Asymmetric addition of diethylzinc to benzaldehyde catalyzed by silica-immobilized titanium(IV) complexes of *N*-sulfonylated amino alcohols

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Abstract

A chiral (1*R*,2*S*)-2-(*p*-toluenesulfonylamino)-1,3-diphenyl-1-propanol derived catalyst was synthesized and successfully grafted onto amorphous silica gel and mesoporous silica (MCM-41) by a facile approach. This is the first use of silica-immobilized titanium(IV) complexes of *N*-sulfonylated amino alcohols for the asymmetric addition of diethylzinc to benzaldehyde with good enantioselectivity (80% e.e.). Particularly, after readily recoverble procedure, the catalyst was able to be reused in multiple catalytic runs (up to 10 times) without loss of enantioselectivity.
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1. Introduction

The asymmetric addition of dialkylzinc to aldehydes, one of the most important asymmetric catalytic reactions, has been studied extensively in the past decade [1]. In recent years, focus of this reaction has shifted from the homogenous system to the heterogeneous one, which has the advantages of easy handling, separation and facilitation of industrial application. Numerous works have described the synthesis of polymer supported amino alcohols with good results in the reaction of asymmetric addition of dialkylzinc to aldehydes [2]. However, there have been far fewer reports on the uses of inorganic supported catalysts, especially silica gel supported ligands and the reported yields and enantioselectivity were generally poor [3]. Until recently, Pericàs [4a] and Hyeon [4b] reported the use of silica-immobilized chiral amino alcohol for this addition, and both of them treated their immobilized ligands with BuLi to afford the good enantioselectiveity. (75% and 77% e.e.).

It has been reported that Ti(IV) accelerates the asymmetric addition of dialkylzinc to aldehydes with excellent yields and e.e. values [5]. Commonly, Ti(IV) complexes of some chiral ligands, such as chiral diols [6], BINOL [7], disulfonamides [8] and *N*-sulfonylated amino alcohols [9], are effective for this catalytic reaction. Seebach and his co-workers successfully used controlled pore glass-bound Ti-TADDOLates for this addition with excellent e.e. values [10]. In this paper, we describe the synthesis of [(1*R*,2*S*)-2-(*p*-toluenesulfonylamino)-1,3-diphenyl-1-propanol]-derived catalyst **4**, and its successful immobilization on amorphous silica gel and mesoporous silica of MCM-41. To the best of our knowledge, this is the first use of Ti(O-*i*-Pr)$_4$ and the silica immobilized sulfonylated amino alcohol together for the asymmetric addition of diethylzinc to benzaldehyde.

2. Experimental

2.1. Materials and analytical methods

Amorphous silica gel (200–400 mesh) and mesoporous silica (MCM-41) were subjected to heat treatment at 150 °C for 3 h and cooled under nitrogen prior to use. Dichloromethane was freshly distilled from phosphorous pentoxide. Toluene, hexane and tetrahydrofuran were freshly distilled from a deep-blue solution of sodium-benzophenone under nitrogen. Titanium isopropoxide was distilled under nitrogen prior to use. Diethylzinc (1 M solution in hexane) was purchased from Acros and

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diethylzinc (1 M solution in dichloromethane) was synthesized according to the literature method [11]. Benzaldehyde was distilled from magnesium sulfate under nitrogen. All catalytic asymmetric addition reactions were carried out under nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury-plus 400 BB with TMS as internal standard. HRMS data were measured with ESI techniques (Bruker Apex II). FT-IR spectra were performed on Nicolet Nexus 670. Elemental analyses were performed on Elementar Vario EL. The pore sizes and surface areas were determined on a Micromeritics ASAP 2010 system. Optical rotation value was measured on a Perkin-Elmer 341 polarimeter. Enantiomeric excess was determined by HPLC (Hewlett Packard 1090 Series) with a Chiralcel OD-H column.

2.2. Synthesis of ligands

2.2.1. Synthesis of (1R,2S)-4

The compound of (1R,2S)-**2** (0.341 g, 1.5 mmol) and triethylamine (0.39 mL) were dissolved in CH_2Cl_2 (19.5 mL), and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilzne (**3**) (0.488 g, 1.5 mmol) in CH_2Cl_2 (19.5 mL) was added dropwise at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. After washed sequentially with 5% $NaHCO_3$ aqueous solution and saturated brine, respectively, the mixture was dried using anhydrous $MgSO_4$. After filtration, the organic solvent was concentrated under vacuum to afford white solid (1R,2S)-**4** (0.687 g, 1.3 mmol) in 89% yield. m.p. 53–55 °C. $[\alpha]_D^{14}$-5 (c = 1.1, CH_2Cl_2). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.87–0.92 (m, 2 H), 2.44 (dd, 1 H, J = 14.2, 10.2 Hz), 2.55 (dd, 1 H, J = 14.6, 4.2 Hz), 2.64–2.67 (m, 2 H), 2.91 (br, 1 H), 3.55 (s, 9 H), 3.47–3.58 (m, 1 H), 4.57 (d, 1 H, J = 7.6 Hz), 5.00 (d, 1 H, J = 2.8 Hz), 6.71–7.31 (m, 14 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 11.0, 28.7, 34.6, 50.6, 61.0, 75.0, 126.2, 126.5, 127.0, 127.8, 128.3, 128.4, 128.5, 129.1, 136.8, 136.9, 140.1, 149.4. IR (KBr): 3466, 3293, 3061, 3028, 2938, 2842, 1600, 1496, 1453, 1411, 1327, 1192, 1155, 1089 cm^{-1}. HRMS (ESI)—m/z calcd. for $C_{26}H_{33}NO_6SSi$: 538.1690 [M + Na]; found 538.1680 [M + Na]. Anal. calcd. for $C_{26}H_{33}NO_6SSi$ (%): C, 60.56; H, 6.45; N, 2.72. Found: C, 60.92; H, 6.77; N, 2.42.

2.2.2. General procedure for the synthesis of immobilized ligands 5a and 5b

The compound (1R,2S)-**4** (0.8 mmol) in CH_2Cl_2 (4 mL) was added to the suspension of pre-dried silica (1.3 g) in anhydrous toluene by syringe under nitrogen. The resulting suspension was heated under refluxing for 6 h and a tolene/methanol mixture (about 10 mL) was distilled off. The same volume of toluene was added and the heating and distillation were repeated twice. After filtration, the white solid was washed using toluene (50 mL) and the mixture of CH_2Cl_2 and CH_3OH (1:1, 50 mL). Then the solid was suspended in the mixture solvent ($CH_2Cl_2:CH_3OH = 1:1$, 50 mL) and stirred for 2 h. After filtration and thorough wash with the mixture solvent ($CH_2Cl_2:CH_3OH = 1:1$, 50 mL) and CH_3OH (50 mL), the solid was dried at 50 °C in vacuo for 24 h to give the immobilized ligands **5a** and **5b**.

- Ligand **5a**—IR (KBr): 3442, 2941, 2844, 1633, 1494, 1098, 959, 808, 703, 469 cm^{-1}. Anal. found: C 11.16, H 1.46, N 0.48. Average pore diameter: 8.01 nm. S_{BET}: 301 m^2/g.
- Ligand **5b**—IR (KBr): 3434, 2981, 2933, 2844, 1634, 1454, 1075, 955, 805, 703, 561, 460 cm^{-1}. Anal. found: C 16.65, H 2.00, N 0.39. Average pore diameter: 1.99 nm. S_{BET}: 1056 m^2/g.

2.2.3. Synthesis of compound 6

2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane (**3**) (0.4 mmol) in CH_2Cl_2 (2 mL) was added to the suspension of pre-dried amorphous silica (0.618 g) in anhydrous toluene by syringe under nitrogen. The resulting suspension was heated under refluxing for 6 h and a tolene/methanol mixture (about 5 mL) was distilled off. The same volume of toluene was added and the heating and distillation were repeated twice. After filtration, the white solid was washed with toluene (50 mL), mixture solvent of CH_2Cl_2 and CH_3OH (1:1, 50 mL). Then the solid was suspended in the mixture solvent ($CH_2Cl_2:CH_3OH = 1:1$, 50 mL) and stirred for 2 h. After filtration and thorough wash with the mixture solvent ($CH_2Cl_2:CH_3OH = 1:1$, 50 mL) and CH_3OH (50 mL), the solid was dried at 50 °C in vacuo for 24 h to give the immobilized compound **6**. IR (KBr): 3431, 2919, 1623, 1101, 804, 577, 468 cm^{-1}. Anal. found: C 6.04, H 0.88.

2.2.4. Synthesis of compound 7

The suspension of compound **6** (0.702 g) in HMDS (30 mL) under nitrogen was heated under rufluxing for 12 h. After filtration, the whitish-brown solid was washed with toluene (25 mL) and $CH_2Cl_2:CH_3OH$ (1:1, 50 mL). Then the solid was suspended in $CH_2Cl_2:CH_3OH$ (1:1, 30 mL) and stirred for 2 h. After filtration and thorough wash with CH_3OH (50 mL), the solid was dried at 50 °C in vacuo for 24 h to give the immobilized compound **7**. IR (KBr): 3424, 2934, 2852, 1622, 1542, 1446, 1397, 1102, 802, 628, 470 cm^{-1}. Anal. found: C 9.10, H 1.43.

2.2.5. Synthesis of ligand 8

(1R,2S)-**2** (0.36 mmol) and triethylamine (1 mL) in CH_2Cl_2 (10 mL) was added to the suspension of compound **7** in CH_2Cl_2 (10 mL) by a syringe under nitrogen. The resulting suspension was heated under refluxing for 12 h. After filtration and thorough wash with CH_2Cl_2 (100 mL) and CH_3OH (100 mL), the whitish-brown solid was dried at 50 °C in vacuo for 24 h to give the immobilized ligand **8**. IR (KBr): 3440, 2964, 1631, 1099, 847, 808, 760, 701, 468 cm^{-1}. Anal. found: C 11.23, H 1.47, N 0.16. Average pore diameter: 7.40 nm. S_{BET}: 279 m^2/g.

2.2.6. General procedure for asymmetric addition of diethylzinc to benzaldehyde

To a suspension of the ligand (required amount for 0.05 mmol sulfonylated amino alcohol) in anhydrous dichloromethane (1.5 mL) under nitroden at room temperature, was added Ti(O-i-Pr)$_4$ (Fig. 1) and the mixture was stirred for 0.5 h. After removal the solvent under vacuo for 2.5 h, fresh dichloromethane (1.5 mL) was added and stirred for 10 min. Another part of Ti(O-i-Pr)$_4$ (150 μL, 0.5 mmol) was added and stirred for 1 h. Then diethylzinc (1.0 M solution in hexane or 1.0 M solution in
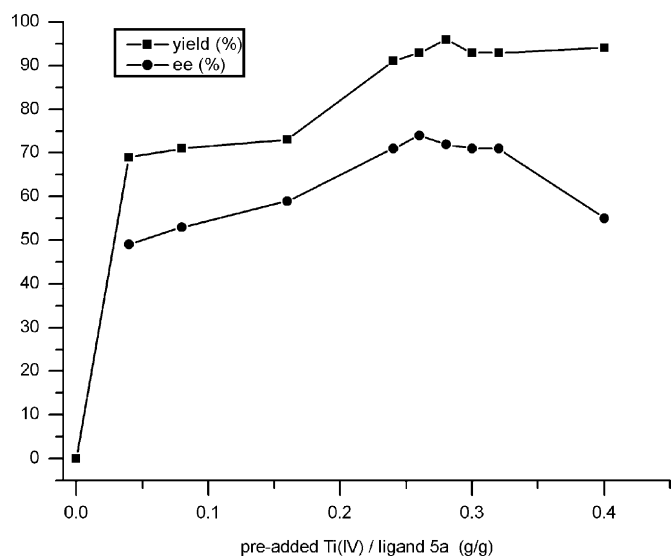
Fig. 1. Effect of amount of pre-added titanium on asymmetric addition of diethylzinc to benzaldehyde catalyzed by silica-immobilized **5a**.

CH_2Cl_2) was added at 0 °C and stirred for 0.5 h. Benzaldehyde (50 μL, 0.5 mmol) was added and the mixture was stirred at 0 °C for 12 h. The reaction was quenched by 1 M HCl and extracted by EA (3× 10 mL). The organic layer was combined, dried and concentrated. The crude product was passed through a short column (silica gel; eluent, PE:EA = 4/1) to afford the *sec*-alcohol.

The e.e. values were determined by HPLC with Chiralcel OD-H column.

2.2.7. General procedure for the restoration of silica-immobilized catalyst

After one catalytic cycle, the silica-immobilized catalyst was washed sequentially with 1 M HCl (30 mL), H_2O (15 mL), MeOH (15 mL), mixture of MeOH and CH_2Cl_2 (1:1, 30 mL), MeOH (30 mL), and dried under vacuum at 50 °C for 18 h. The catalyst could be used for the next catalytic cycle.

3. Results and discussion

The synthetic procedure for various silica-immobilized ligands is shown in Scheme 1. The reaction of (1*R*,2*S*)-2-amino-1,3-diphenyl-1-propanol (**2**), synthesized from (L)-phenylalanine by a literature method [12], with commercially available 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (**3**) yielded *N*-sulfonylated amino alcohol **4**. Ligand **4** was immobilized on amorphous silica gel and MCM-41 by refluxing in toluene to afford the organic-inorganic hybrid ligands **5a** and **5b**. It has been reported that the free hydroxy groups on the silica surface are also able to promote the addition [3c], and therefore is responsible for the null enantioselectivity [4b]. In order to cap the remaining free silanol sites on the walls of amorphous silica, ligand **6** was treated with hexamethyldisiloxane (HMDS) for 12 h as depicted in Scheme 1.
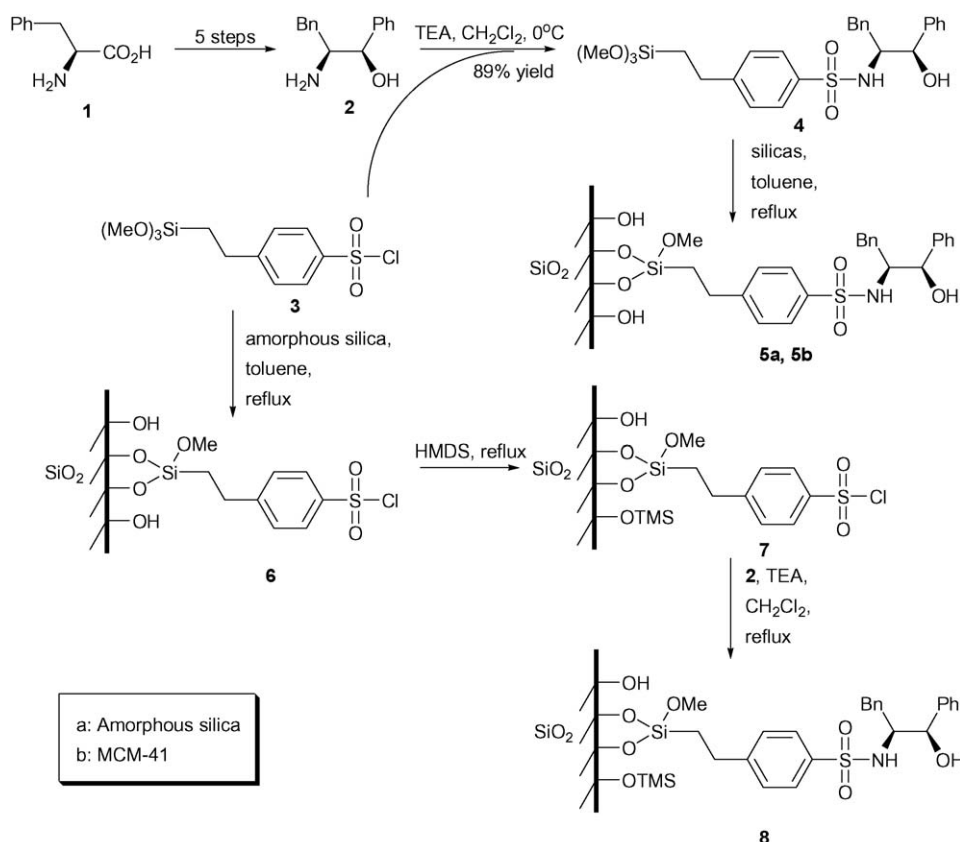
Scheme 1. Synthesis of the immobilized ligands **5a**, **5b** and modified ligand **8**.

Table 1

Characterization of silica-immobilized chiral ligands **5a**, **5b** and modified ligand **8**

Entry	Ligand	Surface area (m^2/g)[a]	Average pore diameter (nm)[a]	Content of **2** (mmol/g)[b]
1	**5a**	301	8.0	0.343
2	**5b**	1056	2.0	0.279
3	**8**	279	7.4	0.117

[a] The surface area and the average pore diameter were calculated by the BET method.

[b] Calculated from nitrogen analysis.

As can be seen from Table 1, mesoporous silica immobilized ligand **5b** presents larger surface area than ligand **5a** prepared from amorphous silica, but a lower content of functionalized amino alcohol groups. Ligand **8** has almost the same surface area and average pore size but a significantly lower immobilization ratio compared with ligand **5a**. The steric hindrance of the bulky TMS groups on the silica walls is likely the main reason for the lower content of sulfonylated amino alcohol.

Ligand **4** was first introduced in the asymmetric addition of diethylzinc to benzaldehyde. After optimization, ligand **4** (0.05 mmol), Ti(O-i-Pr)$_4$ (0.5 mmol), Et$_2$Zn (0.75 mmol, 1 M solution in hexane) and benzaldehyde (0.5 mmol) together yielded the (R)-1-phenylpropan-1-ol with 88% yield and 93% e.e. The same process was carried out using immobilized ligand **5a**, but no expected product was obtained (Fig. 1). It is known that Ti(IV) can form chelate complexes with not only sulfonylated amino alcohol but also silanol groups on the wall of catalysts [13]. In order to overcome this shortage of silica-immobilized ligands, we modified the procedure of this reaction by pre-addition of certain amount Ti(O-i-Pr)$_4$ into the suspension of **5a**, followed by solvent removal. The subsequent processes were the same as those catalyzed by ligand **4** [Ti(O-i-Pr)$_4$/Et$_2$Zn/PhCHO = 1/1.5/1] and the target product was obtained successfully. In view of the relevant role played by Ti(O-i-Pr)$_4$, we decided to explore the influence of the amount of pre-added Ti(O-i-Pr)$_4$ [14] on the results with ligand **5a** (Fig. 1). As can be seen from Fig. 1, the yields and e.e. values were increased rapidly with increasing amount of Ti(IV)/**5a**. The best e.e. value (74% e.e.) was obtained with pre-added Ti(IV)/**5a** of 0.26 g/g. Further increase in the amount of pre-added Ti(IV)/**5a** resulted in a decrease in e.e. However, the reaction yield (95%) remained about the same with the varying amount of pre-added Ti(IV). It is clear that the excessive amount of Ti(O-i-Pr)$_4$ promotes the addition of diethylzinc to benzaldehyde [13b]. The amount of pre-added Ti(IV)/**5a** of 0.26 was chosen for the subsequent studies.

The loading of the chiral ligand is a crucial factor affecting the catalytic activity in this reaction. After screening loadings of **5a** (0.149, 0.273 and 0.387 mmol/g), it was found that **5a** with 0.273 and 0.387 mmol/g sulfonylated amino alcohol presented the same catalytic activity (95% yields and 74% e.e.). However, the lower loading of chiral ligand (0.149 mmol/g) led to an increased portion of silanol groups on the surface which resulted in a lower enantioselectivity (89% yield and 63% e.e.). We chose **5a** with 0.387 mmol/g loading for further studies because the lig-

Table 2

Asymmetric addition of diethylzinc to benzaldehyde using titanium complex of silica-immobilized **5a**[a]
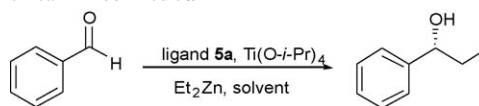
Entry	Solvent	Et$_2$Zn (equiv.)[b]	T (°C)	Yield (%)[c]	e.e. (%)[d]
1	CH$_2$Cl$_2$	1.5	0	95	74
2	CH$_2$Cl$_2$	1.7	0	96	76
3	Toluene	1.7	0	97	52
4	THF	1.7	0	75	6
5	Hexane	1.7	0	97	46
6	CH$_2$Cl$_2$	1.7[e]	0	98	80
7	CH$_2$Cl$_2$	1.7[e]	−15[f]	95	73
8	CH$_2$Cl$_2$	1.7[e]	r.t.	96	73

[a] PhCHO/Ti(O-i-Pr)$_4$/ligand = 1:1:0.1; reaction time: 12 h; pre-added Ti(IV): 26 wt.% of ligand **5a**.

[b] Et$_2$Zn (1 M solution in hexane).

[c] Isolated yield.

[d] Determined by HPLC with a Chiralcel OD-H colume.

[e] Et$_2$Zn (1 M solution in CH$_2$Cl$_2$).

[f] Reaction time: 16 h.

and with higher loadings needed a smaller amount of pre-added Ti(O-i-Pr)$_4$.

Further optimization studies were carried out as shown in Table 2. Increasing the amount of Et$_2$Zn from 1.5 to 1.7 equiv. afforded a slightly increased enantioselectivity (from 74% to 76% e.e.). Four solvents were examined and CH$_2$Cl$_2$ was found to be the best choice (entries 2–5). Obviously, solvents significantly affected the enantioselectivity. The volume of hexane which was introduced with Et$_2$Zn (1 M solution in hexane) led to a decrease in enantioselectivity. We then prepared a 1 M solution of Et$_2$Zn in CH$_2$Cl$_2$ and successfully introduced it into the reaction to obtain the best e.e. value (80% e.e.) (entry 6). The reaction was carried out at −15 °C and ambient temperature (entries 7 and 8). Much to our surprise, temperature effect was not obvious on either the yields or enantioselectivity.

As shown in Table 3, ligand **5b** presented poor catalytic activity (86% yield) and significantly lower enantioselectivity (55% e.e.) (entry 2). To further improve the enantioselectivity in this

Table 3

Asymmetric addition of diethylzinc to benzaldehyde using various catalysts[a]
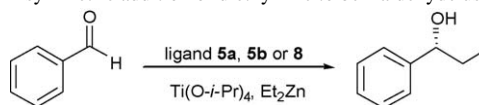
Entry	Ligand	Pre-added Ti(IV) (wt.% of ligand)[b]	Yield (%)[c]	e.e. (%)[d]
1	**5a**	26	98	80
2	**5b**	26	86	55
3	**8**	20	93	68

[a] PhCHO/Ti(O-i-Pr)$_4$/Et$_2$Zn/ligand = 1:1:1.7:0.1; Et$_2$Zn (1 M solution in CH$_2$Cl$_2$); reaction temperature: 0 °C; solvent: CH$_2$Cl$_2$; reaction time: 12 h.

[b] Pre-added Ti(IV) refer to Ti(O-i-Pr)$_4$.

[c] Isolated yield.

[d] Determined by HPLC with a Chiralcel OD-H colume.

Table 4

Reusability of silica-immobilized catalyst **5a** for the asymmetric addition of diethylzinc to benzaldehyde[a]
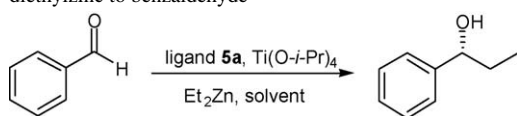
Entry	Run	Yield (%)[b]	e.e. (%)[c]
1	1	97	80
2	2	96	80
3	3	97	79
4	4	97	79
5	5	96	80
6	6	96	80
7	7	95	80
8	8	97	79
9	9	96	80
10	10	95	79

[a] After the general procedure of asymmetric addition, silica-immobilized ligand **5a** was washed sequentially with 1 M HCl (30 mL), H_2O (30 mL), MeOH (30 mL), mixture of MeOH and CH_2Cl_2 (1:1 30 mL) and MeOH (30 mL), then dried under vacuum at 50 °C for 18 h before reusability.

[b] Isolated yield.

[c] Determined by HPLC with a Chiralcel OD-H column.

reaction, modified ligand **8** was used but only 68% e.e. value was obtained (entry 3).

Compared with homogeneous catalytic systems, one of the most advantages for the heterogeneous catalysis is its reusability in the catalytic reaction. For this reason, we also tested the reusability of ligand **5a**. After one catalytic cycle, ligand **5a** can be recovered, and dried for the next catalytic cycle. After 10 runs, the enantioselectivities observed were as good as in the beginning (Table 4).

4. Conclusion

In summary, we report for the first time the use of silica-immobilized Ti(IV) complexes of *N*-sulfonylated amino alcohols as a catalyst for the asymmetric addition of diethylzinc to benzaldehyde. A good yield and enantioselectivity were successfully obtained through a series of optimization studies. The use of titanium tetraisopropoxide is necessary to obtain high yields and enantioselectivity for this silica-immobilized catalytic system. After the restoring procedure, silica-immobilized catalyst can be used in multiple runs (up to 10 times) without loss of enantioselectivity.

Acknowledgements

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