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Synthesis of functionalized trifluorovinyl compounds

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Abstract

Various functionalized trifluorovinyl compounds have been prepared by the addition of $BrCF_2CFClBr$ to functionalized alkenes using bimetal redox systems as initiators, followed by dehalogenation with zinc powder.

Introduction

In recent years, functionalized trifluorovinyl compounds have attracted increasing attention, as they act as monomers in polymerizations and can be expected to undergo selective reactions at the trifluorovinyl or functional group site. However, to date few papers have appeared regarding the preparation of such compounds [1, 2]. We now report a facile and effective synthesis of the title compounds.

Results and discussion

Recently, we have found that certain redox systems can effectively initiate the addition of R_fX to electron-rich as well as to electron-deficient alkenes [3–5] even when such polyfluoroalkyl halides contain vicinal dihalogens. Thus the preparation of trifluorovinyl compounds becomes feasible using $BrCF_2CFClBr$ as a precursor for the trifluorovinyl group.

After screening a series of the reported redox systems, we found bimetal redox systems such as Cp_2TiCl_2/Fe and $CrCl_3 \cdot 6H_2O/Fe$ capable of efficiently promoting the addition of polyfluoroalkyl halide to both electron-rich and electron-deficient alkenes without dehalogenation. The results are listed in Table 1.

$BrCF_2CFClBr$ added readily to electron-rich alkenes (Table 1, Runs No. 1, 2 and 3) giving addition products in excellent yield. With 1,5-hexadiene (Run No. 2), in order to obtain the 1:1 addition product it was necessary to include a slight excess of the 1,5-diene.

In the case of electron-deficient alkenes, a longer reaction time, a higher temperature and usually a greater amount of catalysts were required. Satisfactory results were obtained with an α,β-unsaturated ketone, amide and nitrile. In contrast, ethyl methylacrylate did not significantly affect the reaction (Run No. 5). At the same time, hydrodebromination took place immediately.

The solvent seems to play an important role in such reactions. Experiments showed that when Cp_2TiCl_2/Fe was used as the bimetal redox system, THF was suitable for the reaction. If EtOH was used as the solvent instead of THF in such reactions, complete dehalogenation occurred and very little product could be obtained. When $CrCl_3 \cdot 6H_2O/Fe$ was used as the bimetal redox system, then either THF or EtOH could be used.

In these addition products, vicinal dihalogens could be dehalogenated without any difficulty under mild conditions using zinc powder containing a little $CuCl_2$ in DMF. ^{19}F NMR spectroscopy showed that dehalogenation was complete after stirring for 0.5 h at room temperature. However, in Table 2, Runs No. 1–3, if the bromine atom needed to be reduced during the course of dehalogenation, heating at 50 °C for *c.* 6 h was necessary. The complete results are listed in Table 2.

In summary, functionalized trifluorovinyl compounds may be readily obtained by the addition of $BrCF_2CFClBr$ to various functionalized alkenes promoted by bimetal redox systems, followed by dehalogenation of the adducts with zinc powder.

Experimental

All melting and boiling points are reported uncorrected. ^1H NMR spectra were measured with external TMS as the standard by means of a Varian EM-360A spectrometer at 60 MHz. ^{19}F NMR spectra were mea-

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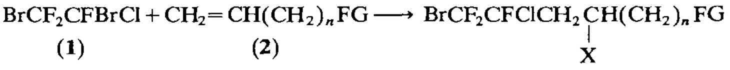
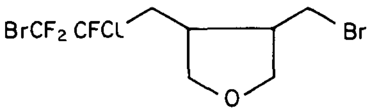
TABLE 1. Addition of $BrCF_2CFClBr$ to functionalized alkenes



$$\underset{(1)}{BrCF_2CFBrCl} + \underset{(2)}{CH_2{=}CH(CH_2)_nFG} \longrightarrow BrCF_2CFClCH_2\underset{X}{CH}(CH_2)_nFG$$

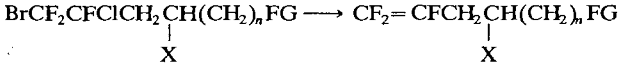
(FG = functional group) (3) (X = H or Br)

Run No.	Alkenes 2	Method[a]	Adducts 3 (% yield)
1	$(CH_2{=}CHCH_2)_2O$ (**2a**)	A, B	 (**3a**) (90%)
2	$CH_2{=}CHCH_2CH_2CH{=}CH_2$ (**2b**)	A, B	$BrCF_2CFClCH_2CHBrCH_2CH_2CH{=}CH_2$ (**3b**) (70%)
3	$CH_2{=}CH(CH_2)_8COOMe$ (**2c**)	A, B	$BrCF_2CFClCH_2CHBr(CH_2)_8COOMe$ (**3c**) (90%)
4	$CH_2{=}CHCOOEt$ (**2d**)	A, B	$BrCF_2CFClCH_2CH_2COOEt$ (**3d**) (90%)
5	$CH_2{=}C(Me)COOEt$ (**2e**)	B	$BrCF_2CFClCH_2CH(Me)COOEt$ (**3e**) (78%)
6	$CH_2{=}CHCONH_2$ (**2f**)	B	$BrCF_2CFClCH_2CH_2CONH_2$ (**3f**) (70%)
7	$CH_2{=}CHCN$ (**2g**)	A, B	$BrCF_2CFClCH_2CH_2CN$ (**3g**) (80%)
8	$CH_2{=}CHCOCH_3$ (**2h**)	B	$BrCF_2CFClCH_2CH_2COCH_3$ (**3h**) (70%)

[a] *Method A*: $Cp_2TiCl_2/Fe/THF$; molar ratio of 1/2/Fe/Cp_2TiCl_2 = 1.2–1.5:1:0.5–1.5:0.02. The reactions were run at 50–60 °C for *c*. 20 h.

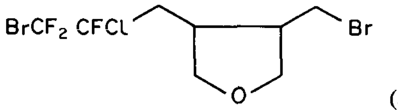
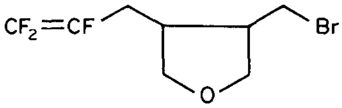
Method B: $CrCl_3{\cdot}6H_2O/Fe/THF$ or EtOH; molar ratio of 1/2/Fe/$CrCl_3{\cdot}6H_2O$ = 1.2–1.5:1:0.5–1.5:0.1–0.2. The reactions were run at 50–60 °C for *c*. 20 h.

TABLE 2. Dehalogenation of **3** with $Zn/CuCl_2/DMF$[a]



$$\underset{(3)}{BrCF_2CFClCH_2\underset{X}{CH}(CH_2)_nFG} \longrightarrow \underset{(4)}{CF_2{=}CFCH_2\underset{X}{CH}(CH_2)_nFG}$$

(X = Br or H)

Run No.	Adducts 3	Time (h)	Products 4 (% yield)
1	 (**3a**)	0.5	 (**4a**) (90%)
2	$BrCF_2CFClCH_2\underset{CH_2CH_2CH{=}CH_2}{CHBr}$ (**3b**)	0.5	$CF_2{=}CFCH_2\underset{CH_2CH_2CH{=}CH_2}{CHBr}$ (**4b**) (80%)
3	$BrCF_2CFClCH_2\underset{(CH_2)_8COOMe}{CHBr}$ (**3c**)	6.0	$CF_2{=}CFCH_2\underset{(CH_2)_8COOMe}{CH_2}$ (**4c**) (85%)[b]
4	$BrCF_2CFClCH_2CH_2COOEt$ (**3d**)	0.5	$CF_2{=}CFCH_2CH_2COOEt$ (**4d**) (95%)
5	$BrCF_2CFClCH_2CH(Me)COOEt$ (**3e**)	0.5	$CF_2{=}CFCH_2CH(Me)COOEt$ (**4e**) (93%)
6	$BrCF_2CFClCH_2CH_2CONH_2$ (**3f**)	0.5	$CF_2{=}CFCH_2CH_2CONH_2$ (**4f**) (92%)
7	$BrCF_2CFClCH_2CH_2CN$ (**3g**)	0.5	$CF_2{=}CFCH_2CH_2CN$ (**4g**) (92%)
8	$BrCF_2CFClCH_2CH_2COCH_3$ (**3h**)	0.5	$CF_2{=}CFCH_2CH_2COCH_3$ (**4h**) (90%)

[a] Reactions performed at room temperature unless otherwise indicated. Molar ratio of 3/Zn/$CuCl_2$ = 1:1:0.05.

[b] Reaction carried out at 50 °C.

sured with external CF_3COOH as the standard with upfield shifts positive using a Varian EM-360L spectrometer at 56.4 MHz. Samples were measured neat unless indicated otherwise. IR spectra were recorded as films for liquid samples on a Shimadzu IR-440 spectrometer. Mass spectra were recorded by means of a Finnigan GC–MS 4021 mass spectrometer. Methyl vinyl ketone was freshly distilled before use. All other chemicals were of analytical grade and were used without further purification.

General procedure for the addition of $BrCF_2CFClBr$ to functionalized alkenes

Method A

A mixture consisting of Fe powder (5–15 mmol), 2 mol% of Cp_2TiCl_2, alkene (10 mmol) and $BrCF_2CFClBr$ (12–15 mmol) was stirred in 25 ml THF at 50–60 °C. The reaction was monitored by GC and ^{19}F NMR methods. After completion of the reaction, the mixture was poured into water (20 ml) and filtered. The residue was washed with ether and the combined filtrates extracted with ether (3×20 ml). The ether extract was washed with brine and dried (Na_2SO_4). Distillation or flash chromatography gave the corresponding product.

Method B

A mixture consisting of Fe powder (5–15 mmol), 10–20 mol% of $CrCl_3 \cdot 6H_2O$, alkene (10 mmol) and $BrCF_2CFClBr$ (12–15 mmol) was stirred in EtOH or THF at 50–60 °C. After the reaction was complete, the mixture was treated in the same manner as in Method A.

3-(3′-Bromo-2′-chloro-2′,3′,3′-trifluoropropyl)-4-bromomethyltetrahydrofuran (**3a**): B.p. 95–95 °C/3 mmHg. ^{1}H NMR δ: 2.00–3.40 (m, 4H); 3.50–4.51 (m, 6H) ppm. ^{19}F NMR δ: −17.0 (s, 2F); 38.8 (m, 1F) ppm. MS (*m/z*): 373 ($M^+ + 1$, 19.25); 293 ($M^+ - HBr$, 64.32); 54 ($CH_2{=}CH{-}CH{=}CH_2$, 100). Analysis: Calc. for $C_8H_{10}Br_2ClF_3O$: C, 25.66; H, 2.67; F, 15.22%. Found: C, 25.72; H, 2.60; F, 15.58%.

5,8-Dibromo-7-chloro-7,8,8-trifluoro-1-octene (**3b**): B.p. 118–120 °C/18 mmHg. IR ν_{max} (cm^{-1}): 1650 ($CH{=}CH_2$). ^{1}H NMR δ: 2.00–3.80 (m, 6H); 4.50–5.00 (m, 1H); 5.10–6.60 (m, 3H) ppm. ^{19}F NMR δ: −14.6 (s, 2F); 40.3 (m, 1F) ppm. MS (*m/z*): 357 ($M^+ + 1$, 1.01); 315 ($M^+ - CH_2CH{=}CH_2$, 2.17); 277 ($M^+ + 1 - HBr$, 14.15); 95 ($CF_2{=}CFCH_2$, 7.71); 81 ($M^+ - BrCF_2CFCl$, 100). Analysis: Calc. for $C_8H_{10}Br_2ClF_3$: C, 26.81; H, 2.79; Fm 15.90%. Found: C, 27.00; H, 2.65; F, 16.11%.

Methyl 10,13-dibromo-12-chloro-12,13,13-trifluorotridecanoate (**3c**): IR ν_{max} (cm^{-1}): 1750 (C=O). ^{1}H NMR δ: 1.30–3.40 (m, 18H); 3.70 (s, 3H); 4.20–4.70 (m, 1H) ppm. ^{19}F NMR δ: −16.0 (s, 2F); 38.2, 40.5 (2 br s, 0.48F+0.52F) ppm. MS (*m/z*): 474 (M^+, 16.65); 395 ($M^+ - Br$, 6.73); 74 ($CH_3CO_2CH_3$, 100). MS (*m/z*): Calc. for $C_{14}H_{22}Br_2ClF_3O_2$, 473.9503. Found, 473.9566.

Ethyl 5-bromo-4-chloro-4,5,5-trifluoro-pentanoate (**3d**): B.p. 102–104 °C/18 mmHg. IR ν_{max} (cm^{-1}): 1740 (C=O). ^{1}H NMR δ: 1.40 (t, *J*=7.0 Hz, 3H); 2.10 (m, 4H, CH_2CH_2); 4.40 (q, *J*=7.0 Hz, 2H) ppm. ^{19}F NMR δ: −16.3 (s, 2F); 41.3 (br s, 1F) ppm. MS (*m/z*): 297 ($M^+ + 1$, 70.50); 271 ($M^+ + 1 - Et$, 17.74); 253 ($M^+ - EtOH$, 72.77). Analysis: Calc. for $C_7H_9BrClF_3O_2$: C, 28.26; H, 3.05; F, 19.16%. Found: C, 28.80; H, 3.19; F, 18.72%.

Ethyl 5-bromo-4-chloro-4,5,5-trifluoro-2-methylpentanoate (**3e**): B.p. 71–72 °C/2 mmHg. IR ν_{max} (cm^{-1}) 1725 (C=O). ^{1}H NMR δ: 1.00–1.35 (m, 6H); 1.55–3.30 (m, 3H); 4.10 (q, *J*=7.0 Hz, 2H) ppm. ^{19}F NMR δ: −16.5 (s, 2F); 39.0, 41.0 (2 br s, 0.45F+0.55F) ppm. MS (*m/z*): 313 ($M^+ + 1$, 100); 265 ($M^+ - EtO$, 18.59). Analysis: Calc. for $C_8H_{11}BrClF_3O_2$: C, 30.85; H, 3.53; F, 18.30%. Found: C, 31.00; H, 3.27; F, 18.56%.

5-Bromo-4-chloro-4,5,5-trifluoro-pentanamide (**3f**): M.p. 54.0–55.2 °C. IR ν_{max} (cm^{-1}): 3300, 3400 (NH_2); 1650 (C=O). ^{1}H NMR δ: 2.20–3.10 (m, 4H); 5.50–6.50 (m, 2H) ppm. ^{19}F NMR δ: −17.0 (s, 2F); 40.7 (m, 1F) ppm. MS (*m/z*): 268 ($M^+ + 1$, 32.91); 251 ($M^+ - NH_2$, 9.00); 232 ($M^+ - HCl$, 90.70); 188 ($M^+ - HCl - CONH_2$, 96.40); 152 ($M^+ - HCl - Br$, 90.12); 55 ($CH_2{=}CHCO$, 100). Analysis: Calc. for $C_5H_6BrClF_3NO$: C, 22.35; H, 2.23; N, 5.21; F, 21.23%. Found: C, 22.73; H, 1.85; N, 5.07; F, 21.10%.

5-Bromo-4-chloro-4,5,5-trifluoro-pentanenitrile (**3g**): B.p. 65–66 °C/2 mmHg. IR ν_{max} (cm^{-1}): 2180 (CN). ^{1}H NMR δ: 2.50–3.50 (m, 4H) ppm. ^{19}F NMR δ: −16.0 (s, 2F); 42.2 (br s, 1F) ppm. MS (*m/z*): 251 (M^+, 100); 216 ($M^+ - Cl$, 2.22). Analysis: Calc. for $C_5H_4BrClF_3$: C, 25.37; H, 1.60; F, 22.76%. Found: C, 25.40; H, 1.60; F, 22.28%.

6-Bromo-5-chloro-5,6,6-trifluoro-2-hexanone (**3h**): B.p. 65–67 °C/2 mmHg. IR ν_{max} (cm^{-1}): 1725 (C=O). ^{1}H NMR δ: 2.37 (s, 3H); 2.57–3.27 (m, 4H) ppm. ^{19}F NMR δ: −17.5 (s, 2F); 39.7 (m, 1F) ppm. MS (*m/z*): 266 (M^+, 1.99); 187 ($M^+ - HCl - CH_3CO$, 3.99); 44 (CH_3CHO, 100). Analysis: Calc. for $C_6H_7BrClF_3O$: C, 26.92; H, 2.62; F, 21.31%. Found: C, 27.06; H, 2.87; F, 21.42%.

General procedure for the dehalogenation of 3 with $Zn/CuCl_2$

To 20 ml DMF was added 0.65 g (10 mmol) of Zn powder, 0.1 g of $CuCl_2$ and 10 mmol of **3**. The whole mixture was stirred at room temperature. ^{19}F NMR spectroscopy showed that dehalogenation was complete after 0.5 h. The reaction mixture was then poured into a 100 ml separating funnel and 10 ml of 5% HCl was added. The whole mixture was then extracted with ether (2×20 ml). The combined extract was washed with a saturated aqueous solution of $NaHCO_3$, brine and dried (Na_2SO_4). Distillation or flash chromatography gave the corresponding product.

3-(2′,3′,3′-Trifluoroallyl)-4-bromomethyltetrahydrofuran (**4a**): B.p. 110–111 °C/20 mmHg. IR ν_{max} (cm^{-1}): 1785 ($CF_2{=}CF$). ^{1}H NMR δ: 2.00–3.10 (m, 4H); 3.20–4.40 (m, 6H) ppm. ^{19}F NMR δ: 28 (dd, *J*=100, 40 Hz, 1F); 47.3 (dd, *J*=120, 100 Hz, 1F); 98.0 (dm, *J*=120 Hz, 1F) ppm. MS (*m/z*): 259 ($M^+ + 1$, 1.95); 179 ($M^+ + 1 - HBr$, 10.41); 165 ($M^+ - CH_2Br$, 100); 95

($CF_2{=}CFCH_2$. 60.94); 81 ($CF_2{=}CF$, 5.48). Analysis: Calc. for $C_8H_{10}BrF_3O$: C, 37.06; H, 3.86; F, 22.01%. Found: C, 37.37; H, 3.55; F, 22.44%.

4-Bromo-1,1,2-trifluoro-1,7-octadiene (**4b**): B.p. 45–47 °C/2 mmHg. IR ν_{max} (cm^{-1}): 1785 ($CF_2{=}CF$); 1630 ($CH{=}CH_2$). ^1H NMR δ: 1.80–3.30 (m, 6H); 4.00–4.50 (m, 1H); 4.90–5.50 (m, 2H); 5.60–6.30 (m, 1H) ppm. ^{19}F NMR δ: 27.3 (dd, $J = 100$, 40 Hz, 1F); 45.9 (dd, $J = 120$, 100 Hz, 1F); 98.5 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 242 (M^+, 2.32); 163 ($M^+ - Br$, 18.44); 121 ($M^+ - Br - CH_2CH{=}CH_2$, 31.34); 108 ($CF_2{=}CFCH{=}CH_2$, 21.83); 95 ($CF_2{=}CFCH_2$, 50.70); 81 ($CF_2{=}CF$, 20.50); 67 ($CH_2{=}CHCH_2CH{=}CH_2$, 100). Analysis: Calc. for $C_8H_{10}BrF_3$: C, 39.67; H, 4.13; F, 23.45%. Found: C, 40.13; H, 4.07; F, 24.76%.

Methyl 12,13,13-trifluoro-12-tridecanoate (**4c**): B.p. 108–110 °C/2 mmHg. IR ν_{max} (cm^{-1}): 1785 ($CF_2{=}CF$); 1750 ($C{=}O$). ^1H NMR δ: 1.07–1.87 (m, 16H); 1.87–2.57 (m, 4H); 3.60 (s, 3H) ppm. ^{19}FNMR δ: 30.5 (dd, $J = 100$, 40 Hz, 1F); 49.3 (dd, $J = 120$, 100 Hz, 1F); 97.3 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 281 ($M^+ + 1$, 20.16); 249 ($M^+ - MeO$, 5.73); 95 ($CF_2{=}CFCH_2$, 29.02); 81 ($CF_2{=}CF$, 7.38); 74 ($CH_3CO_2CH_3$, 100). Analysis: Calc. for $C_{14}H_{23}F_3O_2$: C, 60.02; H, 8.21; F, 20.86%. Found: C, 60.58; H, 8.01; F, 20.86%.

Ethyl 4,5,5-trifluoro-4-pentenoate (**4d**): B.p. 90–92 °C/100 mmHg. IR ν_{max} (cm^{-1}): 1785 ($CF_2{=}CF$); 1725 ($C{=}O$). ^1H NMR δ: 1.00 (t, $J = 7.0$ Hz, 3H); 2.20–2.80 (m, 4H); 3.9 (q, $J = 7.0$ Hz, 2H) ppm. ^{19}F NMR δ: 27.5 (dd, $J = 100$, 40 Hz, 1F); 46.0 (dd, $J = 120$, 100 Hz, 1F); 98.5 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 183 ($M^+ + 1$, 34.96); 182 (M^+, 11.72); 137 ($M^+ - EtO$, 50.24); 109 ($M^+ - CO_2Et$, 44.39); 95 ($CF_2{=}CFCH_2$, 62.77); 81 ($CF_2{=}CF$, 19.30); 42 ($COCH_2$, 100). Analysis: Calc. for $C_7H_9F_3O_2$: C, 46.18; H, 4.94; F, 31.36%. Found: C, 46.40; H, 4.86; F, 31.22%.

Ethyl 4,5,5-trifluoro-2-methyl-4-pentenoate (**4e**): B.p. 83–84 °C/15 mmHg. IR ν_{max} (cm^{-1}): 1785 ($CF_2{=}CF$); 1725 ($C{=}O$). ^1H NMR δ: 0.87–1.27 (m, 6H); 1.97–2.97 (m, 3H); 4.00 (q, $J = 7.0$ Hz, 2H) ppm. ^{19}F NMR δ: 29.7 (dd, $J = 100$, 40 Hz, 1F); 48.2 (dd, $J = 120$, 100 Hz, 1F); 98.1 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 196 (M^+, 3.94); 116 ($M^+ + 1 - CF_2{=}CF$, 100); 111 (CH_3CHCO_2Et, 25.99); 97 (CH_3CO_2Et, 55.35); 95 ($CF_2{=}CFCH_2$, 3.56); 82 ($CF_2{=}CFH$, 43.80). Analysis: Calc. for $C_8H_{11}F_3O_2$: C, 49.00; H, 5.61; F, 29.07%. Found: C, 49.23; H, 5.56; F, 29.23%.

4,5,5-Trifluoro-4-pentenamide (**4f**): M.p. 74.0–75.5 °C. IR ν_{max} (cm^{-1}): 3300, 3400 (NH_2); 1800 ($CF_2{=}CF$); 1650 ($C{=}O$). ^1H NMR ($CDCl_3$) δ: 1.60–2.20 (m, 4H); 6.00–7.20 (m, 2H) ppm. ^{19}F NMR ($CDCl_3$) δ: 27.2 (dd, $J = 100$, 40 Hz, 1F); 45.8 (dd, $J = 120$, 100 Hz, 1F); 98.2 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 153 (M^+, 100); 95 ($CF_2{=}CFCH_2$, 89.72); 81 ($CF_2{=}CF$, 25.69); 58 (CH_2CONH_2, 66.95). Analysis: Calc. for $C_5H_6F_3NO$: C,39.24; H, 3.92; N, 9.15; F, 37.24%. Found: C, 39.68; H, 3.76; F, 37.89; N, 9.25%.

4,5,5-Trifluoro-4-pentenenitrile (**4g**): B.p. 100–102 °C/100 mmHg. IR ν_{max} (cm^{-1}): 2180 (CN); 1785 ($CF_2{=}CF$). ^1H NMR δ: 2.27–2.87 (m, 4H) ppm. ^{19}F NMR δ: 29.1 (dd, $J = 100$, 40 Hz, 1F); 47.4 (dd, $J = 120$, 100 Hz, 1F); 101.1 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 136 ($M^+ + 1$, 9.04); 135 (M^+, 6.46); 109 ($M^+ - CN$, 4.63); 95 ($CF_2{=}CFCH_2$, 77.01); 81 ($CF_2{=}CF$, 8.00); 54 ($M^+ - CF_2{=}CF$, 100). Analysis: Calc. for $C_5H_4F_3N$: C, 44.14; H, 2.94; F, 42.22; N, 10.29%. Found: C, 44.02; H, 2.86; F, 42.07; N, 10.48%.

5,6,6-Trifluoro-5-hexen-2-one (**4h**): B.p. 65–66 °C/30 mmHg. IR ν_{max} (cm^{-1}): 1725 ($C{=}O$); 1810 ($CF_2{=}CF$). ^1H NMR δ: 1.87 (s, 3H); 1.97–2.57 (m, 4H) ppm. ^{19}F NMR δ: 27.8 (dd, $J = 100$, 40 Hz, 1F); 46.7 (dd, $J = 120$, 100 Hz, 1F); 98.0 (dm, $J = 120$ Hz, 1F) ppm. MS (m/z): 152 (M^+, 10.49); 109 ($M^+ - CH_3CO$, 8.62); 95 ($CF_2{=}CFCH_2$, 29.44); 81 ($CF_2{=}CF$, 0.75); 57 ($COCH_3$, 8.19); 44 ($HCOCH_3$, 100). Analysis: Calc. for $C_6H_7F_3O$: C, 47.37; H, 4.60; F, 37.50%. Found: C, 46.99; H, 4.56; F, 37.22%.

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