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Asymmetric C–C bond formation with L-prolinol derived chiral catalysts immobilized on polymer fibers

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Abstract—*N*-(4-Vinylbenzyl)-α,α-diphenyl-L-prolinol was immobilized on polyethylene fibers by electron beam induced pre-irradiation grafting using styrene as a co-monomer. The resulting polymer supported catalyst **P2** was utilized in asymmetric C–C bond forming reactions and its performance compared with those of previously prepared fibrous cross-linked α,α-diphenyl-L-prolinol **P1** and homogeneous model compounds. The fibrous catalyst yields similar enantioselectivities in the asymmetric addition of diethylzinc to benzaldehyde as its homogeneous reference reaction and can be recycled with minimal loss of activity. When **P2** was used as the catalyst in the addition of phenylacetylene to benzaldehyde, the corresponding propargylic alcohol was obtained with enantiomeric excesses of up to 91%.

1. Introduction

Several chiral ligands have proven to be successful in the catalytic enantioselective nucleophilic additions of dialkylzincs[1] and phenylacetylenes[2,3] to aldehydes, some of the most studied, single step, asymmetric carbon–carbon bond forming reactions. The strategy of attaching such chiral ligands to polymeric supports has been widely used to prepare heterogeneous, immobilized catalysts for enantioselective conversions.[4] This approach is advantageous compared to the classical homogeneous version due to: (1) the ease of separation of the expensive chiral catalyst from the reaction system, and hence the possibility of reutilizing the catalyst for successive reactions, (2) convenient operation in flow reactors or flow membrane reactors for continuous production, and (3) for the development of environmentally safe processes for the production of fine chemicals.

Various chiral β-amino alcohols supported on polystyrene (PS) have been used as catalysts[5] and earlier work has been covered in several reviews.[6] The successful design of supported catalysts for the addition of dialkylzincs to aldehydes is a particular challenge: In the absence of added catalysts, these reactions take place slowly to give a racemic product. For example, in toluene at 20 °C, benzaldehyde reacts with diethylzinc to give racemic 1-phenylpropanol in ca. 15% yield after 18 h.[5a] Accordingly, catalysts supported on PS operate in a competitive situation and unless a sufficient proportion of the catalytic sites are readily accessible, the reaction paths yielding racemic products will have a significant contribution to the overall reaction. Consequently, in these cases, relatively low enantioselectivities may be observed.

A significant problem associated with the conventional PS-based supports is their low mechanical strength and often poor thermo-oxidative stability. In a previous paper, we described the facile anchoring of chiral TADDOL and amino alcohol ligands on mechanically stable and chemically inert polyethylene (PE) fibers by electron beam (EB) induced pre-irradiation graft copolymerization.[7] Chiral styrenic ligand derivatives such as **1** (Fig. 1) were successfully immobilized on the fibrous support to generate the corresponding polymeric catalysts, which were then employed in the addition of diethylzinc to benzaldehyde. For example, the fibrous catalyst **P1** gave 1-phenylpropanol in 36% yield and 62:38 ratio of the (*R*)- and (*S*)-enantiomers.[7] The catalyst was successfully recycled without significant losses in activity and enantioselectivity.

The low yield and only moderate stereocontrol obtained with **P1** are possibly associated with the cross-linking nature of the styrenic ligand monomer **1** resulting in the active sites being embedded in the surrounding polymer

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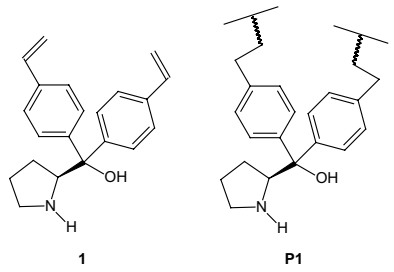


Figure 1. Previously described monomeric and fibrous chiral amino alcohols **1** and **P1**.

matrix. As a continuation of the previous study, we report here the immobilization of the pendantly substituted chiral amino alcohol **2** (Fig. 2) on PE fibers using the previously described EB grafting technique. The corresponding polymeric catalyst **P2** together with several homogeneous reference catalysts was then employed in the addition of diethylzinc and phenylacetylene to benzaldehyde and the results of the former reaction compared with those obtained in our previous study.[7]

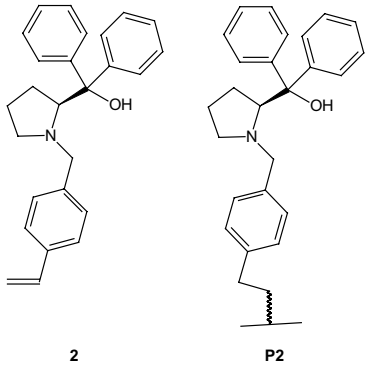
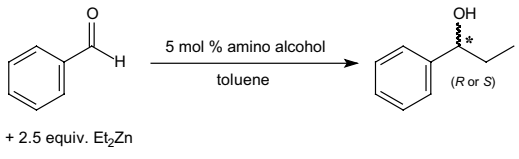


Figure 2. Monomeric and fibrous chiral amino alcohols **2** and **P2** described in the present work.

2. Addition of diethylzinc to benzaldehyde

The addition of diethylzinc to benzaldehyde in the presence of chiral amino alcohol catalysts yields a mixture of (*R*)- and (*S*)-1-phenylpropanols (Scheme 1). The predominant enantiomer is determined by the configuration of the chiral catalyst. Enantioselectivity of the addition is thus highly dependent on the structure of the ligand, especially the substitution pattern of the nitrogen atom[5a,8] and the carbinol carbon. In the case of supported chiral catalysts, architecture, and properties of the support, likewise, play an important role in determining the catalytic performance.



Scheme 1. Addition of diethylzinc to benzaldehyde catalyzed by chiral amino alcohols.

The previously reported monomeric ligand **1** contains two styryl functionalities, thus potentially resulting in a cross-linked polymeric network when subjected to radical polymerization. Such architecture may result in a limited accessibility of the chiral active sites, which in turn may have contributed to the fairly low yields and enantioselectivities observed in the previous study using **P1**.[7] We were thus interested in the opportunity to compare cross-linking versus pendant immobilization of chiral amino alcohols to recyclable fibrous supports and the possible benefits in the site accessibility obtained with the latter.

The styrenic chiral amino alcohol **2** and the reference catalyst **3** were prepared in good yield from α,α-diphenyl-L-prolinol **4** (Fig. 3) and 4-vinylbenzylchloride following a literature procedure.[9] Compound **2** was then immobilized on polyethylene fibers according to the previously described EB pre-irradiation grafting procedure[7] to obtain the polymeric chiral catalyst **P2** with a loading of 0.4 mmol/g as confirmed by elemental nitrogen analysis. Next, the activity and selectivity of **P2** was investigated in the addition of diethylzinc to benzaldehyde at 0 °C and ambient temperature using a catalyst loading of 5 mol %. The monomeric chiral amino alcohols **1**–**5** were studied for comparison. The results are presented in Table 1 together with those previously obtained with **P1**.[7]

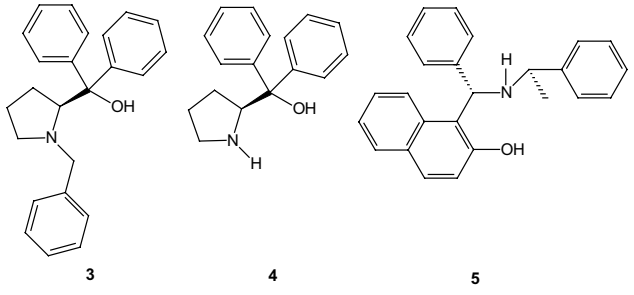


Figure 3. Chiral amino alcohols **3**–**5**.

As evident from Table 1, the pendantly supported catalyst **P2** is superior to the cross-linked catalyst **P1** in terms of reaction yield. In addition, the enantioselectivities obtained with **P2** are slightly higher than those obtained with **P1**. Overall the performance of **P2** is very similar to those of its homogeneous *N*-vinylbenzyl and *N*-benzyl substituted analogues **2** and **3**. The enantioselectivities of all studied *N*-substituted catalysts are slightly lower than those obtained with the homogeneous *N*–H prolinols **1** and **4**. This is in accordance with previous observations by others.[10] Thus, addition of Et_2Zn to benzaldehyde in the presence of 5 mol % **P2** gave (*R*)-1-phenylpropanol in 98% yield and 38% enantiomeric excess. The polymeric catalyst was successfully recycled for two subsequent runs without significant losses in activity and enantioselectivity. The

Table 1. Addition of diethylzinc to benzaldehyde in the presence of homogeneous and heterogeneous chiral amino alcohols

Entry	Ligand	PhCHO (mmol/ml)	Polymer (g)	Loading (mmol/g)	Temperature (°C)	Yield[a] (%)	Ee[d] (*R*)%	Reference
1	**1**	0.38			0	70[b]	76	7
2	**2**	0.42			0	Quant.[c]	44	This work
3	**3**	0.42			0	Quant.[c]	44	This work
4	**4**	0.38			0	97	68	7
5	**5**	0.2			0	89[b]	86	This work
6	**P1**	0.52	1	0.21	0	36	24	7
7	**P1**[e]	0.56	0.8	0.21	0	33	20	7
8	**P1**[f]	0.49	0.7	0.21	0	30	22	7
9	**P2**	0.35	0.53	0.4	0	98	38	This work
10	**P2**[e]	0.35	0.5	0.4	0	95	40	This work
11	**P2**[f]	0.42	0.48	0.4	0	96	36	This work
12	**P2**	0.42	0.53	0.4	25	Quant.[c]	34	This work
13	**3–Li**	0.4			0	97	46	This work
14	**P2–Li**	0.4	0.45	0.4	0	85	25	This work

[a] Estimated by GC after 24 h.
[b] Isolated yield.
[c] No benzaldehyde detected by GC or ^{1}H NMR.
[d] Determined by chiral GC.
[e] First regeneration of the polymeric catalyst.
[f] Second regeneration.

reaction temperature (0 °C vs 25 °C) has only little effect on the performance of **P2** in its present application. The effect of reaction time on the yield approximated of 1-phenylpropanol using **P2** and regenerated **P2** as catalysts in the three successive runs is displayed in Figure 4.

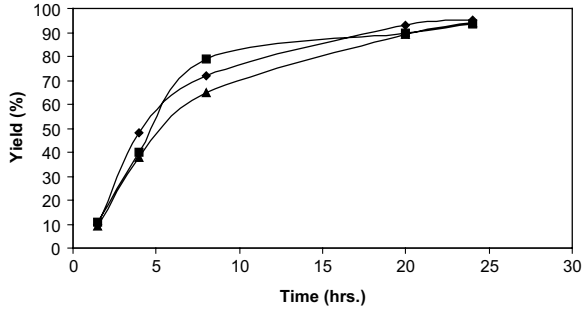
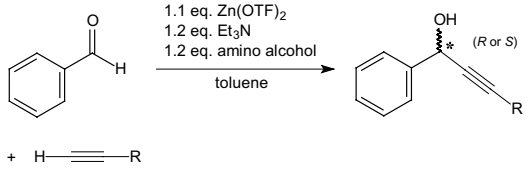


Figure 4. The effect of reaction time on the yield of 1-phenylpropanol using **P2** and regenerated **P2** in the addition of diethylzinc to benzaldehyde. Symbols: (◆) First run, (■) First regeneration, (▲) Second regeneration (entries 9–11 in Table 1).

Two additional experiments were carried out using the lithium salt of the chiral amino alcohols **3** and **P2** (entries 13 and 14 in Table 1). As described previously by Corey et al.,[11] enantioselectivity in the addition of diethylzinc to benzaldehyde may in some cases be improved by the use of the lithium salt derivatives of the chiral β-amino alcohol ligands. Inspired by earlier work,[12] the homogeneous and polymeric ligands **3** and **P2** were treated with an equimolar amount of butyl lithium and employed in the alkylation of benzaldehyde. Thus, when benzaldehyde (1 equiv) was treated with diethylzinc (2.5 equiv) in the presence of **3–Li** (0.1 equiv) in toluene at 0 °C for 22 h, a 97:1.6:1.4 ratio of 1-phenylpropanol (46% ee), benzyl alcohol and unreacted benzaldehyde was detected by GC analysis. Unfortunately, under identical reaction conditions, the performance of the polymeric analogue **P2–Li** was slightly inferior to the homogeneous system producing an 85:5:10 ratio of 1-phenylpropanol (ee = 25%), benzyl alcohol and unreacted benzaldehyde as determined by GC. Thus, contrary to some literature reports, in comparison with **P2**, the use of the lithium salt method does not result in any improvements in terms of yield or enantioselectivity of the polymeric catalyst. One possible explanation may be related to the presence of 'inert' salt effects on the stereochemical outcome of this reaction.[13]

3. Addition of phenylacetylene to benzaldehyde

Due to the promising results obtained in the addition of Et_2Zn to benzaldehyde we decided to extend the application of **P2** to other types of enantioselective transformations. Thus, we undertook a preliminary study of phenylacetylene addition to benzaldehyde in the presence $Zn(OTf)_2$ using **P2** as catalyst (Scheme 2).



Scheme 2. Addition of phenylacetylene to benzaldehyde catalyzed by chiral amino alcohols.

The obtained chiral secondary propargylic alcohols are versatile building blocks for asymmetric synthesis and their utility as key starting materials in a number of applications has been demonstrated in previous works

by other authors.[14] A number of ligands have been employed as chiral mediators in the enantioselective alkynylation of aromatic aldehydes.[2a,b] The relationship between ligand structure, enantioselectivity and catalytic activity in this reaction has been investigated by utilizing various substituted chiral amino alcohols.[2a] In these reports, some problems were encountered: (a) Systems with good enantioselectivity required the use of large quantities of the chiral auxiliary;[3] (b) Formation of considerable amounts of side products and only moderate enantioselectivities for the desired products.[2,3,15]

In our preliminary investigation, the chiral amino alcohol **5** (Fig. 3) was prepared[16] and used as the model catalyst. To our knowledge, compound **5** has not been applied previously for this transformation. In order to find suitable conditions for the application of **P2** in combination with a Zn reagent, we first turned to the procedure described by Moore et al. using $Ti(OiPr)_4$ for activation of the catalyst system.[17] Using this procedure with **5**, 1-phenylpropanol was obtained in low yield without observable formation of the target propargylic alcohol even at prolonged reaction times. Based on these observations, we suspected that diethylzinc is not reactive enough for in situ generation of the zinc phenylacetylide intermedite, which according to the two step reaction mechanism[16] adds to benzaldehyde to produce the chiral secondary propargylic alcohol. Next, following the procedure described by Carreira and co-workers[3a] we were able to successfully carry out this reaction using **P2** in combination with $Zn(OTf)_2$ and Et_3N. Compounds **3** and **5** were used as reference catalysts. The results are summarized in Table 2.

Our results compare favorably with the highest enantioselectivities reported for the addition of terminal alkynes to aromatic aldehydes using either stoichiometric or catalytic amounts of chiral amino alcohols in combination with $Zn(OTf)_2$.[3] As evident from Table 2, grafting of the catalyst to a polymer support significantly decreased the yield of the reaction, whereas the enantioselectivity remained on the same level. Thus, alkynylation of the benzaldehyde using the homogeneous catalyst **3** gave the propargylic alcohol in a quantitative yield with 89% enantiomeric excess, while under identical reaction conditions a <50% yield and 91% ee was obtained with the polymeric catalysts **P2**. Also in this case the fibrous catalyst was successfully recycled without significant losses in catalyst performance. The low yields obtained with the fibrous catalyst are possibly associated with poorer interaction between the reagents in the polymer matrix and the related site accessibility issues and/or the low swelling of the polymer in the solvent employed.

Table 2. Addition of phenylacetylene to benzaldehyde catalyzed by homogeneous and heterogeneous chiral amino alcohols in combination with $Zn(OTf)_2$ and Et_3N

Entry	Ligand	Time (h)	Yield (%)[a]	Ee (%)[c]
1	**3**	15	Quant.[b]	89
2	**5**	23	67	48
3	**P2**	48	45	91
4	**P2**[d]	48	37	90
5	**P2**[e]	48	30	88

[a] Isolated yield after flash chromatography on silica gel.
[b] Estimated by GC after 15 h (no benzaldehyde detected).
[c] Determined by HPLC.
[d] First regeneration of the polymeric catalyst.
[e] Second regeneration.

4. Scanning electron microscope studies

In order to obtain further insight into the morphology of the fibrous catalysts, a scanning electron microscope (SEM) study was carried out on **P2**, the corresponding unfunctionalized parent fiber **P0** and the previously reported catalyst **P1**. SEM micrographs of the fiber surfaces are displayed in Figure 5. Both functionalized fibers **P1** and **P2** show clear evidence of a surface layer when compared to the ungrafted fiber **P0**. For both **P1** and **P2**, grafting has occurred exclusively on the fiber surface and not in the space between the individual fibers. The fibrous morphology is clearly retained in the grafting experiments.

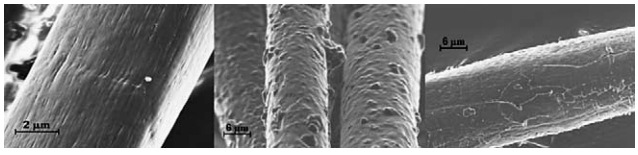


Figure 5. A scanning electron micrograph (SEM) of the unfunctionalized parent fiber **P0** (left) and the fibrous amino alcohol catalysts **P1** (middle) and **P2** (right).

5. Conclusion

The new fibrous chiral amino alcohol catalyst **P2** has been prepared by electron beam induced preirradiation grafting of the corresponding monomer onto mechanically stable polyethylene fibers and utilized in the enantioselective additions of diethyl zinc and phenylacetylene to benzaldehyde. In contrast to catalyst **P1** reported in our previous study,[7] the pendantly immobilized catalyst **P2** provides (*R*)-1-phenylpropanol in excellent yield and slightly higher but similarly moderate enantioselectivity. The higher yield is possibly a consequence of the enhanced site accessibility resulting from the pendant versus cross-linking immobilization of the chiral ligand. The scope of the fibrous catalysts was further broadened by the application of **P2** in the addition of phenylacetylene to benzaldehyde. High enantioselectivities but poor yields were obtained. The fibrous catalyst was, in both applications, successfully recycled twice without significant loss in performance. Polyethylene fibers in combination with the EB-grafting technique thus provides an attractive, morphologically stable, robust, and easily recyclable alternative to the traditional polystyrene based supports, which commonly suffer from poor mechanical and thermal stabilities.

6. Experimental

6.1. General

All reactions were carried out under argon atmosphere using flame-dried glassware. $Ti(OiPr)_4$ (Acros Organics, 98%), Et_2Zn (1.1 M in toluene, Fluka), $Zn(OTf)_2$ (Acros Organics, 98%), and phenylacetylene (Acros Organics, 98%) were used as received. The chiral reference amino alcohol **4** was purchased from Fluka. Synthesis of **1** and **P1** has been described in our previous paper.[7] Compounds **2** and **3**,[9] as well as **5**[13] were prepared according to literature procedures. Triethylamine was dried by distillation over KOH. All organic solvents were dried and distilled under argon prior to use when applicable. Benzaldehyde (Merck) was distilled prior to use. Toluene (Aldrich, anhydrous) was purified by passing through columns containing alumina. All other commercially available chemicals and solvents used were of puriss p.a. quality, or purified and dried according to standard methods. TLC: precoated silica gel 60 F254 (Merck); visualization by irradiation with UV light. Flash chromatography (FC): silica gel 60 (0.04–0.063, Merck). Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded using a Jeol JNM A 500 NMR spectrometer operating at 500.13 MHz for ^1H and 125.78 MHz for ^{13}C, respectively. The chemical shifts are expressed in ppm downfield from internal TMS or referenced against the solvent signal. Polarimetric analyses were performed using a Perkin Elmer 241 polarimeter. Enantioselectivities were determined either by capillary gas chromatography (CGC) on an HP-5 GC (cross-linked 5% PH ME siloxane, column: 15 m × 0.53 mm × 1.5 μm film β-cyclodextrin, 30 m × 0.25 mm × 1.5 μm film thickness) or by HPLC using an HP 1090 liquid chromatograph system equipped with a Chiralcel OD column (Daicel Chemical Industries), 10% IPA in hexane mixture as mobile phase and detection by UV–vis detector at 254 nm. GC/MS analyses were performed using an HP-5890 SERIES II gas chromatograph equipped with a 5971 A mass selective detector (column: 30 m × 0.25 mm × 0.25 μm HP-1MS). Elemental analyses were obtained from the Microanalytical Service of Micro Kemi AB, Uppsala (Sweden).

6.2. Fiber supported chiral catalyst P2

Cut polyethylene fibers (0.7 Dtex) were irradiated in a nitrogen atmosphere to a total dose of 100 kGy using an Electrocurtain electron accelerator (Energy Science Inc.) operating at an acceleration voltage of 175 kV. Immediately after the irradiation, 5 g of the polyethylene fibers were immersed in a nitrogen purged solution of 1.85 g of the monomer **2**, 7.1 g styrene, and 0.14 g divinylbenzene in 35 g ethanol. The reaction was allowed to proceed under nitrogen for 2 h at 60 °C. Next 75 mL of degassed water was added and the temperature increased to reflux for 6 h. The grafted fiber was separated by filtration, washed twice with ethanol, and dried in vacuum. The gravimetrical grafting yield was calculated to 90%. Loading of **P2** was confirmed by nitrogen analysis (average of two runs: 0.57 wt% N, corresponding to a loading of 0.4 mmol ligand per gram of fiber). IR (KBr, cm^{-1}): 3360, 3082, 3025, 2913, 2848, 1600, 1493, 1472, 1451, 1370, 1029, 757, 748, 698, 694, 538 cm^{-1}.

6.3. General procedures for the addition of diethylzinc to benzaldehyde in the presence of chiral amino alcohol catalysts

6.3.1. Homogeneous catalysts. In a typical procedure, to a solution of **3** (72.1 mg, 0.21 mmol) in toluene (10 mL) at 0 °C was added dropwise a solution of Et_2Zn (9.6 mL, 1.1 M in toluene) during a period of 30 min. The mixture was slowly warmed to ambient temperature and stirred for another 30 min. After cooling to 0 °C, benzaldehyde (0.4 mL, 4.21 mmol) was slowly added for 5 min, and the reaction mixture was then stirred at ambient temperature for 24 h. The reaction was then quenched by addition of 2% cold aqueous HCl. After extraction with dichloromethane (2 × 20 mL) the combined organic extracts were washed with brine (10 mL), dried over magnesium sulfate, and evaporated to dryness.

6.3.2. Polymeric catalyst. As described in the previous paper,[7] the calculated amount of the polymeric catalyst **P2** (0.53 g, loading 0.4 mmol/g, 0.21 mmol) was suspended in toluene (15 mL) and stirred for 1 h at ambient temperature. The solvent was stripped off in vacuo to remove traces of water. The catalyst was then suspended again in toluene (10 mL) and treated with a solution Et_2Zn (9.6 mL, 1.1 M in toluene) added dropwise at 0 °C during a period of 30 min. The reaction mixture was slowly warmed to ambient temperature and stirred for an additional 30 min. After cooling to 0 °C, benzaldehyde (0.4 mL, 4.21 mmol) was slowly added for a period of 5 min, and the resulting reaction mixture then left to stir for 24 h at ambient temperature. The reaction was then quenched by the addition of 2 M HCl (10 mL) and stirred for 90 min at ambient temperature. The polymeric catalyst was filtered on a frit and washed with water (20 mL), THF (10 mL), and diethyl ether (50 mL). The filtrate was extracted with diethyl ether (2 × 50 mL) and the combined organic phases washed with brine (50 mL), dried over magnesium sulfate, and evaporated to dryness.

6.3.3. Lithium salts. A solution of the chiral ligand **3** or a suspension of the polymeric catalyst **P2** (0.2 mmol, 10 mol%) in toluene was treated dropwise with an equimolar amount of *n*-BuLi (2.5 M solution in hexanes) at −40 °C. After stirring for 15 min, a solution of Et_2Zn (5 mmol, 1.1 M in toluene) was added for a period of 20 min and the mixture was then allowed to warm up to 0 °C. Next, benzaldehyde (2 mmol) was added and the reaction mixture was stirred for 20 h at 0 °C. The reaction was quenched by the addition of 5M HCl (10 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with $NaHSO_3$ (20 mL), $NaHCO_3$ (20 mL), brine (50 mL), and dried

over magnesium sulfate. Evaporation to dryness afforded the crude products.

6.4. General procedures for the addition of phenylacetylene to benzaldehyde in the presence of chiral amino alcohol catalysts

6.4.1. Homogeneous catalysts. A 50 mL round bottom flask was charged with $Zn(OTf)_2$ (200 mg, 0.55 mmol, 1.1 equiv) and **3** (212 mg, 0.6 mmol, 1.2 equiv) and purged with argon for 30 min. To this mixture was then added toluene (2 mL) and triethylamine (61 mg, 85 μL, 1.2 equiv). The resulting mixture was stirred for 2 h at ambient temperature followed by the addition of phenylacetylene (61.3 mg, 66 μL, 0.6 mmol) in one portion. Next, after stirring for 15 min, benzaldehyde (53 mg, 51 μL, 0.5 mmol) was added in one portion. After an appropriate reaction time, the mixture was quenched by addition of saturated aq NH_4Cl solution (5 mL). The mixture was poured into a separation funnel containing diethyl ether (10 mL). The layers were separated and the aqueous phase was extracted with diethyl ether (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over magnesium sulfate, and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel (pentane/diethyl ether 95:5) afforded the propargylic secondary alcohol.[12,13] The enantiomeric ratio of the product was determined by HPLC (Chiralcel OD, 10% *i*PrOH in hexane, 254 nm); *t*, 13.228 min (major enantiomer), 22.469 min (minor enantiomer).

6.4.2. Polymeric catalyst. A 50 mL RB flask was charged with $Zn(OTf)_2$ (200 mg, 0.55 mmol, 1.1 equiv) and **P2** (0.757 g, loading 0.4 mmol/g, 0.303 mmol, 1.2 equiv), and kept in vacuo (0.03 mbar) for 12 h at ambient temperature. Next, the flask was purged with argon for 30 min followed by the addition of toluene (8 mL), and triethylamine (31 mg, 43 μL, 1.2 equiv). The resulting mixture was stirred for 19 h at ambient temperature before addition of phenylacetylene (31 mg, 33 μL, 0.303 mmol) in one portion. After stirring for 30 min, benzaldehyde (27 mg, 25 μL, 0.252 mmol) was added in one portion. After an appropriate reaction time, the mixture was quenched by the addition of saturated aq NH_4Cl solution (10 mL). The polymeric catalyst was filtered on a frit and washed with water (20 mL), THF (10 mL), and diethyl ether (50 mL). The filtrate was extracted with diethyl ether (2×50 mL) and the combined organic phases washed with brine (50 mL), dried over magnesium sulfate, and evaporated to dryness. Purification of the residue by flash column chromatography on silica gel (pentane/diethyl ether 95:5) afforded the propargylic secondary alcohol. The enantiomeric ratio of the product was determined by HPLC.

6.5. Recycling of the polymeric catalyst

For repeated reactions, the polymeric catalyst was washed subsequently with THF, 5 M aq HCl, methanol, acetone, and dichloromethane followed by drying under high vacuum (oil pump) at ambient temperature for several hours.

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