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Synthesis of α-(Alkoxysilyl)acetic Esters. A Route to 1,2 Diols.

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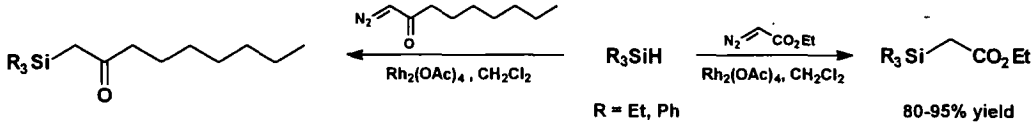
Abstract : An easy route to α-(alkoxysilyl)acetic esters and their utilization is described. It involves a two-step sequence carried out in one pot : Rhodium catalyzed Si-H insertion of a carbenoid, generated by decomposition of N_2CHCO_2Et, followed by a nucleophilic attack onto the Si-Cl bond by an alcohol. Alkylation of the title esters, reduction of the ester function and finally oxidation of the C-Si bond provide a facile entry to 1,2-diols.

α-Silyl carbonyl compounds have been mostly used as enolate equivalents[1] or as precursors of α,β-unsaturated esters and substituted ketones, generated through the Peterson elimination.[2,3] The loss of the silicon moiety in these transformations is greatly facilitated by the presence of the vicinal electron-withdrawing carbonyl group. The discovery that the silicon group could be oxidized into a hydroxyl group[4] and not just eliminated or replaced by a proton, led to a renewed interest in this class of compounds.[5]

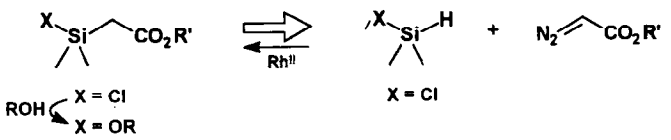
α-Silyl carbonyl compounds are accessible using different approaches, such as oxidation of β-hydroxysilanes,[6] condensation of α-silyl organometallic reagents with carbonyl compounds,[7] rearrangements[8] and C-silylation of esters, carboxylic acids, amide enolates,[9] and hydrazones.[5a,b] This last method is efficient for the preparation of α-silylamides and α-silylhydrazones but is rather limited for the preparation of α-silyl esters due to the large amount of *O*-silylation generally observed in this case. Decomposition of α-diazo carbonyl derivatives in the presence of organosilanes catalyzed by transition metal such as copper (Cu powder ou CuCl) has also been reported but generally gives low yields of the corresponding α-silylacetic esters.[10] In 1988, Doyle and co-workers reexamined this reaction and found that $Rh_2(OAc)_4$ catalyzed decomposition of α-diazocarbonyl compounds led to excellent yields of α-silylesters and α-silyl-ketones through insertion of a rhodium-carbenoid species into the Si-H bond (Scheme 1).[11]



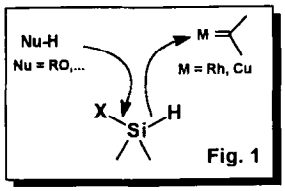
Scheme 1

From the perspective of using the silicon group on the ester fragment as a masked hydroxyl group, we thought that it might be useful to devise an approach to α-silylacetic esters possessing better nucleofugal groups on silicon, than Ph or Et groups used by Doyle et al. Tamao and co-workers effectively demonstrated that the oxidation conditions required for the conversion of a Si-OR group into a OH group are generally very mild and thus leave most functionalities untouched.[4a,b] Our first attempts to prepare α-(alkoxysilyl)acetic esters directly from $(EtO)_3SiH$ and N_2CHCO_2Et catalyzed by $Rh_2(OAc)_4$, failed to afford the desired compounds. Repeating the reaction with (*i*-PrO)Me_2SiH gave only 30% of the α-(isopropyloxydimethylsilyl)acetic ester along with dimerization products from the diazoester. As alkoxy groups might interfere with transition metal catalysis or

decrease the reactivity of the Si-H bond, we turned our attention to the readily available chlorosilanes. Chlorine should not alter the catalyst activity by coordination and can be easily displaced by alkoxy groups after the insertion process to form the desired α-(alkoxysilyl)acetic ester compounds (Scheme 2).

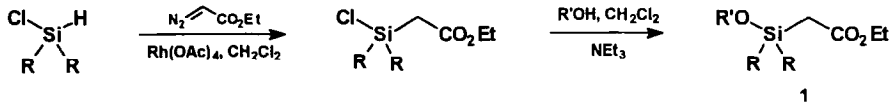


Scheme 2



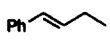
In a preliminary account, we demonstrated that the dual reactivity of chlorosilanes (Fig. 1) affords an efficient approach to the title compounds.[12a] We report herein a full description of our studies directed towards the synthesis of α-(alkoxysilyl)acetic esters and their use as precursors of 1,2-diols.

The synthesis of α-(alkoxysilyl)acetic esters was carried out in one pot (Scheme 3), by slowly adding (using a syringe pump) the α-diazoester to a mixture of chlorosilane and a catalytic amount of $Rh_2(OAc)_4$ in anhydrous CH_2Cl_2. A faster addition usually induced the dimerization of the carbenoid species and the formation of diethyl fumarate and maleate. The chlorosilane intermediate, which can be isolated in quantitative yield in most cases, was then treated with the appropriate alcohol R'OH and a base (e.g. NEt_3) in dry CH_2Cl_2. The workup and distillation gave the desired alkoxysilane in good yields as summarized in Table 1.



Scheme 3

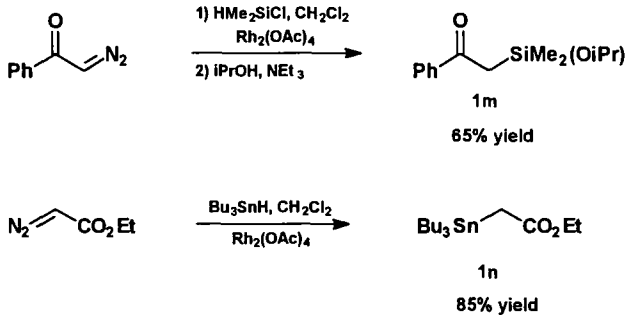
Table 1. Preparation of α-(alkoxysilyl)acetic esters 1 (Scheme 3).

Entry	Chlorosilane (R)	Alcohol (R')	Conditions[a]	Product	Yield[b]
1	Me	i-Pr	A	1a	74
2	Me	Bn	A	1b	76
3	Me	Et	A	1c	73
4	Me	t-Bu	A	1d	78
5	Me	allyl	A	1e	71
6	Ph	Et	A	1f	74
7	Ph	i-Pr	A	1g	65
8	Me		A	1h	80
9	Me		A	1i	82
10	Me		A	1j	75
11	i-Pr	Et	B	1k	70
12	t-Bu	Et	B	1l	62[c]

[a] Conditions A: R_2SiClH (1.05 eq.), $Rh_2(OAc)_4$ (0.3 mol%), N_2CHCO_2Et (1 eq.) then NEt_3 (1.2 eq.) and R'OH (1.2 eq.) in anhydrous CH_2Cl_2.
Conditions B: Insertion carried out as in Conditions A. The chlorosilane was then added to a mixture of EtOH (5 eq.), imidazole (3 eq.) and 4-DMAP (cat.) in dry DMF.

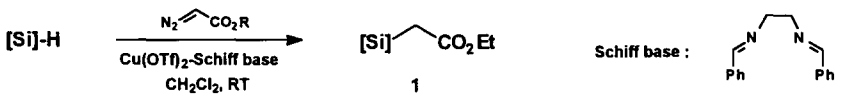
[b] Isolated yields after filtration through Florisil® or distillation. [c] Accompanied together with 20% of the corresponding silanol : ethyl-2-(di-*t*-Butylhydroxysilyl)ethanoate (see Experimental section).

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]



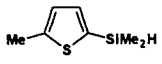
Scheme 4

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]



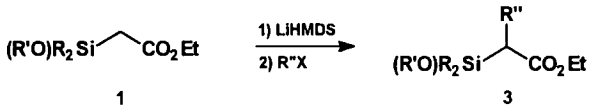
Scheme 5

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.

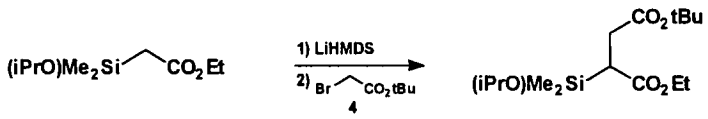
The α-silylacetic esters **1** were then alkylated and allylated via their enolates prepared with LiHMDS in THF (Scheme 6, Table 3). Different attempts to form the enolate using LDA instead of LiHMDS gave complex mixtures. This is presumably due to the presence of diisopropylamine (formed during deprotonation), 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.

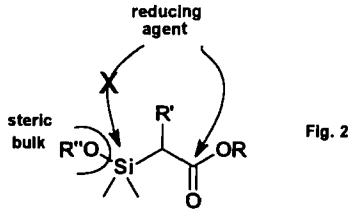


Fig. 2

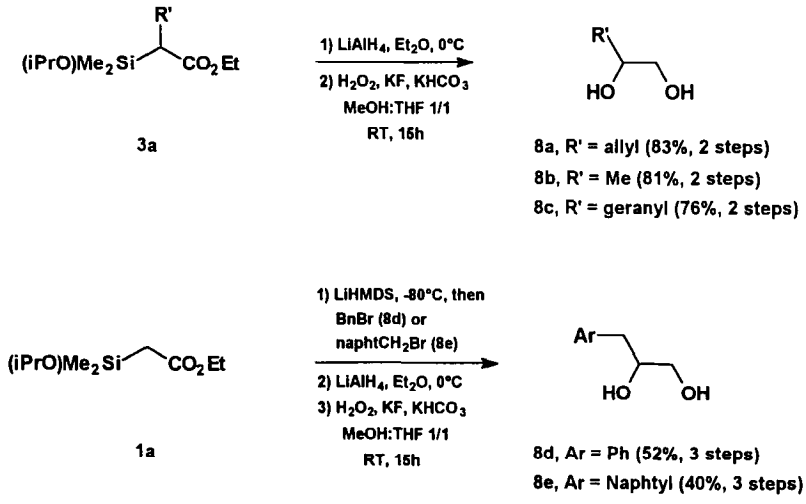
3 6 7

Scheme 8

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

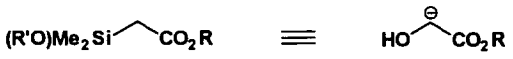
Entry	Substrate	R	R'	Conditions	Ratio (6 : 7)	Yield (%)
1	**3a**	i-Pr	allyl	$LiAlH_4$ (0.6 eq.), ether, 0°C	100 : 0	95
2	**3i**	t-Bu	allyl	$LiAlH_4$ (0.6 eq.), ether, 0°C	100 : 0	92
3	**3a**	i-Pr	allyl	$LiAlH_4$ (2 eq.), ether, reflux	0 : 100	85
4	**3l**	allyl	geranyl	$LiAlH_4$ (0.6 eq.), ether, 0°C	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 ($M^{+\cdot}$+1, 10), 161 ($M^{+\cdot}$ -*i*-Pr, 7), 145 ($M^{+\cdot}$ -*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 ($M^{+\cdot}$+1, 74), 207 ($M^{+\cdot}$-OC_2H_5, 8), 178 (16), 145 ($M^{+\cdot}$-$PhCH_2O$, 8), 108 ($PhCH_2OH$, 8), 91 ($C_7H_7^{+\cdot}$, 100), 75 ($Si(CH_3)OH^{+\cdot}$, 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 ($M^{+\cdot}$+2, 22), 191 ($M^{+\cdot}$+1, 100), 103 ($M^{+\cdot}$-$CH_2CO_2C_2H_5$, 20), 86 ($CHCO_2C_2H_5^{+\cdot}$, 10), 74 ($Si(CH_3)_2O^{+\cdot}$, 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 ($M^{+\cdot}$+1, 100), 203 ($M^{+\cdot}$-CH_3, 13), 161 ($M^{+\cdot}$-*t*-Bu, 10), 145 ($M^{+\cdot}$-$CO_2C_2H_5$ or *t*-BuO, 18), 117 (28), 105 (19), 103 (21), 92 (44), 75 ($Si(CH_3)_2OH^{+\cdot}$, 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 ($M^{+\cdot}$+1, 52), 129 ($M^{+\cdot}$-$CO_2C_2H_5$, 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 ($M^{+\cdot}$+1, 14), 314 ($M^{+\cdot}$, 9), 269 ($M^{+\cdot}$-OC_2H_5, 13), 254 (46), 237 ($M^{+\cdot}$-C_6H_5, 100), 227 ($Ph_2SiOC_2H_5^{+\cdot}$, 49), 199 ($Ph_2SiOH^{+\cdot}$, 18),

195 (39), 183 (30), 105 (14), 77 ($C_6H_5^{+\cdot}$, 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_3CHCH_3), 3.93 (2H, q, J 7.1, $CO_2CH_2CH_3$), 2.53 (2H, s, $SiCH_2$), 1.20 (6H, d, J 6.1, CH_3CHCH_3), 1.02 (3H, t, J 7.1, $CO_2CH_2CH_3$). **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 ($M^{+\cdot}$+1, 17), 328 ($M^{+\cdot}$, 7), 285 ($M^{+\cdot}$-*i*-Pr, 10), 269 ($M^{+\cdot}$-*i*-PrO, 16), 268 (49), 252 (30), 251 ($M^{+\cdot}$-C_6H_5, 100), 241 (60), 227 (20), 222 (19), 209 (39), 199 (70), 183 (16), 105 (14), 91 ($C_7H_7^{+\cdot}$, 15), 77 ($C_6H_5^{+\cdot}$, 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, $CO_2CH_2CH_3$), 2.65 (1H, s, OH), 2.0 (2H, s, $SiCH_2$), 1.26 (3H, t, J 7.1, $CO_2CH_2CH_3$), 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 ($M^{+\cdot}$+1, 100), 217 ($M^{+\cdot}$-C_2H_5, 11), 206 (11), 201 ($M^{+\cdot}$-OC_2H_5, 28), 189 ($M^{+\cdot}$-*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=CH), 4.23-4.13 (2H, m, CH_2OSi), 4.10 (2H, q, J 7.1, $CO_2CH_2CH_3$), 2.02 (2H, s, $SiCH_2$), 1.72 (3H, d, J 1.0, CH_3C=CH), 1.65 (3H, s, CH_3C=CH), 1.24 (3H, t, J 7.1, $CO_2CH_2CH_3$), 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 ($M^{+\cdot}$+1, 3), 230 ($M^{+\cdot}$, 4), 219 (11), 180 (44), 163 ($M^{+\cdot}$-C_5H_7, 47), 145 ($(CH_3)_2SiCH_2CO_2C_2H_5^{+\cdot}$, 25), 127 (10), 117 (18), 103 (32), 92 (43), 85 (29), 83 (48), 75 ($(CH_3)_2SiOH^{+\cdot}$, 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=CH), 5.14 (1H, dd, J 1.3, 17.3, CH_aH_b=CH), 4.96 (1H, dd, J 1.3, 10.6, CH_aH_b), 4.09 (2H, q, J 7.1, $CO_2CH_2CH_3$), 1.99 (2H, s, $SiCH_2$), 1.32 (6H, s, 2 CH_3), 1.24 (3H, t, J 7.1, $CO_2CH_2CH_3$), 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 ($M^{+\cdot}$+1, 11), 219 (33), 215 ($M^{+\cdot}$-CH_3, 13), 187 (12), 180 (47), 163 ($M^{+\cdot}$-C_5H_7, 54), 145 ($(CH_3)_2SiCH_2CO_2C_2H_5^{+\cdot}$, 21), 117 (13), 103 (21), 92 (27), 87 ($CH_2CO_2C_2H_5^{+\cdot}$, 11), 75 ($(CH_3)_2SiOH^{+\cdot}$, 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, PhCH), 6.29 (1H, dt, J 5.4, 15.8, $CHCH_2O$), 4.39 (2H, dd, J 1.5, 5.4, CH_2OSi), 4.12 (2H, q, J 7.1, $CO_2CH_2CH_3$), 2.07 (2H, s, $SiCH_2$), 1.25 (3H, t, J 7.1, $CO_2CH_2CH_3$), 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 ($M^{+\cdot}$+1, 3), 236 (5), 233 ($M^{+\cdot}$-C_2H_5O, 6), 205 ($M^{+\cdot}$-$CO_2C_2H_5$, 18), 204 (14), 191 ($M^{+\cdot}$-$CH_2CO_2C_2H_5$, 11), 146 ($M^{+\cdot}$-PhCH=$CHCH_2OH$, 25), 145 ($M^{+\cdot}$-PhCH=$CHCH_2O$, 42), 118 (53), 117 ($PhCH{=}CHCH_2^{+\cdot}$, 100), 116 (23), 115 (30), 104 (39), 103 (69), 92 (20), 91 (102 (11), 97 (13), 95 (12), 92 (12), 91 ($C_7H_7^{+\cdot}$, 28), 77 ($C_6H_5^{+\cdot}$, 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, $CO_2CH_2CH_3$), 3.79 (2H, q, J 6.9, $SiOCH_2CH_3$), 2.02 (2H, s, $SiCH_2$), 1.25 (3H, t, J 7.1, $CO_2CH_2CH_3$), 1.20 (3H, t, J 6.9, $SiOCH_2CH_3$), 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 ($M^{+\cdot}$+1, 100), 246 ($M^{+\cdot}$, 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, $CO_2CH_2CH_3$), 3.90 (2H, q, J 7.0, $SiOCH_2CH_3$), 2.06 (2H, s, $SiCH_2$), 1.26 (3H, t, J 7.1, $CO_2CH_2CH_3$), 1.20 (3H, t, J 7.0, $SiOCH_2CH_3$), 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 ($M^{+\cdot}$+1, 52), 274 ($M^{+\cdot}$, 7), 229 ($M^{+\cdot}$-C_2H_5O, 27), 217 ($M^{+\cdot}$-C_4H_9, 100), 87 ($CH_2CO_2C_2H_5^{+\cdot}$, 12), 86 ($CHCO_2C_2H_5^{+\cdot}$, 21), 73 ($CO_2C_2H_5^{+\cdot}$, 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 ($PhSi(CH_3)_2^{+\cdot}$, 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 $\underline{H}$-3), 6.86-6.84 (1H, m, Thiophene $\underline{H}$-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 $\underline{H}$-3), 6.86-6.85 (1H, m, Thiophene $\underline{H}$-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 ($M^{+\cdot}$-*t*-Bu, 11), 185 ($M^{+\cdot}$-$CO_2C_2H_5$ or *t*-BuO, 10), 92 (23), 82 (23), 81 (22), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100), 74 ($Si(CH_3)_2O^{+\cdot}$, 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 ($M^{+\cdot}$, 52), 299 ($M^{+\cdot}$-C_2H_5, 19), 283 ($M^{+\cdot}$-C_2H_5O, 24), 255 ($M^{+\cdot}$-$CO_2C_2H_5$, 19), 244 (51), 227 ($M^{+\cdot}$-$(C_2H_5O)SiPh_2$, 100), 199 ($Ph_2SiOH^{+\cdot}$, 39), 183 (66), 167 (16), 105 (26), 91 ($C_7H_7^{+\cdot}$, 10), 77 ($C_6H_5^{+\cdot}$, 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 ($M^{+\cdot}$+2, 21), 287 ($M^{+\cdot}$+1, 32), 286 ($M^{+\cdot}$, 6), 231 ($M^{+\cdot}$-C_4H_7, 52), 229 ($M^{+\cdot}$-*t*-Bu, 10), 213 ($M^{+\cdot}$-$CO_2C_2H_5$ or *t*-BuO, 27), 212 (26), 184 (9), 154 (7), 129 (7), 109 (36), 95 (32), 75 ($(CH_3)_2SiOH^{+\cdot}$, 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 ($M^{+\cdot}$+1, 39), 338 ($M^{+\cdot}$, 9), 293 ($M^{+\cdot}$-C_2H_5O, 36), 280 (34), 265 ($M^{+\cdot}$-$CO_2C_2H_5$, 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 ($(CH_3)_2SiOH^{+\cdot}$, 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 ($M^{+\cdot}$+1, 31), 340 ($M^{+\cdot}$, 6), 295 ($M^{+\cdot}$-C_2H_5O, 12), 281 ($M^{+\cdot}$-*i*-PrO, 6), 266 (9), 212 (21), 211 (20), 183 (7), 117 (25), 92 (19), 81 (37), 75 ($(CH_3)_2SiOH^{+\cdot}$, 100), 74 ($(CH_3)_2SiO^{+\cdot}$, 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 ($M^{+\cdot}$+1, 67), 270 ($M^{+\cdot}$, 7), 255 ($M^{+\cdot}$-CH_3, 17), 225 ($M^{+\cdot}$-C_2H_5O, 50), 213 ($M^{+\cdot}$-AllylO, 33), 212 (31), 195 (29), 183 ($M^{+\cdot}$-$CH_2CO_2C_2H_5$, 13), 129 (11), 115 (35), 103 (30), 99 (28), 83 (42), 81 (41), 75 ($(CH_3)_2SiOH^{+\cdot}$, 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 ($M^{+\cdot}$, 1), 259 ($M^{+\cdot}$-*i*-PrO, 41), 245 ($M^{+\cdot}$-$CO_2C_2H_5$, 12), 220 (33), 217 (48), 203 ($M^{+\cdot}$-CH_2CO_2*t*-Bu, 100), 202 (42), 175 (8), 147 (5), 129 (25), 117 (11), 103 (12), 92 (12), 75 ($(CH_3)_2SiOH^{+\cdot}$, 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 ($M^{+\cdot}$+1, 14), 174 (6), 119 ($C_5H_{15}OSi^{+\cdot}$, 24), 117 ($M^{+\cdot}$-CH(allyl)CH_2OH, 13),

98 (36), 94 (29), 93 (34), 89 (C_3H_9OSi, 12), 85 (CH(allyl)$CH_2OH^{+\cdot}$, 13), 77 (50), 75 ($HOSi(CH_3)_2^{+\cdot}$, 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, $CH_2C\underline{H}$), 5.09-4.95 (2H, m, $C\underline{H}_2CH$), 3.81-3.68 (2H, m, $C\underline{H}_2OH$), 3.08 (1H, broad s, OH), 2.15-2.03 (2H, m, $SiCHC\underline{H}_2$), 1.25 (9H, s, *t*-Bu), 0.94-0.88 (1H, m, $SiC\underline{H}$), 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 ($M^{+\cdot}$+1, 22), 178 (12), 133 ($C_6H_{17}OSi^{+\cdot}$, 18), 94 (20), 93 (21), 92 (79), 91 (17), 85 (CH(allyl)$CH_2OH^{+\cdot}$, 20), 83 (32), 77 (49), 76 (36), 75 ($HOSi(CH_3)_2^{+\cdot}$, 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, $CH_2C\underline{H}$), 5.13-4.98 (2H, m, $C\underline{H}_2CH$), 3.89-3.79 (1H, m, SiH), 3.79 (1H, dd, J 5.0, 10.8, $C\underline{H}_aH_bOH$), 3.72 (1H, dd, J 7.5, 10.8, $CH_a\underline{H}_bOH$), 2.36-2.17 (2H, m, $SiCHC\underline{H}_2$), 1.19-1.06 (1H, m, $SiC\underline{H}$), 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, $C\underline{H}_2OH$), 2.24-2.17 (2H, m, $SiCHC\underline{H}_2$), 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, $SiC\underline{H}$), 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 ($M^{+\cdot}$+NH_4, 11), 240 ($M^{+\cdot}$, 7), 223 ($M^{+\cdot}$-OH, 31), 109 (6), 92 (23), 91 (20), 81 ($C_6H_9^{+\cdot}$, 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, $CH_2C\underline{H}$), 5.30-5.10 (2H, m, $C\underline{H}_2CH$), 3.82-3.73 (1H, m, $C\underline{H}OH$), 3.66 (1H, dd, J 3.1, 11.3, $C\underline{H}_aH_bOH$), 3.47 (1H, dd, J 7.4, 11.3, $CH_a\underline{H}_bOH$), 2.77 (2H, broad s, 2 x OH), 2.27-2.20 (2H, m, $CHC\underline{H}_2CHOH$). **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, $CH_3C\underline{H}OH$), 3.64 (1H, dd, J 2.9, 11.0, $C\underline{H}_aH_bOH$), 3.40 (1H, dd, J 7.8, 11.0, $CH_a\underline{H}_bOH$), 2.51 (2H, broad s, 2 x OH), 1.17 (3H, d, J 6.4, $CHC\underline{H}_3$). **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, $C\underline{H}OH$ and $C\underline{H}_aH_bOH$), 3.48 (1H, dd, J 7.2, 11.1, $CH_a\underline{H}_bOH$), 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 ($M^{+\cdot}$, 2), 155 ($M^{+\cdot}$-C_3H_7, 57), 137 ($M^{+\cdot}$-HOCHCH$_2$OH, 18), 123 ($M^{+\cdot}$-$CH_2CH(OH)CH_2OH$, 56), 109 (26), 107 (35), 95 ($C_7H_{11}^{+\cdot}$, 79), 93 (60), 81 ($C_6H_9^{+\cdot}$, 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, $CH_2C\underline{H}OH$), 3.71 (1H, dd, J 3.2, 11.1, $C\underline{H}_aH_bOH$), 3.53 (1H, dd, J 7.0, 11.1, $CH_a\underline{H}_bOH$), 2.80 (1H, dd, J 5.7, 13.6, $PhC\underline{H}_cH_d$), 2.78 (1H, dd, J 7.7, 13.6, $PhCH_c\underline{H}_d$), 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, $CH_2C\underline{H}OH$), 3.77-3.73 (1H, m, $C\underline{H}_aH_bOH$), 3.58 (1H, dd, J 7.0, 11.0, $CH_a\underline{H}_bOH$), 2.99 (1H, dd, J 5.6, 13.6, $PhC\underline{H}_cH_d$), 2.78 (1H, dd, J 7.6, 13.6, $PhCH_c\underline{H}_d$), 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 ($M^{+\cdot}$+NH_4, 4), 202 ($M^{+\cdot}$, 24), 184 (2), 142 ($M^{+\cdot}$-HOCCH$_2$OH, 100), 141 ($M^{+\cdot}$-$CH(OH)CH_2OH$, 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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