

Chiral polyethers derived from BINOL and ECH as highly enantioselective and efficient catalysts for the borane reduction of prochiral ketones

An-Lin Zhang, Zeng-da Yu, Li-Wen Yang*, Nian-Fa Yang*, Dan Peng

Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Hunan 411105, PR China

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ABSTRACT

Two novel polyethers derived from BINOL were synthesized and used to induce the enantioselective borane reduction of prochiral ketones. The polyethers gave the expected secondary alcohols with up to 98% yields and over 99% ee values. The recovered polyethers could be reused for many times to induce the enantioselective reduction of prochiral ketones without losing their enantioselective induction ability.

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1. Introduction

Asymmetric synthesis of enantiomerically enriched secondary alcohols has been widely studied, because chiral secondary alcohols are important synthetic intermediates for various other functionalities such as halide, amine, ester, and ether, and involved in many natural products and pharmaceuticals [1]. Extensive activities in the field of asymmetric synthesis and catalysis have led to the discovery of many highly enantioselective catalysts [2–5]. A number of effective catalysts have been applied to pharmaceutical and agricultural industries for the asymmetric synthesis of chiral organic molecules. Since it is often quite expensive to prepare the optically active catalysts, their easy recovery and reuse are highly desirable. Because of the significant size difference between polymers and small molecules, using polymer based catalysts greatly simplifies both the recycle of the catalysts and purification of the products [6–9]. Heterogeneous and homogeneous recyclable stereoselective catalysts can be separated by simple filtration or precipitation [10–16]. The traditional approach to constructing polymer-supported chiral catalysts involves the development of

a highly enantioselective monomeric catalyst and then the attachment of this monomeric catalyst to a flexible and sterically irregular polymer backbone. Although a few polymer-supported catalysts have been obtained in this way, a significant drop of enantioselectivity is often observed when a monomeric chiral catalyst is attached to a polymer support due to the changes in the microenvironment of the catalytic sites [17–20].

We have been working on asymmetric syntheses and catalysis using chiral aminoalcohols prepared from chiral epichlorohydrin (ECH), which was cheap and easily available [21,22]. In our previous study, it was found that an amino diol derived from (*S*)-ECH served as an efficient catalyst for the enantioselective alkylation of aldehydes and corresponding chiral secondary alcohols were obtained with moderate to high enantiomeric excesses. We also found that some polymer-supported catalysts derived from chiral ECH gave moderate results for the enantioselective addition of aldehydes with organometallic reagents [23,24].

Chiral 1,1-bi-2-naphthol (BINOL) has occupied a prominent position because of its ability to form highly enantioselective catalysts with main group elements [25,26], transition metals [27,28] and rare earth elements [29,30]. Immobilization of BINOL has earlier been achieved either by grafting onto a sterically irregular polymer backbone [31–34] or by cross-linking copolymerization [35]. However, the random orientation of ligands and the diffusional limitations encountered in such systems make them less

* Corresponding authors. Tel.: +86 15200353035.

E-mail addresses: yangliwen.0519@163.com (L.-W. Yang), nfyang@mail.sdu.edu.cn (N.-F. Yang).

probable candidates for generating catalyst complexes in which two or three BINOL ligands are bound to a central metal ion [36]. We envisaged that the use of soluble polymer derived from BINOL and ECH might allow the ligands to suitably orient themselves during complexation leading to better catalysts. Given these, two BINOL-derived chiral polyethers were designed and synthesised, and then used for inducing the formation of the enantiomerically enriched secondary alcohols. Boron based chiral reducing agents/catalysts occupy a special place in chiral chemistry, particularly in asymmetric reductions, because of their extensive use in efficiently and conveniently transforming prochiral ketones into the corresponding secondary alcohols with high enantioselectivities [37–41]. So that the enantioselective metal-free borane reduction of prochiral ketones was conducted to assess the catalytic activity of the polyethers.

2. Experimental

2.1. General

All reagents were used as supplied commercially unless otherwise noted. THF and toluene were distilled from sodium under N₂ before use. Optically active epichlorohydrin (ECH) was purchased from Yueyang Branch Company, Shenzhen Yawangkangli Technology Co., Ltd. ¹H NMR and ¹³C NMR spectra were performed on a Bruker ARX400 MHz spectrometer using tetramethylsilane (TMS) as internal standard. Optical rotation data was measured on a Perkin Elmer Model 341 LC Polarimeter at 365 nm. GPC analysis was performed with a JASCO-GPC system consisting of DG-1580-53 degasser, PU-980HPLC pump, UV-970 UV-vis detector, RI-930 RI detector, and CO-2065-plus column oven (at 38 °C) using two connected Shodex GPC-KF-804L columns in THF (sample concentration = 1 wt%; flow rate = 1.0 ml/min). The molecular weight was calibrated with a commercially available polystyrene. Melting points were determined with a SGW X-4 melting point apparatus. (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl **2**, (S)-3-iodo-2,2'-bis(methoxymethyl)-1,1'-bi-2-naphthol **3** and (S)-3-hydroxy-2,2'-bis(methoxymethyl)-1,1'-bi-2-naphthol **4** were prepared according to the literatures [42–44].

2.2. (S, R)-3-(glycidyloxy)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **5**

To a solution of (S)-3-hydroxy-2,2'-bis(methoxymethyl)-1,1'-bi-2-naphthol **4** (3.9 g, 10 mmol) in dry THF (30 ml), powdered potassium hydroxide (2.24 g, 40 mmol) and tetrabutylammonium bromide (0.32 g, 1 mmol) was added and stirred for 2 h at room temperature. Then (R)-epichlorohydrin (1.84 g, 20 mmol) was added and stirred for 20 h, mixture was extracted with ethyl acetate and washed with a solution of 1:1 brine and water and the combine organic layers were concentrated. Further purification was accomplished using silica column chromatography with 20% ethyl acetate in petroleum ether to give the corresponding epoxide. Yield, 84%, [α]_D²⁰ 365 = –612.50 (c = 10 mg/ml, THF), Elem. Anal. Calcd for C₂₇H₂₆O₆: C 72.63, H 5.87; Found: C 72.82, H 5.81. ¹H NMR (CDCl₃) δ 7.95–7.93 (d, J = 9.02 Hz, 1H, Ar–H), 7.86–7.84 (d, J = 8.0 Hz, 1H, Ar–H), 7.78–7.76 (d, J = 8.0 Hz, 1H, Ar–H), 7.59–7.56 (d, J = 9.0 Hz, 1H, Ar–H), 7.36–7.12 (m, 7H, Ar–H), 5.15–5.13 (d, J = 6.7 Hz, 1H, CH₂), 5.0–4.9 (d, J = 6.6 Hz, 1H, CH₂), 4.91–4.90 (d, J = 6.4 Hz, 1H, CH₂), 4.88–4.83 (dt, J = 5.6, 10.0 Hz, 2H, CH₂), 4.46–4.43 (d, J = 10.7 Hz, 1H, CH), 4.21–4.18 (m, 1H, CH₂), 3.48 (s, 1H, CH₂), 3.17 (s, 3H, CH₃) 2.95 (s, 1H, CH₂), 2.84 (s, 1H, CH₂), 2.81 (s, 1H, CH₂), 2.63 (s, 3H, CH₃), ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 148.1, 145.0, 133.8, 132.2, 129.9, 129.7, 128.5, 127.9, 126.70, 126.6, 126.0, 125.8, 125.5, 125.3, 124.3, 123.7, 120.4, 116.8, 111.3, 99.6, 95.2, 57.4, 56.0.

In a similar manner, compounds (S,S)-3-(glycidyloxy)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **6** were prepared from (S)-3-hydroxy-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **4** and (S)-epichlorohydrin. Yield, 82%, [α]_D²⁰ 365 = –671.02 (c = 10 mg/ml, THF), Elem. Anal. Calcd for C₂₇H₂₆O₆: C 72.63, H 5.87; Found: C 73.02, H 6.02. ¹H NMR (CDCl₃) δ 7.95–7.93 (d, J = 9.02 Hz, 1H, Ar–H), 7.86–7.84 (d, J = 8.0 Hz, 1H, Ar–H), 7.78–7.76 (d, J = 8.0 Hz, 1H, Ar–H), 7.59–7.57 (d, J = 9.0 Hz, 1H, Ar–H), 7.36–7.13 (m, 7H, Ar–H), 5.15–5.13 (d, J = 6.7 Hz, 1H, CH₂), 5.01–4.99 (d, J = 6.6 Hz, 1H, CH₂), 4.91–4.88 (t, J = 3.4 Hz, 1H, OCH₂), 4.86–4.83 (t, J = 5.6 Hz, 2H, CH₂), 4.46–4.43 (d, J = 10.7 Hz, 1H, CH), 4.21–4.17 (m, 1H, CH₂), 3.48 (s, 1H, CH₂), 3.18 (s, 3H, CH₃) 2.96 (s, 1H, CH₂), 2.84 (s, 1H, CH₂), 2.81 (s, 1H, CH₂), 2.63 (s, 3H, CH₃), ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 148.1, 145.0, 133.8, 132.2, 130.0, 129.7, 128.5, 127.9, 126.70, 126.6, 126.0, 125.9, 125.6, 125.3, 124.4, 123.8, 120.5, 116.7, 111.4, 99.7, 95.1, 57.5, 55.9.

2.3. Solution anionic polymerization

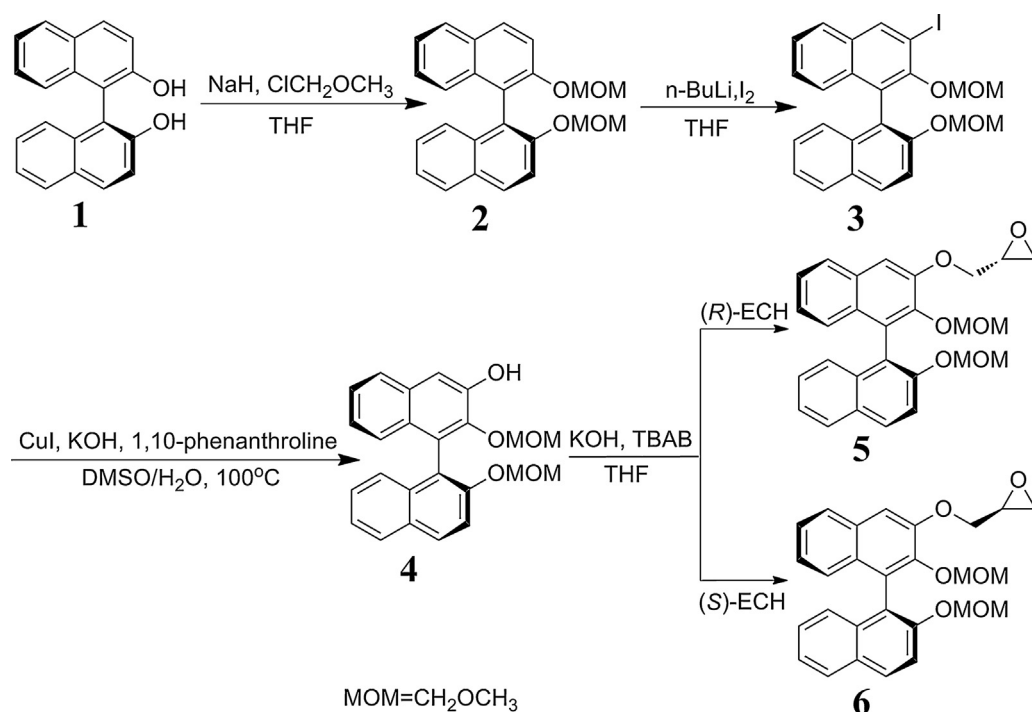
A test tube with stir bar was charged with 10.00 mmol of 3-(glycidyloxy)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **5** or **6** (4.46 g), a desired amount (19 mg, 0.34 mmol for example) of KOH and 1.25 ml xylene under argon atmosphere and then sealed with rubber stopper. The test tube was put into an oil bath thermostated at the desired temperature (such as 140 °C). The reaction mixture was stirred for 48 h. During this time, the mixture turned to auburn and got more and more viscous. After it was complete, 2 ml hydrochloric acid was added dropwise to the tube at 0 °C. After being stirred for 24 h at room temperature. The THF solution was poured into methanol (100 ml). The formed precipitate was filtered and washed with methanol. The above-mentioned precipitation process was repeated, then the obtained precipitate was dried in vacuo at 50 °C to obtain polymer. yield 80–82%. ¹H NMR δ /ppm: 8.02–7.10 [br, 11H, Ar–H], 4.52–3.56 [br, 2H, >CH₂–, CHO–], 3.08–3.01 [br, 3H, CH₂]. Poly-**5**, yield 80%, [α]_D²⁰ 365 = –792.80 (c = 5 mg/ml, THF); Mn = 7.4 × 10³; PDI = Mw/Mn = 2.11. Poly-**6**, yield 82%, [α]_D²⁰ 365 = –912.16 (c = 5 mg/ml, THF); Mn = 7.8 × 10³; PDI = Mw/Mn = 2.02.

2.4. Typical procedure for the reduction of prochiral ketones

BH₃/SME₂ (1.1 ml, 1 M) was added by syringe to a solution of chiral polyether ligand Poly-**6** (0.78 g, 0.1 mmol) in dry THF (5 ml) under nitrogen at 0 °C. The mixture was stirred for 1 h at 0 °C and then a solution of ketone (1 mmol) in dry THF (5 ml) was added dropwise over a period of 1 h at the same temperature and stirred for 6 h, the reaction mixture was then quenched by dropwise addition of 10% NH₄Cl (5 ml). The alcohol product was isolated by extraction with ethyl acetate (10 ml × 3). The organic phase was washed with brine, dried over anhydrous sodium sulfate. After concentration by rotatory evaporation, the product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to afford the corresponding alcohol. The enantiomeric excesses were determined by HPLC with a chiral column (Daicel Chiralcel OD-H; eluent, hexane-isopropyl alcohol; UV detector, 254 nm).

3. Result and discussion

Two new polyether ligands Poly-**5** and Poly-**6** were synthesized from commercially available 1,1'-binaphthol (BINOL) as depicted in Scheme 1. First, chiral (S)-BINOL **1** was reacted with chloromethyl ether to give (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene **2** [42]. (S)-3-iodo-2,2'-bis(methoxymethyl)-1,1'-bi-2-naphthol **3** was easily prepared from readily available **2** through a lithiation-iodination sequence [43]. The copper-mediated (CuI) hydroxy-



Scheme 1. The synthetic route for the monomers 5 and 6.

lation of (*S*)-3-iodo-2,2'-bis(methoxymethyl)-1,1'-bi-2-naphthol **3** with hydroxide salts (KOH and NaOH) as nucleophiles to directly form (*S*)-3-hydroxy-2,2'-bis(methoxymethyl)-1,1'-bi-2-naphthol **4** under mild conditions and in the presence of 1,10-phenanthroline—which is inexpensive and commercially available [44]. The coupling of (*S*)-ECH or (*R*)-ECH with **4** was successfully carried out using KOH as the deprotonation reagent to afford the monomer **5** or **6** with good yield (80–82%) in the presence of tetrabutylammonium bromide (TBAB) (Scheme 1). In most case, the polymerization of optical **5** and **6** were carried out in bulk using KOH as an initiator. In order to obtain higher molecular weight, the solution polymerization of **5** and **6** were conducted in xylene, followed by deprotection of the MOM group to afford Poly-**5** (Mn = 7400,

PDI = 2.11) (Fig. 1) and Poly-**6** (Mn = 7800, PDI = 2.02) (Fig. 2) in high yields, respectively.

It is well known that the enantioselectivity of borane reduction is greatly affected by solvent, temperature, and the amount of catalyst [45–48]. In order to evaluate the above effects, we investigated the reduction of ketone with the chiral polyether ligand Poly-**5** under various reaction conditions and compared the catalytic activity and enantioselectivity of polyether ligand Poly-**6**. The results are summarized in Table 1. After extensively screening, we chose the reaction media of THF, DCM and toluene to examine the solvent effects. At room temperature, the reduction was completed within 6 h in THF and 12 h in toluene and 10 h in DCM with moderate ee values (entries 1–3). As reaction time was shortened to 8 h in toluene,

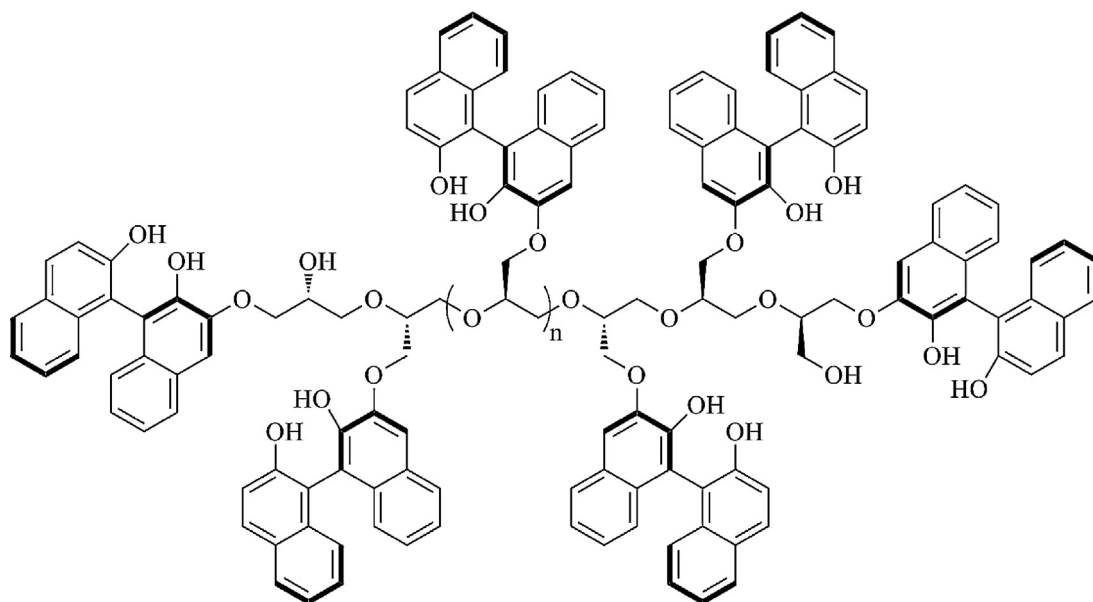
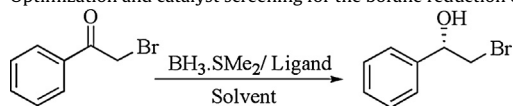


Fig. 1. Poly-(*S,R*)-3-(glycidyoxy)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene Poly-**5**.

Table 1
Optimization and catalyst screening for the borane reduction of 2-bromoacetophenone.^a



Entry	Ligand	Loading(mol%)	Solvent	Reactiontime(h)	Temp(°C)	Yield/% ^b	Ee/% ^{c,d,e}
1	Poly-5	5	Toluene	12	r.t.	93	78
2	Poly-5	5	THF	6	r.t.	90	76
3	Poly-5	5	DCM	10	r.t.	94	70
4	Poly-5	5	Toluene	8	r.t.	80	78
5	Poly-5	5	Toluene	16	r.t.	94	80
6	Poly-5	5	Toluene	12	50	96	72
7	Poly-5	5	THF	12	50	90	66
8	Poly-5	5	Toluene	12	0	92	86
9	Poly-5	10	Toluene	12	0	90	95
10	Poly-5	15	Toluene	12	0	50	95
11	Poly-6	10	Toluene	12	0	95	>99

^a Reaction was carried out on a 1.0 mmol scale in 5 ml of solvent, *n*(2-bromoacetophenone): *n*(BH₃·THF) = 1.0: 1.1.

^b Isolated yields after purification by column chromatography (silica gel, 10% ethyl acetate in petroleum ether).

^c Determined by HPLC analysis using chiral column.

^d Absolute configurations were assigned by comparison with the sign of specific rotations reported in the literature.

^e (S)-product was isolated by column chromatography.

the yield of the product was decrease significantly (entry 4). No expected increase of ee value was observed although a prolonged time was used (entry 5). When the reaction temperature reached 50 °C, the ee values were 72% in toluene and 66% in THF (entries 6 and 7), respectively. By decreasing the reaction temperature to 0 °C, the reaction was completed in toluene within 16 h and 86% ee was obtained. The results showed that toluene is a more effective solvent for the present reduction and the level of enantiometric excess is sensitive to the reaction temperature. Subsequently, the catalyst loading was investigated. It was observed that a increase in the catalyst loading from 5 to 10 mol% at 0 °C resulted in a large increase in the enantioselectivity (95% ee) and a slight loss of yield (entries 8 and 9). By further adding the amount of catalyst to up to 15 mol%, a large decrease in the yield was seen (entry 10), although the ee values were not affected. As a compromise among catalyst loading, the yield and the ee value, a polyether ligand Poly-5 loading of 10 mol% provided the optimum level of enantioselectivity, which is presumably because the rate of the catalyzed reaction in the presence of 10 mol% catalyst is sufficiently faster than the noncatalytic reduction with only BH₃·SMe₂. We also examined the effect of ligand Poly-6 on the reduction of 2-bromoacetophenone, and surprisingly excellent enantiometric excess (over 99%) was obtained. (entry 11). These results indicate that the structural effect of polyether Poly-6

derived from BINOL increase the enantioselectivity of the catalyst greatly.

Under the optimized reaction conditions, the chiral polyether Poly-6 was applied to the asymmetric reduction of a variety of aromatic ketones with BH₃·SMe₂ (Table 2). High yields and enantioselectivities were obtained not only for the prochiral ketones containing electron-donating group (entries 1–3) but also for those with a substitution at the ortho position (entry 4), unlike most of catalyst [49–52], of which the enantioselectivity was highly dependent on steric effects. Over 99% ee values were also observed for prochiral ketones with electron-withdrawing groups (entries 5–9). We also extended the reaction to the reduction of ketones without substituent group under the same conditions, which gave the modest ee values (entries 10, 12 and 14). Raising the amount of catalyst resulted in a slightly increase in the ee values and dramatically decrease in the yields (entries 11, 13 and 15). A simple heteroaromatic ketone 2-acetylpyridine could be reduced in good ee under the influence of catalytic polyether Poly-6 (entry 16). The reduction of aliphatic ketones such as butan-2-one and pentan-3-one gave only 65% and 60% ee, respectively (entries 17 and 18). These indicated that the reactivity and enantioselectivity were significantly affected by a substituent atom of ketone.

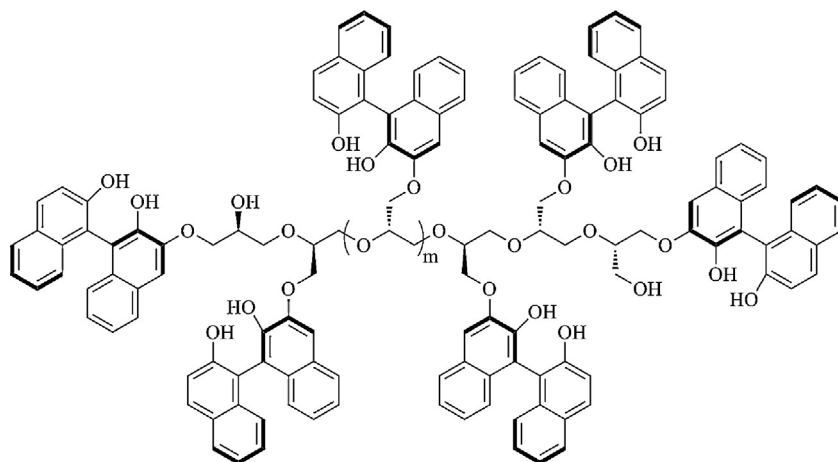


Fig. 2. Poly-(S,S)-3-(glycidyoxy)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene Poly-6.

Table 2
Asymmetric reduction of prochiral ketone.^a

$\text{R}^1-\text{C}(=\text{O})-\text{CH}_2-\text{R}^2 \xrightarrow[\text{Toluene, 0}^\circ\text{C}]{\text{Poly-6, BH}_3\cdot\text{SMe}_2} \text{R}^1-\text{CH}(\text{OH})-\text{CH}_2-\text{R}^2$					
Entry	R ¹	R ²	Yield/% ^b	E.e./% ^c	Config. ^d
1	4-Methylphenyl	H	96	>99	S
2	4-Methoxyphenyl	H	93	>99	S
3	3-Methoxyphenyl	H	95	>99	S
4	Phenyl	Br	95	>99	S
5	4-Chlorophenyl	H	94	>99	S
6	4-Bromophenyl	H	98	>99	S
7	4-Fluorophenyl	H	95	>99	S
8	4-Nitrophenyl	H	98	>99	S
9	4-Chlorophenyl	CH ₃	90	>99	S
10	1-Naphthyl	H	96	76	S
11 ^e	1-Naphthyl	H	50	88	S
12	Phenyl	CH ₃	90	82	S
13 ^e	Phenyl	CH ₃	60	90	S
14	Phenyl	H	92	80	S
15 ^e	Phenyl	H	55	90	S
16	2-Pyridyl	H	92	89	S
17	Ethyl	H	90	65	S
18	Ethyl	CH ₃	88	60	S

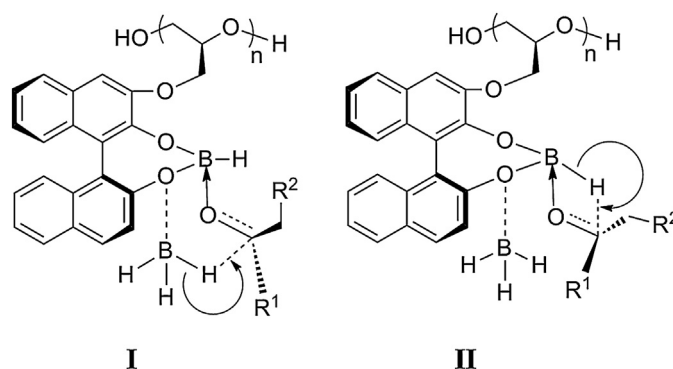
^a n(Ketone): n(BH₃·THF): n(Poly-6) = 1: 1.1: 0.1; reaction time: 12 h.^b Isolated yields after purification by column chromatography (silica gel, 10% ethyl acetate in petroleum ether).^c Determined by HPLC analysis using chiral column.^d Absolute configurations were assigned by comparison with the sign of specific rotations reported in the literature [53,54].^e The amount of catalyst Poly-6 is 15 mol%.

Meanwhile, it is worth noting that the chiral polyether Poly-6 can be easily separated and recycled. After the reduction was completed, the reaction was quenched with water and extracted. After evaporating the solvent, the product was isolated by being redissolved in methanol resulting in the precipitate ligand Poly-6 being obtained. Next, the polyether ligand Poly-6 was washed several times with methanol and dried. Recycling of the polyether ligand Poly-6 was tested by the reduction of 2-bromoacetophenone (Table 3). The results show that ligand Poly-6 could be reused at least six times with no loss of performance (ee over 99%).

The asymmetric borane reduction catalyzed by BINOL derived ligands such as Poly-6 may be rationalized through a proposed mechanism (Fig. 3). Owing to the blocking effect of the polyether segment on the 3-position of BINOL unit, it is likely that two borane molecules cannot complex with the oxygen atom on the 2-position of BINOL unit simultaneously to form a similar transition state proposed by Corey et al. [55–57]. Thus, we proposed that the first borane molecule could combine to two oxygen atom to form a seven-membered ring and that then the secondary borane molecule can only combine to the oxygen atom on 2'-position of BINOL unit. As a result the facial attack of hydride to ketone sub-

Table 3
Recycling experiments of poly-6 in the reduction of 2-bromoacetophenone.

$\text{Ph-CO-CH}_2\text{Br} \xrightarrow[\text{Toluene, 0}^\circ\text{C}]{\text{BH}_3\cdot\text{SMe}_2 / \text{Poly-6}} \text{Ph-CH(OH)-CH}_2\text{Br}$						
Cycle	1	2	3	4	5	6
Recovery(%) ^a	92	94	90	90	88	95
Yield(%) ^b	90	89	92	90	92	94
Ee(%) ^c	>99	>99	>99	>99	>99	>99

^a Reaction was carried out on a 1.0 mmol scale in 5 ml toluene at 0 °C, molar of PhCOCH₂Br, BH₃·SMe₂, Poly-6 = 1.0: 1.1: 0.1; reaction time: 12 h.^b Isolated yield by column chromatography.^c Determined by HPLC analysis using a Daicel Chiralcel column.**Fig. 3.** Presumed transition state for borane reduction.

strates occurs through a macroheterocycle. The transition state I is more favored than II because of the steric interactions between the rigid plane of BINOL and ketones, and hence the attack of hydride occurs on the Si-face of the electronically deficient carbonyl carbon atom to form chiral secondary alcohols. Obviously a more in-depth study is needed to elucidate the mechanism of the asymmetric borane reduction.

4. Conclusion

In conclusion, two new chiral polyether catalysts have been synthesized from commercially available BINOL and epichlorohydrin. The catalytic borane reduction of ketones with these new chiral catalysts was investigated, and high enantioselectivities were obtained (up to over 99%). The results showed that polyether Poly-6 was a very efficient catalyst for the enantioselective borane reduction of ketones. Meanwhile, catalyst Poly-6 can be recovered and reused six times without any significant loss of activity. The development of other asymmetric reactions using these polyethers ligands is currently ongoing in our group.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2015.01.007>.

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