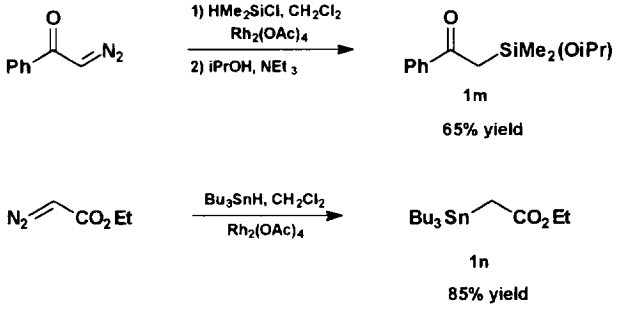
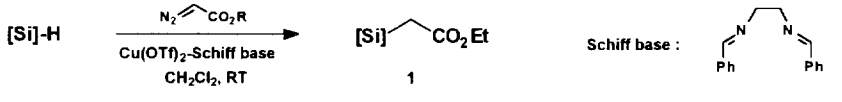
The nucleophilic displacement of the chlorine atom by an alcohol was predictably, more affected than the insertion by steric hindrance around silicon. Thus, with di-*i*-propyl and di-*t*-butylsilylacetic esters, more drastic conditions were required to carry out the alkoxy substitution (entries 11 and 12). The conditions described for the protection of primary alcohols with the bulky *t*-$Bu_2PhSiCl$ were found to be suitable for our purposes (Conditions B).[13] The extension of our method to α-diazoketones was also successful (Scheme 4), but led to lower yields of the insertion products, probably due to Brook Rearrangement[2] occuring during the purification step. Finally, it appeared that the insertion of a carbenoid species into the Si-H bond could also be applied to the Sn-H bond as illustrated by the smooth reaction between Bu_3SnH and N_2CHCO_2Et in the presence of $Rh_2(OAc)_4$ (Scheme 4). We thus have an easy access to a large variety of α-(alkoxysilyl)acetic esters as demonstrated by the examples summarized in Table 1. Interestingly, α-(allyloxysilyl)acetic esters **1h-j** should also be useful intermediates as they can be functionalized further.[14]



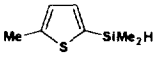
Scheme 4

As rhodium catalysts are generally expensive, we thought it would be particularly convenient to use instead, readily available and cheaper copper salts such as $Cu(acac)_2$ or CuCl. Doyle made use of $Cu(acac)_2$ as a catalyst for the Si-H insertion with Ph_3SiH.[11] He found that the reaction occured in CH_2Cl_2 under reflux and gave the α-silyl esters with yields comparable to those obtained with $Rh_2(OAc)_4$. Attempts to reproduce these results with HMe_2SiCl unfortunately failed. Recent reports on cyclopropanation of olefins by N_2CHCO_2Et catalyzed by Cu(II)-C2-symmetrical diamino ligands retained our attention due to the high efficiency of these catalytic systems in term of yields and stereoselectivities.[15] We thus carried out our insertion reactions as before, but in the presence of a copper catalyst prepared *in situ* from $Cu(OTf)_2$ and an easily available Schiff-base[16] (Scheme 5). We were pleased to find that the expected α-silylacetic ester **1a** was obtained in a yield comparable to the one reported for $Rh_2(OAc)_4$ (compare entry 1 in Table 1 and 2). Extension of the method to various silanes ([Si]) finally demonstrated the higher catalytic activity of this copper catalyst compared to $Cu(acac)_2$ (reaction at RT instead of 40°C) and a similar activity to that of $Rh_2(OAc)_4$ (Table 2).[12c]



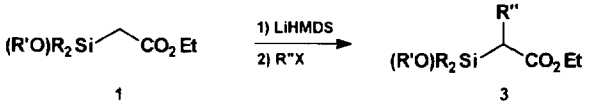
Scheme 5

Table 2. Synthesis of α-silylacetic esters catalysed by a copper-Schiff base complex (Scheme 5).

Entry	[Si]-H	Product[a]	Yield (%)[c]
1	Me_2SiClH	1a[b]	74
2	Et_3SiH	1o	92
3	$PhMe_2SiH$	1p	76
4	Ph_3SiH	1q	70
5	 2	1r	85

[a] Conditions: Chlorosilane (1.1 eq.), $Cu(OTf)_2$ (0.09 eq.), Schiff-base (0.1 eq.), N_2CHCO_2Et (1 eq.) in anhydrous CH_2Cl_2. [b] Same conditions as those described in Table 1 except for the catalyst.
[c] Isolated yields after filtration through Florisil® or distillation.

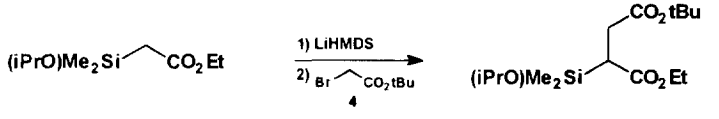
The α-silylacetic esters **1** were then alkylated and allylated via their enolates prepared with LiHMDS in THF (Scheme 6, Table 3). Different attempts to form the enolate using LDA instead of LiHMDS gave complex mixtures. This is presumably due to the presence of diisopropylamine (formed during deprotonation), which is a stronger nucleophile than hexamethyldisilazane and might displace alkoxy groups on silicon. Surprisingly, the formation of the enolate with LiHMDS in ether instead of THF did not occur, showing that alkoxy groups might co-ordinate lithium ions of the amide base, and thus prevent the deprotonation.[17] As already observed for the nucleophilic displacement of chlorine, steric hindrance around silicon retards the formation of the enolate (entry 6, Table 3) and therefore higher temperatures and longer reaction time are required for the deprotonation to occur. The enolates were then trapped with allylic bromides and alkyl iodides to give the desired α-substituted-α-silylesters **3** in good yields after filtration through Florisil® or distillation (Scheme 6). We also noticed that the α-silylacetic esters were relatively prone to dialkylation. Therefore, use of strictly 1.05 equivalents of LiHMDS is generally necessary to avoid dialkylation.



1 3

Scheme 6

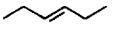
Finally, extension of the sequence to α-halocarbonyl compounds gave Peterson elimination products,[14,18] except for the *t*-butyl α-bromoester **4** which is bulky enough to avoid addition onto the carbonyl group and gives the alkylation product **5** in good yield (Scheme 7).



1a 5 (98% yield)

Scheme 7

Table 3. **Alkylation of α-silylacetic esters 1 (Scheme 6).**

Entry	R	R'	R''	Product	Yield (%)[a]
1	Me	i-Pr	allyl	**3a**	**83**
2	Me	i-Pr	Et	**3b**	**76**
3	Me	i-Pr	Me	**3c**	**79**
4	Me	Et	Me	**3d**	**78**
5	Me	Et	Et	**3e**	**81**
6	i-Pr	Et	Me	**3f**	**71**[b]
7	Me	t-Bu	Me	**3g**	**78**
8	Me	t-Bu	Et	**3h**	**85**
9	Me	t-Bu	allyl	**3i**	**81**
10	Ph	Et	Me	**3j**	**78**
11	Me	t-Bu		**3k**	**88**
12	Me	allyl	geranyl	**3l**	**86**
13	Me	i-Pr	geranyl	**3m**	**77**
14	Me	allyl		**3n**	**83**

Conditions : LiHMDS (1.05 eq.), -60°C, 1h, then R''X (1.2 eq.), -10°C, 2h; [a] Isolated yields after filtration through Florisil® or distillation. [b] The enolate was stirred for 3h at -50°C before addition of MeI.

Direct oxidation of the C-Si bond of α-substituted-α-silylacetic esters **3** was, as expected, unsuccessful due to the easy nucleophilic displacement of the silicon moiety by fluorine ion and formation of the corresponding enolate.[1a,19] Therefore the reduction of the ester function prior to the oxidation of the C-Si bond had to be carried out in order to prevent the competitive desilylation (Scheme 8). However, a competition between the reduction of the carbonyl group and the cleavage of the Si-O bond might also occur and lead to complex mixtures.[20] Fortunately, it was found that $LiAlH_4$ (0.6 eq.) in ether reduced chemoselectively the ester function at 0°C (entry 1 and 2, Table 4) (Fig. 2), higher temperature and an excess of hydride being necessary to reduce both functionalities (entry 3). Again, we noticed a strong influence from the steric hindrance around silicon during the reduction process. Use of a primary alkoxy group on silicon always led to reduction of the ester function accompanied by cleavage of the Si-O bond, whatever the conditions (entry 4 and 5). The isopropyloxy group on silicon was found to be the most convenient and thus reduction of **3a** gave the β-hydroxy-α-(isopropyloxydimethylsilyl) ester **6a** as the sole product in 95% yield (entry 1). The alcohols were generally pure enough after the workup to be used in the oxidation step without purifications.

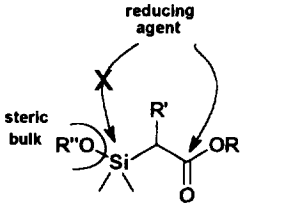
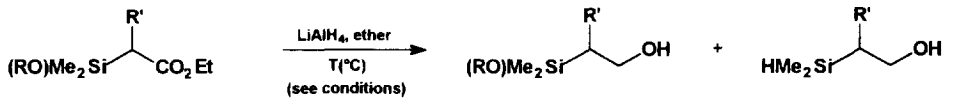


Fig. 2



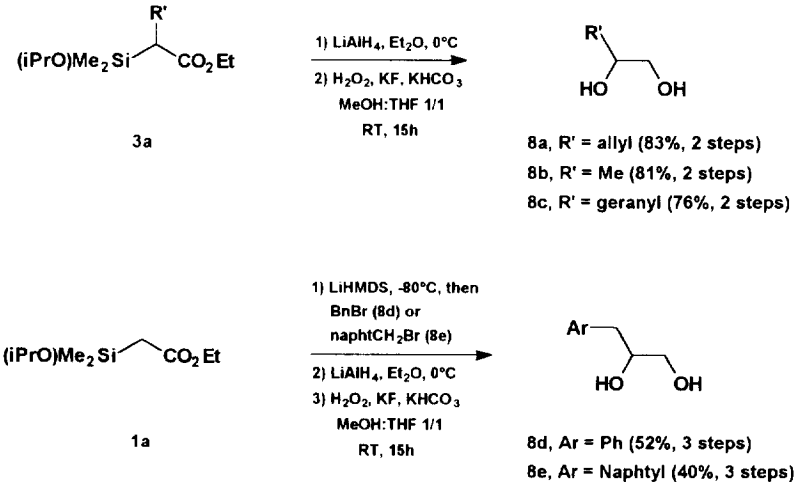
3 6 7

Scheme 8

Table 4. Chemoselective reduction of α-(alkoxysilyl)acetic esters 3 (Scheme 8).

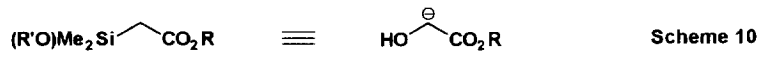
Entry	Substrate	R	R'	Conditions	Ratio (6 : 7)	Yield (%)
1	**3a**	i-Pr	allyl	$LiAlH_4$ (0.6 eq.), ether, 0°C	**100 : 0**	**95**
2	**3i**	t-Bu	allyl	$LiAlH_4$ (0.6 eq.), ether, 0°C	**100 : 0**	**92**
3	**3a**	i-Pr	allyl	$LiAlH_4$ (2 eq.), ether, reflux	**0 : 100**	**85**
4	**3l**	allyl	geranyl	$LiAlH_4$ (0.6 eq.), ether, 0°C	**0 : 50 (50% 3l)**	**96**
5	**3l**	allyl	geranyl	$LiAlH_4$ (2 eq.), ether, 0°C	**0 : 100**	**92**

Oxidation of the β-hydroxysilanes using Tamao conditions[4a] (H_2O_2, KF, $KHCO_3$, THF-MeOH 1:1, RT), afforded the 1,2-diols in good yields (Scheme 9). These mild conditions do not affect homoallylic double bonds (i.e. **8a**) neither do they alter polyenic systems (i.e. **8c**). The isopropyloxy group was again found to be the substituent of choice, allowing a smooth oxidation at room temperature. In contrast, the tertiobutyloxysilyl group was not oxidized using these conditions, probably for steric reasons. Similar observations have been reported by Tamao and co-workers who used H_2O_2 and acidic conditions or *m*-CPBA to carry out the C-Si oxidation with the *t*-$BuOMe_2Si$ group.[4b] Unfortunately, in our hands, these procedures led to extensive decomposition of the starting material, probably due to Peterson elimination.[18] Therefore, the isopropyloxy group is the best candidate for our methodology, since it provides a good balance, possessing enough steric hindrance to prevent attack even by small nucleophiles and, enough reactivity for the Tamao oxidation.



Scheme 9

In summary, we have reported a useful entry to new α-(alkoxy)silylacetic esters in one step from commercially available compounds, and a possible application of these synthons in organic synthesis. Hence, alkylation, followed by reduction of the ester function and Tamao oxidation gives an efficient access to 1,2-diols such as the useful homoallylic 1,2-diols,[21] and it is noteworthy that these last three steps can be carried out on a large scale without purification at any stage. The preparation of a new and cheap copper (II) catalyst will also allow for an application of our method to larger scale. These synthons can thus be regarded as α-hydroxyester carbanion equivalents (Scheme 10). This methodology is an alternative to the one reported previously by Tamao and co-workers[22] and should prove very useful if the required aldehyde in the Tamao procedure is not available.



Scheme 10

EXPERIMENTAL SECTION

^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER 250FT (250 MHz) and BRUKER WH-360FT (360 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer. All commercial products were used without further purifications.

CH_2Cl_2, hexamethyldisilazane and triethylamine were distilled from CaH_2. THF was distilled from sodium and benzophenone. Chlorosilanes were distilled from magnesium before use.

Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (Germany). Mass spectra were recorded on a Nermag R10-10C (Chemical ionization mode, NH_3).

General procedure for the preparation of α-(alkoxysilyl)acetic esters 1. Procedure A. A solution of ethyl diazoacetate (0.9 ml, 8.7 mmol) in CH_2Cl_2 (2 ml) was added slowly at RT, using a syringe pump (2 mmol/h), to a solution of dimethylchlorosilane (1 ml, 9.2 mmol) and $Rh_2(OAc)_4$ (14mg, 0.03 mmol) in dry CH_2Cl_2 (3 ml). The mixture was cooled to 0°C and a solution of triethylamine (1.55 ml, 11 mmol) in CH_2Cl_2 (1 ml) was added, followed by isopropanol (0.85 ml, 11 mmol) in CH_2Cl_2 (1 ml). The suspension was stirred for 3 hours then treated at 0°C with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give a brown oil which was purified by filtration over Florisil® (Petroleum ether/ethyl acetate/NEt_3 98.5/1/0.5) to afford the ester **1a** as a colourless oil (1.32 g, 74%): **^1H NMR** (δ ppm): 4.1 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.05 (1H, sept, J 6.0, $CH_3C\underline{H}CH_3$), 2.0 (2H, s, $SiCH_2$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.16 (6H, d, J 6.0, $C\underline{H}_3CHC\underline{H}_3$), 0.22 (6H, s, $Si(CH_3)_2$). **IR** (CH_2Cl_2) (υ_{max}): 2930 (C-H), 1705 (C=O), 1380, 1365, 1170, 1100, 1030 (Si-O), 950 cm^{-1}. **MS** (CI, NH_3): 205 (M^++1, 10), 161 (M^+ -*i*-Pr, 7), 145 (M^+ -*i*-PrO, 9), 86 (37), 85 (50), 83 (39), 81 (32), 71 (100). **Anal.** Calcd for $C_9H_{20}O_3Si$: C, 52.90; H, 9.86; Si, 13.74. Found : C, 52.89; H, 9.69; Si, 13.66.

1b. ^1H NMR (δ ppm): 7.38-7.24 (5H, m, Aromatic H), 4.77 (2H, s, $PhC\underline{H}_2O$), 4.11 (2H, q, J 7.2, $CO_2C\underline{H}_2CH_3$), 2.06 (2H, s, $SiCH_2$), 1.24 (3H, t, J 7.2, $CO_2CH_2C\underline{H}_3$), 0.27 (6H, s, $Si(CH_3)_2$). **IR** (CH_2Cl_2) (υ_{max}): 2980 (C-H), 1710 (C=O), 1600 (C=C), 1380, 1365, 1100 (Si-O) cm^{-1}. **MS** (CI, NH_3): 253 (M^++1, 74), 207 (M^+-OC_2H_5, 8), 178 (16), 145 (M^+ - $PhCH_2O$, 8), 108 ($PhCH_2OH$, 8), 91 ($C_7H_7^+$, 100), 75 ($Si(CH_3)OH^+$, 15). **Anal.** Calcd for $C_{13}H_{20}O_3Si$: C, 61.87; H, 7.99; Si, 11.13. Found : C, 61.89; H, 7.88; Si, 11.24.

1c. ^1H NMR (δ ppm): 4.11 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.72 (2H, q, J 7.0, $SiOC\underline{H}_2CH_3$), 2.01 (2H, s, $SiCH_2$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.20 (3H, t, J 7.0, $SiOCH_2C\underline{H}_3$), 0.23 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2980 (C-H), 2920, 1710 (C=O), 1360, 1100, 1050, 1030 (Si-O), 830 cm^{-1}. **MS** (CI, NH_3): 192 (M^++2, 22), 191 (M^++1, 100), 103 (M^+-$CH_2CO_2C_2H_5$, 20), 86 ($CHCO_2C_2H_5^+$, 10), 74 ($Si(CH_3)_2O^+$, 97), 71 (21). **Anal.** Calcd for $C_8H_{18}O_3Si$: C, 50.49; H, 9.53; Si, 14.76. Found : C, 50.31; H, 9.64; Si, 14.68.

1d. ^1H NMR (δ ppm): 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 1.98 (2H, s, $SiCH_2$), 1.26 (9H, s, *t*-Bu), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.23 (6H, s, $Si(CH_3)_2$). **IR** (CH_2Cl_2) (υ_{max}): 2900 (C-H), 1710 (C=O), 1600, 1360, 1100, 1050, 1020 (Si-O), 830 cm^{-1}. **MS** (CI, NH_3): 219 (M^++1, 100), 203 (M^+-CH_3, 13), 161 (M^+-*t*-Bu, 10), 145 (M^+-$CO_2C_2H_5$ or *t*-BuO, 18), 117 (28), 105 (19), 103 (21), 92 (44), 75 ($Si(CH_3)_2OH^+$, 67). **Anal.** Calcd for $C_{10}H_{22}O_3Si$: C, 55.00; H,10.15; Si,12.86. Found : C, 54.80; H, 10.12; Si, 12.80.

1e. ^1H NMR (δ ppm): 6.0-5.85 (1H, m, CH_2=C$\underline{H}$), 5.30-5.22 (1H, m, $C\underline{H}_aH_b$=CH), 5.15-5.09 (1H, m, $CH_a\underline{H}_b$=CH), 4.25-4.19 (2H, m, $C\underline{H}_2OSi$), 4.11 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.03 (2H, s, $SiCH_2$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.25 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2980 (C-H), 1710 (C=O), 1640 (C=C), 1370, 1050 (Si-O), 920 cm^{-1}. **MS** (CI, NH_3): 203 (M^++1, 52), 129 (M^+-$CO_2C_2H_5$, 11), 102 (11), 97 (13), 95 (12), 92 (12), 84 (22), 83 (12), 78 (16), 76 (14). **Anal.** Calcd for $C_9H_{18}O_3Si$: C, 53.43; H, 8.97; Si,13.88. Found: C, 53.37; H, 9.08; Si, 13.75.

1f. ^1H NMR (δ ppm): 7.66-7.62 (4H, m, Aromatic H), 7.45-7.36 (6H, m, Aromatic H), 3.95 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.87 (2H, q, J 7.0, $SiOC\underline{H}_2CH_3$), 2.54 (2H, s, $SiCH_2$), 1.25 (3H, t, J 7.0, $SiOCH_2C\underline{H}_3$), 1.03 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$). **IR** (CH_2Cl_2) (υ_{max}): 1710 (C=O), 1590 (C=C), 1365, 1115, 1100, 1030 (Si-O), 950 cm^{-1}. **MS** (CI, NH_3): 315 (M^++1, 14), 314 (M^+, 9), 269 (M^+-OC_2H_5, 13), 254 (46), 237 (M^+-C_6H_5, 100), 227 ($Ph_2SiOC_2H_5^+$, 49), 199 (Ph_2SiOH^+, 18),

195 (39), 183 (30), 105 (14), 77 ($C_6H_5^+$, 22). **Anal.** Calcd for $C_{18}H_{22}O_3Si$: C, 68.76; H, 7.06; Si, 8.91. Found: C, 68.80; H, 6.96; Si, 8.82.

1g. ^{1}**H NMR** (δ ppm): 7.67-7.63 (4H, m, Aromatic H), 7.47-7.35 (6H, m, Aromatic H), 4.19 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 3.93 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.53 (2H, s, $SiCH_2$), 1.20 (6H, d, J 6.1, $C\underline{H}_3CHC\underline{H}_3$), 1.02 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$). **IR** (CH_2Cl_2) (υ_{max}): 1710 (C=O), 1590 (C=C), 1380, 1365, 1120, 1100, 1035 (Si-O), 1025 cm^{-1}. **MS** (CI, NH_3): 329 (M^++1, 17), 328 (M^+, 7), 285 (M^+-*i*-Pr, 10), 269 (M^+-*i*-PrO, 16), 268 (49), 252 (30), 251 (M^+-C_6H_5, 100), 241 (60), 227 (20), 222 (19), 209 (39), 199 (70), 183 (16), 105 (14), 91 ($C_7H_7^+$, 15), 77 ($C_6H_5^+$, 29). **Anal.** Calcd for $C_{19}H_{24}O_3Si$: C, 69.47; H, 7.36; Si, 8.55. Found: C, 69.65; H, 7.35; Si, 8.46.

Ethyl-2-(di-*t*-Butylhydroxysilyl)ethanoate. ^{1}**H NMR** (δ ppm): 4.12 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.65 (1H, s, OH), 2.0 (2H, s, $SiCH_2$), 1.26 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.03 (18H, s, 2 x *t*-Bu). **IR** (CH_2Cl_2) (υ_{max}): 2860, 1710 (C=O), 1470, 1365, 1105, 1030 (Si-O), 825 cm^{-1}. **MS** (CI, NH_3): 247 (M^++1, 100), 217 (M^+-C_2H_5, 11), 206 (11), 201 (M^+-OC_2H_5, 28), 189 (M^+-*t*-Bu, 36), 105 (31), 104 (14), 94 (15). **Anal.** Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.63; Si, 11.40. Found: C, 58.42; H, 10.62; Si, 11.34.

1h. ^{1}**H NMR** (δ ppm): 5.35-5.28 (1H, m, C=C$\underline{H}$), 4.23-4.13 (2H, m, $C\underline{H}_2OSi$), 4.10 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.02 (2H, s, $SiCH_2$), 1.72 (3H, d, J 1.0, $C\underline{H}_3C$=CH), 1.65 (3H, s, $C\underline{H}_3C$=CH), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.23 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2970 (C-H), 2870, 1710 (C=O), 1440, 1380, 1140, 1030 (Si-O), 910 cm^{-1}. **MS** (CI, NH_3): 231 (M^++1, 3), 230 (M^+, 4), 219 (11), 180 (44), 163 (M^+-C_5H_7, 47), 145 (($CH_3)_2SiCH_2CO_2C_2H_5^+$, 25), 127 (10), 117 (18), 103 (32), 92 (43), 85 (29), 83 (48), 75 (($CH_3)_2SiOH^+$, 100). **Anal.** Calcd for $C_{11}H_{22}O_3Si$: C, 57.35; H, 9.63; Si, 12.19. Found: C, 57.47; H, 9.51; Si, 12.30.

1i. ^{1}**H NMR** (δ ppm): 5.94 (1H, dd, J 10.6, 17.3, CH_2=C$\underline{H}$), 5.14 (1H, dd, J 1.3, 17.3, $C\underline{H}_aH_b$=CH), 4.96 (1H, dd, J 1.3, 10.6, $CH_a\underline{H}_b$), 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 1.99 (2H, s, $SiCH_2$), 1.32 (6H, s, 2 CH_3), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.23 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2990 (C-H), 1710 (C=O), 1460, 1400, 1360, 1145, 1035 (Si-O), 910 cm^{-1}. **MS** (CI, NH_3): 231 (M^++1, 11), 219 (33), 215 (M^+-CH_3, 13), 187 (12), 180 (47), 163 (M^+-C_5H_7, 54), 145 (($CH_3)_2SiCH_2CO_2C_2H_5^+$, 21), 117 (13), 103 (21), 92 (27), 87 ($CH_2CO_2C_2H_5^+$, 11), 75 (($CH_3)_2SiOH^+$, 100). **Anal.** Calcd for $C_{11}H_{22}O_3Si$: C, 57.35; H, 9.63; Si, 12.19. Found: C, 57.25; H, 9.47; Si, 11.98.

1j. ^{1}**H NMR** (δ ppm): 7.43-7.21 (5H, m, Aromatic H), 6.59 (1H, dt, J 1.5, 15.8, PhC$\underline{H}$), 6.29 (1H, dt, J 5.4, 15.8, C$\underline{H}$CH$_2$O), 4.39 (2H, dd, J 1.5, 5.4, $C\underline{H}_2OSi$), 4.12 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.07 (2H, s, $SiCH_2$), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.29 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2980 (C-H), 2870, 1710 (C=O), 1600 (C=C), 1490, 1445, 1375, 1250 (Si-C), 1100, 1030 (Si-O), 965, 880, 840 cm^{-1}. **MS** (CI, NH_3): 279 (M^++1, 3), 236 (5), 233 (M^+-C_2H_5O, 6), 205 (M^+-$CO_2C_2H_5$, 18), 204 (14), 191 (M^+-$CH_2CO_2C_2H_5$, 11), 146 (M^+-PhCH=CHCH$_2$OH, 25), 145 (M^+-PhCH=CHCH$_2$O, 42), 118 (53), 117 (PhCH=CHCH$_2^+$, 100), 116 (23), 115 (30), 104 (39), 103 (69), 92 (20), 91 (102 (11), 97 (13), 95 (12), 92 (12), 91 ($C_7H_7^+$, 28), 77 ($C_6H_5^+$, 32), 76 (69), 75 (94), 74 (25). **Anal.** Calcd for $C_{15}H_{22}O_3Si$: C, 64.71; H, 7.96; Si, 10.09. Found: C, 64.94; H, 8.00; Si, 10.20.

Procedure B. The insertion process was carried out as in procedure A, starting from ethyl diazoacetate (0.29 ml, 2.8 mmol) and diisopropylchlorosilane (0.5 ml, 2.93 mmol). The crude product, obtained as an oil after evaporation of the solvent, was diluted with dry DMF (2ml) and then added dropwise to a solution of imidazole (0.57 g, 8.4 mmol), 4-dimethylaminopyridine (5 mg, 0.04 mmol) and dry ethanol (0.82 ml, 14 mmol) in dry DMF (4 ml). The solution was stirred at room temperature for 12 hours then treated at 0°C with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give a residue which was purified by filtration over Florisil® (Petroleum ether/ethyl acetate/NEt_3 98.5/1/0.5) or kugelrohr distillation (60°C, 0.02 mbar) to afford the ester **1k** as a colourless oil (0.48 g, 70%). ^{1}**H NMR** (δ ppm): 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.79 (2H, q, J 6.9, $SiOC\underline{H}_2CH_3$), 2.02 (2H, s, $SiCH_2$), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.20 (3H, t, J 6.9, $SiOCH_2C\underline{H}_3$), 1.08-1.04 (14H, m, 2 x *i*-Pr). **IR** (CH_2Cl_2) (υ_{max}): 3020, 2990 (C-H), 1710 (C=O), 1550, 1420, 1100 (Si-O), 900 cm^{-1}. **MS** (CI, NH_3): 247 (M^++1, 100), 246 (M^+, 1), 220 (7), 203 (13), 201 (18), 84 (8), 77 (11), 74 (13), 73 (9). **Anal.** Calcd for $C_{12}H_{26}O_3Si$: C, 58.50; H, 10.64; Si, 11.37. Found: C, 58.44; H, 10.35; Si, 11.27.

1l. ^{1}**H NMR** (δ ppm): 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.90 (2H, q, J 7.0, $SiOC\underline{H}_2CH_3$), 2.06 (2H, s, $SiCH_2$), 1.26 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.20 (3H, t, J 7.0, $SiOCH_2C\underline{H}_3$), 1.03 (18H, s, 2 x *t*-Bu). **IR** (CH_2Cl_2) (υ_{max}): 2860, 1710 (C=O), 1470, 1390, 1365, 1115, 1090, 1030 (Si-O), 820 cm^{-1}. **MS** (CI, NH_3): 275 (M^++1, 52), 274 (M^+, 7), 229 (M^+-C_2H_5O, 27), 217 (M^+-C_4H_9, 100), 87 ($CH_2CO_2C_2H_5^+$, 12), 86 ($CHCO_2C_2H_5^+$, 21), 73 ($CO_2C_2H_5^+$, 74). **Anal.** Calcd for $C_{14}H_{30}O_3Si$: C, 61.27; H, 11.03; Si, 10.20. Found: C, 61.33; H, 10.93; Si, 10.03.

1m. A solution of α-diazoacetophenone[23] (0.3 g, 2.05 mmol) in dry CH_2Cl_2 (3 ml) was added slowly at room temperature, using a syringe pump (0.02 mmol/min) to a solution of dimethylchlorosilane (0.45 ml, 4.1 mmol) and $Rh_2(OAc)_4$ (7 mg, 0.01 mmol) in dry CH_2Cl_2 (3 ml). The mixture was cooled to 0°C and a solution of triethylamine (0.58 ml, 4.1 mmol) in CH_2Cl_2 (1 ml) was added, followed by isopropanol (0.38 ml, 4.92 mmol) in dry CH_2Cl_2 (1 ml). The suspension was stirred at room temperature for 1.5 hours and petroleum ether was added. The solution was filtered and evaporated in vacuo to

give an oil which was distilled using the kugelrohr (70°C, 0.02 mbar) to afford the ketone **1m** as a colourless oil (0.31 g, 65%): **^{1}H NMR** (δ ppm): 7.97-7.93 (2H, m, Aromatic H), 7.56-7.40 (3H, m, Aromatic H), 4.0 (1H, sept, J 6.0, $CH_3C\underline{H}CH_3$), 2.83 (2H, s, $SiCH_2$), 1.10 (6H, d, J 6.0, $C\underline{H}_3CHC\underline{H}_3$), 0.18 (6H, s, $Si(CH_3)_2$). **IR** (CH_2Cl_2) (υ_{max}): 1660 (C=O), 1600, 1580 (C=C), 1380, 1360, 1020 (Si-O), 950 cm^{-1}. **MS** (CI, NH_3): 238 ($M^{+\cdot}$+2, 20), 237 ($M^{+\cdot}$+1, 100), 221 ($M^{+\cdot}$-CH_3, 4), 194 ($M^{+\cdot}$-C_3H_6, 6), 178 ($M^{+\cdot}$-C_3H_6O, 7), 177 ($M^{+\cdot}$-*i*-PrO, 8), 91 ($C_7H_7^{+\cdot}$, 8), 77 ($C_6H_5^{+\cdot}$, 9), 75 ($Si(CH_3)_2OH^{+\cdot}$, 10). **Anal.** Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.92; H, 8.40.

1n. ^{1}H NMR (δ ppm): 4.06 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 1.92 (2H, s, $SiCH_2$), 1.68-1.24 (12H, m, Aliphatic H), 1.26 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.01-0.83 (15H, m, Aliphatic H). **IR** (CH_2Cl_2) (υ_{max}): 2915, 1690 (C=O), 1080, 1035 cm^{-1}. **MS** (CI, NH_3): 377 ($M^{+\cdot}$, 2), 325 (27), 321 ($M^{+\cdot}$-C_4H_8, 100), 320 ($M^{+\cdot}$-C_4H_9, 28), 319 ($M^{+\cdot}$-C_4H_{10}, 62), 291 ($CHCO_2C_2H_5^{+\cdot}$, 19), 279 (23), 277 (20), 235 (20), 233 (19), 179 (16), 177 (15), 85 (20), 83 (29). **Anal.** Calcd for $C_{16}H_{34}O_2Sn$: C, 50.77; H, 9.06; Sn, 31.71. Found: C, 50.65; H, 9.00; Sn, 31.66.

General procedure for the preparation of α-silylacetic esters 1 using $Cu(OTf)_2$-Schiff-base catalyzed insertion. To a mixture of Schiff-base[16] (114 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (3 ml) was added under stirring at room temperature, $Cu(OTf)_2$ (156 mg, 0.43 mmol) in one portion. The resulting blue mixture was stirred at RT for 1 hour and $PhMe_2SiH$ (0.82 ml, 5.3 mmol) was added. Ethyl diazoacetate (0.5 ml, 5 mmol) in dry CH_2Cl_2 (1 ml) was then added dropwise, using a syringe pump (0.02 mmol/min). After the addition was complete, the mixture was treated with $NaHCO_3$, the organic layer was decanted and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvent was evaporated to give a residue which was chromatographed on silica gel (petroleum light/EtOAc/Et_3N 98:1.5:0.5) to give pure α-silylacetic ester **1p** (0.8 g, 76%).

1o.[11] **^{1}H NMR** (δ ppm): 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 1.88 (2H, s, $SiCH_2$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.97 (3H, q, J 7.9, $SiC\underline{H}_2CH_3$), 0.62 (2H, t, J 7.9, $SiCH_2C\underline{H}_3$). **IR** ($CHCl_3$) (υ_{max}): 2960 (CH), 2910, 2880, 1700 (C=O), 1460, 1410, 1360, 1260 (Si-C), 1140, 1100 975, 860, 690, 600 cm^{-1}.

1p. ^{1}H NMR (δ ppm): 7.56-7.53 (2H, m, Aromatic H), 7.39-7.37 (3H, m, Aromatic H), 4.05 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.12 (2H, s, $SiCH_2$), 1.17 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.42 (6H, s, $Si(CH_3)_2$). **IR** (film) (υ_{max}): 2970 (C-H), 2800, 1720 (C=O), 1600 (C=C), 1430, 1320, 1300, 1250 (Si-C), 1030, 830 cm^{-1}. **MS** (CI, NH_3): 170 (13), 145 ($M^{+\cdot}$-C_6H_5, 100), 130 (7), 116 (14), 135 ($PhSi(CH_3)_2^+$, 4), 103 (28), 86 (7), 74 (64). **Anal.** Calcd for $C_{18}H_{18}O_2Si$: C, 64.82; H, 8.16. Found: C, 64.72; H, 7.98.

1q.[11] **^{1}H NMR** (δ ppm): 7.64-7.58 (6H, m, Aromatic H), 7.49-7.36 (9H, m, Aromatic H), 3.87 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.77 (2H, s, $SiCH_2$), 0.95 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$). **IR** (KBr) (υ_{max}): 3050, 3000 (C-H), 1700 (C=O), 1590 (C=C), 1480, 1430, 1250 (Si-C), 1120, 1100, 1030, 790 cm^{-1}.

1r. ^{1}H NMR (δ ppm): 7.12 (1H, d, J 3.2, Thiophene H-3), 6.86-6.84 (1H, m, Thiophene H-4), 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.53 (3H, d, J 1.1, $C\underline{H}_3$), 2.13 (2H, s, $SiC\underline{H}_2$), 1.21 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.42 (6H, s, $Si(C\underline{H}_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 3000 (C-H), 2960, (C-H), 1710 (C=O), 1440, 1400, 1360, 1250 (Si-C), 1140, 960, 870 cm^{-1}. **MS** (EI): 243 ($M^{+\cdot}$+1, 10), 242 ($M^{+\cdot}$, 37), 228 ($M^{+\cdot}$+1 -CH_3, 20), 227 ($M^{+\cdot}$-CH_3, 100), 197 ($M^{+\cdot}$-CH_2CH_3O, 11), 185 (39), 155 ($M^{+\cdot}$-$CH_2CO_2C_2H_5$, 13), 145 ($M^{+\cdot}$-5-Methylthienyl, 30), 117 (14), 77 (18), 75($Si(CH_3)_2OH^{+\cdot}$, 36). **Anal.** Calcd for $C_{11}H_{18}O_2SSi$: C, 54.50; H, 7.48; S, 13.23; Si, 11.59. Found: C, 54.61; H, 7.45; S, 13.22; Si, 11.64.

Dimethyl-(5-methylthien-2-yl)silane 2. A 1.5M solution of n-BuLi in hexane (81.3 ml, 0.122 mol) was added dropwise at -78°C to a solution of 5-methylthiophene (9.8 ml, 0.1 mol) in dry THF (80 ml). The mixture was allowed to warm at -30°C then stirred 1 hour at this temperature. A solution of 1,1,3,3-tetramethyldisiloxane (23.5 ml, 0.13 mol) in dry THF (50 ml) was then added dropwise at -78°C and the resulting mixture was stirred overnight at room temperature. The mixture was treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give a pale yellow oil which was purified by distillation (115°C, 100 mmHg) to afford the silane **2** as a colourless oil (14.2 g, 89%). **^{1}H NMR** (δ ppm): 7.12 (1H, d, J 3.2, Thiophene H-3), 6.86-6.85 (1H, m, Thiophene H-4), 4.57-4.51 (1H, sept, J 3.7, SiH), 2.54 (3H, d, J 0.8, CH_3), 0.39 (3H, s, $SiCH_3$), 0.37 (3H, s, $SiCH_3$). **IR** (film) (υ_{max}): 3050, 2950 (C-H), 2850, 2150 (Si-H), 1440, 1260 (Si-C), 1220, 800 cm^{-1}.

General procedure for the alkylation of α-(alkoxysilyl)acetic esters 1. To a solution of hexamethyldisilazane (0.26 ml, 1.22 mmol) in dry THF (4 ml) was added at -20°C a 1.6M solution of n-BuLi in hexane (0.64 ml, 1.03 mmol). The solution was stirred at -5°C for 15 minutes then cooled to -60°C and a solution of the ester **1a** (0.2 g, 0.98 mmol) in dry THF (1 ml) was added dropwise. The mixture was stirred at -60°C for one hour, then a solution of allyl bromide (0.41 ml, 4.9 mmol) in dry THF (1 ml) was added dropwise. The mixture was allowed to warm to 0°C over 2 hours then it was treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give a yellow oil which was purified by filtration through florisil® (petroleum light/EtOAc/NEt_3 98:1.5:0.5) or kugelrohr distillation (130°C, 0.3 mbar) to afford the ester **3a** as a colourless oil (0.2 g, 83%). **^{1}H NMR** (δ ppm): 5.90-5.74 (1H, m, $CH_2C\underline{H}$), 5.08-4.93

(2H, m, $C\underline{H}_2CH$), 4.11 (2H, q, J 7.2, $CO_2C\underline{H}_2CH_3$), 4.04 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 2.63-2.49 (1H, m, $SiCHCH_a\underline{H}_b$), 2.31-2.21 (1H, m, $SiCHC\underline{H}_aH_b$), 2.22-2.16 (1H, m, $SiC\underline{H}$), 1.24 (3H, t, J 7.2, $CO_2CH_2C\underline{H}_3$), 1.17 (3H, d, J 6.1, $C\underline{H}_3CHCH_3$), 1.15 (3H, d, J 6.1, $CH_3CHC\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.19 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2980, 2930 (C-H), 2870, 1710 (C=O), 1365, 1230, 1170, 1120, 1030 (Si-O), 920, 880 cm^{-1}. **MS** (CI, NH_3): 246 ($M^{+\cdot}$+2, 26), 245 ($M^{+\cdot}$+1, 93), 244 ($M^{+\cdot}$, 20), 227 (20), 216 ($M^{+\cdot}$-C_2H_5, 17), 199 ($M^{+\cdot}$-C_2H_5O, 18), 176 (10), 156 (10), 121 (14), 117 (*i*-$PrOSi(CH_3)_2^{+\cdot}$, 6), 109 (10), 92 (32), 82 (44), 81 (45), 77 (26), 76 (30), 75 ($HOSi(CH_3)_2^{+\cdot}$, 100), 74 (58). **Anal.** Calcd for $C_{12}H_{24}O_3Si$: C, 58.97; H, 9.90; Si, 11.49. Found: C, 58.74; H, 9.88;Si, 11.55.

3b. ^{1}**H NMR** (δ ppm): 4.11 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.02 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 1.98 (1H, dd, J 3.0, 11.5, $SiC\underline{H}CH_aH_b$), 1.88-1.75 (1H, m, $SiCHC\underline{H}_aH_b$), 1.60-1.49 (1H, m, $SiCHCH_a\underline{H}_b$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.15 (3H, d, J 6.1, $C\underline{H}_3CHCH_3$), 1.13 (3H, d, J 6.1, $CH_3CHC\underline{H}_3$), 0.94 (3H, t, J 7.2, CH_3), 0.16 (6H, s, $Si(CH_3)_2$). **IR** (CH_2Cl_2) (υ_{max}): 2980, 2920 (C-H), 1705 (C=O), 1320, 1130, 1080 (Si-O), 1030 cm^{-1}. **MS** (CI, NH_3): 233 ($M^{+\cdot}$+1, 86), 232 ($M^{+\cdot}$, 43), 217 ($M^{+\cdot}$-CH_3, 14), 173 ($M^{+\cdot}$-*i*-PrO, 25), 145 (16), 117 ($M^{+\cdot}$-$CH(C_2H_5)CO_2C_2H_5$, 13), 93 (22), 86 ($CHCO_2C_2H_5^{+\cdot}$, 24), 85 (24), 75 ($HOSi(CH_3)_2^{+\cdot}$, 100), 74 (18). **Anal.** Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41; Si, 12.09. Found: C, 56.77; H, 10.38; Si, 12.06.

3c. ^{1}**H NMR** (δ ppm): 4.10 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.02 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 2.14 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.21 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.16 (3H, d, J 6.1, $C\underline{H}_3CHCH_3$), 1.14 (3H, d, J 6.1, $CH_3CHC\underline{H}_3$), 0.18 (3H, s, $SiCH_3$), 0.17 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2980, 2920 (C-H), 2870, 1705 (C=O), 1380, 1360, 1320, 1190, 1030 (Si-O), 1025 cm^{-1}. **MS** (CI, NH_3): 245 ($M^{+\cdot}$+1, 65), 218 ($M^{+\cdot}$, 10), 173 ($M^{+\cdot}$-C_2H_5O, 10), 159 ($M^{+\cdot}$-*i*-PrO, 15), 130 (16), 103 (15), 92 (21), 86 ($CHCO_2C_2H_5^{+\cdot}$, 10), 77 (22), 76 (30), 75 ($HOSi(CH_3)_2^{+\cdot}$, 100), 74 (32). **Anal.** Calcd for $C_{10}H_{22}O_3Si$: C, 55.00; H,10.15; Si, 12.86. Found: C, 54.81; H, 10.32; Si, 12.99.

3d. ^{1}**H NMR** (δ ppm): 4.12 (2H, dq, J 1.6, 7.1, $CO_2C\underline{H}_2CH_3$), 3.71 (2H, dq, J 1.5, 7.0, $SiOC\underline{H}_2CH_3$), 2.18 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.22 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.19 (3H, t, J 7.0, $SiOCH_2C\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.18 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2920 (C-H), 1705 (C=O), 1365, 1185, 1100, 1080 (Si-O), 1015, 830 cm^{-1}. **MS** (CI, NH_3): 205 ($M^{+\cdot}$+1, 15), 159 ($M^{+\cdot}$-OC_2H_5, 13), 131 ($M^{+\cdot}$-$CO_2C_2H_5$, 10), 130 (20), 103 ($C_2H_5OSi(CH_3)_2^{+\cdot}$, 63), 101 ($CH_3CHCO_2C_2H_5^{+\cdot}$, 15), 85 (36), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100), 73 ($CO_2C_2H_5^{+\cdot}$ or $SiOC_2H_5^{+\cdot}$, 26). **Anal.** Calcd for $C_9H_{20}O_3Si$: C, 52.90; H, 9.87; Si, 13.74. Found: C, 52.73; H, 9.75; Si, 13.80.

3e. ^{1}**H NMR** (δ ppm): 4.13 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 3.70 (2H, dq, J 2.1, 7.0, $SiOC\underline{H}_2CH_3$), 2.03 (1H, dd, J 3.0, 11.4, $SiC\underline{H}CH_2$), 1.90-1.75 (1H, m, $CHC\underline{H}_aH_b$), 1.62-1.50 (1H, m, $CHCH_a\underline{H}_b$), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.19 (3H, t, J 7.0, $SiOCH_2C\underline{H}_3$), 0.96 (3H, d, J 7.1, $CHCH_2C\underline{H}_3$), 0.18 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2970 (C-H), 1705 (C=O), 1365, 1180, 1140, 1030 (Si-O), 830 cm^{-1}. **MS** (CI, NH_3): 217 ($M^{+\cdot}$-1, 24), 157 ($M^{+\cdot}$-$C_2H_5O_2$, 17), 133 (50), 131 ($M^{+\cdot}$-$CH_2CO_2C_2H_5$, 27), 85 (49), 83 (34), 82 (30), 73 ($CO_2C_2H_5^{+\cdot}$ or $SiOC_2H_5^{+\cdot}$, 100). **Anal.** Calcd for $C_{10}H_{22}O_3Si$: C, 55.00; H, 10.15; Si, 12.86. Found: C, 54.91; H, 10.07; Si, 12.78.

3f. ^{1}**H NMR** (δ ppm): 4.16-3.89 (2H, m, $C\underline{H}_2CH_3$), 3.89-3.71 (2H, m, $C\underline{H}_2CH_3$), 2.34 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 1.28 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.25 (3H, t, J 7.1, $CH_2C\underline{H}_3$), 1.21 (3H, t, J 7.0, $CH_2C\underline{H}_3$), 1.13-1.04 (14H, m, 2 x *i*-Pr). **IR** (CH_2Cl_2) (υ_{max}): 1705 (C=O), 1365, 1310, 1185, 1085 (Si-O), 1015, 950 cm^{-1}. **MS** (CI, NH_3): 261 ($M^{+\cdot}$+1, 17), 247 ($M^{+\cdot}$-CH, 47), 217 ($M^{+\cdot}$-*i*-Pr, 100), 215 ($M^{+\cdot}$-C_2H_5O, 34), 187 ($M^{+\cdot}$-$CO_2C_2H_5$, 19), 161 (61), 133 (26), 115 (19), 95 (36), 85 (34), 73 ($CO_2C_2H_5^{+\cdot}$, 53). **Anal.** Calcd for $C_{13}H_{28}O_3Si$: C, 59.95; H, 10.84; Si, 10.78. Found: C, 59.80; H, 10.76; Si, 10.70.

3g. ^{1}**H NMR** (δ ppm): 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.08 (1H, q, J 7.1, $C\underline{H}CH_3$), 1.24 (9H, s, *t*-Bu), 1.23 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.18 (3H, t, J 7.1, $CHC\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.18 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2920 (C-H), 1705 (C=O), 1365, 1320, 1180, 1050 (Si-O), 1020, 830 cm^{-1}. **MS** (CI, NH_3): 233 ($M^{+\cdot}$+1, 100), 232 ($M^{+\cdot}$, 28), 177 ($M^{+\cdot}$-C_4H_7, 31), 130 (10), 103 ($CH_3CHCO_2C_2H_5^{+\cdot}$, 12), 92 (31), 77 (20), 75 ($Si(CH_3)_2OH^{+\cdot}$, 68). **Anal.** Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41; Si, 12.09. Found: C, 56.62; H, 10.28; Si, 11.97.

3h. ^{1}**H NMR** (δ ppm): 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 1.94 (1H, dd, J 3.0, 11.3, $SiC\underline{H}CH_2$), 1.85-1.72 (1H, m, $CHC\underline{H}_aH_b$), 1.59-1.48 (1H, m, $CHCH_a\underline{H}_b$), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.23 (9H, s, *t*-Bu), 0.92 (3H, t, J 7.1, $CHCH_2C\underline{H}_3$), 0.17 (3H, s, $SiCH_3$), 0.16 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2920 (C-H), 1705 (C=O), 1390, 1365, 1180, 1050 (Si-O), 1020, 830 cm^{-1}. **MS** (CI, NH_3): 247 ($M^{+\cdot}$+1, 100), 246 ($M^{+\cdot}$, 21), 231 ($M^{+\cdot}$-CH_3, 21), 191(37), 129(9), 92 (30), 75 ($Si(CH_3)_2OH^{+\cdot}$, 54), 74 ($Si(CH_3)_2O^{+\cdot}$, 18). **Anal.** Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.63; Si, 11.40. Found: C, 58.29; H, 10.53; Si, 11.44.

3i. ^{1}**H NMR** (δ ppm): 5.86-5.73 (1H, m, $CH_2=C\underline{H}$), 5.06-4.89 (2H, m, $C\underline{H}_2=CH$), 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.60-2.45 (1H, m, $CHC\underline{H}_aH_b$), 2.27-2.19 (1H, m, $CHCH_a\underline{H}_b$), 2.13 (1H, dd, J 3.1, 11.6, $SiC\underline{H}CH_2$), 1.24 (9H, s, *t*-Bu), 1.22 (3H, t, J 7.1 , $CO_2CH_2C\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.18 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2)(υ_{max}): 1705 (C=O), 1630 (C=C), 1365, 1180, 1050 (Si-O), 1020, 910 cm^{-1}. **MS** (CI, NH_3): 259 ($M^{+\cdot}$+1, 69), 258 ($M^{+\cdot}$, 17), 243 ($M^{+\cdot}$-CH_3, 11),

203 (38), 201 (M^+-*t*-Bu, 11), 185 (M^+-$CO_2C_2H_5$ or *t*-BuO, 10), 92 (23), 82 (23), 81 (22), 75 ($Si(CH_3)_2OH^+$, 100), 74 ($Si(CH_3)_2O^+$, 25). **Anal.** Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14; Si, 10.87. Found: C, 60.26; H, 9.98; Si, 10.29.

3j. ^{1}**H NMR** (δ ppm): 7.70-7.62 (4H, m, Aromatic H), 7.49-7.33 (6H, m, Aromatic H), 4.14-3.70 (4H, m, 2 x $C\underline{H}_2CH_3$), 2.76 (1H, q, J 7.2, $SiC\underline{H}CH_3$), 1.30 (3H, d, J 7.2, $SiCHC\underline{H}_3$), 1.23 (3H, t, J 7.0, $CH_2C\underline{H}_3$), 1.02 (3H, t, J 7.1, $CH_2C\underline{H}_3$). **IR** (CH_2Cl_2) (υ_{max}): 1705 (C=O), 1590 (C=C), 1365, 1185, 1080 (Si-O) cm^{-1}. **MS** (CI, NH_3): 328 (M^+, 52), 299 (M^+-C_2H_5, 19), 283 (M^+-C_2H_5O, 24), 255 (M^+-$CO_2C_2H_5$, 19), 244 (51), 227 (M^+-$(C_2H_5O)SiPh_2$, 100), 199 (Ph_2SiOH^+, 39), 183 (66), 167 (16), 105 (26), 91 ($C_7H_7^+$, 10), 77 ($C_6H_5^+$, 53). **Anal.** Calcd for $C_{19}H_{24}O_3Si$: C, 69.47; H, 7.36; Si, 8.55. Found: C, 69.60; H, 7.38; Si, 8.34.

3k. ^{1}**H NMR** (δ ppm): 5.13-5.07 (1H, m, C=C$\underline{H}$), 4.09 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.51-2.38 (1H, m, $CHC\underline{H}_aH_b$), 2.29-2.18 (1H, m, $CHCH_a\underline{H}_b$), 2.03 (1H, dd, J 3.6, 11.2, $SiC\underline{H}CH_2$), 1.66 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.25 (9H, s, *t*-Bu), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.20 (3H, s, $SiCH_3$), 0.19 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}): 2970 (C-H), 1700 (C=O), 1440, 1360, 1250, 1145, 1050 (Si-O), 910 cm^{-1}. **MS** (CI, NH_3): 288 (M^++2, 21), 287 (M^++1, 32), 286 (M^+, 6), 231 (M^+-C_4H_7, 52), 229 (M^+-*t*-Bu, 10), 213 (M^+-$CO_2C_2H_5$ or *t*-BuO, 27), 212 (26), 184 (9), 154 (7), 129 (7), 109 (36), 95 (32), 75 ($(CH_3)_2SiOH^+$, 100). **Anal.** Calcd for $C_{15}H_{30}O_3Si$: C, 62.89; H, 10.55; Si, 9.80. Found: C, 62.79; H, 10.45; Si, 9.95.

3l. ^{1}**H NMR** (δ ppm): 5.99-5.85 (1H, m, CH_2=C$\underline{H}$), 5.27 (1H, dd, J 1.7, 17, $C\underline{H}_aH_b$=CH), 5.14-5.04 (3H, m, vinylic H), 4.22-4.18 (2H, m, $C\underline{H}_2OSi$), 4.11 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.53-2.45 (1H, m, Aliphatic H), 2.32-1.95 (6H, m, Aliphatic H), 1.67 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.22 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2970 (C-H), 2920, 1700 (C=O), 1440, 1325, 1140, 1070 (Si-O), 830 cm^{-1}. **MS** (CI, NH_3): 339 (M^++1, 39), 338 (M^+, 9), 293 (M^+-C_2H_5O, 36), 280 (34), 265 (M^+-$CO_2C_2H_5$, 9), 256 (10), 235 (19), 211 (16), 196 (12), 190 (19), 179 (14), 127 (12), 121 (15), 117 (23), 115 (87), 85 (92), 81 (100), 75 ($(CH_3)_2SiOH^+$, 53). **Anal.** Calcd for $C_{19}H_{34}O_3Si$: C, 67.41; H, 10.12; Si, 8.30. Found: C, 67.26; H, 10.02; Si, 8.28.

3m. ^{1}**H NMR** (δ ppm): 5.14-5.04 (2H, m, vinylic H), 4.10 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 4.05 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 2.56-2.43 (1H, m, Aliphatic H), 2.27-2.17 (1H, m, Aliphatic H), 2.09 (1H, dd, J 3.7, 11.2, $SiC\underline{H}$), 2.09-1.95 (4H, m, Aliphatic H), 1.67 (3H, d, J 0.9, CH_3), 1.61 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.17 (3H, d, J 6.1, $C\underline{H}_3CHCH_3$), 1.16 (3H, d, J 6.1, $CH_3CHC\underline{H}_3$), 0.19 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2970, 2920 (C-H), 1705 (C=O), 1445, 1380, 1370, 1300, 1255 (Si-C), 1145, 1120, 1030 (Si-O), 835 cm^{-1}. **MS** (CI, NH_3): 341 (M^++1, 31), 340 (M^+, 6), 295 (M^+-C_2H_5O, 12), 281 (M^+-*i*-PrO, 6), 266 (9), 212 (21), 211 (20), 183 (7), 117 (25), 92 (19), 81 (37), 75 ($(CH_3)_2SiOH^+$, 100), 74 ($(CH_3)_2SiO^+$, 20). **Anal.** Calcd for $C_{19}H_{36}O_3Si$: C, 67.01; H, 10.65; Si, 8.25. Found: C, 66.91; H, 10.46; Si, 8.29.

3n. ^{1}**H NMR** (δ ppm): 5.99-5.84 (1H, m, CH_2=C$\underline{H}$), 5.41-5.28 (3H, m, Vinylic H), 5.11 (1H, dd, J 1.7, 10.3, $C\underline{H}_aH_b$=CH), 4.21-4.17 (2H, m, $C\underline{H}_2OSi$), 4.11 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.61-2.48 (1H, m, Aliphatic H), 2.30-2.0 (4H, m, Aliphatic H), 1.24 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.95 (3H, t, J 7.5, $CH_2C\underline{H}_3$), 0.22 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2960 (C-H), 1705 (C=O), 1450, 1330, 1250, 1130, 1065 (Si-O), 830 cm^{-1}. **MS** (CI, NH_3): 271 (M^++1, 67), 270 (M^+, 7), 255 (M^+-CH_3, 17), 225 (M^+-C_2H_5O, 50), 213 (M^+-AllylO, 33), 212 (31), 195 (29), 183 (M^+-$CH_2CO_2C_2H_5$, 13), 129 (11), 115 (35), 103 (30), 99 (28), 83 (42), 81 (41), 75 ($(CH_3)_2SiOH^+$, 100). **Anal.** Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69; Si, 10.38. Found: C, 62.04; H, 9.77; Si, 10.49.

5. ^{1}**H NMR** (δ ppm): 4.13 (1H, q, J 7.1, $CO_2C\underline{H}_aH_bCH_3$), 4.12 (1H, q, J 7.1, $CO_2CH_a\underline{H}_bCH_3$), 4.03 (1H, sept, J 6.0, $CH_3C\underline{H}CH_3$), 2.78 (1H, dd, J 11.7, 16.8, $CHC\underline{H}_aH_b$), 2.52 (1H, dd, J 3.2, 11.7, $C\underline{H}CH_aH_b$), 2.38 (1H, dd, J 3.2, 16.8, $CHCH_a\underline{H}_b$), 1.43 (9H, s, *t*-Bu), 1.25 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 1.16 (3H, d, J 6.0, $C\underline{H}_3CHCH_3$), 1.14 (3H, d, J 6.0, $CH_3CHC\underline{H}_3$), 0.21 (3H, s, $SiCH_3$), 0.18 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}): 2980, 2930 (C-H), 1720 (C=O), 1710 (C=O), 1450, 1370, 1255 (Si-C), 1150, 1120, 1020 (Si-O), 840 cm^{-1}. **MS** (CI, NH_3): 318 (M^+, 1), 259 (M^+-*i*-PrO, 41), 245 (M^+-$CO_2C_2H_5$, 12), 220 (33), 217 (48), 203 (M^+-CH_2CO_2*t*-Bu, 100), 202 (42), 175 (8), 147 (5), 129 (25), 117 (11), 103 (12), 92 (12), 75 ($(CH_3)_2SiOH^+$, 46). **Anal.** Calcd for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49; Si, 8.82. Found: C, 56.66; H, 9.49; Si, 8.79.

General procedure for the reduction of α-substituted-α-(alkoxysilyl)acetic esters 3. To a solution of ester **3a** (0.2 g, 0.82 mmol) in dry ether (10ml) was added dropwise at 0°C a 1M solution of $LiAlH_4$ in ether (0.45 ml, 0.45 mmol). The mixture was stirred at 0°C for 10 minutes, then it was treated with a 1M solution of HCl and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated in vacuo to give the alcohol **6** as a colourless oil (0.16 g, 95%), which was used in the next step without further purification. **6a.** ^{1}**H NMR** (δ ppm): 5.89-5.73 (1H, m, $CH_2C\underline{H}$), 5.09-4.96 (2H, m, $C\underline{H}_2CH$), 4.01 (1H, sept, J 6.1, $CH_3C\underline{H}CH_3$), 3.78-3.72 (2H, m, $C\underline{H}_2OH$), 2.25-2.04 (2H, m, $SiCHC\underline{H}_2$), 1.15 (6H, d, J 6.1, $C\underline{H}_3CHC\underline{H}_3$), 1.12-1.01 (1H, m, $SiC\underline{H}$), 0.17 (3H, s, $SiCH_3$), 0.15 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2970 (C-H), 2870, 1380, 1250, 1110, 1020 (Si-O), 845 cm^{-1}. **MS** (CI, NH_3): 203 (M^++1, 14), 174 (6), 119 ($C_5H_{15}OSi^+$, 24), 117 (M^+-CH(allyl)CH_2OH, 13),

98 (36), 94 (29), 93 (34), 89 ($C_3H_9OSi^+$, 12), 85 (CH(allyl)CH_2OH^+, 13), 77 (50), 75 ($HOSi(CH_3)_2^+$, 100). **Anal.** Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96; Si, 13.88. Found: C, 59.28; H, 10.91; Si, 13.79.

6i. ^{1}**H NMR** (δ ppm): 5.88-5.72 (1H, m, CH_2CH), 5.09-4.95 (2H, m, CH_2CH), 3.81-3.68 (2H, m, CH_2OH), 3.08 (1H, broad s, OH), 2.15-2.03 (2H, m, $SiCHCH_2$), 1.25 (9H, s, *t*-Bu), 0.94-0.88 (1H, m, SiCH), 0.19 (3H, s, $SiCH_3$), 0.17 (3H, s, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2980, 2900 (C-H), 2870, 1360, 1240, 1190, 1040 (Si-O), 1015, 840 cm^{-1}. **MS** (CI, NH_3): 217 (M^++1, 22), 178 (12), 133 ($C_6H_{17}OSi^+$, 18), 94 (20), 93 (21), 92 (79), 91 (17), 85 (CH(allyl)CH_2OH^+, 20), 83 (32), 77 (49), 76 (36), 75 ($HOSi(CH_3)_2^+$, 100), 74 (47). **Anal.** Calcd for $C_{11}H_{24}O_2Si$: C, 61.06; H, 11.18; Si, 12.98. Found: C, 61.11; H, 11.22; Si, 13.00.

7a. The ester **3a** (0.5 g, 2.05 mmol) in dry ether (12 ml) was treated with a 1M solution of $LiAlH_4$ in ether (4.1 ml, 4.1 mmol) and the mixture was heated under reflux for 1 hour. The mixture was worked up as above to give **7a** as a pale yellow oil (0.25 g, 85%) which was used in the next step without further purification. ^{1}**H NMR** (δ ppm): 5.95-5.76 (1H, m, CH_2CH), 5.13-4.98 (2H, m, CH_2CH), 3.89-3.79 (1H, m, SiH), 3.79 (1H, dd, J 5.0, 10.8, CH_aH_bOH), 3.72 (1H, dd, J 7.5, 10.8, CH_aH_bOH), 2.36-2.17 (2H, m, $SiCHCH_2$), 1.19-1.06 (1H, m, SiCH), 0.12 (3H, d, J 3.6, $SiCH_3$), 0.11 (3H, d, J 3.8, $SiCH_3$). **IR** (CH_2Cl_2) (υ_{max}): 2980, 2920 (C-H), 2860, 2105 (Si-H), 1640 (C=C), 1310, 1220, 840 cm^{-1}. **Anal.** Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18; Si, 19.46. Found: C, 58.29; H, 11.05; Si, 19.52.

7l. ^{1}**H NMR** (δ ppm): 5.24-5.18 (1H, m, Vinylic H), 5.11-5.05 (1H, m, Vinylic H), 3.88-3.78 (1H, m, SiH), 3.77-3.67 (2H, m, CH_2OH), 2.24-2.17 (2H, m, $SiCHCH_2$), 2.09-1.98 (4H, m, Aliphatic H), 1.68 (3H, d, J 0.6, CH_3), 1.64 (3H, s, CH_3), 1.61 (3H, s, CH_3), 1.16-1.05 (1H, m, SiCH), 0.12 (6H, d, J 3.7, $Si(CH_3)_2$). **IR** ($CHCl_3$) (υ_{max}): 2960, 2920 (C-H), 2860, 2105 (Si-H), 1440, 1380, 1250, 880 (Si-H) cm^{-1}. **MS** (CI, NH_3): 258 (M^++NH_4, 11), 240 (M^+, 7), 223 (M^+-OH, 31), 109 (6), 92 (23), 91 (20), 81 ($C_6H_9^+$, 44), 76 (50), 75 (100). **Anal.** Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74; Si, 11.68. Found: C, 69.74; H, 11.54; Si, 11.72.

General procedure for the preparation of 1,2-diols 8. To a solution of the β-hydroxysilane **6a** (0.155 g, 0.77 mmol) in a 1:1 mixture of MeOH-THF (4 ml), was added at room temperature, $KHCO_3$ (0.23 g, 2.3 mmol), KF (0.133 g, 2.3 mmol), then a 30% wt solution of H_2O_2 (1.53 ml, 14.9 mmol). The mixture was stirred for 15 hours then it was treated cautiously at 0°C with $Na_2S_2O_3$ (1.5 g). The mixture was stirred at room temperature for 30 minutes, then it was diluted with ether, filtered through a plug of celite and was evaporated in vacuo. The residue was diluted with ether, dried ($MgSO_4$) and was evaporated to give a yellow oil which was purified by chromatography on silica gel (CH_2Cl_2/MeOH 98:2) to afford the expected diol **8a** as a colourless oil (59 mg, 76%): ^{1}**H NMR** (δ ppm): 5.91-5.74 (1H, m, CH_2CH), 5.30-5.10 (2H, m, CH_2CH), 3.82-3.73 (1H, m, CHOH), 3.66 (1H, dd, J 3.1, 11.3, CH_aH_bOH), 3.47 (1H, dd, J 7.4, 11.3, CH_aH_bOH), 2.77 (2H, broad s, 2 x OH), 2.27-2.20 (2H, m, $CHCH_2CHOH$). **IR** ($CHCl_3$) (υ_{max}): 3580, 3410 (O-H), 3080, 3000, 2980, 2920 (C-H), 2870, 1640 (C=C), 1430, 1380, 1210 (O-H), 1100, 990, 840 cm^{-1}.

8b. ^{1}**H NMR** (δ ppm): 3.92 (1H, ddq, J 2.9, 6.4, 7.8, CH_3CHOH), 3.64 (1H, dd, J 2.9, 11.0, CH_aH_bOH), 3.40 (1H, dd, J 7.8, 11.0, CH_aH_bOH), 2.51 (2H, broad s, 2 x OH), 1.17 (3H, d, J 6.4, $CHCH_3$). **IR** ($CHCl_3$) (υ_{max}): 3400 (O-H), 2970, 2920 (C-H), 2880, 1450, 1375, 1035, 990, 835 cm^{-1}.

8c. ^{1}**H NMR** (δ ppm): 5.18-5.04 (2H, m, Vinylic H), 3.73-3.66 (2H, m, CHOH and CH_aH_bOH), 3.48 (1H, dd, J 7.2, 11.1, CH_aH_bOH), 2.29-2.02 (6H, m, Aliphatic H), 1.69 (3H, d, J 0.9, CH_3), 1.64 (3H, d, J 0.5, CH_3), 1.61 (3H, d, J 0.7, CH_3). **IR** ($CHCl_3$) (υ_{max}): 3680, 3610, 3440 (O-H), 3020, 2970, 2920 (C-H), 1600 (C=C), 1510, 1210 (O-H), 1040, 930, 880, 850 cm^{-1}. **MS** (CI, NH_3): 198 (M^+, 2), 155 (M^+-C_3H_7, 57), 137 (M^+-$HOCHCH_2OH$, 18), 123 (M^+-$CH_2CH(OH)CH_2OH$, 56), 109 (26), 107 (35), 95 ($C_7H_{11}^+$, 79), 93 (60), 81 ($C_6H_9^+$, 100), 70 (83). **Anal.** Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.61; H, 11.29.

8d.[24] ^{1}**H NMR** (δ ppm): 7.37-7.22 (5H, m, Aromatic H), 3.97 (1H, dddd, J 3.2, 5.7, 7.0, 7.7, CH_2CHOH), 3.71 (1H, dd, J 3.2, 11.1, CH_aH_bOH), 3.53 (1H, dd, J 7.0, 11.1, CH_aH_bOH), 2.80 (1H, dd, J 5.7, 13.6, $PhCH_cH_d$), 2.78 (1H, dd, J 7.7, 13.6, $PhCH_cH_d$), 2.18 (2H, broad s, 2 x OH). **IR** ($CHCl_3$) (υ_{max}): 3400 (O-H), 2970, 2920 (C-H), 2880, 1450, 1375, 1035, 990, 835 cm^{-1}.

8e. **mp**: 94-95°C (CH_2Cl_2/Ether). ^{1}**H NMR** (δ ppm): 7.85-7.78 (3H, m, Aromatic H), 7.68 (1H, s, Aromatic H), 7.52-7.42 (2H, m, Aromatic H), 7.37 (1H, dd, J 1.7, 8.5, Aromatic H), 4.10 (1H, m, CH_2CHOH), 3.77-3.73 (1H, m, CH_aH_bOH), 3.58 (1H, dd, J 7.0, 11.0, CH_aH_bOH), 2.99 (1H, dd, J 5.6, 13.6, $PhCH_cH_d$), 2.78 (1H, dd, J 7.6, 13.6, $PhCH_cH_d$), 2.15 (1H, broad s, OH), 2.03 (1H, broad s, OH). **IR** (film) (υ_{max}): 3450 (O-H), 2940 (C-H), 1600 (C=C), 1450, 1375, 1100, 990, 835 cm^{-1}. **MS** (CI, NH_3): 220 (M^++NH_4, 4), 202 (M^+, 24), 184 (2), 142 (M^+-$HOCCH_2OH$, 100), 141 (M^+-$CH(OH)CH_2OH$, 81), 128 (15), 115 (36). **Anal.** Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.16; H, 6.88.

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Radical Allylation of α-Silylacetic Esters

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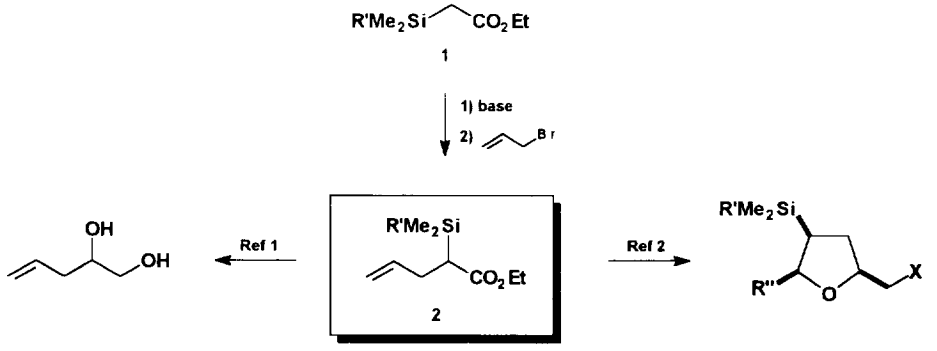
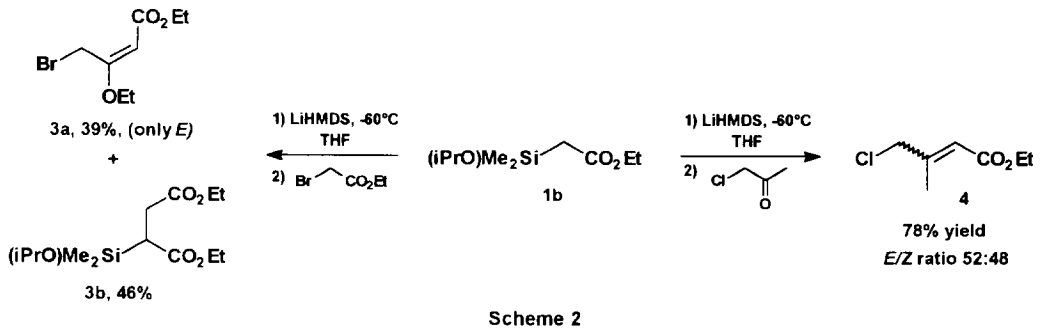
Abstract: Allylation of the radical generated from α-silyl-α-phenylselenoacetic esters with various allyltributyltin substrates led to good yields of the corresponding homoallylsilanes. A study on the nature of the radical thus generated was performed using comparative allylation rates with electronically different allyltributyltin compounds. Finally, these homoallylsilanes were converted into the corresponding homoallylic-1,2-diols after reduction of the ester function and oxidation of the C-Si bond.

Our recent investigations directed towards the development of the potential of α-silylacetic esters **1** have shown that these compounds are useful synthons for organic synthesis. We thus demonstrated that homoallylsilanes such as **2**, readily available by ionic alkylation of **1**, were important precursors in the stereocontrolled synthesis of di- and trisubstituted tetrahydrofurans and for the synthesis of homoallylic-1,2-diols (Scheme 1).[1,2] The straightforward sequence leading to **2** generally affords excellent yields of the desired ester and can be extended to various polyenic systems.[3] In order to apply our methodology to the synthesis of more complex targets, we however required an easy access to a wider range of homoallysilanes. Unfortunately, extension of this methodology to more functionalized substituted α-silylacetic esters met with some restrictions.



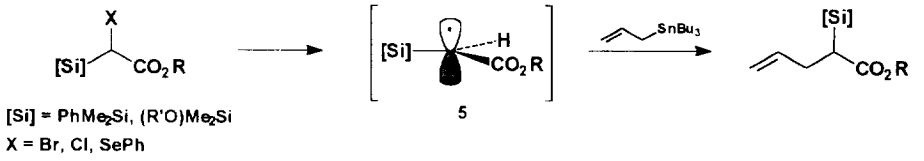
Scheme 1

For instance, alkylation of **1**, using α-chloroketone or α-bromoester resulted in the formation, to a large extent, of Peterson elimination products (e.g. **3a** and **4**) (Scheme 2).[4] Although this problem could be overcome in some cases, for instance by using sterically demanding α-haloesters,[1b] an alternative approach was deemed necessary to enhance the scope of the methodology.



Scheme 2

With this in mind, we explored the possibility of bringing about our carbon-carbon bond formation using a radical process instead of the ionic alkylation described previously.[1b] The generation of a radical and its subsequent reaction with olefins is now known as a general method for the formation of carbon-carbon bonds.[5] Among the most studied of carbon-centred radicals, α-silyl-radicals have received particular attention : their reactions with olefins offer a powerful and stereocontrolled entry to alcohol and polyol systems after the oxidative conversion of the C-Si bond into the corresponding C-OH bond.[6] Application of such a mild radical process to our approach should prevent the troublesome Peterson elimination observed during the ionic process. Therefore, the need for an alternative allylation method, and the absence in the literature of reports concerning this type of radical, prompted us to investigate more in depth the reactivity of radicals such as **5** towards olefins. Among the reactive olefins which could be used, allyltributyltin compounds arouse special interest since they allow for a radical chain reaction without the need of Bu_3SnH, which is a major advantage since it eliminates the possibility of reduction of the α-silyl radical intermediate.[7] We report herein a full account of our studies related to this radical allylations of α-silylacetic esters **1** (Scheme 3).



Scheme 3

The generation of the radical **5** can be carried out using halogeno or phenylseleno precursors.[5] Different attempts to prepare directly the corresponding α-bromo or α-chloroacetic esters using NBS or NCS respectively, led to extensive decomposition of the starting material.[8] An alternative method was found which involves the generation of an ester enolate with LiHMDS which is then quenched with CBr_4 or CCl_4,[9] producing respectively the α-chloro and α-bromo-α-silylacetic esters **6a-b**, in synthetically useful yields (Scheme 4, Table 1). In the same way, selenenylation of the enolate with PhSeCl gave the corresponding α-phenylseleno-α-silyl ester precursor **6c-e**.[10] As summarized in Table 1, the desired substrates were obtained in useful yields, but were also found to be quite sensitive, readily giving desilylated products as a result of chromatography or distillation. Therefore, they were used in the next step without further purification.