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Chiral Polymers via Asymmetric Epoxidation and Asymmetric Dihydroxylation

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Abstract: Asymmetric epoxidation and dihydroxylation performed on suitably substituted styrene-divinylbenzene polymers yielded products which in some cases were difficult to analyze accurately, whereas asymmetric dihydroxylation of a *p*-hydroxycinnamic acid derivative and subsequent reaction with a chloromethylated styrene-1% divinylbenzene polymer afforded a polymer which could be analyzed prior to grafting on the support. Copyright © 1996 Elsevier Science Ltd

Introduction

The development of selective solid phase synthetic processes proceeding in high yield is an important activity in the construction of chemical libraries using combinatorial strategies[1] as well as in cases where solid phase reagents, such as chiral polymer-bound ligands and metal complexes, are desired. Such reagents are finding extensive application in catalytic asymmetric synthesis, primarily since these catalysts are more easily recovered than their monomeric analogues, thus enabling their repeated use.[2] In addition, the polymeric reagents have been found occasionally to exhibit higher selectivity than the corresponding monomers.[3]

Polymers with chiral substituents may be obtained from suitably functionalized non-chiral polymers either by asymmetric modification or by reaction with enantiopure chiral monomers. We have previously devised methods for the preparation of polymer-bound chiral epoxides by asymmetric synthesis[4] as well as by employing the chiral pool.[5] Such polymers are highly useful starting materials for the production of a multitude of enantiopure chiral polymers utilizing the fact that epoxides undergo ring opening reactions with high stereo- and regioselectivity.[6]

Asymmetric epoxidation[7] and dihydroxylation[8] constitute two of the most powerful methods for the synthesis of chiral compounds in stereochemically pure form. It would therefore be of interest to apply these methods to the preparation of polymers containing chiral handles. In principle, it should be possible to achieve this by asymmetric transformations of suitably substituted polymers as well as via asymmetric reactions of appropriate monomers prior to reaction with the polymers. This paper describes the preparation of chiral polystyrenes with 1,2-dihydroxypropionic ester groups obtained by asymmetric dihydroxylation of cinnamic ester derivatives.

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Results and Discussion

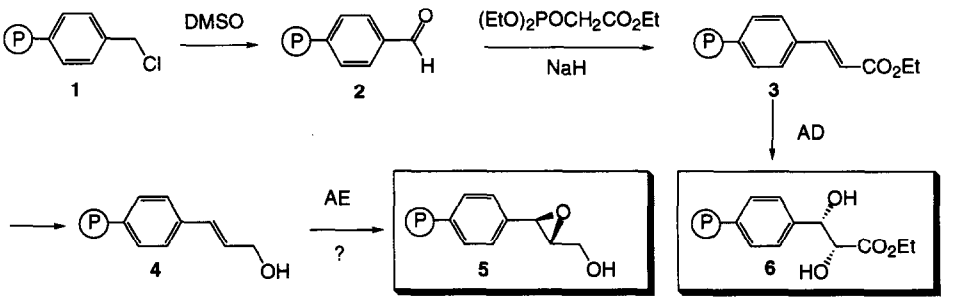
We first attempted to perform the asymmetric reactions directly on polystyrenes containing appropriate functional groups. In order to set the stage for the Sharpless-Katsuki epoxidation procedure, we needed an allylic alcohol group bound to the polymer. For this purpose, polystyrene cross-linked with 1% of divinylbenzene (SX 1) was chloromethylated[9] to yield **1**, and subsequently oxidized to polymeric benzaldehyde **2** using DMSO.[10] The latter conversion was estimated to merely 57% by transformation of the aldehyde to its oxime, followed by nitrogen analysis.[10]

A previously described procedure for the preparation of the desired allylic alcohol involved the condensation of polybenzaldehyde with malonic acid.[10] However, since an olefin with pure *E*-configuration was required in our case, we preferred to use a phosphonate reaction, which was shown on a monomeric analogue to yield only the *E* isomer. Thus, reaction of polybenzaldehyde with triethylphosphonoacetate[11] in the presence of sodium hydride yielded polymeric ethyl cinnamate **3**, as shown both by comparison of the ^{1}H and ^{13}C NMR spectra with those of the monomeric analogue, and by the disappearance of the aldehyde signal at 1698 cm^{-1} in the infrared spectrum and the appearance of a new peak at 1710 cm^{-1}. Finally, the ester was reduced using DIBAL,[12] to yield the desired polymeric allylic alcohol **4**, as indicated by NMR and IR spectroscopy.

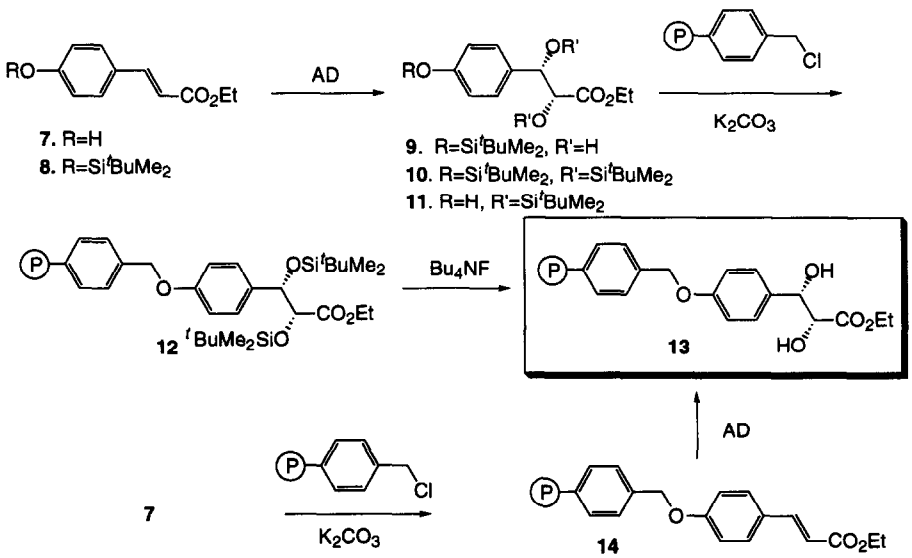
For the asymmetric epoxidation, a stoichiometric reaction was attempted first.[13,14] However, the polymer obtained showed poor swelling capability, which may be due to ring opening during the reaction.[15] This hypothesis was supported by the presence of several signals between δ 3.25 and 4.5 in the ^{1}H NMR spectrum of the polymer. In addition, formation of precipitates containing titanium could not be completely avoided,[16] even when air was excluded during filtering and washing of the polymer after reaction (according to ICP analysis, 42% of the titanium used remained in the polymer in the worst case). In order to avoid these problems, a catalytic reaction was run, which was possible using a column procedure for the reaction (see experimental section). Unfortunately, the polymer obtained after epoxidation was difficult to analyze in detail by NMR spectroscopy due to broadening of peaks, although signals at δ 4.5, 4.2, 3.6 and 3.4 in the ^{1}H NMR spectrum (as compared to 4.18, 3.95, 3.81 and 3.25-3.3 in epoxycinnamyl alcohol[14]) in place of only one signal at δ 4.20 in this region present in the starting alcohol indicated that the desired transformation to **5** had occurred. In order to gain further support for the structure of the polymer, the assumed epoxide was allowed to react with *p*-thiocresol in the presence of titanium tetraisopropoxide under conditions known to result in ring opening of the epoxide by the nucleophile.[14,17] According to sulfur analysis, the product obtained contained 0.32 mmol of thioether groups per g of polymer, whereas 0.42 mmol per g was expected assuming quantitative conversion in all steps starting from the aldehyde.

Attempts were made to determine the enantiomeric purity of the product obtained from asymmetric epoxidation. The product was therefore converted to its Mosher ester by reaction with the acid chlorides derived from both *S*- and *R*-MTPA.[18] In one case, a product was obtained containing 0.48 mmol CF_3 groups per g of polymer. Since the ring opening using thiocresol as nucleophile is expected to proceed in high yield, the high CF_3 content may indicate that some starting allylic alcohol remained after epoxidation, and that this alcohol also reacted with the acid chloride. Unfortunately, it was not possible to obtain separate signals for the two assumed diastereomers in the ^{19}F NMR spectra of the polymers. Attempted analysis of the Mosher derivatives of the bisalcohols obtained after ring opening with *p*-thiocresol gave the same disappointing result.

Attempts were therefore made to dihydroxylate the polymeric cinnamic ester **3** using AD-mix α.[8,19] In this case, the ester was preferred over the alcohol since it was expected to be easier to monitor the reaction by IR spectroscopy in the presence of the ester carbonyl group, and also because dihydroxylation of cinnamic esters has been shown to result in high ee's.[20] The polymer turned out to be quite unreactive in the *t*-butanol/water mixture commonly used for the dihydroxylation reaction, but reacted smoothly in the same mixture if the polymer was initially swollen in THF, to give **6**. Unfortunately, the ee of the polymer could not be determined due to line broadning in the ^{19}F NMR spectrum of the Mosher ester derivative.



We have recently shown that one easy, quite general method for the preparation of functionalized polystyrenes consists of initial preparation of a monomeric phenolic derivative containing the desired functional group and subsequent reaction of this phenol with a chloromethylated polystyrene.[21] This methodology was applied also to the preparation of a dihydroxylated polymer, in order to obtain a product that could be analyzed accurately. For this purpose, commercial *p*-hydroxycinnamic acid was transformed into its ethyl ester **7** and the phenol group protected as its *t*-butyldimethylsilyl ether **8**. Dihydroxylation using AD-mix α yielded dihydroxyester **9** (86%, 75% ee), whereas attempted dihydroxylation of the non-protected phenol resulted in decomposition of the product. The absolute configuration of **9** was assigned using Sharpless' mnemonic



device.[22] Protection of **9**, again using *t*-butyldimethylsilyl chloride (to yield **10**), followed by selective deprotection of the phenolic alcohol group afforded **11**, which was allowed to react with chloromethylated polystyrene-1% divinylbenzene in DMF in the presence of potassium carbonate to yield **12** and, after deprotection, the desired chiral polymer **13**. In this case, the analysis of the enantiomeric purity of the product was straightforward, since it could be performed on the monomer prior to grafting onto the polymer.

A polymer, which according to IR spectroscopy had the same structure, was obtained by initial grafting of ethyl *p*-hydroxycinnamate on chloromethylated SX 1 (to yield **14**) followed by dihydroxylation using AD-mix α in THF/*t*-butanol/ H_2O. The ^{19}F NMR spectrum obtained after transformation of this product to the bis-Mosher ester was badly resolved and separate signals for the diastereomers were not observed.

Summary. Asymmetric epoxidation and dihydroxylation were performed on suitably substituted styrene-divinylbenzene polymers. Since most of the products obtained were difficult to analyze accurately with respect to chemical as well as enantiomeric purity, a method for the dihydroxylation was devised in which the asymmetric reaction and chemical analysis were performed on a monomer prior to reaction with the polymeric support. By this method a chiral polymer with rather high enantiomeric excess, suitable for further manipulation,[23] was readily obtained.

Experimental section

^1H NMR spectra were recorded at 250, 400 or 500 MHz, ^{13}C NMR spectra at 62.9, 100.6 or 125.7 MHz, and ^{19}F NMR spectra at 376.4 or 470.6 MHz. ^{19}F NMR spectra were recorded with MTPA as δ=0. ^{13}C NMR spectra of polymers were recorded either after swelling in $CDCl_3$ at 62.9 or 100.6 MHz or on the dry solids at 75.5 MHz using magic angle spinning at 5.7 kHz, whereas ^1H NMR spectra were recorded at 300 MHz on polymers swollen in $CDCl_3$ using magic angle spinning at 5.7 kHz. The polymer SX 1, obtained from Bio Rad, is polystyrene cross-linked with 1% divinylbenzene. Chloromethylation was performed according to a published procedure.[9] Hexane was distilled from $LiAlH_4$ and methylene chloride was distilled from P_2O_5 and the solvents were stored over 4Å molecular sieves. A FMI Lab Pump, model RP-G400 was used for pumping liquids.

Polymeric benzaldehyde 2. Chloromethylated polystyrene-1% divinylbenzene (**1**, 5.91 g, 0.78 mmol Cl/g) was stirred in DMSO (30 ml) together with $NaHCO_3$ (4 g) at 155 °C for 25 h. The polymer was filtered off and washed in succession with DMSO, hot water, dioxane: H_2O 2:1, dioxane, acetone, ethanol, methylene chloride, toluene and methanol. After drying in vacuum for 16 h at 50 °C, 5.84 g of a white polymer was obtained. IR (KBr): 2729 and 1698 cm^{-1}. (No chlorine according to Beilstein test).

The polymeric aldehyde (0.5 g) was transformed into an oxime by reaction with excess hydroxylamine hydrochloride (0.3 g) in pyridine (5 ml) overnight at 100 °C. The polymer was then filtered off, rinsed with pyridine, DMSO, hot H_2O, dioxane: H_2O 2:1, dioxane, acetone, EtOH, CH_2Cl_2, toluene and MeOH, and finally dried under vacuum at 50 °C overnight to yield 511 mg of polymeric oxime. Found: N, 0.63%, corresponding to 0.45 mmol oxime/g of polymer, and, assuming total conversion of the aldehyde to its oxime, to 0.45 mmol of aldehyde groups/g of **2**, in turn corresponding to 57% conversion from **1**.

Polymeric ethyl cinnamate 3. Triethylphosphonoacetate (2.16 g, 9.6 mmol) in diethyl ether (36 ml) was added dropwise to an ice cooled and stirred suspension of sodium hydride (80% in oil, 0.29 g, 9.6 mmol) in diethyl ether (12 ml) under nitrogen. After stirring for 30 min at 0 °C, polymeric benzaldehyde (3g) was

added and the mixture stirred 4 days at ambient temperature. The polymer was filtered off, washed with H_2O, dioxane, acetone, EtOH, CH_2Cl_2, toluene and MeOH and dried at 50 °C under vacuum for 20 h to yield 3.15 g polymeric ethyl cinnamate. IR (KBr): 1710 and 1634 cm^{-1}. ^1H NMR (300 MHz): δ 7.58, 4.22, 1.30. ^{13}C NMR (75.5 MHz): δ 118, 61, 14. A signal expected from an olefinic proton probably hidden under the signals from the polymer. (^{13}C NMR signals for the corresponding monomeric compound are found at δ 166.87, 144.48, 134.38, 130.14, 128.80, 127.97, 118.21, 60.44 and 14.32).[24]

Polymeric 3-phenyl-2-propenylalcohol 4. DIBAL (1M in hexane, 8.75 ml, 8.75 mmol) was added with a syringe to a stirred suspension of polymeric ethyl cinnamate (2.70 g) in hexane (140 ml) at 0 °C. The mixture was stirred for 2 h at 0 °C and then for 20 h at ambient temperature. The reaction was stopped by the addition of ethyl acetate, followed by ethanol and water. The polymer obtained was filtered off, washed in succession with 2 M HCl, H_2O, dioxane:2M HCl 1:1, acetone, EtOH, CH_2Cl_2, toluene and MeOH and dried at 50 °C under vacuum during 20 h to yield 2.59 g of polymeric 3-phenyl-2-propenylalcohol. ^1H NMR (300 MHz, $CDCl_3$): δ 4.20. IR (KBr): absence of carbonyl band. ^{13}C NMR (75.5 MHz): δ 64 (remaining signals probably hidden under the signals originating from the polymer backbone). (^{13}C NMR signals for the corresponding monomeric compound are found at δ 136.58, 130.91, 128.50, 128.43, 127.57, 126.38 and 63.50).[23]

Epoxidation of polymer 4. Polymeric alcohol **4** (0.5 g) was filled into a column connected to a second column filled with activated 4Å molecular sieves and a reaction flask. The system was purged with nitrogen and CH_2Cl_2 (20 ml) was added. The system was allowed to stabilize at -30 °C during which time the solvent was pumped through the two columns. After ca 2 h, the pump was stopped and the reaction vessel was loaded with L-(+)-diethyl tartrate (30 mg, 0.15 mmol), titanium(IV) tetraisopropoxide (37 µl, 0.125 mmol) and *t*-butylhydroperoxide (4.23 M in isooctane, 0.24 ml, 1 mmol). This mixture was stirred for 0.5 h before pumping through the two columns was continued for another 44 h. While still under nitrogen, the column containing the polymer was rinsed with CH_2Cl_2 and dioxane and then, after allowing air to enter the system, with 1 M NaOH:dioxane 1:1, H_2O, EtOH, toluene, CH_2Cl_2 and MeOH. Drying at 50 °C under vacuum for 19 h afforded 504 mg of a polymer **5**. ^1H NMR (300 MHz, $CDCl_3$): δ 4.5, 4.2, 3.6, 3.4.

Ring opening with *p*-thiocresol.[14,17] Epoxidation and ring opening were performed in a one pot procedure. After the epoxidation had been running for 44 h as described above, pumping was stopped and $P(OMe)_3$ (240 µl, 0.25 g, 2 mmol) was added. After 0.5 h of stirring, pumping was continued for another 3 h, and then *p*-thiocresol (120 mg, 0.97 mmol) was added. After another 2 h of pumping, $Ti(OiPr)_4$ (300 µl, 284 mg, 1 mmol) was added and the reaction allowed to continue for 2 days. While still under nitrogen, the column containing the polymer was rinsed with CH_2Cl_2 and dioxane. After that the polymer obtained was collected on a glass filter, washed with 10% H_2SO_4:dioxane 1:1, H_2O:dioxane 1:1, dioxane, EtOH, toluene, CH_2Cl_2 and MeOH and dried at 50 °C under vacuum overnight. Anal: S, 1.01%, corresponding to 0.32 mmol of functional groups per g of polymer.

Preparation of Mosher ester of 5.[18] To a suspension of polymeric epoxide **5** (200 mg) in CH_2Cl_2 (5 ml) was added *S*- or *R*-MTPA-Cl (250 µl) and pyridine (3 ml) and the resulting mixture stirred under nitrogen at ambient temperature for 1 day. The polymer obtained was filtered off, washed with MeOH, MeOH:H_2O 1:1, CH_2Cl_2, THF and MeOH and then dried at 50 °C under vacuum for 20 h to yield 214 mg of ester. Anal: F, 2.72%, corresponding to 0.48 mmol of functional groups per g of polymer.

Ethyl *p*-hydroxycinnamate 7. *p*-Hydroxycinnamic acid (3 g, 18.3 mmol) was heated at 60 °C in EtOH (150 ml) in the presence of a few drops of conc H_2SO_4 overnight. Extraction with CH_2Cl_2 and washing of the organic phase with aqueous $NaHCO_3$ yielded the desired ester (100%). ^1H NMR (500 MHz, $CDCl_3$): δ

7.64 (d, J = 16.0 Hz, 1H), 7.41 (AA' part of AA'BB' spectrum, 2H), 6.88 (BB' part of AA'BB' spectrum, 2H), 6.30 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 168.20, 158.25, 144.96, 130.01, 126.76, 115.92, 115.07, 60.72, 14.25.

Ethyl *p*-(*t*-butyldimethylsilyloxy)cinnamate 8. To compound **7** (2.4 g, 12.5 mmol) in THF (5 ml) was added Et_3N (3.1 ml, 30 mmol) and then, during 10 min, *t*-butyldimethylsilyl chloride (1.89 g, 12.5 mmol) in THF (5 ml) at 0 °C. After stirring at ambient temperature overnight, the solvent was evaporated, hexane added, and the ammonium chloride filtered off. Evaporation of the solvent yielded **8** (2.77 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.63 (d, J = 15.9 Hz, 1H), 7.41 (AA' part of AA'BB' spectrum, 2H), 6.83 (BB' part of AA'BB' spectrum, 2H), 6.30 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.0 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 167.33, 157.79, 144.30, 129.62, 127.79, 120.48, 115.96, 60.30, 25.60, 18.22, 14.35, -4.39.

Ethyl (2*R*,3*S*)-2,3-dihydroxy-3-[4-(*t*-butyldimethylsilyloxy)phenyl]propanoate 9. AD-mix α (1.4 g) was stirred with *t*-butanol (5 ml) and H_2O (5 ml) for 0.5 h. Methanesulfonamide (95 mg, 1 mmol) was added, the mixture cooled to 0 °C and compound **8** (306 mg, 1 mmol) added. Stirring was continued for 5 h at 0 °C followed by 20 h at rt. $Na_2S_2O_5$ (2.7 g) was added and, after a further 40 min of stirring, the mixture was extracted with EtOAc and the organic phase washed with 2 M KOH. Drying ($MgSO_4$) and evaporation of the solvent yielded **9** (289 mg, 86%). $[\alpha]_D^{20}$ +1 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (AA' part of AA'BB' spectrum, 2H), 6.80 (BB' part of AA'BB' spectrum, 2H), 4.86 (d, J = 3.6 Hz, 1H), 4.26 (d, J = 3.6 Hz, 1H), 4.15 (m, 2H), 1.22 (t, J = 6 Hz, 3H), 0.95 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172.77, 155.49, 132.63, 127.59, 119.91, 74.78, 74.35, 61.96, 25.62, 18.14, 14.02, -4.47.

Ethyl (2*R*,3*S*)-2,3-bis(*t*-butyldimethylsilyloxy)-3-[4-(*t*-butyldimethylsilyloxy)phenyl]-propanoate 10. Compound **9** (590 mg, 1.73 mmol) in dry DMF (2 ml) was added to *t*-butyldimetylsilyl chloride (625 mg, 4.15 mmol) and imidazole (589 mg, 8.65 mmol) under Ar. After stirring at room temperature for 3 days, water (20 ml) was added. The water phase was extracted with ether (3 x 20 ml). The combined ether phases were washed with brine and dried ($MgSO_4$). Evaporation left a clear oil which was purified by column chromatography (6 x 2.5 cm silica gel, continuous gradient from pure hexane to EtOAc:hexane 20:80) resulting in pure **10** (771 mg, 78%) as a clear oil. $[\alpha]_D^{20}$ +43.8 (*c* 5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (AA' part of AA'BB' spectrum, 2H), 6.76 (BB' part of AA'BB' spectrum, 2H), 4.88 (d, J = 4.6 Hz, 1H), 4.14 (d, J = 4,6 Hz, 1H), 4.07-3.91 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H), 0.97 (s, 9H), 0.85 (s, 9H), 0.83 (s, 9H), 0.163 (s, 3H), 0.159 (s, 3H), -0.01 (s, 3H), -0.08 (s, 3H), -0.18 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.85, 155.10, 133.87, 128.46, 119.49, 78.38, 76.79, 60.48, 25.72 (2 *t*-Bu), 25.69, 18.26, 18.22, 18.10, 13.99, -4,49, -4.68, -5.03, -5.32, -5.49.

Ethyl (2*R*,3*S*)-2,3-bis(*t*-butyldimethylsilyloxy)-3-(4-hydroxyphenyl)propanoate 11. A solution of **10** (722 mg, 1.27 mmol) in dry THF (12 ml) was cooled to 0 °C. Tetrabutylammonium fluoride hydrate (401 mg, 1.27 mmol) was added in one portion. The reaction mixture was stirred for 15 min, then 20 ml of saturated aqueous NH_4Cl was added and the water phase was extracted three times with ether. The combined ether phases were washed with brine and dried ($MgSO_4$). Evaporation left a clear oil, which was purified with column chromatography (6 x 2.5 cm silica gel, EtOAc:hexane 20:80), resulting in 489 mg (85%) of **11** as a clear oil. $[\alpha]_D^{20}$ +44.6 (*c* 2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (AA' part of AA'BB' spectrum, 2H), 6.74 (BB' part of AA'BB' spectrum, 2H), 4.86 (d, J = 4.9 Hz, 1H), 4.83 (br s, 1H), 4.14 (d,

J = 4.9 Hz, 1H), 4.06-3.92 (m, 2H), 1.12 (t, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.84 (s, 9H), 0.00 (s, 3H), -0.06 (s, 3H), -0.16 (s, 3H), -0.19 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.85, 155.07, 133.20, 128.62, 114.60, 78.46, 76.74, 60.55, 25.76, 25.72, 18.25, 18.10, 13.96, -4.65, -4.99, -5.29, -5.47.

Grafting of 11, 12. Chloromethylated polystyrene (255 mg, 1.07 mmol of chloromethyl groups) and K_2CO_3 (296 mg, 2.14 mmol) were added to compound **11** (488 mg, 1.07 mmol) in DMF (4 ml). After stirring for 3 days at 80 °C, the polymer was filtered off and washed in succession with DMF, MeOH, H_2O, acetone, MeOH, CH_2Cl_2 and MeOH and then dried to give 557 mg of product (estimated by increase in weight to contain *ca* 1.3 mmol of functional groups per g of polymer). IR (KBr): 1748 cm^{-1}. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172, 129, 114, 78, 60, 26, 18, 14, -4.6, -5.3.

Deprotection of polymer 12, 13. To polymer **12** (513 mg, 0.66 mmol diol groups) suspended in THF (12 ml) was added tetrabutylammonium fluoride hydrate (1.25 g, 3.96 mmol). After stirring for 19 h, 15 ml of saturated aqueous NH_4Cl was added. The polymer was filtered off and washed in succession with H_2O, acetone, MeOH, CH_2Cl_2, MeOH and then dried to give 349 mg of **13**. IR (KBr): 1735 cm^{-1}. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172, 128, 73, 59, 14.

Grafting of ethyl *p*-hydroxycinnamate 14. Chloromethylated polystyrene (2.0 g, 8.4 mmol of chloromethyl groups), compound **7** (1.92 g, 10 mmol) and K_2CO_3 (1.37 g, 10 mmol) were heated in DMF (20 ml) at 80 °C for 40 h. The resulting polymer was filtered off and washed with DMF, H_2O, MeOH, CH_2Cl_2 and MeOH and then dried to yield 2.96 g of **14** (estimated by increase in weight to contain 2.07 mmol of functional groups per g of polymer).

Dihydroxylation of polymer 14, 13. To a mixture of polymer **14** (171 mg, 0.14 mmol of alkene groups), *N*-methylmorpholine (58 mg, 0.43 mmol) and $(DHQ)_2PHAL$ (5.5 mg, 0.007 mmol) was added THF (1 ml), followed by *t*-butanol (5 ml). To the resulting suspension was added K_2OsO_4 x $2H_2O$ (2.6 mg, 0.007 mmol) in water (1 ml) and methanesulfonamide (13.6 mg, 0.14 mmol) as a solid. The reaction mixture was stirred for 6 days at 0 °C. The polymer was filtered off and washed in succession with H_2O, acetone, MeOH, CH_2Cl_2 and MeOH. Drying in air left 150 mg of **13**. IR (KBr): 1735 cm^{-1}.

Dihydroxylation of polymer 3, 6. To **3** (250 mg, *ca* 0.1 mmol of alkene groups), *N*-methylmorpholine (44 mg, 0.32 mmol) and $(DHQ)_2PHAL$ (8.6 mg, 0.011 mmol) in THF (1 ml) and *t*-butanol (5 ml was added K_2OsO_4 x $2H_2O$ (4.1 mg, 0.011 mmol) in water (1 ml) followed by methanesulfonamide (11 mg, 0.11 mmol). The reaction mixture was stirred for 6 days at 0 °C. The polymer was filtered off and washed in succession with H_2O, acetone, MeOH, CH_2Cl_2 and MeOH. Drying in air afforded 193 mg of **6**. IR (KBr): 1735 cm^{-1}. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 146, 115, 70, 62, 55, 14.

Bis-Mosher ester of 9. To a solution of **9** (34 mg, 0.1 mmol), Et_3N (30 mg, 0.3 mmol) and DMAP (1 crystal) in CH_2Cl_2 (1 ml) was added *R*-MTPA-Cl (prepared from 70 mg *R*-MTPA and 381 mg $(COCl)_2$) in CH_2Cl_2 (1 ml). The reaction mixture was stirred at room temperature under N_2 for 2 days, diluted with CH_2Cl_2 (15 ml) and washed in succession with 0.1 M HCl, saturated aqueous $NaHCO_3$ and water. Drying ($MgSO_4$) and evaporation of the solvent left a brown oil, which was filtered through silica to give a clear oil, which according to ^{19}F NMR spectroscopy had an ee of 75%. ^{19}F NMR (470.6 MHz, $CDCl_3$) δ -0.36 (major isomer), -0.43 (minor isomer), -0.46 (major isomer), -0.48 (minor isomer).

Bis-Mosher ester of 13 and cleavage of product. To a suspension of polymer **13** (prepared from **14**, 150 mg, *ca* 0.12 mmol of diol groups), Et_3N (75 mg, 0.74 mmol) and DMAP (1 crystal) in CH_2Cl_2 (2 ml) was added *R*-MTPA-Cl (prepared from 288 mg *R*-MTPA and 780 mg $(COCl)_2$) in CH_2Cl_2 (4 ml). The slurry was stirred at room temperature under N_2 for 7 days. The polymer was filtered off and washed in

succession with MeOH, 0.1 M HCl, H_2O, acetone, MeOH, CH_2Cl_2 and MeOH. Drying in air left 137 mg of polymer. IR (KBr): 1742 cm^{-1}.

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