Supporting Information

Diastereoselective Synthesis of Chiral Oxathiazine 2-Oxide Scaffolds as Sulfinyl Transfer Agents

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General information

General methods

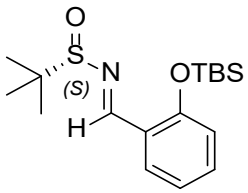
All the commercial chemicals were purchased from Sigma-Aldrich, VWR, Alfa Aesar, or TCI-Chemicals and used without additional purifications. The **^{1}H** and **^{13}C NMR** spectra were recorded on a Varian INOVA 400 NMR instrument with a 5 mm probe. All chemical shifts have been quoted relative to residue solvent signal; chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in hertz (Hz). GC-MS (**GCMS**) spectra were obtained by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection; they are reported as: *m/z* (rel. intensity). High-resolution MS (**HRMS**) ESI analyses were performed on a Xevo G2-XS QTof (Waters) mass spectrometer. Mass spectrometric detection was performed in the full-scan mode from *m/z* 50 to 1200, with a scan time of 0.15 s in the positive ion mode, cone voltage: 40 V, collision energy: 6.00 eV. ESI: capillary: 3kV, cone: 40 V, source temperature: 120 C, desolvation temperature: 600 C, cone gas flow: 50 L/h, desolvation gas flow: 1000 L/h. **CSP-HPLC** analyses were performed on an Agilent Technologies Series 1200 instrument using chiral columns. The enantiomeric compositions were checked against the corresponding racemic products. **Melting point** (m. p.) measurements were performed on Bibby Stuart Scientific SMP3 apparatus. **Optical rotation** measurements were performed on a polarimeter Schmidt+Haensch UniPol L1000. **Flash chromatography** purifications were carried out using VWR silica gel (40 – 63 μm particle size). **Thin-layer chromatography** was performed on Merck 60 F254 plates.

Compounds **2a**[1] and **2b**[2] were synthesized following reported literature procedures and their spectroscopical data matched the reported ones.

General procedure for the synthesis of 3

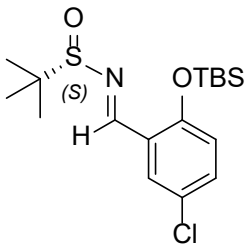
Triethylamine (7 mmol, 0.976 mL, 1.4 eq.), *N,N*-dimethylpyridin-4-amine (0.006 g, 0.01 eq.) and *tert*-butylchlorodimethylsilane (6 mmol, 0.904 g, 1.2 eq) were added at 0 C to a solution of the appropriate sulfinyl imine **2** (5 mmol, 1 eq.) in anhydrous CH_2Cl_2 (10 mL), The reaction mixture was stirred at room temperature for 4 h. After completion, monitored by TLC, the reaction was quenched with saturated aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2 (3x), the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography.

(*S*,*E*)-*N*-(2-((*tert*-butyldimethylsilyl)oxy)benzylidene)-2-methylpropane-2-sulfinamide (3a)



Yellow oil. Column chromatography (CyH/AcOEt 95:5). Yield 95% (1.61 g). $[\alpha]_D^{20}$ = +182 (c = 1.2, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (td, *J* = 8.3, 1.7 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 1.23 (s, 9H), 1.02 (s, 9H), 0.22 (d, *J* = 2.5 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 156.5, 133.5, 128.2, 125.4, 121.5, 120.2, 57.4, 25.6, 22.5, 18.2, -4.3, -4.4. **GC** R_t: 16.5 min. **GCMS** (EI) *m/z* (%) = 57 (14) $[tBu]^+$, 176 (100) $[M – NS(O)tBu – tBu]^+$, 226 (5) $[M – TBS]^+$. **HRMS** (ESI) *m/z* 340.1764, calcd. for $C_{17}H_{30}NO_2SSi$ $[MH]^+$: 340.1761.

(*S*,*E*)-*N*-(2-((*tert*-butyldimethylsilyl)oxy)-5-chlorobenzylidene)-2-methylpropane-2-sulfinamide (3b)

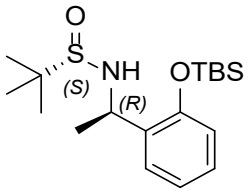


Yellow oil. Column chromatography (CyH/AcOEt 95:5). Yield 95% (1.77 g). $[\alpha]_D^{20}$ = +90 (c = 1.5, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.86 (d, *J* = 2.8 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 1.20 (s, 9H), 0.97 (s, 9H), 0.19 (d, *J* = 1.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 155.0, 133.2, 127.6, 126.9, 126.5, 121.6, 57.7, 25.6, 22.5, 1.0, -4.4, -4.4. **GC** R_t: 16.3 min. **GCMS** (EI) *m/z* (%) 211 (100) [pClPh-SitBu]$^+$, 266 (0.65) $[M – SOtBu]^+$. **HRMS** (ESI) *m/z* 374.1369, calcd. for $C_{17}H_{29}ClNO_2SSi$ $[MH]^+$: 374.1371.

General procedure for the synthesis of 4

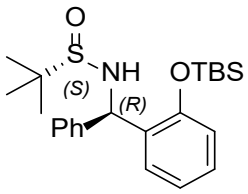
The desired Grignard reagent (1.5 mmol, 1.5 mL 1.5 eq., 1 M solution) was added at −50C to a solution of the sulfinamide **3** (1 mmol) in anhydrous CH_2Cl_2 (3 mL). The reaction mixture was stirred to completion, monitored by TLC. The reaction was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2 (3x), the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography.

(*S*)-*N*-((*R*)-1-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)ethyl)-2-methylpropane-2-sulfinamide (4aA)



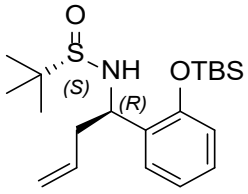
Colorless oil. Column chromatography (CyH/AcOEt 7:3). Yield 95% (0.34g). $[\alpha]_D^{20}$ = +58 (c = 1.2, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.17 – 7.07 (m, 1H), 6.94 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.96 (qd, *J* = 6.7, 4.3 Hz, 1H), 3.35 (d, *J* = 4.5 Hz, 1H), 1.49 (d, *J* = 6.7 Hz, 3H), 1.20 (s, 9H), 1.03 (s, 9H), 0.27 (d, J = 6.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 134.2, 127.8, 127.0, 121.1, 118.9, 118.5, 55.6, 49.0, 25.8, 24.2, 22.6, 22.6, 18.2, -4.0, -4.1. **GC** R_t: 19,1 min. **GCMS** (EI) *m/z* (%) = 235 (100) $[M - NS(O)tBu]^+$. **HRMS** (ESI) *m/z* 356.2083, calcd. for $C_{18}H_{35}NO_2SSi$ $[MH]^+$: 356.2080.

(*S*)-*N*-((*R*)-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)(phenyl)methyl)-2-methylpropane-2-sulfinamide (4aB)



The temperature was allowed to reach 20 C overnight. Colorless oil. Column chromatography (CyH/AcOEt 95:5). Yield 98% (0.41g). $[\alpha]_D^{20}$ = +71 (c = 1.1, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.23 – 7.10 (m, 2H), 7.01 – 6.92 (m, 1H), 6.80 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.02 (d, *J* = 3.7 Hz, 1H), 3.71 (d, *J* = 3.9 Hz, 1H), 1.22 (s, 9H), 0.90 (s, 9H), 0.21 (s, 3H), 0.11 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 142.4, 131.7, 128.8, 128.5, 128.2, 127.6, 127.4, 120.9, 118.6, 56.6, 55.8, 25.8, 22.7, 21.6, 18.2, -4.1, -4.1. **GC** R_t: 20.5 min. **GCMS** (EI) *m/z* (%) = 286 (100) $[M - TBSO]^+$, 302 (50) $[M - TBS]^+$. **HRMS** (ESI) *m/z* 418.2239, calcd. for $C_{23}H_{36}NO_2SSi$ $[MH]^+$: 418.2236.

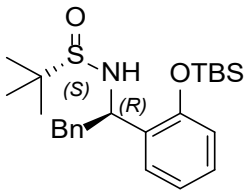
(*S*)-*N*-((*S*)-1-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (4aC)



Colorless oil. Column chromatography (CyH/AcOEt 4:1). Yield 99% (0.38 g). $[\alpha]_D^{20}$ = +85 (c = 1.25, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.11 (ddd, *J* = 8.1, 7.2, 1.8 Hz, 1H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.72 (dddd, *J* = 16.6, 10.2, 8.2, 6.1 Hz, 1H), 5.21 – 5.08 (m, 2H), 4.91 (dq, *J* = 8.3, 4.2, 3.7 Hz, 1H), 3.63 (d, *J* = 3.3 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.39 (dt, *J* = 13.9, 8.3 Hz, 1H), 1.19 (s, 9H),

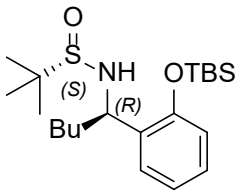
1.02 (s, 9H), 0.26 (d, J = 4.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.98, 134.49, 132.35, 127.88, 127.76, 120.93, 118.95, 118.46, 55.68, 50.81, 41.92, 25.83, 22.62, 18.21, -3.97, -4.24. **GC** R_t: 22.1 min. **GCMS** (EI) *m/z* (%) 268 (100) $[M - TBS]^+$. **HRMS** (ESI) *m/z* 382.2232, calcd. for $C_{20}H_{36}NO_2SSi$ $[MH]^+$: 382.2236.

(*S*)-*N*-((*R*)-1-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-phenylethyl)-2-methylpropane-2-sulfinamide (4aD)



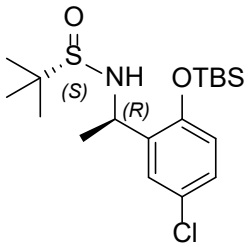
The temperature was allowed to reach 20 C overnight. Colorless oil. Column chromatography (CyH/AcOEt 4:1). Yield 56% (0.24 g). $[\alpha]_D^{20}$ = +74 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 5H), 7.08 – 7.02 (m, 2H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.10 (d, *J* = 8.4 Hz, 1H), 3.55 (d, *J* = 4.1 Hz, 1H), 3.20 (dd, *J* = 13.6, 5.7 Hz, 1H), 3.01 – 2.86 (m, 1H), 1.12 (s, 9H), 1.04 (s, 9H), 0.29 (s, 3H), 0.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 136.9, 131.8, 129.7, 128.5, 128.2, 128.0, 126.7, 120.9, 118.4, 55.6, 43.7, 25.9, 22.6, 18.3, -4.0, -4.1. **GC** R_t: 22.8 min. **GCMS** (EI) *m/z* (%) = 91 (75) $[CH_3Ph]^+$, 300 (63) $[M - TBSO]^+$. **HRMS** (ESI) *m/z* 432.2396, calcd. for $C_{24}H_{38}NO_2SSi$ $[MH]^+$: 432.2393.

(*S*)-*N*-((*R*)-1-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)pentyl)-2-methylpropane-2-sulfinamide (4aE)



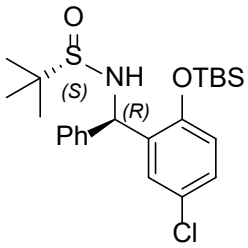
Yellow oil. Column chromatography (CyH/AcOEt 4:1). Yield 60% (0.24 g). $[\alpha]_D^{20}$ = +64 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.3, 1.8 Hz, 1H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.80 (td, *J* = 6.9, 4.3 Hz, 1H), 3.41 (d, *J* = 4.5 Hz, 1H), 1.83 – 1.73 (m, 2H), 1.40 – 1.22 (m, 4H), 1.16 (s, 9H), 1.02 (s, 9H), 0.84 (t, J = 7.1 Hz, 3H), 0.27 (d, *J* = 5.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 133.0, 127.8, 127.7, 121.0, 118.4, 55.6, 53.4, 37.7, 28.2, 25.9, 22.6, 22.5, 18.3, 13.9, -4.0, -4.1. **GC** R_t: 19.9 min. **GCMS** (EI) *m/z* (%) = 226 (70) $[M - TBS - tBu]^+$. **HRMS** (ESI) *m/z* 398.2545, calcd. for $C_{21}H_{40}NO_2SSi$ $[MH]^+$: 398.2549.

(*S*)-*N*-((*R*)-1-(2-((*tert*-butyldimethylsilyl)oxy)-5-chlorophenyl)ethyl)-2-methylpropane-2-sulfinamide (4bA)



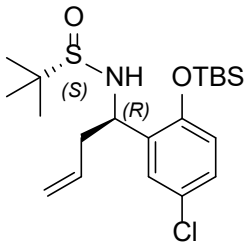
Colorless oil. Column chromatography (CyH/AcOEt 3:2). Yield 90% (0.35 g). $[\alpha]_D^{20}$ = +29 (c = 12.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.7 Hz, 1H), 7.07 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 4.92 (dd, *J* = 6.7, 3.2 Hz, 1H), 3.29 (brs, 1H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.22 (s, 9H), 1.02 (s, 9H), 0.26 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 136.1, 127.5, 127.2, 126.0, 119.6, 55.5, 48.5, 25.7, 24.0, 18.1, -4.2, -4.3. **GC** R_t: 20.4 min. **GCMS** (EI) *m/z* (%) 211 (100) $[pClPh\text{-}SitBu]^+$, 389 (1.4) $[M]^{+\cdot}$. **HRMS** (ESI) *m/z* 390.1686, calcd. for $C_{18}H_{33}ClNO_2SSi$ $[MH]^+$: 390.1690.

(*S*)-*N*-((*R*)-(2-((*tert*-butyldimethylsilyl)oxy)-5-chlorophenyl)(phenyl)methyl)-2-methylpropane-2-sulfinamide (4bB)



The temperature was allowed to reach 20 C overnight. White waxy solid. Column chromatography (CyH/AcOEt 3:2). Yield 95% (0.43 g). $[\alpha]_D^{20}$ = +56 (c = 1.6, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.7 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.28 – 7.20 (m, 1H), 7.11 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 5.98 (d, *J* = 3.1 Hz, 1H), 3.62 (d, *J* = 3.1 Hz, 1H), 1.26 (s, 9H), 0.90 (s, 9H), 0.23 (s, 3H), 0.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 141.3, 133.3, 128.4, 128.3, 127.6, 127.3, 127.1, 125.6, 119.3, 55.7, 55.4, 25.4, 22.2, 17.8, -4.6. **GC** R_t: 23.1 min. **GCMS** (EI) *m/z* (%) 336 (45) $[M - TBS]^+$, 451 (1.7) $[M]^{+\cdot}$. **HRMS** (ESI) *m/z* 452.1851, calcd. for $C_{23}H_{35}ClNO_2SSi$ $[MH]^+$: 452.1846.

(*S*)-*N*-((*R*)-1-(2-((*tert*-butyldimethylsilyl)oxy)-5-chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (4bC)



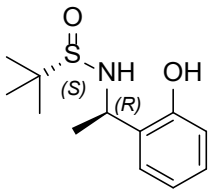
White solid (m. p.: 86 – 88 C). Column chromatography (CyH/AcOEt 3:2). Yield 87% (0.36 g). $[\alpha]_D^{20}$ = +123 (c = 1.4, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (s, overlapped, 1H), 7.08 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 5.71 (ddd, *J* = 17.9, 8.7, 5.7 Hz, 1H), 5.26 – 5.11 (m, 2H), 4.92 – 4.79 (m, 1H), 3.62 (s, 1H), 2.69 – 2.52 (m, 1H), 2.35 (dt, *J* = 15.3, 8.3 Hz, 1H), 1.23 (s, 9H), 1.02 (s, 9H), 0.27 (s, 3H), 0.26 (s, 3H). **^{13}C NMR** (100

MHz, $CDCl_3$) δ 151.2, 134.0, 133.6, 127.5, 127.3, 125.7, 119.3, 119.0, 55.3, 50.0, 41.3, 25.4, 22.2, 17.8, -4.4, -4.7. **GC** R_t: 23.9 min. **GCMS** (EI) *m/z* (%) 302 (100) $[M - TBS]^+$, 344 (2.2) $[M - tBu - Me]^+$, 415 (0.80) $[M]^{+\cdot}$. **HRMS** (ESI) *m/z* 416.1849, calcd. for $C_{20}H_{35}ClNO_2SSi$ $[MH]^+$: 416.1846.

General procedure for the synthesis of 5a and 6b

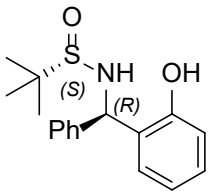
Tetrabutylammonium fluoride (0.314 g, 1.2 mmol, 1.2 eq) was added at 0 C to a solution of the sulfinamide **4a** or the sulfonamide **5b** (1 mmol, 1 eq.) in anhydrous THF (5 mL). The reaction mixture was stirred at room temperature for 1 h. After completion, monitored by TLC, the reaction was washed with water. The organic phase was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography.

(*S*)-*N*-((*R*)-1-(2-Hydroxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (5aA)



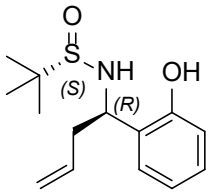
Colorless oil. Column chromatography (CyH/AcOEt 1:1). Yield 92% (0.22 g). $[\alpha]_D^{20}$ = +54 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.20 – 7.09 (m, 2H), 6.84 (t, *J* = 8.6 Hz, 2H), 4.66 (dt, *J* = 11.1, 5.7 Hz, 1H), 4.00 (d, *J* = 4.4 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 128.5, 128.3, 127.6, 119.5, 116.4, 56.0, 53.9, 23.1, 22.6. **GC** R_t: 17.2 min. **GCMS** (EI) *m/z* (%) = 121 (100) $[M\text{-}NS(O)tBu]^+$, 185 (3) $[M - tBu]^+$. **HRMS** (ESI) *m/z* 242.1217, calcd. for $C_{12}H_{20}NO_2S$ $[MH]^+$: 242.1215.

(*S*)-*N*-((*R*)-(2-Hydroxyphenyl)(phenyl)methyl)-2-methylpropane-2-sulfinamide (5aB)



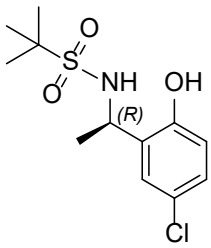
White solid (m. p.: 212 – 217 C). Column chromatography (CyH/AcOEt 1:1). Yield 83% (0.25 g). $[\alpha]_D^{20}$ = +22 (c = 7.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.22 – 7.12 (m, 1H), 6.99 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.80 (td, *J* = 7.5, 1.2 Hz, 1H), 5.89 (d, *J* = 3.8 Hz, 1H), 4.02 (d, *J* = 4.0 Hz, 1H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 141.0, 129.4, 129.2, 128.8, 127.8, 127.5, 126.5, 120.3, 117.7, 56.4, 37.8, 22.7. **GC** R_t: 19.3 min. **GCMS** (EI) *m/z* (%) = 57 (68) $[tBu]^+$, 228 (100) $[M - H2O - tBu]^+$, 285 (51) $[M - H_2O]^+$. **HRMS** (ESI) *m/z* 304.1371, calcd. for $C_{17}H_{22}NO_2S$ $[MH]^+$: 304.1371.

(*S*)-*N*-((*R*)-1-(2-Hydroxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (5aC)



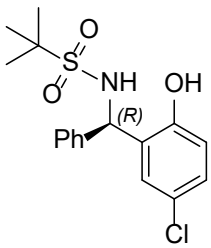
White solid (m.p. 104 – 106 C). Column chromatography (CyH/AcOEt 7:3). Yield 94% (0.25 g). $[\alpha]_D^{20}$ = +81 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.19 (ddd, *J* = 8.9, 7.5, 1.6 Hz, 1H), 7.12 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.90 – 6.82 (m, 2H), 5.85 – 5.70 (m, 1H), 5.22 (d, *J* = 5.7 Hz, 1H), 5.19 (s, 1H), 4.56 (t, *J* = 7.5 Hz, 1H), 4.00 (s, 1H), 2.65 (qt, *J* = 14.2, 7.2 Hz, 2H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 134. 6, 128.9, 128.8, 125.4, 119.7, 119.0, 116.7, 55.9, 55.8, 40.7, 22.5. **GC** R_t: 19.5 min. **GCMS** (EI) *m/z* (%) = 121 (100) $[C_4H_{10}NOS]^+$, 211 (8) $[M - tBu]^+$. **HRMS** (ESI) *m/z* 268.1369, calcd. for $C_{14}H_{22}NO_2S$ $[MH]^+$: 268.1371.

(*R*)-*N*-(1-(5-Chloro-2-hydroxyphenyl)ethyl)-2-methylpropane-2-sulfonamide (6bA)



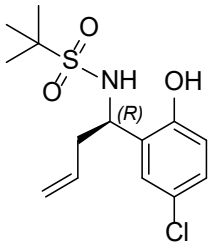
White waxy solid. Column chromatography (CyH/AcOEt 7:3). Yield 82% (0.24 g). $[\alpha]_D^{20}$ = +33 (c = 1.1, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 7.06 (dd, *J* = 2.6, 1.1 Hz, 1H), 6.92 (ddd, *J* = 8.5, 2.7, 1.2 Hz, 1H), 6.60 (dd, *J* = 8.6, 1.2 Hz, 1H), 5.26 (d, *J* = 9.9 Hz, 1H), 4.58 – 4.43 (m, 1H), 1.57 – 1.52 (m, 3H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 130.6, 128.5, 127.3, 125.1, 117.6, 60.0, 53.3, 24.0, 22.5. **GC** R_t: 12.0 min. **GCMS** (EI) *m/z* (%) 154 (61) $[4\text{-Cl-2-}CH_2CH_2\text{Ph-OH}]^+$, 233 (20) $[M - tBu]^+$, 291 (24) $[M]^{+\cdot}$. **HRMS** (ESI) *m/z* 292.0775, calcd. for $C_{12}H_{19}ClNO_3S$ $[MH]^+$: 292.0774.

(*R*)-*N*-((5-Chloro-2-hydroxyphenyl)(phenyl)methyl)-2-methylpropane-2-sulfonamide (6bB)



White solid (m. p.: 66 – 68 C). Column chromatography (CyH/AcOEt 7:3). Yield 93% (0.33 g). $[\alpha]_D^{20}$ = +49 (c = 1.2, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.3 Hz, 4H), 7.30 – 7.22 (m, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 5.67 (s, 1H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 140.7, 129.3, 128.6, 128.4, 128.2, 127.1, 126.5, 124.5, 117.7, 60.0, 59.0, 23.8. **GC** R_t: 9.2 min. **GCMS** (EI) *m/z* (%)57 (100) $[tBu]^+$, 215 (1) $[M - SO_2tBuNH]^+$, 277 (3.2) $[M - Ph]^+$. **HRMS** (ESI) *m/z* 354.0929, calcd. for $C_{17}H_{21}ClNO_3S$ $[MH]^+$: 354.0931.

(*R*)-*N*-(1-(5-Chloro-2-hydroxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfonamide (6bC)

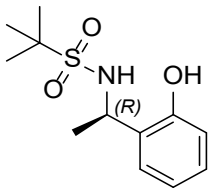


White waxy solid. Column chromatography (CyH/AcOEt 7:3). Yield 91% (0.29 g). $[\alpha]_D^{20}$ = +36 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 2.6 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 5.74 – 5.49 (m, 1H), 5.06 (dd, *J* = 5.8, 1.6 Hz, 1H), 5.03 (s, 1H), 4.40 (t, *J* = 7.3 Hz, 1H), 2.62 (pd, *J* = 13.9, 6.6 Hz, 2H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 134.0, 129.0, 128.4, 128.2, 124.5, 118.4, 117.2, 60.2, 57.7, 40.6, 24.0. **GC** R_t: 18.8 min. **GCMS** (EI) *m/z* (%) 57 (92) $[tBu]^+$, 145 (67) $[M - Cl - SO_2tBuNH]^+$, 282 (7.6) $[M - Cl]^+$. **HRMS** (ESI) *m/z* 318.0934, calcd. for $C_{14}H_{21}ClNO_3S$ $[MH]^+$: 318.0931.

General procedure for the synthesis of 5b and 6a

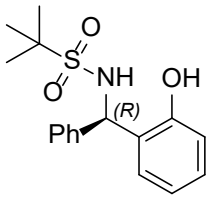
Fresh *meta*-chloroperoxybenzoic acid (0.269 g, 1.2 mmol, 1.2 eq, ≤77%) was added at 0 C to a solution of the sulfinamide **4a** or the sulfonamide **5b** (1 mmol, 1 eq.) in anhydrous CH_2Cl_2 (5 mL). The reaction mixture was stirred at 0 C for 1 h. After completion, monitored by TLC, the reaction was quenched with an aqueous solution of saturated $NaHSO_3$ and $NaHCO_3$ and stirred for 30 minutes. The mixture was extracted with CH_2Cl_2 (3x), the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography.

(*R*)-*N*-(1-(2-Hydroxyphenyl)ethyl)-2-methylpropane-2-sulfonamide (6aA)



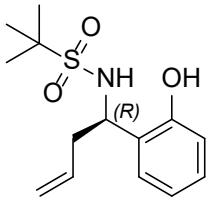
White solid (m. p.: 130 – 135 C). Column chromatography (CyH/AcOEt 7:3). Yield 70% (0.18 g). $[\alpha]_D^{20}$ = +34 (c = 1.1, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (ddd, *J* = 15.2, 7.5, 1.7 Hz, 2H), 6.91 (brs, 1H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.39 (d, *J* = 9.8 Hz, 1H), 4.63 (dq, *J* = 9.8, 6.9 Hz, 1H), 1.60 (d, *J* = 6.9 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 129.0, 128.7, 127.7, 120.6, 116.5, 59.9, 53.8, 24.1, 23.7. **GC** R_t: 18.0 min. **GCMS** (EI) *m/z* (%) = 57 (82) $[tBu]^+$, 120 (80) $[M - tBuS(O)_2NH_2 - H_2]^+$, 122 (100) $[M - tBuS(O)_2NH_2]^+$, 137 (20) $[tBuS(O)_2NH_2]^+$, 257 (5) $[M]^{+\cdot}$. **HRMS** (ESI) *m/z* 258.1167, calcd. for $C_{12}H_{20}NO_3S$ $[MH]^+$: 258.1164.

(*R*)-*N*-((2-Hydroxyphenyl)(phenyl)methyl)-2-methylpropane-2-sulfonamide (6aB)



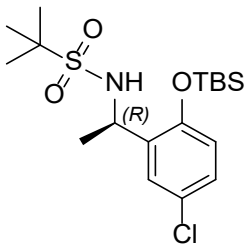
White solid (m. p.: 188 – 189 C). Column chromatography (CyH/AcOEt 7:3). Yield 85% (0.27 g). $[\alpha]_D^{20}$ = +38 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 7.16 – 7.05 (m, 2H), 6.86 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.50 (s, 1H), 5.76 (d, *J* = 9.8 Hz, 1H), 5.54 (d, J = 9.8 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 141.2, 129.3, 129.2, 128.4, 127.9, 127.2, 126.7, 120.8, 117.0, 60.2, 59.3, 24.1. **GC** R_t: 17.4 min. **GCMS** (EI) *m/z* (%) = 57 (100) $[tBu]^+$, 77 (67) $[C_6H_6]^+$. **HRMS** (ESI) *m/z* 320.1324, calcd. for $C_{17}H_{22}NO_3S$ $[MH]^+$: 320.1320.

(*R*)-*N*-(1-(2-Hydroxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfonamide (6aC)



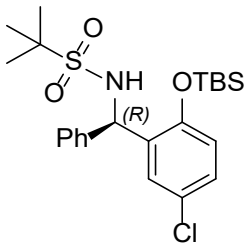
White waxy solid. Column chromatography (CyH/AcOEt 4:1). Yield 65% (0.17 g). $[\alpha]_D^{20}$ = +26 (c = 1.1, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.01 (m, 2H), 6.89 – 6.68 (m, 2H), 5.69 (ddt, J = 17.2, 10.2, 7.2 Hz, 1H), 5.47 (d, J = 9.9 Hz, 1H), 5.11 – 5.02 (m, 1H), 5.03 (dd, J = 6.8, 2.0 Hz, 1H), 4.53 (dt, J = 9.9, 7.2 Hz, 1H) 2.80 – 2.57 (m, 2H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 134.4, 128.7, 128.7, 127.2, 120.3, 118.0, 116.2, 60.0, 57.8, 41.4, 26.9, 24.1. **GC** R_t: 20.4 min. **GCMS** (EI) *m/z* (%) = 122 (100) $[C_4H_9O_2S]^+$, 242 (18) $[M - C_3H_5]^+$. **HRMS** (ESI) *m/z* 284.1317, calcd. for $C_{14}H_{22}NO_3S$ $[MH]^+$: 284.1320.

(*R*)-*N*-(1-(2-((Tert-butyldimethylsilyl)oxy)-5-chlorophenyl)ethyl)-2-methylpropane-2-sulfonamide (5bA)



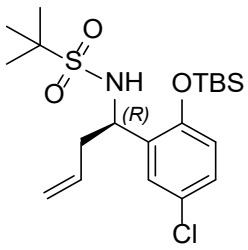
White waxy solid. Column chromatography (CyH/AcOEt 7:3). Yield 92% (0.37 g). $[\alpha]_D^{20}$ = +45 (c = 1.2, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 5.56 (dd, *J* = 7.1, 3.3 Hz, 1H), 3.63 (s, 1H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.22 (s, 9H), 1.02 (s, 9H), 0.26 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 136.7, 128.1, 127.2, 125.0, 119.3, 57.8, 50.3, 25.3, 24.7, 22.2, 18.1, -4.2, -4.3. **GC** R_t: 22.8 min. **GCMS** (EI) *m/z* (%) 211 (100) $[pClPh\text{-}SitBu]^+$, 348 (5.9) $[M - tBu]^+$. **HRMS** (ESI) *m/z* 406.1641, calcd. for $C_{18}H_{33}ClNO_3SSi$ $[MH]^+$: 406.1639.

(*R*)-*N*-((2-((Tert-butyldimethylsilyl)oxy)-5-chlorophenyl)(phenyl)methyl)-2-methylpropane-2-sulfonamide (5bB)



White waxy solid. Column chromatography (CyH/AcOEt 7:3). Yield 97% (0.45 g). $[\alpha]_D^{20}$ = +0.9 (c = 1.5, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 1H), 7.31 – 7.23 (m, 2H), 7.23 – 7.17 (m, 2H), 7.17 – 7.08 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.98 (d, *J* = 9.8 Hz, 1H), 5.75 (d, *J* = 9.9 Hz, 1H), 1.22 (s, 9H), 0.85 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 141.2, 133.6, 128.5, 128.1, 128.1, 127.1, 126.9, 125.9, 59.4, 56.4, 25.4, 23.8, 17.8, -4.4, -4.6. **GC** R_t: 26.2 min. **GCMS** (EI) *m/z* (%) 354 (23) $[M - TBS]^+$, 410 (8.2) $[M - tBu]^+$. **HRMS** (ESI) *m/z* 468.1798, calcd. for $C_{23}H_{35}ClNO_3SSi$ $[MH]^+$: 468.1795.

(*R*)-*N*-(1-(2-((Tert-butyldimethylsilyl)oxy)-5-chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfonamide (5bC)

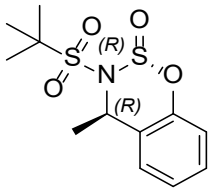


White waxy solid. Column chromatography (CyH/AcOEt 7:3). Yield 92% (0.40 g). $[\alpha]_D^{20}$ = +58 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 2.6 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.75 (d, J = 8.6 Hz, 1H), 5.64 (ddt, *J* = 17.6, 10.5, 7.3 Hz, 1H), 5.29 – 5.06 (m, 2H), 4.81 (d, *J* = 8.3 Hz, 1H), 4.58 (d, *J* = 9.6 Hz, 1H), 2.69 – 2.38 (m, 2H), 1.29 (s, 9H), 1.03 (s, 9H), 0.30 (s, 3H), 0.26 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 134.2, 133.2, 127.8, 127.5, 126.0, 119.2, 119.1, 59.6, 53.3, 41.7, 25.7, 24.0, 18.1, -4.0, -4.4. **GC** R_t: 23.4 min. **GCMS** (EI) *m/z* (%) 270 (100) $[M - CH_2CHCH_2 - SO_2tBu]^+$, 318 (16) $[M - TBS]^+$, 390 (16) $[M - CH_2CHCH_2]^+$. **HRMS** (ESI) *m/z* 432.1791, calcd. for $C_{20}H_{35}ClNO_3SSi$ $[MH]^+$: 432.1795.

General procedure for the synthesis of 7

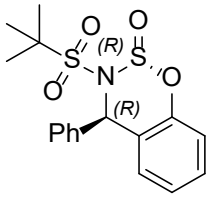
Thionyl chloride (0.150 mL, 2.04 mmol, 1.02 eq.) was added at –15 C to a solution of the sulfonamide **6** (2 mmol, 1 eq.) in anhydrous THF, followed by the slow addition of pyridine (0.372 mL, 4.6 mmol, 2.3 eq.). The reaction mixture was stirred at –15 C for 1 h. After completion, monitored by TLC, the reaction was quenched with water and extracted with AcOEt (3x). The organic phase was then washed with aqueous Na_2HPO_4 solution (5%, 2x), water (2x), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. With the exception of **7aA**, compounds are too unstable to be purified or manipulated, so the crudes were checked by 1H NMR only and readily used in the following step without further purification.

(2*R*,4*R*)-3-(*tert*-butylsulfonyl)-4-methyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2-oxide (7aA)



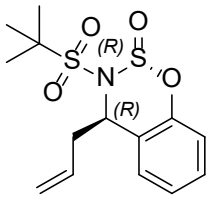
White solid (m. p.: 114 – 115 C). Column chromatography (CyH/AcOEt 9:1). Yield 70% (0.42 g). $[\alpha]_D^{20}$ = −71 (c = 0.75, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (ddd, *J* = 8.5, 6.0, 3.1 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 1H), 5.08 (q, *J* = 7.0 Hz, 1H), 1.95 (d, J = 7.0 Hz, 3H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 129.6, 127.9, 125.2, 124.3, 120.0, 63.3, 54.0, 51.2, 24.3. **GC** R_t: 13.9 min. **GCMS** (EI) *m/z* (%) = 244 (2) $[M - tBu]^+$, 145 (16) $[C_6H_{11}NOS]^+$. **HRMS** (ESI) *m/z* 304.0675, calcd. for $C_{12}H_{18}NO_4S_2$ $[MH]^+$: 304.0677.

(2*R*,4*R*)-3-(*tert*-butylsulfonyl)-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2-oxide (7aB)



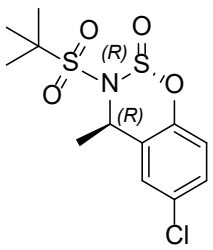
The compound was synthesized and readily used without any purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.39 – 7.28 (m, 4H), 7.18 – 7.09 (m, 2H), 6.96 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.16 (s, 1H), 1.30 (s, 9H).

(2*R*,4*R*)-4-Allyl-3-(*tert*-butylsulfonyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2-oxide (7aC)



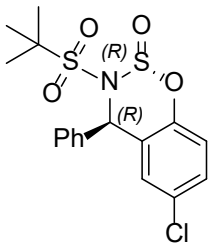
The compound was synthesized and readily used without any purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 1H), 7.17 – 7.07 (m, 3H), 5.91 (ddt, J = 17.3, 10.2, 7.3 Hz, 1H), 5.20 – 5.09 (m, 2H), 4.95 (dd, J = 8.3, 6.8 Hz, 1H), 3.20 – 3.08 (m, 1H), 2.98 – 2.88 (m, 1H), 1.34 (s, 9H).

(2*R*,4*R*)-3-(*tert*-butylsulfonyl)-6-chloro-4-methyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2-oxide (7bA)



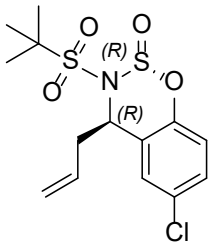
The compound was synthesized and readily used without any purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.7, 2.5 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 1H), 5.04 (q, *J* = 7.1 Hz, 1H), 1.94 (d, *J* = 7.0 Hz, 3H), 1.40 (s, 9H).

(2*R*,4*R*)-3-(*tert*-butylsulfonyl)-6-chloro-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2-oxide (7bB)



The compound was synthesized and readily used without any purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.4 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.30 (dd, J = 8.8, 2.5 Hz, 1H), 7.09 (d, J = 8.7 Hz, 1H), 6.91 (d, J = 2.5 Hz, 1H), 6.10 (s, 1H), 1.28 (s, 9H).

(2*R*,4*R*)-4-Allyl-3-(*tert*-butylsulfonyl)-6-chloro-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2-oxide (7bC)

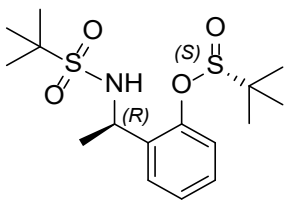


The compound was synthesized and readily used without any purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 5.98 – 5.73 (m, 1H), 5.22 (dt, *J* = 10.2, 0.9 Hz, 1H), 5.17 (dq, *J* = 16.9, 1.5 Hz, 1H), 4.91 (dd, *J* = 8.4, 6.7 Hz, 1H), 3.19 – 3.07 (m, 1H), 3.02 – 2.85 (m, 1H), 1.37 (s, 9H).

General procedure for the synthesis of 8

Tertiary Grignard reagent (1.05 mmol, 1.05 eq., 0.15 to 1 M solution in Et_2O) was slowly added at −40C to a solution of the oxathiozinone **7** (1 mmol) in anhydrous THF (3 mL) for **8aA-C**, **8bA-C** or in anhydrous Et_2O (3 mL) for **8bD,E**. The reaction mixture was stirred at –40 C for 1 h for **8aA-C**, **8bA-C**, at 0 C for **8bD** and at 20 C for **8bE**. After completion, monitored by TLC, the reaction was quenched with aqueous citric acid solution (0.4 eq., 20%) and extracted with AcOEt (3x). The organic phase was then washed with aqueous Na_2HPO_4 solution (5%, 2x), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography.

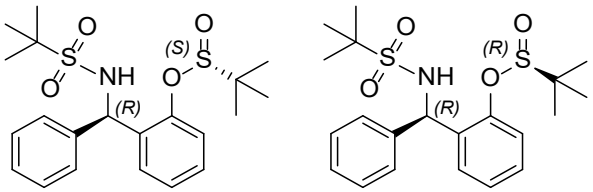
2-((*R*)-1-((1,1-dimethylethyl)sulfonamido)ethyl)phenyl (*S*)-2-methylpropane-2-sulfinate (8aA)



Clear oil. Yield 94% (0.34 g). Column chromatography (CyH/AcOEt 8:2). $[\alpha]_D^{20}$ = +118 (c = 0.9, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.17 (tt, *J* = 8.6, 1.4 Hz, 2H), 5.29 (d, *J* = 9.5 Hz, 1H), 4.79 (dq, *J* = 9.3, 6.9 Hz, 1H), 1.59 (d, *J* = 6.9 Hz, 3H), 1.40 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 129.0, 128.7, 127.7, 120.6, 116.5, 59.9, 53.8, 51.3, 24.1, 23.7, 21,9. **GC** R_t: 12.1 min. **GCMS** (EI)

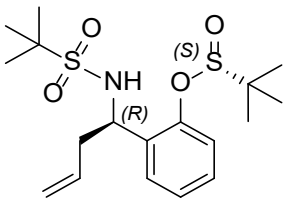
m/z (%) = 57 (100) $[tBu]^+$, 304 (1) $[M - tBu]^+$. **HRMS** (ESI) *m/z* 362.1463, calcd. for $C_{16}H_{28}NO_4S_2$ $[MH]^+$: 362.1460.

2-((*R*)-((1,1-dimethylethyl)sulfonamido)(phenyl)methyl)phenyl 2-methylpropane-2-sulfinate (8ab)



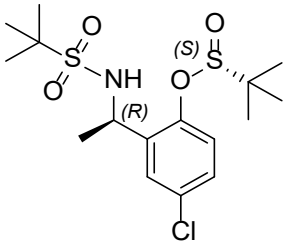
Sulfinate **8aB** was obtained as a hardly separable mixture of two diastereoisomers (Table 2, entry 2). Since it was not reactive in the subsequent ring opening with LiHMDS, no further attempt to separate the diastereoisomeric mixture was made.

2-((*R*)-1-((1,1-dimethylethyl)sulfonamido)but-3-en-1-yl)phenyl (*S*)-2-methylpropane-2-sulfinate (8aC)



Clear oil. Column chromatography (CyH/AcOEt 9:1). Yield 95% (0.37 g). $[\alpha]_D^{20}$ = +97 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 8.6, 7.0, 1.9 Hz, 1H), 7.25 – 7.14 (m, 3H), 5.63 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.12 – 5.02 (m, 2H), 4.74 (d, *J* = 8.6 Hz, 1H), 2.68 (t, *J* = 7.2 Hz, 2H), 1.40 (s, 9H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5m 133.7, 133.5, 129.5, 129.2, 125.6, 120.7, 118.8, 59.7, 59.0, 42.3, 24.3, 22.0. **GC** R_t: 20.3 min. **GCMS** (EI) *m/z* (%) 121 (21) $[C_4H_9O_2S]^+$, 122 (100) $[C_4H_{10}O_2S]^+$, 162 (14) $[C_{10}H_{11}NO]^+$, 283 (1) [M - tBuSO]$^+$. **HRMS** (ESI) *m/z* 388.1612, calcd. for $C_{18}H_{30}NO_4S_2$ $[MH]^+$: 388.1616.

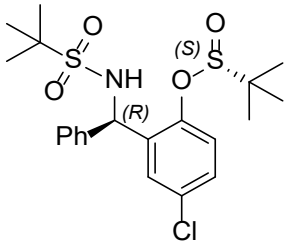
4-Chloro-2-((*R*)-1-((1,1-dimethylethyl)sulfonamido)ethyl)phenyl (*S*)-2-methylpropane-2-sulfinate (8bA)



White waxy solid. Yield 85% (0.34 g). Column chromatography (CyH/AcOEt 9:1). $[\alpha]_D^{20}$ = +126 (c = 0.9, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.5 Hz, 1H), 7.24 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 5.18 (d, *J* = 9.5 Hz, 1H), 4.77 (dq, *J* = 9.6, 7.0 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.39 (s, 9H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 137.5, 131.0, 128.8, 128.4, 122.2, 59.6, 59.1, 51.2, 24.6,

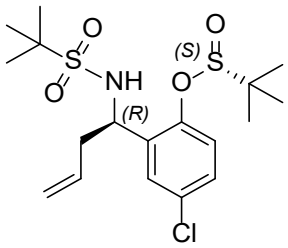
24.2, 21.7. **GC** R_t: 13.9 min. **GCMS** (EI) *m/z* (%) 57 (100) $[tBu]^+$, 338 (1) $[M - tBu]^+$. **HRMS** (ESI) *m/z* 396.1073, calcd. for $C_{16}H_{27}ClNO_4S_2$ $[MH]^+$: 396.1070.

4-Chloro-2-((*S*)-((1,1-dimethylethyl)sulfonamido)(phenyl)methyl)phenyl (*S*)-2-methylpropane-2-sulfinate (8bB)



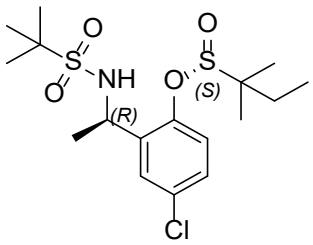
White solid (m. p.: 187 – 189 C). Column chromatography (CyH/AcOEt 9:1). Yield 95% (0.43 g). $[\alpha]_D^{20}$ = +130 (c = 1.4, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.6 Hz, 1H), 7.33 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.26 – 7.18 (m, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 5.79 (d, *J* = 10.0 Hz, 1H), 5.67 (brd, *J* = 10.1 Hz, 1H), 1.36 (s, 9H), 1.11 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.3, 140.8, 135.9, 130.8, 130.4, 129.4, 128.3, 127.1, 126.3, 122.3, 59.8, 59.0, 58.2, 24.1, 21.4. **GC** R_t: 18.5 min. **GCMS** (EI) *m/z* (%) 57 (100) $[tBu]^+$, 400 (4.1) $[M - tBu]^+$, 457 (4.3) $[M]^+$. **HRMS** (ESI) *m/z* 458.1223, calcd. for $C_{21}H_{29}ClNO_4S_2$ $[MH]^+$: 458.1227.

4-Chloro-2-((*R*)-1-((1,1-dimethylethyl)sulfonamido)but-3-en-1-yl)phenyl (*S*)-2-methylpropane-2-sulfinate (8bC)



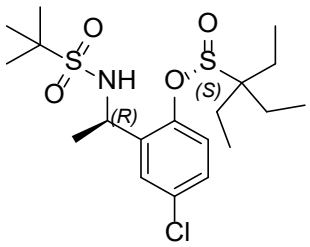
White waxy solid. Column chromatography (CyH/AcOEt 9:1). Yield 86% (0.36 g). $[\alpha]_D^{20}$ = +160 (c = 1.1, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.8 Hz, 1H), 7.23 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 5.64 (brs, 1H), 5.20 – 5.14 (m, 1H), 5.11 (d, *J* = 5.6 Hz, 1H), 5.08 (s, 1H), 4.82 – 4.65 (m, 1H), 2.60 (dtt, *J* = 20.1, 13.5, 6.8 Hz, 2H), 1.37 (s, 9H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 135.8, 133.1, 130.7, 128.8, 121.8, 119.1, 59.6, 59.1, 41.8, 24.1, 21.7. **GC** R_t: 12.1 min. **GCMS** (EI) *m/z* (%) 57 (100) $[tBu]^+$, 421 (4) $[M]^{+\cdot}$. **HRMS** (ESI) *m/z* 422.1230, calcd. for $C_{18}H_{29}ClNO_4S_2$ $[MH]^+$: 422.1227.

4-chloro-2-((R)-1-((1,1-dimethylethyl)sulfonamido)ethyl)phenyl (S)-2-methylbutane-2-sulfinate (8bD)



White solid (m. p.: 64 – 66 C). Yield 90%. Column chromatography (CyH/AcOEt 9:1). $[\alpha]_D^{20}$ = –177 (c = 1.04, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) **)** δ 7.27 (s, 1H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.09 (d, *J* = 9.3 Hz, 1H), 5.06 (d, *J* = 9.5 Hz, 1H), 4.70 – 4.60 (m, 1H), 1.84 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.75 (dq, *J* = 14.5, 7.6 Hz, 1H), 1.58 (d, *J* = 7.0 Hz, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.32 (s, 9H), 1.06 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.9, 137.8, 131.1, 128.9, 128.4, 122.3, 77.5, 77.2, 76.8, 62.8, 59.7, 51.1, 27.9, 24.7, 24.3, 18.6, 7.9. **HPLC** R_t: 9.7 min. **HPLC-MS** (ESI) *m/z* (%) 841.05 (100) $[2M+Na]^+$, 410.10 (11) $[M + H]^+$. **HRMS** (ESI) *m/z* 410.1227, calcd. for $C_{17}H_{29}ClNO_4S_2$ $[MH]^+$: 410.1231.

4-chloro-2-((R)-1-((1,1-dimethylethyl)sulfonamido)ethyl)phenyl (S)-3-ethylpentane-3-sulfinate (8bE)

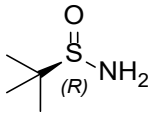


White solid (m. p.: 72 – 74 C). Yield 95%. Column chromatography (CyH/AcOEt 9:1). $[\alpha]_D^{20}$ = –148 (c = 1.07, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) **)** δ 7.27 (d, J = 2.7 Hz, 1H), 7.24 (d, J = 2.6 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 5.06 (d, J = 9.5 Hz, 1H), 4.76 (dq, J = 9.5, 6.9 Hz, 1H), 1.90 (q, J = 7.8 Hz, 6H), 1.58 (d, J = 7.0 Hz, 3H), 1.32 (s, 9H), 1.07 (t, J = 7.5 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.66, 137.93, 130.76, 128.52, 127.81, 121.67, 77.48, 77.16, 76.84, 67.85, 59.52, 50.20, 24.71, 24.12, 23.45, 8.07. **HPLC** R_t: 27.3 min. **HPLC-MS** (ESI) *m/z* (%) 897.15 (100) $[2M+Na]^+$, 438.15 (24) $[M + H]^+$. **HRMS** (ESI) *m/z* 438.1540, calcd. for $C_{19}H_{33}ClNO_4S_2$ $[MH]^+$: 438.1543.

General procedure for the synthesis of 9

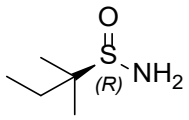
Lithium bis(trimethylsilyl)amide (2.3 mmol, 2.3 mL, 2.3 eq., 1 M solution in THF) was added at 0C to a solution of the compound **8b** (1 mmol) in anhydrous THF (3 mL). The reaction mixture was stirred at 0 C for 1 h. After completion, monitored by TLC, the reaction was quenched with water (1 eq.). The solvent was removed under reduced pressure and the crude was directly purified by column chromatography.

(*R*)-2-Methylpropane-2-sulfinamide (9a)



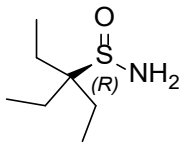
White solid (m. p.: 103 – 106 C). Yield 84% (0.10 g). Column chromatography (CH_2Cl_2/MeOH 95:5). $[\alpha]_D^{20}$ = +4.0 (c = 1.0, $CHCl_3$).**^{1}H NMR** (400 MHz, MeOH-d_4) δ 1.21 (s, 9H). **^{13}C NMR** (100 MHz, MeOH-d_4) δ 56.0, 22.7. **GC** R_t: 9.1 min. **GCMS** (EI) *m/z* (%) 57 (100) $[tBu]^+$. **HRMS** (ESI) *m/z* 122.0638, calcd. for $C_4H_{12}NOS$ $[MH]^+$: 122.0640. **Chiral HPLC** (IA, hex/*i*PrOH 9:1, 1.0 mL/min, 40 C, 220 nm) R_t: 7.0 min.

(*R*)-2-methylbutane-2-sulfinamide (9b)



White waxy solid. Yield 82% (0.11 g). Column chromatography (gradient elution: from 9:1 Cy/AcOEt to 100% AcOEt). $[\alpha]_D^{20}$ = –9.4 (c = 1.06, CH_2Cl_2).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.69 (bs, 2H), 1.76 – 1.66 (app. m, 1H), 1.55 (dq, J = 13.6, 7.4 Hz, 1H), 1.18 (s, 3H), 1.16 (s, 3H), 0.98 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 58.7, 28.6, 18.7, 18.6, 8.0. **HPLC** R_t: 2.0 min. **HPLC-MS** (ESI) *m/z* (%) 293.2 (9) $[2M+Na]^+$, 271.2 (75) $[2M+H]^+$, 136.2 (100) $[M + H]^+$. **HRMS** (ESI) *m/z* 136.0796, calcd. for $C_5H_{14}NOS$ $[MH]^+$: 136.0797. **Chiral HPLC** (AS, Hex/EtOH 9:1, 1.2 mL/min, 30 C, 220 nm) R_t: 7.9 min. Analytical data was found to be in agreement with the literature.[7]

(R)-3-ethylpentane-3-sulfinamide (9c)



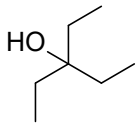
White waxy solid. Yield 43% (0.07 g). Column chromatography (gradient elution: from 9:1 Cy/AcOEt to 100% AcOEt). $[\alpha]_D^{20}$ = –13.9 (c = 1.04, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.75 (bs, 2H), 1.79 – 1.61 (m, 6H), 1.00 (t, J = 7.6 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 63.8, 23.8, 8.4. **HPLC** R_t: 3.7 min. **HPLC-MS** (ESI) *m/z* (%) 349.2 (46) $[2M+Na]^+$, 327.2 (100) $[2M + H]^+$, 164.2 (21) $[M+H]^+$. **HRMS** (ESI) *m/z* 164.1109, calcd. for $C_7H_{18}NOS$ $[MH]^+$: 164.1106. **Chiral HPLC** (OD, hex/*i*PrOH 9:1, 1.0 mL/min, 30 C, 220 nm) R_t: 14.3 min. Analytical data was found to be in agreement with the literature.[7]

Synthesis of tertiary alkyl chlorides and their Grignard reagents

Synthesis of 3-ethylpentan-3-ol (S-1b)

To a cooled (0 C) solution of 3-pentanone (20 mmol, 2.12 mL, 1 eq.) in anhydrous Et_2O (10 mL), ethyl magnesium bromide (22 mmol, 11 mL, 1.1 eq., 2M solution in Et_2O) was added dropwise. The reaction mixture was stirred overnight. After completion, monitored by TLC, the reaction was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with Et_2O (3x), the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and readily used in the following step without further purification.

3-ethylpentan-3-ol (S-1b)

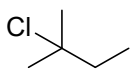


Colorless oil. Yield 96% (2.22 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (q, J = 7.5 Hz, 6H), 0.86 (t, J = 7.5 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 74.75, 30.54, 7.76. **GC** R_t: 7.4 min. **GC-MS** (EI) *m/z* (%) 87 (100) $[M - Et]^+$. Analytical data was found to be in agreement with the literature[3].

General procedure for the synthesis of alkyl chloride S-2

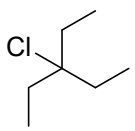
The tertiary alkyl chlorides were synthetized according to literature procedure,[4] modified as follow. HCl 37% (8.21 mL, 100 mmol, 2 eq) was added dropwise to the pure tertiary alcohol (**S-1**, 50 mmol, 1 eq) in an open vial. The reaction was capped and stirred overnight. The upper organic phase was separated from the aqueous phase, diluted with Et_2O (5 mL) and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried (Na_2SO_4), filtered and the desired product was isolated by fractional distillation.

2-chloro-2-methylbutane (S-2a)



Colorless oil. Yield 77% (4.1 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (q, J = 7.4 Hz, 2H), 1.56 (s, 6H), 1.03 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 71.69, 38.90, 32.07, 9.62. Analytical data was found to be in agreement with the literature[5].

3-chloro-3-ethylpentane (S-2b)

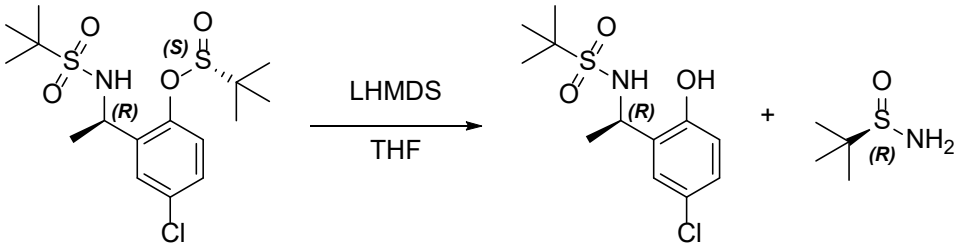


Colorless oil. Yield 85% (5.7 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (q, J = 7.4 Hz, 6H), 0.95 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 80.16 , 33.01, 8.81. **GC** R_t: 9.1 min. **GC-MS** (EI) *m/z* (%) 105.1 (25) $[M - Et]^+$, 99.2 (7) $[M – Cl]^+$, 69.2 (100) $[M – EtCl – H]^+$. Analytical data was found to be in agreement with the literature[6].

General Procedure for the synthesis of tertiary alkyl magnesium chlorides S-3

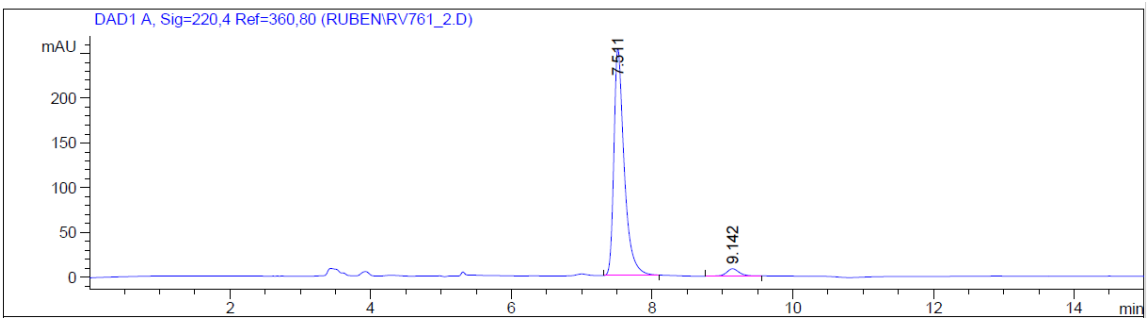
In a dried 25 mL, three-necked, round bottom flask, were placed activated magnesium turnings (15.3 mmol, 0.375 g, 1.03 eq.). Magnesium was covered with anhydrous Et_2O (1 mL) and dibromoetane (0.026 mL, 0.3 mmol) was added. The mixture warmed up and the solvent started refluxing. When the reaction mixture cooled down to room temperature, pure alkyl chloride (**S-2**, 2.5 mmol, 0.5 mL) was added to the magnesium to start the reaction. Stirring was begun and a solution of pure alkyl chloride (**S-2**, 12.5 mmol) in anhydrous Et_2O (6.5 mL) was added dropwise. The reaction was stirred for 2 h and then titrated against salicylaldehyde phenylhydrazone[8] prior to use.

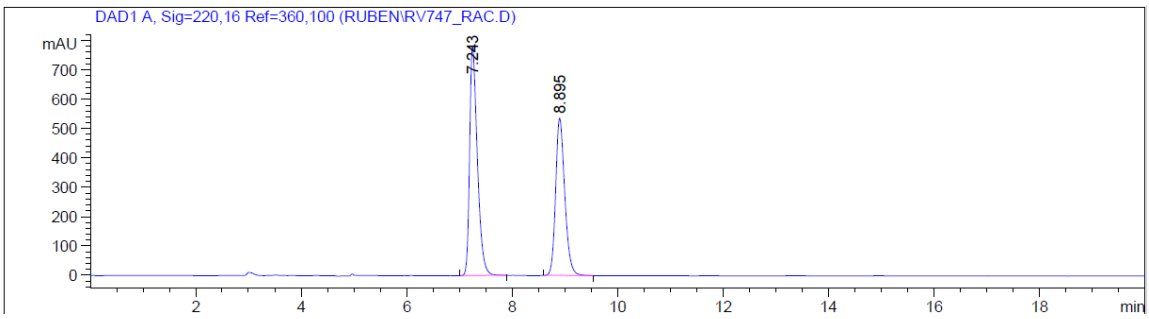
Chiral HPLC analyses



8bA **6bA** **9a**

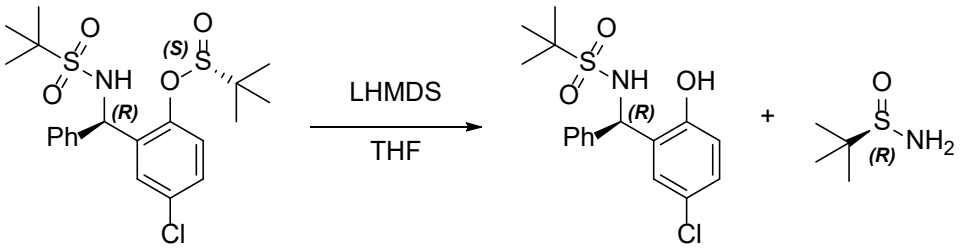
6bA Recovery (%)	**9a** Yield (e.e.) (%)
95	84 (93)



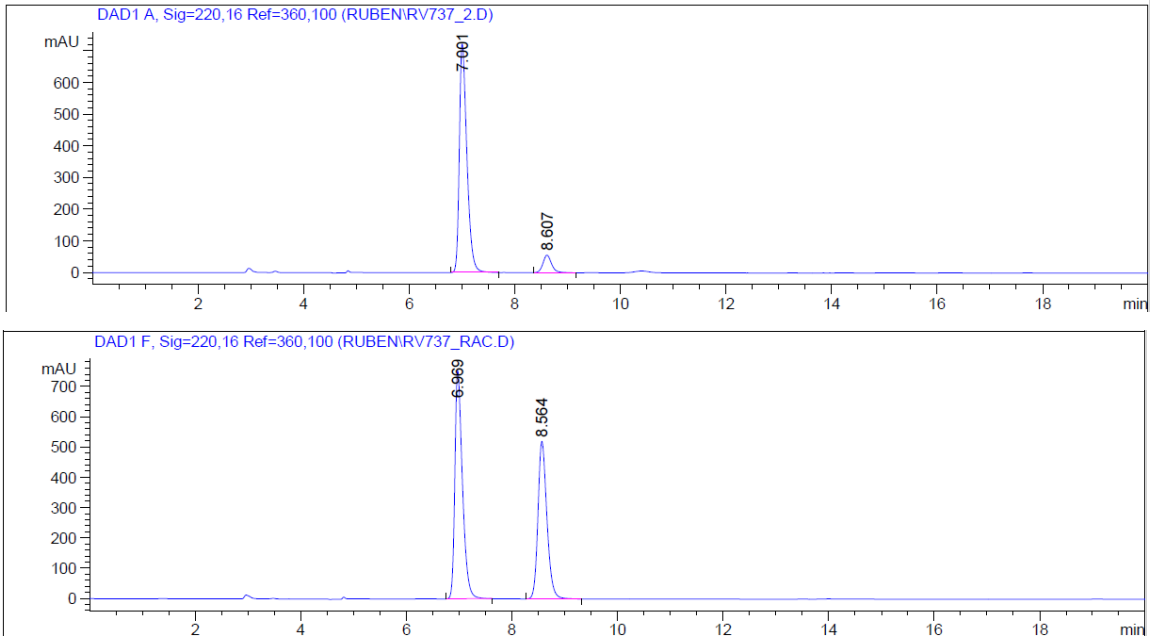


Signal 1: DAD1 A, Sig=220,4 Ref=360,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.511	BB	0.1530	2591.94067	254.04942	96.5170
2	9.142	MM	0.1950	93.53394	7.99371	3.4830

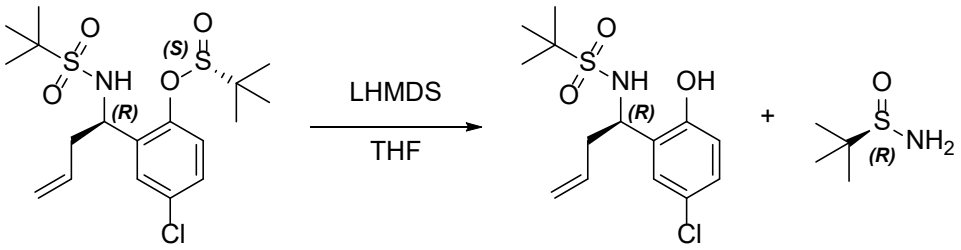


6bB Recovery (%)	**9a** Yield (e.e.) (%)
92	92 (83)



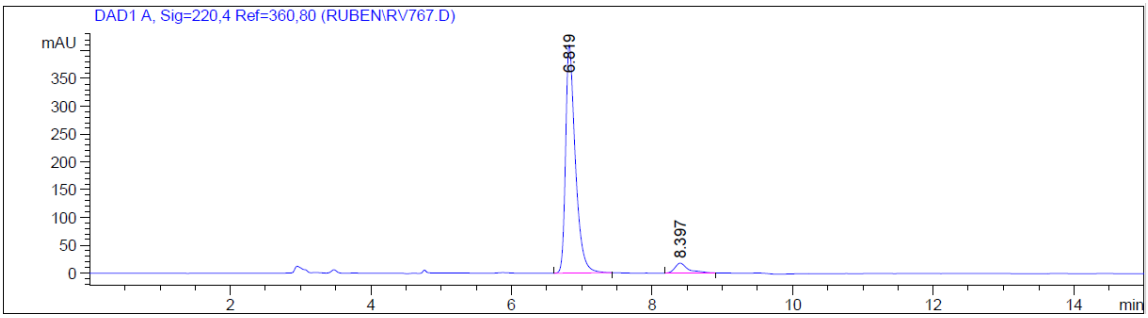
Signal 1: DAD1 A, Sig=220,16 Ref=360,100

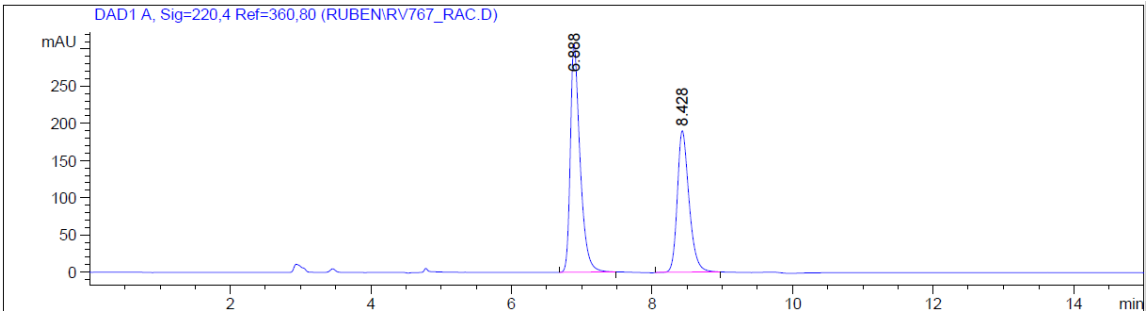
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.001	BB	0.1498	7175.60596	722.81012	91.8077
2	8.607	BB	0.1746	640.30579	55.51767	8.1923



8bC **6bC** **9a**

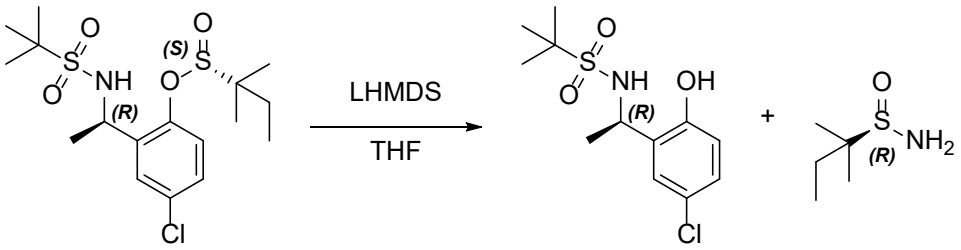
6bC Recovery (%)	**9a** Yield (e.e.) (%)
97	89 (90)





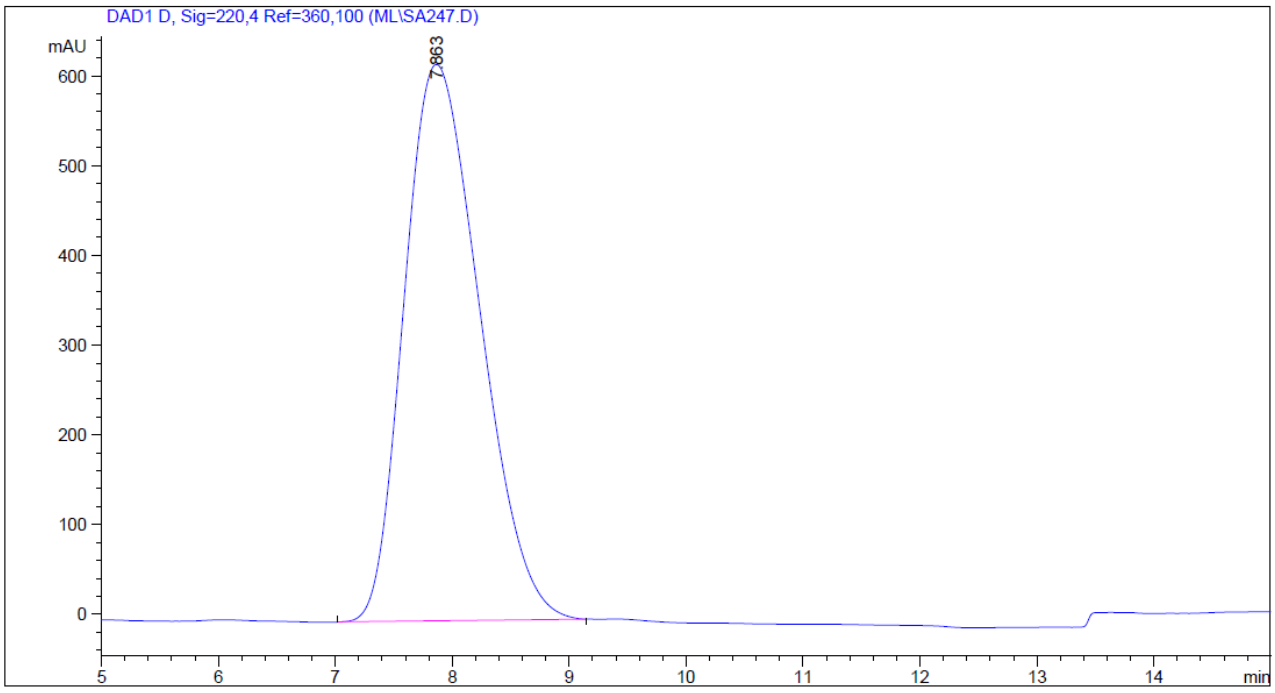
Signal 1: DAD1 A, Sig=220,4 Ref=360,80

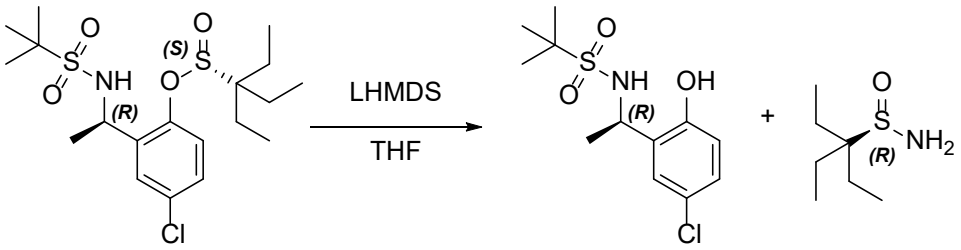
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.819	BB	0.1433	3992.15503	411.13358	95.2084
2	8.397	MM	0.1956	200.91537	17.12121	4.7916
Totals :				4193.07040	428.25479	



8bD **6bA** **9b**

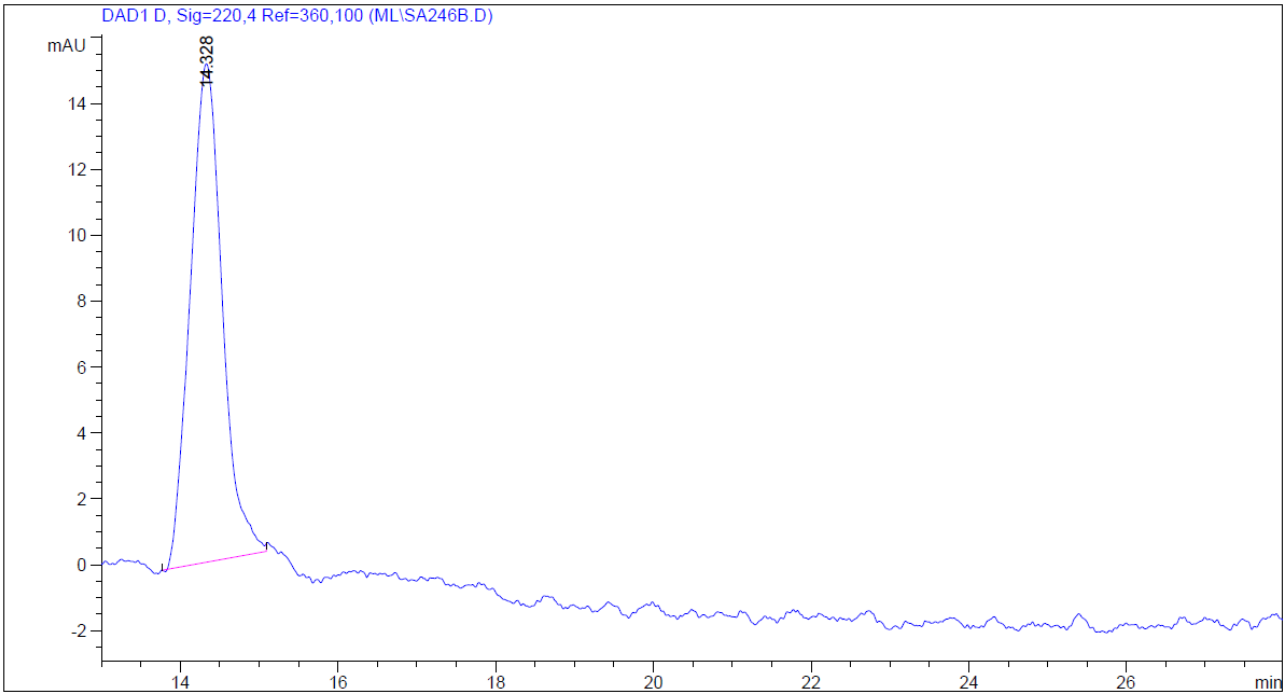
6bA Recovery (%)	**9b** Yield (e.e.) (%)
95	82 (99)





8bE **6bA** **9c**

6bA Recovery (%)	**9c** Yield (e.e.) (%)
95	43 (99)



References

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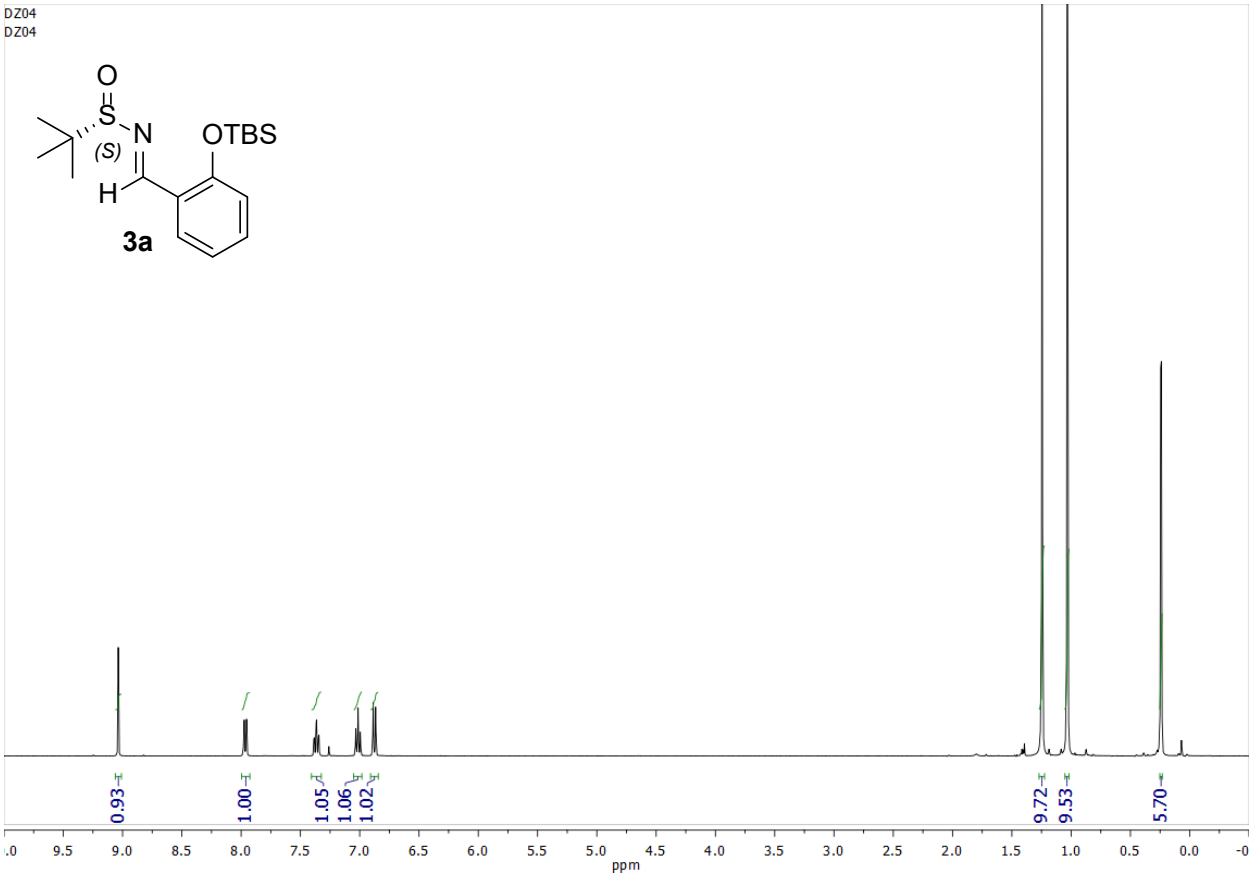
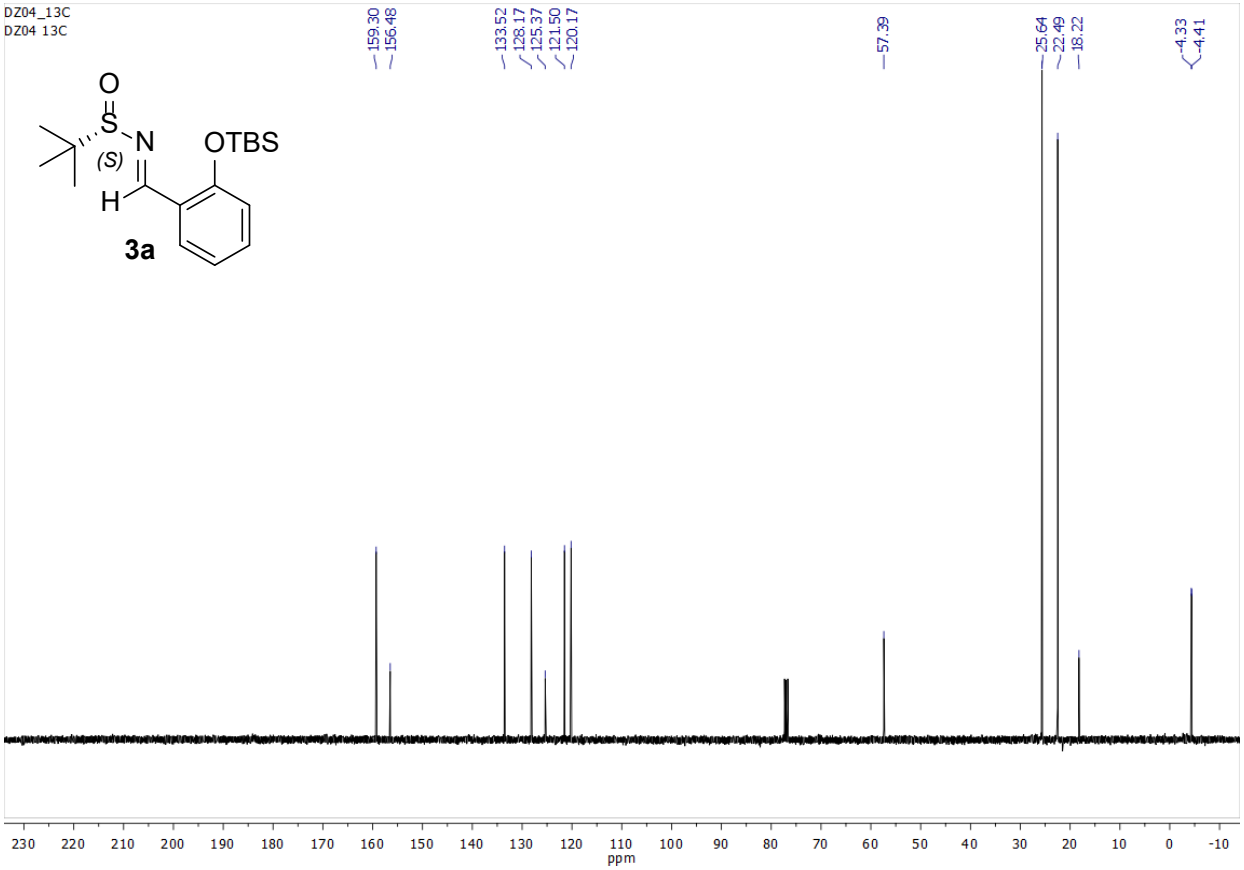
NMR spectra


DZ04
DZ04
O
S
N
(S)
H
OTBS
3a
0.93
1.00
1.05
1.06
1.02
9.72
9.53
5.70
ppm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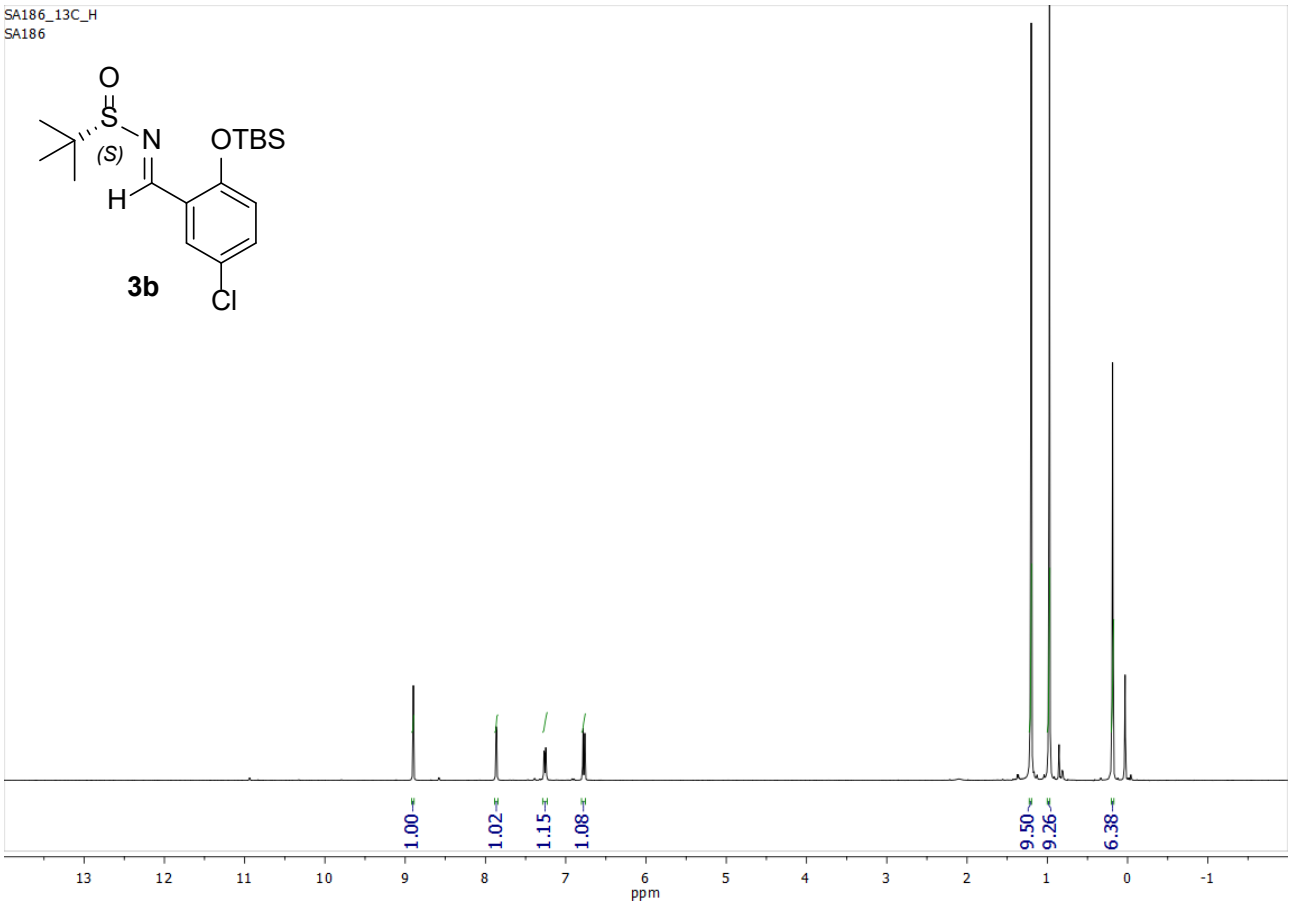
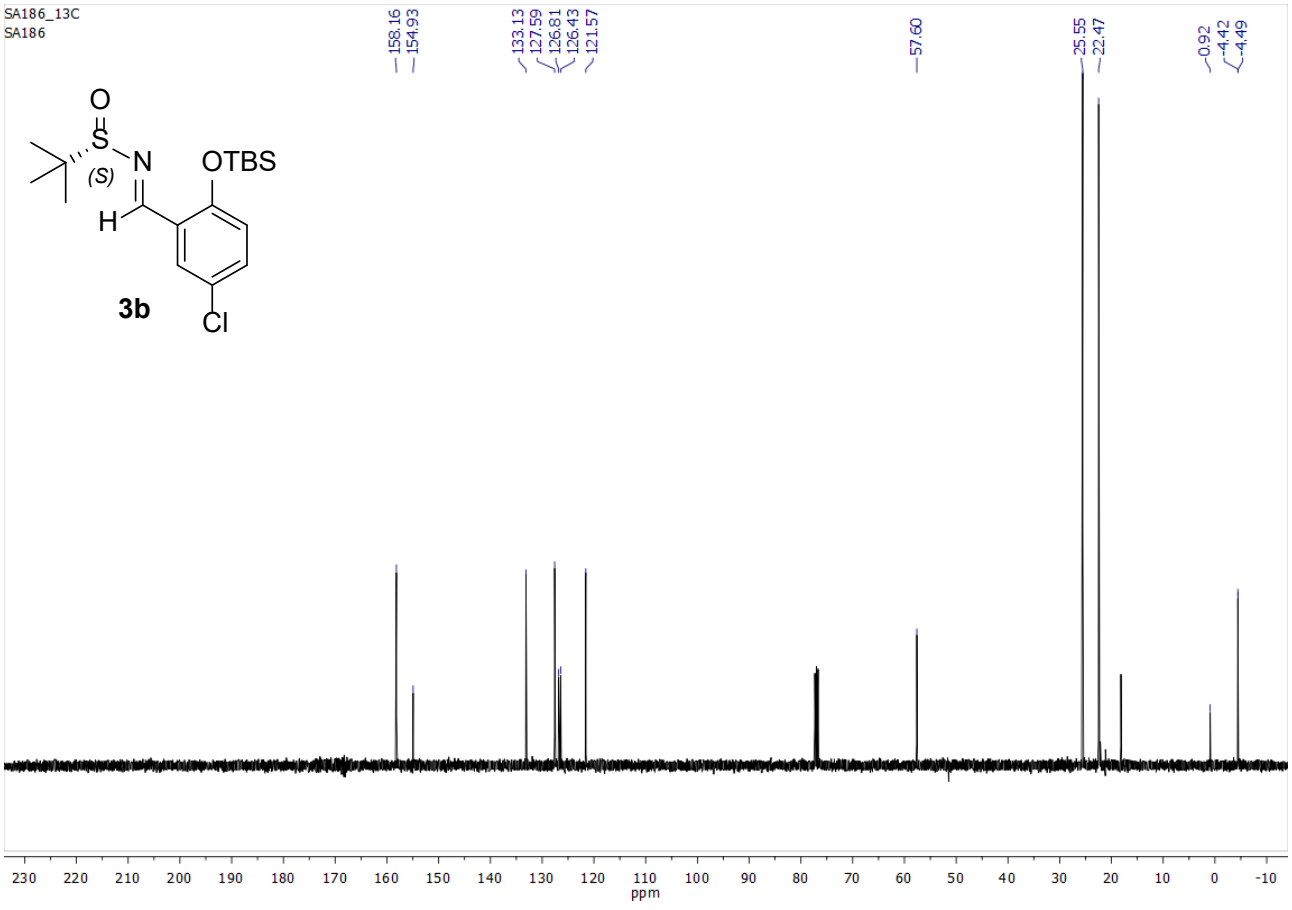
DZ04 13C
159.30
156.48
133.52
128.17
125.37
121.50
120.17
57.39
25.64
22.49
18.22
-4.33
-4.41
O
S
N
(S)
H
OTBS
3a
ppm


SA186_13C_H
SA186
O
S
(S)
N
H
OTBS
Cl
3b
1.00
1.02
1.15
1.08
9.50
9.26
6.38
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
ppm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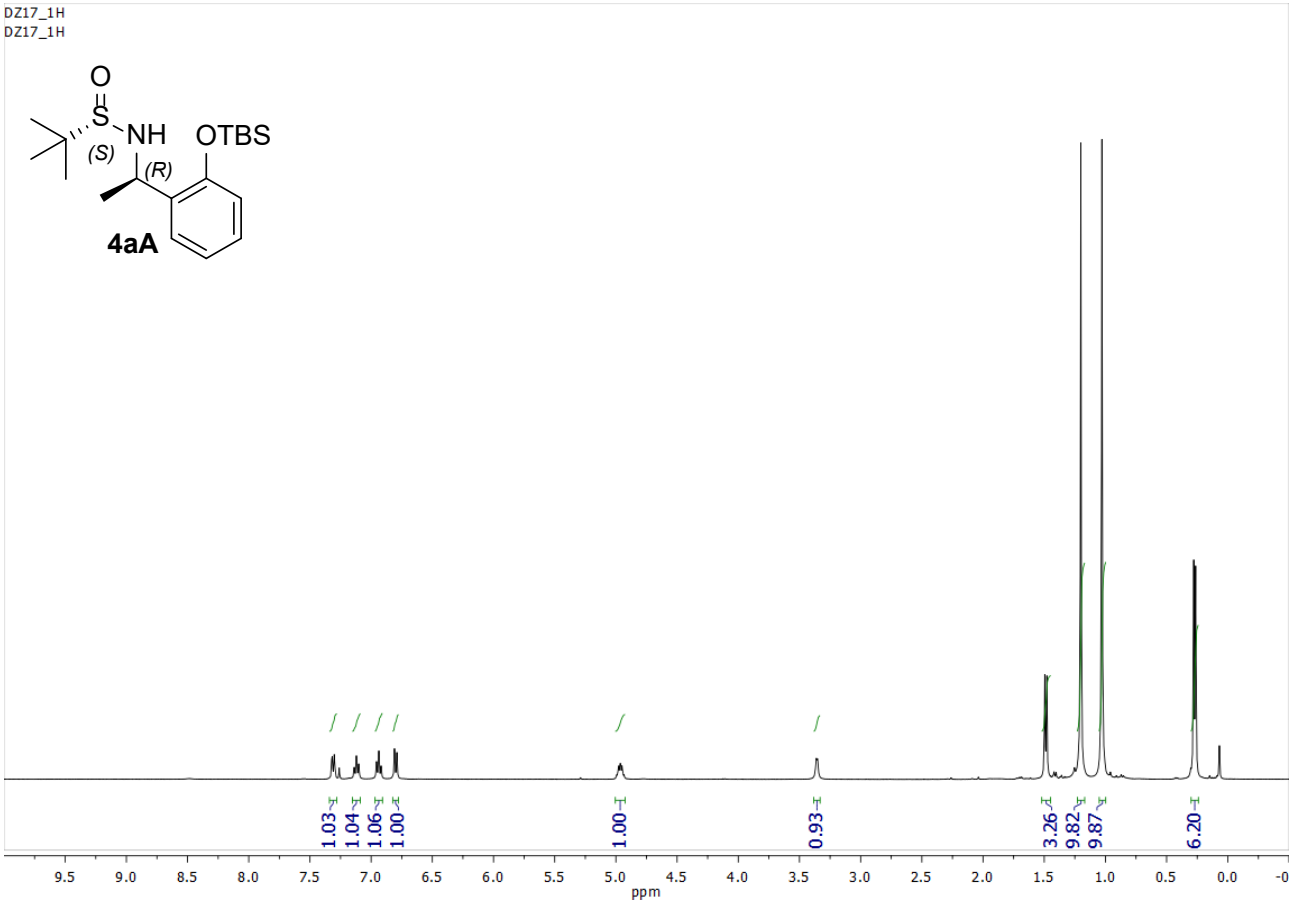
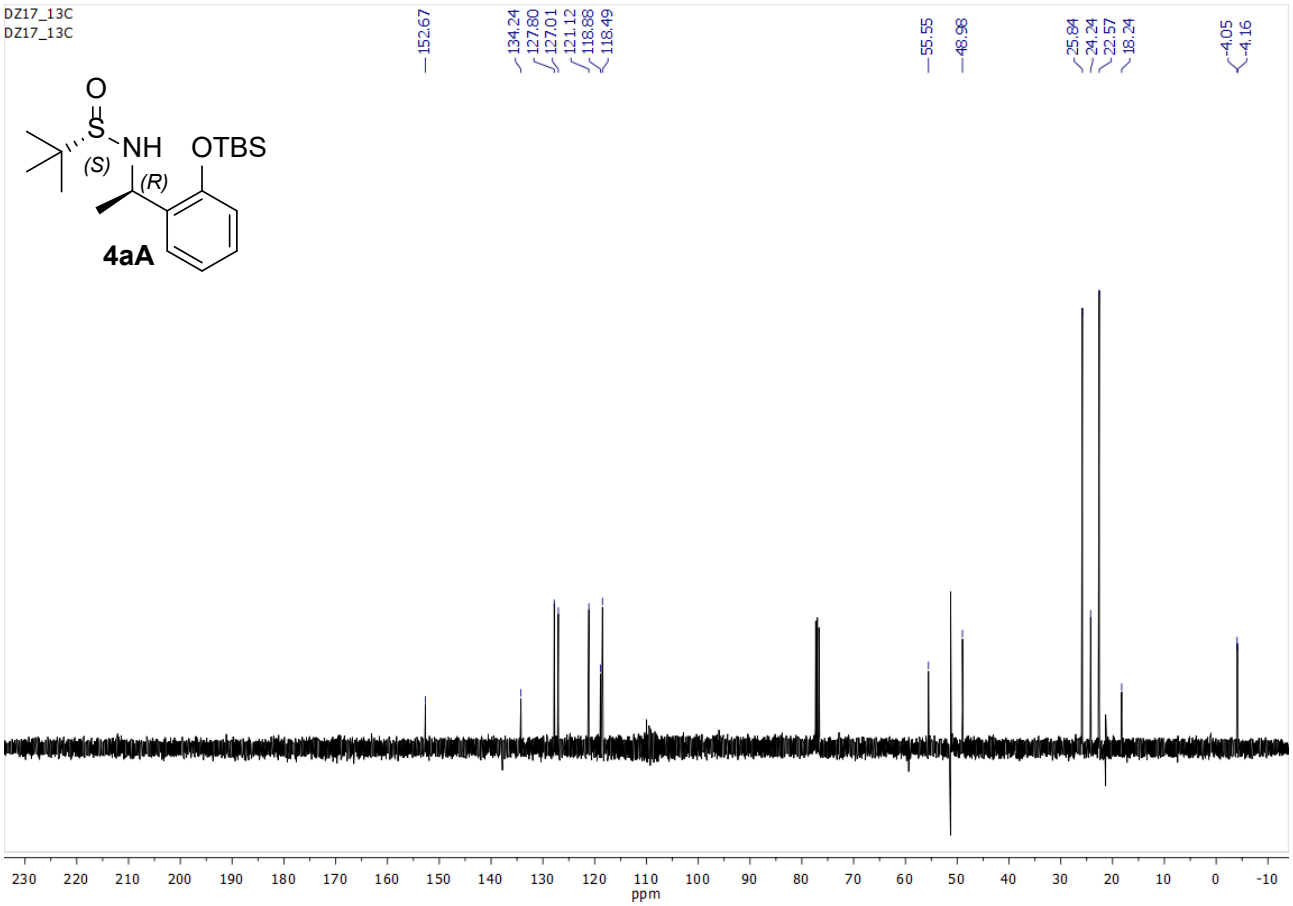
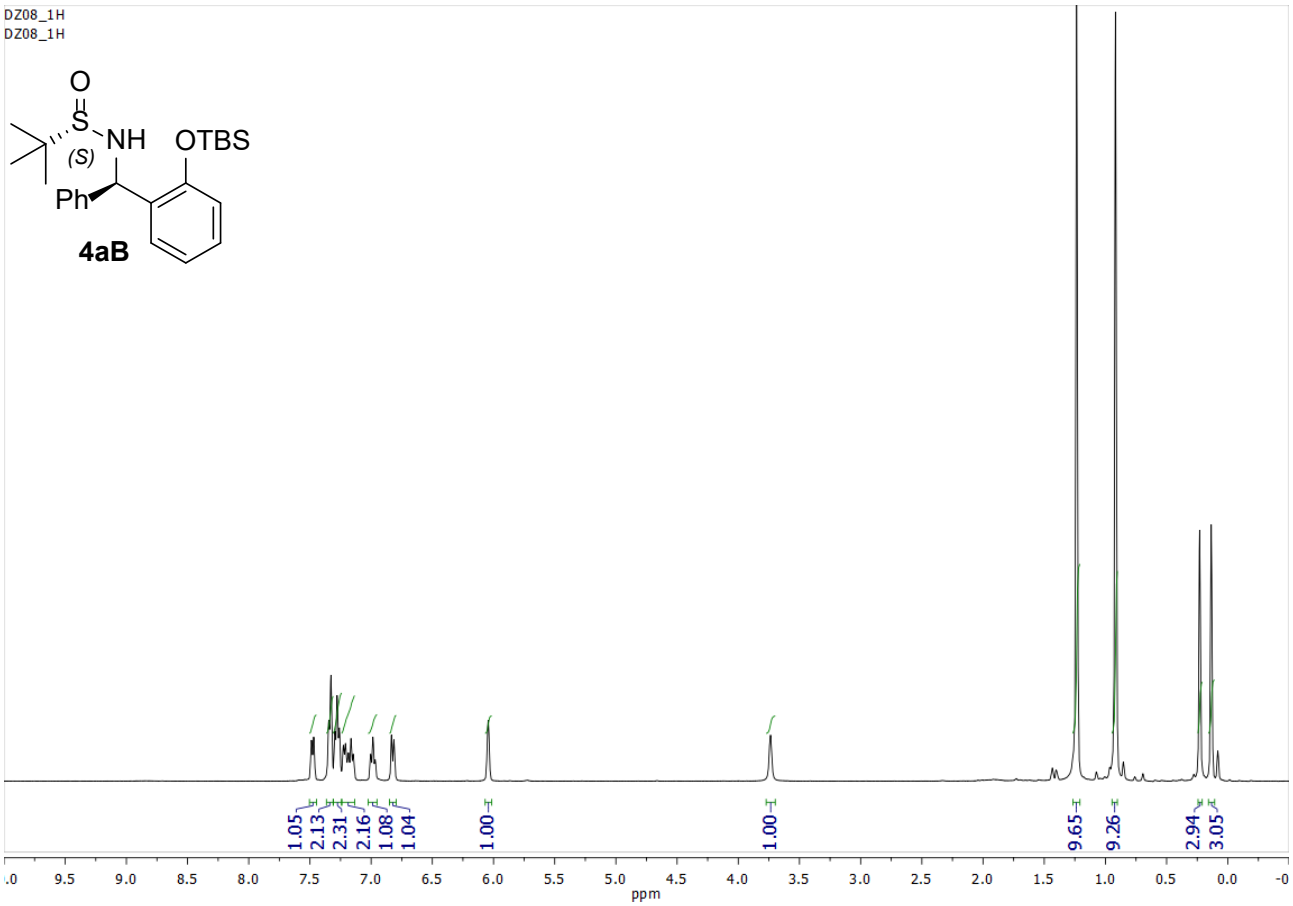
SA186
O
S
(S)
N
H
OTBS
Cl
3b
158.16
154.93
133.13
127.59
126.81
126.43
121.57
57.60
25.55
22.47
0.92
-4.42
-4.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


DZ17_1H
DZ17_1H
O
S
NH
OTBS
(S)
(R)
4aA
1.03
1.04
1.06
1.00
1.00
0.93
3.26
9.82
9.87
6.20
ppm


DZ17_13C
DZ17_13C
152.67
134.24
127.80
127.01
121.12
118.88
118.49
55.55
48.98
25.84
24.24
22.57
18.24
-4.05
-4.16
O
S
NH
OTBS
(S)
(R)
4aA
ppm


DZ08_1H
DZ08_1H
O
S
NH
OTBS
(S)
Ph
4aB
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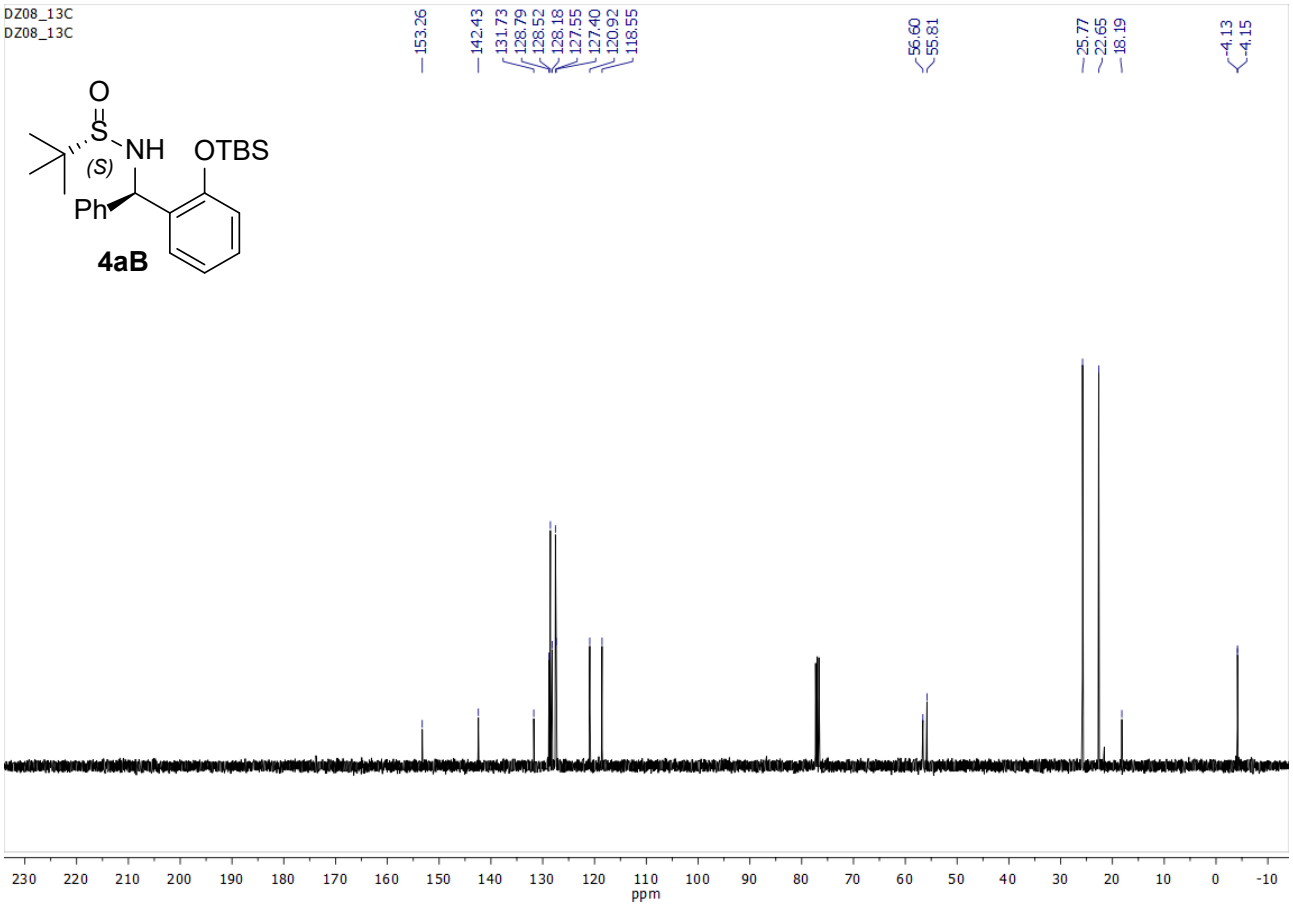
2.13
2.31
2.16
1.08
1.04
1.00
1.00
9.65
9.26
2.94
3.05
ppm


DZ08_13C
DZ08_13C
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142.43
131.73
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128.52
128.18
127.55
127.40
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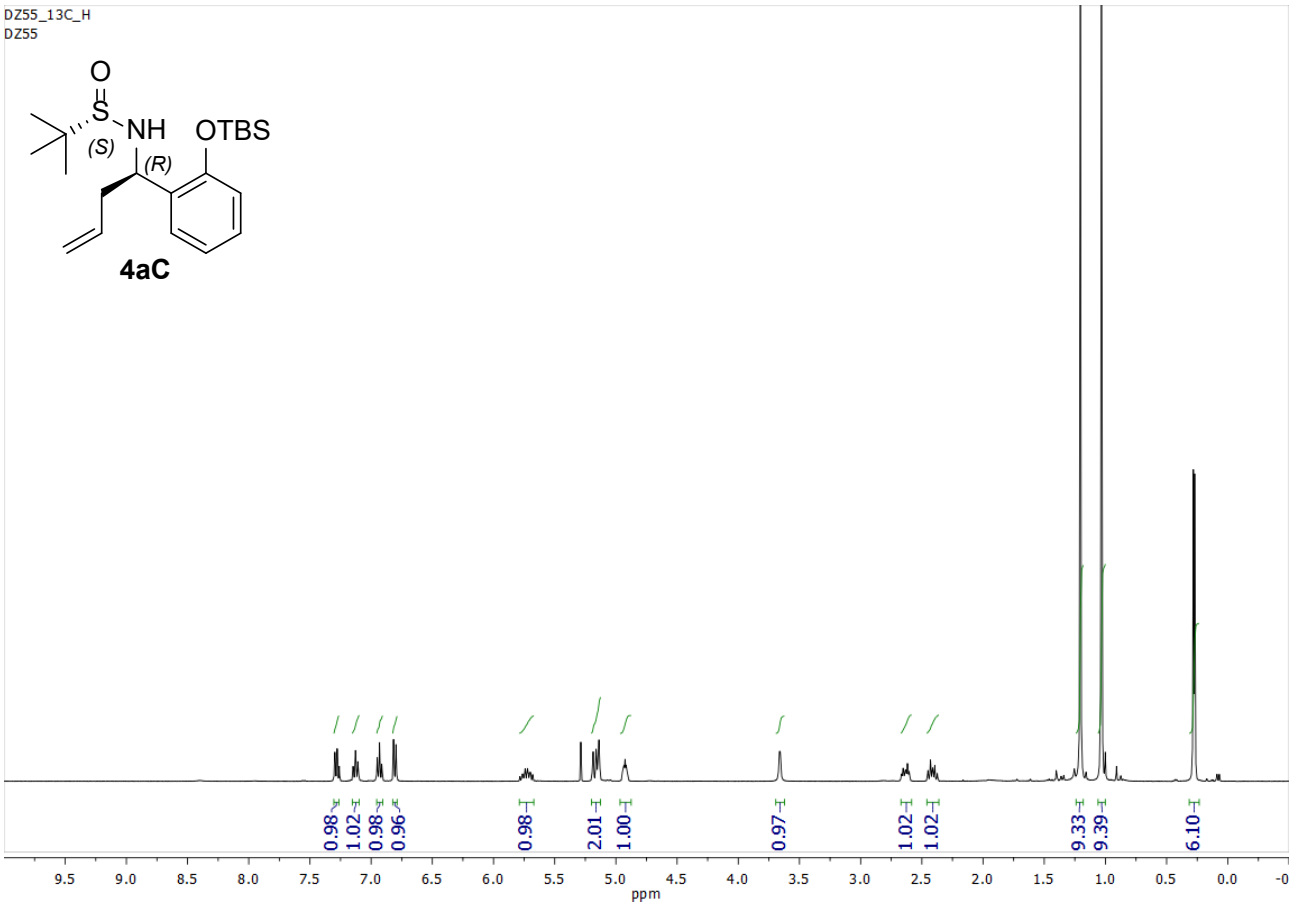
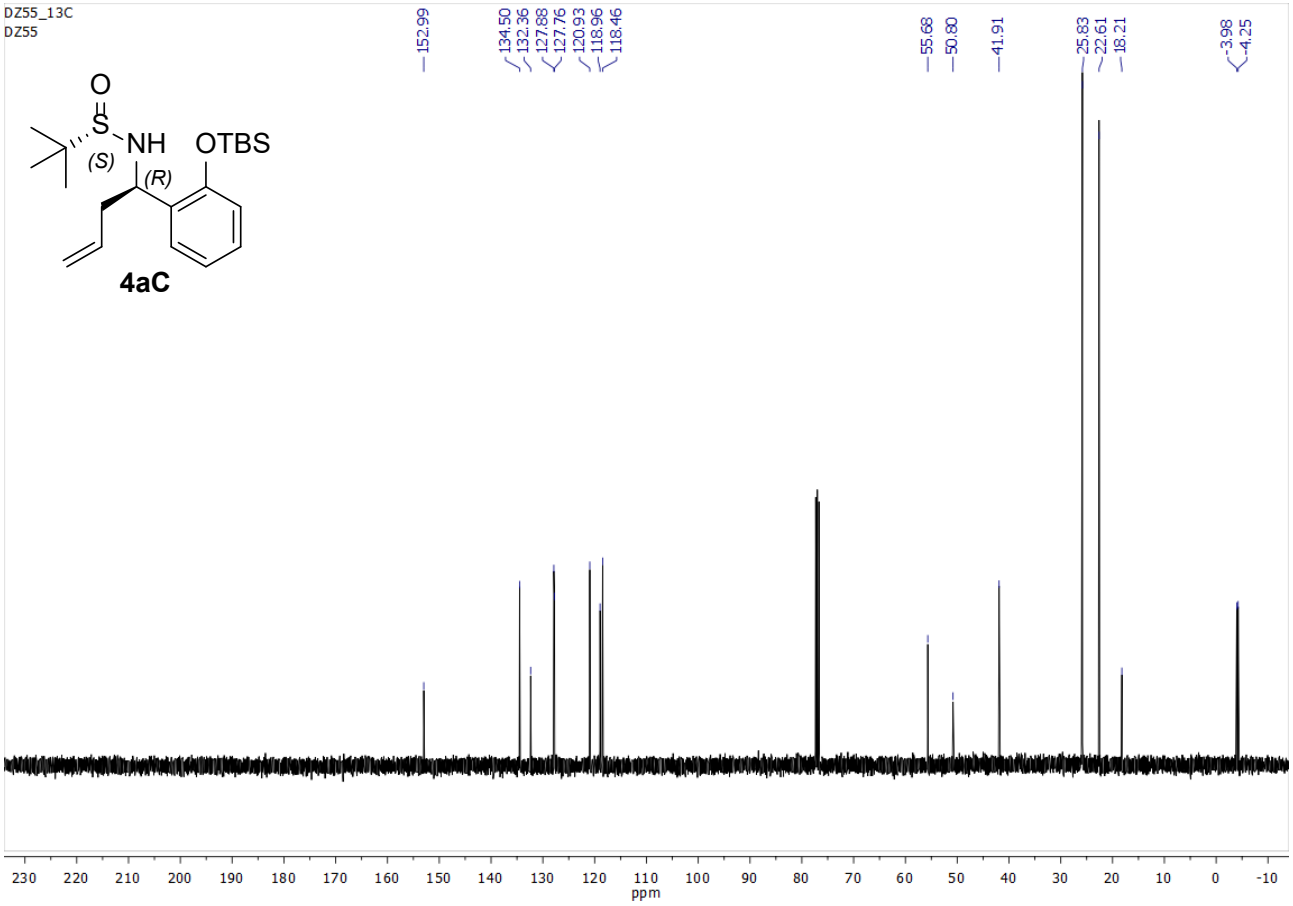
56.60
55.81
25.77
22.65
18.19
-4.13
-4.15
O
S
NH
OTBS
(S)
Ph
4aB
ppm


DZ55_13C_H
DZ55
O
S
NH
OTBS
(S)
(R)
4aC
0.98
1.02
0.98
0.96
0.98
2.01
1.00
0.97
1.02
1.02
9.33
9.39
6.10
ppm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O
S
NH
OTBS
(S)
(R)
4aC
152.99
134.50
132.36
127.88
127.76
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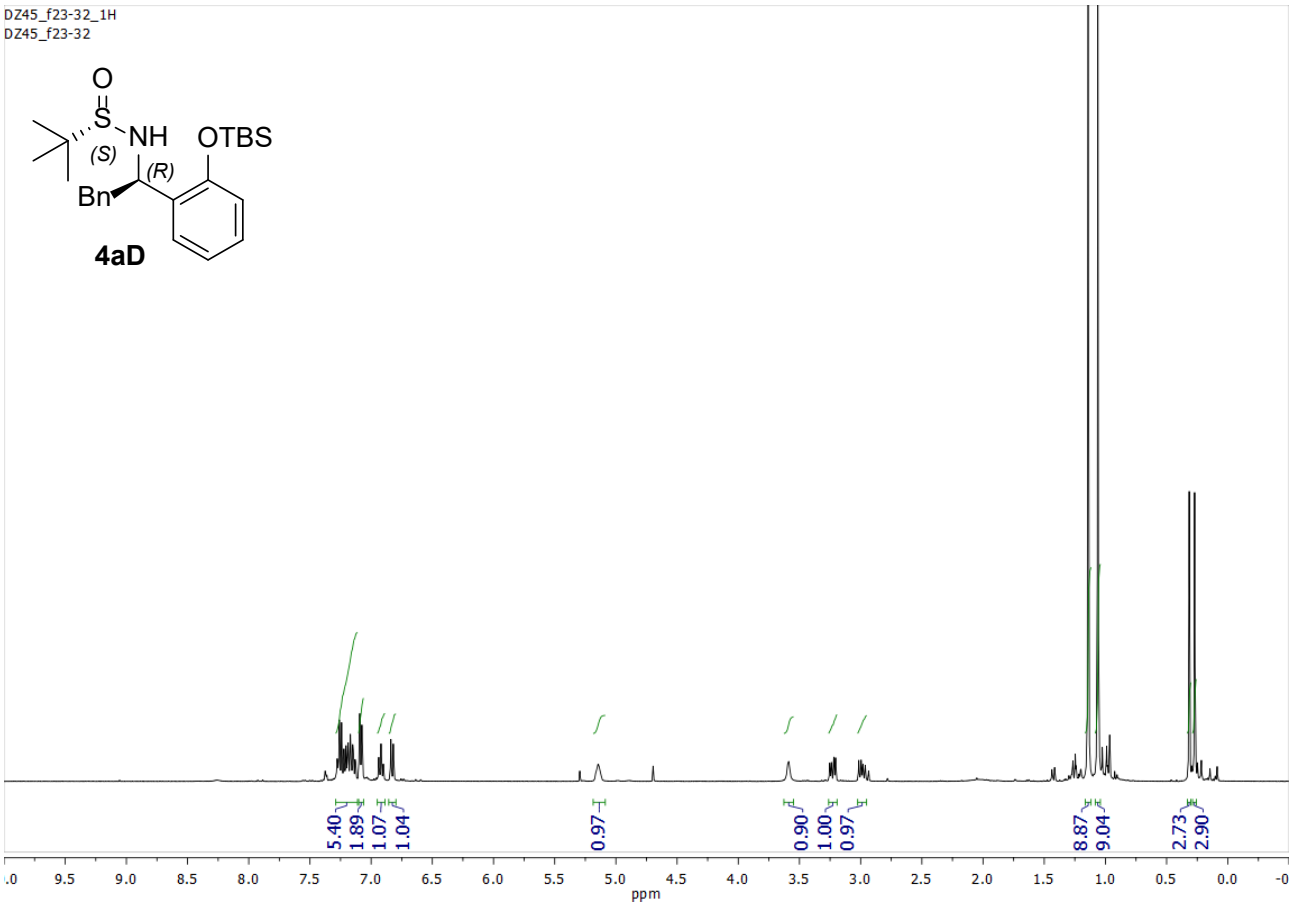
118.96
118.46
55.68
50.80
41.91
25.83
22.61
18.21
-3.98
-4.25
ppm


DZ45_f23-32_1H
DZ45_f23-32
O
S
NH
OTBS
(S)
(R)
Bn
4aD
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1.89
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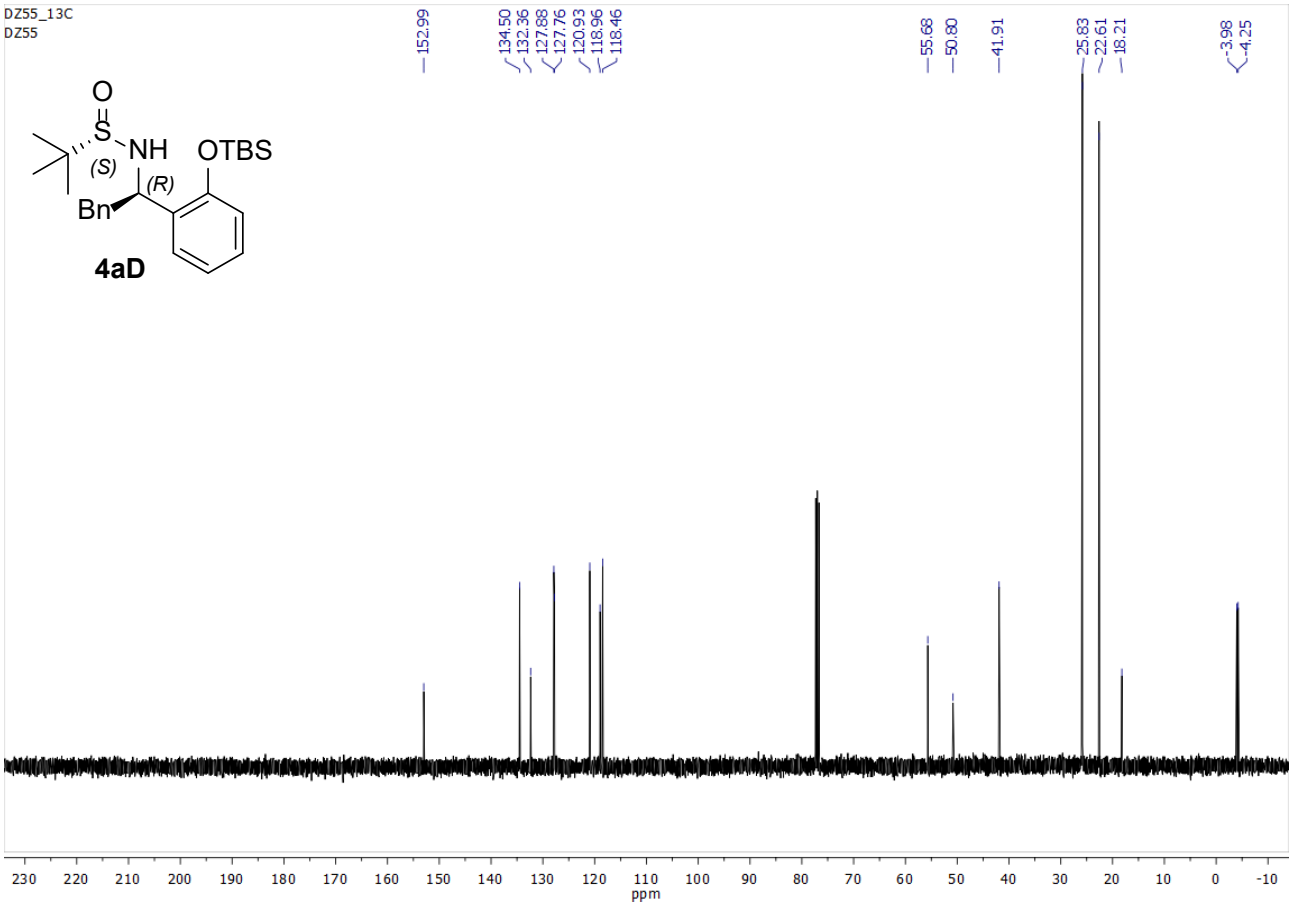
1.04
0.97
0.90
1.00
0.97
8.87
9.04
2.73
2.90
ppm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O
S
NH
OTBS
(S)
(R)
Bn
4aD
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134.50
132.36
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25.83
22.61
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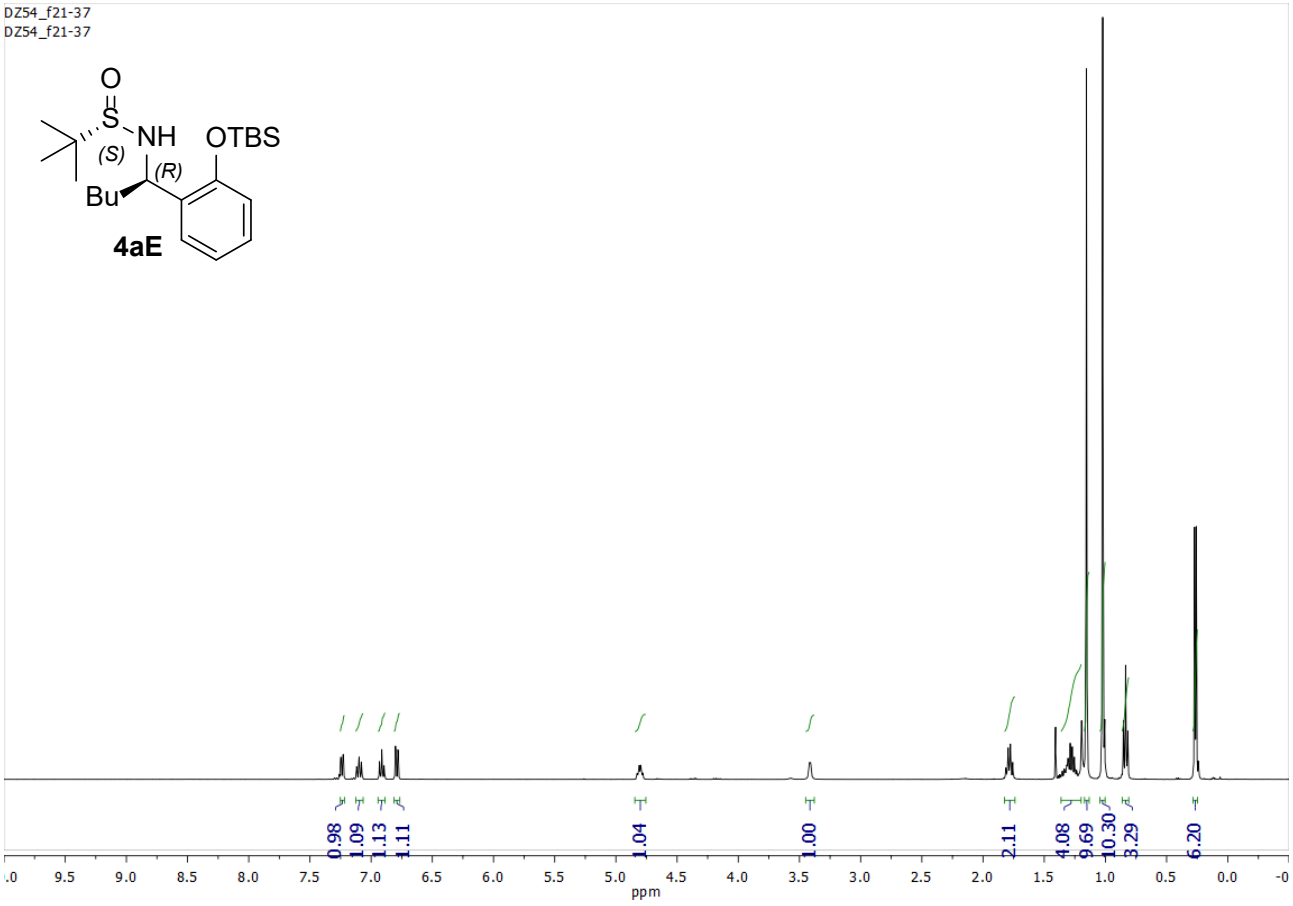
ppm


DZ54_f21-37
DZ54_f21-37
O
S
NH
OTBS
(S)
(R)
Bu
4aE
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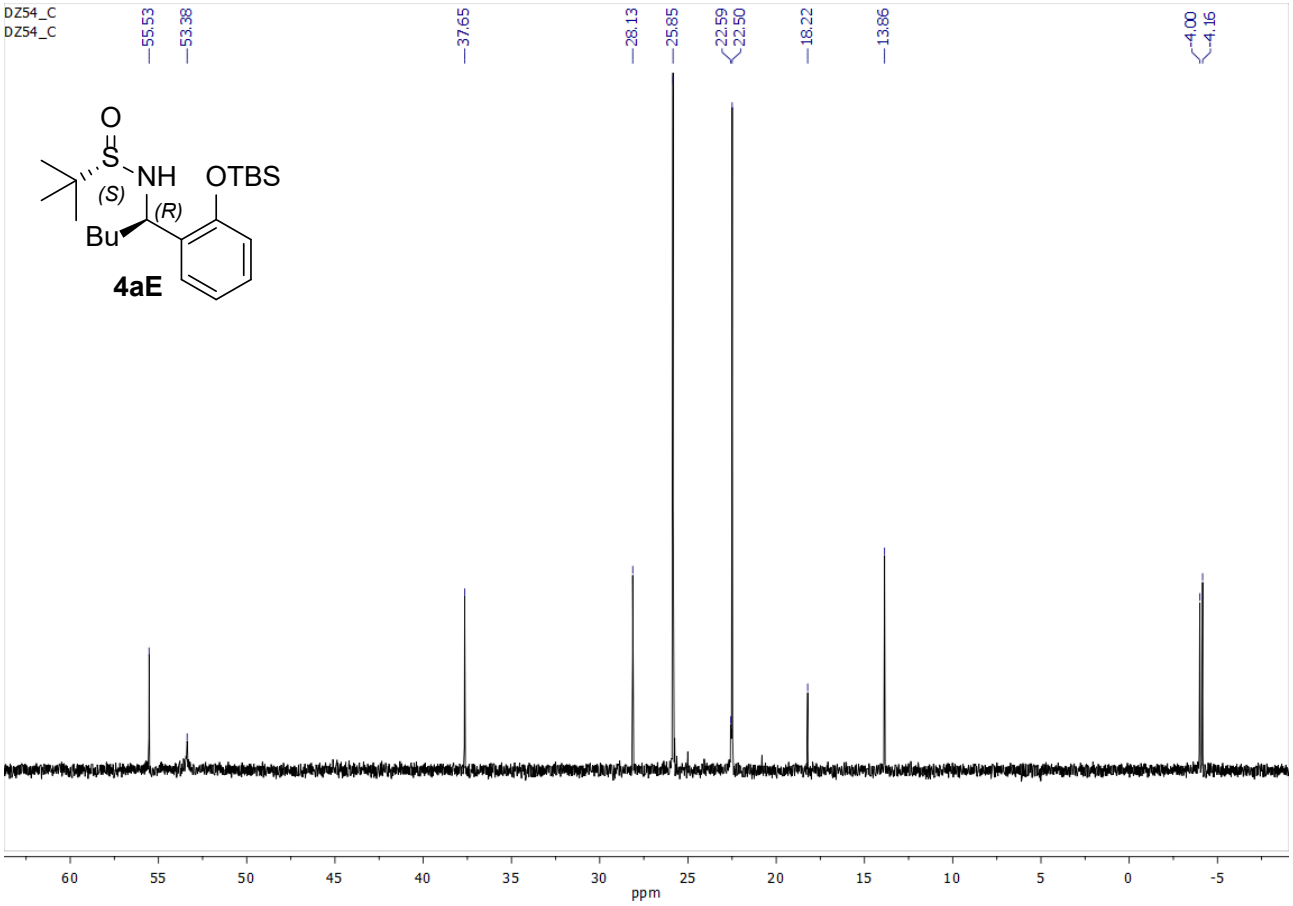
1.13
1.11
1.04
1.00
2.11
4.08
9.69
10.30
3.29
6.20
ppm


DZ54_C
DZ54_C
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53.38
37.65
28.13
25.85
22.59
22.50
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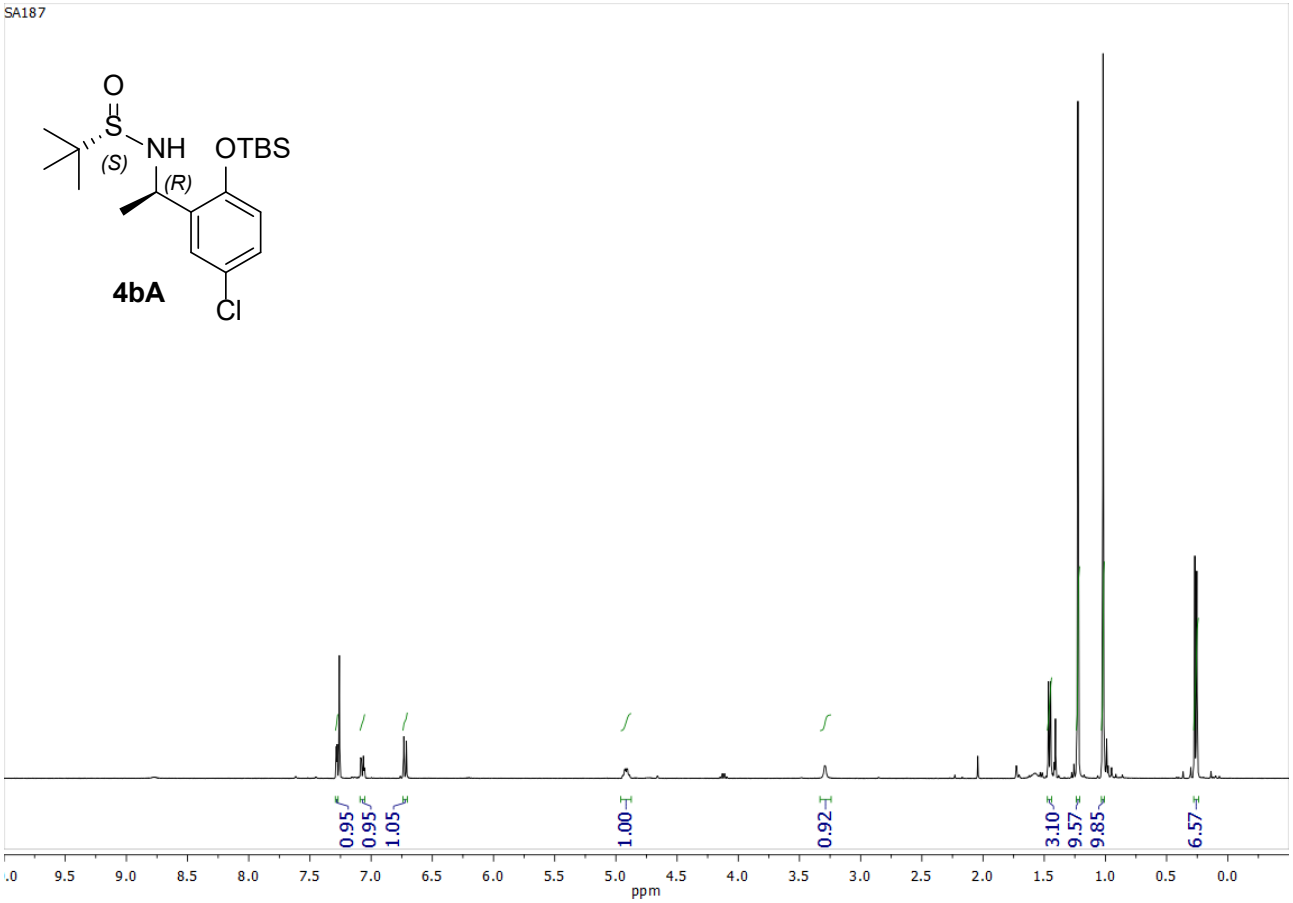
13.86
4.00
-4.16
O
S
NH
OTBS
(S)
(R)
Bu
4aE
ppm


SA187
O
S
NH
OTBS
(S)
(R)
4bA
Cl
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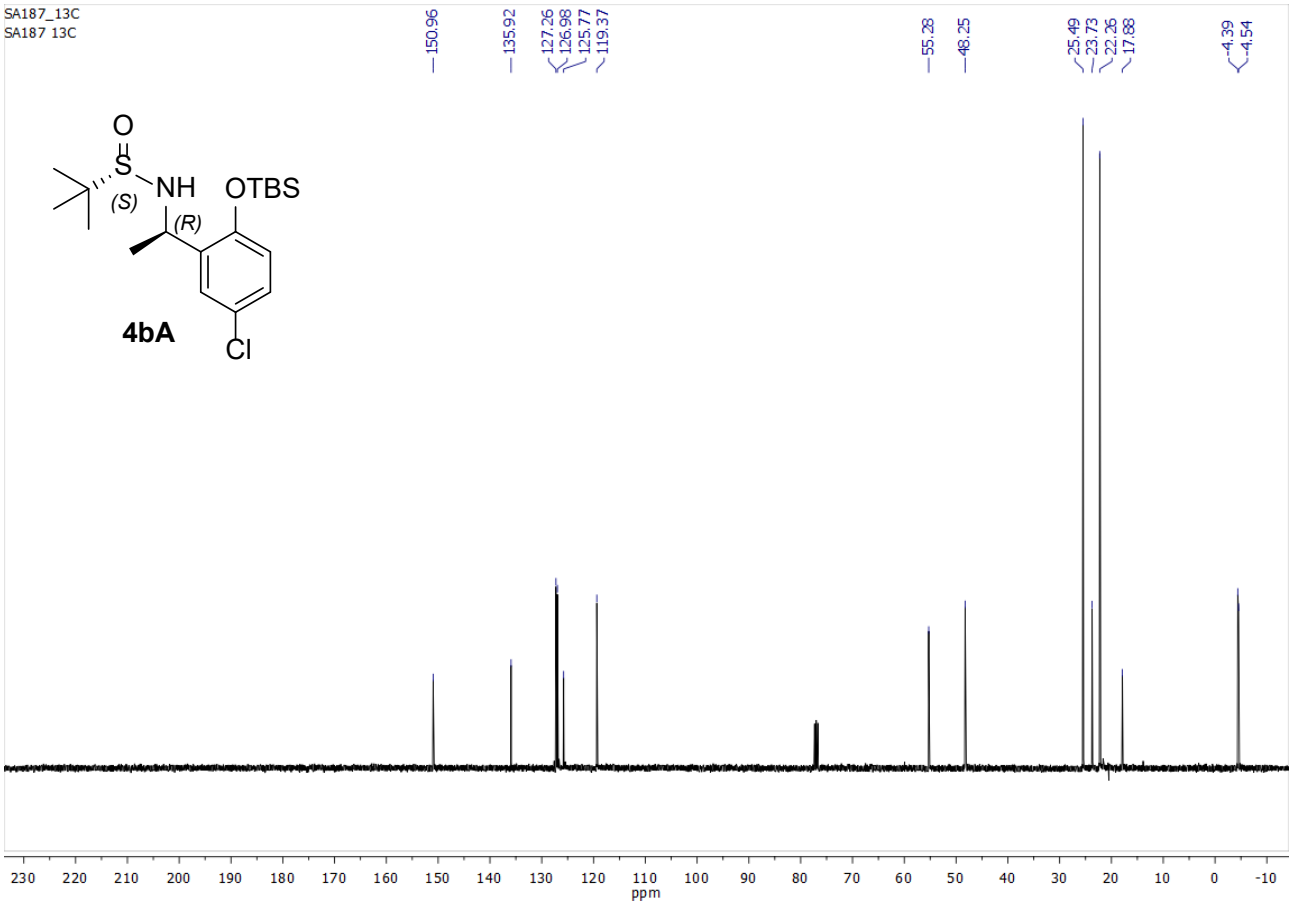
0.95
1.05
1.00
0.92
3.10
9.57
9.85
6.57
ppm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SA187 13C
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127.26
126.98
125.77
119.37
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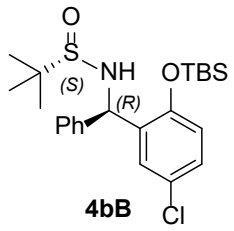
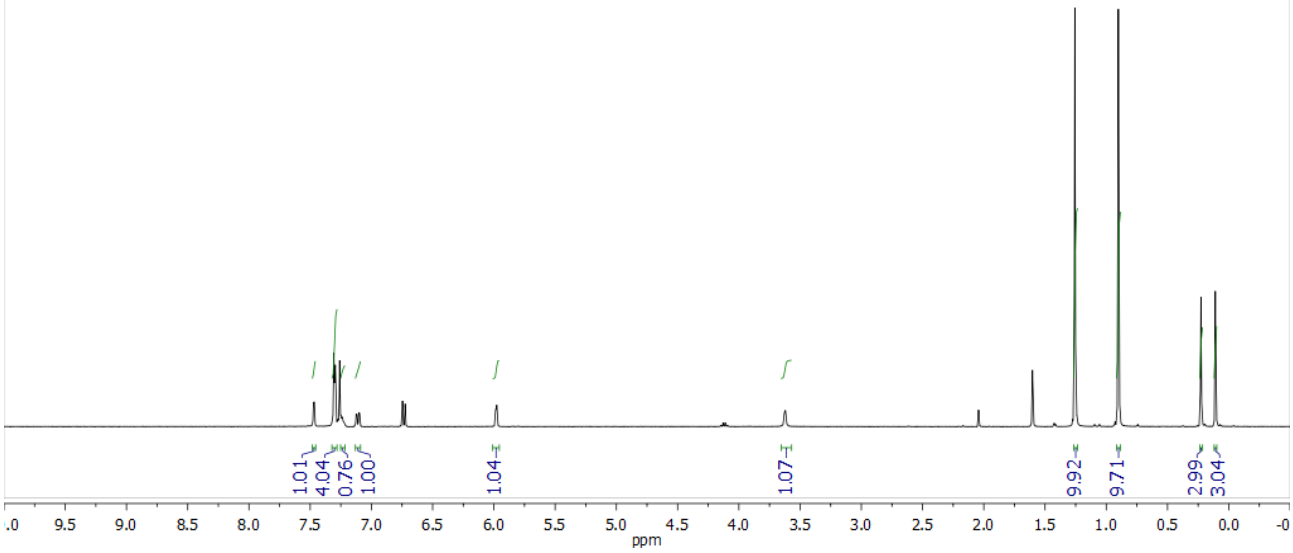
48.25
25.49
23.73
22.26
17.88
-4.39
-4.54
O
S
NH
OTBS
(S)
(R)
4bA
Cl
ppm

SA219
STANDARD FLUORINE PARAMETERS



4bB



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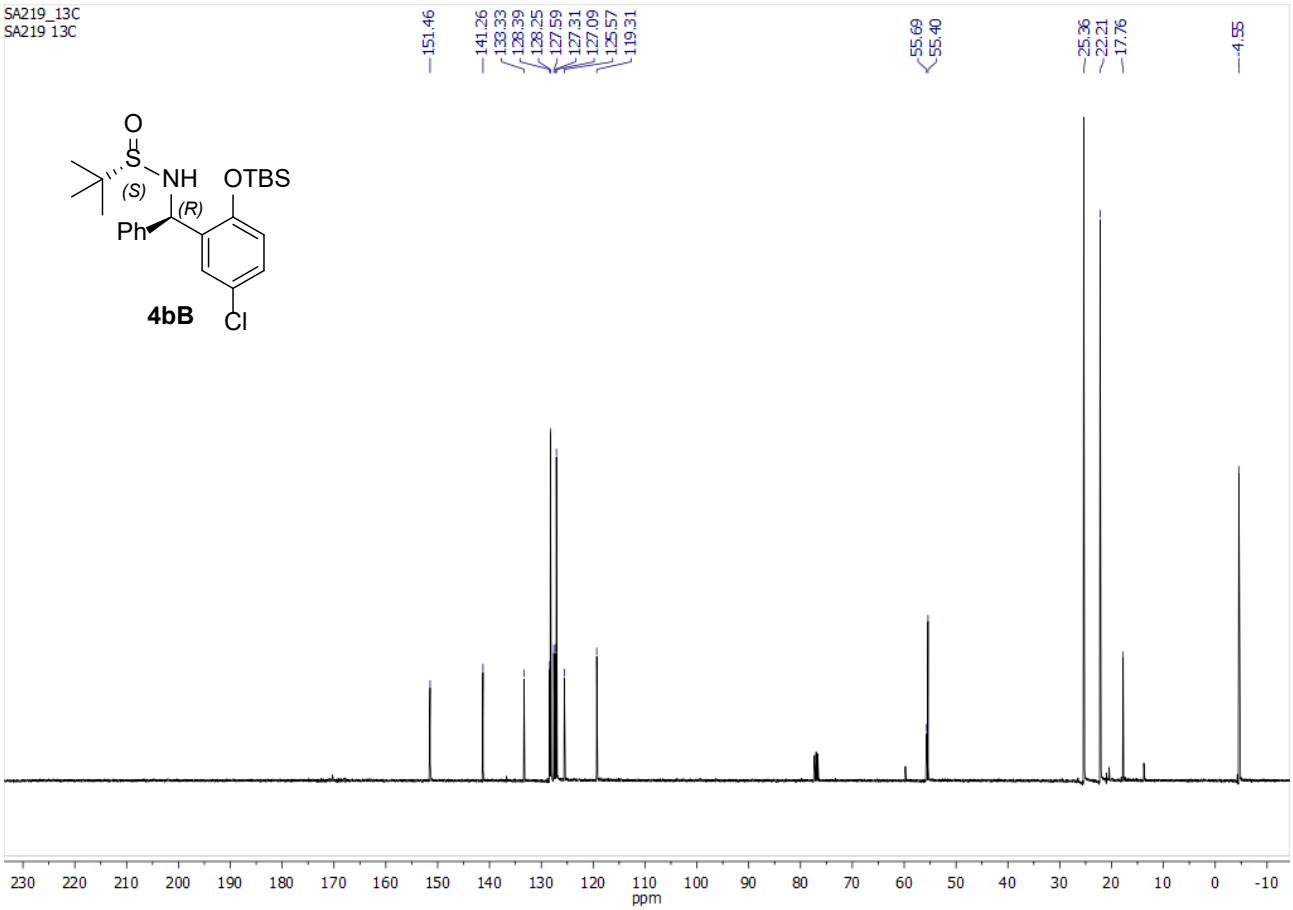
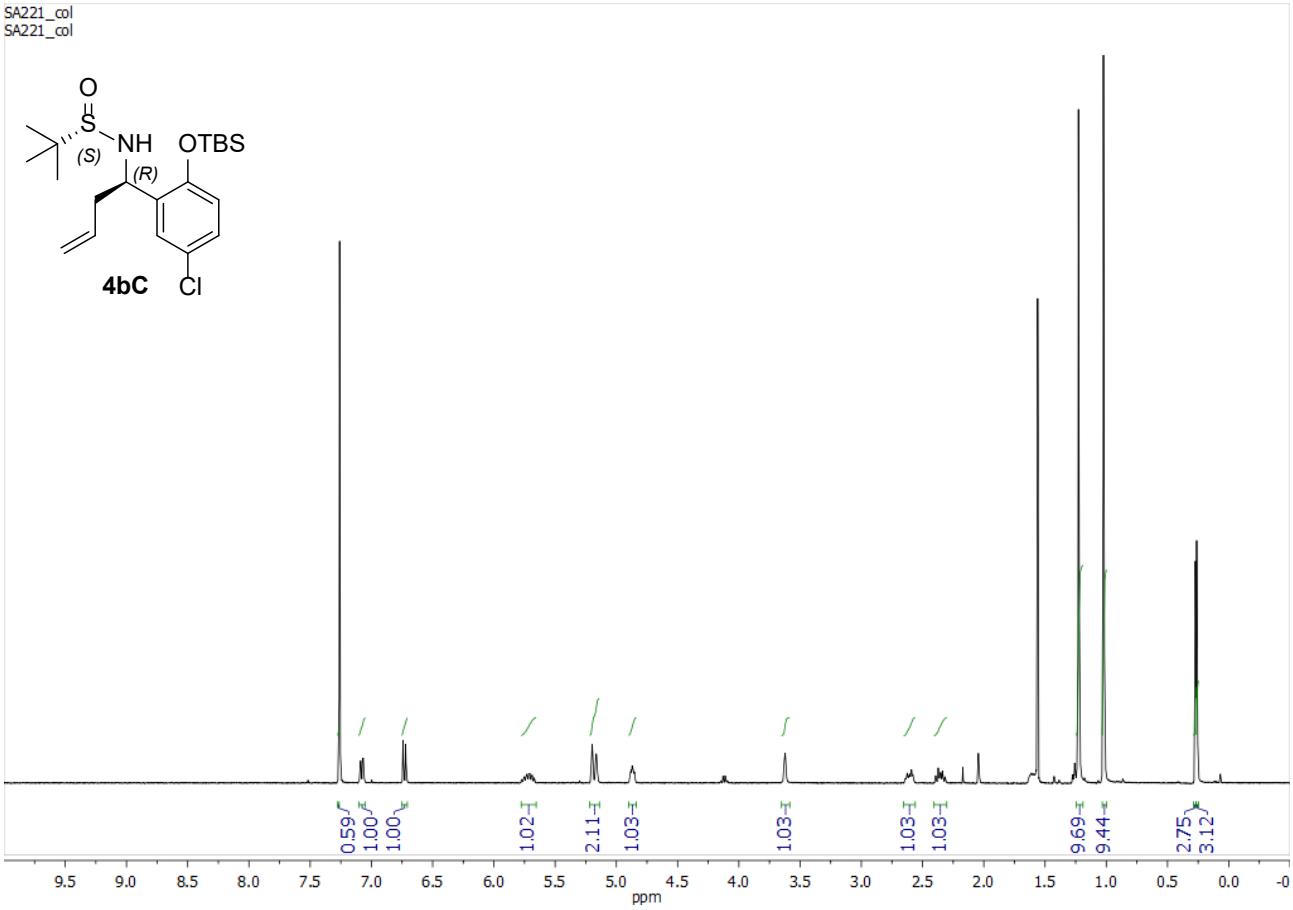
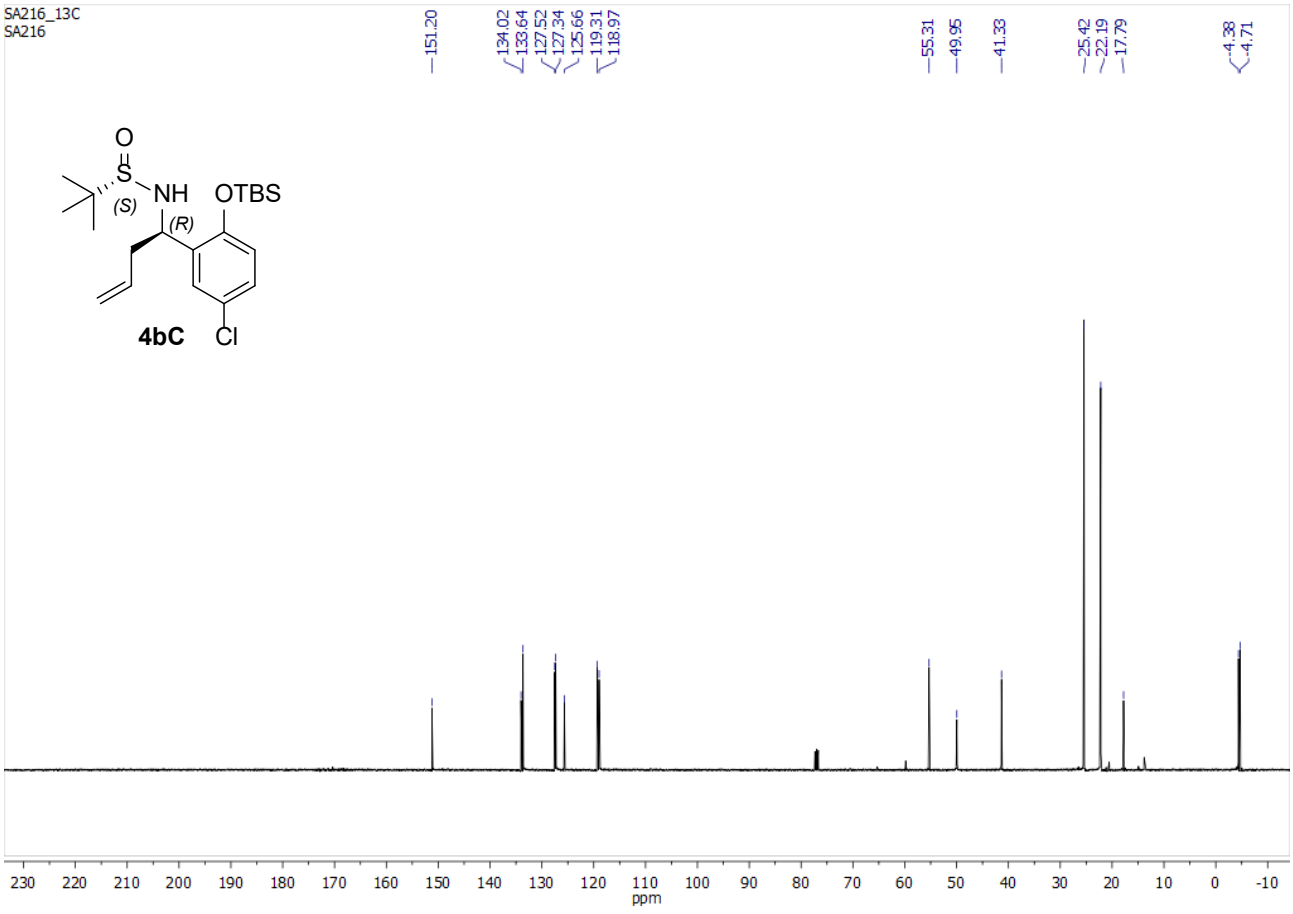
SA219 13C



4bB


SA221_col
SA221_col
O
S
NH
OTBS
(S)
(R)
4bC
Cl
0.59
1.00
1.00
1.02
2.11
1.03
1.03
1.03
1.03
9.69
9.44
2.75
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm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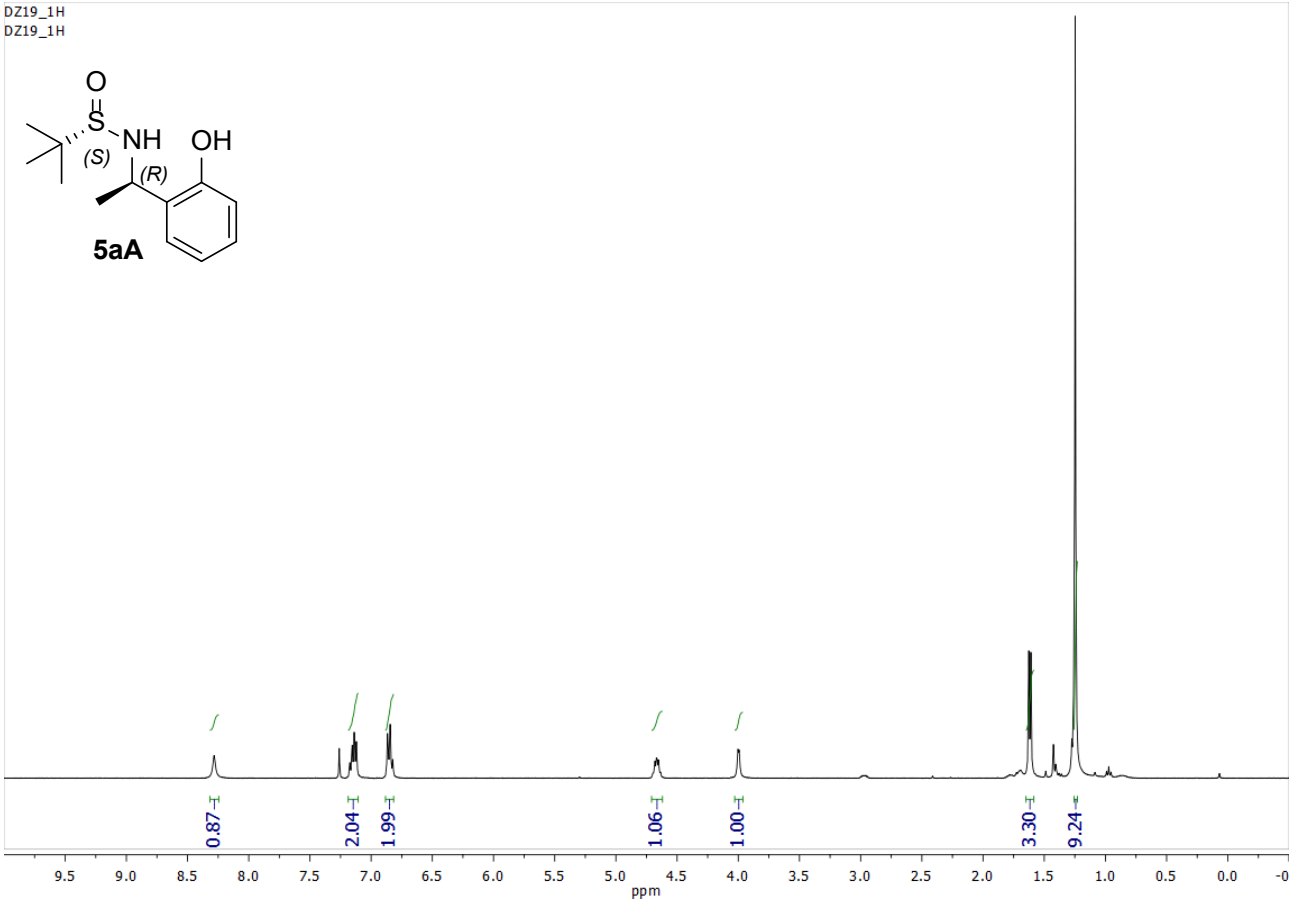
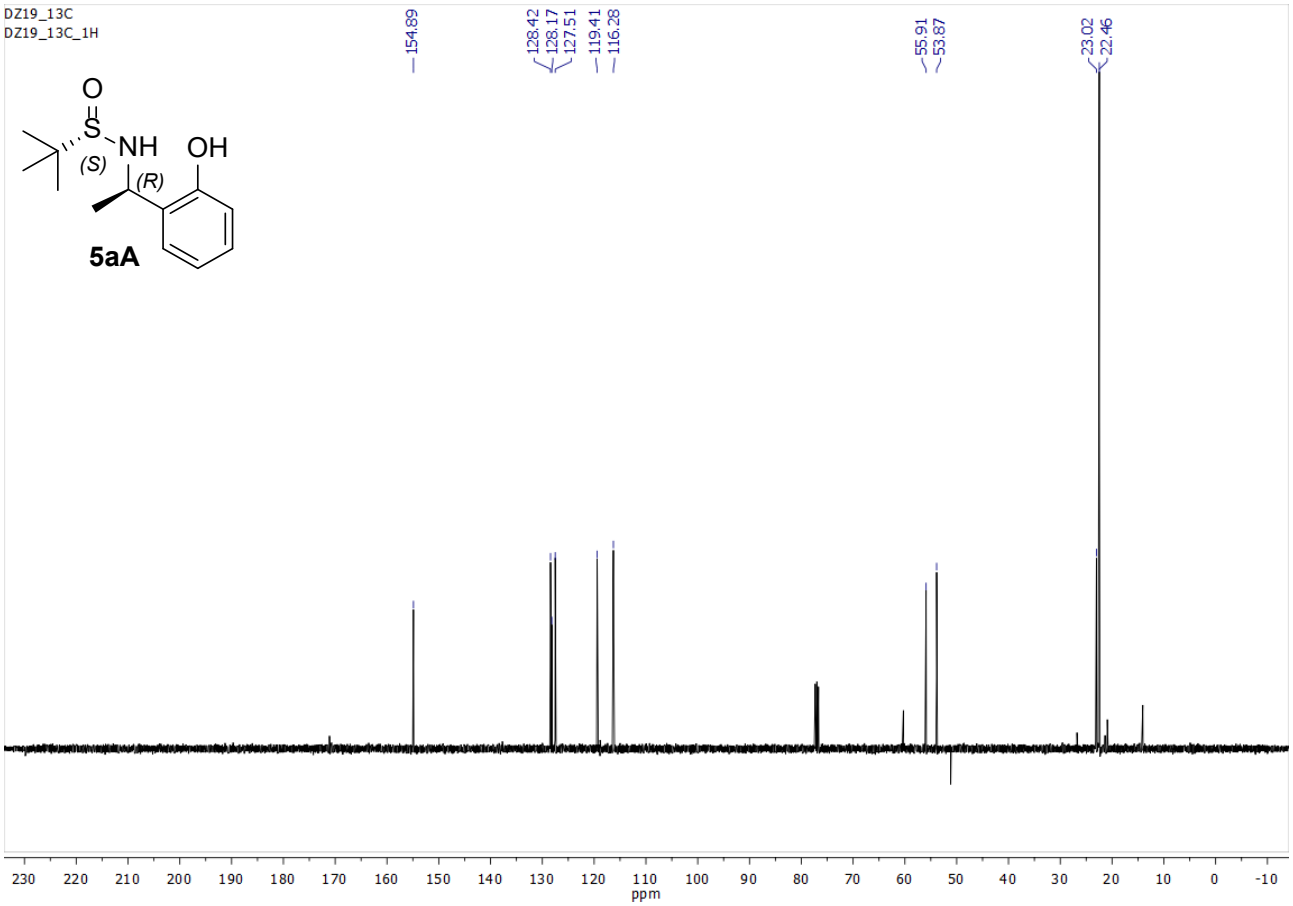
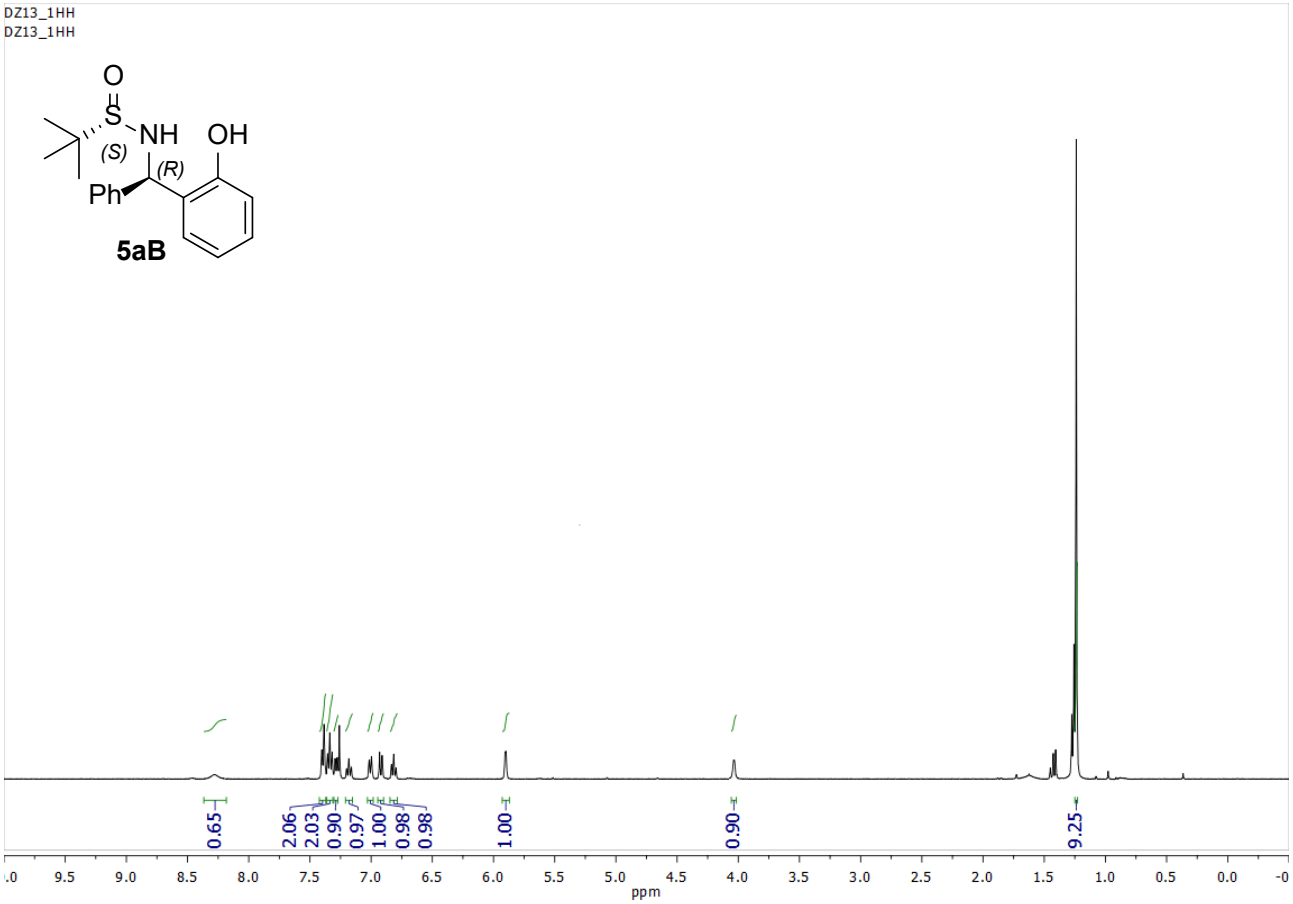
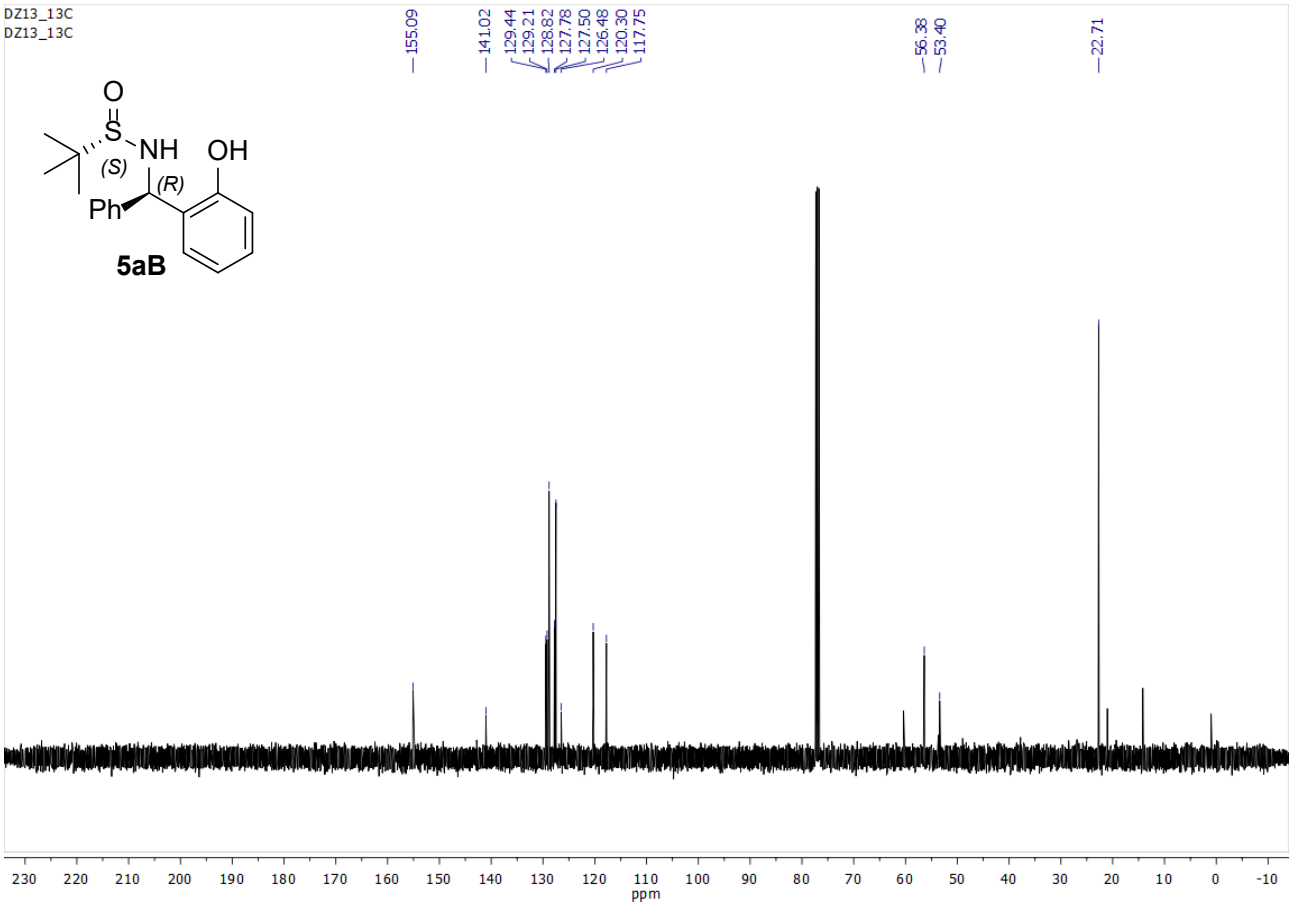
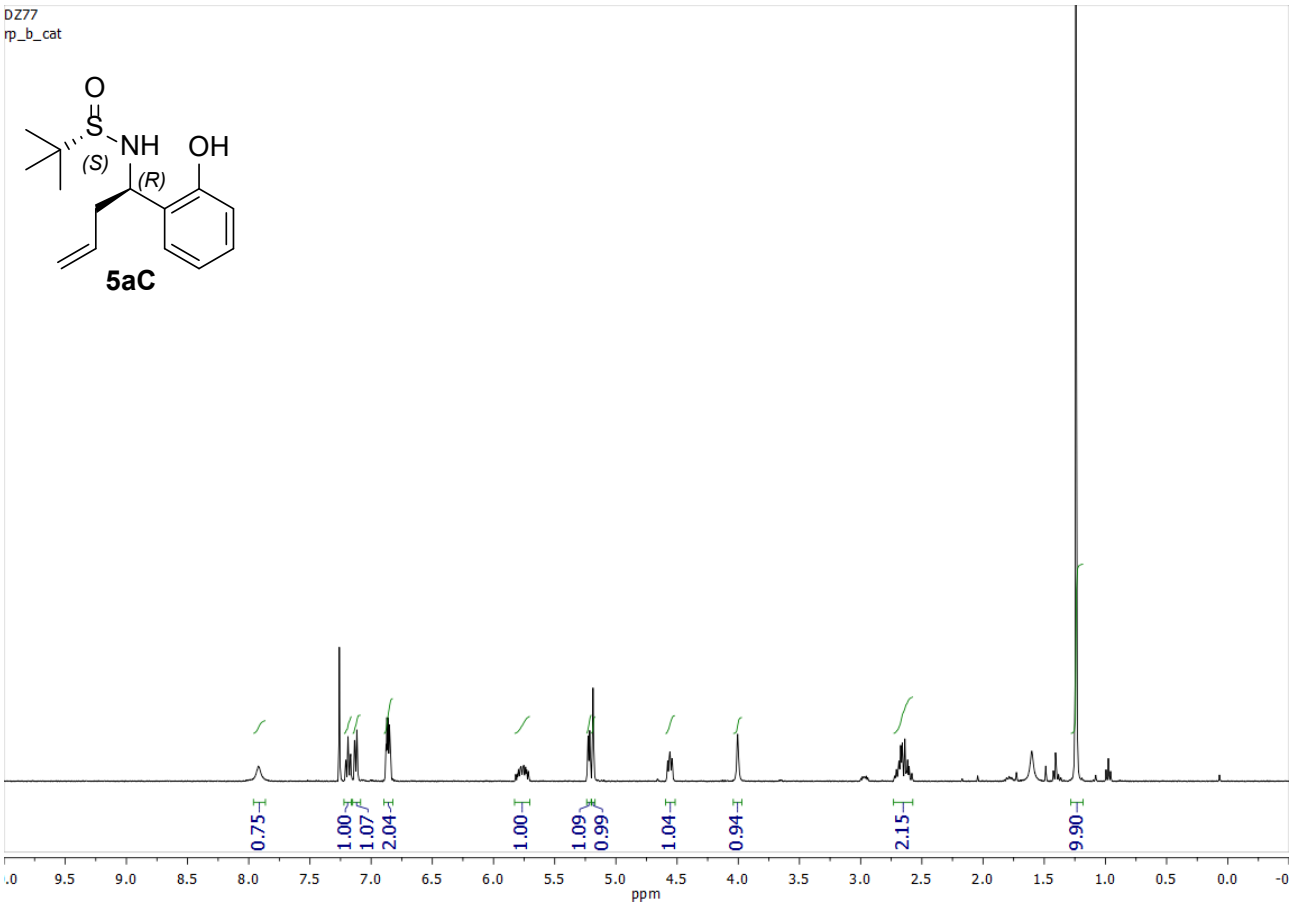
SA216
151.20
134.02
133.64
127.52
127.34
125.66
119.31
118.97
55.31
49.95
41.33
25.42
22.19
17.79
-4.38
-4.71
O
S
NH
OTBS
(S)
(R)
4bC
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

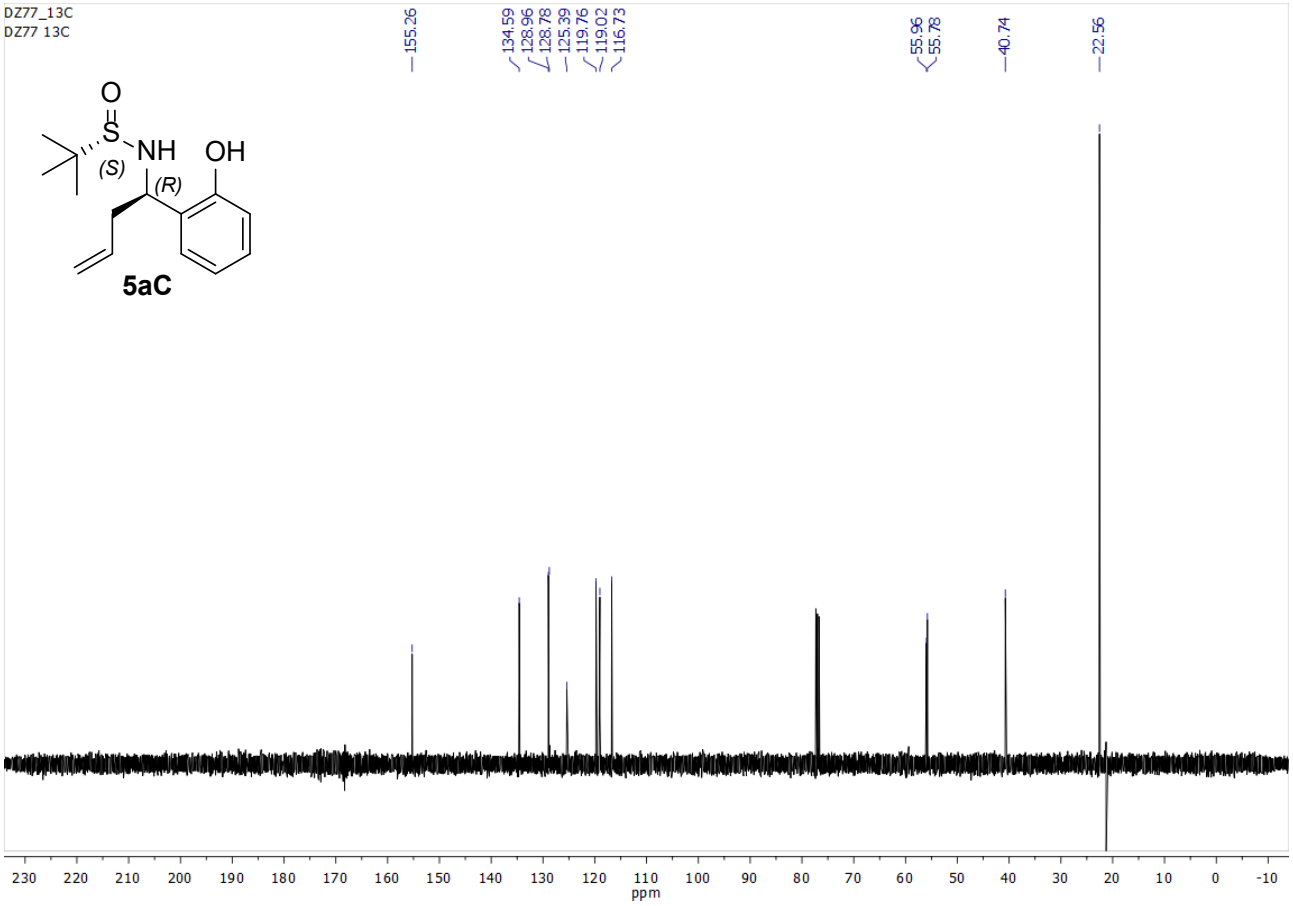

DZ19_1H
DZ19_1H
O
S
NH
OH
(S)
(R)
5aA
0.87
2.04
1.99
1.06
1.00
3.30
9.24
ppm

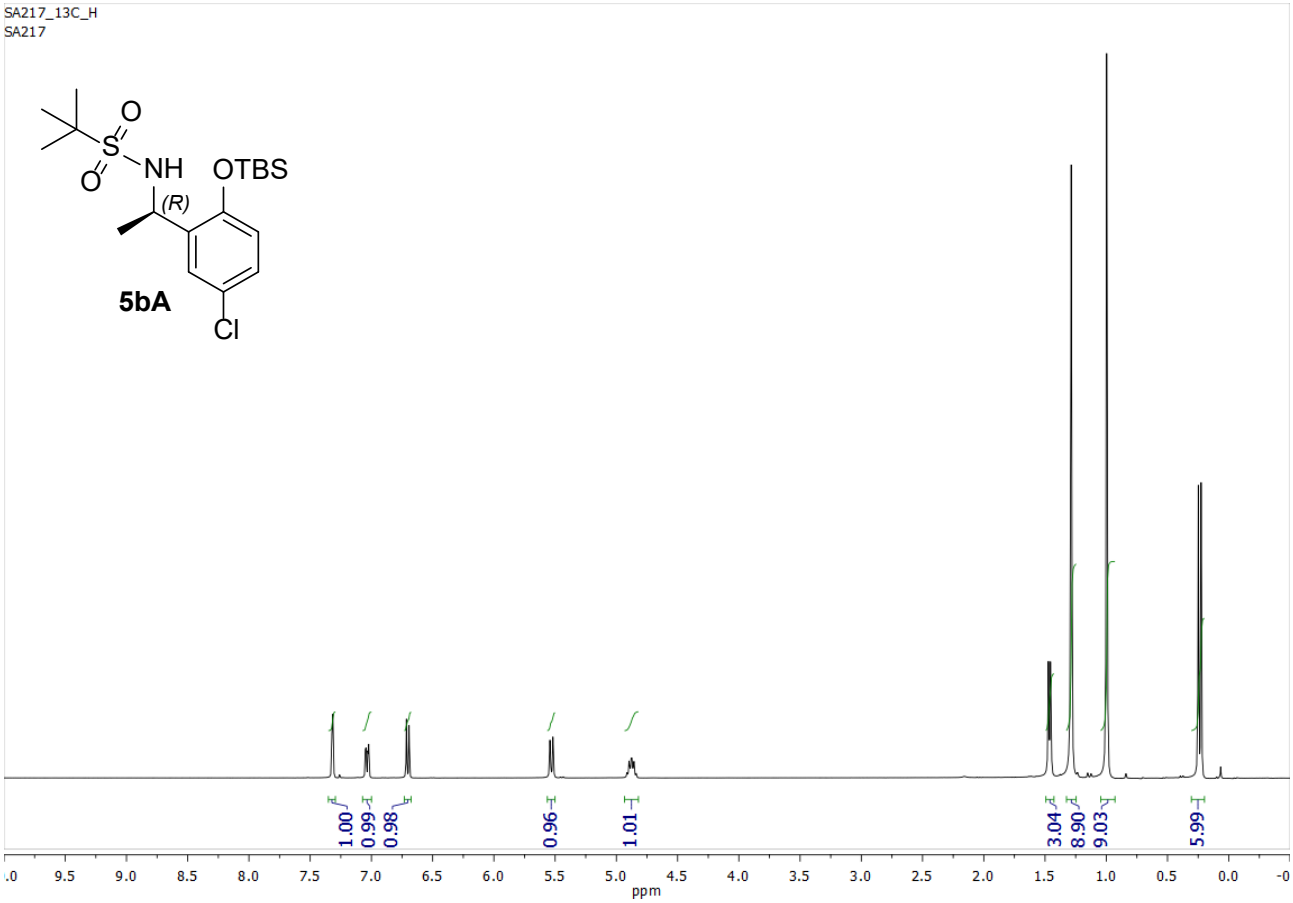

DZ19_13C
DZ19_13C_1H
154.89
128.42
128.17
127.51
119.41
116.28
55.91
53.87
23.02
22.46
O
S
NH
OH
(S)
(R)
5aA
ppm

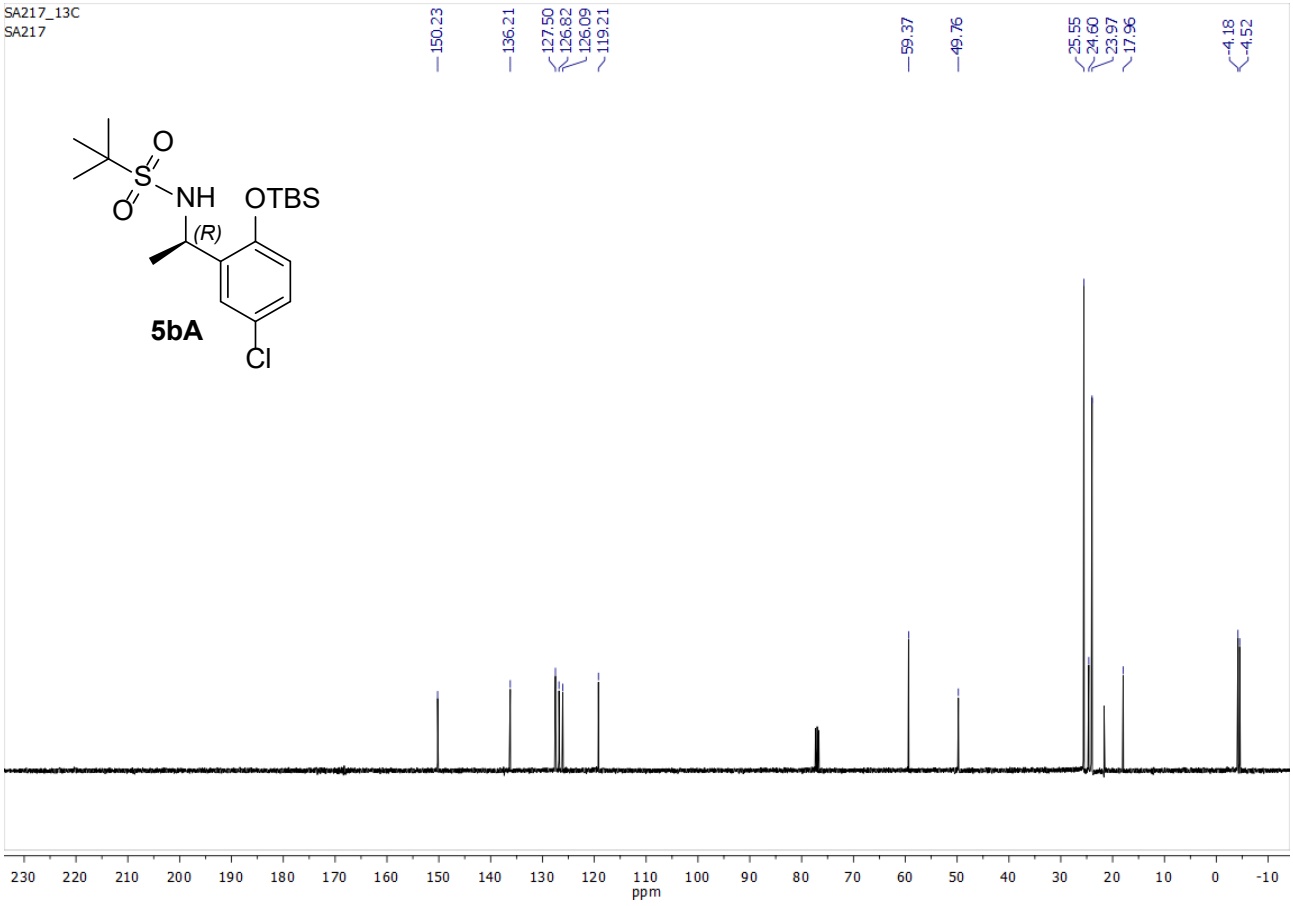

DZ13_1HH
DZ13_1HH
O
S
NH
OH
(S)
(R)
Ph
5aB
0.65
2.06
2.03
0.90
0.97
1.00
0.98
0.98
1.00
0.90
9.25
ppm

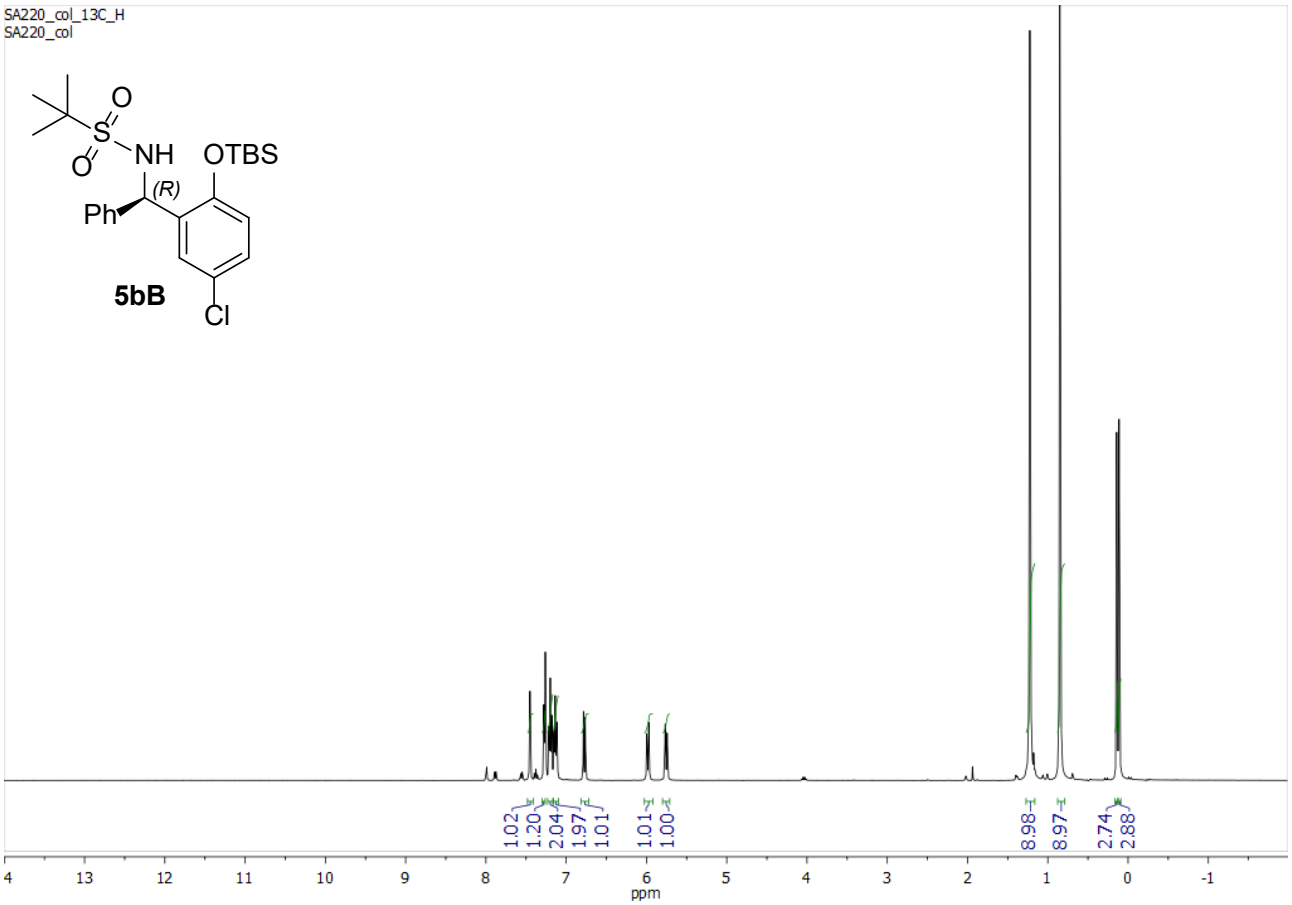

DZ13_13C
DZ13_13C
155.09
141.02
129.44
129.21
128.82
127.78
127.50
126.48
120.30
117.75
56.38
53.40
22.71
O
S
NH
OH
(S)
(R)
Ph
5aB
ppm

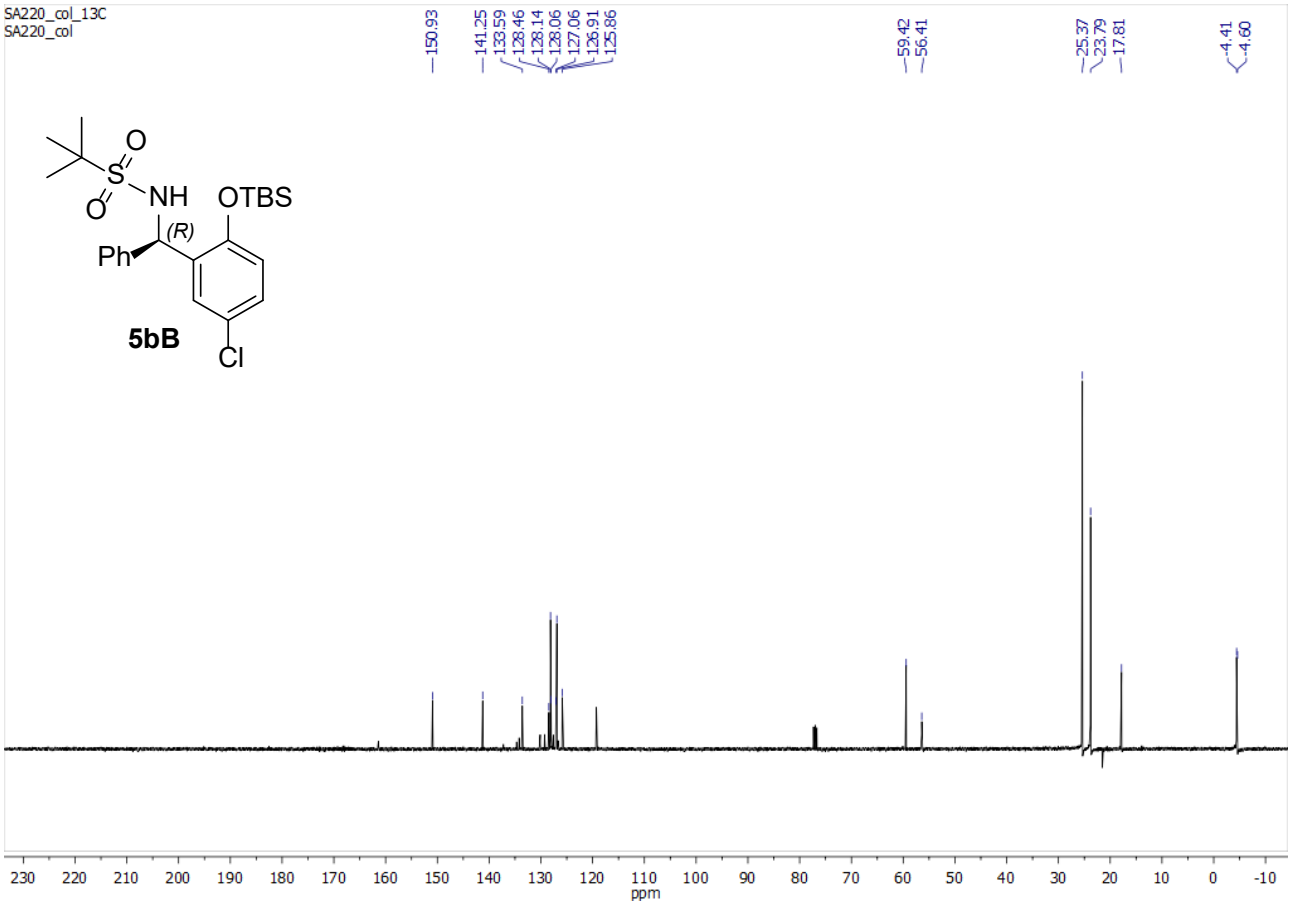

DZ77
rp_b_cat
O
S
NH
OH
(S)
(R)
5aC
0.75
1.00
1.07
2.04
1.00
1.09
0.99
1.04
0.94
2.15
9.90
ppm

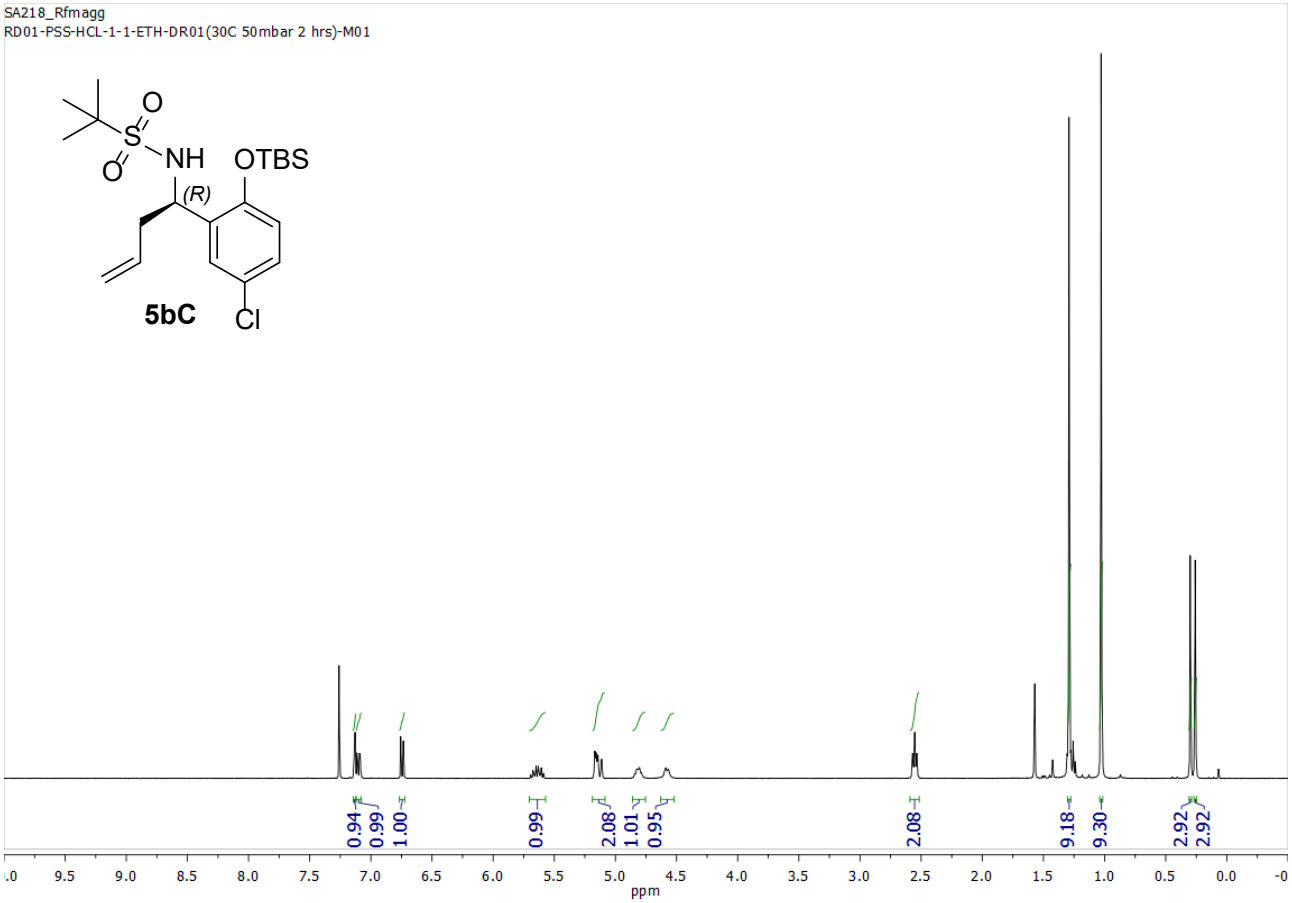

DZ77_13C
DZ77 13C
155.26
134.59
128.96
128.78
125.39
119.76
119.02
116.73
55.96
55.78
40.74
22.56
O
S
NH
OH
(S)
(R)
5aC
ppm

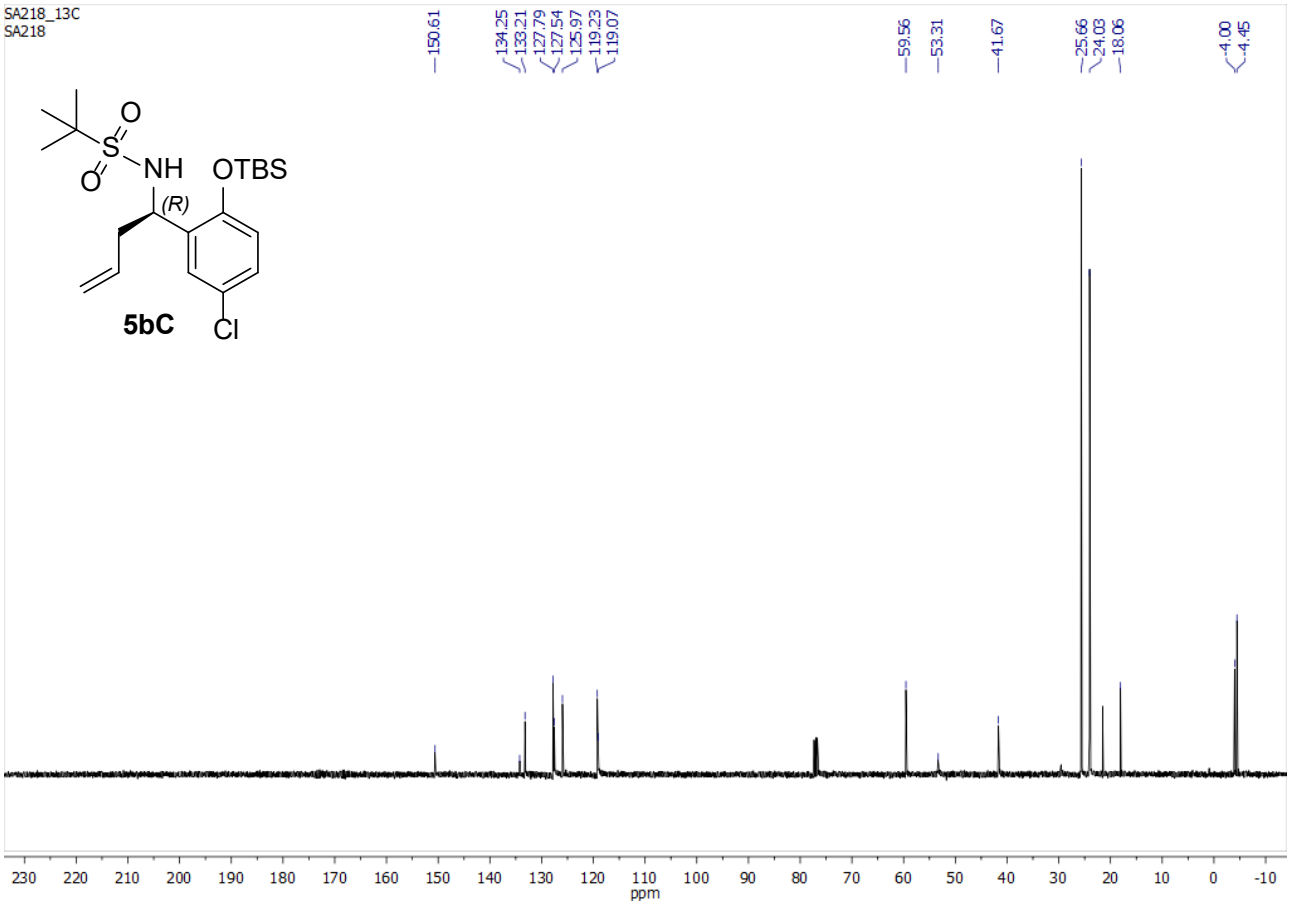

SA217_13C_H
SA217
O
S
O
NH
OTBS
(R)
5bA
Cl
1.00
0.99
0.98
0.96
1.01
3.04
8.90
9.03
5.99
ppm

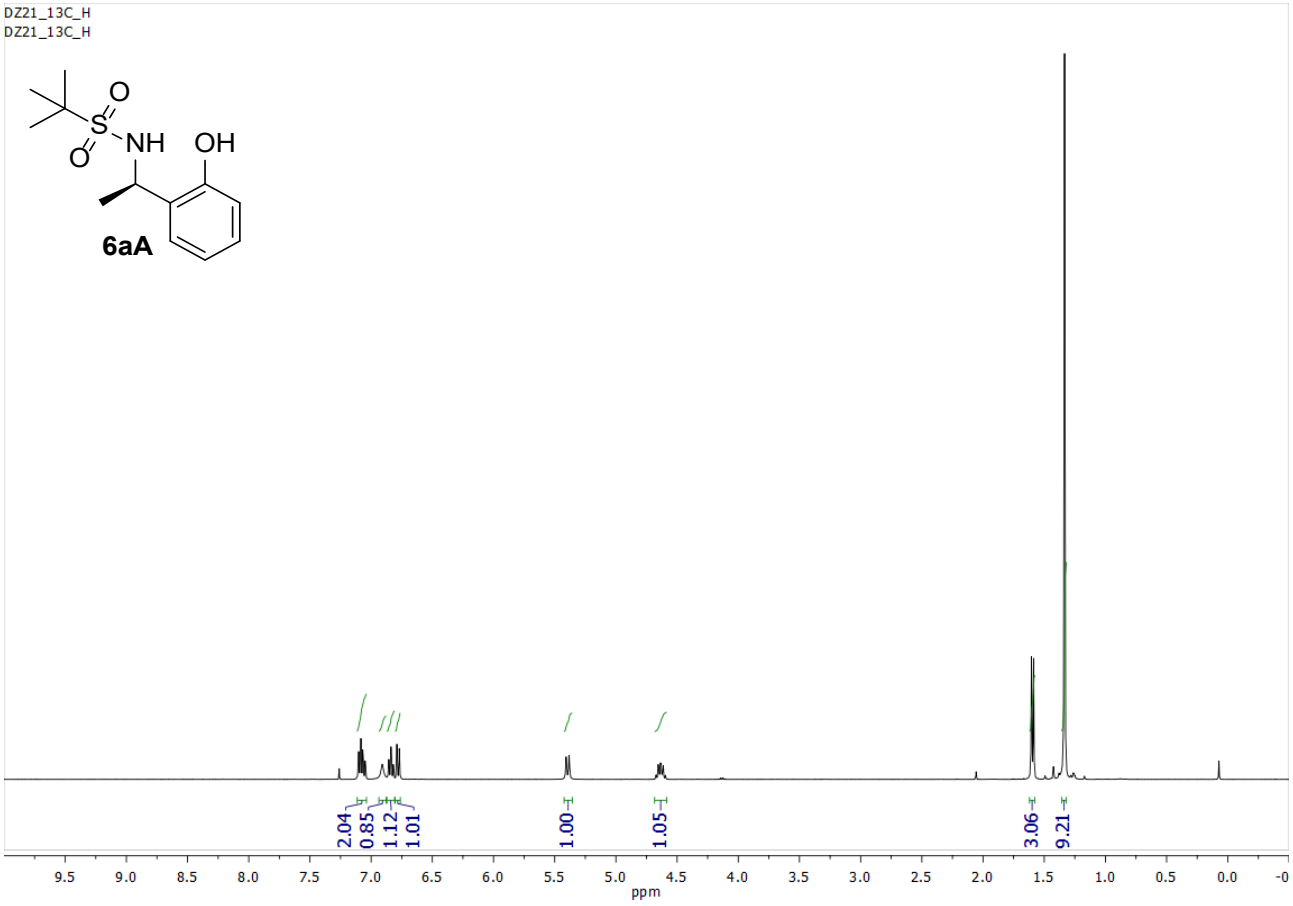

SA217_13C
SA217
150.23
136.21
127.50
126.82
126.09
119.21
59.37
49.76
25.55
24.60
23.97
17.96
-4.18
-4.52
O
S
O
NH
OTBS
(R)
5bA
Cl
ppm

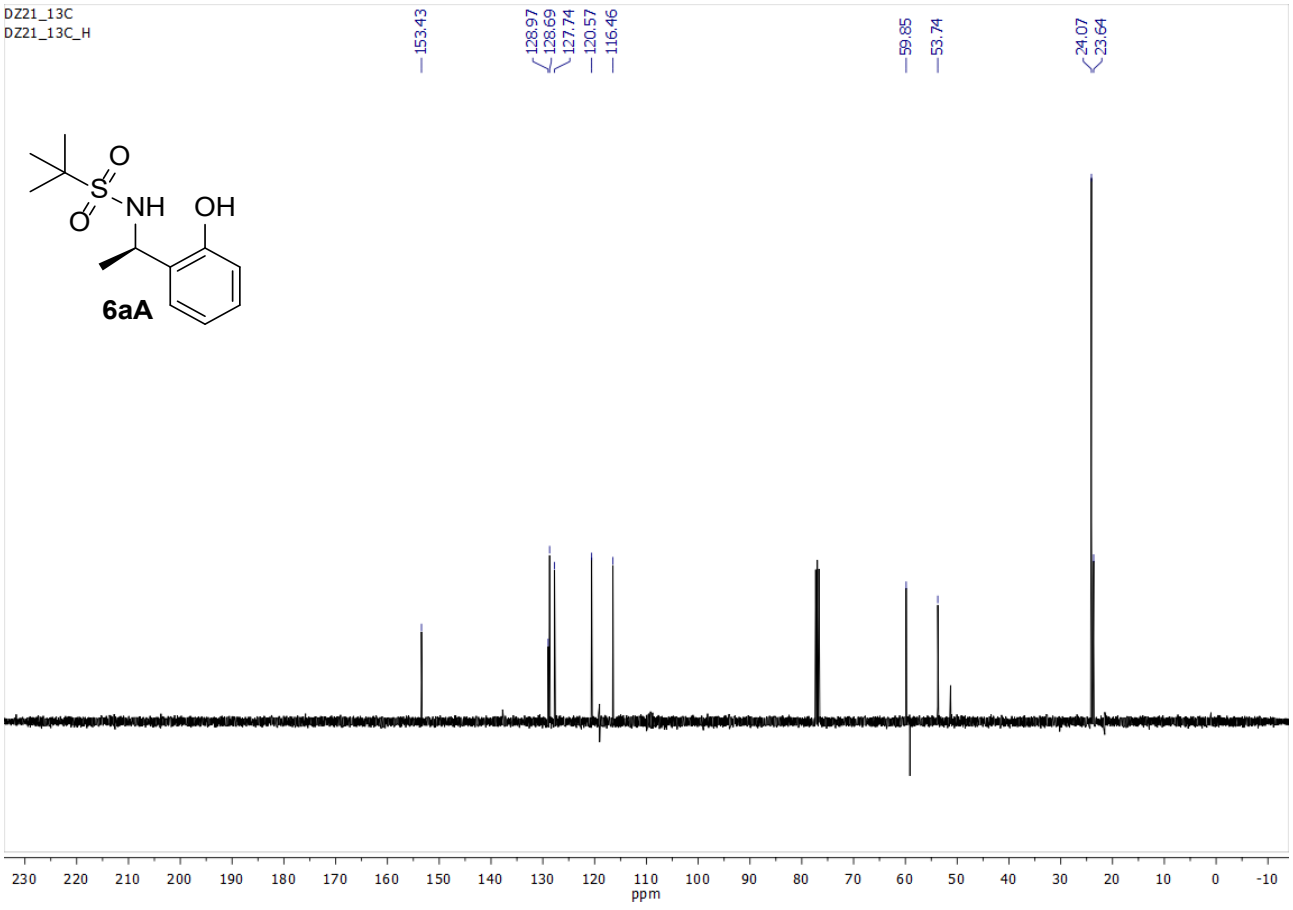

SA220_col_13C_H
SA220_col
O
S
O
NH
OTBS
(R)
Ph
5bB
Cl
1.02
1.20
2.04
1.97
1.01
1.01
1.00
8.98
8.97
2.74
2.88
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

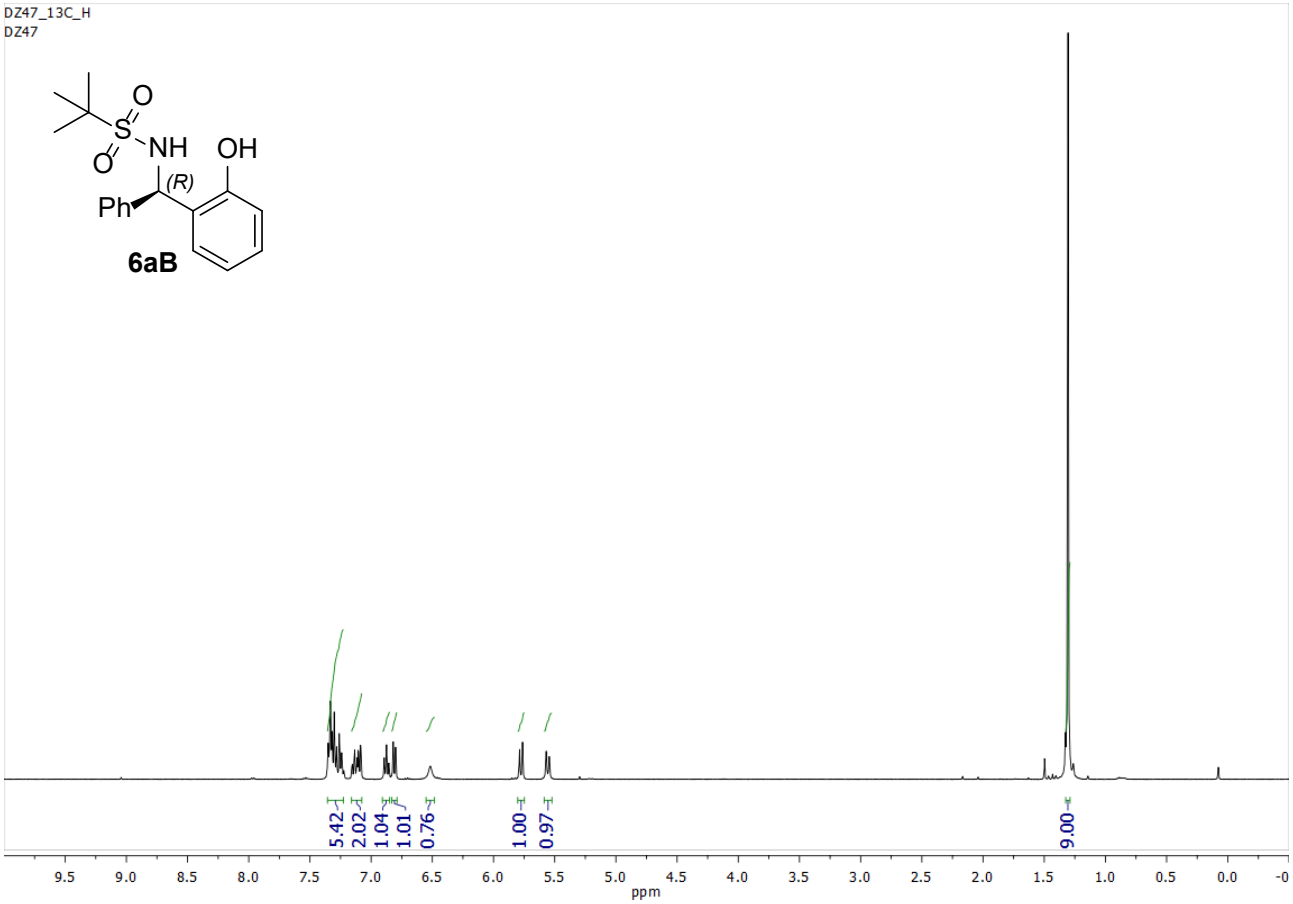

SA220_col_13C
SA220_col
150.93
141.25
133.59
128.46
128.14
128.06
127.06
126.91
125.86
59.42
56.41
25.37
23.79
17.81
-4.41
-4.60
O
S
O
NH
OTBS
(R)
Ph
5bB
Cl
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

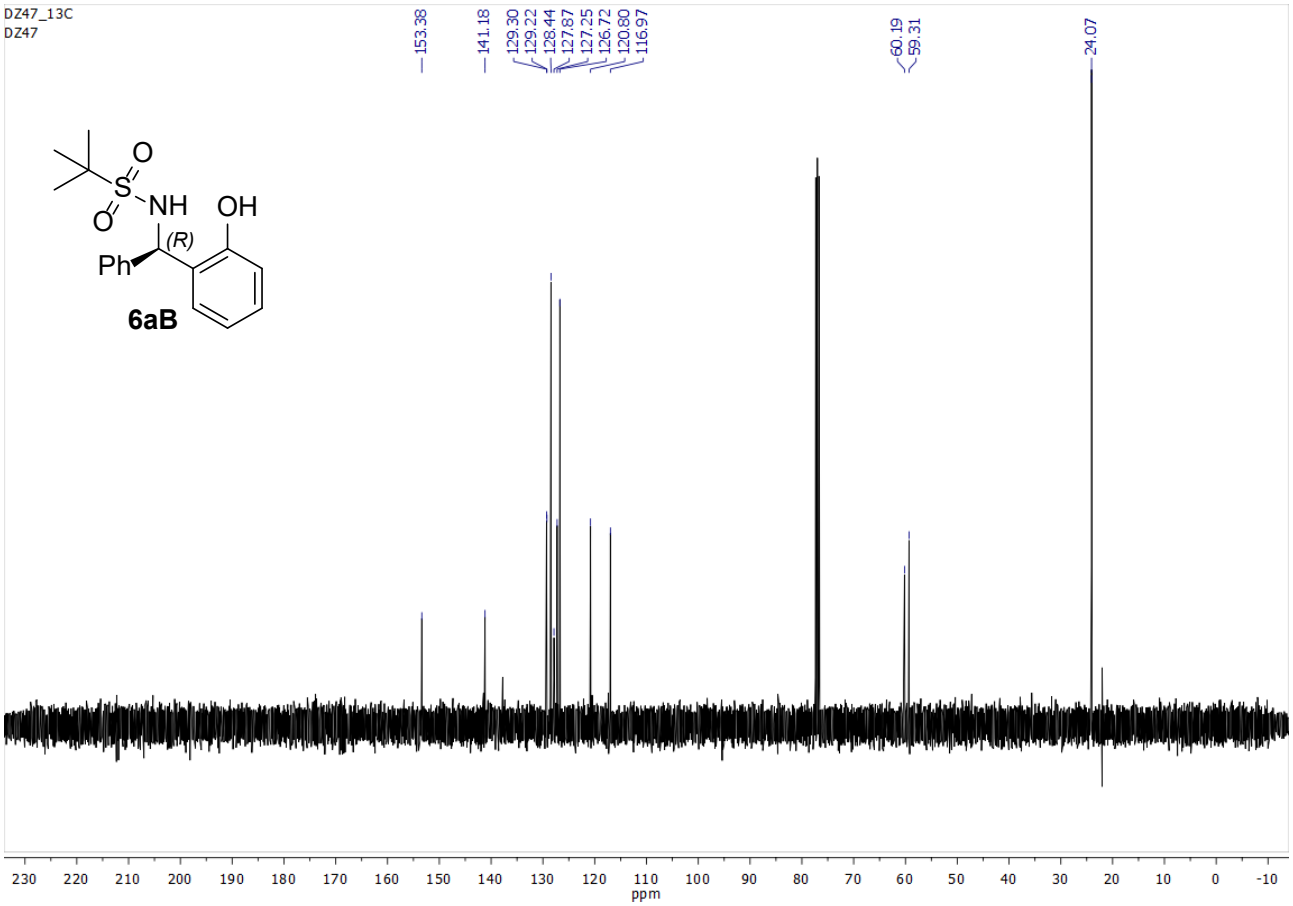

SA218_Rfmagg
RD01-PSS-HCL-1-1-ETH-DR01(30C 50mbar 2 hrs)-M01
O
S
O
NH
OTBS
(R)
5bC
Cl
0.94
0.99
1.00
0.99
2.08
1.01
0.95
2.08
9.18
9.30
2.92
2.92
ppm

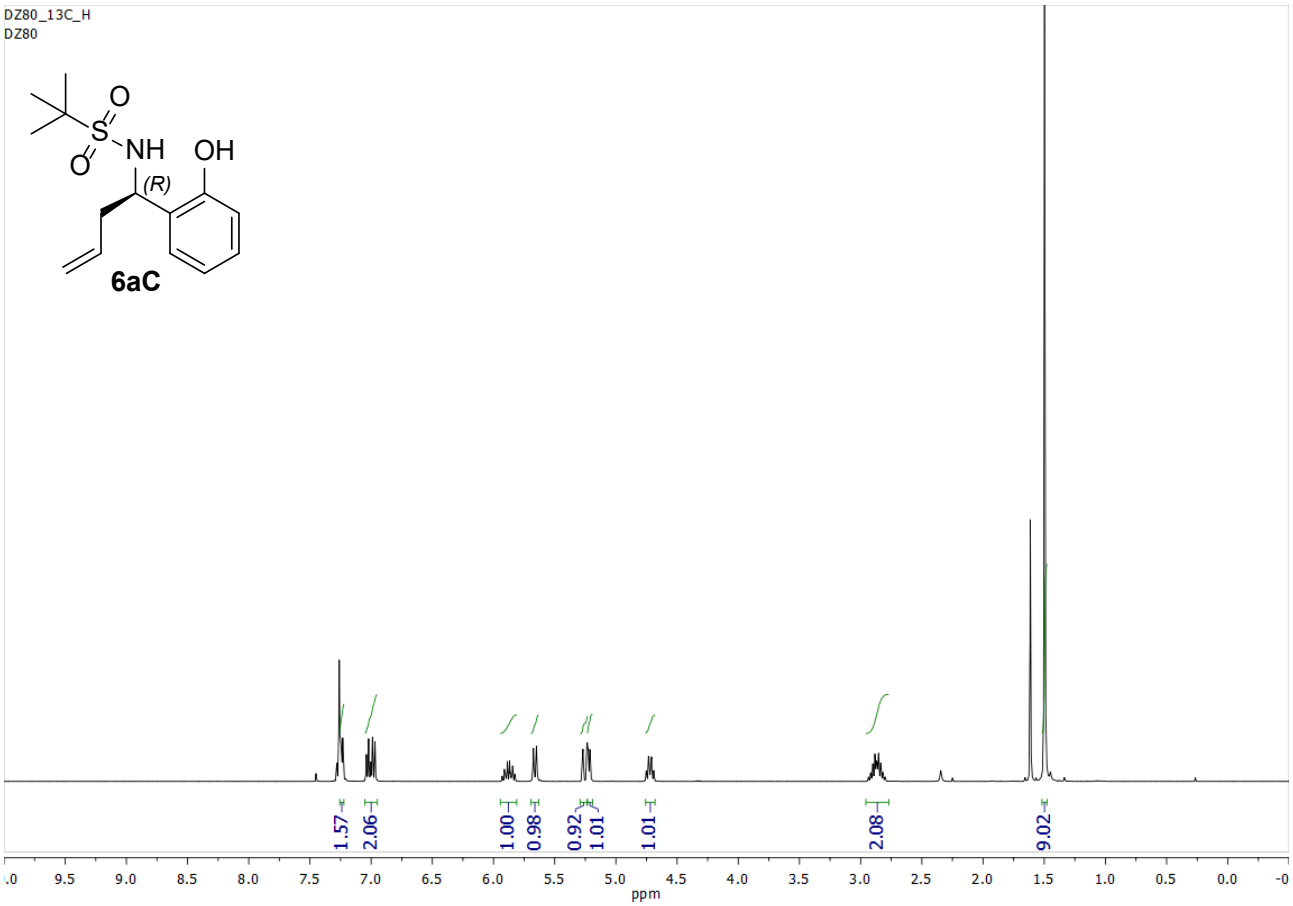

SA218_13C
SA218
150.61
134.25
133.21
127.79
127.54
125.97
119.23
119.07
59.56
53.31
41.67
25.66
24.03
18.06
-4.00
-4.45
O
S
O
NH
OTBS
(R)
5bC
Cl
ppm

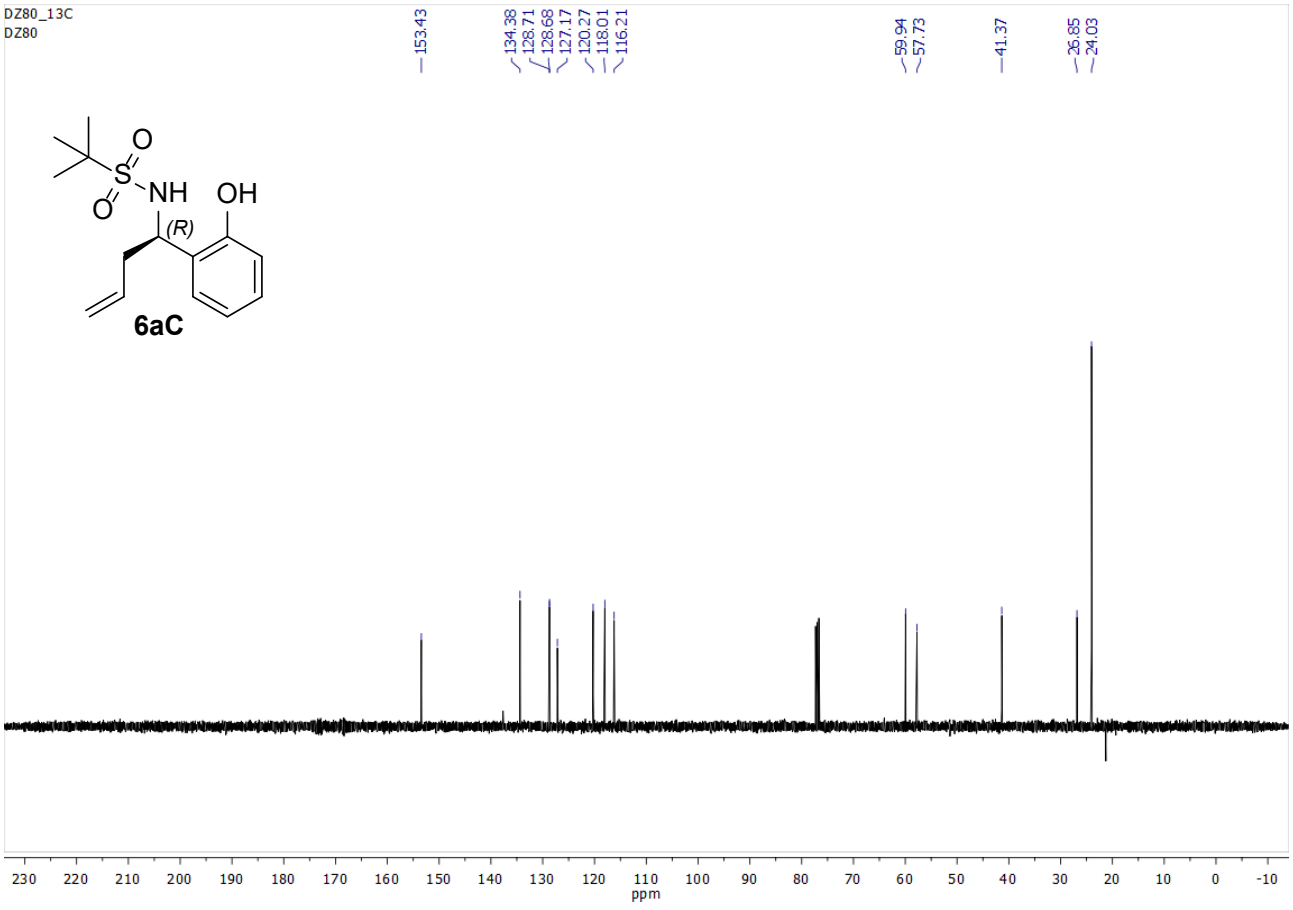

DZ21_13C_H
DZ21_13C_H
O
S
O
NH
OH
6aA
2.04
0.85
1.12
1.01
1.00
1.05
3.06
9.21
ppm

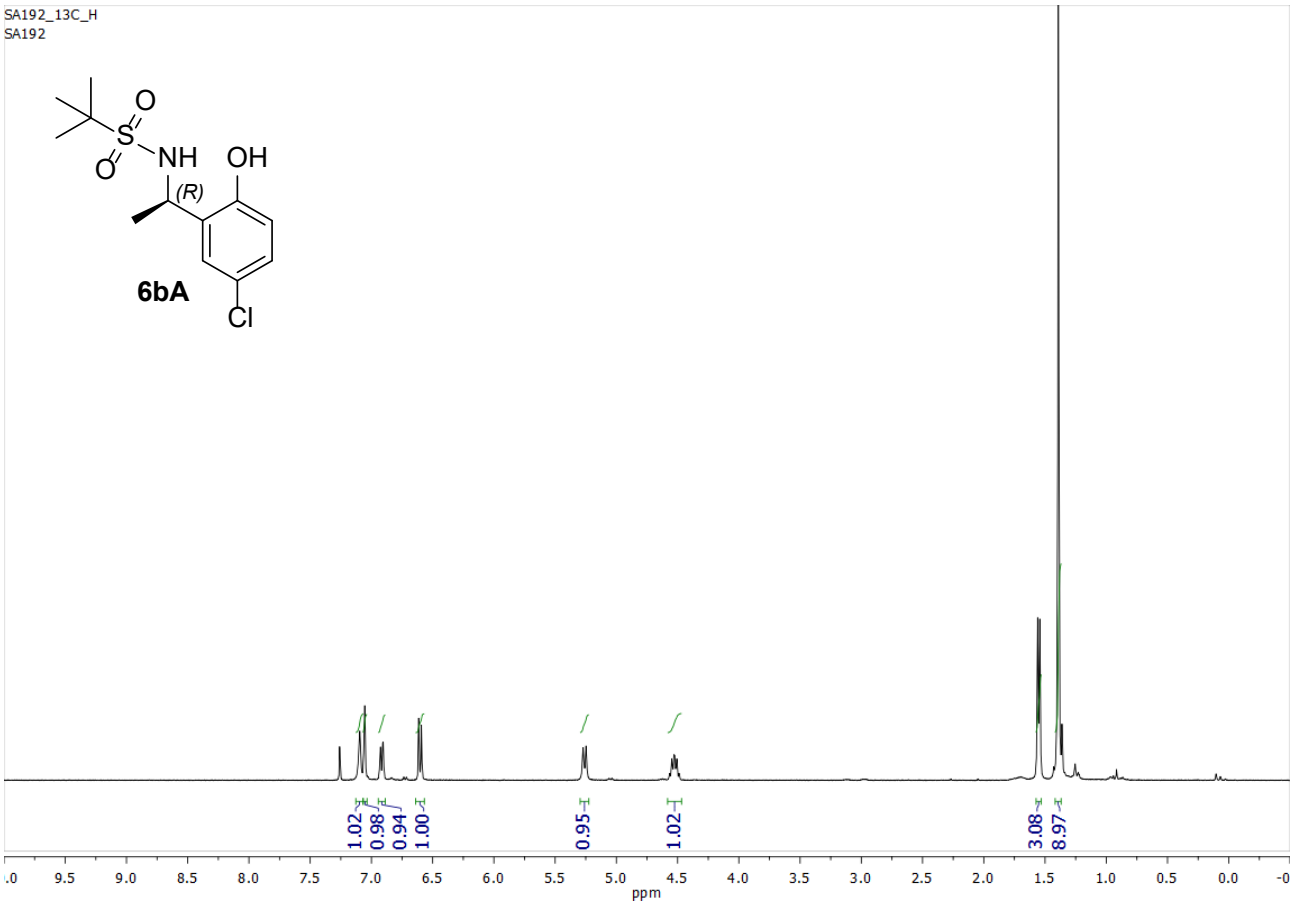

DZ21_13C
DZ21_13C_H
153.43
128.97
128.69
127.74
120.57
116.46
99.85
53.74
24.07
23.64
O
S
O
NH
OH
6aA
ppm

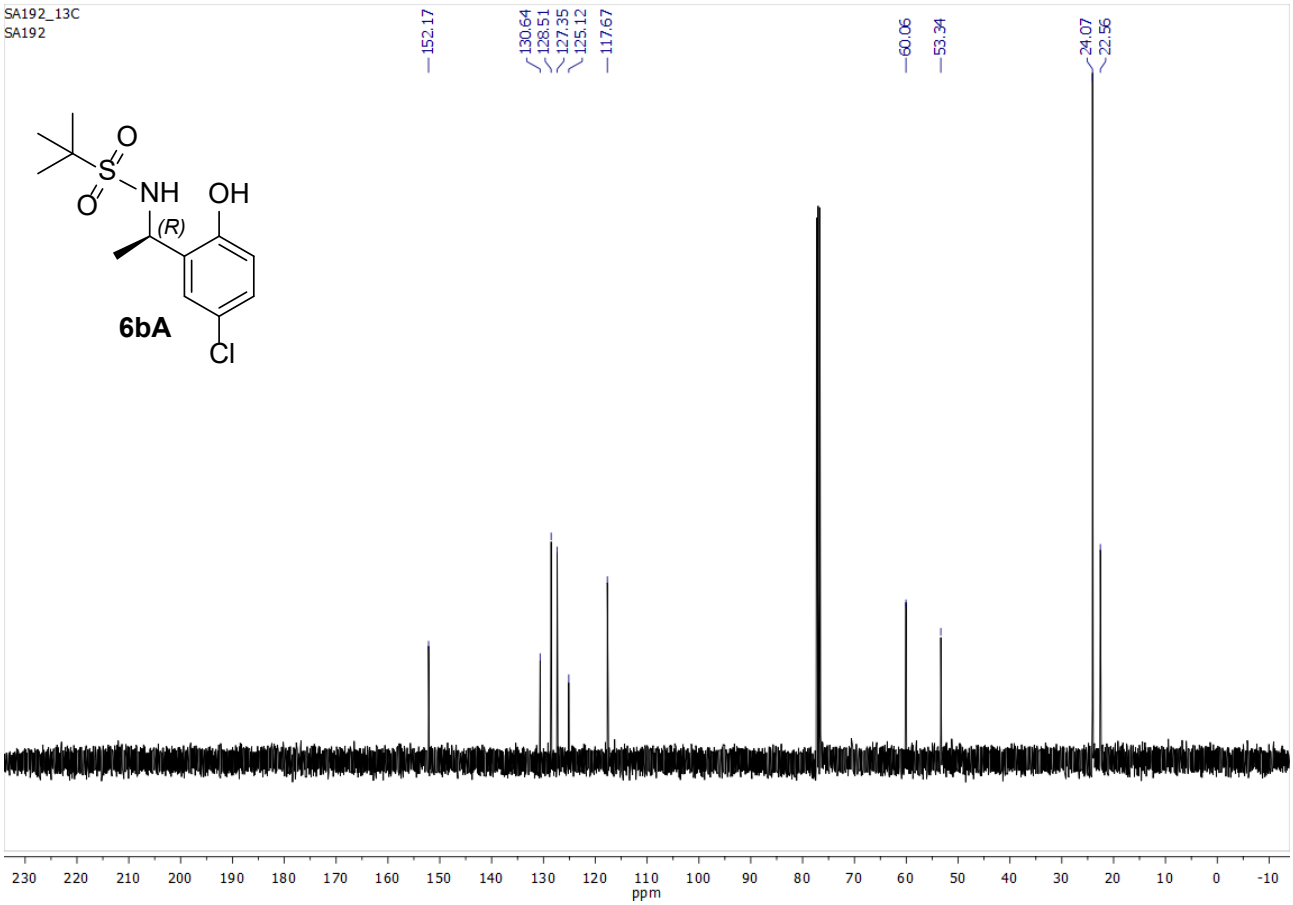

DZ47_13C_H
DZ47
O
S
NH
OH
O
(R)
Ph
6aB
5.42
2.02
1.04
1.01
0.76
1.00
0.97
9.00
ppm

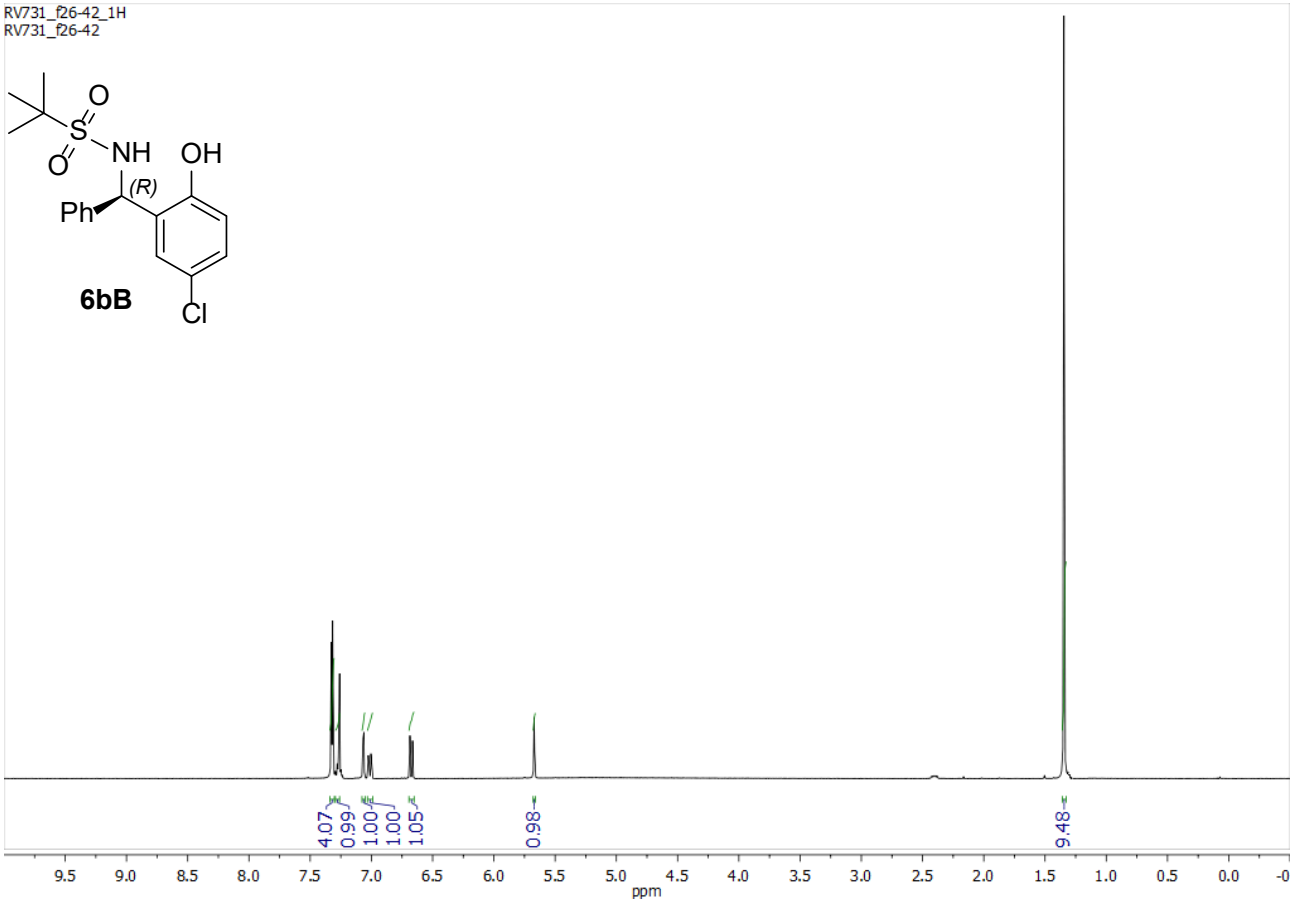

DZ47_13C
DZ47
153.38
141.18
129.30
129.22
128.44
127.87
127.25
126.72
120.80
116.97
60.19
59.31
24.07
O
S
NH
OH
O
(R)
Ph
6aB
ppm

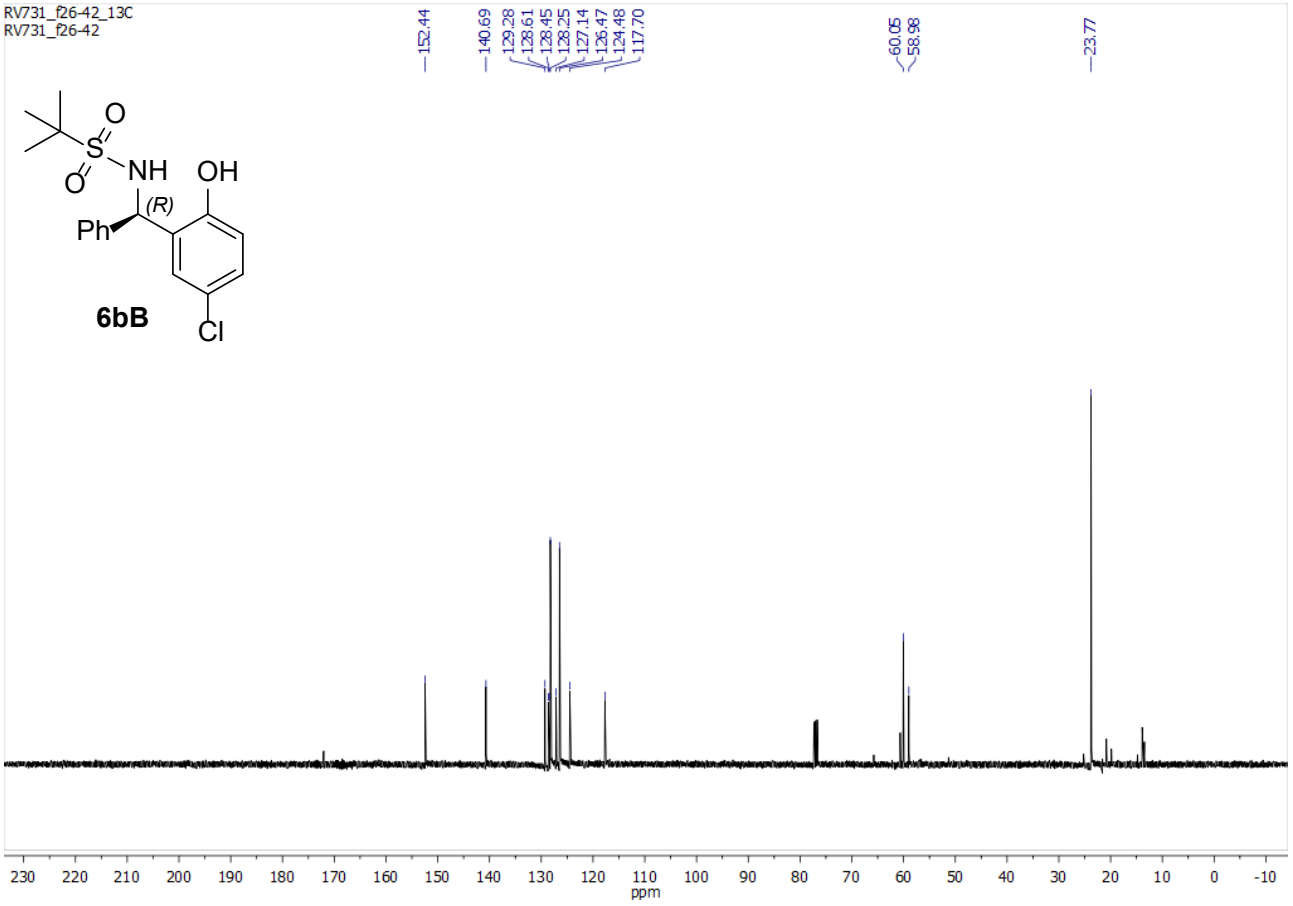

DZ80_13C_H
DZ80
O
S
O
NH
OH
(R)
6aC
1.57
2.06
1.00
0.98
0.92
1.01
1.01
2.08
9.02
ppm

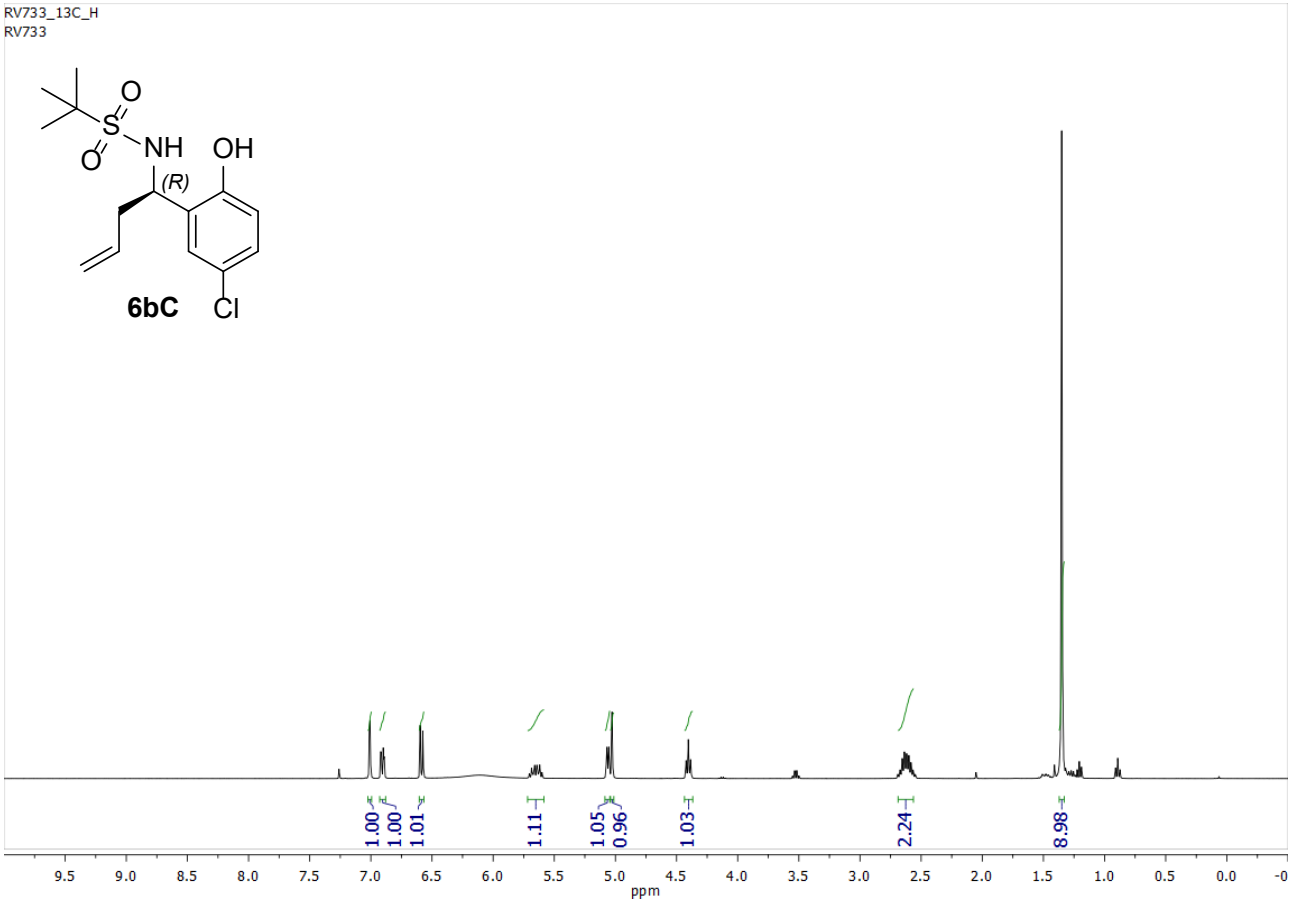

DZ80_13C
DZ80
153.43
134.38
128.71
128.68
127.17
120.27
118.01
116.21
59.94
57.73
41.37
26.85
24.03
O
S
O
NH
OH
(R)
6aC
ppm

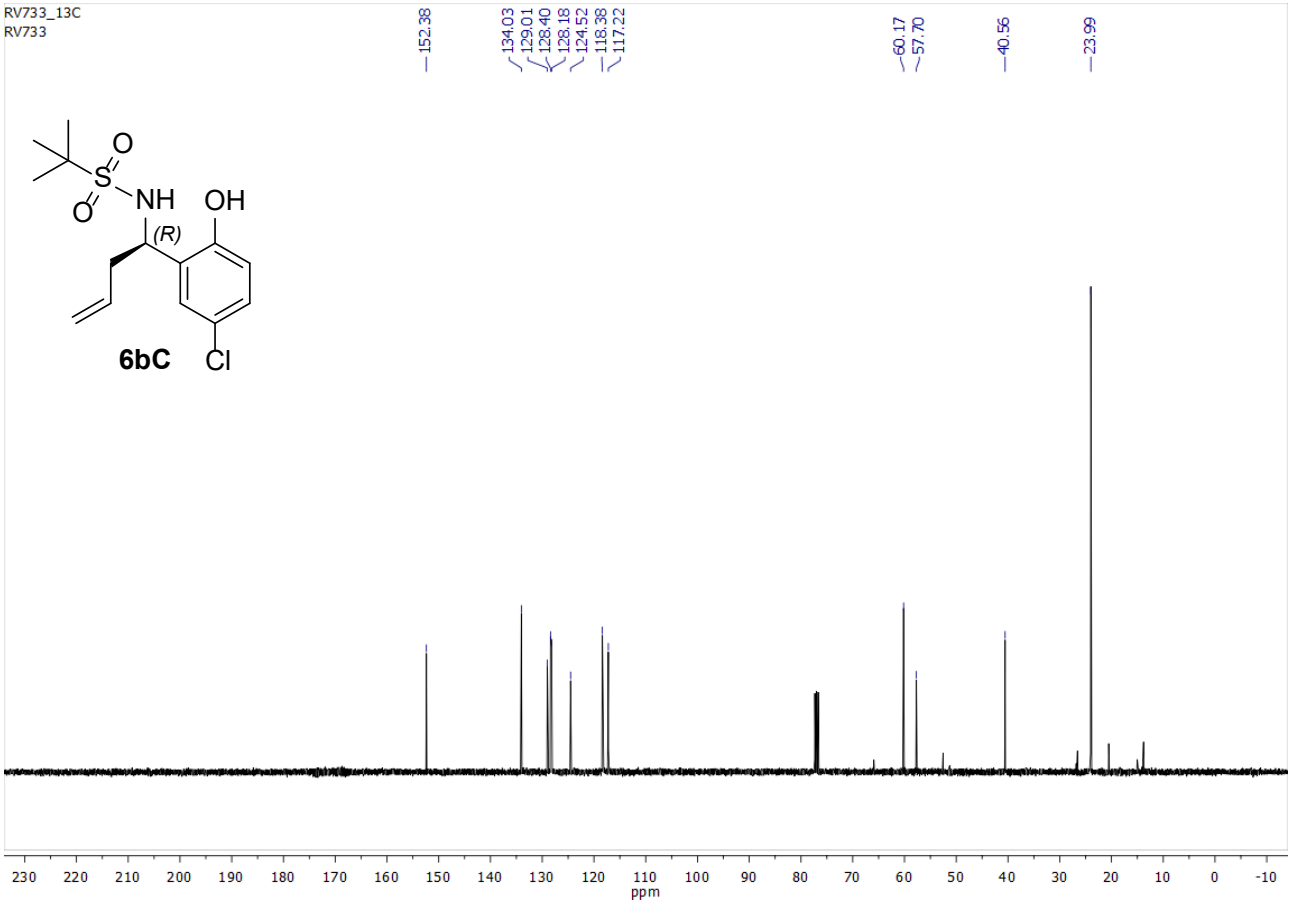

SA192_13C_H
SA192
O
S
O
NH
OH
(R)
6bA
Cl
1.02
0.98
0.94
1.00
0.95
1.02
3.08
8.97
ppm


SA192_13C
SA192
152.17
130.64
128.51
127.35
125.12
117.67
60.06
53.34
24.07
22.56
O
S
O
NH
OH
(R)
6bA
Cl
ppm

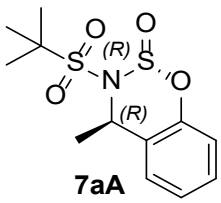

RV731_f26-42_1H
RV731_f26-42
O
S
O
NH
OH
(R)
Ph
6bB
Cl
4.07
0.99
1.00
1.00
1.05
0.98
9.48
ppm


RV731_f26-42_13C
RV731_f26-42
152.44
140.69
129.28
128.61
128.45
128.25
127.14
126.47
124.48
117.70
60.05
58.98
23.77
O
S
O
NH
OH
(R)
Ph
6bB
Cl
ppm


RV733_13C_H
RV733
O
S
O
NH
OH
(R)
6bC
Cl
1.00
1.00
1.01
1.11
1.05
0.96
1.03
2.24
8.98
ppm

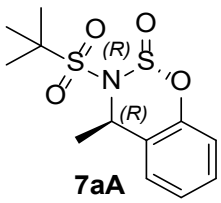

RV733_13C
RV733
152.38
134.03
129.01
128.40
128.18
124.52
118.38
117.22
60.17
57.70
40.56
23.99
O
S
O
NH
OH
(R)
6bC
Cl
ppm

DZ22_13C_H

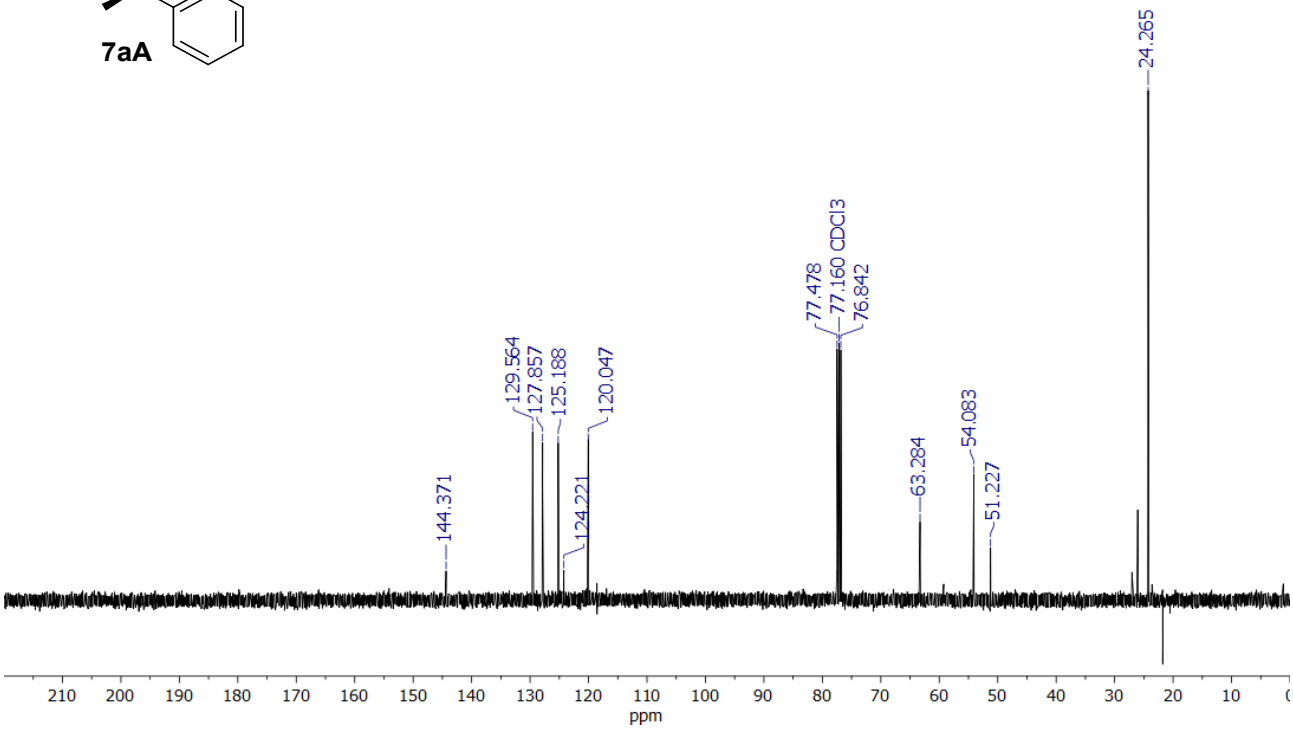


7aA

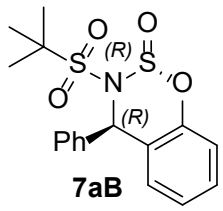
DZ22_13C



7aA

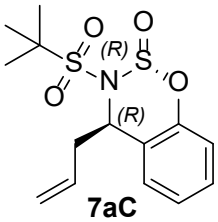


DZ73G_13C_H

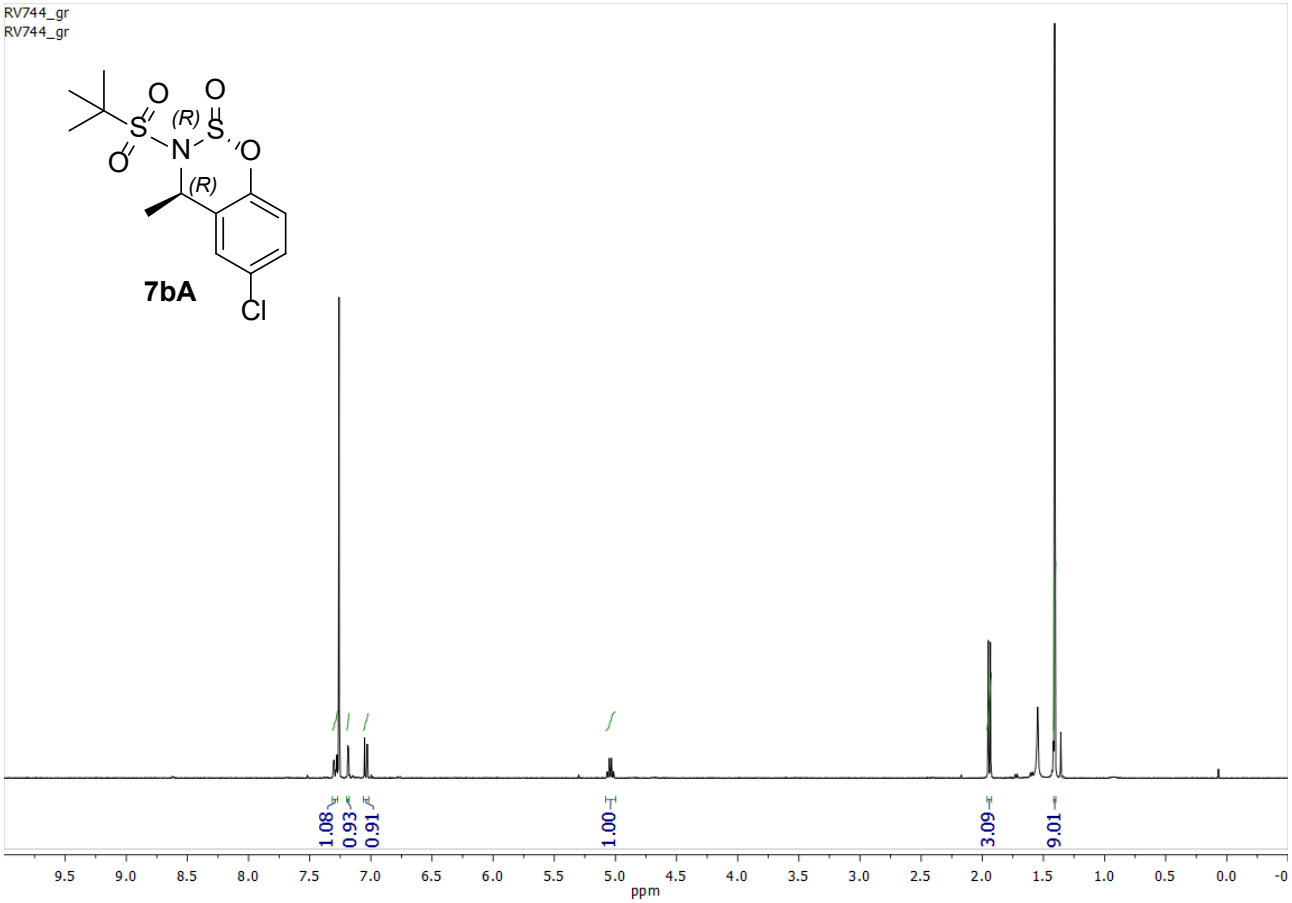


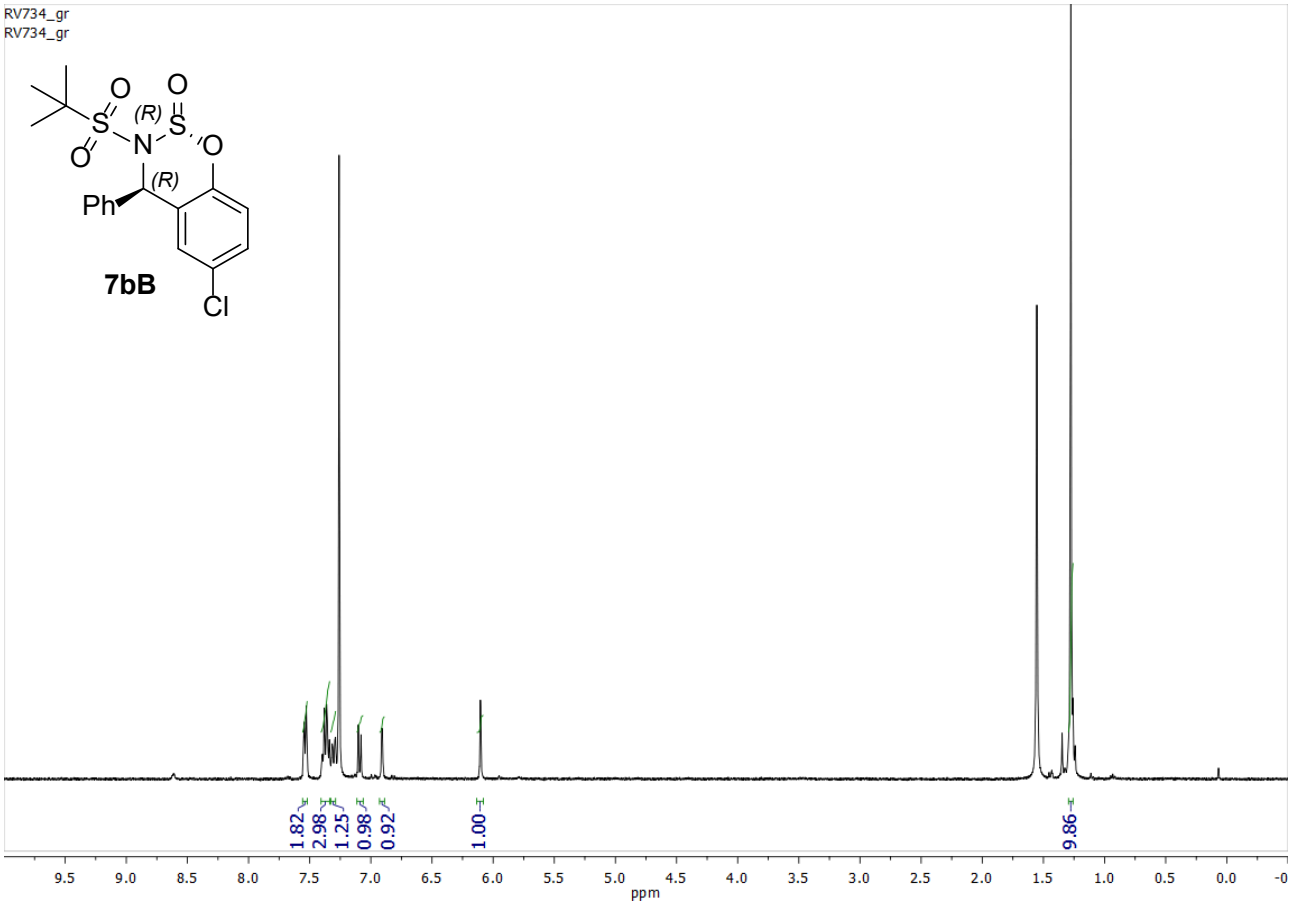
7aB

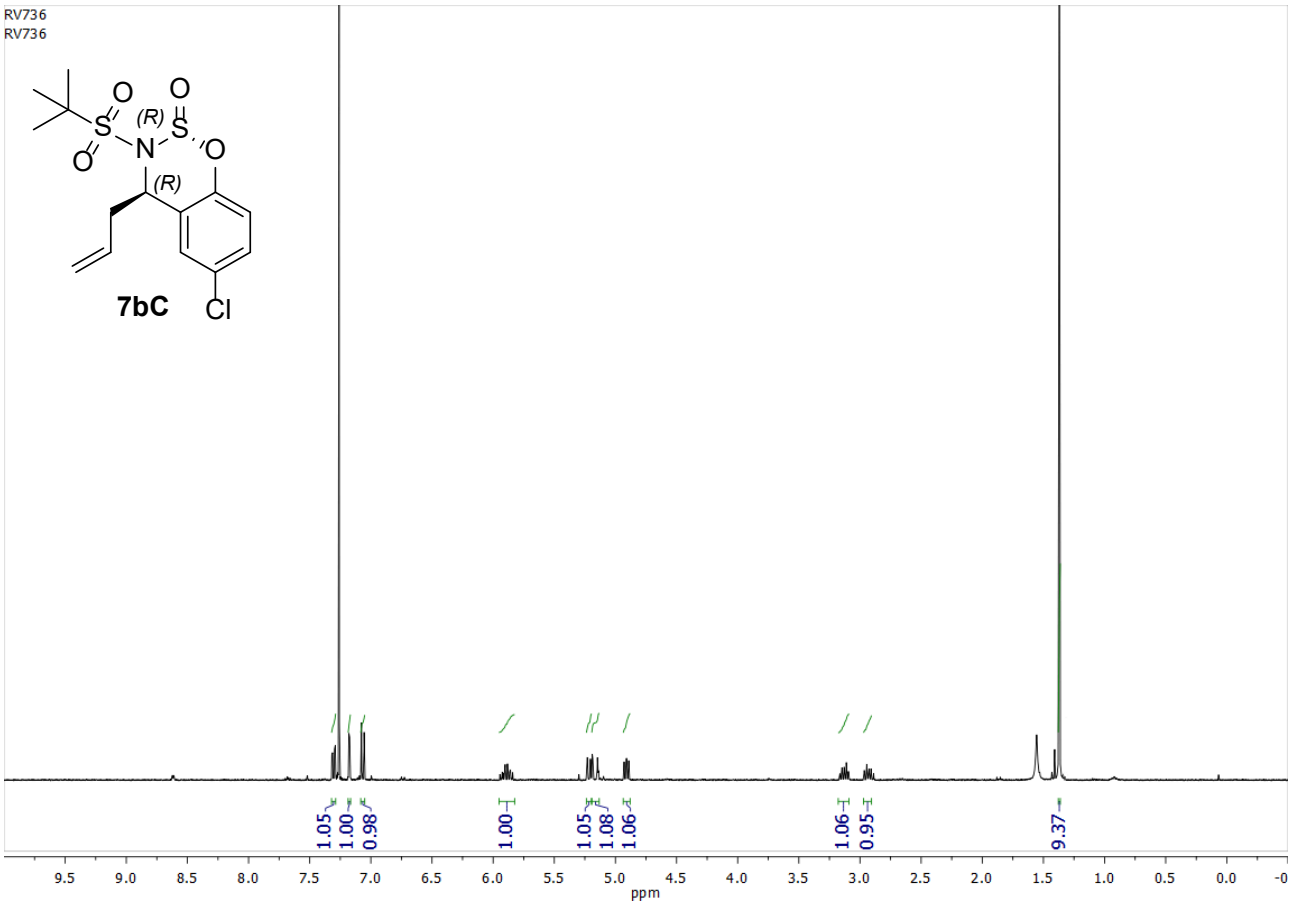
DZ81G_13C_H
DZ81G



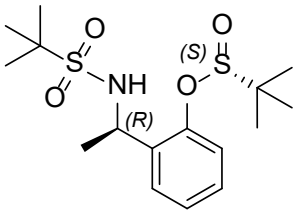
7aC


RV744_gr
RV744_gr
7bA
1.08
0.93
0.91
1.00
3.09
9.01
ppm


RV734_gr
RV734_gr
7bB
1.82
2.98
1.25
0.98
0.92
1.00
9.86
ppm

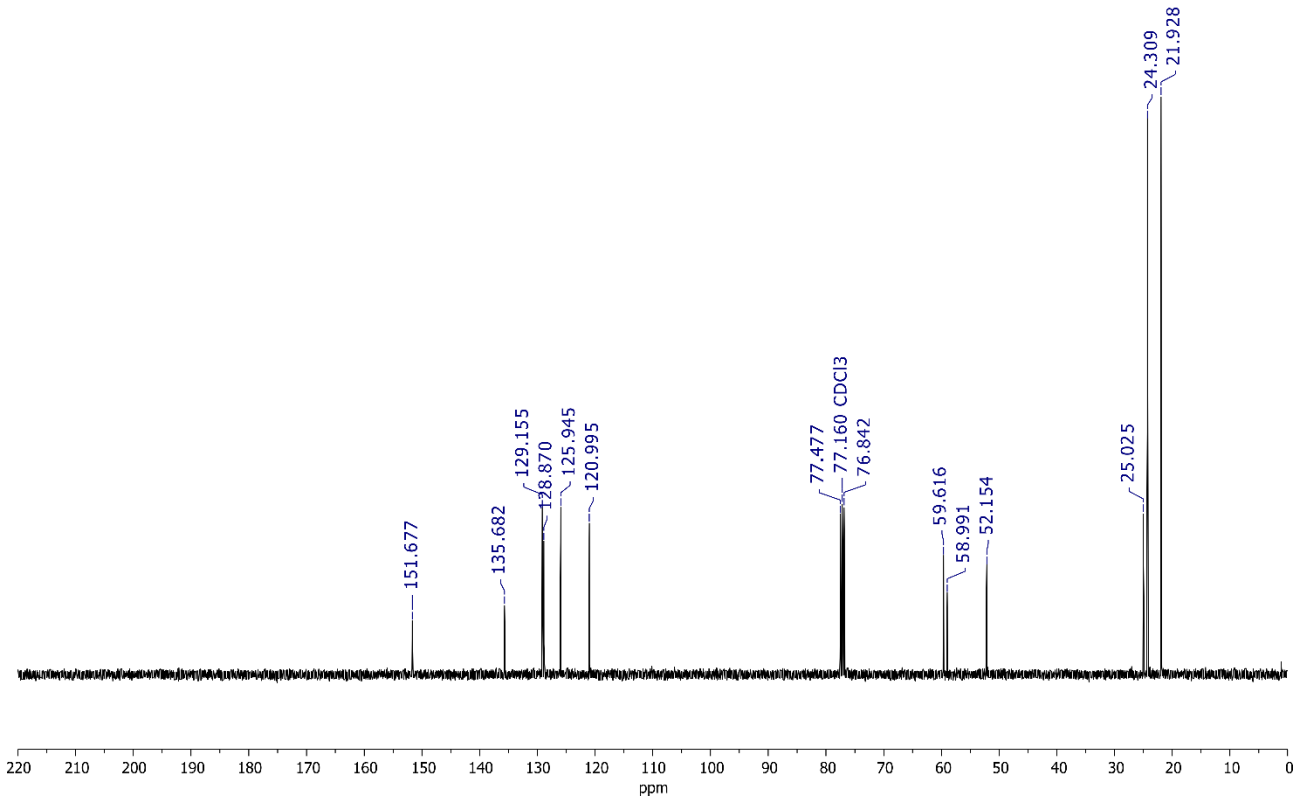

RV736
RV736
(R)
(R)
7bC
Cl
1.05
1.00
0.98
1.00
1.05
1.08
1.06
1.06
0.95
9.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm

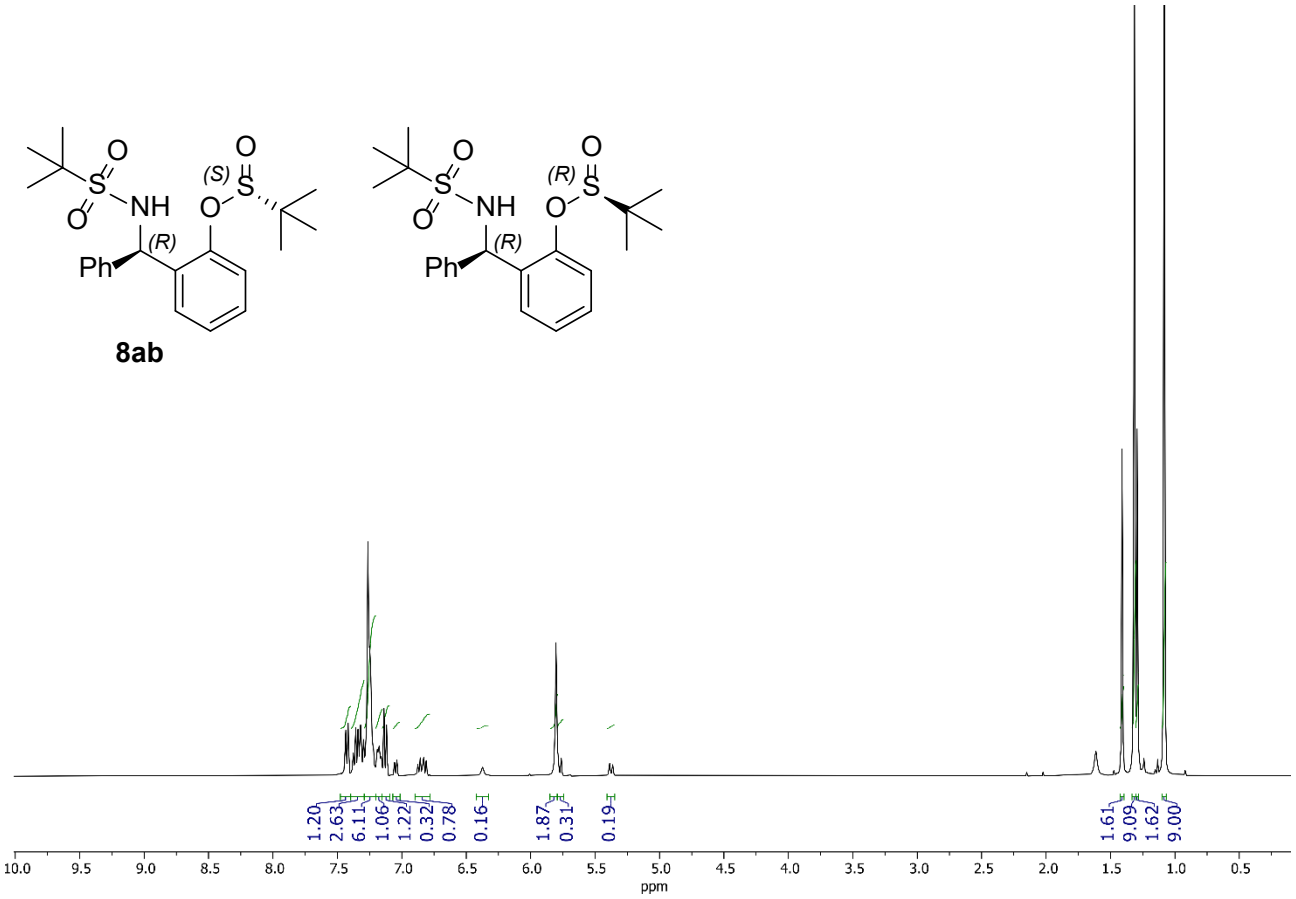
DZ64_H



8aA

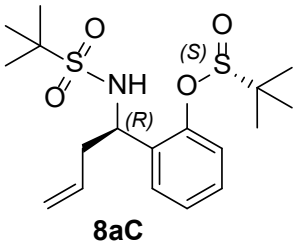
DZ64_13C




(S)
(R)
(R)
(R)
NH
NH
Ph
Ph
1.20
2.63
6.11
1.06
1.22
0.32
0.78
0.16
1.87
0.31
0.19
1.61
9.09
1.62
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

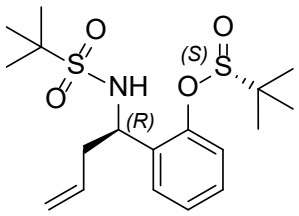
8ab

DZ87

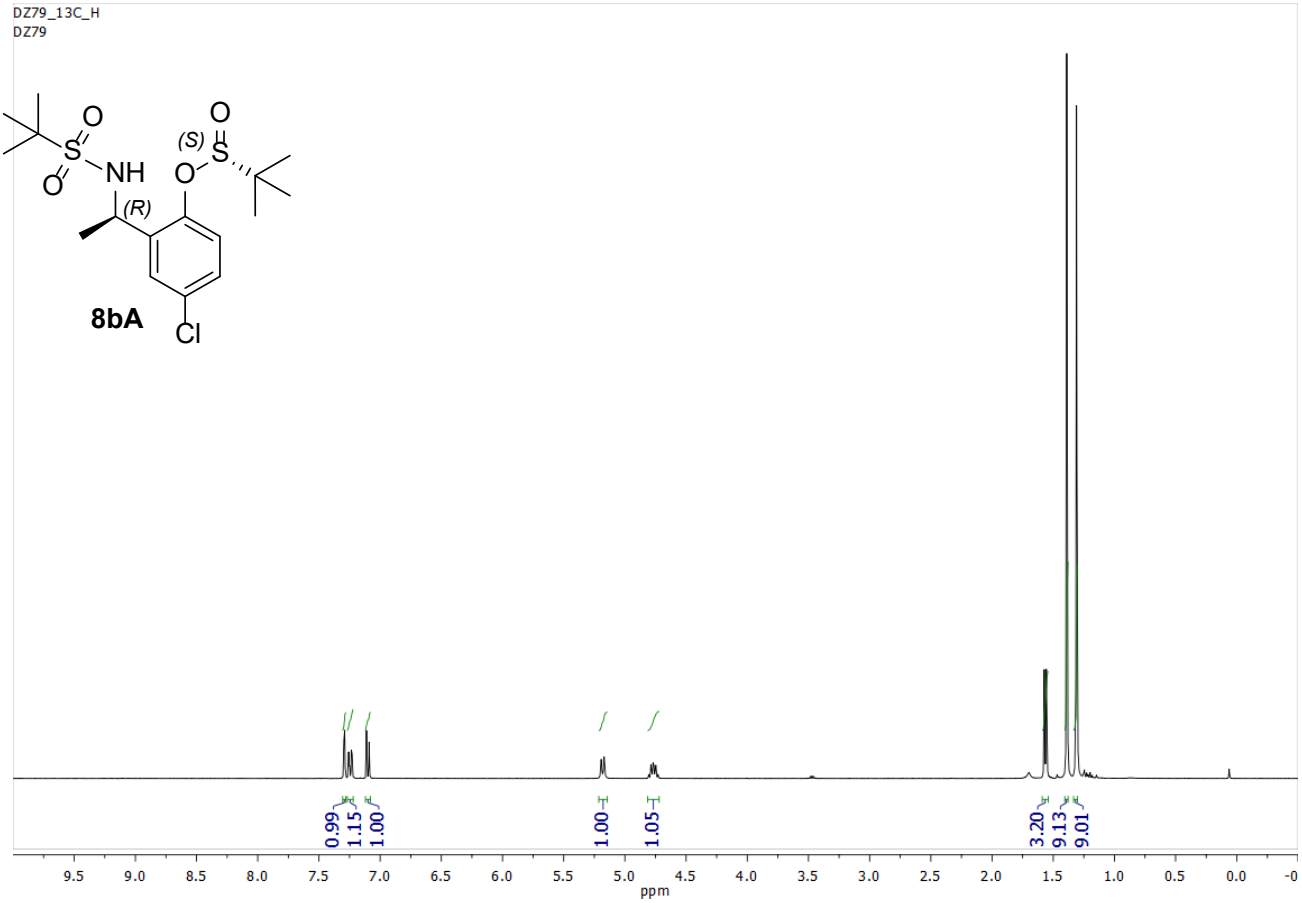


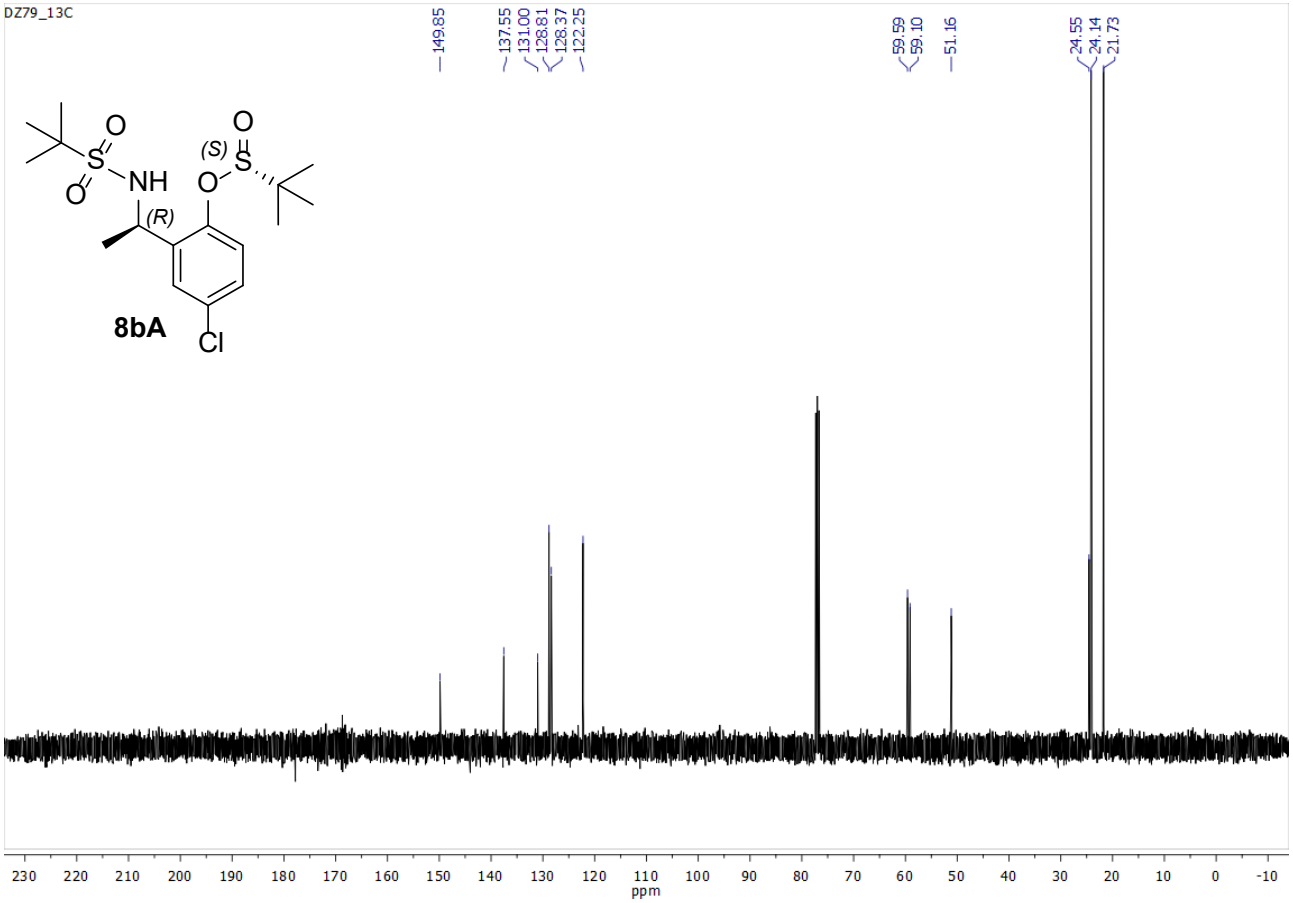
8aC

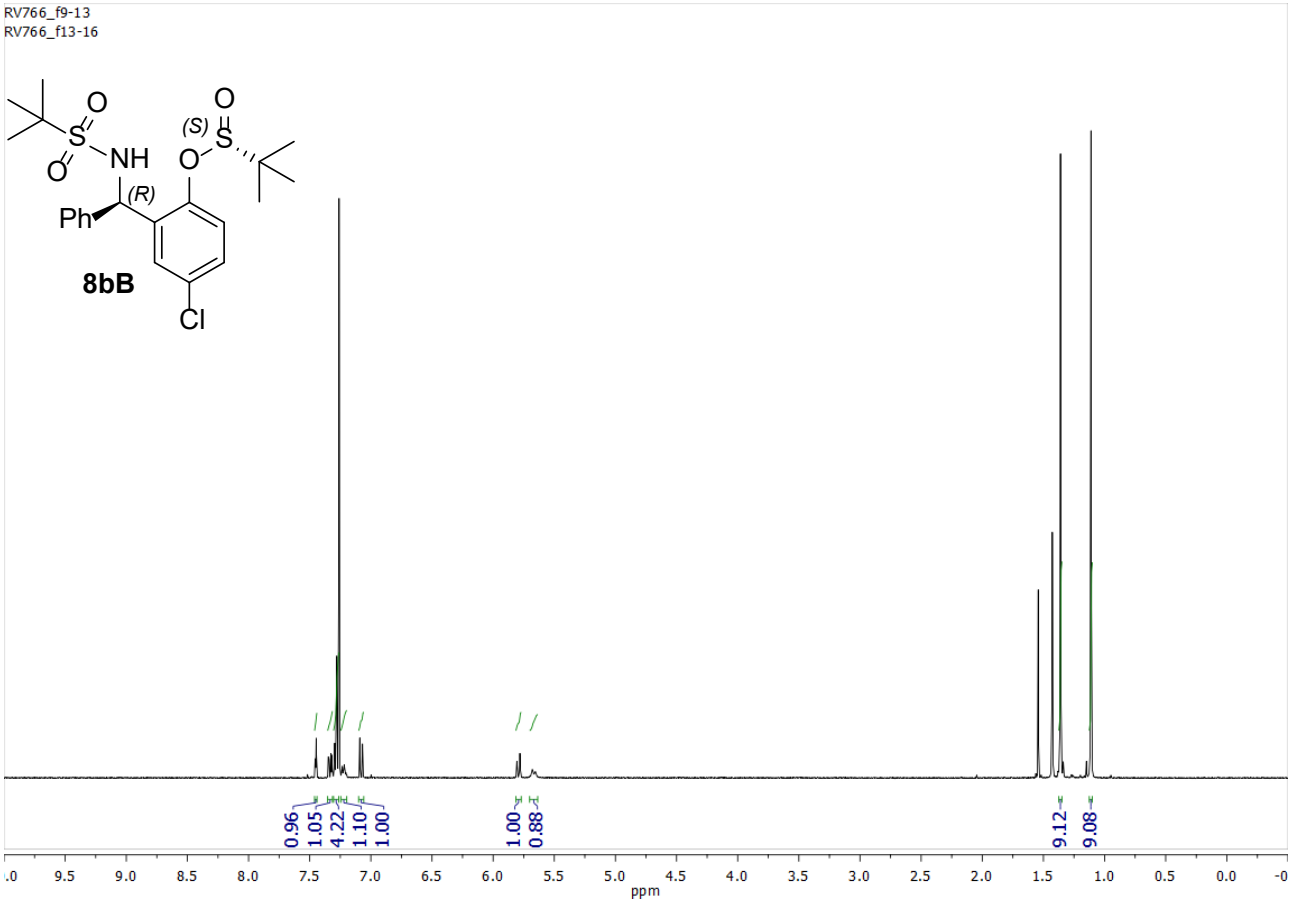
DZ87_13C

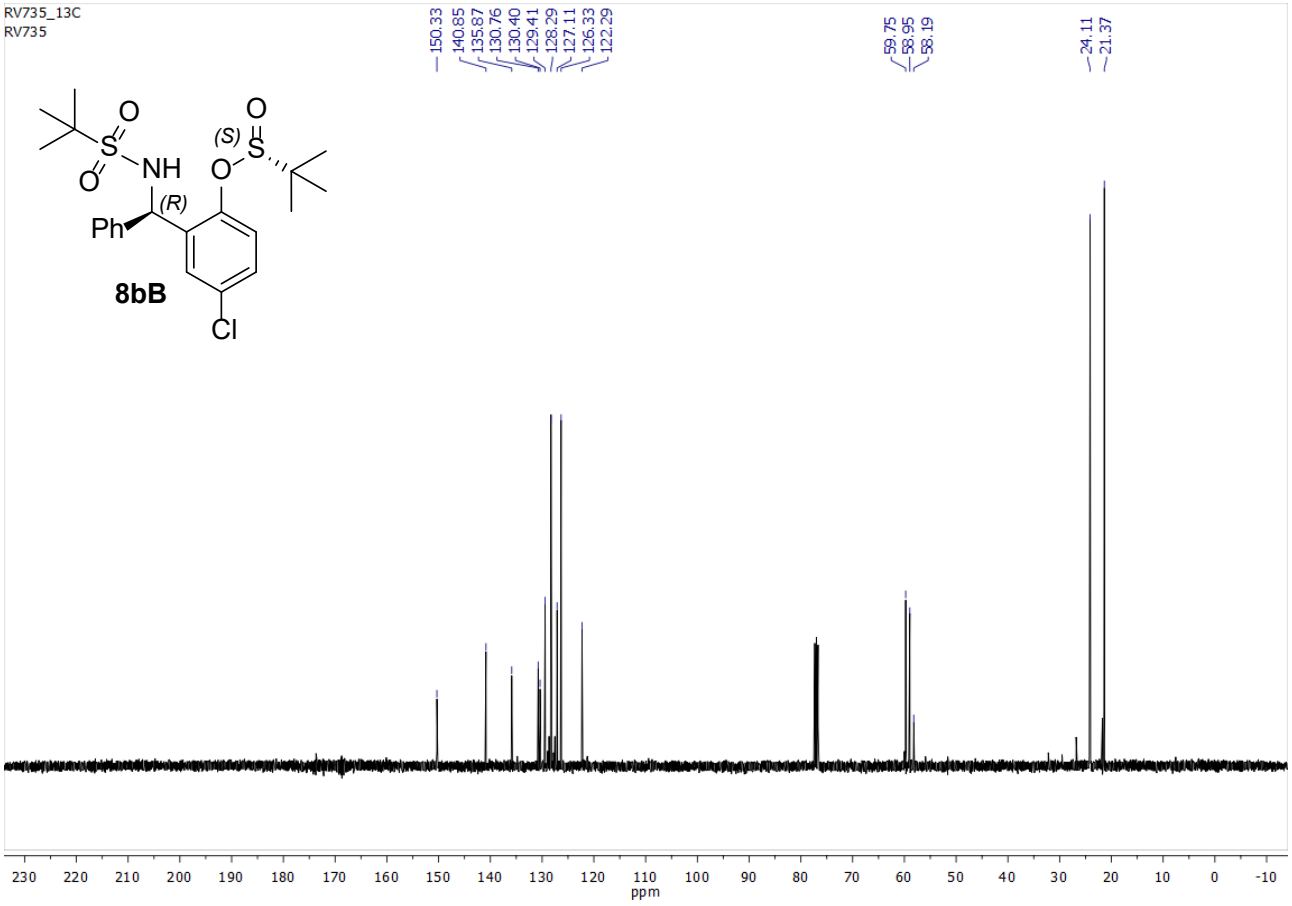


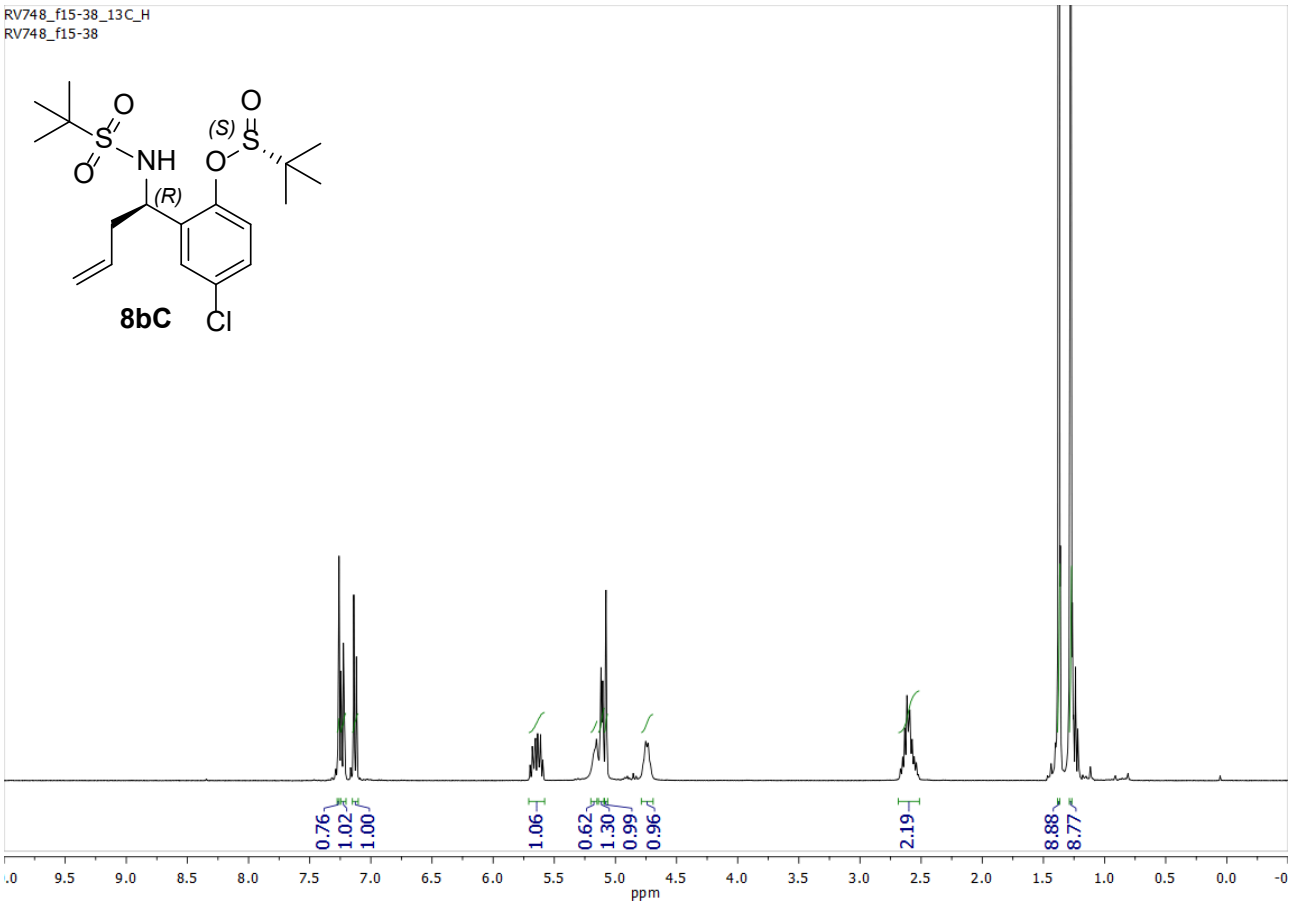
8aC

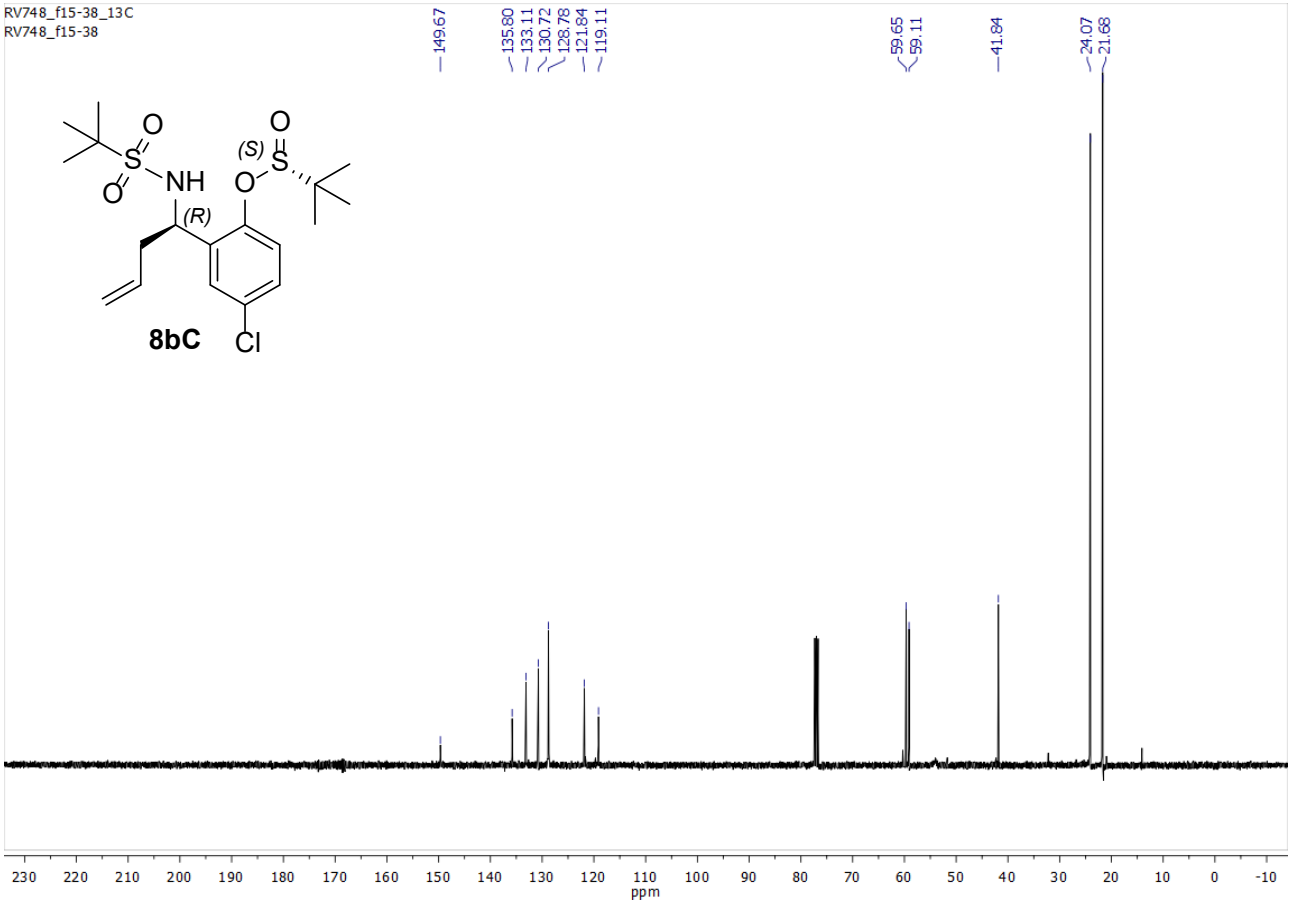

DZ79_13C_H
DZ79
8bA
0.99
1.15
1.00
1.00
1.05
3.20
9.13
9.01
ppm

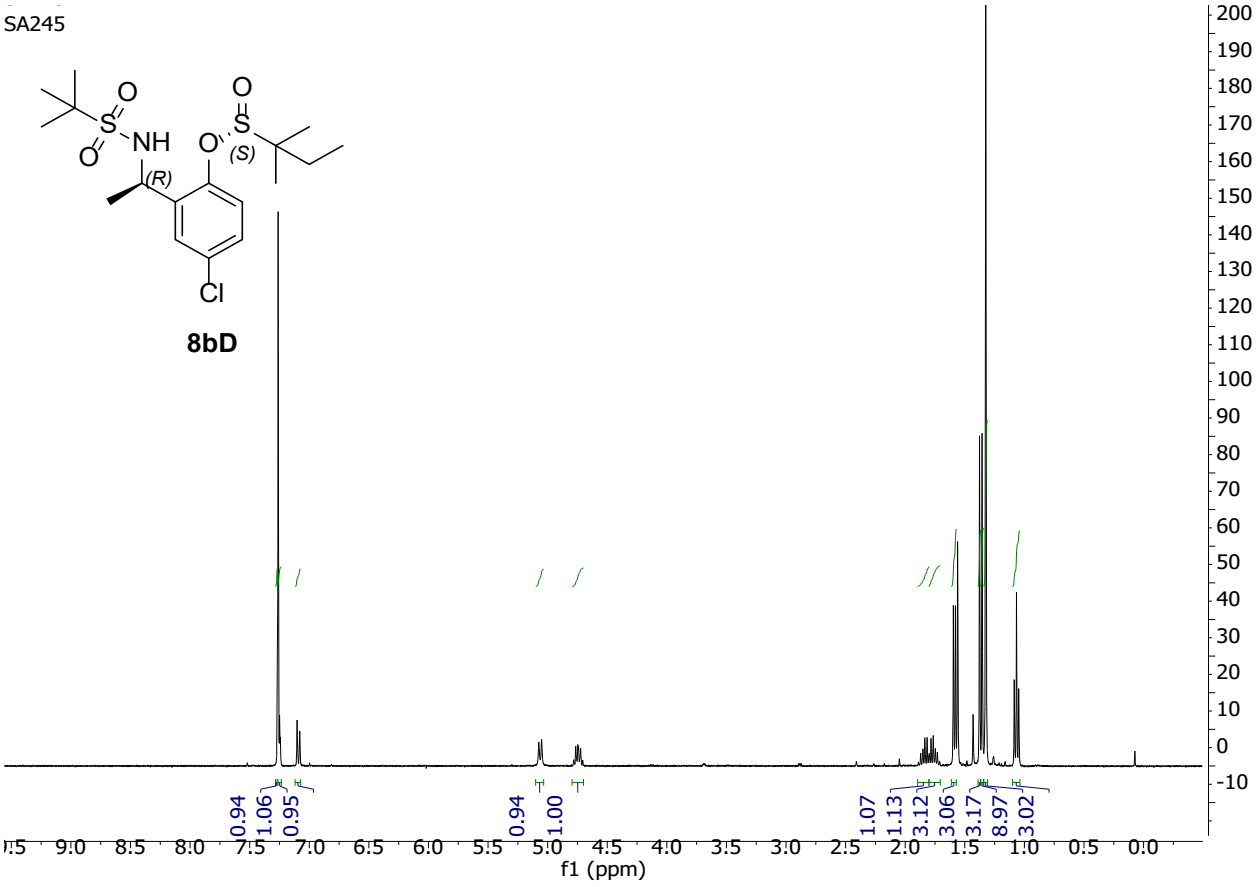

DZ79_13C
8bA
149.85
137.55
131.00
128.81
128.37
122.25
59.59
59.10
51.16
24.55
24.14
21.73
ppm

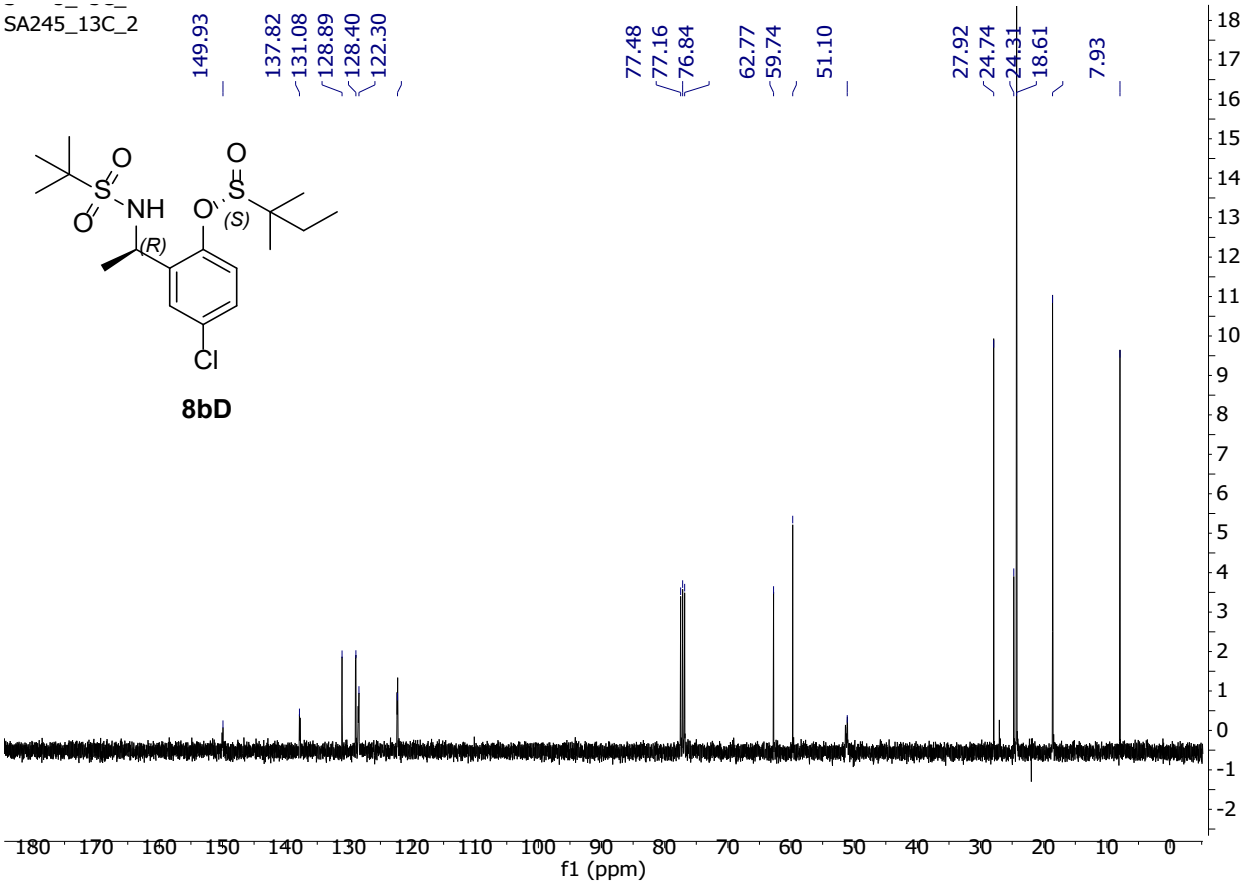

RV766_f9-13
RV766_f13-16
8bB
0.96
1.05
4.22
1.10
1.00
1.00
0.88
9.12
9.08
ppm


RV735_13C
RV735
150.33
140.85
135.87
130.76
130.40
129.41
128.29
127.11
126.33
122.29
59.75
58.95
58.19
24.11
21.37
8bB
ppm

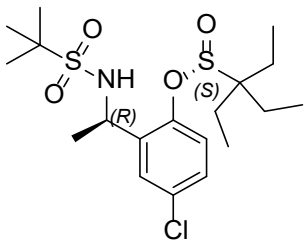

RV748_f15-38_13C_H
RV748_f15-38
8bC
0.76
1.02
1.00
1.06
0.62
1.30
0.99
0.96
2.19
8.88
8.77
ppm


RV748_f15-38_13C
RV748_f15-38
149.67
135.80
133.11
130.72
128.78
121.84
119.11
59.65
59.11
41.84
24.07
21.68
8bC
ppm


SA245
8bD
0.94
1.06
0.95
0.94
1.00
1.07
1.13
3.12
3.06
3.17
8.97
3.02
f1 (ppm)

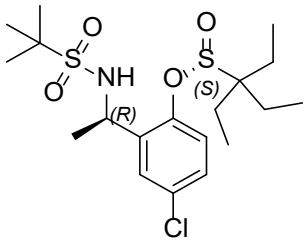

SA245_13C_2
149.93
137.82
131.08
128.89
128.40
122.30
77.48
77.16
76.84
62.77
59.74
51.10
27.92
24.74
24.31
18.61
7.93
8bD
f1 (ppm)

SA241

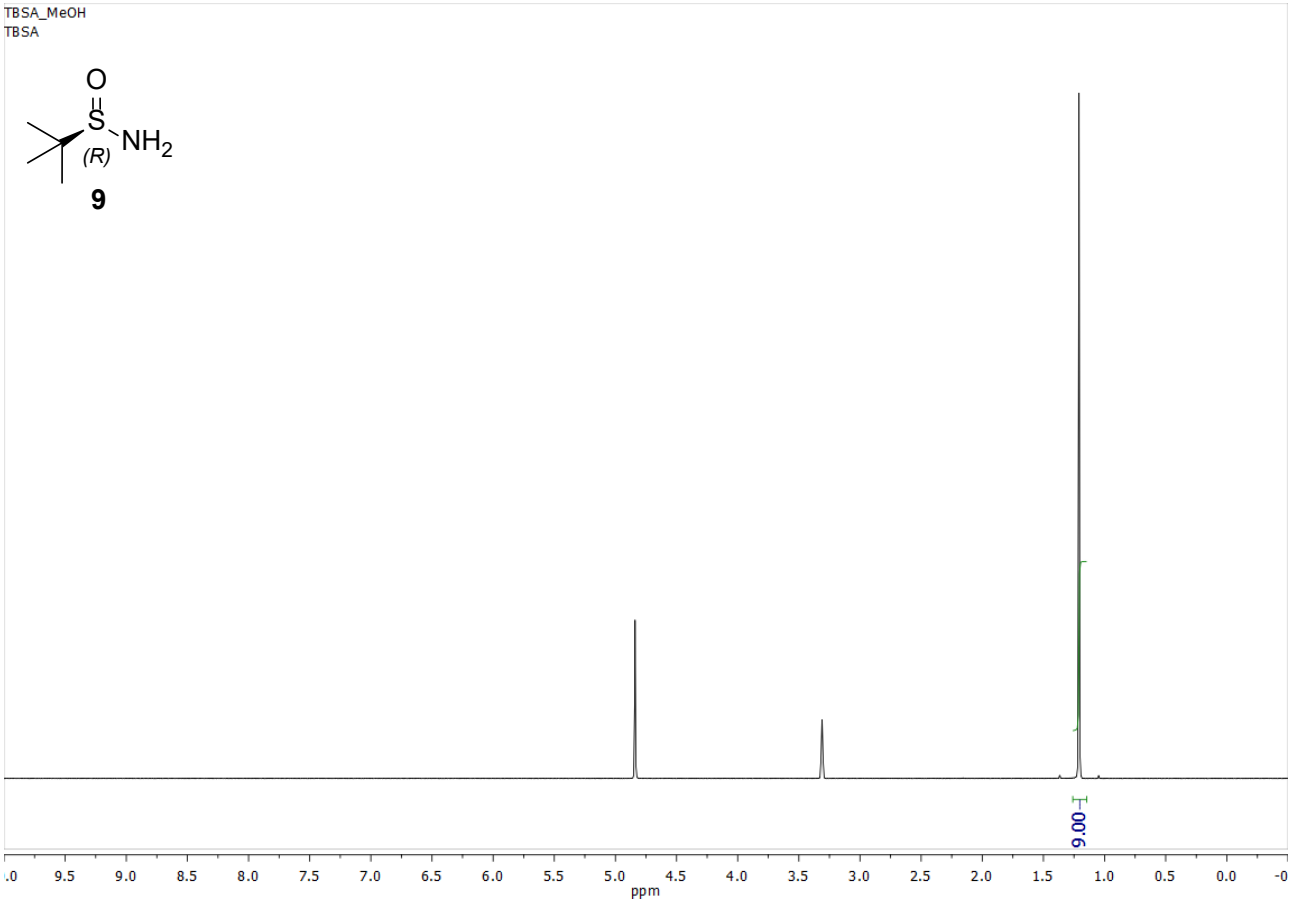


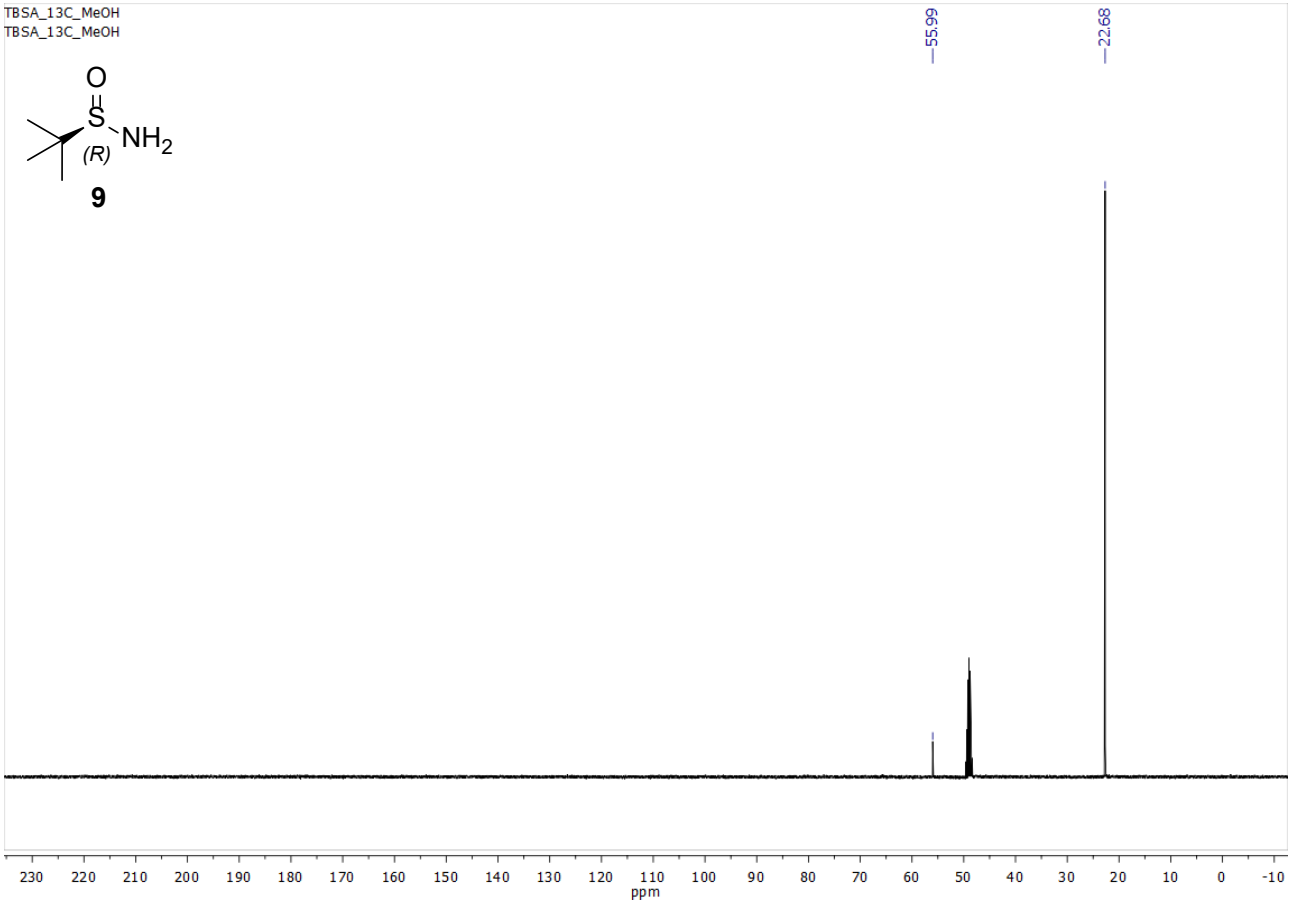
8bE

SA241_13C

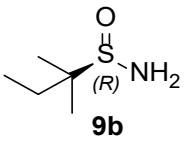


8bE


TBSA_MeOH
TBSA
O
S
NH2
(R)
9
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

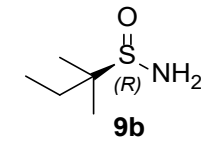

TBSA_13C_MeOH
TBSA_13C_MeOH
55.99
22.68
O
S
NH2
(R)
9
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

SA247_1H



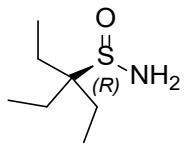
9b

SA247_13C_2



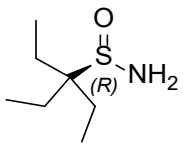
9b

SA246b_1H



9c

data_s2pul_002



9c