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(*E*)-1,2-Difluoro-1-iodo-2-trialkylsilanes—A useful synthon for the addition of the [IFC═CF] unit to activated electrophiles

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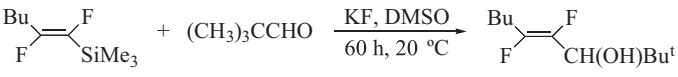
ABSTRACT

Fluoride ion catalyzed reaction of (*E*)-IFC=CFSiR$_3$ with activated aromatic aldehydes and ketones and activated perfluoroaromatics, such as pentafluoropyridine and perfluorotoluenes, transfers the [IFC=CF] unit to the activated electrophiles to stereospecifically provide (*E*)-1,2-difluoro-1-iodosubstituted derivatives. Aluminum chloride catalyzed reaction of (*E*)-1,2-difluoro-1-iodo-2-trialkylsilanes with alkyl or aryl acyl halides gives the corresponding (*E*)-1,2-difluoro-1-iodoketones stereospecifically in excellent yield. The vinyl iodide product formed *via* this methodology could be coupled (with Pd(0)) catalysis to provide an entry to a polyfunctionalized derivative.

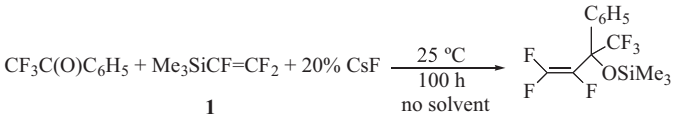
1. Introduction

The development of fluorine-containing synthons has played a significant role in the preparation of organofluorine compounds and has been a valuable addition to the toolbox of the organofluorine chemist [1]. Trialkylsilyl derivatives have been an important component in this methodology. Fluoride ion mediated processes of compounds, such as CF_3SiR_3, have been key to the introduction of trifluoromethyl groups into a variety of non-fluorinated functionalized compounds [2]. In contrast to the use of perfluoroalkylsilanes as synthons, the use of perfluorovinylsilane synthons has received only limited attention. The Normant group first reported the fluoride ion catalyzed reaction of (*Z*)-1,2-difluorotrimethylsilylhexene with pivaldehyde (no yield reported) as illustrated in Eq. (1) [3].



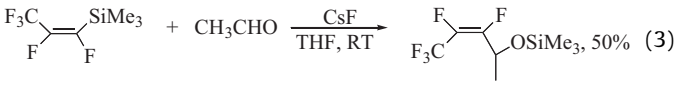
(1)

Subsequently, Yagupolskii studied the fluoride ion catalyzed addition of trialkyl(trifluorovinyl)silanes to aldehydes and ketones, as shown in Eq. (2) [4,5].



(2)

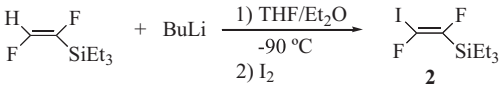
Conditions utilized in this work dictated whether silylated trifluoroallylic alcohols were obtained or whether olefinic products were obtained. More recently, Petrov and Larichev reported similar fluoride ion catalyzed addition reactions of (*E*)-trimethyl(perfluoro-1-propenyl)silane as an agent to transfer the perfluoro-1-propenyl group stereospecifically to aldehydes and ketones, Eq. (3) [6].



(3)

Similar reactions with benzaldehyde gave 66% of the silylated addition adduct.

Another vinylsilane synthon of interest is (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene, **2**, which is readily synthesized by metallation/iodination of (*Z*)-1,2-difluoro-2-triethylsilylethene, Eq. (4) [7].



(4)

2 readily undergoes palladium catalyzed coupling reactions with organozinc reagents [7]. The corresponding (*Z*)-1,2-difluoro-

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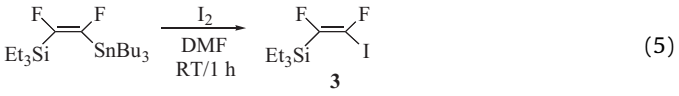
1-iodo-2-triethylsilylethene can be prepared by iodination of (*Z*)-1,2-difluoro-1-tributylstannyl-2-triethylsilylethene as illustrated in Eq. (5) [8].



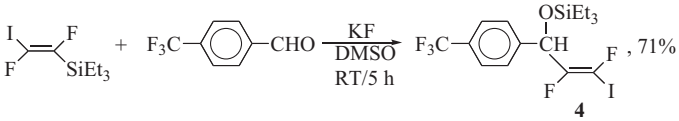
3 (5)

2. Results and discussion

2.1. Fluoride ion catalyzed reaction of 2 with aldehydes and ketones

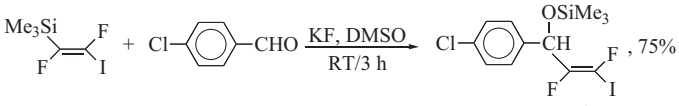
As demonstrated in the previously cited Refs. [2–6], fluoride ion readily attacks the trialkylsilyl group with concomitant transfer of the fluorinated vinyl group to an *in situ* electrophile, such as an aldehyde or ketone. If **2** could be utilized as the vinylsilane component, there is an additional feature present that is not readily available in the $F_2C{=}CF^-$ anion or the *cis*-$CF_3CF{=}CF$ anion – namely, a good leaving group (^-I) at the beta position. Consequently, elimination of the iodide from the anion $[IFC{=}CF]^-$, is more likely than in the previously described reagents [9]. Secondly, the $[IFC{=}CF]^-$ anion can not only attack the electrophilic carbonyl carbon of the aldehyde or ketone, but could also abstract an iodine from **2** to produce (*E*)-IFC=CFI. Thus, our initial focus concentrated on successful capture of the [IFC=CF] moiety and features in the carbonyl component that would promote success in the preparation of the vinyliodide addition product.

When aliphatic aldehydes, such as $C_6H_5CH_2CHO$ and n-octanal were reacted with **2** and KF in DMSO at room temperature for several hours, the main product was (*Z*)-HFC=CFI [10] (90–95%) and the minor product was the expected addition product (5–10%). Traces of (*E*)-IFC=CFI were also detected by NMR [12]. To increase the electrophilicity of the carbonyl group and to avoid abstraction of $[H^+]$ from the aldehyde, we focused on two aromatic aldehydes and one activated ketone containing an electron-withdrawing group. Thus, when p-trifluoromethylbenzaldehyde was reacted with **2** in the presence of dry KF, the addition product was formed in good yield as illustrated in Eq. (6).



4 (6)

Note that similar to Refs. [4–6], the siloxy derivative is initially formed (when the reaction is quenched with water). This protecting group is useful for further functionalization of the addition product (cf. Section 4.8). Hydrolysis to the corresponding alcohol with dilute 3 N HCl is slow. When the reaction mixture was quenched with water, followed by extraction with ether and water, a 71% yield of **4** was isolated. If the reaction mixture was quenched with dilute 3 N HCl followed by extraction with ether and water, a mixture of **4** and the corresponding alcohol, **5**, were isolated (cf. Section 4). If the reaction mixture was treated further with 3 N HCl at RT for 2 h, the alcohol was the sole product in 70% yield. When p-chlorobenzaldehyde was reacted with (*E*)-$Me_3SiCF{=}CFI$ under similar conditions, the addition product, **6**, was obtained in 75% yield, Eq. (7).



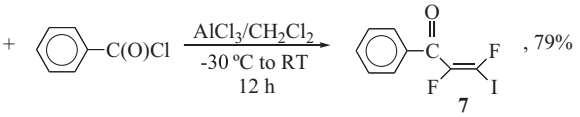
6 (7)

Trifluoroacetophenone, under similar conditions, gave a 60% yield of the addition product. Hiyama has reported that the use of TASF is remarkably efficient for stabilizing carbenoid anions and effecting aldehyde addition reactions [13]. However, when we attempted the reaction of octanal with **2** and TASF, the addition product yield improved slightly. Even with 100 mol% TASF, the addition product/(*Z*)-HFC=CFI ratio was 35:65. Isolation of the addition was complicated; a mixture of the addition product and the aldol condensation product was obtained by column chromatography. Thus, we pursued the aliphatic aldehydes no further.

2.2. Reaction of 2 with acyl chloride (as the electrophile)

Normant reported that difluorovinylsilanes could be reacted with an acyl halide, such as $CH_3C(O)Cl$, in the presence of $AlCl_3$ to yield α,β-unsaturated ketones [3]. Thus, we considered the acyl group as a potentially useful electrophile for transfer of the [ICF=CF] group. Two model acyl halides, $CH_3CH_2C(O)Cl$ and $C_6H_5C(O)Cl$ were selected to evaluate this methodology.

Thus, we added benzoyl chloride to a suspension of $AlCl_3$ in CH_2Cl_2 at 0 °C, followed by addition of **2** at −40 °C to −30 °C. The reaction was allowed to slowly warm to room temperature. The reaction proceeded cleanly as almost no other by-products formed. After quenching the reaction mixture with water, extraction with ether, drying over $MgSO_4$, silica gel chromatography (hexane/ethyl acetate = 10/1) gave the product in 79% isolated yield, Eq. (8).



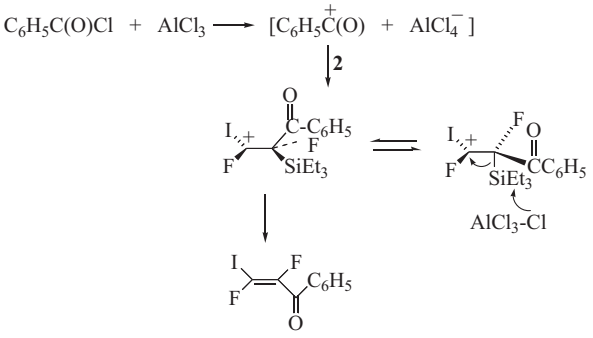
7 (8)

Similarly, propionyl chloride gave the α,β-unsaturated ketone, **8**, in 81% yield. The electrophilic substitution reaction proceeded with retention of stereochemistry. Mechanistically, the reaction proceeds quite differently than the KF reaction of **2** with an activated aldehyde or ketone. Similar to the mechanistic proposal of Normant [3], we propose addition of an acyl cation to **2**, followed by trans-elimination (after rotation) to produce the trans stereochemistry observed in the final product; cf. Scheme 1.

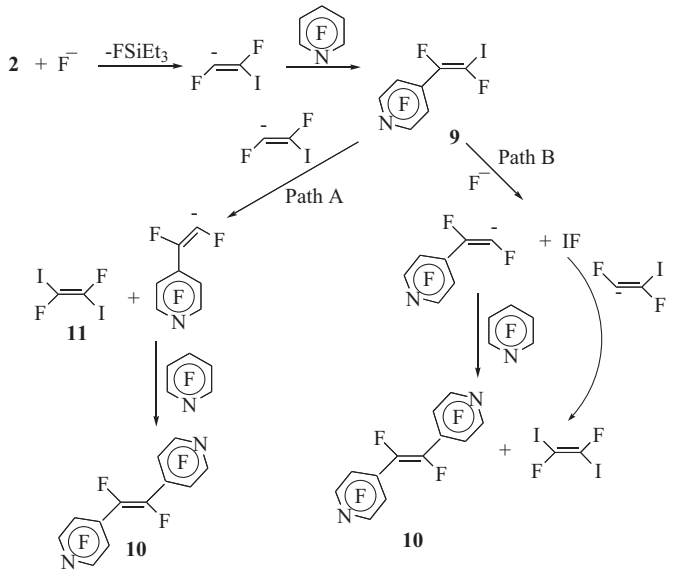
2.3. KF catalyzed reaction of 2 with reactive perfluoroaromatics

Pentafluoropyridine has been shown to be an excellent nucleophilic trapping agent for the unstable halodifluoromethide ion [14]. Thus, we attempted to trap the $[IFC{=}CF]^-$ with pentafluoropyridine. As expected, the trapping reaction was fast.

When **2** was reacted with pentafluoropyridine and KF in DMSO at RT, ^{19}F NMR analysis of the reaction mixture after 10 min showed that all of **2** had been completely consumed. The results of

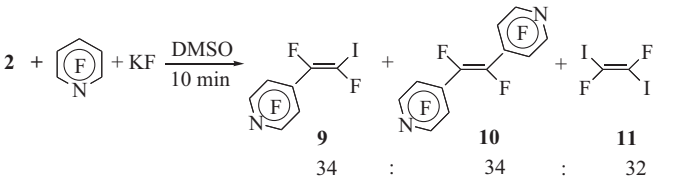


Scheme 1. Mechanism of $AlCl_3$ acylation of an acyl chloride with **2**.



Scheme 2. Mechanism of formation of **9**, **10** and **11**.

this reaction are illustrated in Eq. (9).



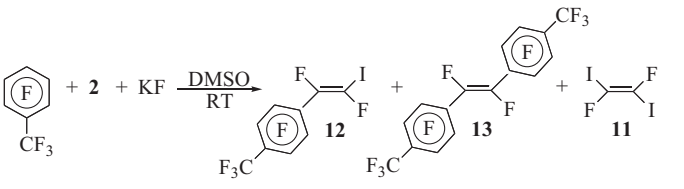
(9)

The ratio of the three products was determined by ^{19}F NMR analysis of the reaction mixture. **9** and **10** were isolated in yields of 26% and 23% respectively. **11** was identified by comparison of its spectroscopic data to a known sample [8]. The products of this reaction are rationalized by the mechanism outlined in Scheme 2.

The possibility of direct attack of F^- on **9** (path B) was excluded by the fact that treatment of **9** with perfluoropyridine and TASF did not afford any **10**.

TASF could also be used as the catalyst in this reaction. Thus, when pentafluoropyridine, TASF and **2** were reacted at RT, the ratio of **9**:**10**:**11** was 43:28:29; 29% isolated yield of **9** and 18% of **10**.

The reaction of perfluorotoluene with **2** and KF in DMSO at RT was slower than the reaction with pentafluoropyridine, but the overall result was similar; cf. Eq. (10).



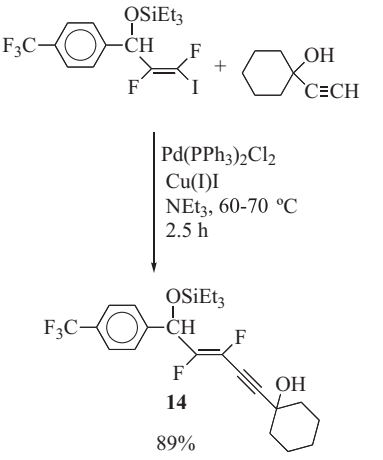
(10)

After 1 h and RT, ^{19}F NMR analysis of the reaction mixture indicated the ratio of **12**:**13**:**11** was 46:30:24. After an additional 2 h at RT, the reaction was complete and the ratio of **12**:**13**:**11** was 33:40:27. The isolated yields of **12** and **13** were 25% and 28% respectively.

With the less reactive hexafluorobenzene, no substitution product was obtained.

2.4. Extension of methodology to polyfunctionalized derivatives

One of the interests in attempting to trap the $[IFC{=}CF]^-$ anion *via* fluoride mediation of **2** with reactive electrophiles was the potential utility of the addition product to be easily functionalized further to provide access to polyfunctional derivatives. The vinyl iodide product could be functionalized *via* two potentially known methods: (1) the vinyl iodide could be directly coupled with other substrates, or (2) the vinyl iodide could be converted *in situ* to a vinylzinc or a vinylcopper reagent that could be elaborated further by known methodology [15,16]. As proof of principle of this expectation, we investigated the functionalization of the addition product of **2** with trifluoroacetophenone, which was obtained in 71% yield (cf. Section 4.2). Thus, **4** was reacted (*via* Pd(0) catalysis) with an acetylenic derivative [18] as illustrated in Eq. (11). The overall yield of **14** *via* a two-step process was 63%.



(11)

3. Conclusions

With fluoride ion catalysis, (*E*)-1,2-difluoro-1-iodotrialkylsilanes have been demonstrated to stereospecifically transfer the [ICF=CF] unit to an activated aldehyde, activated ketone, acylchlorides, or reactive perfluoroaromatics, such as perfluoropyridine or perfluorotoluene. The addition product can be utilized in further transformations to provide a simple two-step route to polyfunctionalized products.

4. Experimental

4.1. General experimental procedures

All glassware were oven-dried before use. ^{19}F NMR (282.44 MHz), ^1H NMR (300.17 MHz) and $\{^1H\}$ ^{13}C NMR (75.48 MHz) were recorded on an AC-300 spectrometer in $CDCl_3$ solvent. The chemical shifts are reported in parts per million downfield to the TMS internal standard for the ^1H NMR and $\{^1H\}$ ^{13}C NMR. The chemical shifts are reported in parts per million upfield to the $CFCl_3$ internal standard for ^{19}F NMR. FTIR spectra were recorded in CCl_4 solutions and reported in wavenumbers (cm^{-1}). Low resolution GC–MS spectra were obtained at 70 eV in the electron-impact mode on a TRIO-1-GC-MS instrument. All reactions were carried out under an atmosphere of nitrogen. Cu(I)Br was treated with aqueous HBr (48%), precipitated with excess cold water, washed with water; acetone, and ether and dried *in vacuo*. KF was dried at 250 °C *in vacuo* for 2 days. **2** was prepared by Normant's procedure [7,8]. (*E*)-IFC=CFSiMe$_3$ was prepared from the corresponding vinylsilane *via* our reported

procedure [17]. All other reagents were obtained from common commercial sources.

4.2. Preparation of (Z)-1,2-difluoro-1-iodo-2(p-trifluoromethylbenzyltriethylsiloxy) ethene, 4

A 2-neck flask equipped with a magnetic stir bar, rubber septum and nitrogen inlet was charged with anhydrous KF (232 mg, 2.87 mmol) in anhydrous DMSO (2 ml). Then, p-trifluoromethylbenzaldehyde (500 mg, 2.87 mmol) and (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene, **2** (700 mg, 2.30 mmol) were added *via* syringe. After the reaction mixture was stirred at RT for 5 h, ^{19}F NMR analysis of the reaction mixture showed the addition product was formed, accompanied by a small amount of the protonated product, while all the starting vinylsilane had been consumed. The reaction was quenched by the addition of diluted HCl (3 N), extracted with ether, the ether extracts washed with dilute HCl (3 N), and water, and the ether layer dried over $MgSO_4$. Column chromatography on silica gel (hexane/ethyl acetate, 9/1) gave a colorless oil (520 mg), **4**, yield: 47% and a white solid (200 mg), **5**, yield: 24%. **4**, ^{1}H NMR: δ 7.57 (m, 4H), 5.88 (dd, $^3J_{HF}$ = 25 Hz, $^4J_{HF}$ = 4.0 Hz, 1H), 0.95 (t, $^3J_{HH}$ = 7.5 Hz, 9H), 0.67 (q, $^3J_{HH}$ = 7.5 Hz, 6H); ^{19}F NMR: δ −63.1 (s, 3F), −123.6 (d, $^3J_{FF}$ = 142.0 Hz, 1F), −145.5 (dd, $^3J_{FF}$ = 142.0 Hz, $^3J_{HF}$ = 25.0 Hz, 1F); ^{13}C NMR: δ 156.3 (dd, $^1J_{CF}$ = 253.0 Hz, $^2J_{CF}$ = 40.4 Hz), 142.9 (s), 130.6 (q, $^2J_{CF}$ = 32 Hz), 126.5 (s), 125.5 (q, $^3J_{CF}$ = 3.5 Hz), 124.2 (q, $^1J_{CF}$ = 272.0 Hz), 99.21 (dd, $^1J_{CF}$ = 314.0 Hz, $^2J_{CF}$ = 67.0 Hz), 66.8 (d, $^2J_{CF}$ = 23.0 Hz), 6.6 (s), 4.6 (s). GC–MS, *m*/*z* (relative intensity): 459 (1), 449 (1), 325 (6), 217 (100), 127 (4), 115 (7), 105 (65), 77 (72). IR (cm^{-1}): 2959 (s), 1324 (vs), 1169 (m), 1134 (vs). **5**, mp 57–58 °C. ^{1}H NMR: δ 7.6 (m, 4H), 5.9 (dm $^3J_{HF}$ = 24.0 Hz, 1H), 2.9 (d, $^4J_{HF}$ = 5.0 Hz, 1H); ^{19}F NMR: δ −63.2 (s, 3F), −122.4 (d, $^3J_{FF}$ = 141.0 Hz, 1F), −146.6 (dd, $^3J_{FF}$ = 142.0 Hz, $^3J_{HF}$ = 25.0 Hz, 1F); ^{13}C NMR: δ 155.2 (dd, $^1J_{CF}$ = 250.0 Hz, $^2J_{CF}$ = 41.0 Hz), 141.4 (s), 130.9 (q, $^2J_{CF}$ = 32 Hz), 126.6 (s), 125.8 (q, $^3J_{CF}$ = 3.5 Hz), 124.2 (q, $^1J_{CF}$ = 273.0 Hz), 100.3 (dd, $^1J_{CF}$ = 316.0 Hz, $^2J_{CF}$ = 67.0 Hz), 66.7 (d, $^2J_{CF}$ = 23.0 Hz). GC–MS, *m*/*z* (relative intensity): 364 (M^+, 3.7), 345 (M^+−F, 5.7), 295 (M^+−CF_3, 0.64), 237 (M^+−I, 100), 219 (M^+−$CF_3C_6H_4$, 20.8), 189 (ICF=CF^+, 48.4), 145 ($CF_3C_6H_4^+$, 34.2), 127 (I^+, 77.8). IR (cm^{+1}): 3613 (br, m), 1325 (vs), 1171 (s), 1136 (vs), 861 (w).

If the reaction was quenched by water followed by extraction with ether and H_2O wash, column chromatography gave only **4**, in 71% isolated yield.

4.3. Preparation of (Z)-1,2-difluoro-1-iodo-3-trimethylsiloxy-3-(p-chlorophenyl) ethene, 6

Similar to Section 4.2, **6** was prepared *via* the reaction of (440 mg, 1.00 mmol) of (*E*)-1,2 difluoro-1-iodo-2-trimethylsilylethene, p-chlorobenzaldehyde (170 mg, 1.20 mmol), KF (116 mg, 2.00 mmol) in DMSO (2 ml) at RT for 3 h. Usual workup gave the addition product, **6**, (300 mg, yield: 75%). ^{1}H NMR: δ 7.3 (s, 4H), 5.80 (dd, $^3J_{HF}$ = 26.0 Hz, $^4J_{HF}$ = 5.5 Hz, 1H), 0.16 (s, 9H); ^{19}F NMR: δ −123.9 (dd, $^3J_{FF}$ = 142.0 Hz, $^4J_{HF}$ = 5.0 Hz, 1F), −145.4 (dd, $^3J_{FF}$ = 142.0 Hz, $^3J_{HF}$ = 25.0 Hz, 1F); ^{13}C NMR: δ 156.1 (dd, $^1J_{CF}$ = 253.0 Hz, $^2J_{CF}$ = 40.0 Hz), 137.0 (s), 133.9 (s), 128.6 (s), 127.5 (s), 99.1 (dd, $^1J_{CF}$ = 314.0 Hz, $^2J_{CF}$ = 67.0 Hz), 66.5 (d, $^2J_{CF}$ = 22.0 Hz), 0.30 (s). GC–MS, *m*/*z* (relative intensity): 405 (M^++1, 1), 403 (M^++1, 1), 367 (M^+−Cl, 1), 275 (26), 73 (100, $^+SiMe_3$). IR (cm^{-1}): 2962 (m), 1491 (m), 1256 (s), 1133 (s), 1090 (s), 875 (s).

4.4. Preparation of (Z)-1,2-difluoro-1-iodo-2-benzoylethene, 7

A 2-neck flask equipped with a magnetic stir bar, rubber septum, and nitrogen inlet was charged with anhydrous $AlCl_3$ (260 mg, 2.00 mmol), in anhydrous CH_2Cl_2 (3 ml). To the above suspension was added benzoyl chloride (252 mg, 1.8 mmol) at 0 °C over a period of 25 min; then 456 mg (1.50 mmol) of **2** was added at −30 to −40 °C within 10 min. The reaction mixture was stirred at −40 °C to RT for 2 h and then at RT overnight. ^{19}F NMR showed that all the vinylsilane, **2**, had been consumed. The reaction mixture was quenched by the addition of water, then extracted with ether, and dried over $MgSO_4$. Column chromatography on silica gel (hexane/ethyl acetate, 10/1) gave 350 mg (yield: 79%) of **7**. ^{1}H NMR: δ 7.81–7.78 (m, 2H), 7.52–7.54 (m, 1H), 7.47–7.42 (m, 2H); ^{19}F NMR: δ −96.6 (d, $^3J_{FF}$ = 148.0 Hz, 1F), −133.8 (d, $^3J_{FF}$ = 148.0 Hz, 1F); ^{13}C NMR: δ 181.9 (dd, $^2J_{CF}$ = 27.0 Hz, $^3J_{CF}$ = 5.0 Hz), 151.6 (dd, $^1J_{CF}$ = 254.0 Hz, $^2J_{CF}$ = 32.0 Hz), 135.0 (d, $^3J_{CF}$ = 5.0 Hz), 133.9 (s), 129.0 (s), 128.5 (s), 113.8 (dd, $^1J_{CF}$ = 339.0 Hz, $^2J_{CF}$ = 67.0 Hz). GC–MS, *m*/*z* (relative intensity): 294 (M^+, 17), 189 (M^+−C_6H_5CO, 3.7), 167 (M^+−I, 71), 127 (I^+, 9), 105 ($C_6H_5CO^+$, 98), 77 ($C_6H_5^+$, 100). IR (cm^{-1}): 1687 (m), 1677 (m), 1581 (m), 1500 (m), 1306 (vs), 1197 (s), 1175 (s).

4.5. Preparation of (Z)-1,2-difluoro-1-iodo-3-pentenone, 8

Similar to Section 4.4, propionyl chloride (184 mg, 2.0 mmol), $AlCl_3$ (390 mg, 3.00 mmol), and **2** (456 mg, 1.50 mmol) in CH_2Cl_2 (3 ml) at −30 °C/RT for 3 h gave 300 mg of **8**, yield: 81%, after the usual workup. ^{1}H NMR: δ 2.70 (qdd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HF}$ = 2.9 Hz, $^5J_{HF}$ = 1.5 Hz, 2H), 1.2 (t, $^3J_{HH}$ = 7.0 Hz, 3H); ^{19}F NMR: δ −94.3 (d, $^3J_{FF}$ = 145.0 Hz, 1F), −139.9 (d, $^3J_{FF}$ = 145.0 Hz, 1F); ^{13}C NMR: 188.8 (dd, $^2J_{CF}$ = 25.0 Hz, $^3J_{CF}$ = 6.0 Hz), 152.0 (dd, $^1J_{CF}$ = 248.0 Hz, $^2J_{CF}$ = 33.0 Hz), 115.5 (dd, $^1J_{CF}$ = 339.0 Hz, $^2J_{CF}$ = 69.0 Hz), 33.6 (d, $^3J_{CF}$ = 4.0 Hz), 6.97 (s). GC–MS, *m*/*z* (relative intensity): 246 (M^+, 9), 217 (M^+−Et, 17), 189 (M^+−EtCO, 10), 127 (I^+, 11), 119 (M^+−I, 15), 57 ($EtCO^+$, 100). IR (cm^{+1}): 1720 (s), 1704 (s), 1616 (s), 1320 (s), 1264 (s), 1184 (vs), 1170 (vs), 2985 (m).

4.6. Reaction of 2 with pentafluoropyridine, preparation of 9 and 10

A 2-neck flask equipped with a magnetic stir bar, rubber septum and nitrogen inlet was charged with anhydrous KF (58 mg, 1.00 mmol). Then pentafluoropyridine (338 mg, 2.00 mmol) and **2** (480 mg, 1.57 mmol) were added *via* syringe. After stirring the reaction mixture at RT for 10 min, ^{19}F NMR analysis of the reaction mixture indicated that all the vinylsilane had been consumed, and three products *A*, *B* and *C*, in the ratio of 34:34:32, had been formed. Product *C* was identified as (*E*)-1,2-difluoro-1,2-diiodoethene, **11**, by comparison of its ^{19}F NMR data with a known sample [12]. The reaction mixture was quenched with H_2O, extracted with ether and dried over $MgSO_4$. Column chromatography on silica gel with hexane gave a white solid product; 140 mg (yield: 26%), identified as (*Z*)-1-iodo-1,2-difluoro-2-tetrafluoropyridylethene, mp = 44.5–45 °C, **9**, and 130 mg (yield, 23%) of a white solid (mp 95–96 °C) identified as (*E*)-1,2-difluoro-1,2-tetrafluoropyridylethene, **10**. ^{19}F NMR of **9**: δ −88.8 (m, 2F), −107.3 (dt, $^3J_{FF}$ = 148.7 Hz, $^4J_{FF}$ 16.3 Hz, 1F), −132.6 (dt, $^3J_{FF}$ = 149.3 Hz, $^5J_{FF}$ = 8.6 Hz, 1F), −137.7 (m, 2F). ^{13}C NMR: δ 143.8 (dm, $^1J_{CF}$ = 246 Hz), 142.0 (dd, $^1J_{CF}$ = 240.9 Hz, $^2J_{CF}$ = 44.5 Hz), 138.8 (dm, $^1J_{CF}$ = 268 Hz), 120.5 (m), 105.5 (dd, $^1J_{CF}$ = 327 Hz, $^2J_{CF}$ = 66.5 Hz). GC–MS, *m*/*z* (relative intensity): 339 (M^+, 100), 212 (M^+−I, 39), 193 (M^+−I−F, 20), 162 (80). IR (cm^{-1}): 1672 (m), 1638 (s), 1484 (vs), 1477 (vs), 1259 (m), 1469 (vs), 1195 (vs), 1166 (vs), 1152 (s), 926 (s). **10**, ^{19}F NMR: δ −87.85 (m, 4F), −137.0 (m, 4F), −138.95 (m, 2F); ^{13}C NMR: δ 143.7 (dtm, $^1J_{CF}$ = 246.5 Hz, $^2J_{CF}$ = 15.0 Hz), 142.9–138.8 (m), 139.3 (dm, $^1J_{CF}$ = 270.0 Hz), 120.0–119.8 (m). GC–MS, *m*/*z* (relative intensity): 362 (M^+, 88), 343 (M^+−F, 13), 293 (100), 262 (26), 248 (79), 181 (11), 117 (22).

When TAFS was used in place of KF, the same reaction was completed at RT in 2 min. The ratio of **9**, **10**, **11**, was 43:28:29. Usual workup gave **9** in 29% isolated yield and **10** in 18% isolated yield.

4.7. Reaction of 2 with perfluorotoluene, preparation of 12 and 13

Similar to Section 4.6, perfluorotoluene (684 mg, 2.9 mmol), anhydrous KF (58 mg, 1.0 mmol) and **2** (760 mg, 2.5 mmol) were stirred at RT for 1 h. ^{19}F NMR analysis of the reaction mixture showed that most of the vinylsilane had been consumed. After stirring the mixture for an additional 2 h at RT, the ratio of products (by ^{19}F NMR), **12** and **13**, **11** was 33:40:27. The reaction was quenched with H_2O, extracted with ether, and dried over $MgSO_4$. Column chromatography on silica gel with hexane gave **12** (250 mg, yield = 25%) and **13** (350 mg, 28%). ^{19}F NMR of **12**: δ −57.2 (t, $^4J_{FF}$ = 22.0 Hz, 3F), −109.3 (dt, $^3J_{FF}$ = 148.0 Hz, $^4J_{FF}$ = 15.0 Hz, 1F), −130.7 (dt, $^3J_{FF}$ = 149.0 Hz, $^5J_{FF}$ = 7.5 Hz, 1F), −134.6 to 134.7 (m, 2F), −139.1 to 139.5 (m, 2F); ^{13}C NMR: δ 156.2–142.1 (m), 141.9 (dd, $^1J_{CF}$ = 246.0 Hz, $^2J_{CF}$ = 45.0 Hz), 120.6 (q, $^1J_{CF}$ = 275 Hz), 112.9–111.4 (m), 104.3 (dd, $^1J_{CF}$ = 325.0 Hz, $^2J_{CF}$ = 67.0 Hz). GC–MS, *m*/*z* (relative intensity): 406 (M^+, 100), 387 (M^+−F, 15), 279 (M^+−I, 25), 260 (M^+−I−F, 13), 241 (M^+−2F, 14), 229 ($CF_3C_6F_4C^+$, 48), 210 (M^+−I−CF_3, 54), 127 (I^+, 8), 69 (CF_3^+, 9). IR (cm^{-1}): 1660 (vs), 1501 (s), 1493 (s), 1348 (s), 1270 (s), 1179 (vs), 1162 (m), 999 (s). **13**, ^{19}F NMR: δ −57.1 (t, $^4J_{FF}$ = 22.0 Hz, 6F), −134.1 to 134.2 (m, 4F), −138.3 (pentet, $^4J_{FF}$ = 12.0 Hz, 2F); −138.7 to −139.0 (m, 4F); ^{13}C NMR: 144.5 (dm, $^1J_{CF}$ = 263.0 Hz), 141.4–137.3 (m), 120.5 (q, $^1J_{CF}$ = 276.0 Hz), 113.4–111.8 (m). GC–MS, *m*/*z* (relative intensity): 496 (M^+, 100), 477 (45), 427 (45), 408 (12), 377 (48), 358 (5), 320 (5), 217 (8). IR (cm^{-1}): 1502 (s), 1493 (s), 1345 (vs), 1299 (s), 1200 (s), 1178 (s), 1163 (s).

4.8. Reaction of 4 with 1-ethynyl-1-cyclohexanol, preparation of 14

A 2-neck flask equipped with a magnetic stir bar, rubber septum, and condenser topped with a nitrogen inlet was charged with $Pd(PPh_3)_2Cl_2$ (50 mg, 0.07 mmol), Cu(I)I (19 mg, 0.10 mmol) and NEt_3 (3 ml). Then 1-ethynyl-1-cyclohexanol (170 mg, 1.37 mmol) and **4** (340 mg, 0.71 mmol) were added to the catalytic mixture *via* syringe. After the reaction mixture was stirred at 60–70 °C for 2.5 h, ^{19}F NMR analysis of the reaction mixture indicated the reaction was complete. Then, the volatile components of the reaction mixture were pumped off. Dilute (3 N) HCl was added to the residue, the residue extracted with ether, washed with water, and dried over $MgSO_4$. Column chromatography on silica gel (hexane/ethyl acetate = 10/1) gave the product **14**, (305 mg) in 89% yield. ^{1}H NMR: δ 7.48 (q, $^{4,5}J_{HF}$ = 8.5 Hz, 4H), 5.76 (dd, $^3J_{HF}$ = 25.0 Hz, $^4J_{HF}$ = 3.5 Hz, 1H), 2.87 (brs, 1H), 1.91–1.83 (m, 2H), 1.54–1.40 (m, 7H), 1.15–1.07 (m, 1H), 0.89 (t, $^3J_{HH}$ = 8.0 Hz, 9H), 0.70 (q, $^3J_{HH}$ = 7.8 Hz, 6H); ^{19}F NMR: δ −63.04 (s, 3F), −152.28 (dd, $^3J_{FF}$ = 135.0 Hz, $^4J_{HF}$ = 3.5 Hz, 1F), −155.77 (dd, $^3J_{FF}$ = 135.0 Hz, $^3J_{HF}$ = 25.0 Hz, 1F); ^{13}C NMR: δ 155.6 (dd, $^1J_{CF}$ = 310.0 Hz, $^2J_{CF}$ = 51.0 Hz), 142.1 (s), 131.99 (dd, $^1J_{CF}$ = 220.0 Hz, $^2J_{CF}$ = 48.0 Hz), 129.4 (q, $^2J_{CF}$ = 32.0 Hz), 125.51 (s), 124.4 (s), 123.14 (q, $^1J_{CF}$ = 272 Hz), 104.84 (dd, $^3J_{CF}$ = 13.0 Hz, $^4J_{CF}$ = 7.6 Hz), 70.15 (dd, $^2J_{CF}$ = 36.6 Hz, $^3J_{CF}$ = 6.4 Hz), 68.22 (s), 38.38 (s), 23.98 (s), 22.06 (s), 5.48 (s), 3.53 (s). GC–MS, *m*/*z* (relative intensity): 455 (M^+−F, 1.5), 359 (M^+−$SiEt_3$, 0.24), 329 (M^+−$CF_3C_6H_4$, 2.4), 275 (11), 201 ($CF_3C_6H_4CHOSi^+$, 17.5), 115 ($SiEt_3^+$, 17), 77 ($C_6H_5^+$, 100). IR (cm^{-1}): 2958 (s), 2877 (m), 1457 (m), 1325 (vs), 1262 (s), 1169 (s), 1134 (vs), 846 (m).

4.9. Reaction of 2 and KF with trifluoroacetophenone, 15

Similar to Section 4.2, **2** (280 mg, 0.92 mmol), trifluoroacetophenone (174 mg, 1.00 mmol) KF (116 mg, 2.00 mmol) in DMSO (2 ml) were reacted for 3 h at RT. After the usual work-up, 260 mg (60%) of (*Z*)-1,2-difluoro-1-iodo-3-phenyl-3-triethylsiloxy-4,4,4-trifluoro-1-butene, **15** was isolated. ^{1}H NMR: δ 7.56–7.53 (m, 2H), 7.40–7.37 (m, 3H), 0.97 (t, $^3J_{HH}$ = 7.5 Hz, 9H), 0.79 (q, $^3J_{HH}$ = 7.5 Hz, 6H); ^{19}F NMR: δ −76.15 (dd, $^4J_{FF}$ = 15.0 Hz, $^5J_{FF}$ = 10.0 Hz, 3F), −106.39 (dq, $^3J_{FF}$ = 150.0 Hz, $^4J_{FF}$ = 15 Hz, 1F), −129.5 (dq, $^3J_{FF}$ = 150.0 Hz, $^5J_{FF}$ = 10.0 Hz, 1F); ^{13}C NMR: δ 159.9 (dd, $^1J_{CF}$ = 285.0 Hz, $^2J_{CF}$ = 36.0 Hz), 135.3 (s), 129.4 (s), 128.3 (s), 126.8 (s), 123.2 (qd, $^1J_{CF}$ = 287.0 Hz, $^3J_{CF}$ = 5.0 Hz), 106.2 (dd, $^1J_{CF}$ = 286 Hz, $^2J_{CF}$ = 71 Hz), 79.40 (m), 6.7 (s), 5.5 (s). IR (cm^{-1}): 2959 (m), 2880 (m), 1207 (m), 1188 (s), 1179 (s), 1151 (m). GC–MS, *m*/*z* (relative intensity): no parent ion, 198 (74), 170, (40, ICF=C^+), 151 (60), 115 (Si^+Et_3, 7), (77, 100, $C_6H_5^+$).

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