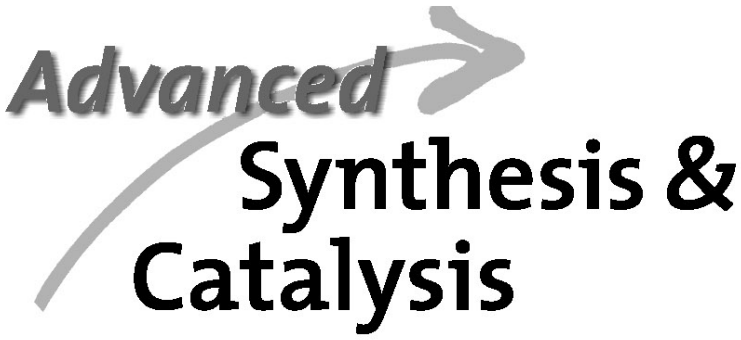


Supporting Information

Enantioselective Addition of Organozinc Reagents to Aldehydes Catalyzed by 3,3'-Bis(diphenylphosphinoyl)-BINOL

Manabu Hatano, Takashi Miyamoto, Kazuaki Ishihara*[a]

[a] Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan
Fax: +81 52 789 3331 / +81 52 789 3222, E-mail: ishihara@cc.nagoya-u.ac.jp

Supporting Information

General Methods. ^{1}H NMR spectra were measured on a Varian Gemini-2000 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the TM scale, multiplicity (s=singlet; d=doublet; t=triplet; q=quartet; m=multiplet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on Varian Mercury-300 (75 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.10 ppm). ^{19}F NMR spectra were measured on Varian Mercury-300 (282 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (BTF at -63.24 ppm in deuterochloroform). ^{31}P NMR spectra were measured on Varian Mercury-300 (121 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (H_3PO_4 at 0 ppm). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. Low-resolution mass analysis (LRMS) and GC analysis were performed with a Shimadzu GC/MS instrument [GC-17A/QP-5050A; column: TC-1 (0.25 mm × 30 m)] by direct insertion for chemical ionization (CI) with isobutane. High performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP and chiral column of Daicel CHIRALCEL, CHIRALPAK; OD-H (4.6 mm × 25 cm), OJ-H (4.6 mm × 25 cm), OB-H (4.6 mm × 25 cm). GC analysis was performed with Shimadzu 17A instruments using CP-Cyclodextrin-β-2,3,6-M-19 (i.d. 0.25 mm × 25 m; CHROMPACK; GL Science Inc.). Optical rotations were measured on Rudolph Autopol IV digital polarimeter. All experiments were carried out under an atmosphere of dry nitrogen. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. 37560). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$ and phosphomolybdic acid. In experiments that required dry solvents, hexane (dehydrate), benzene (dehydrate), toluene (dehydrate), dichloromethane (dehydrate), and tetrahydrofuran (dehydrate) were purchased from Kanto Chemical Co., Inc. Et_2Zn (1.10 *M* in toluene, Aldrich); *n*-Bu_2Zn (1.0 *M* in heptane, Fluka); Ph_2Zn (Strem) were used.

(*R*)-1,1'-Binaphthalene-2,2'-bis(diphenylphosphinate) (5): A solution of (*R*)-BINOL (2.86 g, 10 mmol) and NaH (*ca*. 60%w/w oil suspension) (0.880 g, 22 mmol) in THF (50 mL) was stirred for 15 min at 0 °C under nitrogen atmosphere. To this solution was slowly added diphenylphosphinic chloride (4.19 mL, 22 mmol) at 0 °C. The mixture was stirred for 15 min at 0 °C, then warmed to room temperature, and stirred for 3 h. The resulting mixture was cooled in ice bath, diluted with ether (100 mL) and then water (100 mL). The product was extracted with ether (30 mL × 2) and washed by brine (20 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure to give the crude product ((*R*)-**5**) in quantitiatve yield (6.86 g). This crude was used to next rearrangement without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95-7.44 (m, 26H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?120.0, 120.4, 121.7 (d, *J* = 6.9 Hz), 125.2, 126.1, 126.3, 127.0, 127.9, 128.1, 128.4, 129.7, 129.8, 130.2, 130.7, 131.5, 132,0, 133.7, 147.5 (d, *J* = 8.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 30.18 (s, 2P). HRMS calcd for $C_{44}H_{32}O_4P_2$ $[M+H]^+$ 687.1855, found 687.1854.

(*R*)-3,3'-Bis(diphenylphosphinoyl)-BINOL (3): To a solution of *i*-Pr_2NH (19.2 mL, 137 mmol) in THF (50 mL) was added *n*-BuLi (86.7 mL of 1.58 *M* solution in hexane) at – 78 °C under nitrogen atmosphere. After 30 min at – 78 °C, to this solution was slowly added the THF solution (100 mL) of (*R*)-**5** (13.6 mmol, 9.33 g) *via* cannula. The mixture was stirred for 3 h at – 78 °C. The resulting mixture was diluted with ether (50 mL), with brine (50 mL), and with 1 *M* HCl to acidify to *ca*. pH 1. The product was extracted with ether (30 mL × 2) and washed by brine (20 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure to give the crude product. Recrystallization from toluene/hexane (1/5) give (*R*)-**3** in colorless crystal in quantitative yield (9.33 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.35 (m, 6H), 7.46-7.68 (m, 12H), 7.68-7.87 (m, 12H), 10.57 (bs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?114.8, 116.1, 117.5, 117.6, 123.9, 125.0, 127.2, 127.4, 128.7, 128.9, 130.8, 131.2, 132.2, 132.5, 132.7, 135.0, 135.1, 136.4, 156.3. ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.08 (s, 2P). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 38.82 (s, 2P). IR (KBr) 3055, 1622, 1506, 1436, 1309, 1144, 1119, 1096 cm^{-1}. $[\alpha]_D^{20}$ = + 87.0 (*c* 1.50, $CHCl_3$). HRMS calcd for $C_{44}H_{32}O_4P_2$ $[M+H]^+$ 687.1855, found 687.1854.

(*R*)-3,3'-bis(diphenylphosphino)-1,1'-BINOL (6): To a mixture of (*R*)-**3** (85.3 mg, 0.124 mmol) and *N*,*N*-dimethylaniline (0.63 mL, 4.97 mmol) in toluene (2 mL) was added trichlorosilane (0.125 ml, 1.24 mmol) at 0 °C, and the solution was stirred for 30 min at this temperature. It was then refluxed for 12 h. After cooling to 0 °C, the reaction mixture was diluted with ether and quenched with a small amount of sat. $NaHCO_3$ solution. The resulting suspension was filtered through a pad of Celite and the filter cake was washed with dicholomethane, then the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (eluent:

pentane/EtOAc = 10/1), to afford the titled compound (31.9 mg, 39.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.40 (s, 2H), 7.14 (m, 2H), 7.25-7.50 (m, 26H), 7.63 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$) δ - 16.17 (s, 2P).

(*R*)-3,3'-bis(diphenyphosphinothioyl)-BINOL (4): To a solution of (*R*)-**6** (65.4 mg, 0.10 mmol) in well-deaerated benzene (5 mL) was added elemental sulfur (7.0 mg, 0.22 mmol) under nitrogen atmosphere. The mixture was heated under reflux condition for 24 h. The resulting mixture was concentrated under reduced pressure, and then purified by neutral silica gel column chromatography (eluent: hexane/EtOAc = 5/1), giving the desired products (*R*)-**4** as a white solid in 69% yield (49.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13-7.18 (m, 2H), 7,27-7.31 (m, 4H), 7.42-7.65 (m, 16H), 7.69-7.84 (m, 8H), 8.70(s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?117.5, 118.3, 118.7, 124.3, 124.8, 127.5, 127.7, 128.8, 128.9, 129.3, 130.8, 130.9, 131.9, 132.1, 132.6, 135.2, 136.1, 154.1. ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.89 (s, 2P). $[\alpha]_D^{21}$ = + 98.3 (*c* 0.33, $CHCl_3$). HRMS calcd for $C_{44}H_{32}O_2P_2S_2$ $[M+H]^+$ 719.1398, found 719.1397.

(*R*)-3-(diphenylphosphoryl)-BINOL (10): Titled compound was prepared from (*R*)-1,1'-Binaphthalene-2'-diphenylphosphinate-1-ol *via* phospho-Fries rearrangement described as above in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 1H), 7,16-7.22 (m, 2H), 7.24-7.38 (m, 5H), 7,53-7.59 (m, 4H), 7,62-7.68 (m, 2H), 7,76-7.88 (m, 6H), .7.91 (d, *J* = 9.0 Hz, 1H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.49 (s, 1P).

General Procedure for the Enantioselective Diethylzinc Addition to Aldehydes (Table 1 and 2)

A solution of (*R*)-**3** (0.1 mmol) in THF (3 mL) was stirred in pyrex Schlenk tube at room temperature for 5 min under nitrogen atmosphere. To the solution was added Et_2Zn (2.7 mL of 1.10 *M* solution in toluene) at – 78 °C. This solution was stirred for 30 min, and aldehyde (**1**) (1 mmol) was added. The resulting mixture was then gradually warmed to room temperature or 50 °C, and stirred for 0.1–24 h. After hydrolysis with 10 mL of *sat.* NH_4Cl aqueous solution, the product was extracted with ether (10 mL × 3) and washed by brine (10 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and the crude product was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc or pentane/ether), to give the desired products (**2**). The enantiomeric purity was determined by GC or HPLC on chiral column.

(*R*)-1-phenylpropanol (**2a**)[1,2,3,4,5,6,7,9,10,11]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.91 (t, *J* = 7.5 Hz, 3H), 1.69-1.77 (m, 2H), 2.24 (br, 1H), 4.56 (t, *J* = 6.9 Hz, 1H), 7.25-7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.2, 31.9, 75.9, 126.0, 127.5, 128.4,

144.7. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [115 °C, t_R(*R*) = 13.3 min, t_R(*S*) = 13.7 min].

(*R*)-1-(4-methoxyphenyl)propanol (**2b**)[1,2,3,5,6,7,9]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.90 (t, *J* = 7.5 Hz, 3H), 1.62-1.84 (m, 2H), 2.36 (br, 1H), 3.78 (s, 3H), 4.49 (t, *J* = 6.9 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ? 10.2, 31.7, 55.3, 75.5, 113.8, 127.3, 136.8, 158.9. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [130 °C, t_R(*R*) = 25.1 min, t_R(*S*) = 26.2 min].

(*R*)-1-*p*-tolylpropanol (**2c**)[1,3,7,9,11]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.91 (t, *J* = 7.5 Hz, 3H), 1.68-1.89 (m, 2H), 2.08 (br, 1H), 2.36 (s, 3H), 4.54 (t, *J* = 6.9 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ? 10.2, 21.1, 31.8, 75.9, 126.0, 129.1, 137.1, 141.7. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [120 °C, t_R(*R*) = 14.9 min, t_R(*S*) = 16.0 min].

(*R*)-1-(biphenyl-4-yl)propanol (**2d**)[2,5]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.98 (t, *J* = 7.5 Hz, 3H), 1.76-1.84 (m, 2H), 2.19 (br, 1H), 4.65 (t, *J* = 6.9 Hz, 1H), 7.34-7.50 (m, 5H), 7.58-7.63 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.3, 31.9, 75.8, 126.5, 127.1, 127.2, 127.3, 128.8, 140.4, 140.9, 143.7. Chiral HPLC (OJ-H; hexane/IPA = 20/1, 1.0 mL/min) [t_R(*R*) = 39.0 min, t_R(*S*) = 30.8 min].

(*R*)-1-(4-chlorophenyl)propanol (**2e**)[1,2,7,11]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.89 (t, *J* = 7.5 Hz, 3H), 1.62-1.85 (m, 2H), 2.04 (br, 1H), 4.56 (t, *J* = 6.9 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.0, 32.0, 75.3, 127.4, 128.6, 133.1, 143.1. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [140 °C, t_R(*R*) = 14.8 min, t_R(*S*) = 15.6 min].

(*R*)-1-(4-fluorophenyl)propanol (**2f**)[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.89 (t, *J* = 7.5 Hz, 3H), 1.66-1.84 (m, 2H), 2.18 (br, 1H), 4.56 (t, *J* = 6.9 Hz, 1H), 6.99-7.06 (m, 2H), 7.27-7.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.1, 32.0, 75.5, 115.1 (d, *J* = 21.8 Hz), 127.7 (d, *J* = 5.1 Hz), 140.3, 162.2 (d, *J* = 243.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ?- 115.8 (s, 1F). Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [110 °C, t_R(*R*) = 19.3 min, t_R(*S*) = 21.0 min].

(*R*)-1-(2-fluorophenyl)propanol (**2g**)[1,3]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.93 (t, *J* = 7.5 Hz, 3H), 1.74-1.82 (m, 2H), 2.43 (br, 1H), 4.91 (t, *J* = 6.9 Hz, 1H), 7.00 (ddd, *J* = 10.8, 8.4, 1.2 Hz, 1H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 7.23 (m, 1H), 7.43 (td, *J* = 7.5, 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.1, 32.0, 75.5, 115.5 (d, *J* = 15.5 Hz),

124.2 (d, *J* = 9.8 Hz), 127.4 (d, *J* = 4.8 Hz), 128.7 (d, *J* = 5.7 Hz), 131.5 (d, *J* = 13.2 Hz), 159.9 (d, *J* = 243.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ? - 120.3 (s, 1F). Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [110 °C, t_R(*R*) = 17.2 min, t_R(*S*) = 18.5 min].

(*R*)-1-(4-(trifluoromethyl)phenyl)propanol (**2h**)[4]
^{1}H NMR (300 MHz, $CDCl_3$) δ?0.92 (t, *J* = 7.5 Hz, 3H), 1.70-1.85 (m, 2H), 2.13 (br, 1H), 4.66 (t, *J* = 6.9 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.0, 32.1, 75.4, 124.2 (q, *J* = 270.0 Hz), 125.4 (q, *J* = 4.1 Hz), 126.3, 129.7 (q, *J* = 32.0 Hz), 148.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ?- 63.0 (s, 3F). Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [130 °C, t_R(*R*) = 10.4 min, t_R(*S*) = 11.1 min].

(*R*)-1-(benzo[1,3]dioxol-5-yl)propanol (**2i**)[5]
^{1}H NMR (300 MHz, $CDCl_3$) δ?0.87 (t, *J* = 7.5 Hz, 3H), 1.60-1.85 (m, 2H), 2.08 (br, 1H), 4.47 (t, *J* = 6.9 Hz, 1H), 5.92 (s, 2H), 6.75 (s, 2H), 6.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.2, 31.8, 75.9, 101.0, 106.5, 108.0, 119.5, 138.7, 146.9, 147.7. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [130 °C, t_R(*R*) = 29.9 min, t_R(*S*) = 30.8 min].

(*R*)-1-(1-naphthalenyl)propanol (**2j**)[1,2,5,7]
^{1}H NMR (300 MHz, $CDCl_3$) δ?1.03 (t, *J* = 7.5 Hz, 3H), 1.86-2.07 (m, 2H), 2.45 (br, 1H), 5.26 (t, *J* = 6.9 Hz, 1H), 7.45-7.53 (m, 3H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.76-7.91 (m, 2H), 8.10 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.5, 30.9, 72.5, 122.9, 123.4, 125.4, 125.5, 125.8, 127.7, 128.8, 130.5, 133.8, 140.2. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [160 °C, t_R(*R*) = 27.1 min, t_R(*S*) = 28.0 min].

(*R*)-1-(2-naphthalenyl)propanol (**2k**)[1,5,7,9]
^{1}H NMR (300 MHz, $CDCl_3$) δ?0.96 (t, *J* = 7.5 Hz, 3H), 1.80-1.96 (m, 2H), 2.63 (br, 1H), 4.71 (t, *J* = 6.9 Hz, 1H), 7.45-7.55 (m, 3H), 7.75 (s, 1H), 7.82-7.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ? 10.2, 31.7, 76.0, 124.2, 124.7, 124.8, 125.7, 126.0, 127.7, 128.0, 132.9, 133.2, 142.0. Chiral HPLC (OD-H; hexane/IPA = 9/1, 1.0 mL/min) [t_R(*R*) = 10.1 min, t_R(*S*) = 9.4 min].

(*R*)-1-phenyl-1-pentyn-3-ol (**2l**)[1,9]
^{1}H NMR (300 MHz, $CDCl_3$) δ?1.08 (t, *J* = 7.5 Hz, 3H), 1.76-1.88 (m, 2H), 3.22 (br, 1H), 4.56 (t, *J* = 6.9 Hz, 1H), 7.28-7.34 (m, 3H), 7.37-7.48 (m, 3H), 7.58 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?9.6, 31.0, 64.3, 85.0, 90.0, 122.7, 128.4, 131.7, 133.0. Chiral HPLC (OJ-H; hexane/IPA = 9/1, 1.0 mL/min) [t_R(*R*) = 8.5 min, t_R(*S*) = 10.2 min].

(*R*)-3-phenylpentanol (**2m**)[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.95 (t, *J* = 7.5 Hz, 3H), 1.42 (br, 1H), 1.47-1.58 (m, 2H), 1.71-1.86 (m, 2H), 2.67 (m, 1H), 2.81 (m, 1H), 3.57 (m, 1H), 7.17-7.24 (m, 3H), 7.28-7.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.0, 30.3, 32.2, 38.7, 72.7, 85.0, 90.0, 125.9, 128.5, 128.6, 142.3. Chiral HPLC (OD-H; hexane/IPA = 9/1, 1.0 mL/min) [t_R(*R*) = 5.8 min, t_R(*S*) = 7.3 min].

(*R*)-1-cyclohexylpropanol (**2n**)[1,2,4,5,7,9]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.95 (t, *J* = 7.5 Hz, 3H), 1.11-1.82 (m, 13H), 3.28 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ? 10.0, 26.4, 27.2, 29.0, 31.7, 43.3, 77.8. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 for its acetate [110 °C, t_R(*R*) = 13.0 min, t_R(*S*) = 12.3 min].

(*R*)-3-octanol (**2o**)[1,6]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.86 (t, *J* = 7.5 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 1.22-1.54 (m, 10H), 1.63 (br, 1H), 3.53 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?9.9, 14.0, 22.7, 25.4, 30.2, 32.0, 37.0, 73.3. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 for its acetate [90 °C, t_R(*R*) = 10.5 min, t_R(*S*) = 9.8 min].

(*R*)-3-dodecanol (**2p**)[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.87 (t, *J* = 7.5 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 1.20-1.51 (m, 18H), 1.72 (br, 1H), 3.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?9.9, 14.2, 22.8, 25.8, 29.4, 29.6, 29.7, 29.8, 30.2, 32.0, 37.0, 73.5. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 for its acetate [120 °C, t_R(*R*) = 25.4 min, t_R(*S*) = 26.5 min].

(*R*)-3-tetradecanol (**2q**)[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.87 (t, *J* = 7.5 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 1.16-1.55 (m, 22H), 1.81 (br, 1H), 3.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?9.9, 14.2, 22.8, 25.8, 29.4, 29.7, 30.2, 32.0, 37.0, 73.5. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 for its acetate [140 °C, t_R(*R*) = 28.3 min, t_R(*S*) = 27.5 min].

(*R*)-1-(2-furanyl)propanol (**2r**)[1,8]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.94 (t, *J* = 7.5 Hz, 3H), 1.80-1.93 (m, 2H), 2.04 (br, 1H), 4.59 (t, *J* = 6.9 Hz, 1H), 6.22 (dd, *J* = 3.3, 0.9 Hz, 2H), 6.32 (dd, *J* = 3.3, 1.8 Hz, 2H), 7.36 (dd, *J* = 1.8, 0.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.0, 28.7, 69.2, 105.9, 110.2, 142.0, 156.7. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 for its acetate [90 °C, t_R(*R*) = 12.3 min, t_R(*S*) = 11.5 min].

(*R*)-1-(3-thiophenyl)propanol (**2s**)[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ?0.92 (t, *J* = 7.5 Hz, 3H), 1.75-1.85 (m, 2H), 2.12 (br, 1H), 4.67 (t, *J* = 6.9 Hz, 1H), 7.07 (dd, *J* = 5.4, 1.2 Hz, 2H), 7.16 (dd, *J* = 3.0, 1.2 Hz, 2H), 7.29 (dd, *J* = 5.4, 3.0 Hz,

2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?10.0, 31.3, 72.2, 120.8, 125.6, 126.1, 146.1. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 for its acetate [110 °C, t_R(*R*) = 17.5 min, t_R(*S*) = 16.6 min].

(*R*)-1-(3-pyridinyl)propanol (**2t**)[9]
^{1}H NMR (300 MHz, $CDCl_3$) δ?0.85 (t, *J* = 7.5 Hz, 3H), 1.60-1.81 (m, 2H), 4.10 (br, 1H), 4.56 (t, *J* = 6.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 8.29 (m, 1H), 8.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ? 9.9, 31.9, 72.9, 123.5, 134.1, 140.6, 147.4, 148.0. Chiral GC CP-Cyclodextrin-β-2,3,6-M-19 [120 °C, t_R(*R*) = 28.6 min, t_R(*S*) = 30.0 min].

(*R*)-1-phenylpentanol (**7a**)[10]
^{1}H NMR (300 MHz, $CDCl_3$) δ?0.90 (t, *J* = 7.5 Hz, 3H), 1.22-1.46 (m, 4H), 1.65-1.87 (m, 2H), 2.06 (br, 1H), 4.65 (t, *J* = 6.9 Hz, 1H), 7.24-7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?14.0, 22.7, 28.0, 38.9, 74.8, 126.0, 127.5, 128.5, 145.0. Chiral HPLC (OB-H; hexane/IPA = 80/1, 1 mL/min) [t_R(*R*) = 18.4 min, t_R(*S*) = 13.9 min].

(*R*)-1-(4-chlorophenyl)pentanol (**7e**)[10]
^{1}H NMR (300 MHz, $CDCl_3$) δ?0.87 (t, *J* = 7.5 Hz, 3H), 1.17-1.36 (m, 4H), 1.61-1.74 (m, 2H), 2.51 (br, 1H), 4.57 (t, *J* = 6.9 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?14.0, 22.6, 27.8, 38.8, 74.0, 127.3, 128.5, 133.0, 143.4.? Chiral HPLC (OD-H; hexane/IPA = 80/1, 0.5 mL/min) [t_R(*R*) = 22.5 min, t_R(*S*) = 25.6 min].

(*R*)-phenyl(*p*-tolyl)methanol (**8c**)[11,12,13]
^{1}H NMR (300 MHz, $CDCl_3$) δ?2.28 (br, 1H), 2.37 (s, 3H), 5.81 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.24-7.41 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?21.5, 76.2, 126.6, 127.5, 128.5, 129.2, 129.3, 137.3, 141.0, 144.0. Chiral HPLC (OD-H; hexane/IPA = 40/1, 1 mL/min) [t_R(*R*) = 22.9 min, t_R(*S*) = 20.5 min].

(*R*)-biphenyl-4-yl(phenyl)methanol (**8d**)[11]
^{1}H NMR (300 MHz, $CDCl_3$) δ?2.36 (br, 1H), 5.90 (s, 1H), 7.29-7.67 (m, 12H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?76.2, 126.6, 127.1, 127.2, 127.4, 128.6, 128.7, 128.8, 129.1, 140.6, 140.9, 142.9, 143.8. Chiral HPLC (OD-H; hexane/IPA = 20/1, 0.5 mL/min) [t_R(*R*) = 55.2 min, t_R(*S*) = 59.8 min].

(*R*)-(4-chlorophenyl)(phenyl)methanol (**8e**)[1,11,12,13]
^{1}H NMR (300 MHz, $CDCl_3$) δ?2.69 (br, 1H), 5.78 (s, 1H), 7.18-7.40 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?75.6, 125.4, 126.6, 127.9, 128.6, 128.7, 133.3, 142.3, 143.5. Chiral HPLC (OB-H; hexane/IPA = 9/1, 0.5 mL/min) [t_R(*R*) = 31.5 min, t_R(*S*) = 49.5 min].

(*R*)-(4-fluorophenyl)(phenyl)methanol (**8f**)[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ?2.47 (br, 1H), 5.81 (s, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 7.29-7.37 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?75.6, 115.3 (d, *J* = 18.8 Hz), 126.5, 127.7, 128.3 (d, *J* = 9.8 Hz), 128.7, 139.6 (d, *J* = 3.2 Hz), 143.7, 162.2 (d, *J* = 244.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ?- 115.5 (s, 1F). Chiral HPLC (OB-H; hexane/IPA = 4/1, 0.5 mL/min) [t_R(*R*) = 31.1 min, t_R(*S*) = 38.7 min].

(*R*)-phenyl(4-(trifluoromethyl)phenyl)methanol (**8h**)[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ?2.75 (br, 1H), 5.83 (s, 1H), 7.23-7.38 (m, 5H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?75.8, 124.2 (q, *J* = 270.0 Hz), 125.4 (q, *J* = 3.8 Hz), 126.6, 126.7, 128.2, 128.8, 129.7 (q, *J* = 32.0 Hz), 143.2, 147.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ?- 62.9 (s, 3F). Chiral HPLC (OB-H; hexane/IPA = 20/1, 0.5 mL/min) [t_R(*R*) = 27.2 min, t_R(*S*) = 43.7 min].

(*R*)-2-naphthalenyl(phenyl)methanol (**8k**)[1,12]

^{1}H NMR (300 MHz, $CDCl_3$) δ?2.35 (br, 1H), 6.01 (s, 1H), 7.25-7.38 (m, 3H), 7.41-7.51 (m, 5H), 7.79-7.91 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ?21.5, 76.2, 126.6, 127.5, 128.5, 129.2, 129.3, 137.3, 141.0, 144.0. Chiral HPLC (OD-H; hexane/IPA = 4/1, 0.5 mL/min) [t_R(*R*) = 22.1 min, t_R(*S*) = 19.2 min].

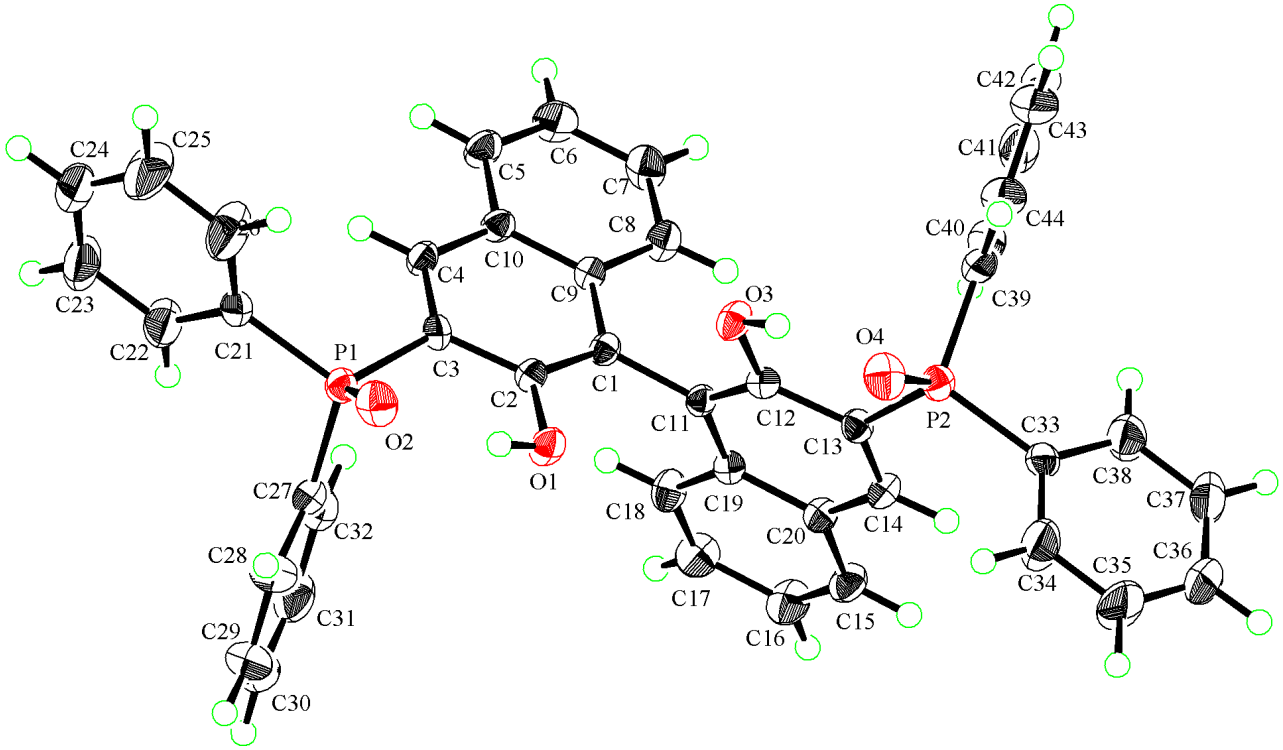
References

1. W.-S. Huang, Q.-S. Hu, L. Pu, *J. Org. Chem.* **1999**, *64*, 7940–7956.
2. W.-P. Deng, X.-L. Hou, L.-X. Dai, *Tetrahedron: Asymmetry* **1999**, *10*, 4689–4693.
3. D. Castellnou, L. Solà, C. Jimeno, J. M. Fraile, J. A. Mayoral, A. Riera, M. A. Pericàs, *J. Org. Chem.* **2005**, *70*, 433–438.
4. K. Biswas, O. Prieto, P. J. Goldsmith, S. Woodward, *Angew. Chem. Int. Ed.* **2005**, *44*, 2232–2234.
5. M. R. Paleo, I. Cabeza, F. J. Sardina, *J. Org. Chem.* **2000**, *65*, 2108–2113.
6. A. L. Braga, M. W. Paixão, D. S, Ludtke, C. C. Silveira, O. E. D. Rodrigues, *Org. Lett.* **2003**, *5*, 2635–2638.
7. Q. Xu, H. Yang, X. Pan, A. S. C. Chan, *Tetrahedron: Asymmetry* **2002**, *13*, 945–951.
8. I. Sato, T, Saito, D. Omiya, Y. Takizawa, K. Soai, *Heterocycles* **1999**, *51*, 2753–2758.
9. P. Västilä, I. M. Pastor, H. Adolfsson, *J. Org. Chem.* **2005**, *70*, 2921–2929.
10. K. H. Yong, N. J. Taylor, J. M. Chang, *Org. Lett.* **2002**, *4*, 3553–3556.
11. J. Rudolph, F. Schmidt, C. Bolm, *Adv. Synth. Catal.* **2004**, *346*, 867–872.
12. G. Zhao, X.-G. Li, X.-R. Wang, *Tetrahedron: Asymmetry* **2001**, *12*, 399–403.
13. J. Wu, J.-X. Ji, A. S. C. Chan, *Proc. Natl. Acad. Sci.* **2005**, *102*, 3570–3575.

X-ray Crystallographic Study:

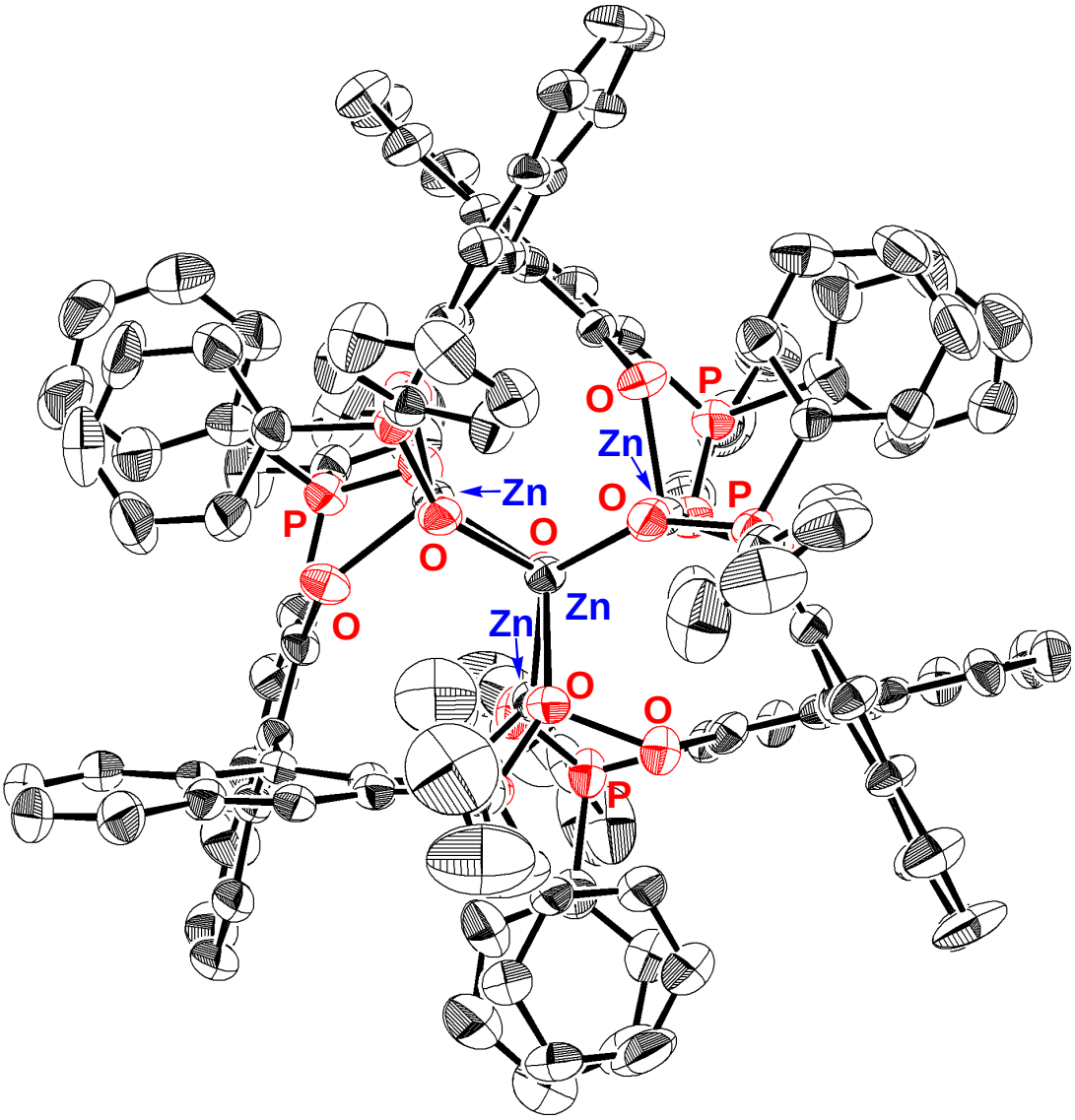
The single crystal growth was grown from a dichloromethane-hexane mixed solvent system at room temperature. X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods and expanded using Fourier techniques.

Crystal data for (*R*)-3,3'-bis(diphenylphosphinoyl)-BINOL ((*R*)-**3**): formula $C_{264}H_{192}O_{24}P_{12}$, colorless, crystal dimensions 0.20×0.20×0.10 mm^3, monoclinic, space group *C*2 (#5), *a* = 10.709(5) Å, *b* = 18.515(5) Å, *c* = 53.426(5) Å, β = 90.282(5) °, *V* = 10593(6) $Å^3$, *Z* = 2, ρ_{calc} = 1.292 g cm^{-3}, μ(MoKα) = 0.167 mm^{-1}, *T* = 173 K. 25528 reflections were independent and unique, and 21519 with $I > 2\sigma(I)$ ($2\theta_{max}$ = 29.31°) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. *R* = 0.0555 and *Rw* = 0.1320. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-262636. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

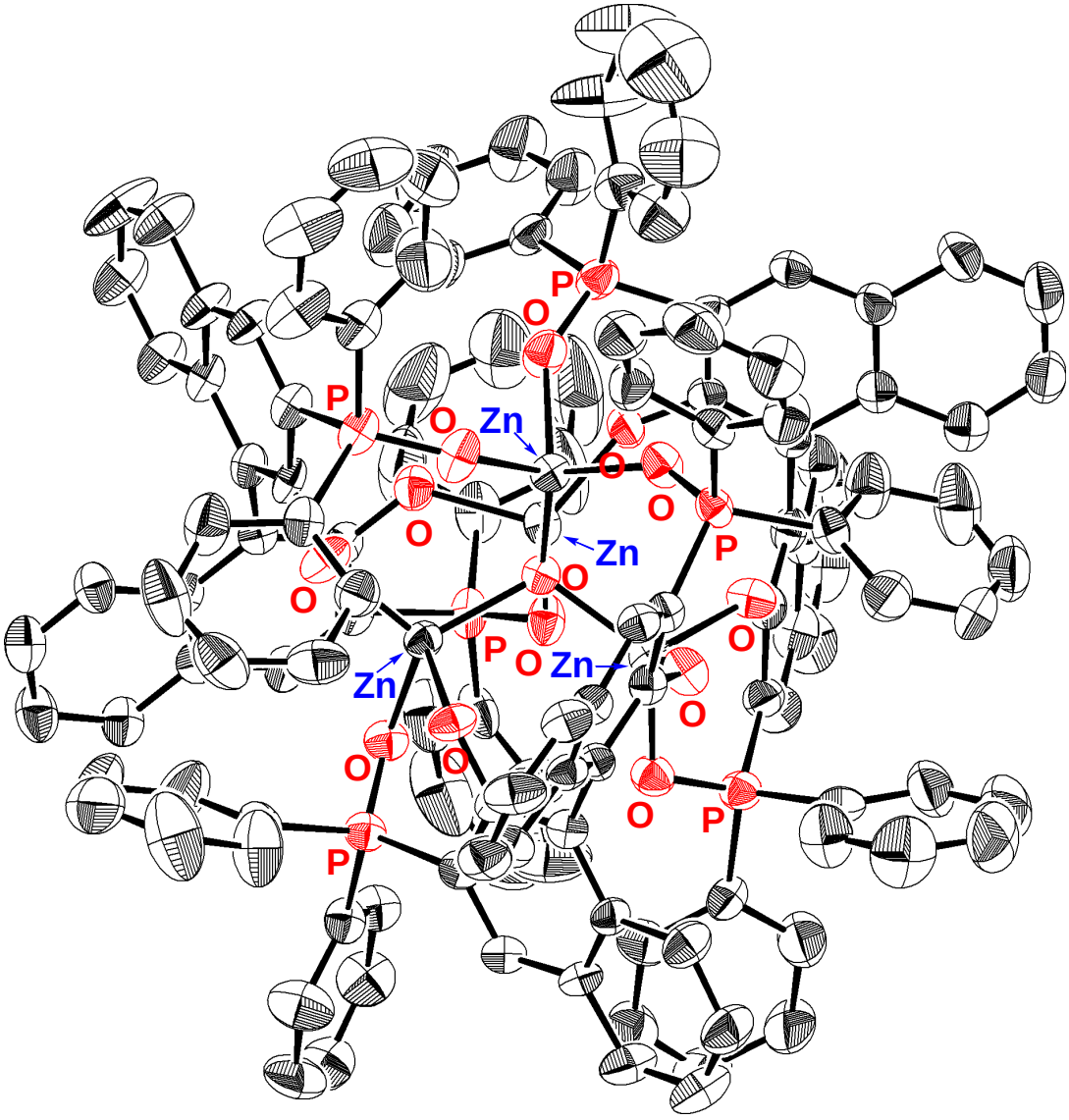


Crystal data for $[Zn_4\{(R)\text{-}3,3'\text{-}bis(Ph_2P{=}O)\text{-}BINOLate\}_3(\mu_4\text{-}O)]\cdot(CH_2Cl_2)_3$ (**11**): formula $C_{132}H_{90}O_{13}P_6Zn_4\cdot C_3H_6Cl_6$, yellow, crystal dimensions 0.25×0.20×0.15 mm^3, monoclinic, space group $P2_1$ (#4), *a* = 15.803(3) Å, *b* = 22.033(4) Å, *c* = 19.949 (3) Å, β = 103.148(4) °, *V* =

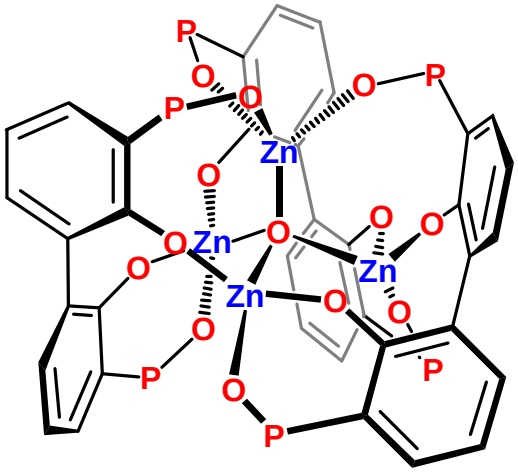
6763.9(19) Å^3, Z = 2, ρ_{calc} = 1.270 g cm^{-3}, μ(MoKα) = 0.946 mm^{-1}, T = 223 K. 33967 reflections were independent and unique, and 22259 with $I > 2\sigma(I)$ ($2\theta_{max}$ = 29.21°) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R = 0.0709 and Rw = 0.1812. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-261552. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].



ORTEP drawing (Top View)



ORTEP drawing (Side View)



Core of the Zn_4 complex