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o-DPPB-Directed Stereoselective Conjugate Addition of Organocuprates

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Abstract—Substrate-directed diastereoselective conjugate addition of Gilman cuprates to acyclic enoates has been achieved with the aid of the substrate-bound reagent-directing *o*-DPPB-group (*o*-DPPB=*ortho*-diphenylphosphanyl benzoate). Combining *o*-DPPB-directed hydroformylation with the *o*-DPPB-directed cuprate addition provides access to building blocks with up to four stereogenic centers, which may be of relevance for polyketide synthesis. Limit and scope of the *o*-DPPB-directed cuprate addition of Gilman cuprates with respect to enoate structure as well as control experiments which probe the role of the *o*-DPPB group are reported.

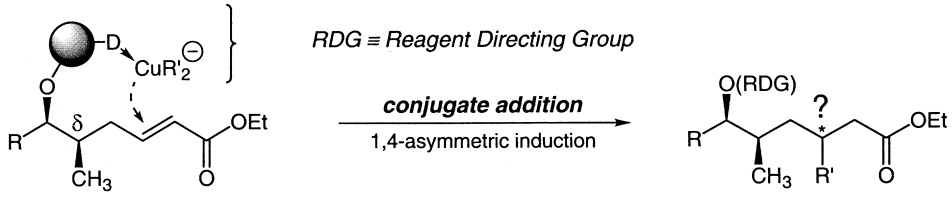
Conjugate additions of organocopper reagents to α,β-unsaturated carbonyl derivatives are widely applicable versatile C–C bond forming reactions.[1] In the course of this reaction a new stereogenic center at the β-position may be formed either under reagent or substrate control. However, the latter is particularly difficult to achieve for acyclic substrates, because of their intrinsic conformational flexibility. As a consequence, the controlling stereocenter should be located in closest proximity relative to the newly formed stereocenter to effect a useful level of facial stereoselection for the conjugate addition reaction. Hence, a stereocenter in γ-position usually provides significant levels of stereocontrol.[2] A modified Felkin–Anh model allows to predict the relative configuration of the newly formed stereocenter.[1e,2a] However, a stereocenter in a δ- or any other remote position does not exert significant levels of stereochemical control if one relies exclusively on passive substrate control.[2a]

One solution to this problem could make use of active substrate control, i.e. to employ a substrate-directed cuprate addition. This general type of reaction usually passes through a cyclic transition state, which is highly ordered, and, as a consequence, allows for an efficient facial diastereoselection[3] (Scheme 1).

Directed allylic substitution of organocuprates has been described employing either carbamates[4] or benzothiazole derivatives[5] as reagent-directing leaving groups. Additionally, carbamates and carbonates have been evaluated as directing groups to control facial stereoselection upon addition of silylcuprate reagents to acyclic enoates.[6]

Recent reports from these laboratories have described the design of a substrate-bound *catalyst-directing group* (CDG) which allows for an efficient control of facial stereoselectivity upon hydroformylation of acyclic allylic and homoallylic alcohol derivatives. As an efficient CDG the *ortho*-diphenylphosphanylbenzoate group (*o*-DPPB) was identified[7] (Scheme 2).

Here we report that the *o*-DPPB group may serve in a



Scheme 1.

Keywords: cuprates; asymmetric synthesis; synthetic methods; reagent-directing group.
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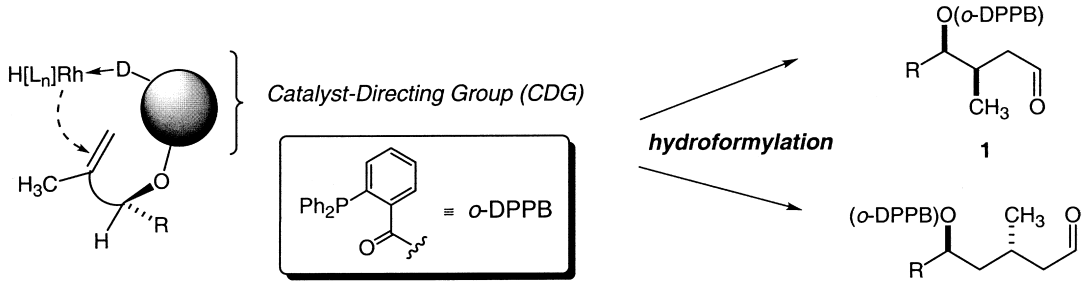


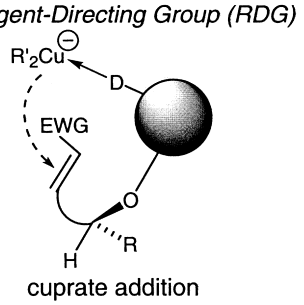
Scheme. 2.

subsequent step, as a *reagent-directing group* (RDG) for the diastereoselective addition of Gilman cuprates to acyclic enoates.[8] Influence of substrate structure is discussed, and experiments that probe the role of the *o*-DPPB group are described.

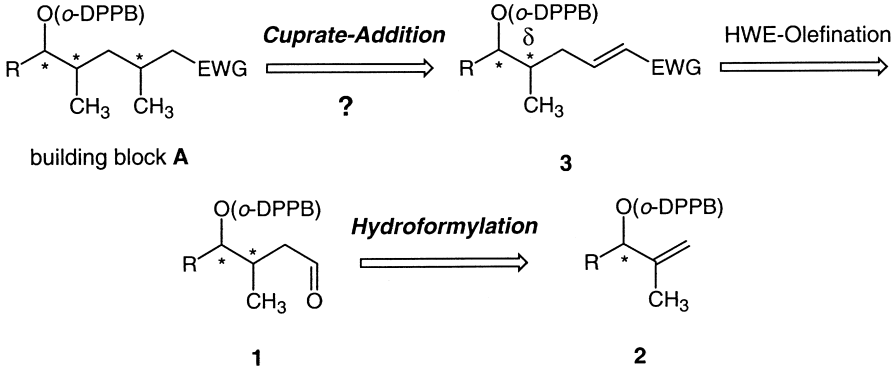
Many biologically interesting natural products of the polyketide class such as the ionophore calcimycin,[9] the antitumor active dictyostatin 1,[10] and venturicidin[11] possess the structural motif **A** as a key element of their structure. We wondered whether the aldehydes **1**, the products of the *o*-DPPB-directed hydroformylation reaction,[7] could serve as a starting point for the construction of building block **A**. Two further C–C bond forming reactions would have to be added to arrive at the desired target. First a Horner–Wadsworth–Emmons (HWE) olefination should transform the aldehyde **1** into an α,β-unsaturated ester **3**. As a second step, the missing methyl group would then have to be introduced by way of a conjugate addition of a methyl group transferring organometallic reagent (Scheme 3).

For the latter step to be efficient it may be desirable to control stereoselectivity making use of only substrate-inherent chirality information. The enoates **3** would possess a stereogenic center in δ-position. However, Lipshutz has noted that conjugate addition reactions of higher order cuprates to acyclic enoates of this structure proceeded non-selective.[12]

To overcome this problem, we speculated that the still present and potentially directing *o*-DPPB group might serve a second time as a directing group, now in the role of an organometallic *reagent-directing group* (RDG). Thus, the *o*-DPPB group would have to precoordinate the organometallic reagent, which should result in positioning and subsequent delivery of this species to hopefully only one of the two diastereotopic enoate faces.



The ideal organometallic reagent would have to undergo clean 1,4-addition reaction, and additionally, would have to realize coordinative interactions with the triphenylphosphane unit of the *o*-DPPB group. Organocopper reagents ideally fulfill both requirements. Thus, Gilman cuprates are known to undergo coordinative interactions with phosphanes. An X-ray structure of a difluorenylcuprate triphenylphosphane adduct has been reported and confirms the possibility of such interactions in the solid state.[13] Additionally, NMR investigations suggest that these interactions occur in solution.[14] On the other hand, reactivity of enoates towards conjugate addition of Gilman cuprates is usually low, and other reaction pathways such as 1,2-addition may compete.[1a,1e,2d,12] However, this low reactivity may turn into an advantage, since the desired intramolecular reaction pathway may now become significantly faster (entropic reasons) compared to the competing intermolecular and presumably non-selective pathway. Hence, with the two assumptions, that enoates of type **3** possess a preferred reactive conformation, and reagent delivery occurs intramolecular, one could expect a stereoselective cuprate addition reaction.

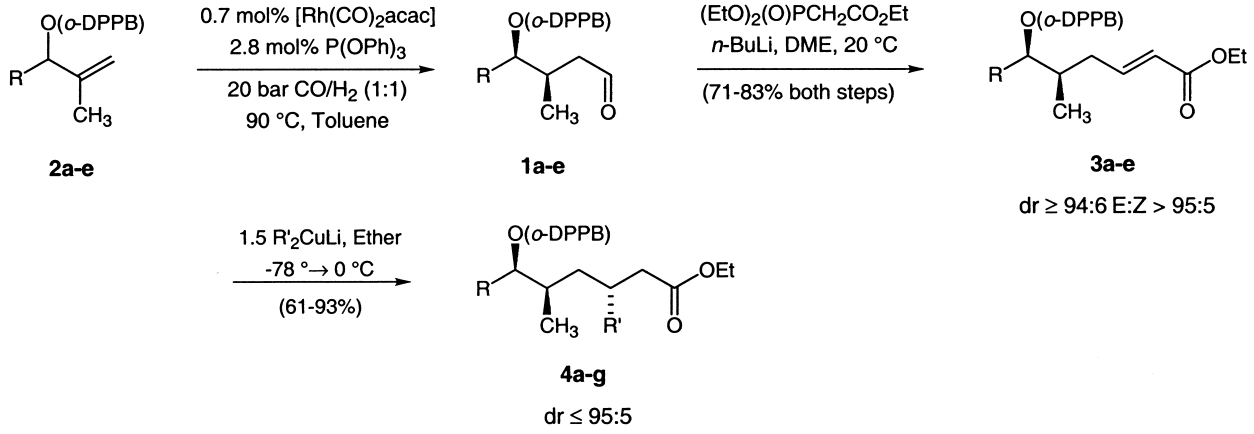


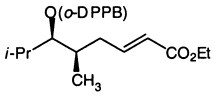
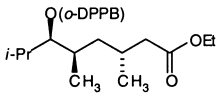
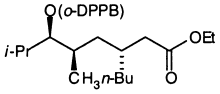
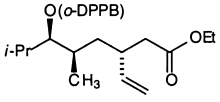
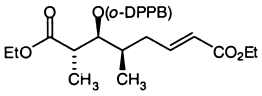
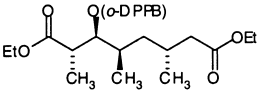
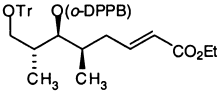
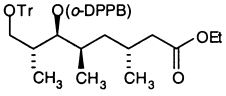
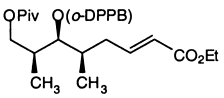
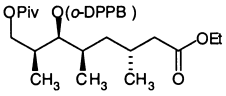
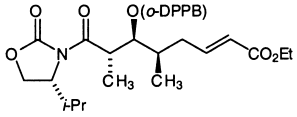
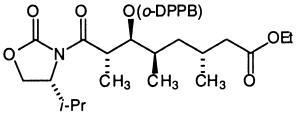
Scheme 3.

The enoates **3** were obtained via *o*-DPPB-directed diastereoselective hydroformylation of alkenes **2** followed by HWE olefination of the crude hydroformylation products (**2→3**) in good yields (71–83%), diastereoselectivities of ≥94:6 (*syn:anti*) and *E*/*Z*-selectivities of >95:5. Treatment of the enoate **3a** with 1.5 equiv. of lithium dimethylcuprate yielded 93% of the 1,4-addition product **4a** in a diastereomer ratio of 95:5 (Table 1, entry 1).

In addition to methyl group transfer, an *n*-butyl side chain

Table 1. Results of the conjugate addition of Gilman cuprates to *E*-enoates **3**



Entry	*E*-enoate	Major diastereomer	Yield [%][a]	dr (*anti*:*syn*)[b]
1	 **3 a**	 **4 a**	93	95:5
2	**3a**	 **4 b**	68	95:5
3	**3a**	 **4 c**	61	80:20
4	 **3 b**	 **4 d**	68	95:5
5	 **3 c**	 **4 e**	71	86:14
6	 **3 d**	 **4 f**	60	85:15
7	 (-)-**3 e**	 (-)-**4 g**	75	95:5

[a] After flash chromatography.
[b] From NMR spectra of the crude product.

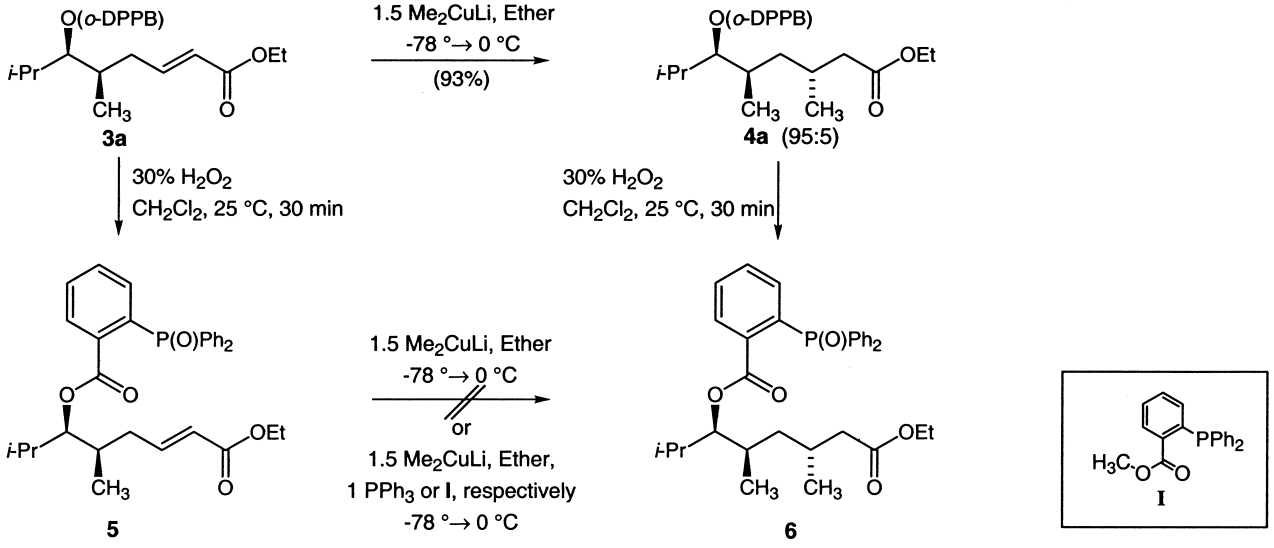
may be introduced employing di-*n*-butyl-cuprate with similar levels of diastereoselectivity (*anti*-**4b**, dr 95:5, entry 2). However, in the case of lithium divinyl cuprate the diastereoselectivity was lower (*anti*-**4c**, dr 80:20, entry 3). With regard to the preparation of important building blocks of polyketide natural products, the addition of dimethylcuprate is clearly the most interesting reaction. Accordingly, combining the stereoselective *o*-DPPB-directed hydroformylation with HWE-olefination and the stereoselective *o*-DPPB-directed dimethylcuprate addition provided access to acyclic building blocks with up to four stereogenic centers (→**4d**–**g**, entries 4–7). The 1,4-addition product **4d** is a potential C13–C20 building block of the ionophor calcimycin with the correct relative configuration of the four stereogenic centers. Additionally, compound **4g** possesses the correct absolute configuration of this polyketide (entries 4 and 7).[9]

Even though the *o*-DPPB group represents an intrinsically coordinating functionality, it has not been proven yet that this is actually the origin of the observed diastereoselectivity. An experiment which could give further mechanistic insight should be the cuprate addition to the enoate **5**, which differs from **3a** only by oxidation of the phosphane functionality to a phosphane oxide. This small structural modification should suppress the ability of the *o*-DPPB group to coordinate a soft cuprate. If the *o*-DPPB group does not play any significant role to control diastereoselectivity, one should observe diastereoselectivity also with derivative **5**. For that reason enoates **3a** and **5** were subjected to identical reaction conditions. Whereas the phosphane **3a** yielded the 1,4-addition product **4a** in 93% yield and a diastereomer ratio of 95:5, the phosphane oxide **5** gave, besides recovered starting material, only non-selective decomposition. No formation of 1,4 addition product **6** could be detected. The latter was prepared independently by oxidation of **4a**. Evidently, the phosphane functionality of the *o*-DPPB group is essential for a successful addition of dimethylcuprate to the enoates **3**. Interestingly, this result is in accord with the low reactivity of Gilman cuprates towards enoates which is frequently observed.[1a,1e,1h,12] In order to increase this reactivity it has been found that additives such as chlorotrimethylsilane,[15] borontrifluoride etherate[16] or even phosphanes[17] could be of benefit. However, at this stage it remained unclear whether the triphenylphosphane moiety of the *o*-DPPB group simply acts as an activating additive. If this would be the case, the intramolecular attachment of the *o*-DPPB group would not be imperative (Scheme 4).

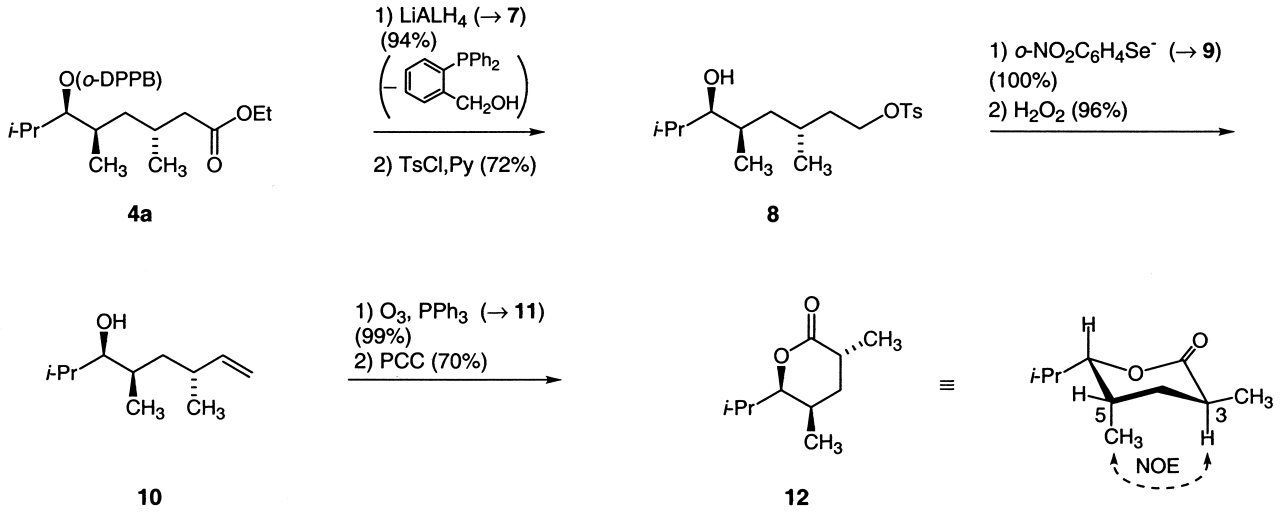
To address this issue, the phosphane oxide **5** was treated again with dimethyl cuprate under the identical conditions used above, but in the presence of an additional equivalent of triphenylphosphane as an external ligand system. Again, besides recovered starting material **5** only unspecified decomposition products were found. However, one may argue that triphenylphosphane does not mimic the ligand properties of the *o*-DPPB group properly. Thus, the ester carbonyl in *ortho*-position reduces the donor capability of the phosphane unit of the *o*-DPPB group. Additionally, the carbonyl oxygen may offer a second binding post for coordination to copper or lithium of the dimethylcuprate reagent. Hence, the methyl ester **I** should be a better mimic for the *o*-DPPB moiety. Thus, the same experiment was repeated with ester **I** replacing triphenylphosphane. However, as before, 1,4-addition product **6** could not be detected and starting material **5** was recovered. These results indicate that the *intramolecular* presence of the *triarylphosphane* is essential for this reaction to proceed. Thus, it is most likely an intramolecular delivery of the dimethylcuprate, caused by precoordination to the triarylphosphane function of the *o*-DPPB group, which controls both reactivity as well as stereoselectivity of the 1,4-addition reaction.

Determination of Relative Configuration of the Cuprate Addition Products 4

In order to determine the relative configuration of the cuprate addition products, **4a** was transformed into the δ-lactone **12**. Reduction of the diester **4a** with lithium



Scheme 4.



Scheme 5.

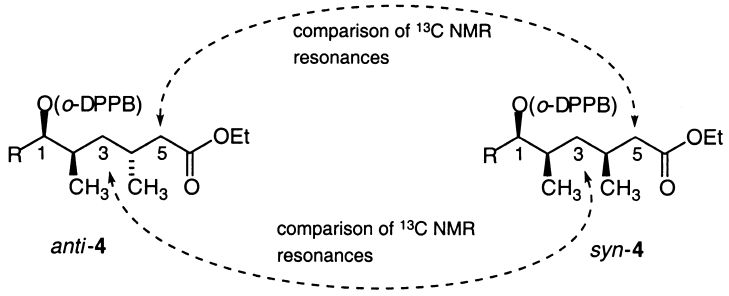
aluminum hydride yielded the diol **7** in addition to *ortho*-diphenylphosphanyl-benzyl alcohol. Next, the primary alcohol in **7** was activated as the toluene sulfonate **8** and transformed into the selenoether **9**. Oxidation to the selenoxide was followed by instantaneous *syn*-elimination to give the terminal olefin **10** in almost quantitative yield.[18] C/C-double bond cleavage via ozonolysis and subsequent oxidation yielded the desired δ-lactone **12**. A 2D-NOESY-NMR experiment with **12** revealed the axial position of the proton at C3 as well as the methyl group at C5, i.e. the *anti*-relation of the two 1,3-positioned methyl groups of the acyclic 1,4-addition product **4a** (Scheme 5).

Characteristically different ^{13}C NMR shifts were observed for the two secondary carbon atoms C3 and C5 of *anti*- and *syn*-**4a**–**g**. Thus, the ^{13}C NMR resonance for C3 of *anti*-**4a**–**g** is always shifted to a higher field compared to *syn*-**4a**–**g**, whereas the ^{13}C NMR signal for C5 in *anti*-**4a**–**g** generally shows a low field shift compared to the *syn* diastereomers of **4a**–**g** (see Table 2). Hence, chemical derivatization of **4a** to the δ-lactone **12** in combination with ^{13}C NMR analysis allows the assignment of relative configuration for conjugate adducts **4a**–**g**.

Influence of Double Bond Geometry of *o*-DPPB-enoates 3 on Reactivity and Stereoselectivity of the Cuprate Addition Reaction

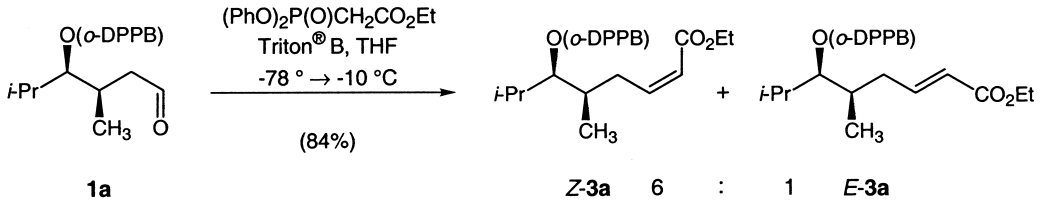
To test the influence of double bond geometry of enoates **3** on the reactive conformation, and hence on reactivity and selectivity of the cuprate addition reaction, the *Z*-enoate **3a** was prepared. Thus, starting from aldehyde **1a**, using the *Z*-selective HWE-olefination protocol developed by Ando,

Table 2. Comparison of selected ^{13}C NMR spectroscopic data of *anti*- and *syn*-esters **4**

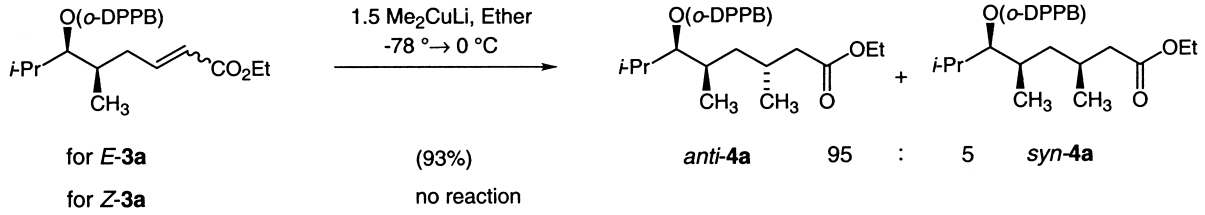


Compound	^{13}C NMR shift of C3		^{13}C NMR shift of C5	
	anti	*syn*	*anti*	*syn*
4a	40.54	40.88	42.62	41.09
4d	40.07	40.54	42.47	40.93
4e	40.33	40.81	42.69	41.06
4f	40.22	40.51	42.58	40.82
4g	40.52	n.d.	42.43	n.d.
4b	38.47[a]	38.37	39.82	39.00
4c	38.45[a]	38.37	40.93	39.95

n.d.: not determined
[a] Trend of chemical shift for C3 of **4b** and **4c** is less clear.



Scheme 6.



Scheme 7.

employing a diphenylphosphonate and Triton® **B** as the base, yielded *Z*-enoate **3a** in good yield and satisfactory *Z*/*E*-selectivity (6:1)[19] (Scheme 6).

However, whereas dimethylcuprate added cleanly to *E*-enoate **3a**, the *Z*-enoate **3a** did not react at all. Starting material *Z*-**3a** could be reisolated (Scheme 7).

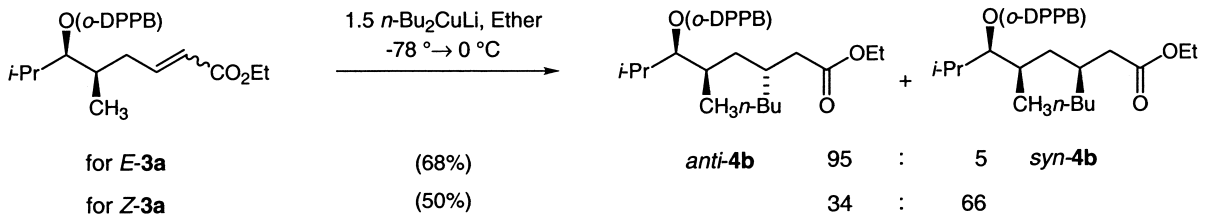
Lower reactivity of *Z*-enoates compared to the corresponding *E*-enoates towards addition of organocopper reagents has been noted.[1a,2d] This observation may account for the lack of reactivity of *Z*-**3a** towards dimethylcuprate. Additionally, one may speculate that *Z*-enoate **3a** does not allow intramolecular dimethylcuprate delivery via the *o*-DPPB group because a suitable reactive conformation may not be available.

However, the more reactive di-*n*-butylcuprate added to both the *E*- as well as the *Z*-enoate **3a**. Whereas addition to the *E*-enoate **3a** showed high *anti*-selectivity in the case of the *Z*-enoate only a 2:1 selectivity in favor of the *syn* isomer **4b** was detected. One may speculate that lack of an appropriate reactive conformation for *Z*-enoate **3a** causes a purely intermolecular, and hence, less selective, reaction pathway (Scheme 8).

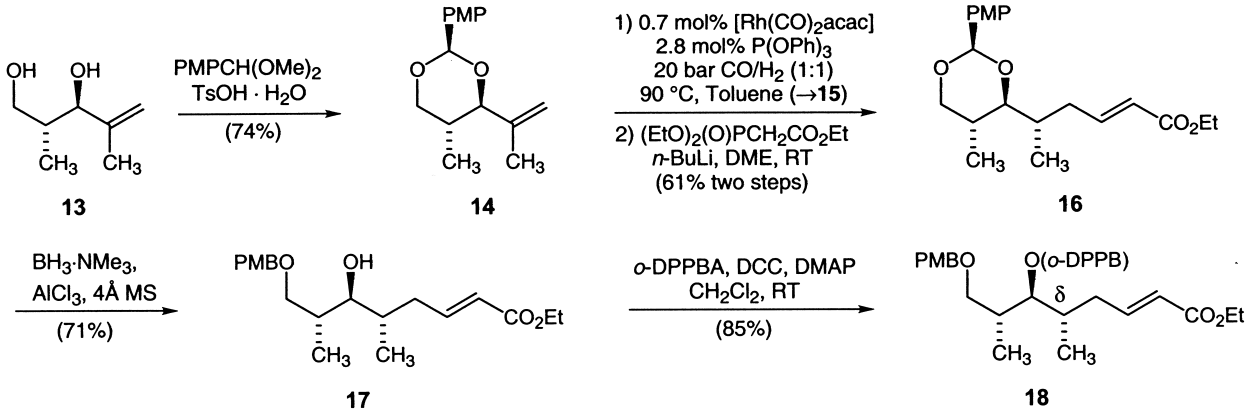
Influence of the Relative Configuration of the δ-Stereocenter

To probe the influence of the relative configuration of the methyl-bearing stereocenter in δ-position on reactivity and selectivity of the cuprate addition reaction an *anti*-configured enoate **3** was required. A representative derivative should be enoate **18** which was obtained starting from the known diol **13**.[7i] Protection as the *para*-methoxybenzylidene acetal was followed by stereoselective hydroformylation with a rhodium/triphenylphosphite catalyst.[20] The crude acid-sensitive aldehyde **15** (dr 93:7) was immediately subjected to HWE olefination conditions to furnish the enoate **16** (61% for two steps, dr *anti:syn*, 93:7). Regioselective ring opening of the acetal was accomplished with the borane trimethylamine/aluminum trichloride reagent combination.[21] This procedure liberated the secondary alcohol selectively (→**17**, 71%, regioisomer ratio, 35:1). Introduction of the *o*-DPPB group employing a standard DCC/DMAP esterification protocol[22] yielded the desired *anti*-*o*-DPPB-enoate **18** (Scheme 9).

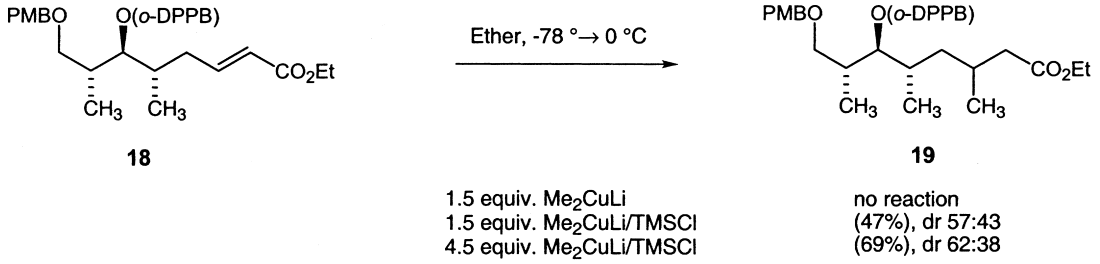
As in the case of *Z*-enoate **3a**, dimethylcuprate could not be added to *anti*-enoate **18** under standard conditions. In order to increase reactivity of the dimethylcuprate reagent, chlorotrimethylsilane was added to the cuprate solution. Interestingly, under these conditions 1,4-addition occurred; however, diastereoselectivity was low. The yield of 1,4-addition product **19** could be improved using an excess of dimethylcuprate reagent. The almost complete lack of diastereoselectivity during the course of this 1,4-addition reaction may be interpreted with the lack of a suitable reactive conformation for *anti*-enoates **18**, which would be mandatory for an intramolecular reagent delivery[23] (Scheme 10).



Scheme 8.



Scheme 9.



Scheme 10.

Conclusion

Experiments described in this paper suggest that the *o*-DPPB group may serve as a *reagent-directing group* for the addition of Gilman cuprates to acyclic enoates. Thus, combining *o*-DPPB-directed hydroformylation with the *o*-DPPB-directed cuprate addition gave access to building blocks with up to four stereogenic centers, which may find application in polyketide synthesis. However, it has been found that stereoselectivity of the *o*-DPPB-directed cuprate addition is a sensitive function of the enoate structure and, thus, limited so far to the *E*-enoates of type **3**.

Experimental

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. ^{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. Elemental analyses: CHN-rapid analyzer (Heraeus). Flash chromatography: Silica gel Si 60, E. Merck AG, Darmstadt, 40–63 μm.

General procedure for the preparation of enoates 3

To a solution of 1.2 equiv. ethyl (diethyoxyphosphoryl) acetate in DME (0.42 M) at 0°C was added dropwise 1.1 equiv. of *n*-BuLi in hexane (1.35 M). After maintaining the reaction at 0°C for 10 min it was allowed to warm to room temperature, followed by dropwise addition of the corresponding aldehyde in DME (1 M). The reaction mixture was maintained for a further 1.5 h at room temperature, and then quenched by addition of water (3 ml/mmol *n*-BuLi). The organic phase was separated and the aqueous phase extracted with *tert*-butyl methyl ether (3×15 ml). The combined organic phases were dried (Na_2SO_4), the solvent evaporated, and the residue purified via flash chromatography with petroleum ether/*tert*-butyl methyl ether. The enoates **3** were obtained as colorless, highly viscous oils.

Ethyl *E*-(5*R,6*R**)-(±)-5,7-diemethyl-6-[2-(diphenylphosphanyl)benzoyloxy]oct-2-enoate (3a).** From 2.693 g (6.227 mmol) aldehyde **1a** was obtained 2.599 g (83%) of enoate **3a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.74 (d, J=6.6 Hz, 3H, CH_3), 0.78 (d, J=6.8 Hz, 3H, CH_3), 1.23 (t, J=7.1 Hz, 3H, CH_3), 1.72–2.1 (m, 4H), 4.09 (q, J=7.1 Hz, 2H, OCH_2), 4.76 (dd, J=8.1, 3.8 Hz, 1H, OCH), 5.66 (d, J=15.6 Hz, 1H, =$CHCO_2$Et), 6.78 (d pseudo t, J=15.6, 6.7 Hz, CH=), 6.86 (m, 1H, ArH), 7.18–7.36 (m, 12H, ArH), 8.04 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=13.41, 14.23, 18.44, 19.11, 29.71, 34.15, 36.64, 60.03, 81.88, 122.89, 128.07, 128.39 (d, $J_{C,P}$=7.2 Hz, 4 C), 128.54 (2 C), 130.48, 131.87, 133.86 (d, $J_{C,P}$=20.7 Hz, 2 C), 133.9 (d, $J_{C,P}$=18.1 Hz), 134.11 (d,

$J_{C,P}$=20.9 Hz, 2 C), 134.19, 138.05 (d, $J_{C,P}$=12.7 Hz), 138.17 (d, $J_{C,P}$=11.6 Hz), 141.37 (d, $J_{C,P}$=28.5 Hz), 146.25, 166.25 (d, $J_{C,P}$=2.9 Hz), 166.34. ^{31}P NMR (161.978 MHz, $CDCl_3$): δ=−3.5. $C_{31}H_{35}O_4P$ (502.6): calcd C 74.08, H 7.02; found C 73.98, H 7.28.

Diethyl *E*-(5*R,6*S**,7*S**)-(±)-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]oct-2-endioate (3b).** From 3.575 g (7.288 mmol) aldehyde **1b** was obtained 3.046 g (74%) of enoate **3b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.76 (d, *J*=6.7 Hz, 3H, CH_3), 1.02 (d, *J*=7.2 Hz, 3H, CH_3), 1.06 (d, *J*=7.2 Hz, 3H, CH_3), 1.22 (t, *J*=7.2 Hz, 3H, CH_3), 1.7–2.8 (m, 3H), 2.77 (dq, *J*=8.2, 7.1 Hz, CH), 3.93 (q, *J*=7.2 Hz, 2H, OCH_2), 4.11 (q, *J*=7.2 Hz, 2H, OCH_2), 5.17 (dd, *J*=8.4, 3.8 Hz, 1H, OCH), 5.68 (d, *J*=15.6 Hz, 1H, =$CHCO_2$Et), 6.76 (ddd, *J*=15.6, 8.0, 6.8 Hz, CH_2–C*H*=), 6.86 (m, 1H, ArH), 7.16–7.31 (m, 12H, ArH), 8.0 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=13.3, 14.06, 14.18, 14.37, 34.09, 36.43, 42.42, 60.27, 60.82, 77.81, 123.25, 128.28, 128.55 (d, *J*=7.2 Hz, 4 C), 128.69 (2 C), 130.86 (d, $J_{C,P}$=2.1 Hz), 132.14, 133.7 (d, $J_{C,P}$=17.7 Hz), 133.96 (d, $J_{C,P}$=21.0 Hz, 2 C), 134.24 (d, $J_{C,P}$=22.0 Hz, 2 C), 134.32, 137.96 (d, $J_{C,P}$=12.3 Hz), 138.32 (d, $J_{C,P}$=11.5 Hz), 141.42 (d, $J_{C,P}$=28.1 Hz), 146.78, 165.65 (d, $J_{C,P}$=2.8 Hz), 166.53, 173.6. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−3.4. $C_{33}H_{37}O_6P$ (560.6): calcd C 70.70, H 6.65; found C 70.75, H 6.44.

Ethyl *E*-(5*R,6*R**,7*R**)-(±)-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]-8-(triphenyl)-methoxy-oct-2-enoate (3c).** From 4.628 g (6.699 mmol) aldehyde **1c** was obtained 3.976 g (78%) of enoate **3c**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.75 (d, *J*=6.7 Hz, 3H, CH_3), 0.95 (d, *J*=6.8 Hz, 3H, CH_3), 1.26 (t, *J*=7.1 Hz, CH_3), 1.65–2.1 (m, 4H), 2.92 (dd, *J*=8.9, 7.7 Hz, 1H, OCH_2), 3.1 (dd, *J*=9.0, 4.2 Hz, 1H, OCH_2), 4.14 (q, *J*=7.2 Hz, 2H, OCH_2), 4.89 (dd, *J*=7.8, 4.2 Hz, 1H, OCH), 5.67 (d, *J*=15.6 Hz, 1H, =$CHCO_2$Et), 6.76 (m, 1H, CH=), 6.86 (m, 1H, ArH), 7.1–7.46 (m, 27H, ArH), 7.73 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=13.63 14.39, 15.09, 34.15, 36.07, 36.56, 60.20, 64.93, 78.90, 86.71, 123.01, 126.9–147.2 (all Aryl-C), 147.2, 165.6 (d, $J_{C,P}$=2.9 Hz), 166.55. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−3.3. $C_{50}H_{49}O_5P$ (760.9): calcd C 78.93, H 6.49; found C 78.76, H 6.50.

Ethyl *E*-(5*R,6*S**,7*S**)-(±)-5,7-dimethyl-8-[2,2-(dimethyl)-propionyloxy]-6-[2-(diphenylphosphanyl)benzoyloxy]-oct-2-enoate (3d).** From 390 mg (0.732 mmol) aldehyde **1d** was obtained 357 mg (81%) of enoate **3d**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82 (d, *J*=6.3 Hz, 3H, CH_3), 0.85 (d, *J*=6.5 Hz, 3H, CH_3), 1.11 [s, 9H, $C(CH_3)_3$], 1.22 (t, *J*=7.1 Hz, 3H, CH_3), 1.84 (m, 2H), 2.08 (m, 2H), 3.8 (m, 2H, OCH_2), 4.1 (q, *J*=7.2 Hz, 2H, OCH_2), 5.01 (dd, *J*=6.4, 4.6 Hz, 1H, OCH), 5.67 (d, *J*=15.6 Hz, 1H, =$CHCO_2$Et), 6.77 (d pseudo t, *J*=15.6, 7.7 Hz, 1H, =CH), 6.87 (m, 1H, ArH), 7.1–7.38 (m, 12H, ArH), 8.02 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=12.65, 14.14, 14.20, 27.05 (3 C), 34.45, 34.50, 36.31, 38.67, 59.99, 65.89, 77.40, 123.14, 128.05, 128.33 (d, $J_{C,P}$=7.2 Hz, 4 C), 128.5 (2 C), 130.45, 131.91, 133.68 (d, $J_{C,P}$=16.3 Hz), 133.84 (d, $J_{C,P}$=20.8 Hz, 2 C), 133.93 (d, $J_{C,P}$=20.9 Hz, 2 C), 134.23, 137.81 (d, $J_{C,P}$=12.2 Hz), 137.94 (d, $J_{C,P}$=9.3 Hz), 141.16 (d, $J_{C,P}$=28.3 Hz), 146.24, 165.93 (d, $J_{C,P}$=2.6 Hz), 166.12, 178.14. ^{13}P NMR (81.015 MHz, $CDCl_3$): δ=−3.7. $C_{36}H_{43}O_6P$ (602.7): calcd C 71.74, H 7.19; found C 71.60; H 6.98.

Ethyl *E*-(5*R*,6*S*,7*S*)-(−)-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]-8-[(4*R*)-isopropyl-2-oxazolidin-3-yl]-oct-2-enoate [(−)-3e]. From 1.147 g (2 mmol) aldehyde (−)-**1e** was obtained 910 mg (71%) of enoate (−)-**3e**. $[\alpha]_D$=−60.0 (*c*=2.0, CH_2C1_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.50 (d, *J*=6.9 Hz, 3H, CH_3), 0.74 (d, *J*=7.0 Hz, 3H, CH_3), 0.87 (d, *J*=6.8 Hz, 3H, CH_3), 1.12 (d, *J*=7.0 Hz, 3H, CH_3), 1.26 (t, *J*=7.0 Hz, 3H, CH_3), 1.67 (d pseudo t, *J*=14.3, 6.5 Hz, 1H, CH_2), 1.92 (m, 1H, CH_2), 2.08 (m, 2H, CH), 4.14 (m, 4H), 4.34 (m, 2H), 5.47 (dd, *J*=9.7, 2.6 Hz, 1H, OCH), 5.65 (d, *J*=15.6 Hz, 1H, =$CHCO_2$Et), 6.77 (ddd, *J*=15.6, 8.3, 6.7 Hz, 1H, CH=), 6.88 (m, 1H, ArH), 7.18–7.36 (m, 12H, ArH), 8.0 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDC1_3$): δ=12.68, 14.16, 14.21, 14.63, 17.97, 28.04, 33.79, 36.37, 39.63, 58.58, 60.05, 62.92, 77.63, 123.0, 127.97, 128.24, 128.38 (d, $J_{C,P}$=6.9 Hz, 4 C), 128.55 (2 C), 130.70 (d, $J_{C,P}$=2.0 Hz), 131.93, 133.52 (d, $J_{C,P}$=17.9 Hz), 133.58 (d, $J_{C,P}$=20.4 Hz, 2 C), 134.20, 134.23 (d, $J_{C,P}$=21.2 Hz, 2 C), 137.97 (d, $J_{C,P}$=16.2 Hz), 138.16 (d, $J_{C,P}$=10.6 Hz), 141.45 (d, $J_{C,P}$=28.8 Hz), 146.77, 153.70, 165.18 (d, $J_{C,P}$=2.6 Hz), 166.41, 173.9. ^{31}P NMR (81.015 MHz, $CDC1_3$): δ=−3.3. $C_{37}H_{42}NO_7P$ (643.7): calcd C 69.04, H 6.58, N 2.18; found C 69.02 H 6.62 N 2.13.

General procedure for the addition of dimethylcuprate to enoates 3 (→4)

A nitrogen flask was loaded with 1.5 equiv. CuI, and evacuated with an oil pump. Subsequently, the flask was heated with a Bunsen burner until the CuI showed a yellowish color, at which time heating was stopped. The flask was allowed to reach room temperature, and subsequently flushed with dry nitrogen. Diethylether (0.1 M) was added, and the suspension was cooled to −5°C, followed by dropwise addition of 3 equiv. of a methyl lithium solution in diethylether. The resulting colorless clear solution was stirred for further 30 min at this temperature. Subsequently, the reaction mixture was cooled to −78°C, and a solution of 1 equiv. of the enoate in diethyl ether (0.2 M) was added dropwise. An immediate color change from colorless to intensive yellow–orange was observed (for some cases the reaction mixture was still homogenous at this point, others turned into a suspension). After maintaining the reaction mixture at this temperature for a further 1 h the cooling bath was removed, and the reaction mixture was allowed to warm within 15 min to 0°C, were it was maintained for a further 90 min. During this period an intensive yellow precipitate was formed. The reaction was quenched by the addition of sat. aqu. NH_4Cl-solution (10 ml/mmol cuprate). The mixture was diluted with *tert*-butyl methyl ether and 15% aqu. NH_3-solution (ca. 25 ml/mmol enoate). The mixture was shaken vigorously until both phases were homogenous. The aqueous phase was separated and extracted two more times with *tert*-butyl methyl ether. The combined organic phases were dried (Na_2SO_4) and the solvent removed in vacuo. NMR spectroscopy of this crude product was used to determine the diastereomer ratio.

Flash chromatography with petroleum ether/*tert*-butyl methyl ether furnished the 1,4-addition products **4a**–**g** as colorless, highly viscous oils.

Ethyl (3*R,5*R**,6*R**)-(±)-6-[2-(diphenylphosphanyl)benzoyloxy]-3,5,7-trimethyloctanoate (4a).** From 2.535 g (5.044 mmol) **3a** was obtained 2.43 g (93%) of **4a**. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn*, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.7 (m, 12H, 4 CH_3), 1.0 (m, 1H), 1.1 (m, 4H), 1.7–2.1 (m, 5H), 4.0 (q, J=7.2 Hz, 2H, OCH_2), 4.7 (dd, J=7.2, 5.0 Hz, 1H, HCO), 6.8 (m, 1H, ArH), 7.2–7.3 (m, 12H, ArH), 8.0 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=13.51, 14.23, 17.98, 19.05, 19.30, 27.62, 29.45, 31.80, 40.54, 42.62, 59.99, 82.80, 128.05, 128.35 (d, $J_{C,P}$=7.2 Hz, 4 C), 129.45 (2 C), 130.45, 131.76, 133.90 (d, $J_{C,P}$=20.8 Hz, 2 C), 134.0 (d, $J_{C,P}$=21.1 Hz, 2 C), 134.21 (C1′ expected at ca. 134 as a doublet is obscured by the signals at 134.0–134.21), 138.21 (d, $J_{C,P}$=12.2 Hz, 2 C), 141.15 (d, $J_{C,P}$=28.3 Hz), 166.30 (d, $J_{C,P}$=2.6 Hz), 172.7 8. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−2.8 $C_{32}H_{39}O_4P$(518.6): calcd C 74.11, H 7.58; found C 74.08, H 7.63.

Diethyl (3*R,5*R**,6*S**,7*S**)-(±)-6-[2-(diphenylphosphanyl)-benzoyloxy]-3,5,7-trimethyloctandioate (4d).** From 670 mg (1.195 mmol) **3b** was obtained 472 mg (68%) of **4d**. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn,* 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.74 (d, J=6.7 Hz, 3H, CH_3), 0.80 (d J=7.2 Hz, 3H, CH_3), 1.05 (d, J=7.2 Hz, 3H, CH_3), 1.06 (t, J=7.1 Hz, 3H, CH_3), 1.15 (t, J=7.3 Hz, 3H, CH_3), 1.0–1.2 (m, 2H), 1.8–2.1 (m, 4H), 2.75 (pseudo quintett, J=7.2 Hz, 1H), 3.93 (q, J=7.1 Hz, 2H, OCH_2), 4.03 (q, J=7.1 Hz, 2H, OCH_2), 5.10 (dd, J=7.4, 4.7 Hz, 1H, OCH), 6.84 (m, 1H, ArH) 7.12–7.35 (m, 12H, ArH), 8.04 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=13.23, 13.86, 13.98, 14.16, 18.87, 27.49, 31.68, 40.06, 41.98, 42.47, 59.97, 60.47, 78.59, 128.10, 128.29 (d, $J_{C,P}$=7.7 Hz, 4 C), 128.38 (2 C), 130.60 (d, $J_{C,P}$=2.2 Hz), 131.85, 133.70 (d, $J_{C,P}$=20.6 Hz, 2 C), 133.82 (d, $J_{C,P}$=18.5 Hz), 133.91 (d, $J_{C,P}$=20.8 Hz, 2 C), 134.19, 138.0 (d, $J_{C,P}$=17.1 Hz), 138.17 (d, $J_{C,P}$=16.7 Hz) 141.0 (d, $J_{C,P}$=28.1 Hz), 165.48 (d, $J_{C,P}$=2.4 Hz), 172.73, 173.47. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−3.8. $C_{34}H_{41}O_6P$ (576.7): calcd C 70.82, H 7.17; found C 70.92, H 7.00.

Ethyl (3*R,5*R**,6*S**,7*R**)-(±)-6-[2-(diphenylphosphanyl)-benzoyloxy]-3,5,7-trimethyl-8-(triphenyl)methoxy-octanoate (4e).** From 1.251 g (1.644 mmol) **3c** was obtained 910 mg (71%) of **4e**. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn,* 86:14). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.76 (d, J=6.2 Hz, 3H, CH_3), 0.77 (d J=6.6 Hz, 3H, CH_3), 1.07, (d, J=6.7 Hz, 3H, CH_3), 1.12 (t, J=7.1 Hz, 3H, CH_3), 1.2–1.4 (m, 2H) 1.7–2.04 (m, 5H), 3.0 (m, 1H), 3.2 (m, 1H), 4.1 (q, J=7.1 Hz, 2H, OCH_2), 4.92 (dd, J=6.8, 5.2 Hz, 1H, OCH), 6.9 (m, 1H, ArH), 7.1–7.5 (m, 27H, ArH), 7.84 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDC1_3$): δ=13.71, 14.33, 15.21, 18.97, 27.62, 31.79, 35.91, 40.33, 42.69, 60.06, 64.77, 80.04, 86.62, 126.83–144.3 (all Aryl-C), 166.0, 172.90. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−3.3. $C_{51}H_{53}O_5P$ (777.0): calcd C 78.84, H 6.88; found C 78.75, H 6.58.

Ethyl (3*R,5*R**,6*S**,7*S**)-(±)-8-[2,2-(dimethyl)propionyloxy]-6-[2-(diphenylphosphanyl)-benzoyloxy]-3,5,7-trimethyloctanoate (4f).** From 280 mg (0.465 mmol) **3d** was obtained 172 mg (60%) of **4f**. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn,* 85:15). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.84 (m, 9H, 3 CH_3), 1.08 (m, 1H) 1.17 [s, 9H, $C(CH_3)_3$], 1.2 (t, J=7.1 Hz, 3H, CH_3), 1.22 (m, 1H), 1.78–2.2 (m, 5H), 3.85 (m, 2 H OCH_2), 4.08 (m, 2H, OCH_2), 5.0 (pseudo t, J=5.8 Hz, 1H, OCH), 6.91 (m, 1H, ArH), 7.2–7.4 (m, 12H, ArH), 8.1 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDC1_3$): δ=12.31, 13.93, 14.18, 18.83, 27.1 (3 C) 27.50, 32.07, 34.27, 38.71, 40.27, 42.64, 60.03, 66.19, 78.65, 128.09, 128.34 (d, $J_{C,P}$=7.3 Hz, 4 C) 128.48 (d, $J_{C,P}$=2.3 Hz, 2 C), 130.49 (d, $J_{C,P}$=2.3 Hz), 131.88, 133.84 (d, $J_{C,P}$=20.7 Hz, 2 C), 133.94 (d $J_{C,P}$=17.9 Hz), 133.96 (d, $J_{C,P}$=21.0 Hz, 2 C), 134.28, 138.0 (d, $J_{C,P}$=12.1 Hz, 2 C), 140.0 (d, $J_{C,P}$=28.0 Hz), 166.03 (d, $J_{C,P}$=2.8 Hz), 172.74, 178.25. ^{31}P NMR (81.015 MHz, $CDCI_3$): δ=−3.3. $C_{37}H_{47}O_6F$ (618.7): calcd C 71.82, H 7.66; found C 71.60, H 7.35.

Ethyl (3*R*,5*R*,6*S*,7*S*)-(−)-6-[2-(diphenylphosphanyl)benzoyloxyl-8-[(4*R*)-isopropyl-2-oxazolidin-3-yl]-3,5,7-trimethyloctanoate [(−)-4g]. From 280 mg (0.435 mmol) (−)-**3e** was obtained 242 mg (85%) of (−)-**4g**. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn*, 95:5). $[\alpha]_D$=−35.7 (c=1.85, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.42 (d, J=6.9 Hz, 3H, CH_3), 0.68 (d, J=7.1 Hz, 3H, CH_3), 0.72 (d, J=6.3 Hz, 3H, CH_3), 0.82 (d, J=6.8 Hz, 3H, CH_3), 1.06 (d, J=7.0 Hz, 3H, CH_3), 1.18 (t, J=7.2 Hz, 3H, CH_3), 1.8–2.1 (m, 7H), 4.1 (m, 4H), 4.30 (m, 2H), 5.36 (dd, J=9.5, 2.8 Hz, 1H, OCH), 6.82 (m, 1H, ArH), 7.1–7.4, m, 12H, ArH 8.0 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=12.91, 14.31 (2 C), 14.82, 18.11, 19.11, 27.61, 28.19, 31.54, 39.73, 40.53, 42.47, 58.66, 60.09, 63.01, 78.57, 128.17, 128.33 (d, $J_{C,P}$=7.1 Hz, 2 C), 128.43 (d, $J_{C,P}$=8.1 Hz, 2 C), 128.58 (2 C), 130.78, 131.97, 133.57 (d, $J_{C,P}$=20.2 Hz, 2 C), 133.94 (d, $J_{C,P}$=18.8 Hz), 134.27 (d, $J_{C,P}$=21.3 Hz, 2 C), 134.41, 138.36 (d, $J_{C,P}$=13.8 Hz), 138.37 (d, $J_{C,P}$=11.0 Hz), 141.21 (d, $J_{C,P}$=28.6 Hz), 153.8, 165.2 (d, $J_{C,P}$=2.5 Hz), 173.0, 174.20. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−3.1 $C_{38}H_{46}NO_7P$ (659.8): calcd C 69.07, H 7.17, N 2.12; found C 68.86, H 7.09, N 2.30.

Ethyl (3*R,5*R**,6*R**)-(±)-3-Butyl-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]-octanoate (4b).** A similar procedure as described for the addition of dimethylcuprate was employed, except di-*n*-butylcuprate was prepared at −30°C. From 251 mg (0.5 mmol) **3a** was obtained 190 mg (68%) of **4b,** as a colorless, highly viscous oil. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn*, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.8 (d, J=6.6 Hz, 3H, CH_3), 0.84–1.5 (m, 19H), 1.6 (m, 1H), 1.8–2.0 (m, 3H), 2.1 (m, 1H), 2.3 (dd, J=14.7, 6.0 Hz, 1H, CH_2), 4.09 (m, 2H, OCH_2), 4.8 (dd, J=7.2, 4.7 Hz, 1H, OCH), 6.92 (m, 1H, ArH), 7.2–7.4 (m, 12H, ArH), 8.1 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=14.03, 14.16, 14.38, 18.22, 19.48, 23.09, 28.34, 29.67, 31.96, 32.44, 33.04, 38.47, 39.82, 60.17, 82.84, 128.2, 128.51 (d, $J_{C,P}$=7.1 Hz, 4 C), 128.56 (2 C), 130.59, 131.89, 133.97 (d, $J_{C,P}$=20.4 Hz), 134.11 (d, $J_{C,P}$=20.8 Hz, 4 C), 134.42, 138.43 (d, $J_{C,P}$=12.8 Hz, 2 C), 144.25 (d, $J_{C,P}$=28.1 Hz),

166.48, 173.35. ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta=-3.1$. $C_{35}H_{45}O_4P$ (560.7): calcd C 74.97, H 8.09; found C 75.20, H 8.23.

Ethyl (3*R,5*R**,6*R**)-(±)-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]-3-vinyloctanoate (*anti*-4c) and ethyl (3*R**,5*S**,6*S**)-(±)-5,7-dimethyl-6-[2-(diphenylphosphanyl)-benzoyloxy]-3-vinyloctanoate (*syn*-4c).** A similar procedure as described for the addition of dimethylcuprate was employed, except divinylcuprate was prepared at −35°C. From 251 mg (0.5 mmol) **3a** was obtained 162 mg (61%) of **4c**, as a colorless, highly viscous oil. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn*, 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.67$ (d, $J=6.6$ Hz, 3H, CH_3), 0.72 (d, $J=6.8$ Hz, 3H, CH_3), 0.76 (d, $J=6.7$ Hz, 3H, CH_3), 0.95–1.1 (m, 2H), 1.12 (t, $J=7.2$ Hz, 3H, CH_3), 1.7–1.88 (m, 3H), 2.14 (m, 1H), 2.5 (m, 1H), 4.0 (q, $J=7.0$ Hz, 2H, OCH_2), 4.67 (dd, $J=7.4$, 4.8 Hz, 1H, OCH), 4.95 (m, 2H, $=CH_2$), 5.40 (ddd, $J=17.2$, 10.1, 9.1 Hz, 1H, =CH), 6.84 (m, 1H, ArH), 7.14–7.32 (m, 12H, ArH), 8.02 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): signals of minor (*syn*) diastereomer in [ ]; $\delta=12.90$, 14.12, 17.91, 19.13, 29.4 1, 31.75, 38.27, 38.45 [38.37], 40.93 [39.95] 60.02, 83.03 [81.21], 115.73, 127.95, 128.27 (d, $J_{C,P}=7.1$ Hz, 4 C), 128.36 (2C), 130.35, 131.67, 133.84 (d, $J_{C,P}=20.8$ Hz, 2 C), 133.89 (d, $J_{C,P}=20.9$ Hz, 2 C), 134.12, (C1′ expected at ca. 134 as a doublet is obscured by the signals at 133.84–134.12), 138.12 (d, $J_{C,P}=12.3$ Hz, 2 C), 140.26, 141.10 (d, $J_{C,P}=28.0$ Hz), 166.25 (d, $J_{C,P}=2.9$ Hz), 172.05. ^{31}P NMR (81.015 MHz, $CDCl_3$): $\delta=-3.1$ [−3.3]. $C_{33}H_{39}O_4P$ (560.7): calcd C 74.70, H 7.41; found C 74.35, H 7.26.

(3*R,5*R**,6*R**)-(±)-3,5,7-Trimethyloctane-1,6-diol (7).** To a magnetically stirred suspension of 574 mg (15.12 mmol) lithium aluminum hydride in 25 ml diethyl ether was added dropwise at 0°C a solution of 2.614 g (5.04 mmol) **4a** in 5 ml diethyl ether. After maintaining the reaction mixture for a further 15 min at 0°C and, subsequently, a further 2 h at room temperature, 0.6 ml H_2O, 0.6 ml of a 15% aqu. NaOH-solution, and Na_2S0_4 (ca. 1 g) were added successively. The reaction mixture was filtered, and the residue was exhaustively washed with *tert*-butyl methyl ether. Solvent was removed in vacuo. Flash chromatography with petroleum ether/*tert*-butyl methyl ether (5:1–1:1 gradient) furnished 1.374 g (93%) [2-(Diphenylphosphanyl)phenyl]methanol as a colorless, highly viscous oil (spectroscopic and analytical data identical to those reported previously),[24] and 895 mg (94%) of the diol **7** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.78$ (d, $J=6.7$ Hz, 3H, CH_3), 0.81 (d, $J=6.5$ Hz, 3H, CH_3), 0.82 (d, $J=6.8$ Hz, 3H, CH_3), 1.0–1.7 (m, 7H, CH, CH_2), 2.2 (m br, 2H, OH), 2.96 (dd, $J=7.3$, 4.1 Hz, 1H, HCOH), 3.6 (m, 2H, CH_2OH). ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta=12.60$, 18.19, 19.17, 19.38, 26.67, 30.73, 32.19, 40.62, 41.65, 60.65, 80.91. MS (70 eV); *m*/*z* (%): 189 (1) [M^++H], 145 (81) [$M^+-C_3H_7$], 127 (75) [M^+-H_2O, $-C_3H_7$], 109 (100) [$M^+-2\times H_2O$, $-C_3H_7$], 73 (95) [$Me_2CHCH(OH)$]. $C_{11}H_{24}O_2$ (188.3): calcd C 70.16, H 12.85; found C 69.77, H 12.80.

(3*R,5*R**,6*R**)-(±)-6-Hydroxy-3,5,7-trimethyloctyl [4-(methyl)phenyl]sulfonate (8).** To a solution of 753 mg (4 mmol) **7**, and 1.266 g (16 mmol) pyridine in CH_2C1_2 (20 ml) was added at 0°C 839 mg (4.4 mmol) *p*-toluene sulfonic acid chloride. The reaction mixture was maintained for a further 3 h at 0°C, and for a further 16 h at room temperature. Subsequently, 10 ml of sat. aqu. NH_4Cl solution was added, the mixture diluted with 200 ml *tert*-butyl methyl ether, and the organic phase was separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2×30 ml), the combined organic phases were dried (Na_2S0_4), and the solvent was evaporated. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (5:1–4:1 gradient) furnished 990 mg (72%) of tosylate **8** as a colorless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.71$ (d, $J=6.6$ Hz, 3H, CH_3), 0.72 (d, $J=6.2$ Hz, 3H, CH_3), 0.79 (d, $J=6.6$ Hz, 3H, CH_3), 0.86 (d, $J=6.6$ Hz, 3H, CH_3), 1.03 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.58 (m, 4H, 3 CH, OH), 2.37 (s, 3H, CH_3), 2.9 (dd, $J=7.1$ Hz, 4.2 Hz, 1H, HCO), 4.0 (m, 2H, CH_2O), 7.28 (d, $J=8.3$ Hz, 2H, ArH), 7.71 (d, $J=8.2$ Hz, 2H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta=12.7$, 18.3, 18.9, 19.6, 21.7, 26.6, 30.9, 32.3, 36.6, 41.3, 69.0, 80.9, 128.0 (2 C), 130.0 (2 C), 133.2, 144.8. HRMS: calcd (for $C_{18}H_{30}SO_4$) 342.1865; found 342.1862. $C_{18}H_{30}SO_4$ (342.5): calcd C 63.12, H 8.83; gef. C 62.92, H 8.93.

(3*R,4*R**,6*R**)-(±)-8-(2-Nitro)phenylselenyl-2,4,6-trimethyloctan-3-ol (9).** To a solution of 125 mg (0.55 mmol) 2-nitrophenyl selenocyanate in 1 ml DMF was added at room temperature 27 mg (0.6 mmol) $NaBH_4$ and maintained for a further 3 h at this temperature. Subsequently, a solution of 171 mg (0.5 mmol) **8** in 1 ml DMF was added dropwise. The reaction mixture was maintained for a further 3 h at room temperature, followed by addition of 5 ml of a sat. aqu. NH_4Cl solution. The mixture was diluted with 30 ml *tert*-butyl methyl ether, the aqueous phase separated, and the organic phase washed with water (2×20 ml). The organic phase was dried (Na_2SO_4), and the solvent evaporated to give 186 mg (quant.) of selenoether **9** as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.78$ (d, $J=6.6$ Hz, 3H, CH_3), 0.79 (d, $J=6.6$ Hz, 3H, CH_3), 0.87 (d, $J=6.4$ Hz, 6H, 2 CH_3), 1.0–1.8 (m, 8H, CH, CH_2, OH), 2.9 (m, 3H, OCH, CH_2Se), 7.2 (m, 1H, ArH), 7.43 (m, 2H, ArH), 8.19 (d, $J=8.4$ Hz, 1H, ArH). ^{13}C NMR (50.329 MHz, $CDCl_3$): $\delta=12.6$, 18.3, 18.9, 19.3, 23.8, 30.6, 30.8, 32.1, 35.9, 41.1, 80.7, 125.1, 126.3, 128.9, 133.5, 133.8, 146.7. $C_{17}H_{27}N^{80}SeO_3$: calcd 373.1156, found 373.1151 (HRMS).

(3*R,4*R**,6*R**)-(±)-Trimethyl-7-octen-3-ol (10).** To a solution of 186 mg (0.5 mmol) selenoether **9** in 3 ml THF was added at room temperature 317 mg (5 mmol) of a 30% aqu. hydrogen peroxide solution, and the reaction was kept at this temperature for a further 3 h. Subsequently, 20 ml of H_2O and 50 ml of *tert*-butyl methyl ether was added, the organic phase separated, and washed with 10 ml sat. aqu. $NaHCO_3$. After drying the organic phase (Na_2SO_4) the solvent was evaporated, and the residue purified via flash chromatography with petroleum ether/*tert*-butyl methyl ether (4:1) to give 82 mg (96%) of alkene **10** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.85$ (d, $J=6.8$ Hz, 3H, CH_3), 0.86 (d, $J=6.7$ Hz, 3H, CH_3), 1.0 (d, $J=6.7$ Hz, 6H, 2 CH_3), 1.21 (d pseudo t, $J=13.5$, 7.5 Hz, 1H, CH_2), 1.38 (d pseudo t, $J=13.5$, 6.9 Hz, 2H, CH_2, OH), 1.74 (m, 2H, CH), 2.26 (pseudo sept, $J=6.8$ Hz, 1H, C*H*–CH=CH_2), 3.12 (dd, $J=7.9$, 3.5 Hz, 1H, HCO), 4.9–5.0 (m, 2H, $=CH_2$), 5.7

(ddd, J=17.2, 10.2, 7.7 Hz, 1H, =CH). ^{13}C NMR (75.469 MHz, $CDC1_3$): δ=13.2, 18.9, 19.3, 20.3, 25.2, 31.2, 32.2, 41.0, 79.6, 112.5, 145.1. $C_{11}H_{22}O$ (170.3): calcd C 77.59, H 13.02; found C 77.43, H 13.14.

(2*R,3*R**,5*R**,6*R**)-(±)-6-Isopropyl-3,5-dimethyl-tetrahydropyran-2-ol and (2*R**,3*R**,5*R**,6*R**)-(±)-6-isopropyl-3,5-dimethyl-tetrahydropyran-2-ol (11).** A solution of 82 mg (0.482 mmol) alkene **10** in 5 ml CH_2Cl_2 was cooled to −78°C and treated with a dilute stream of ozone until the appearance of a faint blue color signaled the complete consumption of the olefin. The solution was purged with oxygen until the blue color bleached and was then treated with 138 mg (0.528 mmol) of triphenyl phosphane. The reaction mixture was allowed to warm (with the cold bath) to room temperature overnight. Silica gel was added, and the mixture was evaporated to dryness. Flash chromatography with petroleum ether/*tert*-butyl methyl ether (10:1–4:1 gradient) furnished 82 mg (99%) of the lactols **11** as a colorless oil. Spectroscopic and analytical data correspond to those previously reported.[25]

(3*R,5*R**,6*R**)-(±)-6-Isopropyl-3,5-dimethyl-tetrahydropyran-2-one (12).** A solution of 82 mg (0.476 mmol) of the lactols **11** in 5 ml CH_2Cl_2, was treated with 960 mg (0.96 mol) of PCC on $A1_2O_3$. The reaction mixture was stirred for 36 h at room temperature and filtered with 150 ml *tert*-butyl methyl ether through a pad of silica. The solvent was evaporated and the residue purified via flash chromatography with petroleum ether/*tert*-butyl methyl ether (5.67:1) to yield 57 mg (70%) of the lactone **12** as a colorless oil. ^{1}H NMR (500 MHz, $CDC1_3$): δ=0.8 (d, J=6.8 Hz, 3H, CH_3), 0.9 (d, J=7.1 Hz, 3H, CH_3), 0.99 (d, J=6.4 Hz, 3H, CH_3), 1.2 (d, J=7.1 Hz, 3H, CH_3), 1.58 (d pseudo t, J=12.3, 3.9 Hz, 1H, CH_2), 1.73 [m, 1H, C*H*$(CH_3)_2$], 1.84 (ddd, J=13.5, 7.2, 3.2 Hz, 1H, CH_2), 2.06 (m, 1H, H at C_5), 2.51 (ddq, J=12.3, 7.2, 7.1 Hz, 1H, CH–C=O). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=10.38, 17.67, 17.71, 19.54, 27.73, 30.02, 30.94, 36.33, 89.2, 174.2. $C_{10}H_{18}O_2$: calcd 170.1307; found 170.1309 (HRMS).

Control experiments probing the role of the *o*-DPPB as a cuprate-directing group

Ethyl *E*-(5*R,6*R**)-(±)-5,7-dimethyl-6-[2-(diphenylphosphinoyl)benzoyloxy]oct-2-enoate (5).** To a solution of 231 mg (0.416 mmol) enoate **3a** in 5 ml CH_2Cl, was added at room temperature 0.3 ml of a 30% aqu. hydrogen peroxide solution. After maintaining the reaction mixture for 2 h at this temperature, it was diluted with 30 ml *tert*-butyl methyl ether, and washed with 10 ml H_2O. The organic phase was separated, dried (Na_2SO_4), and the solvent evaporated to give 240 mg (quant.) of the phosphane oxide **5** as a colorless, highly viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.64 (d, J=6.6 Hz, 3H, CH_3), 0.68 (d, J=6.8 Hz, 3H, CH_3), 0.74 (d, J=6.6 Hz, 3H, CH_3), 1.15 (t, J=7.1 Hz, 3H, CH_3), 1.63–2.0 (m, 4H, CH_2, 2 CH), 4.05 (q, J=7.1 Hz, 2H, OCH_2), 4.54 (dd, J=8.0, 3.6 Hz, 1H, HCO), 5.65 (d, J=15.6 Hz, 1H, =CH–CO_2Et), 6.72 (d pseudo t, J=15.6, 7.7 Hz, 1H, CH=), 7.3 (m, 6H, ArH), 7.55 (m, 6H, ArH), 7.85 (m, 1H, ArH), 8.0 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDC1_3$): δ=13.55, 14.34, 18.49, 19.17, 29.82, 34.19, 36.61, 60.15, 82.38, 123.03, 128.22 (d, $J_{C,P}$=12.6 Hz, 4 C), 128.77 (d, $J_{C,P}$=8.1 Hz), 131.36 (2 C), 131.83 (d, $J_{C,P}$=10.0 Hz, 4 C), 132.06 (d, $J_{C,P}$=2.1 Hz), 132.84, 133.02 (d, $J_{C,P}$=20.0 Hz), 134.37 (d, $J_{C,P}$=10.9 Hz), 134.43 (d, $J_{C,P}$=12.4 Hz), 134.58, 135.96 (d, $J_{C,P}$=9.5 Hz), 147.07, 165.13 (d, $J_{C,P}$=2.1 Hz), 166.45. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=+33.3. $C_{31}H_{35}O_5P$ (518.6): calcd C 71.80, H 6.80; found C 71.61, H 7.03.

Ethyl (3*R,5*R**,6*R**)-(±)-[2-(diphenylphosphinoyl)benzoyloxy]-3,5,7-trimethyloctanoate (6).** Following a procedure as described for the preparation of phosphane oxide **5**, from 470 mg (0.906 mmol) phosphane **4a** and 0.3 ml of a 30% aqu. hydrogen peroxide solution, 468 mg (97%) of phosphane oxide **6** was obtained as a colorless, highly viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.6 (d, J=6.7 Hz, 3H, CH_3), 0.66 (d, J=6.7 Hz, 3H, CH_3), 0.7 (d, J=6.7 Hz, 3H, CH_3), 0.77 (d, J=6.4 Hz, 3H, CH_3), 1.1 (t, J=7.1 Hz, 3H, CH_3), 0.8–2.1 (m, 7H), 3.96 (m, 2H, OCH_2), 4.47 (dd, J=6.5, 5.3 Hz, 1H, OCH), 7.3 (m, 6H, ArH), 7.56 (m, 6H, ArH), 8.0 (m, 2H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=13.68, 14.32, 17.81, 19.15, 19.31, 27.67, 29.50, 31.92, 40.53, 42.72, 60.15, 83.37, 128.19 (d, $J_{C,P}$=12.7 Hz, 4 C), 130.86 (d, $J_{C,P}$=8.1 Hz), 131.3 (m, 2 C), 131.8 (d, $J_{C,P}$=10.0 Hz, 2 C), 131.93 (d, $J_{C,P}$=9.9 Hz, 2 C), 132.08, 132.15, 132.42 (d, $J_{C,P}$=24.5 Hz), 132.47, 134.02 (d, $J_{C,P}$=11.5 Hz), 134.42 (d, $J_{C,P}$=5.1 Hz), 136.22 (d, $J_{C,P}$=9.1 Hz), 164.87, 172.9. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=+33.8. $C_{32}H_{39}O_5P$ (534.6): calcd C 71.89, H 7.35; found C 71.55, H 7.51.

Attempted addition of dimethylcuprate to phosphane-oxide enoate 5

Following exactly the general procedure as described above for the addition of dimethylcuprate to enoates **3** starting from 259 mg (0.5 mmol) phosphane oxide enoate **5** after the usual aqueous work-up the crude NMR-spectra showed in addition to starting material ca. 30% of undefined decomposition products.

Attempted addition of dimethylcuprate to phosphane-oxide enoate 5 with additional triphenylphosphane

As above, but 131 mg (0.5 mmol) triphenyl phosphane was added to the dimethylcuprate solution before adding the enoate **5**. After the usual aqueous work-up the crude NMR-spectra showed, in addition to starting material, ca. 20% of undefined decomposition products.

Attempted addition of dimethylcuprate to phosphane-oxide enoate 5 with additional methyl 2-(diphenyl-phosphanyl) benzoate (I)

As above, but 160 mg (0.5 mmol) of *o*-DPPB-methylester **I**[26] was added to the dimethylcuprate solution before adding the enoate **5**. After the usual aqueous work-up the crude NMR-spectra showed, in addition to starting material, less than 10% of undefined decomposition products.

Ethyl *Z*-(5*R,6*R**)-(±)-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]oct-2-enoate (*Z*-3a).** To a solution of 796 mg (2.615 mmol) (diphenoxy-phosphoryl)-acetic acid ethyl ester in 40 ml THF was added at −78°C 1.15 ml

Triton® B (benzyltrimethylammonium hydroxide, 40 mass% in MeOH) and kept for a further 30 min at this temperature. Subsequently, a solution of 1.028 g (2.377 mmol) of aldehyde **1a** in 8 ml THF was added dropwise, and the resulting solution was maintained for a further 30 min at this temperature. The reaction mixture was allowed to warm within 2.5 h to −10°C, followed by a quench with 10 ml of a sat. aqu. NH_4Cl solution. THF was replaced by 50 ml of *tert*-butyl methyl ether, 30 ml H_2O was added, and the organic phase separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2×50 ml), the combined organic phases were dried (Na_2SO_4) and the solvent evaporated in vacuo. Flash chromatography petroleum ether/*tert*-butyl methyl ether (19:1) yielded 850 mg (71%) *Z*-**3a** and as a second fraction 154 mg (13%) *E*-**3a**. Both compounds were obtained as colorless, highly viscous oils (from NMR spectra of the crude product, *Z*:*E*=6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81 (d, J=6.5 Hz, 3H, CH_3), 0.82 (d, J=6.7 Hz, 3H, CH_3), 1.24 (t, J=6.9 Hz, 3H, CH_3), 1.94 (m, 2H, CH), 2.32 (d pseudo t, J=14.5, 8.0 Hz, 1H, CH_2), 4.12 (q, J=6.9 Hz, 2H, OCH_2), 4.86 (dd, J=7.0, 4.7 Hz, 1H, OCH), 5.76 (d, J=11.7 Hz, 1H, CH=), 6.16 (d pseudo t, J=11.5, 7.3 Hz, 1H, CH=), 6.92 (m, 1H, ArH), 7.26–7.38 (m, 12H, ArH), 8.13 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=14.18, 18.09, 19.24, 29.54, 30.57, 32.60, 35.05, 59.67, 81.43, 120.93, 128.04, 128.35 (d, $J_{C,P}$=7.3 Hz, 4 C), 128.46 (2 C), 130.48 (d, $J_{C,P}$=1.7 Hz), 131.77, 133.85 (d, $J_{C,P}$=20.8 Hz, 2 C), 134.03 (d, $J_{C,P}$=20.7 Hz, 2 C), (C1′ expected at ca. 134 as a doublet is obscured by the signals at 133.85–134.03), 138.14 (d, $J_{C,P}$=12.6 Hz), 138.18 (d, $J_{C,P}$=12.0 Hz), 141.21 (d, $J_{C,P}$=28.1 Hz), 147.86, 166.13, 166.28 (d, $J_{C,P}$=2.9 Hz). ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−2.8. $C_{31}H_{35}O_4P$ (502.6): calcd C 74.08, H 7.02; found C 73.76, H 7.24.

Ethyl (3*R,5*S**,6*S**)-(±)-3-butyl-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]octanoate (*syn*-4b) and ethyl (3*R**,5*R**,6*R**)-(±)-3-butyl-5,7-dimethyl-6-[2-(diphenylphosphanyl)benzoyloxy]octanoate (*anti*-4b).** A similar procedure as described for the addition of dimethylcuprate was employed, except di-*n*-butylcuprate was prepared at −30°C. From 251 mg (0.5 mmol) Z-**3a** was obtained 139 mg (50%) of *syn*/*anti*-**4b**, as a colorless, highly viscous oil. Diastereomer ratio relative to newly formed stereogenic center (*anti*:*syn*, 34:66). NMR data of *syn*-**93**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.6–1.2 (m, 23H), 1.66–1.9 (m, 3H), 1.98 (dd, J=14.8, 7.7 Hz, 1H, CH_2), 2.14 (dd, J=14.6, 5.1 Hz, 1H, CH_2), 3.98 (m, 2H, OCH_2), 4.7 (dd, J=7.1, 4.7 Hz, 1H, OCH), 6.83 (m, 1H, ArH), 7.14–7.34 (m, 12H, ArH), 8.0 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=14.03, 14.16, 14.38, 18.11, 19.44, 22.95, 28.92, 29.67, 32.03, 32.63, 32.78, 38.47, 39.0, 60.17, 83.03, 127.95, 128.24 (d, $J_{C,P}$=7.1 Hz, 4 C), 128.32 (2 C), 130.33, 131.63, 133.81 (d, $J_{C,P}$=20.8 Hz, 2 C), 133.86 (d, $J_{C,P}$=20.8 Hz, 2 C), 134.14, 134.25 (d, $J_{C,P}$=17.5 Hz), 138.12 (d, $J_{C,P}$=12.2 Hz, 2 C), 140.97 (d, $J_{C,P}$=28.0 Hz), 166.24 (d, $J_{C,P}$=2.4 Hz), 173.08. ^{31}P NMR (81.015 MHz, $CDCl_3$): δ=−3.1. $C_{35}H_{45}O_4P$ (560.7): calcd C 74.97, H 8.09; found C 74.69, H 8.19.

(2*R,4*R**,5*R**)-(±)-5-Methyl-2-(4-methoxyphenyl)-4-(prop-2-enyl)-[1,3]-dioxane (14).** To a solution of 2.05 g (15.75 mmol) diol **13**[7i] and 2.86 g (15.69 mmol) 4-methoxy benzaldehyde dimethylacetal in 50 ml CH_2Cl_2 was added at room temperature 0.15 g (0.79 mmol) *p*-toluene sulfonic-acid mono-hydrate. After maintaining the reaction mixture for 48 h at this temperature 100 ml sat. aqu. $NaHCO_3$ solution was added. The organic phase was separated and the aqueous phase extracted with *tert*-butyl methyl ether (3×50 ml). The combined organic phases were dried ($MgSO_4$) and the solvent evaporated. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (9:1) yielded 2.9 g (74%) of the acetal **14**. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.70 (d, J=6.8 Hz, 3H, CH_3–C_{10}), 1.81 (t, J=1.2 Hz, 3H, CH_3–C_8), 2.04 (m, 1H, H–C_5), 3.52 (pt, J=11.2 Hz, 1H, H_{ax}–C_6), 3.77 (s, 3H, CH_3–$C_{7'}$), 3.85 (d, J=10.0 Hz, 1H, H–C_4), 4.15 (dd, J=11.3, 4.7 Hz, 1H, $H_{eq.}$–C_6), 4.95 (m, 2H, CH_2–C_8), 5.49 (s, 1H, H–C_2), 6.87 (m, 2H, ArH), 7.43 (m, 2H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=12.3 (C_{10}), 17.5 (C_9), 31.2 (C_5), 55.2 ($C_{7'}$), 73.0 (C_6), 88.2 (C_4), 101.0 (C_2), 113.5 (2C) and 127.5 (2C) ($C_{2'}$/$C_{6'}$ and $C_{3'}$/$C_{5'}$), 114.8 (C_8), 131.3 ($C_{1'}$), 142.6 (C_7), 159.9 ($C_{4'}$). $C_{15}H_{20}O_3$, (248.3): calcd C 72.55, H 8.12; found C 72.38, H 7.83.

Ethyl *E*-(5*R)-(±)-5-[(2*S**,4*R**,5*S**)-2-[4-methoxyphenyl]-5-methyl-[1,3]dioxan-4-yl]-hex-2-enoate (16).** To a solution of 18.3 mg (70 μmol) [$Rh(CO)_2$acac] in 6 ml toluene was added at room temperature a solution of 2.34 g (9.42 mmol) olefin **14** in 3 ml toluene and, subsequently, 88 mg (0.284 mmol) triphenylphosphite. After 5 min 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 4 ml of toluene. The autoclave was pressurized with synthesis gas (20 bar) and heated at 70°C for 48 h. Subsequently, the autoclave was cooled rapidly to 20°C and depressurized. The reaction mixture was filtered with 200 ml *tert*-butyl methyl ether through a pad of silica, the solvent was evaporated and the crude product aldehyde 15 subjected directly to HWE olefination conditions.

To a solution of 2.73 g (12.18 mmol) (diethoxy-phosphoryl)-acetic acid ethyl ester in 24 ml DME at 0°C was added dropwise 7.7 ml (11.2 mmol) *n*-BuLi in hexane (1.55 M). After maintaining the reaction at 0°C for 10 min it was allowed to warm to room temperature, followed by dropwise addition of the crude aldehyde **15**, as obtained above, in 6 ml DME. The reaction mixture was maintained for a further 2 h at room temperature, and then quenched by addition of 34 ml H_2O. The organic phase was separated and the aqueous phase extracted with *tert*-butyl methyl ether (3×50 ml). The combined organic phases were dried ($MgSO_4$), the solvent evaporated, and the residue purified via flash chromatography with petroleum ether/ethylacetate (9:1) to yield 2.01 g (61%) of enoate **16** as a colorless oil. Diastereomer ratio relative to the newly formed stereogenic center (*anti*:*syn*, 93:7). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.78 (d, J=6.7 Hz, 3H, CH_3–$C_{7'}$), 1.06 (d, J=6.9 Hz, 3H, CH_3–C_6), 1.28 (t, J=7.1 Hz, 3H, CH_3–$C_{2''}$), 2.01 (m, 2H), 2.20 (m, 1H), 2.43 (m, 1H), 3.37 (dd, J=10.0, 2.0 Hz, 1H, H–$C_{4'}$), 3.47 (pt, J=11.1 Hz, 1H, H_{ax}–$C_{6'}$), 3.79 (s, 3H, CH_3–$C_{7'''}$), 4.09 (dd, J=11.4, 4.7 Hz, 1H, H_{eq}–$C_{6'}$), 4.18 (q, J=7 1 Hz, 2H, CH_2–$C_{1''}$), 5.42 (s, 1H, H–$C_{2'}$), 5.85 (d, J=15.6 Hz, 1H, H–C_2), 6.88 (m, 2H, ArH), 6.99 (m, 1H,

H–C_3), 7.40 (m, 2H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=12.2 ($C_{7'}$), 14.2 ($C_{2''}$), 17.3 (C_6), 30.8 (C_4), 32.8 (C_5), 36.6 ($C_{5'}$), 55.2 ($C_{7'''}$), 60.1 ($C_{1''}$), 73.0 ($C_{6'}$), 86.8 ($C_{4'}$), 101.2 ($C_{2'}$), 113.5 (2C, $C_{2'''}$/$C_{6'''}$), 122.4 (C_2), 127.2 (2C, $C_{3'''}$/$C_{5'''}$), 131.4 ($C_{1'''}$), 148.5 (C_3), 159.8 ($C_{4'''}$), 166.5 (C_1). $C_{20}H_{28}O_5$, (348.4): calcd C 68.94, H 8.10; found C 68.63, H 8.12.

Ethyl *E*-(5*R,6*R**,7*S**)-(±)-6-hydroxy-8-(4-methoxy-benzyloxy)-5,7-dimethyl-2-octenoate (17).** To a mixture of 742 mg (2.13 mmol) enoate **16**, 0.5 g molecular sieves (4 Å) in 21 ml THF at 0°C was added successively 934 mg (12.803 mmol) BH_3·NMe_3 and 1.712 g (12.801 mmol) $AlC1_3$ (in small portions, each ca. 30–40 mg). The reaction mixture was maintained for a further 15 min at this temperature, and then warmed to room temperature and kept for a further 1 h at this temperature. The reaction mixture was diluted with 20 ml diethylether followed by careful addition 23 ml of H_2O and 11 ml 2 M aqu. HCl. The organic phase was separated, and the aqueous phase extracted with diethylether (4×15 ml). The combined organic phases were dried ($MgSO_4$) and the solvent were removed in vacuo. The remaining colorless solid was dissolved in 2 ml MeOH and all volatile components removed in vacuo. This operation was repeated two more times. The resulting oil was purified via flash chromatography with petroleum ether/ethyl acetate (4:1) to yield 526 mg (71%) of the secondary alcohol **17**, and 17 mg (2%) of the regioisomeric primary alcohol **17b**. Spectroscopic data of **17**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (d, *J*=6.9 Hz, 3H), 0.95 (d, *J*=7.0 Hz, 3H) (C*H*$_3$–$C_{5'}$/$C_{7'}$), 1.29 (t, *J*=7.1 Hz, 3H, C*H*$_3$–$C_{2''}$), 1.73 (m, 1H), 1.94 (m, 1H), 2.09 (m, 1H), 2.49 (m, 1H), 3.3 (m, 1H, *H*–C_6), 3.44 (dd, *J*=9.1, 6.7 Hz, 1H, *H*–C_8), 3.53 (d, *J*=4.6 Hz, 1H, O*H*), 3.63 (dd, *J*=9.1, 3.8 Hz, 1H, *H*–C_8), 3.80 (s, 3H, C*H*$_3$–$C_{8''}$), 4.18 (q, *J*=7.1 Hz, 2H, C*H*$_2$–$C_{1''}$), 4.44 (s, 2H, C*H*$_2$–$C_{7''}$), 5.89 (m, 1H, *H*–C_2), 6.88 (m, 2H, ArH), 6.98 (m, 1H, *H*–C_3), 7.24 (m, 2H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=14.2 ($C_{2''}$), 14.5 ($C_{7'}$), 16.8 ($C_{5'}$), 33.5 (C_4), 35.2 (C_5), 37.0 ($C_{5'}$), 55.2 ($C_{8''}$), 60.0 ($C_{1''}$), 73.2 (C_8), 74.4 ($C_{7''}$), 80.2 (C_6), 113.8 (2C, $C_{2''}$/$C_{6''}$), 122.3 (C_2), 129.2 (2C, $C_{3''}$/$C_{5''}$), 129.6 ($C_{1''}$), 148.7 (C_3), 159.3 ($C_{4''}$), 166.5 (C_1). $C_{20}H_{30}O_5$, (350.5): calcd C 68.54, H 8.63; found C 68.41, H 8.85. Spectroscopic data of minor product; *Ethyl E-(5R*,6R*,7S*)-(±)-6-(4-Methoxybenzyloxy)-8-hydroxy-5,7-dimethyl-2-octenoate* **(17b)**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86 (d, *J*=6.8 Hz, 3H), 0.89 (d, *J*=7.1 Hz, 3H, C*H*$_3$–$C_{5'}$/$C_{7'}$), 1.15 (t, *J*=7.1 Hz, 3H, C*H*$_3$–$C_{2''}$), 1.61 (m, 1H), 1.81 (m, 1H), 1.97 (m, 1H), 2.39 (m, 1H), 3.10 (pt, *J*=5.7 Hz, 1H), 3.47 (m, 1H), 3.59 (m, 1H), 3.66 (s, 3H, C*H*$_3$–$C_{8''}$), 4.05 (q, *J*=7.1 Hz, C*H*$_2$–$C_{1''}$), 4.41 (m, 2H, C*H*$_2$–$C_{7''}$), 5.70 (d, *J*=15.6 Hz, 1H, *H*–C_2), 6.74 (m, 2H, ArH), 6.81 (m, 1H, *H*–C_3), 7.18 (m, 2H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=14.3 ($C_{7''}$), 15.7 ($C_{2''}$), 17.2 ($C_{5'}$), 34.7 (C_4), 35.8 (C_5), 37.2 ($C_{5'}$), 55.3 ($C_{8''}$), 60.2 ($C_{1''}$), 65.8 (C_8), 75.2 ($C_{7''}$), 88.5 (C_6), 113.9 (2C, $C_{2''}$/$C_{6''}$), 122.7 (C_2), 129.4 (2C, $C_{3''}$/$C_{5''}$), 130.2 ($C_{1''}$), 148.1 (C_3), 159.1 ($C_{4''}$), 166.1 (C_1).

Ethyl *E*-(5*R,6*R**,7*S**)-(±)-6-[2-(diphenylphosphanyl)-benzoyloxyl-8-(4-methoxybenzyloxy)-5,7-dimethyl-2-octenoate (18).** To a solution of 1 equiv. of 406 mg (1.159 mmol) alcohol **17** in 2 ml CH_2Cl_2 were added successively 463 mg (1.51 mmol) *o*-DPPBA,[27] 185 mg (1.514 mmol) DMAP, and 336 mg (1.628 mmol) DCC. The resulting mixture was stirred at room temperature for 48 h. 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/ethyl acetate (9:1) furnished 626 mg (85%) of the *o*-DPPB ester **18**, as a colorless, highly viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81 (d, *J*=6.7 Hz, 3H), 0.91 (d, *J*=6.9 Hz, 3H) (C*H*$_3$–$C_{5'}$/$C_{7'}$), 1.27 (t, *J*=7.1 Hz, 3H, C*H*$_3$–$C_{2'''}$), 1.84 (m, 1H), 1.97 (m, 1H), 2.13 (m, 1H), 2.21 (m, 1H), 3.19 (dd, *J*=9.2, 7.3 Hz, 1H, *H*–C_8), 3.47 (m, 1H, *H*–C_8), 3.78 (s, 3H, C*H*$_3$–$C_{8''}$), 4.16 (q, *J*=7.0 Hz, 2H, C*H*$_2$–$C_{1'''}$), 4.32 (s, 2H, C*H*$_2$–$C_{7''}$), 4.96 (pt, *J*=6.2 Hz, 1H, *H*–C_6), 5.73 (d, *J*=15.6 Hz, 1H, *H*–C_2), 6.83 (m, 3H, ArH), 6.91 (m, 1H, *H*–C_3), 7.14–7.41 (m, 14H, ArH), 7.98 (m, 1H, ArH). ^{13}C NMR (75.469 MHz, $CDCl_3$): δ=14.3 ($C_{2'''}$), 14.9 ($C_{7'}$), 16.5 ($C_{5'}$), 34.1 (C_4), 34.2 (C_5), 35.3 ($C_{5'}$), 55.2 ($C_{8''}$), 60.1 ($C_{1'''}$), 71.5 (C_8), 72.8 ($C_{7''}$), 80.1 (C_6), 113.7 (2C, $C_{2''}$/$C_{6''}$), 122.7 (C_2), 128.2, 128.5 (d, $J_{C,P}$=6.7 Hz, 4C), 128.6 (2C), 129.2 (2C, $C_{3''}$/$C_{5''}$), 130.6, 130.8 ($C_{1''}$), 131.9, 133.9 (d, $J_{C,P}$=20.8 Hz, 2C), 134.0 (d, $J_{C,P}$=20.8 Hz), 134.2 (d, $J_{C,P}$=22.2 Hz, 2C), 134.3, 138.0 (d, $J_{C,P}$=12.2 Hz), 138.1 (d, $J_{C,P}$=11.0 Hz), 141.1 (d, $J_{C,P}$=27.5 Hz), 147.7 (C_3), 159.1 ($C_{4''}$) 166.3. ^{31}P NMR (81.015 MHz, CH_2Cl_2): δ=−2.8. $C_{39}H_{43}O_6P$ (638.7): calcd C 73.34, H 6.79; found C 73.02, H 7.10.

Ethyl (5*R,6*R**,7*S**)-(±)-6-[2-(diphenylphosphanyl)-benzoyloxy]-8-(4-methoxybenzyloxy)-3,5,7-trimethyloctanoate (19).** An ethereal dimethylcuprate solution (0.1 M), prepared from 69 mg (0.362 mmol) CuI, 0.42 ml (0.718 mmol) of MeLi (1.7 M in diethyl ether), was treated with 39 mg (0.36 mmol) chlorotrimethylsilane prior to the addition of 51 mg (0.08 mmol) of enoate **18**. The reaction was performed, as described for the general procedure for the addition of dimethylcuprate to enoates **3**, to give 36 mg (69%) of the addition product **19** as a colorless, highly viscous oil (dr, 62:38, diastereomers not assigned). Physical data given for the mixture of diastereomers: ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.79 (d, *J*=7.0 Hz, 3H), 0.81 (d, *J*=6.9 Hz, 3H), 0.82 (d, *J*=6.9 Hz, 3H), 0.86 (d, *J*=6.6 Hz, 3H), 0.89 (d, *J*=6.9 Hz, 3H), 0.93 (d, *J*=6.3 Hz, 3H) (C*H*$_3$–$C_{3'}$/$C_{5'}$/$C_{7'}$), 1.21 (t, *J*=7.0 Hz, C*H*$_3$–$C_{2'''}$), 0.97–1.37 (m, 2H), 1.72 (m, 5H), 3.13 (m, 1H), 3.43 (m, 1H), 3.77 (s, 3H, C*H*$_3$–$C_{8''}$), 4.10 (q, *J*=7.1 Hz C*H*$_2$–$C_{1'''}$), 4.11 (q, *J*=6.8 Hz, C*H*$_2$–$C_{1'''}$), 4.28 (m, 2H, C*H*$_2$–$C_{7''}$), 4.92 (m, 1H, *H*–C_6), 6.81 (m, 2H, Ar-*H*), 6.93 (m, 1H, Ar-*H*), 7.13–7.41 (m, 14H, Ar-*H*), 7.98 (m, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$. 75 MHz): δ=14.2 [14.6], 14.7 [17.2], 16.9 [18.5], 21.4, 27.8 [27.5], 32.0 [31.7], 35.1, 37.8 [37.1], 40.5 [42.1], 55.2, 60.1, 71.9, 72.7, 80.5, 113.1 (2C, $C_{2''}$/$C_{6''}$), 128.1–159.0 (all Aryl-C), 166.3, 172.9 [173.16] (C_1). ^{31}P NMR ($CDC1_3$, 81.015 MHz): δ=−2.9.

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