**Supporting Information**

# Direct Asymmetric Bromination of Aldehydes Catalyzed by a Binaphthyl-based Secondary Amine: Highly Enantio- and Diastereoselective One-pot Synthesis of Bromohydrins

Taichi Kano, Fumitaka Shirozu, and Keiji Maruoka*

*Department of Chemistry, Graduate School of Science, Kyoto University*
*Sakyo, Kyoto 606-8502, Japan*

**General Information.** Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. $^{1}$H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, ddd= double double doublet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. $^{13}$C NMR spectra were measured on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 20A instruments using Daicel Chiralpak AD-H, AS-H and Chiralcel OD-H, OB-H, OJ-H 4.6mm x 25 cm columns. High-resolution mass spectra (HRMS) were performed on Brucker microTOF. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 $GF_{254}$, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck, 230-400 mesh) without another announce. Neutral silica gel was purchased from Kanto Chemical Co. Inc. For purification with preparative thin layer chromatography (PLC), Merck precoated PLC plates (silica gel 60 $GF_{254}$, 0.5 mm) were used.

Dichloromethane, toluene, and hexane were purchased from Kanto Chemical Co. Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Diethyl ether, and tetrahydrofuran were purchased from Kanto Chemical Co. Inc. as "Dehydrated". Commercially available aldehydes were distilled and stored under argon atmosphere at –17 °C. Commercially available brominating agents and alkylating agents were purchased and used without further purification. Binaphthyl-based amines, rac-**1**,[1] (*S*)-**2**,[2] cyclohexylacetaldehyde,[3] and brominating agents **4f**[4] and **4g**[5] were synthesized according to literature procedures and used after

purification by column chromatography or recrystalization. The $^{1}$H-NMR and $^{13}$C-NMR spectra of known bromohydrines are in agreement with literature values.[6,7]

**Synthesis and characterization of chiral amino alcohol trimethylsilyl ether (*S*)-3:** To a suspension of sodium hydride (60% w/w in oil, 104 mg, 2.6 mmol) in tetrahydrofuran (4 mL) was added amino alcohol (*S*)-**2** (215 mg, 0.33 mmol) at 0 °C under Ar. The mixture was stirred for 3 h at 50 °C. Trimethylsilyl chloride (340 μL, 2.7 mmol) was added to the mixture at 50 °C. After 1 h of stirring at 50 °C, the mixture was diluted with ether at 0 °C, then saturated $NH_4Cl$ was added carefully. The resulting mixture was extracted with ether. The organic layer was washed with brine, dried over $Na_2SO_4$, and then concentrated. The resulting residue was purified by flash column chromatography on neutral silica gel (eluting with hexane/ethyl acetate = 20/1) to give the title compound as a white solid [91% yield (240 mg)]. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.88 (2H, s, Ar-H), 7.76 (2H, d, *J* = 8.0 Hz, Ar-H), 7.42-7.15 (24H, m, Ar-H), 7.10 (2H, d, *J* = 8.5 Hz, Ar-H) 4.00 (2H, d, *J* = 12.8 Hz, -CHH-), 2.82 (2H, d, *J* = 12.8 Hz, -CHH-), –0.11 (18H, s, SiCH$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.5, 142.3, 137.6, 135.2, 131.2 131.1, 129.5, 128.7, 128.6, 128.3, 127.7, 127.6, 127.1, 127.0, 126.8, 125.7, 125.1, 86.2, 45.0, 2.2; IR (neat) 2359, 1491, 1447, 1252, 1105, 1072, 1029, 907, 880, 839, 752, 702 cm$^{-1}$; HRMS (ESI-TOF) Calcd. for $C_{54}H_{54}NO_2Si_2$: 804.3688 ($[M + H]^+$), Found: 804.3682 ($[M + H]^+$).

**Typical procedure for the organocatalytic α-bromination of aldehydes.**

A mixture of (*S*)-**3** (8.0 mg, 0.010 mmol) and 3-phenylpropanal (13 μL, 0.10 mmol) in dichloromethane (2.0 mL) was stirred at –20 °C. To the mixture was then added 4,4-dibromo-2,6-di-*tert*-butylcyclohexa-2,5-dienone **4f** (36.4 mg, 0.10 mmol). After stirring for 24 h at –20 °C, MeOH (1.0 mL) and sodium borohydride (30 mg) were added successively. After 30 min of vigorous stirring at room temperature, saturated $NH_4Cl$ (2.0 mL) was added. The resulting mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $Na_2SO_4$ and then concentrated. The resulting residue was purified by preparative thin layer chromatography (eluting with hexane/ethyl acetate = 3/1) to give 2-bromo-3-phenylpropanol as a pale yellow oil [94% yield (20.2 mg)].

**(*R*)-2-Bromo-3-phenylpropanol**[6a] (Table 2, entry 3): $[\alpha]_D^{18}$ 21.4 (*c* = 1.1, $CHCl_3$; 97% ee); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (5H, m, Ar-H), 4.33 (1H, m, -CHBr-), 3.83 (1H, m, HOCHH-), 3.75 (1H, m, HOCHH-), 3.27 (1H, dd, *J* = 14.4, 7.6 Hz, PhCHH-), 3.18 (1H, dd, *J* = 14.4, 7.6 Hz, PhCHH-), 2.01 (1H, t, *J* = 6.8 Hz -OH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.7, 129.2, 128.6, 127.0, 66.0, 58.7, 41.4; IR (neat) 3410, 2924, 2359, 1495, 1454, 1076, 1041, 748, 700 cm$^{-1}$; HPLC analysis: Daicel Chiralcel OD-H, hexane/*i*-PrOH = 40/1, flow rate = 1.0 mL/min, λ = 208 nm,

retention time; $t_R$(minor) = 22.2 min, $t_R$(major) = 24.3 min.

**(*R*)-2-Bromohexanol**[6b] (Table 2, entry 1): [80% yield (14.4 mg)] $[\alpha]_D^{17}$ 58.3 (*c* = 1.34, $CHCl_3$; 93% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 4.34 (1H, m, -C<u>H</u>Br-), 3.82 (1H, m, HOC<u>H</u>H-), 3.74 (1H, m, HOCH<u>H</u>-), 1.99 (1H, dd, *J* = 8.0, 5.6 Hz, -O<u>H</u>) 1.90-1.80 (2H, m, -CHBrC<u>H</u>$_2$-), 1.47-1.29 (4H, m, -C<u>H</u>$_2$-), 0.92 (3H, t, *J* = 7.4, -C<u>H</u>$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 67.3, 60.2, 34.6, 29.6, 22.1, 13.9; IR (neat) 3354, 2957, 2930, 2870, 1462, 1381, 1252, 1175, 1109, 1072, 1059, 1041, 1016, 881, 839, 752, 702 cm$^{-1}$; HPLC analysis: Daicel Chiralcel OB-H, hexane/*i*-PrOH = 200/1, flow rate = 0.5 mL/min, λ = 204 nm, retention time; $t_R$(minor) = 19.4 min, $t_R$(major) = 20.3 min.

**(*R*)-2-Bromooctanol**[6c] (Table 2, entry 2): [92% yield (19.2 mg)]. $[\alpha]_D^{19}$ 48.6 (*c* = 1.59, $CHCl_3$; 92% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 4.15 (1H, app dd, *J* = 7.0, 4.2 Hz, -C<u>H</u>Br-), 3.82 (1H, m, HOC<u>H</u>H-), 3.74 (1H, m, HOCH<u>H</u>-), 2.00 (1H, dd, *J* = 7.8, 5.8 Hz, -O<u>H</u>), 1.85 (2H, m, -C<u>H</u>$_2$-), 1.38-1.22 (8H, m, -C<u>H</u>$_2$-), 0.89 (3H, t, *J* = 6.8 Hz, -C<u>H</u>$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 67.3, 60.2, 34.9, 31.6, 28.6, 27.4, 22.5, 14.0; IR (neat) 3410, 2955, 2928, 2857, 1716, 1460, 1275, 1057, 1026, 912, 746 cm$^{-1}$; HPLC analysis: Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 1000/1, flow rate = 0.5 mL/min, λ = 203 nm, retention time; $t_R$(minor) = 26.8 min, $t_R$(major) = 28.3 min.

**(*R*)-2-Bromo-3-cyclohexylpropanol** (Table 2, entry 4): [82% yield (18.2 mg)]. $[\alpha]_D^{22}$ 28.7 (*c* = 1.14, $CHCl_3$; 96% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 4.26 (1H, m, -C<u>H</u>Br-), 3.81 (1H, m, HOC<u>H</u>H-), 3.75 (1H, m, HOCH<u>H</u>-), 2.01 (1H, m, -O<u>H</u>), 1.94-1.50 (8H, m, -C<u>H</u>$_2$-), 1.34-1.08 (3H, m, -C<u>H</u>$_2$-), 0.98 (1H, m, -C<u>H</u>$_2$-), 0.84 (1H, m, -C<u>H</u>$_2$-); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 67.7, 58.1, 42.2, 35.4, 33.6, 32.0, 26.4, 26.1, 25.9; IR (neat) 3370, 2920, 2851, 1449, 1277, 1074, 1040, 1016 cm$^{-1}$. The enantiomeric excess was determined by HPLC after conversion to the corresponding benzoate ester.

**(*S*)-3-Benzyloxy-2-bromopropanol**[6d] (Table 2, entry 5): [92% yield (23.5 mg)]. $[\alpha]_D^{23}$ –2.94 (*c* = 1.14, $CHCl_3$; 99% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (5H, m, Ar-<u>H</u>), 4.58 (2H, s, -OC<u>H</u>$_2$Ph), 4.22 (1H, m, -C<u>H</u>Br-), 3.92 (2H, m, -C<u>H</u>$_2$O-), 3.83 (1H, dd, *J* = 10.6, 5.4 Hz, -C<u>H</u>HO-), 3.79 (1H, dd, J = 10.4, 7.2 Hz, -CH<u>H</u>O-), 2.18 (1H, t, *J* = 6.8 Hz, -O<u>H</u>); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.5, 128.0, 127.7, 73.5, 71.7, 65.1, 52.6; IR (neat) 3397, 2866, 1495, 1452, 1364, 1261, 1096, 1074, 1028, 910, 741, 698, 650 cm$^{-1}$; HPLC analysis: Daicel Chiralpak AS-H, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min, λ = 208 nm, retention time; $t_R$(major) = 41.7 min, $t_R$(minor) = 44.2 min.

**(*R*)-2-Bromo-3-methylbutanol**[6c] (Table 2, entry 6): [71% yield (11.8 mg)]. $[\alpha]_D^{21}$ 3.33 (*c* = 0.56, $CHCl_3$; 96% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 4.11 (1H, app q, *J* = 5.6 Hz, -C<u>H</u>Br-), 3.83 (2H, app

t, $J$ = 6.6 Hz, HOC<u>H</u>$_2$-), 2.02 (1H, m, -C<u>H</u>($CH_3$)$_2$), 1.93 (1H, t, $J$ = 6.8 Hz, -O<u>H</u>), 1.05 (3H, d, $J$ = 6.8 Hz, -C<u>H</u>$_3$), 1.03 (3H, d, $J$ = 6.8 Hz, -C<u>H</u>$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 68.3, 65.8, 31.5, 20.8, 19.1; IR (neat) 3358, 2963, 2853, 2363, 1464, 1323, 1254, 1067, 10263 cm$^{-1}$. The enantiomeric excess was determined by HPLC after conversion to the corresponding benzoate ester.

**(*R*)-2-Bromo-2-cyclohexylethanol**[6c] (Table 2, entry 7): [73% yield (15.2 mg)]. $[\alpha]_D^{23}$ 30.9 ($c$ = 0.35, $CHCl_3$; 99% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 4.08 (1H, app q, $J$ = 5.7 Hz, -C<u>H</u>Br-), 3.85 (2H, app t, $J$ = 6.2 Hz, HOC<u>H</u>$_2$-), 1.98 (1H, t, $J$ = 6.8 Hz, -O<u>H</u>), 1.88 (1H, app d, $J$ = 13.6 Hz, -C<u>H</u>-), 1.82-1.62 (5H, m, -C<u>H</u>$_2$-), 1.36-1.08 (5H, m, -C<u>H</u>$_2$-); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 67.5, 65.3, 41.4, 30.9, 30.3, 26.1, 26.0, 25.9; IR (neat) 3356, 2926, 2853, 1449, 1369, 1302, 1240, 1171, 1069, 1015, 957, 891, 878, 785, 660, 627 cm$^{-1}$. The enantiomeric excess was determined by HPLC after conversion to the corresponding benzoate ester. The absolute configuration was determined to be *R* by comparing the sign of optical rotation with literature data, (*S*)-2-bromo-2-cyclohexyletheanol: $[\alpha]_D^{27}$ –20.1 ($c$ = 0.80, $CHCl_3$; 73% ee).[6c]

**Typical procedure for benzoylation of bromohydrins.**

To a solution of 2-bromo-3-cyclohexylpropanol (18.2 mg, 0.082 mmol) and triethylamine (35 μL, 0.25 mmol) in $CH_2Cl_2$ (1.0 mL) was added benzoyl chloride (29 μL, 0.25 mmol) at 0 °C. After stirring for 3 h at room temperature, saturated $NH_4Cl$ (2.0 mL) was added. The resulting mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $Na_2SO_4$ and then concentrated. The resulting residue was purified by preparative thin layer chromatography (eluting with hexane/ethyl acetate = 9/1) to give 2-bromo-3-cyclohexylpropyl benzoate as a pale yellow oil [61% yield (16.4 mg)].

**(*R*)-2-Bromo-3-cyclohexylpropyl benzoate**: $[\alpha]_D^{23}$ 21.9 ($c$ = 1.13, $CHCl_3$; 96% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 (2H, app dd, Ar-<u>H</u>), 7.58 (1H, app tt, $J$ = 7.6, 1.2 Hz, Ar-<u>H</u>), 7.46 (2H, app t, $J$ = 7.6 Hz, Ar-<u>H</u>), 4.54 (2H, d, $J$ = 6.0 Hz, -$CO_2$C<u>H</u>$_2$-), 4.35 (1H, m, -C<u>H</u>Br-), 1.89-1.58 (8H, m, -C<u>H</u>$_2$-), 1.36-1.08 (3H, m, -C<u>H</u>$_2$-), 1.08-0.94 (1H, m, -C<u>H</u>H-), 0.92-0.79 (1H, m, -C<u>H</u>H-); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.2 129.7 (two peaks overlap), 128.5, 68.7 49.5, 42.9 35.4, 33.6, 32.0, 26.4, 26.1, 25.9; IR (neat) 2922, 2851, 1722, 1450, 1315, 1269, 1177, 1115, 1069, 1026, 710 cm$^{-1}$; HPLC analysis: Daicel Chiralcel OD-H, hexane/*i*-PrOH = 200/1, flow rate = 0.5 mL/min, λ = 208 nm, retention time; $t_R$(minor) = 14.6 min, $t_R$(major) = 16.7 min.

**(*R*)-2-Bromo-3-methylbutyl benzoate:** [62% yield (9.8 mg)]. $[\alpha]_D^{22}$ –13.1 ($c$ = 0.91, $CHCl_3$; 96% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08-8.04 (2H, m, Ar-<u>H</u>), 7.58 (1H, app tt, $J$ = 7.6, 1.2 Hz, Ar-<u>H</u>), 7.46 (2H, app t, $J$ = 7.6 Hz, Ar-<u>H</u>), 4.60 (2H, app d, $J$ = 6.6 Hz, -$CO_2$C<u>H</u>$_2$-), 4.28 (1H, m, -C<u>H</u>Br-),

2.09 (1H, m, -C<u>H</u>($CH_3$)$_2$), 1.10 (3H, d, *J* = 6.8 Hz, -C<u>H</u>$_3$), 1.06 (3H, d, *J* = 6.8 Hz, -C<u>H</u>$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.2 129.7 (two peaks overlap), 128.5, 66.7, 59.6, 31.2 20.9, 18.0; IR(neat) 2967, 2928, 2876, 1790, 1724, 1601, 1452, 1389, 1373, 1315, 1269, 1213, 1175, 1113, 1070, 1040, 955, 710 cm$^{-1}$; HPLC analysis Daicel Chiralcel OD-H, hexane/*i*-PrOH = 100/1, flow rate = 0.5 mL/min, λ = 208 nm, retention time; $t_R$(minor) = 12.4 min, $t_R$(major) = 14.2 min.

**(*R*)-2-Bromo-2-cyclohexylethyl benzoate**: [75% yield (4.5 mg)]. $[\alpha]_D^{23}$ –10.3 (*c* = 0.10, $CHCl_3$; 99% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 (2H, dd, *J* = 8.4, 1.6 Hz, Ar-<u>H</u>), 7.58 (1H, app tt, *J* = 7.6, 1.8 Hz, Ar-<u>H</u>), 7.46 (2H, app t, *J* = 7.6 Hz, Ar-<u>H</u>), 4.64 (1H, dd, *J* = 12.2, 5.8 Hz, -$CO_2$C<u>H</u>H-), 4.58 (1H, dd, *J* = 12.2, 7.0 Hz, -$CO_2$CH<u>H</u>-), 4.22 (1H, m, -C<u>H</u>Br-), 1.90 (1H, app d, *J* = 10.0 Hz, -C<u>H</u>-), 1.83-1.65 (5H, m, -C<u>H</u>$_2$-), 1.36-1.22 (5H, m, -C<u>H</u>$_2$-); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.2, 129.8, 129.7, 128.4, 66.5, 58.5, 41.4, 30.9, 29.2, 26.11, 26.07, 25.9; IR (neat) 2928, 2855, 2357, 2328, 1722, 1602, 1450, 1315, 1271, 1177, 1115, 1069, 1026, 712 cm$^{-1}$; HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 200/1, flow rate = 0.5 mL/min, λ = 228 nm, retention time; $t_R$(major) = 18.3 min, $t_R$(minor) = 23.0 min.

**Typical procedure for one-pot alkylation with Grignard reagents.**

A mixture of (*S*)-**3** (8.0 mg, 0.010 mmol) and 3-phenylpropanal (13 μL, 0.10 mmol) in dichloromethane (2.0 mL) was stirred at –20 °C. To the mixture was then added 4,4-dibromo-2,6-di-*tert*- butylcyclohexa-2,5-dienone (36.4 mg, 0.10 mmol). After stirring for 24 h at –20 °C, the reaction mixture was diluted with diethyl ether (2.0 mL) at –78 °C, and stirred for 30 min. A THF solution of Grignard reagent was added to the mixture at –78 °C slowly. After stirring for 2 h at –78 °C, methanol (1 mL) and saturated $NH_4Cl$ (1 mL) were added, and the mixture was stirred for 30 min at room temperature. The resulting mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $Na_2SO_4$, and then concentrated. The resulting residue was purified by preparative thin layer chromatography (eluting with hexane/ethyl acetate = 4/1) to give the 3-bromo-4-phenyl-2-butanol as a pale yellow oil [82% yield (18.7 mg)].

**(2*S*,3*R*)-3-Bromo-4-phenyl-2-butanol**[7a] (Table 3, entry 5, *anti* isomer): $[\alpha]_D^{19}$ 28.0 (*c* = 1.37, $CHCl_3$; 95% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.20 (5H, m, Ar-<u>H</u>), 4.39 (1H, m, -C<u>H</u>Br-), 3.86 (1H, m, -C<u>H</u>OH-), 3.21 (1H, dd, *J* = 15.0, 5.6 Hz, -C<u>H</u>HPh), 3.10 (1H, dd, *J* = 14.6, 9.4 Hz, -CH<u>H</u>Ph), 1.98 (1H, d, *J* = 7.6 Hz, -CHO<u>H</u>-), 1.35 (3H, d, *J* = 6.4 Hz -C<u>H</u>$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.1, 129.0, 128.5, 126.9, 69.8, 65.3, 40.5, 19.1; IR (neat) 3375, 2976, 1495, 1452, 1377, 1256, 1123, 1072, 1032, 959, 918, 748, 698 cm$^{-1}$; HPLC analysis: Daicel Chiralcel OD-H, hexane/*i*-PrOH = 40/1, flow rate = 0.5 mL/min, λ = 208 nm, retention time; $t_R$(minor) = 57.4 min, $t_R$(major) = 70.6 min.

**(1*S*,2*R*)-2-Bromo-1,3-diphenyl-1-propanol**[7b] (Table 3, entry 6, *anti* isomer): [83% yield (24.2 mg)]. $[\alpha]_D^{20}$ 19.3 (*c* = 1.09, $CHCl_3$; 99% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50-7.18 (8H, m, Ar-H), 7.15-7.09 (2H, m, Ar-H), 5.12 (1H, t, *J* = 3.8 Hz, -CHBr-), 4.50 (1H, m, -CHOH-), 3.17 (1H, dd, *J* = 15.2, 3.2 Hz, -CHHPh), 3.01 (1H, dd, *J* = 15.2, 11.2 Hz, -CHHPh), 2.56 (1H, d, *J* = 3.6 Hz, -CHOH-); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.8, 138.4, 129.1, 128.5, 128.3, 128.2, 126.7, 126.5, 63.2, 38.0, 25.4; IR (neat) 3420, 3061, 3028, 2922, 2851, 1603, 1495, 1452, 1391, 1325, 1260, 1225, 1184, 1030, 912, 748, 700 $cm^{-1}$; HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min, λ = 207 nm, retention time; $t_R$(major) = 38.1 min, $t_R$(minor) = 40.8 min.

**(1*S*,2*R*)-2-Bromo-3-methyl-1-phenylbutanol** (Table 3, entry 7, *anti* isomer): [73% yield (17.7 mg)]. $[\alpha]_D^{23}$ 31.6 (*c* = 0.92, $CHCl_3$; 99% ee); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44-7.29 (5H, m, Ar-H), 4.90 (1H, d, *J* = 8.0 Hz, -CHOH-), 4.26 (1H, dd, *J* = 8.0, 2.8 Hz-CHBr-), 2.17 (1H, m, -CH$(CH_3)_2$), 1.06 (3H, d, *J* = 6.4 Hz, -C$H_3$), 1.03 (3H, d, *J* = 6.4 Hz, -C$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.6, 128.5, 128.3, 126.9, 76.4, 69.6, 28.8, 22.5, 17.3; IR (neat) 3431, 3032, 2665, 2874, 2340, 1724, 1495, 1456, 1387, 1369, 1327, 1171, 1032, 1009, 912, 845, 812, 760, 702 $cm^{-1}$; HPLC analysis: Daicel Chiralpak AS-H, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min, λ = 207 nm, retention time; $t_R$(major) = 12.4 min, $t_R$(minor) = 13.6 min. The relative configuration was determined to be *anti* by comparing the $^1$H NMR spectroscopy with literature data after epoxidation.[7c]

**References**

1) T. Ooi, M. Kameda and K. Maruoka, *J. Am. Chem. Soc.*, 2003, **125**, 5139.

2) T. Kano, M. Ueda, J. Takai and K. Maruoka, *J. Am. Chem. Soc.*, 2006, **128**, 6046.

3) M. Stratakis, R. Nencka and C. Rabalakos, *J. Org. Chem*., 2002, **67**, 8758.

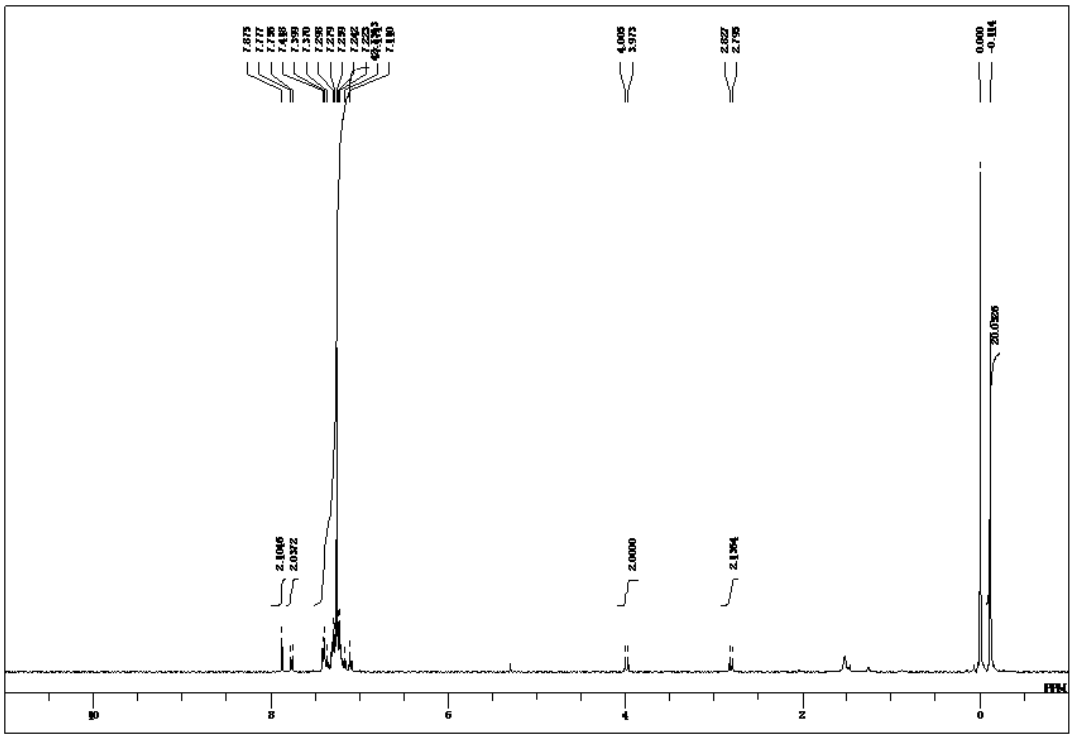
4) K. Omura, *J. Org. Chem*., 1996, **61**, 2006.

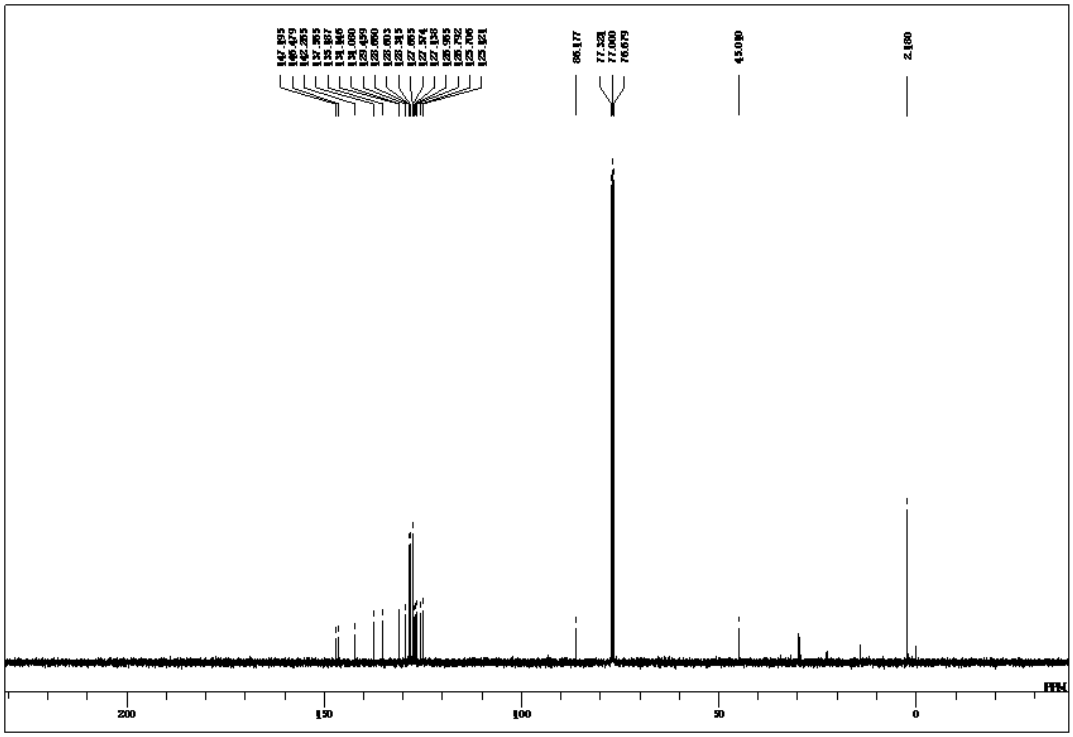
5) A. F. Hegarty and J. P. Keogh, *J. Chem. Soc*., *Perkin Trans. 2*, 2001, 758.

6) (*a*) L. C. Fardelone, J. Augusto, R. Rodrigues and P. J. S. Moran, *Journal of Molecular Catalysis B: Enzymatic*, 2004, **V29**(1-6), 41. (*b*) R. P. Mcgeary, *Tetrahedron Lett.*, 1998, **39**, 3319. (*c*) S. Bertelsen, N. Halland, S. Bachmann, M. Marigo, A. Braunton and K. A. Jørgensen, *Chem. Commun.*, 2005, 4821. (*d*) S. Takano, T. Sugihara, T. Kamikubo and K. Ogasawara, *Heterocycles*, 1991, **32**, 1587.

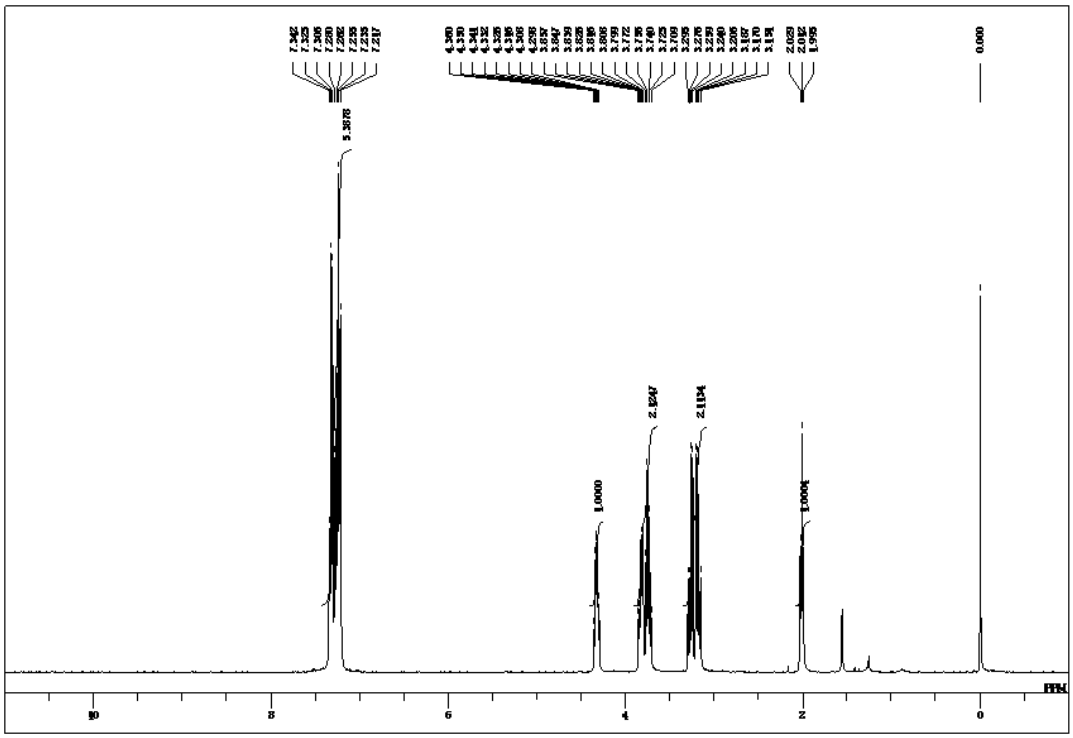
7) (*a*) P. Besse, M. F. Renard and H. Veschambre, *Tetrahedron: Asymmetry*, 1994, **5**, 1249. (*b*) V. Schulze and R. W. Hoffmann, *Chem. Eur. J.*, 1999, **5**, 337. (*c*) V. K. Aggarwal, H. Abdel-Rahman, L. Fan, R. V. H. Jones and M. C. H. Standen, *Chem. Eur. J.*, 1996, **2**, 1024.

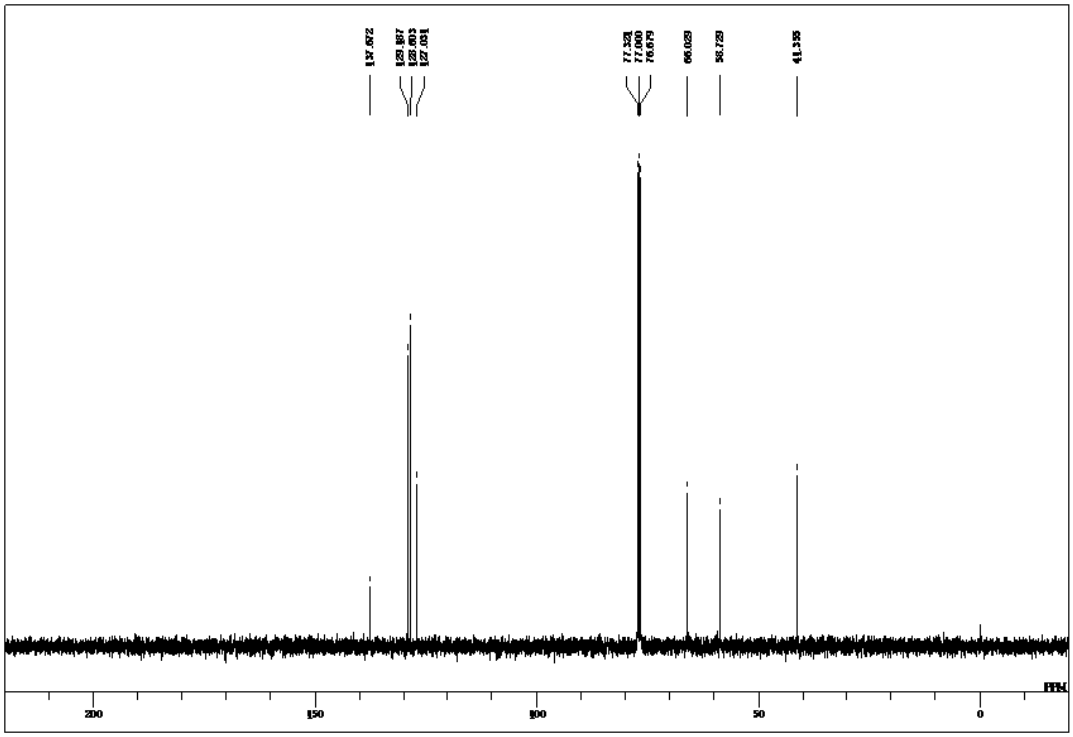
**Amino alcohol trimethylsilyl ether (*S*)-3**



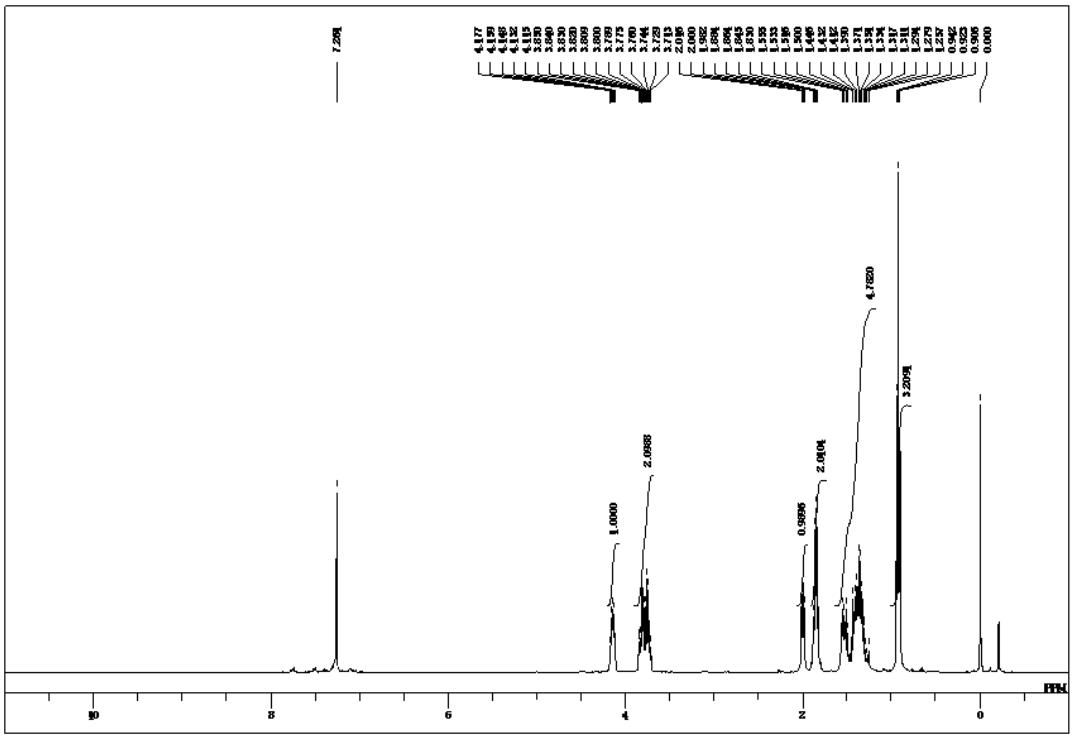


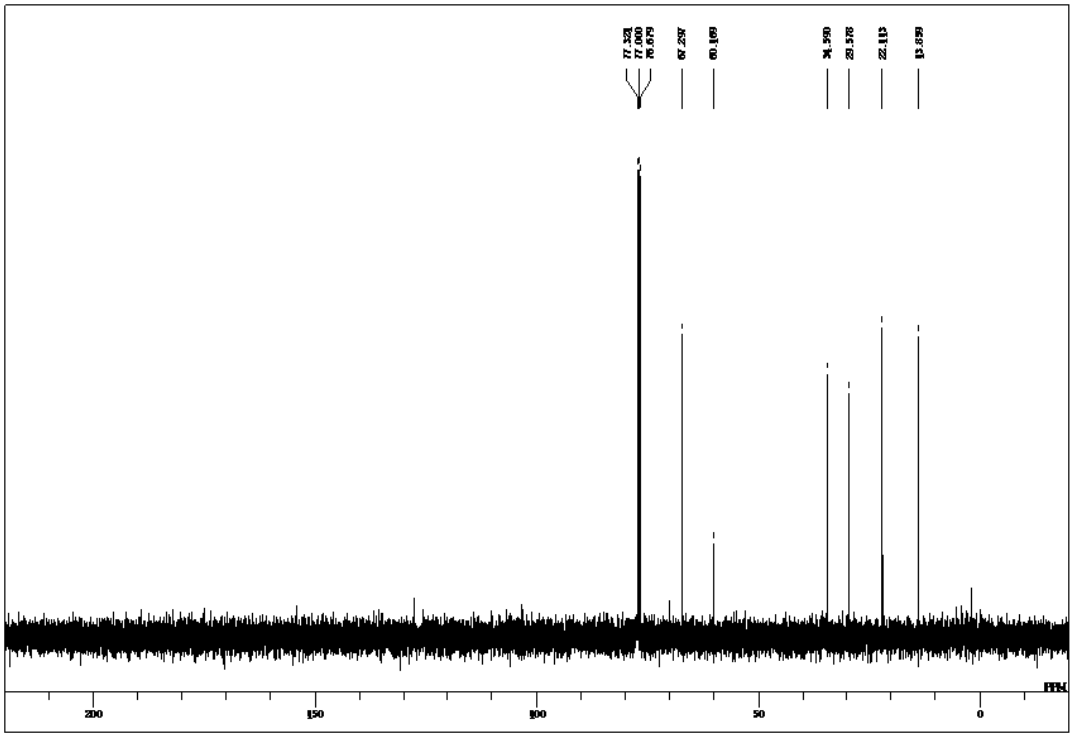
**(*R*)-2-Bromo-3-phenylpropanol** (Table 2, entry 3)



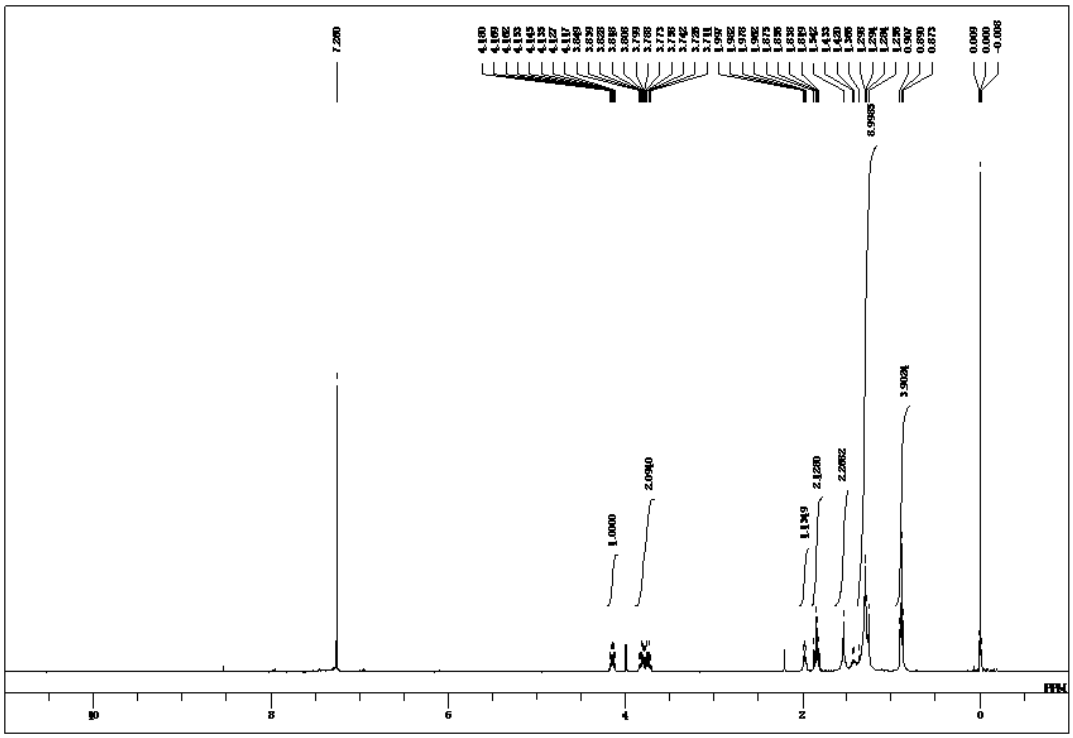


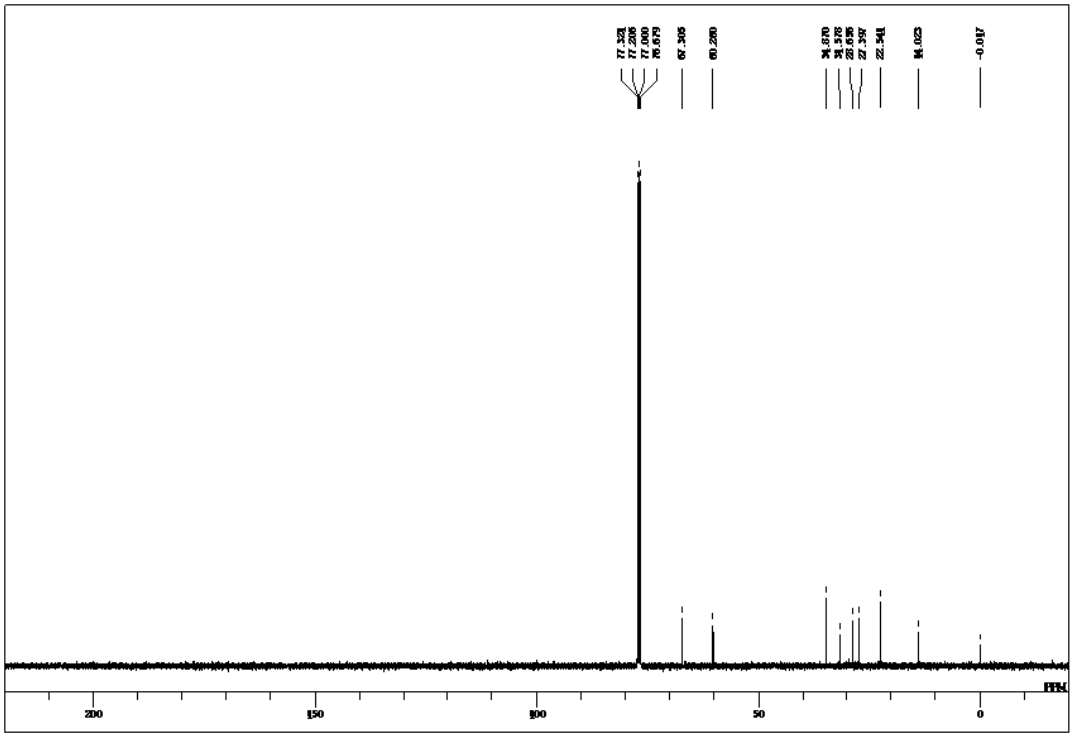
**(*R*)-2-Bromohexanol** (Table 2, entry 1)



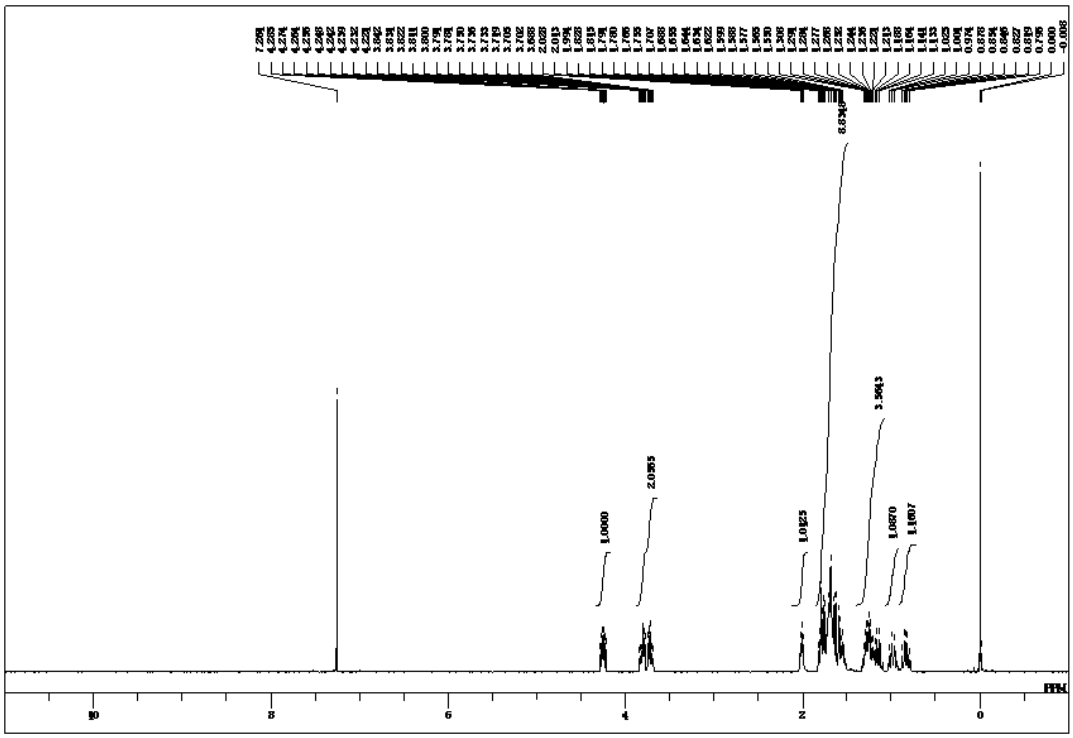



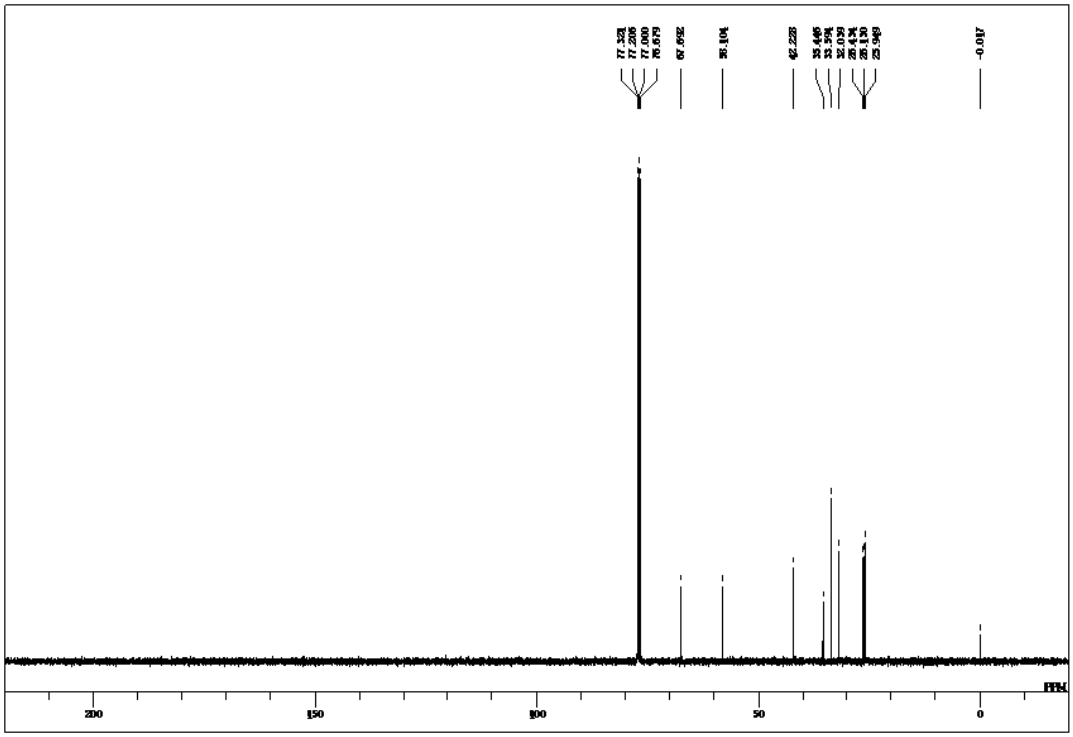
**(*R*)-2-Bromooctanol** (Table 2, entry 2)



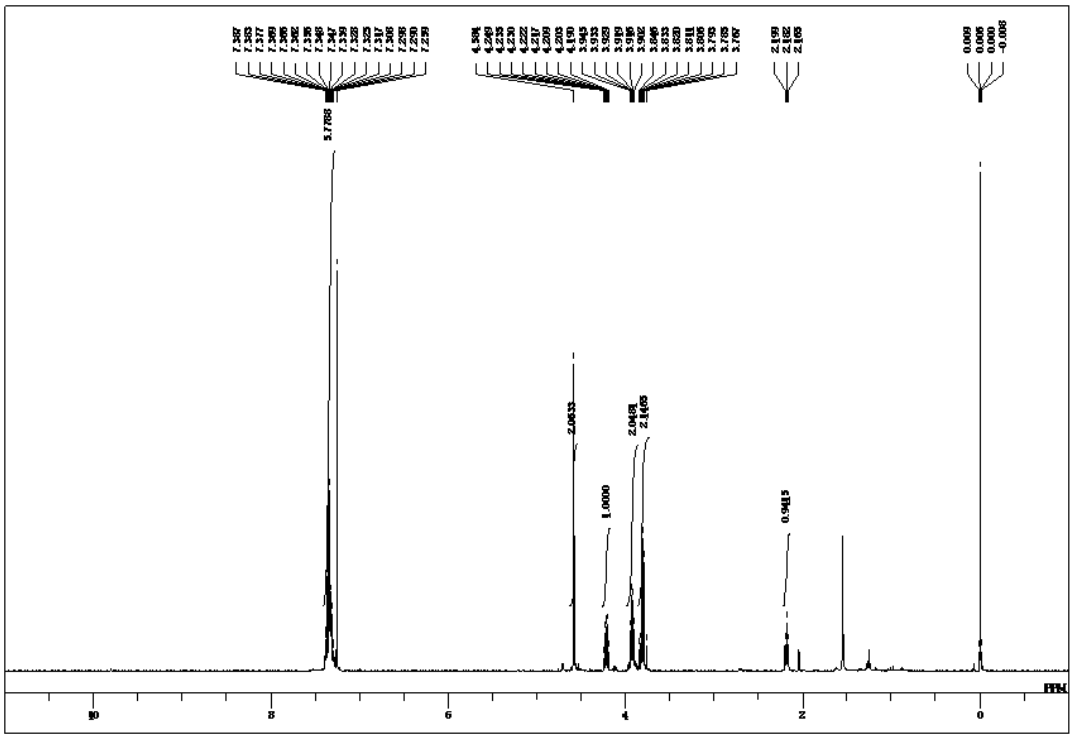


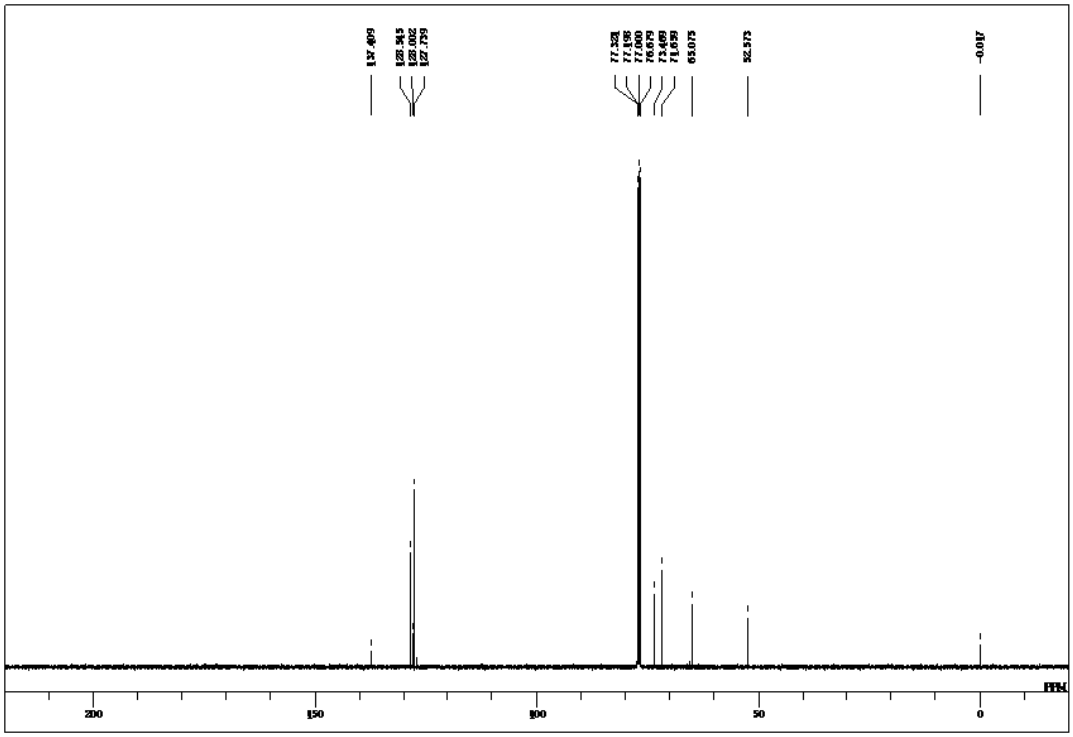
**(*R*)-2-Bromo-3-cyclohexylpropanol** (Table 2, entry 4)



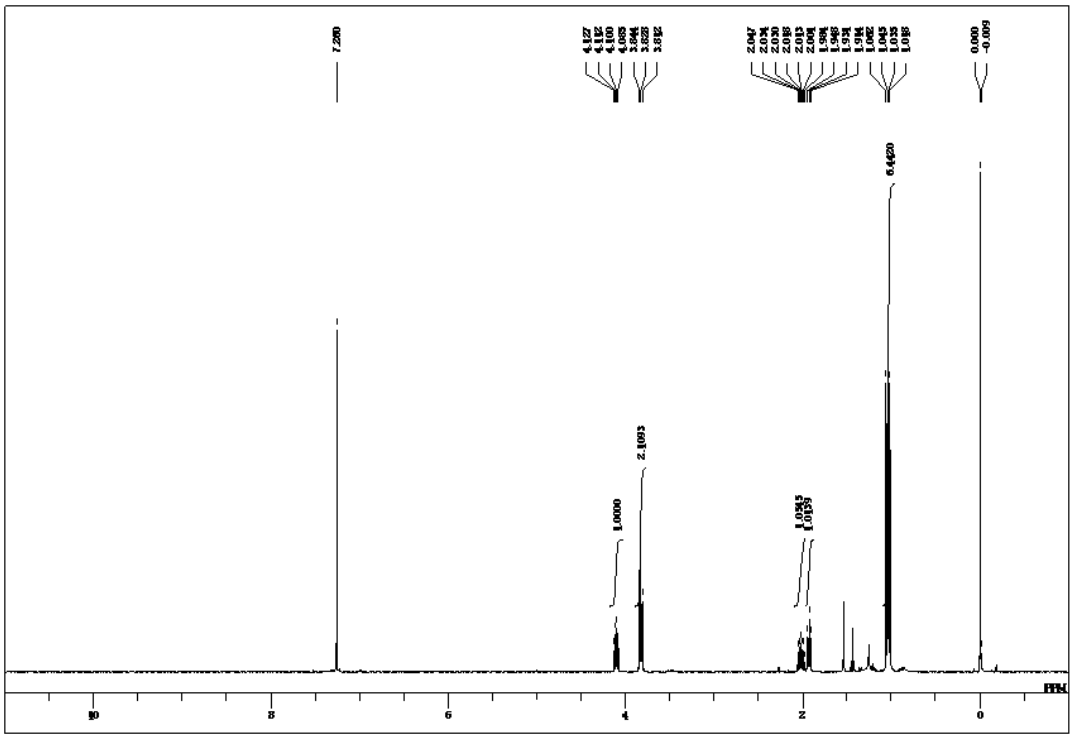



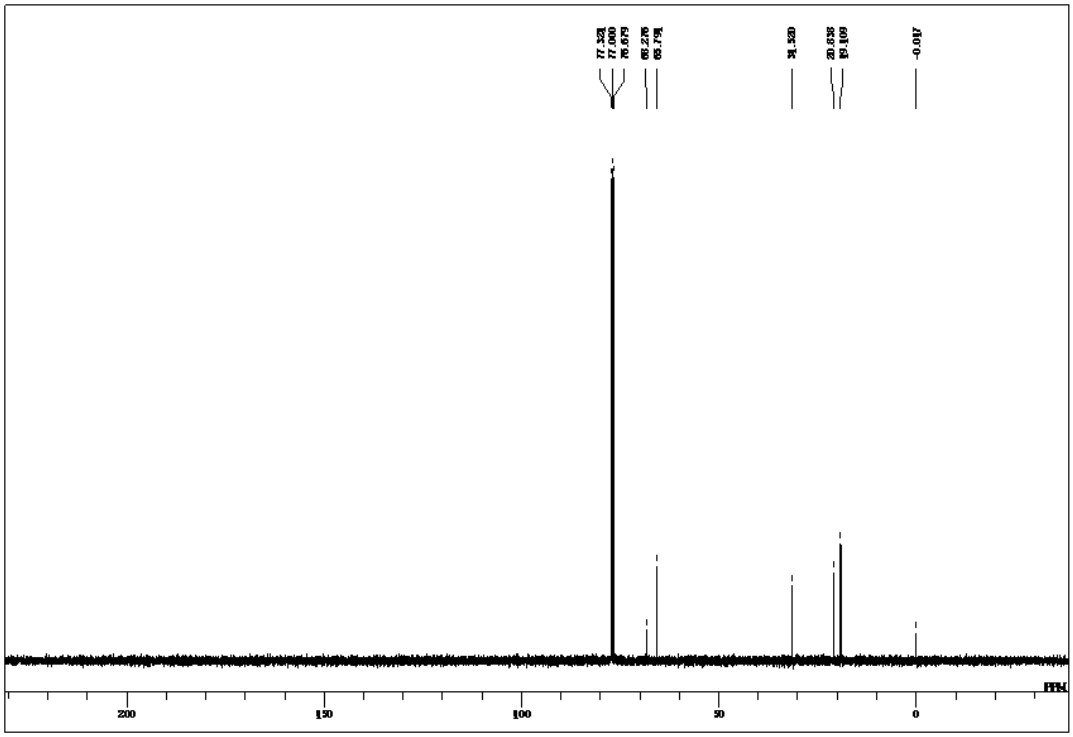
**(*S*)-3-Benzyloxy-2-bromopropanol** (Table 2, entry 5)



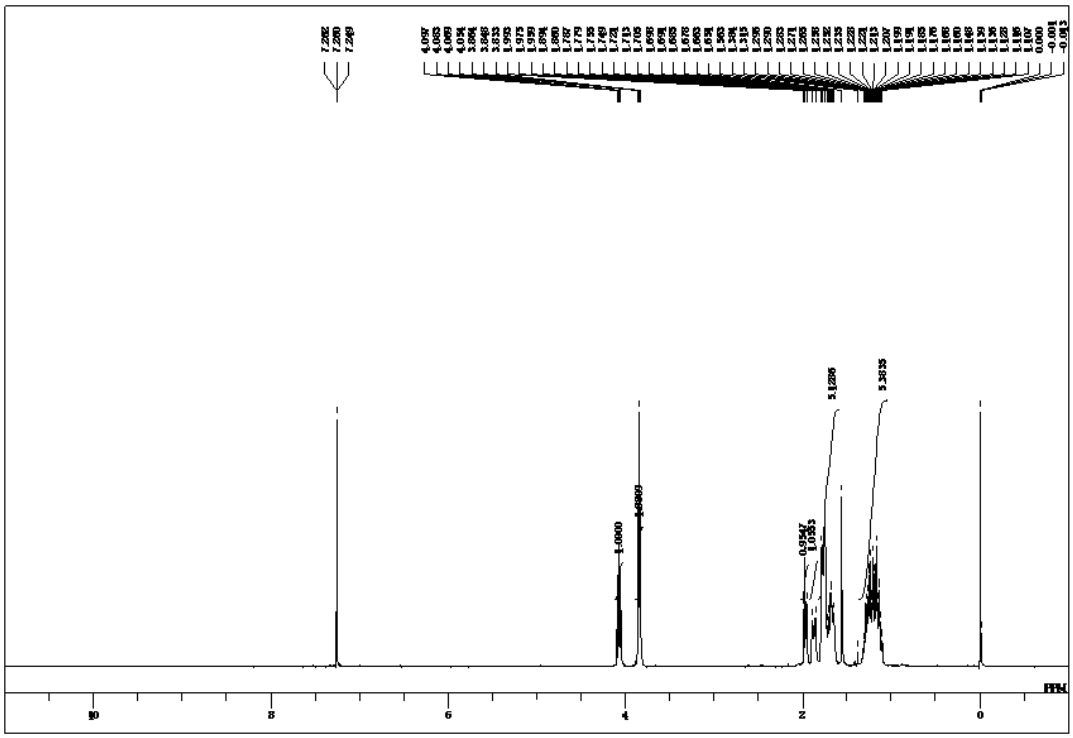


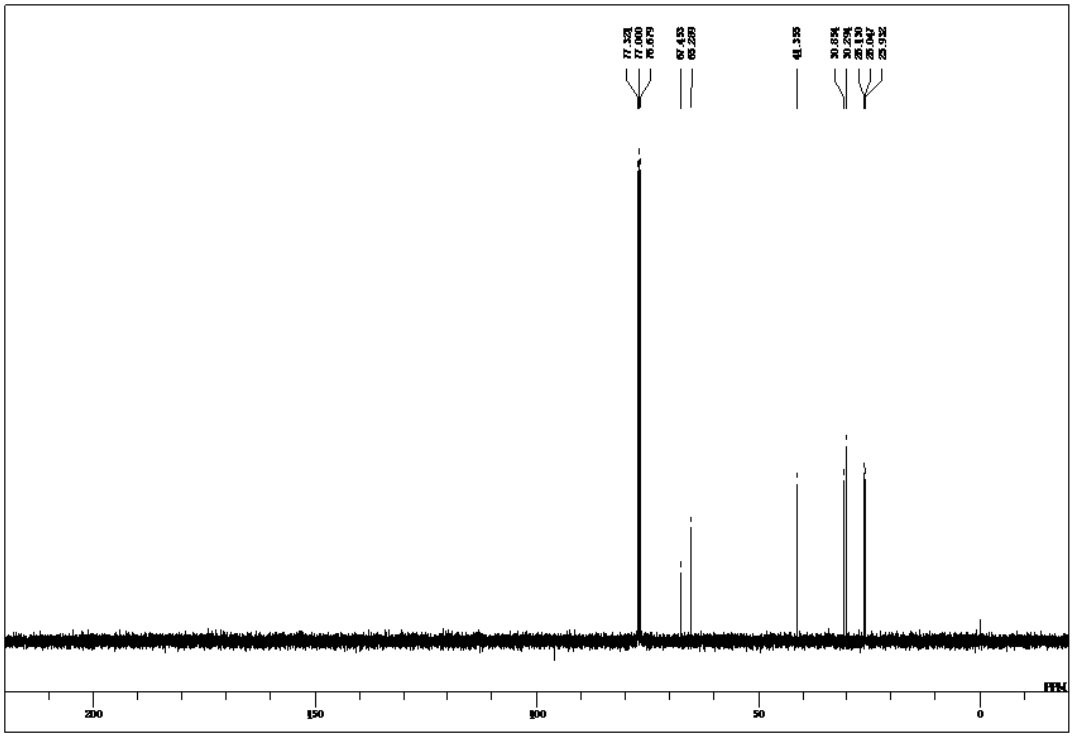
**(*R*)-2-Bromo-3-methylbutanol** (Table 2, entry 6)



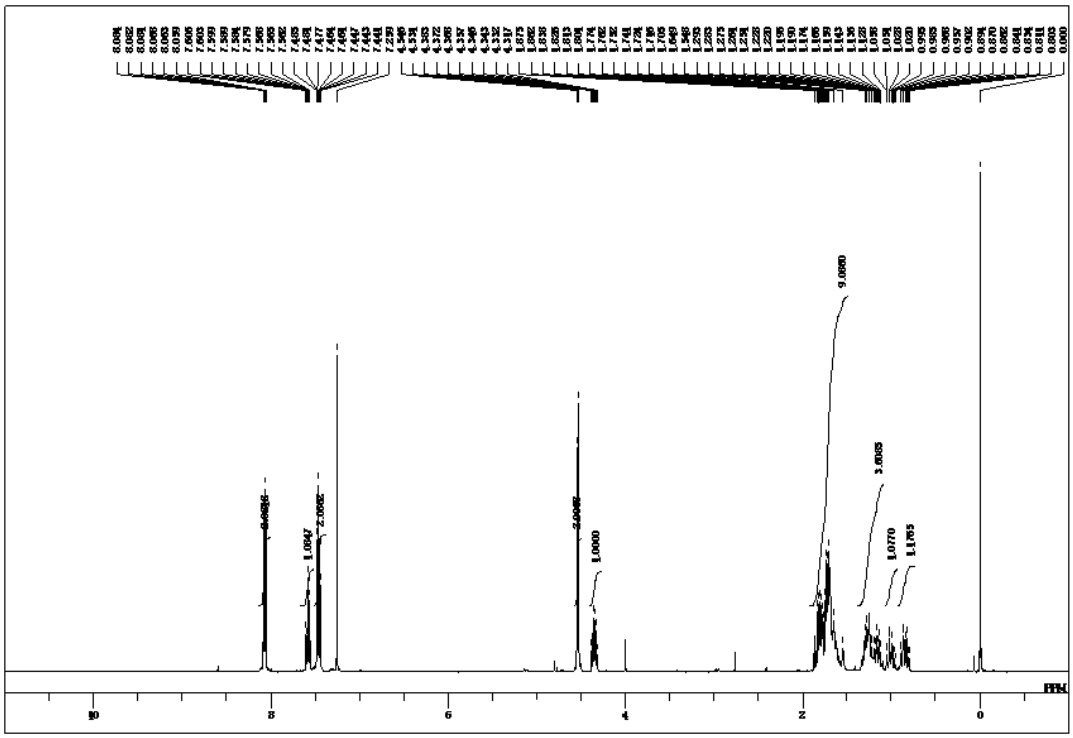


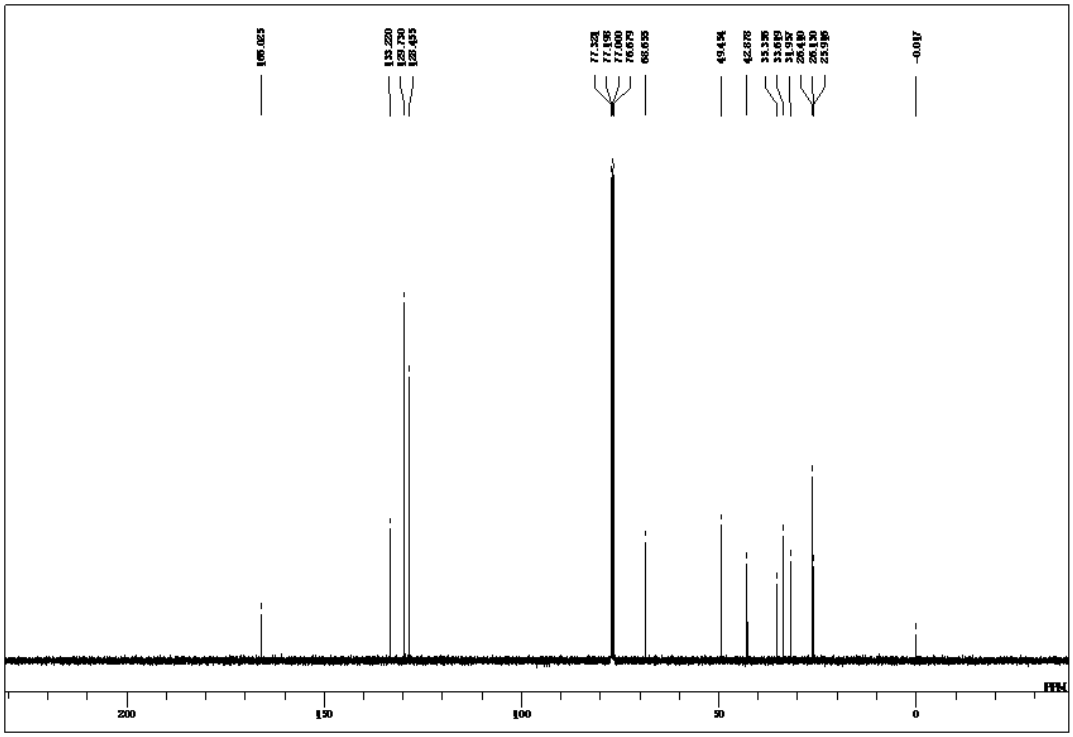
**(*R*)-2-Bromo-2-cyclohexylethanol** (Table 2, entry 7)



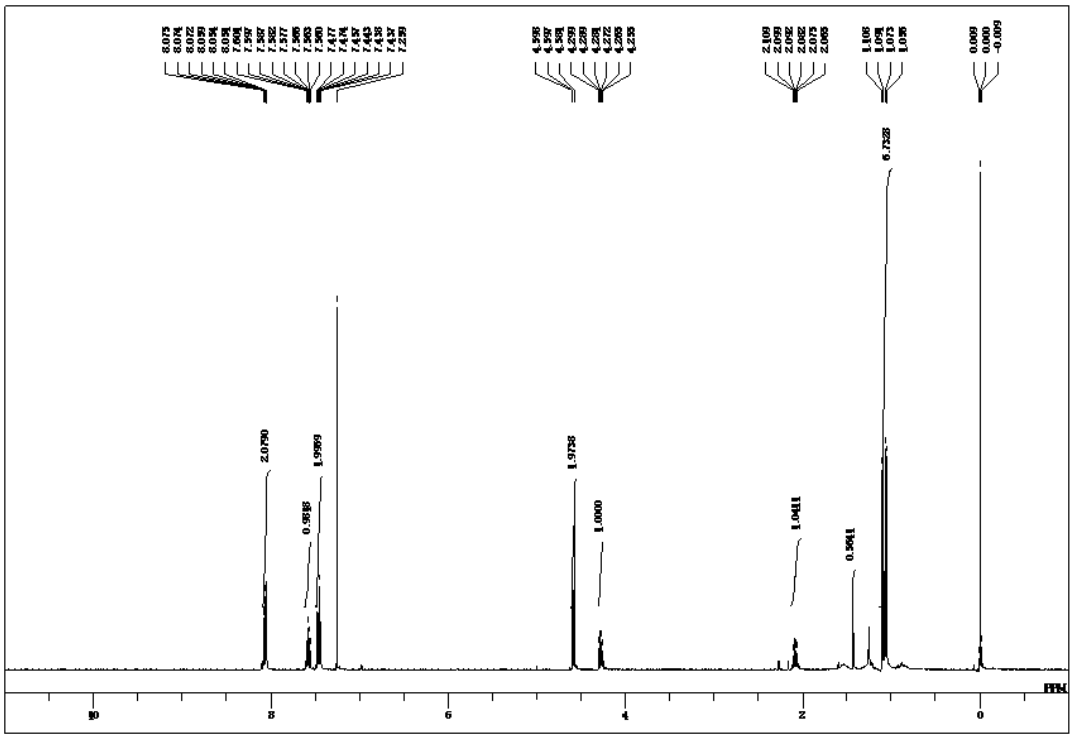


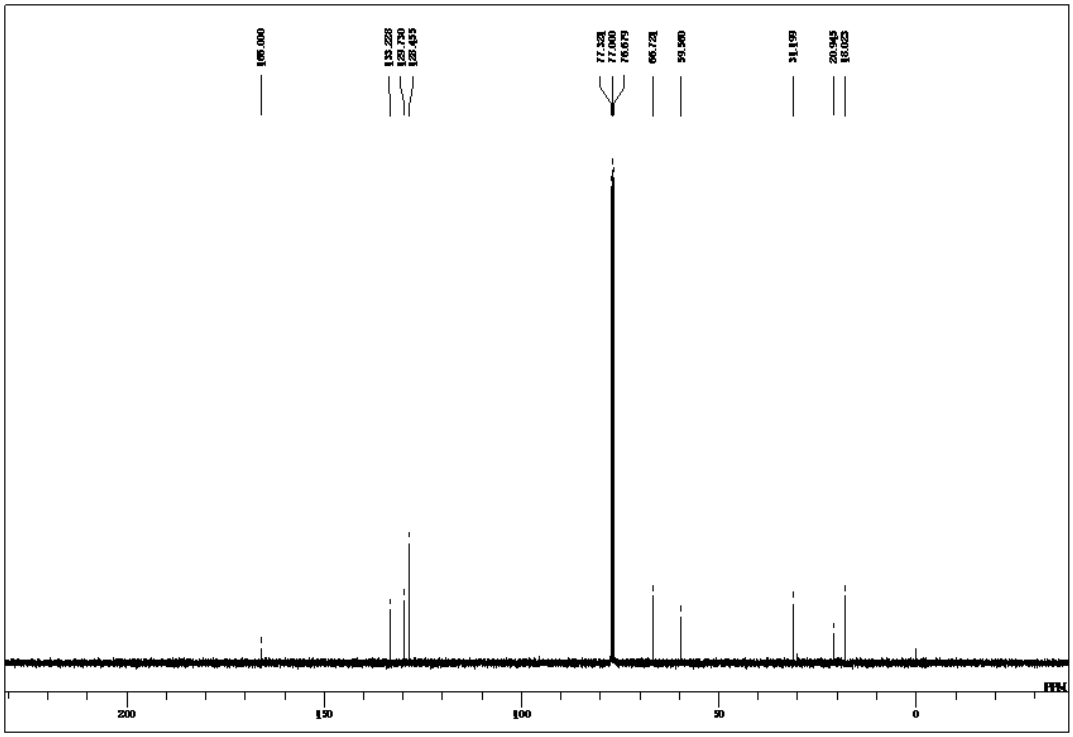
**(*R*)-2-Bromo-3-cyclohexylpropyl benzoate**



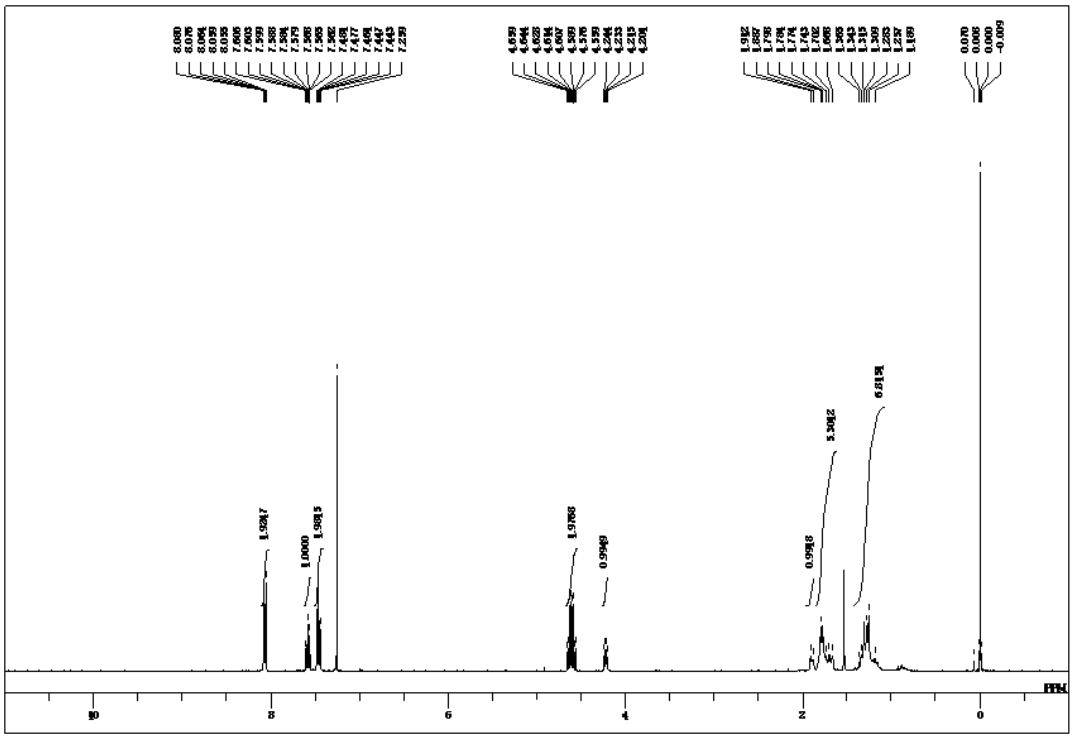



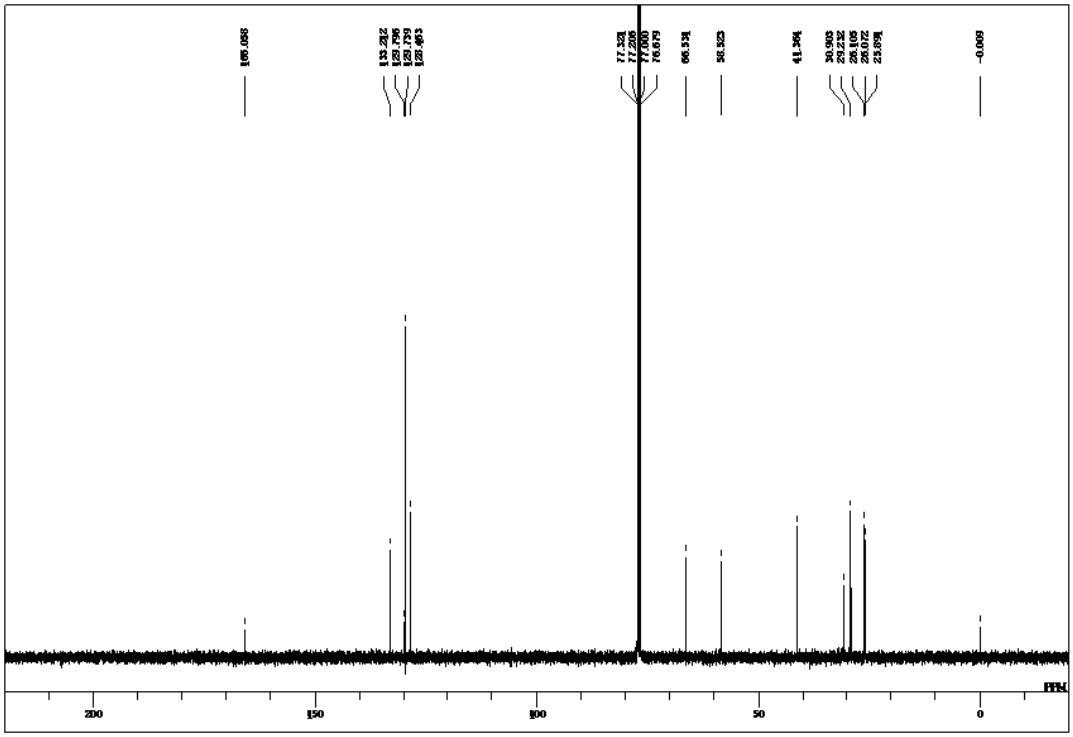
**(*R*)-2-Bromo-3-methylbutyl benzoate**



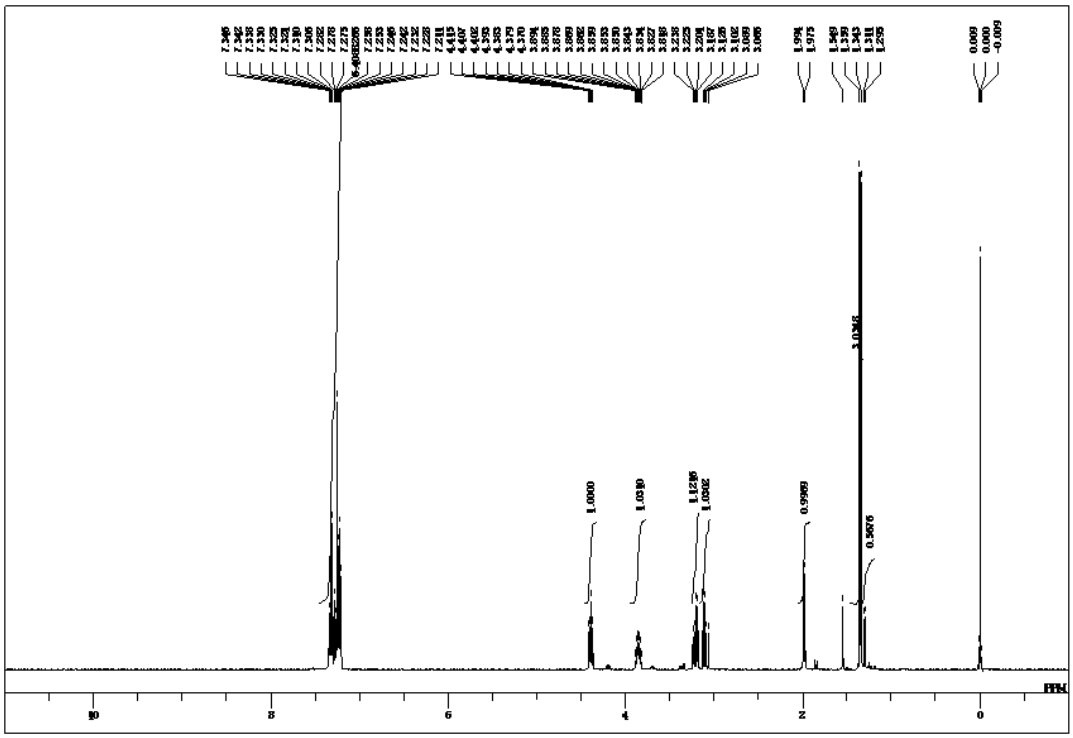


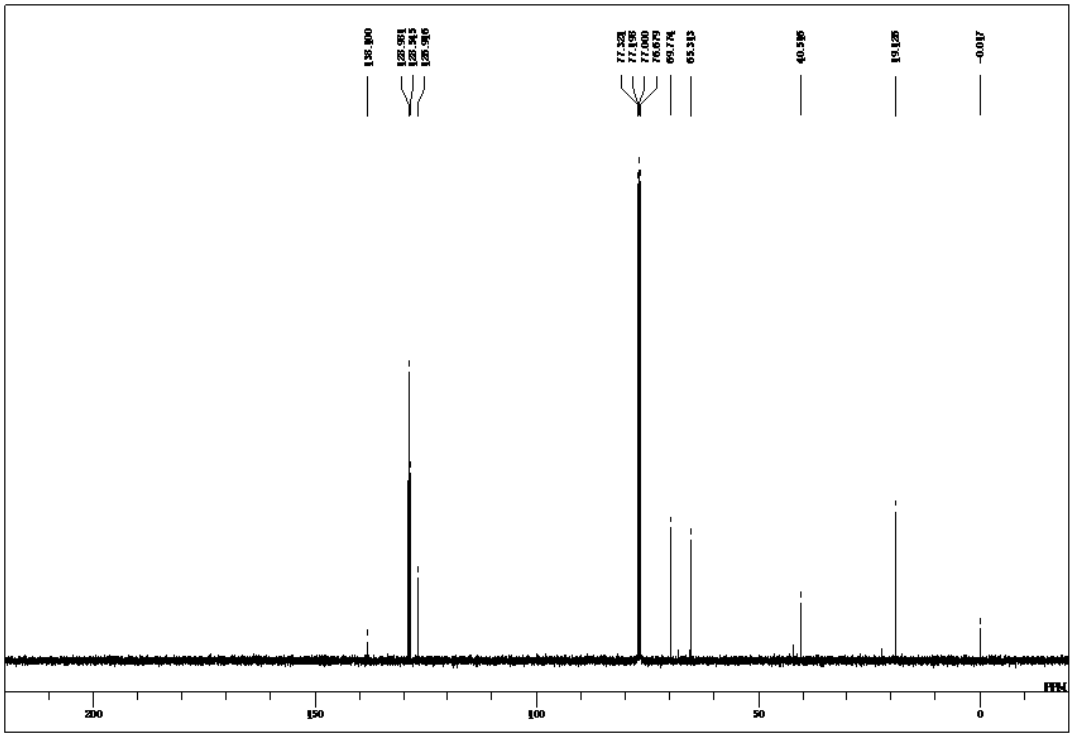
**(*R*)-2-Bromo-2-cyclohexylethyl benzoate**



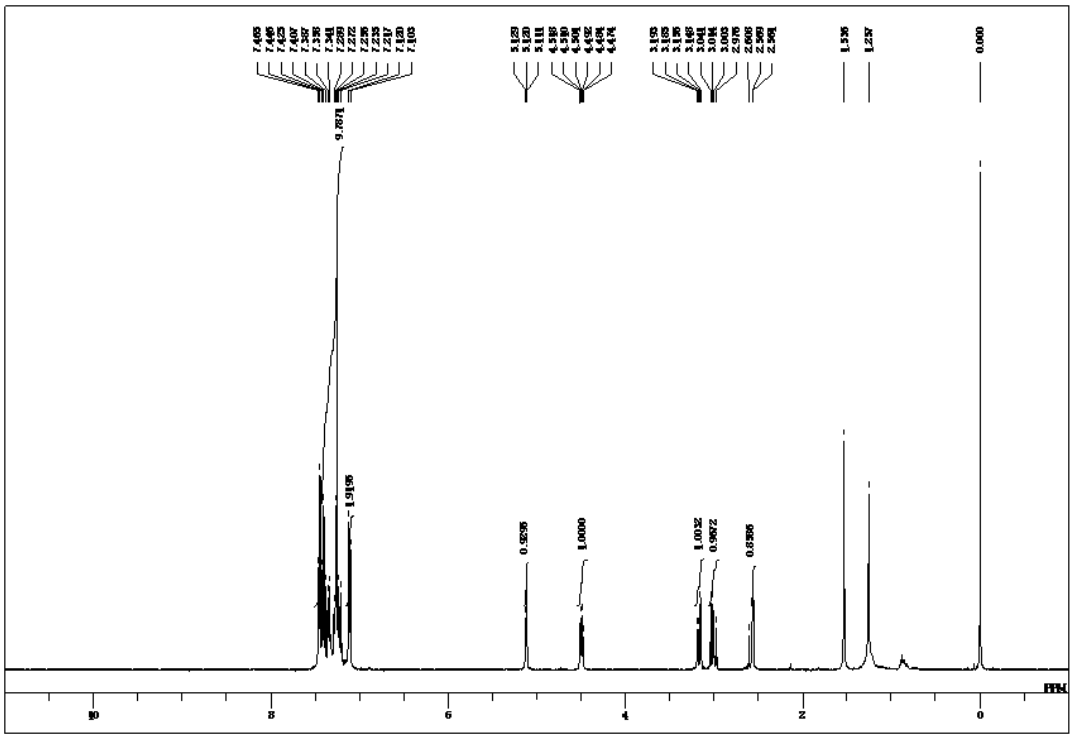


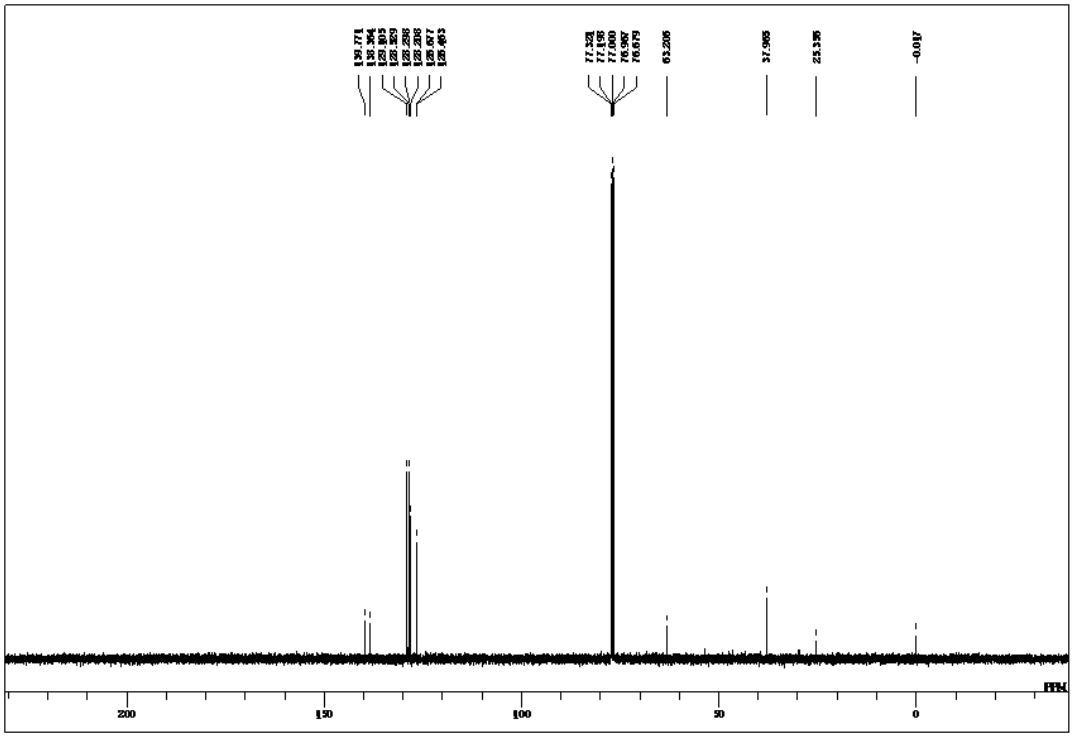
**(2*S*,3*R*)-3-Bromo-4-phenyl-2-butanol** (Table 3, entry 5)





**(1*S*,2*R*)-2-Bromo-1,3-diphenyl-1-propanol** (Table 3, entry 6)





**(1*S*,2*R*)-2-Bromo-3-methyl-1-phenylbutanol** (Table 3, entry 7)