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Highly regio- and stereoselective hydrosilylation of β-fluoroalkylated α,β-unsaturated ketones

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ABSTRACT

Treatment of β-fluoroalkylated α,β-unsaturated ketones with 10.2 equiv of triethylsilane in the presence of 3 mol% of $Co_2(CO)_8$ in dichloroethane at the reflux temperature for 4 h gave 1,4-hydrosilylated adducts in a highly regio- and stereoselective manner. Thus-obtained silyl enol ethers underwent a smooth Mukaiyama aldol reaction with benzaldehyde in the presence of 1.2 equiv of $TiCl_4$ in CH_2Cl_2 at −78 °C for 1 h, affording the corresponding α-(2,2,2-trifluoroethyl)-β-hydroxy ketones with high *syn* stereoselectivity in good yields.

1. Introduction

Transition metal-catalyzed hydrosilylation of α,β-unsaturated carbonyl compounds has been recognized as one of the most important and valuable synthetic methods for the preparation of silyl enol ethers [1]. This is because the reaction generally proceeds in a 1,4-addition manner to produce the corresponding silyl enol ethers, which can participate well in the subsequent various reactions, such as Mukaiyama aldol reaction [2], Michael addition [3], alkylation [4], halogenation [5], oxidation [6], and so on [7] (Scheme 1). Therefore, it is not surprising that there have been voluminous researches on hydrosilylation reactions of *nonfluorinated* α,β-unsaturated carbonyl compounds. However, most of the researches are concerned with the hydrosilylation catalyzed by very expensive rhodium, palladium, platinum, or gold catalysts, and little attention has been paid to inexpensive transition metal-catalyzed hydrosilylation thus far [8]. In addition, to the best of our knowledge, hydrosilylations of *fluorinated* α,β-unsaturated carbonyl compounds have hardly been reported [9].

As a part of our research project on hydrometallation reactions of various fluorinated substances [10], herein is described the highly regio- and stereoselective hydrosilylation reaction of various β-fluoroalkylated α,β-unsaturated ketones **1** in the presence of relatively inexpensive cobalt catalyst in detail (Scheme 2). Moreover, we wish to disclose the highly *syn*-selective aldol reactions using thus-obtained hydrosilylated adducts **2**.

2. Results and discussion

2.1. Preparation of β-fluoroalkylated α,β-unsaturated ketones

Initially, we began with the preparation of various β-fluoroalkylated α,β-unsaturated ketones **1A–H**. As shown in Scheme 3, **1A–C** were easily prepared from commercially available fluorinated hemiacetals **3**, **4** or hydrate **5** and the enamine **6** according to the literature (Scheme 3, eq. 1) [11]. On the other hand, **1D–H** were prepared with slight modifications of the reported procedure (Scheme 3, eq. 2) [12]. Thus, treatment of 2-bromo-3,3,3-trifluoropropene **7** (1.0 equiv) with LDA (2.2 equiv) in THF at −78 °C for 5 min, followed by the addition of various aldehydes (1.0 equiv) into the resultant reaction mixture, gave the corresponding γ-fluoroalkylated propargyl alcohols **8** [12,13]. Without purification, thus-obtained propargyl alcohols **8** were subjected to an excess amount of $NaBH_4$ in ethanol at room temperature for 14 h, affording the corresponding γ-fluoroalkylated allylic alcohols **9** in good yields. Finally, the allylic alcohols were easily oxidized by MnO_2 at the reflux temperature to provide the desired β-fluoroalkylated α,β-unsaturated ketones **1**.

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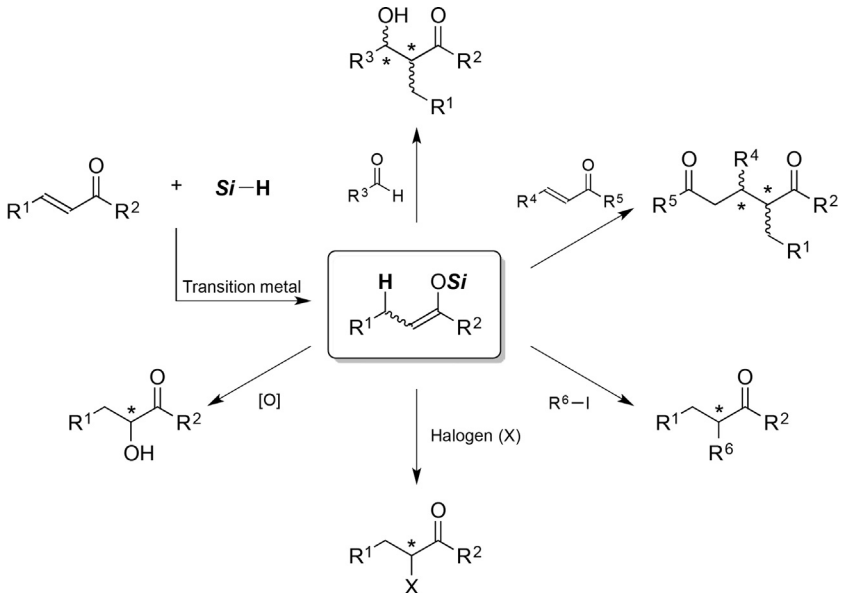
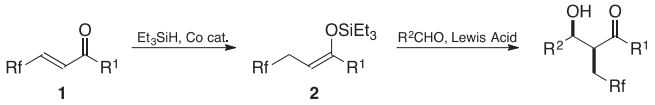


Scheme 1. Hydrosilylation of α,β-unsaturated carbonyl compounds and the synthetic applications.



Scheme 2. Present work.

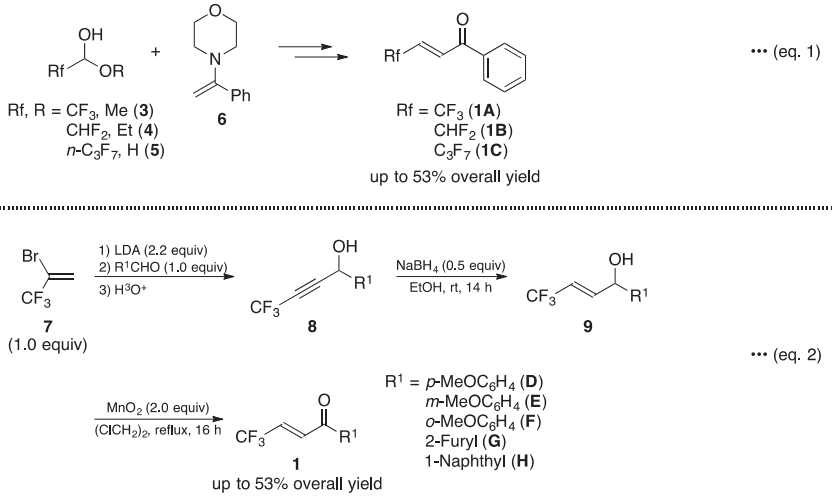
2.2. Hydrosilylation of β-fluoroalkylated α,β-unsaturated ketones

With various types of substrates in hand, our attention was directed toward the examination of the hydrosilylation reaction of **1A**–**H**. First of all, we started the exploitation of the optimum reaction conditions by using **1A**, as shown in Table 1. Thus, treatment of **1A** with 1.2 equiv of Et_3SiH in the presence of 5 mol% of $Co_2(CO)_8$ in dichloroethane at the reflux temperature for 12 h resulted in a complete consumption of the starting ketone, affording the 1,4-hydrosilylated adduct **2Aa** with high *Z* selectivity in 78% yield, together with 7% of the 1,2-hydrosilyated adduct **10Aa** [14]. It was also revealed that the reaction completed within 2 h without any decrease of the yield and the stereoselectivity (Entry 2). Although a lower loading of the catalyst afforded the desired product in only 61% yield (Entry 3), prolonged reaction under 3 mol% loading of the catalyst afforded the desired product quantitatively (Entry 4). At lower temperature, the reaction hardly proceeded (Entry 5). Very interestingly, rhodium or platinum catalysts, very frequently employed for hydrosilylation of the nonfluorinated substances, were found not to be suitable for this reaction (Entries 6–9).

We next examined a series of silanes as summarized in Table 2. In the case of $PhMe_2SiH$, the desired **2Ab** was obtained in only 54% yield though the starting material was completely consumed (Entry 2). Additionally, the stereoselectivity of **2Ab** still remained very high, but the regioselectivity significantly decreased. It was also revealed that use of $(EtO)_2MeSiH$ and $(EtO)_3SiH$ caused a significant decrease of the regioselectivity (Entries 3 and 4) [15].

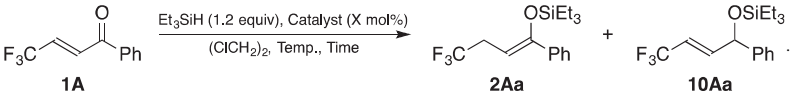
With the best reaction conditions in hand, we next tested a variety of β-fluoroalkylated α,β-unsaturated ketones for the hydrosilylation reaction. The results are summarized in Table 3.

As shown in Entries 2–4, the position of a substituent on the benzene ring in the substrate did not influence on the reaction at all, providing the corresponding silyl enol ethers **2Da**, **2Ea**, **2Fa** in a highly regio- and stereoselective manner. Additionally, the ketones



Scheme 3. Preparation of various β-fluoroalkylated α,β-unsaturated ketones.

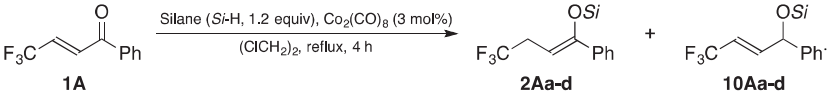
Table 1
Investigation of the reaction conditions.



Entry	Catalyst	X/mol%	Temp.	Time/h	Yield[a]/% of **2Aa**+**10Aa**	Ratio **2Aa**/**10Aa**	Ratio of **2Aa**[a] *E*/*Z*	Recovery[a]/% of **1A**
1	$Co_2(CO)_8$	5	Reflux	12	85 (78+7)	92/8	5/95	0
2	$Co_2(CO)_8$	5	Reflux	2	91 (87+4)	96/4	2/98	0
3	$Co_2(CO)_8$	3	Reflux	2	61 (57+4)	93/7	0/100	39
4	$Co_2(CO)_8$	3	Reflux	4	99 (94+5)	95/5	1/99	0
5	$Co_2(CO)_8$	3	50 °C	4	17 (15+2)	88/12	0/100	81
6	$[Rh(cod)Cl]_2/2PPh_3$	3	Reflux	4	11 (11+0)	100/0	26/74	80
7	$RhCl(PPh_3)_3$	3	Reflux	4	15 (15+9)	100/0	40/60	25
8	$[Rh(cod)_2]BF_4/2PPh_3$	3	Reflux	4	58 (58+0)	100/0	36/64	0
9	$H_2PtCl_6{\cdot}6H_2O$	3	Reflux	4	13 (13+0)	100/0	0/100	0

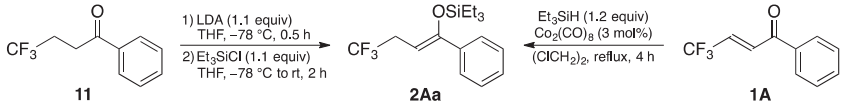
[a] Determined by ^{19}F NMR. The former and the latter values in parentheses are ^{19}F NMR yields of **2Aa** and **10Aa**, respectively.

Table 2
Hydrosilylation using various silanes.



Entry	Silane *Si*-H	Yield[a]/% of **2A**+**10A**	Ratio[a] **2A**/**10A**	Ratio of **2A**[a] *E*/*Z*	Recovery[a]/% of **1A**
1	Et_3SiH (**a**)	99 (94+5)	95/5	1/99	0
2	$PhMe_2SiH$ (**b**)	73 (54+19)	74/26	7/93	0
3	$(EtO)_2MeSiH$ (**c**)	93 (62+31)	69/31	3/97	0
4	$(EtO)_3SiH$ (**d**)	46 (26+20)	57/43	0/100	33

[a] Determined by ^{19}F NMR. The former and the latter values in parentheses are ^{19}F NMR yields of **2A** and **10A**, respectively.



Scheme 4. Determination of the stereochemistry.

having an heteroaromatic ring or a naphthyl group were found to be good substrates as well (Entries 5 and 6) [16]. Changing a fluoroalkyl group from a CF_3 to a C_3F_7 group did not bring about any dramatic change in the reaction (Entry 7). Although use of a CHF_2 group as Rf retarded the reaction proceeding (Entry 8), increasing the amount of the catalyst from 3 to 5 mol% led to a satisfactory result (Entry 9).

2.3. Determination of the stereochemistry

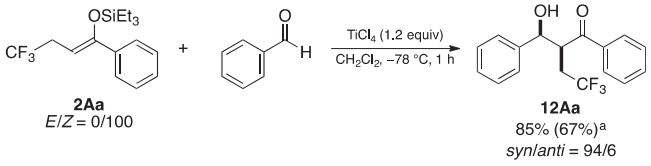
The stereochemical assignment of **2** was made as follows (Scheme 4). In general, it has been well known that treatment of alkyl phenyl ketones with a slight excess of LDA gives the corresponding *Z*-silyl enol ethers preferentially [17]. Then, 4,4,4-trifluoro-1-phenyl-1-butanone **11** was subjected to the enolization using LDA/Et_3SiCl. Thus, on treating **11** with 1.1 equiv of LDA in THF at −78 °C for 0.5 h, followed by the addition of 1.1 equiv of Et_3SiCl and the stirring of the reaction mixture at room temperature, the corresponding *Z*-silyl enol ether was obtained as a single isomer. On the other hand, the silyl enol ether **2Aa**, prepared through the hydrosilylation of **1A** with Et_3SiH in the presence of $Co_2(CO)_8$, was found to be completely identical to the product derived from **11**, indicating unambiguously that the hydrosilylated adduct **2Aa** was a *Z* isomer.

The stereochemistry of other hydrosilylated products **2Da**–**2Ha** was determined as *Z* based on the analogy of the chemical shifts between **2Aa** and **2Da**–**2Ha**.

On the other hand, **2Ba** was also found to be a *Z* isomer because the ^{19}F NMR signal of the *Z* isomer appears at lower field than the one of the *E* isomer. In a manner similar to **2Ba**, the stereochemistry of **2Ca** was determined as *Z* based on the ^{19}F NMR signals for the CF_2 group adjacent to the CH_2 group (−128.33 for *E* isomer, −128.14 for *Z* isomer) (Fig. 1).

2.4. Synthetic application of fluorinated silyl enol ethers

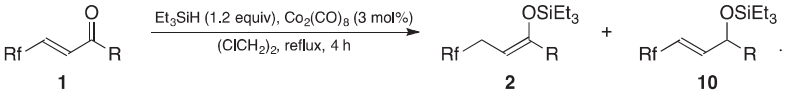
As synthetic application, we attempted the Mukaiyama aldol reaction using the above-obtained silyl enol ethers. Thus, treatment of **2Aa** (1.0 equiv) with 1.2 equiv of benzaldehyde in the presence of 1.2 equiv of $TiCl_4$ in CH_2Cl_2 at −78 °C for 1 h gave the corresponding α-hydroxy-β-(2,2,2-trifluoroethyl)ketone **12Aa** with high *syn* selectivity in 67% isolated yield (Scheme 5) [18]. In terms of efficiency, we also carried out the one-pot procedure for

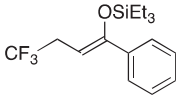
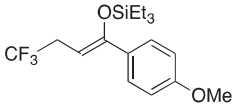
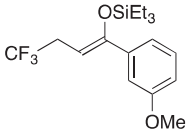
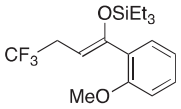
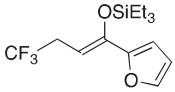
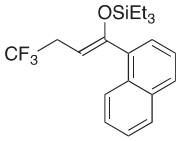
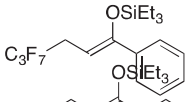
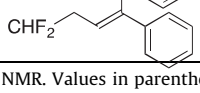


a) Determined by ^{19}F NMR. Value in parentheses is of isolated yield.

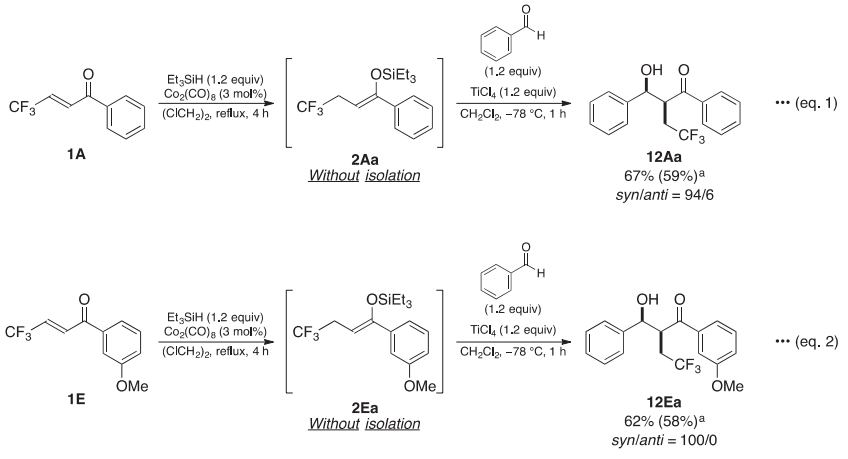
Scheme 5. Mukaiyama aldol reaction of **2Aa** with benzaldehyde.

Table 3
Hydrosilylation of various β-fluoroalkylated α,β-unsaturated ketones.



Entry	Product		Yield[a]/% of **2**+**10**	Ratio[b] **2**/**10**	Ratio of **2**[b] **E**/**Z**
1		**2Aa**	94 (90)	95/5	0/100
2		**2Da**	98 (95)	92/8	3/97
3		**2Ea**	93 (87)	94/6	5/95
4		**2Fa**	92 (90)	93/7	6/94
5		**2Ga**	88 (82)	96/4	10/90
6		**2Ha**	93 (87)	96/4	2/98
7		**2Ca**	91 (87)	100/0	9/91
8		**2Ba**	41	95/5	5/95
9[c]		**2Ba**	96 (92)	96/4	2/98

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yield.
[b] Determined by ^{19}F NMR.
[c] Five mol% of $Co_2(CO)_8$ was used.



a) Determined by ^{19}F NMR. Values in parentheses are of isolated yield.

Scheme 6. One-pot procedures for the hydrosilylation of **1A**, **1E** and the subsequent aldol reaction.

Product	Chemical shift		Product	Chemical shift	
	E	*Z*		*E*	*Z*
2Aa	–	−66.54	**2Ga**	−67.35	−66.52
2Da	−67.14	−66.60	**2Ha**	−67.16	−66.60
2Ea	−67.09	−66.52	**2Ca**	−128.33[a]	−128.14[a]
2Fa	−67.10	−66.59	**2Ba**	−116.43	−115.61 to −115.37

a) ^{19}F NMR signals for the CF_2 group adjacent to the CH_2 group.

Fig. 1. Comparison of chemical shifts in ^{19}F NMR.

the hydrosilylation and the following aldol reaction (Scheme 6, eq. 1). In consequence, the desired aldol adduct **12Aa** was obtained without loss of diastereoselectivity in approximately the same yield as shown in Scheme 5. In addition, changing the substrate from **1A** to **1E** did not influence on the yield as well as the diastereoselectivity (Scheme 6, eq. 2).

3. Conclusion

In summary, we have developed the novel $Co_2(CO)_8$-catalyzed hydrosilylation reaction of various β-fluoroalkylated α,β-unsaturated ketones. It was revealed that this reaction proceeded in a highly *Z*-selective manner to give the corresponding silyl enol ethers in good to high yields. We have also demonstrated the following highly *syn*-selective aldol reaction using thus-obtained hydrosilylated adducts with benzaldehyde. It should be noted that one-pot method for the hydrosilylation of the β-fluoroalkylated α,β-unsaturated ketones and the following aldol reaction also afforded the coupling products in good yields without loss of diastereoselectivity.

4. Experimental

4.1. General

Infrared spectra (IR) were recorded on a Shimadzu FTIR-8200A (PC) spectrophotometer and Thermo Electron Corp AVATAR 370DTGS spectrophotometer. ^1H NMR (500.13 MHz) and ^{13}C NMR (125.75 MHz) spectra were measured with a Bruker DRX500 spectrometer or a JEOL JNM-AL400 spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane (TMS) as an internal reference. ^{19}F NMR spectra were measured with a Bruker DPX300 (282.38 MHz) spectrometer or a JEOL JNM-AL400 spectrometer (376.05 MHz) in a $CDCl_3$ solution containing $CFCl_3$ as an internal reference. A JEOL JNM-EX90A (84.21 MHz, FT) spectrometer was used for determining the yields of the products with internal hexafluorobenzene (C_6F_6), trifluoromethylbenzene (BTF), or ethyl trifluoroacetate (TFA). It was also used for the determining regioselectivity and stereoselectivity. High-resolution mass spectra (HRMS) were measured with a JEOL JMS-700 mass spectrometer by electron impact (EI), chemical ionization (CI), or fast atom bombardment (FAB) method.

4.1.1. Materials

All chemicals were reagent-grade, and if necessary, were purified in the usual manner prior to use. Thin layer chromatography (TLC) was done with Merck 25 aluminium sheets (silica gel 60 F_{254}). Column chromatography was carried out with Wakogel C-200. All reactions were carried out under argon atmosphere.

4.2. Preparation of γ-fluoroalkylated allylic alcohol derivatives

Typical procedure: Diisopropylamine (6.78 mL, 44 mmol) was dissolved in THF (40 mL), and the whole was cooled to −78 °C. Then to this mixture was added *n*-BuLi (1.6 M in *n*-hexane, 27.5 mL, 44 mmol) at that temperature, and the whole was stirred for 30 min. To this reaction mixture was dropwise added 2-bromo-3,3,3-trifluoropropene (3.49 g, 20 mmol) at −78 °C. After stirring of the reaction mixture for 5 min, 4-methoxybenzaldehyde (1.26 mL, 20 mmol) was added into the mixture, and then the whole was stirred at that temperature for 2 h. The mixture was quenched with saturated NH_4Cl aq., and then the whole was extracted with AcOEt three times. The combined organic layers were dried over anhydrous Na_2SO_4, then filtered and concentrated in *vacuo*. The residue was dissolved in ethanol, and to this reaction mixture was added $NaBH_4$ (0.380 g, 10 mmol) at 0 °C. The solution was warmed to room temperature, and stirred for 14 h. The reaction was quenched with saturated NH_4Cl aq. and the whole was extracted with AcOEt three times. The combined organic layers were dried over anhydrous Na_2SO_4, then filtered and concentrated in *vacuo*. The resulting yellow liquid was purified by silica gel column chromatography (Hexane/EtOAc = 5/1) to give the corresponding (*E*)-4,4,4-trifluoro-1-(4-methoxyphenyl)-2-buten-1-ol (**9D**).

4.2.1. (E)-4,4,4-Trifluoro-1-(4-methoxyphenyl)-2-buten-1-ol (*9D*)

Yield 70%; Yellow liquid; IR (neat) 3408, 1683, 1611, 1514, 1465, 1305, 1254, 1176, 1121, 1081, 1034, 977, 834 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{11}H_{11}F_3O_2$: 232.0711, Found 232.0710; ^1H NMR ($CDCl_3$) δ = 2.07 (m, 1H), 3.83 (s, 3H), 5.28 (m, 1H), 6.03 (ddq, *J* = 16.58, 2.00, 6.79 Hz, 1H), 6.51 (ddq, *J* = 16.58, 3.60, 1.79 Hz, 1H), 6.89–6.93 (m, 2H), 7.23–7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 55.2, 72.2, 114.4, 117.5 (q, *J* = 34.7 Hz), 123.3 (q, *J* = 268.7 Hz), 128.0, 132.7, 141.2 (q, *J* = 6.1 Hz), 158.7; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.41 (d, *J* = 6.79 Hz, 3F).

4.2.2. (E)-4,4,4-Trifluoro-1-(3-methoxyphenyl)-2-buten-1-ol (*9E*)

Yield 69%; Yellow liquid; IR (neat) 3410, 2954, 1682, 1603, 1489, 1457, 1438, 1266, 1046, 977, 862, 786, 699 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{11}H_{11}F_3O_2$: 232.0711, Found 232.0705; ^1H NMR ($CDCl_3$) δ = 2.31 (m, 1H), 3.82 (s, 3H), 5.31 (m, 1H), 6.02–6.07 (m, 1H), 6.49–6.54 (m, 1H), 6.87–6.93 (m, 3H), 7.29–7.33 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 55.16–55.18 (m), 72.50–72.51 (m), 112.1, 113.4, 117.6 (q, *J* = 33.9 Hz), 118.7, 123.2 (q, *J* = 269.5 Hz), 130.0, 141.0 (q, *J* = 5.8 Hz), 142.2, 159.9; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.49 (d, *J* = 4.89 Hz, 3F).

4.2.3. (E)-4,4,4-Trifluoro-1-(2-methoxyphenyl)-2-buten-1-ol (*9F*)

Yield 69%; Yellow liquid; IR (neat) 3411, 2955, 1681, 1603, 1489, 1457, 1266, 1117, 1046, 977, 862, 699 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{11}H_{11}F_3O_2$: 232.0711, Found 232.0720; ^1H NMR ($CDCl_3$) δ = 2.89 (m, 1H), 3.87 (s, 3H), 5.55 (m, 1H), 5.99 (ddq, *J* = 16.58, 2.00, 6.79 Hz, 1H), 6.60 (ddq, *J* = 16.58, 5.60, 2.40 Hz, 1H), 6.92–7.01 (m, 2H), 7.26–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 55.2, 68.63–68.66 (m), 110.8, 117.2 (q, *J* = 33.9 Hz), 121.0, 123.4 (q, *J* = 268.9 Hz), 127.2, 128.6, 129.4, 140.9–141.0 (m), 156.4; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.21 (d, *J* = 6.79 Hz, 3F).

4.2.4. (E)-4,4,4-Trifluoro-1-(2-furyl)-2-buten-1-ol (*9G*)

Yield 62%; Yellow liquid; IR (neat) 3408, 1683, 1611, 1514, 1466, 1305, 1254, 1176, 1121, 1080, 1034, 977, 834 cm^{-1}: HRMS (FAB) Calcd for (M+Na) $C_8H_7F_3O_2Na$: 215.0288, Found 215.0296; ^1H NMR ($CDCl_3$) δ = 2.25 (d, *J* = 5.20 Hz, 1H), 5.39–5.39 (m, 1H),

6.10 (ddq, J = 15.59, 2.00, 6.79 Hz, 1H), 6.59 (ddq, J = 15.59, 4.00, 2.00 Hz, 1H), 6.36–6.38 (m, 1H), 6.57–6.62 (m, 1H), 7.425–7.430 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 65.92–65.95 (m), 107.8, 110.5, 119.4 (q, J = 34.2 Hz), 123.0 (q, J = 269.2 Hz), 138.0 (q, J = 6.3 Hz), 143.03–143.07 (m), 152.76–152.79 (m); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.71 (d, J = 6.79 Hz, 3F).

4.3. Preparation of β-fluoroalkylated α,β-unsaturated ketones

Typical procedure: A stirred solution of (*E*)-4,4,4-Trifluoro-1-(4-methoxyphenyl)-2-buten-1-ol (1.16 g, 5.0 mmol, 1.0 equiv) with MnO_2 (0.87 g, 10 mmol, 2.0 equiv) in $ClCH_2CH_2Cl$ (25 mL) was heated at the reflux temperature for 16 h. The reaction was cooled to room temperature, and the reaction mixture was passed through the silica gel, then concentrated *in vacuo*. The resulting yellow solid was purified by silica gel column chromatography (Hexane/EtOAc = 10/1) to give the corresponding (*E*)-4,4,4-Trifluoro-1-(4-methoxyphenyl)-2-buten-1-one (**1D**).

4.4. Hydrosilylation of β-fluoroalkylated α,β-unsaturated ketones

Typical procedure: A stirred solution of (*Z*)-1,1,1-trifluoro-4-phenyl-2-buten-1-one (**1A**, 0.10 g, 0.5 mmol, 1.0 equiv) with triethylsilane (0.1 mL, 0.6 mmol, 1.2 equiv) and $Co_2(CO)_8$ (5 mg, 3 mol%) in $ClCH_2CH_2Cl$ (5 mL) was heated at the reflux temperature for 4 h. The reaction was cooled to room temperature, and the reaction mixture was passed through the silica gel, then concentrated *in vacuo*. The resulting yellow liquid was purified by silica gel column chromatography (Hexane/EtOAc = 20/1) to give the corresponding 4,4,4-trifluoro-1-phenyl-1-triethylsilyloxy-1-butene (**2Aa**).

4.4.1. 4,4,4-Tifluoro-1-phenyl-1-triethylsilyloxy-1-butene (*2Aa*) and (*E*)-1,1,1-trifluoro-4-phenyl-4-triethylsilyloxy-2-butene (*10Aa*)

The products were obtained as an inseparable mixture; Combined yield: 90%; Isomeric ratio: **2Aa**:**10Aa** = 95:5; *E*:*Z* of **2Aa** = 0:100.

Colorless liquid; IR (neat) 3063, 2959, 2914, 2879, 1654, 1458, 1447, 1414, 1362, 1331, 1286, 1258, 1137, 1092, 1005, 828, 767, 731, 698 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{16}H_{23}F_3OSi$: 316.1470, Found 316.1480.

2Aa (*Z* isomer): ^{1}H NMR ($CDCl_3$) δ = 0.59 (q, J = 8.09 Hz, 6H), 0.92 (t, J = 8.09 Hz, 9H), 3.04 (dq, J = 6.99, 10.95 Hz, 2H), 5.05 (t, J = 6.99 Hz, 1H), 7.31–7.33 (m, 3H), 7.44–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 5.3, 6.5, 30.8–31.7 (m), 98.0–98.1 (m), 126.6 (q, J = 276.1 Hz), 128.1, 128.5, 128.6, 138.7, 154.6; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −66.54 (t, J = 10.95 Hz, 3F).

10Aa: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.24 (d, J = 4.89 Hz, 3F).

4.4.2. 4,4,4-Trifluoro-1-(4-methoxyphenyl)-1-triethylsilyloxy-1-butene (*2 Da*) and (*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)-4-triethylsilyloxy-2-butene (*10 Da*)

The products were obtained as an inseparable mixture; Combined yield: 95%; Isomeric ratio: **2Da**:**10Da** = 92:8; *E*:*Z* of **2Da** = 3:97.

Colorless liquid; IR (neat) 2958, 2880, 2839, 1893, 1655, 1577, 1464, 1442, 1415, 1333, 1255, 1137, 1092, 1005, 974, 940, 863, 787, 729 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{17}H_{25}F_3O_2Si$: 346.1576, Found 346.1579.

2 Da (*Z* isomer): ^{1}H NMR ($CDCl_3$) δ = 0.59 (q, J = 8.09 Hz, 6H), 0.92 (t, J = 8.09 Hz, 9H), 3.01 (dq, J = 7.19, 10.99 Hz, 2H), 3.82 (s, 3H), 4.94 (t, J = 7.19 Hz, 1H), 6.83–6.87 (m, 2H), 7.36–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 5.2, 6.5, 31.2 (q, J = 30.1 Hz), 55.2, 96.5–96.6 (m), 113.4, 126.5 (q, J = 276.0 Hz), 127.4, 131.2, 154.2, 159.8; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −66.60 (t, J = 10.99 Hz, 3F).

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −67.14 (t, J = 9.78 Hz, 3F).

10 Da: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.24 (d, J = 4.89 Hz, 3F)

4.4.3. 4,4,4-Trifluoro-1-(3-methoxyphenyl)-1-triethylsilyloxy-1-butene (*2Ea*) and (*E*)-1,1,1-Trifluoro-4-(3-methoxyphenyl)-4-triethylsilyloxy-2-butene (*10Ea*)

The products were obtained as an inseparable mixture; Combined yield: 87%; Isomeric ratio: **2Ea**:**10Ea** = 94:6; *E*:*Z* of **2Ea** = 5:95.

Colorless liquid; IR (neat) 2958, 2879, 1655, 1581, 1488, 1433, 1362, 1330, 1266, 1249, 1213, 1138, 1093, 1052, 1006, 846, 745 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{17}H_{25}F_3O_2Si$: 346.1576, Found 346.1574.

2Ea (*Z* isomer): ^{1}H NMR ($CDCl_3$) δ = 0.60 (q, J = 7.99 Hz, 6H), 0.93 (t, J = 7.99 Hz, 9H), 3.03 (dq, J = 7.09, 10.99 Hz, 2H), 3.82 (s, 3H), 5.06 (t, J = 7.09 Hz, 1H), 6.84–6.87 (m, 1H), 6.98–6.99 (m, 1H), 7.04–7.06 (m, 1H), 7.22–7.25 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 5.2, 6.5, 31.2 (q, J = 30.1 Hz), 55.05–55.11 (m), 98.1–98.2 (m), 111.4, 114.2, 118.6, 126.5 (q, J = 276.4 Hz), 129.2, 140.2, 154.3, 159.4; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −66.52 (t, J = 10.99 Hz, 3F).

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −67.09 (t, J = 12.03 Hz, 3F).

10Ea: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.24 (d, J = 7.14 Hz, 3F).

4.4.4. 4,4,4-Trifluoro-1-(2-methoxyphenyl)-1-triethylsilyloxy-1-butene (*2Fa*) and (*E*)-1,1,1-Trifluoro-4-(2-methoxyphenyl)-4-triethylsilyloxy-2-butene (*10Fa*)

The products were obtained as an inseparable mixture; Combined yield: 90%; Isomeric ratio; **2Fa**:**10Fa** = 93:7; *E*:*Z* of **2Fa** = 6:94.

Colorless liquid; IR (neat) 2958, 2915, 2879, 1661, 1600, 1491, 1464, 1436, 1415, 1361, 1329, 1254, 1135, 1091, 1052, 1029, 1007, 833, 788, 752 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{17}H_{25}F_3O_2Si$: 346.1576, Found 346.1567.

2Fa (*Z* isomer): ^{1}H NMR ($CDCl_3$) δ = 0.48 (q, J = 8.03 Hz, 6H), 0.88 (t, J = 8.03 Hz, 9H), 3.06 (dq, J = 7.19, 11.12 Hz, 2H), 3.83 (s, 3H), 4.88 (t, J = 7.19 Hz, 1H), 6.85–6.93 (m, 2H), 7.27–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 5.0, 6.4, 30.5–31.4 (m), 55.1, 100.09–100.13 (m), 110.6, 120.1, 126.6 (q, J = 276.0 Hz), 127.7, 129.8, 130.3, 151.7, 157.0; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −66.59 (t, J = 11.12 Hz, 3F);

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −67.10 (t, J = 12.40 Hz, 3F).

10Fa: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.02 (m, 3F).

4.4.5. 4,4,4-Trifluoro-1-(2-furyl)-1-triethylsilyloxy-1-butene (*2Ga*) and (*E*)-1,1,1-Trifluoro-4-(2-furyl)-4-triethylsilyloxy-2-butene (*10Ga*)

The products were obtained as an inseparable mixture; Combined yield: 82%; Isomeric ratio: **2Ga**:**10Ga** = 96:4; *E*:*Z* of **2Ga** = 10:90.

Colorless liquid; IR (neat) 2959, 2880, 1686, 1468, 1335, 1258, 1139, 1099, 1012, 805, 740 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{14}H_{21}F_3O_2Si$: 306.1263, Found 306.1266.

2Ga (*Z* isomer): ^{1}H NMR ($CDCl_3$) δ = 0.71 (q, J = 7.99 Hz, 6H), 0.98 (t, J = 7.99 Hz, 9H), 3.00 (dq, J = 7.34, 10.72 Hz, 2H), 5.26 (t, J = 7.34 Hz, 1H), 6.38–6.40 (m, 2H), 7.35 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 5.2, 6.6, 30.7 (q, J = 30.29 Hz), 96.45–96.54 (m), 107.2, 111.1, 126.3 (q, J = 276.10 Hz), 142.2, 145.2, 151.5; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −66.52 (t, J = 10.72 Hz, 3F).

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −67.35 (t, J = 12.40 Hz, 3F).

10Ga: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.42 (d, J = 7.14 Hz, 3F).

4.4.6. 4,4,4-Trifluoro-1-(1-naphthyl)-1-triethylsilyloxy-1-butene (*2Ha*) and (*E*)-1,1,1-Trifluoro-4-(1-naphthyl)-4-triethylsilyloxy-2-butene (*10Ha*)

The products were obtained as an inseparable mixture; Combined yield: 87%; Isomeric ratio: **2Ha**:**10Ha** = 96:4; *E*:*Z* of **2Ha** = 2:98.

Colorless liquid; IR (neat) 3058, 2958, 2914, 2879, 1662, 1366, 1342, 1320, 1289, 1268, 1250, 1184, 1137, 1106, 1074, 1003, 842, 794, 778, 746 cm^{-1}; HRMS (FAB) Calcd for (M^+) $C_{20}H_{25}F_3OSi$: 366.1627, Found 366.1634.

2Ha (*Z* isomer): ^1H NMR ($CDCl_3$) δ = 0.33 (q, *J* = 8.03 Hz, 6H), 0.76 (t, *J* = 8.03 Hz, 9H), 3.15 (dq, *J* = 7.04, 10.92 Hz, 2H), 4.94 (t, *J* = 7.04 Hz, 1H), 7.41–7.51 (m, 4H), 7.82–7.85 (m, 2H), 8.15–8.17 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 5.0, 6.4, 30.9 (q, *J* = 30.0 Hz), 100.6–100.8 (m), 124.9, 126.0, 126.2, 126.3, 126.4, 126.6 (q, *J* = 276.1 Hz), 128.1, 129.0, 131.4, 133.5, 136.8, 154.2; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −66.60 (t, *J* = 10.92 Hz, 3F);

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −67.16 (t, *J* = 12.03 Hz, 3F);

10Ha: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.14 (d, *J* = 7.52 Hz, 3F).

4.4.7. 4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1-triethylsiloxy-1-hexene (**2Ca**)

The products were obtained as an inseparable mixture; Combined yield: 87%; *E*:*Z* = 9:91.

Colorless liquid; IR (neat) 3063, 2960, 2916, 2881, 1655, 1494, 1460, 1447, 1415, 1354, 1325, 1199, 1045, 1006, 857, 809, 698 cm^{-1} HRMS (FAB) Calcd for (M^+) $C_{18}H_{23}F_7OSi$: 416.1406, Found 416.1406.

2Ca (*Z* isomer): ^1H NMR ($CDCl_3$) δ = 0.58 (q, *J* = 7.79 Hz, 6H), 0.91 (t, *J* = 7.79 Hz, 9H), 3.05 (dt, *J* = 6.96, 18.88 Hz, 2H), 5.08 (t, *J* = 6.96 Hz, 1H), 7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 5.3, 6.4, 28.3 (t, *J* = 22.3 Hz), 96.5–96.6 (m), 106.0–112.3 (m), 114.3–120.0 (m), 126.2, 126.3–128.6 (m), 128.2, 128.5, 138.8, 155.2; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −128.14 (s, 2F), −114.54 to −114.35 (m, 2F), −81.08 (t, *J* = 9.78 Hz, 3F).

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −128.33 (s, 2F), −113.89 to −112.12 (m, 2F), −80.88 (t, *J* = 9.78 Hz, 3F).

4.4.8. 4,4-Difluoro-1-phenyl-1-triethylsilyloxy-1-butene (**2Ba**) and (*E*)-1,1-difluoro-4-phenyl-4-triethylsilyloxy-2-butene (**10Ba**)

The products were obtained as an inseparable mixture; Combined yield: 92%; Isomeric ratio: **2Ba**:**10Ba** = 96:4; *E*:*Z* of **2Ba** = 2:98.

Colorless liquid; IR (neat) 3060, 3027, 2960, 2914, 2878, 1652, 1493, 1459, 1414, 1393, 1242, 1179, 1117, 1068, 1006, 974, 834, 742, 698, 649 cm^{-1}; HRMS (FAB) Calcd for (M^+) $C_{12}H_{24}F_2OSi$: 298.1564, Found 298.1572.

2Ba (*Z* isomer): ^1H NMR ($CDCl_3$) δ = 0.62 (q, *J* = 7.83 Hz, 6H), 0.95 (t, *J* = 7.83 Hz, 9H), 2.80 (tdd, *J* = 17.58, 7.33, 4.50 Hz, 2H), 5.10 (t, *J* = 7.33 Hz, 1H), 5.87 (tt, *J* = 57.1, 4.50 Hz, 1H), 7.29–7.49 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 5.3, 6.6, 31.6 (t, *J* = 22.3 Hz), 100.0 (t, *J* = 7.0 Hz), 116.5 (t, *J* = 240.1 Hz), 125.9, 128.1, 128.2, 138.8, 153.6; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −115.61 to −115.37 (m, 2F);

(*E* isomer): ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −116.43 (dt, *J* = 56.03, 16.92 Hz, 2F).

10Ba: ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −111.25 to −111.08 (m, 2F).

4.5. Aldol reaction of the silyl enol ethers with benzaldehyde in the presence of $TiCl_4$

Typical procedure: A stirred solution of (*Z*)-1,1,1-trifluoro-4-phenyl-2-buten-1-one (0.10 g, 0.5 mmol, 1.0 equiv) with triethylsilane (0.1 mL, 0.6 mmol, 1.2 equiv) and $Co_2(CO)_8$ (5 mg, 3 mol%) in $ClCH_2CH_2Cl$ (5 mL) was heated at the reflux temperature for 4 h. Then the mixture was cooled to room temperature and then CH_2Cl_2 (5 mL) was added into the mixture. The whole was cooled to −78 °C, and then $TiCl_4$ (0.07 mL, 0.6 mmol, 1.2 equiv) and PhCHO (0.06 mL, 0.6 mmol, 1.2 equiv) were added into the reaction mixture at that temperature. After being stirred at −78 °C for 1 h, the reaction was quenched with H_2O and the whole was extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4, then filtered and concentrated in *vacuo*. The resulting yellow liquid was purified by silica gel column chromatography (Hexane/EtOAc = 5/1) to give the corresponding 3-hydroxy-1,3-diphenyl-2-(2,2,2-trifluoroethyl)propan-1-one (**12Aa**).

4.5.1. 3-Hydroxy-1,3-diphenyl-2-(2,2,2-trifluoroethyl)propan-1-one (**12Aa**)

Yield: 59%; Diastereomeric ratio = 94:6.

Yellow liquid; IR (neat) 3464, 1670, 1600, 1512, 1456, 1421, 1369, 1311, 1261, 1207, 1173, 1145, 1108, 1027, 979, 771 cm^{-1}: HRMS (FAB) Calcd for (M+Na) $C_{17}H_{15}F_3O_2Na$: 331.0922, Found 331.0916.

Syn isomer: ^1H NMR ($CDCl_3$) δ = 2.06–2.14 (m, 1H), 2.66–2.75 (m, 1H), 3.25–3.56 (m, 1H), 4.10 (ddd, *J* = 2.90, 7.54, 10.49 Hz, 1H), 4.85 (d, *J* = 7.54 Hz, 1H), 7.19–7.51 (m, 8H), 7.85–7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 34.2 (q, *J* = 28.9 Hz), 46.31–46.33 (m), 76.4, 126.2 (q, *J* = 276.0 Hz), 126.3, 128.5, 128.7, 130.1, 133.5, 137.5, 140.9, 171.3, 202.4; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.94 (t, *J* = 9.78 Hz, 3F);

Anti isomer: ^1H NMR ($CDCl_3$) δ = 2.45–2.56 (m, 1H), 2.82–2.95 (m, 1H).

4.5.2. syn-3-Hydroxy-1-(3-methoxyphenyl)-3-phenyl-2-(2,2,2-trifluoroethyl)propan-1-one (**12Ea**)

Yield 58%; Yellow liquid; IR (neat) 3472, 2961, 2839, 1682, 1587, 1257, 1145, 945, 878, 830, 793, 681 cm^{-1}: HRMS (FAB) Calcd for (M^+) $C_{18}H_{17}F_3O_3$: 338.1137, Found 338.1130; ^1H NMR ($CDCl_3$) δ = 2.04–2.10 (m, 1H), 2.64–2.73 (m, 1H), 3.19 (m, 1H), 3.74 (s, 3H), 4.09 (m, 1H), 4.81 (m, 1H), 7.03–7.05 (m, 1H), 7.21–7.31 (m, 5H), 7.40 (s, 1H), 7.48–7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 34.1 (q, *J* = 28.9 Hz), 46.49–46.51 (m), 55.2, 76.4, 112.6, 119.9, 121.2, 126.2 (q, *J* = 276.3 Hz), 126.3, 128.4, 128.7, 129.5, 138.8, 140.9, 159.6, 202.1; ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ = −64.94 (t, *J* = 10.90 Hz, 3F).

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[15] The reaction mechanism of the hydrosilylation has been pooly understood at present. Therefore the high stereoselectivity as well as the low regioselectivity of the hydrosilylation using various silanes also remain unclear.

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