Asymmetric intramolecular Pd(II)-catalysed oxycarbonylation of alkene-1,3-diols

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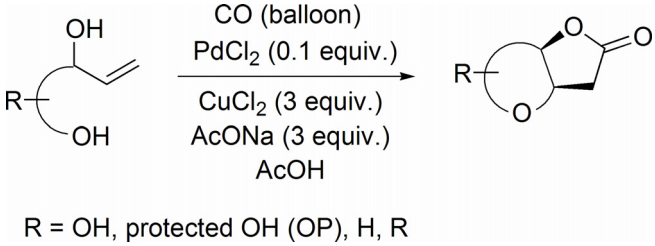
Dedicated to Professor Arlette Solladie-Cavallo on her 70th birthday

Abstract
The first example of asymmetric oxycarbonylative bicyclisation of racemic pent-4-ene-1,3-diol (±)-**1** catalysed by palladium(II) with chiral bis(oxazoline) ligands was investigated. The kinetic resolution of (±)-**1** in the presence of chiral catalyst, *p*-benzoquinone in acetic acid under carbon monoxide atmosphere (balloon) afforded both optically enriched 2,6-dioxabicyclo[3.3.0]octan-3-ones (*R*,*R)*-**2** and (*S*,*S)*-**2**, respectively.

Keywords: Asymmetric catalysis, kinetic resolution, oxycarbonylation, chiral bis(oxazolines), chiral Pd(II)-complexes

Introduction

Intramolecular palladium(II)-catalysed oxycarbonylation of unsaturated polyols is an important transformation of alkenes into bisheterocyclic lactones.[1] The first examples of this domino reaction Pd(II)-promoted cyclisation – intramolecular oxycarbonylation were described for 1,4- and 1,3-alkenediols providing *cis*-fused bicyclic lactones, and involving tetrahydropyran[2] and/or tetrahydrofuran[3] structural motif, respectively (Scheme 1). Such a transformation of optically pure substrates has found numerous applications as the key step in the total syntheses of natural compounds (goniofufurone,[4a,b] goniothalesdiol,[4c,d] erythroskyrine,[4e] kumausyne,[4f] Hagen's gland lactones,[4g] and/or plakortones[4h-j]).



Scheme 1. Intramolecular Pd(II)-catalysed oxycarbonylation of unsaturated polyols.

Typically, alkoxycarbonylation of alkenyl alcohols is catalysed by 10 mol % of the palladium(II)-salt in the presence of an oxidant ($CuCl_2$, *p*-benzoquinone, O_2). Generally, the most efficient catalytic system for intramolecular oxycarbonylation of unsaturated polyols, originally developed for the Wacker process, contains palladium(II) chloride as a catalyst, copper(II) chloride as an oxidant, sodium acetate in acetic acid as a buffer, the reaction taking place under carbon monoxide atmosphere (balloon) at room temperature. In accordance with the diastereoselective *cis*-ring formation, racemic pent-4-ene-1,3-diol (±)-**1** afforded under these reaction conditions racemic 2,6-dioxabicyclo[3.3.0]octan-3-one (±)-**2** in 60% yield.[3] An asymmetric version of this type reaction has not been reported so far. To the best of our knowledge, previously reported works on related asymmetric Wacker-type oxidations have been limited to the monocyclisation of alkenes and alkynes. For instance, Kato, Akita *et al.*[5] described desymmetrisation of cyclic *meso*-2-methyl-2-propargyl-1,3-cyclohexane-diols[5a,c] and -1,3-diones[5b] using methoxycarbonylation catalysed with palladium(II)-complex, bearing chiral bis(oxazoline) ligands. Chiral bis(oxazolines) based on binaphtyl (Boxaxs[6]) or biphenyl backbone[7] were also successfully applied in the asymmetric Wacker-type cyclisation of allylphenols.[8] Sasai and co-workers[9] reported oxidative cyclisation of alkenyl alcohols[9a,b] and aminoalkenes[9c] with spiro bis(isoxazolines) (SPRIXs[9d]). There is no report in the literature dealing with enantioselective oxycarbonylative bicyclisation of unsaturated polyols. We wish to report here the first example of kinetic resolution of alkene-diol by intramolecular Pd(II)-catalysed oxycarbonylation.

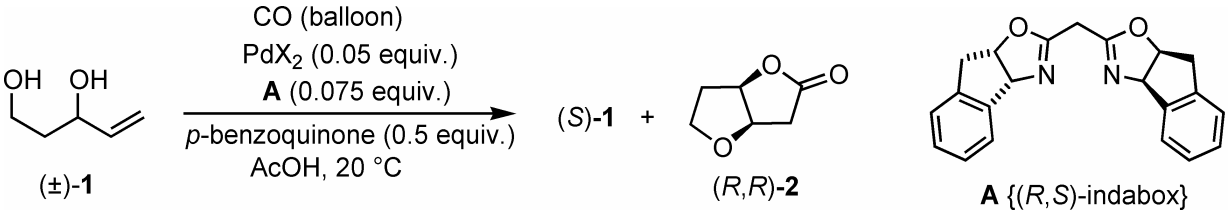
Results and Discussion

Firstly, the catalytic system for kinetic resolution of unsaturated diols was examined. The racemic pent-4-ene-1,3-diol[10] (±)-**1** has been chosen as a model substrate for screening the reaction conditions. The transformation was carried out with different chiral PdX_2-[(*R*,*S*)-indabox] complexes, *p*-benzoquinone in acetic acid under carbon monoxide atmosphere (balloon). Chiral palladium(II)-complexes were generated *in situ* from PdX_2 and a slight excess of chiral ligand **A** {(3a*R*, 8a*S*) -(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazol-2-yl}methane [(*R*,*S*)-indabox]. In accordance with a kinetic resolution process, the reaction was performed with 50%

conversion by use of 0.5 equivalent of *p*-benzoquinone. Conversion control was made by GC with methyl benzoate as an internal standard. The reaction was quenched after 50% of the starting material had been consumed. The bicyclic product **2** and the remaining diol **1** were separated by flash chromatography. The enantiomeric excess of lactone (*R*,*R*)-**2** was determined by GC analysis with a chiral stationary phase (BGB 175 and BGB 173 column). The absolute configuration of (*R*,*R*)-**2** was assigned by comparison of the specific rotation value with the literature data ($[a]_D^{20}$ = +62 (c 0.9, $CHCl_3$) for (*R,R*)-**2** prepared from D-glucose;[11] $[a]_D^{20}$ = -67 (c 0.639, $CHCl_3$) for (*S,S*)-**2** prepared by microbial regiodivergent Baeyer-Villiger oxidation with 99% *ee*[12]).

As shown in Table 1, the reaction catalysed with $PdCl_2$-{(*R*,*S*)-indabox (**A**)} (entry 1) and $Pd(BF_4)_2$-{(*R*,*S*)-indabox} complexes (entry 4) afforded only racemic lactone **2**. Moderate selectivities were achieved using $Pd(OAc)_2$-{(*R*,*S*)-indabox} (entry 2) and $Pd(OCOCF_3)_2$-{(*R*,*S*)-indabox} catalysts (entry 3). It is apparent that catalytic activity of palladium complexes in the present reaction was strongly dependent upon the nature of the anionic part of the catalyst.
It is notable that in transformation of **1** to **2** the use of dichloromethane or tetrahydrofuran as solvents did not give satisfactory results in terms of both conversion and enantioselectivity.

Table 1. Kinetic resolution of pent-4-ene-1,3-diol (±)-**1** in asymmetric Pd(II)-catalysed oxycarbonylation



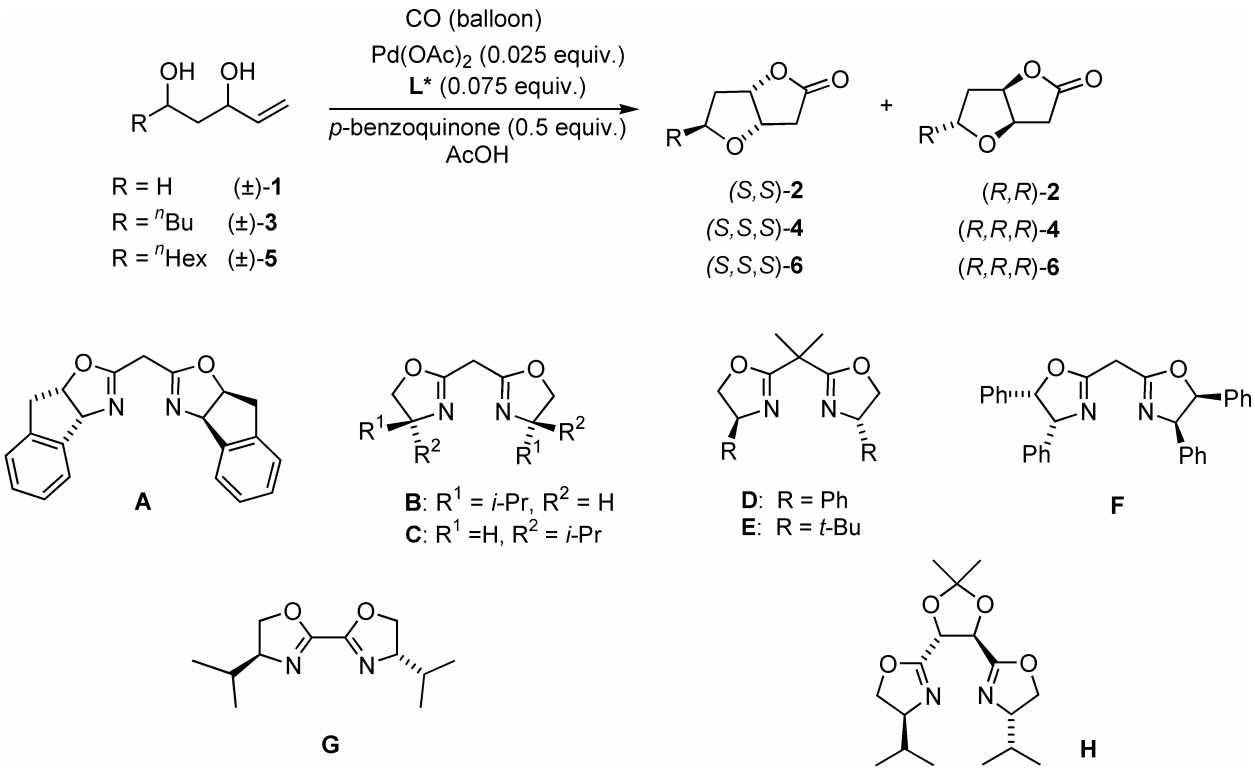
		Diol 1		Lactone 2			
Entry	X	Reaction time[a]	Yield[b] (%)	Yield[b] (%)	% *ee*[c]	$[\alpha]_D$ (25 °C)	Configuration
1	Cl	120 h	58	23	<5	+1 (0.25, $CHCl_3$)	-
2	OAc	30 h	48	33	43	+19 (0.41, $CHCl_3$)	1*R*,5*R*
3	$OCOCF_3$	30 h	48	22	33	+16 (0.26, $CHCl_3$)	1*R*,5*R*
4	BF_4	120 h	33	31	<5	+3 (0.40, $CHCl_3$)	1*R*,5*R*

[a] Reaction was treated after 50% of starting material had been consumed (GC control).
[b] Isolated yield after flash column chromatography.
[b] Enantiomeric excesses were determined using gas chromatography with chiral stationary phase.

Having found reaction conditions for a kinetic resolution process of the diol (±)-**1** by Pd(II)-catalysed oxycarbonylation, our attention was turned to the screening of chiral ligands (Scheme

2). Chiral C_2-symmetric bisoxazolines have been chosen due to their ability to create stable palladium(II)-complexes.[13, 14]

The reaction was carried out under optimised reaction conditions for kinetic resolution of (±)-**1** using 5 mol % of $Pd(OAc)_2$ and 7.5 mol % of ligands **A**-**H** in glacial acetic acid, respectively. A cationic[6b] acetate complex Pd-$(OAc)_2$-{(*R*,*S*)-indabox **A**} was found to be catalytically so highly active that the amount of the catalyst could be reduced to 2.5 mol %. The conversion was controlled by the amount of reoxidant (0.5 equivalents of *p*-benzoquinone). After completion the reaction, the solids were filtered off, solvent was evaporated and the product and remaining substrate were separated by flash column chromatography of the crude reaction mixture. The enantiomeric excesses and absolute configurations of lactones **2** were determined as above. The absolute configurations of lactones **4** and **6** were established by comparison of their specific rotation values with the literature data {for (*R,R,R*)-**4**: $[a]_D^{22}$ = +46.5 (c 1.5, $CHCl_3$) prepared from (*R*)-hexanediol;[4g] $[a]_D^{25}$ = +51 (c 1, $CHCl_3$) from D-glucose;[15] for (*R,R,R*)-**6**: $[a]_D^{22}$ = +39.7 (c 1.05, $CHCl_3$) from (3*R,*5*R*)-undec-1-ene-3,5-diol;[4g] $[a]_D^{25}$ = +50 (c 1, $CHCl_3$) from D-glucose.[15] The NMR spectral data were in good agreement with those reported in the literature.[4g,15]



Scheme 2. Kinetic resolution of alkene-1,3-diols (±)-**1,** (±)-**3** and (±)-**5** in asymmetric Pd(II)-catalysed oxycarbonylation.

Table 2 summarises the results of a series of experiments with several Pd-$(OAc)_2$(L*) complexes. Generally, the enantioselectivity of the reaction was increased by the use of catalyst/ligand in a ratio 1:3. The best result was noted with Pd-$(OAc)_2$-{(*R*,*S*)-indabox} (entry 1). The 50% conversion of substrate was accomplished in 30 h at 18 °C, and racemic diol (±)-**1** was converted into bicyclic lactone (*R*,*R*)-**2** in 29% yield and 62% *ee*. The use of palladium catalysts with ligands **B**, **C** and **F** in the same reaction conditions furnished products **2** in comparable yields (28 - 33%), but with lower enantioselectivity (40 – 45% *ee*, entries 2, 3 and 6). When the reaction was performed in the presence of ligands **D**, **E**, **G**, and **H** the bicycle **2** was obtained with low selectivity, although these chiral bis(oxazolines) have been successfully used for other asymmetric transformations[15] (entries 4, 5, 7 and 8). Similarly, the *syn*-enriched diols (±)-**3**[4g] and (±)-**5**[4g] (*syn*/*anti*, 85:15 for (±)-**3**, 86:14 for (±)-**5**, see experimental part) provided only the corresponding *exo*-lactones **4** and **6**, respectively, with high diastereoselectivity and good yields (35-38%, entries 9-12), however with low enantioselectivities. It is significant, that the reaction proceeding in the presence of *S*-configured bis(oxazoline) **B** provided enriched lactone (*S*,*S*)-**2**, while the opposite enantiomer **C** preferred formation of (*R*,*R*)-**2**.

Table 2. Screening of chiral bis(oxazoline) ligands in the asymmetric Pd(II)-catalysed oxycarbonylation of alkene-1,3-diols (±)-**1**, (±)-**3** and (±)-**5**

Entry	Diol	Ligand	Conditions	Lactone	Yield[a] (%)	% *ee*[b]	$[\alpha]_D$ (25 °C) (*c*, $CHCl_3$)
1	(±)-**1**	A[c]	18 °C, 30 h	(*R*,*R*)-**2**	29	62	+40 (0.19)
2	(±)-**1**	B[16]	18 °C, 48 h	(*S*,*S*)-**2**	30	45	-20 (0.28)
3	(±)-**1**	C[16]	18 °C, 48 h	(*R*,*R*)-**2**	33	45	+20 (0.40)
4	(±)-**1**	D[c]	18 °C, 48 h	**2**	31	<5	-
5	(±)-**1**	E[c]	40 °C, 48 h	**2**	30	16	-
6	(±)-**1**	F[c]	18 °C, 48 h	(*R*,*R*)-**2**	28	40	+19 (0.33)
7	(±)-**1**	G[16]	18 °C, 48 h	**2**	24	<5	-
8	(±)-**1**	H[16]	18 °C, 48 h	**2**	22	<5	-
9	(±)-**3**	A[c]	18°C, 48 h	(*R*,*R*,*R*)-**4**	36	31	+15 (0.41)
10	(±)-**3**	B[16]	18°C, 48 h	(*S*,*S*,*S*)-**4**	36	9	-
11	(±)-**5**	A[c]	18 °C, 30 h	(*R*,*R*,*R*)-**6**	38	41	+17 (0.35)
12	(±)-**5**	B[16]	18°C, 48 h	**6**	35	<5	-

[a] Isolated yield after flash column chromatography.

[b] Enantiomeric excesses were determined using gas chromatography with chiral stationary phase.

[c] Commercially available.

Conclusions

In summary, we have presented a kinetic resolution process of racemic alkene-1,3-diols (±)**-1,** (±)**-3** and (±)**-5** catalysed by palladium(II) with chiral bis(oxazolines). This is the first report of an enantioselective oxycarbonylative bicyclisation. Conversion of substrate is controlled by reoxidant, which represents novelty in kinetic resolution processes. Further studies to improve the performance of asymmetric catalysts for this transformation are now under way.

Experimental Section

General Procedures. Commercial reagents were used without further purification. All solvents were distilled before use. Hexanes refer to the fraction boiling at 60-65^{o}C. Flash column liquid chromatography (FLC) was performed on silica gel Kieselgel 60 (40-63 μm, 230-400 mesh) and analytical thin-layer chromatography (TLC) was performed on aluminium plates pre-coated with either 0.2 mm (DC-Alufolien, Merck) or 0.25 mm silica gel 60 F_{254} (ALUGRAM® SIL G/UV_{254}, Macherey-Nagel). General conversion control and analyses of purified products were performed on a GC Top 8000/MS Voyager (quadropol, EI+) using a standard capillary column BGB5 (30 mP0.32 mm ID). Enantiomeric excesses were determined by chiral-phase GC using a BGB 175 column (30 mP 0.25 mm ID, 0.25 mm film, *50% 2,3-diacetyl-6-tert-butyldimethylsilylated-γ-cyclodextrin* dissolved in BGB-1701 (14% cyanopropylphenyl-, 86% methylpolysiloxane)) and a BGB 173 column (30 mP 0.25 mm ID, 0.25 mm film, *50% 2,3-diacetyl-6-tert-butyldimethylsilylated-α-cyclodextrin* dissolved in BGB-1701 (14% cyanopropylphenyl-, 86% methylpolysiloxane)) on a ThermoQuest Trace GC 2000 and a Thermo Focus GC. Optical rotations were measured with the POLAR L-μP polarimeter (IBZ Messtechnik) with a water-jacketed 10.000 cm cell at the wavelength of sodium line D (λ=589 nm). Specific rotations are given in units of 10^{-1} deg·cm^{2}·g^{-1} and concentrations are given in g/100 mL. Elemental analyses were run on FISONS EA1108 instrument. Infrared spectra were recorded on a Philips Analytical PU9800 FTIR spectrometer as KBr discs (KBr) or as thin films on KBr plates (film). NMR spectra were recorded on a Varian VXR-300 spectrometer. Chemical shifts (δ) are quoted in ppm and are referenced to the tetramethylsilane (TMS) as internal standard. The multiplicites of carbons were assigned from a broadband decoupled analysis used in conjuction with either APT or DEPT programs.

(±)-Non-1-ene-3,5-diol ((±)-3). DIBAL-H (16 mL, 1M in hexane, 2.5 equiv.) was added to a solution of (±)-3-hydroxynon-1-en-5-one[4g] (1.0 g, 6.5 mmol) in anhydrous THF (50 mL) at -90^{o}C during 30 min. The reaction mixture was stirred for additional 2 h at -90^{o}C, quenched with HCl (2M, 25 mL) and extracted with AcOEt (3x20 mL). Organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. Analytically pure product (±)**-3** as the mixture of diastereomers (*syn*/*anti*, 85:15 by ^{13}C NMR) was obtained by FLC (30 g of silica-gel, AcOEt-hexanes, 1:6) as

colourless oil (850 mg, 84%); R_f 0.45 (AcOEt-hexanes, 1:3). Anal. calcd. for $C_9H_{18}O_2$ (158.24): C 68.31, H 11.47; found: C 68.42, H 11.43. Spectral data were in full accordance with lit.[4g]

(±)-Undec-1-ene-3,5-diol ((±)-5). The procedure described above was applied for conversion of (±)-3-hydroxyundec-1-ene-5-one[4g,17] (2.5 g, 13.4 mmol) to nonene-3,5-diol (±)-**5**. The crude product was purified by flash column chromatography (50 g of silica-gel, AcOEt/hexanes, 1:6); yield 1.9 g (76%) of (±)-**5**, colourless oil, R_f 0.27 (AcOEt-hexanes, 1:1). The product consisted of a 86:14 *syn*/*anti* diastereomers (±)-**5** (determined by ^{13}C-NMR). ^{1}H-NMR ($CDCl_3$, 300 MHz, major diastereomer) δ 0.88 (t, 3H, $J_{10,11}$ = 7 Hz, H-11), 1.28-1.70 (m, 12H, H-4, H-6, H-7, H-8, H-9, H-10), 3.61 (bs, 2H, OH), 3.85-3.90 (m, 1H, H-5), 4.32-4.38 (m, 1H, H-3), 5.85 (dt, 1H, $J_{1Z,2}$ = 11 Hz, $J_{1Z,1E}$ = 1 Hz, H-1Z), 5.24 (dt, 1H, $J_{1E,2}$ = 18 Hz, $J_{1Z,1E}$ = 1 Hz, H-1E), 5.81-5.92 (m, 1H, H-2); ^{13}C-NMR ($CDCl_3$, 75 MHz, major diastereomer) δ 14.1 (q, C-11), 22.6, 25.3, 29.3, 31.8, 38.1, 42.7 (all t, C-4, C-6, C-7, C-8, C-9, C-10), 72.5, 73.8 (all d, C-3, C-5), 114.4 (t, C-1), 140.7 (d, C-2). IR (film, cm^{-1}): ν 3346, 2956, 2930, 2858, 1466, 1423. Anal. calcd. for $C_{11}H_{22}O_2$ (186.16): C 70.92, H 11.90; found: C 70.86, H 11.95. This compound (±)-**5** was previously used in the next reaction without characterisation.[4g]

A typical procedure for asymmetric oxycarbonylation of alkenediols (±)-1, (±)-3, (±)-5 with (L*)Pd(OAc)$_2$, (L*)Pd(OCOCF$_3$)$_2$ and (L*)PdCl$_2$

Chiral ligand (0.075 mmol) in AcOH (1 ml) was added to the solution of $Pd(OAc)_2$, or $Pd(MeCN)_2Cl_2$ (0.05 mmol, 0.05 equiv. or 0.025 mmol, 0.025 equiv.) in DCM (1 ml), respectively. The mixture was stirred for 15 min to give a clear solution and DCM was removed *in vacuo*. Resulting chiral palladium complex was dissolved in glacial AcOH (2 ml), substrate **(±)-1** (1.0 mmol) and *p*-benzoquinone (0.5 equiv.) in AcOH (2 ml) were added. The flask was purged with CO from a balloon and the reaction mixture was vigorously stirred until the deposition of black palladium was observed (approx. 1-2 days). The solvent was evaporated and the crude product purified by flash column chromatography.

Asymmetric oxycarbonylation with (±)-1 (L*)Pd(BF$_4$)$_2$

Chiral ligand (0.075 mmol) in DCM (1 ml) was added to the solution of $Pd(MeCN)_2Cl_2$ (0.05 mmol, 0.05 equiv.) in DCM (1 ml). The mixture was stirred for 15 min to give clear solution. This solution was added to a mixture of $AgBF_4$ (0.05 mmol) in DCM (1 ml). Precipitated AgCl was removed by filtration and the filtrate was concentrated. The solid was dissolved in glacial AcOH (2 ml) and substrate **(±)-1** (1.0 mmol) and *p*-benzoquinone (0.5 equiv.) in AcOH (2 ml) were added. The flask was purged with CO from balloon and the mixture was vigorously stirred until black palladium was observed (approx. 1 day). The solvent was then evaporated and the crude product purified by flash column chromatography.

(1*R*,5*R*)- and (1*S*,5*S*)-2,6-Dioxabicyclo[3.3.0]octane-3-one {(*R*,*R*)-2 and (*S*,*S*)-2}. Prepared as described above. Colorless oil, R_f 0.30 (AcOEt-hexanes, 1:1), yield, specific rotation value and %*ee* see tables 1, 2; {lit. $[a]_D^{20}$ = +62 (c 0.9, $CHCl_3$) for (*R,R*)-**2** prepared from D-glucose;[11] $[a]_D^{20}$ = -67 (c 0.639, $CHCl_3$) for (*S,S*)-**2** prepared by microbial regiodivergent Baeyer-Villiger oxidation

with 99% *ee*[12]}. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.05-2.40 (m, 2H, H-8), 2.66 (d, A of ABX, 1H, $J_{A,B}$ = 19 Hz, H-4A), 2.80 (dd, B of ABX, 1H, $J_{A,B}$ = 19 Hz, $J_{B,5}$ = 6 Hz, H-4B), 3.90-4.00 (m, 2H, H-7), 4.70 (dd, dX of ABX, 1H, $J_{B,5} = J_{1,5}$ = 5 Hz, H-5), 5.13 (dd, 1H, $J_{5,8} = J_{1,5}$ = 5 Hz, H-1); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 32.9 (t, C-8), 32.6 (t, C-4), 66.9 (t, C-7), 78.0 (d, C-5), 84.3 (d, C-1), 175.8 (s, C-3). IR (film, cm^{-1}): ν 2966, 2869, 1777. GC/MS for $C_6H_8O_3$ (M^{+1}): calcd. 128.05, found 129.

(1*R*,5*R*,7*R*)- and (1*S*,5*S*,7*S*)-7-Butyl-2,6-dioxabicyclo[3.3.0]octane-3-one {(*R*,*R*,*R*)-4 and (*S*,*S*,*S*)-4}. Prepared according to the typical procedure for asymmetric oxycarbonylation from diol (±)-**3** using $Pd(OAc)_2$ (0.025 mmol), ligand **A** and **B**, respectively (Table 2, entries 9 and 10). Colorless oil, Rf 0.36 (AcOEt-hexanes, 1:2); {lit.:[4g] $[a]_D^{22}$ = +46.5 (c 1.5, $CHCl_3$) for (*R,R,R*)-**4** and $[a]_D^{22}$ = -47.5 (c 1.46, $CHCl_3$) for (*S,S,S*)-**4** prepared from (*R*)- and (*S*)-hexanediol, respectively; lit.:[15] $[a]_D^{25}$ = +51 (c 1, $CHCl_3$) for (*R,R,R*)-**4** from D-glucose. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 3H, $J_{3',4'}$ = 8 Hz, CH_3), 1.21-1.38 (m, 4H, CH_2), 1.40-1.70 (m, 3H, CH_2, H-8A), 2.35 (dd, 1H, $J_{8A,8B}$ = 14 Hz, $J_{1,8B}$ = 4 Hz, H-8B), 2.61 (d, 1H, $J_{A,B}$ = 18 Hz, H-4A), 2.74 (dd, B of ABX, 1H, $J_{A,B}$ = 18 Hz, $J_{B,5}$ = 6 Hz, H-4B), 4.00-4.09 (m, 1H, H-7), 4.79 (dd, dX of ABX, 1H, $J_{B,5} = J_{1,5}$ = 6 Hz, H-5), 5.10 (dd, 1H, $J_{1,8} = J_{1,5}$ = 4 Hz, H-1); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0 (q, CH_3), 22.6, 28.2, 34.4, 36.7, 38.8 (all t, 3xCH_2, C-4), 77.5 (d, C-7), 78.3 (d, C-5), 84.9 (d, C-1), 176.0 (s, C-3). IR (film, cm^{-1}): ν 2959, 2927, 2856, 1770. GC/MS for $C_{10}H_{16}O_3$ (M^{+1}): calcd. 184.11, found 185.

(1*R*,5*R*,7*R*)- and (1*S*,5*S*,7*S*)-7-Hexyl-2,6-dioxabicyclo[3.3.0]octane-3-one {(*R*,*R*,*R*)-6 and (*S*,*S*,*S*)-6}. Prepared according to the typical procedure for asymmetric oxycarbonylation from diol (±)-**5** using $Pd(OAc)_2$ (0.025 mmol), ligand **A** and **B**, respectively (Table 2, entries 11 and 12). Colorless oil, Rf 0.31 (AcOEt-hexanes, 1:2); {lit.:[4g] $[a]_D^{22}$ = +39.7 (c 1.05, $CHCl_3$) for (*R,R,R*)-**6** and $[a]_D^{22}$ = -41.0 (c 1.02, $CHCl_3$) for (*S,S,S*)-**6** prepared from (3*R*,5*R*)- and (3*S*,5*S*)-undec-1-ene-3,5-diol, respectively. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 3H, $J_{5',6'}$ = 8 Hz, CH_3), 1.20-1.72 (m, 11H, CH_2, H-8A), 2.38 (dd, 1H, $J_{8A,8B}$ = 14 Hz, $J_{1,8B}$ = 5 Hz, H-8B), 2.70 (d, 1H, $J_{A,B}$ = 19 Hz, H-4A), 2.78 (dd, B of ABX, 1H, $J_{A,B}$ = 19 Hz, $J_{B,5}$ = 6 Hz, H-4B), 4.02-4.11 (m, 1H, H-7), 4.80-4.84 (m,1H, H-5), 5.13 (dd, 1H, $J_{1,8} = J_{1,5}$ = 5 Hz, H-1); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1 (q, CH_3), 22.6, 26.0, 29.2, 31.7, 34.7, 36.7, 38.8 (all t, 5xCH_2, C-4, C-8), 77.4 (d, C-7), 78.3 (d, C-5), 85.0 (d, C-1), 176.1 (s, C-3). IR (film, cm^{-1}): ν 2956, 2930, 2859, 1785, 1172. GC/MS for $C_{12}H_{20}O_3$ (M^{+1}): calcd. 212.14, found 213.

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References and Notes

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