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Indium- and zinc-mediated allylation of difluoroacetyltrialkylsilanes in aqueous media

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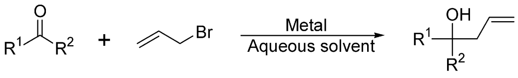
Abstract—Metal-mediated allylations of difluoroacetyltriakylsilanes with various allyl bromides in aqueous media form homoallylic alcohols exclusively. The common Brook rearrangement, carbon to oxygen-silyl migration, is totally suppressed with no detectable formation of silyl enol ether. Influence of solvents on reaction is studied. Reactivity differences between indium and zinc are also described.

1. Introduction

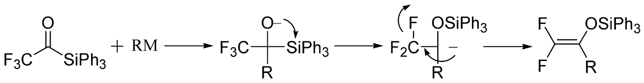
The generation of a hydroxyl group concurrently with the introduction of a carbon–carbon double bond, such as would occur during the allylation reactions[1] of fluorinated carbonyl compounds, suggests that such a process might be especially useful in the preparation of multi-functionalized fluorinated compounds.[2] These molecules are well understood to possess broad utility in the pharmaceutical, agrochemical, and material sciences.[3] As such, these attractive targets have been the aim of many researchers.[4]

Recently, the significant advantages[5] of metal-mediated allylation reactions of carbonyl compounds in aqueous media have attracted considerable attention. These advantages include the avoidance of flammable or anhydrous solvents, reduced environmental and economic impacts and simplified processing in protection–deprotection schemes of reactive functional groups. Allylation reactions of carbonyl compounds using Zn,[6] Bi,[7] Sn,[8] Mg,[9] Mn,[10] Sb,[11] Pb,[12] Hg,[13] and In[14] in aqueous media have been reported (Scheme 1).



Scheme 1. Metal-mediated allylation in aqueous.

Acylsilanes, recognized as synthetic equivalents of aldehydes due to the facile excision of the silyl group by treatment with fluoride ion, have been used as versatile building blocks for the synthesis of complex organic molecules.[15] It is well known that fluorination can impart unexpected and often unique properties to molecules of interest.[16] Not surprisingly, fluorinated acylsilanes have been the subject of increased scrutiny. However, the attempted formation of homoallylic alcohols by the addition of Grignard[17] or lithium reagents[16a] to fluorinated acylsilanes results in the formation of silyl enol ethers via initial Brook rearrangement[18] and subsequent defluorination. (Scheme 2).



Scheme 2. Formation of silyl enol ether via Brook rearrangement and defluorination.

In the course of our research on the development of new fluorinated building blocks and our exploration of the synthetic utility of metal-mediated transformations in aqueous media,[19] we recently reported the synthesis[20] and synthetic applications[21] of novel fluorinated acetyltrialkylsilanes (**1**). In this paper, the results of our studies on the transformation of fluorinated acetyltrialkylsilanes (**1**) via indium and zinc promoted allylation reactions in aqueous media are reported.

2. Results and discussion

2.1. Indium-mediated allylation of difluoroacetyltrialkylsilanes

Allylation reactions mediated by indium have advantages over transformations mediated by other metals. The allylation reaction proceeds in water without activation

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Keywords: difluoroacetyltrialkylsilane; allylation; homoallylic alcohol; Brook rearrangement; silyl enol ether; indium; zinc.

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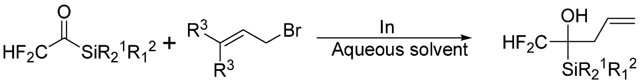
and with only minimal side reactions such as reduction or carbonyl coupling. Indium-mediated allylation reactions of compound (**1a**) with allyl bromide were studied in various concentrations of water in THF. Both water and THF are necessary for the allylation reaction as can be seen from the formation of a trace amount of homoallylic alcohol when pure water or anhydrous THF was employed. However, the influence on this reaction of the relative proportions of THF relative to water is evident in both longer reaction times and lower conversion rates as the concentration of water increased. This outcome may be rationalized by recognizing that solubility of difluoroacetyltrialkylsilanes decreases in increasingly aqueous solvents. The exclusive formation of the homoallylic alcohol under these reaction conditions is worth noting. Enol silyl ethers found as a major product in the reactions of fluorinated acylsilanes with organometallic compounds[16a,17] via Brook rearrangement[18] and defluorination were not detected.

As summarized in Table 1, the generality of the indium-mediated allylation reaction was explored with various difluoroacetyltrialkylsilanes (**1**) in a water and THF (1:1) mixture. Desired homoallylic alcohols were synthesized in good yields without enol silyl ether formation. Substituents on silicon have no effect on the product formation. However, in reaction with a substituted allyl bromide such as 4-bromo-2-methyl-2-butene, the desired homoallylic alcohol was not formed, rather, the acylsilane was recovered.

Table 1. Indium-mediated allylation reaction of difluoroacetyltrialkylsilanes in aqueous media



Entry	R^1	R^2	R^3	Solvent	**2** (Yield %)[a]
1	Phenyl	*t*-Butyl	H	50% THF:50% H_2O	**2a** (97%)
2	Ethyl	Ethyl	H	50% THF:50% H_2O	**2b** (83%)
3	*i*-Propyl	*i*-Propyl	H	50% THF:50% H_2O	**2c** (85%)
4	Ethyl	Ethyl	CH_3	50% THF:50% H_2O	0
5	Ethyl	Ethyl	CH_3	50% THF:50% sat. NH_4Cl	0

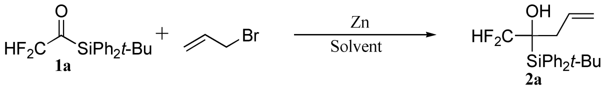
[a] Isolated yield characterized by ^1H, ^{13}C, and ^{19}F NMR.

The reaction mechanism of indium-mediated allylation in aqueous media is not clear. Recently, Chan et al., proposed allylindium(I) as an intermediate species,[22] which on addition to a carbonyl group forms an indium alkoxide that can undergo a simultaneous proton–metal exchange, obviating the Brook rearrangement. However, a parallel process involving a metal surface mediated allyl radical anion cannot be ruled out.

2.2. Zinc-mediated allylation of difluoroacetyltrialkylsilanes

The zinc-mediated allylation reaction gives better results in aqueous saturated ammonium chloride solutions than in water.[23] Addition of ammonium chloride to the medium might not only increase the ionic strength of media but also the change of acidity.[24a] Ammonium chloride while activating the carbonyl group and also activates the metal surface to facilitate the formation of allylating reagent.[25] The zinc-promoted allylation reactions of (**1a**) with allyl bromide were studied in various concentrations of saturated NH_4Cl in THF and the results are summarized in Table 2.

Table 2. The influence of sat. NH_4Cl concentration on zinc-mediated allylation reaction in aqueous THF



Entry	Solvent	Reaction time (min)	Ratio[a]	
			1a (%)	**2a** (%)
1	100% THF	30	>99	<1
2	50% THF:50% sat. NH_4Cl	30	0	100
3	100% sat. NH_4Cl	30	58	42

[a] Determined by GC and ^{19}F NMR.

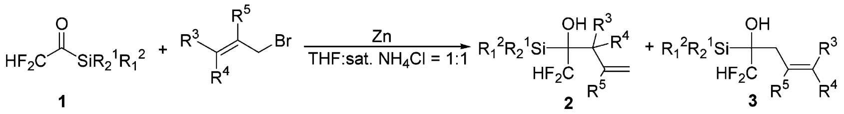
The importance of saturated NH_4Cl is evident as the homoallylic alcohol was not formed when THF alone was solvent. The lower conversions observed in reactions where the solvent was limited to saturated NH_4Cl, are presumably a consequence of the decreased solubility of difluoroacetyltrialkylsilane. Under the optimum conditions found (entry **2**), the zinc-mediated allylation reaction in a mixture of THF and saturated NH_4Cl appeared to be faster (30 min.) than the corresponding indium-promoted process in aqueous THF (24 h).

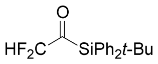
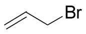
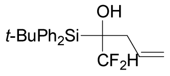
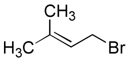
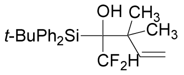
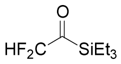
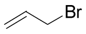
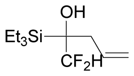
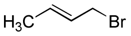
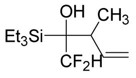
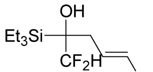
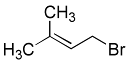
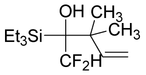
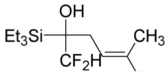
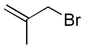
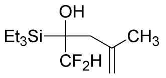
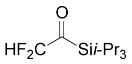
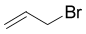
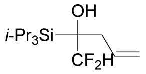
As summarized in Table 3, zinc-mediated allylation reactions of difluoroacetyltrialkylsilanes with various allyl bromides gave homoallylic alcohols in good yields. The steric effect of substituents on silicon was evident in reactions with 4-bromo-2-methyl-2-butene. Reaction with less sterically hindered acylsilane (**1b**) took less time for complete conversion into the desired homoallylic alcohol (entry **5**) than reaction with more hindered silane. The steric influence of the allylic bromide reaction partner was also seen in the transformation where 4-bromo-2-methyl-2-butene was employed. In the case of **1a**, reactions with 4-bromo-2-methyl-2-butene lead to recovery of starting material with formation of only a trace amount of product even at long reaction times (entry **2**). Reactions with non- or mono-substituted allylic bromides (entry **3**, **4** and **6**) required shorter reaction times than with a di-substituted allylic halide. Reaction with 4-bromo-2-methyl-2-butene resulted in formation of regio-isomeric mixture of γ-adduct, **2f**, and α-adduct, **3f** (entry **2**). However, γ-regioselectivity was observed with less hindered allylic bromide such as crotyl bromide(entry **4**).

2.3. Regio- and diastereoselectivity

The regio- and stereoselectivity of metal-mediated allylation reactions in aqueous media is well understood.[6,24] In general, regioselectivity is governed by the substituent on the allyl halide. The formation of γ-adducts was exclusively observed under some conditions, however, allyl halides bearing bulky γ-substituents such as 1-bromo-4,4-dimethyl-2-pentene and (3-bromopropenyl)trimethylsilane resulted in the formation of α-adducts. In contrast, diastereoselectivity is affected by the steric and chelating effect of substituents

Table 3. Zinc-mediated allylation reaction of difluoroacetyltrialkylsilanes in aqueous media



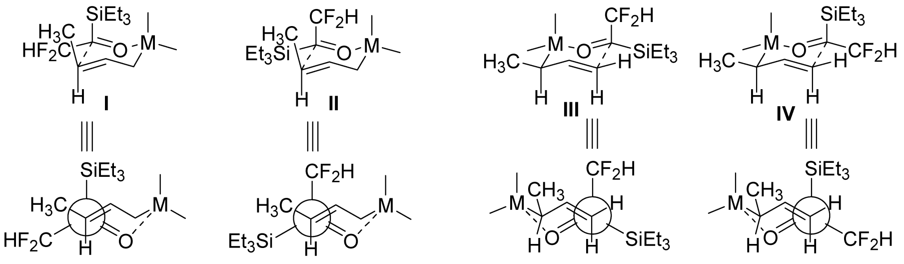
Entry	Acylsilane	Allylic bromide	Reaction time (min)	Yield (%)[a] 2	3
1	 **1a**		30	 **2a (84 %)**	
2			1day	 **2d (trace)**	
3	 **1b**		30	 **2b (88 %)**	
4			30	 **2e (81 %)**	 **3e (trace)**
5			90	 **2f (53 %)**	 **3f (15 %)**
6			30	 **2g (82 %)**	
7	 **1c**		30	 **2c (91 %)**	

[a] Isolated yield characterized by ^{1}H, ^{13}C, and ^{19}F NMR.

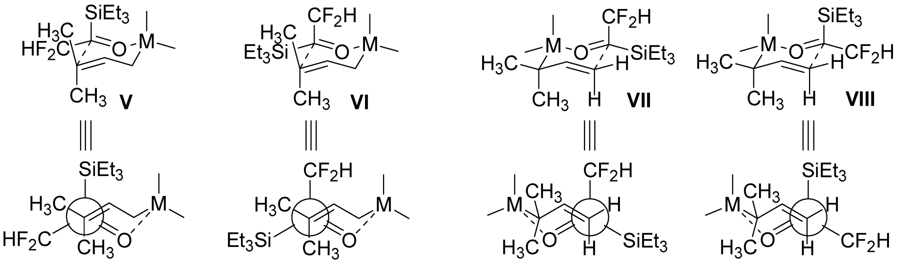
on aldehydes. These observations are consistent with the imposition of classical chair-like Zimmerman type transition state.[26]

The regio- and stereochemistry reported in this work may be rationalized by a cyclic transition state model. The poor diastereoselectivity (60:40) with crotyl bromide (Table 3, entry **4**) can be attributed to the only limited steric influence of a γ-methyl substituent (Scheme 3, transition states **I** versus **II**). Furthermore, γ-regioselective carbon–carbon bond formation is consistent with the minimal steric demand of the methyl group. (Scheme 3, transition states **I** and **II** versus transition states **III** and **IV**). Transition states **III** and **IV** may be disfavored due to congestion of carbon–metal–oxygen coordination even though transition state **I** appears to encounter more steric strain than transition state **III**.

However, reaction with 4-bromo-2-methyl-2-butene results in a mixture of γ-adduct and α-adduct with the γ-adduct favored. Transition state **VII** and **VIII** apparently are less sterically encumbered than transition states **V** and **VI**. This prediction is inconsistent with the experimental findings suggesting that additional γ-methyl substituent increases steric strain promoting the formation of α-adduct but not enough to reverse regioselectivity. Clearly product selectivity is a result of the combination of steric factors



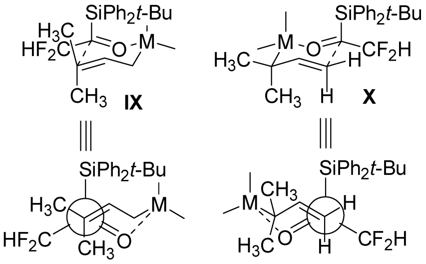
Scheme 3.



Scheme 4.

influencing the reaction, i.e., γ-substituent but also carbon–metal–oxygen coordination both influence the regio- and diastereoselectivity. In addition, from the steric bulk of the acylsilane substituents also modulate the reaction pathway (Scheme 4).

Reaction of more hindered acylsilane (**1a**) with 4-bromo-2-methyl-2-butene resulted in recovery of **1a** with trace formation of γ-adduct even at long reaction times (Table 3, entry **2**). In transition state **X**, γ,γ-dimethyl substituents might interfere carbon–metal–oxygen coordination, forcing transition state **IX** to be favored but the sterically hindered silyl group slows the conversion of acylsilane to γ-adduct (Scheme 5).



Scheme 5.

2.4. Differential reactivities of indium and zinc

In this paper the different reactivities of indium and zinc observed might be derived from the different ionization potentials of these two metals (Table 4).[5b]

Table 4. First to fourth ionization potential of indium and zinc

Metal	Ionization potential (eV)			
	I	II	III	IV
Indium	5.785	18.86	28.03	54.4
Zinc	9.39	17.96	39.7	

Li and Chan[6b] proposed a single-electron transfer (SET) mechanism for the zinc-mediated allylation reaction. They observed dimerization of allyl halides occurs in the absence of electrophiles, suggesting intermediary of the radical anionic species on metal surface and carbon–carbon bond formation occurring prior to the formation of the free organozinc compound. Chan and Yang[22] proposed allylindium(I), preferentially formed due to the low first ionization potential of indium, as an active substrate in aqueous media. Even though, they did not rule out a parallel process involving metal surface-mediated allyl radical processes. However, involvement of indium metal surface for Barbier-type reaction under aqueous conditions may not be necessary as a consequence of the availability of alternative routes to the formation of allylindium(I).

In our observation recovery of unreacted acylsilane (**1a**) on both indium- and zinc-mediated reactions in anhydrous THF might exclude the possible electron transfer from metal surface to acylsilane. However, observation of gas evolution and exothermic reaction on zinc-mediated reaction, but not on indium-mediated processes, suggests possible electron process involving metal surface. Such a route is supported by the improved yields under acidic conditions and those conditions where ultrasound facilitated the electron process by activating the metal surface, as reported elsewhere.[6] We can not exclude the possible involvement of indium surface allyl radical process. Therefore, with the available information no definitive conclusion on the different reactivities between indium and zinc is possible at this time.

3. Conclusion

Homoallylic alcohols were formed by the indium- and zinc-mediated allylation reactions of difluoroacetyltrialkylsilanes, **1**, in aqueous media,. Both indium- and zinc-mediated reactions proceed in good yields without silyl enol ether formation. The importance of the concentration of THF relative to water is evident in the indium-mediated reactions. However, the presence of saturated NH_4Cl is more important than the concentration of THF in zinc-assisted reactions. The improved reactivity of the allylation reagent, especially in the reactions of di-substituted allylic bromides, was observed in zinc-mediated reaction. Steric effects of substituents both on the acetylsilane and on the allylic bromide affected not only reaction times but also the regioselectivity.

4. Experimental

Reagents were purchased from commercial sources and used without further purification. THF was purified by standard methods and freshly distilled under argon from sodium/benzophenone ketyl. ^1H (300 MHz), ^{13}C(75 MHz), and ^{19}F(282 MHz) NMR spectra were measured on a Varian Gemini-300 NMR spectrometer. ^1H and ^{13}C chemical shifts are reported relative to the residual signals of the $CHCl_3$ solvent in $CDCl_3$, taken as δ 7.24 for ^1H and δ 77.0 for ^{13}C. ^{19}F chemical shifts are referenced to $CFCl_3$ as a external standard.

4.1. General procedure for the synthesis of difluoroacetyltrialkylsilanes (1)

Compounds (**1**) were prepared according to the method reported in the literature.[20]

4.2. General procedure for the indium-mediated allylation

To a mixture of allyl bromide (1.1 mmol) and difluoroacetyltrialkylsilanes (**1**) (1 mmol) in THF (5 mL) and water (5 mL) was added indium (1.1 mmol, 126 mg of 100 mesh powder) and the resulting mixture was stirred for 1 day. The reaction was quenched with saturated NH_4Cl solution then extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. Purification by silica gel column chromatography afforded compounds **2**.

4.2.1. 2-(*tert*-Butyldiphenylsilanyl)-1,1-difluoro-4-penten-2-ol (2a). Yield=97%, colorless crystal, mp=62–63°C. ^{1}H NMR: δ 7.86–7.76 (m, 4H), 7.49–7.36 (m, 6H), 6.00 (dd, J_{HF}=55.5, 55.5 Hz, 1H), 5.89–5.71 (m, 1H), 5.24 (dd, J=10.1, 2.2 Hz, 1H), 5.12 (d, J=17.0 Hz, 1H), 2.70 (dd, J=14.1, 9.5 Hz, 1H), 2.50 (dd, J=14.1, 6.0 Hz, 1H), 2.29 (s, 1H), 1.23 (s, 9H); ^{13}C NMR: δ 137.3, 137.0, 132.2, 132.1, 129.5, 129.4, 127.5, 127.4, 121.0, 118.3 (dd, $^{1}J_{CF}$=247.6, 247.7 Hz), 70.5 (dd, $^{2}J_{CF}$=18.9, 18.9 Hz), 37.3 (t, $^{3}J_{CF}$=3.3 Hz), 29.2, 19.6; ^{19}F NMR: δ −122.0 (dd, J=278.9, 55.6 Hz, 1F), −124.0 (ddd, J=278.9, 57.8, 3.7 Hz, 1F); Anal. Calcd For $C_{21}H_{26}F_2OSi$ (%): C, 69.96; H, 7.27. Found (%): C, 70.00; H, 7.16.

4.2.2. 1,1-Difluoro-2-triethylsilanyl-4-penten-2-ol (2b). Yield=83%, clear oil. ^{1}H NMR: δ 5.90–5.75 (m, 1H), 5.71 (t, J_{HF}=57.1 Hz, 1H), 5.20 (d, J=10.4 Hz, 1H), 5.14 (d, J=17.0 Hz, 1H), 2.53 (dd, J=14.0, 6.4 Hz, 1H), 2.36 (dd, J=14.2, 8.9 Hz, 1H), 1.78 (s, 1H), 1.00 (t, J=7.9 Hz 9H), 0.71 (q, J=7.9 Hz, 6H); ^{13}C NMR: δ 132.1, 120.2, 119.1 (t, $^{1}J_{CF}$=247.5 Hz), 69.4 (t, $^{2}J_{CF}$=24.3 Hz), 37.2 (t, $^{3}J_{CF}$=4.1 Hz), 7.5, 2.0; ^{19}F NMR: δ −125.4 (d, J=57.1 Hz, 1F), −125.5 (d, J=57.1 Hz, 1F); Anal. Calcd For $C_{11}H_{22}F_2OSi$ (%): C, 55.89; H, 9.38. Found (%): C, 56.03; H, 9.12.

4.2.3. 1.1-Difluoro-2-triisopropylsilanyl-4-penten-2-ol (2c). Yield=85%, clear oil. ^{1}H NMR: δ 5.93–5.78 (m, 1H), 5.82 (dd, J_{HF}=56.1, 56.0 Hz, 1H), 5.25 (d, J=10.0 Hz, 1H), 5.15 (d, J=17.4 Hz, 1H), 2.69 (dd, J=14.3, 6.0 Hz, 1H), 2.52 (dd, J=14.3, 9.5 Hz, 1H), 1.97 (s, 1H), 1.36–1.26 (m, J=3H), 1.15 (d, J=7.1 Hz, 18H); ^{13}C NMR: δ 132.2, 120.9, 118.5 (dd, $^{1}J_{CF}$=246.3, 246.2 Hz), 70.5 (dd, $^{2}J_{CF}$=19.7, 19.4 Hz), 37.5 (t, $^{3}J_{CF}$=3.7 Hz), 19.3, 19.2, 11.1; ^{19}F NMR: δ −122.5 (dd, J=277.6, 56.0 Hz, 1F), −124.5 (ddd, J=277.7, 58.0, 3.1 Hz, 1F); Anal. Calcd For $C_{14}H_{28}F_2OSi$ (%): C, 60.39; H, 10.14. Found (%): C, 60.41; H, 10.06.

4.3. General procedure for the zinc-mediated allylation

To a mixture of allyl bromide (3 mmol) and difluoroacetyltrialkylsilanes **1** (1 mmol) in THF (5 mL) and saturated NH_4Cl (5 mL) was added zinc (3 mmol, 196 mg, <10 μ powder) and the resulting mixture was stirred for a certain time (Table 3). The reaction was quenched with water then extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. Purification by silica gel column chromatography afforded homoallylic alcohols.

4.3.1. 2-(*tert*-Butyldiphenylsilanyl)-1,1-difluoro-4-penten-2-ol (2a). Yield=84%, colorless crystal, mp=62–63°C.

4.3.2. 1,1-Difluoro-2-triethylsilanyl-4-penten-2-ol (2b). Yield=88%, clear oil.

4.3.3. 1.1-Difluoro-2-triisopropylsilanyl-4-penten-2-ol (2c). Yield=91%, clear oil.

4.3.4. 1,1-Difluoro-3-methyl-2-triethylsilanyl-4-penten-2-ol (2e). Yield=81%, clear oil. First diastereomer. ^{1}H NMR: δ 5.89 (m, 1H), 5.77 (t, J_{HF}=56.7 Hz, 1H), 5.10 (m, 2H), 2.64 (q, J=7.1 Hz, 1H), 1.69 (s, 1H), 1.13 (d, J=7.1 Hz, 3H), 1.00 (t, J=7.8 Hz 9H), 0.76 (q, J=7.8 Hz, 6H); ^{13}C NMR: δ 139.2, 119.1 (t, $^{1}J_{CF}$=245.1 Hz), 116.3, 72.7 (t, $^{2}J_{CF}$=23.0 Hz), 42.5 (t, $^{3}J_{CF}$=3.8 Hz), 14.9, 7.6, 3.2; ^{19}F NMR: δ −123.8 (d, J=56.6 Hz, 1F), −123.9 (d, J=56.8 Hz, 1F); Second diastereomer. ^{1}H NMR: δ 5.78 (t, J_{HF}=55.6 Hz, 1H), 5.76–5.65 (m, 1H), 5.19 (dd, J=10.1, 1.17 Hz, 1H), 5.12 (d, J=17.0 Hz, 1H), 2.56 (q, J=7.4 Hz, 1H), 1.91 (s, 1H), 1.16 (d, J=7.4 Hz, 3H), 1.02 (t, J=7.8 Hz 9H), 0.76 (q, J=7.8 Hz, 6H); ^{13}C NMR: δ 139.2, 118.9 (t, $^{1}J_{CF}$=245.7 Hz), 118.2, 71.6 (t, $^{2}J_{CF}$=21.5 Hz), 44.0 (t, $^{3}J_{CF}$=3.1 Hz), 15.9, 7.6, 3.0; ^{19}F NMR: δ −122.4 (d, J=56.4 Hz, 2F); Anal. Calcd For $C_{12}H_{24}F_2OSi$ (%): C, 57.56; H, 9.66. Found (%): C, 57.39; H, 9.49.

4.3.5. 1,1-Difluoro-3,3-dimethyl-2-triethylsilanyl-4-penten-2-ol (2f). Yield=53%, clear oil. ^{1}H NMR: δ 6.05 (ddd, J=17.5, 10.9, 3.6 Hz, 1H), 5.74 (dd, J_{HF}=55.9, 55.9 Hz, 1H), 5.13 (dd, J=10.9, 1.3 Hz, 1H), 5.03 (d, J=17.5 Hz, 1H), 1.81 (s, 1H), 1.15 (s, 6H), 1.00 (t, J=7.9 Hz 9H), 0.80 (q, J=7.8 Hz, 6H); ^{13}C NMR: δ 145.1, 120.3 (dd, $^{1}J_{CF}$=245.1, 245.0 Hz), 114.1, 75.6 (t, $^{2}J_{CF}$=23.7 Hz), 43.4 (t, $^{3}J_{CF}$=2.2 Hz), 24.4, 23.7, 7.8, 4.5; ^{19}F NMR: δ −117.5 (dd, J=282.7, 56.1 Hz, 1F), −120.6 (dd, J=283.7, 57.6 Hz, 1F); Anal. Calcd For $C_{13}H_{26}F_2OSi$ (%): C, 59.05; H, 9.91. Found (%): C, 59.02; H, 9.78.

4.3.6. 1.1-Difluoro-5-methyl-2-triethylsilanyl-4-hexen-2-ol (3f). Yield=15%, clear oil. ^{1}H NMR: δ 5.68 (t, J_{HF}=57.2 Hz, 1H), 5.24–5.12 (m, 1H), 2.47 (dd, J=14.5, 9.0 Hz, 1H), 2.34 (dd, J=14.7, 7.0 Hz, 1H), 1.74 (s, 3H), 1.73 (s, 1H), 1.63 (s, 3H), 1.00 (t, J=8.0 Hz 9H), 0.72 (q, J=8.0 Hz, 6H); ^{13}C NMR: δ 137.7, 119.4 (t, $^{1}J_{CF}$=246.1 Hz), 116.9, 70.1 (t, $^{2}J_{CF}$=24.1 Hz), 31.2 (t, $^{3}J_{CF}$=4.3 Hz), 26.1, 17.9, 7.5, 2.1; ^{19}F NMR: δ −125.5 (d, J=57.3 Hz, 2F); Anal. Calcd For $C_{13}H_{26}F_2OSi$ (%): C, 59.05; H, 9.91. Found (%): C, 59.02; H, 9.76.

4.3.7. 1,1-Difluoro-4-methyl-2-triethylsilanyl-4-penten-2-ol (2g). Yield=82%, clear oil. ^{1}H NMR: δ 5.66 (t, J_{HF}=57.7 Hz, 1H), 4.98 (s, 1H), 4.76 (s, 1H), 2.38 (m, 2H), 1.94 (s, 1H), 1.82 (s, 3H), 1.01 (t, J=8.0 Hz 9H), 0.72 (q, J=8.0 Hz, 6H); ^{13}C NMR: δ 140.7, 119.2 (dd, $^{1}J_{CF}$=245.9, 243.6 Hz), 115.9, 69.5 (t, $^{2}J_{CF}$=26.9 Hz), 39.6 (dd, $^{3}J_{CF}$=5.7, 5.5 Hz), 24.9, 7.5, 2.1; ^{19}F NMR: δ −123.4

(dd, $J=279.8$, 57.3 Hz, 1F), -125.1 (dd, $J=279.5$, 58.0 Hz, 1F); Anal. Calcd For $C_{12}H_{24}F_2OSi$ (%): C, 57.56; H, 9.66. Found (%): C, 57.80; H, 9.40.

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