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Development of efficient methods for the immobilisation of multicomponent asymmetric catalysts

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Immobilisation of multicomponent asymmetric catalysts has been achieved utilizing soluble polymers and dendrimers containing BINOL ligands. A novel approach based on the use of ''catalyst analogue'' helps to position the ligands suitably on the polymer backbone. Utilizing metal-bridged polymers, a simple and efficient method for immobilisation without the need for a polymer support has also been realized. Heterogeneous Al-Li-bis(binaphthoxide) and μ-oxodititanium complexes thus obtained have been used as catalysts for the asymmetric Michael addition and the asymmetric carbonyl-ene reactions respectively. The catalysts displayed high activity affording the corresponding products with high enantiomeric excesses. In many cases, the catalysts could be recovered and reused.

Keywords: Asymmetric catalysts; Immobilisation; Polymers; Dendrimer; Self-assembly

1. Introduction

Enzymes are capable of promoting various asymmetric transformations with high levels of enantioselectivity through a synergistic cooperation between various active sites that help in the orientation of the substrates around the reactive site and the stabilization of the transition state. In recent years, there has been a growing interest in the development of highly organized multicomponent asymmetric catalysts for a variety of transformations [1–9]. Some of these complexes utilize the synergistic cooperation strategy to facilitate the formation of unique optically active products, which are difficult to obtain even in racemic form [10–13]. While significant progress has been made in exploiting the potential of these catalysts in various asymmetric transformations, their practical utilities are often hampered by their instability to air and moisture. Moreover, the chiral ligands used are either expensive or difficult to synthesize. Hence it is important to develop methods that facilitate the recovery of these catalysts or ligands for subsequent use. Polymer-supported catalysts offer the advantages of easy product

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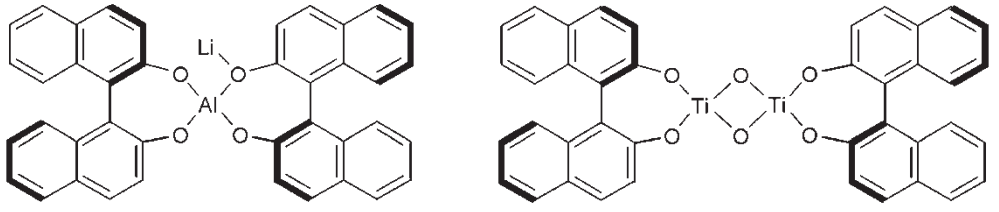


Figure 1. Multicomponent asymmetric catalysts chosen for immobilisation.

separation, recovery and reuse of the catalysts [14–19]. Recently, we have been interested in the development of methods to effectively immobilize multicomponent asymmetric catalysts (MACs) such as Al-Li-bis(binaphthoxide) complex (ALB) reported by us [2] and the μ-oxodititanium complex reported by Nakai *et al.* [9] (figure 1).

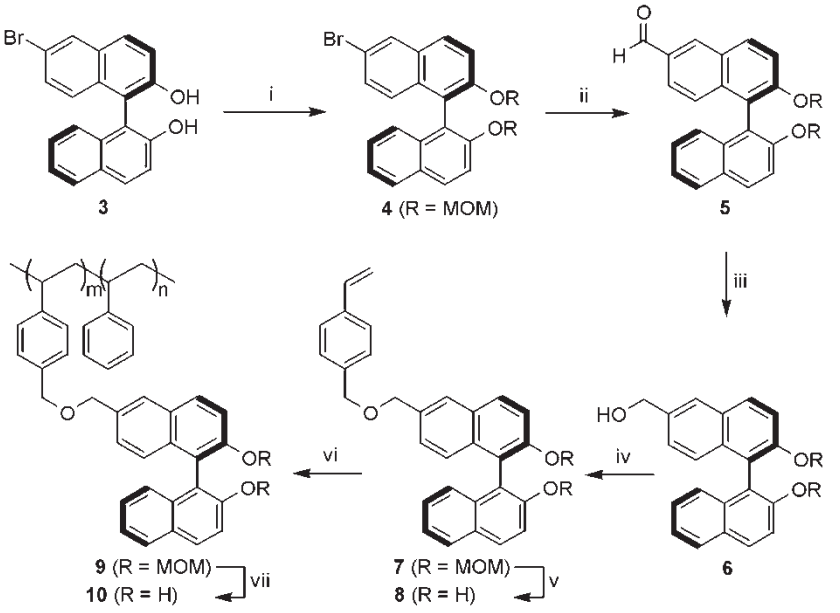
Initial attempts to immobilize catalyst **1** by the conventional approach using commercially available polystyrene resins resulted in less efficient catalysts that afforded racemic products in low yields [20]. In order to realize high activity, it is important to use supports that help in maintaining the organized structure of these catalysts. In this regards, we were interested in exploring the scope of soluble polymer supports that could facilitate the formation of efficient catalysts. Since the complexation occurs essentially in solution, highly active catalysts can be generated. Further, when ligands from different polymer chains are involved in the assembly, cross-linked heterogeneous catalysts will be formed [21, 22]. Herein we describe various strategies developed by us for the immobilisation of these sophisticated multicomponent asymmetric catalysts.

2. Results and discussion

2.1. *Soluble polymer-supported BINOL ligands*

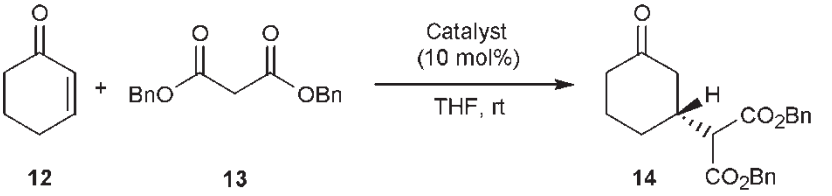
2.1.1. Linear polymers. A soluble, polystyrene supported BINOL derivative was first prepared by the method described in scheme 1. (*R*)-6-bromo-2,2′-dihydroxy-1, 1′-binaphthalene (**3**) [23] was converted to the 6-hydroxymethyl derivative **6** in three steps and subsequently coupled to a styryl derivative by etherification to get the monomer **7**. Polymer **9** [GPC: $M_w = 9585$, PDI = 1.4)] was then obtained by the free radical co-polymerisation of **7** with an excess of styrene. The protecting groups were finally removed by acid treatment to get polymer **10**. Polymer **10** was soluble in solvents such as CH_2Cl_2, toluene and THF and readily precipitated in methanol or hexane.

In a preliminary experiment, monomer **8** was treated with $LiAlH_4$ in THF to generate the soluble ALB complex **11**. This complex promoted the asymmetric Michael reaction of 2-cyclohexen-1-one (**12**) with dibenzyl malonate (**13**) affording the Michael adduct **14** in 42% yield with 99% ee (see table 1, entry 1). This reaction suggested that the loss of



Scheme 1. (i) NaH, THF, 0°C, 30 min; then MOMCl, rt, 3 h, 96%; (ii) *n*-BuLi, THF, −88°C; then DMF, 67%; (iii) $NaBH_4$, THF-MeOH, 0°C, 15 min, 88%; (iv) NaH, THF-DMF, 0°C, 30 min; then 4-vinylbenzylchloride, rt, 72 h, 70%; (v) HCl, THF, 0°C to rt, 15 h, 92%; (vi) styrene, AIBN, toluene, 75°C, 48 h, 81%; (vii) HCl, THF, 0°C to rt, 15 h.

Table 1. Asymmetric Michael reaction catalysed by polymer-supported ALB catalysts.



Entry	Catalyst	Method	Time (h)	Yield (%)	Ee (%)
1	**11**	–	68	42	99
2	**15**	A	96	14	95
3[a]	**15-II**	A	120	25	71
4	**16**	A	48	45	90
5	**16**	B	48	53	95
6[a,b]	**17-II**	B	48	79	81
7	**16**	B	67	68	95
8[c]	**16**	B	89	21	93
9[a]	**16-II**	B	100	72	90
10[c]	**16-II**	B	115	64	45
11[d]	**16**	B	67	59	89

[a]0.9 molar equiv. of *n*-BuLi was added to form the second-generation catalyst.
[b]0.05 mL of dry methanol was added to quench unreacted $LiAlH_4$, if any, before the addition of *n*-BuLi.
[c]Catalyst reused.
[d]Recovered polymer was used to generate the catalyst.

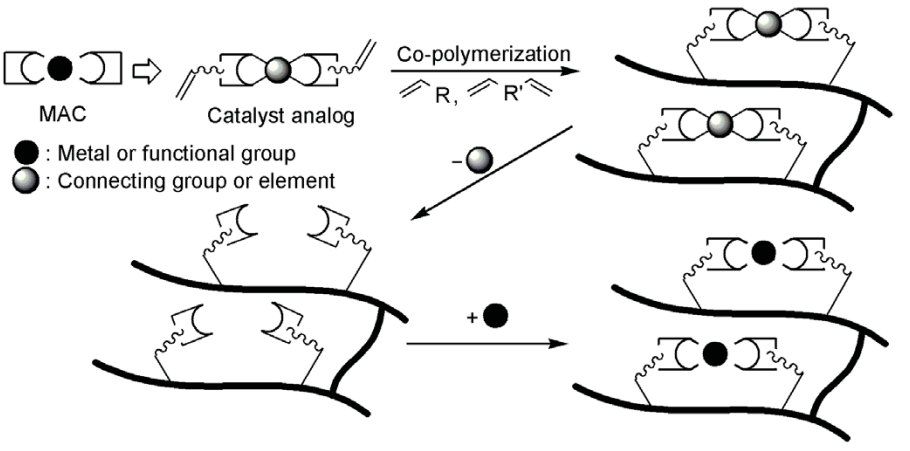
C_2 symmetry due to 6-substitution did not have any adverse effect on the selectivity. Subsequently, the polymer-supported ALB catalyst **15** was obtained as an insoluble solid by the addition of $LiAlH_4$ to a THF solution of polymer **10** (Method A). The solid catalysed the asymmetric Michael reaction affording the product **14** in 14% yield with 95% ee (see table 1, entry 2). While the enantioselectivity was very high, the yield obtained was disappointing. In a bid to improve the yield of **14**, a second-generation catalyst **15-II** was prepared by the addition of 9 mol% of *n*-BuLi to the preformed catalyst [2]. Quite unexpectedly the catalyst afforded the product in 25% yield and the selectivity dropped to 71% ee (see table 1, entry 3). In contrast modest yields were obtained when two equivalents of $LiAlH_4$ was used to generate the catalyst **16**. This result is in contrast to our earlier study with polymeric BINOL derivatives where the chemical yield and selectivity were influenced by the ratio of $LiAlH_4$ used [24].

A slight improvement in the yield and selectivity were observed when the catalyst was generated by the addition of THF to a mixture of the polymer **10** and $LiAlH_4$ (Method B). Addition of methanol to quench the unreacted $LiAlH_4$ resulted in lower selectivity of the product (see table 1, entry 6). Increasing the reaction time resulted in an increase in the product formed with the selectivity remaining unchanged (see table 1, entry 7). In an attempt to reuse the catalyst, the clear supernatant solution was removed with a syringe under argon and the catalyst was washed with THF before addition of substrates. The recovered catalyst provided the product in low yield with comparable ee (see table 1, entry 8). Addition of *n*-BuLi to restore the activity also resulted in products with lower ee (see table 1, entry 10). Nevertheless, the polymer-supported ligand **10** could be recovered by precipitation from hexane and reused to generate the catalyst. Under these conditions the Michael adduct **14** was obtained in 59% yield with 89% ee (see table 1, entry 11).

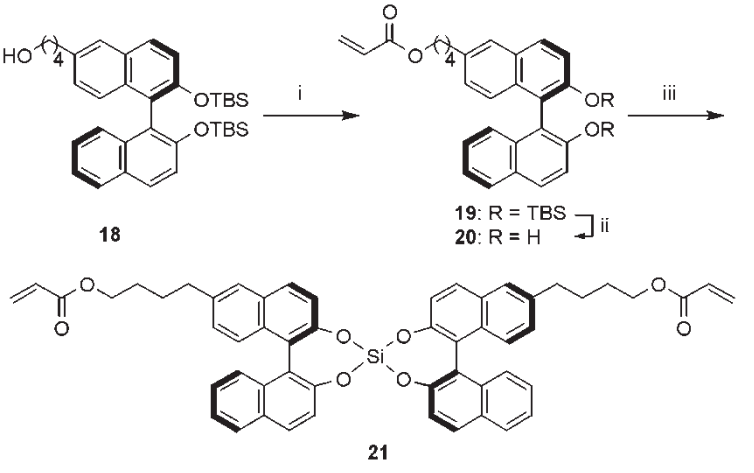
The polymer-supported BINOL **10** could be utilized to generate catalysts that afforded the product in high enantiomeric excesses compared to the catalysts obtained by the conventional method of immobilisation utilizing solid supports. However, a significant decrease in the chemical yield was observed when the catalyst was reused. The lower yields obtained on reuse of the first-generation catalyst could be attributed to the instability of the catalyst or partial leaching of the metal from the polymer surface. Further efforts were thus focused on development of ideal systems that could stabilize the catalyst and maintain the activity over longer durations.

2.1.2. Cross-linked polymers: the catalyst analogue approach. Cross-linked polymers were explored as alternatives to the linear polystyrene derivatives. A novel strategy based on the use of a "catalyst analogue" was developed to fix the position of BINOL ligands on the polymer backbone as described in scheme 2 [25].

The catalyst analogue is a silicon tethered BINOL derivative that closely resembles the parent catalyst in structure and is stable under the polymerisation conditions. Its role is to fix the ligands suitably on the polymer backbone and can be easily replaced with the catalytically active metal species after polymerisation. The synthetic route for the catalyst analogue is described in scheme 3. The 6-substituted BINOL derivative **18** [26] was coupled with acryloyl chloride to give the ester **19**. After removal of the TBS group, the catalyst analogue **21** was almost quantitatively prepared by the reaction of **20** with $SiCl_4$ in THF and used directly in subsequent experiments [27].



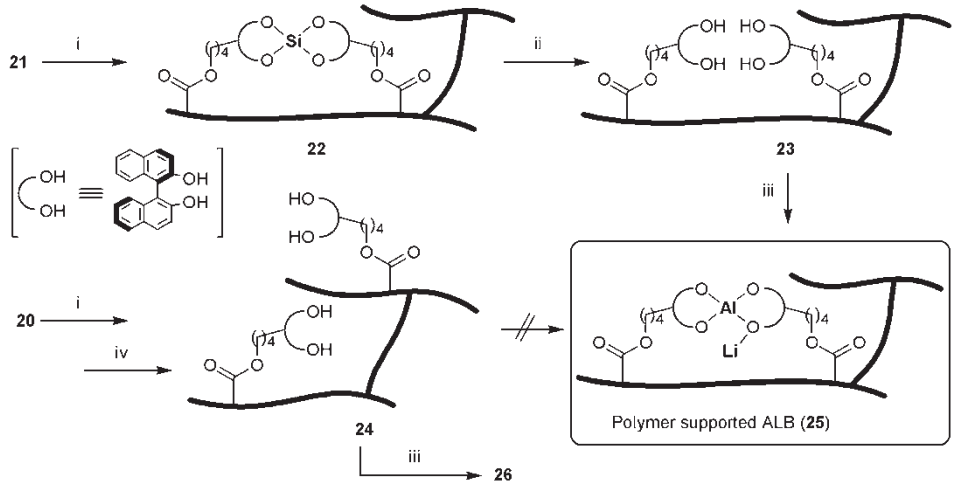
Scheme 2. Construction of a multicomponent asymmetric catalyst by using a polymer support.



Scheme 3. Synthesis of the catalyst analogue **21**. (i) Acryloyl chloride, Et_3N, THF, 0°C; (ii) TBAF, rt, 30 min, obtained quantitatively in two steps; (iii) $SiCl_4$, Et_3N, THF, 0°C.

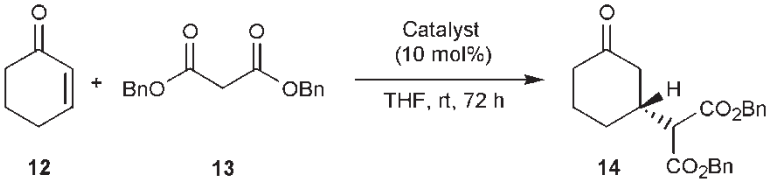
The co-polymerisation of **21** with methyl methacrylate (MMA) at a ratio of 1:20 was initiated by using 5 mol% of AIBN with 1 mol% of ethylene glycol dimethacrylate (EGDMA) as a crosslinker (see scheme 4). After polymerisation, the Si–O bond was cleaved with H_2O to obtain the polymer-supported BINOL **23** (GPC: $M_w = 17800$, PDI = 2.03). For reference, polymer **24** was prepared by the polymerisation of **20**, which has no Si tether, with MMA (**20**:MMA 1:10) and EGDMA. The heterogeneous polymer-supported ALB catalysts were generated by the treatment of a THF solution of the polymer with $AlMe_3$ and *t*-BuLi.

The catalyst **25** generated with polymer **23** promoted the Michael reaction affording the product **14** in 73% yield with 91% ee (see table 2, entry 1). The corresponding catalyst **26**, which was constructed from polymer **24** afforded the product with only 21% ee



Scheme 4. Preparation of polymer-supported ALB. (i) MMA, cross-linker, AIBN, THF, reflux; (ii) H_2O; (iii) $AlMe_3$, *t*-BuLi, THF, −78°C; (iv) TBAF, THF.

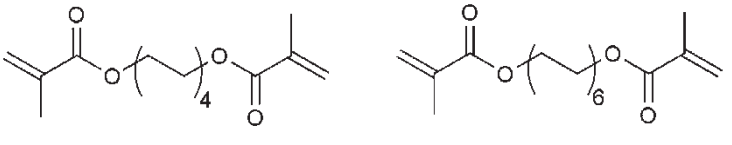
Table 2. Asymmetric Michael reaction catalysed by polymer-supported ALB.



12 13 14

Entry	Polymer supported BINOL[a,b]	Catalyst	Yield of **12** (%)	Ee of **12** (%)
1	**23** (**21** + EGDMA)	**25**	73	91
2	**24** (**20** + EGDMA)	**26**	77	21
3	**27** (**21** + **35**)	**28**	84	80
4	**29** (**20** + **35**)	**30**	20	8
5	**31** (**21** + **36**)	**32**	29	78
6	**33** (**20** + **36**)	**34**	42	34

[a]Polymers for entries 1, 3, and 5 were prepared in the ratio of **21**:MMA = 1:20. Polymers for entries 2, 4, and 6 were prepared in the ratio of **20**:MMA = 1:10.
[b]1 mol% of cross-linker was utilized in each polymerisation.



C8DMA (**35**) C12DMA (**36**)

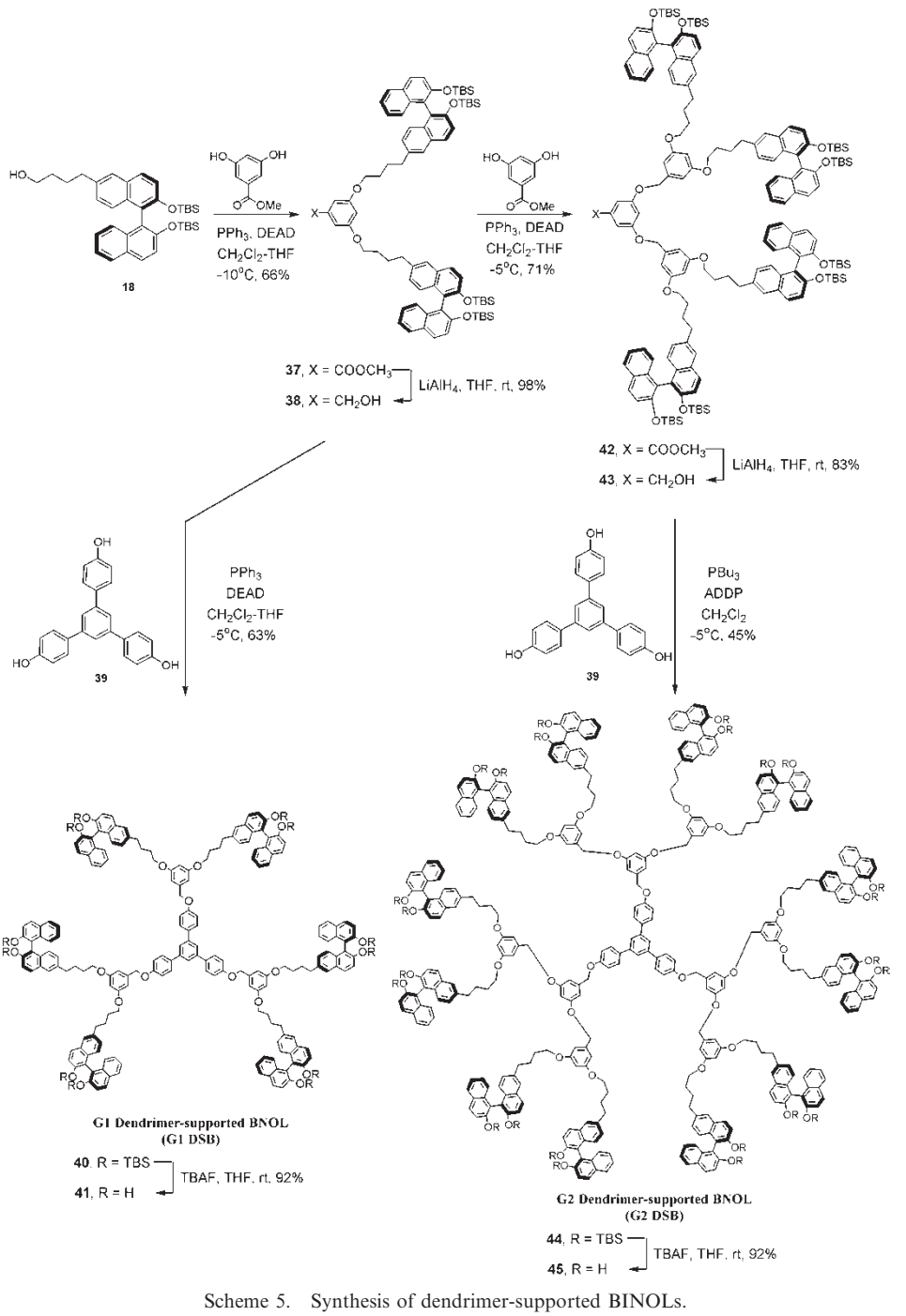
indicating that the use of a catalyst analogue is advantageous for the construction of polymer-supported multicomponent asymmetric catalysts (see table 2, entry 2). An increase in ratio of the cross-linker in the polymer resulted in a reduction of the selectivity [28]. Further, the effect of the length of the cross-linker can also be seen in table 2.

The polymers **27** and **31** were prepared by the use of **35** and **36**. EGDMA proved to be ideal with the selectivities decreasing when **35** and **36** were used as cross-linkers (see table 2, entries 1, 3 and 5). Consistently in all cases, the polymers obtained with the analogue provided better results. As an alternative approach towards the construction of polymer-supported multicomponent asymmetric catalysts, application of the method of molecularly imprinted polymers (MIPs) might be fascinating [29, 30]. In contrast to MIPs, our method using a "catalyst analogue" allowed chiral ligands to be arranged at suitable positions along the polymer chains even in the case of a flexible polymer. The reusability of polymer **23** was investigated by using another batch of polymer **23** (GPC: $M_w = 24{,}000$, PDI = 1.81). After the first and second run, the product was obtained in 74% yield with 89% ee and 76% yield with 88% ee respectively. The polymer **23** was recovered in 97% yield after the second use.

The use of linear as well as cross-linked polymers for immobilisation of the asymmetric catalysts resulted in heterogeneous catalysts with high enantioselectivity and also facilitated the recovery of the ligands at the end of the reaction for subsequent use. However, attempts to reuse the catalysts directly were less successful. Thus our search for systems that would facilitate the recovery and reuse of the catalysts directly continued.

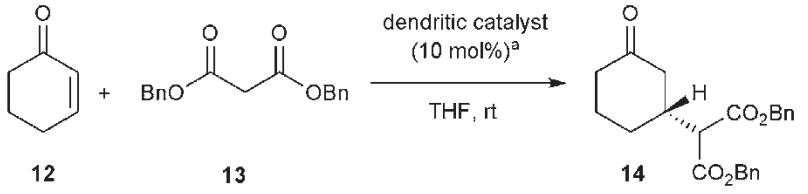
2.2. *Dendrimer-supported BINOL ligands*

Dendrimers are a class of spherical polymers with hyper-branched chains. They possess a central core to which a specific number of dendron units attached. The structure, size, shape and solubility of the dendrimers are readily tunable and hence have attracted considerable attention as a new class of well-defined nanometer-scale materials [31]. Positive effects of dendrimers have already been realized in some cases [32–41]. Jacobsen *et al*. reported on an example in which two catalytic sites at the terminal positions of a dendrimer assisted the ring opening of epoxides [42]. We envisaged that dendrimers containing BINOL ligands at the periphery might be suitable for the construction of an efficient multifunctional catalytic site [43]. Molecular dynamics simulation of the dendrimer-supported ALB catalysts with varying spacer lengths indicated that a C4 to C6 alkyl chain would be optimal [44]. Accordingly the synthesis of the dendrimer was initiated with **18** (see scheme 5) [45]. Two molecules of **18** were reacted with methyl 3,5-dihydroxybenzoate under the Mitsunobu conditions to obtain the terminal unit **37** in 66% yield, which was reduced with $LiAlH_4$ to afford the compound **38** in 98% yield. The resulting alcohol was subsequently coupled with 1,3,5-tris(4-hydroxyphenyl)benzene (**39**) [45] as the core to obtain the first-generation (G1) dendrimer **40**, which contains six BINOL units at the terminal positions, in 63% yield. Deprotection of **40** using TBAF afforded the corresponding dendrimer-supported BINOL (G1 DSB) **41** in 92% yield. Further, a second-generation dendrimer **45** (G2 DSB) containing 12 BINOL units at the terminal positions was prepared using the improved Mitsunobu reagent [46, 47]. Insoluble catalysts were readily obtained by the treatment of **41** or **45** with $AlMe_3$ and *n*-BuLi. The G1 dendritic ALB catalyst **46** afforded the Michael adduct **14** in 63% yield with 91% ee (see table 3, entry 1) [48]. Under similar conditions, the G2 dendritic ALB catalyst **47** afforded the product in 59% yield with 91% ee (see table 3, entry 4). The recovery of G1 dendritic ALB was carried out simply by removing the clear supernatant *via* syringe under a stream of argon. THF and the substrates **12** and **13** were



Scheme 5. Synthesis of dendrimer-supported BINOLs.

Table 3. Asymmetric Michael reaction catalysed by dendritic ALB catalysts.



12 13 14

Entry	Dendritic catalyst	Time (h)	Yield (%)	Ee (%)
1	**46**	48	63	91
2	**46** (2nd use)	48	63	93
3	**46** (3nd use)	48	57	94
4	**47**	72	59	91
5	**46-II**[b]	48	79	89
6	**48**	22	40	92
7	**48-II**[c]	72	83	97

[a]Based on a single catalytic site on the dendrimer.
[b]0.3 equiv. of NaO-*t*-Bu to Al was added. [c]0.5 equiv. of NaO-*t*-Bu to Al was added.

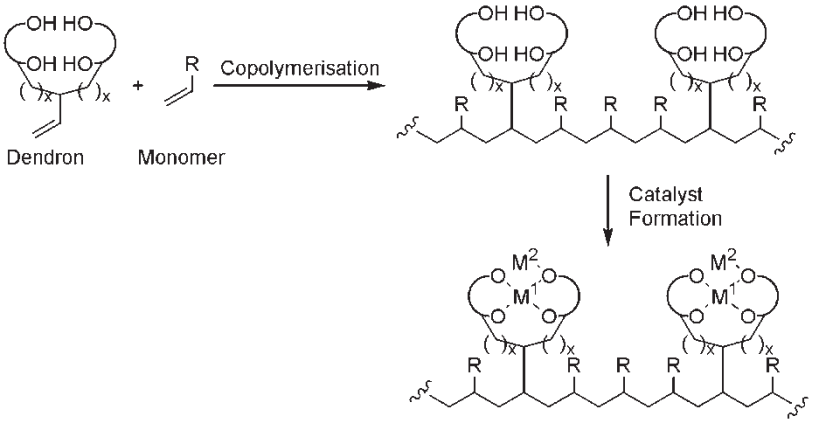
successively added to the residue to carry out the next reaction. The catalyst was found to maintain its activity even during the third use affording the product in 57% yield with 94% ee (see table 3, entry 3) [49]. Thus compared to the polymer supports used earlier, the use of dendrimers to immobilize multifunctional asymmetric catalysts resulted in catalysts that were effectively reusable without any loss in the activity. The activity of the G1 dendritic ALB was improved by the addition of 0.3 equivalent of a basic reagent to the parent ALB catalyst (see table 3, entry 5). Another type of multicomponent catalyst **48**, consisting of gallium, sodium and two BINOL moieties, was also heterogenized using **41**. While the G1 dendritic GaSB provided the adduct in 40% yield with 92% ee (see table 3, entry 6), addition of 0.5 equivalents of the basic reagent resulted in enhanced activity affording the product in 83% yield with 97% ee (see table 3, entry 7).

2.3. *Polymer-supported bisBINOL ligands*

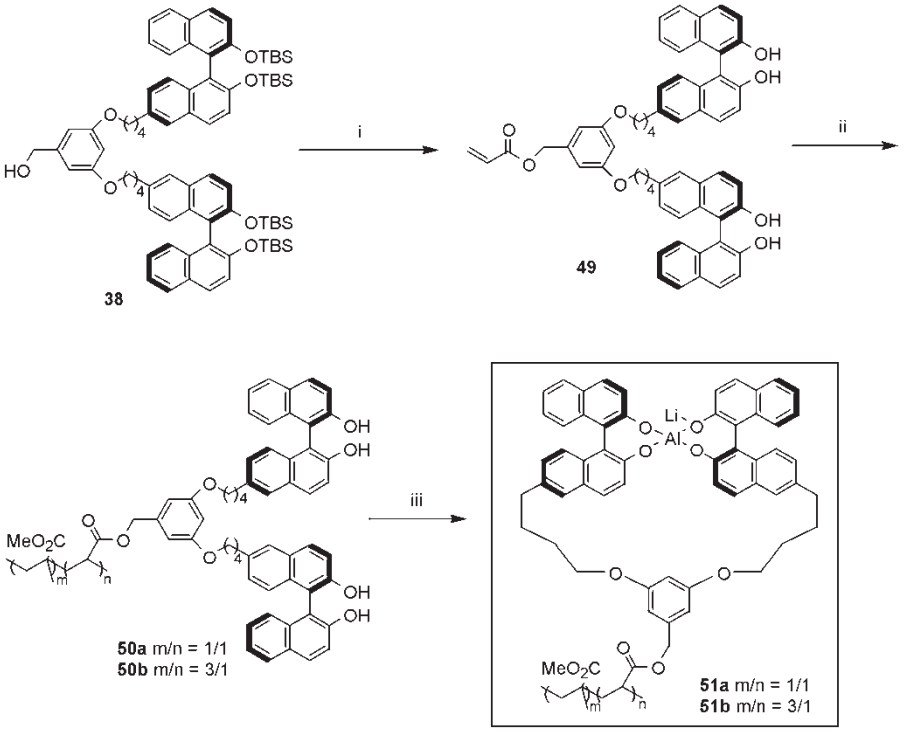
While the use of dendrimers to immobilize multifunctional asymmetric catalysts resulted in catalysts that were effectively reusable, the yields obtained were still modest. Further, the synthesis of dendrimers involves multiple steps and often results in low yields. Dendronized polymers, on the other hand, combine the advantages of both dendrimers and linear polymers [31, 50–54]. They are readily obtained by the polymerisation of a dendron with a comonomer (see scheme 6).

The bisBINOL unit **38**, used for the dendrimer synthesis, was utilized to synthesize such polymers. Accordingly **38** was converted to the monomer **49** by coupling with acryloyl chloride followed by cleavage of the protecting groups. Copolymerisation of **49** with one equivalent of MMA in the presence of AIBN afforded the polymer-supported bisBINOL ligand **50** (GPC: $M_w = 84{,}000$, PDI = 10) (see scheme 7).

The polymer-supported ALB catalyst was obtained as a white precipitate by the addition of $AlMe_3$ and *t*-BuLi to **50a** in THF. The catalyst **51a** promoted



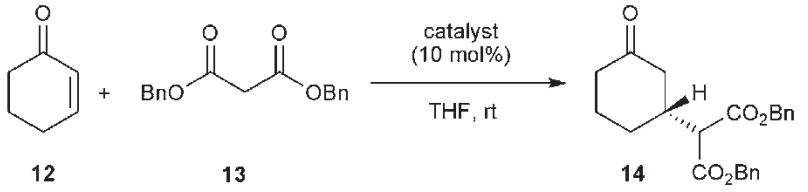
Scheme 6. Representative preparation of polymer containing bisBINOL ligand.



Scheme 7. Synthesis of supported ALB catalyst utilizing polymer-supported bisBINOL ligand; (i) Acryloyl chloride, Et_3N, THF, 79%; (ii) MMA, AIBN, THF, 70°C; (iii) $AlMe_3$, *t*-BuLi, THF.

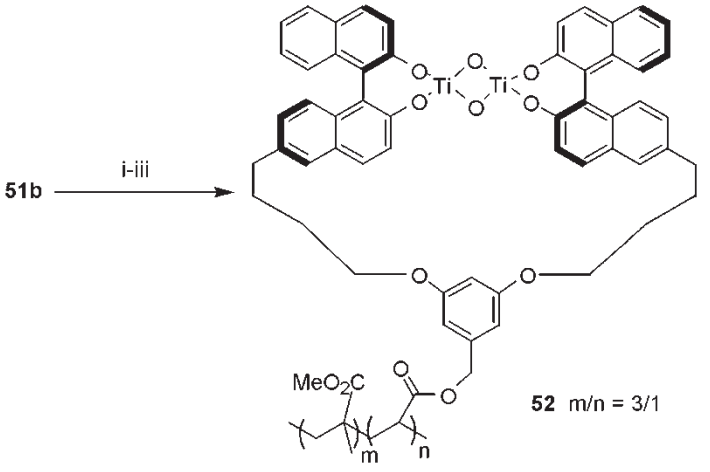
the asymmetric Michael reaction affording the product in 36% yield and 96% ee (see table 4, entry 1). A possible reason for the low yield could be the overcrowding of catalytic sites resulting in diminished reaction rates. To facilitate site separation, monomer **49** was polymerised with three equivalents of MMA to obtain polymer **50b**

Table 4. Asymmetric Michael reaction catalysed by polymer-supported ALB.



12 **13** **14**

Entry	Catalyst	Yield (%)	Ee (%)
1	**51a**	36	96
2	**51b**	91	93

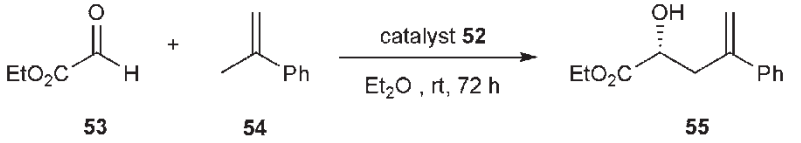


Scheme 8. Preparation of polymer-supported titanium complex (**52**). (i) Ti(O-*i*-Pr)$_4$, CH_2Cl_2; (ii) H_2O; (iii) azeotropic distillation.

(GPC: $M_w = 16{,}000$, PDI = 2.1). As expected the catalyst **51b** obtained with **50b** afforded the product in 91% yield with 93% ee (see table 4, entry 1). Thus the polymers enable easy site separation thereby resulting in enhanced reactivity. While a similar effect could account for lower yields in the case of dendrimer-supported catalysts (see table 3, entry 1), site separation on the periphery with higher generation dendrimers is rather difficult. Thus by virtue of a simpler synthetic route, these polymer-supported catalysts promise better advantages.

To demonstrate the generality of the use of such polymers, **50b** was used to generate the μ-oxodititanium complex [9]. The catalyst **52** was obtained as a reddish brown solid by the reaction of polymer **51b** with one equivalent of Ti(O-*i*-Pr)$_4$ followed by treatment with water (scheme 8). The heterogeneous catalyst **52** promoted the carbonyl-ene reaction of **53** with **54** in Et_2O to give the adduct **55** in 53% yield and 95% ee after 72 h. Addition of MS 4A dramatically improved the catalytic activity. The enantioselectivities obtained with this system are higher than those reported with soluble linear

Table 5. Application and reuse of polymer-supported Ti catalyst (**52**) in asymmetric carbonyl-ene reaction.



53 **54** **55**

Entry	**52** (mol%)	MS 4A	Yield (%)	Ee (%)
1	10	–	53	95
2	10	+	quant	96
3 (2nd use)	20	+	83	98
4 (3rd use)	20	+	74	92

polymers [22] and highlight the advantages of the polymer **50b**. The catalyst **52** was recovered by removing the clear supernatant with a syringe under argon atmosphere. The catalyst maintained high enantioselectivity even during the third use. Although the ICP-AES analysis revealed that less than 2% of the immobilized titanium was lost after the first use, a 17% decrease in chemical yield was observed between the first and the second use of the catalyst. The decrease in yield was unavoidable despite the addition of MS 4A to the reaction during the second use of the catalyst (see table 5, entry 3). The decrease in yield could likely be due to the conversion of the polymer bound complex to a less active form with time.

2.4. *Immobilisation without the use of a support (Self-supported catalysts)*

The results described in the earlier sections indicate that immobilisation of multicomponent asymmetric catalysts can be accomplished by employing a wide range of macromolecules. However, from a practical point of view, it is also important to develop strategies that do not involve the tedious preparation of polymer-supported ligands. In this regards, homochiral metal-organic porous materials appear to be promising alternatives. Although they have been utilized in the recent past for chiral separation and asymmetric transformations, the enantioselectivities of the products obtained have been low [55–57]. Recently BINAP-derived porous zirconium phosphonates [58] have been found to provide enantioselectivities superior to their homogeneous counterparts [59, 60] in the asymmetric hydrogenation reactions. While zirconium is responsible for the immobilisation, BINAP bound ruthenium functions as the asymmetric catalyst. Alternatively, chiral multidentate ligands with attached sites for metals at the opposite sides in the molecular skeleton readily form insoluble metal-bridged polymers in the presence of suitable metal source as described in figure 2. If the chiral metal-bridged regions can function as asymmetric catalyst, a simple and efficient approach for the immobilisation of multicomponent asymmetric catalysts without the need for a polymer support would be realized. The potential of this strategy for the immobilisation of various multicomponent asymmetric catalysts has been demonstrated recently by us [61] and Ding *et al*. [62–64].

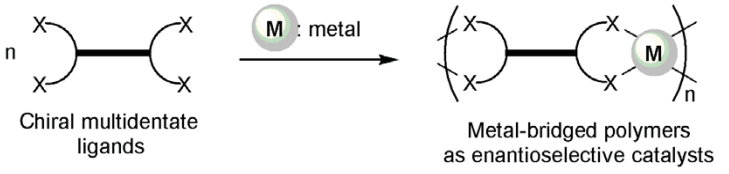


Figure 2. Concept of metal-bridged polymers as enantioselective catalysts.

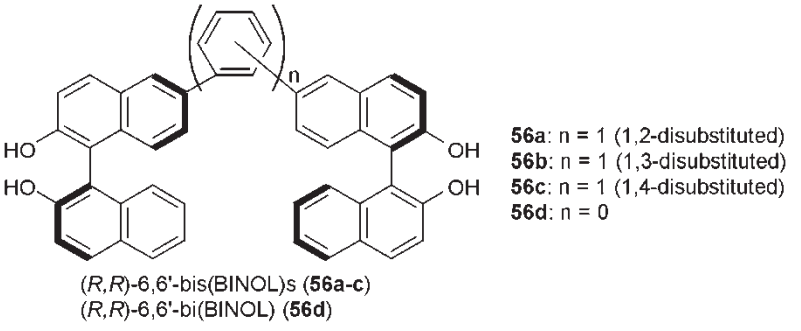
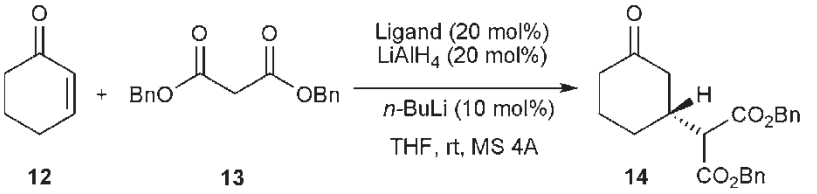


Figure 3. BINOL derivatives (**56a–d**) used to form metal-bridged polymers.

Rigid (*R*,*R*)-6,6′-bis(BINOL) derivatives (**56a–c**) and (*R*,*R*)-6,6′-bi(BINOL) (**56d**) were synthesized by linking the BINOL units at the 6-position (figure 3). All the ligands readily formed the expected metal-bridged polymers as heterogeneous solids upon reaction with $LiAlH_4$ in THF at 0°C. *n*-BuLi was subsequently added to obtain the second-generation catalysts. The catalysts were then used in the enantioselective Michael reaction and the results are summarized in table 6. Catalysts derived from **56a** and **56b** were inferior in activity. While the yields were moderate to good, the enantioselectivities were poor (see table 6, entries 1 and 2). It is presumed that the bent shape of these ligands facilitates the formation of unsuitable aggregates [4]. On the other hand, catalysts obtained with ligands **56c** and **56d** were found to be highly effective, affording the product with 88% and 96% ee respectively (see table 6, entries 3 and 4). The heterogeneous catalyst derived from **56d** and $LiAlH_4$, was characterized by elemental analysis and by comparison of its IR spectrum with that of the ALB complex. Characteristic absorptions for Al-bridged polymer were similar to ALB complex.

The ability of the heterogeneous system to promote this reaction was confirmed by the following experiments: The heterogeneous catalyst derived from **56d** and $LiAlH_4$ was allowed to settle and the clear supernatant solution was removed with a syringe under argon. The supernatant solution exhibited no catalyst activity, whereas the precipitate afforded the product with 91% ee. In addition two reactions were carried out with **12** and **13** under optimized conditions. One reaction was quenched after 8 h during which **14** was obtained in 22% yield with 94% ee. The supernatant solution of the other reaction was separated from the heterogeneous catalyst and stirred further for 40 h. This reaction afforded **14** in 19% yield with 90% ee. In addition, ligand **56d** was

Table 6. Enantioselective Michael reaction catalysed by Al-bridged polymer.



12 13 14

Entry	Ligand	Time (h)	Yield (%)[a]	Ee (%)
1	**56a**	48	94	6
2	**56b**	48	69	17
3	**56c**	48	89	88
4	**56d**	48	86	96

[a]Isolated yield.

Table 7. Reuse of Al-bridged polymer in enantioselective Michael reaction.[a]

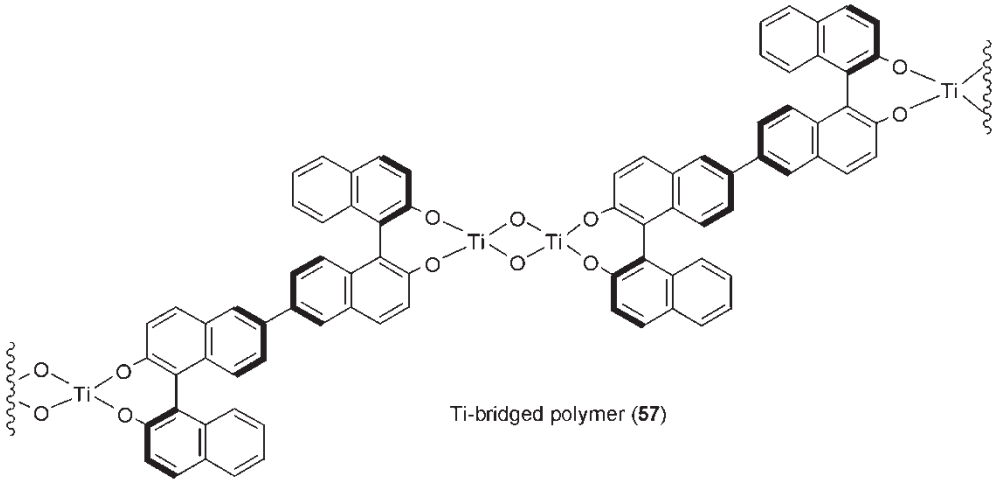
Run	Time (h)	Yield (%)[b]	Ee (%)
1	72	88	96
2	98	86	87
3	98	74	85
4	98	60	77
5	98	59	77

[a]Al-bridged polymer generated from **56d** (1 mol equiv), $LiAlH_4$ (1 mol equiv) and *n*-BuLi (0.5 mol equiv) in the presence of MS 4A was used.
[b]Determined by HPLC (Daicel Chiralpak AS).

not observed in the supernatant solution. These results confirm the absence of catalyst activity in the solution phase.

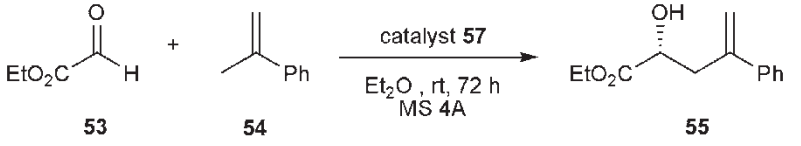
The reuse of the catalyst in asymmetric Michael reaction was then explored by removal of the clear supernatant solution containing the product with a syringe under argon followed by the addition of substrates (see table 7). The metal-bridged polymer maintained its activity even after being reused three times, albeit a slight decrease in enantioselectivity (74%, 85% ee).

The generality of the concept of metal-bridged polymer catalysis has also been demonstrated through the asymmetric carbonyl-ene reaction catalysed by the polymeric μ-oxodititanium catalyst **57**. To a solution of **56d** in CH_2Cl_2 were added $Ti(O\text{-}iPr)_4$ (2 mol equiv) in toluene and H_2O (4 mol equiv). The solution was stirred at room temperature for 24 h to afford the precipitate. After removal of the solvents at 80°C under reduced pressure, the residue was dried *in vacuo* at 80°C for 19 h. The resulting red solid **57**, with a possible structure described in scheme 9, was characterized by elemental analysis and by comparison of its IR spectrum with hitherto known titanium complex [9]. The titanium-bridged polymer **57** catalysed the reaction of aldehyde **53** and olefin **54** to give the product **55** in 81% yield with 90% ee. In contrast to the Al-bridged polymer,



Scheme 9. Possible structure of the Ti-bridged polymer.

Table 8. Reuse of Ti-bridged polymer in enantioselective carbonyl-ene reaction.



53 **54** **55**

Run	Time (h)	Yield (%)[a]	Ee (%)
1	98	88	88
2	98	72	92
3	98	71	89
4	147	88	88
5	147	66	88

[a]Isolated yield.

Ti-bridged polymer could be recovered in air. After being reused four times the Ti-bridged polymer exhibited consistent catalytic activity affording **55** with 88% ee (see table 8).

3. Conclusion

Immobilisation of highly organized multicomponent asymmetric catalysts has been achieved by the use of polymers and dendrimers. The resulting heterogeneous Al-Li-bis(binaphthoxide) and μ-oxodititanium complexes were effective in promoting the asymmetric Michael reaction and the carbonyl-ene reaction respectively.

The corresponding products were obtained in high enantiomeric excess. In spite of its instability towards moisture, the heterogeneous dendrimer-supported Al-Li-bis(binaphthoxide) complex was reused three times without any loss in the catalytic activity. Metal-bridged polymers have also been successfully utilized for the immobilisation of these complexes. These polymers offer a simple and effective method for immobilisation without using any support. Recently, we have demonstrated the immobilisation of Ti-BINOLate complex utilizing monolayer-protected Au cluster [65] and micelle-derived polymers [66]. Encouraged by the success with these systems in the asymmetric alkylation of benzaldehyde, we are presently exploring their potential for the immobilisation of multicomponent asymmetrtic catalysts.

4. Experimental section

4.1. *General*

^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX270 FT NMR system (^{1}H NMR-270 MHz, ^{13}C NMR-67.7 MHz). IR spectra were recorded on Shimadzu FTIR 8300. Optical rotations were measured with a JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as the eluent. Mass spectra were obtained on JEOL JMS-DX300 (for EI-MS), JEOL JMS-700 (for FAB-MS), JEOL JMS-700 equipped with the CSI source (for CSI-MS), and JMS-T100LC (for ESI-MS). Elemental analysis was performed on PERKIN-ELMER 2400. Molecular weights of the polymers were determined by gel permeation chromatography relative to polystyrene standards using SHODEX GPC KF 803L column. All reactions were performed under argon atmosphere. THF was freshly distilled from sodium benzophenone ketyl. MS 4A was dried in vacuum at 180°C for 3 hours before use.

4.2. *Synthesis and characterization*

4.2.1. 4. To an ice cooled solution of **3** (2.86 g, 7.87 mmol) in anhydrous THF (25 mL) was added NaH (1.063 g, 26 mmol as 60% purity in oil). The mixture was stirred for 30 min and chloromethylmethylether (2.3 mL, 30 mmol) was added in drops. After warming to room temperature the mixture was stirred further for 3 h. It was then poured into water (100 mL) and the product extracted with AcOEt. The extract was dried over anhydrous Na_2SO_4 and concentrated to get the product. Drying in vacuo for 3 h at 50°C afforded **4** (3.4 g, 96% yield) as a pale yellow solid. IR (neat) 2898, 2823, 1236, 1145, 1062 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.07 (s, 6 H), 4.88 (d, $J = 6.7$ Hz, 2H), 4.99 (d, $J = 3.6$ Hz, 1H), 5.01 (d, $J = 3.6$ Hz, 1H), 6.93 (d, $J = 9.0$ Hz, 1H), 7.00 (d, $J = 7.9$ Hz, 1H), 7.15–7.26 (m, 3H), 7.47 (d, $J = 7.3$ Hz, 1H), 7.50 (d, $J = 7.1$ Hz, 2H), 7.76 (d, $J = 6.1$ Hz, 1H), 7.79 (d, $J = 4.9$ Hz, 1H), 7.86 (d, $J = 9.1$ Hz, 1H), 7.95 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.8, 95.0, 95.1, 117.0, 117.8, 118.1, 123.9, 124.0, 125.1, 126.3, 127.3, 127.8, 128.3, 129.4, 129.5, 129.6, 130.8, 132.4, 133.7, 152.4, 152.8; MS (EI) m/z 454 [M^{+}]; $[\alpha]_D^{28} + 59.1$ (c = 0.45, $CHCl_3$).

4.2.2. 5. To a solution of **4** (3.3 g, 7.28 mmol) in dry THF was added *n*-BuLi (6.6 mL, 10.8 mmol, 1.6 M solution in hexane) in drops at −88°C. The solution was stirred for 30 min and dry DMF (1.3 mL, 14.6 mmol) was slowly added. After being stirred for 2 h the solution was allowed to warm to −20°C. It was then poured into 1N HCl/ice (100 mL). The product was extracted with AcOEt. The organic layer was washed with saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. The crude product was obtained upon evaporation of the solvent as pale yellow oil. Flash column chromatography afforded **5** (1.95 g, 67% yield) as a colorless solid. IR (neat) 2827, 1689, 1591, 1234, 1145, 1070, 1010, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.14 (s, 3H), 3.19 (s, 3H), 4.97 (d, $J = 6.7$ Hz, 1H), 5.03 (d, $J = 12.9$ Hz, 1H), 5.08 (d, $J = 12.6$ Hz, 1H), 5.13 (d, $J = 7.0$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 7.20 (m, 2H), 7.33 (t, $J = 6.9$ Hz, 1H), 7.56 (d, $J = 9.0$ Hz, 1H), 7.67 (d, $J = 9.1$ Hz, 2H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 9.1$ Hz, 1H), 8.10 (d, $J = 9.0$ Hz, 1H), 8.37 (s, 1H), 10.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 55.8, 56.0, 94.6, 95.0, 116.8, 117.5, 120.0, 123.1, 124.0, 124.9, 126.4, 127.9, 131.0, 132.4, 134.5, 152.5, 155.2, 191.8; MS (EI) m/z 402 (M^+); $[\alpha]_D^{28} + 57.6$ ($c = 0.45$, $CHCl_3$).

4.2.3. 6. To an ice cooled solution of **5** (1.85 g, 4.6 mmol) in THF (12 mL)/MeOH (12 mL) was added $NaBH_4$ (173 mg, 4.6 mmol) and the solution stirred at this temperature for 15 min. The mixture was then poured into water (100 mL) and the product extracted with AcOEt. After drying over anhydrous Na_2SO_4 the solution was concentrated to get **6** (1.63 g, 88% yield) as a colourless foamy solid. A portion of the solid was purified by flash column chromatography for analysis. IR (neat) 3400, 2823, 1591, 1234, 1145, 1066, 1008, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.05 (s, 3H), 3.06 (s, 3H), 4.70 (s, 2H), 4.87 (d, $J = 6.7$ Hz, 2H), 4.96 (d, $J = 3.3$ Hz, 1H), 4.99 (d, $J = 3.3$ Hz, 1H), 7.02–7.17 (m, 4H), 7.23 (t, $J = 6.7$ Hz, 1H), 7.47 (d, $J = 9.0$ Hz, 2H), 7.75 (s, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 5.4$ Hz, 1H), 7.86 (d, $J = 5.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.8, 65.4, 95.1, 95.2, 117.2, 117.4, 121.1, 121.2, 123.9, 125.3, 125.5, 125.6, 125.9, 126.2, 127.7, 129.2, 129.3, 129.6, 129.7, 133.4, 133.8, 136.3, 152.5, 152.6; MS (EI): m/z 404 $[M]^+$; $[\alpha]_D^{29} + 57.0$ ($c = 0.45$, $CHCl_3$).

4.2.4. 7. To an ice cooled solution of **6** (1.54 g, 3.81 mmol) in THF (20 mL)/DMF (20 mL) was added NaH (135 mg, 5.7 mmol as 60% purity in oil) and the mixture was stirred at this temperature for 30 min. 4-Vinylbenzylchloride (0.53 mL, 3.84 mmol) was then added in drops at this temperature and the solution was allowed to warm to room temperature. After stirring for 72 h the mixture was poured carefully into water (100 mL). The product was extracted with AcOEt, dried over anhydrous Na_2SO_4 and concentrated. Flash column chromatography on silica gel (AcOEt/hexane = 1/9) afforded **7** (1.386 g, 70% yield) as a colorless pasty mass. IR (neat) 2825, 1593, 1236, 1147, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.13 (s, 3H), 3.15 (s, 3H), 4.56 (s, 2H), 4.64 (s, 2H), 4.95 (d, $J = 6.7$ Hz, 1H), 4.96 (d, $J = 6.7$ Hz, 1H), 5.05 (d, $J = 6.7$ Hz, 1H), 5.06 (d, 6.7 Hz, 1H), 5.20 (dd, $J = 10.9$, 0.9 Hz, 1H), 5.70 (dd, $J = 17.6$, 0.9 Hz, 1H), 6.65 (dd, $J = 17.6$, 10.9 Hz, 1H), 7.12–7.40 (m, 8H), 7.55 (d, $J = 9$ Hz, 2H), 7.83 (d, $J = 3.8$ Hz, 2H), 7.87 (s, 1H), 7.91 (d, $J = 3.5$ Hz, 1H), 7.94 (d, $J = 3.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.8, 71.8, 72.1, 95.1, 95.2, 113.7, 117.2, 117.4, 121.1, 121.22,

123.9, 125.4, 125.8, 126.1, 126.2, 126.3, 126.5, 127.7, 127.9, 129.2, 129.3, 129.6, 129.7, 133.5, 133.7, 136.4, 136.9, 137.7, 152.5, 152.6; MS (FAB) m/z 521 $[M+H]^+$; $[\alpha]_D^{27}$ + 43.3 (c = 1, $CHCl_3$).

4.2.5. 8. To an ice cooled solution of **7** (250 mg, 3.81 mmol) in THF (2 mL) was added a THF solution of HCl (1 mL conc HCl in 4 mL of THF). The solution was allowed to warm to room temperature slowly. After being stirred for 15 h the solution was poured carefully into water (50 mL). The product was extracted with AcOEt, dried over anhydrous Na_2SO_4 and concentrated. Flash column chromatography on silica gel (AcOEt/hexane = 1/9) afforded **8** (190 mg, 92% yield) as a colorless foamy solid. IR (neat) 3496, 2854, 1618, 1596, 1141, 1014 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57 (s, 2H), 4.65 (s, 2H), 5.04 (s, 2H), 5.21 (dd, J = 10.9, 0.9 Hz, 1H), 5.70 (dd, J = 17.6, 0.9 Hz, 1H), 6.65 (dd, J = 17.6, 10.9 Hz, 1H), 7.12 (d, J = 8.6 Hz), 7.27–7.40 (m, 8H), 7.86 (d, J = 3.3 Hz, 1H), 7.87 (s, 1H), 7.94 (d, J = 4.5 Hz, 1H), 7.97 (d, J = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 71.9, 110.7, 110.8, 113.7, 117.6, 117.9, 123.9, 124.0, 124.4, 126.1, 127.1, 127.4, 127.5, 127.9, 128.3, 129.2, 129.3, 131.2, 131.3, 133.8, 136.4, 137.6, 152.5, 152.6; MS (EI): m/z 432 $[M]^+$; $[\alpha]_D^{28}$ − 46.9 (c = 0.484, $CHCl_3$).

4.2.6. Synthesis of the polymer supported BINOL 9. To a toluene solution of **7** (625 mg in 2 mL) was added AIBN (56 mg) and styrene (0.55 mL, 4.8 mmol). The solution was purged with argon thoroughly. Polymerisation was carried out for 48 h at 75°C. After cooling to room temperature the polymer was first precipitated into methanol followed by hexane. The precipitate was filtered and dried in vacuo at 50°C for 3 h to give the polymer **9** (0.915 g, 81% yield). IR (Neat) 2848, 1598, 1238, 1149, 1014 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.882 (br), 1.42 (br), 1.82 (br), 3.13 (br), 4.58 (br), 4.97 (br), 5.06 (br), 6.56 (br), 7.15 (br), 7.55 (br), 7.91 (br); $[\alpha]_D^{29}$ + 21.1 (c = 0.45, $CHCl_3$).

4.2.7. Removal of the protecting groups in 9. To an ice cooled solution of the polymer **9** (880 mg) in THF (2 mL) was added a THF solution of HCl (1 mL conc HCl in 4 mL of THF). The solution allowed to warm to room temperature. After being stirred for 15 h the solution was poured into water (50 mL). The product was extracted with CH_2Cl_2, washed with saturated $NaHCO_3$ and precipitated into hexane twice. The precipitated polymer **10** was dried in vacuo at 50°C for 3 h (650 mg). IR (neat) 3022, 1598, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.921 (br), 1.10 (br), 1.59 (br), 1.81 (br), 2.17 (br), 4.41 (br), 4.57 (br), 6.56 (br), 7.06 (br), 7.21 (br), 7.33 (br), 7.87 (br); $[\alpha]_D^{29}$ − 23.2 (c = 0.45, $CHCl_3$).

4.2.8. Synthesis of polymer supported ALB catalyst 16. Method A: To an iced cooled solution of polymer **10** (100 mg, 0.1 mmol as a monomer) in THF (1 mL) was added $LiAlH_4$ (3.6 mg, 0.1 mmol). A white precipitate (**16**) was obtained which was stirred for 30 min and used directly as catalyst for the asymmetric Michael reaction.

Method B: To a mixture of the polymer **10** (100 mg, 0.1 mmol as a monomer) and $LiAlH_4$ (3.6 mg, 0.1 mmol) at 0°C was added THF (1 mL). The suspension was stirred

for 30 min and the resulting white precipitate (**16**) was used directly as catalyst for the asymmetric Michael reaction.

4.2.9. Catalytic asymmetric Michael reaction. To a stirred suspension of the catalyst **16** were added 2-cyclohexen-1-one (**12**) (0.05mL, 0.5 mmol) and dibenzyl malonate (**13**) (0.125 mL, 0.5 mmol). After stirring for 48 h at room temperature 1N HCl (5 mL) was added. The product mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The solution was concentrated to 2 mL and added to hexane (100 mL). The precipitated polymer was filtered and dried (92 mg, 92%). The hexane solution was concentrated and purified by flash column chromatography on silica gel (acetone/hexane 1/10) to give the Michael adduct **14**. While the catalyst generated using **Method A** produced the product in 45% yield with 90% ee, the catalyst generated by **Method B** produced the product in 53% yield with 95% ee. The enantiomeric excess was determined by chiral stationary phase HPLC analysis. (DAICEL CHIRALPAK AS, *i*-PrOH/hexane = 1/4, 1.0 mL/min, $\lambda = 254$ nm).

4.2.10. Reuse of the polymer 10. The recovered polymer was dried in vacuo for 3 h at 45°C. The Michael addition catalyst **16** was generated by Method B. The catalyst afforded the product in 59% yield with 89% ee.

4.2.11. 18. To a solution of (*R*)-4-[2,2′-bis(*tert*-butyldimethylsilyloxy)-1,1′-binaphth-6-yl]butanoate (440 mg, 0.7 mmol) in THF (7.0 mL) [26] was added $LiAlH_4$ (40 mg, 1.05 mmol) at 0°C. The reaction mixture was stirred at rt for 30 min and quenched with water at 0°C. The aqueous layer was adjusted to pH 7 with 1N HCl and then extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of solvent, the crude product was purified by flash chromatography on silica gel (AcOEt/hexane = 1/5) to get (*R*)-4-[2,2′-bis(*tert*-butyldimethylsilyloxy)-1,1′-binaphth-6-yl]butan-1-ol (284.2 mg, 69.1%) as colorless oil. IR (neat) 775.3, 806.2, 835.1, 995.2, 1244.0, 1353.9, 1461.9, 1593.1, 2856.6, 2927.7, 3319.3 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.11 (s, 3H), −0.09 (s, 3H), 0.06 (s, 3H), 0.07 (s, 3H), 0.52 (s, 9H),).53 (s, 9H), 1.53 (br-s, 1H), 1.60–1.71 (m, 2H), 1.74–1.85 (m, 2H), 2.79 (t, $J = 8.1$ Hz, 2H), 3.70 (t, $J = 6.8$ Hz, 2H), 7.11 (dd, $J = 8.6$, 1.9 Hz, 1H), 7.20–7.36 (m, 6H), 7.64 (s, 1H), 7.79 (d, $J = 8.6$ Hz, 1H), 7.86 (dd, $J = 8.6$, 1.9 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ −4.35, −4.20, 17.64, 25.09, 27.45, 32.31, 35.48, 72.81, 120.36, 120.29, 121.79, 122.08, 123.09, 125.67, 125.85, 126.05, 127.16, 127.47, 127.97, 128.46, 129.04, 129.20, 132.86, 134.81, 150.35, 150.82; HR-MS (EI) for $C_{36}H_{50}O_3Si_2$, $[M]^+$: m/z Calcd: 586.3298, found: 586.3281; $[\alpha]_D^{25} + 88.5$ (c = 0.694, THF).

4.2.12. 19. To a solution of (*R*)-4-[2,2′-bis(*tert*-butyldimethylsilyloxy)-1,1′-binaphth-6-yl]butan-1-ol (**18**) (2.5 g, 4.26 mmol) in THF (30 mL) were added Et_3N (0.77 mL, 5.5 mmol) and acryloyl chloride (0.38 mL, 4.6 mmol) at 0°C. After being stirred for 30 min, the reaction was quenched with H_2O at 0°C and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, crude product was purified by flash column

chromatography on silica gel (AcOEt/hexane = 1/5) to give **19** (2.73 g, 4.26 mmol, quant) as a pale yellow oil. IR (neat): 1070.4, 1247.8, 1730.0 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.16 (d, J = 4.0 Hz, 6H) 0.01 (d, J = 4.0 Hz, 6H), 0.47 (s, 18H), 1.72–1.77 (m, 4H), 2.75 (d, J = 6.8 Hz, 2H), 4.18 (t, J = 6.1 Hz, 2H), 5.79 (dd, J = 1.5, 10 Hz, 1H), 6.11 (dd, J = 10, 17 Hz, 1H), 6.39 (dd, J = 1.5, 17 Hz, 1H), 7.05 (dd, J = 1.6, 8.6 Hz, 1H), 7.14–7.58 (m, 6H), 7.72 (s, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.80 (d, J = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ −4.4, −4.3, −4.2, 17.7, 25.1, 27.6, 28.2, 35.3, 64.5, 120.3, 120.4, 121.9, 122.1, 123.1, 125.7, 125.8, 125.9, 126.1, 127.1, 127.5, 128.0, 128.5, 129.1, 129.3, 130.3, 133.0, 134.4, 136.5, 150.4, 150.9, 166.1; HR-MS (ESI) for $C_{39}H_{52}O_4Si_2Na$ $[M+Na]^+$: m/z Calcd: 663.3219, found: 663.3236; $[\alpha]_D^{25}$ +35.61 (c = 0.689, $CHCl_3$).

4.2.13. 20. To a solution of **19** (1.9 g, 3.0 mmol) in THF (30 mL) was added 1.0 M TBAF in THF (7.2 mL, 7.2 mmol) drop wise at 0°C. After being stirred for 30 min, the reaction was quenched with H_2O at 0°C and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, crude product was purified by flash column chromatography on silica gel (AcOEt/hexane = 1/3) to give **20** (1.23 g, 3.0 mmol, quant) as pale yellow oil. IR (neat) 1714.6, 3408.0 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.73–1.76 (m, 4H), 2.77 (d, J = 6.8 Hz, 2H), 4.18 (t, J = 6.1 Hz, 2H), 5.80 (dd, J = 1.4, 10 Hz, 1H), 6.10 (dd, J = 10, 17 Hz, 1H), 6.38 (dd, J = 1.4, 17 Hz, 1H), 7.06–7.17 (m, 3H), 7.28–7.40 (m, 6H), 7.67 (s, 1H), 7.88–7.99 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 27.6, 28.3, 35.3, 64.4, 110.8, 111.0, 117.6, 117.7, 123.8, 124.1, 124.2, 126.9, 127.3, 128.2, 128.3, 128.6, 129.3, 129.4, 130.5, 130.7, 131.1, 131.8, 133.3, 137.5, 152.1, 152.5, 166.1; HR-MS (ESI) m/z for $C_{27}H_{24}O_4Na$ $[M+Na]^+$: Calcd. 435.1572, found: 435.1824; $[\alpha]_D^{25}$ −22.66 (c = 2.14, $CHCl_3$).

4.2.14. 21. To a solution of **20** (165 mg, 0.4 mmol) in THF (2.0 mL) were added Et_3N (0.11 mL, 0.8 mmol) and 1.0M tetrachlorosilane in CH_2Cl_2 (0.2 mL, 0.2 mmol) at 0°C. The reaction mixture was stirred for 30 min and used for the next polymerisation. Selected physical properties of **21**: ^1H NMR ($CDCl_3$): δ 1.60–1.70 (m, 8H), 2.59–2.71 (m, 4H), 4.04 (t, J = 6 Hz, 4H), 5.65 (m, 2H), 5.97 (m, 2H), 6.19 (m, 2H), 6.82–7.18 (m, 12H), 7.26–7.40 (m, 2H), 7.49 (s, 2H), 7.57–7.69 (m, 4H), 7.84–8.01 (m, 2H); ^{13}C NMR (THF): δ 28.4, 29.2, 35.9, 64.6, 119.3, 120.8, 121.1, 121.7, 123.2, 125.4, 126.6, 127.1, 127.2, 127.6, 128.0, 128.4, 128.5, 128.8, 128.9, 129.4, 130.2, 131.2, 131.6, 131.8, 132.1, 132.5, 134.0, 139.5, 148.5, 149.0, 165.8.

4.2.15. Polymer 23 from 21. To a cooled (0°C) solution of **21** (0.2 mmol) and AIBN (36 mg, 0.22 mmol) in THF (3.7 mL) were added EGDMA (8 μL, 0.044 mmol) and MMA (430 μL, 4 mmol). The reaction mixture was heated to reflux for 10 h under argon and then H_2O was added to cleave the Si–O bonds. The aqueous layer was extracted with AcOEt and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the polymer was dissolved in ca 2 mL THF, and this mixture was slowly added to 30 mL MeOH under stirring. The precipitated polymer was collected by centrifugation at 3000 rpm for 10 min, and dried *in vacuo* to give light yellow polymer **23**.

4.2.16. Typical procedure for the preparation of polymer supported ALB. Polymer **23** (39.7 mg, 0.04 mmol as BINOL) was dried under reduced pressure at 45°C for 2 h. To a cooled (−78°C) solution of **23** in THF (0.4 mL) were added $AlMe_3$ in hexane (0.98 M, 20.4 μL, 0.02 mmol) and *t*-BuLi in pentane (1.48 M, 13.5 μL, 0.02 mmol). After being stirred for 10 min at the temperature, the reaction mixture was warmed to room temperature. A clear gel precipitated which was directly used as polymer supported ALB **25**.

4.2.17. Typical experimental procedure for polymer supported ALB catalysed asymmetric Michael reaction. To an insoluble polymer supported ALB catalyst **25** (10 mol%) in THF (0.5 M) were added 2-cyclohexen-1-one (**12**) (25 μL, 0.22 mmol) and dibenzyl malonate (**13**) (50 μL, 0.2 mmol). After being stirred at room temperature for 72 h, the reaction mixture was quenched with 1N HCl at 0°C and then extracted with AcOEt. The combined organic extract was washed with saturated $NaHCO_3$ aq. and brine, dried over Na_2SO_4, and concentrated to give an oily residue. The mixture was dissolved in ca 1 mL THF and this solution was slowly added to 30 mL MeOH under stirring. The precipitated polymer was collected by centrifugation at 3000 rpm for 10 min, and the supernatant was evaporated to give a crude product. Purification by flash chromatography on silica gel (acetone/hexane = 1/10) gave **14** in 73% yield with 91% ee. The enantiomeric excess of **14** was determined by chiral HPLC analysis (DAICEL CHIRALPAK AS, *i*-PrOH/hexane = 1/4, 1.0 mL/min, $\lambda = 254$ nm).

4.2.18. 37. To a cooled (−10°C) solution of the 6-substituted BINOL **18** (2.4 g, 4.15 mmol) in $THF/CH_2Cl_2 = 1/10$ (0.3 M) was added PPh_3 (1089 mg, 4.15 mmol, 2.6 equiv), diethyl azodicarboxylate (DEAD) (0.604 mL, 3.84 mmol) (dropwise via a syringe), and 3,5-dihydroxy benzoic acid methyl ester (269 mg, 1.60 mmol). The resulting yellow solution was stirred for 16 h and concentrated to dryness. The product was isolated by flash chromatography on silica gel (AcOEt/hexane = 1/25) to give G1 silyl-protected dendron methyl ester **37**, as a white foam. (1.3 g, 66% yield). IR (neat) 779.2, 810.0, 839.0, 999.1, 1164.9, 1247.9, 1463.9, 1593.1, 1718.5, 2856.4, 2927.7 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.16 (s, 6H), −0.15 (s, 6H), 0.00 (s, 6H), 0.12 (s, 6H), 0.48 (s, 36H), 1.83 (br, 8H), 2.76 (br, 4H), 3.89 (s, 3H), 3.99 (br, 4H), 6.63 (t, $J = 2.1$ Hz, 1H), 7.06 (dd, $J = 8.6$, 1.6 Hz, 2H), 7.14–7.31 (m, 14H), 7.60 (s, 2H), 7.74 (d, $J = 8.9$ Hz, 2H), 7.81 (dd, $J = 8.6$, 2.4 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ −4.36, −4.34, −4.15, 17.67, 25.15, 27.72, 28.74, 35.29, 52.14, 68.08, 106.45, 107.57, 120.35, 120.41, 121.85, 122.12, 123.13, 125.71, 125.88, 125.91, 126.13, 127.17, 127.50, 128.03, 128.50, 129.10, 129.27, 131.71, 132.96, 134.45, 136.63, 150.86, 159.94, 166.71; MS (FAB-HRMS) *m/z* Calcd. for $[M]^+$ 1304.6808, found: 1305.6840; $[\alpha]_D^{25}$ + 32.8 (c = 0.930, $CHCl_3$).

4.2.19. 38. To a cooled (0°C) solution of G1 silyl-protected dendron methyl ester **37** (1.9 g, 1.47 mmol) in THF (0.3 M) was added $LiAlH_4$ (67 mg, 1.764 mmol). The reaction mixture was stirred for 30 min at room temperature and quenched with H_2O at 0°C. The aqueous layer was adjusted to pH 7 with 1N HCl and then extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of solvent, the product was concentrated in *vacuo* to afford G1 silyl-protected

dendron benzyl alcohol **38** as a white foam (1.8 g, 98% yield). IR (neat) 748.3, 779.2, 812.0, 839.0, 997.1, 1080.1, 1161.1, 1220.9, 1357.8, 1417.6, 1506.3, 1593.1, 1708.8, 3649.1 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.19 (s, 6H), −0.17 (s, 6H), −0.03 (s, 6H). 0.00 (s, 6H), 0.45 (s, 36H), 1.80 (br, 8H), 2.75 (br, 4H), 3.93 (br, 4H), 4.58 (s, 2H), 6.35 (t, $J = 1.9$ Hz, 1H), 6.46 (d, $J = 2.1$ Hz, 2H), 7.04 (dd, $J = 8.8$, 1.6 Hz, 2H), 7.11–7.29 (m, 13H), 7.57 (s, 2H), 7.71 (d, $J = 8.9$ Hz, 2H), 7.78 (dd, $J = 8.4$, 1.9 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ −4.38, −4.34, −4.15, 17.70, 25.16, 28.86, 35.44, 65.44, 67.87, 100.55, 105.03, 120.39, 120.42, 121.86, 122.14, 123.12, 125.71, 125.90, 126.12, 127.19, 127.49, 128.01, 128.48, 129.12, 129.27, 132.97, 134.47, 136.72, 143.06, 150.40, 150.89, 160.34; MS (FAB-HRMS) m/z Calcd. for $[M]^+$: 1276.6859, found: 1276.6903; $[\alpha]_D^{25} + 24.4$ ($c = 0.930$, $CHCl_3$).

4.2.20. TBS protected G1 dendrimer-supported BINOL (TBS-G1 DSB) 40. To a cooled (−5°C) solution of the G1 silyl-protected benzyl alcohol **38** (236 mg, 0.185 nmol) in $THF/CH_2Cl_2 = 1/10$ (0.3 M) was added PPh_3 (47.2 mg, 0.180 mmol), diethyl azodicarboxylate (DEAD) (0.027 mL, 0.172 mmol) (dropwise *via* a syringe), and the core unit **39** (14.5 mg, 0.041 mmol). The resulting brown solution was stirred for 16 h and concentrated to dryness. The product was isolated by flash chromatography on silica gel (AcOEt/hexane = 1/15) to give G1 silyl-protected dendrimer-supported BINOL **40**, as a white foam (107 mg, 66% yield). IR (neat) 779.2, 839.0, 999.1, 1163.0, 1247.9, 1267.1, 1355.9, 1463.9, 1508.2, 1593.1 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.18 (s, 18H), −0.17 (s, 18H), −0.01 (s, 18H), 0.00 (s, 18H), 0.46 (s, 108H), 1.82 (br, 24H), 2.77 (br, 12H), 3.95 (br, 12H), 5.00 (s, 6H), 6.39 (s, 3H), 6.60 (d, $J = 1.8$ Hz, 6H), 7.08 (dd, $J = 8.9$, 2.1 Hz, 6H), 7.15–7.29 (m, 42H), 7.69–7.65 (m, 15H), 7.74 (d, $J = 8.7$ Hz, 6H), 7.81 (dd, $J = 10.6$, 2.1 Hz, 12H); ^{13}C NMR ($CDCl_3$): δ −4.37, −4.30, −4.15, 17.69, 25.13, 25.16, 27.77, 28.87, 29.78, 35.46, 67.91, 105.69, 115.09, 120.39, 120.43, 121.86, 122.15, 123.12, 125.71, 125.91, 126.13, 127.20, 127.49, 128.02, 128.24, 128.48, 129.12, 129.28, 132.97, 134.47, 136.72, 150.40, 150.89, 160.37; MS (ESI) m/z Calcd for $[M + C_7H_7]^+$: exact mass: 4221.2064, found: 4225.3; $[\alpha]_D^{25} + 35.9$ ($c = 0.310$, $CHCl_3$); GPC analysis: $M_w = 3800$, $M_w/M_n = 1.02$.

4.2.21. G1 dendrimer-supported BINOL (G1 DSB) 41. To a solution of silyl-protected dendrimer-supported BINOL **40** (227 mg, 0.055 mmol) in THF (0.3 M) was added 1.0 M TBAF (0.99 mL, 0.99 mmol) dropwise *via* a syringe. The reaction mixture was stirred for 12 h at room temperature and quenched with 1N HCl aq. The aqueous layer was extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography on silica gel (toluene/EtOH = 10/1) to give G1 dendrimer-supported BINOL **41** as a white solid (139 mg, 92% yield). IR (neat): 1091.6, 1220.9, 1359.7, 1419.5, 1635.5, 1705.0, 3510.0 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.77 (br, 24H), 2.75 (br, 12H), 2.96 (br, 12H), 3.94 (br, 12H), 5.02 (br, 6H), 6.36 (d, $J = 2.1$ Hz, 3H), 6.59 (dd, $J = 4.9$, 21. Hz, 6H), 6.95 (dd, $J = 8.8$, 2.1 Hz, 6H), 7.00–7.30 (m, 42H), 7.61–7.64 (m, 15H), 7.74 (d, $J = 8.8$ Hz, 6H), 7.82 (dd, $J = 5.9$, 2.9 Hz, 12H); ^{13}C NMR (acetone-d_6): δ 28.58, 30.38, 30.66, 35.87, 67.96, 68.34, 101.12, 106.37, 114.55, 114.90, 115.92, 119.25, 123.44, 123.88, 125.29, 126.82, 127.32, 128.33, 128.64, 128.89, 129.72, 129.89,

129.93, 130.30, 133.69, 134.25, 137.35, 139.80, 140.33, 142.32, 153.68, 154.17, 159.14, 160.50, 161.14; CSI-MS m/z $[M+Na]^+$: 2786; $[\alpha]_D^{25}$ − 21.0 (c = 0.240, $CHCl_3$).

4.2.22. 42. To a cooled (−5°C) solution of the G1 silyl-protected dendron-benzyl alcohol **38** (254 mg, 0.198 mmol) in THF/CH_2Cl_2 = 1/10 (0.3 M) was added PPh_3 (52 mg, 0.198 mmol), diethyl azodicarboxylate (DEAD) (0.028 mL, 0.181 mmol, 2.2 eq) (dropwise *via* a syringe), and 3,5-dihydroxy benzoic acid methyl ester (13.9 mg, 0.083 mmol). The resulting yellow solution was stirred for 18 h and concentrated to dryness. The product was isolated by flash chromatography on silica gel (AcOEt/hexane = 1/20) to give G2 silyl-protected dendron methyl ester **42**, as a white foam. (158 mg, 71% yield). IR (neat) 779.2, 810.0, 839.0, 999.1, 1163.0, 1247.9, 1267.1, 1355.9, 1463.9, 1593.1, 1718.5 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.20 (s, 12H), −0.18 (s, 12H), −0.03 (s, 12H), −0.02 (s, 12H), 0.44 (s, 72H), 1.79 (br, 16H), 2.75 (br, 8H), 3.85 (s, 3H), 3.93 (br, 8H), 4.94 (s, 4H), 6.38 (t, J = 1.8 Hz, 2H), 6.52 (d, J = 1.9 Hz, 4H), 6.75 (t, J = 1.9 Hz, 1H), 7.03 (dd, J = 8.9, 1.9 Hz, 4H), 7.11–7.27 (m, 26H), 7.57 (s, 4H), 7.70 (d, J = 8.9 Hz, 4H), 7.78 (dd, J = 8.9, 2.6 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ −4.37, −4.33, −4.17, −4.15, 17.69, 25.16, 27.76, 28.86, 35.44, 52.24, 67.86, 70.28, 100.88, 105.70, 107.07, 108.30, 120.41, 121.85, 122.13, 123.12, 125.71, 125.90, 126.13, 127.20, 127.49, 128.02, 128.48, 129.10, 129.27, 131.89, 132.95, 134.46, 136.71, 138.45, 150.37, 158.87, 159.60, 160.33, 166.56; MS (ESI) m/z Calcd. for $[M+NH_4]^+$: 2703.4, found: 2704.6; $[\alpha]_D^{24}$ + 34.6 (c = 0.945, $CHCl_3$).

4.2.23. 43. To a cooled (0°C) solution of G2 silyl-protected dendron methyl ester **42** (92 mg, 0.034 mmol) in THF (0.3 M) was added $LiAlH_4$ (1.5 mg, 0.04 mmol). The reaction mixture was stirred for 30 min at room temperature and quenched with H_2O at 0°C. The aqueous layer was adjusted to pH 7 with 1N HCl and then extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of solvent, the product was concentrated in *vacuo* to afford G2 silyl-protected dendron benzyl alcohol **43** as a white foam (76 mg, 83% yield). IR (neat) 779.2, 810.0, 839.0, 999.1, 1163.0, 1249.8, 1340.4, 1463.9, 1593.1 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.18 (s, 12H), −0.17 (s 12H), −0.01 (s, 12H), 0.00 (s, 12H), 0.47 (s, 72H), 1.81 (br, 16H), 2.77 (br, 8H), 3.95 (br, 8H), 4.60 (s, 2H), 4.93 (s, 4H), 6.40 (t, J = 2.2 Hz, 2H). 6.54 (m, 4H), 6.60 (d, J = 1.8 Hz, 2H), 7.07 (dd, J = 8.8, 1.5 Hz, 4H), 7.15–7.21 (m, 16H), 7.24–7.29 (m, 10H), 7.59 (s, 4H), 7.74 (d, J = 8.8 Hz, 4H), 7.81 (dd, J = 8.4, 4.7 Hz, 8H); ^{13}C NMR ($CDCl_3$): δ −0.38, −4.34, −4.15, 17.69, 25.15, 27.78, 28.89, 35.47, 65.35, 67.89, 70.14, 100.78, 105.71, 120.42, 121.86, 122.15, 123.12, 125.71, 125.91, 126.12, 127.20, 127.49, 128.02, 128.48, 129.12, 132.97, 134.47, 136.72, 138.87, 143.22, 150.40, 150.89, 160.03, 160.33; MS (ESI) m/z Calcd. for $[M+NH_4]^+$: 2675.4, found: 2676.6; $[\alpha]_D^{24}$ + 34.9 (c = 0.950, $CHCl_3$).

4.2.24. TBS protected G1 dendrimer-supported BINOL (TBS-G1 DSB) 44. To a cooled (−5°C) solution of the G2 silyl-protected benzyl alcohol **43** (184 mg, 0.069 mmol, 4.5 equiv) in CH_2Cl_2 (0.3 M) was added PBu_3 (0.016 mL, 0.064 mmol, 4.3 equiv), 1,1′-(azodicarbonyl)-dipiperidine (ADDP) (15 mg, 0.062 mmol, 4.1 eq) and the core unit **39** (5 mg, 0.015 mmol, 1.0 eq). The resulting brown solution was stirred for 14 h and

concentrated to dryness. The product was isolated by flash chromatography on silica gel (AcOEt/hexane = 1/15) to give G2 silyl-protected dendrimer-supported BINOL **44**, as a white foam. (56 mg, 45% yield). IR (neat) 779.2, 810.0, 839.0, 1001.0, 1163.0, 1247.9, 1463.9, 1508.2, 1593.1 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.20, (s, 36H), −0.18 (s, 36H), −0.03 (s, 36H), −0.02 (s, 36H), 0.45 (s, 216H), 1.80 (br, 48H), 2.75 (br, 24H), 3.93 (br, 24H), 4.93 (s, 12H), 5.00 (s, 6H), 6.41 (s, 6H), 6.57 (s, 12H), 6.69 (s, 6H), 7.07 (d, J = 8.4 Hz, 12H), 7.15–7.28 (m, 81H), 7.59–7.69 (m, 21H), 7.73 (d, J = 8.7 Hz, 12H), 7.80 (dd, J = 8.3, 4.0 Hz, 24H); ^{13}C NMR ($CDCl_3$): δ −4.37, −4.33, −4.17, 17.70, 25.14, 25.16, 27.77, 28.88, 29.78, 35.46, 67.89, 70.20, 105.79, 115.07, 120.38, 121.85, 122.15, 123.12, 125.71, 125.90, 126.13, 127.20, 127.49, 128.02, 128.26, 128.48, 129.11, 129.27, 132.96, 134.47, 136.72, 138.79, 141.67, 150.38, 150.88, 156.55, 160.05, 160.33; MS (ESI) m/z Calcd. for $[M + Na]^+$: exact 8295.2778, found: 8303.9073; $[\alpha]_D^{24}$ + 30.2 (c = 0.590, $CHCl_3$).

4.2.25. G2 dendrimer-supported BINOL (G2 DSB) 45. To a solution of G2 silyl-protected dendrimer-supported BINOL **44** (389 mg, 0.047 mmol, 1.0 eq) in THF (0.3 M) was added 1.0 M TABF (1.691 mL, 1.691 mmol, 36 eq) dropwise *via* a syringe. The reaction mixture was stirred for 12 h at room temperature and quenched with 1N HCl. The aqueous layer was extracted with AcOEt. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography on silica gel (toluene/EtOH = 10/1) to give G2 dendrimer-supported BINOL **45** as a white solid (244 mg, 94% yield). IR (neat): 819.7, 1126.4, 1145.6, 1458.1, 1508.2, 1596.9, 1701.1, 2923.9, 3410.0 cm^{-1}; ^1H NMR (acetone-d_6): δ 1.73, (br, 48H), 2.70 (br, 24H), 3.07 (br, 24H), 3.90 (br, 24H), 4.93 (s, 12H), 5.02 (s, 6H), 6.43 (s, 6H), 6.59 (s, 12H), 7.10 (d, J = 8.6 Hz, 12H), 7.12–7.32 (m, 81H), 7.57–7.71 (m, 21H), 7.75 (d, J = 8.8 Hz, 12H), 7.85 (dd, J = 8.9, 4.1 Hz, 24H); ^{13}C NMR ($CDCl_3$): δ 28.56, 30.54, 30.65, 35.87, 68.33, 70.37, 101.17, 106.41, 114.51, 114.88, 119.24, 123.45, 125.229, 129.71, 129.87, 129.96, 130.31, 133.65, 135.22, 137.36, 140.17, 153.65, 154.15, 156.55, 160.69, 161.07; CSI-MS m/z $[M + Na]^+$: 5561, $[M + 2Na]^{2+}$ 2792; $[\alpha]_D^{25}$ − 30.9 (c = 0.745, $CHCl_3$).

4.2.26. Preparation of dendritic ALB complex. To a solution of G1 dendrimer-supported BINOL (G1 DSB) **41** (80 mg, 0.029 mmol) in THF (0.96 mL) was added $AlMe_3$ in hexane (2.00 M, 0.043 mL, 0.087 mmol) and *n*-BuLi in hexane (2.66 M, 0.033 mL, 0.087 mmol) at 0°C. After being stirred for 2 h at room temperature, the resulting yellow solid was directly used as a G1 dendritic ALB catalyst (0.03M).

4.2.27. Preparation of dendritic GaSB complex. To a solution of G1 dendrimer-supported BINOL (G1 DSB) **41** (64 mg, 0.023 mmol) in THF (0.3 mL) was added $GaCl_3$ (13 mg, 0.069 mmol) in THF/ether = 10/1 (0.2 mL) and a solution of NaO-*t*-Bu (27 mg, 0.277 mmol) in THF (0.27 mL) at 0°C. After being stirred for 12 h at room temperature, the resulting yellow solid was directly used as a G1 dendritic GaSB catalyst (0.03M).

4.2.28. Preparation of dendritic ALB-II complex (additive: NaO-*t*-Bu). To an insoluble dendritic ALB catalyst in THF was added a solution of NaO-*t*-Bu in THF (0.5 M, 0.092 mL, 0.046 mmol) at 0°C. After being stirred for 2 h at room temperature, the resulting yellow solid was directly used as a G1 dendritic ALB-II catalyst.

4.2.29. Typical experimental procedure for dendritic ALB catalysed asymmetric Michael reaction. To an insoluble dendritic ALB catalyst (0.1 eq) in THF (0.03 M) was added 2-cyclohexen-1-one (**12**) (0.031 mL, 0.317 mmol) and dibenzyl malonate (**13**) 0.072 mL, 0.289 mmol). After being stirred at room temperature for 48 h, the reaction mixture was quenched with 1N HCl at 0°C and then extracted with AcOEt. The combined organic extract was washed with brine, dried (Na_2SO_4) and concentrated to get an oily residue. Purification by flash chromatography on silica gel (acetone/hexane = 1/10) gave the Michael adduct in 64% yield with 91% ee. The enantiomeric purity of **7** was determined by chiral HPLC analysis (Daicel CHIRALPAK AS, *i*-PrOH/hexane = 1/4, 1.0 mL/min, $\lambda = 254$ nm).

4.2.30. Typical procedure for the reuse of the dendritic catalyst. Reuse of the dendritic ALB was carried out after the removal of the clear product solution *via* a syringe under argon, THF, 2-cyclohexen-1-one (**12**) and dibenzyl malonate (**13**) were then added.

4.2.31. 49. To a solution of (*R*,*R*)-3,5-bis-4-[2,2′-bis(*tert*-butyldimethylsilanyloxy)-1,1′-binaphthalenyl-6-yl]-butoxy-benzyl alcohol (**37**) (2.5 g, 4.26 mmol) in THF (30 mL) were added Et_3N (0.77 mL, 5.5 mmol) and acryloyl chloride (0.38 mL, 4.6 mmol) at 0°C. The reaction mixture was stirred at this temperature for 30 min and 1.0 M TBAF in THF (7.2 mL, 7.2 mmol) was added dropwise. After being stirred for 30 min, the reaction was quenched with H_2O at 0°C. The aqueous layer was extracted with AcOEt and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by flash column chromatography on silica gel (AcOEt/hexane = 1/3) to give **49** (1.15 g, 2.79 mmol, 73%) as pale yellow oil. IR (neat) 1596.9, 1716.5, 3417.6, 3489.0 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.75 (s, 8H), 3.89 (s, 4H), 5.02 (s, 2H), 5.23 (s, 4H), 5.78 (dd, $J = 1.4$, 10 Hz, 1H), 6.09 (dd, $J = 10$, 17 Hz, 1H), 6.35 (s, 1H), 6.38 (dd, $J = 1.4$, 17 Hz, 1H), 6.45 (d, $J = 2.0$ Hz, 2H), 7.03 (d, $J = 8.6$ Hz, 2H), 7.11 (dd, $J = 0.8$, 8.9 Hz, 4H), 7.20–7.33 (m, 8H), 7.61 (s, 2H), 7.77–7.88 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 27.7, 28.8, 35.3, 66.2, 67.7, 76.5, 100.8, 106.3, 110.8, 111.1, 117.6, 123.7, 124.1, 126.8, 127.2, 127.9, 128.1, 128.6, 129.1, 129.3, 130.5, 131.0, 131.2, 131.7, 133.3, 137.5, 137.6, 152.0, 152.5, 160.0, 165.8; ESI-MS *m*/*z* $[M+Na]^+$: 897; $[\alpha]_D^{23}$ −13.32 (c 0.058, $CHCl_3$).

4.2.32. Preparation of the polymer-supported BisBINOL ligand 50a. Monomer **49** (88 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), MMA (11 μL, 0.1 mmol) and THF (0.2 mL) were combined in a screw-capped test tube. The reaction mixture was heated at 70°C for 22 h under argon. After removal of the solvent, the polymer was dissolved in THF (2 mL) and to this mixture was slowly added MeOH (30 mL) with stirring. The precipitated polymer was centrifuged at 3000 rpm for 10 min and dried in vacuo to

give a light yellow polymer **50a** (51 mg, 53%). IR (neat): 3510, 2941, 1726, 1596, 1456, 1139, 1058, 813, 748 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.79 (br), 1.56 (br), 1.72 (br), 2.68 (br), 3.48 (br), 3.83 (br), 4.85 (br), 5.19 (br), 5.33 (br), 6.39 (br), 7.05 (br), 7.24 (br), 7.56 (br), 7.78 (br); $[\alpha]_D^{28}$ −18.86 (c 0.058, $CHCl_3$); Amount of BINOL moieties = 2.196 mmol/g.

4.2.33. Preparation of the polymer-supported BisBINOL ligand 50b. Monomer **49** (88 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), MMA (32 μL, 0.3 mmol) and THF (0.3 mL) were combined in a screw-capped test tube. The reaction mixture was heated at 70°C for 22 h under argon. After removal of the solvent, the polymer was dissolved in THF (2 mL) and to this mixture was slowly added MeOH (30 mL) with stirring. The precipitated polymer was centrifuged at 3000 rpm for 10 min and dried in vacuo to give a light yellow polymer **50b** (65 mg, 56%). IR (neat): 3649, 2941, 1716, 1596, 1456, 1145, 1062, 815, 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.82 (br), 1.20 (br), 1.55 (br), 1.79 (br), 2.74 (br), 3.56 (br), 3.90 (br), 4.86 (br), 5.19 (br), 5.40 (br), 6.39 (br), 7.11 (br), 7.26 (br), 7.56 (br), 7.83 (br); $[\alpha]_D^{28}$ −19.41 (c 0.55, $CHCl_3$); Amount of BINOL moieties = 1.098 mmol/g.

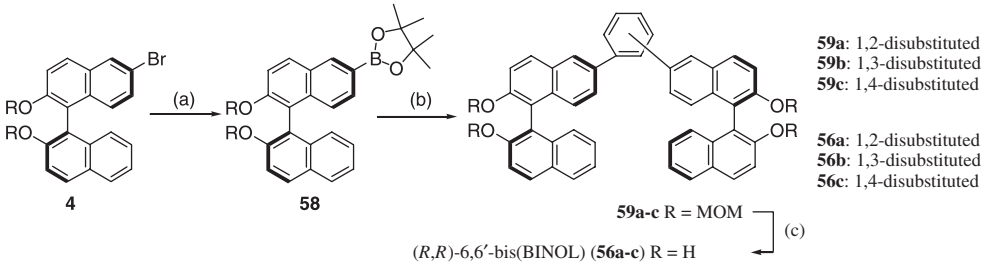
4.2.34. Typical procedure for the preparation of polymer-supported ALB catalyst 51a. Polymer **50a** (18.2 mg, 0.04 mmol as BINOL unit) was dissolved in 0.4 mL of THF after drying at 45°C in vacuo for 2 h. To the solution were added $AlMe_3$ (0.98M, 20.4 μL, 0.02 mmol) and *t*-BuLi (1.49M, 13.5 μL, 0.02 mmol) at −78°C. A white precipitate (**51a**) obtained by warming up to room temperature was directly used as an immobilized ALB catalyst.

4.2.35. Typical procedure for asymmetric Michael reaction. To the polymer-supported ALB catalyst **51a** (0.02 mol as single catalytic site) in THF (0.4 mL) were added **12** (25 μL, 0.22 mmol) and **13** (50 μL, 0.20 mmol) at room temperature. After completion of the reaction, the reaction mixture was quenched with 1N HCl aq. at room temperature and then extracted with AcOEt. The combined organic extracts were neutralized with sat. $NaHCO_3$ aq., washed with brine, dried over Na_2SO_4, and concentrated. Separation of crude Michael product from the polymer **50a** was accomplished by precipitation of the residue from hexane. After concentration of the resulting supernatant, purification by flash chromatography on silica gel (acetone/hexane = 1/10) gave **14**. The enantiomeric purity of **7** was determined by chiral HPLC analysis (Daicel CHIRALPAK AS, *i*-PrOH/hexane = 1/4, 1.0 mL/min, λ = 254 nm).

4.2.36. Typical procedure for reuse of polymer-supported μ-oxodititanium catalyst 52. To the mixture of activated MS 4A (30 mg) and the insoluble polymer-supported μ-oxodititanium catalyst (0.03 mmol as the single catalytic site) in Et_2O (2 mL) were added **53** as 50% toluene solution (92 μL, 0.9 mmol) and **54** (39 μL, 0.3 mmol). After stirring at room temperature for 72 h, the clear supernatant was removed via syringe. The catalyst was repeatedly washed with fresh Et_2O (1 mL × 2) under argon atmosphere. The combined Et_2O extract was concentrated and purified by flash column chromatography on silica gel (AcOEt/hexane = 1/7) to give **55**. To the

catalyst residue were added fresh Et_2O (2 mL), **53** (46 μL, 0.45 mmol) and **54** (20 μL, 0.15 mmol). The enantiomeric purity of **55** was determined by chiral HPLC analysis (Daicel CHIRALPAK AS, *i*-PrOH/hexane = 1/4, 1.0 mL/min, λ = 254 nm).

4.2.37. Synthesis of (*R*,*R*)-6,6′-bis(BINOL) derivatives 56a–c.



(a) i. BuLi, $B(OMe)_3$, -80°C, ii. Pinacol, AcOH, 83%; (b) Dibromobenzene, $Pd(PPh_3)_4$, aq K_2CO_3, THF, reflux, **59a**(67%), **59b**(47%), **59c**(81%); (c) $TsOH\text{-}H_2O$,CH_2Cl_2, RT, **56a**(quant), **56b**(quant), **56c**(90%)

4.2.38. 58. To a THF (65 mL) solution of (*R*)-6-bromo-2,2′-bis(methoxymethyloxy)-1,1′-binaphthalene (**4**) (650 mg, 1.43 mmol) was slowly added *n*-BuLi (0.55 mL, 2.6 M in hexane, 1.43 mmol) at −80°C. After 1.5 h, $B(OMe)_3$ (0.33 mL, 2.87 mmol) was added to the brown solution at −80°C and the reaction mixture was stirred at room temperature for 1 h. To the resulting pale yellow solution was slowly added a THF (2 mL) solution of pinacol (340 mg, 2.87 mmol) and acetic acid (85 μL, 1.49 mmol). After being stirred for 12 h, the mixture was quenched with aq. $NaHCO_3$ at 0°C and extracted with AcOEt and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel (AcOEt/hexane = 1/3) to afford **58** (590 mg, 83% yield) as a white solid. IR (neat) 1477, 1371, 1238, 1144, 1067, 1013, 922 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.35 (s, 12H), 3.13 (s, 3H), 3.14 (s, 3H), 4.95 (d, J = 6.8 Hz, 1H), 4.97 (d, J = 6.8 Hz, 1H), 5.05 (d, J = 6.8 Hz, 1H), 5.08 (d, J = 6.8 Hz, 1H), 7.11–7.22 (m, 3H), 7.30–7.33 (m, 1H), 7.54–7.59 (m, 3H), 7.86 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 9.2 Hz, 1H), 8.40 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 24.9, 25.0, 55.9, 83.8, 94.9, 95.1, 116.9, 117.2, 120.9, 121.1, 123.9, 124.5, 125.4, 126.2, 127.7, 129.1, 129.3, 129.8, 130.2, 130.7, 133.9, 135.6, 136.3, 152.5, 153.4; MS (FAB-HRMS) m/z Calcd. for $C_{30}H_{33}BO_6$ $[M]^+$: 500.2370, found: 500.2358; $[\alpha]_D^{25}$ + 41.4 (c = 1.08, $CHCl_3$).

4.2.39. General procedure for the synthesis of 59. A mixture of **58** (0.36 mmol), corresponding dibromobenzene (0.18 mmol), and $Pd(PPh_3)_4$ (0.036 mmol) in THF (7.5 mL) and 1M aq K_2CO_3 (3.6 mL) was heated to reflux for 24 h. The mixture was extracted with AcOEt, washed with brine, and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel (AcOEt/hexane = 2/5) to afford corresponding **59** as a white solid.

59a (67% yield): IR (neat) 1236, 1148, 1030, 1011, 920, 907 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.89 (s, 6H), 3.12 (s, 6H), 4.82 (d, J = 6.8 Hz, 2H), 4.93 (t, J = 6.8 Hz, 2H), 4.95 (d, J = 6.8 Hz, 2H), 5.04 (d, J = 6.8 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 7.06–7.15 (m, 4H), 7.27–7.33 (m, 2H), 7.39–7.42 (m, 2H),

7.43–7.52 (m, 6H), 7.70–7.90 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 55.7, 55.8, 95.1, 95.3, 117.2, 117.4, 121.0, 121.2, 123.9, 124.8, 125.4, 126.2, 127.3, 127.7, 128.4, 128.5, 129.2, 129.3, 129.6, 129.7, 130.8, 132.4, 133.8, 137.2, 140.4, 152.4, 152.6; FAB-MS m/z 822 $[M]^+$; Anal. Calcd. for $C_{54}H_{46}O_8$: C 78.81; H 5.63, found: C 78.75; H 5.85; $[\alpha]_D^{25} - 0.76$ (c = 1.03, $CHCl_3$).

59b (47% yield): IR (neat) 1236, 1148, 1010, 905, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.14 (s, 6H), 3.16 (s, 6H), 4.97 (d, J = 6.8 Hz, 2H), 4.99 (d, J = 6.8 Hz, 2H), 5.08 (d, J = 6.8 Hz, 4H), 7.21–7.26 (m, 6H), 7.31–7.36 (m, 3H), 7.50–7.64 (m, 9H), 7.86 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 9.4 Hz, 2H), 7.99, (d, J = 9.4 Hz, 2H), 8.13 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 55.8, 55.9, 95.1, 95.2, 117.2, 117.6, 121.1, 124.0, 125.4, 125.8, 125.9, 126.1, 126.2, 127.8, 129.2, 129.3, 129.6, 129.8, 130.0, 133.2, 133.9, 136.5, 141.5, 152.5, 152.7; FAB-MS m/z 822 $[M]^+$. Anal. Calcd. for $C_{54}H_{46}O_8$: C 78.81; H 5.63, found: C 79.04; H 5.83; $[\alpha]_D^{25} + 34.9$ (c = 1.09, $CHCl_3$).

59c (81% yield): IR (neat) 1238, 1148, 1070, 1015, 920 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.16 (s, 6H), 3.18 (s, 6H), 4.98 (d, J = 6.5 Hz, 2H), 5.00 (d, J = 6.5 Hz, 2H), 5.09 (d, J = 6.5 Hz, 2H), 5.10 (d, J = 6.5 Hz, 2H), 7.18–7.27 (m, 6H), 7.32–7.38 (m, 2H), 7.52–7.62 (m, 6H), 7.76 (s, 4H), 7.88 (d, J = 8.1 Hz, 2H), 7.96 (d, J = 9.2 Hz, 2H), 8.01 (d, J = 8.9 Hz), 8.13 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 55.9, 95.2, 117.2, 117.7, 121.1, 124.0, 125.4, 125.5, 125.7, 126.1, 126.3, 127.5, 127.8, 129.3, 129.6, 129.8, 130.0, 133.2. 133.9, 136.0, 139.6, 152.6, 152.7; MS (ESI-HRMS) m/z Calcd. for $C_{54}H_{46}NaO_8$ $[M + Na]^+$: 845.3090, found: 845.3093. Anal. Calcd. for $C_{54}H_{46}O_8$: C 78.81; H 5.63, found: C 78.61; H 5.87; $[\alpha]_D^{25} + 24.4$ (c = 1.07, $CHCl_3$).

4.2.40. General procedure for the synthesis of 56a–c. To an ice cooled solution of **59** (0.061 mmol) in CH_2Cl_2 (10 mL) was added TsOH-H_2O (46 mg, 0.24 mmol). The mixture was stirred at room temperature for 24 h and extracted with AcOEt, washed with brine, and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel (acetone/hexane = 1/2) to afford corresponding **56** as a white solid.

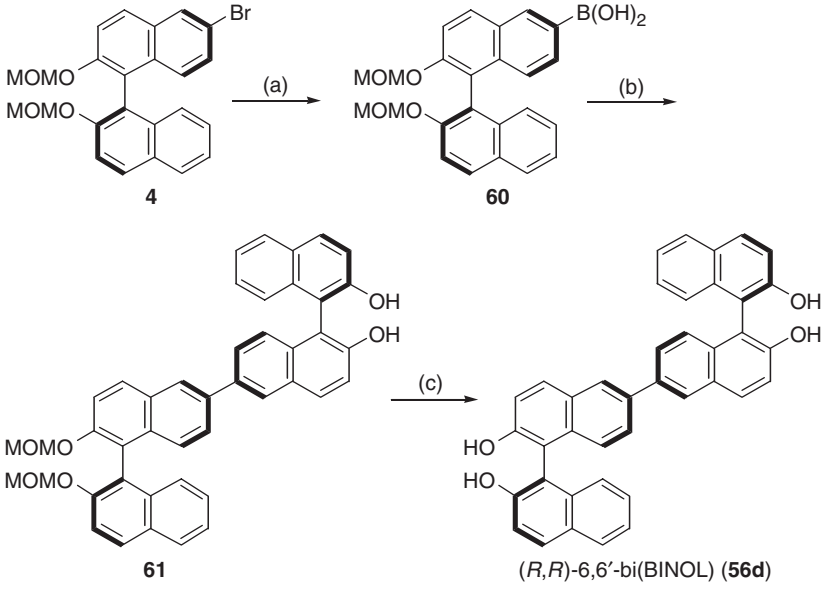
56a (quant): IR (neat) 3483, 3393, 1618, 1593, 1558, 1466, 1381, 1340, 1313, 1256, 1144, 1126, 1072, 932, 905, 864, 814, 725, 692, 648, 565 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.98 (s, 2H), 5.20 (s, 2H), 6.84 (d, J = 8.9 Hz, 2H), 6.94 (dd, J = 8.6, 1.6 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 7.21 (dt, J = 7.0, 1.6 Hz, 2H), 7.29–7.37 (m, 6H), 7.45–7.47 (m, 2H), 7.52–7.56 (m, 2H), 7.79 (d, J = 1.6 Hz, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 7.0 Hz, 2H), 7.91 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 110.8, 117.6, 123.3, 123.8, 123.9, 127.2, 127.5, 128.2, 128.6, 129.1, 129.2, 129.7, 130.5, 131.0, 131.1, 131.7, 133.0, 137.1, 140.1, 152.3. MS (ESI-HRMS) m/z Calcd. for $C_{46}H_{30}NaO_4$ $[M + Na]^+$: 669.2042, found: 669.2035. MS (FAB-HRMS) m/z Calcd. for $C_{46}H_{30}O_4$ $[M]^+$: 646.2144, found: 646.2123. $[\alpha]_D^{25} - 75.1$ (c = 0.460, $CHCl_3$).

56b (quant): IR (neat) 3504, 3413, 1618, 1593, 1466, 1383, 1342, 1312, 1256, 1215, 1144, 1126, 1072, 943, 905, 885, 864, 814, 795, 781, 725, 687, 648, 538 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.18 (s, 4H), 7.16–7.24 (m, 4H), 7.28–7.39 (m, 8H), 7.52–7.65 (m, 5H), 7.88 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.6 Hz, 4H), 8.01 (s, 1H), 8.12 (d, J = 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 110.8, 110.9, 117.7, 118.2, 124.0, 124.1, 124.8, 126.1, 126.4, 127.0, 127.4, 128.3, 129.3, 129.6, 131.3, 131.5, 132.6, 133.3, 136.6, 141.4, 152.6, 152.8; MS (ESI-HRMS) m/z Calcd. for $C_{46}H_{30}NaO_4$ $[M + Na]^+$: 669.2042, found: 669.2036;

MS (FAB-HRMS) m/z Calcd. for $C_{46}H_{30}O_4$ $[M]^+$: 646.2144, found: 646.2169; $[\alpha]_D^{25} - 117$ (c = 0.93, $CHCl_3$).

56c (90% yield): IR (neat) 3501, 3420, 1618, 1595, 1499, 1464, 1383, 1342, 1254, 1213, 1144, 1126, 932, 907, 816, 727 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.14 (s, 4H), 7.18–7.25 (m, 4H), 7.29–7.42 (m, 8H), 7.61 (dd, $J = 8.6$, 1.6 Hz, 2H), 7.76 (s, 4H), 7.90 (d, $J = 7.8$ Hz, 2H), 7.98 (d, $J = 8.6$ Hz, 2H), 7.03 (d, $J = 9.2$ Hz, 2H), 8.13 (d, $J = 1.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 110.7, 110.9, 117.7, 118.2, 124.0, 124.1, 124.8, 126.1, 126.8, 127.4, 127.5, 128.3, 129.4, 129.7, 131.4, 131.6, 132.6, 133.3, 136.2, 138.6, 139.6, 140.5, 152.6, 152.8. MS (ESI-HRMS) m/z Calcd. for $C_{46}H_{30}NaO_4$ $[M + Na]^+$: 669.2042, found: 669.2042; MS (FAB-HRMS) m/z Calcd. for $C_{46}H_{30}O_4$ $[M]^+$: 646.2144, found: 646.2154; $[\alpha]_D^{25} - 152$ (c = 0.445, $CHCl_3$).

4.2.41. Synthesis of (*R*,*R*)-6,6′-bi(BINOL) (56d).



(a) i. BuLi, $B(OMe)_3$, -78°C, ii. 1N HCl, 60 %; (b) (*R*)-6-bromo-1,1′-bi-2-naphthol, $Pd(PPh_3)_4$, aq K_2CO_3, THF, reflux, quant; (c) conc HCl, THF, rt, quant

4.2.42. 60. To a THF (37 mL) solution of **4** (3.3 g, 7.3 mmol) at −78°C was slowly added *n*-BuLi (3.2 mL, 2.6 M in hexane, 8.3 mmol). After stirring at −78°C for 0.5 h, the resulting brown solution was cannulated into $B(OMe)_3$ (2.3 mL, 21 mmol). The mixture was warmed to room temperature and stirred overnight. Excess 1N HCl was then added at 0°C. The mixture was extracted with AcOEt and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel (acetone/hexane = 1/1) to afford **60** (1.83 g, 60% yield) as a white solid. IR (neat) 3422, 1232, 1144, 1007 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.13 (s, 3H), 3.18 (s, 3H), 4.98–5.16 (m, 4H), 7.15–7.28 (m, 4H), 7.32–7.38 (m, 1H), 7.59 (d, $J = 9.2$ Hz, 1H), 7.64 (d, $J = 9.2$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.97 (d, $J = 9.2$ Hz, 1H), 8.00 (d, $J = 8.9$ Hz, 1H), 8.13 (d, $J = 8.9$ Hz, 1H), 8.82 (s, -$B(OH)_2$); ^{13}C NMR ($CDCl_3$): δ 55.9, 94.9, 95.2, 116.9, 117.2, 121.0, 124.0, 124.8,

125.3, 125.4, 126.3, 127.8, 129.1, 129.4, 129.8, 130.6, 131.0, 133.9, 136.5, 137.8, 152.5, 154.0; MS (ESI-HRMS) m/z Calcd. for $C_{26}H_{27}BO_6$ $[M+Na]^+$: 469.1798, found: 469.1798 [M (as the boronic acid dimethylester) + Na]$^+$; The dimethylester was formed when MeOH was used as eluent. $[\alpha]_D^{25}$ + 66.1 (c = 0.290, $CHCl_3$).

4.2.43. 61. A mixture of **60** (300 mg, 0.72 mmol), known (*R*)-6-bromo-2,2′-dihydroxy-1,1′-binaphthalene (262 mg, 0.72 mmol), and $Pd(PPh_3)_4$ (82.9 mg, 0.072 mmol) in THF (14 mL) and 1M aq K_2CO_3 (7.2 mL) was heated to reflux overnight. The mixture was extracted with AcOEt, washed with brine, and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel (AcOEt/hexane = 1/2) to afford **61** as a yellow solid (474 mg, quant). IR (neat) 3389, 1240, 1148, 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.13 (s, 3H), 3.15 (s, 3H), 4.97 (dd, J = 6.8, 3.8 Hz, 2H), 5.07 (d, J = 6.8 Hz, 2H), 5.19 (br-s, 1H), 5.21 (br-s, 1H), 7.16–7.38 (m, 10H), 7.53–7.65 (m, 4H), 7.87 (d, J = 8.1 Hz, 2H), 7.95 (d, J = 9.2 Hz, 2H), 7.99 (d, J = 9.2 Hz, 2H), 8.13 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 55.8, 55.9, 95.1, 95.2, 110.8, 110.9, 117.2, 117.6, 117.7, 118.1, 121.1, 123.9, 124.0, 124.1, 124.8, 125.4, 125.7, 125.9, 126.1, 126.2, 127.0, 127.4, 127.8, 128.3, 129.3, 129.4, 129.6, 129.6, 129.8, 130.0, 131.3, 131.5, 132.4, 133.1, 133.3, 133.9, 136.1, 136.5, 152.5, 152.6; MS (FAB-HRMS) m/z Calcd. for $C_{44}H_{34}O_6$ $[M]^+$: 658.2355, found: 658.2355; $[\alpha]_D^{25}$ − 31.3 (c = 0.670, $CHCl_3$).

4.2.44. 56d. To an ice cooled solution of **61** (299 mg, 0.45 mmol) in THF (3.4 mL) was added conc. HCl (0.58 mL). The solution was allowed to warm to room temperature slowly. After stirring for 24 h the solution was carefully poured into water (10 mL). The mixture was extracted with AcOEt, washed with brine, and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel (AcOEt/hexane = 1/3) to afford known 56d as a white solid (258 mg, quant). Ligand **56d** was identical in all the respects with spectra reported by Lin and co-workers [L. Ma, P. S. White, and W. Lin, *J. Org. Chem.*, 67, 7577 (2002)]. IR (neat) 3385, 1719, 1595, 1508, 1381, 1340, 1144, 905, 818, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.30 (br, OH), 7.15 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.36 (m, 6H), 7.64 (d, J = 8.7 Hz, 4H), 7.90 (d, J = 7.8 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 8.01 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 110.8, 111.0, 117.6, 118.1, 123.8, 124.0, 124.7, 126.1, 126.8, 127.2, 128.1, 129.1, 129.5, 131.1, 131.2, 132.4, 133.2, 136.1, 152.5 FAB-MS m/z 570 $[M]^+$; $[\alpha]_D^{25}$ − 88.3 (c = 0.52, THF).

4.2.45. Preparation of Al-bridged polymer, which functions as an ALB-II catalyst. To a solution of **56d** (10 mg, 0.018 mmol) in THF (1.8 mL) was added $LiAlH_4$ (0.68 mg, 0.018 mmol) at 0°C. After being stirred at room temperature for 0.5 h, Al-bridged polymer was obtained. IR (neat) 2862, 1587, 1499, 1458, 1423, 1339, 1126, 1045, 949, 862, 820, 746 cm^{-1}; Elemental analysis: Calcd. for $[C_{40}H_{22}AlLiO_4 \cdot 3thf]_n$: C 76.46; H 5.68, found: C 76.26; H 5.75.

To the above Al-bridged polymer in THF was added *n*-BuLi (3.4 μL, 2.66 M in THF, 0.009 mmol) at 0°C. After being stirred at room temperature for 1 h, the resulting white solid was directly used as an ALB-II catalyst.

4.2.46. Typical experimental procedure for the polymer catalysed asymmetric Michael reaction. To the obtained polymer and MS 4A (100 mg/mmol) in THF were added **12** (8.5 μL, 0.09 mmol) and **13** (22 μL, 0.09 mmol). After being stirred at room temperature for 48 h, the reaction mixture was quenched with 1N HCl at 0°C and then extracted with AcOEt. The combined organic extract was washed with brine, dried (Na_2SO_4), and concentrated to give an oily residue. Purification by flash chromatography on silica gel (acetone/hexane = 1/10) gave the Michael adduct in 88% yield with 96% ee. (Daicel Chiralpak AS, *i*-PrOH/hexane = 1/4, flow rate: 1.0 mL/min, $\lambda = 254$ nm).

4.2.47. Preparation of Ti-bridged polymer. To a solution of **56d** (10 mg, 0.018 mmol) in CH_2Cl_2 (0.88 mL) were added Ti(O-*i*Pr)$_4$ (10.3 μL, 0.036 mmol) in toluene (2.0 mL) and H_2O (0.63 μL, 0.035 mmol). The solution was stirred at room temperature for 24 h to afford the precipitate. After removal of the solvents at 80°C under reduced pressure, the residue was dried in vacuo at 80°C for 19 h. The resulting red solid **57** was directly used as a Ti-bridged polymer. IR (neat) 1583, 1499, 1454, 1427, 1333, 1236, 1074, 976, 941, 820, 727 cm^{-1}; Anal. Calcd. for $[C_{40}H_{22}O_6Ti_2 \cdot \text{toluene}]_n$: C 71.78; H 3.84, found: C 71.96; H 4.05.

4.2.48. Experimental procedure for the Ti-bridged polymer catalysed asymmetric carbonyl-ene reaction. To an insoluble Ti-bridged polymer and MS 4A (100 mg/mmol) in Et_2O were added a solution of **53** (21.7 μL, 0.09 mmol) in toluene and **54** (11.4 μL, 0.09 mmol) at room temperature under argon. After being stirred at room temperature for 72 h, the reaction mixture was quenched with 1N HCl at 0°C and then extracted with AcOEt. The combined organic extract was washed with brine, dried (Na_2SO_4), and concentrated to give an oily residue. Purification by flash chromatography on silica gel (AcOEt/hexane = 1/15) gave the product **55** in 81% yield with 90% ee. (Daicel Chiralpak AS, *i*-PrOH/hexane = 1/4, flow rate: 1.0 mL/min, $\lambda = 254$ nm).

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