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Synthesis of *anti*-1,3-Diols through $RuCl_3$/PPh_3-Mediated Hydrogenation of β-Hydroxy Ketones: An Alternative to Organoboron Reagents

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Hydrogenation of enantioenriched β-hydroxy ketones promoted by the catalyst generated in situ from commercially available and inexpensive $RuCl_3$ and PPh_3 under hydrogen pressure allowed the efficient preparation of a variety of *anti*-1,3-diols in good yields and with a high level of diastereoselectivity. This method should be an interesting alternative to organoboron reagents for the diastereoselective reduction of β-hydroxy ketones.

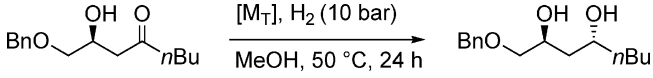
Introduction

Because 1,3-diol units are present in a large variety of polyketide-derived natural products,[1] the development of new methods for their preparation in either a *syn* or *anti* relationship is of great interest.[2] Among the numerous procedures developed for the formation of acyclic 1,3-diols, metal hydride reduction of β-hydroxy ketones has been particularly investigated and allows the stereocontrolled preparation of both *syn* and *anti* compounds.[3,4] In this area, borohydride reagents are commonly used, and the development of selective but less expensive and environmentally more benign procedures is desirable. Towards this end, we published recently an operationally simple and waste-free method for diastereoselective catalytic hydrogenation[5] of β-hydroxy ketones into *anti*-1,3-diols by using an inexpensive $RuCl_3$/phosphane combination.[6,7] Herein, we report an expanded substrate scope as well as additional experiments including the study of various ruthenium sources and other transition-metal complexes. Complementary results obtained with achiral diphosphanes are also described.

Results and Discussion

As a starting point, hydrogenation of β-hydroxy ketone **1** was examined by using various transition-metal complexes associated with PPh_3 as a ligand (Table 1). The reaction was conducted in methanol at 50 °C with 2 mol-% of the metal source and 4 mol-% of PPh_3 under 10 bar of hydrogen for 24 h. With anhydrous $RuCl_3$ under these conditions, the reaction proceeded with full conversion and high diastereomeric excess for the *anti*-1,3-diol **2** (91% *de*, entry 1, Table 1).

Table 1. Catalyst survey.[a]



1 **2**

Entry	Precatalyst	Conv. [%][b]	*de* [%][c]
1	$RuCl_3$ + PPh_3	100	91
2	$[RuCl_2(p\text{-cymene})PPh_3]$	100	82
3	$[RuCl_2(PPh_3)_3]$	100	90
4	[Ru(COD)(2-methylallyl)$_2$] + PPh_3 + HBr	100	91
5	$[RuCl_2(\eta^6\text{-benzene})]_2$ + PPh_3 + $Et_2NH.HCl$	100	89
6	$[Ir(COD)Cl]_2$+ PPh_3	0	–
7	$[Ir(COD)_2Cl]_2$ + PPh_3	0	–
8	$IrCl_3{\cdot}xH_2O$ + PPh_3	0	–
9	$RhCl_3{\cdot}xH_2O$ + PPh_3	0	–
10	$[Rh(COD)Cl]_2$ + PPh_3	0	–
11	$[AuCl_4][Na]$ + PPh_3	0	–
12	[AuHCl] + PPh_3	0	–
13	$[PdCl_2(PPh_3)_2]$	0	–

[a] All reactions were performed with 0.5 mmol of substrate **1** in 2 mL of MeOH by using 10 μmol of the metal complex in the presence of 20 μmol of PPh_3 when necessary. [b] Conversions were determined by ^1H NMR spectroscopy of the crude product. [c] The *de* values were determined by HPLC analysis. For the determination of the diastereomeric excess, an authentic sample of the *anti*-1,3-diol **2** was obtained by reduction of **1** with $Me_4NBH(OAc)_3$,[4b] while an authentic sample of the *syn*-1,3-diol was prepared by reduction with $Et_2BOMe/NaBH_4$.[3b] The identities of the diastereomers were established on the corresponding acetonides by using the protocol reported by Rychnovsky.[10]

A comparative study with other ruthenium sources was then carried out. The hydrogenation reaction catalyzed by commercially available ruthenium(II) complexes [$RuCl_2$(*p*-

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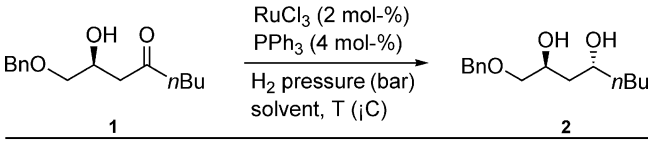
cymene)PPh_3] and [$RuCl_2(PPh_3)_3$] afforded results comparable to those obtained with $RuCl_3/PPh_3$ in terms of both conversion and selectivity (entries 2–3, Table 1). Likewise, with the ruthenium complex prepared by addition of PPh_3 and hydrobromic acid to commercially available [Ru(COD)(2-methylallyl)$_2$],[8] complete conversion and high *de* were obtained (entry 4, Table 1). Similar results were again observed with the ruthenium complex prepared by treatment of [$RuCl_2(\eta^6$-benzene)]$_2$ with PPh_3 and $Et_2NH.HCl$[9] (entry 5, Table 1). Next, other transition-metal complexes were investigated in the model reaction. However, under the standard reaction conditions, the tested iridium, rhodium, gold, and palladium complexes proved to be inefficient, since no conversion was obtained with any of those (entries 6–13, Table 1).

An optimization of the reaction parameters with ruthenium complexes was then undertaken, and the $RuCl_3/PPh_3$ combination was preferred, as $RuCl_3$ is the least expensive of the ruthenium sources (Table 2).

Table 2. Hydrogenation of **1** in the presence of $RuCl_3/PPh_3$.[a]



Entry	Solvent	*P* [bar]	*T* [°C]	*t* [h][b]	Conv. [%][c]	*de* [%][d]
1	MeOH	10	25	72	30	–[e]
2	MeOH	100	25	72	88	83
3	MeOH	10	50	24	100	91
4	MeOH	4	50	48	35	–[e]
5	CH_2Cl_2	10	50	24	61	44
6	hexane	10	50	24	16	59
7	toluene	10	50	24	10	62
8	CH_2Cl_2/MeOH (10:1)	10	50	48	75	83

[a] Conditions: **1** (0.5 mmol), solvent (2 mL), $RuCl_3$ (10 μmol), PPh_3 (20 μmol). [b] Reaction times were not optimized. [c] Conversions were determined by ^{1}H NMR spectroscopy of the crude product. [d] The *de* values were determined by HPLC analysis. [e] Not determined.

The hydrogenation of **1** was carried out in methanol at room temperature for 72 h, under either low or high pressure of hydrogen (10 or 100 bar, respectively, entries 1 and 2, Table 2). However, under these conditions, incomplete conversions were observed. Actually, full conversion was achieved under the previously established standard conditions at a temperature of 50 °C under 10 bar hydrogen pressure (entry 3, Table 2). At a slightly lower hydrogen pressure (4 bar), only 35% conversion was attained after 48 h (entry 4, Table 2). With the above optimized reaction parameters, other solvents were then used. The results in Table 2 indicate that methanol was the solvent of choice for the model reaction, since low conversions and unsatisfactory diastereomeric excesses were obtained in CH_2Cl_2, hexane, and toluene (entries 5–7, Table 2). On the other hand, when the reaction was conducted in dichloromethane, addition of a small amount of methanol allowed a significant increase in diastereoselectivity (from 44% to 83% *de*, entries 5 and 8, Table 2).

The catalytic species involved in the reduction process is most likely the ruthenium hydride complex [RuHCl(PPh_3)$_2$] previously reported in the literature. Indeed, it is well established that reaction of PPh_3 with a methanol solution of $RuCl_3$ leads to the formation of the mononuclear complex [$RuCl_2(PPh_3)_3$].[11] Upon exposure to hydrogen, this complex loses chloride to afford the species [$RuHCl(PPh_3)_3$][12] (Figure 1). The latter in turn forms complex **I**, in which hydroxy ketone **1** is coordinated to the ruthenium center through the keto and hydroxy functions, as in the most commonly considered mechanism for (diphosphane)Ru-catalyzed hydrogenation of functionalized ketone.[13] Further hydride transfer from the ruthenium center to the coordinated ketone function provides ruthenium alkoxide **II**. The 1,3-diol **2** is then released by protonolysis, yielding ruthenium complex **III**, which reacts with hydrogen to complete the catalytic cycle.

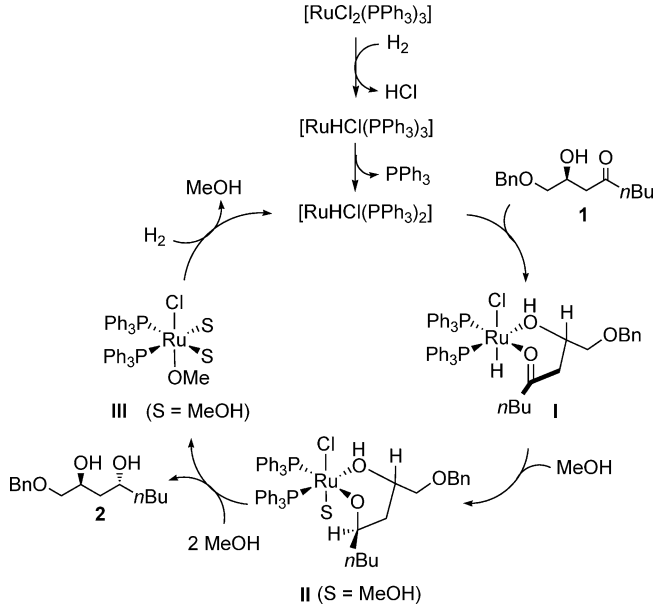


Figure 1. Proposed mechanism for the diastereoselective hydrogenation of **1** in the presence of $RuCl_3/PPh_3$.

The *anti* selectivity observed in the hydrogenation reaction would result from the intramolecular hydride delivery step **I** → **II**. Two chelation modes of hydroxy ketone **1** are possible, via the *re*- or *si*-faces, affording two diastereomers, **I** and **II**, respectively (Figure 2). Energy minimization by using molecular mechanics calculations (CAChe MM2 program) was performed on both structures **I** and **II** and showed that structure **I** displayed a lower relative energy than that of its diastereomer **II** (ΔE = 1.7 kcal mol^{-1}). This difference in relative energy between the two transition states of step **I** → **II** would explain the formation of *anti*-1,3-diol **2** as the major product.

In an attempt to increase the selectivity of the reaction, we next focused our attention on the influence of the monophosphane ligands on the hydrogenation of **1** by using various phosphanes under the optimized conditions (Table 3).

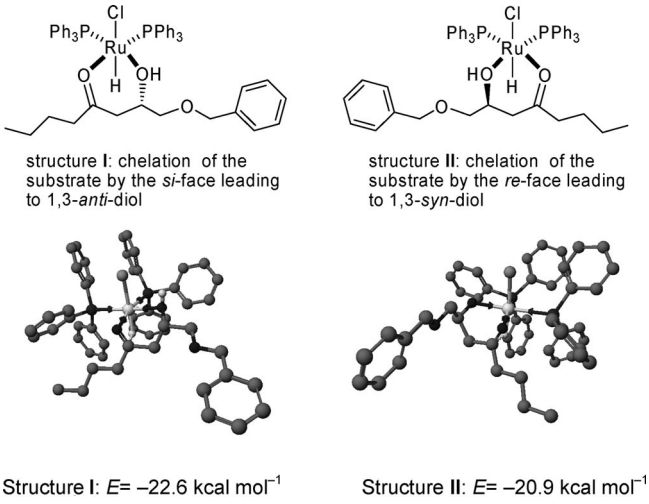


Figure 2. Structures of **I** and **II** minimized by molecular mechanics calculations.

A comparison of various triarylphosphanes was first made (entries 1–7, Table 3). High *anti* diastereoselectivities were obtained by using P(*p*-MeC$_6$H$_4$)$_3$, P(*p*-MeOC$_6$H$_4$)$_3$, or P(*m*-MeC$_6$H$_4$)$_3$, although lower conversions were achieved relative to PPh$_3$ (77–80% conversion and 89–90% *de*, entries 2, 3, and 5 vs. 100% conversion and 91% *de*, entry 1, Table 3). Presumably because of the higher steric hindrance of P(*o*-MeC$_6$H$_4$)$_3$, very poor conversion was obtained in this case (entry 6, Table 3). On the other hand, the less electron-rich phosphanes P(*p*-ClC$_6$H$_4$)$_3$ and P(*m*-NaO$_3$S-C$_6$H$_4$)$_3$ yielded complete conversions, albeit with lower diastereomeric excesses (respectively 74 and 77% *de*, entries 4 and 7, Table 3). The hydrogenation reaction was also performed with monophosphanes bearing one or more alkyl substituents, namely, PPh$_2$Cy, PPhCy$_2$, and PCy$_3$ (entries 8–10, Table 3). In these cases, only moderate conversions were observed (30–75%) because of the steric hindrance brought by the cyclohexyl group.

With PPh$_2$Cy, the formal exchange of a phenyl ring by a cyclohexyl group led to a decrease in diastereoselectivity (from 91% *de* for PPh$_3$ to 83% *de* for PPh$_2$Cy, *anti* isomer,

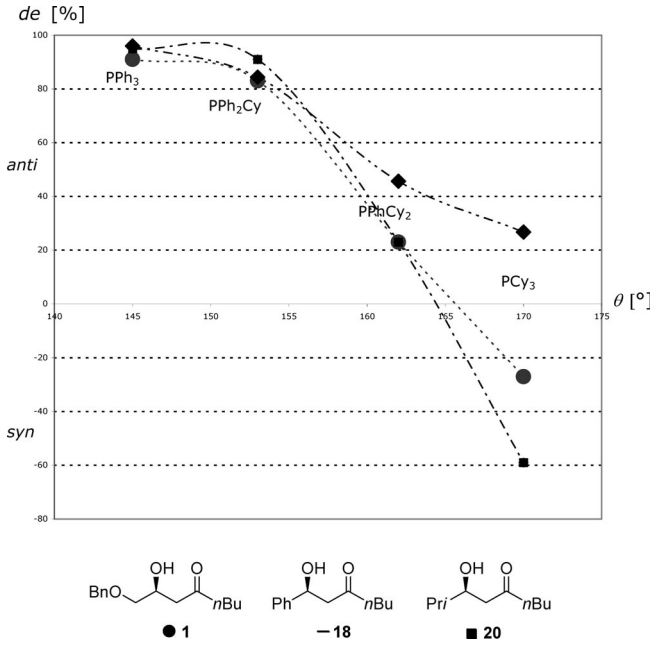
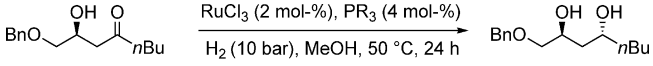


Figure 3. Correlation between the cone angles and the diastereoselectivity of the catalytic hydrogenation of compounds **1**, **18**, and **20** with PPh$_3$, PPh$_2$Cy, PPhCy$_2$ and PCy$_3$.

Table 3. Hydrogenation of **1** in the presence of RuCl$_3$/PR$_3$.

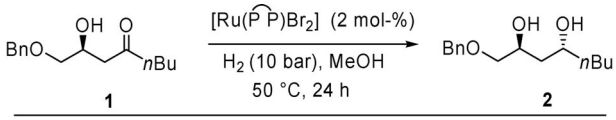


1 **2**

Entry	Phosphane[a]	θ [°][b]	pK_a[b]	Conversion [%][c]	*de*[%][d]
1	PPh$_3$	145	2.73	100	91 (*anti*)
2	P(*p*-MeC$_6$H$_4$)$_3$	145	3.84	80	90 (*anti*)
3	P(*p*-MeOC$_6$H$_4$)$_3$	145	4.59	77	89 (*anti*)
4	P(*p*-ClC$_6$H$_4$)$_3$	145	1.03	100	74 (*anti*)
5	P(*m*-MeC$_6$H$_4$)$_3$	148	3.30	78	90 (*anti*)
6	P(*o*-MeC$_6$H$_4$)$_3$	178	–[e]	10	–[f]
7	P(*m*-NaO$_3$SC$_6$H$_4$)$_3$	166	–[e]	100	77 (*anti*)
8	PPh$_2$Cy	153	5.05	50	83 (*anti*)
9	PPhCy$_2$	162	–[e]	30	23 (*anti*)
10	PCy$_3$	170	9.70	75	27 (*syn*)
11	P(*t*Bu)$_3$	182	11.40	0	–

[a] In the absence of phosphane, no reduction was observed. [b] Values of cone angles (θ) and pK_a were taken from the literature.[14] [c] Conversions were determined by ^{1}H NMR spectroscopy of the crude product. [d] The *de* values were determined by HPLC analysis. [e] Unknown. [f] Not determined.

Table 4. Hydrogenation of **1** in the presence of [Ru(PP)Br$_2$].



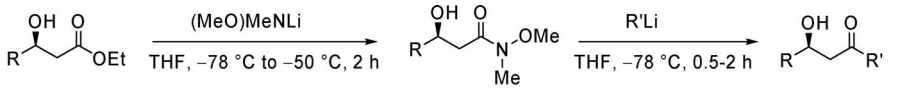
1 **2**

Entry	Diphosphane	Conv [%][a]	*de*, *anti* [%][b]
1	Ph$_2$P–PPh$_2$	45	75
2	Ph$_2$P–(CH$_2$)$_2$–PPh$_2$	100	91
3	Ph$_2$P–(CH$_2$)$_3$–PPh$_2$	100	78
4	Ph$_2$P–(CH$_2$)$_4$–PPh$_2$	100	91
5	Ph$_2$P–(CH$_2$)$_5$–PPh$_2$	100	93
6	Ph$_2$P–(CH$_2$)$_6$–PPh$_2$	65	92
7	Fe(C$_5$H$_4$PPh$_2$)$_2$	100	72
8	1,2-(PPh$_2$)$_2$C$_6$H$_4$	50	89
9	Cy$_2$P–PCy$_2$	30	92

[a] Conversions were determined by ^{1}H NMR spectroscopy of the crude product. [b] The *de* values were determined by HPLC analysis.

entries 1 and 8, Table 3). An even stronger decrease in diastereoselectivity was observed upon switching from PPh_2Cy to $PPhCy_2$ (from 83% to 23% *de*, *anti* isomer, entries 8 and 9, Table 3). Moreover, a reversal of diastereoselectivity was observed in the hydrogenation of **1** with PCy_3, since in this case, the *syn*-1,3-diol was obtained as the major product (27% *de* for the *syn*-1,3-diol, entry 10, Table 3). It appears from these data that an increase in the cone angle values results in a decrease in the diastereoselectivity. With a phosphane bearing a higher cone angle value (θ = 182°) such as

Table 5. Synthesis of variously substituted β-hydroxy ketones from enantiomerically enriched β-hydroxy esters.



Hydroxy ester — Weinreb amide — Hydroxy ketone

Entry	Hydroxy ester	Weinreb amide	Yield	Hydroxy ketone	Yield
1	**3**, 99% *ee*	**10**	87%	**1**	85%
2				**17**	75%
3	**4**, 95% *ee*	**11**	97%	**18**	98%
4				**19**	89%
5	**5**, 98% *ee*	**12**	91%	**20**	80%
6				**21**	64%
7				**22**	81%
8				**23**	80%
9	**6**, 98% *ee*	**13**	77%	**24**	90%
10				**25**	80%
11	**7**, 99% *ee*	**14**	70%	**26**	70%
12	**8**, 99% *ee*, 99% *de*	**15**	91%	**27**	77%
13	**9**, 99% *ee*	**16**	82%	**28**	60%

$P(tBu)_3$, the hydrogenation failed to afford any conversion because the related steric hindrance was the highest (entry 11, Table 3). A correlation between the cone angles and the stereochemical issues of the hydrogenation reaction of compound **1** with PPh_3, PPh_2Cy, $PPhCy_2$, and PCy_3 can be visualized in Figure 3. We have also observed this significant decrease in selectivity upon moving from PPh_3 to PCy_3 in the hydrogenation reactions of β-hydroxy ketones **18** and **20**.

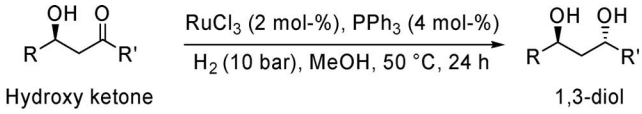
Achiral diphosphanes were also tested in the hydrogenation reaction of compound **1**. However, the $RuCl_3$/diphosphane combination failed to afford complete conversion because of the lower activity of the relevant ruthenium complex. The hydrogenation reactions of **1** were therefore conducted under the standard conditions by using the [Ru(PP)Br_2] complexes,[8] prepared in situ from commercially available [Ru(COD)(2-methylallyl)$_2$] and the diphosphane by addition of hydrobromic acid (Table 4). Thus, with dppe [1,2-bis(diphenylphosphanyl)ethane], dppp [1,3-bis(diphenylphosphanyl)propane], dppb [1,4-bis(diphenylphosphanyl)-butane], or 1,5-bis(diphenylphosphanyl)pentane as diphosphanes, the reaction proceeded quantitatively and delivered the corresponding *anti*-1,3-diol **2** with good diastereoselectivities (91–93% *de*, entries 2, 4–5, Table 4), except for dppp (78% *de*, entry 3, Table 4).

However, hydrogenation of **1** with dppm [bis(diphenylphosphanyl)methane] and 1,6-bis(diphenylphosphanyl)hexane afforded the *anti*-diol **2** with lower conversions and moderate to high diastereoselectivities (75–92% *de*, entries 1 and 6, Table 4). Full conversion was obtained with 1,1′-bis(diphenylphosphanyl)ferrocene, although a lower *de* was observed (72% *de*, entry 7, Table 4). Finally, with the 1,2-bis(diphenylphosphanyl)benzene and 1,2-bis(dicyclohexylphosphanyl)ethane ligands, diol **2** was obtained with good *de* albeit with low conversions (89–92% *de*, entries 8–9, Table 4).

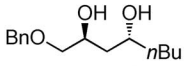
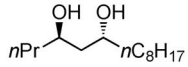
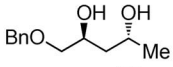
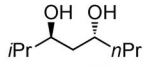
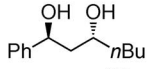
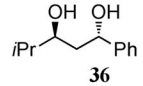
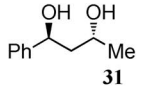
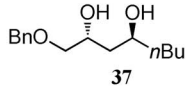
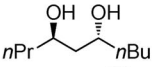
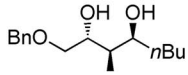
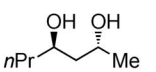
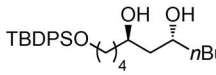
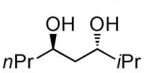
In order to establish the generality of the $RuCl_3/PPh_3$-promoted hydrogenation, the reaction was applied to a series of β-hydroxy ketones **1**, **17**–**28** bearing various substitution patterns. These compounds were first synthesized by starting from enantiomerically pure or enriched β-hydroxy esters **3**–**9** (Table 5).

These readily accessible compounds were first converted into their corresponding Weinreb amides[15] **10**–**16** in yields of 70–97% by reaction with *N*,*O*-dimethylhydroxylamine hydrochloride and *n*-butyllithium.[16] Subsequent addition

Table 6. Substrate scope of the $RuCl_3/PPh_3$ mediated diastereoselective hydrogenation of β-hydroxy ketones.[a]



Hydroxy ketone — 1,3-diol

Entry	Substrate	Product	Yield [%][b]	*de*, *anti* [%]	Entry	Substrate	Product	Yield [%][b]	*de*, *anti* [%]
1	**1**	 **2**	96	91[c] (88)[d]	8	**23**	 **35**	95	98[e]
2	**17**	 **29**	93	95[c]	9	**24**	 **34**	98	94[e]
3	**18**	 **30**	94	96[c] (92)[d]	10	**25**	 **36**	60[f]	85[c]
4	**19**	 **31**	95	97[c] (80)[d]	11	**26**	 **37**	95	89[c]
5	**20**	 **32**	95	97[e] (92)[d]	12	**27**	 **38**	99	94[c]
6	**21**	 **33**	94	98[e]	13	**28**	 **39**	18[g]	94[c]
7	**22**	 **34**	90	95[e]					

[a] All reactions were performed with 0.5 mmol of substrate in 2 mL of MeOH. [b] Isolated yield after column chromatography. [c] The *de* values were determined by HPLC analysis. [d] The *de* values were obtained after reduction of the β-hydroxy ketones with $Me_4NBH(OAc)_3$. [e] The *de* values were determined by GC analysis of the corresponding Mosher diesters. [f] Together with 38% of recovered starting material. [g] Together with 58% of recovered starting material.

of various alkyllithium reagents to these compounds then afforded the corresponding β-hydroxy ketones **1**, **17**–**28** in essentially good yields.

Applying the optimized conditions, these compounds were reduced with good to excellent diastereoselectivities into the corresponding *anti*-1,3-diols **2**, **29**–**39** (Table 6). By using the $RuCl_3/PPh_3$-catalyzed hydrogenation procedure, a series of variously substituted diols bearing phenyl or benzyloxy groups as well as linear and branched alkyl chains were prepared in good yields (entries 1–13, Table 6). Starting from β-hydroxy ketone **26**, which is the antipode of **1**, the corresponding diol **37** was obtained in high yield and with comparable diastereoselectivity (89% *de*, entry 11 vs. 91% *de*, entry 1, Table 6). α-Substituted β-hydroxy ketones were also examined. $RuCl_3/PPh_3$-promoted hydrogenation of compound **27** bearing a methyl substituent in the α position afforded **38** in excellent yield and with high *anti* diastereoselectivity (99% yield, 94% *de*, entry 12, Table 6). Finally, hydrogenation of substrate **28**, bearing a *tert*-butyldiphenylsilyl ether function, under the standard conditions failed to afford the corresponding diol in reasonable yield. In this case, only 18% of diol **39** was obtained together with 58% of recovered starting material and 24% of the triol resulting from deprotection of the silyl ether (entry 13, Table 6). For this compound, the use of the ruthenium complex prepared by treatment of $[RuCl_2(\eta^6\text{-benzene})]_2$ with PPh_3 and $Et_2NH.HCl$[9] at a higher hydrogen pressure (80 bar) allowed the formation of the expected diol in a more reasonable yield of 50%, with no deprotection of the silyl ether observed. For comparison, a number of β-hydroxy ketones were reduced with $Me_4NBH(OAc)_3$. In all cases, the $RuCl_3/PPh_3$-mediated hydrogenation afforded the *anti*-1,3-diols with either comparable selectivities (entries 1, 3, and 5, Table 6) or significantly higher diastereomeric excess (97% vs. 80%, entry 4, Table 6).

Conclusions

In summary, we have shown that the inexpensive $RuCl_3/PPh_3$ combination can be used efficiently for the ruthenium-catalyzed diastereoselective hydrogenation of β-hydroxy ketones. On the basis of the simplicity of the procedure, we think this should be a valuable alternative to well-established methods involving boron reagents for the preparation of *anti*-1,3-diols. Moreover, this catalytic procedure generates no waste, avoids the need for aqueous work-up and is particularly suitable for large-scale reactions. On the other hand, achiral diphosphanes can also be used for the diastereoselective reduction of β-hydroxy ketones by using the related $[Ru(PP)Br_2]$ complexes.

Experimental Section

General: Unless specially mentioned, all reactions were carried out under an argon atmosphere. All solvents were reagent grade and were distilled under a positive pressure of argon prior to use. Amines were dried and then distilled from potassium hydroxide. CH_2Cl_2 was dried and then distilled from calcium hydride. THF and Et_2O were distilled from sodium-benzophenone. *n*-Butyllithium was purchased as 2.5 M solutions in hexanes and titrated before use. Other commercially available reagents were used without further purification. Nuclear magnetic resonance: ^1H and ^{13}C NMR spectra were recorded at room temperature either at 200 MHz and 50 MHz, respectively, with an AC200 Bruker spectrometer, or at 300 MHz and 75 MHz, respectively, with an Avance 300 Bruker spectrometer. The chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm; the signals of residual $CHCl_3$ (δ = 7.26 ppm) and $CDCl_3$ (δ = 77.0 ppm) are used as internal standards. Coupling constants (J) are given in Hertz (Hz). The abbreviations m, s, d, t, q, quint, sext, and sept stand for multiplet, singlet, doublet, triplet, quartet, quintet, sextet, and septet, respectively. Infrared spectra (IR) were recorded with either a Perkin–Elmer 783G spectrometer or an IRFT Nicolet 205 spectrometer. Mass spectra (MS) were measured with a Nermag R10–10C mass spectrometer (DCI/NH_3) and a PE Sciex API 3000 mass spectrometer (ESI). Flash column chromatography was performed with Merck silica gel (0.040–0.063 mesh). TLC analysis was performed with Merck silica gel 60 PF 254 and revealed either by UV light at 254 nm or by a potassium permanganate solution. Optical rotation values were recorded with a Perkin–Elmer 241 polarimeter at 589 nm (sodium lamp). High-performance liquid chromatography analyses (HPLC) were performed with a Waters instrument (Waters 486 detector, 717 autosampler equipped with Daicel Chiralcel OA, OB, OD, OD-H, OJ, and Chiralpack AD and AS-H). Elemental analysis was performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie.

Synthesis of the β-Hydroxy Esters 3–9: Compounds **3**, **4**, **5**, **6**, **7**, and **9** were prepared by ruthenium-mediated asymmetric hydrogenation of the corresponding β-keto esters according to reported procedures.[17,18] The preparation of β-hydroxy ester **8** is described below.

Ethyl (2*R*,3*S*)-4-Benzyloxy-3-hydroxy-2-methylbutyrate (8): A solution of β-hydroxy ester **7** (5.0 g, 21.0 mmol) in THF (40 mL) was added dropwise to a solution (–78 °C) of LDA (50.4 mmol) in THF (30 mL). After stirring at –78 °C for 1 h, HMPA (4.4 mL, 25.2 mmol) and methyl iodide (11.8 mL, 189 mmol) were added. The reaction mixture was gradually warmed to –5 °C over 3.5 h, then cooled to –50 °C and quenched with saturated aqueous NH_4Cl. After extraction with Et_2O, the combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel (elution with cyclohexane/AcOEt: 75:25) afforded **8** (3.6 g, 68%) as a colorless oil. R_f = 0.25 (cyclohexane/AcOEt, 75:25). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.19 (d, J = 7.1 Hz, 3 H, 5-H), 1.26 (t, J = 7.2 Hz, 3 H, 7-H), 2.73 (approx. quint, J = 7.1 Hz, 1 H, 2-H), 3.52 (dd, J = 3.9 and 9.9 Hz, 1 H, 4-H), 3.58 (dd, J = 5.4 and 9.9 Hz, 1 H, 4′-H), 3.88–3.93 (m, 1 H, 3-H), 4.13 (q, J = 7.2 Hz, 2 H, 6-H), 4.53 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.59 (d, J = 12.0 Hz, 1 H, CH_2Ph), 7.28–7.39 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 14.1, 42.4, 60.5, 71.8, 72.3, 73.4, 127.7 (2 C), 128.4, 137.9, 175.4 ppm. $[\alpha]_D^{25}$ = +26.7 (c = 1.4, MeOH), lit.:[19] $[\alpha]_D^{21}$ = +24.6 (c = 1.3, MeOH).

General Procedure for the Preparation of Weinreb Amides from the Corresponding β-Hydroxy Esters: To a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (6.69 g, 67.2 mmol) in THF (120 mL) was added *n*BuLi (134 mmol) at –78 °C. After stirring at room temperature for 10 min, the mixture was cooled to –78 °C, and a solution of the β-hydroxy ester (22.4 mmol) in THF (35 mL) was added. The reaction mixture was stirred at –78 °C for 2 h, then

quenched with saturated aqueous NH_4Cl and warmed to room temperature. After extraction with Et_2O, the combined organic layers were dried with $MgSO_4$ and concentrated. Purification of the residue by flash chromatography on silica gel (elution with cyclohexane/AcOEt) afforded the corresponding pure Weinreb amide (4.5 g, 21.7 mmol, 97%).

(3*S*)-4-(Benzyloxy)-3-hydroxy-*N*-methoxy-*N*-methylbutanamide (10): 4.6 g, 87% yield, pale yellow oil. R_f = 0.63 (cyclohexane/AcOEt, 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.66 (m, 2 H, 2-H), 3.19 (s, 3 H, OMe), 3.54 (d, J = 5.4 Hz, 2 H, 4-H), 3.68 (s, 3 H, NMe), 4.26 (m, 1 H, 3-H), 4.58 (s, 2 H, 5-H), 7.25–7.37 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.8, 35.2, 61.2, 67.2, 73.2, 73.4, 127.6 (2 C), 128.4, 138.1, 173.1 ppm. MS (DCI/NH_3): m/z = 254 $[M + H]^+$, 271 $[M + NH_4]^+$. IR (neat): $\tilde{\nu}$ = 3431, 3063, 3027, 2940, 2858, 1650 cm^{-1}. $[\alpha]_D^{25}$ = –31.3 (c = 1.12, $CHCl_3$), lit.:[20] $[\alpha]_D^{18}$ = –25.7 (c = 3.0, $CHCl_3$). $C_{13}H_{19}NO_4$ (253.29): calcd. C 61.64, H 7.56, N 5.53; found C 61.31, H 7.85, N 5.54.

(3*S*)-3-Hydroxy-*N*-methoxy-*N*-methyl-3-phenylpropanamide (11): 4.5 g, 97% yield, pale yellow oil. R_f = 0.14 (cyclohexane/AcOEt, 6:4). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.78 (dd, J = 16.6 and 9.2 Hz, 1 H, 2-H), 2.88 (dd, J = 16.6 and 2.5 Hz, 1 H, 2′-H), 3.21 (s, 3 H, NMe), 3.63 (s, 3 H, OMe), 5.15 (dt, J = 2.5 and 9.2 Hz, 1 H, 3-H), 7.25–7.42 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.0, 40.6, 61.4, 70.3, 125.8, 127.6, 128.5, 143.1, 173.3 ppm. IR (neat): $\tilde{\nu}$ = 3420, 3070, 3040, 2980, 2940, 1700, 755, 700 cm^{-1}. $[\alpha]_D^{25}$ = –76.7 (c = 1.00, $CHCl_3$), lit.:[21] $[\alpha]_D^{23}$ = –36.6 (c = 1.0, $CHCl_3$), 47% *ee*.

(3*R*)-3-Hydroxy-*N*-methoxy-*N*-methylhexanamide (12): 4.2 g, 91% yield, pale yellow oil. R_f = 0.19 (cyclohexane/AcOEt, 1:1). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.93 (t, J = 6.9 Hz, 3 H, 6-H), 1.50 (m, 4 H, 4-H and 5-H), 2.44 (dd, J = 16.9 and 9.3 Hz, 1 H, 2-H), 2.68 (d, J = 16.9 and 2.0 Hz, 1 H, 2′-H), 3.21 (s, 3 H, NMe), 3.70 (s, 3 H, OMe), 4.04 (m, 1 H, 3-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 18.8, 31.9, 38.3, 38.7, 61.3, 67.7, 174.0 ppm. MS (DCI/NH_3): m/z = 176 $[M + H]^+$, 193 $[M + NH_4]^+$. IR (neat): $\tilde{\nu}$ = 3546, 2959, 2935, 2873, 1654 cm^{-1}. $[\alpha]_D^{25}$ = –53.3 (c = 1.2, $CHCl_3$), lit.:[21] $[\alpha]_D^{23}$ = –2.7 (c = 0.8, $CHCl_3$), 23% *ee*.

(3*S*)-3-Hydroxy-*N*-methoxy-*N*,4-dimethylpentanamide (13): 3.5 g, 77% yield, pale yellow oil. R_f = 0.27 (cyclohexane/AcOEt, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, J = 6.7 Hz, 3 H, MeCH), 0.94 (d, J = 6.7 Hz, 3 H, MeCH), 1.70 (sept, J = 6.7 Hz, 1 H, 4-H), 2.41 (dd, J = 16.5 and 9.9 Hz, 1 H, 2-H), 2.62 (d, J = 16.5 Hz, 1 H, 2′-H), 3.17 (s, 3 H, NMe), 3.67 (s, 3 H, OMe), 3.75 (m, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0, 18.5, 32.0, 33.2, 35.2, 61.3, 72.7, 174.4 ppm. MS (DCI/NH_3): m/z = 176 $[M + H]^+$. IR (neat): $\tilde{\nu}$ = 3470, 2960, 2940, 2875, 1650 cm^{-1}. $[\alpha]_D^{25}$ = –63.3 (c = 1.0, $CHCl_3$), lit.:[21] $[\alpha]_D^{23}$ = –27.8 (c = 0.8, $CHCl_3$), 47% *ee*.

(3*R*)-4-(Benzyloxy)-3-hydroxy-*N*-methoxy-*N*-methylbutanamide (14): 3.7 g, 70% yield, pale yellow oil. R_f = 0.63 (cyclohexane/AcOEt, 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.66 (m, 2 H, 2-H), 3.19 (s, 3 H, NMe), 3.54 (d, J = 5.4 Hz, 2 H, 4-H), 3.68 (s, 3 H, OMe), 4.26 (m, 1 H, 3-H), 4.58 (s, 2 H, 5-H), 7.25–7.37 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.8, 35.2, 61.2, 67.2, 73.2, 73.4, 127.6 (2 C), 128.4, 138.1, 173.1 ppm. MS (DCI/NH_3): m/z = 254 $[M + H]^+$, 271 $[M + NH_4]^+$. IR (neat): $\tilde{\nu}$ = 3431, 3063, 3027, 2940, 2858, 1650 cm^{-1}. $[\alpha]_D^{25}$ = +31.0 (c = 1.10, $CHCl_3$). $C_{13}H_{19}NO_4$ (253.29): calcd. C 61.64, H 7.56, N 5.53; found C 61.31, H 7.85, N 5.54.

(2*S*,3*R*)-4-Benzyloxy-3-hydroxy-*N*-methoxy-2,*N*-dimethylbutanamide (15): 2.5 g, 91% yield, pale yellow oil. R_f = 0.18 (cyclohexane/AcOEt, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.23 (d, J = 7.2 Hz, 3 H, MeCH), 3.17 (s, 3 H, NMe), 3.14–3.23 (m, 1 H, 2-H), 3.47 (dd, J = 5.7 and 9.6 Hz, 1 H, 4-H), 3.53 (dd, J = 5.9 and 9.6 Hz, 1 H, 4′-H), 3.67 (s, 3 H, OMe), 3.88 (q, J = 5.4 Hz, 1 H, 3-H), 4.46 (d, J = 12.0 Hz, 1 H, 5-H), 4.52 (d, J = 12.0 Hz, 1 H, 5′-H), 7.26–7.34 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 31.8, 36.5, 61.5, 72.6, 73.0, 73.4, 127.7 (2 C), 128.3, 138.1, 177.5 ppm.

(3*R*)-7-(*tert*-Butyldiphenylsilyloxy)-3-hydroxy-*N*-methoxy-*N*-methylheptanamide (16): 1.2 g, 82% yield, colorless oil. R_f = 0.20 (cyclohexane/AcOEt, 7:3). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, *t*Bu), 1.35–1.70 (m, 6 H, 4-H, 5-H and 6-H), 2.43 (dd, J = 16.8 and 9.6 Hz, 1 H, 2-H), 2.65 (d, J = 16.8 Hz, 1 H, 2′-H), 3.20 (s, 3 H, NMe), 3.67 (s, 3 H, OMe), 3.67 (t, J = 6.3 Hz, 2 H, 7-H), 3.95–4.05 (m, 1 H, 3-H), 7.34–7.46 (m, 6 H, Ph), 7.64–7.70 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2, 21.8, 26.8, 31.8, 32.4, 36.2, 38.1, 61.2, 63.8, 67.8, 127.5, 129.5, 134.0, 135.5, 173.9 ppm. IR (neat): $\tilde{\nu}$ = 3452, 1648 cm^{-1}. $[\alpha]_D^{25}$ = –20.2 (c = 1.25, $CHCl_3$).

General Procedure for the Preparation of β-Hydroxy Ketones from the Corresponding Weinreb Amides: To a solution of the Weinreb amide (9.6 mmol) in THF (20 mL) at –78 °C was added dropwise a solution of the corresponding alkyllithium (28.7 mmol). After stirring at –78 °C for 0.5–2 h, the reaction mixture was quenched with methanol and saturated aqueous NH_4Cl, then warmed to room temperature and extracted with Et_2O. The combined organic layers were dried with $MgSO_4$ and concentrated. Purification of the residue by flash chromatography on silica gel (elution with cyclohexane/AcOEt) afforded the pure β-hydroxy ketone.

(2*S*)-1-(Benzyloxy)-2-hydroxyoctan-4-one (1):[17] 2.4 g, 85% yield, colorless oil. R_f = 0.47 (cyclohexane/AcOEt, 6:4). ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.90 (t, J = 7.4 Hz, 3 H, 8-H), 1.30 (sext, J = 7.4 Hz, 2 H, 7-H), 1.55 (m, 2 H, 6-H), 2.44 (t, J = 7.4 Hz, 2 H, 5-H), 2.63 (m, 2 H, 3-H), 3.44 (dd, J = 9.6 and 5.8 Hz, 1 H, 1-H), 3.49 (dd, J = 9.6 and 4.8 Hz, 1 H, 1′-H), 4.26 (m, 1 H, 2-H), 4.54 (d, J = 12.4 Hz, 1 H, 9-H), 4.58 (d, J = 12.4 Hz, 1 H, 9′-H), 7.25–7.38 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 22.3, 25.7, 43.5, 45.8, 67.0, 73.3, 73.5, 127.8 (2 C), 128.5, 138.0, 211.2 ppm. MS (DCI/NH_3): m/z = 251 $[M + H]^+$, 268 $[M + NH_4]^+$. IR (thin film): $\tilde{\nu}$ = 3467, 3058, 3027, 2966, 2930, 2868, 1706 cm^{-1}. $[\alpha]_D^{25}$ = –15.2 (c = 0.91, $CHCl_3$).

(4*S*)-5-(Benzyloxy)-4-hydroxypentan-2-one (17): 1.0 g, 75% yield, colorless oil. R_f = 0.64 (cyclohexane/AcOEt, 6:4). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, 1-H), 2.61 (dd, J = 17.4 and 5.2 Hz, 1 H, 3-H), 2.71 (dd, J = 17.4 and 6.6 Hz, 1 H, 3′-H), 3.43 (dd, J = 9.7 and 5.8 Hz, 1 H, 5-H), 3.49 (dd, J = 9.7 and 4.7 Hz, 1 H, 5′-H), 4.26 (m, 1 H, 4-H), 4.52 (d, J = 12.0 Hz, 1 H, 6-H), 4.58 (d, J = 12.0 Hz, 1 H, 6′-H), 7.25–7.3 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.9, 46.7, 66.9, 73.3, 73.5, 127.8, 127.9, 128.5, 138.0, 209.7 ppm. MS (DCI/NH_3): m/z = 209 $[M + H]^+$, 226 $[M + NH_4]^+$. IR (neat): $\tilde{\nu}$ = 3452, 3063, 3032, 2909, 2863, 1721 cm^{-1}. $[\alpha]_D^{25}$ = –15.5 (c = 1.36, $CHCl_3$), lit.:[22] $[\alpha]_D^{25}$ = –13.8 (c = 0.58, CH_2Cl_2), 98% *ee*.

(1*S*)-1-Hydroxy-1-phenylheptan-3-one (18): 1.9 g, 98% yield, pale yellow oil. R_f = 0.31 (cyclohexane/AcOEt, 7:3). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 3 H, 7-H), 1.31 (sext, J = 7.4 Hz, 2 H, 6-H), 1.57 (quint, J = 7.5 Hz, 2 H, 5-H), 2.44 (t, J = 7.3 Hz, 2 H, 4-H), 2.78 (dd, J = 17.2 and 4.1 Hz, 1 H, 2-H), 2.86 (dd, J = 17.2 and 8.3 Hz, 1 H, 2′-H), 5.16 (dt, J = 8.3 and 3.6 Hz, 1 H, 1-H), 7.25–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 22.2, 25.6, 43.4, 51.0, 69.9, 125.6, 127.6, 128.5, 142.9, 211.6 ppm. MS (DCI/NH_3): m/z = 189 $[M – H_2O + H]^+$, 206 $[M + H]^+$, 224 $[M + NH_4]^+$. IR (neat): $\tilde{\nu}$ = 3430,

3070, 3040, 2970, 2940, 1730, 760, 700 cm^{-1}. $[\alpha]_D^{25}$ = –61.6 (c = 1.00, $CHCl_3$), lit.:[21] $[\alpha]_D^{23}$ = –30.8 (c = 0.6, $CHCl_3$), 46% *ee*.

(4*S*)-4-Hydroxy-4-phenylbutan-2-one (19): 0.7 g, 89% yield, pale yellow oil. R_f = 0.21 (cyclohexane/AcOEt, 7:3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3 H, 1-H), 2.81 (dd, J = 17.7 and 3.8 Hz, 1 H, 3-H), 2.90 (dd, J = 17.7 and 8.7 Hz, 1 H, 3′-H), 5.16 (dd, J = 3.8 and 8.7 Hz, 1 H, 4-H), 7.25–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.8, 52.0, 69.9, 125.6, 127.7, 128.6, 142.8, 209.1 ppm. MS (DCI/NH_3): = m/z 147 [M – H_2O + H]$^+$, 164 [M – H_2O + NH_4]$^+$, 182 [M + NH_4]$^+$. IR (thin film): $\tilde{\nu}$ = 3460, 3065, 2980, 2940, 1720, 760, 705 cm^{-1}. $[\alpha]_D^{25}$ = –76.1 (c = 0.50, $CHCl_3$), lit.:[23] $[\alpha]_D^{20}$ = –51.3 (c = 1.0, $CHCl_3$), 79% *ee*.

(7*R*)-7-Hydroxydecan-5-one (20):[24] 3.1 g, 80% yield, pale yellow oil. R_f = 0.65 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 3 H, 1-H or 10-H), 0.92 (t, J = 7.2 Hz, 3 H, 1-H or 10-H), 1.43 (m, 8 H, 2-H, 3-H, 8-H and 9-H), 2.36 (t, J = 7.6 Hz, 2 H, 4-H), 2.52 (dd, J = 17.6 and 8.6 Hz, 1 H, 6-H), 2.60 (dd, J = 17.6 and 3.4 Hz, 1 H, 6′-H), 4.03 (m, 1 H, 7-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 14.0, 18.7, 22.3, 25.7, 38.7, 43.4, 49.1, 67.4, 212.5 ppm. MS (DCI/NH_3): m/z = 173 [M + H]$^+$, 190 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3452, 2966, 2930, 2870, 1711 cm^{-1}. $[\alpha]_D^{25}$ = –38.4 (c = 1.26, $CHCl_3$).

(4*R*)-4-Hydroxyheptan-2-one (21): 0.48 g, 64% yield, pale yellow oil. R_f = 0.10 (cyclohexane/AcOEt, 7:3). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, J = 6.6 Hz, 3 H, 7-H), 1.36 (m, 4 H, 5-H and 6-H), 2.18 (s, 3 H, 1-H), 2.50 (dd, J = 16.4 and 8.4 Hz, 1 H, 3-H), 2.64 (dd, J = 16.4 and 3.5 Hz, 1 H, 3′-H), 4.04 (m, 1 H, 4-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 18.7, 30.8, 38.6, 50.1, 67.3, 210.1 ppm. MS (DCI/NH_3): m/z = 132 [M + H]$^+$, 148 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3426, 2960, 2925, 2873, 1701 cm^{-1}. $[\alpha]_D^{25}$ = –49.6 (c = 0.23, $CHCl_3$), lit.:[25] $[\alpha]_D^{25}$ = –48.0 (c = 0.38, $CHCl_3$).

(5*R*)-5-Hydroxy-2-methyloctan-3-one (22):[24] 0.8 g, 81% yield, colorless oil. R_f = 0.52 (cyclohexane/AcOEt, 8:2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.92 (t, J = 7.0 Hz, 3 H, 8-H), 1.10 (d, J = 6.6 Hz, 6 H, Me_2CH), 1.29–1.45 (m, 4 H, 6-H and 7-H), 2.41–2.61 (m, 3 H, 2-H and 4-H), 3.95–3.98 (m, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 18.0 (2 C), 18.7, 38.6, 41.4, 46.5, 67.4, 216.2 ppm. MS (DCI/NH_3): m/z = 159 [M + H]$^+$, 176 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3430, 2960, 2929, 2873, 1705 cm^{-1}. $C_9H_{18}O_2$ (158.24): calcd. C 68.31, H 11.47; found C 67.96, H 11.74.

(4*R*)-4-Hydroxytetradecan-6-one (23):[17] 1.6 g, 80% yield, pale yellow oil. R_f = 0.63 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 3 H, 1-H or 14-H), 0.95 (t, J = 7.2 Hz, 3 H, 1-H or 14-H), 1.25 (br. s, 12 H, 8-H, 9-H, 10-H, 11-H, 12-H and 13-H), 1.50 (m, 4 H, 2-H and 3-H), 2.41 (t, J = 7.4 Hz, 2 H, 7-H), 2.46 (dd, J = 16.4 and 8.4 Hz, 1 H, 5-H), 2.60 (dd, J = 16.4 and 3.7 Hz, 1 H, 5′-H), 4.05 (m, 1 H, 4-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 14.0, 18.6, 22.6, 23.6, 29.1, 29.2, 29.3, 31.8, 38.6, 43.7, 48.9, 67.3, 212.6 ppm. MS (DCI/NH_3): m/z = 229 [M + H]$^+$, 246 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3518, 2966, 2950, 2827, 1705 cm^{-1}. $[\alpha]_D^{25}$ = –28.7 (c = 1.10, $CHCl_3$).

(6*S*)-6-Hydroxy-7-methyloctan-4-one (24):[27] 0.95 g, 90% yield, pale yellow oil. R_f = 0.22 (petroleum ether/Et_2O, 7:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, J = 6.8 Hz, 3 H, MeCH), 0.92 (t, J = 7.4 Hz, 3 H, 1-H), 0.93 (d, J = 6.8 Hz, 3 H, MeCH), 1.61 (sext, J = 7.4 Hz, 2 H, 2-H), 1.68 (m, 1 H, 4-H), 2.42 (t, J = 7.4 Hz, 2 H, 3-H), 2.47 (dd, J = 17.3 and 9.3 Hz, 1 H, 5-H), 2.58 (dd, J = 17.3 and 2.8 Hz, 1 H, 5′-H), 3.80 (ddd, J = 9.3, 2.8 and 5.9 Hz, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 17.0, 17.7, 18.3, 32.9, 45.5, 45.8, 72.2, 212.7 ppm. MS (DCI/NH_3): m/z = 141 [M – H_2O + H]$^+$, 159 [M + H]$^+$, 176 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3440, 2970, 2940, 2880, 1715 cm^{-1}. $[\alpha]_D^{25}$ = –61.7 (c = 1.60, $CHCl_3$).

(3*S*)-3-Hydroxy-4-methyl-1-phenylpentan-1-one (25): 0.6 g, 80% yield, pale yellow oil. R_f = 0.55 (cyclohexane/AcOEt, 6:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, J = 6.8 Hz, 3 H, 5-H), 1.02 (d, J = 6.8 Hz, 3 H, 5′-H), 1.81 (m, 1 H, 4-H), 3.03 (dd, J = 17.5 and 9.4 Hz, 1 H, 2-H), 3.18 (dd, J = 17.5 and 2.5 Hz, 1 H, 2′-H), 4.00 (ddd, J = 9.4, 5.6 and 2.5 Hz, 1 H, 3-H), 7.40 (m, 2 H, Ph), 7.56 (m, 1 H, Ph), 7.95 (m, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0, 18.6, 33.2, 42.1, 72.5, 128.2, 128.7, 133.5, 137.1, 201.4 ppm. MS (DCI/NH_3): m/z = 193 [M + H]$^+$, 210 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3470, 3070, 2970, 2940, 2880, 1680, 755, 690 cm^{-1}. $[\alpha]_D^{25}$ = –83.0 (c = 0.50, $CHCl_3$), lit.:[27] $[\alpha]_D^{23}$ = –67.7 (c = 1.43, $CHCl_3$), 98% *ee*.

(2*R*)-1-(Benzyloxy)-2-hydroxyoctan-4-one (26):[6] 2.0 g, 70% yield, colorless oil. R_f = 0.47 (cyclohexane/AcOEt, 6:4). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90 (t, J = 7.4 Hz, 3 H, 8-H), 1.30 (sext, J = 7.4 Hz, 2 H, 7-H), 1.55 (m, 2 H, 6-H), 2.44 (t, J = 7.4 Hz, 2 H, 5-H), 2.63 (m, 2 H, 3-H), 3.44 (dd, J = 9.6 and 5.8 Hz, 1 H, 1-H), 3.49 (dd, J = 9.6 and 4.8 Hz, 1 H, 1′-H), 4.26 (m, 1 H, 2-H), 4.54 (d, J = 12.4 Hz, 1 H, 9-H), 4.58 (d, J = 12.4 Hz, 1 H, 9′-H), 7.25–7.38 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 22.3, 25.7, 43.5, 45.8, 67.0, 73.3, 73.5, 127.8 (2 C), 128.5, 138.0, 211.2 ppm. MS (DCI/NH_3): m/z = 251 [M + H]$^+$, 268 [M + NH_4]$^+$. IR (thin film): $\tilde{\nu}$ = 3467, 3058, 3027, 2966, 2930, 2868, 1706 cm^{-1}. $[\alpha]_D^{25}$ = +15.2 (c = 0.9, $CHCl_3$).

(2*R*,3*S*)-1-Benzyloxy-2-hydroxy-3-methyloctan-4-one (27):[6] 0.9 g, 77% yield, colorless oil. R_f = 0.25 (cyclohexane/AcOEt, 8:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.4 Hz, 3 H, 8-H), 1.07 (d, J = 7.3 Hz, 3 H, MeCH), 1.27–1.35 (m, 2 H, 7-H), 1.49–1.57 (m, 2 H, 6-H), 2.37–2.57 (m, 2 H, 5-H), 2.82 (quint, J = 7.2 Hz, 1 H, 3-H), 3.45–3.56 (m, 2 H, 1-H), 3.87–3.90 (m, 1 H, 2-H), 4.48 (d, J = 12.0 Hz, 1 H, 9-H), 4.54 (d, J = 12.0 Hz, 1 H, 9′-H), 7.26–7.37 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 13.8, 22.3, 25.3, 42.6, 47.7, 72.2, 72.7, 73.5, 127.7, 127.8, 128.4, 137.8, 215.3 ppm. $[\alpha]_D^{25}$ = +37.1 (c = 1.1, MeOH).

(7*R*)-11-(*tert*-Butyldiphenylsilyloxy)-7-hydroxyundecan-5-one (28): 0.8 g, 60% yield, colorless oil. R_f = 0.69 (cyclohexane/AcOEt, 7:3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (t, J = 7.4 Hz, 3 H, 1-H), 1.05 (s, 9 H, *t*Bu), 1.25–1.75 (m, 10 H, 2-H, 3-H, 8-H, 9-H and 10-H), 2.43 (t, J = 7.4 Hz, 2 H, 4-H), 2.47 (dd, J = 8.8 and 17.5 Hz, 1 H, 6-H), 2.57 (dd, J = 3.1 and 17.5 Hz, 1 H, 6′-H), 3.67 (t, J = 6.2 Hz, 2 H, 11-H), 3.95–4.05 (m, 1 H, 7-H), 7.32–7.45 (m, 6 H, Ph), 7.62–7.69 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 19.2, 21.7, 22.3, 25.7, 26.9, 32.4, 36.1, 43.4, 48.8, 63.7, 67.5, 127.6, 129.5, 134.1, 135.5, 212.5 ppm. $[\alpha]_D^{25}$ = –17.6 (c = 0.9, $CHCl_3$).

Typical Procedure for the Synthesis of 1,3-*anti*-Diols from the Corresponding β-Hydroxy Ketones: The β-hydroxyketone (0.5 mmol) was purged by three vacuum/argon cycles, dissolved in degassed methanol (2 mL), and transferred by cannula to a round-bottomed tube containing a degassed mixture of $RuCl_3$ (2.1 mg, 10 μmol, purchased from Aldrich Chemicals) and PPh_3 (5.2 mg, 20 μmol). The reaction vessel was placed in a stainless steel autoclave, which was purged with hydrogen and pressurized to 10 bar. The autoclave was heated to 50 °C by circulating thermostatted water in the double wall, and magnetic stirring was started as soon as the required temperature was reached. After stirring for 24 h, the autoclave was cooled to room temperature, hydrogen was vented, and the reaction mixture was concentrated in vacuo. Purification of the residue by flash chromatography on silica gel (elution with cyclohexane/AcOEt) afforded the corresponding pure 1,3-diol.

(2*S*,4*R*)-1-(Benzyloxy)octane-2,4-diol (2):[17] R_f = 0.41 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, J = 7.1 Hz, 3 H, 8-H), 1.19–1.70 (m, 8 H, 3-H, 5-H, 6-H and 7-H), 3.37 (dd, J = 9.5 and 7.3 Hz, 1 H, 1-H), 3.44 (dd, J = 9.5 and 4.0 Hz, 1 H, 1′-H), 3.80 (m, 1 H, 4-H), 4.06 (m, 1 H, 2-H), 4.48 (s, 2 H, 9-H), 7.31 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.7, 27.9, 37.2, 39.1, 67.9, 68.8, 73.3, 74.5, 127.7, 127.8, 128.5, 137.9 ppm. MS (DCI/NH_3): m/z = 235 [M – H_2O + H]$^+$, 253 [M + H]$^+$, 270 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3413, 3054, 3034, 2965, 2930, 2860 cm^{-1}. $[\alpha]_D^{25}$ = –4.2 (c = 1.19, $CHCl_3$). HPLC analysis: Column, Chiralcel OD-H; eluent, hexane/propan-2-ol (95:5); flow rate: 1.0 mL/min; detection: 254 nm; $t_{R(2S,4R)}$ = 17.85 min, $t_{R(2S,4S)}$ = 35.42 min.

(2*S*,4*R*)-1-(Benzyloxy)pentane-2,4-diol (29):[17] R_f = 0.25 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (d, J = 6.4 Hz, 3 H, 5-H), 1.55 (m, 2 H, 3-H), 3.39 (dd, J = 9.5 and 7.3 Hz, 1 H, 1-H), 3.48 (dd, J = 9.5 and 4.0 Hz, 1 H, 1′-H), 4.10 (m, 2 H, 2-H and 4-H), 4.55 (s, 2 H, 6-H), 7.31 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.6, 40.8, 64.9, 67.9, 73.3, 74.5, 127.7, 127.8, 128.5, 137.8 ppm. MS (DCI/NH_3): m/z = 211 [M + H]$^+$, 228 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3410, 3055, 3030, 2980, 2930, 2860, 735, 700 cm^{-1}. $[\alpha]_D^{25}$ = –10.4 (c = 1.17, $CHCl_3$). HPLC analysis: Column, Chiralcel OD-H; eluent, hexane/propan-2-ol (90:10); flow rate: 1.0 mL/min; detection: 254 nm; $t_{R(2S,4R)}$ = 12.36 min, $t_{R(2S,4S)}$ = 19.93 min.

(1*S*,3*R*)-1-Phenylheptane-1,3-diol (30): R_f = 0.41 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.0 Hz, 3 H, 7-H), 1.31 (m, 4 H, 5-H and 6-H), 1.51 (m, 2 H, 4-H), 1.84 (ddd, J = 3.4, 7.9 and 11.5 Hz, 1 H, 2-H), 1.91 (ddd, J = 3.4, 7.9 and 11.5 Hz, 1 H, 2′-H), 3.86 (m, 1 H, 3-H), 5.06 (dd, J = 3.4 and 7.9 Hz, 1 H, 1-H), 7.25–7.35 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.8, 27.9, 37.2, 44.6, 69.4, 71.8, 125.6, 127.4, 128.5, 144.7 ppm. MS (DCI/NH_3): m/z = 209 [M + H]$^+$, 226 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3390, 3070, 3040, 2960, 2935, 2870, 750, 700 cm^{-1}. $[\alpha]_D^{25}$ = –42.9 (c = 0.25, $CHCl_3$), lit.:[28] $[\alpha]_D^{20}$ = –43.4 (c = 0.15, $CHCl_3$). HPLC analysis: Column, Chiralcel OD-H; eluent, hexane/propan-2-ol (95:5); flow rate: 1.0 mL/min; detection: 215 nm; $t_{R(1S,3R)}$ = 12.21 min, $t_{R(1S,3S)}$ = 16.01 min.

(1*S*,3*R*)-1-Phenylbutane-1,3-diol (31): R_f = 0.26 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (d, J = 6.4 Hz, 3 H, 4-H), 1.89 (m, 2 H, 2-H), 4.07 (m, 1 H, 3-H), 5.06 (dd, J = 4.0 and 7.5 Hz, 1 H, 1-H), 7.27–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6, 46.2, 65.5, 71.8, 125.7, 127.4, 128.5, 144.6 ppm. MS (DCI/NH_3): m/z = 167 [M + H]$^+$, 184 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3350, 3070, 3040, 2980, 2935, 755, 700 cm^{-1}. $[\alpha]_D^{25}$ = –67.8 (c = 0.22, $CHCl_3$), lit.:[29] $[\alpha]_D^{25}$ = –61.6 (c = 0.7, $CHCl_3$). HPLC analysis: Column, Chiralcel OD-H; eluent, hexane/propan-2-ol (95:5); flow rate: 1.0 mL/min; detection: 215 nm; $t_{R(1S,3R)}$ = 15.57 min, $t_{R(1S,3S)}$ = 22.25 min.

(4*R*,6*R*)-Decane-4,6-diol (32):[30] R_f = 0.46 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.5 Hz, 3 H, 1-H or 10-H), 0.92 (t, J = 6.8 Hz, 3 H, 1-H or 10-H), 1.39 (m, 10 H, 2-H, 3-H, 7-H, 8-H and 9-H), 1.58 (dd, J = 5.3 and 6.2 Hz, 2 H, 5-H), 3.92 (m, 2 H, 4-H and 6-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (2 C), 18.9, 22.7, 28.0, 37.2, 39.6, 42.3, 69.1, 69.4 ppm. MS (DCI/NH_3): m/z = 175 [M + H]$^+$, 192 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3413, 2959, 2935, 2875 cm^{-1}. $[\alpha]_D^{25}$ = –11.5 (c = 0.99, $CHCl_3$). GC analysis [diester with (*S*)-Mosher chloride]: Column, J&W Scientific DB1701; gas, helium; flow: 1 mL/min; $T_{injector}$: 250 °C; $T_{detector}$: 260 °C; T_{oven}: 210 °C (1 min) then 10 °C/min to 250 °C; $t_{R(4R,6R)}$ = 13.29 min, $t_{R(4R,6S)}$ = 14.32 min.

(2*R*,4*R*)-Heptane-2,4-diol (33): R_f = 0.43 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.8 Hz, 3 H, 7-H), 1.20 (d, J = 6.4 Hz, 3 H, 1-H), 1.40 (m, 4 H, 5-H and 6-H), 1.56 (m, 2 H, 3-H), 3.92 (m, 1 H, 4-H), 4.13 (sext, J = 6.0 Hz, 1 H, 2-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 18.9, 23.5, 39.5, 40.0, 65.4, 69.0 ppm. MS (DCI/NH_3): m/z = 133 [M + H]$^+$, 150 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3398, 2969, 2930, 2875 cm^{-1}. $[\alpha]_D^{25}$ = –21.7 (c = 1.15, $CHCl_3$), lit.:[31] $[\alpha]_D^{22}$ = –8.91 (c = 0.63, $CHCl_3$) for 84% *ee*. GC analysis [diester with (*S*)-Mosher chloride]: Column, J&W Scientific DB1701; gas, helium; flow: 1 mL/min; $T_{injector}$: 250 °C; $T_{detector}$: 260 °C; T_{oven}: 210 °C (1 min) then 10 °C/min to 250 °C; $t_{R(2R,4R)}$ = 9.94 min, $t_{R(2S,4R)}$ = 11.19 min.

(3*S*,5*R*)-2-Methyloctane-3,5-diol (34):[26] R_f = 0.44 (cyclohexane/AcOEt, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, J = 6.9 Hz, 3 H, 8-H), 0.94 (d, J = 6.9 Hz, 6 H, Me_2CH), 1.20–1.65 (m, 7 H, 2-H, 4-H, 6-H and 7-H), 3.66 (m, 1 H, 3-H), 3.94 (m, 1 H, 5-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 18.0, 18.6, 19.0, 33.7, 39.4, 39.5, 69.1, 73.8 ppm. IR (neat): $\tilde{\nu}$ = 3420, 2970, 2940 cm^{-1}. $[\alpha]_D^{25}$ = –22.6 (c = 0.50, $CHCl_3$). GC analysis [diester with (*S*)-Mosher chloride]: Column, J&W Scientific DB1701; gas, helium; flow: 1 mL/min; $T_{injector}$: 250 °C; $T_{detector}$: 260 °C; T_{oven}: 210 °C (1 min) then 5 °C/min to 250 °C; $t_{R(3S,5R)}$ = 11.55 min, $t_{R(3S,5S)}$ = 12.21 min.

(4*R*,6*R*)-Tetradecane-4,6-diol (35):[17] R_f = 0.49 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.6 Hz, 3 H, 1-H or 14-H), 0.93 (t, J = 6.6 Hz, 3 H, 1-H or 14-H), 1.26 (br. s, 10 H, 9-H, 10-H, 11-H, 12-H and 13-H), 1.43 (m, 8 H, 2-H, 3-H, 7-H and 8-H), 1.58 (dd, J = 6.0 and 5.1 Hz, 2 H, 5-H), 3.92 (m, 2 H, 4-H and 6-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1 (2C), 18.9, 22.6, 25.8, 29.2, 29.5, 29.6, 31.8, 37.5, 39.6, 42.3, 69.1, 69.4 ppm. MS (DCI/NH_3): m/z = 231 [M + H]$^+$, 248 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3437, 2984, 2954, 2830 cm^{-1}. $[\alpha]_D^{25}$ = –12.0 (c = 1.11, $CHCl_3$). GC analysis [diester with (*S*)-Mosher chloride]: Column, J&W Scientific DB1701; gas, helium; flow: 1 mL/min; $T_{injector}$: 250 °C; $T_{detector}$: 260 °C; T_{oven}: 210 °C (1 min) then 2 °C/min to 250 °C; $t_{R(4R,6R)}$ = 27.52 min, $t_{R(4R,6S)}$ = 30.22 min.

(1*S*,3*S*)-4-Methyl-1-phenylpentane-1,3-diol (36):[32] R_f = 0.19 (cyclohexane/AcOEt, 75:25). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, J = 6.8 Hz, 3 H, MeCH), 0.91 (d, J = 6.8 Hz, 3 H, MeCH), 1.68 (oct, J = 6.5 Hz, 1 H, 4-H), 1.86 (m, 2 H, 2-H), 3.59 (dt, J = 6.0 and 5.8 Hz, 1 H, 3-H), 5.04 (dd, J = 5.0 and 6.5 Hz, 1 H, 1-H), 7.20–7.36 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8, 18.6, 33.8, 41.8, 71.8, 73.9, 125.6, 127.3, 128.5, 144.8 ppm. IR (neat): $\tilde{\nu}$ = 3450, 3070, 3040, 2970, 2945 cm^{-1}. $[\alpha]_D^{25}$ = –73.5 (c = 0.50, $CHCl_3$). HPLC analysis: Column, Chiralcel AS-H; eluent, hexane/propan-2-ol (95:5); flow rate: 1.0 mL/min; detection: 215 nm; $t_{R(1R,3S)}$ = 11.11 min, $t_{R(1S,3S)}$ = 12.14 min.

(2*R*,4*S*)-1-(Benzyloxy)octane-2,4-diol (37):[6] R_f = 0.41 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, J = 7.1 Hz, 3 H, 8-H), 1.19–1.70 (m, 8 H, 3-H, 5-H, 6-H and 7-H), 3.37 (dd, J = 9.5 and 7.3 Hz, 1 H, 1-H), 3.44 (dd, J = 9.5 and 4.0 Hz, 1 H, 1′-H), 3.80 (m, 1 H, 4-H), 4.06 (m, 1 H, 2-H), 4.48 (s, 2 H, 9-H), 7.31 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.7, 27.9, 37.2, 39.1, 67.9, 68.8, 73.3, 74.5, 127.7, 127.8, 128.5, 137.9 ppm. MS (DCI/NH_3): m/z = 235 [M – H_2O + H]$^+$, 253 [M + H]$^+$, 270 [M + NH_4]$^+$. IR (neat): $\tilde{\nu}$ = 3413, 3054, 3034, 2965, 2930, 2860 cm^{-1}. $[\alpha]_D^{25}$ = –10.5 (c = 1.05, $CHCl_3$). HPLC analysis: Column, Chiralcel OD-H; eluent, hexane/propan-2-ol (95:5); flow rate: 1.0 mL/min; detection: 254 nm; $t_{R(2R,4S)}$ = 17.26 min, $t_{R(2R,4R)}$ = 23.29 min.

(2*R*,3*R*,4*S*)-1-Benzyloxy-3-methyloctane-2,4-diol (38):[33] R_f = 0.53 (cyclohexane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91

(d, J = 6.8 Hz, 3 H, MeCH), 0.91 (t, J = 6.8 Hz, 3 H, 8-H), 1.26–1.49 (m, 6 H, 5-H, 6-H and 7-H), 1.69–1.72 (m, 1 H, 3-H), 3.48 (dd, J = 9.5 and 7.6 Hz, 1 H, 1-H), 3.58 (dd, J = 9.5 and 3.6 Hz, 1 H, 1′-H), 3.81–3.85 (m, 2 H, 2-H and 4-H), 4.56 (s, 2 H, OCH_2Ph), 7.31 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.6, 13.8, 22.5, 28.3, 33.2, 38.8, 72.4, 72.7, 73.2, 73.7, 127.5, 127.6, 128.2, 137.6 ppm. IR (neat): $\tilde{\nu}$ = 3413, 3054, 3034, 2965, 2930, 2860 cm^{-1}. $[a]_D^{25}$ = –12.0 (c = 0.5, $CHCl_3$). HPLC analysis: Column, Chiralcel OD-H; eluent, hexane/propan-2-ol (95:5); flow rate: 1.0 mL/min; detection: 254 nm; $t_{R(2R,3R,4R)}$ = 14.48 min, $t_{R(2R,3R,4S)}$ = 17.46 min.

(5*R*,7*R*)-1-(*tert*-Butyldiphenylsilyloxy)undecane-5,7-diol (39): R_f = 0.30 (cyclohexane/AcOEt, 7:3). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.0 Hz, 3 H, 11-H), 1.05 (s, 9 H, *t*Bu), 1.20–1.70 (m, 14 H, 2-H, 3-H, 4-H, 6-H, 8-H, 9-H and 10-H), 3.67 (t, J = 6.2 Hz, 2 H, 1-H), 3.85–3.95 (m, 2 H, 5-H and 7-H), 7.33–7.45 (m, 6 H, Ph), 7.64–7.69 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 19.2, 22.0, 22.7, 26.9, 27.9, 32.4, 37.1, 37.2, 42.2, 63.8, 69.4, 127.6, 129.9, 134.0, 135.6 ppm. MS (DCI/NH_3): m/z = 443 [M + H]$^+$. $[a]_D^{25}$ = –5.9 (c = 0.63, $CHCl_3$). HPLC analysis: Column, Chiralpak AD-H; eluent, hexane/propan-2-ol (98:2); flow rate: 1.0 mL/min; detection: 254 nm; $t_{R(5R,7S)}$ = 14.79 min, $t_{R(5R,7R)}$ = 18.92 min.

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