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Selective formation of alkenes from trimethylsilylmethyl ketones and from acylsilanes

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Abstract

Trimethylsilylmethyl ketones, readily available from acyl chlorides, undergo a Reformatsky–Peterson reaction sequence to give 3-alkenoates regioselectively. Acylsilanes, however, react with either zinc ester enolates or trimethylsilylmethylmagnesium chloride to give the corresponding tertiary alcohols which, depending on their structure, spontaneously undergo either elimination or a Brook rearrangement–Peterson olefination sequence. These reactions allow the selective formation of vinylsilanes.

Introduction

Part of the importance of organosilicon compounds in organic synthesis stems from the pronounced propensity of the silyl group to migrate to neighbouring oxygen [1]. This property constitutes the driving force for the Peterson elimination [2] as well as for the closely related Brook rearrangement [3]; both are well established and widely used reactions. However, despite considerable advances, compounds containing neighbouring carbonyl and silyl groups have hithero rarely been considered as substrates for such transformations, which allow the formation of C–C bonds by nucleophilic reactions with the carbonyl group, followed by migration of the silyl group in a single step [4]. We describe below some of our studies of this aspect of organosilicon chemistry.

Results and discussion

As a result of our study of the nucleophilic silylation of organic compounds acylsilanes **2** became readily available by reactions of acyl halides with different silyl metallates [5]. This procedure compares favourably with and complements other syntheses of this interesting group of compounds [6]. Similarly trimethylsilylmethyl ketones **4** are formed by cuprous iodide mediated reactions of trimethylsilylmethylmagnesium chloride **3** and acyl chlorides [7,8]. Reinvestigation of this procedure has revealed that the precautions previously taken, such as the choice of particular solvents or reverse addition, were quite unnecessary. Since compounds **4**

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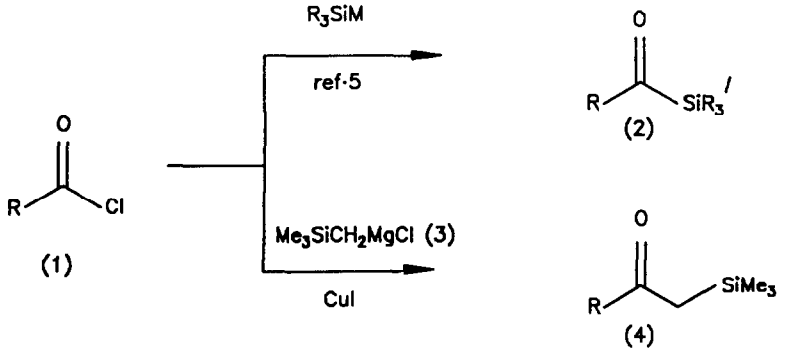


Scheme 1.

do not react with either the manganese diiodide [9] or preferably cuprous iodide mediated reagent **3**, these Grignard reactions can be conducted under conventional conditions to give good yields from sterically crowded, α,β-unsaturated and variously functionalized acyl chlorides, respectively (Table 1).

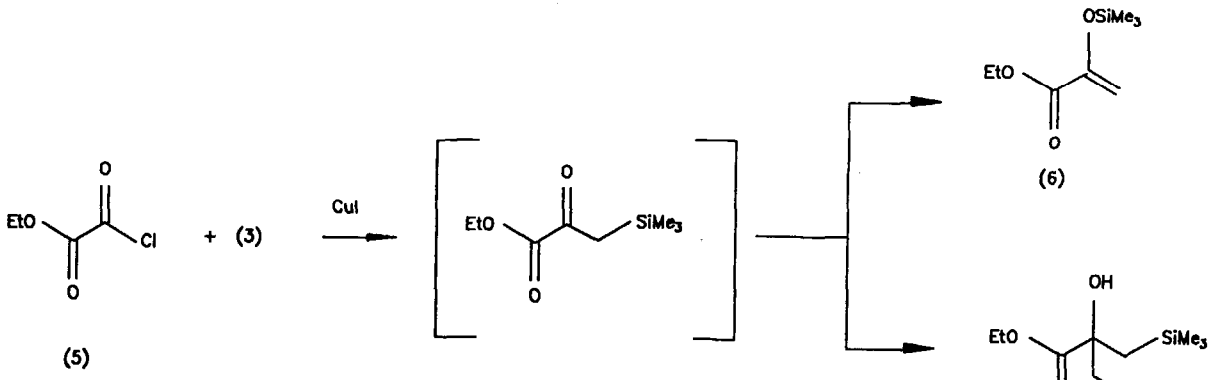
Only ethyloxycarbonyl chloride afforded ethyl trimethylsilyl acetate (**4i**) [10] in somewhat lower yield, and the intermediate product resulting from the reaction of the acyl chloride of monoethyl oxalate (**5**) rearranged partly to give the trimethylsilyl enolether (**6**). The remainder gave 2-hydroxy-2-(trimethylsilylmethyl)-3-trimethylsilyl propanoate (**7**), a valuable precursor of 2-(trimethylsilylmethyl) propenoate [11] (Scheme 2). The results are summarized in Table 1.

For further exploration of the utility of trimethylsilylmethyl ketones and acylsilanes in organic synthesis Reformatsky reactions appeared to be of particular interest because of the substantial advances in this field [12]. Thus, treatment of trimethylsilylmethyl ketones with preformed zinc ethyl acetate enolate in tetrahydrofuran at room temperature afforded the corresponding Reformatsky products (**8**) in fair to good yields (Scheme 3). Traces of boron trifluoride etherate caused immediate elimination, with regioselective formation of ethyl 3-alkenoates (**9**) (cf. Table 2). However, attempts to perform either the Reformatsky reaction [13] or the Reformatsky and elimination reaction in a one-pot procedure led either to desilylation (Scheme 4) (as confirmed by NMR spectroscopy) or gave inferior yields.

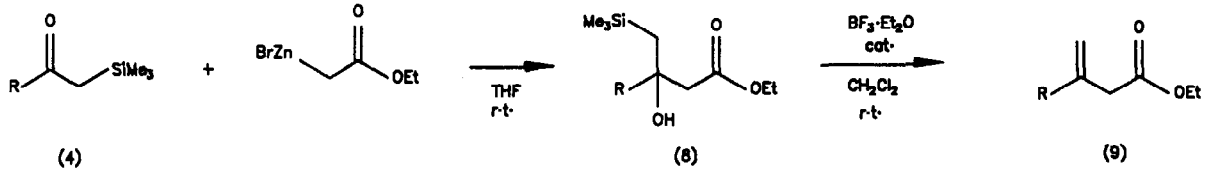
These results are in agreement with recent observations that in the synthesis of allylsilanes from alkanoates and the trimethylsilyl Grignard reagent (**3**) cerium (III) chloride is needed to assist the transformation of the intermediate from silylmethyl ketones into bis(trimethylsilylmethyl)alkyl carbinols [14] (Scheme 5).

The regioselective synthesis of 3-alkenoates by the Reformatsky reaction/Peterson olefination sequence depicted in Scheme 3 complements that of 2-alkenoates from carbonyl compounds by reaction with the zinc enolate of ethyl trimethylsilylacetate described recently [15] (Scheme 6).

Reformatsky reactions of acylsilanes not only require more forcing conditions but also give results that depend on the structure of the substrates (Scheme 7). While compound **2a** cleanly affords the expected aldol **10**, benzoyl methyldiphenylsilane (**2b**) under the same conditions gave ethyl cinnamate **11** by elimination of methyldiphenylsilanolate.



Scheme 2.



Scheme 3.

Table 1

Synthesis of trimethylsilylmethyl ketones **4**

Substrate	R	Product	Yield (%)	B.p. (°C/Torr)	n_{20}^{D}	^{29}Si (δ)
1a	C_6H_{11}	**4a**	70	82– 86/1,5	1.4619	1.92
1b	Ph	**4b**	70	67– 70/0,3	1.5105	1.76
1c	$CH_3(CH_2)_3$	**4c**	90	68– 70/10	1.4338	1.66
1d	$(CH_3)_3C$	**4d**	55	66– 70/15	1.4290	2.29
1e	$PhCH_2$	**4e**	70	90– 94/0.4	1.5028	2.68
1f	$CH_3CH{=}CH$	**4f**	80	103–104/46	1.4515	1.97
1g	$ClCH_2$	**4g**	61	72– 74/14	1.4486	2.86
1h	$EtOOC(CH_2)_3$	**4h**	86	112–114/1.5	1.4429	1.65
1i	EtO	**4i**	60	82– 84/47	1.4153	2.71

Table 2

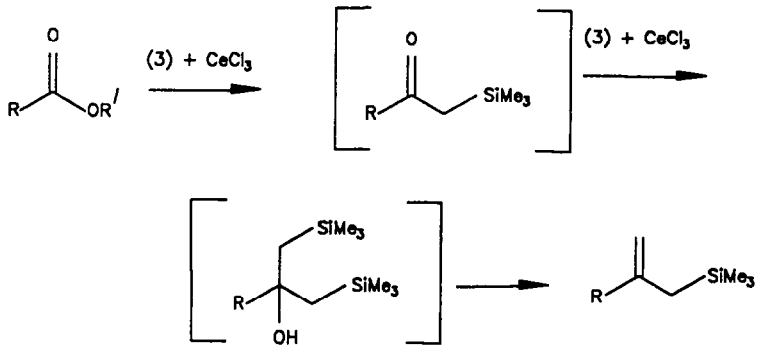
Reformatsky reaction/ Peterson elimination sequences

Substrate	Reaction time (min)	Aldol (Yield %)	Reaction time (min)	Alkene (Yield %)
4a	60	**8a** (70)	5	**9a** (75)
4b	30	**8b** (50)	30	**9b** (95)
4c	90	**8c** (30)	45	**9c** (97)
4e	60	**8e** (60)	30	**9e** (90)
4f	–	– [a]	10	**9f** (50)
2a	120	**10** (77)	–	–
2b	–	–	120	**11** (81)

[a] Spontaneous elimination.

This difference in the behaviour of cycloalkylcarbonylsilanes and aroylsilanes is even more pronounced in the reactions with trimethylsilylmethylmagnesium chloride. Thus, as shown in Scheme 8, the intermediate addition product of the former (**12e**) undergoes a direct Peterson elimination to give the vinylsilane (**13**), while each of the products formed from the latter (**12b–d**) initially undergoes Brook rearrangement [16] immediately followed by migration of the TMS-group and final Peterson elimination. Thus, 1-(trimethylsilyl)vinylbenzene (**14**) is the product invariably formed from compounds **2b–d**. This sequence of two consecutive silanotropic shifts is, to our knowledge, the first example of a structure-dependent competition

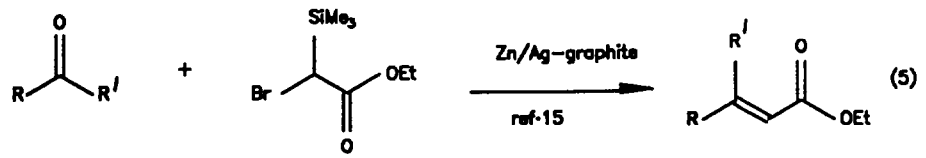
Scheme 4.



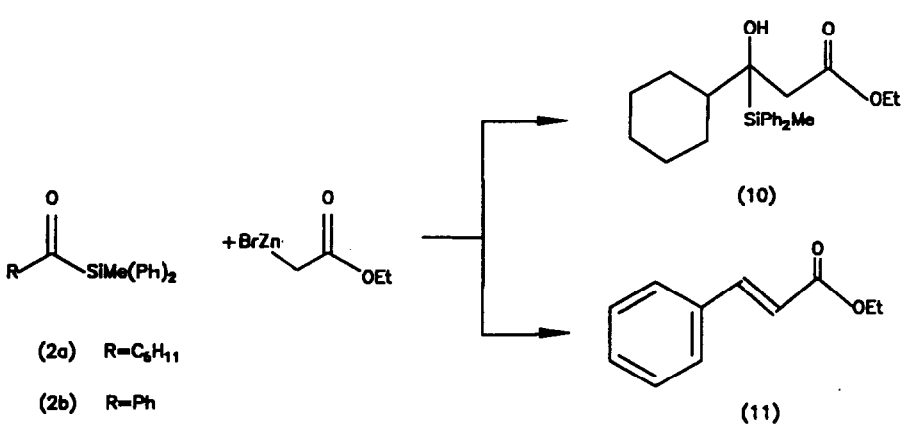
Scheme 5.

between a Brook rearrangement and a Peterson elimination reaction [17*]. The results are summarized in Table 3.

This investigation has shown that reactions of silylcarbonyl compounds with organometallic reagents followed by Peterson elimination are especially satisfactory for the selective synthesis of alkenes.

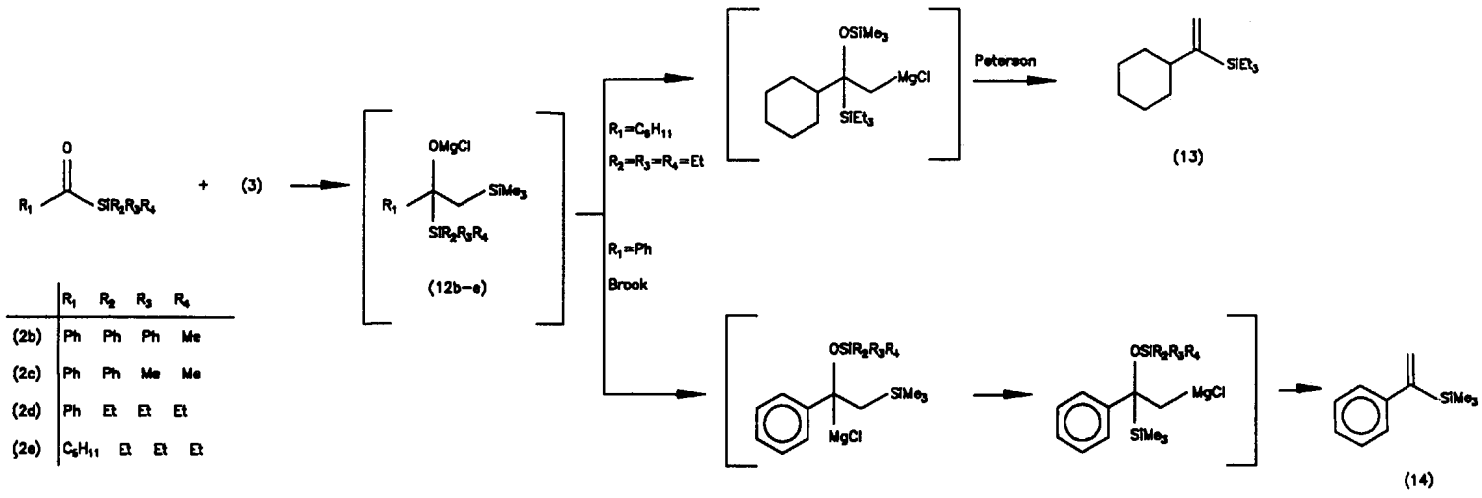


Scheme 6.



Scheme 7.

* Reference number with asterisk indicates a note in the list of references.



	R_1	R_2	R_3	R_4
(2b)	Ph	Ph	Ph	Me
(2c)	Ph	Ph	Me	Me
(2d)	Ph	Et	Et	Et
(2e)	C_6H_{11}	Et	Et	Et

Scheme 8.

Experimental

General

Tetrahydrofuran was dried over sodium/benzophenone and CH_2Cl_2 over CaH_2 prior to use. For TLC precoated silica gel plates (Merck 60 F254) were used and column chromatography was performed on silica gel (Merck 230–400 mesh). ^1H NMR spectra were recorded with a Hitachi Perkin Elmer R24B (60 MHz) or a Bruker MSL 300 (300 MHz) spectrometer. The latter was also used for ^{13}C and ^{29}Si NMR spectroscopy. All spectra were recorded in $CDCl_3$ (Aldrich) unless stated otherwise. IR spectra were taken with films of the respective product on a NaCl plate on a Beckman IR33 instrument.

CuI, $ZnCl_2$, $BF_3 \cdot Et_2O$, and the chlorosilanes were purchased from Fluka AG Switzerland, trimethylsilylmethyl chloride and trimethylsilylmethylmagnesium chloride from Aldrich, and were used without further purification. The acylsilanes **2a–e** were prepared by published procedures [5,18].

*Preparation of trimethylsilylmethyl ketones (**4a–i**). General procedure*

Solutions of 35.6 mmol each of the corresponding acyl chloride (**1a–i**) in tetrahydrofuran (20 ml) were added dropwise to solutions of 40 mmol each of trimethylsilylmethylmagnesium chloride and cuprous iodide in tetrahydrofuran (35 ml) at $-40\,^\circ C$ under nitrogen. After 90 min stirring at this temperature water (50 ml) was added, the mixture filtered, and the filtrate extracted several times with diethyl ether. The extract was dried and evaporated and the residue distilled under reduced pressure. Yields of the products and physical data are given in Table 1.

*Ethyl 3-enoates from trimethylsilylmethyl ketones (**4a–i**). General procedure*

Ethyl bromoacetate (25 mmol) in tetrahydrofuran (10 ml) was added dropwise during 15 min to a refluxing suspension of zinc powder and a few crystals of iodine in tetrahydrofuran (20 ml). The mixture was heated for a further 15 min under nitrogen and then allowed to cool to ambient temperature. A solution of trimethylsilylmethyl ketone (10 mmol) in tetrahydrofuran (10 ml) was added dropwise during 15 min, and the mixture stirred until the reaction was complete (cf. Table 2). Water (50 ml) was then added and the mixture filtered through a pad of charcoal. The charcoal was washed with diethyl ether and the filtrate extracted several times with diethyl ether. The combined organic layers were dried, and the resulting Reformatsky products (**8a–e**) subjected to column chromatography.

Table 3

Synthesis of vinylsilanes **13** and **14**

Substrate	Product	Reaction time (h)	Yield (%)	^{29}Si (δ)
2b	**14**	0.5	70	−4.20
2c	**14**	0.5	40	−4.20
2d	**14**	2	50	−4.20
2e	**13**	6	30	−12.80

For their transformation into ethyl 3-enoates solutions of each of the compounds **8a–e** in dichloromethane (10 ml) were treated with 0.5 ml of a solution of boron trifluoride etherate (1% v/v) in dichloromethane (5 ml). After completion of the Peterson elimination, the solution) was extracted with water (10 ml) and the aqueous phase then extracted with dichloromethane. The combined organic solutions were dried and evaporated and the residues chromatographically purified. Reaction times and yields for the Reformatsky and the Peterson reactions are given in Table 2.

Reformatsky reaction of acylsilanes

Zinc/silver graphite, prepared as described [13] from potassium-graphite laminate (15.5 mmol), zinc chloride (7.4 mmol) and silver acetate (0.6 mmol) in tetrahydrofuran (25 ml), was stirred at −40 °C for 30 min under argon with ethyl bromoacetate (7.4 mmol) in tetrahydrofuran (15 ml). The acylsilane (**2a–b**) (7.4 mmol each) in tetrahydrofuran (15 ml) was added and the mixture stirred for 2 h at ambient temperature under argon. After filtration and evaporation of the filtrate the residue was purified by column chromatography. Thus, ethylcinnamate (**11**) was obtained from **2b** and product **10** from **2a**.

Selective formation of vinylsilanes from acylsilanes. General procedure

Trimethylsilylmethylmagnesium chloride (10 ml, 1 *M* in diethylether) was added in one portion to a solution of the acylsilane (5 mmol) in tetrahydrofuran (20 ml) at ambient temperature with stirring under nitrogen. After completion of the reaction, water (30 ml) was added, the layers separated, the aqueous phase extracted repeatedly with diethyl ether, and the combined ethereal solutions dried. The residue obtained after evaporation of the solvent was subjected to column chromatography. The yields, reaction times, and ^{29}Si-NMR data of products **13** and **14** are given in Table 3.

*Cyclohexyl(trimethylsilylmethyl) ketone (**4a**).* ^{1}H NMR (60 MHz): δ −0.1 (s, 9H, $SiMe_3$); 0.9–2.1 (m, 11H, cyclohexyl); 2.2 (s, 2H, CH_2SiMe_3). ^{13}C NMR: δ −0.74 ($SiMe_3$); 25.98; 26.09; 28.78 (cyclohexyl); 36.25 (CH_2SiMe_3); 52.20 (*C*HCO); 212.79 (CO).

*Phenyl(trimethylsilylmethyl)ketone (**4b**).* ^{1}H NMR (60 MHz): δ 0.0 (s, 9H, $SiMe_3$); 2.35 (s, 2H, CH_2SiMe_3); 7.0–8.0 (m, 5H, Ph). ^{13}C NMR: δ −0.9 ($SiMe_3$); 33.10 (CH_2SiMe_3); 127.84; 128.16; 128.48; 128.70; 132.46 (Ph); 197.96 (CO).

*1-Trimethylsilyl-2-hexanone (**4c**).* ^{1}H NMR: δ −0.06 (s, 9H, $SiMe_3$); 0.73 (t, 3H, CH_3); 1.13 (tq. 2H, $CH_3CH_2CH_2$); 1.38 (tt, 2H, $CH_2CH_2CH_2CO$); 2.04 (s, 2H, CH_2SiMe_3); 2.17 (t, 2H, CH_2CO). ^{13}C NMR: δ −1.15 ($SiMe_3$); 13.79 (CH_3); 22.37; 26.15 (CH_2CH_2); 37.90 (CH_2SiMe_3); 44.08 (CH_2CO); 208.96 (CO).

*3,3-Dimethyl-1-trimethylsilyl-2-butanone (**4d**).* ^{1}H NMR: δ −0.02; 0.05 (s, 9H, $SiMe_3$, rotamers); 1.05; 1.08 (s, 9H, $(CH_3)_3$, rotamers); 2.07; 2.14 (s, 2H, $COCH_2SiMe_3$, rotamers). ^{13}C NMR: δ −0.31; 2.03 ($SiMe_3$, rotamers); 26.52; 26.75 (CH_3, rotamers); 30.42 (CH_2SiMe_3); 44.41; 44.64 ($(CH_3)_3C$–, rotamers).

*3-Phenyl-1-trimethylsilyl-propanone (**4e**).* ^{1}H NMR (60 MHz): δ 0.0 (s, 9H, $SiMe_3$); 2.2 (s, 2H, CH_2SiMe_3); 3.6 (s, 2H, $PhCH_2$); 7.2 (bs, 5H, Ph). ^{13}C NMR: δ −0.80 ($SiMe_3$); 37.39 (CH_2SiMe_3); 51.81 ($PhCH_2$); 124.87; 127.24; 128.02; 128.75; 129.81; 134.83 (Ph); 206.67 (CO).

*1-Trimethylsilyl-3-penten-2-one (**4f**).* ^{1}H NMR: δ 0.01 (s, 9H, $SiMe_3$); 1.78 (dd,

3H, CH_3CH_2=, $^4J(CH_3,CHCO) = 1.6$); 2.21 (s, 2H, CH_2SiMe_3); 5.97 (dd, 1H, CHCO, $^4J(=CH,CH_3) = 1.6$); 6.64 (dq, 1H, CH_3CH=CH, $J(CH$=$CH) = 15.5$, $J(CH$=,$CH_3) = 6.7$). ^{13}C NMR: δ −1.06 ($SiMe_3$); 17.92 (CH_3); 35.57 (CH_2SiMe_3); 133.18 (CHCO); 141.35 (CH=CHCO), 198.72 (CO).

*1-Chloro-3-trimethylsilyl-propanone (**4g**).* ^{1}H NMR (60 MHz): δ 0.1 (s, 9H, $SiMe_3$); 2.3 (s, 2H, CH_2SiMe_3); 3.9 (s, 2H, $ClCH_2$). ^{13}C NMR: δ −1.12 ($SiMe_3$); 34.75 (CH_2SiMe_3); 49.06 ($ClCH_2$); 200.71 (CO).

*Ethyl 5-oxo-6-trimethylsilyl-hexanoate (**4h**).* ^{1}H NMR: δ −0.07 (s, 9H, $SiMe_3$); 1.06 (t, 3H, CH_3CH_2O); 1.69 (tt, 2H, $CH_2CH_2CH_2$); 2.03 (s, 2H, CH_2SiMe_3); 2.15 (t, 2H, $EtOOCCH_2$); 2.25 (t, 2H, CH_2COCH_2); 3.93 (q, 2H, CH_3CH_2O). ^{13}C NMR: −1.09 ($SiMe_3$); 14.25 (CH_3CH_2O); 19.22 ($CH_2CH_2CH_2$); 33.45 ($EtOOCCH_2$); 38.05 (CH_2SiMe_3); 43.19 (CH_2COCH_2); 60.20 (CH_3CH_2COO); 173.11 (EtOOC); 209.19 ($COCH_2SiMe_3$).

*Ethyl trimethylsilylacetate (**4i**).* ^{1}H NMR: δ 0.11 (s, 9H, $SiMe_3$); 1.09 (t, 3H, CH_3CH_2O); 1.67 (s, 2H, CH_2SiMe_3); 4.02 (q, 2H, CH_2O). ^{13}C NMR: δ −1.53 ($SiMe_3$); 14.40 (CH_3CH_2); 26.82 ($EtOOCCH_2$); 59.65 (CH_3CH_2O); 172.72 (EtOOC).

*Ethyl 3-cyclohexyl-3-hydroxy-4-trimethylsilyl butanoate (**8a**).* ^{1}H NMR: δ 0.10 (s, 9H, $SiMe_3$); 0.88–1.82 (m, 13H, cyclohexyl, CH_2SiMe_3); 1.31 (t, 3H, CH_3CH_2O); 2.69; 2.83 (AB-System, 2H, CH_2COOEt, $J_{AB} = 16$); 3.50 (s, 1H, OH); 4.23 (q, 2H, CH_2O). ^{13}C NMR: δ 0.85 ($SiMe_3$); 14.34 (CH_3CH_2O); 26.75; 26.84; 26.90; 27.04; 27.67; 28.00; 28.20 (cyclohexyl, CH_2SiMe_3); 48.25 (CH_2COOEt); 61.67 (CH_2O); 77.07 (COH); 167.10 (COOEt).

*Ethyl 3-hydroxy-3-phenyl-4-trimethylsilyl butanoate (**8b**).* ^{1}H NMR: δ −0.20 ($SiMe_3$); 1.13 (t, 3H, CH_3CH_2O); 1.19; 1.22 (AB-system, 2H, CH_2SiMe_3, $J_{AB} = 9$); 2.78; 2.95 (AB-system, 2H, CH_2COOEt, $J_{AB} = 15$); 3.22 (s, 1H, OH); 4.04 (q, 2H, CH_2O); 7.15–7.48 (m, 5H, Ph). ^{13}C NMR: δ −0.05 ($SiMe_3$); 14.05 (CH_3CH_2O); 30.64 (CH_2SiMe_3); 46.71 (CH_2COOEt); 60.71 (CH_2O); 72.83 (COH); 124.84; 126.90; 128.00; 128.28 (Ph); 172.62 (COOEt).

*Ethyl 3-hydroxy-3-(trimethylsilylmethyl)heptanoate (**8c**).* ^{1}H NMR: δ 0.06 (s, 9H, $SiMe_3$); 0.90 (t, 3H, CH_3); 1.02 (s, 2H, CH_2SiMe_3); 1.27 (t, 3H, CH_3CH_2O); 1.24–1.33 (m, 4H, $CH_3CH_2CH_2CH_2$); 1.51 (t, 2H, CH_2COH); 2.47; 2.50 (AB-system, 2H, CH_2COOEt, $J_{AB} = 12$); 3.58 (bs, 1H, OH); 4.16 (q, 2H, CH_2O). ^{13}C NMR: δ 0.65 ($SiMe_3$); 14.25; 14.45 (CH_3); 23.37; 26.73; 29.87 ($CH_3CH_2CH_2CH_2$, CH_2SiMe_3); 42.49 (CH_2COH); 45.99 (CH_2COOEt); 60.69 (CH_2O); 73.92 (COH); 173.48 (COOEt).

*Ethyl 3-hydroxy-4-phenyl-3-(trimethylsilylmethyl)butanoate (**8e**).* ^{1}H NMR: δ 0.18 (s, 9H, $SiMe_3$); 1.09; 1.14 (AB-system, 2H, CH_2SiMe_3, $J_{AB} = 15$); 1.29 (t, 3H, CH_3CH_2O); 2.49 (s, 2H, CH_2COOEt); 2.86; 3.02 (AB-system, 2H, CH_2Ph, $J_{AB} = 13.5$); 3.77 (bs, 1H, OH); 4.17 (q, 2H, CH_2O); 7.23–7.36 (m, 5H, Ph). ^{13}C NMR: δ 0.73 ($SiMe_3$); 14.25 (CH_3CH_2O-); 30.36 (-CH_2SiMe_3); 45.01 (CH_2COOEt); 48.92 (-CH_2Ph); 60.49 (-CH_2O-); 73.83 (-COH-); 126.55; 128.14; 130.82; 137.75 (Ph-); 173.05 (COOEt).

*Ethyl 3-cyclohexyl-3-butenoate (**9a**).* ^{1}H NMR: δ 1.10–1.86 (m, 11H, cyclohexyl); 1.27 (t, 3H, OCH_2CH_3); 3.48 (s, 2H, CH_2COOEt); 4.18 (q, 2H, OCH_2); 4.85; 5.00 (s, 1H each, $=CH_aH_b$). ^{13}C NMR: δ 14.27 (OCH_2CH_3); 26.41; 26.52; 29.66; 32.24; 32.47 (cyclohexyl); 44.38 (CH_2COOEt); 61.44 (OCH_2); 113.45 (C=CH_2); 147.80 (C=CH_2); 167.36 (COOEt).

*Ethyl 3-phenyl-3-butenoate (**9b**).* ^{1}H NMR: δ 1.21 (t, 3H, CH_3); 3.42 (s, 2H, CH_2COOEt); 4.13 (q, 2H, OCH_2); 5.22; 5.50 (s, 1H each, $=CH_aH_b$); 7.22–7.52 (m, 5H, Ph). ^{13}C NMR: δ 14.04 (CH_2CH_3); 48.03 (CH_2COOEt); 61.27 (OCH_2); 117.19 ($C=CH_2$); 125.84; 126.35; 127.80; 128.41; 128.55 (Ph); 140.81 ($C=CH_2$); 167.05 (COOEt).

*Ethyl 3-n-butyl-3-butenoate (**9c**).* ^{1}H NMR: δ 0.87 (t, 3H, $CH_3CH_2CH_2$); 1.23 (t, 3H, OCH_2CH_3); 1.20–1.47 (m, 4H, $CH_3CH_2CH_2$); 2.07 (t, 2H, $CH_3CH_2CH_2CH_2$); 2.99 (s, 2H, CH_2COOEt); 4.12 (q, 2H, OCH_2); 4.85; 4.88 (s, 1H each, $=CH_aH_b$). ^{13}C NMR: δ 14.01; 14.34 (CH_3); 22.48; 30.53; 35.87 (CH_2); 42.24 (CH_2COOEt); 60.64 (OCH_2); 113.38 ($C=CH_2$); 142.95 ($C=CH_2$); 171.66 (COOEt).

*Ethyl 3-(phenylmethyl)-3-butenoate (**9e**).* ^{1}H NMR: δ 1.28 (t, 3H, OCH_2CH_3); 3.19 (1H); 3.39 (2H); 3.40 (1H) (CH_2COOEt, PhCH_2); 4.19 (q, 2H, OCH_2); 4.98; 5.03 (d, 1H each, $=CH_aH_b$, $J(H_a,H_b) < 1$); 7.17–7.53 (m, 5H, Ph). ^{13}C NMR: δ 14.30 (OCH_2CH_3); 43.10 (CH_2COOEt); 48.65 (PhCH_2); 61.53 (OCH_2); 116.75 ($CH=CH_2$); 126.72; 128.32; 129.41; 129.76 (Ph); 142.37 ($CH=CH_2$); 167.22 (COOEt).

*Ethyl 3-methylene-4(E)-hexenoate (**9f**).* ^{1}H NMR: δ 1.20 (t, 3H, OCH_2CH_3); 1.71 (d, 3H, $CH_3CH=$, $J = 6.7$); 3.15 (s, 2H, CH_2COOEt); 4.09 (q, 2H, OCH_2); 4.94; 5.02 (s, 1H each, $C=CH_aH_b$); 5.66 (dq, 1H, $CH_3CH=CH$, $J(CH_3CH=CH, CH_3CH=CH) = 15.8$); 6.08 (d, 1H, $CH_3CH=CH$). ^{13}C NMR: 14.32 (OCH_2CH_3); 16.09 ($CH_3CH=$); 38.88 (CH_2COOEt); 60.54 (OCH_2); 116.64 ($C=CH_2$); 126.03; 132.58 ($CH_3CH=CH$); 139.28 ($C=CH_2$); 171.26 (COOEt).

*Ethyl 3-cyclohexyl-3-hydroxy-3-(diphenylmethylsilyl)propanoate (**10**).* ^{1}H NMR: δ 0.77 (s, 3H, SiMe); 0.90–1.90 (m, 11H, cyclohexyl); 2.69; 2.71 (AB-system, 2H, CH_2COOEt, $J_{AB} = 10$); 3.90 (q, 2H, OCH_2); 3.96 (bs, 1H, OH); 7.35–7.81 (m, 10H, Ph). ^{13}C NMR: δ −3.89 (SiMe); 14.20 (CH_2CH_3); 26.84; 27.18; 27.85; 29.67; 38.96 (cyclohexyl); 47.75 (CH_2COOEt); 60.75 (OCH_2); 71.64 (COH); 127.87; 127.99; 129.38; 129.47; 135.62; 135.85; 136.12; 136.22 (Ph); 173.97 (COOEt).

*1-Cyclohexyl-1-triethylsilylethene (**13**).* ^{1}H NMR: δ 0.65 (q, 6H, $SiCH_2$); 0.95 (t, 9H, $SiCH_2CH_3$); 1.20–2.05 (m, 11H, cyclohexyl); 5.32; 5.68 (d, 1H each, $C=CH_aH_b$, $J(H_a,H_b) = 2.4$). ^{13}C NMR: δ 3.43 ($SiCH_2$); 7.64 ($SiCH_2CH_3$); 26.37; 26.94; 27.17; 27.58; 32.99; 33.80 (cyclohexyl); 123.66 ($C=CH_2$); 142.87 ($C=CH_2$).

*1-Phenyl-1-trimethylsilylethene (**14**).* ^{1}H NMR: δ 0.37 (s, 9H, $SiMe_3$); 5.80; 6.02 (d, 1H each, $C=CH_aH_b$, $J = 3.0$); 7.36–7.50 (m, 5H, Ph). ^{13}C NMR: δ −0.62 ($SiMe_3$); 126.50; 127.00; 127.36; 128.39; 128.51; 129.32 (Ph, $C=CH_2$).

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