Chirality Transfer in the Formation of Poly(oxymethylene) Helices by Anionic Polymerization

by **Christian Miculka**, **Christian R. Noe***, and **Simon Eppacher**

Department of Medicinal Chemistry, University of Vienna, Althanstrasse 14, A-1090 Wien (phone: +43 1 427 55103; fax: +43 1 427 79551; e-mail: christian.noe@univie.ac.at)

In this article, we present the synthesis of a series of oligo(oxymethylenes) capped with 1-phenylethanol and MeOH. The anionic condition affords enantiomerically pure oligo(oxymethylene) oligomers, while the cationic oligomerization leads to a racemic mixture of the oligo(oxymethylene) chain.

Introduction and Concept. – Formaldehyde was first discovered by *A. M. Butlerow* in 1855 and synthesized in 1867 by *A. W. Hoffmann* by dehydrogenation of MeOH. The structure of formaldehyde was first investigated by *H. Staudinger* in 1925 [1–3]. It is well-accepted that paraformaldehyde forms a helix as it was shown by theoretical calculations [4], by IR spectroscopy [5], and by X-ray analysis [6–11]. By insertion of a poly(oxymethylene) into a diamond lattice, an idealized 2_1 helix can be found (*Fig. 1*).

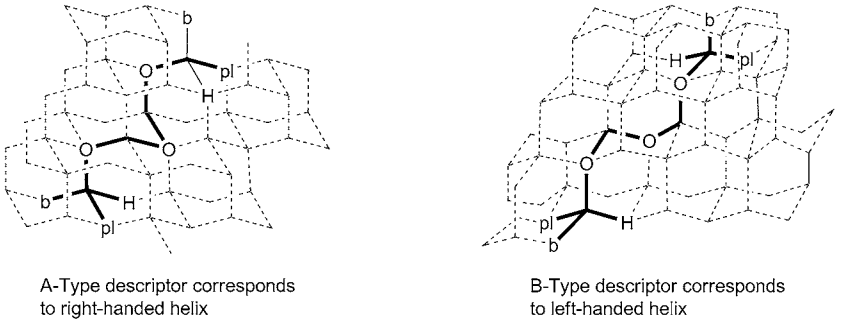


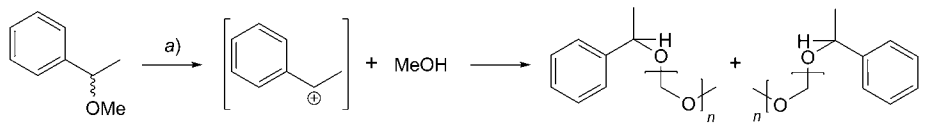
Fig. 1. *Idealized oligo(oxymethylene) helices fitted into a diamond lattice.* Right handed helix capped with an A and a left handed helix with a B descriptor, respectively.

By applying the b, pl, H-rule [12][13], a right handed helix is observed when the starting and the end group has an A descriptor [14], whereas a left-handed helix is obtained with a B descriptor as start and end group, respectively. Poly(oxymethylene) serves as the most general model of the anomeric effect, namely the interaction of the n_o lone pair of the O-atom and the σ^* orbital of the C–O bond [15]. This interaction causes the continuous *gauche*-orientiation of the dihedral angles and a shortening of the C–O bonds in the helix, as it was established by the synthesis and X-ray analysis of 1,13-diphenyl-2,4,6,8,10,12-hexaoxatridecane [15] and its corresponding heptamer [16]. We synthesized the enantiomerically pure oligo(oxymethylene) helix by cationic oligome-

rization of paraformaldehyde with (1*S*)-2,2-dimethyl-1-phenylpropan-1-ol (B descriptor) as starter and end group, respectively [17]. By calculations, NMR spectroscopy, optical rotation, as well by X-ray crystallography, we could show the expected left handed helical structure. Remarkable is the stability of this carbinol under acidic condition. Since we isolated only the enantiomerically pure helix, we can conclude that the formation of the carbocation is slower than the addition to the formaldehyde. The present work aims at enantiomerically pure oligo(oxymethylene) helices, which are capped with a chiral inducer at one end and a Me group at the other end.

Results and Discussion. – 1. *Cationic Polymerization.* In a first experiment, we investigated the cationic oligomerization to obtain oligo(oxymethylene) helices capped with (±)-1-phenylethanol and MeOH by the reaction of 1-phenylethanol, paraformaldehyde, and MeOH catalyzed by H_2SO_4. In this reaction, we found a complex mixture of products. We found the twofold 1-phenylethanol-capped oligomer, the expected oligomers in small amounts, and a series of non-identified products. Next, we examined the insertion reaction of (±)-methyl 1-phenylethyl ether and paraformaldehyde (*Scheme 1*).

Scheme 1



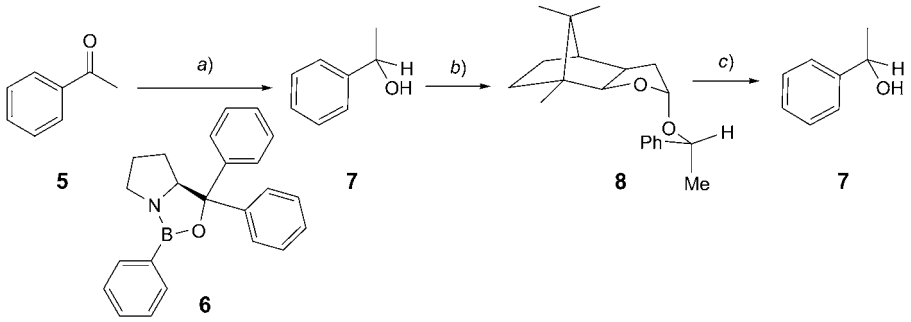
1 *n* = 1 **1a** *n* = 1
2 *n* = 2 **2a** *n* = 2
3 *n* = 3 **3a** *n* = 3
4 *n* = 4 **4a** *n* = 4

a) Cat. H_2SO_4 paraformaldehyde, CH_2Cl_2, 3% of **1**/**1a**, 0.8% of **2**/**2a**, 0.6% of **3**/**3a**, 0.6% of **4**/**4a**, and *ca.* 14.5% mixed fractions.

In this reaction, we obtained the desired 1-phenylethyl/Me-capped racemic oligomers up to the tetramer *i.e.*, **1**/**1a** to **4**/**4a**, which could be separated by flash chromatography. In contrast to our experiment with (1*S*)-2,2-dimethyl-1-phenylpropan-1-ol, the reaction with the methyl ether of (±)-1-phenylethanol must proceed *via* a carbocation, followed by the insertion of formaldehylde (HCHO). In fact, this should happen regardless whether the starting material is enantiomerically pure or a racemic mixture. In the NMR spectrum of the tetramer **4**/**4a**, the CH_2 H-atoms showed signals of four *AB* systems. The NMR spectra in different solvents (CD_3OD, $CDCl_3$, and (D_8)toluene) displayed a better resolution in the less polar solvent where all 16 signals could be resolved. The assignment of the signals was achieved by $^1H,^1H$ and $^1H,^{13}C$ correlated spectroscopy. For the tetramer **4**/**4a** in (D_8)toluene, a temperature-dependent recording was performed at 295, 315, 335, and 355 K. As expected, the shift difference of the diastereotopic H-atoms of the CH_2 units decreased. The H-atoms corresponding to the *A* part are shifted to higher field, while the signals corresponding to the *B* part are shifted to lower field.

2. *Anionic Polymerization*. To obtain a new enantiomerically pure poly(oxymethylene) helix, we investigated the anionic polymerization. Therefore, we synthesized enantiomerically pure (*R*)-1-phenylethanol (**7**) by reduction of acetophenone (**5**) with BH_3 and the *Corey* catalyst (**6**; *Scheme 2*) [18–20] in 91% ee.

Scheme 2



a) THF, BH_3; 95%. *b*) $(MBE)_2O$, cat. TsOH; 82%. *c*) MeOH, cat. TsOH; 83%.

The (*R*)-1-phenylethanol was enantiomerically enriched by mixed acetal formation with the terpene carbohydrate mimic $(MBE)_2O$ (= [2*S*,2′*S*-(2α,2′α,3aα,3′aα,4β,4′β,7β,7′β,7aα,7′aα)]-2,2′-oxybis[octahydro-7,8,8-trimethyl-4,7-methanobenzofuran] [21] to **8**, followed by crystallization of **8** from MeOH for two times and then methanolysis [14]. By this protocol, we obtained the required (*R*)-1-phenylethanol (**7**) in an overall yield of 67% and an enantiomeric purity of 99.8% ee.

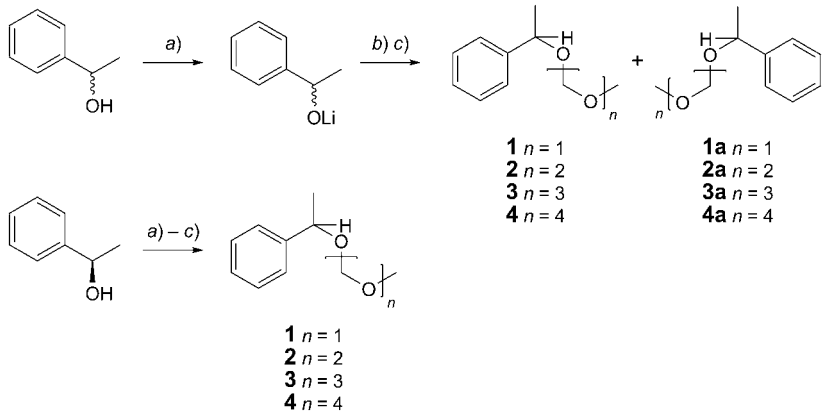
The experiments by *Vogl* and co-workers provided the starting point for the anionic polymerization [22–27]. In a first experiment, the racemic carbinol was used. The oligomerization of (±)-1-phenylethanol was started by deprotonation with BuLi in THF at −20°, followed by treatment at −95° with gaseous HCHO, which was obtained from carefully dried poly(oxymethylene) (*Scheme 3*).

After removal of the cooling bath, we observed a remarkable increase of the temperature between −40 and −30°, indicating the start of the reaction. The reaction was quenched with distilled Me_2SO_4. By this protocol, we could again obtain oligomers up to the tetramer, **1**/**1a**–**4**/**4a**. In the case of the reaction with enantiomerically pure (*R*)-1-phenylethanol, we investigated the enantiomeric purity of the reaction by quenching a part of the lithium alkoxide with H_2O. This product showed no change of the enantiomeric excess according to the investigation with a chiral column (*Chiralcel OD*).

The resolution of the racemic poly(oxymethylenes) (**1**/**1a**–**4**/**4a**) with a chiral column (*Chiralcel OD*) led to a good separation of **2**/**2a** and a slight separation of **4**/**4a**, while **1**/**1a** and **3**/**3a** could not be resolved even when the column was adjusted to 0°. The elution sequence of the racemic mixture showed a faster elution for the (*S*)- than for the (*R*)-product as was shown by the addition of the enantiomerically pure **2**. The elution sequence of the oligomers was opposite to the starting unit 1-phenylethanol.

The assignment of the conformation of the chain was investigated as described by *Anderson et al.* [28]. They reported a dependence of the direct C,H coupling constants

Scheme 3



a) THF, BuLi. *b*) HCHO gas. *c*) Me_2SO_4; 0.7% of **1**, 15% of **2**, 6.1% of **3**, 2.8% of **4**, and 26% of mixed fractions.

in fixed $R^{13}C^{1}H(OR')_2$ fragments in dependence of the H-atoms *syn*-clinal and *anti*-periplanar to the non-bonding orbitals of the O-atom. By consideration of a O–CH_2–O section of the oligo(oxymethylene) chain, it is possible to formulate four possible diastereoisomerically different conformations (*Fig. 2*).

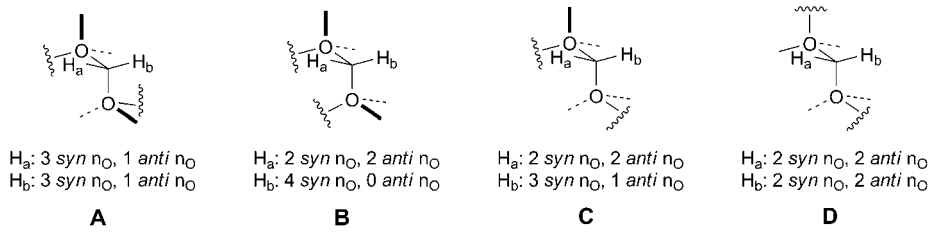


Fig. 2. *Four possible conformations of a O–CH_2–O section and the* syn- *and* anti-*arrangement of the diastereoisomerically different H-atoms*

These four conformations should give rise to different ^{1}J(C,H) coupling constants. Therefore, the helical $+sc$, $+sc$ as the continuous *ap* conformation should give only one coupling constant. Only in conformation **A**, we find a combination of the diasterotopic H-atoms, and the lone pairs resulting in three *syn*- and one *anti*-orientations. For this conformation, a ^{1}J(C,H) value of 162 Hz is proposed.

In all of our synthesized oligo(oxymethylene) helices, we obtained only one value for the coupling constants with an overall value of 164.3 Hz. This value is in accordance with a continuous *syn* orientation leading to a helical conformation and excludes the *ap* conformation of the oligo(oxymethylene) chain.

4. Conclusion. – In this communication, we presented the synthesis of oligo(oxymethylene) helices capped with 1-phenylethyl and Me groups by cationic and anionic oligomerization. While the cationic oligomerization of the methyl ether of (±)-1-

phenylethanol yielded racemic oligomers, the anionic oligomerization afforded in an enantiomerically selective way, as we could demonstrate by the reaction with (*R*)-1-phenylethanol. By investigation of the ^1J(C,H) coupling constants, we could establish the *gauche*-orientation of the chain and exclude the *anti*-orientation.

Experimental Part

General. THF was distilled on Na/benzophenone, toluene on Na, and petroleum ether (PE; b.p. 50–75°). TLC: Precoated silica-gel plates (*Merck* silica gel *60* F_{254}); detection by spraying with 'Mostain' soln. (400 ml of 10% aq. H_2SO_4, 20 g of $(NH_4)_6Mo_7O_{24}\cdot H_2O$, and 0.4 g of $Ce(SO_4)_2$). Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). ^{1}H- and ^{13}C-NMR spectra: at 300 and 75 MHz, resp. Poly(oxymethylene) was dried in an exsiccator over P_2O_5. HPLC: with a 25 cm column of *Chiralcel OD*, 5 μm; eluent: hexane/10 vol-% *t*-BuOMe/3.5 vol-% i-PrOH.

[1-(Methoxymethoxy)ethyl]benzene (*rac*-**1**/**1a**), *[1-[(Methoxymethoxy)methoxy] ethyl]benzene* (*rac*-**2**/**2a**), *9-Phenyl-2,4,6,8-tetraoxadecane* (*rac*-**3**/**3a**), *and 11-Phenyl-2,4,6,8,10-pentaoxadodecane* (*rac*-**4**/**4a**). A suspension of paraformaldehyde (6.0 g, 0.2 mol) and (±)-(1-methoxyethyl)benzene (2.72 g, 0.02 mol) in CH_2Cl_2 (30 ml) was treated dropwise with H_2SO_4 (2 ml), stirred for 30 min, treated with solid $NaHCO_3$, filtered over 15 g of SiO_2, and evaporated. FC (PE/Et_2O 19:1 → 8:1) gave *rac*-**1**/**1a** (89 mg, 2.68%), *rac*-**2**/**2a** (31 mg, 0.79%), *rac*-**3**/**3a** (26 mg, 0.57%), *rac*-**4**/**4a** (32 mg (0.62%), and 570 mg of mixed fractions (corresponding of 62% of the material before the FC).

*(*R*)-[1-(Methoxymethoxy)ethyl]benzene* (**1**), *(*R*)-{1-[(Methoxymethoxy)methoxy]ethyl}benzene* (**2**), *(*R*)-9-Phenyl-2,4,6,8-tetraoxadecane* (**3**), *and (*R*)-11-Phenyl-2,4,6,8,10-pentaoxadodecane* (**4**). A soln. of (*R*)-1-phenylethanol (4.0g, 33 mmol) in abs. THF (70 ml) under N_2 was cooled to −20° and treated dropwise with BuLi (2.5M soln. in hexane; 13.6 ml, 34 mmol). After 30 min, the completeness of the deprotonation was established by quenching the reaction of one drop of the mixture with Ac_2O in Et_2O, followed by extraction with $NaHCO_3$ and TLC control. The rest of the mixture was cooled to −105° and treated with monomeric HCHO (obtained by heating of carefully dried oligo(oxymethylene) (9.9 g, 330 mmol; dried over P_2O_5 in the exsiccator)) in a way that the temp. of the reaction mixture did not exceed −95°. After the treatment with HCHO, the cooling bath was removed, the mixture was stirred for 2.5 h at r.t. (at −30°, an exothermic reaction was observed), treated with Me_2SO_4 (4.2 g, 33 mmol), and stirred overnight at r.t. The suspension was filtered, concentrated, dissolved in CH_2Cl_2, and extracted with $NaHCO_3$. The org. phase was dried (Na_2SO_4) and concentrated. FC (1:80; PE/Et_2O 19:1 → 8:1 gave **1** (37 mg, 0.7%), **2** (950 mg, 15%), **3** (457 mg, 6.1%), **4** (207 mg, 2.8%), and 1.7 g of mixed fractions (corresponding to 61% of the material before FC).

Data of **1**. Colorless liquid. $[\alpha]_D^{20} = +180$ ($c = 0.62$; Et_2O). ^{1}H-NMR ($CDCl_3$): 7.26–7.37 (*m*, 5 arom. H); 4.76 (*q*, $J = 6.6$, PhC*H*–O); 4.56, 4.59 (*AB*, $J = 6.7$, OCH_2O); 3.38 (*s*, MeO); 1.50 (*d*, $J = 6.6$, Me). ^{1}H-NMR ((D$_8$)toluene): 6.98–7.24 (*m*, 5 arom. H); 4.58 (*q*, $J = 6.6$, PhC*H*–O); 4.41, 4.48 (*AB*, $J = 6.7$, OCH_2O); 3.17 (*s*, MeO); 1.38 (*d*, $J = 6.6$, Me). ^{13}C-NMR ($CDCl_3$): 143.4 (*s*, C(1)); 128.3 (*d*, C(3) and C(5)); 127.4 (*d*, C(4)); 126.1 (*d*, C(2) and C(6)); 94.2 (*t*, ^1J(C,H) = 162.9, OCH_2O); 73.7 (*d*, PhCH–O); 55.2 (*q*, MeO); 23.5 (*q*, Me). ^{13}C-NMR ((D$_8$)toluene): 144.1 (*s*, C(1)); 128.5 (*d*, C(3) and C(5)); 127.6 (*d*, C(4)); 126.6 (*d*, C(2) and C(6)); 94.2 (*t*, ^1J(C,H) = 162.0, OCH_2O); 73.9 (*d*, PhCH–O); 55.9 (*q*, MeO); 24.0 (*q*, Me). Anal. calc. for $C_{10}H_{14}O_2$: C 72.26, H 8.49; found: C 72.50, H 8.25.

Data of **2**. Colorless liquid. $[\alpha]_D^{20} = +188$ ($c = 0.69$, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): 7.26–7.34 (*m*, 5 arom. H); 4.60, 4.82 (*AB*, $J = 6.9$, CH_2(1)); 4.78 (*q*, $J = 6.6$, PhC*H*–O); 4.66, 4.78 (*AB*, $J = 6.5$, CH_2(2)); 3.37 (*s*, MeO); 1.48 (*d*, $J = 6.6$, Me). ^{1}H-NMR ((D$_8$)toluene): 6.98–7.23 (*m*, 5 arom. H); 4.50, 4.73 (*AB*, $J = 6.6$, CH_2(1)); 4.52, 4.70 (*AB*, $J = 6.3$, CH_2(2)); 4.68 (*q*, $J = 6.5$, PhC*H*–O); 3.13 (*s*, MeO); 1.35 (*d*, $J = 6.5$, Me). ^{13}C-NMR ($CDCl_3$): 143.1 (*s*, C(1)); 128.3 (*d*, C(3) and C(5)); 127.4 (*d*, C(4)); 126.2 (*d*, C(2) and C(6)); 93.3 (*t*, ^1J(C,H) = 163.5, CH_2(2)); 89.7 (*t*, ^1J(C,H) = 164.0, CH_2(1)); 74.6 (*d*, PhCH–O); 55.6 (*q*, MeO); 23.5 (*q*, Me). ^{13}C-NMR ((D$_8$)toluene): 144.0 (*s*, C(1)); 128.6 (*d*, C(3) and C(5)); 127.6 (*d*, C(4)); 126.7 (*d*, C(2) and C(6)); 93.0 (*t*, ^1J(C,H) = 163.2, CH_2(2)); 89.3 (*t*, ^1J(C,H) = 163.6, CH_2(1)); 74.6 (*d*, PhCH–O); 55.3 (*q*, MeO); 24.0 (*q*, Me). Anal. calc. for $C_{11}H_{16}O_3$ (196.24): C 67.32, H 8.22; found: C 67.10, H 8.15.

Data of **3**. Colorless liquid. $[\alpha]_D^{20} = +160$ ($c = 0.72$, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): 7.26–7.35 (*m*, 5 arom. H); 4.84, 4.89 (*AB*, $J = 6.5$, CH_2(2)); 4.61, 4.83 (*AB*, $J = 6.6$, CH_2(1)); 4.78 (*q*, $J = 6.6$, PhC*H*–O); 4.68, 4.73 (*AB*, $J = 6.5$, CH_2(3)); 3.37 (*s*, MeO); 1.47 (*d*, $J = 6.6$, Me). ^{1}H-NMR ((D_8)toluene): 6.98–7.22 (*m*, 5 arom. H); 4.78, 4.85 (*AB*, $J = 6.5$, CH_2(2)); 4.54, 4.75 (*AB*, $J = 6.9$, CH_2(1)); 4.67 (*q*, $J = 6.5$, PhC*H*–O); 4.51, 4.61 (*AB*, $J = 6.8$, CH_2(3)); 3.12 (*s*, MeO); 1.31 (*d*, $J = 6.5$, Me). ^{13}C-NMR ($CDCl_3$): 143.0 (*s*, arom C(1)); 128.4 (*d*, C(3) and C(5)); 127.5 (*d*, C(4)); 126.2 (*d*, arom. C(2) and C(6)); 93.6 (*t*, ^1J(C,H) = 164.6, CH_2(3)); 90.0 (*t*, ^1J(C,H) = 164.6, CH_2(1)); 88.6 (*t*, ^1J(C,H) = 165.7, CH_2(2)); 74.6 (*d*, PhC*H*–O); 55.6 (*q*, MeO); 23.5 (*q*, Me). ^{13}C-NMR ((D_8)toluene): 143.8 (*s*, arom C(1)); 128.6 (*d*, C(3) and C(5)); 127.6 (*d*, C(4)); 126.7 (*d*, C(2) and C(6)); 93.4 (*t*, ^1J(C,H) = 163.4, CH_2(3)); 89.8 (*t*, ^1J(C,H) = 163.9, CH_2(1)); 88.1 (*t*, ^1J(C,H) = 164.4, CH_2(2)); 74.7 (*d*, PhC*H*–O); 55.3 (*q*, MeO); 23.9 (*q*, Me). Anal. calc. for $C_{12}H_{18}O_4$ (226.27): C 63.70, H 8.02; found: C 63.99, H 7.85.

Data of **4**. Colorless liquid. $[\alpha]_D^{20} = +142$ ($c = 0.38$, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): 7.26–7.34 (*m*, 5 arom. H); 4.84, 4.91 (*AB*, $J = 6.7$, CH_2(2)); 4.86, 4.86 (*AB*, $J = 6.6$, CH_2(3)); 4.60, 4.83 (*AB*, $J = 6.9$, CH_2(1)); 4.77 (*q*, $J = 6.5$, PhC*H*–O); 4.71, 4.72 (*AB*, $J = 6.5$, CH_2(4)); 3.37 (*s*, MeO); 1.46 (*d*, $J = 6.6$, Me). ^{1}H-NMR ((D_8)toluene): 7.26–7.34 (*m*, 5 arom. H); 4.79, 4.86 (*AB*, $J = 6.6$, CH_2(2)); 4.76, 4.79 (*AB*, $J = 6.6$, CH_2(3)); 4.53, 4.74 (*AB*, $J = 6.8$, CH_2(1)); 4.67 (*q*, $J = 6.5$, PhC*H*–O); 4.53, 4.57 (*AB*, $J = 6.5$, CH_2(4)); 3.12 (*s*, MeO); 1.35 (*d*, $J = 6.5$, Me). ^{13}C-NMR ($CDCl_3$): 143.8 (*s*, arom C(1)); 128.3 (*d*, arom. C(3) and C(5)); 127.4 (*d*, arom. C(4)); 126.6 (*d*, arom. C(2), arom. C(6)); 93.6 (*t*, ^1J(C,H) = 164.6, CH_2(4)); 90.0 (*t*, ^1J(C,H) = 164.6, CH_2(1)); 88.69 (*t*, ^1J(C,H) = 165.7, CH_2(2)); 88.62 (*t*, ^1J(C,H) = 165.7, CH_2(3)); 74.6 (*d*, PhC*H*–O); 55.6 (*q*, MeO); 23.5 (*q*, Me). ^{13}C-NMR ((D_8)toluene): 143.0 (*s*, arom. C(1)); 128.6 (*d*, arom. C(3) and C(5)); 127.6 (*d*, arom. C(4)); 126.7 (*d*, arom. C(2) and C(6)); 93.4 (*t*, ^1J(C,H) = 163.6, CH_2(4)); 89.8 (*t*, ^1J(C,H) = 163.9, CH_2(1)); 88.56 (*t*, ^1J(C,H) = 164.5, CH_2(2)); 88.45 (*t*, ^1J(C,H) = 164.5, CH_2(4)); 74.7 (*d*, PhC*H*–O); 55.3 (*q*, MeO); 23.9 (*q*, Me). Anal. calc. for $C_{13}H_{20}O_5$ (256.30): C 60.92 H, 7.87; found: C 61.15, H 7.80.

*(*R*)-1-Phenylethanol* (**7**). A soln. of **6** (2.27g, 6.7 mmol) in THF (13 ml) and 1N $BH_3 \cdot$THF (6.5 ml, 6,5 mmol) was cooled to 0° and simultaneously treated with acetophenone (8.0 g, 67 mmol) dissolved in Et_2O (30 ml) and 1N $BH_3 \cdot$THF (33.5 ml, 33.5 mmol) in a way that the temp. did not exceed 2–7°. After addition, the mixture was stirred for 3 min and treated dropwise, under cooling, with 10 ml of abs. MeOH during 10 min. The soln. was treated with 2 ml of HCl sat. in Et_2O, stirred for 30 min, concentrated, dissolved in benzene, again concentrated, and dissolved in Et_2O (70 ml). The soln. was stored overnight in the refrigerator, the precipitated hydrochloride of **6** was filtered (1.64 g; 85% catalyst recovery), and the Et_2O phase was extracted with $NaHCO_3$, dried ($NaSO_4$), and concentrated to yield **7** (7.7 g, 95%) with 91% ee according to HPLC control (*Chiralcel OD*, 5 μm).

According to the procedure described in [21], a soln. of **7** (7.4 g, 60.2 mmol) and $(MBE)_2O$ (11.8 g, 32 mmol) in CH_2Cl_2 (70 ml) was treated with 1 g of Na_2SO_4 and *ca.* 20 mg of TsOH, stirred for 2 h, treated with $NaHCO_3$, filtered, concentrated, and crystallized two times with MeOH to yield **8** (14.9 g, 82%) with de > 99.8%.

A soln. of these crystals in MeOH and *ca.* 20 mg of TsOH was stirred for 40 min, the reaction was quenched with solid $NaHCO_3$, and the mixture was concentrated. FC (PE/Et_2O 20:1 → Et_2O) gave **7** (5.0 g, 83%), ee > 99.8% according to HPLC (*Chiralcel OD* 5 μm).

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