Diastereoselective Hydroformylation of 2-Substituted Allylic *o*-DPPB-Esters—On the Origin of 1,2-Asymmetric Induction**

Bernhard Breit,* Golo Heckmann, and Stephan K. Zahn[a]

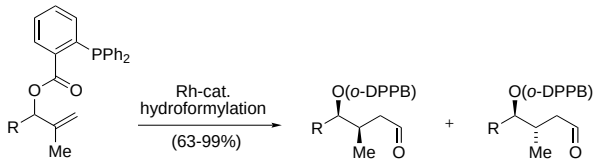
Abstract: 2-Substituted secondary alcohol *o*-DPPB esters (*o*-DPPB = *ortho*-diphenylphosphanylbenzoyl) have been prepared and their *o*-DPPB-directed diastereoselective hydroformylation examined. It was found that the diastereoselectivity increased as a function of the steric demand of the substituents both at the stereogenic center and in the alkene 2-position. Hydrolytic cleavage of the *o*-DPPB group afforded—via the lactols **29**—the corresponding lactones **30**, the relative configurations of the vicinal stereogenic centers of which were ascertainable by 2D-NOESY spectroscopy. In addition, a crystal structure analysis of the hydroformylation product **2d** provided further confirmation of the relative configuration. Replacement of the ester carbonyl group of the *o*-DPPB by a methylene unit resulted in significantly worse diastereoselectivity in the course of the hydroformylation (**34** → **35**), which indicates a decisive role for the ester carbonyl function. All the experimental observations were combined in a model of the origin of the 1,2-asymmetric induction during the title reaction. The key feature is the consideration of diastereomeric trigonal-bipyramidal rhodium-hydrido-olefin complexes **I** and **II**, capable on the basis of the Hammond postulate of acting as good models for the transition states of the selectivity-determining hydrometalation step. Investigation of these complexes by force-field methods indicated good correlation between theoretically predicted and experimentally determined diastereoselectivities.

Keywords: asymmetric synthesis · catalysis · catalyst directing group · C–C coupling · hydroformylation

Introduction

The hydroformylation of alkenes is an attractive C/C bond-forming reaction, since it is not only an atom-economic addition reaction but also provides the aldehyde function, which itself is an ideal platform for further synthetic operations.[1] However, hydroformylation has not yet been of frequent use in organic synthesis, although it is one of the industrially most important reactions relying on homogenous catalysis.[2] This discrepancy is primarily due to the difficulty in control of selectivity, in particular stereoselectivity, in the course of the hydroformylation reaction.

We[3] and others[4] recently devised solutions to this selectivity problem, relying on specifically introduced substrate-bound catalyst-directing groups. Such a function enforces attractive substrate–catalyst interaction and enables efficient substrate-directed hydroformylation of, for instance, methallylic and homomethallylic alcohols. As an ideal catalyst-directing group we identified the *ortho*-diphenylphosphanylbenzoyl function (*o*-DPPB), attached to a hydroxy group of the substrate through an ester linkage (see Scheme 1). In



Scheme 1. Diastereoselective hydroformylation of metallylic *o*-DPPB esters (*o*-DPPB = *ortho*-diphenylphosphinobenzoate).

the case of the hydroformylation of methallylic *o*-DPPB systems **1**, diastereoselectivity of up to 96:4 in favor of the *syn*-aldehyde **2** was observed.[5] The reaction has also been used as a key step for the construction of stereotriad building blocks for polyketide synthesis,[6] and additionally, was able to serve as a key step in Domino-type reaction sequences.[7]

However, previous studies with this system have shown that diastereoselectivity of the *o*-DPPB-directed hydroformyla-

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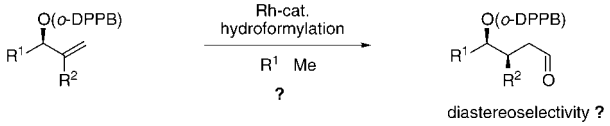
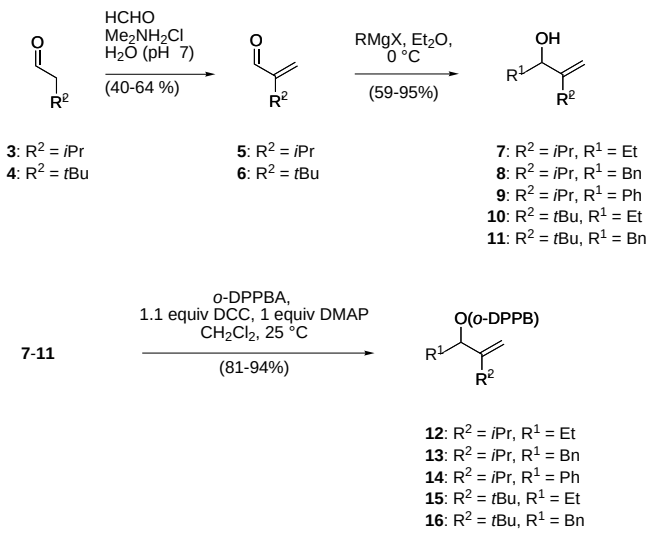
tion is a function of the nature of the substituent at the stereogenic center of the methallylic *o*-DPPB ester **1**, with secondary alkyl substituents showing the highest selectivities.[5] To learn more about the scope of this stereoselective hydroformylation and to obtain insights into the origin of 1,2-asymmetric induction, we have initiated studies on the influence of the substituent R^2 on the diastereoselectivity of the *o*-DPPB-directed hydroformylation described (see Scheme 2). The results of these investigations, together with a model for the origin of 1,2-asymmetric induction in the course of the *o*-DPPB-directed hydroformylation, are reported here.



Scheme 2. Influence of the 2-substituent R^2 on the diastereoselectivity of 2-substituted allylic *o*-DPPB esters.

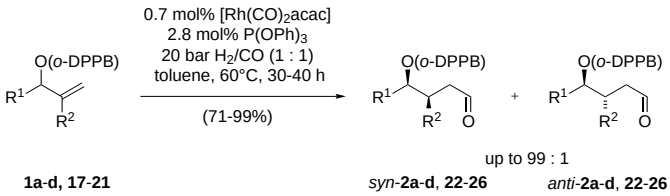
Preparation of 2-alkyl-substituted allylic alcohol *o*-DPPB esters: The synthesis of 2-alkyl-substituted allylic alcohol derivatives started from aldehydes **3** and **4** (Scheme 3). Mannich reactions provided enals **5** and **6**, and chemoselective addition of the corresponding Grignard reagent gave the desired 2-substituted allylic alcohol derivatives **7**–**11**. Subsequent esterification with *ortho*-diphenylphosphinobenzoic acid by the DCC/DMAP coupling protocol[8] furnished the *o*-DPPB esters in good to excellent yields. Stoichiometric amounts of DMAP as the acylation catalyst were essential to ensure good yields for the esterification step.



Scheme 3. Preparation of 2-substituted allylic *o*-DPPB esters.

Hydroformylation of 2-alkyl-substituted allylic alcohol *o*-DPPB esters: To preclude alkene isomerization as a potential side reaction, mild reaction conditions (60 °C, 20 bar CO/H_2, 1:1) for the hydroformylation of the 2-alkyl-substituted allyl-*o*-DPPB esters were selected.

Hydroformylation occurred smoothly at 20 bar syngas pressure with a catalyst loading of 0.7 mol% $[Rh(CO)_2acac]$ in the presence of 2.8 mol% of triphenylphosphite. The addition of a co-ligand was found to be beneficial with respect to yield and diastereoselectivity in the course of the *o*-DPPB-directed hydroformylation reaction. Aldehydes **2a**–**d** and **22**–**26** were formed in good to excellent yields. In each case the *syn* diastereomer was obtained as the major product, with diastereoselectivities of up to 99:1 (Scheme 4, Table 1).



Scheme 4. Hydroformylation of 2-substituted allylic *o*-DPPB esters.

Determination of relative configuration: In the case of the aldehydes **2a**–**d**, derived from methallylic alcohol, the relative configurations of the hydroformylation products had been determined previously, by transformation into the corresponding γ-lactones.[5] In addition, we were able to obtain an X-ray crystal structure analysis of aldehyde **2d**, which further confirms the stereochemical assignment of aldehydes **2a**–**d**. The structure of **2d** in the solid state is depicted in Figure 1.

Abstract in German: *2-Substituierte sekundäre Allylalkohol o-DPPB Ester (o-DPPB = ortho-diphenylphosphanylbenzoyl) wurden präpariert und deren o-DPPB-dirigierte diastereoselektive Hydroformylierung untersucht. Dabei wurde gefunden, dass die Diastereoselektivitäten mit steigendem sterischen Anspruch der Substituenten sowohl am stereogenen Zentrum als auch in der 2-Position des Alkens zunahmen. Durch hydrolytische Abspaltung der o-DPPB-Gruppe gelangte man über die γ-Lactole **29** zu den entsprechenden γ-Lactonen **30**. An diesen konnte die relative Konfiguration der vicinalen stereogenen Zentren durch 2D-NOESY Spektroskopie aufgeklärt werden. Darüberhinaus lieferte eine Kristallstrukturanalyse des Hydroformylierungsproduktes **2d** eine weitere Absicherung der relativen Konfiguration. Der Ersatz der Estercarbonylgruppe der o-DPPB-Funktion durch eine Methyleneinheit führte zu einer deutlich schlechteren Diastereoselektivität im Verlauf der Hydroformylierung (**34** → **35**), was der Estercarbonylfunktion eine entscheidende Rolle zuweist. Alle experimentellen Beobachtungen wurden in einem Modell zum Ursprung der 1,2-asymmetrischen Induktion im Verlauf der Titelreaktion zusammengefasst. Kerngedanke ist die Betrachtung der diastereomeren trigonal-bipyramidalen Rhodium-Hydrido-Olefin-Komplexe **I** und **II**, die aufgrund des Hammond-Postulats als gute Modelle für den Übergangszustand des Selektivitäts-bestimmenden Hydrometallierungsteilschrittes dienen können. Untersuchungen dieser Komplexe mit Kraftfeldmethoden ergaben eine gute Korrelation zwischen theoretisch erwarteter und experimentell gefundener Diastereoselektivität.*

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Table 1. Results from the substrate-directed diastereoselective hydroformylation of 2-substituted allylic *o*-DPPB esters.

Entry	Allylic *o*-DPPB ester	R^1	R^2	Product (yield/%[a])	*dr* (*syn*:*anti*[b])
1	**1a**	Et	Me	**2a** (99)	60:40[c]
2	**1b**	Bn	Me	**2b** (75)	72:28[c]
3	**1c**	Ph	Me	**2c** (98)	90:10[c]
4	**1d**	*i*Pr	Me	**2d** (97)	96:4[c]
5	**17**	Et	*i*Pr	**22** (81)	84:16
6	**18**	Bn	*i*Pr	**23** (96)	92:8
7	**19**	Ph	*i*Pr	**24** (97)	99:1
8	**20**	Et	*t*Bu	**25** (71)	94:6
9	**21**	Bn	*t*Bu	**26** (95)	99:1

[a] Isolated yield after column chromatography. In all cases the branched regioisomer could not be detected. [b] Determined by NMR spectroscopic analysis of the crude product. [c] For hydroformylations run at 90 °C diastereomeric ratios obtained for **2a–d** were 73:27, 80:20, 92:8, and 96:4, respectively.

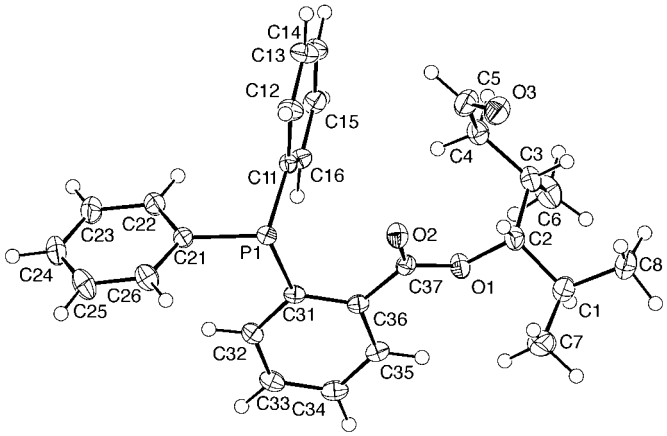
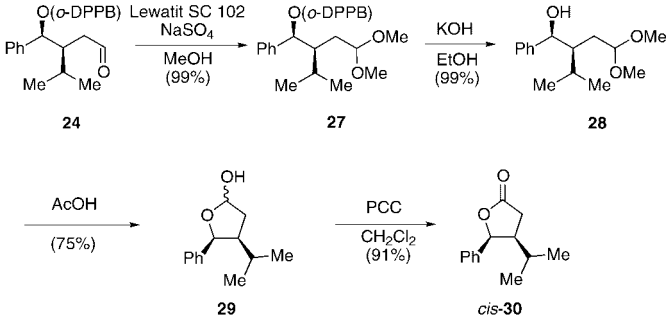


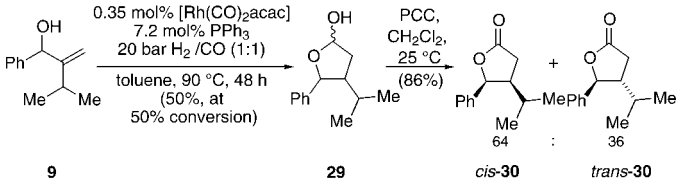
Figure 1. Structure of **2d** in the solid state.

To ensure the relative configurations of the 2-isopropyl- and 2-*tert*-butyl-substituted derivatives, aldehyde **24** was selected for transformation into the corresponding γ-lactone (see Scheme 5). The derivatization sequence commenced with protection of aldehyde **24** as the dimethylacetal **27**. Alkaline hydrolysis with potassium hydroxide in ethanol gave alcohol **28**, together with the *ortho*-diphenylphosphinobenzoic acid, in quantitative yield. Deprotection of the dimethyl acetal in **28** occurred upon treatment with 80% acetic acid to furnish the γ-lactols **29**, which were smoothly oxidized in the presence of PCC to furnish the *cis*-γ-lactone **30**.



Scheme 5. Derivatization of aldehyde **24** to the γ-lactone *cis*-**30**.

To clarify the relative configuration of lactone *cis*-**30** unambiguously by use of NOE experiments, it became necessary to have access to the *trans* diastereomer of **30**. A non-directed hydroformylation of the allylic alcohol **9** was decided upon. From previous experience, this was expected to furnish the lactols **29** without significant diastereoselectivity. Subjection of allylic alcohol **9** to standard hydroformylation conditions (see Scheme 6) for 48 h gave a 50% conversion and a theoretical yield of 50% for the γ-lactols **29**. Oxidation with PCC revealed a 64:33 mixture of the *cis* and *trans* diastereomers of lactone **30**.



Scheme 6. Hydroformylation of allylic alcohol **9** and oxidation to give the γ-lactones *cis*- and *trans*-**30**.

Two-dimensional NOESY NMR spectra showed distinct NOE contacts for both diastereomeric γ-lactones **30**, which allowed the relative configurations to be determined. Thus, *cis*-**30** showed a NOE contact between protons attached to C4 and C5 (Figure 2), whereas *trans*-**30** revealed a NOE contact between the proton at C5 and the methine unit of the isopropyl substituent.

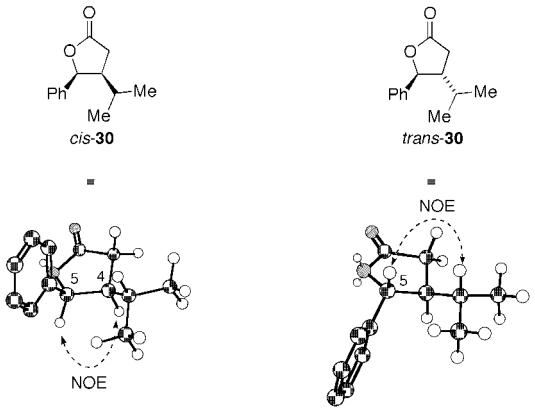


Figure 2. Observed NOE contacts for *cis*- and *trans*-**30**, illustrated with the corresponding MM2 minimized geometries.

Comparison of the NMR spectra of the aldehydes **22–26** revealed characteristic differences between the *syn* (major) and the *anti* (minor) diastereomers. For instance, the ^{13}C NMR resonances of the isopropyl methine carbon atoms are shifted to higher field in *syn*-**22–24** than in *anti*-**22–24** (see Table 2). The same holds for the proton NMR resonances of the aldehyde protons, which are shifted to higher field in *syn*-**22**, **23**, and **25** than in *anti*-**22**, **23**, and **25**. With derivatization of **24** to the *cis*-γ-lactone **30** as a point of reference, NMR spectroscopy allows the assignment of *syn* and *anti* configurations for aldehydes **22–26**.

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Table 2. Comparison of selected NMR data of *syn* and *anti* aldehydes **22**–**26**.

Compound	^{13}C NMR shifts for R^2		^{1}H NMR shift of aldehyde proton	
	syn	*anti*	*syn*	*anti*
22	28.0 (*C*H) 19.1, 21.2 [CH(*C*H$_3$)$_2$]	28.8 (*C*H) 18.9, 20.7 [CH(*C*H$_3$)$_2$]	9.50	9.64
23	28.0 (*C*H) 19.4, 21.3 [CH(*C*H$_3$)$_2$]	29.4(*C*H) 19.2, 20.7 [CH(*C*H$_3$)$_2$]	9.53	9.70
24	27.0 (*C*H) 17.1, 21.3 [CH(*C*H$_3$)$_2$]	–	9.18	–
25	32.8 [*C*(CH$_3$)$_3$] 28.6 [C(*C*H$_3$)$_3$]	n. d.	9.42	9.66
26	33.0 [*C*(CH$_3$)$_3$] 28.8 [C(*C*H$_3$)$_3$]	–	9.40	–

n.d. = not detectable.

Discussion

The hydroformylation of 2-substituted allyl alcohol *o*-DPPB esters proceeded in all cases with good to excellent yields at low temperatures (60 °C) and within 30–48 h. In each case the *syn* diastereomer was formed as the major product. For the methallylic ester derivatives **1a**–**d** the diastereoselectivity for the reactions run at 60 °C was in some cases somewhat lower than obtained for the same reactions run at 90 °C (see Scheme 4, Table 1).[5] The diastereoselectivities show a clear dependence on the size of the substituents both at the stereogenic center (= R^1) and at the 2-position of the allylic alcohol system (= R^2). Thus, a combination of the sterically least demanding substituents—R^1 = Et and R^2 = Me—gave the lowest diastereomer ratio for **2a**, at *syn*/*anti* 60:40 (Figure 3, Table 1, entry 1). However, an increase in the steric demand of R^1—as an isopropyl substituent—with R^2 maintained as Me increased the diastereoselectivity to 96:4 for **2d** (Figure 3, Table 1, entry 4). Similarly, maintenance of R^1 as Et while increasing the size of the R^2 substituent to a *tert*-butyl group increased diastereoselectivity from 60:40 to 94:6 for **25** (Figure 3, Table 1, entry 8). Optimum results were obtained for derivatives **24** (R^1 = Ph, R^2 = *i*Pr) and **26** (R^1 = Bn, R^2 = *t*Bu) (Figure 3, Table 2, entries 7 and 9), the minor *anti* diastereomer being undetectable in each case.

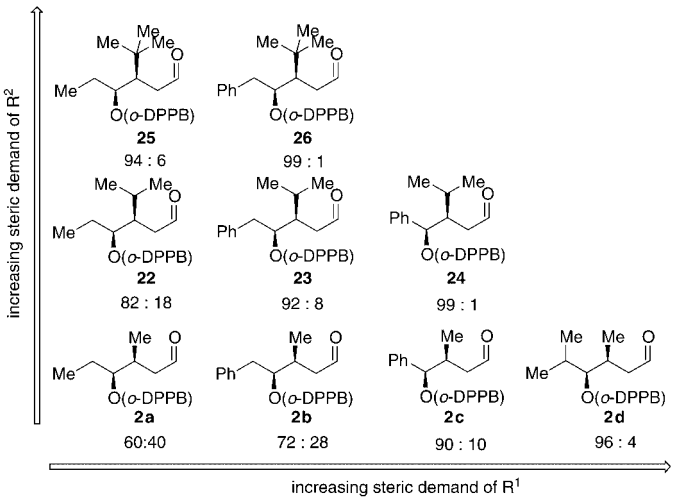

Figure 3. Graphical summary of the results of the *o*-DPPB-directed hydroformylation of 2-substituted allylic *o*-DPPB esters.

In general, an increase in the steric demand of either of the substituents R^1 and R^2 significantly increased the diastereoselectivity of the hydroformylation of 2-substituted allylic *o*-DPPB esters.

Model for 1,2-asymmetric induction: To understand these trends in the diastereoselectivity and to provide a more detailed insight into the factors governing 1,2-asymmetric induction, one has to consider the rate and selectivity-determining step of the hydroformylation, which is the hydrometalation step.[9] According to the generally accepted mechanism of the hydroformylation, the hydrometalation occurs from a trigonal-bipyramidal rhodium(I)-hydrido-olefin complex. Stereoelectronic reasons cause the alkene to align coplanar with the rhodium–hydride bond to allow for efficient orbital overlap. The hydrometalation is known to be exothermic.[10] Hence, according to Hammond's postulate,[11] the transition state is early, making the starting hydrido–alkene rhodium complex a good model for the corresponding hydrometalation transition state.

How, though, do *o*-DPPB esters of 2-substituted allylic alcohols bind with a trigonal-bipyramidal rhodium center?

From previous experiments we already know that the presence of the phosphine function is essential to produce diastereoselectivity in the course of the hydroformylation reaction.[5] Hence, binding of the phosphine to the catalytically active rhodium center throughout the selectivity-determining step is reasonable. The ester linkage should adopt the energetically preferred conformation expected for an ester of a secondary alcohol, based on minimization of allylic 1,3-strain (see Figure 4; consider for example the *o*-DPPB ester conformation in the X-ray structure plot of **1d** depicted in Figure 1). This would reduce the number of degrees of freedom, and hence should lead to a highly ordered transition state for the hydrometalation step.

To probe this role of the *o*-DPPB linkage, a substrate in which the carbonyl group of the ester was replaced by a CH_2 unit was needed (→**31**). Such a benzyl ether linkage should lack the conformational preference of the *o*-DPPB ester linkage present in *o*-DPPB substrates **1** (Figure 4).

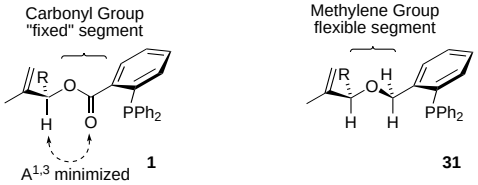

Figure 4. Proposed influence of the linkage of the catalyst-directing group on the conformational properties of the alkene substrates.

Synthesis of a corresponding benzyl ether substrate was achieved by starting from *ortho*-diphenylphosphinobenzoic acid (Scheme 7). Reduction with lithium aluminum hydride and oxidation with hydrogen peroxide gave the known

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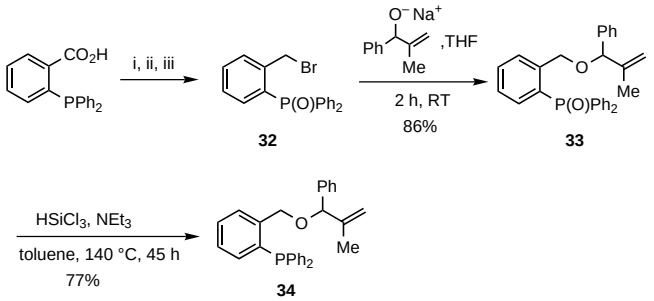
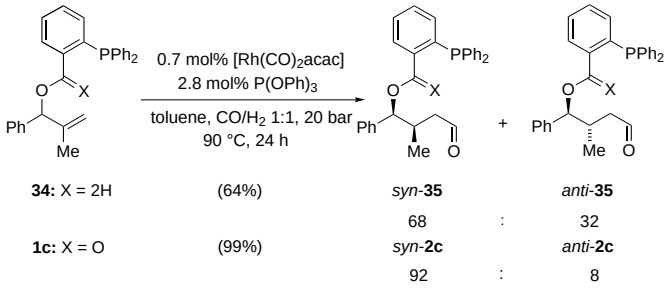


Scheme 7. Preparation of benzyl ether **34**: i) $LiAlH_4$; ii) H_2O_2; iii) PBr_3.

phosphane oxide alcohol.[12] Treatment with phosphorus bromide furnished bromide **32**, which could be coupled to produce the allylic ether **33** by use of the Williamson etherification protocol. Reduction of the phosphane oxide proceeded upon treatment with trichlorosilane in the presence of triethylamine at higher temperatures to give the desired test substrate **34**.

Next, *ortho*-diphenylphosphinobenzyl allylic ether **34** was subjected to rhodium-catalyzed hydroformylation under our standard conditions at 90 °C and 20 bar syngas pressure. Formation of the two diastereomeric aldehydes **35** was observed, in a *syn*/*anti* diastereomer ratio of 68:32 (Scheme 8). The corresponding hydroformylation with the *o*-DPPB **1c** substrate at 90 °C occurred with a much higher *syn*/*anti* diastereoselectivity of 92:8. This showed that the ester linkage was essential for achievement of high levels of diastereoselectivity.



Scheme 8. Hydroformylation of benzyl ether **34** and *o*-DPPB ester **1c**: influence of the carbonyl group.

What remained to be clarified was the coordination mode of the *o*-DPPB allylic esters within the trigonal-bipyramidal geometry of the starting hydrido-olefin-rhodium(I) complexes. Three possible bidentate binding modes of olefin and phosphine had to be considered: a) equatorial–equatorial, b) axial–equatorial, or c) axial–axial coordination (Figure 5).

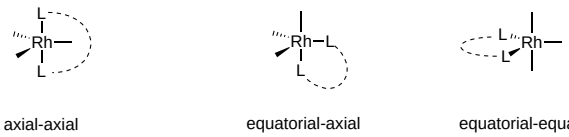


Figure 5. Possible binding modes of a bidentate ligand in a trigonal-bipyramidal rhodium(I) complex.

Since rhodium(I)-hydrido-alkene complexes are too reactive to be isolated and investigated experimentally,[13] a theoretical study of the preferred binding mode of the *o*-DPPB substrates was undertaken. For this reason we employed a modified version of Casey and Whiteker's concept of the natural bite angle for bidentate ligands.[14] This method was originally developed to determine natural bite angles of diphosphine ligands. We extrapolated this method to the bidentate phosphine/alkene rhodium complexes **A** of the *o*-DPPB esters **1**. The force-field parameters used are given in Table 3. The potential energy as a function of the bite angle is shown in Figure 6.[15]

Table 3. Force-field parameters used to determine the natural bite angle β_n of methallylic *o*-DPPB esters **1**.

Rh–P bond	$d = 230$ pm, $k = 440$ nm^{-1}
Rh–C_{olefin} bonds	$d = 200$ pm (locked)
P-Rh-C_{olefin} angle	$k = 0$
r_0 (Rh) (van der Waals)	200 pm
ε (hardness factor)	0.255

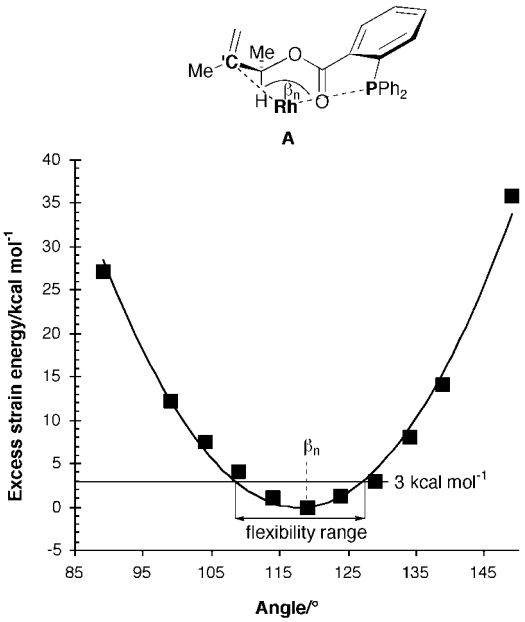
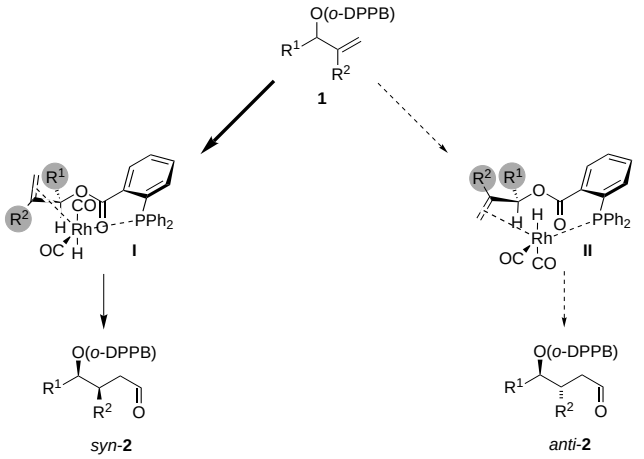


Figure 6. Relative energies of complex **A** as a function of the C'_{olefin}-Rh-P bite angle.

Clearly, the preferred bite angle β_n for substrates **1** is close to 120°. Going either to 90° (required for axial–equatorial binding) or to 180° (required for diaxial binding) is associated with a large energy penalty. Hence, allylic *o*-DPPB esters should adopt the equatorial–equatorial binding mode as a bidentate ligand in trigonal-bipyramidal rhodium(I) complexes.

As a result, only two diastereomeric rhodium(I) alkene complexes leading to the corresponding hydrometalation transition states remained to be considered: complex **I**, characterized by minimization of allylic 1,2-strain, and complex **II**, which shows a minimization of allylic 1,3-strain within the allylic part of the molecule (Scheme 9, Figure 7). The



Scheme 9. Assumed chelate complexes **I** and **II** for hydroformylation of *o*-DPPB esters **1**.

relative axial position of the hydrido ligand is a consequence of the formation only of the linear regioisomer, as observed experimentally. Since both alkene complexes should represent good models for the corresponding diastereomorphic transition states, inspection of the relative stabilities of complexes **I** and **II** was carried out by use of the MMFF94 force-field, as implemented in the Spartan molecular package. Table 4 shows the results and Figure 7 displays the calculated structures for complexes **I** and **II** of derivative **1d**.

In accordance with the experimental results, complex **I**, leading to the *syn* diastereomer, is the energetically more stable in all cases. Furthermore, the energy differences between the two alkene complexes increase with the steric demand of the substituents R^1 and R^2. Interestingly, the calculated diastereomer ratios based on these energy differences are very close to the experimental observations (Table 4).

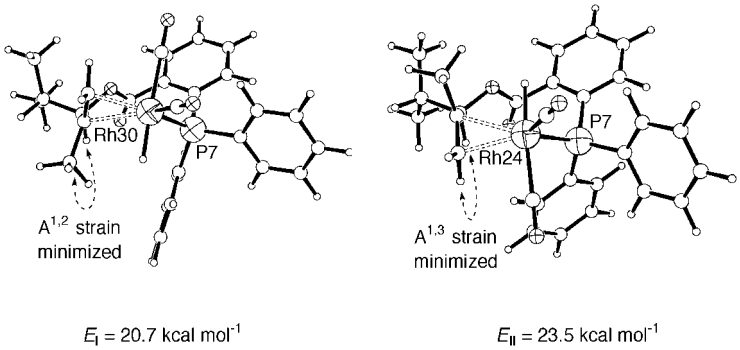


Figure 7. MMFF-minimized geometries for rhodium complexes **I** and **II** derived from *o*-DPPB ester **1d**.

Table 4. MMFF force-field calculations for complexes **I** and **II**.

R^1	R^2	E_I [kcal mol^{-1}]	E_{II} [kcal mol^{-1}]	$E_{II}-E_I$ [kcal mol^{-1}]	N_I/N_{II}[a]	*dr* (exptl)
Me	Me	13.7	15.2	1.5	88:12	73:27[b]
Ph	Me	30.5	32.2	1.7	91:9	92:8
*i*Pr	Me	20.7	23.5	2.8	98:2	96:4
*t*Bu	Me	29.9	34.1	4.2	>99:<1	n.d.[c]
Me	*t*Bu	37.4	39.3	1.9	94:6	94:6[b]

[a] from $[\ln(N_{II}/N_I) = -(E_{II}-E_I)/RT)]$ at 363 K; [b] For $R^1 = Et$; [c] not determined.

The diastereoselectivities of the *o*-DPPB-directed hydroformylation of 2-substituted allylic alcohol derivatives are thus governed by a repulsive interaction between substituents R^1 and R^2 (Scheme 9). This repulsive interaction is minimized in alkene complexes **I** (and in the corresponding transition state) because both substituents have dihedral angles of ca. $+86^\circ$. Conversely, in alkene complexes **II** this dihedral angle is much smaller, at ca. -53°. Hence, the two substituents R^1 and R^2 are in spatial proximity. The repulsive interaction increases with increasing size of R^1 and R^2 and results in higher diastereoselectivity.

Conclusion

In conclusion, the hydroformylation of *o*-DPPB esters of 2-substituted allylic alcohols occurs as a substrate-directed diastereoselective reaction. The diastereoselectivities can be interpreted by employing the diastereomeric hydrido-alkene-rhodium(I) complexes as good models for the corresponding competing diastereomorphic hydrometalation transition states. Two-point binding of the substrate through phosphine and alkene, a preferred conformation induced by the ester linkage of the *o*-DPPB group, and minimization of repulsive interaction of substituents R^1 and R^2 are the basis and origin of diastereoselectivity in these reactions. In some cases perfect diastereoselectivity could be observed, which is now not only theoretically understandable but also makes this variant of the hydroformylation a preparatively interesting method for the construction of building blocks with vicinal stereocenters.

Experimental Section

General: Reactions were performed in flame-dried glassware either under argon (purity >99.998%) or under nitrogen. The solvents were dried by standard procedures, distilled, and stored under nitrogen. All temperatures quoted are uncorrected. ^{1}H, ^{13}C NMR spectra: Bruker ARX 200, Bruker AC 300, Bruker WH 400, or Bruker AMX 500, with tetramethylsilane (TMS), chloroform ($CHCl_3$), or benzene (C_6H_6) as internal standards. ^{31}P NMR spectra: Bruker WH 400 (161.978 MHz) with 85% H_3PO_4 as external standard. Melting points: Dr. Tottoli (Büchi) melting point apparatus. Elemental analyses: CHN-rapid analyzer (Heraeus). Flash chromatography: Si 60 silica gel, E. Merck AG, Darmstadt, 40–63 μm. Hydroformylation reactions were performed in 100 and 200 mL stainless steel autoclaves equipped with magnetic stirrers. Gases: carbon monoxide 2.0 (Messer–Griesheim), hydrogen 3.0 (Messer–Griesheim). The following compounds were prepared by literature procedures: 3,3-dimethylbutyraldehyde (**4**),[16] methallylic *o*-DPPB esters **1a–d**,[5] [2-(diphenylphosphinoyl)phenyl] methanol.[12]

2-Isopropylpropenal (5): A solution of dimethylammonium chloride (32.62 g, 0.40 mol) in 37% aqueous formaldehyde (32.5 mL, 0.40 mol) was adjusted to pH 7 with powdered sodium bicarbonate. After addition of 3-methylbutyraldehyde (**3**, 28.42 g, 0.33 mol) the reaction mixture was heated at 70 °C for 22 h. The reaction mixture was subsequently steam

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distilled until organic material no longer separated from the distillate. The distillate (ca. 500 mL) was extracted with diethyl ether (3 × 150 mL), the combined organic phases were dried (Na_2SO_4), and the solvent was removed in vacuo. Distillation of the residue at normal pressure (15 cm Vigreux) furnished enal **5** (20.52 g, 64 %) as a colorless liquid. B.p. 109 °C (1013 mbar). The analytical and spectroscopic data correspond to those reported previously.[17]

2-*tert*-Butylpropenal (6): The procedure used was analogous to that described for the preparation of enal **5**. Treatment of 3,3-dimethylbutyraldehyde (**4**, 3.51 g, 35.5 mmol), dimethylammonium chloride (3.43 g, 42 mmol), and 37 % aqueous formaldehyde solution (3.4 mL, 42 mmol) gave enal **6** (1.53 g, 40 %) as a colorless liquid. B.p. 124 °C (1013 mbar). The analytical and spectroscopic data correspond to those reported previously.[17]

2-Isopropylpent-1-en-3-ol (7): A solution of 2-isopropylpropenal (**5**, 2.75 g, 8 mmol) in ether (8 mL) was added dropwise over 15 min to a 1 M solution of ethyl magnesium bromide in diethyl ether (35 mL, 35 mmol). The reaction mixture was stirred at room temperature for 3 h; followed by addition of saturated aqueous NH_4Cl solution (30 mL). The reaction mixture was extracted with *tert*-butyl methyl ether (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), the solvent was removed in vacuo, and the residue was purified by distillation (15 cm Vigreux) to give allyl alcohol **7** (2.21 g, 62 %) as a colorless oil. B.p. 70–71 °C (24–25 mbar); ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.88$ (pseudo t, $J = 7.4$ Hz, 3H; CH_2CH_3), 1.01 [d, $J = 7.2$ Hz, 3H; $CH(CH_3)_2$], 1.04 [d, $J = 7.1$ Hz, 3H; $CH(CH_3)_2$], 1.42–1.66 (m, 2H; CH_2CH_3), 1.71 (br s, 1H; OH), 2.23 [m, 1H; $CH(CH_3)_2$], 3.98 (pseudo t, $^3J = 6.1$ Hz, 1H; CHOH), 4.87 (s, 1H, =CH_2), 4.98 (s, 1H; =CH_2); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 9.99$, 22.70, 23.15, 28.83, 30.18, 75.75, 106.97, 158.88; analytical data correspond to those reported previously.[18]

3-Isopropyl-1-phenyl-but-3-en-2-ol (8): A solution of 2-isopropylpropenal (**5**, 3.93 g, 40 mmol) in diethyl ether (5 mL) was added at 0 °C to a solution of benzylmagnesium chloride [prepared from benzyl chloride (6.33 g, 50 mmol) and magnesium (1.34 g, 55 mmol)] in diethyl ether (25 mL). The reaction mixture was stirred at room temperature for 4 h, followed by addition of saturated aqueous NH_4Cl (30 mL). The resulting precipitate was removed by filtration over Celite. The organic phase was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 40 mL). The solvent was removed in vacuo and the residue was purified by distillation to give allyl alcohol **8** (7.19 g, 94 %) as a 10:1 mixture of 1,2- and 1,4-addition product, which was used as such in the subsequent esterification step. B.p. 80–84 °C (1 mbar); ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta =$ 1.13 [d, $J = 6.9$ Hz, 6H; $CH(CH_3)_2$], 1.15 [d, $J = 6.7$ Hz, 6H; $CH(CH_3)_2$], 1.77 (br s, 1H; OH), 2.36 [m, 1H; $CH(CH_3)_2$], 2.75 (dd, $J = 13.7$, 8.8 Hz, 1H; CH_2), 2.98 (dd, $J = 13.6$, 4.2 Hz, 1H; CH_2), 4.32 (m, 1H; CHOH), 4.99 (m, 1H; =CH_2), 5.15 (m, 1H; =CH_2), 7.21–7.37 (m, 5H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 22.35$, 22.98, 30.73, 43.41, 74.79, 107.29, 125.94, 128.35 (2C), 129.34 (2C), 138.58, 158.33 (C3).

2-Isopropyl-1-phenyl-prop-2-en-1-ol (9): The procedure was analogous to that used for the preparation of **8**. Allyl alcohol **9** (5.71 g, 81 %) was obtained from magnesium (1.34 g, 55 mmol), bromobenzene (7.85 g, 50 mmol), and 2-isopropylpropenal (**5**, 3.93 g, 40 mmol) as a colorless oil. B.p. 85–90 °C (1 mbar); ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.95$ [pseudo d, $J = 6.6$ Hz, 6H; $CH(CH_3)_2$], 1.96 (br s, 1H; OH), 2.08 [m, 1H; $CH(CH_3)_2$], 5.01 (m, 1H; =CH_2), 5.15 (s, 1H; CHOH), 5.22 (m, 1H; =CH_2), 7.23–7.32 (m, 5H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 22.37$, 23.10, 30.10, 76.61, 107.71, 126.95 (2C), 127.13, 128.34 (2C), 142.39, 157.76; elemental analysis calcd (%) for $C_{12}H_{16}O$ (176.3): C 81.77, H 9.15; found C 81.90, H 9.18.

2-*tert*-Butyl-pent-1-en-3-ol (10): The procedure was analogous to that used for the preparation of **7**. Allyl alcohol **10** (0.90 g, 79 %) was obtained from ethylmagnesium bromide solution in diethyl ether (1 M, 10 mL, 10 mmol) and 2-*tert*-butylpropenal (**6**, 0.90 g, 8.0 mmol), as a colorless oil. B.p. 74 °C (25 mbar); ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.88$ (pseudo t, $J = 7.4$ Hz, 3H; CH_2CH_3), 1.02 [s, 9H; $C(CH_3)_3$], 1.49–1.59 (m, 2H; CH_2CH_3), 1.86 (br s, 1H; OH), 4.04 (pseudo t, $J = 6.6$ Hz, 1H; CHOH), 4.95 (s, 1H; =CH_2), 5.06 (s, 1H; =CH_2); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 10.88$ (C5), 29.16 (3C), 31.50, 35.57, 71.52, 107.32, 162.10; analytical data correspond to those reported previously.[18]

3-*tert*-Butyl-1-phenylbut-3-en-2-ol (11): The procedure was analogous to that used for the preparation of **8**. Allyl alcohol **9** (721 mg, 59 %) was obtained from magnesium (201 mg, 8.3 mmol), benzyl chloride (949 mg, 7.5 mmol), and 2-*tert*-butyl-propenal (**6**, 673 mg, 6.0 mmol), as a colorless oil. $R_f = 0.33$ (petrol ether/*tert*-butyl methyl ether 4:1); ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 1.12$ [s, 9H; $C(CH_3)_3$], 1.66 (br s, 1H; OH), 2.80 (dd, $J = 13.8$ Hz, 8.9 Hz, 1H; CH_2Ph), 2.94 (dd, $J = 13.8$ Hz, 3.9 Hz, 1H; CH_2Ph), 4.43 [dd, $J = 8.9$, 3.9 Hz, 1H; CHOH), 5.15 (s, 1H =CH_2), 5.30 (s, 1H; =CH_2), 7.23–7.36 (m, 5H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 28.98$ (3C), 35.64, 45.39, 71.04, 108.19, 126.38, 128.37(2C), 129.38 (2C), 139.10, 161.11; IR (film): $\tilde{\nu} = 3500$ (m, b), 2965 (s), 2908 (s), 1454 (m), 1363 (m), 1047 (m), 1031 (m), 908 (m), 751 (m), 699 (s) cm^{-1}; MS (EI, 70 eV): m/z(%): 204 (1) $[M]^+$, 113 (25) $[M - C_7H_7]^+$, 92 (100) $[C_7H_8]^+$, 57 (44) $[C(CH_3)_3]^+$; found: 204.1516 $[M]^+$; $C_{14}H_{20}O$ calcd 204.1514.

General procedure for synthesis of *o*-DPPB esters 12–16: *o*-DPPBA (1 equiv), DMAP (1 equiv), and DCC (1.1 equiv) were successively added to a solution of allylic alcohol in CH_2Cl_2 (0.5 M, 1 equiv) and the resulting mixture was stirred at room temperature until TLC showed complete consumption of the starting material. The reaction mixture was subsequently filtered through a plug of CH_2Cl_2-wetted Celite and washed with additional CH_2Cl_2. An appropriate amount of silica gel was added to the filtrate, which was then concentrated to dryness. Flash chromatography with petroleum ether/*tert*-butyl methyl ether (9:1) provided the *o*-DPPB esters **12–16** either as slightly yellow to colorless, highly viscous oils or as colorless solids.

(*1RS*)-(±)-1-Ethyl-2-isopropyl-prop-2-enyl 2-(diphenylphosphanyl)benzoate (12): *o*-DPPB ester **12** (1.84 g, 88 %) was obtained from 2-isopropylpent-1-en-3-ol (**7**, 0.64 g, 5.0 mmol), *o*-DPPBA (1.53 g, 5.0 mmol), DMAP (0.61 g, 5.0 mmol), and DCC (1.08 g, 5.3 mmol), as a colorless solid. M.p. 77–78 °C; ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.80$(pseudo t, $J = 7.4$ Hz, 3H; CH_2CH_3), 0.99 [d, $J = 6.8$ Hz, 3H; $CH(CH_3)_2$], 1.01 [d, $J =$ 6.9 Hz, 3H; $CH(CH_3)_2$], 1.64 (m, 2H; CH_2CH_3), 2.20 [m, 1H; $CH(CH_3)_2$], 4.89 (m, 1H; =CH_2), 5.00 (m, 1H; =CH_2), 5.30 (pseudo t, $J = 6.6$ Hz, 1H; CHOR), 6.89–6.92 (m, 1H; Ar-H), 7.25–7.38 (m, 12H; Ar-H), 8.06–8.13 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 9.89$, 22.55, 22.78, 26.57, 30.41, 78.28, 109.28, 128.10, 128.29–128.45 (6 Aryl-*C*), 130.46 (d, J(C,P) = 2.6 Hz), 131.67, 133.87 (d, J(C,P) = 20.7 Hz, 2C), 133.97 (d, J(C,P) = 20.8 Hz, 2C), 134.26, 134.83 (d, J(C,P) = 18.9 Hz), 138.10 (d, J(C,P) = 11.7 Hz), 138.19 (d, J(C,P) = 12.2 Hz), 140.49 (d, J(C,P) = 27.9 Hz), 153.86 (C2′), 165.95 (d, ^3J(C,P) = 2.4 Hz); ^{31}P NMR (161.978 MHz, $CDCl_3$): $\delta = -4.2$; elemental analysis calcd (%) for $C_{27}H_{29}O_2P$ (416.5): C 77.85, H 7.03; found C 77.86, H 6.98.

(1*RS*)-(±)-1-Benzyl-2-isopropyl-prop-2-enyl 2-(diphenylphosphanyl)benzoate (13): *o*-DPPB ester **13** (2.20 g, 92 %) was obtained from 2-isopropyl-4-phenylbut-1-en-3-ol (**8**, 1.05 g, 5.5 mmol), *o*-DPPBA (1.53 g, 5.0 mmol), DMAP (0.61 g, 5.0 mmol), and DCC (1.08 g, 5.3 mmol), as a highly viscous, slightly yellow oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.94$ [d, $J = 6.9$ Hz, 3H; $CH(CH_3)_2$], 0.97 [d, $J = 6.9$ Hz, 3H; $CH(CH_3)_2$], 2.15 [m, 1H; $CH(CH_3)_2$], 2.87–2.99 (m, 2H; CH_2Ph), 4.86 (s, 1H; =CH_2), 4.96 (s, 1H; =CH_2), 5.53 (pseudo t, $J = 6.7$ Hz, 1H; CHOR), 6.87–6.90 (m, 1H; Ar-H), 7.14–7.30 (m, 17H; Ar-H), 7.97–8.02 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 22.25$, 22.59, 31.00, 40.61, 77.26, 109.78, 126.41, 128.19 (2C), 128.37–128.55 (7 Aryl-*C*), 129.54 (2C), 130.51(d, J(C,P) = 2.3 Hz), 131.79, 133.98 (d, J(C,P) = 20.8 Hz, 2C), 134.07 (d, J(C,P) = 20.8 Hz, 2C), 134.28, 134.60 (d, J(C,P) = 18.5 Hz), 137.46 (C5), 138.16 (d, J(C,P) = 11.7 Hz), 138.19 (d, J(C,P) = 12.3 Hz), 140.75 (d, J(C,P) = 27.5 Hz), 153.82, 165.95 (d, J(C,P) = 2.4 Hz); ^{31}P NMR (161.978 MHz, $CDCl_3$): $\delta = -4.3$; elemental analysis calcd (%) for $C_{32}H_{31}O_2P$ (478.6): C 80.31, H 6.53; found C 80.28, H 6.68.

(1*RS*)-(±)-2-Isopropyl-1-phenyl-prop-2-enyl 2-(diphenylphosphanyl)benzoate (14): *o*-DPPB ester **14** (2.18 g, 94 %) was obtained from 2-isopropyl-3-phenylprop-2-en-1-ol (**9**, 0.88 g, 5.0 mmol), *o*-DPPBA (1.53 g, 5.0 mmol), DMAP (0.61 g, 5.0 mmol), and DCC (1.08 g, 5.3 mmol), as a highly viscous, slightly yellow oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.97$ [d, $J = 6.8$ Hz, 3H; $CH(CH_3)_2$], 1.01 [d, $J = 6.9$ Hz, 3H; $CH(CH_3)_2$], 2.14 [m, 1H; $CH(CH_3)_2$], 5.04 (s, 1H; =CH_2), 5.14 (s, 1H; =CH_2), 6.44 (s, 1H; CHOR), 6.92–6.96 (m, 1H; Ar-H), 7.21–7.35 (m, 17H; Ar-H), 8.15–8.18 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 22.17$, 22.67, 30.46, 77.75, 109.60, 127.82 (2C), 127.90, 128.14, 128.21–128.48 (6 Aryl-*C*), 128.31 (2C), 130.59 (d, J(C,P) = 2.3 Hz), 131.88, 133.94 (d, J(C,P) = 20.8 Hz, 4C), 134.31, 134.31 (d, J(C,P) = 18.8 Hz), 137.99 (d, J(C,P) = 12.2 Hz), 138.08 (d,

J(C,P) = 12.2 Hz), 138.61 (C4), 140.99 (d, J(C,P) = 27.8 Hz), 153.69 (C2), 165.29; ^{31}P NMR (161.978 MHz, $CDCl_3$): $\delta = -4.2$; elemental analysis calcd (%) for $C_{31}H_{29}O_2P$ (464.6): C 80.15, H 6.29; found C 79.98, H 6.42.

(1*RS*)-(±)-2-*tert*-Butyl-1-ethyl-prop-2-enyl 2-(diphenylphosphanyl)benzoate (15): *o*-DPPB ester **15** (1.39 g, 81%) was obtained from 2-*tert*-butylpent-1-en-3-ol (**10**, 0.22 g, 4.0 mmol), *o*-DPPBA (1.22 g, 4.0 mmol), DMAP (0.61 g, 5.0 mmol), and DCC (1.08 g, 5.3 mmol), as a highly viscous, slightly yellow oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.76$ (pseudo t, J = 7.4 Hz, 3H; CH_2CH_3), 0.98 [s, 9H; $C(CH_3)_3$], 1.63 (pseudo quint, J = 7.2 Hz, 2H; CH_2CH_3), 5.00 (s, 1H; =CH_2), 5.07 (s, 1H; =CH_2), 5.42 (t, ^3J = 6.6 Hz, 1H; CHOR), 6.85–6.89 (m, 1H; Ar-H), 7.19–7.37 (m, 12H; Ar-H), 8.01–8.05 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 10.36$, 28.92, 29.14 (3C), 35.44, 74.40, 109.86, 128.05, 128.26–128.47 (6Aryl-*C*), 130.49 (d, J(C,P) = 2.3 Hz), 131.61, 133.80 (d, J(C,P) = 21.1 Hz, 2C), 134.09 (d, J(C,P) = 21.5 Hz), 134.12, 134.79 (d, J(C,P) = 18.5 Hz, 2C), 138.10 (d, J(C,P) = 10.0 Hz), 138.24 (d, J(C,P) = 12.5 Hz), 140.47 (d, J(C,P) = 27.4 Hz), 156.37, 165.94; ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta = -3.1$; elemental analysis calcd (%) for $C_{28}H_{31}O_2P$ (430.5): C 78.11, H 7.26; found C 77.84, H 7.10.

(1*RS*)-(±)-1-Benzyl-2-*tert*-butyl-prop-2-enyl 2-(diphenylphosphanyl)benzoate (16): *o*-DPPB ester **16** (1.03 g, 84%) was obtained from 2-*tert*-butyl-4-phenyl-but-1-en-3-ol (**11**, 511 mg, 2.5 mmol), *o*-DPPBA (765 mg, 2.5 mmol), DMAP (305 mg, 2.5 mmol), and DCC (540 mg, 2.6 mmol), as a highly viscous, slightly yellow oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.94$ [s, 9H; $CH(CH_3)_3$], 2.91–3.05 (m, 2H; CH_2Ph), 5.10 (s, 1H; =CH_2), 5.21 (s, 1H; =CH_2), 5.71 (pseudo t, J = 6.6 Hz, 1H; CHOR), 6.90–6.94 (m, 1H; Ar-H), 7.19–7.43 (m, 17H; Ar-H), 8.02–8.06 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 28.96$ (3C), 35.48 (C9), 42.01 (C4), 73.51 (C1), 110.87 (C3), 126.32, 128.06 (2C), 128.26–128.50 (7Aryl-*C*), 129.66 (2C), 130.41 (d, J(C,P) = 2.2 Hz), 131.66, 133.79 (d, J(C,P) = 20.8 Hz, 2C), 133.99, 134.13 (d, J(C,P) = 20.9 Hz, 2C), 134.45 (d, J(C,P) = 18.9 Hz), 137.46, 138.07 (d, J(C,P) = 11.5 Hz), 138.19 (d, J(C,P) = 12.8 Hz), 140.65 (d, J(C,P) = 27.8 Hz), 155.79, 165.59 (d, J(C,P) = 2.6 Hz); ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta = -3.1$; elemental analysis calcd (%) for $C_{33}H_{33}O_2P$ (492.6): C 80.46, H 6.75; found C 80.46, H 6.55.

General procedure for hydroformylation of methallylic o-DPPB esters 1a–d and 12—16: $P(OPh)_3$ (4.5 mg, 1.4×10^{-2} mmol) was added at room temperature to a solution of $[Rh(CO)_2acac]$ (0.9 mg, 3.5×10^{-3} mmol) in toluene (3 mL) (exclusion of air and moisture), and the mixture was stirred for 15 min. The corresponding allylic *o*-DPPB ester (0.5 mmol) was subsequently added, and the resulting solution was cannulated into a stainless steel autoclave, followed by rinsing with additional toluene (2 mL). The autoclave was heated to 60 °C and then pressurized successively with 20 bar of a 1:1 mixture of hydrogen and carbon monoxide. The reaction was monitored by TLC and was stopped after complete consumption of starting material. The autoclave was allowed to cool to room temperature, and the reaction mixture was filtered through a small plug of silica with *tert*-butyl methyl ether (30 mL). After evaporation of the solvent in vacuo, the crude product was analyzed by NMR to determine conversion and diastereomer ratio. Subsequent flash chromatography with petroleum ether/*tert*-butyl methyl ether (9:1) provided the corresponding aldehydes **2a–d**[5] and **22–26** as highly viscous oils.

Crystal structure analysis of (±)-**2d**: $C_{27}H_{29}O_3P$, M_r = 432.47; monoclinic, space group: $P21/n$; a = 12.2840(2), b = 11.6675(2), c = 17.0825(3) Å, β = 103.6533(12)°, V = 2379.14(7) Å^3, ρ_{calcd} 1.207 g cm^{-3}; Z = 4, F(000) = 920, crystal dimensions: 0.45 × 0.35 × 0.2 mm. A total of 11422 reflections were collected at 100 K with a Nonius Kappa CCD area-detector diffractometer, by use of ω scans in the theta range of 3.16 to 30.03°, 6939 reflections were unique (R_{int} = 0.0217). The structure was solved by direct methods.[19] Full matrix, least-squares refinement[20] was based on F^2, with all non-hydrogen atoms anisotropic and hydrogens isotropic. The refinement converged at $R1$ = 0.0592 and $wR2$ = 0.1380 for all data; final GOF 1.012; largest peak and hole in the final difference Fourier: 0.315 and −0.315 e Å^{-3}.

CCDC-194956 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

(1*R,2*S**)-(±)-1-Ethyl-2-isopropyl-4-oxobutyl 2-(diphenylphosphanyl)-benzoate (*syn*-22) and (1*R**,2*R**)-(±)-1-ethyl-2-isopropyl-4-oxobutyl 2-(diphenylphosphanyl)benzoate (*anti*-22)**: Compound **22** (180 mg, 81%) was obtained from **17** (208 mg, 0.50 mmol) after 46 h, as a colorless, highly viscous oil. Diastereomer ratio 84:16 (*syn*/*anti*). ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.74–0.86$ (m, 9H; 3 × CH_3), 1.35–1.76 [m, 3H; $CH(CH_3)_2$ and CH_2CH_3], 2.15–2.38 [m, 3H; $CHCH_2$CHO), 5.11–5.19 (m, 1H; CHOR), 6.94–6.98 (m, 1H; Ar-H), 7.28–7.42 (m, 12H; Ar-H), 8.00–8.10 (m, 1H; Ar-H), 9.50 (pseudo t, J = 2.0 Hz, 1H; CHO-*syn*); [minor diastereomer: 9.64 (pseudo t, J = 1.7 Hz, 1H; CHO-*anti*)]; ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 10.25$, 19.14, 21.23, 23.56, 28.02, 41.65, 41.84, 77.49, 128.11–140.67 (18Aryl-*C*), 166.23 (d, J(C,P) = 2.9 Hz), 201.93 [minor diastereomer: 9.53, 18.88, 20.67, 25.77, 28.82, 41.29, 41.52, 76.83]; ^{31}P NMR (161.978 MHz, $CDCl_3$): $\delta = -4.1$; elemental analysis calcd (%) for $C_{28}H_{31}O_3P$ (446.6): C 75.30, H 7.00; found C 75.15, H 7.08.

(1*R,2*S**)-(±)-1-Benzyl-2-isopropyl-4-oxobutyl 2-(diphenylphosphanyl)-benzoate (*syn*-23) and (1*R**,2*R**)-(±)-1-benzyl-2-isopropyl-4-oxobutyl 2-(diphenylphosphanyl)benzoate (*anti*-23)**: Compound **23** (244 mg, 96%) was obtained from **18** (239 mg, 0.50 mmol) after 36 h, as a yellow, highly viscous oil. Diastereomer ratio 92:8 (*syn*/*anti*). ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.86$ [d, J = 6.8 Hz, 3H; $CH(CH_3)_2$-*syn*], 0.95 [d, J = 6.7 Hz, 3H; $CH(CH_3)_2$-*syn*], 1.79–1.90 [m, 1H; $CH(CH_3)_2$], 2.11–2.42 (m, 3H; $CHCH_2$CHO), 2.76–2.89 (m, 2H; $PhCH_2$), 5.40–5.46 (m, 1H; CHOR), 6.86–6.91 (m, 1H; Ar-H), 7.13–7.44 (m, 17H; Ar-H), 7.82–7.86 (m, 1H; Ar-H), 9.53 (br s, 1H; CHO-*syn*); [minor diastereomer: 0.73 (d, J = 6.8 Hz, 3H; $CH(CH_3)_2$-*anti*), 0.77 (d, J = 6.7 Hz, 3H; $CH(CH_3)_2$-*anti*), 9.70 (br s, 1H; CHO-*anti*]; ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 19.44$, 21.31, 28.04, 36.73, 41.74, 41.83, 76.55, 126.47, 128.15, 128.38 (2C), 128.38–128.60 (6Aryl-*C*), 129.11 (2C), 130.36 (d, J(C,P) = 2.2 Hz), 131.84, 133.91 (d, J(C,P) = 20.8 Hz, 2C), 134.07 (d, J(C,P) = 21.0 Hz, 2C) (C1′, expected at $\delta \approx 134$ as a doublet, is obscured by the signals at 133.91–134.14), 134.14, 137.47, 137.59 (d, J(C,P) = 12.8 Hz), 138.18 (d, J(C,P) = 11.5 Hz), 140.61 (d, J(C,P) = 27.6 Hz), 165.95 (d, J(C,P) = 2.6 Hz), 201.76 [minor diastereomer: 19.20, 20.14, 29.15, 38.93, 40.42, 41.39, 75.73]; ^{31}P NMR (161.978 MHz, $CDCl_3$): $\delta = -4.1$; elemental analysis calcd (%) for $C_{33}H_{33}O_3P$ (508.6): C 77.93, H 6.54; found C 77.69, H 6.34.

(1*R,2*R**)-(±)-2-Isopropyl-1-phenyl-4-oxobutyl 2-(diphenylphosphanyl)-benzoate (*syn*-24)**: Compound **24** (239 mg, 97%) was obtained from **19** (232 mg, 0.50 mmol) after 33 h, as a yellow, highly viscous oil. Diastereomer ratio 99:1 (*syn*/*anti*). ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.73$ (d, J = 7.0 Hz, 3H; $CH(CH_3)_2$), 0.88 (d, J = 6.9 Hz, 3H; $CH(CH_3)_2$), 1.96–2.20 (m, 3H; CH_2 and $CH(CH_3)_2$), 2.58–2.63 (m, 1H; $CHCH_2$), 5.89 (d, J = 8.4 Hz, 1H; CHOR), 6.89–6.93 (m, 1H; Ar-H), 7.19–7.35 (m, 17H; Ar-H), 8.07–8.12 (m, 1H; Ar-H), 9.18 (dd, ^3J = 1.9, 1.7 Hz, 1H; CHO); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 17.06$, 21.28, 27.00, 40.44, 43.52, 77.60, 127.51 (2C), 128.11, 128.14, 128.32 (2C), 128.25–128.50 (6Aryl-*C*), 130.58 (d, J(C,P) = 2.3 Hz), 131.88, 133.66 (d, J(C,P) = 20.5 Hz, 2C), 133.91 (d, J(C,P) = 20.8 Hz, 2C), 134.05 (d, J(C,P) = 18.0 Hz), 134.22, 137.61 (d, J(C,P) = 12.9 Hz), 138.09 (d, J(C,P) = 11.5 Hz), 138.24, 140.56 (d, J(C,P) = 28.0 Hz), 165.58 (d, J(C,P) = 2.5 Hz), 200.60; ^{31}P NMR (161.978 MHz, $CDCl_3$): $\delta = -4.2$; elemental analysis calcd (%) for $C_{32}H_{31}O_3P$ (494.6): C 77.71, H 6.32; found C 77.52, H 6.58.

(1*R,2*S**)-(±)-2-*tert*-Butyl-1-ethyl-4-oxobutyl 2-(diphenylphosphanyl)benzoate (*syn*-25) and (1*R**,2*R**)-(±)-2-*tert*-butyl-1-ethyl-4-oxobutyl 2-(diphenyl-phosphanyl)benzoate (*anti*-25)**: Compound **25** (163 mg, 71%) was obtained from **20** (208 mg, 0.50 mmol) after 30 h, as a colorless, highly viscous oil. Diastereomer ratio 94:6 (*syn*/*anti*). ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.74$ (pseudo t, J = 7.4 Hz, 3H; CH_2CH_3), 0.85 [s, 9H; $C(CH_3)_3$], 1.41 (m, 2H; CH_2CH_3), 1.96 [m, 1H; $CHC(CH_3)_3$], 2.23 (ddd, J = 16.0, 5.2, 2.0 Hz, 1H; CH_2CHO), 2.34 (ddd, J = 16.0, 8.1, 3.3 Hz, 1H; CH_2CHO), 5.18 (m, 1H; CHOR), 6.83–6.87 (m, 1H; Ar-H), 7.19–7.35 (m, 12H; Ar-H), 7.90–7.94 (m, 1H; Ar-H), 9.42 (m, 1H; CHO-*syn*) [minor diastereomer: 9.66 (br s, 1H; CHO-*anti*)]; ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 10.72$, 23.82, 28.61 (3C), 32.80, 41.04, 46.77, 77.48, 128.15–128.57 (7Aryl-*C*), 130.45 (d, J(C,P) = 2.0 Hz), 131.78, 133.79 (d, J(C,P) = 20.5 Hz, 2C), 133.93, 134.06 (d, J(C,P) = 20.9 Hz, 2C) (C1′, expected at $\delta \approx 134$ as a doublet, is obscured by the signals at 133.93–134.06), 137.73 (d, J(C,P) = 12.7 Hz), 138.23 (d, J(C,P) = 11.3 Hz), 140.69 (d, J(C,P) = 27.5 Hz), 166.00 (d, J(C,P) = 2.9 Hz), 202.56 [minor diastereomer: 201.93 (C4-*anti*)]; ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta = -2.9$ [minor diastereomer: −3.6]; elemental analysis calcd (%) for $C_{29}H_{33}O_3P$ (460.6): C 75.63, H 7.22; found C 75.56, H 7.30.

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(1*R,2*S**)-(±)-1-Benzyl-2-*tert*-butyl-4-oxobutyl 2-(diphenylphosphanyl)-benzoate (*syn*-26)**: Compound **26** (247 mg, 95%) was obtained from **21** (246 mg, 0.50 mmol) after 40 h, as a colorless, highly viscous oil. Diastereomer ratio 99:1 (*syn*/*anti*). ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.97$ [s, 9H; $C(CH_3)_3$], 1.99 [ddd, $J = 8.7$, 5.1, 2.7 Hz, 1H; $CHC(CH_3)_3$], 2.34 (ddd, $J = 15.8$, 5.1, 1.8 Hz, 1H; CH_2CHO), 2.52 (ddd, $J = 15.8$, 5.1, 3.3 Hz, 1H; CH_2CHO), 2.80 (dd, $J = 14.6$, 10.4 Hz, 1H; $PhCH_2$), 2.89 (dd, $J = 14.6$, 2.8 Hz, 1H; $PhCH_2$), 5.55 (ddd, $J = 10.3$, 2.8, 2.6 Hz, 1H; CHOR), 6.80–6.84 (m, 1H; Ar-H), 7.09–7.33 (m, 17H; Ar-H), 7.71–7.75 (m, 1H; Ar-H), 9.40 (dd, $J = 3.8$, 1.8 Hz, 1H; CHO); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta =$ 28.79 (3C), 33.02, 36.88, 41.18, 46.93, 76.27, 126.40, 128.14, 128.35 (2C), 128.35–128.59 (6Aryl-*C*), 128.83 (2C), 130.40, 131.80, 133.53 (d, J(C,P) = 17.1 Hz), 133.86, 133.89(d, J(C,P) = 20.6 Hz, 2C), 134.16 (d, J(C,P) = 20.8 Hz, 2C), 137.54 (d, J(C,P) = 13.2 Hz), 138.36, 138.43 (d, J(C,P) = 10.9 Hz), 140.89 (d, J(C,P) = 27.5 Hz), 166.00 (d, J(C,P) = 2.9 Hz), 202.59 (C4); ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta = -2.8$; elemental analysis calcd (%) for $C_{34}H_{35}O_3P$ (522.6): C 78.14, H 6.75; found C 77.88, H 6.66.

(1*R,2*R**)-(±)-2-Isopropyl-4-dimethoxy-1-phenylbutyl 2-(diphenylphosphanyl)benzoate (27)**: A mixture of aldehyde **24** (1.30 g, 2.6 mmol), Bayer Lewatit SC 102 (200 mg), and Na_2SO_4 (1.85 g, 13.0 mmol) in methanol (22 mL) was stirred for 3 h at room temperature. The reaction mixture was filtered through basic alumina. Evaporation of the solvent afforded **27** (1.41 g, >99%) as a yellow, highly viscous oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.83$ [d, $J = 6.8$ Hz, 3H; $CH(CH_3)_2$], 0.89 [d, $J = 6.8$ Hz, 3H; $CH(CH_3)_2$], 1.28–1.37 (m, 1H; CH_2), 1.52–1.60 (m, 1H; CH_2), 1.96–2.11 [m, 2H; $CHCH(CH_3)_2$], 2.99 (s, 3H; OCH_3), 3.18 (s, 3H; OCH_3), 3.50 [m, 1H; $CH(OCH_3)_2$], 5.89 (d, $J = 8.4$ Hz, 1H; CHOR), 6.93–6.97 (m, 1H; Ar-H), 7.27–7.34 (m, 17H; Ar-H), 8.16–8.20 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 17.06$, 21.20, 27.12, 29.10, 44.15, 53.13, 53.43, 78.33, 103.77, 127.28 (2C), 127.68, 128.14, 128.19 (2C), 128.28–128.49 (6Aryl-*C*), 130.57 (d, J(C,P) = 2.3 Hz), 131.86, 133.86 (d, J(C,P) = 20.9 Hz, 2C), 134.00 (d, J(C,P) = 21.4 Hz, 2C), 134.33 (C1′, expected at $\delta \approx 134$ as a doublet, is obscured by the signals at 133.86–134.33), 137.92 (d, J(C,P) = 13.1 Hz), 138.22 (d, J(C,P) = 11.7 Hz), 139.89, 140.83 (d, J(C,P) = 28.1 Hz), 165.61 (d, J(C,P) = 2.5 Hz); ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta = -3.5$.

(3*R,4*R**)-(±)-4-Hydroxy-3-isopropyl-4-phenylbuten-1-al dimethylacetal (28)**: A saturated solution of ethanolic potassium hydroxide (15 mL) was added to a solution of ester **27** (1.08 g, 2.0 mmol), and the resulting mixture was heated at reflux for 3 h. Water (30 mL) and *tert*-butyl methyl ether (20 mL) were added, and the phases were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 15 mL) and the combined organic phases were dried (Na_2SO_4). The solvent was removed in vacuo, and the residue was purified by flash chromatography with petroleum ether/*tert*-butyl methyl ether (4:1) to furnish alcohol **28** (0.58 g, 99%) as a yellowish oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.83$ [d, $^3J = 6.8$ Hz, 3H; $CH(CH_3)_2$], 0.87 [d, $^3J = 6.9$ Hz, 3H; $CH(CH_3)_2$], 1.35–1.53 (m, 2H; CH_2), 1.69–1.74 [m, 1H; $CH(CH_3)_2$], 1.94–2.00 [m, 1H; $CHCH(CH_3)_2$], 2.36 (br s, 1H; OH), 3.05 (s, 3H; OCH_3), 3.15 (s, 3H; OCH_3), 3.69 [pseudo t, $J =$ 6.0 Hz, 1H; $CH(OCH_3)_2$], 4.60 (dd, $J = 7.0$, 2.4 Hz, 1H; CHOH), 7.25–7.32 (m, 5H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 17.65$, 21.57, 27.15, 29.08, 46.27, 52.87, 53.39, 75.99, 104.34, 126.75 (2C), 127.37, 128.24 (2C), 143.93.

(4*R,5*R**)-(±)-4-Isopropyl-5-phenyl-tetrahydrofuran-2-one (*cis*-30)**: A solution of dimethylacetal **28** was dissolved in acetic acid (80%, 5 mL) and stirred for 24 h at room temperature. The reaction was terminated by cautious addition of aqueous saturated $NaHCO_3$ solution (30 mL). The reaction mixture was extracted with *tert*-butyl methyl ether (3 × 15 mL) and the combined organic phases were dried ($MgSO_4$). Evaporation of the solvent in vacuo and purification of the residue by flash chromatography with petroleum ether/*tert*-butyl methyl ether (4:1) furnished the lactols **29** (44 mg, 75%) as a colorless oil. Lactols **29** were used directly in the subsequent oxidation.

PCC on Al_2O_3 (1 mmol g^{-1}, 630 mg) was added to a magnetically stirred solution of lactols **29** (44 mg, 0.21 mmol) in CH_2Cl_2 (8 mL), and the resulting suspension was stirred for 26 h at room temperature. The reaction mixture was filtered through silica gel with CH_2Cl_2 (200 mL). After evaporation of the solvent in vacuo, the residue was purified by flash chromatography with petroleum ether/*tert*-butyl methyl ether (4:1) to furnish lactone *cis*-**30** (39 mg, 91%) as a colorless oil. ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.70$ [d, $J = 6.7$ Hz, 3H; $CH(CH_3)_2$], 0.78 [d, $J = 6.5$ Hz, 3H; $CH(CH_3)_2$], 1.20–1.27 [m, 1H; $CH(CH_3)$], 2.47–2.58 (m, 3H; $CHCH_2$), 5.54 (d, $^3J = 6.4$ Hz, 1H; CHPh), 7.18–7.35 (m, 5H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 19.90$, 21.22, 27.49, 31.79, 47.54, 84.27, 126.51 (2C), 128.32, 128.47 (2C), 136.34, 176.83; MS (EI, 70 eV, m/z (%): 204 (29), 107 (60) $[C_7H_7O]^+$, 98 (19), 70 (100), 55 (55), 42 (19), 28 (24) $[CO]^+$; found 204.1151 $[M]^+$ (HRMS, EI); $C_{13}H_{16}O_2$ calcd 204.1150.

(4*R,5*R**)-(±)-4-Isopropyl-5-phenyl-tetrahydrofuran-2-one (*cis*-30) and (4*R**,5*S**)-(±)-4-isopropyl-5-phenyl-tetrahydrofuran-2-one (*trans*-30)**: PPh_3 (74.9 mg, 0.286 mmol) was added at room temperature (exclusion of air and moisture) to a solution of $[Rh(CO)_2acac]$ (0.9 mg, 3.5×10^{-3} mmol) in toluene (3 mL), and the mixture was stirred for 15 min. Subsequently, 2-isopropyl-1-phenylprop-2-en-1-ol (**9**, 705 mg, 4.0 mmol) was added, and the resulting solution was cannulated into a stainless steel autoclave, followed by rinsing with an additional toluene (2 mL). The autoclave was heated to 90 °C and then pressurized successively with 20 bar of a 1:1 mixture of hydrogen and carbon monoxide. After 48 h under these conditions, the autoclave was allowed to cool to room temperature, and the reaction mixture was filtered through a small plug of silica with *tert*-butyl methyl ether (30 mL). After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography with petroleum ether/*tert*-butyl methyl ether (4:1) to give lactols **29** (207 mg, 50% based on recovered starting material 350 mg, 2.0 mmol).

The lactols **29** (103 mg, 0.5 mmol) were oxidized as described above for the preparation of *cis*-**30** to give a mixture of *cis*- and *trans*-lactone **30** (88 mg, 86%) in a diastereomer ratio *cis*/*trans* 64:36.

NMR data for *trans*-**30**: ^{1}H NMR (300.133 MHz, $CDCl_3$): $\delta = 0.82$ (d, $J =$ 6.8 Hz, 3H; $CH(CH_3)_2$), 0.93 (d, $J = 6.8$ Hz, 3H; $CH(CH_3)_2$), 1.72–1.83 (m, 1H; $CH(CH_3)$), 2.31–2.64 (m, 3H; $CHCH_2$), 5.14 (d, $J = 6.6$ Hz, 1H; CHPh), 7.18–7.33 (m, 5H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta =$ 18.85, 20.63, 29.61, 31.66, 49.97, 84.62, 126.05, 128.45, 128.63 (2C), 139.31, 176.25. The analytical data correspond to those reported for *cis*-**30**.

1-Bromomethyl-2-(diphenylphosphinoyl)benzene (32): Phosphorus tribromide (0.7 mL, 7.4 mmol) was added dropwise at 0 °C to a suspension of [2-(diphenylphosphinoyl)-phenyl] methanol[12] (2.87 g, 9.3 mmol) in THF (50 mL) and CH_2Cl_2 (10 mL). After the mixture had been stirred for 15 min at this temperature and for a further 2 h at room temperature, TLC showed complete consumption of starting material. Water (5 mL) was added, and the reaction mixture was poured into water (100 mL). After extraction with CH_2Cl_2 (3 × 50 mL), the combined organic phases were dried ($MgSO_4$) and the solvent was evaporated. Purification of the residue by flash chromatography with petroleum ether/ethyl acetate (1:1) furnished bromide **32** (3.3 g, 96%) as a colorless waxy solid. ^{1}H NMR (500.130 MHz, $CDCl_3$): $\delta = 4.93$ (s, 2H; CH_2), 6.97 (m, 1H; Ar-H), 7.17 (m, 1H; Ar-H), 7.39–7.51 (m, 8H; Ar-H), 7.56–7.60 (m, 4H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 60.2$, 127.4 (d, = 12.4 Hz), 128.6 (d, J(C,P) = 12.0 Hz, 4C), 130.7 (d, J(C,P) = 72.3 Hz, 2C), 132.0 (d, J(C,P) = 10.2 Hz, 4C), 132.1 (d, J(C,P) = 2.9 Hz), 132.5 (d, J(C,P) = 2.8 Hz), 133.0 (d, J(C,P) = 6.3 Hz), 133.2 (d, J(C,P) = 11.9 Hz), 133.5 (s), 142.9 (d, J(C,P) = 6.8 Hz, C1); ^{31}P NMR (121.495 MHz, $CDCl_3$): $\delta = 32.3$ (s); analytical data correspond to those reported previously.[12]

(±)-1-{[(2-Methyl-1-phenylallyl)oxy]methyl}-2-(diphenylphosphinoyl)-benzene (33): Sodium hydride (84 mg, 2.1 mmol, 60% in oil, 1.1 equiv) was washed oil-free with petroleum ether (2 mL) and suspended in THF (4 mL). Subsequently, a solution of (±)-2-methyl-1-phenylprop-2-en-1-ol[21] (311 mg, 2.1 mmol) in THF (2 mL) was added dropwise at 0 °C, and the mixture was stirred for ca. 10 min at this temperature until gas evolution had ceased. A solution of bromide **32** (650 mg, 1.75 mmol) in THF (5 mL) was added over 5 min, and the resulting mixture was stirred at room temperature for a further 2 h until TLC showed complete consumption of the starting material. The reaction mixture was poured into water (30 mL) and extracted with CH_2Cl_2 (5 × 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography with petroleum ether/ethyl acetate (1:1) yielded allylic ether **33** (660 mg, 86%) as a highly viscous, colorless oil. ^{1}H NMR (300.130 MHz, $CDCl_3$): $\delta = 1.42$ (s, 3H; CH_3), 4.65 (s, 1H; CH_2=), 4.74 (d, $J = 14.1$ Hz, 1H; CH_2), 4.83 (s, 1H), 4.85 (d, $J = 14.0$ Hz, 1H; CH_2), 4.99 (s, 2H; CH_2=), 7.05 (m, 1H; Ar-H), 7.20–7.39 (m, 6H; Ar-H), 7.45–7.67 (m, 11H; Ar-H), 7.91 (m, 1H; Ar-H); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 17.2$, 67.9 (d, J(C,P) = 4.8 Hz, CH_2), 85.0, 113.1, 126.2–128.5 (15 Ar-C), 129.5, 131.8–133.9 (7 Ar-C), 140.3, 144.3 (d, J(C,P) = 3.8 Hz); ^{31}P NMR

(121.495 MHz, $CDCl_3$): $\delta = 31.4$ (s); found 439.1792 $[M+H]^+$ (HRMS, FAB); $C_{29}H_{28}O_2P$ calcd 439.1827.

(±)-2-{[(2-Methyl-1-phenylallyl)oxy]methyl}phenyl-(diphenyl)-phosphane (34): Triethylamine (9.92 g, 98 mmol) was added to a solution of phosphane oxide **33** (2.07 g, 4.9 mmol) in toluene (15 mL). The solution was cooled to 0 °C, and trichlorosilane (3.32 g, 24.5 mmol) was added. The reaction mixture was heated at 140 °C in a sealed tube for 45 h. After cooling to room temperature, the reaction mixture was poured into aqueous sodium hydroxide solution (5%, 100 mL). After addition of brine (30 mL), the mixture was extracted with ether (4×100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography with petroleum ether/*tert*-butyl methyl ether (98:2) to furnish phosphine **34** (1.56 g, 77%) as a viscous, colorless oil. ^{1}H NMR (500.130 MHz, $CDCl_3$): $\delta = 1.49$ (s, 3H; CH_3), 4.66 (d, $J = 12.6$ Hz, 1H), 4.74–4.77 (m, 2H), 4.91 (s, 1H), 5.06 (s, 1H), 6.88 (m, 1H; Ar-H), 7.16–7.30 (m, 16H; Ar-H), 7.35 (m, 1H; Ar-H), 7.63 (m, 1H; Ar-H); ^{13}C NMR (125.758 MHz, $CDCl_3$): $\delta = 17.4$ (CH_3), 68.5 (d, J(C,P) = 25.0 Hz), 85.0, 113.3 (CH_2=), 126.5 (s, 2C), 127.1 (s), 127.5, 127.8 (d, J(C,P) = 5.7 Hz), 128.0 (s, 2C), 128.5 (d, J(C,P) = 7.0 Hz, 4C), 128.6 (s, 2C), 128.9 (s), 133.4 (s), 133.8 (d, J(C,P) = 19.6 Hz, 4C), 135.1 (d, J(C,P) = 15.3 Hz), 136.6 (d, J(C,P) = 10.2 Hz, 2C), 140.5 (s), 143.1 (d, J(C,P) = 23.6 Hz), 144.9; ^{31}P NMR (121.495 MHz, $CDCl_3$): $\delta = -16.1$ (s); elemental analysis calcd (%) for $C_{29}H_{27}PO$ (422.5): C 82.44, H 6.44; found C 82.16, H 6.56.

(3*R,4*S**)-4-[2-(Diphenylphosphanyl)-benzyloxy]-3-methyl-4-phenylbutyraldehyde (*syn*-35) and (3*R**,4*R**)-4-[2-(diphenylphosphanyl)-benzyloxy]-3-methyl-4-phenyl-butyraldehyde (*anti*-35)**: This compound was obtained from allylic ether **34** (211 mg, 0.5 mmol) after 24 h at 90 °C and 20 bar syngas pressure, by the procedure described for the hydroformylation of *o*-DPPB esters **1a–d** and **17–21**, a quantitative conversion of starting material according to NMR analysis of the crude reaction product. The diastereomer ratio was *syn*/*anti* 68:32. Flash chromatography of the crude product with petroleum ether/*tert*-butyl methyl ether (9:1) gave aldehydes **35** (154 mg, 64%) as a highly viscous colorless oil. Signals of the minor (*anti*) diastereomer in square brackets. ^{1}H NMR (500.130 MHz, $CDCl_3$): $\delta = 0.76$ (d, $J = 6.9$ Hz, 3H; CH_3), [0.69 (d, $J = 6.8$ Hz, 3H; CH_3], 1.96 (ddd, $J = 18.4$, 8.0, 1.8 Hz, 1H), [2.07 (m, 1H)], 2.26 (m, 1H)], 2.34 (dd, $J = 16.6$ Hz, 5.4 Hz, 1H), [2.51 (dd, $J = 16.5$ Hz, 5.1 Hz, 1H)], 4.25 (d, $J =$ 5.1 Hz, 1H) [4.01 (d, $J = 7.0$ Hz, 1H)], 4.47–4.64 (m, 2H), 6.91 (m, 1H; Ar-H), 7.15–7.36 (m, 17 Ar-H), 7.48 (m, 1H; Ar-H), 9.47 (s, 1H; CHO), [9.54 (s, 1H; CHO)]; ^{13}C NMR (125.758 MHz, $CDCl_3$): $\delta = 15.6$ [16.9], 34.4 [35.4], 46.8 [47.5], 69.4 [69.2], 84.7 [86.2], 127.3 [127.4] (2C), 127.8 [127.7], 128.1 [128.2] (2C), 128.4–128.7 (4 Ar-C), 129.0, 133.7 (d, J(C,P) = 19.6 Hz, 4C), 135.4 [135.2], 135.5, 136.6 (d, J(C,P) = 10.1 Hz, 2C), 136.7 (d, J(C,P) = 10.3 Hz, 2C), 139.2 [140.1], 142.8 [142.5], 142.9, 202.4 [202.6]; ^{31}P NMR (202.457 MHz, $CDCl_3$): $\delta = -18.7$ (s); elemental analysis calcd (%) for $C_{30}H_{29}PO_2$ (452.3): C 79.62, H 6.46; found C 79.73, H 6.51.

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