# Ruthenium(II) complexes of monodonor ligands; efficient reagents for asymmetric ketone hydrogenation.

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**Supporting information.**

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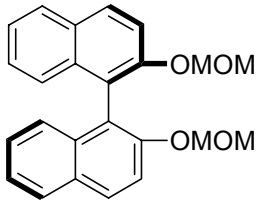
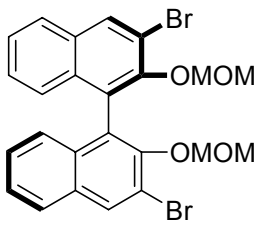
**Synthesis of (*R*)-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl**



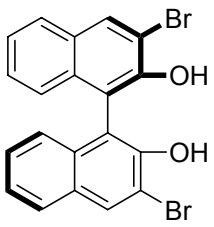

(*R*)-BINOL (5g, 0.017452 mol) in anhydrous THF (30 mL) was added dropwise at 0 $^{o}$C to a stirred suspension of NaH (2.79 g, 0.069808 mol, 4 e.q., 60% dispersion in mineral oil, prewashed using hexane) in anhydrous THF (50 mL). After H2 evolution ceased (~ 1.5 h), solution was stirred for an additional 0.5 h, and then bromomethyl methyl ether (4.58 g, 2.99 mL, 0.0366492 mol, 2.1 e.q.) was added dropwise. The reaction mixture was stirred overnight at room temperature. It was diluted with ether (130 mL), washed with water (2 x 40 mL), and then dried over $MgSO_4$. The mixture was filtered through silica gel and dried under high vacuo for 30 min to give (*R*)-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (6 g, 92%). m.p. 103 $^{o}$C-105 $^{o}$C; $[\alpha]_D^{21}$= + 84.0 (*c* 0.1, THF); IR: $\nu_{max}$ solid($cm^{-1}$) = 2904, 1590, 1505, 1236, 1146, 1010, 808; $^{1}$H NMR (250MHz, $CDCl_3$): δ= 7.78 (2H, d, *J* = 9.2 Hz), 7.70 (2H, d, *J* = 7.9 Hz), 7.43 (2H, d, *J* = 8.9), 7.17 (2H, m), 7.05 (4H, m), 4.86 (4H, dd, *J* = 6.7 Hz, *J* = 27.5 Hz), 2.97 (6H, s); $^{13}$C NMR (75MHz, $CDCl_3$) = 151.5 (s), 132.9 (s), 128.8 (s), 128.3 (s), 126.8 (s), 125.2 (s), 124.4 (s), 123.0 (s), 120.1 (s), 116.1 (s), 94.0 (s), 54.7 (s); MS: *m/z* ($EI^+$) =374 ($[M]^+$, 60%), 298 (75%), 269 (100%); HRMS: calc for $C_{24}H_{22}O_4$ : 374.1518 ($[M]^+$). Found 374.1527.

**Synthesis of (*R*)-3,3'-dibromo-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl**



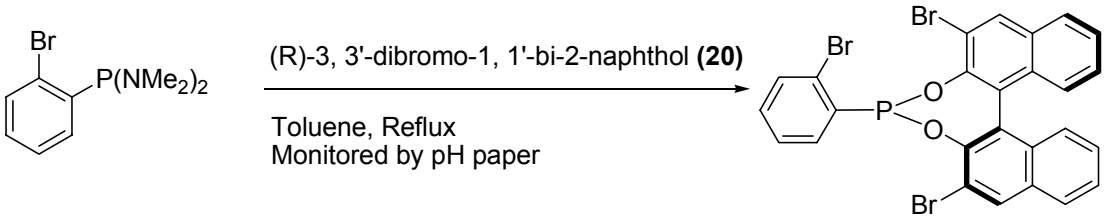

To a solution of (*R*)-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (3.0 g, 0.00801196 mol) in anhydrous THF (30 mL), n-BuLi (7.69 mL, 2.5 M, 0.0192287 mol, 2.4 e.q.) was added dropwise at -78 $^{o}$C under argon, and the solution colour changed from dark brown to yellow brown. The mixture was allowed to warm to 0 $^{o}$C, and stirred for 1 h, and then cooled to – 78 $^{o}$C again. To the mixture was added a solution of bromine (1.23 mL, 3.84 g, 0.024 mol, 3 e.q.) in pentane (10 mL) dropwise over 15 min and then let it warm to room temperature. After stirring over night at room temperature, the resulting mixture was poured into saturated $Na_2SO_3$. The organic layer was separated and aqueous phase was extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over $Na_2SO_4$. The mixture was filtered and evapourated, the resulting crude product was purified by column chromatography on silica gel (ethyl acetate / hexane = 1 : 10) to give the final product (*R*)-3, 3'-dibromo-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (2.17 g, 61.1%). $[\alpha]_D^{22}$= + 38.8 (*c* 0.17, THF); IR: $\nu_{max}$ neat($cm^{-1}$) = 2957, 1703, 1450, 1349, 1120, 748; $^1$H NMR (250MHz, $CDCl_3$): δ= 8.27 (2H, s), 7.81 (2H, d, *J* = 7.9 Hz), 7.44 (2H, dt, *J* = 1.2 Hz, *J* = 6.7 Hz), 7.26-7.34 (2H, m), 7.19 (2H, d, *J* = 8.3 Hz), 4.82-4.83 (4H, m), 2.56 (6H, s); $^{13}$C NMR (75MHz, $CDCl_3$) δ= 149.9 (s), 132.9 (s), 132.8 (s), 131.3 (s), 127.6 (s), 127.2 (s), 127.1 (s), 126.3 (s), 125.8 (s), 117.1 (s), 98.9 (s), 56.1 (s); MS: *m/z* (EI$^+$) = 531 ([M]$^+$, 10%), 456 (30%), 85 (100%); HRMS: calc for $C_{24}H_{20}O_4Br_2$ : 529.9728 ([M]$^+$). Found 529.9734.

**Synthesis of (*R*)-3, 3'-dibromo-1, 1'-bi-2-naphthol**




A mixture of (*R*)-3, 3'-dibromo-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (4.32 g, 0.008117 mol) and concentrated HCl (0.5 mL, 0.016234 mol, 2 e.q.) in 1, 4-dioxane (35 mL) was heated to 50 $^{o}$C and stirred overnight. The resulting mixture was poured into water (25 mL) and extracted with ethyl acetate. The organic extracts were washed with brine and dried over $Na_2SO_4$. The solvents were evapourated to give the crude product **(***R*)-3, 3'-dibromo-1, 1'-bi-2-naphthol (3.38 g, 93.5%). m.p. 208 $^{o}$C- 210 $^{o}$C; $[\alpha]_D^{22}$= + 38.5 (*c* 0.1, THF); IR: $\nu_{max}$ neat($cm^{-1}$) = 3213, 1578, 1495, 1219, 747; $^{1}$H NMR (300 MHz, $CDCl_3$): δ= 8.25 (2H, s), 7.80-7.82 (2H, d, *J* = 7.5 Hz), 7.28-7.41 (4H, m), 7.08-7.11 (2H, d, *J* = 8.5 Hz), 5.35 (2H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ= 148.4 (s), 137.7 (s), 133.2 (s), 130.2 (s), 128.0 (s), 127.8 (s), 125.3 (s), 125.1 (s), 115.0 (s), 112.7 (s); MS: *m/z* ($EI^+$) =444 ($[M]^+$, 100%), 364 (30%), 226 (47%); HRMS: calc for $C_{20}H_{12}O_2{}^{79}Br^{81}Br$: 443.9184 ($[M]^+$). Found 443.9188.

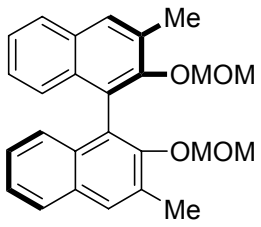
**Synthesis of (*R*)-3, 3'-dibromo-Br-XuPHOS 45**




To the dibromobinaphthol (0.380 g, 0.856 mmol) dissolved in anhydrous toluene (15 ml), a solution of *ortho*-bis(dimethylamino)phosphinobromobenzene (0.235 g, 0.856 mmol, 1 e.q.) in anhydrous toluene (10 ml) was slowly added. The reaction flask was stirred at

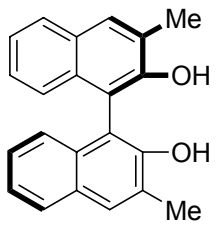
room temperature for 10 mins before being heated up to reflux for 16 h. Once complete, the mixture was allowed to cool to room temperature and the solvent removed (high vacuo, 40 °C oil bath). The yellow solid was dried to yield 275 mg (51%) of **45**, which was stored under argon. $^{1}$H NMR (400MHz, $CDCl_3$): δ = 8.33 (1H, s), 7.99 (1H, s), 7.88 (1H, d, *J* = 8.2 Hz), 7.76 (1H, d, *J* = 8.2 Hz), 7.59-7.62 (1H, m), 7.42-7.49 (2H, m), 7.25-7.34 (4H, m), 7.16-7.19 (1H, m), 7.09-7.11 (1H, m), 7.00 (1H, dt, *J* = 0.9 Hz, *J* = 7.3 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$): δ = 175 ppm. Prone to decomposition hence no MS or HRMS.

**Synthesis of (*R*)-3, 3'-dimethyl-2, 2'-bis(methoxymethoxy)-1,1'-binaphthyl**



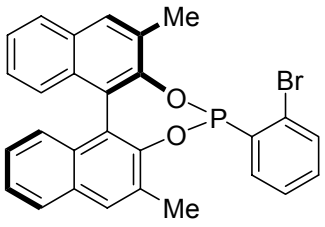

(*R*)-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (2.0 g, 5.34 mmol) was treated with n-BuLi (6.4 mL, 2.5 M in hexane, 16.0 mmol, 3 e.q.) at room temperature and stirred for 1 h. The resulting mixture was quenched with iodomethane (2.27 g, 1.0 mL, 16.0 mmol, 3 e.q.) for an addition of 1 h. The solution was washed with ethyl acetate (2 x 50 mL), $Na_2SO_3$ (30 mL) and brine (2 x 50 mL). The mixture was evapourated under reduced vacuo to give the product (*R*)-3, 3'-dimethyl-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (1.74 g, 81.0 %). m.p. 90 $^{o}$C- 92 $^{o}$C; $[\alpha]_D^{21}$= - 47.5 (*c* 0.1, THF); IR: $\nu_{max}$ neat($cm^{-1}$) = 2924, 1596, 1425, 1237, 1148, 950, 741; $^{1}$H NMR (300 MHz, $CDCl_3$): δ= 7.77-7.80 (4H, m), 7.31-7.38 (2H, m), 7.18 (4H, d, *J* = 4.4 Hz), 4.54 (4H, dd, *J* = 5.9 Hz, *J* = 34.9 Hz), 2.83 (6H, s), 2.57 (6H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ= 153.0 (s), 132.8 (s), 131.4 (s), 130.8 (s), 129.6 (s), 126.9 (s), 126.0 (s), 125.4 (s), 125.2 (s), 124.7 (s), 98.5 (s), 56.3 (s), 17.7 (s); MS: *m/z* (EI$^+$) = 402 ([M]$^+$, 100%); HRMS: calc for $C_{26}H_{26}O_4$ : 402.1831 ([M]$^+$). Found 402.1820.

**Synthesis of (*R*)-3, 3'-dimethyl-1, 1'-bi-2-naphthol**




(*R*)-3, 3'-dimethyl-2, 2'-bis(methoxymethoxy)-1, 1'-binaphthyl (1.5 g, 0.004 mol) treated with Amberlyst 15 (2.0 g) in THF/MeOH (30 mL, 1: 1). The reaction mixture was heated to reflux for 17 hours. Purification was carried out by column chromatography (ethyl acetate / hexane = 1: 5) to give slightly yellow solid (*R*)-3, 3'-dimethyl-1, 1'-bi-2-naphthol (540 mg, 47.7%). m.p. 206 $^{o}$C- 208 $^{o}$C; $[\alpha]_D^{17}$= + 58.5 (*c* 0.1, THF); IR: $\nu_{max}$ neat($cm^{-1}$) = 3371, 2915, 1625, 1432, 1210, 869; 7.80 (4H, s, Ar-H), 7.31-7.36 (2H, m, Ar-H), $^{1}$H NMR (300 MHz, $CDCl_3$): δ= 7.20-7.26 (2H, d, *J* = 4.4 Hz), 7.07 (2H, d, *J* = 8.3 Hz), 5.11 (2H, s), 2.51 (6H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ= 151.9 (s), 132.5 (s), 131.9 (s), 130.5 (s), 129.2 (s), 127.3 (s), 126.8 (s), 126.2 (s), 123.7-123.8 (d, *J* = 10.1 Hz), 110.2 (s), 16.8 (s); MS: *m/z* ($EI^+$) = 314 ($[M]^+$, 75%), 312 (40%), 296 (100%); HRMS: calc for $C_{22}H_{18}O_2$ : 314.1307 ($[M]^+$). Found 314.1312.

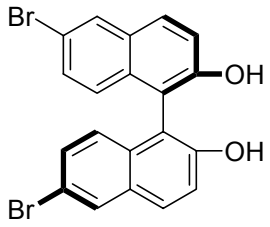
**Synthesis of (*R*)-3, 3'-dimethyl-Br-XuPHOS 46.**




To a solution containing 2-bis-(dimethylaminophosphino)-bromobenzene (0.455 g, 0.00165mol) dissolved in anhydrous toluene (25ml) was charged the (*R*)-3, 3'-dimethyl-1, 1'-bi-2-naphthol (0.520 g, 0.00165 mol) dissolved in anhydrous toluene (25ml). The

reaction flask was placed under argon in an oil bath and stirred at room temperature for 10 mins. It was heated up to reflux for 5 days. The reaction was monitored by $^{31}P$ NMR, and also the releasing dimethylamine gas was monitored by wet pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed under high vacuum to give a yellow solid (0.68 g, 82.6 %). m.p. 91 $^{o}$C- 95 $^{o}$C; $[\alpha]_D^{18}$= - 160.1 (*c* 0.14, DCM); IR: $\nu_{max}$ neat($cm^{-1}$) = 2918, 1501, 1413, 1238, 1096, 903, 740; $^{1}$H NMR (400 MHz, $CDCl_3$): δ= 7.87 (1H, s), 7.80-7.85 (1H, m), 7.74 (1H, d, *J* = 8.2 Hz), 7.58-7.61 (1H, m), 7.50 (1H, s), 7.06-7.41 (8H, m), 6.98 (1H, dt, *J* = 0.9 Hz, *J* = 7.3 Hz), 2.60 (6H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ= 151.9 (s), 148.4 (s), 147.3 (s), 137.7 (d, $J_{CP}$ = 41.6 Hz), 132.8 (d, $J_{CP}$ = 29.9 Hz), 131.5 (d, $J_{CP}$ = 17.2 Hz), 130.9 (d, $J_{CP}$ = 3.4 Hz), 130.5 (d, $J_{CP}$ = 33.9 Hz), 130.0 (s), 129.1 (s), 128.5 (d, $J_{CP}$ = 39.1 Hz), 127.3-127.4 (m), 126.6-126.7 (m), 125.0 (d, $J_{CP}$ = 17.2 Hz), 124.7 (d, $J_{CP}$ = 20.1 Hz), 123.8 (d, $J_{CP}$ = 21.8 Hz), 17.0 (d, $J_{CP}$ = 20.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) δ= 167.4; MS: *m/z* (EI$^+$) = 499 ([M]$^+$, 60%), 314 (75%), 83 (100%); HRMS: calc for $C_{28}H_{20}BrO_2P$ : 497.0306 ([M-H]$^+$). Found 497.0306.

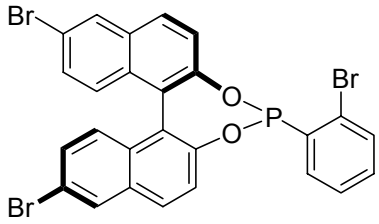
**Synthesis of (*R*)-6, 6'-dibromo-1, 1'-bi-2-naphthol.**




To a solution of (*R*)-BINOL (1.43 g, 0.005 mol) in DCM (50 mL) at – 78 $^{o}$C, bromine (2.4 g, 0.015 mol, 3 e.q., 0.78 mL) in DCM (5 mL) was added dropwise. The resulting brown solution was stirred at room temperature for 24 h. Saturated sodium thiosulfate was added and the solution was stirred for 30 min. The organic layer was separated and aqueous layer was extracted with EtOAc (3 x 30 mL), the combined organic layer was washed with water, ether (3 x 50 mL), brine and dried over $MgSO_4$. The mixture was filtered, vacuumed down and purified by column chromatography (ethyl acetate / hexane

= 3: 10) to give clear brown oil, and it was percipitated by doing azeotrop with ether to give light brown powder (1.85 g, 39.8%). m.p. 93 $^{o}$C- 95 $^{o}$C; $[\alpha]_D^{17}$= - 24.6 (*c* 0.126, $CH_3COOH$); IR: $\nu_{max}$ neat($cm^{-1}$) = 3395, 1905, 1703, 1587, 1493, 1266, 1143, 811, 668; $^{1}$H NMR (400 MHz, $CDCl_3$): δ= 8.04 (2H, d, *J* = 2.0 Hz), 7.88 (2H, d, *J* = 9.0 Hz), 7.38 (2H, d, *J* = 9.0 Hz), 7.37 (2H, dd, *J* = 2.0 Hz, *J* = 8.8 Hz), 6.96 (2H, d, *J* = 9.0 Hz), 5.0 (2H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ= 153.0 (s), 131.9 (s), 130.9 (s), 130.7 (s), 130.6 (s), 130.5 (s), 125.9 (s), 119.0 (s), 118.0 (s), 110.7 (s); MS: *m/z* ($CI^+$) = 444 ($[M]^+$, 100%), 142 (20%); HRMS: calc for $C_{20}H_{12}Br_2O_2$ : 443.9184 ($[M]^+$). Found 443.9191.

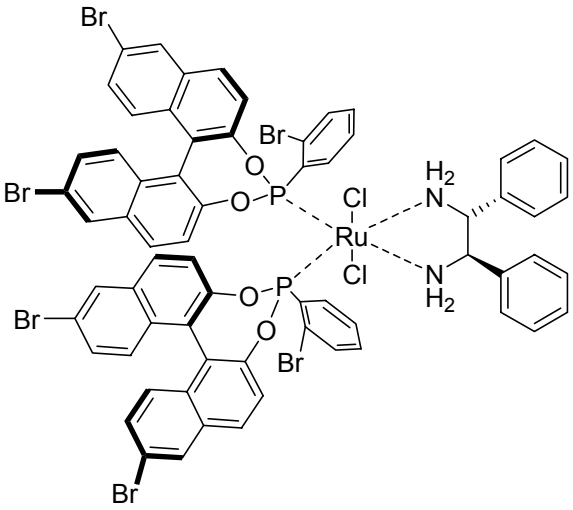
**Synthesis of (*R*)-6, 6'-dibromo-Br-XuPHOS 47.**




To a solution containing 2-bis-(dimethylaminophosphino)-bromobenzene (0.285 g, 0.001013 mol) dissolved in anhydrous toluene (25ml) was charged the (*R*)-3, 3'-dimethyl-1, 1'-bi-2-naphthol (0.451 g, 0.001013 mol) dissolved in anhydrous toluene (25ml). The reaction flask was placed under argon in an oil bath and stirred at room temperature for 10 mins. It was heated up to reflux for 10 hrs. The reaction was monitored by $^{31}$P NMR, and also the releasing dimethylamine gas was monitored by wet pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed under high vacuum to give a white solid (0.45 g, 71.0 %). m.p. 116 $^{o}$C-118 $^{o}$C; $[\alpha]_D^{17}$= - 56.7 (*c* 0.10, DCM); IR: $\nu_{max}$ neat($cm^{-1}$) = 2917, 1580, 1491, 1323, 1230, 934, 817, 751, 691; $^{1}$H NMR (400 MHz, $CDCl_3$): δ= 8.10 (1H, d, *J* = 2.2 Hz), 7.95 (1H, d, *J* = 2.16 Hz), 7.61-7.59 (2H, m), 7.50 (1H, d, *J* = 8.8 Hz), 7.39-7.13 (7H, m), 7.00 (1H, t, *J* = 7.6 Hz), 6.80 (1H, d, *J* = 8.8 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ= 153.1 (s), 150.1 (s), 149.2 (d, $J_{CP}$ = 6.1 Hz), 137.5 (d, *JCP* = 41.0 Hz), 133.0 (s), 132.9 (d, $J_{CP}$

= 60.9 Hz), 131.4 (d, $J_{CP}$ = 5.0 Hz), 130.4-130.8 (m), 129.9-130.1 (m), 128.9 (s), 128.3 (d, $J_{CP}$ = 6.5 Hz), 127.5 (d, $J_{CP}$ = 35.3 Hz), 127.0 (s), 124.5 (d, $J_{CP}$ = 5.4 Hz), 123.6 (d, $J_{CP}$ = 1.9 Hz), 122.8 (s), 119.2 (d, $J_{CP}$ = 25.0 Hz), 119.2 (s); $^{31}$P NMR (162 MHz, $CDCl_3$) δ= 175.5; LSIMS: *m/z* ($E^+$) = 630 ($[M+H]^+$, 100%), 549 (65%), 470 (50%); HRMS: calc for $C_{26}H_{14}Br_3O_2P$ : 625.8282 ($[M]^+$). Found 625.8281.

**Synthesis of (*R, R, RR*) 6, 6'-diBr BrXuPHOS (47)-Ru-DPEN**




$[RuCl_2(C_6H_6)]_2$ (111 mg, 0.223 mmol) and *(R)* 6, 6'-diBr BrXuPHOS (561 mg, 0.892 mmol, 4e.q.) were placed in a 50-ml schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (10 ml) was added, the mixture was degassed and stirred under argon at 100 $^oC$ for 15 min to form a reddish brown solution. After the solution was cooled down to the room temperature, *(R)*-DPEN (95 mg, 0.446 mmol, 2e.q.) was added and the mixture was degassed again before it was stirred for 3h. During the reaction, yellow solid precipitated out. After the reaction finished, DCM (30—60ml) was added into the reaction mixture for several times, and at each time it was turned on the high vacuum and back to argon, to do azeotrope to get rid of remaining DMF. The resulting dark brown solid was dried under the high vacuum to give the final product (*R, R, RR*) 6, 6-diBr BrXuPHOS-Ru-DPEN (0.447 g, 76.1 %). m.p. 200-202 $^oC$ (dec.); $[\alpha]_D^{20}$= + 96.7 (*c* 0.14, $CH_2Cl_2$); IR: $\nu_{max}$ solid($cm^{-1}$) = 3058, 1668, 1491, 1322, 1226, 820, 698; $^1$H NMR

(400 MHz, $CDCl_3$) δ= 8.18-8.01 (4H, m), 7.89-7.71 (6H, m), 7.54-7.52 (2H, m), 7.41-6.87 (22H, m), 6.67-6.58 (2H, m), 6.22-6.17 (2H, m), 4.52-4.57 (2H, m), 4.18-4.35 (2H, m), 2.73-2.76 (2H, m); $^{31}P$ NMR (162 MHz, $CDCl_3$) δ= 205.3.

**2) Data for reduction products.**

**(*R*)-(+)-1-phenylethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 95 % and 93.0 % by chiral GC analysis. $[\alpha]_D^{26}$ +46.0 (*c* 0.84, $CH_2Cl_2$) (lit.[1] $[\alpha]_D^{23}$ +48.6 (*c* 1.0, $CH_2Cl_2$), 96% e.e. (*R*)), 93.0 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 115 °C, P = 7 psi, *R* isomer 20.0 min, *S* isomer 21.3 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.32-7.24 (4H, m), 7.21-7.16 (1H, m), 4.76 (1H, q, *J* 6.4 Hz), 4.40 (1H, bs), 1.40 (3H, d, J 6.6 Hz).

**(*R*)-(+)-1-(2'-fluorophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 68 % and 54 % by chiral GC analysis. $[\alpha]_D^{18}$ +23.0 (*c* 0.774, MeOH) (lit.[2] $[\alpha]_D^{25}$ -44.5 (*c* 0.782, MeOH), 99 % e.e. (*S*)), 54 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 120 °C, *R* isomer 13.1 min, *S* isomer 13.9 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.41 (1H, td, *J* 1.3 Hz, *J* 7.5 Hz), 7.22-7.13 (1H, m), 7.07 (1H, t, *J* 7.35 Hz), 6.94 (1H, t, *J* 9.1 Hz), 5.09 (1H, q, *J* 6.4 Hz), 3.51 (1H, bs), 1.40 (3H, d, *J* 6.6 Hz).

**(*R*)-(+)-1-(4'-chlorophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 99 % and 86 % by chiral GC analysis. $[\alpha]_D^{22}$ +40.4 (*c* 0.74, ether) (lit.[2] $[\alpha]_D^{25}$ -49 (*c* 1.84, ether), 99 % e.e. (*S*)), 86% e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 150 °C, *R* isomer 16.5 min, *S* isomer 17.1 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.23-7.21 (2H, m), 7.16-7.13 (2H, m), 4.68 (1H, q, *J* 6.4 Hz), 3.86 (1H, bs), 1.33 (3H, d, *J* 6.4 Hz).

**(*R*)-(+)-1-(3'-chlorophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 96.2 % and 88 % by chiral GC analysis. $[\alpha]_D^{19}$ +31.4 (*c* 0.74, $CHCl_3$) (lit.[2] $[\alpha]_D^{25}$ -43.5 (*c* 1.08, $CHCl_3$), 99% e.e. (*S*)), 88% e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 150 °C, P = 10 psi, *R* isomer 16.4 min, *S* isomer 16.9 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.27 (1H, s), 7.20-7.15 (2H, m), 7.14-7.10 (1H, m), 4.70 (1H, q, *J* 6.4 Hz), 3.71 (1H, bs), 1.35 (3H, d, *J* 6.6 Hz).

**(*R*)-(+)-1-(2'-chlorophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 97 % and 95 % by chiral GC analysis. $[\alpha]_D^{19}$ +61.0 (*c* 0.74, $CHCl_3$) (lit.[2] $[\alpha]_D^{25}$ -62.7 (*c* 0.894, $CHCl_3$), 99 % e.e. (*S*)), 95% e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 150 °C, P = 10 psi, *R* isomer 11.2 min, *S* isomer 12.1 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.41 (1H, dd, *J* 1.9 Hz, *J* 7.7 Hz), 7.18-7.09 (2H, m), 7.05-7.00 (1H, m), 5.11 (1H, dq, *J* 3.0 Hz, *J* 6.2 Hz), 3.87 (1H, d, *J* 3.2 Hz), 1.29 (3H, d, *J* 6.4 Hz).

**(*R*)-(+)-1-(2'-bromophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 93 % and 99 % by chiral GC analysis. $[\alpha]_D^{25}$ +54.1 (*c* 1.18, $CHCl_3$) (lit.[3a,b] $[\alpha]_D^{24}$ -54.6 (*c* 1.23, $CHCl_3$), 99 % e.e. (*S*)), 99.0 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 145 °C, P = 10 psi, *R* isomer 26.2 min, *S* isomer 30.7 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.53 (1H, dd, *J* 1.7 Hz, *J* 7.7 Hz), 7.46 (1H, dd, *J* 1.32 Hz, *J* 7.9 Hz), 7.32-7.26 (1H, m), 7.10-7.05 (1H, m), 5.17 (1H, dq, $J_{Br\text{-}H}$ 3.0 Hz, *J* 6.4 Hz), 2.98 (1H, d, *J* 2.8 Hz), 1.41 (3H, d, *J* 6.4 Hz).

**(*R*)-(+)-1-(4'-iodophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 89 % by chiral GC analysis. $[\alpha]_D^{21}$ +25.3 (*c* 0.632, $CHCl_3$) (lit.[4a] $[\alpha]_D^{26}$ +35.0 (*c* 1.0, $CHCl_3$), 99 % e.e. (*R*)), 89.0 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 160 °C, P = 10 psi, *R* isomer 28.6 min, *S* isomer 29.6 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.67 (2H, d, *J* 8.3 Hz), 7.12 (2H, d, *J* 8.1 Hz), 4.84 (1H, q, *J* 6.4 Hz), 1.96 (1H, bs), 1.46 (3H, d, *J* 6.6 Hz).

**(*R*)-(+)-1-(2'-iodophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 98 % and 99 % by chiral GC analysis. $[\alpha]_D^{18}$ +43.9 (*c* 0.50, $CHCl_3$) (lit.[2,3c] $[\alpha]_D^{24}$ +37.7 (*c* 0.934, $CHCl_3$), 86 % e.e. (*R*)), 99 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 160 °C, P = 10 psi, *R* isomer 18.9 min, *S* isomer 21.5 min). $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.79 (1H, d, *J* 7.7 Hz), 7.55 (1H, dd, *J* 1.7 Hz, *J* 7.7 Hz), 7.37 (1H, td, *J* 1.1 Hz, *J* 7.7 Hz), 6.96 (1H, td, *J* 1.7 Hz, *J* 7.5 Hz), 5.06 (1H, q, *J* 6.2 Hz), 2.15 (1H, bs), 1.45 (3H, d, *J* 6.4 Hz).

**(*R*)-(+)-1-(2'-methylphenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 99 % and 95 % by chiral GC analysis. $[\alpha]_D^{20}$ +60.6 (*c* 0.71, EtOH) (lit.[2] $[\alpha]_D^{25}$ -64.3 (*c* 1.04, EtOH), >99 % e.e. (*S*)), 95 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 125 $^oC$, P = 10 psi, *R* isomer 19.9 min, *S* isomer 22.7 min). $^1H$ NMR (300 MHz, $CDCl_3$) δ = 7.39 (1H, dd, *J* 1.5 Hz, *J* 7.4 Hz), 7.15-7.00 (3H, m), 4.90 (1H, q, *J* 6.4 Hz), 3.47 (1H, s), 2.20 (3H, s), 1.30 (3H, d, *J* 6.4 Hz).

**(*R*)-(+)-1-(3'-trifluoromethylphenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 83 % by chiral GC analysis. $[\alpha]_D^{21}$ +20.6 (*c* 0.56, MeOH) (lit.[2] $[\alpha]_D^{22}$ -28.4 (*c* 1.26, MeOH), >99 % e.e. (*S*)), 83.3 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 120 $^oC$, P = 10 psi, *R* isomer 17.3 min, *S* isomer 18.6 min). $^1H$ NMR (300 MHz, $CDCl_3$) δ = 7.59 (1H, s), 7.48 (2H, t, *J* 7.5 Hz), 7.40 (1H, t, *J* 7.7 Hz), 4.84 (1H, q, *J* 6.6 Hz), 3.35 (1H, bs), 1.41 (3H, d, *J* 6.6 Hz).

**(*R*)-(+)-1-(2', 3'-difluorophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 97.0 % and 62.0 % by chiral GC analysis. $[\alpha]_D^{23}$ + 25.1 (*c* 0.5, $CH_2Cl_2$), 62.0 % e.e. (*R*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), 15 psi, T = 120 $^oC$, *S* isomer 14.4 min, *R* isomer 15.1 min). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.20-7.16 (1H, m), 7.06-6.99 (2H, m), 5.15-5.09 (1H, m), 3.47 (1H, d, *J* = 3.76 Hz), 1.44 (3H, d, *J* = 6.5 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ= 150.6 (dd, *J* = 13.2 Hz, *J* = 247.7 Hz), 147.8 (dd, *J* = 13.2 Hz, *J* = 247.7 Hz), 135.5 (d, *J* = 9.8 Hz), 124.5 (d, *J* = 6.3 Hz), 121.6 (s), 116.2 (d, *J* = 16.7 Hz), 64.3 (s), 24.3 (s); IR: $\nu_{max}$ neat/$cm^{-1}$ = 3331, 2978, 1482, 1275, 783, 725; MS: *m/z* ($EI^+$) = 158 ($[M]^+$, 15%), 143 (100%); HRMS: calc for $C_8H_8F_2O$: 158.0543 ($[M]^+$). Found 158.0549.

**(*R*)-(+)-1-(2', 3'-dichlorophenyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 95.1 % by chiral GC analysis. $[\alpha]_D^{23}$ + 53.9 (*c* 0.46, $CH_2Cl_2$), 95.1 % e.e. (*R*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), 15 psi, T = 160 $^oC$, *S* isomer 17.5 min, *R* isomer 18.4 min). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.39 (1H, dd, *J* = 1.5 Hz, *J* = 7.8 Hz), 7.31 (1H, dd, *J* = 1.5 Hz, *J* = 7.8 Hz), 5.20-5.15 (1H, m), 3.70 (1H, d, *J* = 2.2 Hz), 1.37 (3H, d, *J* = 6.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ= 145.3 (s), 132.6 (s), 129.4 (s), 128.8 (s), 127.4 (s), 124.2 (s), 67.1 (s), 23.2 (q); IR: $\nu_{max}$ neat/$cm^{-1}$ = 3319,

2974, 1417, 1181, 782, 718; MS: *m/z* ($EI^+$) = 190 ($[M-H]^+$, 20%), 175 (100%); HRMS: calc for $C_8H_8Cl_2O$: 189.9952 ($[M]^+$). Found 189.9943.

**(*R*)-(+)-1-(1'-naphthyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 92 % and 99 % by chiral GC analysis. $[\alpha]_D^{28}$ +77.2 (*c* 0.67, ether) (lit.[4b] $[\alpha]_D^{25}$ +77.0 (*c* 1.02, ether), 98 % e.e. (*R*)), 99 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 155 $^oC$, P = 10 psi, *S* isomer 60.4 min, *R* isomer 62.3 min). $^1H$ NMR (300 MHz, $CDCl_3$) δ = 7.87-7.83 (1H, m), 7.73-7.70 (1H, m), 7.60 (1H, d, *J* 8.10 Hz), 7.48 (1H, d, *J* 7.0 Hz), 7.36-7.33 (2H, m), 7.27 (1H, t, *J* 7.7 Hz), 5.35 (1H, q, *J* 6.4 Hz), 3.32 (1H, bs), 1.43 (3H, d, *J* 6.6 Hz).

**(*R*)-(+)-1-phenylpropan-1-ol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 97.2 % and 90.0 % by chiral GC analysis. $[\alpha]_D^{19}$ +42.3 (*c* 0.78, $CHCl_3$) (lit.[2] $[\alpha]_D^{25}$ -47.2 (*c* 0.643, $CHCl_3$), >99 % e.e. (*S*)), 90.0 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 115 $^oC$, P = 15 psi, *R* isomer 20.7 min, *S* isomer 21.8 min). $^1H$ NMR (300 MHz, $CDCl_3$) δ = 7.25-7.16 (5H, m), 4.41 (1H, t, *J* 6.0 Hz), 2.94 (1H, s), 1.75-1.58 (2H, m), 0.81 (3H, t, *J* 7.4 Hz).

**(*R*)-(+)-2-methyl-1-phenyl-propan-1-ol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 99 % and 75 % by chiral GC analysis. $[\alpha]_D^{21}$ +31.6 (*c* 1.24, ether) (lit.[2] $[\alpha]_D^{26}$ -49.1 (*c* 0.828, ether), 99 % e.e. (*S*)), 75.0 % e.e. (*R*) by GC (Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 120 $^oC$, P = 15 psi, *R* isomer 22.4 min, *S* isomer 23.0 min). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.26-7.22 (5H, m), 4.31 (1H, d, *J* 7.0 Hz), 2.26 (1H, bs), 1.95-1.89 (1H, m), 0.98 (3H, d, *J* 6.7 Hz), 0.78 (3H, d, *J* 7.0 Hz).

**(*S*)-(+)-2-phenoxy-1-phenylethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 76 % by $^1H$ NMR and chiral HPLC analysis. $[\alpha]_D^{20}$ + 29.2 (*c* 0.44, $CHCl_3$) (lit.[3d] $[\alpha]_D^{20}$ + 19 (*c* 2, $CHCl_3$), 99% e.e. (*S*)), 76% e.e. (*S*) by HPLC (column, Chiralcel OD, ethanol/hexane = 7 : 93), 1.0 mL $min^{-1}$, *R* isomer 12.8 min, *S* isomer 16.8 min). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.34-7.14 (7H, m), 6.88-6.78 (3H, m), 4.98 (1H, dd, *J* = 3.0 Hz, *J* = 8.5 Hz), 3.95-3.85 (2H, m), 3.02 (1H, s).

**(*R*)-(+)-1-(2-thienyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 52 % by chiral GC analysis. $[\alpha]_D^{20}$ +15.2 (*c* 0.5, $CHCl_3$) (lit.[4c] $[\alpha]_D^{25}$ –26.0 (*c* 1.02, $CH_3Cl_3$), 99% e.e. (*S*)), 52% e.e. (*R*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 125 $^oC$, P = 7 psi, *R* isomer 14.6 min, *S* isomer 15.2 min). $^1H$ NMR (400 MHz, $CDCl_3$) 7.27-7.21 (1H, m), 6.93-6.97 (2H, m), 5.12 (1H, q, *J* 6.0 Hz), 2.20 (1H, bs), 1.59 (3H, d, J 6.8 Hz).

**(*R*)-(+)-1-(3-thienyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 91 % by chiral GC analysis. $[\alpha]_D^{24}$ +33.8 (*c* 0.43, $CH_3CH_2OH$) (lit.[4c] $[\alpha]_D^{25}$ –44.7 (*c* 1.00, EtOH), 99% e.e. (*S*)), 86% e.e. (*R*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), T = 125 $^oC$, P = 7 psi, *R* isomer 15.9 min, *S* isomer 16.5 min). $^1H$ NMR (300 MHz, $CDCl_3$) δ = 7.25 (1H, dd, *J* 3.0 Hz, *J* 5.1 Hz), 7.12-7.11 (1H, m), 7.05 (1H, dd, *J* 1.3 Hz, *J* 5.1 Hz), 4.87 (1H, m), 3.19 (1H, d, *J* 3.9 Hz), 1.45 (3H, d, *J* 6.4 Hz).

**(*R*)-(+)-1-(2, 5-dichloro-3-thienyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 92.1 % by chiral GC analysis. $[\alpha]_D^{21}$ + 6.75 (*c* 0.2, $CHCl_3$) 92.1% e.e. (*R*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), 15 psi, T = 160 $^oC$, *R* isomer 11.4 min, *S* isomer 12.2 min). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 6.83 (1H, s), 4.92 (1H, dq, *J* = 2.0 Hz, *J* = 6.5 Hz), 3.25 (1H, d, *J* = 2.0 Hz), 1.38 (3H, d, *J* = 6.5 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ= 143.2 (s), 126.2 (s), 124.7 (s), 120.4 (s), 120.4 (s), 63.4 (s), 23.2 (s); IR: $\nu_{max}$ neat/$cm^{-1}$ = 3295, 2974, 2361, 1433, 1109, 1036; MS: *m/z* ($EI^+$) = 196 ([M-H]$^+$, 45%), 181 (100%); HRMS: calc for $C_6H_6Cl_2OS$: 195.9516 ($[M]^+$). Found 195.9507.

**(*R*)-(+)-1-(2, 5-dimethyl-3-thienyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 96.0 % and 97.0 % by chiral GC analysis. $[\alpha]_D^{21}$ + 7.0 (*c* 0.45, $CHCl_3$) 97.0 % e.e. (*R*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), 15 psi, T = 145 $^oC$, *R* isomer 10.7 min, *S* isomer 11.1 min). (400 MHz, $CDCl_3$) δ = 6.64 (1H, s), 4.82 (1H, q, *J* = 6.5 Hz), 2.41 (1H, d, *J* = 3.3 Hz), 2.37 (3H, s), 2.31 (3H, s), 1.39 (3H, d, J = 6.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ= 141.5 (s), 135.2 (s), 130.6 (s), 123.9 (s), 63.7 (s),

23.8 (s), 14.8 (s), 12.3 (s); IR: $\nu_{max}$ neat/cm$^{-1}$ = 3364, 2970, 2918, 1444, 1366, 1068; MS: *m/z* (EI$^+$) = 156 ([M]$^+$, 45%), 138 (100%); HRMS: calc for $C_8H_{12}OS$: 156.0609 ([M]$^+$). Found 156.0613.

**(*R*)-(+)-1-(3-pyridyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 99 % and 70 % by chiral GC analysis. $[\alpha]_D^{20}$ +37.0 (*c* 1.46, EtOH) (lit.[4c] $[\alpha]_D^{25}$ –56.3 (*c* 1.00, EtOH), 99% e.e. (*S*)), 70% e.e. (*R*) by GC (column, Chirasil-DEX CB), T = 120 $^o$C, *R* isomer 13.9 min, *S* isomer 14.9 min). $^1$H NMR (300 MHz, $CDCl_3$) 8.42 (1H, d, *J* 2.3 Hz), 8.32 (1H, dd, *J* 1.7 Hz, *J* 4.9 Hz), 7.74 (1H, dd, *J* 1.9 Hz, *J* 7.9 Hz), 7.24 (1H, dd, *J* 4.9 Hz, *J* 7.9 Hz), 4.88 (1H, q, *J* 6.2 Hz), 4.60 (1H, bs), 1.47 (3H, d, *J* 6.6 Hz).

**(*R*)-(+)-1-(4-pyridyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 93 % by chiral HPLC analysis. $[\alpha]_D^{21}$ +51.2 (*c* 0.122, EtOH) (lit.[4c] $[\alpha]_D^{25}$ –54.9 (*c* 1.02, EtOH), 99% e.e. (*S*)), 93% e.e. (*R*) by HPLC (column, Chiralcel OD-H, 10% isopropanol/hexane), 0.5 mL min$^{-1}$, *R* isomer 22.4 min, *S* isomer 32.3 min). $^1$H NMR (400 MHz, $CDCl_3$) 8.44 (2H, dd, *J* 1.7 Hz, *J* 4.5 Hz), 7.30 (2H, dd, *J* 1.5 Hz, *J* 4.7 Hz), 4.88 (1H, q, J 6.5 Hz), 4.10 (1H, bs), 1.48 (3H, d, *J* 6.5 Hz).

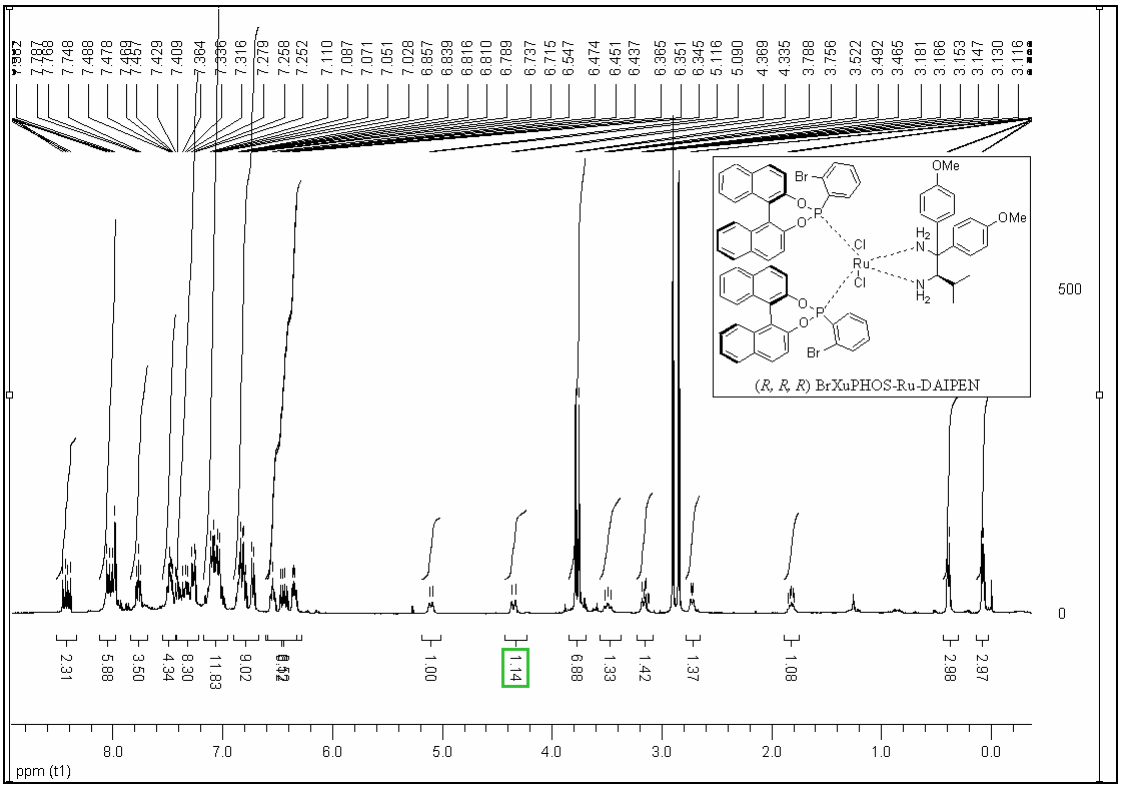
***(S)*-(+)-1-(cyclohexyl)ethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 99 % and 68 % by chiral GC analysis. $[\alpha]_D^{29}$ +1.82 (*c* 0.3, $CHCl_3$) (lit.[5] $[\alpha]_D^{25}$ +3.51 (*c* 3.1, $CHCl_3$), 95% e.e. (*S*)), 68% e.e. (*S*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), 10 psi, T = 100 $^o$C, *R* isomer 22.1 min, *S* isomer 22.4 min). $^1$H NMR (400 MHz, $CDCl_3$) δ = 3.51 (1H, quin, *J* 6.3 Hz), 2.70 (1H, bs), 1.87-1.84 (1H, m), 1.78-1.73 (2H, m), 1.68-1.65 (2H, m), 1.29-1.12 (4H, m), 1.13 (3H, d, *J* 6.5 Hz), 1.04-0.90 (2H, m).

**(*S*)-(-)-1-Admantanylethanol:** The conversion and the enantiomeric excess of the product were respectively determined to be of 100 % and 61 % by chiral GC analysis. $[\alpha]_D^{21}$ -0.95 (*c* 0.16, $CHCl_3$) (lit.[6] $[\alpha]_D^{25}$ -1.6 (*c* 2.2, $CHCl_3$), 99% e.e. (*S*)), 61% e.e. (*S*) by GC (column, Cyclodextrin-β-236M-19 (CHROMPAC, 50m), 15 psi, T = 135 $^o$C, *R* isomer 38.7 min, *S* isomer 39.0 min). $^1$H

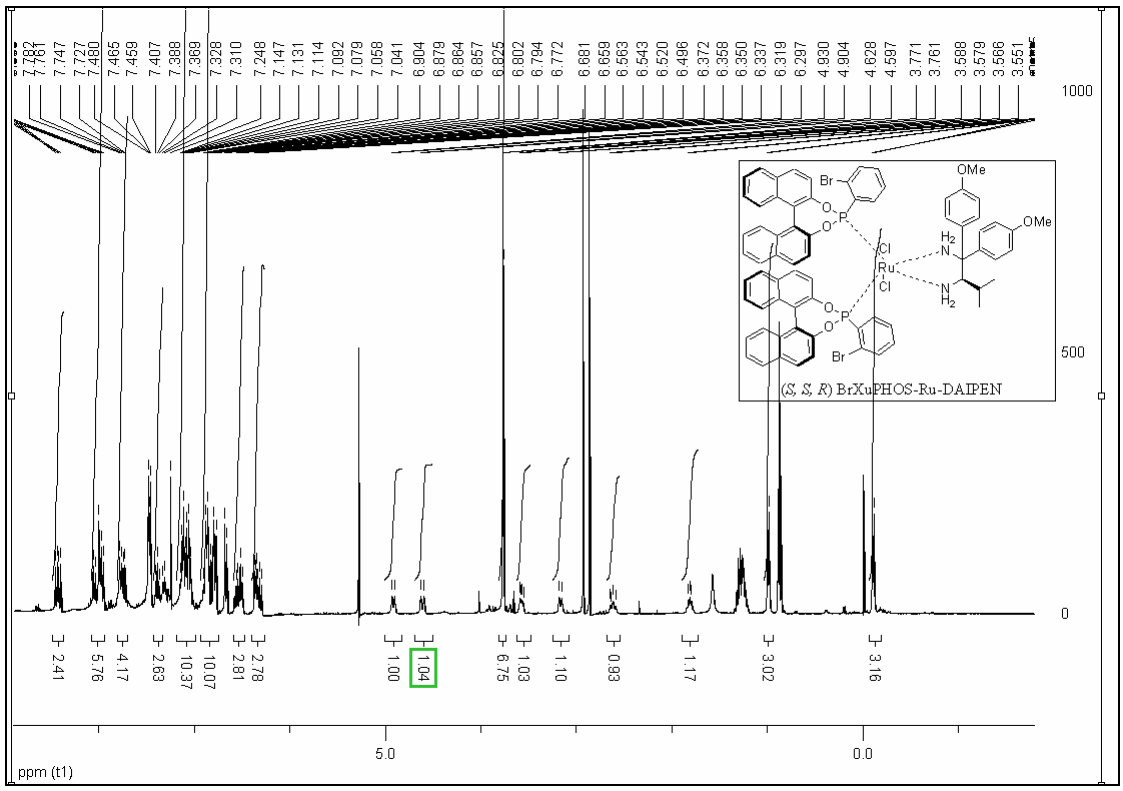
NMR (400 MHz, $CDCl_3$) δ = 3.27 (1H, q), 1.99 (3H, m), 1.73-1.70 (3H, m), 1.66-1.57 (6H, m), 1.50-1.46 (3H, m), 1.25 (1H, bs), 1.09 (3H, d, J 6.8 Hz).

**3) 1H-NMR and 13C-NMR of all new compounds lacking CHN analysis:**

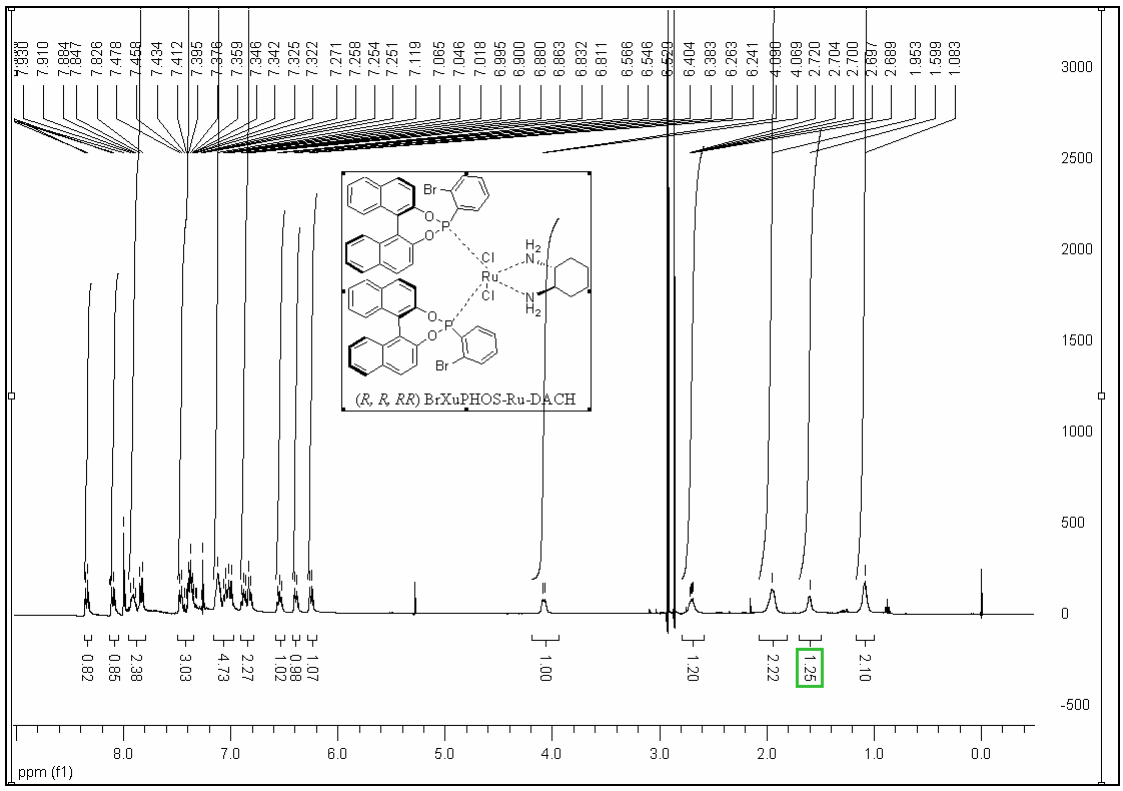
$^{1}$H NMR of (*R, R, R*) BrXuPHOS-Ru-DAIPEN



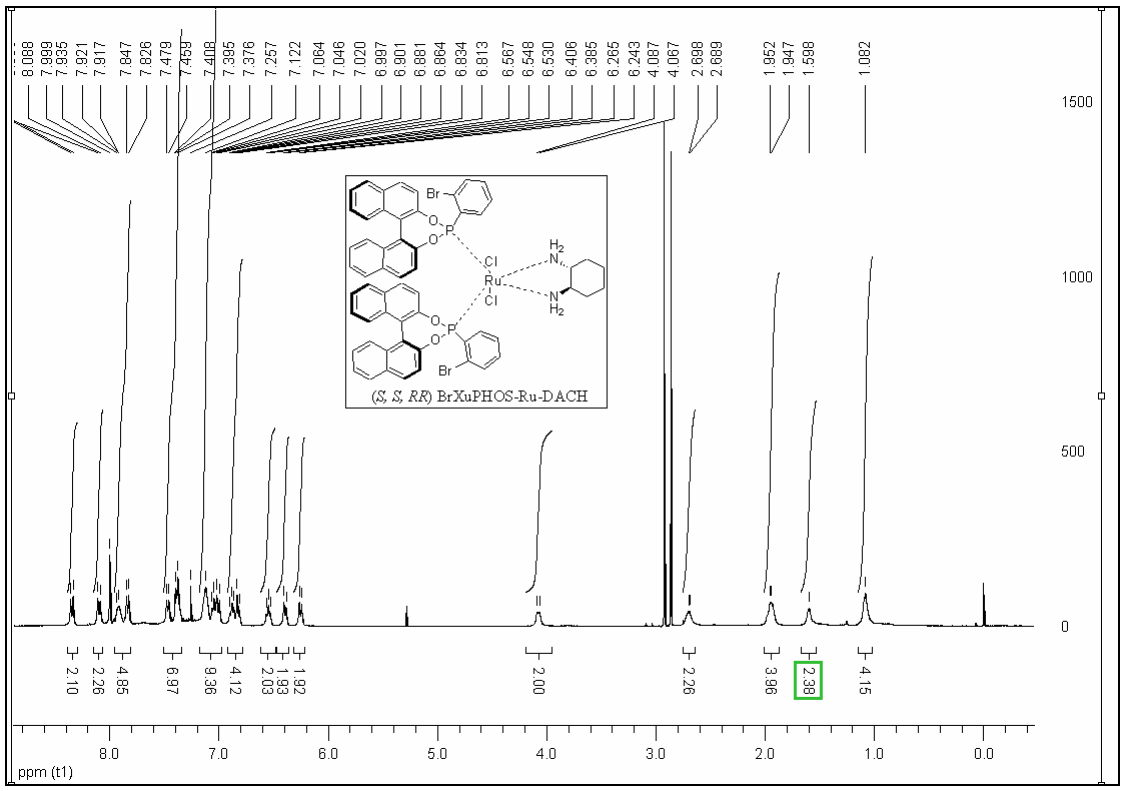
$^{1}$H NMR of (*S, S, R*) BrXuPHOS-Ru-DAIPEN



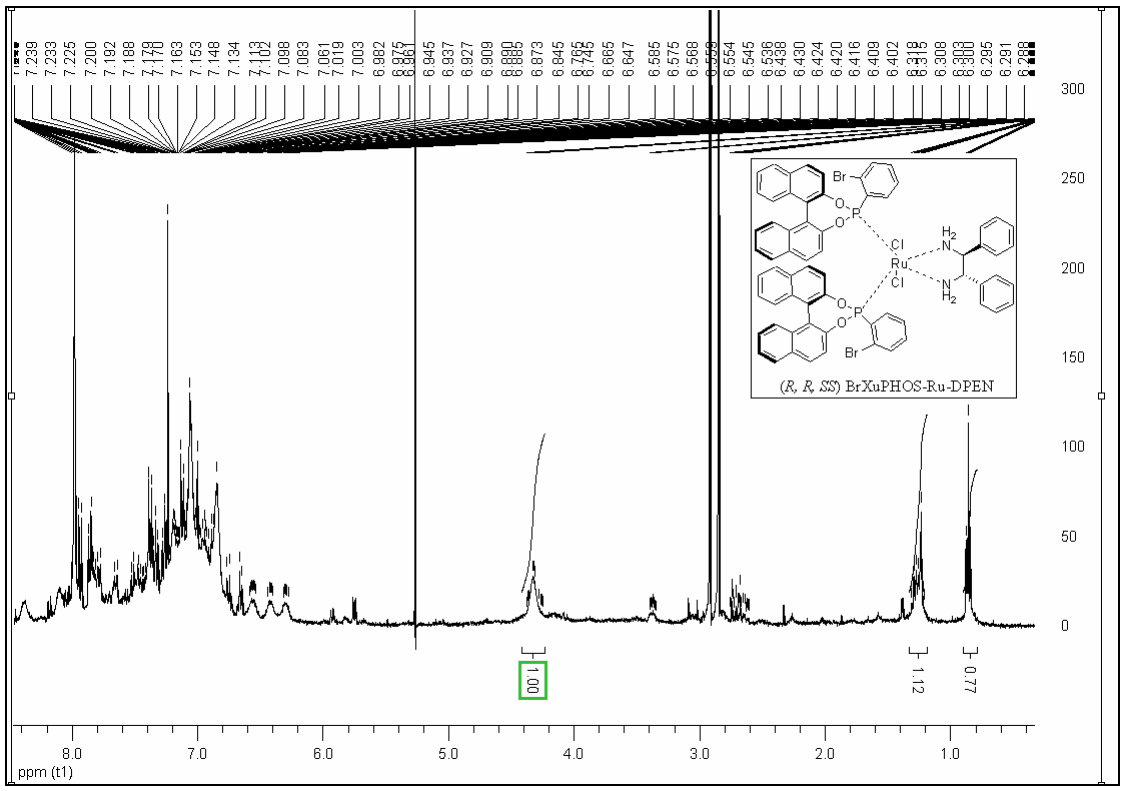
$^{1}$H NMR of (*R, R, RR*) BrXuPHOS-Ru-DACH



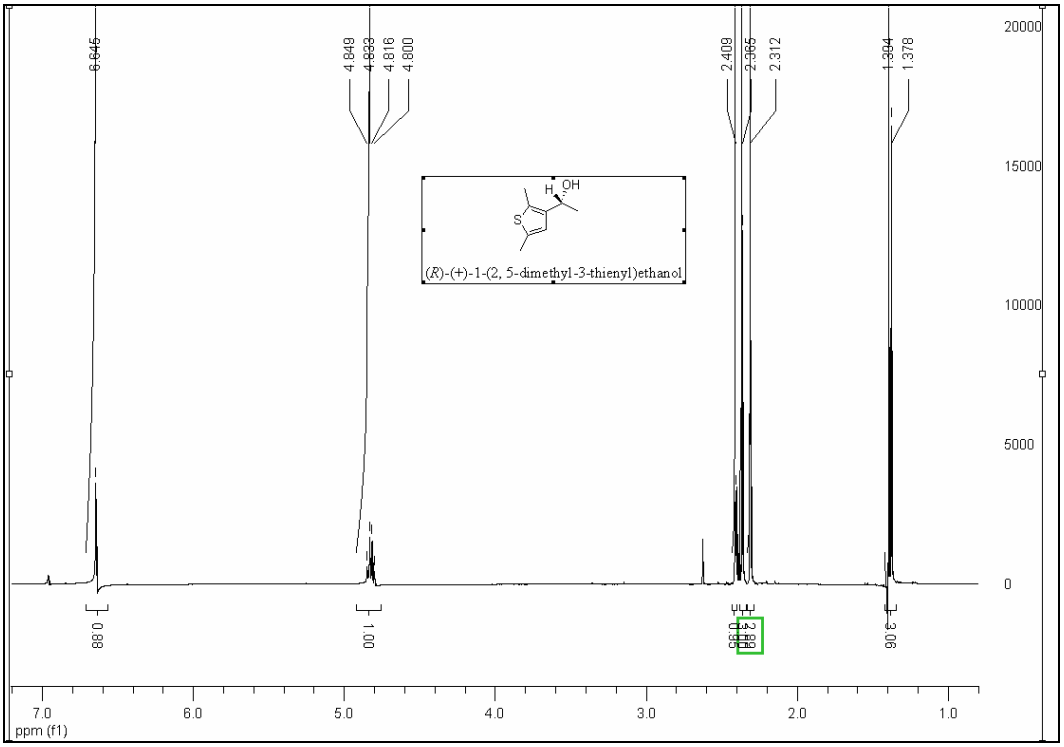
$^{1}$H NMR of (*S, S, RR*) BrXuPHOS-Ru-DACH



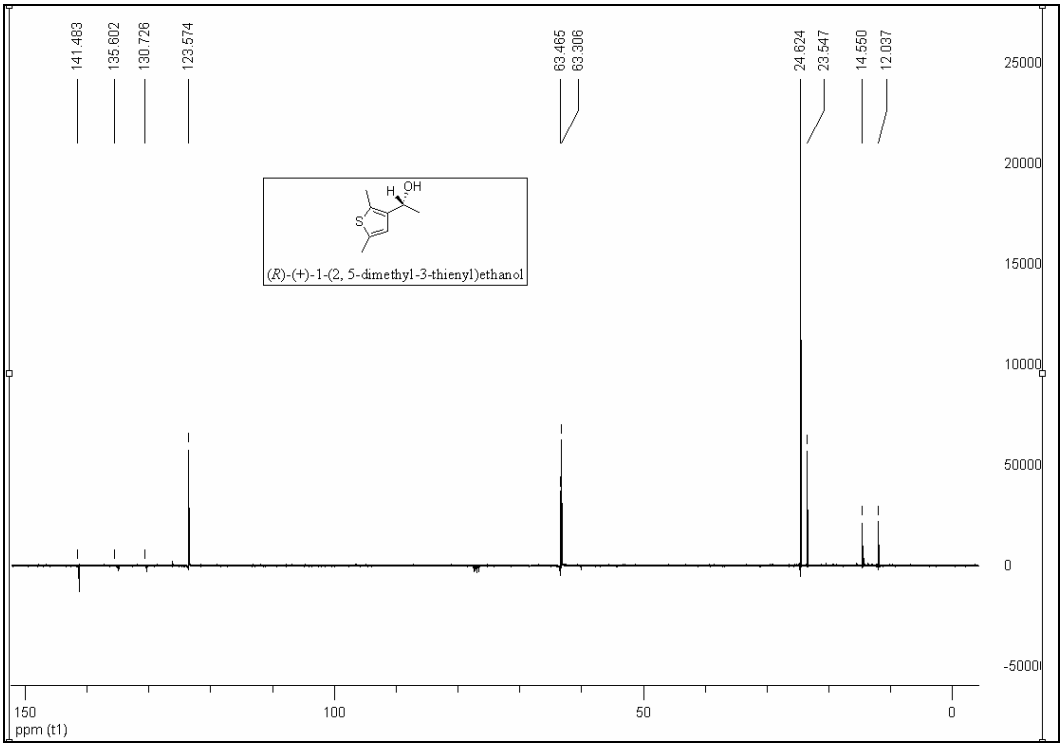
$^{1}$H NMR of (*R, R, SS*) BrXuPHOS-Ru-DPEN



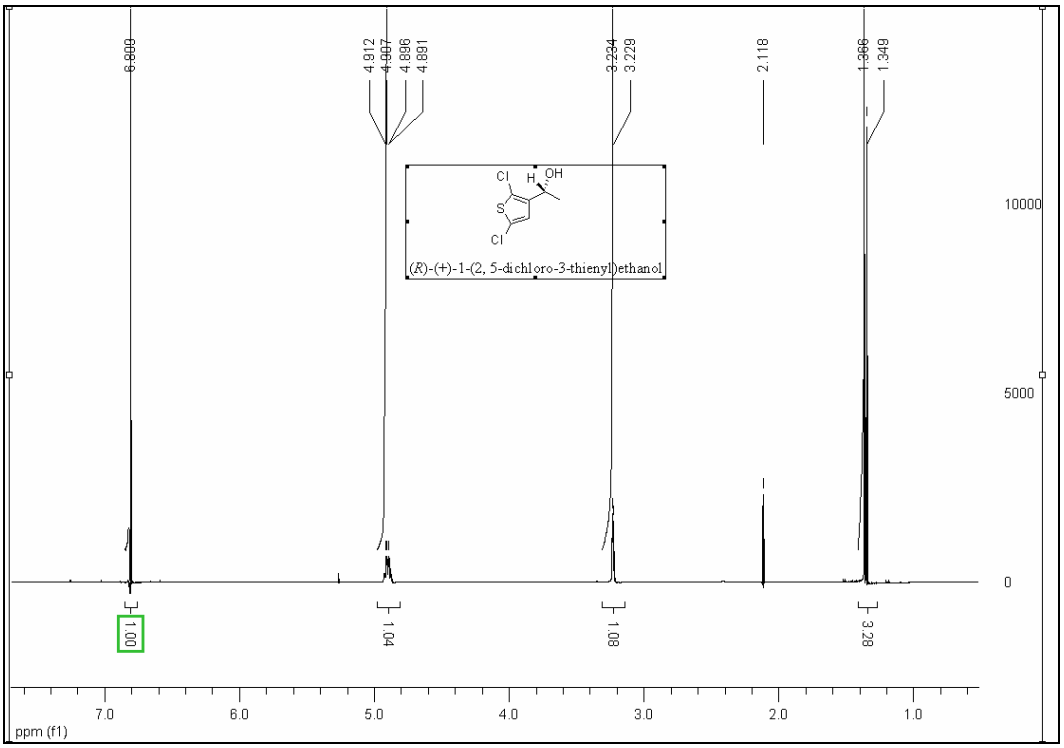
$^{1}$H NMR of (*R*)-(+)-1-(2,5-dimethyl-3-thienyl)ethanol



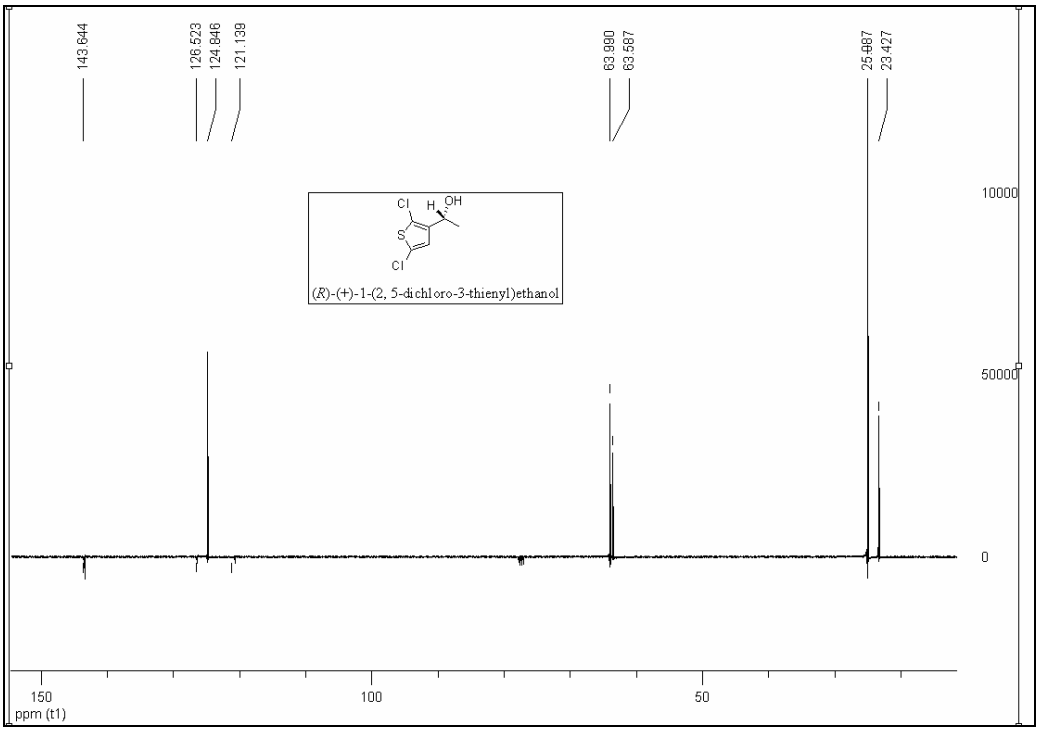

$^{13}$C NMR of (*R*)-(+)-1-(2,5-dimethyl-3-thienyl)ethanol



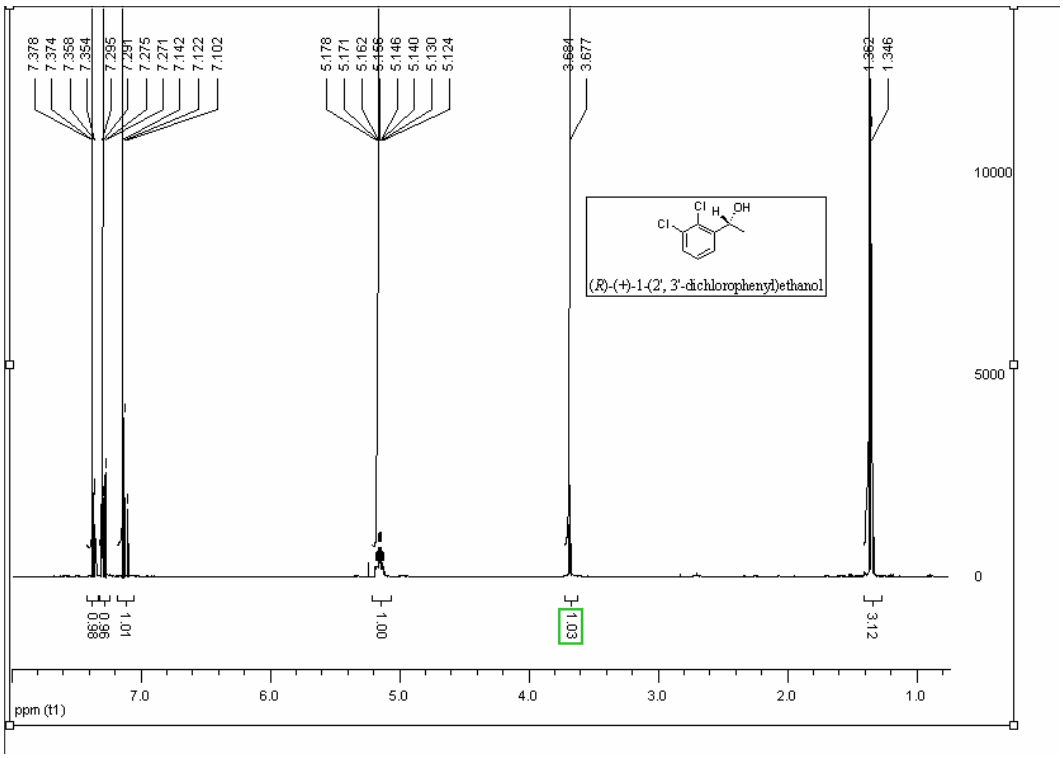
$^{1}$H NMR of (*R*)-(+)-1-(2,5-dichloro-3-thienyl)ethanol



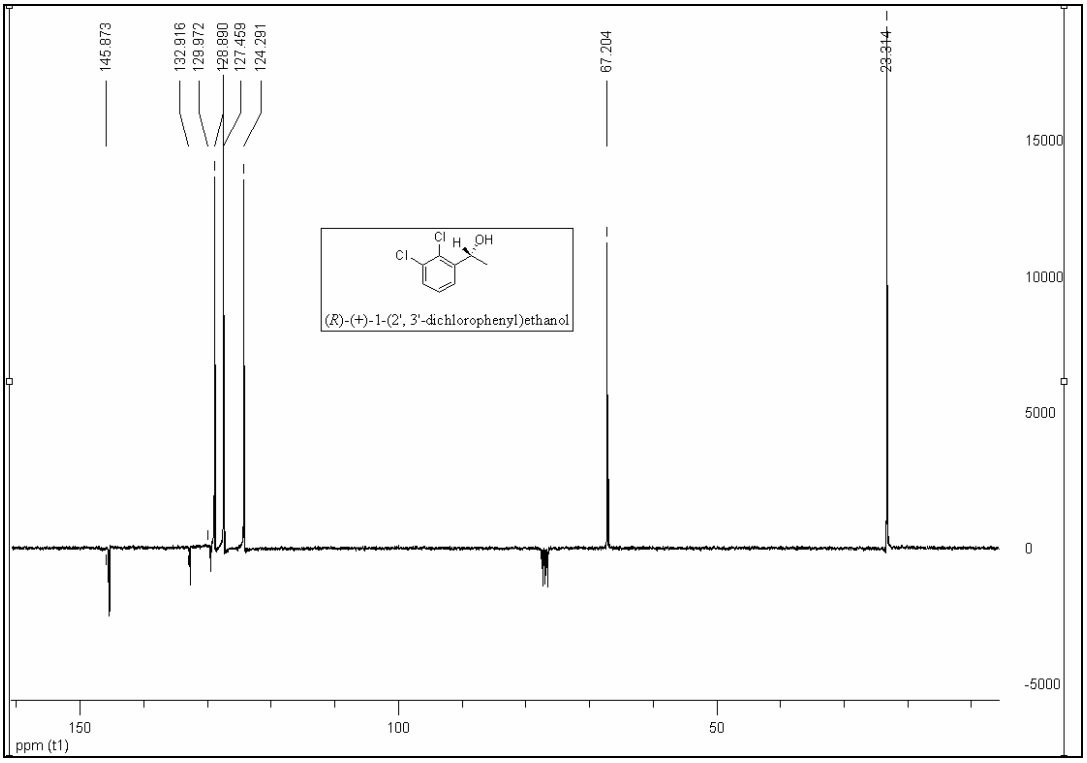

$^{13}$C NMR of (*R*)-(+)-1-(2,5-dichloro-3-thienyl)ethanol



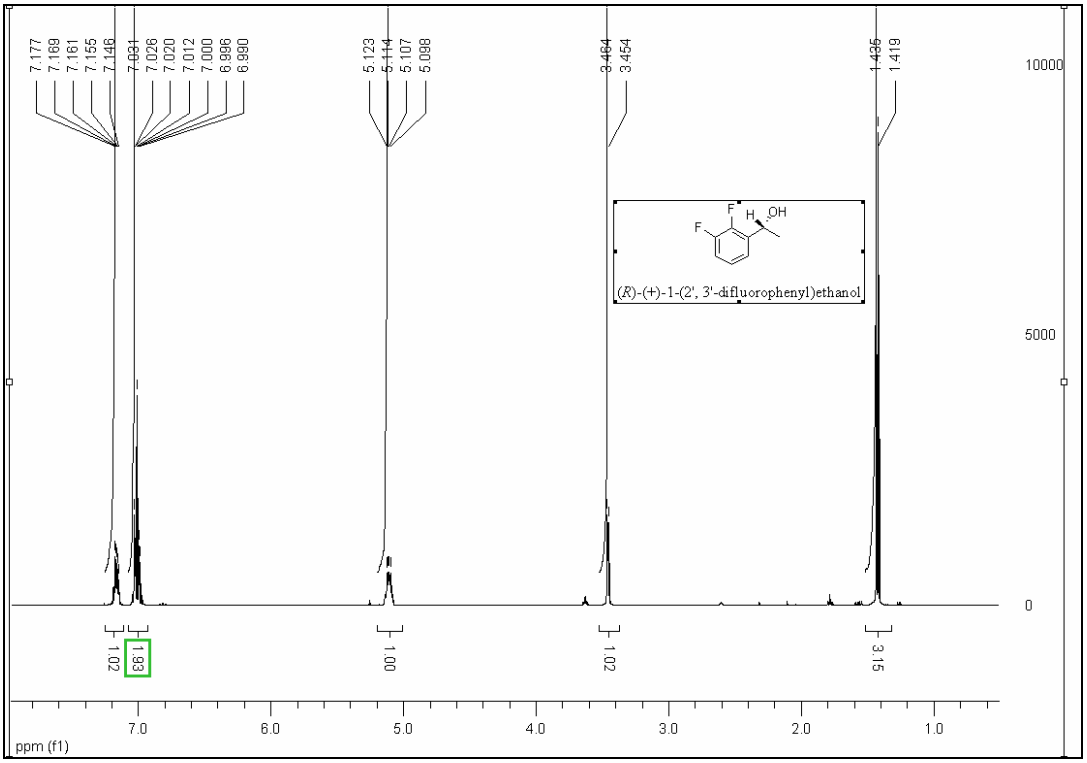
$^{1}$H NMR of (*R*)-(+)-1-(2,3-dichlorophenyl)ethanol



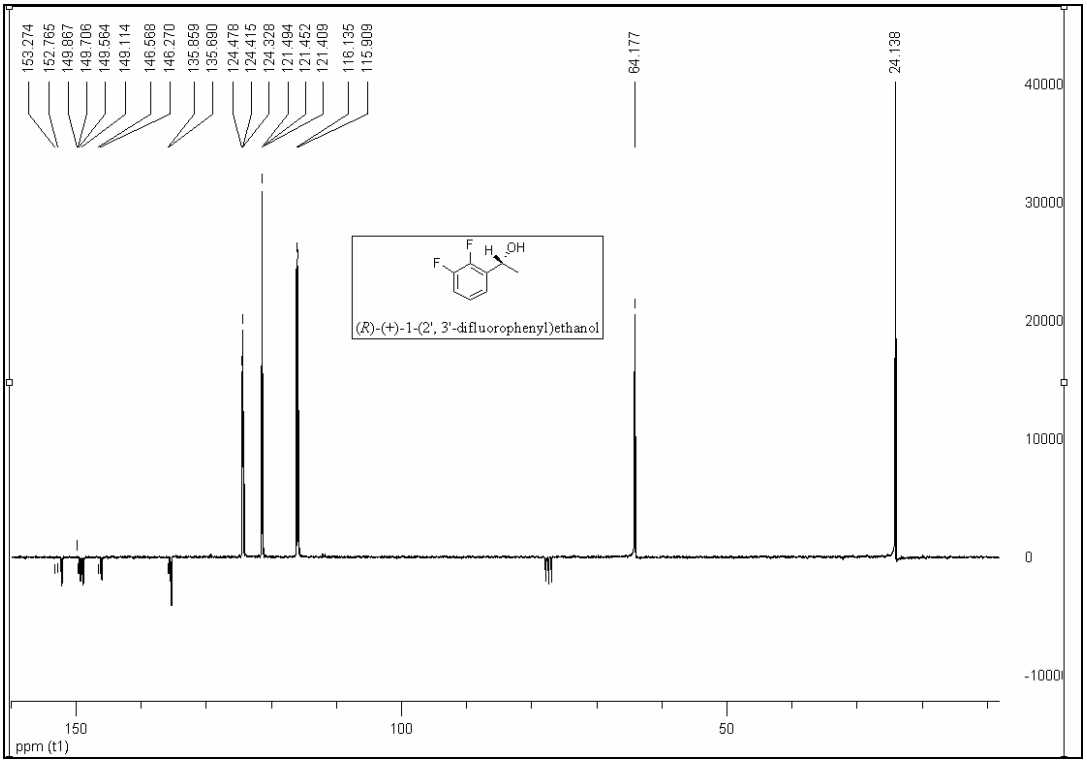

$^{13}$C NMR of (*R*)-(+)-1-(2,3-dichlorophenyl)ethanol



$^{1}$H NMR of (*R*)-(+)-1-(2,3-difluorophenyl)ethanol




$^{13}$C NMR of (*R*)-(+)-1-(2,3-difluorophenyl)ethanol



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