Tetrahedron 66 (2010) 8562–8568

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Magnesium-induced regiospecific C-silylation of suitably substituted enoates and dienoates

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ARTICLE INFO

Article history:
Received 7 May 2010
Received in revised form 27 August 2010
Accepted 1 September 2010
Available online 9 September 2010

Keywords:
Regiospecific
Reductive C-silylation
Unsaturated esters
Magnesium
Allyl silane

ABSTRACT

The β-aryl–β-silyl and β,β-disilyl propionates have been synthesized from cinnamates and β-silyl acrylates by a regiospecific reductive C-silylation using Mg/silyl chloride/DMF system at room temperature. These reductive C-silylation conditions have also been applied to δ-aryl substituted dienoates wherein silylation took place at the δ-position leading to the synthesis of single regioisomeric allylsilanes with very high stereoselectivity.

1. Introduction

The unique properties of silicon[1] have led to its wide utilization in organic chemistry ranging from protecting functional groups[2] to temporary tether[3] in general and as masking hydroxyl group,[4] to highly controlled and selective organic reactions[1,5] in particular. A silicon group is known to stabilize either an electron deficient centre such as a carbocation at the β-position (β-effect)[6,7] or a carbanion at the α-position (α-effect)[8] with respect to it. These stabilizing effects play important roles in directing the regioselectivity in various organic reactions, especially in β-silyl carbonyl compounds. Some recent examples include Baeyer–Villiger oxidation,[9] Bamford–Stevens reaction,[10] Beckmann fragmentation,[11] Curtius reaction,[12] Norrish type I and II cleavages,[13] palladium-catalyzed nucleophilic substitution,[14] Nazarov cyclizations,[15] decarboxylation reactions,[16] stereospecific 1,2-silyl shifts,[17] and cyclobutane[18] formation.

Carbonyl compounds having a silyl group at β-position are popular targets because of their versatile nature[19] as stated earlier and also excellent surrogate for the acetate aldol[20] reaction. The available methods of preparation of β-silyl carbonyl compounds include hydrosilylation of unsaturated carbonyl compounds,[21] silylmetalation of unsaturated carbonyl compounds[22,23] and methods based on the use of various transition metal catalysts.[24–27] Amongst these, silylmetalation of unsaturated carbonyl compounds using dimethyl (phenyl)silyl lithium ($Me_2PhSiLi$)[28] as a source reagent is widely used. The choice of Me_2PhSi group is due to its convertibility to the corresponding alcohol under oxidative conditions (Fleming–Tamao)[29] with complete retention of stereochemistry. Although Me_2PhSi group is an equivalent to a hydroxyl group, it is not the most easily oxidizable group. The proposed mechanism[29c] shows that the phenyl group undergoes an *ipso*-substitution by first reacting with an electrophile such as bromine or mercuric acetate. It is therefore expected that electron rich aryl ring would make this *ipso*-substitution more facile. This has been demonstrated by converting dimethyl(*p*-tolyl)silyl[30] and (2-methoxyphenyl)dimethylsilyl groups[31] to a hydroxyl functionality under milder conditions and better yields. But the major hurdle was the preparation of dimethyl(aryl)silyl lithiums from the corresponding silyl chlorides, which does not occur[32] for electron rich aryl groups. So the popularity of Me_2PhSi group remained because of the easy preparation of $Me_2PhSiLi$[33] from the commercially available silyl chloride and facile conjugate additions of mono-[34] and bis-silylcuprate[22,28] reagents derived from it to unsaturated carbonyl compounds.

Reductive silylation of α,β-unsaturated carbonyl compounds is known to be mediated by metals, notably by lithium,[35] ytterbium,[36] and magnesium.[37] Electrochemical methods[38] have also been used, although, rarely. The outcome of these reactions depended upon the functionalities attached to the double bond, metal, and the solvent used in these reactions. Picard et al.[37a,b] have shown that α,β-unsaturated esters in the presence of Mg and trimethylsilyl chloride (TMSCl) in hexamethylphosphoric triamide (HMPA) can produce three different types of products viz. C-silylation at the β-position with respect to the ester moiety, reductive dimerization

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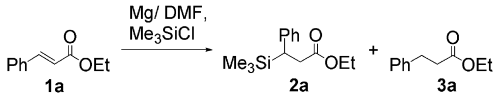
doi:10.1016/j.tet.2010.09.001

or simple saturation of the double bond. The quantum of each product depended on the functionalities attached to the double bond. The C-silylation at the β-position was the main product obtained with cinnamic esters. Similar results were obtained when β-aryl α-phosphorylacrylate derivatives[37c] were subjected under reductive silylation conditions using TMSCl/Mg/DMF system. Arylidene malonates/aceto acetates/cyanoacetates were not so selective under these conditions and produced in addition to the *C*-silylated product, a significant amount of double bond reduced product. Reductive trimethylsilylation of β-aryl-α,β-unsaturated ketones, esters, and nitriles using a Mg anode in an undivided electrochemical cell[38] mainly produced the β-*C*-silylated products in moderate yields. While α,β-unsaturated aldehydes and ketones under these conditions preferred for reductive dimerization[39] to generate bis-(enol silyl) ethers with very high regioselectivity. We have also recently shown[40] that the reductive conditions using Mg/TMSCl/DMF system on silicon-tethered diacrylic esters or amides preferred for intramolecular reductive coupling of the two acrylic units leading to 3,4-bis-silyl substituted adipic acid derivatives with very high selectivity with no C-silylation at the β-position. We, therefore, became curious to know the outcome of this reductive dimerization protocol on β-dimethyl(aryl)silylacrylates. Which pathway it would follow, reduction, C-silylation or dimerization? Herein, we report our successful approach to the reductive C-silylation of β-dimethyl(aryl)silylacrylates/cinnamates at β-position and reductive C-silylation of δ-phenyldienoate at δ-position leading to functionalized allylsilanes.

2. Results and discussion

Prior to work with β-dimethyl(aryl)silylacrylates, we decided to find out suitable conditions for the reductive silylation of ethyl cinnamate as it is known[37b] to react in this fashion under Mg/TMSCl/HMPA system. When ethyl cinnamate **1a** was subjected under our reported[40] conditions (reactant concentration 0.1 M in DMF, 12 equiv each of Mg and TMSCl with respect to ethyl cinnamate, at 0 °C), it was gratified to note that the reaction took place with complete consumption of starting material (Scheme 1). The crude reaction product indeed showed the formation of ethyl β-phenyl β-trimethylsilyl propionate **2a** associated with a small amount of double bond reduced product, ethyl dihydrocinnamate **3a** (**2a**:**3a**=9/1 as revealed by ^{1}H NMR). No reductive dimerization product could be detected from the crude product. The *C*-silylated product **2a** was also isolated in 76% yield. To improve upon the yield and selectivity, the procedure was then modified by adding ethyl cinnamate to the mixture of Mg and TMSCl under various conditions as presented in Table 1. As our study aimed to introduce various silyl groups, optimization of the quantity of silyl chloride was therefore essential. We began our studies with the use of 3 equiv of TMSCl with respect to ethyl cinnamate at 0 °C (Table 1, entry 1). Increasing the proportion of TMSCl from 3 equiv to 6 equiv reduced the formation of the reduction product **3a** and the overall yield was also improved (Table 1, entry 2). Further increase in TMSCl quantity did not improve the yield of the silylated product **2a** much (Table 1, entries 3–5). Increasing the reactant concentration did not change the selectivity or the yield while reactions under dilute conditions produced more double bond reduction product **3a** (Table 1, entries 6–8). When the reaction temperature was lowered, the selectivity of C-silylation versus double bond reduction detoriated (Table 1, entry 9) and also the isolated yield of **2a** decreased significantly. Interestingly, carrying out the reaction at room temperature (30 °C) increased the reaction rate, the yield of product **2a** and the selectivity of the reaction (Table 1, entry 10). Further increase in the reaction temperature shortened the reaction time but yield and selectivity dropped marginally (Table 1, entry 11). We also varied the quantity of magnesium (9–3 equiv; Table 1, entries 12–14) and carried out the silylation reaction of ethyl cinnamate with 6 equiv of TMSCl in each case at room temperature. The β-silylated product **2a** was formed in all cases but required longer reaction time. Although, the ratio of silylation to reduction, i.e., the formation of **2a**:**3a** did not change, significant drop in the isolated yield of **2a** was observed. The best condition is therefore to add the ethyl cinnamate to a mixture of 6 equiv of TMSCl, 12 equiv of Mg in DMF (0.2 M) at 30 °C for 0.5 h (Table 1, entry 10). Under these conditions the *C*-silylated product **2a** was isolated in 84% yield with the double bond reduction product **3a** now found to be negligible (~5%). The double bond reduction product **3a** was also easily separated from *C*-silylated product **2a** by column chromatography.



Scheme 1. Reductive silylation of ethyl cinnamate.

Table 1
Optimization of conditions for the reductive silylation of ethyl cinnamate[a]

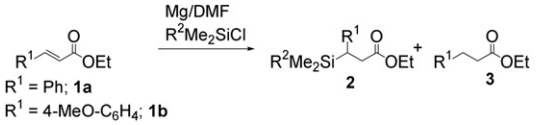
Entry	Me_3SiCl equiv	Concn of **1a** (M) in DMF	Temperature (°C)/time (h)	**2a**:**3a**[b]	Yield (%)[c] of **2a**
1	3	0.1	0/1.5	85:15	68
2	6	0.1	0/1.5	91:9	75
3	12	0.1	0/1.5	91:9	76
4	15	0.1	0/1.5	91:9	76
5	20	0.1	0/1.5	91:9	76
6	6	0.2	0/1.5	92:8	77
7	6	0.06	0/1.5	90:10	73
8	6	0.05	0/1.5	89:11	72
9	6	0.1	−15/1.5	71:19	50
10	6	0.2	30/0.5	95:5	84
11	6	0.2	65/0.15	91:9	79
12	6	0.2	30/0.5	94:6	78[d]
13	6	0.2	30/1	94:6	73[e]
14	6	0.2	30/1.5	93:7	70[f]

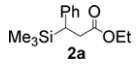
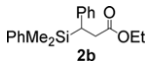
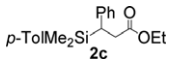
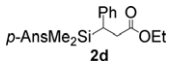
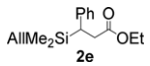
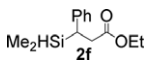
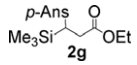
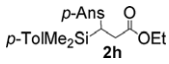
[a] Unless stated, Mg (12 equiv) metal was used.
[b] Ratio determined by ^{1}H NMR.
[c] Yield of homogeneous material obtained after silica-gel chromatography.
[d] Mg (9 equiv) metal was used.
[e] Mg (6 equiv) metal was used.
[f] Mg (3 equiv) metal was used.

As mentioned earlier, suitable substituents on silicon, especially aryl groups make the silyl group as a masked hydroxyl group. To generalize the Mg/TMSCl/DMF system for efficient reductive C-silylation at the β-position of ethyl cinnamates, reductive silylation with $PhMe_2SiCl$ and silyl chlorides, which do not form the corresponding silyl lithium easily, such as *p*-$TolMe_2SiCl$, *p*-$AnsMe_2SiCl$, and $AllMe_2SiCl$ were pursued. All these silyl groups[30,41] are also known to be the surrogate of the hydroxyl group. The results of reductive silylation under the optimized conditions are presented in Table 2. In all cases the β-silylated product was obtained in very good yield and purity (Table 2, entries 1–6). Even, chlorodimethylsilane reacts very cleanly to produce the corresponding β-silylated product in high yield (Table 2, entry 6). Electron donating substituent at the phenyl ring of the substituted ethyl cinnamate did not hinder the reaction (Table 2, entries 7 and 8).

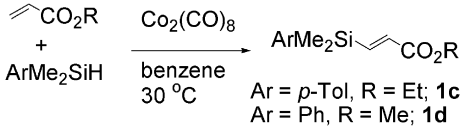
We next turned our attention to know the fate of β-silyl acrylates under these optimized reductive silylation conditions using Mg/chlorosilane/DMF system at 30 °C. We prepared two β-silyl acrylates **1c** and **1d** as the substrates following the reported procedures[42] using cobalt carbonyl mediated silylation of ethyl/methyl acrylate with appropriate dimethyl(aryl)silanes (Scheme 2). When β-dimethyl(phenyl)silyl acrylate **1c** was subjected under the reductive silylation conditions using Mg/TMSCl/DMF system, the β,β-disilylated product **4a** was isolated in good yield (Table 3, entry 1).

Table 2
Reductive silylation of cinnamates with various silyl chlorides[a]



Entry	Cinnamate	Silyl chloride	Product	Yield (%)[b] of **2**
1	**1a**	Me_3SiCl	 **2a**	84
2	**1a**	$PhMe_2SiCl$	 **2b**	75
3	**1a**	*p*-$TolMe_2SiCl$	 **2c**	75
4	**1a**	*p*-$AnsMe_2SiCl$	 **2d**	80
5	**1a**	$AllMe_2SiCl$	 **2e**	89
6	**1a**	Me_2SiHCl	 **2f**	85
7	**1b**	Me_3SiCl	 **2g**	70
8	**1b**	*p*-$TolMe_2SiCl$	 **2h**	71

[a] Mg (12 equiv) metal and silyl chloride (6 equiv) were used in all experiments.
[b] Yield of homogeneous material obtained after silica-gel chromatography.

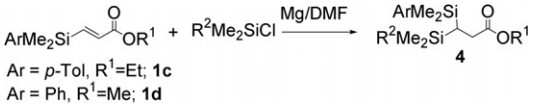


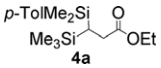
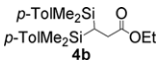
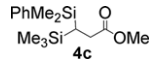
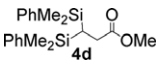
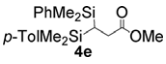
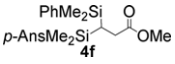
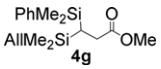
Scheme 2. Synthesis of β-silyl substituted acrylates.

Although a trace amount (<5%) of reductive dimerization product was formed, no double bond reduction could be seen in the crude reaction product. A similar clean reaction took place for **1c** when TMSCl was replaced by dimethyl(*p*-tolyl)silyl chloride (Table 3, entry 2). The reductive C-silylation was then repeated with the silyl acrylate methyl ester **1d** using various silyl chlorides as presented in Table 3. The desired β,β-disilylated products **4c**–**g** were formed in moderate to good yield. Compared to ethyl ester **1c**, methyl ester **1d** produced slightly more amount of the reductive dimerization products (10–15%) as judged from the crude reaction product by ^{1}H NMR affecting the isolated yields of β,β-disilylated products **4c**–**g** (Table 3, entries 3–7). Acrylates with a β-alkyl group viz. ethyl crotonate or ethyl 5-phenyl-2-pentenoate under the same conditions did not react. After prolonged stirring at room temperature some unidentified products were formed presumably by cross reaction with the solvent, i.e., DMF under the reaction conditions.

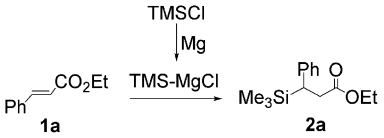
The reductive β C-silylation of cinnamate can occur by two pathways. The silyl chloride can react with magnesium metal to give intermediate silyl Grignard species, which then undergo 1,4-addition to cinnamate **1a** to give the product **3a** (Scheme 3). The other possibility is the single electron transfer from Mg metal to the cinnamate, activated by silyl chloride, to generate a benzyl radical,

Table 3
Reductive silylation of β-silyl substituted acrylates with various silyl chlorides[a]



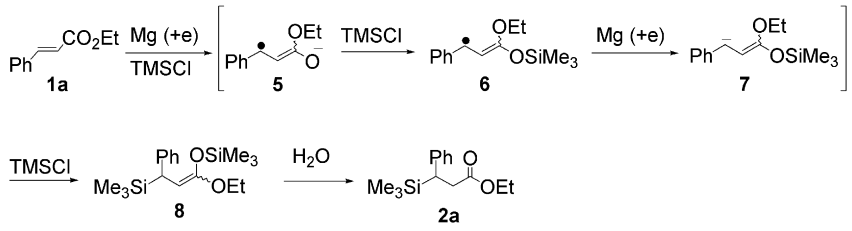
Entry	Acrylate	Silyl chloride	Product	Yield (%)[b]
1	**1c**	Me_3SiCl	 **4a**	81
2	**1c**	*p*-$TolMe_2SiCl$	 **4b**	79
3	**1d**	Me_3SiCl	 **4c**	70
4	**1d**	$PhMe_2SiCl$	 **4d**	71
5	**1d**	*p*-$TolMe_2SiCl$	 **4e**	70
6	**1d**	*p*-$AnsMe_2SiCl$	 **4f**	70
7	**1d**	$AllMe_2SiCl$	 **4g**	72

[a] Mg (12 equiv) metal and silyl chloride (6 equiv) were used in all experiments.
[b] Yield of homogeneous material obtained after silica-gel chromatography.



Scheme 3. Silyl Grignard route to reductive β-C-silylation.

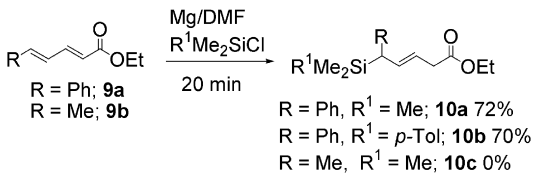
which accepts another electron from Mg to give the anion species, that is, quenched by the silyl chloride to give the β *C*-silylated product. The former pathway seems to be not operative in the present case. This was augmented by the following experiments. When a mixture of TMSCl and Mg metal in DMF was stirred at room temperature and the supernatant was added to ethyl cinnamate **1a**, no silyl addition product **3a** was observed. No reaction also took place when a DMF solution of ethyl cinnamate was added to the residual Mg metal. But the desired product **3a** was formed when 6 equiv of TMSCl was added to this mixture. Although silyl Grignard reagents are known to be produced from silyl chlorides having aryl substitutions, trialkylsilyl chlorides do not form such species under normal conditions.[43] The alternate and most plausible mechanism for the reductive C-silylation is depicted in Scheme 4. Without TMSCl, there was no reaction including the double bond reduction. The role of the silyl chloride was manifold. First, it probably activates the metal by cleaning the oxide/hydroxide/carbonate coating from the surface. TMSCl is also known to increased the reduction potential value of octanoylimidazole from −2.00 to −1.04 V versus SCE[44] or acetophenone −2.34 to −1.38 V versus SCE.[45] It is logically expected that TMSCl would increased the reduction potential value of the cinnamate substrate thus accelerates the single electron transfer from Mg to the substrate. Its presence also increases the chemoselectivity of the reaction in favor of the C-silylation products over double bond reduction product or dimerization. The reductive C-silylation process was probably accelerated by quenching



Scheme 4. Plausible mechanism of reductive β-C-silylation.

the radical anion **5**, formed by electron transfer from Mg to the acrylate **1a**, with TMSCl to give the ketene silyl acetal radical **6**. One more electron transfer from Mg to **6** provided the intermediate anion **7**, which was then quenched by silyl chloride to give the β-C-silylated silyl ketene acetal **8**. The silyl acetal **8** underwent hydrolysis during aqueous work-up conditions and provided the β-silyl propionate **2a**. By this process, TMSCl also protected the reductive silylation product from further reactions like Claisen condensation or oligomerizations. The C-silylation took place only with β-aryl/silyl acrylates and not with β-alkyl acrylates. The aryl groups are known to stabilize the carbanion at the benzylic positions and a silicon group is also known to stabilize a carbanion α to it. As the reduction potential of benzyl radical (−1.45 V vs SCE)[46] and α-silyl radical (−1.51 V vs SCE)[47] is higher compared to alkyl radicals (−2.0 V vs SCE),[46] the reductive silylation process was favored with these two classes of substrates.

We turned our attention to study this reductive silylation on dienic esters because these substrates can react in different modes to produce regio-isomeric *C*-silylated products. When the diene ester **9a** was treated under the optimized reductive silylation conditions as described for ethyl cinnamate, (Scheme 5) using TMSCl, the allyl silane **10a** was formed without a trace of the other regioisomer. Moreover, the allyl silane was also formed with high stereoselectivity where (*E*)-isomer was found to be the major product (*E*/*Z*=86/14 by GC) as revealed from the ^{1}H NMR coupling constant values of the olefinic protons (J=16 Hz). While changing the silyl chloride from TMSCl to *p*-TolMe$_2$SiCl, the corresponding allyl silane **10b** was formed in good yield and also contaminated with a small amount of the (*Z*)-isomer (19%). Interestingly, alkyl substituted dienoate **9b** under the same conditions did not provide the desired allyl silane **10c**. Instead, some unidentified oligomeric products were formed.



Scheme 5. Regiospecific reductive silylation of dienoates.

3. Conclusions

In conclusion, we have successfully developed a Mg/silyl chloride/DMF system for the reductive C-silylation at the β-position of β-aryl and β-silyl substituted enoates with very good yields. The C-silylation selectivity was very high over the reductive dimerization or the simple double bond reduction. The reductive silylation conditions are applicable to δ-aryl substituted dienoates wherein silylation took place at the δ-position leading to the synthesis of allylsilanes as single regioisomer and with very high stereoselectivity. The β-aryl–β-silyl and β,β-disilyl propionates can be considered as a ester homoenolate because tetrabutylammonium triphenyldifluorosilicate[48] can cause desilylation to generate aryl and silyl stabilized carbanion which can be trapped with electrophiles. As homoenolates are considered equivalent to umpolung of acrylates, the present methodology is thus amounted to overall umpolung generation while making the silylated compounds from the acrylates as well their possible uses. The allylsilanes are known as useful synthetic intermediates and the additional ester functionality at the terminal of the allysilane would enhance their utility. The C-silylations described here is electrophilic. Thus, there is no limitation for the choice of silyl groups, a crucial factor for nucleophilc silylation reactions. Although β-silylation using the silyl chloride like *p*-TolMe$_2$SiCl, *p*-AnsMe$_2$SiCl, AllMe$_2$SiCl etc. are not possible by using the conventional procedure of 1,4 addition using silylcuprate reagents, it is easily done by using Mg/silyl chloride/DMF system.

4. Experimental

4.1. General methods

DMF was dried over CaH_2 followed by storage over 4 Å molecular sieves. Mg turnings were purified by washing with dilute hydrochloric acid, water followed by washing with acetone and dried under vacuum. TMSCl was distilled over CaH_2 before use. Silylated acrylates **1c** and **1d** were prepared following the reported procedure[42] and not included in the experimental.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometers. Spectra were referenced to residual chloroform (δ 7.25 ppm, ^{1}H; 77.00 ppm, ^{13}C). Chemical shifts are reported in parts per million (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (pentet), m (multiplet), and br (broad). Coupling constants, J, are reported in Hertz. C, H, and N analyses were performed at the Indian Institute of Technology, Mumbai and at the Hydrometallurgy Division, BARC, Mumbai. High resolution mass spectra were recorded at 60–70 eV on a Waters Micromass Q-TOF spectrometer (ESI, Ar). Infrared spectra (IR) were recorded on a JASCO FTIR spectrophotometer in NaCl cells or in KBr discs. Peaks are reported in cm^{-1}. The mass spectra were recorded on a Shimadzu GC–MS 2010 mass spectrometer (EI 70 eV). Gas chromatography (GC) studies were carried out using Younglin Acme 6000 M Gas Chromatograph fitted with a capillary column (WCOT Fused Silica, CP-SIL-5-CB, 50 m×0.25 mm/0.39 mm, 0.25 μm; Carrier: helium 1 mL/min). Analytical thin-layer chromatography was performed using home made silica gel plates (about 0.5 mm).

4.1.1. General procedure: preparation of (3RS)-ethyl 3-phenyl-3-trimethylsilylpropionate ***2a***[38]. Freshly distilled TMSCl (3.8 mL, 30 mmol) was added to a stirred suspension of magnesium turnings (1.46 g, 60 mmol) in dry DMF (20 mL) at room temperature under an argon atmosphere. After 15 min, a solution of *trans*-ethyl cinnamate **1a** (0.88 g, 5 mmol) in dry DMF (5 mL) was added to the reaction mixture, stirred for 0.5 h, and poured into cold saturated sodium bicarbonate solution. The reaction mixture was extracted

with 15% ethyl acetate/hexane. The organic extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica using hexane/EtOAc (98:2) as eluent to give the product **2a** (1.05 g, 84%) as a colorless liquid; R_f (95% hexane/EtOAc) 0.52; ν_{max} (liquid film) 3026, 2956, 2899, 1736, 1601, 1495, 1450, 1250, 1163, 1034, 839, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.26–7.18 (2H, m, Ph), 7.11–7.00 (3H, m, Ph), 3.99 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 2.81–2.59 (3H, m, Ph$CHCH_2CO$), 1.08 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), −0.04 (9H, s, Me_3Si); δ_C (50 MHz, $CDCl_3$) 173.1, 142.4, 128.0 (2C), 127.3 (2C), 124.7, 60.1, 34.8, 32.5, 14.0, −3.2 (3C).

4.1.2. (3RS)-Ethyl 3-dimethyl(phenyl)silyl-3-phenylpropionate ***2b***[23]. Yield 75%, colorless liquid; R_f (95% hexane/EtOAc) 0.53; ν_{max} (liquid film) 3069, 3025, 2959, 2901, 1733, 1600, 1494, 1450, 1251, 1167, 1114, 1033, 908, 835, 699 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.38–7.30 (4H, m, Ph), 7.26–7.07 (4H, m, Ph), 6.96–6.92 (2H, m, Ph), 3.90 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 2.88–2.56 (3H, m, Ph$CHCH_2CO$), 1.03 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.25 (3H, s, $SiMe_AMe_BPh$), 0.21 (3H, s, $SiMe_AMe_BPh$); δ_C (50 MHz, $CDCl_3$) 172.7, 141.6, 136.3, 134.0 (2C), 129.1, 127.9 (2C), 127.6 (2C), 127.4 (2C), 124.8, 60.0, 34.8, 32.2, 13.8, −4.3, −5.6.

4.1.3. (3RS)-Ethyl 3-dimethyl(4-methylphenyl)silyl-3-phenylpropionate ***2c***. Yield 75%, colorless liquid; R_f (95% hexane/EtOAc) 0.50; ν_{max} (liquid film) 3062, 3025, 2958, 1735, 1602, 1494, 1450, 1250, 1164, 1106, 1034, 836, 796 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.30 (2H, d, J=7.6 Hz, Ar), 7.27–7.06 (5H, m, Ph), 6.95 (2H, d, J=7.6 Hz, Ar), 3.91 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 2.96–2.50 (3H, m, Ph$CHCH_2CO$), 2.36 (3H, s, Ar–Me), 1.04 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.23 (3H, s, $SiMe_AMe_BAr$), 0.20 (3H, s, $SiMe_AMe_BAr$); δ_C (50 MHz, $CDCl_3$) 172.9, 141.8, 139.0, 134.1 (2C), 132.7, 128.5 (2C), 127.9 (2C), 127.5 (2C), 124.8, 60.0, 34.8, 32.3, 21.3, 13.9, −4.1, −5.5; HRMS (ESI): M^+, found 326.1727. $C_{20}H_{26}O_2Si$ requires 326.1702.

4.1.4. (3RS)-Ethyl 3-dimethyl(4-methoxyphenyl)silyl-3-phenylpropionate ***2d***. Yield 80%, colorless liquid; R_f (95% hexane/EtOAc) 0.36; ν_{max} (liquid film) 3060, 3023, 2957, 2903, 2837, 1732, 1595, 1504, 1278, 1250, 1183, 1112, 1033, 822 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.32 (2H, d, J=8.5 Hz, Ar), 7.20–6.90 (3H, m, Ph), 6.97–6.90 (2H, m, Ph), 6.89 (2H, d, J=8.5 Hz, Ar), 3.95 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 3.82 (3H, s, OMe), 2.86–2.57 (3H, m, Ph$CHCH_2CO$), 1.04 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.22 (3H, s, $SiMe_AMe_BAr$), 0.20 (3H, s, $SiMe_AMe_BAr$); δ_C (50 MHz, $CDCl_3$) 173.0, 160.5, 141.8, 135.5 (2C), 127.9 (2C), 127.5 (2C), 127.1, 124.8, 113.4 (2C), 60.1, 54.9, 34.9, 32.5, 13.9, −4.0, −5.3; m/z (EI) 342 (M, 15), 327 (M−Me, 4), 297 (5), 207 (5), 195 (14), 165 (100), 135 (13), 122 (8), 104 (11); HRMS (ESI): MNa^+, found 365.1542. $C_{20}H_{26}O_3SiNa$ requires 365.1543.

4.1.5. (3RS)-Ethyl 3-dimethyl(2-propenyl)silyl-3-phenylpropionate ***2e***. Yield 89%, colorless liquid; R_f (95% hexane/EtOAc) 0.52; ν_{max} (liquid film) 3078, 3060, 3026, 2958, 2901, 1736, 1630, 1600, 1370, 1251, 1163, 1035, 897, 838, 701 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.26–7.20 (2H, m, Ph), 7.13–7.02 (3H, m, Ph), 5.76–5.60 (1H, m, $SiCH_2CH{=}CH_2$), 4.87–4.81 (2H, m, $SiCH_2CH{=}CH_2$), 3.98 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 2.89–2.66 (3H, m, Ph$CHCH_2CO$), 1.47 (2H, d, J=7.9 Hz, $SiCH_2CH{=}CH_2$), 1.08 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), −0.01 (3H, s, $SiMe_AMe_B$), −0.06 (3H, s, $SiMe_AMe_B$); δ_C (50 MHz, $CDCl_3$) 172.8, 141.9, 134.1, 128.1 (2C), 127.3 (2C), 124.8, 113.5, 60.1, 34.8, 31.4, 21.4, 13.9, −5.3 (2C); m/z (EI) 276 (M, 1), 261 (M−Me, 5), 235 (M−C_3H_5, 100), 207 (27), 171 (9), 147 (9), 99 (60), 75 (66); HRMS (ESI): MNa^+, found 299.1411. $C_{16}H_{24}O_2SiNa$ requires 299.1444.

4.1.6. (3RS)-Ethyl 3-dimethyl(hydro)silyl-3-phenylpropionate ***2f***. Yield 85%, colorless liquid; R_f (95% hexane/EtOAc) 0.56; ν_{max} (liquid film) 3061, 3025, 2961, 2903, 2116, 1734, 1601, 1494, 1450, 1371, 1252, 1166, 1034, 908, 881, 758 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.28–7.20 (2H, m, Ph), 7.14–7.04 (3H, m, Ph), 4.02 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 3.93–3.85 (1H, m, Me_2SiH), 2.89–2.68 (3H, m, Ph$CHCH_2CO$), 1.11 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.11 (3H, s, J=3.5 Hz, $SiMe_AMe_BH$), -0.02 (3H, s, J=3.5 Hz, $SiMe_AMe_BH$); δ_C (50 MHz, $CDCl_3$) 172.7, 142.1, 128.2 (2C), 127.2 (2C), 125.0, 60.2, 35.5, 30.5, 14.0, −5.7, −6.1; m/z (EI) 236 (M, 11), 221 (M−Me, 6), 207 (7), 193 (17), 163 (17), 147 (11), 135 (52), 117 (33), 104 (100), 91 (16), 75 (41).

4.1.7. (3RS)-Ethyl 3-(4-methoxyphenyl)-3-trimethylsilylpropionate ***2g***[38]. Yield 70%; colorless liquid; R_f (90% hexane/EtOAc) 0.58; ν_{max} (liquid film) 3069, 2955, 2901, 2835, 1733, 1610, 1510, 1249, 1162, 1108, 1038, 841, 758 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.95 (2H, d, J=8.5 Hz, Ar), 6.78 (2H, d, J=8.5 Hz, Ar), 3.99 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 3.76 (3H, s, OMe), 2.80–2.50 (3H, m, Ar$CHCH_2CO$), 1.09 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), −0.05 (9H, s, $SiMe_3$); δ_C (50 MHz, $CDCl_3$) 173.0, 156.8, 134.1, 128.0 (2C), 113.3 (2C), 60.0, 54.9, 34.9, 31.3, 13.9, −3.3 (3C).

4.1.8. (3RS)-Ethyl 3-dimethyl(4-methylphenyl)silyl-3-(4-methoxyphenyl)propionate ***2h***. Yield 71%; colorless liquid; R_f (90% hexane/EtOAc) 0.56; ν_{max} (liquid film) 3065, 3032, 2956, 2904, 2834, 1734, 1606, 1509, 1442, 1247, 1162, 1107, 1038, 842, 795, 778 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.30 (2H, d, J=7.6 Hz, Ar), 7.16 (2H, d, J=7.6 Hz, Ar), 6.86 (2H, d, J=8.6 Hz, Ar), 6.74 (2H, d, J=8.6 Hz, Ar), 3.91 (2H, q, J=7.1 Hz, $CO_2CH_2CH_3$), 3.76 (3H, s, OMe), 2.79–2.52 (3H, m, Ar$CHCH_2CO$), 2.35 (3H, s, ArMe), 1.04 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.21 (3H, s, $SiMe_AMe_B$), 0.18 (3H, s, $SiMe_AMe_B$); δ_C (50 MHz, $CDCl_3$) 173.0, 157.0, 139.0, 134.1 (2C), 133.60, 132.8, 128.5 (2C), 128.4 (2C), 113.4 (2C), 60.0, 55.0, 35.1, 31.2, 21.3, 13.9, −4.1, −5.5; m/z (EI) 356 (M, 6), 149 (100), 134 (22), 121 (13), 91 (4); HRMS (ESI): MNa^+, found 379.1696. $C_{21}H_{28}O_3SiNa$ requires 379.1705.

4.1.9. (3RS)-Ethyl 3-dimethyl(4-methylphenyl)silyl-3-trimethylsilylpropionate ***4a***. Yield 81%; colorless liquid; R_f (95% hexane/EtOAc) 0.65; ν_{max} (liquid film) 3067, 2955, 2899, 1736, 1369, 1252, 1199, 1105, 1037, 837, 734 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.41 (2H, d, J=7.6 Hz, Ar), 7.15 (2H, d, J=7.6 Hz, Ar), 4.06–3.92 (2H, m, $CO_2CH_2CH_3$), 2.37 (2H, d, J=6.4 Hz, CH_2CO), 2.33 (3H, s, ArMe), 1.19 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.76 (1H, t, J=6.4 Hz, $SiCHCH_2CO$), 0.30 (3H, s, $SiMe_AMe_B$), 0.28 (3H, s, $SiMe_AMe_B$), −0.06 (9H, s, $SiMe_3$); δ_C (50 MHz, $CDCl_3$) 174.6, 138.5, 135.4, 133.8 (2C), 128.4 (2C), 60.3, 30.9, 21.4, 14.1, 8.6, −0.4 (3C), −1.4, −2.4; m/z (EI) 307 (M−Me, 70), 249 (8), 231 (43), 149 (100), 133 (19), 121 (11), 103 (12), 73 (19).

4.1.10. Ethyl 3,3-bis-dimethyl(4-methylphenyl)silylpropionate ***4b***. Yield 79%; colorless liquid; R_f (95% hexane/EtOAc) 0.60; ν_{max} (liquid film) 3066, 3010, 2955, 1734, 1603, 1251, 1104, 1036, 835, 796 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.36 (4H, d, J=7.5 Hz, Ar), 7.13 (4H, d, J=7.5 Hz, Ar), 3.84 (2H, q, J=7.2 Hz, $CO_2CH_2CH_3$), 2.34 (2H, d, J=6.5 Hz, $SiCHCH_2CO$), 2.33 (6H, s, 2×ArMe), 1.20 (3H, t, J=7.2 Hz, $CO_2CH_2CH_3$), 1.05 (1H, t, J=6.5 Hz, $SiCHCH_2CO$), 0.20 (6H, s, 2×$SiMe_BMe_A$), 0.18 (6H, s, 2×$SiMe_BMe_A$); δ_C (50 MHz, $CDCl_3$) 174.2, 138.5 (2C), 135.3 (2C), 133.8 (4C), 128.4 (4C), 60.2, 31.0, 21.3 (2C), 13.9, 8.1, −1.5 (2C), −2.5 (2C); m/z (EI) 398 (M, 1), 383 (M−Me, 45), 308 (17), 307 (54), 249 (11), 207 (14), 149 (100), 133 (26), 121 (16), 103 (11); HRMS (ESI): MNa^+, found 421.1977. $C_{23}H_{34}O_2Si_2Na$ requires 421.1995.

4.1.11. (3RS)-Methyl 3-dimethyl(phenyl)silyl-3-trimethylsilylpropionate ***4c***. Yield 70%; colorless liquid; R_f (95% hexane/EtOAc) 0.58; ν_{max} (liquid film) 3069, 2999, 2952, 2898, 1739, 1428, 1348, 1252, 1204, 1050, 1032, 837, 815 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.54–7.47 (2H, m, Ph), 7.35–7.32 (3H, m, Ph), 3.53 (3H, s, CO_2CH_3), 2.38 (2H, d, J=6.5 Hz, $SiCHCH_2CO$), 0.77 (1H, t, J=6.5 Hz, $SiCHCH_2CO$), 0.32 (3H, s, $SiMe_AMe_B$), 0.30 (3H, s, $SiMe_AMe_B$), −0.06 (9H, s, $SiMe_3$);

δ_C (50 MHz, $CDCl_3$) 174.8, 139.0, 133.7 (2C), 128.8, 127.6 (2C), 51.4, 30.6, 8.7, −0.5 (3C), −1.5, −2.6; *m/z* (EI) 294 (M, 2), 279 (M−Me, 80), 217 (50), 163 (19), 151 (27), 135 (100), 121 (26), 89 (41), 73 (30).

4.1.12. Methyl 3,3-bis-dimethyl(phenyl)silylpropionate ***4d***. Yield 71%; colorless liquid; R_f (95% hexane/EtOAc) 0.56; ν_{max} (liquid film) 3069, 3049, 2952, 2899, 2843, 1738, 1427, 1349, 1253, 1206, 1112, 1048, 1027, 838, 813, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.49−7.44 (4H, m, Ph), 7.34−7.30 (6H, m, Ph), 3.38 (3H, s, CO_2CH_3), 2.38 (2H, d, *J*=6.6 Hz, $SiCHCH_2CO$), 1.07 (1H, t, *J*=6.6 Hz, $SiCHCH_2CO$), 0.30 (6H, s, $2\times SiMe_AMe_B$), 0.20 (6H, s, $2\times SiMe_BMe_A$); δ_C (50 MHz, $CDCl_3$) 174.6, 138.9 (2C), 133.8 (4C), 128.9 (2C), 127.6 (4C), 51.4, 30.8, 8.3, −1.6 (2C), −2.6 (2C); *m/z* (EI) 356 (M, 3), 341 (M−Me, 59), 279 (60), 231 (15), 221 (34), 193 (13), 151 (23), 135 (100), 121 (22), 107 (11), 89 (14); HRMS (ESI): MNa^+, found 379.1510. $C_{20}H_{28}O_2Si_2Na$ requires 379.1526.

4.1.13. (3RS)-Methyl 3-dimethyl(4-methylphenyl)silyl-3-dimethyl(phenyl)silylpropionate ***4e***. Yield 70%; colorless liquid; R_f (95% hexane/EtOAc) 0.57; ν_{max} (liquid film) 3068, 3011, 2952, 2900, 1739, 1428, 1348, 1252, 1204, 1105, 1048, 1032, 831, 815, 797 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.49−7.28 (7H, m, Ar), 7.14 (2H, d, *J*=7.5 Hz, Ar), 3.39 (3H, s, CO_2CH_3), 2.38 (2H, d, *J*=6.6 Hz, $SiCHCH_2CO$), 2.34 (3H, s, Ar*Me*), 1.05 (1H, t, *J*=6.6 Hz, $SiCHCH_2CO$), 0.23 (3H, s, $SiMe_BMe_A$), 0.20 (6H, s, $2\times SiMe_AMe_B$), 0.18 (3H, s, $SiMe_BMe_A$); δ_C (50 MHz, $CDCl_3$) 174.7, 139.0, 138.7, 135.2, 133.9 (4C), 128.8, 128.5 (2C), 127.6 (2C), 51.4, 30.8, 21.4, 8.4, −1.5 (2C), −2.5, −2.6; *m/z* (EI) 370 (M, 1), 355 (M−Me, 56), 280 (15), 279 (53), 235 (17), 193 (11), 165 (18), 149 (100), 135 (80), 121 (30), 105 (15), 89 (23); HRMS (ESI): MNa^+, found 393.1665. $C_{21}H_{30}O_2Si_2Na$ requires 393.1682.

4.1.14. (3RS)-Methyl 3-dimethyl(4-methoxyphenyl)silyl-3-dimethyl (phenyl)silylpropionate ***4f***. Yield 70%; colorless liquid; R_f (95% hexane/EtOAc) 0.47; ν_{max} (liquid film) 3068, 3019, 2999, 2952, 2902, 2837, 1738, 1503, 1428, 1278, 1249, 1205, 1183, 1111, 1032, 834, 810 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.48−7.32 (7H, m, Ar), 6.88 (2H, d, *J*=8.2 Hz, Ar), 3.81 (3H, s, CO_2CH_3), 3.41 (3H, s, ArO*Me*), 2.38 (2H, d, *J*=6.5 Hz, $SiCHCH_2CO$), 1.04 (1H, t, *J*=6.5 Hz, $SiCHCH_2CO$), 0.28 (3H, s, $SiMe_BMe_A$), 0.20 (6H, s, $2\times SiMe_AMe_B$), 0.18 (3H, s, $SiMe_BMe_A$); δ_C (50 MHz, $CDCl_3$) 174.7, 160.2, 139.0, 135.2 (2C), 133.8 (2C), 129.6, 128.8, 127.6 (2C), 113.3 (2C), 54.9, 51.4, 30.8, 8.5, −1.5, −1.6, −2.4, −2.6; *m/z* (EI) 371 (M−Me, 58), 231(11), 181 (14), 165 (100), 151 (32), 135 (65), 121 (23), 89 (21).

4.1.15. (3RS)-methyl 3-dimethyl(2-propenyl)silyl-3-dimethyl(phenyl) silylpropionate ***4g***. Yield 72%; colorless liquid; R_f (95% hexane/EtOAc) 0.57; ν_{max} (liquid film) 3070, 2952, 2901, 1739, 1630, 1428, 1254, 1204, 1157, 1112, 1028, 814, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.54−7.49 (2H, m, Ph), 7.36−7.33 (3H, m, Ph), 5.81−5.59 (1H, m, $SiCH_2CH{=}CH_2$), 4.84−4.75 (2H, m, $SiCH_2CH{=}CH_2$), 3.51 (3H, s, CO_2CH_3), 2.41 (2H, d, *J*=6.4 Hz, $SiCHCH_2CO$), 1.48−1.43 (2H, m, $SiCH_2CH{=}CH_2$), 0.84 (1H, t, *J*=6.4 Hz, $SiCHCH_2CO$), 0.34 (3H, s, $SiMe_AMe_B$), 0.32 (3H, s, $SiMe_AMe_B$), −0.05 (3H, s, $SiMe_BMe_A$), −0.06 (3H, s, $SiMe_BMe_A$); δ_C (50 MHz, $CDCl_3$) 174.7, 138.8, 134.7, 133.8 (2C), 128.9, 127.6 (2C), 113.2, 51.5, 30.5, 23.6, 7.5, −1.5, −2.4, −2.5, −3.1; *m/z* (EI) 305 (M−Me, 3), 279 (M−C_3H_5, 94), 231 (23), 163 (41), 151 (25), 135 (100), 121 (31), 89 (62); HRMS (ESI): MNa^+, found 343.1526. $C_{17}H_{28}O_2Si_2Na$ requires 343.1526.

4.1.16. (3E,5RS)-Ethyl 5-phenyl-5-trimethylsilylpentanoate ***10a***. Yield 72%; colorless liquid; contains 14% of (3*Z*,5*RS*)-isomer; R_f (95% hexane/EtOAc) 0.58; ν_{max} (liquid film) 3061, 3026, 2980, 2957, 2898, 2871, 1737, 1638, 1600, 1495, 1368, 1249, 1159, 1031, 968, 839, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.29−7.04 (5H, m, Ph), 5.93 (1H, dd, *J*=15.0, 10.0 Hz, $SiCHCH{=}CHCH_2$), 5.57−5.43 (1H, m, $SiCHCH{=}CHCH_2$), 4.13 (2H, q, *J*=7.1 Hz, $CO_2CH_2CH_3$), 3.06 (2H, d, *J*=6.9 Hz, $CHCH{=}CHCH_2$), 2.96 (1H, d, *J*=10.0 Hz, $CHCH{=}CHCH_2$), 1.25 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), −0.04 (9H, s, $SiMe_3$); δ_C (50 MHz, $CDCl_3$) 171.9, 142.2, 133.7, 128.2 (2C), 127.0 (2C), 124.5, 120.0, 60.4, 42.9, 38.3, 14.1, −3.1 (3C); GC−MS (EI) (column: WCOT Fused Silica, CP-SIL-5-CB, 50 m×0.25 mm/0.39 mm, 0.25 μm; Carrier: helium 1 mL/min; temp: 60 °C-2 min-10 °C/min-300 °C): t_R 16.57 min, (3*E*,5*RS*)-**10a** (86%); t_R 16.79 min, (3*Z*,5*RS*)-**10a** (14%); *m/z* for (3*E*,5*RS*)-**10a**: 276 (M, 11), 261 (M−Me, 3), 158 (21), 130 (99), 115 (23), 73 (100); *m/z* for (3*Z*,5*RS*)-**10a**: 276 (M, 11), 261 (M−Me, 3), 158 (10), 130 (67), 115 (19), 73 (100).

4.1.17. (3E,5RS)-Ethyl 5-dimethyl(4-methylphenyl)silyl-5-phenylpentanoate ***10b***. Yield 70%; colorless liquid; contains 19% of (3*Z*,5*RS*)-isomer; R_f (95% hexane/EtOAc) 0.57; ν_{max} (liquid film) 3061, 3025, 2979, 2871, 1733, 1659, 1601, 1494, 1369, 1248, 1157, 1106, 1030, 967, 831, 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.41−7.04 (7H, m, Ph and Ar), 6.90 (2H, d, *J*=7.3 Hz, Ar), 5.85 (1H, dd, *J*=15.0, 9.9 Hz, $SiCHCH{=}CHCH_2$), 5.51−5.36 (1H, m, $SiCHCH{=}CHCH_2$), 4.13 (2H, q, *J*=7.1 Hz, $CO_2CH_2CH_3$), 3.12 (1H, d, *J*=9.9 Hz, $SiCHCH{=}CHCH_2$), 3.03 (2H, d, *J*=7.1 Hz, $SiCHCH{=}CHCH_2$), 2.35 (3H, s, Ar*Me*), 1.25 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 0.23 (6H, s, $SiMe_2$); δ_C (50 MHz, $CDCl_3$) 171.8, 141.6, 138.8, 134.3 (2C), 133.6, 132.8, 128.2 (2C), 128.0 (2C), 127.3 (2C), 124.6, 120.2, 60.4, 42.7, 38.3, 21.4, 14.1, −4.3, −4.8; GC−MS (EI) (column: WCOT Fused Silica, CP-SIL-5-CB, 50 m×0.25 mm/0.39 mm, 0.25 μm; Carrier: helium 1 mL/min; temp: 60 °C-2 min-10 °C/min-300 °C): t_R 21.6 min, (3*E*,5*RS*)-**10b** (80%); t_R 21.94 min, (3*Z*,5*RS*)-**10b** (20%); *m/z* for (3*E*,5*RS*)-**10b**: 352 (M, 7), 149 (100), 130 (28), 121 (11); *m/z* for (3*Z*,5*RS*)-**10b**: 352 (M, 13), 149 (100), 130 (41), 121 (15); HRMS (ESI): MH^+, found 353.1921. $C_{22}H_{29}O_2Si$ requires 353.1937.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.09.001. These data include MOL files and InChIKeys of the most important compounds described in this article.

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