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Preparation of a polymer-supported chiral 1,2-diamine and its application to the asymmetric hydrogenation of aromatic ketones

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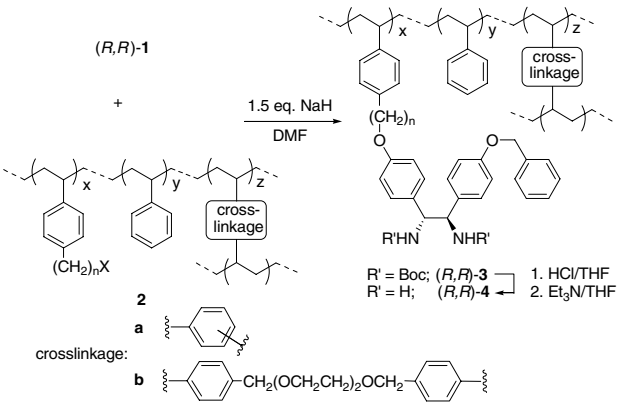
Abstract—Polymer-supported chiral 1,2-diamines were prepared by two methods including (1) chemical modification of a Merrifield-type resin with a chiral 1,2-diamine and (2) polymerization of a 1,2-diamine monomer. The polymeric complex formed by the polymer-supported 1,2-diamine and $RuCl_2$-BINAP was used for the asymmetric hydrogenation of aromatic ketones to afford the corresponding secondary alcohols in quantitative yields with high enantioselectivities up to 99% ee in the asymmetric hydrogenation. The polymeric catalyst could be reused many times without any loss of activity or enantioselectivity.

1. Introduction

Over the last few decades, many examples of asymmetric reactions using chiral 1,2-diamines as chiral ligands have been reported.[1] One of the most efficient chiral 1,2-diamines is 1,2-diphenyl-1,2-ethylenediamine (DPEN), which was originally developed by Corey.[2] High levels of enantioselectivities were obtained when DPEN and its derivatives were used as chiral ligands for catalysts for various kinds of asymmetric transformations including epoxidation,[3] Diels–Alder reaction,[4] aldol reaction,[5] hydrogenation,[6] transfer hydrogenation,[7] and Michael addition.[8] If DPEN is immobilized onto a polymer-support, the reaction process in most of the above reactions can be facilitated mainly due to its easy separation and recyclability.[9] The use of polymer-supported catalysts has become a standard technique in modern organic synthesis. Although various kinds of chiral ligands have been immobilized on polymers,[10] there have been only limited examples on the polymer-supported chiral primary diamines.[11,12] We have synthesized new polymer-supported 1,2-diamines **4** and **9** by means of the two following methods. One involves a polymer reaction between **1** and a Merrifield-type resin to prepare the polymeric 1,2-diamine **4** (Scheme 1). Chiral monomers **7** were also prepared from **5**, which were copolymerized with styrene and divinylbenzene to give the crosslinked polymer **9** (Schemes 2 and 3). To evaluate



Scheme 1. Preparation of chiral 1,2-diamine polymers through a polymer reaction.

the efficiency of these polymeric chiral ligands in an asymmetric reaction, we chose asymmetric hydrogenation as a model reaction. Herein, we report the preparation of polymer-supported chiral catalysts derived from chiral polymers **4** and **9** and their use in the asymmetric hydrogenation of aromatic ketones.

2. Results and discussion

We first prepared the polymer-supported chiral 1,2-diamines **4** through the reaction between halogenoalkyl polymer **2** and chiral 1,2-diamine (*R*,*R*)-**1** with a hydroxyl

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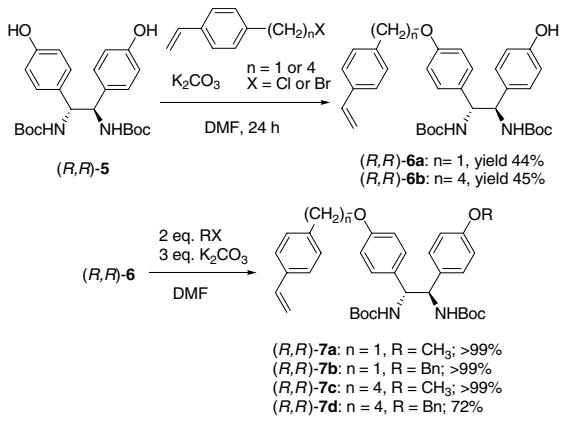
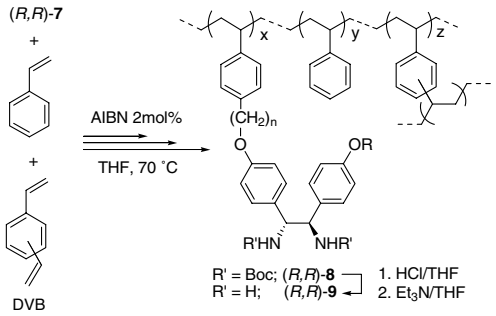
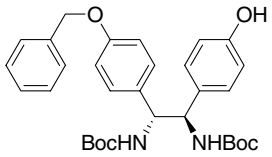


Scheme 2. Preparation of chiral 1,2-diamine monomers.



Scheme 3. Polymerization of a chiral 1,2-diamine monomer.

group. Crosslinked polymer **2** reacted smoothly with the sodium phenoxide of **1** to give **3** in quantitative yield. Since a degree of crosslinkage higher than 10% divinylbenzene (DVB) caused incomplete conversion of chloromethyl groups on the polymer, we have prepared polymers **2a** containing less than 5% DVB. The use of a flexible crosslinkage **2b** resulted in the complete conversion of the polymer reaction. An alkyl chain spacer arm in **2** ($n = 4$) was also introduced between the polymer-support and chiral 1,2-diamine moiety. Removal of the Boc protecting group from polymer **3** was conducted by treatment with HCl in THF to give the desired polymer-supported primary 1,2-diamine **4** after neutralization. Disappearance of the C=O absorption in the IR and positive bromophenol blue test[13] confirmed that the deprotection occurred smoothly on the polymers.



(*R*,*R*)-**1**: yield 39%

An alternative method to prepare the chiral 1,2-diamine polymer involves the terpolymerization of 1,2-diamine monomer **7**, styrene and a crosslinking agent. The novel chiral monomers (*R*,*R*)-**7** were easily prepared from **5** (Scheme 2). Radical polymerization of **7**, styrene and DVB gave the polymer-supported chiral 1,2-diamine **8**. Deprotection of the obtained polymers **8** was carried out in the same manner as that described above (Scheme 3). The structure of the polymers obtained **9** (R = Bn) is the same as that of **4**.

We then complexed these polymeric 1,2-diamines to the $RuCl_2$-(*R*)-BINAP[14] complex, which was used for the asymmetric hydrogenation of aromatic ketones. First, the 1,2-diamine polymers and $RuCl_2\{(R)\text{-BINAP}\}(dmf)_n$ were heated to 80 °C in DMF to form the chiral complex. During the heating of the mixture, the polymer color was changed to reddish brown, which indicated the formation of the BINAP-Ru-1,2-diamine complex on the polymer. After the removal of solvent the polymeric chiral complex was rinsed with DMF. The polymeric complex was then subjected to the asymmetric hydrogenation of acetophenone. Although 2-propanol is the choice solvent under the original reaction conditions reported by Noyori et al.,[7] almost no reaction occurred in 2-propanol by using the polymeric catalyst, mainly due to shrinkage of the hydrophobic polystyrene chain in this solvent. We found that the use of a 2-propanol–DMF (1:1) mixed solvent system was suitable for the reaction in the case of the polymeric catalyst. The result of the hydrogenation of acetophenone using the polymer-immobilized catalyst is shown in Tables 1 and 2. Asymmetric hydrogenation of acetophenone smoothly occurred by means of the polymeric chiral

Table 1. Asymmetric hydrogenation of acetophenone with (*R*)-BINAP/$RuCl_2$/(*R*,*R*)-**4**[a]

Entry	(*R*,*R*)-**4**					Conv.[b] %	ee[c] (%)
		Cross-linkage	*n*	*x*	*z*		
1	**4a**	**a**	1	0.05	0.01	>99	76
2	**4b**	**a**	1	0.10	0.01	91	70
3	**4c**	**a**	1	0.10	0.05	46	67
4	**4d**	**a**	1	0.20	0.01	93	75
5	**4e**	**a**	1	0.30	0.01	>99	74
6	**4f**	**a**	4	0.05	0.01	>99	60
7	**4g**	**a**	4	0.10	0.01	>99	73
8	**4h**	**a**	4	0.20	0.01	>99	72
9	**4i**	**b**	1	0.05	0.02	>99	63
10	**4j**	**b**	1	0.10	0.02	>99	72
11	**4k**	**b**	1	0.10	0.05	>99	70
12	**4l**	**b**	1	0.10	0.10	23	65
13	**4m**	**b**	1	0.20	0.02	>99	72
14	**4n**	**b**	1	0.30	0.02	>99	70
15	**4o**	**b**	4	0.05	0.02	>99	74
16	**4p**	**b**	4	0.10	0.02	>99	75
17	**4q**	**b**	4	0.20	0.02	>99	76

[a] Unless otherwise noted, reactions were carried out at 1 MPa of H_2 and at room temperature for 24 h with a solution of acetophenone (5 mmol) in 4 mL of solvent (2-propanol–DMF = 1:1), 1,2-diamine (0.01 mmol), and (*R*)-BINAP/$RuCl_2$ (0.005 mmol) in the presence of $(CH_3)COK$ (1 M, 100 μL). Diamine/BINAP/$RuCl_2$/ketone/base = 2:1:1:1000:20.

[b] Determined by GC analysis.

[c] Determined by LC analysis using a chiral column (chiral OD).

Table 2. Asymmetric hydrogenation of acetophenone with (*R*)-BINAP/$RuCl_2$/(*R*,*R*)-**9**[a]

Entry	(*R*,*R*)-**9**					Conv.[b] %	ee[c] (%)
		R	*n*	*x*	*z*		
1	**9a**	CH_3	1	0.10	0	>99	74
2	**9b**	CH_3	1	0.05	0.01	>99	80
3	**9c**	CH_3	1	0.10	0.01	>99	75
4	**9d**	CH_3	1	0.05	0.05	>99	78
5	**9e**	CH_3	1	0.10	0.05	>99	78
6	**9f**	CH_3	4	0.10	0	>99	78
7	**9g**	CH_3	4	0.05	0.01	>99	80
8	**9h**	CH_3	4	0.10	0.01	>99	79
9	**9i**	CH_3	4	0.05	0.05	>99	78
10	**9j**	CH_3	4	0.10	0.05	>99	78
11[d]	**9j**	CH_3	4	0.10	0.05	>99	99
12	**9k**	$C_6H_5CH_2$	1	0.10	0.01	>99	77
13	**9l**	$C_6H_5CH_2$	1	0.10	0.05	>99	76
14	**9m**	$C_6H_5CH_2$	1	0.10	0.10	39	73
15	**9n**	$C_6H_5CH_2$	4	0.10	0.01	>99	73
16	**9o**	$C_6H_5CH_2$	4	0.10	0.05	>99	75
17[e]	DPEN	—	—	—	—	>99	80

[a] Unless otherwise noted, reactions were conducted at 1 MPa of H_2 and at room temperature for 24 h with a solution of acetophenone (5 mmol) in 4 mL of solvent (2-propanol–DMF = 1:1), 1,2-diamine (0.01 mmol), and (*R*)-BINAP/$RuCl_2$ (0.005 mmol) in the presence of $(CH_3)COK$ (1 M, 100 μL). Diamine/BINAP/$RuCl_2$/ketone/base = 2:1:1:1000:20.
[b] Determined by GC analysis.
[c] Determined by LC analysis using a chiral column (chiral OD).
[d] (*R*)-xylBINAP was used instead of (*R*)-BINAP.
[e] Reaction was conducted for 1 h. Diamine/BINAP/$RuCl_2$/ketone/base = 2:1:1:200:4.

catalyst prepared from **4** to give (*S*)-1-phenylethanol with 76% ee in quantitative conversion (Table 1, entry 1). Higher crosslinkage of the polymeric chiral ligand resulted in both a lower reactivity and a decrease in the enantioselectivity (entries 3 and 12). In the case of DVB the crosslinkage alkyl spacer did not influence the catalytic activity. When a flexible crosslinkage was used, somewhat higher ees were obtained with polymer having a longer alkyl spacer **4** ($n = 4$).

Polymers **9**, prepared from the polymerization method, were subjected to the same reaction. Overall, relatively higher reactivities were obtained by using **9**. For example, the use of **9b** as a chiral 1,2-diamine ligand afforded 80% ee in the hydrogenation (Table 2, entry 2), which is the same as that obtained from the low-molecular-weight counterpart (DPEN) in the same solvent system (Table 2, entry 17). Some differences in the enantioselectivities observed between the results obtained from polymers **4** and **9** might be caused by their slight variation of the ligand conformation in the polymer network based on the preparation method. While quantitative conversion was always obtained by using **9** containing less than 5% DVB, the conversion decreased in the case of 10% DVB crosslinked polymer (entry 14). Relatively higher ees were obtained when methoxy derivatives (**9**, R = Me) were used in comparison to the benzyloxy derivative (**9**, R = Bn) (entry 5 vs 13, 10 vs 16). In the case of the polymer reaction method, we could not obtain the methoxy derivative due to the difficulty of the synthesis of a chiral 1,2-diamine having a monomethoxy derivative corresponding to **1**. The structure of the chiral diphosphine ligand is also a very important factor for controlling the enantioselectivity in this catalyst, as expected from the original study of Noyori. Instead of BINAP, when (*R*)-xylBINAP[15] was used, the polymeric catalyst gave nearly perfect enantioselectivity (entry 11). The results of the asymmetric hydrogenation of other aromatic ketones are shown in Table 3. Enantioselectivities obtained by means of the polymer-immobilized catalyst developed in this study were as high as those obtained from the low-molecular-weight catalyst derived from DPEN. For example, the hydrogenation of 1′-acetonaphthone with the polymeric catalyst gave 97% ee, while the low-molecular-weight catalyst gave the same enantioselectivity (Table 3, entry 4). The reuse of polymer-immobilized catalyst (*R*)-BINAP/$RuCl_2$/(*R*,*R*)-**9c** was also examined. Since the crosslinked polymers were insoluble in the solvent used, it was easy to separate the polymeric catalyst from the reaction mixture. The recovered polymer-immobilized catalyst could be reused at least 16 times without any loss of activity or enantioselectivity.

Table 3. Asymmetric hydrogenation of aromatic ketones with (*R*)-BINAP/$RuCl_2$/(*R*, *R*)-**9e**[a]

Entry	Ketone	Conv.[b] (%)	ee[c] (%)
1	Propiophenone	99 (87)[d]	82 (84)[d]
2	Butyrophenone	97 (>99)[d]	84 (83)[d]
3	Valerophenone	>99 (>99)[d]	88 (91)[d]
4	1′-Acetonaphthone	>99 (>99)[d]	97 (97)[d]

[a] Unless otherwise noted, reactions were conducted at 1 MPa of H_2 and at room temperature for 24 h with a solution of acetophenone (5 mmol) in 4 mL of solvent (2-propanol–DMF = 1:1), 1,2-diamine (0.01 mmol), and (*R*)-BINAP/$RuCl_2$ (0.005 mmol) in the presence of $(CH_3)COK$ (1M, 100 μL). Diamine/BINAP/$RuCl_2$/ketone/base = 2:1:1:1000:20.
[b] Determined by GC analysis.
[c] Determined by LC analysis using a chiral column (chiral OD).
[d] Reactions were conducted by using DPEN for 3 h. DPEN/(*R*)-BINAP/$RuCl_2$/ketone/base = 2:1:1:200:4.

3. Conclusion

We have developed the preparation of a polystyrene-immobilized enantiopure 1,2-diamine either by polymer reaction method or the copolymerization method. The polymer reaction method involves coupling of a Merrifield-like resin and chiral 1,2-diamine (*R*,*R*)-**1** having a phenolic hydroxyl group. The copolymerization method involves the copolymerization of 1,2-diamine monomer **7** with styrene in the presence of a crosslinking agent, followed by the deprotection reaction. The polymeric primary 1,2-diamines **4** and **9** obtained were used as ligands of the catalyst in the hydrogenation of aromatic ketones to afford the corresponding secondary alcohols in quantitative yield. High levels of enantioselectivities (up to 99% ee) were obtained by using the polymeric catalyst, which are the same as those obtained from the corresponding low-molecular weight catalyst in solution system. The polymeric catalyst could be

reused many times without any loss of activity or enantioselectivity. Our results demonstrate that these polymeric chiral 1,2-diamines could be used as efficient chiral ligands or an auxiliary for other asymmetric reactions.

4. Experimental

4.1. General

Tetrahydrofuran (THF) was freshly distilled form sodium benzophenone ketyl under nitrogen. *N*,*N*-Dimethylformamide (DMF) was freshly distilled form calcium hydride under argon immediately before use. 4-(Chloromethyl)-styrene and 4-(4-bromobutyl)styrene were distilled from calcium hydride. Ketones used were distilled from calcium hydride. Reactions were monitored by TLC using Merk precoated silica gel plates (Merk 5554, 60F254). Column chromatography was performed with a silica gel column (Wakogel C-200, 100–200 mesh). Melting points were taken on a Yanaco micro melting apparatus and are uncorrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were measured on a Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard, and *J* values are reported in Hz. ^{31}P (162 MHz) spectra were measured on a Varian Inova 400 spectrometer. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and were reported in reciprocal centimeters (cm^{-1}). Elemental analyses were performed at the Microanalytical Center of Kyoto University. GC analyses were performed with a Shimadzu Capillary Gas Chromatograph 14B equipped with a capillary column (Supelco β-DEX325, 30 m × 0.25 mm). 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 eluent, column temperature was at 30 °C. UV detector (JASCO UV-975 for JASCO HPLC system) was used for the peak detection. Optical rotations were taken on a JASCO DIP-149 digital polarimeter using 10 cm thermostated microcell. Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution of linear polymers was conducted at 40 °C with a JASCO PU-980 as a pump, JASCO UVI-DEC-100-III as a UV detector, and Shodex column A-802 (pore size: 20 Å) and A-803 (pore size: 100 Å) as columns. The eluent was THF, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained by using a series of polystyrene standards (Tosoh Co., Japan).

4.2. Preparation of polymer-supported 1,2-chiral diamine 4

4.2.1. A 20 mL round-bottomed flask, equipped with a magnetic stirring bar was charged with 0.10 g (0.19 mmol) of 1 and 5 mL of DMF under nitrogen. To this solution, 7 mg (0.28 mmol) of NaH was added and stirred for 10 min, added 0.32 g (0.15 mmol Cl) of **2a** ($n = 1$). After the mixture was stirred for 48 h, the polymer was poured into methanol and washed with THF, water, hexane, and methanol, and dried under reduced pressure to give 0.39 g of **3a** as pale yellow beads. IR (KBr): 1714 cm^{-1}.

A 10 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 0.39 g of **3a** and 5 mL of a 4 M-HCl/THF solution. After the reaction mixture was stirred for 12 h, polymer was collected by filtration, and washed with water and THF. The polymer was transferred to a 10 mL round-bottomed flask equipped with a magnetic stirring bar and suspended in 5 mL of THF, and then 5 mL of triethylamine added. After 12 h stirring, the polymer was collected by filtration, washed with water, THF and methanol, and dried under reduced pressure to give 0.36 g (>99%) of **4a** as a pale yellow solid. Bromophenol blue test: positive. Diamine content was determined to be 0.41 mmol/g from nitrogen analysis. Crosslinked polymers **4b**, **4c**, **4d** and **4e** were obtained by the same procedure as described above.

4.2.2. Compound 4f. The reaction of **1** and **2a** ($n = 4$) was carried out by the same procedure as described above for the preparation of **4a** and produced **4f** in 98% yield. Diamine content was determined to be 0.40 mmol/g from nitrogen analysis. Crosslinked polymers **4g** and **4h** were obtained by the same procedure as described above.

4.2.3. Compound 4i. The reaction of **1** and **2b** ($n = 1$) was carried out by the same procedure as described above for the preparation of **4a** and produced **4i** in 98% yield. Diamine content was determined to be 0.40 mmol/g from nitrogen analysis. Crosslinked polymers **4j**–**n** were obtained by the same procedure as described above.

4.2.4. Compound 4o. The reaction of **1** and **2b** ($n = 4$) was carried out by the same procedure as described above for the preparation of **4a** and produced **4o** in 98% yield. Diamine content was determined to be 0.39 mmol/g from nitrogen analysis. Crosslinked polymers **4p** and **4q** were obtained by the same procedure as described above.

4.3. Preparation of chiral 1,2-diamine monomers

4.3.1. (*R*,*R*)-*N*,*N*′-Di(*tert*-butoxycarbonyl)-1-(*p*-hydroxyphenyl)-2-(*p*-(*p*-vinyl-benzyloxy)phenyl)-1,2-diaminoethane 6a. A 30 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 1.5 g (3.37 mmol) of (*R*,*R*)-*N*,*N*′-di(*tert*-butoxycarbonyl)-1,2-bis(*p*-hydroxyphenyl)-1,2-diaminoethane **5** and 5 mL of DMF under nitrogen. To this solution, 0.565 g (3.71 mmol) of 4-(chloromethyl)styrene and 1.40 g (10.1 mmol) of K_2CO_3 were added. After the mixture was stirred for 24 h, the DMF was evaporated under reduced pressure. The residual solid was washed with water and hexane, and the yellow solid was purified by silica gel column chromatography (hexane–EtOAc 3:1). Removal of solvent under reduced pressure gave 0.828 g (1.48 mmol) of **6a** as a white solid. Yield 44%. $R_f = 0.15$ (hexane–EtOAc 3:1). Mp 123–125 °C. $[\alpha]_D = -15.7$ (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.40 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.33 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.95–6.87 (m, 4H, Ar-H), 6.77 (d, $J = 9.0$ Hz, 2H, Ar-H), 6.71 (dd, $J = 18.0$, 11.0 Hz, 1H, CH_2=CH), 6.62 (d, $J = 6.9$ Hz, 2H, Ar-H), 5.75 (d, $J = 18.0$ Hz, 1H, CH_2=CH), 5.51 (br s, 2H, NH), 5.25 (d, $J = 12.0$ Hz, 1H, CH_2=CH), 4.96 (s, 2H,

CH_2), 4.75 (br s, 2H, CH), 1.43 (s, 18H, CH_3). Anal. Calcd for $C_{33}H_{40}N_2O_6$: H, 7.19; C, 70.69; N, 5.00. Found for $C_{33}H_{40}N_2O_6$: H, 7.15; C, 70.64; N, 5.02.

4.3.2. Compound 6b. Prepared according to the above procedure using 2.8 g (6.30 mmol) of **5**, 10 mL of DMF, 1.66 g (6.93 mmol) of 4-(4-bromobutyl)styrene and 2.61 g (18.9 mmol) of K_2CO_3 gave 1.72 g (2.85 mmol) of **2c** as a white solid. Yield 45%. $R_f = 0.20$ (hexane–EtOAc 3:1). Mp 77–78 °C. $[\alpha]_D = -9.6$ (c 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.32 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.90 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.85 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.68 (dd, $J = 18.0$, 11.0 Hz, 1H, CH_2=CH), 6.65 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.61 (d, $J = 8.7$ Hz, 2H, Ar-H), 5.69 (d, $J = 18.0$ Hz, 1H, CH_2=CH), 5.66 (br s, 2H, NH), 5.18 (d, $J = 12.0$ Hz, 1H, CH_2=CH), 4.74 (br s, 2H, CH), 3.85 (br s, 2H, CH_2), 2.64 (br s, 2H, CH_2), 3.85 (br s, 2H, CH_2), 1.89 (br s, 2H, CH_2), 1.43 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.1, 136.9, 128.8, 126.4, 118.5, 115.6, 110.6, 88.9, 67.9, 35.5, 29.0, 28.6, 28.0. Anal. Calcd for $C_{36}H_{46}N_2O_6$: H, 7.69, C, 71.73, N, 4.65. Found for $C_{36}H_{46}N_2O_6$: H, 7.78, C, 70.26, N, 5.09.

4.3.3. (*R*,*R*)-*N*,*N*′-Di(*tert*-butoxycarbonyl)-1-(*p*-methoxyphenyl)-2-(*p*-(*p*-vinyl-benzyloxy)phenyl)-1,2-diaminoethane 7a. A 30 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 0.728 g (1.30 mmol) of **6a** and 5 mL of DMF under nitrogen. To this solution, 0.16 mL (0.37 g; 2.60 mmol) of CH_3I and 0.539 g (3.90 mmol) of K_2CO_3 was added. After the mixture was stirred for 24 h, DMF was evaporated under reduced pressure. The residual solid was dissolved in chloroform, and washed with water three times, dried over anhydrous magnesium sulfate. After the solvent was removed in vacuo, the residue was purified by silica gel column chromatography (hexane–EtOAc 3:1). Removal of solvent under reduced pressure gave 0.748 g (1.30 mmol) of **7a** as a white solid. Yield >99%. $R_f = 0.30$ (hexane–EtOAc 3:1). Mp 158–160 °C. $[\alpha]_D = -4.2$ (c 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.41 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.34 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.96 (d, $J = 8.7$ Hz, 4H, Ar-H), 6.78 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.71 (d, $J = 6.9$ Hz, 2H, Ar-H), 6.71 (dd, $J = 18.0$, 11.9 Hz, 1H, CH_2=CH), 5.75 (d, $J = 17.4$ Hz, 1H, CH_2=CH), 5.49 (br s, 2H, NH), 5.25 (d, $J = 11.1$ Hz, 1H, CH_2=CH), 4.96 (s, 2H, CH_2), 4.79 (br s, 2H, CH), 3.73 (s, 3H, CH_3), 1.43 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.0, 137.5, 136.6, 128.7, 127.9, 126.6, 114.9, 114.0, 69.9, 55.4, 28.6. Anal. Calcd for $C_{34}H_{42}N_2O_6$: H, 7.37, C, 71.06, N, 4.87. Found for $C_{34}H_{42}N_2O_6$: H, 7.40, C, 71.10, N, 4.90.

4.3.4. Compound 7b. In the same manner, 0.35 g (0.62 mmol) of **6a**, 5 mL of DMF, 0.15 mL (0.21 g; 1.25 mmol) of benzylbromide and 0.52 g (3.7 5 mmol) of K_2CO_3 gave 0.41 g (0.63 mmol) of **7b** as a white solid. Yield >99%. $R_f = 0.45$ (hexane–EtOAc 3:1). Mp 200–202 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.40–7.33 (m, 9H, Ar-H), 6.96 (d, $J = 8.1$ Hz, 4H, Ar-H), 6.79 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.78 (d, $J = 9.0$ Hz, 2H, Ar-H), 6.71 (dd, $J = 18.0$, 10.8 Hz, 1H, CH_2=CH), 5.75 (d, $J = 18.0$ Hz, 1H, CH_2=CH), 5.49 (br s, 2H, NH), 5.25 (d, $J = 12.0$ Hz, 1H, CH_2=CH), 4.98 (s, 2H, CH_2), 4.97 (s, 2H, CH_2), 4.78 (br s, 2H, CH), 1.43 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 128.8, 128.2, 128.0, 127.7, 126.6, 114.9, 70.1, 28.6. Anal. Calcd for $C_{40}H_{46}N_2O_6$: H, 7.12; C, 73.82; N, 4.30. Found for $C_{40}H_{46}N_2O_6$: H, 7.11; C, 73.82; N, 4.25.

4.3.5. Compound 7c. In the same manner, 0.633 g (1.05 mmol) of **6b**, 5 mL of DMF, 0.13 mL (0.30 g; 2.10 mmol) of CH_3I and 0.435 g (3.15 mmol) of K_2CO_3 gave 0.506 g (0.82 mmol) of **7c** as a white solid. Yield >99%. $R_f = 0.40$ (hexane–EtOAc 3:1). Mp 133–134 °C. $[\alpha]_D = -6.5$ (c 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.32 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.14 (d, $J = 7.8$ Hz, 2H, Ar-H), 6.97–6.93 (m, 4H, Ar-H), 6.71 (d, $J = 5.4$ Hz, 2H, Ar-H), 6.69 (dd, $J = 18.0$, 11.0 Hz, 1H, CH_2=CH), 6.68 (d, $J = 4.8$ Hz, 2H, Ar-H), 5.70 (d, $J = 17.4$ Hz, 1H, CH_2=CH), 5.47 (br s, 2H, NH), 5.19 (d, $J = 11.1$ Hz, 1H, CH_2=CH), 4.77 (br s, 2H, CH), 3.87 (br s, 2H, CH_2), 3.72 (s, 3H, CH_3), 2.65 (br s, 2H, CH_2), 1.89 (br s, 2H, CH_2), 1.43 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.2, 136.9, 135.4, 128.8, 126.4, 114.5, 114.0, 113.2, 55.4, 35.5, 28.6, 28.0. Anal. Calcd for $C_{36}H_{48}N_2O_6$: H, 7.84; C, 72.05; N, 4.54. Found for $C_{36}H_{48}N_2O_6$: H, 7.85; C, 71.18; N, 4.61.

4.3.6. Compound 7d. In the same manner, 0.35 g (0.58 mmol) of **6 b**, 5 mL of DMF, 0.14 mL (0.20 g; 1.16 mmol) of benzyl bromide and 0.48 g (3.48 mmol) of K_2CO_3 gave 0.29 g (0.42 mmol) of **7d** as a white solid. Yield 72%. $R_f = 0.50$ (hexane–EtOAc 3:1). Mp 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.39–7.37 (m, 5H, Ar-H), 7.33 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.15 (d, $J = 8.1$ Hz, 2H, Ar-H), 6.99-6.94 (m, 4H, Ar-H), 6.80 (d, $J = 8.1$ Hz, 2H, Ar-H), 6.70 (dd, $J = 18.0$, 10.0 Hz, 1H, CH_2=CH), 6.70 (d, $J = 8.4$ Hz, 2H, Ar-H), 5.71 (d, $J = 15.0$ Hz, 1H, CH_2=CH), 5.51 (br s, 2H, NH), 5.20 (d, $J = 9.0$ Hz, 1H, CH_2=CH), 4.97 (br s, 2H, CH), 3.88 (br s, 2H, CH_2), 2.66 (br s, 2H, CH_2), 1.77 (br s, 2H, CH_2), 1.44 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.2, 137.1, 136.9, 135.5, 128.8, 128.2, 127.7, 126.4, 114.9, 113.2, 70.1, 67.9, 35.5, 29.0, 28.6, 28.0. Anal. Calcd for $C_{43}H_{52}N_2O_6$: H, 7.56; C, 74.54; N, 4.04. Found for $C_{43}H_{52}N_2O_6$: H, 7.53, C, 74.52l; N, 4.09.

4.4. Preparation of polymeric chiral 1,2-diamine 9

4.4.1. Compound 9a. An ample tube equipped with a magnetic stirring bar was charged with 0.1 g (0.17 mmol) of **7a**, 0.16 g (1.57 mmol) of styrene, 0.006 g (0.035 mmol) of AIBN and 1.3 mL of THF. The ample tube was degassed three times by freeze-thaw in vacuo, sealed off, and placed in an oil bath (70 °C) and stirred for four days. The polymer solution obtained was then poured into 100 mL of methanol. The precipitated polymer was collected by filtration, washed with methanol, and dried under reduced pressure to give 0.193 g (73%) of (*R*,*R*)-**8a** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.5–6.3 (br, Ar-H), 5.5 (br, NH), 4.8 (br, CH), 3.7 (br, CH_3), 2.1–1.0 (br, CH_2, CH). Anal. Calcd for: H, 7.60; C, 84.2; N, 1.85. Found: H, 7.58; C, 84.35; N, 1.80.

A 10 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 0.11 g of **8a** and 5 mL of HCl/THF solution. After stirring for 12 h, 5 mL of triethylamine was added and the mixture was stirred for another 12 h. The mixture was added into 100 mL of methanol. The precipitate was collected by filtration, washed with water and methanol, and dried under reduced pressure to give 0.10 g (>99%) of **9a** as a white solid. $M_n = 10{,}900$, $M_w/M_n = 2.25$. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.5–6.3 (br, Ar-H), 4.9 (br, CH), 4.5 (br, NH), 3.8 (br, CH_3), 2.0–1.0 (br, CH_2, CH).

4.4.2. Preparation of crosslinked polymer-supported chiral 1,2-diamine 9e. An ample tube equipped with a magnetic stirring bar was charged with 0.20 g (0.35 mmol) of **7a**, 0.33 g (3.13 mmol) of styrene, 0.022 g (0.17 mmol) of divinylbenzene, 0.012 g (0.70 mmol) of AIBN and 1.8 mL of THF. The ample tube was degassed three times by freeze-thaw in vacuo, sealed off, and placed in an oil bath (70 °C) and stirred for four days. The obtained polymer solution was poured into 100 mL of methanol. The polymer was then collected by filtration, washed with THF and methanol, and dried under reduced pressure to give 0.59 g (>99%) of **8e** as a white solid. IR (KBr): 1714 cm^{-1}.

A 10 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 0.20 g of **8e** and 5 mL of HCL/THF solution. After stirring for 12 h, the polymer was collected by filtration, and then washed with water and THF. The polymer was transferred to a 10 mL round-bottomed flask equipped with a magnetic stirring bar and suspended in 5 mL of THF, and then 5 mL of triethylamine was added. After stirring for 12 h, the polymer was collected by filtration, washed with water, THF and methanol, and dried under reduced pressure to give 0.18 g (>99%) of **9e** as a pale yellow solid. Bromophenol blue test: positive. Diamine content was determined to be 0.72 mmol/g from nitrogen analysis. Crosslinked polymers **9b**, **9c**, and **9d** were obtained by the same procedure as described above.

4.4.3. Compound 9g. The polymerization of **7c**, styrene, and divinylbenzene was carried out by the same procedure for the preparation of **9e** and produced **9g** in 97% yield. Diamine content was determined to be 0.42 mmol/g from nitrogen analysis. Crosslinked polymers **9h**, **9i**, and **9j** were obtained by the same procedure as described above.

4.4.4. Compound 9k. The polymerization of **7b**, styrene, and divinylbenzene was carried out by the same procedure for the preparation of **9e** and produced **9k** in 92% yield. Diamine content was determined to be 0.71 mmol/g from nitrogen analysis. Crosslinked polymers **9l** and **9m** were obtained by the same procedure as described above.

4.4.5. Compound 9n. The polymerization of **7d**, styrene, and divinylbenzene was carried out by the same procedure for the preparation of **9e** and produced **9n** in 99% yield. Diamine content was determined to be 0.69 mmol/g from nitrogen analysis. Crosslinked polymer **9o** was obtained by the same procedure as described above.

4.5. General procedure for asymmetric hydrogenation of acetophenone with $RuCl_2$\{(*R*)-BINAP[(*R*,*R*)-polymeric diamine]\}$(dmf)_n$

A 20 mL Schlenk flask equipped with a magnetic stirring bar was charged with 4 mg (5 μmol) of $RuCl_2$\{(*R*)-BINAP\}$(dmf)_n$, 10 μmol of polymeric (*R*,*R*)-1,2-diamine and 2 mL of degassed DMF under argon. Then the flask placed in a bath heated at 80 °C and stirred for 2.5 h. The whole mixture was cooled to room temperature. DMF was then evaporated under reduced pressure to give $RuCl_2$\{(*R*)-BINAP[polymeric (*R*,*R*)-1,2-diamine]\}$(dmf)_n$ as a red brown solid. The polymeric Ru complex was then placed in a 100 mL glass autoclave equipped with a magnetic stirring bar under argon. To the autoclave, a solution of 0.58 mL (5 mmol) of acetophenone in 4 mL of solvent (2-propanol–DMF = 1:1) and 100 μL (100 μmol) of 1.0 M *t*-C_4H_9OK solution in 2-methyl-2-propanol. After the mixture was degassed by vacuum-filling argon cycles, hydrogen gas was introduced and released. This process was repeated three times and the vessel was pressurized to 1 MPa by the introduction of hydrogen gas. The mixture was stirred for 24 h at room temperature. After carefully venting the hydrogen gas, the reaction mixture was purified by a short silica gel column using ethyl acetate as eluent. The solvent was removed under reduced pressure. The conversion was determined by GC analysis. The enantioselectivity of the product 1-phenylethanol was determined by LC analysis. LC: eluent, 2-propanol–hexane (1:20); flow rate, 0.4 mL/min; retention time (t_R) of (*R*)-1-phenylethanol, 22 min; (t_R) of (*S*)-1-phenylethanol, 25 min. ^{31}P NMR of $RuCl_2$\{(*R*)-BINAP[polymeric (*R*,*R*)-1,2-diamine]\}-$(dmf)_n$ (162 MHz, $CDCl_3$, δ): 46.6 (s).

4.6. Reuse of catalyst

Hydrogenation was performed by the general procedure using 23 mg (25 μmol) of $RuCl_2$\{(*R*)-BINAP\}$(dmf)_n$, 69 mg (50 μmol) of (*R*,*R*)-**9c**, 0.58 mL (5 mmol) of acetophenone in 8 mL of solvent (2-propanol–DMF, 1:1) and 100 μL (100 μmol) of 1.0 M *t*-C_4H_9OK solution in 2-methyl-2-propanol. After 6 h stirring at room temperature, the mixture was allowed to settle for 30 min to precipitate the polymer. The autoclave was carefully opened, and supernatant solution was removed. The product (*S*)-1-phenylethanol was obtained from the solution. To the polymeric catalyst remaining in the autoclave, a solution of 0.58 mL (5 mmol) of acetophenone in 5 mL of solvent (2-propanol–DMF = 1:1) and 100 μL (100 μmol) of 1.0 M *t*-C_4H_9OK solution in 2-methyl-2-propanol, which had been degassed by bubbling argon, were added. The second run of the asymmetric hydrogenation was conducted using the same procedure as that outlined above. The reaction was repeated 16 times by using the same catalyst. The results are as follows: from the first cycle to the forth cycle, (*S*)-1-phenylethanol (>99% conv., 76% ee); from the fifth cycle to the tenth cycle, (*S*)-1-phenylethanol (>99% conv., 75% ee); from the 11th cycle to the 16th cycle, (*S*)-1-phenylethanol (>99% conv., 76% ee).

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