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Low-temperature ^{19}F NMR spectroscopy of 1-fluoro-1-lithioethenes Stability, shifts and unexpected coupling constants☆

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Abstract

Half-lives and fluorine atom shifts of stabilized 1-fluoro-1-lithioethenes bearing hydrogen, fluorine, phenyl, and/or dimethylphenylsilyl groups in the β-positions have been determined by a low-temperature ^{19}F NMR spectroscopy. Some 1-fluoro-1-lithioethenes displayed an exceptionally low value of the *trans*-$^{3}J_{FF}$ coupling constant. Stereoselectivity of carbenoid formation, as well as an effect of configuration on the stability is discussed.

Keywords: 1-Fluoro-1-lithioalkene; Fluoroethenyllithium; Fluorovinyllithium; Fluorinated carbanion; Fluorinated carbenoid; ^{19}F NMR spectroscopy

1. Introduction

Aims to synthesize novel compounds with significant biological activity has resulted in a rapid development of the chemistry of fluorinated organic compounds. This effort has led both to the introduction of new, often rather sophisticated fluorinating reagents or fluorinated synthons [1,2], and to attempts to understand more deeply the changes caused by the presence of fluorine in molecules [3–5].

Carbanion chemistry is a powerful tool for organic synthesis. Carbanions bearing both electropositive metal and electronegative halogen atoms at the central atom show low stability [6–8] due to the strong interaction between the metal and halogen atoms, which limits their synthetic use. Although bromo- and chlorocarbanions have been intensively studied [6–8], little attention has been paid to fluorocarbenoids [9]. Organolithium compounds are widely used in synthetic organic chemistry [10] and are suitable both for analysis by NMR spectroscopy [11] and for computational chemistry [12–14]. However, in contrast to other metals such as zinc or cadmium, the highly electropositive lithium brings additional instability to the fluorocarbanion molecule and the way of decomposition of both alkane- [15] and alkene-based [16] fluorocarbenoids have been studied. As the only example of the synthetic use of a non-stabilized alkane-based fluorocarbanion, dibromofluoromethyllithium, at low temperature is known [17], and few others rely on adjacent heteroatom, like sulfur [18,19], phosphorus [20] or silicon [21], stabilization, efforts concentrated on more stable alkenyl fluorocarbenoids. Their stability depends mostly on the properties of the β-substituents [22–24] and further factors, e.g. the stabilizing role of fluorine atoms in trifluoromethyl groups *cis* to the lithium atom or the destabilizing role of the fluorine atom *trans* to the lithium atom has been recognized. Recently, surprisingly a stabilizing role of an oxygen substituent at a greater distance from the carbanion center has been reported [25,26]. However, all information concerning the stability of fluorocarbanions is indirect and based on a decrease of the yield in a series of trapping experiments. No attempts have been made to summarize the role of individual β-substituents. We reported that low-temperature ^{19}F NMR spectroscopy can be employed with advantage for the direct observation of fluorocarbenoids with limited stability [27]. In this paper, we wish to report how the properties of β-substituents influence the stability of 1-fluoro-1-lithioalkenes and also present our experimental approach in detail.

☆ Part 1 in the series "Fluorinated carbanions".

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2. Results and discussion

2.1. Choice of the β-substituents

We have selected four substituents for a study of the role of β-substitution on the stability of 1-fluoro-1-lithioalkenes, viz. hydrogen (basic substituent), fluorine (σ-acceptor and π-donor), substituted silyl group (σ-donor and π-acceptor), and phenyl group (aromatic substituent). Where possible, attempts to prepare pure stereoisomers have been made, in other cases mixtures of stereoisomers have been used.

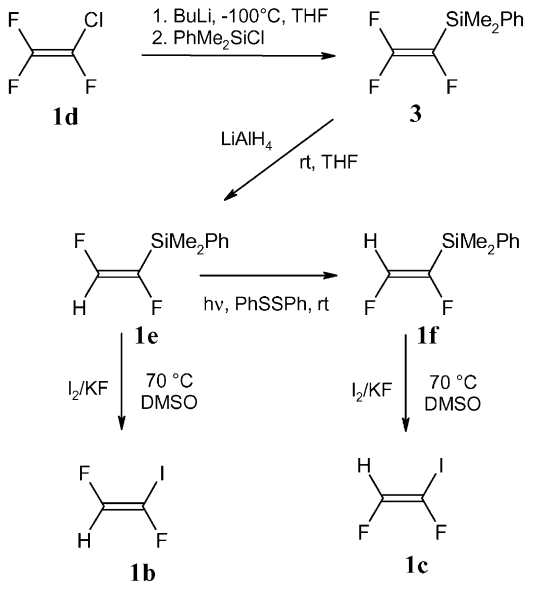
2.2. Syntheses of precursors of 1-fluoro-1-lithioethenes

1-Fluoro-1-lithioalkenes can be generated in two main ways, viz. by an exchange of lithium for either hydrogen or halogen atoms. The later method is more selective, can be accomplished more rapidly under low temperatures and hence has been used preferentially. As a rule [10], the rate of the exchange for halogen decreases in the order from iodine to chlorine.

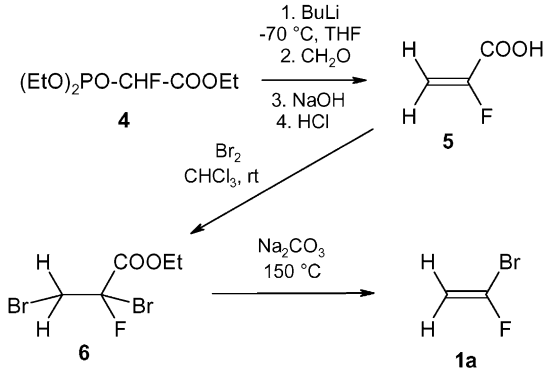
1-Chlorotrifluoroethene (**1d**) is commercially available and a cheap direct precursor of trifluorovinyllithium (**2d**) [22]. Trapping of trifluorovinyllithium with substituted silyl chloride leads to substituted trifluoroethenylsilane, which in turn can be reduced with lithium aluminum hydride to the corresponding (*Z*)-1,2-difluoroethenylsilane (**1e**, 94% stereo purity) [28]. Iododesilylation of **1e** afforded (*Z*)-1,2-difluoro-1-iodoethene (**1b**, 94% stereo purity) [28]. In analogy to [23], fluoroethenylsilane (**1e**) undergoes isomerization in the presence of ultraviolet light and a catalytic amount of diphenyldisulfide to the opposite stereoisomer (*E*)-1,2-difluoroethenylsilane (**1f**, 95% stereo purity). The fluorosilane **1f** can be similarly iododesilylated to (*E*)-1,2-difluoroiodoethene (**1c**, 95% stereo purity). We used dimethylphenylsilyl chloride instead of the previously reported [23] triethylsilyl chloride to exclude the formation of volatile triethylsilyl fluoride as a by-product, which can contaminate [23] difluoroiodoethenes **1b** and **1c** (Scheme 1).

The precursor of the simplest member of the series, 1-fluoroethenyllithium (**2a**), is 1-bromo-1-fluoroethene (**1a**), synthesis of which has been reported by Drakesmith et al. [29]. As no analysis is given in [29] and we were in doubt whether the published structure is correct, we decided to prepare fluoroethene **1a** by Eddarir's approach [30] based on ethyl (diethoxyphosphoryl)fluoroacetate (**4**). This procedure afforded the expected fluoroethene **1a** in low yield (Scheme 2).

(*E*)-1-Bromo-1-fluoro-2-phenylethene (**1g**, 87% stereo purity) has been synthesized according to Eddarir's procedure [30]. Surprisingly, all effort to isomerize the fluoroethene **1g** to the corresponding (*Z*)-isomer **1h** by palladium acetate according to [30] resulted only in a mixture of bromofluoroethenes **1g**, **1h** with stereoisomer ration *Z*/*E* = 75:25. On the other hand, distilled fluoroethene **1g** was spontaneously isomerized to (*Z*)-1-bromo-1-fluoro-2-phenylethene (**1h**, 87% stereo purity) on standing at RT for 1 week. A procedure analogous to [30] was also used by us for the preparation of 1-bromo-1-fluoro-2,2-diphenylethene (**1i**) [27] (Scheme 3).

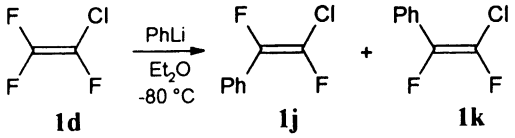


Scheme 1.



Scheme 2.

Finally, 1-chloro-1,2-difluoro-2-phenylethene (**1j**, **1k**) was prepared as a mixture of stereoisomers (*Z*/*E* = 26:74) by the reaction of phenyllithium with 1-chlorotrifluoroethene (**1d**) as in [31].

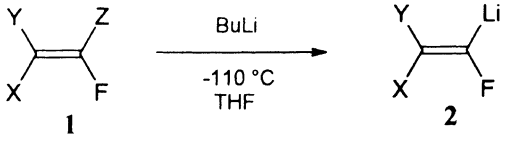


(1)

2.3. Formation of 1-fluoro-1-lithioethenes

1-Fluoro-1-lithioethenes **2b**, **2d**, **2e**, **2i**–**2k** were prepared by the reaction of precursors **1b**, **1d**, **1e**, **1i**–**1k** with commercial 2.5 M BuLi solution in hexanes at −110 °C directly in special NMR tube with the upper capillary part fitted with

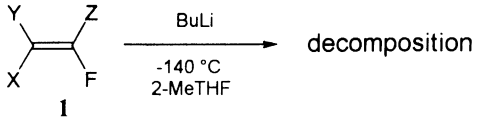
Wilmad Omnifit valve (Eq. (2)).



	X	Y	Z
1b,2b	H	F	I
1d,2d	F	F	Cl
1e,2e	Me_2PhSi	F	H
1i,2i	Ph	Ph	Br
1j,2j	Ph	F	Cl
1k,2k	F	Ph	Cl

(2)

The use of this equipment allowed sufficient mixing of the reaction components without risk of overheating. As solvent, a mixture of THF/THF-d_8 (2.5:1) was used. In the case of the unstable fluorolithioethenes **2a**, **2c**, **2f–2h**, we tried to reduce the temperature of carbanion formation to −140 °C and hence used the mixture 2-methyltetrahydrofuran (MTHF)/THF-d_8 (2.5:1), but only products of decomposition of fluorolithioethenes **2** were observed in the NMR spectra.



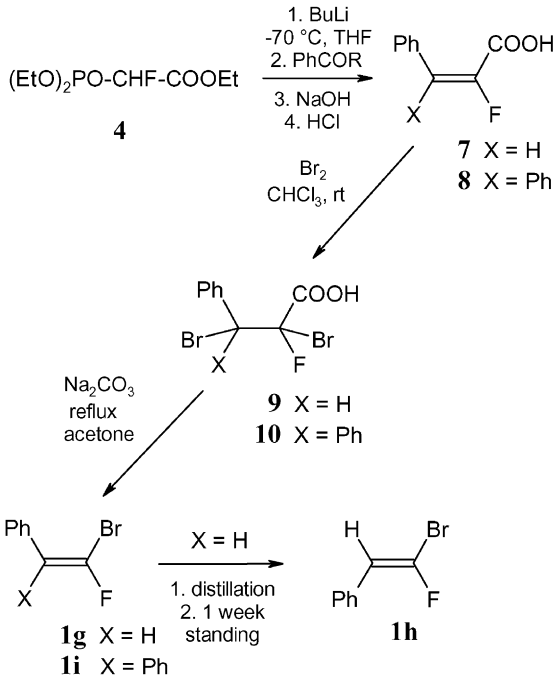
	X	Y	Z
1a,2a	H	H	Br
1c,2c	F	H	I
1f,2f	F	Me_2PhSi	H
1g,2g	H	Ph	Br
1h,2h	Ph	H	Br

(3)

As the commonly used internal standard, trichlorofluoromethane, is not stable under the reaction conditions, we looked for another internal standard to obtain both chemical shifts and quantitative stability data for fluorolithioethenes **2b**, **2d**, **2e**, **2i–2k**. Bis(2,2,2-trifluoroethyl)ether[1] proved to be a successful candidate and is sufficiently stable. Moreover, this ether can trap excess butyllithium and thus, lower risk of negative influence on stability by "metal assisted ionization" [16]. Cooling was provided by an external bath consisting of an ethanol–liquid N_2 mixture for −110 °C or isopentane–liquid N_2 mixture for −140 °C. All NMR experiments were performed 15 min after mixing the reaction components and the lithiations were then complete in all cases.

2.4. Stereoselectivity in the formation of 1-fluoro-1-lithioalkenes

Although in all cases, the rate of the lithiation was too high to be followed directly, remarkable stereoselectivity has been observed when the substituted atom was not too reactive, viz. for Z = H or Cl in Eq. (2) (precursors **1e**, **1f**, **1j**, **1k**).



Scheme 3.

When the precursor **1e** (*Z*/*E* mixture 94:6) was reacted with a little less than one equivalent of butyllithium, it was observed in the ^{19}F NMR spectra that all (*Z*)-isomer **2e** had been lithiated. On the other hand, a significant amount of (*E*)-isomer **1f** remained unchanged pointing, thus, to its lower rate of lithiation. Surprisingly just the opposite stereoselectivity was observed in the lithiation of the mixture of precursors **1j** and **1k** (*Z*/*E* = 26:74). In the course of partial lithiation, 97% of the major (*E*)-isomer, but only 13% of the (*Z*)-isomer were lithiated.

2.5. Stability of 1-fluoro-1-lithioethenes

For all stable fluorolithioethenes **2b**, **2d**, **2e**, **2i–2k**, the starting temperature for measurements was −110 °C. In the case of unstable fluorolithioethenes **2a**, **2c**, **2f–2h**, decrease of the measurement temperature to −120 °C had no apparent influence on their stability in solution. The temperature was then raised by 10 °C steps until measurable decomposition started. Approximate half-lives of carbanions at these temperatures are listed in Table 1.

Some trends in the stability of fluorolithioethenes **2** can be recognized in the NMR data: fluorine *cis* to lithium stabilizes the carbanion more than a phenyl group in this position. Hydrogen and silyl groups show no stabilizing effect. On the other hand, in *trans*-difluorolithioethenes, a hydrogen atom is the most stabilizing substituent *trans* to lithium as probably both lithium fluoride elimination and Fritz–Buttenberg–Wiechell rearrangement as the main decomposition

[1] Caution! Bis(2,2,2-trifluoroethyl) ether is highly toxic and all manipulations should be made with gloves in an efficient fume cupboard.

Table 1
Half-lives, shifts and $^3J_{FF}$ coupling constants of 1-fluoro-1-lithioethenes **2** ()

	X	Y	Temperature (°C)	Half-life (min)	δ (ppm)	$^3J_{XF}$ (Hz)	$^3J_{YF}$ (Hz)
2a	H	H	−120	Unstable			
2b	H	F	−70	80	−171.2		58
2c	F	H	−120	Unstable			
2d	F	F	−70	15	−194.4	54	88
2e	$SiMe_2Ph$	F	−90	20	−143.2		27
2f	F	$SiMe_2Ph$	−120	Unstable			
2g	H	Ph	−100	Unstable			
2h	Ph	H	−100	Unstable			
2i	Ph	Ph	−80	10	−66.0		
2j	Ph	F	−90	55	−133.1		38
2k	F	Ph	−90	55	−127.2	50	

mechanisms [6–8,22,24] are disadvantageous. Observed trends are depicted in Fig. 1.

In most cases, the rate of decomposition of fluorolithioethenes **2** corresponded to a monomolecular reaction. On the other hand, the decomposition of trifluorovinyllithium (**2d**) was probably autocatalyzed by the decomposition

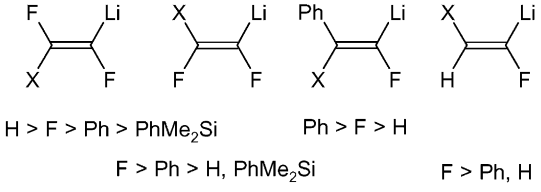


Fig. 1. Comparison of the stabilizing effect of various substituents X in fluorolithioethenes **2**.

products. An example of a series of low-temperature ^{19}F NMR spectra depicting the course of decomposition of fluorolithioethenes (in this case (*E*)-difluoroethenyllithium, **2b**), is given in Fig. 2. The first line shows the ^{19}F NMR spectrum observed at −100 °C, when the fluorolithioethene **2b** is stable. The second line is measured after 1 h at −80 °C and slow decomposition can be observed. The third to sixth line show the course of the decomposition at −70 °C in 20 min intervals, which takes place at a reasonable rate. The final line shows the ^{19}F NMR spectrum of the mixture at −60 °C, when all fluorolithioethene **2b** has decomposed.

It is rather surprising that the stability of some fluorolithioethenes significantly varies with configuration (couples **2b**, **2c** and **2e**, **2f**) while other fluorolithioethenes show low sensitivity to configuration of β-substituents (couples **2g**, **2h**

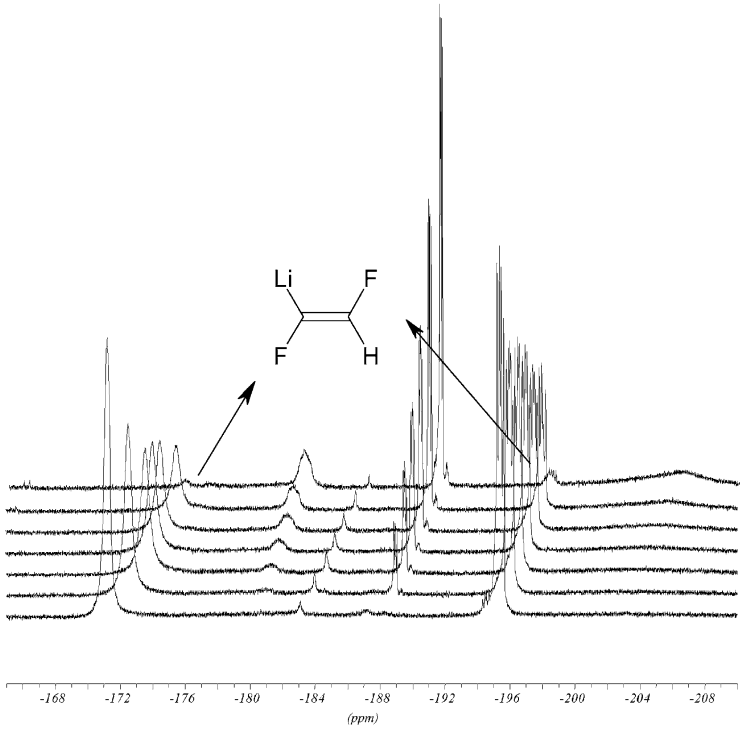


Fig. 2. Monitoring of the decomposition of (*E*)-difluoroethenyllithium by the low-temperature ^{19}F NMR.

and **2j**, **2k**). This is probably caused by various decomposition mechanisms of the fluorolithioethenes **2** and calculations which should clarify these differences are in progress.

Our data on the stability of carbanions **2j**, **2k** differ significantly from those published by Normant [22]. This can be caused either by a different method of formation of the present fluorolithioethenes or by the fact that we worked with the mixture of stereoisomers.

2.6. ^{19}F NMR shifts of 1-fluoro-1-lithioethenes

The ^{19}F NMR shifts of the fluorolithioethenes **2**, which did not decompose immediately at −120 °C, are listed in Table 1. The ^{19}F NMR shifts varies significantly depending on its environment and hence for most organofluorine compounds they can be observed over a wide range between +40 and −230 ppm. Nevertheless, each grouping containing a fluorine atom has a characteristic shift with the shift differences not higher than 40 ppm [32]. Surprisingly, the =CFLi grouping is the exception with the ^{19}F NMR shifts varying over an extraordinarily wide range between −65 and −195 ppm. Calculations attempting to explain the reasons for this unprecedented sensitivity are in progress.

2.7. Trans-fluorine–fluorine coupling constants of 1-fluoro-1-lithioethenes

Coupling constants between two vicinal fluorine atoms on a double bond are characteristic features of ^{19}F NMR spectroscopy. As a rule, *trans*-$^3J_{FF}$ coupling constants are significantly larger than the corresponding *cis*-$^3J_{FF}$ coupling constants and range between about 100 and 150 Hz [32]. Hence, it was rather unexpected that in the case of fluorolithioethenes **2**, we found extremely low values of *trans*-$^3J_{FF}$ coupling constants (see Table 1), which are in some cases even smaller than those of the corresponding *cis*-$^3J_{FF}$ coupling constants. To be completely sure that no isomerization proceeded during the carbanion formation, we trapped the fluorolithioethenes after observation with chlorotrimethylsilane. In all cases, the characteristically large *trans*-$^3J_{FF}$ coupling constants were observed with all integral characteristics unchanged confirming unequivocally that the configuration at the double bond did not change during the NMR experiment.

3. Conclusions

We confirmed in agreement with our previous results [27] that ^{19}F NMR spectroscopy is highly efficient tool for the estimation of stability of 1-fluoro-1-lithioalkenes **2** providing that these are sufficiently stable at −100 °C. We found that the ^{19}F NMR shifts of the carbenoid fluorine vary widely depending on the nature of the β-substituents. Fluorolithioethenes **2** containing a *trans*-difluoroethenyl grouping exhibit small values for coupling constants. These exclusive magnetic properties of fluorolithioethenes **2** make them attractive compounds for further synthetic, computational and analytical studies.

4. Experimental details

4.1. General comments

Temperature data are uncorrected with the exception of low-temperature NMR experiments, where the temperatures were calibrated. All NMR spectra were recorded with a Bruker AM 400 spectrometer, ^1H NMR spectra at 400.1 MHz using TMS as internal standard, ^{13}C NMR spectra at 100.6 MHz using TMS as internal standard and ^{19}F NMR at 376.5 MHz using $CFCl_3$ as internal standard with upfield values designated negative, except for NMR spectra of fluorolithioethenes **2**, where bis(2,2,2-trifluoroethyl)ether was used. FT-IR spectra were recorded with a Nicolet 740 instrument in KBr.

4.2. Preparation of precursors of fluorolithioalkenes

4.2.1. 1-Bromo-1-fluoroethene (*1a*)

*4.2.1.1. 2-Fluoroprop-2-enoic acid (**5**).* A 100 ml two-necked round bottom flask was charged with ethyl (diethoxyphosphoryl)fluoroacetate (**4**, 3.45 g, 14.3 mmol) and dried THF (40 ml). The mixture was cooled to −80 °C and butyllithium (5.73 ml, 2.5 M solution in hexanes, 14.3 mmol) was added to it. After stirring for 15 min, depolymerized (170–210 °C) formaldehyde (0.98 g, 32 mmol) was introduced into the mixture over 1.5 h. When the addition was finished, the mixture was stirred at −40 °C for 15 min and allowed to warm to room temperature. Water (30 ml) was then added to the mixture, the water layer was separated and extracted with diethyl ether. The organic layers were combined and washed with water. A mixture of this solution of crude ethyl 2-fluoroprop-2-enoate (60 ml), water (40 ml) and NaOH (2.3 g, 51 mmol) was stirred overnight at room temperature and then neutralized with aqueous HCl (6 M, 14 ml). The organic layer was separated, the water layer extracted with diethyl ether, organic layers were combined, washed with water and dried over anhydrous $MgSO_4$. Removal of drying agent by filtration and of solvents in vacuo afforded crystalline 2-fluoroprop-2-enoic acid (**5**, 0.30 g, 23%, mp 48–51 °C, [29] 52 °C). ^1H NMR ($CDCl_3$) δ: 5.25 (dd, 1H, $^3J_{HF} = 12.9$ Hz, $^2J_{HH} = 2.8$ Hz); 5.62 (dd, 1H, $^3J_{HF} = 43.4$ Hz, $^2J_{HH} = 2.8$ Hz); 9.50 (bs, 1H).

*4.2.1.2. 2,3-Dibromo-2-fluoroprop-2-enoic acid (**6**).* A 50 ml round bottom flask was charged with 2-fluoroprop-2-enoic acid (**5**, 0.30 g, 3.3 mmol), diethyl ether (20 ml), cooled to 0 °C and bromine (1.12 g, 7.0 mmol) was added dropwise. The flask was then allowed to warm to room temperature,

stoppered and stirred for 3 days. Removal of solvents in vacuo afforded crystalline 2,3-dibromo-2-fluoroprop-2-enoic acid (**6**, 0.79 g, 95%, mp 68–71 °C, [33] 71–72.5 °C). ^{1}H NMR ($CDCl_3$ [34]) δ: 4.08 (dd, 1H, $^2J_{HH} = 11.5$ Hz, $^3J_{HF} = 7.7$ Hz); 4.24 (dd, 1H, $^3J_{HF} = 29.1$ Hz, $^2J_{HH} = 11.5$ Hz); 9.65 (bs, 1H).

*4.2.1.3. 1-Bromo-1-fluoroethene (**1a**).* A 50 ml round bottom flask was charged with dried acetophenone (15 ml), 2,3-dibromo-2-fluoroprop-2-enoic acid (**6**, 0.79 g, 3.2 mmol), followed by $NaHCO_3$ (0.6 g, 7 mmol) in small portions while stirring. The mixture was heated slowly to 150 °C for 3 h and outgoing 1-bromo-1-fluoroethene (**1a**, 50 mg, 13%) was trapped in the cooled (−80 °C) receiver. ^{1}H NMR (2-methyltetrahydrofuran/THF-d_8 1:1) δ: 4.91 (dd, 1H, $^3J_{HF} = 42.3$ Hz, $^2J_{HH} = 4.4$ Hz); 5.34 (dd, 1H, $^3J_{HF} = 9.9$ Hz, $^2J_{HH} = 4.4$ Hz). ^{19}F NMR (2-methyltetrahydrofuran/THF-d_8 1:1) δ: −61.8 (dd, 1F, $^3J_{HF} = 42$ Hz, $^3J_{HF} = 10$ Hz).

*4.2.2. Preparation of (Z)-(1,2-difluoroethenyl)-dimethylphenylsilane (**1e**)*

*4.2.2.1. Dimethylphenyl(1,2,2-trifluoroethenyl)silane (**3**).* From chlorotrifluoroethene (17.5 g, 150 mmol), chlorodimethylphenylsilane (17.1 g, 100 mmol) and butyllithium (48 ml, 2.5 M in hexanes, 120 mmol), dimethylphenyl-(1,2,2-trifluoroethenyl)silane (**3**, 17.51 g, 76.8%, bp 81–86 °C/2.4 kPa, [28] 82–83 °C/2.3 kPa) was prepared according to [35]. ^{1}H NMR ($CDCl_3$) δ: 0.76 (d, 6H, $^4J_{HF} = 1.1$ Hz); 7.64 (m, 3H); 7.83 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: −4.4 (s); 128.2 (s); 130.1 (s); 131.4 (ddd, $^1J_{CF} = 256$ Hz, $^2J_{CF} = 83$ Hz, $^2J_{CF} = 65$ Hz); 133.8 (s); 134.2 (s); 161.6 (ddd, $^1J_{CF} = 317$, $^1J_{CF} = 277$, $^2J_{CF} = 40$).

*4.2.2.2. (Z)-(1,2-Difluoroethenyl)dimethylphenylsilane (**1e**).* From dimethylphenyl(1,2,2-trifluoroethenyl)silane (**3**, 12.17 g, 56.3 mmol) and lithium aluminum hydride (2.67 g, 70.3 mmol), (*Z*)-(1,2-difluoroethenyl)dimethylphenylsilane (**1e**, 9.95 g, 89.2%, bp 87–94 °C/2.7 kPa [28] not given, *Z*/*E* = 94:6) was prepared according to [23]. ^{1}H NMR ($CDCl_3$) δ: 0.54 (s, 6H); 7.42 (m, 3H); 7.61 (m, 2H); 7.64 (dd, 1H, $^2J_{HF} = 79.1$ Hz, $^3J_{HF} = 11.0$ Hz). ^{13}C NMR ($CDCl_3$) δ: −4.2 (s); 128.1 (s); 129.8 (s); 133.8 (s); 133.9 (s); 154.1 (dd, $^1J_{CF} = 244$ Hz, $^2J_{CF} = 56$ Hz); 160.5 (dd, $^1J_{CF} = 259$ Hz, $^2J_{CF} = 55$ Hz). ^{19}F NMR (THF-d_8 [28]) δ: −171.0 (dd, 1F, $^3J_{FF} = 130$ Hz, $^2J_{HF} = 79$ Hz); −179.9 (dd, 1F, $^3J_{FF} = 130$ Hz, $^3J_{HF} = 11$ Hz).

*4.2.3. (Z)-1,2-Difluoro-1-iodoethene (**1b**)*

A 25 ml round bottom flask charged with (*Z*)-(1,2-difluoroethenyl)dimethylphenylsilane (**1e**, 1.99 g, 10.0 mmol), dry DMSO (10 ml), dried potassium fluoride (1.74 g, 30 mmol) and iodine (5.08 g, 20.0 mmol) was attached to the source of vacuum (2.5 kPa) and heated while stirred at 70 °C for 1.5 h. Crude product (1.40 g) collected in a cooled trap (−80 °C) afforded on short path distillation (*Z*)-1,2-difluoro-1-iodoethene (**1b**, 1.079 g, 56.8%, bp 43–48 °C, [28] 49–50 °C, *Z*/*E* = 94:6). ^{1}H NMR ($CDCl_3$ [28]) δ: 7.50 (d, 1H, $^2J_{HF} = 76.4$ Hz). ^{13}C NMR ($CDCl_3$ [28]) δ: 104.1 (dd, $^1J_{CF} = 316$ Hz, $^2J_{CF} = 57$ Hz); 146.2 (dd, $^1J_{CF} = 248$ Hz, $^2J_{CF} = 56$ Hz). ^{19}F NMR (THF-d_8 [28]) δ: −133.8 (d, 1F, $^3J_{FF} = 145$ Hz); −159.8 (dd. 1F, $^3J_{FF} = 145$ Hz, $^2J_{HF} = 76$ Hz).

*4.2.4. (E)-Dimethylphenyl(1,2-difluoroethenyl)silane (**1f**)*

A 2 ml quartz cell was charged with (*Z*)-(1,2-difluoroethenyl)dimethylphenylsilane (**1e**, 1.98 g, 10.0 mmol) and diphenyl disulfide (66 mg, 0.30 mmol) and irradiated by a medium pressure UV lamp at room temperature for 2 days. (*E*)-Dimethylphenyl(1,2-difluoroethenyl)silane (**1f**) was obtained in good yield by distillation (1.82 g, 91.5%, bp 85–91 °C/2.7 kPa [23] not given, *Z*/*E* = 5:95). ^{1}H NMR ($CDCl_3$) δ: 0.48 (s, 6H); 6.21 (dd, 1H, $^2J_{HF} = 74.7$ Hz, $^3J_{HF} = 22.0$ Hz); 7.42 (m, 3H); 7.59 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: −4.6 (s); 128.0 (s); 130.1 (s); 133.9 (s); 133.9 (s); 143.7 (dd, $^1J_{CF} = 277$ Hz, $^2J_{CF} = 9$ Hz); 152.3 (dd, $^1J_{CF} = 277$ Hz, $^2J_{CF} = 5$ Hz). ^{19}F NMR (THF-d_8) δ: −134.5 (dd, 1F, $^2J_{HF} = 75$ Hz, $^3J_{FF} = 21$ Hz); −158.1 (dd, 1F, $^3J_{FF} = {}^3J_{HF} = 22$ Hz).

*4.2.5. (E)-1,2-Difluoro-1-iodoethene (**1c**)*

A 20 ml round bottom flask charged with (*E*)-(1,2-difluoroethenyl)dimethylphenylsilane (**1f**, 1.53 g, 7.72 mmol), dry DMSO (8 ml), dried potassium fluoride (1.34 g, 23 mmol) and iodine (3.95 g, 15.6 mmol) was attached to the source of vacuum (2.5 kPa) and heated while stirred at 70 °C for 1.5 h. Crude product (1.18 g) collected in a cooled trap (−80 °C) afforded on short path distillation (*E*)-1,2-difluoro-1-iodoethene (**1c**, 963 mg, 65.7%, bp 48–51 °C, *Z*/*E* = 5:95). ^{1}H NMR ($CDCl_3$) δ: 6.32 (dd, 1H, $^2J_{HF} = 73.6$, $^3J_{HF} = 25.4$ Hz). ^{13}C NMR ($CDCl_3$) δ: 97.9 (dd, $^1J_{CF} = 331$ Hz, $^2J_{CF} = 19$ Hz); δ: 138.5 (dd, $^1J_{CF} = 273$ Hz, $^2J_{CF} = 9$ Hz). ^{19}F NMR (THF-d_8) δ: −109.2 (m, 1F); −135.5 (d, 1F, $^2J_{HF} = 75$ Hz).

*4.2.6. (Z)-1-Bromo-1-fluoro-2-phenylethene (**1g**)*

Preparation of (*Z*)-1-bromo-1-fluoro-2-phenylethene (**1g**) was accomplished according to [30]. From ethyl (diethoxyphosphoryl)fluoroacetate (**4**, 5.33 g, 22.0 mmol), benzaldehyde (2.12 g, 20.0 mmol) and butyllithium (2.25 ml, 9.85 M in hexanes, 22.0 mmol), ethyl (*E*)-2-fluoro-3-phenylprop-2-enoate (3.38 g, 87.1%, bp 90–104 °C/100 Pa, [36] 73–77 °C/100 Pa, *Z*/*E* = 5:95) was prepared, which (3.38 g, 17.4 mmol) afforded by hydrolysis with sodium hydroxide (2.78 g, 69.6 mmol) crude (*E*)-2-fluoro-3-phenylprop-2-enoic acid (**7**, 2.79 g, 96.5%, *Z*/*E* = 5:95) as colorless oil. Bromination (2.95 g, 18.5 mmol) of (*E*)-2-fluoro-3-phenylprop-2-enoic acid (**7**, 2.79 g, 16.8 mmol) yielded 2,3-dibromo-2-fluoro-3-phenylpropanoic acid (**9**, 5.28 g, 96.5%), which (5.28 g, 16.2 mmol) was reacted with $NaHCO_3$ (2.72 g, 32.4 mmol) in acetone (50 ml) to afford

after purification by column chromatography (silica, eluent petroleum ether) (*Z*)-1-bromo-1-fluoro-2-phenylethene (2.66 g, 81.7%, *Z*/*E* = 90:10). ^{1}H NMR ($CDCl_3$ [30]) δ: 6.65 (d, 1H, $^3J_{HF}$ = 15.1 Hz); 7.29 (m, 1H); 7.33 (m, 2H); 7.48 (m, 2H). ^{19}F NMR ($CDCl_3$ [30]) δ: −65.7 (d, 1F, $^3J_{HF}$ = 15 Hz).

*4.2.7. (E)-1-Bromo-1-fluoro-2-phenylethene (**1h**)*

(*Z*)-1-Bromo-1-fluoro-2-phenylethene (4.26 g, 21.2 mmol) afforded by distillation a product (3.88 g, 91.1%, bp 60–62 °C/2 kPa, [30] 96 °C/2.9 kPa), which after 1 week standing at RT afforded (*E*)-1-bromo-1-fluoro-2-phenylethene (**1h**, *Z*/*E* = 13:87). ^{1}H NMR ($CDCl_3$ [30]) δ: 5.97 (d, 1H, $^3J_{HF}$ = 32.9 Hz); 7.27 (m, 1H); 7.33 (m, 2H); 7.38 (m, 2H). ^{19}F NMR ($CDCl_3$ [30]) δ: −68.2 (d, 1F, $^3J_{HF}$ = 33 Hz).

*4.2.8. Preparation of 1-bromo-1-fluoro-2,2-diphenylethene (**1i**)*

4.2.8.1. Ethyl 2-fluoro-3,3-diphenylprop-2-enoate. A mixture of dry THF (100 ml) and ethyl (diethoxyphosphoryl)-fluoroacetate (**4**, 12.1 g, 50.0 mmol) was cooled to −70 °C while stirring and butyllithium (20.3 ml, 2.48 M in hexanes, 50.0 mmol) was added. After stirring for 30 min at −30 °C, a THF (40 ml) solution of benzophenone (8.20 g, 45.0 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight (12 h). Solvents were then removed in vacuo, water (200 ml) was added and the mixture was extracted with dichloromethane. The organic layer was separated and dried over anhydrous $MgSO_4$. Solids were filtered off and dichloromethane removed in vacuo to afford 13.2 g of crude ethyl 2-fluoro-3,3-diphenylprop-2-enoate, which was directly used for the next reaction step. ^{1}H NMR ($CDCl_3$ [37]) δ: 1.02 (t, 3H, $^3J_{HH}$ = 7.1 Hz); 4.07 (q, 2H, $^3J_{HH}$ = 7.1 Hz); 7.31 (m, 10H). ^{19}F NMR ($CDCl_3$ [37]) δ: −122.4 (s, 1F).

*4.2.8.2. 2-Fluoro-3,3-diphenylprop-2-enoic acid (**8**)*. A mixture of crude ethyl 2-fluoro-3,3-diphenylprop-2-enoate (2.70 g), water (20 ml), dioxane (20 ml) and sodium hydroxide (1.60 g, 40.0 mmol) was stirred overnight (12 h) at room temperature, then acidified with hydrochloric acid (10 ml, 2 M) and extracted with dichloromethane. Solvents were removed in vacuo and the crude product was treated with petroleum ether to afford 1.84 g of crude 2-fluoro-3,3-diphenylprop-2-enoic acid (**8**, 1.84 g), which was recrystallized from petroleum ether/chloroform mixture to afford pure product **8** (1.30 g, combined yield 58.2%, mp 166–168 °C). ^{1}H NMR ($CDCl_3$) δ: 7.17 (m, 2H); 7.32 (m, 8H); 9.89 (bs, 1H). ^{19}F NMR ($CDCl_3$) δ: −123.5 (s, 1F).

*4.2.8.3. 1-Bromo-1-fluoro-2,2-diphenylethene (**1i**)*. A mixture of 2-fluoro-3,3-diphenylprop-2-enoic acid (**7**, 1.30 g, 5.37 mmol), chloroform (10 ml) and bromine (6.2 g, 38.8 mmol) in a stoppered 50 ml round bottom flask was stirred for 1 week at RT. The solvent was removed in vacuo and the crude product was purified by column chromatography (silica, eluent petroleum ether) to afford a mixture of 1-bromo-1-fluoro-2,2-diphenylethene (**1i**) and 1,1,2-tribromo-1-fluoro-2,2-diphenylethane (1.18 g), which was dissolved in dichloromethane (25 ml) and stirred for 3 days with saturated aqueous solution of sodium sulfite (25 ml). The organic layer was separated and the water layer was extracted with dichloromethane. The combined organic layers were dried with anhydrous $MgSO_4$, solids were filtered off and solvents were removed in vacuo to afford 1-bromo-1-fluoro-2,2-diphenylethene (**1i**, 818 mg, 55.0%, mp 58–60 °C, [38] 59–60 °C). ^{1}H NMR ($CDCl_3$ [38]) δ: 7.28 (m, 7H); 7.35 (m, 3H). ^{19}F NMR ($CDCl_3$ [38]) δ: −71.4 (s, 1F).

*4.2.9. 1-Chloro-1,2-difluoro-2-phenylethene (**1j, 1k**)*

From phenyllithium (27.8 ml, 1.8 M in hexanes, 50.0 mmol) and chlorotrifluoroethene (7.0 g, 60 mmol), 1-chloro-1,2-difluoro-2-phenylethene (4.23 g, 48.4%, bp 70–80 °C/3 kPa, *Z*/*E* = 26:74) was obtained according to [39]. ^{1}H NMR ($CDCl_3$) δ: 7.35 (m, 3H); 7.63 (m, 3H). ^{19}F NMR ($CDCl_3$ [40]) (*Z*)-isomer δ: −118.6 (d, 1F, $^3J_{FF}$ = 127 Hz); −148.0 (d, 1F, $^3J_{FF}$ = 127 Hz); (*E*)-isomer δ: −102.6 (d, 1F, $^3J_{FF}$ = 12 Hz); −131.2 (d, 1F, $^3J_{FF}$ = 12 Hz).

*4.3. Formation of 1-fluoro-1-lithioethenes (**2**)*

*4.3.1. Typical procedure: formation of (E)-1,2-difluoro-1-lithioethene (**2b**)*

The NMR tube with narrow upper part (Wilmad) equipped with Omnifit Valve (Wilmad) was charged with (*Z*)-1,2-difluoro-1-iodoethene (**2b**) (38 mg, 0.20 mmol), dry THF (0.35 ml), dry THF-d_8 (0.35 ml) and bis(2,2,2-trifluoroethyl)ether (10 μl). The tube was cooled to −110 °C (ethanol/liquid N_2) and BuLi (128 μl, 2.5 M in hexanes, 0.32 mmol) was added into the tube. After 2 min cooling, the cooled mixture was repetitively shaken vigorously. After 15 min, NMR spectra were taken.

*4.3.2. (E)-1,2-Difluoro-1-lithioethene (**2b**)*

^{19}F NMR (THF/THF-d_8) δ: −171.2 (bs, 1F); −195.4 (dd, 1F, $^2J_{HF}$ = 96 Hz, $^3J_{FF}$ = 58 Hz).

*4.3.3. 1,1,2-Trifluoro-2-lithioethene (**2d**)*

^{19}F NMR (THF/THF-d_8) δ: −96.8 (dd, 1F, $^2J_{FF}$ = 118 Hz, $^3J_{FF}$ = 54 Hz); −138.7 (dd, 1F, $^2J_{FF}$ = 118 Hz, $^3J_{FF}$ = 88 Hz); −194.4 (dd, 1F, $^3J_{FF}$ = 54 Hz, $^3J_{FF}$ = 88 Hz).

*4.3.4. (Z)-1-(Dimethylphenylsilyl)-1,2-difluoro-2-lithioethene (**2e**)*

^{19}F NMR (THF/THF-d_8) δ: −143.2 (bs, 1F); −187.1 (d, 1F, $^3J_{FF}$ = 27 Hz).

*4.3.5. 1-Fluoro-1-lithio-2,2-diphenylethene (**2i**)*

^{19}F NMR (THF/THF-d_8) δ: −66.0 (s, 1F).

4.3.6. 1,2-Difluoro-1-lithio-2-phenylethene

(E)-isomer (**2j**) ^{19}F NMR (THF/THF-d_8) δ: −133.1 (d, 1F, $^3J_{FF} = 38$ Hz); −171.4 (d, 1F, $^3J_{FF} = 38$ Hz); *(Z)*-isomer (**2k**) ^{19}F NMR (THF/THF-d_8) δ: −127.2 (d, 1F, $^3J_{FF} = 50$ Hz); −142.2 (d, 1F, $^3J_{FF} = 50$ Hz).

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