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Hiyama coupling reaction of fluorous alkenyl-fluorosilanes: Scope and mechanistic considerations

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ABSTRACT

Novel fluorous alkenyl-fluorosilanes ($C_nF_{2n+1}CH{=}CHSiMe_2F$; n = 4, 6, 8; **5a**–**c**) were synthetized in a three step procedure from perfluoroalkyliodides and dimethylvinylchlorosilane. They were first reacted with iodobenzene at room temperature in Hiyama coupling reaction (DMF, $Pd(OAc)_2$, TBAF, 72 h) to afford the appropriate ω-perfluoroalkyl-styrenes ($C_nF_{2n+1}CH{=}CHC_6H_5$, n = 4, 6, 8); then the reactivity of **5a** with monosubstituted iodobenzenes was studied. The coupling reaction of **5a** with o-substituted iodobenzenes usually failed, while that of with the m- and p-substituted ones gave fluorous styrenes [m- or p-$(C_4F_9CH{=}CH)C_6H_4X$], independently of the electronic effect of their substituent (X = Br, CF_3, CH_3, OCH_3). These volatile products can easily be isolated by steam-distilltaion and purified further by distillation.

The mechanism of the above coupling reactions was a pure Hiyama type involving fluoride-ion induced transmetallation without any Heck type contribution, since no coupling product of $C_6F_{13}CH{=}CH_2$ and C_6H_5I was observed in blank control experiments using similar conditions (DMF, TBAF, $Pd(OAc)_2$, 72 h, 25 °C).

1. Introduction

The Hiyama cross-coupling reaction is an important palladium catalyzed carbon–carbon bond formation reaction, where the coupling of *aryl* and *alkenyl-halogenides* or *-triflates* with *organo-silanes* constitutes its early examples [1]. The scope of this silicon-based reaction is summarized below to disclose that a large variety of organic groups bonded to silicon (R^1) are suitable transferable groups ($TG{=}R^1$) (Scheme 1) [2].

Various organosilicon reagents are now commercially available that are stable under normal conditions but can be activated to provide the requisite TG's. Moreover silicon is an environmentally benign element, since organosilicon compounds are ultimately oxidized to biologically inactive silica gel. Since the Si–C bond is quite stable, it has to be polarized for the success of the Hiyama-coupling. The activation of the silicon compound (R^1–SiY_3) by fluoride ions involves the formation of a pentacoordinated siliconate, which then initiates the transmetallation step. The reactivity of the silanes (R^1–SiY_3) can be increased if the spectator methyl ligands at (R^1–$SiMe_3$) are substituted for alkoxides [3], chlorines [3], fluorines [3,4], or for heterocycles, like the 2-pyridyl-group [5] and the 2-thienyl-group (Scheme 2) [6].

The expansion of the scope of the Hiyama cross-coupling reaction by the introduction of organosiletanes, -silanols, and -siloxanes, was executed in the last decades by Denmark [7], and others [8]. The fluoride-free activation of silanolates accessable from the base treatment of the latter silicon compounds allowed the simultanous use of silyl-protected substrates which are necessary for natural products synthesis. Thus the latter variant, the *Hiyama-Denmark coupling reaction* [9] is considered as a practical alternative to the boron- and tin-based cross-coupling reactions [10].

Recent improvements of this coupling reaction allow the use of milder conditions with good functional group tolerance. Lee and Fu developed the first method for the Hiyama coupling of unactivated alkyl bromides and iodides [11]. Sarkar and others introduced Pd nanoparticles for the coupling of arylsiloxanes with benzyl halides [12].

Novák and coworkers disclosed that Pd/C catalysts could also be applied effectively in Hiyama and other cross-coupling reactions but their activity is dependent on the kind of support and their processing method [13].

However, fluorous-alkenyl fluorosilanes ($R_{fn}CH{=}CHSiMe_2F$; n = 4, 6, 8) are unknown in the literature and not tested yet for Hiyama cross-coupling reaction as (perfluoroalkyl)-alkenyl-TG precursors. Only a recent article reports on the use of some light fluorous-tagged alkenylgermanes in a palladium-catalyzed reaction with aryl-bromides [14].

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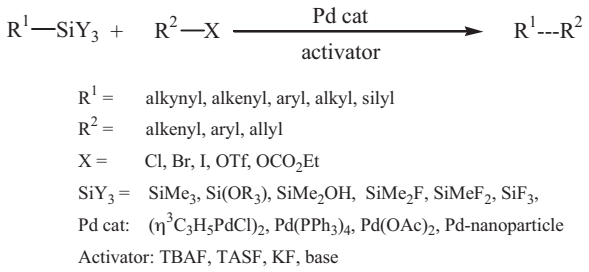


Scheme 1. The scope and the requisite catalysts and activators of the Hiyama coupling reaction.

Our aim was to develop an easy access to fluorous-alkenyl fluorosilanes (R^1–SiY_3: $R_{fn}CH{=}CHSiMe_2F$; Schemes 1 and 2) starting from perfluoroalkyl iodides, then to study their suitability for using as perfluoroalkylalkenyl-group transfer reagents under Hiyama cross-coupling conditions with aryl iodides. This study could also result in the addition of novel protocols for the synthesis of fluorous compounds [15].

We also aimed at devising reaction condition that ensure that the formation of our model fluorous styrenes proceeds with a clear transmetallation step, without any percent contribution of a Heck type pathway (Scheme 3) [16].

2. Results and discussion

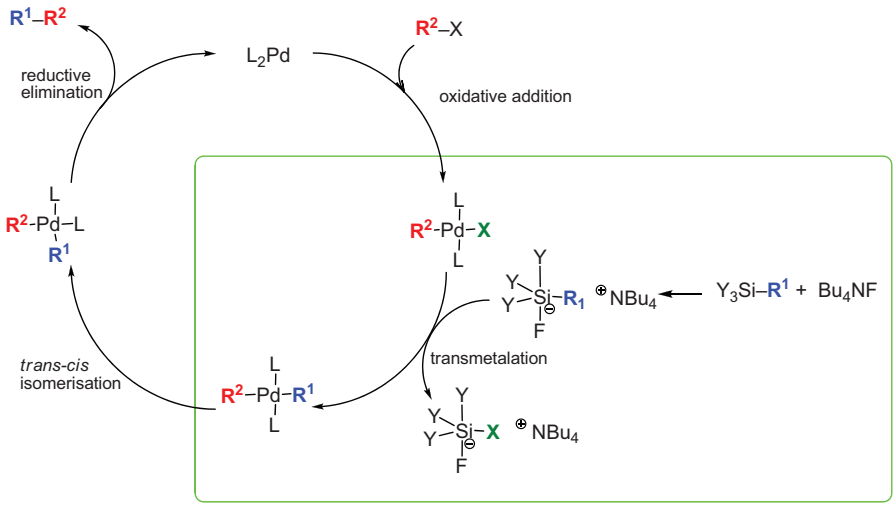
We disclose here new and optimized procedures for the preparation of fluorous organosilicon compounds which can be used effectively in Hiyama coupling reaction. The *in situ* hydrolysis of dimethylvinylchlorosilane (**1**) to tetramethyldivinyldisiloxane [$(CH_2{=}CHSiMe_2)O$] was accompanied by the regioselective addition of perfluoroalkyl-iodides (**2**), initiated with AIBN, to afford fluorous diiodo-disiloxanes (**3**) (Scheme 4; and Section 4, GP-1). This reaction with longer perfluoroalkyl-iodides gave good yields at 80 °C, but in the case of C_4F_9I the yield decreased. It can be caused by the lower boiling point of C_4F_9I. When the latter reaction was performed at 70 °C with longer time the yield increased as expected. The synergic effect of aqueous $K_2S_2O_5$ solution on the AIBN initiated additions of perfluoro alkyliodides has already been discussed [17], and exploited for the synthesis of fluorous iodohydrines [18].

The ^{1}H NMR and the ^{13}C NMR spectra of compounds **3** showed some unexpected features as compared to the previously described assignments by Beyou and co-workers [19].

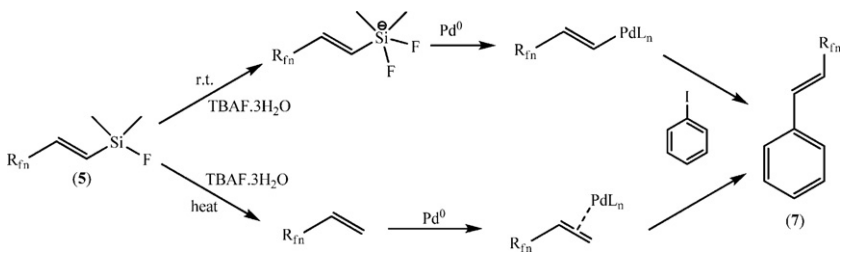
For example, in the ^{1}H NMR (700 MHz) spectra of **3a**, four distinct signals with the same intensity appear in the highly shielded methyl region at 0.6 ppm, and the corresponding ^{13}C NMR signals appear as two groups at −1.39 ppm and −1.41 ppm, and two overlapping signals at −1.86 ppm, respectively (Scheme 5).

This pattern could be interpreted on the one hand that the molecule is not symmetric (alike to compounds **4** and **5**), and this asymmetry is due to the presence of the steric effect of the iodine atom, and also to the chirality centers at the C_α carbons. On the other hand the two methine-carbons (–*CHI–) are also not equivalent but highly shielded; see the very low ^{13}C chemical shift at −0.18 ppm and broad signal with a line width of 4.7 Hz, compared to the 1.0 Hz line width of the methyl carbons.

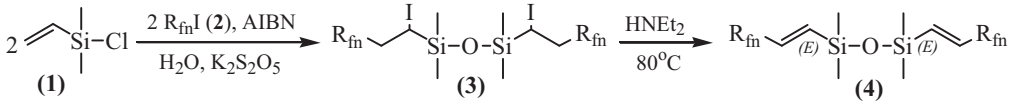
The corresponding ^{1}H resonances show a multiplet structure. The broadening effect is detected also on the adjacent CH_2 carbons that has a multiplet splitting due to the $^3J_{CF}$ coupling (cf. Section 4). The two H atoms are not equivalent as shown on their ^{1}H spectra (cf. Supplementary material).



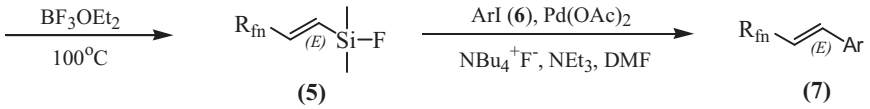
Scheme 2. A simplified mechanism for the Hiyama coupling reaction.



Scheme 3. Two simplified pathways to ω-perfluoroalkyl-styrenes in a fluorous Hiyama coupling reaction. Upper path: clear Hiyama mechanism, lower path: coupling with Heck mechanism.



2, 3, 4, 5, and **7:** R_{fn} = *n*-C_4F_9 (**a**), *n*-C_6F_{13} (**b**), and *n*-C_8F_{17} (**c**)



7a-c: Ar = Ph; **7d-q**: R_{fn} = *n*-C_4F_9, Ar = XC_6H_4, X = *m*-CF_3 (**e**), *p*-CF_3 (**f**), *m*-OCH_3 (**h**), *p*-OCH_3 (**i**), *o*-CH_3 (**n**), *p*-CH_3 (**o**), *p*-Br (**p**), 1-$C_{10}H_7$ (**q**) yields: 17-91%; while X = *o*-CF_3 (**d**), *o*-OCH_3 (**g**), *o*-Cl (**j**), *o*-Br (**k**), *o*-NH_2 (**l**), *o*-NHAc (**m**), yields: 0 %

Scheme 4. Synthesis of (polyfluoroalkenyl)-fluorosilanes (**5**) and their coupling with iodobenzenes (**6**).

The dehydro-halogenation of **3** with $HNEt_2$ results in the formation of the appropriate fluorous alkenyl-disiloxanes (**4**). This reaction can be completed with other organic bases as well. We chose diethyl-amine because it can be easy separated from the reaction mixture and to a literature precedent (Scheme 5; Section 4, GP-2) [20].

However, dehydrohalogenation has a simplifying effect on the NMR spectra, because the disappearance of the chirality centers leads to one resonance for all the methyl groups of disiloxanes **4**.

In the next step disiloxanes **4** are effectively converted to fluorous alkenyl-fluorosilanes (**5**) by heating them with borontrifluoride-ether at 100 °C without any solvents (Section 4; GP-3) [21].

Due to the formation of a new Si–*F* bond in **5**, new couplings appear in their NMR spectra. The ^{1}H NMR sign of Si–C**H** become a ddt (doublet–doublet–triplet), while both CF_2–**C**H and Si–**C**H carbons show a dt (doublet–triplet) in their ^{13}C NMR. The Si–**C**H_3 become also a doublet in ^{13}C NMR because of the Si–*F* bond ($^3J_{CF}$ = 15 Hz).

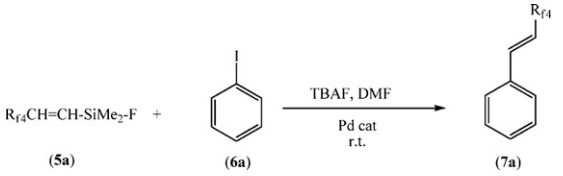
Alkenyl-fluorosilanes are good candidates for Hiyama coupling reactions. We tried to apply these fluorosilane-derivatives as coupling reagents with halobenzenes. The first exercise was to choose the appropriate reaction conditions. Since iodobenzenes are the most reactive partners in the Pd-catalyzed reactions our experiments are centered on the coupling of these compounds. The efficiency of various Pd catalysts (4 mol% catalyst) was tested on the reaction of iodobenzene and (perfluorobutylvinyl)-dimethyl-fluorosilane (Scheme 6 and Table 1).

After comparing the results of the five commercial Pd catalysts, $Pd(OAc)_2$ was selected for further studies, since it gave the purest isolated product within an acceptable reaction time and with the lowest unit price. It should be noted that Pd/C and $Pd(PPh_3)_4$ were found inactive under the mild experimental conditions used (cf. Section 4).

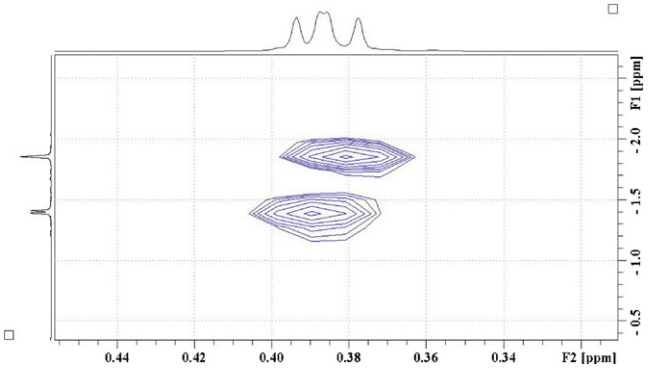
During the setting of the experimental conditions we observed that the Si–C bond of these alkenyl-silanes can be cleaved at higher temperatures with the activator TBAF. Thus we heated a solution of 1,3-divinyltetramethyl-disiloxane and TBAF in DMF for 1 h at 90 °C in a closed Pyrex pressure tube. Then the headspace of the pressure tube was sampled and analyzed by GC–MS to indicate that it contains approximately 90% of ethene (Scheme 7).

We also found that the silicon–carbon bond in fluorous alkenylfluorosilanes **5** could be cleaved by TBAF at elevated temperatures. Thus a protodesilylation reaction of fluorosilane **5a** (R_{f4}=C_4F_9) with excess TBAF in DMF at 90 °C gave the corresponding fluorous olefin in 90% yield (Scheme 8).

These are qualitative evidences of our theory that the fluoride source might cleave the Si–C bonds in some alkenylsilanes at elevated temperatures and thus it could generate *in situ* the appropriate olefins [22]. These olefins then may couple in a Heck type mechanism with iodobenzenes to afford the same products as if they were reacted with a pure Hiyama type coupling mechanism. This observation made it clear that the coupling reaction of some



Scheme 6. Model reaction for testing catalysts efficiency (cf. Table 1).

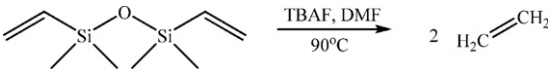


Scheme 5. Part of ^{1}H–^{13}C HSQC spectra of **3a** at 700 MHz.

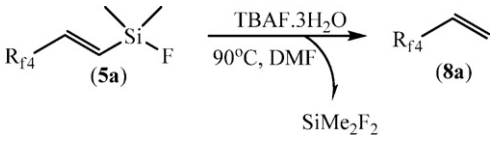
Table 1
Efficiency of Pd-catalysts on the formation and purity of ω-perfluorobutyl-styrene at 20 °C in DMF.

Entry	Catalyst[a] (4 mol%)	Conversion of **6a** after 20 h (%)	100% Conversion of **6a** (day(s))	Isolated yield of **7a** (%)	Purity of **7a** (GC %)
1	10% Pd/C	0	–	–	–
2	$Pd(PPh_3)_4$	0	–	–	–
3	$Pd(OAc)_2$	15	3	60%	90%
4	Pd_2dba_3	99.5	1	47%	83%
5	[(η^3-allyl)PdCl]$_2$	92	1	60%	72%

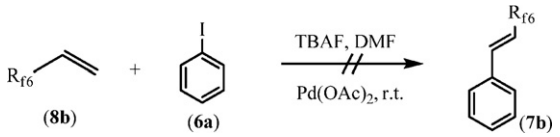
[a] Entries 1–2 and 3–5 are heterogeneous or homogeneous systems at 0.025 mmol catalyst/1.0 ml DMF loading, respectively.



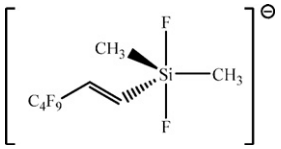
Scheme 7. The reaction of a vinylsiloxane with TBAF at higher temperature.



Scheme 8. The reaction of a fluorous alkenylfluorosilane (**5a**) with TBAF at higher temperature.



Scheme 9. Blank experiment to exclude the possibility of Heck type contribution.



Scheme 10. HRMS evidence for the formation of a fluorous pentacoordinated silicate [**5a**+F$^-$]. Calculated mass [M+F]$^-$ = 341.0225, measured mass [M+F]$^-$ = 341.0224, mass difference: −0.2 ppm.

structural type organosilanes at higher temperature not necessarily follow a pure Hiyama type mechanism, which involves a transmetallation step through a pentacoordinate silicate-anion.

A blank experiment was also performed to exclude the possibility of a Heck type mechanism in our room temperature Hiyama coupling protocol (Scheme 9). Here we kept all conditions unchanged, but substituted perfluorohexylethene ($R_{f6}CH{=}CH_2$) for (perfluorohexylethenyl)-dimethylfluorosilane ($R_{f6}CH{=}CHSiMe_2F$, **5b**). There was no formation of fluorous styrene in this control experiment during one week stirring at room temperature, but 90% of the starting iodobenzene was recovered in 98% chemical purity (GC).

Consequently we choose room temperature for our further experiments with the above fluorous alkenyl-fluorosilanes to be able to scope the nature of the Hiyama coupling reaction without any Heck type contributions (cf. Scheme 3). We performed an HPLC–TOF MS measurement to determine the exact mass of the complex formed by the reaction of **5a** and TBAF. The result obtained was agreeable with the formation of a pentacoordinated silicate-anion; a possible intermediate of transmetallation according to Hiyama and co-workers (Scheme 10).

Then we studied the Hiyama coupling of selected alkenyl-fluorosilanes (**5**) and iodobenzenes (**6**) in DMF solution using $Pd(OAc)_2$ as precatalyst and TBAF as an activator at room temperature (Table 2; Section 4, GP-4). Different fluorosilanes and iodoarenes were used to learn the reaction scope.

First the reaction of fluorosilanes **5a–c** and iodobenzene **6a** was investigated (Table 2, Entries 1–3) to reveal the effect of the length of fluorous-chains on product **7a–c** yields. However, no significant effect was observed. Some alternative methods for the synthesis fluorous styrenes **7a–c** are known in the literature [15e,f,23–26].

We tried to apply substituted iodobenzenes as coupling reagents as well. First, a series of CF_3- (**6d–f**) and CH_3O-substituted (**6g–i**) iodobenzenes were tested (Table 2, Entries 4–9). Both series show the same results, the yields increase in the *ortho*, *meta*, *para* direction, independently of the electronic effect of the substituent. These results may suggest, that the reaction of the halobenzene is controlled by steric factors.

To collect more evidences some other *ortho* substituted iodobenzenes were tested (Table 2, Entries 10–14). The selected substituents represent different sizes and electronic effects. With *ortho*-Cl-(**6j**) and *ortho*-Br-(**6k**) derivatives the formation of **7j** and **7k** was detected with ^{1}H NMR, via a typical *doublet–triplet* sign at ~6 ppm, but their isolation was not performed because of their trace amounts. With *ortho*-NH_2-(**6l**) and *ortho*-NHAc-(**6m**) derivatives no formation of the appropriate styrenes was observed at all. Only exception is *ortho*-iodotoluene (**6n**), which allowed the isolation of styrene **7n** in 17% with 90% purity (GC assay).

Then the reaction of some other *para*-substituted iodobenzenes – 4-iodotoluene (**6o**) and 4-iodobromo-benzene (**6p**) – was studied

Table 2
Reaction of fluorosilanes (**5**) with aryl iodides (**6**) under '*room temperature Hiyama coupling*' conditions.

Entry	Ar-	R_{fn}	(*E*)-R_{fn}CH=CHAr (**7**)	Yield (%)[a]	Purity (%)[b]	Lit. data[c] (bp °C/kPa) (mp °C/^{solvent})
1	C_6H_5 (**6a** = 6b = 6c)	*n*-C_4F_9	**7a** colorless oil	61	91	bp = 76–78/3.1 [27]
2	C_6H_5 (6a = **6b** = 6c)	*n*-C_6F_{13}	**7b** colorless oil	63	95	mp = 38–39.5/^{hexane} [28]
3	C_6H_5 (6a = 6b = **6c**)	*n*-C_8F_{17}	**7c** colorless oil	50	90	mp = 59–61/^{hexane} [28]
4	*o*-CF_3–C_6H_4 (**6d**)	*n*-C_4F_9	**7d** –	0[d]	–	–
5	*m*-CF_3–C_6H_4 (**6e**)	*n*-C_4F_9	**7e** colorless oil	35	82	n. c.
6	*p*-CF_3–C_6H_4 (**6f**)	*n*-C_4F_9	**7f** colorless oil	47	78	n. c.
7	*o*-CH_3O–C_6H_4 (**6g**)	*n*-C_4F_9	**7g** –	0[d]	–	–
8	*m*-CH_3O–C_6H_4 (**6h**)	*n*-C_4F_9	**7h** colorless oil	11	91	n. c.
9	*p*-CH_3O–C_6H_4 (**6i**)	*n*-C_4F_9	**7i** colorless oil	56	98	n. c.
10	*o*-Cl–C_6H_4 (**6j**)	*n*-C_4F_9	**7j** –	0[d]	–	–
11	*o*-Br–C_6H_4 (**6k**)	*n*-C_4F_9	**7k** –	0[d]	–	–
12	*o*-H_2N–C_6H_4 (**6l**)	*n*-C_4F_9	**7l** –	0[d]	–	–
13	*o*-AcNH–C_6H_4 (**6m**)	*n*-C_4F_9	**7m** –	0[d]	–	–
14	*o*-CH_3–C_6H_4 (**6n**)	*n*-C_4F_9	**7n** colorless oil	17	90	n. c.
15	*p*-CH_3–C_6H_4 (**6o**)	*n*-C_4F_9	**7o** colorless oil	91	93	n. c.
16	*p*-Br–C_6H_4 (**6p**)	*n*-C_4F_9	**7p** colorless oil	25	90	n. c.
17	1-$C_{10}H_7$ (**6q**)	*n*-C_4F_9	**7q** yellow oil	51	94	n. c.

[a] Isolated yield.
[b] Determined by GC.
[c] n. c., new compound.
[d] Unchanged aryl iodide was recovered.

(Table 2, Entries 15–16). Here, the coupling reaction takes place in the presence of both electron withdrawing and electron donating groups in *para* position. These results show clearly, that the reaction is controlled mostly by steric factors among others. Finally the reaction of 1-iodonaphtalene (**6q**) was tested. The expected fluorous naphthalene derivative (**7q**) was isolated in good yield and purity.

All the new compounds including fluorous fluorosilanes and -styrenes were characterized by ^{1}H, ^{13}C and ^{19}F NMR spectra, and their purity assayed by GC analysis (cf. Section 4). The fluorous styrenes shown above are liquids or low melting solids, volatile with steam and easily soluble in common organic solvents (*e.g.*, ether, acetone, benzene, ethyl acetate, dichloromethane and chloroform).

3. Conclusions

A simple route for the synthesis of novel fluorous alkenyl fluorosilanes was developed and these products were used as the source of transferable groups for a fluorous Hiyama-reaction.

Experimental evidence was given that the fluoride activators used in the Hiyama cross-coupling reaction at higher temperatures could initiate the protodesilylation reaction of the silicon substrate to afford fluorous alkenes [29].

Iodoarenes were coupled effectively with fluorous alkenyl-fluorosilanes yielding ω-perfluoroalkyl-styrenes under conditions where the formation of terminal fluorous alkenes could be definitely excluded.

4. Experimental

4.1. Materials and methods

Catalysts Pd_2dba_3 and $Pd(OAc)_2$ (99.9+%), 10%Pd/C [$(\eta^3$-allyl)$PdCl]_2$, and $Pd(PPh_3)_4$ were purchased from Aldrich, Merck, Strem and Alfa Aesar, respectively. The other reagents and solvents were purchased from Alfa Aesar or Molar, but **6m** prepared from **6l** as reported [30]. DMF was distilled from CaH_2 prior to use. NMR spectra were recorded at 298 K on Bruker Avance 250 MHz and Avance III 700 MHz spectrometers equipped with a QNP $^{1}H/^{13}C/^{19}F/^{31}P$ and a triple-resonance *z*-axis pulsed field gradient probe-head, respectively. ^{1}H and ^{13}C spectra were referenced to the signal of chloroform. Standard Bruker pulse sequences were run, spectra analysis was performed with TopSpin. Chemical shifts (δ) are given in parts per million (ppm) units relatively to the internal standard TMS (δ = 0.00 for ^{1}H, δ = 0.00 for ^{13}C) and to $CFCl_3$ as external standard (δ = 0.00 for ^{19}F). HPLC-TOF analysis was performed on an Agilent 1200 series HPLC coupled to an Agilent 6210 Time of Flight mass spectrometer. Dual ESI ion source was operated in negative mode. GCMS SHS measurement was performed on an Agilent 7890A chromatograph coupled to an Agilent 5975C inert XL mass spectrometer. GC analyses were performed on a Hewlett-Packard 5890 Series II chromatograph, Column: PONA [crosslinked methylsilicone gum], 50 m × 0.2 mm × 0.5 μm, carrier gas: H_2, FID detection (detector: 280 °C). Temperature program: 120, 5, 10, 280, 10. Injector: 250 °C.

4.2. Development of room temperature cross-coupling protocol

4.2.1. Catalyst-testing – the model reaction

A mixture of $R_{f4}CH{=}CHSiMe_2F$ (**5a**, 0.20 g, 0.62 mmol), iodobenzene (**6a**, 0.13 g, 0.62 mmol), TBAF·$3H_2O$ (0.39 g, 1.24 mmol), 1.00 ml DMF and 4.0 mol% Pd-catalyst [5.60 mg (0.0249 mmol, 0.0249 mmol Pd atom) of $Pd(OAc)_2$; 26.4 mg (0.0248 mmol Pd atom) of 10%Pd/C; 9.10 mg (0.0248 mmol, 0.0496 mmol Pd atom) of $(\eta^3$-allyl-$PdCl)_2$; 22.7 mg (0.0247 mmol, 0.0494 mmol Pd atom) of or Pd_2dba_3; or 28.6 mg (0.0247 mmol, 0.0247 mmol Pd atom) of $Pd(PPh_3)_4$] was stirred at room temperature in an argon atmosphere. The reactions were monitored with GC. After the reaction completed the mixture was diluted with 50 ml of water and distilled. The distillate was extracted with diethyl ether, dried (Na_2SO_4) and the solvent was removed in vacuo.

Yields of **7a**: 0 mg (0%) for 10%Pd/C and 0 mg (0%) for $Pd(PPh_3)_4$; 120 mg (60%) (GC assay: 90%) for $Pd(OAc)_2$; 95 mg (47%) (GC assay: 83%) for Pd_2dba_3; and 120 mg (60%) (GC assay: 72%) for (η^3-allyl-$PdCl)_2$.

4.2.2. Formation of 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene by TBAF cleavage of fluorosilane 5a

A round bottomed flask was charged with $R_{f4}CH{=}CHSiMe_2F$ (3.22 g, 10 mmol), TBAF·$3H_2O$ (4.73 g, 15 mmol) and DMF (10 ml), then it was set for distillation. The mixture was stirred and heated at 80–90 °C until all the generated *F*-olefin (R_{f4}–CH=CH_2) distilled. Yield: 2.20 g (89.4%) colorless oil, bp = 59–60 °C/1 atm (GC assay: 98%).

4.2.3. Cross-coupling experiment of $R_{f6}CH{=}CH_2$ and C_6H_5I

A mixture of iodobenzene (0.48 g, 2.37 mmol), perfluorohexyl-ethene (0.82 g, 2.37 mmol), TBAF·$3H_2O$ (1.50 g; 4.74 mmol), $Pd(OAc)_2$ (0.021 g, 4 mol%) and 3.0 ml DMF was stirred at room temperature for 7 days under an argon atmosphere. Then the reaction mixture was partitioned between water (30 ml) and ether (30 ml). The aqueous phase was washed with ether (3× 10 ml), and then the combined ethereal extracts were washed with water (3× 10 ml). The ether layer was separated, dried (Na_2SO_4) and the solvent was removed by distillation. The residual oil (1.2 g) was analyzed by GC, which indicated the presence of iodobenzene and perfluorohexyl-ethene as main components, but no peak for the formation of the corresponding ω-perfluorohexylstyrene was detected. Short path distillation allowed the recovery of 0.43 g (90%) iodobenzene (GC assay: 98%).

4.3. Reaction of 1,3-divinyltetramethyldisiloxane with TBAF

1,3-Divinyltetramethyldisiloxane (0.46 g, 2.5 mmol), TBAF·$3H_2O$ (3.15 g, 10 mmol) and DMF (5.0 ml) was stirred under an argon atmosphere in a closed tube at 80 °C for 1.5 h. The mixture was cooled to room temperature. The head-space gas formed was passed into a sample tube and analyzed by GC–MS. The measurement showed 90% ethylene (cf. Supplementary).

4.4. Preparation of 1,3-bis(1-iodo-2-perfluoroalkyl-ethyl)-tetramethyldisiloxanes (3a–c); general procedure 1 (GP-1)

A 250 ml round-bottomed two-necked flask was provided with a magnetic stirrer bar, equipped with a thermometer and a condenser. Dimethylvinylchlorosilane (**1**) (5.00 g; 41.4 mmol), perfluoroalkyl-iodide (**2a–c**) and the aqueous solution of $K_2S_2O_5$ (3.20 g, 14.4 mmol salt in 10 ml water) was placed in the flask. The mixture was stirred and heated to 70 or 80 °C and AIBN (0.50 g, 3.0 mmol) was added in small portions during 1.5–2.5 h. The mixture was further stirred on 70 or 80 °C for 4 h. After cooling the mixture to r.t. it was partitioned between water and ether. The aqueous phase was washed with ether, than the collected ethereal phase was washed with water 3 times. The organic layer was separated, dried (Na_2SO_4) and compound **3** was isolated by fractional vacuum-distillation.

4.4.1. 1,3-Bis(1-Iodo-3,3,4,4,5,5,6,6-nonafluoro-hexan-1-yl)-tetramethyldisiloxane; ($(R_{f4}CH_2CH(I)SiMe_2)_2O$ (3a)

The reaction was performed according to GP-1 using **2a** (21.59 g; 62.4 mmol). The reaction temperature was 70 °C, AIBN

addition: 2.5 h. Yield: 15.28 g (84.0%) light-purple oil. Bath temperature = 140–150 °C/13 Pa. Fw: 878.22 g/mol; calculated iodine%: 28.9%; found iodine%: 28.19%; purity: 97.5% (microanalytical iodine%).

^{1}H NMR ($CDCl_3$; 700 MHz): δ = 0.332 (s, 3H, CH_3), 0.340 (s, 3H, CH_3), 0.341 (s, 3H, CH_3), 0.348 (s, 3H, CH_3); 2.500–2.600 (m; 2H, CH_2); 2.750–2.850 (m; 2H, CH_2), 3.150–3.180 (m; 2H, two C*H*). (cf. Supplementary) ^{13}C NMR ($CDCl_3$; 700 MHz): δ = −1.86 (s, two overlapping CH_3), −1.41 (s, CH_3), −1.39 (s, CH_3), −0.18 (s, broad signal of C*H*-s), 34.5 (t, $^2J_{CF}$ = 21.5 Hz, broad signal of CH_2-s). ^{19}F NMR ($CDCl_3$; 250 MHz): δ = −81.62 (t; $^3J_{FF}$ = 10.5 Hz; 3F);−115.62 (m; 2F); −125.2 (m; 2F); −126.51 (m; 2F).

4.4.2. 1,3-Bis(1-Iodo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-1-yl)-tetramethyldisiloxane; ($R_{f6}CH_2CH(I)SiMe_2)_2O$ (3b)

The reaction was performed according to GP-1 using **2b** (27.82 g; 62.4 mmol). The reaction temperature was 80 °C, AIBN addition: 1.5 h. Yield: 19.35 g (86.7%) light-purple oil. Bath temperature = 170–180 °C/13 Pa. Fw: 1078.22 g/mol; calculated iodine%: 23.54%, found iodine%: 23.24%; purity: 98.7% (microanalytical iodine%).

^{1}H NMR ($CDCl_3$): δ = 0.32 (s, 3H, CH_3), 0.33 (s, 6H, two overlapping CH_3), 0.34 (s, 3H, CH_3), 2.40–2.65 (m; 2H, CH_2); 2.65–2.95 (m; 2H, CH_2), 3.10–3.20 (m; 2H, two C*H*). ^{13}C NMR ($CDCl_3$): δ = −1.63 (m; two overlapping CH_3); −1.13 (m, two overlapping CH_3), 0.08 (s, broad signal of C*H*-s), 34.77 (t, $^2J_{CF}$ = 21.5 Hz, broad signal of CH_2-s). ^{19}F NMR ($CDCl_3$): δ = −81.42 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −115.35 (m; 2F); −122.4 (m; 2F); −123.45 (m; 2F); −124.2 (m; 2F); −126.75 (m; 2F).

4.4.3. 1,3-Bis(1-Iodo-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decan-1-yl)-tetramethyldisiloxane; ($R_{f8}CH_2CH(I)SiMe_2)_2O$ (3c)

The reaction was performed according to GP-1 using **2c** (34.00 g; 62.4 mmol). The reaction temperature was 80 °C, AIBN addition: 1.5 h. Yield: 21.80 g (82.4%) light-purple oil. Bath temperature = 190–200 °C/13 Pa. Fw: 1278.34 g/mol; calculated iodine%: 19.86%; found iodine%: 20.98%; purity: 94.6% (microanalytical iodine%).

^{1}H NMR ($CDCl_3$): δ = 0.32 (s, 3H, CH_3), 0.33 (s, 6H, two overlapping CH_3), 0.34 (s, 3H, CH_3), 2.40–2.65 (m; 2H, CH_2); 2.65–2.95 (m; 2H, CH_2), 3.10–3.20 (m; 2H, two C*H*). ^{13}C NMR ($CDCl_3$): δ = −1.68 (m; two overlapping CH_3); −1.17 (m, two overlapping CH_3), 0.05 (s, broad signal of C*H*-s), 34.8 (t, $^2J_{CF}$ = 21.5 Hz, broad signal of CH_2-s). ^{19}F NMR ($CDCl_3$): δ = −81.59 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −115.5 (m; 2F); −122.5 (m; 6F); −123.5 (m; 2F); −124.3 (m; 2F); −126.9 (m; 2F).

4.5. Preparation of 1,3-bis(2-perfluoroalkyl-ethen-1-yl)-tetramethyldisiloxanes (4a–c); general procedure 2 (GP-2)

A mixture of the appropriate iodo-adduct **3** and diethylamine was stirred and refluxed for 7 h with an ~100 °C temperature oil bath. Then the mixture was cooled to room temperature and the excess of $HNEt_2$ was evaporated (Rotavap). The residue obtained was partitioned between water and ether. The ether extracts were combined, washed with water and dried (Na_2SO_4), then product **4** was isolated by fractional distillation.

4.5.1. 1,3-Bis(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-tetramethyldisiloxane ($R_{f4}CH{=}CHSiMe_2)_2O$ (4a)

The reaction was performed according to GP-2 using **3a** (12.00 g, 13.66 mmol) and $HNEt_2$ (3.24 g, 44.4 mmol). Yield: 7.15 g (84.1%) colorless oil. Bath temperature = 145–155 °C/~2.3 kPa. GC assay: 90%.

^{1}H NMR ($CDCl_3$): δ = 0.21 (s; 12H, Si–CH_3); 6.06 (dt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 11 Hz, 2H, CF_2–C*H*); 6.60 (dt; $^3J_{HH}$ = 19.0 Hz; $^4J_{HF}$ = 2.3 Hz; 2H, Si–C*H*). ^{13}C NMR ($CDCl_3$): δ = 0.21 (s; Si–CH_3); 131.3 (t; $^3J_{CF}$ = 24 Hz; CF_2–C*H*); 141.9 (t; $^4J_{CF}$ = 6 Hz; Si–C*H*). ^{19}F NMR ($CDCl_3$): δ = −81.71 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −114.53 (m; 2F); −125.1 (m; 2F); −126.4 (m; 2F).

4.5.2. 1,3-Bis(3,3,4,4,5,5,6,6,6,7,7,8,8,8-tridecafluoro-octen-1-yl)-tetramethyldisiloxane ($R_{f6}CH{=}CHSiMe_2)_2O$ (4b)

The reaction was performed according to GP-2 using **3b** (5.00 g; 4.64 mmol), and $HNEt_2$ (1.1 g, 15 mmol). Yield: 2.90 g (76.0%) colorless oil. Bath temperature = 170 °C/~2.3 kPa. GC assay: 92%.

^{1}H NMR ($CDCl_3$): δ = 0.21 (s; 12H, Si–CH_3); 6.06 (dt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 11 Hz, 2H, CF_2–C*H*); 6.60 (dt; $^3J_{HH}$ = 19.0 Hz; $^4J_{HF}$ = 2.3 Hz; 2H, Si–C*H*). ^{13}C NMR ($CDCl_3$): δ = 0.21 (s; Si–CH_3); 131.3 (t; $^3J_{CF}$ = 24 Hz; CF_2–C*H*); 141.9 (t; $^4J_{CF}$ = 6 Hz; Si–C*H*). ^{19}F NMR ($CDCl_3$): δ = −81.6 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −114.3 (m; 2F); −122.3 (m; 2F); −123.6 (m; 2F); −124.1 (m; 2F); −126.8 (m; 2F).

4.5.3. 1,3-Bis(3,3,4,4,5,5,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decen-1-yl)-tetramethyldisiloxane ($R_{f8}CH{=}CHSiMe_2)_2O$ (4c)

The reaction was performed according to GP-2 using **3c** (10.0 g; 7.82 mmol), and $HNEt_2$ (2.0 g, 27.4 mmol). Yield: 6.86 g (85.75%) colorless oil. Bath temperature = 190 °C/~2.3 kPa. GC assay: 88%.

^{1}H NMR ($CDCl_3$): δ = 0.21 (s; 12H, Si–CH_3); 6.06 (dt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 11 Hz, 2H, CF_2–C*H*); 6.60 (dt; $^3J_{HH}$ = 19.0 Hz; $^4J_{HF}$ = 2.3 Hz; 2H, Si–C*H*). ^{13}C NMR ($CDCl_3$): δ = 0.21 (s; Si–CH_3); 131.3 (t; $^3J_{CF}$ = 24 Hz; CF_2–C*H*); 141.9 (t; $^4J_{CF}$ = 6 Hz; Si–C*H*). ^{19}F NMR ($CDCl_3$): δ = −81.56 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −114.56 (m; 2F); −122.3 (m; 2F); −122.8 (m; 6F); −123.6 (m; 2F); −127.1 (m; 2F).

4.6. Preparation of dimethyl-(2-perfluoroalkyl-ethen-1-yl)-fluorosilanes (5a–c); general procedure 3 (GP-3)

A 100 ml round-bottomed flask was provided with a magnetic stirrer bar and equipped with a condenser. The alkenyl-disiloxane (**4a**–**c**) and $BF_3{\cdot}OEt_2$ was placed in the flask and the mixture was stirred on 100 °C bath for 5 h. After cooling to r.t. the mixture was partitioned between water and ether, the aqueous phase was washed with ether, than the collected ethereal phase was washed with water 3 times. The organic layer was separated, dried (Na_2SO_4), than ether was removed by atmospheric distillation. Compound **5** was isolated by fractional distillation.

4.6.1. Dimethyl-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-fluorosilane (5a)

The reaction was performed according to GP-3 using disiloxane **4a** (4.00 g; 6.43 mmol), and BF_3OEt_2 (2.3 g, 16.21 mmol). Yield: 2.95 g (71.25%) colorless oil. Bath temperature = 140–145 °C/101.3 kPa. GC assay: 97%.

^{1}H NMR ($CDCl_3$): δ = 0.36 (d; $^3J_{HF}$ = 7.3 Hz; 6H, Si–CH_3); 6.21 (dt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 11 Hz, 1H, CF_2–C*H*); 6.64 (ddt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 5 Hz, $^4J_{HF}$ = 2.3 Hz, 1H, Si–C*H*). ^{13}C NMR ($CDCl_3$): δ = −1.3 (d; $^3J_{CF}$ = 15 Hz; Si–CH_3); 133.0 (td, $^3J_{CF}$ = 3.5, $^2J_{CF}$ = 24, CF_2–C*H*), 138.8 (dt; $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 6 Hz, Si–C*H*). ^{19}F NMR ($CDCl_3$): δ = −81.67 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −114.85 (m; 2F); −124.97 (m; 2F); −126.40 (m; 2F); −163.82 (m; 1F).

4.6.2. Dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octen-1-yl)-fluorosilane (5b)

The reaction was performed according to GP-3 using disiloxane **4b** (14.0 g; 17.0 mmol), and BF_3OEt_2 (7.00 g, 49.3 mmol). Yield: 10.07 g (70.05%) colorless oil. Bath = 70–75 °C/~2.3 kPa. GC assay: 96%.

^{1}H NMR ($CDCl_3$): δ = 0.36 (d; $^3J_{HF}$ = 7.3 Hz; 6H, Si–CH_3); 6.21 (dt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 11 Hz, 1H, CF_2–C*H*); 6.64 (ddt; $^3J_{HH}$ = 19 Hz,

$^3J_{HF}$ = 5 Hz, $^4J_{HF}$ = 2.3 Hz, 1H, Si–C*H*). ^{13}C NMR ($CDCl_3$): δ = −1.3 (d; $^3J_{CF}$ = 15 Hz; Si–*C*H$_3$); 133.0 (td, $^3J_{CF}$ = 3.5, $^2J_{CF}$ = 24, CF_2–*C*H), 138.8 (dt; $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 6 Hz, Si–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.45 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −114.60 (m; 2F); −122.25 (m; 2F); −123.51 (m; 2F); −124.0 (m; 2F); −126.79 (m; 2F); −163.81 (m; 1F).

4.6.3. Dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decen-1-yl)-fluorosilane (**5c**)

The reaction was performed according to GP-3 using disiloxane **4c** (10.0 g; 9.78 mmol) and BF_3OEt_2 (4.2 g, 29.6 mmol). Yield: 7.50 g (73.4%) colorless oil. Bath temperature = 95–100 °C/ ~2.3 kPa. GC assay: 96%.

^{1}H NMR ($CDCl_3$): δ = 0.36 (d; $^3J_{HF}$ = 7.3 Hz; 6H, Si–C*H*$_3$); 6.21 (dt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 11 Hz, 1H, CF_2–C*H*); 6.64 (ddt; $^3J_{HH}$ = 19 Hz, $^3J_{HF}$ = 5 Hz, $^4J_{HF}$ = 2.3 Hz, 1H, Si–C*H*). ^{13}C NMR ($CDCl_3$): δ = −1.3 (d; $^3J_{CF}$ = 15 Hz; Si–*C*H$_3$); 133.0 (td, $^3J_{CF}$ = 3.5, $^2J_{CF}$ = 24, CF_2–*C*H), 138.8 (dt; $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 6 Hz, Si–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.42 (t; $^3J_{FF}$ = 10.5 Hz; 3F); −114.56 (m; 2F); −122.04 (m; 2F); −122.5 (m; 4F); −123.35 (m; 2F); −123.89 (m; 2F); −126.73 (m; 2F); −163.83 (m; 1F).

4.7. Hiyama coupling reactions with iodobenzene and its derivatives; general procedure 4 (GP-4)

A mixture of the appropriate fluorosilanes (**5a**–**c**, 2.37 mmol) and iodoarenes (**6a**–**q**, 2.37 mmol), TBAF·3H$_2$O (1.5 g; 4.74 mmol), $Pd(OAc)_2$ (0.021 g, 4 mol%) and DMF or DMF/BTF as solvent was stirred at room temperature during 3–7 days in an argon atmosphere. (Due to the lower miscibility of the R_{f8}-substituted fluorosilane in DMF, that reaction must be done in DMF/BTF.) The mixture was diluted with 100 ml water and steam-distilled. The distillate was extracted with ether, the organic layer was separated, dried (Na_2SO_4) and the solvent was removed under vacuo (Rotavap). The product was purified with flash column chromatography (silica 60, eluent: 100 ml *n*-hexan, column: 2.5 cm × 6 cm).

4.7.1. (E)-(3,3,4,4,5,5,6,6,6-Nonafluoro-hexen-1-yl)-benzene (**7a**)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodobenzene **6a** (0.48 g, 2.37 mmol), TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 3 days. Yield: 0.46 g (60.5%) colorless oil. GC assay: 91%.

^{1}H NMR ($CDCl_3$): δ = 6.19 (dt; $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.17 (dt, $^3J_{HH}$ = 16 Hz, $^4J_{HF}$ = 2.3 Hz; 1H, Ar–C*H*); 7.3–7.6 (m; 5H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 114.6 (t; $^3J_{CF}$ = 23 Hz; *C*H–CF_2); 127.5 (s; C_{Ar}); 128.9 (s; C_{Ar}); 130.4 (s; C_{Ar}); 133.8 (s; $C_{Ar,ipso}$), 140.0 (t; $^4J_{CF}$ = 10 Hz; Ar–*C*H =). ^{19}F NMR ($CDCl_3$): δ = −81.6 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −111.8 (m; 2F); −124.6 (m; 2F); −126.2 (m; 2F). In agreement with the published data [27].

4.7.2. (E)-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-octen-1-yl)-benzene (**7b**)

The reaction was performed according to GP-4 using fluorosilane **5b** (1.00 g, 2.37 mmol) and iodobenzene **6b** (0.48 g, 2.37 mmol), TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 3 days. Yield: 0.63 g (63%) colorless oil. GC assay: 95%.

^{1}H NMR ($CDCl_3$): δ = 6.19 (dt; $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.17 (dt, $^3J_{HH}$ = 16 Hz, $^4J_{HF}$ = 2.3 Hz; 1H, Ar–C*H*); 7.3–7.6 (m; 5H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 114.6 (t; $^3J_{CF}$ = 23 Hz; *C*H–CF_2); 127.8 (s; C_{Ar}); 129.2 (s; C_{Ar}); 130.4 (s; C_{Ar}); 133.8 (s; $C_{Ar,ipso}$), 140.0 (t; $^4J_{CF}$ = 10 Hz; Ar–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.4 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −111.7 (m; 2F); −122.2 (m; 2F); −123.4 (m; 2F); −123.8 (m; 2F); −126.8 (m; 2F). In agreement with the published data [28].

4.7.3. (E)-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decen-1-yl)-benzene (**7c**)

The reaction was performed according to GP-4 using fluorosilane **5c** (1.24 g, 2.37 mmol) and iodobenzene **6c** (0.48 g, 2.37 mmol), TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$ (0.021 g, 4 mol%) in 1.5 ml of BTF and 1.5 ml of DMF for 3 days. Yield: 0.62 g (50%) colorless oil. GC assay: 90%.

^{1}H NMR ($CDCl_3$): δ = 6.19 (dt; $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.17 (dt, $^3J_{HH}$ = 16 Hz, $^4J_{HF}$ = 2.3 Hz; 1H, Ar–C*H*); 7.3–7.6 (m; 5H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 114.6 (t; $^3J_{CF}$ = 23 Hz; *C*H–CF_2); 127.9 (s; C_{Ar}); 129.2 (s; C_{Ar}); 130.4 (s; C_{Ar}); 133.8 (s; $C_{Ar,ipso}$), 140.0 (t; $^4J_{CF}$ = 10 Hz; Ar–*C*H=). ^{19}F NMR ($CDCl_3$): δ = −81.25 (t, $^3J_{FF}$ = 10.5 Hz, 3F), −111.56 (m; 2F), −121.86 (m; 2F), −122.38 (m; 4F), −123.19 (m; 2F), −123.66 (m; 2F), −126.59 (m; 2F). In agreement with the published data [28].

4.7.4. (E)-1-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-3-trifluoromethyl-benzene (**7e**)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6e** (0.64 g, 2.37 mmol), TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 5 days. The product was distilled in vacuo (bath: 120–125 °C/~2.3 kPa). Yield: 0.32 g (35%) colorless oil. GC assay: 82%.

^{1}H NMR ($CDCl_3$): δ = 6.2 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.05–7.70 (m; 5H, Ar–C*H* overlaps with the aromatic protons). ^{13}C NMR ($CDCl_3$): δ = 116.6 (t, $^2J_{CF}$ = 24 Hz, CF_2–CH); 124.6 (m; C_{Ar}); 127.0 (m; C_{Ar}); 129.8 (s; C_{Ar}); 130.9 (s; C_{Ar}); 134.5 (s; $C_{Ar,ipso}$); 138.6 (t; $^3J_{CF}$ = 10 Hz, *C*H=CH–CF_2), ^{19}F NMR ($CDCl_3$): δ = −63.5 (m; 3F); −81.59 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −112.27 (m; 2F); −124.58 (m; 2F); −126.27 (m; 2F).

4.7.5. (E)-1-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-4-trifluoromethyl-benzene (**7f**)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6f** (0.64 g, 2.37 mmol), TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 5 days. Yield: 0.43 g (46.7%) colorless oil. GC assay: 78%.

^{1}H NMR ($CDCl_3$): δ = 6.28 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.15–7.7 (m; 5H, Ar–CH overlaps with the aromatic protons). ^{13}C NMR ($CDCl_3$): δ = 117.2 (t; $^2J_{CF}$ = 24 Hz; CH=*C*H–CF_2); 126.2 (m; C_{Ar}); 128.1 (s; C_{Ar}); 137.0 (s; $C_{Ar,ipso}$); 138.6 (t; *J* = 10 Hz; *C*H=CH–CF_2). ^{19}F NMR ($CDCl_3$): δ = −63.49 (s; 3F); −81.59 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −112.42 (m; 2F); −124.60 (m; 2F); −126.28 (m; 2F).

4.7.6. (E)-1-Methoxy-3-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**7h**)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6h** (0.55 g, 2.37 mmol). TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 7 days. Yield: 0.10 g (10.5%) colorless oil. GC assay: 91%.

^{1}H NMR ($CDCl_3$): δ = 4.03 (s, 3H, OC*H*$_3$) 6.35 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.1–7.55 (m; 5H, Ar–CH overlaps with the aromatic protons). ^{13}C NMR ($CDCl_3$): δ = 55.52 (s, O*C*H$_3$), 113.0 (s, C_{Ar}), 114.7 (t, $^2J_{CF}$ = 23 Hz, CF_2–*C*H), 116.0 (s, C_{Ar}), 120.4 (s, C_{Ar}), 130.2 (s, C_{Ar}), 135.1 (s; $C_{Ar,ipso}$), 140.0 (t, $^3J_{CF}$ = 10 Hz, Ar–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.55 (t, $^3J_{FF}$ = 10.5 Hz, 3F), −111.9 (m; 2F), −124.6 (m; 2F), −126.2 (m; 2F).

4.7.7. (E)-1-Methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**7i**)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6i** (0.55 g, 2.37 mmol). TBAF·3H$_2$O (1.5 g; 4.74 mmol) and $Pd(OAc)_2$

(0.021 g, 4 mol%) in 3 ml of DMF for 7 days. Yield: 0.47 g (56%) colorless oil. GC assay: 98%.

^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3H, OC*H*$_3$), 6.05 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 6.85–6.95 (m; 2H, aromatic protons), 7.1 (dt, $^3J_{HH}$ = 16 Hz, $^4J_{HF}$ = 2.3 Hz, Ar–C*H*), 7.38–7.44 (m; 2H, aromatic protons). ^{13}C NMR ($CDCl_3$): δ = 55.5 (s, O*C*H$_3$); 111.8 (t; $^2J_{CF}$ = 23 Hz, CF_2–*C*H); 114.5 (s; C_{Ar}); 126.5 (s; $C_{Ar(ipso)}$); 129.4 (s; C_{Ar}); 139.4 (t; $^3J_{CF}$ = 10 Hz; Ar–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.58 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −111.32 (m; 2F); −124.62 (m; 2F); −126.25 (m; 2F).

4.7.8. (E)-1-Methyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (7n)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6n** (0.52 g, 2.37 mmol). TBAF·3H$_2$O (1.5 g; 4.74 mmol) and Pd(OAc)$_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 7 days. Yield: 0.13 g (16.5%) colorless oil. GC assay: 90%.

^{1}H NMR ($CDCl_3$): δ = 2.66 (s, 1H, CH_3), 6.35 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.4–7.75 (m; 5H, Ar–C*H* overlaps with the aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 19.7 (s, *C*H$_3$), 115.8 (t, $^2J_{CF}$ = 23 Hz, CF_2–CH), 126.4 (s, C_{Ar}), 126.7 (s, C_{Ar}), 130.1 (s, C_{Ar}), 130.9 (s, C_{Ar}), 133.0 (s, $C_{Ar/ipso}$), 137.2 (s, $C_{Ar/ipso}$), 138.0 (t, $^3J_{CF}$ = 10 Hz, Ar–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.56 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −111.82 (m; 2F); −124.66 (m; 2F); −126.15 (m; 2F).

4.7.9. (E)-1-Methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (7o)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6o** (0.52 g, 2.37 mmol). TBAF·3H$_2$O (1.5 g; 4.74 mmol) and Pd(OAc)$_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 7 days. Yield: 0.72 g (91.3%) colorless oil. GC assay: 93%.

^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 3H, CH_3), 6.05 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–C*H*); 7.00–7.30 (m; 5H, Ar–C*H* overlaps with the aromatic protons). ^{13}C NMR ($CDCl_3$): δ = 21.5 (s, *C*H$_3$), 113.3 (t; $^2J_{CF}$ = 23 Hz, CF_2–CH); 127.8 (s; C_{Ar}); 129.8 (s; C_{Ar}); 131.0 (s; $C_{Ar(ipso)}$); 140.8 (t; $^3J_{CF}$ = 10 Hz; Ar–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.58 (t; J = 10.25 Hz, 3F); −111.62 (m; 2F); −124.62 (m; 2F); −126.23 (m; 2F).

4.7.10. (E)-1-Bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (7p)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6p** (0.67 g, 2.37 mmol). TBAF·3H$_2$O (1.5 g; 4.74 mmol) and Pd(OAc)$_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 7 days. Yield: 0.24 g (25%) colorless oil. GC assay: 90%.

^{1}H NMR ($CDCl_3$): δ = 6.22 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–*C*H); 7.14 (dt;, $^3J_{HH}$ = 16 Hz, $^4J_{HF}$ = 2.3 Hz, Ar–C*H*), 7.20–7.60 (m; 4H, aromatic protons). ^{13}C NMR ($CDCl_3$): δ = 115.1 (t, $^2J_{CF}$ = 23 Hz, CF_2–*C*H), 124.7 (s; $C_{Ar,ipso}$), 129.2 (s, C_{Ar}), 132.4 (s, C_{Ar}), 132.6 (s; $C_{Ar,ipso}$), 138.7 (t, $^3J_{CF}$ = 10 Hz, Ar–*C*H). ^{19}F NMR ($CDCl_3$): δ = −81.56 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −112.0 (m; 2F); −124.5 (m; 2F); −126.2 (m; 2F).

4.7.11. (E)-1-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-naphtalene (7q)

The reaction was performed according to GP-4 using fluorosilane **5a** (0.76 g; 2.37 mmol) and iodoarene **6q** (0.60 g, 2.37 mmol). TBAF·3H$_2$O (1.5 g; 4.74 mmol) and Pd(OAc)$_2$ (0.021 g, 4 mol%) in 3 ml of DMF for 5 days. Yield: 0.45 g (51%), yellow liquid, GC: 94%.

^{1}H NMR ($CDCl_3$): δ = 6.15 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, CF_2–*C*H); 7.20–8.0 (m; 9H, Ar–C*H* overlaps with the aromatic protons). ^{13}C NMR: δ = 117.73 (t; $^2J_{CF}$ = 24 Hz; CH=*C*H–CF_2); 123.56 (s, C_{Ar}); 125.38 (s; $C_{Ar,ipso}$), 125.86 (s; C_{Ar}); 126.77 (s; C_{Ar}); 127.42 (s; C_{Ar}); 129.20 (s; C_{Ar}); 130.82 (s; C_{Ar}); 131.52, (s, C); 131.67 (s, C); 137.96 (t; J = 10 Hz; *C*H=CH–CF_2). ^{19}F NMR: δ = 81.43 (t; $^3J_{FF}$ = 10.5 Hz, 3F); −111.67 (m; 2F); −124.49 (m; 2F); −126.05 (m; 2F).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2012.03.007.

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