ROMP-Polymers in Asymmetric Catalysis: The Role of the Polymer Backbone

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Abstract: Ring-opening metathesis polymerization (ROMP) is utilized for the synthesis of highly functionalized polymers with covalently bound chiral prolinol units. The linear macromolecules act as multifunctional ligands in homogeneous asymmetric catalysis. The solubility of the polymers and their catalytic performance can be tuned by random co-polymerization with achiral units in a simple and flexible manner. Use of norbornenes with additional well-defined stereogenic centers in the polymerizable core of the monomers leads to polymers which show cooperative effects between the various elements of chirality during the course of the catalysis.

Keywords: asymmetric synthesis; catalysis; cooperative effects; polymer support; ROMP

Introduction

Asymmetric catalysis has been one of the fastest growing fields in organic chemistry in recent years.[1] Besides the development of novel catalysts and the search for entirely new chemical transformations, the improvement of known catalytic systems has been of interest. The aim of these efforts is then to increase turnover numbers (TON) and turnover frequencies (TOF)[2] of established catalysts, in order to render them more attractive for large-scale production in industrial applications.[3,4] One approach to this goal is the immobilization of catalysts enabling their easy recovery and recycling.[5] For this purpose, various ligands have been attached onto solid supports, and the resulting catalysts performed well with respect to durable catalytic activity. However, when it came to asymmetric catalysis, only very few of these heterogeneous systems were effective in terms of enantioselectivity.[6] In contrast, immobilized ligands for asymmetric catalysis under homogeneous reaction conditions often retained their stereochemistry-directing properties and behaved analogously to their parent systems.[5c, d,7] Bearing this in mind, we have now developed highly functionalized chiral polymers and investigated their application in a homogeneous catalytic enantioselective C-C-bond formation. The general concept involved the synthesis of the macromolecules by ring-opening metathesis polymerization (ROMP)[8,9] of norbornenes bearing catalytically active prolinol units.[10,11] The resulting polymers had high molecular weight and were soluble in organic solvents such as toluene. In a highly modular approach the properties of the polymers could be modified by random co-polymerization with catalytically inactive achiral monomers. By changing the achiral to chiral monomer ratio, a large number of such co-polymers was obtained, each having its own unique distribution of catalytically active sites along the polymer chain. For allowing a comparison with known systems, the well-established catalytic addition of diethylzinc to benzaldehyde[12,13] was chosen as test reaction, and each polymer was included in a standard test protocol for the enantioselectivity in this catalytic asymmetric transformation.

Results and Discussion

Due to the known efficiency of 4-hydroxyproline derivatives in the catalyzed diethylzinc addition to benzaldehyde,[13p–r] we chose (2*S*,4*R*)-diphenyl-(1-methyl-4-hydroxypyrrolidin-2-yl)methanol {**1**, H[OPyrr]} as the basic structure for the catalytically active site. For polymers with a linker a three-carbon chain was introduced by allylation of the secondary hydroxy group of **1** followed by regioselective hydroboration of the resulting product with catecholborane and subsequent oxidation to give **2**.

Mono- and double-functionalized bicyclic olefins **4** and **6** were regarded as appropriate ROMP monomers. For the synthesis of **4a** and **4b**, *endo*-norbornene anhydride **3** was reacted with 2 equivalents of **1** or **2**, respectively, under Mukaiyama esterification conditions.[14] This route was a short and efficient way to obtain monomers bearing two identical chiral prolinol moieties as catalytically active sites. The preparation of

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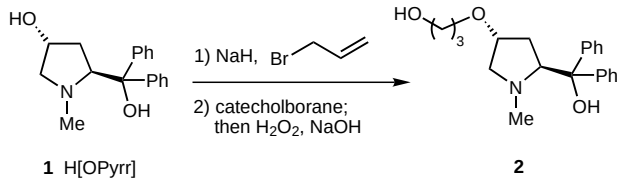
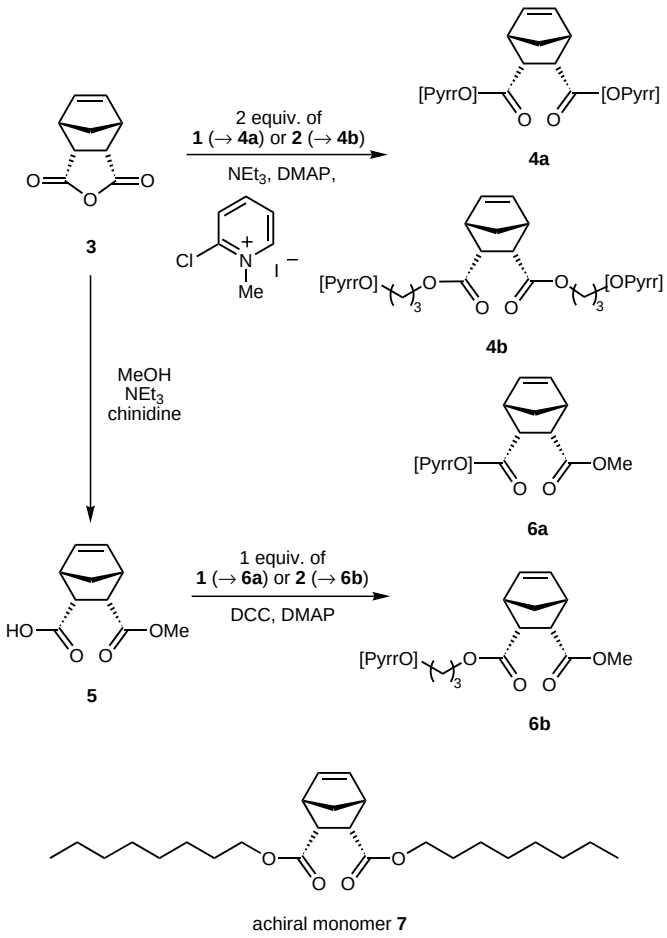


1 H[OPyrr] **2**

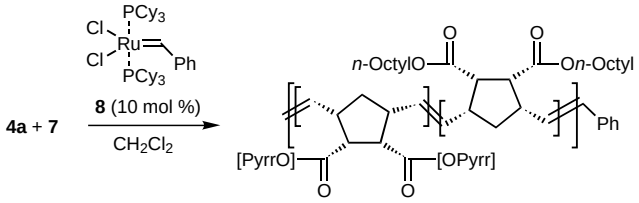
Scheme 1. Precursors for the catalytically active sites of the polymers.



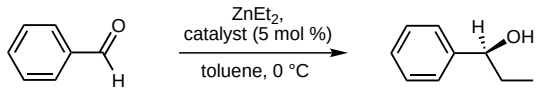
Scheme 2. Syntheses of monomers **4** and **6** bearing catalytically active sites derived from chiral hydroxyprolinol **1**.

the unsymmetrical bicyclic monomers **6a** and **6b** started with an alkoloid-mediated enantioselective anhydride opening of **3** to give monomethyl ester **5**.[15] Subsequent DCC coupling of **5** with 1 equivalent of **1** or **2** yielded **6a** or **6b**, respectively. *endo*-Bicyclic dioctyl ester **7** was used as achiral monomer in the random co-polymerizations, allowing a modification of the overall catalyst composition and an increase of the polymer solubility due to the lipophilicity of the *n*-octyl side chains.

Treatment of various mixtures of chiral monomers **4a**, **4b**, **6a**, **6b** and achiral **7** with Grubbs' ROMP catalyst **8**[16] (10 mol %) in dichloromethane afforded 24 different macromolecules resulting from homo- and random co-polymerizations (Scheme 3).[17]



Scheme 3. Representative example of a random co-polymerization (here: reaction between chiral monomer **4a** and achiral **7** catalyzed by Grubbs' ROMP catalyst **8**).



9 (*S*)-**10**

Scheme 4. Test reaction for the polymeric catalysts obtained by ROMP.

The polymeric products were analyzed by ^{1}H NMR spectroscopy and gel permeation chromatography. The latter revealed the complete polymerization of all monomers. The PDI[18] values varied from 1.3 to 4.8 depending on the nature of the chiral starting material. In particular, the products resulting from polymerizations of **4a** and **6a** without linker had high PDI values. Presumably, this effect was due to the steric bulk of the hydroxyprolinol unit, because it was not observed in reactions of the more flexible systems **4b** and **6b**, which gave PDI values < 2 in most experiments. The molecular masses of the polymers exceeded 6×10^3 g/mol. Compounds of this size can be recovered by ultrafiltration techniques and might find application in continuously operating flow reactors.[19]

Next, all 24 polymers were screened for catalytic activity in the addition of diethylzinc to benzaldehyde (Scheme 4). For obtaining a reference ee value the catalysis was first performed with 5 mol % of **1** giving (*S*)-1-phenylpropanol [(*S*)-**10**] with 89% ee.[20]

In order to achieve a rapid evaluation of their catalytic properties, the polymers were tested in a parallel format in 24 separate reaction vessels. Each catalysis was performed under homogeneous reaction conditions with toluene as solvent, employing a polymer amount corresponding to 5 mol % of catalytically active chiral prolinol units and a 2.5-fold excess of diethylzinc with respect to benzaldehyde. The results of this study are summarized in Table 1.

Several interesting results emerged from that screening: (1) In general, random co-polymers derived from 1:1 mixtures of the chiral and achiral monomers gave the highest enantiomeric excesses. Those obtained from 1:4 and 1:8 molar ratios of chiral monomer and achiral **7** afforded (*S*)-**10** with lower ee values. The homopolymer of **4a** was a remarkable exception, yielding the product with 87% ee. (2) Most of the polymers gave lower

Table 1. Enantiomeric excesses of (*S*)-**10** obtained in catalytic reactions with various ROMP polymers.[a]

Equiv. of **7**[b]	Chiral monomers used for the ROMP			
	4a	**4b**	**6a**	**6b**
0	87	82	67	50
0.5	86	86	79	58
1	**87**	**84**	**87**	**89**
2	81	86	80	72
4	84	75	25	76
8	83	29	18	60

[a] ee values of (*S*)-**10** obtained in catalytic reactions with the corresponding monomers: **4a**: 72% ee; **4b**: 80% ee; **6a**: 71% ee; **6b**: 82% ee.
[b] With respect to chiral monomers used in the ROMP.

Table 2. Enantiomeric excesses of (*S*)-**10** obtained in test reactions with various catalysts.

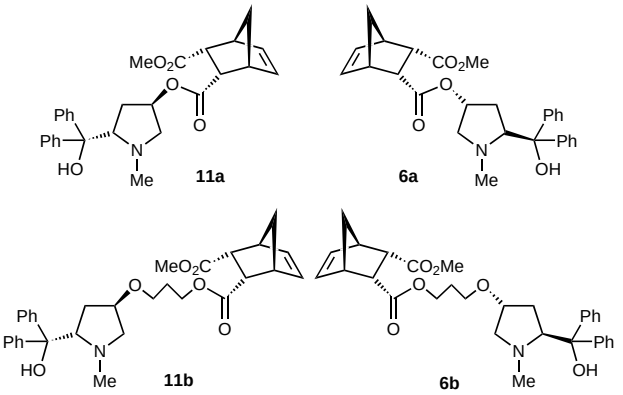
	chiral catalysts based on					
	11a	**11a + 6a**[a]	**6a**	**11b**	**11b + 6b**[a]	**6b**
monomer	**88**	88	71	**90**	90	82
homopolymer	**51**	20	67	**48**	45	50
random co-polymer[b]	**50**	25	87	**50**	44	89

[a] Mixtures of both diastereomers were used in equimolar amounts (de = 0).
[b] Generated by using a 1:1 molar ratio of the chiral monomer and achiral **7**.

enantioselectivities than achieved in the reference catalysis with **1** [(*S*)-**10** with 89% ee]. However, this loss of selectivity could fully be compensated by using a catalytically active polymer composed of **6b** and **7** in a 1:1 ratio. Most interestingly, compared to the results obtained with monomers **4a**, **4b**, **6a**, and **6b** (see Table 1, footnote [a]), the ee values achieved with the corresponding optimal polymers were significantly better. (3) Random co-polymers prepared by ROMP from high achiral-to-chiral monomer ratios dissolved more easily than others in the test reaction.[21]

These results suggested that only some polymers were able to create distinct microenvironments, which provided excellent geometrical orientations for achieving high enantioselectivities. Others disfavored an efficient asymmetric catalysis. Taking into account that each polymer contained a large number of unequal catalytically active sites along the polymer chain, it was apparent that the random co-polymer derived from a 1:1 molar ratio of **6b** and **7** contained the largest statistical number of most suited mircroenvironments leading to a catalyst for the formation of the product with the highest enantiomeric excess.

Assuming that the enantioselectivity of the catalysis was (at least in part) influenced by the stereogenic centers in the polymer backbone, we decided to investigate the impact of an altered polymer backbone chirality on the enantioselectivity of the catalysis. For this purpose, monofunctionalized monomers **6a** and **6b** appeared most appropriate. Both were stereochemically well-defined norbornenes, which upon polymerization allowed obtention of a restricted number of isomeric polymer backbone fragments.[22,23] Now, the synthesis of stereoisomers of **6a** and **6b** was envisaged, and hence, diastereomeric monomers **11a** and **11b** became the targets of choice. Both had the same prolinol units derived from (2*S*,4*R*)-diphenyl-(1-methyl-4-hydroxypyrrolidin-2-yl)methanol (**1**) as **6a** and **6b**, but the polymerizable norbornene parts of **11a** and **11b** were the mirror images of the ones in **6a** and **6b** (Scheme 5).



Scheme 5. Representation of the diastereomeric relationship between monomers **6a** and **11a** as well as **6b** and **11b**.

The test reaction was first conducted with the monomers, **11a** and **11b**. Interestingly, compared to the results with the diastereomeric systems **6a** and **6b** the enantioselectivities were now significantly higher (e.g., 90% ee for **11b** versus 82% ee for **6b**; Table 2). This indicated that the stereogenic centers in the more remote bicyclic part of the catalyst had also an influence on the enantioselectivity of the test reaction.

As before, the standard procedure for the ROMP using 10 mol % of Grubbs' catalyst **8** in dichloromethane afforded polymeric structures either from **11a** and **11b** alone or in combination with achiral monomer **7** (1:1 ratio), giving homopolymers and random co-polymers, respectively. Unfortunately, neither of these gave better results in the test reaction. In contrast, and to our greatest surprise, all catalyses with polymers derived from **11a** and **11b** revealed a much lower enantioselectivity compared to the corresponding polymers obtained from diastereomeric monomers **6a** and **6b** (Table 2).

Apparently, the enantioselectivity in the asymmetric catalysis did not only depend on the directing effect of the catalytically active site at the prolinol unit but also on the stereogenic centers in the norbornene part of the molecules as well as those in the polymer backbone.

Thus, while monomers **11a** and **11b** led to products with higher ee values than their diastereomeric counterparts **6a** and **6b**, the situation reversed when the corresponding polymers were used. Then, those derived from **6a** and **6b** were better than the ones obtained from **11a** and **11b**. Apparently, matched and mismatched arrangements occurred, and cooperative effects between the various stereogenic elements (in the monomers and polymers) led to enhanced (or reduced) enantioselectivities.

In order to further demonstrate the interplay between the various elements of chirality, test reactions with polymers derived from mixtures of diastereomeric monomers were performed. These results were then compared to those obtained in catalytic reactions with 1:1 combinations of monomer **6a** and its diastereomer **11a** as well as **6b** and **11b** (Table 2, columns 2 and 5). In the latter case the ee values obtained with monomer mixtures were identical to the ones observed with those monomers, which gave the higher enantioselectivity (matched cases). For example, whereas the catalysis with **6b** gave (*S*)-**10** with only 82% ee, both the one with **11b** alone as well as mixtures of **6b** and **11b** gave (*S*)-**10** with 90% ee. Such behavior has previously been observed in applications of non-diastereomerically pure planar chiral ferrocenes[24] and can be explained by a kinetic phenomenon involving drastically different rates of the diastereomeric catalysts derived from **6b** and **11b**. Thus, the faster reacting system (the one with **11b** as ligand) dominates the catalysis which is then reflected by the stereochemical outcome of the test reaction. Apparently, the situation is different in catalytic reactions with the polymers obtained from the diastereomeric monomer mixtures. There, the various stereogenic elements at the catalytically active site and along the polymer chain interact with each other and lead to species which are less enantioselective. Thus, all four polymers derived from mixtures of **6a**/**11a** and **6b**/**11b** as well as combinations of those with achiral monomer **7** gave low ee values in the test reaction (Table 2, lines 2 and 3). Obviously, for getting the maximal beneficial effect from possible cooperative interactions between the various stereogenic elements of the polymers, the monomers used in the polymer preparation should be diastereomerically pure. Stereochemically inhomogeneous mixtures should be avoided.

Conclusion

We have developed polymeric chiral catalysts for enantioselective C-C-bond formations, which are easily accessible by ROMP. Their properties can be modified by a modular approach in which the catalytically active sites are combined with achiral units bearing lipophilic side chains. The ratio between the chiral and the achiral units in the polymer is decisive for their catalytic behavior. Appropriately composed random co-polymers perform as well as their low-molecular counterparts in terms of enantioselectivity in the asymmetric catalysis. The stereogenic centers in the polymer backbone and their mutual interplay have a major impact on the microenvironment along the polymer chain. Thus, only the right combination of the various elements of chirality leads to positive cooperative effects which are essential for achieving a high enantioselectivity in the catalysis. These findings will now serve as guidelines for the ongoing studies on the design and construction of modified polymeric catalysts, which operate under homogeneous conditions in other asymmetric transformations.

Experimental Section

General Remarks

(*S*)-4-*trans*-Hydroxyproline and diethylzinc were generous gifts from Degussa AG and Witco, respectively. Bis(tricyclohexylphosphine)benzylidene-ruthenium(II) dichloride was purchased from Strem and dry DMF from Fluka. THF and toluene were distilled from sodium/benzophenone ketyl radical under argon. Dichloromethane was distilled from CaH_2 under nitrogen. All other chemicals were reagent grade and used as received.

If not stated otherwise, the term "standard work-up" refers to the following procedure: After being quenched with distilled water the reaction mixture was extracted with an organic solvent. The organic layer was washed sequentially with brine and water, and after drying with anhydrous $MgSO_4$ the solvent was evaporated under reduced pressure to yield the crude product. All syntheses of the monomers and their precursors were repeated at least twice to ensure reproducibility. Given yields are average values. The enantiomeric excess of 1-phenyl propanol was determined by means of HPLC using a chiral column (Chiralcel OD). All NMR measurements were done in $CDCl_3$.

(2*S*,4*R*)-4-Hydroxymethylazolan-2-yl-diphenylmethanol (1)

Synthesized following standard literature procedures. Accordingly, (*S*)-4-*trans*-hydroxyproline was transformed into its methyl ester hydrochloride followed by *N*-methylation.[25] Subsequent treatment with an excess of phenylmagnesium bromide afforded **1**. No epimerization was observed. All analytical data were in accordance with those previously reported;[13p] mp 119 °C; $[\alpha]_D^{20}$: 0.8 ± 0.3 (*c* 2, $CHCl_3$). ^{1}H NMR (300 MHz): δ = 1.72 (m, 1H), 1.84 (m, 1H), 1.89 (s, 3H), 2.25 (bs, *sec*-OH), 2.48 (dd, J = 5.0, 10.4 Hz, 1H), 3.32 (dd, J = 5.0, 10.4 Hz, 1H), 3.99 (t, J = 7.7 Hz, 1H), 4.20 (dt, J = 5.0, 5.4 Hz, 1H), 4.80 (bs, *tert*-OH), 7.12 (m, 2H), 7.25 (m, 4H), 7.51 (m, 2H), 7.65 (m, 2H); anal. calcd. for $C_{18}H_{21}NO_2$: C 76.29, H 7.47, N 4.94; found: C 75.97, H 7.33, N 5.09.

3-[(5*S*,3*R*)-5-Hydroxy(diphenyl)methyl-1-methylazolan-3-yloxy]-1-propanol (2)

a) (2*S*,4*R*)-4-Allyoxy-1-methylazolan-2-yl(diphenyl)methyl alcohol: In a 50-mL Schlenk flask **1** (3.0 g, 10.6 mmol) was placed under Ar and dissolved in dry dimethylformamide (30 mL). NaH (279 mg, 11.7 mmol) was added, and after stirring for 2 h at room temperature allyl bromide (985 μL, 11.7 mmol) was injected in one portion. Stirring overnight and followed by the standard work-up with diethyl ether afforded the crude product. Purification by column chromatography (silica gel, ethyl acetate/petroleum ether, 4:1) gave (2*S*,4*R*)-4-allyoxy-1-methylazolan-2-yl(diphenyl)methyl alcohol as a colorless oil; yield: 2.22 g (65%); $[\alpha]_D^{20}$: 1.8 ± 0.3 (*c* 1.9, $CHCl_3$). ^{1}H NMR (400 MHz): δ = 1.85 (m, 1H), 1.87 (m, 1H), 1.89 (s, 3H), 2.59 (dd, *J* = 5.4, 10.3 Hz, 1H), 3.34 (dd, *J* = 5.4, 10.3 Hz, 1H), 3.90 (m, 4H), 4.74 (bs, OH), 5.14 (d, *J* = 10.0 Hz, 1H), 5.23 (d, *J* = 17 Hz, 1H), 5.86 (m, 1H), 7.13 (m, 2H), 7.26 (m, 4H), 7.53 (m, 2H), 7.66 (m, 2H); ^{13}C NMR (100 MHz): δ = 36.5, 43.9, 63.6, 70.3, 71.6, 76.8, 77.0, 117.1, 125.5, 125.7, 126.5, 126.6, 128.3, 135.1, 146.4, 148.2; MS (CI, *i*-butane): *m/z* (%) = 380 (5), 324 (100); IR (neat): $\tilde{\nu}$ = 3357, 3086, 2945, 2856, 2796, 1597, 1492, 1450, 1196, 1177, 922, 748, 735, 707, 698 cm^{-1}; anal. calcd. for $C_{21}H_{25}NO_2$: C 77.98, H 7.79, N 4.33; found: C 77.81, H 7.94, N 4.56.

b) 3-[(5*S*,3*R*)-5-Hydroxy(diphenyl)methyl-1-methylazolan-3-yloxy]-1-propanol (2): (2*S*,4*R*)-4-Allyloxy-1-methylazolan-2-yl(diphenyl)methyl alcohol (2.2 g, 6.8 mmol) was treated with catecholborane (20 mL, 20 mmol, 1 M in THF) for 4 d at room temperature. Addition of 3 N NaOH (20 mL) and aqueous H_2O_2 (5 mL; 35 wt %) followed by the standard work-up with ethyl acetate afforded the crude product. Purification by column chromatography (silica gel, ethyl acetate/petroleum ether, 4:1) afforded the title compound as a colorless oil; yield: 1.6 g (69%); $[\alpha]_D^{20}$: 5.4 ± 0.3 (*c* 2.1, $CHCl_3$). ^{1}H NMR (400 MHz): δ = 1.71 (m, 2H), 1.83 (m, 2H), 1.84 (s, 3H), 2.51 (dd, *J* = 5.5, 10.4 Hz, 1H), 3.28 (dd, *J* = 5.2, 10.2 Hz, 1H), 3.42 (m, 2H), 3.65 (m, 2H), 3.82 (m, 1H), 3.91 (m, 1H), 4.60 (bs, OH), 7.10 (m, 2H), 7.23 (m, 4H), 7.53 (m, 2H), 7.65 (m, 2H); ^{13}C NMR (100 MHz): δ = 32.5, 36.4, 43.9, 61.4, 63.5, 67.9, 71.6, 76.9, 77.8, 125.5, 125.7, 126.5, 126.6, 128.3, 146.4, 148.0; MS (CI, *i*-butane): *m/z* (%) = 398 (16), 342 (95), 284 (100); IR (neat): $\tilde{\nu}$ = 3401, 2946, 2870, 2796, 1597, 1492, 1450, 1096, 1063, 1035, 749, 707 cm^{-1}; HRMS: calcd. for $C_{21}H_{27}NO_3$: 342.2069; found: 342.2059.

Bis[(*S*)-5-hydroxy(diphenyl)methyl-1-methyl-*trans*-3-azolanyl] Bicyclo[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (4a)

An oven-dry, 25-mL Schlenk flask was charged with acid anhydride **3** (289 mg, 1.8 mmol), **1** (1.0 g, 3.5 mmol) and dichloromethane (15 mL). Triethylamine (0.75 mL, 5.4 mmol), 4-DMAP (88 mg, 0.7 mmol) and 2-chloro-1-methylpyridinium iodide (552 mg, 2.2 mmol) were added, and the resulting mixture was stirred for 48 h at room temperature. Standard work-up with dichloromethane followed by column chromatography (silica gel, ethyl acetate/petroleum ether, 3:1) afforded **4a** as a pale yellow solid; yield: 950 mg (76%); mp 77 °C. $[\alpha]_D^{20}$: –0.9 ± 0.3 (*c* 1.9, $CHCl_3$). ^{1}H NMR (300 MHz): δ = 1.23 (d, *J* = 8.4 Hz, 1H), 1.39 (d, *J* = 8.4 Hz, 1H), 1.68 (m, 2H), 1.77 (s, 3H), 1.82 (m, 2H), 1.84 (s, 3H), 2.44 (m, 2H), 3.07 (s, 2H), 3.15 (s, 2H), 3.31 (m, 1H), 3.41 (m, 1H), 3.85 (m, 2H), 4.60 (bs, 2 OH), 4.85 (m, 2H), 6.14 (s, 2H), 7.05 (m, 4H), 7.17 (m, 8H), 7.45 (m, 4H), 7.60 (m, 4H); ^{13}C NMR (75.4 MHz): δ = 35.7, 36.0, 43.8, 44.0, 46.5, 46.6, 48.2, 48.8, 62.9, 63.5, 71.4, 71.6, 73.2, 73.7, 76.1, 76.2, 125.3, 125.6, 126.4, 126.5, 128.2, 134.8, 135.1, 146.0, 147.8, 171.9, 171.9; MS (FAB, neg. ion): *m/z* (%) = 711 (M – 2, 46), 446 (100), 267 (2), 183 (4), 163 (21); IR (KBr): $\tilde{\nu}$ = 3421, 2980, 2863, 2797, 1781, 1739, 1493, 1450, 1253, 1187, 1078, 1064, 1033, 749, 706 cm^{-1}; FAB-HRMS: calcd. for $C_{45}H_{49}N_2O_6$: 713.3591; found: 713.3599.

Bis{3-[(*S*)-5-hydroxy(diphenyl)methyl-1-methyl-*trans*-3-azolanyloxy]propyl} Bicyclo[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (4b)

The title compound was synthesized in the same manner as **4a** using **3** (328 mg, 2.2 mmol), **2** (1.5 g, 4.4 mmol), triethylamine (0.84 mL, 6 mmol), 4-DMAP (98 mg, 0.8 mmol), and 2-chloro-1-methylpyridinium iodide (612 mg, 2.4 mmol) affording **4b** as a white solid; yield: 1.04 g (63%); mp 48 – 50 °C; $[\alpha]_D^{20}$: + 6.0 ± 0.3 (*c* 2, $CHCl_3$). ^{1}H NMR (400 MHz): δ = 1.20 – 1.57 (m, 4H), 1.66 – 1.79 (m, 6H), 1.80 (s, 6H), 2.45 (m, 2H), 2.92 – 3.08 (m, 2H), 3.16 (m, 2H), 3.22 – 3.33 (m, 6H), 3.47 – 3.66 (m, 2H), 3.75 – 4.05 (m, 6H), 4.60 (bs, 2OH), 6.13 (m, 2H), 7.06 (m, 4H), 7.18 (m, 8H), 7.46 (m, 4H), 7.58 (m, 4H); ^{13}C NMR (75 MHz): δ = 29.2, 36.3, 43.8, 46.5, 48.3, 48.8, 61.7, 63.4, 65.5, 71.5, 77.4, 77.5, 125.4, 125.6, 126.4, 126.4, 128.2, 134.9, 135.0, 146.3, 148.0, 172.4; MS (FAB, neg. ion.): *m/z* (%) = 827 (M – 1, 100), 740 (4), 504 (46), 450 (16), 297 (20), 239 (23), 223 (67), 163 (47); IR (KBr): $\tilde{\nu}$ = 3393, 2952, 2869, 2796, 1780, 1740, 1598, 1492, 1450, 1370, 1253, 1193, 1135, 1112, 1064, 749, 707 cm^{-1}. FAB-HRMS: calcd. for $C_{51}H_{61}N_2O_8$: 829.4428; found: 829.4414.

(2*R*,3*S*)-2-[(*S*)-5-Hydroxy(diphenyl)methyl-1-methyl-*trans*-3-azolanyl] 3-Methyl Bicyclo[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (6a)

An oven-dry, 50-mL Schlenk flask was charged with **5** (620 mg, 3.2 mmol), **1** (700 mg, 2.5 mmol) and dichloromethane (20 mL). After addition of 4-DMAP (110 mg, 0.9 mmol) and dicyclohexylcarbodiimide (510 mg, 3.2 mmol) the solution was stirred at room temperature for 48 h. Standard work-up with dichloromethane followed by purification by column chromatography (silica gel, ethyl acetate/petroleum ether, 3:1) afforded **6a** as a colorless oil; 853 mg (75%); $[\alpha]_D^{20}$: –2.1 ± 0.3 (*c* 1.9, $CHCl_3$). ^{1}H NMR (500 MHz): δ = 1.21 (m, 1H), 1.37 (m, 1H), 1.71 (m, 1H), 1.84 (s, 3H), 1.85 (m, 1H), 2.50 (dd, *J* = 4.0, 11.3 Hz, 1H), 3.06 (m, 2H), 3.17 (m, 2H), 3.38 (dd, *J* = 4.0, 11.3 Hz, 1H), 3.48 (s, 3H), 3.87 (t, *J* = 7.9 Hz, 1H), 4.60 (bs, *tert*-OH), 6.12 (dd, *J* = 3.1, 5.5 Hz, 1H), 6.19 (dd, *J* = 3.1, 5.5 Hz, 1H), 7.04 (m, 2H), 7.17 (m, 4H), 7.46 (m, 2H), 7.61 (m, 2H); ^{13}C NMR (125.6 MHz): δ = 36.1, 43.8, 46.4, 46.5, 46.7, 48.2, 48.8, 51.6, 63.0, 71.5, 73.3, 76.2, 125.3, 125.6, 126.4, 126.5, 128.2, 134.7, 134.9, 139.2, 146.1, 147.9, 172.1, 172.8; MS (EI, 70 eV): *m/z* (%) = 462 (M + 1, 1), 278 (29), 266 (5), 82 (100); IR (neat): $\tilde{\nu}$ = 3384, 2948, 2856, 1740, 1661, 1450, 1341, 1253, 1196, 1168, 1077, 753, 707 cm^{-1}; HRMS: calcd. for $C_{28}H_{32}NO_5$: 462.2280; found: 462.2272.

(2*R*,3*S*)-2-{3-[(*S*)-5-Hydroxy(diphenyl)methyl-1-methyl-*trans*-3-azolanyloxy]propyl} 3-Methyl Bicyclo-[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (6b)

Synthesized in the same manner as **6a** using **5** (334 mg, 1.7 mmol), **2** (640 mg, 1.9 mmol), 4-DMAP (62 mg, 0.5 mmol) and dicyclohexylcarbodiimide (421 mg, 2.0 mmol) giving **6b** as a colorless oil; yield: 550 mg (68%); $[\alpha]_D^{20}$: –10.1 ± 0.3 (*c* 2.2, $CHCl_3$). ^{1}H NMR (400 MHz): δ = 1.31 (m, 1H), 1.46 (m, 1H), 1.82 (m, 4H), 1.90 (s, 3H), 2.55 (dd, *J* = 5.4, 10.3 Hz, 1H), 3.13 (bs, 1H), 3.15 (bs, 2H), 3.26 (m, 2H), 3.37 (m, 3H), 3.58 (s, 3H), 3.86 (m, 1H), 3.94 (m, 1H), 4.07 (m, 2H), 6.21 (m, 1H), 6.26 (m, 1H), 7.13 (m, 2H), 7.26 (m, 4H), 7.53 (m, 2H), 7.66 (m, 2H); ^{13}C NMR (100 MHz): δ = 29.0, 36.1, 43.8, 46.3, 46.4, 48.0, 48.2, 48.6, 51.5, 61.7, 63.3, 65.5, 71.5, 76.7, 77.4, 152.3, 152.5, 126.3, 126.4, 128.0, 134.7, 135.0, 146.1, 147.8, 172.7, 172.9; MS (CI, *i*-butane): *m/z* (%) = 520 (M + 1, 100), 336 (11), 255 (3), 183 (30); IR ($CHCl_3$): ṽ = 3019, 2952, 2873, 2116, 1738, 1341, 1254, 1216, 1197, 1175, 744, 707, 669 cm^{-1}; HRMS: calcd. for $C_{31}H_{38}NO_6$: 520.2699; found: 520.2679.

Dioctyl Bicyclo[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (7)

In a 100-mL flask bicyclo[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylic acid anhydride (**3**; 3.9 g, 23.7 mmol), *n*-octanol (7.2 g, 55.3 mmol), and 4-DMAP (600 mg, 4.9 mmol) were dissolved in dichloromethane (25 mL). The solution was cooled to 0 °C before dicyclohexylcarbodiimide (5.8 g, 27.9 mmol) was added. The solution was allowed to warm to room temperature overnight. Standard work-up with dichloromethane followed by purification by column chromatography (first, silica gel, petroleum ether/tetrahydrofuran, 9:1, then, silica gel, ethyl acetate/petroleum ether, 1:4) afforded **7** as a colorless oil; yield: 5.6 g (58%). ^{1}H NMR (400 MHz): δ = 0.88 (t, *J* = 7.2 Hz, 6H), 1.20 – 1.40 (m, 21H), 1.46 (m, 1H), 1.58 (m, 2H), 3.15 (m, 2H), 3.27 (t, *J* = 1.7 Hz, 2H), 3.91 – 4.05 (m, 4H), 6.25 (t, *J* = 1.7 Hz, 2H); ^{13}C NMR (100 MHz): δ = 14.1, 22.7, 26.0, 23.6, 29.2, 29.2, 31.8, 46.4, 48.3, 48.7, 64.6, 134.9, 172.5; MS (EI, 70 eV): *m/z* (%) = 406 (2), 342 (5), 276 (10), 249 (32); IR (neat): ṽ = 2954, 2927, 2856, 2120, 1745, 1467, 1340, 1253, 1191, 1165, 1079, 719 cm^{-1}; anal. calcd. for $C_{25}H_{42}O_4$: C 73.85, H 10.41; found: C 74.00, H 10.52.

(2*S*,3*R*)-2-[(*S*)-5-Hydroxy(diphenyl)methyl-1-methyl-*trans*-3-azolanyl] 3-Methyl Bicyclo[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (11a)

Synthesized in the same manner as 6a using *ent*-**5** (151 mg, 0.77 mmol), **1** (262 mg, 0.92 mmol), 4-DMAP (28 mg, 0.23 mmol) and dicyclohexylcarbodiimide (191 mg, 0.92 mmol) giving **11a** as a white solid; yield: 232 mg (65%); mp 28 – 31 °C; $[\alpha]_D^{20}$: –12.0 ± 0.4 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (m, 1H), 1.35 (m, 1H), 1.71 – 1.84 (m, 2H), 1.85 (s, 3H), 2.50 (dd, *J* = 4.8, 11.4 Hz, 1H), 3.05 (m, 2H), 3.18 (m, 2H), 3.40 (dd, *J* = 5.2, 11.4 Hz, 1H), 3.44 (s, 3H), 3.88 (t, *J* = 8.0 Hz, 1H), 4.60 (bs, *tert*-OH), 4.87 (m, 1H), 6.13 (m, 1H), 6.21 (m, 1H), 7.04 (m, 2H), 7.16 (m, 4H), 7.47 (m, 2H), 7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.1, 44.3, 46.6, 46.7, 48.4, 48.5, 49.0, 51.8, 63.6, 71.8, 73.8, 76.4, 125.5, 125.7, 126.5, 126.6, 128.2, 128.3, 134.7, 135.5, 146.1, 148.0, 172.2, 172.9; MS (CI, *i*-butane): *m/z* (%) = 462 (M + 1, 100), 444 (2), 278 (12); IR ($CHCl_3$): ṽ = 2947, 2857, 2797, 2117, 1742, 1450, 1341, 1253, 1196, 1167, 1077, 751, 707 cm^{-1}; FAB-HRMS: calcd. for $C_{28}H_{32}NO_5$: 462.2280; found: 462.2272.

(2*S*,3*R*)-2-{3-[(*S*)-5-Hydroxy(diphenyl)methyl-1-methyl-*trans*-3-azolanyloxy]propyl} 3-Methyl Bicyclo-[2.2.1]hept-5-ene-(2-*endo*,3-*endo*)-dicarboxylate (11b)

The title compound was synthesized according to the same protocol as **6a** using *ent*-**5** (200 mg, 1.0 mmol), 2 (512 mg, 1.5 mmol), 4-DMAP (38 mg, 0.3 mmol) and dicyclohexylcarbodiimide (252 mg, 1.2 mmol) giving **11b** as a colorless oil; yield: 234 mg (45%); $[\alpha]_D^{20}$: + 4.7 ± 0.3 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (m, 1H), 1.37 (m, 1H), 1.68 – 1.78 (m, 4H), 1.79 (s, 3H), 2.46 (dd, *J* = 5.5 Hz, *J* = 10.1 Hz, 1H), 3.05 (m, 1H), 3.17 (m, 2H), 3.20 – 3.40 (m, 4H), 3.49 (s, 3H), 3.72 (m, 1H), 3.84 (m, 1H), 3.98 (m, 2H), 4.65 (bs, *tert*-OH), 6.16 (m, 1H), 6.18 (m, 1H), 7.04 (m, 2H), 7.17 (m, 4H), 7.46 (m, 2H), 7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5, 36.5, 44.1, 46.6, 46.7, 48.3, 48.5, 49.0, 51.8, 61.9, 63.6, 65.8, 71.7, 76.9, 77.2, 125.5, 125.7, 126.4, 126.5, 128.3, 128.3, 134.9, 135.2, 146.4, 148.1, 172.5, 173.0; MS (CI, methane): *m/z* (%) = 520 (M + 1, 46), 336 (11), 225 (32), 183 (100), 129 (33), 89 (82), 73 (93); IR ($CHCl_3$): ṽ = 2948, 2869, 2796, 1743, 1493, 1450, 1436, 1365, 1341, 1254, 1196, 1169, 1112, 750, 708 cm^{-1}; FAB-HRMS: calcd. for $C_{31}H_{38}NO_6$: 520.2699; found: 520.2706.

General Procedure for the Random Co-Polymerization of Bicyclic Olefins

The chiral monomer (**4a**, **4b**, **6a, 6b**, **11a**, or **11b**) was placed in a small reaction vessel and **7** was added (in a 1:0; 2:1; 1:1; 1:2; 1:4, or 1:8 chiral-to-achiral monomer ratio). The mixture was evaporated to dryness under reduced pressure at room temperature. Then, 10 mol % of bis(tricyclohexylphosphine)-benzylidene-ruthenium(II) dichloride (**8**) and dichloromethane (1 mL) were added. The solution was stirred under inert atmosphere for 6 d. The reaction was then quenched with ethyl vinyl ether (1 mL) and stirred for additional 2 h. The solvent was removed under vacuum furnishing the random co-polymers. In all cases no starting material was left as proven by ^{1}H NMR spectroscopy. The polymers were used as such without further purification in the catalytic addition of diethylzinc to benzaldehyde.

General Procedure for the Diethylzinc Addition to Benzaldehyde (9)

A Schlenk flask under argon was charged with the polymer (0.05 equiv. based on the amount of prolinol units) using Schlenk techniques. Then freshly distilled toluene (5 mL) was added followed by neat diethylzinc (2.5 equiv.). After stirring for 30 min at ambient temperature the solution was cooled to 0 °C, and 1 equiv. of freshly distilled benzaldehyde (**9**) was added. The reaction was quenched after 48 h by careful addition of 2 M aqueous HCl (5 mL). The resulting mixture was extracted with dichloromethane (4 × 25 mL), and the

combined organic layers were dried with anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure the crude product was purified by column chromatography (silica gel, petroleum ether/methyl *tert*-butyl ether,10:1) giving 1-phenylpropanol (**10**) in 70 – 85% yield. The enantiomeric excess of **10** was determined by HPLC using a chiral stationary phase [Chiralcel OD, *n*-hexane/2-propanol, 98:2 (premixed); 1.0 mL/min; $t_R = 12.5$ min (*R*) and 14.7 min (*S*)]. The absolute configuration was determined by correlation with the values reported in the literature.[26]

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