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Supporting Information

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Design of Axially Chiral Amino Acid with Binaphthyl Backbone as an Organocatalyst for Direct Asymmetric Aldol Reaction

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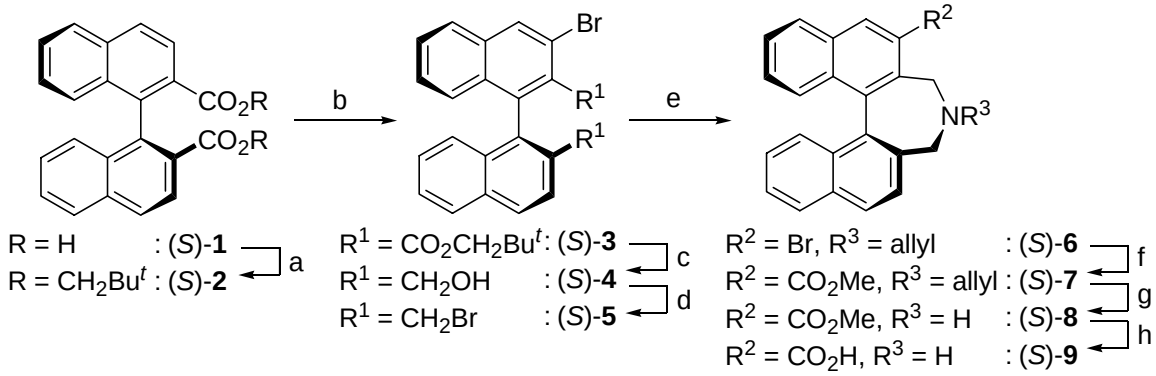
General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-FX400 NMR spectrometer at ambient temperature. ^{1}H NMR data were reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were determined with complete proton decoupling. Chemical shifts are reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel CHIRALPAK AS-H or AD-H, 4.6 mm × 25 cm column. High-resolution mass spectra (HRMS) were performed on Applied Biosystems Mariner biospectrometry workstation. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. 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 1.09386.9025, 230-400 mesh).

(±)-1,1'-Binaphthyl-2,2'-dicarboxylic acid **1** was provided from Tanabe Seiyaku Co., Ltd. and was resolved by the reported procedure[1] to give (*S*)-**1**. (*S*)-**1** is also commercially available from Ivy Chiral Chemical Synthesis Co., Ltd. and NetQem. Acetone was distilled from K_2CO_3. 2-(Trifluoromethanesulfonyloxy)benzaldehyde[2] and ethyl (*E*)-3-methyl-4-oxo-2-butenoate[3] were synthesized according to the literature procedure and purified by flash column chromatography. 2-Chlorobenzaldehyde and 4-pyridinecarboxaldehyde were purified by distillation prior to use. Other simple chemicals were purchased and used as such.

4-(4-Nitrophenyl)-4-hydroxybutan-2-one (Table 2, entry 1), 4-(4-cyanophenyl)-4-hydroxybutan-2-one (Table 2, entry 2) and 4-(2-chlorophenyl)-4-hydroxybutan-2-one (Table 2, entry 4) are reported in the literature.[4]

Synthetic Route of Catalyst (*S*)-9



a) $SOCl_2$; then neopentyl alcohol; b) $Mg(TMP)_2$, THF; then Br_2; c) LAH, THF; d) BBr_3, CH_2Cl_2; e) allylamine, CH_3CN; f) 5 mol% $Pd(OAc)_2$, dppp, *i*Pr_2NEt, CO, DMSO, MeOH; g) $Pd(OAc)_2$, PPh_3, NDMBA, CH_2Cl_2; h) 1 N NaOH, MeOH-THF.

Synthesis and Characterization of Binaphthyl-Based Amino Acid (*S*)-9:

Diester (*S*)-2. A mixture of (*S*)-**1** (1.7 g, 5.0 mmol) and thionyl chloride (5 mL) was refluxed for 2 h and excess thionyl chloride was removed under reduced pressure. 2,2-Dimethylpropanol (1.3 g, 15 mmol), pyridine (1.1 mL) and THF (15 mL) were added into the residue. The mixture was refluxed for 3 h. The resulting mixture was poured into 1 N HCl and then extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:30 as eluent) to give (*S*)-**2** (2.2 g, 4.6 mmol, 91% yield). $[\alpha]_D^{28}$ -19.0° (*c* 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.64 (d, *J* = 10.8 Hz, 2H), 3.60 (d, *J* = 10.8 Hz, 2H), 0.64 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 139.7, 134.9, 132.9, 127.8 (two peaks overlap), 127.6, 127.5, 127.2 , 126.6, 126.2, 74.5, 31.2, 26.3; IR (neat) 2955, 1724, 1703, 1464, 1368, 1321, 1277, 1236, 1215, 1152, 1136, 1119, 993, 976, 766 cm^{-1}; HRMS (FAB) Calcd. for $C_{32}H_{34}O_4$: 482.2457 (M^+), Found: 482.2457 (M^+).

Diol (*S*)-4. To a solution of magnesium bis(2,2,6,6-tetramethylpiperidide) (4.0 mmol)[5] in THF was added (*S*)-**2** in THF (3.8 mL) dropwise at 0 °C. The mixture was stirred for 3 h at room temperature. After cooling to -78 °C, Br_2 (411 μL, 8.0 mmol) was added. After stirring for 1 h at room temperature, the reaction mixture was poured into cooled 1 N HCl, washed with saturated Na_2SO_3 and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and then concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:10 as eluent) to give a mixture including the desired (*S*)-**3**. This mixture (548 mg), which consisted of three components (3,3'-dibromo, 3-bromo and non-substituted forms), was used for next step without further purification.

The mixture in THF (20 mL) obtained above was added into a suspension of lithium aluminum hydride (114 mg, 3.0 mmol) in THF (10 mL) dropwise at 0 °C and kept stirring at the same temperature until the starting material was completely consumed (checked by TLC). The reaction mixture was carefully poured into cooled 1 N HCl and

extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:4 as eluent) to give (*S*)-**4** (166 mg, 0.42 mmol, 42% yield). $[\alpha]_D^{28}$ -93.7° (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.45-7.49 (m, 2H), 7.22-7.27 (m, 2H), 6.95-6.99 (m, 2H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.38 (d, *J* = 12.2 Hz, 1H), 4.07 (dd, *J* = 12.2, 2.4 Hz, 2H), 3.49 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.5, 135.4, 133.8, 133.6, 132.9, 132.6, 132.2, 131.9, 129.0, 128.0, 127.8, 127.3, 127.0, 126.94, 126.88, 126.6, 126.14, 126.10, 122.7, 62.7, 62.4; IR (neat) 3284, 1015, 980, 968, 908, 883, 825, 752, 731 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{17}BrNaO_2$: 415.0305 ($[M+Na]^+$), Found: 415.0304 ($[M+Na]^+$).

Tribromide (*S*)-5. A mixture of (*S*)-**4** and boron tribromide (86 mg, 0.22 mmol) in CH_2Cl_2 was stirred for 1 h at 0 °C. Then, water was carefully added dropwise. After extraction with CH_2Cl_2, the organic layer was washed with brine and dried over Na_2SO_4. The organic layer was concentrated and the resulting residue was purified by flash column chromatography on silica gel (hexane only as eluent) to give (*S*)-**5** (98 mg, 0.19 mmol, 86% yield). $[\alpha]_D^{29}$ -140.6° (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.48-7.53 (m, 2H), 7.21-7.33 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 2H), 4.48 (d, *J* = 10.6 Hz, 1H), 4.33 (d, *J* = 10.0 Hz, 1H), 4.25 (d, *J* = 10.0 Hz, H), 4.18 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 134.03, 133.97, 133.5, 133.1, 132.8, 132.0, 131.5, 129.7, 128.0, 127.8, 127.7, 127.3, 127.0, 126.92, 126.90, 126.8, 126.6, 122.5, 33.0, 32.6 (The signal for an aromatic carbon was not identified due to the overlap of peaks.); IR (Neat) 3055, 1580, 1558, 1497, 1427, 1263, 1215, 1024, 984, 880, 853, 821, 748, 725 cm^{-1}; HRMS (FAB) Calcd. for $C_{22}H_{15}Br_3$: 517.8703 ($[M]^+$), Found: 517.8702 ($[M]^+$).

Allylamine (*S*)-6. To a solution of (*S*)-**5** (77 mg, 0.15 mmol) in THF (3 mL) was added allylamine (56 μL, 0.74 mmol) at room temperature. The mixture was heated at 50 °C, stirred there for 5 h, and then poured into water. After extraction with ethyl acetate, the organic layer was washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by flash column chromatography on silica gel (ethyl acetate/hexane = 1:20~1:4 as eluent) afforded (*S*)-**6** (54.5 mg, 0.13 mmol, 89% yield). $[\alpha]_D^{29}$ 331.2° (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.95 (t, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43-7.48 (m, 2H), 7.35 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.21-7.27 (m, 2H), 5.95-6.05 (m, 1H), 5.25 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.35 (d, *J* = 12.6 Hz, 1H), 3.77 (d, *J* = 12.6 Hz, 1H), 3.42 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.03-3.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.0, 134.4, 133.7, 133.5, 132.9, 132.6, 131.4, 131.1, 130.4, 128.8, 128.2, 127.7, 127.4, 127.2, 127.0, 126.4, 126.0, 125.9, 125.4, 123.0, 117.6, 58.8, 54.9, 53.8; IR (neat) 3053, 2805, 1555, 1497, 1464, 1418, 1329, 1263, 1238, 1136, 1098, 991, 966, 916, 881, 845, 814, 748, 737 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{21}BrN$: 414.0853 ($[M+H]^+$), Found: 414.0852 ($[M+H]^+$).

Methyl ester (*S*)-7. Compound (*S*)-**6** (238 mg, 0.57 mmol), $Pd(OAc)_2$ (13 mg, 0.057 mmol), bis(diphenylphosphino)propane (dppp) (24 mg, 0.057 mmol) and ^{i}Pr$_2$NEt (427 μL, 2.5 mmol) in DMSO (10 mL) and

MeOH (10 mL) were charged into autoclave under argon atmosphere. After pressurized with CO (10 atm), the mixture was heated to 80 °C with stirring for 24 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and then concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:9~1:4 as eluent) to give (*S*)-**7** (150 mg, 0.38 mmol, 67% yield) with recovery of starting material (*S*)-**6** (29 mg, 12% yield). $[\alpha]_D^{30}$ 334.7° (*c* 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.94-8.00 (m, 3H), 7.38-7.56 (m, 3H), 7.22-7.36 (m, 4H), 5.94-6.03 (m, 1H), 5.16-5.21 (m, 2H), 4.75 (d, *J* = 12.8 Hz, 1H), 4.00 (s, 3H), 3.75 (d, *J* = 12.4 Hz, 1H), 3.23 (dd, *J* = 13.6, 6.8 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.98-3.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 137.3, 136.2, 134.3, 133.2, 132.9, 132.6, 131.9, 131.6, 131.2, 129.1, 128.61, 128.56, 128.2, 127.7, 127.44, 127.35, 127.0, 126.2, 125.8, 125.3, 117.3, 58.7, 54.8, 52.5, 49.8 (The signal for an aromatic carbon was not identified due to the overlap of peaks.); IR (neat) 3053, 2947, 2803, 1721, 1441, 1335, 1296, 1287, 1263, 1240, 1207, 1194, 1180, 1136, 1072, 1042, 1028, 920, 816, 787, 779, 752, 735 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{24}NO_2$: 394.1802 ($[M+H]^+$), Found: 394.1802 ($[M+H]^+$).

Amino ester (*S*)-8. A mixture of (*S*)-**7** (1.1 g, 2.7 mmol), *N*,*N*-dimethylbarbituric acid (NDMBA) (1.3g, 8.1 mmol), $Pd(OAc)_2$ (30 mg, 0.135 mmol), and triphenylphosphine (142 mg, 0.50 mmol) in CH_2Cl_2 (15 mL) was heated at 35 °C and stirred there for 2 h under argon atmosphere. After cooling to room temperature, CH_2Cl_2 was removed under vacuum and replaced by benzene. After addition of saturated $NaHCO_3$, the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (MeOH/CH_2Cl_2 = 1:50 as eluent) to give (*S*)-**8** (0.95 g, 2.7 mmol, quantitative yield): $[\alpha]_D^{30}$ 361.7° (*c* 0.47, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.44-7.52 (m, 2H), 7.31-7.38 (m, 3H), 7.23-7.27 (m, 1H), 4.68 (d, *J* = 13.4 Hz, 1H), 4.00 (s, 3H), 3.91 (d, *J* = 11.6 Hz, 1H), 3.49 (d, *J* = 11.6 Hz, 1H), 3.26 (d, *J* = 13.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 136.8, 134.5, 134.4, 133.2, 133.1, 132.6, 131.9, 131.6, 131.2, 129.24, 129.15, 128.3, 127.9, 127.8, 127.4, 127.2, 127.0, 126.2, 125.8, 125.4, 52.5, 48.4, 44.2; IR (neat) 3310, 3053, 2949, 2839, 1715, 1674, 1611, 1441, 1296, 1263, 1242, 1207, 1136, 1053, 908, 810, 789, 731 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{20}NO_2$: 354.1490 ($[M+H]^+$), Found: 354.1489 ($[M+H]^+$).

Amino acid (*S*)-9. A mixture of (*S*)-**8** (177 mg, 0.5 mmol) and 1 N NaOH (1.0 mL) in MeOH (1.5 mL) and THF (1.0 mL) was refluxed for 1 h. After cooling to room temperature, CH_2Cl_2 (1 mL) was added and the mixture was acidified with 1 N HCl. This mixture was then concentrated and the residue was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The acquired residue was purified by using ion exchange resin (Dowex® 50W-X, supplied by Dow chemical Co. Ltd.) (1~5 % ammonium hydroxide as eluent) to give (*S*)-**9** (153 mg, 0.45 mmol, 90 % yield). $[\alpha]_D^{31}$ 232.2° (*c* 0.36, $CHCl_3$/MeOH = 2:1); ^{1}H NMR (400 MHz, CD_3OD/$CDCl_3$ = 2:1) δ 8.41 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 8.4, 1H), 7.52-7.58 (m, 2H), 7.27-7.37 (m, 4H), 5.24 (d, *J* = 12.8 Hz, 1H), 4.33 (d, *J* = 13.2 Hz, 1H), 3.83 (d, *J* = 31.2 Hz, 1H), 3.48 (d, *J* = 12.8 Hz,

1H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ = 2:1) δ 174.5, 136.4, 135.9, 134.2, 133.4, 131.4, 131.3, 130.1, 129.9, 129.1, 128.5, 128.3, 127.4, 127.20, 127.18, 127.1, 126.92, 126.90, 126.8, 126.3, 46.2, 42.8 (The signal for an aromatic carbon was not identified due to the overlap of peaks.); IR (neat) 3410, 3049, 2957, 1595, 1558, 1441, 1369, 1321, 812, 791, 750, 723, cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{18}NO_2$: 340.1319 ($[M+H]^+$), Found: 340.1332 ($[M+H]^+$); The optical purity of (*S*)-**9** was determined to be >99% ee by treatment of (*S*)-**9** in MeOH and benzene with trimethylsilyldiazomethane[6] and HPLC analysis of the resulting methyl ester (*S*)-**8**. HPLC analysis; Daicel Chiralpak IA, CH_2Cl_2/methanol = 20:1, flow rate = 0.5 mL/min, UV 254 nm, retention time; 7.5 min (*R*) and 8.2 min (*S*).

General Procedure for an Aldol Reaction: To a mixture of binaphthyl-based amino acid (*S*)-**9** (8.5 mg, 0.025 mmol) in anhydrous acetone (1 mL) and anhydrous DMF (4 mL) was added an aldehyde (0.5 mmol) at room temperature. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was then treated with saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 1:3 as eluent) to give an aldol product.

4-(4-Acetylphenyl)-4-hydroxybutan-2-one (Table 2, entry 3). $[\alpha]^{30}_D$ 69.3˚ (*c* 1.00, $CHCl_3$; 95% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, *J* = 8.0 Hz, Ar-H), 7.45 (2H, d, *J* = 8.0 Hz, Ar-H), 5.19-5.23 (1H, m, Ar-CH), 3.56 (1H, br, OH), 2.84-2.86 (2H, m, CH_2), 2.59 (3H, s, CH_3), 2.20 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 197.5, 147.9, 136.3, 128.5, 125.6, 69.3, 51.7, 30.8, 26.6; IR (neat) 3446, 2918, 1705, 1674, 1606, 1359, 1267, 1072, 833, 597 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{12}H_{14}NaO_3$: 229.0835 ($[M + Na]^+$), Found: 229.0836 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AS-H, hexane/ethanol = 6:1, flow rate = 1.0 mL/min, UV 254 nm, retention time; 17.3 min (major) and 19.0 min.

4-(2-Trifluoromethanesulfonyloxyphenyl)-4-hydroxybutan-2-one (Table 2, entry 5). $[\alpha]^{30}_D$ 43.0˚ (*c* 1.00, $CHCl_3$; 94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, d, *J* = 8.0 Hz, Ar-H), 7.35-7.44 (2H, m, Ar-H), 7.27 (1H, d, *J* = 8.0 Hz, Ar-H), 5.44-5.46 (1H, m, Ar-CH), 3.61 (1H, d, *J* = 3.6 Hz, OH), 2.77-2.94 (2H, m, CH_2), 2.21 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 145.6, 135.3, 129.2, 128.7, 128.3, 121.0, 118.4 (q, $J_{C\text{-}F}$ = 321 Hz), 64.1, 50.3, 30.5; IR (neat) 3435, 1712, 1417, 1207, 1136, 1062, 891, 767, 596 cm^{-1}; HRMS (ESI) Calcd. for $C_{11}H_{11}F_3NaO_3S$: 335.0172 ($[M + Na]^+$), Found: 335.0172 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AD-H, hexane/2-propanol = 6:1, flow rate = 0.5 mL/min, UV 210 nm, retention time; 10.7 min (major) and 11.8 min.

4-Hydroxy-4-(pyridin-4'-yl)butan-2-one (Table 2, entry 6). $[\alpha]^{30}_D$ 91.1˚ (*c* 1.00, $CHCl_3$; 95% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (2H, d, *J* = 6.0 Hz, Ar-H), 7.29 (2H, d, *J* = 6.0 Hz, Ar-H), 5.17 (1H, dd, *J* = 8.8 Hz, 4.0 Hz, Ar-CH), 4.54 (1H, br, OH), 2.77-2.90 (2H, m, CH_2), 2.21 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 152.2, 149.5, 120.5, 68.2, 51.5, 30.8; IR (neat) 3219, 1707, 1604, 1415, 1359, 1066, 582, 557 cm^{-1}; HRMS (ESI) Calcd. for $C_9H_{12}NO_2$: 166.0863 ($[M + H]^+$), Found: 166.0860 ($[M + H]^+$); HPLC analysis: Daicel Chiralpak AS-H,

hexane/ethanol = 6:1, flow rate = 1.0 mL/min, UV 254 nm, retention time; 10.3 min (major) and 15.1 min.

(*Z*)-5-Chloro-4-hydroxy-6-phenylhex-5-en-2-one (Table 2, entry 7). $[\alpha]^{27}_{D}$ 40.5˚ (*c* 1.00, $CHCl_3$; 90% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (2H, d, *J* = 7.6 Hz, Ar-H), 7.25-7.37 (3H, m, Ar-H), 6.88 (1H, s, PhCH), 4.76-4.81 (1H, m, CH), 3.42 (1H, br, OH), 2.86-3.01 (2H, m, CH_2), 2.23 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 133.9, 133.3, 129.1, 128.1, 128.0, 124.9, 72.0, 48.1, 30.9; IR (neat) 3392, 1708, 1361, 1163, 1076, 756, 694 cm^{-1}; HRMS (ESI) Calcd. for $C_{12}H_{13}ClNaO_2$: 247.0496 ($[M + Na]^+$), Found: 247.0493 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AD-H, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, UV 254 nm, retention time; 23.6 min and 26.1 min (major).

Ethyl (*E*)-4-hydroxy-3-methyl-6-oxo-hept-2-enoate (Table 2, entry 8). $[\alpha]^{30}_{D}$ 55.0˚ (*c* 1.00, $CHCl_3$; 96% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (1H, s, CH=C), 4.54 (1H, d, *J* = 9.2 Hz, CH), 4.16 (2H, q, *J* = 7.2 Hz, OCH_2), 3.25 (1H, br, OH), 2.59-2.76 (2H, m, CH_2), 2.22 (3H, s, CH_3), 2.11 (3H, s, CH_3), 1.28 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 166.5, 157.3, 115.3, 71.7, 59.8, 48.1, 30.8, 15.3, 14.3; IR (neat) 3458, 2981, 1707, 1653, 1365, 1220, 1145, 1039 cm^{-1}; HRMS (ESI) Calcd. for $C_{10}H_{16}NaO_4$: 223.0941 ($[M + Na]^+$), Found: 223.0940 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AS-H, hexane/2-propanol = 8:1, flow rate = 1.0 mL/min, UV 210 nm, retention time; 11.4 min (major) and 14.6 min.

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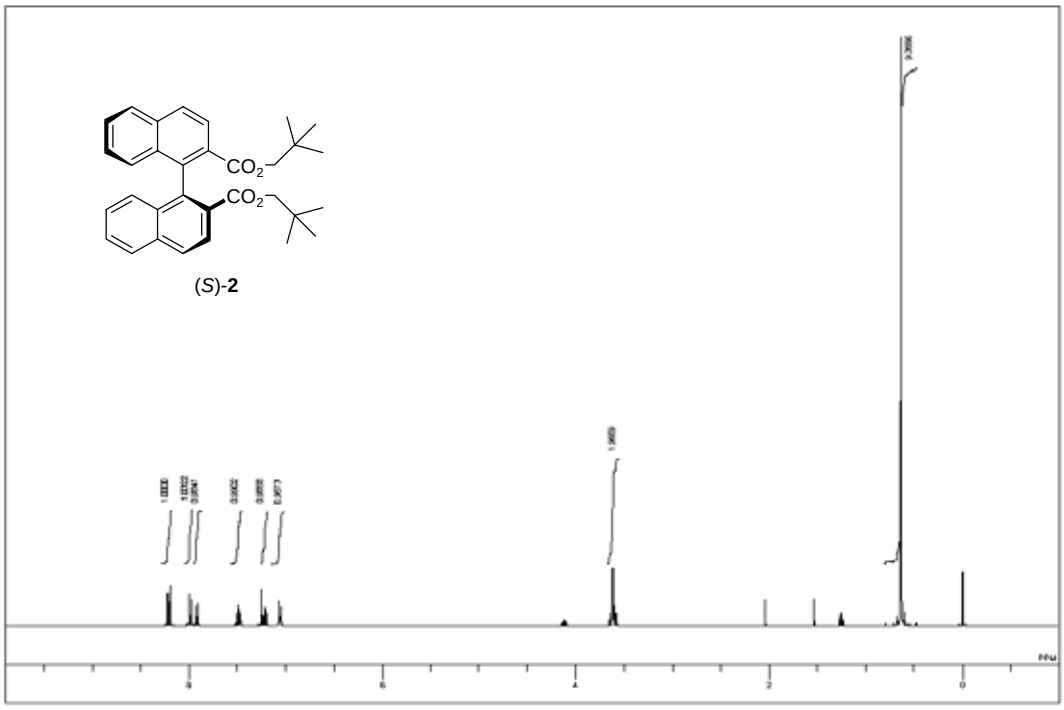

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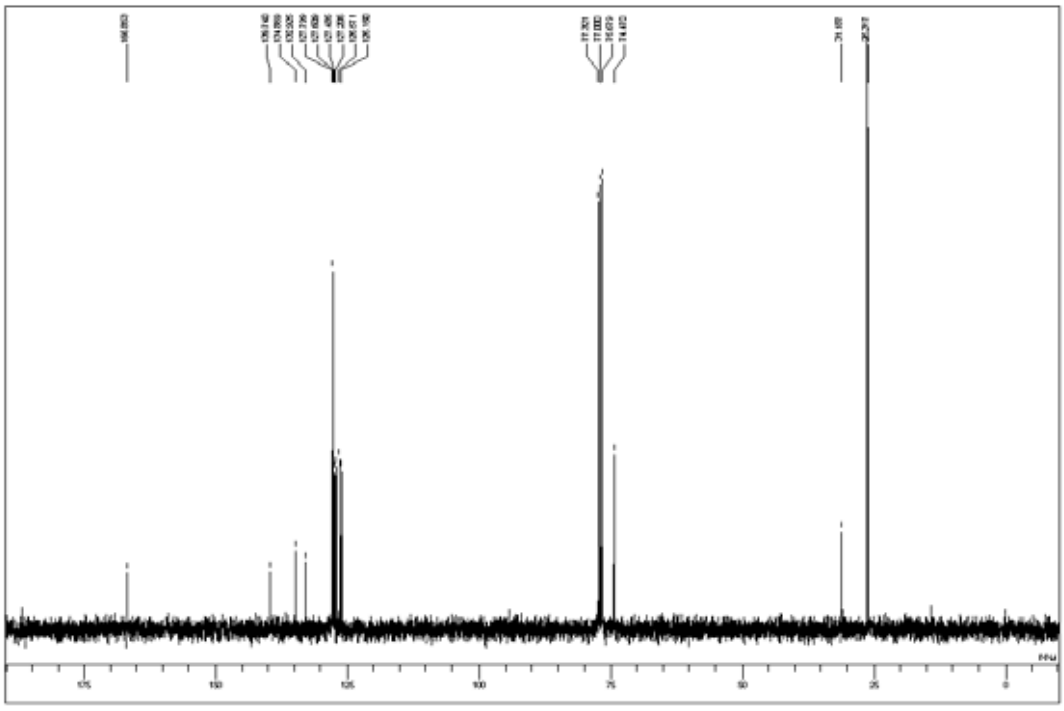

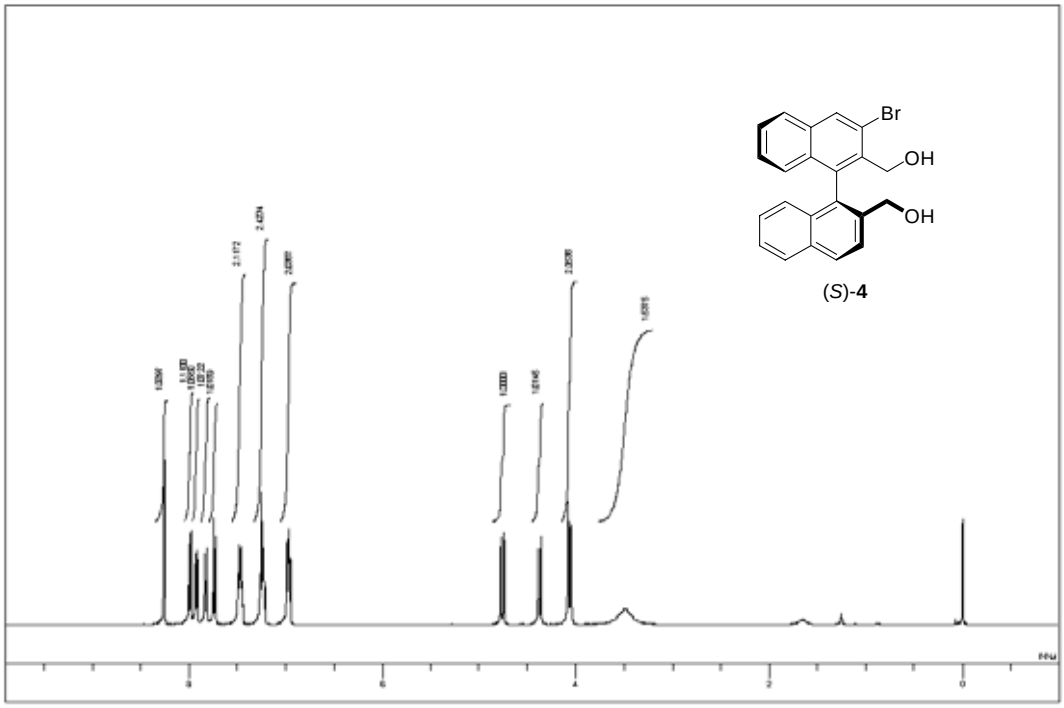

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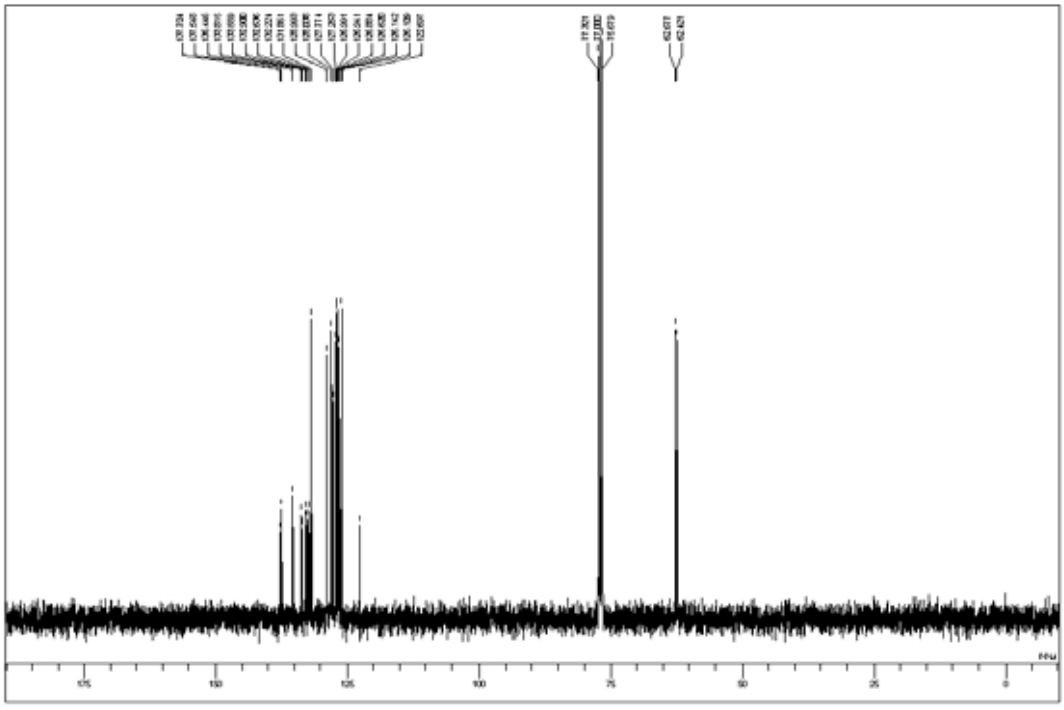

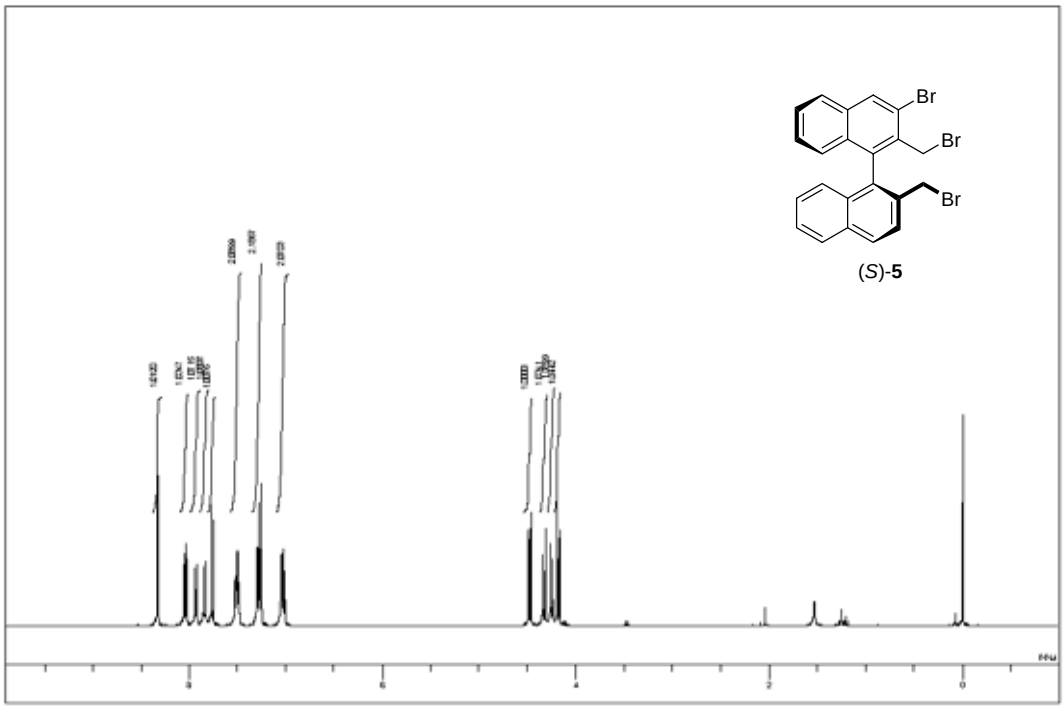

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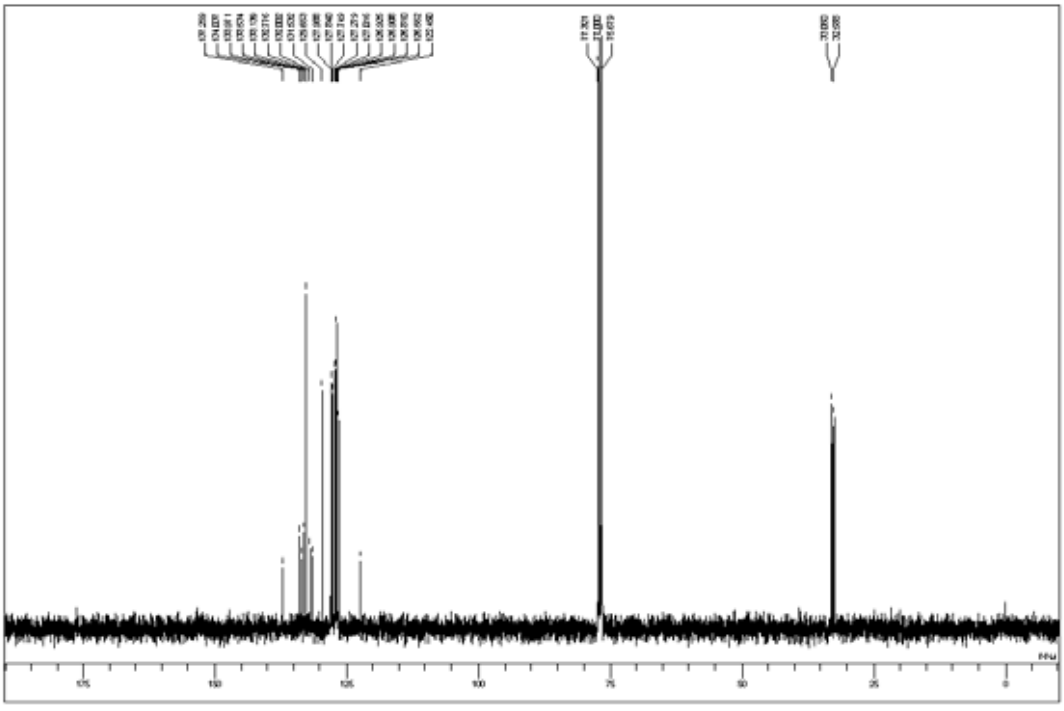

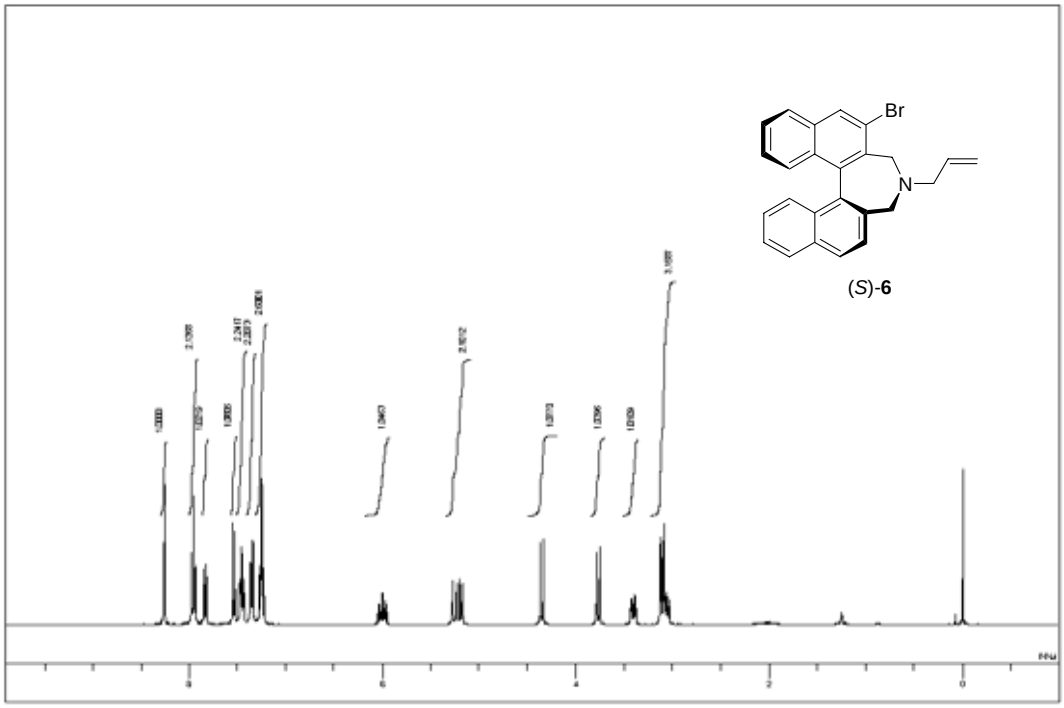

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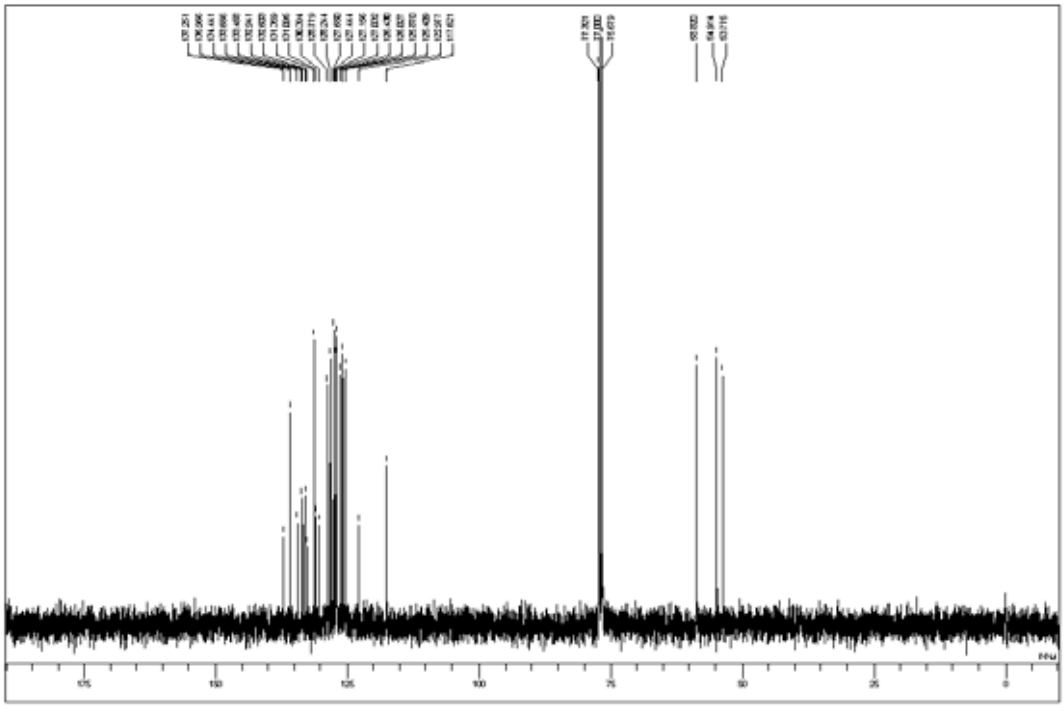

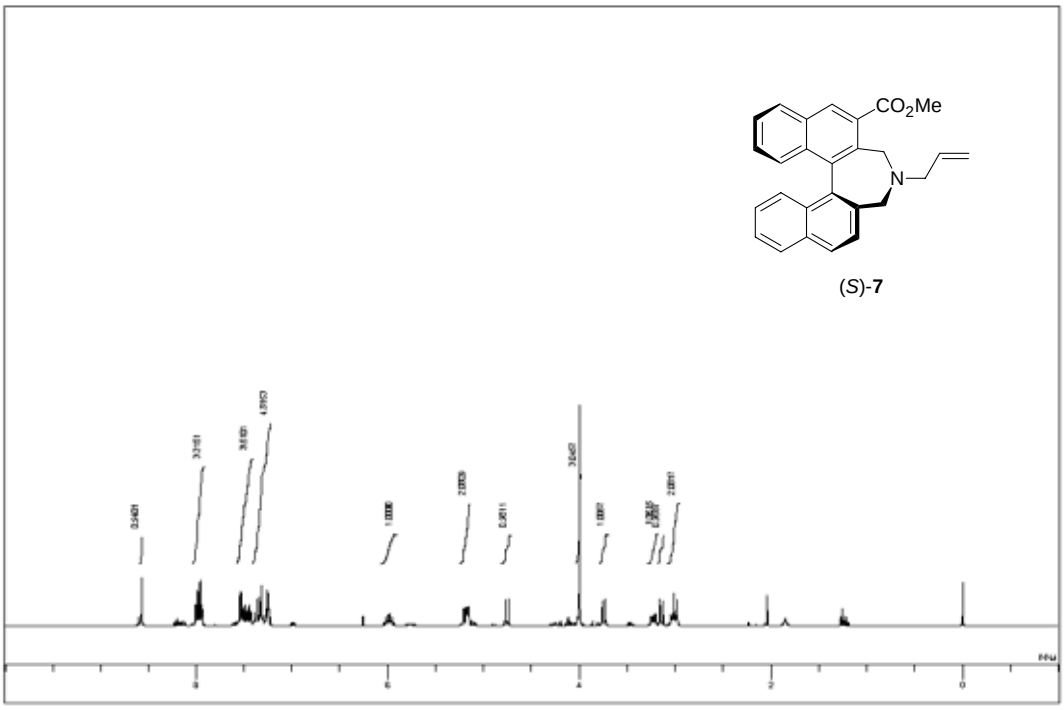

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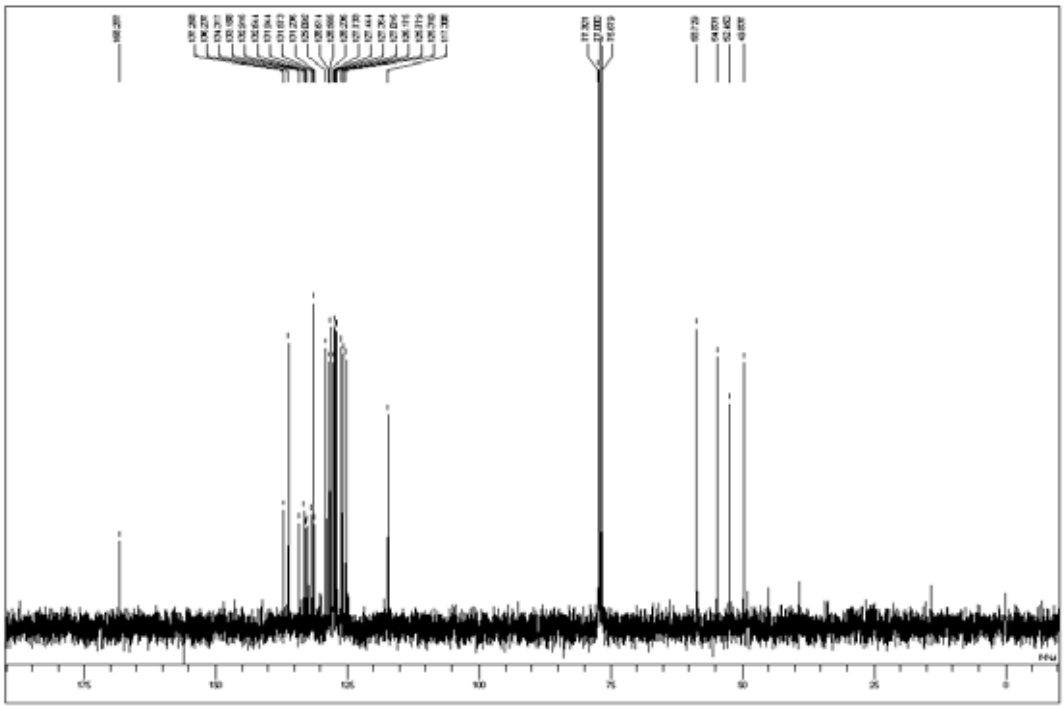

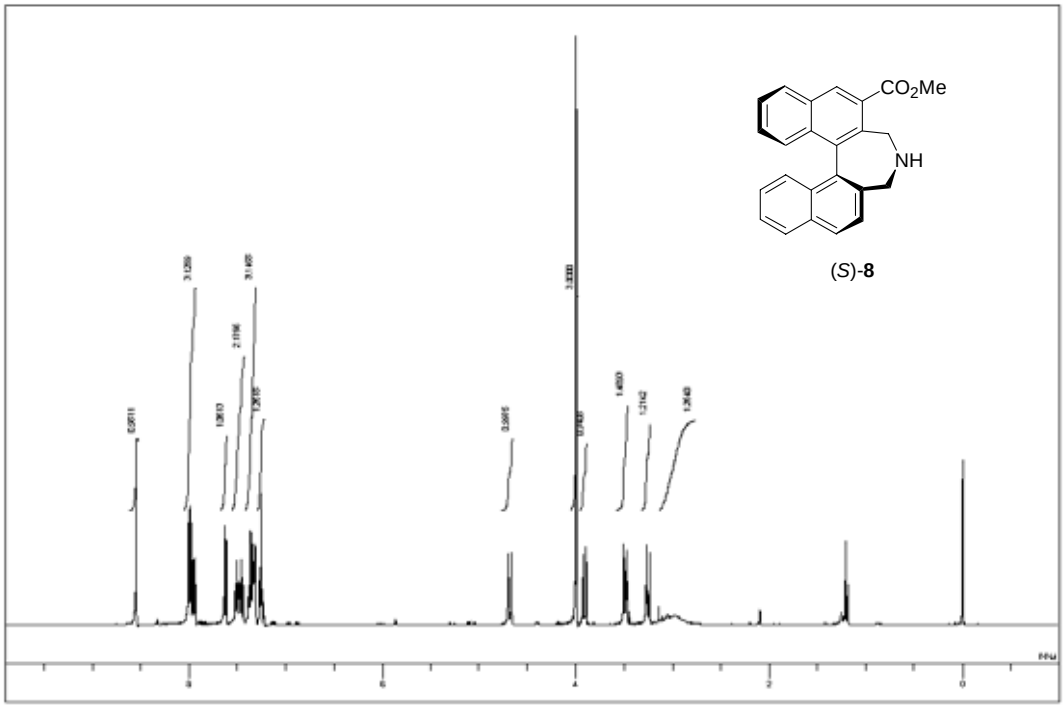

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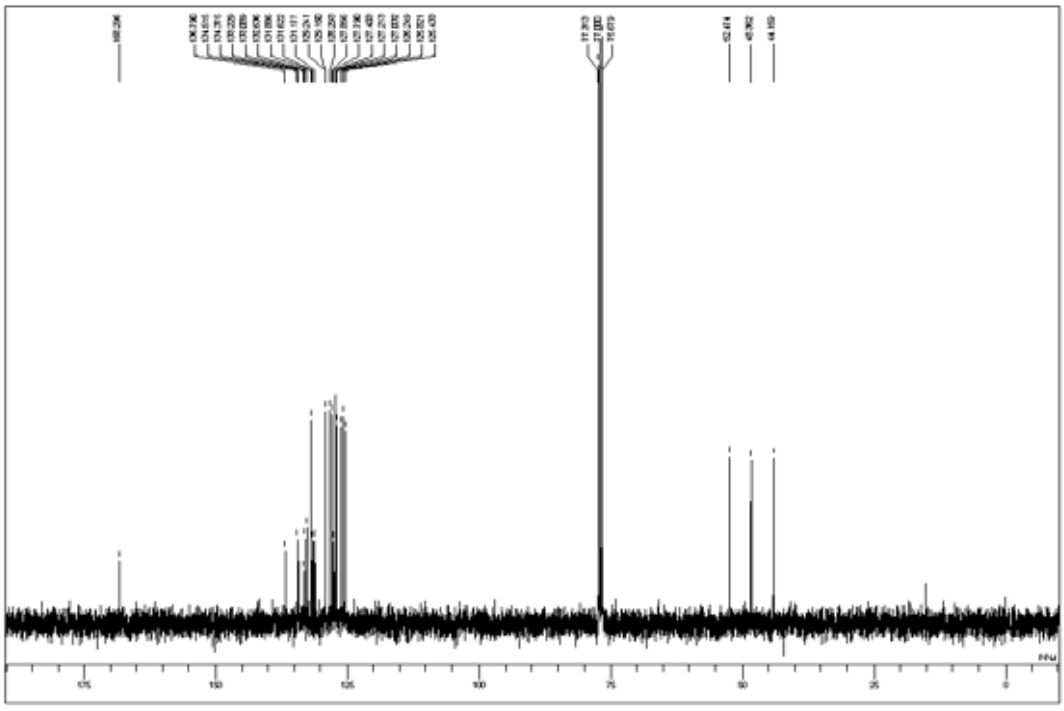

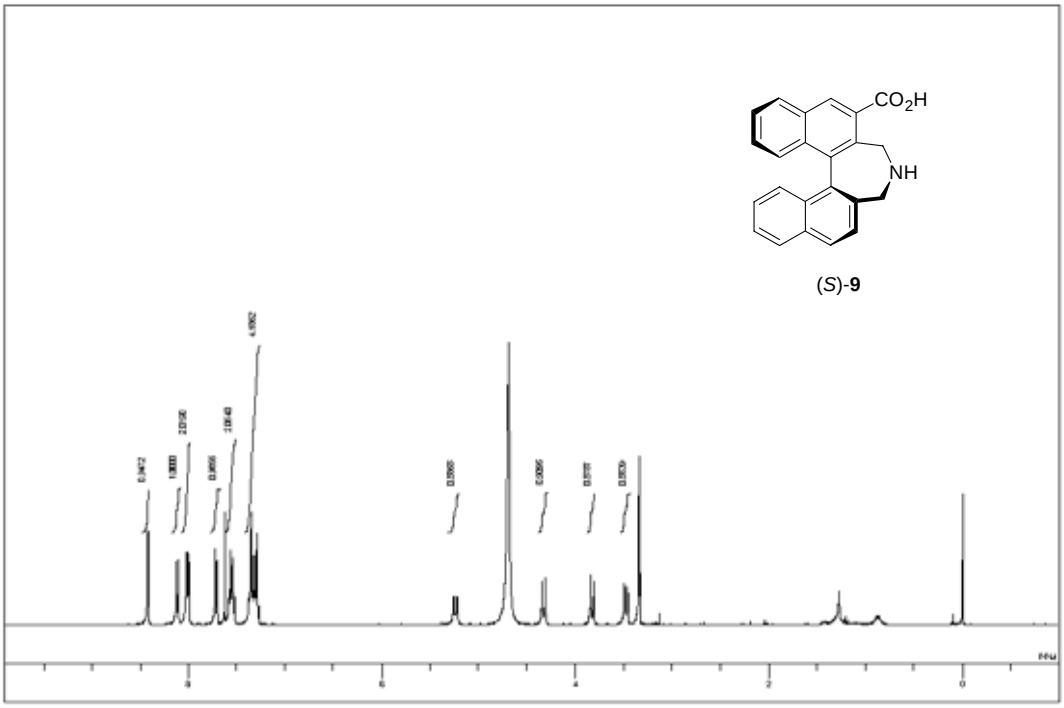

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