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Directed Branched-Regioselective Hydroformylation of 2-Substituted Allylic *o*-DPPB Esters[‡]

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Keywords: Homogeneous catalysis / Hydroformylation / C–C coupling / Catalyst-directing group

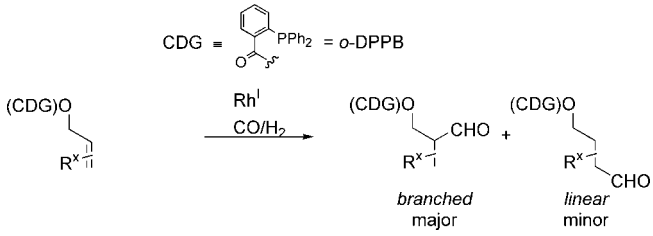
Branched-regioselective hydroformylation of allylic *o*-DPPB esters has been accomplished with mono- and disubstituted alkene functions in good to excellent yields and selectivities. Optimized reaction conditions allowed the reaction of even trisubstitued alkenic functions. These reactions occur as a result of a significant rate-accelerating effect exerted by the catalyst-directing *o*-DPPB group, as exemplified by highly position-, regio-, and diastereoselective hydroformylation of the geranyl and neryl *o*-DPPB esters.

Introduction

The hydroformylation of alkenes is one of the most important applications of homogeneous catalysis in industry, although its use in laboratory organic synthesis is still rare.[1,2] Hydrogen and carbon monoxide are added in the presence of a transition-metal catalyst across the double bond of an alkene. A new carbon–carbon and carbon–hydrogen bond are formed with concomitant introduction of the aldehyde function, which itself can serve as a versatile starting point for subsequent skeleton-expanding synthetic transformations. Today, rhodium catalysts with tailor-made bidentate ligands allow for a highly linear-selective hydroformylation of terminal alkenes.[3] However, branched-regioselective hydroformylation of an alkyl-substituted terminal alkene and position-selective hydroformylation of an internal unsymmetrical alkene are challenging tasks for which, to date, no general solution exists.[4]

We recently showed that specific incorporation of substrate-bound catalyst-directing groups into alkenes allows for high levels of diastereoselective control in the hydroformylation of allylic, methallylic, and homomethallylic *o*-DPPB esters [*o*-DPPB = *ortho*-(diphenylphosphanyl)benzoyl].[5] Furthermore, desymmetrizing hydroformylation of bis(alkenyl)- and bis(allyl)carbinols has been developed employing the planar chiral *ortho*-(diphenylphosphanyl)ferrocenecarboxylate (*o*-DPPF) as a directing group.[6]

We herein report on the use of the *o*-DPPB group as an efficient catalyst-directing group (CDG) allowing for highly branched-selective hydroformylation of allylic *o*-DPPB esters (Scheme 1). Terminal, 1,2-disubstituted, and even trisubstituted alkene functions react with exceptional levels of regiocontrol.



Scheme 1. Concept of a branched-regioselective hydroformylation of allylic alcohol derivatives with the aid of a substrate-bound catalyst-directing group (CDG).

Results and Discussion

The *o*-DPPB function was readily incorporated into a range of alkenes in good yields upon reaction of the corresponding allylic alcohol with *ortho*-(diphenylphosphanyl)-benzoic acid under Steglich esterification conditions[7] (Table 1).

In a first set of experiments crotyl *o*-DPPB ester **3** was subjected to hydroformylation conditions. The catalyst loading was 0.7 mol-% [$Rh(CO)_2acac$] and the syngas pressure was 40 bar. In order to identify the best solvent in terms of reaction rate and regioselectivity the reaction temperature was chosen such that the reaction did not reach complete conversion.

In all cases high regioselectivity in favor of aldehyde **11** was observed. However, a significant effect of the solvent on reaction rate was noted. Thus, among the solvents investigated (toluene, THF, Et_2O, CH_2Cl_2) toluene, THF, and Et_2O gave the best reaction rates (Table 2, Entries 1–4). At room temperature, full conversion was reached with both

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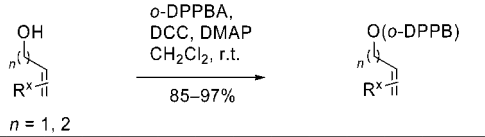
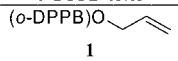
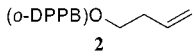
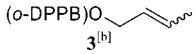
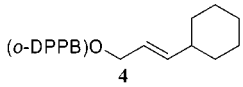
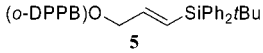
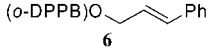
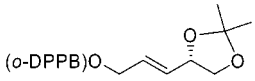
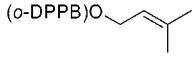
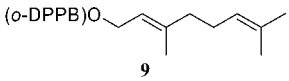
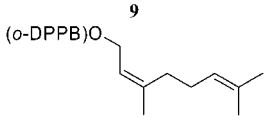
Table 1. Preparation of allylic and homoallylic *o*-DPPB esters.



Entry	*o*-DPPB ester	Yield (%)[a]
1	 **1**	96
2	 **2**	85
3	 **3**[b]	88
4	 **4**	91
5	 **5**	97
6	 **6**	80
7	 **7**	88
8	 **8**	91
9	 **9**	85
10	 **10**	93

[a] Isolated yield after column chromatography. [b] (*E*)/(*Z*) = 70:30.

THF and toluene (Entries 5 and 6). However, toluene was finally chosen as the optimal solvent due to a slightly higher regioselectivity under these conditions. Interestingly, when increasing the temperature to 30 °C, the regioselectivity decreased. Thus, as optimized reaction conditions we used 0.7 mol-% catalyst loading, 40 bar syngas pressure, and toluene as the reaction solvent at room temperature with an initial substrate concentration of 0.1 mol/L.

With these optimized conditions in hand, we turned our attention to the scope and limitations of the substrates. Thus, *o*-DPPB esters **1**–**7** were subjected to these hydroformylation conditions and the results are depicted in Table 3.

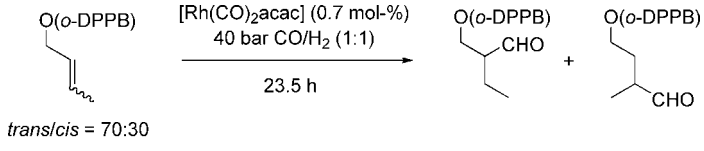
Excellent yield and regioselectivity were achieved for the parent allylic *o*-DPPB ester **1**.[8] However, hydroformylation of the homologous homoallylic *o*-DPPB ester **2** resulted in a completely region-random reaction. Clearly, during the selectivity-determining hydrometallation step this system can efficiently discriminate between eight- and nine-membered chelate ring formation, but fails to discriminate between nine- and ten-membered chelate ring formation.

When increasing the steric demand of substituent R in allylic *o*-DPPB esters, the regioselectivity decreases (Entries 3–6). In the case of styrene derivative **6** it was of interest to learn whether the *o*-DPPB directing group is capable of overruling the intrinsic *iso*-directing effect of the phenyl substituent. Thus, styrene derivatives usually display regioselectivities that favor the *iso*-aldehyde by more than 90%. Unfortunately, a mixture of **16** and *iso*-**16** was obtained indicating that the *o*-DPPB group and the styrene substituent have opposite directing effects of similar strength. Regioselective hydroformylation can also be accomplished in a more complex environment, as exemplified with enantiomerically pure allylic *o*-DPPB ester **7** (entry 7).

Trisubstituted alkenes are usually tough substrates to hydroformylate as the reaction rate of hydroformylation drops exponentially with the number of substituents at the alkene function.[2] However, we speculated that the rate-accelerating effect typical for a directed reaction may allow regioselective hydroformylation of trisubstituted alkene functions in an allylic position relative to the directing *o*-DPPB group. As a model substrate, prenyl *o*-DPPB ester **8** was chosen.

Subjecting **8** to the standard optimized reaction conditions used before gave a conversion after 23.5 h of only 4%

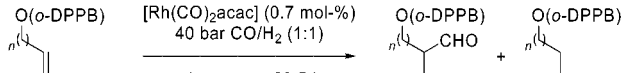
Table 2. Directed-regioselective hydroformylation of crotyl *o*-DPPB ester **3**: Solvent and temperature screening.

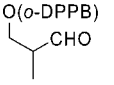
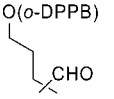
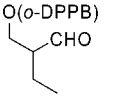
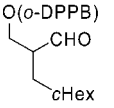
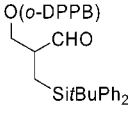
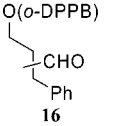
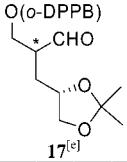


Entry[a]	Solvent	*T* [°C]	Conversion[b] [%]	Yield[c] [%]	Regioselectivity[b] (**11**/*iso*-**11**)
1	toluene	10	53	n.d.	97:3
2	THF	10	68	n.d.	94:6
3	Et_2O	10	52	n.d.	92:8
4	CH_2Cl_2	10	21	n.d.	95:5
5	toluene	r.t.	quant.	97	97:3
6	THF	r.t.	quant.	97	94:6
7	toluene	30	30	quant.	92:8

[a] Initial substrate concentration: c_0 = 0.1 M. [b] Determined by NMR analysis of the crude reaction mixture. [c] Isolated yield after column chromatography.

Table 3. Directed hydroformylation of allyl and homoallyl *o*-DPPB esters **1**–**7** with mono- and disubstituted alkene functions.



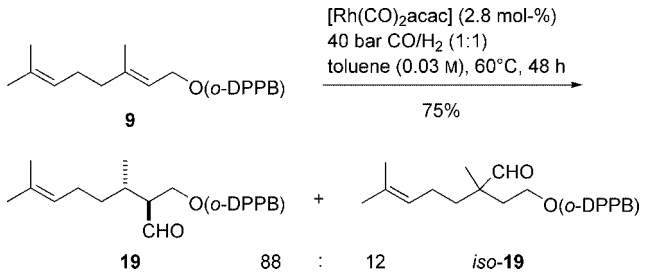
Substrate[a]	Major product	Conversion[b] (%)	Yield[c] (%)	rs[b] (**ald**/*iso*-**ald**)
	1–7		**11–17**	*iso*-**11–17**
1	 **12**	quant.	quant.	97:3
2	 **13**	quant.	89	58:42
3	 **11**	quant.	97	97:3
4	 **14**	quant.	84	81:19
5	 **15**	quant.	87	90:10
6[d]	 **16**	quant.	quant.	48:52
7	 **17**[e]	quant.	94	93:7

[a] Initial substrate concentration: c_0 = 0.1 M. [b] Determined by NMR analysis of the crude reaction mixture. [c] Isolated yield after chromatographic workup. [d] c_0 = 0.03 M, [Rh(CO)$_2$acac] = 1.8 mol-%. [e] *dr* of **17** = 81:19.

(Table 4, Entry 1). This result indicates the level of difficulty one encounters when dealing with trisubstituted alkene functions.

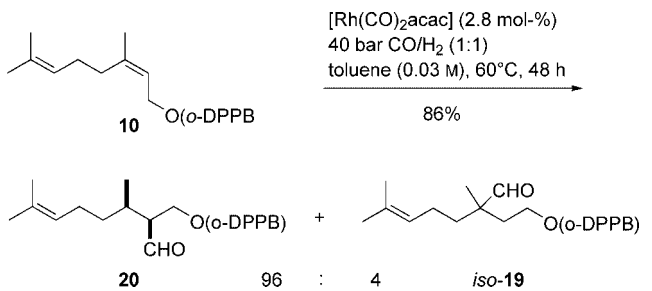
Increasing the reaction temperature to 60 °C gave a much better conversion (56%) and an excellent regioselectivity in favor of aldehyde **18**. Raising the temperature to 100 °C did not improve the reaction rate but reduced the regioselectivity of the reaction (Entry 3). Employing THF as the solvent did not lead to any improvement either (Entry 4), nor did employing an increased syngas pressure (Entry 5). Also, addition of co-ligands, which proved beneficial in an earlier investigation with respect to reaction rate and selectivity,[5a] only resulted in a decrease of regioselectivity. Thus, a reaction temperature of 60 °C and a syngas pressure of 40 bar with toluene as the solvent seemed to offer the best conditions so far. Finally, in order to achieve complete consumption of the starting material in a reasonable reaction time, catalyst loading was increased to 1.8 and 2.8 mol-% (Entries 7–9). However, only when the initial substrate concentration was simultaneously reduced from 0.1 to 0.03 M was a quantitative conversion of the starting material **8** observed after 48 h with good regioselectivity (Entry 10).

Note that in this particular case the reaction regioselectivity is certainly primarily a result of Keuleman's rule, which states that hydroformylation of alkene functions occurs so as to avoid the formation of a quaternary carbon atom. However, it is likely that the directing effect of the *o*-DPPB group is responsible for a significant rate acceleration of the hydroformylation process in the allylic position in order for hydroformylation of a trisubstituted alkene to occur under fairly mild conditions. In order to probe this notion we subjected geranyl and neryl *o*-DPPB esters **9** and **10** to the reaction conditions optimized for the hydroformylation of trisubstituted alkene functions [Equation (1)]. If the rate-accelerating effect of the *o*-DPPB group is significant, position-selective hydroformylation of the allylic alkene function in the presence of an additional trisubstituted alkene function should be possible.



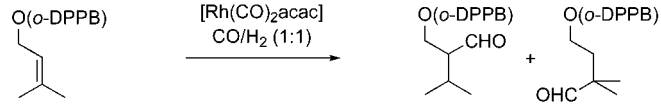
(1)

In fact, subjecting **9** and **10** to similar reaction conditions led to position-selective as well as diastereoselective hydroformylation of the allylic alkene function [Equation (2)]. The diastereoselectivity observed is of course a result of a stereoelectronically controlled and irreversible *syn* hydrometallation step. Better regioselectivity was noted for the neryl system with a ratio for **20**/*iso*-**19** of 96:4 and an isolated yield of 86%.



(2)

Table 4. Directed hydroformylation of allyl *o*-DPPB ester **8** with a trisubstituted alkene function.



8 **18** ***iso*-18**

Entry	Solvent	*T* [°C]	*P* [bar]	[Rh] [mol-%]	*t* [h]	c_0[a] [M]	Conversion[b] [%]	Regioselectivity[b] (**18**/*iso*-**18**)
1	toluene	r.t.	40	0.7	23.5	0.1	4	n.d.
2	toluene	60	40	0.7	23.5	0.1	56	99:1
3	toluene	100	40	0.7	23.5	0.1	51	92:8
4	THF	60	40	0.7	23.5	0.1	51	99:1
5	toluene	70	70	0.7	23.5	0.1	48	97:3
6	toluene	60	35	1.8	23.5	0.1	78	98:2
7[c]	toluene	60	40	1.8	23.5	0.1	49	94:6
8	toluene	60	65	1.8	23.5	0.1	80	98:2
9	toluene	60	40	2.8	48	0.1	93	94:6
10	toluene	60	40	2.8	48	0.03	quant.	96:4

[a] Initial substrate concentration. [b] Determined by NMR analysis of the crude reaction mixture. [c] With addition of 5.4 mol-% P(OPh)$_3$.

Conclusions

Branched-regioselective hydroformylation of allylic *o*-DPPB esters could be accomplished with mono- and disubstituted alkene functions in good to excellent yields and selectivities. Optimized reaction conditions allowed the reaction of even trisubstituted alkenic functions. These reactions occur as a result of a significant rate-accelerating effect exerted by the catalyst-directing *o*-DPPB group, as exemplified by highly position- and regioselective hydroformylation of the geranyl and neryl *o*-DPPB esters.

Experimental Section

General Remarks: Reactions were performed in flame-dried glassware under argon (purity >99.998%). The solvents were dried by standard procedures, distilled, and stored under argon. All temperatures quoted are uncorrected. ^{1}H and ^{13}C NMR spectra: Bruker AM-400 or DRX-500 spectrometer with tetramethylsilane (TMS), chloroform ($CHCl_3$), or benzene (C_6H_6) as internal standards. ^{31}P NMR spectra: Varian Mercury 300 spectrometer with 85% H_3PO_4 as external standard. Melting points: Melting point apparatus by Dr. Tottoli (Büchi). Elemental analyses: Elementar Vario EL apparatus. Flash chromatography: silica gel Si 60, E. Merck AG, Darmstadt, 40–63 μm. Hydroformylation reactions were performed in 50- and 100-mL stainless-steel autoclaves equipped with magnetic stirrers. Gases: Carbon monoxide 3.7, hydrogen 4.3 (1:1, Messer-Griesheim). The following compounds were prepared according to literature procedures: (*E*)-3-Cyclohexylprop-2-en-1-ol,[9] (*E*)-3-(*tert*-butyldiphenylsilyl)prop-2-en-1-ol,[10] (*E*,*S*)-3-(2′,2′-dimethyl-1,3-dioxolan-4′-yl)prop-2-en-1-ol,[11] and *ortho*-(diphenylphosphanyl)benzoic acid.[12]

General Procedure for the Preparation of *o*-DPPB Esters 1–10: *o*-DPPBA (1.05 equiv.), DMAP (0.1 equiv.), and DCC (1.1 equiv.) were successively added to a solution of allylic alcohol (1 equiv.) in CH_2Cl_2 (0.3 M) and the resulting mixture was stirred at room temperature until TLC showed 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 cyclohexane/ethyl acetate (98:2–95:5) provided the *o*-DPPB esters **1**–**10**.

Allyl *o*-(Diphenylphosphanyl)benzoate (1): *o*-DPPB ester **1** (655 mg, 96%) was obtained as a colorless solid from allylic alcohol (116 mg, 2.00 mmol), *o*-DPPBA (643 mg, 2.10 mmol), DMAP (24 mg, 0.20 mmol), and DCC (454 mg, 2.20 mmol). M.p. 87 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.68 (ddd, J = 5.8, 1.4, 1.4 Hz, 2 H), 5.21 (ddt, J = 10.4, 1.4, 1.4 Hz, 1 H), 5.32 (ddt, J = 17.2, 1.4, 1.4 Hz, 1 H), 5.88 (ddt, J = 17.2, 10.4, 5.8 Hz, 1 H), 6.95–7.00 (m, 1 H, Ar-H), 7.28–7.46 (m, 12 H, Ar-H), 8.09–8.14 (m, 1 H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 65.9, 118.5, 128.3, 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.8 (d, $J_{C,P}$ = 2.7 Hz), 132.0, 132.1, 134.0 (d, $J_{C,P}$ = 20.8 Hz, 4 C) 134.3 (d, $J_{C,P}$ = 18.8 Hz), 134.4, 137.8 (d, $J_{C,P}$ = 10.1 Hz, 2 C), 140.4 (d, $J_{C,P}$ = 25.6 Hz), 166.5 (d, $J_{C,P}$ = 2.2 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.4 ppm. $C_{22}H_{19}O_2P$ (346.4): calcd. C 76.29, H 5.49; found C 76.11, H 5.53.

Homoallyl *o*-(Diphenylphosphanyl)benzoate (2): *o*-DPPB ester **2** (918 mg, 85%) was obtained as a slightly yellow solid from homoallylic alcohol (216 mg, 3.00 mmol), *o*-DPPBA (964 mg, 3.15 mmol), DMAP (36 mg, 0.30 mmol), and DCC (681 mg, 3.30 mmol). M.p. 72 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.37 (dtdd, J = 6.8, 6.8, 1.4, 1.4 Hz, 2 H), 4.24 (d, J = 6.7 Hz, 2 H), 5.06 (ddt, J = 10.3, 1.9, 1.1 Hz, 1 H), 5.10 (dtd, J = 17.1, 1.7, 1.6 Hz, 1 H), 5.77 (ddt, J = 17.1, 10.3, 6.7 Hz, 1 H), 6.94–6.99 (m, 1 H, Ar-H), 7.27–7.45 (m, 12 H, Ar-H), 8.05–8.10 (m, 1 H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 33.0, 64.3, 117.2, 128.3, 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.7 (d, $J_{C,P}$ = 2.9 Hz), 132.0, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.0, 134.5, 134.7 (d, $J_{C,P}$ = 19.1 Hz), 137.9 (d, $J_{C,P}$ = 10.4 Hz, 2 C), 140.2 (d, $J_{C,P}$ = 25.4 Hz), 166.8 (d, $J_{C,P}$ = 1.9 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. $C_{23}H_{21}O_2P$ (360.1): calcd. C 76.65, H 5.87; found C 76.58, H 5.96.

(*E*)/(*Z*)-Crotyl *o*-(Diphenylphosphanyl)benzoate (3): *o*-DPPB ester **3** (1.72 g, 88%) was obtained as a slightly yellow solid from (*E*)/(*Z*)-crotyl alcohol (389 mg, 5.40 mmol), *o*-DPPBA (1.73 g, 5.67 mmol), DMAP (66 mg, 0.54 mmol), and DCC (1.23 g, 5.94 mmol). M.p. 93 °C. (*Z*)-**3**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.68 (ddt, J = 7.0, 1.8, 0.9 Hz, 3 H), 4.74 (ddq, J = 6.8, 1.4, 0.9 Hz, 2 H), 5.50–5.57 (m, 1 H)*, 5.70 (dqt, J = 10.6, 6.7, 1.4 Hz, 1 H), 6.93–6.99 (m, 1 H, Ar-H)*, 7.27–7.45 (m, 12 H, Ar-H)*, 8.06–8.12 (m, 1 H, Ar-H)* ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2, 60.9, 124.1,

128.3, 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 129.5, 130.8 (d, $J_{C,P}$ = 2.9 Hz), 131.9, 134.0 (d, $J_{C,P}$ = 20.8 Hz, 4 C), 134.3, 134.6 (d, $J_{C,P}$ = 18.8 Hz), 138.0 (d, $J_{C,P}$ = 10.6 Hz, 2 C), 140.3 (d, $J_{C,P}$ = 26.1 Hz), 166.9 (d, $J_{C,P}$ = 1.9 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.5 ppm. (*E*)-**3**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.70 (ddt, *J* = 6.6, 1.6, 1.2 Hz, 3 H), 4.61 (ddq, *J* = 6.6, 1.1, 1.1 Hz, 2 H), 5.52 (dtq, *J* = 15.3, 6.6, 1.6 Hz, 1 H), 5.77 (dqt, *J* = 15.3, 6.6, 1.2 Hz, 1 H), 6.93–6.99 (m, 1 H, Ar-H)*, 7.27–7.45 (m, 12 H, Ar-H)*, 8.06–8.12 (m, 1 H, Ar-H)* ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.8, 60.0, 125.0, 128.3, 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.8 (d, $J_{C,P}$ = 2.9 Hz), 131.4, 131.9, 134.0 (d, $J_{C,P}$ = 20.8 Hz, 4 C), 134.3, 134.6 (d, $J_{C,P}$ = 18.8 Hz), 138.0 (d, $J_{C,P}$ = 10.6 Hz, 2 C), 140.3 (d, $J_{C,P}$ = 26.1 Hz), 166.7 (d, $J_{C,P}$ = 1.9 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.4 ppm. *Signals overlapping with those of the other isomer. $C_{23}H_{21}O_2P$ (360.4): calcd. C 76.65, H 5.87; found C 76.59, H 6.14.

(*E*)-3-Cyclohexylprop-2-enyl *o*-(Diphenylphosphanyl)benzoate (4): *o*-DPPB ester **4** (1.17 g, 91%) was obtained as a slightly yellow viscous oil from (*E*)-3-cyclohexylprop-2-en-1-ol (420 mg, 3.00 mmol), *o*-DPPBA (964 mg, 3.15 mmol), DMAP (36 mg, 0.30 mmol), and DCC (681 mg, 3.30 mmol). For analytical data see ref.[13]

(*E*)-3-(*tert*-Butyldiphenylsilyl)prop-2-enyl *o*-(Diphenylphosphanyl)benzoate (5): *o*-DPPB ester **5** (307 mg, 97%) was obtained as a slightly yellow viscous oil from (*E*)-3-(*tert*-butyldiphenylsilyl)prop-2-en-1-ol (160 mg, 0.541 mmol), *o*-DPPBA (258 mg, 0.930 mmol, 1.70 equiv.), DMAP (11 mg, 0.089 mmol, 0.20 equiv.), and DCC (202 mg, 0.980 mmol, 1.80 equiv.). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 1.1 Hz, 9 H), 4.78 (dd, *J* = 4.8, 1.6 Hz, 2 H), 6.11 (dtd, *J* = 18.7, 4.8, 1.4 Hz, 1 H), 6.43 (dtd, *J* = 18.7, 1.5, 1.5 Hz, 1 H), 6.93–7.01 (m, 1 H), 7.20–7.47 (m, 18 H), 7.58–7.63 (m, 4 H), 8.09–8.14 (m, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.2, 27.8 (3 C), 67.4, 126.6, 127.7 (4 C), 128.4, 128.5 (2 C), 128.6 (2 C), 128.8 (2 C), 129.3 (2 C), 130.8 (d, $J_{C,P}$ = 2.7 Hz), 132.1 (1 C, Ar-C), 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.0 (d, $J_{C,P}$ = 20.5 Hz), 134.3, 134.5 (2 C), 136.3 (4 C), 138.0 (d, $J_{C,P}$ = 11.3 Hz, 2 C), 140.6 (d, $J_{C,P}$ = 27.0 Hz), 144.6, 166.5 (d, $J_{C,P}$ = 2.2 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. $C_{38}H_{37}O_2PSi$ (584.8): calcd. C 78.05, H 6.38; found C 78.31, H 6.12.

(*E*)-Cinnamyl *o*-(Diphenylphosphanyl)benzoate (6): *o*-DPPB ester **6** (1.68 g, 80%) was obtained as a slightly yellow solid from (*E*)-cinnamyl alcohol (670 mg, 5.00 mmol), *o*-DPPBA (1.61 g, 5.25 mmol), DMAP (60 mg, 0.50 mmol), and DCC (1.14 g, 5.50 mmol). For analytical data see ref.[13]

(*E*,*S*)-3-(2′,2′-Dimethyl-1,3-dioxolan-4′-yl)prop-2-enyl *o*-(Diphenylphosphanyl)benzoate (7): *o*-DPPB ester **7** (1.48 g, 88%) was obtained as a slightly yellow viscous oil from (*E*,*S*)-3-(2′,2′-dimethyl-1,3-dioxolan-4′-yl)prop-2-en-1-ol (598 mg, 3.76 mmol), *o*-DPPBA (1.21 g, 3.95 mmol), DMAP (45 mg, 0.38 mmol), and DCC (853 mg, 4.14 mmol). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.42 (d, *J* = 0.6 Hz, 3 H), 1.46 (d, *J* = 0.6 Hz, 3 H), 3.59 (dd, *J* = 8.2, 7.6 Hz, 1 H), 4.10 (dd, *J* = 8.2, 6.2 Hz, 1 H), 4.50 (ddd, *J* = 7.3, 6.8, 6.4 Hz, 1 H), 4.69 (d, *J* = 5.7 Hz, 2 H), 5.75 (dddd, *J* = 15.5, 6.8, 1.0, 1.0 Hz, 1 H), 5.32 (dtd, *J* = 15.5, 5.7, 0.6 Hz, 1 H), 6.93–6.98 (m, 1 H), 7.20–7.45 (m, 12 H), 8.07–8.12 (m, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.9, 26.7, 64.6, 69.3, 76.2, 109.5, 127.8, 128.3, 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.8 (d, $J_{C,P}$ = 2.7 Hz), 131.8, 132.1, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 20.8 Hz, 2 C), 134.2 (d, $J_{C,P}$ = 19.1 Hz), 134.4, 137.9 (d, $J_{C,P}$ = 10.9 Hz, 2 C), 140.5 (d, $J_{C,P}$ = 26.8 Hz), 166.4 (d, $J_{C,P}$ = 2.2 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.5 ppm. $C_{27}H_{27}O_4P$ (446.5): calcd. C 72.63, H 6.10; found C 72.72, H 5.93.

3-Methylbut-2-enyl *o*-(Diphenylphosphanyl)benzoate (8): *o*-DPPB ester **8** (1.02 g, 91%) was obtained as a slightly yellow solid from 3-methylbut-2-en-1-ol (258 mg, 3.00 mmol), *o*-DPPBA (964 mg, 3.15 mmol), DMAP (36 mg, 0.30 mmol), and DCC (681 mg, 3.30 mmol). M.p. 58 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.67 (d, *J* = 1.3 Hz, 3 H), 1.74 (d, *J* = 1.3 Hz, 3 H), 4.68 (d, *J* = 7.1 Hz, 2 H), 5.28 (tqq, *J* = 7.1, 1.3, 1.3 Hz, 1 H), 6.92–6.97 (m, 1 H), 7.27–7.44 (m, 12 H), 8.06–8.10 (m, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.1, 25.8, 62.2, 118.5, 128.2, 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 130.7 (d, $J_{C,P}$ = 2.9 Hz), 131.8, 134.0 (d, $J_{C,P}$ = 20.8 Hz, 4 C), 134.3, 134.8 (d, $J_{C,P}$ = 19.3 Hz), 138.1 (d, $J_{C,P}$ = 11.4 Hz, 2 C), 138.9, 140.3 (d, $J_{C,P}$ = 26.6 Hz), 167.0 (d, $J_{C,P}$ = 2.2 Hz) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.5 ppm. $C_{24}H_{23}O_2P$ (360.1): calcd. C 76.99, H 6.19; found C 76.72, H 6.25.

Geranyl *o*-(Diphenylphosphanyl)benzoate (9): *o*-DPPB ester **9** (756 mg, 85%) as a slightly yellow viscous oil from geraniol (309 mg, 2.00 mmol), *o*-DPPBA (643 mg, 2.10 mmol), DMAP (24 mg, 0.20 mmol), and DCC (454 mg, 2.20 mmol). For analytical data see ref.[13]

Neryl *o*-(Diphenylphosphanyl)benzoate (10): *o*-DPPB ester **10** (821 mg, 93%) as a slightly yellow viscous oil from nerol (309 mg, 2.00 mmol), *o*-DPPBA (643 mg, 2.10 mmol), DMAP (24 mg, 0.20 mmol), and DCC (454 mg, 2.20 mmol). For analytical data see ref.[13]

General Procedure (GP) 1 for the Hydroformylation of *o*-DPPB Esters 1–7 (Mono- and Disubstituted Alkene Functions): [$Rh(CO)_2$acac] (0.70 mol-%) was added to a solution of the *o*-DPPB ester (1 equiv.) in toluene (0.1 M) and the reaction mixture was stirred until the catalyst had completely dissolved. The resulting solution was transferred by syringe into an oven-dried stainless-steel tube autoclave. The argon in the autoclave was removed by a pressurizing/depressurizing cycle (three times 20 bar H_2/CO) and finally the autoclave was pressurized with 40 bar H_2/CO (1:1). The reaction mixture was stirred at room temperature for 23.5 h. After releasing the pressure, the solvent was removed in vacuo and CH_2Cl_2 (30 mL) was added to the reaction mixture. This solution was filtered through silica gel (esters **11**–**14**, **16**) or Celite (esters **15**, **17**), which was washed with additional CH_2Cl_2 (30 mL). The solvent of the filtrate was removed in vacuo, providing aldehydes **11**–**17** as slightly yellow highly viscous oils.

General Procedure (GP) 2 for the Hydroformylation of *o*-DPPB Esters 8–10 (Trisubstituted Alkene Functions): [$Rh(CO)_2$acac] (2.8 mol-%) was added to a solution of the *o*-DPPB ester (1 equiv.) in toluene (0.033 M) and the reaction mixture was stirred until the catalyst had completely dissolved. The resulting solution was transferred by syringe into an oven-dried stainless-steel tube autoclave. The argon in the autoclave was removed by a pressurizing/depressurizing cycle (three times 20 bar H_2/CO) and finally the autoclave was pressurized with 40 bar H_2/CO (1:1). The reaction mixture was stirred at 60 °C for 48 h. After releasing the pressure, the solvent was removed in vacuo and CH_2Cl_2 (30 mL) was added to the reaction mixture. This solution was filtered through silica gel, which was washed with additional CH_2Cl_2 (30 mL). The solvent of the filtrate was removed in vacuo, providing aldehydes **8**–**10** as slightly yellow highly viscous oils.

2-Formylbutyl *o*-(Diphenylphosphanyl)benzoate (11): According to GP 1, hydroformylation of **3** (216 mg, 0.600 mmol) was carried out with [$Rh(CO)_2$acac] (1.1 mg, 4.2 μmol) in toluene (6 mL), giving **11** (227 mg, 97%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (dd, *J* = 7.5, 7.5 Hz, 3 H), 1.52 (ddq, *J* = 14.2, 7.4, 7.3 Hz, 1 H), 1.71 (ddq, *J* = 14.4, 7.2, 7.1 Hz, 1 H), 2.51 (ddddd, *J* = 6.9, 6.9, 6.8, 5.0, 2.0 Hz, 1 H), 4.37 (dd, *J* = 11.4, 5.0 Hz, 1 H), 4.42 (dd, *J* = 11.5,

7.2 Hz, 1 H), 6.89–6.97 (m, 1 H), 7.22–7.42 (m, 12 H), 7.95–8.01 (m, 1 H), 9.60 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.3, 19.1, 52.3, 62.7, 128.4, 128.6 (2 C), 128.6 (2 C), 128.8 (2 C), 130.8 (d, $J_{C,P}$ = 2.9 Hz), 132.2, 133.9 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.0 (d, $J_{C,P}$ = 19.3 Hz), 134.5, 137.9 (d, $J_{C,P}$ = 11.1 Hz), 137.9 (d, $J_{C,P}$ = 11.1 Hz), 140.6 (d, $J_{C,P}$ = 26.8 Hz), 166.6 (d, $J_{C,P}$ = 2.2 Hz), 202.4 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.6 ppm. $C_{24}H_{23}O_3P$ (390.1): calcd. C 73.83, H 5.94; found C 73.96, H 5.91.

2-Formylpropyl *o*-(Diphenylphosphanyl)benzoate (12): According to GP 1, hydroformylation of **1** (208 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (1.1 mg, 4.2 μmol) in toluene (6 mL), giving **12** (226 mg, quant.). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.13 (d, J = 7.1 Hz, 3 H), 2.69 (dddq, J = 7.0, 7.0, 5.4, 1.4 Hz, 1 H), 4.37 (dd, J = 11.3, 5.2 Hz, 1 H), 4.43 (dd, J = 11.2, 6.8 Hz, 1 H), 6.92–6.99 (m, 1 H), 7.16–7.45 (m, 12 H), 7.98–8.06 (m, 1 H), 9.64 (d, J = 1.3 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.7, 45.7, 64.4, 128.4, 128.6 (2 C), 128.6 (2 C), 128.8 (2 C), 130.8 (d, $J_{C,P}$ = 2.9 Hz), 132.2, 133.9 (d, $J_{C,P}$ = 20.5 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 20.8 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 19.3 Hz), 134.5, 137.8 (d, $J_{C,P}$ = 11.1 Hz, 2 C), 140.5 (d, $J_{C,P}$ = 26.8 Hz), 166.6 (d, $J_{C,P}$ = 1.9 Hz), 202.1 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.6 ppm. $C_{23}H_{21}O_3P$ (376.4): calcd. C 73.39, H 5.62; found C 73.16, H 5.60.

3- and 4-Formylbutyl *o*-(Diphenylphosphanyl)benzoate (13): According to GP 1, hydroformylation of **2** (216 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (1.1 mg, 4.2 μmol) in toluene (6 mL), giving **13** (208 mg, 89%). Major regioisomer [3-formylbutyl *o*-(diphenylphosphanyl)benzoate, 58%]: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.07 (d, J = 7.1 Hz, 3 H), 2.05 (dqd, J = 7.1, 7.0, 6.8 Hz, 1 H), 2.33–2.42 (m, 2 H)*, 4.24 (ddd, J = 6.8, 6.0, 1.9 Hz, 2 H), 6.90–6.95 (m, 1 H)*, 7.22–7.44 (m, 12 H)*, 8.98–8.06 (m, 1 H)*, 9.56 (d, J = 1.3 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2, 28.0, 43.4, 62.7, 128.4, 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.7 (d, $J_{C,P}$ = 3.1 Hz), 132.0, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.5, 134.5 (d, $J_{C,P}$ = 19.5 Hz), 137.9 (d, $J_{C,P}$ = 11.1 Hz, 2 C), 140.2 (d, $J_{C,P}$ = 26.3 Hz), 167.0 (d, $J_{C,P}$ = 1.9 Hz), 203.9 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. Minor regioisomer [4-formylbutyl *o*-(diphenylphosphanyl)benzoate, 42%]: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.55–1.65 (m, 4 H), 2.33–2.42 (m, 2 H)*, 4.18 (tt, J = 4.0, 2.0 Hz, 2 H), 6.90–6.95 (m, 1 H)*, 7.22–7.44 (m, 12 H)*, 8.98–8.06 (m, 1 H)*, 9.73 (t, J = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.7, 29.2, 43.4, 64.7, 128.4, 128.6 (2 C), 128.6 (2 C), 128.8 (2 C), 130.7 (d, $J_{C,P}$ = 2.7 Hz), 132.1, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.5, 134.7 (d, $J_{C,P}$ = 19.5 Hz), 138.0 (d, $J_{C,P}$ = 10.9 Hz, 2 C), 140.2 (d, $J_{C,P}$ = 26.3 Hz), 167.0 (d, $J_{C,P}$ = 2.2 Hz), 202.1 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.6 ppm. *Signals overlapping with those of the other isomer. $C_{24}H_{23}O_3P$ (390.4): calcd. C 73.83, H 5.94; found C 73.57, H 5.78.

3-Cyclohexyl-2-formylpropyl *o*-(Diphenylphosphanyl)benzoate (14): According to GP 1, hydroformylation of **4** (241 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (1.1 mg, 4.2 μmol) in toluene (6 mL), giving **14** (216 mg, 84%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79–2.06 (m, 13 H), 2.67 (ddddd, J = 7.1, 6.9, 6.9, 5.0, 2.1 Hz, 1 H), 4.33 (dd, J = 11.3, 5.2 Hz, 1 H), 4.36 (dd, J = 11.4, 7.1 Hz, 1 H), 6.89–6.95 (m, 1 H), 7.22–7.42 (m, 12 H), 7.94–7.99 (m, 1 H), 9.57 (d, J = 2.4 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.1, 26.2, 26.4, 33.3, 33.4, 33.4, 35.0, 48.4, 63.5, 128.4, 128.6 (2 C), 128.6 (2 C), 128.8 (2 C), 130.8 (d, $J_{C,P}$ = 2.7 Hz), 132.2, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.0 (d, $J_{C,P}$ = 18.6 Hz), 134.5, 137.9 (d, $J_{C,P}$ = 11.1 Hz), 137.9 (d, $J_{C,P}$ = 10.9 Hz), 140.6 (d, $J_{C,P}$ = 26.8 Hz), 166.6 (d, $J_{C,P}$ = 1.9 Hz), 202.7 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.6 ppm.

3-(*tert*-Butyldiphenylsilyl)-2-formylpropyl *o*-(Diphenylphosphanyl)-benzoate (15): According to GP 1, hydroformylation of **5** (205 mg, 0.351 mmol) was carried out with [Rh(CO)$_2$acac] (0.6 mg, 2 μmol) in toluene (4 mL), giving **15** (188 mg, 87%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 1.19 (dd, J = 15.5, 6.8 Hz, 1 H), 1.60 (dd, J = 15.3, 6.6 Hz, 1 H), 2.60 (ddddd, J = 6.5, 6.5, 6.5, 5.1, 1.4 Hz, 1 H), 4.08 (dd, J = 11.3, 6.4 Hz, 1 H), 4.11 (dd, J = 11.3, 4.9 Hz, 1 H), 6.88–6.95 (m, 1 H), 7.15–7.45 (m, 18 H), 7.55–7.61 (m, 4 H), 7.90–7.95 (m, 1 H), 9.24 (d, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 5.8, 18.3, 27.8 (3 C), 46.8, 64.9, 128.0 (4 C), 128.4, 128.5 (2 C), 128.6 (2 C), 128.7 (d, $J_{C,P}$ = 2.2 Hz, 2 C), 129.7, 129.7, 130.8 (d, $J_{C,P}$ = 2.9 Hz), 132.2, 133.4, 133.6, 133.9 (d, $J_{C,P}$ = 20.8 Hz, 2 C), 133.9 (d, $J_{C,P}$ = 20.8 Hz, 2 C), 134.1 (d, $J_{C,P}$ = 19.6 Hz), 134.5, 136.0 (2 C), 136.1 (2 C), 137.9 (d, $J_{C,P}$ = 11.3 Hz), 137.9 (d, $J_{C,P}$ = 11.3 Hz), 140.5 (d, $J_{C,P}$ = 27.0 Hz), 166.3 (d, $J_{C,P}$ = 1.9 Hz), 202.0 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.9 ppm. $C_{39}H_{39}O_3PSi$ (614.78): calcd. C 76.19, H 6.39; found C 76.48, H 6.39.

2- and 3-Formyl-3-phenylpropyl *o*-(Diphenylphosphanyl)benzoate (16): Owing to the reduced reactivity of the starting material **6** in the hydroformylation reaction the GP 2, featuring a higher catalyst loading and a lower concentration of the *o*-DPPB ester, was employed. Hydroformylation of **6** (205 mg, 0.332 mmol) was carried out with [Rh(CO)$_2$acac] (1.5 mg, 6.0 μmol, 1.8 mol-%) in toluene (10 mL, 0.03 M), giving **16** (149 mg, 99%). 2-Formyl-3-phenylpropyl *o*-(diphenylphosphanyl)benzoate: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.76 (dd, J = 13.9, 7.8 Hz, 1 H), 2.90 (ddddd, J = 7.6, 6.2, 6.0, 5.5, 1.5 Hz, 1 H), 3.04 (dd, J = 13.9, 6.4 Hz, 1 H), 4.37–4.40 (m, 2 H), 6.91–6.97 (m, 1 H)*, 7.09–7.15 (m, 2 H)*, 7.20–7.43 (m, 15 H)*, 7.94–7.99 (m, 1 H)*, 9.67 (d, J = 1.4 Hz, 1 H) ppm. 3-Formyl-3-phenylpropyl *o*-(diphenylphosphanyl)benzoate: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.95 (dddd, J = 14.4, 8.7, 5.7, 5.7 Hz, 1 H), 2.39 (dddd, J = 14.4, 8.2, 6.0, 6.0 Hz, 1 H), 3.55 (dd, J = 8.7, 6.0 Hz, 1 H), 4.09 (ddd, J = 11.2, 8.1, 5.5 Hz, 1 H), 4.20 (ddd, J = 11.3, 5.8, 5.8 Hz, 1 H), 6.91–6.97 (m, 1 H)*, 7.09–7.15 (m, 2 H)*, 7.20–7.43 (m, 15 H)*, 7.94–7.99 (m, 1 H)*, 9.59 (d, J = 1.1 Hz, 1 H) ppm. *Signals overlapping with those of the other isomer. ^{13}C NMR (100.6 MHz, $CDCl_3$) of the mixture of regioisomers (doubled signal set): δ = 28.6, 32.0, 52.4, 55.8, 62.6, 62.8, 126.8, 127.9, 128.4, 128.4, 128.5 (2 C), 128.6 (2 C), 128.6 (2 C), 128.6 (2 C), 128.7 (d, $J_{C,P}$ = 4.8 Hz, 2 C), 128.7 (d, $J_{C,P}$ = 4.8 Hz, 2 C), 128.8 (2 C), 129.0 (2 C), 129.1 (2 C), 129.3 (2 C), 130.7 (d, $J_{C,P}$ = 2.7 Hz), 130.8 (d, $J_{C,P}$ = 2.4 Hz), 132.1, 132.3, 133.9 (d, $J_{C,P}$ = 20.8 Hz, 2 C), 133.9 (d, $J_{C,P}$ = 20.8 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 20.5 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 20.5 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 19.1 Hz), 134.5, 134.5, 134.6 (d, $J_{C,P}$ = 21.0 Hz), 135.2, 137.7, 137.8 (d, $J_{C,P}$ = 10.9 Hz), 137.8 (d, $J_{C,P}$ = 10.9 Hz), 137.9 (d, $J_{C,P}$ = 8.0 Hz), 138.0 (d, $J_{C,P}$ = 7.7 Hz), 140.0 (d, $J_{C,P}$ = 26.6 Hz), 140.6 (d, $J_{C,P}$ = 26.8 Hz), 166.5 (d, $J_{C,P}$ = 2.2 Hz), 166.9 (d, $J_{C,P}$ = 2.2 Hz), 199.6, 201.6 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$) of the mixture of regioisomers: δ = –4.6, –4.7 ppm. $C_{29}H_{25}O_3P$ (452.5): calcd. C 76.98, H 5.57; found C 76.72, H 5.64.

(2*RS*,4S)-3-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-2-formylpropyl *o*-(Diphenylphosphanyl)benzoate (17) (81:19 Mixture of Diastereomers): According to GP 1, hydroformylation of **7** (268 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (1.1 mg, 4.2 μmol) in toluene (6 mL), giving **17** (269 mg, 94%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.33 (d, J = 0.6 Hz, 3 H), [1.33 (d, J = 0.5 Hz, 3 H)], 1.39 (d, J = 0.5 Hz, 3 H), [1.40 (d, J = 0.5 Hz, 3 H)], 1.66 (ddd, J = 14.2, 9.1, 4.8 Hz, 1 H), 1.98 (ddd, J = 14.2, 8.1, 3.7 Hz, 1 H), 2.80–2.89 (m, 1 H), [3.51 (dd, J = 8.1, 6.8 Hz, 1 H)], 3.52 (dd, J = 8.1, 6.8 Hz, 1 H), [4.04 (dd, J = 8.0, 6.1 Hz, 1 H)], 4.05 (dd, J = 8.1, 6.1 Hz, 1 H), 4.11–4.21 (m, 1 H), 4.48 (dd, J =

11.4, 6.3 Hz, 1 H), 4.53 (dd, *J* = 11.4, 5.2 Hz, 1 H), 6.92–6.99 (m, 1 H), 7.15–7.44 (m, 12 H), 7.97–8.03 (m, 1 H), 9.68 (d, *J* = 1.3 Hz, 1 H), [9.70 (d, *J* = 1.3 Hz, 1 H)] ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.6, 27.0, [30.1], 30.3, 48.2, [48.5], [62.7], 63.5, 69.4, [69.5], [73.3], 73.5, 109.4, 128.4, 128.6 (2 C), 128.6 (2 C), 128.7 (2 C), 130.8 (d, $J_{C,P}$ = 2.9 Hz), 132.3, 133.6 (d, $J_{C,P}$ = 19.3 Hz), 133.9 (d, $J_{C,P}$ = 20.8 Hz, 4 C), 134.5, 137.8 (d, $J_{C,P}$ = 11.1 Hz, 2 C), 140.6 (d, $J_{C,P}$ = 26.8 Hz), 166.5 (d, $J_{C,P}$ = 1.9 Hz), 201.5 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. The NMR signals in brackets are the signals of the minor diastereomer if distinguishable from the signals of the major diastereomer. $C_{28}H_{29}O_5P$ (476.5): calcd. C 70.58, H 6.13; found C 70.66, H 5.94.

2-Formyl-3-methylbutyl *o*-(Diphenylphosphanyl)benzoate (18): According to GP 2, hydroformylation of **8** (224 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (4.3 mg, 17 μmol) in toluene (18 mL), giving **18** (184 mg, 76%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.8 Hz, 3 H), 1.00 (d, *J* = 6.8 Hz, 3 H), 2.10 (qqd, *J* = 6.8, 6.8, 6.8 Hz, 1 H), 2.44 (dddd, *J* = 8.5, 6.3, 4.5, 2.5 Hz, 1 H), 4.39 (dd, *J* = 11.4, 4.5 Hz, 1 H), 4.51 (dd, *J* = 11.4, 8.4 Hz, 1 H), 6.91–6.97 (m, 1 H), 7.24–7.44 (m, 12 H), 7.96–8.02 (m, 1 H), 9.64 (d, *J* = 2.5 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.9, 20.3, 26.5, 56.7, 61.9, 128.4, 128.6 (2 C), 128.6 (2 C), 128.7 (d, $J_{C,P}$ = 1.5 Hz, 2 C), 130.7 (d, $J_{C,P}$ = 2.7 Hz), 132.2, 133.9 (d, $J_{C,P}$ = 20.7 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 20.5 Hz, 2 C), 134.0 (d, $J_{C,P}$ = 19.1 Hz), 134.5, 137.8 (d, $J_{C,P}$ = 7.0 Hz), 137.9 (d, $J_{C,P}$ = 6.8 Hz), 140.5 (d, $J_{C,P}$ = 26.6 Hz), 166.6 (d, $J_{C,P}$ = 1.9 Hz), 202.8 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. $C_{25}H_{25}O_3P$ (404.4): calcd. C 74.24, H 6.23; found C 74.07, H 6.16.

(2,3-*anti*)-2-Formyl-3,7-dimethyloct-6-enyl *o*-(Diphenylphosphanyl)-benzoate (19): According to GP 2, hydroformylation of **9** (265 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (4.3 mg, 17 μmol) in toluene (18 mL), giving **19** (213 mg, 75%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.9 Hz, 3 H), 1.21–1.48 (m, 3 H), 1.60 (d, *J* = 0.8 Hz, 3 H), 1.68 (d, *J* = 1.3 Hz, 3 H), 1.96–2.08 (m, 2 H), 2.52 (dddd, *J* = 8.6, 5.1, 4.4, 2.1 Hz, 1 H), 4.35 (dd, *J* = 11.4, 4.4 Hz, 1 H), 4.50 (dd, *J* = 11.4, 8.6 Hz, 1 H), 5.05 (tqq, *J* = 7.1, 1.4, 1.4 Hz, 1 H), 6.89–6.97 (m, 1 H), 7.22–7.43 (m, 12 H), 7.94–8.00 (m, 1 H), 9.59 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4, 17.8, 25.6, 25.8, 30.8, 34.6, 55.2, 62.3, 123.7, 128.4, 128.5 (2 C), 128.6 (2 C), 128.7 (d, $J_{C,P}$ = 3.4 Hz, 2 C), 130.7 (d, $J_{C,P}$ = 2.9 Hz), 132.2, 132.2, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.3 (d, $J_{C,P}$ = 25.3 Hz), 134.5, 137.9 (d, $J_{C,P}$ = 7.7 Hz), 138.0 (d, $J_{C,P}$ = 7.5 Hz), 140.5 (d, $J_{C,P}$ = 26.6 Hz), 166.7 (d, $J_{C,P}$ = 1.7 Hz), 202.6 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. $C_{30}H_{33}O_3P$ (472.6): calcd. C 76.25, H 7.04; found C 75.89, H 6.98.

(2,3-*syn*)-2-Formyl-3,7-dimethyloct-6-enyl *o*-(Diphenylphosphanyl)-benzoate (20): According to GP 2, hydroformylation of **10** (265 mg, 0.600 mmol) was carried out with [Rh(CO)$_2$acac] (4.3 mg, 17 μmol) in toluene (18 mL), giving **20** (244 mg, 86%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.9 Hz, 3 H), 1.19–1.49 (m, 3 H), 1.59 (d, *J* = 0.9 Hz, 3 H), 1.67 (d, *J* = 1.1 Hz, 3 H), 1.90–1.99 (m, 2 H), 2.54 (dddd, *J* = 8.7, 5.1, 4.9, 2.3 Hz, 1 H), 4.32 (dd, *J* = 11.4, 4.7 Hz, 1 H), 4.52 (dd, *J* = 11.4, 8.5 Hz, 1 H), 5.05 (tqq, *J* = 7.1, 1.4, 1.4 Hz, 1 H), 6.90–6.97 (m, 1 H), 7.22–7.42 (m, 12 H), 7.94–8.00 (m, 1 H), 9.63 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.0, 17.8, 25.6, 25.8, 31.4, 34.1, 55.4, 62.1, 123.7, 128.4, 128.5 (2 C), 128.6 (2 C), 128.7 (d, $J_{C,P}$ = 2.9 Hz, 2 C), 130.7 (d, $J_{C,P}$ = 2.7 Hz), 132.2, 132.3, 134.0 (d, $J_{C,P}$ = 20.5 Hz, 4 C), 134.4 (d, $J_{C,P}$ = 32.4 Hz), 134.5, 137.9 (d, $J_{C,P}$ = 8.2 Hz), 138.0 (d, $J_{C,P}$ = 8.0 Hz), 140.5 (d, $J_{C,P}$ = 26.6 Hz), 166.7 (d, $J_{C,P}$ = 1.9 Hz), 202.9 ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = –4.7 ppm. $C_{30}H_{33}O_3P$ (472.6): calcd. C 76.25, H 7.04; found C 76.01, H 6.92.

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