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Stereoselective and Diversity-Oriented Synthesis of Trisubstituted Allylic Alcohols and Amines

Yvonne Schmidt and Bernhard Breit*[a]

Abstract: Stereoselective and diversity-oriented synthesis of trisubstituted olefins was achieved by using *ortho*-diphenylphosphanyl benzoate (*o*-DPPB) as a directing group for allylic substitution. The starting point of this methodology was a set of α-methylene aldehydes derived from Baylis–Hillman adducts. Subsequent addition of different organometallic reagents led to a variety of allylic alcohol substrates. After introduction of the reagent-directing *o*-DPPB group, copper-mediated allylic substitution with a wide range of Grignard reagents enabled the stereoselective construction of a large number of *E*-configured trisubstituted allylic alcohols and amines in excellent yields and stereoselectivities. Remarkable is the synthetic flexibility, which allows a wide range of permutations starting from an aldehyde followed by successive introduction of the substituents R^2 and R^3 from organometallic Grignard based reagents. Thus, starting from only a few precursors, a diversity-oriented synthesis of stereodefined trisubstituted allylic alcohols and amines becomes possible.

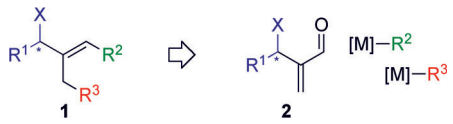
Keywords: allylation · allylic compounds · directed reactions · diversity-oriented synthesis · trisubstituted olefins

Introduction

Trisubstituted allylic alcohols are abundant structural motives in natural products.[1–6] Not only are they recognized as valuable target molecules, but allylic alcohols also represent highly valuable intermediates for asymmetric synthesis. Strategic applications of allylic alcohols include enantioselective epoxidation,[2,3,7] cyclopropanation,[2,4] hydrogenation,[2,5] and allylic substitution,[2,6] en route to chiral building blocks. Allylic amines, on the other hand, are particularly useful starting materials for the preparation of amino acids, amino alcohols, and heterocycles.[8] Additionally, they can be applied as dipeptide isosteres.[9,10] Peptides possess a broad variety of physiological properties and can be applied as enzyme inhibitors, growth factors, antimicrobiotics, and many more.[11] A major drawback regarding the use of peptides as pharmaceuticals is their limited bioavailability due to the instability of the peptide bond.[12] Therefore, the development of peptide isosteres plays an important role in medicinal chemistry.[10,13]

Despite such high demands, synthesis of trisubstituted olefins in a stereodefined manner is still an unsolved problem for a wide range of substrates. Many existing methods are restricted to the necessary presence of adjacent electron-withdrawing groups for control of the geometry of the newly formed double bond.[14] To date, modern methods used to prepare trisubstituted allylic alcohols are alkyne hydrometalation or carbometalation, mediated by stoichiometric organometallic reagents.[15–17] In a similar fashion, allylic amines are accessible by use of imines are used as the electrophile instead of aldehydes.[18] Most of these methods only warrant regioselectivity in the metalation step for selected examples and, thus, the product range of trisubstituted allylic alcohols and amines is limited.

In this work, we present the use of a directed allylic substitution for the stereoselective synthesis of trisubstituted allylic alcohols and amines **1** (Scheme 1). Additionally, the diversity-oriented approach gives rise to a wide variety of alkene products from simple starting materials and uses inexpensive copper as the transition-metal reagent. The presented methodology allows for the synthesis of stereodefined backbones, which are not currently available with a broad side-chain scope.[19,20] Especially, substituents with further heteroatom substitution, such as oxygen or nitrogen atoms, are of interest for potential pharmaceutical applications.[21] In only a few steps, a large number of products with high levels of complexity and selectivity can be generated, which can then be tested for their pharmacological effects.[19,20]



Scheme 1. Retrosynthetic analysis of trisubstituted allylic alcohols and amines **1**, which leads to α-methylene aldehydes **2** (X = NHR, X = OR).

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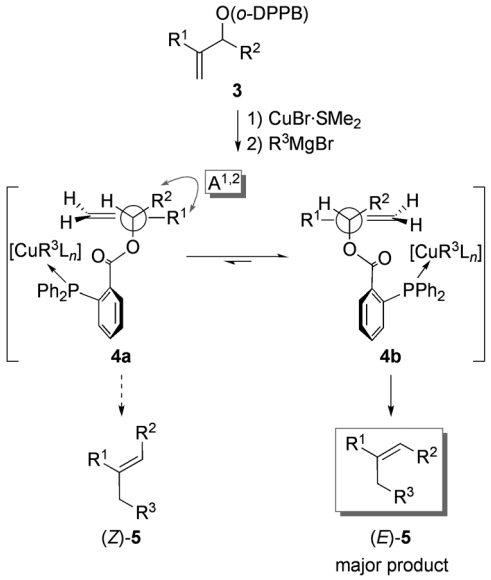
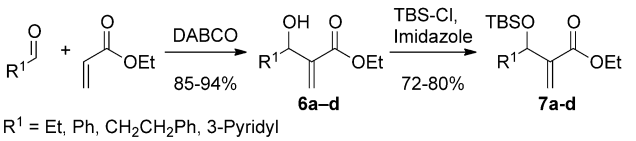


Scheme 2. Reactive conformations in the *o*-DPPB-directed allylic substitution.

In a previous report, we described the development of an *ortho*-diphenylphosphanyl benzoate (*o*-DPPB)-directed allylic substitution for the stereoselective synthesis of trisubstituted olefins **5** (Scheme 2).[22] In the course of the reaction, the organocopper reagent, generated in situ, is bound to the directing group of the substrate and subsequently delivered intramolecularly via the sterically and stereoelectronically favored reactive conformation **4b** to furnish (*E*)-**5** as the major product stereoisomer. A prerequisite for the successful substitution reaction is the extent of 1,2-allylic strain posed by the substituents R^1 and R^2 in conformation **4a**. Therefore, we envisioned the use of a stereogenic center as the controlling factor in the *o*-DPPB-directed allylic substitution, as shown for the heteroatom branching of **1** in Scheme 1.

Results and Discussion

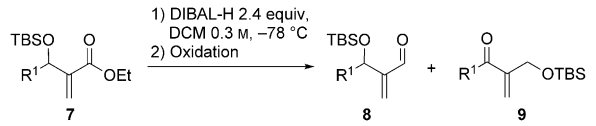
Substrate synthesis: The atom economic,[23] organocatalyzed[24] the Morita–Baylis–Hillman (MBH) reaction represents an ideal method for the preparation of α-methylene aldehydes **2** (Scheme 1).[25] Thus, starting from Michael acceptors and aldehyde or imine electrophiles, in the presence of a nucleophilic organocatalyst, the corresponding geminally substituted allylic alcohols or amines are potentially available.[26] However, the desired reaction with acrolein itself as the Michael acceptor was not possible due to polymerization under the reaction conditions.[27] Therefore, we employed a standard protocol for the MBH reaction of aldehydes with ethyl acrylate, furnishing the desired products **6** in very good yields (Scheme 3). In the following step, the adducts **6** were protected as the corresponding *tert*-butyldimethylsilyl (TBS) ethers **7** and, finally, oxidation state adjustment



Scheme 3. Synthesis of the protected MBH adducts **7**. (DABCO = 1,4-diazabicyclo[2.2.2]octane.)

should deliver the desired α-methylene aldehydes **8**. Accordingly, the esters **7** were reduced with diisobutylaluminum hydride (DIBAL) to the corresponding alcohols in quantitative yields. Unexpectedly, oxidation of the allylic alcohols to the corresponding aldehyde turned out to be problematic (Table 1).

Table 1. Reduction/oxidation sequence for the protected MBH adducts **7**.

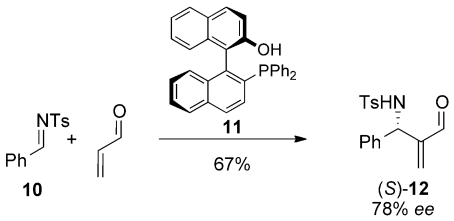


Entry	R^1	Oxidation method	*t* [h]	**8**/**9**	Yield [%][a]
1	Et	MnO_2[b]	24	5:1	< 10
2	Et	PCC[c]	2	> 98:2	64
3	Et	Swern[d]	0.083	> 98:2	70
4	Ph	Swern[e]	1.5	2:1	35
5	Ph	PCC	2	n.d.	23
6	Ph	PCC	1	> 98:2	65
7	$PhCH_2CH_2$	PCC	2	> 98:2	34
8	$PhCH_2CH_2$	Swern	0.083	> 98:2	61
9	3-pyridyl	PCC	1	> 98:2	23

[a] Isolated yields. [b] $c = 1$ M in CH_2Cl_2, MnO_2 (6 equiv), RT. [c] PCC (2.0 equiv), AloxN (1 g mmol^{-1}), PCC, NaOAc (0.2 equiv), RT. [d] DMSO (2.4 equiv), oxalyl chloride (1.2 equiv); then −78 °C, alcohol (1 equiv), 5 min, NEt_3 (5 equiv). [e] DMSO (2.4 equiv), oxalyl chloride (1.2 equiv); then −78 °C, alcohol (1 equiv),1 h, NEt_3 (5 equiv).

Initial attempts with manganese dioxide gave low yield and concomitant decomposition of the starting material was observed (Table 1, entry 1). Furthermore, the reaction furnished a mixture of the desired aldehyde **8** and the isomeric ketone **9**. Presumably, this side product is formed by silyl group migration prior to oxidation.[28] Classical Swern oxidation conditions with a reaction time of 90 min at −78 °C also led to a mixture of **8** and **9** (Table 1, entry 4). Improved yields could be obtained upon addition of triethylamine after 5 min. This procedure suppressed the undesired isomerization (Table 1, entries 3 and 8). A pyridinium chlorochromate (PCC) oxidation protocol was also tested for the allylic oxidation and good yields were obtained upon careful monitoring of the conversion by TLC (Table 1, entries 2 and 6). Again, prolonged reaction times led to inferior results (Table 1, entry 5 versus 6).

Furthermore, the enantiomerically enriched β-aminoaldehyde (*S*)-**12** was prepared from the tosyl imine **10** and acro-

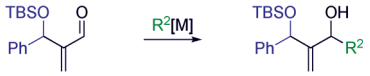


Scheme 4. Preparation of the enantiomerically enriched α-methylene aldehyde (*S*)-**12**.

lein by using the known asymmetric Baylis–Hillman protocol (Scheme 4). In this reaction, the axially chiral, bifunctional organocatalyst **11** delivers the aldehyde (*S*)-**12** with an enantiomeric excess (*ee*) of 78%.[29]

Next, 1,2-addition of an organometallic reagent to aldehydes **8** or **12** to furnish the corresponding *gem*-disubstituted allylic alcohols **13**–**17** was explored (Tables 2 and 3). However, initial experiments that employed *n*-butylmagnesium bromide proved cumbersome. Under the basic conditions, product mixtures due to silyl group migration were obtained (Table 2, entries 1 and 2). Fortunately, lowering the addition temperature to −20 °C, together with a shortened reaction time, furnished **13a** in good yield without concomitant silyl group migration (Table 2, entry 3). However, for the reaction with the benzyl Grignard reagent these optimized conditions only gave modest yields, presumably due to competitive 1,4-addition (Table 2, entry 6). To improve the selectivity for 1,2-addition, we used benzyl lithium as a harder nucleophile and obtained the desired product **13b** in 59% yield (Table 2, entry 7). Notably, the monoprotected diols were obtained as diastereomeric mixtures in all cases, and they can be used as such. We have previously shown that the absolute and relative configurations of such stereocenters do not affect the *E*/*Z* selectivity of the directed allylic substitution reaction.[22]

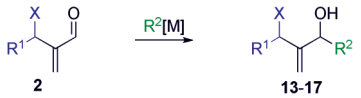
Table 2. Optimization of the reaction conditions for the addition of organometallic reagents to α-methylene aldehydes.[a]

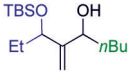
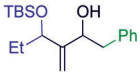
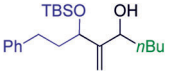
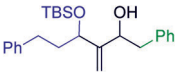
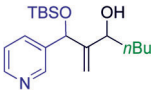
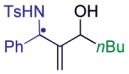
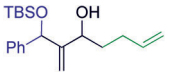
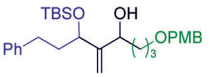


Entry	R^2[M]	*t* [h]	*T* [°C]	Yield [%][b]
1	*n*BuMgBr	12	0–RT	51[c]
2	*n*BuMgBr	0.25	0	16[c]
3	*n*BuMgBr	0.05	−20	64 (d.r.[d] = 52:48)
4	BnMgBr	12	0–RT	30[c]
5	BnMgBr	4	0	37[c]
6	BnMgBr	0.05	−20	44
7	BnLi	0.05	−20	59 (d.r. = 79:21)

[a] Conditions: $c = 0.5$ M in diethyl ether, R^2[M] (1.1–1.3 equiv). [b] Isolated yield. [c] Yields refer to inseparable mixtures of isomers due to silyl group migration. [d] Diastereomeric ratio.

Table 3. Addition of organometallic reagents to α-methylene aldehydes.[a]

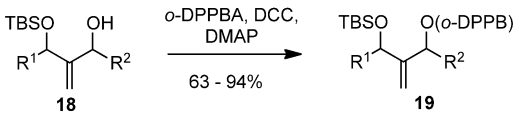


Entry	Product		[M]	*t* [min]	*T* [°C]	Yield [%][b]	d.r.
1		**14a**	Mg	3	−20	79	83:17
2		**14b**	Li	3	−20	71	80:20
3		**15a**	Mg	3	−20	69	70:30
4		**15b**	Li	3	−20	70	60:40
5		**16**	Mg	720	0–RT	36	80:20
6		**17**	Mg	720	−20–RT	53	77:23
7		**13c**	Mg	3	−20	51	56:44
8		**15c**	Mg	3	−20	44 (80)[c]	66:34

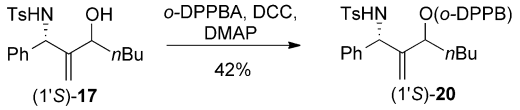
[a] Conditions: $c = 0.5$ M in diethyl ether, organometallic reagent (1.1–1.3 equiv). [b] Isolated yield. [c] Yield in brackets refers to the yield based on recovered aldehyde due to incomplete conversion of the bromide reagent into the Grignard reagent.

Next, the optimized reaction conditions were applied to prepare a broad range of differently substituted allylic alcohols (Table 3). Simple alkyl- and aryl-substituted aldehydes gave the corresponding products in good yields under the optimized conditions (Table 3, entries 1–4, 7 and 8). For nitrogen-functionalized substrates, such as the pyridine or tosyl amine derivatives, prolonged reaction times were necessary to obtain full conversion (Table 3, entries 5 and 6). The enantiomerically enriched aldehyde (*S*)-**12** furnished (1′*S*)-**17** in good yield as a mixture of *syn*- and *anti*-diastereomers (Table 3, entry 6). As noted earlier, the configuration of the stereocenter formed after Grignard addition is irrelevant to the stereochemical course of the alkene-forming allylic substitution reaction.

To activate the thus obtained *gem*-disubstituted allylic alcohols for the directed allylic substitution they were transformed into the corresponding *o*-DPPB esters **18** (Scheme 5). Standard Steglich esterification conditions furnished the desired products in moderate to very good yields.[30] Additionally, the enantiomerically enriched *o*-DPPB ester (1′*S*)-**19** was obtained by using the same procedure (Scheme 6). Following this route, we were able to access eleven different *o*-DPPB esters as starting materials for the directed allylic substitution. All of these examples



Scheme 5. Esterification of monoprotected allylic alcohols with *o*-DPPBA under Steglich conditions. (*o*-DPPBA = *ortho*-diphenylphosphanyl benzoic acid, DCC = *N*,*N*-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine)



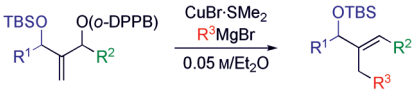
Scheme 6. Esterification of the enantiomerically enriched amine (1′*S*)-**17**.

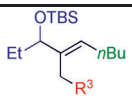
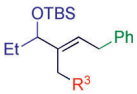
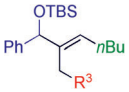
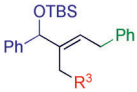
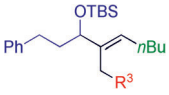
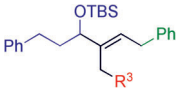
were accessible in just three steps from only four different α-methylene aldehydes.

Next, *o*-DPPB esters **18** were examined in the directed allylic substitution with different alkyl Grignard reagents (Table 4). With all of the alkyl- and phenyl-substituted esters good yields were observed under standard conditions. Additionally, excellent *E*/*Z* selectivities ranging between 95:5 and >98:2 were obtained for the reactions with both the *n*-butyl- and isopropyl Grignard reagents. In most cases, only the *E* isomer could be detected. The observed high stereoselectivity is presumably a consequence of the high steric demand of the OTBS group, thus reactive conformation **4b** is favored due to the minimization of $A^{1,2}$ strain (see Scheme 2). Compared to our previous results with methyl substituents in this position,[22] the OTBS group yielded superior selectivities. Even the less sterically demanding methyl Grignard reagent gave rise to a high *E* selectivity of 95:5 (Table 4, entry 3).

Furthermore, several side-chain functionalized *o*-DPPB esters **26** were tested as substrates for the directed allylic substitution (Table 5). Both the olefin- and oxygen-functionalized esters (Table 5, entries 1 and 2) showed no significant difference in reactivity and selectivity compared to the results shown in Table 4. Accordingly, the corresponding products **27** and **28** were isolated in high yields and with excellent *E* selectivity. Initially, in the case of the tosyl amine, an additional equivalent of Grignard reagent was used to deprotonate the amine. Directed allylic substitution then yielded the allylic amine **29** with high diastereoselectivity (Table 5, entry 3). However, further experiments showed that the substitution reaction is faster than deprotonation of the amine. Thus, the enantiomerically enriched product (*R*)-**29** (Table 5, entry 4) was isolated in excellent yield and selectivity by using only a slight excess of Grignard reagent. HPLC analysis proved the preservation of the stereochemi-

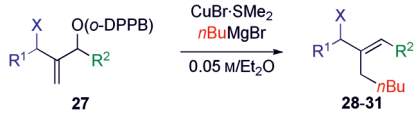
Table 4. Directed allylic substitution with functionalized *o*-DPPB esters.[a]

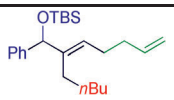
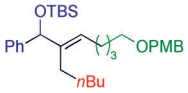
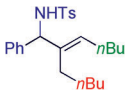
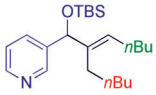


Entry	Product		R^3	*E*/*Z*[b]	Yield [%][c]
1		**20a**	*n*Bu	>98:2	72
2		**20b**	*i*Pr	>98:2	83
3		**20c**	Me	95:5	91
4		**21a**	*n*Bu	>98:2	52
5		**21b**	*i*Pr	>98:2	66
6		**22a**	*n*Bu	97:3	91
7		**22b**	*i*Pr	95:5	85
8		**23a**	*n*Bu	>98:2	81
9		**23b**	*i*Pr	>98:2	71
10		**24a**	*n*Bu	>98:2	66
11		**24b**	*i*Pr	97:3	89
12		**25a**	*n*Bu	>98:2	88
13		**25b**	*i*Pr	>98:2	97

[a] Conditions: $c = 0.05$ M in diethyl ether, Grignard reagent (1.1–1.3 equiv), RT. [b] The *E*/*Z* ratio was determined from the 500 MHz ^{1}H NMR spectra, the assignment of the *E*- or *Z*-isomer was determined by measurement of NOE contacts. [c] Isolated yields. The S_N2'/S_N2 selectivity was >98:2 in all cases.

Table 5. Directed allylic substitution with functionalized *o*-DPPB esters.[a]



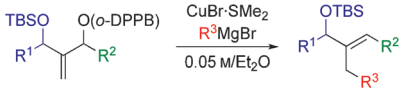
Entry	Product		*E*/*Z*	S_N2'/S_N2	Yield [%][b]
1		**27**	96:4	>98:2	82
2		**28**	>98:2	>98:2	91
3		**29**	>98:2	97:3	86[c]
4		(*R*)-**29**	>98:2	98:2	100 (83 % *ee*)[d]
5		**30**	60:40	84:16	68

[a] Conditions: $c = 0.05$ M in diethyl ether, Grignard reagent (1.1–1.3 equiv), RT. [b] Isolated yield. [c] The reaction was performed with Grignard reagent (2 equiv). [d] Determined by chiral HPLC.

cal information of the allylic amine during the course of the directed allylic substitution reaction. A 3-pyridyl substituent turned out to be inferior in terms of selectivity and reactivity in the directed allylic substitution. Thus, not only was the *E*/*Z* selectivity lower for this example, but the S_N2 side reaction was also observed (Table 5, entry 5). To rationalize this result, a competing coordination of the copper reagent with the pyridyl substituent may be envisioned. As such, the directing function of the *o*-DPPB group is disturbed by this interaction with an alternative ligand. The use of directing pyridine groups in copper-mediated reactions has been described previously by Itami and Yoshida.[17,31]

Finally, the reactions with functionalized Grignard reagents were examined (Table 6). As previously found, the Grignard reagents with remote oxygen and olefin functionality gave excellent results in the directed allylic substitution (Table 6, entries 1 and 2).[22] Additionally, we were able to apply a benzyl Grignard reagent which yielded alkene **23c** with excellent *E*/*Z* selectivity and in quantitative yield (Table 6, entry 3). With sp^2-hybridized Grignard reagents it was found that both the inverse addition method and a high dilution of the Grignard reagent were crucial to obtain high *E*/*Z* selectivity (Table 6, entry 5 versus 6 for phenyl Grignard reagent). However, the reaction with a simple, unsubstituted vinyl Grignard reagent was unsuccessful, even under optimized reaction conditions; only 1,2-addition of the organometallic reagent to the ester carbonyl was observed (Table 6, entry 7). In general, when applying sp^2 Grignard reagents the yields were normally lower. Furthermore, as observed previously, the reaction with phenyl Grignard occurred with inverted *Z* selectivity, presumably due to a change in mechanism toward a carbometalation pathway.[22]

Table 6. Directed allylic substitution with functionalized *o*-DPPB esters.[a]



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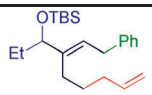
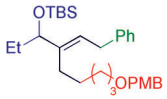
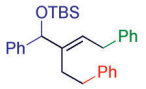
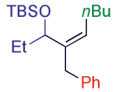
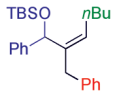
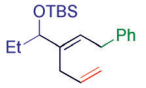
Entry	Product		*E*/*Z*	Addition	Yield [%][b]
1		**21c**	97:3	normal 30 min	60
2		**21d**	97:3	normal 30 min	99
3		**23c**	94:6	normal 30 min	100
5		**20d**	2:98	inverse 90 min	36[c]
6		**22c**	21:79	inverse 90 min	24[d]
7		**21e**	–	inverse 30 min	0[e]

[a] Conditions: $c = 0.05$ M in diethyl ether, Grignard reagent (1.1–1.3 equiv), RT. [b] Isolated yields. The S_N2'/S_N2-selectivity was >98:2 in all cases. [c] [Grignard] = 0.10 M, [ester/Cu] = 0.056 M. [d] [Grignard] = 0.15 M, [ester/Cu] = 0.21 M. [e] Only 1,2-addition of organometallic reagent to the ester was observed.

Conclusion

We have developed a stereoselective and flexible synthetic methodology for the divergent construction of stereodefined trisubstituted allylic alcohols and amines. A key component of the methodology is the *o*-DPPB-directed allylic substitution with Grignard-derived organocopper reagents to furnish the corresponding *E* alkenes in excellent yield and selectivity. The starting point of this diversity-oriented methodology is α-methylene aldehydes derived from Baylis–Hillman adducts. The successive addition of organometallic reagents (mostly inexpensive and readily available Grignard reagents) allows highly flexible access to a wide range of trisubstituted allylic alcohols and amines. The latter have found use as peptide isosteres, therefore, this approach might be ideally suited to generate a library of such compounds for evaluation in medicinal chemistry.

Experimental Section

General remarks: All reactions were carried out under an atmosphere of argon 5.0 (Südwest-Gas) in dried glassware. Air- and moisture-sensitive liquids and solutions were transferred by syringe. All solvents were dried and distilled by standard procedures. Solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished on Merck silica gel 60 Å (200–400 mesh). ^1H and ^{13}C NMR spectra were acquired on a Varian Mercury spectrometer (300 MHz and 75 MHz, respectively) or a Bruker AMX 400 spectrometer (400 MHz and 101 MHz, respectively) and are referenced to an internal TMS standard or solvent signals ($CDCl_3$: $\delta = 7.26$ ppm; C_6D_6: $\delta = 7.16$ ppm). Data for ^1H NMR spectra are reported as follows: chemical shift (δ, in ppm), multiplicity (s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; sept, septet; m_c, centered multiplet; m, multiplet; app, apparent signal), coupling constant (Hz), integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ, in ppm). *E*/*Z* ratios were determined from the ^1H NMR spectra. Assignment of the ^1H NMR spectra were accomplished by H,H-COSY experiments and the ^{13}C NMR spectra by C,H-COSY experiments. The shift values, given in square brackets, refer to the differing values for the second isomer. Stereogenic centers are represented by an asterisk (*). 2D-NOESY or 2D-ROESY experiments confirmed the assignment of *E* and *Z* configurations, respectively. HRMS were obtained on a Finnigan MAT 8200 instrument. Elemental analysis was performed on an Elementar vario instrument (Fa. Elementar Analysensysteme GmbH).

Typical procedure for the preparation of MBH adducts 6, in particular for; ethyl-2-(hydroxy(phenyl)methyl)acrylate (6b): A mixture of ethyl acrylate (8.3 mL, 7.6 g, 76 mmol, 1.5 equiv), benzaldehyde (5.2 mL, 5.5 g, 51 mmol), and DABCO (841 mg, 7.5 mmol, 15 mol%) was stirred at RT until complete conversion of the aldehyde was observed (NMR control, 10 d). The reaction mixture was quenched with water, extracted with

ethyl acetate, and dried under high vacuum (to remove excess ethyl acrylate). Compound **6b** (9.0 g, 85%) was obtained as a colorless liquid. R_f = 0.08 (petroleum ether/*tert*-butyl methyl ether (TBME) 10:1). The product was used without further purification. An analytical sample was purified by flash chromatography on silica (petroleum ether/TBME 5:1). R_f = 0.08 (petroleum ether/TBME 10:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.4 Hz, 3H; 2′-H), 3.05 (d, ^3J = 5.7 Hz, 1H; O*H*), 4.18, (q, ^3J = 7.1 Hz, 2H; 1′-H), 5.56 (d, ^3J = 5.7 Hz, 1H; 2-C*H*OH), 5.81 (dd, ^2J = 1.2 Hz, ^4J = 1.2 Hz, 1H; 3-H_AH_B), 6.34 (dd, ^2J = 1.2 Hz, ^4J = 0.7 Hz, 1H; 3-H_AH_B) 7.27–7.31 (m, 1H; Ar-H), 7.32–7.40 ppm (m, 4H; Ar-H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = 14.1 (C-2′), 61.0 (C-1′), 73.5 (2-*C*HOH), 126.0, 126.7 (2C), 127.9, 128.5 (2C), 141.4, 142.2, 166.4 ppm (C-1). The analytical data match those reported previously.[32]

Typical procedure for the protection with TBS Cl; in particular ethyl 2-[(*tert*-butyldimethylsilyloxy)(phenyl)methyl]acrylate (7b): A solution of the Baylis–Hillman adduct **6b** (4.60 g, 22.3 mmol) in CH_2Cl_2 (135 mL) was stirred over 4 Å molecular sieves for 30 min at RT. Imidazole (1.82 g, 26.7 mmol, 1.2 equiv) was added and the mixture was cooled to 0°C, then TBSCl (3.91 g, 24.5 mmol, 1.1 equiv) was added. After stirring for 24 h at RT, the molecular sieves was filtered off and the reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. Purification by flash chromatography (silica, petroleum ether/TBME 20:1) furnished **7b** (5.67 g, 79%) as a colorless oil. R_f = 0.51 (petroleum ether/TBME 15:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = −0.12 (s, 3H; Si−CH_3), 0.05 (s, 3H; Si−CH_3), 0.87 (s, 9H; *t*Bu), 1.22 (t, ^3J = 7.1 Hz, 3H; 2″-H), 4.08 (dq, ^2J = 10.8 Hz, ^3J = 7.1 Hz, 1H; 1″-H_A), 4.16 (dq, ^2J = 10.8 Hz, ^3J = 7.1 Hz, 1H; 1″-H_B), 5.60 (pseudo s, 1H; 1′-H), 6.05 (dd, ^2J = 1.7 Hz, ^4J = 1.7 Hz, 1H, 3-H_A), 6.25 (dd, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 1H; 3-H_B), 7.19–7.24 (m, 1H), 7.25–7.30 (m, 2H), 7.33–7.37 ppm (m, 2H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −4.9 (Si−*C*H_3), −4.8 (Si−*C*H_3), 14.2 (C-2″), 18.3 (Si−C_q), 25.9 (3C; *t*Bu), 60.6, 72.9, 123.7, 127.2 (2C), 127.4, 128.1 (2C), 142.8, 144.3, 166.1 (C-1); MS (CI, NH_3, 130 eV): *m*/*z* (%): 275 (20), 274 (71), 273 (100), 243 (13), 215 (68), 187 (14), 169 (12); MS (EI, 70 eV): *m*/*z* (%): 243 (31), 216 (15), 215 (100), 187 (39), 169 (59), 75 (20), 73 (17); HRMS: *m*/*z* calcd for $C_{18}H_{29}O_3Si$: 321.18860 $[M+H]^+$; found: 321.18930 (−2.2 ppm); elemental analysis (%) calcd for $C_{18}H_{28}O_3Si$ (320.50): C 67.46, H 8.81; found: C 67.36, H 8.99.

Typical procedure for DIBAL reduction/Swern oxidation, in particular for 3-(*tert*-butyldimethylsilyloxy)-2-methylenepentanal (8a): A solution of ester **7a** (6.96 g, 25.6 mmol) in CH_2Cl_2 (80 mL) was cooled to −78°C and a solution of DIBAL in CH_2Cl_2 (44 mL, 62 mmol, 2.4 equiv) was added. The reaction mixture was stirred at −78°C until complete conversion of the ester was observed (TLC). The reaction mixture was quenched at −78°C by addition of a saturated aqueous solution of sodium acetate (8 mL mmol^{-1}), a saturated aqueous solution of NH_4Cl (1.5 mL mmol^{-1}), and EtOAc (8 mL mmol^{-1}). The mixture was stirred at RT for 1 h. The resulting gel was filtered over Celite and rinsed with EtOAc. If no gelation occurred, the phases were separated and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The obtained alcohol was used directly in the next step. A solution of oxalyl chloride (0.52 mL, 0.77 g, 6.1 mmol) in CH_2Cl_2 (8 mL) was cooled to −50°C and DMSO (0.85 mL, 0.94 g, 12 mmol) in CH_2Cl_2 (8 mL) was added. After stirring for 15 min at −50°C a solution of the alcohol (1.16 g, 5.02 mmol) in CH_2Cl_2 (8 mL) was added. Immediately after the addition, triethylamine (3.5 mL, 2.5 g, 25 mmol) was added and the mixture was stirred for 5 min at −50°C. The reaction mixture was warmed to RT, diluted with water, and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. Purification by flash chromatography (silica, petroleum ether/TBME 50:1) furnished **8a** (796 mg, 70%) as a colorless oil. R_f = 0.74 (petroleum ether/TBME 10:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = −0.03 (s, 3H; Si−CH_3), 0.05 (s, 3H; Si−CH_3), 0.84 (t, ^3J = 7.4 Hz, 3H; 5-H), 0.91 (s, 9H; *t*Bu), 1.47 (ddq, ^2J = 13.8 Hz, ^3J = 7.4, 6.4 Hz, 1H; 3-H_A), 1.64 (ddq, ^2J = 14.3 Hz, ^3J = 7.2, 4.1 Hz, 1H; 3-H_B), 4.59 (m_c, 1H; 3-H), 6.08 (dd, ^2J = 1.0 Hz, ^4J = 0.9 Hz, 1H; 2-CH_AH_B), 6.52 (dd, ^2J = 1.4 Hz, ^4J = 1.4 Hz, 1H; 2-CH_AH_B), 9.57 ppm (s, 1H; 1-H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −4.9 (Si−*C*H_3), −4.8 (Si−*C*H_3), 9.0 (C-5), 18.2 (Si−C_q), 25.7 (3C, *t*Bu), 30.1 (C-4), 69.2 (C-3), 134.5 (2-*C*H_2), 153.4 (C-2), 193.7 ppm (C-1); MS (EI, 70 eV): *m*/*z* (%): 230 (19) $[M+2H]^+$, 229 (100) $[M+H]^+$, 171 (38); HRMS: *m*/*z*: calcd for $C_{12}H_{25}O_2Si$: 229.16238 $[M+H]^+$; found: 229.16200 (+1.7 ppm).

Typical procedure for DIBAL reduction/PCC oxidation, in particular for 2-[(*tert*-butyldimethylsilyloxy)(phenyl)methyl]acrylaldehyde (8b): A solution of the ester **7b** (1.60 g, 5.00 mmol) in CH_2Cl_2 (16 mL) was cooled to −78 C and a solution of DIBAL in CH_2Cl_2 (12 mL, 12 mmol 1.0 M, 2.4 equiv) was added. The reaction mixture was stirred at −78 C until complete conversion of the ester was observed (TLC). The reaction mixture was quenched at-78°C by addition of a saturated aqueous solution of sodium acetate (8 mL mmol^{-1}), a saturated aqueous solution of NH_4Cl (1.5 mL mmol^{-1}), and EtOAc (8 mL mmol^{-1}) and the mixture was stirred at room temperature for 1 h. The resulting gel was filtered over Celite and rinsed with EtOAc. If no gelation occurred, the phases were separated and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The obtained alcohol was used directly in the next step. Sodium acetate (324 mg, 3.94 mmol, 0.340 equiv) was added to a suspension of PCC (8.51 g, 39.5 mmol, 3.4 equiv) and AloxN (40 g) in CH_2Cl_2 (80 mL) at RT. Then, a solution of the alcohol (3.24 g, 11.6 mmol) in CH_2Cl_2 was added slowly. After the reaction time indicated (see Table 1), the reaction mixture was filtered over Celite, rinsed with CH_2Cl_2, and the solvent was evaporated under reduced pressure. Compound **8b** (2.1 g, 65%) was obtained as a colorless oil. An analytical sample was purified by flash chromatography (silica, petroleum ether/TBME 20:1). R_f = 0.56 (petroleum ether/TBME 15:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 0.10 (s, 3H; Si−CH_3), 0.04 (s, 3H; Si−CH_3), 0.88 (s, 9H; *t*Bu), 5.63 (s, 1H; 1′-H), 6.07 (dd, ^2J = 1.0 Hz, ^4J = 1.0 Hz, 1H; 3-H_A), 6.66 (dd, ^2J = 1.3 Hz, ^4J = 1.3 Hz, 1H; 3-H_B), 7.19–7.24 (m, 1H), 7.25–7.30 (m, 2H), 7.35–7.38 (m, 2H), 9.53 ppm (s, 1H; 1-H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −5.1 (Si−*C*H_3), −4.9 (Si−*C*H_3), 18.2 (Si−C_q), 25.7 (3C; *t*Bu), 70.5 (C-1′), 126.6 (2C), 127.4, 128.1 (2C), 133.0, 142.5, 153.3, 192.8 ppm (C-1); MS (CI, NH_3, 130 eV): *m*/*z* (%): 278 (14), 277 (82), 220 (18), 219 (100), 162 (82), 145 (56); MS (EI, 70 eV): *m*/*z* (%): 220 (13), 219 (100), 189 (10), 115 (35), 113 (47), 75 (64), 73 (17), 59 (16); HRMS calcd for $C_{16}H_{25}O_2Si$: 277.16238 $[M+H]^+$; found: 277.16210 (+1.0 ppm).

Typical procedure for the addition of alkyl Grignard reagent to TBS-protected aldehydes, in particular 3-(*tert*-butyldimethylsilyloxy)-4-methylenenonan-5-ol (14a): A solution of aldehyde **8a** (200 mg, 0.88 mmol) in diethyl ether (2 mL) was cooled to −20°C and the Grignard reagent (0.55 M in diethyl ether, 2.0 mL, 1.1 mmol) was added dropwise. After complete addition, the reaction was immediately quenched with a saturated aqueous solution of NH_4Cl and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, the combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Purification by flash chromatography (silica, petroleum ether/TBME 30:1) furnished **14a** (200 mg, 79%, d.r. = 83:17) as a colorless oil. R_f = 0.22 (petroleum ether/TBME 15:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 0.03[0.05] (s, 3H; Si−CH_3), 0.07[0.08] (s, 3H; Si−CH_3), 0.87[0.83] (t, ^3J = 7.4 Hz, 3H; 9-H), 0.89–0.94 (m, 3H; 1-H), 0.90 (s, 9H; *t*Bu), 1.27–1.40[1.42–1.50] (m, 4H; 7-H, 8-H), 1.58–1.70[1.98–2.09] (m, 4H; 2-H, 6-H), 4.16[3.99] (t, ^3J = 7.6 Hz, 1H; 3-H)*, 4.18[4.11] (t, ^3J = 7.4 Hz, 1H; 5-H)*, 5.02[5.03] (dd, ^4J = 1.2, 1.2 Hz, 1H; 4-CH_AH_B), 5.05 ppm [5.09] (dd, ^4J = 1.2, 1.2 Hz, 1H; 4-CH_AH_B); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −4.80[−4.77] (Si−*C*H_3), −4.5 (Si−*C*H_3), 10.2-[10.1] (C-9), 14.2 (C-1), 18.22[18.18] (Si−C_q), 22.8[22.9], 25.9 (3C, *t*Bu), 28.4[28.1], 30.3[29.5], 36.8[35.4], 72.5[70.3], 77.3[78.7], 111.3[111.2] (4-*C*H_2), 153.4 ppm [152.0] (C-4); MS (CI, NH_3, 130 eV): *m*/*z* (%): 287 (34) $[M+H]^+$, 229 (25), 138 (11), 137 (100); MS (EI, 70 eV): *m*/*z* (%): 257 (23), 229 (28), 211 (24), 201 (11), 173 (12), 147 (12), 143 (21), 137 (26), 133 (30), 115 (14), 95 (81), 81 (58), 75 (100), 73 (41), 69 (14), 67 (14), 52 (19), 55 (15), 41 (17); HRMS: *m*/*z*: calcd for $C_{16}H_{35}O_2Si$: 287.24063 $[M+H]^+$; found: 287.24030 (+1.2 ppm); elemental analysis (%) calcd for $C_{16}H_{34}O_2Si$ (286.52): C 67.07, H 11.96; found: C 67.21, H 12.00.

Typical procedure for the addition of benzyllithium to TBS-protected aldehydes, in particular for 4-(*tert*-butyldimethylsilyloxy)-3-methylene (14b): *n*BuLi (0.48 mL, 1.1 mmol, 1.2 equiv) was added to a solution of TMEDA (0.16 mL, 0.12 g, 1.1 mmol, 1.2 equiv) in toluene (1.1 mL, 11 mmol, 12 equiv) at RT. After stirring for 30 min, the reaction mixture was cooled to −20 °C and a solution of aldehyde **8a** (200 mg, 0.88 mmol) in THF (1 mL) was added. The reaction was quenched immediately with a saturated aqueous solution of NH_4Cl and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, the combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Purification by flash chromatography (silica, petroleum ether/TBME 15:1) furnished **14b** (200 mg, 71 %, d.r. = 80:20) as a colorless oil. R_f = 0.47 (petroleum ether/TBME 15:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 0.05 (s, 3H; Si−CH_3), 0.07[0.09] (s, 3H; Si−CH_3), 0.80[0.87] (t, ^3J = 7.4 Hz, 3H; 6-H), 0.905[0.915] (s, 9H; *t*Bu), 1.56–1.71 (m, 2H; 5-H), 2.63[1.54] (br s, 1H; OH), 2.86[2.80] (dd, ^2J = 13.7 Hz, ^3J = 8.6 Hz, 1H; 1-H_A), 2.97[3.06] (dd, ^2J = 13.8 Hz, ^3J = 4.5 Hz, 1H; 1-H_B), 4.12 (t, ^3J = 6.4 Hz, 1H; 4-H), 4.37 (ddd, ^3J = 9.2, 4.0 Hz, ^4J = 1.0 Hz, 1H; 2-H), 5.11[5.10] (dd, ^2J = 1.1 Hz, ^4J = 1.1 Hz, 1H; 3-C$H_A$$H_B$), 5.22-[5.17] (dd, ^2J = 1.1 Hz, ^4J = 1.1 Hz, 1H; 3-C$H_A$$H_B$), 7.19–7.35 ppm (m, 5H; Ar-H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −4.8 (Si−*C*H_3), −4.55-[−4.47] (Si−*C*H_3), 10.0[10.2] (C-6), 18.2 (Si−C_q), 25.9[26.0] (3C; *t*Bu), 29.6[30.0] (C-5), 42.8[44.2] (C-1), 71.2[72.5] (C-2)*, 78.1[77.6] (C-4)*, 111.7[111.9] (3-*C*H_2), 126.4[126.5], 128.5[128.6] (2C), 129.45[129.50] (2C), 139.0[139.1] (Ar-C_q), 152.0 ppm (C-3); MS (CI, NH_3, 130 eV): *m*/*z* (%): 312 (14), 311 (20), 310 (100), 245 (14); MS (EI, 70 eV): *m*/*z* (%): 273 (27), 263 (19), 229 (31), 172 (14), 171 (100), 143 (44), 133 (21), 129 (66), 115 (18), 97 (10), 91 (34), 75 (41), 73 (23); elemental analysis (%) calcd for $C_{19}H_{32}O_2Si$ (320.54): C 71.19, H 10.06; found: C 71.17, H 10.29.

Typical procedure for the preparation of *o*-DPPB esters 19 from allylic alcohols 13–16, in particular 3-(*tert*-butyldimethylsilyloxy)-4-methylenenonan-5-yl 2-(diphenylphosphanyl) benzoate (19c): A solution of allylic alcohol **14a** (150 mg, 0.66 mmol) in CH_2Cl_2 was added to a suspension of *o*-DPPBA (244 mg, 0.80 mmol, 1.2 equiv), DCC (165 mg, 0.80 mmol, 1.2 equiv), and DMAP (99 mg, 0.81 mmol, 1.2 equiv) in CH_2Cl_2 (3.5 mL) at RT. The reaction mixture was stirred until complete conversion of the allylic alcohol was observed (TLC). The mixture was filtered over Celite, rinsed with CH_2Cl_2, and the filtrate was evaporated under reduced pressure. Purification by flash chromatography (silica, petroleum ether/TBME 20:1) furnished **18c** (271 mg, 72 %, d.r = 43:57) as yellow oil. R_f = 0. 76 (petroleum ether/TBME 15:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = −0.05[−0.06] (s, 3H; Si−CH_3), 0.01[0.00] (s, 3H; Si−CH_3), 0.77[0.73] (t, ^3J = 7.3 Hz, 3H; 1/9-H), 0.81–0.92 (m, 3H; 9/1-H), 0.88[0.87] (s, 9H; *t*Bu), 1.09–1.33 (m, 6H) [1.37–1.48 (m, 2H)], 1.53–1.69 (m, 2H) [1.72–1.88 (m, 2H)], 4.08[4.01] (dd, ^3J = 6.0, 6.0 Hz, 1H; 3-H), 5.12[5.11] (m_c, 1H; 4-C$H_A$$H_B$), 5.16[5.13] (dd, ^2J = 1.5 Hz, ^4J = 1.5 Hz, 1H; 4-C$H_A$$H_B$), 5.37[5.30] (dd, ^3J = 8.0, 5.0 Hz, 1H; 5-H), 6.89–6.96 (m, 1H; Ar-H), 7.20–7.33 (m, 10H; Ar-H), 7.35–7.44 (m, 2H; Ar-H), 8.08–8.12[8.03–8.07] ppm (m, 1H; Ar-H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −4.91[−4.52] (Si−*C*H_3), −4.52[−4.49] (Si−*C*H_3), 9.2[9.6], 14.0[14.1], 18.3 (Si−C_q), 22.6, 25.95[25.97] (3C; *t*Bu), 27.6[28.1], 30.0[29.5], 34.5[34.3], 73.9[74.1], 74.8-[75.5], 110.9[112.9], 128.3, 128.48 (d, J = 7.1 Hz, 2C), 128.50 (d, J = 7.2 Hz, 2C), 128.6, 130.62[130.65] (d, J = 4.6 Hz), 130.7, 131.90[131.85], 133.9 (d, J = 20.6 Hz, 4C), 134.19[134.15] (d, J = 20.7 Hz, 4C), 134.4-[134.5], 150.4[150.2], 165.8 ppm (d, J = 2.9 Hz); ^{31}P NMR (161.976 MHz, $CDCl_3$): δ = −4.7[−5.0] ppm; MS (CI, NH_3, 130 eV): *m*/*z* (%): 592 (20) $[M+NH_4]^+$, 591 (49) $[M+NH_3]^+$, 576 (31) $[M+H]^+$[M+H]$^+$, 575 (80) $[M]^+$, 533 (10), 379 (14), 323 (22), 306 (20), 305 (100); MS (EI, 70 eV): *m*/*z* (%): 306 (21), 305 (100), 213 (20); HRMS: *m*/*z*: calcd for $C_{35}H_{48}O_3PSi$: 575.31104 $[M+H]^+$; found: 575.31100; elemental analysis (%) calcd for $C_{35}H_{47}O_3PSi$ (574.80): C 73.13, H 8.24; found: C 73.00, H 8.39.

Typical procedure for allylic substitution with *o*-DPPB esters 18, normal addition method, in particular for (*E*)-*tert*-butyldimethyl(4-pentylnon-4-ene-3-yloxy)silane (20a): CuBr·SMe_2 (6.2 mg, 0.030 mmol, 0.51 equiv) was added to a solution of **19c** (34 mg, 0.059 mmol) in diethyl ether (1.2 mL) at RT. The Grignard reagent (0.55 M in diethyl ether, 0.082 mmol, 1.4 equiv) was added to this intensely yellow solution over 30 min by syringe pump. After stirring overnight, the conversion was determined by TLC and the reaction mixture was directly applied onto a silica gel column. Purification by flash chromatography (silica, petroleum ether/TBME 100:1) furnished **20a** (14 mg, 72 %, E/Z > 98:2) as a colorless oil. R_f = 0.87 (petroleum ether/TBME 100:1); ^{1}H NMR (400.132 MHz, $CDCl_3$): δ = −0.02 (s, 3H; Si−CH_3), 0.02 (s, 3H; Si−CH_3), 0.81 (t, ^3J = 7.4 Hz, 3H; 1-H), 0.87–0.92 (m, 6H; 9-H, 5′-H), 0.89 (s, 9H; *t*Bu), 1.21–1.41 (m, 10H; 2′-H, 3′-H, 4′-H, 7-H, 8-H), 1.47 (m_c, 2H; 2-H), 1.86–2.04 (m, 4H; 6-H, 1′-H), 3.87 (t, ^3J = 6.2 Hz, 1H; 3-H), 5.28 ppm (t, ^3J = 6.9 Hz, 1H; 5-H); ^{13}C NMR (100.613 MHz, $CDCl_3$): δ = −4.9 (Si−*C*H_3), −4.4 (Si−*C*H_3), 10.4 (C-1), 14.1 (C-9/5′), 14.2 (C-5′/9), 18.4 (Si−C_q), 22.55, 22.62, 26.0 (3C; *t*Bu), 27.28 (C-6/1′), 27.32 (C-1′/6), 29.7, 29.9 (C-2), 32.2, 32.7, 79.1 (C-3), 126.3 (C-5), 141.4 ppm (C-4); MS (CI, NH_3, 130 eV): *m*/*z* (%): 297 (15), 269 (23), 212 (11), 196 (14), 195 (100); MS (EI, 70 eV): *m*/*z* (%): 298 (26), 297 (88), 270 (28), 269 (100), 75 (32), 73 (11); elemental analysis (%) calcd for calcd for $C_{20}H_{42}OSi$ (326.63): C 73.54, H 12.96; found: C 73.14, H 13.08.

Typical procedure for allylic substitution with *o*-DPPB esters 18, inverse addition method, in particular for (*Z*)-(4-benzylnon-4-ene-3-yloxy)-(*tert*-butyl)dimethylsilane (20d): The Grignard reagent (0.72 M, in diethyl ether, 0.072 mmol, 1.3 equiv) was diluted with diethyl ether (0.62 mL) to 0.1 M concentration. A solution of **19c** (32 mg, 0.056 mmol) and CuBr·SMe_2 (5.8 mg, 0.028 mmol, 0.50 equiv) in diethyl ether (1.0 mL) was added by syringe pump at RT over 30 min. After stirring overnight, the conversion was determined by TLC and the reaction mixture was applied onto a silica gel column. Purification by flash chromatography (silica, petroleum ether) furnished **20d** (10.8 mg, contained biphenyl, 36 %, E/Z 98:2) as a colorless oil. R_f = 0.44 (petroleum ether); ^{1}H NMR (499.630 MHz, $CDCl_3$): δ = −0.09 (s, 3H; Si−CH_3), −0.05 (s, 3H; Si−CH_3), 0.77 (t, ^3J = 7.4 Hz, 3H; 9-H), 0.87 (s, 9H; *t*Bu), 0.89 (t, ^3J = 7.1 Hz, 3H; 1-H), 1.29–1.40 (m, 6H; 2-H, 7-H, 8-H), 2.09 (td, ^3J = 7.2, 7.2 Hz, 1H; 6-H_A), 2.10 (td, ^3J = 7.1, 7.1 Hz, 1H; 6-H_B), 3.28 (d, ^2J = 15.4 Hz, 1H; 1′-H_A), 3.52 (d, ^2J = 15.4 Hz, 1H; 1′-H_B), 3.90 (dd, ^3J = 6.1, 5.3 Hz, 1H; 3-H), 5.59 (dd, ^3J = 7.3, 7.3 Hz, 1H; 5-H), 7.13–7.19 (m, 3H; Ar-H), 7.22–7.25 ppm (m, 2H; Ar-H); ^{13}C NMR (125.312 MHz, $CDCl_3$): δ = −5.0 (Si−*C*H_3), −4.6 (Si−*C*H_3), 10.1 (C-1), 14.1 (C-9), 18.3 (Si−C_q), 22.6, 26.0 (3C; *t*Bu), 27.8 (C-6), 29.8, 32.0, 33.1 (C-1′), 77.9 (C-3), 125.7, 127.8 (C-5), 128.2 (2C), 128.6 (2C), 139.3, 140.7 ppm; MS (EI, 70 eV): *m*/*z* (%): 317 (22), 290 (24), 289 (100) $[M-C_4H_9]^+$, 75 (16), 44 (27); HRMS: *m*/*z*: calcd for $C_{22}H_{38}OSi-C_4H_9^+$: 289.19877 $[M-C_4H_9]^+$, found: 289.19900 (+ 0.8 ppm).

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