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Highly Porous Cross-Linked Polymers for Catalytic Asymmetric Diethylzinc Addition to Aldehydes

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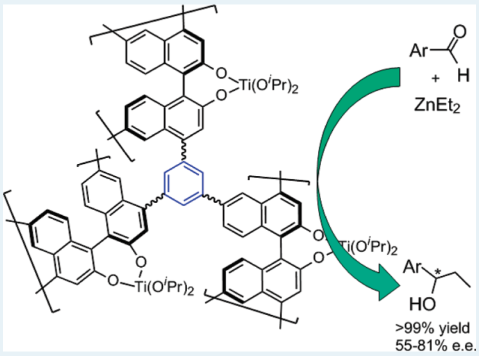
ABSTRACT: A series of five chiral cross-linked polymers (CCPs) based on the 1,1′-binaphthyl building blocks have been synthesized via the trimerization reaction of terminal alkyne groups, catalyzed by octacarbonyldicobalt complex ($Co_2(CO)_8$). The CCPs were highly porous, with surface areas of 689 to 974 m^2/g and pore volumes of 0.87 to 1.23 cm^3/g. The CCPs were insoluble in all solvents tested, including concentrated hydrochloric acid. The CCPs containing chiral dihydroxy functionalities were treated with Ti(O^{i}Pr)$_4$ to generate chiral Lewis acid catalysts for the asymmetric diethylzinc addition to aldehydes. The enantioselectivity of these reactions is modest to good (55 to 81 e.e.%), but the CCPs could be readily recycled and reused for the asymmetric diethylzinc addition reactions for up to 10 times without loss of conversion or enantioselectivity.



KEYWORDS: porous materials, crosslinked polymers, heterogeneous catalysis, asymmetric catalysis, chirality

INTRODUCTION

The field of porous materials has undergone revolutionary growth in the past decade.[1] For example, numerous metal–organic frameworks (MOFs) with unprecedentedly high porosity have been designed[2] and evaluated for a host of applications including gas separation and storage,[3–6] catalysis,[7–11] molecular sensing,[12–15] and biomedical applications.[16–18] Inspired by the advances in MOF design, framework materials with more robust linkages such as covalent-organic frameworks (COFs)[19,20] and porous cross-linked polymers (PCPs)[1,21–25] have recently emerged. In particular, PCPs can be built from well-designed organic precursors via strong covalent bonds and represent a new class of robust, nanoporous materials showing great promise in light harvesting, gas storage, and separation.[26–29]

Although homogeneous asymmetric catalysis has witnessed tremendous growth over the past three decades, a relatively small percentage of homogeneous asymmetric catalytic reactions have been scaled up to industrial processes, primarily owing to the high costs of the chiral ligands and precious metals typically used in these reactions.[30,31] Heterogenization of these homogeneous asymmetric catalysts presents an interesting solution to both recycling and reusing expensive chiral ligands/catalysts.[32–35] To this end, a number of strategies have been developed to heterogenize homogeneous asymmetric catalysts, including attachment to porous inorganic oxide[36–39] and insoluble organic polymer supports,[40,41] incorporation into soluble organic macromolecules and membranes,[42,43] immobilization via biphasic systems,[44–46] and incorporation into chiral MOFs or coordination polymers.[47–49] As a result of their high porosity, PCPs present an excellent platform for engineering recyclable and reusable heterogeneous catalysts by incorporating catalytically relevant moieties into the frameworks. The catalytic performance of such PCPs can be rationally tuned by adjusting the monomeric units.[50–55] PCPs are potentially advantageous over MOFs as heterogeneous catalysts because of their enhanced stability, which greatly facilitates the recovery and reuse of PCP catalysts.

In this work, we report the successful incorporation of chiral dihydroxy functional monomers into robust PCPs by $Co_2(CO)_8$-mediated alkyne trimerization reactions.[56,57] The resulting PCPs were postsynthetically modified with Ti(O^{i}Pr)$_4$ to provide active catalysts for asymmetric addition of diethylzinc to aldehydes to produce chiral secondary alcohols upon hydrolytic workup. The PCP materials are highly recyclable and reusable materials for catalyzing the diethylzinc addition reactions.

RESULTS AND DISCUSSION

$Co_2(CO)_8$-mediated alkyne trimerization reactions have recently been used to form highly porous PCPs for gas storage[56] and efficient photocatalysis.[57] We reasoned that tetraalkynyl derivatives of the chiral 1,1′-binaphthyl system can provide an ideal monomer for homopolymerization to afford highly cross-linked chiral polymers that can find applications in asymmetric catalysis. Three new tetraalkynyl derivatives of the chiral 1,1′-binaphthyl system were synthesized in this work.

Tetraalkynyl monomers (*R*)-2,2′-diethoxy-4,4′,6,6′-tetraethynyl-1,1′-binaphthylene (**1**) and (*R*)-4,4′,6,6′-tetraethynyl-1,1′-binaphthyl-2,2′-diol (**2**) were synthesized by Pd-catalyzed Sonagashira coupling reactions between the corresponding tetrabromo starting materials and trimethylsilylacetylene followed by base-assisted deprotection of the trimethylsilyl groups (Scheme 1).

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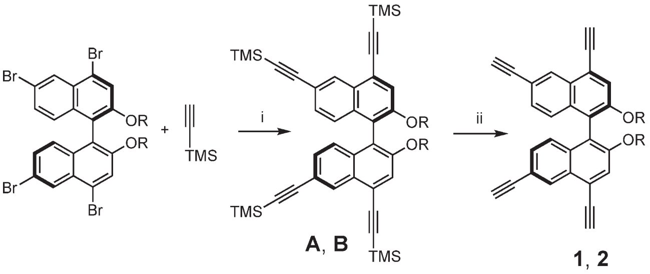
1 was obtained in 72% overall yield whereas **2** was obtained in 37% overall yield. All of the new tetraethynyl products were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry.

The longer tetraalkynyl monomer (*R*)-2,2′-diethoxy-4,4′,6,6′-tetrakis((4-ethynylphenyl)ethynyl)-1,1′-binaphthyl (**3**) was synthesized by a Pd-catalyzed Sonagashira coupling reactions between **1** and 4-(4-iodophenyl)-2-methylbut-3-yn-2-ol followed by base-assisted deprotection of the acetone moieties in a 54% overall yield (Scheme 2). The intermediate **C** and the tetraethynyl product **3** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry.

Trimerization reactions of **1**−**3** were carried out by heating a solution of the tetraethynyl monomer and $Co_2(CO)_8$ in anhydrous dioxane at 115 °C for 30 min (Scheme 3). The resulting black precipitate was filtered and washed several times with tetrahydrofuran (THF), H_2O, EtOH, and pentane, and then stirred vigorously in conc. HCl for 2 h. Chiral cross-linked polymers (CCP **1**−**3**) were obtained as yellow powder in quantitative yields after additional washing with H_2O, THF, and pentane, and drying under vacuum. The use of tetra-alkynyl monomers **1**−**3** led to high connectivity in the resulting polymers CCP **1**−**3**.

Scheme 1. Synthesis of Chiral Tetraethynyl Monomers 1 and 2^a



(R=Et for **A** and **1**; R=H for **B** and **2**)

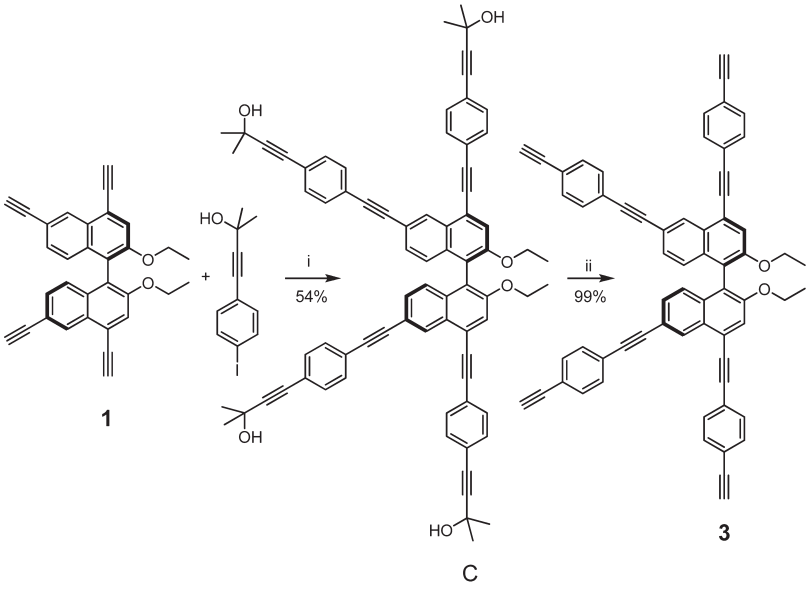
^{a} Synthetic conditions: (i) $Pd(PPh_3)_4$ (19 mol %), CuI (50 mol %), THF/Et_3N, Argon, 80 °C, 1 d; (ii) K_2CO_3 (7 equiv), MeOH, THF, rt, 1 h.

CCP-**1** was characterized by scanning electron microscopy (SEM), nitrogen adsorption, and infrared spectroscopy (IR). SEM images showed that the CCPs appear as aggregates of several micrometers (μm) in size that are composed of smaller particles with diameters range from 10 to 30 nm (Figure 1). These materials are insoluble in all of the solvents tested, presumably owing to the high connectivity of the cross-linked polymers. Nitrogen adsorption measurements indicated that CCPs are highly porous with Brunauer−Emmett−Teller (BET) surface areas of 689 to 974 m^2/g (Figure 2 and Table 1). As expected, the elongated monomer **3** led to the more porous CCP-**3**. Pore size distributions shown in Figure 2 suggest that the majority of the porosity is in the micropore regime. A small percentage of the porosity is in the mesopore regime (<40 Å), likely coming from the interparticle spacing in the CCPs. The IR spectra of CCPs **1**−**3** are consistent with a high degree of trimerization of the terminal alkynes as the carbon−hydrogen stretching peak of the C≡C−H group around 3300 cm^{-1} is absent in the IR spectra. This result suggests that most of the alkyne groups in the starting materials have been consumed to form benzene rings in the CCPs (Figure 3).

CCP-**2** contains extremely high densities of chiral dihydroxyl groups (∼2.62 mmol/g) as it is a simple homopolymer of **2**. This chiral dihydroxy group density is slightly higher than those of previously reported polymeric BINOL systems.[40] The ethoxy groups of CCPs **1** and **3** were deprotected by treatment with BBr_3 in CH_2Cl_2 to afford CCP-**1d** and CCP-**3d** that contain chiral dihydroxy groups. CCPs **1d**, **2**, and **3d** were used as heterogenized BINOL ligands for the formation of chiral Lewis acid catalysts by treating with excess $Ti(O^iPr)_4$ (Scheme 4).

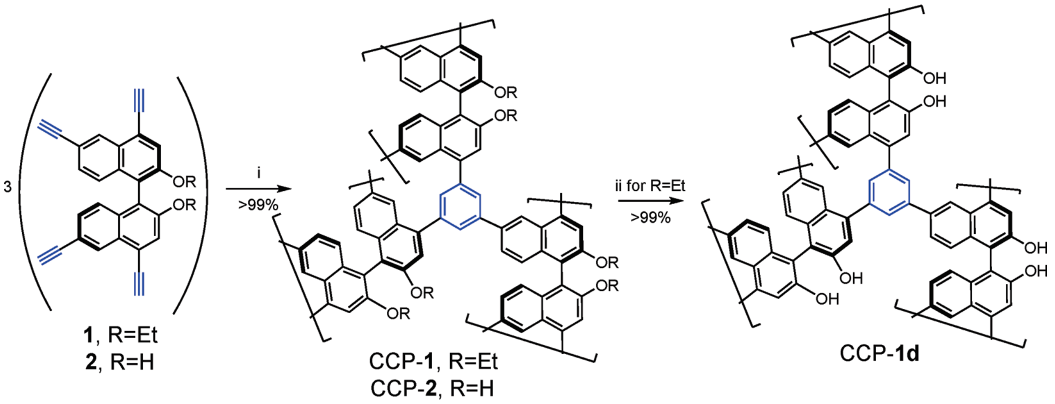
As shown in Table 2, $Ti(O^iPr)_4$-treated CCP-**1d**, CCP-**2**, and CCP-**3d** are highly active in the addition of diethylzinc to aromatic aldehydes to afford secondary alcohols. The CCP/Ti catalyzed reactions gave quantitative conversions and exclusive selectivity for secondary alcohols. The enantiomeric excesses (e.e.'s) of the CCP/Ti catalysts ranged from 55% to 81%, depending on the aromatic substrates. The CCP-**2**/Ti system

Scheme 2. Synthesis of Chiral Tetraethynyl Monomer 3^a



^{a} Synthetic conditions: (i) $Pd(PPh_3)_4$ (24 mol %), CuI (80 mol %), THF/Et_3N, Argon, 80 °C, 1 d; (ii) KOH (32 equiv), toluene, reflux, 16 h.

Scheme 3. Synthesis of CCPs 1 and 2 by Co-Mediated Trimerization of Tetraethynyl Monomers 1 and 2[a]



[a] CCP-**1** was further deprotected to form chiral-dihydroxyl-containing CCP-**1d**. Synthetic conditions: (i) $Co_2(CO_8)$ (1.5 equiv), dioxane, Argon, 115 °C, 30 min; (ii) BBr_3 (excess), CH_2Cl_2, Argon, rt, 4 days.

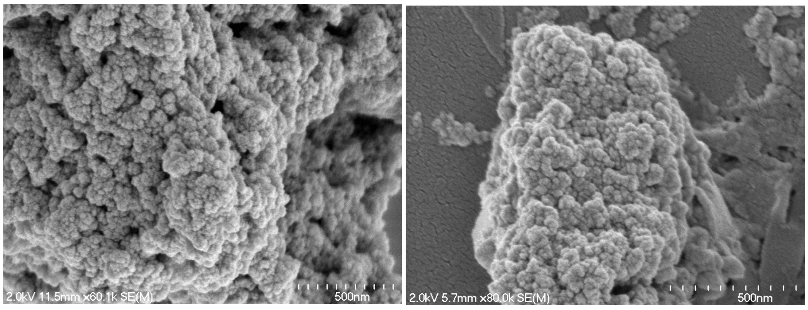


Figure 1. SEM images of CCP-**1** (left) and CCP-**2** (right).

gave higher e.e.'s than the CCP-**1d**/Ti and CCP-**3d**/Ti systems. For benzaldehyde, the CCP-**2**/Ti system gave an e.e. of 68% (Table 2, entry 3), which is comparable to a previously reported polymeric BINOL system,[40] but much lower than the homogeneous counterpart- and MOF-catalyzed diethylzinc additions (~93% e.e.).[9,11,59] We believe that the lower e.e.'s observed for the CCP/Ti catalysts could be in part because of the close proximity of the hydroxy moieties in such amorphous, cross-lined polymers, allowing the reaction of $Ti(O^iPr)_4$ with two different BINOL moieties to form intermolecular $[(O^iPr)_2Ti\text{-}(BINOLate)_2]$ complexes that were recently found to be responsible for low e.e.'s in a crystalline MOF.[58] The present CCP/Ti catalysts have higher secondary alcohols selectivities and e.e.'s than previously reported zirconium phosphonate-based Ti-BINOlate catalysts.[60]

We have examined recyclability and reusability of the CCP-**2** catalyst system. CCP-**2** was readily recovered from the reaction mixtures via centrifugation, followed by repeated washing with toluene. The recovered catalyst was able to perform diethylzinc addition to benzaldehyde with no loss of conversion or enantioselectivity after recycling 10 times (Table 3).

CONCLUSIONS

We have synthesized chiral cross-linked polymers based on the 1,1′-binaphthyl building blocks via efficient Co-mediated trimerization of terminal alkyne groups. The CCPs were highly porous and insoluble in all solvents tested. Treatment of chiral dihydroxyl-containing CCPs with $Ti(O^iPr)_4$ led to highly active Lewis acid catalysts for the asymmetric diethylzinc addition to aldehydes. The CCP/Ti catalysts gave secondary alcohols in quantitative yields with modest to good e.e.'s (55 to 81%), and could be readily recycled and reused for the asymmetric diethylzinc addition reactions for up to 10 times without loss of conversion or enantioselectivity.

EXPERIMENTAL SECTION

Materials and General Procedures. All of the chemicals were obtained from commercial sources and used without further purification unless otherwise noted. All of the reactions and manipulations were carried out under Argon with the use of standard inert atmosphere and Schlenk techniques or inside a nitrogen-filled drybox. Toluene was distilled with sodium/benzophenone. ^1H and $^{13}C\{^1H\}$ NMR spectra were collected on a Bruker 300 or 400 MHz NMR spectrometer. Mass Spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF mass spectrometer. Nitrogen adsorption experiments were performed with Autosorb-1C from Quantachrome, Inc. SEM was used to image the particles, using a Hitachi 4700 Field Emission Scanning Electron Microscope. A Cressington 108 Auto Sputter Coater equipped with a Au/Pd (80/20) target and an MTM-10 thickness monitor was used to coat the samples with a conductive layer before taking SEM images. Each SEM sample was prepared by first suspending the material in mesitylene, then a drop of the suspension was placed on a glass slide, and the solvent was allowed to evaporate. Chiral GC analyses of the secondary alcohols were carried out in the same manner as those reported earlier.[9]

*Synthesis of (R)-4,4′,6,6′-tetrakis((trimethylsilyl)ethynyl)-2,2′-diethoxy-1,1′-binaphthylene (**A**).* To a solution of (*R*)-4,4′,6,6′-tetrabromo-2,2′-diethoxy-1,1′-binapthalene (2.00 g, 3.04 mmol) in 20 mL of THF and

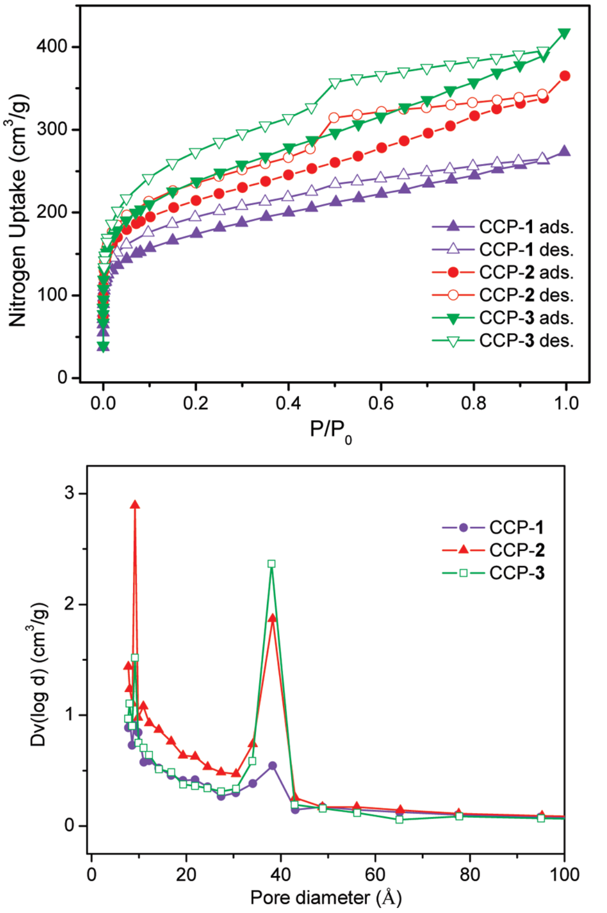


Figure 2. N_2 adsorption isotherms at 77 K (top) and Barret–Joyner–Halenda (BJH) pore size distribution (bottom) of CCPs **1**–**3**. The desorption data were used to calculate pore size distributions.

Table 1. Surface Areas and Pore Volumes of CCPs

catalyst	BET surface area (m^2/g)	pore volume (cm^3/g)
CCP-**1**	689	0.87
CCP-**2**	851	0.84
CCP-**3**	974	1.23

20 mL of Et_3N in a pressure reaction vessel, trimethylsilyl-acetylene (4.0 mL, 28 mmol) was added. The mixture was then degassed by Argon for 10 min, followed by the addition of $Pd(PPh_3)_4$ (0.60 g, 0.52 mmol) and CuI (0.20 g, 1.1 mmol). The resulting mixture was further degassed for 10 min, sealed and heated to 80 °C for one day, with stirring. After cooling to room temperature, the solvent was removed by rotary evaporator. The resulting solid was dissolved in ethyl acetate and washed several times with 1 M HCl, water, and brine. The organic layer was collected and dried with $MgSO_4$, and the solvent was removed by rotary evaporator. The crude product was purified by silica gel column chromatography with ethyl acetate/hexanes (1:9) as eluent. Pale orange solid was obtained (1.58 g, yield: 72%). ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.46 (d, $J = 2$ Hz, 2H), 7.59 (s, 2H), 7.24 (dd, $J = 2$ Hz, 9 Hz, 2H), 6.97 (d, 9 Hz, 2H), 4.02 (m, 4H), 1.03 (t, $J = 7$ Hz, 6H), 0.39 (s, 18H), 0.27 (s, 18H).

*Synthesis of (R)-2,2′-diethoxy-4,4′,6,6′-tetraethynyl-1,1′-binaphthylene (**1**).* To a solution of **A** (1.58 g, 2.17 mmol) in 60 mL of THF and 60 mL of MeOH, K_2CO_3 (2.0 g, 14.5 mmol) was added. After the reaction mixture was stirred at room temperature for 1 h, the remaining solid was removed by filtration, and the organic solvent was removed by rotary evaporator. The resulting solid was dissolved by ethyl acetate (200 mL) and washed several times by water and brine. The organic layer was collected and dried with $MgSO_4$, and the solvent was removed by rotary evaporator. Light orange solid (0.95 g, yield 99%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.56 (d, $J = 2$ Hz, 2H); 7.65 (s, 2H); 7.30 (dd, $J = 2$ Hz, 9.0 Hz, 2H); 7.05 (d, $J = 9$ Hz, 2H); 4.07 (q, $J = 7.2$ Hz, 4H); 3.59 (s, 2H); 3.14 (s, 2H); 1.08 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (75 Mz, $CDCl_3$), δ 154.5, 133.7, 130.9, 129.8, 129.1, 125.9, 121.4, 121.3, 120.6, 118.3, 84.3, 83.2, 81.5, 65.3, 15.0. MS (ESI/BioToF + CsAc): 438.18, calc. 438.16.

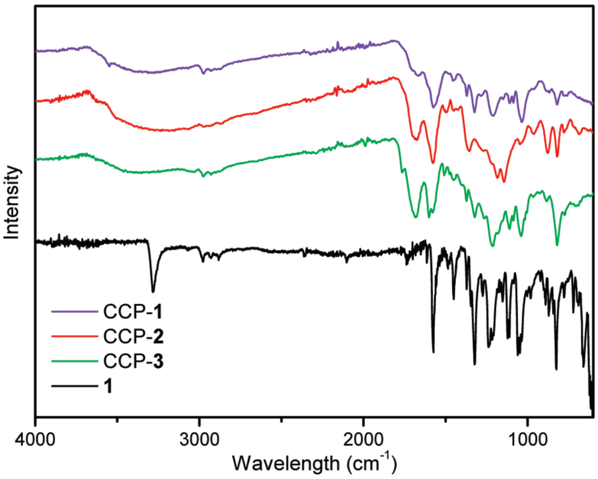


Figure 3. IR spectra of **1** and CCPs **1**–**3**. The characteristic carbon–hydrogen stretching peak of the C≡C–H group around 3300 cm^{-1} is absent in CCPs **1**–**3**, indicating a high degree of trimerization of the terminal alkynes in CCPs.

*Synthesis of (R)-4,4′,6,6′-tetrakis((trimethylsilyl)ethynyl)-1,1′-binaphthyl-2,2′-diol (**B**).* Compound (**B**) was synthesized in a similar way as compound (**A**). 4,4′,6,6′-tetrabromo-1,1′-binaphthyl-2,2′-diol (0.60 g, 1.0 mmol), trimethylsilyl -acetylene (3.0 mL, 21 mmol), Pd(PPh3)4 (0.22 g, 0.19 mmol), CuI (0.10 g, 0.5 mmol) and THF/Et_3N (15 mL/15 mL) were used. Pale yellow powder was obtained (0.25 g, yield: 37%) after silica gel column chromatography with ethyl acetate/hexanes (1:4) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.48 (s, 2H), 7.57 (s, 2H), 7.32 (d, $J = 9$ Hz, 2H), 6.99 (d, $J = 9$ Hz, 2H), 4.11 (q, $J = 7$ Hz, 4H), 1.26 (t, $J = 7$ Hz, 6H). ^{13}C NMR (100 Mz, $CDCl_3$), δ 152.6, 132.7, 131.1, 130.8, 129.1, 124.4, 122.6, 119.7, 112.0, 105.2, 102.2, 101.6, 95.2, 0.0.

*Synthesis of (R)-4,4′,6,6′-tetraethynyl-1,1′-binaphthyl-2,2′-diol (**2**).* **2** was synthesized in a similar way as **1**. Quantitative yield of light yellow solid product was obtained after the deprotection of TMS groups. ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.56 (d, $J = 2$ Hz, 2H), 7.61 (s, 2H), 7.38 (dd, $J = 7$ Hz, 2 Hz, 2H), 7.05 (d, $J = 7$ Hz, 2H), 5.44 (s, 2H), 3.61 (s, 2H), 3.16 (s, 2H). ^{13}C NMR (75 Mz, $CDCl_3$), δ 152.9, 133.1, 131.3, 131.2, 129.4, 124.8, 123.6, 123.5, 119.1, 112.5, 84.4, 83.8, 80.5, 78.3. MS (ESI/BioToF + CsAc): 382.12, calc. 438.10.

*Synthesis of (R)-4,4′,4″,4‴-(4,4′,4″,4‴-(2,2′-diethoxy-1,1′-binaphthyl-4,4′,6,6′-tetrayl)tetrakis(ethyne-2,1-diyl)tetrakis(benzene-4,1-diyl))tetrakis-(2-methylbut-3-yn-2-ol) (**C**).* To a solution of **1** (0.20 g, 0.46 mmol) in 15 mL of THF and 15 mL of Et_3N in a pressure reaction vessel, 4-(4-iodophenyl)-2-methylbut-3-yn-2-ol (4.0 mL, 28 mmol) was added. The mixture then was degassed with Argon for 10 min, followed by the addition of $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol) and CuI (0.070 g, 0.37 mmol). The resulting mixture was further degassed for 10 min, sealed and heated to 80 °C for one day, with stirring. After cooling to room temperature, the solvent was removed by rotary evaporator, and the resulting solid was dissolved in ethyl acetate and washed several times with 1 M HCl, water, and brine. The organic layer was collected and dried with $MgSO_4$, and the solvent was removed by rotary evaporator.

Scheme 4. Generation of Chiral Lewis Acid by Treating CCPs 1d, 2, and 3d with $Ti(O^iPr)_4$

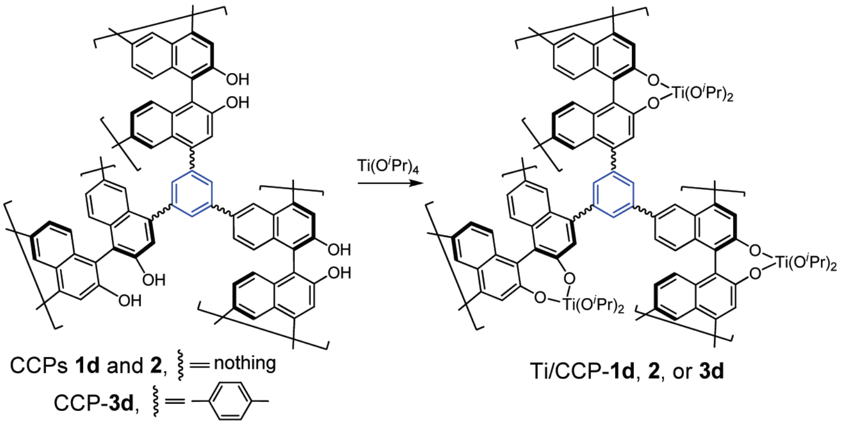
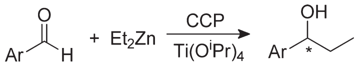


Table 2. Diethylzinc Additions to Aromatic Aldehydes Catalyzed by CCP-1d, CCP-2, and CCP-3d[a]



entry	CCP	Ar	conversion (%)	selectivity (%)	e.e. (%)
1	CCP-**1d**	Ph	99	>99	58
2[b]	CCP-**1d**	Ph	99	>99	60
3	CCP-**2**	Ph	94	>99	68
4	CCP-**2**	*p*-Cl-Ph	>99	>99	71
5	CCP-**2**	*p*-Br-Ph	>99	>99	71
6	CCP-**2**	1-Naph	>99	>99	81
7	CCP-**3d**	Ph	>99	>99	55
8	CCP-**3d**	*p*-Cl-Ph	>99	>99	59
9	CCP-**3d**	*p*-Br-Ph	>99	>99	60
10	CCP-**3d**	1-Naph	>99	>99	63

[a] All the reactions were carried out with vigorous stirring in toluene at r.t. for 16 h; catalyst loading is 13 mol % with excess $Ti(O^iPr)_4$ (1.3 equiv) and $ZnEt_2$ (3.0 equiv). [b] 2.6 equiv $Ti(O^iPr)_4$ was used.

The crude product was purified by silica gel column chromatography with ethyl acetate/CH_2Cl_2 (1:1) as eluent. Pale orange solid was obtained (0.27 g, yield: 54%). ^1H NMR (400 MHz, $CDCl_3$), δ 8.61 (s, 2H), 7.71 (s, 2H), 7.68 (d, *J* = 8 Hz, 4H), 7.53 (d, *J* = 8 Hz, 4H), 7.51 (d, *J* = 8 Hz, 4H), 7.42 (d, *J* = 8 Hz, 4H), 7.38 (d, *J* = 9 Hz, 2H), 7.15 (d, *J* = 9 Hz, 2H), 4.12 (m, 4H), 2.17 (br, 4H), 1.68 (s, 12H), 1.65 (s, 12H), 1.13 (t, *J* = 7 Hz, 6H). ^{13}C NMR (75 Mz, $CDCl_3$), δ 133.7, 132.0. 131.9. 131.8, 131.7, 130.1, 129.7, 129.0, 126.1, 123.5, 123.3, 123.1, 122.2, 121.4, 119.9, 119.1, 95.2, 95.9, 95.0, 92.1, 89.8, 89.2, 82.13, 82.07, 65.9, 65.3, 31.7, 15.1. MS (ESI/BioToF + CsAc): 1070.49, calc. 1070.45.

*Synthesis of (R)-2,2′-diethoxy-4,4′,6,6′-tetrakis((4-ethynylphenyl)ethynyl)-1,1′-binaphthyl (**3**).* To a solution of **C** (0.120 g, 0.112 mmol) in toluene (80 mL), ground KOH (0.20 g, 3.6 mmol) was added. The mixture was stirred and heated to reflux for 16 h. After cooling down to room temperature, the organic layer was washed with 1 M HCl, H_2O, and brine. The organic layer was collected and dried with $MgSO_4$, and the solvent was removed by rotary evaporator. Light yellow powder (0.094 mg, 99%) was obtained. ^1H NMR (400 MHz, $CDCl_3$), δ 8.60 (d, *J* = 1.2 Hz, 2H), 7.73 (s, 2H), 7.70 (d, *J* = 8 Hz, 4H), 7.59 (d, *J* = 8 Hz, 4H), 7.55 (d, *J* = 8 Hz, 4H), 7.50 (d, *J* = 8 Hz, 4H), 7.38 (dd, *J* = 1.2 Hz, 9 Hz, 2H), 7.16 (d, *J* = 9 Hz, 2H), 4.14 (m, 4H), 3.25 (s, 2H), 3.20 (s, 2H), 1.13 (t, *J* = 7 Hz, 6H). ^{13}C NMR (75 Mz, $CDCl_3$), δ 154.7, 133.7, 132.5, 132.3, 131.9, 131.8, 130.1, 129.7, 129.0, 126.1, 124.1, 123.8, 122.2, 120.0, 119.1, 92.3, 89.6, 89.4, 83.54, 83.46, 79.4, 79.1, 65.3, 15.1, 1.2. MS (ESI/BioToF + CsAc): 838.32, calc. 838.29.

Table 3. Diethylzinc Additions to Benzaldehyde Catalyzed by CCP-2[a]

run	conversion (%)	selectivity (%)	e.e. (%)
1	>99	>99	61
2	>99	>99	63
3	>99	>99	63
4	>99	>99	63
5	>99	>99	63
6	>99	>99	65
7	>99	>99	65
8	>99	>99	64
9	>99	>99	64
10	>99	>99	65

[a] All the reactions were carried out with vigorous stirring in toluene at r.t. for 1 h; catalyst loading is 65 mol % with excess $Ti(O^iPr)_4$ (4.1 equiv) and $ZnEt_2$ (3.0 equiv).

Synthesis of Chiral Covalent Frameworks. *CCP-1.* To an anhydrous dioxane (10 mL) solution of **1** (200 mg, 0.46 mmol), $Co_2(CO)_8$ (200 mg, 0.71 mmol) was added. The reaction mixture was then placed in a preheated oil bath (115 °C) under argon. Black precipitate was observed after 5 min. The heating was stopped 30 min later, and the resulting mixture was allowed to cool to room temperature. The precipitate was filtered and washed several times with THF, H_2O, EtOH, and pentane. The obtained black solid was stirred with conc. HCl for 2 h. After washing several times with H_2O, THF, and pentane, a pale orange powder of CCP-**1** was obtained in quantitative yield (200 mg). CCPs **2** and **3** were similarly prepared in quantitative yields from the corresponding monomers **1** and **2**, respectively.

CCP-**1d** and CCP-**3d** were obtained by stirring the suspended CCP-**1** or CCP-**3** in CH_2Cl_2 with excess BBr_3 for 4 days. After filtration and washing repeatedly with H_2O, THF, EtOH, and pentane, ethoxy-deprotected CCP-**1d** and CCP-**3d** were obtained quantitatively.

General Procedure for CCP/$Ti(O^iPr)_4$ Catalyzed Diethylzinc Addition Reactions. To a dry sample of CCP-**2** (3 mg, 8 μmol) in 1 mL of dry toluene was added $Ti(O^iPr)_4$ (24 μL, 81 μmol), and the resulting mixture was stirred for 1 h. Benzaldehyde (6 μL, 59 μmol) and diethylzinc in toluene (177 μL, 1.0 M, 177 μmol) were then added sequentially to the stirring suspension and allowed to react for 16 h. The reaction mixture was quenched by the addition of 1 mL of 3 M HCl. The organic layer was passed down a short silica column and analyzed by chiral GC to give conversion, selectivity, and e.e.

Recycling Experiments. To a dry suspension of CCP-**2** (15 mg, 38 mmol) in 1 mL of toluene was added $\mathrm{Ti(O^{i}Pr)_4}$ (72 μL, 243 μmol), and the mixture was allowed to stir for 2 h. To the stirring suspension was then added $\mathrm{Et_2Zn}$ (1.0 M in toluene, 177 μL, 177 μmol), followed by the addition of benzaldehyde (6 μL, 59 μmol) a minute later. The reaction was allowed to run for 1 h. The reaction mixture was treated with 3 M HCl, and organic fraction was filtered through a short silica plug. Conversion, selectivity, and e.e. values were determined by chiral GC. The CCP material was recovered by centrifugation and dried for subsequent rounds of reactions.

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