Probing the Scope of the Asymmetric Dihydroxylation of Polymer-Bound Olefins. Monitoring by HRMAS NMR Allows for Reaction Control and On-Bead Measurement of Enantiomeric Excess

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Abstract: The aim of this study was (I) to define the scope and limitations of the Sharpless asymmetric dihydroxylation (AD) for polymer-bound olefins of different structural types and (II) to elaborate HRMAS NMR methods for the direct on-bead monitoring of the asymmetric dihydroxylation, including the on-bead determination of enantiomeric excess (ee). (I) 2-Methoxy-4-(2-propenyl)phenol (eugenol, **E**), 10-undecenoic acid (**U**), and *(E)*-4-hydroxystilbene (**S**) were bound to Wang-resin or TentaGel S-OH. These olefins gave low (**E**, 32%), intermediate (**U**, 88%), and very high enantiomeric excesses (**S**, >99%) when treated with AD mix β in solution. When bound to the polymers, the trend of the enantioselectivities remained the same [**S** (97%) > **U** (20−45%) > **E** (0−3%)]. However, the absolute ee values demonstrate that only the most selective types of substrates in homogeneous solution have practical potential for enantioselective AD on solid phase. (II) HRMAS NMR was successfully used for on-bead monitoring and for the first time for the ee measurement of the polymer-bound dihydroxylation product. As an example, the full assignment of all resonances of polymer-bound 10-undecenoic acid (**U**) and its dihydroxylation product is presented. For the ee measurement, the polymer-bound dihydroxylation product was derivatized with Mosher's acid. The integration of seven different pairs of resonances in the ^{13}C HRMAS NMR of the diastereomeric Mosher esters gave (in each case) an ee value that agreed within <1% with that determined by chiral HPLC after cleavage of the AD product.

Introduction

In the rapidly developing field of combinatorial chemistry,[1−3] libraries of low molecular weight organic compounds are in most cases synthesized on solid polymeric supports. As a consequence, the two steps crucial to every synthetic operation, i.e., (I) the efficient transformation of a given starting material and (II) the analysis of the resulting product, need to be adapted from the conditions of the homogeneous solution to those of the polymer-bound compound. In fact, quite a number of reactions have already been optimized for solid-phase synthesis.[1−3] (I) Interestingly, the potential of the Sharpless asymmetric dihydroxylation (AD),[4,5] which has proven extremely valuable in "normal" solution-phase organic synthesis, has been investigated only in two instances: Moberg et al. prepared polymeric ethyl cinnamate in which the phenyl ring was part of the polystyrene support and treated it with AD mix α.[6a] Unfortunately, they were not able to determine the enantiomeric excess of the resulting diol. Han and Janda reported that *(E)*-cinnamic acid—bound to various polymers—can be dihydroxylated with enantiomeric excesses (88−99%) reaching or even surpassing those of the solution phase AD of ethyl *(E)*-cinnamate (97%).[6b] Obviously, this one data point of the solution-/solid-phase correlation does not allow for the conclusion that, in the Sharpless AD, every given olefin will afford the same enantiomeric excess (ee) when polymer supported or when in homogeneous solution. We selected 2-methoxy-4-(2-propenyl)-phenol (eugenol, **1a**), 10-undecenoic acid (**2b**), and *(E)*-4-hydroxystilbene (**1c**) as representative olefins: allylbenzene is known to give intermediate ee values (78%),[7] long-chain α-olefins give quite satisfactory ee values (e.g., 1-decene, 92%),[7] and *(E)*-stilbenes are dihydroxylated with extreme selectivity [*(E)*-stilbene, 99.8% ee][5] in the solution-phase Sharpless AD. Our results suggest that only those olefins that perform best in solution (e.g., stilbenes) are reasonable substrates for solid-phase AD. (II) The monitoring of solid-supported transformations is in most instances carried out *post festum*, by cleaving the reaction products off the polymer, followed by standard solution-phase methods (mostly NMR). Only few publications deal with nondestructive on-bead analyses by NMR-methods.[8] To the best of our knowledge, no method for the nondestructive on-bead determination of enantiomeric excess has been reported as yet. In high-resolution magic angle spinning (HRMAS) NMR, the combination of reduced but sufficient mobility of the polymer-bound molecules in the swelling agent and magic angle spinning

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(3) (a) Hermkens, P. H. H.; Ottenheijm, H. C. J.; Rees, D. C. *Tetrahedron* **1996**, *52*, 4527−4554. (b) Hermkens, P. H. H.; Ottenheijm, H. C. J.; Rees, D. C. *Tetrahedron* **1997**, *53*, 5643−5678.

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(5) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483−2547.

(6) (a) Cernerud, M.; Reina, J. A.; Tegenfeldt, J.; Moberg, C. *Tetrahedron: Asymmetry* **1996**, *7*, 2863−2870. (b) Han, H.; Janda, K. D. *Angew. Chem.* **1997**, *109*, 1835−1837; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1731−1733.

(7) Becker, H.; Sharpless, K. B. *Angew. Chem.* **1996**, *108*, 447−449; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 448−451.

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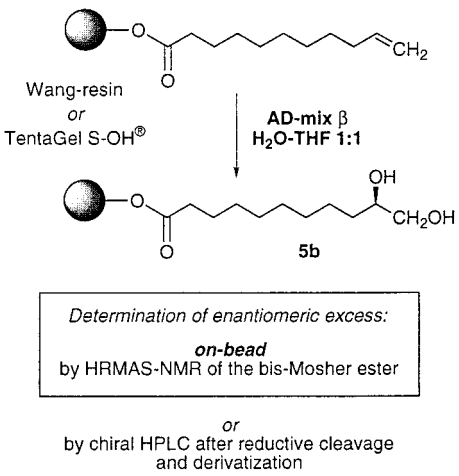
Table 1. Asymmetric Dihydroxylation on Polymeric Supports and in Homogeneous Solution[a]

entry	substrate[b]	polymer[c]	ligand	yield[d] [%]	ee [%]
1	**4a**	solution	$(DHQD)_2AQN$[e]	75	32[h]
2	**3a**	W	$(DHQD)_2AQN$[e]	83	0[h]
3	**3a**	W	$(DHQD)_2PYR$[f]	62	0[h]
4[i]	**3a**	W	$(DHQD)_2PHAL$[g]	73	3[h]
5[j]	**3a**	W	$(DHQD)_2PHAL$[g]	8	0[h]
6[m]	**4b**	solution	$(DHQD)_2AQN$[e]	78	88[k]
7	**3b**	W	$(DHQD)_2AQN$[e]	52	32[k]
8	**3b**	W	$(DHQD)_2PYR$[f]	44	34[k]
9[i]	**3b**	W	$(DHQD)_2PHAL$[g]	96	41[k]
10[l]	**3b**	W	$(DHQD)_2PHAL$[g]	96	20[k]
11[m]	**3b**	T	$(DHQD)_2PHAL$[g]	44	45[k]
12	**4c**	solution	$(DHQD)_2PHAL$[g]	61	>99[n]
13	**3c**	W	$(DHQD)_2PHAL$[g]	41	97[n]
14	**3c**	T	$(DHQD)_2PHAL$[g]	21	97[n]

[a] If not mentioned otherwise, the reactions were run at room temperature for 18 h. [b] See Scheme 2 for the structures of the substrates. [c] W: Wang-resin. T: TentaGel S-OH. [d] Yields refer to the pure, isolated triols **6a**−**c**/*ent*-**6a**−**c** (see Scheme 2). [e] Dihydroquinidine 1,4-anthraquinonediyl diether.[7] [f] Dihydroquinidine 2,5-diphenyl-4,6-pyrimidinediyl diether.[5] [g] Dihydroquinidine 1,4-phthalazinediyl diether.[5] [h] ChiraSpher-type column (Merck; methyl-*tert*-butyl ether−THF 20:80). [i] Reaction run at room temperature for 12 h. [j] Reaction run at 0 °C for 24 h. [k] ChiraSpher-type column (Merck; methyl-*tert*-butyl ether−THF 70:30). [l] Reaction run at room temperature for 6 d. [m] Reaction run at room temperature for 24 h. [n] CHIRALCEL OD-H column (Daicel; hexane−2-propanol 80:20).

Scheme 1

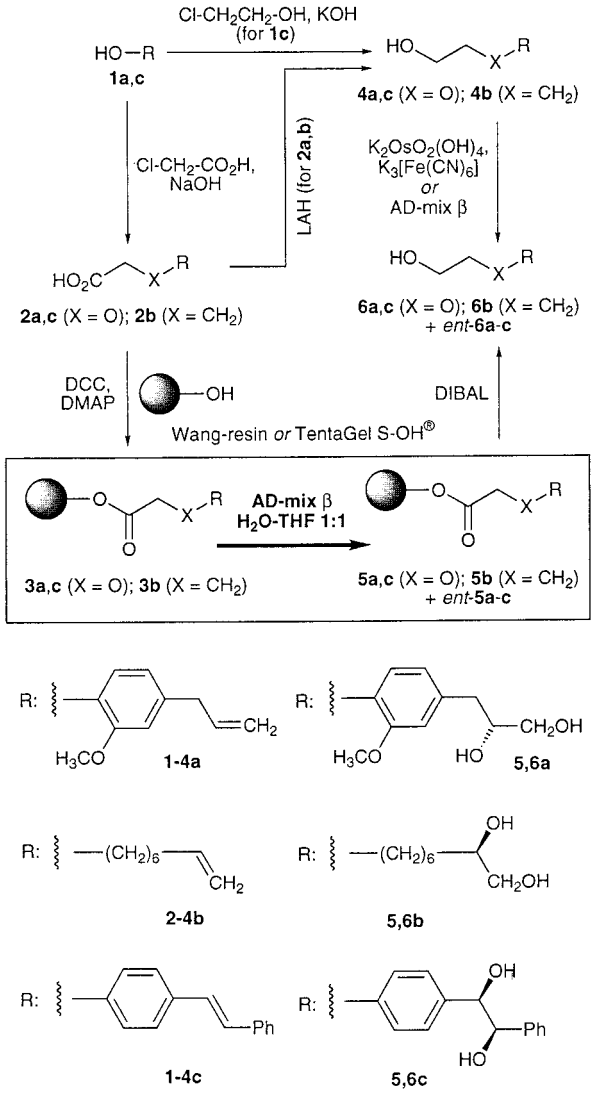


leads to NMR spectra approaching the quality of solution-phase NMR. We herein describe the application of homo- and heteronuclear HRMAS NMR for the monitoring of the AD of polymer-bound 10-undecenoic acid (**2b**) and for the determination of the ee of the dihydroxylation product **5b**. For the latter purpose, the product diol **5b** was derivatized on the solid support with Mosher's acid. As expected, this fast on-bead method gave ee values that agreed within <1% with those determined by chiral HPLC after cleavage (Scheme 1).

Results

Wang-resin[9] and TentaGel S-OH were selected as polymeric supports. As a prerequisite for the attachment to the polymers,

Scheme 2



eugenol (**1a**) and *(E)*-4-hydroxystilbene (**1c**) were reacted with chloroacetic acid, affording the carboxylic acids **2a** and **2c**. In the next step, the resins were loaded with the acids **2a** and **2c** and with 10-undecenoic acid (**2b**), using dicyclohexyl carbodiimide (DCC) as the coupling agent (Scheme 2). Substrate loadings were typically in the range of 0.7−1.0 mmol/g (Wang-resin) and 0.3 mmol/g (TentaGel S−OH).[10]

The Sharpless AD was carried out with three different ligands [$(DHQD)_2AQN$,[7] $(DHQD)_2PYR$,[5] $(DHQD)_2PHAL$[4,5]] in a 1:1-mixture of water and THF. In our hands, this solvent system was the only one affording reasonable conversions of the polymer-bound substrates **2a**−**c**.[11] Under the reaction conditions given in the Experimental Section, the prochiral olefins **3a**−**c** were transformed into the diols **5a**−**c**/*ent*-**5a**−**c**. The cleavage of the dihydroxylation products **5a**−**c**/*ent*-**5a**−**c** from the polymeric supports was done in a reductive manner (DIBAL), affording the corresponding triols **6a**−**c**/*ent*-**6a**−**c**. The yields and enantiomeric excesses of the isolated triols **6a**−

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(10) Loadings were determined by cleaving the substrates off the resins and gravimetry of the chromatographically pure materials.

(11) *tert*-Butyl alcohol−water and acetone−water mixtures proved inappropriate for the AD of Wang-resin-supported *(E)*-cinnamic acid, using $K_3[Fe(CN)_6]$ as terminal oxidant.

Table 2. ^{13}C NMR Data of **3b**, **5b**/*ent*-**5b**, **8**/**9**, and **10**/**11**[a]

ar	1	2/6	3/5	4	α	ar′	1	2/6	3/5	4	α
all	145.5	*b*	128.1	134.6	70.3		159.3	115.1	130.3	129.1	66.1

	1	2	3	4	5	6	7	8	9	10	11
3b	173.8	34.7	25.4	29.5	29.5[c]	29.6[c]	29.7[c]	29.3	34.2	139.6	114.4
5b/*ent*-**5b**	174.0	34.6	25.3	30.0	29.5[c]	29.6[c]	29.7[c]	25.9	33.5	72.6	67.1
8/**9**	173.8	34.6	25.3	29.4	29.4	29.4	29.4	24.9	30.7[d]	74.2[d]	66.7[d]
								25.3	30.6	74.4	66.3
10/**11**[f,g]								25.0[d]	30.7[d]	74.2[d]	66.7[d]
								25.3	30.5	74.4	66.3

ar″/ar‴	1	2	3	4	5	6/10	7/9	8
8/9[e]	166.7[d]	85.0	123.7	55.8	132.6[d]	127.78	128.91	130.19
	166.6			55.6	132.4	127.71	128.83	130.10
	166.4				132.3	127.59	128.78	130.08
	166.3[d]				132.2[d]	127.53	128.67	130.06

[a] Polymer beads were swollen in CD_2Cl_2 prior to measurement. $T = 298$ K. δ: (ppm). [b] Unambiguous assignment was not possible. [c] Assignment of resonances may be opposite. [d] Resonances of the main diastereomer [*R*-configuration at the diol's center of chirality (**8**, **10**)]. [e] The resolution of the 2D experiments did not allow for a full assignment to ar″/ar‴ of the two diastereomers. [f] Recorded in homogeneous CD_2Cl_2 solution. [g] For the sake of clarity, atoms are numbered as in the Mosher esters **8** and **9**.

Table 3. ^{1}H NMR Data of **3b**, **5b**/*ent*-**5b**, **8**/**9**, and **10**/**11**[a]

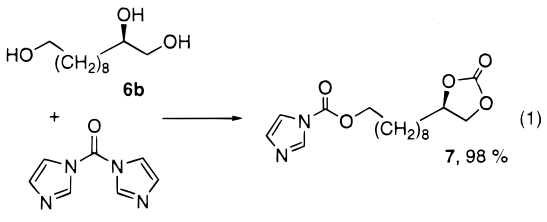
ar	2/6	3/5	α	ar′	2/6	3/5	α
all	6.57[b]	7.05[b]	4.94		6.94	7.27	5.02

	2	3	4	5	6	7	8	9	10	11a	11b
3b	2.30	1.60	1.29	1.29	1.29	1.29	1.37	2.04	5.81	4.97	4.91
5b/*ent*-**5b**	2.30	1.60	1.29	1.29	1.29	1.29	1.39	1.39	3.63	3.36	3.57
8/**9**	2.30	1.59	1.27	(1.25	/	1.18)[c]	1.27	1.57	5.32[d]	4.30[d]	4.62[d]
							1.17		5.31	4.27	4.54
10/**11**[f,g]									5.32[d]	4.32[d]	4.64[d]
									5.33	4.30	4.55

ar″/ar‴	4	6/10	7/9	8
8/9[e]	3.47	7.48	7.35	7.37
	3.41	7.44		
	3.38			

[a] Polymer beads were swollen in CD_2Cl_2 prior to measurement. $T = 298$ K. δ: (ppm). [b] Very broad. [c] Unambiguous assignment was not possible. [d] Resonances of the main diastereomer [*R*-configuration at the diol's center of chirality (**8**, **10**)]. [e] The resolution of the 2D experiments did not allow for a full assignment to ar″/ar‴ of the two diastereomers. [f] Recorded in homogeneous CD_2Cl_2 solution. [g] For the sake of clarity, atoms are numbered as in the Mosher esters **8** and **9**.

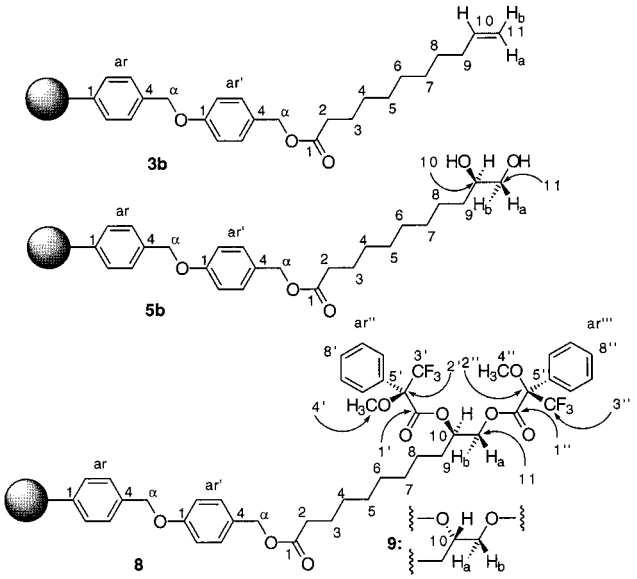
c/*ent*-**6a**−**c** are summarized in Table 1. In the cases of **6a**/*ent*-**6a** and **6c**/*ent*-**6c**, the enantiomeric excesses of the triols could be determined directly by chiral HPLC (see Experimental Section for conditions). The triol **6b**/*ent*-**6b** had to be derivatized first: Treatment with carbonyldiimidazole afforded the cyclic carbonate **7**/*ent*-**7**, which could again be analyzed by chiral HPLC (eq 1).



For comparison, the racemic triols *rac*-**6a**−**c** were also prepared by conventional solution-phase chemistry (Scheme 2): First, the unsaturated alcohols **4a**−**c** were prepared either by LAH reduction of the carboxylic acids **2a**,**b** (**4a** 46%, **4b** 77%) or by reacting the phenol **1c** with 2-chloroethanol (**4c** 39%). The subsequent dihydroxylation with $K_2OsO_2(OH)_4$/$K_3[Fe(CN)_6]$ afforded the racemic triols *rac*-**6a**−**c** (**6a** 75%, **6b** 78%, **6c** 55%). When the dihydroxylation of the olefins **4a**−**c** was carried out using AD mix β under standard conditions[5] in *tert*-butanol/water, the triols **6a**−**c** were obtained in the yields and enantiomeric excesses stated in Table 1.

The formulas **5a**−**c** and **6a**−**c** in Scheme 2 represent the major enantiomers expected according to the Sharpless mnemonic,[5] which in turn is derived from experiments in homogeneous solution. In fact, solution-phase asymmetric dihydroxylation and AD on solid support gave the same major enantiomer in the cases of **5b**,**c** and **6b**,**c** (**3a** gave the racemic diol *rac*-**5a**, see Table 1, entries 2−5). The assignment of (*R*,*R*)-configuration to the triol **6c** (obtained enantiomerically pure from solution-phase AD, see Table 1, entry 12) is further supported by the fact that both **6c** and unsubstituted (*R*,*R*)-hydrobenzoin have the same sense of optical rotation (+).[5]

HRMAS NMR was used for the characterization of 10-undecenoic acid supported on Wang-resin (**3b**), for monitoring the dihydroxylation of this material (**3b** → **5b**/*ent*-**5b**, Scheme 2) and for the characterization of the dihydroxylation product **5b**/*ent*-**5b**. For the HRMAS NMR characterization of polymer-bound dihydroxylation product, the material processed according to entry 10, Table 1, was used (i.e., dihydroxylation for 6 d at room temperature, affording 20% ee of **5b**). We found later that a higher enantiomeric excess (41%) of the dihydroxylation product **5b** can be achieved by shortening the reaction time (12 h, entry 9, Table 1). The ^{1}H and ^{13}C NMR data of the polymer-supported compounds **3b**, **5b**/*ent*-**5b**, and **8**/**9** (see below) are summarized in Tables 2 and 3. An almost complete assignment of the resonances was possible by a combination of ^{1}H-DQF−COSY, ^{1}H−HOHAHA, ^{1}H,^{13}C−HSQC, and HMBC experi-



ments. In the case of the HMBC experiments, the use of a delay of 60 ms for the evolution of the long-range couplings gave better results than longer evolution delays that fit better the expected *J*-couplings. This observation is most likely due to fast t_2-relaxation of the protons. As shown in Figure 1, the HMBC experiment with **3b** even proved the attachment of the substrate 10-undecenoic acid (**2b**) to the Wang-resin by a cross-peak ar′-Hα/-C1 and the connection between rings ar and ar′ of the Wang-linker by a cross-peak ar-Hα/ar′-C1.

Whereas the lines of the ^{1}H-spectra were still somewhat broadened by, e.g., inhomogeneities of the surroundings of the individual molecules, the ^{13}C-spectra showed line widths of 3−6 Hz for carbon atoms of ar′ and the attached molecules (Figure 2). First of all, the spectra summarized in Figure 2 prove the complete dihydroxylation of the substrate **3b** to the diols **5b**/*ent*-**5b**, with basically no byproducts being formed. The very high quality of the broadband (bb)-decoupled ^{13}C spectra (with or without heteronuclear NOE transfer) furthermore enabled us to use HRMAS NMR as a fast method for the determination of the enantiomeric excess achieved in the reaction **3b** → **5b**/*ent*-**5b** (Scheme 2): First, the dihydroxylation product **5b**/*ent*-**5b** was derivatized with (*R*)-(+)-Mosher's acid, affording the diastereomers **8** and **9**. The accumulation of 12 k scans gave a signal-to-noise ratio sufficient for the reliable determination of enantiomeric excess. The peak intensities of seven relevant pairs of resonances (Figure 3) were used to calculate an ee of 20−21% of the mixture **5b**/*ent*-**5b**. Comparison with entry 10 of Table 1 reveals that this is exactly the enantiomeric excess determined by the more time-consuming three-step procedure of cleaving the triol **6b**/*ent*-**6b** off of the resin, derivatization according to eq 1, and subsequent analysis by chiral HPLC.

For comparison, 1-undecene was dihydroxylated under standard conditions[5] using AD mix *β*, too. The resulting diols were derivatized to the bis-Mosher esters **10** and **11**, and their NMR spectra were recorded in homogeneous solution (not shown). As it turned out, the chemical shifts of the nuclei at or next to the diol's center of chirality in the polymer-bound bis-Mosher esters **8** and **9** are at most slightly affected by the polymeric matrix (Tables 2 and 3). Most likely, the Wang-linker plus the substrate's long alkyl chain account for this "solution-like" behavior.

Discussion

For the sake of clarity, the most important results of our study are again summarized:

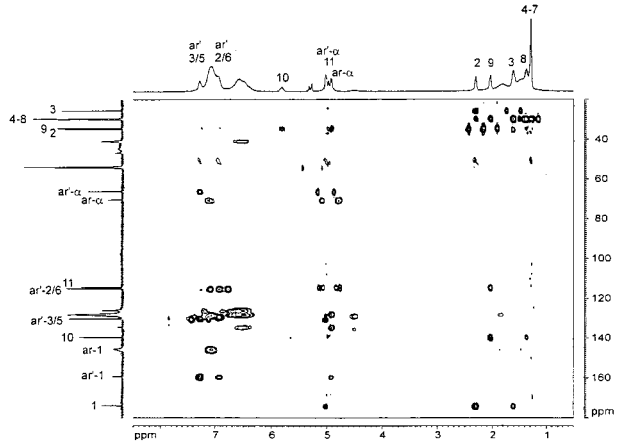


Figure 1. ^{1}H,^{13}C-HMBC spectrum of the substrate **3b**.

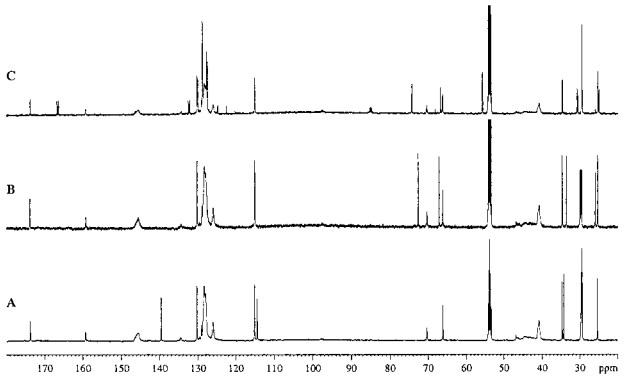


Figure 2. Monitoring solid-phase reactions by HRMAS NMR: ^{13}C NMR spectra of the substrate **3b** (trace A), the dihydroxylation product **5b**/*ent*-**5b** (trace B), and the bis-Mosher esters **8** and **9** (trace C).

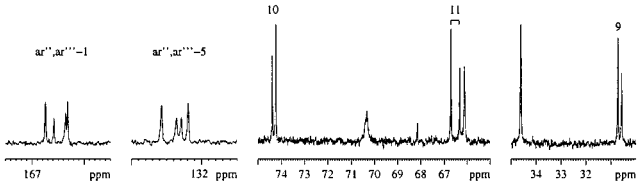


Figure 3. Determination of enantiomeric excesses of polymer-bound products by HRMAS NMR: relevant sections of the ^{13}C NMR spectrum of the bis-Mosher esters **8** and **9**.

(I) HRMAS NMR Spectroscopy. We were able to elaborate experimental conditions that afford ^{1}H and in particular ^{13}C NMR spectra of the polymer-supported substrates that are comparable in quality to the spectra of the low-molecular weight substrates in homogeneous solution. We believe that HRMAS NMR allows for the rapid and reliable monitoring of solid-phase reactions. With this improvement, one of the major drawbacks of solid-phase synthesis, i.e., the nonapplicability of advanced NMR techniques for homogeneous solutions, has been removed.[12] We are convinced that HRMAS NMR will allow for the rapid development of further methods of organic synthesis on solid supports. Due to the high qualitiy of the spectra, we could even determine enantiomeric excesses of reaction products *on the solid support*.[12]

(II) Scope and Limitations of the Sharpless AD for Polymer-Bound Substrates. (II.1) Olefinic substrates that give almost perfect enantioselectivities (> 99% ee) in the Sharpless

(12) For a related *exo*/*endo*-analysis of norbornane-2-carboxylic acid on solid support by MAS ^{13}C-NMR, see ref 8c. In this case, the norbornane derivative analyzed did not result from a solid-phase reaction.

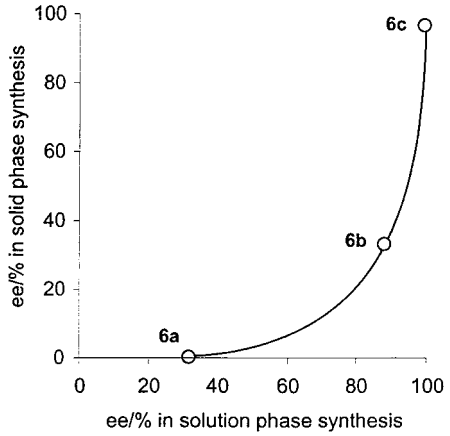


Figure 4. Enantiomeric excesses achieved in the asymmetric dihydroxylation of olefins: homogeneous solution vs solid-phase reactions.

AD in solution still afford diols that are basically enantiomerically pure when bound to polymeric supports (ee = 97%). Typical examples are *(E)*-stilbenes (this work) or *(E)*-cinnamates.[6] (II.2) Less selective olefins such as 10-undecen-1-ol (88% ee in solution) are dihydroxylated with moderate ees when bound to polymers (20−45% ee). (II.3) Almost no enantioselectivity is retained when polymer-bound olefins are used that give moderate selectivities in homogeneous solution, e.g. 2-methoxy-4-(2-propenyl)phenol (eugenol), 32% ee in homogeneous solution, 0−3% ee when bound to Wang-resin. The correlation of ee values found in homogeneous solution and in solid-phase AD is shown in Figure 4. As a consequence, only olefins of the first category are reasonable substrates, e.g., for the construction of combinatorial libraries of polyols by repetitive olefination/dihydroxylation.[13]

Experimental Section

General Methods. Commercially available chemicals were used as purchased. Diethyl ether and toluene were distilled from sodium; CH_2Cl_2 was distilled from $CaCl_2$. Merrifield resin (chloromethyl polystyrene, cross-linked with 2% divinylbenzene, 2.1 mmol of Cl/g, 200−400 mesh) was purchased from Fluka, TentaGel S-OH was purchased from Rapp-Polymere (loading capacity 0.3 mmol/g). Wang resin was prepared as reported elsewhere.[9] All reactions in solution were monitored by thin-layer chromatography (TLC), using Macherey-Nagel precoated silica gel plates. Chromatography was performed using Macherey-Nagel silica gel 60 (particle size 0.04−0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds. Melting points were measured on a Büchi apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC 300 spectrometer using solvent signals as internal standard. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra were taken on a Finnigan MAT H-SQ 30 (CI), JEOL JMS-700 (FAB), or VG ZAB-2F (EI) instrument. Combustion analyses were carried out on an Elementar Vario EL instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. HPLC analyses were carried out using a Merck/Hitachi L-6200A pump and a Merck/Hitachi L-4500 diode array detector, together with a CHIRALCEL OD-H column (DAICEL Chemical Industries).

[2-Methoxy-4-(2-propenyl)phenoxy]acetic Acid (2a). 2-Methoxy-4-(2-propenyl)phenol (eugenol, **1a**, 9.85 g, 60.0 mmol), chloroacetic acid (5.67 g, 60.0 mmol), and NaOH (5.28 g, 132 mmol) were dissolved in 30 mL of water and heated to reflux for 6 h. The solution was allowed to cool to room temperature. It was then acidified to pH = 1 with concentrated HCl, and the precipitate was separated by filtration. Recrystallization of the crude product from water furnished the analytically pure acid as a colorless solid (7.13 g, 53% yield): mp 97 °C (lit.[14] 96.5−97.5 °C); IR (KBr) 3000−2500 (s), 1754 (s), 1634 (s), 1593 (s), 1518 (s), 1430 (s), 1300 (m), 1262 (s), 1151 (s), 1031 (s), 912 (s), 812 (s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ = 3.28 (d, J = 6.6 Hz, 2H), 3.74 (s, 3H), 4.60 (s, 2H), 4.98−5.11 (m, 2H), 5.86−6.01 (m, 1H), 6.65 (dd, J = 8.1 Hz, 1.5 Hz, 1H), 6.74−6.82 (m, 2H), 12.98 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 39.0 (t), 55.5 (q), 65.3 (t), 112.8 (d), 113.6 (d), 115.5 (t), 120.1 (d), 133.1 (s), 137.8 (d), 145.5 (s), 148.8 (s), 170.3 (s); FAB-MS [*m*/*z* (% intensity)] 222.0 (100) [M^+], 163.0 (70) [$C_{10}H_{11}O_2^+$], 137.1 (54) [$C_8H_9O_2^+$], 91 (46) [$C_6H_3O^+$]. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.70; H, 6.29.

2-[2-Methoxy-4-(2-propenyl)phenoxy]ethanol (4a). $LiAlH_4$ (0.51 g, 13.5 mmol) was suspended in 50 mL of Et_2O and cooled to 0 °C. A solution of [2-methoxy-4-(2-propenyl)phenoxy]acetic acid (**2a**) (2.00 g, 9.00 mmol) in 80 mL of Et_2O was added dropwise. The mixture was stirred for 16 h at room temperature. Ice was added, followed by sufficient 10% H_2SO_4 to dissolve the white precipitate. The ether phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Purification of the residue by silica gel chromatography (MeOH−CH_2Cl_2 1:9, v/v) afforded the pure product as a colorless oil which solidified upon cooling (870 mg, 46%): mp 31 °C (lit.[15] 33−34 °C); IR (neat) 3486 (s), 3075 (s), 3001(s), 2935 (m), 2873 (m), 1636 (m), 1591 (m), 1514 (s), 1456 (s), 1420 (s), 1335 (m), 1261 (s), 1232 (s), 1140 (s), 1034 (s), 914 (s), 806 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 2.92 (br s, 1H), 3.32 (d, J = 6.7 Hz, 2H), 3.83 (s, 3H), 3.88−3.96 (m br, 2H), 4.06−4.09 (m, 2H), 5.05−5.14 (m, 2H), 5.89−6.04 (m, 1H), 6.71−6.75 (m, 2H), 6.85−6.89 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ =39.61 (t), 55.62 (q), 61.09 (t), 71.71 (t), 112.26 (d), 115.43 (d), 115.50 (t), 120.56 (d), 134.00 (s), 137.26 (d), 146.18 (s), 149.79 (s); FAB-MS [*m*/*z* (% intensity)] 208.1 (100) [M^+], 164.0 (90) [$C_{10}H_{12}O_2^+$], 149.1 (50) [$C_9H_9O_2^+$], 131.1 (30) [$C_9H_7O^+$], 103.1 (30) [$C_8H_7^+$], 91.1 (30) [$C_6H_3O^+$]; HRMS *m*/*z* (M^+) calcd 208.10994, obsd 208.11100.

(*R*,*S*)-3-[4-(2-Hydroxyethoxy)-3-methoxyphenyl]-1,2-propanediol (*rac*-6a). $K_3[Fe(CN)_6]$ (1.10 g, 3.30 mmol), K_2CO_3 (0.46 g, 3.30 mmol) and $K_2OsO_2(OH)_4$ (0.81 mg, 2.20 μmol) were dissolved in 12.0 mL of a 1:1-mixture of *tert*-butyl alcohol and water (v/v). 2-[2-Methoxy-4-(2-propenyl)phenoxy]ethanol (**4a**, 0.23 g, 1.10 mmol) was added, and the mixture was stirred at room temperature for 20 h. Na_2SO_3 (1.68 g, 13.3 mmol) was added, and stirring was continued for 1 h. The solution was extracted with EtOAc (5 × 50 mL), and the combined organic layers were dried over $MgSO_4$. Concentration in vacuo afforded the crude product. Purification by silica gel chromatography (MeOH−$CHCl_3$ 1:9, v/v) afforded the pure triol as a colorless solid (200 mg, 75% yield): mp 78 °C; IR (KBr) 3530 (s), 3372 (s), 2928 (m), 2879 (m), 2832 (m), 1592 (m), 1515 (s), 1464 (m), 1438 (m), 1420 (m), 1260 (s), 1229 (s), 1156 (m), 1139 (s), 1103 (m), 909 (m), 896 (m), 816 (m) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ = 2.45 (dd, J = 13.8, 7.6 Hz, 1H), 2.67 (dd, J = 13.8, 5.5 Hz, 1H), 3.24−3.28 (m, 2H), 3.55−3.65 (m, 1H), 3.65−3.70 (m, 2H), 3.72 (s, 3H), 3.89−3.92 (m, 2H), 4.48−4.53 (m, 2H), 4.80 (t, J = 5.5 Hz, 1H), 6.68 (dd, J = 8.1 Hz, J = 1.9 Hz 1H), 6.80−6.84 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ =39.3 (t), 55.4 (q), 59.7 (t), 65.3 (t), 70.3 (t), 72.6 (d), 113.2 (d), 113.5 (d), 121.2 (d), 132.3 (s), 146.3 (s), 148.6 (s); FAB-MS [*m*/*z* (% intensity)] 242 (96.7) [M^+], 211(2.7) [$C_{11}H_{15}O_4^+$], 198 (3.7) [$C_{10}H_{14}O_4^+$], 181 (53.4) [$C_{10}H_{13}O_3^+$], 167 (3.3) [$C_9H_{11}O_3^+$], 137 (100.0) [$C_8H_9O_2^+$], 107 (3.5) [$C_7H_7O^+$], 77 (3.1) [$C_6H_5^+$], 57 (3.8) [$C_3H_5O^+$], 45 (8.8) [$C_2H_5O^+$], 31 (34.3) [CH_3O^+]. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.41; H, 7.50.

10-Undecen-1-ol (4b).[16] $LiAlH_4$ (3.42 g, 90.0 mmol) was suspended in 150 mL of absolute Et_2O under nitrogen. The suspension was cooled to 0 °C, and a solution of 10-undecenoic acid (**2b**, 11.06 g, 60.0 mmol) in 20.0 mL of absolute Et_2O was added in a dropwise manner. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. Ice was added, followed by sufficient 10% H_2SO_4 to dissolve

(13) For the synthesis of the complete series of unnatural L-aldohexoses by repetitive Sharpless epoxidation/olefination, see: Ko, S. Y.; Lee, A. W.; Masamune, S.; Reed, L. A., III; Sharpless, K. B.; Walker, F. J. *Science* **1983**, *220*, 949−951.

(14) Hickey, M. J. *J. Org. Chem.* **1948**, *13*, 443−446.

(15) West, T. F. *J. Chem. Soc.* **1945**, 490.

(16) Bunnell, R. H.; Shirley, D. A. *J. Org. Chem.* **1952**, *17*, 1545−1550.

the white precipitate. The ether phase was separated, and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by distillation (0.35 mbar; 100 °C), affording the analytically pure product **4b** as a colorless liquid (7.80 g, 77% yield): IR (neat) 3334 (m), 2926 (s), 2855 (s), 1435 (m), 1371 (m), 1056 (m), 994 (m), 909 (m), 722 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 1.10−1.45 (br m, 12H), 1.46−1.52 (m, 2H), 1.72−1.95 (br s, 1H), 1.97−2.09 (m, 2H), 3.63 (t, J = 6.6 Hz, 2H), 4.87−5.03 (m, 2H), 5.73−5.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ =25.73, 28.93, 29.11, 29.40, 29.41, 29.54, 32.79, 33.79, 63.07, 114.10 (all t), 139.21 (d); FAB-MS [*m*/*z* (% intensity)] 151.9 (5.2) [M − H_2O^+], 123.9 (60), 109.9 (95) [$C_8H_{14}^+$], 108.9 (95) [$C_8H_{13}^+$], 54.9 (85) [$C_3H_3O^+$], 40.9 (100) [$C_3H_5^+$]. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.44; H, 13.01.

(*R*,*S*)-1,2,11-Undecanetriol (*rac*-6b). $K_3[Fe(CN)_6]$ (19.56 g, 60.0 mmol), K_2CO_3 (8.22 g, 60.0 mmol), and $K_2OsO_2(OH)_4$ (29.5 mg, 0.4 mol % Os) were dissolved in 200 mL of a 1:1-mixture of *tert*-butyl alcohol and water (v/v). 10-Undecen-1-ol (**4b**, 3.40 g, 20.0 mmol) was added, and the mixture was stirred at room temperature for 24 h. The reaction was quenched by the addition of Na_2SO_3 (30.0 g, 238 mmol), and the mixture was extracted with CH_2Cl_2 (4 × 200 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. Column chromatography of the residue on silica gel (MeOH−$CHCl_3$ 1:9, v/v) furnished the pure triol *rac*-**6b** as a colorless solid (3.19 g, 78%): mp 75 °C (lit.[17] 74−75 °C); IR (KBr) 3290 (s), 2917 (s), 2850 (s), 1471 (s), 1332 (m), 1086 (s), 1065 (s), 1009 (s); 720 (m) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ = 1.22−1.48 (br s, 16H), 3.16−3.28 (m, 2H), 3.33−3.40 (m, 3H), 4.31−4.34 (m, 2H), 4.41 (t, J = 5.6 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ = 26.68, 26.93, 30.57, 30.65, 30.68, 30.82, 33.66, 34.46, 63.02, 67.42 (all t), 73.28 (d); FAB-MS [*m*/*z* (% intensity)] 205.1 (0.1) [M + 1^+], 173.1 (7) [$C_{10}H_{21}O_2^+$], 137.1 (31) [$C_{10}H_{17}^+$], 95.1 (100) [$C_7H_{11}^+$], 81.1 (99) [$C_6H_9^+$], 55.0 (78) [$C_4H_7^+$], 41 (62) [$C_3H_5^+$]. Anal. Calcd for $C_{11}H_{24}O_3$: C, 64.67; H, 11.84. Found: C, 64.53; H, 11.81.

***(E)*-[4-(2-Phenylethenyl)phenoxy]acetic Acid (2c).** *(E)*-4-Hydroxystilbene (**1c**, 1.00 g, 5.00 mmol), chloroacetic acid (945 mg, 10.0 mmol), and KOH (1.12 g, 20.0 mmol) were dissolved in 100 mL of EtOH and heated to reflux for 5 h. The colorless precipitate was collected by filtration and dissolved in 500 mL water with heating. This solution was acidified to pH = 1 with concentrated HCl. Upon cooling to 4 °C, the analytically pure acid precipitated as a colorless solid (650 mg, 51%): mp 207 °C (lit.[18] 208 °C); IR (KBr) 3000−2500 (s), 1706 (s), 1610 (s), 1582 (s), 1433 (s), 1295 (s), 1239 (s), 1180 (s), 1085 (s), 970 (s), 831 (s), 800 (s), 758 (s), 693 (s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ = 4.69 (s, 2H), 6.91 (d, J = 8.8 Hz, 2H), 7.05−7.30 (m, 3H), 7.31−7.40 (m, 2H), 7.50−7.70 (m, 4H), 13.00 (br s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 64.5 (t), 114.7 (d), 126.2 (d), 126.4 (d), 127.3 (d), 127.8 (d), 127.9 (d), 128.7 (d), 130.2 (s), 137.3 (s), 157.5 (s), 170.2 (s); CI-MS [*m*/*z* (% intensity)] 255 (100) [M + 1^+], 196 (40) [$C_{14}H_{12}O^+$], 165 (15) [$C_{10}H_{13}O_2^+$], 107 (20) [$C_7H_7O^+$]. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.39; H, 5.55.

***(E)*-2-[4-(2-Phenylethenyl)phenoxy]ethanol (4c).** *(E)*-4-Hydroxystilbene (**1c**, 580 mg, 2.96 mmol), KOH (253 mg, 4.44 mmol), and 2-chloroethanol (715 mg, 8.88 mmol) were dissoloved in 100 mL of MeOH and heated to reflux for 8 h. Evaporation of the solvent gave a colorless residue. Purification by silica gel chromatography (EtOAc) afforded 275 mg (39%) of the analytically pure product as a colorless powder: mp 148−149 °C; IR (KBr) 3421 (m), 3297 (m), 1605 (s), 1512 (m), 1255 (m), 1180 (m), 1096 (m), 1052 (m), 966 (m), 924 (m), 815 (s), 693 (m) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ = 3.68−3.75 (m, 2H), 4.01 (m, 2H), 4.88 (t, J = 5.5 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 7.03−7.29 (m, 3H), 7.30−7.41 (m, 2H), 7.47−7.58 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 59.6 (t), 69.6 (t), 114.7 (d), 126.1 (d), 126.2 (d), 127.2 (d), 127.8 (d), 128.1 (d), 128.7 (d), 129.6 (s), 137.4, (s) 158.4 (s); EI-MS [*m*/*z* (% intensity)] 240 (99) [M^+], 196 (100) [$C_{14}H_{12}O^+$], 165 (40) [$C_{10}H_{13}O_2^+$], 152 (30) [$C_9H_{12}O_2^+$], 89 (20) [$C_7H_5^+$], 45 (28) [$C_2H_5O^+$]. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.71; H, 6.87.

(*R*,*R*)-(+)-1-[4-(2-Hydroxyethoxy)phenyl]-2-phenyl-1,2-ethanediol (6c). AD-Mix β (252 mg) was dissolved in 4.00 mL of a 1:1-mixture of *tert*-butyl alcohol and water (v/v). *(E)*-2-[4-(2-Phenylethenyl)phenoxy]ethanol (**4c**, 43.3 mg, 0.18 mmol) was added, and the mixture was stirred for 18 h at room temperature. The reaction was quenched by addition of Na_2SO_3 (270 mg, 2.14 mmol). The resulting mixture was stirred for 1 h and extracted with CH_2Cl_2 (5 × 20 mL). The organic phases were combined, dried over $MgSO_4$, and concentrated in vacuo. Silica gel chromatography of the residue (MeOH−$CHCl_3$ 1:9, v/v) furnished the analytically pure triol as a colorless solid (30.0 mg, 61% yield): mp 81 °C; $[\alpha]^{21}_D$ +108.5° (*c* 0.254, $CHCl_3$); IR (KBr) 3416 (s), 3030 (m), 2928 (m), 1613 (m), 1513 (s), 1454 (m), 1388 (m), 1249 (s), 1177 (m), 1080 (s), 1052 (s), 915 (m), 812 (m), 726 (m), 698 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 1.57 (br s, 1H), 2.02 (br s, 1H), 2.85 (br s, 1H), 3.90−3.94 (m, 2H), 3.99−4.02 (m, 2H), 4.65 (s, 2H), 6.75 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 7.08−7.11 (m, 2H), 7.18−7.23 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 61.3 (t), 69.0 (t), 78.6 (d), 79.1 (d), 114.1 (d), 127.0 (d), 127.8 (d), 128.1 (d), 128.2 (d), 132.5 (s), 139.9 (s), 158.2 (s); CI-MS [*m*/*z* (% intensity)] 274 (1) [M^+], 257 (100) [$C_{16}H_{17}O_3^+$], 167 (70) [$C_9H_{11}O_3^+$]. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.80; H, 6.55.

(*R*,*R*;*S*,*S*)-1-[4-(2-Hydroxyethoxy)phenyl]-2-phenyl-1,2-ethanediol (*rac*-6c). $K_3[Fe(CN)_6]$ (178 mg, 0.54 mmol), K_2CO_3 (75.6 mg, 0.54 mmol) and $K_2OsO_2(OH)_4$ (0.25 mg, 0.40 mol-% Os) were dissolved in 4.00 mL of a 1:1-mixture of *tert*-butyl alcohol and water (v/v). *(E)*-2-[4-(2-Phenylethenyl)phenoxy]ethanol (**4c**, 43.3 mg, 0.18 mmol) was added, and the solution was stirred for 18 h at room temperature. Workup and chromatography as described above for **6c** afforded the racemic triol *rac*-**6c** as a colorless solid (27.3 mg, 55% yield); IR and NMR data were identical to those of **6c**.

Derivatization of 1,2,11-Undecanetriol *rac*-6b with *N*,*N*′-Carbonyldiimidazole for HPLC Analysis. (*R*,*S*)-9-(2-Oxo-1,3-dioxolan-4-yl)nonyl-1*H*-imidazole-1-carboxylate (*rac*-7). A solution of (*R*,*S*)-1,2,11-Undecanetriol (*rac*-**6b**, 100 mg, 0.49 mmol) and *N*,*N*′-carbonyldiimidazole (160 mg, 0.98 mmol) in 20.0 mL of CH_2Cl_2 was stirred for 5 h at room temperature. The solution was washed with saturated aqueous $NaHCO_3$ solution (2 × 10 mL), and the organic layer was separated. The organic phase was dried over $MgSO_4$ and evaporated in vacuo. Purification of the residue by silica gel chromatography (MeOH−$CHCl_3$ 1:9, v/v) furnished the cyclic carbonate *rac*-**7** as a colorless oil (156 mg, 98%): IR (neat) 2928 (s), 2856 (s), 1798 (s), 1761 (s), 1471 (m), 1405 (s), 1376 (m), 1318 (m), 1291 (s), 1241 (s), 1174 (s), 1061 (s), 1003 (s), 772 (m), 650 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ =1.20−1.56 (br s, 12 H), 1.60−1.90 (br s, 4H), 4.02 (dd, J = 8.3 Hz, 7.2 Hz, 1H), 4.37 (t, J = 6.7 Hz, 2H), 4.48 (dd, J = 8.3 Hz, 7.8 Hz, 1H), 4.62−4.71 (m, 1H), 7.04 (s, 1H), 7.39 (s, 1H), 8.10(s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 24.30 (t), 25.60 (t), 28.37 (t), 28.99 (t), 29.02 (t), 29.16 (t), 29.17 (t), 33.82 (t), 68.22 (t), 69.19 (t), 76.95 (d), 116.87 (d), 130.38 (d), 136.84 (d), 148.53 (s), 154.82 (s); CI-MS [*m*/*z* (% intensity)] 325 (100) [M + 1^+]. Anal. Calcd for $C_{16}H_{24}N_2O_5$: C, 59.24; H, 7.46; N, 8.64. Found: C, 59.16; H, 7.34; N, 8.57.

Immobilization of Alkenes 2a−c on the Solid Support. The alkenes **2a**−**c** (2.00 mmol) were dissolved in 50.0 mL of absolute CH_2Cl_2 (in the case of *(E)*-[4-(2-phenylethenyl)phenoxy]acetic acid **2c**, absolute DMF was used). DCC (2.00 mmol), a catalytic amount of DMAP, and Wang-resin or TentaGel S-OH (1.00 mmol OH) were added, and the resulting suspension was shaken overnight. The resin was finally filtered off and washed successively with CH_2Cl_2, DMF, and MeOH.

Dihydroxylation of Polymer-Bound Alkenes 3a−c. AD mix β (1.40 g) [contains 0.4 mol % Os, 3.00 mmol $K_3[Fe(CN)_6]$, 3.00 mmol K_2CO_3, and 1.0 mol % $(DHQD)_2PHAL$; same composition when the ligands $(DHQD)_2AQN$ or $(DHQD)_2PYR$ were used, see Table 1] and 95.0 mg (1.00 mmol) $MeSO_2NH_2$ were dissolved in 30.0 mL of a 1:1-mixture of THF and H_2O (v/v). The polymer-bound alkenes **3a**−**c** (1.00 mmol) were added, and the suspension was stirred for the period of time stated in Table 1. The resin **5a**−**c**/*ent*-**5a**−**c** was collected by

(17) Sisido, K.; Kawanisi, M.; Kondo, K.; Morimoto, T.; Saito, A.; Hukue, N. *J. Org. Chem.* **1962**, *27*, 4073−4076.

(18) Cavallini, G.; Massarani, E.; Nardi, D.; D'Ambrosio, R. *J. Am. Chem. Soc.* **1957**, *79*, 3514−3517.

filtration and washed successively with a 1:1 mixture of THF and H_2O (v/v) and with CH_2Cl_2. The resin was dried in vacuo over P_2O_5.

Release of the Dihydroxylation Products from the Polymer. The dried resin **5a**−**c**/*ent*-**5a**−**c** was suspended in 50.0 mL of absolute toluene, and 5.00 mL of 1.00 M DIBAL in *n*-hexane was added at room temperature under argon. The suspension was stirred at 0 °C for 6 h. The reaction was quenched with MeOH. Sufficient 1.00 M HCl was added to dissolve the white precipitate. The resin was filtered off and washed successively with a 1:1 mixture of THF and H_2O (v/v) and with MeOH. The filtrate was extracted with $CHCl_3$ until no more product could be detected by TLC. The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. Silica gel chromatography (MeOH−$CHCl_3$ 1:9, v/v) furnished the pure dihydroxylation products **6a**−**c**/*ent*-**6a**−**c** (yields and enantiomeric excesses are summarized in Table 1).

Derivatization of the Polymer-Bound Dihydroxylation Product 5b/*ent*-5b with (*R*)-(+)-Mosher's Acid. The polymer-bound dihydroxylation product **5b**/*ent*-**5b** (80.0 mg, 0.13 mmol) was suspended in 3.00 mL of absolute CH_2Cl_2 and 120 mg (0.51 mmol, 4 equiv) of (*R*)-(+)-Mosher's acid and 160 mg (0.78 mmol, 6 equiv) of DCC was added. The suspension was shaken for 10 h at room temperature. The polymer (mixture of the diastereomers **8**, **9**) was collected by filtration and washed with CH_2Cl_2.

HRMAS NMR Spectroscopy. HRMAS NMR experiments were carried out on a BRUKER-AVANCE DRX 500 instrument using a 4 mm ^1H,^{13}C,^{15}N HRMAS probe with deuterium-lock. Samples of the Wang-resins **3b**, **5b**/*ent*-**5b**, and **8**/**9** were swollen in CD_2Cl_2 and measured at a sample rotation rate of 5500 Hz, $T = 298$ K. ^1H,^1H DQF−COSY:[19] 256 t_1 experiments with 16 scans each and 2k data points in t_2; 3 s pre-scan delay, phase sensitive in t_1 using TPPI. ^1H−HOHAHA:[20] 160 t_1 experiments with 16 scans each and 2k data points in t_2, 3 s pre-scan delay, 43 ms mixing time, phase sensitive in t_1 using TPPI. Spectral width of both experiments: 5000 Hz. Processing included the application of squared sinebell window functions shifted by $\pi/2$ in both dimensions and zero-filling to obtain a matrix of 2k × 512 real data points after Fourier transformation. Nondecoupled ^1H,^{13}C−HMBC:[21] 128 t_1 experiments with 96 scans each and 2k data points in t_2, 3 s pre-scan delay, 60 ms delay for the evolution of longrange couplings ($J_{H,C} = 8.3$ Hz). Nonshifted sinebell window functions and zero-filling were applied to obtain a matrix of 2k × 512 real data points after Fourier transformation. The spectrum was calculated in the magnitude mode. ^1H,^{13}C−HSQC:[22] 128 t_1 experiments with 40 scans each and 2k data points in t_2, 3 ms pre-scan delay, phase sensitive in t_1 using TPPI. In both dimensions, squared sinebell window functions shifted by $\pi/3$ and zero filling were applied to obtain a matrix of 2k × 512 real data points after Fourier transformation. Spectral widths were 5000 Hz in F_2 and 15 000 Hz (HSQC) or 22 500 Hz (HMBC) in F_1.

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