Desymmetrizing Hydroformylation of Diallylcarbinols with the Aid of a Planar-Chiral, Catalyst-Directing Group[‡]

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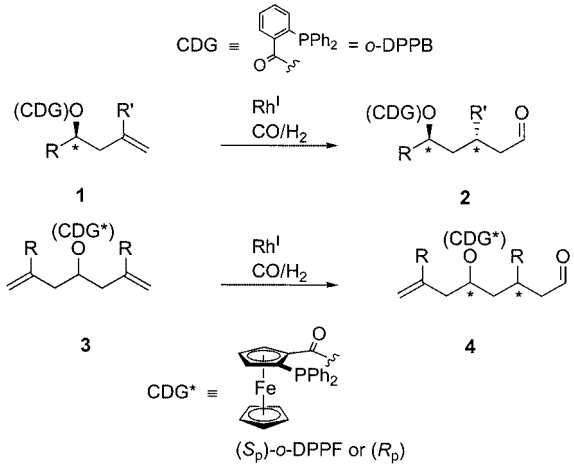
The desymmetrizing hydroformylation of diallylcarbinols has been achieved by employing a planar-chiral, substrate-bound catalyst-directing group – the *ortho*-(diphenylphosphanyl)ferrocenylcarbonyl group (*o*-DPPF). The method allows the simultaneous construction of two stereogenic centers in a 1,3-relative position with high levels of stereocontrol. The diastereoselectivity was investigated as a function of substrate structure. Determination of the relative and absolute configuration of the product aldehydes (chemical derivatization and X-ray crystallographic studies), as well as the conditions for removal and recovery of the catalyst-directing *o*-DPPF group, are described. Furthermore, a model is suggested that rationalizes the experimentally observed stereochemical result based on the minimization of *syn*-pentane interactions.

Introduction

The hydroformylation of alkenes is a synthetically attractive catalytic carbon–carbon bond-forming reaction which is in agreement with the criteria of atom economy.[1] The control of stereochemistry can be achieved either by employing catalysts modified with chiral phosphorus-based ligands[2] or, alternatively, by relying on substrate-bound catalyst-directing groups (CDG).[3,4] In the latter case, efficient 1,2- and 1,3-asymmetric induction employing chiral allylic or homoallylic alcohol derivatives has been achieved using the *ortho*-(diphenylphosphanyl)benzoate function (*o*-DPPB) as the catalyst-directing group.[4] For instance, hydroformylation of homomethallylic *o*-DPPB esters **1** furnishes the *anti*-aldehydes **2** with good levels of acyclic stereocontrol.[5] However, if prochiral substrates are to be employed, the chirality information has to reside in the catalyst-directing group. As a first example of this approach, we recently introduced the planar-chiral *ortho*-(diphenylphosphanyl)ferrocenylcarbonyl function (*o*-DPPF),[6–8] which was used successfully as a chiral catalyst-directing group to achieve desymmetrizing hydroformylation of dialkenylcarbinols (see preceding paper in this journal).[7] Furthermore, the same group has been successfully applied as a reagent-directing leaving group for enantioselective allylic substitution with organocopper reagents.[8]

We report herein, in full detail, the extension of this concept to a desymmetrizing hydroformylation of diallylcarbinols **3**.[9] This allows for the preparation of enantiomerically and diastereomerically pure acyclic aldehyde building blocks **4** with two new stereogenic centers − a secondary alcohol and a tertiary carbon center − in a 1,3-position, a structural motif which is found in a number of biologically important natural products (Scheme 1).



Scheme 1. Concept of desymmetrizing hydroformylation of diallylcarbinols with the aid of *o*-DPPF as a planar-chiral, substrate-bound catalyst-directing group (CDG*).

Results

Diallylcarbinols of structure **6** are rare in the literature. A general procedure for their preparation involves addition of allylmetal reagents derived from bromides **5a**–**e** to ethyl formate (Table 1). Notably, reactions involving allylzinc rea-

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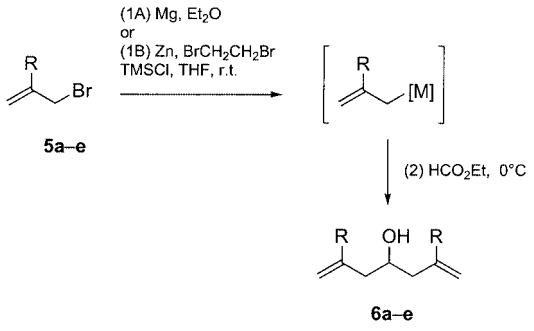
gents proceeded with best chemoselectivity due to the significantly reduced amount of homocoupling products.[10]

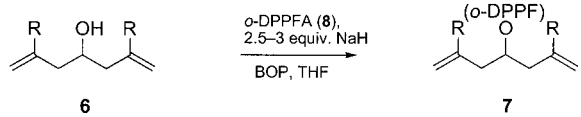
Table 1. Preparation of diallylcarbinols **6a**–**e**.



Entry	R	Product	Method	Yield [%]
1	Me	**6a**	1A	52
2	Et	**6b**	1B	96
3	*i*Pr	**6c**	1B	98
4	Ph	**6d**	1B	93
5	CH_2OTBS	**6e**	1B	39

Since traditional esterification protocols failed to form reasonable amounts of the desired diallylcarbinol *o*-DPPF esters **7**, we employed our recently developed dual activation strategy.[7] In situ activation of the carboxylic acid with BOP as the hydroxybenzotriazol ester, followed by addition of the alcohol **6** activated as the corresponding sodium alkoxide, led to the formation of the desired bis(homoallylic) *o*-DPPF esters **7** in satisfactory to good yields (Table 2). These compounds were obtained as orange solids or oils, which needed to be stored under argon to avoid phosphane oxidation. HPLC analysis on chiral columns (see Exp. Sect.) established enantiomeric purities of >99%.

Table 2. Prepartion of diallylcarbinol *o*-DPPF esters **7**.



Entry	R	Product	*ee* [%][a]	Yield [%][b]
1	Me	*rac*-**7a**	–	64
2	Me	(R_p)-**7a**	>99	61
3	Et	*rac*-**7b**	–	69
4	Et	(R_p)-**7b**	>99	85
5	*i*Pr	*rac*-**7c**	–	67
6	*i*Pr	(R_p)-**7c**	>99	93
7	Ph	*rac*-**7d**	–	67
8	Ph	(R_p)-**7d**	>99[c]	69
9	CH_2OTBS	*rac*-**7e**	–	64
10	CH_2OTBS	(R_p)-**7e**	>99	83

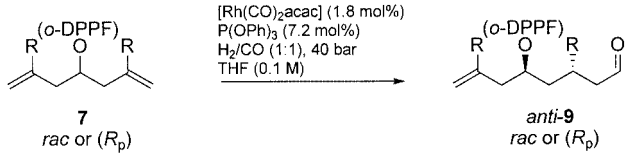
[a] Determined by HPLC. [b] Isolated yield after chromatographic separation. [c] Determined at the stage of diol *anti*-**11d** by HPLC (OD-H).

Hydroformylation of Diallylcarbinol *o*-DPPF Esters

Stereoselective mono(hydroformylation) of diallylcarbinol *o*-DPPF esters requires a simultaneous differentiation of diastereotopic alkene faces and diastereotopic alkene groups. Hence, four different diastereomeric monoaldehydes may be formed. Additionally, the situation may be complicated by dialdehyde formation.

With these difficulties in mind it is remarkable to note that hydroformylation of *o*-DPPF ester **7** proceeded smoothly at temperatures between 40 and 60 °C and 40 bar of syngas at catalyst loadings of 1.8 mol-% to give essentially a single monoaldehyde diastereomer *anti*-**9** in good yield (Table 3). The reactions were complete in most cases after approximately 24 h. However, since at conversions

Table 3. Desymmetrizing hydroformylation of diallylcarbinol *o*-DPPF esters **7**.

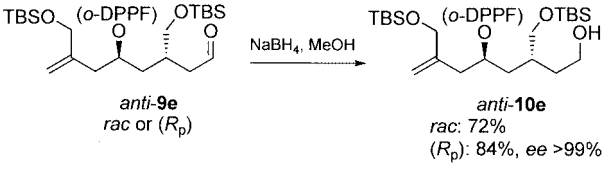


Entry	Substrate	R	*T* [°C]	*t* [h]	Conv.[a] [%]	*dr*[a] *anti*-**9**/*syn*-**9**	Yield[b] [%]
1	*rac*-**7a**	Me	50	21.5	88	96:4	89[c]
2	*rac*-**7a**	Me	40	48	80	97:3	79[c]
3	(R_p)-**7a**	Me	50	21.5	91	96:4	83[c]
4	*rac*-**7b**	Et	50	21	84	95:5	88[c]
5	(R_p)-**7b**	Et	50	21	83	95:5	85[c]
6	*rac*-**7c**	*i*Pr	60	24	87	87:13	91[c]
7	*rac*-**7c**	*i*Pr	50	48	72	87:13	91[c]
8	(R_p)-**7c**	*i*Pr	60	24	81	86:14	84[c]
9	*rac*-**7d**	Ph	70	24	81	94:6	84[c]
10	(R_p)-**7d**	Ph	70	24	82	94:6	90[c]
11	*rac*-**7e**	CH_2OTBS	50	16	quant.	95:5	85
12	(R_p)-**7e**	CH_2OTBS	50	16	quant.	96:4	80

[a] Determined from the ^1H NMR spectrum of the crude product. [b] Isolated yield after chromatographic purification. [c] Based on recovered starting material.

greater than 90% unselective dialdehyde formation could be detected, the reactions were usually stopped at conversions of less than 90%. The diastereoselectivity was found to be almost independent of the nature of the substituent R. Thus, **7** with methyl, ethyl, phenyl, and (silyloxy)methyl substituents yielded diastereoselectivities in the order of >94:6. An exception is the isopropyl substituent (Table 3, Entries 6–8), which gave a slightly reduced diastereoselectivity of 87:13.

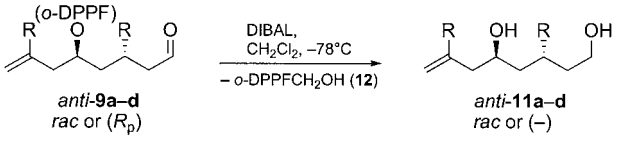
In order to check that hydroformylation with enantiomerically pure derivatives **7** proceeded without racemization, the enantiomeric purity of the aldehyde products **9** had to be determined. Unfortunately, these aldehydes were not stable enough under the conditions of HPLC analysis, which required subsequent transformation to a derivative more suitable to chromatographic analysis. In the case of *anti*-**9e** the aldehyde was reduced to the corresponding primary alcohol, and HPLC analysis showed *anti*-**10e** to be an essentially enantiomerically pure compound [Equation (1)].



(1)

In all other cases (**9a**–**d**) the *o*-DPPF group was removed reductively with DIBAL prior to analysis of the enantiomeric purity of the resulting diols **11a**–**d** (Table 4).

Table 4. Reductive removal of *o*-DPPF and determination of *ee*.

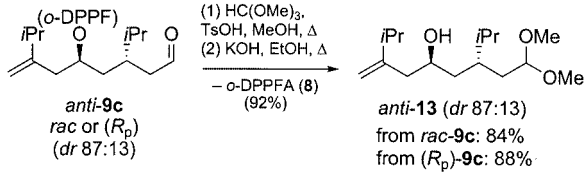


Entry	Substrate	Yield [%] *o*-DPPFCH$_2$OH (**12**)	Yield [%] **11**	*ee* [%]
1	*rac*-**9a**	78	90	–
2	(R_p)-**9a**	79	91	>99[a]
3	*rac*-**9b**	54	86	–
4	(R_p)-**9b**	74	78	>99[a]
5	*rac*-**9c**	89	63	–
6	(R_p)-**9c**	91	82	>99[a]
7	*rac*-**9d**	75	96	–
8	(R_p)-**9d**	78	86	>99[b]

[a] Determined by GC (Supelco BetaDex110). [b] Determined by HPLC (OD-H).

Removal and Recovery of the Catalyst-Directing *o*-DPPF Group

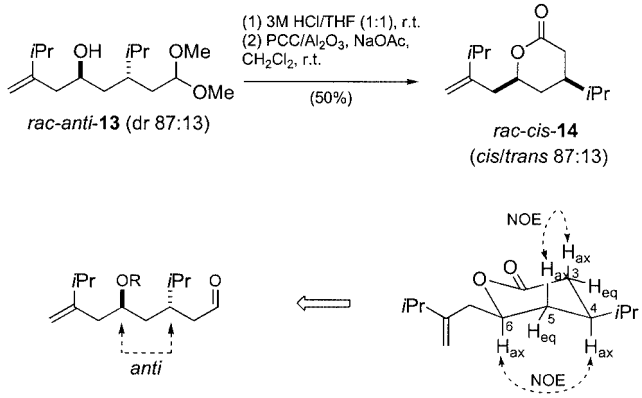
The *o*-DPPF group could be removed and recovered after protection of the aldehyde as the dimethyl acetal. Saponification of the ester function with ethanolic potassium hydroxide solution gave the alcohols **13** as well as *o*-DPPFA (**8**) [Equation (2)] in good yields.



(2)

Determination of the Relative and Absolute Configuration of Product Aldehydes 9

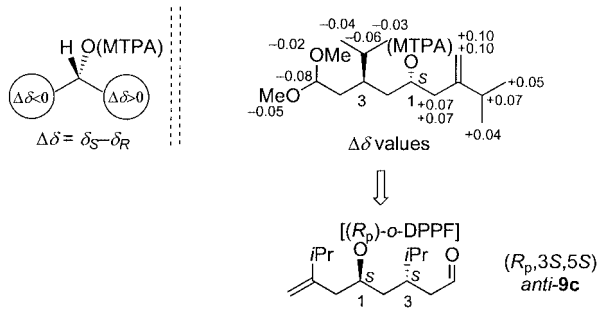
In order to determine the relative and absolute configuration of aldehydes **9**, the aldehyde function from *rac*-*anti*-**13** was liberated and the resulting lactol was oxidized to give the δ-lactone **14**. NOESY experiments established the diequatorial arrangement of the substituents at C-4 and C-6, which is equivalent to the *anti* relation for the acyclic structure (Scheme 2).



Scheme 2. Determination of the relative configuration.

In order to determine the absolute configuration of the hydroformylation products **9**, alcohol (–)-**13c** [*dr* 95:5, obtained from the hydroformylation of (R_p)-**7c**] was subjected to a Mosher ester analysis. Comparison of the chemical-shift differences in both diastereomeric Mosher esters allowed us to assign the (*S*)-configuration for the stereogenic center at C1 (Scheme 3).[11] Hence, the major diastereomeric aldehyde *anti*-**9c** obtained by hydroformylation of the dipropenylcarbinol *o*-DPPF ester (R_p)-**7c** has the configuration (R_p,3*S*,5*S*)-**9c**. The absolute and relative configuration of aldehydes **9a**,**b**,**d**,**e** was assigned by analogy.

Final unequivocal proof for the relative configuration of stereogenic centers at C-1 and C-3 came from an X-ray crystal structure analysis of *rac*-*anti*-**9a** (Figure 1). The absolute configuration of the minor diastereomer *syn*-**9** has not been determined explicitly. However, it is likely that the minor diastereomer will have the same absolute configuration at C-1 (Scheme 3) as determined for the major diastereomer *anti*-**9c**. This assumption is reasonable since previous investigations on hydroformylation of the closely re-



Scheme 3. Determination of the absolute configuration of (–)-**13** [obtained from (R_p)-**7c**] by Mosher ester analysis [δ_S and δ_R refer to the absolute configuration of the Mosher acid (MTBA) employed].

lated chiral homomethallylic *o*-DPPB esters **1** (Scheme 1) have shown that a minor *syn* diastereomer of aldehyde **2** is expected from imperfect diastereofacial discrimination.

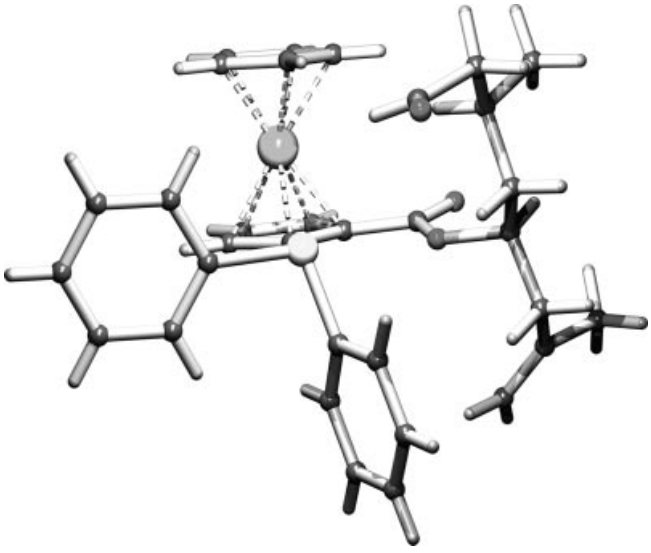


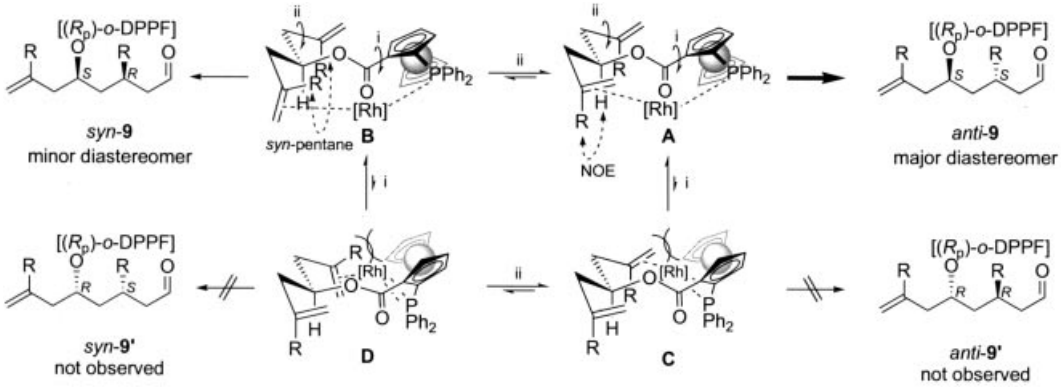
Figure 1. X-ray crystal structure analysis of *rac-anti*-**9a**.

Discussion and Model for 1,3-Asymmetric Induction

From the absolute and relative configuration of monoaldehydes **9a** it follows that the hydroformylation of diallylcarbinol *o*-DPPF esters **7** occurs with excellent diastereotopic face discrimination and presumably perfect diastereotopic group discrimination. Diastereotopic face discrimination is almost independent of the nature of the R substituent: only in the case of the isopropyl substituent, which has an increased steric demand (Table 3, Entries 6–8), was a diminished diastereoselection noted. Hence, discrimination of the diastereomeric alkene faces seems to be inherent to the 2-substituted homoallylic system. A similar observation has been made previously when studying the *o*-DPPB-directed hydroformylation of chiral homomethallylic alcohol *o*-DPPB esters (Scheme 1, **1** → **2**).[5] In this case a stereochemical model based on force-field conformational studies as well as NMR studies in solution could be devised. Thus, a chelating binding mode of the substrate through coordination of the alkene and the catalyst-directing *o*-DPPB group, which provides the most stable hydrometalation transition state, controls the stereochemical outcome of the *o*-DPPB-directed hydroformylation reaction.[4,5,12] In the course of this model minimization of the *syn*-pentane interaction in the substrate skeleton between the 2-substituent at the alkene and the C–O bond attached to the catalyst-directing group proved decisive.

A similar model, modified by exchanging *o*-DPPB with the planar-chiral *o*-DPPF group, allows us to rationalize the stereochemical outcome of the directed desymmetrizing hydroformylation of diallylcarbinol *o*-DPPF esters **7** (Scheme 4).

Comparison of the relative stabilities of the chelating (alkene)rhodium complexes **A**–**D**, which serve as models for the competing rate- and selectivity-determining hydrometalation transition states, should allow us to predict the stereochemistry of the directed hydroformylation. Thus, for (R_p)-*o*-DPPF esters **7** the relative stabilities of the two diastereomeric complexes **A** and **B**, and the corresponding transition states for hydrometalation, decide the alkene face



Scheme 4. Model for desymmetrizing hydroformylation of dialkenylcarbinol *o*-DPPF esters **7**.

diastereoselectivity of the reaction. Minimization of the *syn*-pentane interaction should lead, via **A**, to the major diastereomer *anti*-**9**. The reaction via chelation mode **B** presumably furnishes the minor diastereomer *syn*-**9**. In fact, NOESY experiments indicate a preferred ground-state conformation similar to the one depicted for **A**. Interestingly, inspection of the X-ray plot of *anti*-**9a** depicted in Figure 1 shows the same conformation for the alkene moiety of *anti*-**9a** in the solid state.

Group diastereoselectivity is determined by the relative stabilities of the hydrometalation transition states resulting from chelate complexes **C** and **D** vs. **A** and **B**. Thus, coordination of the opposite diastereotopic alkene group requires a bond-rotation process (i in Scheme 4). However, such a chelating binding mode is prohibited because of severe steric hindrance between the ferrocene nucleus and the rhodium center.[7] Hence, alkene group diastereoselectivity is perfect and neither the diastereomer *syn*-**9a′** nor *anti*-**9a′** is observed.

Conclusions

Use of the chiral, substrate-bound, catalyst-directing *o*-DPPF group allows a desymmetrizing hydroformylation of diallylcarbinols to be achieved with excellent levels of stereocontrol. Thus, two new stereogenic centers in a 1,3-relation, namely a tertiary carbon center and a secondary *O*-substituted stereocenter, are formed simultaneously. The catalyst-directing *o*-DPPF group can be removed and recovered easily, thus furnishing interesting chiral building blocks in enantiomerically pure form.

Experimental Section

General: Reactions were performed in flame-dried glassware under argon. The solvents were dried by standard procedures, distilled, and stored under argon. All temperatures quoted are not corrected. NMR spectra were obtained with a Varian Mercury spectrometer (300 MHz, 121.5 MHz, and 75.5 MHz for ^{1}H, ^{31}P, and ^{13}C respectively), a Bruker AMX 400 (400 MHz and 100.6 MHz for ^{1}H and ^{13}C, respectively), or a Bruker DRX 500 (500 MHz and 125 MHz for ^{1}H and ^{13}C, respectively) and are referenced internally according to residual protonated solvent signals (^{31}P NMR: 85% H_3PO_4 as external standard). Melting points: Melting point apparatus by Dr. Tottoli (Büchi). Elemental analyses: Elementar Vario EL (Elementar-Analysensysteme GmbH). Flash chromatography: Silica gel Si 60, E. Merck AG, Darmstadt, 40–63 μm. High-resolution mass spectra were obtained with a Finnigan MAT 8200 instrument. Enantiomeric excesses (*ee*) were determined by HPLC using Daicel Chiralpak AD, AD-H, and Chiralcel OD-H columns (wavelengths 245 nm) with 2-propanol/heptane as the eluent or by GC using a Supelco Betadex 110 (30 m × 0.25 mm, 0.25 μm film thickness) with helium 4.6 (Messer-Griesheim). Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Hydroformylation reactions were performed in 50- and 100-mL stainless-steel autoclaves equipped with magnetic stirrers. Gases: carbon monoxide 3.7, hydrogen 4.3 (1:1, Messer-Griesheim). The following compounds were prepared according to literature procedures: 2-(bromomethyl)-1-butene (**5b**),[13] 2-(bromomethyl)-3-methyl-1-butene (**5c**),[14] 1-bromo-2-phenyl-2-propene (**5d**),[15] 2-[(*tert*-butylsilyloxy)-methyl]-2-propen-1-ol,[16] and *o*-DPPFA (**8**).[17] PE = petroleum ether; MTBE = *tert*-butyl methyl ether; Cy = cyclohexane; EE = ethyl acetate; BOP = (benzotriazol-1-yloxy)tris(dimethylamino)-phosphonium hexafluorophosphate; PCC = pyridinium chlorochromate.

Synthesis of Diallylcarbinols 6

2,6-Dimethylhepta-1,6-dien-4-ol (6a): Freshly distilled 3-bromo-2-methylprop-1-ene (**5a**; 6.70 g, 0.05 mol) in Et_2O (40 mL) was added, over 2 h, to magnesium turnings (3.61 g, 0.149 mol, 3.0 equiv.) in Et_2O (20 mL) while the temperature was kept at 25 °C. After stirring for an additional 10 min, the supernatant solution was transferred into a separate flask, cooled to 0 °C, and a solution of ethyl formate (1.83 g, 0.025 mol, 0.5 equiv.) in Et_2O (4 mL) was added slowly. The solution was allowed to warm to room temperature and was stirred for 1 h. The reaction mixture was quenched by addition of satd. aqueous NH_4Cl solution (100 mL), the organic phase was separated, and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phases were dried (Na_2SO_4), concentrated, and purified by flash chromatography (PE/MTBE, 50:1) to furnish **6a** (1.81 g, 0.013 mol, 52%) as a colorless liquid. R_f (PE/MTBE, 50:1) = 0.05. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 6 H), 1.83 (br. s, 1 H), 2.15 (dd, J = 14.0, 8.2 Hz, 2 H), 2.20 (dd, J = 14.0, 5.2 Hz, 2 H), 3.89 (tt, J = 8.2, 5.2 Hz, 1 H), 4.80 (s, 2 H), 4.87 (quint, 2 H, J = 1.7 Hz) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.6 (2 C), 45.8 (2 C), 66.6, 113.3 (2 C), 142.8 (2 C) ppm.

General Procedure 1 (GP1). Reaction of Allylzinc Reagents with Ethyl Formate: In a three-necked flask equipped with a reflux condenser and argon inlet, zinc dust (<45 μm, 2.0 equiv.) was flame-dried under vacuum until sublimation occurred. After cooling to 25 °C, the thermally activated zinc was suspended in THF (2 mL/mmol allyl bromide) and subsequently treated with 1,2-dibromoethane (3 cycles, total 0.2 equiv.) followed by refluxing. Then, TMSCl was added (3 cycles, total 0.08 equiv.) without external heating and, after cooling to 25 °C, allyl bromide (**5**) was added (1 equiv.) dropwise from a syringe and the mixture was stirred for the indicated period of time. Then, ethyl formate (0.3 equiv.) was added in one portion and the mixture was again stirred at 25 °C for 6–8 h until complete consumption of the starting material. After quenching of the reaction mixture with satd. aqueous NH_4Cl (2 mL/mmol allyl bromide) and addition of MTBE (2 mL/mmol allyl bromide), the phases were separated. The aqueous phase was extracted with MTBE (4 times) and the combined organic phases were dried (Na_2SO_4), concentrated, and the residue was purified by flash chromatography to furnish the diallylcarbinols **6** in analytically pure form.

3,7-Dimethylenenonan-5-ol (6b): Zinc dust (990 mg, 15.1 mmol, 2.0 equiv.) in THF (15 mL) was activated with dibromoethane (129 μL, 1.5 mmol, 0.20 equiv.) and TMSCl (75 μL, 0.6 mmol, 0.08 equiv.) according to GP1. After addition of 2-(bromomethyl)-1-butene (**5b**; 1.112 g, 7.5 mmol) and stirring for 16 h, ethyl formate (166 mg, 2.2 mmol, 0.30 equiv.) was added to the mixture by syringe. After workup and flash chromatography (PE/MTBE, 25:1), the title compound **6b** (361 mg, 2.1 mmol, 95%) was isolated as a colorless liquid. R_f (Cy/EE, 10:1) = 0.14. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, J = 7.5 Hz, 6 H), 1.86 (d, J = 2.1 Hz, 1 H), 2.00–2.30 (m, 8 H), 3.87 (m_c, 1 H), 4.83 (s, 2 H), 4.88 (q, J = 1.6 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.4 (2 C), 28.9 (2 C), 44.4 (2 C), 67.0, 111.0 (2 C), 148.4 (2 C) ppm. $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 78.25, H 11.68.

2,8-Dimethyl-3,7-dimethylenenonan-5-ol (6c): Zinc dust (6.664 g, 101.9 mmol, 2.0 equiv.) in THF (100 mL) was activated with dibromoethane (0.87 mL, 10.1 mmol, 0.20 equiv.) and TMSCl (0.53 mL, 4.1 mmol, 0.08 equiv.) according to GP1. After addition of 2-(bromomethyl)-3-methyl-1-butene (**5c**; 8.281 g, 50.8 mmol) and stirring for 12.5 h, ethyl formate (1.19 g, 16.1 mmol, 0.30 equiv.) was added to the mixture by syringe. After workup and flash chromatography (PE/MTBE, 25:1), the title compound **6c** (3.089 g, 15.7 mmol, 98%) was isolated as a colorless liquid. R_f (Cy/EE, 10:1) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (d, J = 6.9 Hz, 6 H), 1.06 (d, J = 6.9 Hz, 6 H), 1.92 (d, J = 1.7 Hz, 1 H), 2.16 (dd, J = 14.2, 8.2 Hz, 2 H), 2.26 (sept, J = 6.9 Hz, 2 H), 2.28 (dd, J = 14.2, 0.9 Hz, 2 H), 3.88 (m_c, 1 H), 4.82 (d, J = 1.3 Hz, 2 H), 4.91 (s, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (2 C), 22.0 (2 C), 33.7 (2 C), 42.9 (2 C), 67.6, 109.5 (2 C), 153.0 (2 C) ppm. $C_{13}H_{24}O$ (196.3): calcd. C 79.53, H 12.32; found C 79.33, H 12.46.

2,6-Diphenyl-1,6-heptadien-4-ol (6d): Zinc dust (3.52 g, 53.8 mmol, 2.0 equiv.) in THF (54 mL) was activated with dibromoethane (465 µL, 5.4 mmol, 0.20 equiv.) and TMSCl (270 µL, 2.1 mmol, 0.08 equiv.) according to GP1. After addition of 1-bromo-2-phenyl-2-propene (**5d**; 5.31 g, 26.9 mmol) and stirring for 14 h, ethyl formate (0.66 mL, 8.2 mmol, 0.30 equiv.) was added to the mixture by syringe. After workup and flash chromatography (PE/MTBE, 10:1), the title compound **6d** (2.01 g, 7.6 mmol, 93%) was isolated as a white solid. R_f (Cy/EE, 10:1) = 0.10; m.p. 55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.84 (br. s, 1 H), 2.69 (dd, J = 14.2, 7.3 Hz, 2 H), 2.80 (ddd, J = 14.2, 5.2, 0.9 Hz, 2 H), 3.79 (m_c, 1 H), 5.18 (d, J = 0.9 Hz, 2 H), 5.43 (d, J = 1.3 Hz, 2 H), 7.25–7.36 (m, 10 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.1 (2 C), 67.8, 115.2 (2 C), 126.2 (4 C), 127.7 (2 C), 128.4 (4 C), 140.3 (2 C), 145.3 (2 C) ppm. $C_{19}H_{20}O$ (264.4): calcd. C 86.32, H 7.63; found C 85.93, H 7.83.

[2-(Bromomethyl)allyloxy](*tert*-butyl)dimethylsilane (5e): PPh_3 (6.460 g, 24.6 mmol, 1.3 equiv.) in CH_2Cl_2 (80 mL) was cooled to –78 °C and NBS (4.399 g, 24.7 mmol, 1.3 equiv.) was added in one portion. After stirring for 15 min, 2-[(*tert*-butylsilyloxy)methyl]-2-propen-1-ol (3.910 g, 19.3 mmol) was added and the solution was allowed to warm to –60 °C and was stirred for 1 h. Then, the mixture was allowed to warm to –20 °C during 1 h, stirred at this temperature for another 30 min, and was then quenched with satd. aqueous $NaHCO_3$ solution (80 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography (neutral Al_2O_3, deactivated with 10% water, PE/MTBE, 25:1) afforded the title compound **5e** (3.814 g, 14.4 mmol, 75%) as a colorless liquid. R_f (Cy/EE, 5:1) = 0.61. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, 6 H), 0.92 (s, 9 H), 4.01 (s, 2 H), 4.27 (s, 2 H), 5.22–5.26 (m, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.3 (2 C), 18.4, 26.0 (3 C), 32.9, 63.6, 114.9, 145.0 ppm. $C_{10}H_{21}BrOSi$ (265.3): calcd. C 45.28, H 7.98; found C 45.34, H 7.94.

2,6-Bis[(*tert*-butyldimethylsilyloxy)methyl]hepta-1,6-dien-4-ol (6e): Zinc dust (1.875 g, 28.7 mmol, 2.0 equiv.) in THF (29 mL) was activated with dibromoethane (0.25 mL, 2.9 mmol, 0.20 equiv.) and TMSCl (0.15 mL, 1.2 mmol, 0.08 equiv.) according to GP1. After addition of [2-(bromomethyl)allyloxy](*tert*-butyl)dimethylsilane (**5e**; 3.81 g, 14.4 mmol) and stirring for 14 h, ethyl formate (0.36 g, 4.8 mmol, 0.30 equiv.) was added to the mixture by syringe. After workup, the crude product was stirred with K_2CO_3 (0.50 g) in methanol (5 mL) for 90 min. Filtration, removal of the solvent, and flash chromatography (PE/TBME, 50:1) afforded the title compound **6e** (0.752 g, 1.9 mmol, 39%) as a colorless liquid. R_f (Cy/EE, 10:1) = 0.12. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 12 H), 0.92 (s, 18 H), 2.16 (dd, J = 14.1, 8.2 Hz, 2 H), 2.30 (dd, J = 14.1, 4.3 Hz, 2 H), 3.01 (d, J = 2.8 Hz, 1 H), 3.87 (m_c, 1 H), 4.11 (s, 4 H), 4.93 (s, 2 H), 5.14 (d, J = 1.6 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.3 (4 C), 18.5 (2 C), 26.0 (6 C), 41.6 (2 C), 66.6 (2 C), 69.0, 112.8 (2 C), 145.8 (2 C) ppm. $C_{21}H_{44}O_3Si_2$ (400.8): calcd. C 62.94, H 11.07; found C 63.12, H 11.20.

General Procedure 2 (GP2). Esterification Protocol: Under light protection, *o*-DPPFA (**8**) and the alcohol **6** were dissolved in THF (10 mL/mmol *o*-DPPFA) and BOP (1.0–1.1 equiv.) was added. NaH (2.5–3.0 equiv.) was added to this mixture and the reaction mixture was stirred at 25 °C for the indicated period of time. The reaction mixture was quenched with water (2 equiv.), silica gel was added, and all volatile components were removed in vacuo. Flash chromatography [the product fraction (orange) was collected in a flask under argon and the solvents were removed in an argon-purged rotary evaporator due to the air sensitivity of the *o*-DPPF esters] furnished the corresponding ester **7**, which was dried at 60 °C/0.1 mbar overnight.

[3-Methyl-1-(2-methylallyl)but-3-enyl] (R_p)-2-(Diphenylphosphanyl)-ferrocenecarboxylate (7a). *rac*-7a: As described in GP2, *rac*-*o*-DPPFA (**8**; 563 mg, 1.36 mmol), alcohol **6a** (212 mg, 1.51 mmol, 1.1 equiv.), BOP (644 mg, 1.46 mmol, 1.1 equiv.), and NaH (135 mg, 60% in mineral oil, 3.41 mmol, 2.5 equiv.) in THF (14 mL) gave, after 19.5 h and flash chromatography (PE/EE, 25:1), the title compound *rac*-**7a** (470 mg, 0.88 mmol, 64%) as an orange solid. **(R_p)-7a:** (R_p)-*o*-DPPFA (**8**; 532 mg, 1.28 mmol, *ee* > 99%) in THF (13 mL) was deprotonated with *t*BuLi (0.78 mL, 1.65 M in pentane, 1.29 mmol, 1.01 equiv.) at –78 °C and was then added to a solution of BOP (612 mg, 1.38 mmol, 1.08 equiv.) in THF (13 mL) at 25 °C over 30 min. After stirring for 1 h, the alcohol **6a** (213 mg, 1.52 mmol, 1.19 equiv.) in THF (6 mL) was deprotonated with *t*BuLi (0.92 mL, 1.65 M in pentane, 1.52 mmol, 1.19 equiv.) in a separate flask at –78 °C and the alkoxide solution was then added to the reaction mixture. After stirring for 2 h, workup as described in GP2, and flash chromatography (PE/EE, 25:1), the title compound (R_p)-**7a** (420 mg, 0.78 mmol, 61%, *ee* > 99%) was obtained as an orange solid. **Data for 7a:** R_f (Cy/EE, 10:1) = 0.38; m.p. 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (s, 3 H), 1.71 (s, 3 H), 1.88 (dd, J = 14.2, 5.6 Hz, 1 H), 2.04 (dd, J = 14.2, 7.3 Hz, 1 H), 2.18 (dd, J = 14.2, 4.2 Hz, 1 H), 2.31 (dd, J = 14.2, 8.6 Hz, 1 H), 3.64 (br. s, 1 H), 4.17 (s, 5 H), 4.38 (pseudo t, J = 2.5 Hz, 1 H), 4.53 (s, 1 H), 4.69 (s, 1 H), 4.76 (s, 1 H), 4.84 (s, 1 H), 5.01 (br. s, 1 H), 5.29 (m_c, 1 H), 7.15–7.20 (m, 2 H), 7.21–7.25 (m, 3 H), 7.32–7.36 (m, 3 H), 7.41–7.47 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.46, 22.53, 42.6, 42.8, 70.2, 71.1 (5 C), 71.5, 74.0, 75.2 (d, $J_{C,P}$ = 4.4 Hz), 76.1 (d, $J_{C,P}$ = 14.5 Hz), 79.4 (d, $J_{C,P}$ = 17.4 Hz), 113.1, 113.5, 127.9, 128.1 (d, $J_{C,P}$ = 5.8 Hz, 2 C), 128.2 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.0, 132.5 (d, $J_{C,P}$ = 18.9 Hz, 2 C), 135.1 (d, $J_{C,P}$ = 21.8 Hz, 2 C), 138.6 (d, $J_{C,P}$ = 14.6 Hz), 139.9 (d, $J_{C,P}$ = 14.6 Hz), 141.8, 141.9, 170.7 (d, $J_{C,P}$ = 2.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –15.8 ppm. $C_{32}H_{33}FeO_2P$ (536.4): calcd. C 71.65, H 6.20; found C 71.30, H 6.30. HPLC [AD, heptane/2-propanol (99:1), 15 °C, 0.8 mL min^{-1}]: t_R[(S_p)-**7a**] = 10.25 min; t_R[(R_p)-**7a**] = 13.05 min. $[\alpha]_D^{20}$ = +153 (c = 0.875, $CHCl_3$).

3-Methylene-1-(2-methylenebutyl)pentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (7b). *rac*-7b: As described in GP2, *rac*-*o*-DPPFA (**8**; 565 mg, 1.36 mmol), alcohol **6b** (248 mg, 1.47 mmol, 1.1 equiv.), BOP (627 mg, 1.42 mmol, 1.0 equiv.), and NaH (131 mg, 60% in mineral oil, 3.30 mmol, 2.4 equiv.) in THF (11 mL) gave, after 16 h and flash chromatography (PE/EE, 50:1), the title compound *rac*-**7b** (529 mg, 0.94 mmol, 69%) as an orange solid. **(R_p)-7b:** As described in GP2, (R_p)-*o*-DPPFA (460 mg,

1.11 mmol, *ee* > 99%), alcohol **6b** (201 mg, 1.19 mmol, 1.07 equiv.), BOP (527 mg, 1.19 mmol, 1.1 equiv.), and NaH (113 mg, 60% in mineral oil, 2.85 mmol, 2.57 equiv.) in THF (11 mL) gave, after 19.5 h and flash chromatography (PE/EE, 50:1), the title compound (R_p)-**7b** (535 mg, 0.95 mmol, 85%, *ee* > 99%) as an orange solid. **Data for 7b:** R_f (Cy/EE, 10:1) = 0.45; m.p. 91–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.4 Hz, 3 H), 0.99 (t, J = 7.4 Hz, 3 H), 1.88 (dd, J = 14.2, 5.8 Hz, 1 H), 1.94–2.13 (m, 5 H), 2.23 (dd, J = 14.3, 4.5 Hz, 1 H), 2.29 (dd, J = 14.3, 8.5 Hz, 1 H), 3.64 (ddd, J = 2.5, 1.4, 0.9 Hz, 1 H), 4.19 (s, 5 H), 4.40 (pseudo t, J = 2.5 Hz, 1 H), 4.60 (s, 1 H), 4.72 (d, J = 1.5 Hz, 1 H), 4.77 (d, J = 1.5 Hz, 1 H), 4.89 (s, 1 H), 5.02 (pseudo quint, J = 1.2 Hz, 1 H), 5.27 (m_c, 1 H), 7.17–7.21 (m, 2 H), 7.22–7.26 (m, 3 H), 7.34–7.38 (m, 3 H), 7.44–7.49 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.23, 12.26, 28.67, 28.70, 41.1, 41.4, 70.7, 71.1 (5 C), 71.6, 74.0, 75.3 (d, $J_{C,P}$ = 4.8 Hz), 76.1 (d, $J_{C,P}$ = 14.5 Hz), 79.4 (d, $J_{C,P}$ = 16.7 Hz), 110.7, 111.0 (d, $J_{C,P}$ = 1.8 Hz), 128.0, 128.1 (d, $J_{C,P}$ = 6.7 Hz, 2 C), 128.2 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.0, 132.5 (d, $J_{C,P}$ = 19.7 Hz, 2 C), 135.1 (d, $J_{C,P}$ = 21.8 Hz, 2 C), 138.6 (d, $J_{C,P}$ = 14.5 Hz), 139.9 (d, $J_{C,P}$ = 13.9 Hz), 147.3, 147.4, 170.8 (d, $J_{C,P}$ = 3.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.8 ppm. $C_{34}H_{37}FeO_2P$ (564.5): calcd. C 72.34, H 6.61; found C 72.18, H 6.71. HPLC [AD, heptane/2-propanol (200:1), 15 °C, 0.5 mL min^{-1}]: t_R[(R_p)-**7b**] = 9.71 min; t_R[(S_p)-**7b**] = 15.31. $[\alpha]_D^{20}$ = +140 (c = 0.735, $CHCl_3$).

4-Methyl-3-methylene-1-(3-methyl-2-methylenebutyl)pentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (7c). *rac*-7c: As described in GP2, *rac*-*o*-DPPFA (**8**; 1.61 g, 3.89 mmol), alcohol **6c** (0.84 g, 4.27 mmol, 1.1 equiv.), BOP (1.90 g, 4.30 mmol, 1.1 equiv.), and NaH (0.41 g, 60% in mineral oil, 10.3 mmol, 2.6 equiv.) in THF (40 mL) gave, after 15 h, workup, flash chromatography (PE/EE, 50:1), and drying of the product at 80 °C/0.1 mbar, the title compound *rac*-**7c** (1.55 g, 2.62 mmol, 67%) as an orange oil, which crystallized slowly on standing at 4 °C. **(R_p)-7c:** As described in GP2, (R_p)-*o*-DPPFA (**8**; 424 mg, 1.02 mmol, *ee* > 99%), alcohol **6c** (213 mg, 1.08 mmol, 1.06 equiv.), BOP (482 mg, 1.09 mmol, 1.07 equiv.), and NaH (119 mg, 60% in mineral oil, 2.99 mmol, 2.94 equiv.) in THF (10 mL) gave, after 16.5 h, workup, flash chromatography (PE/EE, 50:1), and drying of the product at 80 °C/0.1 mbar, the title compound (R_p)-**7c** (563 mg, 0.95 mmol, 93%, *ee* > 99%) as an orange oil, which crystallized slowly on standing at 4 °C. **Data for 7c:** R_f (Cy/EE, 10:1): 0.59; m.p. 70–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (d, J = 6.9 Hz, 3 H), 0.98 (d, J = 7.3 Hz, 3 H), 1.00 (d, J = 7.3 Hz, 3 H), 1.01 (d, J = 6.9 Hz, 3 H), 1.84 (dd, J = 14.6, 6.4 Hz, 1 H), 2.07 (dd, J = 14.6, 6.9 Hz, 1 H), 2.20 (sept, J = 6.9 Hz, 1 H), 2.28 (d, J = 6.5 Hz, 2 H), 2.30 (m, 1 H), 3.65 (br. s, 1 H), 4.20 (s, 5 H), 4.40 (pseudo t, J = 2.6 Hz, 1 H), 4.63 (s, 1 H), 4.78 (s, 1 H), 4.80 (s, 1 H), 4.91 (s, 1 H), 5.03 (pseudo quint, J = 1.3 Hz, 1 H), 5.29 (pseudo quint, J = 6.6 Hz, 1 H), 7.18–7.26 (m, 5 H), 7.34–7.38 (m, 3 H), 7.44–7.49 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.7, 21.8 (2 C), 22.0, 33.3, 33.5, 39.4, 39.7, 71.1 (5 C), 71.3, 71.5, 74.0, 75.2 (d, $J_{C,P}$ = 4.4 Hz), 76.1 (d, $J_{C,P}$ = 14.5 Hz), 79.5 (d, $J_{C,P}$ = 17.4 Hz), 109.4, 109.6, 128.0, 128.1 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 128.2 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.0, 132.5 (d, $J_{C,P}$ = 20.3 Hz, 2 C), 135.1 (d, $J_{C,P}$ = 10.4 Hz, 2 C), 138.7 (d, $J_{C,P}$ = 14.5 Hz), 139.9 (d, $J_{C,P}$ = 14.5 Hz), 151.7, 151.9, 170.8 (d, $J_{C,P}$ = 2.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.8 ppm. $C_{36}H_{41}FeO_2P$ (592.5): calcd. C 72.97, H 6.97; found C 72.82, H 6.99. HPLC [AD-H, heptane/2-propanol (400:1), 20 °C, 0.5 mL min^{-1}]: t_R[(R_p)-**7c**] = 9.25 min; t_R[(S_p)-**7c**] = 12.84 min. $[\alpha]_D^{20}$ = +129 (c = 1.435, $CHCl_3$, *ee* > 99%).

3-Phenyl-1-(2-phenylallyl)but-3-enyl (R_p)-2-(Diphenylphosphanyl)-ferrocenecarboxylate (7d). *rac*-7d: As described in GP2, *rac*-*o*-DPPFA (**8**; 425 mg, 1.02 mmol), alcohol **6d** (297 mg, 1.12 mmol, 1.1 equiv.), BOP (518 mg, 1.17 mmol, 1.2 equiv.), and NaH (107 mg, 60% in mineral oil, 2.69 mmol, 2.6 equiv.) in THF (20 mL) gave, after 18 h, workup, and flash chromatography (PE/EE, 25:1), the title compound *rac*-**7d** (453 mg, 0.69 mmol, 67%) as an orange solid. **(R_p)-7d:** As described in GP2, (R_p)-*o*-DPPFA (**8**; 569 mg, 1.37 mmol, *ee* > 99%), alcohol **6d** (403 mg, 1.52 mmol, 1.11 equiv.), BOP (628 mg, 1.42 mmol, 1.04 equiv.), and NaH (140 mg, 60% in mineral oil, 3.52 mmol, 2.57 equiv.) in THF (14 mL) gave, after 19 h, workup, and flash chromatography (PE/EE, 25:1) the title compound (R_p)-**7d** (620 mg, 0.94 mmol, 69%, *ee* > 99%) as an orange solid. **Data for 7d:** R_f (Cy/EE, 10:1) = 0.35; m.p. 119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (dd, J = 14.2, 7.1 Hz, 1 H), 2.65 (dd, J = 14.2, 6.9 Hz, 1 H), 2.76 (d, J = 6.5 Hz, 2 H), 3.65 (br. s, 1 H), 4.16 (s, 5 H), 4.39 (pseudo t, J = 2.5 Hz, 1 H), 4.93 (m, 2 H), 5.12 (quint, J = 6.9 Hz, 1 H), 5.32 (d, J = 0.9 Hz, 1 H), 5.34 (s, 1 H), 5.40 (d, J = 1.3 Hz, 1 H), 7.17–7.51 (m, 20 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 39.2, 39.4, 71.2 (5 C), 71.5, 71.6, 74.0, 75.4 (d, $J_{C,P}$ = 4.4 Hz), 75.7 (d, $J_{C,P}$ = 13.1 Hz), 79.5 (d, $J_{C,P}$ = 16.0 Hz), 115.0, 115.6, 126.18 (2 C), 126.21 (2 C), 127.5, 127.7, 128.2, 128.26 (d, $J_{C,P}$ = 6.7 Hz, 2 C), 128.28 (d, $J_{C,P}$ = 7.0 Hz, 2 C), 128.4 (2 C), 128.5 (2 C), 129.0, 132.6 (d, $J_{C,P}$ = 18.9 Hz, 2 C), 135.0 (d, $J_{C,P}$ = 20.4 Hz, 2 C), 138.5 (d, $J_{C,P}$ = 13.1 Hz), 139.9, 140.1 (d, $J_{C,P}$ = 13.1 Hz), 140.2, 144.32, 144.36, 170.8 (d, $J_{C,P}$ = 2.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.5 ppm. $C_{42}H_{37}FeO_2P$ (660.6): calcd. C 76.37, H 5.65; found C 76.13, H 5.80. HPLC: baseline separation of the enantiomers could not be achieved. $[\alpha]_D^{20}$ = +107 (c = 0.62, $CHCl_3$).

3-[(*tert*-Butyldimethylsilyloxy)methyl]-1-{2-[(*tert*-butyldimethylsilyloxy)methyl]allyl}but-3-enyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (7e). *rac*-7e: As described in GP2, *rac*-*o*-DPPFA (**8**; 622 mg, 1.50 mmol), alcohol **6e** (605 mg, 1.51 mmol, 1.0 equiv.), BOP (698 mg, 1.58 mmol, 1 equiv.), and NaH (150 mg, 60% in mineral oil, 3.79 mmol, 2.5 equiv.) in THF (15 mL) gave, after 21 h, workup, and flash chromatography (PE/EE, 50:1), the title compound *rac*-**7e** (766 mg, 0.96 mmol, 64%) as an orange oil. **(R_p)-7e:** As described in GP2, (R_p)-*o*-DPPFA (**8**; 424 mg, 1.02 mmol, *ee* > 99%), alcohol **6e** (410 mg, 1.02 mmol, 1.00 equiv.), BOP (476 mg, 1.08 mmol, 1.06 equiv.), and NaH (116 mg, 60% in mineral oil, 2.92 mmol, 2.87 equiv.) in THF (10 mL) gave, after 18 h, workup, and flash chromatography (PE/EE, 50:1), the title compound (R_p)-**7e** (678 mg, 0.85 mmol, 83%, *ee* > 99%) as an orange oil. **Data for 7e:** R_f (Cy/EE, 10:1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 6 H), 0.07 (s, 6 H), 0.90 (s, 9 H), 0.91 (s, 9 H), 1.98 (d, J = 6.4 Hz, 2 H), 2.26 (dd, J = 14.6, 8.2 Hz, 1 H), 2.34 (dd, J = 14.6, 4.3 Hz, 1 H), 3.66 (br. s, 1 H), 3.97 (d, J = 14.0 Hz, 1 H), 4.04 (d, J = 10.3 Hz, 2 H), 4.12 (d, J = 14.0 Hz, 1 H), 4.18 (s, 5 H), 4.40 (pseudo t, J = 2.6 Hz, 1 H), 4.67 (s, 1 H), 5.00–5.04 (m, 3 H), 5.10 (d, J = 1.7 Hz, 1 H), 5.25 (m_c, 1 H), 7.16–7.26 (m, 5 H), 7.34–7.37 (m, 3 H), 7.44–7.50 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –5.26 (2 C), –5.23 (2 C), 18.4 (2 C), 26.03 (3 C), 26.06 (3 C), 37.8, 37.9, 65.7, 65.9, 70.6, 71.2 (5 C), 71.6, 74.1, 75.3 (d, $J_{C,P}$ = 4.4 Hz), 76.0 (d, $J_{C,P}$ = 14.5 Hz), 79.3 (d, $J_{C,P}$ = 17.4 Hz), 111.6, 112.1, 128.0, 128.17 (d, $J_{C,P}$ = 5.8 Hz, 2 C), 128.23 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.0, 132.5 (d, $J_{C,P}$ = 20.3 Hz, 2 C), 135.1 (d, $J_{C,P}$ = 21.8 Hz, 2 C), 138.6 (d, $J_{C,P}$ = 14.5 Hz), 140.0 (d, $J_{C,P}$ = 13.1 Hz), 144.5, 144.6, 170.7 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –17.01 ppm. $C_{44}H_{61}FeO_4PSi_2$ (797.0): calcd. C 66.31, H 7.71; found C 66.53, H 7.70. HPLC [AD-H, heptane/2-propanol (400:1), 20 °C, 0.5 mL min^{-1}]: t_R[(S_p)-**7e**] = 9.36 min; t_R[(R_p)-**7e**] = 11.51 min. $[\alpha]_D^{20}$ = +110 (c = 0.73, $CHCl_3$).

Rhodium-Catalyzed Desymmetrizing Hydroformylation of Diallylcarbinol *o*-DPPF Esters 7

General Procedure 3 (GP3). Hydroformylation Protocol: The ester **7** was dissolved in THF and $[Rh(CO)_2acac]$ was added (a small gas evolution of CO was visible). After addition of $P(OPh)_3$, the orange solution was transferred with a syringe into an oven-dried (70 °C) stainless-steel tube autoclave; the flask and syringe were rinsed twice with THF (final ester concentration: 0.1 M). The argon in the autoclave was removed by a pressurizing/depressurizing cycle (three times 20 bar H_2/CO), and finally the autoclave was pressurized with 40 bar H_2/CO and heated in an oil bath to the reaction temperature for the indicated period of time. Subsequently, the autoclave was cooled to 25 °C, depressurized, and the solution was filtered through a plug of Celite, washed with MTBE, and the solvents were removed in vacuo. Conversion and diastereoselectivity were determined by NMR analysis of the crude mixture (in $CDCl_3$, conversion was determined by integration of the aldehyde signals relative to the NMR signals of the olefinic protons of the starting material; diastereoselecitivity was determined by integration of the aldehyde signals). Purification of the products was achieved by flash chromatography (the orange fraction was collected in a flask under argon and the solvents were removed in an argon-purged rotary evaporator) followed by drying of the product aldehyde **9** at 60 °C/0.1 mbar for several hours.

(1*S*,3*S*)-3-Methyl-1-(2-methylallyl)-5-oxopentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (9a)

***rac*-9a. Variation 1:** According to GP3, hydroformylation of *rac*-**7a** (261.3 mg, 0.49 mmol) was carried out with $[Rh(CO)_2acac]$ (2.3 mg, 8.9 μmol, 0.018 equiv.) and $P(OPh)_3$ (9.2 μL, 0.035 mmol, 0.072 equiv.) in THF (4.9 mL) at 50 °C for 21.5 h. The NMR spectrum of the crude product showed a conversion of 88% and the resulting aldehydes were obtained in a diastereomeric ratio of 96:4. Flash chromatography (PE/EE, 20:1), furnished starting material (25.5 mg, 0.05 mmol, 10%) and after increasing the polarity of the eluent (PE/EE, 10:1) the aldehyde *rac*-**9a** (222.2 mg, 0.39 mmol, 89% based on recovered starting material, *dr* 97:3) as an orange solid. **Variation 2:** According to GP3, hydroformylation of *rac*-**7a** (209.7 mg, 0.39 mmol) was carried out with $[Rh(CO)_2acac]$ (1.8 mg, 7.0 μmol, 0.018 equiv.) and $P(OPh)_3$ (7.4 μL, 0.028 mmol, 0.072 equiv.) in THF (3.9 mL) at 40 °C for 48 h. The NMR spectrum of the crude product showed a conversion of 80% and the resulting aldehydes were obtained in a diastereomeric ratio of 97:3. Flash chromatography (PE/EE, 20:1) furnished the starting material (40.3 mg, 0.08 mmol, 19%) and, after increasing the polarity of the eluent (PE/EE, 10:1), the aldehyde *rac*-**9a** (140.6 mg, 0.25 mmol, 79% based on recovered starting material, *dr* 97:3) as an orange solid.

(R_p)-9a: According to GP3, hydroformylation of (R_p)-**7a** (262.4 mg, 0.49 mmol) was carried out with $[Rh(CO)_2acac]$ (2.3 mg, 8.9 μmol, 0.018 equiv.) and $P(OPh)_3$ (9.3 μL, 0.036 mmol, 0.072 equiv.) in THF (4.9 mL) at 50 °C for 21.5 h. The NMR spectrum of the crude product showed a conversion of 91% and the resulting aldehydes were obtained in a diastereomeric ratio of 96:4. Flash chromatography (PE/EE, 20:1) furnished starting material (16.3 mg, 0.03 mmol, 6%) and, after increasing the polarity of the eluent (PE/EE, 10:1), the aldehyde (R_p)-**9a** (217.3 mg, 0.38 mmol, 83% based on recovered starting material, *dr* 96:4) as an orange solid.

Data for 9a: R_f (Cy/EE, 5:1) = 0.26; m.p. 117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (d, J = 6.3 Hz, 3 H), 1.32 (ddd, J = 13.9, 9.7, 2.6 Hz, 1 H), 1.60 (ddd, J = 13.9, 10.6, 3.1 Hz, 1 H), 1.68 (s, 3 H), 1.71 (dd, J = 13.7, 7.4 Hz, 1 H), 2.02 (dd, J = 13.7, 6.9 Hz, 1 H), 2.30–2.45 (m, 3 H), 3.67 (br. s, 1 H), 4.22 (s, 5 H), 4.43 (pseudo t, J = 2.5 Hz, 1 H), 4.48 (s, 1 H), 4.69 (s, 1 H), 5.06 (br. s, 1 H), 5.21 (m_c, 1 H), 7.18–7.22 (m, 2 H), 7.23–7.26 (m, 3 H), 7.34–7.38 (m, 3 H), 7.43–7.48 (m, 2 H), 9.86 (pseudo t, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.3, 22.4, 24.9 (d, $J_{C,P}$ = 3.3 Hz), 41.3, 43.4, 51.7, 69.7, 71.1 (5 C), 71.7, 74.2, 75.4 (d, $J_{C,P}$ = 4.2 Hz), 75.9 (d, $J_{C,P}$ = 14.8 Hz), 79.4 (d, $J_{C,P}$ = 15.4 Hz), 113.4, 128.1, 128.2 (d, $J_{C,P}$ = 7.0 Hz, 2 C), 128.3 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.1, 132.5 (d, $J_{C,P}$ = 19.7 Hz, 2 C), 135.0 (d, $J_{C,P}$ = 21.5 Hz, 2 C), 138.2 (d, $J_{C,P}$ = 13.6 Hz), 139.8 (d, $J_{C,P}$ = 13.2 Hz), 141.5, 171.0 (d, $J_{C,P}$ = 3.0 Hz), 202.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.3 ppm. $C_{33}H_{35}FeO_3P$ (566.5): calcd. C 69.97, H 6.23; found C 69.81, H 6.19. $[\alpha]_D^{20}$ = +121 (c = 0.79, $CHCl_3$, *dr* 96:4).

(1*S*,3*S*)-3-Ethyl-1-(2-methylenebutyl)-5-oxopentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (9b). *rac*-9b: According to GP3, hydroformylation of *rac*-**7b** (290.3 mg, 0.51 mmol) was carried out with $[Rh(CO)_2acac]$ (2.4 mg, 9.3 μmol, 0.018 equiv.) and $P(OPh)_3$ (9.6 μL, 0.037 mmol, 0.072 equiv.) in THF (5.1 mL) at 50 °C for 21 h. The NMR spectrum of the crude product showed a conversion of 84% and the resulting aldehydes were obtained in a diastereomeric ratio of 95:5. Flash chromatography (PE/EE, 50:1) furnished starting material (35.1 mg, 0.06 mmol, 12%) and, after increasing the polarity of the eluent (PE/EE, 10:1), the aldehyde *rac*-**9b** (235.2 mg, 0.40 mmol, 88% based on recovered starting material, *dr* 96:4) as an orange solid. **(R_p)-9b:** According to GP3, hydroformylation of (R_p)-**7b** (482.8 mg, 0.86 mmol) was carried out with $[Rh(CO)_2acac]$ (4.0 mg, 15.5 μmol, 0.018 equiv.) and $P(OPh)_3$ (16.1 μL, 0.061 mmol, 0.072 equiv.) in THF (8.6 mL) at 50 °C for 21 h. The NMR spectrum of the crude product showed a conversion of 83% and the resulting aldehydes were obtained in a diastereomeric ratio of 96:4. Flash chromatography (PE/EE, 50:1) furnished starting material (59.5 mg, 0.11 mmol, 12%) and, after increasing the polarity of the eluent (PE/EE, 10:1), the aldehyde (R_p)-**9b** (380.1 mg, 0.64 mmol, 85% based on recovered starting material, *dr* 96:4) as an orange solid. **Data for 9b:** R_f (Cy/EE, 10:1) = 0.20; m.p. 96–97 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, J = 7.4 Hz, 3 H), 0.99 (t, J = 7.4 Hz, 3 H), 1.29 (dq, J = 21.1, 7.4 Hz, 1 H), 1.46–1.56 (m, 3 H), 1.69 (dd, J = 14.1, 6.9 Hz, 1 H), 1.99 (m_c, 2 H), 2.08 (dd, J = 14.1, 6.7 Hz, 1 H), 2.15–2.23 (m_c, 1 H), 2.30 (ddd, J = 16.0, 7.4, 2.8 Hz, 1 H), 2.46 (ddd, J = 16.0, 6.2, 2.2 Hz, 1 H), 3.66 (ddd, J = 2.5, 1.5, 0.9 Hz, 1 H), 4.21 (s, 5 H), 4.43 (d pseudo t, J = 2.5, 0.5 Hz, 1 H), 4.57 (s, 1 H), 4.72 (d, J = 1.7 Hz, 1 H), 5.06 (ddd, J = 2.5, 1.4, 1.1 Hz, 1 H), 5.16 (m_c, 1 H), 7.17–7.22 (m, 2 H), 7.23–7.26 (m, 3 H), 7.34–7.38 (m, 3 H), 7.43–7.48 (m, 2 H), 9.86 (dd, J = 2.8, 2.2 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.4, 12.3, 25.6, 28.7, 30.8 (d, $J_{C,P}$ = 2.4 Hz), 38.4, 41.8, 48.3, 70.2, 71.1 (5 C), 71.7, 74.1, 75.4 (d, $J_{C,P}$ = 4.5 Hz), 75.8 (d, $J_{C,P}$ = 14.8 Hz), 79.4 (d, $J_{C,P}$ = 15.7 Hz), 111.1, 128.1, 128.2 (d, $J_{C,P}$ = 7.0 Hz, 2 C), 128.3 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.1, 132.5 (d, $J_{C,P}$ = 19.4 Hz, 2 C), 135.0 (d, $J_{C,P}$ = 21.5 Hz, 2 C), 138.2 (d, $J_{C,P}$ = 13.6 Hz), 139.8 (d, $J_{C,P}$ = 13.4 Hz), 147.0, 171.1 (d, $J_{C,P}$ = 3.0 Hz), 203.3 (d, $J_{C,P}$ = 1.8 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.5 ppm. $C_{35}H_{39}FeO_3P$ (594.5): calcd. C 70.71, H 6.61; found C 70.48, H 6.63. $[\alpha]_D^{20}$ = +111 (c = 0.61, $CHCl_3$, *dr* 96:4).

(1*S*,3*S*)-4-Methyl-1-(3-methyl-2-methylenebutyl)-3-(2-oxoethyl)pentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (9c)

***rac*-9c. Variation 1:** According to GP3, hydroformylation of *rac*-**7c** (337.2 mg, 0.57 mmol) was carried out with $[Rh(CO)_2acac]$ (2.6 mg, 10.1 μmol, 0.018 equiv.) and $P(OPh)_3$ (10.7 μL, 0.041 mmol, 0.072 equiv.) in THF (5.7 mL) at 60 °C for 24 h. The NMR spectrum of the crude product showed a conversion of 87% and the resulting aldehydes were obtained in a diastereomeric ratio of 87:13. Flash chromatography (PE/EE, 50:1, stationary phase neutral Al_2O_3 deactivated with 10% water) furnished starting mate-

rial (29.7 mg, 0.05 mmol, 9%) and, after increasing the polarity of the eluent (PE/EE, 25:1), the aldehyde *rac*-**9c** (294.0 mg, 0.47 mmol, 91% based on recovered starting material, *dr* 87:13) as an orange oil which crystallized slowly on standing at 4 °C. **Variation 2:** According to GP3, hydroformylation of *rac*-**7c** (297.1 mg, 0.50 mmol) was carried out with $[Rh(CO)_2acac]$ (2.3 mg, 8.9 μmol, 0.018 equiv.) and $P(OPh)_3$ (9.5 μL, 0.036 mmol, 0.072 equiv.) in THF (5.0 mL) at 50 °C for 48 h. The NMR spectrum of the crude product showed a conversion of 72% and the resulting aldehydes were obtained in a diastereomeric ratio of 87:13. Flash chromatography (PE/EE, 50:1, stationary phase neutral Al_2O_3 deactivated with 10% water) furnished starting material (75.4 mg, 0.13 mmol, 25%) and, after increasing the polarity of the eluent (PE/EE, 25:1), the aldehyde *rac*-**9c** (211.0 mg, 0.34 mmol, 91% based on recovered starting material, *dr* 87:13) as an orange oil which crystallized slowly on standing at 4 °C.

(R_p)-9c: According to GP3, hydroformylation of (R_p)-**7c** (301.1 mg, 0.51 mmol) was carried out with $[Rh(CO)_2acac]$ (2.4 mg, 9.3 μmol, 0.018 equiv.) and $P(OPh)_3$ (9.6 μL, 0.037 mmol, 0.072 equiv.) in THF (5.1 mL) at 60 °C for 24 h. The NMR spectrum of the crude product showed a conversion of 81% and the resulting aldehydes were obtained in a diastereomeric ratio of 86:14. Flash chromatography (PE/EE, 50:1, stationary phase neutral Al_2O_3 deactivated with 10% water) furnished starting material (45.1 mg, 0.08 mmol, 15%) and, after increasing the polarity of the eluent (PE/EE, 25:1), the aldehyde (R_p)-**9c** (227.5 mg, 0.37 mmol, 84% based on recovered starting material, *dr* 86:14) as an orange oil.

Data for 9c: R_f (Cy/EE, 5:1) = 0.44; m.p. 70–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.75 (d, J = 6.4 Hz, 3 H), 0.84 (d, J = 6.9 Hz, 3 H), 0.97 (d, J = 7.3 Hz, 3 H), 0.99 (d, J = 7.3 Hz, 3 H, 3 H), 1.36 (ddd, J = 14.2, 9.9, 4.3 Hz, 1 H), 1.53–1.67 (m, 2 H), 1.88 (m_c, 1 H), 2.09–2.33 (m, 4 H), 2.43 (dd, J = 10.8, 1.7 Hz, 1 H), 3.67 (br. s, 1 H), 4.22 (s, 5 H), 4.43 (pseudo t, J = 2.6 Hz, 1 H), 4.61 (s, 1 H), 4.78 (s, 1 H), 5.06 (pseudo quint, J = 1.3 Hz, 1 H), 5.14 (m_c, 1 H), 7.17–7.26 (m, 5 H), 7.34–7.38 (m, 3 H), 7.43–7.48 (m, 2 H), 9.87 (pseudo t, J = 2.4 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.9, 20.5, 21.7, 21.8, 28.6, 33.6, 34.9, 36.3, 40.0, 44.9, 70.5, 71.1 (5 C), 71.7, 74.1, 75.4 (d, $J_{C,P}$ = 4.4 Hz), 75.9 (d, $J_{C,P}$ = 14.5 Hz), 79.5 (d, $J_{C,P}$ = 16.0 Hz), 109.7, 128.1, 128.2 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 128.3 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 129.1, 132.5 (d, $J_{C,P}$ = 18.9 Hz, 2 C), 135.0 (d, $J_{C,P}$ = 21.8 Hz, 2 C), 138.3 (d, $J_{C,P}$ = 14.5 Hz), 139.8 (d, $J_{C,P}$ = 14.5 Hz), 151.5, 171.1 (d, $J_{C,P}$ = 2.9 Hz), 203.6 (CHO) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.6 ppm. $C_{37}H_{43}FeO_3P$ (622.6): calcd. C 71.38, H 6.96; found C 71.11, H 6.99. $[\alpha]_D^{20}$ = +106 (c = 0.39, $CHCl_3$, *dr* 86:14).

[(1*S*,3*S*)-5-Oxo-3-phenyl-1-(2-phenylallyl)pentyl] (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (9d). *rac*-9d: According to GP3, hydroformylation of *rac*-**9d** (431.0 mg, 0.65 mmol) was carried out with $[Rh(CO)_2acac]$ (3.0 mg, 11.6 μmol, 0.018 equiv.) and $P(OPh)_3$ (12.3 μL, 0.047 mmol, 0.072 equiv.) in THF (6.5 mL) at 70 °C for 24 h. The NMR spectrum of the crude product showed a conversion of 81% and the resulting aldehydes were obtained in a diastereomeric ratio of 94:6. Flash chromatography (PE/EE, 10:1) furnished starting material (63.5 mg, 0.10 mmol, 15%) and, after increasing the polarity of the eluent (PE/EE, 5:1), the aldehyde *rac*-**9d** (321.0 mg, 0.47 mmol, 84% based on recovered starting material, *dr* 94:6) as an orange solid. **(R_p)-9d:** According to GP3, hydroformylation of (R_p)-**9d** (433.2 mg, 0.66 mmol) was carried out with $[Rh(CO)_2acac]$ (3.0 mg, 11.6 μmol, 0.018 equiv.) and $P(OPh)_3$ (12.4 μL, 0.047 mmol, 0.072 equiv.) in THF (6.6 mL) at 70 °C for 24 h. The NMR spectrum of the crude product showed a conversion of 82% and the resulting aldehydes were obtained in a diastereomeric ratio of 94:6. Flash chromatography (PE/EE, 10:1) furnished starting material (59.5 mg, 0.09 mmol, 14%) and, after increasing the polarity of the eluent (PE/EE, 5:1), the aldehyde (R_p)-**9d** (352.2 mg, 0.51 mmol, 90% based on recovered starting material, *dr* 94:6) as an orange solid. **Data for 9d:** R_f (Cy/EE, 10:1) = 0.16; m.p. 158–162 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (ddd, J = 14.2, 9.9, 3.9 Hz, 1 H), 1.80 (m, 2 H), 2.59 (ddd, J = 16.1, 6.9, 2.6 Hz, 1 H), 2.67 (ddd, J = 16.1, 8.2, 2.2 Hz, 1 H), 2.78 (dd, J = 14.2, 6.6 Hz, 1 H), 3.55 (m_c, 1 H), 3.68 (br. s, 1 H), 4.25 (s, 5 H), 4.45 (pseudo t, J = 2.6 Hz, 1 H), 4.68 (m_c, 1 H), 4.81 (s, 1 H), 5.05 (br. s, 1 H), 5.23 (s, 1 H), 6.86–7.53 (m, 20 H), 9.73 (t, J = 2.2 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 36.7 (d, $J_{C,P}$ = 2.9 Hz), 39.2, 39.7, 51.3, 71.06, 71.13 (5 C), 71.8, 74.4, 75.6 (d, $J_{C,P}$ = 4.4 Hz), 75.9 (d, $J_{C,P}$ = 14.5 Hz), 79.2 (d, $J_{C,P}$ = 16.0 Hz), 115.0, 126.2 (2 C), 126.7, 127.4 (2 C), 127.7, 128.2, 128.3 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 128.37 (d, $J_{C,P}$ = 8.7 Hz, 2 C), 128.42 (2 C), 128.7 (2 C), 129.2, 132.5 (d, $J_{C,P}$ = 18.9 Hz, 2 C), 135.1 (d, $J_{C,P}$ = 20.3 Hz, 2 C), 138.2 (d, $J_{C,P}$ = 13.1 Hz), 139.9, 140.0 (d, $J_{C,P}$ = 13.1 Hz), 142.2, 144.3, 170.9 (d, $J_{C,P}$ = 2.9 Hz), 201.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –15.8 ppm. $C_{43}H_{39}FeO_3P$ (690.6): calcd. C 74.79, H 5.69; found C 74.56, H 5.74. $[\alpha]_D^{20}$ = +48 (c = 0.67, $CHCl_3$, *dr* 94:6).

(1*S*,3*S*)-3-[(*tert*-Butyldimethylsilyloxy)methyl]-1-{2-[(*tert*-butyldimethylsilyloxy)methyl]allyl}-5-oxopentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (9e). *rac*-9e: According to GP3, hydroformylation of *rac*-**7e** (327.4 mg, 0.41 mmol) was carried out with $[Rh(CO)_2acac]$ (1.9 mg, 7.4 μmol, 0.018 equiv.) and $P(OPh)_3$ (7.8 μL, 0.030 mmol, 0.072 equiv.) in THF (4.1 mL) at 50 °C for 16 h. The NMR spectrum of the crude product showed a quantitative conversion and the resulting aldehydes were obtained in a diastereomeric ratio of 95:5. Flash chromatography (PE/EE, 10:1) furnished the aldehyde *rac*-**9e** (287.8 mg, 0.35 mmol, 85%, *dr* 95:5) as an orange oil which crystallized slowly upon standing at 4 °C. **(R_p)-9e:** According to GP3, hydroformylation of (R_p)-**7e** (592.5 mg, 0.74 mmol) was carried out with $[Rh(CO)_2acac]$ (3.5 mg, 13.6 μmol, 0.018 equiv.) and $P(OPh)_3$ (14.0 μL, 0.053 mmol, 0.072 equiv.) in THF (7.4 mL) at 50 °C for 16 h. The NMR spectrum of the crude product showed a quantitative conversion and the resulting aldehydes were obtained in a diastereomeric ratio of 96:4. Flash chromatography (PE/EE, 10:1) furnished the aldehyde (R_p)-**9e** (492.5 mg, 0.60 mmol, 80%, *dr* 96:4) as an orange oil which crystallized slowly upon standing at 4 °C. **Data for 9e:** R_f (Cy/EE, 10:1) = 0.35; m.p. 93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.007 (s, 3 H), 0.014 (s, 3 H), 0.046 (s, 3 H), 0.050 (s, 3 H), 0.86 (s, 9 H), 0.89 (s, 9 H), 1.47 (ddd, J = 14.3, 10.4, 3.8 Hz, 1 H), 1.67 (ddd, J = 14.3, 9.5, 2.9 Hz, 1 H), 1.82 (dd, J = 14.3, 6.1 Hz, 1 H), 1.94 (dd, J = 14.3, 7.2 Hz, 1 H), 2.36–2.44 (m, 2 H), 2.56 (ddd, J = 17.7, 9.1, 2.5 Hz, 1 H), 3.48 (dd, J = 10.0, 5.8 Hz, 1 H), 3.58 (dd, J = 10.0, 3.5 Hz, 1 H), 3.67 (ddd, J = 2.5, 1.5, 0.9 Hz, 1 H), 3.95 (d, J = 14.1 Hz, 1 H), 4.01 (d, J = 14.1 Hz, 1 H), 4.21 (s, 5 H), 4.43 (pseudo t, J = 2.5 Hz, 1 H), 4.62 (d, J = 0.8 Hz, 1 H), 5.00 (q, J = 1.7 Hz, 1 H), 5.05 (pseudo quint, J = 1.4 Hz, 1 H), 5.13 (m_c, 1 H), 7.17–7.26 (m, 5 H), 7.34–7.38 (m, 3 H), 7.43–7.48 (m, 2 H), 9.87 (pseudo t, J = 2.3 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.47, –5.45, –5.28, –5.25, 18.3, 18.4, 25.97 (3 C), 26.00 (3 C), 32.9 (d, $J_{C,P}$ = 2.7 Hz), 35.9, 38.4, 47.3, 64.2, 65.6, 70.1, 71.1 (5 C), 71.7, 74.3 (d, $J_{C,P}$ = 4.2 Hz), 75.9 (d, $J_{C,P}$ = 14.8 Hz), 79.2 (d, $J_{C,P}$ = 15.7 Hz), 111.9, 128.1, 128.2 (d, $J_{C,P}$ = 7.0 Hz, 2 C), 128.3 (d, $J_{C,P}$ = 7.0 Hz, 2 C), 129.1, 132.5 (d, $J_{C,P}$ = 19.7 Hz, 2 C), 135.0 (d, $J_{C,P}$ = 21.5 Hz, 2 C), 138.1 (d, $J_{C,P}$ = 13.3 Hz), 139.9 (d, $J_{C,P}$ = 13.0 Hz), 144.1, 171.0 (d, $J_{C,P}$ = 2.7 Hz), 202.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.6 ppm. $C_{45}H_{63}FeO_5PSi_2$ (827.0): calcd. C 65.36,

H 7.68; found C 65.34, H 7.65. $[\alpha]_D^{20}$ = +86 (*c* = 0.92, $CHCl_3$, *dr* 97:3).

Determination of the Enantiomeric Purity of the Hydroformylation Products. $NaBH_4$ Reduction of 9e

(1*S*,3*R*)-3-[(*tert*-Butyldimethylsilyloxy)methyl]-1-{2-[(*tert*-butyldimethylsilyloxy)methyl]allyl}-5-hydroxypentyl (R_p)-2-(Diphenylphosphanyl)ferrocenecarboxylate (10e). *rac*-10e: *rac*-**9e** (73.0 mg, 0.088 mmol, *dr* 96:4) in methanol (2.0 mL) was treated with $NaBH_4$ (3.5 mg, 0.100 mmol, 1.1 equiv.) at room temperature for 120 min. Quenching with water (4 equiv.), removal of all volatile components in vacuo, and subsequent flash chromatography (PE/EE, 25:1) furnished the title compound *rac*-**10e** (52.8 mg, 0.064 mmol, 72%, *dr* > 99:1) as an orange solid. **(R_p)-10e:** (R_p)-**9e** (109.3 mg, 0.132 mmol, *dr* 97:3) in methanol (2.5 mL) was treated with $NaBH_4$ (5.8 mg, 0.153 mmol, 1.2 equiv.) at room temperature for 80 min. Quenching with water (4 equiv.), removal of all volatile material, and subsequent flash chromatography (PE/EE, 25:1) furnished the title compound (R_p)-**10e** (91.9 mg, 0.111 mmol, 84%, *dr* > 99:1, *ee* > 99%) as an orange solid. **Data for 10e:** R_f (Cy/EE, 10:1) = 0.23; m.p. 87–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03 (s, 3 H), 0.04 (s, 3 H), 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 0.89 (s, 9 H), 1.51–1.58 (m, 3 H), 1.63 (dd, *J* = 14.2, 7.2 Hz, 1 H), 1.74 (dd, *J* = 14.2, 7.2 Hz, 1 H), 1.84 (m_c, 1 H), 2.06 (br. s, 1 H), 3.48 (dd, *J* = 13.2, 7.2 Hz, 1 H), 3.60–3.65 (m, 3 H), 3.73–3.88 (m, 2 H), 3.91 (d, *J* = 14.1 Hz, 1 H), 3.97 (d, *J* = 14.1 Hz, 1 H), 4.23 (s, 5 H), 4.44 (pseudo t, *J* = 2.5 Hz, 1 H), 4.48 (s, 1 H), 4.93 (s, 1 H), 5.09 (s, 1 H), 5.19 (pseudo quint, *J* = 6.6 Hz, 1 H), 7.21–7.30 (m, 5 H), 7.34–7.38 (m, 3 H), 7.43–7.48 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.40, –5.37, –5.30, –5.27, 18.3, 18.4, 26.0 (6 C), 33.4 (d, $J_{C,P}$ = 2.7 Hz), 34.7, 36.2, 38.6, 59.9, 65.1, 65.5, 70.2, 71.2 (5 C), 71.7, 74.8, 75.6 (d, $J_{C,P}$ = 3.9 Hz), 76.0 (d, $J_{C,P}$ = 15.2 Hz), 79.9 (d, $J_{C,P}$ = 15.4 Hz), 111.7, 128.3, 128.4 [d, $J_{C,P}$ = 6.7 Hz, 4 C], 129.3, 132.5 (d, $J_{C,P}$ = 19.4 Hz, 2 C), 135.0 (d, $J_{C,P}$ = 20.9 Hz, 2 C), 138.2 (d, $J_{C,P}$ = 9.1 Hz), 139.1 (d, $J_{C,P}$ = 8.8 Hz), 144.2, 170.9 (d, $J_{C,P}$ = 2.7 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.6 ppm. $C_{45}H_{65}FeO_5PSi_2$ (829.0): calcd. C 65.20, H 7.90; found C 65.26, H 7.84. HPLC [AD-H, heptane/2-propanol (98:2), 20 °C, 0.8 mL min^{-1}]: t_R[(R_p,1*S*,3*R*)-**10e**] = 8.56 min; t_R[(S_p,1*R*,3*S*)-**10e**] = 12.21 min. $[\alpha]_D^{20}$ = +89 (*c* = 0.515, $CHCl_3$, *dr* > 99:1).

General Procedure 4 (GP4). DIBALH Reduction of 9a–d: The corresponding aldehyde **9** was dissolved in CH_2Cl_2 and the solution was cooled to –78 °C. DIBALH (1 M solution in cyclohexane) was added dropwise with a syringe and the reaction mixture was stirred at –78 °C. The reaction mixture was allowed to warm to 0 °C and was subsequently quenched with satd. aqueous NH_4Cl solution (6 mL/mmol) and 1 M HCl (12 mL/mmol). The aqueous phase was extracted four times with CH_2Cl_2, dried (Na_2SO_4), and all volatile components removed in vacuo. Purification of the residue by flash chromatography furnished *o*-DPPF-CH_2OH (**12**) as well as the corresponding diol **11**.

(4*S*,6*R*)-2,6-Dimethyloct-1-ene-4,8-diol (11a). *rac*-11a: *rac*-**9a** (85.4 mg, 0.15 mmol, *dr* 96:4) in CH_2Cl_2 (2 mL) was treated with DIBALH (0.53 mL, 0.53 mmol, 3.5 equiv.) for 2 h as described in GP4. Flash chromatography (PE/TBME, 1:1) furnished *rac*-**12** (54.2 mg, 0.14 mmol, 90%) and, after increasing the polarity of the eluent (PE/TBME, 1:2), *rac*-**11a** (20.3 mg, 0.12 mmol, 78%, *dr* > 99:1) as a colorless liquid. **(–)-11a:** (R_p)-**9a** (85.7 mg, 0.15 mmol, *dr* 96:4) in CH_2Cl_2 (2 mL) was treated with DIBALH (0.57 mL, 0.57 mmol, 3.8 equiv.) for 2 h as described in GP4. Flash chromatography (PE/TBME, 1:1) furnished (R_p)-**12** (55.2 mg, 0.14 mmol, 91%) and, after increasing the polarity of the eluent (PE/TBME, 1:2), (–)-**11a** (20.6 mg, 0.12 mmol, 79%, *dr* > 99:1, *ee* > 99%) as a colorless liquid. **Data for 11a:** R_f (Cy/EE, 5:1) = 0.08. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.6 Hz, 3 H), 1.18 (ddd, *J* = 12.2, 6.5, 2.8 Hz, 1 H), 1.48–1.54 (m, 3 H), 1.75 (s, 3 H), 1.87 (m_c, 1 H), 2.11–2.14 (m, 2 H), 2.1–2.4 (br. s, 1 H), 3.66 (dt, *J* = 10.9, 3.7 Hz, 1 H), 3.71 (dt, *J* = 10.9, 6.7 Hz, 1 H), 3.82 (m_c, 1 H), 4.77 (s, 1 H), 4.86 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0, 22.5, 26.2, 40.5, 44.0, 47.1, 60.5, 66.8, 113.5, 142.8 ppm. HRMS (EI; $C_{10}H_{20}O_2$ [M – C_4H_7], 172.3): calcd. 117.0913; found 117.0916. GC (Betadex 110, 105 °C, 18 psi): t_R[(4*R*,6*S*)-**11a**] = 99.4 min; t_R[(4*S*,6*R*)-**11a**] = 104.0 min. $[\alpha]_D^{20}$ = –32 (*c* = 0.895, $CHCl_3$, *dr* > 99:1). **Data for 12:** R_f (Cy/EE, 1:1) = 0.38; m.p. 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (br. t, *J* = 6.0 Hz, 1 H), 3.76 (br. s, 1 H), 4.10 (s, 5 H), 4.30 (pseudo t, *J* = 2.6 Hz, 1 H), 4.42 (dd, *J* = 12.5, 6.0 Hz, 1 H), 4.52 (br. s, 1 H), 4.54 (ddd, *J* = 12.5, 6.0, 1.7 Hz, 1 H), 7.19–7.24 (m, 2 H), 7.25–7.29 (m, 3 H), 7.37–7.41 (m, 3 H), 7.50–7.56 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 60.0 (d, $J_{C,P}$ = 10.2 Hz), 69.5 (5 C), 69.7, 71.6 (d, $J_{C,P}$ = 4.4 Hz), 71.7 (d, $J_{C,P}$ = 2.9 Hz), 76.2 (d, $J_{C,P}$ = 7.3 Hz), 92.8 (d, $J_{C,P}$ = 23.3 Hz), 128.31 (d, $J_{C,P}$ = 7.3 Hz, 2 C), 128.32, 128.5 (d, $J_{C,P}$ = 5.8 Hz, 2 C), 129.3, 132.5 (d, $J_{C,P}$ = 17.4 Hz, 2 C), 134.9 (d, $J_{C,P}$ = 20.3 Hz, 2 C), 137.0 (d, $J_{C,P}$ = 8.7 Hz), 139.7 (d, $J_{C,P}$ = 10.2 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –22.4 ppm. $C_{23}H_{21}FeOP$ (400.2): calcd. C 69.02, H 5.29; found C 68.81, H 5.49. $[\alpha]_D^{20}$ = +273 (*c* = 0.78, $CHCl_3$).

(3*R*,5*S*)-3-Ethyl-7-methylenenonane-1,5-diol (11b). *rac*-11b: *rac*-**9b** (117.2 mg, 0.20 mmol, *dr* 96:4) in CH_2Cl_2 (4 mL) was treated with DIBALH (0.70 mL, 0.70 mmol, 3.5 equiv.) for 2.5 h as described in GP4. Flash chromatography (PE/TBME, 1:1) furnished *rac*-**12** (68.2 mg, 0.17 mmol, 86%) and, after increasing the polarity of the eluent (PE/TBME, 1:2), *rac*-**11b** (21.2 mg, 0.11 mmol, 54%, *dr* 96:4) as a colorless liquid. **(–)-11b:** (R_p)-**9b** (187.4 mg, 0.32 mmol, *dr* 95:5) in CH_2Cl_2 (6 mL) was treated with DIBALH (1.10 mL, 1.10 mmol, 3.5 equiv.) for 2 h as described in GP4. Flash chromatography (PE/TBME, 1:1) furnished (R_p)-**12** (93.4 mg, 0.23 mmol, 74%) and, after increasing the polarity of the eluent (PE/TBME, 1:2), (–)-**11b** (49.0 mg, 0.25 mmol, 78%, *dr* 98:2, *ee* > 99%) as a colorless liquid. **Data for 11b:** R_f (Cy/EE, 1:1) = 0.16. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 3 H), 1.04 (t, *J* = 7.4 Hz, 3 H), 1.29–1.48 (m, 5 H), 1.63–1.72 (m, 2 H), 1.97–2.12 (m, 4 H), 2.21 (dd, *J* = 13.7, 3.5 Hz, 1 H), 2.37 (br. s, 1 H), 3.63–3.80 (m, 3 H), 4.82 (s, 1 H), 4.88 (d, *J* = 1.5 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.8, 12.3, 27.4, 28.7, 32.8, 36.9, 40.8, 45.7, 60.6, 67.9, 111.3, 148.3 ppm. HRMS (EI; $C_{12}H_{24}O_2$ [M – C_5H_9], 200.3): calcd. 131.1066; found 131.1072. GC (Betadex 110, 140 °C, 10 psi): t_R[(3*S*,5*R*)-**11b**] = 58.8 min; t_R[(3*R*,5*S*)-**11b**] = 60.3 min. $[\alpha]_D^{20}$ = –40 (*c* = 1.395, $CHCl_3$, *dr* 98:2).

(3*R*,5*S*)-3-Isopropyl-8-methyl-7-methylenenonane-1,5-diol (11c). *rac*-11c: *rac*-**9c** (171.3 mg, 0.28 mmol, *dr* 87:13) in CH_2Cl_2 (6 mL) was treated with DIBALH (1.10 mL, 1.10 mmol, 4.0 equiv.) for 4 h as described in GP4. Flash chromatography (PE/TBME, 1:1) furnished *rac*-**12** (69.0 mg, 0.17 mmol, 63%) and *rac*-**11c** (69.0 mg, 0.25 mmol, 89%, *dr* = 95:5) as a colorless liquid. Separation of the diastereomers by a second flash chromatography step (PE/TBME, 2:1) delivered a diastereomeric mixture of *rac*-*anti*/*syn*-**11c** (9.5 mg, 0.04 mmol, 15%, *dr* 85:15) and then pure *rac*-**11c** (44.0 mg, 0.19 mmol, 70%, *dr* > 99:1) as colorless liquids. **(–)-11c:** (R_p)-**9c** (80.3 mg, 0.13 mmol, *dr* 87:13) in CH_2Cl_2 (3 mL) was treated with DIBALH (0.52 mL, 0.52 mmol, 4.0 equiv.) for 4 h as described in GP4. Flash chromatography (PE/TBME, 2:1) furnished (R_p)-**12** (42.2 mg, 0.11 mmol, 82%), a diastereomeric mixture of *anti*-/*syn*-**11c** (5.7 mg, 0.03 mmol, 19%, *dr* 81:19), and (–)-**11c** (21.3 mg, 0.09 mmol, 72%, *dr* > 99:1, *ee* > 99%) as a colorless liquid. **Data for 11c:** R_f (Cy/EE, 1:1) = 0.15. ^{1}H NMR (500 MHz, $CDCl_3$): δ =

0.82 (d, J = 6.8 Hz, 3 H), 0.86 (d, J = 6.9 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.03 (d, J = 6.9 Hz, 3 H), 1.25–1.35 (m, 2 H), 1.42 (ddd, J = 14.5, 6.2, 3.2 Hz, 1 H), 1.57–1.65 (m, 2 H), 1.70 (m_c, 1 H), 2.07 (dd, J = 14.2, 9.1 Hz, 1 H), 2.21 (sept, J = 6.8 Hz, 1 H), 2.24 (ddd, J = 14.2, 4.0, 0.8 Hz, 1 H), 2.4–2.9 (br. s, 2 H), 3.60–3.75 (m, 3 H), 4.78 (s, 1 H), 4.90 (pseudo t, J = 1.2 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.6, 19.4, 21.7, 22.0, 31.2, 33.6, 34.1, 37.1, 37.9, 44.0, 60.9, 69.4, 109.8, 152.9 ppm. HRMS (EI; $C_{14}H_{28}O_2$ [M – C_6H_{11}], 228.4): calcd. 145.1229; found 145.1229. GC (Betadex 110, 130 °C, 20 psi): t_R[(3*S*,5*R*)-**11c**] = 85.7 min; t_R[(3*R*,5*S*)-**11c**] = 90.4 min. $[\alpha]_D^{20}$ = –27 (c = 0.80, $CHCl_3$, *dr* > 99:1).

(4*S*,6*R*)-2,6-Diphenyloct-1-ene-4,8-diol (11d). *rac*-11d: *rac*-**9d** (168.1 mg, 0.24 mmol, *dr* 94:6) in CH_2Cl_2 (4 mL) was treated with DIBALH (0.84 mL, 0.84 mmol, 3.5 equiv.) for 2.5 h as described in GP4. Flash chromatography (PE/EE, 1:2) furnished *rac*-**12** (93.3 mg, 0.23 mmol, 96%) and, after increasing the polarity of the eluent (PE/EE, 1:4), *rac*-**11d** (53.2 mg, 0.18 mmol, 75%, *dr* 94:6) as a white solid. **(–)-11d:** (R_p)-**9d** (199.3 mg, 0.29 mmol, *dr* 94:6) in CH_2Cl_2 (5 mL) was treated with DIBALH (1.01 mL, 1.01 mmol, 3.5 equiv.) for 2.5 h as described in GP4. Flash chromatography (PE/EE, 1:2) furnished (R_p)-**12** (99.7 mg, 0.25 mmol, 86%) and, after increasing the polarity of the eluent (PE/EE, 1:4), (–)-**11d** (67.1 mg, 0.23 mmol, 78%, *dr* 98:2, *ee* > 99%) as a white solid. **Data for 11d:** R_f (Cy/EE, 1:1) = 0.12; m.p. 83 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (br. s, 1 H), 1.64 (br. s, 1 H), 1.77–1.86 (m, 4 H), 2.54 (ddd, J = 14.2, 8.2, 0.8 Hz, 1 H), 2.61 (ddd, J = 14.2, 4.9, 1.1 Hz, 1 H), 3.01 (m_c, 1 H), 3.40–3.57 (m, 3 H), 5.06 (d, J = 1.3 Hz, 1 H), 5.35 (d, J = 1.6 Hz, 1 H), 7.09–7.18 (m, 3 H), 7.20–7.35 (m, 7 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.1, 40.3, 43.6, 44.4, 61.1, 67.8, 115.2, 126.2 (2 C), 126.4, 127.71 (2 C), 127.72, 128.4 (2 C), 128.6 (2 C), 140.5, 144.5, 145.3 ppm. HRMS (EI; $C_{20}H_{24}O_2$ [M – C_9H_9], 296.4): calcd. 179.1068; found 179.1073. HPLC [OD-H, heptane/2-propanol (95:5), 20 °C, 0.8 mL min^{-1}, 242 nm]: t_R[(4*R*,6*S*)-**11d**] = 30.24 min; t_R[(4*S*,6*R*)-**11d**] = 35.39. $[\alpha]_D^{20}$ = –21 (c = 0.835, $CHCl_3$, *dr* 98:2).

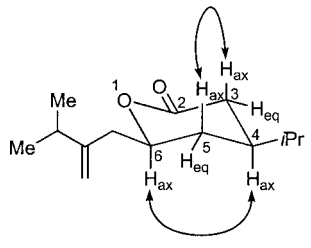
Cleavage and Recovery of the Catalyst-Directing Group

General Procedure 5 (GP5). Aldehyde Protection and Alkaline Ester Hydrolysis: The aldehyde **9** was suspended in methanol (10 mL/mmol), trimethyl orthoformate (5 equiv.) and *para*-toluenesulfonic acid monohydrate (0.05 equiv.) were added, and the mixture was heated to reflux for 2 h. After cooling to 25 °C, all volatile material was evaporated at 0.1 mbar and satd. KOH/EtOH (10 mL/mmol, degassed) was added to the red-brown solid residue. After heating again to reflux for several hours, satd. aqueous $NaHCO_3$ solution (30 mL/mmol) and Et_2O (30 mL/mmol) were added to the brown reaction mixture and the mixture was stirred until a brown solid precipitated. The solid material was collected by filtration and washed several times with water and Et_2O. The solid was then suspended in 1 N HCl (20 mL/mmol) and CH_2Cl_2 (20 mL/mmol) and the mixture was stirred until the solid had completely dissolved in the organic phase. The aqueous phase was extracted with CH_2Cl_2 (10 mL/mmol), the combined organic phases were dried (Na_2SO_4), and the solvent was removed in vacuo (employing an argon-purged rotary evaporator) to give *o*-DPPFA (**8**) as an orange-brown solid (partially oxidized). The aqueous phase of the filtrate was extracted three times with Et_2O (10 mL/mmol), the combined organic phases were dried (Na_2SO_4), and the solvent was removed in vacuo. Flash chromatography of the residue gave the pure dimethyl acetal **13**.

(3*S*,5*S*)-3-Isopropyl-1,1-dimethoxy-8-methyl-7-methylenenonan-5-ol (13). *rac*-13: The aldehyde *rac*-**9c** (224 mg, 0.36 mmol, *dr* 87:13) was treated with $HC(OMe)_3$ (0.20 mL, 1.83 mmol, 5 equiv.) and *para*-toluenesulfonic acid monohydrate (3.3 mg, 0.02 mmol, 0.05 equiv.) in methanol (5 mL) and then with satd. ethanolic KOH (5 mL) for 14 h as described in GP5. Workup and flash chromatography (PE/MTBE, 5:1) furnished *rac*-**13** (83 mg, 0.30 mmol, 84%, *dr* 87:13) as a colorless liquid. *o*-DPPFA was not isolated in this case. **(–)-13:** The aldehyde (R_p)-**9c** (159 mg, 0.26 mmol, *dr* 86:14) was treated with $HC(OMe)_3$ (0.14 mL, 1.28 mmol, 5 equiv.) and *para*-toluenesulfonic acid monohydrate (2.5 mg, 0.01 mmol, 0.05 equiv.) in methanol (4 mL) and then with satd. ethanolic KOH (4 mL) for 13 h as described in GP5. Workup gave (R_p)-*o*-DPPFA (**8**; 98 mg, 0.24 mmol, 92%) and flash chromatography (PE/MTBE, 5:1) furnished a diastereomeric mixture of *anti*/*syn*-**13** (15 mg, 0.05 mmol, 21%, *dr* 51:49) and (–)-**13** (47 mg, 0.17 mmol, 67%, *dr* 96:4) as a colorless liquid. **Data for 13:** R_f (Cy/EE) = 0.09. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (d, J = 6.9 Hz, 3 H), 0.86 (d, J = 6.9 Hz, 3 H), 1.02 (d, J = 6.9 Hz, 3 H), 1.04 (d, J = 6.8 Hz, 3 H), 1.33 (ddd, J = 14.2, 8.3, 5.8 Hz, 1 H), 1.42–1.49 (m, 2 H), 1.50–1.56 (m, 1 H), 1.64 (ddd, J = 13.8, 6.3, 4.6 Hz, 1 H), 1.75 (dsept, J = 6.9, 3.4 Hz, 1 H), 2.07 (ddd, J = 14.2, 8.8, 0.6 Hz, 1 H), 2.19–2.27 (m, 3 H), 3.28 (s, 3 H), 3.32 (s, 3 H), 3.73 (m_c, 1 H), 4.46 (pseudo t, J = 6.2 Hz, 1 H), 4.78 (s, 1 H), 4.88 (t, J = 1.3 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.3, 19.2, 21.7, 22.0, 30.4, 33.5, 34.0, 36.6, 39.0, 43.7, 51.8, 53.4, 68.5, 103.8, 109.5, 153.1 ppm. HRMS (EI; $C_{16}H_{32}O_3$ [M – MeOH], 272.4): calcd. 241.2170; found. 241.2168. $[\alpha]_D^{20}$ = –11.6 (c = 0.86, CH_2Cl_2, *dr* 96:4).

Determination of the Relative and Absolute Configuration of Product Aldehydes 9

(4*S,6*S**)-4-Isopropyl-6-(3-methyl-2-methylenebutyl)tetrahydropyran-2-one (14):** The dimethyl acetal *rac*-**13** (71.4 mg, 0.26 mmol, *dr* 87:13) in THF (3 mL) was treated with aqueous HCl (3 mL, 3 M) at 25 °C for 16 h. The reaction mixture was then poured into satd. aqueous $NaHCO_3$ solution (20 mL) and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The crude product was dissolved in CH_2Cl_2 (4 mL), NaOAc (15.0 mg, 0.18 mmol) and PCC/Al_2O_3 (532.7 mg, 1 mmol PCC/g, 0.53 mmol) were added, and the mixture was stirred for 24.5 h. The solids were removed by filtration, washed with Et_2O, and the filtrate was concentrated. Flash chromatography of the residue (PE/MTBE, 5:1) furnished *rac*-**14** (30.1 mg, 0.134 mmol, 50%, *dr* 94:6) as a colorless liquid. **Data for 14:** R_f (Cy/EE, 5:1) = 0.19. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.8 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3 H), 1.03 (d, J = 6.9 Hz, 6 H), 1.16 (dt, J = 13.8, 11.7 Hz, 1 H), 1.50 (oct, J = 6.8 Hz, 1 H), 1.72 (m, 1 H), 1.97 (dquint, J = 13.8, 2.0 Hz, 1 H), 2.14 (dd, J = 17.8, 10.4 Hz, 1 H), 2.23 (sept, J = 6.9 Hz, 1 H), 2.27 (dd, J = 14.8, 7.1 Hz, 1 H), 2.53 (ddd, J = 14.8, 6.2, 0.6 Hz, 1 H), 2.64 (ddd, J = 17.8, 6.5, 1.8 Hz, 1 H), 4.37 (m_c, 1 H), 4.79 (q, J = 0.8 Hz, 1 H), 4.89 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.1, 19.3, 21.7, 21.8, 32.3, 32.4, 33.83, 33.84, 37.9, 41.3, 79.4, 110.2, 150.7, 172.1 ppm. HRMS (EI; $C_{14}H_{24}O_2$, 224.3): calcd. 224.1780; found 224.1776. 2D NMR experiments and coupling constants established the *syn* relationship of the two substituents in the lactone **14**.



Determination of the Absolute Configuration of (–)-13. Preparation of (*R*) Mosher Ester: The alcohol (–)-**13** (5.6 mg, 21 μmol) in CH_2Cl_2 (1 mL) was treated with pyridine (0.50 mL), DMAP (4.7 mg, 39 μmol, 1.9 equiv.), and (+)-(*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (19.2 μL, 103 μmol, 5 equiv.) at 25 °C for 3 h. The reaction was quenched with satd. aqueous $NaHCO_3$ (2 mL), stirred for 30 min, and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic phases were dried (Na_2SO_4), concentrated, and the residue was dissolved in benzene (10 mL) and again concentrated in vacuo (two times) to remove excess pyridine. Flash chromatography of the residue (PE/MTBE, 10:1) furnished the (*R*) Mosher ester (8.7 mg, 18 μmol, 86%) as a colorless liquid. R_f (Cy/EE, 10:1) = 0.18. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (d, J = 6.9 Hz, 3 H), 0.87 (d, J = 6.9 Hz, 3 H), 0.98 (d, J = 6.9 Hz, 3 H), 1.01 (d, J = 6.9 Hz, 3 H), 1.30–1.40 (m, 1 H), 1.44–1.53 (m, 1 H), 1.57–1.71 (m, 3 H), 1.84 (dsept, 1 H, J = 6.9, 2.9 Hz), 2.22 (sept, J = 6.9 Hz, 1 H), 2.26 (dd, J = 14.2, 6.3 Hz, 1 H), 2.39 (dd, J = 14.2, 7.0 Hz, 1 H), 3.26 (s, 3 H), 3.30 (s, 3 H), 3.54 (q, J = 1.0 Hz, 1 H), 4.39 (pseudo t, J = 6.2 Hz, 1 H), 4.70 (s, 1 H), 4.78 (s, 1 H), 5.31 (quint, J = 6.7 Hz, 1 H), 7.35–7.43 (m, 3 H), 7.50–7.57 (m, 2 H) ppm. **Preparation of (*S*) Mosher Ester:** As described above, the alcohol (–)-**13** (6.0 mg, 22 μmol) in CH_2Cl_2 (1 mL) and pyridine (0.5 mL) was converted with DMAP (5.4 mg, 44 μmol, 2 equiv.) and (–)-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (20.7 μL, 111 μmol, 5 equiv.) into the corresponding (*S*) Mosher ester (9.7 mg, 20 μmol, 89%, colorless liquid). R_f (Cy/EE, 10:1) = 0.13. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (d, J = 6.9 Hz, 3 H), 0.83 (d, J = 6.9 Hz, 3 H), 1.03 (d, J = 6.8 Hz, 3 H), 1.05 (d, J = 6.8 Hz, 3 H), 1.25–1.37 (m, 2 H), 1.51–1.65 (m, 3 H), 1.78 (dsept, 1 H, J = 6.9, 2.3 Hz), 2.29 (sept, J = 6.8 Hz, 1 H), 2.33 (dd, J = 14.4, 6.0 Hz, 1 H), 2.46 (dd, J = 14.4, 7.2 Hz, 1 H), 3.21 (s, 3 H), 3.28 (s, 3 H), 3.54 (q, J = 1.0 Hz, 3 H), 4.31 (t, J = 5.5 Hz, 1 H), 4.80 (s, 1 H), 4.88 (s, 1 H), 5.34 (quint, J = 7.2 Hz, 1 H), 7.36–7.41 (m, 3 H), 7.51–7.57 (m, 2 H) ppm.

Crystal Structure Analysis of *rac*-9a: $C_{33}H_{35}FeO_3P$, M_r = 566.43, monoclinic, space group: $P2_1/a$, a = 8.6402(2), b = 33.3015(8), c = 10.0997(3) Å, β = 96.4913(14)°, V = 2887.97(13) Å^3, $\rho_{calcd.}$ = 1.303 g cm^{-3}, Z = 4, F(000) = 1192; crystal dimensions: 0.30 × 0.15 × 0.10 mm. A total of 21143 reflections were collected at 293 K with a Nonius Kappa CCD area detector diffractometer using ω-scans in the θ range 2.12–27.45°, 6532 reflections were unique (R_{int} = 0.0513). The structure was solved by direct methods.[18] Full-matrix least-squares refinement[19] was based on F^2, with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The refinement converged at R_1 = 0.0683, wR_2 = 0.1209 for all data; final GOF: 1.052; largest peak/hole in the final difference Fourier map: 0.988/–0.547 e Å^{-3}. CCDC-270161 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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