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Enantioselective addition of diethylzinc to aldehydes using immobilized chiral BINOL–Ti complex on ordered mesoporous silicas

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Abstract—A chiral (*S*)-BINOL ligand has been covalently grafted on ordered mesoporous silicas—MCM-41 and SBA-15 and the resulting inorganic–organic hybrid materials used as chiral auxiliaries in Ti-promoted enantioselective addition of diethyl zinc to aldehydes under heterogeneous conditions. These heterogeneous catalysts showed promising activity and enantioselectivity. The catalyst having a larger pore diameter with capping of free silanol moiety with trimethylsilyl (TMS) group was found to be more active with enantioselectivities up to 81% being achieved. The catalyst worked well up to three cycles with retention of enantioselectivity after washing with 10% HCl in methanol.

1. Introduction

Optically active secondary alcohols are important intermediates in the synthesis of many naturally occurring compounds, biologically active intermediates, and materials, such as liquid crystals. Enantioselective addition of diethylzinc to aldehydes is one of the most fundamental methods that afford optically active secondary alcohols through a C–C bond formation reaction.[1,2] Chiral 1,1′-bi-2-naphthol (BINOL) is one of the most useful ligands and has made a considerable contribution to asymmetric synthesis under homogeneous conditions.[3–5] It has also contributed to the catalytic asymmetric addition of diethylzinc to aldehydes utilizing a BINOL–Ti complex as an efficient catalyst under homogeneous systems,[6–8] although the heterogeneous asymmetric catalytic system has an inherent advantage in its easy recovery, product separation from the reaction mixture and reuse of the expensive chiral catalyst,[9–11] that can narrow the gap between homogeneous and heterogeneous catalysis. In this direction, some attempts have been made for heterogenization of chiral BINOL on organic polymers by grafting it onto polymer back bone,[12–14] cross-linking co-polymerization,[15] and BINOL with an ionic tag.[16] Its immobilization on inorganic support has been scarcely explored.[17,18] Inorganic supports have many advantages over most polymers because of their superior mechanical and thermal stability.[19] Recently, ordered mesoporous solids such as MCM-41 and SBA-15, with their well-defined uniform mesopores and facile surface modification, were shown to be potential materials for the heterogenization of valuable chiral homogeneous catalyst.[20–25] Various ligand systems such as β-amino alcohols based *N*-alkylnorephedrine, ephedrine, proline, and dendrimers immobilized on inorganic supports, have been investigated for the enantioselective alkylation of aldehydes.[26,27] In continuation of our earlier works on the heterogenization of chiral BINOL on siliceous support for La catalyzed enantioselective nitroaldol reaction,[28] we herein report, the immobilization of chiral BINOL ligand covalently bonded to mesoporous silicas such as MCM-41 and SBA-15. The active heterogeneous catalyst for enantioselective addition of diethylzinc to various aldehydes was generated in situ by the interaction of bonded BINOL ligand with $Ti(O^iPr)_4$. The study deals with (a) strategy to support chiral BINOL on mesoporous silicas, (b) catalytic activity of these supported catalysts, (c) minimizing undesired catalytic activity on the silica surface by capping of free hydroxyl groups of silica surface with (TMS) group,[29] and (d) regeneration of the expensive chiral catalyst.

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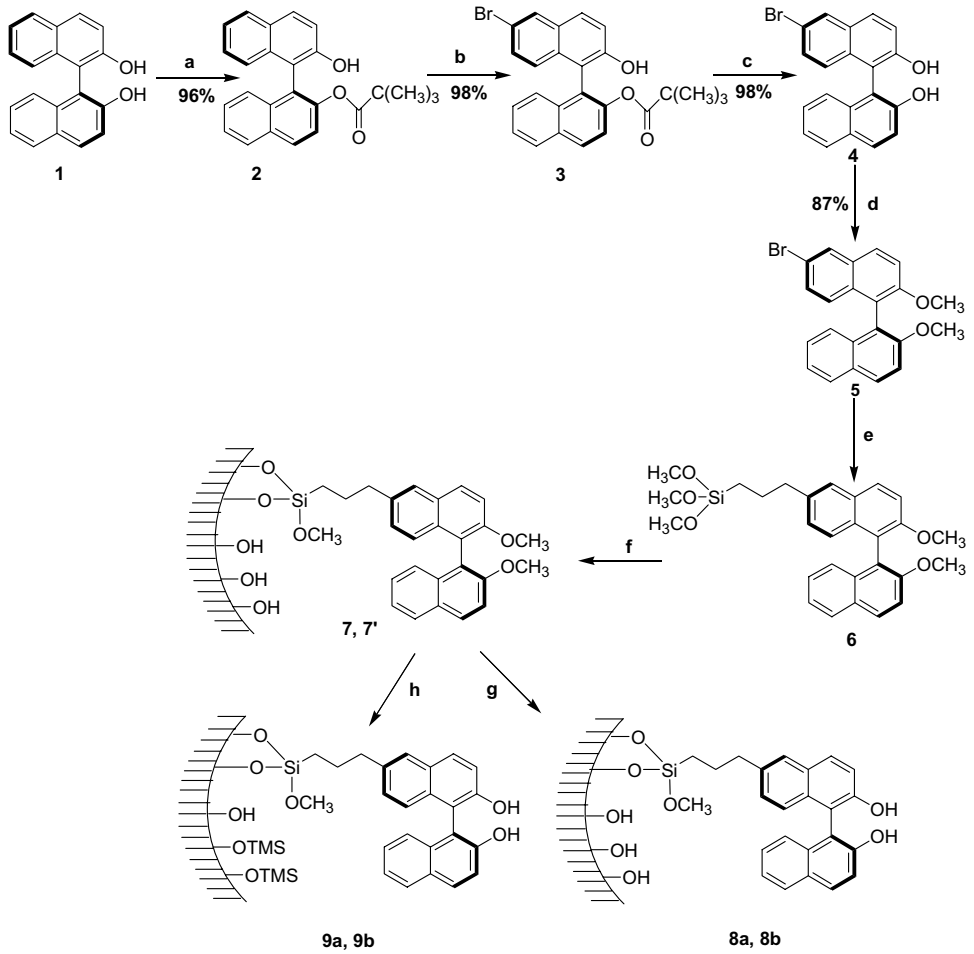
2. Results and discussion

2.1. Modification and immobilization of chiral BINOL

In order to retain the flexibility of the free BINOL and to develop the catalyst system akin to the structure that was used under homogeneous condition, we synthesized **8a**, **9a** and **8b**, **9b** according to the steps shown in Scheme 1. Thus monoesterification of (*S*)-1,1′-bi-2-naphthol was achieved leading to the formation of compound **2** in excellent selectivity. Bromination of **2** yielded exclusively monobrominated product with the bromine attached on the 6th position of the non-esterified naphthyl moiety **3**. The brominated product upon saponification afforded (*S*)-6-monobromo-1,1′-bi-2-naphthol **4**. Protection of the hydroxyl groups of **4** with CH_3I under basic conditions yielded (*S*)-6-bromo-2,2′-dimethoxy-1,1′-binaphthyl **5**. To achieve covalent grafting to mesoporous silica, compound **5** was treated with Mg/I_2 and 3-chloropropyltrimethoxysilane to obtain O-methylated BINOL **6** with a silanol arm. Compound **6** was then refluxed with calcined MCM-41/SBA-15 in toluene to afford **7**/**7**′. Demethylation of compounds **7** and **7**′ afforded **8a** and **8b**, respectively. The silica matrix bears many hydroxyl groups that may react with Ti metal ions in order to create non-chiral catalyst sites on silica support. Therefore, in order to understand the role of hydroxyl groups belonging to silica's, compounds **7** and **7**′ were capped with a TMS group and then demethylated to give solid ligands **9a** and **9b**.

The characterization of the mesoporous silica-supported ligands was accomplished by various physico-chemical techniques. The grafted amount of chiral auxiliary was found to be 16–18 mg/100 mg of solid support calculated from elemental analysis and thermal gravimetric data. FT-IR spectra of immobilized ligands **8a** and **9a** showed the characteristic bands of CH_2 for aliphatic C–H stretching vibrations at 3000–2900 cm^{-1} and bands at ~1465 and 1454 cm^{-1} due to the C=C stretching vibration of the attached BINOL group implying that the modified BINOL was covalently grafted to the mesoporous silicas MCM-41. Furthermore, the FT-IR spectra for compound **9a**



8a, **9a**: MCM-41 supported ligand
8b, **9b**: SBA-15 supported ligand

Scheme 1. The synthetic route for anchoring of BINOL with functional groups onto silica surface. Reagents and conditions: (a) pivaloyl chloride, Et_3N, CH_3CN, 0 °C; (b) Br_2, CH_3CN, 0 °C, 3 h; (c) KOH, H_2O, THF, rt, 24 h; (d) CH_3I, K_2CO_3, acetone, 18 h; (e) (i) Mg/I_2, THF, reflux, 9 h; (ii) chloropropyltrimethoxysilane, toluene, reflux, 12 h; (f) calcined MCM-41/SBA-15, toluene, 48 h; (g) BBr_3, CH_2Cl_2, −78 °C; (h) (i) HMDS, reflux, 12 h; (ii) BBr_3, CH_2Cl_2, −78 °C.

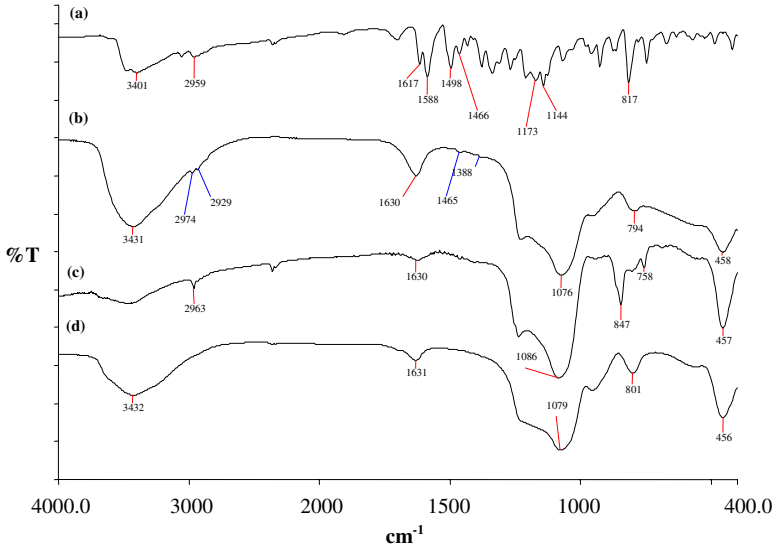


Figure 1. Representative IR spectra of ligand **4** (a), ligand **8a** (b), ligand **9a** (TMS capped) (c), and calcined MCM-41 (d).

showed a remarkable reduction in the intensity of –OH band at 3432 cm^{-1} due to the capping of –Si–OH with TMS (Fig. 1(c)).

^{13}C CP MAS NMR spectra of immobilized modified BINOL on SBA-15 peaks in the range $\delta = 8$–35 ppm due to the propyl group of the silanol arm and $\delta = 109$–155 ppm aromatic carbons due to the naphthyl groups of BINOL, respectively, additionally support our view of successful anchoring of BINOL on mesoporous silicas[12] (Fig. 2).

The textural characteristics of this supported chiral ligand were obtained by an N_2 sorption study. Typical adsorption and desorption isotherm (type IV) were retained after immobilization of the organic functions on the surface, the conservation of the same type of isotherms indicates that the structure of the inorganic surface remain intact after modification. However, a decrease in BET surface area (S_{BET}), total pore volume, and BJH average pore diameter were observed, which can be attributed to the presence of a chiral BINOL auxiliary in the mesopores that partially blocks the adsorption of nitrogen molecules (Table 1). TEM images for large pore sized mesoporous silica SBA-15 showed two dimensional hexagonal symmetry that remained unaffected on immobilization of chiral BINOL and also after reusing the supported catalyst (Fig. 3). Powder X-ray diffraction of the supported chiral auxiliary confirmed structural hexagonal space group (*p6mm*) of the inorganic support that remain preserved after immobilization even after successive reuse experiment (Fig. 4).

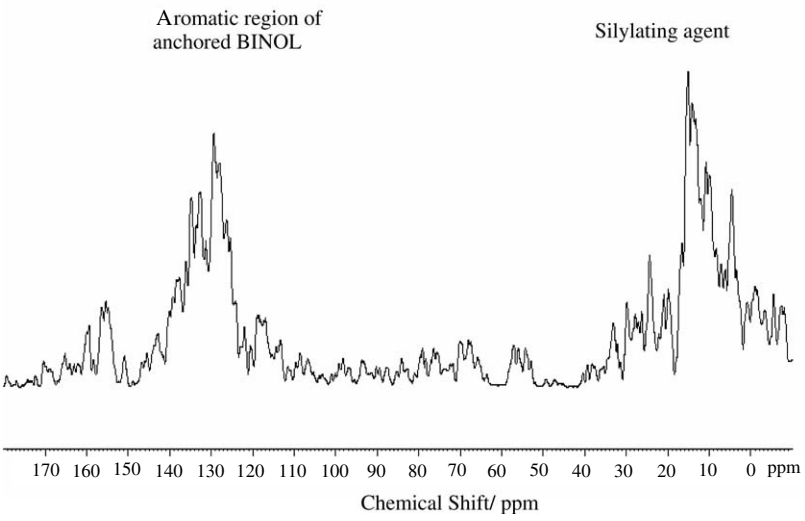


Figure 2. ^{13}C MAS NMR spectra of ligand **8b** immobilized on SBA-15.

Table 1. Textural characterization of mesoporous silicas and immobilization of BINOL during various synthetic steps

Compound	BET surface area (m^2/g)	Total pore volume (cm^3/g)	BJH pore diameter (Å)
MCM-41	998	0.9875	35
8a	864	0.6142	29
9a	842	0.5142	26
SBA-15	797	1.1327	68
8b	493	0.6768	63
9b	443	0.5667	59

2.2. Enantioselective addition of diethylzinc to aldehydes

Enantioselective addition of diethylzinc to various aldehydes such as benzaldehyde, 3-methoxy benzaldehyde, and 4-fluoro benzalaldehyde was carried out using an immobilized chiral modified BINOL–Ti complex, generated in situ to give the respective secondary alcohols (Table 2). To compare the catalytic efficacy of the immobilized catalyst, we used ligand **4** as the catalyst precursor under homogeneous conditions by keeping other reaction parameters constant for the enantioselective addition of diethylzinc to various aldehydes to give excellent conversion (95–99%), selectivity (95–100%), and enantioselectivity (88–89%) for the secondary alcohols (entries 1, 6, and 11) in 7 h. However, when the same reaction was conducted with MCM-41 immobilized ligand **8a** under heterogeneous conditions, conversions of 78–88% with selectivities of 80–89% and enantioselectivities of 37–45% were obtained for the respective secondary alcohols (entries 2, 7, and 12) in 24 h. The longer reaction times under heterogeneous conditions were possibly due to the slow diffusion of reactants to the catalytic sites in the mesopores of silica.

SBA-15 immobilized ligand **8b** resulted in conversions of up to 94% with high selectivity of 92% and good enantioselectivity of 69% in the product 1-phenyl 1-propanol using benzaldehyde as a substrate (entry 4). These improvements over MCM-41 based catalysts were attributed to the bigger pore size of the SBA-15 support facilitating the diffusion of reactants. Significant improvement in conversion (82–98%), selectivity (87–99%), and enantioselectivity (51–81%) (entries 3, 5, 8, 10, 13, and 15) were observed when TMS-capped silicas **9a** and **9b** were used as catalyst precursors for the addition of diethyl zinc with various aldehydes under heterogeneous reaction conditions. The overall performance was better for larger pore sized SBA-15 supported catalysts **8b** and **9b** than MCM-41 based catalyst

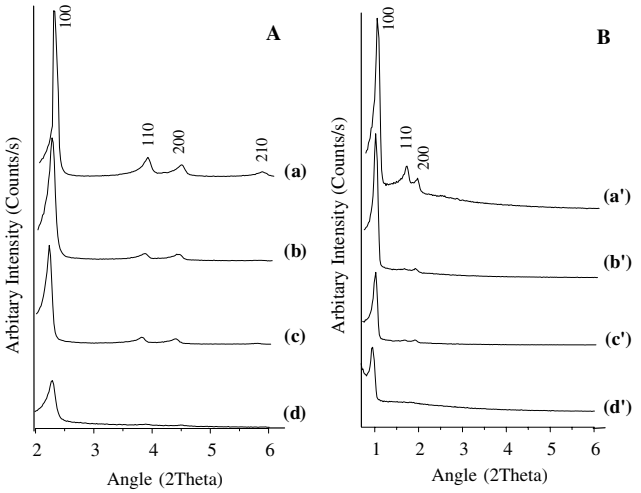


Figure 4. (A) XRPD pattern of calcined MCM-41 (a), ligand **8a** (b), ligand **9a** (TMS capped) (c), and reused catalyst **9a** (d). (B) XRPD pattern of calcined SBA-15 (a′), ligand **8b** (b′), ligand **9b** (TMS capped) (c′), and reused catalyst **9b** (d′).

8a and **9a**. Highest enantioselectivity (81%) was achieved with TMS capped SBA-15 supported BINOL ligand **9b** (entry 5) with conversion and selectivity almost similar to the homogeneous catalytic system. The catalytic activity of the TMS-capped silica without a chiral ligand showed only 10% conversion of the product under similar reaction conditions (entry 16). This residual activity of the silica possibly causes a reduction of the enantioselectivity.[26d]

After the first use of immobilized catalysts, compounds **9a** and **9b** were filtered before quenching the reaction mixture by NH_4Cl solution. Their recovered catalyst was washed with toluene and dried under vacuum at 110 °C for 4–5 h for reuse. In the second run, with catalyst **9a**, the conversion decreased markedly (from 90% to 60%), similarly with catalyst **9b** (from 98% to 67%), (Table 3, catalytic runs 1 and 2) probably due to the blockage of catalytic sites with the reactants. Therefore, the recovered catalyst was washed sequentially with 10% HCl in MeOH, H_2O, and finally with acetone under centrifugation.[30] This treatment resulted in the restoration of activity and selectivity of the immobilized catalyst. The hexagonal porosity of the dried material was intact as confirmed by XRPD analysis (Fig. 4d and d′) and TEM image (Fig. 3C). The catalytic system worked well for two more repeat catalytic experiments with some loss in activity for the enantioselective addition of diethyl

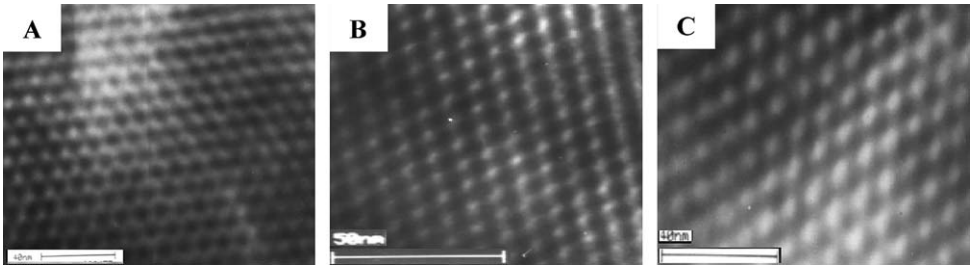
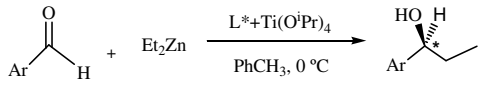


Figure 3. Representative TEM images of calcined SBA-15 (A), ligand **9b** (TMS capped) (B), and reused catalyst **9b** (C).

Table 2. Enantioselective addition of diethylzinc to aromatic aldehydes using immobilized (*S*)-BINOL–Ti complexes[a]



Entry	ArCHO	L*	Conversion[c] (%)	Selectivity[d] (%)	ee[e] (%)	Config[e]
1		**4**	99	100	89	*S*
2		**8a**	82	88	45	*S*
3	C_6H_5CHO	**9a**	90	92	62	*S*
4		**8b**	94	92	69	*S*
5		**9b**	98	99	81	*S*
6		**4**	95	95	88	*S*
7		**8a**	78	80	37	*S*
8	*m*-$MeOC_6H_4CHO$	**9a**	82	87	51	*S*
9		**8b**	76	80	58	*S*
10		**9b**	86	90	70	*S*
11		**4**	97	98	89	*S*
12		**8a**	88	89	41	*S*
13	*p*-FC_6H_4CHO	**9a**	90	91	57	*S*
14		**8b**	90	93	63	*S*
15		**9b**	96	98	78	*S*
16[b]	C_6H_5CHO	TMS capped SBA-15	10	—	—	—

[a] Reactions were carried out with 8 mol % of **4** at 0 °C for 7 h (entries 1, 6, and 11) under homogeneous condition and **8a**, **8b**, **9a**, and **9b** for 24 h under heterogeneous reaction condition using 1.5 mmol $Ti(O^iPr)_4$, 3.0 mmol Et_2Zn, and 1.0 mmol substrate in 2 mL toluene.
[b] Reaction performed with TMS capped surface SBA-15 without ligand for 24 h.
[c] Determined by ^1H NMR spectroscopy.
[d] % Selectivity: $100([R]+[S])/([R]+[S]+[PhCH_2OH])$.
[e] Determined by HPLC using Daicel Chiralcel OD column.

Table 3. Recycling data for addition of diethylzinc to benzaldehyde as representative substrate using immobilized ligand with $Ti(O^iPr)_4$ as catalyst[a]

Catalytic run	L + $Ti(O^iPr)_4$	Conversion (%)	ee (%)
1	**9a** (**9b**)	90 (98)	62 (81)
2	**9a** (**9b**)	60 (67)	58 (76)
3*	**9a** (**9b**)	85 (94)	60 (80)
4*	**9a** (**9b**)	77 (89)	59 (78)

[a] Using 8 mol % ligand at 0 °C, reaction time—24 h.
* After washing with 10% HCl in MeOH, H_2O, and acetone.

zinc to benzaldehyde (Table 3, catalytic runs 3* and 4*). This approach simplifies the recovery of chiral auxiliaries, and can be transposed and reused.

3. Conclusion

In conclusion, mesoporous silica-supported BINOL has been synthesized, which can be used to generate Ti–BINOL complexes. These silica-supported chiral catalysts were used for the enantioselective addition of diethylzinc to aldehydes with moderate conversions for the secondary alcohols under heterogeneous reaction condition. The TMS capped catalyst **9b** with a larger pore size gave excellent conversions and higher enantioselectivities (up to 81%) in the product 1-phenyl 1-propanol. The reuse of expensive chiral BINOL based catalyst was effectively worked out by washing the used catalyst with 10% HCl in methanol while the regenerated catalyst was used for further catalytic runs with the retention of enantioselectivity.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded using a Bruker, F113V (200 and 50 MHz) FT-NMR spectrometer. The IR spectra were recorded on a Perkin–Elmer Spectrum GX spectrophotometer in KBr/Nujol mull. Microanalysis of the complex was carried out on a CHNS analyzer, Perkin–Elmer model 2400. Inductive coupled plasma spectrometer (Perkin–Elmer Instrument, Optical Emission spectrometer, Optima 2000 DV) was used for Ti estimation, X-ray powder diffraction patterns of the samples were recorded on Philips X″ pert MPD diffractometer using Cu Kα (= 1.5405 Å) radiation with 2θ step size of 0.02° and step time of 5 s of curved Cu Kα monochromator under identical conditions. Specific rotation was measured by polarimeter model Digipol 781 Rudolph instruments, USA. Thermal measurements of the samples were carried out on a Mettler Toledo (TGA/SDTA 851°) instrument. N_2 gas adsorption–desorption isotherms were performed using Micromeritics ASAP-2010 at 77 K. The pore diameter of the samples was determined from the desorption branch of the N_2 adsorption isotherm employing the Barret, Joyner, and Halenda (BJH) method. TEM analysis was accomplished by transmission electron microscope Philips Tecnai 20. The conversion and ee of secondary

alcohols were determined by HPLC (Shimadzu SCL-10AVP) using Chiralcel OD column. All reagents were obtained from commercial sources and used without purification. All the solvents used in the present study were purified by the known methods.[31]

4.2. (*S*)-2-Hydroxy-2′-pivaloyloxy-1,1′-binaphthyl 2

Compound **2** was synthesized according to a reported procedure.[32] (*S*)-2,2′-Dihydroxy-1,1′-binaphthyl **1** (4.0 g, 14.0 mmol) and $(C_2H_5)_3N$ (5.9 mL, 42.0 mmol) were added to pivaloyl chloride (1.68 g, 14.0 mmol) in CH_3CN (45 mL) at 0 °C. The mixture was allowed to warm to rt and stirred for 6 h. The crude mixture was dissolved in diethyl ether and washed with aq 1 M HCl (20 mL), saturated aq $NaHCO_3$ (20 mL), and brine. The organic phase was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded the desired product that was purified by column chromatography [silica gel, *n*-hexane/EtOAc (6:1)] to give **2** (yield; 4.96 g, 96%). $[\alpha]_D^{25} = -54.5$ (*c* 0.5, THF); IR (KBr) 3414, 2969, 1720, 1509, 1280, 1154, 813 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.75 (s, 9H), 5.08 (s, 1H), 7.01 (d, $J = 8.4$ Hz, 1H), 7.15–7.34 (m, 6H), 7.46 (t, $J = 5.8$ Hz, 1H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR δ 27.31, 39.59, 115.10, 119.0, 122.69, 123.94, 124.37, 125.4, 126.50, 127.10, 127.54, 128.28, 128.76, 129.18, 129.89, 131.13, 131.55, 133.05, 134.37, 134.51, 149.19, 152.65, 178.66. Anal. Calcd for $C_{25}H_{22}O_3$: C, 81.08; H, 5.95. Found: C, 80.91; H, 5.90.

4.3. (*S*)-6-Bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl 3

Compound **3** was synthesized according to a known procedure.[32] To a solution of **2** (4 g, 10.8 mmol) in CH_3CN (50 mL) was added bromine (1.10 mL, 21.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h, quenched with aqueous Na_2SO_3, and extracted with diethyl ether. The organic phase was washed sequentially with saturated aq $NaHCO_3$, aqueous 1 M HCl, brine and dried over anhydrous Na_2SO_4. After removal of the solvent, **3** was obtained as white solid (yield, 3.92 g, 98%). $[\alpha]_D^{25} = +6.0$ (*c* 0.52, THF); IR (KBr) 3404, 2969, 1720, 1494, 1152, 815, 489, 422 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.76 (s, 9H), 5.13 (s, 1H), 6.87 (d, $J = 8.8$ Hz, 1H), 7.20–7.35 (m, 5H), 7.48 (td, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.92 (m, 2H), 8.04 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR δ 27.32, 39.59, 115.36, 118.15, 119.0, 120.26, 122.66, 126.22, 127.14, 128.41, 129.24, 130.17, 130.72, 131.81, 133.0, 133.78, 134.07, 134.90, 135.1, 149.16, 153.0, 178.61. Anal. Calcd for $C_{25}H_{21}O_3Br$: C, 66.82; H, 4.67. Found: C, 66.12; H, 4.50.

4.4. (*S*)-6-Bromo-2,2′-dihydroxy-1,1′-binaphthyl 4

A mixture of **3** (3.5 g, 7.78 mmol), KOH (1.3 g, 23 mmol), THF (25 mL), and water (10 mL) was stirred for 16 h at ambient temperature under N_2. The reaction mixture was diluted with EtOAc and the organic phase washed with aqueous 1 M HCl (25 mL), saturated aq $NaHCO_3$, and brine in that order. The organic phase was then dried over Na_2SO_4 and concentrated in vacuum to give **4** as a yellow solid. (Yield; 2.8 g, 98%) $[\alpha]_D^{25} = +6.35$ (*c* 0.55, THF); IR (KBr) 3476, 3401, 1587, 1496, 1144, 816, 749, 421 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.94 (s, 1H), 5.04 (s, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 7.25–7.37 (m, 5H), 7.48 (t, $J = 5.8$ Hz, 1H), 7.82–7.85 (m, 2H), 7.93 (d, $J = 8.6$ Hz, 1H), 8.0 (s, 1H); ^{13}C NMR δ 111.05, 112.11, 118.25, 118.91, 119.85, 124.20, 124.65, 126.3, 127.98, 128.65, 130.10, 130.61, 131.11, 132.40, 132.65, 133.10, 133.65, 133.9, 153.0, 153.5. Anal. Calcd for $C_{20}H_{13}O_2Br$: C, 65.76; H, 3.56. Found: C, 65.60; H, 3.45.

4.5. (*S*)-6-Bromo-2,2′-dimethoxy-1,1′-binaphthyl 5

To a solution of **4** (2.5 g, 6.84 mmol) in anhydrous acetone (80 mL) were added anhydrous K_2CO_3 (2.83 g, 20.5 mmol) and methyl iodide (2.91 g, 20.5 mmol) at room temperature and the mixture refluxed for 18 h under dry conditions. The solvent was completely removed under vacuum and the residue dissolved in CH_2Cl_2 (80 mL) and H_2O (70 mL). The aqueous layer was further extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After the removal of the solvent, the pale yellow product was washed with methanol to give **5** as white solid (yield; 2.34 g, 87%). $[\alpha]_D^{25} = +48.1$ (*c* 0.5, $CHCl_3$); IR (KBr) 2933, 1586, 1492, 1265, 1251, 807, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.75 (s, 6H), 6.94 (d, $J = 9.2$ Hz, 1H), 7.11 (d, $J = 9.2$ Hz, 1H), 7.18–7.27 (m, 3H), 7.47 (d, $J = 9$ Hz, 2H), 7.84 (d, $J = 6.6$ Hz, 1H), 7.89 (d, $J = 5.7$ Hz, 1H), 7.95 (d, $J = 10.8$ Hz, 1H), 8.01 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 57.3, 110.1, 111.3, 117.1, 118.2, 123.8, 124.0, 125.7, 127.1, 128.3, 129.5, 129.8, 130.2, 130.6, 130.8, 131.3, 132.3, 152.1, 152.7, Anal. Calcd $C_{22}H_{17}BrO_2$: C, 67.17; H, 4.33. Found: C, 67.02; H, 4.30.

4.6. (*S*)-6-(1-Propyltrimethoxy silane)-2,2′-dimethoxy-1,1′-binaphthyl 6

Compound **6** was synthesized according to a literature procedure.[28] Magnesium turnings (0.92 g, 38 mmol), 65 mL of dried and degassed THF and a crystal of iodine were allowed to react with **5** (2 g, 5.8 mmol) in 15 mL of THF under a dry argon atmosphere for 30 min at ambient temperature, followed by its gentle refluxing for 9 h. The resulting mass was cooled to room temperature and a solution of 3-chloropropyltrimethoxysilane (1.15 g, 1 equiv, in 25 mL of dry THF) then added dropwise over a period of 40 min. The reaction mixture was then refluxed for 12 h and the solvent distilled out completely under an inert atmosphere. Dry toluene (30 mL) was added to the resulting residue that was stirred for 2 h and filtered under inert atmosphere to afford **6** in solution. Compound **6** is highly moisture sensitive and hence an aliquot from the above solution was taken for spectroscopic characterization, while the rest of the solution was used directly for subsequent synthesis. ^1H NMR ($CDCl_3$) δ 0.92 (broad t, $J = 7$ Hz, 2H), 0.75–0.85 (m, 2H), 1.84 (broad t, $J = 7$ Hz, 2H), 3.56 (s, 9H), 3.75 (s, 6H), 6.95 (d, $J = 9$ Hz, 1H), 7.02 (d, $J = 9$ Hz, 1H), 7.17–7.35 (m, 3H), 7.42 (d, $J = 3.8$ Hz, 1H), 7.48 (d, $J = 3.5$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.88 (d, $J = 9$ Hz, 1H), 7.95 (d, $J = 9$ Hz, 1H), 8.0 (d, $J = 2$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.4, 8.7,

26.9, 47.8, 50.9, 51.3, 114.9, 115.8, 124.0, 125.6, 125.9, 126.7, 126.8, 127.0, 127.5, 127.8, 128.5, 128.6, 129.1, 129.4, 130.0, 130.2, 130.4, 130.5, 149.9, 150.1. Anal. Calcd $C_{28}H_{32}O_5Si$: C, 70.58; H, 6.72. Found: C, 70.12; H, 6.44.

4.7. Synthesis of ordered mesoporous silicas MCM-41/SBA-15 (a,b)

Ordered mesoporous silicas MCM-41 was synthesized by using cetyltrimethyl ammonium bromide (CTAB) as surfactant and sodium silicate as silica source in a molar ratio $1SiO_2$–$0.33Na_2O$–0.5CTAB–$74H_2O$ under a hydrothermal crystallization method, while SBA-15 was synthesized by using triblock copolymer P123 as a structure directing agent and TEOS as silica source.[20] The calcined mesoporous silicas were characterized by powder XRD, IR, N_2 sorption study, SEM, and TEM analysis.

4.8. Immobilization of modified BINOL on mesoporous silicas 7 and 7′

Calcined MCM-41/SBA-15 (1.8 g) was added to the above-synthesized solution of **6** and the suspension allowed to stir at reflux temperature under an argon atmosphere for 48 h. After cooling, the powder was collected by filtration, washed successively with dry toluene, and then dried under vacuum. Dried material was subjected to soxhlet-extraction with dichloromethane for 24 h. Finally the sample was dried under vacuum at 45–50 °C. Yield; 1.85 g, IR (KBr) cm^{-1}: 3439, 2959, 2857, 2358, 1635, 1439, 1251, 1084, 964, 807, 796, 689, 558, 461. Anal. Found: C, 5.0; H, 0.88.

4.9. Removal of the protecting group 8a and 8b

2,2′-Dimethoxy-1,1′-bi-naphthalene supported silicas **7** and **7′** (2.0 g) were taken in dried CH_2Cl_2 (20 mL) and cooled to −78 °C. BBr_3 (3 mL, 3.0 mmol, 1 M solution in CH_2Cl_2) was added to the cooled suspension dropwise with continuous stirring for 2 h, after which the reaction mixture was brought to room temperature, stirred for an additional 2 h and an aqueous saturated solution of $NaHCO_3$ was slowly added to it. The resulting solid was filtered off, washed successively with water, acetone, and CH_2Cl_2, and finally dried at 55 °C under vacuum for 10 h. Yield; 1.93 g, IR (KBr) cm^{-1}: 3418, 2959, 2358, 1636, 1383, 1231, 1076, 963, 800, 579, 454. Anal. Found: C, 6.68; H, 0.51.

4.10. End-capping of silanol groups (trimethylsilylation) 9a and 9b

Under extremely dry conditions, a suspension of **7/7′** (0.5 g), $(CH_3)_3SiCl$ (TMSCl) (10 g), and $((CH_3)_3Si)_2O$ (HMDS) (15 g) were refluxed overnight with stirring under an argon atmosphere. The volatiles were stripped on a rotary evaporator and the dry powder was washed two or three times with 10 mL of dry acetone by centrifugation and finally dried under vacuum at 75–80 °C for 6 h. Material recovery was >98%. After successful TMS capping of compounds **7** and **7′**, the resulting compounds were demethylated to give the desired compounds **9a** and **9b** (Scheme 1). IR (KBr) cm^{-1}: 2963, 2361, 1627, 1236, 1085, 840, 457. Anal. Found: C, 9.92; H, 2.35.

4.11. General procedure for the enantioselective addition of diethylzinc to aromatic aldehydes

Immobilized ligands **8a** and **8b** and **9a** and **9b** (8 mol %) were dried under vacuum for 6 h at 110 °C after they were taken in 2 mL of dry toluene and stirred with $Ti(O^iPr)_4$ (1.5 mmol) for 2 h at room temperature under an argon atmosphere. To the above suspension, a solution of Et_2Zn (1 M solution in hexane, 3.0 mmol) was added, cooled to 0 °C, appropriate aromatic aldehydes were added (1.0 mmol) and the resulting mixture was stirred for 24 h at 0 °C. The progress of the catalytic reaction was monitored on HPLC. After completion of the reaction, the immobilized catalyst was filtered off from the reaction mixture, washed with toluene, dried under vacuum, and kept for reuse experiments. The filtrate and combined washings were quenched with saturated NH_4Cl solution (10 mL), washed with water, and dried over anhydrous Na_2SO_4. This was then filtered and concentrated to provide a colorless oil, which was analyzed on HPLC chiralcel OD column to determine the enantiomeric purity.

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References

1. Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49.
2. Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833.
3. Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: New York, 1999.
4. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.
5. Pu, L. *Chem. Rev.* **1998**, *98*, 2405.
6. Zhang, F. Y.; Yip, C.-W.; Chan, A. C. *Tetrahedron: Asymmetry* **1997**, *8*, 585.
7. Mori, M.; Nakai, T. *Tetrahedron Lett.* **1997**, *38*, 6233.
8. Balsells, J.; Davis, T. J.; Carroll, P.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 10336.
9. *Heterogeneous Catalysis and Fine Chemicals*; Blaser, H., Bailker, A., Prins, R., Eds.; Elsevier: Amsterdam, 1997; Vol. IV.
10. Clark, J. H.; Macquarrie, D. J. *Org. Process Res. Dev.* **1997**, *1*, 149.
11. Ernst, S.; Gläser, R.; Selle, M. *Stud. Surf. Sci. Catal.* **1997**, *105*, 1021.
12. Hesemann, P.; Moreau, J. J. E. *C.R. Chim.* **2003**, *6*, 199.
13. Jayaprakash, D.; Sasai, H. *Tetrahedron: Asymmetry* **2001**, *12*, 2589.
14. Matsanuga, S.; Ohshimi, T.; Shibasaki, M. *Tetrahedron Lett.* **2000**, *41*, 8473.
15. Sellner, H.; Faber, C.; Rheuner, P. B.; Seebach, D. *Eur. J. Org. Chem.* **2000**, *6*, 3692.

16. Gadenne, B.; Hesemann, P.; Moreau, J. J. E. *Tetrahedron: Asymmetry* **2005**, *16*, 2001.
17. Macquarrie, D. J. *Chem. Commun.* **1997**, *601*, 886.
18. Hesemann, P.; Moreau, J. J. E. *Tetrahedron: Asymmetry* **2000**, *11*, 2183.
19. Jorna, A. M. J.; Boelrijk, A. E. M.; Hoorn, H. J.; Reedijk, J. *React. Funct. Polym.* **1996**, *29*, 101.
20. (a) Kureshy, R. I.; Ahmad, I.; Khan, N. H.; Abdi, S. H. R.; Singh, S.; Pandya, P. H.; Jasra, R. V. *J. Catal.* **2005**, *235*, 28; (b) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548; (c) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
21. Hultman, H. M.; de Lang, M.; Nowotny, M.; Arends, I. W. C. E.; Hanefeld, U.; Sheldon, R. A.; Maschmeyer, T. *J. Catal.* **2003**, *217*, 264.
22. Davis, M. E. *Nature* **2002**, *417*, 813.
23. Kim, G.-J.; Park, D.-W. *Catal. Today* **2000**, *63*, 537.
24. Crosman, A.; Hoelderich, W. F. *J. Catal.* **2005**, *232*, 43.
25. (a) Kureshy, R. I.; Ahmad, I.; Khan, N. H.; Abdi, S. H. R.; Pathak, K.; Jasra, R. V. *Tetrahedron: Asymmetry* **2005**, *16*, 3562; (b) Kureshy, R. I.; Ahmad, I.; Khan, N. H.; Abdi, S. H. R.; Pathak, K.; Jasra, R. V. *J. Catal.* **2006**, *238*, 134.
26. (a) Soai, K.; Wattanabe, M.; Yamamoto, A. *J. Org. Chem.* **1990**, *55*, 4832; (b) Abramson, S.; Lasperas, M.; Galarneau, A.; Giscard, D. D.; Brunel, D. *Chem. Commun.* **2000**, 1773.29; (c) Bellocq, N.; Abramson, S.; Lasperas, M.; Brunel, D.; Moreau, P. *Tetrahedron: Asymmetry* **1999**, *10*, 3229; (d) Kim, S. W.; Bae, S. J.; Hyeon, T.; Kim, B. M. *Microporous Mesoporous Mater.* **2001**, *44*, 523.
27. Chung, Y.-M.; Rhee, H.-Ku. *Chem. Commun.* **2002**, 238.
28. Bhatt, A.; Pathak, K.; Jasra, R. V.; Kureshy, R. I.; Khan, N. H.; Abdi, S. H. R. *J. Mol. Catal. A: Chem.* **2006**, *244*, 110.
29. Tatsumi, T.; Koyano, K. A.; Tanaka, Y.; Nakata, S. *J. Phys. Chem. B* **1997**, *101*, 943.
30. Heckel, A.; Seebach, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 163.
31. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1981.
32. Hocke, H.; Uozumi, Y. *Tetrahedron* **2003**, *59*, 619.