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Allyl 1,1-Bimetallic Species: Their Preparation and Reactivity Profile.

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Abstract:

A synthesis of novel allyl 1,1-hetero- and homobimetallic compounds where M=Sn or Si' and M'=Si via a palladium catalyzed reduction employing ammonium formate is described. The regioselectivity in the reductions is routinely >99:1.

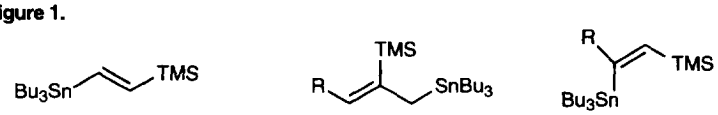
Reaction of these novel reagents was also investigated with various electrophiles and compared to the well studied crotyl- and allylstannane and silanes. Copyright © 1996 Elsevier Science Ltd

Introduction:

Bimetallic compounds are potentially valuable synthetic intermediates when selective reaction of one metal over the other is possible. Within recent years selectivity of this type has been achieved, leading to several useful applications in organic synthesis.[1a,b] Bimetallic compounds can be divided into homobimetallic compounds, where M=M' (although the substituents on the metal may be different) and heterobimetallic compounds where M and M' are two different metals.

There are several ways to effect a selective reaction of one metal over another in a bimetallic compound. For homobimetallic reagents, selective reaction may be achieved by employing a stoichiometric amount of the reagent, by utilizing the different reactivity of an allylic vs. a vinylic metal bond or by varying the substituents on the metal. When M and M' are different, selective reaction of one metal over another is more easily accomplished. In cases where one metal is allylic and the other is vinylic, the allylic metal will typically react first in analogy to the homobimetallic case. In examples where both metals are allylic or vinylic, the weaker carbon-metal bond will be broken preferentially. For instance, in the examples shown in Figure 1, the carbon-tin bond reacts preferentially over the carbon-silicon bond. This selective reactivity is attributed to the fact that the carbon-tin bond is weaker than the carbon-silicon bond.

Figure 1.



Whereas several examples of 1,2- and 1,3-bimetallic reagents are known, less information on the preparation of 1,1-heterobimetallic reagents has been obtained. This may be because 1,1-heterobimetallic compounds are generally less stable and often are prepared and reacted *in situ*. Several groups have

successfully synthesized 1,1-heterobimetallic compounds, where M=Sn and M'=Si and subsequently studied their reactions with various organolithium reagents.[1c-g]

The preparation and reactivity of allyl 1,1-heterobimetallic compounds is a new and potentially fruitful area of research. With the exception of Yamamoto's preparation of α-silyl or α-stannyl substituted crotyl-9-borabicyclo[3.2.1]nonane[2a-c] and Matteson's pinanediol [α-(trimethylsilyl)allyl]boronate esters,[2d] little is known about reactions of allyl 1,1-bimetallic compounds.

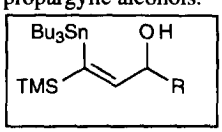
We have begun to explore the synthesis and reactions of allyl 1,1-bimetallic compounds containing Si and Sn and describe our results herein. In particular, we focus on their reactivity with different electrophiles and compare these results with the well studied allylstannane and allylsilane systems.

Results and Discussion:

The synthesis of allyl 1,1-heterobimetallic reagents.

Vinyl 1,1-bimetallic compounds of the general structure **1a-c** were synthesized using the titanium catalyzed hydromagnesiation-stannation sequence on a series of propargylic alcohols.[3]

Figure 2. **1a** R = H
1b R = *n*-propyl
1c R = cyclohexyl



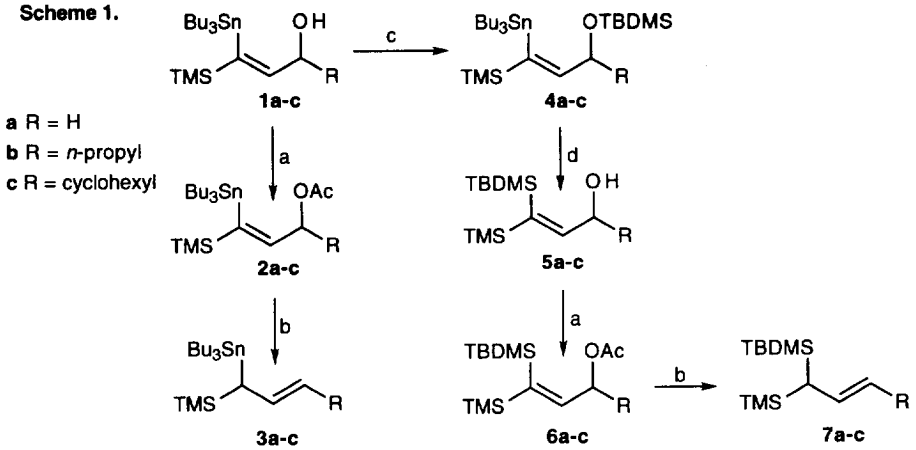
Conversion of the vinylbimetallic alcohols **1a-c** into the desired allylbimetallic derivatives required two steps, Scheme 1. The allylic alcohols were acetylated and then subjected to a highly regioselective palladium catalyzed reduction of an allylic acetate to furnish the desired allyl 1,1-bimetallic compounds, **3a-c** in quantitative yield.[4] It should be noted that the selectivity of the reduction, as determined by 400 MHz ^1H NMR, was typically >99:1 in favor of the allyl 1,1-bimetallic rather than the vinyl 1,1-bimetallic regioisomer.

The 1,1-heterobimetallic compounds containing two different silicon groups were prepared by a similar route following a 1,4-silyl migration reaction.[5] Alcohols **1a-c**, were silylated with TBDMSCl and the resulting silylethers where treated with 1.2 eq of MeLi to effect a tin-lithium exchange and subsequent *in situ* 1,4-migration of the TBDMS group. After aqueous work-up and purification, compounds **5a-c** were obtained in 90-97% yield. These intermediates were then acetylated and the allylic acetate was reduced in the presence of palladium to furnish **7a-c** in yields ranging from 40-91%. Again, as with compounds **3a-c,** the palladium catalyzed reduction was highly regioselective (>99:1) and favored formation of the allylic silane isomer.

This sequence represents a relatively efficient route to allyl 1,1-heterobimetallic compounds where M=Sn or Si' and M'=Si. Four steps are required to prepare **3a-c** and six steps are required for **7a-c** from commercially available starting materials. It should be emphasized that these compounds are not readily available using a simple deprotonation-trapping sequence. For instance, it is known that treatment of allyltrimethylsilane with base then tributyltin chloride gives 3-trimethylsilyl allylstannane rather than **3a** as the major product.[6]

Prior to the discovery of the route outlined above, we had explored other methods of preparing the target compounds. For example, we envisioned that reduction of vinyl 1,1-bimetallic compounds having the general structure of **1a-c**, followed by mesylation and treatment with base would furnish the desired species. Although

Scheme 1.



Reagents: a) Ac_2O, DMAP, Pyridine; b) $Pd_2(dba)_3$, PPh_3, HCO_2H, Et_3N; c) TBDMSCl, DMF, imidazole; d) MeLi (1.2 eq), THF, 0°C; H_2O

the hydrogenation using a cationic rhodium catalyst produced the desired 1-hydroxy-3,3-heterobimetallic compounds,[7] mesylation and treatment with a base such as DBU or triethylamine failed to produce the desired products.[8] Furthermore, conversion of the hydroxy group to a bromine and treatment with base also failed to produce the desired product.

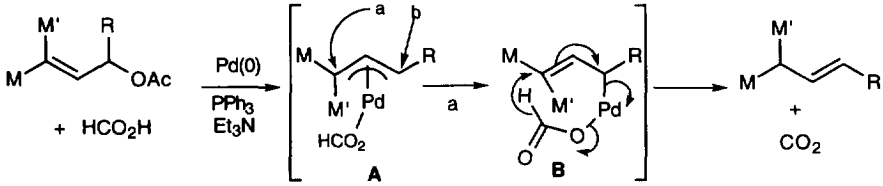
In contrast, the palladium catalyzed hydrogenolysis of allylic acetates with ammonium formate is an efficient and mild method. The regioselectivities obtained are dependent upon the substrate, the nature of the palladium catalyst and phosphine ligand employed. Ammonium formate was chosen as the hydride source, since other hydride sources including lithium aluminum hydride, sodium borohydride and lithium triethylborohydride are known to produce the more substituted olefin.[9]

A typical procedure for the reduction of allylic acetates **2a-c** and **6a-c** utilizes $Pd_2(dba)_3$ (1 to 10 mol%), formic acid-triethylamine (3 eq) as the reductant and triphenylphosphine (4 to 40 mol%) as a ligand. The reactions are carried out in refluxing dioxane and are usually complete in 3-48 hours providing the terminal olefins in 40-99% yield. The high level of regioselectivity in the reductions (>99:1) is particularly noteworthy.

The mechanism of these reductions is believed to proceed as outlined in Scheme 2.[10] The palladium (0) forms a π-complex with the olefin, followed by backside displacement of the acetate form a π-allyl complex (**A**). In theory, the hydride may be delivered to either end of the π-allyl complex (i.e. path a or b) and the pathway followed is influenced by significant steric interactions between the palladium complex and the M and M' subsituents. As a result of this constraint, complex **B** is formed preferentially, which delivers the hydride to the more substituted end of the allylic system (path a) with subsequent generation of carbon dioxide and reductive elimination of Pd(0). Generally, allylic acetates which are disubstituted in the 3-position give the highest selectivities (99:1) when using tributylphosphine as a ligand.[9] In the substrates we examined, excellent selectivities were obtained even when Ph_3P was used as a ligand. While it is apparent that the large tributyltin and trimethylsilyl groups located on C-1 have a pronounced effect on the regiochemistry of the reduction, the magnitude of this effect is not obvious until the selectivities in the reduction of compounds **2c** and **6c** are examined. In these cases, the desired allyl 1,1-heterobimetallic compounds are formed with >99:1 selectivity.

The high regioselectivity and mild reaction conditions make this an attractive route for the preparation of both substituted and unsubstituted allyl 1,1-heterobimetallic compounds.

Scheme 2

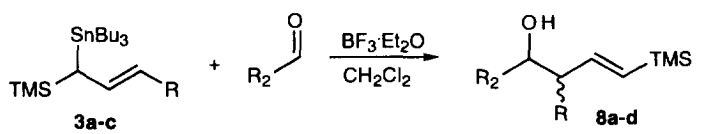


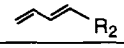
Preliminary reactions of allyl 1,1-heterobimetallic reagents.

With a synthesis of allyl 1,1-heterobimetallic compounds in hand, a preliminary investigation into the reactivity of these compounds was undertaken. The reaction of allylstannanes and allysilanes with various electrophiles has been extensively studied, which allows a direct comparison with the 1,1-bimetallic compounds.

As shown in Table 1a and 1b, compounds **3a-c** reacted with aryl or aliphatic aldehydes as well as acetals. Aldehydes underwent 1,2-addition with substituted and unsubstituted bimetallic reagents to furnish products **8a-d** in 52-91% chemical yield. The aldehyde and Lewis acid (1 eq) were premixed at -78 °C and a solution of **3a-c** was added. Generally, the reaction was complete within 15 min. Selective cleavage of the

Table 1a. Reaction of **3a-c** with aldehydes.



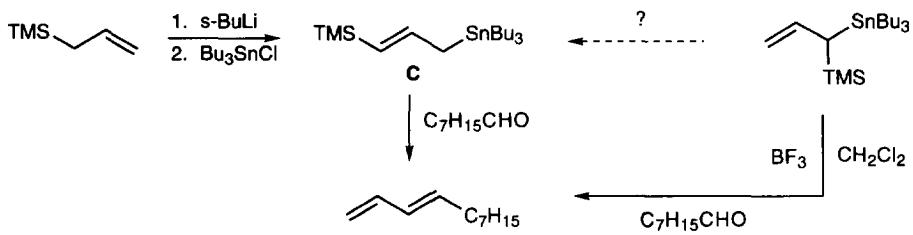
	R	R_2	Product	yield (%)	diastereomeric ratio
3a	H	C_7H_{15}	**8a**	52	NA
				33	
3a	H	Ph	**8b**	91	NA
3b	*n*-propyl	C_7H_{15}	**8c**	72	8:1
3c	cyclohexyl	C_7H_{15}	**8d**	62	4:1

carbon-tin bond was observed in all cases, with no products resulting from cleavage of the carbon-silicon bond detected in the crude reaction mixtures. The weaker carbon-tin bond appears to be responsible for this result. Rate constants for the reaction of allyltributylstannanes and allyltrimethylsilanes with diaryl carbenium ions have been measured and the allylstannane is approximately 2000 times more reactive.[11] The configuration of the double bond in all cases was *trans* based on a 17 Hz coupling constant in the ^1H NMR spectrum. Examination of the possible transition states reveals a plausible explanation for this result. Based upon an antiperiplanar orientation[12], formation of the *trans* olefin is favored over the *cis* because of significant 1,3-allylic strain.

In our preliminary report, we showed that reaction of **3a** with an aliphatic aldehyde led to a mixture of **8a** and undeca-1,3-diene.[4] The stereochemistry of the diene was shown to be *(E)* based on a 17 Hz coupling constant in the ^{1}H NMR spectrum. We proposed that the diene was formed when **3a** underwent a 1,3-tin shift, followed by addition to the aldehyde and Peterson elimination. This result suggested that the silyl stannyl bimetallic compounds might not be useful for simple carbonyl addition reactions. However, it appears that the tin shift is not a major side reaction when the olefin bears a substituent at the terminus. Allylbimetallic reagents **3b** and **3c** reacted efficiently with alkyl or aryl aldehydes and produced no diene.

To confirm that the rearranged 1,3-bimetallic reagent was responsible for formation of the diene, **C** was prepared as described by Keck[6] and treated with octanal, Scheme 3. At -78 °C the *(E)*-diene was isolated in 95% yield. It is interesting to note that reaction of **3a** with benzaldehyde produced no diene. This may be because addition to the aryl aldehyde is a much faster reaction than the 1,3-tin shift.

Scheme 3.



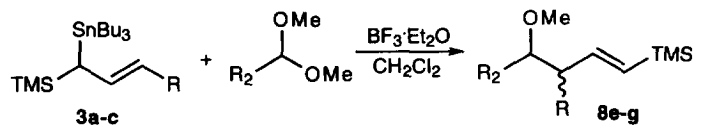
1,3-Tin shifts are well documented in the literature.[13] For instance, Marshall reported that on treatment of optically active (*E*)-α-(alkoxy)allyl stannanes with $BF_3{\cdot}Et_2O$ at -78 °C, a 1,3-isomerization of these compounds occurs stereospecifically to produce the (*Z*)-γ-(alkoxy)allyl stannanes.[14] The process occurs through an intramolecular *anti-* S_E' mechanism and involves a 1,3 migration of the Bu_3Sn group. Similar migrations have also been reported in the reaction of allyl- and crotylstannanes in the presence of Lewis acids other than $BF_3{\cdot}Et_2O$.[15] In the case of **3a**, weaker Lewis acids were examined which might induce formation of the desired product and be less efficient at promoting the 1,3 migration. Unfortunately, the bimetallic compound **3a** was recovered or was destroyed on work-up in all cases.[16]

The stereochemistry of the diene produced when **3a** reacts with octanal is interesting when compared to other work with related compounds.[17, 18] Yamamoto demonstrated that the stereochemistry of the non-terminal double bond is dependent upon both the nature of the Lewis acid employed and the geometry of the double bond in the allylmetal.[19] When Yamamoto reacted **C** with aliphatic aldehydes in the presence of $BF_3{\cdot}Et_2O$ at -78 °C, he obtained substituted dienes with exclusively the *(Z)* stereochemistry. Formation of the *syn*-intermediate which then underwent an *anti*-Peterson elimination to give the *(Z)* diene was proposed.[19] Other variations on this theme have been described.[20]

The diastereomeric ratios of the products in Table 1a and 1b were measured by ^{1}H and ^{13}C NMR and capillary GC and ranged from 4:1 to 8:1. Reaction of crotylstannane with aldehydes typically gives much higher diastereomeric ratios (90 to 99:1) than we observed.[21] Reactions of α-(alkoxy)allylstannanes, where the alkoxy group presumably occupies the same position as the TMS in the transition state, were also highly selective.[22] Further studies are required to understand the cause of the decrease in selectivity in the presence of the silicon functionality.

Compounds **3a-c** also reacted with aryl dimethyl acetals as shown in Table 1b. Again, selective cleavage of the carbon-tin bond was observed and only the *trans* olefin was produced. Reaction of **3b** with aliphatic dimethyl acetals and pyruvic aldehyde dimethylacetal failed when BF_3 etherate was employed as a Lewis acid. More reactive Lewis acids and different reaction temperatures, have to date been unsuccessful in promoting the desired reaction.

Table 1b. Reaction of **3a-c** with dimethyl acetals.

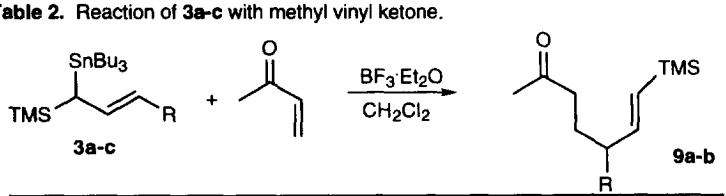


	R	R_2	Product[a]	yield (%)	diastereometic ratio
3a	H	Ph	**8e**	72	NA
3b	n-propyl	Ph	**8f**	83	5:1
3b	n-propyl	$CH_3C(O)$	NR	NA	NA
3b	n-propyl	C_7H_{15}	NR	NA	NA
3c	cyclohexyl	Ph	**8g**	66	4:1

a) In all cases where no reaction was observed the bimetallic reagent decomposed on work-up.

Bimetallic compounds **3b-c** did undergo 1,4- addition to methyl vinyl ketone as shown in Table 2. In a typical procedure, the enone was premixed at -40 °C with the Lewis acid and then a solution of the appropriate bimetallic reagent was added. Enones **9a-b** were formed via exclusive cleavage of the carbon-tin bond as in earlier examples with the *trans*-olefin obtained as the sole product.

Table 2. Reaction of **3a-c** with methyl vinyl ketone.

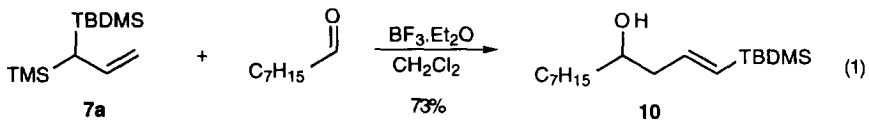


	R	Product[a]	yield (%)
3a	H	NR	NA
3b	n-propyl	**9a**	84
3c	cyclohexyl	**9b**	61

a) In all cases where no reaction was observed the bimetallic reagent decomposed on work-up.

To our surprise **3a** failed to react with either methyl vinyl ketone (MVK) or other β,β-disubstituted enones. While we can expect that **3a** may form **C** in analogy to our previous results (see Scheme 3), this intermediate was shown to be unreactive toward MVK after 48 h at -78 or -40 °C.

Reaction of allyl 1,1-bis-silyl-bimetallic reagents **7a-c** was also investigated. Initial results with **7a** (R=H) and octanal were very promising since **10** was formed in 73% yield.[4] Selective cleavage of the C-TMS bond was observed[11] and the *trans*-olefin (J=18.6 Hz) was formed exclusively. It is noteworthy that the reaction of **7a** with octanal was slower and took place at higher temperature than the analogous reaction of **3a**.



7a 73% **10**

Thus far we have not found a Lewis acid which will promote the addition of **7b** and **7c** to aliphatic or aryl aldehydes or MVK. In our preliminary studies, the bimetallic reagent was routinely recovered in quantitative yield. These results, along with the fact that bimetallic compound **7a** required elevated temperature and increased reaction time suggested that the bis-silyl bimetallics are significantly less reactive than the tin-silicon compounds.

Our current efforts are directed toward examining the intramolecular reactions and fluoride promoted reactions.

Conclusion:

We have described an efficient and general synthetic procedure allowing for the synthesis of unsubstituted and substituted allyl 1,1-hetero- and homobimetallic compounds where M=Sn or Si' and M'=Si. This transformation is effected by a palladium catalyzed reduction using ammonium formate. The regioselectivities in the reduction are consistently better than 99:1 and the chemical yields of the products obtained range from 40-99%.

The initial studies indicate that a delicate balance between 1,3-migration, reactivity and stereoselectivity must be achieved and that neither Si, Sn or Si, Si' reagents are as reactive as the simple allyl metal analogues bearing a silicon or tin. Further investigations into the reactivities and possible applications of these novel 1,1-heterobimetallic compounds are ongoing in our laboratory.

Experimental:

General procedure A for the acetylation of allylic alcohols:

The alcohol was dissolved in dry freshly distilled pyridine and acetic anhydride (1.5 eq) and 4-dimethylaminopyridine (0.1 eq) was added. When TLC showed that the starting material had been consumed, the mixture was diluted with diethyl ether, washed consecutively with sat. $NaHCO_3$, sat. $CuSO_4$ (until a completely colorless organic layer was obtained upon addition of fresh $CuSO_4$) and finally brine. After drying over $MgSO_4$, the solvent was evaporated *in vacuo* and the resulting oil was purified by flash chromatography on silica gel.

General procedure B for the palladium-catalyzed reduction of allylic acetates.

Tris(dibenzylideneacetone)dipalladium(0) was added (1-10 mole%) to a flame dried flask, followed by triphenylphosphine (8-40 mole%) and dioxane. The resulting purple colored solution was stirred at room

temperature under a nitrogen atmosphere until it became yellow. At this point, a solution of substrate in dioxane was added followed by a rapid, sequential addition of triethylamine (3.0 eq) and freshly distilled formic acid (3.0 eq). The solution was heated to reflux. When all of the allylic alcohol was consumed, the reaction mixture was diluted with hexanes, washed several times with sat. $NaHCO_3$, brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting yellow coloured liquid was purified by flash chromatography on silica gel.

General procedure C for the reaction of allyl-1,1-heterobimetallic reagents with various electrophiles.

A flask was charged with 5 mL of CH_2Cl_2 and cooled to either -40 or -78°C. The appropriate electrophile (1.05 equiv) was added, followed by $BF_3{\cdot}Et_2O$ (1.0 equiv, 1M solution in CH_2Cl_2 unless stated otherwise) and the mixture was allowed to stir for 5 min. A CH_2Cl_2 solution of the bimetallic reagent was then added by syringe. The reaction mixture was monitored by TLC and when the starting materials had been consumed, 2 mL of sat. NH_4Cl was added and the solution was allowed to warm to room temperature. Extraction of the aqueous phase with CH_2Cl_2, drying over $MgSO_4$ and removal of the solvent *in vacuo* produced the crude product which was purified by flash column chromatography using the appropriate eluent.

(*Z*)-3-Tributylstannyl-3-trimethylsilyl-2-propenyl acetate (2a). According to the general procedure A, the allylic alcohol (3.3 g, 7.9 mmol) was dissolved in 10 mL of pyridine, followed by the addition of acetic anhydride (0.89 mL, 9.4 mmol) and DMAP (48 mg, 0.4 mmol). After stirring at room temperature for 30 min and aqueous workup, acetate **2a** (3.6 g) was obtained in 99% yield as a colorless oil of sufficient purity to continue on to the next step. IR (neat, cm^{-1}) 2959, 2924, 2875, 2854, 1743, 1462, 1377, 1244, 1230, 1026, 864, 836; ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 (1H, t, J = 5.9 Hz)(J_{Sn-H} = 164.4, 157.1 Hz), 4.53 (1H, d, J = 5.9 Hz), 4.50 (1H, d, J = 5.9 Hz), 2.06 (3H, s), 1.43 (6H, m), 1.29 (6H, m), 0.93 (6H, m), 0.86 (9H, t, J = 7.3 Hz), 0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 149.83 (J_{Sn-C} = 224.8, 214.5 Hz), 147.6 (J_{Sn-C} = 22.7 Hz), 68.3 (J_{Sn-C} = 11.0 Hz), 29.1 (J_{Sn-C} = 19.0 Hz), 27.4 (J_{Sn-C} = 101.1, 59.3 Hz), 20.9, 13.6, 11.3 (J_{Sn-C} = 323.7, 310.5 Hz), -0.48 (J_{Si-C} = 9.5 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ -51.73;

(*Z*)-1-Tributylstannyl-1-trimethylsilyl-1-hexen-3-yl acetate (2b). According to the general procedure A, the allylic alcohol (3.0 g, 6.5 mmol) was dissolved in 20 mL of pyridine, followed by the addition of acetic anhydride (0.74 mL, 7.8 mmol) and DMAP (40 mg, 0.32 mmol). After stirring at room temperature for 12 h and an aqueous workup, the crude mixture was purified by flash chromatography (hexanes:diethyl ether 20:1), to yield 3.03 g (98%) of acetate **2b**. IR (neat, cm^{-1}) 2959, 2931, 2875, 2861, 1743, 1466, 1373, 1239, 1018, 874, 833; ^1H NMR (400 MHz, CDCl3) δ 6.55 (1H, d, J = 8.5 Hz)(J_{Sn-H} = 175.8, 168.1 Hz), 5.06 (1H, ddd, J = 8.5, 7.8, 5.0 Hz), 2.02 (H, s), 1.64 (1H, m), 1.50-1.39 (7H, m), 1.34-1.24 (8H, m), 0.95 (6H, m), 0.89 (3H, t, J = 7.0 Hz), 0.86 (9H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 152.2 (J_{Sn-C} = 21.2 Hz), 147.7, 78.7 (J_{Sn-C} = 58.5 Hz), 37.3, 29.1 (J_{Sn-C} = 19.0 Hz), 27.5 (J_{Sn-C} = 63.0 Hz), 21.4, 18.5, 14.21, 13.7, 11.38 (J_{Sn-C} =324.4, 309.8 Hz), -0.23; ^{119}Sn NMR (112, MHz, $CDCl_3$) δ -53.4; Anal. Calcd for $C_{23}H_{48}O_2SiSn$: C, 54.88; H, 9.61. Found: C, 55.07; H, 9.29.

(*Z*)-3-Tributylstannyl-3-trimethylsilyl-1-cyclohexyl-2-propenyl acetate (2c). According to the general procedure A, the allylic alcohol (550 mg, 1.10 mmol), was dissolved in 10 mL of pyridine, followed by the addition of acetic anhydride (0.16 mL, 1.65 mmol) and DMAP (13 mg, 0.11 mmol). After stirring at room

temperature for 17 h and an aqueous workup, the crude mixture was purified by flash chromatography (hexanes:diethyl ether 20:1), to yield 561 mg (97%) of acetate **2c** as a colourless oil. IR (neat, cm^{-1}) 2959, 2931, 2845, 1735, 1574, 871, 836; ^1H NMR (400 MHz, $CDCl_3$) δ 6.62 (1H, d, J = 8.4 Hz)(J_{Sn-H} = 175.4, 158.2 Hz), 4.92 (1H, dd, J = 8.4 5.7 Hz), 2.02 (3H, s), 1.76-0.95 (21H, m), 0.87 (9H, t, J = 7.3 Hz), 0.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 151.6 (J_{Sn-C} = 20.6 Hz), 148.7, 82.1 (J_{Sn-C} = 57.1 Hz), 29.3, 29.2 (J_{Sn-C} = 19.0 Hz), 27.9, 27.5 (J_{Sn-C} = 63.0 Hz), 26.5, 26.2, 21.31, 13.7, 11.6 (J_{Sn-C} = 322.7, 309.8 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ -54.4; HRMS calcd for $C_{22}H_{43}O_2SiSn$ $(M-C_4H_9)^+$ 487.2054, found 487.2068.

(Z)-3-*tert*-Butyldimethylsilyl-3-trimethylsilyl-2-propenyl acetate (6a). According to the general procedure A, the alcohol (100 mg, 0.41 mmol) was dissolved in 2 mL of pyridine, followed by the addition of acetic anhydride (58 μL, 0.61 mmol) and DMAP (5 mg, 0.04 mmol). After stirring at room temperature for 1 h and an aqueous workup, the crude mixture was purified by flash chromatography (eluting with hexanes:diethyl ether 20:1), to yield 105 mg (90% yield) of acetate **6a** as a colourless oil. IR (neat, cm^{-1}) 2956, 2859, 1742, 1249, 1227, 880, 836; ^1H NMR (400 MHz, $CDCl_3$) δ 6.69 (1H, t, J = 6.2 Hz), 4.65 (2H, d, J = 6.2 Hz), 2.06 (3H, s), 0.87 (9H, s), 0.15 (6H, s), 0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 151.6, 143.5, 66.9, 27.5, 20.9, 18.3, 1.01, -1.59; HRMS calcd for $C_{10}HO_2Si_2$ $(M-C_4H_9)^+$ 229.1080, found 229.1075.

(Z)-3-*tert*-Butyldimethylsilyl-3-trimethylsilyl-1-hexen-3-yl acetate (6b). According to the general procedure A, the alcohol (1.54 g, 5.38 mmol) was dissolved in 16 mL of pyridine, followed by the addition of acetic anhydride (1.0 mL, 2 equiv) and DMAP (65 mg, 0.53 mmol). After stirring at room temperature for 24 h, and an aqueous workup, the crude reaction mixture was purified by flash chromatography (eluting with hexanes:ethyl acetate 15:1) to yield 1.26 g (73%) of the acetate **6b** as a colourless oil. IR (neat, cm^{-1}) 2957, 1739, 1386, 1235, 1032, 878, 836; ^1H NMR (200 MHz, $CDCl_3$) δ 169.8, 155.3, 142.2, 75.8, 37.4, 27.4, 21.3, 18.2 17.7, 14.3, 1.2, -0.4, -1.8; HRMS calcd for $C_{16}H_{33}O_2Si$ $(M-CH_3)^+$ 313.20188, found 313.2019.

(Z)-3-*tert*-Butyldimethylsilyl-3-trimethylsilyl-1-cyclohexyl-2-propenyl acetate (6c). According to the general procedure A, the alcohol (1.01 g, 2.1 mmol) was dissolved in 25 mL of pyridine, followed by the addition of acetic anhydride (0.31 mL, 1.6 eq) and DMAP (26 mg, 0.21 mmol). After stirring at room temperature for 24 h and an aqueous workup, the crude mixture was purified by flash chromatography (hexanes:ethyl acetate 15:1) to yield 742 mg (72%) of acetate **6c** as a colourless oil. IR (neat, cm^{-1}) 2925, 1742, 1652, 1242, 1013; ^1H NMR (400 MHz, $CDCl_3$) δ 6.70 (1H, d, J = 9.2 Hz), 5.30 (1H, dd, J = 4.8, 9.6 Hz), 2.00 (3H, s), 1.64 (6H, m), 1.11 (5H, m), 0.82 (9H, s), 0.20, 0.12, 0.10 (total 15H, all s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 154.8, 143.0, 78.5, 43.6, 29.2, 27.8, 27.4, 26.2, 26.1, 21.0, 17.5, 1.4, 0.0, -0.18; HRMS calcd for $C_{20}H_{40}O_2Si_2$ $(M)^+$ 368.2566, found 368.2566.

3-Tributylstannyl-3-trimethylsilyl-1-propene (3a). Using general procedure B, **2a** (2.0g, 4.3 mmol), $Pd_2(dba)_3$ (39 mg, 2 mol%), PPh_3 (90 mg, 8.0 mol%), formic acid (0.5 mL, 3 equiv) and triethylamine (1.8 mL, 3 equiv) in dioxane (15 mL) were heated for 3 h. The crude product was purified by flash chromatography (hexanes) to yield 1.73 g (99%) of **3a** as a colourless oil. IR (neat, cm^{-1}) 2961, 2927, 2873, 2854, 1609, 1463, 1379, 1248, 1078; ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (1H, ddd, J = 16.5, 21.1, 9.8 Hz), 4.66 (1H, dd, J = 16.5, 2.2 Hz), 4.62 (1H, dd, J = 9.8, 2.2 Hz), 1.46 (7H, m), 1.29 (6H, sext, J = 7.3 Hz), 0.88 (9H, t, J = 7.3 Hz), 0.86 (6H, m), 0.00 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (J_{Sn-C}

= 42.5 Hz), 109.2 (J_{Sn-C} = 46.1 Hz), 29.2 (J_{Sn-C} = 19.0 Hz), 27.5 (J_{Sn-C} = 59.3 Hz), 22.6 (J_{Sn-C} = 183.1, 174.3 Hz), 13.7, 9.9 (J_{Sn-C} = 314.2, 301.0 Hz), -0.45 (J_{Sn-C} = 10.3 Hz); ^{119}Sn (112 MHz, $CDCl_3$) δ -16.8; ^{29}Si NMR (80 MHz, $CDCl_3$) δ 1.18; HRMS calcd for $C_{14}H_{31}SiSn$ $(M-C_4H_9)^+$ 347.1217, found 347.1219.

(*E*)-1-Tributylstannyl-1-trimethylsilyl-2-hexene (3b). Using general procedure B, **2b** (238 mg, 0.5 mmol), $Pd_2(dba)_3$ (4.6 mg, 2.0 mol%), PPh_3 (4.6 mg, 7 mol%), formic acid (0.06 mL, 3 equiv) and triethylamine (0.21 mL, 3 equiv) in dioxane (3 mL) were heated for 17 h. The crude product was purified by flash chromatography (hexanes) to yield 220 mg (99%) of **3b** as a colourless oil. IR (neat cm^{-1}) 2960, 2924, 2866, 2852, 1481, 1377, 1246, 1073; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (1H ddd, J = 15.0, 11.7, 1.5 Hz), 5.08 (1H, ddd, J = 15.0, 6.9, 6.6 Hz), 1.92 (2H, m), 1.45 (7H, m), 1.35-1.24 (8H, m), 0.88 (9H, t, J = 7.3 Hz), 0.86-0.82 (9H, m), -0.02 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.9 (J_{Sn-C} = 44.7 Hz), 125.8 (J_{Sn-C} = 47.6), 35.0 (J_{Sn-C} = 10.2 Hz), 29.3 (J_{Sn-C} = 19.1 Hz), 27.6 (J_{Sn-C} = 58.6 Hz), 23.58, 20.01, 113.7, 10.0 (J_{Sn-C} = 310.5, 296.6 Hz), -0.38; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ -15.0; HRMS calcd for $C_{20}H_{43}SiSn$ $(M-CH_3)^+$ 431.2156, found 431.2156.

(*E*)-1-Cyclohexyl-3-tributylstannyl-3-trimethylsilyl-1-propene (3c). Using general procedure B, **2c** (310 mg, 0.59 mmol), $Pd_2(dba)_3$ (28 mg, 10 mol%), PPh_3 (31 mg, 20 mol%), formic acid (0.06 μL, 3 equiv) and triethylamine (245 μL, 3 equiv) in dioxane (5 mL) were heated for 17 h. The crude product was purified by flash chromatography (hexanes) to yield 280 mg (98%) of **3c** as a colourless oil. IR (neat, cm^{-1}) 2959, 2924, 2854, 1462, 1448, 1244, 998, 857, 836; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (1H, ddd, J = 15.0, 11.9, 1.1 Hz), 5.04 (1H, dd, J = 15.0, 7.1 Hz) 1.86 (1H, m), 1.67 (5H, m), 1.51-0.94 (18H, m), 0.88 (9H, t, J = 7.3 Hz), 0.82 (6H, m), -0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4 (J_{Sn-C} = 46.8 Hz), 127.1 (J_{Sn-C} = 44.6 Hz), 41.2, 34.0 (J_{Sn-C} = 11.7 Hz), 33.91 (J_{Sn-C} = 19.0 Hz), 27.6 (J_{Sn-C} = 57.1 Hz), 26.4, 26.2 (2), 19.8 (J_{Sn-C} = 196.3, 186.7 Hz), 13.7, 10.0 (J_{Sn-C} = 310.5, 296.6 Hz, -0.45 (J_{Sn-C} = 10.3 Hz); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ -15.8; HRMS calcd for $C_{23}H_{47}SiSn$ $(M-CH_3)^+$ 471.2469, found 471.2476.

3-*tert*-Butyldimethylsilyl-3-trimethylsilyl-1-propene (7a). Using general procedure B, **6a** (200 mg, 0.70 mmol), $Pd_2(dba)_3$ (6.5 mg, 2 mol%), PPh_3 (13 mg, 7 mol%), formic acid (79 μL, 3 equiv) and triethylamine (0.29 mL, 3 equiv) in dioxane (3 mL) was heated for 4 h. The crude product was purified by flash chromatography (hexanes) to yield 145 mg (90%) of **7a** as a colourless oil. IR (neat, cm^{-1}) 3079, 2957, 2930, 2896, 2856, 1615, 1464, 1460, 1250, 1071, 885; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (1H, ddd, J = 16.5, 11.9, 9.9 Hz), 4.77 (1H, dd, J = 9.9, 2.2 Hz), 4.71 (1H, dd, J = 16.5, 2.2 Hz), 1.30 (1H, d, J = 11.9 Hz), 0.86 (9H, s, 0.02 (9H, s), 0.00 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 127.1, 112.0, 27.0, 24.2, 18.8, -0.24, -3.50, -5.54; HRMS calcd for $C_{12}H_{28}Si_2$ $(M)^+$ 228.1730, found 228.1729.

3-*tert*-Butyldimethylsilyl-3-trimethylsilyl-1-hexene (7b). Using general procedure B, **6b** (500 mg, 1.52 mmol), $Pd_2(dba)_3$ (139 mg, 10 mol%), PPh_3 (160 mg, 40 mol%), formic acid (0.17 mL, 3 equiv) and triethylamine (0.63 mL, 3 equiv) in dioxane (5 mL) were heated for 24 h. The crude product was purified by flash chromatography (hexanes) to yield 365 mg (89%) of **7b** as a colourless oil. IR (neat, cm^{-1}) 2955, 1467, 1245, 1044, 842; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (1H, dd, J = 15.7, 10.0 Hz), 5.13 (1H, dt, J = 15.7, 5.2 Hz), 1.95 (2H, q, J = 7.9 Hz), 1.30 (3H, m), 0.85 (15H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 129.1, 128.5, 35.6, 27.5, 23.7, 21.9, 19.1, 14.3, 0.30, -2.9, -5.0; HRMS calcd for $C_{15}H_{34}Si_2$ $(M)^+$ 270.2198, found 270.2199.

1-Cyclohexyl-3-*tert*-butyldimethylsilyl-3-trimethylsilyl-1-propene (7c). Using general procedure B, **6c** (100 mg, 0.27 mmol), $Pd_2(dba)_3$ (25 mg, 10 mol%), PPh_3 (29 mg, 40 mol%), formic acid (0.03 mL, 3 equiv) and triethylamine (0.11 mL, 3 eq) in dioxane (5 mL) were heated for 24 h. The crude product was purified by flash chromatography (hexanes) to yield 34 mg (40%) of **7c** as a colourless oil. IR (neat, cm^{-1}) 2917, 1461, 1252, 1035, 861, 842; ^1H NMR (400 MHz, $CDCl_3$) δ 5.24 (1H, ddd, J = 15.0, 11.0, 1.1 Hz), 5.13 (1 H, dd, J = 15.0, 7.1 Hz), 1.60 (5H, m), 1.30-1.00 (6H, m), 0.83 (9H, s), 0.00 (15H, 3s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 126.2, 41.1, 33.8, 32.2, 30.2, 27.2, 26.3, 26.1, 21.3, 0.0, -4.2, -6.1; HRMS calcd for $C_{18}H_{38}Si_2$ $(M)^+$ 310.2511, found 310.2512.

(*E*)-1-Trimethylsilyl-1-undecen-4-ol (8a). According to general procedure C, octanal (0.16 mL, 1.0 mmol), BF_3 etherate and **3a** (403 mg, 1.0 mmol) were stirred in 3 mL of dry CH_2Cl_2 at -78 °C. After 10 min, the reaction was subjected to aqueous workup and purification by flash chromatography (pentane) to yield 52 mg (33%) yield of the diene. Further elution with pentane:diethyl ether (10:1) afforded 126 mg (52%) of **8a.** IR (neat, cm^{-1}) 3360, 2959, 2924, 2854, 1616, 1462, 1251, 991, 865, 836; ^1H NMR (400 MHz, $CDCl_3$) δ 6.01 (1H, ddd, J = 18.7, 7.3, 6.2 Hz), 5.75 (1H, ddd, J = 18.7, 1.5, 1.1 Hz), 3.64 (1H, m), 2.16 (1H, m), 1.55 (1H, d, J = 4.0 Hz), 1.44-1.22 (12H, m), 0.86 (3H, t, J = 7.3 Hz), 0.04 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 134.3, 70.5, 44.9, 36.6, 31.8, 29.6, 29.3, 25.6, 22.6, 14.1, -1.2; HRMS calcd for $C_{14}H_{29}OSi$ $(M-H)^+$ 241.1987, found 241.1987.

(*E,E*)-1,3-undecadiene. IR (neat, cm^{-1}), 2959, 2931, 2854, 1263, 1378, 1250, 997, 903; ^1H NMR (400 MHz, $CDCl_3$) δ 6.63 (1H, ddd, J = 17.0, 11.0, 9.9 Hz), 5.97 (1H, dd, J = 11.0, 9.9 Hz), 5.44 (1H, ddd, J = 9.9, 7.7, 7.5), 5.16 (1H, dd, J = 17.0, 2.0 Hz), 5.05 (1H, d, J = 9.9 Hz), 2.16 (2H, dt, J = 9.1, 7.7 Hz), 1.36 (2H, m), 1.20 (8H, m), 0.86 (3H, t, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 132.3, 129.1, 116.6, 31.8, 29.6, 29.2, 29.2, 27.8, 22.7, 14.1.

4-Phenyl-(*E*)-1-trimethylsilyl-1-buten-4-ol (8b). According to general procedure C, benzaldehyde (26.5 mg, 0.25 mmol), BF_3 etherate (1.05 equiv) and **3a** (100 mg, 0.25 mmol) were stirred in 3 mL of dry CH_2Cl_2 at -78°C. After 15 min, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:diethyl ether 20:1) to furnish 50 mg (91%) of **8b** as a colourless oil. IR (neat, cm^{-1}) 3391, 2952, 1617, 1451, 1248, 1052, 990, 864, 839; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (5H, m), 6.03 (1H, dt, J = 18.0, 7.2 Hz), 5.78 (1H, dm, J = 18.0 Hz), 4.74 (1H, m), 2.56 (2H, m), 2.00 (1H, br. s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.2, 134.4, 129.1, 127.8, 126.1, 73.2, 47.3, -1.0; HRMS calcd for $C_{13}H_{19}OSi$ $(M-H)^+$ 219.1204, found 219.1205.

(*E*)-1-Trimethylsilyl-3-propyl-1-undecen-4-ol (8c). According to general procedure C, octanal (0.7 mL, 0.20 mmol), BF_3 etherate (0.18 mL, 1.05 equiv) and **3b** (87 mg, 0.20 mmol) were stirred in 5 mL of dry CH_2Cl_2 at -78 °C. After 1.5 h, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:diethyl ether 15:1) to furnish 41 mg (72%) of **8c** as a colourless oil and a 8:1 mixture of diastereomers. IR (neat, cm^{-1}) 3362, 2293, 1613, 1462, 1251, 980, 832; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (1H, dd, J = 18.6, 8.0 Hz), 5.67 (1H, dd, J = 18.6 Hz), 3.46 (1H, q, J = 6.9 Hz), 2.10 (1H, m), 1.60-1.10 (6H, m), 0.85 (6H, m), 0.50 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 147.1, 134.3, 133.0, 74.4, 74.3, 53.2, 34.1, 32.8, 31.8, 29.6, 29.3, 26.0, 20.7, 20.6, 14.3, 14.2, 0.5, -1.1; HRMS calcd for $C_{17}H_{35}OSi$ $(M-H)^+$ 283.2457, found 283.2457.

(*E*)-1-Trimethylsilyl-3-cyclohexyl-1-undecen-4-ol (8d). According to general procedure C, octanal (0.04 mL, 0.22 mmol), BF_3 etherate (0.23 mL, 1.05 equiv) and **3c** (110 mg, 0.22 mmol) were stirred in 5 mL of dry CH_2Cl_2 at -78 °C. After 2.5 h, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:diethyl ether 20:1) to furnish 44 mg (62%) of **8d** as a colourless oil as a 4:1 mixture of diastereomers. IR (neat, cm^{-1}) 2917, 1447, 1251, 998, 867; ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, J = 17.6, 9.4 Hz) and 5.65 (m), 1H in total, 3.65 (1H, m), 1.94 (1H, q, J = 7.3 Hz), 1.80-0.80 (27 H, m), 0.60 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 145.0, 135.0 (2), 70.1 (2), 60.0, 55.9, 37.8, 37.7, 35.4, 34.0, 31.9, 31.8, 31.6, 30.3, 31.1, 29.8 (2), 29.4, 26.8, 26.7, 26.6 (2), 26.0, 27.7, 22.6, 14.2, 0.0; HRMS calcd for $C_{20}H_{40}OSi$ $(M-H)^+$ 323.2770, found 323.2772.

(*E*)-1-Trimethylsilyl-4-phenyl-4-methoxy-1-butene (8e). According to general procedure C, benzaldehyde dimethyl acetal (45 mg, 0.29 mmol), BF_3 etherate (0.22 mL, 1.05 equiv) and **3a** (100 mg, 0.25 mmol) were stirred in 5 mL of dry CH_2Cl_2 at -78 °C. After 10 min, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:diethyl ether 20:1) to furnish 42 mg (72%) of **8e** as a colourless oil. IR (neat, cm^{-1}) 2949, 1631, 1464, 1247, 1099, 868; ^1H NMR (200 MHz, $CDCl_3$) δ 7.30 (5H, m), 5.95 (1H, dt, J = 18.6 Hz), 5.63 (1H, d, J = 18.0 Hz), 4.20 (1H, t, J = 6.0 Hz), 3.21 (3H, s), 2.50 (2H, m), 0.50 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.1, 133.2, 128.0, 127.2, 126.1, 84.2, 56.3, 46.8, -1.0.

(*E*)-1-Trimethylsilyl-4-phenyl-4-methoxy-3-propyl-1-butene (8f). According to general procedure C, benzaldehyde dimethyl acetal (52 mg, 0.38 mmol), BF_3 etherate (0.22 mL, 1.05 equiv) and **3b** (106.5 mg, 0.25 mmol) were stirred in 5 mL of dry CH_2Cl_2 at -78 °C. After 30 min, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:diethyl ether 40:1) to furnish 55 mg (83%) of **8f** as a colourless oil in a 5:1 mixture of diastereomers. IR (neat, cm^{-1}) 2920, 1441, 2530, 982, 832; ^1H NMR (200 MHz, $CDCl_3$) δ 7.30 (5H, m), 5.80, 5.62 (total 1H, both dd, J = 18.4, 9.5 Hz), 5.35 (1H, d, J = 18.4 Hz) 4.10 , 3.95 (total 1H, both d, J = 7.8 Hz), 3.20 (3H, s), 2.35 (1H, m), 1.82 (2H, m), 1.35 (2H, m), 0.90 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.8, 141.3, 132.3, 127.9, 127.5, 127.1, 87.3, 53.5, 20.5, 17.5, 14.3, 13.7, -1.2, -1.4.

(*E*)-1-Trimethylsilyl-4-phenyl-4-methoxy-3-cyclohexyl-1-butene (8g). According to general procedure C, benzaldehyde dimethyl acetal (40 mg, 0.20 mmol), BF_3 etherate (0.17 mL, 1.05 equiv) and **3c** (82 mg, 0.17 mmol) were stirred in 5 mL of dry CH_2Cl_2 at -78 °C. After 16 h, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes) to furnish 35 mg (66%) of **8g** as a colourless oil in a 4:1 mixture of diastereomers. IR (neat, cm^{-1}) 2917, 1626, 1446, 1257, 1104, 870, 842; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (5H, m), 5.90 (dd, J = 18.5, 9.6 Hz) and 5.55 (dd, J = 18.5, 9.6 Hz), total of 1H, 5.20 (1H, d, J = 18.5 Hz), 4.10, 4.20 (total 1H, J = 7.0 Hz), 3.18 (3H, s), 2.10 (1H, m), 1.92-0.80 (11H, m), 0.0, -1.0 (total 9H, both s); ^{13}C NMR (200 MHz, $CDCl_3$) δ 145.2, 145.0, 142.1, 141.8, 134.0, 133.8, 127.8, 127.5, 126.3, 84.2, 82.0, 66.3, 64.3, 64.2, 61.0, 60.1, 57.8, 57.3, 38.0, 37.8, 32.1, 31.8, 31.2, 28.1, 27.2, 15.8, 0.0, -1.1; HRMS calcd for $C_{20}H_{31}OSi$ $(M-H)^+$ 315.2143, found 315.2144.

(*E*)-Trimethylsilyl-6-keto-3-propyl-1-heptene (9a). According to general procedure C, methyl vinyl ketone (0.014 mL, 0.16 mmol), BF_3 etherate (0.34 mL, 1.05 equiv) and **3b** (70 mg, 0.16 mmol) were stirred in 8 mL of dry CH_2Cl_2 at -40 °C. After 2 h, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:ethyl acetate 15:1) to furnish 30 mg (84%) of **9a** as a colourless oil. IR

(neat, cm^{-1}) 2945, 1728, 1623, 1433, 1243, 850; ^1H NMR (400 MHz, $CDCl_3$) δ 5.65 (1H, dd, *J* = 18.0, 7.1 Hz), 5.53 (1H, d, *J* = 18.0 Hz), 2.35 (2H, t, *J* = 7.3 Hz), 2.10 (3H, s), 1.90 (1H, m), 1.65 (1H, m), 1.43 (1H, m), 1.23 (4H, m), 0.85(3H, t, *J* = 6.5 Hz), 0.50 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 246.0, 150.9, 131.1, 46.7, 42.0, 37.6, 30.2, 28.9, 20.7, 14.6, -0.60; HRMS calcd for $C_{13}H_{26}OSi$ $(M)^+$ 226.1752, found 226.1752.

(*E*)-Trimethylsilyl-6-keto-3-cyclohexyl-1-heptene (9b). According to general procedure C, methyl vinyl ketone (0.013 mL, 0.16 mmol), BF_3 etherate (0.16 mL, 1.05 equiv) and **3c** (77 mg, 0.16 mmol) were stirred in 8 mL of dry CH_2Cl_2 at -40 °C. After 14 h, the reaction was worked up and the crude product was purified by flash column chromatography (hexanes:ethyl acetate 20:1) to furnish 26 mg (61%) of **9b** as a colourless oil. IR (neat, cm^{-1}) 2970, 1730, 1640, 1422, 1200, 842; ^1H NMR (400 MHz, $CDCl_3$) δ 5.68 (1H, dd, *J* = 18.5, 8.8 Hz), 5.50 (1H, d, *J* = 18.5 Hz), 2.31 (2H, m), 1.80-0.82 (17H, m), 0.20 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 149.1, 131.8, 77.2, 52.6, 48.1, 42.1, 31.3, 30.2, 30.0, 26.7, 26.6, 25.3, -2.0.

(*E*)-1-*tert*-Butyldimethylsilyl-1-undecen-4-ol (10). According to general procedure C, octanal (68 μL, 0.44 mmol), BF_3 etherate (0.88 mL of 0.5 M solution in CH_2Cl_2, 1.05 equiv) and **7a** (100 mg, 0.22 mmol) were stirred in 5 mL of dry CH_2Cl_2 at -40 °C. After 2.0 h, the reaction was worked up and the crude product was purified by flash column chromatography (pentane:diethyl ether 10:1) to furnish 91 mg (73%) of **10** as a colourless oil. IR (neat, cm^{-1}) 3347, 2956, 2927, 2858, 1618, 1469, 1360, 1248, 994, 827, 780; ^1H NMR (400 MHz, $CDCl_3$) δ 6.02 (1H, ddd, *J* = 18.6, 7.3, 5.9 Hz), 5.73 (1H, ddd, *J* = 18.6, 1.5, 1.1 Hz), 3.64 (1H, m), 2.37 (1H, dddd, *J* = 13.6, 5.9, 4.4, 1.4 Hz), 2.19 (1H, dddd, *J* = 13.6, 8.7, 7.3, 1.1 Hz), 1.54 (1H, d, *J* = 3.7 Hz), 1.43 (4H, m), 1.26 (8H, m), 0.86 (3H, t, *J* = 7.3 Hz), 0.84 (9H, s), 0.00 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 131.6, 70.5, 45.2, 36.8, 31.8, 29.6, 29.3, 26.4, 25.7, 22.7, 16.5, 14.1, -6.06; HRMS calcd for $C_{17}H_{35}OSi$ $(M-H)^+$ 282.2451, found 283.2451.

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