Highly Selective *C*-Silylation of Fatty Acid Methyl Esters

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New silylated saturated and unsaturated fatty acid methyl esters (FAMEs) possessing a hydrophobic frame and a hydrophilic core were prepared. *C*-silylations of the ester group were achieved either by treating FAMEs with various alkyl- and chlorosilyl triflates or by subjecting various chlorosilanes to reaction with the corresponding FAME lithium enolates. Both routes led to the exclusive formation of one isomer identified as the *C*-silylated form on the basis of the analytical results.

Introduction

In recent years, much attention has been directed to functional silicones[1] as sources of novel materials (conductive[2] and electroluminescent[3] polymers, nonlinear optical materials,[4] and liquid crystals[5]). The development of organosilicon polymer chemistry has required not only new synthetic methods for generating specific chains but also appropriate substituents on the silicon atom. Indeed, chemical and physical properties are directly determined by the substituents (or side chains) linked to the silicon of the siloxane backbone. This has stimulated research and has resulted in a flurry of materials based on functional polysiloxanes. Surprisingly, despite the abundant literature on this topic, there is, to the best of our knowledge, no report on side chains incorporating FAMEs. Fatty-acid derivatives have been shown to exhibit unique properties of self-organization,[6] surface adsorption and, more obviously, biocompatibility, since they display characteristics that are nearly identical to those of oils and fats from plants and animals. In addition, oils and fats are among the most important renewable raw materials for the chemical industry and are thus of great significance for economic and ecological reasons.[7]

Hitherto, the efforts of industrial oleochemistry have mainly concentrated on the carboxy functionality of fatty-acid derivatives, but more recently, a variety of studies have been conducted on the selective functionalization of the alkyl chain. For example, various radical, electrophilic, nucleophilic, and pericyclic additions to the C–C double bond of unsaturated fatty-acid derivatives have led to a series of new fatty compounds.[8] Moreover, transition-metal-catalyzed hydrosilylation of olefins, which has been the methodology of choice to attach an organic group on a chain,[9] has also been explored in the case of fatty compounds.[10] In this context, we recently reported the syntheses of organohalosilyl FAMEs by hydrosilylation of unsaturated FAMEs (methyl undecenoate and 9-methyl oleate) for the preparation of ambiphilic polysiloxanes.[11] This study has allowed silylation both at the terminal and at various internal positions of the FAMEs. In contrast, the functionalization of the saturated hydrocarbon chain has been poorly developed and remains a stimulating challenge, in particular for saturated aliphatic fatty acids, since they are present in non-negligible amounts in oils and fats. Among the methylene groups, the one located α to a carboxy functionality possesses higher reactivity, but has only been exploited in halogenations, sulfonations, the Guerbet reaction, and Claisen condensations.[7] We herein describe a new, selective, and general strategy of silylation of FAMEs in the α position to the carboxy functionality.

Results and Discussion

α-Silylation of FAMEs by Using Silyl Triflates

The use of trialkylsilyl triflates for the silylation of aldehydes and ketones is well known,[12] and it was shown that these reactions are accelerated in the presence of triethylamine and preferentially lead to trialkylsilylenol ethers.[13] In the case of carboxylic acid esters, the two *O*- and *C*-silyl forms are obtained depending on the structures of the acyl and alkoxy groups.[12,13] The reaction probably proceeds through a six-membered transition state leading to the ketene acetal (Scheme 1). Rearrangements of ketene *O*-trimethylsilyl acetals to give the trimethylsilyl carboxylates are observed if the mesomerism of alkoxycarbonyl groups is not disturbed by electronic or steric effects.

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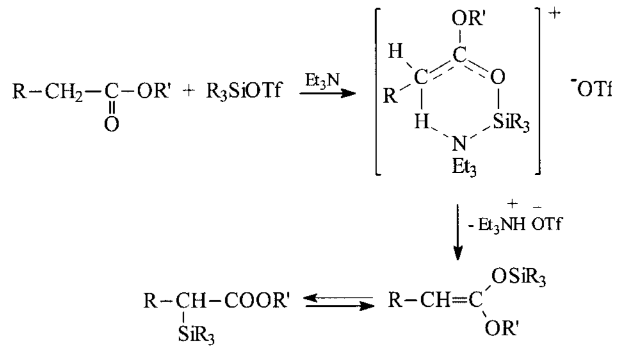


Scheme 1.

Similarly, the use of an excess of trialkylsilyl triflate results in the conversion of the *O*-silylated product into the *C*-silylated one.[14]

Before testing these reactions with FAMEs, we first synthesized a series of functionalized silyl triflates. They were prepared by treating stoichiometric amounts of triflic acid with various phenylsilanes[15–18] by substitution of the phenyl by a trifluoromethanesulfonyl group [Equation (1)]. They were generated in situ and used immediately after evaporation of the benzene.

$$Z_3SiPh + TfOH \longrightarrow Z_3SiOTf + C_6H_6$$

$Z_3Si = Me_2HSi, MeH_2Si, Me_2ClSi, MeCl_2Si$ (1)

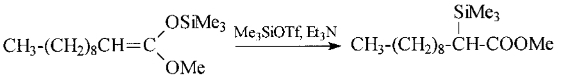
Compared to organic esters, the silylation of saturated FAMEs (methyl undecanoate and methyl palmitate) required a longer reaction time and the use of excess (4 equiv.) Me_3SiOTf in the presence of triethylamine at room temperature. Using these reaction conditions, high yields of silylated compounds were obtained [Equation (2)].

$$CH_3\text{-}(CH_2)_n\text{-}CH_2\text{-}COOMe + Me_3SiOTf \xrightarrow[\text{- }Et_3N,\ HOTf]{Et_3N,\ ether} CH_3\text{-}(CH_2)_n\text{-}CH(SiMe_3)\text{-}COOMe$$

1: $n = 8$ (67%)
2: $n = 13$ (75%) (2)

Silyl compounds **1** and **2** were isolated as analytically pure liquids by distillation. The analyses (^1H, ^{13}C and ^{29}Si NMR and IR) revealed the exclusive formation of one isomer: the *C*-silylated derivative. In the ^1H NMR spectra, we effectively observed the disappearance of the characteristic signal of the CH_2CO group (triplet) at 2.20–2.30 ppm and the appearance of a new signal at $\delta = 1.95$ ppm assigned to the Me_3SiCH group. The ^{13}C NMR and IR studies unequivocally established the presence of the ester function, as evidenced by the resonance of the carbonyl groups at $\delta = 174$ ppm and the strong absorption at 1715 cm^{-1}. ^{29}Si NMR resonances were observed in the expected region for alkylated silicon atoms ($\delta = 7.0$ ppm). The elemental analyses and mass spectra were also consistent with a silylation reaction.

The prevalence of the *C*-silylated form probably results from the use of excess silyl triflate, as was previously mentioned in the case of aliphatic esters.[14] We have verified that adding the complex, trimethylsilyl triflate/triethylamine, to the *O*-silylated [(*Z*) isomer] compound, which was prepared separately, gave the *C*-silylated form **1** quantitatively, in good yield [Equation (3)].



$$CH_3\text{-}(CH_2)_8CH{=}C(OSiMe_3)(OMe) \xrightarrow{Me_3SiOTf,\ Et_3N} CH_3\text{-}(CH_2)_8\text{-}CH(SiMe_3)\text{-}COOMe$$

1 (3)

Ab initio calculations (RHF, 6-31G*) were performed in order to evaluate the influence of the length of the alkyl chain on the difference of energy between silyl carboxylates and ketene acetals [(*Z*) isomers] (R = methyl and longer alkyl chain). The *C*-silylated isomer was found to be slightly more stable compared to the *O*-silylated form regardless of the length of the chain (Table 1). This observation is consistent with previous results from the ketone or carboxylic acid ester series.[12]

Table 1. Relative energies of *C*- and *O*-silylated compounds.

$R\text{–}CH(SiMe_3)\text{–}COOMe$ $R\text{–}CH{=}C(OSiMe_3)(OMe)$

C-silylated compound *O*-silylated compound[a]

R	Δ*E* (kcal/mol)[b]
CH_3	–5.19
$CH_3\text{–}CH_2$	–3.22
$CH_3\text{–}(CH_2)_2$	–5.29
$CH_3\text{–}(CH_2)_3$	–3.13
$CH_3\text{–}(CH_2)_8$	–3.16
$CH_3\text{–}(CH_2)_{13}$	–3.16

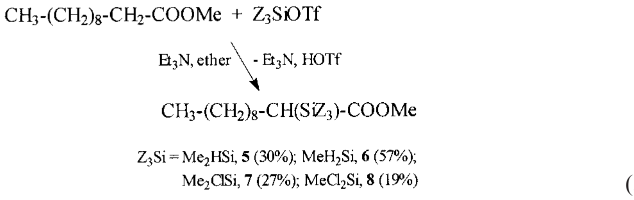
[a] (*Z*) isomer. [b] $\Delta E = E_{(C\text{-silylated})} - E_{(O\text{-silylated})}$.

In the case of unsaturated FAMEs (*cis*-oleate and *cis*-linoleate), the reaction with excess Me_3SiOTf also led to the corresponding α-silylated compounds. Compounds **3** and **4** contained the same olefin geometry as the parent substrate [Equation (4)].

$$R\text{-}CH{=}CH\text{-}(CH_2)_6\text{-}CH_2\text{-}COOMe + Me_3SiOTf \xrightarrow[\text{- }Et_3N,\ HOTf]{Et_3N,\ ether} R\text{-}CH{=}CH\text{-}(CH_2)_6\text{-}CH(SiMe_3)\text{-}COOMe$$

3: $R = CH_3\text{-}(CH_2)_7$ (71%)
4: $R = CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2$ (60%) (4)

In the case of methyl undecanoate, this reaction can be extended to various silicon-functionalized silyl triflates. The same work-up procedure resulted in the exclusive formation of the *C*-silylated compounds, but with moderate yield [Equation (5)]. The chlorosilyl triflates are shown to be curiously less reactive than their hydrosilyl analogues. This low yield may be attributed on one hand to their lower thermal stability and on the other hand to the side reaction with triethylamine showing the difficulty of using chlorosilyl triflate for such reactions.



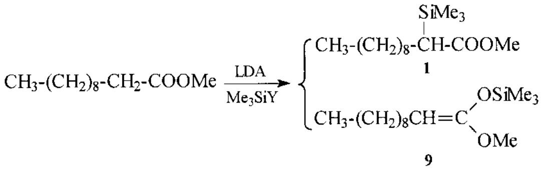
$$CH_3\text{-}(CH_2)_8\text{-}CH_2\text{-}COOMe + Z_3SiOTf \xrightarrow[\text{- }Et_3N,\ HOTf]{Et_3N,\ ether} CH_3\text{-}(CH_2)_8\text{-}CH(SiZ_3)\text{-}COOMe$$

$Z_3Si = Me_2HSi$, **5** (30%); MeH_2Si, **6** (57%); Me_2ClSi, **7** (27%); $MeCl_2Si$, **8** (19%) (5)

α-Silylation of FAMEs from the Corresponding Lithium Enolates

As triflates are reactive and not easy to handle from an industrial standpoint, we tried to prepare some of the α-silylated FAMEs, already obtained by the triflate method, by treating chlorosilanes with the corresponding lithium enolates. The best method to prepare FAME lithium enolates is to react the FAME with LDA.[19] Less bulky lithium amides undergo a modification of the ester function to the amide function,[20] and the alkyllithiums lead to alkylation of the carbonyl group.

In the case of methyl undecanoate, lithium enolates gave *O*- and/or *C*-silylation depending on the trimethylhalosilanes (chloro-, bromo-, and iodosilane) [Equation (6)] (Table 2).



$$CH_3\text{-}(CH_2)_8\text{-}CH_2\text{-}COOMe \xrightarrow[Me_3SiY]{LDA} \begin{cases} CH_3\text{-}(CH_2)_8\text{-}CH(SiMe_3)\text{-}COOMe & \mathbf{1} \\ CH_3\text{-}(CH_2)_8CH{=}C(OSiMe_3)(OMe) & \mathbf{9} \end{cases} \quad (6)$$

Table 2. Halosilane effect on the silylation of methyl undecanoate.

Halosilane	Solvent	Reaction time (h)[a]	**1/9** (%)
Me_3SiCl	THF	24	18:72
Me_3SiCl	THF/HMPA[b]	6	0:100
Me_3SiBr	THF	12	77:23
Me_3SiI	THF	4	100:0

[a] Reaction time of the silylation, for the reaction conditions see the Experimental Section. [b] HMPA: hexamethylphosphoramide.

Whereas the reaction with bromosilane was nonselective, Me_3SiI led to the *C*-silylated product, and Me_3SiCl gave the *O*-silylated compound as the exclusive product, thus revealing the dramatic effect of the halogen. In addition, in the case of Me_3SiCl, changing the solvent from THF to THF–HMPA leads to selective *O*-silylation. A drastic effect of the solvent was previously reported with the reaction of methyldiphenylchlorosilane with lithium ester enolates which gave *C*-silylation in THF and *O*-silylation in THF–HMPA.[21] After isolation of the *O*-silylated product **9**, comparison of the ^1H and ^{13}C NMR with literature data[22] revealed the exclusive formation of the (*Z*) isomer. The silylation of esters depends on several factors: (1) the choice of halosilane and the ester and (2) the reaction conditions (lithiating reagent, solvent, reaction temperature, addition mode, reaction time etc.). Optimal conditions to obtain *C*-silylation products selectively are the choice of organochlorosilane, THF as solvent, iPr_2NLi as lithiating reagent, low temperature (–78 °C) to avoid Claisen's condensation.[19] A reaction time of at least four hours at –78 °C is necessary for preparing the lithiated FAME. Following this procedure, compounds **5**, **7**, and **8** were obtained in higher yields [Equation (7)] relative to those obtained previously by reaction with silyl triflates.

$$CH_3\text{-}(CH_2)_8\text{-}CH_2\text{-}COOMe \xrightarrow[2\text{ - }Z_3SiCl]{1\text{ - }LDA} CH_3\text{-}(CH_2)_8\text{-}CH(SiZ_3)\text{-}COOMe$$

$Z_3Si = Me_2HSi$, **5** (67%); Me_2ClSi, **7** (41%); $MeCl_2Si$, **8** (61%) (7)

In the case of methyl palmitate, the α-silylated FAME is formed in good yield [Equation (8)].

$$CH_3(CH_2)_{13}\text{-}CH_2COOMe \xrightarrow[2\text{ - }Me_2HSiCl]{1\text{ - }LDA} CH_3(CH_2)_{13}\text{-}CH(SiHMe_2)COOMe$$

10 (66%) (8)

In conclusion, we have developed facile and selective routes for *C*-silylation in the α position of the carbonyl group of FAMEs. Moreover, these methodologies allow unsaturated carbon–carbon bonds to remain intact and could be generalized for use with unsaturated FAMEs. In addition, the introduction of the functionalized halosilylated moiety on FAME opens up the scope of this reaction to access new FAME-substituted polysiloxanes.

Experimental Section

All reactions were performed under nitrogen using standard Schlenk tube techniques and dry solvents. NMR spectra were recorded with Bruker AC 250 (250.13 MHz) and AC 300 (300.13 MHz) (^1H), AC 250 (62.89 MHz) and AC 300 (75.47 MHz) (^{13}C), and AC 300 (133.71 MHz) (^{29}Si) spectrometers. Mass spectra were recorded with a Hewlett Packard HP5989 spectrometer in the EI mode or a Rybermag R10–10 spectrometer operating in the EI mode. Infrared spectra were recorded with a Perkin–Elmer 1600FT spectrometer. Elemental analyses were done at the Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse. Ab initio calculations have been performed with the program GAMESS[23a] using HF/6-31G* basis sets.[23b] Zero-point vibrational energies were included in the relative energies. Harmonic frequency calculations HF/6-31G* were also performed to establish whether a given conformer is at an energy minimum. The FAMEs and halosilanes were purchased from commercial sources (Aldrich or Acros). All the silanes were distilled before use. The silyl triflates were prepared according to the published procedures: $Me_2HSiOTf$,[16] MeH_2SiOTf,[17] $MeCl_2SiOTf$[18] (OTf: OSO_2CF_3).

$Me_2ClSiOTf$: Triflic acid (1.20 g, 8 mmol) was added dropwise to chlorodimethylphenylsilane (1.37 g, 8 mmol). After stirring for

10 min at ambient temperature, the produced benzene was removed at reduced pressure, and the resulting silyl triflate was analyzed. ^{1}H NMR (200 MHz, C_6D_6, 20 °C): δ = 0.15 (s, 6 H, SiMe$_2$) ppm. ^{13}C NMR (62.89 MHz, C_6D_6, 20 °C): δ = 2.01 (SiMe$_2$), 118.86 (q, $^{1}J_{\mathrm{C,F}}$ = 317.8 Hz, CF$_3$) ppm. ^{29}Si NMR (133.71 MHz, C_6D_6, 20 °C): δ = 28.44 ppm.

2-Trimethylsilylmethyl Undecanoate (1): Et$_3$N (3.32 g, 32.80 mmol) was added dropwise to a solution of trimethylsilyl triflate (7.30 g, 32.80 mmol) in diethyl ether (8 mL). The mixture was cooled to 0 °C, and a solution of methyl undecanoate (1.64 g, 8.20 mmol) in diethyl ether (3 mL) was then added. The mixture was left at 0 °C whilst stirring for 3 h then at room temperature for 48 h. After filtration, the filtrate was distilled to give **1** as colorless liquid. Yield: 1.50 g (67%). B.p. 102 °C/0.08 Torr. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): δ = 0.02 (s, 9 H, SiMe$_3$), 0.80 (t, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, CH_3-CH$_2$), 1.16–1.20 [m, 16 H, (CH_2)$_8$], 1.91 (t, $^{3}J_{\mathrm{H,H}}$ = 5.6 Hz, 1 H, CHSiMe$_3$), 3.55 (s, 3 H, OCH_3) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 20 °C): δ = –2.81 (SiMe_3), 14.07 (CH$_3$), 22.64, 22.71, 24.67, 26.73, 29.31, 29.61, 30.52, 31.95 (CH$_2$)$_8$, 37.71 (CHSiMe$_3$), 50.75 (OCH$_3$), 175.92 (CO) ppm. ^{29}Si NMR (133.71 MHz, CDCl$_3$, 20 °C): δ = 7.23 ppm. IR (CDCl$_3$): $\tilde{\nu}$ = 1716 (C=O) cm^{-1}. MS (EI): *m*/*z* = 272 [M$^+$]. $C_{15}H_{32}O_2Si$ (272.50): calcd. C 66.11, H 11.84; found C 66.10, H 12.10.

2-Trimethylsilylmethyl Palmitate (2): Following the same procedure as that described for compound **1**, a mixture of triethylamine (3.32 g, 32.80 mmol), trimethylsilyl triflate (7.30 g, 32.80 mmol), and methyl palmitate (2.22 g, 8.20 mmol) gives compound **2**. Yield: 2.81 g (75%). B.p. 118 °C/0.01 Torr. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): δ = 0.02 (s, 9 H, SiMe$_3$), 0.84 (t, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, CH_3-CH$_2$), 1.14–1.42 [m, 26 H, (CH_2)$_{13}$], 1.94 (t, $^{3}J_{\mathrm{H,H}}$ = 5.8 Hz, 1 H, CHSiMe$_3$), 3.59 (s, 3 H, OCH_3) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 20 °C): δ = –2.83 (SiMe_3), 14.10 (CH$_3$), 22.71, 25.06, 26.81, 29.25, 29.34, 29.46, 29.71, 30.65, 31.96 (CH$_2$)$_{13}$, 37.73 (CHSiMe$_3$), 50.81 (OCH$_3$), 175.84 (CO) ppm. ^{29}Si NMR (133.71 MHz, CDCl$_3$, 20 °C): δ = 7.13 ppm. IR (CDCl$_3$): $\tilde{\nu}$ = 1719 (C=O) cm^{-1}. MS (EI): *m*/*z* = 342 [M$^+$]. $C_{20}H_{42}O_2Si$ (342.63): calcd. C 70.11, H 12.36; found C 70.07, H 12.75.

Action of Excess Trimethylsily Triflate on the Trimethylsilyl Ketene Acetal: Triethylamine (0.54 g, 5.34 mmol) was added dropwise to a solution of trimethylsilyl triflate (1.18 g, 5.34 mmol) in diethyl ether (1 mL). The mixture was cooled to 0 °C, and a solution of trimethylsilyl ketene acetal (1.04 g, 3.81 mmol) in diethyl ether (1.5 mL) was then added. The mixture was left at 0 °C whilst stirring for 3 h and then at room temperature for 24 h. After filtration, the filtrate was analyzed by ^{1}H and ^{29}Si NMR spectroscopy, which showed the exclusive formation of **1**.

2-Trimethylsilylmethyl Oleate (3): Following the same procedure as that described for compound **1**, a mixture of triethylamine (3.32 g, 32.80 mmol), trimethylsilyl triflate (7.30 g, 32.80 mmol), and methyl oleate (2.43 g, 8.20 mmol) gives compound **3**. Yield: 2.15 g, (71%). B.p. 157 °C/0.25 Torr. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): δ = 0.04 (s, 9 H, SiMe$_3$), 0.85 (t, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, CH_3-CH$_2$), 1.18–1.34 [m, 22 H, (CH_2)$_5$ and (CH_2)$_6$], 1.95 (t, $^{3}J_{\mathrm{H,H}}$ = 5.6 Hz, 1 H, CHSiMe$_3$), 1.92–1.94 (m, 4 H, CH_2-CH=CH), 3.60 (s, 3 H, OCH_3), 5.28–5.40 (m, 2 H, CH=CH) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 20 °C): δ = –2.76 (SiMe_3), 14.13 (CH$_3$), 22.71, 25.23, 27.37, 27.45, 29.28, 29.47, 29.61, 29.87, 31.90 [(CH$_2$)$_7$ and (CH$_2$)$_6$], 37.75 (CHSiMe$_3$), 50.81 (OCH$_3$), 129.75, 129.92 (CH=CH), 175.84 (CO) ppm. ^{29}Si NMR (133.71 MHz, CDCl$_3$, 20 °C): δ = 7.06 ppm. IR (CDCl$_3$): $\tilde{\nu}$ = 1723 (C=O), 1462 (C=C) cm^{-1}. MS (EI): *m*/*z* = 368 [M$^+$]. $C_{22}H_{44}O_2Si$ (368.67): calcd. C 71.67, H 12.03; found C 71.82, H 12.15.

2-Trimethylsilylmethyl Linoleate (4): Following the same procedure as that described for compound **1**, a mixture of triethylamine (3.32 g, 32.80 mmol), trimethylsilyl triflate (7.30 g, 32.80 mmol), and methyl linoleate (2.42 g, 8.20 mmol) gives compound **4**. Yield: 1.80 g (60%). B.p. 180 °C/0.20 Torr. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): δ = 0.04 (s, 9 H, SiMe$_3$), 0.86 (t, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, CH_3-CH$_2$), 1.16–1.36 [m, 16 H, (CH_2)$_3$ and (CH_2)$_5$], 1.94 (t, $^{3}J_{\mathrm{H,H}}$ = 5.9 Hz, 1 H, CHSiMe$_3$), 1.98–2.04 (m, 4 H, CH_2-CH=CH), 2.73 (m, 2 H, =CH-CH_2-CH=), 3.59 (s, 3 H, OCH_3), 5.25–5.40 (m, 2 H, CH=CH) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 20 °C): δ = –2.70 (SiMe_3), 14.12 (CH$_3$), 22.71, 25.06, 25.69, 27.42, 29.19, 29.38, 29.72, 31.55, 31.89 [(CH$_2$)$_4$, CH$_2$ and (CH$_2$)$_6$], 37.78 (CHSiMe$_3$), 50.82 (OCH$_3$), 129.74, 130.24 (CH=CH), 175.86 (CO) ppm. ^{29}Si NMR (133.71 MHz, CDCl$_3$, 20 °C): δ = 6.98 ppm. IR (CDCl$_3$): $\tilde{\nu}$ = 1722 (C=O), 1462 (C=C) cm^{-1}. MS (EI): *m*/*z* = 366 [M$^+$]. $C_{22}H_{42}O_2Si$ (366.65): calcd. C 72.07, H 11.55; found C 71.66, H 11.93.

2-Dimethylsilylmethyl Undecanoate (5): Using the same procedure as that described for compound **1**, only 30% of **5** was obtained with byproducts resulting from the decomposition of the initial silyl triflate. In this case, it will be better to start from FAME lithium enolate. A solution of methyl undecenoate (1.39 g, 6.96 mmol) in THF (3 mL) was added at –78 °C to a solution of *i*Pr$_2$NLi (6.96 mmol) in THF (6 mL) [prepared from *i*Pr$_2$NH (0.70 g, 6.96 mmol) and *n*BuLi (9.39 mmol, 1.6 M in hexane)]. The mixture was stirred at this temperature for 5 h. Dimethylchlorosilane (1.07 g, 11.36 mmol) was added. After 20 min at –78 °C, the temperature was raised to room temperature, and the mixture was stirred for 24 h. The solvents were removed under reduced pressure, and pentane (5 mL) was added giving a white precipitate. After filtration, the filtrate was evaporated and distilled. Compound **5** was obtained as a colorless liquid. Yield: 1.20 g (67%). B.p. 95 °C/0.03 Torr. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): δ = 0.07 (d, $^{3}J_{\mathrm{H,H}}$ = 3.5 Hz, 6 H, SiMe_2H), 0.84 (t, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, CH_3-CH$_2$), 1.17–1.36 [s, 16 H, (CH_2)$_8$], 2.03 (m, 1 H, CHSiMe$_2$H), 3.45 (m, 1 H, SiMe$_2$$H$), 3.65 (s, 3 H, OC$H_3$) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 20 °C): δ = 0.91 (SiMe_2H), 14.02 (CH$_3$), 22.61, 23.42, 24.89, 27.32, 28.27, 29.14, 30.24, 31.92 (CH$_2$)$_8$, 35.47 (CHSiMe$_2$H), 51.23 (OCH$_3$), 174.18 (CO) ppm. ^{29}Si NMR (133.71 MHz, CDCl$_3$, 20 °C): δ = 5.16 ppm. IR (CDCl$_3$): $\tilde{\nu}$ = 1709 (C=O), 2119 (Si–H) cm^{-1}. MS (EI): *m*/*z* = 258 [M$^+$]. $C_{14}H_{30}O_2Si$ (258.47): calcd. C 65.06, H 11.70; found C 64.79, H 11.97.

2-Methylsilylmethyl Undecanoate (6): Using the same procedure as that described for compound **1**, a mixture of triethylamine (3.32 g, 32.80 mmol), methylsilyl triflate (6.37 g, 32.80 mmol), and methyl undecanoate (1.64 g, 8.20 mmol) gives compound **6** as a colorless liquid. Yield: 1.14 g (57%). b.p. 100 °C/0.04 Torr. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): δ = 0.46 (m, 3 H, SiMeH$_2$), 0.86 (t, $^{3}J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, CH_3-CH$_2$), 1.25 [s, 16 H, (CH_2)$_8$], 1.79 (m, 1 H, CHSiMeH$_2$), 3.17 (m, 2 H, SiMeH_2), 3.66 (s, 3 H, OCH_3) ppm. ^{13}C NMR (62.89 MHz, CDCl$_3$, 20 °C): δ = 0.71 (SiMeH$_2$), 14.07 (CH$_3$), 21.88, 22.65, 24.95, 25.35, 27.87, 28.42, 30.54, 31.87 (CH$_2$)$_8$, 47.14 (CHSiMeH$_2$), 51.70 (OCH$_3$), 174.65 (CO) ppm. ^{29}Si NMR (133.71 MHz, CDCl$_3$, 20 °C): δ = 8.65 ppm. IR(CDCl$_3$): $\tilde{\nu}$ = 1715 (C=O), 2115 (Si–H) cm^{-1}. MS (EI): *m*/*z* = 244 [M$^+$]. $C_{13}H_{28}O_2Si$ (244.44): calcd. C 63.88, H 11.55; found C 62.65, H 11.13.

2-Dimethylchlorosilylmethyl Undecanoate (7): Using the same procedure as that described for compound **1**, **7** was obtained with a low yield (27%; identified by GC). This chlorosilyl ester was obtained in pure form starting from FAME lithium enolate. A solution of methyl undecenoate (1.39 g, 6.96 mmol) in THF (3 mL) was added at –78 °C to a solution of $i\mathrm{Pr_2NLi}$ (6.96 mmol) in THF (6 mL) [prepared from $i\mathrm{Pr_2NH}$ (0.70 g, 6.96 mmol) and nBuLi (9.39 mmol, 1.6 M in hexane)]. The mixture was stirred at this temperature for 5 h. A large excess of dimethyldichlorosilane (3.56 g, 27.84 mmol) was then added. After 20 min at –78 °C, the temperature was raised to room temperature, and the mixture was stirred for 24 h. The solvents were removed under reduced pressure, and pentane (3 mL) was added giving a white precipitate. After filtration, the filtrate was evaporated and distilled. Compound **7** was obtained as a colorless liquid. Yield: 0.83 g (41%). B.p. 81 °C/0.01 Torr. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 0.45 (s, 6 H, Si*Me*$_2$), 0.86 (t, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, C*H*$_3$-CH$_2$), 1.24 [s, 16 H, (C*H*$_2$)$_8$], 1.90 (m, 1 H, C*H*SiMe$_2$Cl), 3.70 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (62.89 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 0.83 (Si*Me*$_2$Cl), 14.07 (*C*H$_3$), 22.65, 23.47, 24.70, 25.40, 27.50, 28.31, 29.43, 31.87 (*C*H$_2$)$_8$, 51.50 (O*C*H$_3$), 54.65 (*C*HSiMe$_2$Cl), 175.40 (*C*O) ppm. ^{29}Si NMR (133.71 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 8.33 ppm. IR ($\mathrm{CDCl_3}$): $\tilde{\nu}$ = 1720 (C=O) cm^{-1}. MS (EI): m/z = 292 [M$^+$]. $\mathrm{C_{14}H_{29}ClO_2Si}$ (292.92): calcd. C 57.41, H 9.98; found C 58.11, H 10.45.

2-Methyldichlorosilylmethyl Undecanoate (8): Using the same procedure as that described for **1**, **8** was observed with a low yield (19%; identified by GC). This chlorosilyl ester was obtained in pure form starting from FAME lithium enolate. A mixture of methyl undecenoate (1.39 g, 6.96 mmol), $i\mathrm{Pr_2NLi}$ (6.96 mmol), and a large excess of methyltrichlorosilane (5.15 g, 34.80 mmol) gives compound **8** as a colorless liquid. Yield: 1.32 g (61%). B.p. 93 °C/0.01 Torr. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 0.63 (s, 3 H, Si*Me*Cl$_2$), 0.86 (t, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, C*H*$_3$-CH$_2$), 1.25 [s, 16 H, (C*H*$_2$)$_8$], 1.96 (m, 1 H, C*H*SiMeCl$_2$), 3.64 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (62.89 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 1.06 (Si*Me*Cl$_2$), 14.15 (*C*H$_3$), 22.71, 25.01, 26.31, 28.31, 29.13, 29.35, 30.27, 31.92 (*C*H$_2$)$_8$, 51.69 (O*C*H$_3$), 56.44 (*C*HSiMeCl$_2$), 174.34 (*C*O) ppm. ^{29}Si NMR (133.71 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 9.93 ppm. IR ($\mathrm{CDCl_3}$): $\tilde{\nu}$ = 1722 (C=O) cm^{-1}. MS (EI): m/z = 312 [M$^+$]. $\mathrm{C_{13}H_{26}ClO_2Si}$ (313.33): calcd. C 49.83, H 8.36; found C 49.69, H 8.72.

Trimethylsilyl Ketene Acetal (9): A solution of methyl undecanoate (1.39 g, 6.96 mmol) in THF (3 mL) was added dropwise to a solution of LDA [prepared from $i\mathrm{Pr_2NH}$ (0.70 g, 6.96 mmol) and nBuLi (6.96 mmol, 1.6 M in hexane) in THF (6 mL)] at –78 °C. The mixture was stirred at this temperature for 30 min and HMPA (0.1 mL) was then added. After 3 h, whilst stirring at –78 °C, Me$_3$SiCl (0.90 g, 8.35 mmol) was introduced. The mixture was slowly brought to ambient temperature and stirred for 2.5 h. After evaporation of the solvents under reduced pressure, the residue was treated by pentane and filtered. The filtrate was concentrated and distilled giving compound **9** as a colorless liquid. Yield: 0.96 g (51%). B.p. 85 °C/0.01 Torr. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 0.10 (s, 9 H, Si*Me*$_3$), 0.87 (t, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, C*H*$_3$-CH$_2$), 1.15 [s, 14 H, (C*H*$_2$)$_7$], 1.68 (m, 2 H, C*H*$_2$-CH=C), 3.31 (s, 3 H, OC*H*$_3$), 3.45 (t, $^3J_{\mathrm{H,H}}$ = 4.8 Hz, 1 H, CH$_2$-C*H*=C) ppm. ^{13}C NMR (62.89 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = –0.04 (Si*Me*$_3$), 14.23 (*C*H$_3$), 22.64, 22.71, 24.67, 26.73, 29.31, 29.61, 30.52, 31.95 (*C*H$_2$)$_8$, 51.30 (O*C*H$_3$), 85.40 (*C*H=C), 153.49 (CH=*C*) ppm. ^{29}Si NMR (133.71 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 19.90 ppm. IR ($\mathrm{CDCl_3}$): $\tilde{\nu}$ = 1681 (C=C) cm^{-1}. MS (EI): m/z = 272 [M$^+$]. $\mathrm{C_{15}H_{32}O_2Si}$ (272.50): calcd. C 66.11, H 11.84; found C 66.84, H 12.01.

Reaction of Me$_3$SiY with FAME Lithium Enolate: Using the same procedure as that described for compound **9**, but without HMPA, this reaction leads to a mixture of **1** and **9** in 18 and 72% yield, respectively (determined by ^{1}H NMR spectroscopy). Starting from Me$_3$SiBr, **1** and **9** were obtained in 77 and 23% yield, respectively. With Me$_3$SiI, only the formation of **1** was observed after 4 h at room temperature.

2-Dimethylsilylmethyl Palmitate (10): Using the same procedure as that described for compound **1**, only 35% of **10** was obtained (identified by GC). This silyl ester was obtained in pure form starting from FAME lithium enolate. A mixture of methyl palmitate (1.87 g, 6.96 mmol), $i\mathrm{Pr_2NLi}$ (6.96 mmol), and dimethylchlorosilane (0.78 g, 8.35 mmol) gives compound **10** as a viscous oil. Yield: 1.50 g (66%). B.p. 138 °C/0.01 Torr. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 0.06 (d, $^3J_{\mathrm{H,H}}$ = 3.4 Hz, 6 H, Si*Me*$_2$H), 0.85 (t, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, 3 H, C*H*$_3$-CH$_2$), 1.15–1.46 [m, 26 H, (C*H*$_2$)$_{13}$], 2.06 (m, 1 H, C*H*SiMe$_2$H), 3.46 (m, 1 H, SiMe$_2$*H*), 3.62 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (62.89 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 0.90 (Si*Me*$_2$H), 14.02 (*C*H$_3$), 22.76, 25.09, 26.46, 29.13, 29.25, 29.31, 29.49, 31.63, 31.87 (*C*H$_2$)$_{13}$, 35.47 (*C*HSiMe$_2$H), 51.22 (O*C*H$_3$), 174.13 (*C*O) ppm. ^{29}Si NMR (133.71 MHz, $\mathrm{CDCl_3}$, 20 °C): δ = 4.17 ppm. IR ($\mathrm{CDCl_3}$): $\tilde{\nu}$ = 1710 (C=O), 2117 (Si–H) cm^{-1}. MS (EI): m/z = 328 [M$^+$].

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