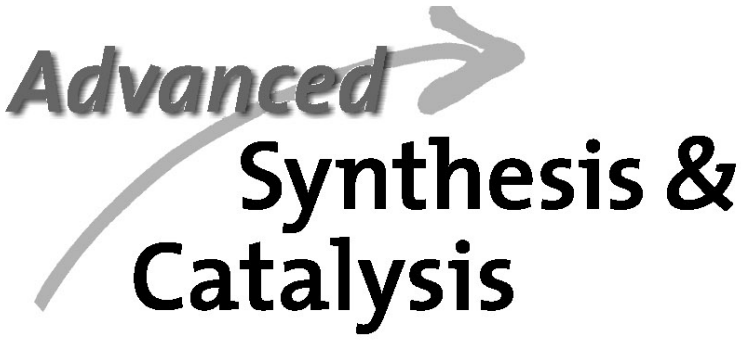


Supporting Information

Supporting Information

Chiral phosphine Lewis bases bearing multiple phenol groups catalyzed asymmetric aza-Morita-Baylis-Hillman reaction of *N*-sulfonated imines with activated olefins

*Ying-Hao Liu, Lian-Hui Chen and Min Shi**

State Key Laboratory of Organometallic Chemistry,

Shanghai Institute of Organic Chemistry,

Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032 China,

Fax: 86-21-64166128, mshi@pub.sioc.ac.cn.

Content

General Remarks. MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were purified by distillation. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer as a solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. *N*-Sulfonated imines **1** were prepared according to the literature. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. The optical purities of the aza-Morita-Baylis-Hillman adducts were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel AD, AS, TBB and OJ; eluent: hexane/2-propanol mixture; flow rate, 0.7 mL min^{-1}; detection, 254 nm or 220 nm light) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.

Figures of ^{31}P-NMR spectroscopy

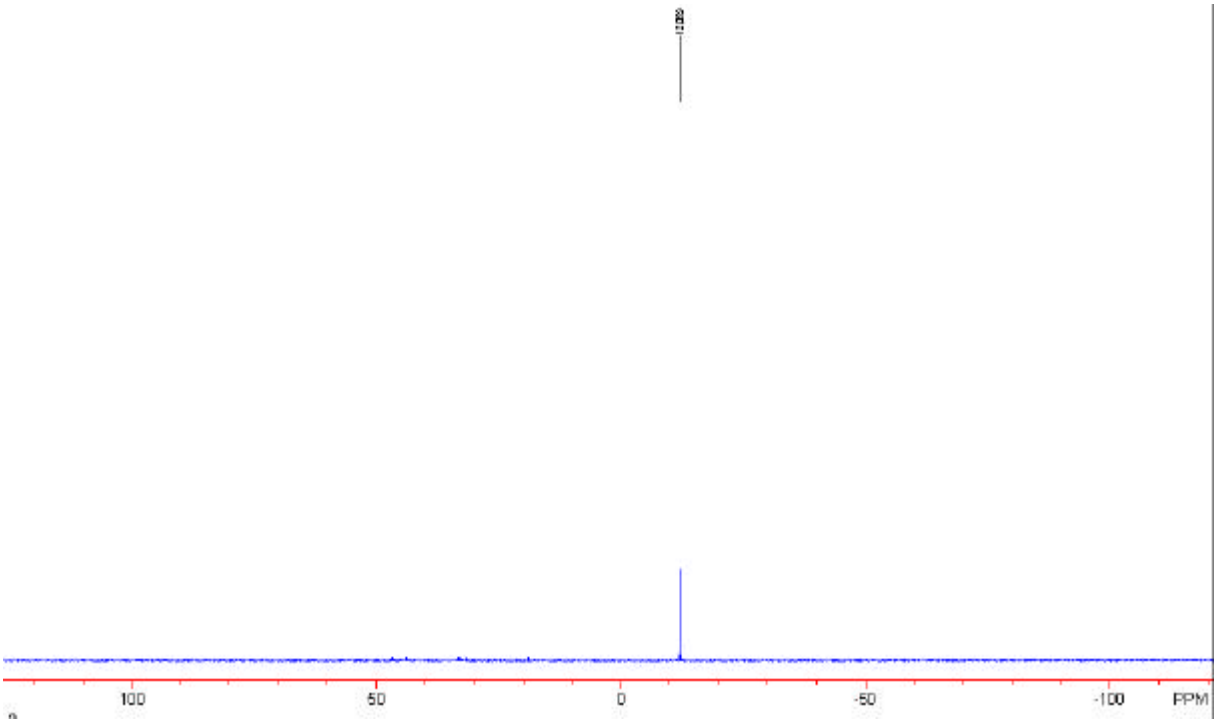


Figure S1. ^{31}P NMR spectrum of **CPLB1** in $CDCl_3$.

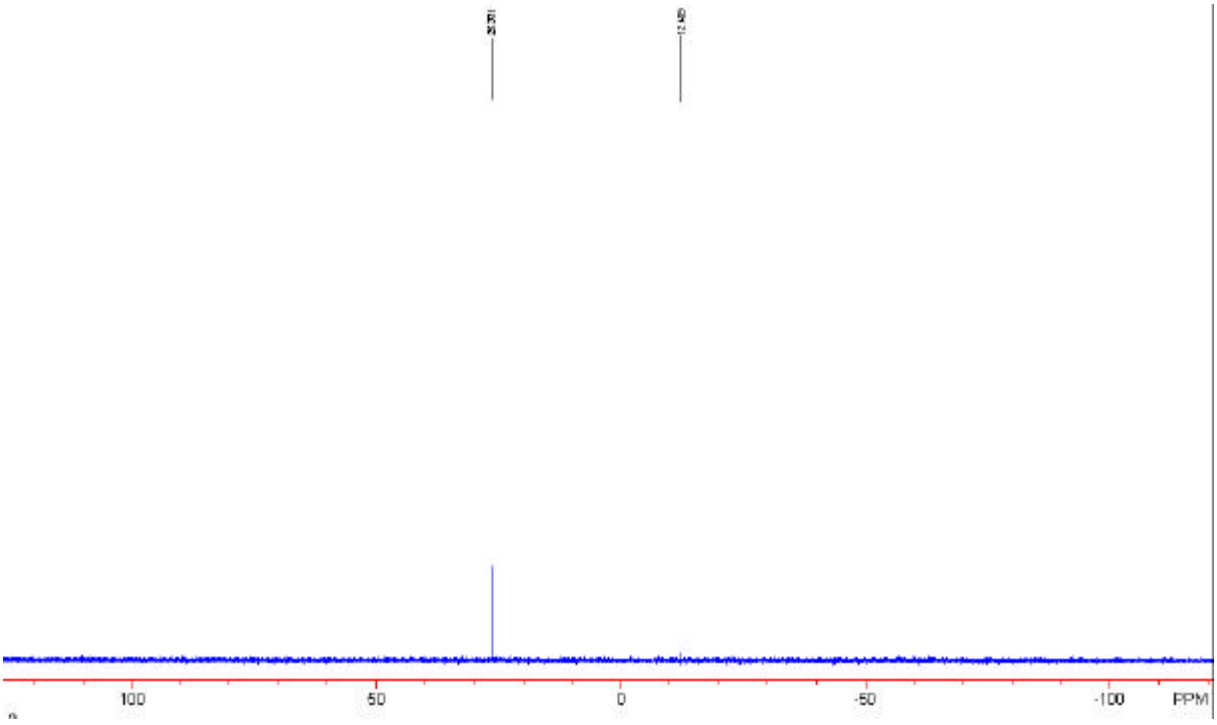


Figure S2. ^{31}P NMR spectrum of **CPLB1** with MVK in $CDCl_3$.

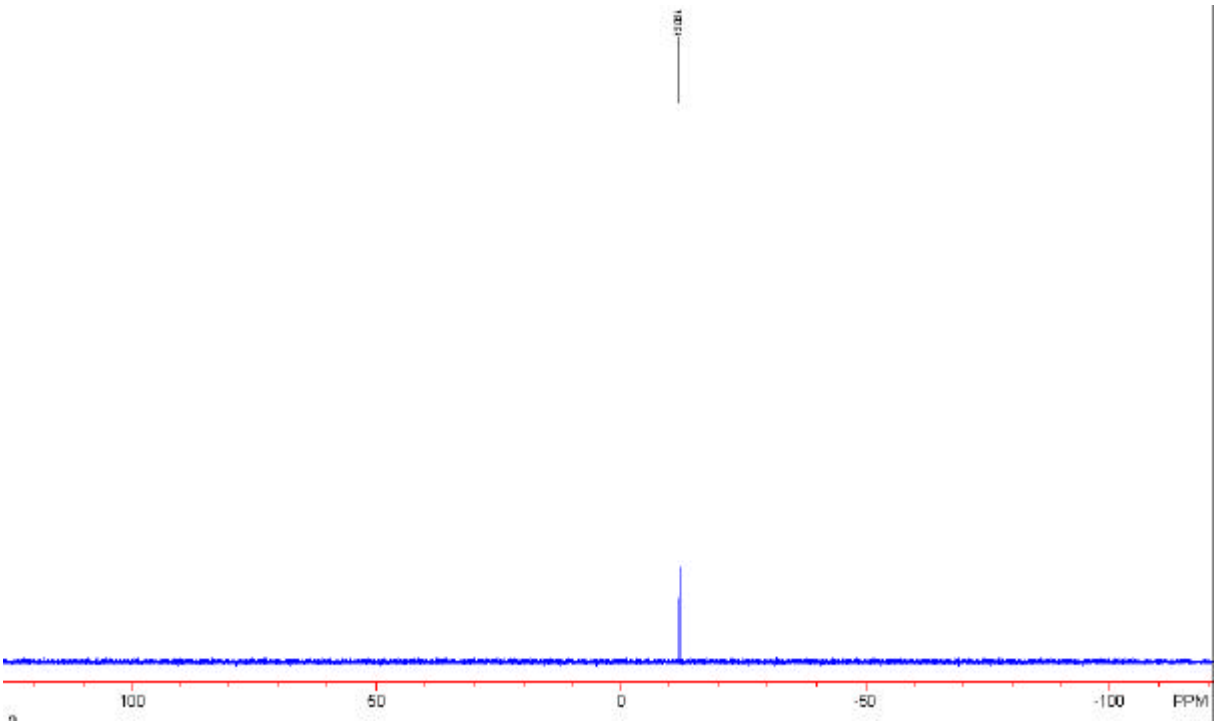


Figure S3. ^{31}P NMR spectrum of **CPLB6** in $CDCl_3$.

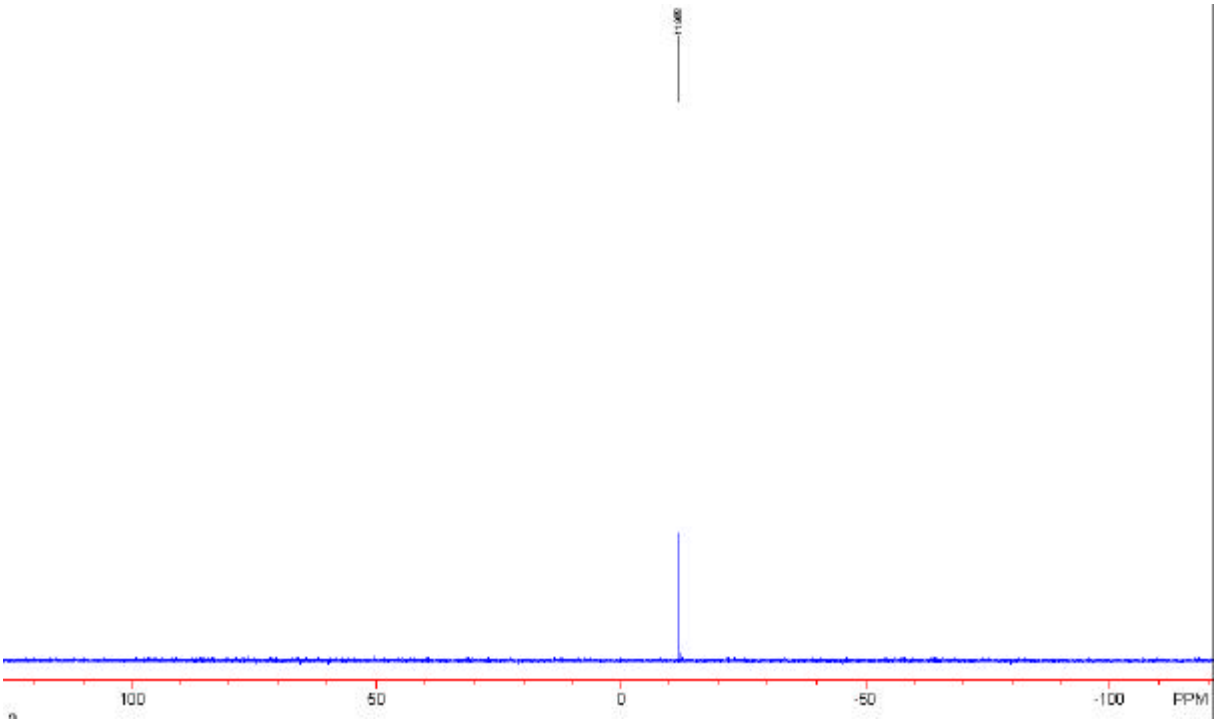
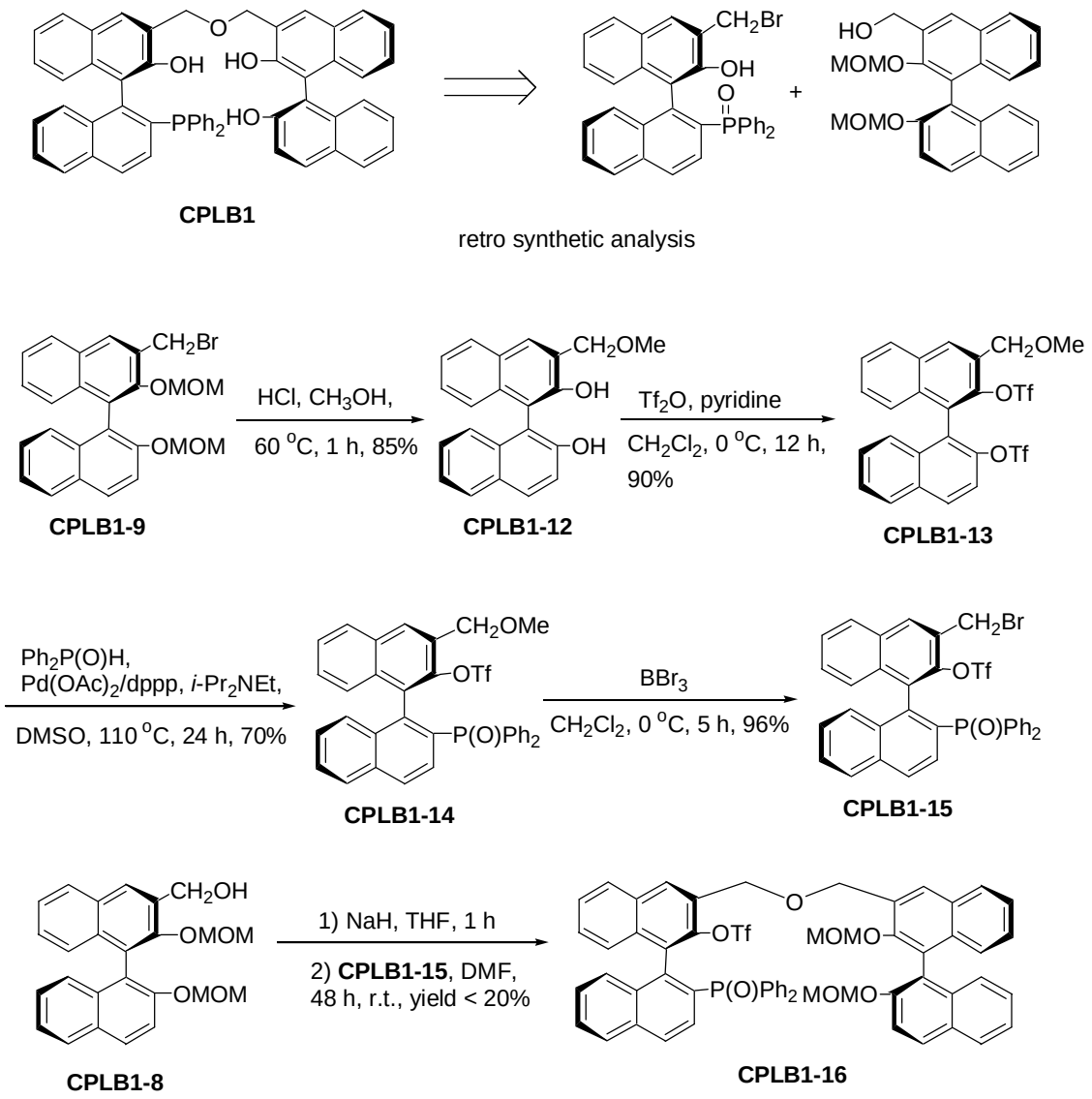


Figure S4. ^{31}P NMR spectrum of **CPLB6** with MVK in $CDCl_3$.

Preparation of chiral phosphine Lewis bases (CPLB1) bearing multiple phenol groups.

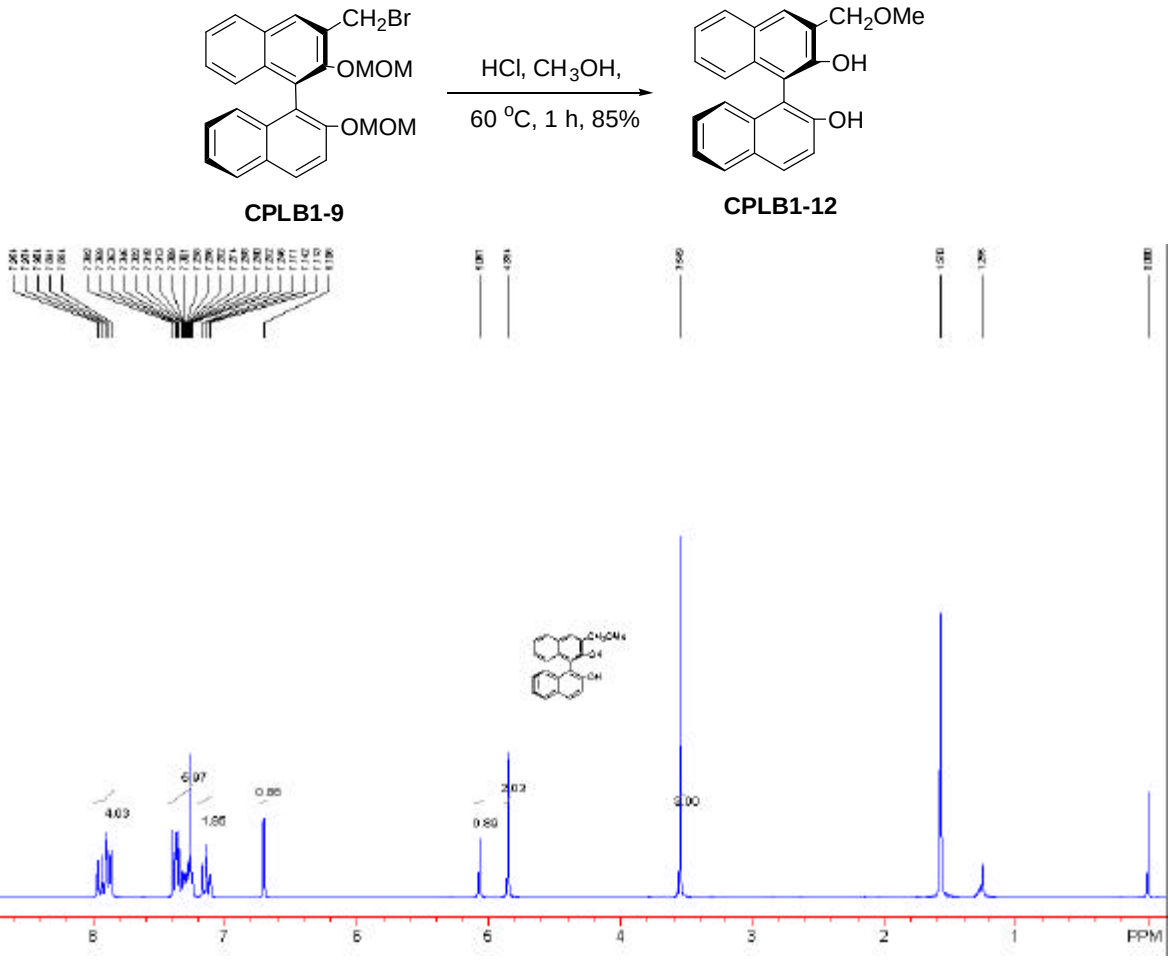
*The primary synthetic strategies of chiral phosphine Lewis bases (**CPLB1**) bearing multiple phenol groups*.



Scheme Sl-1

On the basis of this synthetic strategy, the desired product **CPLB1-16** was obtained in less than 20% yield and the starting material **CPLB1-15** was consumed when the nucleophilic substitution reaction of **CPLB1-8** treated with NaH in THF and **CPLB1-15** was performed in DMF for 48 hours. Therefore, we attempted another synthetic strategy shown in Scheme 1 in main text.

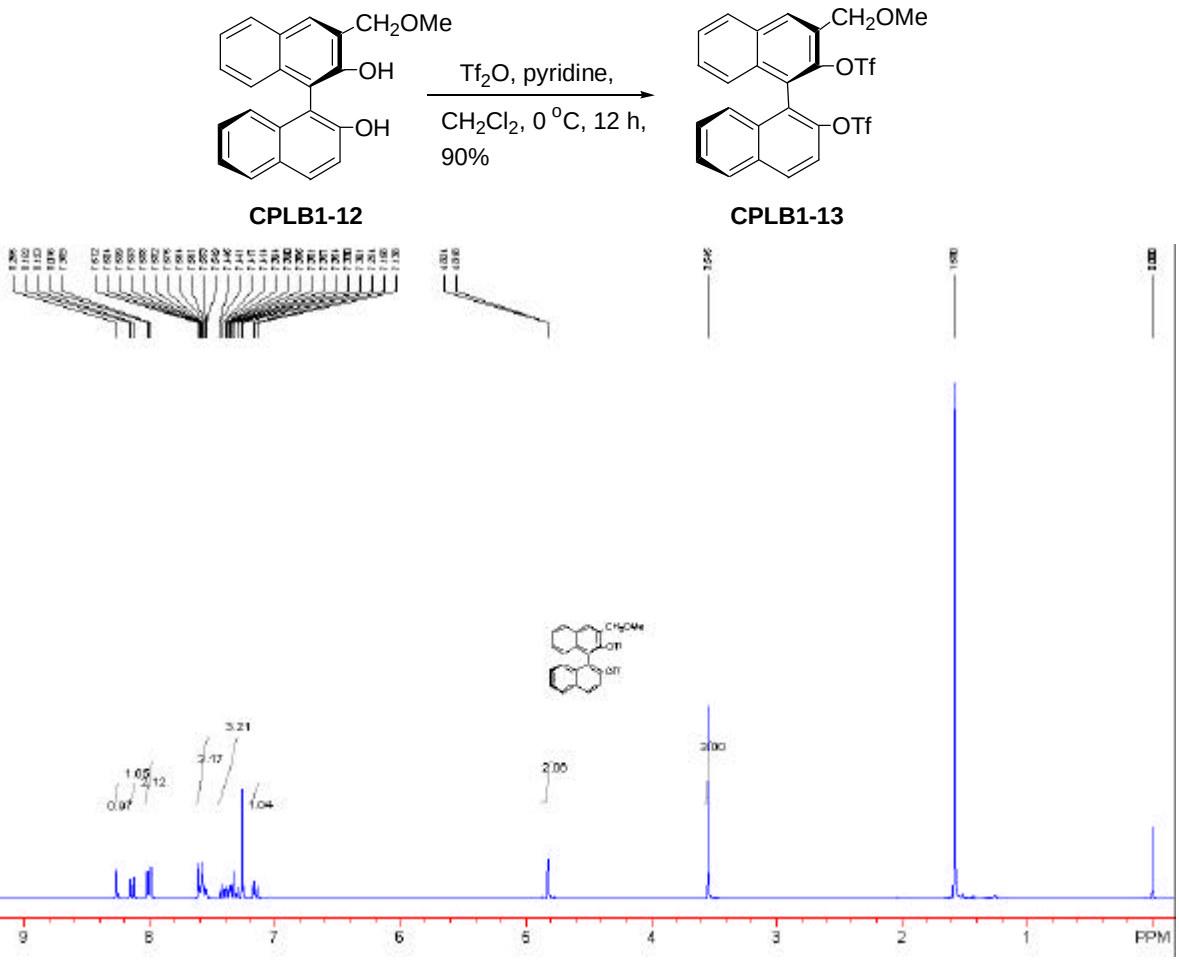
*Preparation of compound **CPLB1-12**.*



3-Methoxymethyl-[1,1']binaphthalenyl-2,2'-diol CPLB1-12.

To a solution of **CPLB1-9** (866 mg, 1.86 mmol) in CH_3OH (50 mL) was added aqueous hydrochloric acid and the temperature was raised to 60 ^oC. After stirring for 1 hour, the solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/4) to give product **CPLB1-12** (521 mg, 85%) as a colorless oil. $[\alpha]_D^{20}$ +16.0 (c 1.05, $CHCl_3$). mp: 133-135 ^oC. IR (KBr): ν 3521, 3213, 3057, 2928, 2826, 1620, 1596, 1506, 1467, 1433, 1386, 1341, 1275, 1197, 1108, 1086, 820, 753 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.55 (3H, s), 4.86 (2H, s), 5.06 (1H, s), 6.70 (1H, s), 7.15 (2H, t, *J* = 8.7 Hz), 7.25-7.31 (2H, m), 7.34 (1H, d, *J* = 6.9 Hz), 7.36 (2H, d, *J* = 9.0 Hz), 7.87 (2H, d, *J* = 7.8 Hz), 7.89 (1H, s), 7.94 (1H, d, *J* = 9.0 Hz). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 58.5, 72.0, 112.3, 112.5, 117.6, 123.5, 124.0, 124.3, 124.4, 125.7, 126.9, 127.1, 128.1, 128.2, 128.8, 129.0, 129.2, 130.6, 133.4, 133.5, 151.7, 152.0. MS (EI): *m/e* 331 (M^++1, 13.95), 330 (M^+, 57.87), 311 (M^+-19, 12.43), 298 (M^+-32, 100), 269 (M^+-61, 61.84), 253 (M^+-77, 58.02), 235 (M^+-95, 43.11), 197 (M^+-133, 49.62), 77 ($C_6H_5^+$, 13.41). Anal. Calcd. for $C_{22}H_{18}O_3$: requires C, 79.98; H, 5.49%; Found: C, 79.56; H, 5.83%.

*Preparation of compound **CPLB1-13**.*

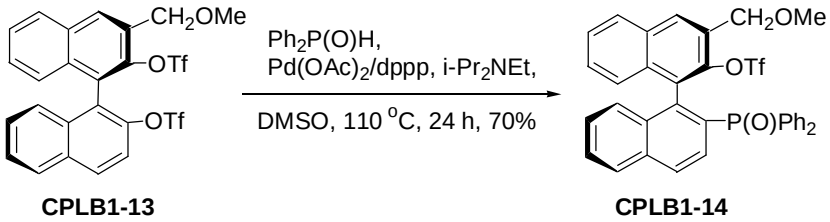


Trifluoromethanesulfonic acid 3'-methoxymethyl-2'-trifluoromethanesulfonyloxy-[1,1'] binaphthalenyl-2-yl ester CPLB1-13.

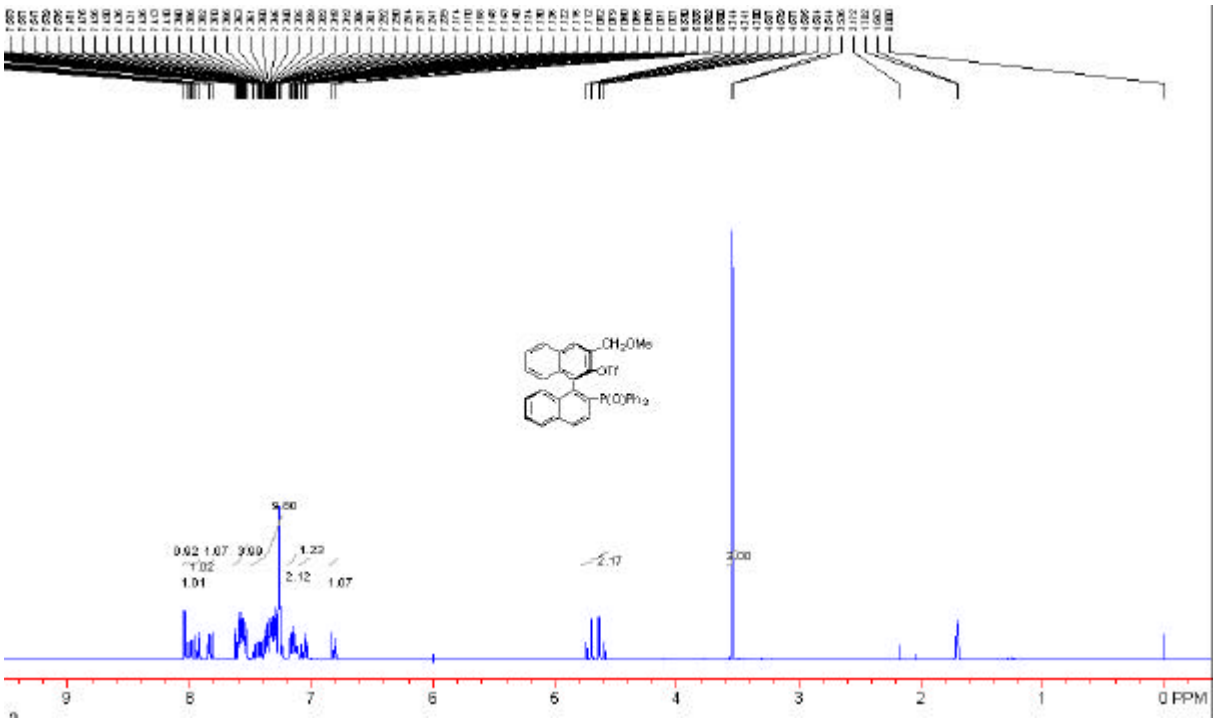
To a solution of **CPLB1-12** (522 mg, 1.58 mmol) and pyridine (0.40 mL, 4.74 mmol) in CH_2Cl_2 (20 mL) was added Tf_2O (0.28 mL, 1.67 mmol) dropwise at 0 °C for 10 minutes. After stirring for 6 hours, the reaction was quenched with H_2O (10 mL). After extraction with ethyl acetate (10 mL x 2), the organic layer was washed with aqueous hydrochloric acid (10 mL), saturated aqueous $NaHCO_3$ (15 mL) and brine (10 mL), then dried over anhydrous $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/10) to give product **CPLB1-13** (890 mg, 89%) as a colorless oil. $[\alpha]_D^{20}$ –157.3 (c 1.39, $CHCl_3$). IR (KBr): ν 3066, 2992, 2933, 2895, 2827, 1625, 1595, 1580, 1510, 1466, 1427, 1362, 1327, 1248, 1149, 1106, 1077, 1038, 948, 820 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.54 (3H, s), 4.82 (2H, d, *J* = 1.9 Hz), 7.15 (1H, d, *J* = 8.7 Hz), 7.32 (1H, d, *J* = 8.7 Hz), 7.35-7.44 (2H, m), 7.51-7.61 (3H, m), 8.00 (2H, d, *J* = 8.4 Hz), 8.14 (1H, d, *J* = 9.0 Hz), 8.27 (1H, s). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ

58.54, 69.44, 117.90 (d, J_{F-C} = 318.5 Hz), 118.09 (d, J_{F-C} = 318.0 Hz), 119.2, 123.7, 124.4, 126.7, 127.1, 127.2, 127.5, 127.6, 127.9, 128.2, 128.3, 129.9, 131.0, 132.0, 132.3, 132.4, 132.6, 133.6, 143.3, 145.5. MS (EI): *m/e* 594 (M^+, 46.69), 563 (M^+-31, 6.06), 461 (M^+-133, 8.74), 429 (M^+-133-32, 8.47), 328 (M^+-266, 8.64), 312 (M^+-149-133, 100), 296 (M^+-149-149, 16.72), 282 (M^+-149-133-30, 34.46), 281 (M^+-149-133-31, 28.30), 69 (CF_3^+, 42.90), 45 (M^+-549, 57.16). Anal. Calcd. for $C_{24}H_{16}F_6O_7S_2$: requires C, 48.49; H, 2.71%; Found: C, 48.79; H, 2.77%.

Preparation of compound ***CPLB1-14****.*



CPLB1-13 **CPLB1-14**

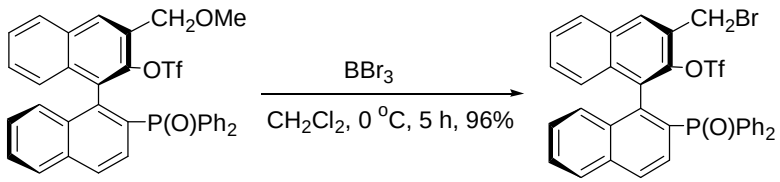


Trifluoromethanesulfonic acid 2'-(diphenyl-phosphinoyl)-3-methoxymethyl-[1,1']binaphthalenyl-2-yl ester CPLB1-14.

To a solution of **CPLB1-13** (890 mg, 1.40 mmol), $Ph_2P(O)H$ (566 mg, 2.80 mmol), $Pd(OAC)_2$ (32 mg, 0.14 mmol) and 1,4-bis(diphenylphosphanyl)butane (dppb) (60 mg, 0.14 mmol) in DMSO (15 mL) was added *i*-Pr_2NEt (1.0 mL, 5.6 mmol) under argon atmosphere. After stirring at 120 ^oC for 12 hours, DMSO was removed under reduced pressure. The mixture was resolved with ethyl acetate (100 mL), and washed with water (30 mL x 3). The organic layer was dried over anhydrous $MgSO_4$ and removed under reduced pressure. The residue was

further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/1) to give product **CPLB1-14** as a colorless solid (633 mg, 70%). $[\alpha]_D^{20}$ –34.7 (c 1.01, $CHCl_3$). mp: 209-211 ^oC. IR (KBr): ν 3054, 2993, 2922, 2889, 2814, 1589, 1557, 1503, 1483, 1436, 1410, 1368, 1219, 1136, 1117, 1072, 936, 904, 822, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.61 (3H, s), 4.74 (2H, m), 6.82 (1H, d, *J* = 8.7 Hz), 7.10-7.13 (1H, m), 7.18-7.24 (2H, m), 7.33-7.52 (9H, m), 7.60-7.69 (4H, m), 7.89 (1H, d, *J* = 8.1 Hz), 8.00 (1H, d, *J* = 8.1 Hz), 8.06 (1H, dd, J_1 = 8.1 Hz, J_2 = 2.4 Hz), 8.11 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +28.57. ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ -74.44 (3F, s). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 58.3 (d, *J* = 3.0 Hz), 69.3, 117.6 (d, J_{F-C} = 319.4 Hz), 126.3, 126.4, 126.5, 126.8, 127.3, 127.49, 127.54, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.46, 128.51, 129.18, 129.22, 129.6, 130.5, 130.87, 130.90, 131.1, 131.17, 131.2, 131.3, 131.39, 131.42, 131.5, 131.6, 131.8, 132.8, 133.2, 133.3, 133.5, 134.10, 134.13, 137.0, 137.1, 143.5. MS (EI): *m/e* 615 (M^+-31, 0.66), 513 (M^+-133, 3.58), 497 (M^+-149, 100), 481 (M^+-133-32, 18.69), 465 (M^+-149-32, 3.77), 296 (M^+-149-32-201, 2.50), 281 (M^+-133-31-201, 10.47), 201 (Ph_2PO^+, 24.58), 77 (Ph^+, 8.24), 45 (M^+-601, 11.14). Anal. Calcd. for $C_{35}H_{26}F_3O_5PS$: requires C, 65.01; H, 4.05%; Found: C, 65.28; H, 4.07%.

*Preparation of compound **CPLB1-15**.*



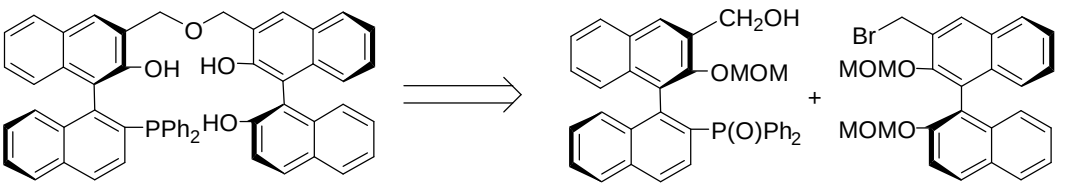
CPLB1-14 **CPLB1-15**

Trifluoromethanesulfonic acid 3-bromomethyl-2'-(diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-yl ester CPLB1-15.

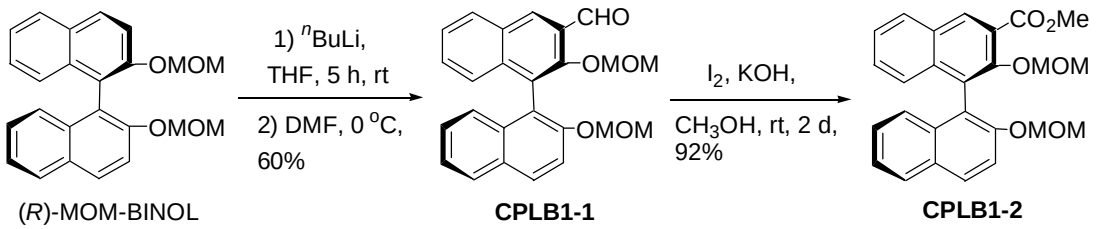
To a solution of **CPLB1-14** (1.93 g, 3.0 mmol) in CH_2Cl_2 (20 mL) was added BBr_3 (1.0 mL, 2.5 g, 10 mmol) at 0 ^oC, then the reaction temperature was raised to room temperature slowly. And after stirring for 5 hours, water (10 mL) was added to quench the reaction. After extraction with ethyl acetate (10 mL x 2), the organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/1) to give product **CPLB1-15** (2.0 g, 96%) as a colorless solid: $[\alpha]_D^{20}$ +18.2 (c 1.01, $CHCl_3$). mp: 207-209 ^oC. IR (KBr): ν 3055, 1590, 1557, 1502, 1483, 1437, 1408, 1313, 1281, 1213, 1133, 1118, 1074, 1037, 936, 899, 821, 751, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): 4.77 (2H, d, *J* = 11.4 Hz), 6.87 (1H, d, *J* = 8.1 Hz),

7.10 (1H, t, J = 8.0 Hz), 7.19-7.47 (11H, m), 7.58-7.75 (4H, m), 7.84 (1H, d, J = 8.1 Hz), 7.99 (1H, d, J = 7.8 Hz), 8.07 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz), 8.10 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +28.23. ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ -74.39 (3F, s). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 27.9 (d, J = 1.1 Hz), 117.8 (d, $J_{F\text{-}C}$ = 318.6 Hz), 126.9, 127.0, 127.1, 127.2, 127.3, 127.7, 127.78, 127.80, 127.88, 127.94, 128.0, 128.2, 128.36, 128.43, 128.6, 128.7, 128.9, 129.5, 129.86, 129.92, 130.8, 131.15, 131.18, 131.3, 131.4, 131.5, 131.59, 131.63, 131.7, 131.8, 132.87, 132.91, 133.0, 133.3, 133.5, 134.3, 134.33, 136.7, 136.8, 143.2, 143.2. MS (EI): *m/e* 615 (M^+-Br, 8.94), 563 (M^++2-133, 4.29), 561 (M^+-133, 4.22), 547 (M^++2-149, 100), 545 (M^+-149, 96.79), 467 (M^+-149-Br, 55.8), 282 (M^++1-133-80-201, 48.83), 281 (M^+-133-80-201, 42.12), 252 (M^+-442, 35.23), 233 (M^+-461, 47.09), 201 (Ph_2PO^+, 89.61), 77 (Ph^+, 24.37). Anal. Calcd. for $C_{34}H_{23}BrF_3O_4PS$: requires C, 58.72; H, 3.33%; Found: C, 58.63; H, 3.18%.

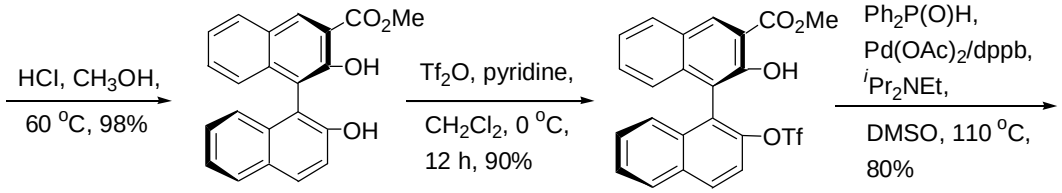
*The improved preparation strategies of chiral phosphine Lewis bases (**CPLB1**) bearing multiple phenol groups.*



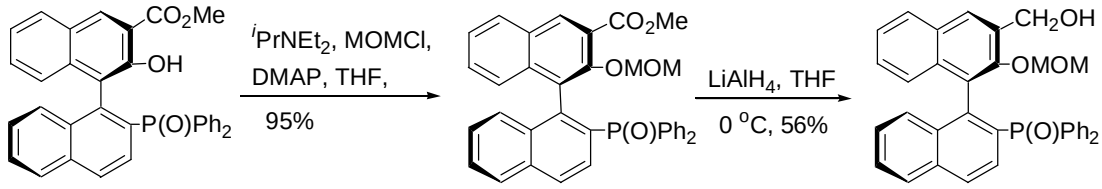
CPLB1 **CPLB1-7** **CPLB1-9**



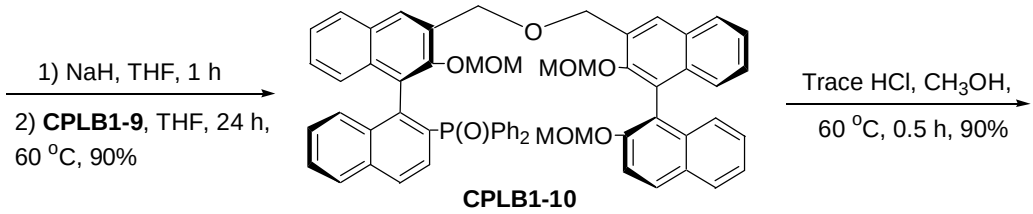
(*R*)-MOM-BINOL **CPLB1-1** **CPLB1-2**



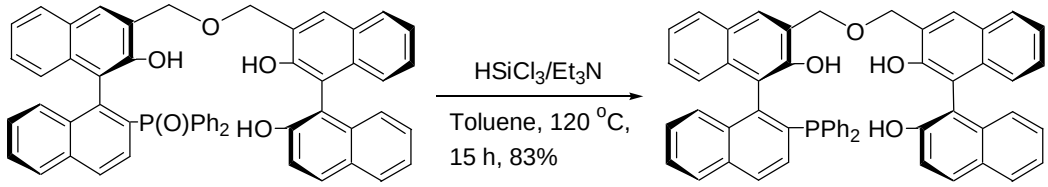
CPLB1-3 **CPLB1-4**



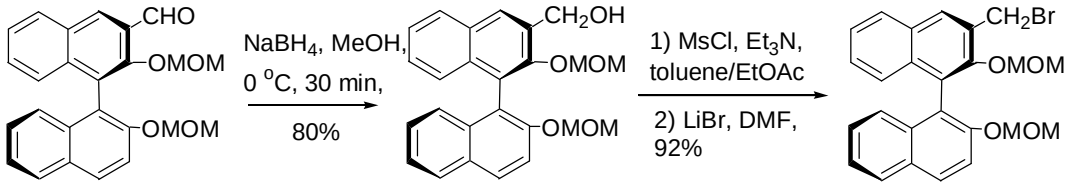
CPLB1-5 **CPLB1-6** **CPLB1-7**



CPLB1-10



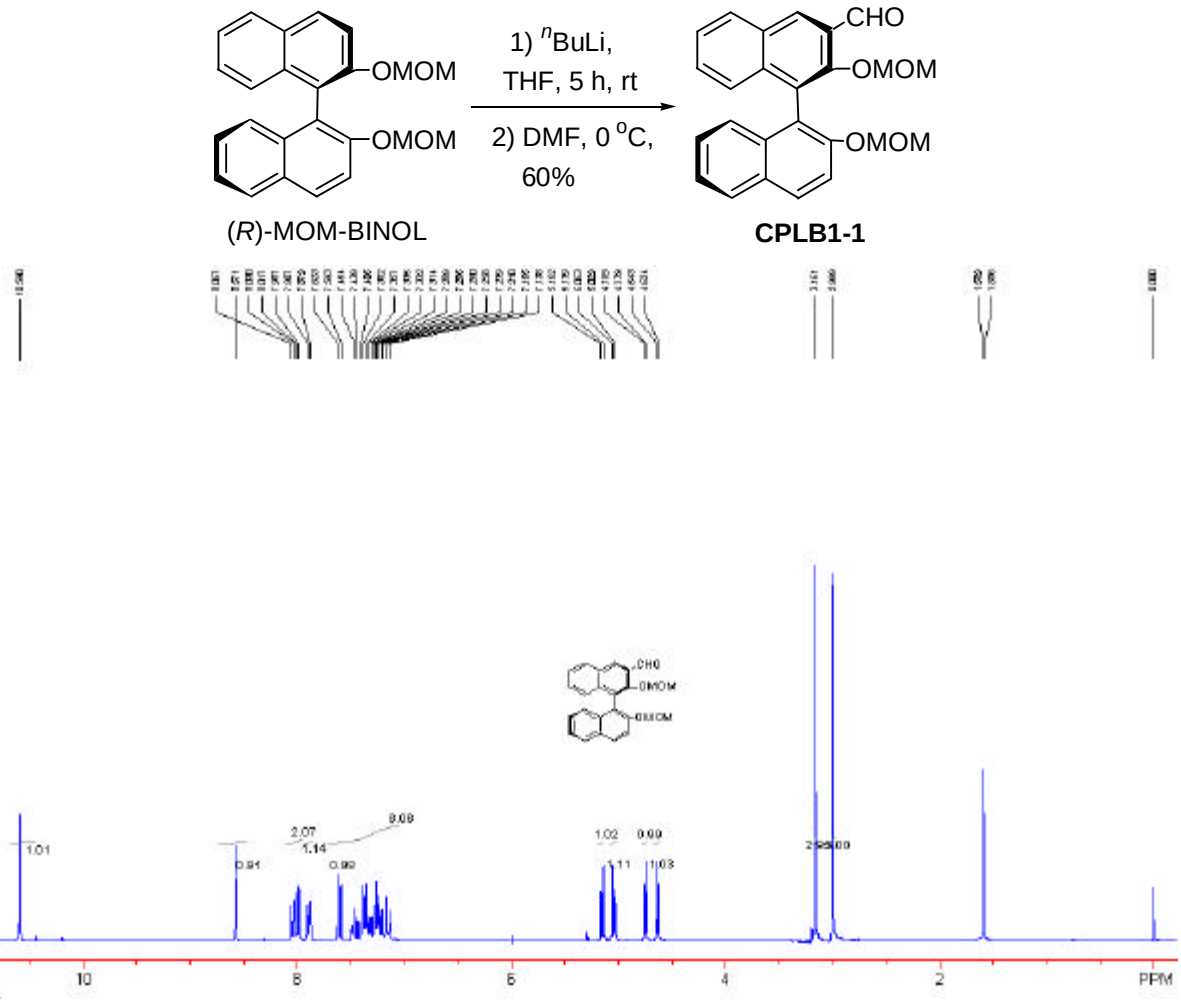
CPLB1-11 (*R,R*)-**CPLB1**



CPLB1-1 **CPLB1-8** **CPLB1-9**

Scheme SI-2

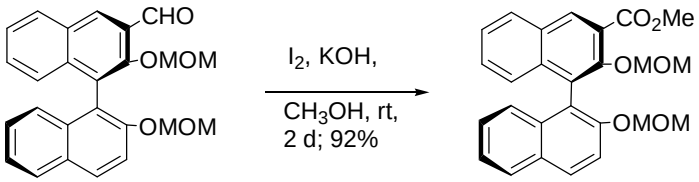
Preparation of compound ***CPLB1-1***.



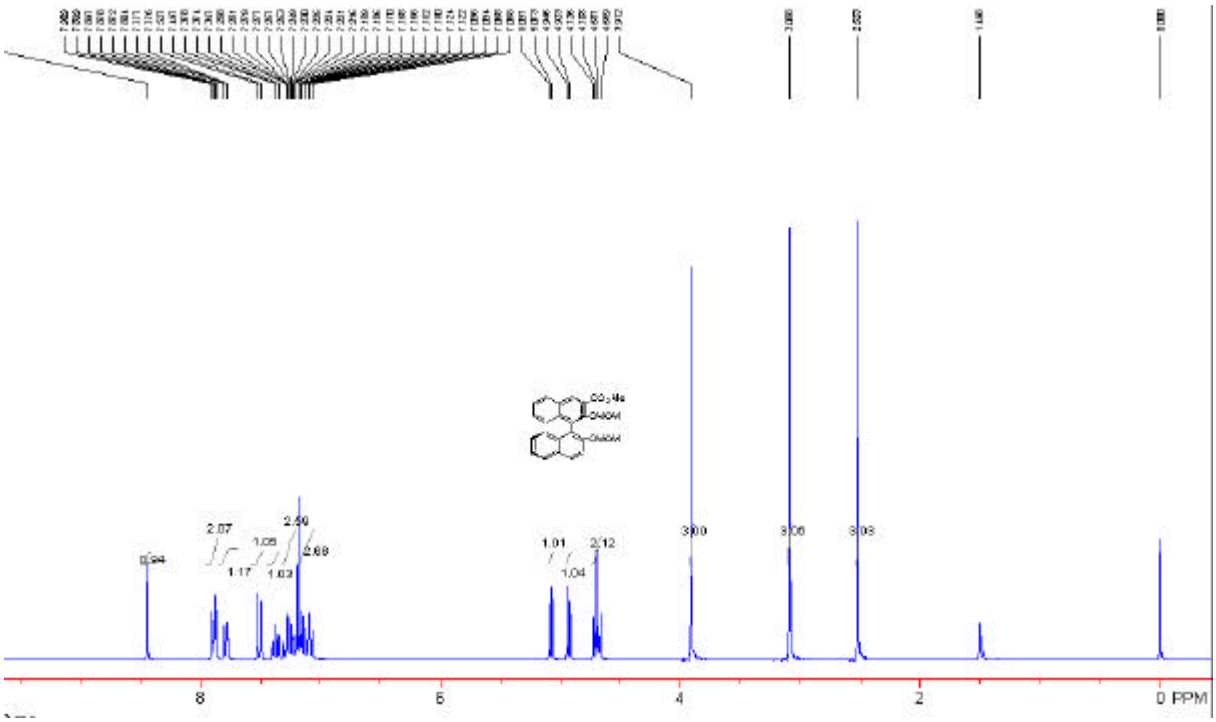
2,2'-Bis-methoxymethoxy-[1,1']binaphthalenyl-3-carbaldehyde CPLB1-1.

To a solution of (*R*)-MOM-BINOL (7.6 g, 20 mmol) in THF (40 mL) was added n-BuLi (1.6 M in hexane, 13.75 mL, 22 mmol) dropwise. After stirring for 5 hours, DMF (1.73 mL, 22 mmol) was added at 0 °C. The reaction was quenched with water (10 mL) after 4 hours. After extraction with ethyl acetate (20 mL x 3) and drying over anhydrous $MgSO_4$, the organic solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/20) to give product **CPLB1-1** (4.8 g, 60%) as a yellow solid. This is a known compound.[1] $[\alpha]_D^{20}$ +81.0 (c 1.03, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.01 (3H, s), 3.15 (3H, s), 4.63 (1H, d, *J* = 6.0 Hz), 4.74 (1H, d, *J* = 6.0 Hz), 5.04 (1H, d, *J* = 7.0 Hz), 5.15 (1H, d, *J* = 7.0 Hz), 7.16 (1H, d, *J* = 8.4 Hz), 7.23 (1H, d, *J* = 8.4 Hz), 7.27-7.50 (5H, m), 7.62 (1H, d, *J* = 9.0 Hz), 7.90 (1H, d, *J* = 8.3 Hz), 8.01 (1H, d, *J* = 9.1 Hz), 8.05 (1H, d, *J* = 8.3 Hz), 10.60 (1H, s).

*Preparation of compound **CPLB1-2**.*



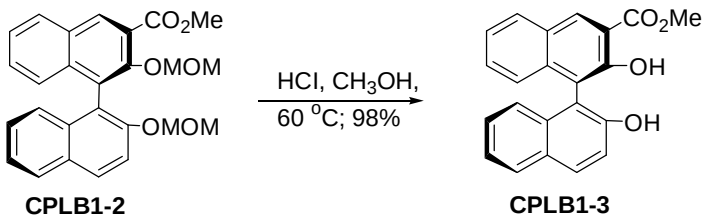
CPLB1-1 **CPLB1-2**



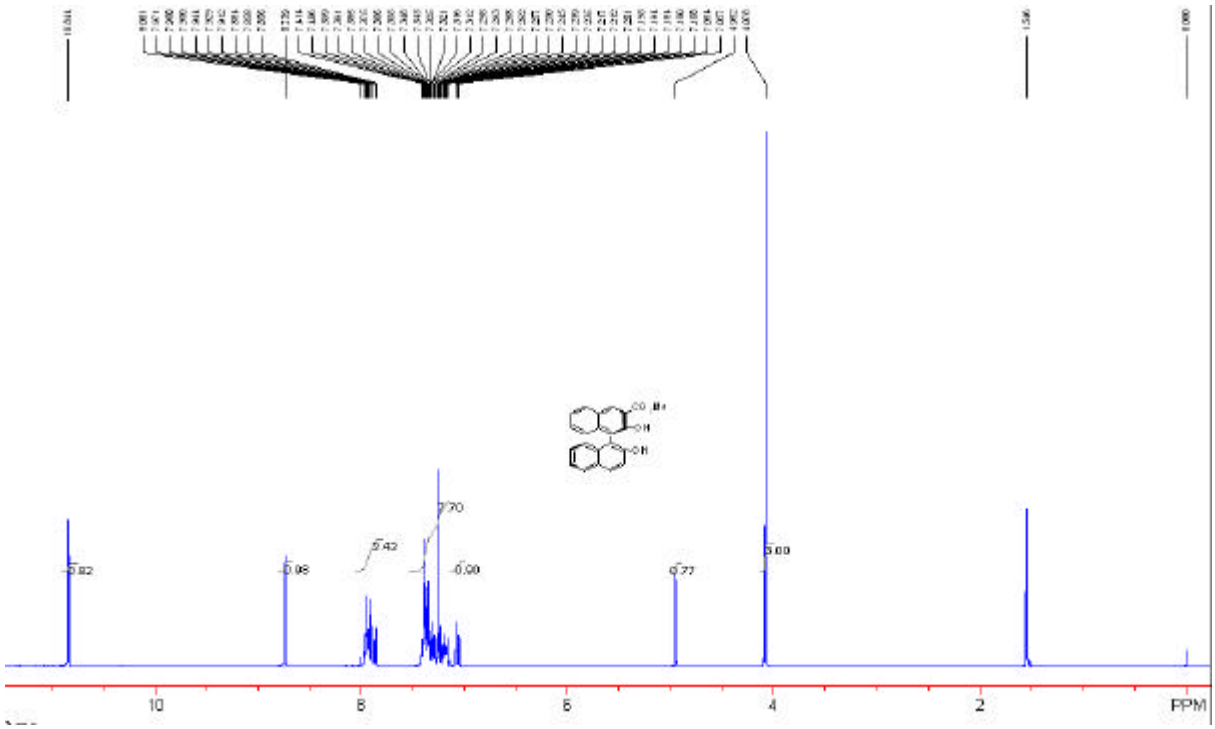
2,2'-Bis-methoxymethoxy-[1,1']binaphthalenyl-3-carboxylic acid methyl ester CPLB1-2.

To a solution of **CPLB1-1** (2.0 g, 5.0 mmol) in methanol (30 mL) were added KOH (60 mmol, 3.4 g) and I_2 (30 mmol, 7.6 g) in portions at 0 ^{o}C. The temperature was raised to room temperature slowly, and the mixture was stirred for 1-2 days. Saturated aqueous Na_2SO_3 was added to quench the reaction, and after extraction with ethyl acetate (10 mL x 3), drying over anhydrous Na_2SO_4, the organic solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/10) to give product **CPLB1-2** (2.0 g, 92%) as a white solid. This is a known compound.[2] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.59 (3H, s), 3.16 (3H, s), 3.98 (3H, s), 4.77 (2H, d, *J* = 5.4 Hz), 4.93 (1H, d, *J* = 6.0 Hz), 5.08 (1H, d, *J* = 6.0 Hz), 7.14-7.38 (5H, m), 7.42-7.47 (1H, m), 7.58 (1H, d, *J* = 9.0 Hz), 7.86 (1H, d, *J* = 8.1 Hz), 7.95 (1H, d, *J* = 8.1 Hz), 7.96 (1H, d, *J* = 8.1 Hz), 8.51 (1H, s).

*Preparation of compound **CPLB1-3**.*



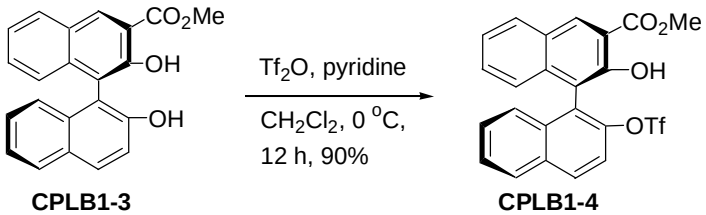
CPLB1-2 **CPLB1-3**



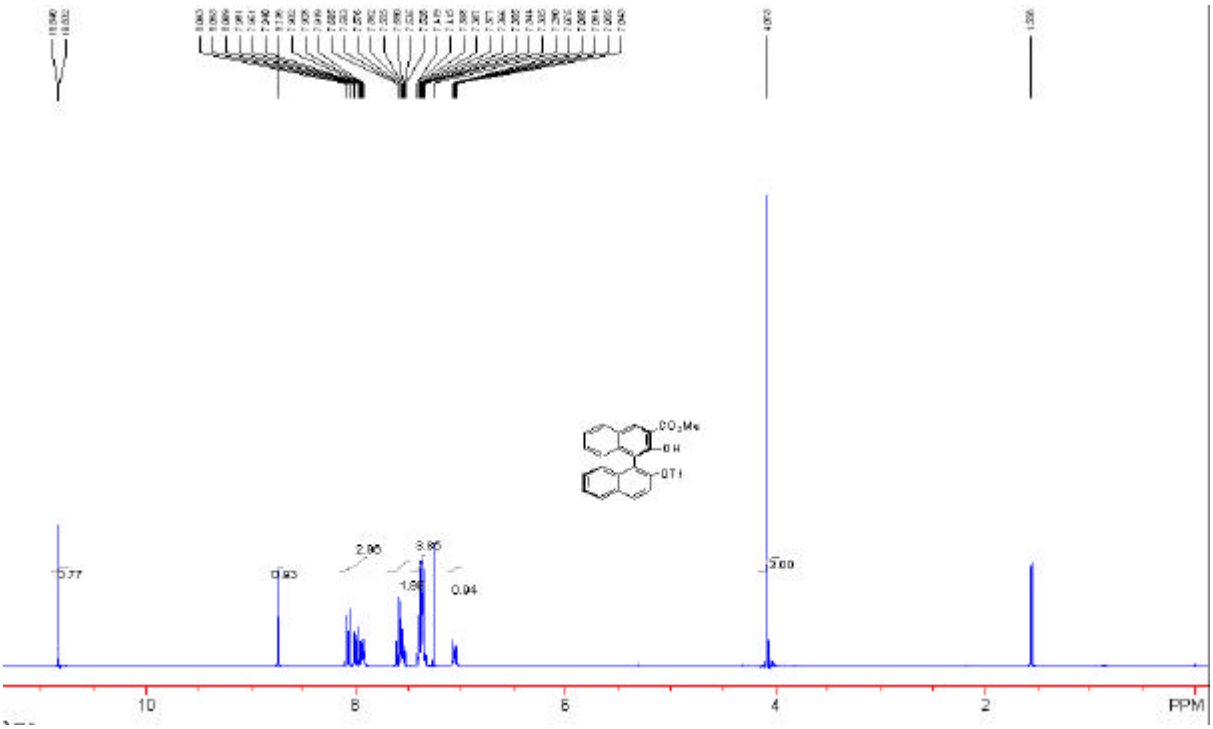
2,2'-Dihydroxy-[1,1']binaphthalenyl-3-carboxylic acid methyl ester CPLB1-3.

The procedure for the preparation of **CPLB1-12** was generally followed. This is a known compound.[3] Yield: 98%. $[\alpha]_D^{20}$ +21.6 (c 1.12, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.08 (3H, s), 4.95 (1H, s), 7.07 (1H, d, *J* = 8.4 Hz), 7.17-7.41 (6H, m), 7.87 (1H, d, *J* = 8.4 Hz), 7.91-7.96 (2H, m), 8.74 (1H, s), 10.84 (1H, s).

*Preparation of compound **CPLB1-4**.*



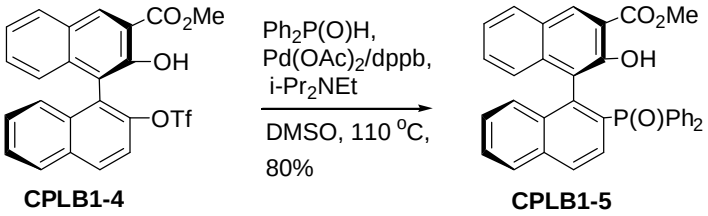
CPLB1-3 **CPLB1-4**



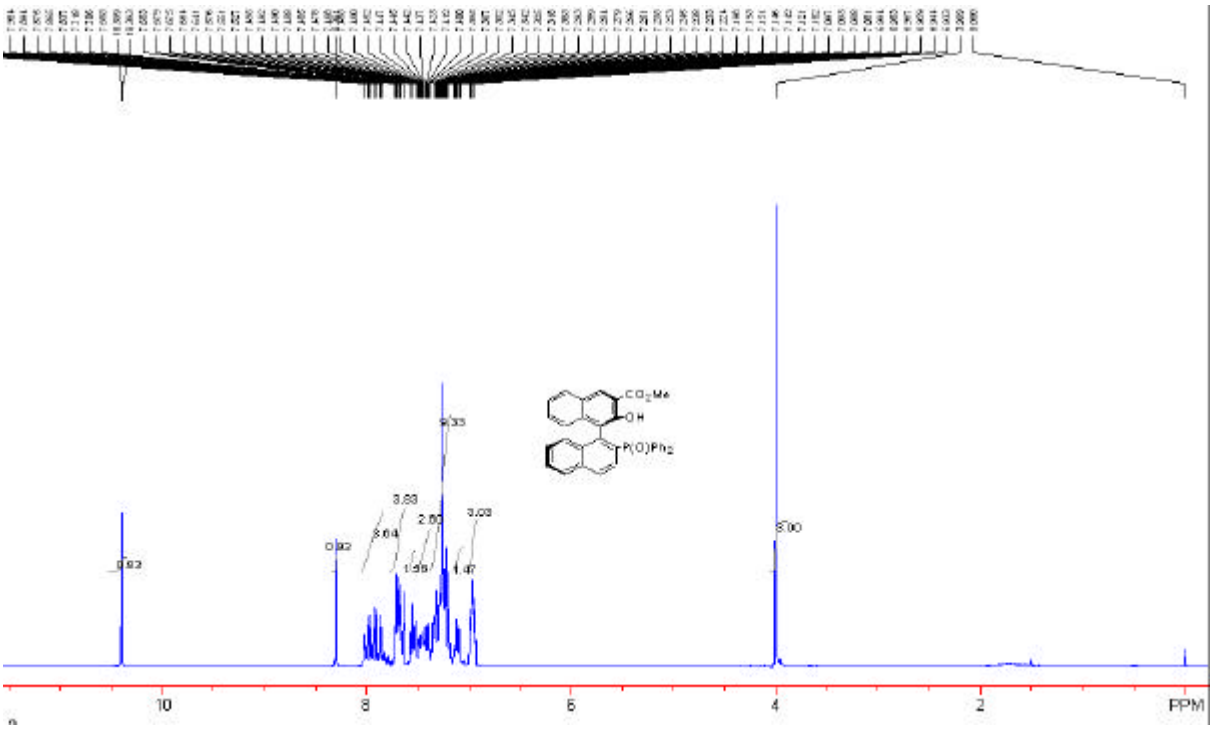
2-Hydroxy-2'-trifluoromethanesulfonyloxy-[1,1']binaphthalenyl-3-carboxylic acid methyl ester CPLB1-4.

The procedure for the preparation of **CPLB1-13** was generally followed. This is a known compound.[4] Yield: 90%. $[\alpha]_D^{20}$ +108.4 (c 1.14, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.00 (3H, s), 6.94-6.99 (1H, m), 7.34-7.42 (4H, m), 7.53-7.61 (2H, m), 7.92-7.95 (1H, m), 7.99 (1H, d, *J* = 8.1 Hz), 8.08 (1H, d, *J* = 9.0 Hz), 8.73 (1H, s), 10.83 (1H, s).

*Preparation of compound **CPLB1-5**.*



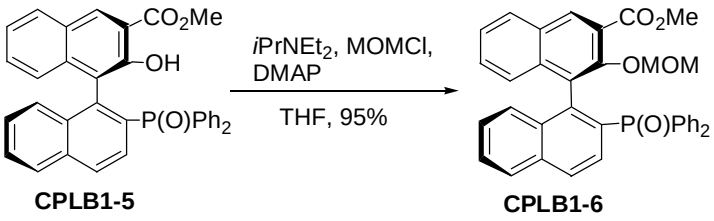
CPLB1-4 **CPLB1-5**



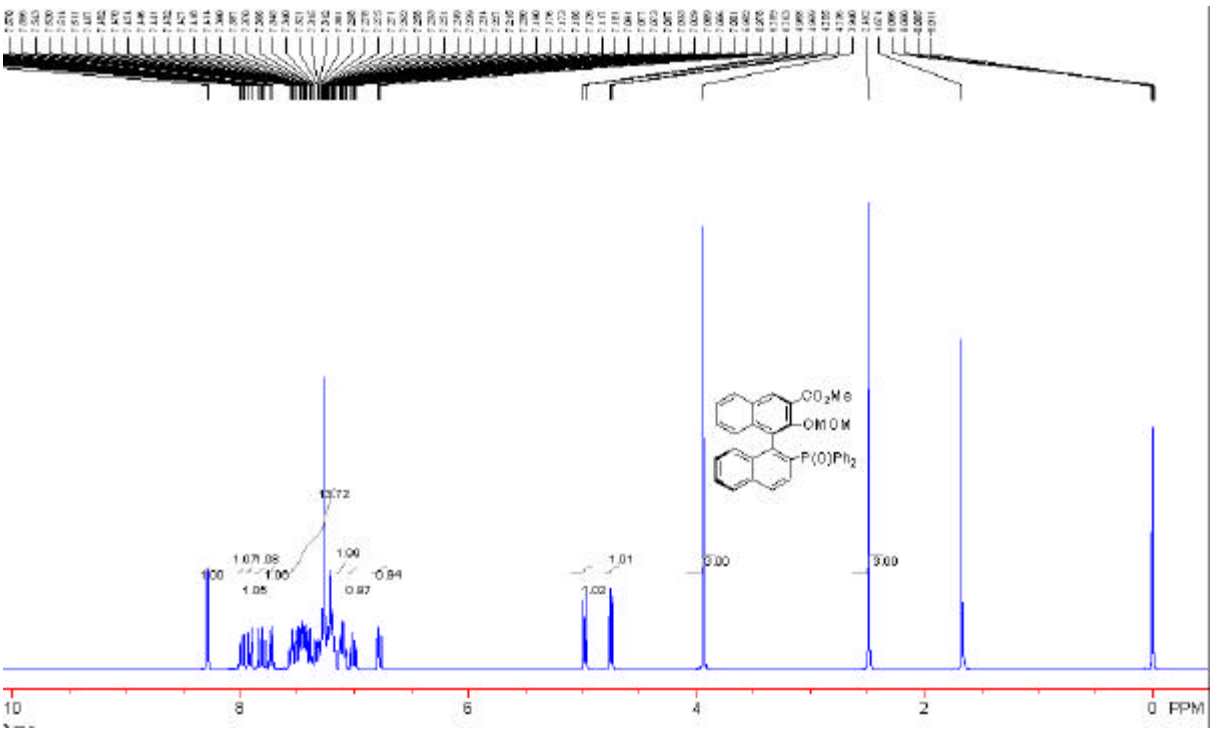
2'-(Diphenyl-phosphinoyl)-2-hydroxy-[1,1']binaphthalenyl-3-carboxylic acid methyl ester CPLB1-5.

The procedure for the preparation of **CPLB1-14** was generally followed. This is a known compound.[4] Yield: 80%. $[\alpha]_D^{20}$ –55.0 (c 1.05, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.07 (3H, s), 6.94-7.00 (3H, m), 7.09-7.13 (1H, m), 7.20-7.35 (6H, m), 740-7.57 (3H, m), 7.63-7.72 (4H, m), 7.83-8.02 (3H, m), 8.30 (1H, s), 10.38 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +29.27.

*Preparation of compound **CPLB1-6**.*



CPLB1-5 **CPLB1-6**

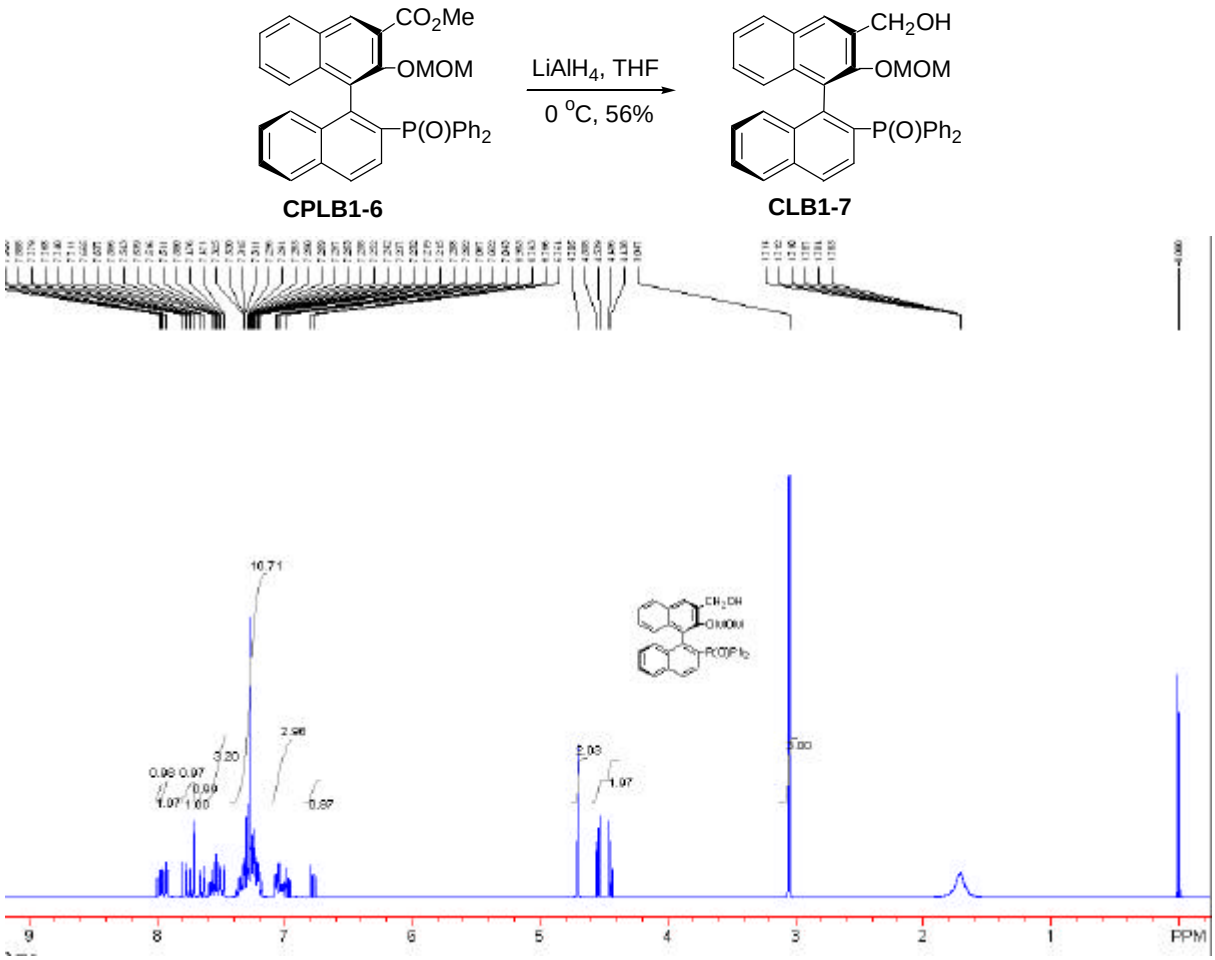


2'-(Diphenyl-phosphinoyl)-2-methoxymethoxy-[1,1']binaphthalenyl-3-carboxylic acid methyl ester CPLB1-6.

To a solution of **CPLB1-5** (1.24 g, 2.3 mmol) in CH_2Cl_2 (30 mL) were added DMAP (107 mg, 0.87 mmol), *i*-Pr_2NEt (3.5 mL, 20 mmol) and MOMCl (1.05 mL, 13.8 mmol). The solution was refluxed for 3 hours, and quenched with water (5.0 mL). The mixture was washed with water (10 mL x 2) and extracted with CH_2Cl_2. After drying over anhydrous $MgSO_4$, the organic solvent was evaporated under reduced pressure. The residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/1) to give product **CPLB1-6** (1.3 g, 95%) as a white solid: $[\alpha]_D^{20}$ +124.0 (c 1.01, $CHCl_3$). mp: 169-171 ^oC. IR (KBr): ν 3055, 2950, 1725, 1701, 1623, 1589, 1554, 1499, 1436, 1397, 1339, 1289, 1237, 1203, 1158, 1114, 1070, 974, 752, 699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.49 (3H, s), 3.94 (3H, s), 4.75 (1H, d, *J* = 6.0 Hz), 4.98 (1H, d, *J* = 6.0 Hz), 6.78 (1H, d, *J* = 8.1 Hz), 6.98-7.04 (1H, m), 7.07-7.13 (2H, m), 7.15-7.57 (12H, m), 7.73 (1H, d, *J* = 8.1 Hz), 7.81 (1H, dd, J_1 = 11.4 Hz, J_2 = 9.0 Hz), 7.91 (1H, d, *J* = 8.4 Hz), 7.99 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 8.28 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +29.66. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 52.2, 55.7, 99.6, 123.7, 125.1, 126.0, 126.8, 127.3, 127.4, 127.5, 127.6, 127.65, 127.69, 127.7, 127.8, 127.9, 128.2, 128.3, 128.5, 128.7, 128.8, 129.0, 130.2, 130.8, 130.9, 130.95, 130.99, 131.5, 131.56, 131.6, 131.63, 131.8, 131.9, 132.3, 133.2, 133.30, 133.32, 133.7, 134.1, 134.27, 134.30, 135.21, 135.23, 139.4, 139.5, 151.47, 151.48, 166.3. MS (EI): *m/e* 572 (M^+, 16.98), 557 (M^+-15, 1.66), 529 (M^+-44+1, 9.76), 512 (M^+-60, 5.00), 326 (M^+-45-201, 70.75), 295 (M^+-45-201-31, 9.59), 267 (M^+-201-45-59, 20.28), 216 (M^+-356, 21.48), 201 (Ph_2PO^+, 89.61),

77 (Ph^+, 24.37), 45 (572-527, 62.58). Anal. Calcd. for $C_{36}H_{29}O_5P$: requires C, 75.51; H, 5.10%; Found: C, 75.26; H, 5.04%.

*Preparation of compound **CPLB1-7**.*

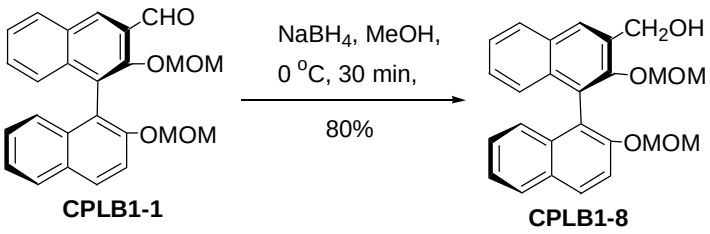


[2'-(Diphenyl-phosphinoyl)-2-methoxymethoxy-[1,1']binaphthalenyl-3-yl]-methanol CPLB1-7.

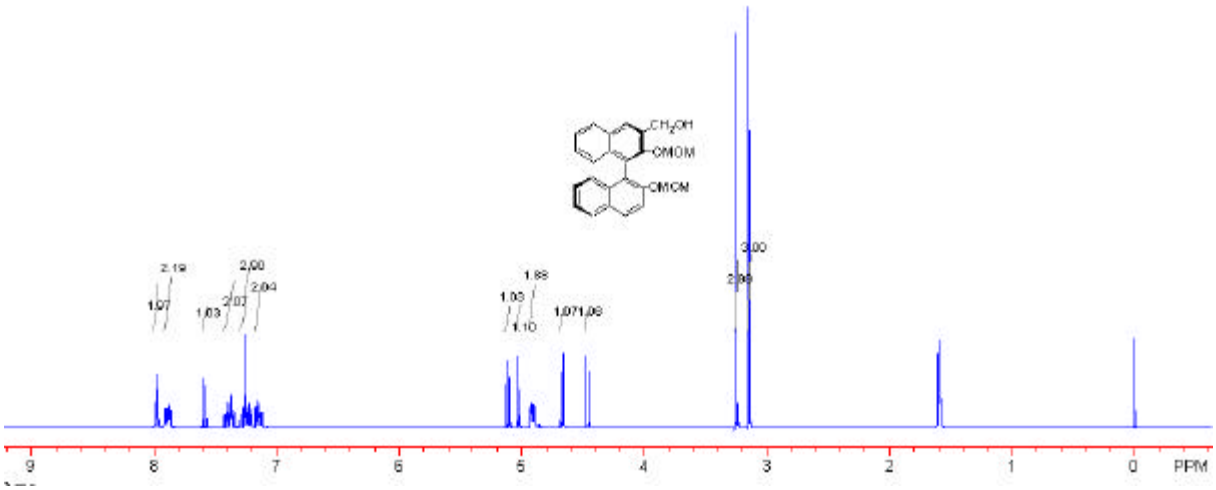
To a stirred solution of **CPLB1-6** (1.3 g, 2.2 mmol) in THF (30 mL) at ice bath $LiAlH_4$ (152 mg, 4.0 mmol) was added slowly. After completion of the reaction, it was quenched with water (10 mL). After extraction with CH_2Cl_2 (10 mL x 2), drying over anhydrous $MgSO_4$ and evaporation, the crude mixture was further purified by silica gel column chromatography (Eluent: EtOAc/PE/CH_3OH = 10/40/1) to give product **CPLB1-7** (680 mg, 56%) as a white solid: $[\alpha]_D^{20}$ –42.1 (c 1.08, $CHCl_3$). mp: 144-146 °C. IR (KBr): ν 3297 (br), 3054, 2930, 1590, 1560, 1500, 1436, 1398, 1378, 1354, 1309, 1180, 1156, 1114, 1098, 1070, 1022, 969, 922, 749, 723, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.06 (3H, s), 3.55 (1H, s, br), 4.44 (1H, d, *J* = 5.7 Hz), 4.52 (1H, d, *J* = 5.7 Hz), 4.71 (2H, s), 6.78 (1H, d, *J* = 8.1 Hz), 6.96-6.99 (1H, m), 7.00-7.08 (2H, m), 7.17-7.38 (9H, m), 7.47-7.59 (3H, m), 7.65 (1H, d, *J* = 8.1 Hz), 7.71 (1H, s),

7.77 (1H, dd, J_1 = 11.7 Hz, J_2 = 8.4 Hz), 7.94 (1H, d, J = 8.1 Hz), 7.99 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +29.27. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 56.2, 61.1, 98.3, 124.4, 125.6, 125.7, 125.98, 126.04, 126.9, 127.3, 127.4, 127.5, 127.6, 127.7, 127.74, 127.8, 127.83, 127.9, 128.92, 129.1, 129.7, 129.9, 130.3, 130.7, 130.8, 130.9, 131.0, 131.1, 131.2, 131.2, 131.3, 131.4, 131.5, 132.3, 132.6, 133.0, 133.2, 133.3, 133.7, 134.0, 134.3, 134.32, 139.9, 140.0, 152.5. MS (EI): *m/e* 482 (M^+-62, 6.26), 298 (M^+-62-30-77-77, 8.44), 282 (M^+-62-30-77-77-16, 15.91), 281 (M^+-263, 22.35), 268 (M^+-62-30-77-77-31+1, 12.29), 252 (M^+-201-62-30+1, 25.56), 239 (M^+-305, 25.32), 201 (Ph_2PO^+, 86.84), 77 (Ph^+, 18.77), 45 (572-469, 100). Anal. Calcd. for $C_{35}H_{29}O_4P$: requires C, 77.19; H, 5.37%; Found: C, 76.76; H, 5.55%.

*Preparation of compound **CPLB1-8**.*



CPLB1-1 **CPLB1-8**

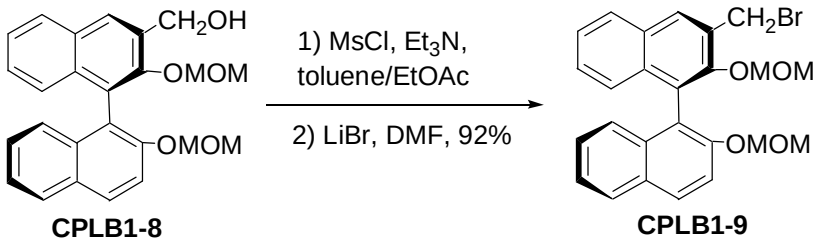


(2,2'-Bis-methoxymethoxy-[1,1']binaphthalenyl-3-yl)-methanol CPLB1-8.

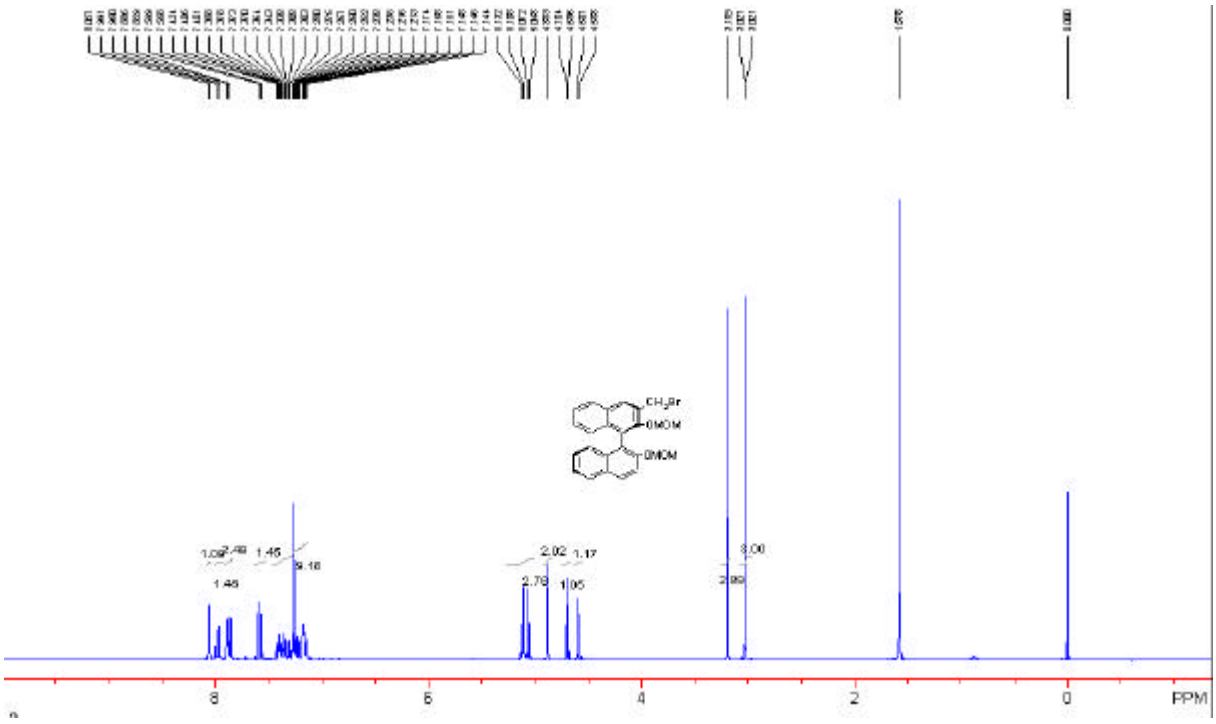
To a solution of **CPLB1-1** (3.74 g, 9.3 mmol) in methanol (30 mL) was added $NaBH_4$ (1.14 g, 30 mmol) slowly at ice bath. After stirring for 1.5 hours, water (5.0 mL) was added to quench the reaction. After extraction with ethyl acetate (10 mL x 2), drying over anhydrous $MgSO_4$,

the organic solvent was removed under reduced pressure. The residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/4) to give product **CPLB1-8** (3.1 g, 83%) as a white solid. This is a known compound.[5] $[\alpha]_D^{20}$ +63.4 (c 0.96, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.15 (3H, s), 3.26 (3H, s), 3.49 (1H, t, *J* = 6.6 Hz), 4.46 (1H, d, *J* = 6.0 Hz), 4.67 (1H, d, *J* = 6.0 Hz), 4.88-4.94 (2H, m), 5.05 (1H, d, *J* = 6.3 Hz), 5.11 (1H, d, *J* = 6.3 Hz), 7.12-7.30 (4H, m), 7.35-7.41 (2H, m), 7.59 (1H, d, *J* = 9.0 Hz), 7.89 (1H, d, *J* = 8.1 Hz), 7.90 (1H, d, *J* = 8.4 Hz), 7.97 (1H, s), 7.98 (1H, d, *J* = 9.1 Hz).

*Preparation of compound **CPLB1-9**.*



CPLB1-8 **CPLB1-9**

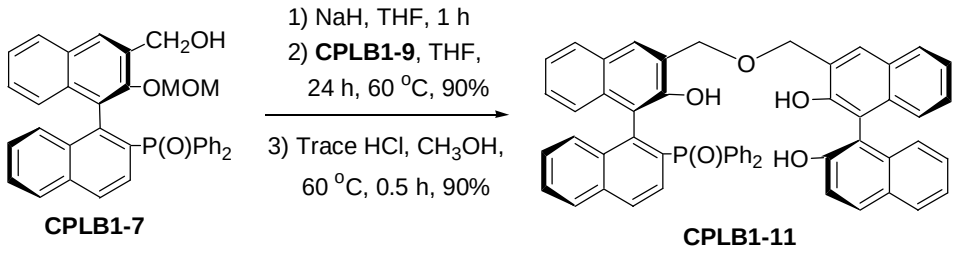


3-Bromomethyl-2,2'-bis-methoxymethoxy-[1,1']binaphthalenyl CPLB1-9.

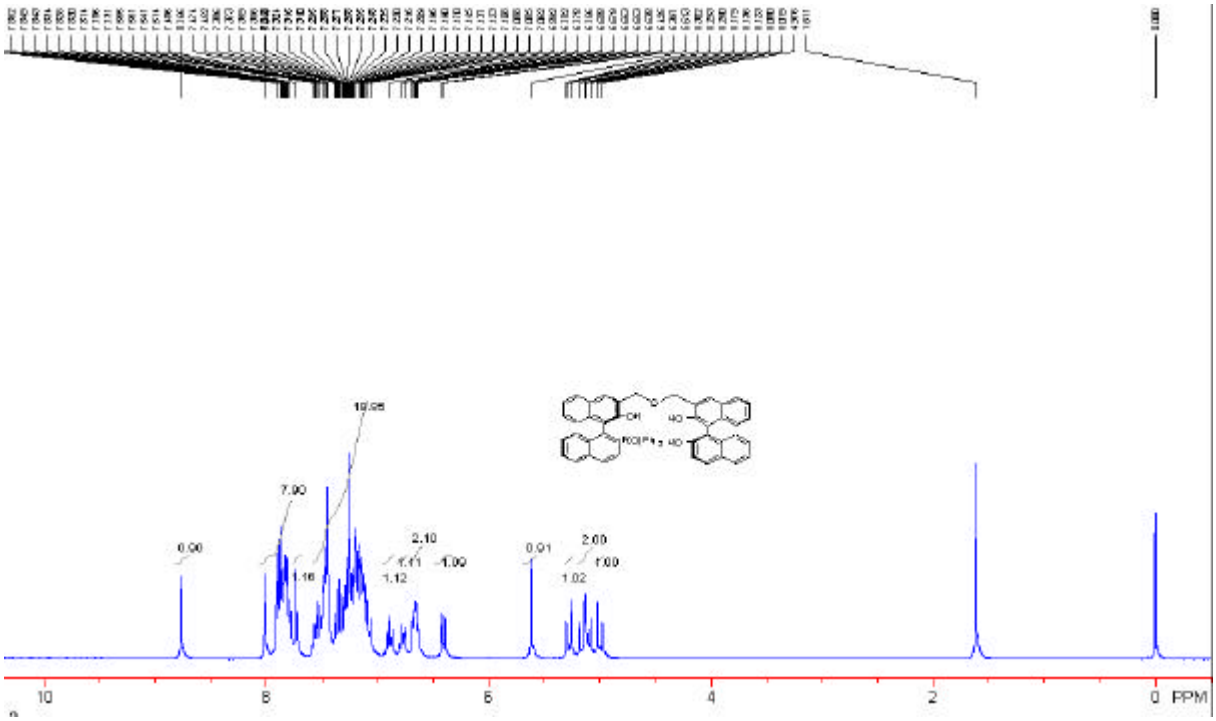
To a solution of **CPLB1-8** (1.9 g, 4.7 mmol) in toluene (30 mL) and ethyl acetate (30 mL) was added triethylamine (1.4 mL, 9.4 mmol) at ice bath, then methanesulfonyl chloride (0.45 mL, 6.0 mmol) was added slowly. After stirring for 90 minutes, the mixture was filtrated and the organic solvent in the filtrate was removed under reduced pressure. DMF (20 mL) and LiBr (4.3 g, 50 mmol) was added to the residue. The mixture was stirred for 12 hours, and the DMF was removed under reduced pressure. After washing with water (10 mL), extraction with ethyl

acetate (10 mL x 2) and evaporation, the residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/8) to give product **CPLB1-9** (2.0 g, 92%) as a white solid. This is a known compound.[5] $[\alpha]_D^{20}$ +60.0 (c 0.96, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.03 (3H, s), 3.19 (3H, s), 4.59 (1H, d, *J* = 6.0 Hz), 4.69 (1H, d, *J* = 6.0 Hz), 4.89 (2H, s), 5.05 (1H, d, *J* = 7.2 Hz), 5.11 (1H, d, *J* = 7.2 Hz), 7.14-7.69 (7H, m), 7.59 (1H, d, *J* = 9.0 Hz), 7.87 (2H, d, *J* = 8.4 Hz), 7.98 (1H, d, *J* = 9.0 Hz), 8.06 (1H, s).

*Preparation of compound **CPLB1-11**.*



CPLB1-7 **CPLB1-11**

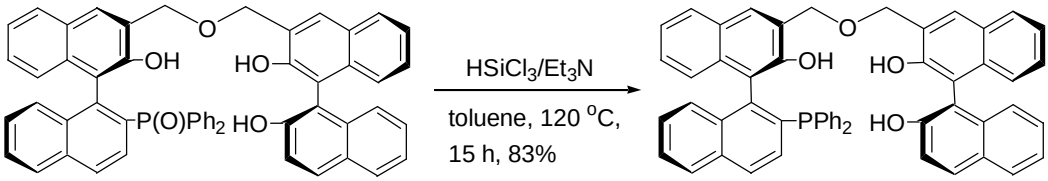


3-[2'-(Diphenyl-phosphinoyl)-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxymethyl]-[1,1'] binaphthalenyl-2,2'-diol CPLB1-11.

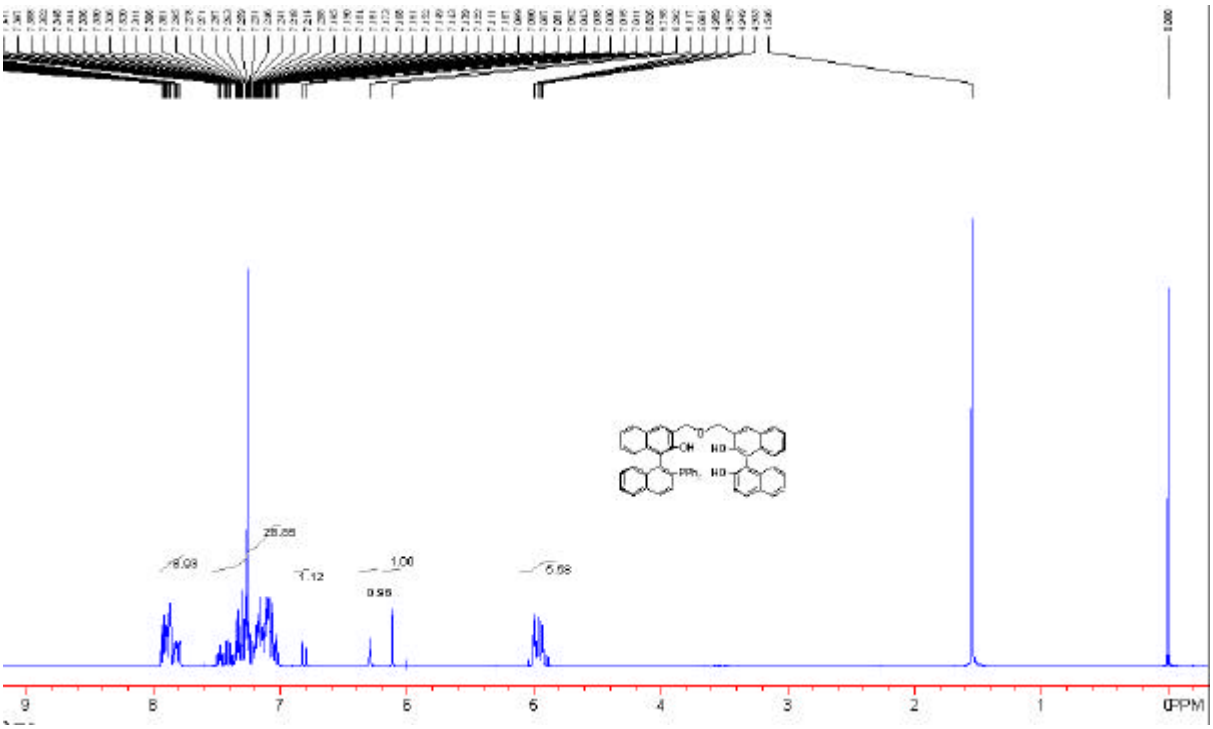
To a suspension of NaH (60 mg, 2.5 mmol) in THF (10 mL) was added dropwise the solution of **CPLB1-7** (680 mg, 1.25 mmol) in THF (40 mL). After stirring for 1 hour, **CPLB1-9** (582 mg, 1.25 mmol) was added. The mixture was refluxed for 20 hours, quenched with water (10 mL). After extraction with ethyl acetate (40 mL x 2) and evaporation, the crude product was obtained as a white solid. The solid was dissolved in methanol (60 mL), and 5-10 drops hydrochloric acid was added at 60 °C. When the starting materials disappeared, the organic

solvent was removed under reduced pressure. The crude product was washed with water (10 mL x 2), extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. After evaporation, the residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/1) to give product **CPLB1-11** (799 mg, 80%) as a white solid: $[\alpha]_D^{20}$ –25.3 (c 1.06, $CHCl_3$). mp: 273-275 ^oC. IR (KBr): ν 3529, 3272 (br), 3055, 1620, 1597, 1505, 1468, 1438, 1383, 1356, 1129, 1114, 1090, 818, 749, 724, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.99 (1H, d, *J* = 12.6 Hz), 5.13 (2H, d, *J* = 12.6 Hz), 5.28 (1H, d, *J* = 12.6 Hz), 5.67 (1H, s), 6.41 (1H, d, *J* = 8.4 Hz), 6.63-6.69 (2H, m), 6.76-6.81 (1H, m), 6.89 (1H, dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz), 7.06-7.56 (19H, m), 7.73-7.91 (8H, m), 8.01 (1H, s), 8.75 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +32.44. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 69.0, 70.8, 113.5, 113.8, 117.9, 123.25, 123.32, 123.5, 123.9, 124.5, 124.8, 125.4, 125.6, 126.1, 126.7, 127.0, 127.3, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.16, 128.18, 128.3, 128.6, 128.7, 128.73, 128.9, 129.1, 129.3, 129.4, 129.6, 129.8, 123.0, 130.1, 130.2, 130.3, 130.35, 130.37, 131.0, 131.4, 132.0, 132.06, 132.10, 132.14, 133.11, 133.4, 133.5, 133.69, 133.72, 135.1, 135.2, 141.2, 141.3, 151.8, 152.1, 152.4. MS (EI): *m/e* 500 (M^+-298, 7.64), 482 (M^+-500-18, 28.85), 316 (M^+-482, 19.41), 298 (M^+-500, 39.79), 282 (M^+-316-201+1, 69.75), 281 (M^+-316-201, 45.24), 252 (M^+-201-316-30+1, 25.56), 239 (M^+-559, 68.40), 201 (Ph_2PO^+, 100), 77 (Ph^+, 37.57). HRMS (MALDI) for $C_{54}H_{39}O_5PNa^{+1}$: requires 821.2427; Found: 821.2415.

*Preparation of compound **CPLB1**.*



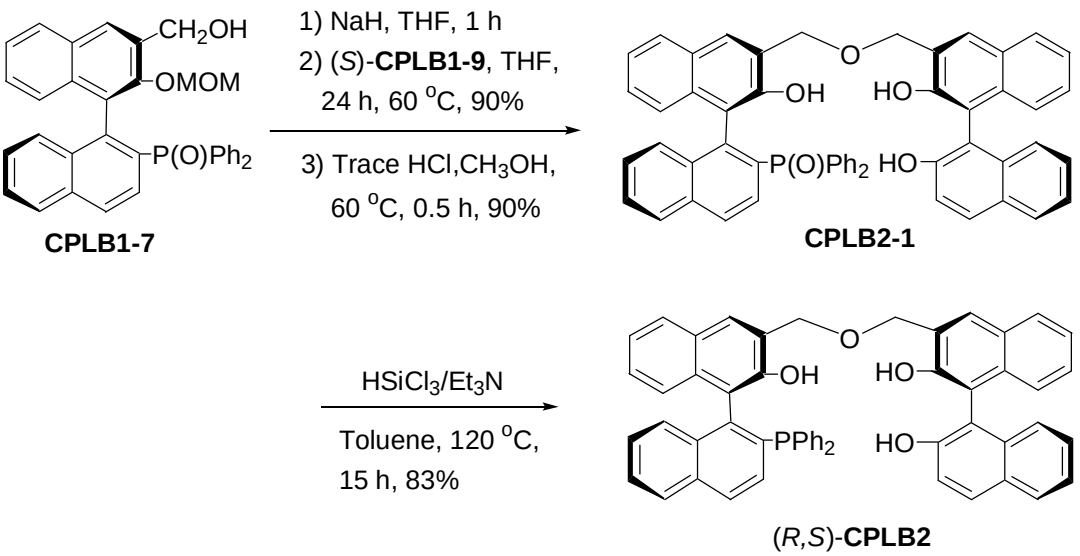
CPLB1-11 (*R*,*R*)-**CPLB1**



3-(2'-Diphenylphosphanyl-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxymethyl)-[1,1']bin aphthalenyl-2,2'-diol CPLB1.

To a solution of **CPLB1-11** (799 mg, 1.0 mmol) and Et_3N (0.67 mL, 5.6 mmol) in toluene (30 mL) was added $HSiCl_3$ (0.45 mL, 4.4 mmol) at 0 ^oC. The temperature was raised to 120 ^oC, and after 12 hours, the mixture was cooled to room temperature, then diluted with CH_2Cl_2 (100 mL). Saturated aqueous Na_2CO_3 was added to quench the reaction. After stirring for 15 minutes and extraction with water (3 x 30 mL), the organic layer was washed with aqueous hydrochloric acid (10 mL), saturated aqueous $NaHCO_3$ (30 mL) and brine (20 mL). After drying over anhydrous $MgSO_4$ and evaporation, the residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/1) to give product **CPLB1** (650 mg, 83%) as a white solid: $[\alpha]_D^{20}$ +32.4 (c 1.04, $CHCl_3$). mp: 168-170 ^oC. IR (KBr): ν 3514, 3373 (br), 3052, 2923, 1725, 1621, 1594, 1504, 1466, 1434, 1385, 1338, 1256, 1211, 1108, 1067, 817, 746, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.89-5.04 (5H, m), 6.12 (1H, s), 6.29 (1H, s), 6.81 (1H, d, *J* = 8.1 Hz), 7.01-7.50 (23H, m), 7.79-7.94 (8H, m). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.22. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 69.6, 70.7, 112.2, 112.4, 117.7, 119.6, 119.7, 123.4, 123.6, 124.1, 124.3, 124.4, 124.6, 124.9, 125.6, 126.2, 126.2, 126.4, 126.9, 127.0, 127.2, 127.8, 128.0, 128.0, 128.1, 128.1, 128.1, 128.2, 128.2, 128.6, 128.8, 129.1, 129.2, 129.8, 130.1, 130.7, 132.9, 133.0, 133.2, 133.3, 133.4, 133.46, 133.47, 133.6, 133.7, 134.01, 134.04, 137.0, 137.2, 137.3, 137.40, 137.43, 137.6, 139.4, 139.8, 150.66, 150.69, 151.7, 152.0. MS (MALDI): *m/e* 783 (M^+), 781 (M^+-2). HRMS (MALDI) for $C_{54}H_{40}O_4P^{+1}$: requires 783.2659; Found: 783.2633.

***Preparation of chiral phosphine Lewis bases (CPLB2) bearing multiple phenol groups*.**



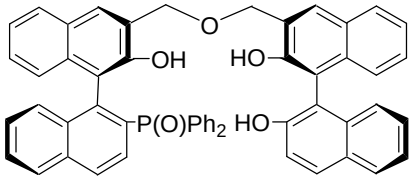
CPLB1-7

CPLB2-1

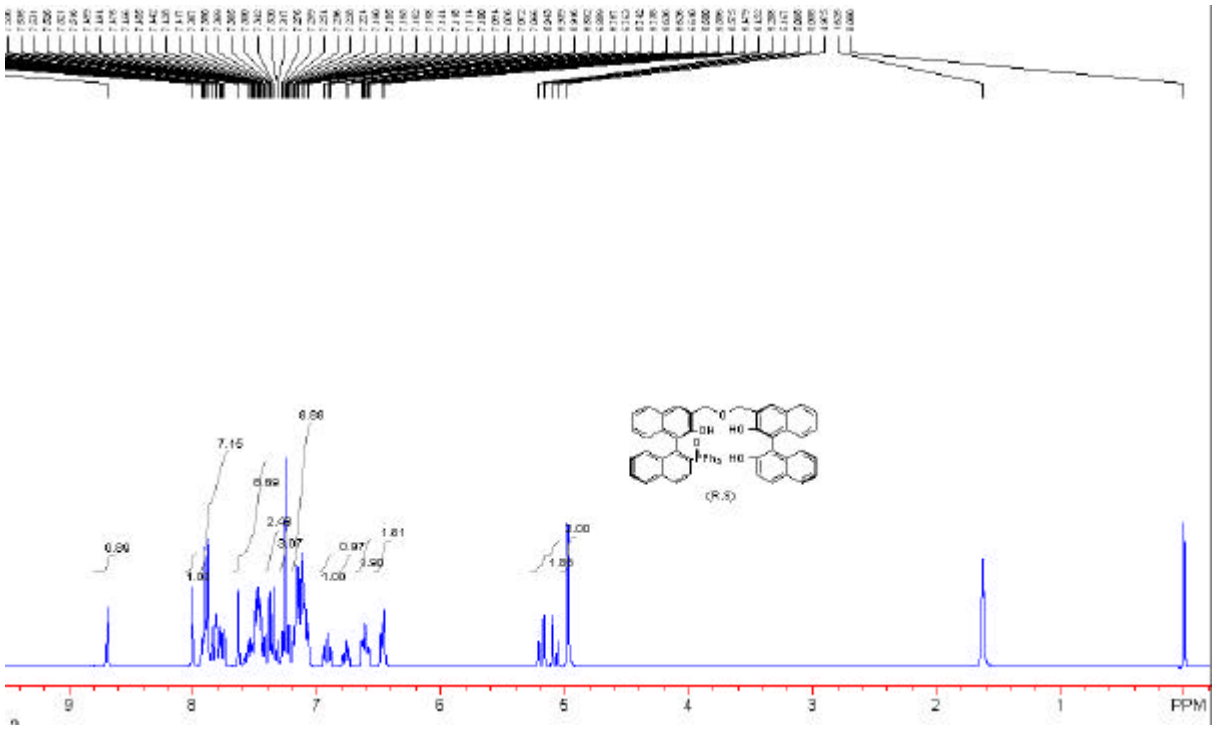
(*R,S*)-**CPLB2**

Scheme SI-3

*Preparation of compound **CPLB2-1**.*



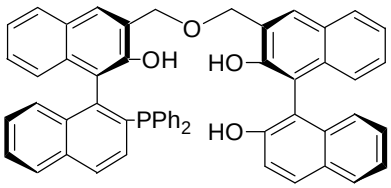
CPLB2-1



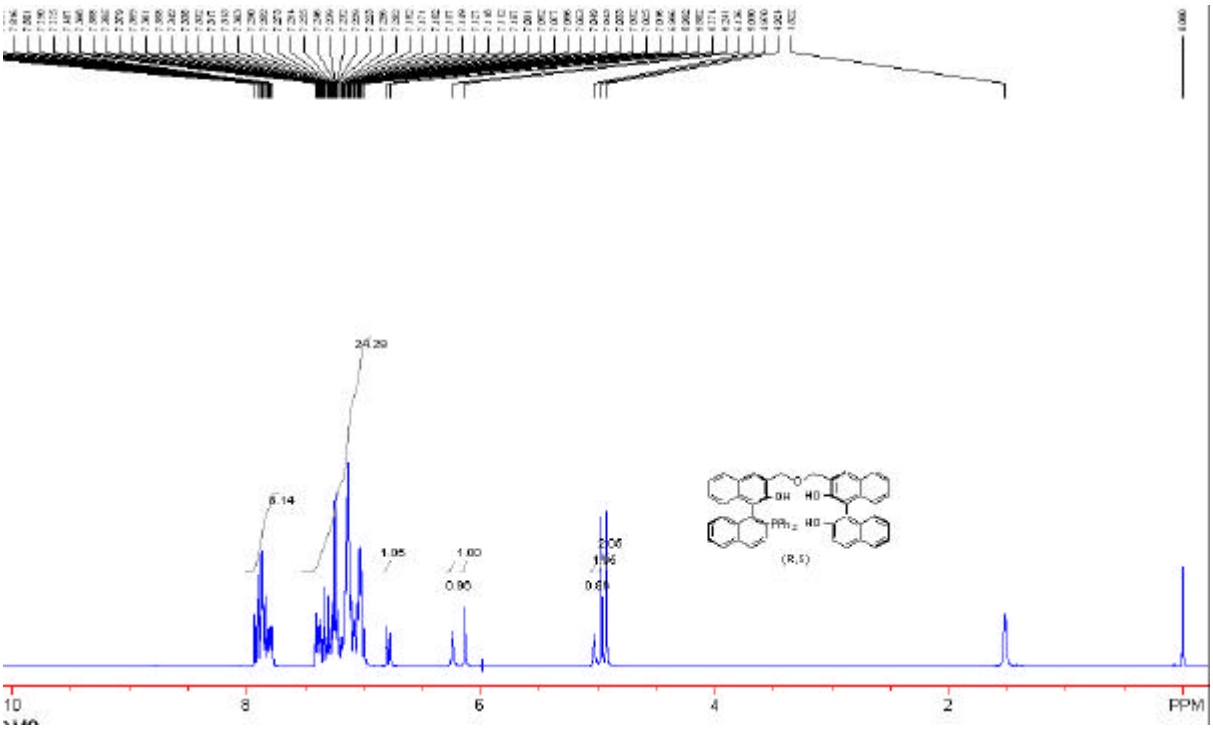
3-[2'-(Diphenyl-phosphinoyl)-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxymethyl]-[1,1'] binaphthalenyl-2,2'-diol CPLB2-1.

The procedure for the preparation of **CPLB1-11** was generally followed. Yield: 81%. $[\alpha]_D^{20}$ –51.2 (c 1.08, $CHCl_3$). mp: 180-182 ^oC. IR (KBr): ν 3525, 3363 (br), 3058, 2926, 1622, 1597, 1505, 1437, 1386, 1345, 1276, 1169, 1150, 1113, 1071, 817, 748, 724, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.98 (2H, s), 5.07 (1H, d, *J* = 12.3 Hz), 5.18 (1H, d, *J* = 12.3 Hz), 6.45 (1H, s), 6.48 (1H, s), 6.57-6.64 (2H, m), 6.74-6.79 (1H, m), 6.89-6.92 (1H, m), 7.07-7.19 (9H, m), 7.22-7.28 (2H, m), 7.32-7.56 (8H, m), 7.63 (1H, s), 7.74-7.93 (7H, m), 8.00 (1H, s), 8.69 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +32.24. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 69.3, 70.4, 113.2, 114.3, 118.2, 121.8, 121.9, 123.1, 123.16, 123.21, 123.6, 124.7, 125.1, 125.3, 125.5, 126.0, 126.5, 126.7, 127.0, 127.1, 127.2, 127.3, 127.5, 127.8, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.8, 128.9, 129.1, 129.3, 129.4, 129.6, 129.7, 129.8, 130.1, 130.15, 130.22, 130.3, 130.6, 131.7, 131.8, 131.9, 133.1, 133.2, 133.3, 133.7, 133.8, 134.9, 135.0, 140.9, 141.1, 151.7, 151.9, 152.6. MS (MALDI): *m/e* 799.3 (M^++1). HRMS (MALDI) for $C_{54}H_{39}O_5PNa^{+1}$: requires 821.2427; Found: 821.2417.

*Preparation of compound **CPLB2**.*



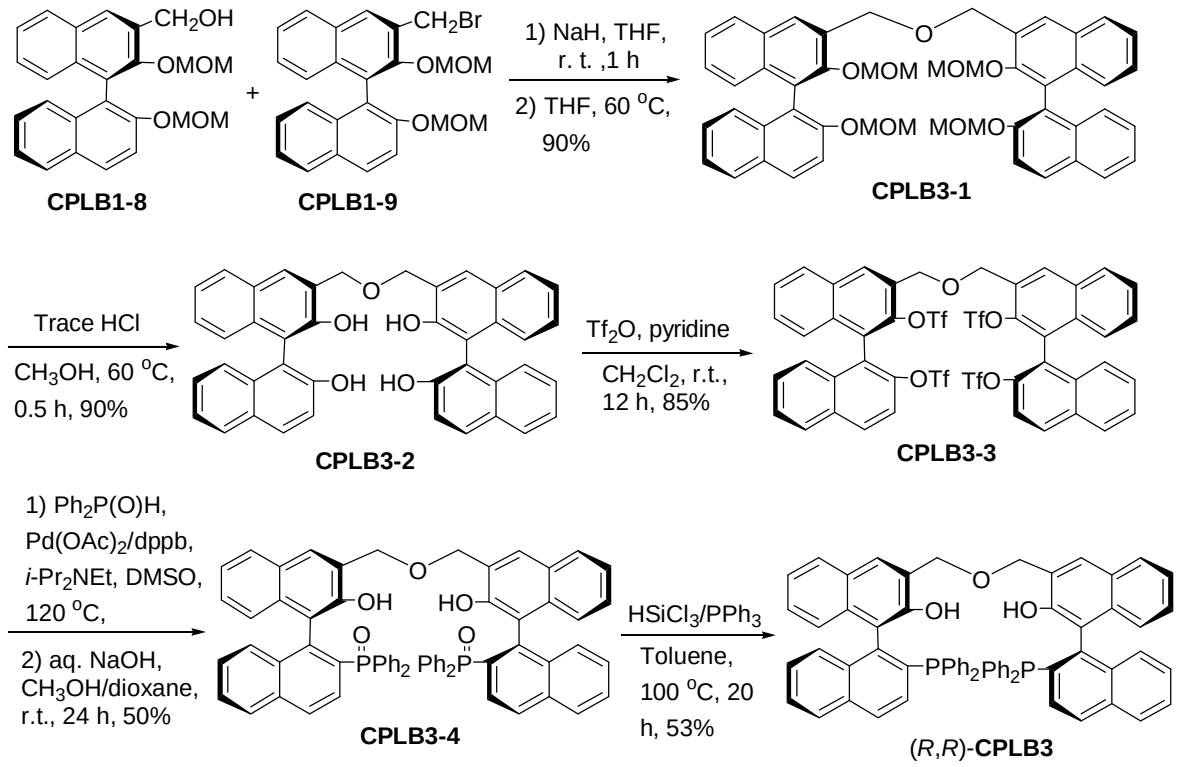
(*R,S*)-**CPLB2**



3-(2'-Diphenylphosphanyl-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxymethyl)-[1,1']bin aphthalenyl-2,2'-diol CPLB2.

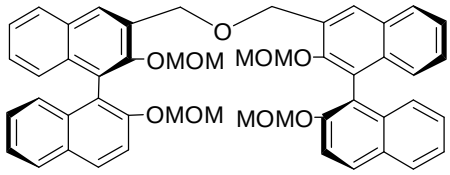
The procedure for the preparation of **CPLB1** was generally followed. Yield: 83%. $[\alpha]_D^{20}$ –20.0 (c 0.99, $CHCl_3$). mp: 180-183 ^oC. IR (KBr): ν 3519, 3383 (br), 3053, 2922, 2852, 1621, 1596, 1504, 1465, 1435, 1385, 1340, 1258, 1211, 1108, 1068, 1025, 817, 746, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 4.93 (2H, s), 4.97 (2H, s), 5.03 (1H, s), 6.14 (1H, s), 6.24 (1H, s), 6.79 (1H, d, *J* = 8.4 Hz), 6.99-7.41 (23H, m), 7.78-7.93 (8H, m). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.12. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 69.6, 70.7, 112.1, 112.4, 117.6, 119.6, 119.7, 123.4, 123.6, 124.1, 124.2, 124.3, 124.5, 124.9, 125.5, 126.2, 126.3, 126.7, 126.8, 126.9, 127.3, 127.8, 127.9, 128.0, 128.1, 128.16, 128.21, 128.5, 128.7, 129.1, 129.2, 130.0, 130.1, 130.6, 132.8, 132.9, 133.2, 133.3, 133.38, 133.44, 133.5, 133.6, 133.7, 134.0, 134.1, 137.0, 137.1, 137.2, 137.3, 137.4, 137.6, 139.4, 139.9, 150.7, 150.8, 151.8, 152.1. MS (MALDI): *m/e* 821.4 (M^++23), 783.5 (M^+), 782.5 (M^+-1), 781.5 (M^+-2). HRMS (MALDI) for $C_{54}H_{40}O_4P^{+1}$: requires 783.2659; Found: 783.2656.

Preparation of chiral phosphine Lewis bases CPLB3.

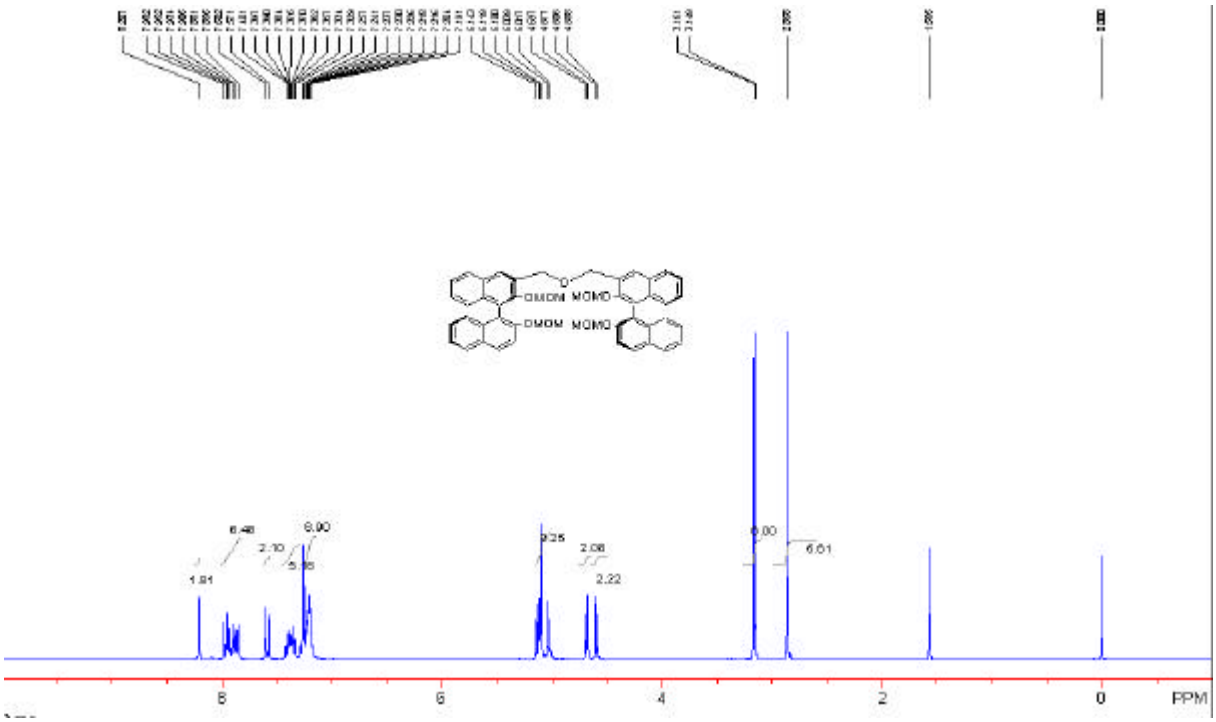


Scheme SI-4

*Preparation of compound **CPLB3-1**.*



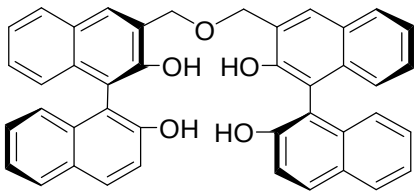
CPLB3-1



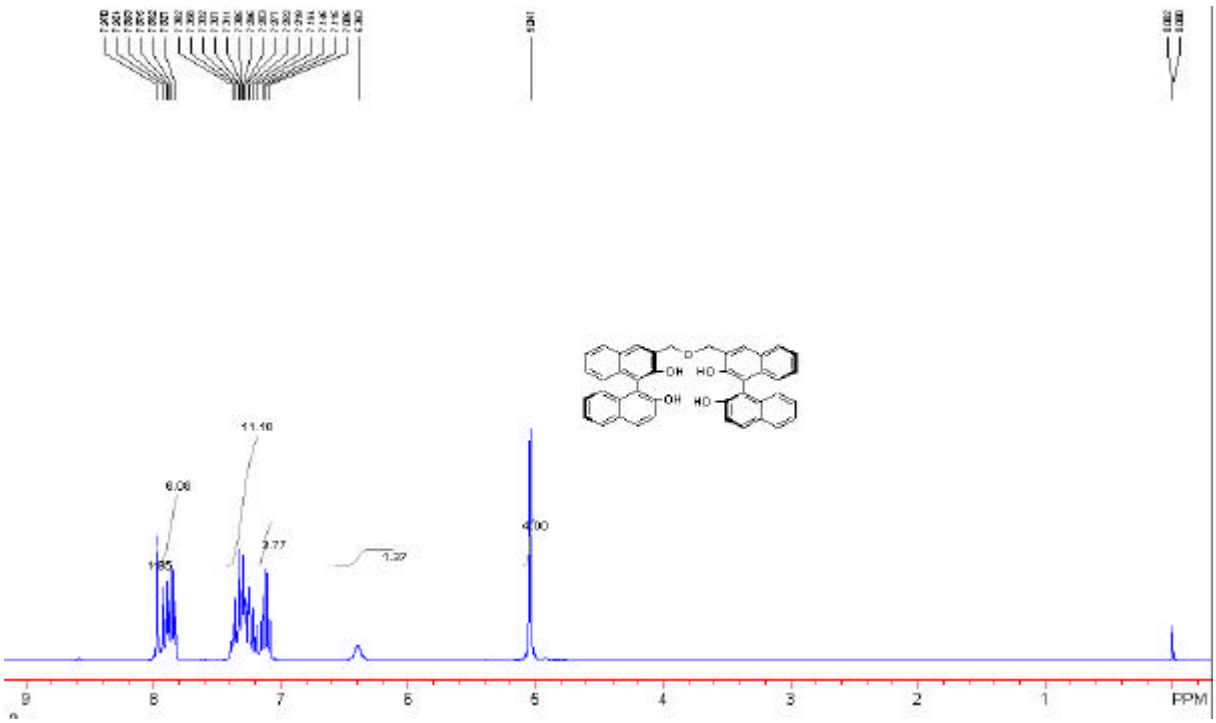
2-(methoxymethoxy)-3-(((3-(methoxymethoxy)-4-(2-(methoxymethoxy)naphthalen-1-yl) naphthalen-2-yl)methoxy)methyl)-1-(2-(methoxymethoxy)naphthalen-1-yl)naphthalene CPLB3-1.

The procedure for the preparation of **CPLB1-11** was generally followed. This is a known compound.[4] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.86 (6H, s), 3.16 (6H, s), 4.58 (2H, d, *J* = 5.4 Hz), 4.70 (2H, d, *J* = 5.4 Hz), 5.00 (2H, d, *J* = 6.9 Hz), 5.12 (2H, d, *J* = 6.9 Hz), 5.10 (4H, s), 7.18-7.24 (8H, m), 7.33-7.40 (4H, m), 7.59 (2H, d, *J* = 9.0 Hz), 7.87 (2H, d, *J* = 7.8 Hz), 7.92 (2H, d, *J* = 8.1 Hz), 7.97 (2H, d, *J* = 9.0 Hz), 8.21 (2H, s).

*Preparation of compound **CPLB3-2**.*



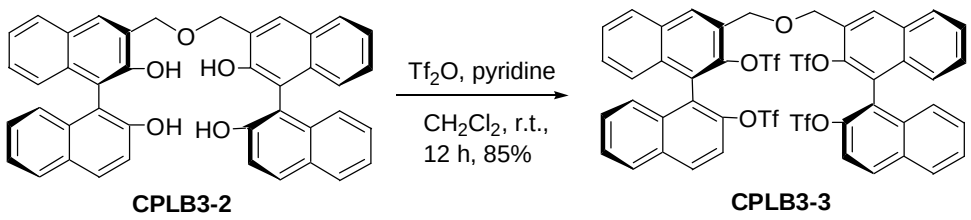
CPLB3-2



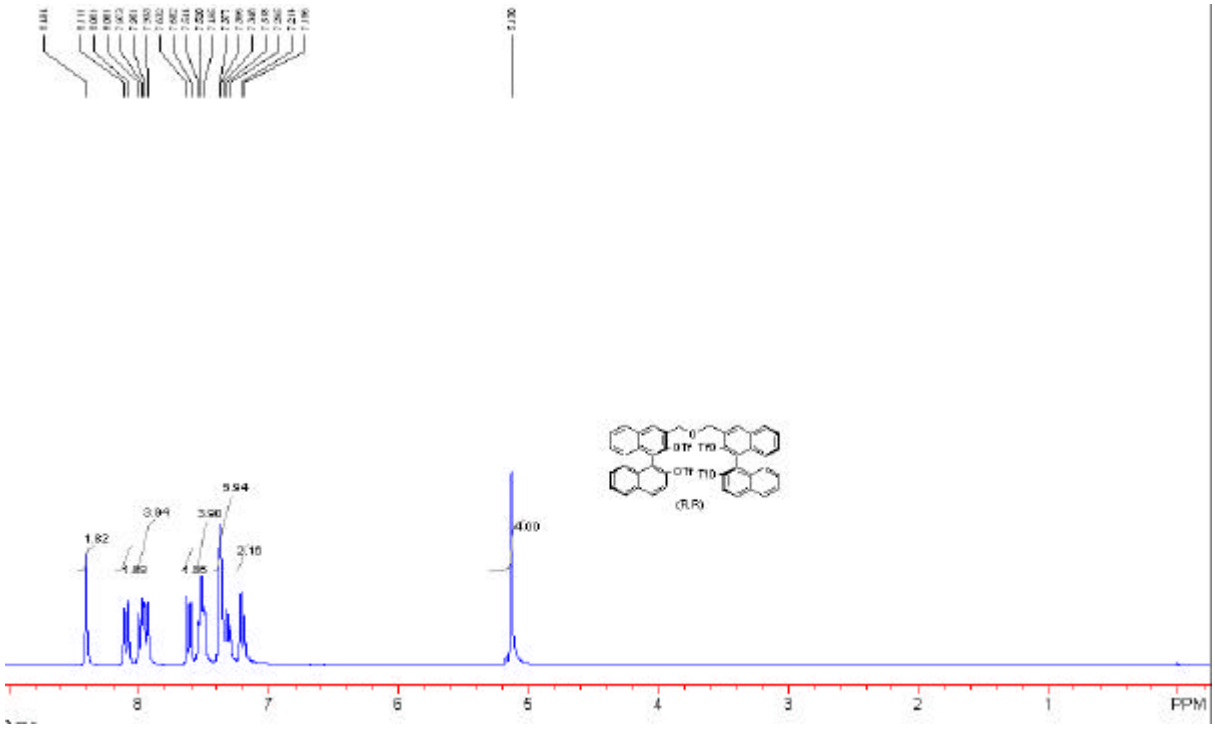
3,3''-(oxydimethylene)-di-1,1'-bi-2-naphthol CPLB3-2.

The procedure for the preparation of **CPLB1-11** was generally followed. $[\alpha]_D^{20}$ +60.6 (c 1.07, $CHCl_3$). This is a known compound.[4] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.04 (4H, s, br), 6.34 (2H, s), 7.09 (2H, d, *J* = 8.7 Hz), 7.12 (2H, d, *J* = 9.3 Hz), 7.20 (2H, dd, J_1 = 7.2 Hz, J_2 = 1.8 Hz), 724-7.38 (8H, m), 7.84 (2H, d, *J* = 7.8 Hz), 7.86 (2H, d, *J* = 7.2 Hz), 7.91 (1H, d, *J* = 9.0 Hz), 7.97 (2H, s).

*Preparation of compound **CPLB3-3**.*



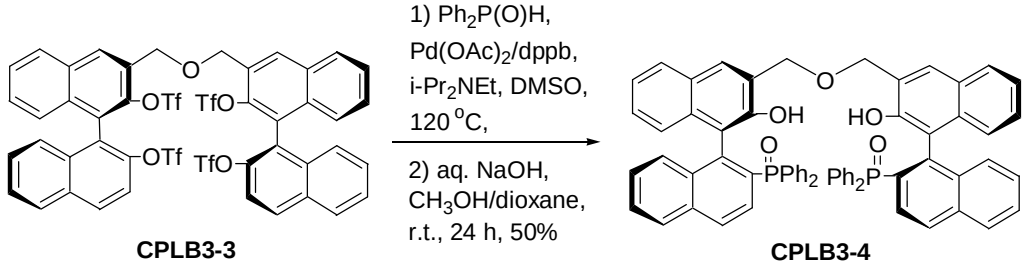
CPLB3-2 **CPLB3-3**



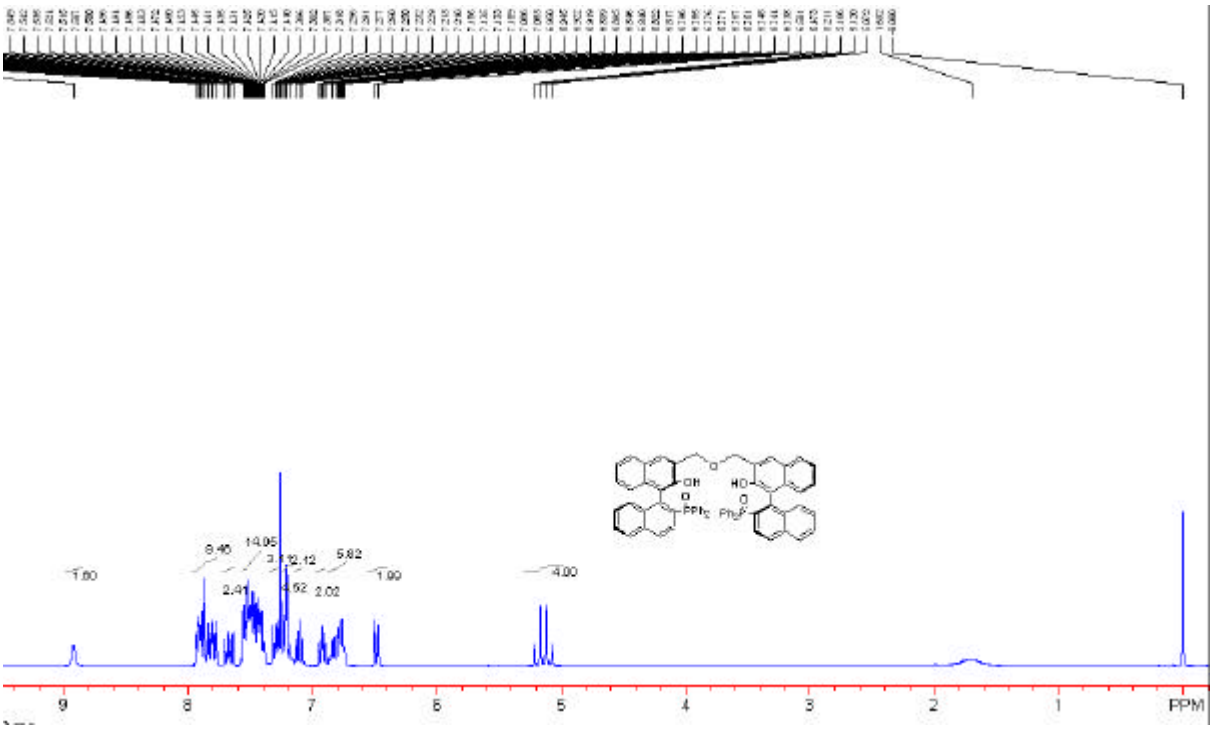
Trifluoromethanesulfonic acid 3'-(2,2'-bis-trifluoromethanesulfonyloxy-[1,1'] binaphthalenyl-3-ylmethoxymethyl)-2'-trifluoromethanesulfonyloxy-[1,1']binaphthalenyl-2-yl ester CPLB3-3.

The procedure for the preparation of **CPLB1-4** was generally followed. $[\alpha]_D^{20}$ –143.0 (c 1.08, $CHCl_3$). IR (KBr): ν 3066 1595, 1510, 1418, 1361, 1217, 1137, 940, 890, 822, 751 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 5.08 (4H, s), 7.18 (2H, d, J = 8.7 Hz), 7.35-7.46 (6H, m), 7.56-7.64 (6H, m), 8.02 (4H, d, J = 8.4 Hz), 8.15 (2H, d, J = 9.3 Hz), 8.38 (2H, s). ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ –75.1 (6F, s), -74.4 (6F, s). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 67.9, 118.0 (d, J_{C-F} = 318.9 Hz), 118.4 (d, J_{C-F} = 317.7 Hz), 119.3, 123.7, 124.7, 126.7, 127.1, 127.3, 127.6, 127.8, 128.0, 128.2, 128.4, 129.4, 131.7, 132.1, 132.3, 132.5, 132.8, 133.6, 143.4, 145.5. MS (ESI): *m/e* 1160 (M^++18). Anal. Calcd. for $C_{46}H_{26}F_{12}O_4S_4$: requires C, 48.34; H, 2.29%; Found: C, 48.04; H, 2.40%.

*Preparation of compound **CPLB3-4**.*



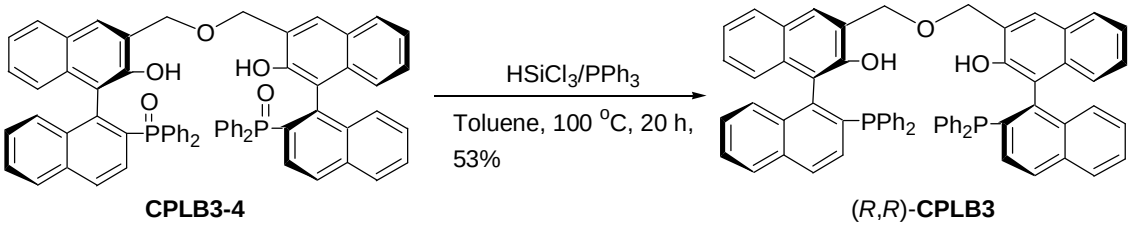
CPLB3-3 **CPLB3-4**



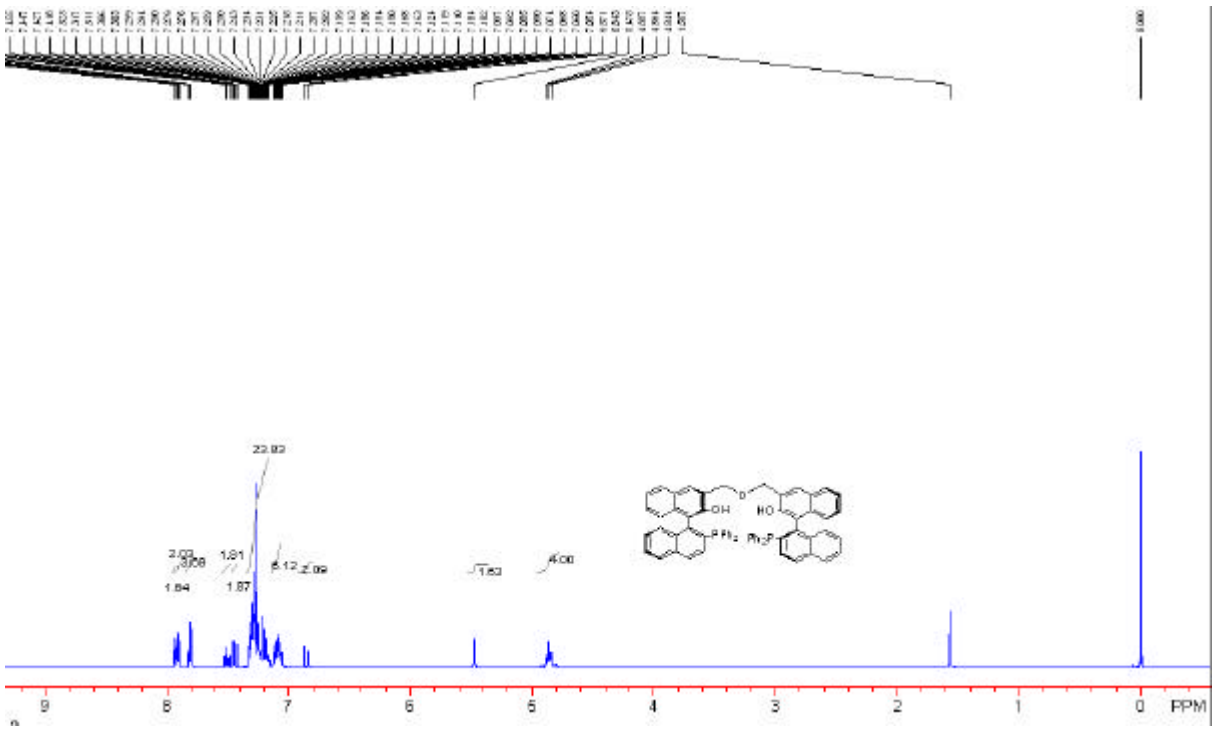
1-(2-(diphenylphosphoryl)naphthalen-1-yl)-3-(((4-(2-(diphenylphosphoryl)naphthalen-1-yl)-3-hydroxynaphthalen-2-yl)methoxy)methyl)naphthalen-2-ol CPLB3-4.

The procedure for the preparation of **CPLB1-5** was generally followed. $[\alpha]_D^{20}$ –37.8 (c 0.86, $CHCl_3$). IR (KBr): ν 3360 (br), 3055, 2924, 2853, 1624, 1590, 1533, 1503, 1438, 1383, 1354, 1311, 1237, 1152, 1115, 1091, 817, 747, 724, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 5.14 (4H, d, *J* = 11.4 Hz), 6.49 (2H, d, *J* = 8.4 Hz), 6.74-6.84 (6H, m), 6.92 (2H, t, *J* = 7.0 Hz), 7.11 (2H, t, *J* = 7.5 Hz), 7.18-7.32 (8H, m), 7.38-7.55 (12H, m), 7.77-7.94 (10H, m), 8.92 (2H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ 31.75. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 69.0, 122.6, 122.7, 123.2, 125.0, 125.5, 127.0, 127.2, 127.3, 127.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.35, 128.41, 128.5, 128.6, 129.7, 129.8, 129.9, 130.1, 131.0, 131.1, 131.5, 131.7, 131.8, 131.86, 131.93, 132.9, 133.2, 133.4, 134.9, 135.0, 141.2, 141.3, 151.6. MS (MALDI): *m/e* 1006 (M^++23), 1023 (M^++39+1). HRMS (MALDI) for $C_{66}H_{49}O_5P_2^{+1}$: requires 983.3049; Found: 983.3050.

*Preparation of compound **CPLB3**.*



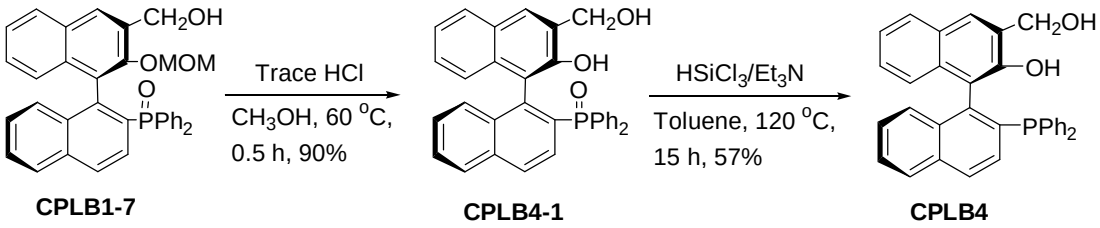
CPLB3-4 (*R*,*R*)-**CPLB3**



1-(2-(diphenylphosphino)naphthalen-1-yl)-3-(((4-(2-(diphenylphosphino)naphthalen-1-yl)-3-hydroxynaphthalen-2-yl)methoxy)methyl)naphthalen-2-ol CPLB3.

The procedure for the preparation of **CPLB1** was generally followed. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.87 (4H, d, J = 12.3 Hz), 5.56 (2H, s), 6.85 (2H, d, J = 8.7 Hz), 7.06-7.18 (6H, m), 7.20-7.33 (22H, m), 7.44 (2H, dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 7.48-7.53 (2H, m), 7.80 (2H, s), 7.81 (2H, d, J = 6.6 Hz), 7.91 (2H, d, J = 8.1 Hz), 7.93 (2H, d, J = 8.4 Hz). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.27. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 54.9, 56.0, 118.4, 118.5, 122.6, 124.2, 152.1, 125.7, 126.2, 126.5, 126.9, 127.5, 127.7, 127.9, 128.0, 128.1, 128.2, 128.2, 128.3, 130.4, 130.9, 132.5, 132.7, 132.9, 133.00, 133.04, 133.5, 135.7, 135.9, 137.1, 137.3, 138.1, 138.3, 141.5, 142.0, 150.6. MS (MALDI): *m/e* 983 (M^++1). HRMS (MALDI) for $C_{66}H_{49}O_3P_2^{+1}$: requires 951.3152; Found: 951.3137.

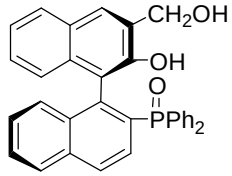
Preparation of chiral phosphine Lewis bases CPLB4.



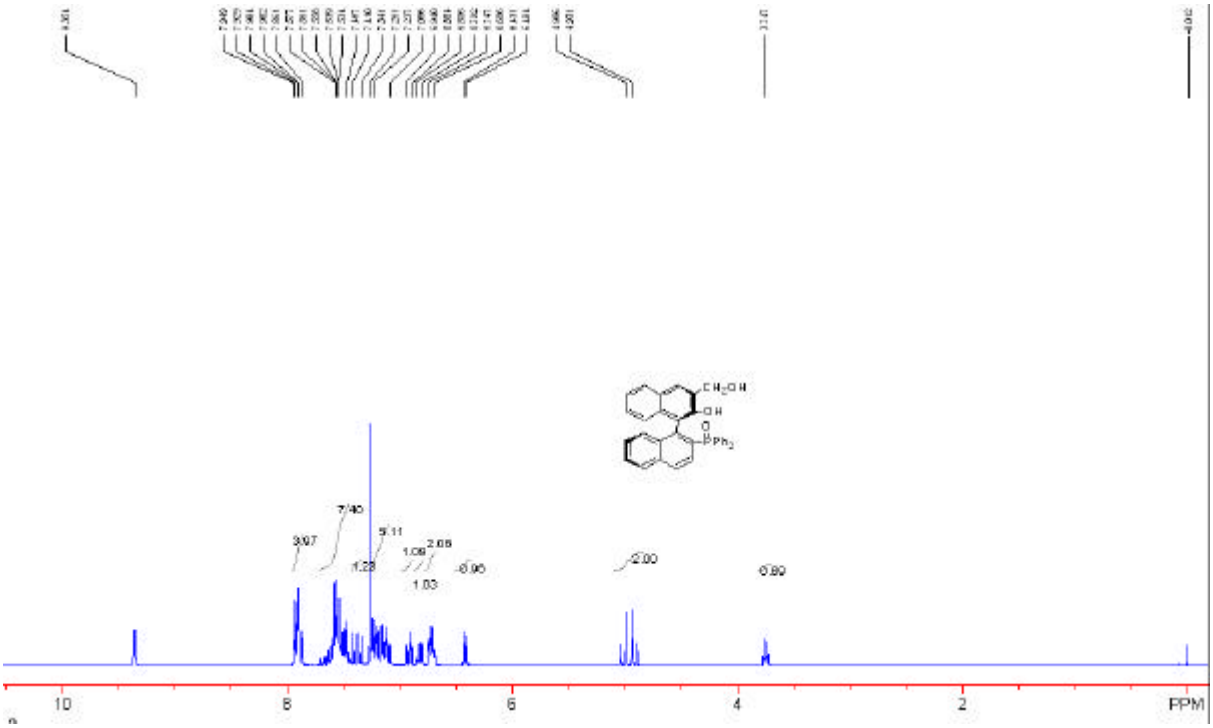
CPLB1-7 **CPLB4-1** **CPLB4**

Scheme SI-5

*Preparation of compound **CPLB4-1**.*



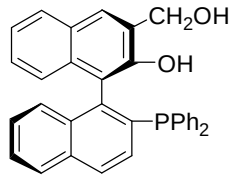
CPLB4-1



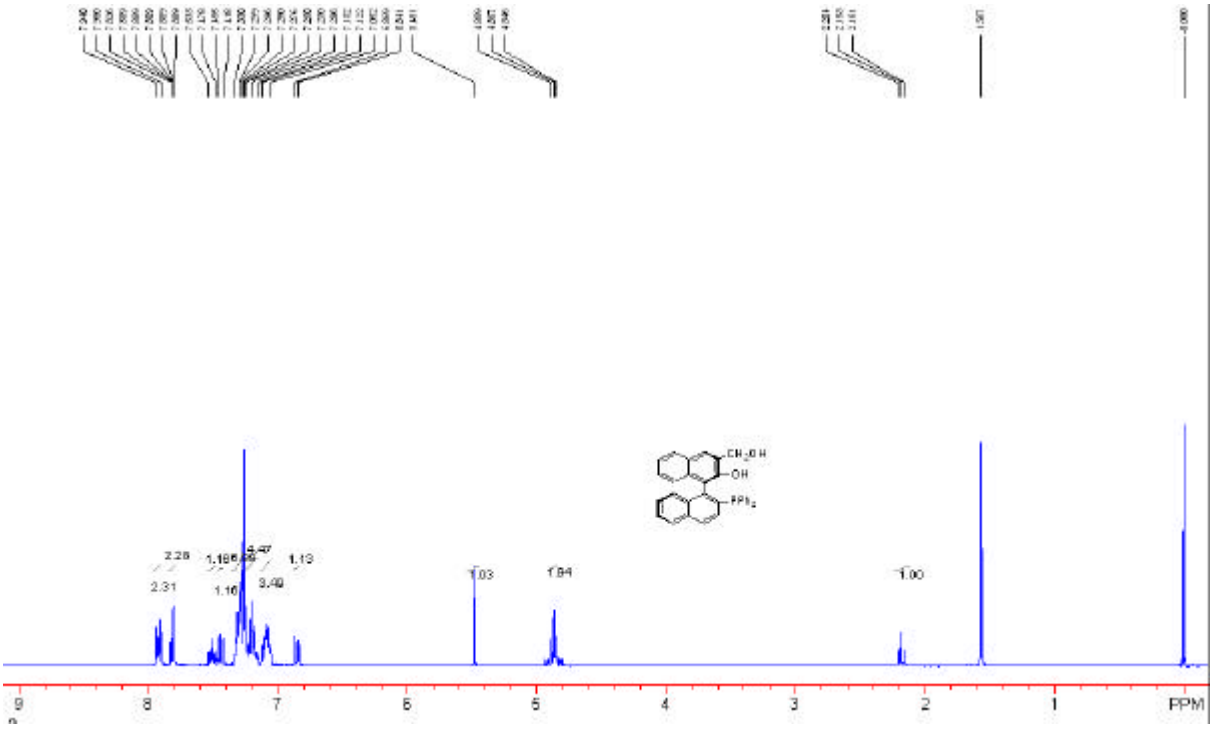
2'-(Diphenyl-phosphinoyl)-3-hydroxymethyl-[1,1']binaphthalenyl-2-ol CPLB4-1.

The procedure for the preparation of **CPLB1-11** was generally followed. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.75 (1H, m), 4.96 (2H, d, J = 12.9 Hz), 6.42 (1H, d, J = 8.7 Hz), 6.68-6.75 (2H, m), 6.78-6.84 (1H, m), 6.86-6.94 (1H, m), 7.09-7.24 (5H, m), 7.38 (1H, dd, J_1 = 12.0 Hz, J_2 = 7.8 Hz), 7.47-7.60 (6H, m), 7.86-7.94 (4H, m), 9.35 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ +32.69.

*Preparation of compound **CPLB4**.*



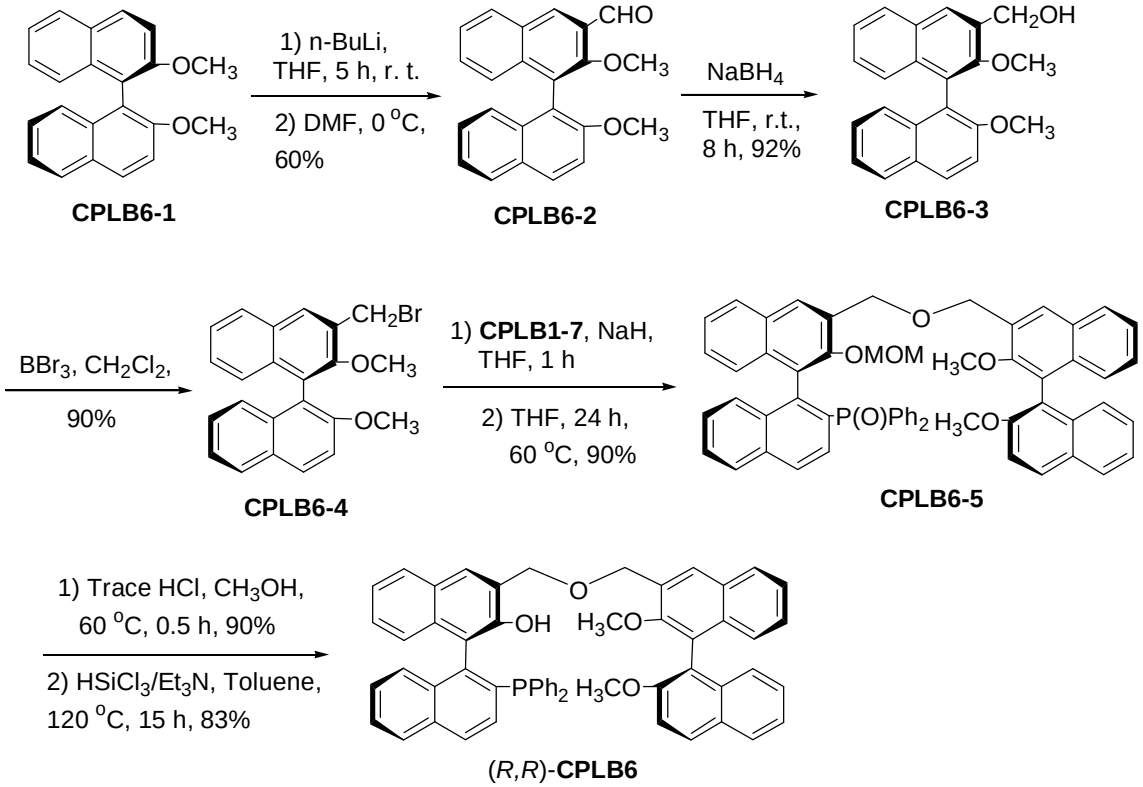
CPLB4



2'-Diphenylphosphanyl-3-hydroxymethyl-[1,1']binaphthalenyl-2-ol CPLB4.

The procedure for the preparation of **CPLB1** was generally followed. mp: 222-225 ^{o}C. IR (KBr): ν 3279 (br), 3051, 1633, 1583, 1504, 1479, 1434, 1390, 1352, 1256, 1203, 1104, 1045, 1025, 939, 817, 743, 696 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.18 (1H, t, *J* = 6.6 Hz, OH), 4.87 (2H, m), 5.48 (1H, s), 6.86 (1H, d, *J* = 8.4 Hz) 7.05-7.12 (3H, m), 7.16-7.32 (11H, m), 7.44 (1H, dd, J_1 = 8.4 Hz, J_1 = 2.4 Hz), 7.48-7.53 (1H, m), 7.81 (1H, s), 7.82 (1H, d, *J* = 5.1 Hz), 7.91 (1H, d, *J* = 8.1 Hz), 7.93 (1H, d, *J* = 9.0 Hz). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.24. MS (EI): *m/e* 485 (M^++1, 30.91), 484 (M^+, 89.02), 483 (M^+-1, 30.26), 467 (M^+-17, 70.73), 377 (M^+-107, 44.11), 298 (M^+-186, 90.24), 282 (M^+-202, 97.95), 281 (M^+-203, 68.73), 265 (M^+-219, 59.19), 252 (M^+-232, 46.47), 233 (M^+-251, 100), 202 (Ph_2PO^++1, 50.05), 183 (M^+-301, 48.79), 77 (Ph^+, 11.29). HRMS (MALDI) for $C_{33}H_{26}O_2P^{+1}$: requires 485.1644; Found: 485.1665.

Preparation of chiral phosphine Lewis bases CPLB6.



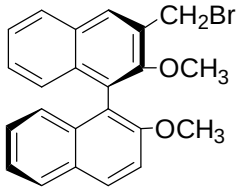
CPLB6-1 **CPLB6-2** **CPLB6-3**

CPLB6-4 **CPLB6-5**

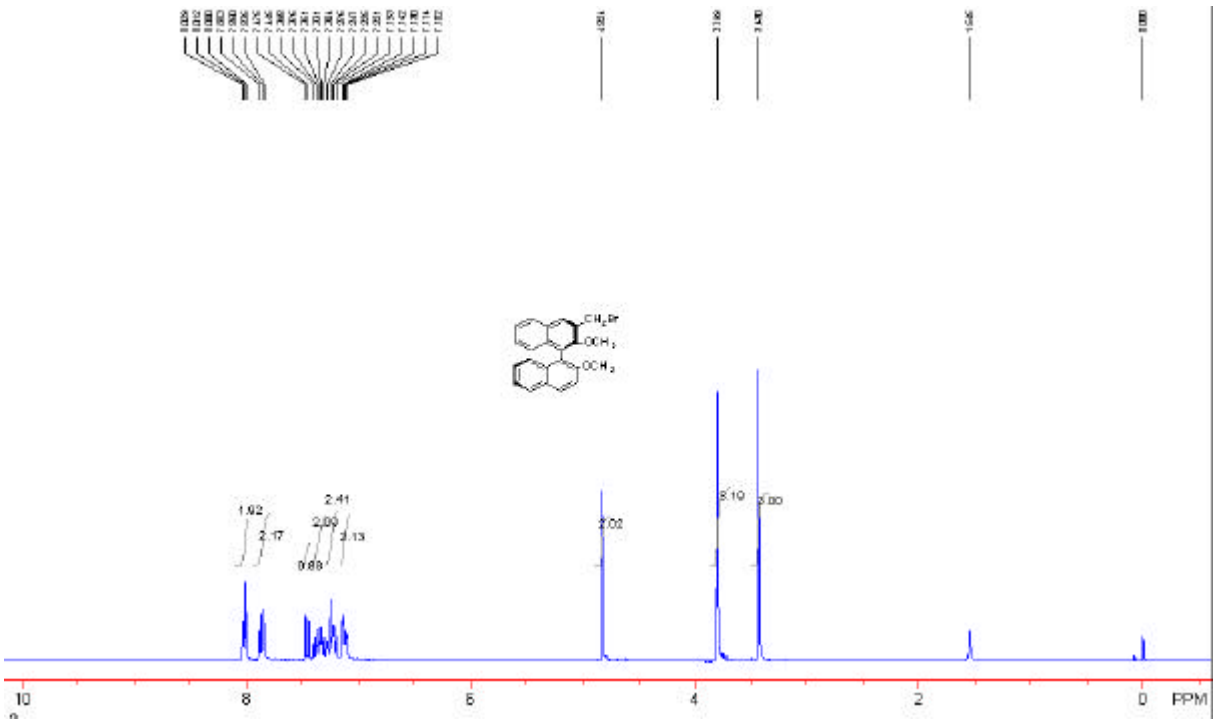
(*R,R*)-**CPLB6**

Scheme SI-6

*Preparation of compound **CPLB6-4**.*



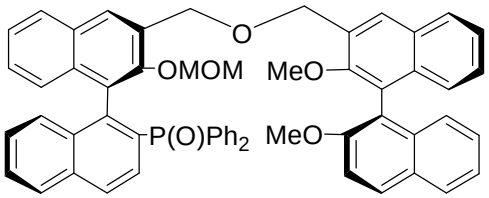
CPLB6-4



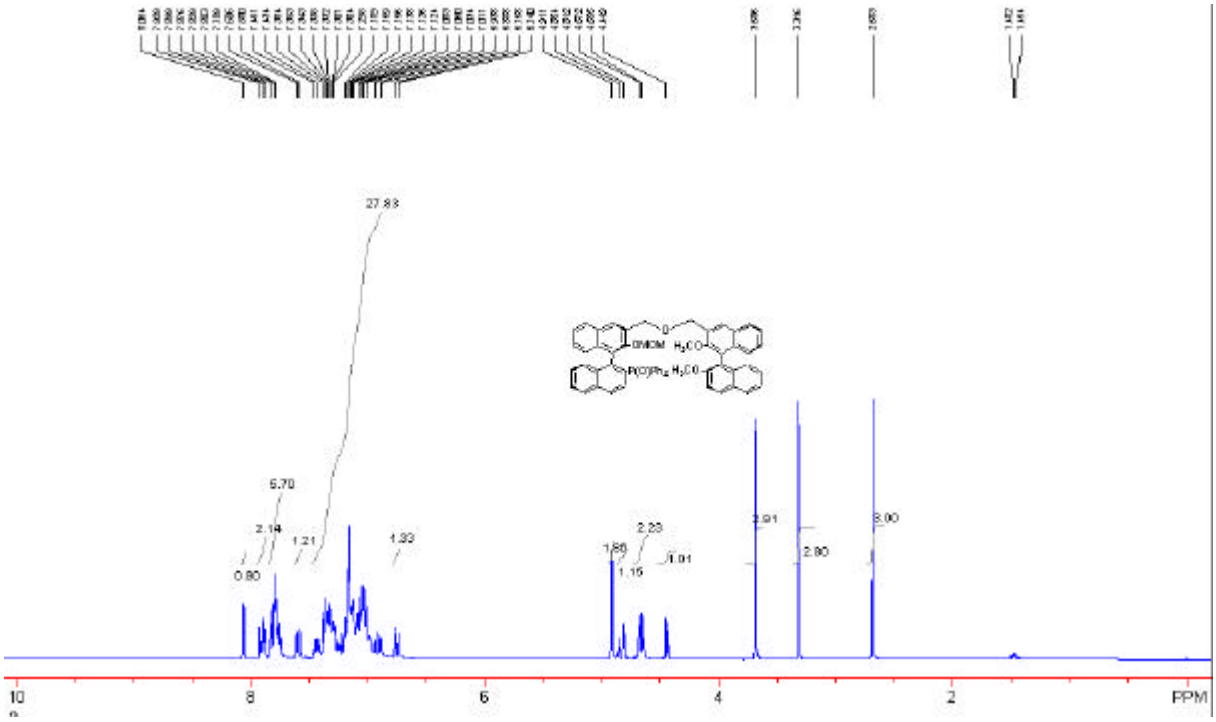
3-Bromomethyl-2,2'-dimethoxy-[1,1']binaphthalenyl CPLB6-4.

To a solution of **CPLB6-3** (69 mg, 0.2 mmol) in CH_2Cl_2 (3.0 mL) was added PBr_3 (28 μL, 0.3 mmol). The mixture was stirred for 1 hour at room temperature. Water (2.0 mL) was added to quench the reaction. After extraction with CH_2Cl_2 (5.0 mL x 2), the organic layer was removed under reduced pressured and the residue was further purified by silica gel column chromatography (Eluent: EtOAc/PE = 1/20) to give product **CPLB6-4** (67 mg, 83%) as a white solid. $[\alpha]_D^{20}$ +56.1 (c 1.0, $CHCl_3$). mp: 162-164 ^oC. IR (KBr): ν 2924, 2854, 1735, 1690, 1620, 1591, 1497, 1461, 1433, 1357, 1265, 1249, 1221, 1190, 1079, 804, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.43 (3H, s), 3.80 (3H, s), 4.83 (2H, s), 7.10-7.14 (2H, m), 7.19-7.28 (2H, m), 7.30-7.40 (2H, m), 7.46 (1H, d, *J* = 9.0 Hz), 7.86 (2H, m), 8.01 (2H, m). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 31.9, 56.5, 61.0, 113.5, 118.7, 118.9, 123.7, 125.0, 125.1, 125.4, 126.7, 126.8, 127.9, 128.0, 129.0, 130.1, 130.4, 130.7, 131.1, 133.9, 134.4, 154.6, 154.9. MS (EI): *m/e* 408 (M^++2, 61.27), 406 (M^+, 74.62), 327 (M^+-79, 100), 296 (M^+-110, 69.24), 282 (M^+-124, 35.08), 252 (M^+-154, 36.26), 239 (M^+-167, 40.10), 145 (M^+-261, 64.99), 126 (M^+-280, 38.85), 70 (M^+-336, 33.96), 45 (M^+-361, 42.73). Anal. Calcd. for $C_{22}H_{18}O_3$: requires C, 67.82; H, 4.70%; Found: C, 67.49; H, 4.63%.

Preparation of compound ***CPLB6-5***.



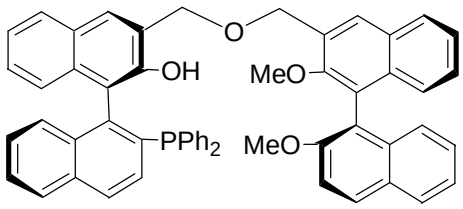
CPLB6-5



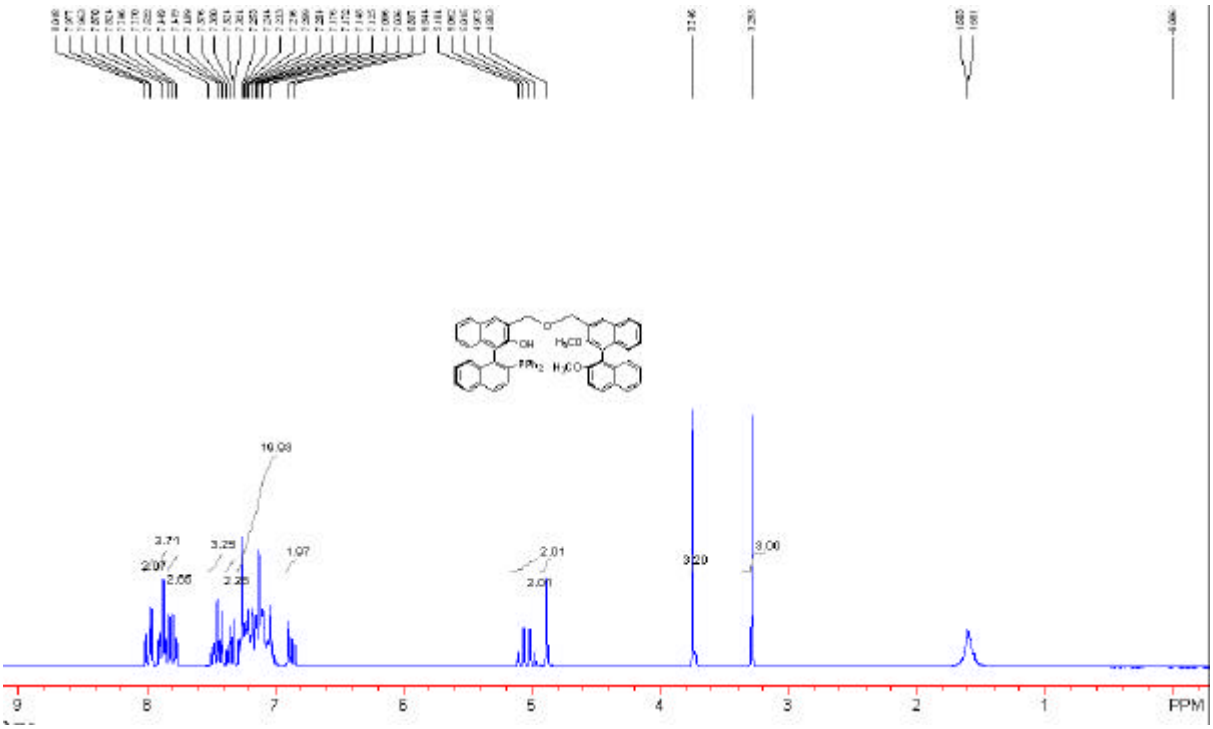
3-(2,2'-Dimethoxy-[1,1']binaphthalenyl-3-ylmethoxymethyl)-2'-(diphenyl-phosphinoyl)-2-methoxylmethyl[1,1']binaphthalenyl-2-ol CPLB6-5.

The procedure for the preparation of **CPLB1-11** was generally followed. A white solid. Yield: 55%. $[\alpha]_D^{20}$ +16.0 (c 1.0, $CHCl_3$). mp: 162-164 ^oC. IR (KBr): ν 3055, 2925, 2853, 1722, 1677, 1622, 1593, 1503, 1462, 1436, 1357, 1266, 1115, 970, 915, 890 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.77 (3H, s), 3.40 (3H, s), 3.77 (3H, s), 4.44 (1H, d, *J* = 5.1 Hz), 4.66 (2H, m), 4.84 (1H, d, *J* = 12.6 Hz), 4.92 (2H, s), 6.77 (1H, d, *J* = 15.6 Hz), 6.89-7.40 (22H, m), 7.61 (1H, d, *J* = 5.1 Hz), 7.78-8.07 (7H, m), 8.07 (1H, s). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ 29.90. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): 56.5, 60.9, 61.8, 68.6, 71.0, 71.6, 98.7, 113.5, 114.0, 119.0, 123.6, 124.6, 124.65, 124.70, 125.2, 125.3, 125.8, 126.0, 126.3, 126.4, 126.6, 126.9, 127.5, 127.6, 127.8, 127.9, 128.0, 128.5, 128.96, 129.04, 129.2, 129.7, 129.8, 130.1, 130.3, 130.6, 131.0, 131.2, 131.5, 131.6, 132.5, 133.1, 133.3, 133.5, 133.6, 133.7, 133.9, 134.0, 134.4, 139.2, 139.8, 139.9, 151.7, 154.5, 154.9. MS (ESI): *m/e* 893.3 (M^++23). HRMS (MALDI) for $C_{58}H_{47}PO_6Na^{+1}$: requires 893.3003; Found: 893.3004.

*Preparation of compound **CPLB6**.*



CPLB6

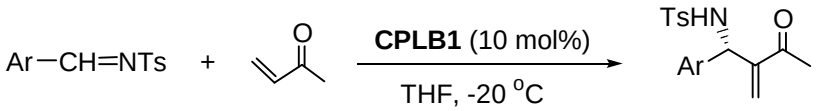


3-(2,2'-Dimethoxy-[1,1']binaphthalenyl-3-ylmethoxymethyl)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol CPLB6.

The procedure for the preparation of **CPLB1** was generally followed. A white solid. yield: 87%. $[\alpha]_D^{20}$ +10.2 (c 0.55, $CHCl_3$). mp: 138-140 ^oC. IR (KBr): ν 3369, 3054,2925, 2850, 1623, 1593, 1508, 1460, 1434, 1357, 1265, 1248, 1109, 1108, 1049, 1005, 893 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.30 (3H, s), 3.75 (3H, s), 4.88 (2H, s), 4.99 (1H, d, *J* = 12.6 Hz), 5.08 (1H, d, *J* = 12.6 Hz), 6.87 (2H, m), 7.01-7.28 (17H, m), 7.35 (2H, m), 7.45 (3H, m), 7.77-7.91 (6H, m), 8.07 (2H, m). ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.02. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): 56.4, 60.9, 68.6, 71.0, 113.4, 118.9, 119.8, 123.3, 123.6, 124.7, 124.72, 125.0, 125.2, 125.3, 126.2, 126.5, 126.5, 126.9, 126.8, 127.7, 127.9, 128.0, 128.05, 128.08, 128.1, 128.3, 128.9, 129.1, 129.8, 130.3, 130.5, 132.9, 133.0, 133.1, 133.3, 133.4, 133.6, 133.86, 133.93, 134.1, 136.7, 136.9, 137.5, 137.7, 137.8, 138.0, 140.6, 141.0, 151.31, 151.33, 154.7, 154.8. MS (ESI): *m/e* 811 (M^++1). HRMS (MALDI) for $C_{56}H_{44}PO_4^{+1}$: requires 811.2971; Found: 811.2935.

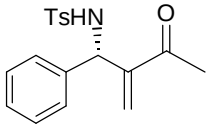
Typical reaction procedure for CPLB catalyzed aza-Baylis-Hillman reaction of N-sulfonated Imines with MVK.

A 10 mL Schlenk tube containing *N*-(benzylidene)-4-chlorobenzenesulfonamide **1e** (0.5 mmol) 3-(2'-diphenylphosphanyl-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxymethyl)-[1,1']binaphth alenyl-2,2'-diol **CPLB1** (0.05 mmol) was degassed and the reaction vessel was protected under argon atmosphere. Then, THF (1.0 mL) was added. After the reaction mixture was cooled to -30 °C, methyl vinyl ketone (MVK) (1.5 mmol) was added into the Schlenk tube. The reaction mixture was stirred at -20 °C for 24-48 hours. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, eluent: EtOAc/Petroleum ether = 1/5) to yield the corresponding aza-Baylis-Hillman adduct as a colorless solid, which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For microanalysis, all these products were recrystallized from acetone and n-hexane.



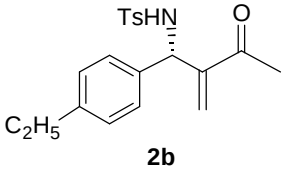
1a-m **2a-m**

a: Ar = C_6H_5, b: Ar = *p*-EtC_6H_4, c: Ar = *p*-$MeOC_6H_4$, d: Ar = *p*-FC_6H_4, e: Ar = *p*-ClC_6H_4, f: Ar = *p*-BrC_6H_4, g: Ar = *o*-ClC_6H_4, h: Ar = *m*-ClC_6H_4,i: Ar = *p*-$NO_2C_6H_4$, j: Ar = *o*-$NO_2C_6H_4$, k: Ar = *m*-$NO_2C_6H_4$, l: Ar = *trans*-C_6H_5-CH=CH, R = $MeC_6H_4SO_2$, m: R = $MeSO_2$, Ar = *p*-ClC_6H_4.



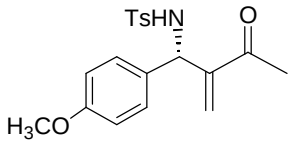
2a

4-Methyl-*N*-(2-methylene-3-oxo-1-phenylbutyl)benzenesulfonamide 2a: a colorless solid, yield: 97%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.16 (3H, s, Me), 2.42 (3H, s, Me), 5.26 (1H, d, *J* = 8.6 Hz), 5.61 (1H, d, *J* = 8.6 Hz), 6.10 (1H, s), 6.11 (1H, s), 7.11 (2H, m, Ar), 7.20-7.27 (5H, m, Ar), 7.66 (2H, d, *J* = 8.1 Hz, Ar). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{major} = 17.14 min, t_{minor} = 18.80 min; *ee*% = 92%.



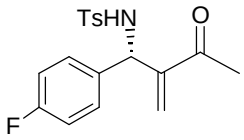
2b

***N*-[1-(4-Ethylphenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2b**: a colorless solid, yield: 94%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.23 (3H, t, *J* = 7.6 Hz, Me), 2.15 (3H, s, Me), 2.39 (3H, s, Me), 2.54 (2H, q, *J* = 7.6 Hz, CH_2), 5.20 (1H, d, *J* = 6.1 Hz, NH), 5.51 (1H, d, *J* = 8.4 Hz, CH), 6.09 (2H, s), 6.97 (2H, d, *J* = 6.1 Hz, Ar), 6.98 (2H, *J* = 6.1 Hz, Ar), 7.21 (2H, d, *J* = 8.4 Hz, Ar), 7.63 (2H, d, *J* = 8.4 Hz). HPLC: TBB column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{minor} = 10.84 min; t_{major} = 11.52 min, *ee*% = 96%.



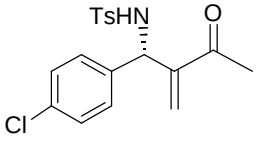
2c

***N*-[1-(4-Methoxyphenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2c**: a colorless solid, yield: 70%.^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.17 (3H, s, Me), 2.41 (3H, s, Me), 3.74 (3H, s, Me), 5.21 (1H, d, *J* = 8.3 Hz, NH), 5.49 (1H, d, *J* = 8.3 Hz, CH), 6.10 (2H, s), 6.73 (2H, d, *J* = 6.8 Hz, Ar), 6.99 (2H, d, *J* = 6.8 Hz, Ar), 7.25 (2H, d, *J* = 9.3 Hz, Ar), 7.65 (2H, d, *J* = 9.3 Hz, Ar). HPLC: TBB column; λ = 220 nm; eluent: Hexane/Isopropanol/TBME = 75/5/20; Flow rate: 0.7 mL/min; t_{minor} = 11.83 min; t_{major} = 12.67 min, *ee*% = 95%.



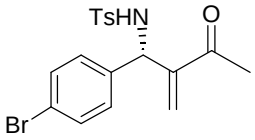
2d

***N*-[1-(4-Fluorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2d**: a colorless solid, yield: 83%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.15 (3H, s, Me), 2.41 (3H, s, Me), 5.24 (1H, d, *J* = 8.7 Hz), 5.75 (1H, d, *J* = 8.7 Hz), 6.07 (1H, s), 6.09 (1H, s), 6.84-6.9 (2H, dd, J_1 = 9.0 Hz, J_2 = 8.6 Hz), 7.04-7.09 (2H, dd, J_1 = 8.6 Hz, J_2 = 5.2 Hz), 7.23 (2H, d, *J* = 8.1 Hz), 7.63 (2H, *J* = 8.1 Hz). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{major} = 13.15 min, t_{minor} = 14.26 min; *ee*% = 96%.



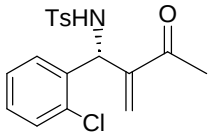
2e

***N*-[1-(4-Chlorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2e**: a colorless solid, yield: 94%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.11 (3H, s, Me), 2.38 (3H, s, Me), 5.24 (1H, d, *J* = 9.1 Hz, NH), 5.99 (1H, d, *J* = 9.1 Hz, CH), 6.03 (1H, s), 6.06 (1H, s,), 7.01 (2H, d, *J* = 8.6 Hz, Ar), 7.12 (2H, d, *J* = 8.6 Hz, Ar), 7.19 (2H, d, *J* = 8.1 Hz, Ar), 7.59 (2H, d, *J* = 8.1 Hz, Ar). HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min; t_{major} = 24.437 min, t_{minor} = 32.41 min; *ee*% = 96%.



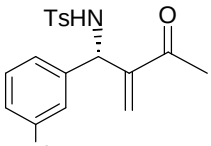
2f

***N*-[1-(4-Bromophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2f**: a colorless solid, yield: 85%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.15 (3H, s, Me), 2.41 (3H, s, Me), 5.19 (1H, d, *J* = 9.1 Hz), 5.71 (1H, d, *J* = 9.1 Hz), 6.06 (1H, s), 6.09 (1H, s), 6.98 (2H, d, *J* = 7.8 Hz), 7.26 (2H, d, *J* = 8.0 Hz), 7.31 (2H, dd, J_1 = 7.8 Hz, J_2 = 2.0 Hz), 7.62 (2H, *J* = 8.0 Hz). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{major} = 23.16 min, t_{minor} = 25.65 min; *ee*% = 95%.



2g

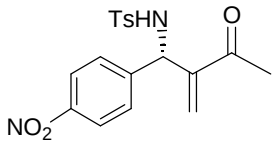
***N*-[2-Acetyl-1-(2-chloro-phenyl)-allyl]-4-methylbenzenesulfonamide 2g**: a colorless solid, yield: 97%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.21 (3H, s, Me), 2.37 (3H, s, Me), 5.68 (1H, d, *J* = 8.6 Hz), 5.78 (1H, d, *J* = 8.6 Hz), 6.16 (1H, s), 6.17 (1H, s,), 7.06-7.15 (2H, m, Ar), 7.20 (2H, d, *J* = 8.4 Hz, Ar), 7.21-7.24 (1H, m, Ar), 7.30-7.33 (1H, m, Ar), 7.63 (2H, d, *J* = 8.4 Hz, Ar). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{major} = 22.13 min, t_{minor} = 24.46 min; *ee*% = 92%.



2h

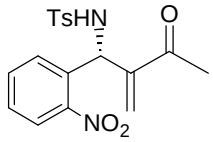
***N*-[1-(3-Chlorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2h**: a colorless solid, yield: 87%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.16 (3H, s, Me), 2.41 (3H, s, Me), 5.20 (1H, d, *J* = 9.0 Hz), 5.69 (1H, d, *J* = 9.0 Hz), 6.08 (1H, s), 6.12 (1H, s), 7.0-7.03 (2H,

m), 7.13-7.15 (2H, m), 7.24 (2H, d, *J* = 8.2 Hz), 7.63 (2H, *J* = 8.2 Hz). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{major} = 17.65 min, t_{minor} = 20.81 min; *ee*% = 94%.



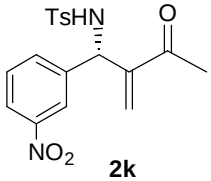
2i

4-Methyl-*N*-[2-methylene-1-(4-nitrophenyl)-3-oxobutyl]benzenesulfonamide 2i: a colorless solid, yield: 93%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.15 (3H, s, Me), 2.44 (3H, s, Me), 5.32 (1H, d, *J* = 9.4 Hz), 5.94 (1H, d, *J* = 9.4 Hz), 6.08 (1H, s), 6.14 (1H, s), 7.25 (2H, d, *J* = 8.3 Hz, Ar), 7.34 (2H, d, *J* = 8.7 Hz, Ar), 7.65 (2H, d, *J* = 8.3 Hz, Ar), 8.07 (2H, d, *J* = 8.7 Hz). HPLC: OJ column; λ = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min; t_{major} = 13.15 min, t_{minor} = 14.26 min; *ee*% = 93%.



2j

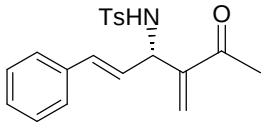
***N*-[2-Acetyl-1-(2-nitro-phenyl)-allyl]-4-methylbenzenesulfonamide 2j**: a yellow solid, yield: 85%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.17 (3H, s, Me), 2.40 (3H, s, Me), 5.91 (1H, d, *J* = 9.0 Hz), 5.96 (1H, s), 5.97 (1H, d, *J* = 9.0 Hz), 6.08 (1H, s), 7.23 (2H, d, *J* = 8.1 Hz, Ar), 7.36 (1H, ddd, J_1 = 7.8 Hz, J_2 = 7.5 Hz, J_3 = 1.5 Hz, Ar), 7.50 (1H, ddd, J_1 = 7.8 Hz, J_2 = 7.5 Hz, J_3 = 1.2 Hz, Ar), 7.64 (1H, dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, Ar), 7.68 (2H, d, *J* = 8.1 Hz, Ar), 7.75 (1H, dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, Ar). HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min; t_{major} = 30.88 min, t_{minor} = 78.03 min; *ee*% = 90%.



2k

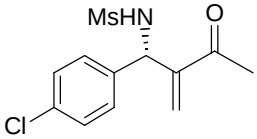
4-Methyl-*N*-[2-methylene-1-(3-nitrophenyl)-3-oxobutyl]benzenesulfonamide 2k: a colorless solid, yield: 89%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.18 (3H, s, Me), 2.41 (3H, s, Me), 5.32 (1H, d, *J* = 9.4 Hz), 5.89 (1H, d, *J* = 9.4 Hz), 6.12 (1H, s), 6.18 (1H, s), 7.25 (2H, d, *J* = 8.6 Hz), 7.44 (1H, dd, J_1 = 8.2 Hz, J_2 = 7.8 Hz), 7.61 (1H, d, *J* = 7.8 Hz), 7.65 (2H, d, *J* = 8.6 Hz), 7.89 (1H, s), 8.05 (1H, d, *J* = 8.2 Hz). HPLC: AD column; λ = 254 nm; eluent:

Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{major} = 23.60 min, t_{minor} = 29.04 min; *ee*% = 96%.



2l

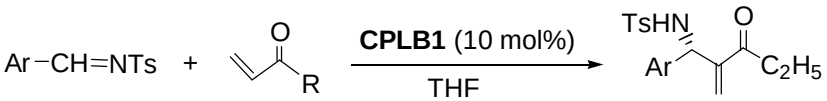
***N*-[2-Acetyl-1-styryl-allyl]-4-methylbenzenesulfonamide 2l**: a colorless solid, yield: 97%.^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.19 (3H, s, Me), 2.33 (3H, s, Me), 4.76 (1H, dd, J_1 = 6.9 Hz, J_2 = 9.6 Hz, CH), 5.61 (1H, d, J = 9.6Hz, NH), 5.98 (1H, s), 5.99 (1H, dd, J_1 = 6.9 Hz, J_2 = 15.9 Hz), 6.00 (1H, s), 6.28 (1H, d, J = 15.9 Hz), 7.14-7.28 (7H, m, Ar), 7.69 (2H, d, J = 8.1 Hz, Ar). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{major} = 23.30 min, t_{minor} = 26.88 min; *ee*% = 90%.



2m

***N*-[2-Acetyl-1-(4-chloro-phenyl)-allyl]-methanesulfonamide 2m**: a colorless solid, yield: 92%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.34 (3H, s, Me), 2.88 (3H, s, Me), 5.41 (1H, d, J = 9.0 Hz), 5.64 (1H, d, J = 9.0 Hz), 6.18 (1H, s), 6.29 (1H, s), 7.25-7.34 (4H, m, Ar). HPLC: OD column; λ = 254 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.7 mL/min; t_{minor} = 24.03 min, t_{major} = 25.54 min; *ee*% = 91%.

Typical reaction procedure for CPLB catalyzed aza-Morita-Baylis-Hillman reaction of N-Sulfonated Imines with Acrolein or EVK.

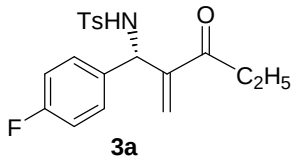


Ia-g **3a-g**

a: Ar = *p*-FC_6H_4, b: Ar = *m*-FC_6H_4,c: Ar = *m*-ClC_6H_4, d: Ar = *p*-BrC_6H_4, R = C_2H_5;
e: Ar = *p*-BrC_6H_4, f: Ar = *p*-FC_6H_4, g: Ar = *p*-ClC_6H_4, R = H.

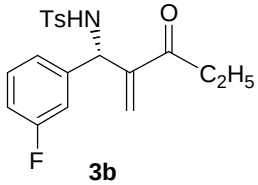
A 10 mL Schlenk tube contained with *N*-(benzylidene)-4-chlorobenzenesulfonamide **1g** (0.5 mmol) and 3-(2'-diphenylphosphanyl-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxy methyl)-[1,1'] binaphthalenyl-2,2'-diol **CPLB1** (0.05 mmol) was degassed and the reaction

vessel was protected under argon atmosphere. Then, THF (1.0 mL) and acrolein (1.0 mmol) was added into the Schlenk tube at room temperature. The reaction was monitored by TLC, when the imine disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (SiO_2, EtOAc-Petroleum ether = 1/5) to yield the product as a colorless solid, which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For microanalysis, all these products were recrystallized from acetone and n-hexane.



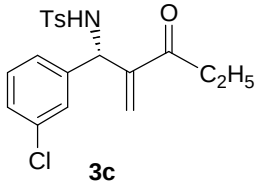
3a

4-Methyl-*N*-[1-(4-fluorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3a: a colorless solid, yield: 86%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.95 (3H, t, *J* = 7.2 Hz, Me), 2.43 (3H, s, Me), 2.44-2.62 (2H, m, CH_2), 5.26 (1H, d, *J* = 9.0 Hz), 5.77 (1H, d, *J* = 9.0 Hz), 6.04 (1H, s), 6.10 (1H, s), 6.87-6.93 (2H, m, Ar), 7.08-7.12 (2H, m, Ar), 7.26 (2H, d, *J* = 8.1 Hz, Ar), 7.66 (2H, d, *J* = 8.1 Hz, Ar). HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.7 mL/min; t_{major} = 22.56 min, t_{minor} = 25.86 min; *ee*% = 92%.



3b

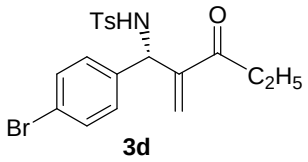
4-Methyl-*N*-[1-(3-fluorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3b: a colorless solid , yield: 83%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.94 (3H, t, *J* = 7.2 Hz, Me), 2.41 (3H, s, Me), 2.43-2.60 (2H, m, CH_2), 5.23 (1H, d, *J* = 9.1 Hz), 5.77 (1H, d, *J* = 9.1 Hz), 6.01 (1H, s), 6.10 (1H, s), 6.79-6.93 (3H, m, Ar), 7.17-7.26 (3H, m, Ar), 7.65 (2H, d, *J* = 8.0 Hz, Ar). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t_{major} = 18.57 min, t_{minor} = 20.24 min; *ee*% = 90%.



3c

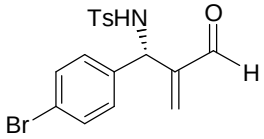
4-Methyl-*N*-[1-(3-chlorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3c: a colorless solid , yield: 83%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.94 (3H, t, *J* = 7.2 Hz, Me),

2.41 (3H, s, Me), 2.44-2.61 (2H, m, CH_2), 5.22 (1H, d, *J* = 9.2 Hz), 5.72 (1H, d, *J* = 9.2 Hz), 6.03 (1H, s), 6.11 (1H, s), 7.01-7.04 (2H, m, Ar), 7.14-7.16 (2H, d, m, Ar), 7.24 (2H, d, *J* = 8.2 Hz, Ar), 7.64 (2H, d, *J* = 8.2 Hz, Ar). HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.7 mL/min; t_{major} = 13.05 min, t_{minor} = 14.85 min; *ee*% = 90%.



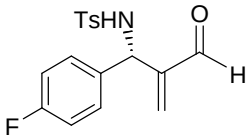
3d

4-Methyl-*N*-[1-(4-bromophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3d: a colorless solid , yield: 88%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.93 (3H, t, *J* = 7.3 Hz, Me), 2.41 (3H, s, Me), 2.46-2.61 (2H, m, CH_2), 5.20 (1H, d, *J* = 8.9 Hz), 5.73 (1H, d, *J* = 8.9 Hz), 6.00 (1H, s), 6.08 (1H, s), 6.99 (2H, d, *J* = 8.3 Hz, Ar), 7.22 (2H, d, *J* = 8.0 Hz, Ar), 7.32 (2H, d, *J* = 8.3 Hz, Ar), 7.63 (2H, d, *J* = 8.0 Hz, Ar). HPLC: OD column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 11.89 min; t_{major} = 13.12 min, *ee*% = 93%.



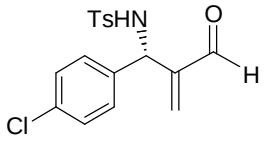
3e

***N*-[1-(4-Bromophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 3e**: a colorless solid , yield: 90%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.45 (3H, s, Me), 5.25 (1H, d, *J* = 8.3 Hz), 5.56 (1H, d, *J* = 8.3 Hz), 6.14 (1H, s), 6.53 (1H, s), 7.00 (2H, d, *J* = 8.4 Hz, Ar), 7.27 (2H, d, *J* = 8.5 Hz, Ar), 7.36 (2H, d, *J* = 8.4 Hz, Ar), 7.65 (2H, d, *J* = 8.5 Hz, Ar), 9.40 (1H, s). HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{major} = 30.78 min, t_{minor} = 42.31 min; *ee*% = 90%.



3f

***N*-[1-(4-Fluorophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 3f**: a colorless solid, yield: 75%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.42 (3H, s, Me), 5.26 (1H, d, *J* = 7.8 Hz), 5.61 (1H, d, *J* = 7.8 Hz), 6.12 (1H, s), 6.52 (1H, s), 6.90 (2H, dd, *J* = 8.4, 8.3 Hz, Ar), 7.07 (2H, dd, *J* = 8.3, 5.8 Hz, Ar), 7.25 (2H, d, *J* = 8.4 Hz, Ar), 7.64 (2H, d, *J* = 8.4 Hz, Ar), 9.38 (1H, s). HPLC: OJ column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 28.84 min; t_{major} = 32.41 min, *ee*% = 99%.



3g

***N*-[1-(4-Chlorophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 3g**: a colorless solid , yield: 67%. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.46 (3H, s, Me), 5.26 (1H, d, *J* = 8.6 Hz), 5.62 (1H, d, *J* = 8.6 Hz), 6.12 (1H, s), 6.52 (1H, s), 7.04 (2H, d, *J* = 8.4 Hz, Ar), 7.19 (2H, d, *J* = 8.4 Hz, Ar), 7.25 (2H, d, *J* = 8.6 Hz, Ar), 7.64 (2H, d, *J* = 8.6 Hz, Ar), 9.38 (1H, s). HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{major} = 31.18 min, t_{minor} = 44.35 min; *ee*% = 85%.

REFERENCE

1. Ahn, K. H.; Park, S. W.; Choi, S.; Kim, H. J.; Moon, C. J. *Tetrahedron Lett.* **2001**, *42*, 2485-2488.
2. Hodacova, J.; Stibor, I. *Collect. Czech. Chem. Commun.* **2000**, 83-98.
3. Smrcina, M.; Vyskocil, S.; Maca, B.; Polasek, M.; Claxton, T. A.; Abbott, A. P.; Kocovsky, P. *J. Org. Chem.* **1994**, 59, 2156-2163.
4. Martorell, G.; Garcias, X.; Janura, M.; Saa, J. M. *J. Org. Chem.* **1998**, *63*, 3463-3467.
5. Vogl, E. M.; Matsunaga, S.; Kanai, M.; Iida, T.; Shibasaki, M. *Tetrahedron Lett.* **1998**, *39*, 7917-7920.

Chiral HPLC analysis.

色谱分析报告

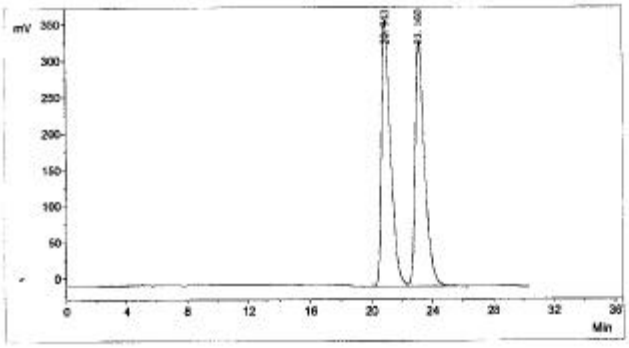
样品名称:分析谱图　　样品文件名:clh-041216-4.che

样品批号:　　分析者:

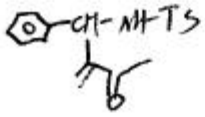
分析日期:2005-01-19　　分析时间:14:00

色谱柱:　　流动相:

流速:　　检测波长:

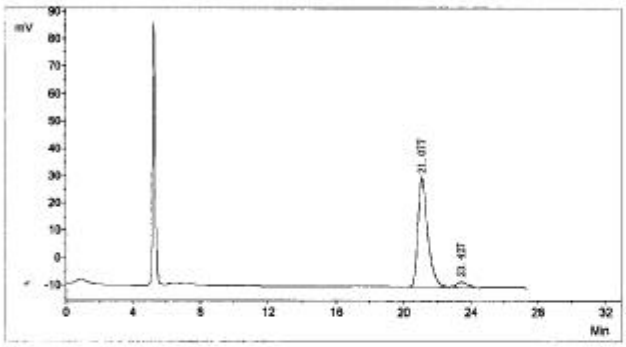


No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	20.943	365494.3	14738630.5	49.7402
2	2	Unknown	23.160	336787.8	14892606.0	50.2598
Total				702282.1	29631235.5	100.0000



色谱分析报告

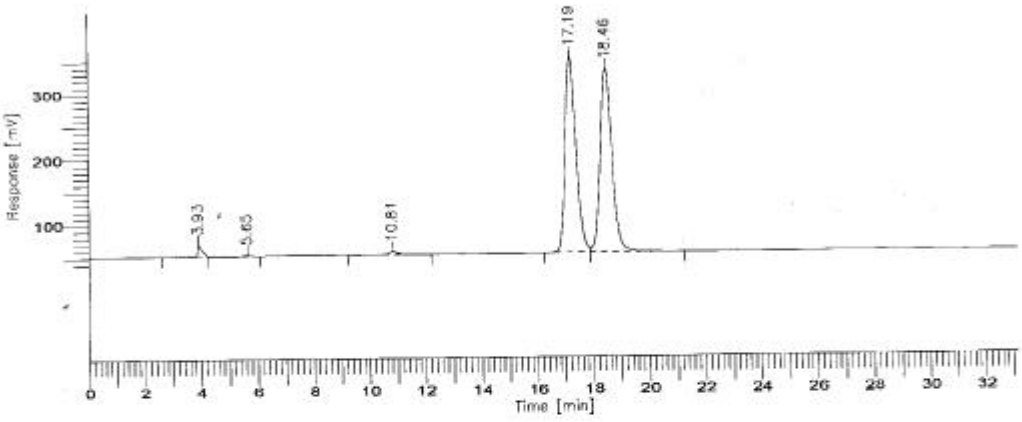
样品名称:分析谱图　　样品文件名:clh-050221-1.che
样品批号:　　分析者:
分析日期:2005-03-02　　分析时间:15:27
色谱柱:　　流动相:
流速:　　检测波长:



No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	21.077	39597.8	1827841.1	95.8753
2	2	Unknown	23.427	1652.7	70031.6	4.1247
Total				41250.5	1697872.7	100.0000

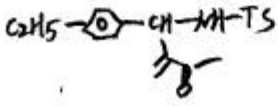
ee% 92%

Software Version: 4.1<2F12>
Date: 05-1-25 9:34
Sample Name : Clh-050106-2+/-
Data File : D:\CS\D-2_107.RAW Date: 05-1-25 9:00
Sequence File: D:\CS\D-2.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: DING-1
Sample Amount : 1.0000 Dilution Factor : 1.00

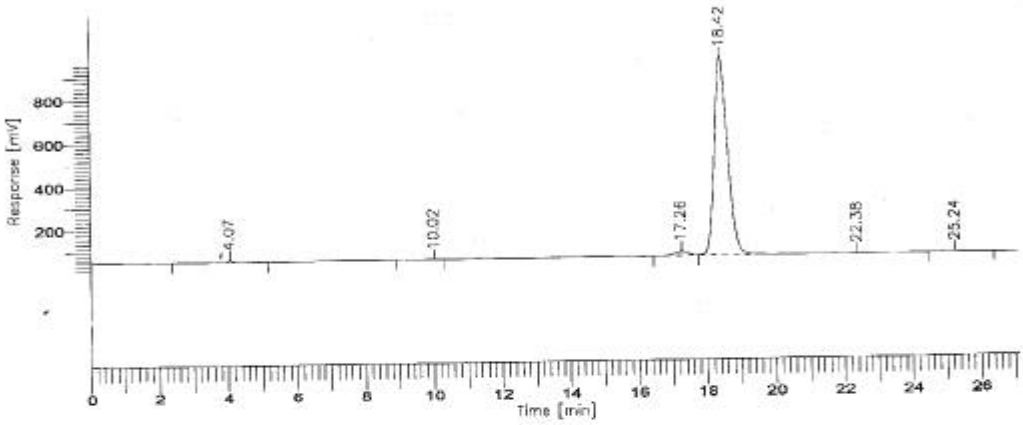


DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Area/Height [sec]
1	3.925	246194.00	18332.15	1.47	BB	13.4296
2	5.652	73578.00	1782.41	0.44	BB	41.2801
3	10.813	105270.50	4568.61	0.63	BB	23.0421
4	17.190	8072907.78	299489.22	48.22	BV	26.9556
5	18.461	8243486.72	279905.55	49.24	VB	29.4510
		16741437.00	604077.94	100.00		



Software Version: 4.1<2F12>
Date: 05-1-25 10:08
Sample Name : Clh-050104-1
Data File : D:\CS\D-2_108.RAW Date: 05-1-25 9:40
Sequence File: D:\CS\D-2.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: DING-1
Sample Amount : 1.0000 Dilution Factor : 1.00



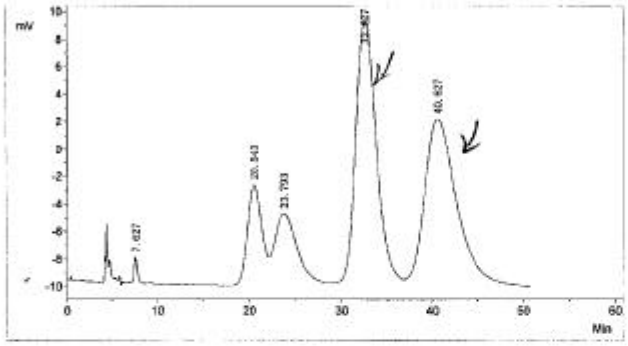
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Area/Height [sec]
1	4.068	111555.50	7538.92	0.44	BB	14.7973
2	10.019	5594.00	212.15	0.02	BB	26.3679
3	17.255	502253.67	19738.20	1.98	BV	25.4458
4	18.422	24777925.33	912612.50	97.46	VE	27.1505
5	22.379	20578.00	175.36	0.08	EB	117.3444
6	25.242	6639.00	127.05	0.03	BB	52.2536
		25424545.50	940404.19	100.00		

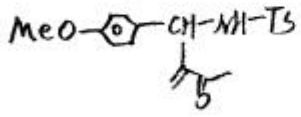
ee% 96%

色谱分析报告

样品名称:分析谱图　　样品文件名:clh-050104-3.che
样品批号:　　分析者:
分析日期:2005-01-20　　分析时间:14:13
色谱柱:　　流动相:
流速:　　检测波长:

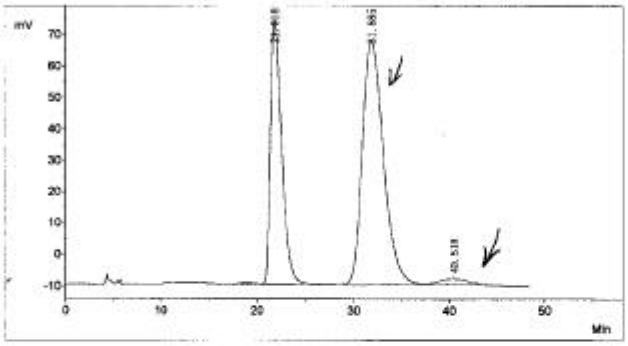


序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	7.627	1823.6	45856.7	0.6449
2	2	Unknown	20.543	7198.1	783300.5	11.0164
3	3	Unknown	23.793	5003.9	792398.5	11.1443
4	4	Unknown	32.627	18662.0	2745364.1	38.6109
5	5	Unknown	40.627	11761.1	2743413.3	38.5835
合计:				44448.8	7110333.0	100.0000



色谱分析报告

样品名称:分析谱图　　样品文件名:clh-050104-2.che
样品批号:　　分析者:
分析日期:2005-01-20　　分析时间:15:06
色谱柱:　　流动相:
流速:　　检测波长:

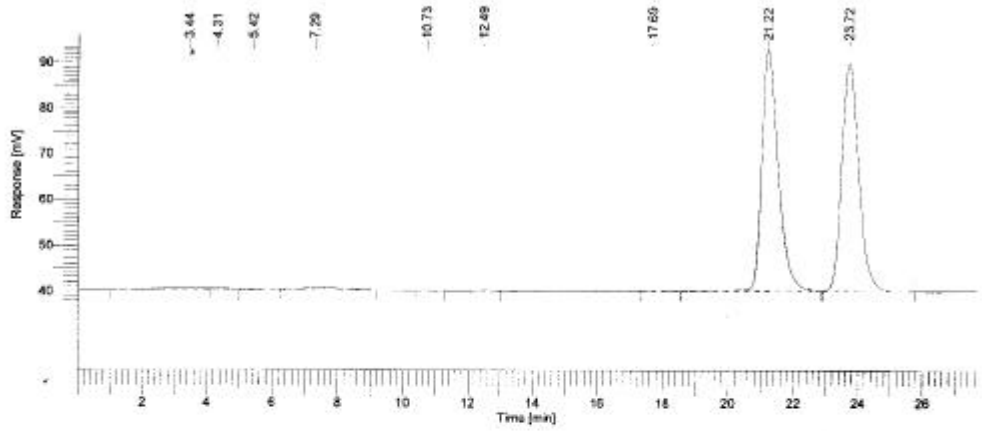


No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	21.818	84106.2	6720685.1	35.7710
2	2	Unknown	31.885	77280.7	11763492.6	62.6115
3	3	Unknown	40.518	1635.9	303892.4	1.6175
Total				163022.8	18788070.1	100.0000

ee%: 95%

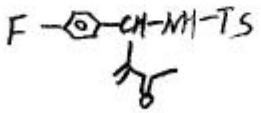
Software Version : 6.2.0.0.0:R27		Date : 2005-1-11 16:12:45	
Sample Name : clh-020128-1		Data Acquisition Time : 2005-1-11 15:36:07	
Instrument Name : NCI901		Channel : A	
Rack/Vial : 0/0		Operator : manager	
Sample Amount : 1.000000		Dilution Factor : 1.000000	
Cycle : 1			

Result File : E:\hplc\A051011-010.rst
Sequence File : E:\hplc\A041011-.seq



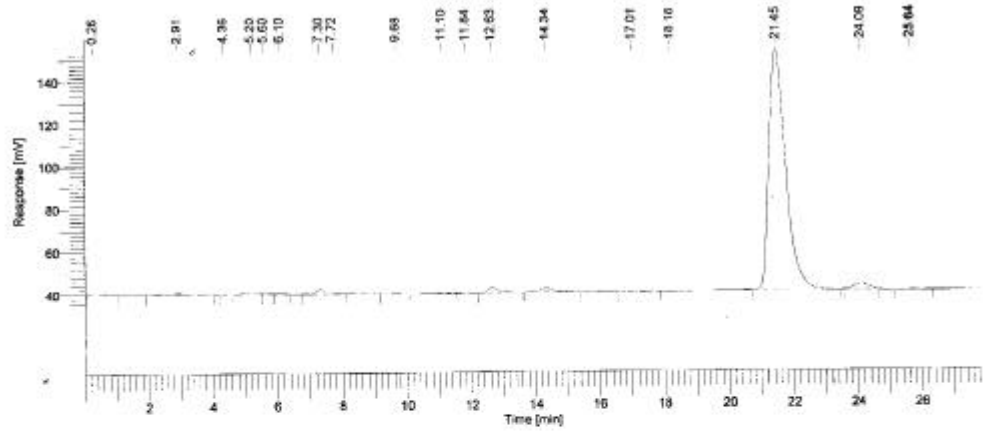
HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Norm. Area [%]
1		3.443	15357.63	129.63	0.411	BV	0.41
2		4.305	2730.83	266.19	0.073	VB	0.07
3		5.419	13897.74	248.41	0.372	BV	0.37
4		7.291	48449.17	662.88	1.296	VB	1.30
5		10.730	1821.46	112.79	0.049	BB	0.05
6		12.491	3333.00	168.65	0.089	BB	0.09
7		17.693	3913.19	118.38	0.105	BB	0.10
8		21.219	1834565.72	52640.17	49.075	BB	49.08
9		23.720	1814198.72	49887.16	48.530	BB	48.53
			3738267.47	104234.26	1e+02		100.00



Software Version	: 6.2.0.0.0:B27	Date	: 2005-1-12 14:24:37
Sample Name	: clh-041230-3	Data Acquisition Time	: 2005-1-11 16:05:39
Instrument Name	: NCI901	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File :
Sequence File : E:\hplc\A041011-.seq



HPLC REPORT

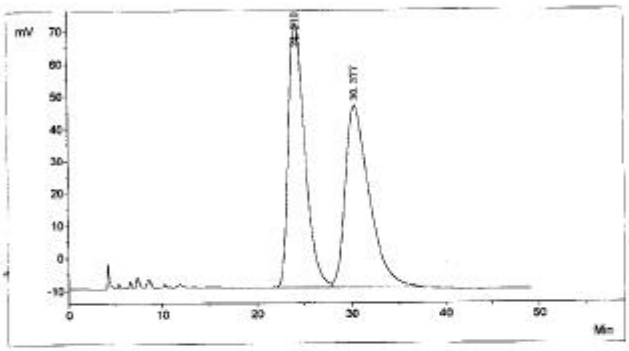
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Norm. Area [%]
1		0.264	11604.22	368.33	0.266	BB	0.27
2		2.913	32299.04	614.61	0.741	BB	0.74
3		4.360	3057.93	227.74	0.070	BV	0.07
4		5.200	30867.47	1196.31	0.708	VV	0.71
5		5.596	7140.58	401.24	0.164	VV	0.16
6		6.096	5780.53	347.62	0.133	VB	0.13
7		7.304	36189.35	2238.48	0.830	BE	0.83
8		7.725	3345.55	246.17	0.077	BB	0.08
9		9.680	2438.55	92.91	0.056	BB	0.06
10		11.098	4728.89	89.06	0.109	BV	0.11
11		11.836	4607.66	260.21	0.106	VV	0.11
12		12.628	51776.66	2533.29	1.188	VB	1.19
13		14.338	55925.13	1885.23	1.283	BB	1.28
14		17.008	3444.64	81.45	0.079	BV	0.08
15		18.182	2383.50	92.48	0.055	VB	0.05
16		21.447	4011256.34	113001.15	92.043	BB	92.04
17		24.089	88299.57	2782.07	2.026	*BB	2.03
18		25.639	2889.45	73.52	0.066	BB	0.07
			4358035.08	126531.89			100.00

ee%: 96%

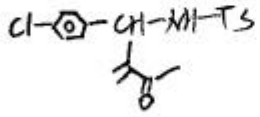
色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2004-12-30
色谱柱:
流速:

样品文件名:clh-041127-1.che
分析者:
分析时间:09:02
流动相:
检测波长:

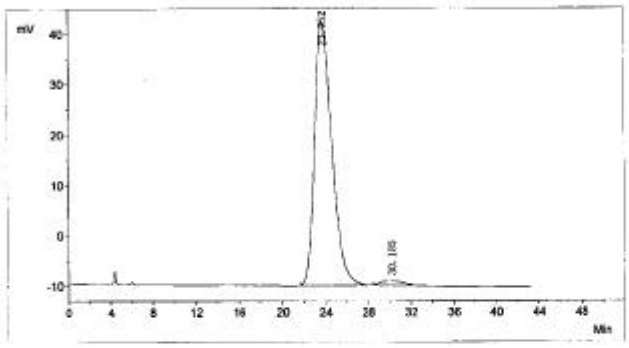


No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	24.210	81394.8	9729638.3	49.5959
2	2	Unknown	30.377	55850.9	9888088.2	50.4041
Total				137245.7	19617626.5	100.0000



色谱分析报告

样品名称:分析谱图
样品文件名:clh-041226-2.che
样品批号:
分析者:
分析日期:2004-12-30
分析时间:10:38
色谱柱:
流动相:
流速:
检测波长:

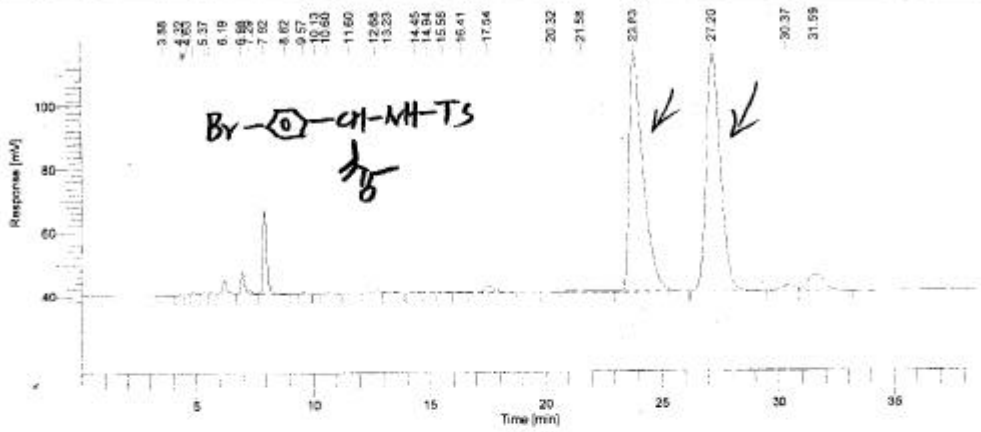


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.752	52182.8	5823902.3	98.0023
2	2	Unknown	30.185	879.6	118717.3	1.9977
Total				53062.4	5942619.6	100.0000

ee%: 96%

Software Version	: 6.2.0.0.0:B27	Date	: 2005-1-11 14:54:30
Sample Name	: clh-020220-1+/-	Data Acquisition Time	: 2005-1-11 14:11:08
Instrument Name	: NCI901	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : E:\hplc\A051011-009.rst
Sequence File : E:\hplc\A041011-.seq

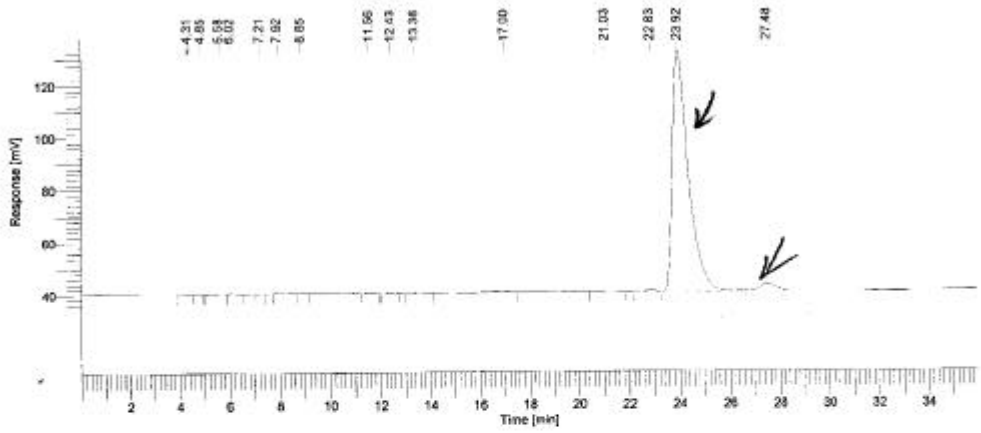


HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Norm. Area [%]
1		3.585	622.48	26.65	0.009	BB	0.01
2		4.321	2064.00	203.01	0.029	BV	0.03
3		4.633	5069.79	407.00	0.070	VV	0.07
4		4.880	14544.91	1254.52	0.201	VV	0.20
5		5.365	11718.39	729.60	0.162	VV	0.16
6		5.586	12983.22	714.21	0.179	VV	0.18
7		6.191	60478.41	4599.86	0.836	VV	0.84
8		6.980	77925.92	6869.55	1.077	VE	1.08
9		7.293	11586.43	940.57	0.160	EV	0.16
10		7.922	301081.87	26578.37	4.160	VE	4.16
11		8.819	1773.00	81.78	0.024	EB	0.02
12		9.567	4161.89	307.18	0.057	BB	0.06
13		10.130	1593.03	137.37	0.022	BV	0.02
14		10.604	5207.51	225.19	0.072	VB	0.07
15		11.600	2107.92	74.23	0.029	BV	0.03
16		12.676	16967.53	843.27	0.235	VV	0.23
17		13.228	12668.17	406.08	0.175	VB	0.18
18		14.450	4828.06	168.30	0.067	BV	0.07
19		14.936	6023.32	289.90	0.083	VV	0.08
20		15.585	3350.98	152.87	0.046	VV	0.05
21		16.413	2727.48	100.61	0.038	VV	0.04
22		17.539	56955.34	1846.90	0.787	VB	0.79
23		20.317	2073.03	67.13	0.029	BV	0.03
24		21.577	19585.87	261.41	0.271	VV	0.27
25		23.825	3144599.27	75410.03	43.444	VB	43.44
26		27.199	3143241.30	75035.43	43.425	BV	43.43
27		30.368	63263.26	1468.17	0.874	VV	0.87
28		31.589	249925.18	5188.26	3.440	VB	3.44
			7238247.56	204387.47	1e+02		100.00

Software Version	: 6.2.0.0.0:827	Date	: 2005-1-12 14:10:07
Sample Name	: clh-041230-4	Data Acquisition Time	: 2005-1-11 14:54:37
Instrument Name	: NCI901	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File :
Sequence File : E:\hplc\A041011-.seq



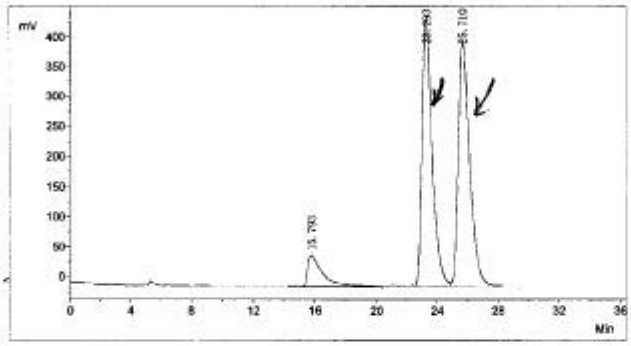
HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Norm. Area [%]
1		4.313	2632.08	179.38	0.063	BV	0.06
2		4.850	2352.39	118.32	0.056	VB	0.06
3		5.581	8922.13	247.62	0.213	BV	0.21
4		6.023	4684.12	263.11	0.112	VB	0.11
5		7.211	1115.26	98.49	0.027	BB	0.03
6		7.916	7786.75	723.58	0.186	BB	0.19
7		8.849	741.48	54.58	0.018	BB	0.02
8		11.562	2443.16	149.07	0.058	BB	0.06
9		12.425	1037.15	52.87	0.025	BV	0.02
10		13.376	5330.85	221.52	0.127	VB	0.13
11		16.997	12978.67	166.56	0.310	BB	0.31
12		21.032	6123.72	176.77	0.146	BB	0.15
13		22.831	13640.22	429.60	0.326	BV	0.33
14		23.922	4014963.40	91838.30	95.916	VB	95.92
15		27.483	101174.48	2536.71	2.417	*BB	2.42
			4185925.87	97256.48	1e+02		100.00

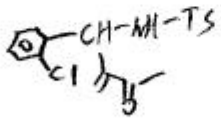
ee% . 95 %

色谱分析报告

样品名称:分析谱图　　样品文件名:clh-041121-1.che
样品批号:　　分析者:
分析日期:2005-01-21　　分析时间:15:33
色谱柱:　　流动相:
流速:　　检测波长:



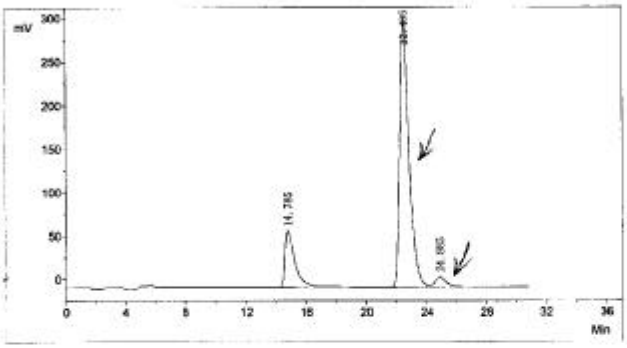
No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	15.793	51104.3	3347684.0	7.5133
2	2	Unknown	23.293	443044.4	20488844.1	45.9836
3	3	Unknown	25.710	406344.5	20720361.5	46.5032
Total				900493.3	44556889.6	100.0000



色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2005-01-31
色谱柱:
流速:

样品文件名:clh-050116-2.che
分析者:
分析时间:15:26
流动相:
检测波长:

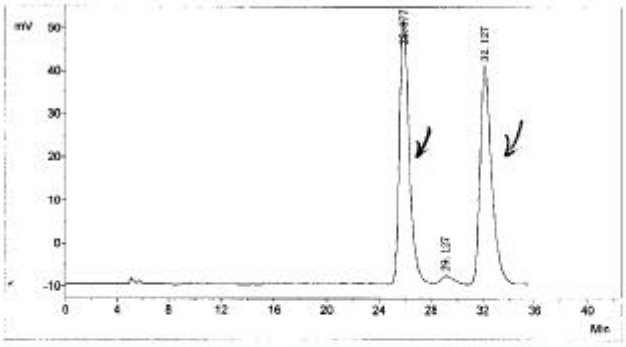


No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	14.785	63808.5	2761010.3	16.4587
2	2	Unknown	22.485	305511.8	13470594.8	80.2997
3	3	Unknown	24.885	10877.0	543796.8	3.2416
Total				380197.4	16775401.9	100.0000

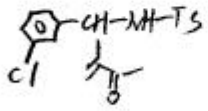
ee%. 92%

色谱分析报告

样品名称:分析谱图　　样品文件名:clh-020127-1..che
样品批号:　　分析者:
分析日期:2005-02-02　　分析时间:11:02
色谱柱:　　流动相:
流速:　　检测波长:

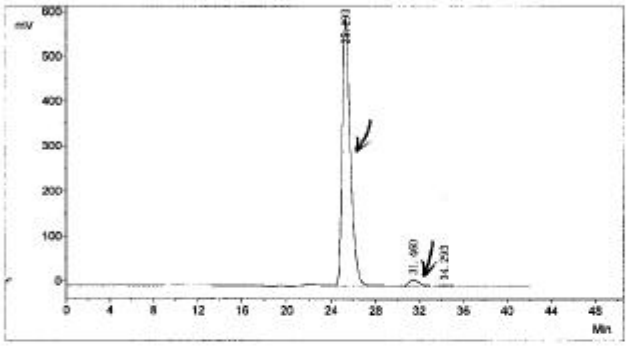


序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	25.877	61134.0	3192139.2	49.2432
2	2	Unknown	29.127	1671.6	110124.2	1.6988
3	3	Unknown	32.127	50602.1	3180137.2	49.0580
合计:				113407.7	6482400.6	100.0000



色谱分析报告

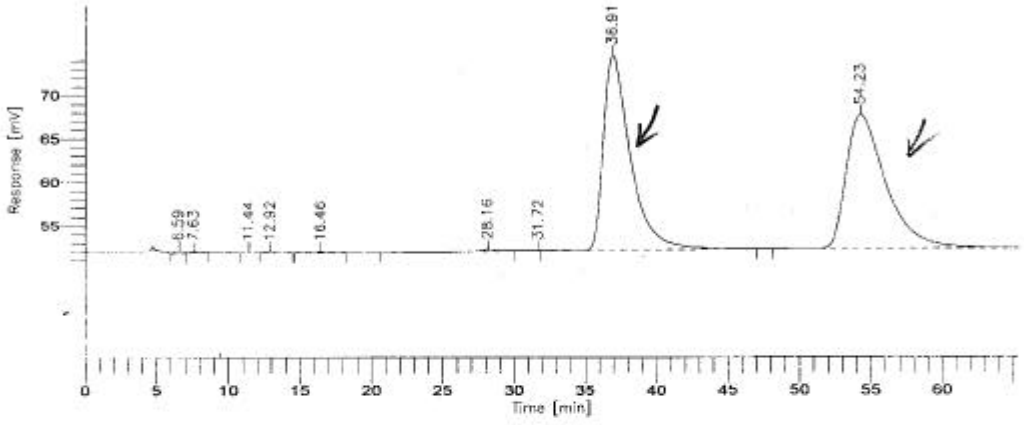
样品名称:分析谱图　　样品文件名:clh-050116-1.che
样品批号:　　分析者:
分析日期:2005-02-02　　分析时间:13:41
色谱柱:　　流动相:
流速:　　检测波长:



No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	25.293	591380.5	29543736.4	97.0447
2	2	Unknown	31.460	13969.3	838797.5	2.7553
3	3	Unknown	34.293	685.0	60896.2	0.2000
Total				606034.8	30443430.1	100.0000

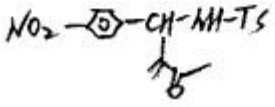
ee%: 94%

Software Version: 4.1<2F12>
Date: 05-1-12 10:09
Sample Name : clh-031216-3+/-
Data File : D:\CS\D-2_049.RAW Date: 05-1-12 9:03
Sequence File: D:\CS\D-2.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: DING-1
Sample Amount : 1.0000 Dilution Factor : 1.00

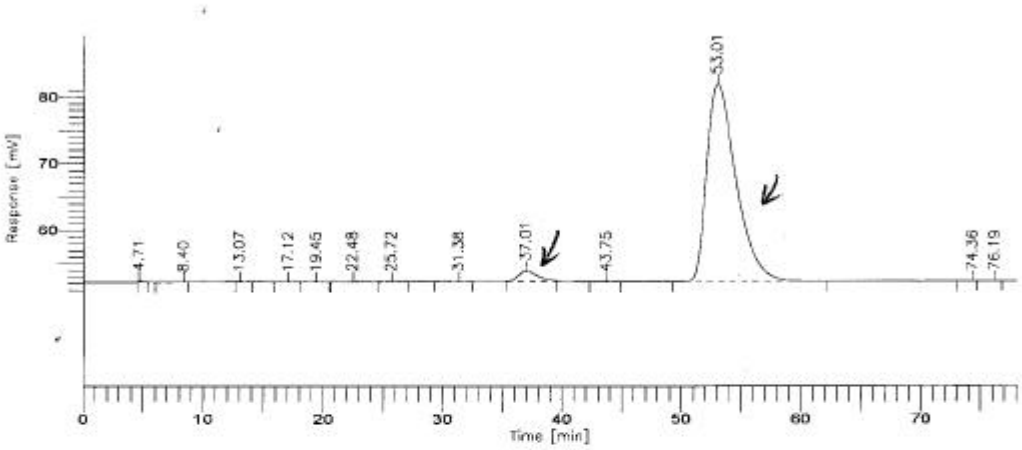


DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Area/Height [sec]
1	6.586	16952.44	310.16	0.28	BV	54.6564
2	7.625	9642.06	149.66	0.16	VB	64.4261
3	11.438	1372.43	31.84	0.02	BV	43.0979
4	12.922	7228.57	140.23	0.12	VB	51.5491
5	16.458	6694.00	88.73	0.11	BB	75.4431
6	28.158	27020.09	222.64	0.45	BV	121.3649
7	31.717	6035.02	60.58	0.10	VV	99.6140
8	36.910	2974709.39	22413.23	49.43	VB	132.7211
9	54.232	2968544.00	15435.23	49.33	BB	192.3227
		6018198.00	38852.30	100.00		



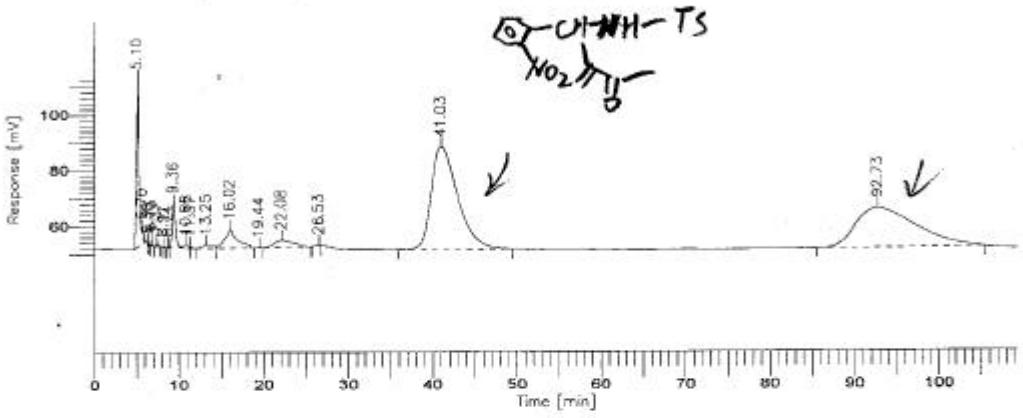
Software Version: 4.1<2F12>
Date: 05-1-12 14:37
Sample Name : clh-041230-5
Data File : D:\CS\D-2_050.RAW Date: 05-1-12 10:11
Sequence File: D:\CS\D-2.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: DING-1
Sample Amount : 1.0000 Dilution Factor : 1.00



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	BL	Area/Height [sec]	
1	4.711	4363.00	258.22	0.08	BB	16.8966	
2	8.396	10399.50	47.00	0.20	BB	221.2838	
3	13.071	961.00	26.12	0.02	BB	36.7847	
4	17.117	1341.00	19.00	0.03	BB	70.5789	
5	19.447	1851.00	20.04	0.04	BB	92.3576	
6	22.483	2768.50	25.96	0.05	BB	106.6327	
7	25.721	2569.00	30.54	0.05	BB	84.1084	
8	31.383	1747.50	20.33	0.03	BB	85.9426	
9	37.008	175000.00	1566.58	3.33	*BB	111.7082	
10	43.747	2461.00	28.44	0.05	BB	86.5280	
11	53.006	5056459.00	29645.46	96.08	BB	170.5643	ee%: 93%
12	74.358	990.62	19.15	0.02	BV	51.7371	
13	76.188	1609.38	22.39	0.03	VB	71.8740	
		5262520.50	31729.25	100.00			

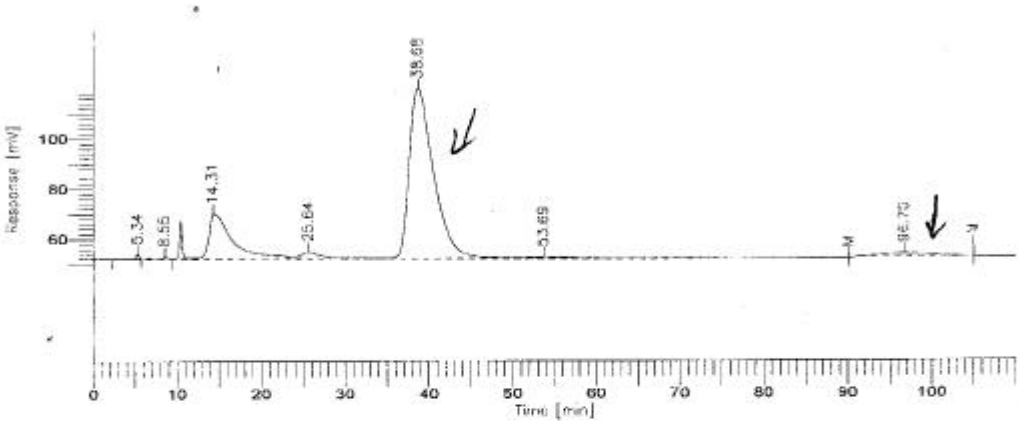
Software Version: 4.1<2F12>
Date: 05-3-14 10:26
Sample Name : CIL-050224-3+/-
Data File : D:\CS\D___031.RAW Date: 05-3-11 11:43
Sequence File: D:\CS\D.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: DING
Sample Amount : 1.0000 Dilution Factor : 1.00



DEFAULT REPORT

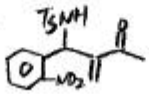
Peak #	Time [min]	Area [uv*sec]]	Height [uv]	Area [%]	Norm Area [%]	BL	Area/Height [s]
1	5.095	1303102.00	60324.26	7.14	0.00	BE	21.60
2	5.702	55299.00	2912.84	0.30	0.00	EB	18.98
3	6.378	1880.00	287.88	0.01	0.00	BB	6.53
4	6.725	17794.00	1566.35	0.10	0.00	BB	11.36
5	7.374	18629.50	1100.91	0.10	0.00	BB	16.92
6	8.205	3015.00	251.62	0.02	0.00	BB	11.98
7	8.744	7052.17	463.18	0.04	0.00	BV	15.23
8	9.360	437532.37	15825.84	2.40	0.00	VE	27.65
9	10.881	48916.00	1096.76	0.27	0.00	EV	44.60
10	11.368	12044.96	625.27	0.07	0.00	VB	19.26
11	13.247	117306.51	1254.25	0.64	0.00	BV	93.53
12	16.021	682060.99	6641.75	3.74	0.00	VB	102.69
13	19.438	4954.00	156.09	0.03	0.00	BB	31.74
14	22.083	420167.00	2603.30	2.30	0.00	BB	161.40
15	26.528	7487.50	154.10	0.04	0.00	BB	48.59
16	41.025	8027218.00	36852.09	43.99	0.00	BB	217.82
17	92.725	7085375.00	14271.20	38.82	0.00	BB	496.48

Software Version: 4.1<2F12>
Date: 05-3-14 10:58
Sample Name : CIL-050306-2
Data File : D:\CS\D___033.RAW Date: 05-3-11 15:25
Sequence File: D:\CS\D.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: DING
Sample Amount : 1.0000 Dilution Factor : 1.00



DEFAULT REPORT

Peak #	Time [min]	Area [uv*sec]]	Height [uv]	Area [%]	Norm Area [%]	BL	Area/Height [s]
1	5.338	54699.68	2111.05	0.28	0.00	BV	25.91
2	8.551	75001.91	998.30	0.38	0.00	VV	75.13
3	14.312	3988208.03	18266.68	20.19	0.00	VE	218.33
4	25.644	673635.00	2628.23	3.41	0.00	EV	256.31
5	38.683	13796889.86	67768.58	69.85	0.00	VE	203.59
6	53.685	385596.00	678.49	1.95	0.00	EB	568.31
7	96.697	776978.89	1652.27	3.93	0.00	*BB	470.25
		19751009.37	94103.61	100.00	0.00		

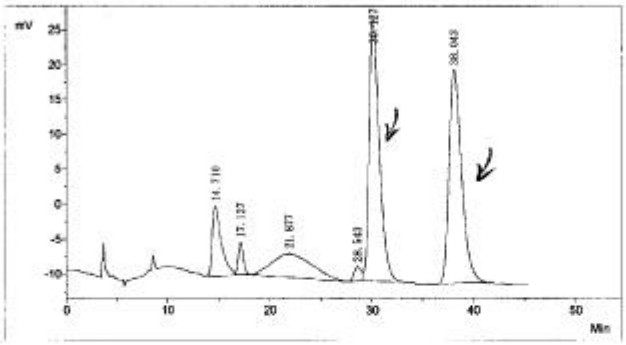


ee%: 90%

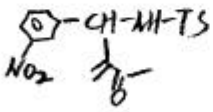
色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2005-01-26
色谱柱:
流速:

样品文件名:clh-020128-[redacted].che
分析者:
分析时间:09:01
流动相:
检测波长:

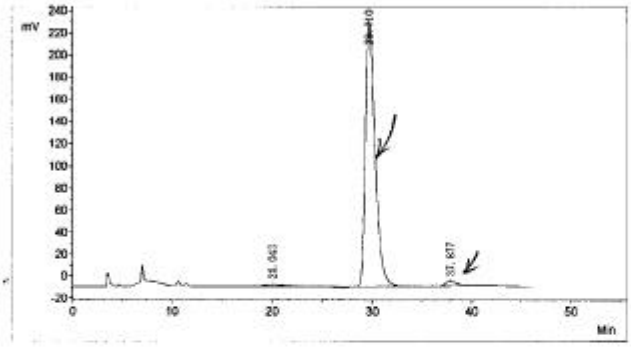


No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	14.710	9898.1	624432.4	9.0181
2	2	Unknown	17.127	4654.6	159971.0	2.3103
3	3	Unknown	21.877	3266.0	892150.8	12.8845
4	4	Unknown	28.543	1932.9	89218.7	1.2885
5	5	Unknown	30.127	37325.9	2565295.3	37.0482
6	6	Unknown	38.043	30510.2	2593136.3	37.4503
Total				87587.7	6924204.5	100.0000



色谱分析报告

样品名称:分析谱图
样品文件名:clh-050116-3.dc
样品批号:
分析者:
分析日期:2005-01-26
分析时间:09:50
色谱柱:
流动相:
流速:
检测波长:

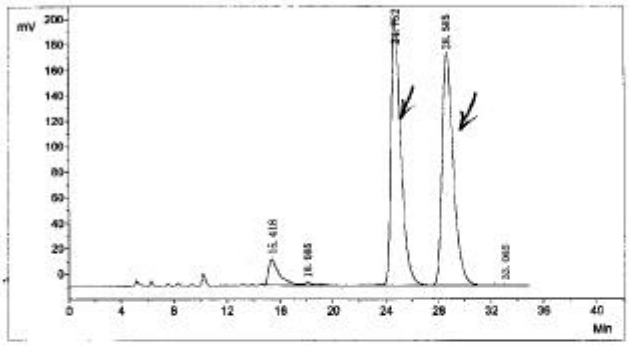


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	20.043	1898.0	242392.7	1.4895
2	2	Unknown	29.710	238738.3	15748247.8	96.7722
3	3	Unknown	37.877	3948.8	282878.0	1.7383
Total				244575.1	16273518.5	100.0000

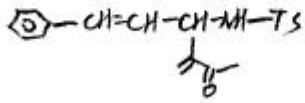
ee% : 96%

色谱分析报告

样品名称:分析谱图
样品文件名:clh-041124-2.che
样品批号:
分析者:
分析日期:2005-01-24
分析时间:08:54
色谱柱:
流动相:
流速:
检测波长:



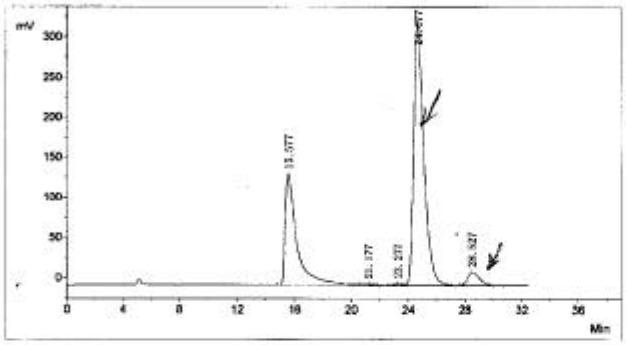
序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	15.418	19470.8	1078409.1	4.7347
2	2	Unknown	18.085	1882.2	121563.0	0.5337
3	3	Unknown	24.752	204978.4	10762615.5	47.2532
4	4	Unknown	28.585	180874.9	10780587.4	47.3321
5	5	Unknown	33.085	594.9	33313.3	0.1463
合计:				407811.3	22776488.3	100.0000



色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2005-03-21
色谱柱:
流速:

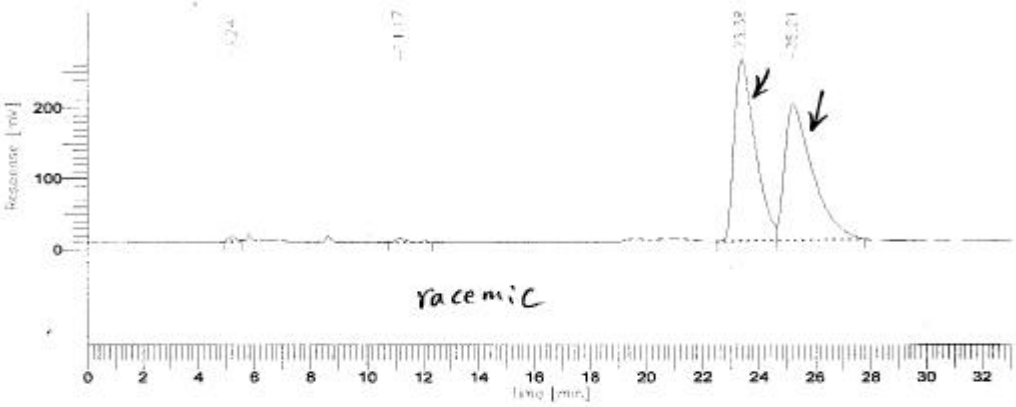
样品文件名:clh-050306-1.chc
分析者:
分析时间:14:14
流动相:
检测波长:



No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	15.577	138324.8	8264743.5	32.0511
2	2	Unknown	21.177	761.5	30218.6	0.1172
3	3	Unknown	23.277	1704.0	70904.6	0.2750
4	4	Unknown	24.677	325620.8	16536741.5	64.1304
5	5	Unknown	28.527	15858.2	883504.0	3.4263
Total				482269.3	25786112.1	100.0000

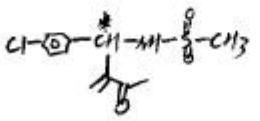
ee%: 9°%

Software Version: 4.1<2F12>
Date: 04-12-3 13:43
Sample Name : clh041126-1
Data File : D:\TC4\DATA\CAO\CAP_070U.RAW Date: 04-12-3 11:36
Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator:
Sample Amount : 1.0000 Dilution Factor : 1.00



REPORT

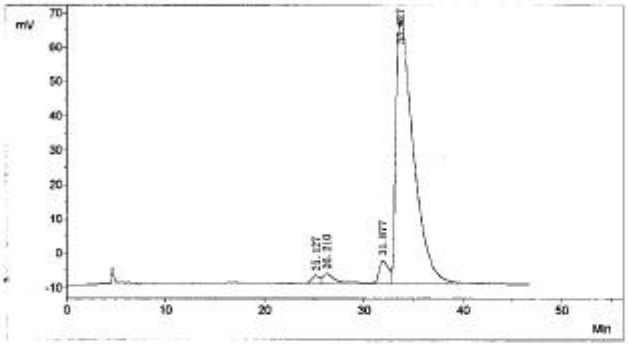
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	5.240	137027.50	7433.01	0.51	0.00	BB	18.4350
2	11.168	144321.00	6068.88	0.54	0.00	BB	23.7805
3	23.384	13228442.07	253822.58	49.30	0.00	BV	52.1169
4	25.206	13321416.93	191764.10	49.65	0.00	VB	69.4677
		26831207.50	459088.58	100.00	0.00		



OD column λ=254 nm
Hexane/isopropanol = 85/15 0.7mL/min

色谱分析报告

样品名称:分析谱图　　样品文件名:clh-050118-3.che
样品批号:　　分析者:
分析日期:2005-02-01　　分析时间:15:44
色谱柱:　　流动相:
流速:　　检测波长:

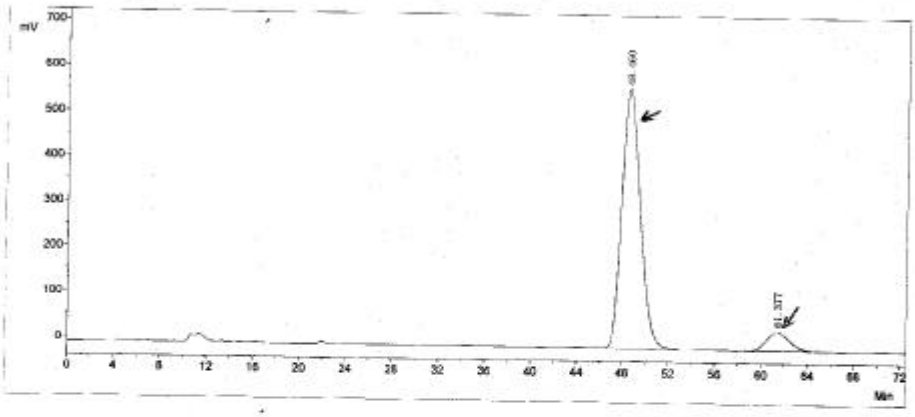


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	25.127	2078.9	105963.5	1.0366
2	2	Unknown	26.210	2579.3	189095.6	1.8498
3	3	Unknown	31.877	6674.0	434058.6	4.2461
4	4	Unknown	33.627	76551.6	9493492.2	92.8676
Total				87883.8	10222609.9	100.0000

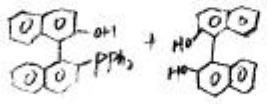
ee%: 91%

金属有机HPLC分析报告

样品文件名:lyh3021-2.che　　分析者:
分析日期:2005-10-20　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:

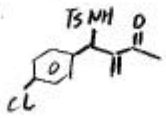


No.	R.Time	PeakHeight	PeakArea	PerCent
1	48.460	567780.3	63368556.2	92.0458
2	61.377	40028.7	5476095.2	7.9542
Total		607809.0	68845651.4	100.0000



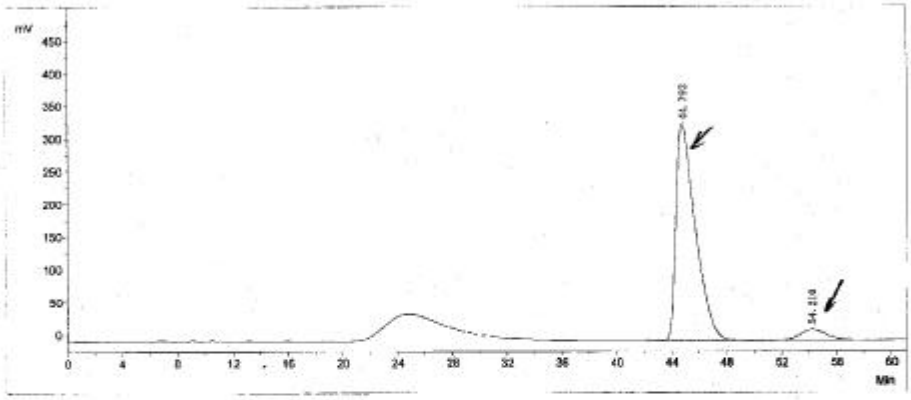
(R)

ee=84%

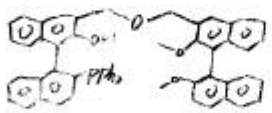


金属有机HPLC分析报告

样品文件名:lyh3016-2.che　　分析者:
分析日期:2005-10-14　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:

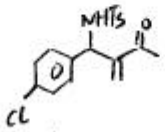


No.	R.Time	PeakHeight	PeakArea	PerCent
1	44.793	329545.9	32282560.5	94.1164
2	54.210	15677.3	2018100.9	5.8836
Total		345223.2	34300661.4	100.0000



(R,R)

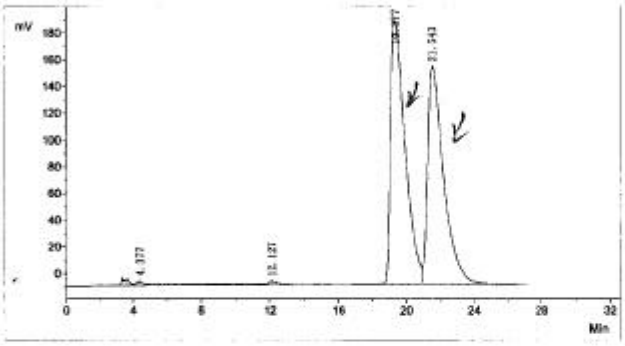
ee%: 88%



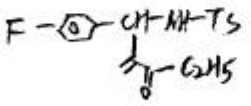
色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2005-03-09
色谱柱:
流速:

样品文件名:xu-7-25.che
分析者:
分析时间:15:12
流动相:
检测波长:

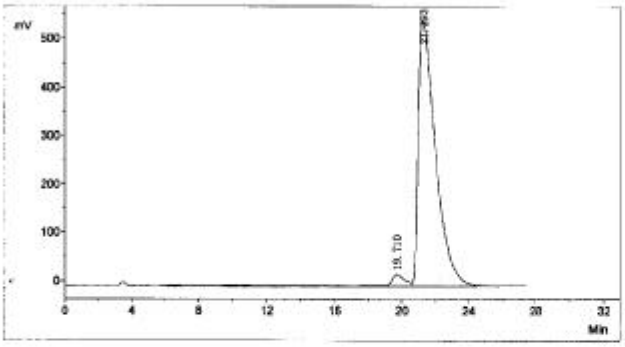


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	4.377	3047.2	246519.5	1.0785
2	2	Unknown	12.127	1952.5	196235.2	0.8585
3	3	Unknown	19.377	197017.2	11749132.6	51.4024
4	4	Unknown	21.543	162432.5	10665276.0	46.6605
Total				364449.4	22857163.2	100.0000



色谱分析报告

样品名称:分析谱图　　样品文件名:clh-050225-1.che
样品批号:　　分析者:
分析日期:2005-03-09　　分析时间:15:42
色谱柱:　　流动相:
流速:　　检测波长:

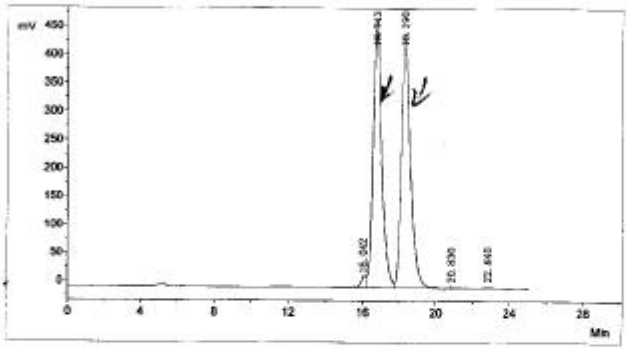


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	19.710	22368.3	1617798.2	4.0250
2	2	Unknown	21.293	547288.0	38575645.2	95.9750
Total				569656.3	40193443.4	100.0000

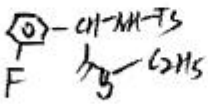
ee%. 92%

色谱分析报告

样品名称:分析谱图
样品文件名:clh-0211017-2 ad 80.che
样品批号:
分析者:
分析日期:2005-03-09
分析时间:13:28
色谱柱:
流动相:
流速:
检测波长:

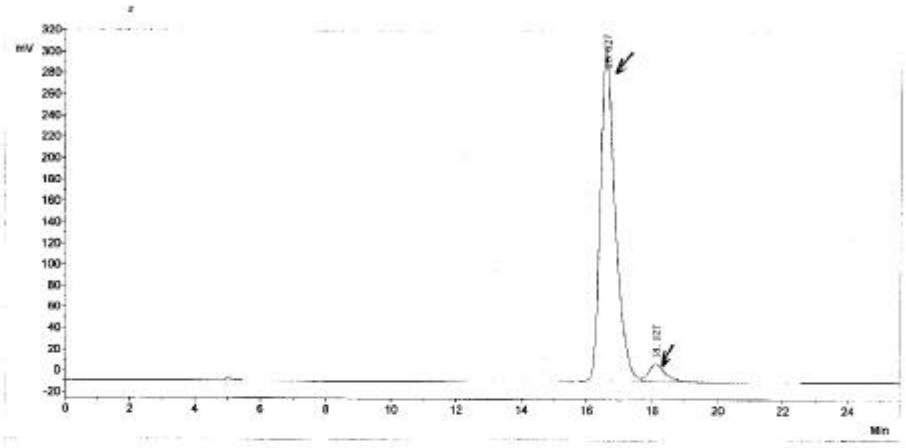


No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	16.042	19041.7	315160.0	1.0017
2	2	Unknown	16.743	468814.0	15388882.8	48.9096
3	3	Unknown	18.290	446210.1	15701021.4	49.9016
4	4	Unknown	20.830	20.6	255.6	0.0008
5	5	Unknown	22.840	1205.9	58663.0	0.1864
Total				936092.3	31463982.8	100.0000

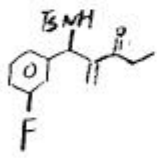


高效液相色谱分析报告

样品名称:分析谱图
样品文件名:clh-050225-2.che
分析日期:2005-03-09
分析时间:14:25
色谱柱:
流动相:
流速:
检测波长:



No	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	16.627	310172.1	10053178.3	94.7942
2	2	18.127	16419.3	552089.5	5.2058
Total			326591.4	10605267.7	100.0000

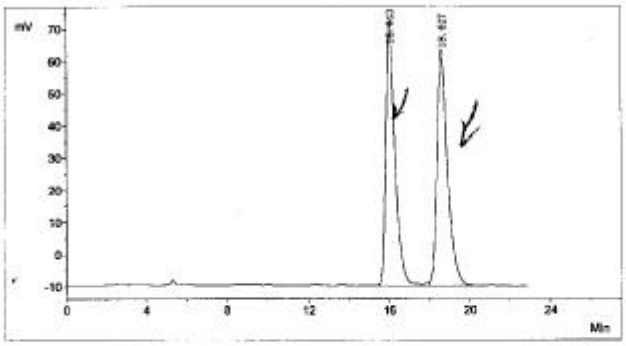


ee% = 90%

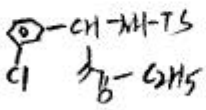
色谱分析报告

样品名称:分析谱图
样品批号:
分析日期:2005-03-09
色谱柱:
流速:

样品文件名:c1h021017-3.che
分析者:
分析时间:10:53
流动相:
检测波长:

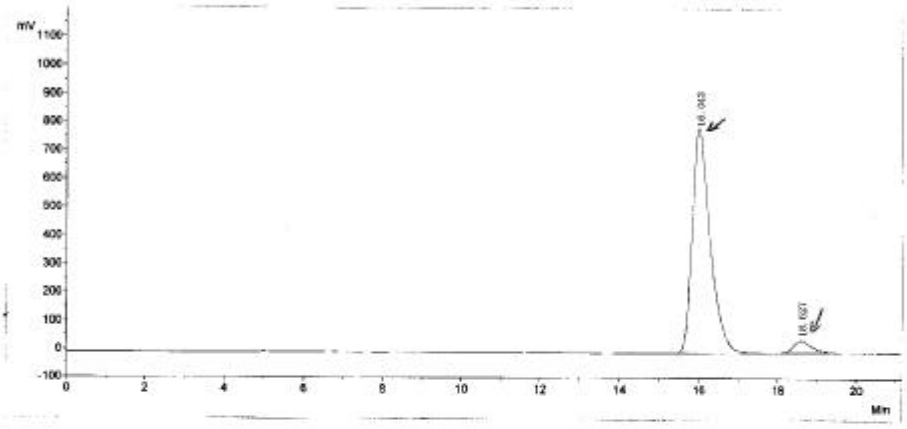


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	16.043	81458.7	2643047.0	49.5086
2	2	Unknown	18.627	72145.8	2695513.3	50.4914
Total				153604.5	5338560.3	100.0000

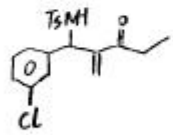


高效液相色谱分析报告

样品名称:分析谱图　　样品文件名:clh-050225-4.che
分析日期:2005-03-09　　分析时间:11:19
色谱柱:　　流动相:
流速:　　检测波长:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	16.043	781596.2	25025374.2	94.7385
2	2	18.627	41486.5	1389848.2	5.2615
Total			823081.7	26415222.4	100.0000



ee%: 90%

色谱分析报告

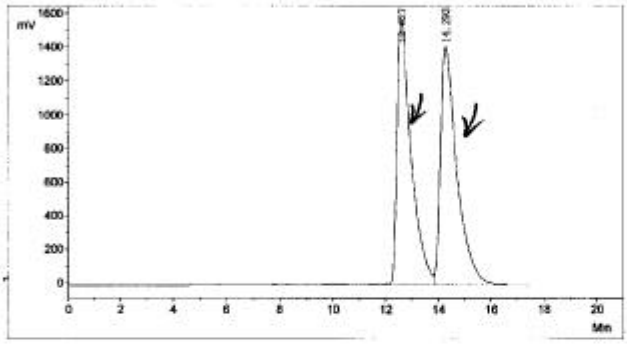
样品名称:分析谱图　　样品文件名:clh-021017-1.che

样品批号:　　分析者:

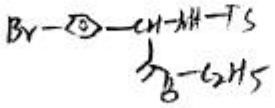
分析日期:2005-03-02　　分析时间:08:54

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.627	1559104.8	59016029.2	49.5464
2	2	Unknown	14.293	1402517.3	60096543.8	50.4536
Total				2961622.1	119112573.0	100.0000



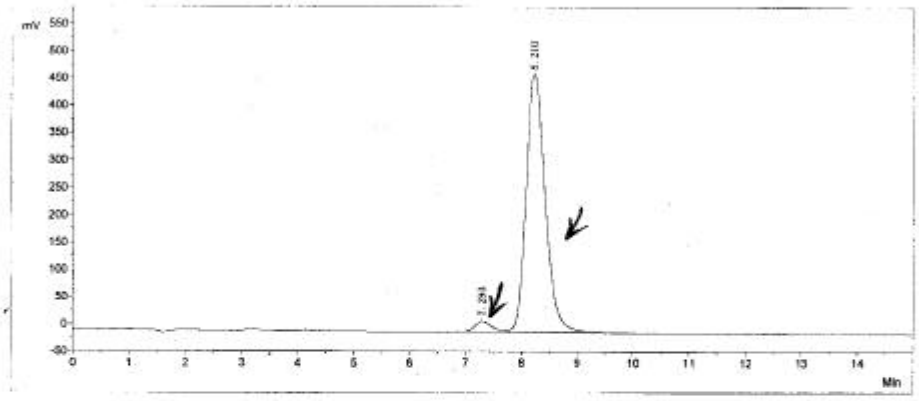
金属有机HPLC分析报告

样品文件名:clh-050221-3.che　　分析者:

分析日期:2005-03-25　　色谱柱:

流动相:　　流速:

检测波长:　　柱压:

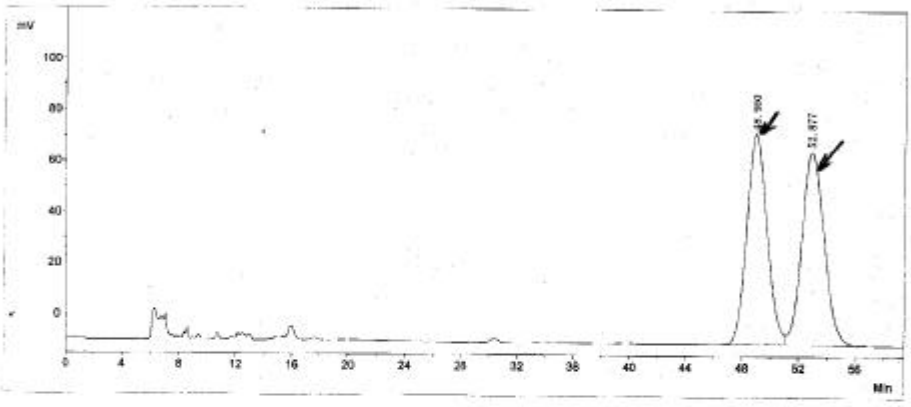


No.	R.Time	PeakHeight	PeakArea	PerCent
1	7.293	19529.0	399145.3	3.4537
2	8.210	470514.9	11157913.3	96.5463
Total		490043.9	11557058.6	100.0000

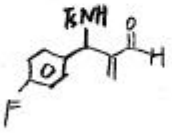
ee%. 93

金属有机HPLC分析报告

样品文件名:lyh-3020.che　　分析者:
分析日期:2005-10-18　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:

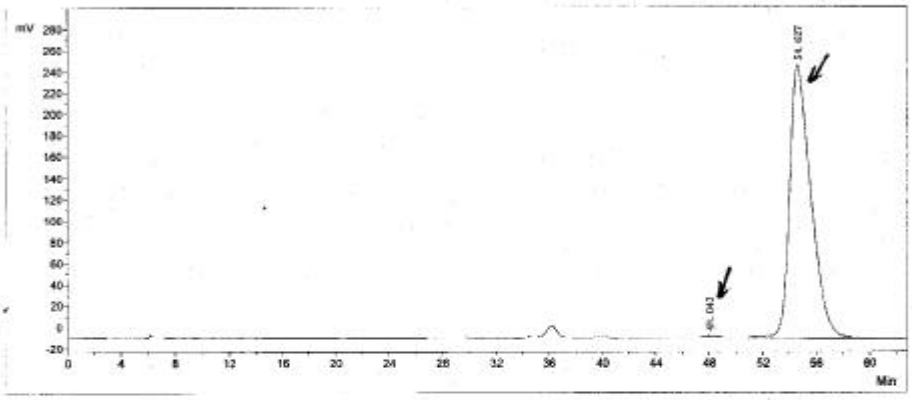


No.	R.Time	PeakHeight	PeakArea	PerCent
1	48.960	82140.9	8238396.1	50.0542
2	52.877	75100.6	8220555.2	49.9458
Total		157241.5	16458951.3	100.0000

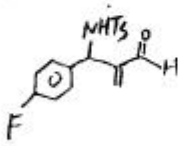


金属有机HPLC分析报告

样品文件名:clh050303-5.che　　分析者:
分析日期:2005-10-18　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



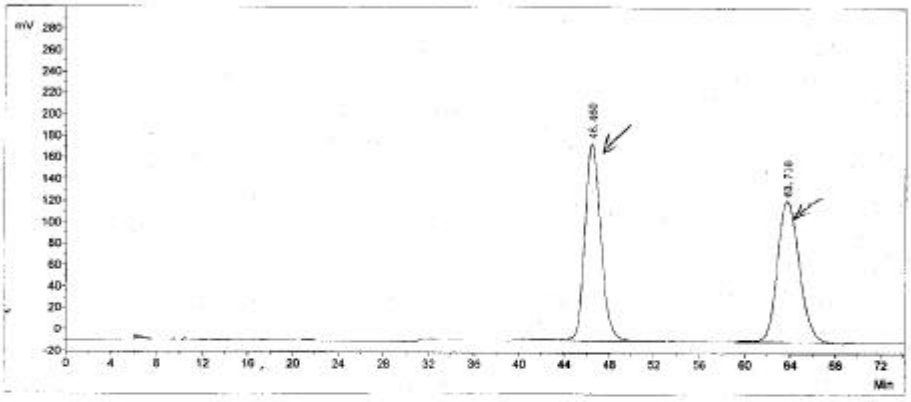
No.	R.Time	PeakHeight	PeakArea	PerCent
1	48.043	1229.6	89692.8	0.3164
2	54.627	255430.2	28255671.6	99.6836
Total		256659.8	28345364.4	100.0000



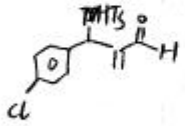
ee%: 99%

金属有机HPLC分析报告

样品文件名:lyh050303-3wx.che　　分析者:
分析日期:2005-10-20　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



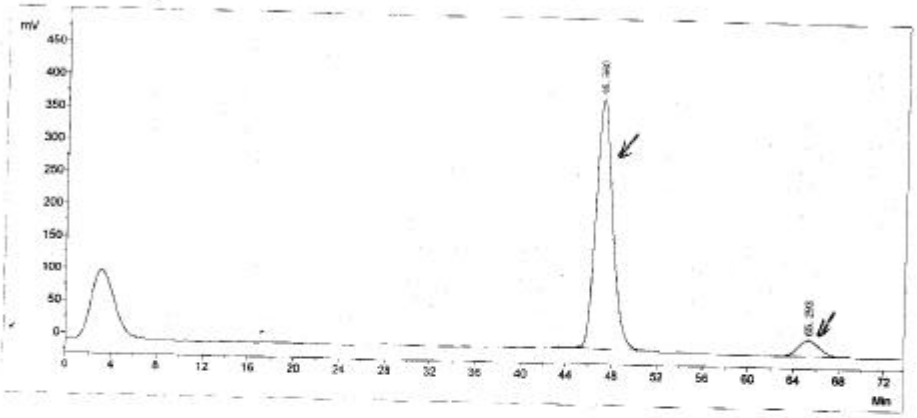
No.	R.Time	PeakHeight	PeakArea	PerCent
1	46.460	183038.6	17995291.8	50.1280
2	63.710	131513.1	17903406.0	49.8720
Total		314551.7	35898697.8	100.0000



金属有机HPLC分析报告

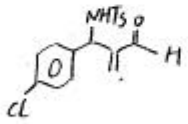
样品文件名:lyh050303-3.che
分析日期:2005-10-20
流动相:
检测波长:

分析者:
色谱柱:
流速:
柱压:



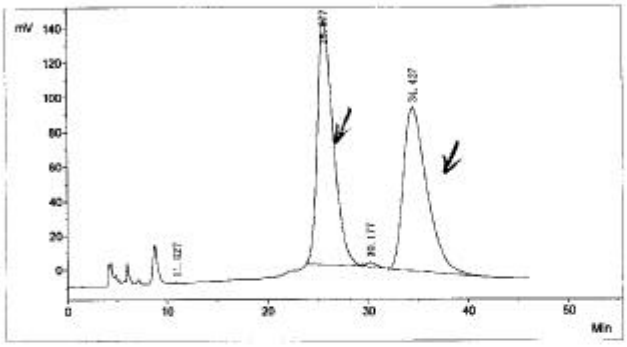
No.	R.Time	PeakHeight	PeakArea	PerCent
1	46.960	383638.3	39603193.8	92.5366
2	65.293	24204.6	3194123.7	7.4634
Total		407842.9	42797317.5	100.0000

ee=85%

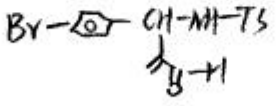


色谱分析报告

样品名称:分析谱图　　样品文件名:c1h021106-2.che
样品批号:　　分析者:
分析日期:2005-01-24　　分析时间:14:35
色谱柱:　　流动相:
流速:　　检测波长:



序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	11.027	410.3	8591.1	0.0276
2	2	Unknown	25.577	140827.4	15512957.1	49.8251
3	3	Unknown	30.177	1952.8	135722.2	0.4359
4	4	Unknown	34.427	94089.5	15477545.2	49.7114
合计:				237280.0	31134815.6	100.0000



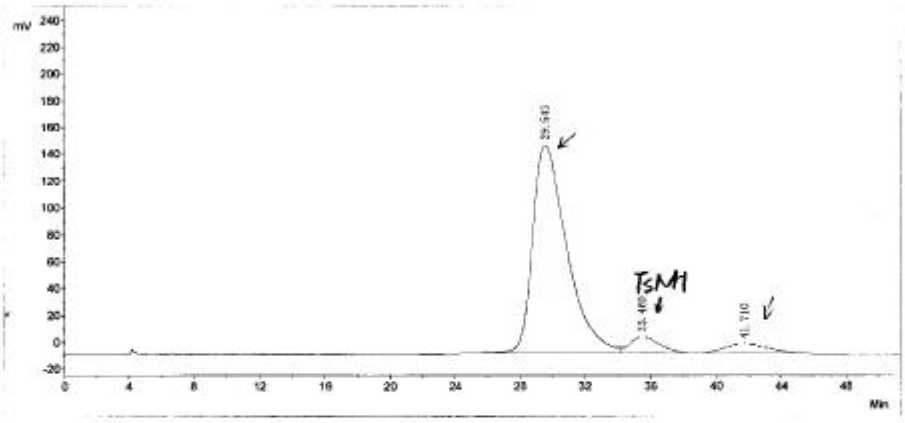
高效液相色谱分析报告

样品名称:分析谱图　　样品文件名:clh-050301-2.che

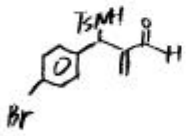
分析日期:2005-03-07　　分析时间:09:42

色谱柱:　　流动相:

流速:　　检测波长:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	29.543	154485.7	22507302.5	89.1826
2	2	35.460	12028.0	1505227.7	5.9643
3	3	41.710	6725.1	1224796.7	4.8531
Total			173238.8	25237326.9	100.0000



ee%: 90%