Preparation of Polymer-Supported Chiral 1,2-Diamine as an Efficient Ligand for Asymmetric Hydrogenation Catalyst

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Summary: An enantiopure 1,2-diamine having two phenolic hydroxy groups was synthesized, and attached to chloromethylated poly(styrene) through a benzyl ether linkage. The polymer-supported Ru precatalysts were prepared from the polymeric chiral 1,2-diamine and $RuCl_2$/BINAP complex. In the presence of *t*-BuOK the polymeric catalyst system worked well in asymmetric hydrogenation of aromatic ketones in a mixed solvent of 2-propanol and DMF. The insoluble polymeric catalyst was readily separated from the reaction mixture and reused at least several times without loss of the catalytic activity.

Keywords: asymmetric hydrogenation; 1,2-diamine; ketone; polymer-support

Introduction

Recently enantiopure 1,2-diamines and their derivatives[1] have attracted much attention as efficient chiral auxiliary in various kinds of chiral catalysts and reagents. For example, asymmetric reactions in which chiral 1,2-diamines takes part include hydrogenation of simple nonfunctionalized ketones with $RuCl_2$/diphosphine/1,2-diamine/alkaline base catalysts.[2] Chiral salene-metal complexes are also composed of a chiral 1,2-diamine, and have been successfully used in various kinds of asymmetric transformations including epoxidation,[3, 4] ring opening of meso epoxide,[5] kinetic resolution of terminal epoxides,[5] aziridination,[6] cyclopropanation,[7] and borohydride reduction.[8] On the other hand, the cross-linked polymers offer a well-documented advantage in purification since separation of the chiral reaction product from the polymer-supported catalyst is simply achieved by filtration. The polymeric catalysts can be recycled many times. A large number of polymer-supported chiral ligands or auxiliaries for asymmetric reaction have been developed.[9] However, to our knowledge, there is no report on the immobilization of a chiral 1,2-diamine. Here, the development of the polymer-supported chiral 1,2-diamine-Ru-BINAP catalyst for the enantioselective hydrogenation of simple ketones is presented.[10]

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Experimental Part

General Method and Materials

All reactions were carried out under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was freshly distilled from calcium hydride under argon immediately before use. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under nitrogen. Ketones used were distilled from calcium hydride. Reactions were monitored by TLC using Merck Precoated silica-gel plates (Merck 5554, 60F254). Column chromatography was performed with a silica gel column (Wakogel C-200, 100-200 mesh).

Measurements

Melting points were determined on a Yanaco micromelting apparatus and are uncorrected. Optical rotations were measured on a JASCO-DIP-140 digital polarimeter using a 10 cm thermomtated microcell. Both ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were recorded on Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard, and *J* values are recorded in Hz. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). Elemental analyses were performed at the Microanalytical Center of Kyoto University. HPLC analyses were performed with a JASCO HPLC system composed of 3-line degasser DG-980-50, HPLC pump PV 980, column oven CO-965, equipped with a chiral column (Chiralcel OD, Daicel) using hexane/2-propanol as an eluent. A UV detector (JASCO UV-975) was used for the peak detection. GC analyses of reaction conversion were performed with a Shimadzu Capillary Gas Chromatograph 14A equipped with a capillary column (Astec Chiraldex G-TA, 30 m x 0.25 mm).

Synthesis of 2,2-spirocyclohexane-4,5-bis(*p*-methoxyphenyl)-2H-imidazole (2)

A 200 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 60 mL of glacial acetic acid, 10.5 g (38.8 mmol) of 4,4'-dimethoxybenzil, 29.9 g (0.39 mol) of ammonium acetate and 4.03 mL (38.8 mmol) of cyclohexanone. The mixture was stirred at reflux temperature for 1.5 h and then poured into 300 mL of vigorously stirred water.

The mixture was left overnight and extracted with ethyl acetate. The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by chromatography (benzene/ethylacetate = 6:1) to afford compound **2** (10.5 g, 77%). Mp 109-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, 4H, *J*=8.8 Hz, ArH), 6.87 (d, 4H, *J*=8.8 Hz, ArH), 3.83 (s, 6H, OCH_3), 2.00-1.65 (m, 10H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.8, 161.2, 130.7, 126.0, 113.9, 103.6, 55.5, 35.1, 26.0, 24.4.

Synthesis of 1,2-bis(*p*-methoxyphenyl)-1,2-diaminoethane (3)

A 300 mL three-necked, round-bottomed flask equipped with a magnetic stirring bar, thermometer and dry ice condenser was charged with 9.9 g (28.4 g) of **2**. The flask was flashed with argon, and 80 mL of THF was added. The mixture was stirred until all solids dissolved, cooled to –78 °C and treated with a stream of gaseous ammonia until the volume of liquid increased by about 80 mL. Lithium (0.79 g, 113 mmol) was slowly introduced by cutting the wire with a scissor in a gentle stream of argon. The rate of lithium addition was such that the temperature did not rise above –65 °C. Following the addition of lithium, the mixture was stirred for 30 min and 10 mL of ethanol was slowly added. The mixture was stirred for an additional 20 min and 13 g of ammonium chloride was added. The cooling bath was removed, the mixture was allowed to warm to 0 °C, 100 mL of water was carefully introduced, and the phases were separated. The aqueous phase was washed with diethyl ether and the combined organic extracts were washed with brine and concentrated. The residue was treated with 2N HCl and extracted with dichloromethane. Aqueous phase was neutralized with ammonium hydroxide and extracted with dichloromethane. The combined extracts were washed with brine, dried ($MgSO_4$) and filtered. Removal of volatile material under reduced pressure gave 6.2 g (80%) of racemic diamine. Mp 112-113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, 4H, *J*=8.7 Hz, ArH), 6.87 (d, 4H, *J*=8.7 Hz, ArH), 4.00 (s, 2H, CH), 3.83 (s, 6H, OCH_3), 1.55 (br s, 4H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.8, 128.2, 113.8, 55.4.

Optical resolution of 1,2-diamine 3

A 200 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 16.2 g (60 mmol) of the racemic 1,2-diamine **3** and 80 mL of ethanol. A hot (70 °C), homogeneous

solution of L-(+)-tartaric acid (8.9 g, 60 mmol) in ethanol (80 mL) was added dropwise to the diamine solution. The tartrate salts precipitated immediately, after the mixture was cooled to room temperature, the crystals were collected by filtration, washed with ethanol, and dried under reduced pressure. The obtained solid was dissolved in 75 mL of boiling water, 75 mL of ethanol was added and the homogeneous solution was allowed to cool slowly to room temperature. The crystals were collected by filtration, washed with ethanol and dried under reduced pressure. The recrystallization procedure was then repeated twice to give 8.4 g (34%) of the tartrate salt as colorless crystals.

The salt was transferred to a 500 mL round-bottomed flask and suspended in 150 mL of water. After the mixture was vigorously stirred and then cooled to 0-5 °C, 50 mL of 50% aqueous sodium hydroxide was added dropwise followed by 200 mL of dichloromethane, and stirring was continued for 30 min. The phases were separated, the aqueous phase was washed with dichloromethane and the combined organic extracts were washed with brine, dried ($MgSO_4$) and filtered. Removal of the volatile materials under reduced pressure gave 4.44 g (27%) of (*S*,*S*)-**3**, $[\alpha]_D$ 106.5° (*c* 1.0, CH_3OH). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, 4H, *J*=8.7 Hz, ArH), 6.87 (d, 4H, *J*=8.7 Hz, ArH), 4.00 (s, 2H, CH), 3.83 (s, 6H, OCH_3), 1.55 (br s, 4H, NH_2).

Synthesis of (*S*,*S*)-1,2-bis(*p*-hydroxyphenyl)-1,2-diaminoethane ((*S*,*S*)-5)

A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with (*S*,*S*)-**3** (1.0 g, 3.68 mmol) and 10 mL of dichloromethane. After the mixture was cooled to –78 °C, of BBr_3 (1N dichloromethane solution, 14.72 mL, 14.72 mmol) was added to the above mixture and stirred for 48 h at room temperature. The whole mixture was then evaporated to dryness. The corresponding HBr salt **4** (1.477 g, 99%) was obtained. Mp 240-241 °C. ^1H NMR (300 MHz, DMSO-d_6) δ: 9.70 (br s, 2H, OH), 8.60 (br s, 6H, NH_3), 7.01 (d, 4H, *J*=8.3 Hz, ArH), 6.67 (d, 4H, *J*=8.3 Hz, ArH), 4.70 (br s, 2H, CH). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 158.5, 130.6, 115.8, 57.1.

The HBr salt **4** was then dissolved in 20 mL of methanol and treated with cross-linked polymer-supported amine base (3.5 g, piperazine content = 4.2 mmol/g, 2% cross-link) for 24 h at room temperature. The polymeric base was removed by filtration and washed with methanol. Methanol was then evaporated and the obtained solid was dried in vacuo to give the desired free 1,2-diamine (*S*,*S*)-**5** (0.886 g, 99%). Mp 189-190 °C. $[\alpha]_D$–91.4° (*c* 1.0, MeOH). ^1H NMR (300

MHz, DMSO-d_6) δ: 6.95 (d, 4H, J=8.1 Hz, ArH), 6.55 (d, 4H, J=8.1 Hz, ArH), 3.94 (s, 2H, CH), 3.30-3.50 (br, 4H, NH_2). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 157.4, 129.5, 115.6, 59.9. Anal. Calcd for $C_{14}H_{16}N_2O_6$ C, 68.33; H, 6.60; N, 11.47, Found C, 68.25; H, 6.72; N, 11.51.

Synthesis of polymer-supported chiral 1,2-diamine 5P

A 50 mL round-bottomed flask equipped with magnetic stirring bar was charged with 1,2-diamine (*S*,*S*)-**5** (0.183 g, 0.75 mmol) and 10 mL of dry DMF. After addition of NaH (27 mg, 1.125 mmol) to the above mixture, 1 % cross-linked chloromethylated polystyrene beads (0.20 g, 1.75 meq Cl/g) was added and stirred slowly for 24 h at room temperature. The polymer was filtered and washed with water, ether and methanol and dried in vacuo for 24 h at 40 °C to give the polymer-supported 1,2-diamine (*S*,*S*)-**5Pc** (0.221 g). Calcd for $(C_8H_8)_{0.79}(C_{10}H_{10})_{0.01}(C_{32}H_{32}N_2O_4)_{0.10}$ C, 88.0; H, 7.39; N, 2.15. Found C, 88.0; H, 7.38; N, 2.14.

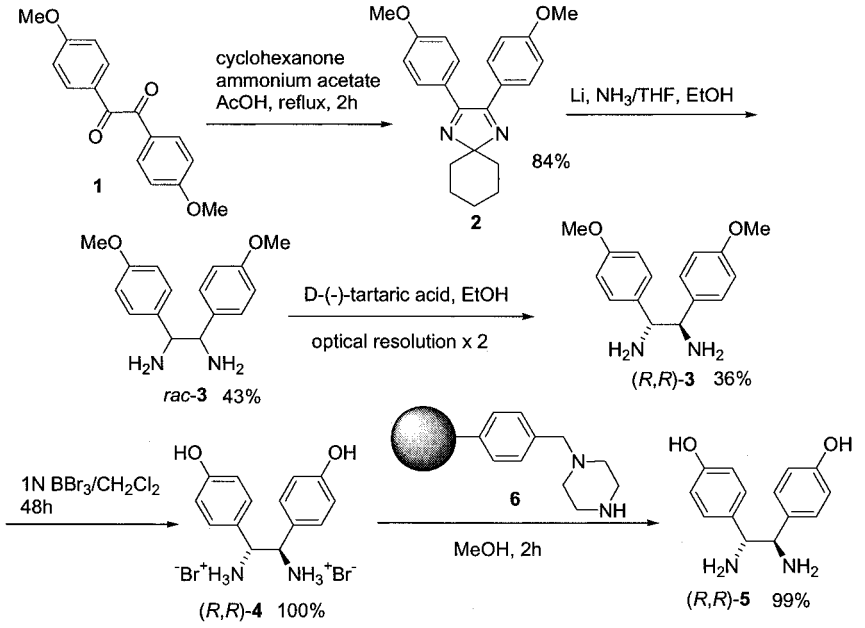
Asymmetric hydrogenation of acetophenone with polymeric catalyst prepared from (*S*,*S*)-5Pc

A 20 mL Schlenk vessel equipped with a Teflon-coated magnetic stirring bar was charged with polymer-supported chiral 1,2-diamine (*S*,*S*)-**5Pc** (29 mg, 0.025 mmol), $RuCl_2$/(*S*)-BINAP(dmf)$_n$ (23 mg, 0.025 mmol) and 2 mL of dry DMF. The above mixture was degassed and heated at 80 °C for 2.5 h. After removal of DMF under reduced pressure, the solid obtained was transferred to a 100 mL glass autoclave equipped with a pressure gauge and a gas inlet tube attached to a hydrogen source. Air present in the autoclave was replaced by argon. A solution of acetophenone (0.58 mL, 5 mmol) in a 1 : 1 mixture of 2-propanol (2 mL) and DMF (2 mL), and a 1.0 M *t*-BuOK solution in *t*-BuOH (0.1 mL), which had been degassed, were added to the autoclave. Hydrogen was then introduced into the autoclave and pressurized to 1 MPa. The reaction mixture was stirred for 1 h at room temperature. After carefully venting the hydrogen gas, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a glass filter equipped with silica gel. The solvent was removed under reduced pressure. The yield determined by GC was 100 %. Enantioselectivity of 1-phenylethanol was determined by HPLC analysis using chiral stationary phase (Chiralcel OD, Daicel): hexane/2-propanol = 20:1, flow rate, 0.4 mL/min, temp. 30 °C, $t_R(R)$ = 22.8 min, $t_R(S)$ = 25.9 min.

Results and Discussion

Synthesis of enantiopure diamine

Enantiopure 1,2-bis(*p*-hydroxyphenyl)-1,2-diaminoethane **5** was synthesized as shown in Scheme 1.[11] 4,4'-Dimethoxybenzil **1** was treated with cyclohexanone and ammonium acetate in acetic acid to give imidazole derivative **2**, which was subjected to Birch reduction to give the racemic 1,2-diamine **3**. This method yielded no *meso* isomer of **3**, which is contaminated by usual reductive coupling of aldimine derivatives[12] and must be removed before optical resolution. Optical resolution of the racemic 1,2-diamine **3** was efficiently performed by using tartaric acid. While (*R*,*R*)-**3** was obtained with D-tartaric acid, (*S*,*S*)-**3** was retrieved by treatment with L-tartaric acid, respectively. Enantiopurity of the 1,2-diamine was determined by means of chiral HPLC analysis of its *N*,*N*'-di-BOC (di-*tert*-butoxycarbonyl) derivative. The methoxy groups were easily transformed into hydroxy groups by treatment with BBr_3 in dichloromethane. Neutralization of the obtained dihydrobromide **4** with usual aqueous workup followed by extraction gave no

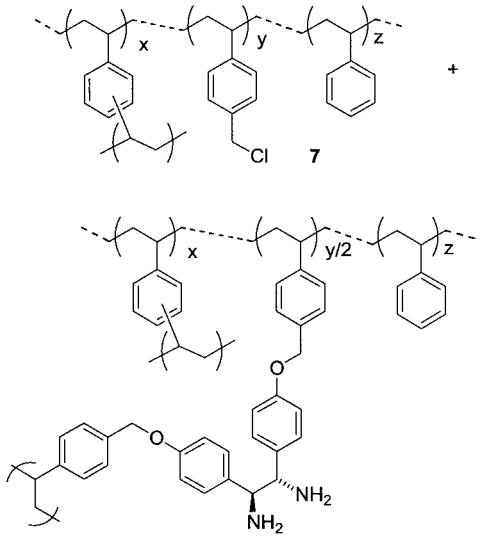


Scheme 1: Preparation of enantiopure 1,2-diamine.

product since the bisphenol **5** having free diamino group is miscible with aqueous phase. The use of polymer-supported amine base **6** in organic solvent without aqueous workup is necessary to obtain the desired free diamine **5** in quantitative yield.

Synthesis of Polymer-supported Chiral 1,2-Diamine

In our previous reports on polymer-supported chiral ligands, we have found that a phenolic functionality is quite suitable for immobilization reactions to functional poly(styrene)s having electrophilic reactive groups such as chloromethyl group.[13-15] For example, chiral amino alcohols having phenol hydroxy groups were easily introduced into chloromethylated poly(styrene) in quantitative conversion without any side reaction.[15] Protection of the amino functionality is not necessary due to the highly reactive phenoxide, which was rapidly and exclusively consumed with the formation of benzyl phenyl ether linkage. Thus, the sodium phenoxide derived from (*S*,*S*)-**5** was allowed to react with a crosslinked chloromethylated poly(styrene) **7** to give polymer-supported chiral 1,2-diamine (*S*,*S*)-**5P** (Scheme 2). In this



5P

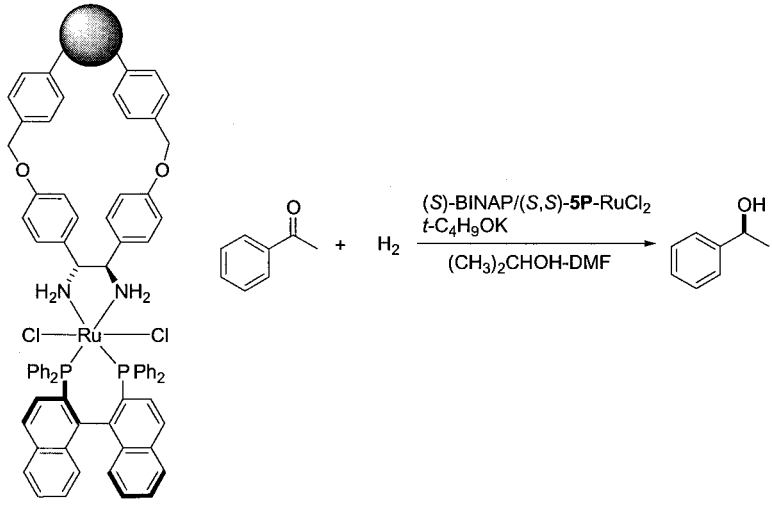
(*S*,*S*)-**5P**	x	y	z
(*S*,*S*)-**5Pa**	0.01	0.05	0.94
(*S*,*S*)-**5Pb**	0.01	0.10	0.89
(*S*,*S*)-**5Pc**	0.01	0.20	0.79
(*S*,*S*)-**5Pd**	0.02	0.20	0.78
(*S*,*S*)-**5Pe**	0.05	0.20	0.75
(*S*,*S*)-**5Pf**	0.01	0.30	0.69
(*S*,*S*)-**5Pg**	0.01	0.40	0.59
(*S*,*S*)-**5Ph**	0.01	0.50	0.49

Scheme 2: Preparation of polymer-supported chiral diamine.

immobilization reaction, both hydroxy groups of (*S*,*S*)-**5** seem to react with the chloromethyl groups in **7** based on the 1,2-diamine loading % of **5P** calculated by nitrogen analysis.

Asymmetric Hydrogenation of Acetophenone using Polymer-supported Chiral 1,2-Diamine-BINAP-$RuCl_2$ Complex

Noyori et al. have developed an excellent chiral catalyst system effective for the hydrogenation of simple ketones.[2] Aromatic ketones can be smoothly hydrogenated with (*S*)-BINAP-$RuCl_2$ complexed with (*S*,*S*)-diphenylethylenediamine in the presence of *t*-BuOK to give the corresponding secondary alcohol in quantitative yield with a high level of enantioselectivity.[2] We have used the catalyst system based on the polymer-supported chiral 1,2-diamine for the same reaction. Since the polymeric 1,2-diamines have been prepared from insoluble cross-linked poly(styrene), a choice of solvent used for the reaction is important. In most cases in the hydrogenation with $RuCl_2$/diphosphine/diamine/alkaline base catalyst system 2-propanol gives good result.[2] First we used 2-propanol as a solvent of the catalyst prepared from the polymeric 1,2-diamine. Unfortunately, no reaction occurred in 2-propanol mainly due to the shrinkage of the



Scheme 3: Asymmetric hydrogenation using polymer-supported catalyst.

insoluble polystyrene network in this solvent, which would interfere the access of the substrate to the catalytic site. When DMF was added as a solvent the reaction took place to give the corresponding chiral secondary alcohol with reasonable enatioselectivity. Hydrogenation of unfunctionalized ketones could not proceed with $RuCl_2$/BINAP complex alone. The above result shows that the chiral catalyst is formed on the polymer. The best result was obtained from 1 : 1 mixture of 2-propanol and DMF (Table 1).

Table 1. Solvent effect on asymmetric hydrogenation of acetophenone using the catalyst prepared from polymer-supported 1,2-diamine[a]

1,2-diamine	Solvent (2-propanol : DMF)	1-phenylethanol		
		Yield %[b]	Ee %[c]	Config.
(*S*,*S*)-**5Pc**	2-propanol	0	-	-
(*S*,*S*)-**5Pc**	2 : 1	46	71	*R*
(*S*,*S*)-**5Pc**	1 : 1	100	73	*R*
(*S*,*S*)-**5Pc**	1 : 2	100	70	*R*
(*S*,*S*)-**6Pc**	DMF	38	75	*R*
(*S*,*S*)-DPEN[d]	2-propanol	100	80	*R*
(*R*,*R*)-DPEN[e]	1 : 1	92	81	*S*
(*R*,*R*)-DPEN[e]	DMF	100	72	*S*

[a] Reactions were conducted at 1 Mpa of H_2 and at room temperature for 1 h using acetophenone (5 mmol), *t*-BuOK (1M, 100 μL), 1,2-diamine (0.025 mmol) and (*S*)-BINAP/$RuCl_2$ (0.025 mmol).
[b] Determined by GC analysis.
[c] Determined by HPLC using Chiralcel OD.
[d] See ref. [16]. tolBINAP (2,2'-bis(di-4-tolylphosphino)-1,1'-binaphthyl) was used.
[e] (*R*)-BINAP was used.

Both a degree of cross-linking of the polymeric support and the catalyst loading in the polymer often influence the performance of a polymeric catalyst. We have prepared chiral 1,2-diamine polymers **5P** having different degrees of cross-linking and diamine content. Table 2 summarizes the effect of the degree of crosslinking and the diamine content in the polymeric 1,2-diamine. Relatively high yields were obtained with lightly crosslinked polymers. Higher loading of 1,2-diamine resulted in lower enantioselectivity. The polymer *rac*-**5Pc** consists of racemic 1,2-diamine and also acted as a catalyst in the hydrogenation of acetophenone with lower

enantioselectivity. Instead of BINAP the use of xylBINAP yielded the same product in higher enantioselectivity as expected from the asymmetric hydrogenation data reported by Noyori.[17]

Table 2. Effect of crosslinking degree and 1,2-diamine content in the polymer[a]

Diamine polymer	**5P**			1-Phenylethanol		
	x	y	z	Yield %	Ee %	Config
(*S*,*S*)-**5Pa**	0.01	0.05	0.94	87	73	*R*
(*S*,*S*)-**5Pb**	0.01	0.10	0.89	86	74	*R*
(*S*,*S*)-**5Pc**	0.01	0.20	0.79	100	73	*R*
(*R*,*R*)-**5Pc**[b]	0.01	0.20	0.79	100	73	*S*
(*S*,*S*)-**5Pc**[a,c]	0.01	0.20	0.79	100	93	*R*
rac-**5Pc**	0.01	0.20	0.79	100	21	*R*
(*S*,*S*)-**5Pd**	0.02	0.20	0.78	69	73	*R*
(*S*,*S*)-**5Pe**[d]	0.05	0.20	0.75	39	68	*R*
(*S*,*S*)-**5Pf**[d]	0.01	0.30	0.69	91	69	*R*
(*S*,*S*)-**5Pg**	0.01	0.40	0.59	78	67	*R*
(*S*,*S*)-**5Ph**[d]	0.01	0.50	0.49	43	63	*R*

[a] Reaction conditions: See footnote in Table 1.
[b] (*R*)-BINAP was used.
[c] xylBINAP (2,2'-bis(di-3,5-xylylphosphino)-1,1'-binaphthyl was used.
[d] Contains unreacted chloromethyl groups.

Table 3 shows that several other aromatic ketones can be asymmetrically hydrogenated with the polymeric chiral catalyst with good enantioselectivities. Reactions occurring in the polymer network are sometimes affected by substrate accessibility to the catalytic site in the polymer network. Ketones having bulky alkyl chain showed lower reactivity.

One of the most important feature by using polymeric catalyst is its recyclability (Table 4). Once the chiral catalyst was formed on the insoluble polymer the alcohol product was easily separated from the catalyst. The polymeric catalyst was then used for the next reaction. We have performed four recycling experiment for the asymmetric hydrogenation of acetophenone with the polymeric catalyst prepared from **5Pc**. No damage and loss of catalytic activity was observed on the polymeric catalyst during the recycling experiment.

Table 3. Asymmetric hydrogenation of aromatic ketones using polymer-supported catalyst[a]

Ketone	Reaction time h	Alcohol produced		
		Yield %	Ee %	Config
acetophenone	1	100	73	*S*
4-methoxyacetophenone	3	98	75	*R*
4-chloroacetophenone	1	87	47	*S*
4-bromoacetophenone	1	99	45	*R*
propiophenone	1	93	76	*S*
butyrophenone	4	98	72	*S*
isobutyrophenone	4	95	47	*R*
valerophenone	15	33	81	*S*
1-acetonaphthone	1	90	90	*S*

[a] Reaction conditions: See footnote in Table 1.

Table 4. Recycle use of the polymeric chiral catalyst[a]

Recycle	1-Phenylethanol		
	Yield %	Ee %	Config.
1	100	73	*S*
2	100	73	*S*
3	100	73	*S*
4	100	74	*S*

[a] Reaction conditions: See footnote in Table 1.

Conclusions

We have successfully synthesized enantiopure 1,2-diamine having two phenolic functionalities, which was quite useful for immobilization reaction into chloromethylated polystyrene. The chiral 1,2-diamine moiety was readily immobilized into crosslinked poly(styrene) through a benzyl ether linkage. Hydrogenation of ketones smoothly occurred with the polymeric catalyst system prepared from the polymeric chiral 1,2-diamine, $RuCl_2$/BINAP and *t*-BuOK in 2-propanol/DMF mixed solvent. The polymeric catalyst can be recycled several times without any loss of activity.

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