Electronic Supporting Information

Cyclopent-2-enylaluminium as allylzinc precursor for the diastereoselective allylmetallation of non-racemic imines: Applications to the synthesis of enantiomerically enriched heterocycles

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Experimental procedures and characterization of compounds.

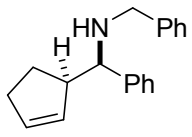
All reactions were conducted under an atmosphere of argon. Prior to use, THF was distilled under argon from sodium benzophenone ketyl, and CH_2Cl_2 was distilled under argon from CaH_2, reagents were used as received. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless specified, on a Brucker AC-250. Mass spectra were recorded on a Micromass Q-TOF micro MS spectrometer.

X-ray diffraction measurement was performed on a Bruker D8 Venture diffractometer equipped with a kappa goniometer and a PHOTON100 CMOS detector and using Cu Kα radiation (from a microsource tube with multi-layer mirror focalizing opticals). Data were collected using Bruker Apex2 software, on the full sphere, with omega and phi scans, 1°/frame, 25 s/frame, with the detector placed at 35mm. The sample temperature was maintained at 100K using a Cryostream700 (Oxford Cryosystems).

General procedure for the allylmetallation of achiral imines. Procedure A

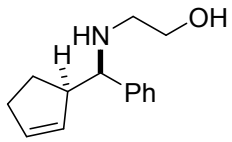
To a solution of Cp_2TiCl_2 (25 mg, 0.1 mmol) and freshly cracked cyclopendiene (0.4 mL) in THF (10 mL) was added dropwise a solution of DIBAL-H (1M in THF, 1.2 mmol, 1.2 mL) at rt. The resulting solution was stirred for 4h at 40°C. The mixture was cooled down to -78°C, and a solution of imine (1 mmol) in THF (2 mL) was slowly added. After 2 h of stirring at -78°C, the solution was slowly warmed to rt, then the reaction was quenched by carefully adding a saturated aqueous solution of $NaHCO_3$ (10 mL). The aqueous layer was extracted with Et_2O (2 x 10 mL), the organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether and AcOEt to give the corresponding homoallylic amine.

(*RS*)-*N*-Benzyl-1-[(*RS*)-cyclopent-2-en-1-yl]-1-phenylmethanamine 2a



Yield = 83%. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.39 (ddd, J = 13.0, 8.7, 6.5 Hz, 1 H), 1.51-1.65 (m, 2 H), 1.97-2.20 (m, 2 H), 2.84 (m, 1 H), 3.03-3.56 (m, 2 H), 3.33 (d, J = 13.2 Hz, 1 H), 3.34 (d, J = 7.8 Hz, 1 H), 3.52 (d, J = 13.3 Hz, 1 H), 5.67 (ddd, J = 5.7, 3.8, 1.8 Hz, 1 H), 5.73 (dq, J = 5.7, 2.0 Hz, 1 H), 7.10-7.20 (m, 10 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ : 27.2, 31.9, 51.3, 52.9, 66.8, 126.7, 126.8, 127.7, 128.10, 128.15, 128.20, 131.8, 132.7, 140.8, 143.2; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{19}H_{22}N$: 264.1747; found: 264.1742.

2-([(*RS*)-[(*RS*)-Cyclopent-2-en-1-yl](phenyl)methyl]amino)ethanol 2b



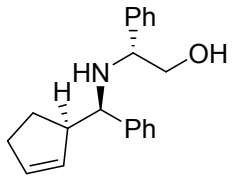
Obtained according to the above procedure using 0.5 mmol (75 mg) of imine.

Yield = 74%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.42 (m, 1 H), 1.66 (dtd, J = 14.0, 8.4, 5.8 Hz, 1 H), 2.10-2.40 (m, 2 H), 2.45-2.51 (m, 2 H), 2.54 (m, 2 H), 2.92 (m, 1 H), 3.37 (d, J = 7.7 Hz, 1 H), 3.40-3.56 (m, 2 H), 5.74-5.82 (m, 2 H), 7.14-7.24 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.2, 31.8, 48.7, 52.6, 60.8, 67.3, 126.9, 127.4, 128.2, 131.5, 132.9, 142.8; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{14}H_{20}NO$: 218.1539; found: 218.1541.

General procedure for the allylmetallation of non-racemic imines. Procedure B

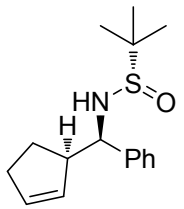
To a solution of Cp_2TiCl_2 (60 mg, 0.24 mmol) and freshly cracked cyclopendiene (0.5 mL) in THF (10 mL) was added dropwise a solution of DIBAL-H (1M in THF, 2.4 mL, 2.4 mmol) at rt, then the resulting solution was stirred for 4h at 40°C. The mixture was cooled down to 0°C then, a solution of Et_2Zn (1M in hexanes, 2,4 mL, 2.4 mmol) was added. The stirring was continued for 1h at rt, then cooled down to -78°C, and a solution of imine (1 mmol) in THF (2 mL) was slowly added. After 2 h of stirring at -78°C, the solution was slowly warmed to rt, then the reaction was quenched by carefully adding a saturated aqueous solution of $NaHCO_3$(10 mL). The aqueous layer was extracted with Et_2O (2 x 10 mL), the organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether and AcOEt to give the corresponding homoallylic amine.

(*R*)-2-[(*R*)-[(*R*)-cyclopent-2-enyl](phenyl)methylamino]-2-phenylethanol 3a



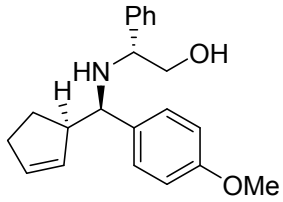
Yield = 74%. White solid; mp 93°C; $[\alpha]_D$ = +19.6 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.64 (m, 1 H), 1.85 (m, 1 H), 2.24-2.42 (m, 2 H), 2.55 (br s, 2 H), 3.11 (m, 1 H), 3.60 (dd, J = 10.3, 4.9 Hz, 1 H), 3.66 (d, J = 7.5 Hz, 1 H), 3.77 (t, J = 4.7 Hz, 1H), 3.84 (dd, J = 10.2, 4.5 Hz, 1 H), 5.91 (m, 1 H), 5.97 (m, 1 H), 7.19-7.36 (m, 10 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.3, 32.0, 52.6, 61.0, 64.4, 65.1, 126.9, 127.1, 127.3, 128.2, 128.4, 133.0, 141.9, 142.9 ; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{20}H_{24}NO$: 294.1858; found: 294.1853.

(*S*)-*N*-[(*R*)-[(*R*)-cyclopent-2-en-1-yl](phenyl)methyl]-2-methylpropane-2-sulfinamide 3'a



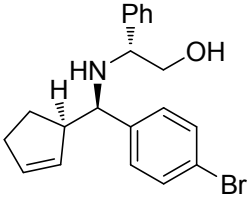
Yield = 76%. Colorless oil; $[\alpha]_D$ = +211 (*c* 1, CH_2Cl_2); NMR ^{1}H (250 MHz, $CDCl_3$) δ: 1.12 (s, 9 H), 1.68 (m, 1 H), 1.85 (m, 1 H), 2.12-2.36 (m, 2 H), 3.05 (m, 1 H), 3.48 (d, *J* = 3.2 Hz, 1 H), 4.26 (dd, *J* = 5.7, 3.8 Hz, 1 H), 5.61 (dq, *J* = 5.7, 1.9 Hz, 1 H), 5.84 (dq, *J* = 5.7, 2.1 Hz, 1 H), 7.13-7.27 (m, 5 H); NMR ^{13}C (62.5 MHz, $CDCl_3$) δ: 22.6, 26.7, 32.1, 53.1, 55.6, 62.4, 127.1 , 127.4, 128.1, 129.4, 134.8, 142.1; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{16}H_{23}NNaOS$: 300.1398; found: 300.1401.

(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](4-methoxyphenyl)methylamino]-2-phenylethanol 3b



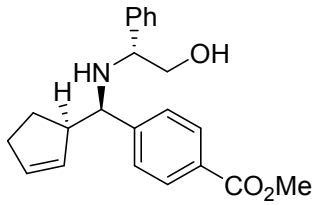
Yield = 63%. White solid; mp 68°C; $[\alpha]_D$ = +17.3 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.54 (m, 1 H), 1.76 (m, 1 H), 1.96-2.64 (br m, 4 H), 3.01 (m, 1 H), 3.47-3.54 (m, 2 H) ; 3.68 (t, *J* = 4.6 Hz, 1 H), 3.72-3.77 (m, 4 H), 5.82 (dq, *J* = 5.7, 2.0 Hz, 1 H), 5.89 (dq, *J* = 5.7, 1.9 Hz, 1 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 7.05 (d, *J* = 8.6 Hz, 2 H), 7.14-7.25 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.2, 31.9, 52.6, 55.1, 60.8, 64.3, 64.4, 113.5, 113.6, 127.1, 127.2, 127.3, 128.25, 128.35; 131.8, 132.8, 135.1, 142.0, 158.4; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{21}H_{25}NO_2Na$ 294.1858; found: 294.1853.

(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](4-bromophenyl)methylamino]-2-phenylethanol 3c



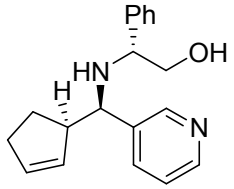
Yield = 62%. Yellow oil; $[\alpha]_D$ = +14.9 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.54 (m, 1 H), 1.78 (m, 1 H), 2.12-2.32 (m, 4 H), 2.99 (m, 1 H), 3.51-3.57 (m, 2 H), 3.64-3.76 (m, 2 H), 5.84 (s, 2 H), 7.00 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.12-7.24 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.1, 32.1, 52.6, 61.6, 64.8, 65.0, 120.6, 127.2, 127.4, 128.5, 129.2, 131.2, 131.3, 133.3, 141.69, 142.3; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{20}H_{23}BrNO$: 372.0963; found: 372.0964.

Methyl 4-[(*R*)-[(*R*)-cyclopent-2-enyl][(*R*)-2-hydroxy-1-phenylethylamino]methyl]benzoate 3d



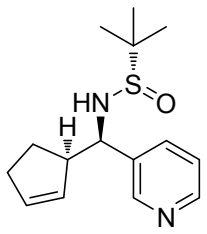
Yield = 58%. White solid; mp 59°C; $[\alpha]_D$ = +37 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.57 (m, 1 H), 1.77 (m, 1 H), 2.68 (br s, 1 H), 3.03 (m, 1 H), 3.55 (dd, *J* = 10.0, 5.3 Hz, 1 H), 3.64-3.69 (m, 2 H), 3.75 (dd, *J* = 10.1, 4.4 Hz, 1 H), 3.89 (s, 3 H), 5.84 (m, 2 H), 7.11-7.22 (m, 7 H), 7.90 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.0, 32.0, 52.0, 52.5, 61.8, 65.0, 65.2, 127.1, 127.4, 128.4, 128.7, 129.4, 131.1, 133.3, 141.5, 148.4, 166.9; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{22}H_{26}NO_3$: 352.1913; found: 352.1911.

(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](pyridin-3-yl)methylamino]-2-phenylethanol 3e



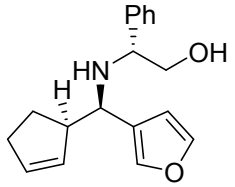
Yield = 49%. Yellow oil; $[\alpha]_D$ = +54.8 (*c* 0.25, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.56 (m, 1 H), 1.79 (m, 1 H), 2.23 (td, *J* = 7.0, 1.8 Hz, 2 H), 2.34 (br s, 2 H), 3.06 (m, 1 H), 3.57-3.63 (m, 2 H), 3.70-3.77 (m, 2 H), 5.85 (m, 2 H), 7.07-7.20 (m, 7 H), 7.43 (dt, *J* = 7.8, 1.7 Hz, 1 H), 8.36 (m, 2 H) ; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 26.9, 32.0, 52.4, 62.7, 63.4, 65.6, 123.0, 127.3, 127.4, 128.4, 131.0, 133.6, 134.8, 138.7, 141.3, 148.1, 149.4; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{19}H_{23}N_2O$: 295.1810; found: 295.1804.

(*S*)-*N*-[(*R*)-[(*R*)-cyclopent-2-en-1-yl](pyridin-3-yl)methyl]-2-methylpropane-2-sulfinamide 3'e



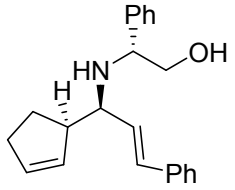
Isolated as 5.8:1 mixture of isomers. Yield = 57%. Colorless oil; NMR ^{1}H (250 MHz, $CDCl_3$) δ: 1.21 (s, 9 H), 1.78 (m, 1 H), 1.95 (m, 1 H), 2.29 (m, 2 H), 3.14 (m, 1 H), 3.61 (m, 1 H), 4.41 (dd, *J* = 4.7, 3.8 Hz, 1 H), 5.66 (m, 1 H), 5.95 (m, 1 H), 7.27 (dd, *J* = 7.3, 4.9 Hz, 1 H), 7.62 (d, *J* = 7.4 Hz, 1 H), 8.52-8.58 (m, 2 H); NMR ^{13}C (62.5 MHz, $CDCl_3$) δ: 22.5, 26.3, 32.0, 52.8, 55.7, 60.1, 123.0, 128.6, 134.9, 135.4, 137.2, 148.5, 149.1; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{15}H_{22}N_2NaOS$: 301.1351; found: 301.1343.

(*R*)-2-[(*R*)-[(*R*)-cyclopent-2-enyl](furan-3-yl)methylamino]-2-phenylethanol 3f



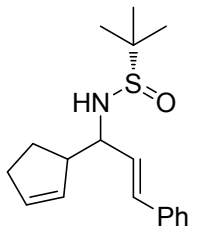
Isolated as 11 : 1 mixture of isomers. Yield = 78%. Yellow oil; $[\alpha]_D$ = +41.4 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.58 (m, 1 H), 1.86 (m, 1 H), 2.26 (m, 2 H), 2.36 (br s, 2 H), 3.03 (m, 1 H), 3.51 (dd, *J* = 10.7, 6.2 Hz, 1 H), 3.56 (d, *J* = 7.2 Hz, 1 H), 3.71 (dd, *J* = 10.7, 4.6 Hz, 1 H), 3.80 (dd, *J* = 6.1, 4.6 Hz, 1 H), 5.81 (m, 2 H), 6.17 (s, 1 H), 7.18-7.30 (m, 7 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 26.5, 31.9, 51.2, 56.0, 61.3, 65.1, 109.0, 127.1, 127.3, 128.3, 128.4, 131.6, 132.7, 139.5, 141.6, 142.8; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{18}H_{22}NO_2$: 284.1651; found: 284.1642.

(*R*)-2-[(*S,E*)-1-[(*R*)-Cyclopent-2-enyl]-3-phenylallylamino]-2-phenylethanol 3g



Isolated as a 5: 1 mixture of isomers. Yield = 56%. Yellow oil. Major Isomer : ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.74 (m, 1 H), 1.95 (m, 1 H), 2.24-2.37 (m, 2 H), 2.54 (br s, 2 H), 2.94 (m, 1 H), 3.23 (dd, *J* = 7.8, 6.6 Hz, 1 H), 3.52 (dd, *J* = 10.5, 6.7 Hz, 1 H), 3.72 (dd, *J* = 10.6, 4.6 Hz, 1 H), 3.87 (dd, *J* = 6.7, 4.7 Hz, 1 H), 5.76-5.91 (m, 3 H), 6.36 (d, *J* = 15.9 Hz, 1 H), 7.17-7.32 (m, 10 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 26.0, 32.2, 50.6, 61.3, 63.0, 65.4, 126.2, 127.2 (2C), 127.3, 128.4, 128.5, 130.8, 131.3, 131.7, 132.9, 137.0, 142.1; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{22}H_{26}NO$: 320.2014; found: 320.2014.

(*S*)-*N*-[(*E*)-1-(Cyclopent-2-enyl)-3-phenylallyl]-2-methylpropane-2-sulfinamide 3'g



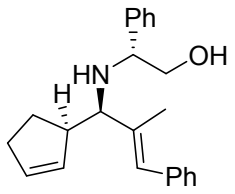
Combined yield of anti isomers: 51%.

Less polar diastereomer : Yellow oil; $[\alpha]_D$ = +95.7 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.23 (s, 9 H), 1.73 (m, 1 H), 2.01 (m, 1 H), 2.34 (m, 2 H), 3.12 (m, 1 H), 3.28 (d, *J* = 8.3 Hz, 1 H), 3.90 (m, 1 H), 5.71 (dq, *J* = 5.6, 2.1 Hz, 1 H), 5.89 (dq, *J* = 5.6, 2.1 Hz, 1 H), 6.23 (dd, *J* = 15.9, 7.1 Hz, 1 H), 6.63 (d, *J* = 15.9 Hz, 1 H), 7.21-7.40 (m, 10 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 22.6, 25.9, 32.3, 51.1, 56.1, 62.2, 126.5, 127.5, 128.4, 130.0, 130.4, 131.5, 133.9, 136.7.

More polar diastereomer : Yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.23 (s, 9 H), 1.80 (m, 1 H), 2.01 (m, 1 H), 2.27-2.42 (m, 2 H), 3.04 (m, 1 H), 3.33 (d, *J* = 3.8 Hz, 1 H), 3.96 (m, 1 H), 5.71 (dq, *J* = 5.7, 2.0 Hz, 1 H), 5.91 (dq, *J* = 5.7, 2.1 Hz, 1 H), 6.07 (dd, *J* = 15.8, 7.3 Hz, 1 H), 6.57 (d, *J* = 15.8 Hz, 1 H), 7.20-

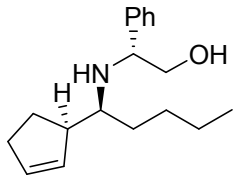
7.39 (m, 10 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 22.6, 25.8, 32.2, 55.6, 60.9, 126.4, 127.5, 128.5, 129.5, 129.7, 131.9, 134.4, 136.7.

(*R*)-2-[(*R,E*)-1-[(*R*)-Cyclopent-2-enyl]-2-methyl-3-phenylallylamino]-2-phenylethanol 3h



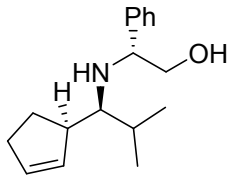
Yield = 76%. White solid; mp 52°C; $[\alpha]_D$ = -42.7 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.55 (d, *J* = 1.1 Hz, 3 H), 1.60 (m, 1 H), 1.87 (m, 1 H), 2.26 (m, 1 H), 2.41 (m, 1 H), 2.80 (m, 1 H), 3.01 (d, *J* = 9.2 Hz, 1 H), 3.55 (dd, *J* = 11.8, 7.4 Hz, 1 H), 3.72 (t, *J* = 4.6 Hz, 1 H), 3.76 (d, *J* = 4.6 Hz, 1 H), 5.87 (dq, *J* = 5.7, 2.0 Hz, 1 H), 6.03 (dq, *J* = 5.7, 2.0 Hz, 1 H), 6.30 (s, 1 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 7.19-7.33 (m, 8 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 12.9, 27.2, 31.9, 49.3, 61.7, 64.9, 71.4, 126.2, 127.30, 127.35, 128.0, 128.3, 128.4, 128.9, 132.40, 132.45, 137.6, 138.5, 142.5; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{23}H_{28}NO$: 334.2171; found: 334.2173.

(*R*)-2-[(*S*)-1-[(*R*)-Cyclopent-2-enyl]pentylamino]-2-phenylethanol 3i



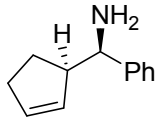
Isolated as a 5: 1 mixture of isomers. Yield = 29%. Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.78 (d, *J* = 6.7 Hz, 3 H), 1.01-1.31 (m, 7 H), 1.67 (m, 1H), 1.93 (m, 1 H), 2.22-2.53 (m, 4 H), 3.00 (m, 1 H), 3.47 (dd, *J* = 10.2, 8.9 Hz, 1 H), 3.66 (dd, *J* = 10.5, 4.6 Hz, 1 H), 3.87 (dd, *J* = 8.5, 4.5 Hz, 1 H), 5.60 (m, 1 H), 5.79 (m, 1 H), 7.25-7.36 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 13.9, 22.7, 24.9, 28.2, 31.4, 32.3, 48.8, 57.8, 62.0, 66.5, 127.2, 127.4, 128.5, 131.8, 132.2, 141.7; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{18}H_{28}NO$: 274.2171; found: 274.2162.

(*R*)-2-[(*S*)-1-[(*R*)-Cyclopent-2-enyl]-2-methylpropylamino]-2-phenylethanol 3j



Yield = 60%. Colorless oil; $[\alpha]_D$ = +18.8 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.68 (d, *J* = 6.9 Hz, 3 H), 0.82 (d, *J* = 6.9 Hz, 3 H), 1.55 (m, 1 H), 1.71 (m, 1 H), 2.00 (m, 1 H), 2.21-2.47 (m, 3 H), 2.91 (m, 1 H), 3.53 (dd, *J* = 10.5, 8.2 Hz, 1 H), 3.66 (dd, *J* = 10.5, 4.7 Hz, 1 H), 3.83 (dd, *J* = 8.1, 4.7 Hz, 1 H), 5.82 (dq, *J* = 5.7, 2.1 Hz, 1 H), 5.88 (dq, *J* = 5.7, 1.9 Hz, 1 H), 7.22-7.34 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 17.7, 19.7, 28.5, 31.0, 31.9, 48.7, 63.6, 64.4, 66.4, 127.4, 127.5, 128.3, 131.8, 133.0, 141.9; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{17}H_{26}NO$: 260.2014; found: 260.2006.

(*R*)-[(*R*)-Cyclopent-2-enyl](phenyl)methanamine

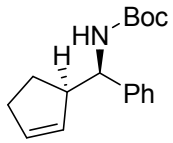


To a solution of **3a** (273 mg, 1 mmol) in a 1 : 1 mixture of MeOH /CH_2Cl_2 (10 mL), was added $Pb(OAc)_4$ (555 mg, 1.25 mmol) in one portion at 0°C. The resulting mixture was stirred for 30 min then $NH_2OH{\cdot}HCl$ (690 mg, 10 mmol) was added. The stirring was continued for 1h at rt. The solvents were removed under reduced pressure. The white solid was washed with CH_2Cl_2 (30 mL) and filtered off. The filtrate was washed with an aqueous solution of NaOH (1M, 3 x 5 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound which was used in the next step without purification.

To a solution of **3'a** (150 mg, 0.54 mmol) in dry MeOH (2 mL), was added a solution of HCl (2M in Et_2O, 0.4 mL) at 0°C, then the mixture was stirred for 1h at rt. The solvent was removed under reduced pressure. The residue was diluted in CH_2Cl_2, then, washed with a saturated aqueous solution of Na_2CO_3. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound which was used in the next step without purification.

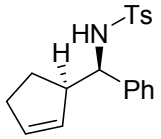
$[\alpha]_D$ = +119 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.55 (m, 1 H), 1.80 (m, 1 H), 2.17-2.38 (m, 2 H), 2.30 (m, 1 H), 3.75 (d, *J* = 7.4 Hz, 1 H), 5.80 (m, 1 H), 5.88 (m, 1 H), 7.23-7.33 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.1, 32.1, 53.7, 60.5, 126.70, 126.75, 128.2, 131.2, 133.2, 145.7.

***Tert*-Butyl (*R*)-((*R*)-cyclopent-2-enyl)(phenyl)methylcarbamate 4**



To a solution of the above primary amine (173 mg, 1 mmol) and Et_3N (0.14 mL, 1 mmol) in CH_2Cl_2 (10 mL), was added Boc_2O (218 mg, 1 mmol). The resulting mixture was stirred for 4h at rt. The crude mixture was concentrated to dryness and purified by flash column chromatography on silica gel (eluting with a mixture of petroleum ether and AcOEt to give **4**. Yield = 69% from **3a**. White solid; mp 99 °C; $[\alpha]_D$ = +145 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.27 (br s, 1.5 H), 1.42 (s, 7.5 H), 1.01-1.31 (m, 7 H), 1.69 (m, 1 H), 1.98 (m, 1 H), 2.21-2.45 (m, 2 H), 3.14 (m, 1 H), 4.40-5.00 (m, 2 H), 5.53 (m, 1 H), 5.90 (m, 1 H), 5.79 (m, 1 H), 7.19-7.34 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.0, 28.3, 32.3, 51.9, 57.7, 79.3, 126.1, 126.7, 128.2, 129.4, 134.5, 142.6, 155.5; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{17}H_{23}NO_2Na$: 296.1626; found: 296.1620.

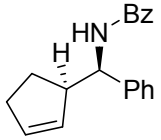
***N*-[(*R*)-[(*R*)-Cyclopent-2-en-1-yl](phenyl)methyl]-4-methylbenzenesulfonamide 6**



To a solution of the above primary amine (173 mg, 1 mmol) and Et_3N (0.14 mL, 1 mmol) in CH_2Cl_2 (10 mL), was added TsCl (190 mg, 1 mmol). The resulting mixture was stirred at rt overnight. Water (5 mL) was added, and the organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluting with a mixture of petroleum ether and AcOEt to give the title compound.

Yield = 87%. White solid; $[\alpha]_D$ = +114 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.52 (m, 1 H), 1.82 (m, 1 H), 2.15-2.40 (m, 2 H), 2.30 (s, 3 H), 3.05 (m, 1 H), 4.30 (dd, *J* = 7.8, 6.7 Hz, 1 H), 5.40 (d, *J* = 8.7 Hz, 1 H), 5.59 (m, 1 H), 5.86 (m, 1 H), 6.96-7.13 (m, 7 H), 7.52 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 21.8, 26.7, 32.2, 52.5, 61.5, 126.4, 126.7, 128.0, 129.0, 129.2, 134.8, 137.7, 140.4, 142.6; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{19}H_{21}NO_2SNa$: 350.1191; found: 350.1199.

***N*-[(*R*)-[(*R*)-Cyclopent-2-enyl](phenyl)methyl]benzamide 8**

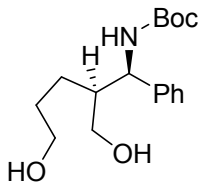


To a solution of the above primary amine (173 mg, 1 mmol) and Et_3N (0.14 mL, 1 mmol) in CH_2Cl_2 (10 mL), was added benzoylchloride (0.12 mL, 1 mmol). The resulting mixture was stirred for 2h at rt then water (5 mL) was added. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with a mixture of petroleum ether and AcOEt to give the title compound. Yield = 90%. White solid, mp 137°C; $[\alpha]_D$ = +116 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.90 (m, 1 H), 2.26 (m, 2 H), 2.44-2.67 (m, 2 H), 3.52 (m, 1 H), 5.40 (dd, *J* = 8.7, 5.2 Hz, 1 H), 5.80 (dq, *J* = 5.7, 2.1 Hz, 1 H), 6.18 (dq, *J* = 5.7, 2.1 Hz, 1 H), 6.80 (d, *J* = 8.7 Hz, 1 H), 7.38-7.70 (m, 8 H), 7.94 (dd, *J* = 8.3, 1.6 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 27.1, 32.5, 51.5, 56.5, 126.3, 126.8, 126.9, 128.4, 128.5, 129.4, 131.4, 134.5, 135.0, 141.8, 166.8; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{19}H_{19}NONa$: 300.1364; found: 300.1367.

General procedure for ozonolysis. Procedure C

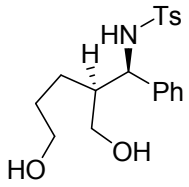
O_3 was bubbled through a solution of **4** or **6** or **8** (1.3 mmol) in a 1 : 1 mixture of MeOH / CH_2Cl_2 (10 mL) until a blue color persists. The solution was stirred for 30 min, then, degassed with a flow of N_2. A solution of $NaBH_4$ (195 mg, 5.2 mmol) in MeOH (10 mL) was added and the resulting mixture was stirred for 30 min. Water (10 mL) and CH_2Cl_2 (10 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL), the organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the corresponding diol which was used in the next step without purification.

***Tert*-Butyl (1*R*,2*S*)-5-hydroxy-2-(hydroxymethyl)-1-phenylpentylcarbamate**



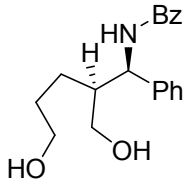
Yield = 77%. Yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.42 (s, 9 H), 1.54-1.69 (m, 4 H), 3.18 (br s, 2 H), 3.50-3.69 (br m, 4 H), 4.66 (t, J = 7.8 Hz, 1 H), 5.66 (d, J = 8.0 Hz, 1 H), 7.24-7.36 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 24.8, 28.8, 30.5, 45.9, 57.4, 60.8, 63.0, 80.2, 127.1, 127.7, 129.1, 142.1, 157.0. HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{17}H_{27}NO_4Na$: 332.1838; found: 332.1845.

***N*-[(1*R*,2*S*)-5-Hydroxy-2-(hydroxymethyl)-1-phenylpentyl]-4-methylbenzenesulfonamide**



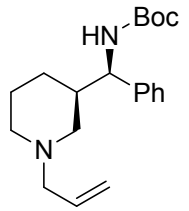
Yield = 88%. NMR ^{1}H (250 MHz, $CDCl_3$) δ: 1.25-1.72 (m, 5 H), 2.29 (s, 3 H), 3.05 (br s, 1 H), 3.46-3.61 (m, 3 H), 3.76 (d, J = 10.8 Hz, 1 H), 4.43 (t, J = 6.1 Hz, 1 H), 6.66 (d, J = 7.7 Hz, 1 H), 6.98-7.08 (m, 7 H), 7.46 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 21.3, 24.5, 29.7, 45.4, 60.4, 60.9, 62.4, 126.80, 126.85, 128.0, 129.0, 137.5, 139.8, 142.6; HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{19}H_{25}NO_4SNa$: 386.1402; found: 386.1408.

***N*-[(1*R*,2*S*)-5-Hydroxy-2-(hydroxymethyl]-1-phenylpentyl)benzamide**



Yield = 74%. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.37-1.74 (m, 5 H), 2.89 (br s, 1H), 4.18 (br s, 1H), 3.34-3.62 (m, 4 H), 5.17 (dd, J = 7.5, 5.8 Hz, 1 H), 7.14-7.42 (m, 8 H), 7.72 (d, J = 7.3 Hz, 2 H), 7.95 (d, J = 7.5 Hz, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 25.0, 29.9, 44.6, 56.9, 60.7, 62.4, 126.4, 126.9, 127.1, 128.5, 131.5, 134.0, 141.4, 167.4.

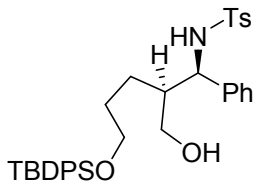
***Tert*-Butyl (*R*)-[(*R*)-1-allylpiperidin-3-yl](phenyl)methylcarbamate 5**



To a solution of the crude diol obtained from **4** (116 mg, 0.37 mmol) and Et_3N (0.14 mL, 1 mmol) in CH_2Cl_2 (5 mL) was slowly added MsCl (0.06 mL, 0.86 mmol) at 0°C. The resulting mixture was stirred for 2h at rt, then water (5 mL) was added. The organic layer was dried over Na_2SO_4, filtered and

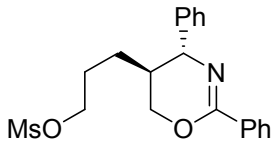
concentrated under reduced pressure. Allylamine (1 mL, 13 mmol) was added then the mixture was heated to reflux overnight. The excess of amine was removed under reduced pressure. The residue was diluted in CH_2Cl_2 (10 mL) washed with a saturated aqueous solution of Na_2CO_3, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with a mixture of petroleum ether and AcOEt to give **6**. Yield = 62%. Yellow oil; $[\alpha]_D$ = +23.4 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.22-1.60 (m, 13 H), 1.75-1.89 (m, 3 H), 2.72 (d, *J* = 11.1 Hz, 1 H), 2.85-2.99 (m, 3 H), 4.44 (br t, *J* = 7.4 Hz, 1 H), 4.99-5.13 (m, 3 H), 5.81 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1 H), 7.11-7.27 (m, 5 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 24.8, 28.3, 41.9, 53.8, 56.8, 58.4, 62.2, 79.3, 117.8, 126.8, 128.5, 135.1, 141.6, 155.3; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{20}H_{31}N_2O_2$: 331.2386; found: 331.2382.

_N_-[(1_R_,2_S_)-5-[(_Tert_-Butyldiphenylsilyl)oxy]-2-(hydroxymethyl)-1-phenylpentyl]-4-methylbenzenesulfonamide 7



To a solution of the crude diol obtained from **6** (256 mg, 0.7 mmol) and DBU (140 µL, 0.9 mmol) in DMF (3.2 mL) was added TBDPSCl (183 µL, 0.7 mmol) at -30°C. The reaction mixture was stirred at -30°C for 30 min, then 1h at rt. Water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with a mixture of petroleum ether and AcOEt to give the title compound. Yield = 72%. Colorless oil; $[\alpha]_D$= +22.3 (*c* 1, CH_2Cl_2); NMR ^{1}H (250 MHz, $CDCl_3$) δ: 1.15 (s, 9 H), 1.20-1.51 (m, 5 H), 1.63 (m, 1 H), 2.34 (s, 3 H), 3.34-3.43 (m, 3 H), 3.56 (d, *J* = 10.5 Hz, 1 H), 4.64 (t, *J* = 5.6 Hz, 1 H), 6.72 (d, *J* = 6.7 Hz, 1 H), 7.08-7.12 (m, 7 H), 7.33-7.44 (m 6 H), 7.54 (d, *J* = 8.1 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 4 H); NMR ^{13}C (62.5 MHz, $CDCl_3$) δ: 19.1, 21.3, 24.6, 26.9, 30.0, 45.5, 60.5, 62.5, 63.6, 126.7, 126.9, 127.7, 127.8, 128.0, 129.1, 129.9, 130.0, 132.2, 132.4, 135.6, 135.7, 138.3, 140.2, 142.6.

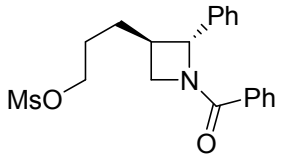
3-[(4_R_,5_S_)-2,4-Diphenyl-5,6-dihydro-4_H_-1,3-oxazin-5-yl]propyl methanesulfonate 9



To a solution of the crude diol obtained from **8** (200 mg, 0.64 mmol) and Et_3N (0.23 mL, 1.65 mmol) in CH_2Cl_2 (5 mL) was added MsCl (0.12 mL, 1.53 mmol) at rt, The resulting solution was stirred overnight at rt, then, water (5 mL) was added. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluting with a mixture of petroleum ether and AcOEt to give **9** (67%) and benzoylazetidine (11%).

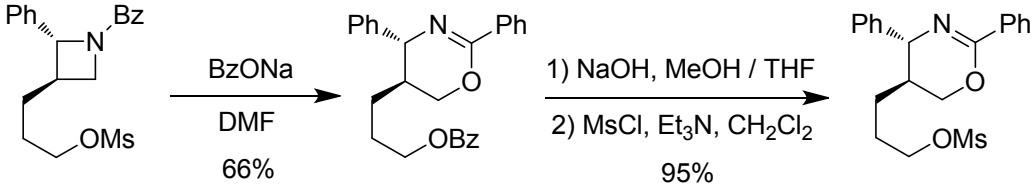
Yield = 67%. Yellow oil; $[\alpha]_D$ = +11.8 (*c* 1, CH_2Cl_2); NMR ^{1}H (250 MHz, $CDCl_3$) δ: 1.40-1.92 (m, 5 H), 2.92 (s, 3 H), 4.04 (dd, *J* = 10.6, 7.5 Hz, 1 H), 4.10-4.22 (m, 2 H), 4.32 (dd, *J* = 10.9 3.6 Hz, 1 H), 4.44 (d, *J* = 6.4 Hz, 1 H), 7.23-7.45 (m, 5 H), 8.00 (dd, *J* = 8.1, 1.5 Hz, 2 H); NMR ^{13}C (62.5 MHz, $CDCl_3$) δ: 25.8, 26.5, 37.2, 38.2, 61.2, 66.2, 69.4, 127.1, 127.2, 127.4, 128.0, 128.4, 130.6, 133.3, 143.3, 155.3.

3-[(2*R*,3*R*)-1-Benzoyl-2-phenylazetidin-3-yl]propyl methanesulfonate



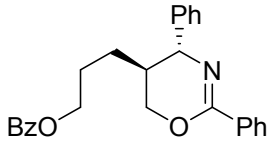
Yield = 11%. ^{1}H NMR (250 MHz, $CDCl_3$) δ:1.66-1.93 (m, 4 H), 2.37 (m, 1 H), 2.94 (s, 3 H), 3.59-3.69 (m, 2 H), 4.21 (t, *J* = 6.1 Hz, 1 H), 5.48 (dd, *J* = 9.1, 6.4 Hz, 1 H), 7.28-7.53 (m, 8 H), 7.81 (dd, *J* = 8.3, 1.5 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 25.1, 26.3, 37.4, 43.8, 45.8, 55.2, 69.4, 126.4, 126.9, 127.7, 128.7, 128.9, 131.7, 134.0, 140.0, 166.8.

Conversion of 3-[(2*R*,3*R*)-1-Benzoyl-2-phenylazetidin-3-yl]propyl methanesulfonate into 9.



9

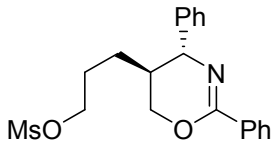
3-[(4*R*,5*S*)-2,4-Diphenyl-5,6-dihydro-4*H*-1,3-oxazin-5-yl]propyl benzoate



A mixture of **3-[(2*R*,3*R*)-1-Benzoyl-2-phenylazetidin-3-yl]propyl methanesulfonate** (83 mg, 0.22 mmol) and sodium benzoate (144 mg, 1 mmol) in DMF (2 mL) was stirred for 12 h at 80°C. The reaction mixture was diluted with AcOEt (10 mL) then washed with water (5 x 1 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether and AcOEt to give the title compound.

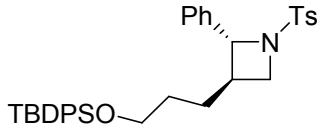
Yield = 66%. Colorless oil; $[\alpha]_D$ = -6.2 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.37-1.88 (m, 5 H), 4.00 (dd, *J* = 10.6, 7.8 Hz, 1 H), 4.19 (t, *J* = 5.8 Hz, 2 H), 4.29 (dd, *J* = 10.9, 3.6 Hz, 1 H), 4.39 (d, *J* = 6.6 Hz, 1 H), 7.17-7.36 (m, 10 H), 7.47 (t, *J* = 7.3 Hz, 1 H), 7.89 (d, *J* = 8.3 Hz, 2 H), 7.93 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 26.0, 26.3, 38.4, 61.3, 64.4, 66.5, 127.0, 127.3, 127.4, 128.0, 128.3, 129.5, 132.9, 133.5, 143.4, 155.4, 166.5; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{26}H_{26}NO_3$: 400.1913; found: 400.1925.

3-[(4*R*,5*S*)-2,4-Diphenyl-5,6-dihydro-4*H*-1,3-oxazin-5-yl]propyl methanesulfonate 9



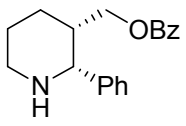
To a solution of the above oxazine ester (60 mg, 0.15 mmol) in a mixture of MeOH (3 mL) and THF (0.5 mL), was added an aqueous solution of NaOH (10%, 1 mL) and the resulting mixture was stirred for 2h at rt then, the solvents were removed under reduced pressure. The residue was diluted in CH_2Cl_2 (5 mL) and washed with water (2 x 2 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Dry CH_2Cl_2 was added followed by Et_3N (80 µL, 0.57 mmol) and MsCl (25 µL, 0.32 mmol). The mixture was stirred for 3h at rt, then, water (2 mL) was added. The organic layer was washed with water (2 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **9** in 95% yield.

(2*R*,3*R*)-3-(3-[(*Tert*-Butyldiphenylsilyl)oxy)propyl]-2-phenyl-1-tosylazetidine 10



To a solution of **7** (223 mg, 0.37 mmol) and Et_3N (95 µL, 0.6 mmol) in CH_2Cl_2 (7 mL) was added MsCl (35 µL, 0.48 mmol) at 0°C. The resulting mixture was stirred for 3h at rt, then water (2 mL) was added. The organic layer was washed with water (2 x 2 mL) dried over Na_2SO_4, filtered and concentrated under reduced pressure. Dry THF (3 mL) and NaH (20 mg, 0.83 mmol) were added and the resulting mixture was stirred for 1h at rt under Ar. Water (2 mL) was carefully added. The aqueous layer was extracted with Et_2O (3 x 2 mL). The organic phases were combined, washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with a mixture of petroleum ether and AcOEt to **10**. Yield = 88%. Pale yellow oil; $[\alpha]_D$ = +1.2 (*c* 1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.02 (s, 9 H), 1.37-1.46 (m, 2 H), 1.66 (m, 1 H), 1.83 (d, *J* = 12.7 Hz, 1 H), 2.21 (m, 1 H), 2.32 (s, 3 H), 3.11-3.26 (m, 3 H), 3.86 (dd, *J* = 13.2, 2.1 Hz, 1 H), 5.43 (d, *J* = 5.6 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 7.13-7.41 (m, 15 H), 7.57 (d, *J* = 7.2 Hz, 2 H); NMR ^{13}C (62.5 MHz, $CDCl_3$) δ: 19.1, 21.1, 21.4, 24.5, 26.8, 41.8, 42.6, 57.9, 65.2, 127.1, 127.3, 127.5, 127.6, 128.0, 129.0, 129.6, 129.7, 133.3, 133.4, 135.4, 135.5, 137.1, 137.7, 142.3. HRMS-ESI : *m/z* $[M+Na]^+$calcd for $C_{35}H_{41}NO_3SSiNa$: 606.2474; found: 606.2479.

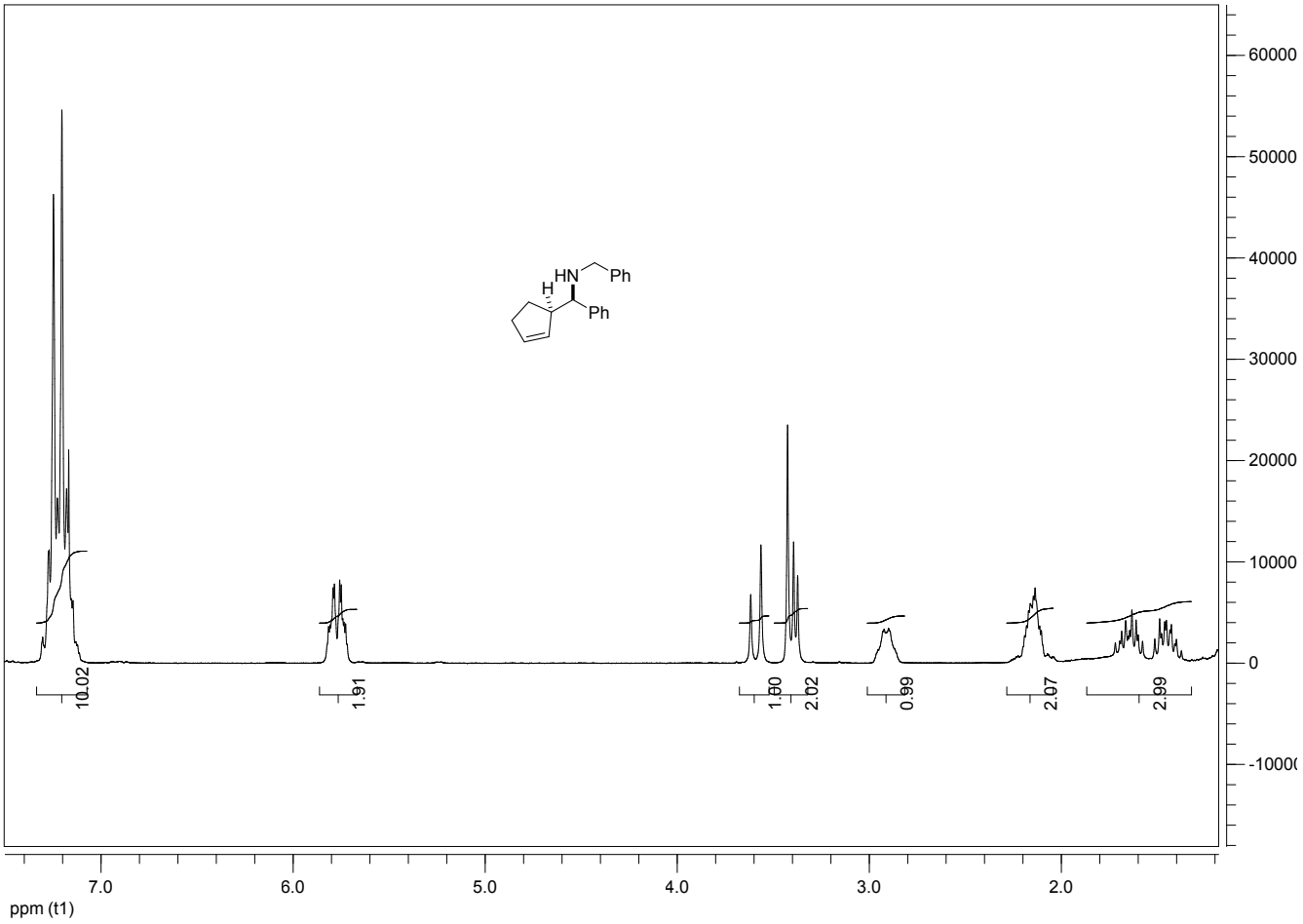
[(2*R*,3*S*)-2-Phenylpiperidin-3-yl]methyl benzoate 11

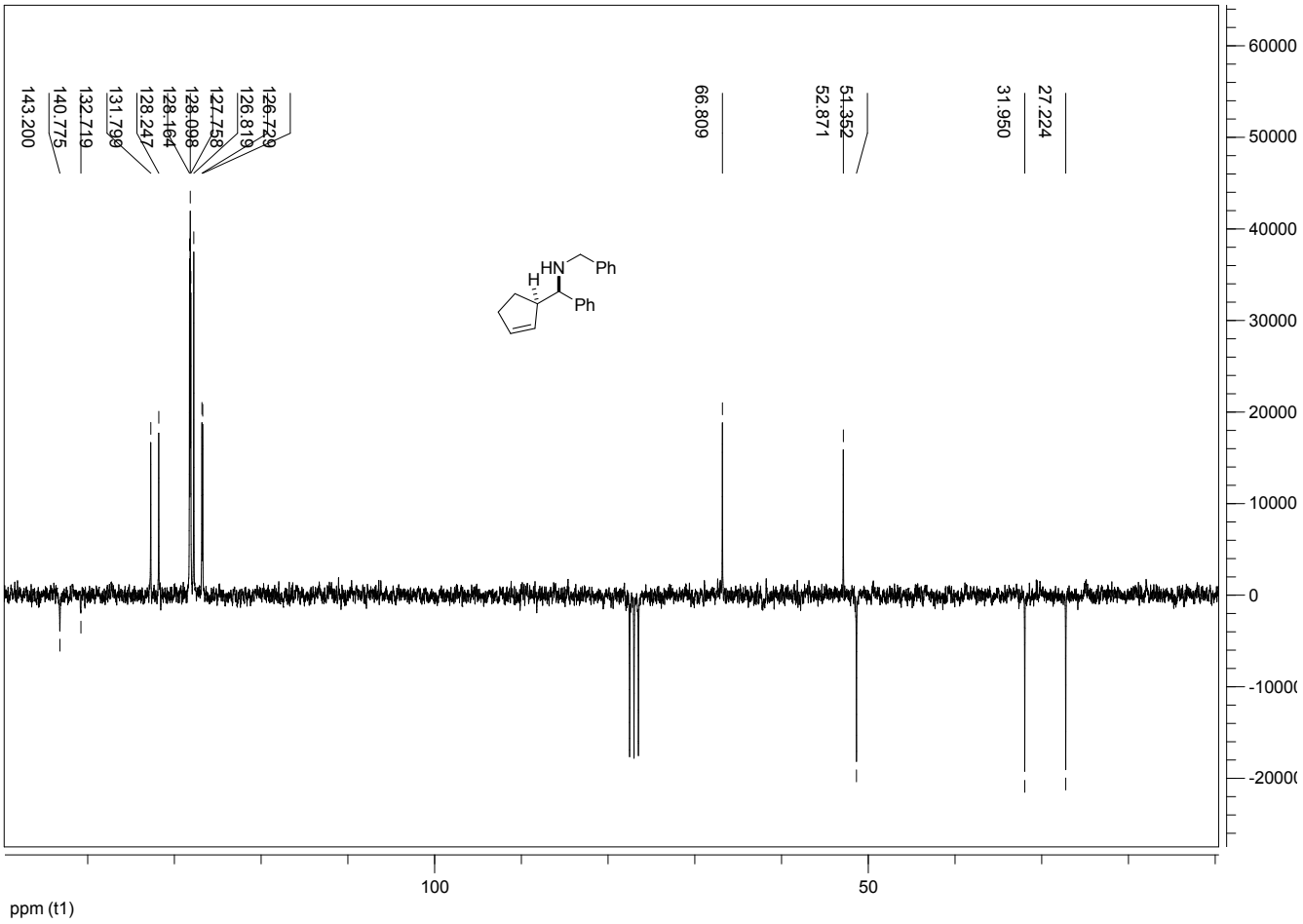


To a solution of **9** (71 mg, 0.19 mmol) in dioxane (5 mL) was added an aqueous solution of HCl (1M, 5 mL) and the resulting solution was stirred overnight at rt. The solution was concentrated to dryness, then diluted in CH_2Cl_2 (5 mL). An aqueous solution of NaOH (1M, 3 mL) was added and the biphasic media

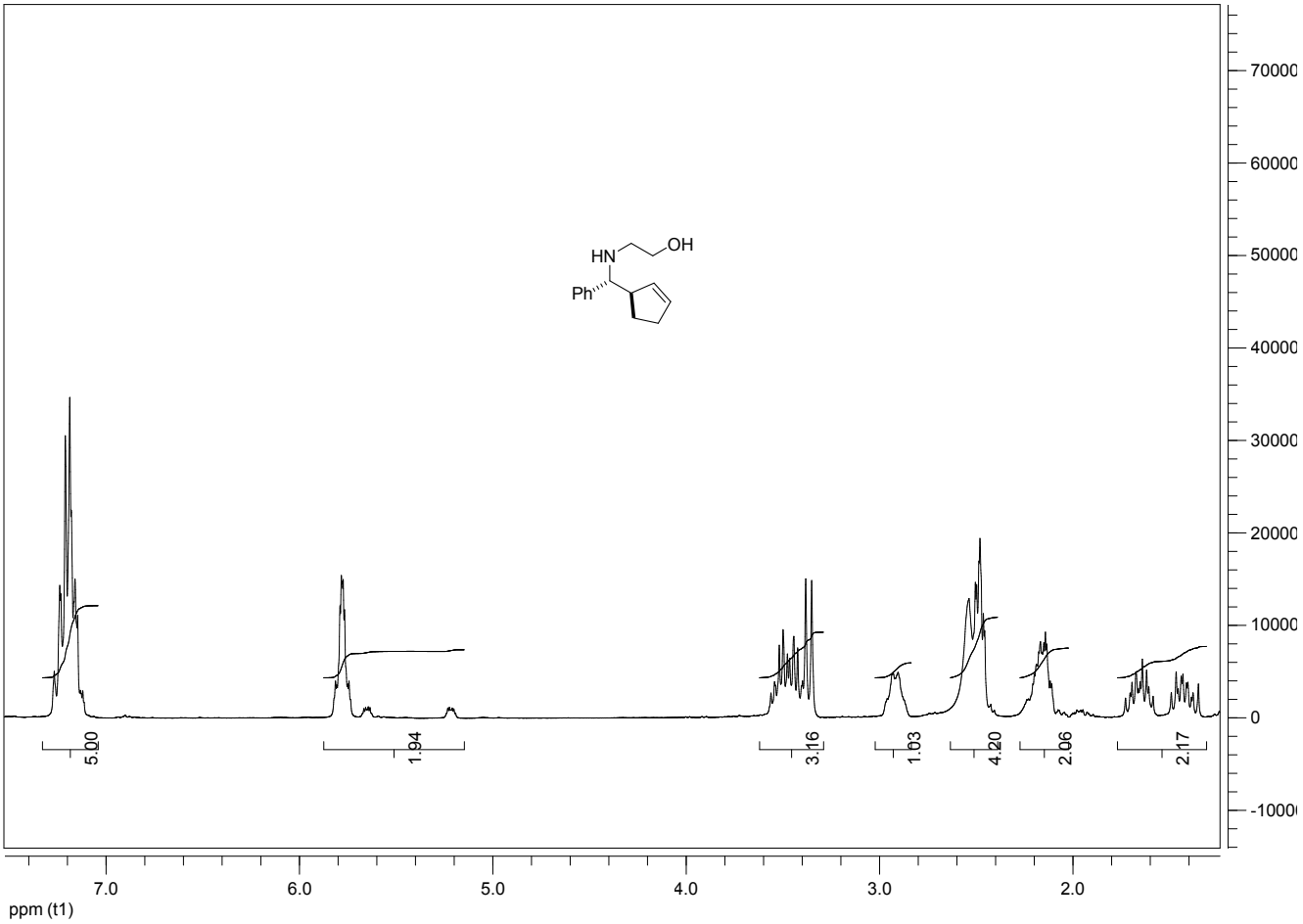
was stirred vigorously for 2h. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with a mixture of petroleum ether and AcOEt to give **11**. Yield = 61%. Yellow oil; $[\alpha]_D$ = +15.7 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.45 (m, 1 H), 1.63 (dd, *J* = 12.9, 3.7 Hz, 1 H), 1.70 (m, 1 H), 1.80 (br s, 1 H), 2.00 (m, 1 H), 2.27 (m, 1 H), 2.78 (m, 1 H), 3.20 (m, 1 H), 3.94 (d, *J* = 3.0 Hz, 1 H), 4.11 (dd, *J* = 11.1, 5.5 Hz, 1 H), 4.50 (dd, *J* = 11.1, 8.6 Hz, 1 H), 7.09-7.30 (m, 7 H), 7.40 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.68 (dd, *J* = 8.2, 1.4 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 20.9, 27.6, 39.4, 48.0, 62.9, 63.1, 126.3, 126.8, 128.0, 128.4, 129.4, 130.4, 132.5, 143.1, 166.4; HRMS-ESI : *m/z* $[M+H]^+$calcd for $C_{19}H_{22}NO_2$: 296.1651; found: 296.1646.

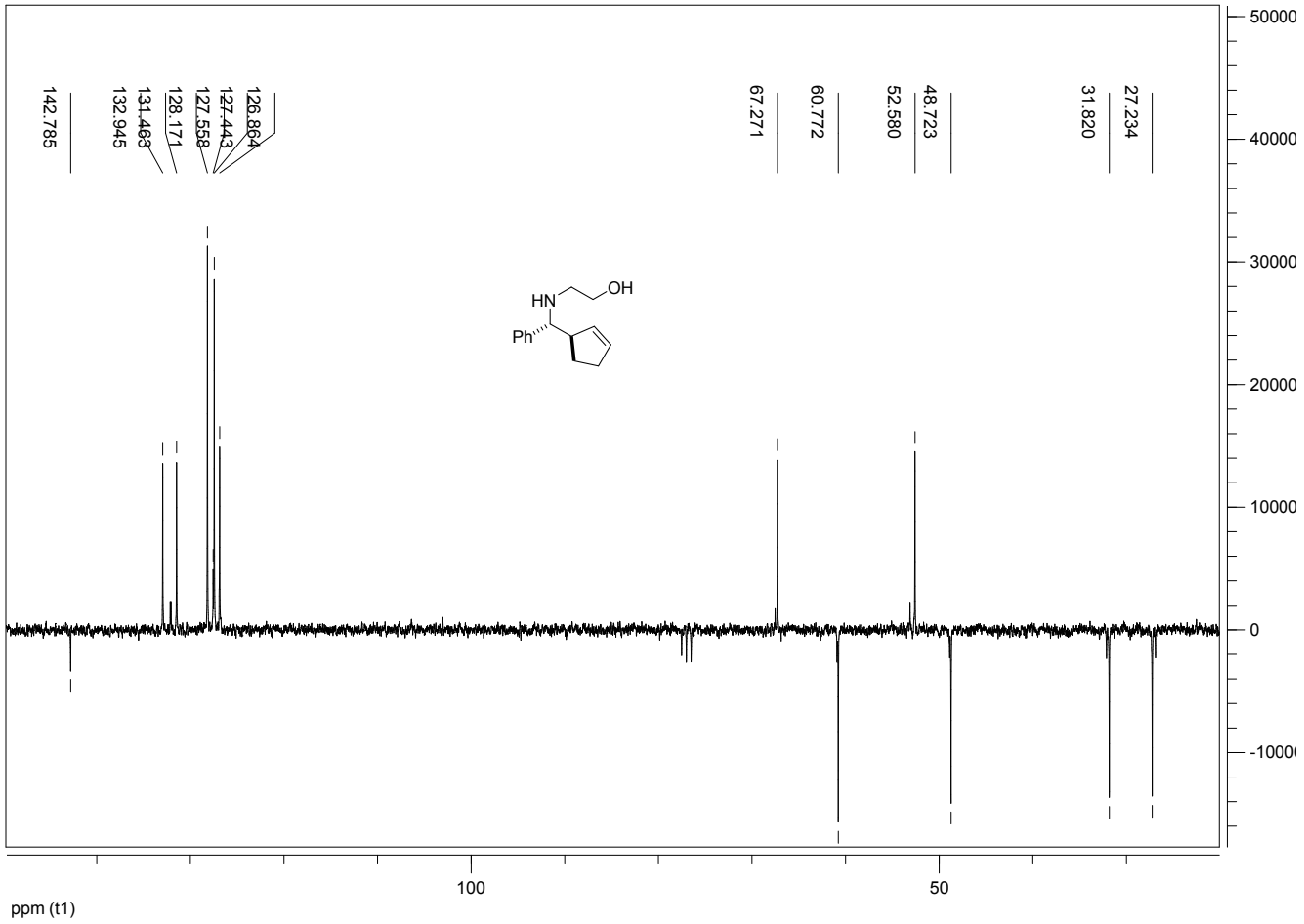
(*RS*)-*N*-Benzyl-1-[(*RS*)-cyclopent-2-enyl]-1-phenylmethanamine 2a



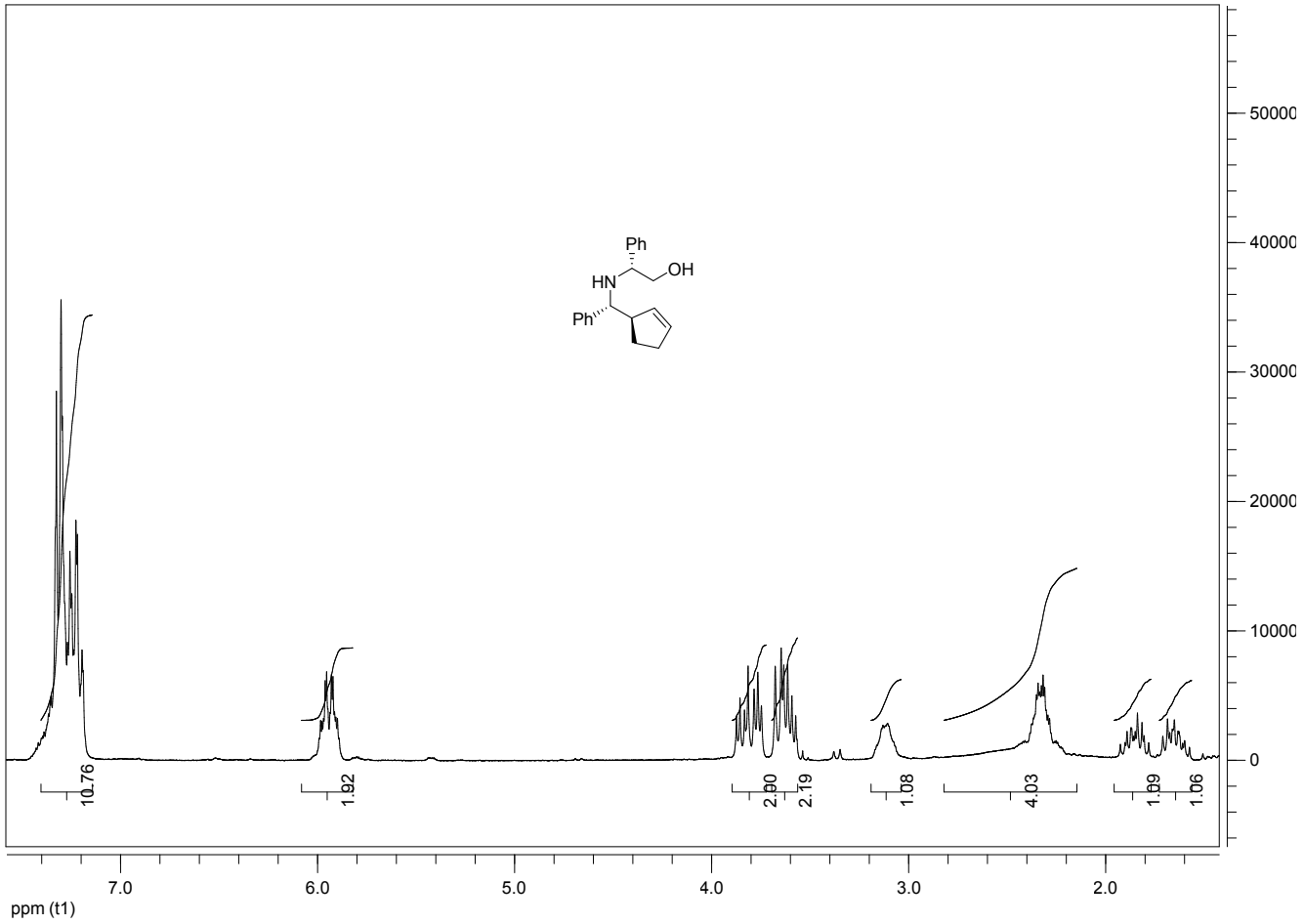


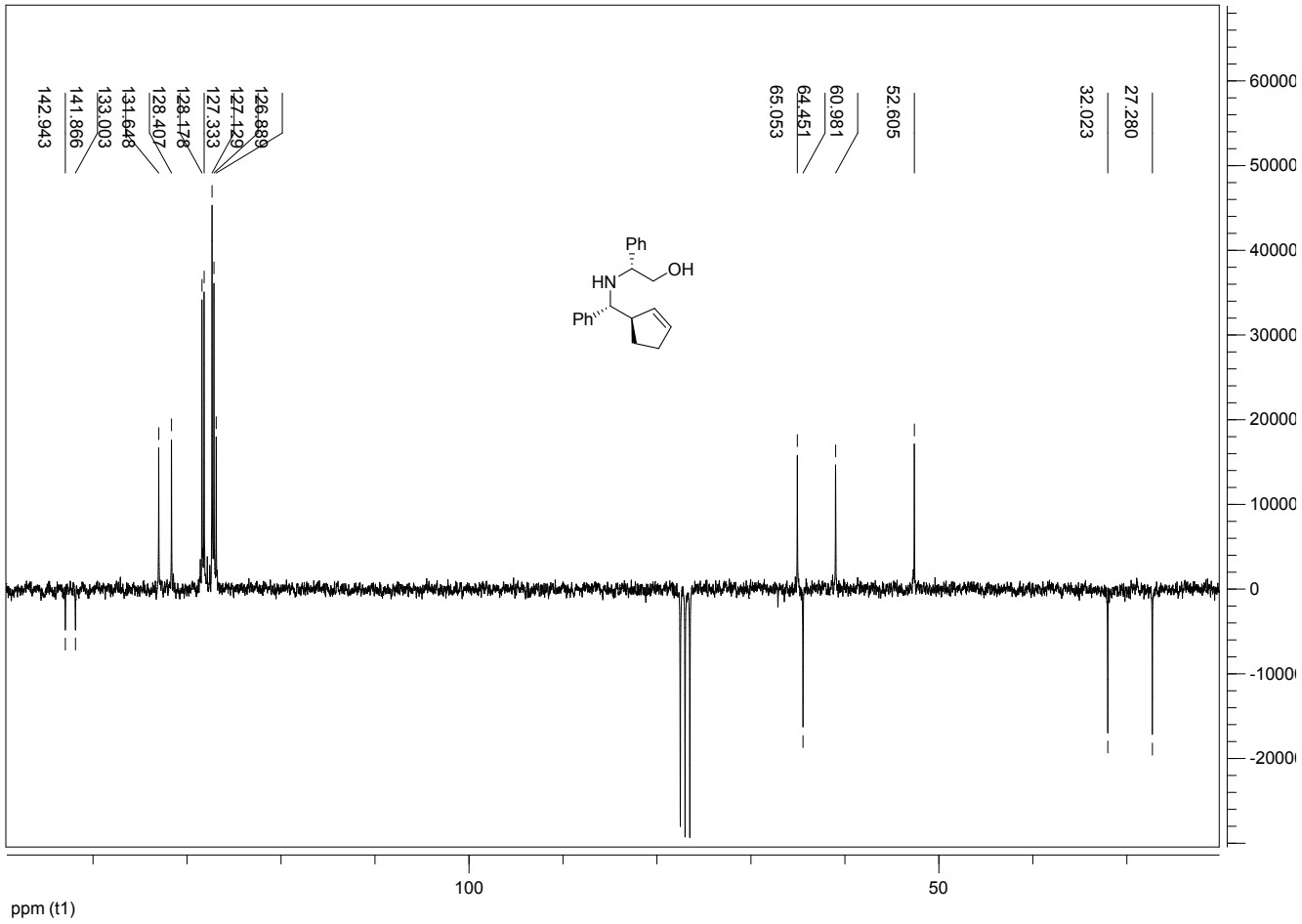
2-[(*RS*)-[(*RS*)-Cyclopent-2-enyl](phenyl)methylamino]ethanol 2b



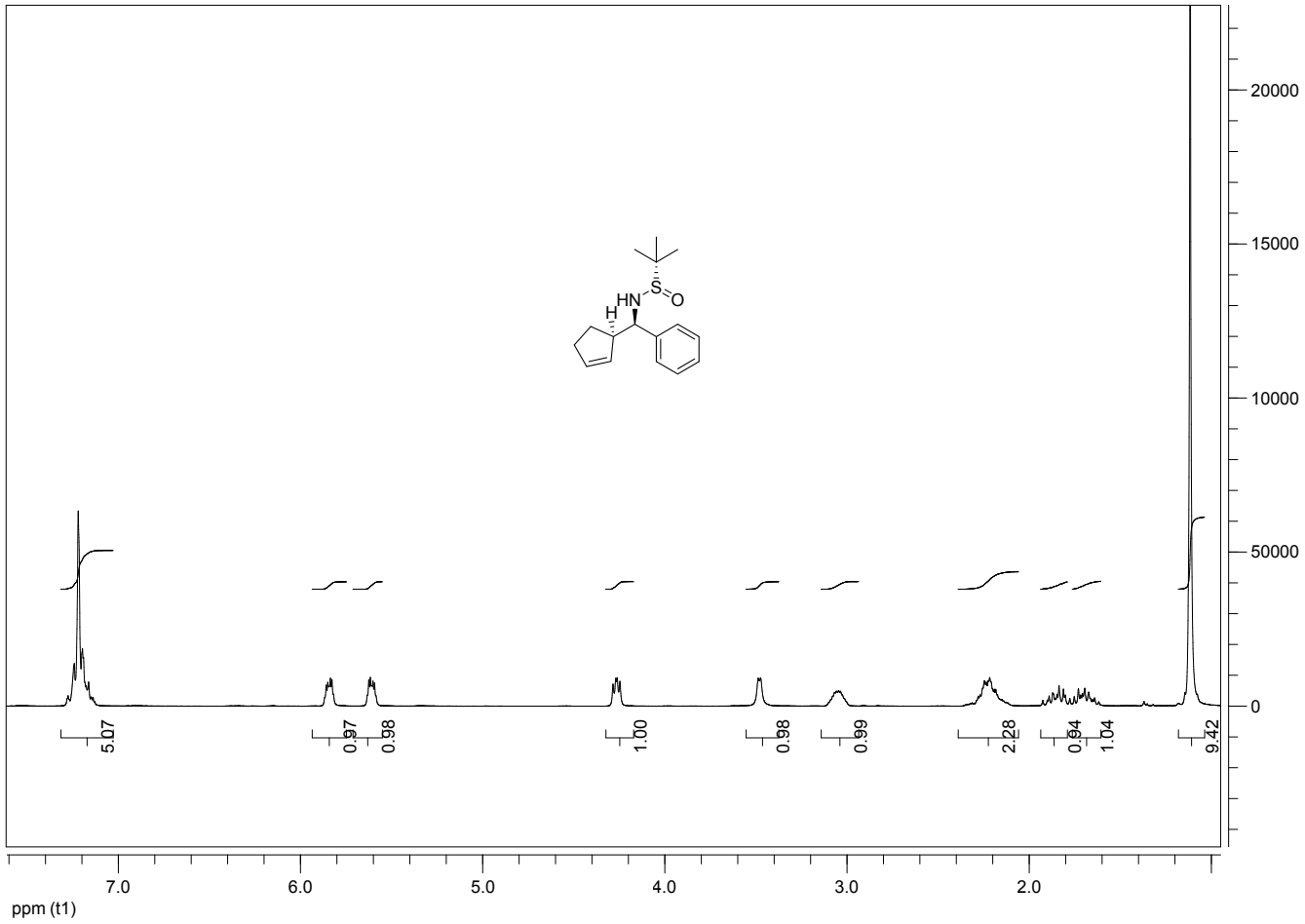


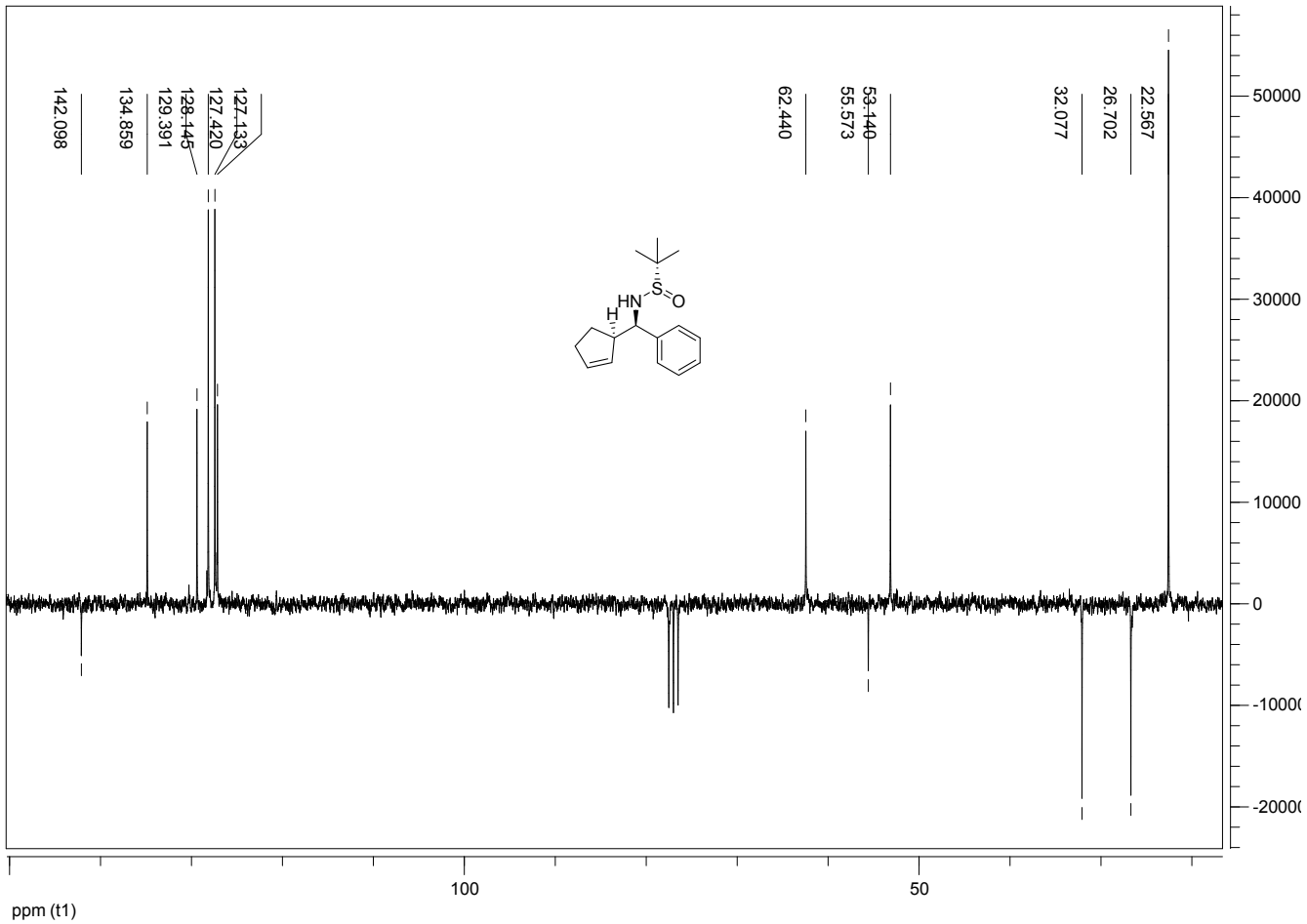
(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](phenyl)methylamino]-2-phenylethanol 3a



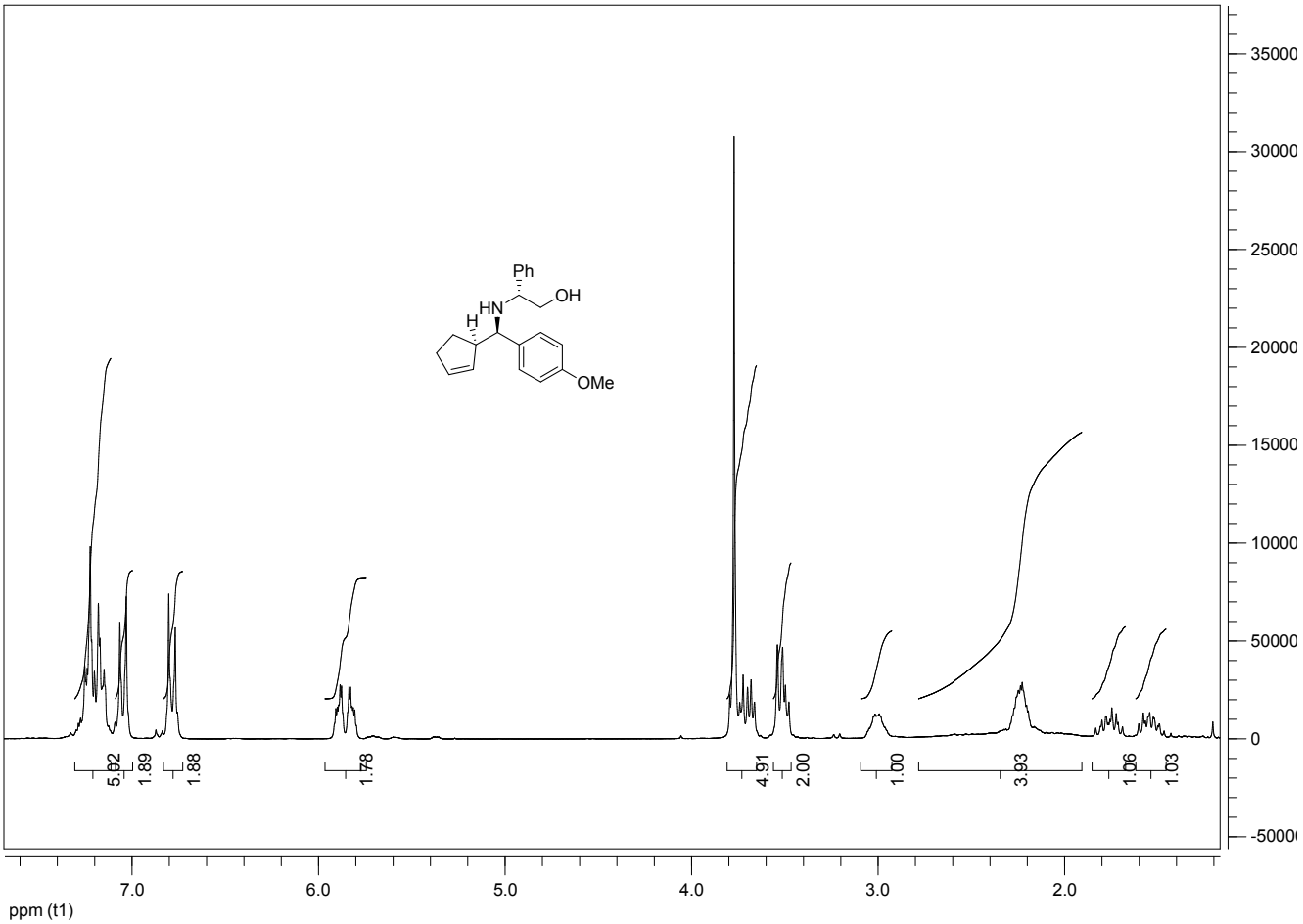


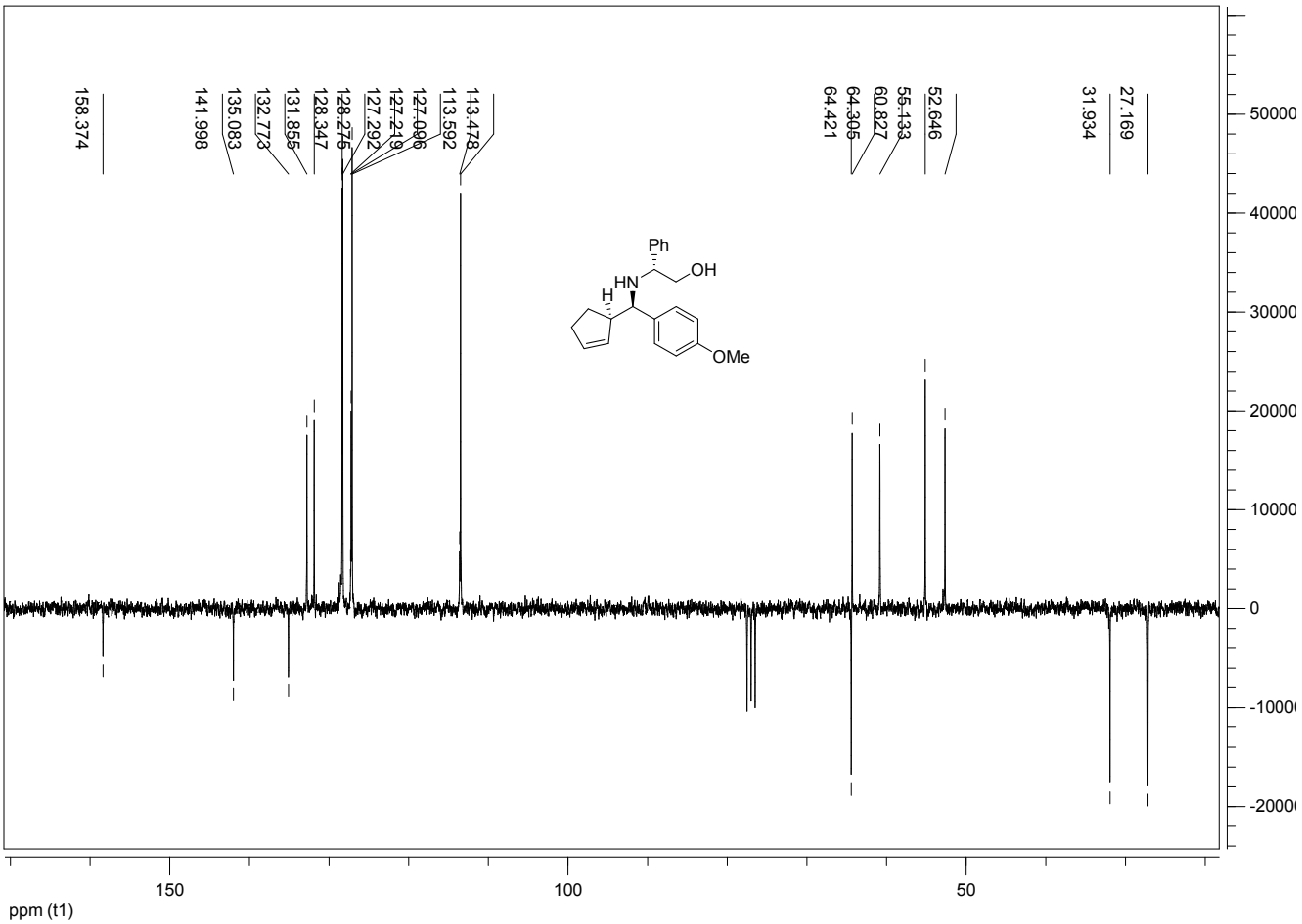
(*R*)-*N*-[(*S*)-[(*S*)-cyclopent-2-en-1-yl](phenyl)methyl]-2-methylpropane-2-sulfinamide 3'a



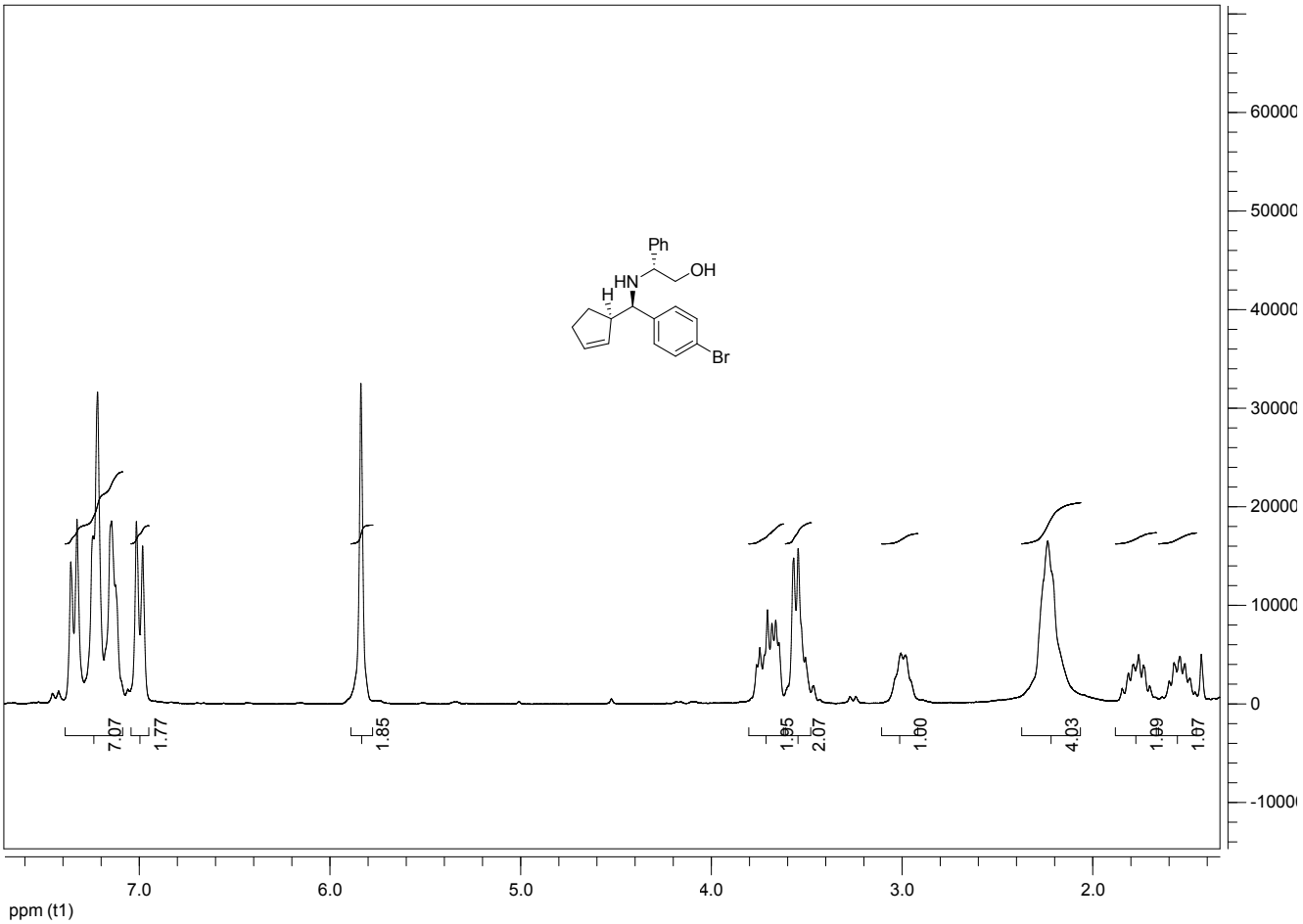


(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](4-methoxyphenyl)methylamino]-2-phenylethanol 3b





(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](4-bromophenyl)methylamino]-2-phenylethanol 3c


Ph
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HN
H
Br
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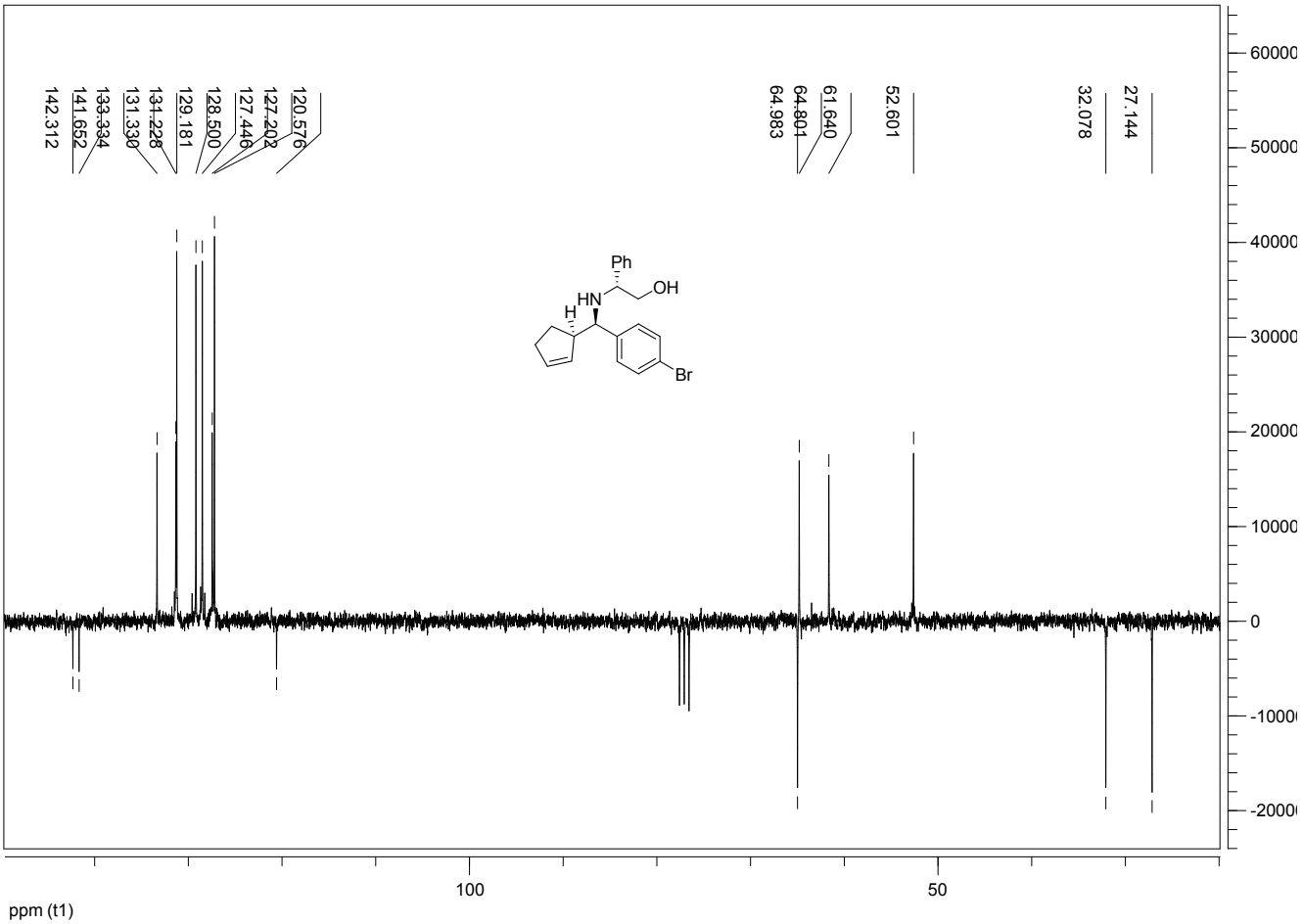
1.85
1.95
2.07
1.90
4.03
1.96
1.97
60000
50000
40000
30000
20000
10000
0
-10000
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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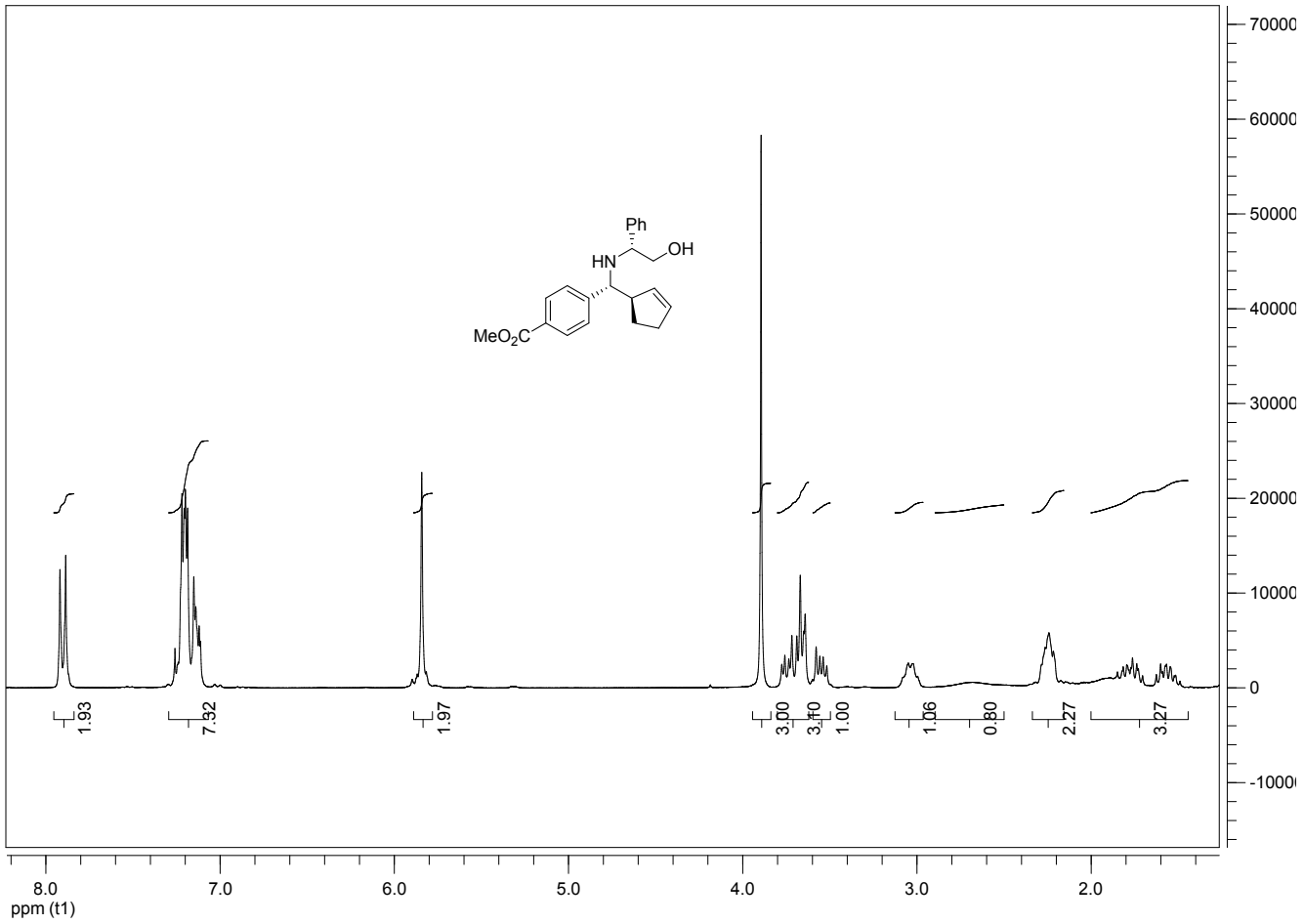
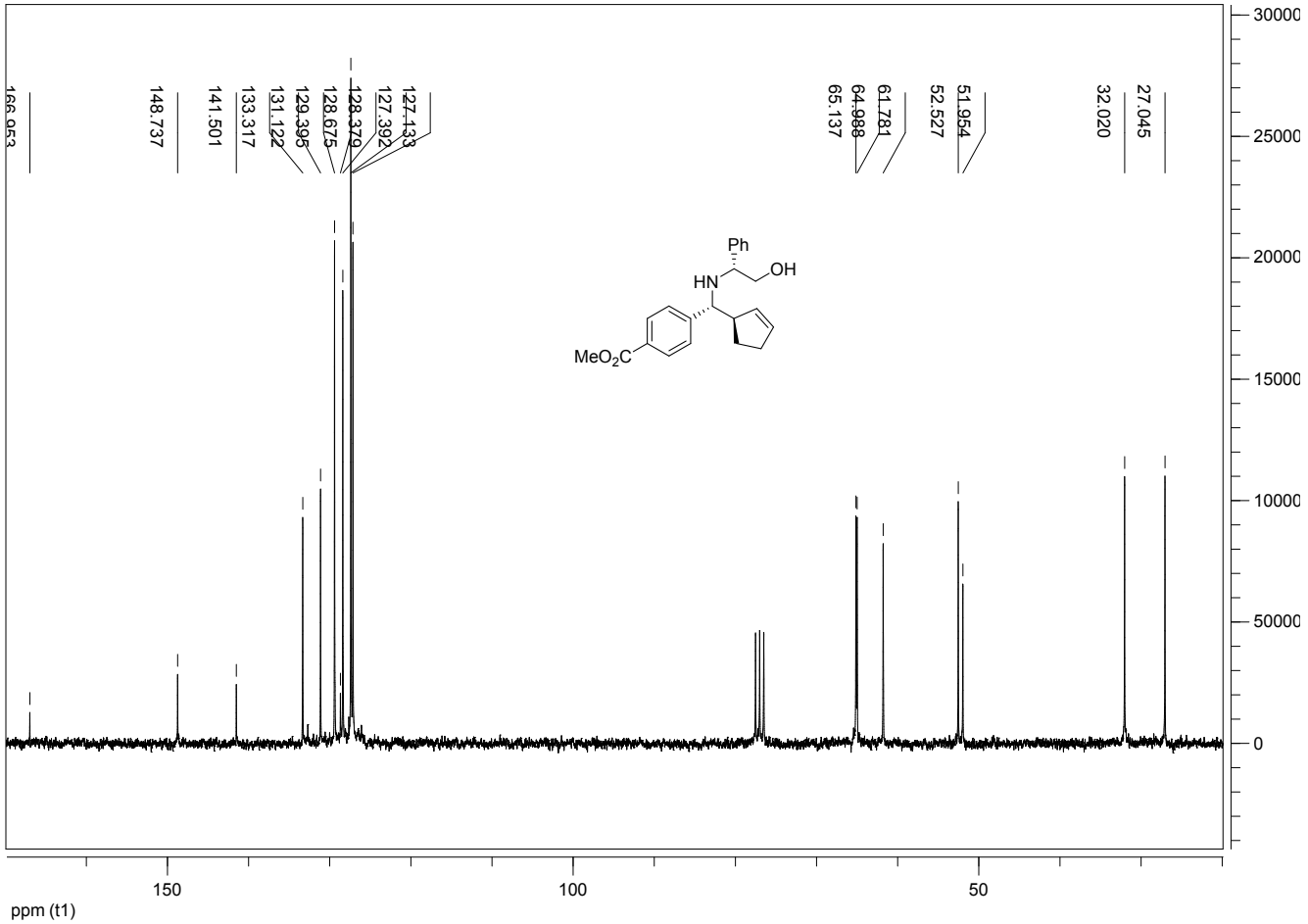
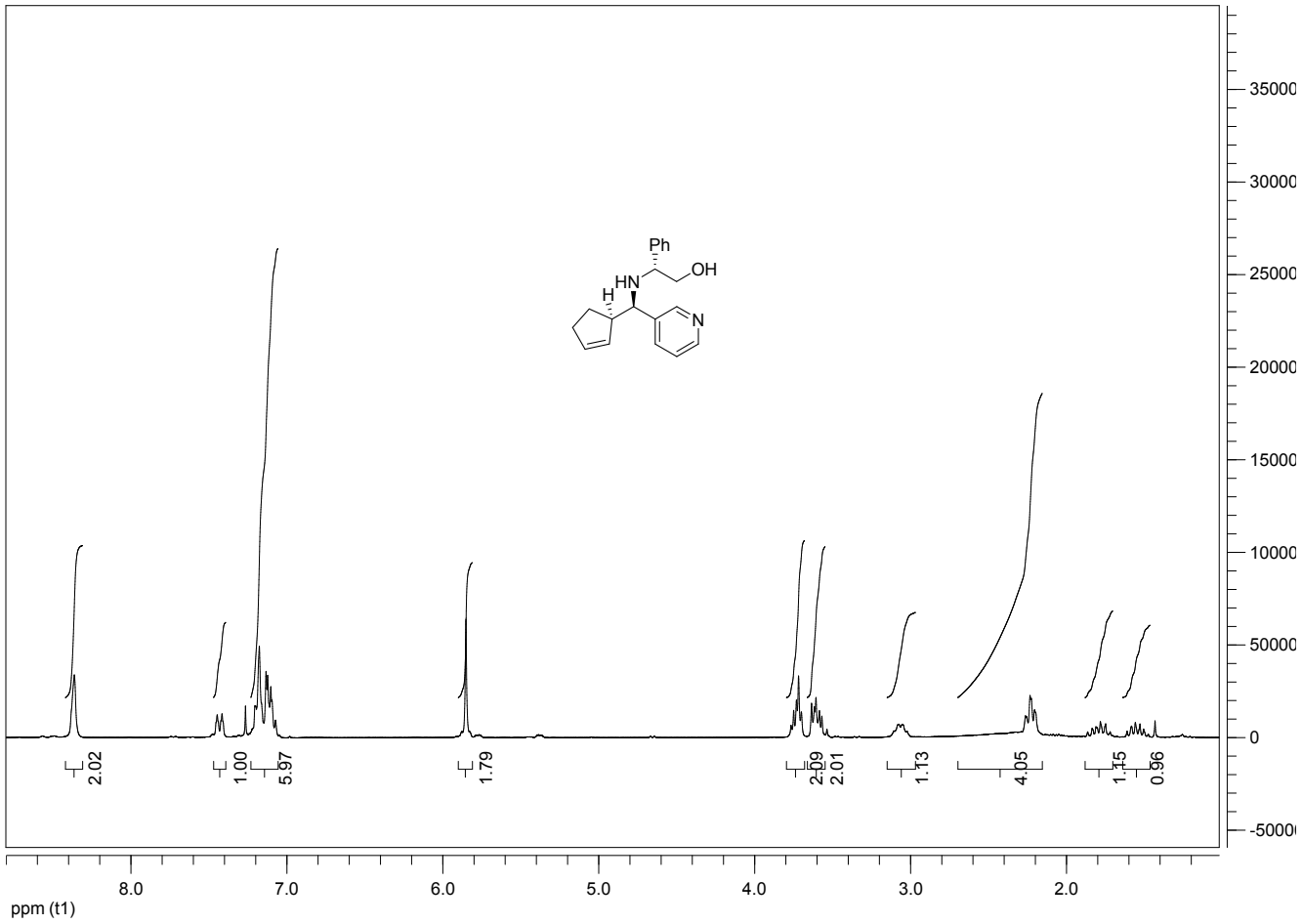
133.334
131.330
131.228
129.181
128.500
127.446
127.202
120.576
64.983
64.801
61.640
52.601
32.078
27.144
Ph
OH
HN
H
Br
60000
50000
40000
30000
20000
10000
0
-10000
-20000
100
50
ppm (t1)

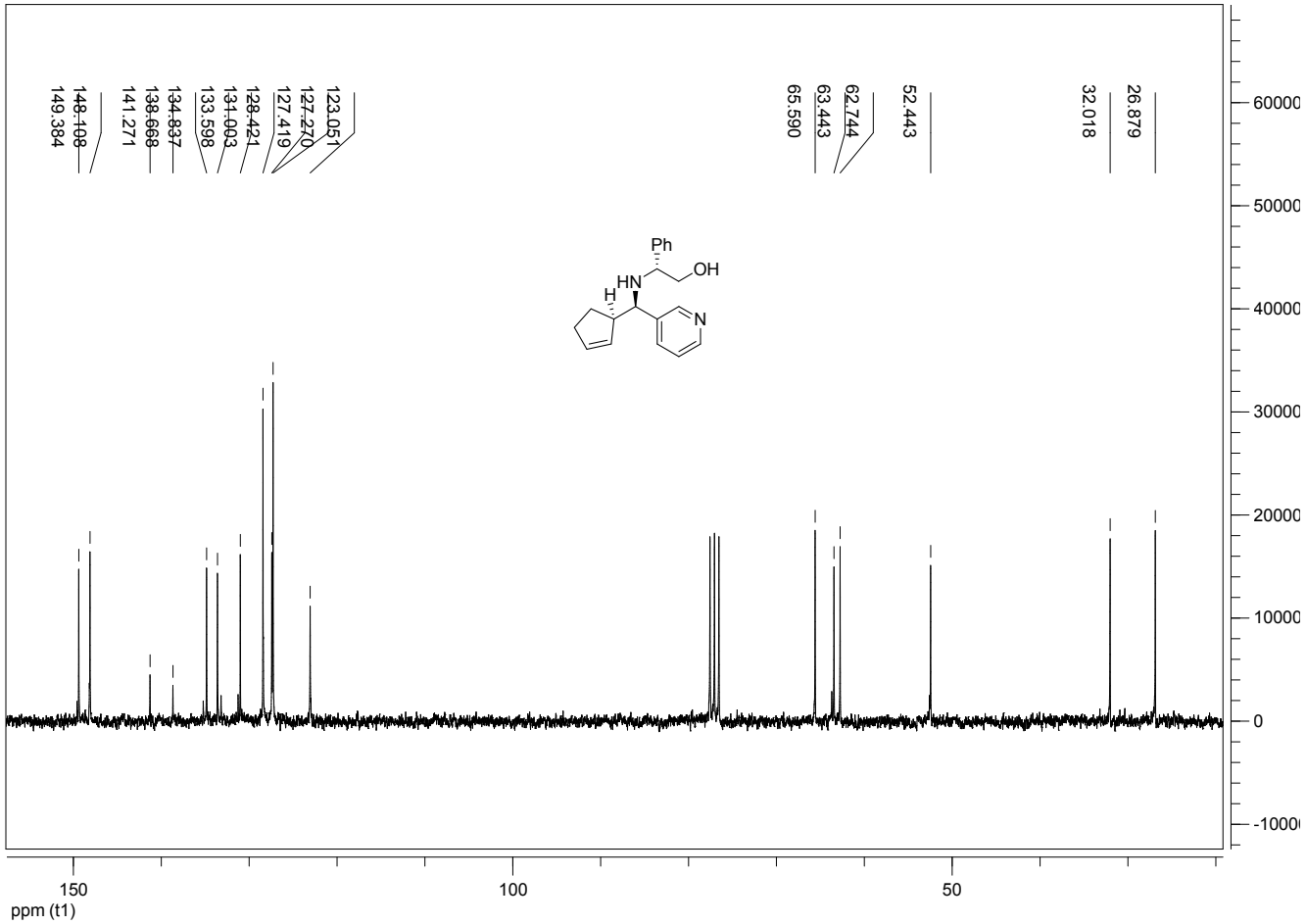
Methyl 4-[(*R*)-[(*R*)-cyclopent-2-enyl][(*R*)-2-hydroxy-1-phenylethylamino]methyl]benzoate 3d



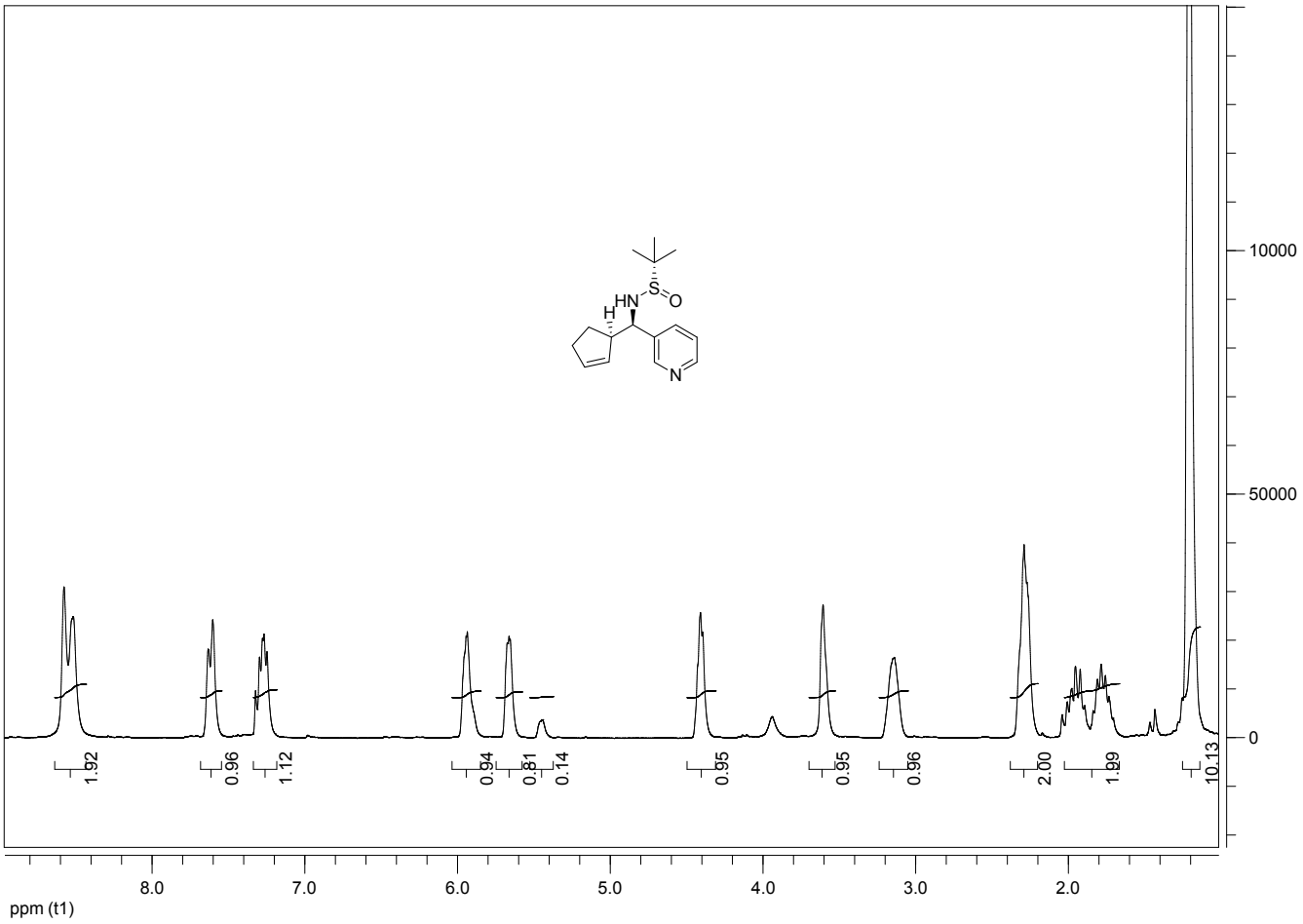


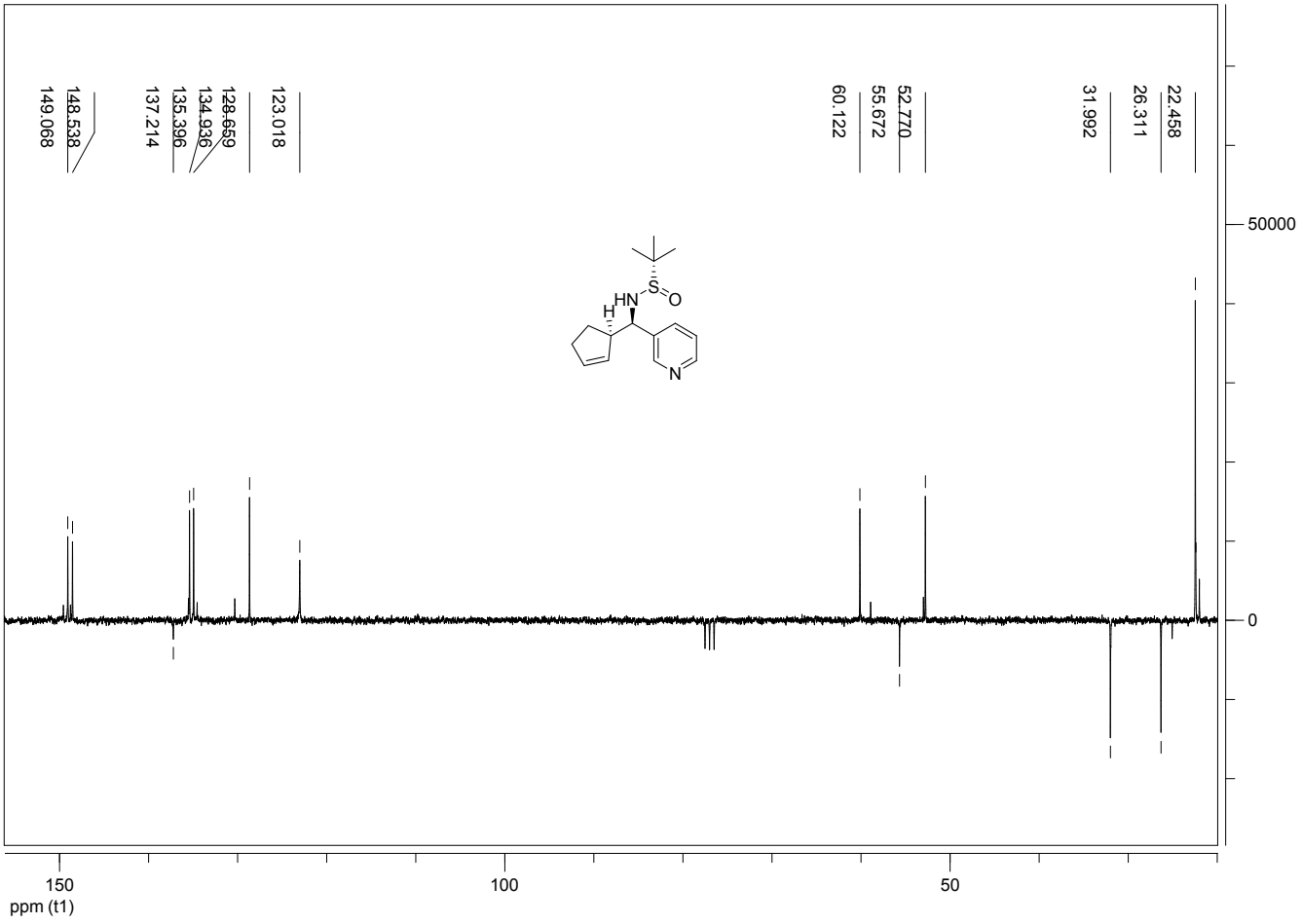
(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](pyridin-3-yl)methylamino]-2-phenylethanol 3e



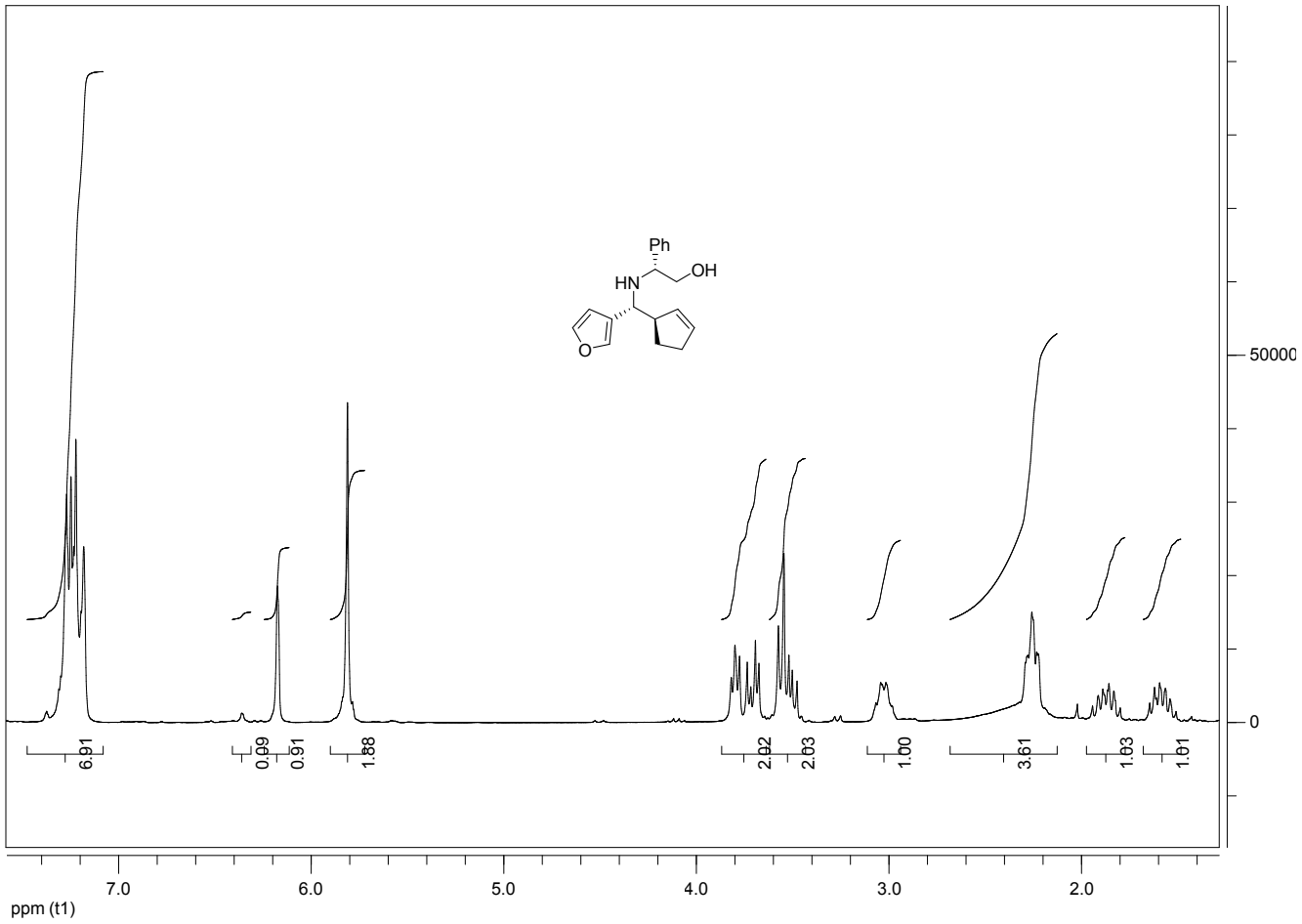


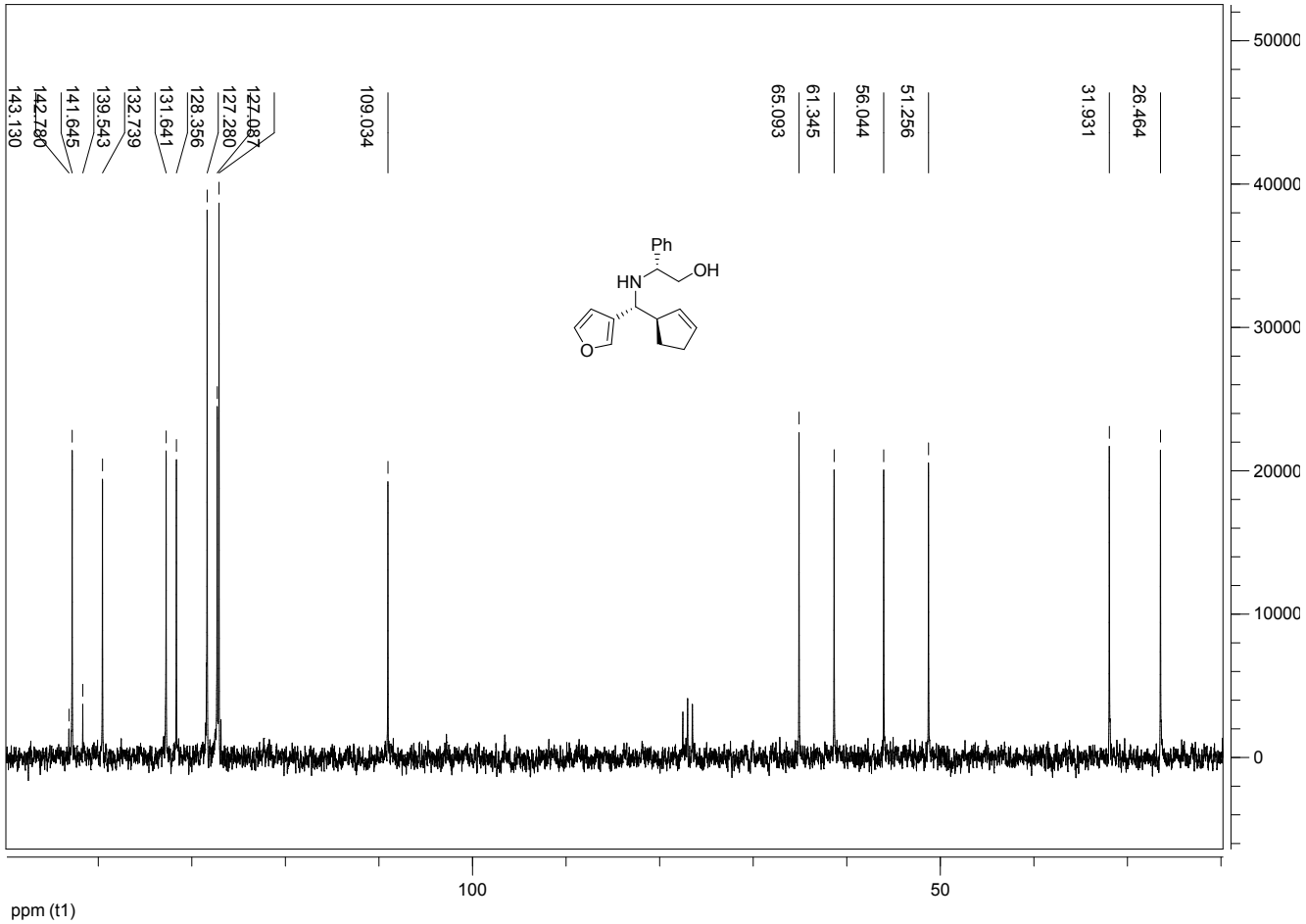
(*R*)-*N*-[(*S*)-[(*S*)-cyclopent-2-en-1-yl](pyridin-3-yl)methyl]-2-methylpropane-2-sulfinamide 3'e



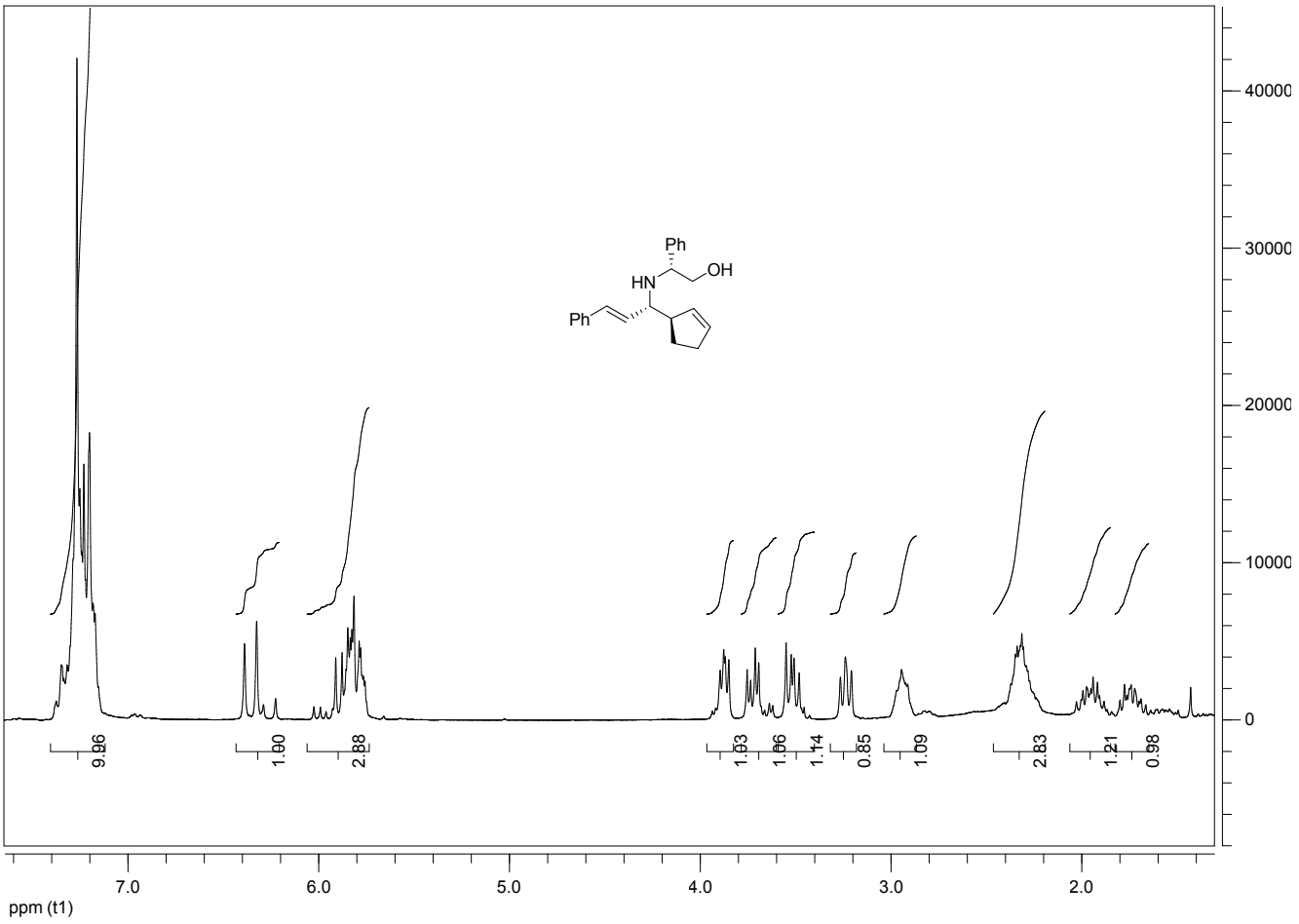


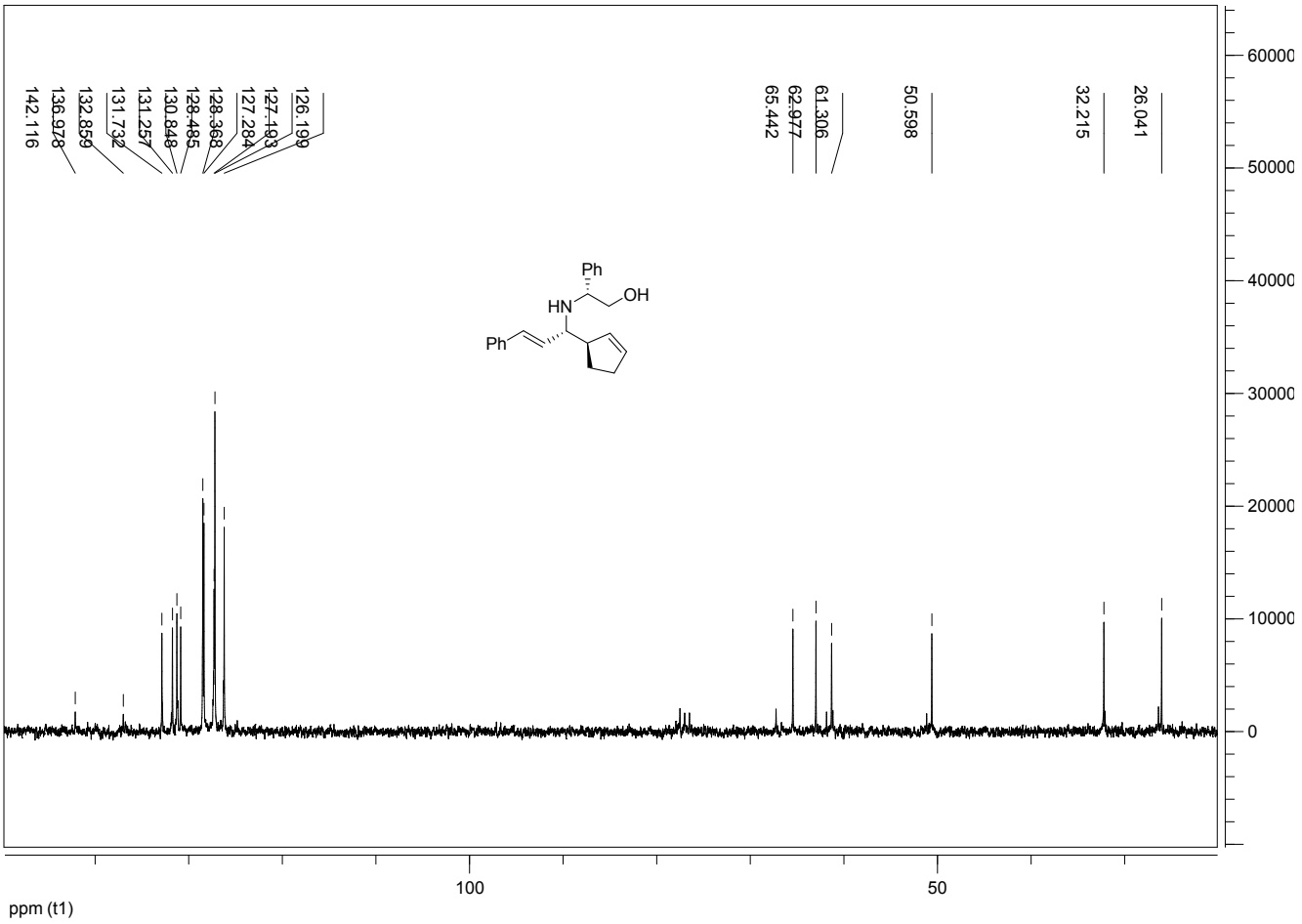
(*R*)-2-[(*R*)-[(*R*)-Cyclopent-2-enyl](furan-3-yl)methylamino]-2-phenylethanol 3f



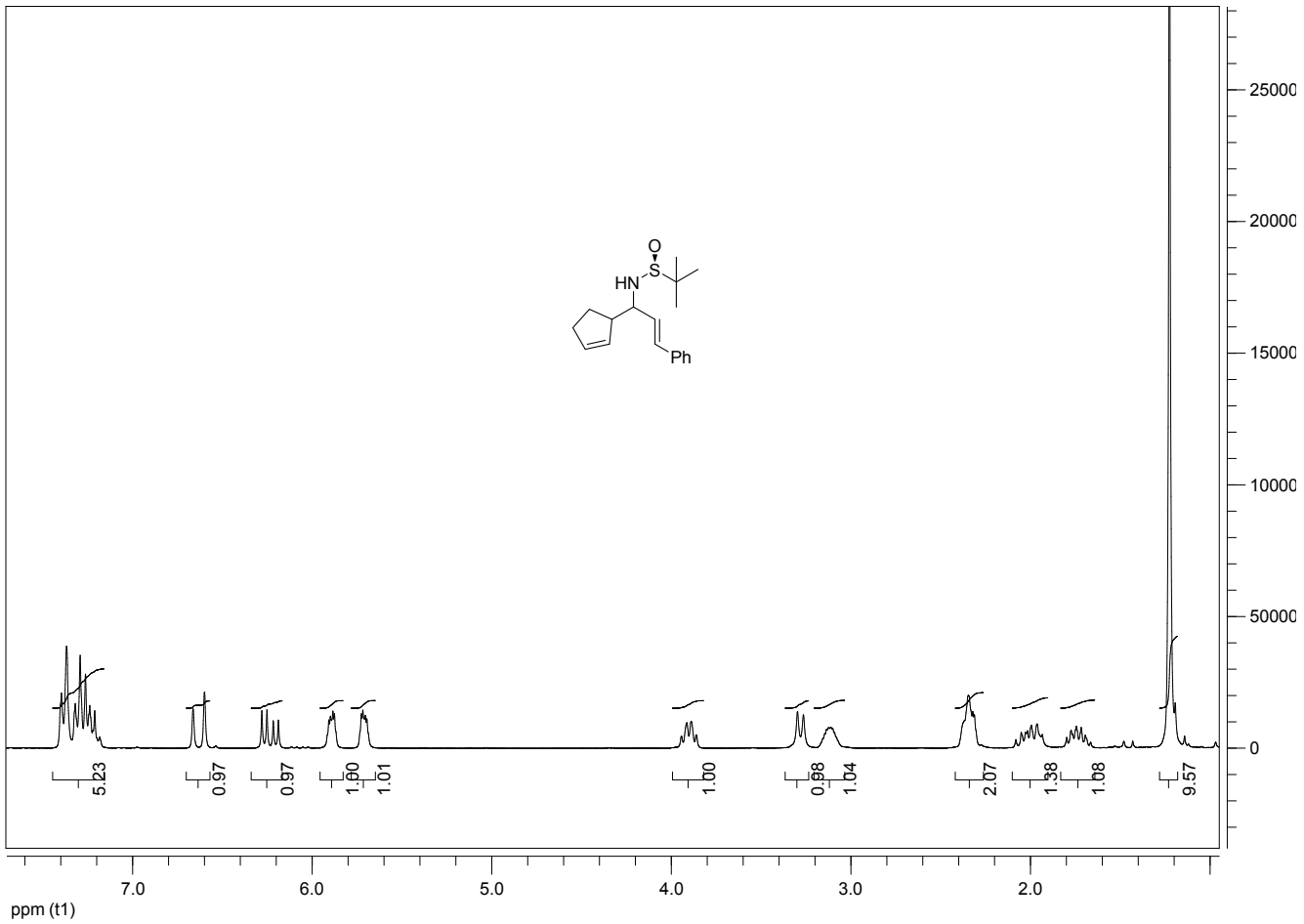


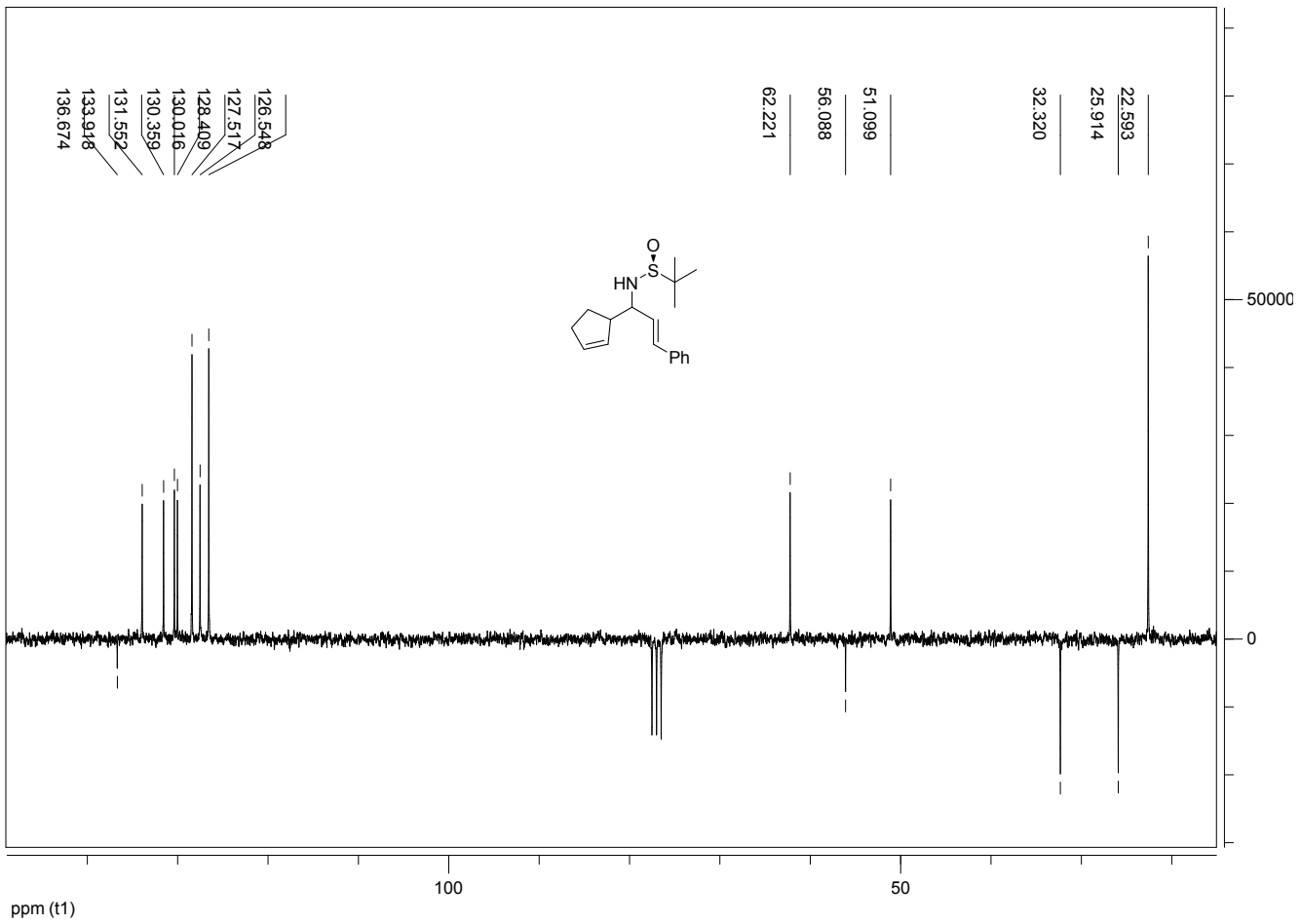
(*R*)-2-[(*S*,*E*)-1-[(*R*)-Cyclopent-2-enyl]-3-phenylallylamino]-2-phenylethanol 3g



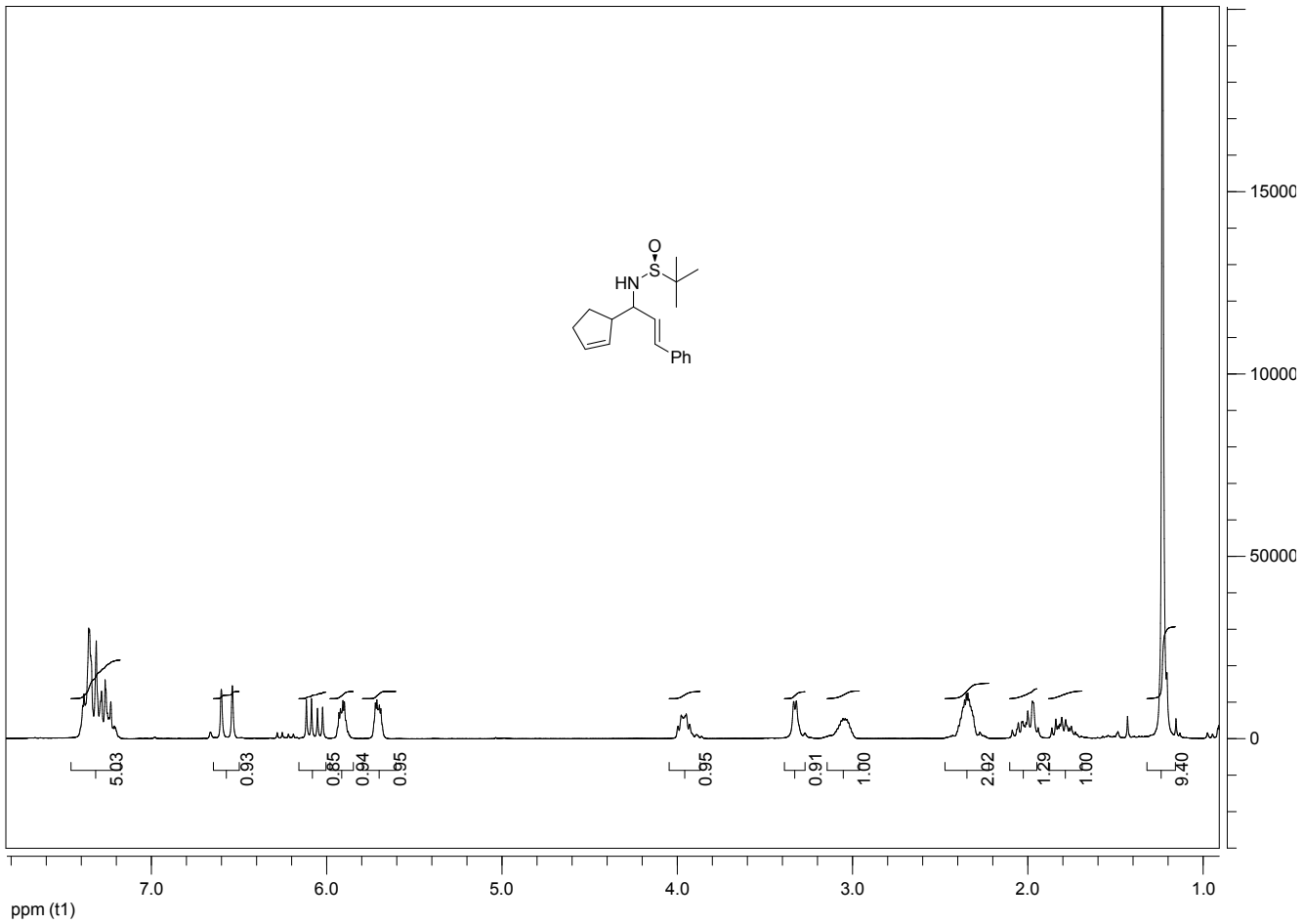


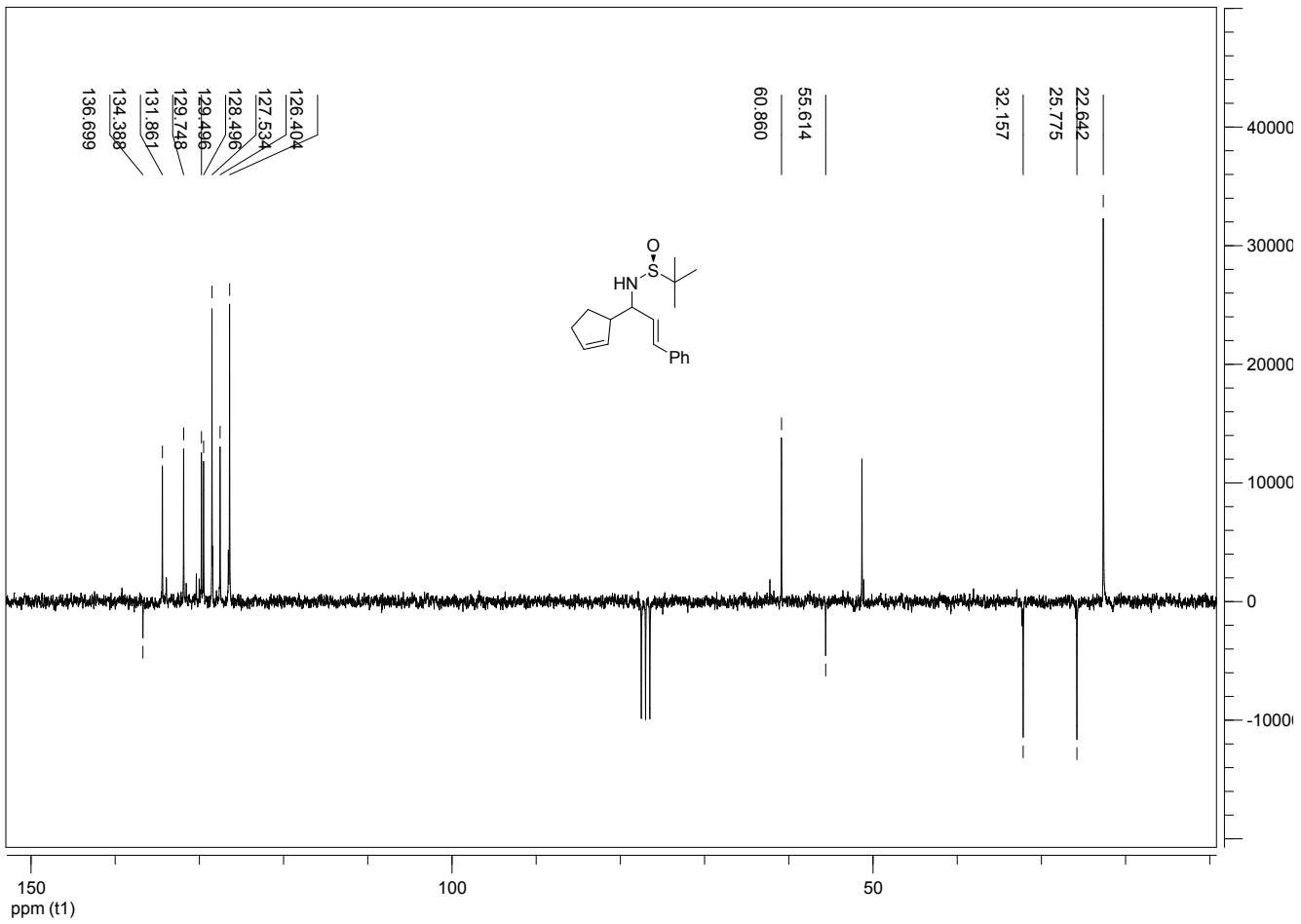
(*S*)-*N*-[(*E*)-1-(Cyclopent-2-enyl)-3-phenylallyl]-2-methylpropane-2-sulfinamide 3'g (less polar isomer)



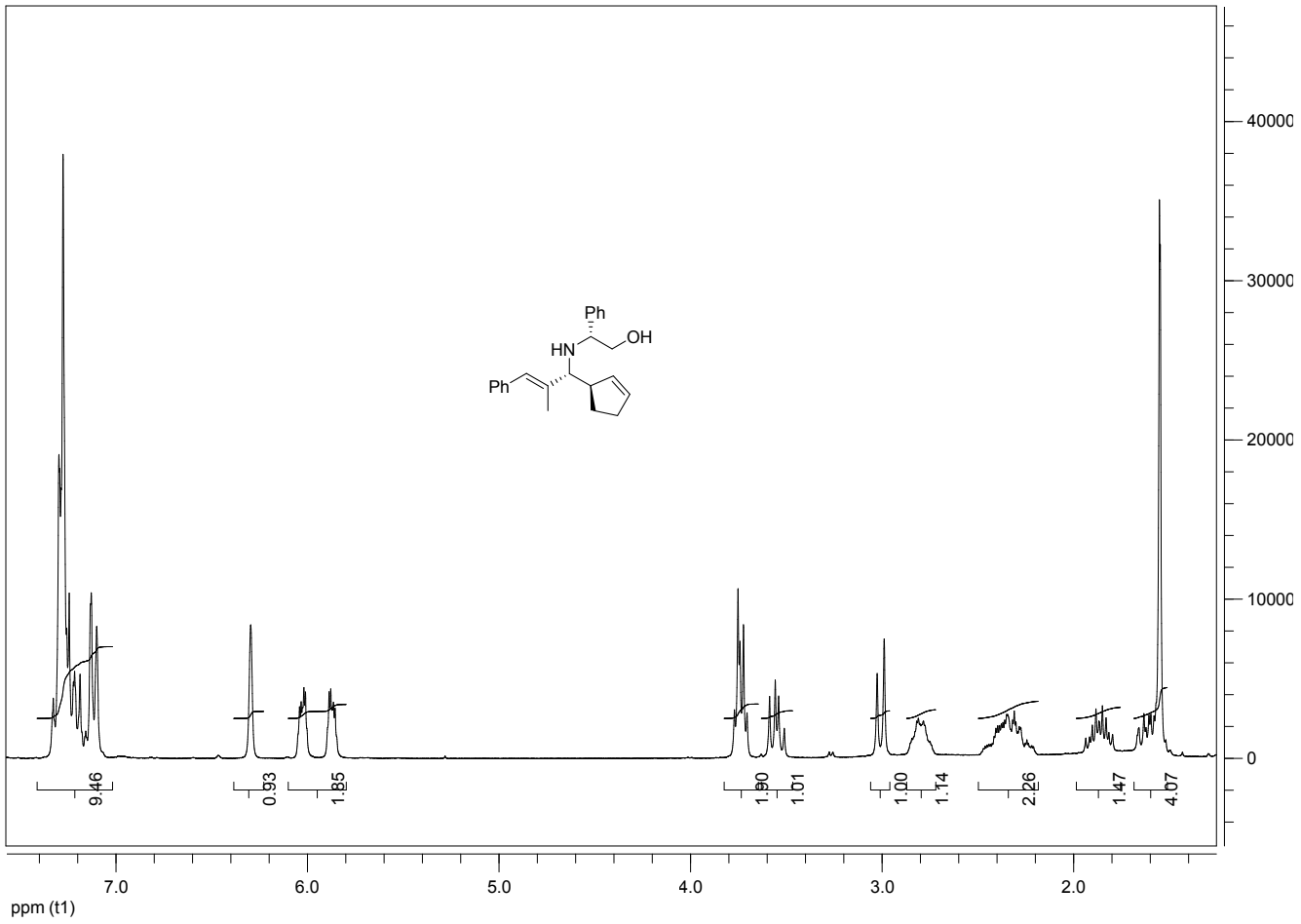


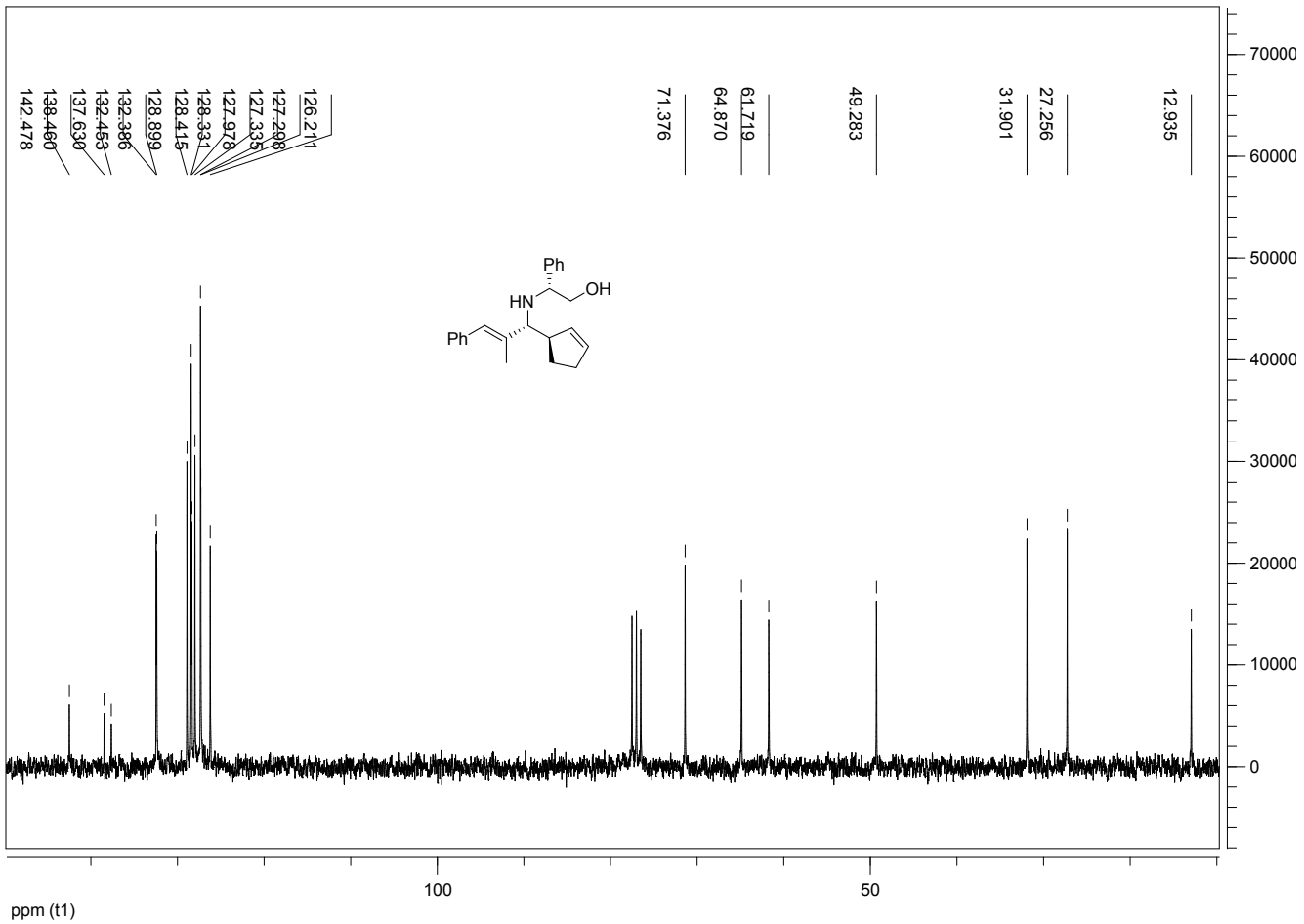
(*S*)-*N*-[(*E*)-1-(Cyclopent-2-enyl)-3-phenylallyl]-2-methylpropane-2-sulfinamide 3'g (more polar isomer)



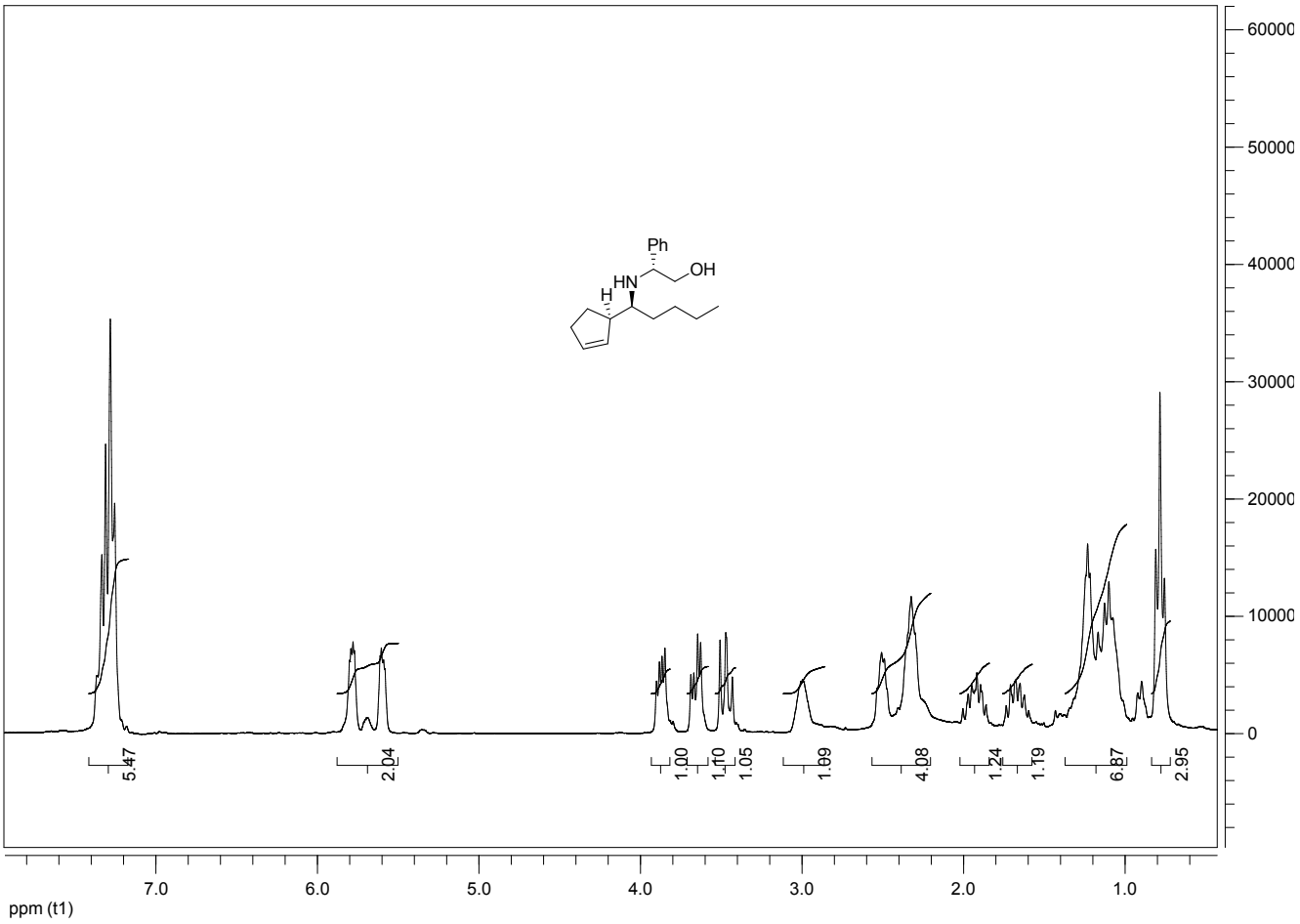


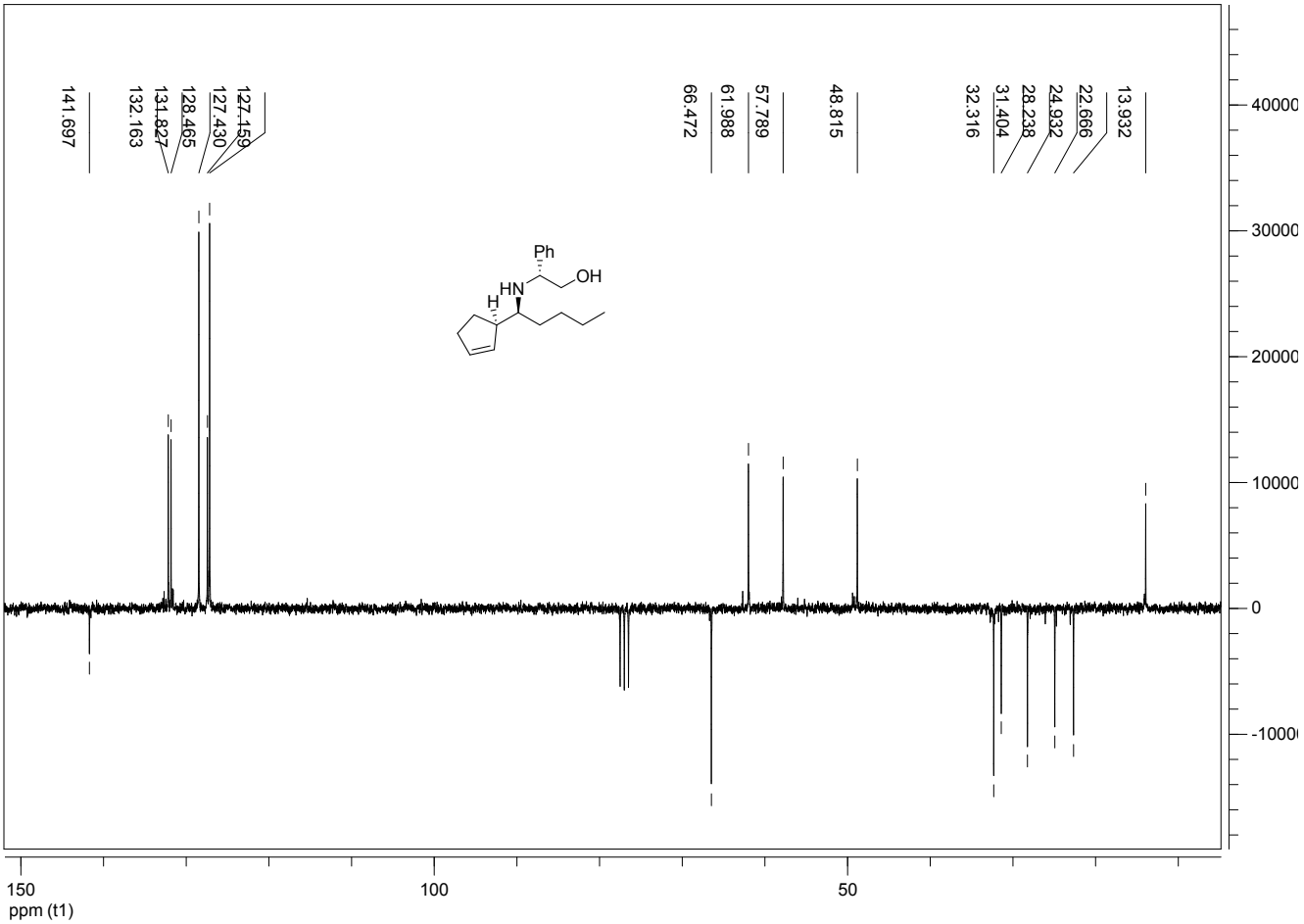
(*R*)-2-[(*R*,*E*)-1-[(*R*)-Cyclopent-2-enyl]-2-methyl-3-phenylallylamino]-2-phenylethanol 3h



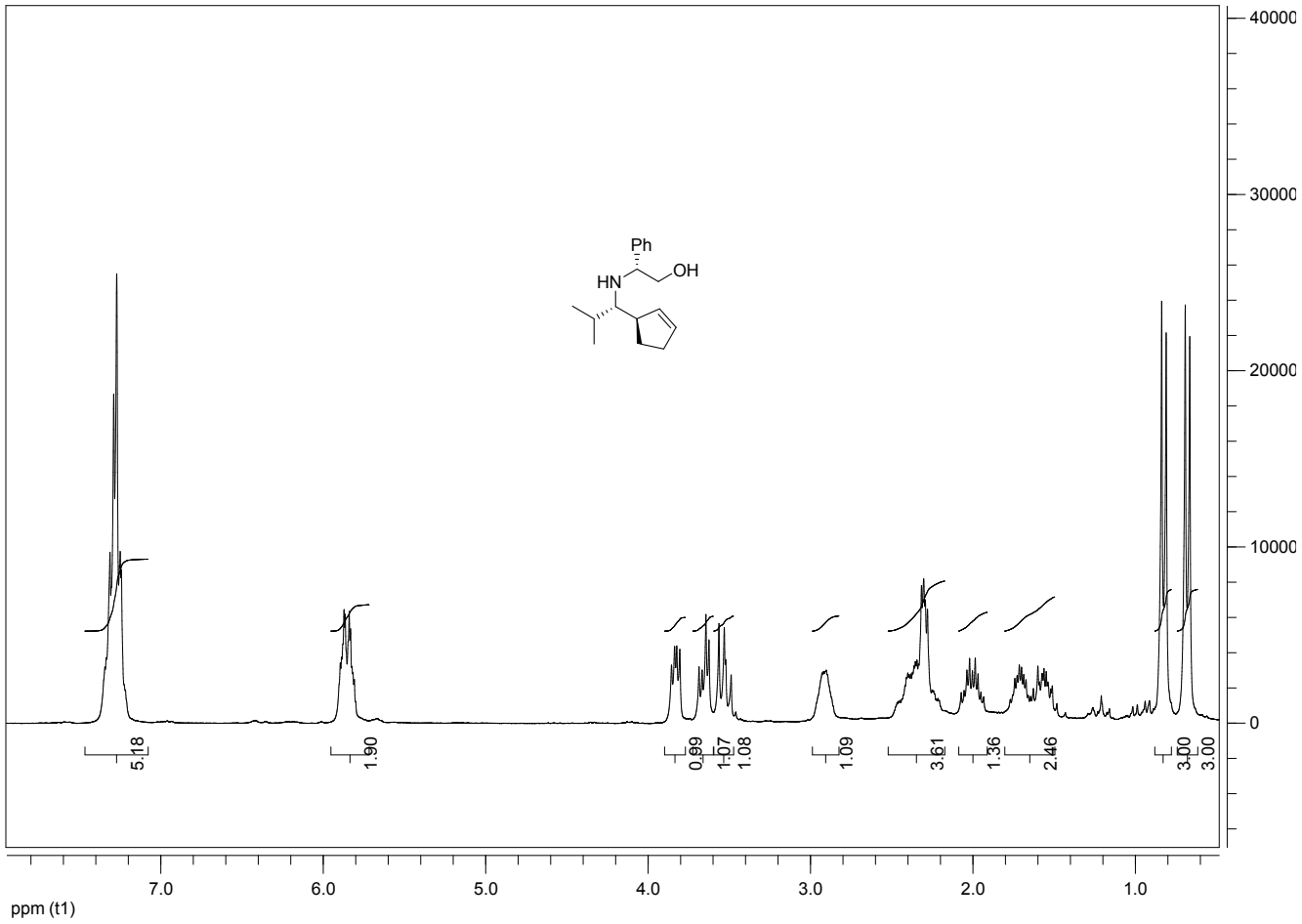


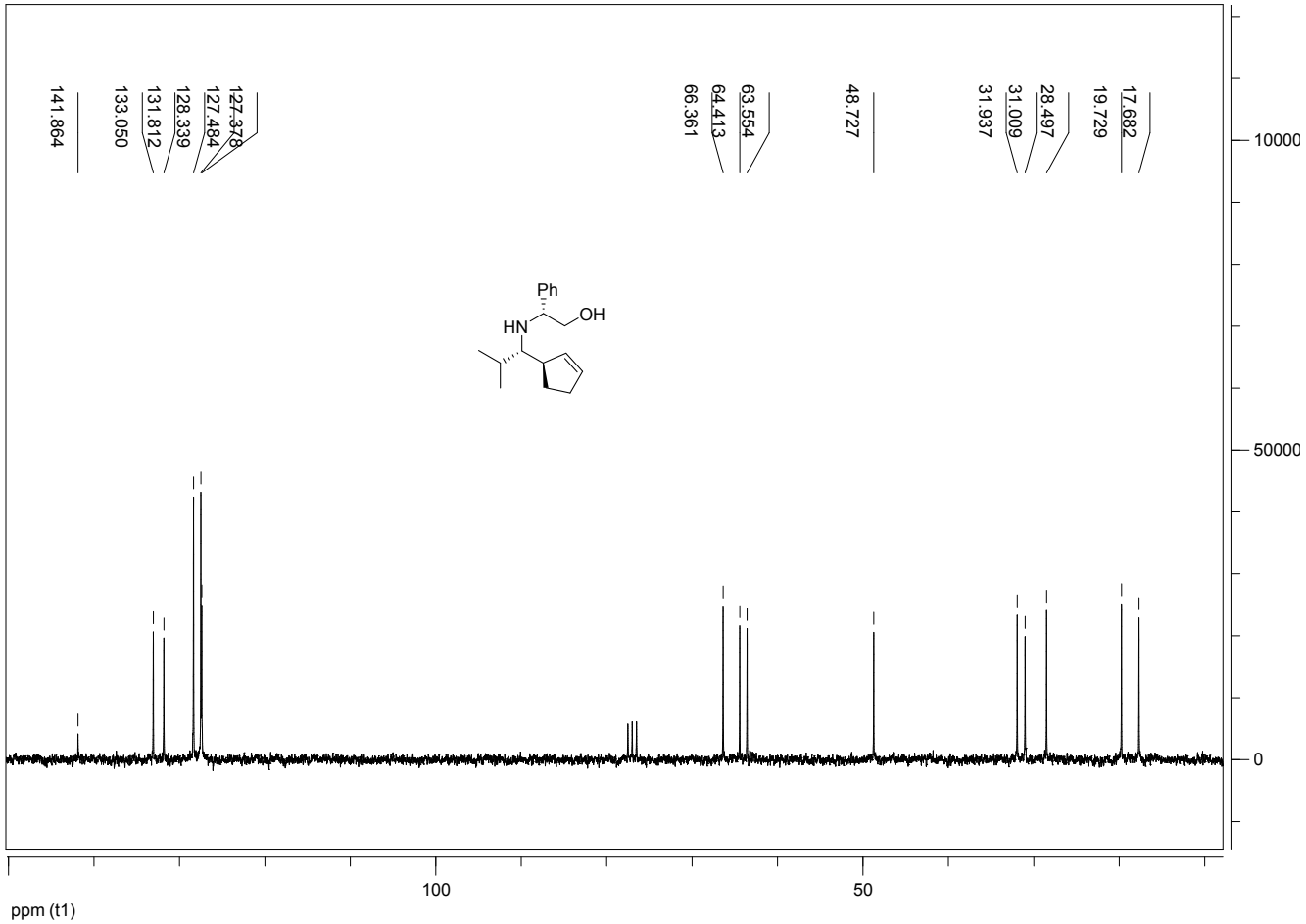
(*R*)-2-[(*S*)-1-[(*R*)-Cyclopent-2-enyl]pentylamino]-2-phenylethanol 3i



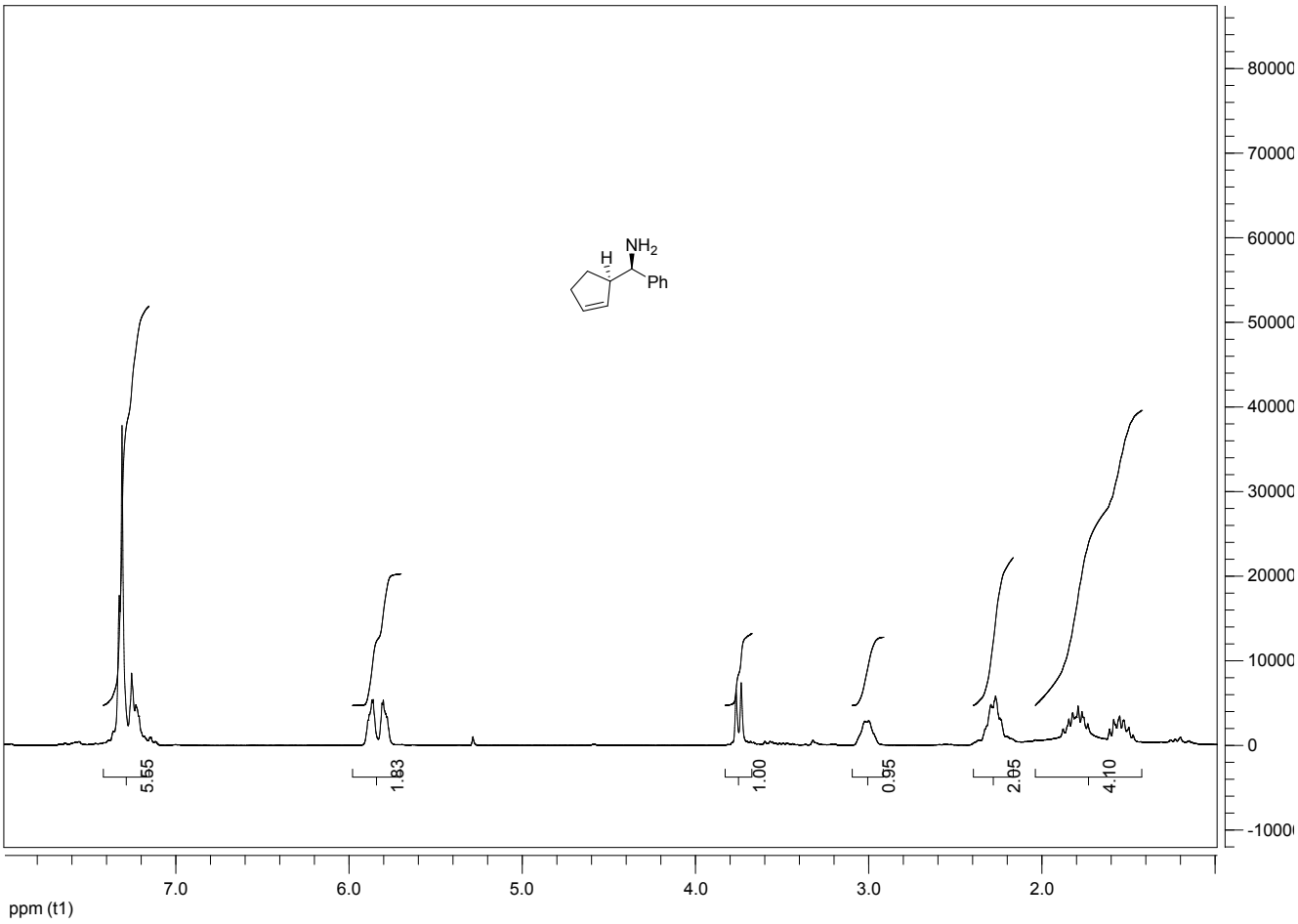


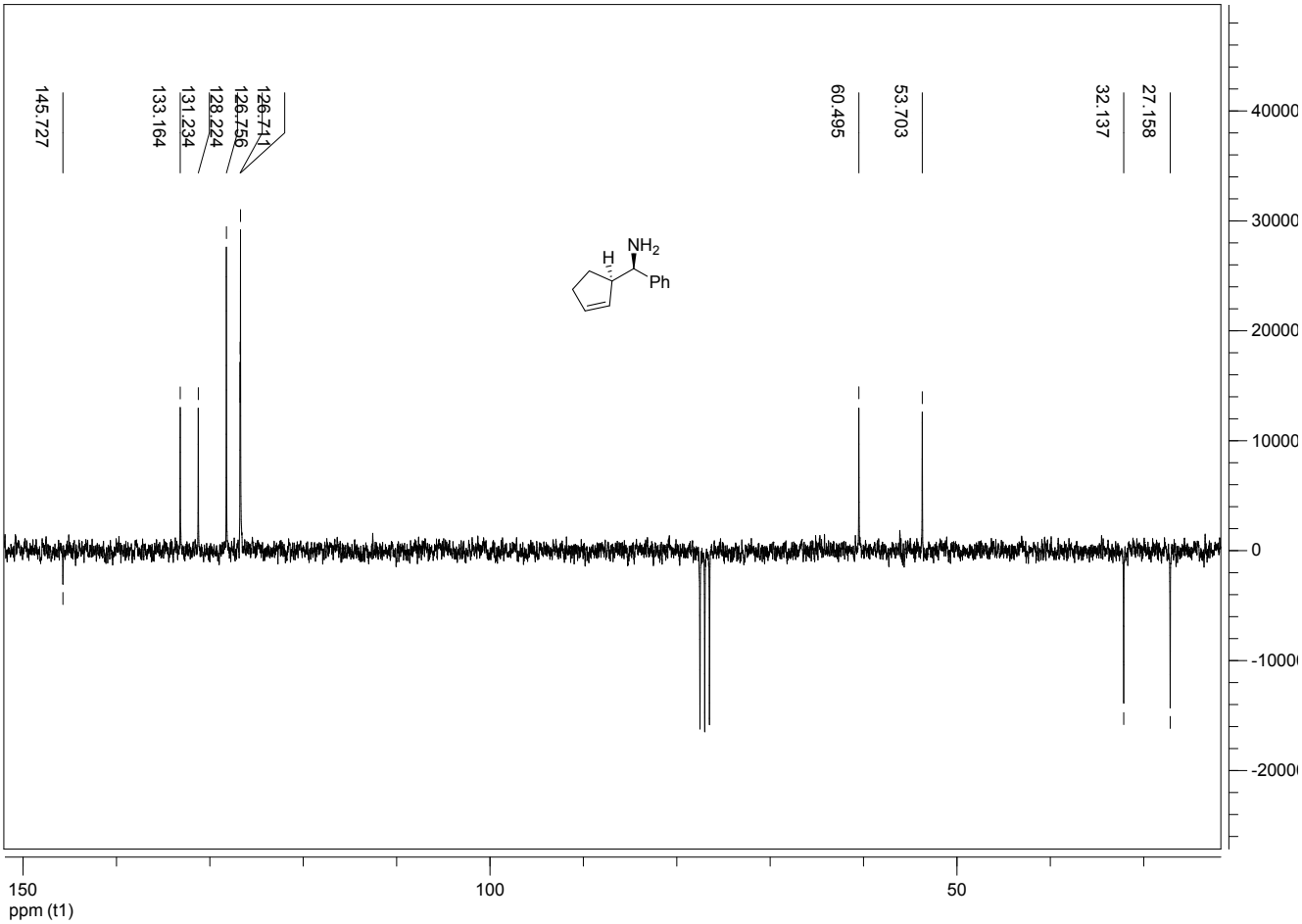
(*R*)-2-[(*S*)-1-[(*R*)-Cyclopent-2-enyl]-2-methylpropylamino]-2-phenylethanol 3j



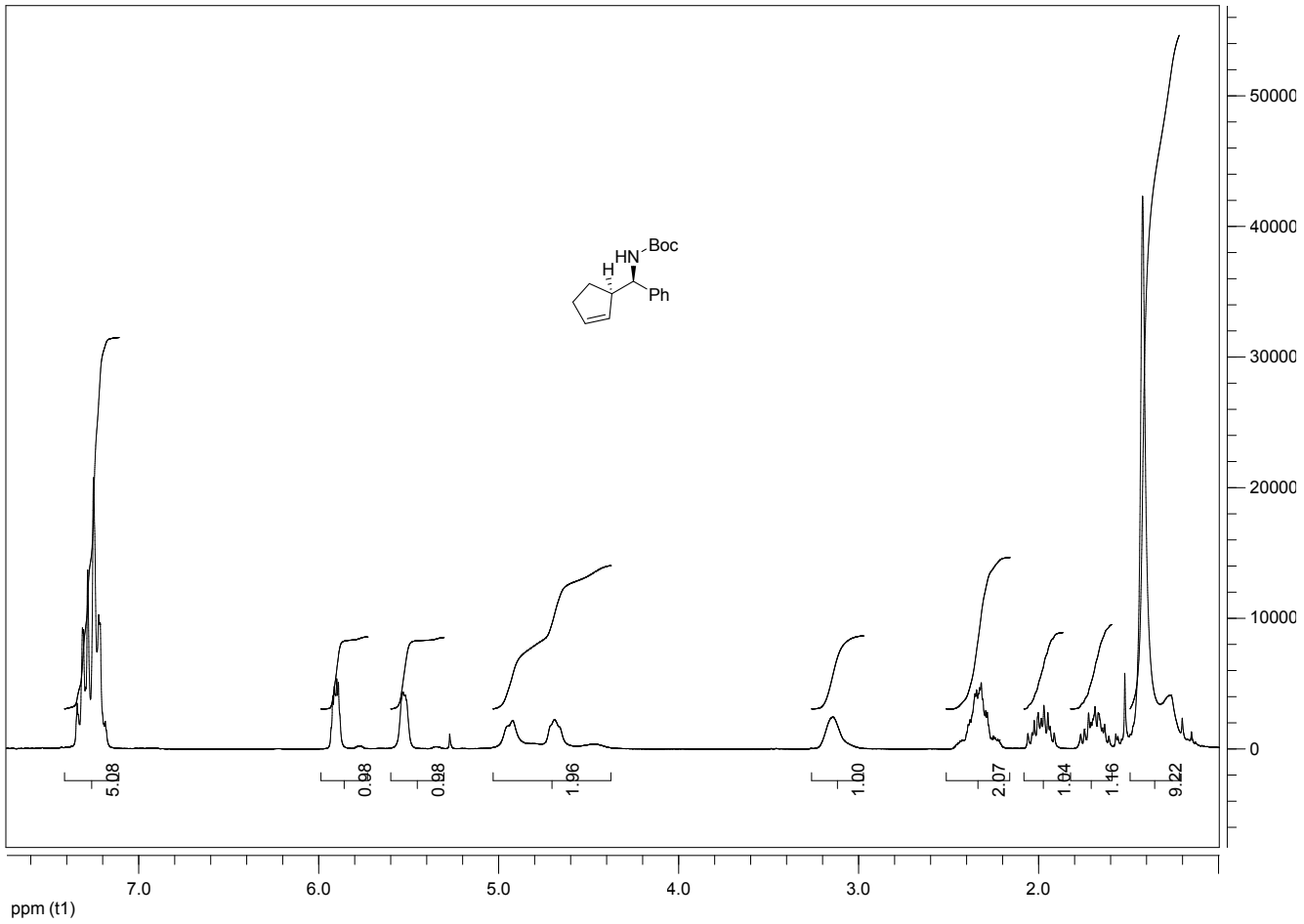


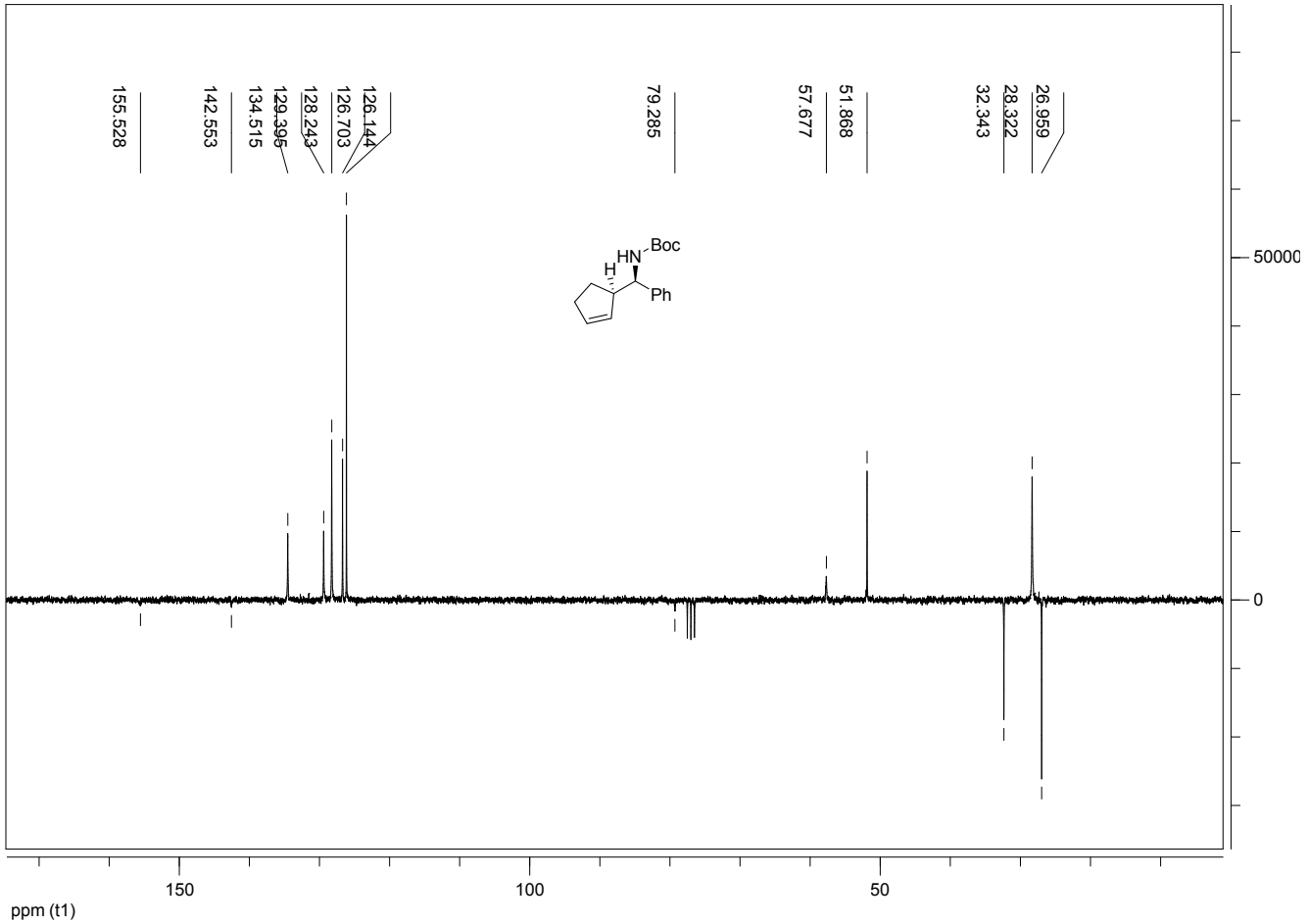
(*R*)-[(*R*)-Cyclopent-2-enyl](phenyl)methanamine



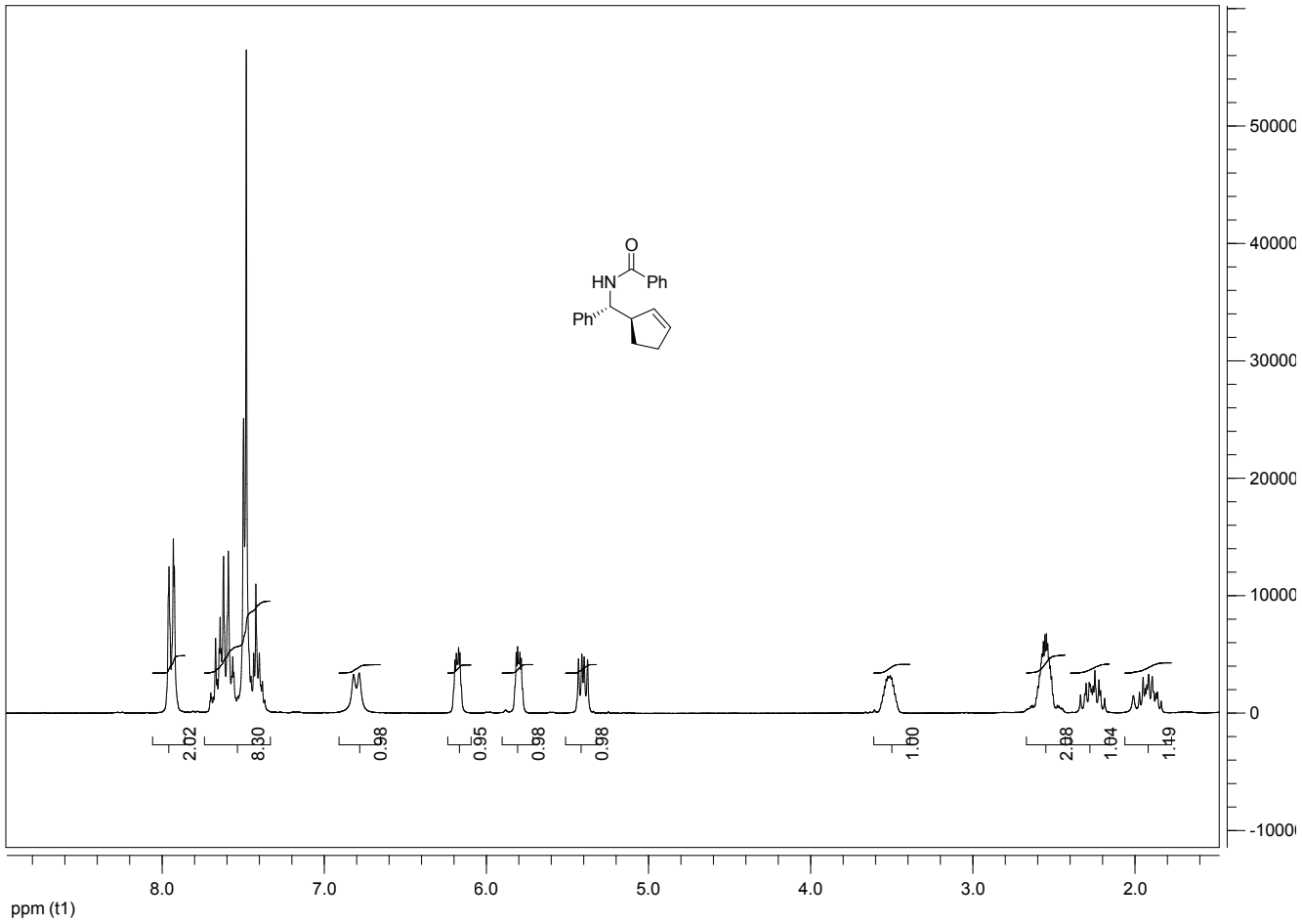


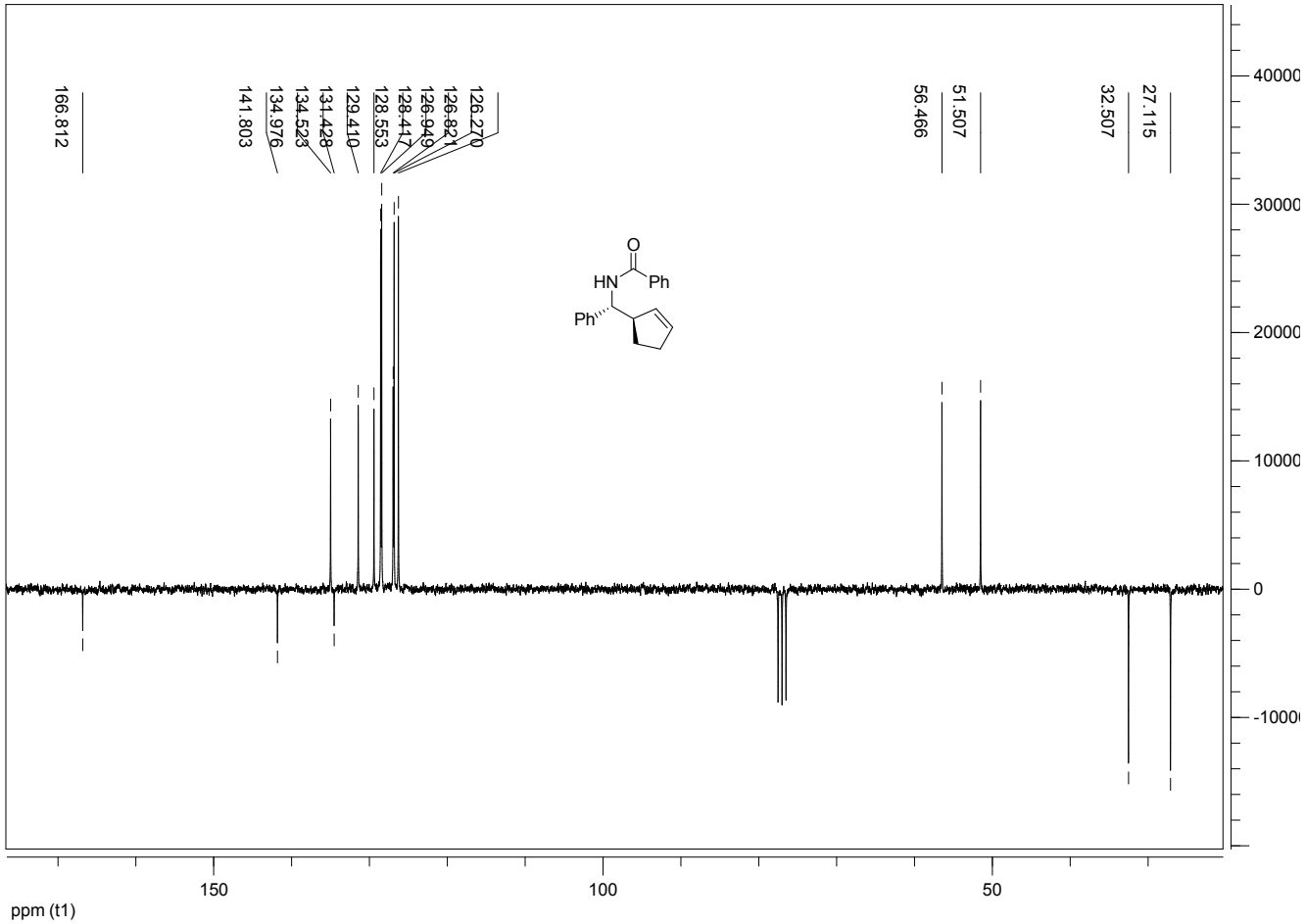
***Tert*-Butyl (*R*)-[(*R*)-cyclopent-2-enyl](phenyl)methylcarbamate 4**



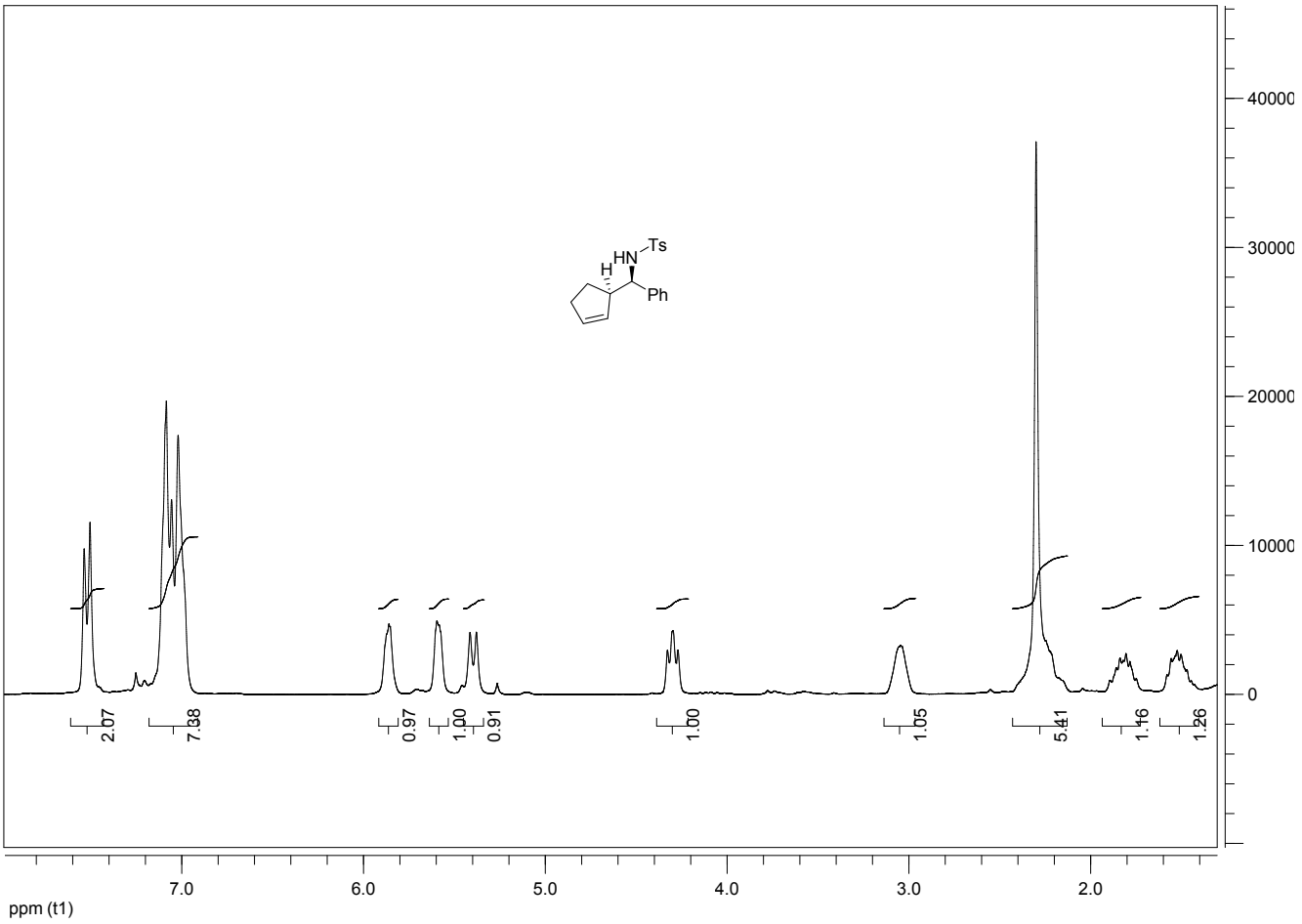


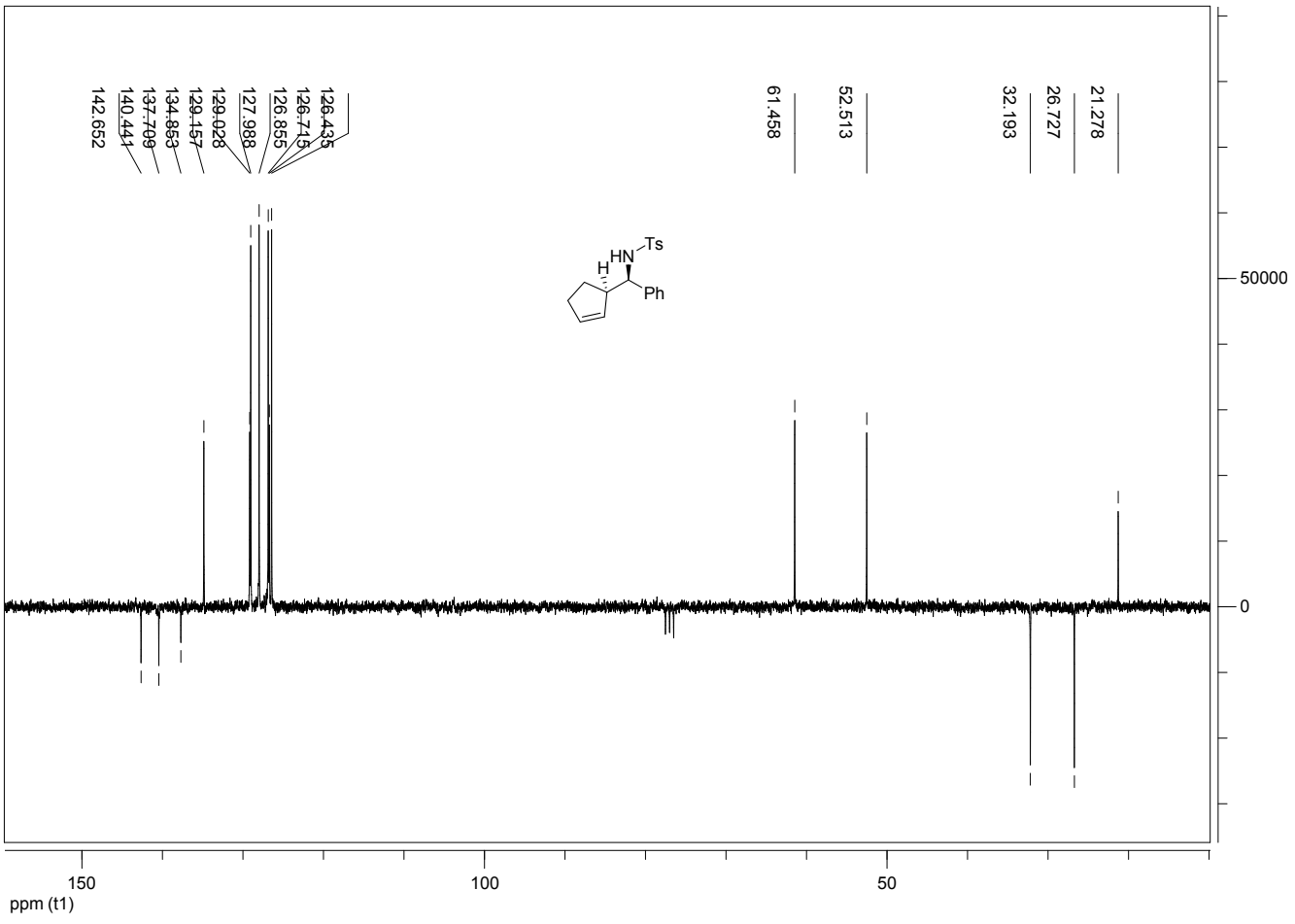
***N*-[(*R*)-[(*R*)-Cyclopent-2-enyl](phenyl)methyl]benzamide**



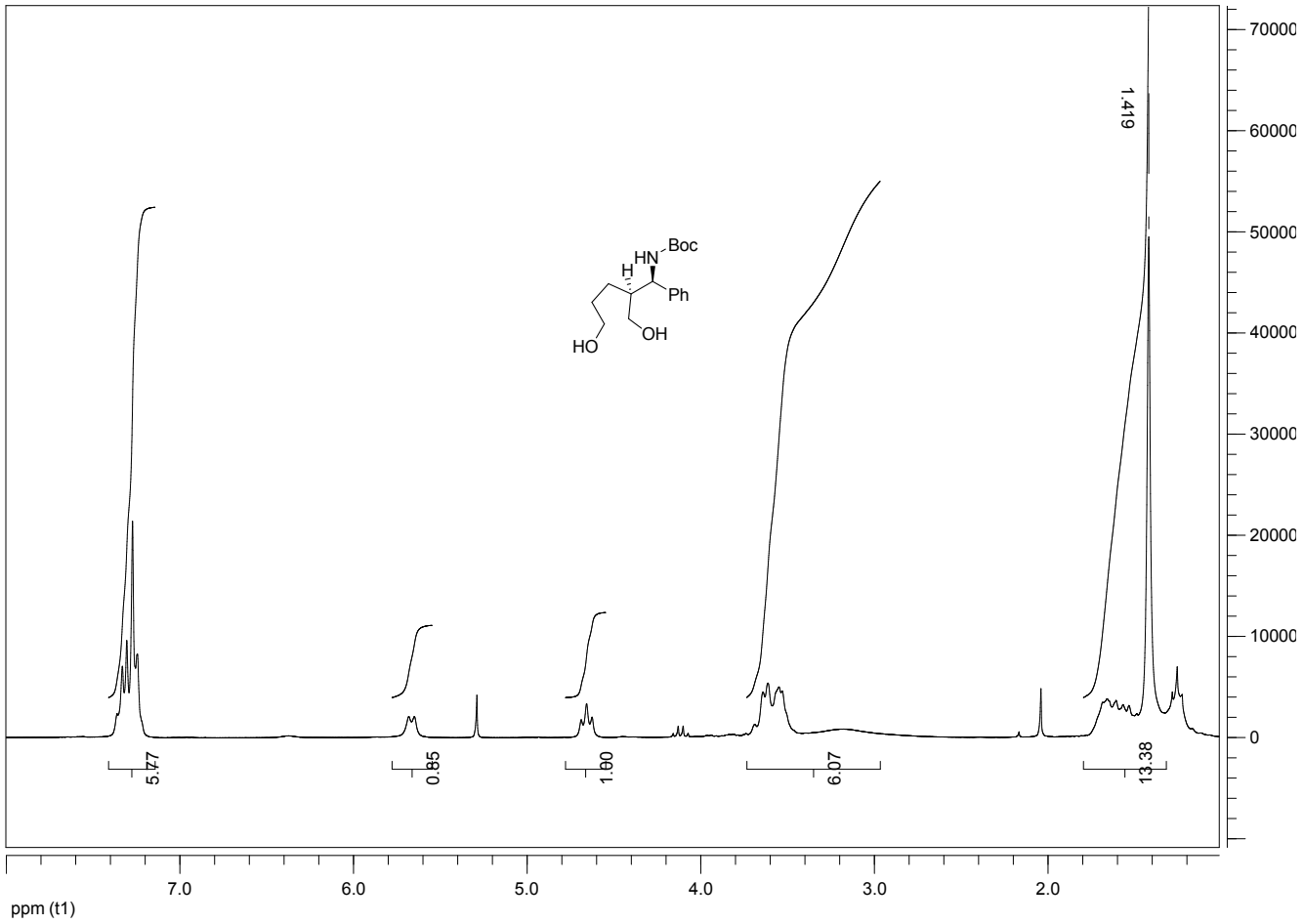


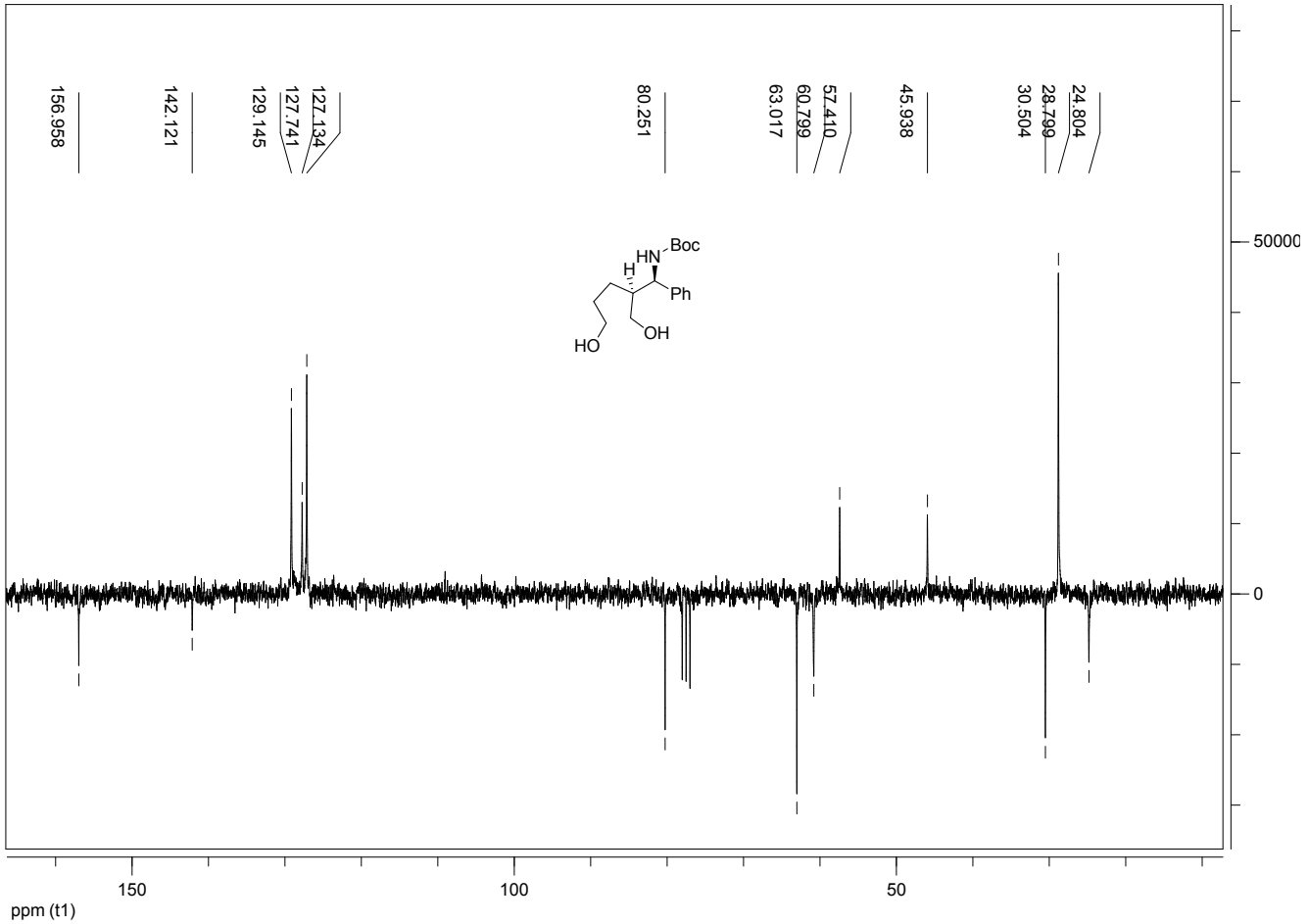
***N*-[(*R*)-[(*R*)-Cyclopent-2-en-1-yl](phenyl)methyl]-4-methylbenzenesulfonamide**



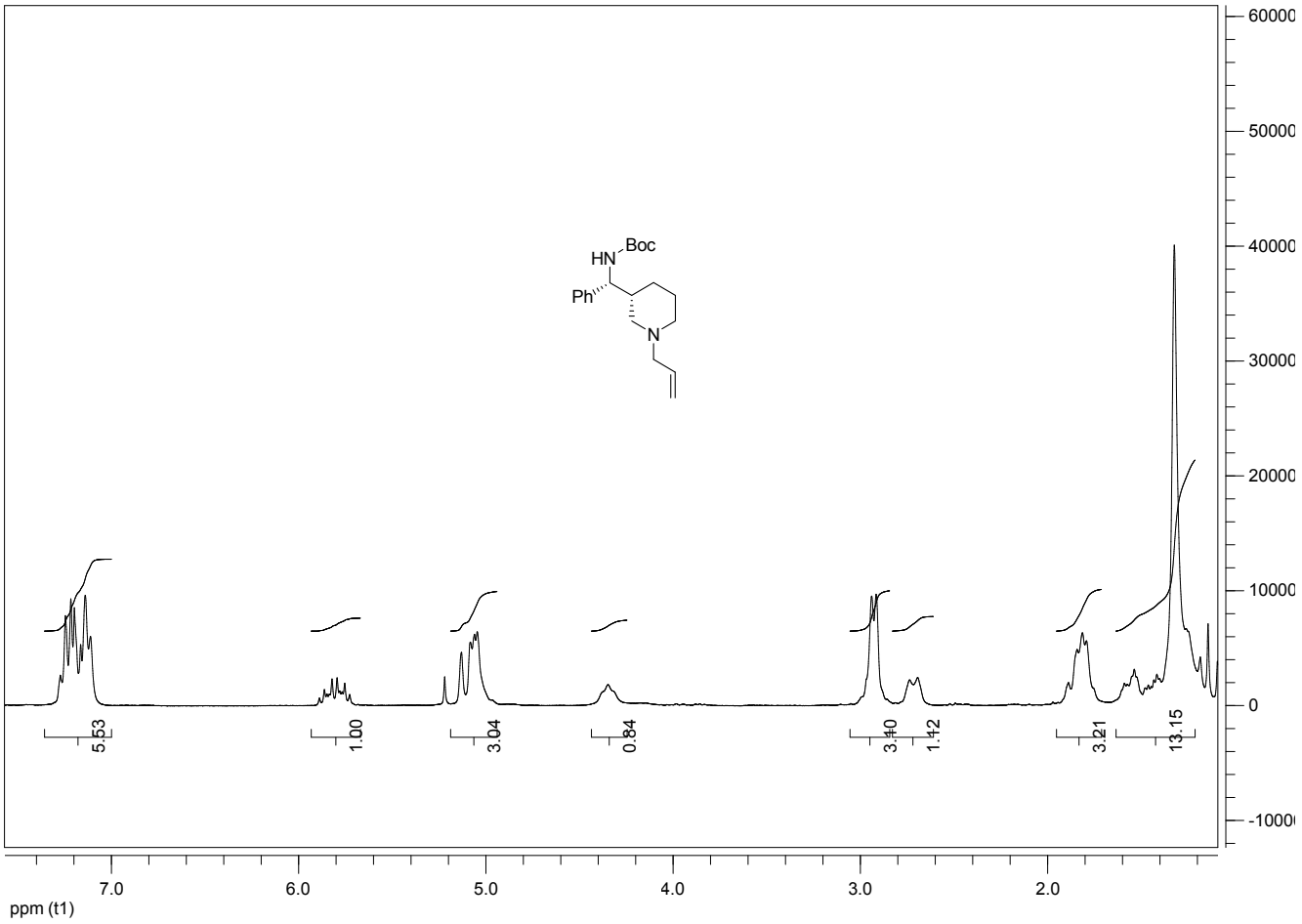


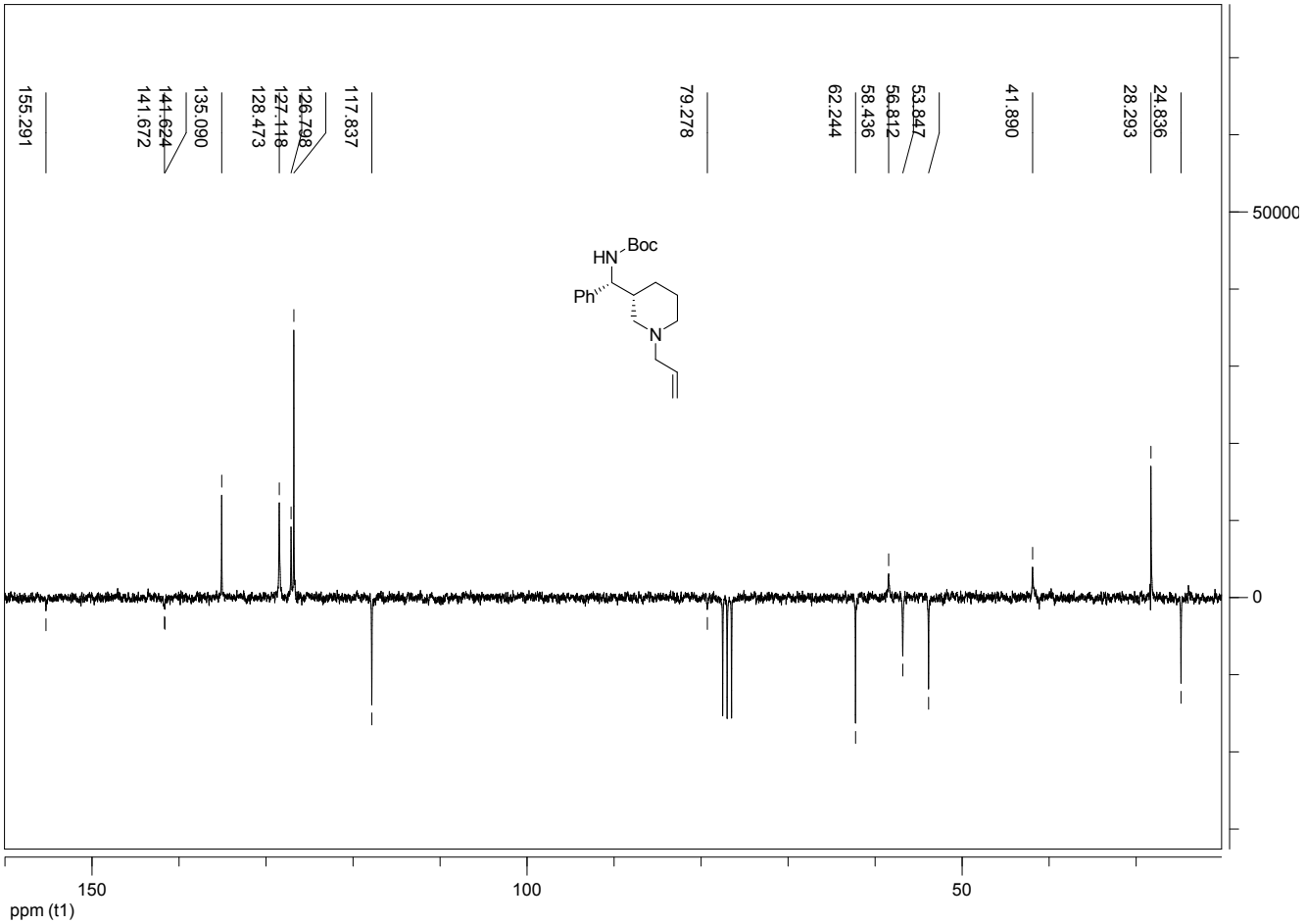
***Tert*-Butyl (1*R*,2*S*)-5-hydroxy-2-(hydroxymethyl)-1-phenylpentylcarbamate**



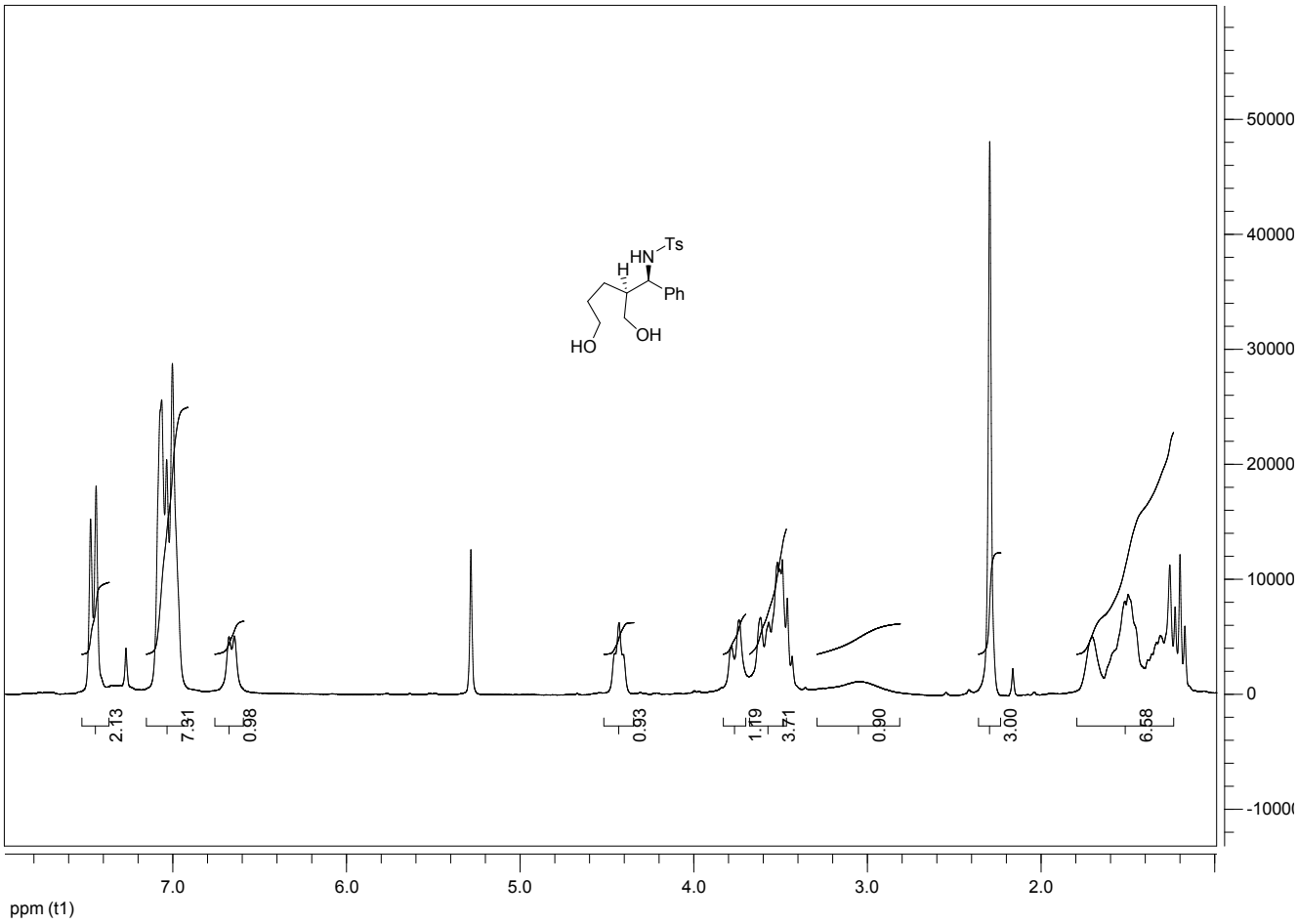


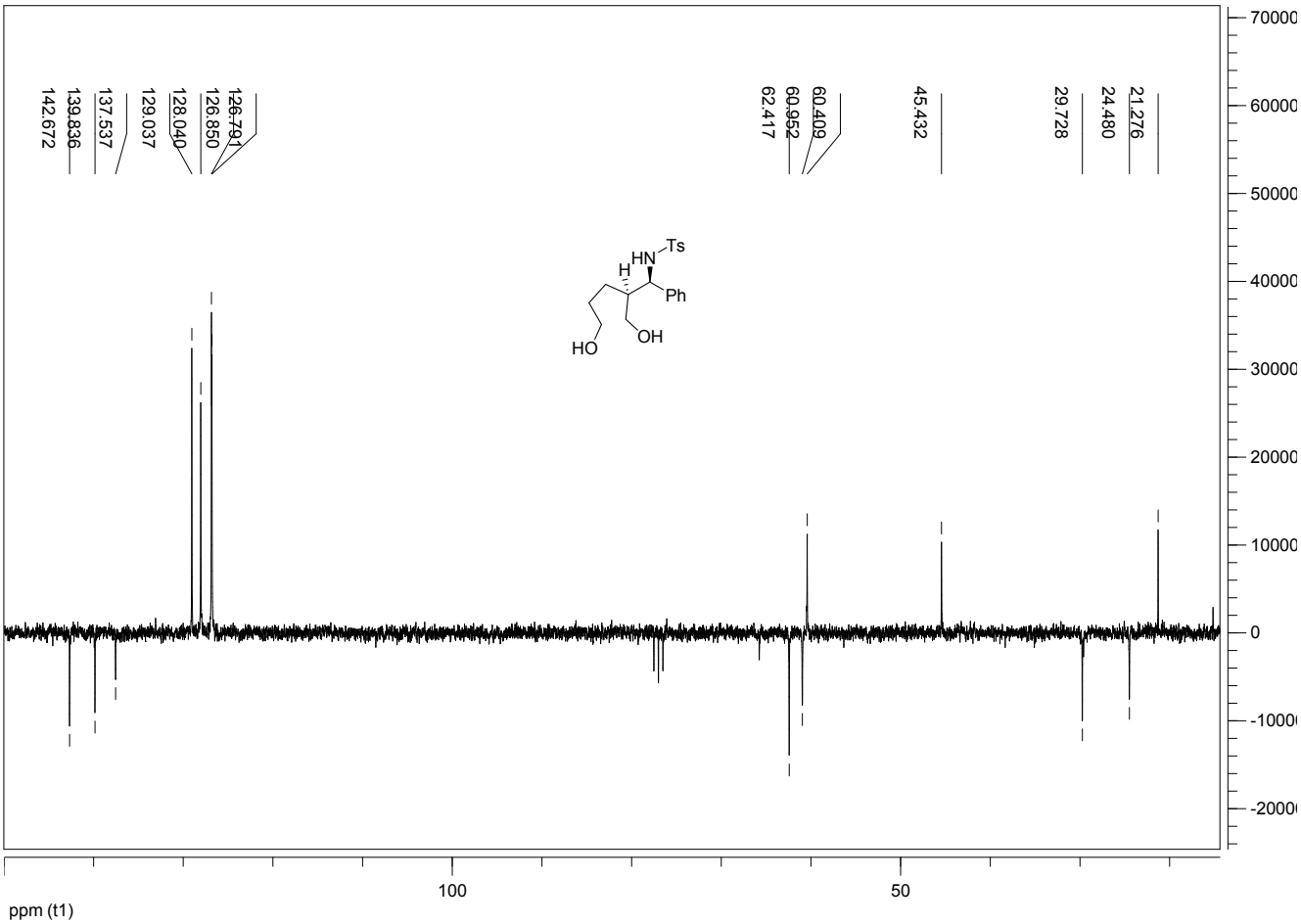
***Tert*-Butyl (*R*)-[(R)-1-allylpiperidin-3-yl](phenyl)methylcarbamate 5**



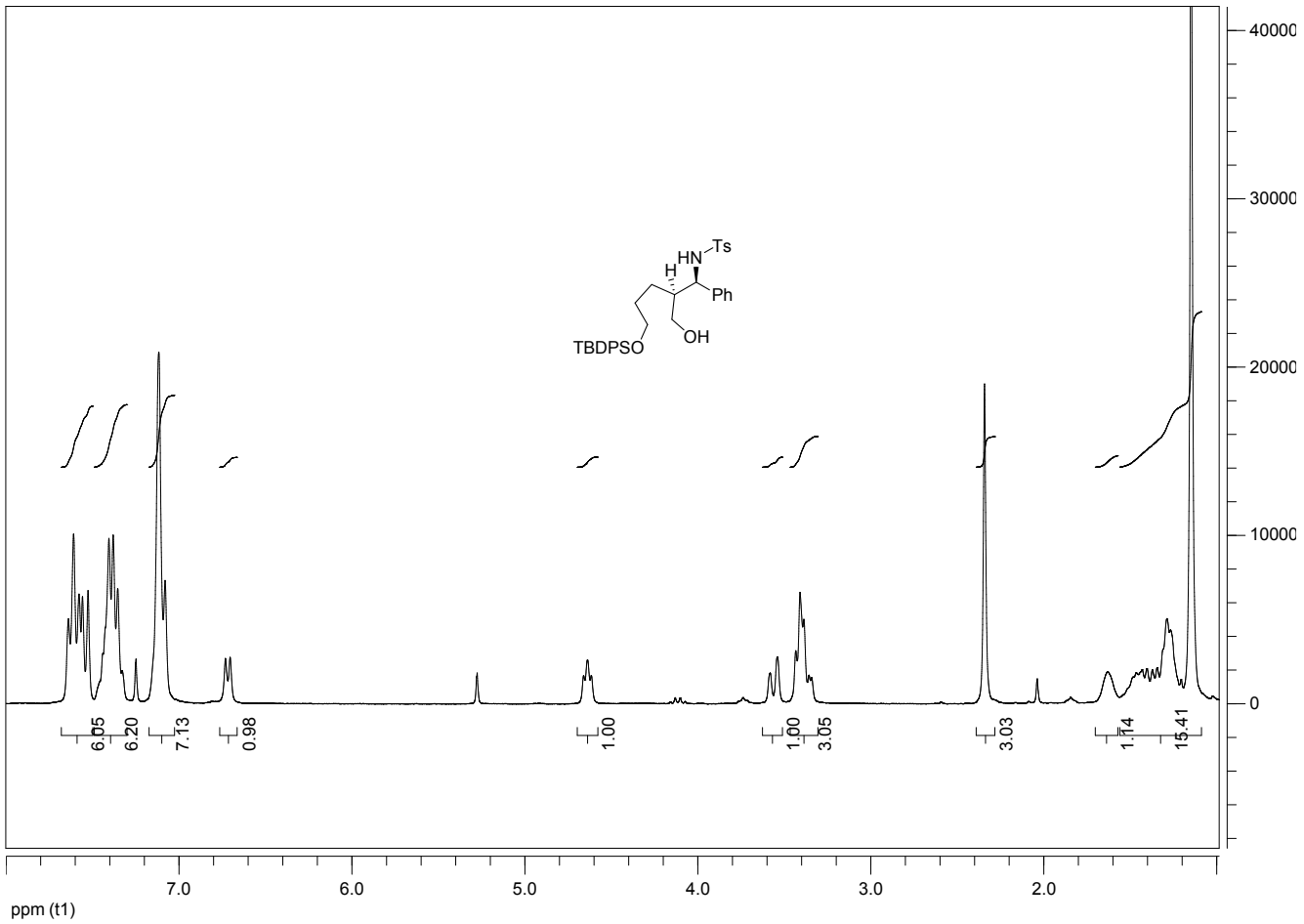


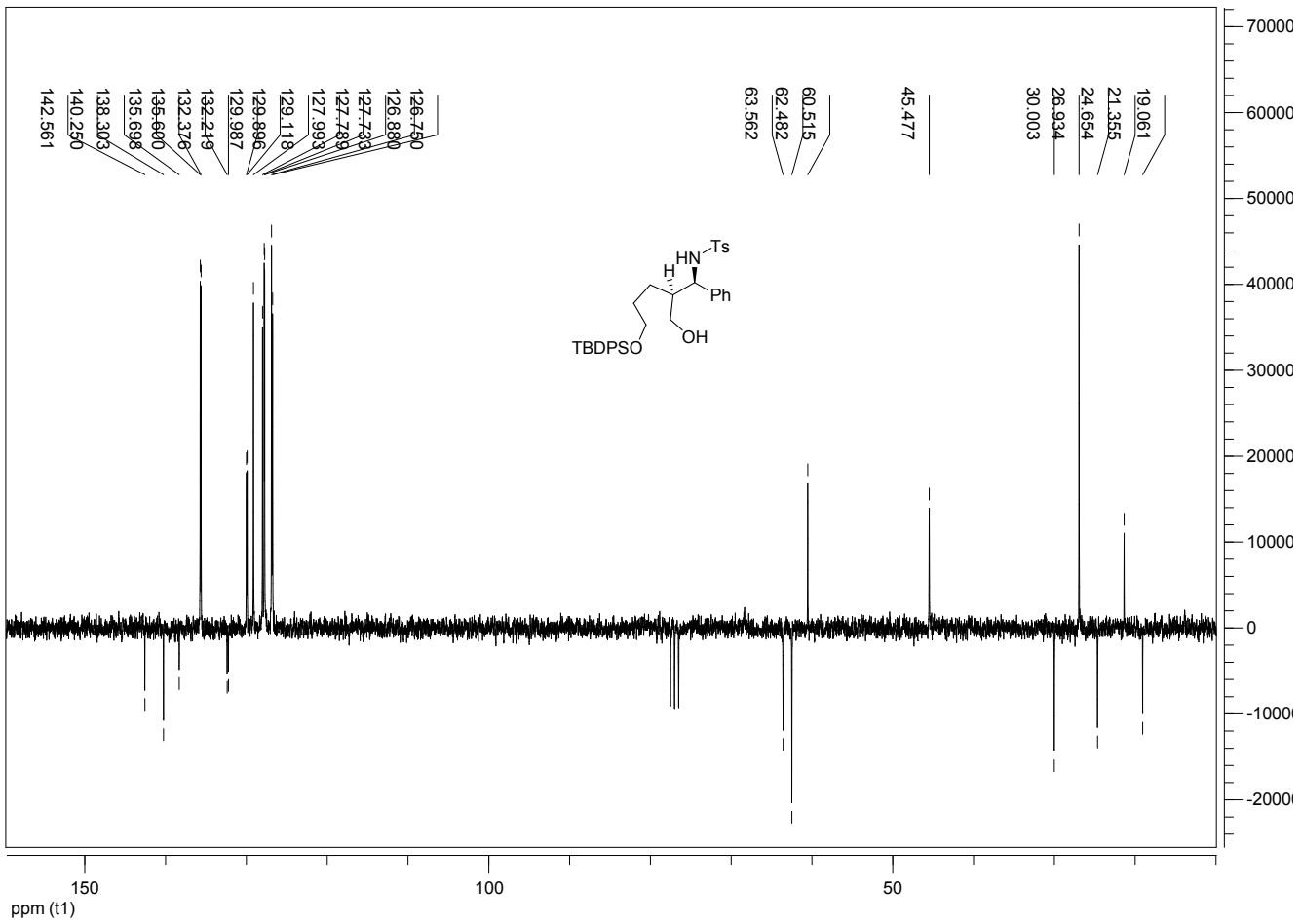
***N*-[(*R*)-[(*R*)-Cyclopent-2-en-1-yl](phenyl)methyl]-4-methylbenzenesulfonamide**



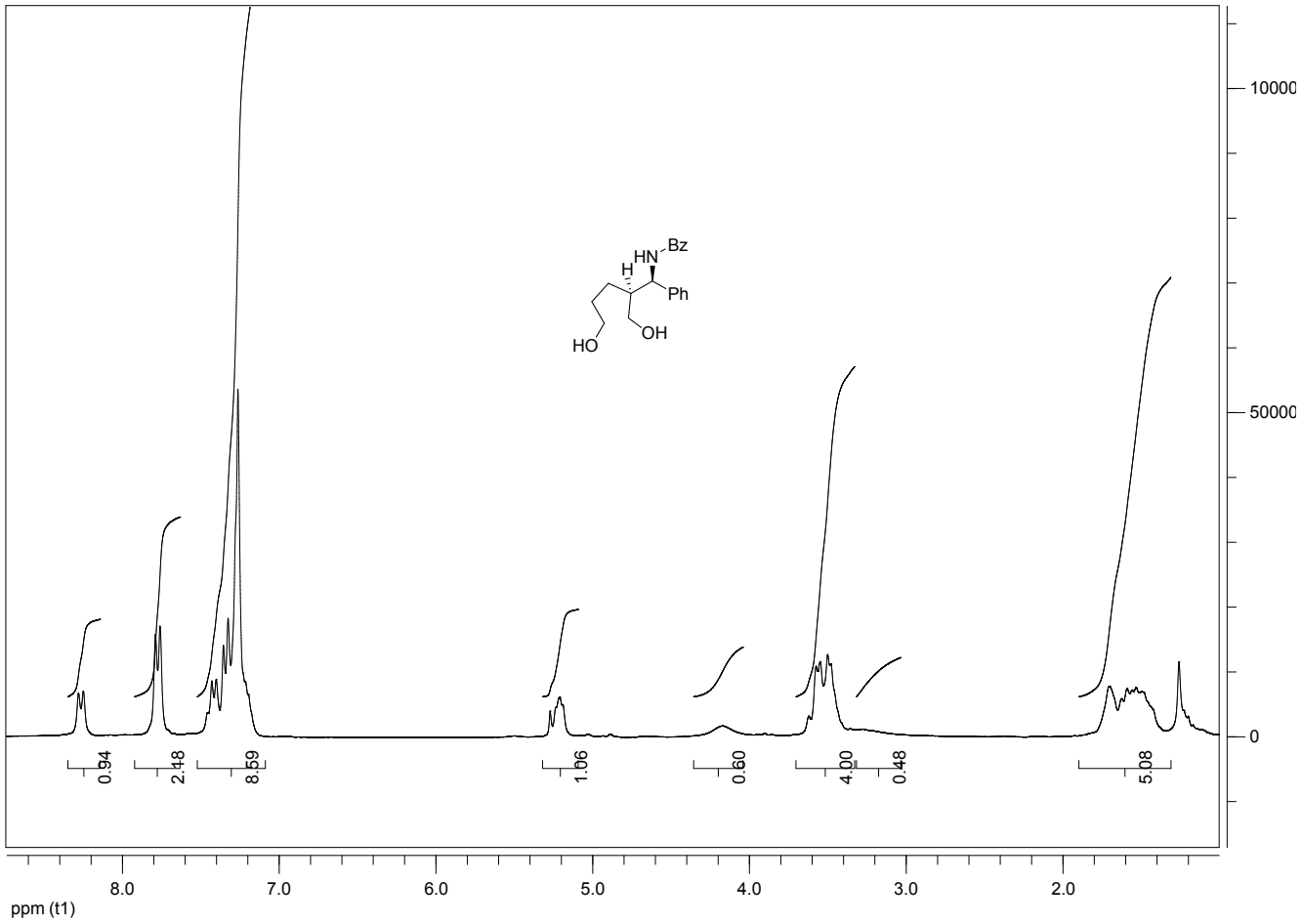


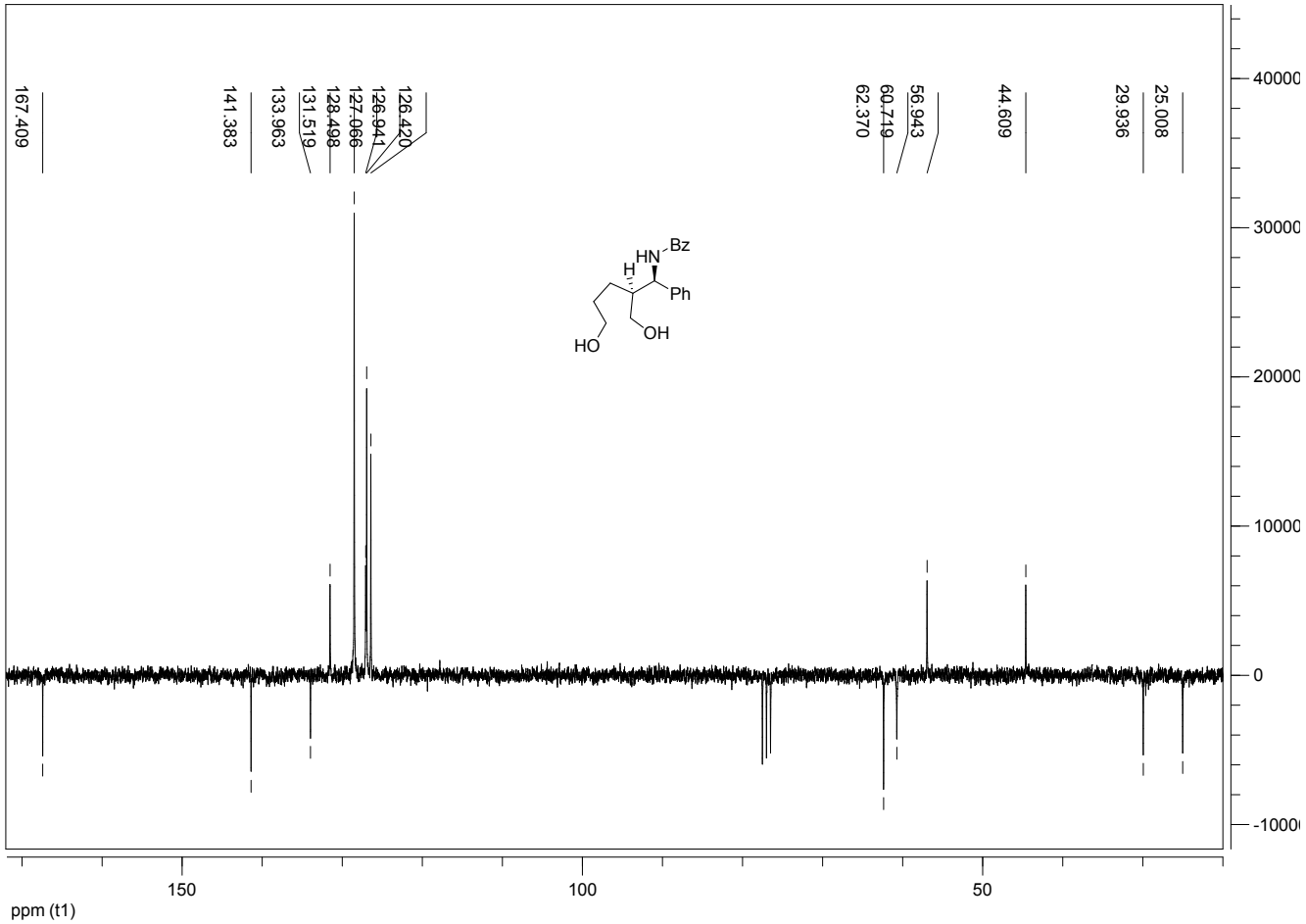
***N*-[(1*R*,2*S*)-5-(*Tert*-Butyldiphenylsilyloxy)-2-(hydroxymethyl)-1-phenylpentyl]-4-methylbenzenesulfonamide**



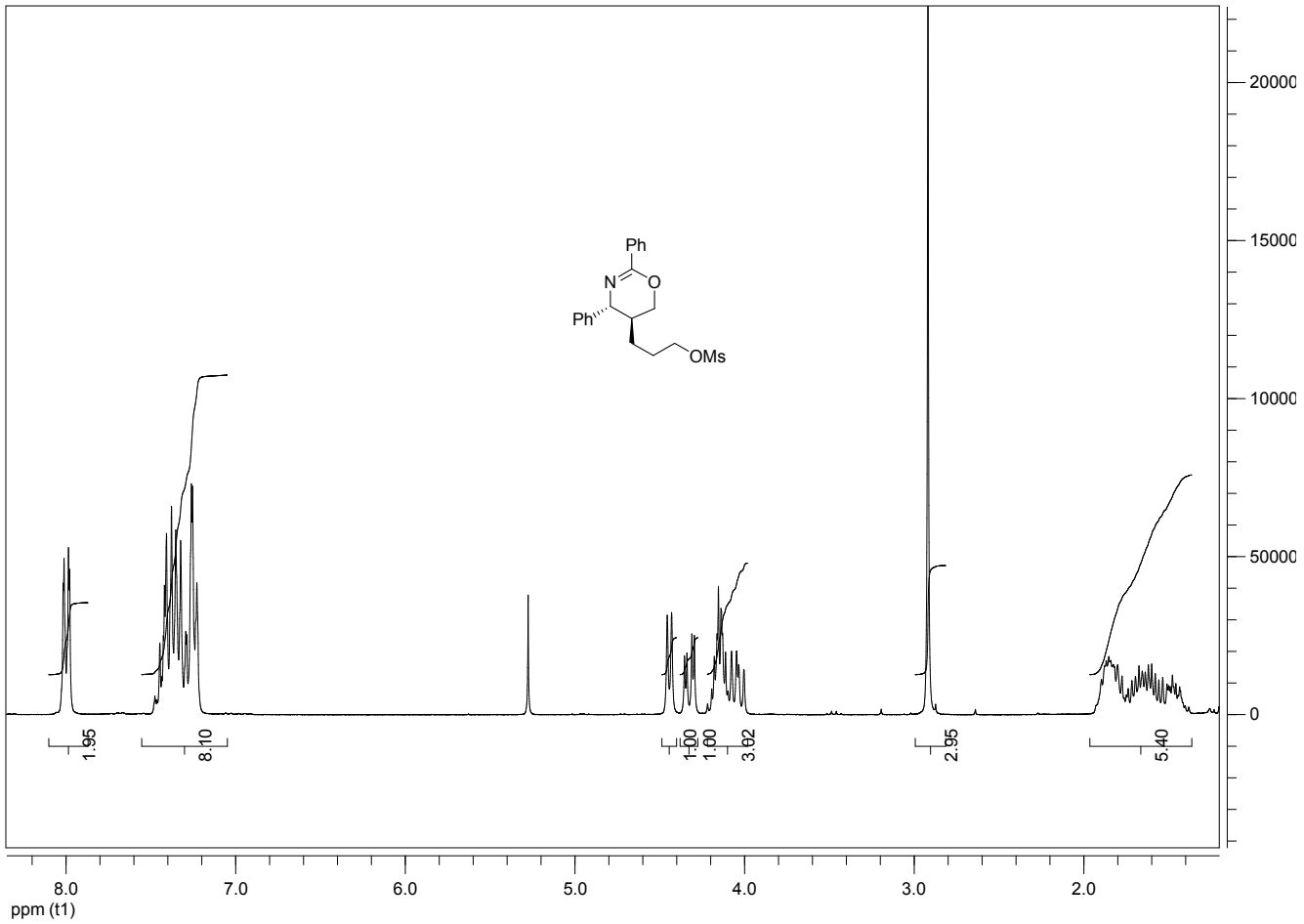


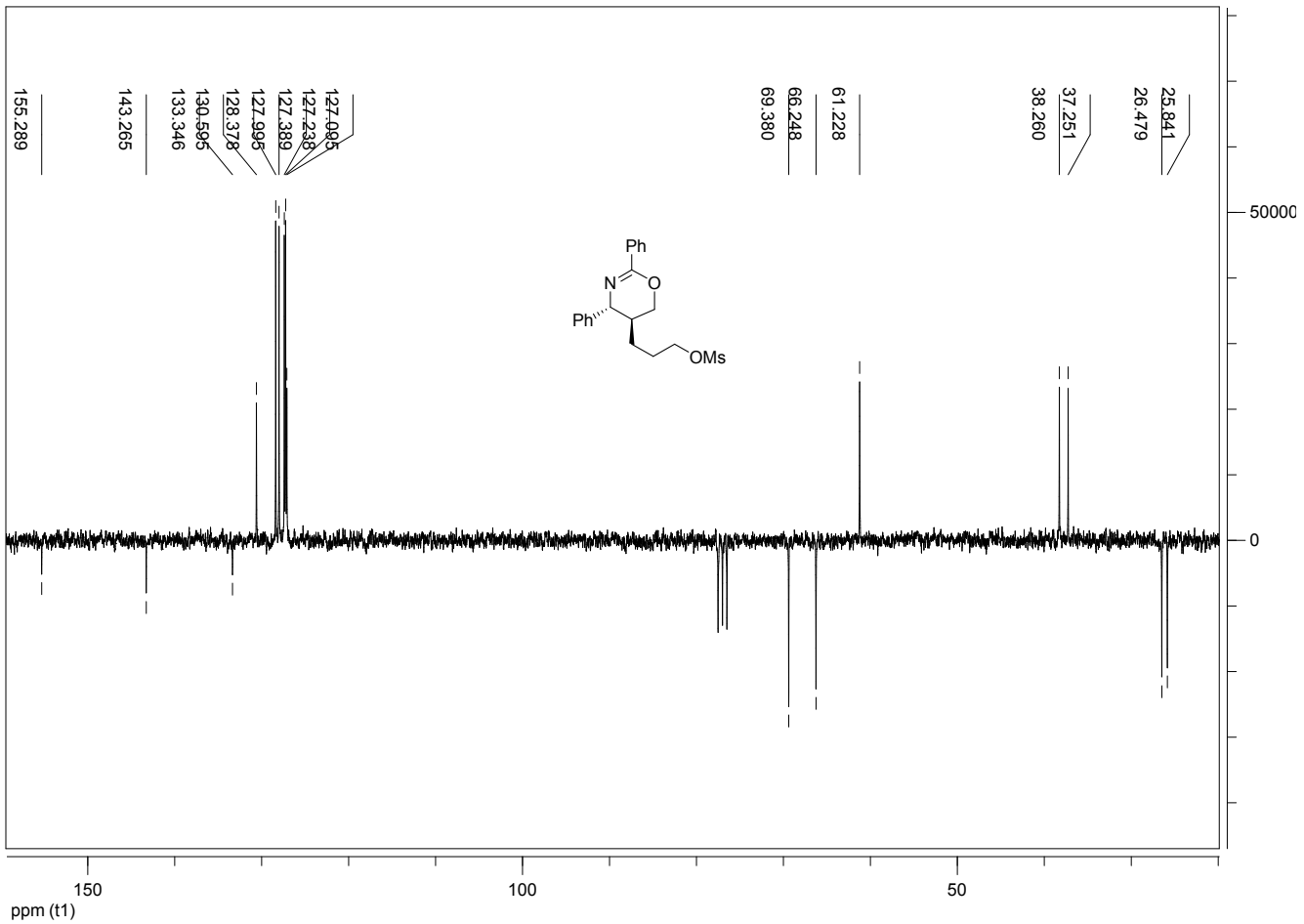
***N*-[(1*R*,2*S*)-5-Hydroxy-2-(hydroxymethyl)-1-phenylpentyl]benzamide**



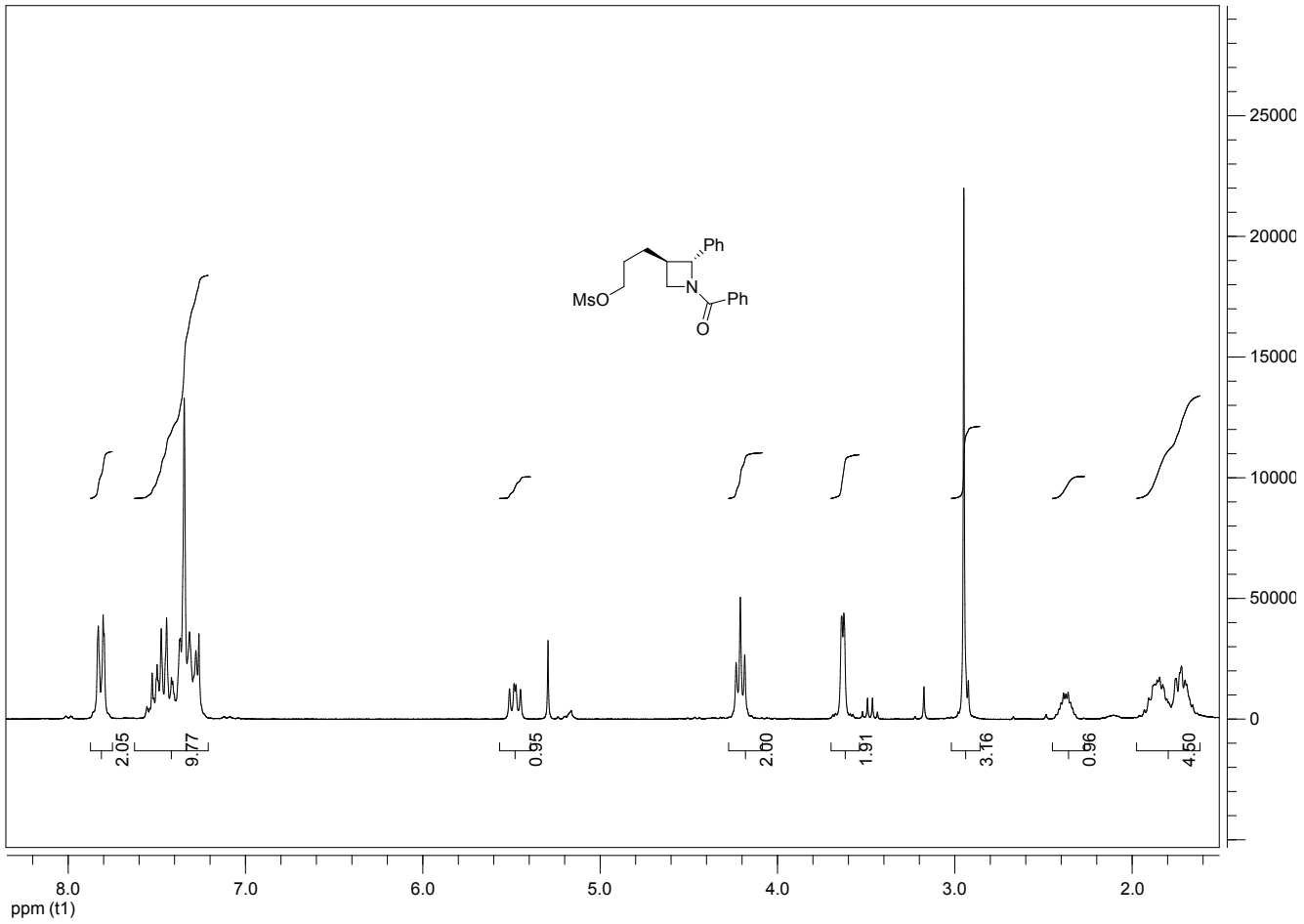


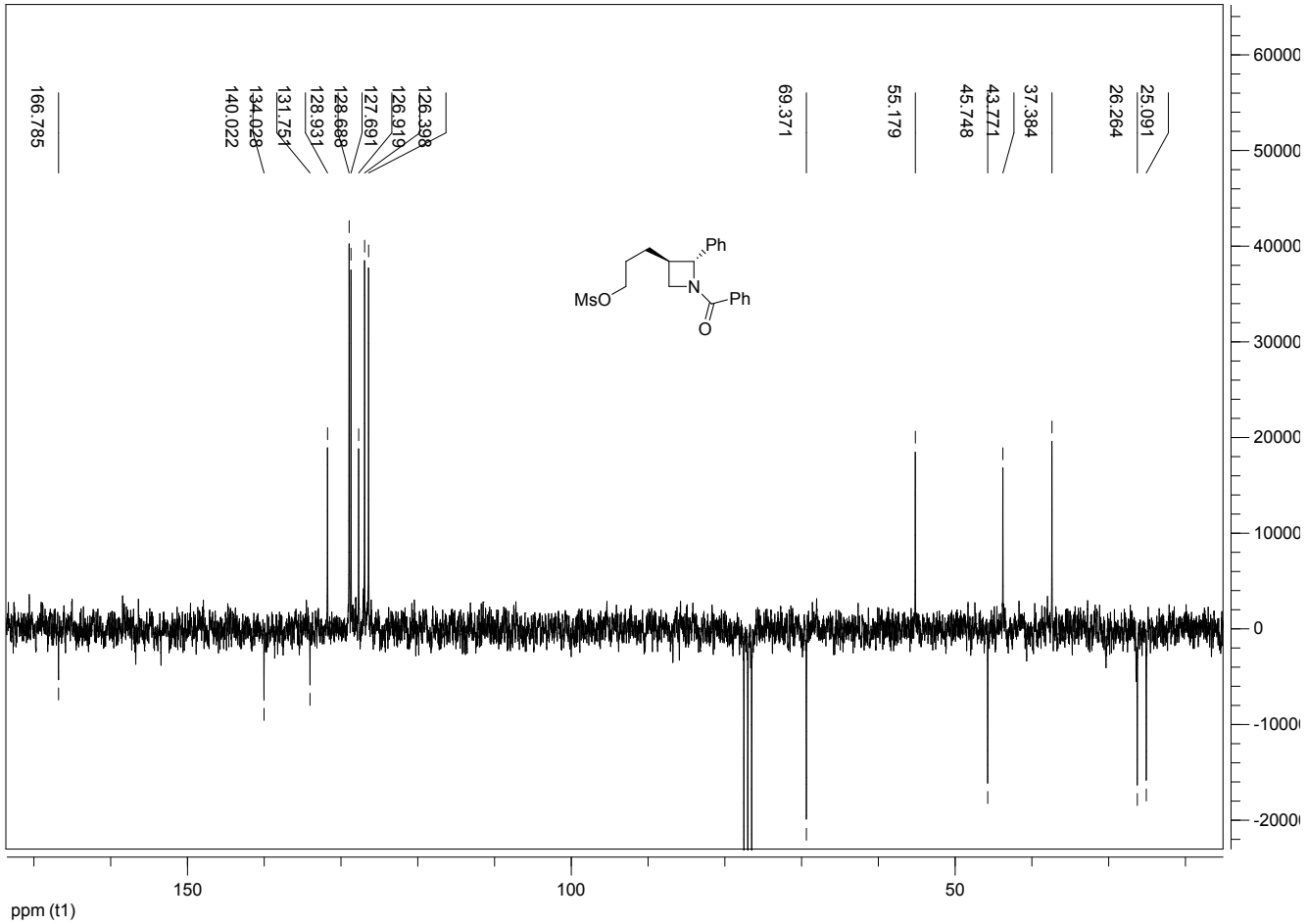
3-[(4*R*,5*S*)-2,4-Diphenyl-5,6-dihydro-4*H*-1,3-oxazin-5-yl]propyl methanesulfonate 9



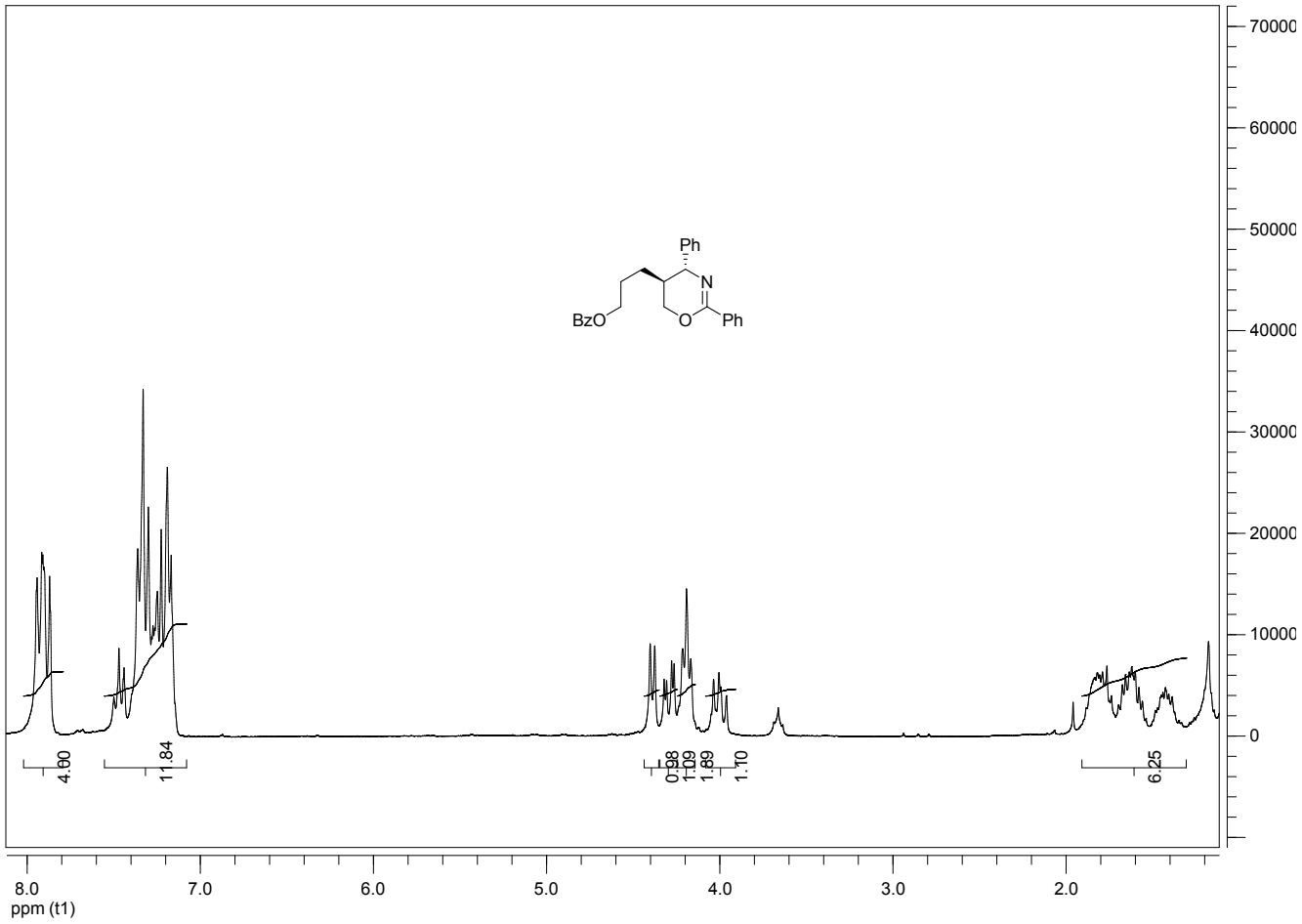


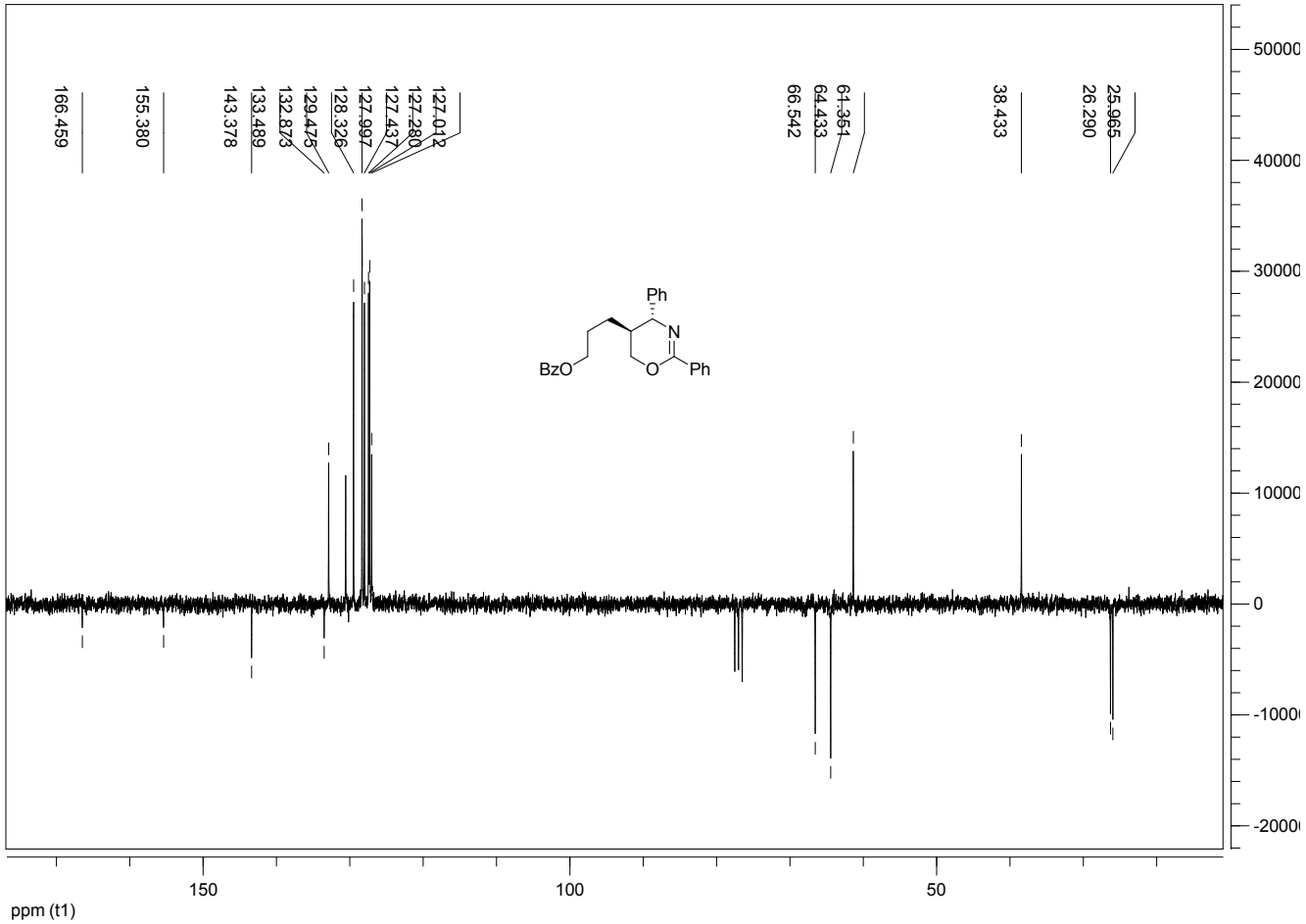
3-[(2*R*,3*R*)-1-Benzoyl-2-phenylazetidin-3-yl]propylmethanesulfonate



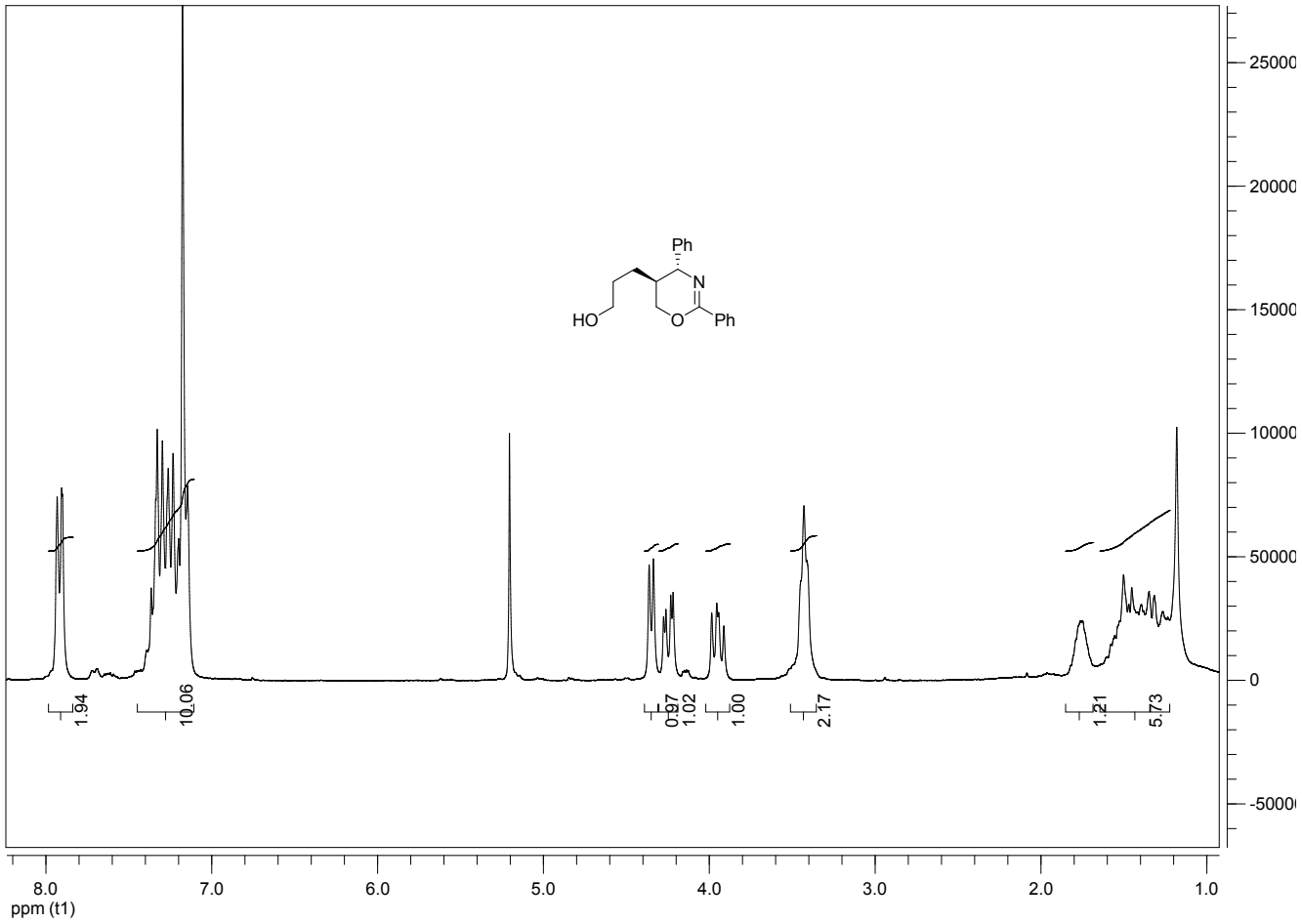


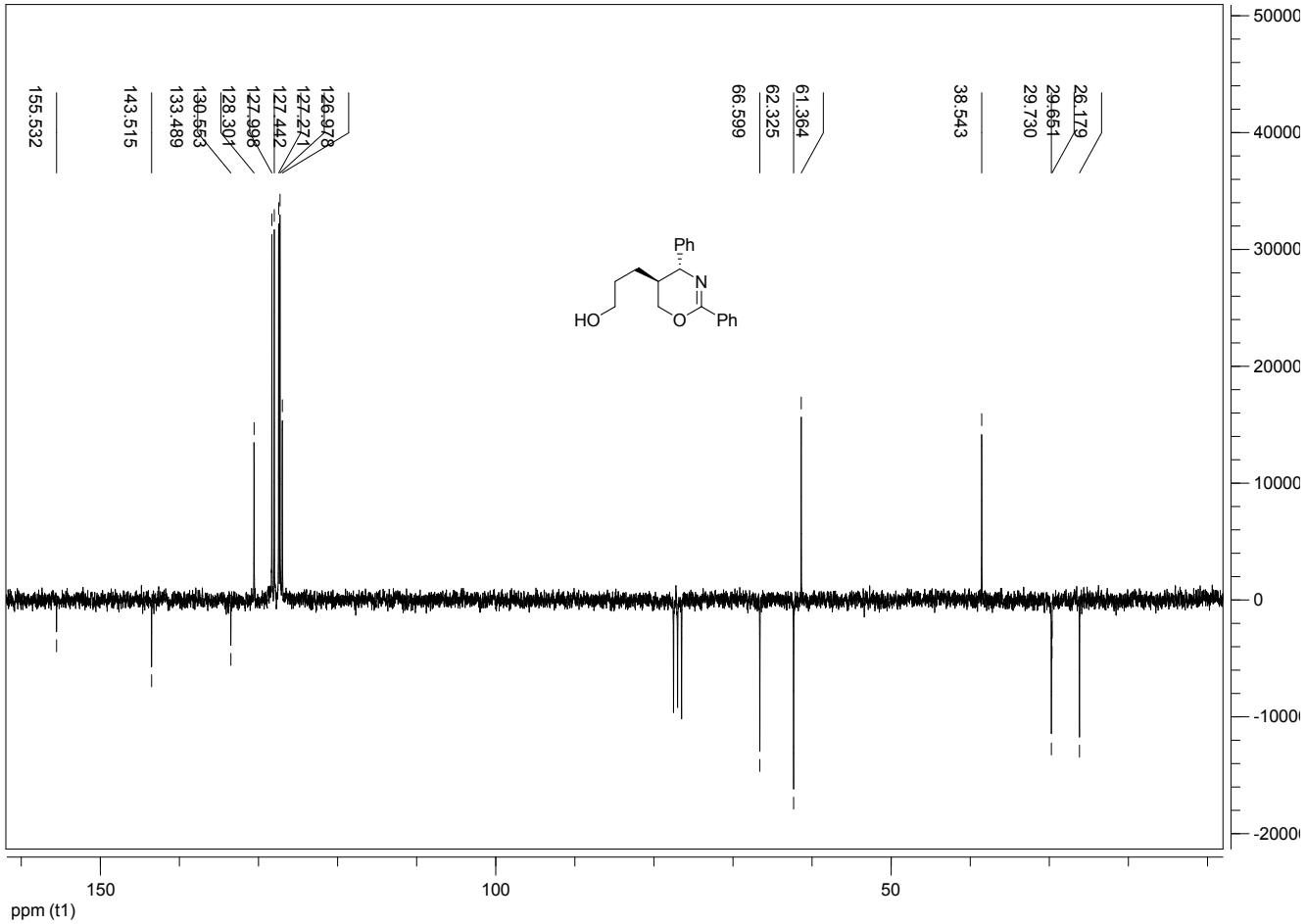
3-[(4*R*,5*S*)-2,4-Diphenyl-5,6-dihydro-4*H*-1,3-oxazin-5-yl]propyl benzoate



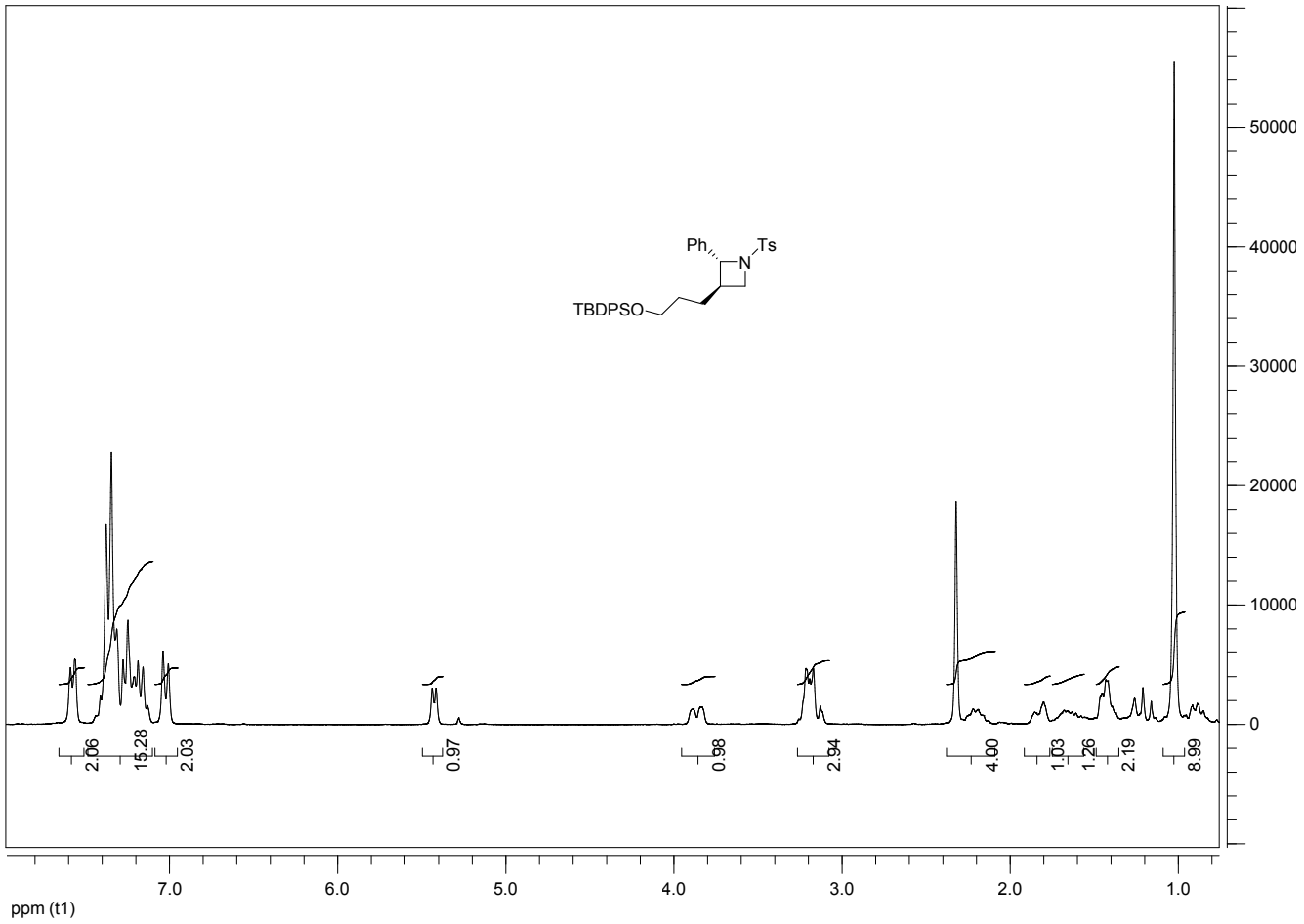


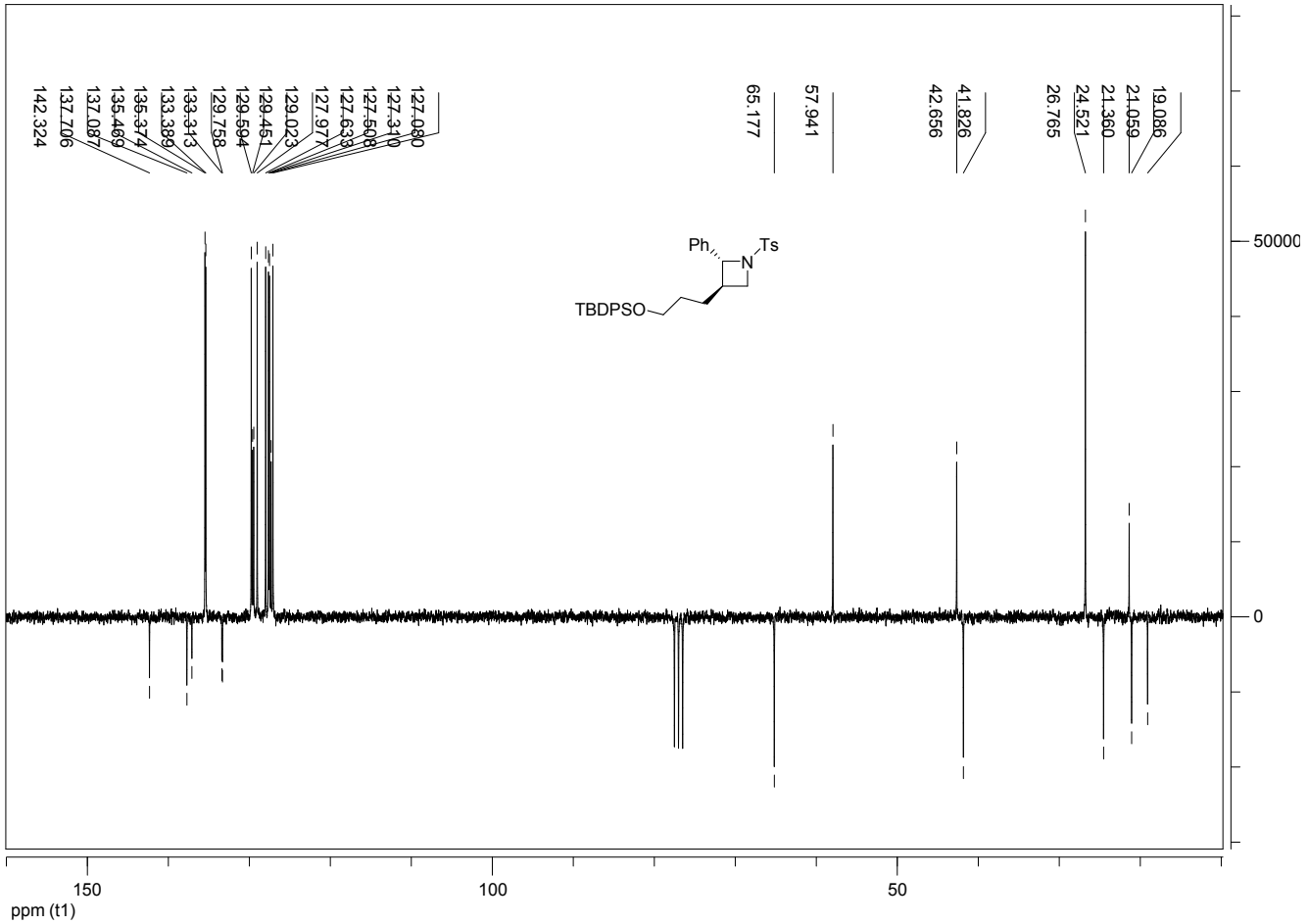
3-[(4*R*,5*S*)-2,4-Diphenyl-5,6-dihydro-4*H*-1,3-oxazin-5-yl]propan-1-ol





(2*R*,3*R*)-3-(3-(*Tert*-Butyldiphenylsilyloxy)propyl)-2-phenyl-1-tosylazetidine 10





[(2*R*,3*S*)-2-Phenylpiperidin-3-yl]methyl benzoate 11