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Synthesis, Characterization and Catalytic Properties of Chiral BINOL Functionalized Mesoporous Silicas for Enantioselective Morita-Baylis-Hillman Reaction

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Abstract Several Chiral BINOL functionalized mesoporous silicas were prepared by post grafting of organosilane derivatives of (*S*)-BINOL (1,1′-bi-2-naphthol) on SBA-15 and characterized by ^{13}C CP/MAS NMR, FT-IR, UV–visible absorption spectra, elemental analysis, powder XRD, nitrogen adsorption–desorption isotherms and TEM techniques. Their catalytic properties were demonstrated in enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and cyclohexenone. Among them, 3BSBA-15 linked through the 3 position of BINOL exhibit higher enantioselectivity (26% e.e.) and yield (88%) which are similar to the homogeneous catalyst (*S*)-BINOL (27% e.e. and 92% yield) as Brønsted acids catalyst, while complex of 3BSBA-15 and calcium 3BSBA-15-Ca show lower enantioselectivity (21% e.e.) than its homogeneous complex (*S*)-BINOL-Ca (32% e.e.) as ligand catalyst. 3BSBA-15 and 3BSBA-15-Ca can be reused with no significant decrease in enantioselectivity and yield.

Keywords Chiral organosilane derivatives · BINOL · SBA-15 as support · Chiral Brønsted acids · Enantioselective Morita-Baylis-Hillman reaction

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1 Introduction

Mesoporous silicas, as a group of inorganic supports, have unique properties such as well-ordered pore arrays, large surface area, uniform pore size distributions and tunable pore diameters causing fascination and drawing public attention [1]. Many homogeneous chiral catalysts, usually transition-metal complexes, have been immobilized on mesoporous silicas through adsorption, covalent grafting, encapsulation and electrostatic interaction strategies [2]. Recent literature discussed the confinement effects, the properties of the linkages and the microenvironment in nanopores that affect the activity and enantioselectivity of chiral catalysts in channels of mesoporous silicas [3]. The most effective method for immobilization of chiral catalysts into the nanopores of mesoporous materials is post-grafting method [2, 4–6]. Generally, pre-grafting method of chiral ligands on mesoporous silicas and coordination with mental ions afterwards [7] has been predominantly applied. However, it is inevitable that some metal ions could not coordinate with the chiral ligands pre-grafted on the mesoporous silicas [8] since they react with Si–OH groups of the supports which would influence the activity and enantioselectivity of the catalytic reactions at the final stage [9, 10].

Recently, advancement in the development of asymmetric catalytic reactions with chiral organic catalysts has been reported [11–13]. Chiral Brønsted acids were acknowledged as efficient organocatalysts for asymmetric additions of nucleophiles to imines [14–17]. Specifically, chiral BINOLs were accepted as optimal candidates for the asymmetric Morita-Baylis-Hillman reaction [18] and asymmetric allylboration of ketones [19, 20] as chiral Brønsted acids even though they have been widely used in metal-centered Lewis acid catalysts [21]. Various supports such as organic polymers [22–30], inorganic materials

[31–33], dendrimers [34], have been investigated to immobilize BINOLs as metal-centered Lewis acid catalysts in a lot of asymmetric catalytic reactions. Meanwhile, one organosilane derivative of chiral BINOL was post-grafted onto ordered mesoporous silicas MCM-41 [35] and SBA-15 [36] by Abdi and coworkers to catalyze asymmetric nitroaldol reaction [37] and enantioselective addition of diethylzinc to aldehydes [38] centered with different metal ions. However, that organosilane derivative of chiral BINOL could not be purified because of its instability to moisture. Furthermore, additional titanium ions and diethylzinc were required in the enantioselective addition of diethylzinc to aldehydes since they could react with Si–OH groups on mesoporous silicas. To date, there is no report about chiral BINOL supported mesoporous silicas that used as organocatalyst. We now used new immobilized BINOLs as chiral Brønsted acids to investigate their properties in asymmetric reactions.

In this paper, we synthesized a series of new chiral triethoxysilane derivatives of (*S*)-BINOL substituted at different positions of binaphthyl backbone and immobilized them on mesoporous silica SBA-15 and amorphous silica gel as a comparison. The resulting chiral BINOL functionalized silicas were used as chiral Brønsted acids to promote enanitoselective Morita-Baylis-Hillman reaction [39, 40] of 3-phenylpropanal and cyclohexenone with tri-*n*-butylphosphine as Lewis base at room temperature. In contrast with these results, coordinate complex of chiral BINOL functionalized silicas and calcium expanded as metal-centered Lewis acids to catalyze this reaction [41]. These immobilized BINOLs might be used as organocatalysts to catalyze other asymmetric catalytic reactions.

2 Results and Discussion

2.1 Preparation and Characterization of Organosilane Derivatives of (S)-BINOL

In order to study the properties of immobilized BINOLs linked at different positions of binaphthyl backbone, different triethoxysilane derivatives of (*S*)-BINOL **2a**, **2b**, **2c**, and **2d** were synthesized from hydroxylmethyl derivatives **1a**, **1b**, **1c** and **1d** at 3, 3,3′, 6 and 6,6′ positions by coupling with 3-chloropropyltriethoxysilane under conditions of NaH/THF in Scheme 1. Compounds **1a**, **1b**, **1c** and **1d** were obtained according to the references [23, 27, 34] from (*S*)-BINOL and bromides of (*S*)-BINOL through only three steps including protection by MOMCl (CH_3OCH_2Cl), carbonylation at its 3, 3,3′, 6 and 6,6′ positions and reducation to hydroxylmethyl groups, respectively. The products **2a**, **2b**, **2c** and **2d** can be purified by flash column chromatography, with the following corresponding yields: 84%, 62%, 82% and 67%. The yield of single triethoxysilane derivatives is higher than that of double derivatives due to the low activity of the second hydroxylmethyl group in compounds **1b** and **1d**. The chains introduced at different positions of BINOL were $–CH_2O(CH_2)_3–$ with longer lengths than the organosilane derivative of BINOL reported [37, 38] to retain the flexibility of BINOL. The obtained triethoxysilane derivatives of (*S*)-BINOL were characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, FT-IR, ESI-MS and elemental analyses.

2.2 Immobilization of (S)-BINOL Onto Mesoporous Silica SBA-15 and Amorphous Silica Gel

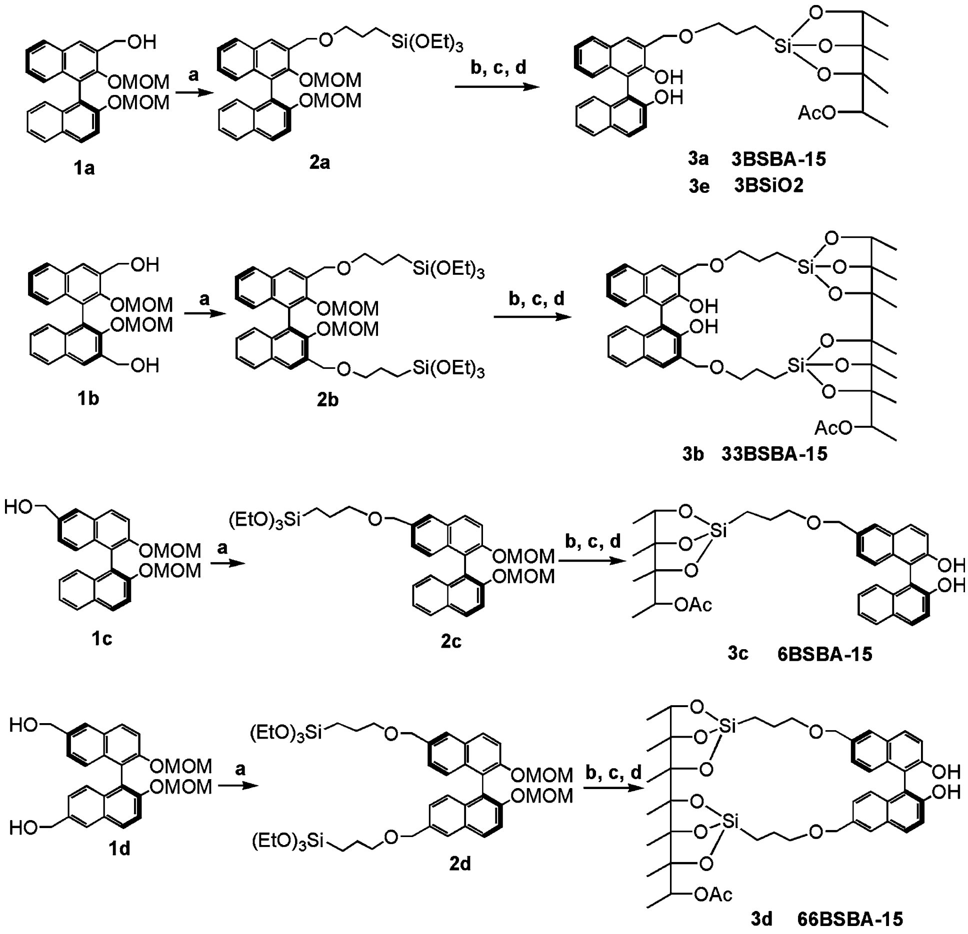
The as-synthesized triethoxysilane derivatives of (*S*)-BINOL **2a**, **2b**, **2c** and **2d** were post-grafted onto mesoporous silica SBA-15 [42] and amorphous silica gel (200–300 mesh) respectively by refluxing in anhydrous toluene for 48 h under nitrogen. The solids were filtered and washed with toluene, extracted with dichloromethane and dried under vacuum. The resulting organic–inorganic compounds were protected by steady AcO group with $(AcO)_2O$ and pyridine under room temperature [43]. The MOM groups of BINOL unit were deprotected by $(CH_3)_3SiCl$ and Bu_4NBr [44] under mild conditions to prevent the disconnection of propyl methyl ether in the linkage. The final chiral BINOL functionalized silicas were labeled as 3BSBA-15 **3a**, 33BSBA-15 **3b**, 6BSBA-15 **3c**, 66BSBA-15 **3d** and 3BSiO2 **3e**, respectively and were shown in Scheme 1. To compare with properties of supported chiral organocatalysts and metal-centered catalysts, complex of chiral BINOL functionalized mesoporous silica 3BSBA-15 and calcium ions were prepared and named as **3f** 3BSBA-15-Ca in Scheme 2 [45].

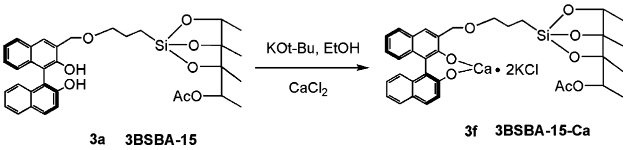
2.3 Characterization of the Chiral BINOL Functionalized Silicas **3a**, **3b**, **3c**, **3d** and **3e**

The characterizations of the chiral BINOL functionalized silicas were accomplished by various physicochemical techniques. The ^{13}C CP/MAS NMR spectrum of solid **3a** indicates the maintenance of BINOL units in the organic–inorganic hybrid mesoporous silicas (Fig. 1). The spectra of the other four products **3b**, **3c**, **3d** and **3e** are similar to product **3a**. Chemical shifts at 70.22, 59.23, 46.85, 25.36 and 16.53 ppm represent the propyl methyl ether groups of the linkage [46]. Chemical shifts between 170.18 and 127.23 ppm are due to the binaphthyl group of BINOL [22]. These results were further confirmed by the corresponding FT-IR spectra of the chiral BINOL functionalized silicas in Fig. 2.

FT-IR spectra of chiral BINOL functionalized silicas **3a**, **3b**, **3c** and **3d** show two characteristic peaks of asymmetric

Scheme 1 The synthetic route for organosilane derivatives of (*S*)-BINOL and post grafting on mesoporous silica SBA-15 and amorphous silica gel. (**a**) NaH, $Cl(CH_2)_3Si(OEt)_3$, reflux; (**b**) SBA-15 and silica gel, toluene, reflux; (**c**) $(AcO)_2O$, pyridine, rt; (**d**) $(CH_3)_3SiCl$, Bu_4NBr, CH_2Cl_2, rt





Scheme 2 Preparation of 3f 3BSBA-15-Ca

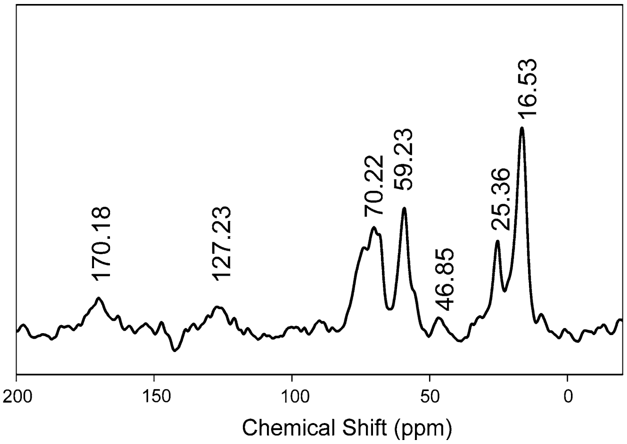


Fig. 1 ^{13}C CP/MAS NMR spectrum of chiral BINOL functionalized silica 3a (3BSBA-15)

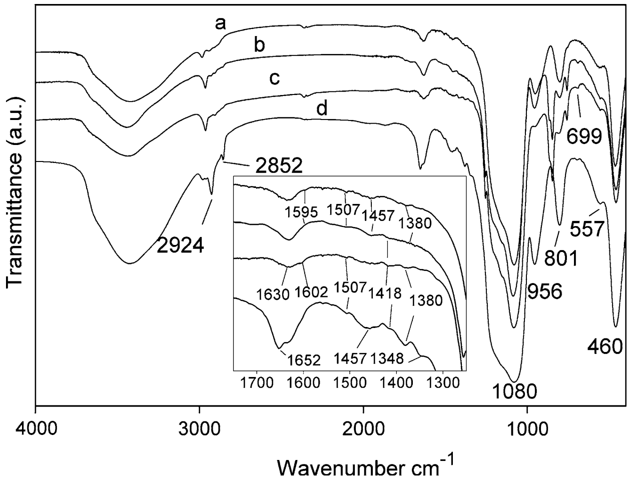


Fig. 2 FT-IR spectra of chiral BINOL functionalized silicas (**a**) 3BSBA-15, (**b**) 33BSBA-15, (**c**) 6BSBA-15 and (**d**) 66BSBA-15

and symmetric stretching vibrations of –CH_2– groups at 2924 and 2852 cm^{-1} [47]. Less intense peaks at 1506 and 1601 cm^{-1} ascribe to the C=C stretching vibration of the attached BINOL group [23], implying that the modified BINOLs have been covalently grafted to the mesoporous silica SBA-15. Peaks at 699 and 557 cm^{-1} are assigned to

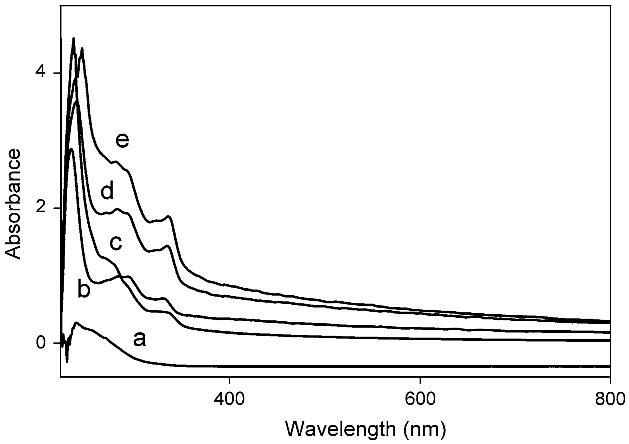


Fig. 3 UV-visible absorption spectra of (**a**) pure SBA-15, and chiral BINOL functionalized silicas (**b**) 3BSBA-15, (**c**) 33BSBA-15, (**d**) 6BSBA-15 and (**e**) 66BSBA-15

bending vibration of C–H in binaphthyl group [27]. In addition, the main bands at 1068 cm^{-1} and around 801 cm^{-1} are associated with the asymmetric and symmetric stretching vibrations of Si–O–Si. Bands at 460 cm^{-1} and 956 cm^{-1} are attributed to Si–O–Si symmetric bending and silanol (Si–OH) stretching vibrations respectively [48].

The presence of binaphthyl units in chiral BINOL functionalized silicas **3a**, **3b**, **3c**, **3d** is also shown in UV-visible absorption spectra in Fig. 3, a sharp peak at 235 nm along with two broad bands at about 280 and 335 nm. These absorption bands are totally absent in pure SBA-15 and attributed to the $\pi \rightarrow \pi^*$ transitions of the organic aromatic compounds BINOL [49].

The loading of the chiral BINOL functionalized silicas **3a**, **3b**, **3c** and **3d** resulted to 0.48, 0.33, 0.41, 0.40 mmol/g, respectively as calculated from elemental analysis. However, the load of **3e** was half of **3a** and may be attributed to the lower surface area of amorphous silica gel (395 m^2/g) in Table 1. Different loads lead to different pore diameters and pore volumes corroborate with the results of XRD in Fig. 4 and nitrogen adsorption/desorption isotherms in Fig. 5.

Table 1 Structural parameters of as-synthesized chiral BINOL-grafted silicas

Compound	BINOL loading (mmol/g)	BJH average pore diameter (nm)	BET specific surface area (m^2/g)	Total pore volume (cm^3/g)
SBA-15	0	6.64	980	1.45
3a	0.48	5.73	592	0.82
3b	0.33	6.35	706	1.12
3c	0.41	6.03	437	0.66
3d	0.40	6.16	480	0.78
3e	0.24	8.19	395	0.81

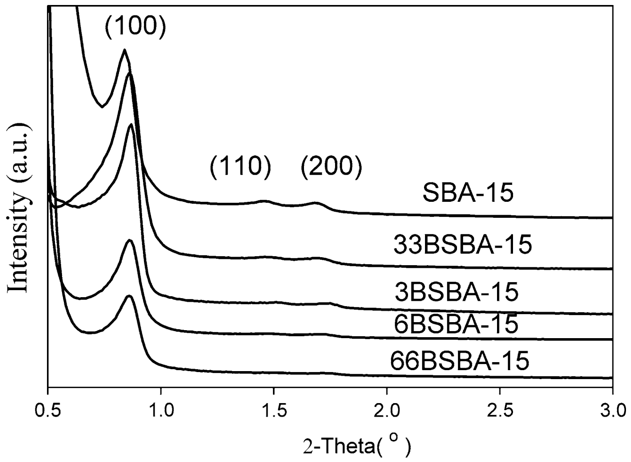


Fig. 4 Low-angle powder X-ray diffraction patterns for SBA-15 and chiral BINOL functionalized silicas 3BSBA-15, 33BSBA-15, 6BSBA-15 and 66BSBA-15

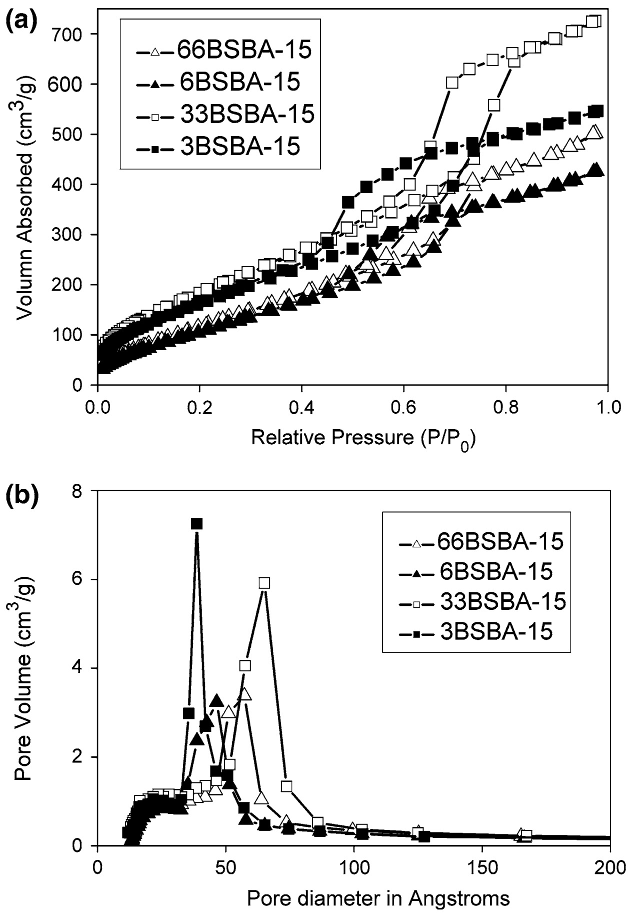


Fig. 5 (**a**) Nitrogen adsorption–desorption isotherms for chiral BINOL functionalized silicas 3BSBA-15, 33BSBA-15, 6BSBA-15 and 66BSBA-15 and (**b**) corresponding pore size distribution by BJH model

The pure mesoporous SBA-15 and chiral BINOL functionalized silicas **3a**, **3b**, **3c** and **3d** were characterized by low-angle powder X-ray diffraction appeared as structural hexagonal space group (p6 mm) confirmed by TEM images in Fig. 6. XRD pattern for pure SBA-15 exhibited in Fig. 4 shows the presence of the three reflection peaks corresponding to 100, 110 and 200 reflections, usual result for SBA-15, confirmed the presence of ordered hexagonal mesoporous structure [50]. For SBA-15 and BINOL functionalized samples **3a, 3b, 3c, 3d**, the d_{100} spacings are 10.50, 10.14, 10.26, 10.21 and 10.24 nm, respectively. The difference of d_{100} spacing between pure SBA-15 and BINOL functionalized silicas is due to the introduction of organic BINOL molecule into the pore channels, leads to a slight decrease in *d*-spacing. The d_{100} spacing of sample **3a** that contains highest loading of BINOL is the smallest and the BJH average pore diameter outcome of **3a** is the smallest among the four chiral BINOL-functionalized silicas too.

The characterization of pore properties of chiral BINOL functionalized silicas was obtained by an N_2 sorption study in Fig. 5. Typical adsorption and desorption isotherm exhibits type IV curves and BINOL functionalized silica samples keep the same type of isotherms. The conservation of the same type of isotherms indicated that the structure of the inorganic surface remained constant and unchanged after modification. Some decreases in BET specific surface area (S_{BET}), total pore volume, and BJH average pore diameter were discovered compared with pure SBA-15 and may be attributed to the presence of chiral BINOL that occupy the pore spaces (Table 1). The BJH average pore diameter of pure SBA-15 was 6.64 nm, with an increase of BINOL loading from 0.33 to 0.48 mmol/g, the BJH average pore diameters of chiral BINOL functionalized silicas decreased from 6.35 to 5.73 nm.

TEM image for pure SBA-15 shows two dimensional hexagonal symmetry, whereas, the chiral BINOL functionalized hybrid SBA-15 persisted as an ordered hexagonal pore structure as illustrated in Fig. 6. Figure 6a–d present TEM image of the chiral BINOL functionalized silicas **3a** 3BSBA-15, **3b** 33BSBA-15, **3c** 6BSBA-15 and **3d** 66BSBA-15 respectively.

The catalytic activity of the chiral BINOL functionalized silicas **3a**, **3b**, **3c**, **3d** and **3e** as chiral Brønsted acids and Lewis acid **3f** 3BSBA-15-Ca was evaluated in the enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and cyclohexenone in THF with tributylphosphane as mild Lewis base at room temperature (Scheme 3). The results were summarized in Table 2 using 10 mol% of BINOL functionalized silicas and 20 mol% of tri-n-butylphosphine. Immobilized catalyst **3a** linked at 3 position of binaphthyl backbone resulted to a higher e.e. and yield (23% and 88%) than **3c** (12% and 87%) and **3d** (13% and 86%) linked at 6 and 6,6′ positions of binaphthyl backbone respectively. Possibly, the substitution at 3 position of binaphthyl backbone could

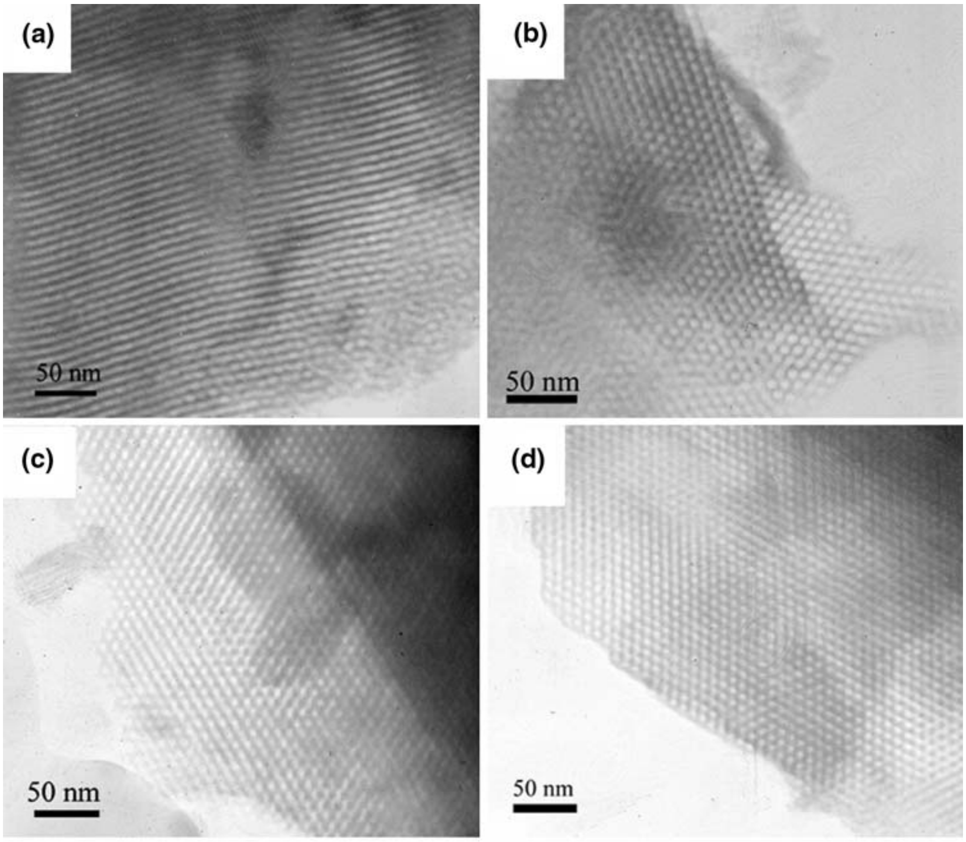
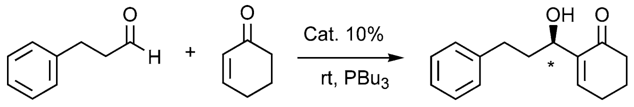


Fig. 6 TEM images of chiral BINOL functionalized silicas (**a**) 3BSBA-15, (**b**) 33BSBA-15, (**c**) 6BSBA-15 and (**d**) 66BSBA-15



Scheme 3 Enantioselective Morita-Baylis-Hillman reaction

Table 2 Catalytic enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and cyclohexenone[a]

Entry	Brønsted acids	PBu_3 (mol%)	Time (h)	Yield (%)[c]	E.e. (%)[d]	Confign[e]
1	**3a**	20	72	88	23	*R*
2	**3b**	20	72	90	1.7	*R*
3	**3c**	20	72	87	13	*R*
4	**3d**	20	72	86	12	*R*
5	**3e**	20	72	77	7.4	*R*
6	(*S*)-BINOL	20	48	92	27	*R*
7	**3f**[b]	10	72	86	21	*R*
8	(*S*)-BINOL-Ca[b]	10	48	89	32	*R*

[a] Reactions were run with 0.9 mmol of 3-phenylpropanal, 0.5 mmol of cyclohexenone, and 10 mol% chiral Brønsted acids in THF at room temperature under nitrogen

[b] Reactions were run with 16 mol% ligands

[c] Isolated yield

[d] Determined by HPLC analysis using a chiralcel OD-H column

[e] Educe from comparation with references reported

partially enhance the enatioselectivity of products. However, immobilized catalyst **3b** linked at 3,3′positions of binaphthyl backbone caused the lowest e.e. (1.7%) that was not clarified. Catalyst **3e** with lower e.e. (7.4%) was used as a comparison with **3a** supported on mesoporous silica SBA-15 to imply the advantage of mesopores of SBA-15 for this reaction. When 16 mol% of complex of chiral BINOL functionalized silica **3f** 3BSBA-15-Ca and 10 mol% of tributylphosphane were used to catalyze this reaction, e.e. value of the product was lower (21%) than its homegenous catalyst (S)-BINOL-Ca (32%). This may be due to the fact that some calcium ions cannot coordinate with the chiral BINOL functionalized silicas.

Different amounts of tributylphosphane (10, 20, 50, 200 mol%) were used as cooperative catalyst with invariable 10 mol% amount of **3a**. The more tributylphosphane were used, the lower the e.e. of the products gathered. With the increase in the amounts of tributylphosphane, the e.e. of products (26%, 23%, 16% and 7%) gradually decreased (Table 3). The highest e.e. of 26% was obtained when 10 mol% PBu_3 was used similar to that of homogenous catalyst (S)-BINOL (27%).

Recyclability of the immobilized catalyst **3a** and **3f** was assessed for enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and cyclohexenone using 10 mol% amounts of tributylphosphane as Lewis base. After the first catalytic run, the catalyst was easily separated by filtration, washed thoroughly with THF, dried in vacuum and subjected to another cycle of experimentation with fresh reaction mixture under similar reaction conditions. While the homogenous catalyst (*S*)-BINOL were difficult to separate from the product using column chromatography. The enantioselectivity resulted in a little decrease for the following three reused experiments. For catalyst **3a**, the e.e. values of product in the three recycled uses are 24%, 24% and 23% respectively, which are a little lower than that of the first use (26%). For catalyst **3f**, the e.e. values and yields of product for the three recycled runs are 21%, 85%, 20%, 85%, 19% and 83% respectively, which are closer to that of the first use (21%, 86%) in Table 4.

Table 3 Enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and using different amounts of PBu_3[a]

Entry	Brønsted acids	PBu_3 (mol%)	Time (h)	Yield (%)[b]	E.e. (%)[c]
1	3a	10	72	85	26
2	3a	20	72	88	23
3	3a	50	72	90	16
4	3a	200	72	91	7.0

[a] Using 10 mol% chiral Brønsted acids

[b] Isolated yield

[c] Determined by chiral HPLC analysis

3 Experimental

3.1 Materials and Methods

All chemicals were purchased from commercial suppliers and used without further purification. Toluene and tetrahydrofuran were dried and distilled before utilization. Amorphous silica gel (200–300 mesh) and mesoporous silica (SBA-15) were subjected to heat treatment at 150 °C for 3 h and cooled under nitrogen prior to experimentation. The NMR spectra (^{1}H NMR, ^{29}Si NMR, ^{13}C NMR, ^{13}C CP/MAS NMR) were recorded on Bruker-AV 400 and

Table 4 Recycling test for enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and cyclohexenone[a]

Run	Brønsted acids	PBu_3 (mol%)	Time (h)	Yield (%)[b]	e.e. (%)[c]
1	3a	10	72	85	24
2	3a	10	72	84	24
3	3a	10	72	84	23
1	3f[b]	10	72	85	21
2	3f[b]	10	72	85	20
3	3f[b]	10	72	83	19

[a] Using 10 mol% chiral Brønsted acids

[b] Reactions were run with 16 mol% ligands, isolated yield

[c] Determined by chiral HPLC analysis

600 MHz spectrometers using TMS as internal standard. FT-IR spectra were recorded on a Boi-Rad FTS135 infrared spectrometer. Optical rotation value was measured on a Perkin-Elmer 341 polarimeter. Elemental analyses were carried out with a GmbH VarioEL V2.8 instrument. Room temperature transmission UV-visible spectra of chiral BINOL functionalized silicas in dichloromethane were recorded in Shimadzu UV-2550 spectrophotometers. ESI-MS quantities were measured with an LCQ instrument. X-ray diffraction (XRD) patterns were recorded on a D8 X-ray Thin Film Reflector using Cu Ka radiation at 40 kV and 40 mA. As a standard procedure, the data of low-angle XRD patterns were collected in the range of $0.5^{o} < 2\theta < 3^{o}$ with a step size of 0.01^{o} and a calculated time of 1 s per step. Transmission electron microscope (TEM) images were taken with a JEOL 1011 electron microscope with an accelerating voltage of 100 kV. The samples were prepared by dispersing the powder samples directly on copper grids. Nitrogen adsorption–desorption isotherms at 77 K for mesoporous samples were obtained using a micromeritics ASAP 2010. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method while the pore size was obtained from the Barrett-Joyner-Halenda (BJH) model. Enantiomeric excess was determined by HPLC (Hewlett Packard 1090 Series) with a Chiralcel OD-H column.

3.2 Synthesis of (S)-3-(3-Triethoxysily)propoxy methyl-2,2′-bis(methoxymethy)-1,1′-binaphthol (S)-**2a**

A solution of compound **1a** (*S*)-3-hydroxymethyl-2,2′-bis(methoxymethy)-1,1′- binaphthol (4.04 g, 10 mmol) in anhydrous THF (50 mL) was added with NaH (0.83 g, 20 mmol, 60% dispersion in mineral oil) with constant stirring. The mixture was stirred for 2 h at 70–80 °C, then 3-chloropropyltriethoxysilane (5.06 mL, 20 mmol) was added dropwise into the mixture within 15 min. After stirring under constant temperature for 6 h, the mixture was cooled to room temperature and filtered. Organic solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (ethyl acetate/petroleum ether (v/v), 1/10) to obtain (*S*)-**2a** as pale yellow oil (4.86 g, 84%). $[\alpha]_{D}^{20} + 28.8$ (*c* 0.448, CH$_2$Cl$_2$); ^{1}H NMR (CDCl$_3$): δ = 8.14 (s, 1H), 7.99 (d, *J* = 9 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.61(d, *J* = 9.0 Hz, 1H), 7.37–7.46 (m, 2H), 7.18–7.32 (m, 4H), 5.27 (s, 2H), 5.15 (d, *J* = 6.9 Hz, 1H), 5.05 (d, *J* = 6.9 Hz, 1H), 4.66 (d, *J* = 5.4 Hz, 1H), 4.55 (d, *J* = 5.6 Hz, 1H), 3.95 (q, 6H), 3.61 (t, 2H), 3.19 (s, 3H), 2.99 (s, 3H), 2.05 (m, 2H), 1.27 (t, 9H), 0.93 (t, 2H); ^{13}C NMR (CDCl$_3$): δ = 152.86, 151.40, 133.97, 133.81, 133.16, 130.94, 129.83, 129.67, 127.91, 127.86, 126.68, 126.44, 125.79, 125.63, 125.50, 124.88, 124.80, 124.14, 120.72, 116.55, 99.12, 94.92, 60.71, 58.68, 56.61, 55.90, 47.45, 26.51, 18.33, 8.11 ppm; ^{29}Si NMR (CDCl$_3$): −45.44 ppm; IR (KBr disk): v = 2972, 2890, 1624, 1594, 1508, 1358, 1246, 1151, 1083, 1012, 976, 749 cm^{-1}; ESI-MS: m/z 609.2 (M + 1); Anal. Found: C, 66.87; H, 7.65; Si, 4.23%; Calc. for C$_{34}$H$_{44}$O$_8$Si: C, 67.11; H, 7.24; Si, 4.61%.

3.3 Synthesis of (S)-3,3′-Di[(3-triethoxysilyl)propoxy methyl]-2,2′-bis(methoxymethy)-1,1′-binaphthol (S)-**2b**

A solution of Compound **1b** (*S*)-3,3′-di(hydroxymethyl)-2,2′-bis(methoxymethy)-1,1′- binaphthol (4.34 g, 10 mmol) in anhydrous THF (50 mL) was added with NaH (1.66 g, 40 mmol, 60% dispersion in mineral oil) with continuous stirring. This time, the mixture was stirred for 4 h at 70–80 °C, then 3-chloropropyltriethoxysilane (10.1 mL, 40 mmol) was added dropwise into the concoction within 30 min. After stirring at a steady temperature for 12 h, the mixture was cooled to room temperature and filtered. Organic solvent was removed under reduced pressure and the residue was purified by flash column chromatography (ethyl acetate/petroleum ether (v/v), 1/5) to obtain (*S*)-**2b** as pale yellow oil (5.22 g, 62%). $[\alpha]_{D}^{20}$ 61.1 (*c* 0.458, CH$_2$Cl$_2$); ^{1}H NMR (CDCl$_3$): δ = 8.07 (s, 2H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.11–7.18 (m, 4H), 5.14 (s, 4H), 4.30 (d, 2H), 4.39 (d, 2H), 3.79 (q, 12H), 3.40 (t, 4H), 2.84 (s, 6H), 2.05 (m, 4H), 1.17 (t, 18H), 0.89 (t, 4H); ^{13}C NMR (CDCl$_3$): δ = 151.63, 133.98, 133.37, 132.34, 130.83, 127.99, 126.04, 125.01, 124.68, 120.54, 99.22, 60.63, 58.32, 56.60, 47.42, 26.50, 18.21, 8.07 ppm; ^{29}Si NMR (CDCl$_3$): −45.03 ppm; IR (KBr disk): v = 2973, 2890, 1624, 1594, 1508, 1358, 1246, 1152, 1084, 1012, 976, 769, 749 cm^{-1}; ESI-MS: m/z 843.4 (M + 1), 797.4 (M–OCH$_2$CH$_3$); Anal. Found: C, 62.34; H, 8.23; Si, 6.35%; Calc. for C$_{44}$H$_{66}$O$_{12}$Si$_2$: C, 62.71; H, 7.84; Si, 6.65%.

3.4 Synthesis of (S)-6-(3-Triethoxysily)propoxy methyl-2,2′-bis(methoxymethy)-1,1′-binaphthol (S)-**2c**

A solution of compound (*S*)-**1c** (S)-6-hydroxymethyl-2,2′-bis(methoxymethy)-1,1′- binaphthol (3.23 g, 8 mmol) in anhydrous THF (40 mL) was added with NaH (0.66 g, 16 mmol, 60% dispersion in mineral oil) with incessant stirring. The mixture was stirred for 2 h at 70–80 °C, then 3-chloropropyltriethoxysilane (4.05 mL, 16 mmol) was added dropwise into the mixture in 15 min. The concoction was constantly mixed under an even temperature for 6 h, the mixture was cooled to room temperature and filtered. Organic solvent was removed under reduced pressure and the residue was purified by flash column chromatography (ethyl acetate/petroleum ether (v/v), 1/10) to obtain (*S*)-**2c** as pale yellow oil (3.81 g, 82%). $[\alpha]_{D}^{20}$ −61.0 (*c* 0.426,

CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 7.99$ (d, $J = 3.8$ Hz, 1H), 7.96 (d, $J = 3.8$ Hz, 1H), 7.92 (d, $J = 3.8$ Hz, 1H), 7.89 (s, 1H), 7.63 (d, $J = 1.3$ Hz, 1H), 7.60 (d, $J = 1.4$ Hz, 1H), 7.38 (t, $J = 6.8$ Hz, 1H), $7.15 - 7.28$ (m, 4H), 5.12 (d, 1H), 5.10 (d, 1H), 5.01 (d, 2H), 4.84 (s, 2H), 3.81 (q, 6H), 3.48 (t, 2H), 3.18 (s, 3H), 3.15(s, 3H), 1.88 (m, 2H), 1.25(t, 9H), 0.87 (t, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 153.01$, 152.63, 135.89, 133.73, 133.30, 131.41, 129.68, 129.51, 129.39, 129.29, 127.47, 126.41, 125.96, 125.60, 125.47, 125.15, 121.23, 121.01,117.58, 117.45, 99.22, 95.12, 66.38, 64.65, 58.47, 55.77, 47.39, 26.39, 18.21, 8.04 ppm; ^{29}Si NMR ($CDCl_3$): -45.69 ppm; IR (KBr disk): $v = 2972$, 2890, 1594, 1508, 1358, 1263, 1246, 1152, 1083, 1012, 976, 812, 749 cm^{-1}; ESI-MS: m/z 609.2 (M + 1); Anal. Found: C, 66.95; H, 7.54; Si 4.33%; Calc.for $C_{34}H_{44}O_8Si$: C, 67.11; H, 7.24; Si, 4.61%.

3.5 Synthesis of (S)-6,6′-Di[(3-triethoxysilyl)propoxy methyl]-2,2′-bis(methoxymethy)-1,1′-binaphthol (S)-**2d**

A solution of Compound (*S*)-**1d** (*S*)-6,6′-di(hydroxymethyl)-2,2′-bis(methoxymethy)-1,1′-binaphthol (4.34 g, 10 mmol) in anhydrous THF (50 mL) was added with NaH (1.66 g, 40 mmol, 60% dispersion in mineral oil) with continuous stirring. The mixture was stirred for 4 h at 70–80 °C, then 3-chloropropyltriethoxysilane (10.1 mL, 40 mmol) was added by dropping into the mixture within 30 min. After stirring under continual temperature for 12 h, the mixture was cooled to room temperature and filtered. Organic solvent was removed under reduced pressure and the residue was purified by flash column chromatography (ethyl acetate/petroleum ether (v/v), 1/5) to obtain (*S*)-**2d** as pale yellow oil (5.64 g, 67%). $[\alpha]_{D}^{20}$ −28.2 (*c* 0.216, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 7.96$ (d, $J = 4.2$ Hz, 2H), 7.84 (s, 2H), 7.58 (d, $J = 9$ Hz, 2H), 7.21(dd, $J = 8.0$ and 1.2 Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 5.07 (d, 2H), 4.97 (d, 2H), 4.96 (s, 4H), 3.86 (q, 12H), 3.50 (t, 4H), 3.16 (s, 6H), 1.86 (m, 4H), 1.19 (t, 18H), 0.79 (t, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 152.63$, 135.87, 133.37, 129.70, 129.29, 125.71, 125.43, 125.14, 121.30, 117.51, 95.24, 64.60, 58.47, 55.77, 47.39, 26.40, 18.23, 8.06 ppm; ^{29}Si NMR ($CDCl_3$): -45.70 ppm; IR (KBr disk) $v = 2973$, 2925, 2890, 2831, 1944, 1624, 1594, 1509, 1358, 1246, 1150, 1084, 1041, 1012, 976, 812, 769, 749 cm^{-1}; ESI-MS: m/z 843.4 (M + 1); Anal. Found: C, 62.45; H, 8.14; Si, 6.28%; Calc.for $C_{44}H_{66}O_{12}Si_2$: C, 62.71; H, 7.84; Si, 6.65%.

3.6 General Procedure for the Synthesis of (S)-BINOL Functionalized Silica/SBA-15 **3a**, **3b**, **3c**, **3d** and **3e**

Four portions of SBA-15/Silica (freshly activated at 150 °C) (1.0 g) were added to the anhydrous toluene solution of 1.0 g **2a**, **2b**, **2c** and **2d** respectively, and the mixture was stirred under reflux temperature with nitrogen atmosphere for 48 h. After cooling, the powder was collected by filtration, washed successively with dry toluene and dichloromethane. After drying under vacuum, the solids were subjected to Soxhlet-extraction with dichloromethane for 24 h. Finally the resulting 2,2′-bis(methoxy methy)-1,1′-bi- naphthalene supported samples were dried under vacuum at 70–80 °C. 1.0 g were taken in anhydrous pyridine (10 mL) and $(AcO)_2O$ (1 mL, 9.0 mmol) was added by dropping with continuous stirring. The mixture was stirred for an additional 24 h at rt. The resulting solids were filtered off, washed successively with pyridine, dried with dichloromethane and finally subjected to Soxhlet-extraction with dichloromethane for 24 h. Vacuum dried samples were produced at 50 °C for 10 h, they were deposited in 15 mL dichloromethane. Bu_4NBr (0.64 g, 2 mmol) and $(CH_3)_3SiCl$ (0.28 g, 2.5 mmol) were added to be stirred for an additional 24 h at rt. After being filtered off, washed with CH_2Cl_2 and subjected to Soxhlet-extraction with THF for 24 h, the samples were finally dried under vacuum at 80 °C. Henceforth, denoted as 3BSBA-15 **3a**, 33BSBA-15 **3b**, 6BSBA-15 **3c**, 66BSBA-15 **3d** and 3BSiO2 **3e**, respectively. The loading of these chiral BINOL functionalized silicas were calculated from elemental analysis.

3.7 Preparation of Supported Complex Catalyst **3BSBA-15-Ca 3f**

To a solution of **3BSBA-15** (0.5 g, 0.24 mmol) in anhydrous ethanol (10 mL) was added t-BuOK (58 mg, 0.48 mmol) at room temperature under argon atmosphere. After stirring for 2 h, the ethanol was evaporated under reduced pressure and the residue solid was added anhydrous $CaCl_2$ (29 mg, 0.24 mmol). After a few minutes, the mixture was dried under vacuum and followed by again addition of anhydrous EtOH (10 mL) resulted in the formation of white suspension, which was stirred for 4 h at ambient temperature. Subsequent evaporation of ethanol under vacuum produced a white solid powder, toluene (10 mL) was added under argon atmosphere, mixed for 12 h at ambient temperature, evaporation of it resulted in complex catalyst **3BSBA-15-Ca 3f** at last.

3.8 General Procedure for Enantioselective Morita-Baylis-Hillman Reaction of 3-Phenylpropionaldehyde with 2-Cyclohexen-1-One under 20 mol% PBu_3

An oven-dried 10 mL flask was charged with catalyst **3a** (104 mg, 0.05 mmol, 0.48 mmol/g) under nitrogen atmosphere. The catalyst was dissolved in THF (2.0 mL), 2-Cyclohexen-1-one (48 mg, 0.5 mmol), 3-phenylpropionaldehyde (121 mg, 0.9 mmol), and n-tributylphosphane (20.2 mg, 0.1 mmol, 20 mol%) were added successively at room temperature. After the flask was constantly stirred for 72 hs, the catalyst 3a was filtered and the reaction mixture was subjected to flash chromatography on silica gel and eluted with petroleum ether and ethyl acetate (5:1) to afford (*R*)-2-(1-hydroxy-3-phenylpropyl)- cyclohex-2-enone (101 mg, 0.44 mmol, 88% yield) as a colorless oil which was determined to be 23% e.e. by chiral HPLC analysis (Chiralcel OD-H, 9:1 hexanes: *i*-PrOH, 1 mL/min, *t*r(minor) = 10.4 min, *t*r(major) = 13.0 min). $[\alpha]_D^{20} = +9.6$ (*c* 1.05, $CHCl_3$) characterization and spectroscopic data was in agreement with literature values [51].

3.9 Recycled Process for Enantioselective Morita-Baylis-Hillman Reaction of 3-Phenylpropion Aldehyde and 2-Cyclohexen-1-One using **3a**, **3f** and 10 mol% PBu_3

The catalyst **3a** or **3f** was effortlessly separated by filtration after its first thorough employment with THF, dried in vacuum and subjected to another cycle of test with fresh reaction mixture under similar reaction conditions. An oven-dried 10 mL flask was charged with reused catalyst **3a** or **3f** under nitrogen atmosphere which was dissolved in THF (2.0 mL), 2-Cyclohexen-1-one (48 mg, 0.5 mmol), 3-phenylpropionaldehyde (121 mg, 0.9 mmol), and n-tributylphosphane (10.1 mg, 0.05 mmol, 10 mol%) were mixed successively at room temperature. After it was stirred for 72 h in a flask, the reused catalyst **3a** or **3f** was filtered and the reaction mixture was subjected directly to flash chromatography on silica gel, and eluted with petroleum ether and ethyl acetate (5:1) to afford (*R*)-2-(1-hydroxy-3-phenylpropyl)-cyclohex-2-enone (98 mg, 0.44 mmol, 85% yield) as a colorless oil which was determined to be 24% e.e. by chiral HPLC analysis.

4 Conclusions

A series of pure chiral organosiliane derivatives of (S)-BINOL **2a**, **2b**, **2c** and **2d** substituted at different positions of binaphthyl backbone have been synthesized conveniently and immobilized on mesoporous silica SBA-15 and amorphous silica gel. The resulting chiral BINOL functionalized silicas were then used as asymmetric Brønsted acids to catalyze enantioselective Morita-Baylis-Hillman reaction of 3-phenylpropanal and cyclohexenone with tributylphosphane as Lewis base. The easily achieved chiral BINOL functionalized silica **3BSBA-15** linked at 3-position of binathphyl backbone has shown higher e.e. of 26% and yield of 88% than the others, namely, **6BSBA-15**, **66BSBA-15**, **33BSBA-15** linked at 6, 6,6′ and 3,3′ positions. Its catalytic properties in enantioselectivity and yield were analogous with that of homogeneous catalyst (*S*)-BINOL. While complex of chiral BINOL functionalized silica **3BSBA-15-Ca** was used as chiral Lewis acid to catalyze this reaction, e.e. value of the product was lower (21%) than that of its homegenous catalyst (*S*)-BINOL-Ca (32%). These results imply that chiral BINOL functionalized mesoporous silicas can serve as a good candidate of organocatalysts which are better than its corresponding complex of calcium for this reaction. Catalysts **3BSBA-15** and **3BSBA-15-Ca** were recycled and there was no significant decrease in enantioselectivity and yield.

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