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Stereoselective synthesis of 1-bromo- (or 1-chloro-) 1,1-difluoro-2-alkenes

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Abstract

A highly regio- and stereo-selective method for the introduction of a bromo- (or chloro-) difluoromethylene group into various unsaturated systems is described. The key step is the treatment of 1,1-difluoro-1-alken-3-ols with thionyl bromide (or chloride).

Keywords: Stereoselective synthesis; Bromo- (or chloro-) difluoroalkenes; NMR spectroscopy; IR spectroscopy

1. Introduction

Fluorinated organic molecules attract much attention due to their unique biological properties. The replacement of hydrogen atoms by fluorine atoms in biological molecules causes a relatively small steric perturbation but leads to major changes in hydrophobicity and polarity of the hydrocarbon chain [1,2]. Some syntheses allowing the preparation of products in which a methylene group α to the double bond is replaced by a CF_2 group have been described [3–6]. The incorporation of the CF_2X ($X = Br$, Cl) moiety in an allylic position in intermediate synthons appears to be a potent tool for the construction of more elaborate molecules [7–9].

Herein we report an efficient method for the incorporation of a difluorobromo- (or chloro-) methyl group in various products such as alkenes, styrenes, dienes and enynes.

2. Results and discussion

Previously, we have described S_N2' substitution reactions on 1,1-difluoro-1-alken-3-ols **1** (readily obtained by the addition of difluorovinyllithium to carbonyl compounds [10]) by a fluorinating agent [11] or a hydride [12]. We now show that similar alcohols **1** can react with thionyl bromide (or chloride) by substitution of the hydroxy moiety by bromide or chloride to afford the corresponding 1-bromo- (or 1-chloro-)-1,1-difluoro-2-alkenes **2**.

$$R^1R^2C{=}O \xrightarrow[\text{2) } H_3O^+]{\text{1) } CF_2{=}CHLi} R^1R^2C(OH)CH{=}CF_2\ (\mathbf{1}) \xrightarrow[\text{2) } H_2O]{\text{1) } SOX_2} R^1R^2C{=}CH\text{-}CF_2X\ (\mathbf{2})\quad (X{=}Br,Cl)$$

1a: R^1=n-Hex, R^2=H

1b: R^1,R^2=$(CH_2)_5$

1c: R^1=Thienyl, R^2=H

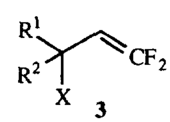
1d: R^1=Me-CH=CH, R^2=H

1e: R^1= n-Bu-C≡C, R^2=H

The reaction proceeds in diethyl ether in a few hours at room temperature and the alkenes **2** are afforded pure with a high stereoselectivity (if R^2=H, the *E* isomer is major) except when R^1 = alkynyl.

The results of the halogenation reactions are summarized in Table 1.

It is interesting to note from Table 1 that besides products **2** (S_N2' products), products **3** (S_N2 products) and **4** (acid fluorides) were also obtained in variable ratios.



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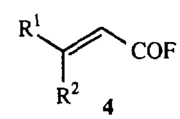

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From the various results obtained, the following comments may be made.

1. Since the S_N2 products **3** are very unstable (in contrast to products **2**), the ratio of these products was difficult to determine. This ratio could be accurately determined via the ^{19}F NMR spectra of the crude reaction product only in the

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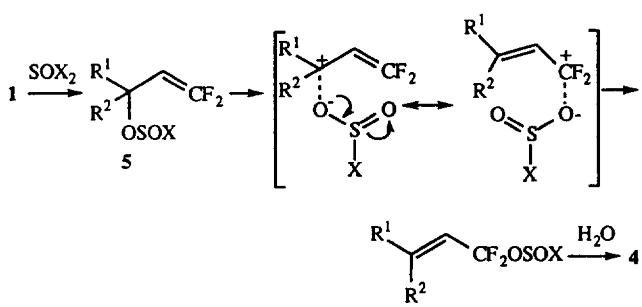
Table 1

R^1	R^2	X	Ratios 2/3/4 [a] 2	3	4	Compound 2 Yield (%) [b]	E/Z [c]	Experimental conditions (h at 20 °C)
^{n}Hex	H	Br	92	3	5	**2a**:81	99:1	3
^{n}Hex	H	Cl	90	5	5	**2a′**:76	99:1	24
$(CH_2)_5$		Br	100	0	0	**2b**:75	–	1
$(CH_2)_5$		Cl	5	0	95	**2b′**:5	–	6
thienyl	H	Br	95	0	5	**2c**:60	100:0	3
thienyl	H	Cl	75	0	25	**2c′**:50	100:0	6
Me–CH=CH	H	Br	90	0	10	**2d**:56	99:1	3
Me–CH=CH	H	Cl	70	0	30	**2d′**:50 [d]	99:1	6
^{n}Bu–C≡C	H	Br	90	0	10	**2e**:68	88:12	3
^{n}Bu–C≡C	H	Cl	18	2	80	**2e′**:13	92:8	6

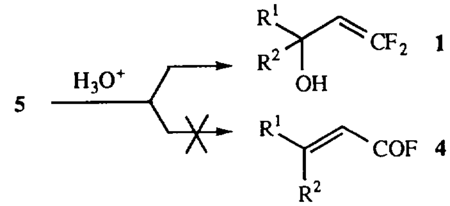
[a] Ratio **2/3/4** determined by ^{19}F NMR spectroscopy.
[b] Yield for the second step (reaction with SOX_2) in distilled product (except for **2b′**, **2c**, **2c′** and **2d′**).
[c] E/Z Ratio determined by ^{19}F NMR spectroscopy.
[d] 1:1 Mixture of the two possible S_N2' regioisomers: MeCHClCH=CH–CH=CF_2/Me(CH=CH)$_2CF_2$Cl.

case of alcohol **1a**. In other cases, the 'zero' value indicated in Table 1 does not mean that the S_N2 products were not obtained but that these were not observed in the NMR spectra. However, the yields of these products relative to **2** and **4** show that this ratio must be always low. (In addition, these S_N2 products can be destroyed by filtration through a small column packed with silica and so the S_N2' products can be afforded pure.)

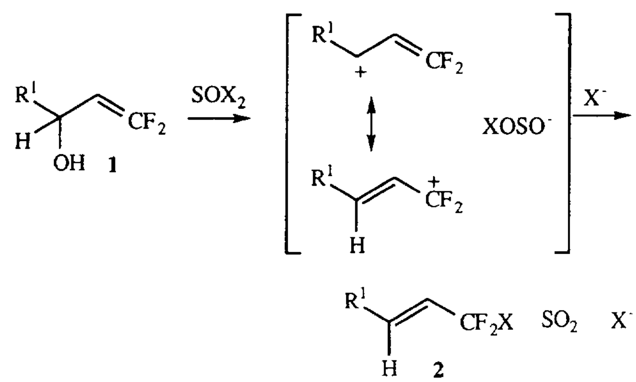
2. In the cases of tertiary (**1b**), allyl aromatic (**1c**), bis-allylic (**1d**) and allyl propargylic (**1e**) alcohols, the amount of **4** generated in addition to **2** can sometimes be significant, particularly when X = Cl. In these cases, the $XOSO^-$ moiety is readily released (at low temperature) and hence $XOSO^-$ is in competition with the halogenide used. If X = Br, the desired product **2** is mainly obtained because Br^- is a good nucleophile. In contrast, if X = Cl, since the Cl^- ion is not such a good nucleophile, attack of $XOSO^-$ is competitive and leads after hydrolysis to the acid fluoride **4**.



It appears that the acid fluoride **4** does not come from unreacted intermediate **5**. We have shown that after a short reaction time, hydrolysis leads to the alcohol **1** and not the acid fluoride **4**.



3. In the case of secondary alcohols (**1a**), the release of $XOSO^-$ is more difficult (only at room temperature) and the ratio of acid fluoride **4** afforded is very low (5%) whatever X may be. This means that there is no competition between the $XOSO^-$ and X^- ions (especially if X = Cl) because $XOSO^-$ must be in an inactive form ($SO_2 + X^-$) in the reaction mixture. Here, the low ratio of acid fluoride formed must be due to the small amount of free $XOSO^-$ remaining.



Although the mechanism has not been determined, the results obtained suggest that the halogenation process involves a transition state with a significant carbocation character [13,14]. Thus, if CF_2^+ is stabilized by the two fluorine atoms, **2** is the principal product.

In conclusion, the reaction of thionyl bromide (or chloride) with 1,1-difluoro-1-alken-3-ols **1** allows the formation of 1-bromo- (or 1-chloro-)-1,1-difluoro-2-alkenes **2** with good stereospecificity. If a choice is possible, it is preferable to use thionyl bromide because this halogenide gives little or no acid fluoride besides the desired product and moreover, the halogenation reaction is more rapid than with thionyl chloride. This method constitutes a useful means for synthesizing more complex fluorinated molecules.

3. Experimental details

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL GSX 400 spectrometer [$CDCl_3$: δ(ppm) from TMS, J(Hz)] and ^{19}F NMR spectra on a JEOL FX 90 spectrometer [$CDCl_3$: δ(ppm) from $CFCl_3$, J(Hz)]. Infrared spectra were measured on a Perkin-Elmer 397 spectrometer (neat, cm^{-1}).

3.1. Preparation of the intermediate difluorinated alcohols 1

To a solution of $F_2C{=}CH_2$ (2.4 g, 37.5 mmol) in THF (60 ml) and Et_2O (15 ml) was added 30 mmol of ^{s}BuLi in cyclohexane at −100 °C. The reaction mixture was stirred at −90 °C for 20 min, and then a solution of the carbonyl compound (25 mmol) in Et_2O (10 ml) was added at −100 °C. After 30 min at −90 °C, the temperature was raised to 0 °C (over 20 min). The solution was hydrolyzed by the addition of H_2SO_4 solution (1 N) and extracted with Et_2O. The organic phase was successively washed with saturated aqueous solutions of $NaHCO_3$ and NaCl, and dried over $MgSO_4$. After evaporation of the solvents, the corresponding alcohol was obtained. Alcohols **1** are unstable in the pure state but can be stored without any problem in Et_2O solution (with the addition of a small amount of $NaHCO_3$).

3.2. Preparation of the bromo- or chloro-difluorinated alkenes 2

$SOBr_2$ (1.94 ml, 25 mmol) or $SOCl_2$ (1.82 ml, 25 mmol) was added (over 5 min) at −80 °C (for $SOBr_2$) or at −20 °C (for $SOCl_2$) to a solution of the crude alcohol **2** (prepared from 25 mmol of the carbonyl derivative) in Et_2O (50 ml). After 15 min, the temperature was allowed to warm up to 20 °C (over 15 min) and the reaction mixture stirred over the time indicated in Table 1. The reaction mixture was hydrolyzed by the addition of H_2O (30 ml) at −10 °C and extracted with Et_2O. The organic phase was successively washed with sat. aq. $NaHCO_3$ and NaCl solutions. It was then dried over $MgSO_4$ and concentrated in vacuo. To the crude product thus obtained was quickly added 30 ml of a mixture of pentane (cyclohexane for R^1 = thienyl) and Et_2NH in a 95:5 ratio. After 2 min, this solution was filtered through a small column packed with silica. The solvent was evaporated and the residue distilled to afford the desired product **2**.

1-Bromo-1,1-difluoro-2-nonene (**2a**): yield, 81%; b.p. 38–42 °C/0.5 Torr. Steric purity: E/Z = 99:1. IR (cm^{-1}): 2940; 2915; 2840; 1725; 1660; 1455; 1225; 1080; 960; 920; 730. ^{19}F NMR δ: −44.3 (d, J = 10 Hz, E-isomer); −39.0 (Z-isomer) ppm. ^{1}H NMR δ: E-isomer: 0.9 (t, 3H); 1.3 (m, 6H); 1.45 (m, 2H); 2.15 (m, 2H); 5.85 (dtt, H^2); 6.2 (dtt, H^3) [$J(H^2/H^3)$ = 15.5 Hz, $J(H^2/F)$ = 9.9 Hz, $J(H^3/H^4)$ = 6.9 Hz, $J(H^3/F)$ = 2.2 Hz, $J(H^2/H^4)$ = 1.5 Hz] ppm. ^{13}C NMR δ: E-isomer: 14.0, 22.6, 28.0, 28.8, 31.2, 31.6, 117.2 (t, C^1, J = 301 Hz); 126.8 (t, C^2, J = 23 Hz); 137.2 (t, C^3, J = 8 Hz) ppm. Analysis: Calc. for $C_9H_{15}BrF_2$: C, 44.83; H, 6.27%. Found: C, 44.92; H, 6.35%.

1-Chloro-1,1-difluoro-2-nonene (**2a'**): yield, 76%; b.p. 68–70 °C/ 10 Torr. Steric purity: E/Z = 99:1. IR (cm^{-1}): 2950; 2920; 2850; 1740; 1670; 1460; 1230; 1080; 940. ^{19}F NMR δ: −49.8 (d, J = 9 Hz, E-isomer); −45.2 (Z-isomer) ppm. ^{1}H NMR δ: E-isomer: 0.95 (t, 3H); 1.3 (m, 6H); 1.4 (m, 2H); 2.15 (m, 2H); 5.8 (dtt, H^2); 6.3 (dtt, H^3) [$J(H^2/H^3)$ = 15.4 Hz, $J(H^2/F)$ = 8.8 Hz, $J(H^3/H^4)$ = 6.6 Hz, $J(H^3/F)$ = 2.2 Hz, $J(H^2/H^4)$ = 1.6 Hz] ppm. ^{13}C NMR δ: E-isomer: 14.0, 22.6, 28.0, 28.7, 31.3, 31.6, 124.6 (t, C^2, J = 27 Hz); 125. 1 (t, C^1, J = 287 Hz); 138.0 (t, C^3, J = 7 Hz) ppm. Analysis: Calc. for $C_9H_{15}ClF_2$: C, 54.96; H, 7.69%. Found: C, 54.86; H, 7.87%.

3-Bromo-1,1-difluoro-1-nonene (**3a**): ^{19}F NMR δ: −86.5 [d, F^1, $J(F^1/F^2)$ = 30 Hz]; −84.4 [dd, F^2, $J(F^2/F^1)$ = 30 Hz, $J(F^2/H^2)$ = 22 Hz] ppm. ^{1}H NMR δ: 4.6 (ddd, H^2); 4.7 (dtt, H^3) [$J(H^2/F^2)$ = 22 Hz, $J(H^2/H^3)$ = 11 Hz, $J(H^3/H^4)$ = 7.1 Hz, $J(H^3/F)$ = 1.5 Hz, $J(H^2/F^1)$ = 1 Hz] ppm.

3-Chloro-1,1-difluoro-1-nonene (**3a'**): ^{19}F NMR: −87.0 [d, F^1, $J(F^1/F^2)$ = 33 Hz]; −85.5 [dd, F^2, $J(F^2/F^1)$ = 33 Hz, $J(F^2/H^2)$ = 21 Hz] ppm. ^{1}H NMR δ: 4.5 (ddd, H^2); 4.6 (dtm, H^3) [$J(H^2/F^2)$ = 21 Hz, $J(H^2/H^3)$ = 10 Hz, $J(H^3/H^4)$ = 7 Hz, $J(H^2/F^1)$ = 1 Hz] ppm.

1-Bromo-2-cyclohexylidene-1,1-difluoroethane (**2b**): yield, 75%; b.p. 38–40 °C/1 Torr. IR (cm^{-1}): 2930; 2850; 1660; 1445; 1220; 1190; 1090; 945. ^{19}F NMR δ: −35.7 (d, J = 12 Hz) ppm. ^{1}H NMR δ: 1.6 (m, 6H); 2.15 (m, 2H); 2.4 (m, 2H); 5.65 (t, H^2, J = 12.4 Hz) ppm. ^{13}C NMR δ: 26.0, 27.0; 28.3; 30.1; 36.8; 116.8 (t, C^1, J = 301 Hz); 119.9 (t, C^2, J = 25 Hz); 152.9 (t, C^3, J = 6 Hz) ppm. Analysis: Calc. for $C_8H_{11}BrF_2$: C, 42.69; H, 4.93%. Found: C, 42.83; H, 5.02%.

1-Chloro-2-cyclohexylidene-1,1-difluoroethane (**2b'**): yield, 5%. ^{19}F NMR δ: −41.6 (dt, J = 9, 2 Hz) ppm.

(E)-1-Bromo-1,1-difluoro-3-thienyl-2-propene (**2c**): crude yield, 60%. Steric purity: E = 100%. IR (cm^{-1}): 3100; 3060; 2910; 2840; 1635; 1595; 1220; 1090; 1085; 915; 850; 815; 700. ^{19}F NMR δ: −44.1 (d, J = 10 Hz) ppm. ^{1}H NMR δ: 6.3 (dt, H^2); 7.05 (dd, H^6); 7.15 (dt, H^3); 7.2 (d, H^5); 7.4 (d, H^7) [$J(H^2/H^3)$ = 15.6 Hz, $J(H^2/F)$ = 10.1 Hz, $J(H^6/H^7)$ = 5.1 Hz, $J(H^5/H^6)$ = 3.6 Hz, $J(H^3/F)$ = 2.0 Hz] ppm. ^{13}C NMR δ: 116.7 (t, C^1, J = 301 Hz); 122.6 (t, C^2, J = 24 Hz); 126.9 (t, C^3, J = 9 Hz); 127.6, 127.7, 129.8, 137.5 (s, C^4) ppm.

(E)-1-Chloro-1,1-difluoro-3-thienyl-2-propene (**2c'**): crude yield, 50%. Steric purity: E = 100%. IR (cm^{-1}): 3105; 3065; 2960; 2840; 1645; 1600; 1230; 1195; 1085; 950; 700. ^{19}F NMR δ: −49.1 (d, J = 9 Hz) ppm. ^{1}H NMR δ: 6.2 (dt, H^2); 7.05 (dd, H^6); 7.20 (dt, H^3); 7.21 (d, H^5); 7.35 (d, H^7) [$J(H^2/H^3)$ = 15.7 Hz, $J(H^2/F)$ = 9.1 Hz, $J(H^6/H^7)$ = 5.1 Hz, $J(H^5/H^6)$ = 3.6 Hz, $J(H^3/F)$ = 2.0 Hz] ppm. ^{13}C NMR δ: 120.5 (t, C^2, J = 27 Hz); 125.3 (t, C^1, J = 283 Hz); 127.8 (t, C^3, J = 5 Hz); 127.6, 127.8, 129.9, 137.7 (s, C^4) ppm.

1-Bromo-1,1-difluoro-2,4-hexadiene (**2d**): yield, 56%; b.p. 40 °C/10 Torr. Steric purity: $E,E/Z,E$ = 99:1. IR (cm^{-1}): 2960; 1650; 1625; 1220; 1070; 985; 915; 785; 725. ^{19}F NMR δ: −43.6 (d, J = 10 Hz, E,E-isomer); −38.0 (d, J ≈ 12 Hz, Z,E-isomer) ppm. ^{1}H NMR δ: E,E-isomer: 1.85 (d, 3H, J = 4.6 Hz); 5.85 (dt, H^2); 6.1 (m, H^4 and H^5); 6.6 (ddt, H^3) [$J(H^2/H^3)$ = 15.2 Hz, $J(H^2/F)$ = 10.6 Hz, $J(H^3/H^4)$ = 9.7 Hz, $J(H^3/F)$ = 2.0 Hz] ppm. ^{13}C NMR δ: E,E-isomer: 17.8 (s); 117.0 (t, C^1, J = 300 Hz); 124.4 (t, C^2, J = 24 Hz); 127.7 (s); 133.8 (t, C^3, J = 8 Hz); 137.3 (s) ppm. Analysis: Calc. for $C_6H_7BrF_2$: C, 36.58; H, 3.58%. Found: C, 36.28; H, 3.65%.

1-Chloro-1,1-difluoro-2,4-hexadiene (**2d'**): crude yield, 50% (1:1 mixed with the other S_N2' product: 1,1-difluoro-5-chloro-1,3-hexadiene). Steric purity: $E,E/Z,E$ = 99:1. IR

(cm^{-1}): 1655. ^{19}F NMR δ: −49.0 (d, J=9 Hz, E,E-isomer); −44.2 (d, Z,E-isomer) ppm. ^{1}H NMR δ: E,E-isomer: 1.85 (d, 3H, J=6 Hz); 5.8 (dt, H^2); 6.1 (dq, H^5); 6.2 (ddq, H^4); 6.65 (ddm, H^3) [$J(H^4/H^5)$ = 15.0 Hz, $J(H^2/H^3)$ = 15.5 Hz, $J(H^3/H^4)$ = 9.7 Hz, $J(H^2/F)$ = 9.4 Hz, $J(H^5/H^6)$ = 6.5 Hz, $J(H^4/H^6)$ = 1.0 Hz] ppm.

1,1-Difluoro-5-chloro-1,3-hexadiene: IR (cm^{-1}): 1720. ^{19}F NMR δ: −85.3 (t, J=24 Hz); −86.7 (d, J=24 Hz) ppm. ^{1}H NMR δ: 1.65 (d, $3H^6$, J=6.6 Hz); 4.6 (dq, H^5, J=7 Hz); 4.95 (dd, H^2); 5.75 (dd, H^4); 7.3 (dd, H^3) [$J(H^2/F)$ = 23.9 Hz, $J(H^3/H^4)$ = 15 Hz, $J(H^2/H^3)$ = 10.8 Hz, $J(H^4/H^5)$ = 8.0 Hz] ppm.

1-Bromo-1,1-difluoro-2,4-nonenyne (**2e**): yield, 68%; b.p. 56–58 °C/1 Torr. Steric purity: E/Z = 88:12. IR (cm^{-1}): 2950; 2925; 2860; 2210; 1630; 1460; 1270; 1220; 1090; 925; 725; 700. ^{19}F NMR δ: −42.6 (d, J=11 Hz, Z-isomer); −46.6 (d, J=10 Hz, E-isomer) ppm. ^{1}H NMR δ: 0.9 (t, 3H); 1.4 (m, 2H); 1.55 (m, 2H); E-isomer: 2.35 (t, 2H); 6.10 (dtt, H^3); 6.22 (dt, H^2) [$J(H^2/H^3)$ = 15.9 Hz, $J(H^2/F)$ = 9.9 Hz, $J(H^3/H^6)$ = 2 Hz, $J(H^3/F)$ = 2 Hz]; Z-isomer: 2.40 (t, 2H); 5.8 (dtt, H^3); 6.05 (dt, H^2) [$J(H^2/H^3)$ = 11.5 Hz, $J(H^2/F)$ = 11 Hz, $J(H^3/H^6)$ = 2 Hz, $J(H^3/F)$ = 2 Hz] ppm. ^{13}C NMR δ: E-isomer: 13.5, 19.2, 22.0, 30.3, 75.7, 99.1, 115.9 (t, C^3, J = 8 Hz); 116.3 (t, C^1, J = 301 Hz); 134.4 (t, C^2, J=24 Hz) ppm. Analysis: Calc. for $C_9H_{11}BrF_2$: C, 45.59; H, 4.67%; Found: C, 45.38; H, 4.85%.

1-Chloro-1,1-difluoro-2,4-nonenyne (**2e'**): yield, 13%; b.p. 70–72 °C/11 Torr. Steric purity: E/Z=92:8. ^{19}F NMR δ: −51.4 (E-isomer); −48.0 (Z-isomer) ppm. ^{1}H NMR δ: E-isomer: 0.9 (t, 3H); 1.4 (m, 2H); 1.55 (m, 2H); 2.35 (t, 2H); 6.15 (m, 2H) ppm. ^{13}C NMR δ: E-isomer: 13.5, 19.2, 22.0, 30.3, 75.8, 98.7, 116.9 (t, C^3, J=8 Hz); 124.5 (t, C^1, J=287 Hz); 132.4 (t, C^2, J=27 Hz) ppm.

(E)-2-nonenoyl fluoride (**4a**): IR (cm^{-1}): 1790. ^{19}F NMR δ: +24.4 [d, $J(F/H^2)$ = 9 Hz] ppm. ^{1}H NMR δ: 5.8 (ddt, H^2); 7.2 (dt, H^3) [$J(H^2/H^3)$ = 15.4 Hz, $J(H^2/F)$ = 8.8 Hz, $J(H^3/H^4)$ = 7.1 Hz, $J(H^2/H^4)$ = 1.6 Hz] ppm.

2-Cyclohexylidene ethanoyl fluoride (**4b**): IR (cm^{-1}): 1800; 1630. ^{19}F NMR δ: +42.9 (s) ppm. ^{1}H NMR δ: 1.6 (m, 6H); 2.3 (t, 2H); 2.8 (t, 2H); 5.6 (m, H^2) ppm. ^{13}C NMR δ: 25.6, 27.6, 28.3, 30.3, 37.8 (d, C^4, J=3 Hz); 107.2 (d, C^2, J=73 Hz); 155.4 (d, C^1, J=335 Hz); 173.5 (d, C^3, J=17 Hz) ppm.

(E)-3-thienyl-2-propenoyl fluoride (**4c**): IR (cm^{-1}): 1785; 1615. ^{19}F NMR δ: +23.9 (d, J=7 Hz) ppm. ^{1}H NMR δ: 6.15 (dd, H^2); 7.15 (dd, H^6); 7.4 (d, H^5); 7.55 (d, H^7); 7.95 (d, H^3) [$J(H^2/H^3)$ = 15.7 Hz, $J(H^2/F)$ = 7.2 Hz, $J(H^6/H^7)$ = 5.0 Hz, $J(H^5/H^6)$ = 3.6 Hz] ppm. ^{13}C NMR δ: 110.0 (d, C^2, J=69 Hz); 128.4, 130.8, 133.6, 138.1 (s, C^4); 143.1 (d, C^3, J=7 Hz); 156.7 (d, C^1, J=336 Hz) ppm.

(E,E)-2,4-Nonadienoyl fluoride (**4d**): IR (cm^{-1}): 1790; 1635; 1605. ^{19}F NMR δ: +23.8 (d, J=9 Hz) ppm.

2,4-Nonenynoyl fluoride (**4e**): Steric purity: E/Z=96:4. IR (cm^{-1}): 2950; 2920; 2860; 2205; 1800; 1610; 1450; 1280; 1200; 1100; 960; 850; 700; 640. ^{19}F NMR δ: +23.8 (d, J=8 Hz, E-isomer); +35.9 (dd, J=5, 3 Hz, Z-isomer) ppm. ^{1}H NMR δ: 0.9 (t, 3H); 1.4 (m, 2H); 1.55 (m, 2H); E-isomer: 2.43 (td, $2H^6$); 6.1 (dd, H^2); 6.9 (dt, H^3) [$J(H^2/H^3)$ = 15.4 Hz, $J(H^2/F)$ = 7.7 Hz, $J(H^6/H^7)$ = 7.1 Hz, $J(H^3/H^6)$ = 2.2 Hz]; Z-isomer: 2.49 (td, $2H^6$); 6.0 (dd, H^2); 6.45 (ddt, H^3) [$J(H^2/H^3)$ = 11 Hz, $J(H^6/H^7)$ = 7.1 Hz, $J(H^3/F)$ = 5 Hz, $J(H^2/F)$ = 3 Hz, $J(H^3/H^6)$ = 2.2 Hz] ppm. ^{13}C NMR δ: E-isomer: 13.2, 19.3, 21.8, 30.0, 77.3, 106.0, 123.1 (d, C^2, J=68 Hz); 132.8 (d, C^3, J=6 Hz); 155.8 (d, C^1, J=336 Hz) ppm.

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