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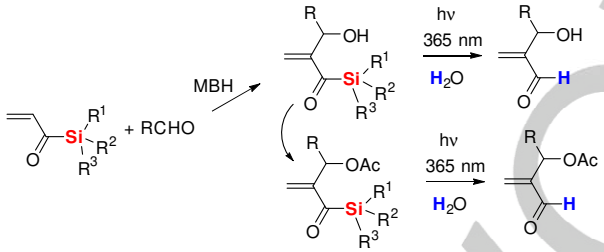
Gangababu Marri,[a] Frédéric Justaud,[b] Saibal Das,*[a] and René Grée*[b]

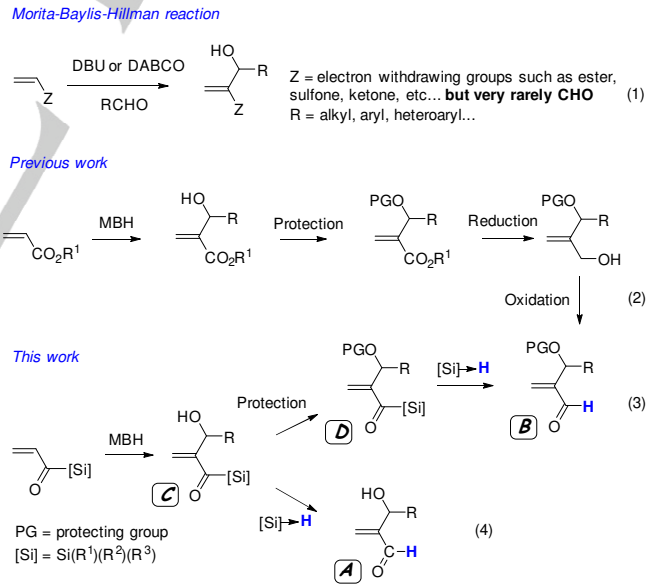


Abstract: α-β unsaturated acylsilanes are excellent substrates for Morita-Baylis-Hillman (MBH) reactions, affording the expected adducts in good to excellent yields. In these derivatives, as well as the corresponding acetates, the acylsilanes can be smoothly transformed into aldehydes by irradiation at 365 nm in acetone or THF/water mixtures. Therefore α-β unsaturated acylsilanes are very useful surrogates for acrolein in MBH reactions, allowing easy preparation of simple and highly functionalized new building blocks for synthetic applications.

Introduction

The Morita-Baylis-Hillman (MBH) reaction has been established as a major C-C bond forming reaction and the corresponding adducts proved to be particularly useful for the preparation of a very large number of molecules (Scheme 1, Eq. 1).[1] Since this umpolung-type transformation involves the base-mediated condensation of an electrophilic alkene, such as an acrylate, with an aldehyde, the use of acrolein in this process is, at best, very difficult. In fact, only few papers reports such an application and important limitations have been usually observed.[2] Therefore, in order to obtain the corresponding target molecules containing both an allylic alcohol and a vicinal aldehyde (Scheme 1, type-***A*** and -***B***), the classical process will be to transform another function, such as an ester group into the aldehyde by a reduction-reoxidation process (Scheme 1, Eq. 2).[3]

On the other hand, the acylsilanes are well recognized as highly versatile functional groups with many applications in organic synthesis.[4] Since the acylsilane group can be transformed to aldehydes under very mild and neutral conditions (photolysis in water/organic solvents mixtures),[5-6] we designed a strategy where α-β unsaturated acylsilanes could be employed in the MBH reaction and the adducts could be transformed directly and efficiently into the target molecules (Scheme 1, Eq. 3 and 4). The goal of this paper is to demonstrate**,** for the first time**,** that α-β unsaturated acylsilanes can be used in MBH reactions affording derivatives ***C*** and ***D*** and to validate this strategy towards type-***A*** and -***B*** functionalized enals which appear as versatile synthetic intermediates.



Scheme 1. Morita-Baylis-Hillman reaction and our working hypothesis toward the *A* and *B* target molecules

Results and Discussion

To the best of our knowledge, only one method has been reported to date for the preparation of molecules ***A***. It involves the condensation of the lithium anion of acrolein acetal with aldehydes, followed by deprotection of the acetal. (Scheme 2, Eq. 5).[7] To be mentioned also, is the elegant method described

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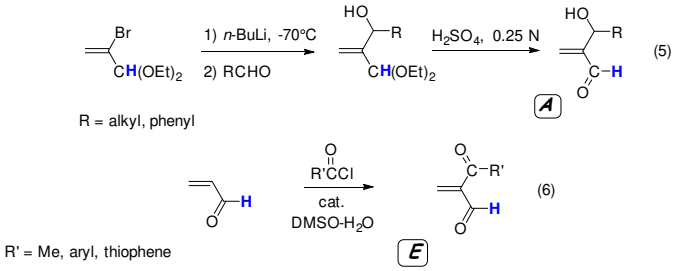
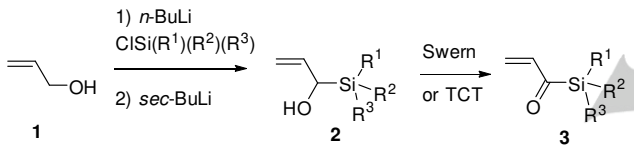
recently which affords highly electrophilic 2-methylene-1,3-dicarbonyl compounds ***E*** (Scheme 2, Eq. 6).[8]



Scheme 2. Alternative methods reported for the synthesis of target molecules *A* and alkenes *E*

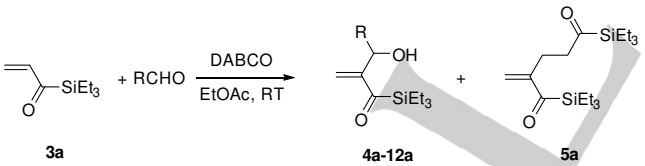
The synthesis of the α-β unsaturated acylsilanes **3** has been performed by using slight optimizations (see Scheme 3 and experimental section) of literature procedures. Starting from allylic alcohol **1**, and using retro-Brook reactions, the α-silyl allyl alcohols **2** have been obtained in good yields. The oxidation of alcohols **2** to the desired products **3** was performed efficiently by Swern method, or by using DMSO activated by 2,4,6-Trichloro-1,3,5-Triazine (TCT).[9] Latter method proved to be more convenient on large scale reactions.



a: $R^1 = R^2 = R^3$ = Et; **b**: $R^1 = R^2$ = Me, R^3 = Ph; **c**: $R^1 = R^2 = R^3$ = Me; **d**: $R^1 = R^2 = R^3$ = *i*Pr; **e**: $R^1 = R^2$ = Me, R^3 = *t*Bu; **f**: R^1 = Me, $R^2 = R^3$ = Ph

Scheme 3. Synthesis of the α-β unsaturated acylsilanes

The α-β unsaturated acylsilane **3a** and benzaldehyde were selected to explore the MBH reaction with a vinylic acylsilane (Scheme 4).[10]



Scheme 4. Reactivity studies starting from acylsilane **3a**

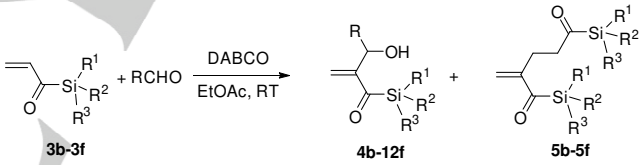
After some experiments it was found that using DABCO as the nucleophilic catalyst and ethylacetate as the solvent, the desired adduct **4a** was obtained in 60% yield after six days at room temperature in the dark (Table 1, entry 1). As a byproduct the dimer **5a** was also obtained, through a Rauhut-Currier (RC) type reaction.[11] The MBH reaction was successfully extended to other aromatic aldehydes with nitro- and bromo-substituents (entries 2-5), as well as to the pyridine-3-carboxaldehyde (entry 6). Further, after two days reaction, the glyoxylate ethylester gave the MBH adduct only and in excellent yield (entry 7). The less reactive pentanal afforded the adduct **12a**, but in lower yield and as a mixture with the dimer **5a** (entry 8). Clearly, the α-β unsaturated acylsilane **3a** follows the general trends of the MBH reactions: the reactions are faster, and giving higher yields, with aldehydes bearing strong electron-withdrawing substituents. When the MBH reaction becomes slower and more difficult, the dimerization of the unsaturated starting material becomes competitive and affords higher yields of the Rauhut-Currier (RC) product.

Table 1. MBH reaction studies with acylsilane **3a** as model

Entry	RCHO (equiv.)	Time (days)	Ratio [a] (MBH:RC)	Adduct (%)	**5a**(%)
1	PhCHO (1.5)	6	72:28	**4a** (60)	16
2	4-NO_2PhCHO (1.2)	2	100:00	**6a** (88)	0
3	4-BrPhCHO (1.5)	7	68:32	**7a** (53)	20
4	2-BrPhCHO (1.5)	6	80:20	**8a** (63)	14
5	3-BrPhCHO (1.5)	6	96:4	**9a** (75)	9
6	3-PyrCHO (1.5)	7	82:18	**10a** (68)	13
7	EtO_2CCHO (1.2)	1.5	100:00	**11a** (93)	0
8	C_4H_9CHO (2.0)	10	50:50	**12a** (37)	26

[a] Ratios between products resulting from Morita-Baylis-Hillman adducts (MBH, **4a**-**12a**) and Rauhut-Currier (RC, **5a**) reaction, established by ^{1}H NMR analysis on the crude reaction mixtures.

In a next step, the MBH reaction was successfully extended to other acylsilanes (Scheme 5 and Table 2). On reaction with a few representative examples of aldehydes, this process could be developed with acylsilanes bearing five other commonly used groups: TMS, TIPS, TBDMS, $SiMe_2Ph$ and $SiPh_2Me$.



Scheme 5. Extension to other acylsilanes **3b**-**3f**

Table 2. MBH reactions with acylsilanes **3a**-**3e**

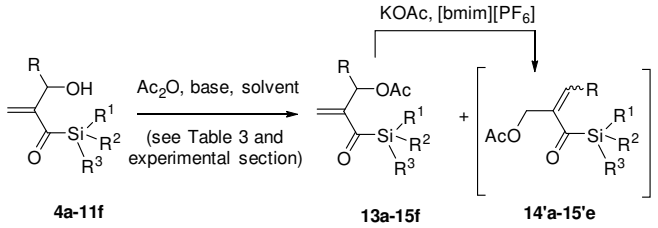
Entry	RCHO (equiv.)	$Si(R^1)(R^2)(R^3)$	Adduct (%)[a]	**5a-5f** (%)
1	PhCHO (1.5)	$SiMe_2Ph$	**4b** (40)	**5b** (11)
2	4-NO_2PhCHO (1.1)	$SiMe_2Ph$	**6b** (77)	0
3	4-BrPhCHO (1.2)	$SiMe_2Ph$	**7b** (34)	**5b** (20)
4	EtO_2CCHO (1.2)	$SiMe_2Ph$	**11b** (88)	0
5	4-NO_2PhCHO (1.2)	$Si(Me)_3$	**6c** (92)	0
6	EtO_2CCHO (1.5)	$Si(Me)_3$	**11c** (22)	0
7	PhCHO (1.5)	$Si(iPr)_3$	**4d** (10)	**5d** (20)
8	4-NO_2PhCHO (1.2)	$Si(iPr)_3$	**6d** (30)	**5d** (25)
9	EtO_2CCHO (1.5)	$Si(iPr)_3$	**11d** (70)	0
10	4-NO_2PhCHO (1.2)	Si-$tBuMe_2$	**6e** (34)	0
11	EtO_2CCHO (1.5)	Si-$tBuMe_2$	**11e** (54)	0
12	4-NO_2PhCHO (1.2)	$SiPh_2Me$	**6f** (72)	0
13	EtO_2CCHO (1.5)	$SiPh_2Me$	**11f** (32)	0

[a] isolated yields of products resulting from Morita-Baylis-Hillman adducts (MBH, **4b**-**11f**) and Rauhut-Currier (RC, **5b-5d**) reactions.

The results obtained show in general a similar tendency to those obtained with the TES group, and the MBH adducts **4b**-**12f** were

usually isolated in fair to good yields. However, in few cases (entries 6-8, 10 and 13), lower yields were obtained due to the lability of corresponding adducts.

The next step involved the protection of the allylic alcohol function. Based on our previous work in acylsilane chemistry,[5] we selected the acetate group and the results are given in Scheme 6 and Table 3. The reactions gave the desired acetates **13a**-**15f** in fair to good yields, although systematic optimization studies had to be performed and several conditions (A, B and C) were used depending upon the nature of the R group and the silyl substituents (see Table 3 and experimental section).



Scheme 6. Protection of acylsilanes MBH adducts

Table 3. Protection of MBH adducts

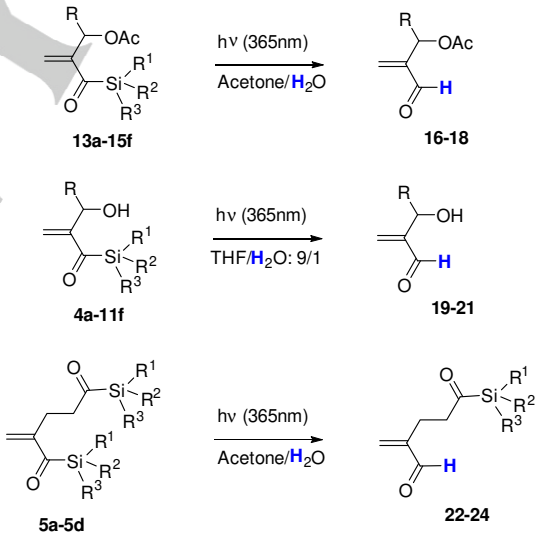
Entry	R	Si(R^1) (R^2(R^3)	Cond. [a]	Time (h)	Adduct	Yield (%)
1	Ph	$SiEt_3$	A	20	**13a**	63
2	4-NO_2Ph	$SiEt_3$	A	6	**14a**	92
3	4-NO_2Ph	$SiEt_3$	A	48	**14a +(14'a)**	81 (18)
4	4-NO_2Ph	$SiEt_3$	C	6	**14a**	82
5	4-NO_2Ph	$SiEt_3$	D	2	**14'a**	64
6	EtO_2C	$SiEt_3$	A	40	**15a**	88
7	Ph	$SiPhMe_2$	B	6	**13b**	76
8	4-NO_2Ph	$SiPhMe_2$	B	5	**14b**	80
9	EtO_2C	$SiPhMe_2$	B	5	**15b**	67
10	4-NO_2Ph	$SiMe_3$	A	0.5	**14c**	72
11	4-NO_2Ph	$SiMe_3$	D	2	**14'c**	72
12	EtO_2C	$SiMe_3$	A	5	**15c**	67
13	EtO_2C	$SiMe_3$	C	24	**15c**	75
14	4-NO_2Ph	Si^iPr_3	B	5	**14d**	51
15	EtO_2C	Si^iPr_3	B	3	**15d**	70
16	4-NO_2Ph	Si^tBuMe_2	C	48	**14e**	68
17	4-NO_2Ph	Si^tBuMe_2	D	2	**14'e**	81
18	EtO_2C	Si^tBuMe_2	C	24	**15e**	84
19	EtO_2C	Si^tBuMe_2	D	2	**15'e**	64
20	4-NO_2Ph	$SiPh_2Me$	A	0.2	**14f**	79[b]
21	4-NO_2Ph	$SiPh_2Me$	C	48	**14f**	54
22	EtO_2C	$SiPh_2Me$	C	48	**15f**	77

[a] Conditions A: Ac_2O (2 equiv), Et_3N (3 equiv), DMAP (0.1 equiv) DCM, 0 °C to rt.; B: Ac_2O (2 equiv), DMAP (0.1 equiv), DCM, rt; C: Ac_2O (5 equiv), $NaHCO_3$ (2 equiv), DCM, rt ; D: KOAc (1.5 equiv), [bmim]PF_6, 50 °C, 2 h.

[b] Temperature of the reaction: -10 °C.

The main reason was that, in several cases, during this protection step, the products resulting from an allylic transposition **14'**-**15'** were also obtained. For instance, acetates **13a** and **14a** were easily obtained from **4a** and **6a** using conditions A (Table 3, entries 1 and 2). However, increasing the reaction time afforded some transposed allylic derivative **14'a** (18% of *E* isomer) (entry 3). Therefore, we had to use, in parallel, a method to isolate the transposed products in order to have authentic samples of such molecules. Reaction of allylic acetate **14a** with potassium acetate in ionic liquids (conditions D),[12] afforded efficiently the transposition product **14'a** (entry 5, *E* isomer only). The stereochemistry of the *E* isomer of **14'a** was established by NoE experiments. By using these methods, all desired derivatives **13**-**15** could be prepared under appropriate conditions (Table 3), while the regioisomeric derivatives **14'**, **15'** were obtained as well by using conditions D.

The, final, key step involved the transformation of the acylsilane units into aldehydes (Scheme 7). Based on our recent work, we have employed photolytic conditions in a (1: 2) water: acetone mixture and classical UV lamps at 365 nm.[13] By using these very simple conditions the target molecules **16**-**18**, with three representative R groups (Ph, 4-NO_2Ph and EtO_2C) were obtained in excellent yields from derivatives **13a**-**15f** (Table 4). Importantly this method proved to be successful, independently of the nature of the silicon protecting groups (TES, TMS, TIPS and $SiPhMe_2$) and the enals **16**-**18** were obtained in good to excellent yields (69-95%, Table 4, entries 1-13).



Scheme 7. Conversion of acylsilanes MBH and RC adducts into enals

Further, it proved to be even possible to perform this transformation directly on the first, non-protected, MBH adducts **4a**-**11f**. In that case we changed the organic co-solvent from acetone to THF, for solubility reasons. These reactions afforded in fair to good yields the target molecules **19**-**21,** with the same three R groups as before (Table 4, entries 14-22).

Finally, to complete this study we considered the possibility to use the same transformation of acylsilanes into aldehydes on the Rauhut-Currier adducts **5a** to **5d** (Scheme 7). The reaction

afforded cleanly, and in good to excellent yields, the desired compounds **22** - **24** with both an enal and a remote acylsilane unit.

Table 4. Transformation of acylsilanes MBH adducts into enals.

Entry	Starting Material	Product	R	Time (h)	Yield (%)
1	**13a**	**16**	Ph	48	95
2	**14a**	**17**	4-NO_2Ph	48	92
3	**15a**	**18**	EtO_2C	40	53
4	**13b**	**16**	Ph	24	88
5	**14b**	**17**	4-NO_2Ph	40	88
6	**15b**	**18**	EtO_2C	20	83
7	**15c**	**18**	EtO_2C	40	95
8	**14d**	**17**	4-NO_2Ph	20	75
9	**15d**	**18**	EtO_2C	6	80
10	**14e**	**17**	4-NO_2Ph	20	91
11	**15e**	**18**	EtO_2C	24	95
12	**14f**	**17**	4-NO_2Ph	20	69
13	**15f**	**18**	EtO_2C	24	81
14	**4a**	**19**	Ph	20	61
15	**6a**	**20**	4-NO_2Ph	48	78
16	**11a**	**21**	EtO_2C	48	81
17	**6c**	**20**	4-NO_2Ph	48	86
18	**11c**	**21**	EtO_2C	48	53
19	**6e**	**20**	4-NO_2Ph	48	86
20	**11e**	**21**	EtO_2C	48	63
21	**6f**	**20**	4-NO_2Ph	48	93
22	**11f**	**21**	EtO_2C	48	74
23	**5a**	**22**	-	24	60
24	**5b**	**23**	-	40	90
25	**5d**	**24**	-	8	90

This result is in agreement with literature data indicating that conjugated acylsilanes are more easily cleaved under photolytic conditions that non conjugated substrates.[6] Similar reactions have been performed starting from the transposed (*E*) acylsilane **14'a**. However, they did not afford the expected conjugated aldehyde, and they gave only *E-Z* equilibration of this molecule, without hydrolysis of the acylsilane unit.

Conclusions

In summary, we have disclosed a short and efficient approach toward new acrolein-type derivatives, functionalized in position 2. Taking into account their multiple reactivity profile, these molecules appear as versatile building blocks [14] for the preparation of natural products, as well as various type of bioactive compounds.

Experimental section

General Information: All anhydrous reactions were performed in oven-dried round-bottomed flasks under a dry argon atmosphere. Air and moisture-sensitive compounds were introduced via syringes or cannulae, using standard inert atmosphere techniques. Reactions were monitored by thin layer chromatography (TLC) using E. Merck silica gel plates and components were visualized by illumination with short-wavelength UV light and/or staining (*p*-anisaldehyde or basic $KMnO_4$). All reagents were used as they were received from commercial suppliers, unless otherwise noted. THF was dried in the presence of sodium metal using benzophenone as indicator and distilled prior to use. Anhydrous CH_2Cl_2 was prepared by refluxing in the presence of CaH_2 and distilled right before use. We used a Vilber Lourmat VL-6.LC lamp equiped with two 6W bulbs at 365 nm for the small scale reactions, or a LT5W T8/010 UV Dudexa lamp from Narva for the larger scale reactions. ^1H NMR spectra were recorded at 300, 400 and 500 MHz, and ^{13}C NMR spectra were recorded at 75, 101 and 126 MHz, respectively in $CDCl_3$. The residual peak of $CHCl_3$ was set at 7.26 ppm for ^1H NMR and the central peak of $CDCl_3$ was set at 77.0 ppm for ^{13}C NMR. All products were purified by flash column chromatography on silica gel (100 – 200 mesh).

General experimental procedure for the preparation of α-hydroxyallylsilanes (2): to a solution of allyl alcohol **1** (1 equiv) in anhydrous THF was added *n*-BuLi (1.2 equiv) at -78 °C. After 30 min stirring at the same temperature, $SiR^1R^2R^3Cl$ (1 equiv) in dry THF was added in dropwise. Then, the reaction was warmed to room temperature and stirred for 18 h. Next, *sec*-BuLi (1.05 equiv) was added in dropwise at -78 °C. After stirring for 2 h at -50 °C, the reaction mixture was quenched with aqueous NH_4Cl at -78 °C, and then diluted with Et_2O. The organic phase was collected and the aqueous phase was extracted with Et_2O for twice. Combined organic phases were dried with Na_2SO_4, concentrated under reduce pressure. The residue was purified by column chromatography on silica gel to afford (**2)** as a colourless oil. With this procedure we prepared all *α*-hydroxyallylsilanes (**2a** to **2f**).

General experimental procedure for preparation of acryloylsilanes by Swern protocol (3a-3f): to a solution of trifluoroacetic anhydride (1.5 equiv) in CH_2Cl_2 was added DMSO (2 equiv) dropwise at -78 °C. After 30 min stirring at the same temperature, α- hydroxyallylsilanes (**2a-2f)** (1 equiv) in CH_2Cl_2 were added in dropwise. Then the reaction was stirred for 1 h at -78 °C, and followed by adding TEA (3 equiv) slowly. After stirring for another 1 h at -78 °C, the reaction mixture was quenched with water and warmed to room temperature. The organic phase was collected and the aqueous phase was extracted twice with CH_2Cl_2. The organic phases were combined, dried with $MgSO_4$ and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford acryloylsilanes (**3a-3f**) as bright yellow liquids.

General experimental procedure for preparation of acryloylsilanes by using TCT (3a-3f): DMSO (5 equiv) was added slowly to a solution of 2,4,6-Trichloro-1,3,5-Triazine (TCT,1.2 equiv) in THF, stirred and maintained at -30 °C for 30 min. Then, a solution of *α*-hydroxyallylsilane **3** (1.0 equiv) in dry THF was added dropwise and stirring continued for a further 30 min. Finally Et_3N (4 equiv) was added with an additional 30 min of stirring. The mixture was poored in pentane under vigourous stirring with appearance of a sticky mass of TEA salt, which was discarded. The rest of the cloudy solution was stirred with an excess of $MgSO_4$ while addition of a small amount of water (0.5 to 1.0 ml) permitted the clearance of this solution. Then, it was filtrated and the volatiles were evaporated at 450 Mbar with a water bath at 45°C. Additional pentane was added twice to ensure the total impoverishment of the solvent by azeotropic distillation.

The product was purified by column chromatography on silica gel to afford acryloylsilanes (**3a-3f**) as bright yellow liquids.

1-(Triethylsilyl)prop-2-en-1-one (3a): R_f: 0.8 (5:95 EtOAc/n-Hexane); Yield 88%, as a yellow oil; FT-IR (film) 2954, 2876, 1598, 1180, 1002, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.44 (dd, *J* = 17.9, 10.8 Hz, 1H), 6.03 (dd, *J* = 17.9, 1.1 Hz 1H), 5.83 (dd, *J* = 10.8, 1.1 Hz, 1H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.75 (2 x q, *J* = 7.8, 1.0 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 237.7, 142.1, 127.2, 7.1, 2.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_9H_{18}ONaSi$ $[M+Na]^+$: 193.1019, found: 193.1022.

1-(Dimethyl(phenyl)silyl)prop-2-en-1-one (3b): R_f: 0.6 (5:95 EtOAc/n-Hexane); Yield 80% as a yellow oil; FT-IR (film) 2960, 2871, 1600, 1428, 1250, 1183, 1110, 1024, 955, 815, 783, 697, 653 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.56-7.51 (m, 2H), 7.43-7.34 (m, 3H), 6.41 (dd, *J* = 17.9, 10.8 Hz, 1H), 5.99 (dd, *J* = 17.9, 0.9 Hz, 1H), 5.86 (dd, *J* = 10.8, 0.9 Hz, 1H), 0.53 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.8, 141.2, 135.1, 133.9, 129.9, 129.4, 128.2, -3.6 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{11}H_{15}OSi$ $[M+H]^+$; 191.0892, found: 191.0890.

1-(Trimethylsilyl)prop-2-en-1-one (3c): R_f : 0.7 (5:95 EtOAc/n-Hexane); Yield 91% as a yellow oil; FT-IR (film) 2960, 1734, 1460, 1259, 1083, 842, 800 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.43 (dd, *J* = 18.0, 10.7 Hz, 1H), 6.12 (dd, *J* = 18.0, 1.0 Hz, 1H), 5.97 (dd, *J* = 10.7, 1.0 Hz, 1H), 0.27 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 237.8, 141.4, 128.5, -2.3 ppm; HRMS (ESI +ve) Exact mass calculated for $C_6H_{13}OSi$ $[M+H]^+$; 129.0730, found: 129.0731.

1-(Triisopropylsilyl)prop-2-en-1-one (3d): R_f: 0.8 (5:95 EtOAc/n-Hexane); Yield 55% as a yellow oil; FT-IR (film) 2944, 2867, 1637, 1576, 1464, 1390, 1177, 986, 882, 677, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.70 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.96 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.56 (dd, *J* = 10.6, 1.5 Hz, 1H), 1.34 (hept, *J* = 7.5 Hz, 3H), 1.11 (d, *J* = 7.5 Hz, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 236.7, 141.0, 123.6, 18.5, 11.1 ppm; HRMS: (ESI -ve) Exact mass calculated for $C_{12}H_{25}OSi$ $[M+H]^+$; 213.1675, found: 213.1678.

1-(Tert-butyldimethylsilyl)prop-2-en-1-one (3e): R_f : 0.75 (5:95 EtOAc/n-Hexane); Yield: 89% as a yellow oil; FT-IR (film) 2854, 1644, 1463, 1259, 1082, 1018, 800 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 6.59 (dd, *J* = 17.7, 10.7 Hz, 1H), 6.04 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.77 (dd, *J* = 10.7, 1.3 Hz, 1H), 0.95 (s, 9H), 0.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 236.9, 141.4, 126.4, 26.5, 16.6, -6.2 ppm; HRMS (ESI -ve) Exact mass calculated for $C_9H_{19}OSi$ $[M+H]^+$; 171.1199, found: 171.1202.

1-(Methyldiphenylsilyl)prop-2-en-1-one (3f): R_f : 0.6 (5:95 EtOAc/n-Hexane); Yield 73% as a yellow oil; FT-IR (film) 3048, 1638, 1486, 1427, 1251, 1185, 1110, 997, 790, 727, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.58 (m, 4H), 7.50-7.35 (m, 6H), 6.57 (dd, *J* = 17.8, 10.8 Hz, 1H), 6.02 (dd, *J* = 17.8, 0.9 Hz, 1H), 5.85 (dd, *J* = 10.8, 0.9 Hz, 1H), 0.81 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 233.7, 141.4, 135.1, 133.2, 130.1, 129.6, 128.2, -4.3 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{16}ONaSi$ $[M+Na]^+$; 275.0862, found: 275.0864.

General experimental procedure for the preparation of *α*-functional *α,β*-unsaturated acylsilanes *via* MBH reactions:

To a solution of acryloylsilane **3** in EtOAc was added the aldehyde, followed by DABCO at 0 °C and reached room temperature with stirring. After consumption of the starting material, water was added and the organic phase was separated and washed with water. Aqueous phases were extracted with EtOAc twice and the organic phases gathered, dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography.

2-(Hydroxy(phenyl)methyl)-1-(triethylsilyl)prop-2-en-1-one (4a): yield 60% as a yellow oil. FT-IR (film) 3447, 2954, 2875, 1594, 1454, 1019, 734, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.32 – 7.25 (m, 4H), 7.23-7.19 (m, 1H), 6.14 (d, *J* = 1.3 Hz, 1H), 6.09 (s, 1H), 5.53 (d, *J* = 4.6 Hz, 1H), 3.51 (d, *J* = 4.9 Hz, 1H), 0.90 (t, *J* = 7.8 Hz, 9H), 0.75-0.77 (2 x q, *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 239.3, 155.7, 141.9, 128.2, 127.9, 127.4, 126.6, 72.2, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{24}O_2NaSi$ $[M+Na]^+$: 299.1437, found: 299.1438.

2-methylene-1,5-bis(triethylsilyl)pentane-1,5-dione (5a): yield 16% as a yellow oil. FT-IR (film) 2954, 2876, 1641, 1595, 1414, 1004, 719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 6.04 (broad s, 1H), 5.95 (s, 1H), 2.68-2.60 (t, *J* = 7.4 Hz ,2H), 2.39 (tq, *J* = 7.4, 1.2 Hz, 2H), 0.94 (t, *J* = 6.5 Hz, 18H), 0.82-0.66 (2 x q, *J* = 6.5 Hz, 2 x 6H); ^{13} ppm C NMR (126 MHz, $CDCl_3$) δ = 246.4, 237.5, 154.4, 128.6, 48.8, 22.1, 7.4, 7.3, 3.9, 2.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{36}O_2NaSi_2$ $[M+Na]^+$: 363.2146, found: 363.2150.

2-(Hydroxy(4-nitrophenyl)methyl)-1-(triethylsilyl)prop-2-en-1-one (6a): yield 88% as a yellow oil. FT-IR (film) 3464, 2956, 2876, 1594, 1519, 1344, 1014, 851, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 6.21 (s, 1H), 6.17 (d, *J* = 1.1 Hz, 1H), 5.63 (d, *J* = 5.5 Hz, 1H), 3.37 (dt, *J* = 5.2, 2.7 Hz, 1H), 0.93 (t, *J* = 7.5 Hz, 9H), 0.83 - 0.75 (3 x q , *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 239.6, 154.3, 149.1, 147.2, 129.6, 127.2, 123.5, 72.2, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{23}NO_4NaSi$ $[M+Na]^+$: 344.1288, found: 344.1289.

2-((4-Bromophenyl)(hydroxy)methyl)-1-(triethylsilyl)prop-2-en-1-one (7a): yield 53% as a yellow oil. FT-IR (film) 3435, 2954, 2875, 1590, 1486, 1010, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 6.15 (s, 1H), 6.13 (d, *J* = 1.2 Hz, 1H), 5.51 (s, 1H), 0.93 (t, *J* = 7.5 Hz, 9H), 0.79 (q , *J* = 7.5 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 239.7, 154.9, 140.7, 131.4, 128.8, 128.2, 121.3, 72.1, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{23}O_2BrNaSi$ $[M+Na]^+$: 377.0542, found: 377.0543.

2-((2-Bromophenyl)(hydroxy)methyl)-1-(triethylsilyl)prop-2-en-1-one (8a): yield 63% as a yellow oil. FT-IR (film) 3065, 2960, 2912, 2876, 1596, 1466, 1020, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.59 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (td, *J* = 7.6, 1.7 Hz, 1H), 6.12 (s, 1H), 5.87 (d, *J* = 3.3 Hz, 1H), 5.80 (d, *J* = 1.0 Hz, 1H), 3.52 (d, *J* = 3.7 Hz, 1H), 0.98 (t, *J* = 7.2 Hz, 9H), 0.83 - 0.75 (2 x

q , J = 7.8 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 239.8, 153.8, 140.0, 132.6, 129.5, 129.0, 128.5, 127.5, 122.6, 70.8, 7.3, 3.6 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{23}O_2BrNaSi$ $[M+Na]^+$: 377.0542, found: 377.0542.

2-((3-Bromophenyl)(hydroxy)methyl)-1-(triethylsilyl)prop-2-en-1-one (9a): yield 75% as a yellow oil. FT-IR (film) 3435, 2954, 1875, 1590, 1486, 1403, 1234, 1070, 815, 731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.40-7.33 (dd, J = 7.8, 1.5 Hz, 1H, 1H), 7.24 (dd, J = 7.8, 1.5 Hz, 1H), 7.17 (td, J = 7.8, 1.0 Hz, 1H), 6.15-6.12 (m, 2H), 5.49 (d, J = 4.2 Hz, 1H), 3.49-3.42 (m, 1H), 0.91 (t, J = 7.8 Hz, 9H), 0.77 (q , J = 7.8 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 239.7, 154.8, 144.1, 130.5, 129.8, 129.5, 128.8, 125.2, 122.4, 71.9, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{23}O_2BrNaSi$ $[M+Na]^+$: 377.0542, found: 377.0542.

2-(Hydroxy(pyridin-3-yl)methyl)-1-(triethylsilyl)prop-2-en-1-one (10a): yield 68% as a yellow oil. FT-IR (film) 3170, 2954, 2875, 1593, 1424, 948, 711 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.46 (d, 0.9 Hz, 1H), 8.38 (dd, J = 4.8, 1.9 Hz, 1H), 7.68 (ddt, J = 7.8, 1.9, 0.9 Hz, 1H), 7.21 (dd, J = 7.8, 4.8, Hz, 1H), 6.27 (s, 1H), 6.18 (s, 1H), 5.58 (s, 1H), 0.88 (t, J = 6.9, 9H), 0.77 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 238.2, 155.5, 148.1, 147.9, 138.4, 134.7, 128.1, 123.2, 68.9, 7.1, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{23}NO_2NaSi$ [M+Na]+: 300.1390, found: 300.1390.

Ethyl 2-hydroxy-3-((triethylsilyl)carbonyl)but-3-enoate (11a): yield 93% as a yellow oil. FT-IR (film) 3492, 2956, 2877, 1736, 1598, 1234, 1086, 1019, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.31 (s, 1H), 6.19 (s, 1H), 4.79 (d, J = 6.3 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 3.38 (d, J = 6.3 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H), 0.97 (t, J = 8.2, 9H), 0.81 (q, J = 8.2 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 236.2, 172.6, 151.3, 129.9, 69.9, 61.7, 13.9, 7.1, 3.4 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{24}O_4NaSi$ $[M+Na]^+$: 295.1336, found: 295.1335.

3-Hydroxy-2-methylene-1-(triethylsilyl)heptan-1-one (12a): yield 37% as a yellow oil. FT-IR (film) 3435, 2955, 2875, 1592, 1414, 1017, 731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 6.05 (s, 1H), 4.39 (q, J = 6.4 Hz, 1H), 1.60-1.53(m, 2H), 1.42-1.23 (m, 4H), 0.98 (t, J = 8.2 Hz, 9H), 0.90 (t, J = 7.0 Hz, 3H), 0.81 (q, J = 8.2 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 240.1, 155.9, 127.7, 71.2, 35.9, 28.0, 22.5, 14.0, 7.3, 3.7 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{14}H_{28}O_2NaSi$ $[M+Na]^+$: 279.1750, found: 279.1753.

1-(Dimethyl(phenyl)silyl)-2-(hydroxy(phenyl)methyl)prop-2-en-1-one (4b): yield 40% as a yellow oil. FT-IR (film) 3493, 2959, 1597, 1427, 1251, 1112, 1058, 814, 781, 695, 650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51-7.46 (m, 2H), 7.44-7.37 (m, 3H), 7.34-7.26 (m, 5H), 6.05 (s, 1H), 6.02 (d, J = 1.2 Hz, 1H), 5.55 (d, J = 4.7 Hz, 1H), 3.08 (d, J = 5.0 Hz, 1H), 0.53 and 0.51 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 237.4, 153.9, 141.4, 135.3, 133.8, 130.2, 129.9, 128.3, 128.2, 127.5, 126.5, 72.5, -3.1, -3.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{20}O_2NaSi$ $[M+Na]^+$: 319.1130, found: 319.1134.

1,5-Bis(dimethyl(phenyl)silyl)-2-methylenepentane-1,5-dione (5b): yield 11% as a yellow oil. FT-IR (film) 2960, 1642, 1596, 1427, 1251, 1109, 812, 781, 730, 697, 649 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50 (m, 4H), 7.36 (m, 6H), 5.81 (d, J = 2.3 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 0.49 and 0.45 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 244.5, 235.2, 152.5, 136.0, 134.3, 133.9, 133.8, 130.0, 129.9, 129.7, 128.2, 47.2, 22.2, -2.7, -4.7 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{22}H_{28}O_2NaSi_2$ $[M+Na]^+$: 403.1526, found: 403.1522.

1-(Dimethyl(phenyl)silyl)-2-(hydroxy(4-nitrophenyl)methyl) prop-2-en-1-one (6b): yield 77% as a yellow oil. FT-IR (film) 3486, 2959, 1688, 1596, 1518, 1344, 1252, 1109, 1066, 818, 786, 735, 652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.7 Hz, 2H), 7.29 - 7.24 (m, 4H), 7.23 - 7.13 (m, 3H), 5.92 (s, 1H), 5.89 (s, 1H), 5.39 (d, J = 5.4 Hz, 1H), 3.15 (d, J = 5.4, 1H), 0.33 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 237.3, 152.9, 148.9, 147.2, 134.7, 133.7, 130.9, 130.1, 128.3, 127.2, 123.5, 72.0 -3.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{19}NO_4NaSi$ $[M+Na]^+$: 364.0981, found: 364.0981.

2-((4-Bromophenyl)(hydroxy)methyl)-1-(dimethyl(phenyl) silyl)prop-2-en-1-one (7b): yield 34% as a yellow oil. FT-IR (film) 3449, 2959, 1690, 1593, 1485, 1252, 1112, 1069, 1009, 818, 734, 652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.49-7.30 (m, 7H), 7.17-7.10 (d, J = 8.7 Hz, 2H), 6.03 (s, 1H), 6.00 (d, J = 1.2 Hz, 1H), 5.45 (s, 1H), 3.18 (s, 1H), 0.50 (s, 3H), 0.49 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 234.8, 150.9, 137.9, 132.5, 131.2, 128.8, 127.7, 127.4, 125.7, 125.7, 118.9, 69.4, -5.6, -5.7 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{19}O_2NaSiBr$ $[M+Na]^+$: 397.0235, found: 397.0241.

Ethyl-3-((dimethyl(phenyl)silyl)carbonyl)-2-hydroxybut-3-enoate (11b): yield 88% as a yellow oil. FT-IR (film) 3491, 2853, 1608, 1428, 1249, 1029, 827, 733, 647 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.59-7.49 (m, 2H), 7.45-7.33 (m, 3H), 6.20 (s, 1H), 6.06, (s, 1H), 4.79 (d, J = 4.2 Hz, 1H), 4.29-4.05 (m, 2H), 3.43 (d, J = 5.8 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H), 0.56 (s, 3H), 0.54 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 234.4, 172.6, 149.9, 135.2, 133.8, 131.5, 129.9, 128.3, 70.1, 61.9, 14.0, -3.1, -3.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{20}O_4NaSi$ $[M+Na]^+$: 315.1029, found: 315.1032.

2-(Hydroxy(4-nitrophenyl)methyl)-1-(trimethylsilyl)prop-2-en-1-one (6c): yield 92% as a yellow oil. FT-IR (film) 2960, 1596, 1518, 1410, 1343, 1249, 1014, 986, 839, 755, 700, 624 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.17 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 6.24 (s, 1H), 6.18 (d, J = 1.1 Hz, 1H), 5.59 (d, J = 4.50 Hz, 1H), 0.26 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 239.2, 153.0, 149.0, 147.2, 130.2, 127.2, 123.5, 71.9, -1.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{17}NO_4NaSi$ [M+H]+: 302.0819, found: 302.0818.

Ethyl-2-hydroxy-3-((trimethylsilyl)carbonyl)but-3-enoate (11c): yield 22% as a yellow oil. FT-IR (film) 3451, 2982, 2930, 1742, 1701, 1451, 1372, 1207, 1020, 759, 691 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.27 (d, J = 0.9 Hz, 1H), 6.16 (s, 1H), 4.78 (d, J = 5.2 Hz, 1H), 4.29 – 3.99 (m, 2H), 3.44 (d, J = 6.2 Hz, 1H), 1.18

(t, J = 7.1 Hz, 3H), 0.25 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 236.3, 172.6, 150.1, 129.9, 70.1, 61.7, 14.0, -1.7 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{10}H_{18}O_4Na$ Si [M+H]+: 253.0866, found: 253.0866.

2-(Hydroxy(phenyl)methyl)-1-(triisopropylsilyl)prop-2-en-1-one (4d): yield 10% as a yellow oil. FT-IR (film) 3493, 2944, 2894, 1659, 1465, 1113, 992, 882, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35-7.30 (m, 3H), 7.27-7.23 (m, 2H), 6.10 (d, J = 1.0 Hz, 1H), 6.05 (s, 1H), 5.58 (s, 1H), 3.34-3.01 (m, 1H), 1.30-1.20 (m, 3H), 095 (s, J = 6.2 Hz, 9H), 0.98 (s, J = 6.2 Hz, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 239.6, 156.3, 141.5, 128.2, 127.5, 126.6, 73.0, 29.7, 18.5, 12.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{19}H_{31}O_2Si$ [M+H]$^+$: 319.2093, found: 319.2086.

2-methylene-1,5-bis(triisopropylsilyl)pentane-1,5-dione (5d): yield 20% as a yellow oil. FT-IR (film) 2944, 2867, 1639, 1594, 1464, 1256, 1168, 922, 882, 675 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.02 (s, 1H), 5.82 (s, 1H), 2.60 (t, J = 7.1 Hz, 2H), 2.36 (t, J = 7.1 Hz, 2H), 1.41-1.18 (m, 6H), 1.07 (d, J = 2.6 Hz, 18H), 1.04 (d, J = 2.6 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 245.5, 236.8, 155.2, 128.1, 50.1, 22.1, 18.7, 18.5, 12.3, 10.7 ppm; HRMS: (ESI +ve) Exact mass calculated for $C_{24}H_{48}O_2NaSi_2$ [M+Na]$^+$: 447.3091, found: 447.3084.

2-(Hydroxy(4-nitrophenyl)methyl)-1-(triisopropylsilyl)prop-2-en-1-one (6d): yield 30% as a yellow oil. FT-IR (film) 3486, 2944, 2892, 1600, 1465, 1250, 1177, 1015, 920, 882, 677, 642 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.02 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 6.0 (s, 1H), 5.97 (s, 1H), 5.47 (d, J = 5.5 Hz, 1H), 3.21 (d, J = 5.6 Hz, 1H), 1.22-1.11 (m, 3H), 0.88 (d, J = 7.5Hz, 9H), 0.86 (d, J = 7.5Hz, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 236.8, 152.5, 146.6, 144.6, 126.8, 124.7, 120.9, 69.8, 16.0, 9.6 ppm; HRMS (ESI -ve) Exact mass calculated for $C_{19}H_{30}NO_4Si$ [M+H]$^+$: 364.1944, found: 364.1947.

Ethyl -2-hydroxy-3-((triisopropylsilyl)carbonyl)but-3-enoate (11d): yield 70% as a yellow oil. FT-IR (film) 3491, 2944, 1602, 1371, 1190, 1026, 857, 741, 635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.33 (s, 1H), 6.16 (s, 1H), 4.77 (d, J = 6.4 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.41 (d, J = 6.5 Hz, 1H), 1.44-1.27 (m, 3H), 1.20 (t, J = 7.2 Hz, 3H), 1.10 (dd, J = 7.5, 1.2 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.8, 172.8, 151.9, 130.3, 70.5, 61.8, 18.6, 13.9, 12.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{30}O_4NaSi$ [M+Na]$^+$: 337.1811, found: 337.1811.

1-(Tert-butyldimethylsilyl)-2-(hydroxy(4-nitrophenyl)methyl) prop-2-en-1-one (6e): yield 34% as a yellow oil. FT-IR (film) 3480, 2930, 28602, 1590, 1520, 1345, 1250, 821, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.22 (d, J = 0.5 Hz, 1H), 6.18 (d, J = 1.1 Hz, 1H), 5.63 (d, J = 4.1 Hz, 1H), 3.42 (d, J = 5.2 Hz, 1H), 0.86 (s, 9H), 0.26 (s, 3H), 0.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 247.5, 238.9, 154.6, 149.1, 147.2, 130.3, 127.2, 123.49, 72.1, 16.7, -4.8 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{16}H_{23}NO_4NaSi$ [M+Na]$^+$: 344.1288, found: 344.1289.

Ethyl-3-((tert-butyldimethylsilyl)carbonyl)-2-hydroxybut-3-enoate (11e): yield 54% as a yellow oil. FT-IR (film) 3445, 2929, 2857, 1743, 1253, 1089, 1040, 840, 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.33 (s, 1H), 6.22 (s, 1H), 4.76 (d, J = 6.1 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.37 (d, J = 6.0 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 0.94 (s, 9H), 0.30 (s, 3H), 0.29 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.9, 172.8, 151.4, 131.1, 70.6, 61.9, 26.5, 16.8, 14.0, -4.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{13}H_{24}O_4NaSi$ [M+Na]$^+$: 295.1341, found: 295.1339.

2-(Hydroxy(phenyl)methyl)-1-(methyldiphenylsilyl)prop-2-en-1-one (6f): yield 72% as a yellow oil. FT-IR (film) 3070, 1688, 1596, 1518, 1428, 1344, 1109, 792, 728, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.7 Hz, 2H), 7.55 – 7.31 (m, 12H), 6.15 (s, 1H), 6.11 (s, 1H), 5.67 (s, 1H), 3.60 (s, 1H), 0.80 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.3, 153.7, 149.2, 147.2, 135.0, 134.9, 134.0, 133.0, 132.9, 131.7, 130.3, 128.4, 128.3, 127.3, 123.5, 71.7, -3.6 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{23}H_{21}NO_4NaSi$ [M+Na]$^+$: 426.1132, found: 426.1129.

Ethyl-2-hydroxy-3-((methyldiphenylsilyl)carbonyl)but-3-enoate (11f): yield 32% as a yellow oil. FT-IR (film) 3450, 3070, 2981, 1734, 1694, 1428, 1254, 1112, 1024, 790, 724, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.62-7.56 (m, 4H), 7.48 – 7.32 (m, 6H), 6.24 (s, 1H), 6.10 (s, 1H), 4.86 (s, 1H), 4.20 (m, 2H), 3.55 (d, J = 5.6 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H), 0.81 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 232.7, 172.6, 150.5, 135.0, 133.3, 133.2, 132.7, 130.2, 128.3, 70.2, 62.0, 14.0, -3.6 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{20}H_{22}O_4NaSi$ [M+Na]$^+$: 377.1179, found: 377.1177.

General experimental procedure for the protection of MBH adducts as acetates:

Three methods have to been employed to protect the previous MBH products. After some time we found that the use of TEA was not necessary and induced the formation of transposed product. Finally $NaHCO_3$ was found to be more efficient for sensitive substrates. We described the three methods which were used:

Method A: a round bottom flask was charged with *β*-hydroxyacryloylsilane (1 equiv), acetic anhydride (2 equiv), in dry DCM under nitrogen flush at 0 °C. Then DMAP (0.1 equiv) and TEA (3 equiv) were added to the solution and stirring was continued at room temperature and monitored by TLC using 10% EtOAc/pentane. After aqueous workup and concentration, the compound was purified by column chromatography.

Method B: a round bottom flask was charged with *β*-hydroxyacryloylsilane (1 equiv), acetic anhydride (1,2 – 1,5 equiv) in dry DCM under nitrogen flush at 0 °C. Then DMAP (0.2 equiv) was added to the solution and stirring was continued at room temperature and monitored by TLC using 10 % EtOAc/pentane. After aqueous workup and concentration, the compound was purified by column chromatography.

Method C: a round bottom flask was charged with *β*-hydroxyacryloylsilane (1 equiv), acetic anhydride (5 equiv) in dried DCM under nitrogen flush at 0°C. Then, $NaHCO_3$ (2.0 equiv) was added to the solution and stirring was continued at room temperature and the reaction monitored by TLC using 10 %

EtOAc/pentane. After aqueous workup and concentration, the compound was purified by column chromatography.

1-Phenyl-2-((triethylsilyl)carbonyl)allylacetate (13a): method A: yield 63% as a yellow oil. FT-IR (film) 2955, 2876, 1740, 1599, 1369, 1223, 1026, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.38-7.24 (m, 5H), 6.69 (s, 1H), 6.23 (d, *J* = 1.5 Hz, 1H), 6.16 (s, 1H), 2.10 (s, 3H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.78 (q, *J* = 7.7 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 235.5, 169.3, 153.4, 138.4, 128.3, 128.0, 127.5, 126.6, 72.1, 21.1, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{26}O_3NaSi$ $[M+Na]^+$: 341.1543, found: 341.1545.

1-(4-Nitrophenyl)-2-((triethylsilyl)carbonyl)allyl acetate (14a): method A: yield 92% as a yellow thick oil. When time was prolonged from 6 h to 48 h isomerisation of **14a** to **14'a** took place and this compound (**14'a**, *E* isomer) was obtained in 18% yield together with compound (**14a**) in 81%. Method C: yield: 82% as a yellow solid. FT-IR (film) 2596, 2876, 1745, 1598, 1521, 1345, 1220, 735, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 6.69 (s, 1H), 6.34 (d, *J* = 1.4 Hz, 1H), 6.25 (s, 1H), 2.12 (s, 3H), 0.96 – 0.84 (m, 9H), 0.81 – 0.71 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 235.3, 169.1, 152.3, 147.4, 145.8, 128.2, 127.9, 123.6, 71.1, 21.0, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{25}NO_5NaSi$ $[M+Na]^+$: 386.1394, found: 386.1390.

(*E*)-3-(4-Nitrophenyl)-2-((triethylsilyl)carbonyl)allyl acetate (14a'): ^1H NMR (300 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 3H), 4.86 (s, 2H), 2.03 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 9H), 0.90 (q, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.3, 170.3, 148.0, 144.0, 143.0, 140.8, 130.0, 123.9, 57.0, 20.7, 7.4, 3.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{25}NO_5NaSi$ $[M+Na]^+$: 386.1394, found: 386.1392.

Ethyl 2-acetoxy-3-((triethylsilyl)carbonyl)but-3-enoate (15a): method A: yield 88% as a yellow liquid. FT-IR (film): 2956, 2877, 1746, 1606, 1371, 12118, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 6.39 (d, *J* = 0.8 Hz, 1H), 6.28 (s, 1H), 5.97 (d, *J* = 0.8 Hz, 1H), 4.28 – 4.04 (m, 2H), 2.14 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 9H, 6H), 0.77 (q, *J* = 7.0 Hz, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 233.4, 169.6, 168.3, 148.2, 130.5, 68.6, 61.4, 20.5, 13.8, 7.2, 3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{26}O_5NaSi$ [M+Na]+: 337.1441, found: 337.1446.

2-((Dimethyl(phenyl)silyl)carbonyl)-1-phenylallyl acetate (13b): method B: yield 76%. FT-IR (film) 2955, 2911, 2876, 1740, 1599, 1369, 1223, 10226, 735, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.46-7.42 (m, 2H), 7.41-7.32 (m, 3H), 7.31-7.23(m, 5H), 6.60 (s, 1H), 6.10 (s, 1H), 6.02 (s, 1H), 2.04 (s, 3H), 0.51 (s, 3H), 0.45 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 233.5, 169.3, 151.8, 138.2, 135.4, 133.8, 129.8, 128.4, 128.3, 128.2, 128.1, 127.5, 71.9, 21.1, -3.0, -3.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{20}H_{22}O_3NaSi$ $[M+Na]^+$: 361.1236, found: 361.1238.

2-((Dimethyl(phenyl)silyl)carbonyl)-1-(4-nitrophenyl)allyl acetate (14b): method B: yield 80% as a yellow liquid. FT-IR (film) 2919, 2850, 1745, 1600, 1521, 1371, 1346, 1223, 1110, 1039, 834, 787, 734, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.09-8.02 (m, 2H), 7.42-7.25 (m, 7H), 6.60 (s, 1H), 6.13 (d, *J* = 1.3 Hz, 1H), 6.04 (s, 1H), 2.10 (s, 3H), 0.46 (s, 3H), 0.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 233.3, 169.1, 150.7, 147.5, 145.6, 134.9, 133.7, 130.0, 129.3, 128.3, 128.2, 123.6, 71.0, 20.9, -3.1, -3.3 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{20}H_{21}NO_5NaSi$ $[M+Na]^+$: 406.1087, found: 406.1071.

Ethyl-2-acetoxy-3-((dimethyl(phenyl)silyl)carbonyl)but-3-enoate (15b): method B: yield 67% as a yellow liquid.FT-IR (film) 2924, 2853, 1745, 1608, 1372, 1217, 1115, 1060, 827, 788, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.41 (m, 2H), 7.33-7.25 (m, 3H), 6.14 (d, *J* = 0.8 Hz, 1H), 6.03 (s, 1H), 5.85 (d, *J* = 0.8 Hz, 1H), 4.06 (q, *J* = 7.0 , 2H), 2.01 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 3H), 0,46 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 231.7, 169.7, 168.3, 146.7, 135.1, 133.8, 132.2, 130.0, 128.3, 68.6, 61.6, 20.6, 13.9, -3.1, -3.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{17}H_{22}O_5NaSi$ $[M+Na]^+$: 357.1134, found: 357.1134.

1-(4-Nitrophenyl)-2-((trimethylsilyl)carbonyl)allylacetate (14c): method A: yield 72% as a yellow liquid. FT-IR (film) 1741, 1598, 1519, 1370, 1345, 1221, 1108, 992, 839, 750, 698, 622, 530 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H, 2H), 6.67 (s, 1H), 6.36 (d, *J* = 1.3 Hz, 1H), 6.28 (d, *J* = 0.7 Hz, 1H), 2.12 (s, 3H), 0.25 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.1, 169.1, 150.9, 147.5, 145.8, 128.5, 123.6, 70.9, 20.9, -1.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{19}NO_5NaSi$ $[M+Na]^+$: 344.0924, found: 344.0928.

Ethyl-2-acetoxy-3-((trimethylsilyl)carbonyl)but-3-enoate (15c): method A: yield 67%, method C: yield: 75% as a yellow liquid. FT-IR (film) 1742, 1608, 1371, 842, 620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 6.38 (s, 1H), 6.30 (s, 1H), 5.97 (s, 1H), 4.21 (q, *J* = 7.6 Hz, 2H), 2.15 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H), 0.33 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 233.4, 169.7, 168.4, 146.9, 130.9, 68.6, 61.6, 20.6, 13.9, -1.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{12}H_{20}O_5NaSi$ $[M+Na]^+$: 295.0972, found: 295.0971.

1-(4-Nitrophenyl)-2-((triisopropylsilyl)carbonyl)allyl acetate (14d): method B: yield 51% as a yellow liquid. FT-IR (film) 2945, 2867, 1748, 1600, 1524, 1347, 1226, 1113, 1048, 849, 751, 684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 1H), 6.24 (s, 1H), 6.11 (s, 1H), 2.05 (s, 3H), 1.31-1.20 (m, 3H), 0.97 (d, *J* = 7.4 Hz, 9H), 0.94 (d, *J* = 7.4 Hz, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 234.9, 169.1, 153.2, 147.4, 145.9, 128.3, 127.6, 123.6, 71.3, 21.0, 18.6, 12.2 ppm; HRMS: (ESI +ve) Exact mass calculated for $C_{21}H_{31}NO_5NaSi$ $[M+Na]^+$: 428.1869, found: 428.1869.

Ethyl-2-acetoxy-3-((triisopropylsilyl)carbonyl)but-3-enoate (15d): method B: yield 70% as a yellow liquid. FT-IR (film) 2944, 2867, 1748, 1602, 1464, 1371, 1216, 1062, 982, 882, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.31 (d, *J* = 0.8 Hz, 1H), 6.15 (s, 1H), 5.89 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.30 (m, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.04 (d, *J* = 7.5 Hz, 9H), 1.03 (d, *J* = 7.5 Hz, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 233.0, 169.7,

168.4, 148.9, 130.6, 69.0, 61.5, 20.6, 18.6, 18.6, 13.9, 12.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{32}O_5NaSi$ $[M+Na]^+$: 379.1917, found: 379.1915.

2-((Tert-butyldimethylsilyl)carbonyl)-1-(4-nitrophenyl)allyl acetate (14e): method C: yield 68% as a yellow liquid. FT-IR (film) 2930, 2858, 1746, 1522, 1346, 1224, 1041, 836, 780 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 1.1 Hz, 1H), 6.32 (d, *J* = 1.3 Hz, 1H), 6.25 (d, *J* = 0.7 Hz,), 2.12 (s, 3H), 0.84 (s, 9H), 0.25 (s, 3H), 0.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 234.7, 217.1, 210.3, 169.1, 152.6, 147.4, 145.8, 128.6, 128.2, 123.5, 71.1, 26.5, 20.9, 16.7, -4.8, -4.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{25}NO_5NaSi$ [M+Na]+: 386.1394, found: 386.1397.

Ethyl-2-acetoxy-3-((tert-butyldimethylsilyl)carbonyl)but-3-enoate (15e): method C: yield 84% as a yellow liquid. FT-IR (film) 2928, 2857, 1749, 1602, 1465, 1370, 1248, 1220, 839, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 6.35 (d, *J* = 0.7 Hz, 1H), 6.27 (s, 1H), 5.94 (d, *J* = 0.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.11 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.28 (d, *J* = 2.9 Hz, 3H), 0.27 ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 233.0, 169.6, 168.4, 148.4, 131.4, 68.9, 61.5, 26.5, 20.6, 16.8, 13.9, -5.0 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{26}O_5NaSi$ [M+Na]+: 337.1441, found: 337.1440.

2-((Methyldiphenylsilyl)carbonyl)-1-(4-nitrophenyl)allyl acetate (14f): method A: yield: 79%, method C: yield 54% as a yellow liquid. FT-IR (film) 2953, 2923, 2878, 17448, 1599, 1522, 1343, 1218, 851, 742, 684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.34 – 7.90 (m, 2H), 7.71 – 7.14 (m, 10H), 6.78 (s, 1H), 6.27 (d, *J* = 1.4 Hz, 1H), 6.19 (s, 1H), 2.12 (s, 3H), 0.78 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 231.7, 169.1, 151.3, 147.5, 145.6, 134.9, 134.9 (2C), 133.1, 132.9, 130.3, 130.2, 128.3(3C), 123.6, 71.1, 21.0, -3.6 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{25}H_{23}NO_5NaSi$ $[M+Na]^+$: 468.1237, found: 468.1237.

Ethyl-2-acetoxy-3-((methyldiphenylsilyl)carbonyl)but-3-enoate (15f): method C: yield 77% as a yellow liquid. FT-IR (film) 2959, 2925, 2853, 1746, 1020, 800, 722, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.67 – 7.56 (m, 4H), 7.51 – 7.29 (m, 6H), 6.29 (s, 1H), 6.19 (s, 1H), 6.03 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.14 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.83 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 230.1, 169.7, 168.3, 147.4, 135.0, 133.3, 133.2, 133.1, 130.3, 128.3, 128.3, 68.7, 61.7, 20.7, 14.0, -3.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{22}H_{24}O_5NaSi$ $[M+Na]^+$: 419.12852, found: 419.1282.

(*E*)-3-(4-Nitrophenyl)-2-((triethylsilyl)carbonyl)allylacetate (14'a): in a 10 mL round bottomed was added compound (**14a**) (610 mg, 1.67 mmol) and 1.5 ml of $[BMiM],PF_6$ followed by addition of KOAc (214 mg, 2.2 mmol, 1.5 equiv) at 50 °C.The reaction mixture was kept for 2 hours at this temperature. The product was extracted with diethyl ether and purified by column chromatography with 20% diethyl ether/cyclohexane as eluent to afford pure product (**14'a**) (386 mg, 64% yield) as a yellow solid. FT-IR (Film) 2956, 2876, 1738, 1597, 1522, 1339, 1222, 1097, 1020, 856, 724, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.30 (d, *J*= 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.57 (s, 1H), 4.86 (s, 2H), 2.03 (s, 3H), 1.04 (t, *J*= 6.7 Hz, 9H), 0.90 (q, *J*= 6.7 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.3, 170.3, 148.0, 144.0, 143.0, 140.8, 130.0, 123.9, 57.0, 20.7, 7.4, 3.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{25}NO_5NaSi$ [M+Na]+: 386.13942 found: 386.1392.

(*E*)-3-(4-nitrophenyl)-2-((trimethylsilyl)carbonyl)allylacetate (14'c): yield 72% as a yellow thick oil. FT-IR (Film) 2960, 1738, 1597, 1517, 1350, 1229, 1028, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.25 (d, *J*= 8.8 Hz, 2H), 7.60 (d, *J*= 8.8 Hz, 2H), 7.56 (s, 1H), 4.81(s, 2H), 2.03 (s, 3H), 0.31 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 235.0, 170.3, 147.9, 143.7, 142.6, 140.7, 130.1, 123.8, 57.0, 20.7, -1.2 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{19}NO_5NaSi$ [M+Na]+: 344.1924, found: 344.0925.

(*E*)-2-((tert-butyldimethylsilyl)carbonyl)but-2-en-1-ylacetate (14'e): yield 81% as a yellow thick oil. FT-IR (Film) 2960, 2931, 2855, 1739, 1512, 1345, 1227, 735cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.29 (d, *J*= 8.8 Hz, 2H), 7.59 (d, *J*= 8.8 Hz, 2H), 7.56 (d, *J* = 2.1 Hz, 1H), 4.85 (s, 2H), 2.04 (s, 3H), 1.00 (s, 9H), 0.38 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 234.9, 170.4, 148.0, 144.2, 143.7, 140.8, 129.9, 123.9, 57.2, 26.7, 20.8, 17.0, -4.5 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{18}H_{25}NO_5NaSi$ [M+Na]+: 386.1394, found: 386.1392.

Ethyl-(*E*)-4-acetoxy-3-((tert-butyldimethylsilyl)carbonyl)pent-2-enoate (15'e): yield 64% as a yellow thick oil. FT-IR (Film) 2945, 2932, 2859, 1751, 1226, 1202, 1032, 838, 779 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 6.35 (s, 1H), 5.19 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.01 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.31 (s, 6H) ppm;^{13}C NMR (75 MHz, $CDCl_3$) δ = 237.5, 170.2, 165.3, 153.1, 128.2, 61.3, 58.0, 26.5, 20.7, 17.0, 14.1, -5.3 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{26}O_5NaSi$ [M+Na]+: 337.14417, found: 337.1438.

General experimental procedure for the transformation of MBH adducts into aldehydes:

A round bottom flask was charged with an acetyl protected *β*-hydroxyacryloylsilane dissolved in acetone/water 2:1 or THF/water 9:1. The solution was degasified then enlightened at 365 nm under stirring at room temperature. After completion of the reaction as monitored by TLC, solvents were removed in vacuum. The residue was dissolved in DCM and an aqueous workup done. The organic layer was dried with $MgSO_4$ and after concentration under reduced pressure the corresponding aldehyde was obtained.

2-Formyl-1-phenylallyl acetate (16): from compound (**13a**): yield 95%; from compound (**13b**): yield 88% as colourless oil. FT-IR (film) 2960, 1737, 1688, 1222, 1025, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.56 (s, 1H), 7.44 – 7.27 (m, 5H), 6.68 (s, 1H), 6.51 (d, *J* = 1.4 Hz, 1H), 6.22 (s, 1H), 2.13 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 191.7, 169.3, 148.7, 137.4, 133.6, 128.5, 128.4, 127.4, 71.4, 21.0 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{12}H_{12}O_3Na$ $[M+Na]^+$: 227.0678, found: 227.0681.

2-Formyl-1-(4-nitrophenyl)allyl acetate (17): from compound (**14a**): yield 92%; (**14b**): yield 88%; (**14d**): yield 75%; (**14e**): yield 91%; (**14f**): yield 69% as a colourless oil. FT-IR (film) 3088, 2935, 2858, 1741, 1687, 1602, 1518, 1335, 1225, 967, 848, 747, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 8.17 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.69 (s, 1H), 6.60 (d, *J* = 1.3 Hz, 1H), 6.29 (s, 1H), 2.15 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 191.4, 169.1, 147.7, 144.7, 134.5, 128.2, 123.7, 70.4, 20.8 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{12}H_{11}NO_5Na$ [M+Na]+: 272.05294, found: 272.0528.

Ethyl 2-acetoxy-3-formylbut-3-enoate (18): from compound (**15a**): yield 53%; (**15b**): yield 83%; (**15c**): yield 95%; (**15d**): yield 80%; (**15e**): yield 95%; (**15f**): yield 81% as a colourless oil. FT-IR (film) 2924, 2852, 1723, 1450, 1370, 1210, 1158, 1030, 883 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.52 (s, 1H), 6.55 (s, 1H), 6.29 (s, 1H), 5.89 (d, *J* = 1.0 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.20-1.16 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.6, 169.6, 167.6, 143.5, 137.3, 67.5, 62.0, 20.6, 13.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_9H_{12}O_5Na$ $[M+Na]^+$: 223.0582, found: 223.0584.

2-(Hydroxy(phenyl)methyl)acrylaldehyde (19): from compound (**4a)**: yield 61% as a colourless oil. FT-IR (film) 3412, 2922, 1682, 1453, 958, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.59 (s, 1H), 7.41-7.27 (m, 5H), 6.47 (d, *J* = 1.4 Hz, 1H), 6.18 (s, 1H), 5.64 (s, 1H), 2.88 (d, *J* = 3.5 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.9, 151.3, 140.8, 134.5, 128.5, 128.0, 126.6, 71.1 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{10}H_{10}O_2Na$ $[M+Na]^+$: 185.0573, found: 185.0574.

2-(Hydroxy(4-nitrophenyl)methyl) acrylaldehyde (**20):** from compound (**6a**): yield 78%; (**6c**): yield 86%; (**6e**): yield 86%; (**6f**): yield 93% as a colourless oil. FT-IR (film) 3071, 2958, 2855, 1688, 1600, 1515, 1428, 1343, 1255, 1111, 850, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 9.56 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 1.3 Hz, 1H), 6.23 (d, *J* = 0.7 Hz, 1H), 5.71 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.6, 150.5, 148.4, 147.4, 135.3, 127.4, 123.6, 69.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{10}H_8NO_3$ $[M-H_2O+H]^+$: 190.0498, found: 191.0498.

Ethyl 3-formyl-2-hydroxybut-3-enoate (**21**)**:** from compound (**11a**): yield 81%; (**11c**): yield 53%; (**11e**): yield 63%; (**11f**): yield 74% as a colourless oil. FT-IR (film) 3458, 2982, 2936, 1734, 1687, 1446, 1200, 1022, 969 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.60 (s, 1H), 6.58 (d, *J* = 0.9 Hz, 1H), 6.27 (s, 1H), 4.94 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 172.2, 146.7, 136.3, 68.2, 62.4, 13.9 ppm; HRMS: (ESI +ve) Exact mass calculated for $C_7H_{10}O_4Na$ [M+Na]+: 181.04713, found: 181.0474.

2-Methylene-5-oxo-5-(triethylsilyl)pentanal (22): from compound **5a**: yield 60% as a colourless oil. FT-IR (film) 2954, 2876, 1689, 1639, 1414, 1016, 945, 719 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.51 (s, 1H), 6.26 (s, 1H), 5.99 (s, 1H), 2.75 (t, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.73 (q, *J* = 8.0 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 245.7, 194.7, 149.6, 134.9, 47.9, 20.7, 7.2, 2.0 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{12}H_{22}O_2NaSi$ $[M+Na]^+$: 249.1281, found: 249.1281.

5-(Dimethyl(phenyl)silyl)-2-methylene-5-oxopentanal (23): from compound **5b**: 90% yield as a colourless oil. FT-IR (film) 2924, 2859, 1690, 1642, 1428, 1252, 1112, 950, 815, 783, 736, 649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 9.43 (s, 1H), 7.57-7.46 (m, 2H), 7.46-7.29 (m, 3H), 6.13 (s, 1H), 5.91 (s, 1H), 2.75 (t, *J* = 7.0 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 0.49 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 244.2, 194.3, 149.0, 134.8, 133.9, 133.0, 129.9, 128.2, 46.3, 20.8, -4.9 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{14}H_{18}O_2NaSi$ $[M+Na]^+$: 269.0974, found: 269.0977.

2-Methylene-5-oxo-5-(triisopropylsilyl)pentanal (24): from compound **5d**: yield 90% as a colourless oil. FT-IR (film) 2942, 2866, 1692, 1636, 1464, 1251, 881, 828, 674 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 9.44 (s, 1H), 6.22 (s, 1H), 5.93 (s, 1H), 2.68 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.28-1.14 (m, 3H), 1.02 (s, 9H), 0.98 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 245.3, 194.4, 149.4, 134.9, 49.1, 20.6, 18.5, 17.6, 10.7 ppm; HRMS (ESI +ve) Exact mass calculated for $C_{15}H_{28}O_2NaSi$ $[M+Na]^+$: 291.1756, found: 291.1756.

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Keywords: Morita-Baylis-Hillman • Rauhut-Currier • Acylsilanes • Photolysis • Enals

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FULL PAPER

Key Topic: Synthetic Methodology

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α-β Unsaturated Acylsilanes as Surrogates of Acrolein for Morita-Baylis-Hillman Reactions

A short approach toward new acrolein-type derivatives, functionalized in position 2 is described. It involves as the key step, a smooth transformation of acylsilanes into aldehydes by irradiation in water-organic solvent mixtures. The functionalized enals obtained by this new route appear as versatile building blocks for the preparation of natural products and/or bioactive compounds.