Substrate-Directed Diastereoselective Hydroformylations, 1

Substrate-Directed Diastereoselective Hydroformylation of Methallylic Alcohols – Development of an Efficient Catalyst-Directing Group for Rhodium-Catalyzed Hydroformylation

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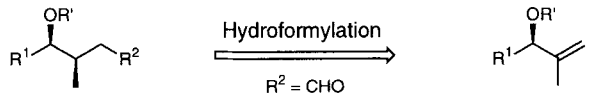
The development of an efficient catalyst-directing group based on *ortho*-diphenylphosphanyl benzoate (*o*-DPPB) for the substrate-directed, diastereoselective hydroformylation of methallylic alcohols **5** is described. The hydroformylation of methallylic *o*-DPPB esters **9** provides the corresponding *syn*-aldehydes **10** with diastereoselectivities of up to 96:4. A specific steric demand of the substituent at the stereogenic center of the methallylic derivatives **9** was found to be necessary to achieve a high degree of stereoselectivity. Experiments have been performed that prove that the *o*-DPPB group acts as a catalyst-directing group by reversibly coordinating to the catalyst. The removal of the *o*-DPPB group was accomplished by means of alkaline hydrolysis, thereby furnishing the lactols **6**. Oxidation of **6** provides the corresponding γ-lactones **7**.

Introduction

Transition-metal-catalyzed reactions represent uniquely efficient tools for the construction of carbon backbones in organic synthesis. They allow also the generation of new stereocenters, either with the aid of a chiral catalyst[1] or by substrate-based asymmetric induction[2]. Despite the fact that the latter approach seems attractive with respect to synthetic efficiency, somewhat surprisingly such reactions do not appear to be utilized very frequently[3].

Many synthetic targets contain the acyclic structural fragment **1**, a commonly encountered structural motif found especially in the polyketide class of natural products[4]. The stereoselective synthesis of this particular unit, which possesses two adjacent stereocenters, has been a yardstick by which the efficiencies of new methodologies for controlling stereoselectivity in reactions of acyclic substrates have been compared. Successful approaches to this fragment via C–C bond-forming reactions include the addition of organometallic reagents to aldehydes possessing a stereocenter in the α position[5], homo-aldol-type processes developed by Hoppe and Thomas[6], as well as the recently discovered zirconium-catalyzed carbomagnesation[3,7]. A common disadvantage of all three of these methods is that stoichiometric amounts of the organometallic reagents are required.

The two faces of the double bond in an α-substituted methallylic alcohol **2** are diastereotopic in nature. In addition reactions, efficient differentiation of these two faces is desirable, so that the new stereocenter is generated stereoselectively. Such an approach has already been realized for transition-metal-catalyzed reduction processes, such as rhodium-catalyzed hydroboration[8] as well as rhodium-catalyzed hydrogenation of 2-substituted allylic alcohols, as developed by Brown and Evans[9]. Thus, it was of interest to ascertain whether this type of reaction could be extended to a transition-metal-catalyzed C–C bond-forming process. If successful, such a transformation could provide an efficient access to the building block **1**.



1 **2**

As a particularly appealing homogeneously catalyzed C–C bond-forming reaction, the industrially important rhodium-catalyzed hydroformylation of olefins[10] was selected for study. This reaction makes use of inexpensive "synthesis gas" as a carbon source and leads overall to a one-carbon extension of the carbon framework, introducing the synthetically useful aldehyde functionality. Although hydroformylation has been known for almost 60 years, no efficient variants allowing control of diastereoselectivity for acyclic substrates are known[11]. For the development of a stereoselective hydroformylation reaction, methallylic alcohols **2** seemed to be ideal substrates. Thus, the 1,2 relation of the directing stereocenter to the new stereocenter formed in the course of the hydroformylation reaction might give

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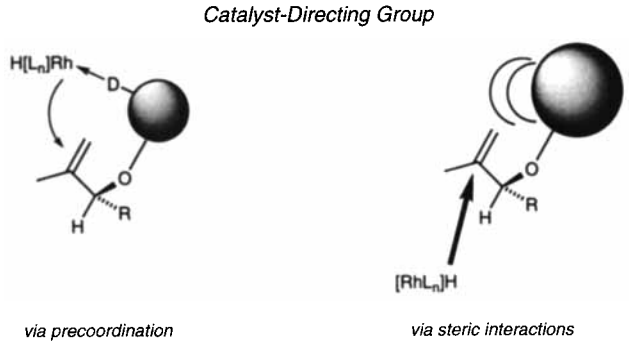
rise to a strong asymmetric induction. Furthermore, the presence of a 1,1-disubstituted double bond in a methallylic alcohol avoids the problem of regioselectivity, which usually accompanies the hydroformylation reaction. Based on Keulemans' rule, the formyl group will be attached exclusively at the less substituted olefin terminus[12]. Consequently, the only type of selectivity that remains to be controlled is diastereoselectivity. To address this challenge, the concept of a catalyst-directing group in rhodium-catalyzed hydroformylation of methallylic alcohols has been evaluated. Such a group, which might easily be attached to the hydroxy function of the methallylic alcohol, could, in principle, exert an influence in two different ways (see Scheme 1).

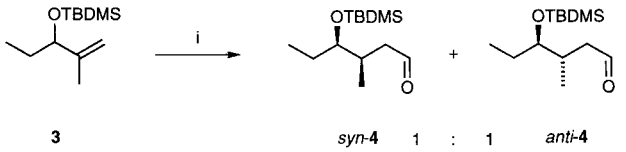
Scheme 1. Concepts employing a catalyst-directing group for the development of a substrate-directed hydroformylation of acyclic methallylic alcohols



One mode of action, based on attractive interactions, would be a precoordination of the catalytically active rhodium species by the catalyst-directing group, which must therefore possess a suitable coordination site. In this scenario, the catalyst would be positioned at one of the diastereotopic olefin faces. On the other hand, an alternative mode of action would be repulsive in nature and based on steric interactions. Thus, if a sterically demanding substituent were to be attached at the hydroxy functionality, and if 1,2-allylic strain were to favor a particular conformation (as indicated in Scheme 1), one could assume an efficient shielding of one of the two diastereotopic olefin faces. In this paper, these two possibilities are considered in the context of a diastereoselective hydroformylation of acyclic methallylic alcohols with the aid of an efficient catalyst-directing group[13].

Exploratory Studies

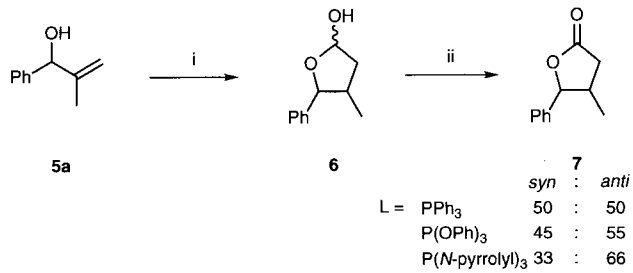
For rhodium-catalyzed hydroboration of methallylic alcohols, it is known that the presence of an unprotected allylic hydroxy substituent does not lead to useful levels of diastereoselectivity, but that, on the other hand, protection of this alcohol as a silyl ether with bulky substituents at the silicon atom, gives rise to high 1,2-asymmetric induction[8]. In view of this, investigations were carried out to ascertain whether the same bulky silyl protecting group (TBDMS) also has a beneficial effect on stereoselectivity in rhodium-catalyzed hydroformylation.



Reagents and conditions: i, 0.7 mol% $Rh(CO)_2acac/4P(OPh)_3$, 20 bar H_2/CO (1 : 1), toluene, 80 °C, 48 h (35%, 63% recovered **3**).

In a first experiment, the TBDMS ether **3** was subjected to hydroformylation conditions. This resulted in a 1:1 *syn/anti* mixture of the corresponding aldehydes **4**, as determined by NMR spectroscopic analysis of the crude reaction product. Thus, in contrast to rhodium-catalyzed hydroboration, a bulky silyl substituent is not a useful catalyst-directing group for rhodium-catalyzed hydroformylation.

Secondly, a catalyst-directing group expected to act via precoordination of the catalyst was evaluated. Such investigations were made in the light of the known, highly stereoselective, hydroxy-directed, rhodium-catalyzed hydrogenations of allylic and homoallylic alcohols[9]. In these cases, high levels of stereoselectivity are presumably due to a precoordination of the catalytically active rhodium species to the hydroxy function. The question arose as to whether the same principle could be used to achieve a stereoselective hydroformylation[14].



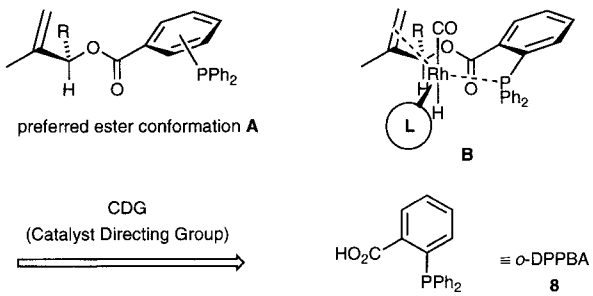
Reagents and conditions: i, 0.35 mol% $Rh(CO)_2acac$/n eq ligand, 20 bar H_2/CO (1 : 1), toluene, 90°C, 6-24 h (83-95%); ii, 2 eq pyridinium chloro chromate (PCC) on Al_2O_3, CH_2Cl_2, 25°C, 16 h (95%).

Thus, the unprotected methallylic alcohol **5a** was subjected to hydroformylation conditions, employing 0.35 mol-% $Rh(CO)_2(acac)/PPh_3$ (1:20) as the catalyst. The lactols **6** were isolated in 83% yield and then oxidized with pyridinium chlorochromate (PCC) to the known lactones *syn*- and *anti*-**7**[15]. NMR analysis again revealed a disappointing 1:1 *syn/anti* ratio, i.e. no diastereoselectivity. The catalyst properties were then modified by varying the π acceptor ability of the phosphane ligand[16]. On going from triphenylphosphite to tris(pyrrolyl)phosphane, an increase was observed in the amount of the *anti* product formed, such that the *syn/anti* ratio was shifted towards 1:2. However, in spite of this degree of dependence of the diastereoselectivity of hydroformylation of **5a** on the π acceptor ability of the phosphorus ligands, it seems unlikely that synthetically useful levels of diastereoselectivity could be achieved by modifications of this kind.

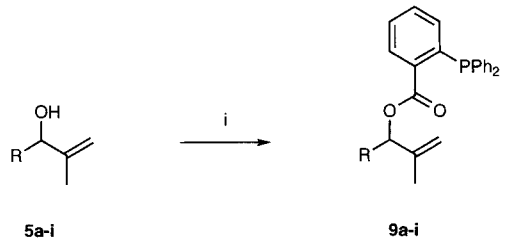
Development of an Efficient Catalyst-Directing Group for Rhodium-Catalyzed Hydoformylation of 2-Substituted Allylic Alcohols

The main point to emerge from the aforementioned experiments is that a hydroxy substituent is not an efficient catalyst-directing group for rhodium-catalyzed hydroformylation, in contrast to rhodium-catalyzed hydrogenation reactions of similar substrates[9]. This might be due to the presence of a large excess of carbon monoxide under hydroformylation conditions, which itself is a much better ligand for rhodium than a hydroxy group. These findings indicated that for a catalyst-directing group to be effective, it would have to be as good a ligand for rhodium as carbon monoxide. Simultaneously, a reversible coordination of the catalyst-directing group has to be ensured, because otherwise stoichiometric amounts of rhodium-catalyst would be consumed, or, in other words, there would be no turnover. A system combining both properties is a monodentate triarylphosphane. The ability of such ligands to coordinate reversibly to rhodium under hydroformylation conditions is well documented[17]. Another requisite feature of the catalyst-directing group is its facile attachment to, as well as its removal from, the methallylic alcohol substrate. In this respect, the formation of an ester bond between the hydroxy function of the methallylic alcohol and a corresponding carboxylic acid function attached to the triarylphosphane seemed to be particularly attractive. In addition to its ease of formation, an ester connection to an α-substituted methallylic alcohol would be expected to induce the energetically preferred, well-defined conformation **A** (see Scheme 2)[18].

Scheme 2. Preferred ester conformation **A** and hypothetical intermediate **B**

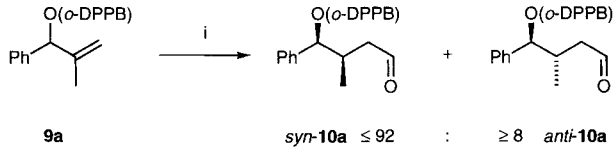


The attachment of the carboxylic acid functionality at one of the aromatic rings of the triarylphosphane seemed to be straightforward. Clearly, three options were available, i.e. introduction of the substituent at the *ortho*, *meta* or *para* position. In choosing between these positions it had to be borne in mind that both the olefin and the catalyst-directing group should coordinate to the same catalytically active rhodium center. This is mandatory if the stereochemistry-defining, hydrometallation step is to pass through a cyclic transition state. A cyclic transition state is particularly desirable, since these are generally highly ordered and consequently often provide high selectivities. In the present system, only an *ortho* orientation of the carboxylic ester functionality would allow such a bidentate binding mode as in the proposed arrangement **B** (see Scheme 2), suggesting that *ortho*-(diphenylphosphanyl)benzoic acid (**8**) would be the catalyst-directing group of choice. Fortunately, compound **8** is readily available by reaction of the inexpensive *ortho*-chlorobenzoic acid and triphenylphosphane with sodium in liquid ammonia[19]. The corresponding methallylic *ortho*-(diphenylphosphanyl)benzoates **9** were readily obtained using the dicyclohexylcarbodiimide/DMAP esterification protocol[20].



Reagents and Conditions: i, 1 eq *ortho*-diphenylphosphino benzoic acid (*o*-DPPBA), 1.1 eq dicyclohexyl carbodiimide (DCC), 0.1 eq 4-*N*,*N*-dimethylamino pyridine (DMAP), CH_2Cl_2, 25°C (67-99%).

To evaluate the concepts outlined above, the methallylic *o*-DPPB ester **9a** was subjected to hydroformylation conditions. Gratifyingly, hydroformylation was found to proceed smoothly, furnishing the aldehyde *syn*-**10a** with diastereoselectivities of up to 92:8 when $Rh(CO)_2(acac)$/$P(OPh)_3$ (1:4) was used as the catalyst system.



Reagents and Conditions: i, see table 1 [a] and table 2 [a] for details.

This optimized catalyst system was arrived at after much careful consideration and numerous experiments. Thus, as a working hypothesis, complex **B** (Scheme 2) was envisaged as a likely intermediate in the catalytic cycle for hydroformylation of methallylic *o*-DPPB esters **9**. For standard rhodium/phosphane hydroformylation catalysts, it has been shown that, in general, two P-donor ligands are coordinated to rhodium within the catalytically active species[17]. Consequently, another P-donor ligand is required to occupy the coordination position of L within the arrangement **B**. For this reason, a systematic investigation was made on the influence of a monodentate coligand on reactivity and selectivity in hydroformylation of the *o*-DPPB ester **9a** as a model system (see Table 1).

When using $Rh(CO)_2(acac)$ as the hydroformylation catalyst without a coligand, conversion at 90°C and 20 bar CO/H_2 (1:1) was low after 24 h (35%), as was the diastereoselectivity (81:19). With triphenylphosphane as the coligand, the conversion was quantitative and the diastereoselectivity improved to 88:12. However, the best result was obtained with triphenylphosphite – a stronger π acceptor – as the coligand. A quantitative conversion combined with the highest

diastereomer ratio of 92:8 was found. The steric demand of the phosphite π acceptor coligand was then varied. It was found that both a smaller phosphite, such as triethylphosphite, as well as the extremely bulky tris(2,6-di-*tert*-butyl) phosphite[21] gave inferior results, with regard to both reactivity and diastereoselectivity (entries 4 and 5). Subsequently, a coligand with an extremely strong π acceptor ability, the tris(1-pyrrolyl)phosphane, was evaluated. Although reactivity was satisfactory, the observed diastereoselectivity (81:19) was inadequate.

Table 1. Influence of a coligand on conversion and diastereoselectivity for rhodium-catalyzed hydroformylation of the methallylic *o*-DPPB ester **9a**

Entry[a]	Ligand	X[b]	θ[c]	Conversion[d]	dr[d] **10a** *syn/anti*
1				35	81:19
2	PPh_3	12.8	145	quant.	88:12
3	$P(OPh)_3$	29.2	128	quant.	92:8
4	P[O-(2,6-di-*tert*-butyl-phenyl)]$_3$	28.5	180	70	80:20
5	$P(OEt)_3$	23.4	109	62	86:14
6	P(*N*-pyrrolyl)$_3$	36	145	quant.	81:19

[a] All hydroformylation reactions were performed in a 100 ml stainless-steel autoclave at 90°C and 20 bar of CO/H_2 (1:1) for 24 h; all reactions were carried out on a 0.5−mmol scale for **9a** with 0.7 mol-% of $Rh(CO)_2(acac)$ in 5 ml of toluene; ligand/rhodium ratio = 4. − [b] Electronic Tolman parameter describes the π-acceptor ability of a ligand[22]. − [c] Tolman cone angle[22]. − [d] Determined by NMR spectroscopy of the crude reaction mixture.

Table 2. Influence of the reaction temperature on conversion and diastereoselectivity of hydroformylation of **9a** with $Rh(CO)_2acac/P(OPh)_3$ (1:4) as the catalyst

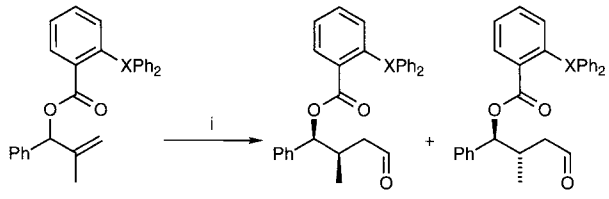
Entry[a]	T [C]	Conversion[b]	dr[b] **10a** *syn/anti*
1	110	quant.	87:13
2	90	quant.	92:8
3	70	80	91:9
4	50	70	87:13

[a] All hydroformylation reactions were performed in a 100 ml stainless-steel autoclave at 20 bar of CO/H_2 (1:1) for 24 h at the indicated temperature; all reactions were carried out on a 0.5-mmol scale for **9a** with 0.7 mol-% of $Rh(CO)_2acac/P(OPh)_3$ (1:4) in 5 ml of toluene. − [b] Determined by NMR spectroscopy of the crude reaction mixture.

A next step on the way to optimized reaction conditions was the optimization of the reaction temperature with respect to the diastereoselectivity of the hydroformylation reaction of derivative **9a** (see Table 2). Thus, 90°C was found to be the optimal reaction temperature with regard to both conversion (quantitative) as well as diastereoselectivity (92:8, see Table 2, entry 2).

Probing the Role of *o*-DPPB as a Catalyst-Directing Group

Although the *o*-DPPB group is an intrinsically good coordinating functionality, that this role is responsible for the observed diastereoselectivity in hydroformylation of methallylic *o*-DPPB ester **9a** had yet to be proven. To gain further mechanistic insight into the mode of action of the *o*-DPPB group, derivative **11** was prepared. Compound **11** possesses an *ortho*-diphenylmethyl-substituted benzoate substituent, which differs from the *o*-DPPB group only in that the phosphane unit is absent. Accordingly, this benzoate substituent does not have the ability to temporarily coordinate to the catalytically active transition metal center, but both benzoate groups should have almost the same steric demand. Thus, if only steric factors are responsible for the observed diastereoselectivity with the *o*-DPPB group, then at least some degree of diastereoselectivity should also be detected on hydroformylation of derivative **11**.



		TOF [h^{-1}]				
X = P:	**9a**	21	*syn*-**10a**	92	: 8	*anti*-**10a**
X = CH:	**11**	1.4	*syn*-**12**	50	: 50	*anti*-**12**

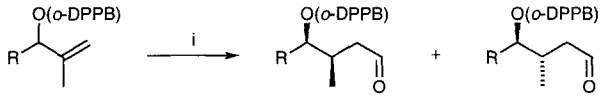
Reagents and Conditions: i, 0.7 mol% $Rh(CO)acac/4P(OPh)_3$, 20 bar H_2/CO (1 : 1), toluene (0.1 M), 90°C, 2h.

To examine this question, the two compounds were subjected to identical hydroformylation conditions. While **9a** reacted to give **10a** (*syn/anti* = 92:8), **11** afforded a mixture of *syn*-**12** and *anti*-**12** in a ratio of 1:1, i.e. *with no diastereoselectivity*. Determination of turnover frequencies of the two reactions showed the reaction with the phosphane-containing substrate **9a** to be 15 times faster than that with derivative **11**. A similar rate enhancement due to a reagent-coordinating hydroxy substituent was reported by Winstein in 1961 in the case of a hydroxy-directed Simmons-Smith reaction[23]. Both of these observations, i.e. the dramatic differences in diastereoselectivity as well as the significant differences in rate, strongly support the hypothesis that the *o*-DPPB group functions as a catalyst-directing group by reversibly coordinating to the catalyst. A second conclusion that can be drawn from the results of these experiments is that the sole presence of a sterically demanding substituent is not adequate to achieve useful levels of diasteroselectivity in the hydroformylation of methallylic alcohol derivatives.

Limit and Scope

To explore limit and scope of this substrate-directed diastereoselective hydroformylation reaction, investigations were made concerning the influence of the nature of the substituent R at the stereogenic center of the methallylic alcohol derivatives **9** (see Table 3). Hydroformylation proceeded smoothly in all cases to afford good to quantitative yields of the corresponding *syn*-aldehydes **10** as the major

products. The highest diastereoselectivities were obtained with branched substituents at the α position, these being attached either via an sp^2- or an sp^3-hybridized carbon atom. In these cases, diastereomer ratios between 90:10 and 96:4 (entries 1–7) were obtained. Even a carboxylic ester function as well as a furan heterocycle were tolerated (entries 5 and 6). Diastereoselectivities were somewhat lower when the α substituent was a primary alkyl group (entry 8) or a benzyl substituent (entry 9). Evidently, this α substituent must exert a certain steric demand for effective differentiation of the two diastereotopic faces of the olefin.



9 *syn*-**10** *anti*-**10**

Reagents and conditions: i, 0.7 mol% $Rh(CO)_2acac/4P(OPh)_3$, 20 bar H_2/CO (1 : 1), toluene, 90°C, 24h.

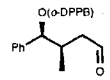
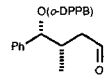
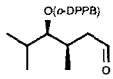
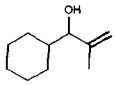
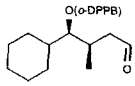
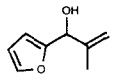
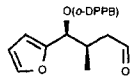
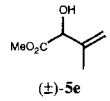
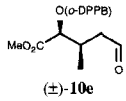
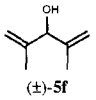
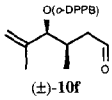
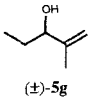
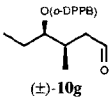
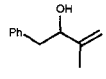
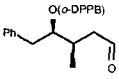
To demonstrate that these reaction conditions are compatible with enantiomerically pure building blocks, the methallylic alcohol (+)-**5a** was prepared by kinetic resolution of (±)-**5a** via asymmetric epoxidation[24]. Enantiomeric purity was checked by diastereomeric derivatization forming the Mosher ester (ee ≥ 95%). Hydroformylation of the corresponding *o*-DPPB ester furnished the *syn*-(+)-aldehyde **10a** in a diastereomer ratio of 92:8 (entry 2), i.e. exactly the same ratio as had been obtained in the racemic case (entry 1). To ensure that the hydroformylation reaction proceeded without racemization, the cyclic acetal (+)-**14** was prepared from the enantiomerically pure, C_2-symmetrical diol (*R,R*)-**13**.

Removal of the Catalyst-Directing *o*-DPPB Group

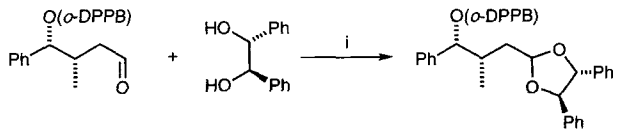
After having performed its function, a useful catalyst-directing group should be readily removable from the substrate. In practice, this may be accomplished by means of alkaline hydrolysis. This process was evaluated using **10a** as a model substrate, by treatment with potassium hydroxide in THF/methanol/water. As a result, both the lactols *syn*-**6** as well as the (phosphanyl)carboxylic acid were recovered in quantitative yields. Oxidation of the lactols **6** furnished the known lactone *syn*-**7** in a diastereomer ratio of 92:8. Hence, the overall process of catalyst-directing group removal occurs without loss of stereochemical information.

In conclusion, the introduction of a catalyst-directing group based on the concept of a reversible catalyst coordination has proved to be effective in the development of a substrate-directed, diastereoselective, rhodium-catalyzed hydroformylation of acyclic methallylic alcohols. This homogeneously-catalyzed carbon–carbon bond-forming reaction provides stereoselective access to acyclic building blocks with two adjacent stereocenters, enantiomerically pure if desired, by introducing the synthetically useful aldehyde functionality in a one-carbon extension of the carbon framework. Subsequent transformation to the corresponding γ-lactones was readily achieved.

Table 3. Results of diastereoselective hydroformylation of acyclic methallylic alcohol *o*-DPPB ester (**9** → **10**)

Entry	Alcohol **5**	Major diastereomer **10** [a]	Yield **10** [%] [b]	dr (*syn*/*anti*) [c]
1	 (±)-**5a**	 (±)-**10a**	99	92 : 8
2	 (+)-**5a**	 (+)-**10a**	98	92 : 8
3	 (±)-**5b**	 (±)-**10b**	97	96 : 4
4	 (±)-**5c**	 (±)-**10c**	81	95 : 5
5	 (±)-**5d**	 (±)-**10d**	63[d]	93 : 7
6	 (±)-**5e**	 (±)-**10e**	80	90 : 10
7	 (±)-**5f**	 (±)-**10f**	90 [e]	96 : 4
8	 (±)-**5g**	 (±)-**10g**	83	73 : 27
9	 (±)-**5h**	 (±)-**10h**	75	80 : 20

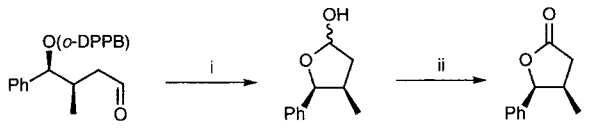
[a] Hydroformylations of the corresponding *o*-DPPB esters **9** were performed under identical reaction conditions according to the General Procedure described in the Experimental Section. – [b] After column chromatographic work-up. – [c] Determined from ^{1}H-NMR spectra of the crude product. – [d] Hydroformylation performed at 70°C. – [e] At 40% conversion.



(+)-*syn*-**10a** (92 : 8) (ee≥ 95%) *(R,R)*-**13** (+)-**14** (92 : 8)

Reagents and conditions: i, TsOH(cat.), $MgSO_4$, toluene, 110°C, 1 h (99%).

This work was supported by the *Fonds der Chemischen Industrie* (Liebig fellowship for B. B.), the *Otto Röhm Gedächtnisstiftung*, and by the *Deutsche Forschungsgemeinschaft* (SFB 260). The author thanks Prof. *R. W. Hoffmann* for his generous support, the com-



(±)-*syn*-**10a** (92 : 8) *syn*-**6** *syn*-**7** (92 : 8)

Reagents and conditions: i, THF/MeOH/H_2O (2 : 2 : 1), KOH, 50°C, 2.5 h (99%); ii, 2eq pyridinium chloro chromate (PCC) on Al_2O_3, 25°C, 16 h (95%).

panies *BASF* and *Degussa* for their gifts of chemicals, and *M. Dauber* for his skillful experimental assistance.

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 not corrected. – ^{1}H-, ^{13}C-NMR spectra: Bruker ARX-200, Bruker AC-300, Bruker WH-400, 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: Melting point apparatus by Dr. Tottoli (Büchi). – Optical rotations: Perkin-Elmer 241. – Mass spectra: MAT CH7A, MAT 711. – Elemental analyses: CHN-rapid analyzer (Heraeus). – Flash chromatography: Silica gel Si 60, 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). – Compounds (±)-**5a**[25], (±)-**5b**[26], (±)**5c**[26], (±)-**5e**[26], (±)-**5f**[27], (±)-**5g**[26], (±)-**5h**[28], **8**[19] and (*R,R*)-**13**[29] were prepared by published methods.

1-Furanyl-2-methylprop-2-en-1-ol [(±)-**5d**]: To a solution of 10 ml (19 mmol) of a 1.9 M solution of *n*BuLi in hexane in 125 ml of THF, 6.3 g (92.53 mmol) of furan was added dropwise at –15°C. After stirring for 5 h at –15°C, the solution was cooled to –78°C and 1.33 g (19 mmol) of methacrolein was added dropwise. The solution was allowed to warm to room temp. over a period of 12 h, and was subsequently quenched by the addition of 5 ml of water. THF was replaced by 200 ml of *tert*-butyl methyl ether and 100 ml of water was added. The ethereal phase was separated and the aqueous phase was extracted with two further 50 ml portions of *tert*-butyl methyl ether. 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 ethyl ether (5:1) to give 2.6 g (99%) of (±)-**5d** as a yellow oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 3H, CH_3), 2.64 (s, br, 1H, OH), 4.93 (m, 1H, OCH), 5.04 (s, 1H, =CH_2), 5.1 (s, 1H, =CH_2), 6.18 (d, *J* = 3.2 Hz, 1, furyl-H), 6.26 (m, 1H, furyl-H), 7.29 (m, 1H, furyl-H). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.4, 71.27, 106.71, 110.09, 111.87, 141.97, 144.29, 154.82. – $C_8H_{10}O_2$ (138.2): calcd. C 69.55, H 7.29; found C 69.50, H 7.29.

*Kinetic Resolution of Alcohol (±)-***5a**. – *(R)-(+)-2-Methyl-1-phenylprop-2-en-1-ol* [(±)-**5a**]: To a solution of 7.39 g (31.55 mmol) of D-(–)-diisopropyl tartrate in 150 ml of CH_2Cl_2 at –25°C, 7.223 g (25.4 mmol) of titanium tetraisopropoxide was added and the mixture was stirred for 15 min at –25°C. Subsequently, 3.167 g (21.37 mmol) of the methallylic alcohol (±)-**5a** was added, stirring was continued at –25°C for a further 15 min, and then 9.2 ml (64.4 mmol) of a 7 M solution of *tert*-butyl hydroperoxide in CH_2Cl_2 was added dropwise. After storing the reaction mixture for 3 d at –30°C, it was poured at –20°C into a cooled solution of 7.5 ml water in 250 ml of acetone and allowed to warm to room temp. The mixture was filtered, the solvent was removed in vacuo and the residue was dissolved in 150 ml of diethyl ether. After cooling to 0°C, 60 ml of a 1 N NaOH solution was added and the mixture was stirred at this temp. for 30 min. The organic phase was then separated, washed with brine, dried (Na_2SO_4), and the ether was removed in vacuo. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (9:1) furnished 377 mg (12%) of (+)-**5a** as a colorless oil. Enantiomeric purity (>95% ee) was determined by formation of the Mosher ester (see below). – $[\alpha]_D$ = +19.3 (*c* = 3.3, CH_2Cl_2). – IR (neat): $\tilde{\nu}$ = 3380 cm^{-1} (OH), 1660 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 3H, CH_3), 2.14 (s, br, 1H, OH), 4.93 (s, br, 1H, OCH), 5.09 (s, 1H, =CH_2), 5.17 (d, *J* = 0.64 Hz, 1H, =CH_2), 7.22–7.3 (m, 5H, Ph). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.1, 77.8, 111.1, 126.4, 127.5, 128.2, 141, 146. – MS (70 eV); *m/z* (%): 148 (89.6) [M^+], 133 (80.29) [$M^+ - CH_3$], 105 (93.1) [C_6H_5CO], 77 (100) [C_6H_5]. – $C_{10}H_{12}O$ (148.2): calcd. C 81.04, H 8.16; found C 81.23, H 7.96.

(S)-(+)-(R)-2-Methyl-1-phenylprop-2-enyl α-Methoxy-α-(trifluoromethyl)phenylacetate [Mosher ester of (+)-**5a**]: To a solution of 28 mg (0.189 mmol) of methallylic alcohol (+)-**5a** in 1 ml CH_2Cl_2/0.5 ml pyridine, 48 mg (0.189 mmol) of (*S*)-(+)-Mosher acid chloride was added and the mixture was stirred for 18 h at room temp. The solvent was then evaporated and the residue was filtered through a plug of silica gel with 50 ml *tert*-butyl methyl ether. The solvent was removed in vacuo to give 64 mg (93%) of the Mosher ester as a colorless oil. NMR analysis showed the presence of only one diastereomer. – $[\alpha]_D$ = + 18.6 (*c* = 2.65, CH_2Cl_2). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 3H, CH_3), 3.43 (s, 3H, OCH_3), 4.91 (m, 1H, =CH_2), 4.99 (d, *J* = 0.95 Hz, 1H, =CH_2), 6.35 (s, br, 1H, OCH), 7.26–7.32 (m, 10H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.43, 55.29, 80.35, 86.5 (m), 113.56, 123.1 (q, *J* = 357 Hz, CF_3), 127.19, 127.27, 128.15, 128.22, 128.31, 129.38, 134.47, 137.13, 141.69, 165.55. – MS (70 eV), *m/z* (%): 364 (2.6) [M^+], 189 (60) [$(F_3C)(OMe)CPh$], 131 (100) [$PhCHC(CH_3)CH_2$], 77 (100). – $C_{20}H_{19}O_3F_3$: calcd. 364.1286; found 364.1267 (HRMS).

tert-Butyldimethylsilyl-(1RS)-(±)-1-Ethyl-2-methylprop-2-enyl Ether (**3**): To a magnetically stirred solution of 1.002 g (10 mmol) of methallylic alcohol **5g** and 183 mg (1.5 mmol) of 4-(dimethylamino)pyridine in 10 ml CH_2Cl_2/3.5 ml triethylamine, 4.52 g of a 50% solution of *tert*-butyldimethylsilyl chloride in toluene was added at room temp. After stirring for 4 d, the reaction mixture was diluted with 50 ml CH_2Cl_2, and then washed successively with 20 ml of satd. aq. $NaHSO_4$ solution and 20 ml of satd. aq. $NaHCO_3$ solution. The organic phase was dried (Na_2SO_4), the solvent was evaporated and the residue was purified by flash chromatography with petroleum ether to give 1.367 g (64%) of **3** as a colorless oil. – IR (neat): $\tilde{\nu}$ = 3073 cm^{-1} (w), 2959 (s), 2932 (s), 2885 (m), 2858 (s), 1652 (w), 1472 (m), 1463 (m), 1256 (s), 1067 (s), 1018 (m), 864 (s), 836 (s), 775 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.33, 0.0 [each s, each 3H, $Si(CH_3)_2$], 0.79 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 0.83 [s, 9H, $C(CH_3)_3$], 1.45 (m, 2H, $CHCH_2CH_3$), 1.61 (pseudo t, *J* = 1.1, 0.9 Hz, 3H, =C–CH_3), 3.89 (t, *J* = 6.3 Hz, 1H, OCH), 4.71 (m, 1H, =CH_2), 4.8 (m, 1H, =CH_2). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = –5.17, –4.91, 9.72, 17.0, 18.13, 25.72, 28.85, 77.93, 110.36, 147.53. – $C_{12}H_{26}OSi$ (214.4): calcd. C 67.16, H 12.22; found C 66.86, H 12.15.

(3R,4R*/3R*,4S*)-4-(tert-Butyldimethylsiloxy)-3-methylhexan-1-al* (**4**): To a solution of 1.8 mg (7.1×10^{-3} mmol) of $[Rh(CO)_2(acac)]$ in 2 ml of toluene at 20°C (exclusion of air and

moisture), 8.8 mg (2.84×10^{-2} mmol) of $P(OPh)_3$ was added and the mixture was stirred for 15 min at 20°C. Subsequently, 214 mg (1 mmol) of **3** was added and the resulting solution was cannulated into a stainless-steel autoclave, which had been evacuated and refilled with argon several times. The flask and the cannula were rinsed with an additional 1 ml of toluene. The autoclave was heated to 80°C, then pessurized successively with carbon monoxide (10 bar) and hydrogen (10 bar) and the reaction solution was stirred under these conditions for 48 h. Subsequently, the autoclave was cooled rapidly to 20°C and depressurized, and the contents were filtered through a small plug of silica gel with *tert*-butyl methyl ether (30 ml). After evaporation of the solvent in vacuo, the crude product was analyzed by NMR to determine the conversion (37%) and the diastereomer ratio (1:1). Subsequent flash chromatography with petroleum ether/*tert*-butyl methyl ether (19:1) furnished 127 mg of starting material **3** and 85 mg (35%) of **4** as a colorless oil. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1} (s), 2932 (s), 2710 (w), 1710 (s), 1256 (m), 1089 (m), 860 (m), 837 (m), 774 (m). – ^1H NMR (300 MHz, $CDCl_3$): δ = −0.01, 0.0 [each s, each 3H, $Si(CH_3)_2$], 0.8−0.92 (m, 6H, 2 CH_3), 0.84 [s, 9H, $C(CH_3)_3$], 1.27−1.46 (m, 2H, CH_2CH_3), 2.14−2.2 [m, 2H, $CHO(CH_2)$], 2.48 (m, 1H, $CHCH_3$), 3.39−3.45 (m, 1H, OCH), 9.71 (m, 1H, CHO). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = −4.3, −4.37, −4.5, −4.62, 9.13, 10.43, 14.76, 16.81, 18.06, 25.63, 25.83, 26.51, 32.2, 32.83, 46.42, 47.02, 76.86, 76.62, 202.71, 208.87. – $C_{13}H_{28}O_2Si$ (244.4): calcd. C 63.88, H 11.54; found C 63.65, H 11.30.

General Procedure for the Hydroformylation of (RS)-(±)-2-Methyl-1-phenylprop-2-en-1-ol [(±)-**5a**]. – *Synthesis of (2RS,4R*,5R*)- and (2RS,4R*,5S*)-2-Hydroxy-4-methyl-5-phenyloxolane* (**6**): To a solution of 2 mg (7.7×10^{-3} mmol) of $[Rh(CO)_2(acac)]$ in 2 ml of toluene at 20°C (exclusion of air and moisture), 40.5 mg (1.55×10^{-1} mmol) of PPh_3 was added and the mixture was stirred for 15 min at 20°C. Subsequently, 322 mg (2.17 mmol) of (±)-**5a** was added and the resulting solution was cannulated into a stainless-steel autoclave, which had been evacuated and refilled with argon several times. The flask and the cannula were rinsed with an additional 1 ml of toluene. The autoclave was heated to 90°C, then pressurized successively with carbon monoxide (10 bar) and hydrogen (10 bar), and the reaction solution was stirred under these conditions for 6 h. Subsequently, the autoclave was cooled rapidly to 20°C and depressurized. The solvent was evaporated and the residue was purified by flash chromatography with petroleum ether/*tert*-butyl methyl ether to give 321 mg (83%) of the known lactols **6**[30] as a colorless oil, which was used directly in the subsequent oxidation step. Spectroscopic data were identical to those reported in the literature.

Lactones, PCC Oxidation. – cis- and trans-β-Methyl-γ-phenyl-γ-lactones (**7**): To a solution of 321 mg (1.8 mmol) of lactols **6** in 5 ml of CH_2Cl_2, 3.6 g of PCC on Al_2O_3 (1 mmol/g) was added and the suspension was stirred for 16 h at room temp. The reaction mixture was then filtered through silica gel with an additional 50 ml of CH_2Cl_2, the solvent was evaporated and the residual product was analyzed by NMR to determine the diastereomer ratio [50:50 (*anti*/*syn*)]. Yield of lactones after purification by flash chromatography with petroleum ether/*tert*-butyl methyl ether (4:1) 301 mg (95%). Spectroscopic and analytical data correspond to those reported previously[15].

Run 2: 9.6 mg (0.0308 mmol) of $P(OPh)_3$, reaction time for hydroformylation 24 h, 90°C; yield of lactols **6** 367 mg (95%); diastereomer ratio of lactones **7**: 55:45 (*anti*/*syn*).

Run 3: 7.1 mg (0.031 mmol) of tris(pyrrolyl)phosphane, reaction time for hydroformylation 24 h; yield of lactols **6** 320 mg (83%); diastereomer ratio of lactones **7**: 66:33 (*anti*/*syn*).

General Procedure for Synthesis of o-DPPB Esters: To a solution of 1 equiv. of methallylic alcohol in CH_2Cl_2 (0.5 M), 1 equiv. of *o*-DPPBA **8**, 0.1 equiv. of DMAP and 1.1 equiv. of DCC were successively added and the resulting mixture was stirred at room temp. until TLC analysis indicated complete consumption of the starting material. Subsequently, the reaction mixture was 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 **9**, usually as slightly yellow to colorless, highly viscous oils.

(1RS)-(±)-2-Methyl-1-phenylprop-2-enyl 2-(Diphenylphosphanyl)benzoate [(±)-**9a**]: From 445 mg (3 mmol) of methallylic alcohol (±)-**5a**, 1.3 g (97%) of (±)-**9a** was obtained as a pale-yellow, viscous oil. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.64 (s, 3H, $=C-CH_3$), 4.94 (s, 1H, $=CH_2$), 5.1 (s, 1H, $=CH_2$), 6.28 (s, 1H, OCH), 6.94 (m, 1H, ArH), 7.21−7.38 (m, 17H, ArH), 8.16 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.92, 79.0, 112.9, 127.17, 127.85, 128.16, 128.25, 128.34 (d, $J_{C,P}$ = 7.0 Hz), 128.38 (d, $J_{C,P}$ = 7.0 Hz), 128.48, 130.58 (d, $J_{C,P}$ = 2.5 Hz), 131.92, 133.84 (d, $J_{C,P}$ = 20.7 Hz), 133.92 (d, $J_{C,P}$ = 20.7 Hz), 134.3 (d, $J_{C,P}$ = 18 Hz), 134.39, 137.96 (d, $J_{C,P}$ = 12.0 Hz), 138.02 (d, $J_{C,P}$ = 11.8 Hz), 138.3, 140.91 (d, $J_{C,P}$ = 27.8 Hz), 142.88, 165.3. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = −4.3. – $C_{29}H_{25}O_2P$ (436.5): calcd. C 79.80, H 5.77; found C 79.75, H 5.95.

(1R)-(+)-2-Methyl-1-phenylprop-2-enyl 2-(Diphenylphosphanyl)-benzoate [(+)-**9a**]: From 247 mg (2.16 mmol) of methallylic alcohol (+)-**5a**, 669 mg (71%) of (+)-**9a** was obtained as a pale-yellow, viscous oil. – $[\alpha]_D$ = +45.3 (*c* = 6.8, CH_2Cl_2). Analytical and spectroscopic data were identical to those for (±)-**9a**.

(1RS)-(±)-1-Isopropyl-2-methylprop-2-enyl 2-(Diphenylphosphanyl)benzoate (**9b**): From 1.14 g (10 mmol) of methallylic alcohol **5b**, 3.02 g (75%) of **9b** was obtained as colorless crystals, m.p. 98−99°C. – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.9 [d, *J* = 6.8 Hz, 3H, $CH(CH_3)_2$], 0.94 [d, *J* = 6.6 Hz, 3H, $CH(CH_3)_2$], 1.74 (s, 3H, CH_3), 2.0 [pseudo sext, *J* = 6.8 Hz, $CH(CH_3)_2$], 4.92 (s, 1H, $=CH_2$), 4.99 (s, 1H, $=CH_2$), 5.18 (d, *J* = 7.5 Hz, 1H, OCH), 7.0 (m, 1H, ArH), 7.32−7.42 (m, 12H, ArH), 8.2 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.05, 18.52, 19.03, 29.87, 83.06, 114.08, 128.17, 128.39 (d, $J_{C,P}$ = 7.1 Hz), 128.48 (d, $J_{C,P}$ = 1.5 Hz), 130.43 (d, $J_{C,P}$ = 2.3 Hz), 131.77, 133.84 (d, $J_{C,P}$ = 20.7 Hz), 133.97 (d, $J_{C,P}$ = 20.8 Hz), 134.34, 134.73 (d, $J_{C,P}$ = 18.9 Hz), 138.14 (d, $J_{C,P}$ = 12.5 Hz), 138.26 (d, $J_{C,P}$ = 11.9 Hz), 140.75 (d, $J_{C,P}$ = 27.9 Hz), 141.9, 165.78. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = −4.3. – $C_{26}H_{27}O_2P$ (402.5): calcd. C 77.59, H 6.76; found C 77.32, H 6.80.

(1RS)-(±)-1-Cyclohexyl 2-methylprop-2-enyl 2-(Diphenylphosphanyl)benzoate (**9c**): From 463 mg (3 mmol) of methallylic alcohol **5c**, 969 mg (73%) of **9c** was obtained as a colorless, viscous oil. – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.8−1.2 (m, 5H, cyclohexyl-H), 1.5−1.85 (m, 6H, cyclohexyl-H), 1.81 (s, 3H, Me), 4.89 (pseudo t, *J* = 1.5 Hz, 1H, $=CH_2$), 4.93 (s, 1H, $=CH_2$), 5.14 (d, *J* = 7.8 Hz, 1H, OCH), 6.94 (m, 1H, ArH), 7.27−7.46 (m, 12H, ArH), 8.2 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.24, 25.73, 25.89, 26.13, 28.34, 29.07, 39.03, 82.39, 114.24, 127.96, 128.32 (d, $J_{C,P}$ = 7.0 Hz), 128.28, 130.28, 131.54, 133.75 (d, $J_{C,P}$ = 20.5 Hz), 133.85 (d, $J_{C,P}$ = 20.7 Hz), 134.19, 135.02 (d, $J_{C,P}$ = 18.9 Hz), 138.29 (d, $J_{C,P}$ = 11.8 Hz), 138.44 (d, $J_{C,P}$ = 11.8 Hz), 140.74 (d, $J_{C,P}$ = 27.6 Hz), 141.5, 166.02. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = −4.4. – $C_{29}H_{31}O_2P$ (442.5): calcd. C 78.71, H 7.06; found C 78.72, H 7.05.

(1RS)-(±)-1-(2-Furyl)-2-methylprop-2-enyl 2-(Diphenylphosphanyl)benzoate (**9d**): From 1.38 g (10 mmol) of methallylic alcohol **5d**, 2.838 g (67%) of **9d** was obtained as a yellow, viscous oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (s, 3H, =C–CH_3), 4.98 (s, 1H, =CH_2), 5.1 (s, 1H, =CH_2), 6.17 (m, 2H, OCH and furyl-H), 6.28 (m, 1H, furyl-H), 6.94 (m, 1H, ArH), 7.22–7.38 (m, 12H, ArH), 7.33 (s, 1H, furyl-H), 8.13 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 19.21, 72.04, 109.27, 110.09, 113.34, 128.16, 128.35 (d, J = 7.1 Hz), 128.48, 130.73 (d, J = 2.3 Hz), 131.08, 133.82 (d, J = 20.7 Hz), 133.88 (d, J = 20.5 Hz), 133.94 (d, J = 18.6 Hz), 134.33, 137.91 (d, J = 11.7 Hz), 137.97 (d, J = 12.1 Hz), 140.5, 141.0 (d, J = 28.1 Hz), 142.67, 151.04, 165.08 (d, J = 2.3 Hz). – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –3.9. – $C_{27}H_{23}O_3P$ (426.5)[31].

Methyl (RS)-(±)-2-[2-(Diphenylphosphanyl)benzoyloxy]-3-methylbut-3-enoate (**9e**): From 651 mg (5 mmol) of methallylic alcohol **5e**, 1.82 g (87%) of **9e** was obtained as a pale-yellow, viscous oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (s, 3H, =C–CH_3), 3.64 (s, 3H, OCH_3), 5.06 (pseudo t, J = 1.2 Hz, 1H, =CH_2), 5.16 (s, 1H, OCH), 6.92 (m, 1H, ArH), 7.21–7.39 (m, 12H, ArH), 8.16 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.64, 26.96, 49.38, 76.36, 117.27, 128.25, 128.38 (d, $J_{C,P}$ = 7.2 Hz), 128.41 (d, $J_{C,P}$ = 7.1 Hz), 128.6, 130.93 (d, $J_{C,P}$ = 2.5 Hz), 132.24, 133.46 (d, $J_{C,P}$ = 18.8 Hz), 133.81 (d, $J_{C,P}$ = 20.5 Hz), 134.01 (d, $J_{C,P}$ = 20.8 Hz), 134.32, 137.68 (d, $J_{C,P}$ = 11.1 Hz), 137.86 (d, $J_{C,P}$ = 12.2 Hz), 137.89, 141.09 (d, $J_{C,P}$ = 28.0 Hz), 165.41 (d, $J_{C,P}$ = 2.0 Hz), 168.66. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.3. – $C_{25}H_{23}O_4P$ (418.4): calcd. C 71.76, H 5.54; found C 71.64, H 5.72.

(1RS)-(±)-2-Methyl-1-(prop-2-enyl)prop-2-enyl 2-(Diphenylphosphanyl)benzoate (**9f**): From 1.12 g (10 mmol) of methallylic alcohol **5f**, 2.77 g (69%) of **9f** was obtained as a colorless, viscous oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73 (s, 6H, 2 CH_3), 4.91 (s, 2H, =CH_2), 5.01 (s, 2H, =CH_2), 5.68 (s, 1H, HCO), 6.93 (m, 1H, ArH), 7.23–7.38 (m, 12H, ArH), 8.12 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.36, 80.44, 113.35, 128.1, 128.28 (d, $J_{C,P}$ = 7.2 Hz), 128.39, 130.32 (d, $J_{C,P}$ = 2.6 Hz), 131.78, 133.81 (d, $J_{C,P}$ = 20.7 Hz), 134.32, 134.43 (d, $J_{C,P}$ = 17.6 Hz), 138.0 (d, $J_{C,P}$ = 12.1 Hz), 140.85 (d, $J_{C,P}$ = 27.5 Hz), 140.99, 164.98. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.6. – $C_{26}H_{25}O_2P$ (400.5): calcd. C 77.98, H 6.29; found C 77.68, H 6.56.

(1RS)-(±)-1-Ethyl-2-methylprop-2-enyl 2-(Diphenylphosphanyl)-benzoate (**9g**): From 1.002 g (10 mmol) of methallylic alcohol **5g**, 2.7 g (70%) of **9g** was obtained as colorless crystals, m.p. 75–80°C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.65 (m, 2H, CH_2CH_3), 1.72 (s, 3H, =CCH_3), 4.9 (pseudo t, J = 1.4 Hz, 1H, =CH_2), 4.98 (s, 1H, =CH_2), 5.32 (pseudo t, J = 6.6 Hz, 1H, OCH), 6.97 (m, 1H, ArH), 7.29–7.44 (m, 12H, ArH), 8.14 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 9.72, 18.32, 25.54, 80.3, 113.33, 128.28, 128.52 (d, $J_{C,P}$ = 7.1 Hz), 128.61, 130.64 (d, $J_{C,P}$ = 2.6 Hz), 131.41, 134.05 (d, $J_{C,P}$ = 20.6 Hz), 134.5, 135.14 (d, $J_{C,P}$ = 19.3 Hz), 138.26 (d, $J_{C,P}$ = 12.0 Hz), 138.35 (d, $J_{C,P}$ = 12.0 Hz), 140.5 (d, $J_{C,P}$ = 27.2 Hz), 142.64, 166.08. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.5. – $C_{25}H_{25}O_2P$ (388.4): calcd. C 77.3, H 6.49; found C 77.35, H 6.38.

(1RS)-(±)-1-Benzyl-2-methylprop-2-enyl 2-(Diphenylphosphanyl)benzoate (**9h**): From 1.62 g (10 mmol) of methallylic alcohol **5h**, 4.489 g (99.6%) of **9h** was obtained as a pale-yellow, viscous oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 3H, =C–CH_3), 2.92 (m, 2H, CH_2Ph), 4.81 (d, J = 1.34 Hz, 1H, =CH_2), 4.84 (s, 1H, =CH_2), 5.54 (pseudo t, J = 6.9 Hz, OCH), 6.92 (m, 1H, ArH), 7.16–7.29 (m, 17H, ArH), 8.0 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 18.63, 39.39, 78.78, 113.89, 126.47, 128.22, 128.25, 128.46 (d, $J_{C,P}$ = 7.2 Hz), 128.61, 129.43, 130.54 (d, $J_{C,P}$ = 2.5 Hz), 131.84, 133.96 (d, $J_{C,P}$ = 20.7 Hz), 134.05 (d, $J_{C,P}$ = 20.8 Hz), 134.39, 134.83 (d, $J_{C,P}$ = 19.2 Hz), 137.25, 138.17 (d, $J_{C,P}$ = 12.3 Hz), 140.54 (d, $J_{C,P}$ = 27.4 Hz), 142.15, 165.79. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.4. – $C_{30}H_{27}O_2P$ (450.5): calcd. C 79.98, H 6.04; found C 80.00, H 6.19.

(1RS)-(±)-2-Methyl-1-phenylprop-2-enyl 2-(Diphenylmethyl)benzoate (**11**): According to the General Procedure described for the preparation of the *o*-DPPB esters **9**, reaction of 296 mg (2 mmol) of methallylic alcohol (±)-**5a**, 577 mg (2 mmol) of 2-(diphenylmethyl)benzoic acid[32], 24 mg (0.2 mmol) of DMAP and 433 mg (2.1 mmol) of DCC in 10 ml of CH_2Cl_2 afforded 683 mg (82%) of **11** as a colorless, viscous oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (s, 3H, =C–CH_3), 4.96 (s, 1H, =CH_2), 5.05 (s, 1H, =CH_2), 6.3 (s, 1H, OCH), 6.68 (s, 1H, $CHPh_2$), 7.04–7.44 (m, 18H, ArH), 7.95 (dd, J = 7.8, 1.5 Hz, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$). δ = 18.72, 51.74, 78.92, 112.88, 126.09, 126.14, 126.96, 127.82, 128.11, 128.28, 129.61, 129.63, 130.29, 130.77, 130.95, 131.36, 138.23, 142.78, 143.63, 143.67, 144.78, 166.43. – $C_{30}H_{26}O_2$ (418.5): calcd. C 86.09, H 6.26; found C 85.96, H 6.35.

Hydroformylation of Methallylic o-DPPB Esters (**9**). – *General Procedure:* To a solution of 0.9 mg of $Rh(CO)_2(acac)$ (3.5×10^{-3} mmol) in 3 ml of toluene at 20°C (exclusion of air and moisture), 4.5 mg (1.4×10^{-2} mmol) of $P(OPh)_3$ was added and the resulting mixture was stirred at this temp. for 15 min. Subsequently, 0.5 mmol of *o*-DPPB ester **9** was added and the resulting solution was cannulated into a stainless-steel autoclave, which had been evacuated and refilled with argon several times. The flask and cannula were rinsed with an additional 2 ml of toluene. The autoclave was heated to 90°C, then pressurized successively with carbon monoxide (10 bar) and hydrogen (10 bar), and the reaction mixture was stirred under these conditions for 24 h. The autoclave was then cooled rapidly to 20°C and the contents were filtered through a small plug of silica gel with 30 ml of *tert*-butyl methyl ether. After evaporation of the solvent in vacuo, the crude product was analyzed by NMR to determine the conversion and diastereomer ratio. Subsequent flash chromatography with petroleum ether/*tert*-butyl methyl ether (9:1) provided the aldehydes **10** as highly viscous oils.

(1R,2S*)-(±)-2-Methyl-4-oxo-1-phenylbutyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10a**): From 218 mg (0.5 mmol) of **9a**, 231 mg (99%) of *syn*-**10a** was obtained. Diastereomer ratio 92:8 (*syn*/*anti*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (d, J = 6.8 Hz, 3H, CH_3), 2.12 (ddd, J = 17.1, 8.6, 1.8 Hz, 1H, CH_2CHO), 2.39 (dd, J = 17.1, 4.6 Hz, 1H, CH_2CHO), 2.63 (m, 1H, $CHCH_3$), 5.9 (d, J = 6.0 Hz, 1H, HCO), 6.96 (m, 1H, ArH), 7.25–7.5 (m, 17H, ArH), 8.15 (m, 1H, ArH), 9.57 (s, 1H, CHO-*syn*), [9.65 (s, 1H, CHO-*anti*)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 15.78, 33.67, 47.06, 79.5, 127.01, 127.99, 128.36, 128.4, 128.5 (d, $J_{C,P}$ = 7.1 Hz), 128.52 (d, $J_{C,P}$ = 7.0 Hz), 128.66, 130.71 (d, $J_{C,P}$ = 2.3 Hz), 133.13, 133.93 (d, $J_{C,P}$ = 20.6 Hz), 134.03 (d, $J_{C,P}$ = 20.8 Hz), 134.19 (d, $J_{C,P}$ = 18.9 Hz), 134.53, 137.68 (d, $J_{C,P}$ = 12.6 Hz), 138.09 (d, $J_{C,P}$ = 13.8 Hz), 138.25, 140.69 (d, $J_{C,P}$ = 27.6 Hz), 201.04 (CHO-*syn*), [201.5 (CHO-*anti*)]. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.2 [–4.4]. – $C_{30}H_{27}O_3P$ (466.5): calcd. C 77.24, H 5.83; found C 77.18, H 5.93.

(1R,2S)-(+)-2-Methyl-4-oxo-1-phenylbutyl 2-(Diphenylphosphanyl)benzoate [(+)-*syn*-**10a**]: From 218 mg (0.5 mmol) of (+)-**9a**, 228 mg (98%) of (+)-*syn*-**10a** was obtained. Diastereomer ratio 92:8 (*syn*/*anti*). – $[\alpha]_D$ = +43.3 (*c* = 3.75, CH_2Cl_2). Analytical and specctroscopic data were identical to those reported for (±)-**10a**.

(4R,5R,3'R,2'S)-(+)-1-{3'-[2-(Diphenylphosphanyl)benzoyl]-2'-methyl-3'-phenylpropyl}-4,5-diphenyl-1,3-dioxolane [(+)-**14**]: To a solution of 75 mg (0.16 mmol) of (+)-*syn*-**10a** in 3 ml of toluene were added 34.3 mg (0.16 mmol) of (*R,R*)-**13**, 50 mg of $MgSO_4$ and a small crystal of *p*-toluenesulfonic acid. The mixture was heated to reflux for 1 h, cooled to room temp., the solvent was evaporated and the residue was filtered through basic alumina with 20 ml of *tert*-butyl methyl ether. After evaporation of the solvent, 106 mg (99%) of (+)-**14** was obtained as a colorless glass. – $[\alpha]_D$ = +27.9 (*c* = 5.7, CH_2Cl_2). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 6.7 Hz, 3H, CH_3), 1.71 (m, 1H, CH_2CHO), 2.0 (d pseudo t, *J* = 13.9, 5.0 Hz, 1H, CH_2CHO), 2.5 (m, 1H, C*H*CH_3), 4.71 (AB system, *J* = 7.8 Hz, 2H, 2 × OCHPh), 5.51 (t, *J* = 5.2 Hz, 1H, OCHO), 6.0 (d, *J* = 6.2 Hz, 1H, HCO), 6.98 (m, 1H, ArH), 7.2–7.48 (m, 27H, ArH), 8.23 (m, 1H, ArH). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 15.8, 34.96, 37.88, 80.18, 84.83, 86.68, 104.48, 126.32–141.1 (all aryl–C), 165.79 (d, $J_{C,P}$ = 2.4 Hz). – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.2. – $C_{44}H_{39}O_4P$ (662.8): calcd. C 79.74, H 5.93; found C 79.97, H 6.11.

(1R,2R*)-(±)-1-Isopropyl-4-oxo-2-methylbutyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10b**): From 201 mg (0.5 mmol) of **9b**, 210 mg (97%) of *syn*-**10b** was obtained. Diastereomer ratio 96:4 (*syn/anti*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (d, *J* = 6.6 Hz, 3H, CH_3), 0.97 [d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$], 0.98 [d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$], 1.94 [m, 1H, C*H*(CH$_3$)$_2$], 2.11 (ddd, *J* = 17.6, 8.3, 1.8 Hz, 1H, CH_2CHO), 2.30 (dd, *J* = 17.6, 5.3 Hz, 1H, CH_2CHO), 2.52 (m, 1H, H at C2), 4.87 (dd, *J* = 8.9, 3.3 Hz, 1H, OCH), 7.02 (m, 1H, ArH), 7.22–7.47 (m, 12H, ArH), 8.2 (m, 1H, ArH), 9.57 (d, *J* = 0.7 Hz, 1H, CHO-*syn*), [9.68 (CHO-*anti*)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 13.69, 19.15, 29.09, 29.83, 48.33, 82.07, 125.47, 128.62 (d, $J_{C,P}$ = 2.1 Hz), 128.81 (d, $J_{C,P}$ = 7.3 Hz), 130.72 (d, $J_{C,P}$ = 1.7 Hz), 132.23, 133.85 (d, $J_{C,P}$ = 18 Hz), 134.08 (d, $J_{C,P}$ = 20.8 Hz), 134.28, (d, $J_{C,P}$ = 21.1 Hz), 134.41, 138.04 (d, $J_{C,P}$ = 13.6 Hz), 138.48 (d, $J_{C,P}$ = 11.3 Hz), 141.54 (d, $J_{C,P}$ = 28.2 Hz), 166.62, 201.47 (CHO-*syn*), [202.03 (CHO-*anti*)]. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –3.1. – $C_{27}H_{29}O_3P$ (432.5): calcd. C 74.98, H 6.76; found C 74.91, H 6.90.

(1R,2S*)-(±)-1-Cyclohexyl-2-methyl-4-oxobutyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10c**): From 221 mg (0.5 mmol) of **9c**, 191 mg (81%) of *syn*-**10c** was obtained. Diastereomer ratio 95:5 (*syn/anti*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67–1.3 (m, 5H, cyclohexyl-H), 0.86 (d, *J* = 6.8 Hz, 3H, CH_3), 1.5–1.7 (m, 6H, cyclohexyl-H), 1.89 (ddd, *J* = 17.6, 8.1, 1.7 Hz, 1H, CH_2CHO), 2.2 (dd, *J* = 17.6, 5.4 Hz, 1H, CH_2CHO), 2.43 (m, 1H, C*H*CH_3), 4.8 (dd, *J* = 8.6 Hz, 2.8 Hz, 1H, HCO), 6.88 (m, 1H, ArH), 7.24–7.34 (m, 12H, ArH), 8.08 (m, 1H, ArH), 9.46 (d, *J* = 1.0 Hz, 1H, CHO), [9.59 (d, *J* = 1.4 Hz, CHO-*anti*)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 13.56, 25.62, 25.93, 26.24, 27.07, 28.4, 29.06, 29.14, 38.9, 48.22, 80.97, 128.22, 128.54 (d, $J_{C,P}$ = 7.2 Hz), 128.7 (d, $J_{C,P}$ = 6.2 Hz), 130.68, 132.1, 133.71 (d, $J_{C,P}$ = 20.7 Hz), 133.99 (d, $J_{C,P}$ = 20.8 Hz), 134.28, 134.31 ($J_{C,P}$ = 21.2 Hz), 138.0 (d, $J_{C,P}$ = 12.9 Hz), 138.36 (d, $J_{C,P}$ = 11.5 Hz), 141.52 (d, $J_{C,P}$ = 28.3 Hz), 166.56 (d, $J_{C,P}$ = 3.1 Hz), 201.36 [201.93 (CHO-*anti*)]. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –3.2. – $C_{30}H_{33}O_3P$ (472.6): calcd. C 76.25, H 6.93; found C 75.98, H 7.21.

(1R,2S*)-(±)-1-(2-Furyl) 2-methyl-4-oxobutyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10d**): The reaction was performed at 70°C. From 213 mg (0.5 mmol) of **9d**, 144 mg (63%) of *syn*-**10d** was obtained. Diastereomer ratio 93:7 (*syn/anti*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.8 Hz, 3H, CH_3), 2.23 (ddd, *J* = 17.2, 8.7, 2.1 Hz, 1H, CH_2CHO), 2.48 (dd, *J* = 17.2, 4.7 Hz, 1H, CH_2CHO), 2.8 (m, 1H, C*H*CH_3), 5.93 (d, *J* = 6.8 Hz, 1H, HCO), 6.25 (m, 2H, furyl-H), 6.93 (m, 1H, ArH), 7.17–7.4 (m, 13H, ArH and 1 furyl-H), 8.05 (m, 1H, ArH), 9.57 (pseudo t, *J* = 2.6 Hz, 1H, CHO-*syn*), [9.60 (m, CHO-*anti*)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 16.23, 31.57, 46.87, 72.63, 109.67, 110.26, 128.27, 128.5 (d, $J_{C,P}$ = 7.1 Hz), 128.66, 130.78 (d, $J_{C,P}$ = 2.3 Hz), 132.2, 133.92 (d, $J_{C,P}$ = 20.6 Hz), 134.03 (d, $J_{C,P}$ = 20.8 Hz), 134.0, 134.4, 137.9 (d, $J_{C,P}$ = 13.5 Hz), 138.02 (d, $J_{C,P}$ = 11.2 Hz), 141.0 (d, $J_{C,P}$ = 27.7 Hz), 142.52, 150.8, 165.74, 200.95. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –3.9 [–4.4]. – $C_{30}H_{27}O_3P$ (466.5)[31].

Methyl (2R,3S*)-(±)-2-[2-(Diphenylphosphanyl)benzoyloxy]-3-methyl-5-oxopentanoate* (*syn*-**10e**): From 209 mg (0.5 mmol) of **9e**, 179 mg (80%) of *syn*-**10e** was obtained. Diastereomer ratio 90:10 (*syn/anti*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.9 Hz, 3H, CH_3), 2.26 (ddd, *J* = 17.9, 8.2, 1.6 Hz, 1H, CH_2CHO), 2.54 (dd, *J* = 17.8, 5.4 Hz, 1H, CH_2CHO), 2.77 (m, 1H, C*H*CH_3), 3.66 (s, 3H, OCH_3), 5.05 (d, *J* = 3.6 Hz, 1H, HCO), 6.92 (m, 1H, ArH), 7.22–7.42 (m, 12H, ArH), 8.15 (m, 1H, ArH), 9.62 (s, 1H, CHO-*syn*), [9.67 (s, CHO-*anti*)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 15.06, 29.68, 46.84, 52.26, 75.36, 128.36, 128.49 ($J_{C,P}$ = 7.2 Hz, 128.69, 130.88 (d, $J_{C,P}$ = 2.5 Hz), 132.36, 133.47 (d, $J_{C,P}$ = 19.3 Hz), 133.93 (d, $J_{C,P}$ = 20.8 Hz), 133.98 (d, $J_{C,P}$ = 20.6 Hz), 134.37, 137.43 (d, $J_{C,P}$ = 11.5 Hz), 137.89 (d, $J_{C,P}$ = 11.6 Hz), 140.93 (d, $J_{C,P}$ = 27.9 Hz), 165.88, 169.18, 200.23 (CHO-*syn*), [200.3 (CHO-*anti*)]. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.3. – $C_{26}H_{25}O_5P$ (448.5): calcd. C 69.64, H 5.62; found C 69.78, H 5.70.

(1R,2R*)-(±)-2-Methyl-4-oxo-1-prop-2-enyl)butyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10f**): From 200 mg (0.5 mmol) of **9f**, 77 mg (90%, calculated for 40% conversion) of *syn*-**10f** was obtained, along with 120 mg of recovered **9f** (40% conversion). Diastereomer ratio 96:4 (*syn/anti*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.7 Hz, 3H, CH_3), 1.65 (s, 3H, =CCH_3), 2.12 (ddd, *J* = 17.2, 8.4, 1.9 Hz, 1H, CH_2CHO), 2.3–2.5 (m, 2H, CH_2CHO and C*H*CH_3), 4.86 (s, 1H, =CH_2), 4.89 (s, 1H, =CH_2), 5.19 (d, *J* = 5.7 Hz, 1H, HCO), 6.87 (m, 1H, ArH), 7.2–7.4 (m, 12H, ArH), 8.1 (m, 1H, ArH), 9.58 (s, 1H, CHO). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 15.06, 19.16, 29.85, 47.67, 80.48, 114.12, 128.35, 128.58 (d, $J_{C,P}$ = 7.1 Hz), 128.72 (d, $J_{C,P}$ = 3.9 Hz), 130.58 (d, $J_{C,P}$ = 2.3 Hz), 133.98 (d, $J_{C,P}$ = 20.7 Hz), 134.22 (d, $J_{C,P}$ = 20.8 Hz), 134.54, 137.94 (d, $J_{C,P}$ = 12.2 Hz), 138.24 (d, $J_{C,P}$ = 11.5 Hz), 141.14 (d, $J_{C,P}$ = 28 Hz), 141.35, 165.82, 201.24. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –4.3. – $C_{27}H_{27}O_3P$ (430.5): calcd. C 75.33, H 6.32; found C 75.13, H 6.47.

(1R,2R*)-(±)-1-Ethyl-2-methyl-4-oxobutyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10g**) *and (1R*,2S*)-(±)-1-Ethyl-2-methyl-4-oxobutyl 2-(Diphenylphosphanyl)benzoate* (*anti*-**10g**): From 194 mg (0.5 mmol) of **9g**, 173 mg (83%) of *syn*- and *anti*-**10g** was obtained. Diastereomer ratio 73:27 (*syn/anti*). NMR data of the mixture of diastereomers is given with signals of the minor diastereomer (*anti*-**10g**) in square brackets. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7–0.8 (m, 6H, 2 CH_3), 1.5–1.59 (m, 2H, CH_2CH$_3$), 2.0–2.4 (m, 3H, H at C2 and C3), 4.83–4.96 (m, 1H, OCH), 6.88–6.92 (m, 1H, ArH), 7.22–7.34 (m, 12H, ArH), 8.0–8.06 (m, 1H, ArH), 9.52 (dd, *J* = 1.9, 1.0 Hz, 1H, CHO-*syn*), [9.58 (dd, *J* = 2.3, 1.3 Hz, CHO-*anti*)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 10.32, 14.57, 24.08, 30.88, 47.32, 79.02, 125.3–140.9 (all aryl-C), 166.57, 201.43, [9.72, 16.7, 24.5, 31.11, 46.59, 79.45, 125.3–140.9, 166.57, 201.68]. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –3.75 [–3.91]. – $C_{26}H_{27}O_3P$ (418.5): calcd. C 74.63, H 6.50; found C 74.98, H 6.41.

(1R,2R*)-(±)-1-Benzyl-2-methyl-4-oxobutyl 2-(Diphenylphosphanyl)benzoate* (*syn*-**10h**) *and (1R*,2S*)-(±)-1-Benzyl-2-methyl-4-oxobutyl 2-(Diphenylphosphanyl)benzoate* (*anti*-**10h**): From 225

mg (0.5 mmol) of **9h**, 180 mg (75%) of *syn*- and *anti*-**10h** was obtained. Diastereomer ratio 80:20 (*syn*/*anti*). NMR data of the mixture of diastereomers is given with signals of the minor diastereomer (*anti*-**10h**) in square brackets. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = [0.97 (d, *J* = 6.6 Hz, 3H, CH_3)], 1.02 (d, *J* = 6.8 Hz, 3H, CH_3), 2.08–2.55 (m, 3H, H at C2 and C3), 2.85 (m, 2H, H at C5), [5.22 (dd, *J* = 12.4, 6.7 Hz, HCO)], 5.31 (ddd, *J* = 9.4, 7.6, 2.7 Hz, HCO), 6.94 (m, 1H, ArH), 7.16–7.42 (m, 17H, ArH), 7.94 (m, 1H, ArH), 9.53 (m, 1H, CHO), [9.64 (dd, *J* = 2.4, 1.3 Hz, CHO)]. – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 14.25, 30.35, 37.42, 47.6, 78.05, 126.61–140.81 (all aryl-C), 166.31, 201.27; [16.97, 30.86, 37.75, 46.31, 78.69, 126.61–140.81 (all aryl-C), 166.31, 201.54]. – ^{31}P NMR (161.978 MHz, $CDCl_3$): δ = –3.9 [–4.2]. – $C_{31}H_{29}O_3P$ (480.5): calcd. C 77.48, H 6.08; found C 77.29, H 6.00.

(1R,2S*)-(±)-2-Methyl-4-oxo-1-phenylbutyl 2-(Diphenylmethyl)benzoate* (*syn*-**12**) *and (1R*,2R*)-(±)-2-Methyl-4-oxo-1-phenylbutyl 2-(Diphenylmethyl)benzoate* (*anti*-**12**): From 209 mg (0.5 mmol) of **11**, 140 mg (62%), conversion 67%) of *syn*/*anti*-**12** was obtained. Diastereomer ratio 50:50 (*syn*/*anti*). Spectroscopic data of the 1:1 *syn*/*anti*-**12** mixture is given. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (d, *J* = 6.6 Hz, 3H, CH_3), 0.85 (d, *J* = 7 Hz, 3H, CH_3), 2.04 (m, 1H, C*H*$_2$CHO), 2.24 (m, 1H, C*H*$_2$CHO), 2.54 (m, 1H, C*H*CH$_3$), 5.63 (d, *J* = 7.8 Hz, 1H, HCO), 5.79 (d, *J* = 5.7 Hz, HCO), 6.62 (s, 1H, $CHPh_2$), 6.65 (s, 1H, $CHPh_2$), 7.01–7.4 (m, 36H, ArH), 7.79 (d, *J* = 7.5 Hz, 1H, ArH), 7.88 (d, *J* = 7.5 Hz, 1H, ArH), 9.52 (s, 2H, CHO). – ^{13}C NMR (75.469 MHz, $CDCl_3$): δ = 15.3, 16.56, 33.48, 46.53, 46.89, 51.76, 78.85, 79.63, 126.21, 126.63, 126.87, 127.89, 128.08, 128.18, 128.38, 128.47, 129.64, 129.67, 129.72, 130.09, 130.64, 130.82, 130.92, 131.47, 131.49, 138.35, 138.52, 143.39, 143.46, 143.79, 144.64, 144.77, 166.67, 166.72, 200.93, 201.33. – $C_{31}H_{28}O_3$ (448.6): calcd. C 83.01, H 6.29; found C 82.90, H 6.35.

Cleavage of the o-DPPB Group: A solution of 120 mg (0.26 mmol) of (±)-*syn*-**10a** and 100 mg of KOH in THF (2 ml)/MeOH (2 ml)/water (1 ml) was stirred at 50°C for 2.5 h, and then diluted with 20 ml of *tert*-butyl methyl ether/10 ml of water. The organic phase was separated and the aqueous phase extracted with two further 10 ml portions of *tert*-butyl methyl ether. The combined organic phases were dried (Na_2SO_4) and concentrated to dryness to give 46 mg (99%) of the crude lactol as a yellow oil, which was directly used in the following oxidation step with PCC (see below). The aqueous phase was acidified to pH = 1 with conc. HCl and extracted with three 20 ml portions of CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and the solvent was evaporated to give 78 mg (98%) of *o*-DPPBA as a pale-yellow solid. Spectroscopic and analytical data were identical to those reported previously[8]. Crude lactol (46 mg, 0.26 mmol) was oxidized with 112 mg (0.52 mmol) of PCC on Al_2O_3 (1 g/mmol) according to the General Procedure described for *syn*- and *anti*-**6**, to give 44 mg (95%) of *syn*-lactone **7** as a colorless oil, diastereomer ratio (92:8). Spectroscopic data were identical to those reported previously[15]. – $C_{11}H_{12}O_2$ (176.2): calcd. C 74.98, H 6.86; found C 74.73, H 6.97.

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