Convenient Stereoselective Syntheses of (6*E*)- and (6*Z*)-5,6-Dimethyl-8-silyl-6-octenals

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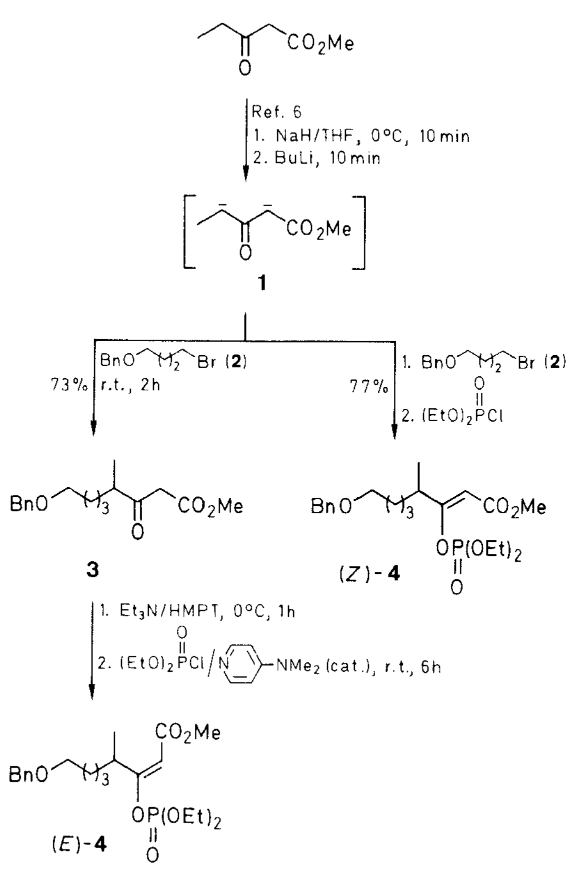
A stereoselective synthetic method for the title compounds, *E*- and *Z*- allylsilanes, which would be generally applicable for the preparation of other trisubstituted allylsilanes, has been elaborated. The key steps are the following: (i) stereoselective preparation of (2*Z*)- and (2*E*)-3-[(diethoxy)phosphoryloxy]-2-octenoates (*Z*)- and (*E*)-**4**, (ii) substitution of 3-phosphoryloxy group with methyl in the presence of palladium catalyst [(*Z*/*E*)-**4** → (*E*/*Z*)-**5**]; and (iii) substitution reaction of the desired allyl chlorides with appropriate silyllithiums [(*E*/*Z*)-**7** → (*E*/*Z*)-**8**].

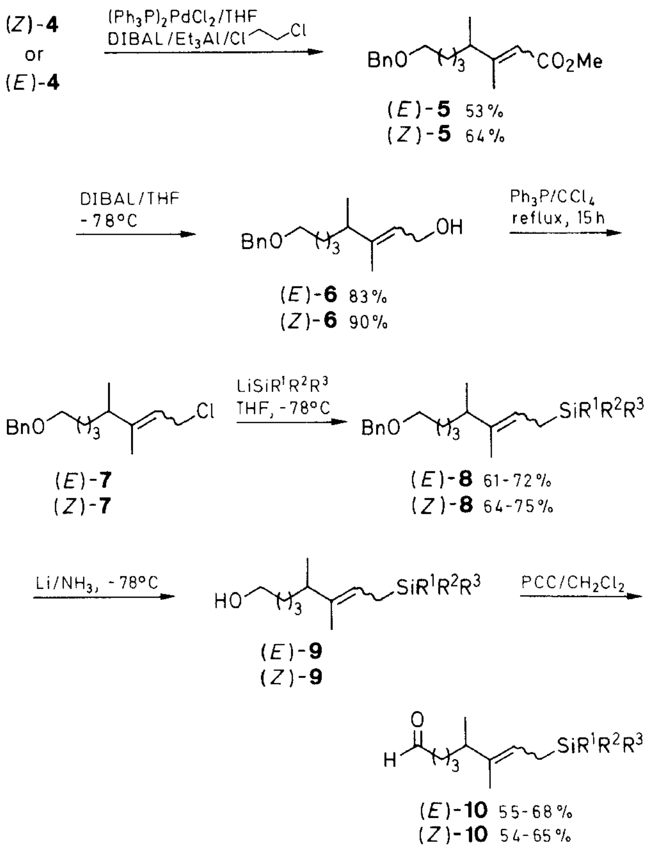
Much attention has been recently focused on the syntheses of allylsilanes and their applications as synthetic reagents or intermediates.[1] Although the stereoselective method for the synthesis of *E*- and *Z*-disubstituted allylsilanes seems to be established,[2] the method for trisubstituted compounds is very limited.[3] In connection with our studies on the stereoselective allylsilane carbocyclization,[4] we investigated the stereoselective syntheses of title allylsilanes and developed a convenient method,[5] which would be generally applicable for the syntheses of similar types of trisubstituted allylsilanes.

First, the stereoisomeric enol phosphates (*Z*)- and (*E*)-**4** were prepared smoothly by alkylation of the dianion **1**, generated from 3-oxopentanoate, with 4-benzyloxybutyl bromide (**2**) according to the procedure of Weiler[6] (Scheme A). Stereochemical purity of the *Z*- and *E*-enol phosphates (*Z*)- and (*E*)-**4** was over 99 % in both cases as checked by 400 MHz ^{1}H-NMR spectra. The substitution reactions of (*E*)-**4** with lithium dimethylcuprate or the combination of methylmagnesium iodide/methylcopper[6] or nickel acetylacetonate[7] were sluggish and gave no appreciable amount of the methylated product (*Z*)-**5**. Although the reaction of (*Z*)-**4** with dimethylcuprate afforded the substitution product in 58 % yield, it was found to be a mixture of the desired ester (*E*)-**5** and the product of deoxygenation in 1 : 1 ratio. These difficulties[8] were circumvented by the application of Oshima–Nozaki procedure.[9] The reaction was conducted in the presence of palladium(0) catalyst (0.1 mol equiv) prepared *in situ*



Bn = CH$_2$Ph

Scheme A



8–10	R^1	R^2	R^3
a	Me	Me	Me
b	Ph	Me	Me
c	Ph	Ph	Me
d	Ph	Ph	Ph

Scheme B

by the reduction of bis(triphenylphosphine)palladium(II) chloride $[(Ph_3P)_2PdCl_2]$ or [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) chloride with diisobutylaluminum hydride (DIBAL)[10] using 3 molar equivalents of trimethylaluminum. The enol phosphate (*Z*)-**4** gave the desired product (*E*)-**5** with the stereochemical purity (*E*/*Z*) over 99 %, the former catalyst resulting in slightly better yield. In the case of enolphosphate (*E*)-**4** the reaction was slower and, interestingly, when $(Ph_3P)_2PdCl_2$-DIBAL was used, the reaction almost stopped at about 20 % conversion. However the renewed addition of trimethylaluminum (1 mol equiv) effected completion of the reaction. The stereochemical purity of the product was better (*E*/*Z* = 4 : 96 vs 8 : 92) when $(Ph_3P)_2PdCl_2$-DIBAL was used.

The *E*- and *Z*-trisubstituted α,β-unsaturated esters (*E*)- and (*Z*)-**5** thus obtained stereoselectively, were converted to the allyl chlorides (*E*)- and (*Z*)-**7**, respectively, by reduction with DIBAL and subsequent chlorination. Next the silylation of (*E*)- and (*Z*)-**7** was performed by treatment with appropriate silyllithiums in tetrahydrofuran.[11] The silyllithiums were prepared by the Gilman procedure[12] except trimethylsilyllithium, which was produced from hexamethyldisilane and methyllithium.[13] In the Gilman procedure it was pertinent to treat metallic lithium in hexane twice with ultrasound before use. The reaction of (*E*)- and (*Z*)-**7** with silyllithiums proceeded smoothly to afford the allylsilanes (*E*)- and (*Z*)-**8**, respectively. Finally on deprotection and oxidation with pyridinium chlorochromate (PCC) (*E*)- and (*Z*)-**8** furnished the target aldehydes (*E*)- and (*Z*)-**10**, respectively.

The syntheses of the trisubstituted *E*- and *Z*-allylsilanes described above start from common material and involve the same type of reactions, being stereodivergent and concise. Thus the method will be generally applicable for the stereoselective synthesis of trisubstituted allylsilanes.

IR spectra were recorded on a JASCO A-100 spectrophotometer. NMR spectra were obtained on a Hitachi R-90H or a JEOL GX-400 spectrometer. Chemical shifts are reported in δ units relative to internal TMS for ^{1}H-NMR spectra and relative to internal TMS (0.00) or $\underline{C}DCl_3$ (δ = 77.03) for ^{13}C-NMR spectra. Mass spectra were obtained on a JEOL D-300 apparatus by GC introduction at 20 eV. Column chromatography was performed on Fuji-Davison Chemicals BW-820 MH and for preparative TLC Merck Art 7747 Kieselgel $60F_{254}$ was used.

Methyl (2*Z*)-8-Benzyloxy-3-[(diethoxy)phosphoryloxy]-4-methyl-2-octenoate [(*Z*)-4]:

To a suspension of NaH (60 % oil dispersion, 2.07 g, 45 mmol) in THF (10 mL), cooled to 0 °C, is added dropwise methyl 3-oxopentanoate (5.2 g, 40 mmol). After stirring for 10 min, BuLi (1.5 M

Table 1. Spectral Data of Intermediate 8-Benzyloxy-3,4-dimethyl-1-silyl-2-octenes (*E*)- and (*Z*)-**8**

Product	Yield (%)	IR (film) ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, *J*(Hz)
(*E*)-**8a**	66	2960, 2860, 1460, 1250, 1160, 840	0.00 (s, 9H), 0.96 (d, 3H, *J* = 6.8), 1.20–1.70 (m, 8H), 1.43 (d, 3H, *J* = 1), 2.02 (sext, 1H, *J* = 6.8), 3.42 (t, 2H, *J* = 6.2), 4.46 (s, 2H), 5.13 (t, 1H, *J* = 7), 7.30 (s, 5H)
(*E*)-**8b**	61	2970, 2870, 1960, 1900, 1850, 1430, 1250, 1120, 830	0.25 (s, 6H), 0.94 (d, 3H, *J* = 6.8), 1.10–1.70 (m, 6H), 1.37 (s, 3H), 1.62 (d, 2H, *J* = 8), 2.01 (m, 1H), 3.38 (t, 2H, *J* = 7), 4.43 (s, 2H), 5.13 (t, 1H, *J* = 8), 7.20–7.55 (m, 10H)
(*E*)-**8c**	62	2970, 2870, 1960, 1880, 1820, 1430, 1250, 1110	0.52 (s, 3H), 0.89 (d, 3H, *J* = 7), 1.05–1.70 (m, 6H), 1.34 (s, 3H), 1.93 (d, 2H, *J* = 8), 1.98 (m, 1H), 3.36 (t, 2H, *J* = 7), 4.33 (s, 2H), 5.15 (t, 1H, *J* = 8), 7.18–7.60 (m, 15H)
(*E*)-**8d**	72	2970, 2860, 2140, 1960, 1890, 1820, 1430, 1100, 800	0.84 (d, 3H, *J* = 7), 1.05–2.00 (m, 7H), 1.26 (s, 3H), 2.22 (d, 2H, *J* = 8), 3.30 (t, 2H, *J* = 7), 4.40 (s, 2H), 5.22 (t, 1H, *J* = 8), 7.1–7.7 (m, 20H)
(*Z*)-**8a**	68	2970, 2860, 1460, 1250, 1160, 840	0.00 (s, 9H), 0.93 (d, 3H, *J* = 7), 1.15–1.70 (m, 8H), 1.52 (d, 3H, *J* = 1), 2.55 (m, 1H), 3.43 (t, 2H, *J* = 6), 4.46 (s, 2H), 5.07 (t, 1H, *J* = 7), 7.28 (s, 5H)
(*Z*)-**8b**	64	2970, 2860, 1960, 1880, 1820, 1430, 1250, 1120, 830	0.26 (s, 6H), 0.84 (d, 3H, *J* = 6.8), 1.24 (m, 4H), 1.53 (s, 3H), 1.48–1.62 (m, 3H), 1.72 (dd, 1H, *J* = 9.2, 14.2), 2.52 (sext, 1H, *J* = 6.8), 3.43 (t, 2H, *J* = 6.6), 4.48 (s, 2H), 5.11 (t, 1H, *J* = 9.0), 7.22–7.34 (m, 8H), 7.50 (m, 2H)
(*Z*)-**8c**	75	2970, 2870, 1960, 1890, 1820, 1430, 1250, 1110	0.53 (s, 3H), 0.78 (d, 3H, *J* = 6.8), 1.21 (m, 4H), 1.51 (s, 3H), 1.55 (t, 2H, *J* = 6.6), 1.91 (dd, 1H, *J* = 7.4, 14.4), 2.04 (dd, 1H, *J* = 9.0, 14.4), 2.54 (sext, 1H, *J* = 6.8), 3.42 (t, 2H, *J* = 6.6), 4.49 (s, 2H), 5.15 (dd, 1H, *J* = 7.4, 9.0), 7.22–7.37 (m, 11H), 7.55 (m, 4H)
(*Z*)-**8d**	73	2970, 2860, 2140, 1960, 1890, 1820, 1425, 1100, 800	0.68 (d, 3H, *J* = 7), 1.05–1.70 (m, 6H), 1.48 (d, 3H, *J* = 1), 2.28 (m, 2H), 2.55 (m, 1H), 3.38 (t, 2H, *J* = 7), 4.47 (s, 2H), 5.24 (t, 1H, *J* = 8), 7.2–7.8 (m, 20H)

[a] All the products were obtained as oils. They were characterized spectroscopically; no microanalyses were performed.

[b] ^{13}C-NMR (100 MHz, $CDCl_3$/TMS)

8b: δ = −3.1 (2q), 17.0 (t), 18.2 (q), 18.9 (q), 24.4 (t), 30.0 (t), 33.4 (d), 34.7 (t), 70.5 (t), 72.9 (t), 119.4 (d), 127.4 (d), 127.6 (2d), 127.7 (2d), 128.3 (2d), 128.8 (d), 133.6 (2d), 137.5 (s), 138.8 (s), 139.3 (s)

8c: δ = −5.4 (q), 15.5 (t), 18.2 (q), 18.7 (q), 24.4 (t), 30.1 (t), 33.6 (d), 34.7 (t), 70.5 (t), 72.9 (t), 118.9 (d), 127.5 (d), 127.5 (d, 127.6 (2d), 127.7 (4d), 128.3 (2d), 129.2 (2d), 134.6 (4d), 137.1 (2s), 138.3 (s), 138.8 (s) solution in hexane, 34 mL, 51 mmol) is added and the solution is stirred further for 10 min. To a solution of the dianion **1** thus prepared is added 4-benzyloxy-1-bromobutane (**2**; 7.3 g, 30 mmol) and the mixture is stirred at r.t. for 2 h, when the complete consumption of **2** is confirmed by TLC. Diethyl chlorophosphate (2.9 g, 60 mmol) is added and the mixture is allowed to react for 2 h. The reaction is quenched by the addition of sat. NH_4Cl solution and the mixture is extracted with Et_2O (3 x 80 mL). The combined Et_2O layers are washed with 1 N HCl, sat. aq $NaHCO_3$ and brine, and dried ($MgSO_4$). The residue obtained after evaporation of the solvent is purified by chromatography (silica gel, 150 g, hexane/EtOAc, 1 : 1) to give the enol phosphate (*Z*)-**4** as a colorless oil; yield: 9.73 g; (77 %); bp 210°C/0.05 Torr (Kugelrohr).

$C_{21}H_{33}O_7P$	calc.	C 58.87	H 7.76
(428.2)	found	58.50	7.75

IR (film): ν = 2980, 2950, 2870, 1730, 1664, 1455, 1435, 1370, 1272, 1030 cm^{-1}.

^{1}H-NMR (90 MHz): δ = 1.11 (d, 3 H, J = 7 Hz), 1.30–1.80 (m, 6 H), 1.32 (t, 6 H, J = 7 Hz), 2.59 (m, 1 H), 3.41 (t, 2 H, J = 6.5 Hz), 3.64 (s, 3 H), 4.19 (dq, 4 H, J = 7.5, 7.1 Hz), 4.43 (s, 2 H), 5.31 (s, 1 H), 7.27 (s, 5 H).

^{13}C-NMR: δ = 16.0 (q), 16.1 (q), 17.9 (q), 23.4 (t), 29.7 (t), 34.1 (t), 39.1 (d), 51.1 (q), 64.6 (2t), 70.1 (t), 72.8 (t), 104.0 (d), 127.4 (d), 127.6 (2d), 128.3 (2d), 138.6 (s), 164.5 (s), 166.1 (s).

Methyl 8-Benzyloxy-4-methyl-3-oxooctanoate (3):

To a solution of the dianion **1**, prepared in the same way as above from methyl 3-oxopentanoate (6.50 g, 50 mmol), NaH (2.9 g, 60 mmol) and BuLi (1.5 M in hexane, 34 mL, 51 mmol), is added 4-benzyloxy-1-bromobutane (**2**; 10 g, 41 mmol). The mixture is al-

Table 2. Spectral Data of Allylsilanes (*E*)- and (*Z*)-**10** Prepared

Product	Yield (%)	Molecular Formula[a]	IR (film) ν(cm^{-1})	^{1}H-NMR (400 MHz, $CDCl_3$/TMS) δ, J(Hz)	^{13}C-NMR (100 MHz, $CDCl_3$), δ
(*E*)-**10a**	55	$C_{13}H_{26}OSi$ (226.2)	2970, 2900, 2720, 1730, 1250, 860, 840	0.00 (s, 9 H), 0.99 (d, 3 H, J = 6.6), 1.20–1.60 (m, 6 H), 1.47 (s, 3 H), 2.12 (sext, 1 H, J = 6.6), 2.39 (dt, 2 H, J = 1.8, 7.1), 5.21 (t, 1 H, J = 8.2), 9.75 (t, 1 H, J = 1.8)	−1.68 (3q), 11.8 (q), 18.4 (t), 20.1 (q), 20.4 (t), 34.4 (t), 42.8 (d), 43.9 (t), 120.2 (d), 135.7 (s), 202.7 (d)
(*E*)-**10b**	61	$C_{18}H_{28}OSi$ (288.2)	2960, 2880, 2720, 1960, 1880, 1820, 1730, 1250, 840	0.26 (s, 6 H), 0.94 (d, 3 H, J = 7.0), 1.17–1.52 (m, 4 H), 1.38 (s, 3 H), 1.66 (ABX, 2 H, J = 8.2, 13.3), 2.07 (sext, 1 H, J = 7.0), 2.35 (br t, 2 H, J = 7.3), 5.18 (t, 1 H, J = 8.2), 7.33–7.51 (m, 5 H), 9.71 (t, 1 H, J = 1.4)	−3.2 (2q), 11.9 (q), 17.5 (t), 20.1 (q), 20.4 (t), 34.4 (t), 42.8 (d), 43.9 (t), 119.5 (d), 127.7 (2d), 128.9 (d), 133.6 (2d), 136.6 (s), 139.2 (s), 202.8 (d)
(*E*)-**10c**	68	$C_{23}H_{30}OSi$ (350.2)	2960, 2860, 2730, 1960, 1890, 1820, 1730, 1430, 1250, 1110	0.53 (s, 3 H), 0.91 (d, 3 H, J = 7.0), 1.13–1.45 (m, 4 H), 1.35 (s, 3 H), 1.97 (ABX, 2 H, J = 8.1, 13.3), 2.04 (sext, 1 H, J = 7.0), 2.29 (dt, 2 H, J = 1.8, 7.1), 5.21 (t, 1 H, J = 8.1), 7.31–7.53 (m, 10 H), 9.66 (t, 1 H, J = 1.8)	−5.3 (q), 12.0 (q), 16.0 (t), 20.0 (q), 20.3 (t), 34.3 (t), 42.9 (d), 43.9 (t), 118.9 (d), 127.7 (4d), 129.2 (2d), 134.6 (4d), 137.1 (2s), 137.4 (s), 202.8 (d)
(*E*)-**10d**	62	$C_{28}H_{32}OSi$ (412.2)	2980, 2940, 2880, 2740, 1960, 1890, 1820, 1720, 1430, 1260, 1110	0.86 (d, 3 H, J = 7.0), 1.04–1.40 (m, 4 H), 1.29 (s, 3 H), 2.02 (sext, 1 H, J = 7.0), 2.26 (t, 2 H, J = 7.9), 2.27 (ABX, 2 H, J = 7.9, 13.3), 5.32 (t, 1 H, J = 7.9), 7.31–7.53 (m, 15 H), 9.61 (t, 1 H, J = 1.8)	12.0 (q), 14.9 (t), 19.7 (q), 20.2 (t), 34.3 (t), 42.9 (d), 43.9 (t), 118.6 (d), 127.8 (6d), 129.4 (3d), 135.0 (3s), 135.7 (6d), 137.9 (s), 202.8 (d)
(*Z*)-**10a**	54	$C_{13}H_{26}OSi$ (226.2)	2970, 2900, 2720, 1730, 1250, 860, 840	0.00 (s, 9 H), 0.96 (d, 3 H, J = 6.6), 1.28–1.60 (m, 6 H), 1.57 (d, 3 H, J = 1.1), 2.41 (dt, 2 H, J = 2.0, 7.2), 2.61 (sext, 1 H, J = 6.6), 5.15 (t, 1 H, J = 8.4), 9.76 (t, 1 H, J = 2)	−1.71 (3q), 18.0 (t), 18.1 (q), 19.0 (q), 20.4 (t), 33.2 (d), 34.4 (t), 44.1 (t), 120.8 (d), 135.9 (s), 202.7 (d)
(*Z*)-**10b**	65	$C_{18}H_{28}OSi$ (288.2)	2970, 2880, 2720, 1960, 1880, 1820, 1730, 1250, 840	0.27 (s, 6 H), 0.85 (d, 3 H, J = 6.6), 1.25 (m, 2 H), 1.46 (m, 2 H), 1.53 (s, 3 H), 1.59 (dd, 1 H, J = 8.8, 14.3), 1.71 (dd, 1 H, J = 9.2, 14.3), 2.33 (dt, 2 H, J = 1.4, 7.3), 2.54 (sext, 1 H, J = 6.6), 5.15 (t, 1 H, J = 8.2), 7.32–7.51 (m, 5 H), 9.71 (t, 1 H, J = 1.4)	−3.2 (2q), 17.2 (t), 18.1 (q), 18.8 (q), 20.4 (t), 33.3 (d), 34.4 (t), 44.1 (t), 120.1 (d), 127.7 (2d), 128.9 (d), 133.6 (2d), 136.8 (s), 139.1 (s), 202.7 (d)
(*Z*)-**10c**	59	$C_{23}H_{30}OSi$ (350.2)	2970, 2880, 2730, 1960, 1725, 1430, 1250, 1110	0.54 (s, 3 H), 0.78 (d, 3 H, J = 7.0), 1.22 (m, 2 H), 1.42 (m, 2 H), 1.51 (d, 3 H, J = 1.1), 1.92 (dd, 1 H, J = 7.7, 14.3), 2.03 (dd, 1 H, J = 9.2, 14.3), 2.31 (dt, 2 H, J = 1.8, 7.0), 2.54 (sext, 1 H, J = 7.0), 5.19 (t, 1 H, J = 7.9), 7.31–7.53 (m, 10 H), 9.69 (t, 1 H, J = 1.8)	−5.3 (q), 15.6 (t), 18.1 (q), 18.6 (q), 20.4 (t), 33.5 (d), 34.3 (t), 44.1 (t), 119.4 (d), 127.8 (4d), 129.2 (2d), 134.6 (4d), 137.0 (2s), 137.5 (s), 202.8 (d)
(*Z*)-**10d**	60	$C_{28}H_{32}OSi$ (412.2)	2950, 2730, 1960, 1890, 1820, 1720, 1430, 1260, 1110	0.69 (d, 3 H, J = 6.6), 1.07–1.43 (m, 4 H), 1.49 (d, 3 H, J = 1.1), 2.24 (m, 1 H), 2.26 (dt, 2 H, J = 1.8, 7.3), 2.35 (dd, 1 H, J = 8.8, 14.1), 2.54 (sext, 1 H, J = 6.6), 5.29 (t, 1 H, J = 8.8), 7.31–7.59 (m, 15 H), 9.66 (t, 1 H, J = 1.8)	14.6 (t), 18.1 (q), 18.4 (q), 20.3 (t) 33.6 (d), 34.3 (t), 44.0 (t), 119.3 (d) 127.8 (6d), 129.5 (3d), 134.9 (3s) 135.8 (6d), 138.0 (s), 202.7 (d)

[a] HRMS gave a mass value for the molecular ion within ± 3.0 amu of the calculated value.

lowed to react at r.t. for 2 h. The reaction is quenched by the addition of sat. aq NH_4Cl and the product is extracted with Et_2O (3 × 80 mL). The combined Et_2O layers are washed (1 N HCl, sat. aq $NaHCO_3$ and brine), and dried ($MgSO_4$). The solvent is evaporated *in vacuo* and the residue is purified by chromatography (silica gel, 120 g, 1 : 1 hexane EtOAc to yield the β-keto ester **3** as a colorless oil; yield: 8.76 g (73 %); bp 170 °C/0.02 Torr (Kugelrohr).

$C_{17}H_{24}O_4$	calc.	C 69.84	H 8.27
(292.2)	found	69.67	8.32

IR (film): ν = 2950, 2860, 1750, 1710, 1650, 1628, 1455, 1100 cm^{-1}.

^{1}H-NMR (400 MHz): δ = 1.10 (d, 3 H, J = 6.6 Hz), 1.30–1.43 (m, 3 H), 1.57–1.65 (m, 3 H), 2.62 (sext, 1 H, J = 6.8 Hz), 3.46 (t, 2 H, J = 6.6 Hz), 3.48 (s, 2 H), 3.72 (s, 3 H), 4.49 (s, 2 H), 7.33 (s, 5 H).

^{13}C-NMR: δ = 15.9 (q), 23.7 (t), 29.7 (t), 32.3 (t), 46.5 (t), 47.4 (d), 52,2 (q), 70.0 (t), 72.9 (t), 127.5 (d), 127.6 (2d), 128.3 (2d), 138.8 (s), 167.7 (s), 206.2 (s).

MS: m/z = 292 (M$^+$).

Methyl (2*E*)-8-Benzyloxy-4-methyl-3-[(diethoxy)phosphoryloxy]-2-octenoate [(*E*)-4]:

The β-keto ester **3** (11.4 g, 39 mmol) is dissolved in HMPT (100 mL) and the solution is cooled to 0 °C. After addition of Et_3N (5.05 g, 50 mmol) and stirring the mixture for 1 h, diethyl chlorophosphate (8.6 g, 50 mmol) and 4-dimethylaminopyridine (150 mg) are added and the mixture is allowed to react at r.t. for 6 h. Sat. aq NH_4Cl solution is added and the product is extracted with Et_2O (3 × 150 mL). The combined Et_2O layers are washed successively twice each with 1 N HCl, water, sat. aq $NaHCO_3$ and brine, and dried. Removal of the solvent furnishes the enol phosphate (*E*)-**4** as a colorless oil; yield: 15.47 g (92 %); bp 210 °C/0.09 Torr (Kugelrohr).

$C_{21}H_{33}O_7P$	calc.	C 58.87	H 7.76
(428.2)	found	58.57	7.76

IR (film): ν = 2980, 2940, 2870, 1720, 1644, 1455, 1435, 1370, 1272, 1144, 1030 cm^{-1}.

^{1}H-NMR (90 MHz): δ = 1.10 (d, 3 H, J = 7 Hz), 1.30–1.90 (m, 6 H), 1.34 (t, 6 H, J = 7 Hz), 3.41 (t, 2 H, J = 6.5 Hz), 3.64 (s, 3 H), 3.85 (m, 1 H), 4.14 (dq, 4 H, J = 7.6, 7.1 Hz), 4.44 (s, 2 H), 5.86 (d, 1 H, J = 1.2 Hz), 7.37 (s, 5 H).

^{13}C-NMR: δ = 16.0 (q), 16.1 (q), 17.6 (q), 23.8 (t), 29.7 (t), 33.5 (t), 34.3 (d), 51.2 (q), 64.8 (2t), 70.2 (t), 72.8 (t), 103.6 (d), 127.4 (d), 127.5 (2d), 128.3 (2d), 138.7 (s), 166.6 (s), 169.7 (s).

Methyl (2*E*)- and (2*Z*)-8-Benzyloxy-3,4-dimethyl-2-octenoates [(*E*)- and (*Z*)-5]:

To a suspension of $(Ph_3P)_2PdCl_2$ (320 mg, 0.4 mmol) in THF (4 mL) under argon at 0 °C is added DIBAL (1 M solution in toluene, 0.8 mL) and the mixture is stirred for 10 min. 1,2-dichloroethane (40 mL), enol phosphate (*Z*)-**4** (8 g, 19 mmol) and Me_3Al (1 M solution in hexane, 60 mL, 60 mmol) are added successively at 0 °C and the mixture is stirred at r.t. for 5 d. After the addition of Et_2O (100 mL), the mixture is poured into a mixture of 1 N HCl and ice. The layers are separated and the aqueous phase is extracted with Et_2O (3 × 100 mL). The combined organic layers are washed with 1 N HCl, sat. aq $NaHCO_3$ and brine, and dried ($MgSO_4$). The solvent is removed and the resulting oil was chromatographed on silica gel (100 g) using hexane/Et_2O (9 : 1) as eluent to afford the ester (*E*)-**5** as a colorless oil; yield: 2.89 g (53 %). The analysis by 400 MHz ^{1}H-NMR shows the product is stereochemically > 99 % pure.

HRMS calc. for $C_{18}H_{26}O_3$ (M$^+$): 290.1882; found: 290.1898.

IR (film): ν = 2950, 2860, 1720, 1645, 1500, 1440, 1380, 1100 cm^{-1}.

^{1}H-NMR (400 MHz): δ = 1.03 (d, 3 H, J = 6.8 Hz), 1.22–1.50 (m, 4 H), 1.59 (quint, 2 H, J = 6.6 Hz), 2.08 (d, 3 H, J = 1.2 Hz), 2.20 (sext, 1 H, J = 6.8 Hz), 3.44 (t, 2 H, J = 6.6 Hz), 3.67 (s, 3 H), 4.48 (s, 2 H), 5.67 (s, 1 H), 7.32 (s, 5 H).

^{13}C-NMR: δ = 15.3 (q), 19.1 (q), 24.1 (t), 29.7 (t), 34.5 (t), 43.9 (q), 50.7 (d), 70.1 (t), 72.8 (t), 114.7 (d), 127.4 (d), 127.6 (2d), 128.3 (2d), 138.6 (s), 164.5 (s), 167.3 (s).

MS: m/z (%) = 290 (M$^+$, 3), 258 (8), 199 (18), 184 (20), 167 (53), 91 (100).

The corresponding ester (*Z*)-**5** is prepared from (*E*)-**4** in the same way except that the reaction slows down midway and the addition of further amount (1 mol. equiv) of Me_3Al is necessary for the completion of the reaction (see text); colorless oil; yield: 64 %.

HRMS calc. for $C_{18}H_{26}O_3$ (M$^+$): 290.1882, found: 290.1899

IR (film): ν = 2950, 2860, 1715, 1640, 1440, 1370, 1100 cm^{-1}.

^{1}H-NMR: δ = 1.01 (d, 3 H, J = 6.8 Hz), 1.24–1.70 (m, 6 H), 1.76 (d, 3 H, J = 1.4 Hz), 3.45 (t, 2 H, J = 6.6 Hz), 3.66 (s, 3 H), 3.89 (sext, 1 H, J = 6.8 Hz), 4.48 (s, 2 H), 5.64 (d, 1 H, J = 1.2 Hz), 7.32 (s, 5 H).

^{13}C-NMR: δ = 18.8 (q), 19.1 (q), 24.2 (t), 29.8 (t), 34.2 (d), 34.6 (t), 50.7 (q), 70.3 (t), 72.8 (t), 116.0 (d), 127.4 (d), 127.6 (2d), 128.3 (2d), 138.7 (s), 164.5 (s), 166.7 (s).

MS: m/z = 290 (M$^+$, 6), 258 (37), 199 (18), 184 (100), 167 (75), 91 (88).

(2*E*)- and (2*Z*)-8-Benzyloxy-3,4-dimethyl-2-octen-1-ols (*E*)- and (*Z*)-6:

To a solution of the (*E*)-5 (4.86 g, 17 mmol) in THF (35 mL), cooled to −78 °C, is added DIBAL solution (1 M in toluene, 36 mL). After 10 min, the mixture is quenched by the addition of MeOH and extracted with Et_2O (3 × 100 mL). The extract solution is washed with 1 N HCl, sat. aq $NaHCO_3$ and brine, and dried ($MgSO_4$). Evaporation of the solvent affords (*E*)-**6** as a colorless oil; yield: 3.53 g (83 %).

HRMS calc. for $C_{17}H_{24}O$ (M$^+$ − H_2O): 244.1827, found: 244.1847.

IR (film): ν = 3390, 2940, 2860, 1670, 1455, 1365, 1100, 1000 cm^{-1}.

^{1}H-NMR (400 MHz): δ = 0.98 (d, 3 H, J = 6.8 Hz), 1.22–1.42 (m, 4 H), 1.56 (d, 3 H, J = 0.5 Hz), 1.58 (m, 2 H), 1.86 (br s, 1 H), 2.09 (sext, 1 H, J = 6.8 Hz), 3.44 (t, 2 H, J = 6.6 Hz), 4.12 (d, 2 H, J = 6.8 Hz), 4.48 (s, 2 H), 5.39 (t, 1 H, J = 6.8 Hz), 7.32 (s, 5 H).

^{13}C-NMR: δ = 12.6 (q), 19.4 (q), 24.1 (t), 29.7 (t), 34.6 (t), 42.5 (d), 59.2 (t), 70.3 (t), 72.8 (t), 123.1 (d), 127.4 (d), 127.6 (2d), 128.3 (2d), 138.6 (s), 142.3 (s).

MS: m/z = 244 (M$^+$ − H_2O, 3), 200 (12), 153 (25), 135 (34), 109 (50), 91 (100).

The corresponding *Z*-allyl alcohol (*Z*)-**6** is obtained in the same way as a colorless oil; yield: 90 %.

HRMS calc. for $C_{17}H_{24}O$ (M$^+$ − H_2O): 244.1827, found: 244.1839.

IR (film): ν = 3400, 2950, 2870, 1665, 1455, 1365, 1100, 1000 cm^{-1}.

^{1}H-NMR (400 MHz): δ = 0.97 (d, 3 H, J = 6.8 Hz), 1.20–1.40 (m, 4 H), 1.50–1.62 (m, 2 H), 1.60 (s, 3 H), 1.80 (br s, 1 H), 2.64 (sext, 1 H, J = 6.8 Hz), 3.44 (AB part of ABX_2, J = 6.5, 9.1 Hz), 4.11 (AB part of ABX, 2 H, J = 6.9, 12.5 Hz), 4.48 (s, 2 H), 5.39 (t, 1 H, J = 6.9 Hz), 7.32 (s, 5 H).

^{13}C-NMR: δ = 17.9 (q), 19.5 (q), 24.4 (t), 29.7 (t), 34.0 (d), 34.3 (t), 58.4 (t), 70.2 (t), 72.9 (t), 124.6 (d), 127.5 (d), 127.6 (2d), 128.3 (2d), 138.5 (s), 143.3 (s).

MS (20 eV): m/z = 244 (M$^+$ − H_2O, 3), 200 (11), 153 (35), 135 (35), 109 (65), 91 (100).

(2*E*)- and (2*Z*)-Benzyloxy-3,4-dimethyl-2-octenyl Chlorides [(*E*)- and (*Z*)-7]:

A mixture of the allyl alcohol (*E*)-**6** (1.295 g, 5 mmol) and Ph_3P (1.57 g, 6 mmol) in CCl_4 (8 mL) is refluxed for 15 h. After cooling, the precipitate is removed by filtration and the solvent is evaporated to leave (*E*)-**7** which is sufficiently pure for further reaction.

IR (film): ν = 2945, 2860, 1660, 1455, 1362, 1255, 1120 cm^{-1}.

^{1}H-NMR (90 MHz): δ = 0.97 (d, 3 H, J = 7 Hz), 1.20–1.81 (m, 6 H), 1.60 (d, 3 H, J = 1.0 Hz), 2.10 (sext, 1 H, J = 7 Hz), 3.39 (t, 2 H, J = 7 Hz), 4.03 (d, 2 H, J = 8 Hz), 4.43 (s, 2 H), 5.38 (t, 1 H, J = 8 Hz), 7.26 (s, 5 H).

The *Z*-allyl chloride (*Z*)-**7** is prepared from the corresponding *Z*-allyl alcohol (*Z*)-**6**.

IR (film): ν = 2945, 2860, 1656, 1455, 1365, 1255, 1110 cm^{-1}.

^{1}H-NMR (90 MHz): δ = 0.97 (d, 3H, J = 7 Hz), 1.20–1.75 (m, 6H), 1.61 (s, 3H), 2.64 (sext, 1H, J = 7 Hz), 3.40 (t, 2H, J = 6 Hz), 4.03 (d, 2H, J = 8 Hz), 4.42 (s, 2H), 5.37 (t, 1H, J = 8 Hz), 7.26 (s, 5H).

Preparation of Silyllithium Derivatives:

A suspension of pieces of metallic lithium (350–500 mg atom) in hexane is irradiated with ultrasound and this operation is repeated in renewed hexane. Lithium, thus activated, is added to a stirred solution of silyl chlorides ($PhMe_2SiCl$ and Ph_3SiCl, 8–10 mmol) or disilane [$(Ph_2MeSi)_2$, 4 mmol] in THF (15 mL) at 0–10 °C for 6 h. The supernatant solutions (0.5–0.6 M) are used for the reaction.

(2*E*)- and (2*Z*)-8-Benzyloxy-3,4-dimethyl-1-silyl-2-octenes [(*E*)- and (*Z*)-8]; General Procedure:

To a solution of the appropriate allyl chloride. (*E*)- or (*Z*)-**7** (730 mg, 3 mmol) in THF (10 mL), cooled to − 78 °C, is added any one of the above described silyllithium solution in THF (3.4 mmol) and the mixture is stirred for 1 h. The mixture is quenched by the addition of sat. aq NH_4Cl and the product is extracted with Et_2O (30 mL). Combined Et_2O layers are washed with brine and the solvent is evaporated. The crude product is chromatographed on silica gel (30 g) using hexane/Et_2O as eluent to give, after removal of solvents, the corresponding (*E*)- or (*Z*)-**8** allylsilanes as colorless oil. (Table 1)

(6*E*)- and (6*Z*)-5,6-Dimethyl-8-silyl-6-octenals; General Procedure:

To liquid NH_3 (10–15 mL) under N_2 at − 78 °C is added metallic lithium (60 mg, 9 mg atoms). When the mixture attains deep blue in color, a solution of allylsilane (*E*)-**8** or (*Z*)-**8** (1–3 mmol) in Et_2O (2–3 mL) is added. After stirring for 10 min, the reaction mixture is quenched by the addition of NH_4Cl and NH_3 is allowed to evaporate. Et_2O and water were added cautiously and the layers are separated. The aqueous layer is extracted with Et_2O (3 × 30 mL). The combined Et_2O layers are washed with brine and dried ($MgSO_4$). Evaporation of the solvent furnishes the crude alcohol (*E*)- or (*Z*)-**9**, which are oxidized without further purification.

*Oxidation of Alcohols (E)- and (Z)-***9**: To a solution (*E*)- or (*Z*)-**9**, as obtained above (400–700 mg) in CH_2Cl_2 (5 mL) is added pyridinium chlorochromate and the mixture is stirred at r. t. for 6–12 h. Et_2O (10 mL) is added and the mixture is filtered through a column of Florisil and the solvent is removed from the filtrate by evaporation *in vacuo*. The resulting oil is chromatographed on silica gel (20 g) using hexane Et_2O (92:8–80:20) to afford the aldehydes (*E*)- or (*Z*)-**10**, respectively (Table 2).

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