Chiral primary amine mediated conjugate addition of branched aldehydes to vinyl sulfone: asymmetric generation of quaternary carbon centers

Qiang Zhu[a,b] and Yixin Lu[*a,b]

[a]*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543*

[b]*Medicinal Chemistry Program, Life Sciences Institute, National University of Singapore*

Email: chmlyx@nus.edu.sg

Supplementary Information

A. General Information S2

B. Preparation of the Catalysts (**11a-c** & **12a-c**) S3

C. Representative Procedure S14

D. Preparation of Chiral Alcohol **15**, Acid **16** & Determination of the Absolute Configuration of the Conjugate Addition products S15

E. Analytical Data and HPLC Chromatogram of Conjugate Addition Products S19

F. NMR Spectra of the Products S27

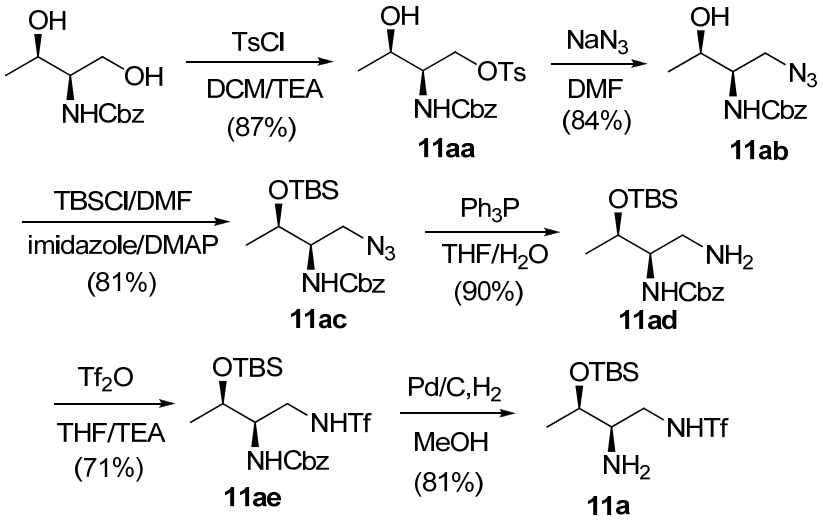
A. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF300 or DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin-layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F_{254}) were used, and compounds were visualized under a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063 mm) mesh silica gel. The enantiomeric excesses of the products were determined by chiral-phase HPLC analysis.

All the branched aldehydes were prepared following the literature procedures[1] and 1,2-bis(phenylsulfonyl)ethylene was purchased from Sigma-Aldrich.

B. Preparation of the Catalysts

B1. Preparation of L-threonine-derived catalyst **11a**



(2*R*,3*R*)-2-(Benzyloxycarbonyl)-3-hydroxybutyl 4-methylbenzenesulfonate **11aa**

To an ice-cold solution of benzyl (2*R*,3*R*)-1,3-dihydroxybutan-2-ylcarbamate (2.39 g, 10.0 mmol) and triethylamine (15 mmol, 2.1 mL) in dichloromethane (50 mL) at 0 ^{o}C was added 4-toluenesulfonyl chloride (2.28 g, 12.0 mmol). The reaction mixture was stirred at room temperature for 6 h and then diluted with dichloromethane (50 mL). The organic phase was washed with aqueous $NaHCO_3$ (3 X 50 mL) and brine (2 X 50 mL), and dried over Na_2SO_4. The solution was filtered and concentrated under the reduced pressure to afford the crude product, which was subjected to flash chromatographic separation on silica gel (ethyl acetate/hexanes = 1:15 to 1:4) to afford **11aa** as a colorless oil (3.41 g, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14-1.16 (d, *J* = 6.3 Hz, 3H), 2.41 (s, 3H), 3.00 (s, 1H), 3.71-3.78 (m, 1H), 4.00-4.07 (m, 2H), 4.11-4.14 (m, 1H), 5.06 (s, 2H), 5.51-5.52 (d, *J* = 8.9 Hz, 1H), 7.28-7.35 (m, 7H), 7.76-7.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.93, 21.63, 54.69, 65.38, 66.97, 68.90, 127.91, 127.93, 128.17, 128.55, 130.00, 132.52, 136.26, 145.15, 156.63; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_6S$ $[M+H]^+$ 416.1129, found 416.1118.

Benzyl (2*R*,3*R*)-1-azido-3-hydroxybutan-2-ylcarbamate **11ab**

Sodium azide (1.95 g, 30.0 mmol) was added to **11aa** (1.97 g, 5.0 mmol) in *N,N*-dimethylformamide (15 mL), and the resulting mixture was heated at 70 ^{o}C for 14 hrs. The reaction mixture was then allowed to cool to room temperature and diluted with ethyl acetate (75 mL). The organic phase was washed with H_2O (3 X 30 mL) and brine (3 X 30 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure to afford the crude product as a colorless oil (1.11 g, 84%). The crude product was used in the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18-1.20 (d, *J* = 6.4 Hz, 3H), 2.82-2.83 (m, 1H), 3.42-3.45 (m, 2H), 3.62-3.67 (m, 1H), 3.97 (br, 1H), 5.11 (s, 2H), 5.50-5.53 (d, *J* = 8.7 Hz, 1H), 7.31-7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.23, 52.57, 55.13, 66.67, 67.03, 127.97, 128.18, 128.51, 136.13, 156.68; HRMS (ESI) m/z calcd for $C_{12}H_{16}N_4O_3$ $[M-H]^-$ 263.1150, found 263.1149.

Benzyl (2*R*,3*R*)-1-azido-3-(*tert*-butyldimethylsilyloxy)butan-2-ylcarbamate **11ac**

To a stirred solution of the azide **11ab** (1.27 g, 5 mmol) in freshly distilled *N,N*-dimethylformamide (5 mL) was added *tert*-butylchlorodimethylsilane (900 mg, 6.0 mmol), imidazole (680 mg, 10 mmol) and DMAP (120 mg, 1.0 mmol). After stirring at room temperature for 12 hrs, ethyl acetate (50 mL) was added to the reaction mixture and the mixture was washed with water (5 X 20 mL) and brine (2 X 20 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under the reduced pressure to afford the crude product, which was purified by flash column chromatography (ethyl acetate/hexanes = 1:20 to 1:5) to afford the desired product as a colorless oil (1.53 g, 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.90 (s, 9H), 1.16-1.19 (d, *J* = 6.4 Hz, 3H), 3.27-3.31 (m, 1H), 3.41-3.44 (m, 1H), 3.68-3.71 (m, 1H), 4.01-4.05 (m, 1H), 5.10-5.15 (m, 3H), 7.31-7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.11, -4.28, 17.90, 20.65, 25.76, 51.89, 55.62, 66.41, 66.95, 128.17, 128.51, 136.27, 156.27; HRMS (ESI) m/z calcd for $C_{18}H_{30}N_4O_3Si$ $[M+Na]^+$ 401.1979, found 401.1980.

Benzyl (2*R*,3*R*)-1-amino-3-(*tert*-butyldimethylsilyloxy)butan-2-ylcarbamate **11ad**

Triphenylphosphine (629 mg, 2.4 mmol) was added to azide **11ac** (756 mg, 2.0 mmol) in tetrahedrofuran (15 mL) and H_2O (5.0 mL). The reaction mixture was brought to reflux for 2 hours. Solvent was removed under reduced pressure, and extra water (15 mL) was added. The aqueous layer was extracted with ethyl acetate several times (3 X 15 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1:2 to triethylamine/ethyl acetate = 1:10) to afford the desired amine **11ad** as a colorless oil (634 mg, 90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02-0.03 (d, *J* = 2.3 Hz, 3H), 0.85 (s, 9H), 1.10-1.12 (d, *J* = 6.2 Hz, 3H), 1.19 (br, 2H), 2.69-2.71 (d, *J* = 6.9 Hz, 2H), 3.42-3.45 (m, 1H), 3.97-3.99 (m, 1H), 5.07-5.10 (s, 3H), 7.31-7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.06, -4.30, 17.86, 20.89, 25.74, 44.31, 59.30, 66.66, 67.48, 128.02, 128.44, 131.92, 132.06, 136.51, 156.99; HRMS (ESI) m/z calcd for $C_{18}H_{32}N_2O_3Si$ $[M+H]^+$ 353.2264, found 353.2262.

Benzyl(2*R*,3*R*)-3-(*tert*-butyldimethylsilyloxy)-1-(trifluoromethylsulfonamido)butan-2-ylcarbamate **11ae**

Trifluoromethanesulfonic anhydride (0.2 mL, 1.2 mmol) was added to amine **11ad** (0.35 g, 1.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in anhydrous dichloromethane (5 mL) at 0 ^{o}C, and the mixture was stirred at room temperature for 5 hours. After diluting with dichloromethane (10 mL), the mixture was washed with aqueous $NaHCO_3$ (3 X 5 mL) and brine (2 X 5 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography (ethyl acetate/hexanes = 1:10 to 1:2) to afford **11ae** as a white solid (344 mg, 71%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 6H), 0.93 (s, 9H), 1.21-1.23 (d, *J* = 6.2 Hz, 3H), 3.39-3.41 (m, 2H), 3.73-3.76 (m, 1H), 4.01-4.05 (m, 1H), 5.17 (s, 2H), 5.29-5.32 (d, *J* = 9.0 Hz, 1H), 7.39-7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.21, -4.24, 17.83, 20.87, 25.65, 25.79, 47.45, 55.95, 67.47,

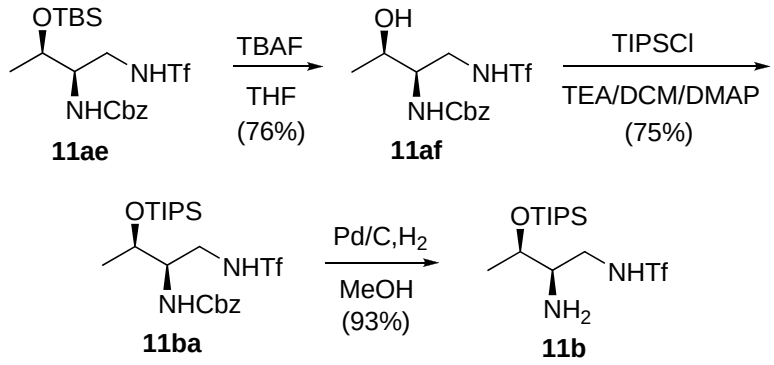
67.68, 128.05, 128.29, 128.56, 135.79, 157.65; HRMS (ESI) m/z calcd for $C_{19}H_{31}F_3N_3O_5SSi$ $[M-H]^-$ 483.1602, found 483.1580.

N-((2*R*,3*R*)-2-Amino-3-(*tert*-butyldimethylsilyloxy)butyl)trifluoromethanesulfonamide **11a**

To the solution of carbamate **11ae** (194 mg, 0.4 mmol) in methanol (3 mL) was added 10% Pd/C (20 mg). The flask was then flushed with hydrogen, and a hydrogen balloon was connected. After the mixture was stirred for one hour, the catalyst was removed by filtration through Celite, the filtrate was concentrated *in vacuo* to yield **11a** as a white solid (113 mg, 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 1.15-1.17 (d, *J* = 6.2 Hz, 3H), 2.69-2.75 (m, 1H), 3.04-3.11 (m, 1H), 3.17 (s, 3H), 3.29-3.33 (m, 1H), 3.74-3.77 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.82, 20.04, 25.62, 29.59, 46.95, 56.57, 69.49, 117.68, 121.95; HRMS (ESI) m/z calcd for $C_{11}H_{25}F_3N_2O_3SSi$ $[M+H]^+$ 351.1375, found 351.1374.

B2. Preparation of L-threonine-derived catalyst **11b**



Benzyl (2*R*,3*R*)-3-hydroxy-1-(trifluoromethylsulfonamido)butan-2-ylcarbamate **11af**

To a stirred solution of **11ae** (484 mg, 1.0 mmol) in THF was added TBAF (1M in THF, 3 mL). After stirring at room temperature for 5 hours, the solvent was removed. The residue was

taken up in ethyl acetate (30 mL), and s washed with water (3 X 15 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under the reduced pressure to afford the crude product, which was purified by flash column chromatography (ethyl acetate/hexanes = 1:10 to 1:4) to afford the desired product as a white solid (281 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.22 (d, *J* = 6.3 Hz 6H), 3.34-3.42 (m, 2H), 3.65-3.67 (m, 1H), 4.04-4.06 (m, 1H), 4.39 (br, 2H), 5.10 (s, 2H), 5.50-5.53 (d, *J* = 9.0 Hz, 1H), 7.30-7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.30, 46.24, 55.06, 66.55, 67.39, 117.55, 121.80, 127.87, 128.27, 128.54, 135.72, 157.37; HRMS (ESI) m/z calcd for $C_{13}H_{17}F_3N_2O_5S$ $[M-H]^-$ 369.0733, found 369.0729.

Benzyl(2*R*,3*R*)-1-(trifluoromethylsulfonamido)-3-(triisopropylsilyloxy)butan-2-ylcarbamate **11ba**

Chlorotriisopropylsilane (134 mg, 0.7 mmol) was added to a solution of alcohol **11af** (178 mg, 0.5 mmol), triethylamine (0.14 mL, 1.0 mmol) and DMAP (12 mg, 0.1 mmol) in anhydrous dichloromethane (5 mL) at 0 ^{o}C. The mixture was then allowed to stir at room temperature for 5 hours and diluted with dichloromethane (10 mL). The mixture was washed with water (3 X 10 mL) and brine (2 X 10 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography (ethyl acetate/hexanes = 1:10 to 1:3) to afford **11ba** as a colorless oil (197 mg, 75%).

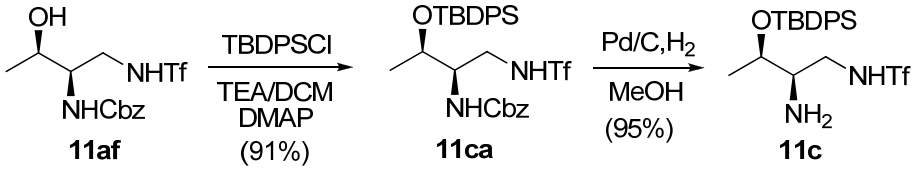
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (m, 21H), 1.27-1.30 (m, 3H), 3.47-3.51 (m, 2H), 3.70-3.79 (m, 1H), 4.15-4.17 (m, 1H), 5.17 (s, 2H), 5.26-5.29 (d, *J* = 8.6 Hz, 1H), 7.39-7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.47, 17.95, 18.00，20.81，47.86, 56.00, 67.47，68.62，117.56, 121.82, 128.06，128.30，128.55，135.79, 157.70; HRMS (ESI) m/z calcd for $C_{22}H_{37}F_3N_2O_5S$ Si $[M+Na]^+$ 549.2043, found 549.2041.

N-((2*R*,3*R*)-2-Amino-3-(triisopropylsilyloxy)butyl)trifluoromethanesulfonamide **11b**

Following the same procedure as described for the preparation of **11a**, **11b** was obtained as a white solid (73 mg, 93%) from the carbamate **11ba** (105 mg, 0.2mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (m, 21H), 1.21-1.23 (d, *J* = 8.4 Hz, 3H), 2.70-2.74 (m, 4H), 3.12-3.19 (m, 1H), 3.33-3.39 (m, 1H), 3.93-3.96 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.51, 17.97, 18.03，19.76，46.76, 56.47, 70.22，117.65, 121.92; HRMS (ESI) m/z calcd for $C_{14}H_{31}F_3N_2O_3SSi$ $[M+H]^+$ 393.1838, found 393.1842.

B3. Preparation of L-threonine-derived catalyst **11c**



Benzyl 3-(*tert*-butyldiphenylsilyloxy)-1-(trifluoromethylsulfonamido)butan-2-ylcarbamate **11ca**

Following the same procedure as described for the preparation of **11ba**, the carbamate **11ca** was obtained as a colorless oil (278 mg, 91% yield) from the alcohol **11af** (178 mg, 0.5mmol).

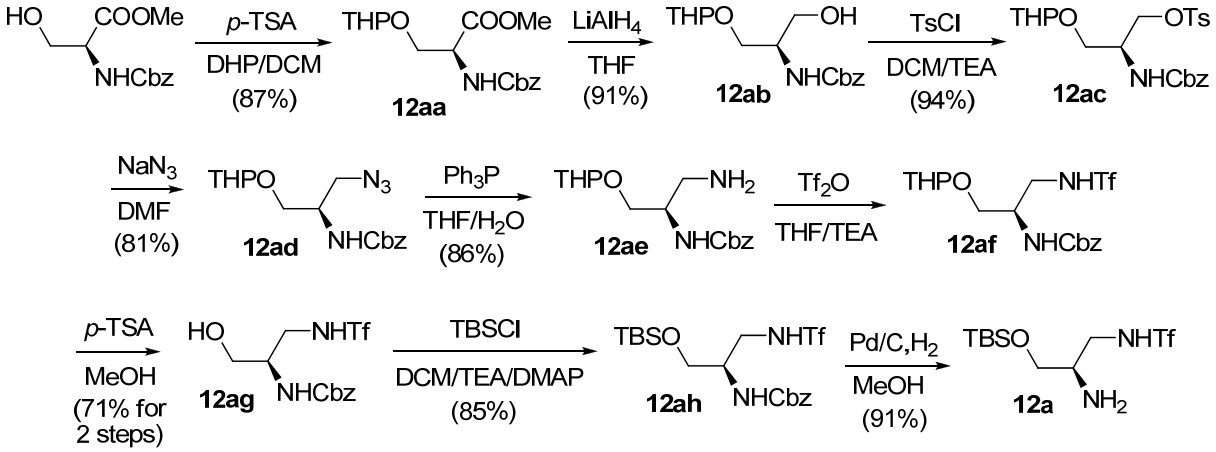
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08-1.12 (m, 12H), 3.10-3.12 (m, 1H), 3.40-3.43 (m, 1H), 3.64-3.65 (m, 1H), 3.88-3.89 (m, 1H), 5.14 (s, 2H), 5.29-5.31 (d, *J* = 8.8 Hz, 1H), 7.39-7.49 (m, 11H), 7.63-7.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.24, 20.83, 27.06, 47.43, 56.31, 67.56, 67.80, 80.49, 127.71, 128.11, 128.18, 128.40, 128.70, 130.05, 130.37, 132.34, 133.30, 135.87, 135.90, 157.75, 173.18; HRMS (ESI) m/z calcd for $C_{29}H_{35}F_3N_2O_5SSi$ $[M-H]^-$ 607.1915, found 607.1931.

N-((2R,3*R*)-2-Amino-3-(tert-butyldiphenylsilyloxy)butyl)trifluoromethanesulfonamide **11c**

Following the same procedure as described for the preparation of **11a**, the catalyst **11c** was obtained as a colorless oil (180 mg, 95% yield) from the carbamate **11ca**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 12H), 2.65-2.71 (m, 1H), 3.04-3.16 (m, 5H), 3.72-3.75 (m, 1H), 7.39-7.45 (m, 6H), 7.63-7.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.21, 19.75, 27.01, 25.79, 46.63, 56.82, 70.62, 127.58, 127.89, 129.84, 130.08, 132.84, 133.61, 135.71, 135.79; HRMS (ESI) m/z calcd for $C_{21}H_{29}F_3N_2O_3SSi$ $[M+Na]^+$ 475.1702, found 475.1710.

B4. Preparation of L-serine-derived catalyst **12a**



(2*S*)-Methyl 2-(benzyloxycarbonyl)-3-(tetrahydro-2H-pyran-2-yloxy)propanoate **12aa**

To a stirred solution of (*S*)-methyl 2-(benzyloxycarbonyl)-3-hydroxypropanoate (5.06 g, 20.0 mmol) and freshly distilled dihydropyran (10 mL) in anhydrous dichloromethane (50 mL) was added *p*-toluenesulfonic acid monohydrate (95 mg, 0.5 mmol). After stirring at room temperature for 3 hours, triethylamine (3 mmol, 0.42 mL) was added the reaction mixture. The reaction mixture was concentrated, and the residue was taken up in EtOAc (100 mL). The organic extracts were washed with brine (3 X 50 mL), and dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography (ethyl acetate /hexanes = 1/15 to 1/5) to afford the desired product as a white solid (5.86 g, 87%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51-1.55 (m, 6H), 3.44-3.51 (m, 1H), 3.75-3.79 (m, 4.5H), 3.96-3.97 (m, 1H), 4.16-4.19 (m, 0.5H), 4.55-4.61 (m, 2H), 5.16 (s, 2H), 5.70-5.92 (m, 1H), 7.35-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.83, 19.29, 25.08, 25.17, 30.03, 30.28, 52.35, 52.39, 54.14, 54.39, 61.65, 62.47, 66.89, 66.98, 67.09, 68.04, 98.43, 98.44, 128.00, 128.04, 128.11, 128.41,

128.44, 136.18, 155.95, 170.69, 170.82; HRMS (ESI) m/z calcd for $C_{17}H_{23}NO_6$ $[M+Na]^+$ 360.1418, found 360.1435.

Benzyl (*R*)-1-hydroxy-3-(tetrahydro-2H-pyran-2-yloxy)propan-2-ylcarbamate **12ab**

$LiAlH_4$ (760 mg, 20.0 mmol) was added to a solution of **12aa** (3.37 g, 10.0 mmol) in anhydrous tetrahydrofuran (40 mL) at -20 ^oC. After stirring at the same temperature for 1 hour, the excess of the hydride was destroyed by slow addition of water (10.0 mL). The reaction mixture was filtered through Celite, and the filtrate was concentrated *in vacuo*. Water (60 mL) was added to the residue, and the aqueous layer was extracted with ethyl acetate several times (3 X 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1:5 to 1:2) afforded the desired product as a colorless oil (2.81 g, 91%).

^1H NMR (300 MHz, $CDCl_3$) δ 1.48-1.51 (m, 4H), 1.72-1.81 (m, 2H), 3.13-3.15 (m, 1H), 3.51-3.71 (m, 3H), 3.80-3.94 (m, 4H), 4.55-4.57 (m, 1H), 5.13 (s, 2H), 5.52-5.63 (m, 1H), 7.35-7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.64, 25.11, 30.39, 30.55, 52.06, 62.59, 62.83, 62.96, 63.19, 66.71, 66.77, 67.23, 67.46, 99.45, 99.86, 127.98, 128.02, 128.06, 128.41, 128.44, 136.32, 136.38, 156.37. HRMS (ESI) m/z calcd for $C_{16}H_{23}NO_5$ $[M+Na]^+$ 332.1468, found 332.1475.

(*S*)-2-(Benzyloxycarbonyl)-3-(tetrahydro-2H-pyran-2-yloxy)propyl-4-methylbenzeneSulfonate **12ac**

Following the same procedure as described for the preparation of **11aa**, tosylate **12ac** was obtained as a colorless oil (4.35 g, 94% yield) from **12ab** (3.09 g, 10.0 mmol).

^1H NMR (300 MHz, $CDCl_3$) δ 1.39-1.51 (m, 6H), 2.39 (s, 3H), 3.35-3.52 (m, 2H), 3.67-3.80 (m, 2H), 4.06-4.18 (m, 3H), 4.40-4.46 (m, 1H), 5.03 (s, 2H), 5.16-5.34 (m, 1H), 7.28-7.37 (m, 7H), 7.73-7.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.16, 19.05, 19.52, 20.98, 21.58, 25.13, 25.18, 28.14,

30.17, 30.32, 49.50, 60.33, 61.99, 62.66, 65.16, 65.56, 66.90, 67.74, 68.18, 98.79, 99.51, 127.93, 128.03, 128.17, 128.51, 129.86, 132.63, 136.16, 144.93, 155.65; HRMS (ESI) m/z calcd for $C_{23}H_{29}NO_7S$ $[M+Na]^+$ 486.1557, found 486.1583.

Benzyl (*R*)-3-azido-1-(tetrahydro-2H-pyran-2-yloxy)propan-2-ylcarbamate **12ad**

Following the same procedure as described for the preparation of **11ab**, azide **12ad** was obtained as a colorless oil (1.35 g, 81% yield) from tosylate **12ac** (1.67 g, 5.0 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47-1.53 (m, 4H), 1.70-1.78 (m, 2H), 3.46-3.55 (m, 4H), 3.61-3.83 (m, 2H), 3.85-3.94 (m, 1H), 4.54-4.57 (m, 1H), 5.10 (s, 2H), 5.25-5.46 (m, 1H), 7.30-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.24, 19.69, 25.12, 25.18, 30.27, 30.45, 50.29, 51.34, 51.62, 62.23, 62.88, 66.20, 66.76, 66.88, 98.91, 99.67, 128.03, 128.09, 128.14, 128.46, 128.48, 136.22, 136.30, 155.77; HRMS (ESI) m/z calcd for $C_{16}H_{22}N_4O_4$ $[M+Na]^+$ 357.1547, found 357.1542.

Benzyl (*R*)-1-amino-3-(tetrahydro-2H-pyran-2-yloxy)propan-2-ylcarbamate **12ae**

Following the same procedure as described for the preparation of **11ad**, amine **12ae** was obtained as a colorless oil (1.06 g, 86% yield) from azide **12ad** (1.34 g, 4.0 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26-1.29 (m, 2H), 1.47-1.53 (m, 4H), 1.67-1.71 (m, 2H), 2.84-2.86 (d, *J* = 5.9 Hz, 2H), 3.41-3.60 (m, 2H), 3.71-3.84 (m, 3H), 4.52-4.54 (m, 1H), 5.10 (s, 2H), 5.48-5.63 (m, 1H), 7.30-7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.34, 19.69, 25.17, 25.22, 30.34, 30.51, 43.01, 43.31, 52.85, 62.22, 62.72, 66.20, 66.49, 66.57, 67.38, 67.66, 98.88, 99.51, 127.93, 127.99, 128.38, 128.40, 136.48, 136.56, 156.26; HRMS (ESI) m/z calcd for $C_{16}H_{24}N_2O_4$ $[M+H]^+$ 309.1809, found 309.1808.

Benzyl(*R*)-1-(tetrahydro-2H-pyran-2-yloxy)-3-(trifluoromethylsulfonamido)propan-2-ylcarbamate **12af**

Following the same procedure as described for the preparation of **11ae**, the curde sulfonamide **12af** was obtained as a white solid from amine **12ae** (310 mg, 1.0 mmol). The crude product was used directly in the next step.

(*R*)-Benzyl 1-hydroxy-3-(trifluoromethylsulfonamido)propan-2-ylcarbamate **12ag**

p-Toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) was added to the crude sulfonamide **12af** in methanol (5 mL). After stirring at room temperature for 4 hours, the solvent was evaporated to afford the crude product, which was purified by flash column chromatography (ethyl acetate/hexanes = 1:5 to 1:2) to afford **12ag** as a colorless oil (0.25 g, 71% for two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33-3.39 (m, 2H), 3.64-3.71 (m, 2H), 3.81-3.82 (m, 1H), 5.09 (s, 2H), 5.75-5.77 (d, *J* = 4.9 Hz, 1H), 7.29-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.88, 52.14, 61.81, 62.46, 118.47, 121.02, 127.93, 128.40, 128.64, 135.76, 157.20; HRMS (ESI) m/z calcd for $C_{12}H_{15}F_3N_2O_5S$ $[M-H]^-$ 355.0576, found 355.0564.

(*R*)-Benzyl-1-(*tert*-butyldimethylsilyloxy)-3-(trifluoromethylsulfonamido)propan-2-ylcarbamate **12ah**

Following the same procedure as described for the preparation of **11ba**, the carbamate **12ah** was obtained as a colorless oil (0.8 g, 85% yield) from the alcohol **12ag** (720 mg, 2.0 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.93 (s, 9H), 3.47-3.52 (m, 2H), 3.74-3.81 (m, 2H), 3.91-3.93 (m, 1H), 5.16 (s, 2H), 5.33-5.36 (d, *J* = 8.0 Hz, 1H), 6.53 (br, 1H), 7.35-7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.69, 18.09, 25.70, 29.66, 46.77, 51.27, 63.51, 67.41, 117.59, 121.85, 128.15, 128.35, 128.59, 135.82, 156.84; HRMS (ESI) m/z calcd for $C_{18}H_{29}F_3N_2O_5SSi$ $[M+Na]^+$ 493.1411, found 493.1418.

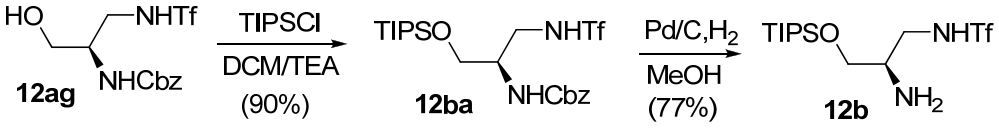
(*R*)-*N*-(2-Amino-3-(*tert*-butyldimethylsilyloxy)propyl)trifluoromethanesulfonamide **12a**

Following the same procedure as described for the preparation of **11a**, the catalyst **12a** was obtained as a white solid (153 mg, 91% yield) from the carbamate **12ah** (235 mg, 0.5 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.90 (s, 9H), 3.07-3.09 (m, 1H), 3.14-3.18 (m, 1H), 3.35-3.39 (m, 1H), 3.57-3.61 (m, 1H), 3.94 (br, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.63, -5.61, 18.15,

25.74, 46.74, 52.52, 65.541, 118.76, 1218.32; HRMS (ESI) m/z calcd for $C_{10}H_{23}F_3N_2O_3SSi$ $[M+H]^+$ 337.1230, found 337.1230.

B5. Preparation of L-serine-derived catalyst **12b**



(*R*)-Benzyl3-(trifluoromethylsulfonamido)-1-(triisopropylsilyloxy)propan-2-ylcarbamate **12ba**

Following the same procedure as described for the preparation of **11ba**, carbamate **12ba** was obtained as a colorless oil (230 mg, 90% yield) from alcohol **12ag** (178 mg, 0.5mmol).

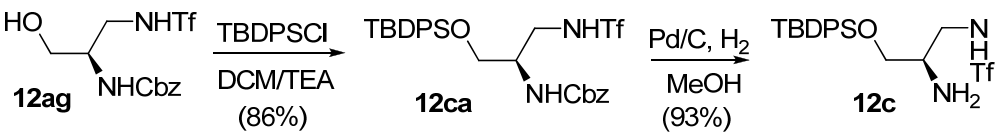
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05-1.11 (m, 21H), 3.47-3.51 (m, 2H), 3.80-3.88 (m, 3H), 5.12 (s, 2H), 5.36-5.39 (m, 1H), 7.34-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.64, 17.76, 46.74, 51.46, 64.04, 67.30, 117.57, 121.83, 127.97, 128.22, 128.51, 135.84, 156.81; HRMS (ESI) m/z calcd for $C_{21}H_{35}F_3N_2O_5SSi$ $[M+Na]^+$ 535.1880, found 535.1868.

(*R*)-N-(2-amino-3-(triisopropylsilyloxy)propyl)trifluoromethanesulfonamide **12b**

Following the same procedure as described for the preparation of **11a**, the catalyst **12b** was obtained as a colorless oil (116 mg, 77% yield) from carbamate **12ba** (205 mg, 0.4mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (m, 21H), 3.08-3.21 (m, 2H), 3.36-3.40 (m, 1H), 3.68-3.70 (m, 2H), 4.17 (br, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.70, 17.78, 46.88, 52.49, 66.15, 117.73, 122.00; HRMS (ESI) m/z calcd for $C_{13}H_{29}F_3N_2O_3SSi$ $[M+H]^+$ 379.1702, found 379.1707.

B6. Preparation of L-serine-derived catalyst **12c**



(*R*)-Benzyl1-(*tert*-butyldiphenylsilyloxy)-3-(trifluoromethylsulfonamido)propan-2-ylcarbamate

12ca

Following the same procedure as described for the preparation of **11ba**, the carbamate **12ca** was obtained as a white solid (255 mg, 86% yield) from alcohol **12ag** (178 mg, 0.5mmol).

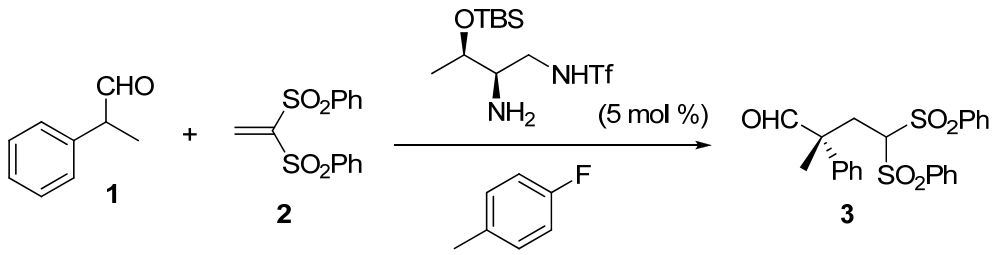
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (s, 9H), 3.44-3.46 (m, 2H), 3.78-3.88 (m, 3H), 5.12-5.14 (d, *J* = 2.8 Hz, 2H), 5.28-5.31 (m, 1H), 6.53 (br, 1H), 7.40-7.47 (m, 11H), 7.64-7.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.10, 26.78, 46.46, 51.70, 63.71, 67.35, 117.59, 127.98, 128.00, 128.05, 128.26, 128.52, 130.16, 130.21, 132.10, 132.19, 135.39, 135.44, 135.80, 156.85; HRMS (ESI) m/z calcd for $C_{38}H_{33}F_3N_2O_5SSi$ $[M+Na]^+$ 617.1724, found 617.1716.

(*R*)-*N*-(2-Amino-3-(*tert*-butyldiphenylsilyloxy)propyl)trifluoromethanesulfonamide **12c**

Following the same procedure as described for the preparation of **11a**, the catalyst **12c** was obtained as a colorless oil (171 mg, 93% yield) from carbamate **12ca** (238 mg, 0.4mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 9H), 3.10-3.18 (m, 6H), 3.38-3.41 (m, 1H), 3.61-3.63 (m, 2H), 7.42-7.50 (m, 6H), 7.66-7.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.11, 26.74, 46.72, 52.25, 66.53, 127.84, 129.99, 132.60, 135.43; HRMS (ESI) m/z calcd for $C_{20}H_{27}F_3N_2O_3SSi$ $[M+H]^+$ 461.1537, found 461.1544.

C. Representative Procedure

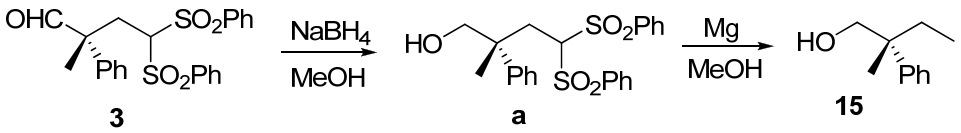


1,1-Bis(benzenesulfonyl)ethylene **2** (15.4 mg, 0.05 mmol) was added to a mixture of 2-phenylpropanal **2** (14 mg, 0.10 mmol) and *N*-((2*R*,3*R*)-2-amino-3-(*tert*-butyldimethylsilyloxy)butyl)-trifluoromethanesulfonamide **11a** (0.9 mg, 0.0025mmol) in *para*-fluorotoluene (0.8 mL) in a

sample vial at room temperature. The vial was then sealed, and the reaction mixture was stirred for 4 hours and then quenched by addition of 1N aqueous HCl (2 mL). The mixture was extracted with ethyl acetate several times (3 x 3 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1:5 to 1:2) to afford **3** as a white solid (20 mg, 93%). The enantiometric excess of **3** was determined by chiral HPLC analysis.

D. Preparation of Chiral Alcohol 15, Acid 16 & Determination of the Absolute Configuration of the Conjugate Addition Products

D1. Conversion of Michael adduct to Alcohol and Absolute Configuration Determination



3 **a** **15**

Following the representative procedure illustrated in section B, Michael addition of 2-phenyl propanal to vinyl sulfone **2** yielded the adduct **3**, which was reduced to the alcohol **a** by $NaBH_4$. Removal of sulfone groups afforded the alcohol **15**, the configuration of which was determined by comparing the specific rotation value with that in the literature.[2]

(*R*)-2-Methyl-2-phenyl-4,4-bis(phenylsulfonyl)butan-1-ol **a**

$NaBH_4$ (24 mg, 0.5 mmol) was added to the aldehyde **3** (133 mg, 0.3 mmol) in methanol (3 mL) at 0 °C. After one hour, the methanol was removed and saturated NH_4Cl solution (4 mL) was added to the mixture. The aqueous phase was extracted with ethyl acetate several times (3 x 5 mL), and the organic extracts were combined and dried over Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography (EtOAc/Hexanes = 1:5 to 1:3) to afford **a** as a colorless oil (128 mg, 96%).

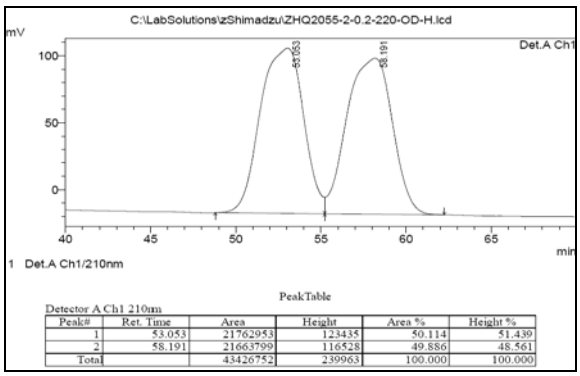
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (s, 3H), 2.65-2.72 (m, 3H), 3.72-3.74 (d, *J* = 12.0 Hz, 1H), 4.07-4.09 (d, *J* = 12.0 Hz, 1H), 4.74-4.76 (m, 1H), 7.27-7.29 (m, 1H), 7.35-7.39 (m, 4H), 7.47-7.52 (m,

4H), 7.62-7.68 (m, 4H), 7.78-7.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.79, 32.43, 42.94, 68.77, 81.27, 126.83, 126.99, 128.66, 128.97, 129.03, 129.65, 129.91, 134.42, 134.56, 137.69, 137.85, 143.78; $[\alpha]_D$ = - 0.78 (c = 0.40, $CHCl_3$); HRMS (ESI) m/z calcd for $C_{23}H_{24}O_5S_2$ $[M+Na]^+$ 467.0957, found 467.0963.

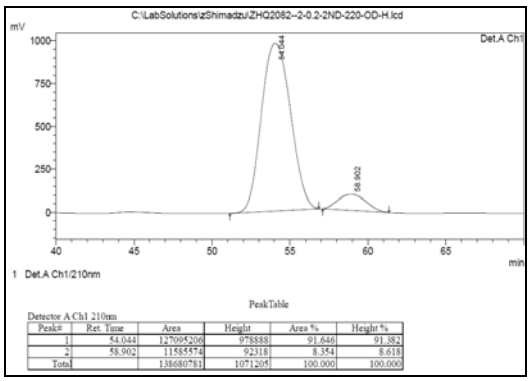
(*R*)-2-Methyl-2-phenylbutan-1-ol **15**

The activated magnesium metal (108 mg, 4.5 mmol) was added into a solution of compound **a** (85 mg, 0.15 mmol) in anhydrous methanol (10 mL) with stirring. After 30 minutes, the reaction mixture was brought to gentle reflux for 2 hrs. After cooling down to room temperature, the mixture was poured into an aqueous solution of 2 N HCl (10 mL), and extracted with diethyl ether (3 X 10 mL). The organic extracts were combined, dried over Na_2SO_4 and filtered. Solvent was removed *in vacuo*, and the residue was purified by column chromatography (ethyl acetate /hexanes = 1/15 to 1/5) to afford **15** as a colorless oil (35 mg, 83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74-0.79 (t, *J* = 7.4 Hz, 3H), 1.38 (s, 3H), 1.58-1.65 (m, 1H), 1.81-1.89 (m, 1H), 3.57-3.61 (d, *J* = 10.8 Hz, 1H), 3.76-3.79 (d, *J* = 10.8 Hz, 1H), 7.19-7.24 (m, 1H), 7.29-7.42 (m, 4H); $[\alpha]_D$ = - 3.6 (c = 0.80, $CHCl_3$, *lit*^{2} $_{neat}$ = - 1.77); The ee value of **15** is 83%, t_R (major) = 53.1 min, t_R (minor) = 58.2 min (Chiralcel OD-H, λ = 220 nm, 2% *i*PrOH/hexanes, flow rate = 0.2 mL/min).

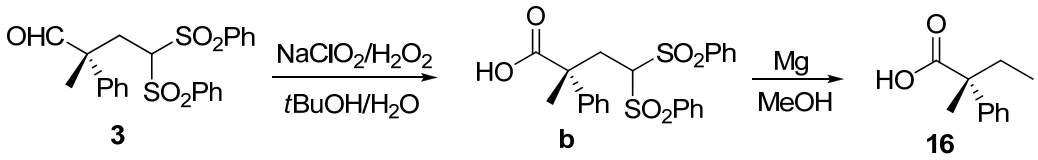


Racemic **15**



Enantiomeric enriched **15**

D2. Conversion of Michael adduct to Chiral Carboxylic Acid 16



3 b 16

(*R*)-2-Methyl-2-phenyl-4,4-bis(phenylsulfonyl)butanoic acid **b**

To a stirred solution of the (*R*)-2-benzyl-4,4-bis(phenylsulfonyl)butanal **3** (133 mg, 0.30 mmol) in a mixture of *tert*-butanol/water (4.0 mL, v/v = 1:1) were added sodium chlorite (78.0 mg, 0.90 mmol) and 30% aqueous solution of H_2O_2 (0.17 mL, 1.50 mmol), and the resulting mixture was stirred at room temperature for 3 hours. The reaction mixture was then concentrated, and the residue was taken up in ethyl acetate (10 mL), washed with water (2 x 5 mL). The organic extract was dried over Na_2SO_4 and concentrated, and the residue was purified by column chromatography (ethyl acetate /hexanes = 1/2 to ethyl acetate) to afford the desired acid product **b** as a white foam (120 mg, 87%).

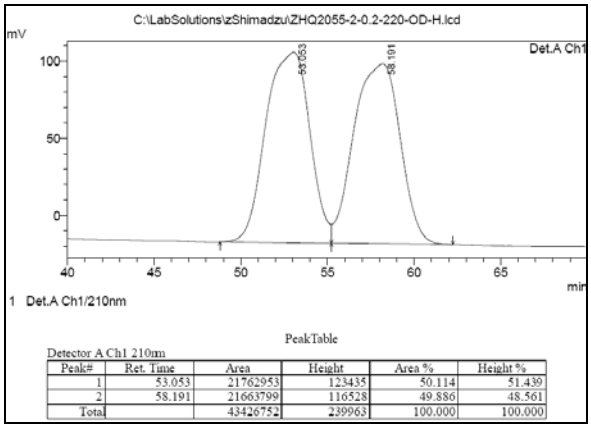
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 3H), 2.83-2.91 (m, 1H), 3.17-3.24 (m, 1H), 4.52-4.54 (m, 1H), 7.27-7.29 (m, 5H), 7.46-7.69 (m, 8H), 7.94-7.97 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.94, 32.64, 49.67, 80.77, 127.07, 127.70, 128.60, 128.91, 129.33, 130.15, 134.24, 134.52, 137.34, 138.02, 140.06, 180.68; $[\alpha]_D$ = - 26.3 (c = 1.70, $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{23}H_{22}O_6S_2$ $[M+Na]^+$ = 481.0750, found = 481.0756.

(*R*)-2-Methyl-2-phenylbutanoic acid **16**

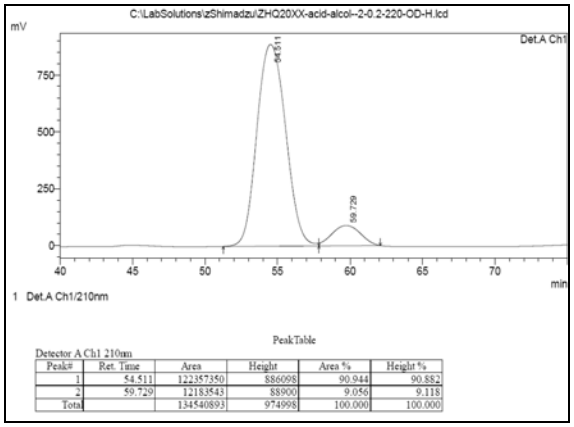
The activated magnesium metal (0.18 g, 7.5 mmol) was added into a solution of (*R*)-2-benzyl-4,4-bis(phenylsulfonyl)butanoic acid **b** (92 mg, 0.20 mmol) in anhydrous methanol (15 ml) with stirring. The mixture was heated to 50 ^{o}C to initiate continuous hydrogen generation, and then the heating was then discontinued. After 40 minutes, the reaction mixture was brought to reflux for 4 hours. After cooling down to room temperature, the mixture was poured into 2 N HCl solution (10 mL) and extracted with diethyl ether (3 X 10 mL). The organic extracts were combined, dried over Na_2SO_4 and filtered. Solvent was removed *in vacuo*, and the residue

was purified by column chromatography (ethyl acetate/hexanes = 1/10 to 1/1) to afford the desired acid as a colorless oil (30 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83-0.88 (t, *J* = 7.4 Hz, 3H), 1.56 (s, 3H), 2.00-2.10 (m, 2H), 7.34-7.37 (m, 5H); $[\alpha]_D$ = - 17.4 (c = 2.70, $CHCl_3$). For the enantiomeric excess determination, Acid **16** was difficult to be resolved by chiral HPLC analysis. Acid **16** was reduced to corresponding alcohol **15'** with $LiAH_4$, and the ee was determined accordingly. The ee value of **15'** is 82%, t_R (major) = 53.1 min, t_R (minor) = 58.2 min (Chiralcel OD-H, λ = 220 nm, 2% *i*PrOH/hexanes, flow rate = 0.2 mL/min).



Racemic **15'**



Enantiomeric enriched **15'**

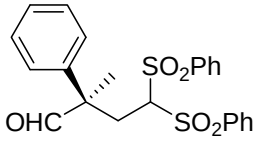
References:

[1] Baumann, T.; Vogt, H.; Bräse, S. *Eur. J. Org. Chem*. **2007**, 266.

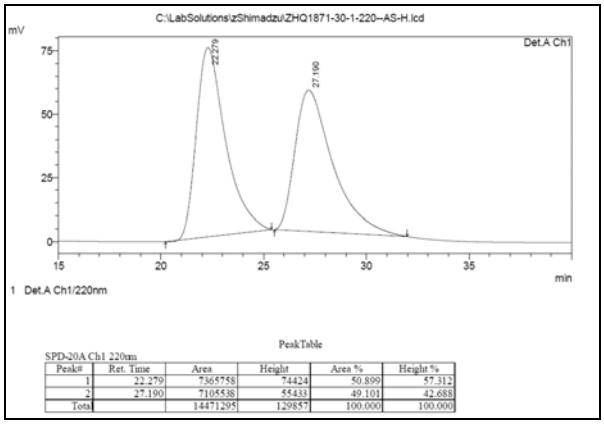
[2] Paquette, L. A.; Gilday, J. P.; Ra, C. S. *J. Am. Chem.Soc.* **1987**, *109*, 6858.

E. Analytical Data and HPLC Chromatogram of the Conjugate Addition Products

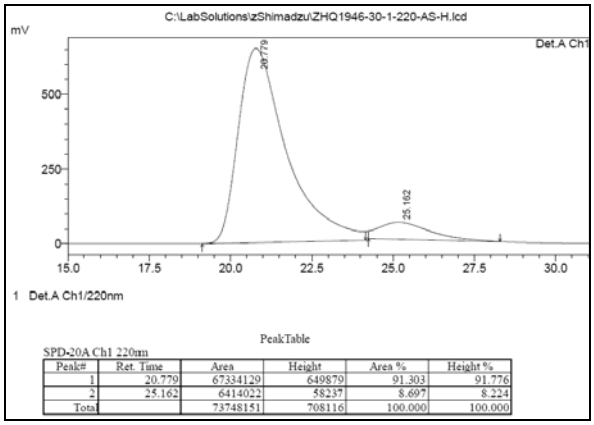
(*R*)-2-Methyl-2-phenyl-4,4-bis(phenylsulfonyl)butanal **3**



A white solid; $[\alpha]_D$ = - 1.78 (c = 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3H), 2.79-3.00 (m, 2H), 4.41-4.44 (m, 1H), 7.24-7.27 (m, 2H), 7.40-7.56 (m, 7H), 7.64-7.67 (m, 4H), 7.85-7.87 (m, 2H), 9.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.54, 30.84, 53.03, 80.14, 127.55, 128.06, 129.03, 129.04, 129.22, 129.63, 129.71, 134.51, 134.54, 137.34, 137.80, 138.27, 201.26; HRMS (ESI) m/z calcd for $C_{23}H_{22}O_5S_2$ $[M+Na]^+$ 465.0801, found 465.0808; The ee value of **3** is 83%, t_R (major) = 22.3 min, t_R (minor) = 27.2 min (Chiralcel AS-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).

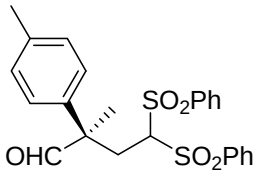


Racemic **3**

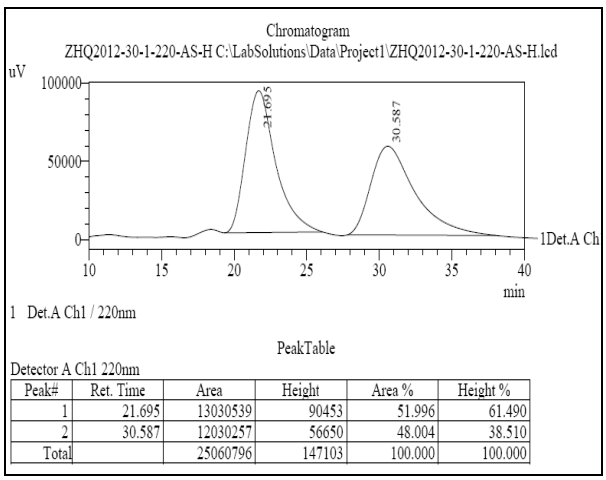


Enantiomeric enriched **3**

(*R*)-2-Methyl-4,4-bis(phenylsulfonyl)-2-p-tolylbutanal **14a**



A white solid; $[\alpha]_D$ = +31.0 (c = 1.40, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 3H), 2.39 (s, 3H), 2.75-2.96 (m, 2H), 4.40-4.43 (m, 1H), 7.12-7.15 (m, 2H), 7.21-7.24 (m, 2H), 7.26-7.58 (m, 4H), 7.64-7.6 (m, 4H), 7.86-7.89 (m, 2H), 9.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.51, 20.92, 30.80, 52.75, 80.31, 127.44, 128.96, 129.71, 129.76, 129.85, 134.43, 135.11, 137.42, 137.84, 137.91, 201.26; HRMS (ESI) m/z calcd for $C_{24}H_{24}O_5S_2$ $[M+Na]^+$ 479.0948, found 79.0942; The ee value of **14a** is 81%, t_R (major) = 21.7 min, t_R (minor) = 30.6 min (Chiralcel AS-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

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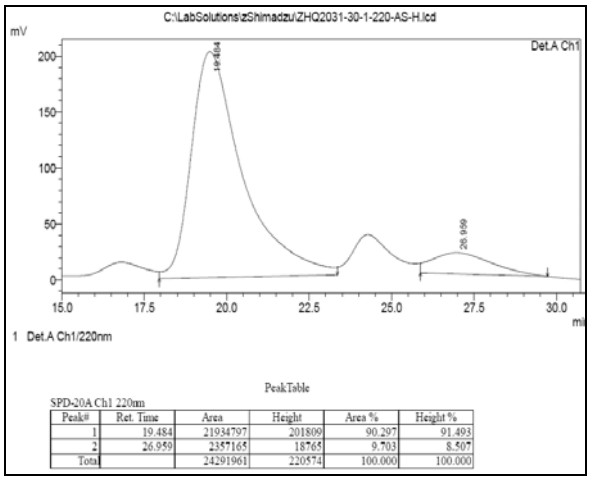
2	30.587	12030257	56650	48.004	38.510
Total		25060796	147103	100.000	100.000



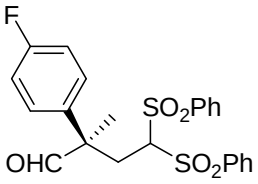
PeakTable

SPD-20A Ch1 220nm

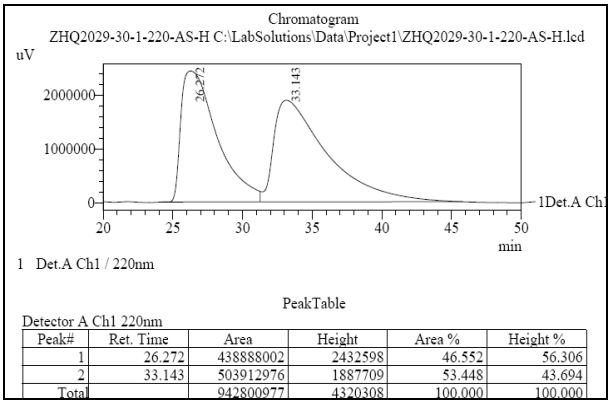
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.484	21934797	201809	90.297	91.493
2	26.959	2357165	18765	9.703	8.507
Total		24291961	220574	100.000	100.000

Racemic **14a** Enantiomeric enriched **14a**

(*R*)-2-(4-Fluorophenyl)-2-methyl-4,4-bis(phenylsulfonyl)butanal **14b**



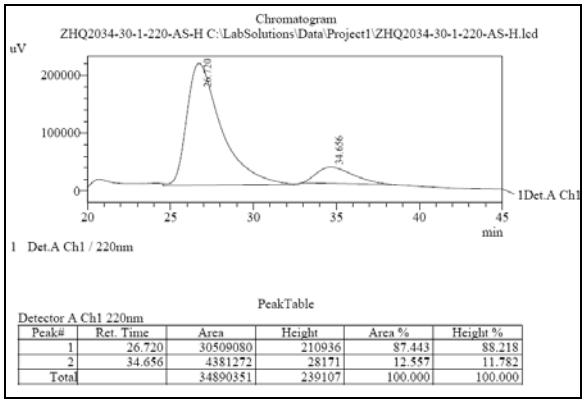
A white solid; $[\alpha]_D$ = +18.8 (c = 1.83, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 3H), 2.80-2.98 (m, 2H), 4.41-4.44 (m, 1H), 7.15-7.18 (m, 2H), 7.27-7.29 (m, 2H), 7.54-7.62 (m, 4H), 7.72-7.75 (m, 4H), 7.89-7.92 (m, 2H), 9.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.72, 31.15, 52.55, 80.14, 115.95, 116.24, 129.04, 129.26, 129.37, 129.66, 129.71, 134.07, 134.56, 137.30, 137.73, 200.84; HRMS (ESI) m/z calcd for $C_{23}H_{21}FO_5S_2$ $[M+Na]^+$ 483.0707, found 483.0710; The ee value of **14b** is 75%, t_R (major) = 26.3 min, t_R (minor) = 33.1 min (Chiralcel AS-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.272	438888002	2432598	46.552	56.306
2	33.143	503912976	1887709	53.448	43.694
Total		942800977	4320308	100.000	100.000



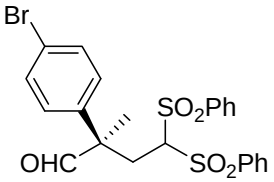
PeakTable

Detector A Ch1 220nm

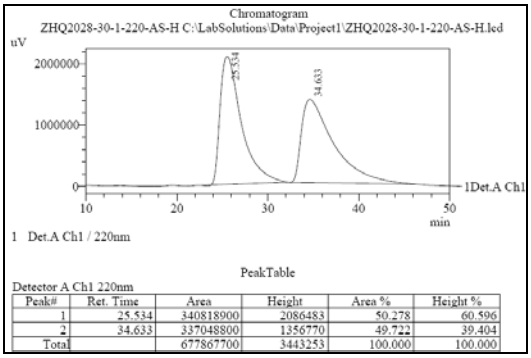
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.720	30509080	210936	87.443	88.218
2	34.656	4381272	28171	12.557	11.782
Total		34890351	239107	100.000	100.000

Racemic **14b** Enantiomeric enriched **14b**

(*R*)-2-(4-Bromophenyl)-2-methyl-4,4-bis(phenylsulfonyl)butanal **14c**



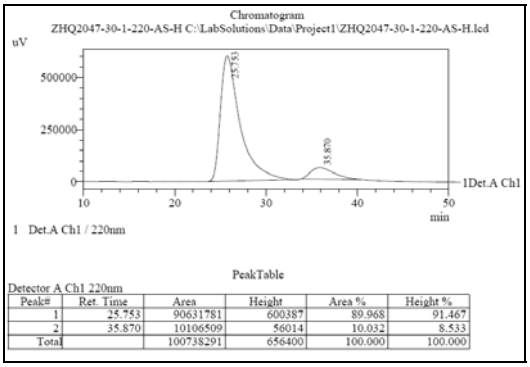
A white solid; $[\alpha]_D$ = -125.4 (c = 1.50, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 3H), 2.80-2.97 (m, 2H), 4.40-4.43 (m, 1H), 7.16-7.19 (m, 2H), 7.54-7.70 (m, 6H), 7.70-7.73 (m, 4H), 7.88-7.91 (m, 2H), 9.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.55, 31.03, 52.76, 80.11, 122.40, 129.04, 129.07, 129.24, 129.63, 129.73, 134.57, 137.28, 137.34, 137.68, 200.55; HRMS (ESI) m/z calcd for $C_{23}H_{21}BrO_5S_2$ $[M+Na]^+$ 542.9906, found 542.9906; The ee value of **14c** is 80%, t_R (major) = 25.5 min, t_R (minor) = 34.6 min (Chiralcel AS-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.534	340818900	2086483	50.278	60.596
2	34.633	337048800	1356770	49.722	39.404
Total		677867700	3443253	100.000	100.000



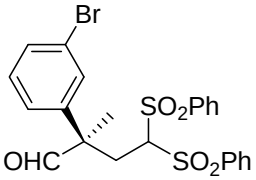
PeakTable

Detector A Ch1 220nm

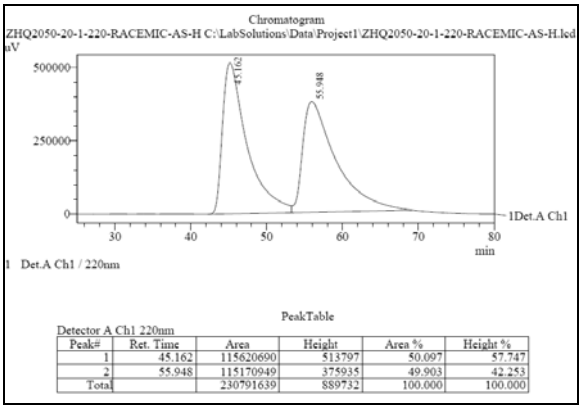
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.753	90631781	600387	89.968	91.467
2	35.870	10106509	56014	10.032	8.533
Total		100738291	656400	100.000	100.000

Racemic **14c** Enantiomeric enriched **14c**

(*R*)-2-(3-Bromophenyl)-2-methyl-4,4-bis(phenylsulfonyl)butanal **14d**

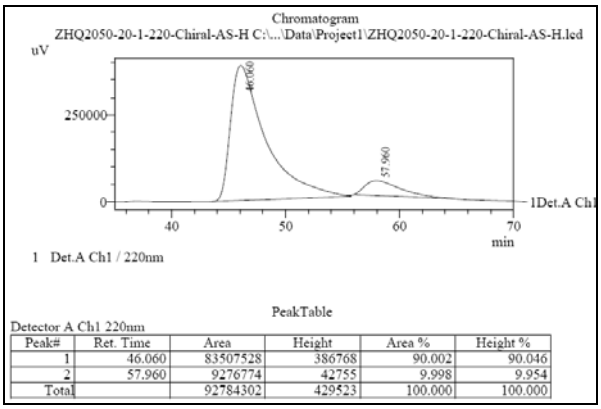


A white solid; $[\alpha]_D$ = -67.0 (c = 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 3H), 2.87-2.90 (m, 2H), 4.42-4.45 (m, 1H), 7.29-7.44 (m, 3H), 7.54-7.63 (m, 5H), 7.71-7.76 (m, 4H), 7.89-7.93 (m, 2H), 9.63 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.53, 31.15, 52.88, 79.98, 123.42, 126.36, 129.05, 129.10, 129.66, 129.71, 130.43, 130.68, 131.26, 134.56, 134.63, 137.24, 137.66, 140.91, 200.51; HRMS (ESI) m/z calcd for $C_{23}H_{21}BrO_5S_2$ $[M+Na]^+$ 542.9906, found 542.9927; The ee value of **14d** is 80%, t_R (major) = 45.2 min, t_R (minor) = 55.9 min (Chiralcel AS-H, λ = 220 nm, 20% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.162	115620690	513797	50.097	57.747
2	55.948	115170949	375935	49.903	42.253
Total		230791639	889732	100.000	100.000

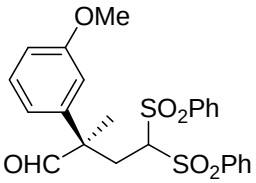


PeakTable
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.060	83507528	386768	90.002	90.046
2	57.960	9276774	42755	9.998	9.954
Total		92784302	429523	100.000	100.000

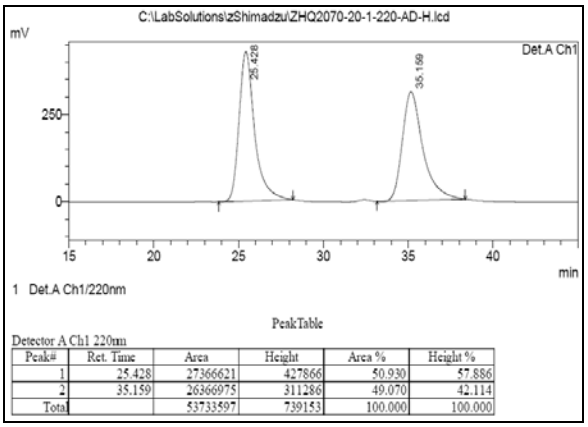
Racemic **14d** Enantiomeric enriched **14d**

(*R*)-2-(3-Methoxyphenyl)-2-methyl-4,4-bis(phenylsulfonyl)butanal **14e**



A colorless oil; $[\alpha]_D$ = +2.86 (c = 1.40, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3H), 2.74-2.98 (m, 2H), 3.83 (s, 3H), 4.41-4.44 (m, 1H), 6.79-6.92 (m, 3H), 7.31-7.34 (m, 1H), 7.46-7.69 (m, 8H),

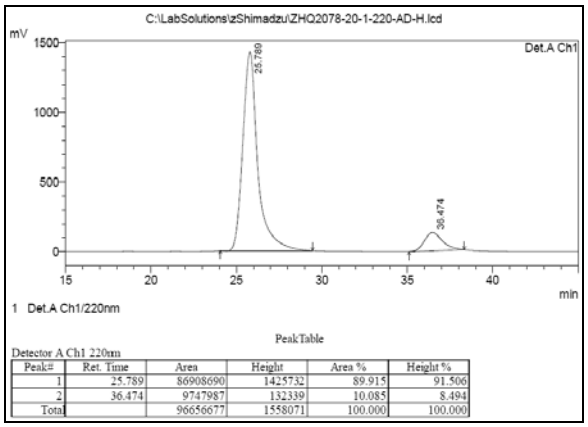
7.87-7.89 (m, 2H), 9.58 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.60, 30.77, 53.10, 55.30, 80.27, 113.23, 113.80, 119.70, 129.02, 129.70, 129.80, 130.22, 134.50, 201.07; HRMS (ESI) m/z calcd for $C_{24}H_{24}O_6S_2$ $[M+Na]^+$ 495.0907, found 495.0906; The ee value of **14e** is 80%, t_R (major) = 25.4 min, t_R (minor) = 35.2 min (Chiralcel AD-H, λ = 220 nm, 20% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.428	27366621	427866	50.930	57.886
2	35.159	26366975	311286	49.070	42.114
Total		53733597	739153	100.000	100.000



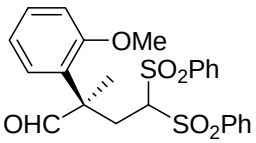
PeakTable

Detector A Ch1 220nm

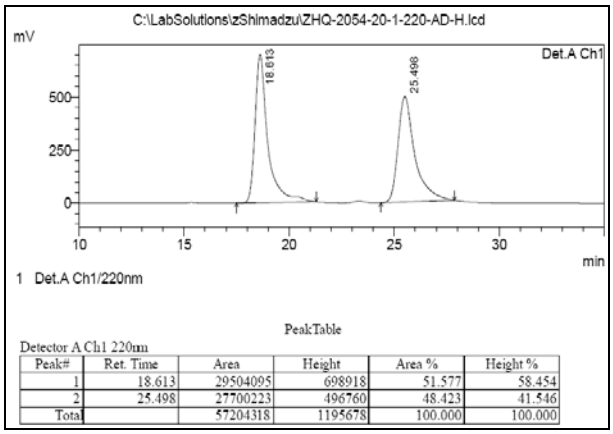
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.789	86908690	1425732	89.915	91.506
2	36.474	9747987	132339	10.085	8.494
Total		96656677	1558071	100.000	100.000

Racemic **14e** Enantiomeric enriched **14e**

(*R*)-2-(2-Methoxyphenyl)-2-methyl-4,4-bis(phenylsulfonyl)butanal **14f**



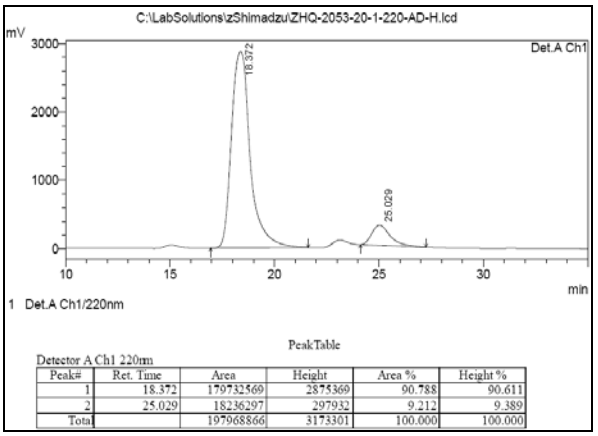
A colorless oil; $[\alpha]_D$ = -78.50 (c = 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3H), 2.71-2.78 (m, 1H), 3.17-3.24 (m, 1H), 3.82 (s, 3H), 4.37-4.40 (m, 1H), 6.96-6.99 (m, 1H), 7.12-7.14 (m, 1H), 7.33-7.34 (m, 1H), 7.45-7.73 (m, 9H), 7.97-8.00 (m, 2H), 9.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.61, 27.56, 51.11, 55.17, 80.75, 111.25, 120.84, 127.42,127.93, 128.72, 128.84, 129.41, 129.86, 130.27, 134.08, 134.40, 137.42, 138.23, 157.30, 201.27 HRMS (ESI) m/z calcd for $C_{24}H_{24}O_6S_2$ $[M+Na]^+$ 497.0907, found 497.0918; The ee value of **14f** is 82%, t_R (major) = 18.6 min, t_R (minor) = 25.5 min (Chiralcel AD-H, λ = 220 nm, 20% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.613	29504095	698918	51.577	58.454
2	25.498	27700223	496760	48.423	41.546
Total		57204318	1195678	100.000	100.000



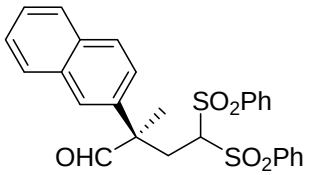
PeakTable

Detector A Ch1 220nm

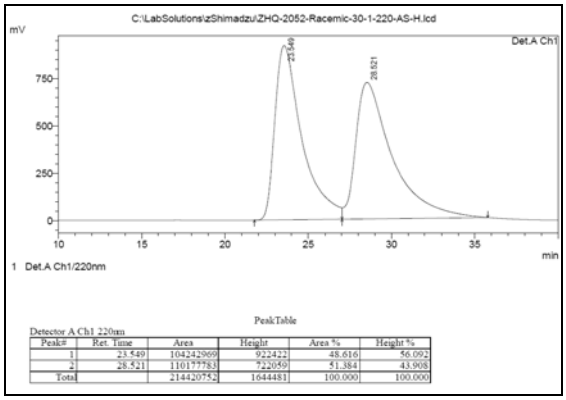
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.372	179732569	2875369	90.788	90.611
2	25.029	18236297	297932	9.212	9.389
Total		197968866	3173301	100.000	100.000

Racemic **14f** Enantiomeric enriched **14f**

(*R*)-2-Methyl-2-(naphthalen-2-yl)-4,4-bis(phenylsulfonyl)butanal **14g**



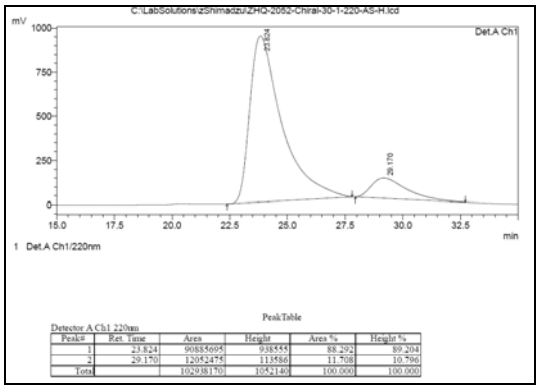
A white solid; $[\alpha]_D$ = +64.20 (c = 0.50, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3H), 2.96-3.09 (m, 2H), 4.48-4.51 (m, 1H), 7.35-7.38 (m, 3H), 7.55-7.61 (m, 7H), 7.74-7.77 (m, 2H), 7.89-7.94 (m, 5H), 9.71 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.64, 30.83, 53.29, 80.42, 125.20, 126.71, 126.78, 127.54, 128.12, 128.88, 128.95, 128.99, 129.47, 129.82, 132.62, 133.27, 134.35, 134.47, 135.47, 137.46, 137.75, 201.05; HRMS (ESI) m/z calcd for $C_{27}H_{24}O_5S_2$ $[M+Na]^+$ 515.0957, found 515.0948; The ee value of **14g** is 77%, t_R (major) = 23.5 min, t_R (minor) = 28.5 min (Chiralcel AS-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.549	104242969	922422	48.616	56.092
2	28.521	110177783	722059	51.384	43.908
Total		214420752	1644481	100.000	100.000



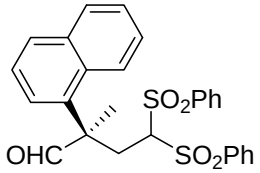
PeakTable

Detector A Ch1 220nm

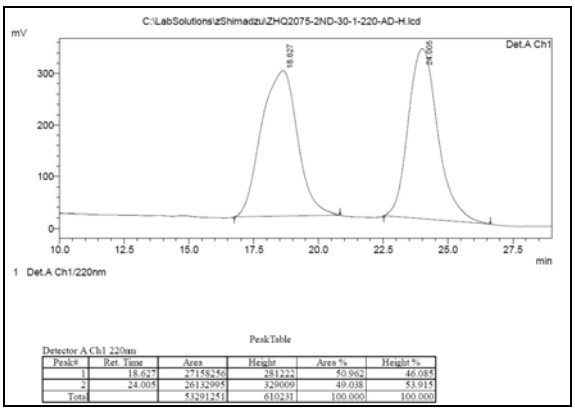
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.824	90835695	938555	88.292	89.204
2	29.170	12052475	113586	11.708	10.796
Total		102938170	1052140	100.000	100.000

Racemic **14g** Enantiomeric enriched **14g**

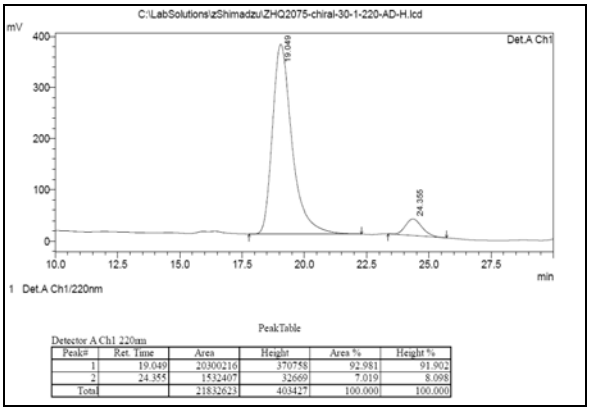
(*R*)-2-Methyl-2-(naphthalen-1-yl)-4,4-bis(phenylsulfonyl)butanal **14h**



A white solid; $[\alpha]_D$ = -12.50 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (s, 3H), 3.19-3.24 (m, 2H), 4.68-4.71 (m, 1H), 7.35-7.40 (m, 2H), 7.49-7.62 (m, 9H), 7.69-7.77 (m, 2H), 7.95-7.98 (m, 4H), 9.74 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.46, 29.93, 53.14, 80.57, 123.92, 125.21, 125.89, 125.97, 127.02, 128.70, 128.89, 129.53, 129.60, 129.78, 129.85, 134.24, 134.36, 134.47, 134.51, 134.78, 137.10, 138.06, 203.53; HRMS (ESI) m/z calcd for $C_{27}H_{24}O_5S_2$ $[M+Na]^+$ 515.0981, found 515.0981; The ee value of **14h** is 86%, t_R (major) = 18.6 min, t_R (minor) = 24.0 min (Chiralcel AD-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).

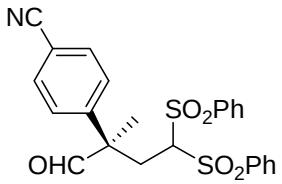


Racemic **14h**



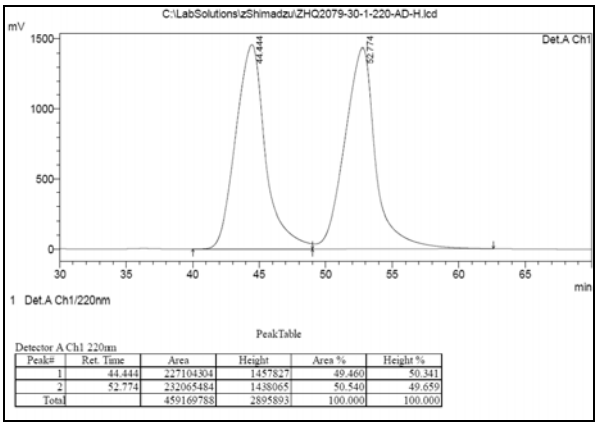
Enantiomeric enriched **14h**

(*R*)-4-(2-Methyl-1-oxo-4,4-bis(phenylsulfonyl)butan-2-yl)benzonitrile **14i**

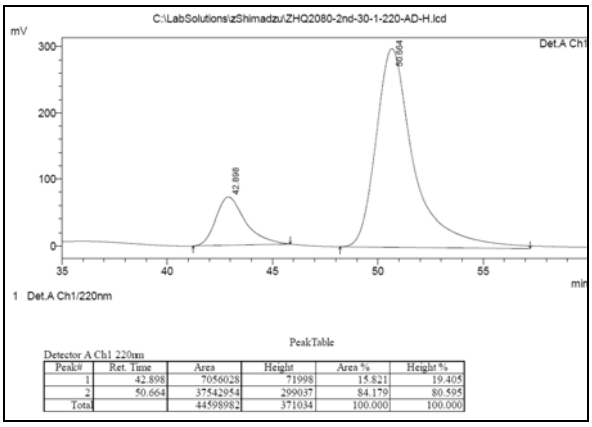


A colorless oil; $[\alpha]_D$ = +14.6 (c = 1.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 3H), 2.88-2.94 (m, 2H), 4.43-4.44 (m, 1H), 7.45-7.47 (m, 2H), 7.53-7.58 (m, 4H), 7.73-7.75 (m, 6H), 7.85-7.87 (m,

2H), 9.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.64, 31.47, 53.24, 79.73, 112.27, 118.11, 126.58, 128.36, 129.22, 129.25, 129.68, 129.78, 132.59, 132.88, 134.75, 134.88, 137.06, 137.62, 144.26, 200.38; MS (ESI) m/z calcd for $C_{24}H_{21}NO_5S_2$ $[M-H]^-$ 467.1, found 466.1; The ee value of **14i** is 68%, t_R (minor) = 44.4 min, t_R (major) = 52.8 min (Chiralcel AD-H, λ = 220 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).

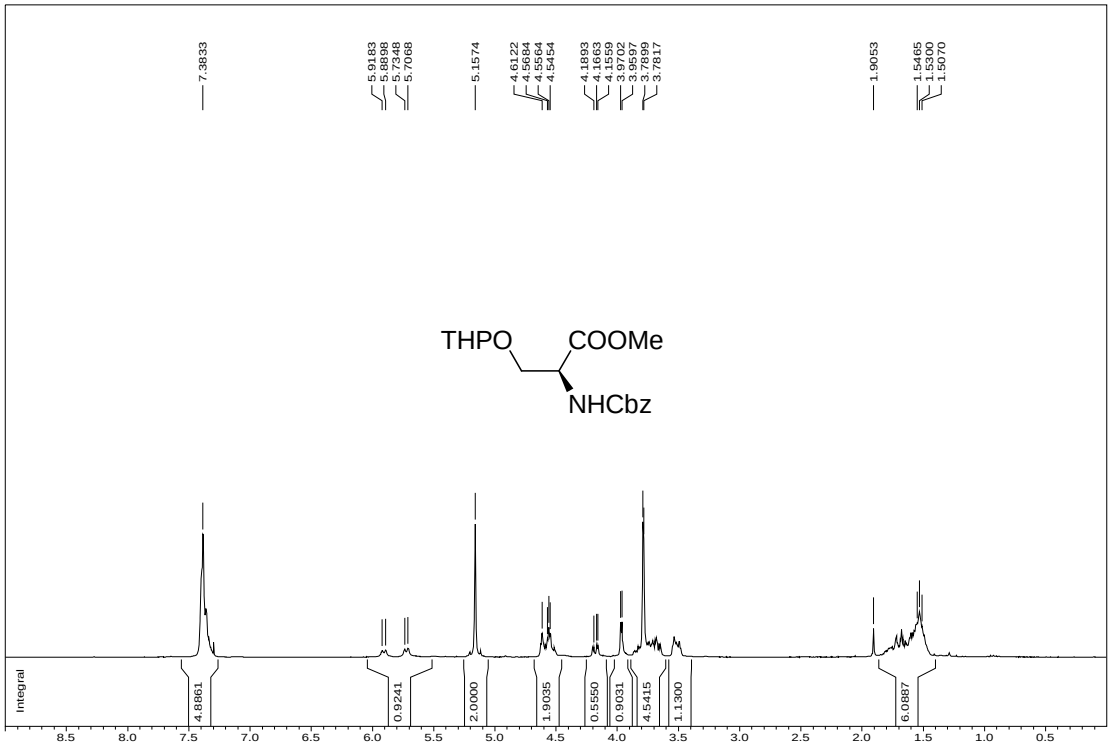


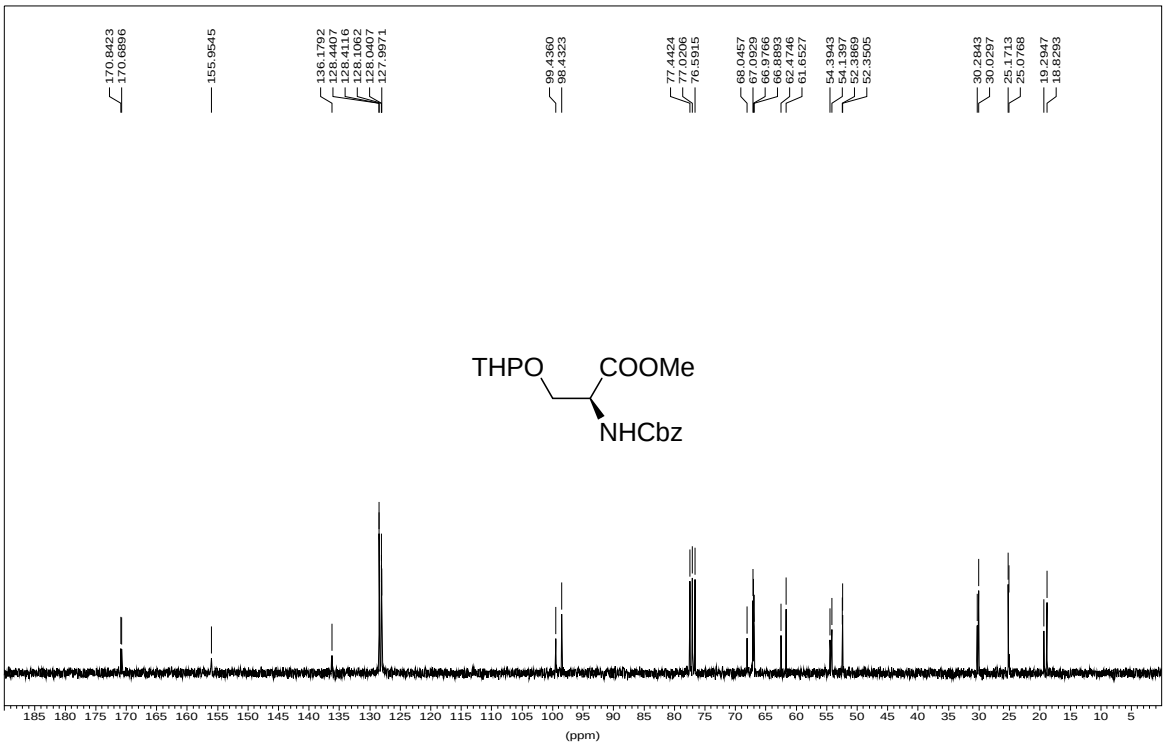
Racemic **14i**

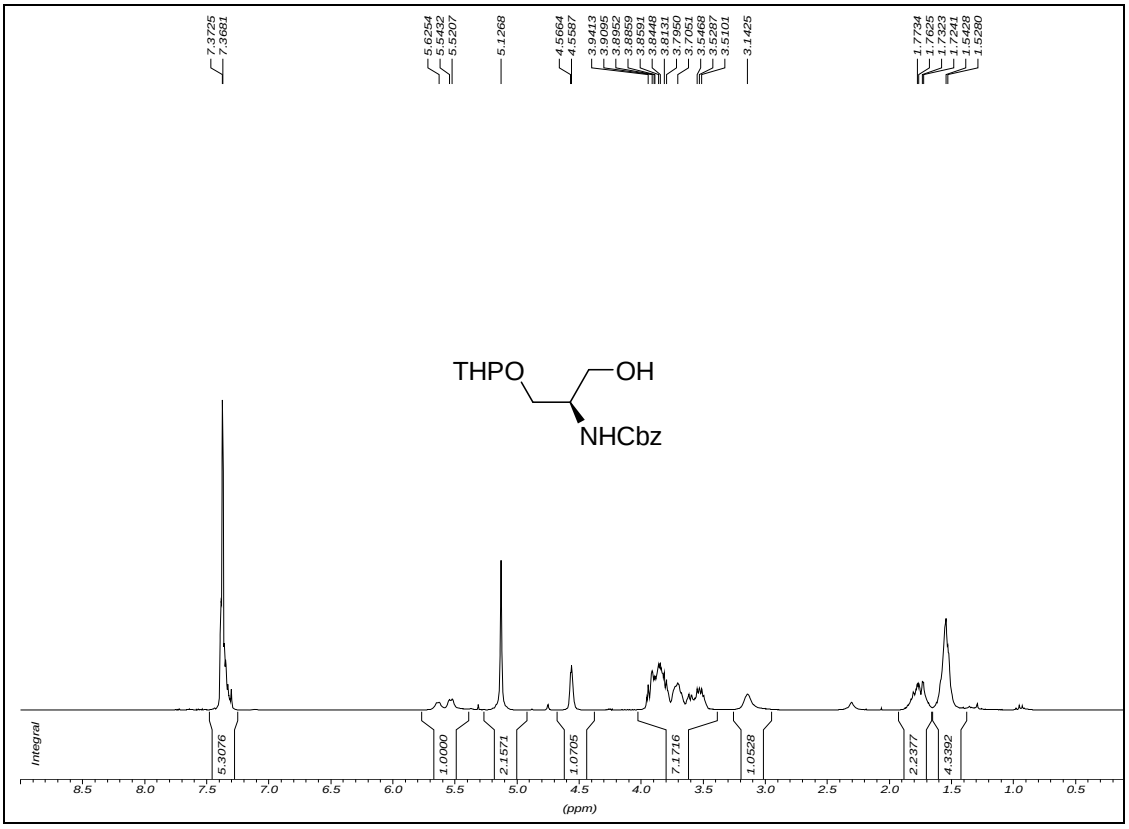


Enantiomeric enriched **14i**

F. NMR Spectra of Products



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5.6254
5.5432
5.5207
5.1268
4.5664
4.5587
3.9413
3.9095
3.8952
3.8859
3.8591
3.8448
3.8131
3.7950
3.7051
3.5468
3.5287
3.5101
3.1425
1.7734
1.7625
1.7323
1.7241
1.5428
1.5280
THPO
OH
NHCbz
Integral
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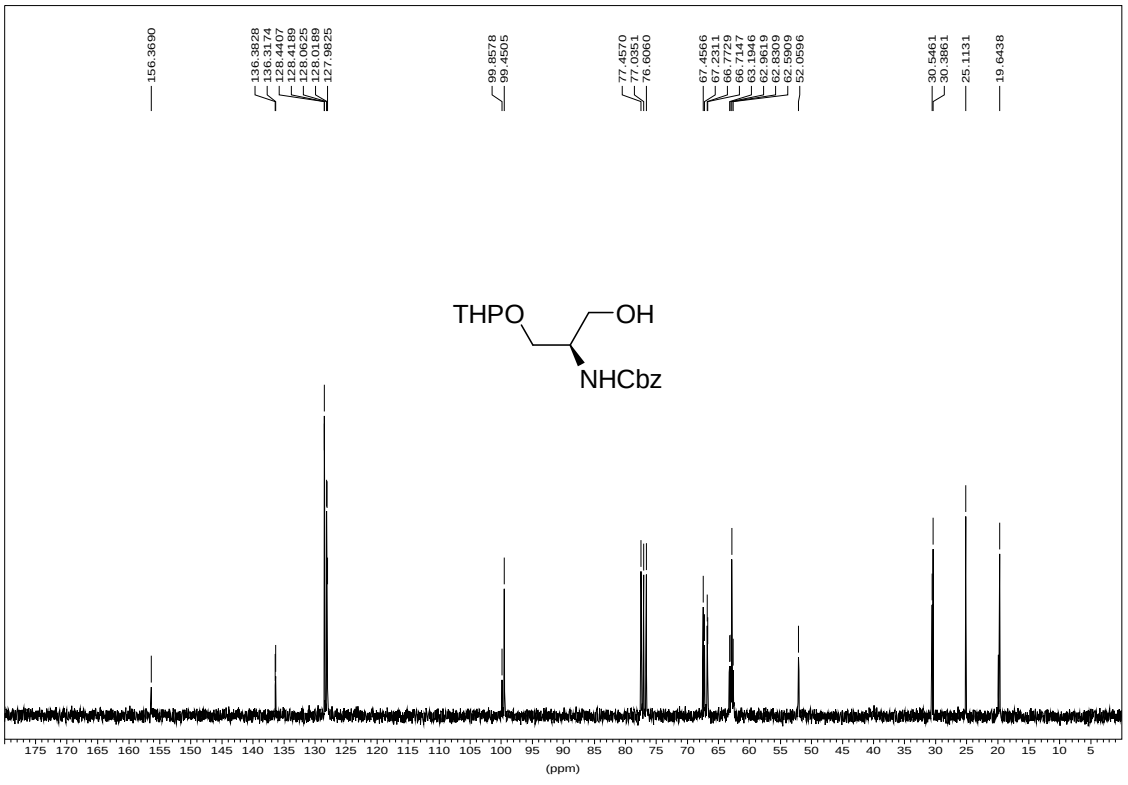
1.0000
2.1571
1.0705
7.1716
1.0528
2.2377
4.3392
(ppm)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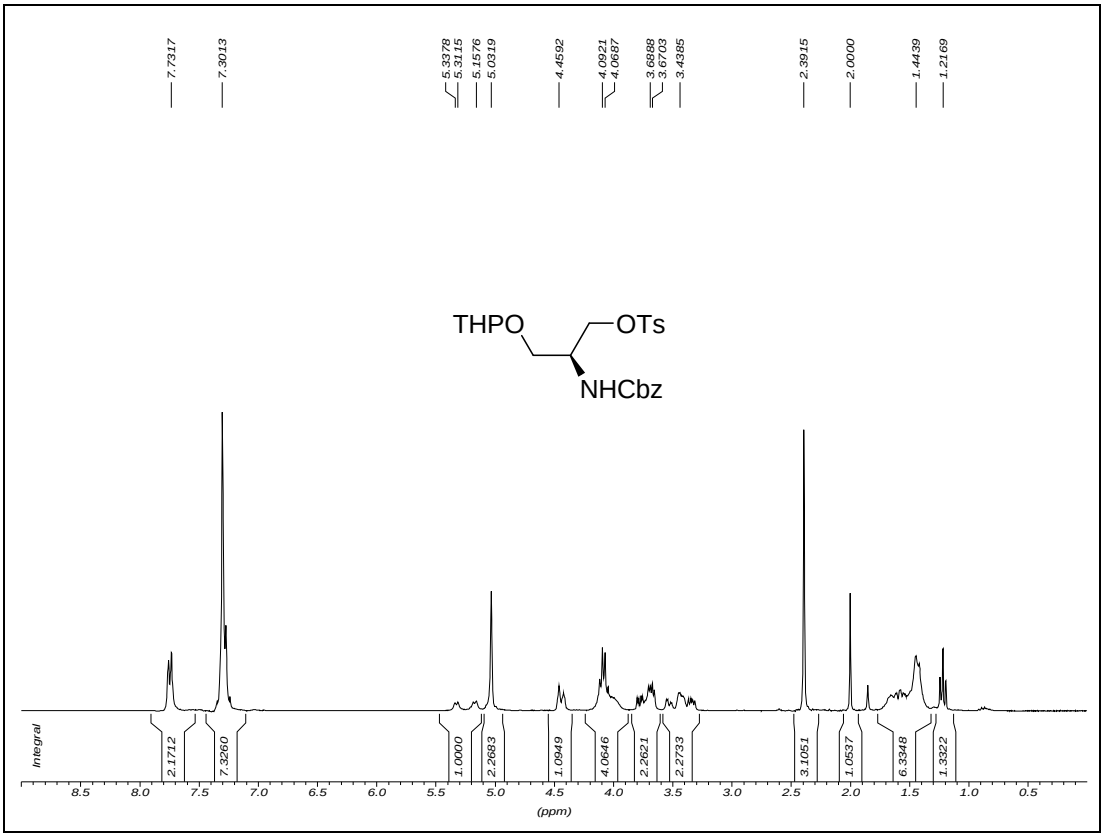
136.3174
128.4407
128.4189
128.0625
128.0189
127.9825
99.8578
99.4505
77.4570
77.0351
76.6060
67.4566
67.2311
66.7729
66.7147
63.1946
62.8659
62.8309
62.5909
52.0596
30.5461
30.3861
25.1131
19.6438
THPO
OH
NHCbz
(ppm)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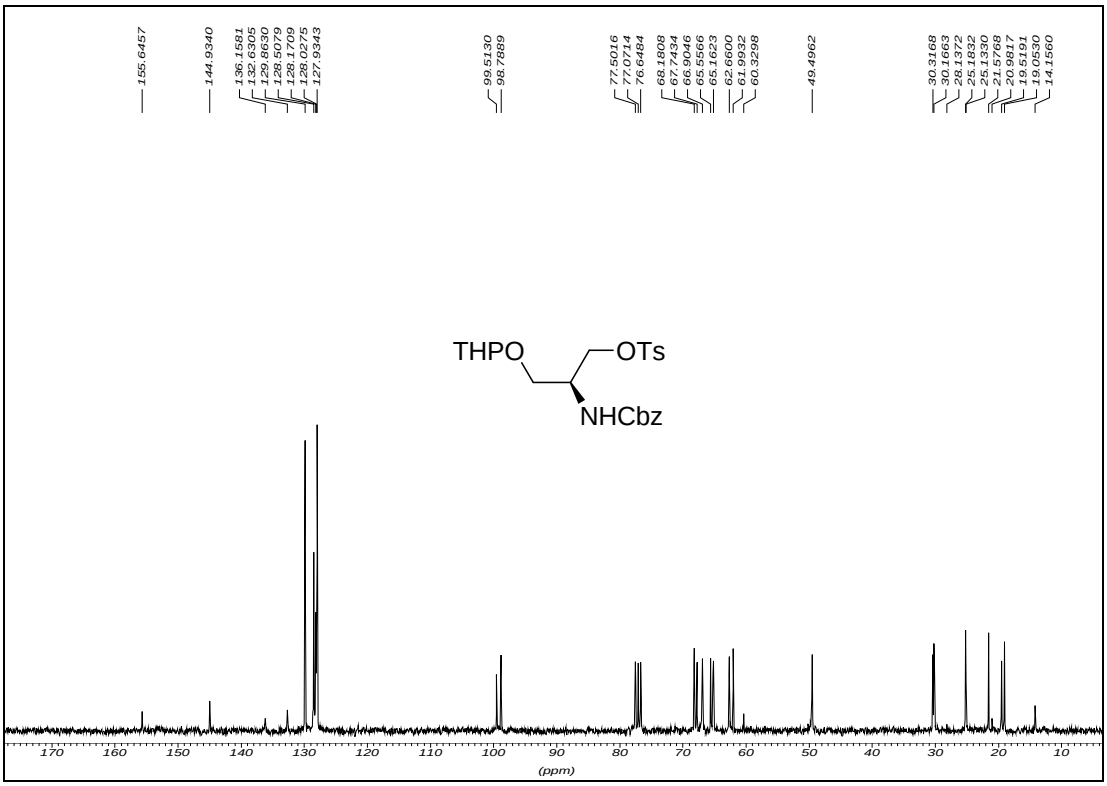
7.3013
5.3378
5.3115
5.1576
5.0319
4.4592
4.0921
4.0687
3.6888
3.6703
3.4385
2.3915
2.0000
1.4439
1.2169
THPO
OTs
NHCbz
Integral
2.1712
7.3260
1.0000
2.2683
1.0949
4.0646
2.2621
2.2733
3.1051
1.0537
6.3348
1.3322
(ppm)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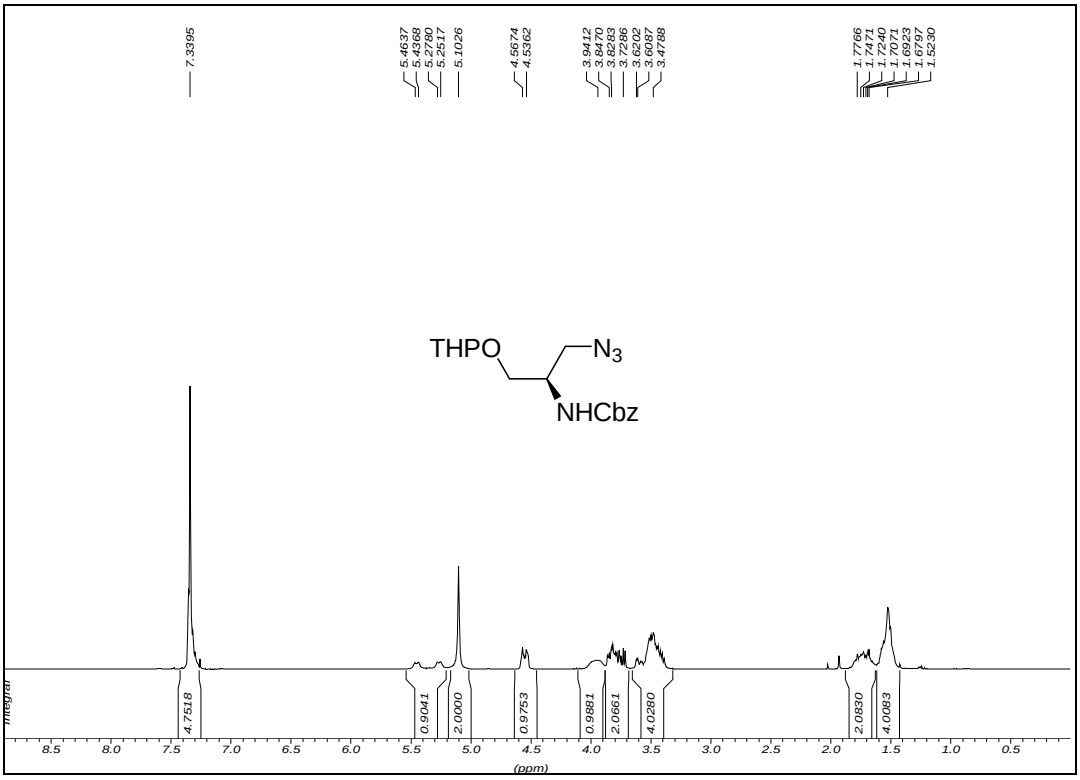
136.1581
132.6305
129.8630
128.5079
128.1709
128.0275
127.9343
99.5130
98.7889
77.5016
77.0714
76.6484
68.1808
67.7434
66.9046
65.5566
65.1623
62.6600
61.9932
60.3298
49.4962
30.3168
30.1663
28.1372
25.1832
25.1330
21.5768
20.9817
19.5191
19.0530
14.1560
THPO
OTs
NHCbz
(ppm)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5.2780
5.2517
5.1026
4.5674
4.5562
3.9412
3.8470
3.8283
3.7288
3.6202
3.6087
3.4788
1.7766
1.7471
1.7240
1.7071
1.6923
1.6797
1.5230
THPO
N3
NHCbz
Integral
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2.0000
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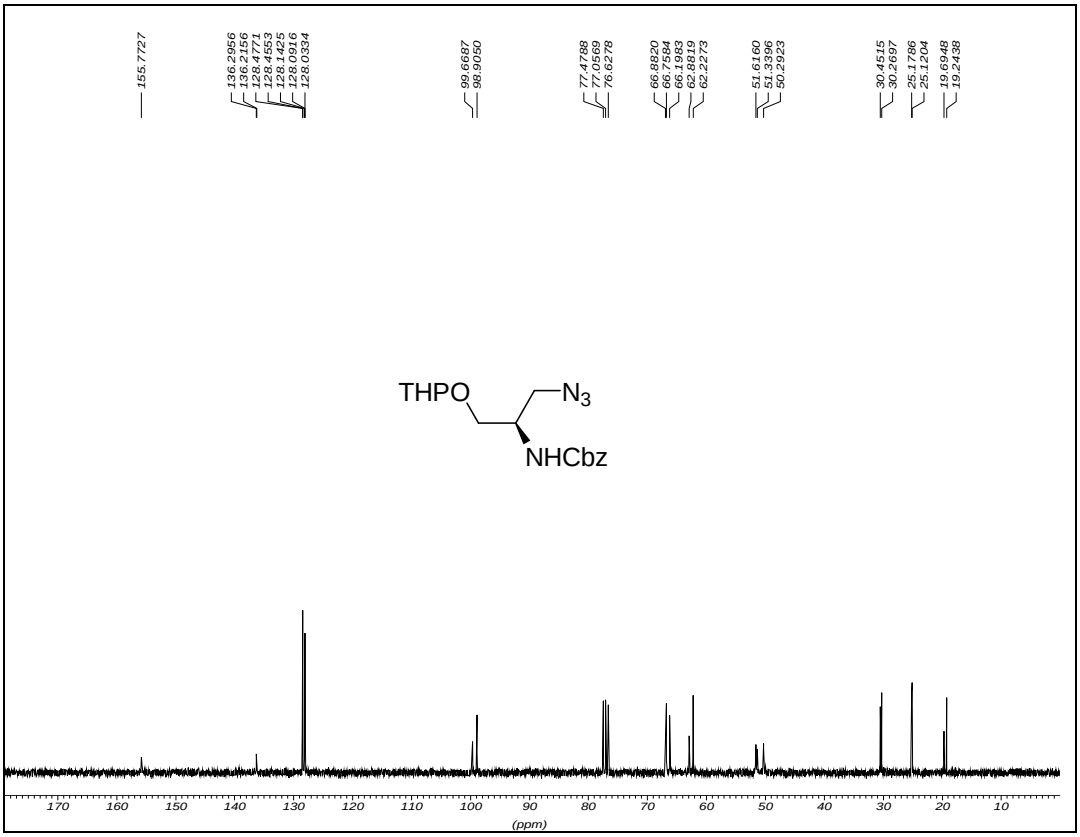
0.9881
2.0661
4.0280
2.0830
4.0083
(ppm)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136.2956
136.2156
128.4771
128.4553
128.1425
128.0916
128.0334
99.6687
98.9050
77.4788
77.0569
76.6278
66.8820
66.7584
66.1983
62.8819
62.2273
51.6160
51.3396
50.2923
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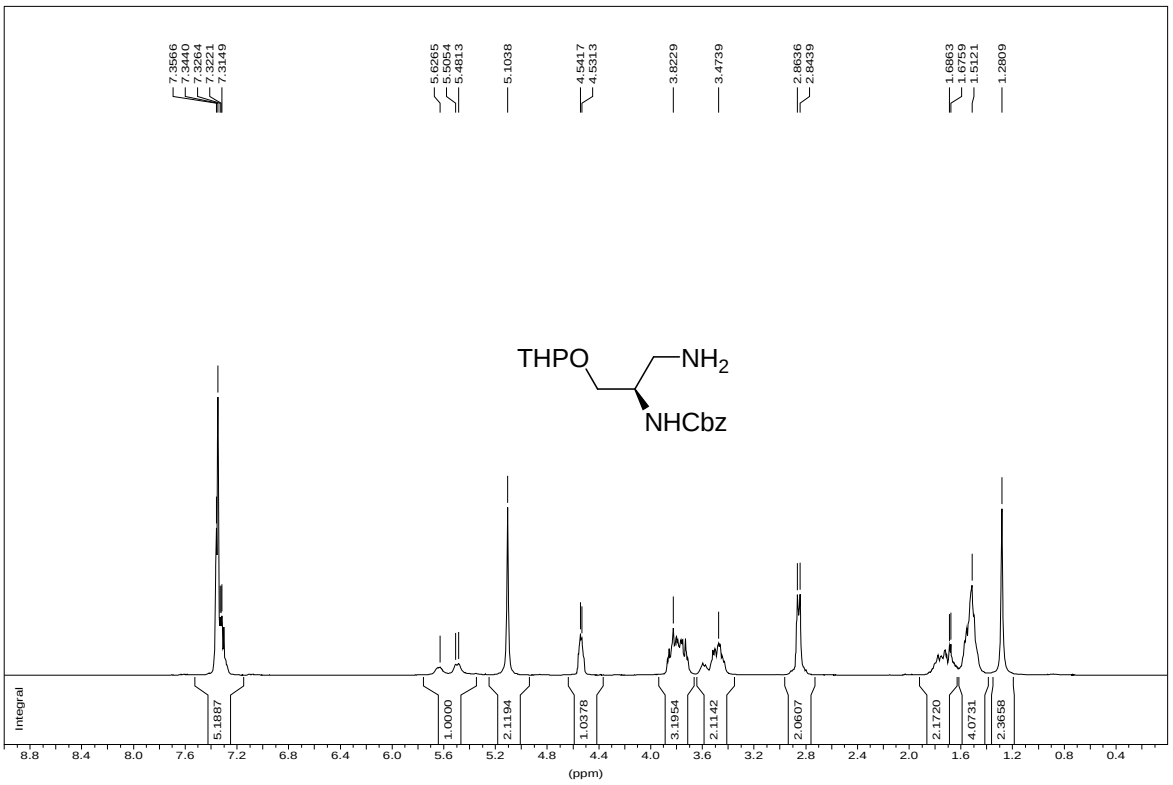
30.2697
25.1796
25.1204
19.6948
19.2438
THPO
N3
NHCbz
(ppm)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7.3440
7.3264
7.3221
7.3149
5.6265
5.5054
5.4813
5.1038
4.5417
4.5313
3.8229
3.4739
2.8636
2.8439
1.6863
1.6759
1.5121
1.2809
THPO
NH2
NHCbz
Integral
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1.0378
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2.1142
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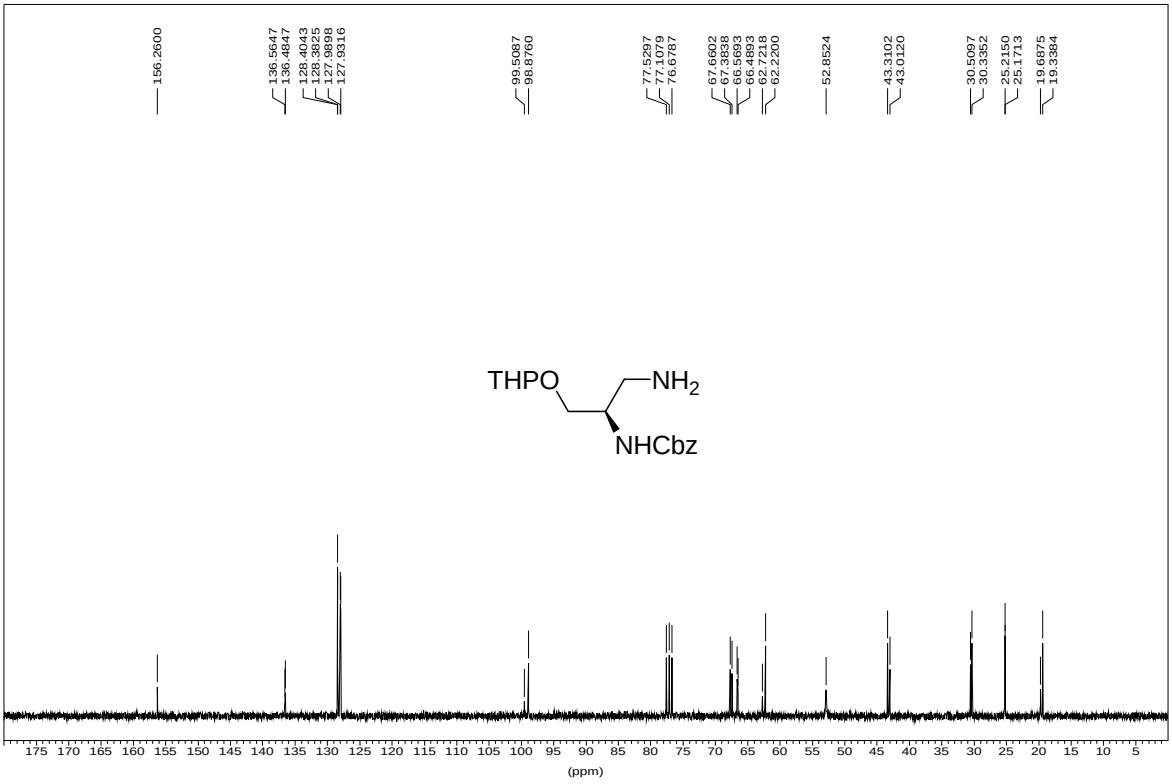
2.1720
4.0731
2.3658
(ppm)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136.4847
128.4043
128.3825
127.9898
127.9316
99.5087
98.8760
77.5297
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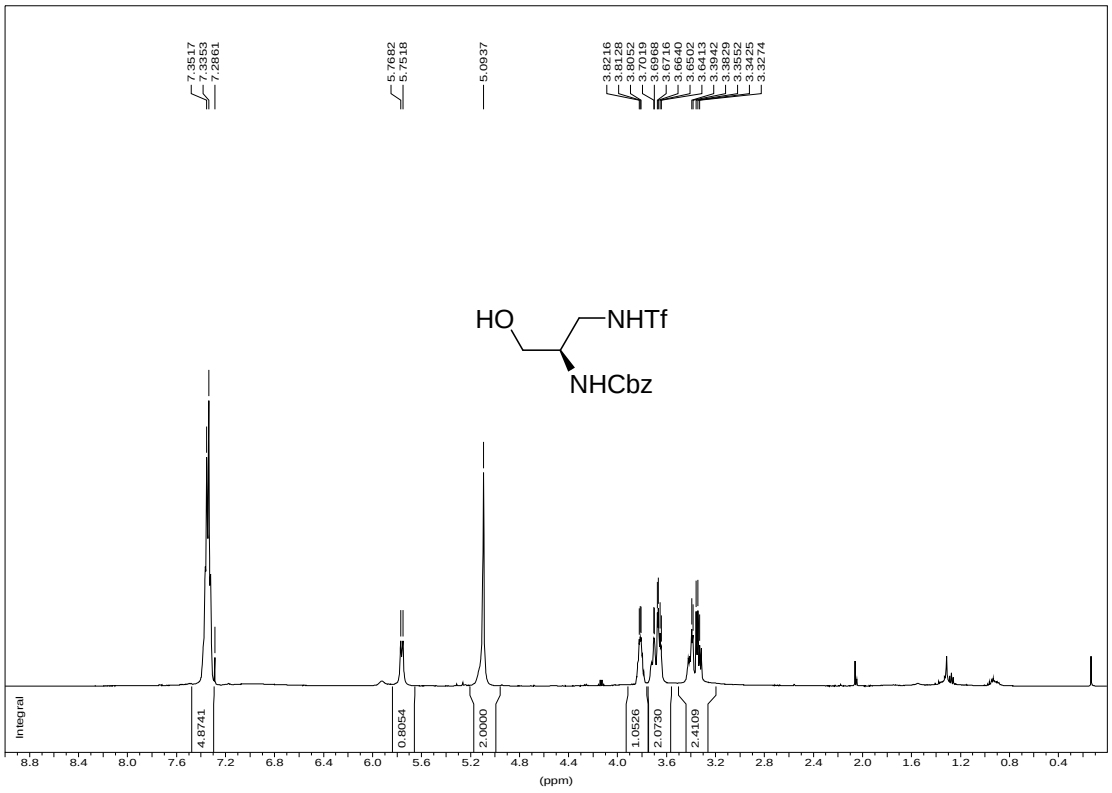
76.6787
67.6602
67.3838
66.5693
66.4893
62.7218
62.2200
52.8524
43.3102
43.0120
30.5097
30.3352
25.2150
25.1713
19.6875
19.3384
THPO
NH2
NHCbz
(ppm)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7.2861
5.7682
5.7518
5.0937
3.8216
3.8078
3.6952
3.6852
3.7019
3.6968
3.6716
3.6640
3.6502
3.6413
3.3942
3.3829
3.3552
3.3425
3.3274
HO
NHTf
NHCbz
Integral
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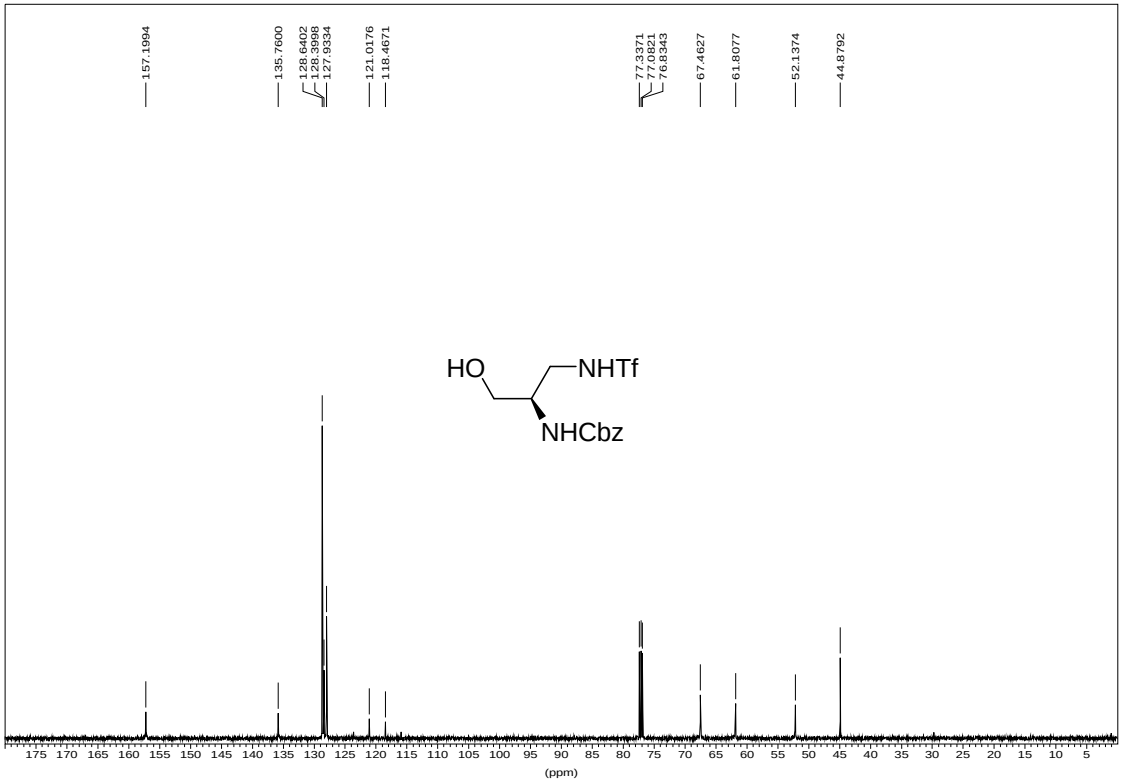
0.8054
2.0000
1.0526
2.0730
2.4109
(ppm)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128.3998
127.9334
121.0176
118.4671
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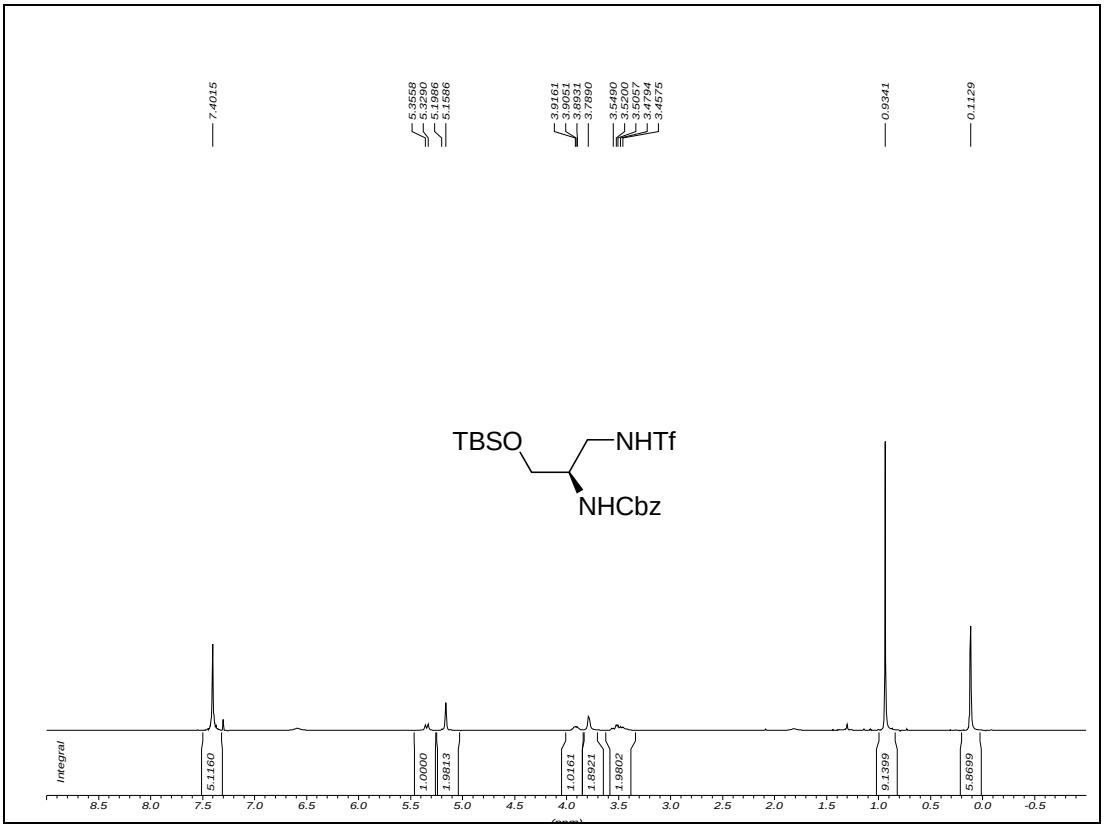
76.8343
67.4627
61.8077
52.1374
44.8792
HO
NHTf
NHCbz
(ppm)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5.3558
5.3290
5.1986
5.1586
3.9161
3.9051
3.8931
3.7990
3.5490
3.5200
3.5057
3.4794
3.4575
0.9341
0.1129
TBSO
NHTf
NHCbz
Integral
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1.9813
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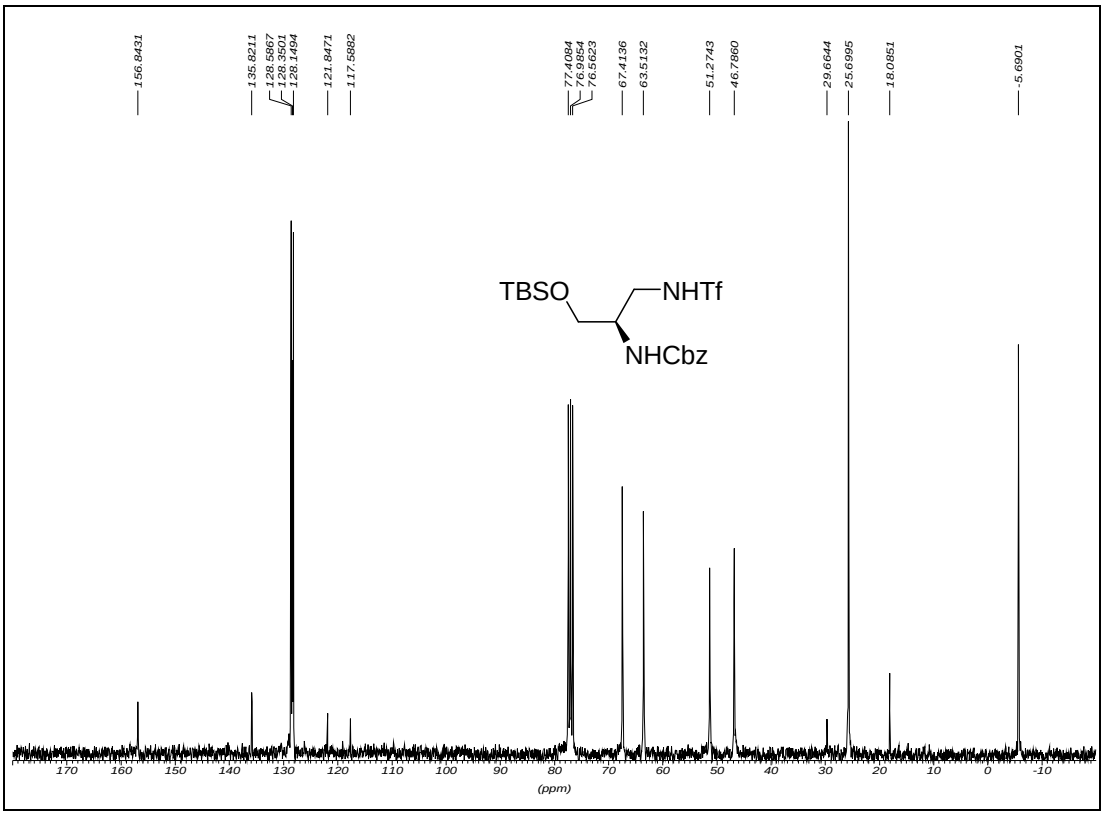
1.8921
1.9802
9.1399
5.8699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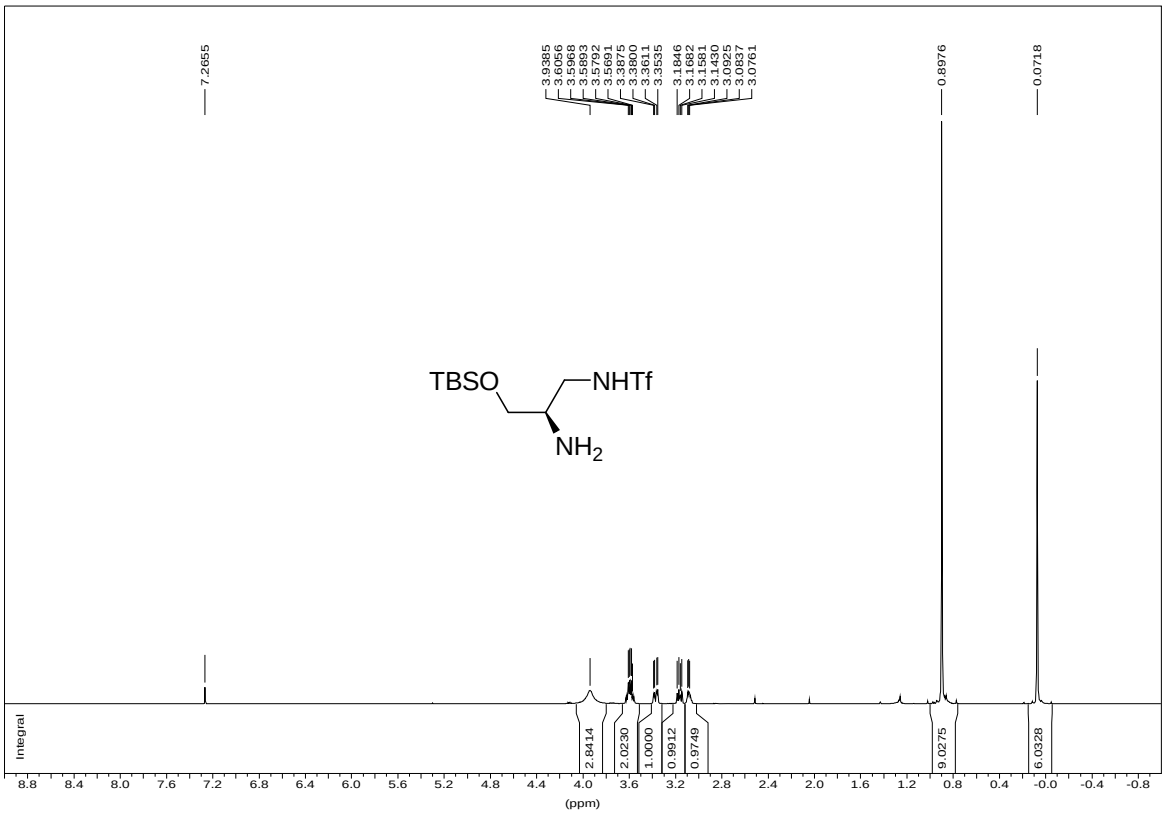
128.5867
128.3501
128.1494
121.8471
117.5882
77.4084
76.9854
76.5623
67.4136
63.5132
51.2743
46.7860
29.6644
25.6995
18.0851
-5.6901
TBSO
NHTf
NHCbz
(ppm)


7.2655
3.9385
3.6056
3.5968
3.5893
3.5722
3.5691
3.3875
3.3800
3.3611
3.3535
3.1846
3.1682
3.1581
3.1430
3.0925
3.0837
3.0761
0.8976
0.0718
TBSO
NHTf
NH2
Integral
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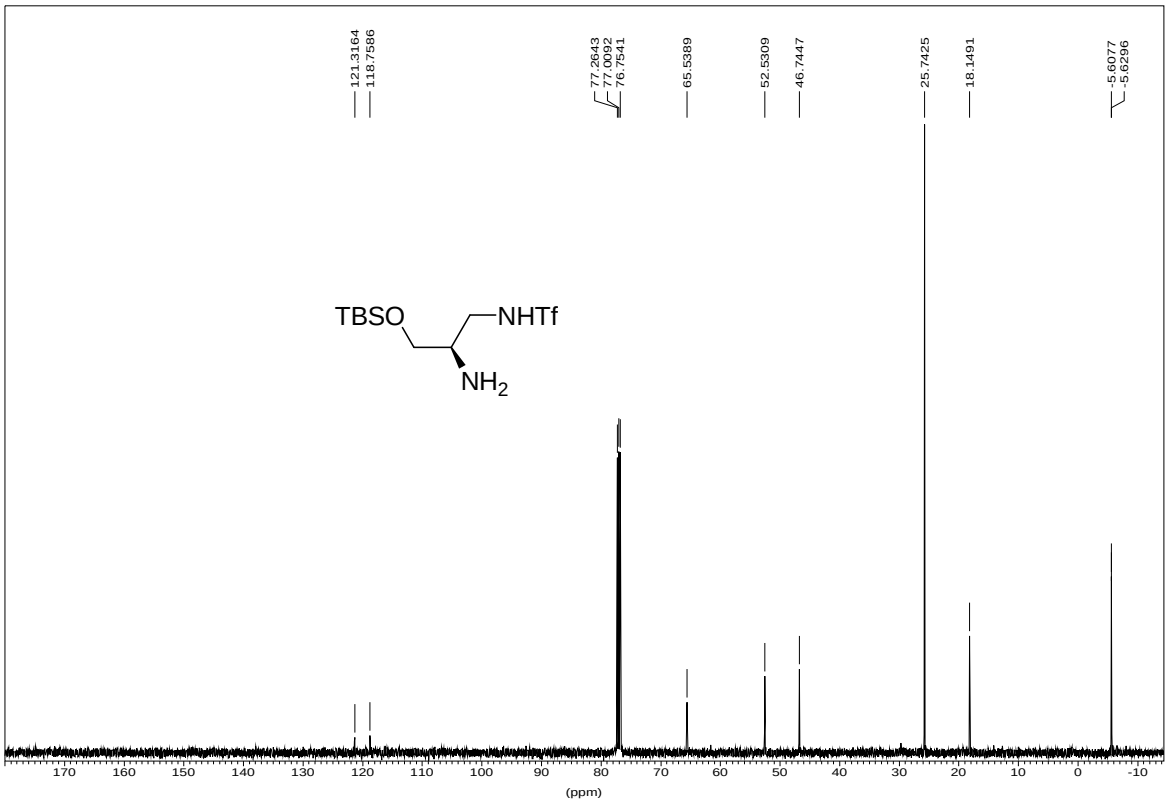
1.0000
0.9912
0.9749
9.0275
6.0328
(ppm)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76.7541
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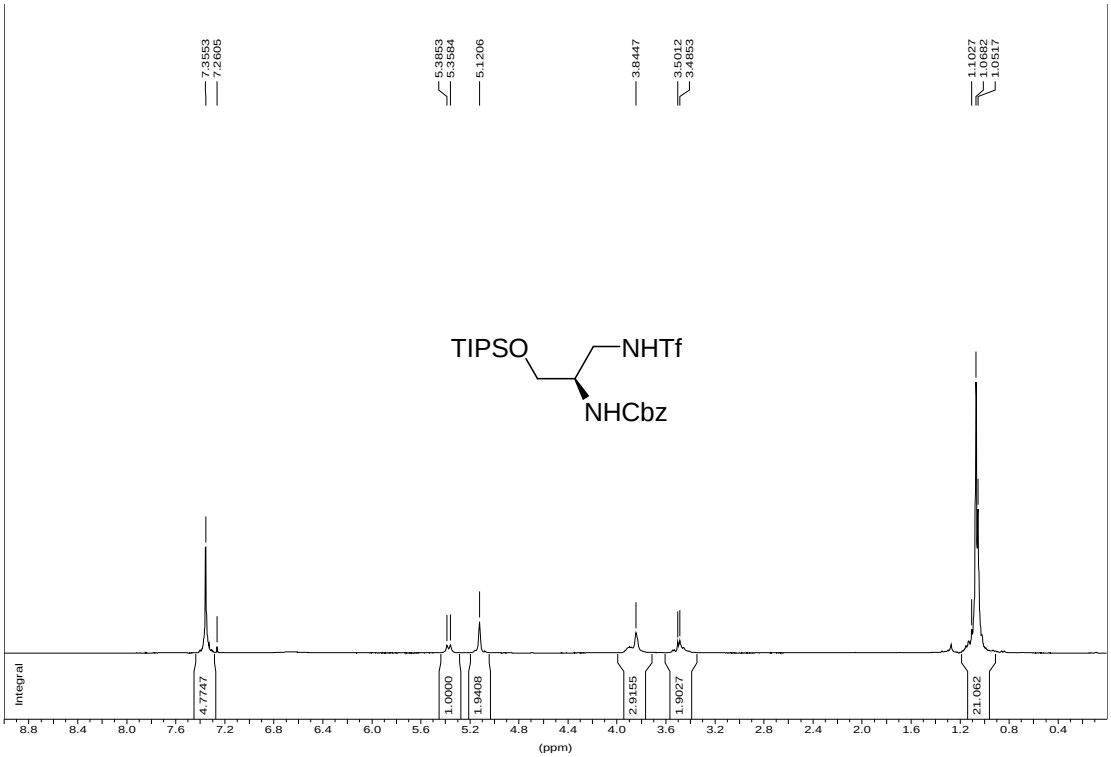
-5.6296
TBSO
NHTf
NH2
(ppm)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5.3853
5.3584
5.1206
3.8447
3.5012
3.4853
1.1027
1.0682
1.0517
TIPSO
NHTf
NHCbz
Integral
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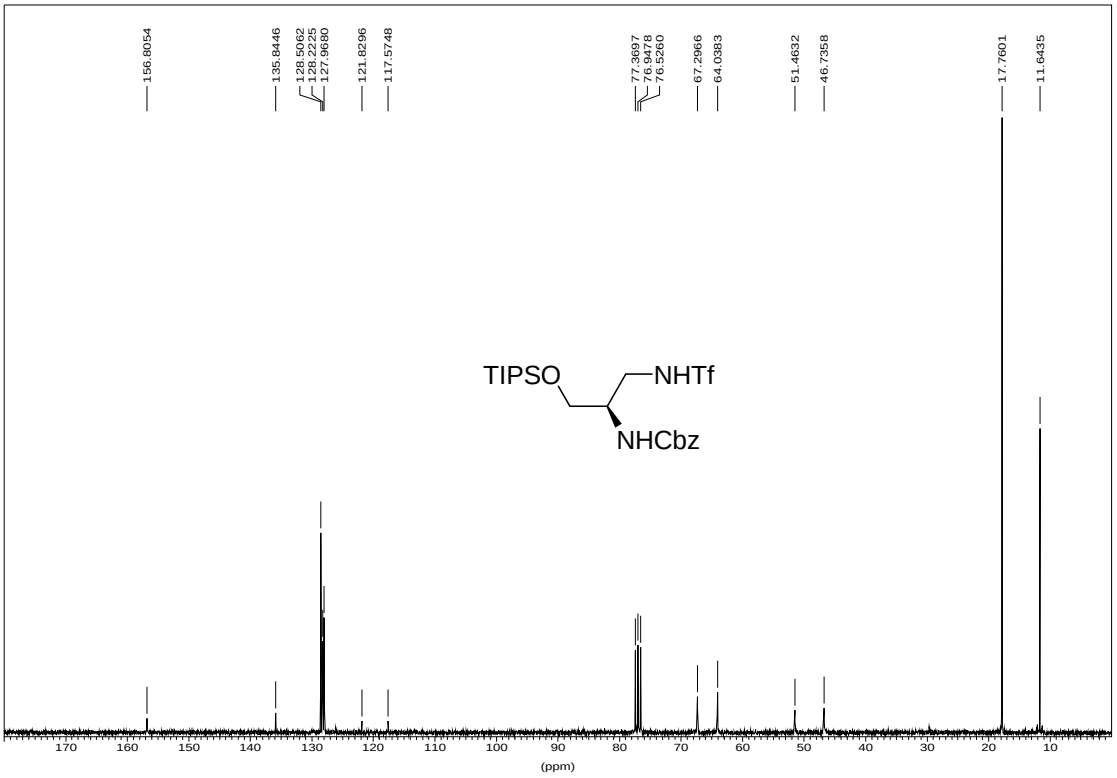
21.062
(ppm)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128.2225
127.9680
121.8296
117.5748
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76.9478
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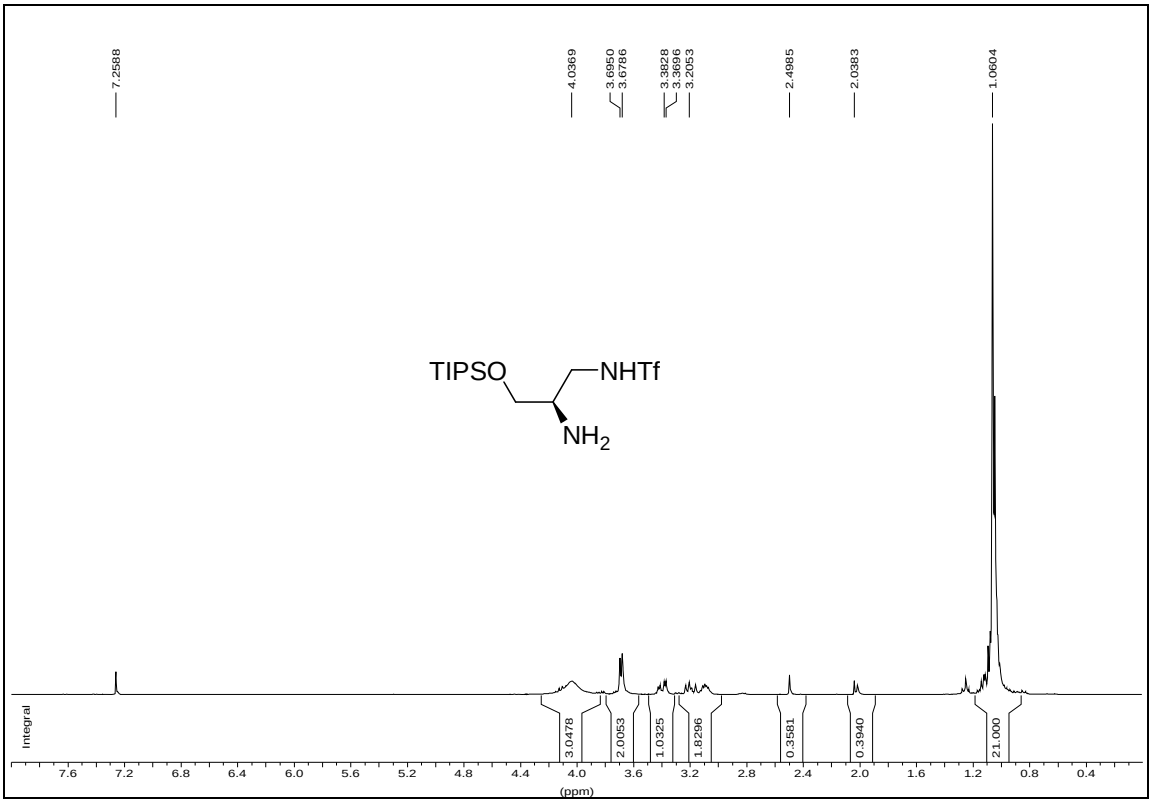
51.4632
46.7358
17.7601
11.6435
TIPSO
NHTf
NHCbz
(ppm)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3.6950
3.6786
3.3828
3.3696
3.2053
2.4985
2.0383
1.0604
TIPSO
NHTf
NH2
Integral
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1.0325
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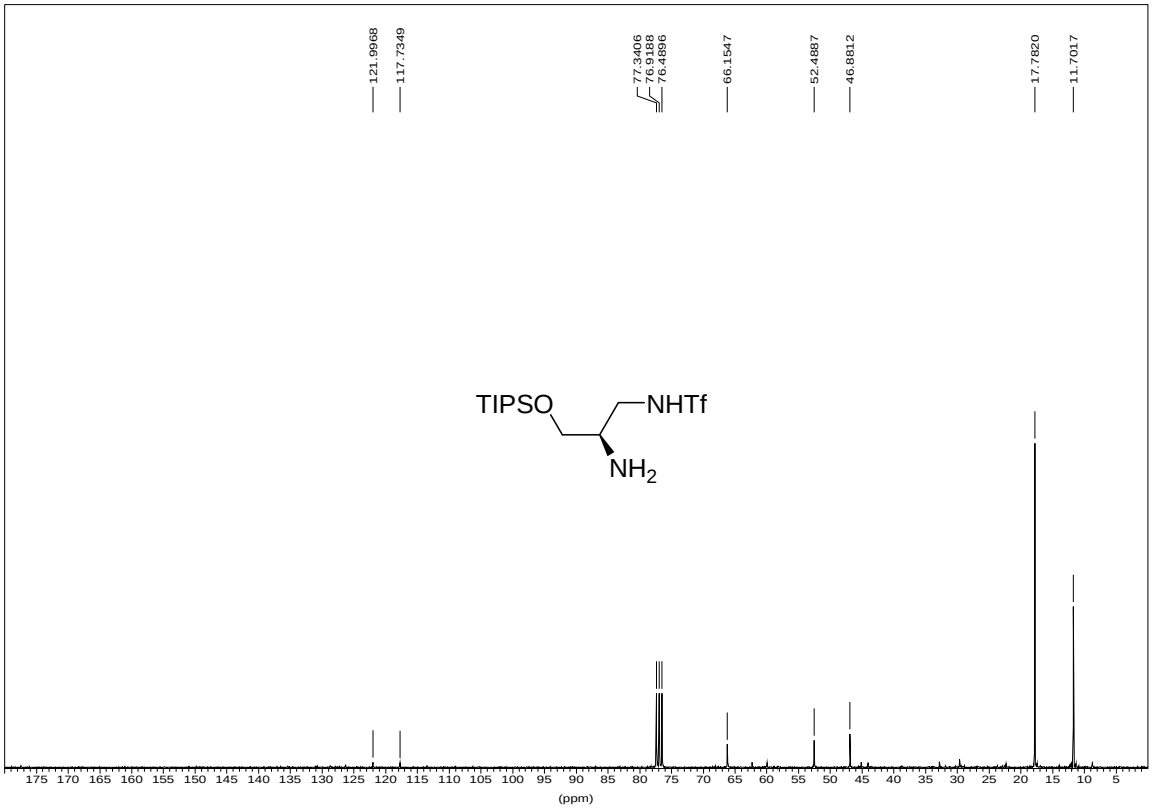
0.3581
0.3940
21.000
(ppm)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17.7820
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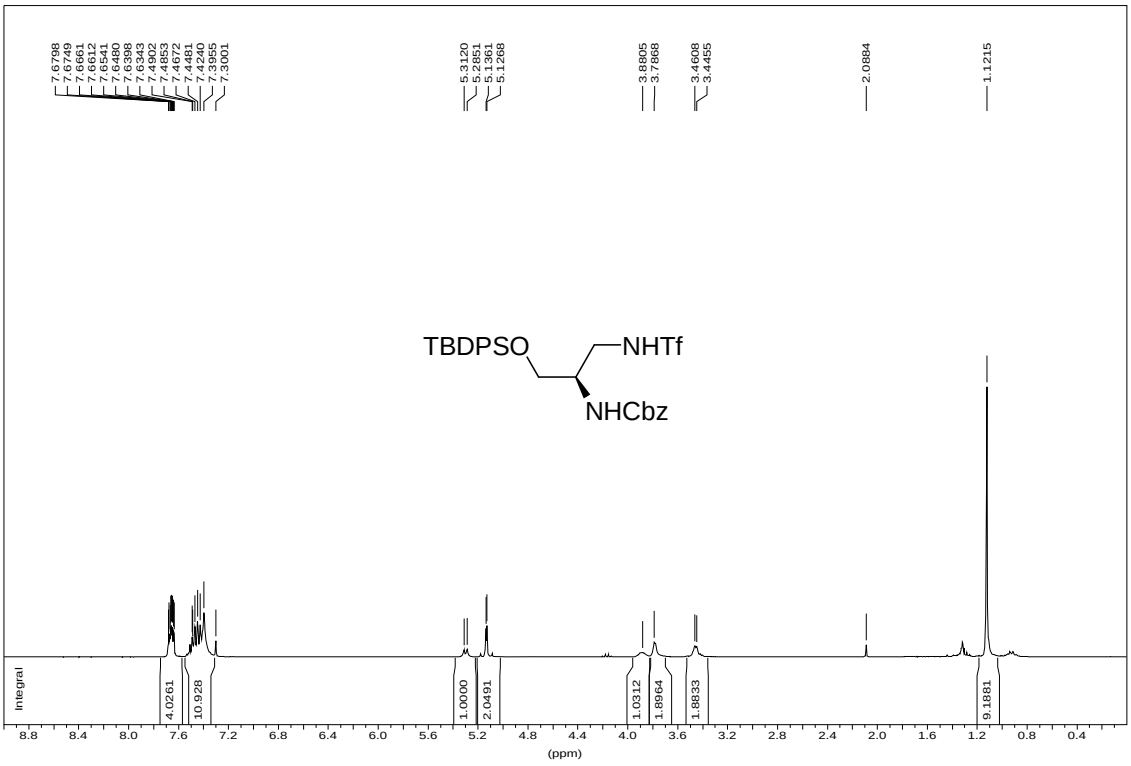
NHTf
NH2
(ppm)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7.6661
7.6612
7.6541
7.6480
7.6398
7.6343
7.4902
7.4853
7.4672
7.4481
7.4240
7.3955
7.3801
5.3120
5.2951
5.1361
5.1268
3.8805
3.7868
3.4608
3.4455
2.0884
1.1215
TBDPSO
NHTf
NHCbz
Integral
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1.0000
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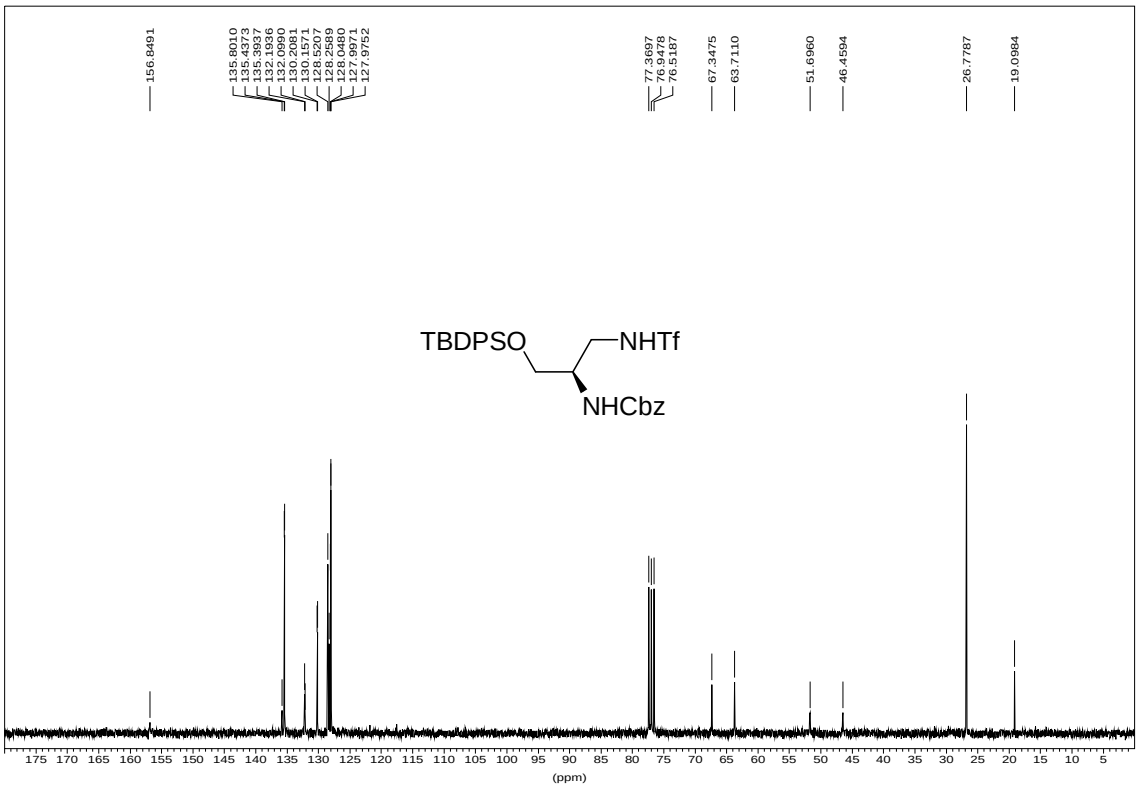
1.0312
1.8964
1.8833
9.1881
(ppm)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135.3937
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127.9971
127.9752
77.3697
76.9478
76.5187
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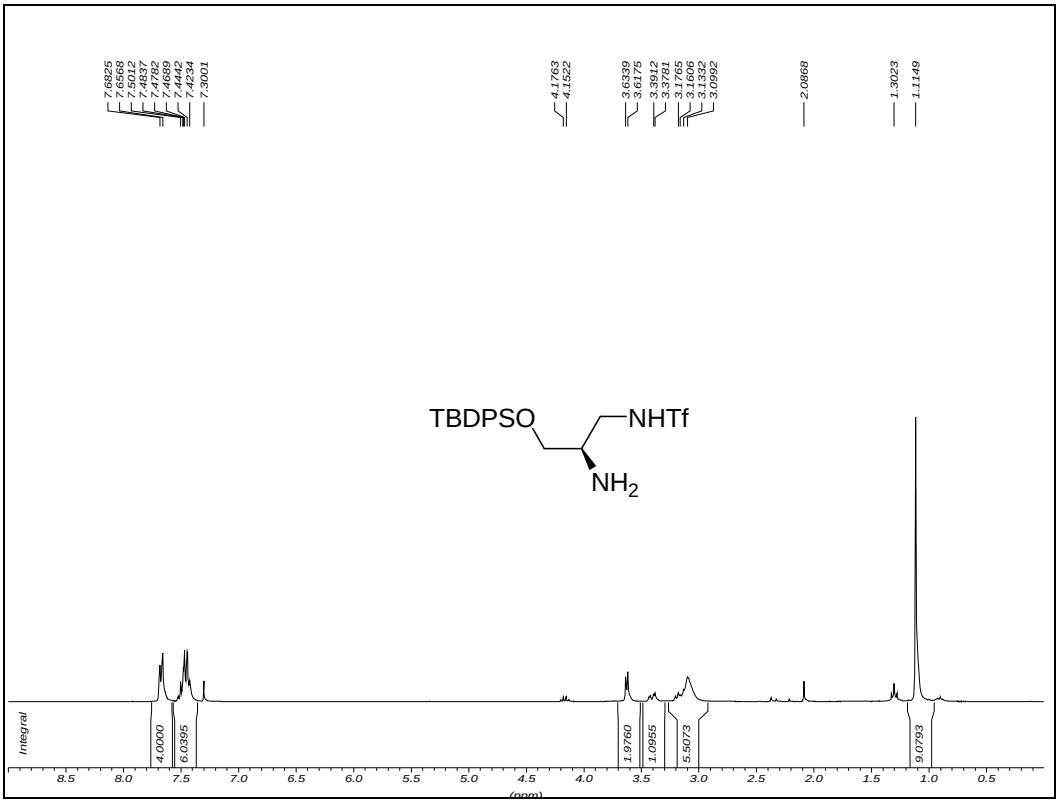
63.7110
51.6960
46.4594
26.7787
19.0984
TBDPSO
NHTf
NHCbz
(ppm)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7.4837
7.4782
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7.4442
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7.3001
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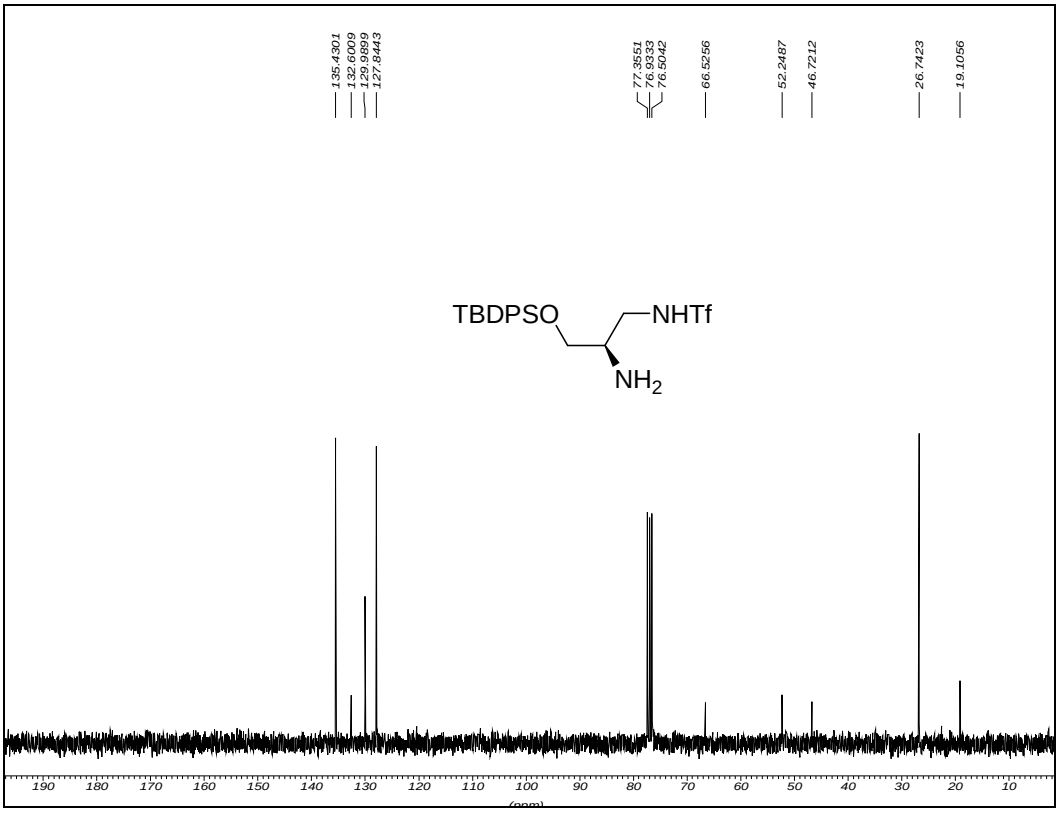
4.1522
3.6339
3.6175
3.3912
3.3781
3.1765
3.1606
3.1332
3.0992
2.0868
1.3023
1.1149
TBDPSO
NHTf
NH2
Integral
4.0000
6.0395
1.9760
1.0955
5.5073
9.0793
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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129.9899
127.8443
77.3551
76.9333
76.5042
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52.2487
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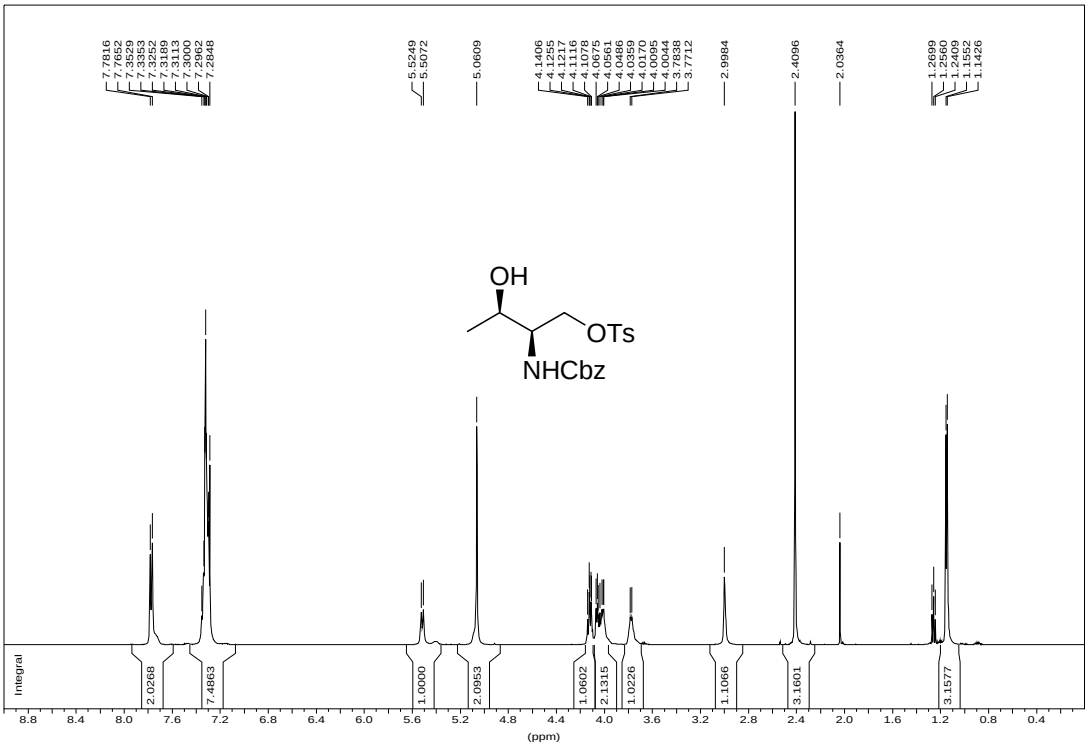
19.1056
TBDPSO
NHTf
NH2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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7.3353
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7.3113
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7.2962
7.2848
5.5249
5.5072
5.0609
4.1406
4.1255
4.1217
4.1118
4.1078
4.0675
4.0561
4.0486
4.0359
4.0170
4.0095
4.0044
3.7838
3.7712
2.9984
2.4096
2.0364
1.2699
1.2560
1.2409
1.1552
1.1426
OH
OTs
NHCbz
Integral
2.0268
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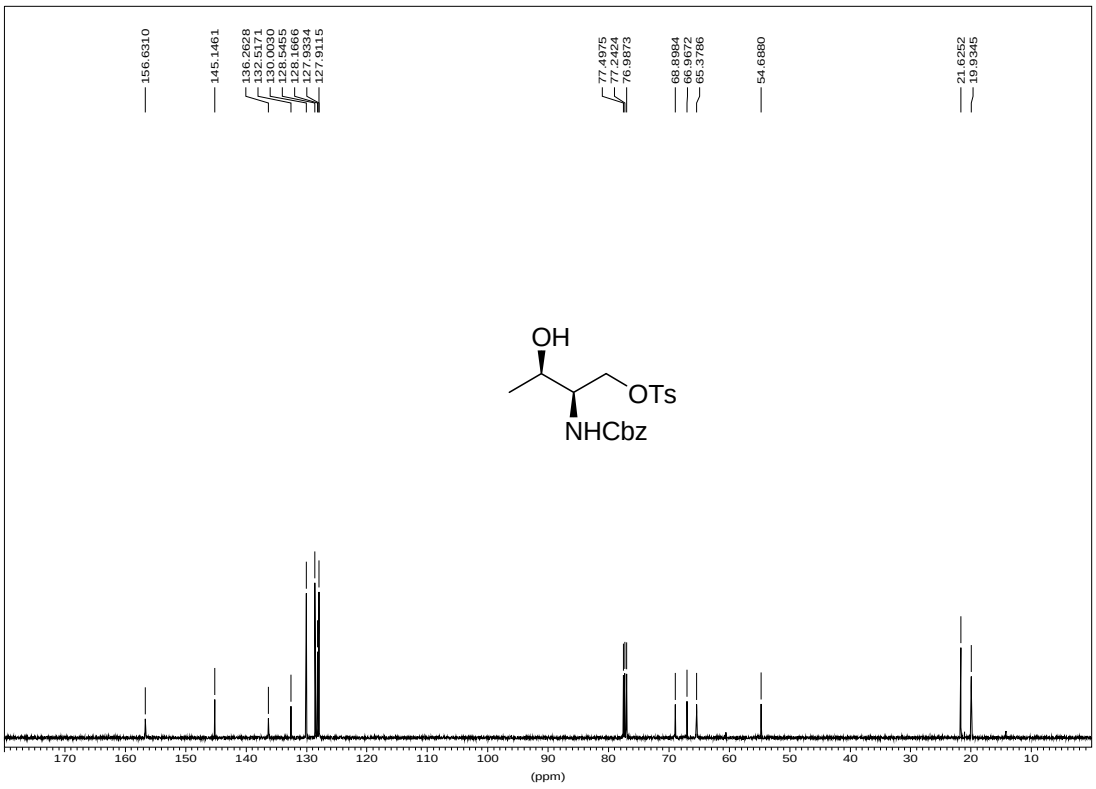
(ppm)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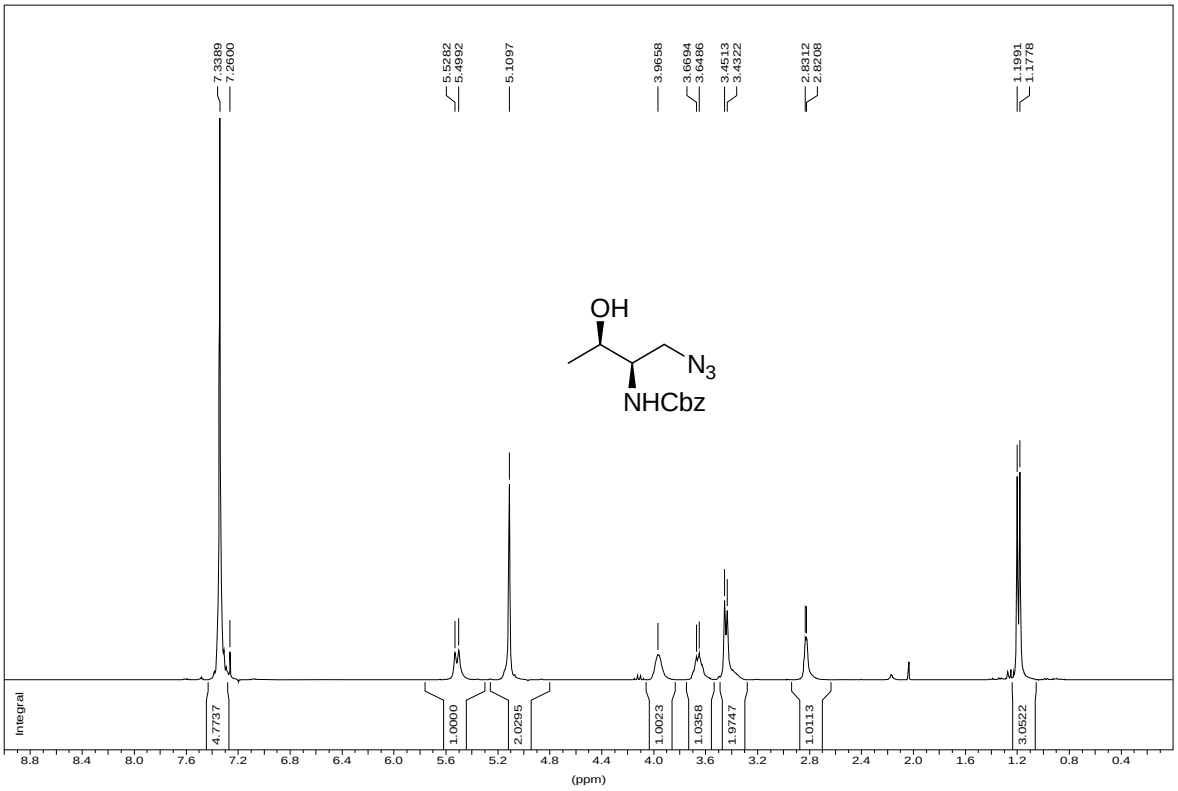
136.2628
132.5171
130.0030
128.5455
128.1666
127.9334
127.9115
77.4975
77.2424
76.9873
68.8984
66.9672
65.3786
54.6880
21.6252
19.9345
OH
OTs
NHCbz
(ppm)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3.6694
3.6486
3.4513
3.4322
2.8312
2.8208
1.1991
1.1778
OH
N3
NHCbz
Integral
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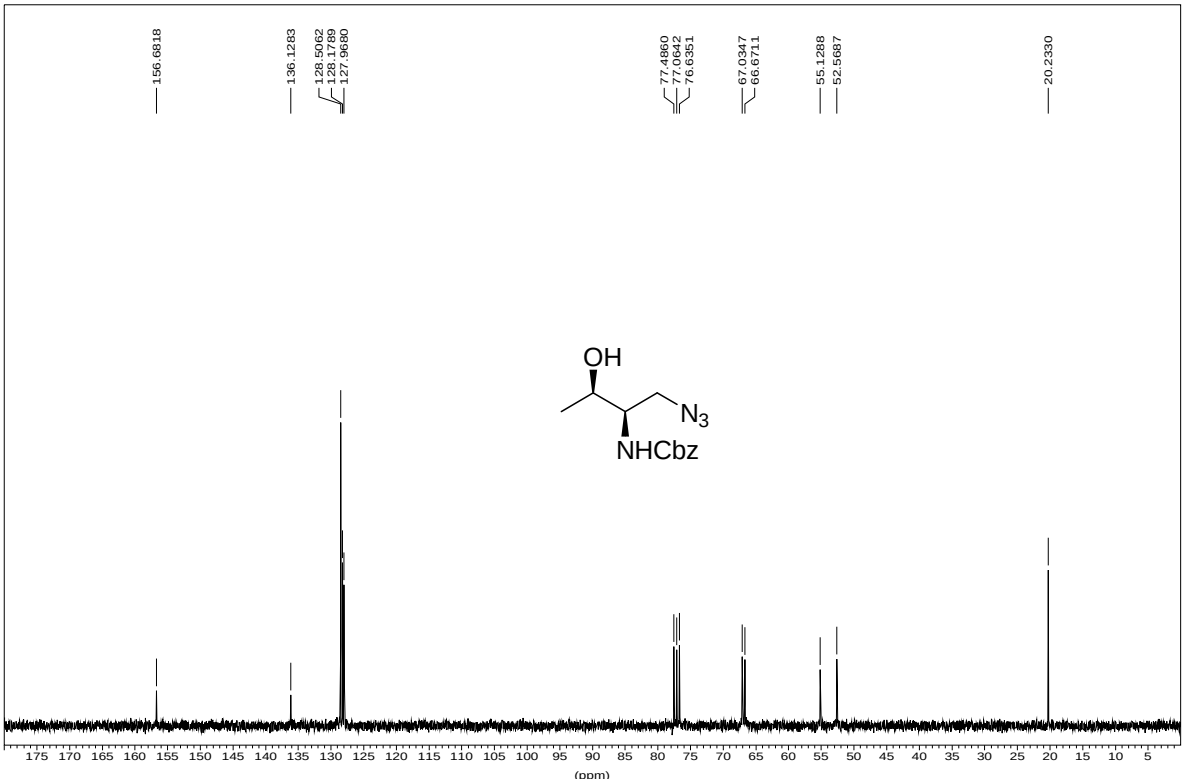
1.0000
2.0295
1.0023
1.0358
1.9747
1.0113
3.0522
(ppm)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127.9680
77.4860
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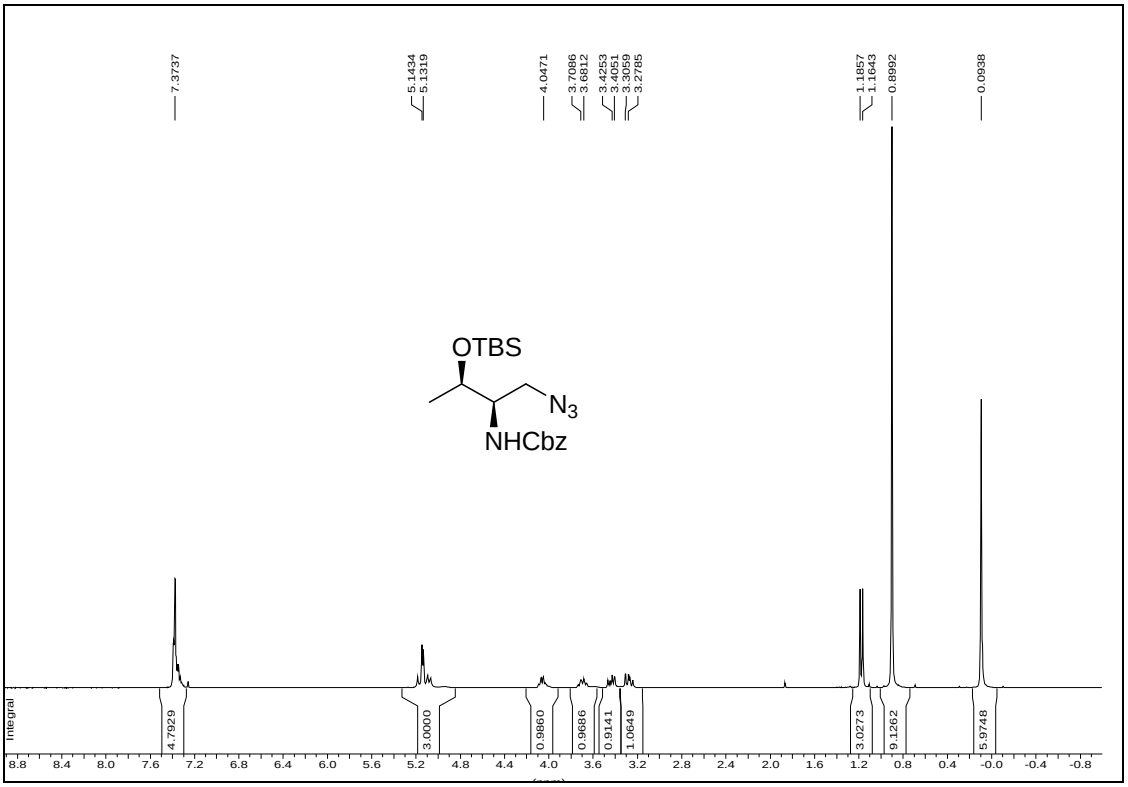
55.1288
52.5687
20.2330
OH
N3
NHCbz
(ppm)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5.1319
4.0471
3.7086
3.6812
3.4253
3.4051
3.3059
3.2785
1.1857
1.1643
0.8992
0.0938
OTBS
N3
NHCbz
Integral
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0.9686
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1.0649
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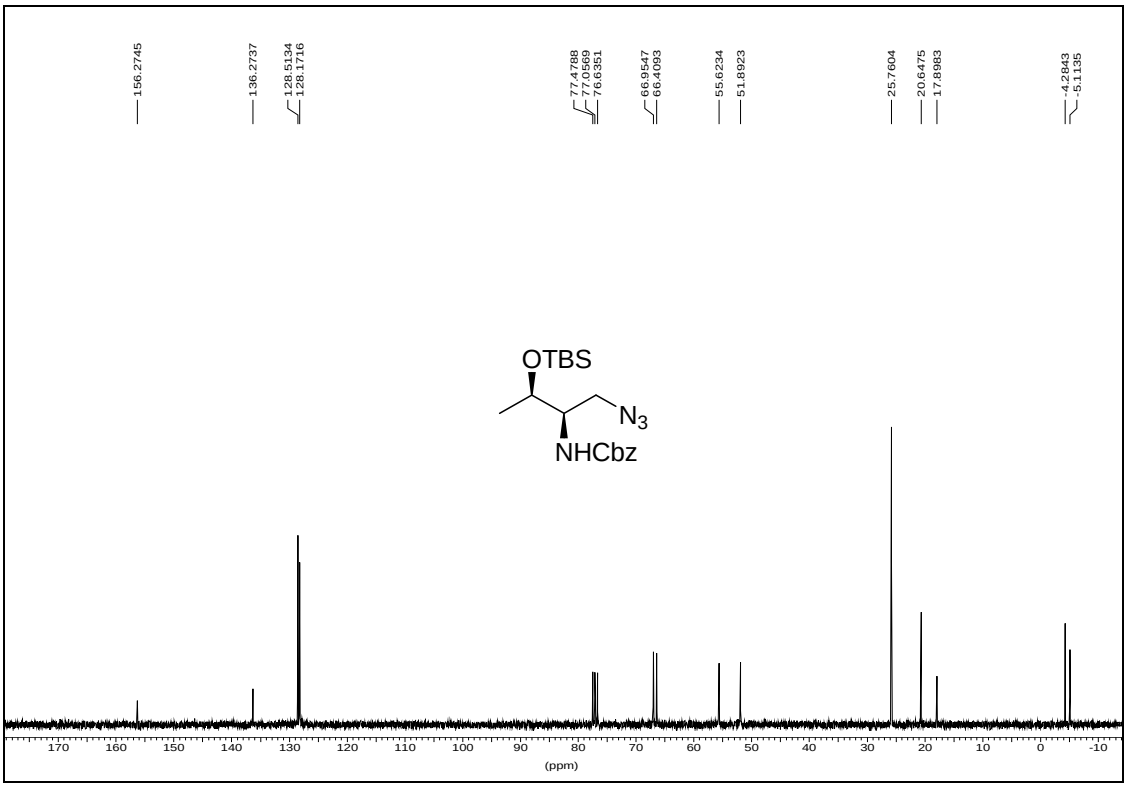
9.1262
5.9748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128.5134
128.1716
77.4788
77.0569
76.6351
66.9547
66.4093
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51.8923
25.7604
20.6475
17.8983
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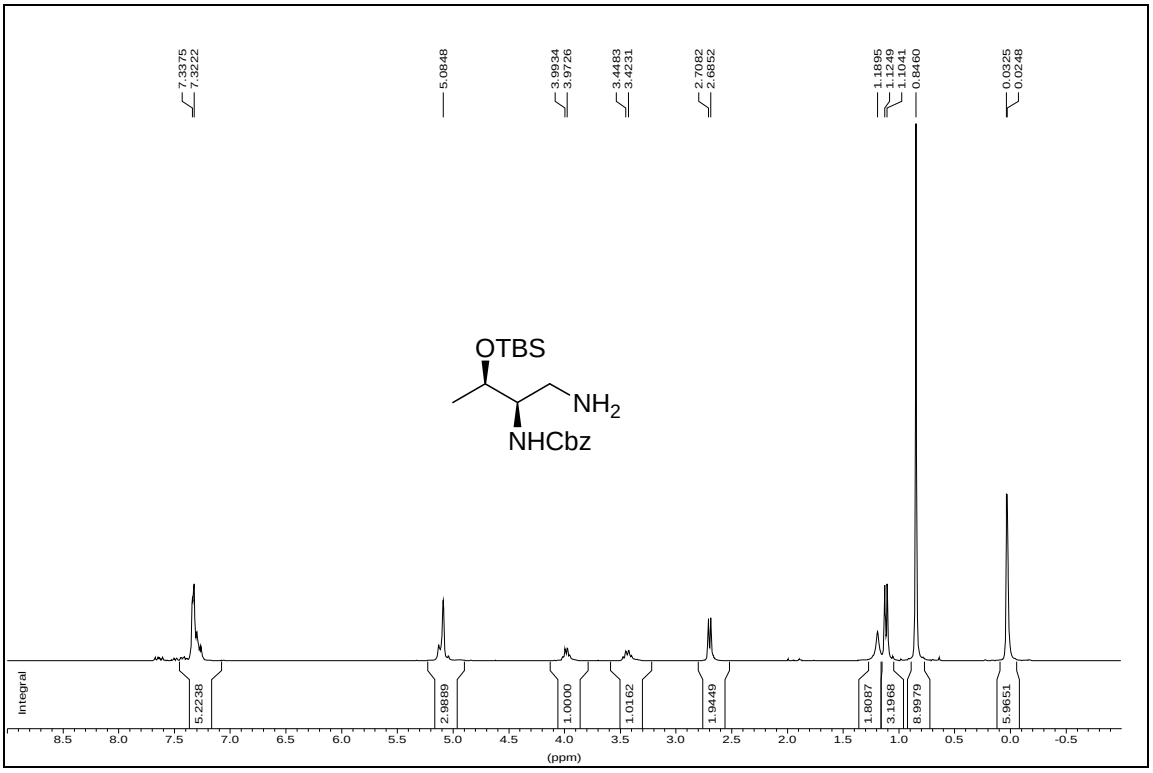
-5.1135
OTBS
N3
NHCbz
(ppm)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5.0848
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3.9726
3.4483
3.4231
2.7082
2.6852
1.1895
1.1749
1.1041
0.8460
0.0325
0.0248
OTBS
NH2
NHCbz
Integral
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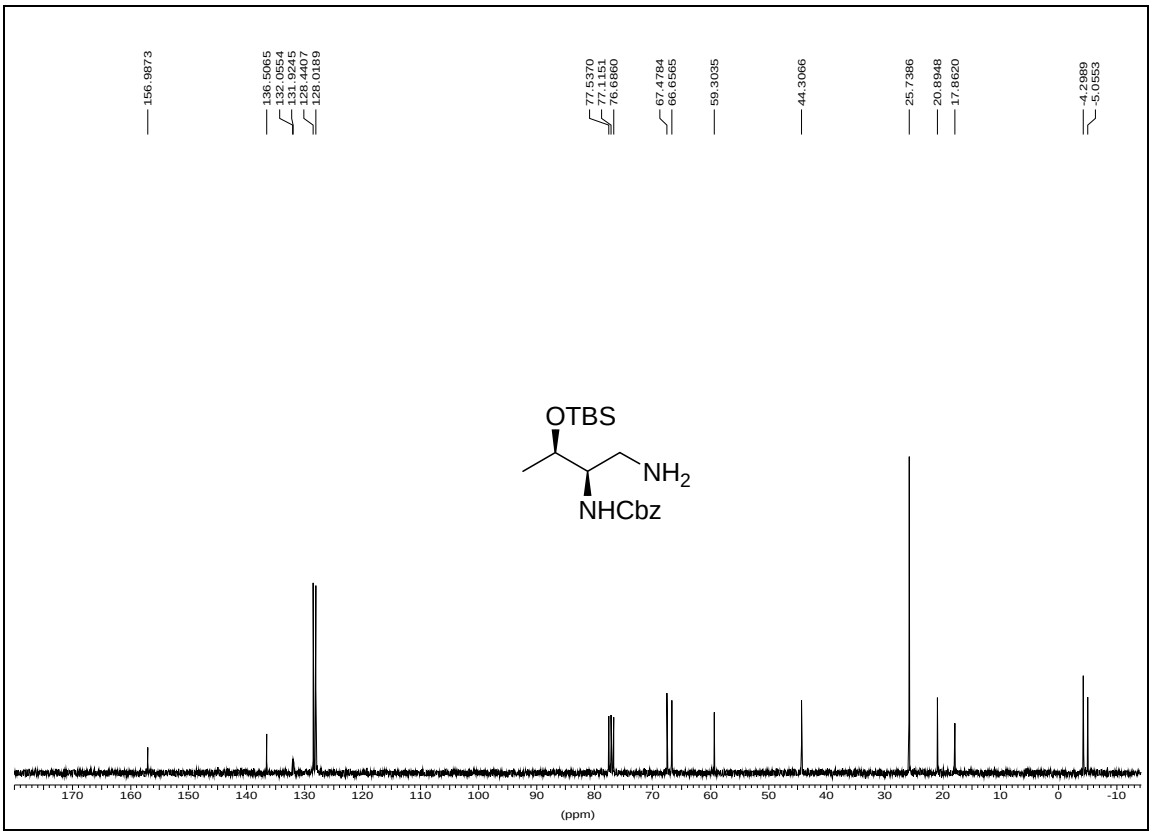
2.9889
1.0000
1.0162
1.9449
1.8087
3.1968
8.9979
5.9651
(ppm)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44.3066
25.7386
20.8948
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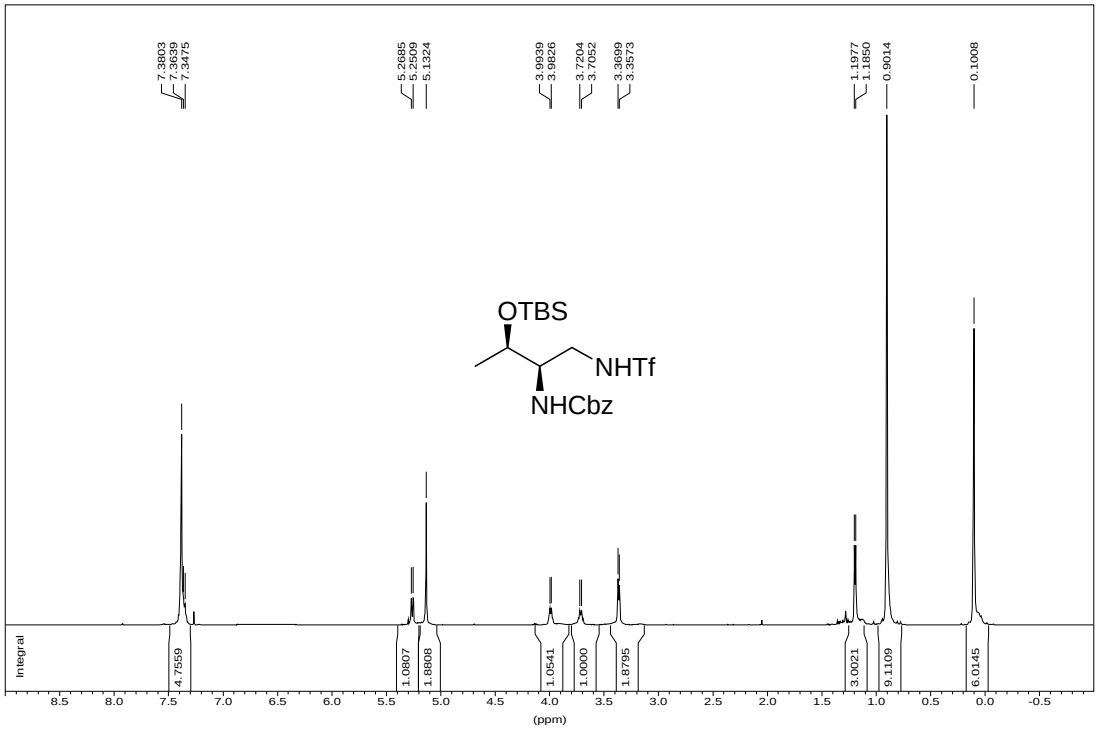
-5.0553
OTBS
NH2
NHCbz
(ppm)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3.7204
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3.3699
3.3573
1.1977
1.1850
0.9014
0.1008
OTBS
NHTf
NHCbz
Integral
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1.8808
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1.0000
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3.0021
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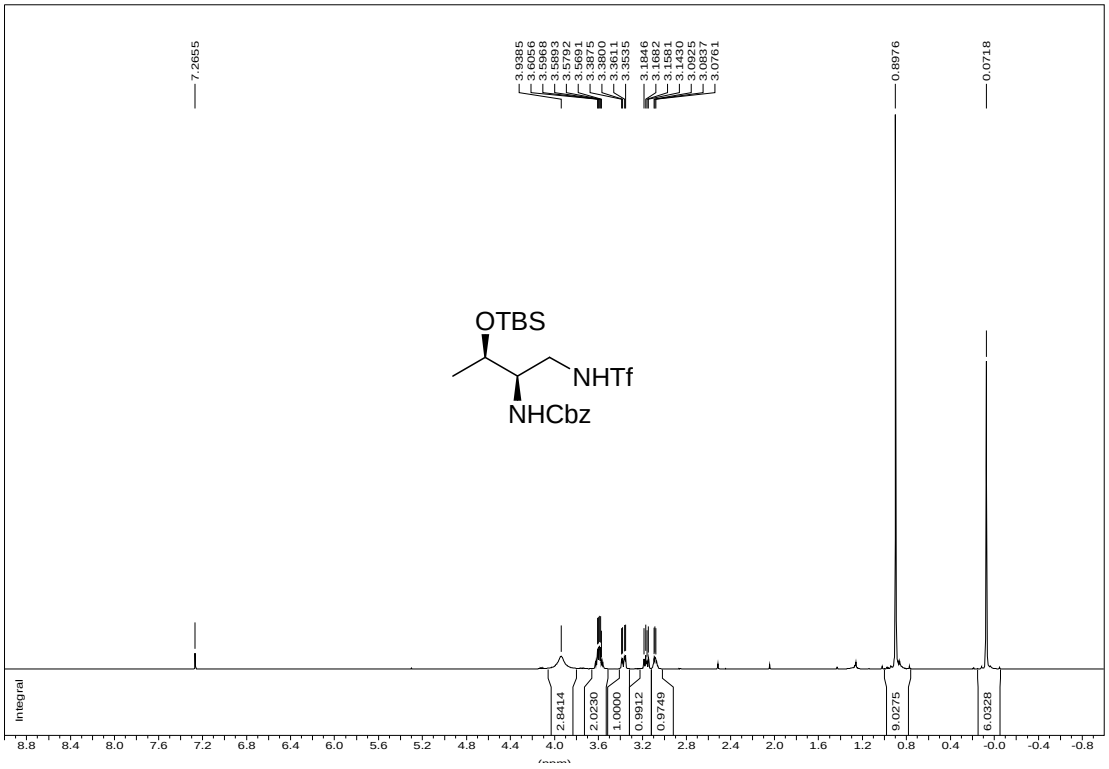
(ppm)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3.6056
3.5968
3.5993
3.5792
3.5691
3.3875
3.3800
3.3611
3.3535
3.1846
3.1682
3.1581
3.1430
3.0925
3.0837
3.0761
0.8976
0.0718
OTBS
NHTf
NHCbz
Integral
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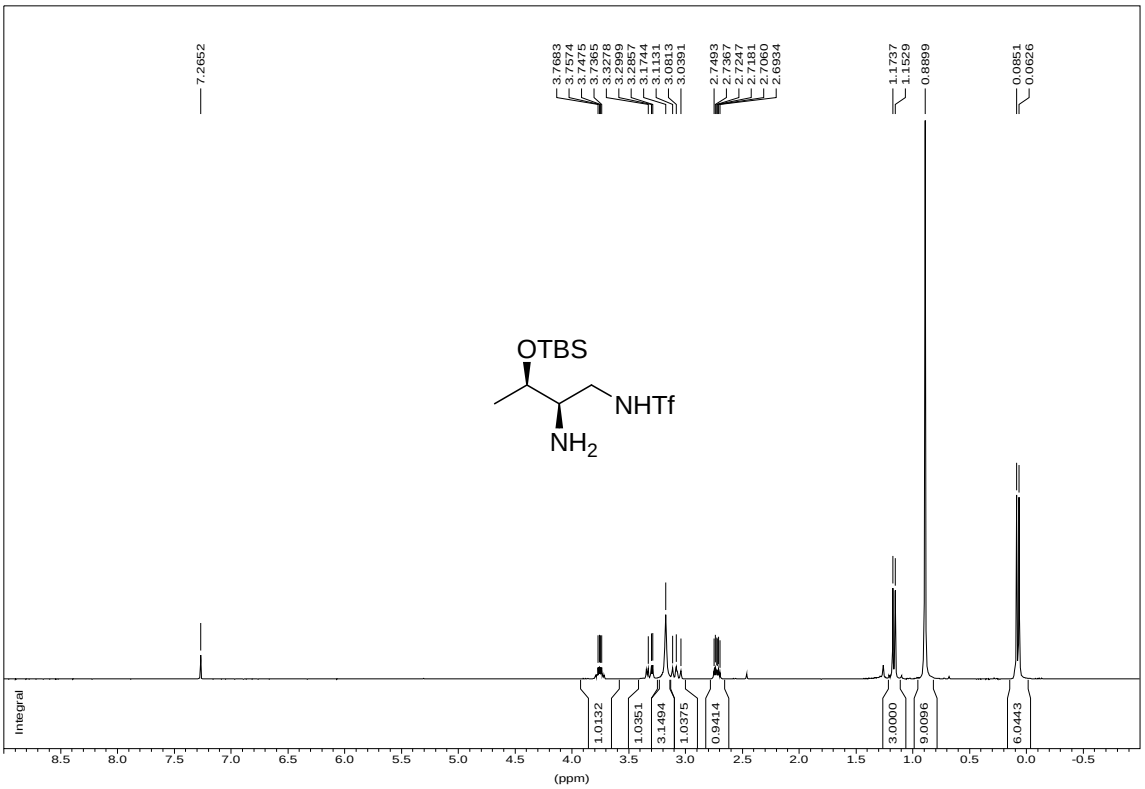
2.0230
1.0000
0.9912
0.9749
9.0275
6.0328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3.7683
3.7574
3.7475
3.7365
3.3278
3.2999
3.2857
3.1744
3.1131
3.0813
3.0391
2.7493
2.7367
2.7247
2.7181
2.7060
2.6934
1.1737
1.1529
0.8899
0.0851
0.0626
OTBS
NHTf
NH2
Integral
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1.0351
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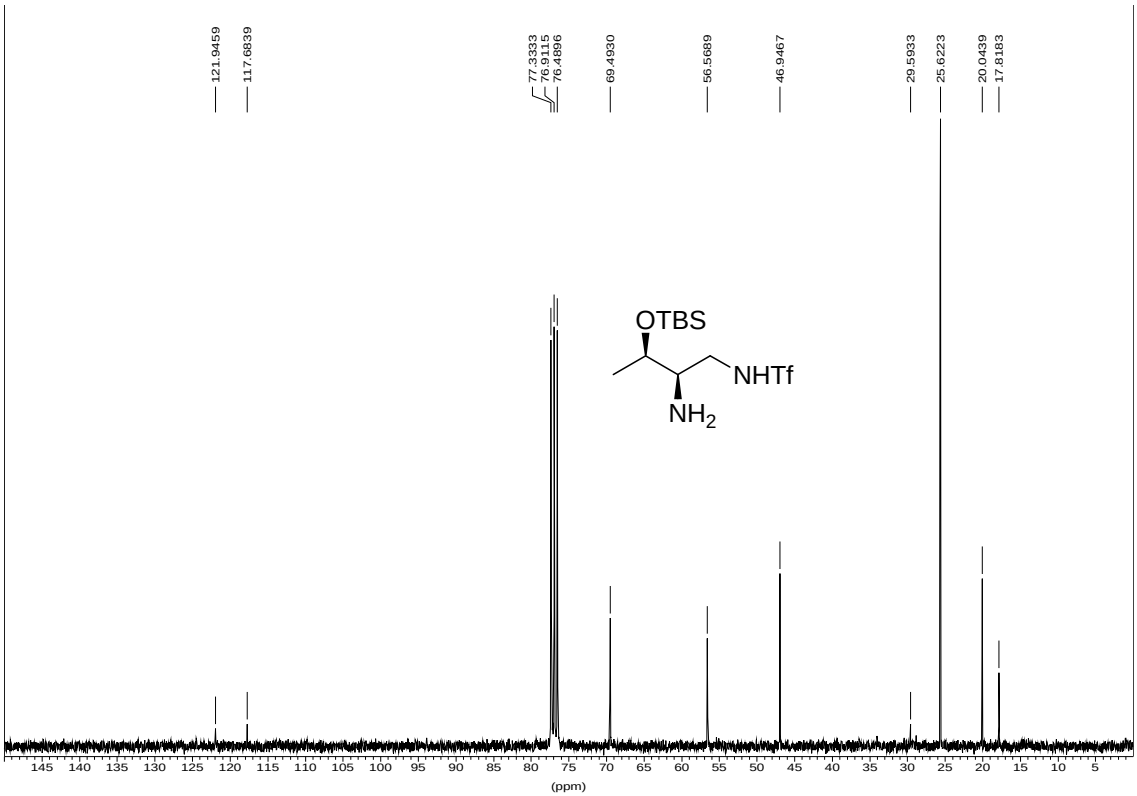
1.0375
0.9414
3.0000
9.0096
6.0443
(ppm)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77.3333
76.9115
76.4896
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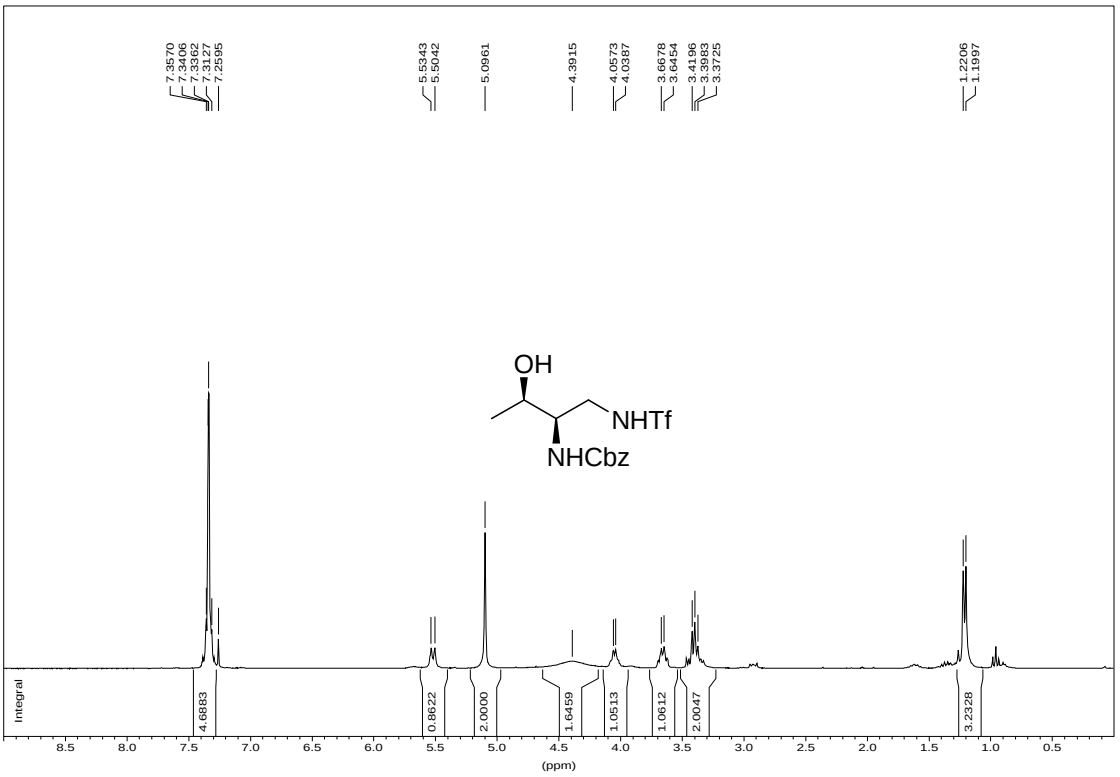
17.8183
OTBS
NHTf
NH2
(ppm)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7.3362
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7.2595
5.5343
5.5042
5.0961
4.3915
4.0573
4.0387
3.6678
3.6454
3.4196
3.3983
3.3725
1.2206
1.1997
OH
NHTf
NHCbz
Integral
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0.8622
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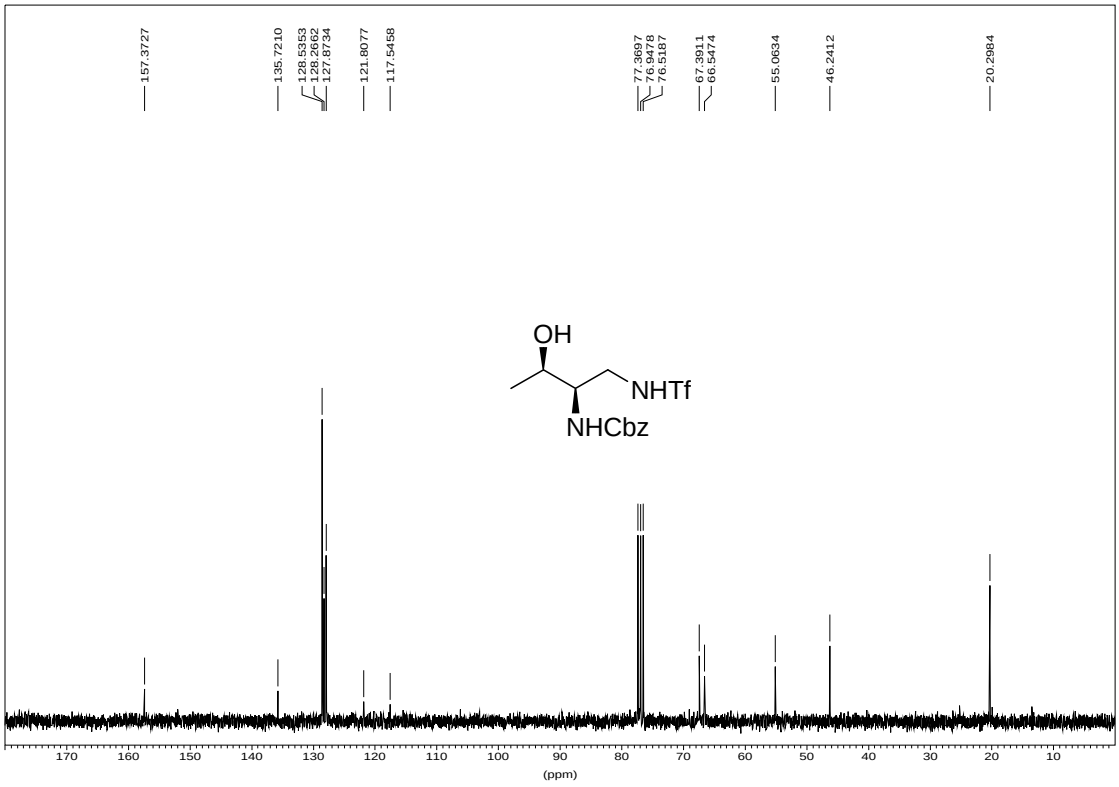
1.0612
2.0047
3.2328
(ppm)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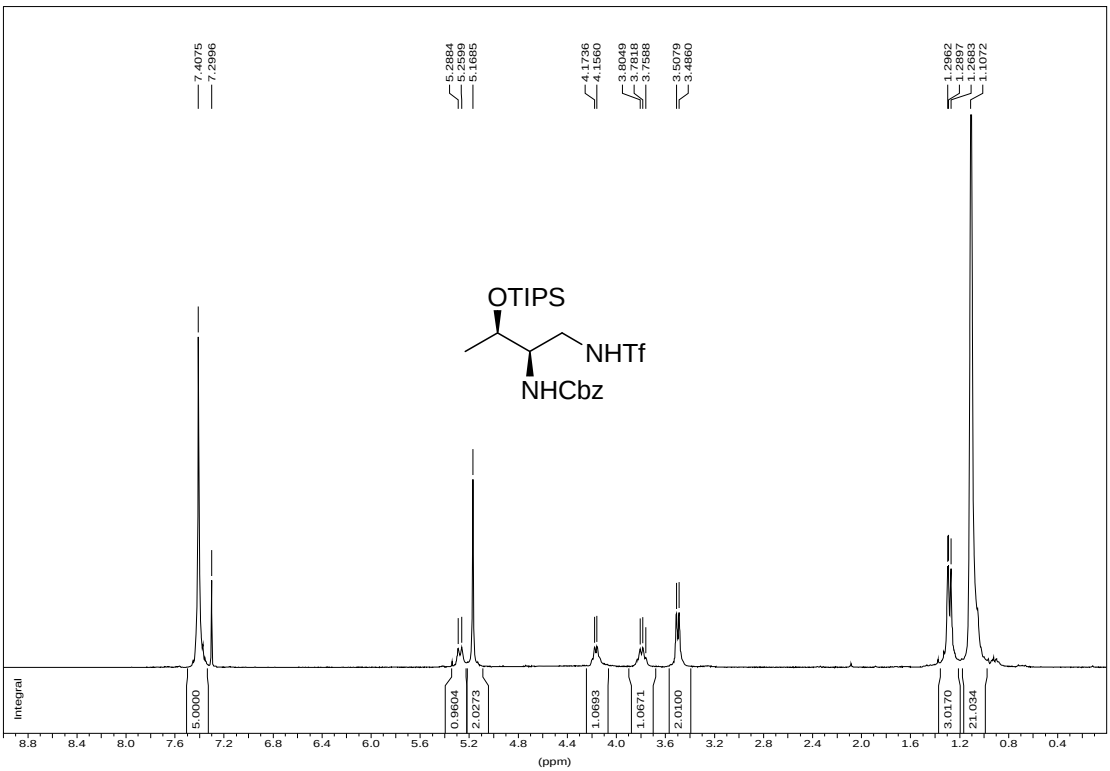
67.3911
66.5474
55.0634
46.2412
20.2984
OH
NHTf
NHCbz
(ppm)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5.2884
5.2599
5.1685
4.1736
4.1560
3.8049
3.7818
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3.5079
3.4860
1.2962
1.2897
1.2683
1.1072
OTIPS
NHTf
NHCbz
Integral
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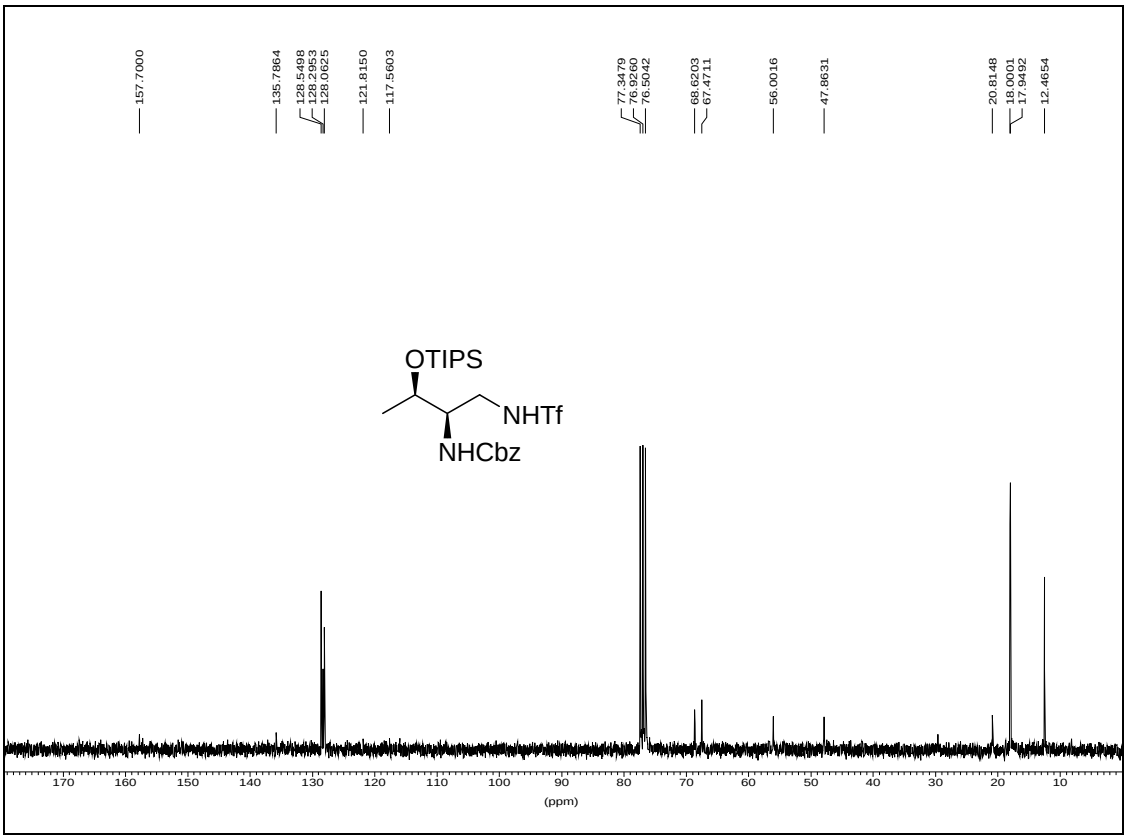
0.9604
2.0273
1.0693
1.0671
2.0100
3.0170
21.034
(ppm)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117.5603
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68.6203
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47.8631
20.8148
18.0001
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12.4654
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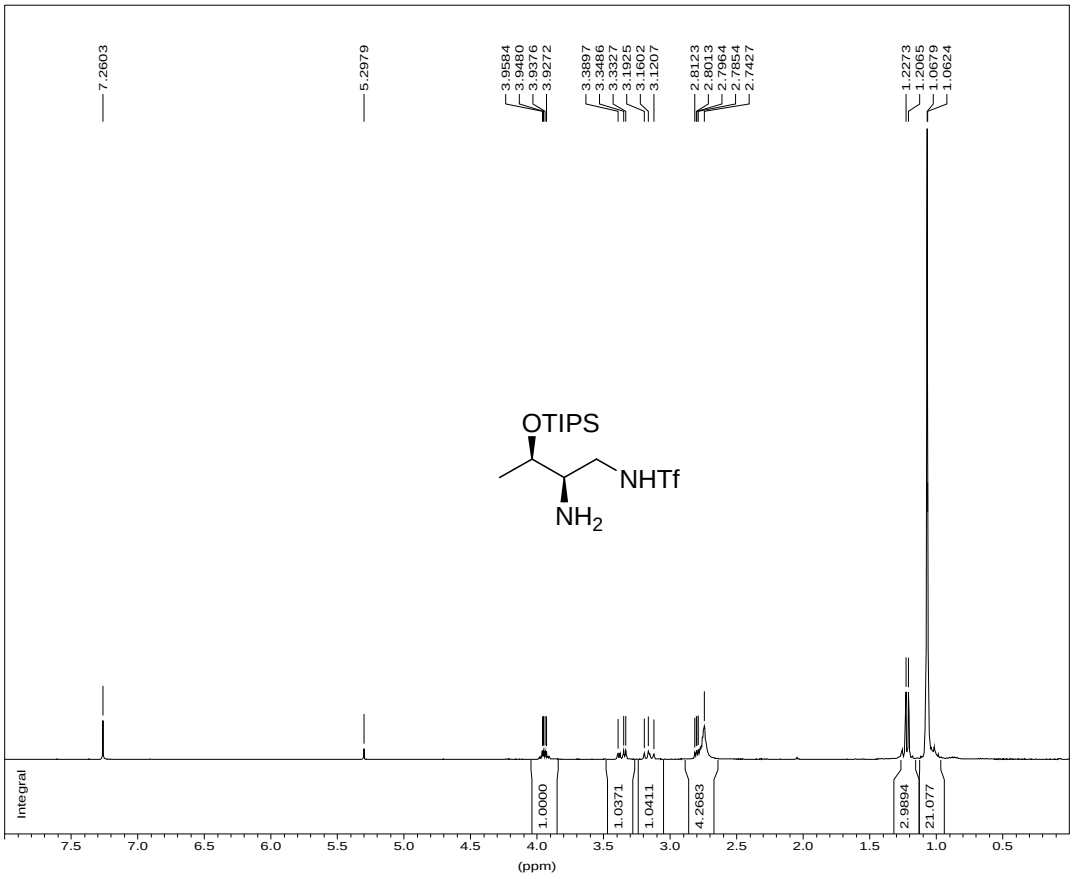
NHTf
NHCbz
(ppm)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3.9376
3.9272
3.3897
3.3486
3.3327
3.1925
3.1602
3.1207
2.8123
2.8013
2.7964
2.7854
2.7427
1.2273
1.2065
1.0679
1.0624
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NHTf
NH2
Integral
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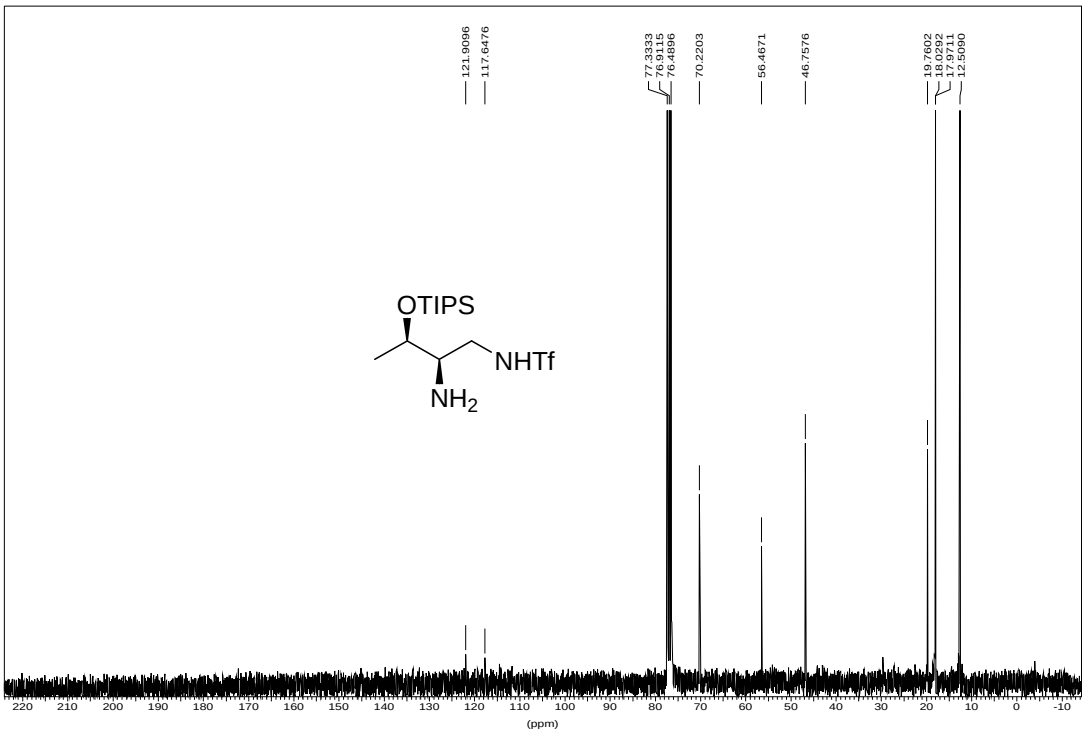
4.2683
2.9894
21.077
(ppm)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77.3333
76.9115
76.4896
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46.7576
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18.0232
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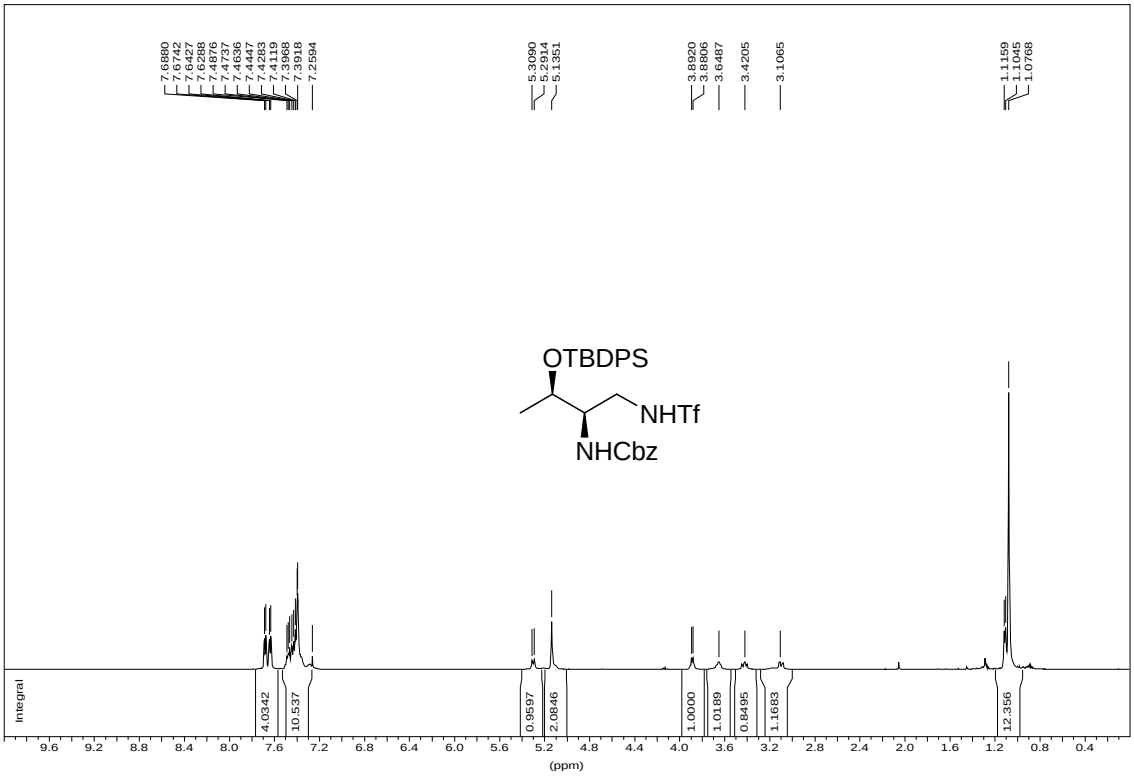
12.5090
OTIPS
NHTf
NH2
(ppm)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7.4283
7.4119
7.3968
7.3818
7.2594
5.3090
5.2914
5.1351
3.8920
3.8806
3.6487
3.4205
3.1065
1.1159
1.1045
1.0768
OTBDPS
NHTf
NHCbz
Integral
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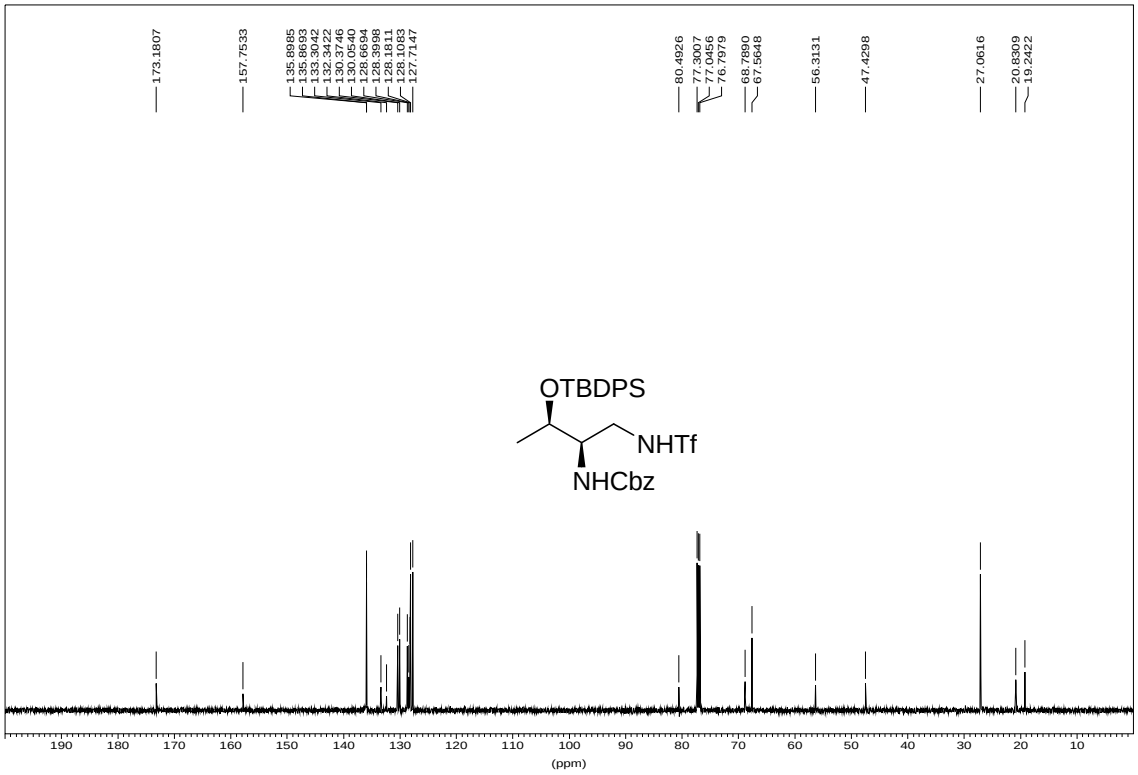
(ppm)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128.1811
128.1083
127.7147
80.4926
77.3007
77.0456
76.7979
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47.4298
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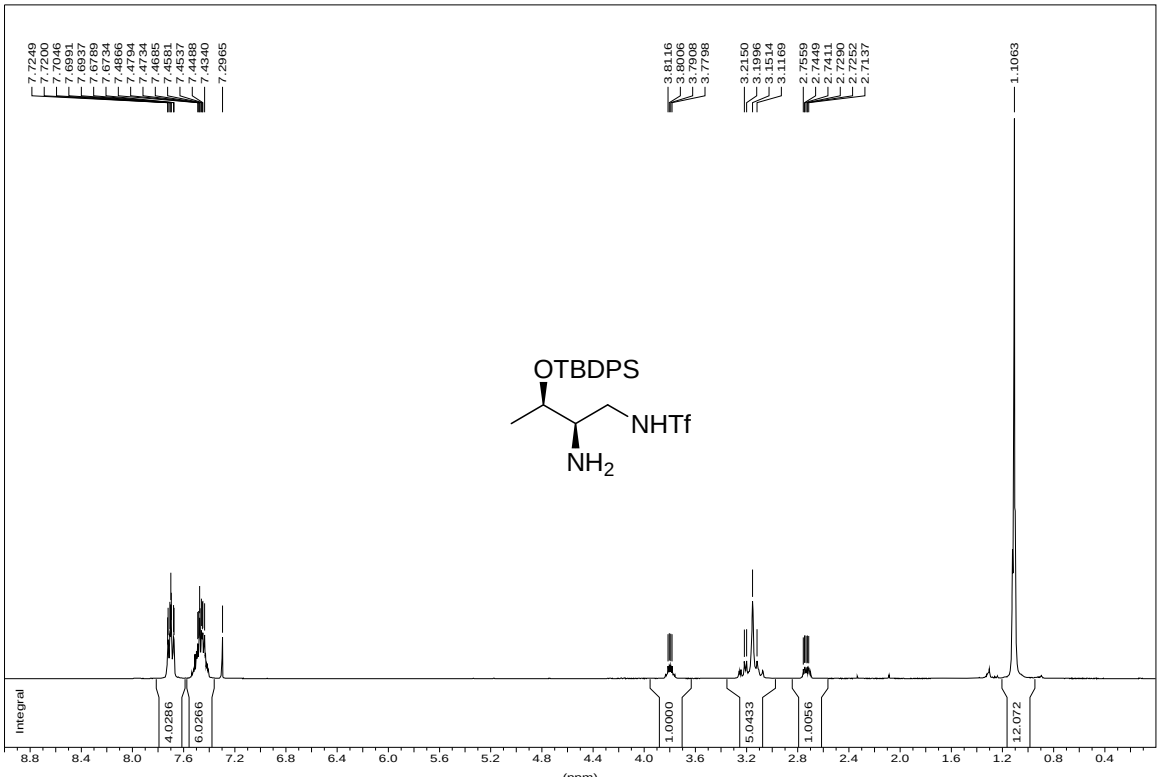
20.8309
19.2422
OTBDPS
NHTf
NHCbz
(ppm)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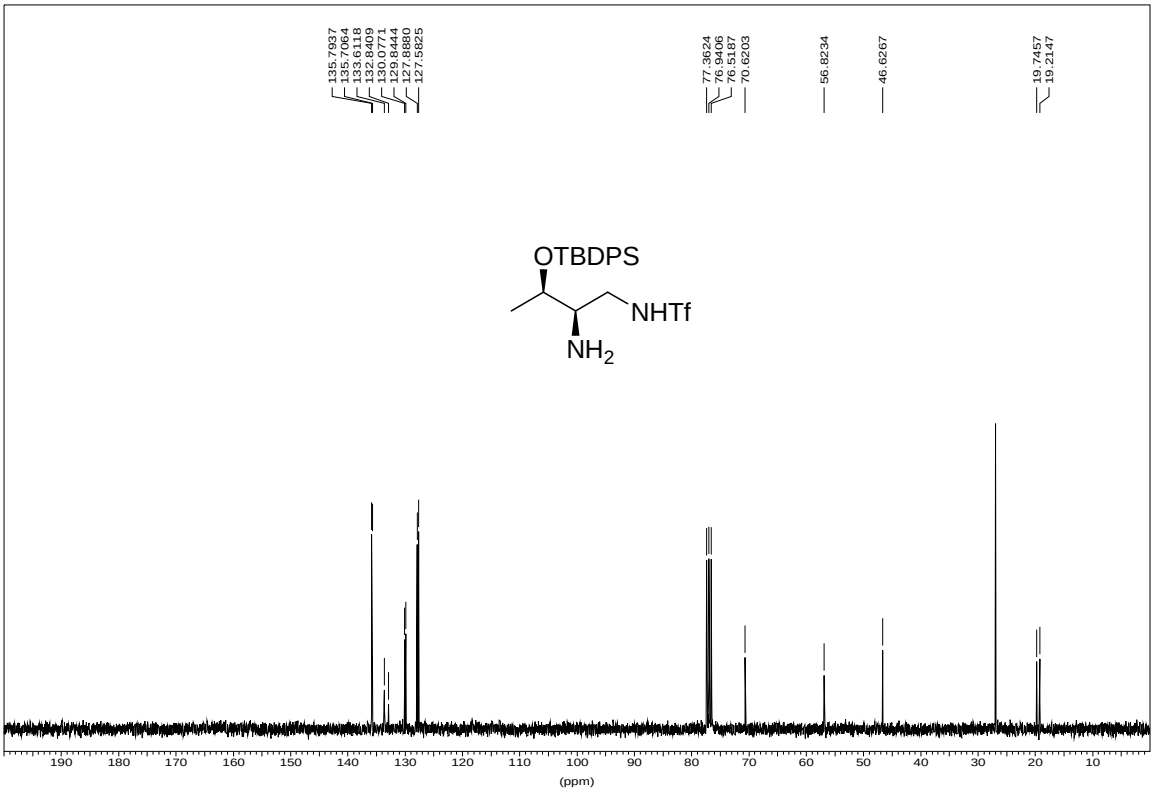
7.4794
7.4734
7.4685
7.4581
7.4537
7.4488
7.4340
7.2965
3.8116
3.8006
3.7908
3.7798
3.2150
3.1996
3.1514
3.1169
2.7559
2.7449
2.7411
2.7290
2.7252
2.7137
1.1063
OTBDPS
NHTf
NH2
Integral
4.0286
6.0266
1.0000
5.0433
1.0056
12.072
8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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130.0771
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127.8880
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77.3624
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76.5187
70.6203
56.8234
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OTBDPS
NHTf
NH2
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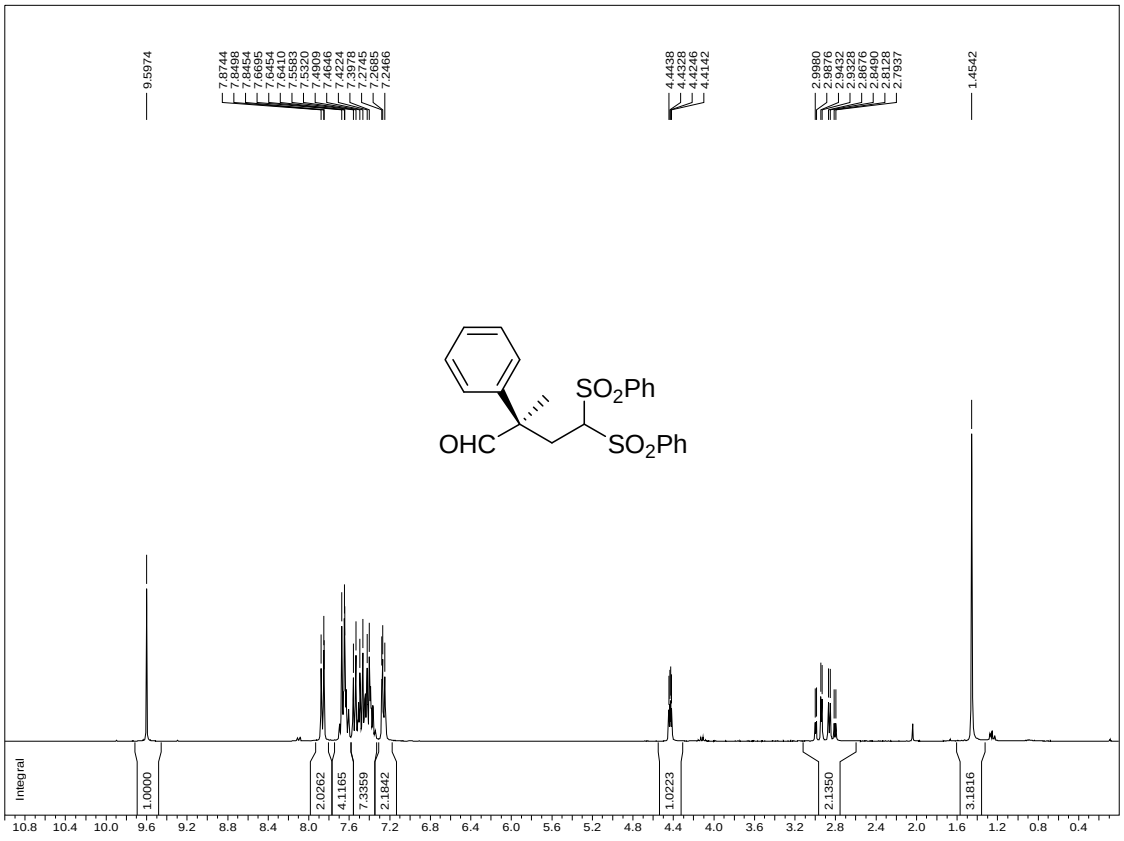
(ppm)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7.5320
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7.4566
7.4224
7.3978
7.2745
7.2685
7.2466
4.4438
4.4328
4.4246
4.4142
2.9980
2.9876
2.9432
2.9328
2.8676
2.8490
2.8128
2.7937
1.4542
SO2Ph
OHC
SO2Ph
Integral
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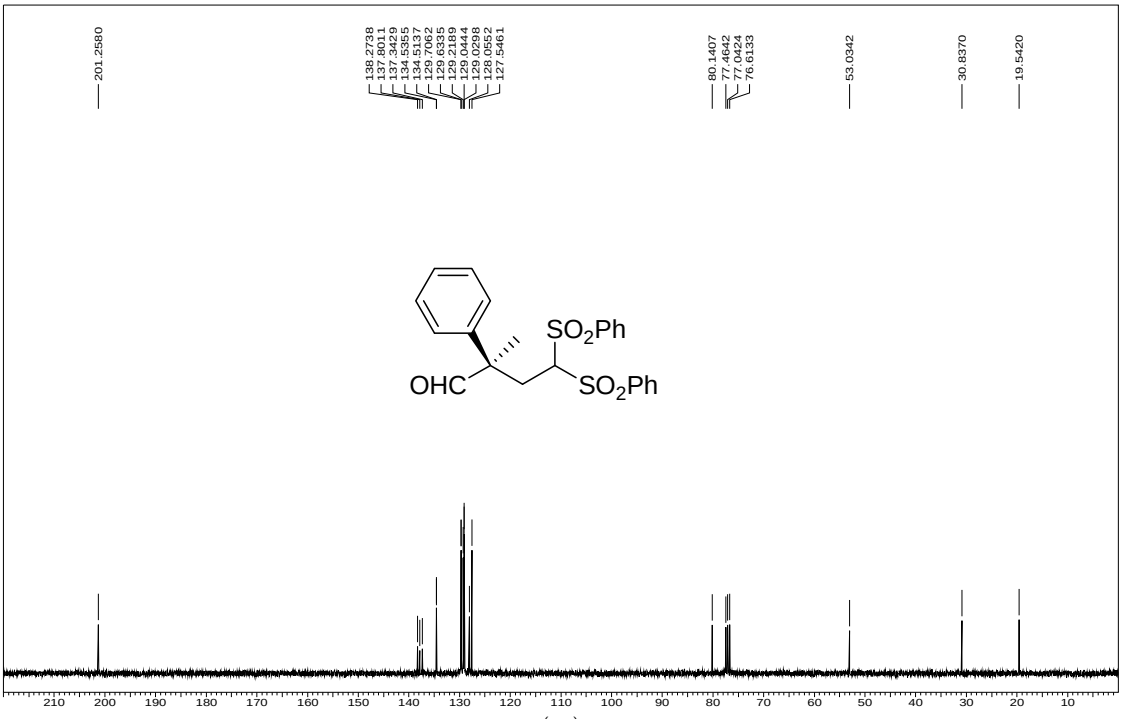
3.1816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128.0952
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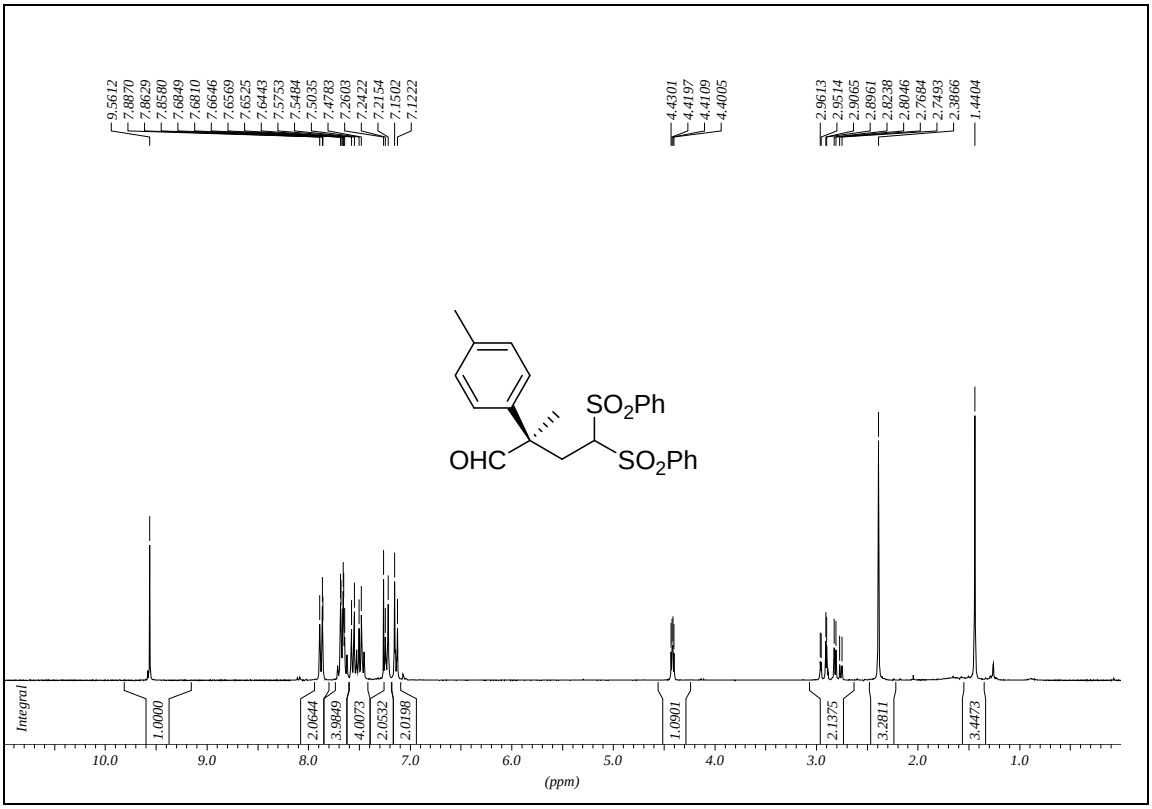
53.0342
30.8370
19.5420
SO2Ph
OHC
SO2Ph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7.5484
7.5035
7.4783
7.2603
7.2422
7.2154
7.1502
7.1222
4.4301
4.4197
4.4109
4.4005
2.9613
2.9514
2.9065
2.8961
2.8238
2.8046
2.7684
2.7493
2.3866
1.4404
SO2Ph
OHC
SO2Ph
Integral
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3.9849
4.0073
2.0532
2.0198
1.0901
2.1375
3.2811
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8.0
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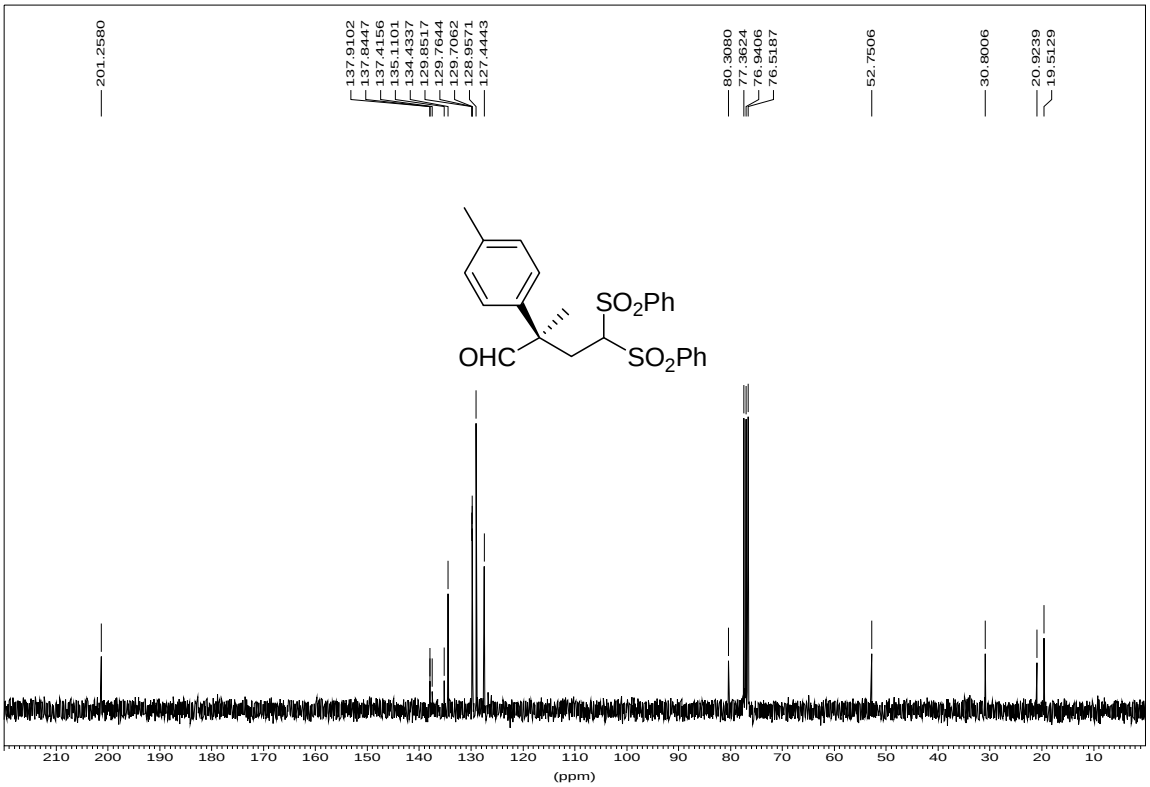
(ppm)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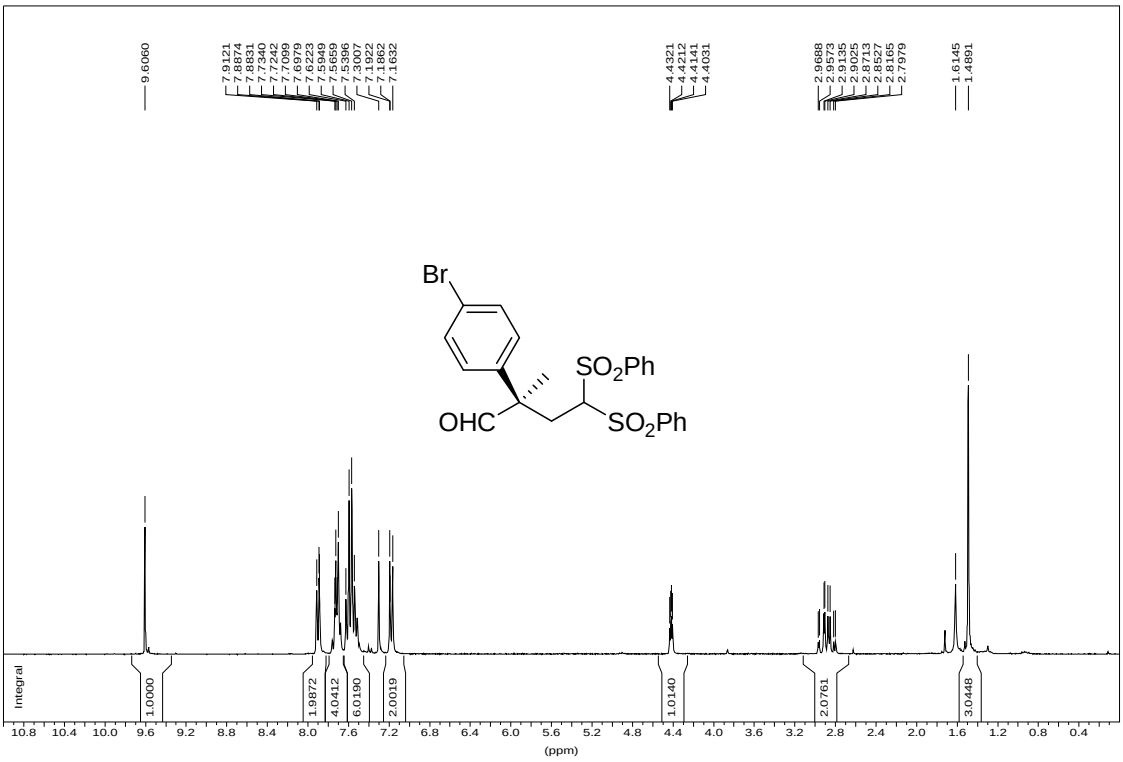
127.4443
80.3080
77.3624
76.9406
76.5187
52.7506
30.8006
20.9239
19.5129
SO2Ph
OHC
SO2Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)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7.8874
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7.7340
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7.7099
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7.6223
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7.5669
7.5396
7.3007
7.1922
7.1862
7.1632
4.4321
4.4212
4.4141
4.4031
2.9688
2.9573
2.9135
2.9025
2.8733
2.8527
2.8165
2.7979
1.6145
1.4891
Br
SO2Ph
OHC
SO2Ph
Integral
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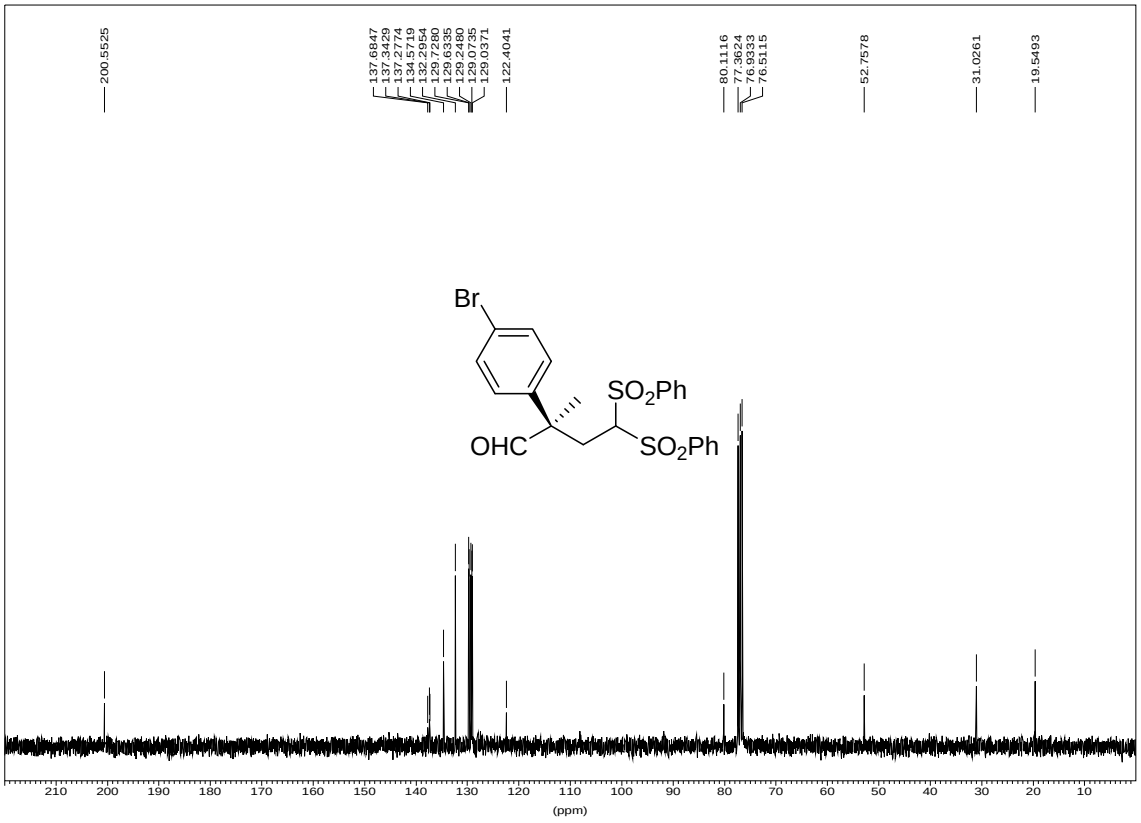
(ppm)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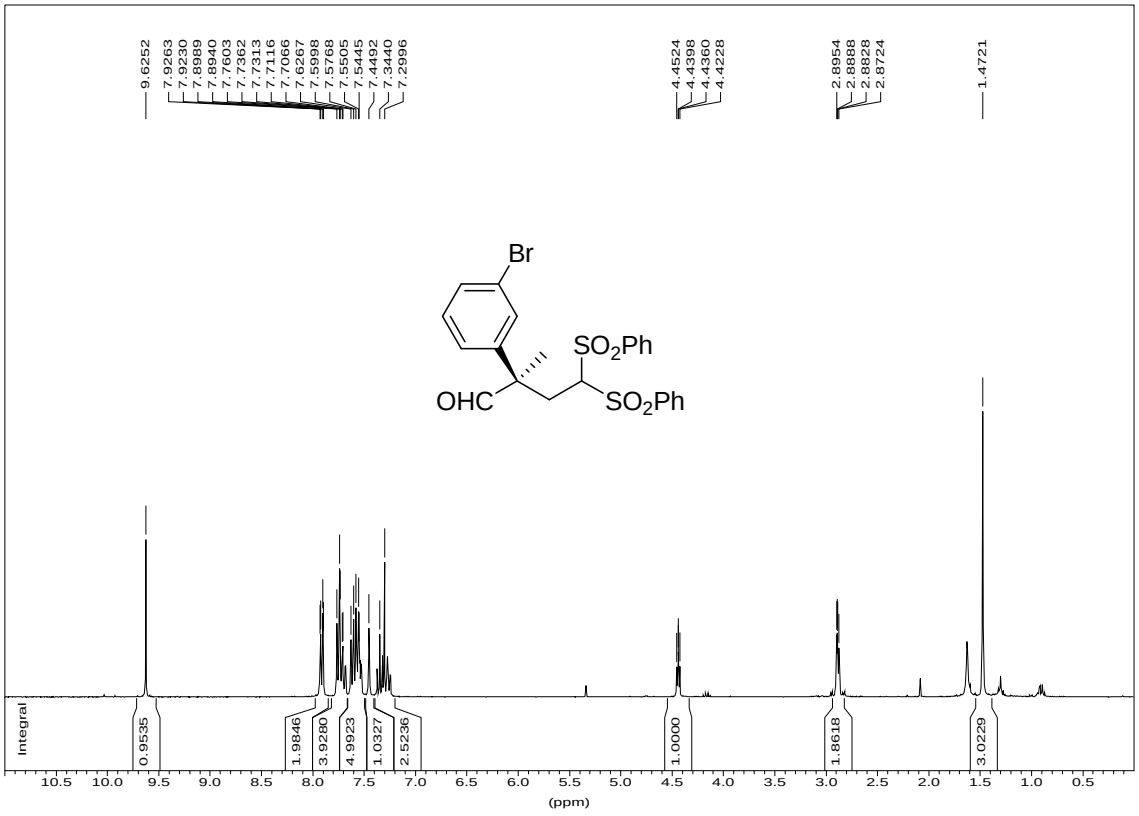
122.4041
80.1116
77.3624
76.9333
76.5115
52.7578
31.0261
19.5493
Br
SO2Ph
OHC
SO2Ph
(ppm)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7.6267
7.5998
7.5768
7.5505
7.5445
7.4492
7.3440
7.2996
4.4524
4.4398
4.4360
4.4228
2.8954
2.8888
2.8828
2.8724
1.4721
Br
SO2Ph
OHC
SO2Ph
Integral
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3.9280
4.9923
1.0327
2.5236
1.0000
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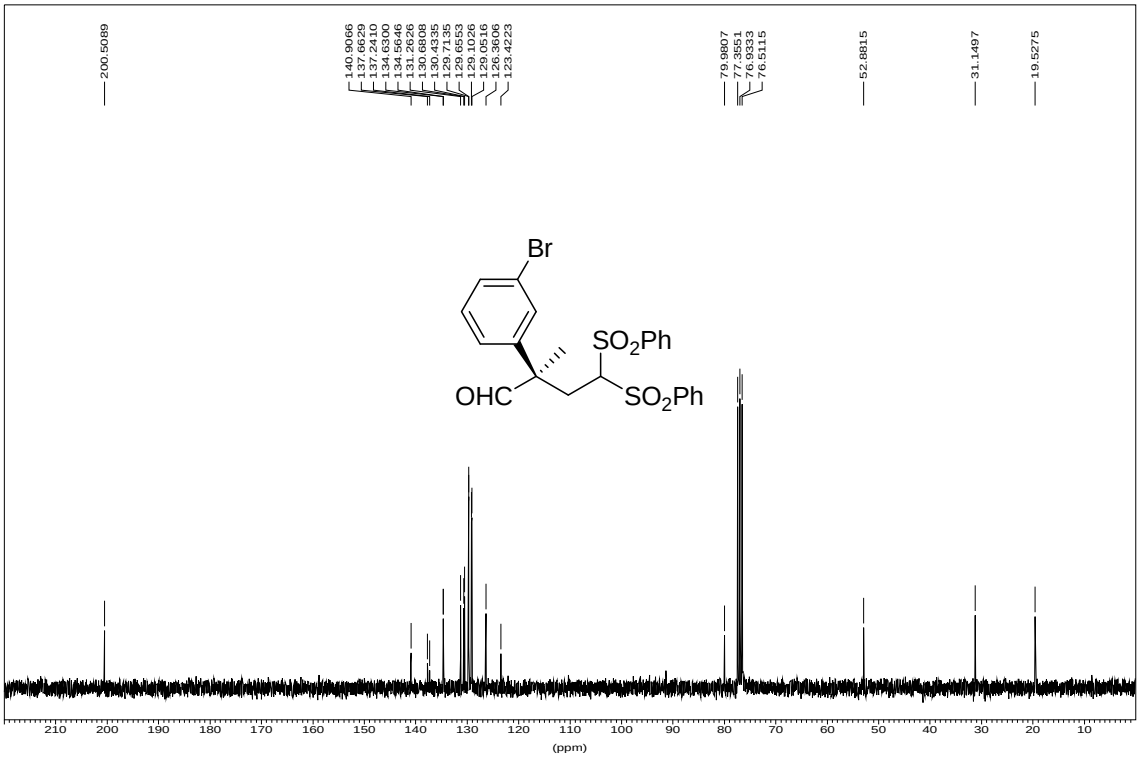
3.0229
(ppm)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129.1026
129.0516
126.3606
123.4223
79.9807
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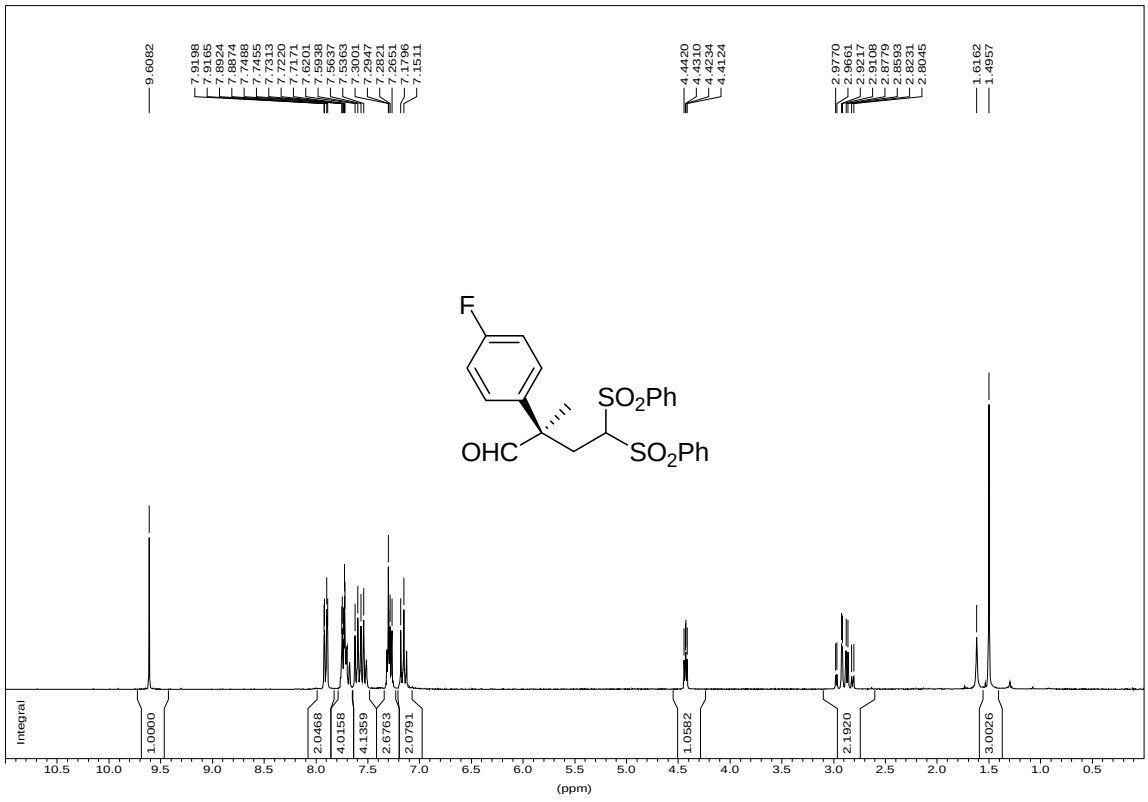
76.5115
52.8815
31.1497
19.5275
Br
SO2Ph
OHC
SO2Ph
(ppm)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7.6201
7.5938
7.5637
7.5563
7.3001
7.2947
7.2821
7.2651
7.1796
7.1511
4.4420
4.4310
4.4234
4.4124
2.9770
2.9651
2.9217
2.9108
2.8779
2.8593
2.8231
2.8045
1.6162
1.4957
F
SO2Ph
OHC
SO2Ph
Integral
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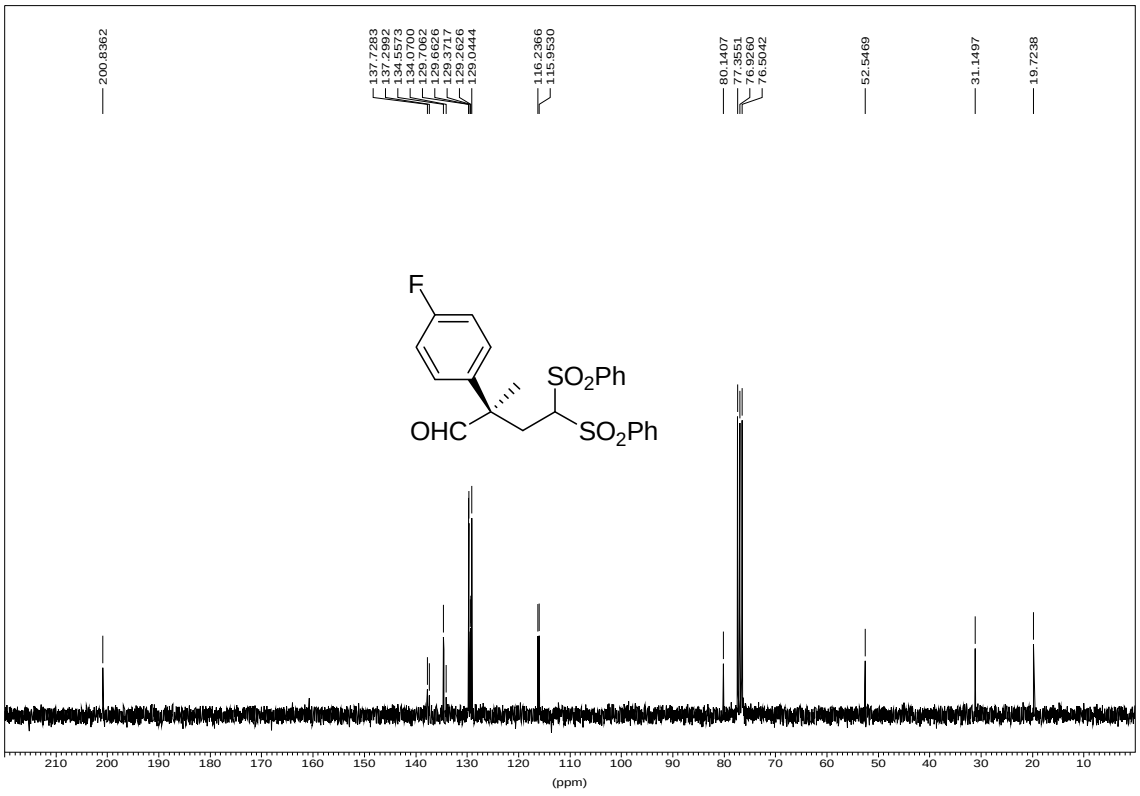
4.0158
4.1359
2.6763
2.0791
1.0582
2.1920
3.0026
(ppm)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115.9530
80.1407
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76.5042
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31.1497
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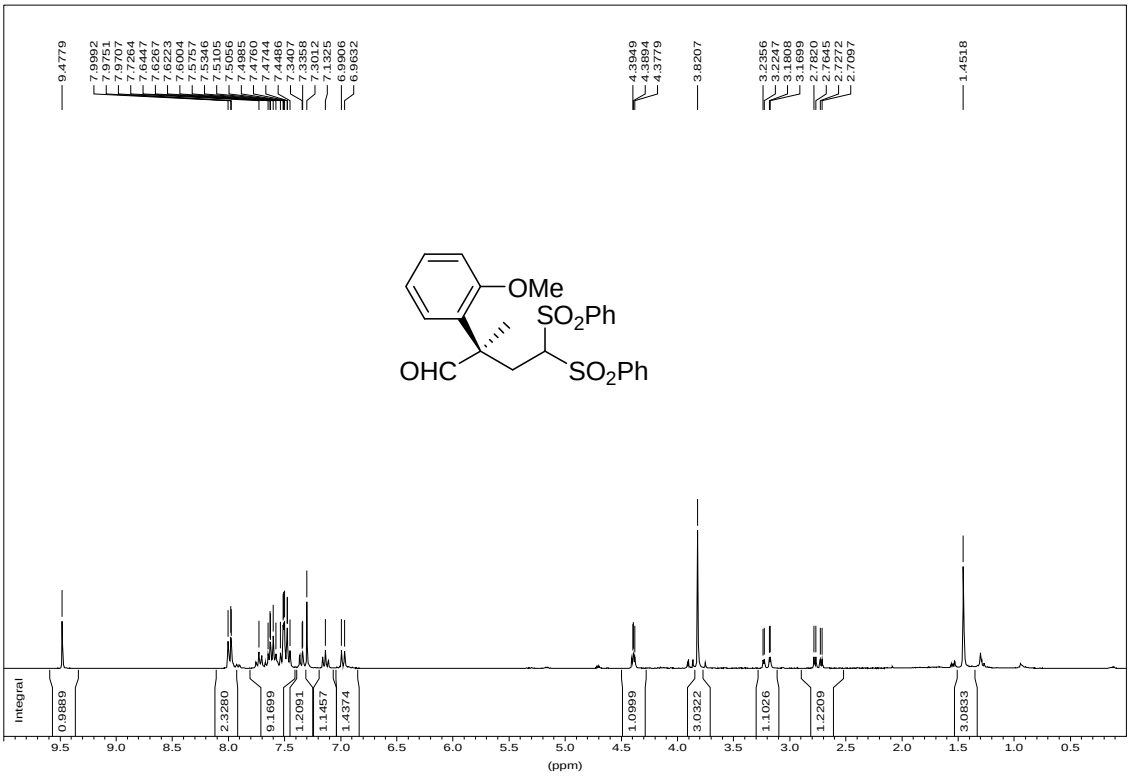
F
SO2Ph
OHC
SO2Ph
(ppm)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7.5155
7.5056
7.4985
7.4760
7.4744
7.4486
7.3407
7.3358
7.3012
7.1325
6.9906
6.9632
4.3949
4.3894
4.3779
3.8207
3.2356
3.2247
3.1808
3.1699
2.7820
2.7645
2.7272
2.7097
1.4518
OMe
SO2Ph
OHC
SO2Ph
Integral
0.9889
2.3280
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1.1457
1.4374
1.0999
3.0322
1.1026
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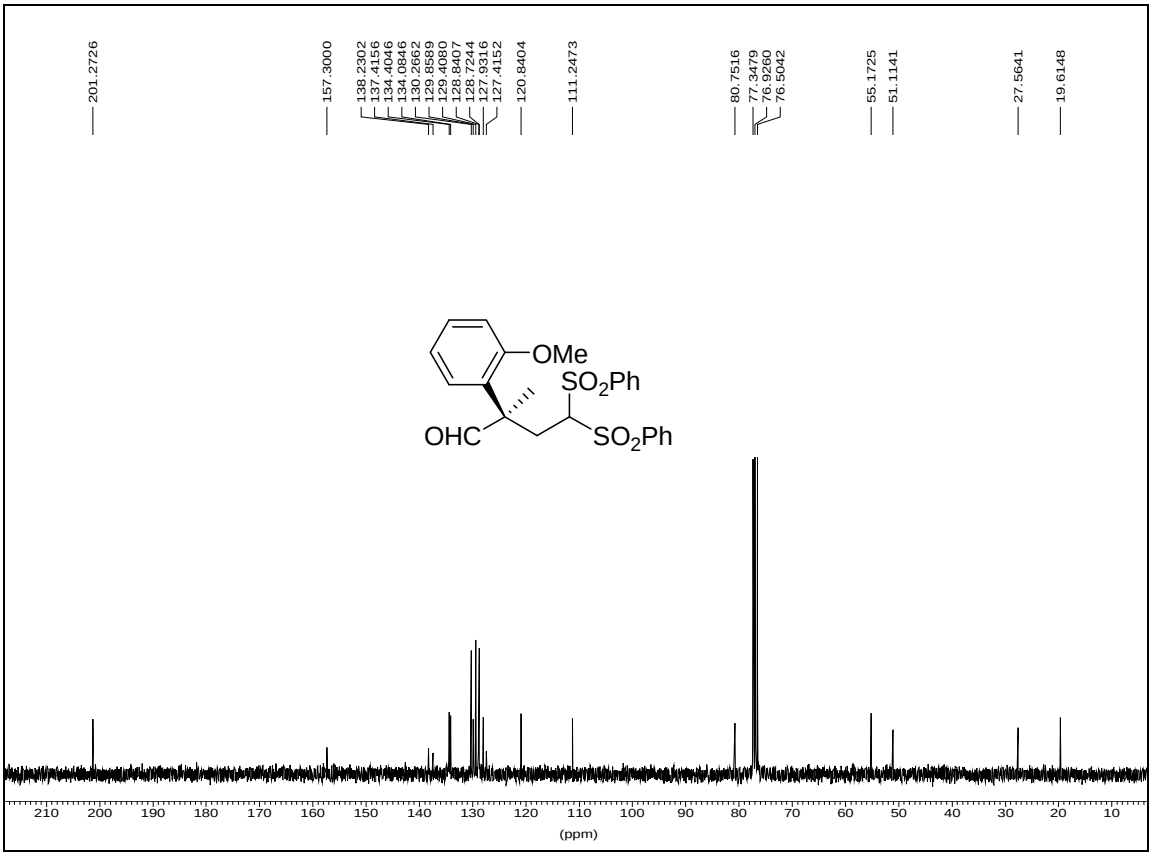
3.0833
(ppm)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128.7244
128.3216
127.4152
120.8404
111.2473
80.7516
77.3479
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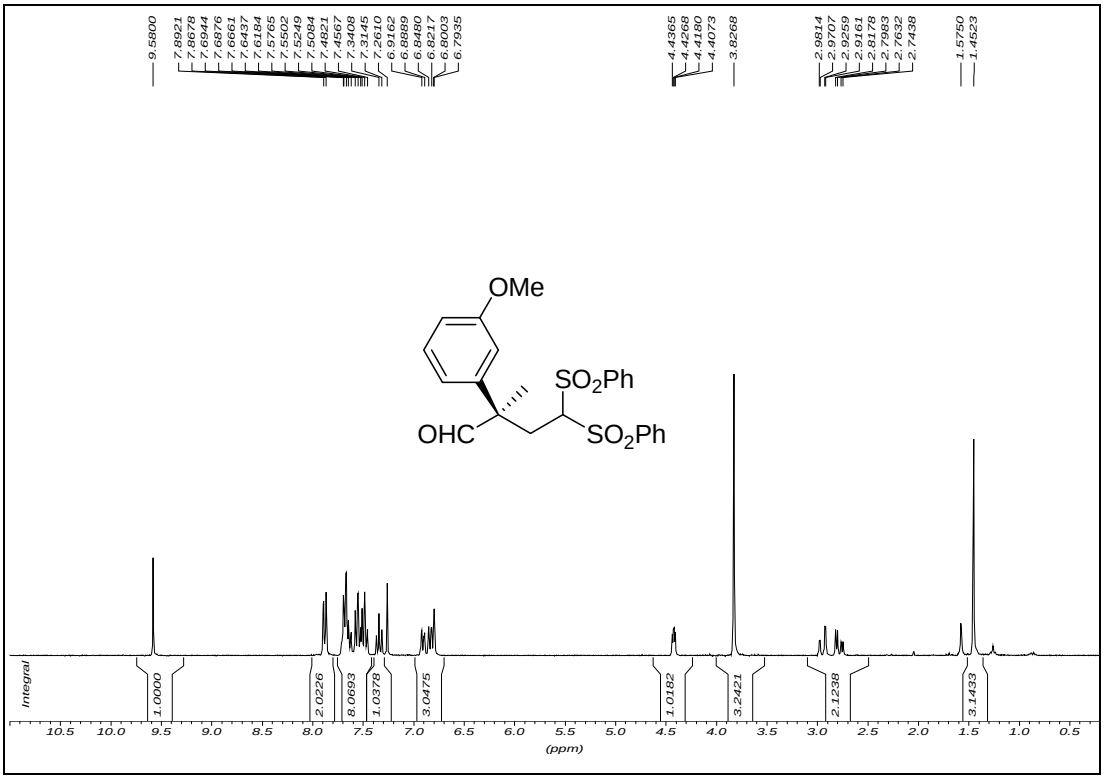
55.1725
51.1141
27.5641
19.6148
OMe
SO2Ph
OHC
SO2Ph
(ppm)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7.8644
7.8476
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7.6437
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7.5765
7.5502
7.5249
7.5084
7.4821
7.4567
7.3408
7.3145
7.2610
6.9162
6.8889
6.8480
6.8217
6.8003
6.7935
4.4365
4.4268
4.4180
4.4073
3.8268
2.9814
2.9707
2.9259
2.9161
2.8178
2.7983
2.7632
2.7438
1.5750
1.4523
OMe
SO2Ph
OHC
SO2Ph
Integral
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8.0693
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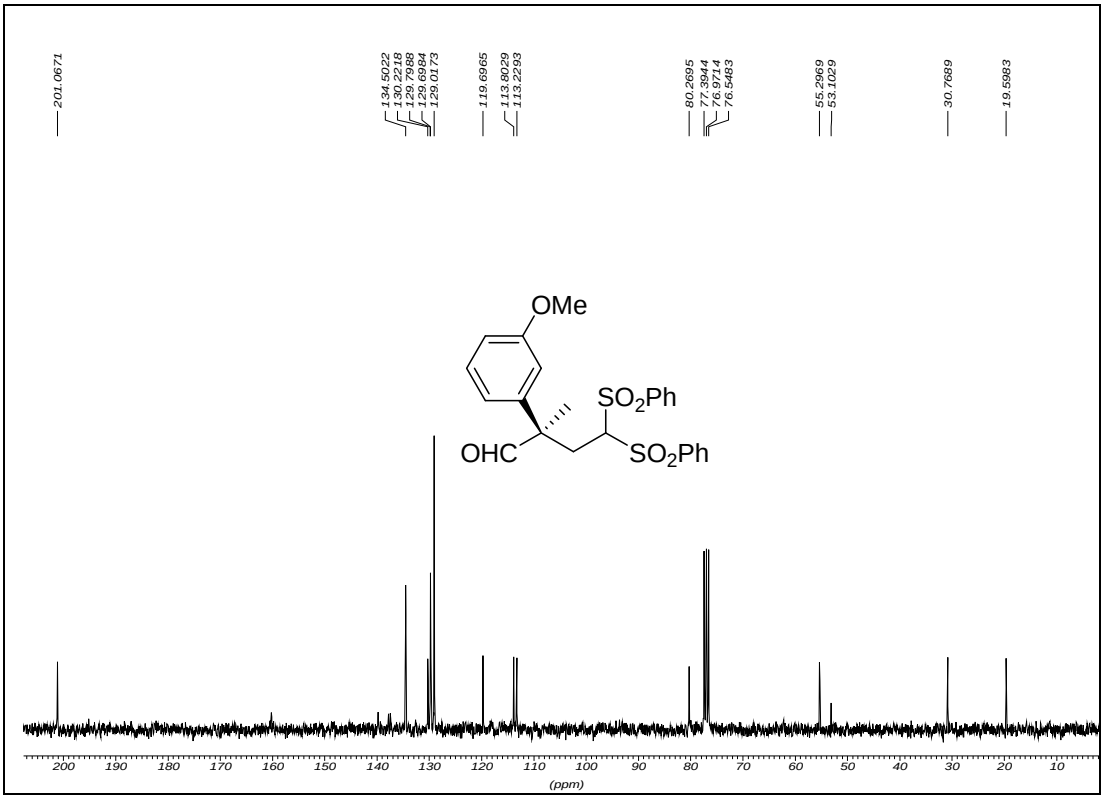
3.0475
1.0182
3.2421
2.1238
3.1433
(ppm)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130.2218
129.7988
129.6984
129.0173
119.6965
113.8029
113.2293
80.2695
77.3944
76.9714
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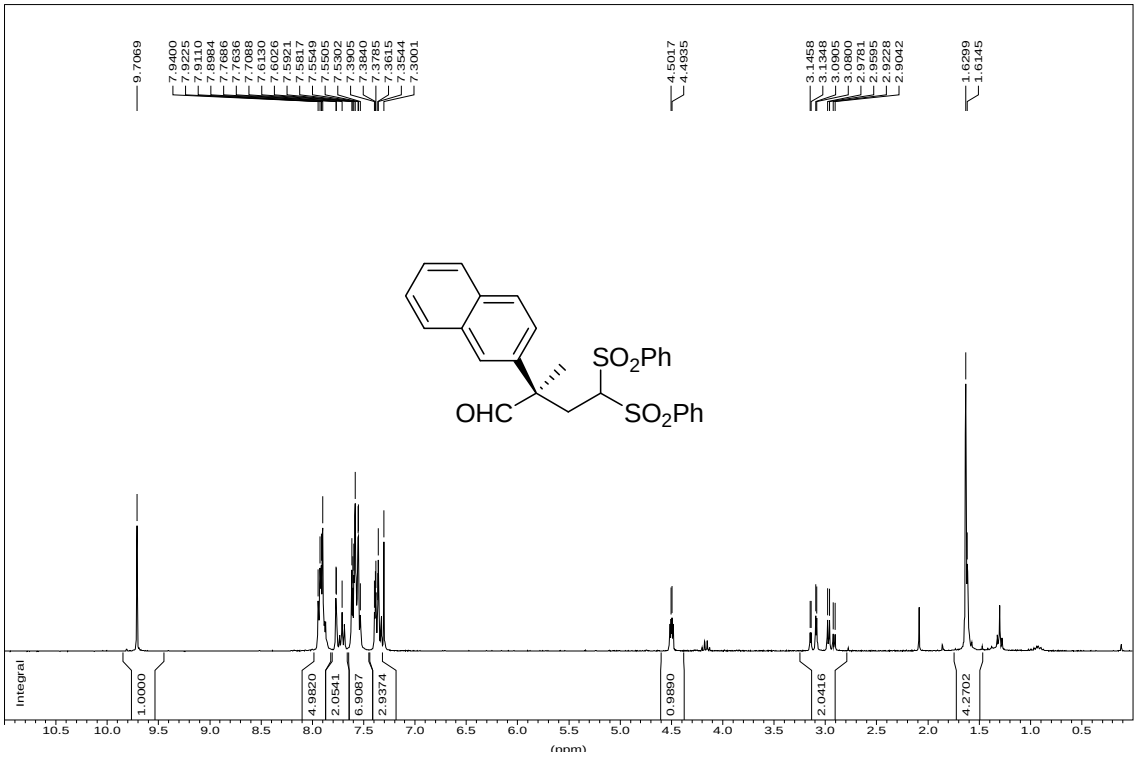
55.2969
53.1029
30.7689
19.5983
OMe
SO2Ph
OHC
SO2Ph
(ppm)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7.9225
7.9110
7.8984
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7.7636
7.7088
7.6130
7.6026
7.5921
7.5817
7.5549
7.5505
7.5302
7.3945
7.3840
7.3785
7.3615
7.3544
7.3001
4.5017
4.4935
3.1458
3.1348
3.0905
3.0800
2.9781
2.9595
2.9228
2.9042
1.6299
1.6145
SO2Ph
OHC
SO2Ph
Integral
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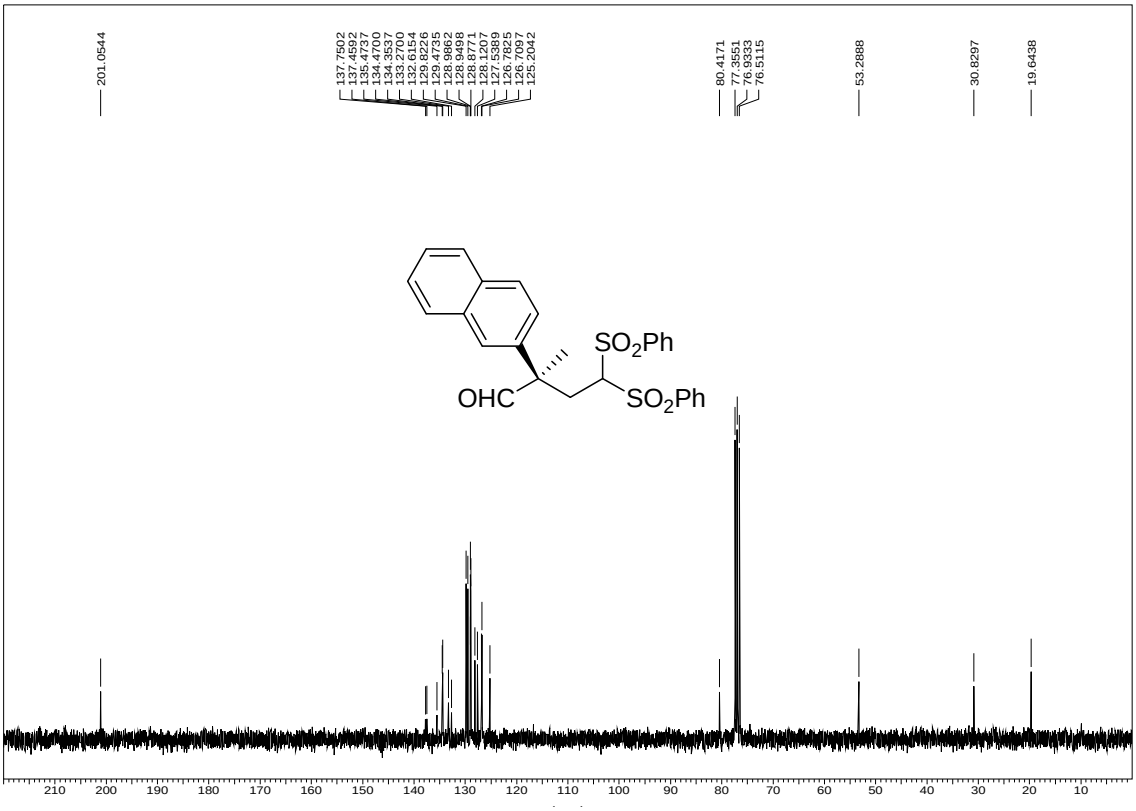
6.9087
2.9374
0.9890
2.0416
4.2702
(ppm)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133.2700
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128.8771
128.1207
127.5389
126.7825
126.7097
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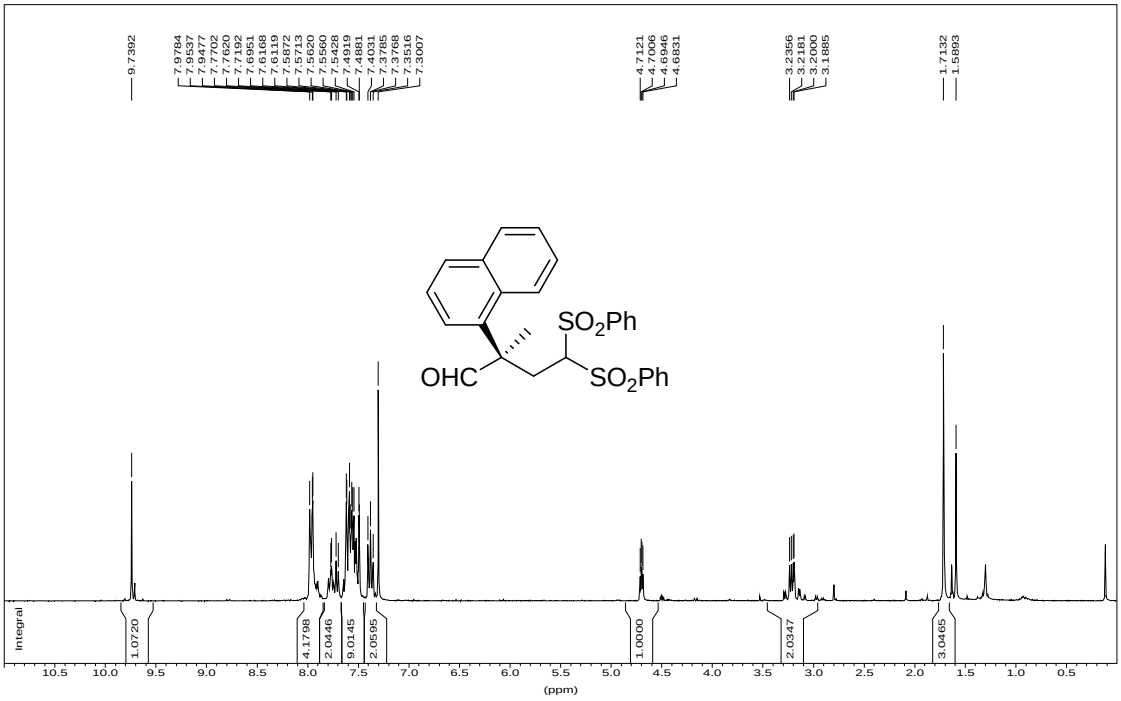
76.9333
76.5115
53.2888
30.8297
19.6438
SO2Ph
OHC
SO2Ph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7.6168
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7.5872
7.5713
7.5650
7.5560
7.5428
7.4919
7.4881
7.4031
7.3785
7.3768
7.3516
7.3007
4.7121
4.7006
4.6946
4.6831
3.2356
3.2181
3.2000
3.1885
1.7132
1.5893
SO2Ph
OHC
SO2Ph
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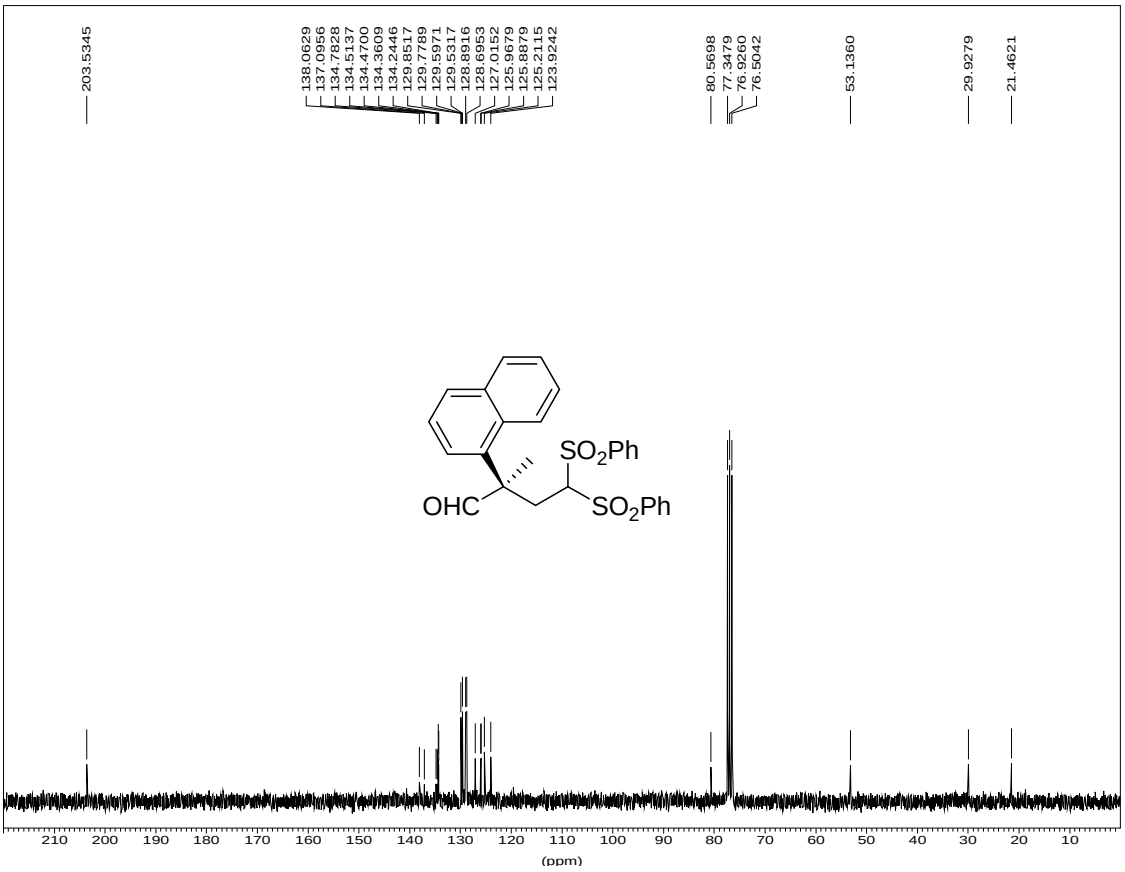
(ppm)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137.0956
134.7828
134.5137
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134.3609
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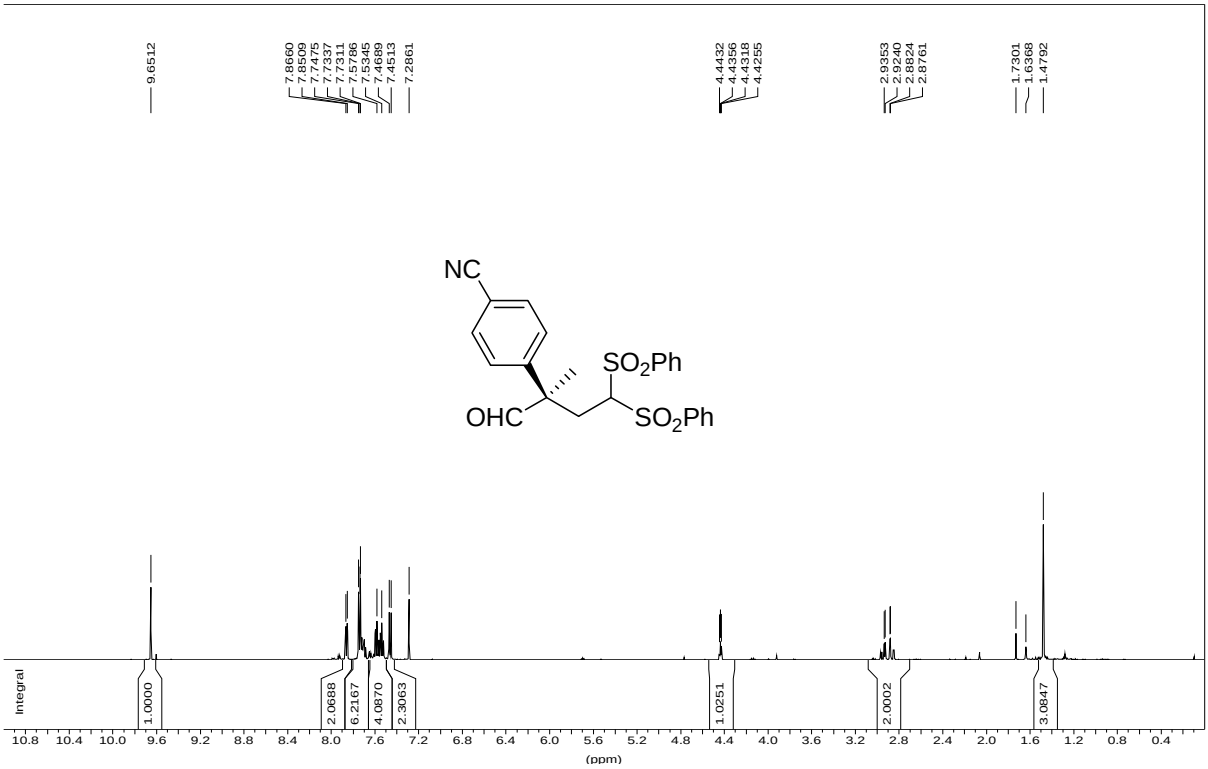
129.5317
128.8916
128.6953
127.0152
125.9679
125.8879
125.2115
123.9242
80.5698
77.3479
76.9260
76.5042
53.1360
29.9279
21.4621
SO2Ph
OHC
SO2Ph
(ppm)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7.5786
7.5345
7.4689
7.4513
7.2861
4.4432
4.4356
4.4318
4.4255
2.9353
2.9240
2.8824
2.8761
1.7301
1.6368
1.4792
NC
SO2Ph
OHC
SO2Ph
Integral
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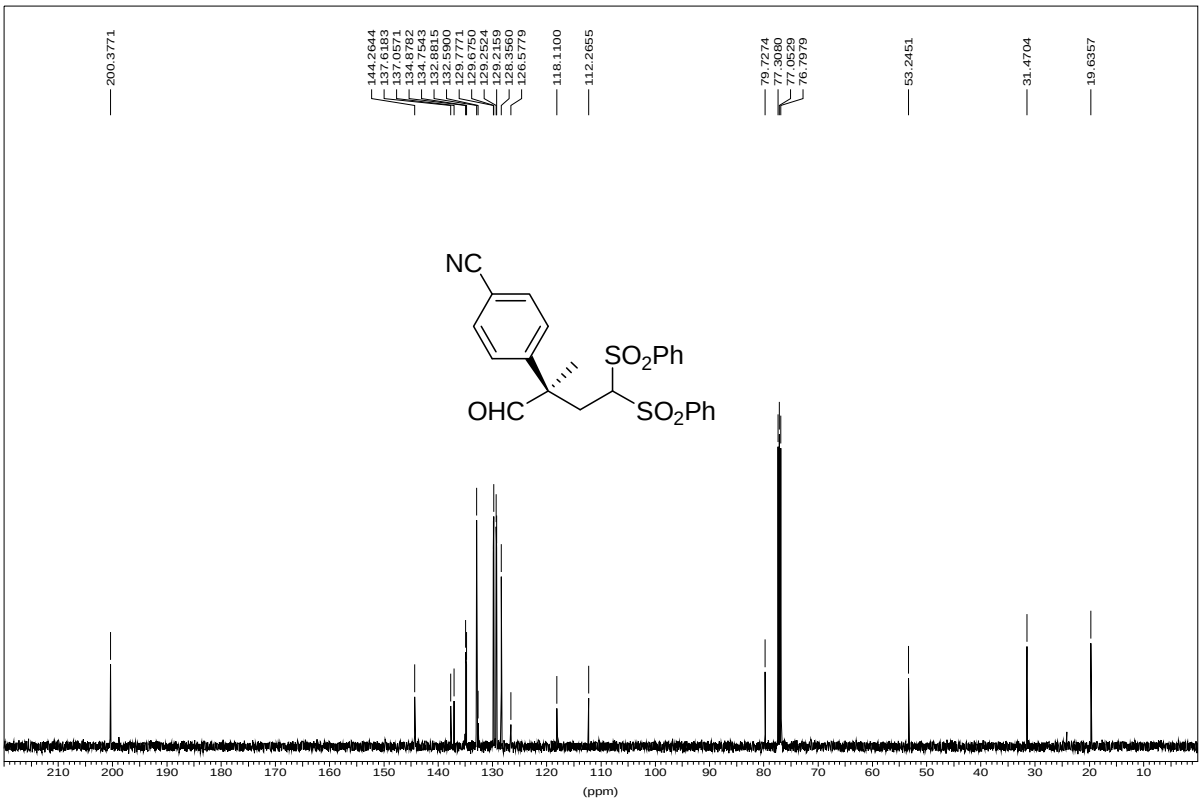
2.0002
3.0847
(ppm)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129.2524
129.2159
128.3560
126.5779
118.1100
112.2655
79.7274
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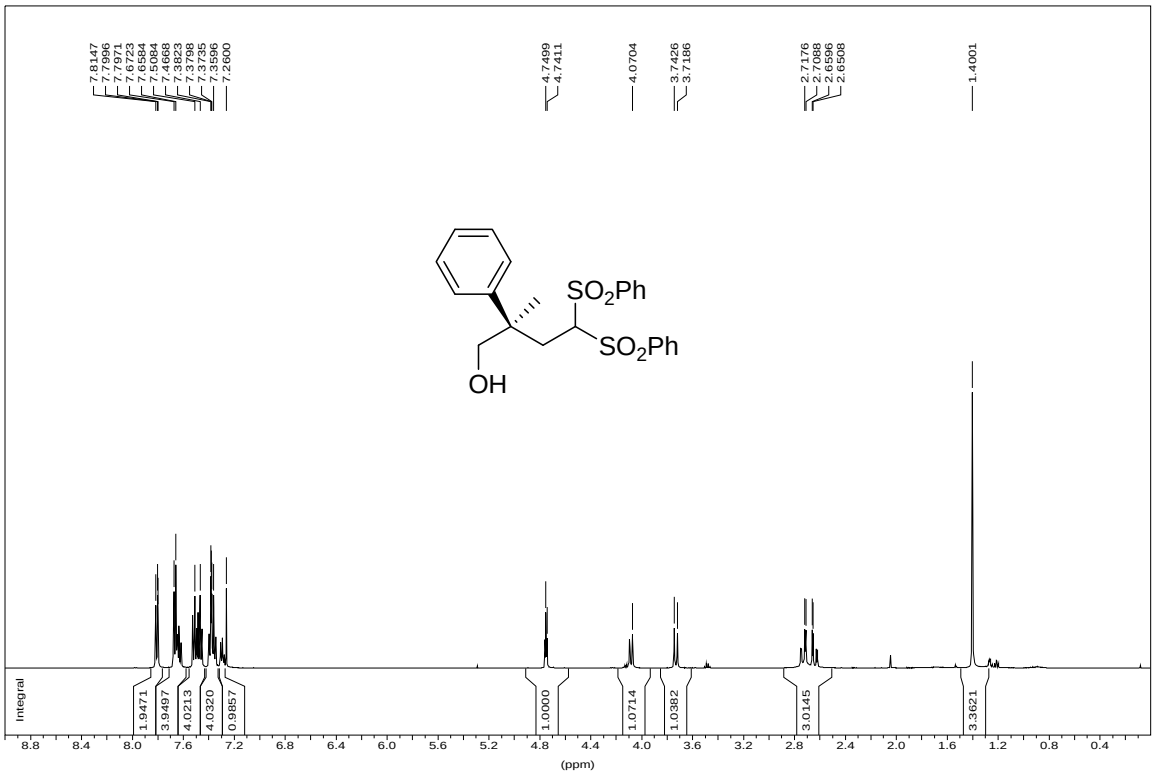
SO2Ph
OHC
SO2Ph
(ppm)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7.3596
7.2600
4.7499
4.7411
4.0704
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3.7186
2.7176
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2.6596
2.6508
1.4001
SO2Ph
SO2Ph
OH
Integral
1.9471
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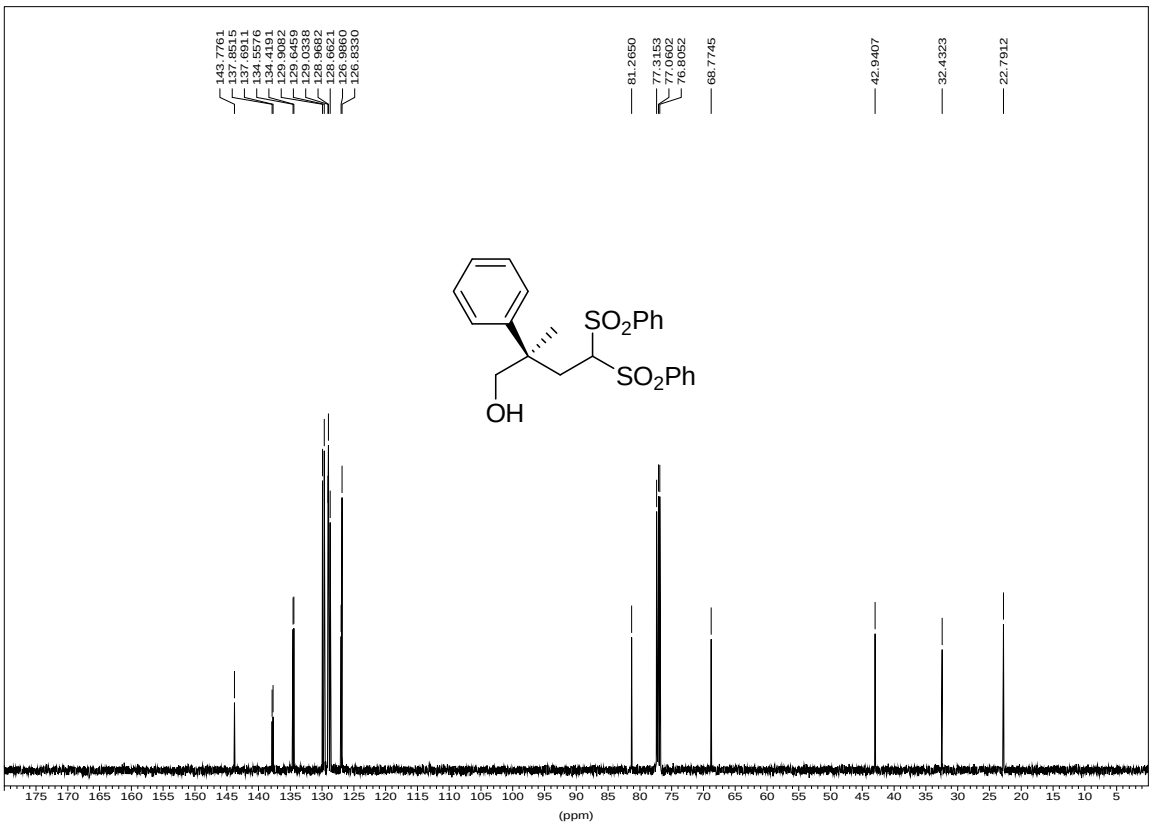
3.3621
(ppm)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126.9960
126.8330
81.2650
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76.8052
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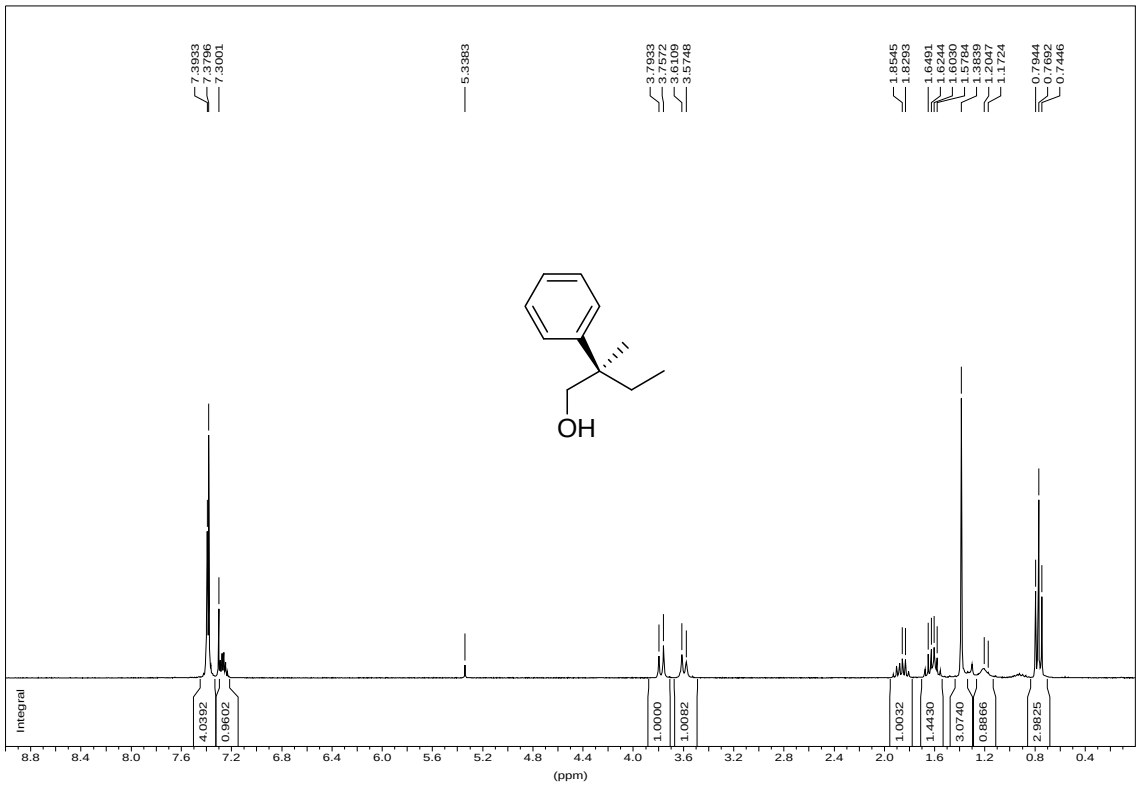
42.9407
32.4323
22.7912
SO2Ph
SO2Ph
OH
(ppm)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3.7933
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3.6109
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1.8293
1.6491
1.6244
1.6030
1.5784
1.3839
1.2047
1.1724
0.7944
0.7692
0.7446
OH
Integral
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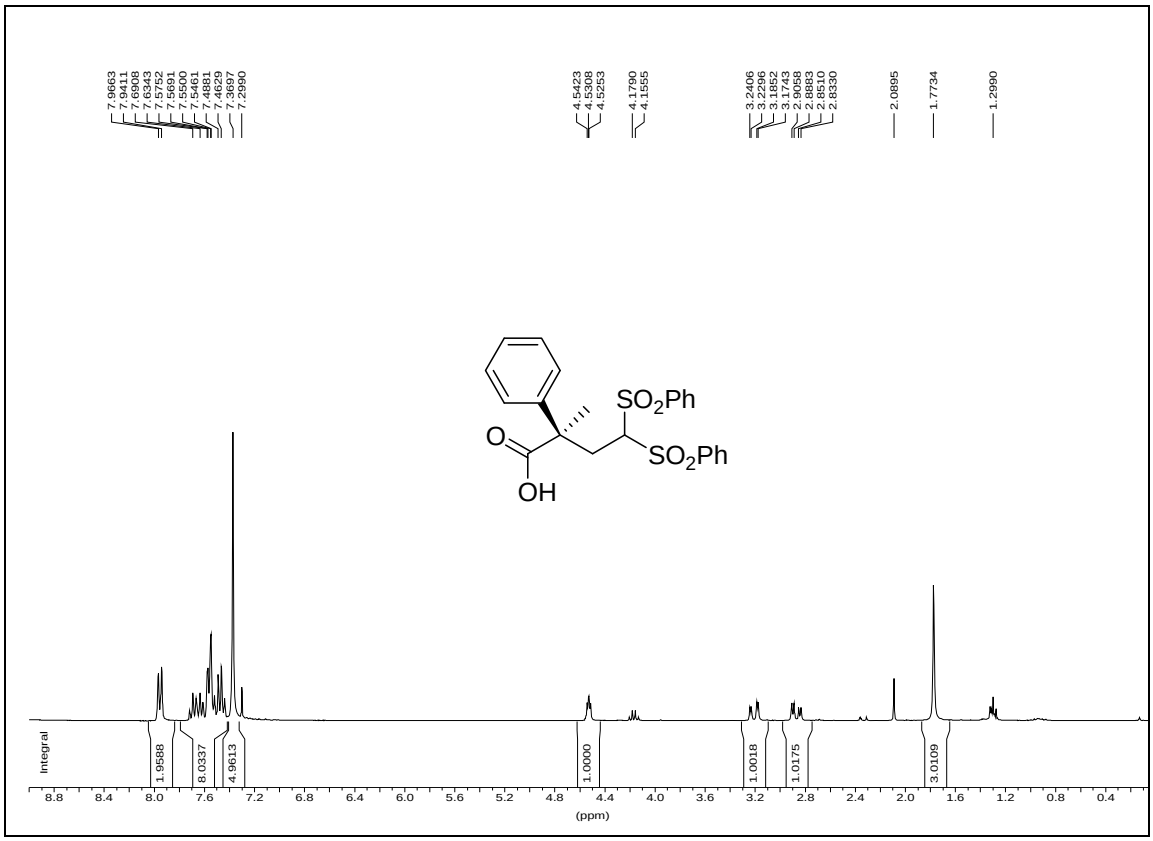
2.9825
(ppm)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7.3697
7.2990
4.5423
4.5308
4.5253
4.1790
4.1555
3.2406
3.2296
3.1852
3.1743
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2.8983
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2.8330
2.0895
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1.2990
SO2Ph
O
SO2Ph
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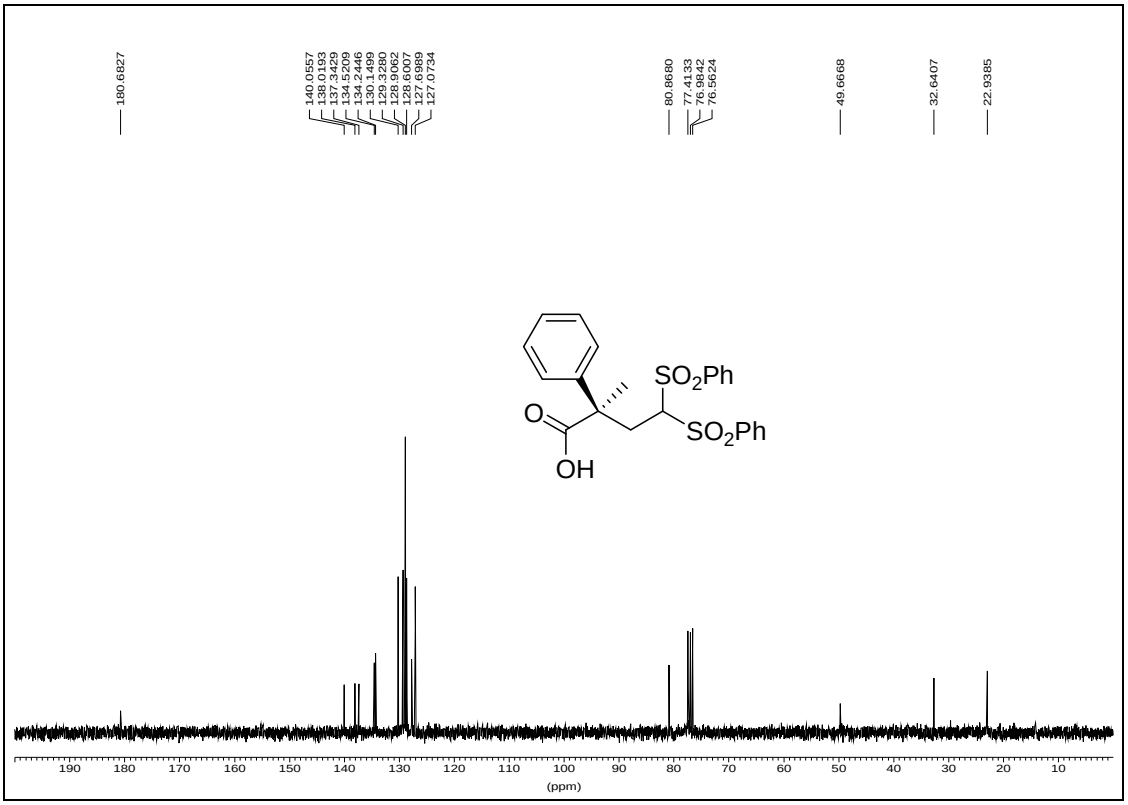
(ppm)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127.0734
80.8680
77.4133
76.9842
76.5624
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SO2Ph
O
SO2Ph
OH
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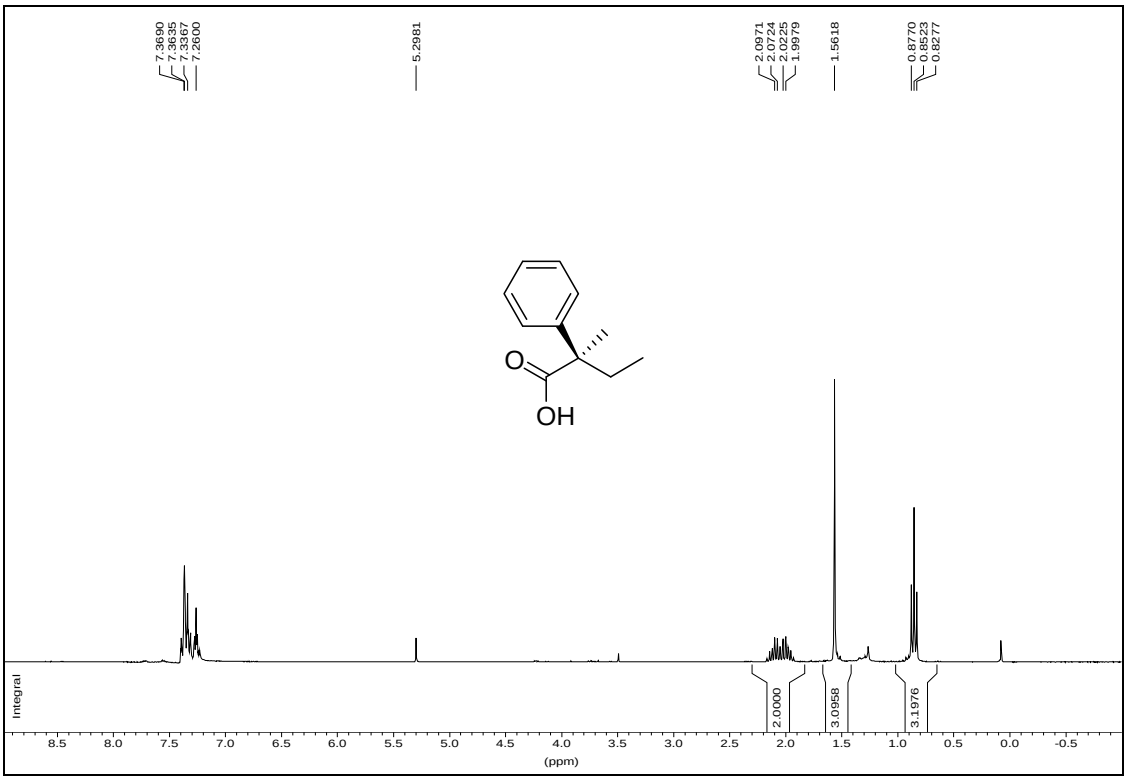
(ppm)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0.8770
0.8523
0.8277
O
OH
Integral
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3.0958
3.1976
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
(ppm)