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Molecular building block approaches to chiral porous zirconium phosphonates for asymmetric catalysis

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Abstract

Porous zirconium phosphonates containing chiral dihydroxy functionalities have been synthesized via a building block approach. Enantiopure atropisomeric bisphosphonic acids of various lengths, L_1–L_3, were first synthesized starting from 1,1′-bi-2-naphthol (BINOL) in multi-step sequences. Amorphous chiral porous zirconium phosphonates were then obtained by refluxing BINOL-derived bisphosphonic acids with $Zr(O^nBu)_4$ in *n*-BuOH, and have been characterized by powder X-ray diffraction, solid-state CP-MAS ^{31}P NMR, IR, TGA, adsorption measurements, circular dichroism spectroscopy, and microanalyses. These zirconium phosphonates have empirical formulae of $(Zr\text{-}L_{1–3})\cdot xH_2O$ ($x = 4$ or 5), and exhibit BET surface areas ranging from 431 to 586 m^2/g. In combination with $Ti(O^iPr)_4$, these zirconium phosphonates have been used to heterogeneously catalyze the additions of diethylzinc to a wide range of aromatic aldehydes with high conversions and e.e. of up to 72%. This work represents a novel approach towards heterogeneous asymmetric catalysis. The tunability of such a molecular building block approach promises to lead to practically useful heterogeneous asymmetric catalytic processes.

Keywords: Molecular building block; Zirconium phosphonates; Asymmetric catalysis

1. Introduction

The ability to predictably synthesize materials with desired chemical and physical properties constitutes a central theme of contemporary chemical research. Hybrid organic-inorganic materials have recently attracted great attention from synthetic chemists because of the propensity of engineering interesting properties via judicious combinations of a vast array of organic ligands and diverse metal coordination geometries [1–4]. The synthesis of porous crystalline solids based on metal-organic coordination networks (MOCNs) has been particularly successful; some of these crystalline hybrid organic-inorganic solids have been shown to exhibit porosity exceeding that of inorganic counterparts [5,6]. Tunability of MOCNs also allows the design of chiral pores and functionalities exploitable for enantioselective processes. A straightforward strategy involves the incorporation of chiral bridging ligands into the metal-organic frameworks, which will necessarily result in chiral solids that can possess chiral pockets or functionalities that are accessible to prochiral substrates in the events of asymmetric catalyses or racemic compounds in the events of chiral separations. Such a molecular building block approach towards heterogeneous asymmetric catalysis and chiral separations will represent a major advance in chirotechnology owing to both its tunability as well as re-usability of the resulting chiral porous materials.

While Aoyama et al. have extensively investigated the catalytic behaviors of hydrogen-bonded anthracene-bis(resorcinol) systems and zirconium complexes of anthracene-bis-(resorcinol) [7,8], Seo et al. provided the first example of asymmetric catalyses of transesterification reactions with a modest enantio excess (e.e.) of 8% [9]. We have recently reported the design of a series of chiral porous lamellar lanthanide phosphonates and their applications in heterogeneous catalyses of cyanation of aldehydes, Diels–Alder reactions, and ring-opening of carboxylic anhydrides [10]. We wish to report in this paper the synthesis and characterization of a series of chiral porous zirconium phosphonates that possess chiral dihydroxy functionalities. We also present the preliminary results on the applications of these chiral porous solids in asymmetric catalyses of the additions of

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diethylzinc to aromatic aldehydes to afford chiral secondary alcohols.

2. Experimental

2.1. Materials and general procedures

All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used in the reactions were dried by standard procedures. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(phosphonic acid) was synthesized by an improved procedure as shown below.

Circular dichroism (CD) spectra were recorded on a Jasco J-720 spectropolarimeter. The IR spectra were recorded from KBr pellets on a Nicolet Magna-560 FTIR spectrometer. NMR spectra were recorded on a Bruker NMR 400 DRX spectrometer and a Bruker NMR 360 MHz spectrometer. ^{1}H NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform or methanol. $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of chloroform-d_1 or CD_3OD. Solution ^{31}P NMR spectra were recorded at 161 MHz, while CP-MAS ^{31}P NMR spectra were recorded at 121 MHz with a spinning rate of 8 KHz. Thermogravimetric analysis was performed in air at a scan speed of 4 °C/min on a Shimadzu TGA-50 analyzer. Microanalysis was performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign, while FAB HR-MS data spectra were obtained in UIUC mass spectrometry laboratory.

Nitrogen adsorption experiments were performed on a Quantachrome-1C surface area analyzer at liquid nitrogen temperature. All the surface areas were calculated based on multi-point BET plots, while the pore volumes were estimated based on BJH method.

2.2. 6,6′-Dibromo-2,2′-diacetyl-1,1′-binaphthalene

To a mixture of acetic anhydride (9.5 ml, 99 mmol) and pyridine (8.0 ml, 99 mmol) was added a solution of 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene (8.8 g, 19.8 mmol) in 200 ml of distilled CH_2Cl_2. The mixture was allowed to stir at RT for 24 h, extracted with CH_2Cl_2, and washed with water three times. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to afford the crude product which was washed with 1 L of water to give pure 6,6′-dibromo-2,2′-diacetyl-1,1′-binaphthalene. Yield: 10.5 g (99%). Spectroscopic data are identical to those reported in the literature [11].

2.3. 2,2′-Diacetyl-1,1′-binaphthyl-6,6′-bis(diethylphosphonate)

A mixture of 6,6′-dibromo-2,2′-diacetyl-1,1′-binaphthalene (5.6 g, 10.6 mmol), diethylphosphite (3.4 ml, 24 mmol), and $Pd(PPh_3)_4$ (0.61 g, 0.53 mmol) in NEt_3 (15 ml) and benzene (120 ml) was refluxed for 3 days. Upon cooling to RT, the organic volatiles were removed under reduced pressure, and the residue was extracted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$, and the removal of organic volatiles afforded the crude product which is pure enough for subsequent reactions. Yield: 6.8 g (100%). The crude product can be purified by column chromatography (CH_2Cl_2/acetone 1:1 (v/v)). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.51 (s, 2H, H_5), 8.12 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_3), 7.56 (dd, $^3J_{H-H}$ = 8.8 Hz, $^4J_{H-H}$ = 0.9 Hz, 2H, H_7), 7.51 (d, $^3J_{H-H}$ = 8.8, 2H, H_4), 7.20 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_8), 4.14 (m, 8H, –OCH_2CH_3), 1.87 (s 6H, CO_2CH_3), 1.32 (t, $^3J_{H-H}$ = 7.1 Hz, 12 H, –OCH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169 (s), 148.6 (s), 134.9 (d, J_{c-p} = 2.7 Hz), 133.9 (d, J_{c-p} = 11 Hz), 130.7 (s), 133.3 (s), 127.5 (d, J_{c-p} = 10 Hz), 126.6 (s), 126.3 (d, J_{c-p} = 15 Hz), 123.9 (d, J_{c-p} = 175 Hz), 123 (d, J_{c-p} = 3.8 Hz), 62.2 (d, J_{c-p} = 6.8 Hz, $POCH_2CH_3$), 20.5 (s, CO_2CH_3), 16.3 (d, J_{c-p} = 6.8 *Hz*, $POCH_2CH_3$).

2.4. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylphosphonate)

A mixture of crude 2,2′-diacetyl-1,1′-binaphthyl-6,6′-bis-(diethylphosphonate) (6.8 g, 11 mmol) from the above reaction and KOH (1.8 g, 32 mmol) in MeOH (95 ml), THF (95 ml), and water (95 ml) was stirred at RT for 24 h. The solvents were removed under reduced pressure and the residue was extracted with EtOAc and washed with copious amounts of water. The organic layer was dried over $MgSO_4$, and the organic volatiles were removed under reduced pressure. Column chromatography with silica gel using CH_2Cl_2/acetone (1:1 (v/v)) gave pure solid of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylphosphonate). Yield: 5.6 g (95%). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.36 (s, 2H, H_5), 7.92 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_3), 7.50 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_4), 7.46 (dd, $^3J_{H-H}$ = 8.8 Hz, $^4J_{H-H}$ = 0.9 Hz, 2H, H_7), 7.15 (d, $^3J_{H-H}$ = 8.8, 2H, H_8), 4.11 (m, 8H, –OCH_2CH_3), 1.28 (m, 12H, –OCH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.3 (s), 136.5 (d, J_{c-p} = 2.8 Hz), 134.1 (d, J_{c-p} = 11 Hz), 131.1 (s), 127.7 (d, J_{c-p} = 17 Hz), 126.9 (d, J_{c-p} = 10 Hz), 125 (d, J_{c-p} = 14 Hz), 121.1 (d, J_{c-p} = 191 Hz), 119.3 (s), 113.4 (s), 62.2 (m), 16.5 (d, J_{c-p} = 7.3 Hz).

2.5. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(phosphonic acid)

A solution of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylphosphonate) ((1.0 g, 1.8 mmol) and $(CH_3)_3SiBr$

(1.2 ml, 9.1 mmol) in CH_2Cl_2 (50 ml) was stirred at RT. After 12 h, the volatiles were removed under reduced pressure and the residue was dissolved in 50 ml of MeOH and stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure and pure product of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(phosphonic acid) was obtained in quantitative yield. $^1H\{^{31}P\}$ NMR (CD_3OD): δ 8.35 (s, 2H, H_5) 8.00 (d, $^3J_{H-H} = 8.7$ Hz, 2H, H_3), 7.49 (dd, $^3J_{H-H} = 8.7$ Hz, $^4J_{H-H} = 1.6$ Hz, 2H, H_7), 7.38 (d, $^3J_{H-H} = 8.7$ Hz, 2H, H_4), 7.08 (d, $^3J_{H-H} = 8.7$ Hz, 2H, H_8), 4.90 (s, 6H, OH). These spectroscopic data are identical to those previously reported [12].

2.6. 2,2′-Diacetyl-1,1′-binaphthyl-6,6′-dialdehyde

To a mixture of acetic anhydride (8.4 ml, 89 mmol) and pyridine (7.2 ml, 89 mmol) was added a solution of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-dialdehyde (6.08 g, 18 mmol) in 250 ml of CH_2Cl_2 under N_2 gas flow. The mixture was allowed to stir at RT for 12 h, extracted with CH_2Cl_2, and washed with water three times. The organic layer was dried with $MgSO_4$, and the organic volatiles were removed under reduced pressure. The crude product was washed with 2 L of water to give pure 2,2′-diacetyl-1,1′-binaphthyl-6,6′-dialdehyde in quantitive yield. ^1H NMR ($CDCl_3$): δ 10.2 (s, 2H, CHO), 8.47 (s, 2H, H_5), 8.21 (d, $^3J_{H-H} = 9.1$ Hz, 2H, H_3), 7.76 (dd, $^3J_{H-H} = 8.9$ Hz, $^4J_{H-H} = 1.1$ Hz, 2H, H_7), 7.56 (d, $^3J_{H-H} = 8.9$ Hz, 2H, H_4), 7.24 (d, $^3J_{H-H} = 9.0$ Hz, 2H, H_8), 1.89 (s, 6H, CO_2CH_3). ^{13}C NMR ($CDCl_3$): δ 191.8 (s, CHO), 168.9 (s), 149.3 (s), 136.4 (s), 134.1 (s), 134 (s), 131.5 (s), 130.8 (s), 127 (s), 124.2 (s), 123.3 (s), 20.5 (s, CO_2CH_3).

2.7. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylvinylphosphonate)

A mixture of diacetyl-1,1′-binaphthyl-6,6′-dialdehyde (6.5 g, 15 mmol), tetraethylmethylenebisphosphonate (7.8 ml, 31 mmol), and NaH (60% dispersion in mineral oil, 2.6 g, 65 mmol) in 200 ml of anhydrous THF was stirred at RT for 4 h, and then quenched with 200 ml of water. Removal of the volatiles afforded crude product of 2,2′-diacetyl-1,1′-binaphthyl-6,6′-bis(diethylvinylphosphonate).

A mixture of this crude product (10.5 g, 15 mmol) and KOH (2.5 g, 45 mmol) in THF (200 ml), water (200 ml), and MeOH (200 ml) was sitrred at RT for 24 h. The solvents were removed under reduced pressure, and the residue was extracted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$. Column chromatography with silica gel using CH_2Cl_2/acetone (3:1 (v/v)) gave pure solid of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylvinylphosphonate). Yield: 6.5 g (70%). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 7.91 (d, $^3J_{H-H} = 9.2$ Hz, 2H, H_3), 7.81 (s, 2H, H_5), 7.54 (d, $^3J_{H-H} = 17$ Hz, 2H, $-CH_2CH_2-$), 7.45 (d, $^3J_{H-H} = 8.8$ Hz, 2H, H_7), 7.36 (d, $^3J_{H-H} = 8.6$ Hz, 2H, H_4), 7.08 (d, $^3J_{H-H} = 8.8$ Hz, 2H, H_8), 6.71 (s, 2H, OH), 6.17 (d, $^3J_{H-H} = 17$ Hz, 2H, $-CH_2CH_2-$), 4.10 (m, 8H, OCH_2CH_3), 1.32 (t, $^3J_{H-H} = 7.0$ Hz, 12H, $-OCH_2CH_3$). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 20.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.2 (s), 148.9 (d, $^1J_{c-p} = 8.8$ Hz), 134.7 (s), 131.6 (s), 130.2 (d, $^2J_{c-p} = 24$ Hz), 129.9 (s), 128.9 (s), 118.9 (s), 112.6 (d, $^3J_{c-p} = 190$ Hz), 112.4 (s), 61.9 (m, OCH_2CH_3), 16.3 (d, $^4J_{c-p} = 6.4$ Hz, OCH_2CH_3).

2.8. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(vinylphosphonic acid)

A solution of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylvinylphosphonate) (500 mg, 0.82 mmol) and $(CH_3)_3SiBr$ (0.6 ml, 4.5 mmol) in CH_2Cl_2 (50 ml) was stirred at RT. After 36 h, the solvent was removed under reduced pressure and the residue was dissolved in 50 ml of MeOH and stirred at RT for 0.5 h. The volatiles were removed under reduced pressure and a pure product of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(vinylphosphonic acid) was obtained in quantitative yield. $^1H\{^{31}P\}$ NMR (CD_3OD): δ 7.99 (s, 2H, H_5), 7.96 (d, $^3J_{H-H} = 8.9$ Hz, 2H, H_3), 7.52 (d, $^3J_{H-H} = 18$ Hz, 2H, H_a), 7.49 (d, $^3J_{H-H} = 9.3$ Hz, 2H, H_4), 7.35 (d, $^3J_{H-H} = 8.9$ Hz, 2H, H_7), 7.08 (d, $^3J_{H-H} = 8.8$ Hz, 2H, H_8), 6.46 (d, $^3J_{H-H} = 17$ Hz, 2H, H_b). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 18.9 (s). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 155.7 (s), 147.3 (d, $^1J_{c-p} = 6.0$ Hz), 136.7 (s), 131.5 (s), 131.2 (d, $^2J_{c-p} = 23$ Hz), 130.7 (s), 130.1 (s), 126.6 (s), 124.6 (s), 120.1 (s), 116.4 (d, $^3J_{c-p} = 166$ Hz), 116.5 (s). HR–MS (FAB) m/z $[M + H]^+$ 499.0712 (Calcd m/z 499.0711). $[\alpha]_D^{20} = +104.8$ (c 0.05 in MeOH) for *S*-enantiomer.

2.9. (4-Diethylphosphonobenzyl)diethylphosphonate

A mixture of diethyl 4-bromobenzyl phosphonate (10 g, 33 mmol), diethylphosphite (6.3 ml, 49 mmol), and $Pd(PPh_3)_4$ (1.9 g, 1.7 mmol) in NEt_3 (15 ml) and toluene (250 ml) was refluxed for 2 days. Upon cooling to RT, the organic volatiles were removed under reduced pressure, and the residue was extracted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$. The crude product obtained upon removal of the organic solvent under reduced pressure was purified by column chromatography using CH_2Cl_2/acetone (1:1 (v/v)) to give a pure liquid of (*p*-diethylphosphono)benzyldiethylphosphonate. Yield: 6.4 g (54%). ^1H $\{^{31}P\}$ NMR ($CDCl_3$): δ 7.75 (d, $^3J_{H-H} = 8.1$ Hz, 2H, H_a), 7.4 (d, $^3J_{H-H} = 8.1$ Hz, 2H, H_b), 4.06 (m, 8H, $-OCH_2CH_3$), 3.18 (s, 2H, PCH_2), 1.31 (t, $^3J_{H-H} = 7.1$ Hz, 6H, $-OCH_2CH_3$), 1.24 (t, $^3J_{H-H} = 6.9$ Hz, 6 H, $-OCH_2CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.2 (d, $^1J_{c-p} = 2$ Hz) & 19.6 (d, $^2J_{c-p} = 3$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.2 (m), 131.4 (m), 129.3 (m), 126.4 (d, $^1J_{c-p} = 190$ Hz), 61.6 (m, OCH_2CH_3), 33.4 (d, $^2J_{c-p} = 137$ Hz, $-CH_2$), 15.8 (m, OCH_2CH_3). The spectroscopic data for the product from this improved procedure are identical to those reported in the literature [13,14].

2.10. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylstyrylphosphonate)

To a mixture of 2,2′-diacetyl-1,1′-binaphthalene-6,6′-dialdehyde (3.0 g, 7.0 mmol), (*p*-diethylphosphono)benzyldiethylphosphonate (5.1 g, 14 mmol) in 200 ml of anhydrous THF at 3 °C was added 35 ml of 0.9 M KO^{t}Bu (32 mmol) in THF. The mixture was allowed to warm to RT and stirred for 45 min, and then quenched with water. The solvents were removed under reduced pressure, and the residue was extracted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$. The volatiles were removed under reduced pressure to afford a crude product of 2,2′-diacetyl-1,1′-binaphthyl-6,6′-bis(diethylstyrylphosphonate).

A mixture of the crude product from above (6.2 g, 7.3 mmol) and KOH (1.3 g, 23 mmol) of MeOH (150 ml), THF (150 ml), and water (150 ml) was stirred at RT for 24 h. The solvents were removed under reduced pressure and the residue was extracted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$, and the organic volatiles were removed under reduced pressure. Column chromatography with silica gel using CH_2Cl_2/acetone (2:1 (v/v)) gave 45–50% yield of pure solid of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylstyrylphosphonate). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 7.97 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, H_3), 7.94 (s, 2H, H_5), 7.76 (d, $^3J_{H-H}$ = 8.0 Hz, 4H, H_a′), 7.57 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, H_b′), 7.54 (d, $^3J_{H-H}$ = 9.3 Hz, 2H, H_4), 7.43 (d, $^3J_{H-H}$ = 9.2 Hz, 2H, H_7), 7.33 (d, $^3J_{H-H}$ = 17 Hz, 2H, H_a), 7.17 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, H_8), 7.12 (d, $^3J_{H-H}$ = 17 Hz, 2H, H_b), 5.90 (s, 2H, OH), 4.10 (m, 8H, OCH_2CH_3), 1.32 (t, $^3J_{H-H}$ = 7.4 Hz & 6.7 Hz, 12 H, OCH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.4 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.5 (s), 141.5 (d, $^1J_{c-p}$ = 3 Hz), 133.9 (s), 132.1 (d, $^2J_{c-p}$ = 10 Hz), 131.6 (s), 131.3 (s), 130.7 (d, $^3J_{c-p}$ = 9 Hz), 130.3 (s), 129.0 (s), 128.5 (d, $^4J_{c-p}$ = 11 Hz), 127.5 (s), 126.3 (d, $^5J_{c-p}$ = 189 Hz), 126.5 (s), 126.1 (d, $^6J_{c-p}$ = 17 Hz), 125.2 (s), 124.1 (s), 118.7 (s), 113.4 (s), 62.1 (m, OCH_2CH_3), 16.1 (d, $^7J_{c-p}$ = 6.0 Hz, OCH_2CH_3).

2.11. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid)

A solution of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylstyrylphosphonate) (710 mg, 0.93 mmol) and $(CH_3)_3SiBr$ (0.74 ml, 5.6 mmol) in anhydrous CH_2Cl_2 (100 ml) was stirred at RT for 12 h. The organic volatiles were removed under reduced pressure and the residue was dissolved in 100 ml of MeOH and stirred at RT for an additional 0.5 h. The solvent was removed under reduced pressure and pure product of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid) was obtained in quantitative yield. $^1H\{^{31}P\}$ NMR (CD_3OD): δ 7.98 (d, $^4J_{H-H}$ = 1.4 Hz, 2H, H_5), 7.95 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_3), 7.80 (d, $^3J_{H-H}$ = 8.3 Hz, 4H, H_a′), 7.7 (d, $^3J_{H-H}$ = 8.3 Hz, 4H, H_b′), 7.59 (d, $^3J_{H-H}$ = 9.1 Hz & $^4J_{H-H}$ = 1.5 Hz, 2H, H_7), 7.48 (d, $^3J_{H-H}$ = 16 Hz, 2H, H_a), 7.34 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, H_4), 7.26 (d, $^3J_{H-H}$ = 16 Hz, 2H, H_b), 7.10 (d, $^3J_{H-H}$ = 8.9 Hz, 2H, H_8), 4.90 (m, 6H, OH). $^{31}P\{^1H\}$ NMR (CD_3OD): 17.1 (s). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 154.9 (s), 142.7 (d, $^1J_{c-p}$ = 4 Hz), 135.8 (s), 133.0 (s), 132.4 (d, $^2J_{c-p}$ = 11 Hz), 131.5 (d, $^3J_{c-p}$ = 186 Hz), 131.0 (s), 128.9 (s), 127.6 (s), 127.2 (d, $^4J_{c-p}$ = 18 Hz), 126.5 (s), 124.8 (s), 119.8 (s), 116.6 (s). HR–MS (FAB) *m/z* [*M* + H]$^+$ 651.1338 (Calcd *m/z* 651.1339). $[\alpha]_D^{20}$ = +247.2 (c 0.05 in MeOH) for *S*-enantiomer.

2.12. 2,2′-Diethoxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid)

To a mixture of 6,6′-dialdehyde-2,2′-diethoxy-1,1′-binaphthalene (3.0 g, 7.5 mmol), (4-diethylphosphonobenzyl) diethylphosphonate (6.0 g, 16.5 mmol) in 150 ml of anhydrous THF at 3 °C was added 23 ml of 0.97 M KO^{t}Bu (23 mmol) in THF. The mixture was allowed to warm up to room temperature and stirred for 1/2 h, and then quenched with water. The solvent was removed under reduced pressure, and the residue was extracted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product 2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(diethylstyrylphosphonate). Column chromatography with silica gel using CH_2Cl_2/acetone (4:1 (v/v)) gave 60% yield of pure solid of 2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis (diethylstyrylphosphonate). ^1H $\{^{31}P\}$ NMR ($CDCl_3$): δ 7.95 (d, $^3J_{H-H}$ = 9.2 Hz, 4H, H_a′, 7.91 (d, $^4J_{H-H}$ = 1.4 Hz, 2H, H_5), 7.79 (m), 7.60 (m), 7.47 (d, $^3J_{H-H}$ = 8.2 Hz & $^4J_{H-H}$ = 1.2 Hz, H_4), 7.43 (d, $^3J_{H-H}$ = 9.6 Hz, H_b′), 7.34 (d, $^3J_{H-H}$ = 16 Hz, H_a), 7.15 (s), 7.11 (d, $^3J_{H-H}$ = 16 Hz, H_b), 4.11 (m, -OCH_2CH_3), 1.33 (t, $^3J_{H-H}$ = 6.8 Hz & 7.6Hz, OCH_2CH_3), 1.08 (t, $^3J_{H-H}$ = 7.6 Hz & 6.4 Hz, OCH_2CH_3). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ 20.1 (s). HR–MS (MALDI) *m/z* [*M* + H]$^+$ 651.2 (Calcd *m/z* 651.1).

A solution of 2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(diethylstyrylphosphonate) (3.8 g, 4.7 mmol) and $(CH_3)_3SiBr$ (2.6 ml, 19 mmol) in anhydrous CH_2Cl_2 (100 ml) was stirred at RT for 12 h. The organic volatiles were removed under reduced pressure and the residue was dissolved in 100 ml of MeOH and stirred at RT for an additional 0.5 h. The solvent was removed under reduced pressure and pure product of 2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid) was obtained in quantitative yield. ^1H $\{^{31}P\}$ NMR (CD_3OD): δ 8.73 (m, 4H, H_3 & H_5), 8.61 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, H_a′), 8.41 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, H_b′), 8.26 (m, 4H), 8.18 (d, $^3J_{H-H}$ = 16 Hz, 2H, H_a), 7.93 (d, $^3J_{H-H}$ = 16.8 Hz, 4H, H_b), 7.86 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_8), 4.85 (m, 4H, OCH_2CH_3), 1.85 (t, $^3J_{H-H}$ = 6.4 Hz & 6.4 Hz, 6H, OCH_2CH_3). ^{31}P $\{^1H\}$ NMR (CD_3OD): δ 16.0 (s). ^{13}C $\{^1H\}$ NMR (CD_3OD): δ 156.2 (s), 142.5 (s),

135.3 (s), 133.5 (s), 132.4 (s), 132.3 (s), 132.1 (s), 130.8 (s), 127.9 (s), 127.3 (s), 127.2 (s), 126.8 (s), 124.6 (s), 121.6 (s), 116.9 (s), 66.0 (s), 15.4 (s). IR (KBr, cm^{-1}): (s, 3444.1), (m, 2975.4), (w, 2338.4), (s, 1597.6), (s, 1467.3), (w, 1385.1), (w, 1336.1), (s, 1233.5), (s, 1136.7), (s, 925.9), (m, 823.7), (m, 684.1), (s, 535.4), (w, 450.6). MS (MALDI) *m*/*z* $[M + H]^+$ 706.6 (Calcd *m*/*z* 706.7).

2.13. A typical procedure for the synthesis of zirconium(IV) phosphonates

To a solution of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis-(phosphonic acid) (1.95 g, 4.4 mmol) in 15 ml of *n*-BuOH was added a solution of $Zr(O^nBu)_4$ (1.93 g, 4.4 mmol) in 100 ml of *n*-BuOH at RT. The reaction mixture was heated to reflux overnight. The reaction mixture was cooled to room temperature, centrifuged, and washed with methanol three times to afford a white solid of zirconium(IV) phosphonate. The yields range from 90–95%.

2.14. Zirconium(IV) 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(phosphonate)

Zr-L_1. Anal. Calcd for $C_{20}H_{20}O_{12}P_2Zr$, Zr-L_1·$4H_2O$: C, 39.7; H, 3.33. Found: C, 39.2; H, 3.34. IR (KBr, cm^{-1}): (s, 3365.6, OH), (s, 2978.6), (s, 2931.2), (w, 2361.5), (s, 1653.3) (s, 1617.3), (s, 1559.8), (w, 1495.6), (s, 1390.6), (s, 1323.7), (w, 1261.5), (s, 1228.9), (s, 1110.9), (s, 1089.7), (s, 1057.9), (s, 1042.2), (m, 894.3), (m, 797.7), (m, 761.6), (s, 699.3), (w, 668.5), (w, 629.6), (w, 516.7), (w, 423.4).

2.15. Zirconium(IV) 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(vinylphosphonate)

Zr-L_2. Anal. Calcd for $C_{24}H_{26}O_{13}P_2Zr$, Zr-L_2·$5H_2O$: C, 42.7; H, 3.88. Found: C, 41.2; H, 3.52. IR (KBr, cm^{-1}): (s, 3400.0, OH), (w, 2959.9), (s, 1608.4), (m, 1515.8), (m, 1477.7), (m 1346.9), (s, 1149.2), (s, 1050), (m, 829.5), (m, 508.9).

2.16. Zirconium(IV) 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonate) Zr-L_3

Anal. Calcd for $C_{36}H_{32}O_{12}P_2Zr$, Zr-L_3·$4H_2O$: C, 53.4; H, 3.98. Found: C, 52.1; H, 3.80. IR (KBr, cm^{-1}): (s, 3359.9, OH), (s, 1597.8), (w, 1506.8), (m, 1473.8), (m, 1347.8), (w, 1279.0), (s, 1138.6), (s, 1030.6), (s, 1006.6), (w, 864.5), (m, 825.1), (m, 683.4), (w, 652.4), (m, 557.3).

2.17. Zirconium(IV) 2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonate) Zr-L_3-Et_2

IR (KBr): (s, 2974.2, OH), (w, 1654.1), (s, 1597.2), (s, 1467.1), (w, 1400.3), (m, 1339.4), (s, 1233.8), (s, 1138.5), (s, 1035.3), (s, 1006.5), (w, 864.7), (m, 824.2), (m, 691.2), (w. 624.8), (m, 555.8).

2.18. A typical procedure for the catalytic reactions

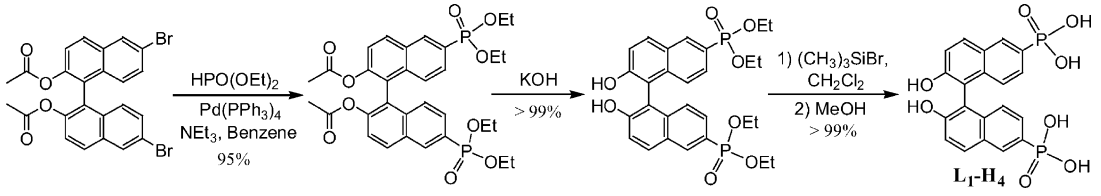
(18.5 mg, 0.025 mmol) of the zirconium(IV) phosphonate was vacuum dried at 80 °C. After 24 h, the solid was allowed to cool down to RT and (0.518 ml, 0.18 mmol) of $Ti(O^iPr)_4$ and 1 ml of toluene was added. The reaction mixture was allowed to stir at for an additional 1 h at RT (0.068 ml, 0.5 mmol) and then 1-naphthaldehyde (6.3 microlitre, 0.046 mmol) and (0.2 ml, 0.22 mmol) of 1.1 M $ZnEt_2$ in toluene were added. The reaction mixture was allowed to stir at RT for 24 h. The crude product was purified by prep-scale silica gel chromatography using diethyl ether as the eluent, and then analyzed by chiral gas chromatography.

3. Results and discussion

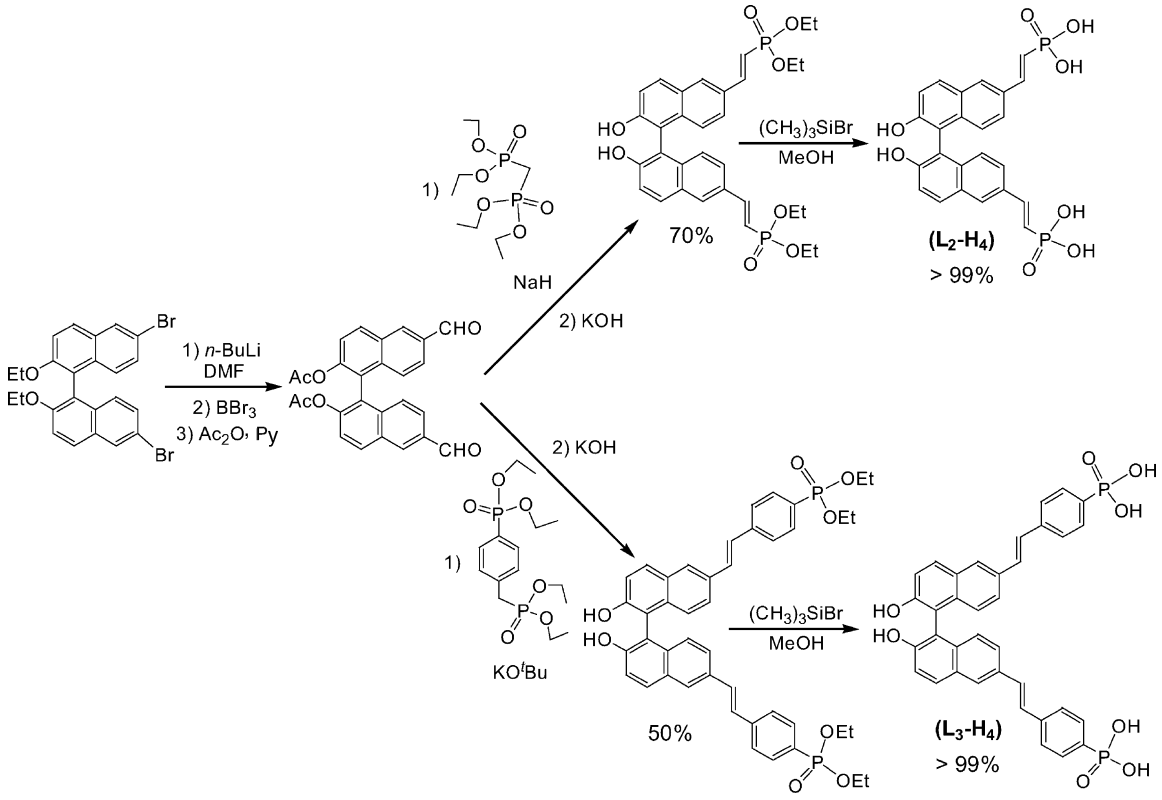
3.1. Synthesis of BINOL-derived bisphosphonic acids

2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(phosphonic acid), L_1-H_4, was synthesized according to Scheme 1. Palladium-catalyzed phosphonation of 6,6′-dibromo-2,2′-diacetyl-1,1′-binaphthalene gave 2,2′-diacetyl-1,1′-binaphthyl-6,6′-bis(diethylphosphonate), which was directly deprotected with KOH to afford 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylphosphonate) in ∼95% overall yield. Treatment of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(diethylphosphonate) with $(CH_3)_3SiBr$ followed by MeOH afforded the desired product L_1-H_4 in quantitative yield. This sequence afforded L_1-H_4 in a much higher yield than the literature procedure [12].

2,2′-Diethoxy-1,1′-binaphthalene-6,6′-dialdehyde was obtained by treating 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene with *n*-BuLi at −78 °C in THF, and followed by the addition of dimethylformamide (DMF) and quenching of the mixture with water (Scheme 2). The ethoxy groups were



Scheme 1.



Scheme 2.

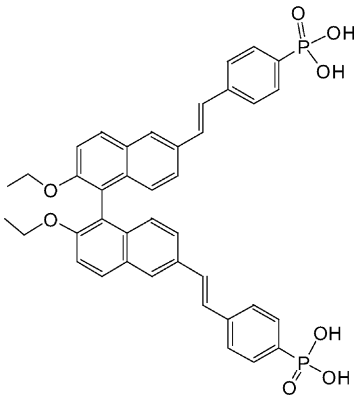
deprotected with BBr_3 in CH_2Cl_2 [15] and then reacted with acetic anhydride to give 2,2′-diacetyl-1,1′-binaphthalene-6,6′-dialdehyde. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis-(vinyldiethylphosphonate) was synthesized in 70% yield by a Wittig–Horner coupling between 2,2′-diacetyl-1,1′-binaphthalene-6,6′-dialdehyde and tetraethylmethylenediphosphonate in the presence of NaH, followed by treatment with KOH to remove the acetyl protecting groups.

Treatment of 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(vinyldiethylphosphonate) with Me_3SiBr followed by MeOH led to 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis(vinylphosphonic acid), L_2-H_4, in quantitative yield. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(styryldiethylphosphonate) was similarly obtained by a Wittig–Horner reaction between 2,2′-diacetyl-1,1′-binaphthalene-6,6′-dialdehyde and (4-diethylphosphonobenzyl)-diethylphosphonate in the presence of KO^tBu in THF, followed by treatment with KOH to remove the acetyl protecting groups. 2,2′-Dihydroxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid), L_3-H_4, was obtained quantitatively by treating 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-bis-(styryldiethylphosphonate) with Me_3SiBr and then MeOH. All the intermediates and phosphonic acid products were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. L_2-H_4 and L_3-H_4 were also characterized by HR-MS.

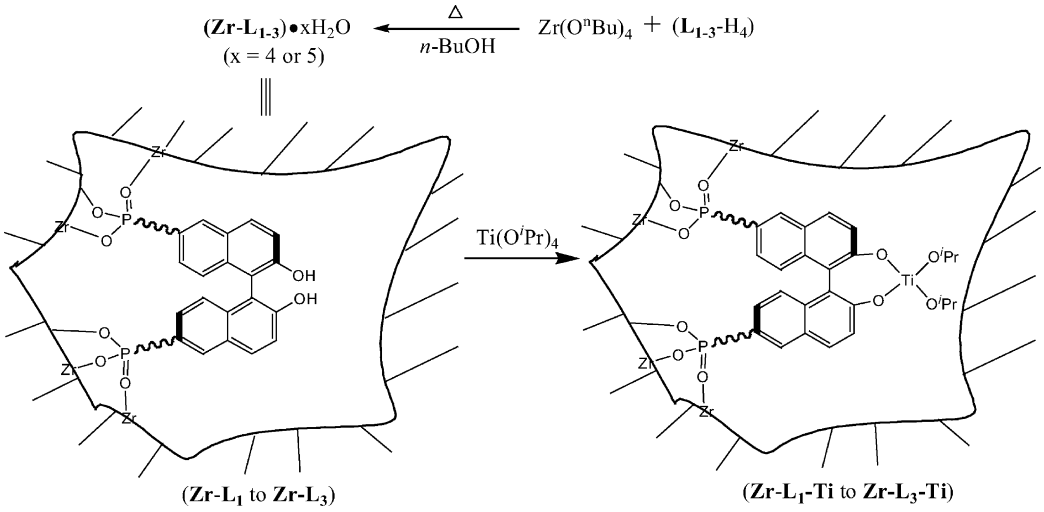
2,2′-Diethoxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid), L_3-Et_2-H_4, was similarly prepared via a Wittig-Horner coupling between 6,6′-dialdehyde-2,2′-diethoxy-1,1′-binaphthalene and diethylphosphonobenzyl)diethylphosphonate, followed by deprotection of the phosphonate esters with Me_3SiBr (Scheme 3). L_3-Et_2-H_4 was characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies.

3.2. Synthesis and characterization of chiral porous zirconium bis(phosphonates)

Chiral porous zirconium bis(phosphonates), Zr-L_1 to Zr-L_3, were obtained by refluxing BINOL-derived bis(phosphonic acids) with $Zr(O^nBu)_4$ in *n*-BuOH (Scheme 4). In a typical synthesis, a mixture of bis(phosphonic acid)



Scheme 3.



Scheme 4.

and $Zr(O^nBu)_4$ in *n*-BuOH in a 1:1 molar ratio was refluxed overnight. The resulting colorless suspension was centrifuged and the clear solution was siphoned away. The resulting solid was washed with three fractions of MeOH and centrifuged. Regardless the bis(phosphonic acid) used, amorphous solids based on zirconium-bis(phosphonates) were obtained in higher than 95% yield. These solids have been characterized by powder X-ray diffraction, solid-state CP-MAS ^{31}P NMR, IR, TGA, BET, and circular dichroism spectroscopy.

Powder X-ray diffraction studies indicated that these solids based on zirconium bis(phosphonates) are amorphous. CP-MAS ^{31}P NMR spectra show one broad peak between 0–20 ppm (which can be deconvoluted to two peaks at ~9 ppm and ~17 ppm with a half-width of 7 ppm). The breadth of these peaks is consistent with the presence of many possible microenvironments of the zirconium bis(phosphonate) moieties. TGA results show the loss of 4–5 water molecules upon heating the Zr-L_1 to Zr-L_3 solid to 200 °C in air (Fig. 1). The frameworks of these solids are stable up to 300 °C. IR spectra of these solids exhibit strong peaks at 915–1050 cm^{-1} owing to the P–O stretches, which have shifted to lower wave numbers after the formation of Zr phosphonates. The very broad peaks at ~3000 cm^{-1} correspond to OH stretches. SEM results show that these materials are featureless and are submicron in size (Fig. 2). Adsorption isotherms of these solids performed using nitrogen gas as the adsorbate at liquid nitrogen temperature have been very informative (Fig. 3). Detailed BET analyses show that these materials are highly porous with total surface areas ranging from 431 to 586 m^2/g and pore volumes ranging from 0.63 to 1.23 cm^3/g (by BJH method). They contain both micropores and mesopores (Table 1). CD spectra of the zirconium bis(phosphonates) made from opposite enantiomers of the bisphosphonic acids exhibit opposite cotton effects, and thus indicate the enantiomeric nature of these solids (Fig. 4).

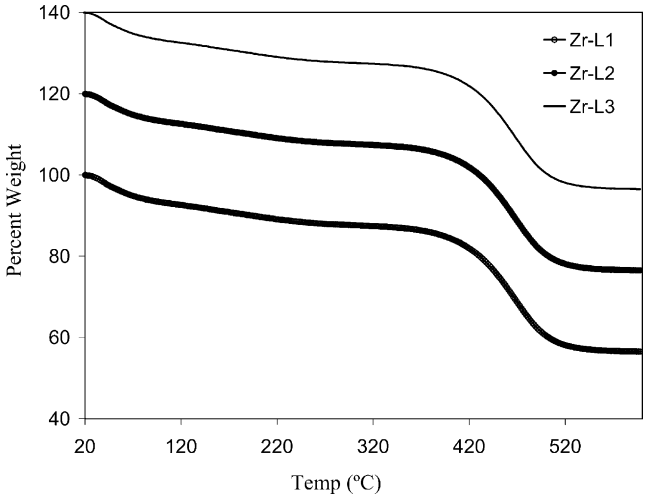


Fig. 1. TGA curves for Zr-L_1 to Zr-L_3. For clarity, the pink and green curves have been shifted up by 20 and 40%, respectively.

3.3. Heterogeneous catalysis for addition of diethylzinc to benzaldehyde with enantioselectivity

With high surface areas and accessible chiral dihydroxy groups, we have tested chiral porous zirconium bis(phosphonates) Zr-L_1 to Zr-L_3 for applications in hetero-

Table 1
Surface areas and pore volumes

Solid	A_{total} (m^2/g)	$A_{micropore}$ (m^2/g)	Pore volume (cm^3/g)
Zr-L_1	431	134	0.63
Zr-L_2	438	94	0.92
Zr-L_3	586	239	1.23
Zr-L_3-Et_2	467	165	1.12

Surface areas were determined using multi point BET method, while pore volumes were determined based on BJH method.

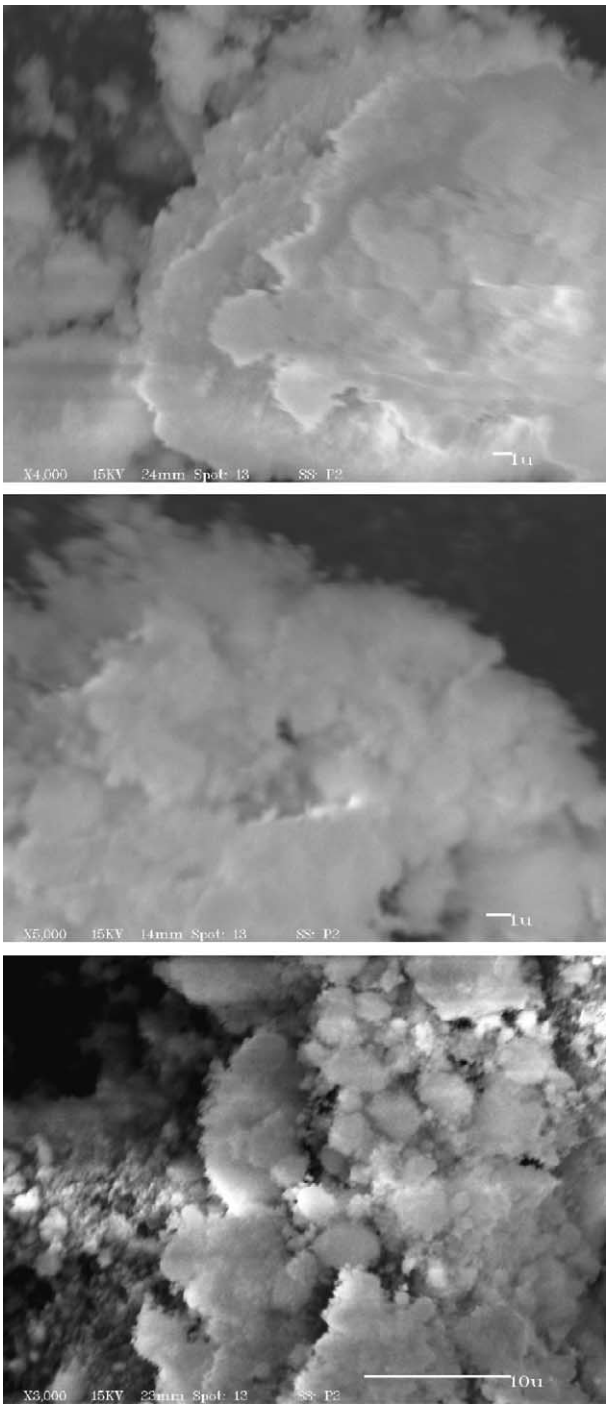
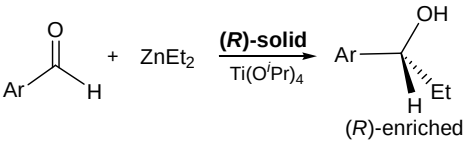


Fig. 2. SEM micrographs of Zr-L_1, Zr-L_2, and Zr-L_3 (from top to bottom).

geneous asymmetric catalysis. After drying at 80 °C under vacuum, Zr-L_1 to Zr-L_3 was treated with excess Ti(O^iPr)$_4$ to generate active catalysts for the additions of diethylzinc to aromatic aldehydes to afford chiral secondary alcohols. While the Zr-L_1-Ti(IV) combination catalyzed the addition of $ZnEt_2$ to 1-naphthaldehyde in toluene in >95% yield and 59% e.e., the same reaction in dichloromethane only gave α-(1-naphthyl)propanol in 80% yield and 55% e.e. (Table 2). All the subsequent reactions were thus carried

Table 2
Diethylzinc additions to aromatic aldehydes



(*R*)-enriched

Solid	Ar	Time (h)	Conversion (%)	e.e. (%)
Zr-L_1	1-Naphthyl	17	80[a]	55
Zr-L_1	1-Naphthyl	20	>95	59
Zr-L_1	1-Naphthyl	15	>95	59
Zr-L_2	1-Naphthyl	15	70	61
Zr-L_3	1-Naphthyl	15	>95	72
Zr-L_3	Ph	16	>95	59
Zr-L_3	4′-Cl-Ph	20	95[b]	43[b]
Zr-L_3	4′-Me-Ph	20	92[b]	45[b]
Zr-L_3	4′-F-Ph	20	96[b]	48[b]
Zr-L_3	4′-CF_3-Ph	20	>99[b]	29[b]
Zr-L_3	3′-Br-Ph	20	>99[b]	46[b]
Zr-L_3-OEt	1-Naphthyl	20	68[b]	0[b]

The e.e. values were determined by GC on a Supelco γ-Dex 120 column, while the conversions were determined by the integrations of ^{1}HNMR spectra and GC traces. All the reactions were carried out with 20 mol% solid loading in toluene at RT.

[a] The reaction is carried in DCM.

[b] The reactions were carried out with 50 mol% solid loading at RT.

out in toluene. The heterogeneous nature of the present systems was supported by the fact that the supernatant from the above was not capable of activating Ti(O^iPr)$_4$ for catalyzing $ZnEt_2$ additions.

A comparison among the solid catalysts showed that the highest e.e. value was obtained for the $ZnEt_2$ addition to 1-naphthaldehyde catalyzed by the Zr-L_3-Ti(IV) combination, presumably a result of its higher surface areas and larger pores. We have thus focused mostly on the Zr-L_3-Ti(IV) catalyst system. As shown in Table 2, the Zr-L_3-Ti(IV) system catalyzed the addition of $ZnEt_2$ to a wide range of aromatic aldehydes with high conversions in e.e. values up to 72% (with the same stereochemistry as that obtained by the parent homogeneous Ti-BINOL catalytic system). ^{1}H NMR and GC studies show that reduced primary alcohols are the major byproducts in these heterogeneously catalyzed diethylzinc addition reactions. This level of enantioselectivity exceeds that of other heterogeneous asymmetric catalysts made by immobilization of homogeneous catalysts on mesoporous inorganic supports [16], but is still inferior to those of homogeneous Ti-BINOL catalytic systems [17,18].

In an effort to understand the different performance of our solid catalysts vs. those of homogeneous systems, we have carried out control experiments using the solid derived from 2,2′-ethoxy-1,1′-binaphthyl-6,6′-bis(styrylphosphonic acid), L_3-Et_2-H_4. Interestingly, although there are not chiral dihydroxy groups in the Zr-L_3-Et_2 solid, its combination with Ti(O^iPr)$_4$ is active catalyst for the addition of $ZnEt_2$ to 1-naphthaldehyde to result in racemic α-(1-naphthyl)pro-

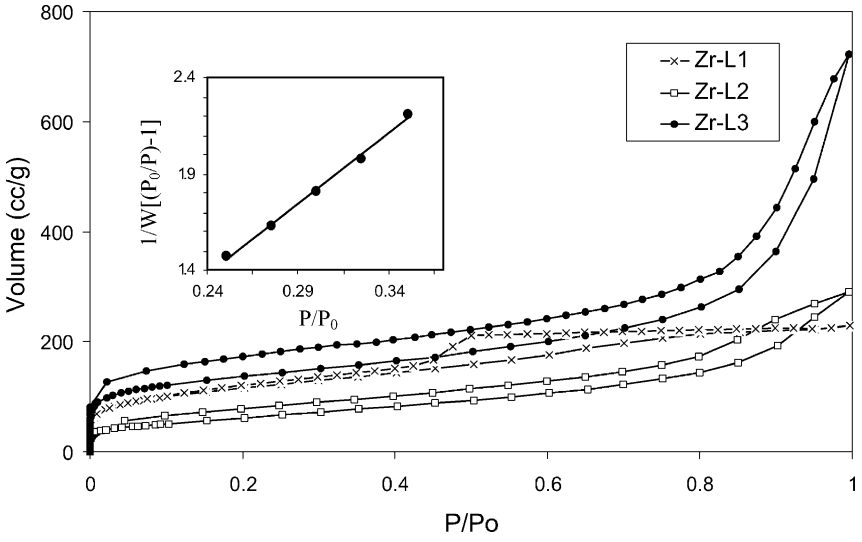
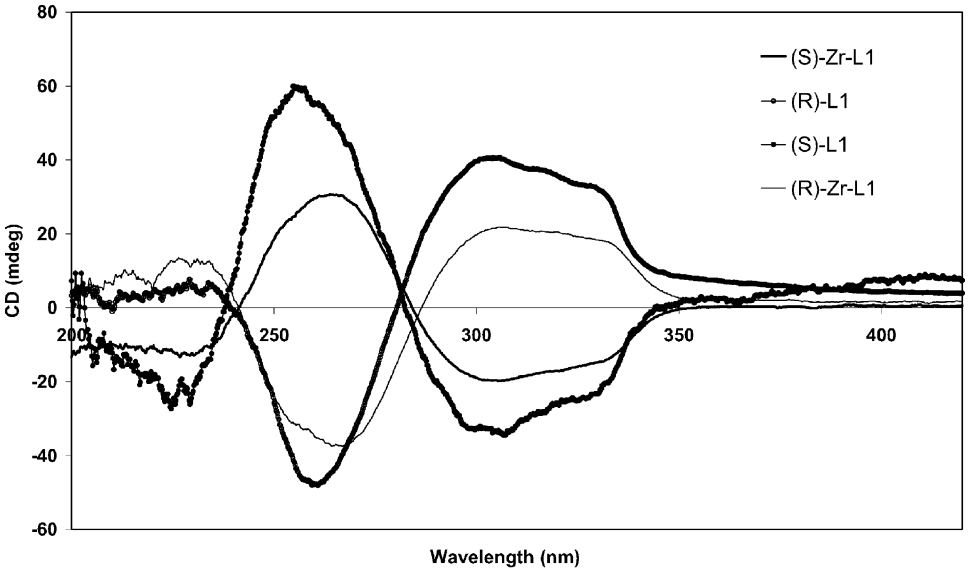


Fig. 3. Adsorption isotherms for Zr-L_1 to Zr-L_3. The inset shows the BET curve for Zr-L_3.



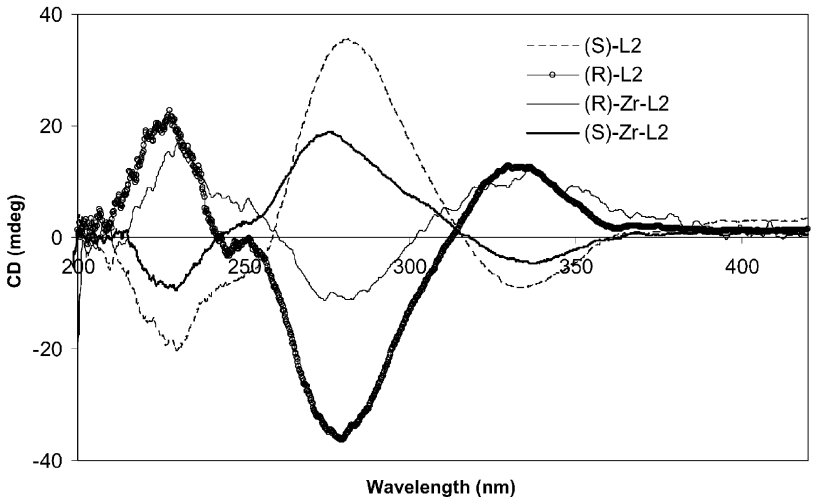


Fig. 4. Solid-state CD spectra of BINOL-derived phosphonic acids and their Zr(IV) phosphonate solids.

panol (Table 2). We believe that there are residual phosphonic acid protons in the Zr-L_3-Et_2 solid which can activate $Ti(O^iPr)_4$ for non-enantioselective $ZnEt_2$ addition. This type of background reaction explains lower e.e. values observed for our solid catalysts than those of homogeneous Ti-BINOL catalytic systems. Future work is directed at selective scavenging of the residual phosphonic acid protons in order to enhance the enantioselectivity of these solid catalysts.

4. Conclusions

We have synthesized chiral porous solids based on BINOL-derived Zr phosphonates via a molecular building block approach. Coordination of Ti(IV) centers to these dihydroxy functionalities leads to active heterogeneous catalysts for asymmetric additions of diethylzinc to aromatic aldehydes with high conversions and e.e. values of up to 72%.

Acknowledgements

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