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Synthesis and Catalytic Application of Chiral 1, 1′-Binaphthyl Polymers

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Abstract: The synthesis of a new type of polymers with main chain chirality based on BINOL skeleton is described. Titanium-BINOLate catalysts are easily generated from these polymers and applied to the asymmetric reaction of Et_2Zn with benzaldehyde. The products are obtained in good yields with moderate enantioselectivities.

Keywords: Asymmetric catalysis, chiral polymers, BINOL.

Polymer-supported reagents and catalysts have attracted considerable attention as they offer alternative methods to separate and reuse expensive and often toxic chemicals[1]. Traditionally, the polymer-supported chiral catalysts are prepared by anchoring highly enantioselective monomeric catalysts to flexible and sterically irregular polymer supports. Because of the stereo-irregularity and flexibility of the traditional polymeric chiral catalysts, their catalytic sites do not have well-defined microenvironment. It is very difficult to systematically modify the microenvironment of the catalytic sites in these polymers to improve their enantioselectivity. However, the rigidity and stereoregularity of the chiral conjugated polymers make it possible to systematically adjust the microenvironment of the catalytic sites. Thus preparation of chiral conjugated polymers where the catalytic sites are expected to be highly organized along the rigid and the sterically regular backbone is necessary.

It is well known that axially dissymmetric 1, 1′-binaphthalene-derivatives serve as highly efficient chiral inducers for a wide range of asymmetric reactions[2]. A variety of 2, 2′-dihydroxy-1,1′-binaphthalene (BINOL) ligands applied to catalytic asymmetric organozinc additions to carbonyl compounds have been recently reported[3]. It is also reported that the introduction of bulky substituents to the 3, 3′-positions of BINOL can lead to better steric control and consequently increase enantioselctivity because the positions are closest to the chiral catalytic center[4]. In order to modify the microenvironment of the catalytic sites, we reported the synthesis of polymers **6a-d** from optically pure **4** and 1, 2-phenylene diamine **5a**, 1, 3-phenylene **5b**, 1, 4-phenylene diamine **5c** and 4-aminophenyl ether **5d**, respectively.

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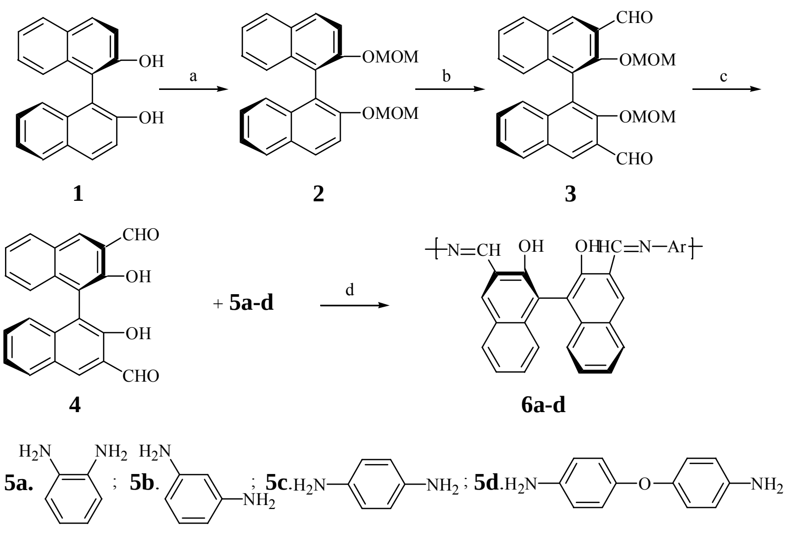
Scheme 1



(a) NaH, CH_3OCH_2Cl, DMF/THF= 1:2, 86%; (b) *n*-BuLi, ether, 0°C; Then DMF, 72%; (c) HCl, THF, 0°C, 80%; (d) THF/glacial acetic acid= 1:4, **5a-d**, 85-97%.

The synthetic route is outlined in **Scheme 1**. The key BINOL derivative (R)–3, 3′–diformyl–2, 2′–dihydroxy–1, 1′–binaphthyl **4** was synthesized according to the method reported by Lin Pu[5]. The commercially available (R)–BINOL **1** was used as starting material. The hydroxyl group of **1** was protected with the methoxyl methyl (MOM) group, and the resulting protected BINOL **2** was lithiated with *n*-BuLi followed by carbonylation to give MOM-protected 3, 3′-diformyl–BINOL **3**. The protecting groups were removed by acid treatment to afford **4**. Reaction of **4** with **5a-d** at 40°C gave polymers **6a-d** in 85-97% yield. IR, ^{1}H NMR and MS spectra confirmed the structures of **2-4**. Polymers **6a-d** were found to be insoluble in regular organic solvents and basic water solution, and their structures were confirmed by IR.

In order to evaluate the efficiency of these polymeric BINOL ligands, the titanium complex-catalyzed reaction of Et_2Zn with benzaldehyde **7** was chosen as a model reaction[6] (**Scheme 2**). In a typical experimental procedure, a mixture of polymer catalyst (0.063 mmol, based on the repeated unit) and 0.15 mL Ti $(O^iPr)_4$ (0.44 mmol) in 5 mL CH_2Cl_2 was stirred at rt for 12 hr under nitrogen. Then 0.78 mL of 1.2 mol/L $ZnEt_2$ (0.94 mmol) was added and the mixture was stirred for another 30 min. The solution was cooled to 0°C and 0.032 mL benzaldehyde (0.312 mmol) was added to the solution and the final solution was allowed to stir at 0°C for 12 hr. The reaction was stopped by addition of saturated NH_4Cl. The polymer was removed by filtration. The ethyl acetate extract was dried over $MgSO_4$ and the yield of the product was determined by GC, the e.e. was analyzed by Chiralcel OD column. The preliminary results are summarized in **Table 1**. Polymer **6d** was found to have the highest enantioselectivity.

In summary, a new kind of chiral polymers **6a-d** was synthesized and applied to the

Scheme 2

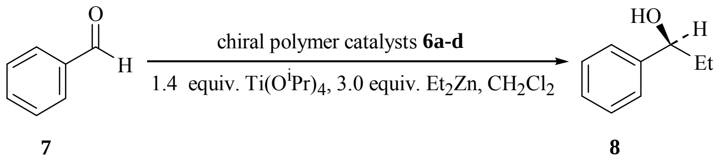


Table 1 Asymmetric reaction of diethylzinc with benzaldehyde catalyzed by polymeric Ti-BINOLate catalysts

Entry[a]	Polymer	Conv. (%)[b]	Config.	e.e. (%)[c]
1	**6a**	80	S	26
2	**6b**	96	S	46
3	**6c**	99	S	43
4	**6d**	99	S	60

[a] Benzaldehyde/chiral catalyst/$Ti(O^iPr)_4/Et_2Zn$= 1.0:0.2 (per BINOL unit):1.4:3.0 (molar ratio); solvent=dichloromethane; 0°C; 24 hrs. [b] Conv. determined by capillary GC. [c] e.e. was determined by HPLC analysis using Chiracel OD.

asymmetric reaction of Et_2Zn with benzaldehyde **7**. The product **8** with high yields and moderate e.e. was achieved.

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