79 mg, 57%) as a colourless oil. $[\alpha]_D^{25}$ -59 (c 0.25, $CHCl_3$); IR ($CHCl_3$) 3007, 2931, 2855, 1741, 1602, 1449, 1380, 1192, 1092; ^{1}H NMR (400 MHz, $CDCl_3$) 6.82 (2H, s), 4.17 (2H, q, *J* 7.1), 3.47 (1H, d, *J* 7.3), 2.57 (6H, s), 2.28 (1H, dd, *J* 9.4, 7.3), 2.26 (3H, s), 1.81-1.43 (7H, m), 1.22 (3H, t, *J* 7.2), 1.22-0.99 (4H, m); ^{13}C NMR (101 MHz, $CDCl_3$) 167.6, 141.5, 138.0, 136.4, 130.9, 61.2, 46.6, 35.9, 35.8, 30.8, 29.9, 26.07, 25.4, 25.3, 21.0, 19.3, 14.1; m/z (ES+) 386 ($[M+Na]^+$, 100%), 364 ($[M+H]^+$, 3); HRMS: Found: 386.1755 $C_{20}H_{29}NNaO_3S$ 386.1760.

(2*R*,3*R*)-Ethyl *N*-[2,4,6-trimethylbenzene-(*R*)-sulfinyl]-3-phenylaziridine 2-carboxylate 6g



Method C was followed using (*R*,*E*)-*N*-(benzylidene)-2,4,6-trimethylbenzenesulfinamide (250 mg, 0.92 mmol) and gave the crude product (433 mg , >98% dr, 98:2 cis/trans) as a pale yellow oil. Purification by column chromatography over silica gel (eluting with 20:1 petroleum ether/ethyl acetate (1% Et_3N)) gave the *title compound* **6g** (238 mg, 72%) as a white solid. $[\alpha]_D^{25}$ -39 (c 0.25, $CHCl_3$); IR ($CHCl_3$) 3008, 1745, 1602, 1498, 1374, 1192, 1095; ^{1}H NMR (300 MHz, $CDCl_3$) 7.44-7.41 (2H, m), 7.33-7.28 (3H, m), 6.89 (2H, s), 3.92 (2H, qd, *J* 7.2, 3.9), 3.79 (1H, d, *J* 7.3), 3.74 (1H, d, *J* 7.3), 2.66 (6H, s), 2.31 (3H, s), 0.94 (3H, t, *J* 7.2); ^{13}C NMR (75 MHz, $CDCl_3$) 166.0, 141.6, 138.1, 135.7, 133.0, 131.0, 128.1, 128.0, 127.8, 61.0, 42.1, 38.1, 21.0, 19.3, 13.8; m/z (ES+) 380 ($[M+Na]^+$, 100%), 358 ($[M+H]^+$, 2); HRMS: Found: 380.1283 $C_{20}H_{23}NNaO_3S$ 380.1291.

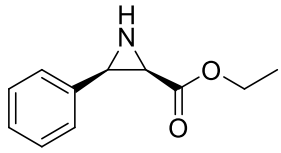
(2*R*,3*R*)-Ethyl *N*-[2,4,6-trimethylbenzene-(*R*)-sulfinyl]-3-[(2)-furfuryl]aziridine 2-carboxylate 6h



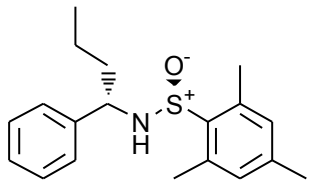
Method C was followed using (*R*,*E*)-*N*-(furan-2-ylmethylene]-2,4,6-trimethylbenzenesulfinamide (38 mg, 0.14 mmol) at room temperature and gave the crude product (27 mg , 97:3 dr, 92:8 cis/trans) as a brown oil. Purification by column chromatography over silica gel (eluting with 15:1 petroleum ether/ethyl acetate (1% Et_3N)) gave the title compound **6h** (25 mg, 50%) as a yellow oil. $[\alpha]_D^{25}$ -115 (c 0.25, $CHCl_3$); IR ($CHCl_3$) 3008, 1747, 1602, 1466, 1380, 1192, 1096; ^{1}H NMR (400 MHz, $CDCl_3$) 7.35 (1H, d, *J* 0.9), 6.85 (2H, s), 6.36-6.32 (2H, m), 4.07 (2H, q, *J* 7.1), 3.78 (1H, d, *J* 7.1), 3.65 (1H, d, *J* 7.1), 2.59 (6H, s), 2.28 (3H, s), 1.11 (3H, t, *J* 7.1); ^{13}C NMR (101 MHz, $CDCl_3$) 165.9, 147.6, 142.8, 141.8, 138.2, 135.5, 131.1, 110.6, 110.0, 61.4, 37.1, 36.3, 21.1, 19.3, 13.9; m/z

(ES+) 370 ([M+Na]$^+$, 100%), 348 ([M+H]$^+$, 2); HRMS: Found:350.1083 $C_{18}H_{21}NNaO_4S$ 370.1089.

(2*R*,3*R*)-Ethyl 3-phenyl-1*H*-aziridine 2-carboxylate



To a solution of (2*R*,3*R*)-Ethyl *N*-[2,4,6-trimethylbenzene-(*R*)-sulfinyl]-3-phenylaziridine 2-carboxylate **6g** (61 mg, 0.17 mmol) in a 1:1 water/acetone solution (2.5 mL) was added, dropwise, trifluoroacetic acid (0.065 mL, 0.85 mmol). Once the reaction was completed a saturated solution of sodium bicarbonate was added until pH was brought to 10 and the crude product was extracted with dichloromethane (3 mL) and dried over sodium sulfate. The organic fractions were concentrated *in vacuo* to yield the crude product (34 mg). Purification by column chromatography over neutralised silica gel (eluting with 7:3 petroleum ether/ethyl acetate) gave the *title compound* (28 mg, 87%) as a white solid. M.p. 65-70 ºC; $[\alpha]_D^{25}$ -11 (c 0.25, $CHCl_3$); IR ($CHCl_3$) 3275, 2987, 1728, 1383, 1192, 1028; ^{1}H NMR (300 MHz, $CDCl_3$) 7.34-7.27 (5H, m), 3.99 (2H, qd, *J* 7.2, 2.4), 3.50 (1H, d, *J* 6.4), 3.02 (1H, d, *J* 6.4), 1.71 (1H, bs), 1.03 (3H, t, *J* 7.2); ^{13}C NMR (75 MHz, $CDCl_3$) 169.0, 134.8, 128.0, 127.6, 127.5, 61.1, 40.0, 37.1, 13.9; m/z (ES+) 214 ([M+Na]$^+$, 100%), 192 ([M+H]$^+$, 11); HRMS: Found: 192.1026 $C_{11}H_{14}NO_2$ 192.1019.



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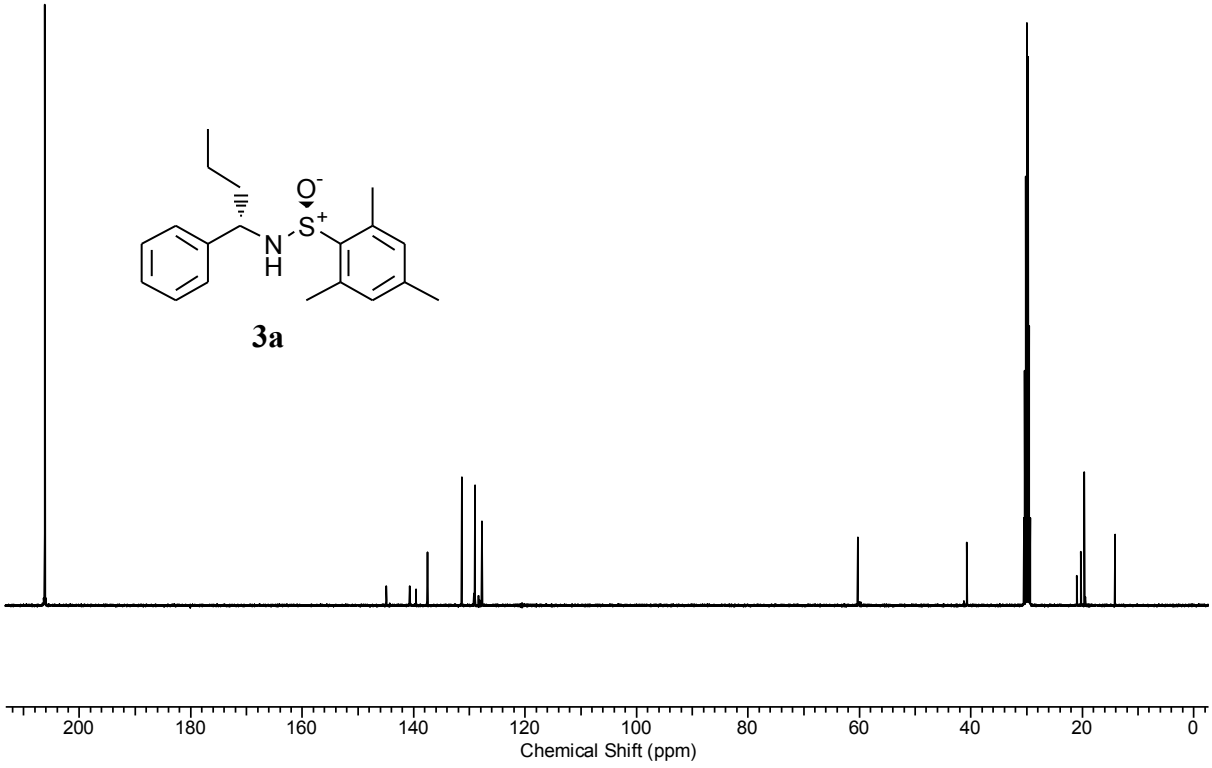
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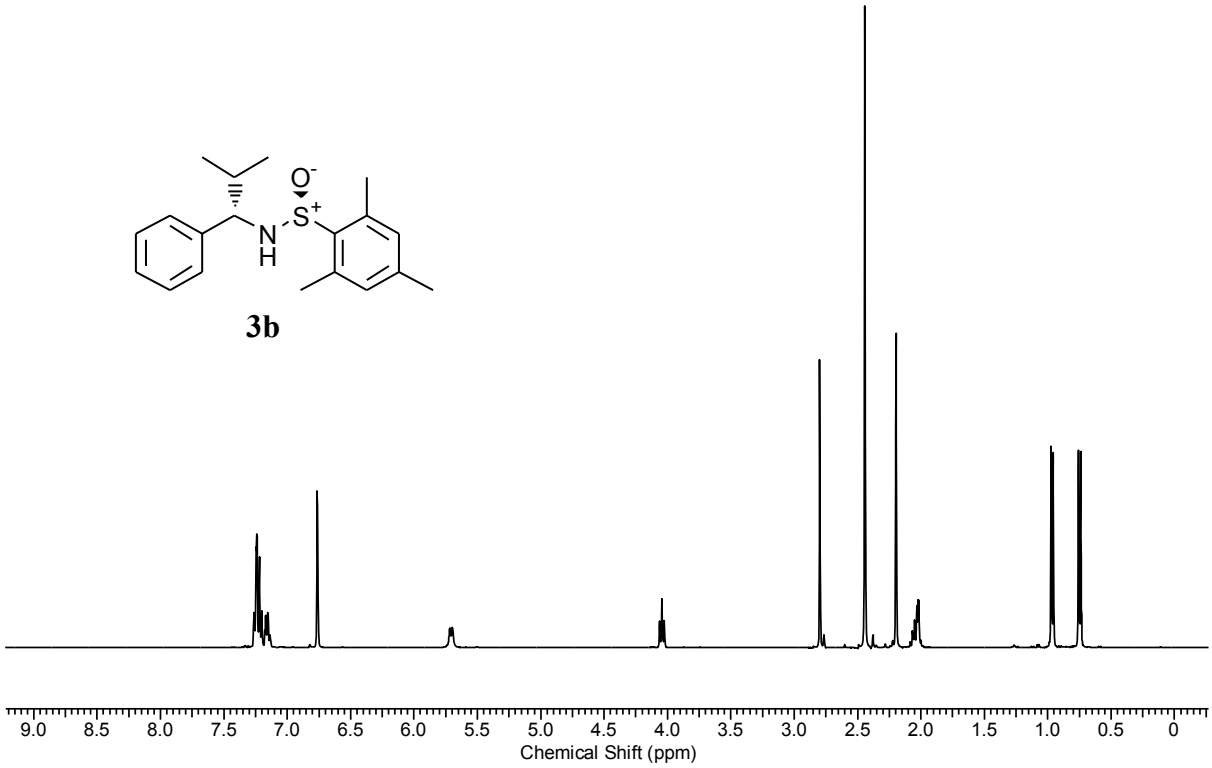
Chemical Shift (ppm)

3a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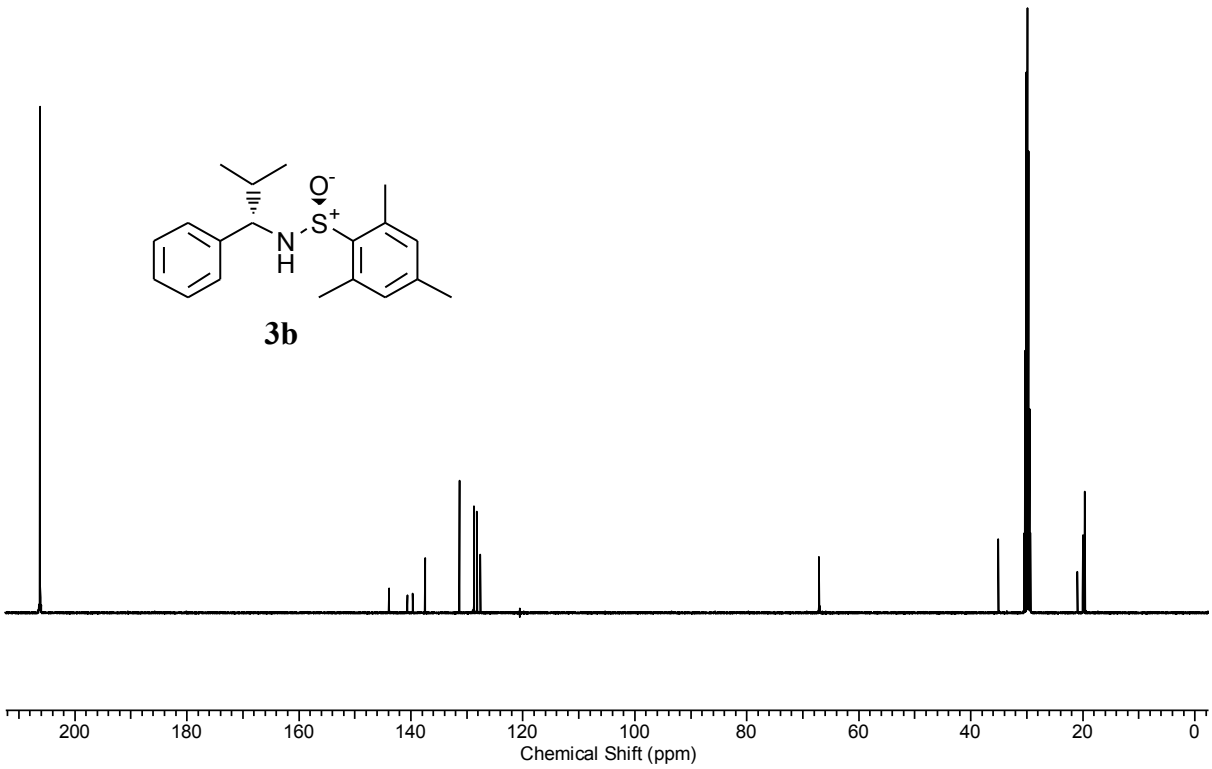
0
Chemical Shift (ppm)

3b



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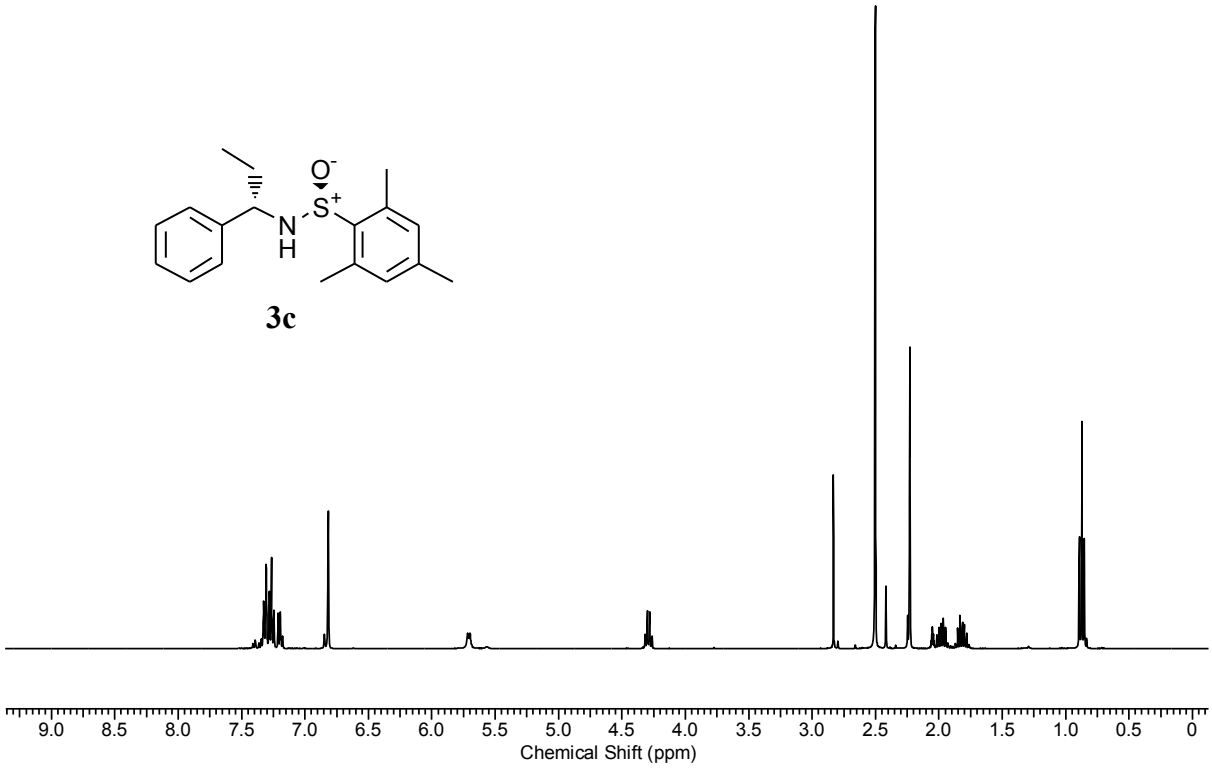

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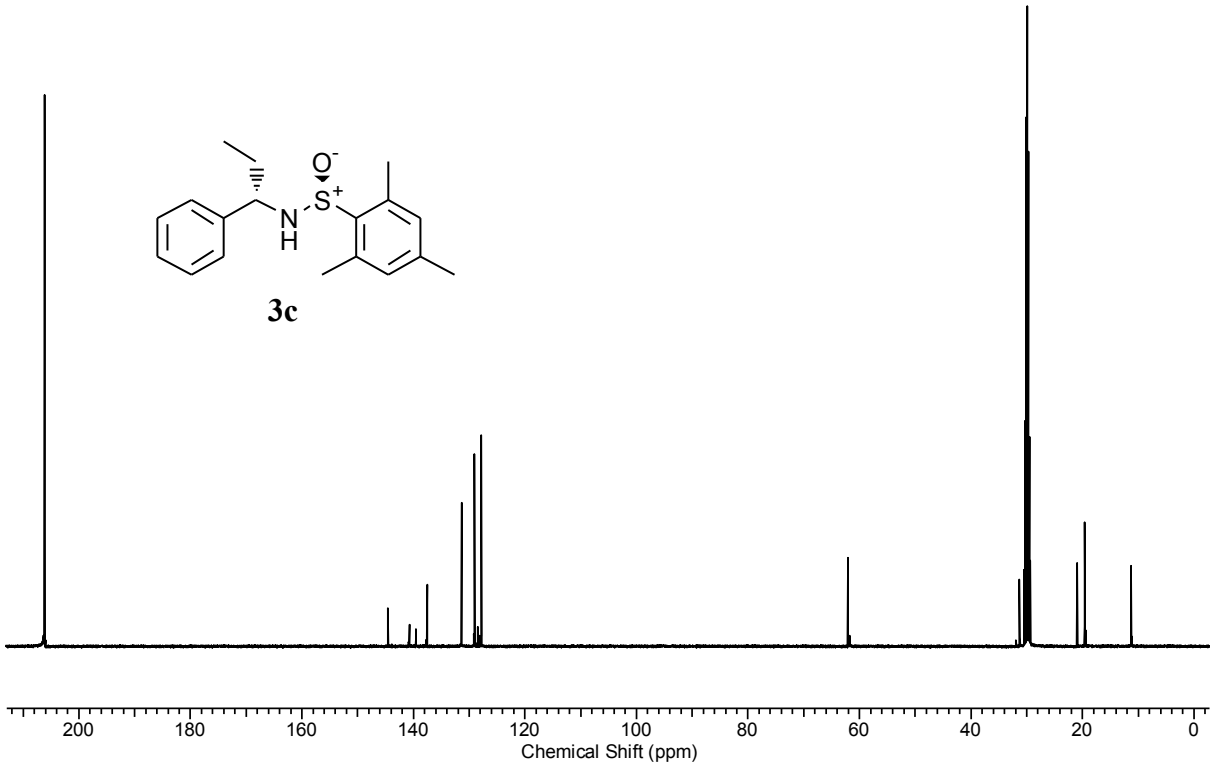

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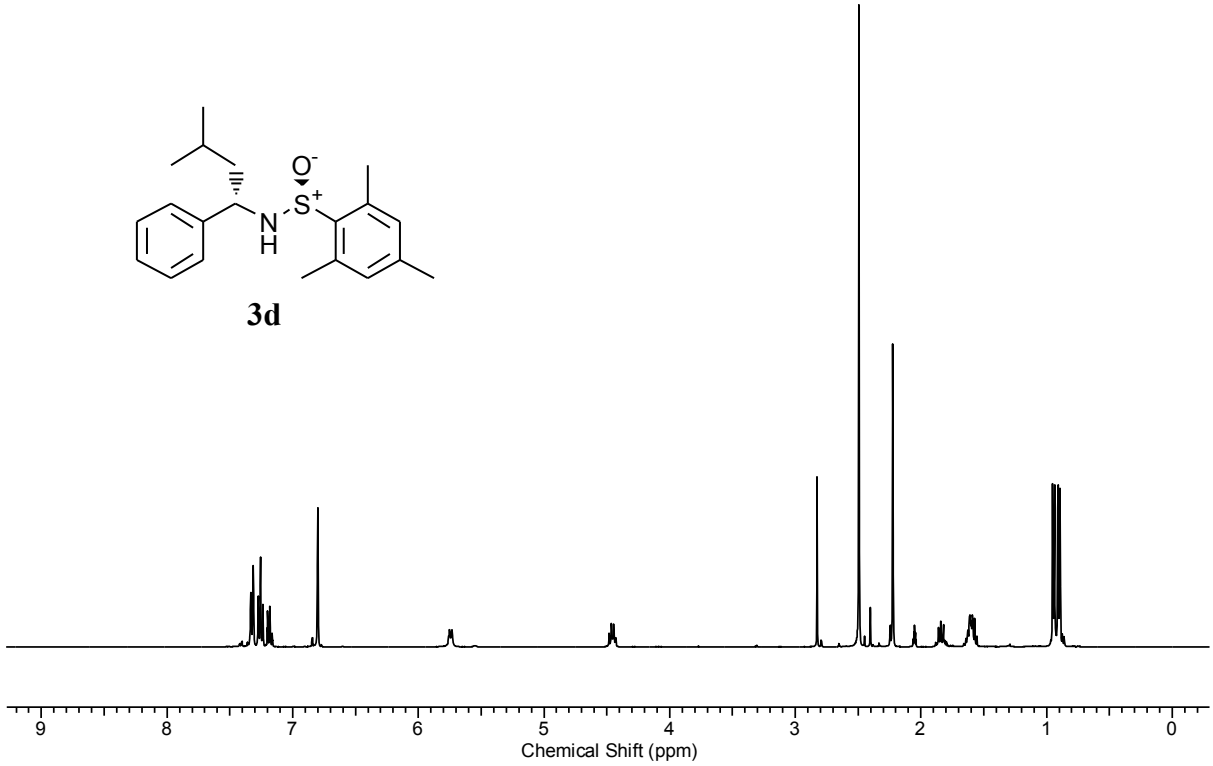

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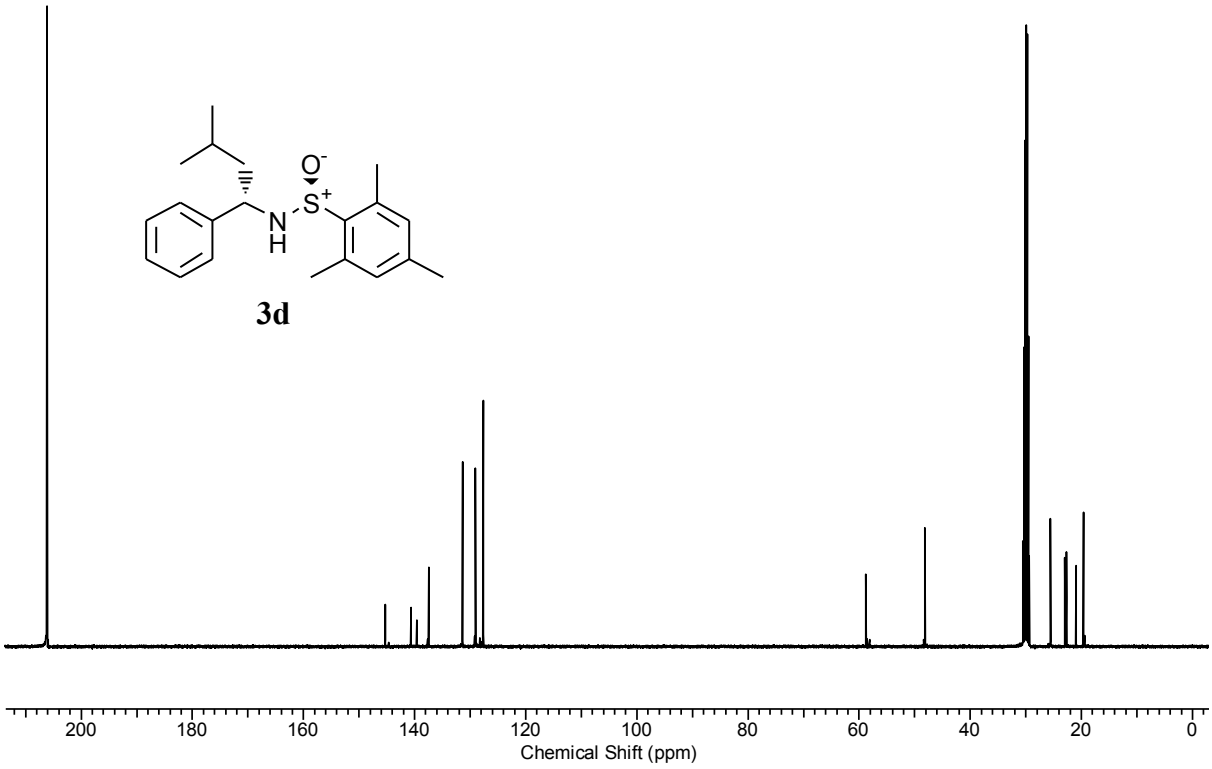

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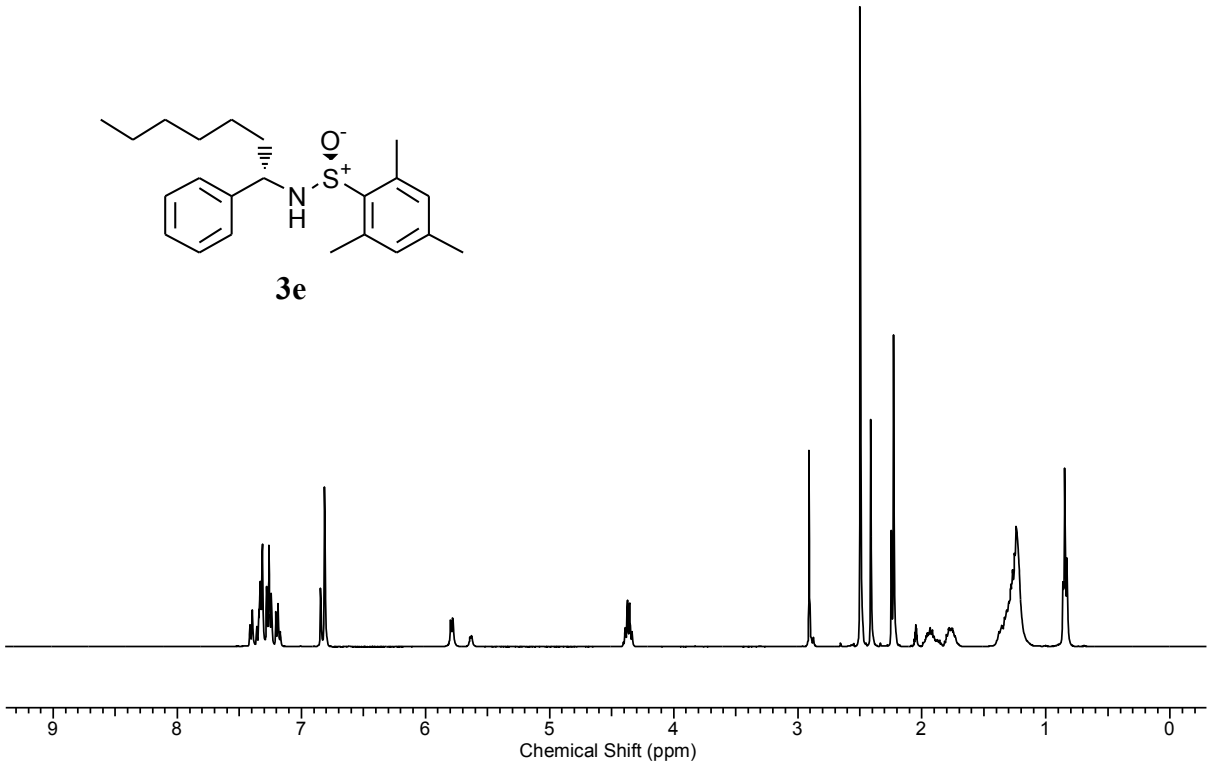

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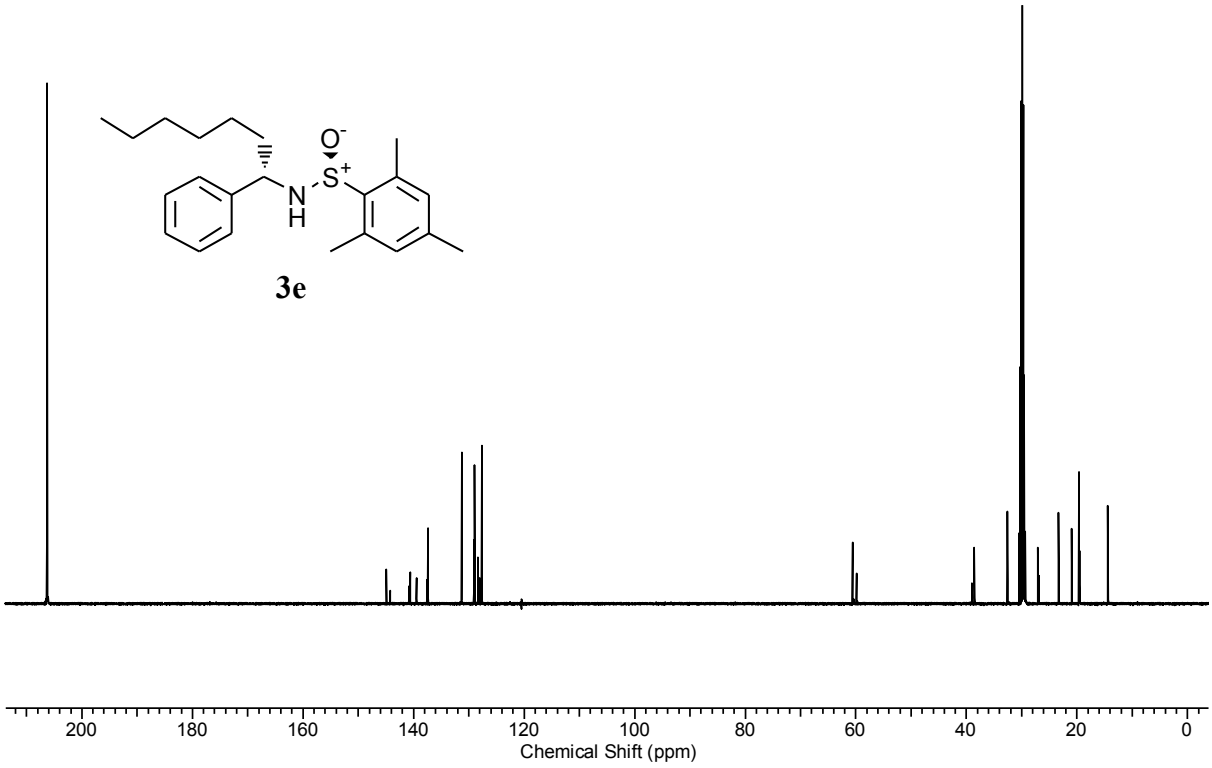

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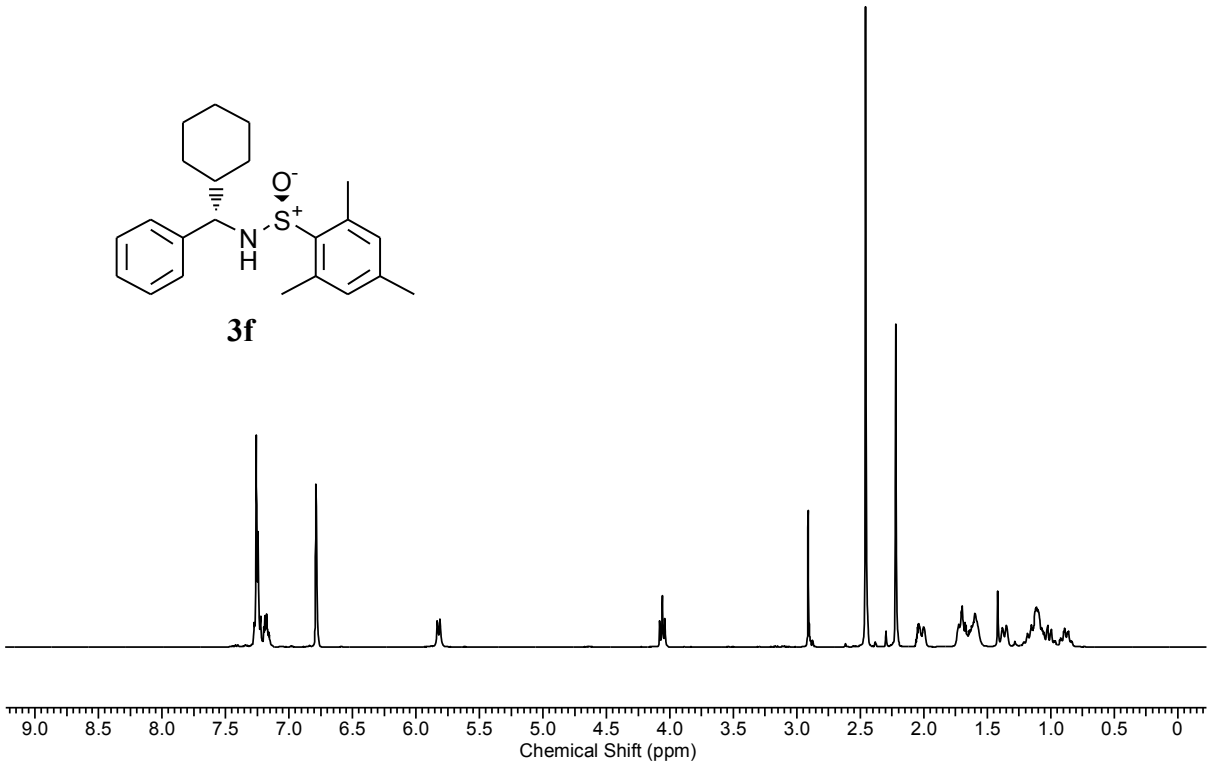

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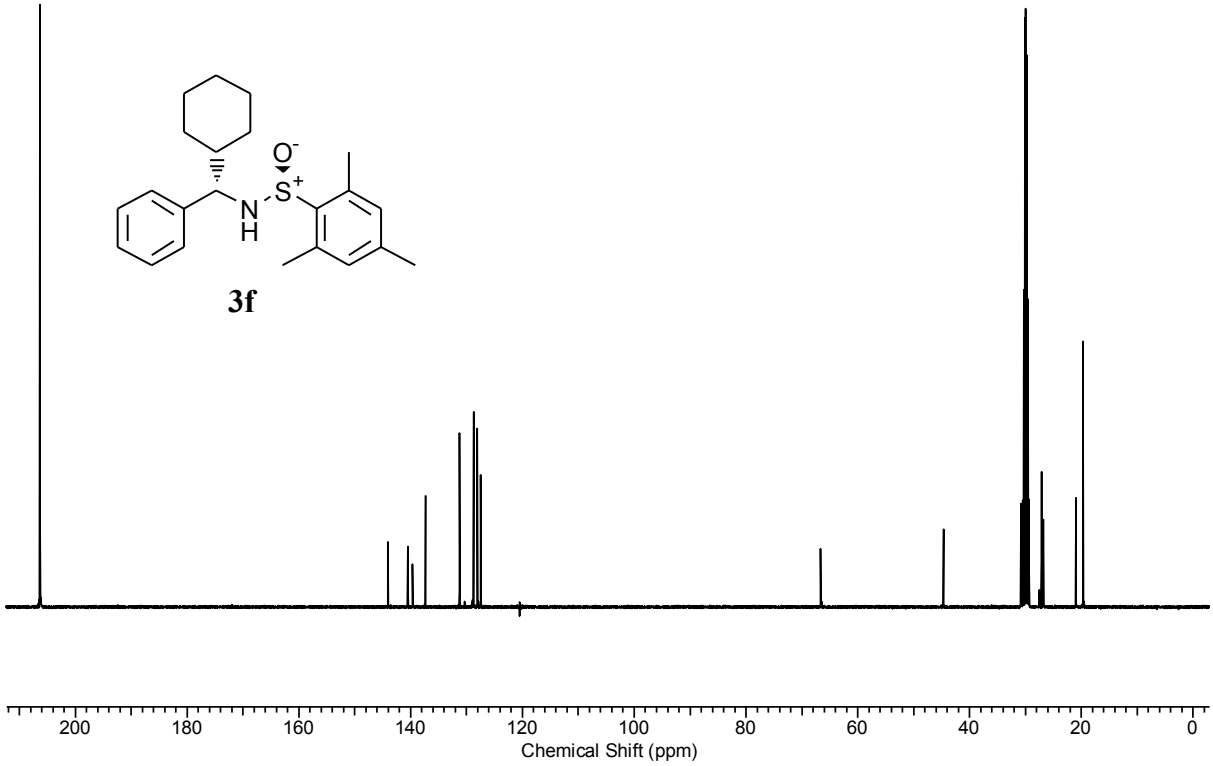

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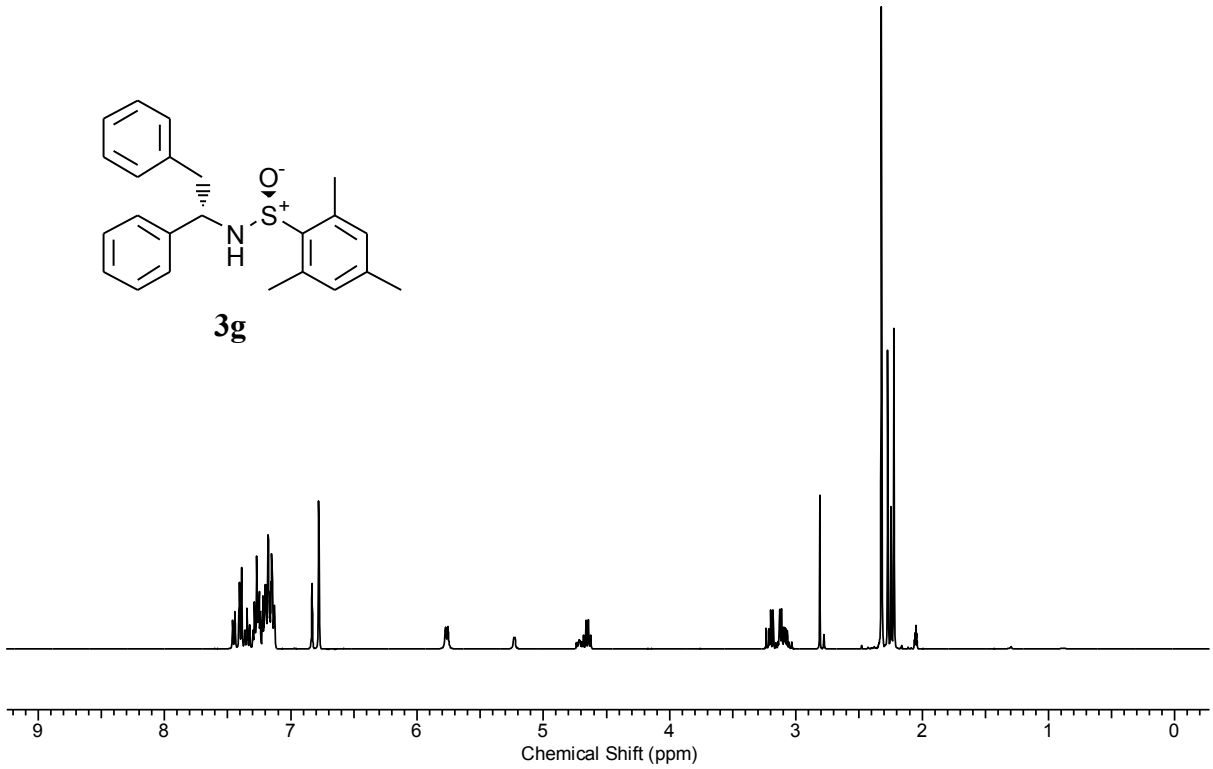

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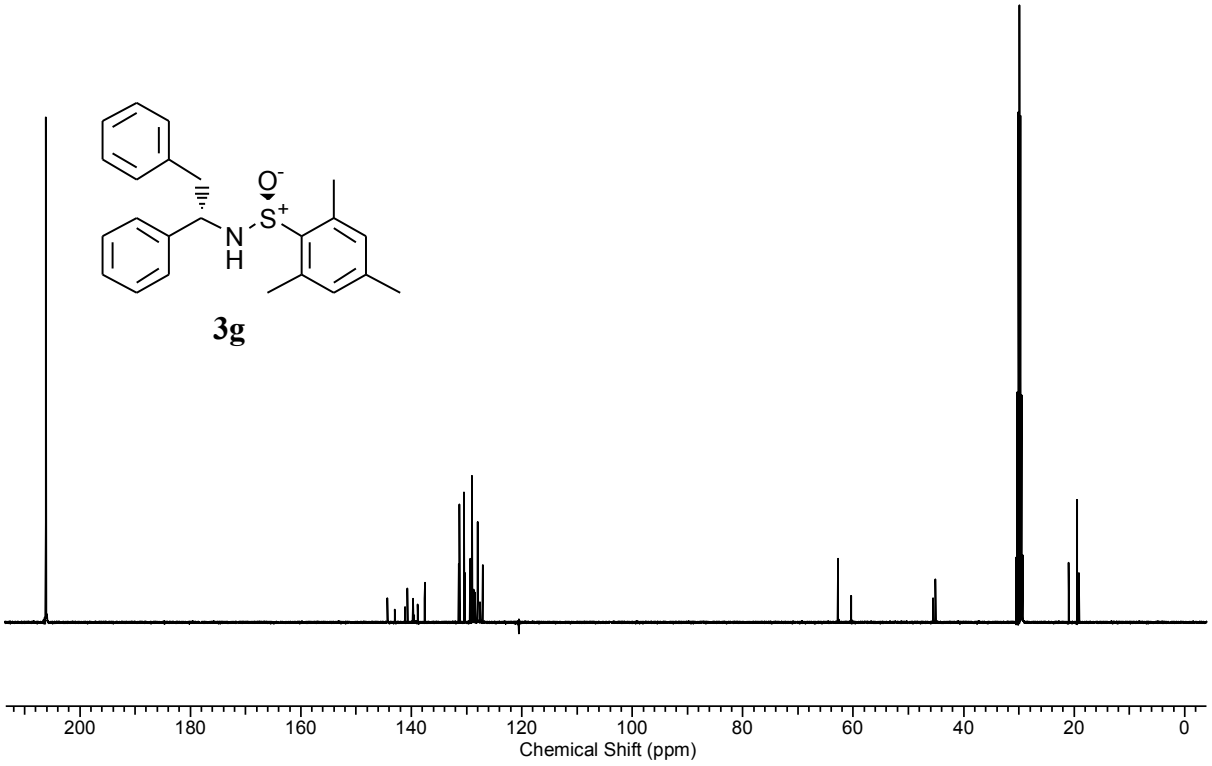

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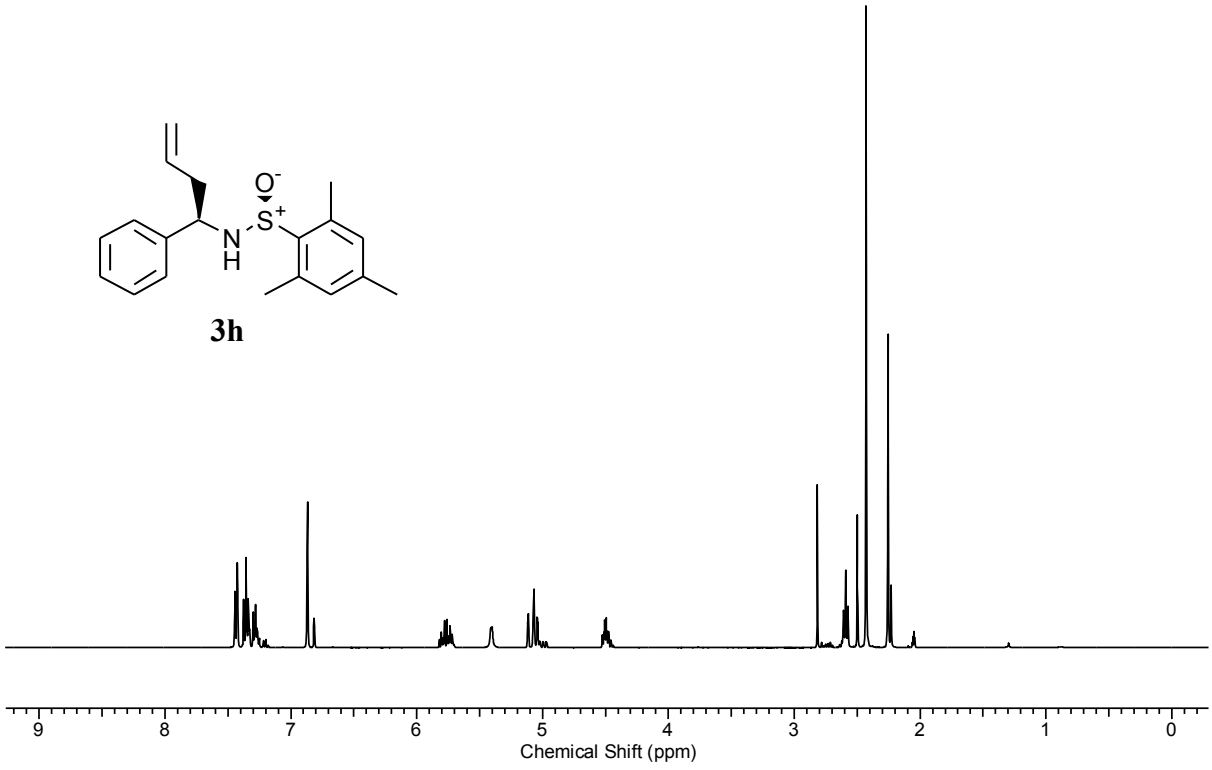

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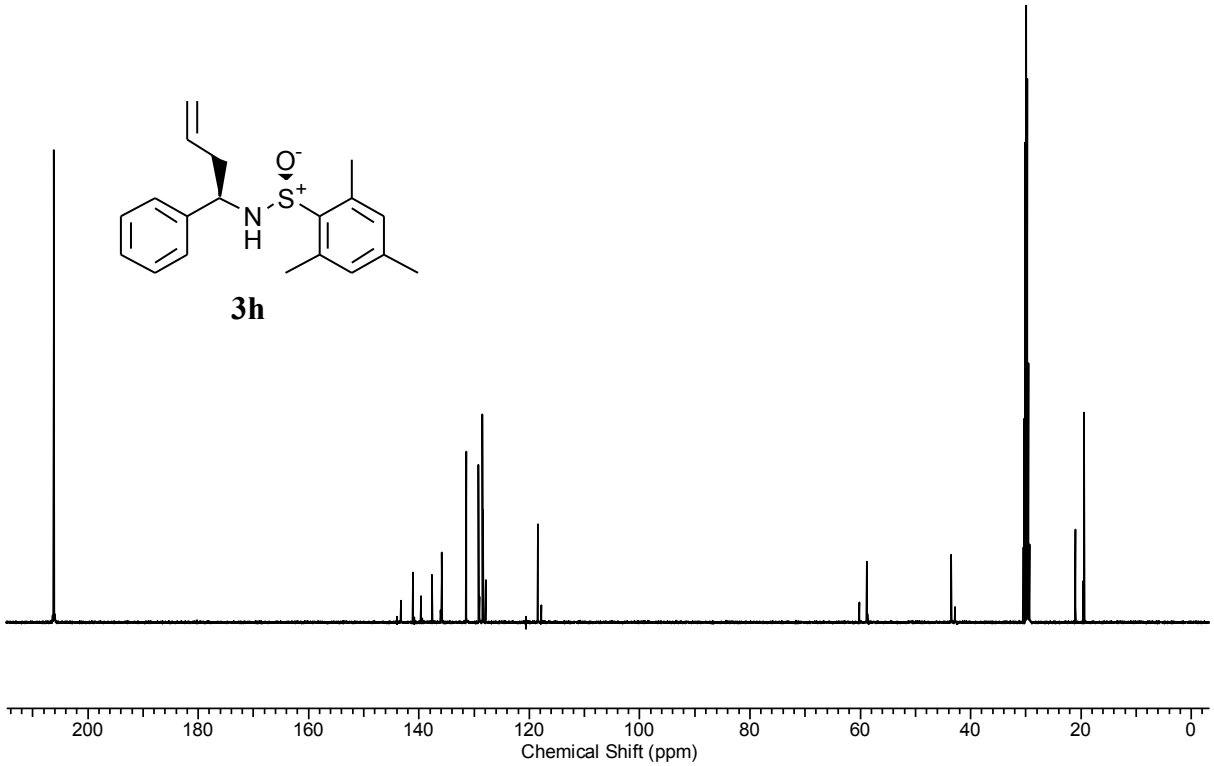

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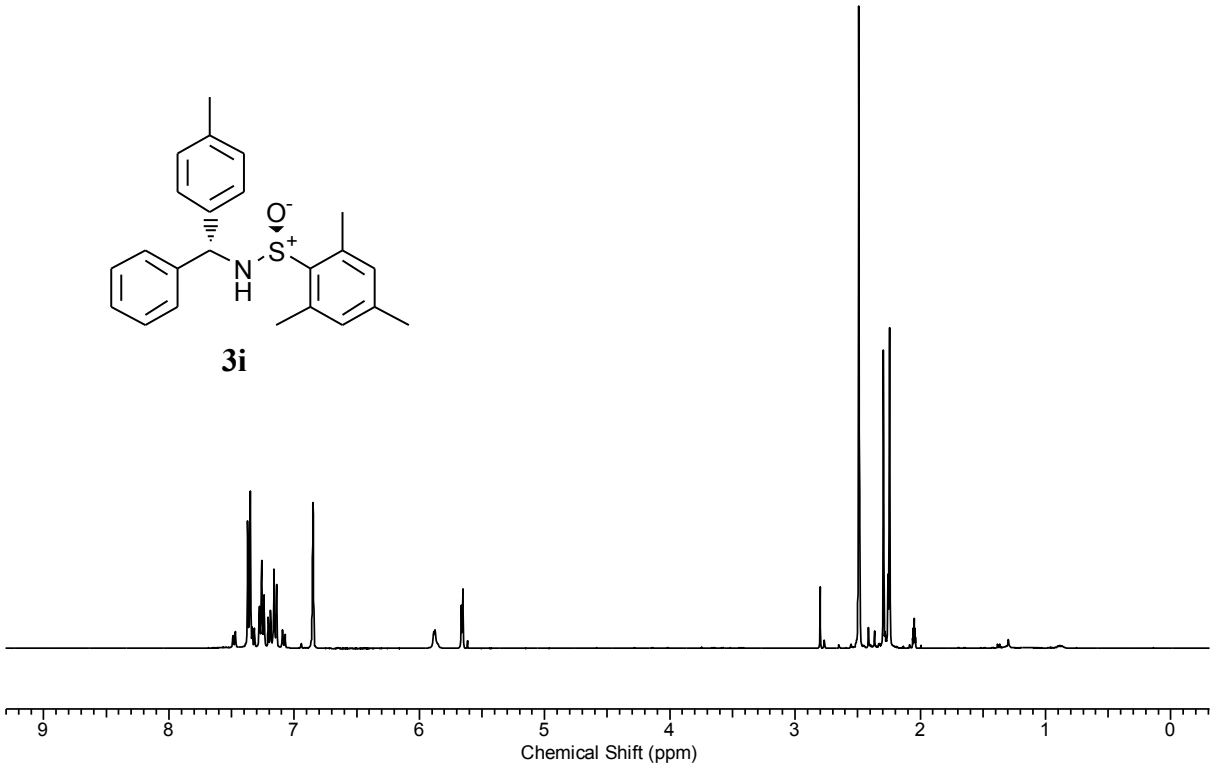

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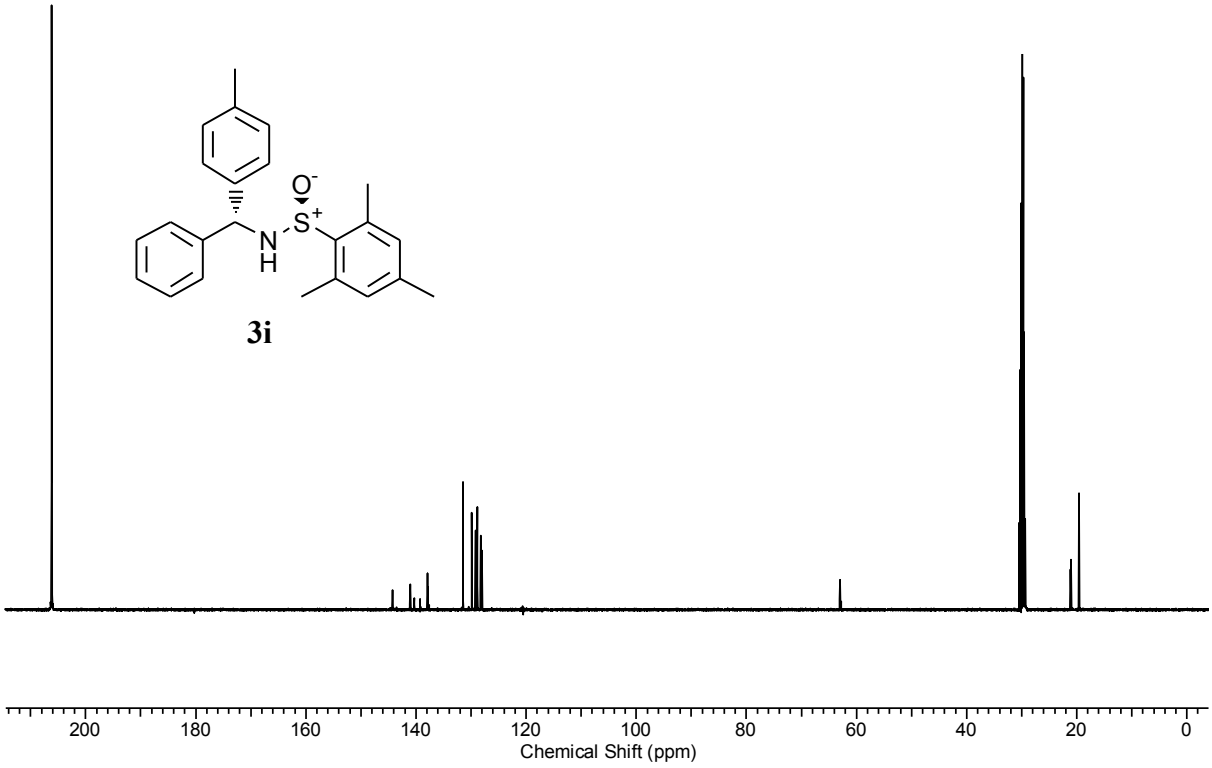

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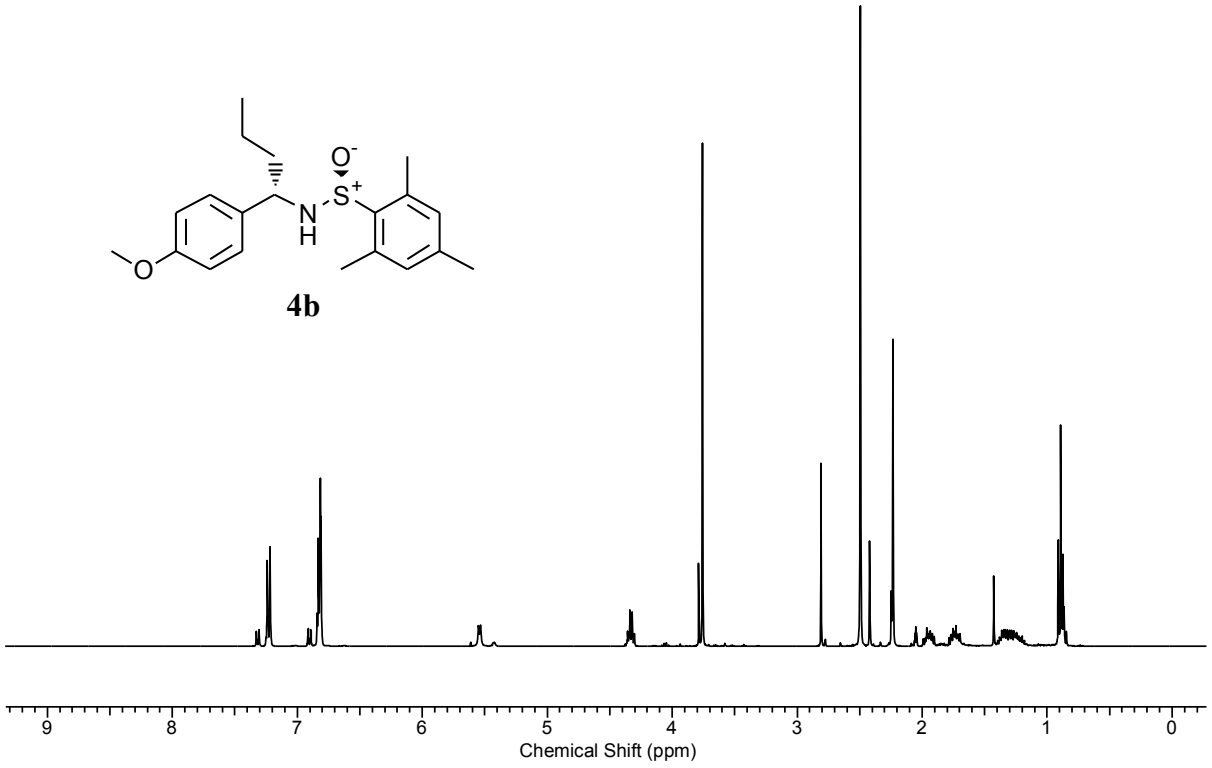

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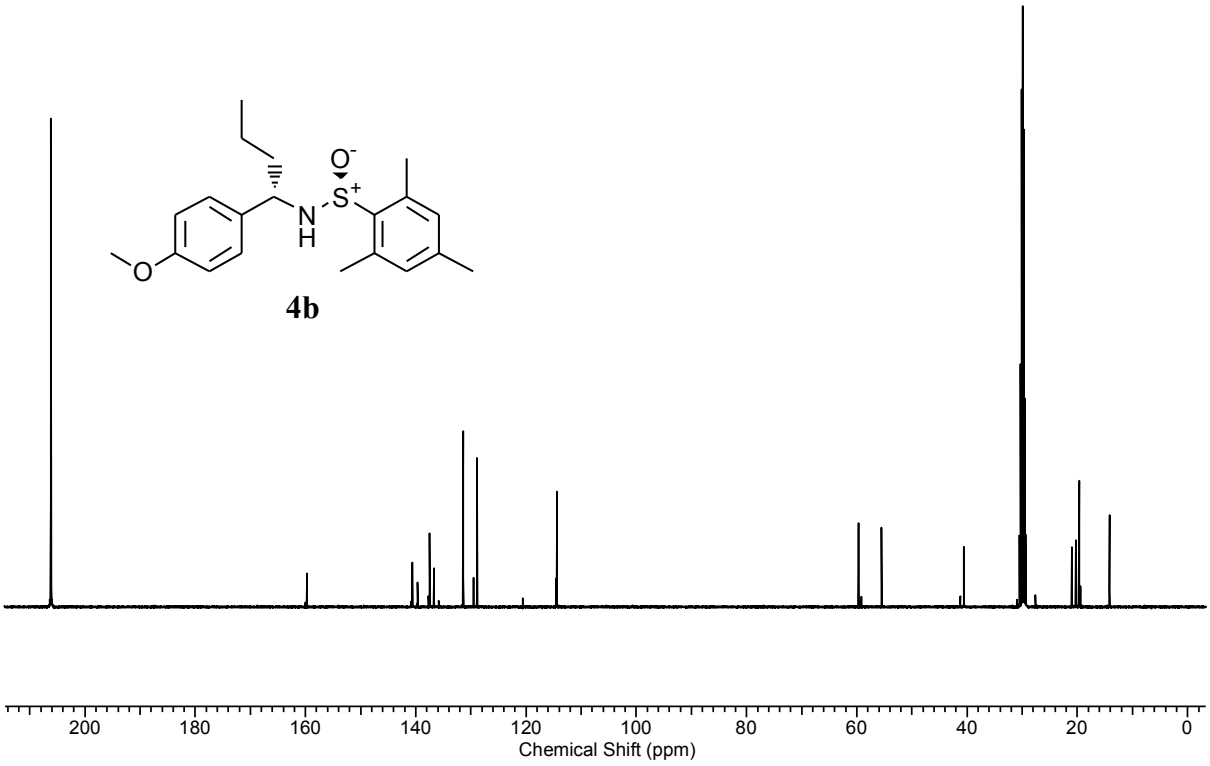

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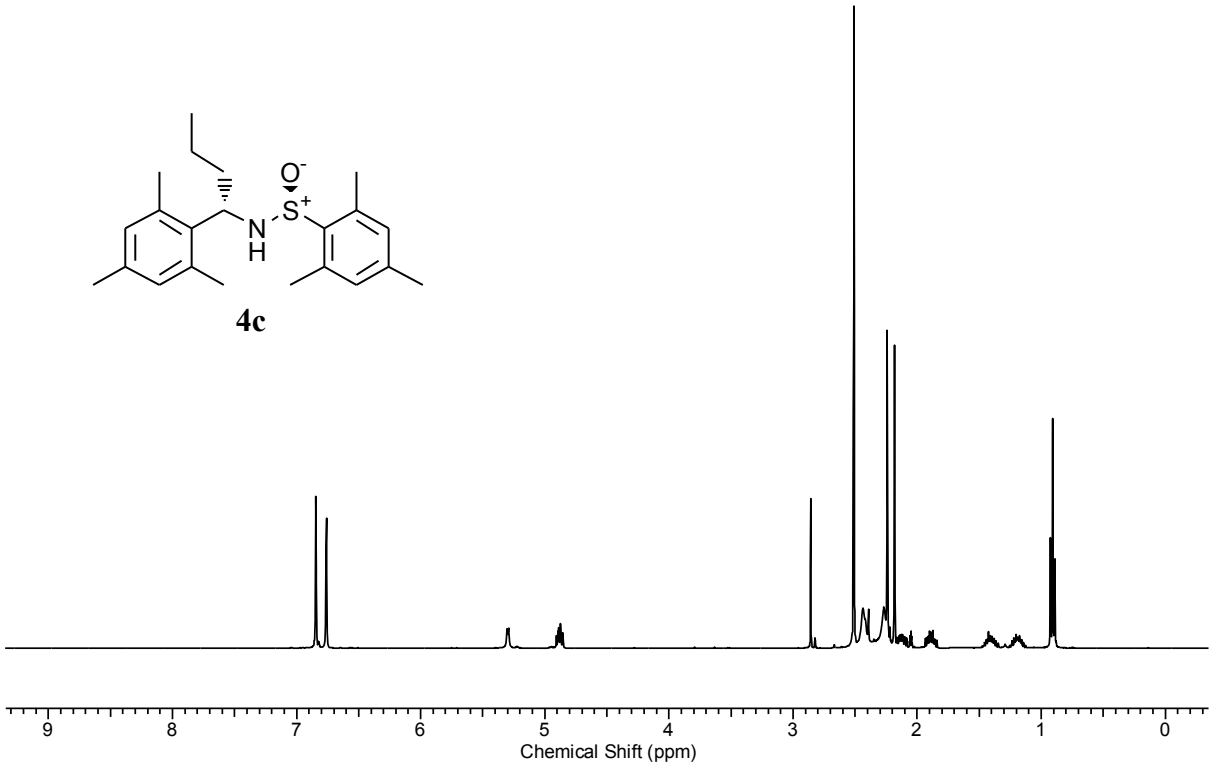

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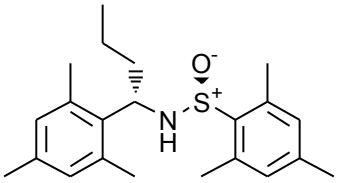

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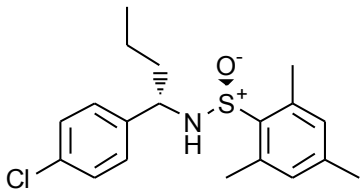

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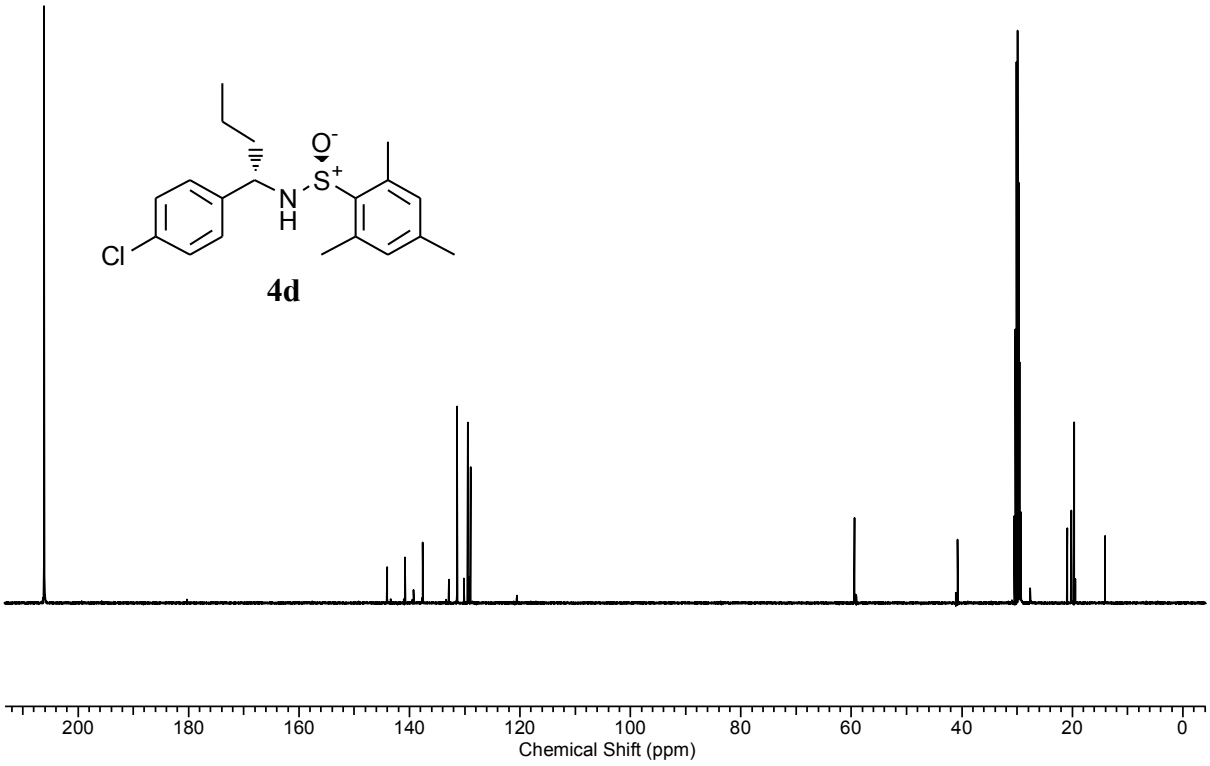

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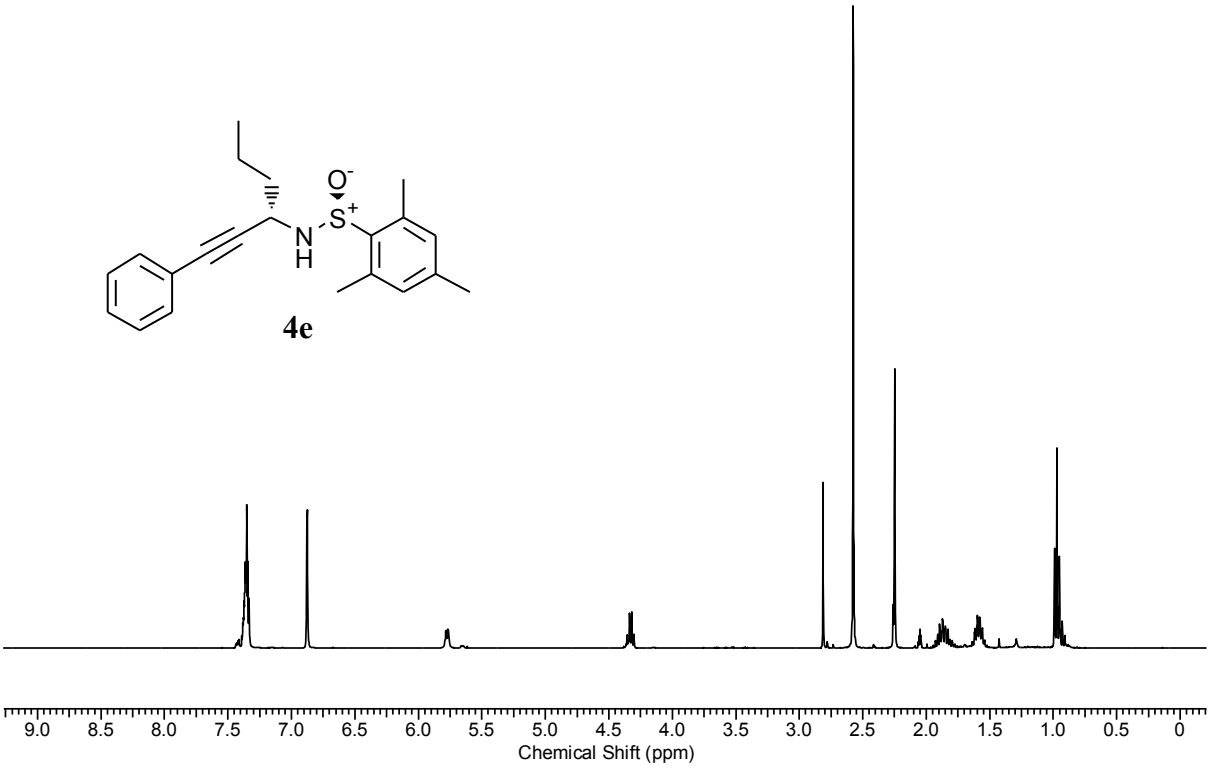

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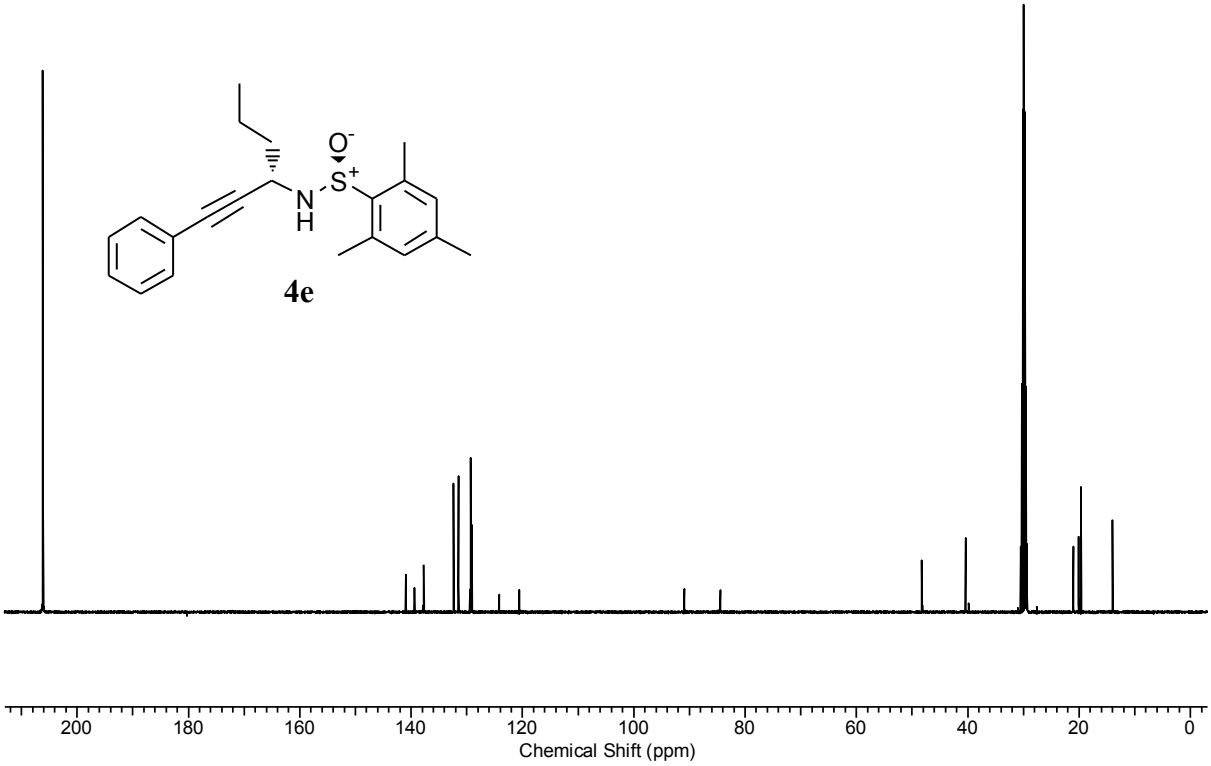

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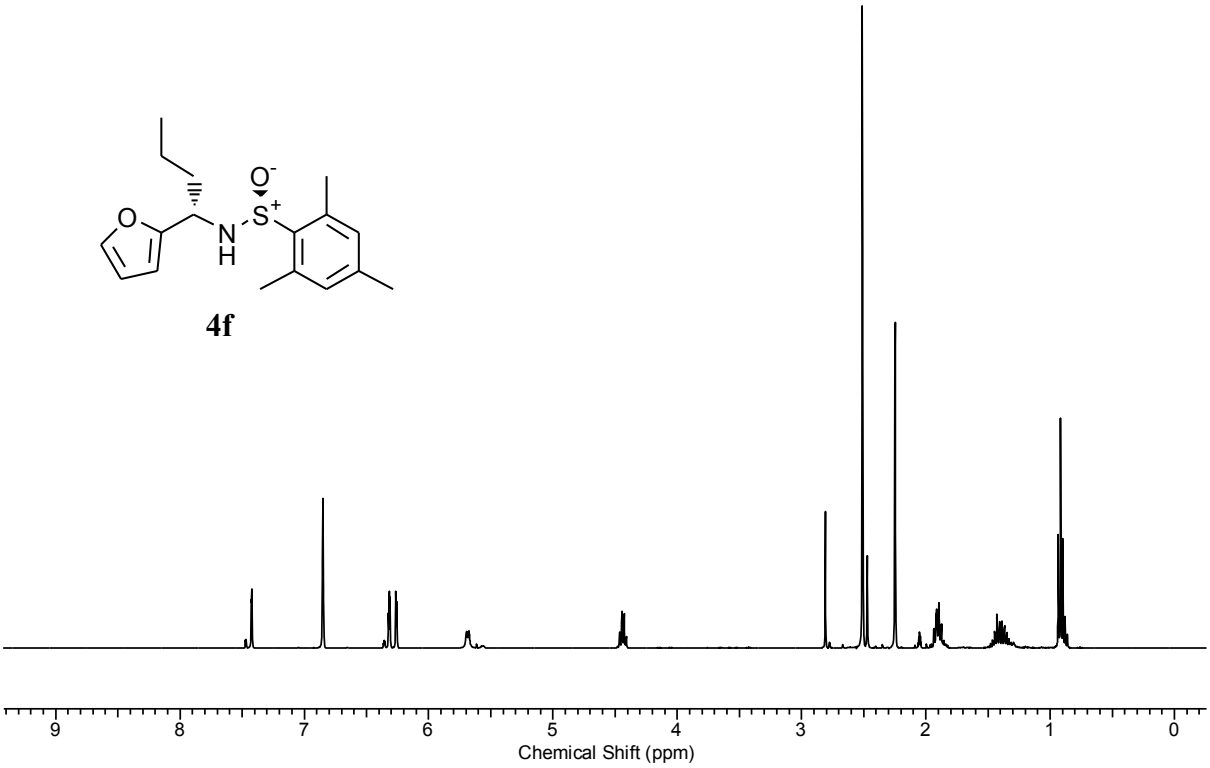

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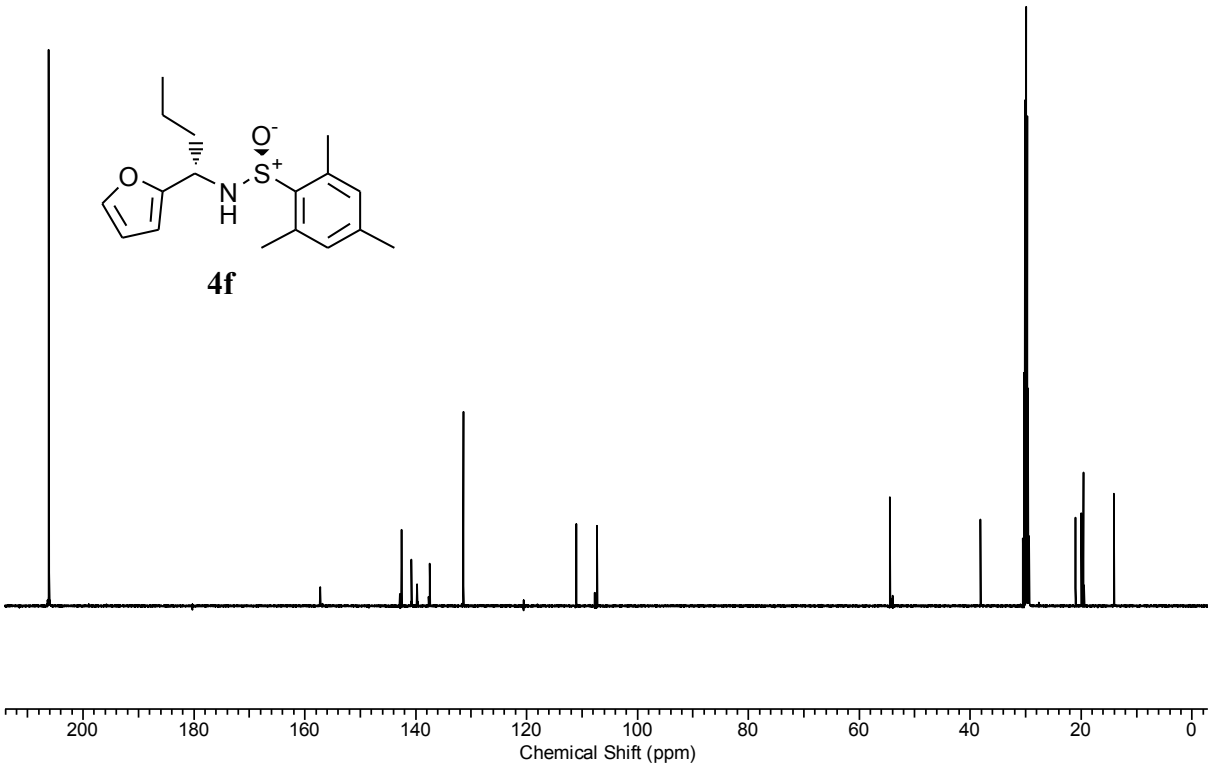

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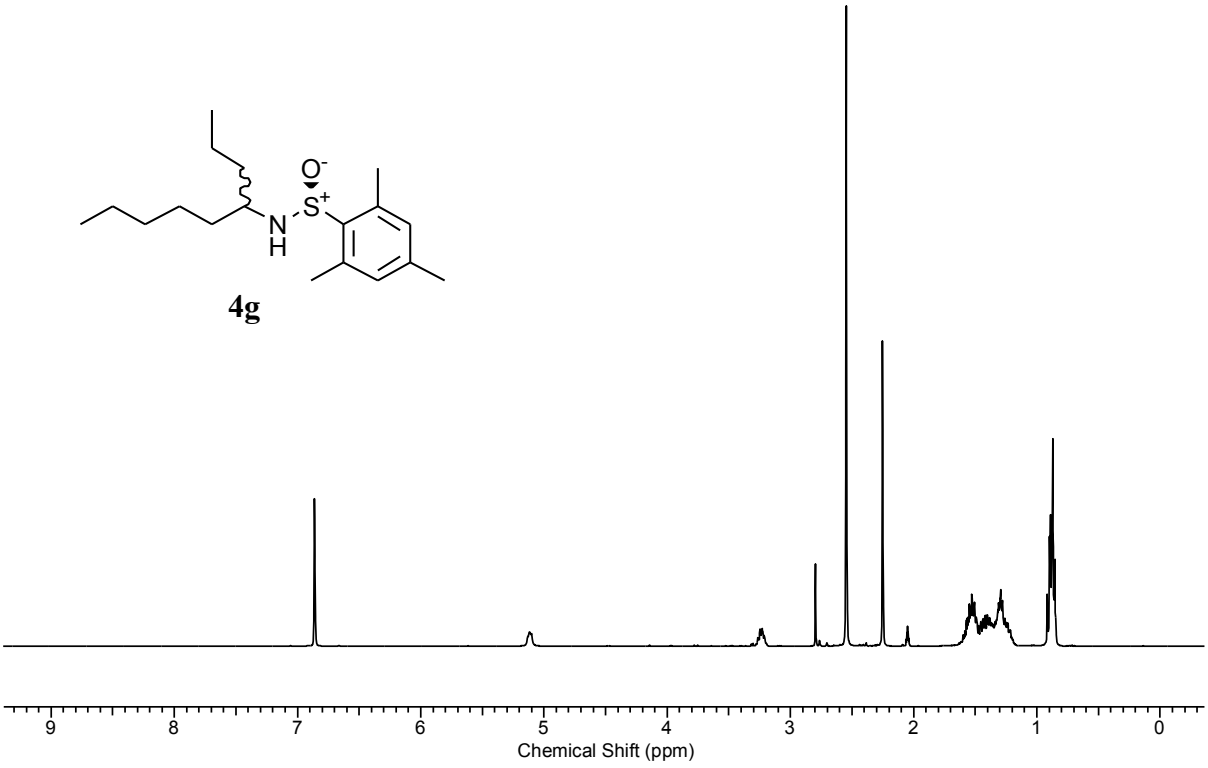

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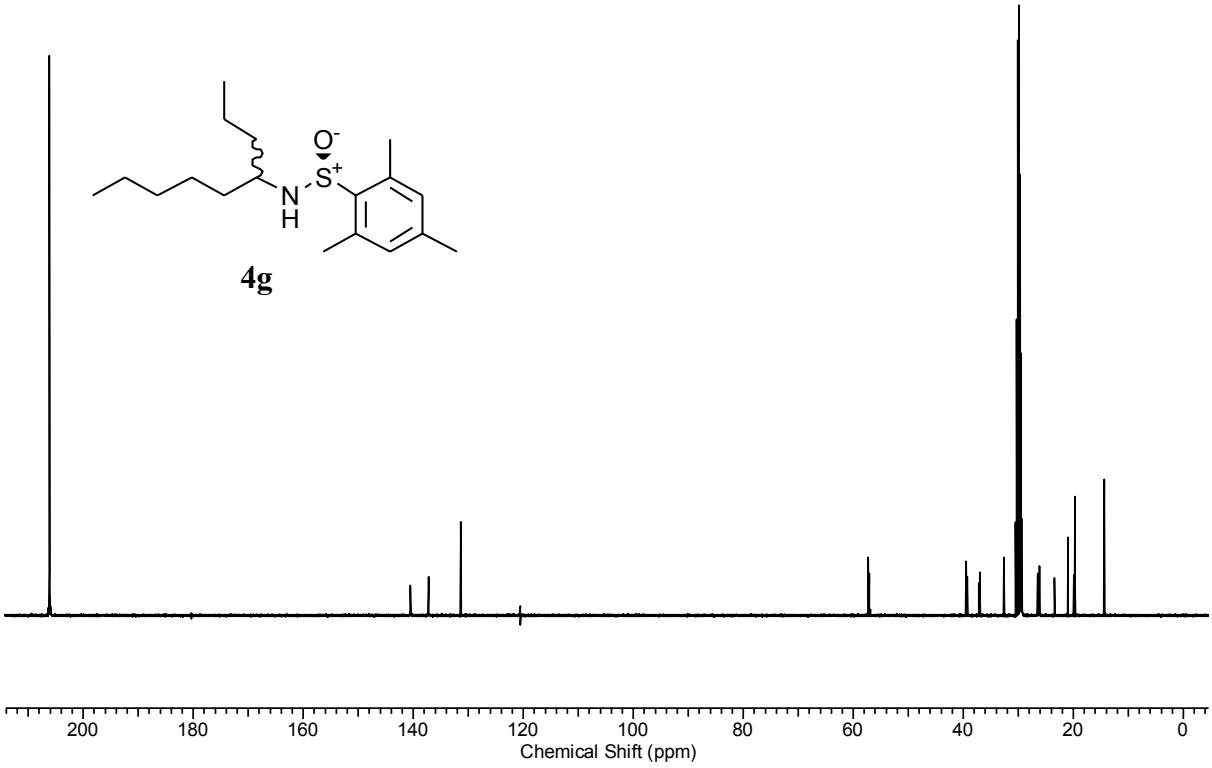

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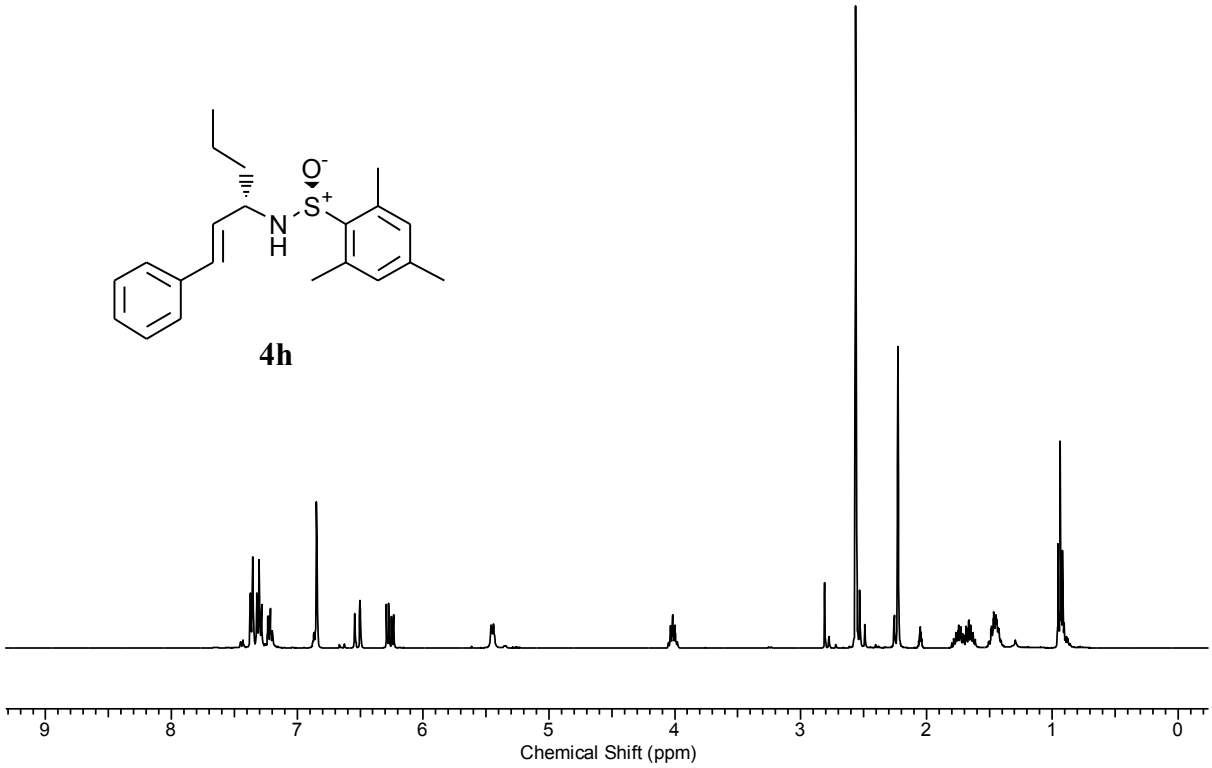
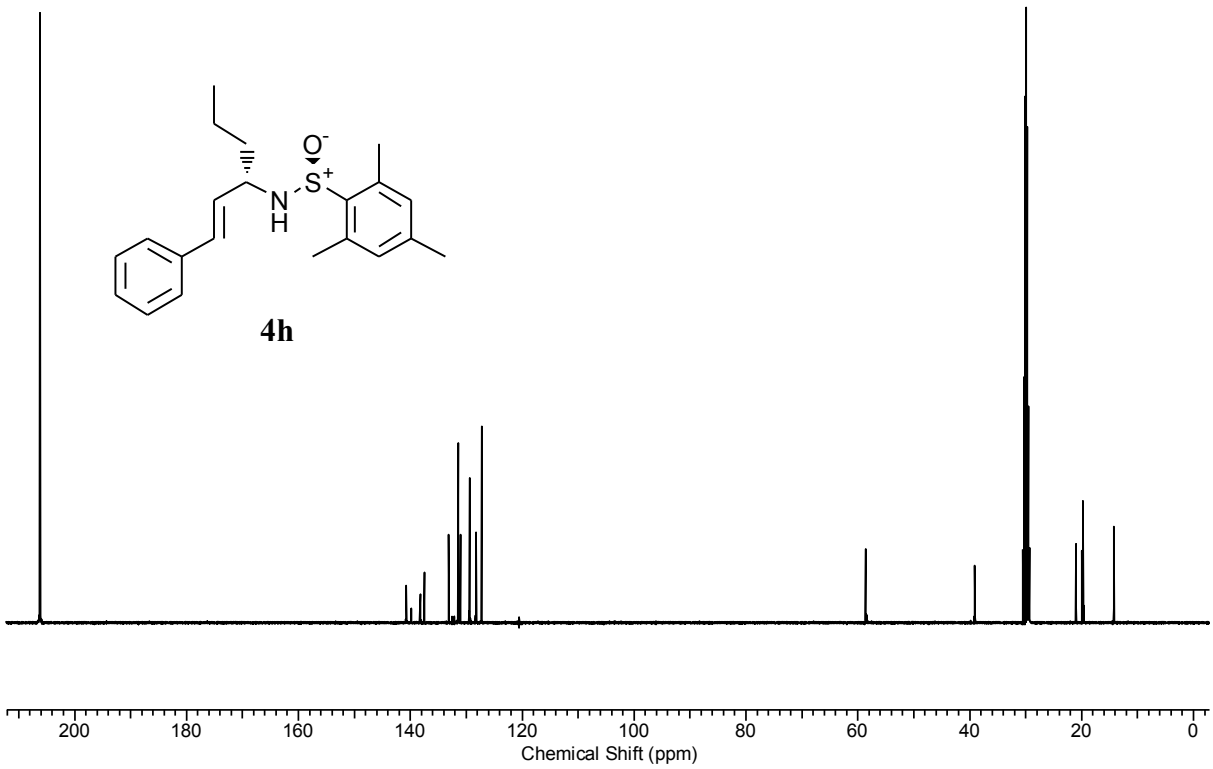


4h



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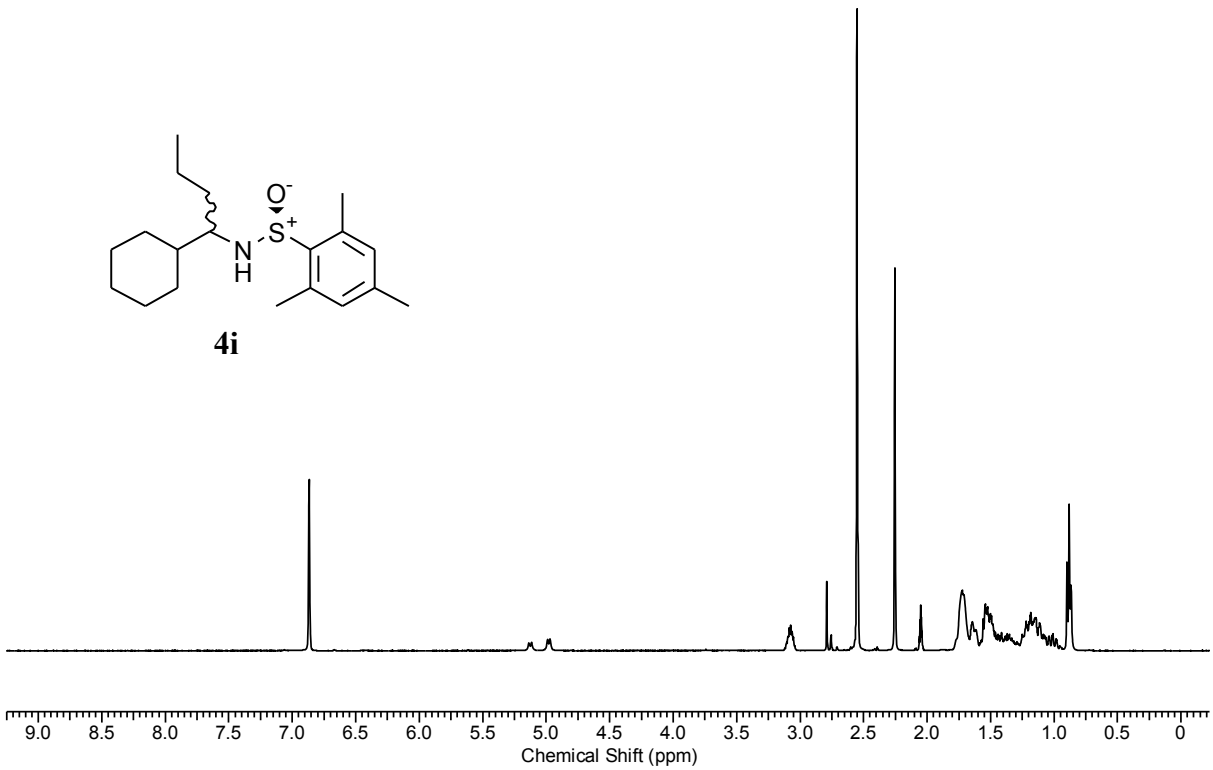

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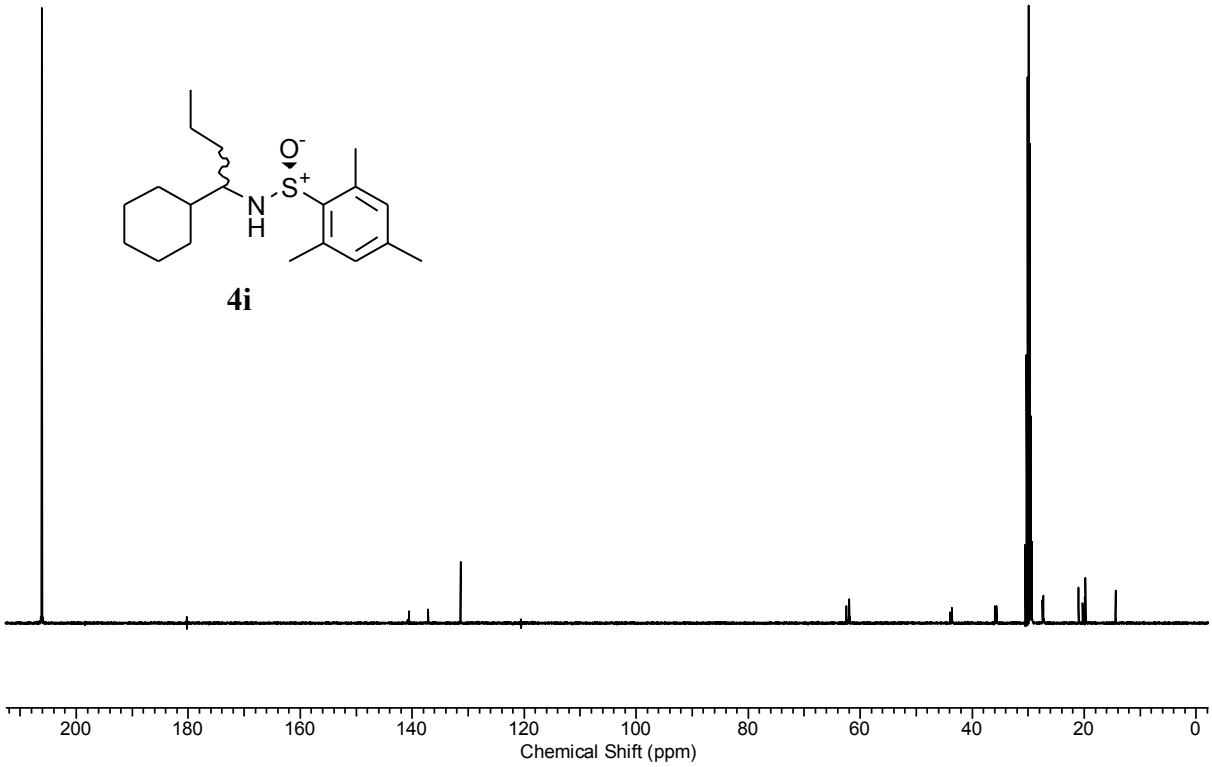

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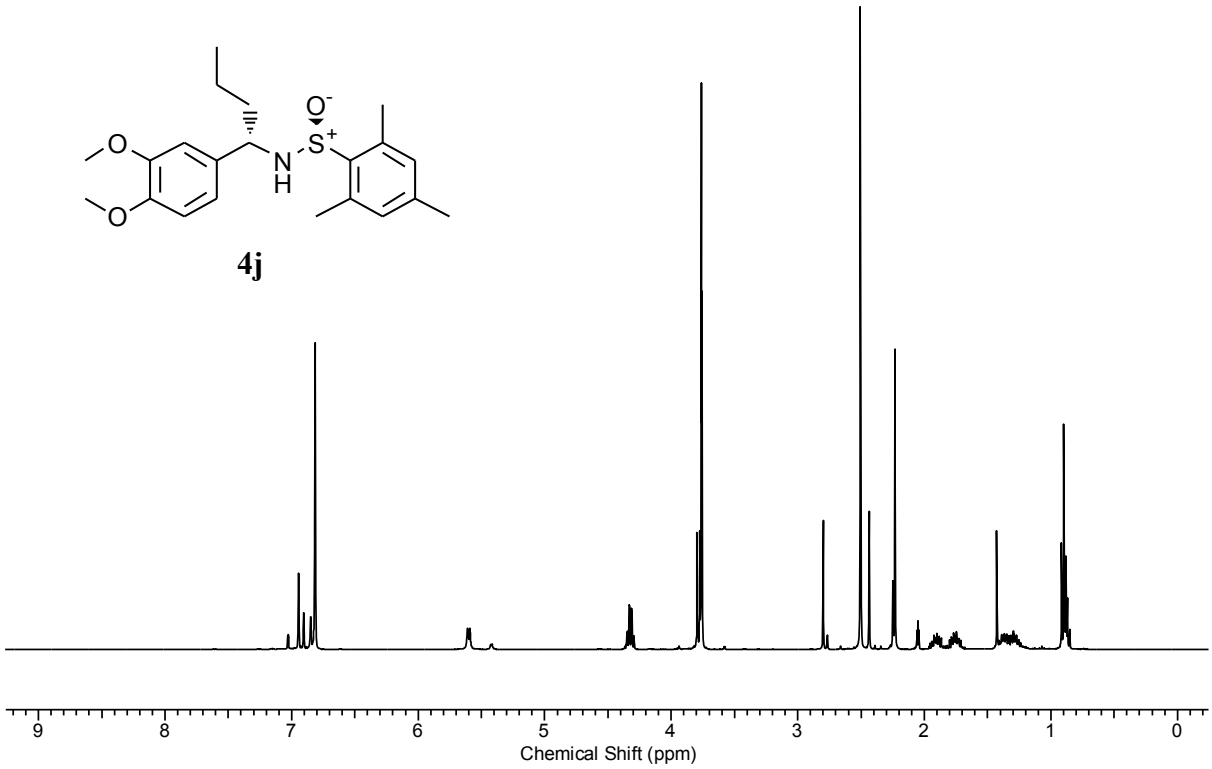

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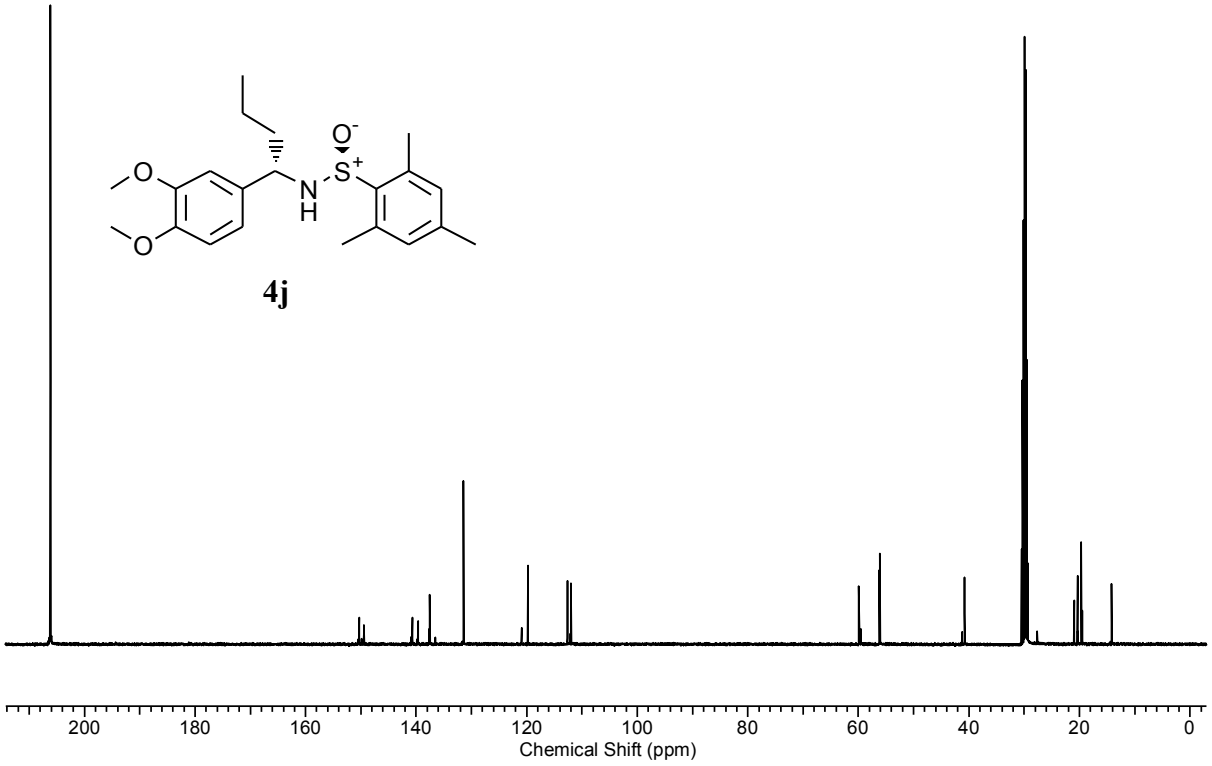

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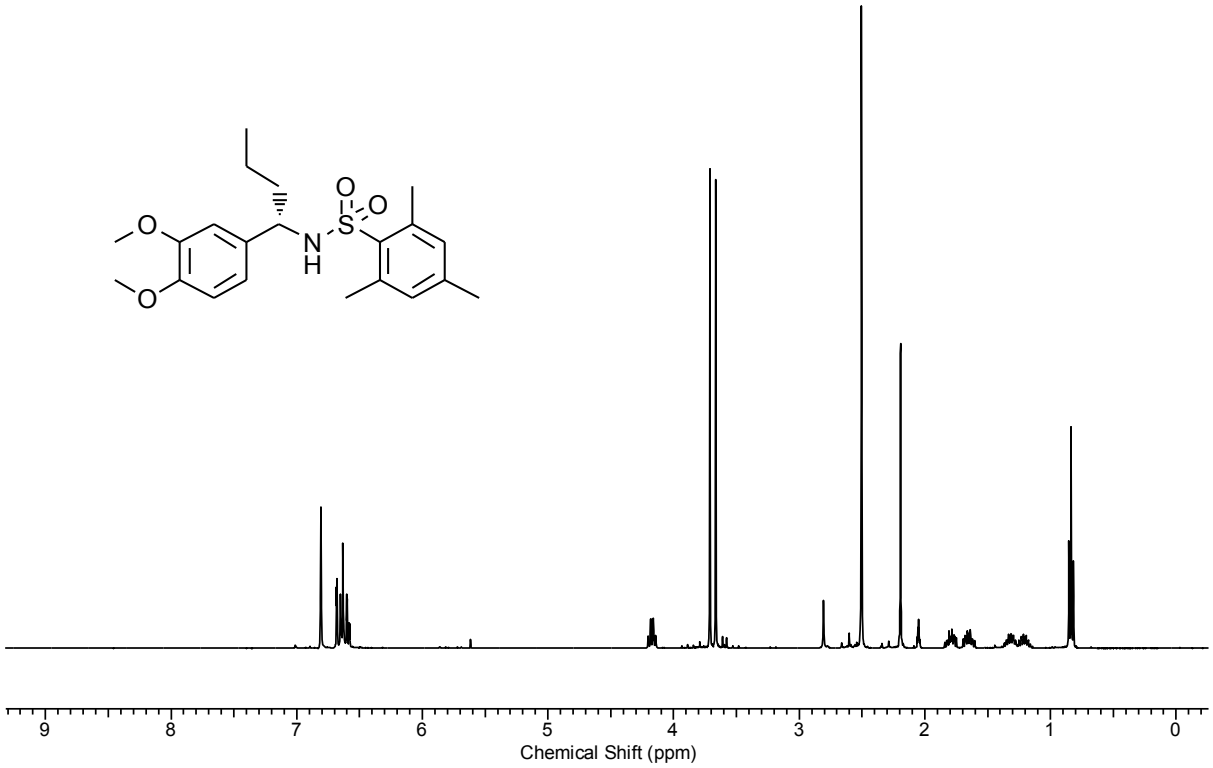

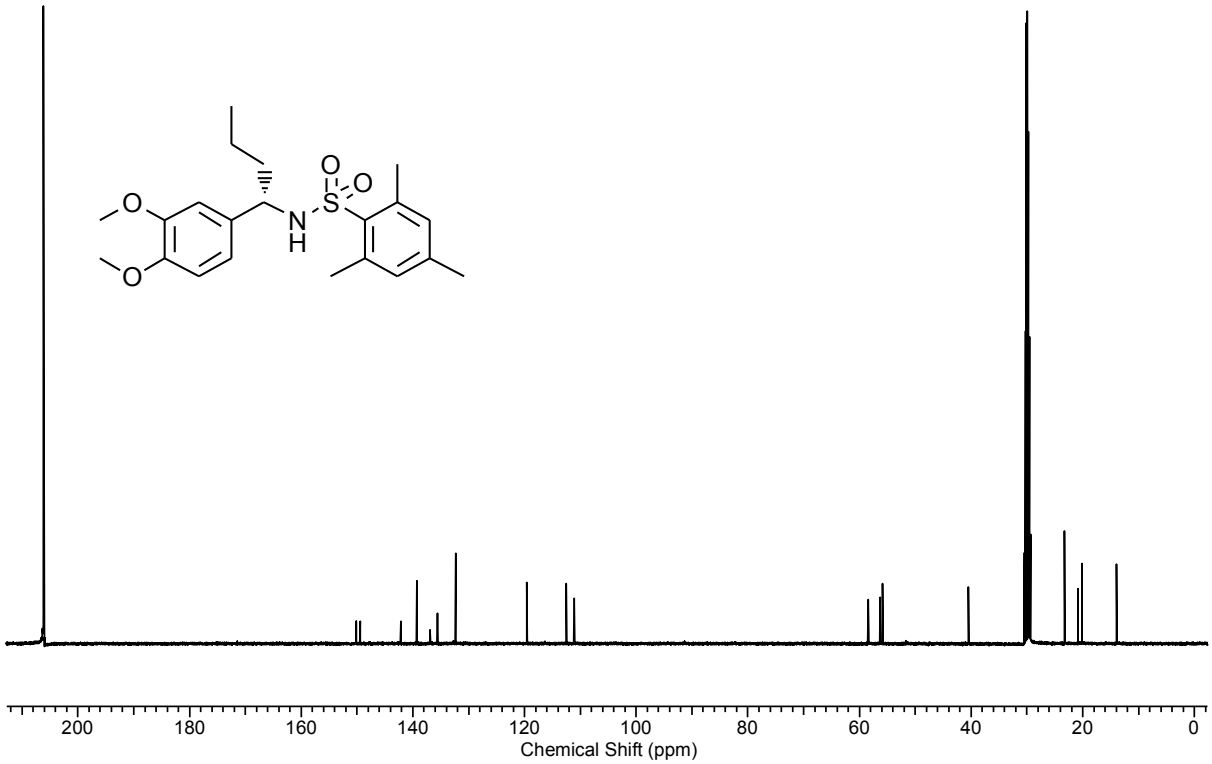

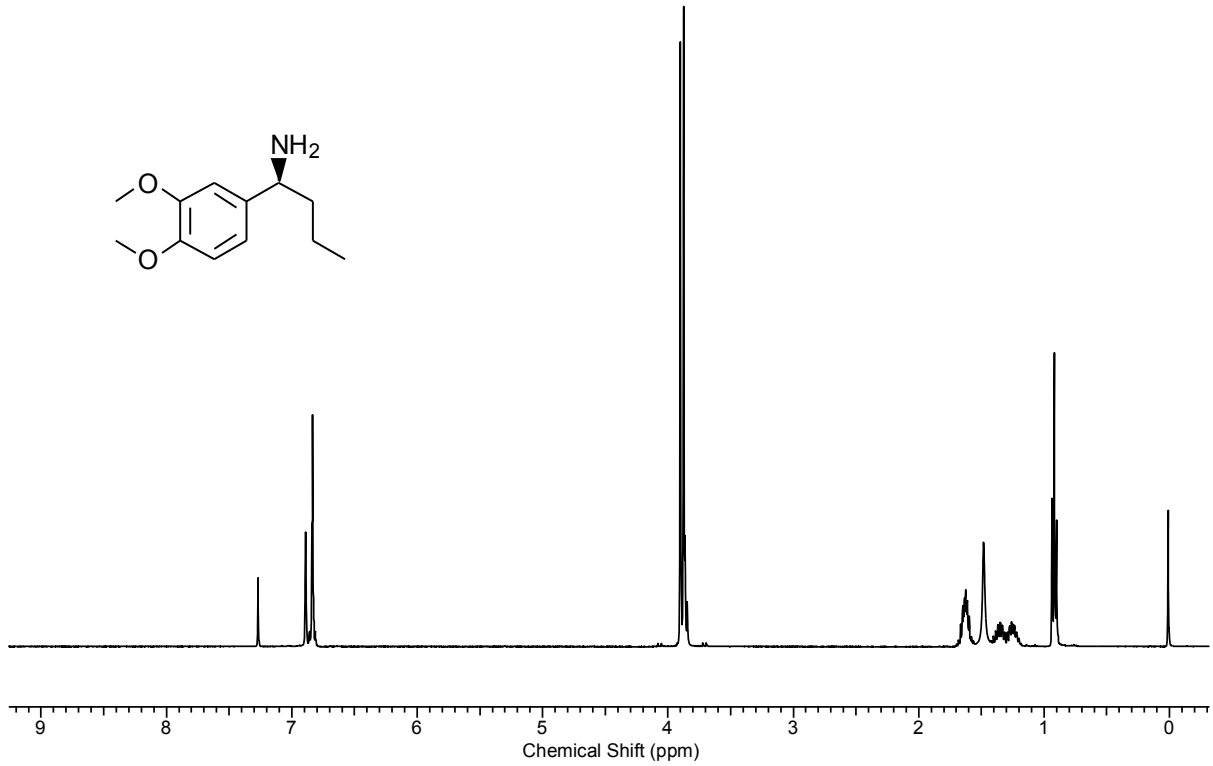

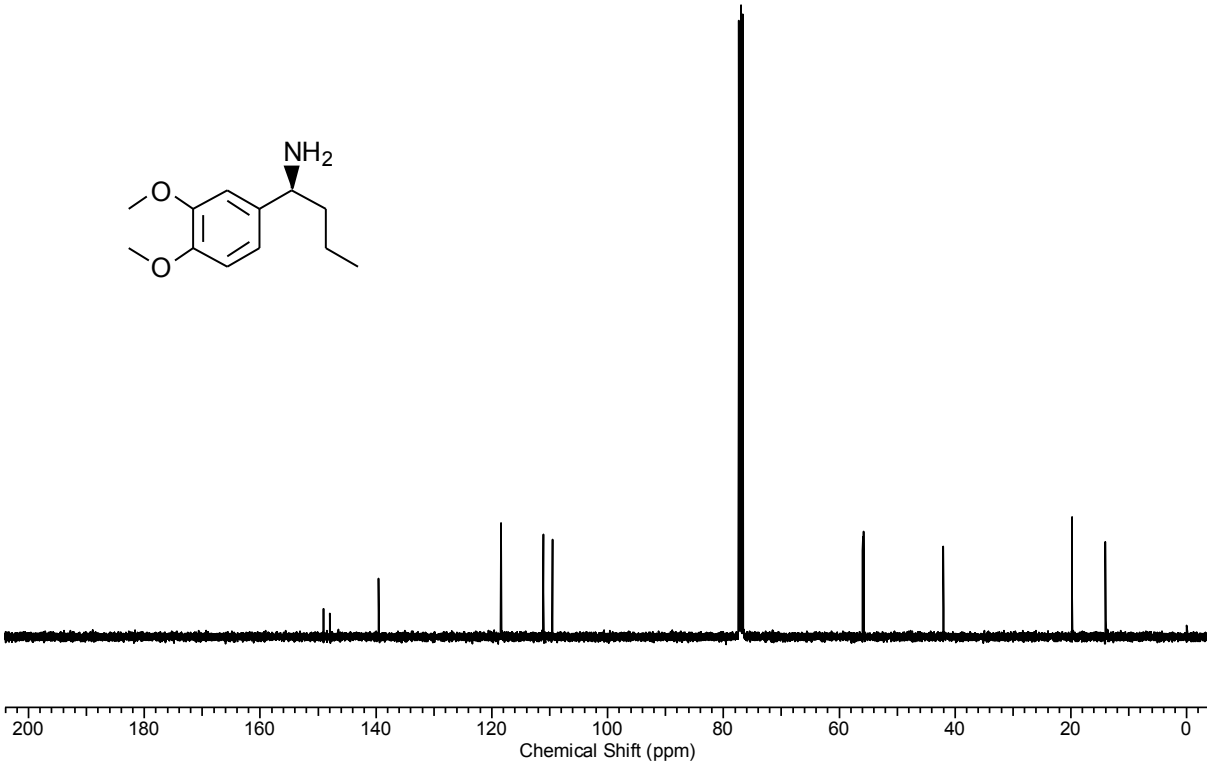

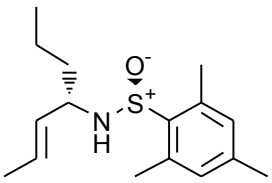

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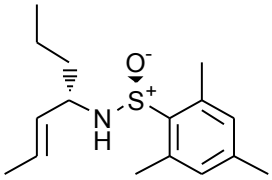

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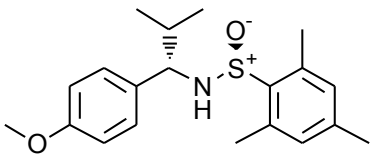

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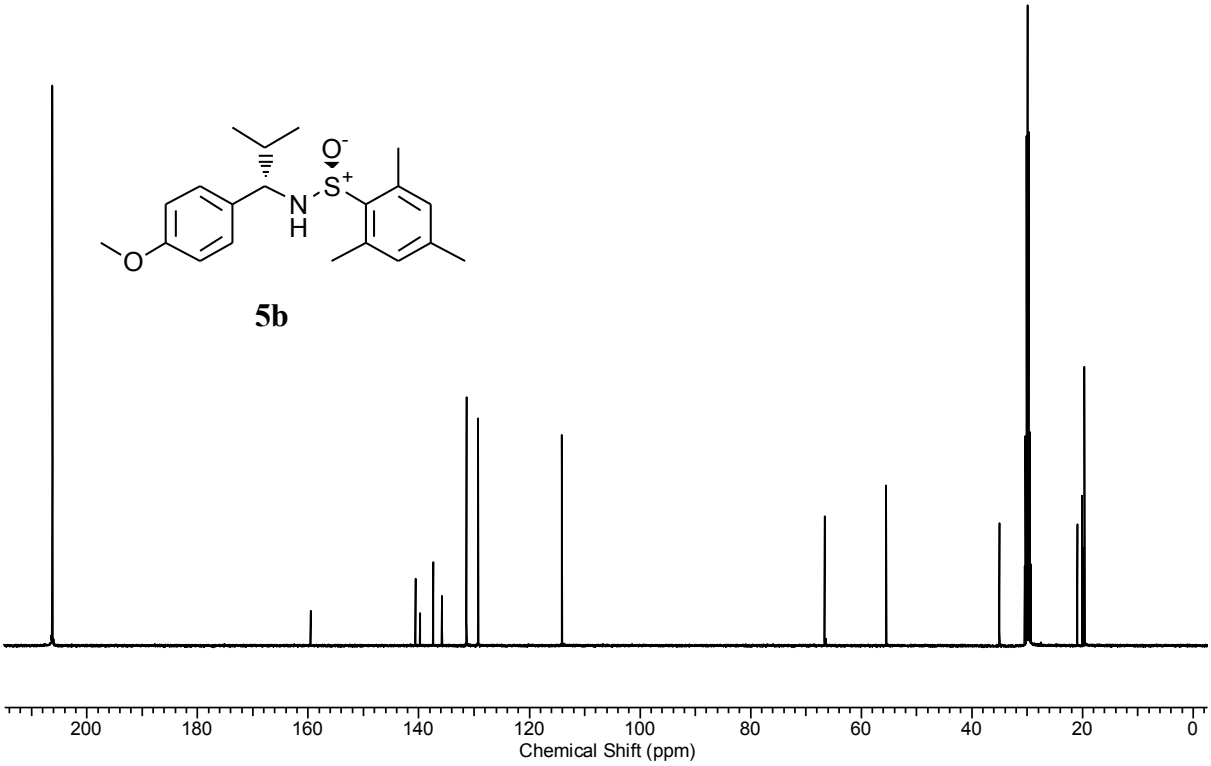

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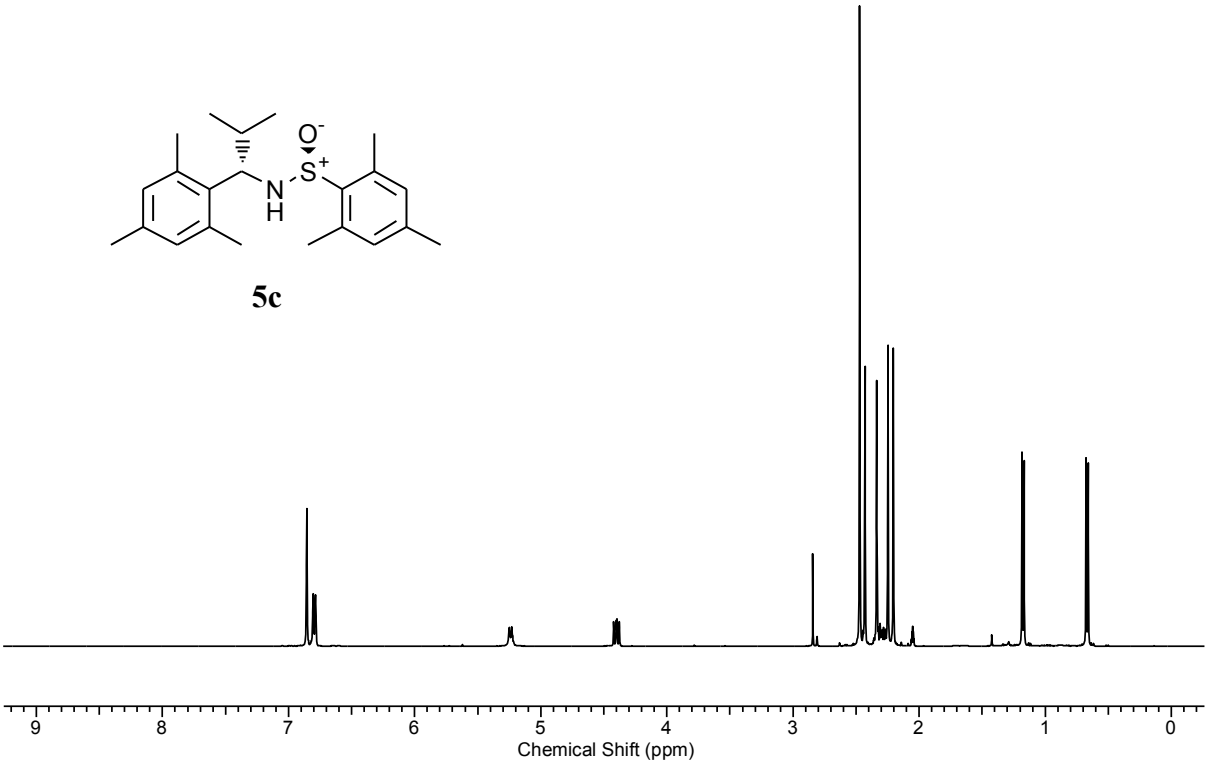

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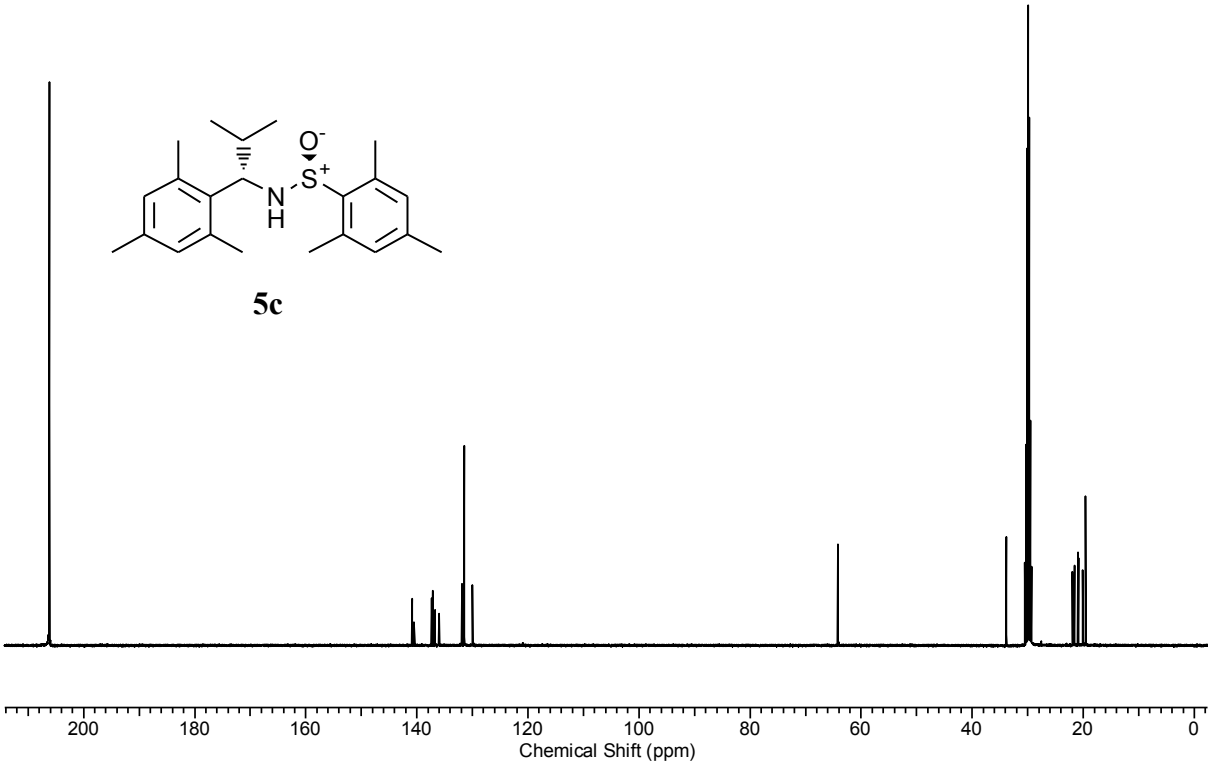

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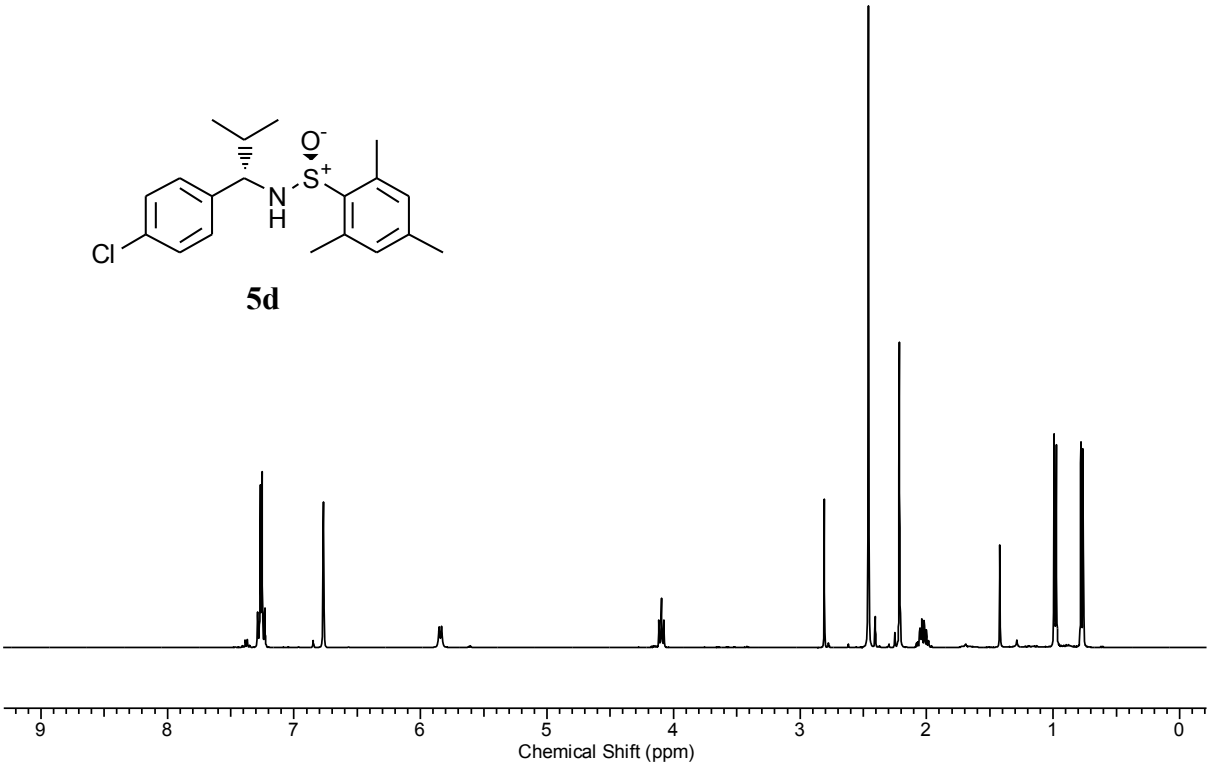

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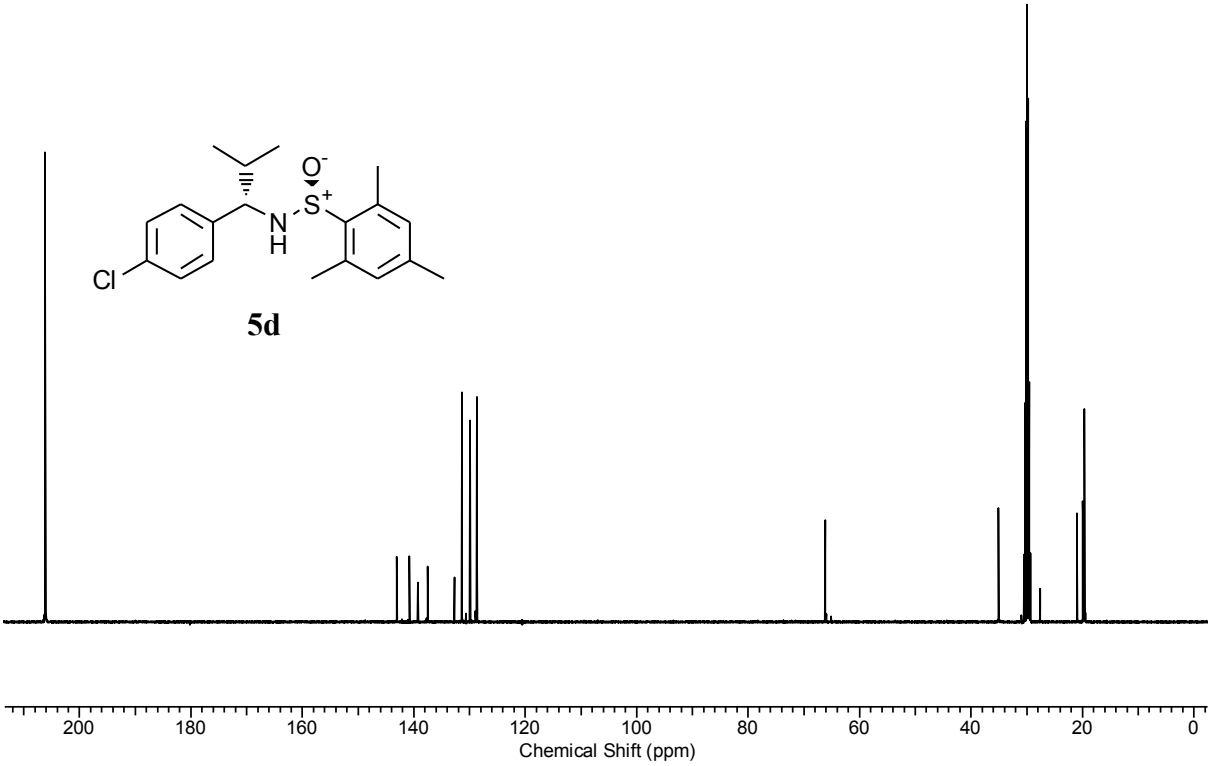

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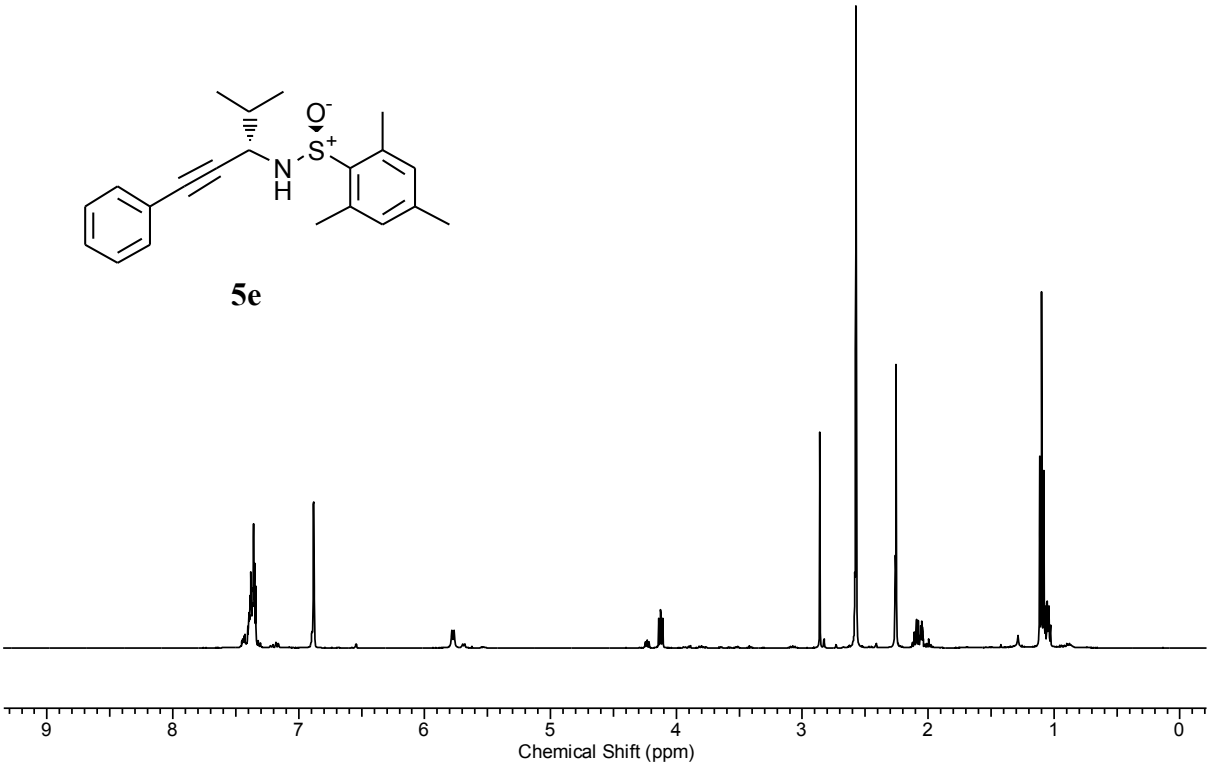

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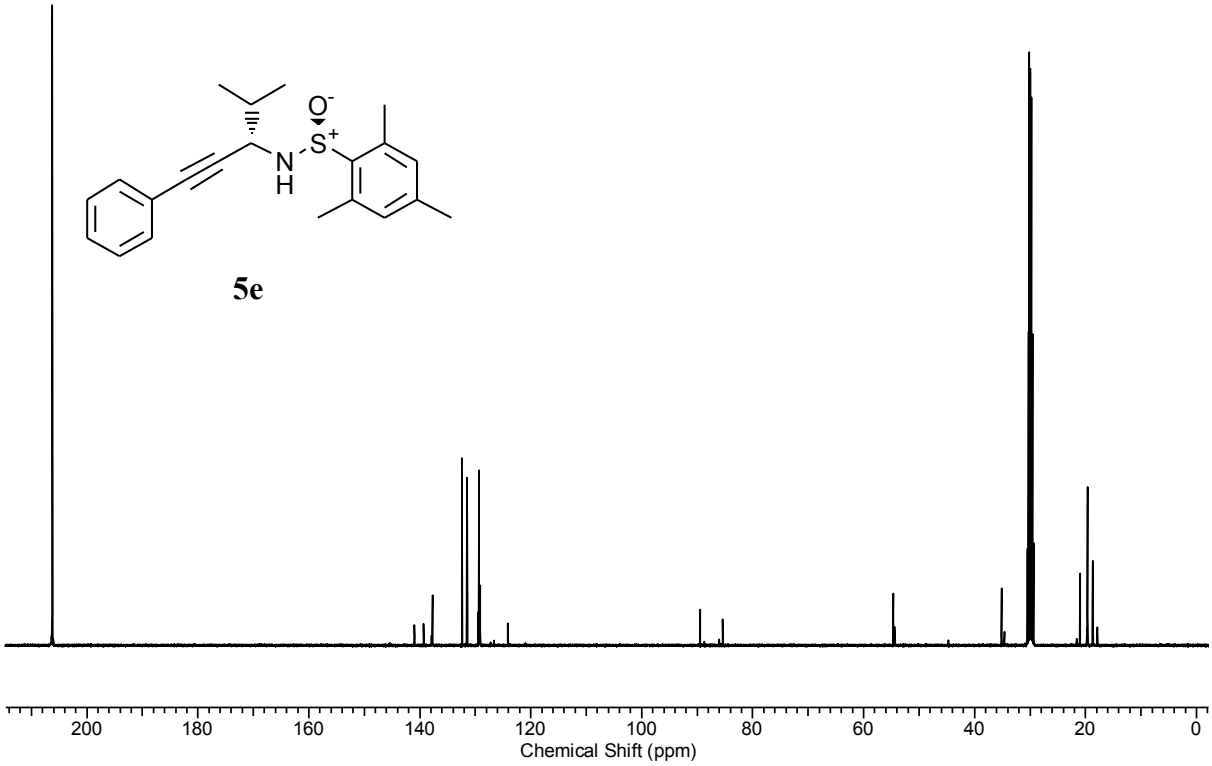

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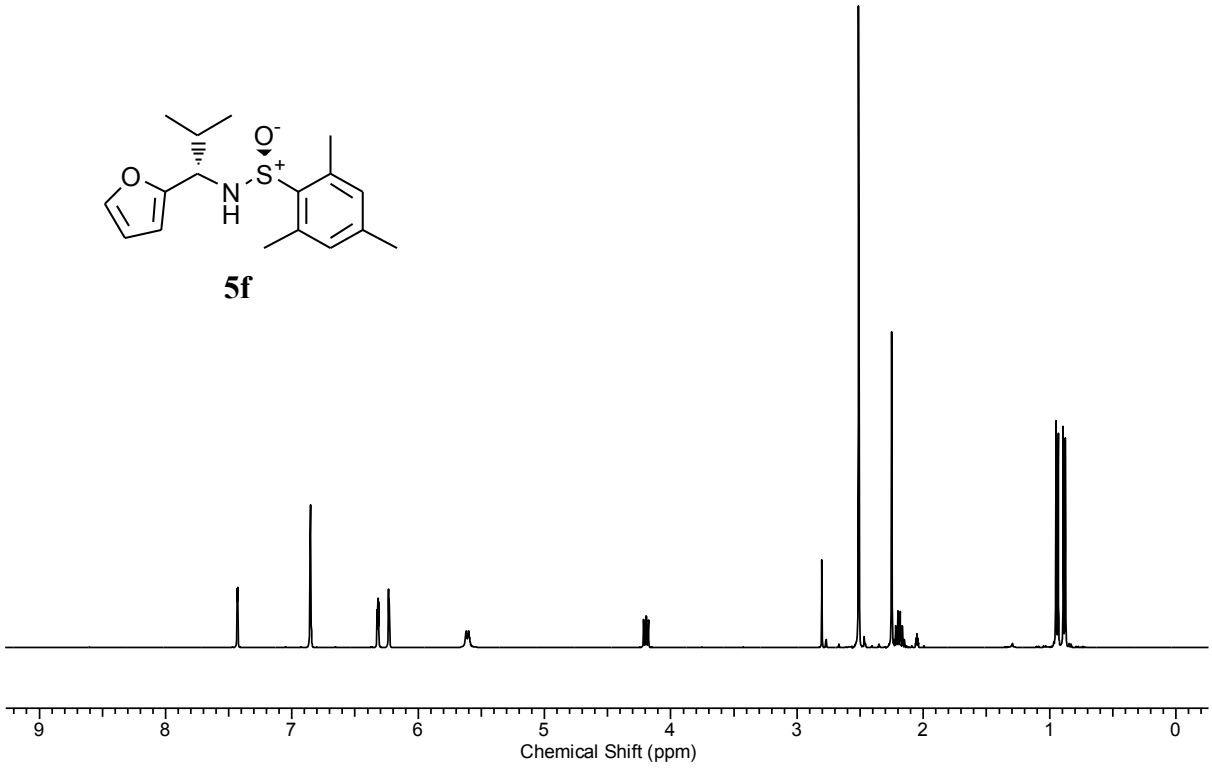

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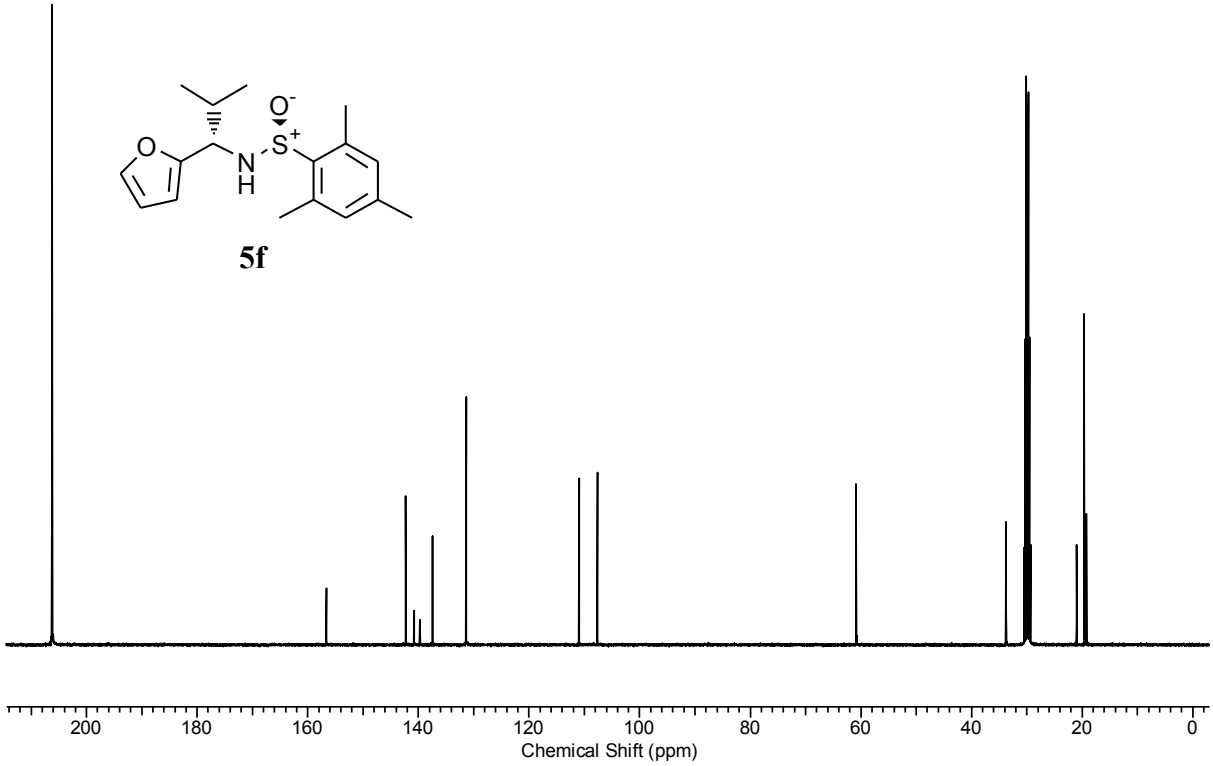
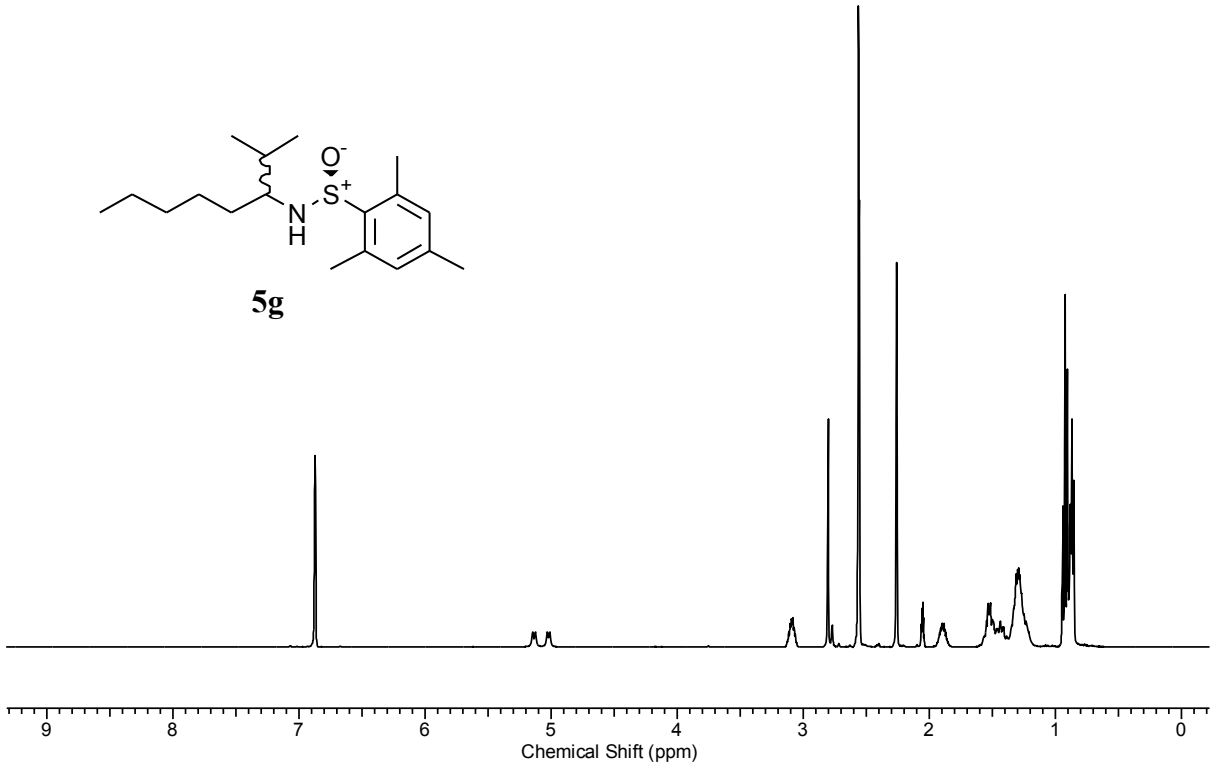
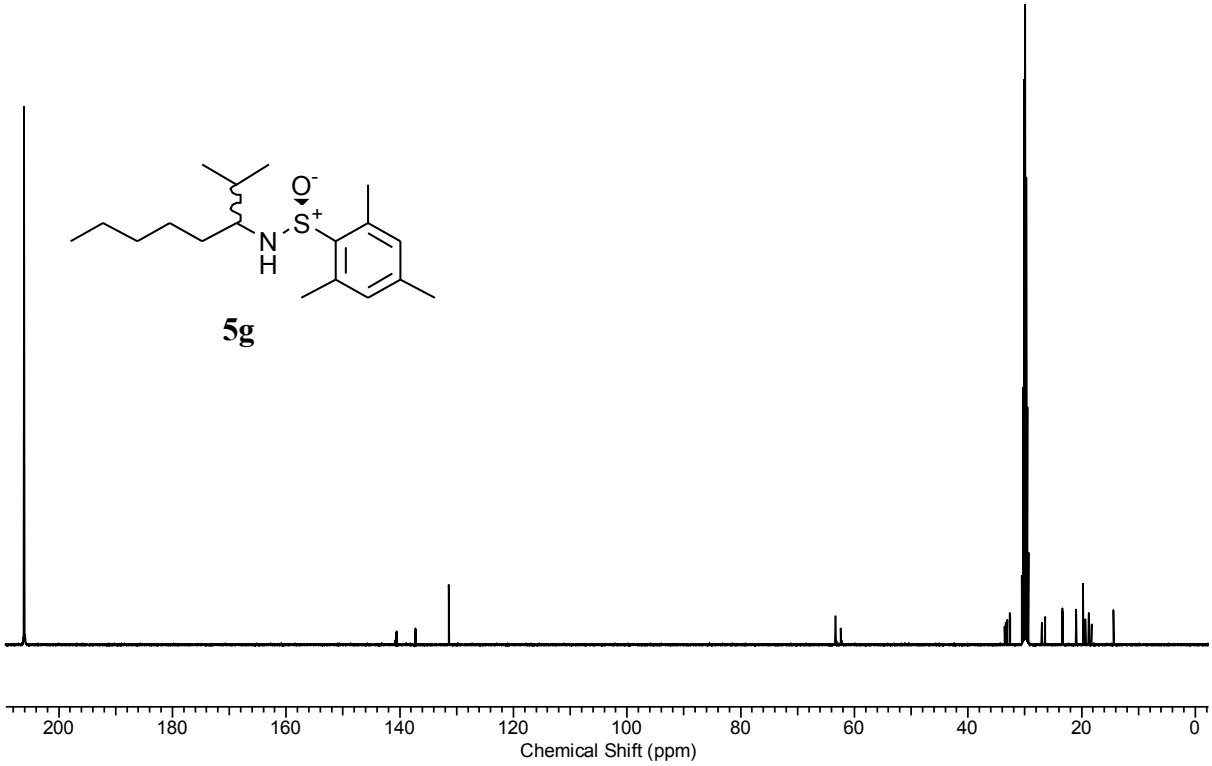

O
N
H
O-
S+
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

5f


N
H
O-
S+
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

5g



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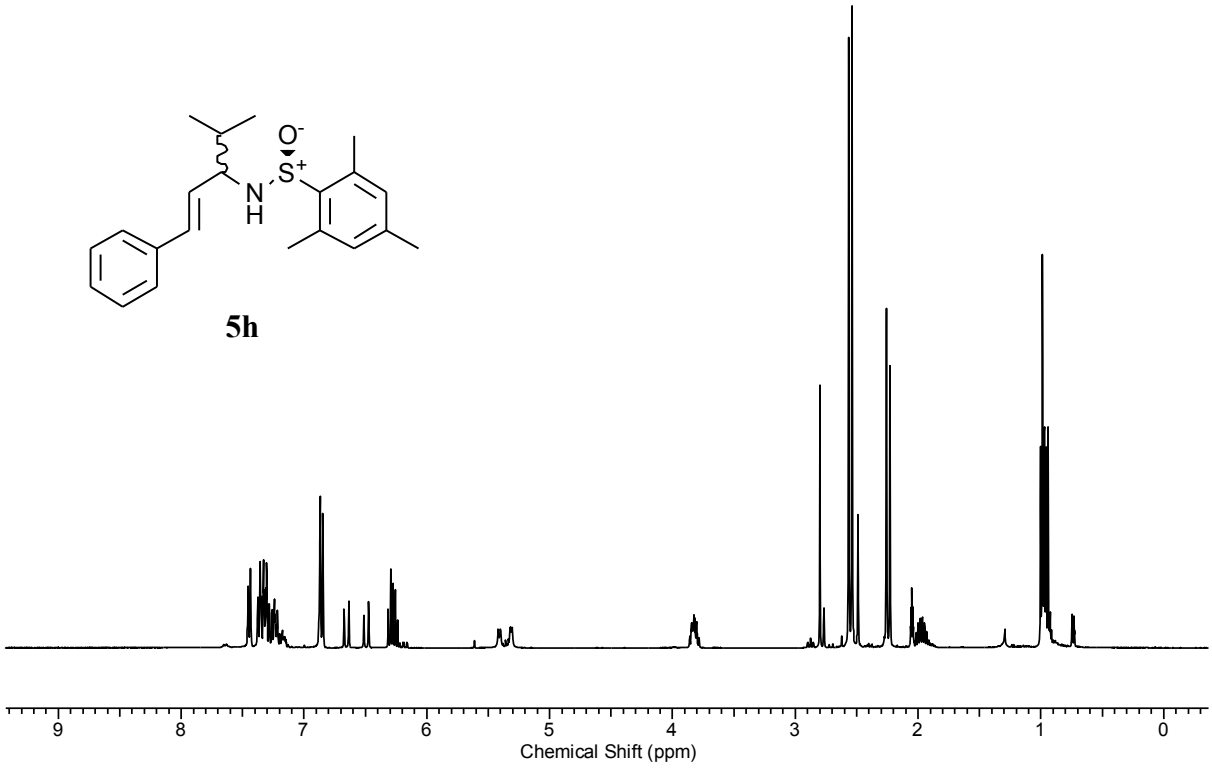

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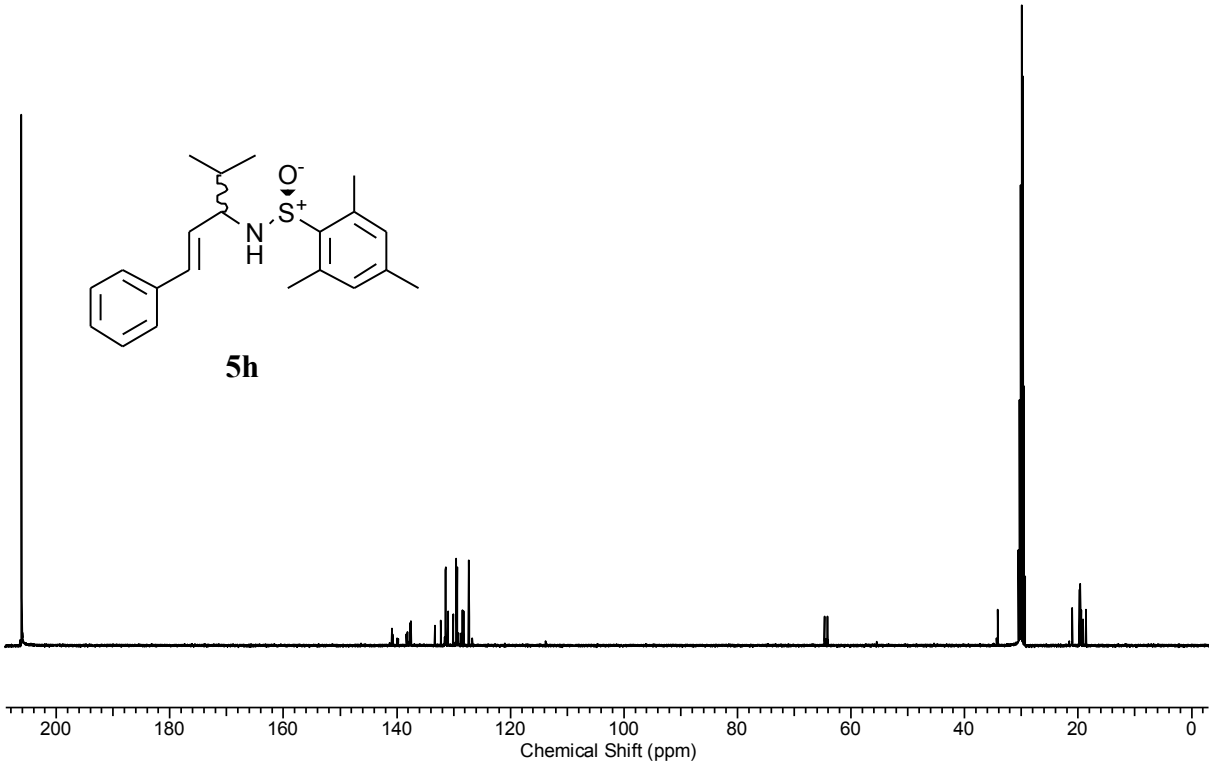

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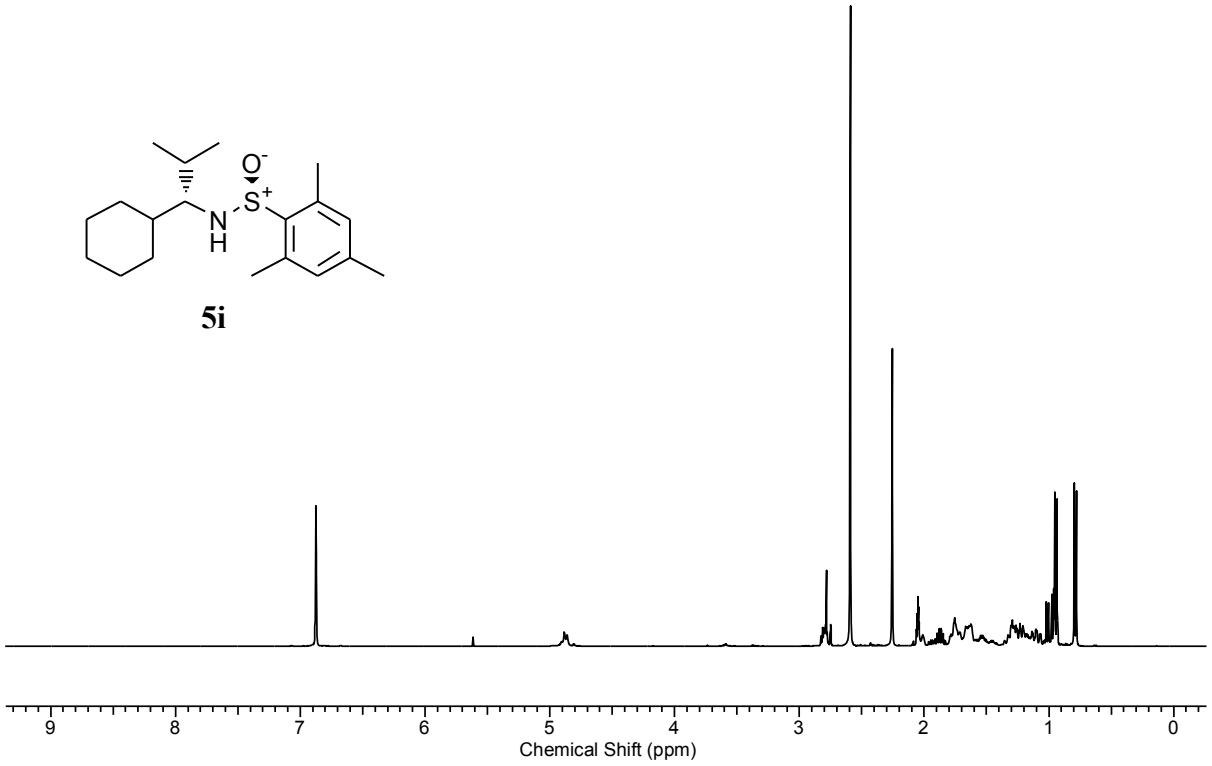

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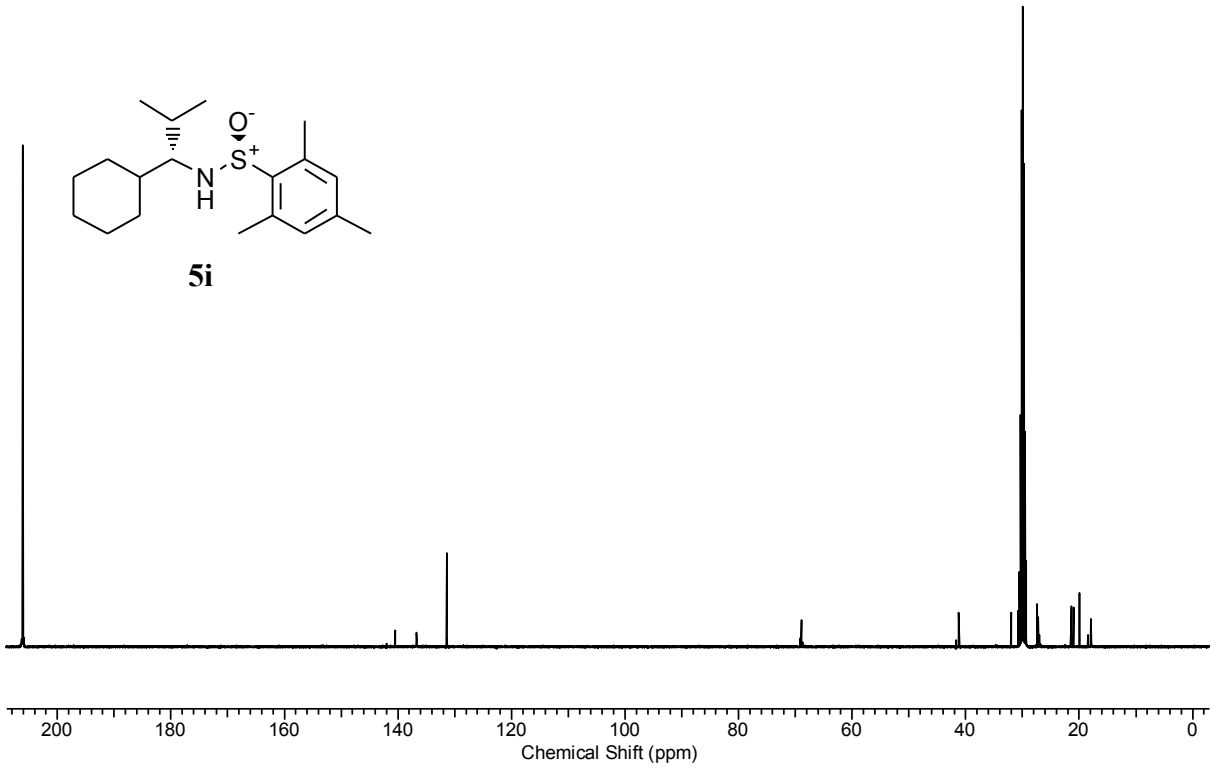

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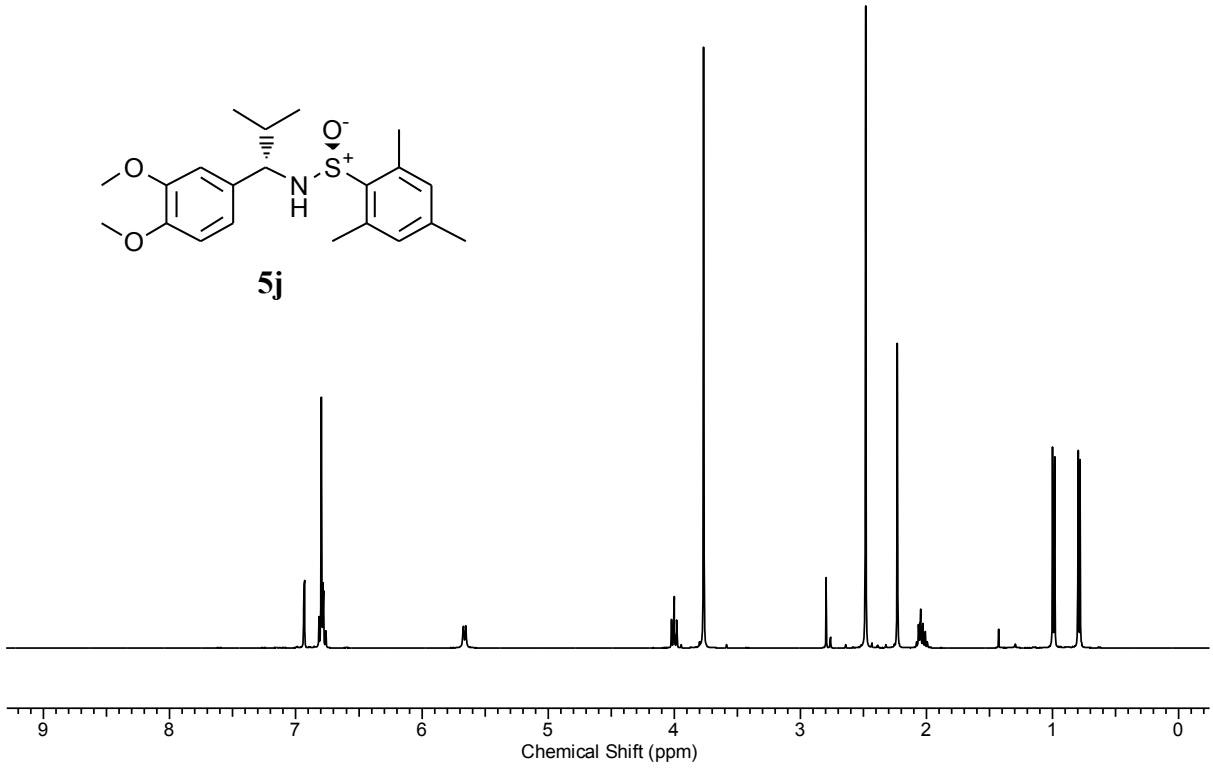

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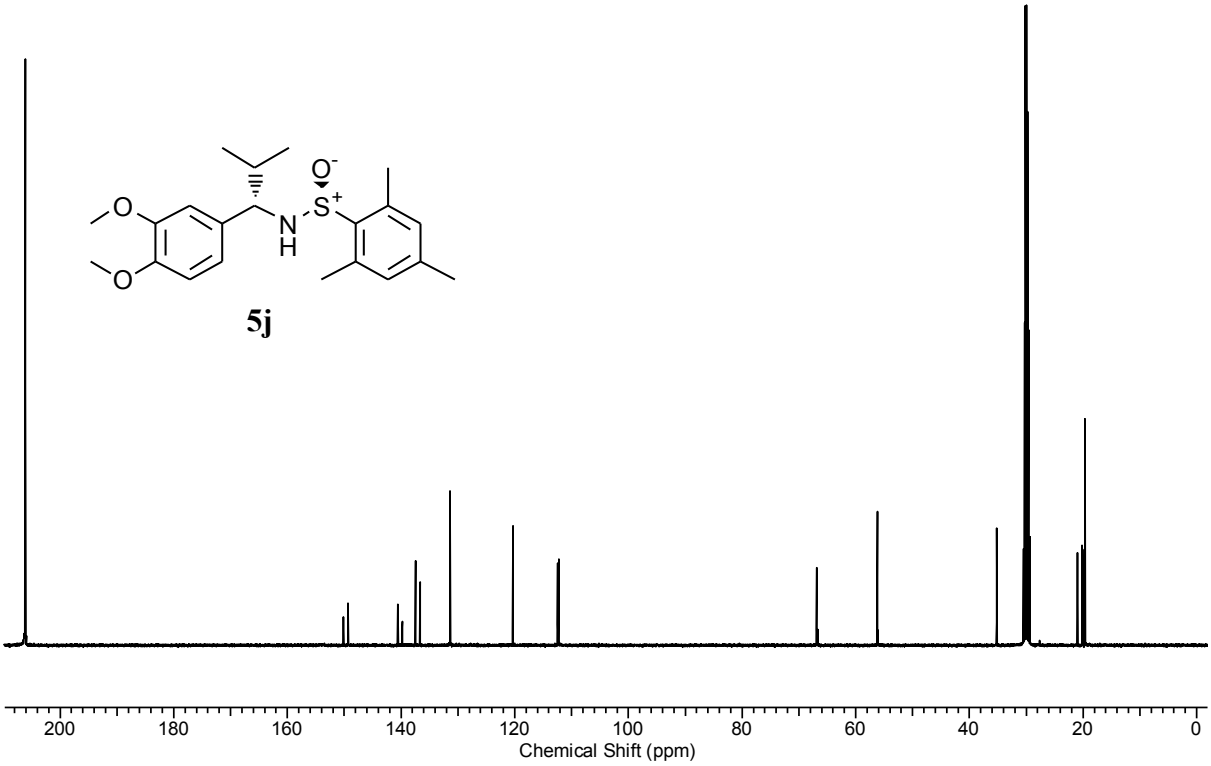

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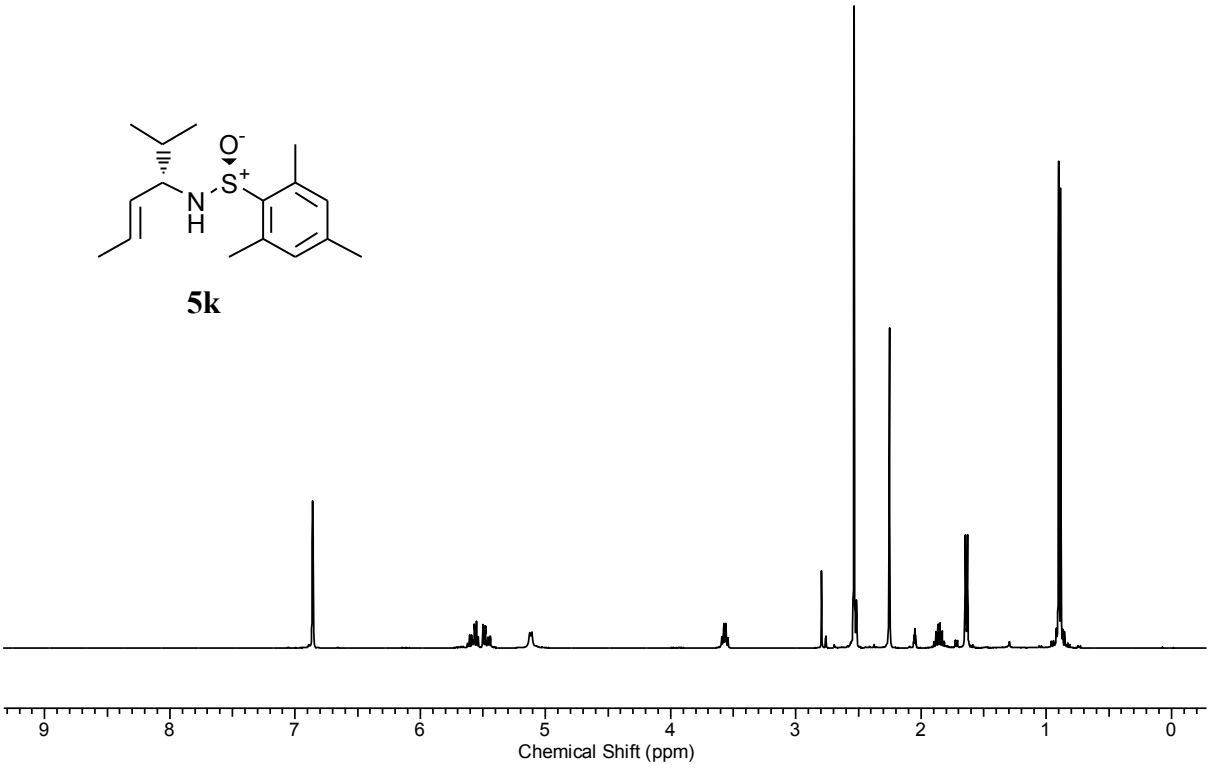

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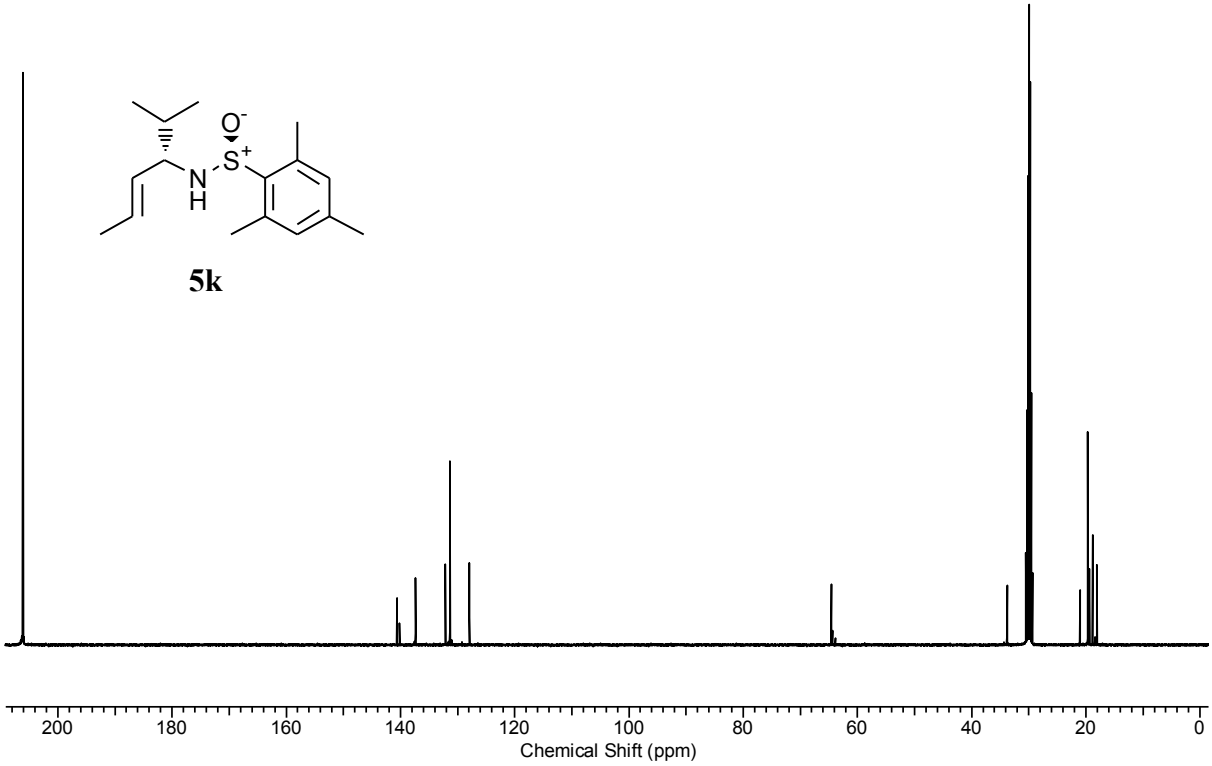
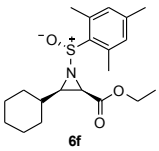
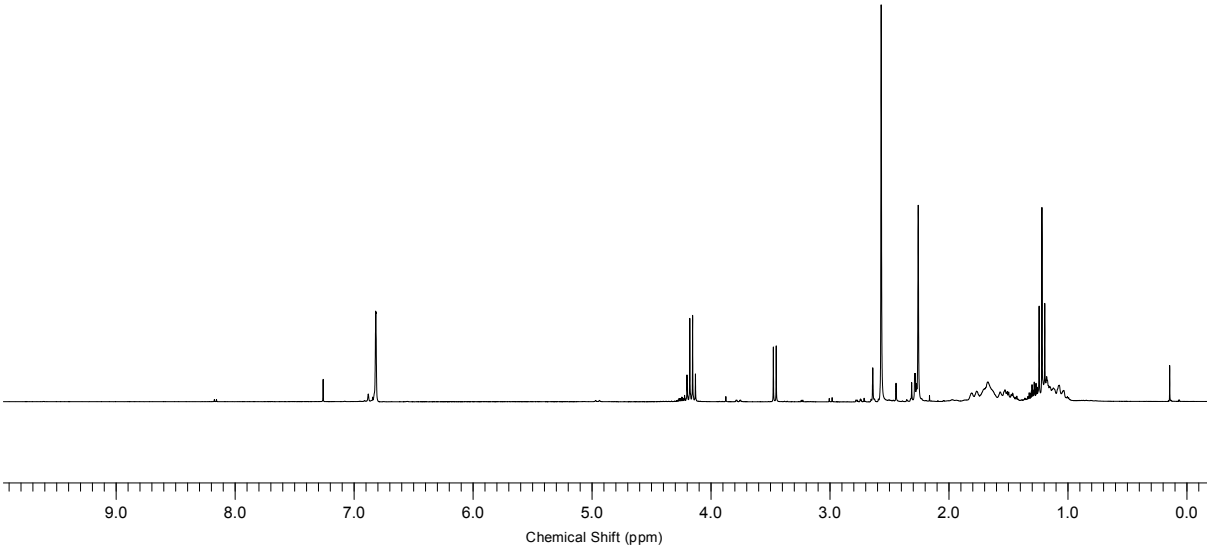
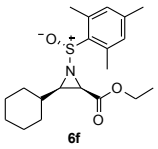

O⁻
S⁺
N
H
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

5k

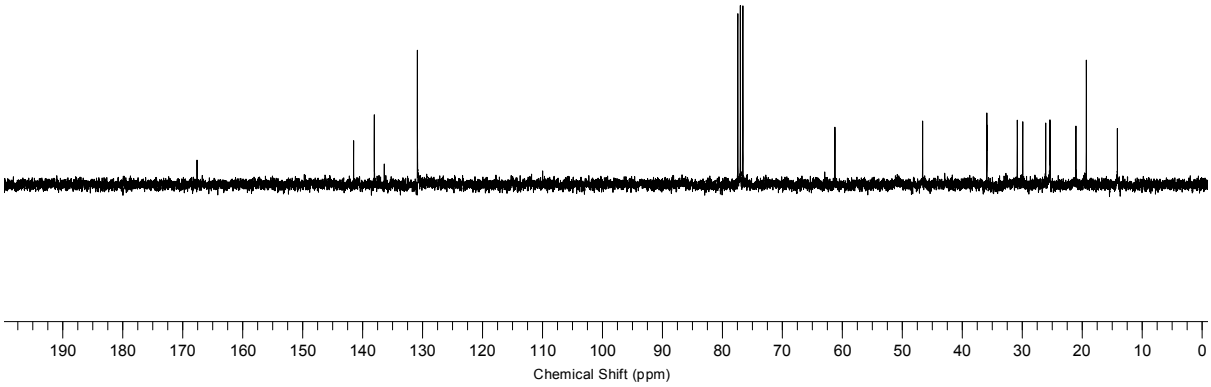

⁻O
S⁺
N
O
O

6f


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical Shift (ppm)



6f


190
180
170
160
150
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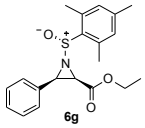
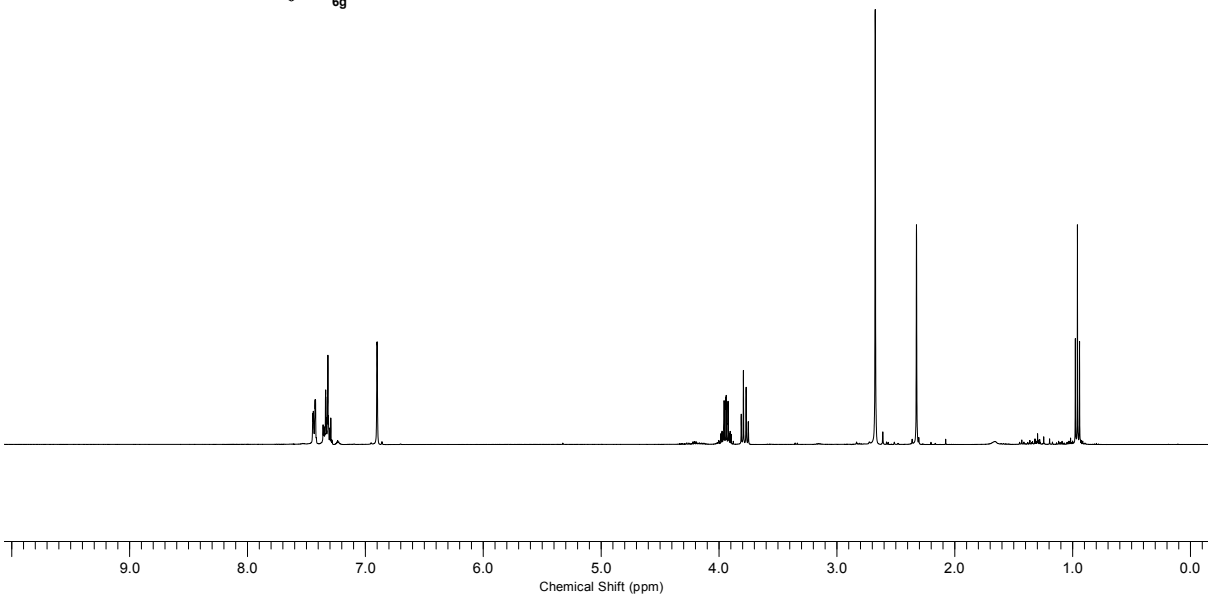
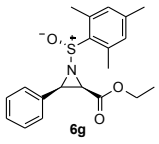
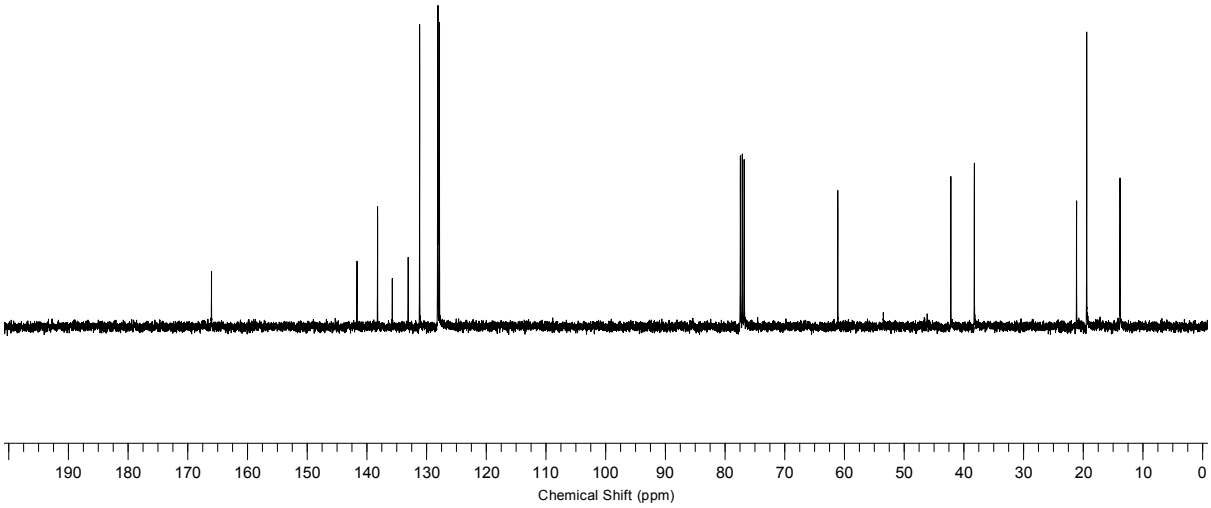
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

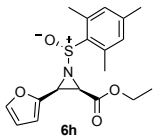


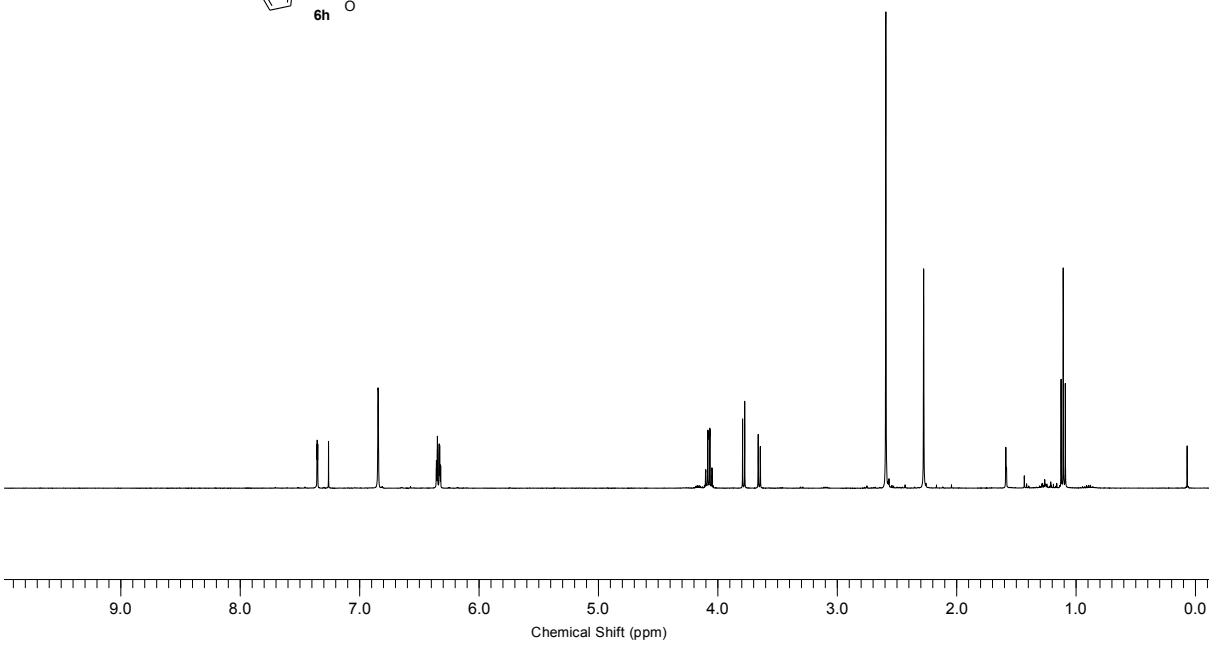
6g

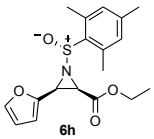

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical Shift (ppm)



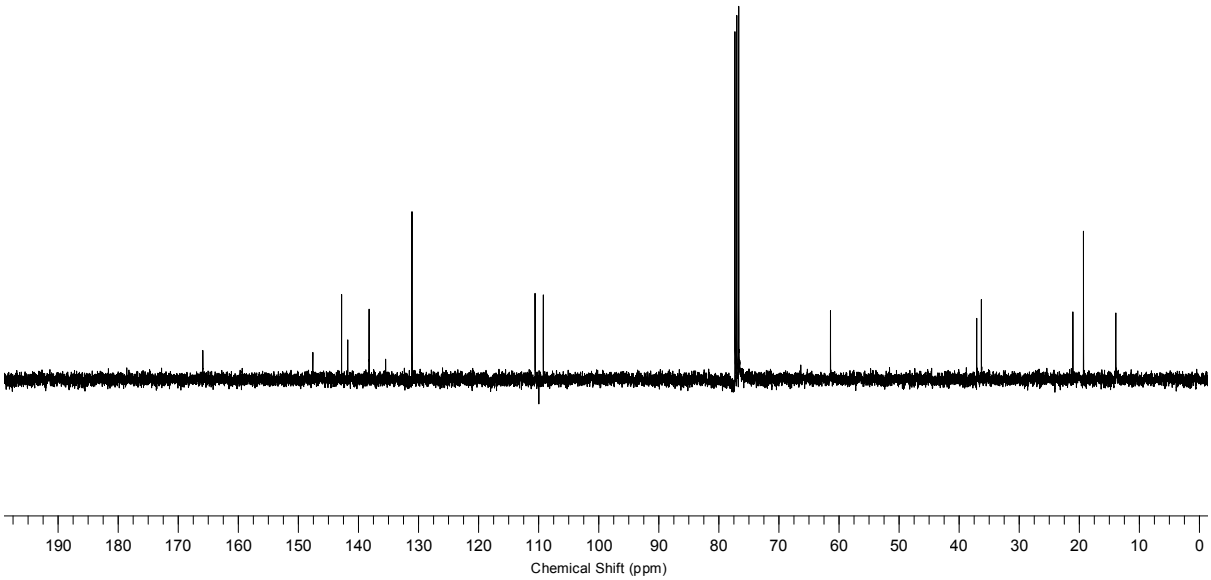


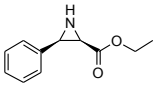


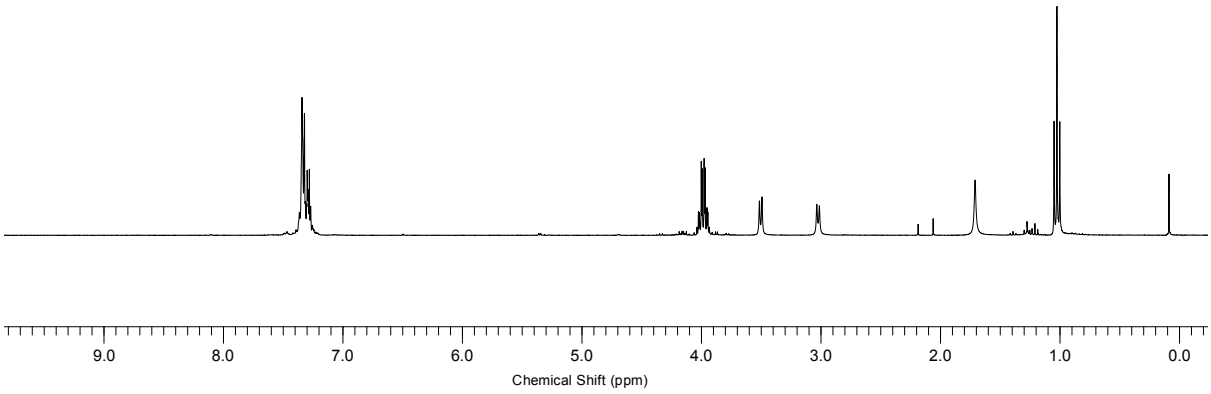


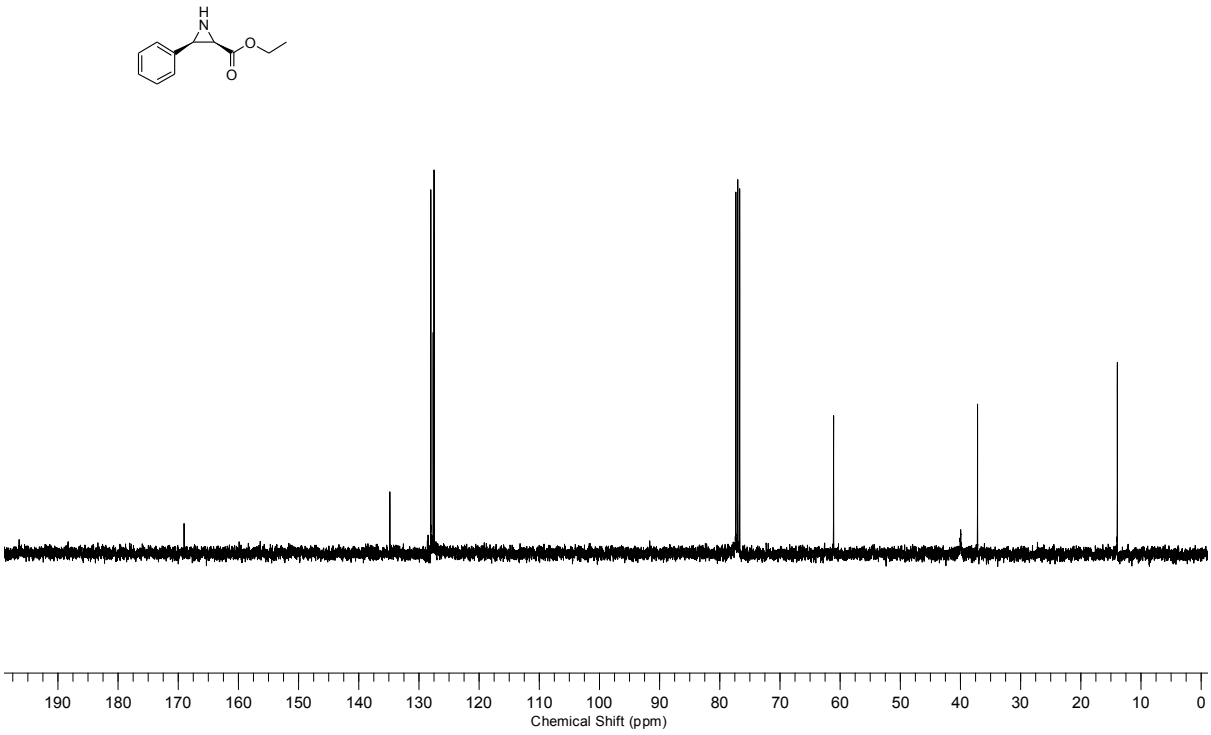


6h









References

1. C. Roe, H. Hobbs and R. A. Stockman, *Chem. Eur. J.*, 2011, **17**, 2704.
2. For 1-phenylpropan-1-amine hydrochloride, observed $[\alpha]_D^{20}$ +16 (*c* 1.0, EtOH). Lit.: $[\alpha]_D^{23}$ +17.8 [(*c* 2.08, EtOH) (S)]. Ref.: A. Côté and A. B. Charette, *J. Org. Chem.*, 2005, **70**, 10864.
3. For 2-methyl-1-phenylpropan-1-amine, observed $[\alpha]_D^{20}$ -10 (*c* 0.1, $CHCl_3$). Lit.: $[\alpha]_D^{23}$ -12.4 [(*c* 0.97, $CHCl_3$) (S)]. Ref.: Z. L. Shen, T. P. Loh, *Org. Lett.*, 2007, **9**, 5413.
4. For 1,2-diphenylethanamine, observed $[\alpha]_D^{20}$ +8 (*c* 0.5, $CHCl_3$). Lit.: $[\alpha]_D^{25}$ -10.9 [(*c* 1.6, $CHCl_3$) (R)]. Ref.: M. J. Wu and L. N. Pridgen, *J. Org. Chem.*, 1991, **56**, 1340.
5. For 1-phenylbut-3-en-1-amine hydrochloride, observed $[\alpha]_D^{20}$ +14 (*c* 1.1, $CHCl_3$). Lit.: $[\alpha]_D^{25}$ +36.2 [(*c* 1.4, $CHCl_3$) (R)]. Ref.: M.J. Wu and L. N. Pridgen, *Synlett*, 1990, 636.
6. For 1-(4-methoxyphenyl)butan-1-amine, observed $[\alpha]_D^{21}$ -10 (*c* 1.1, $CHCl_3$). Lit.: $[\alpha]_D^{24}$ -11.2 [(*c* 0.82, $CHCl_3$) (S)]. Ref.: Y. Chu, Z. Shan, D. Liu and N. Sun, *J. Org. Chem.*, 2006, **71**, 3998.
7. For 1-(4-chlorophenyl)butan-1-amine, observed $[\alpha]_D^{21}$ -9 (*c* 0.8, $CHCl_3$). Lit.: $[\alpha]_D^{25}$ +11.2 [(*c* 6.35, $CHCl_3$) (R)]. Ref.: J. Dalmolen, M. van der Sluis, J. W. Nieuwenhuijzen, A. Meetsma, B. de Lange, B. Kaptein, R. M. Kellogg and Q. B. Broxterman, *Eur. J. Org. Chem.*, 2004, 1544.

8. For 1-(furan-2-yl)-2-methylpropan-1-amine, observed $[\alpha]_D^{20}$ -7 (*c* 0.2, $CHCl_3$). Lit.: $[\alpha]_D^{20}$ +6.4 [(*c* 0.6, $CHCl_3$) (R)]. Ref.: R. Almansa, J. F. Collados, D. Guijarro, M. Yus, *Tetrahedron: Asymmetry*, 2010, **21**, 1421.
9. For ethyl 3-phenyl-1*H*-aziridine 2-carboxylate, observed $[\alpha]_D^{25}$ -11 (c 0.25, $CHCl_3$). Lit: $[\alpha]_D^{25}$ -12.4 [c 1, EtOAc) (2R,3R)]. Ref: A. P. Patwardhan, Z. Lu, V. R. Pulgam, W. D. Wulff, *Org. Lett.,* 2005, **7**, 2201.
10. Y. Pérez-Fuertes, A. M. Kelly, A. L. Johnson, S. Arimori, S. D. Bull and T. D. James, *Org. Lett.*, 2006, **8**, 609.