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Characterization of *gem*-difluoropropargyl synthons through HF loss from protonated molecules in methane chemical ionization mass spectra

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Abstract

Electron impact and methane chemical ionization mass spectra were obtained following gas chromatography/mass spectrometry for several *gem*-difluoropropargyl compounds, which had been synthesized as potential intermediates for synthesis of *gem*-difluoromethylene-containing C-3 acetylenes. EI spectra were variable with respect to the presentation of molecular ions, depending on substituent functional groups present. Methane-CI spectra were characterized by loss of 19 mass units from molecular weight with all compounds examined. These $[M - 19]^+$ ions often presented as base peaks of the CI spectra, and were more reliably present and abundant than $[M + 1]^+$ ions for these compounds. These ions could have been formed by elimination of HF from the protonated molecules under conditions of methane chemical ionization. \bigcirc 2005 Elsevier B.V. All rights reserved.

Keywords: CF bond activation; gem-Difluoropropargyl; Neutral loss of HF; Fast atom bombardment; Fluoroorganic

1. Introduction

Mass spectrometry has been increasingly used in the analysis of fluorinated compounds. It has been used in the determination of stability of fluorinated surfactants in advanced oxidation processes [1], and their metabolites in sewage sludge [2]; in the characterization of fluorinated copolymers [3]; or in the separation and detection of oxidation products of fluorodeoxyglucose [4]. Some of the techniques used in these analyses include flow injection-mass spectrometry, liquid chromatography with mass spectrometry and tandem mass spectrometry, and liquid chromatography-electrospray ionization mass spectrometry. In the cases of small, partially fluorinated organic compounds, the mass spectrometric behavior, under electron impact and fast atom bombardment, has been studied for fluorinated steroids [5], deoxofluorinated sugars [6], and epoxyethers [7]. In none of these cases, however, $[M - 19]^+$ ions have been presented as base peaks of the chemical ionization mass spectra.

During our investigations on the synthesis of silylated or stannylated *gem*-difluoropropargyl synthons, $RC \equiv C-CF_2Si(Sn)$ [8], we noticed that the analysis of products **1–4** using mass spectrometry did not yield the expected M + 1 peak under conditions of methane chemical ionization (methane-CI). We now report the phenomenon of C–F bond cleavage under methane-CI conditions, which leads to characteristic ions definitive of several *gem*-difluoropropargyl synthetic intermediates. Additionally, electron-impact ionization (EI) spectra of these fluorinated compounds are presented for comparison.

2. Results and discussion

We recently reported [8] a practical synthesis of *gem*difluoropropargylsilanes **1**, **3**, **4** and *gem*-difluoropropargyl stannane **2** using Mg(0)-promoted reductive debromometalation of 3-bromo-3,3-difluoropropyne (Eq. (1)). The γ -alkyl, silyl or -aryl-substituted difluoropropargyl bromide precursor was prepared in high yield by monitoring concentration and temperature in the reaction between CF₂Br₂ and γ -substituted lithium acetylide [9]. These compounds are fitted with synthetically useful acetylene functionality and therefore could

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be key synthetic intermediates in the synthesis of *gem*-difluoromethylene-containing C-3 derivatives.

in which the opposing alkyne substituent was aromatic. With compounds **1d** and **1e**, which included aliphatic (hexyl) or tri-



Table 1 shows the structures, formulae, molecular weights, and GC retention times of *gem*-diffuoropropargyl synthons **1–4**. Their EI and CI mass spectra are presented in Fig. 1. Prominent ions, their formulae, and assignments are given in Table 2. When methane-CI ionization was employed, all *gem*-diffuor-opropargyl synthons produced ions at $[M - 19]^+$. These presented as base peaks in the CI spectra of all compounds

isopropylsilyl functional groups, intensities of $[M - 19]^+$ ions were much less, 6 and 13%, respectively. These $[M - 19]^+$ ions likely result from loss of a neutral species (HF, 20 Da) during methane-CI. Although C–F bond cleavage has been considered difficult in general due to the high C–F bond strength, the strong association of fluorine with boron and aluminum reagents promotes sometimes the heterolysis of C–F bond. The present

Table 1

Structures, formulae, molecular weights, and GC retention times of gem-difluoropropargyl synthons

Compound Number	Structure	Molecular formula	Molecular weight	GC retention time (min)
1a	F	$C_{12}H_{14}F_2Si$	224.2	8.57
1b	⊧	$C_{13}H_{16}F_2Si$	238.3	10.1
1c		$C_{13}H_{16}F_2Si$	238.3	10.1
1d		C ₁₂ H ₂₂ F ₂ Si	232.4	7.80
1e	F −Si- F Si-	$C_{15}H_{30}F_2Si$	304.2	10.2
2		$C_{12}H_{14}F_2Sn$	314.9	10.7
3		$C_{16}H_{12}F_2$	242.3	12.9
4		C ₁₂ H ₁₀ F ₂	192.2	7.45
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Fig. 1. EI and CI mass spectra of gem-difluoropropargyl compounds. MM*, mono-isotopic mass.

C–F bond activation may arise through proton-assisted C–F bond cleavage, which would be favorable from the point of view of higher H–F bond energy (BDE for C–F, H–F, B–F, and Al-F, 132, 136, 181, and 159 kcal/mol, respectively). Fig. 2

proposes a mechanism for the formation and stabilization of the resulting $[M - 19]^+$ ions using **1a** as an example. In the first step, the addition of a proton to the triple bond in **1a** produces species **A**. This is followed by HF elimination to form the

Table 2 Mass assignments for selected ions of *gem*-difluoropropargyl compounds

Compound	<i>m/z</i> ; <u>BP</u>	EI		<i>m/z</i> ; <u>BP</u>	CI	
		Formula	Assignment		Formula	Assignment
1a	224 151 <u>132</u> 73	$\begin{array}{c} C_{12}H_{14}F_{2}Si\\ C_{9}H_{5}F_{2}\\ C_{9}H_{5}F\\ C_{3}H_{9}Si \end{array}$	M^{+} [M - Si(CH ₃) ₃] ⁺ [M - Si(CH ₃) ₃ - F] ⁺ [Si(CH ₃) ₃] ⁺	225 209 <u>205</u> 147 132 73	$\begin{array}{c} C_{12}H_{15}F_{2}Si_{2}\\ C_{11}H_{11}F_{2}Si\\ C_{12}H_{14}FSi\\ C_{6}H_{9}F_{2}Si\\ C_{9}H_{5}F\\ C_{3}H_{9}Si \end{array}$	$[M + H]^{+}$ $[M - CH_{3}]^{+}$ $[M - F]^{+}$ $[M - C_{6}H_{5}]^{+}$ $[M - Si(CH_{3})_{3} - F]^{+}$ $[Si(CH_{3})_{3}]^{+}$
1b	238 223 165 <u>146</u> 115 73	$\begin{array}{c} C_{13}H_{16}F_{2}Si\\ C_{12}H_{13}F_{2}Si\\ C_{10}H_{7}F_{2}\\ C_{6}H_{8}F_{2}Si\\ C_{9}H_{7}\\ C_{3}H_{9}Si \end{array}$	$M^{+} [M - CH_3]^{+} [M - Si(CH_3)_3]^{+} [M - Si(CH_3)_3 - F]^{+} [M - Si(CH_3)_3 - CF_2]^{+} [Si(CH_3)_3]^{+}$	239 223 219 147 146 73	$\begin{array}{c} C_{13}H_{17}F_2Si_2\\ C_{12}H_{13}F_2Si\\ C_{13}H_{16}FSi\\ C_6H_9F_2Si\\ C_{10}H_7F\\ C_3H_9Si \end{array}$	$[M + H]^{+}$ $[M - CH_{3}]^{+}$ $[M - F]^{+}$ $[M - CH_{3}C_{6}H_{5}]^{+}$ $[M - Si(CH_{3})_{3} - F]^{+}$ $[Si(CH_{3})_{3}]^{+}$
1c	238 223 165 <u>146</u> 115 73	$\begin{array}{c} C_{13}H_{16}F_2Si\\ C_{12}H_{13}F_2Si\\ C_{10}H_7F_2\\ C_6H_8F_2Si\\ C_9H_7\\ C_3H_9Si \end{array}$	$M^{+} [M - CH_3]^{+} [M - Si(CH_3)_3]^{+} [M - Si(CH_3)_3 - F]^{+} [M - Si(CH_3)_3 - CF_2]^{+} [Si(CH_3)_3]^{+}$	239 223 219 147 146 73	$\begin{array}{c} C_{13}H_{17}F_2Si_2\\ C_{12}H_{13}F_2Si\\ C_{13}H_{16}FSi\\ C_6H_9F_2Si\\ C_{10}H_7F\\ C_3H_9Si \end{array}$	$[M + H]^{+}$ $[M - CH_{3}]^{+}$ $[M - F]^{+}$ $[M - CH_{3}C_{6}H_{5}]^{+}$ $[M - Si(CH_{3})_{3} - F]^{+}$ $[Si(CH_{3})_{3}]^{+}$
1d	162 109 97 <u>73</u>	$\begin{array}{c} C_{7}H_{12}F_{2}Si\\ C_{8}H_{13}\\ C_{7}H_{13}\\ C_{3}H_{9}Si \end{array}$	$[M - C_5H_{11}]^+$ $[M - Si(CH_{3)3}CF_2]^+$ $[C_7H_{13}]^+$ $[Si(CH_3)_3]^+$	213 <u>93</u> 73	C ₁₂ H ₂₂ FSi C ₂ H ₃ F ₂ Si C ₃ H ₉ Si	$[M - F]^+$ [Si(CH ₃) ₃] ⁺
1e	<u>157</u> 73	C9H21Si C3H9Si	$[M - (CH_3)_3 SiCF_2]^+$ $[Si(CH_3)_3]^+$	285 261 <u>193</u> 137 73	$\begin{array}{c} C_{15}H_{30}FSi_2\\ C_{12}H_{23}F_2Si_2\\ C_{12}H_{21}Si\\ C_8H_{13}Si\\ C_3H_9Si \end{array}$	$[M - F]^+$ $[M - C_3H_7]^+$ $[Si(CH_3)_3]^+$
2	301 <u>165</u> 113	$C_1^{\ 1}H_{11}F_2Sn$ C_3H_9Sn C_9H_5	$[M - CH_3]^+$ $[(CH_3)_3Sn]^+$	301 <u>297</u> 165	$C_1^{\ 1}H_{11}F_2Sn$ $C_{12}H_{14}FSn$ C_3H_9Sn	$[M - CH_3]^+$ $[M - F]^+$ $[(CH_3)_3Sn]^+$
3	242 <u>151</u> 91	$\begin{array}{c} C_{16}H_{12}F_2 \\ C_9H_5F_2 \\ C_7H_7 \end{array}$	M^+ [$M - C_6H_5CH_2$] ⁺ [$C_6H_5CH_2$] ⁺	243 223	$\begin{array}{c} C_{16}H_{13}F_{2} \\ C_{16}H_{12}F \end{array}$	$\begin{bmatrix} M + H \end{bmatrix}^+ \\ \begin{bmatrix} M - F \end{bmatrix}^+$
4	192 <u>151</u> 128	$\begin{array}{c} C_{12}H_{10}F_2\\ C_9H_6F_2\\ C_{10}H_8 \end{array}$	$\frac{M^+}{[M-C_3H_5]^+}$	193 <u>173</u> 151 129	$\begin{array}{c} C_{12}H_{11}F_2\\ C_{12}H_{10}F\\ C_9H_5F_2\\ C_{10}H_9 \end{array}$	$[M + H]^+$ $[M - F]^+$ $[M - C_3H_5]^+$

corresponding allenyl cation **B**, which is stabilized through resonance with its canonical structure C. Alternatively, if one of the fluorine atoms present in the difluoromethylene moiety of 1a could accept a proton via a hydrogen bonding-type mechanism, it would promote dehydrofluorination and formation of carbocation C $[M - 19]^+$. Loss of neutral molecules from the molecular ion during ion formation in mass spectrometry is common. As stated by McLafferty and Tureček [10], loss of 20 mass units under such conditions almost always represents loss of HF as a neutral species, and such loss is of major significance in confirming the molecular structure. Taken together, these CI spectra of gem-difluoropropargyl compounds indicate cleavage of the C-F bond is a likely event under conditions of methane chemical ionization. However, such C-F bond cleavage is not common in spectra of fluorinated carbon structures due to the strength of the C-F bond. The $[M+1]^+$ ions were observed at relatively low

abundance with structures **1a–c**, **3**, and **4**, while no protonated molecular species were observed with compounds **1d**, **1e**, and **2** [11].

In summary, these $[M - 19]^+$ ions offer more reliable, definitive information with respect to the molecular weights of these *gem*-difluoropropargyl structures than the usual protonated molecules that often are used for determination of molecular weight with chemical ionization. Given these observations, $[M - 19]^+$ ions may be useful for confirmation of synthesis of similar compounds in the future.

3. Experimental

3.1. General

¹H, ¹³C, and ¹⁹F NMR spectra were recorded at 500, 126, and 470 MHz, respectively, using CDCl₃ as a solvent.



Fig. 2. Proposed mechanism for the formation and stabilization of $[M - 19]^+$ during methane-CI-MS using **1a** as model.

The chemical shifts are reported in δ (ppm) values relative to CHCl₃ (δ 7.26 ppm for ¹H NMR and δ 77.0 ppm for ¹³C NMR) and C₆F₆ (δ 0 ppm for ¹⁹F NMR). Coupling constants are reported in hertz (Hz). All air and/or moisture sensitive reactions were carried out under argon atmosphere with dry solvents using PuresolvTM solvent purification systems. All other reagents and solvents were employed without further purification.

3.2. Conditions employed in the mass spectral analysis

Methane chemical ionization (CI) and electron-impact ionization (EI) mass spectra were obtained using a Hewlett-Packard (HP) 5973 mass spectrometer operated with the respective CI or EI source. The instrument was tuned to standard operating parameters using the Autotune software for EI and methane-CI modes. CI spectra were produced at 10^{-4} Torr source pressure using an instrumental methane flow setting of 20 mL/min, with source and quadrupole temperatures set at 250 and 106 °C, respectively. EI spectra relied on the standard 70 eV electron energy, with source and quadrupole temperatures of 230 and 150 °C, respectively. Spectra were acquired by scanning from m/z 50 to 400 with 4 A/D samples and a digital threshold of 150. These conditions enabled acquisition of 4.1 scans/s throughout the GC/MS analysis.

The inlet was a directly coupled $15 \text{ m} \times 0.25 \text{ mm}$ i.d. $\times 0.25 \mu\text{m}$ film thickness ZB-5 ms (5%-polysilarylene 95%-polydimethylsiloxane stationary phase, Phenomenex, Torrance, CA, USA) capillary column installed in a HP 6890 gas chromatograph. Compounds were diluted to 500 μ g/ mL hexane, and 1 μ L injections were made via a 250 °C injector in splitless mode. He carrier gas at 20 kPa pressure gave an average column velocity of 58 cm/s. The oven temperature program ramped from 50 to 200 °C at 10 °C/min. Compounds eluted according to retention times listed in Table 1.

3.3. A typical procedure for the synthesis of 3,3difluoropropargylsilanes (1)

To the mixture of Mg (194 mg, 8.0 mmol) and chlorotrimethylsilane (0.51 mL, 4.0 mmol) in dry THF (10 mL), 3bromo-3,3-difluoro-1-(4-methylphenyl)propyne (**7b**) (245 mg, 1.0 mmol) was added dropwise at 0 °C under an argon atmosphere. The reaction mixture was stirred for 30 min at 0 °C. The residual Mg was removed by decantation, the THF solution was washed with H₂O (5 mL). The aqueous layer was extracted with hexane (5 mL ×2) and the combined organic layer was dried over Na₂SO₄. After evaporation of the solvent, the crude product was purified by silica gel treated with Et₃N/ hexane = 1/9 column chromatography (hexane) to afford **1b** (193 mg, 81%) as a colorless oil.

3.4. 3,3-Difluoro-1-phenyl-3-trimethylsilylpropyne (1a)

Colorless oil; 51% yield; IR (neat) 2225 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.29 (s, 9H), 7.34–7.50 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ –5.0, 82.2 (t, *J* = 31.8 Hz), 91.0 (t, *J* = 9.6 Hz), 120.5 (t, *J* = 255 Hz), 120.8 (t, *J* = 3.5 Hz), 128.4, 129.6 132.0; ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 57.1 (s, 2F); Anal. Calcd. for C₁₂H₁₄F₂Si: C, 64.25; H, 6.29. Found: C, 64.60; H, 6.23.

3.5. 3,3-Difluoro-1-(4-methyl)phenyl-3trimethylsilylpropyne (**1b**)

IR (neat) 2225 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.29 (s, 9H), 2.37 (s, 3H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ -4.9,

21.6, 81.6 (t, J = 30.6 Hz), 91.4 (t, J = 9.6 Hz), 111.7, 120.6 (t, J = 254 Hz), 129.2, 131.9, 140.0; ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 56.8 (s, 2F); Anal. Calcd. for C₁₃H₁₆F₂Si: C, 65.51; H, 6.77. Found: C, 65.24; H, 6.94.

3.6. 3,3-Difluoro-1-(2-methyl)phenyl-3trimethylsilylpropyne (**1***c*)

Colorless oil; 77% yield; IR (neat) 2222 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.29 (s, 9H), 2.38 (s, 3H), 7.16 (d, J = 7.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ -5.0, 21.5, 81.6 (t, J = 31.8 Hz), 91.4 (t, J = 9.7 Hz), 111.7, 120.6 (t, J = 255 Hz), 129.2, 131.9, 140.0; ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 57.5 (s, 2F); Anal. Calcd. for C₁₃H₁₆F₂Si: C, 65.51; H, 6.77. Found: C, 65.52; H, 6.69.

3.7. 1,1-Difluoro-1-trimethylsilyl-2-nonyne (1d)

Colorless oil; 63% yield; IR (neat) 2234 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.22 (s, 9H), 0.89 (t, J = 7.0 Hz, 3H), 1.26–1.33 (m, 4H), 1.40 (q, J = 7.0 Hz, 2H), 1.55 (q, J = 7.0 Hz, 2H), 2.31 (q, J = 7.0 H, 2H); ¹³C NMR (126 MHz, CDCl₃) δ –5.1, 14.0, 18.7, 22.5, 28.0, 28,4, 31.2, 74.4 (t, J = 31.8 Hz), 93.0 (t, J = 8.7 Hz), 120.4 (t, J = 253 Hz); ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 58.8 (t, J = 7.0 Hz, 2F); Anal. Calcd. for C₁₂H₂₂F₂Si: C, 62.02; H, 9.54. Found: C, 62.40; H, 9.44.

3.8. 3,3-Difluoro-1-triisopropylsilyl-3trimethylsilylpropyne (1e)

Colorless oil; 82% yield; IR (neat) 1863 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.24 (s, 9H), 1.08–1.11 (m, 21H); ¹³C NMR (126 MHz, CDCl₃) δ –5.0, 11.0, 18.5, 94.0 (t, J = 7.1 Hz) 99.8 (t, J = 28.9 Hz), 119.8 (t, J = 254 Hz); ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 56.7 (s, 2F); Anal. Calcd. for C₁₅H₃₀F₂Si₂: C, 59.15; H, 9.93. Found: C, 59.22; H, 10.09.

3.9. A typical procedure for the synthesis of 3,3difluoropropargylstannane (2)

To the mixture of Mg (194 mg, 8.0 mmol) and chlorotrimethyltin (4.0 mL of 1.0 M solution) in dry THF (10 mL), 3bromo-3,3-difluoro-1-phenylpropyne (231 mg, 1.0 mmol) was added dropwise at 0 °C under an argon atmosphere. The reaction mixture was stirred for 1 h at 0 °C. The residual Mg was removed by decantation. After evaporation of the solvent and removal of excess amount of chrolotrimethyltin in vacuo (<0.1 mmHg, r.t.), the hexane solution was washed with H₂O (5 mL), aqueous layer was extracted with hexane (5 mL ×2) and combined organic layer was dried over Na₂SO₄. The crude product was chromatographed on silica gel (hexane) treated with Et₃N/hexane = 1/9 to afford **2** (236 mg, 75%) as a colorless oil.

3.10. 3,3-Difluoro-1-phenyl-3-trimethylstannylpropyne (2)

IR (neat) 2223 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.41 (s, 9H), 7.33–7.49 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ –9.5, 83.9 (t, *J* = 27.8 Hz), 92.5 (t, *J* = 10.6 Hz), 121.0, 124.0 (t, *J* = 279 Hz), 128.4, 129.5, 131.8; ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 68.0 (s, 2F); Anal. Calcd. for C₁₂H₁₄F₂Sn: C, 45.76; H, 4.48. Found: C, 46.24; H, 4.42.

3.11. Fluoride ion promoted alkylation of **2a** with allyl halide

A solution of **1a** (224 mg, 1.0 mmol), allyl bromide (605 mg, 5.0 mmol), KF (70 mg, 1.2 mmol), and CuI (286 mg, 1.5 mmol) in DMF (1.5 mL) under an argon atmosphere was stirred for 5 h at 55 °C. The usual workup procedure of the mixture provided the crude product. The crude mixture was chromatographed on silica gel (hexane) to give **3** (125 mg, 65%) as a colorless oil.

3.12. 4,4-Difluoro-6-phenyl-1-hexen-5-yne (3)

IR (neat) 2243, 1230 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.87–2.94 (m, 2H), 5.30–5.33 (m, 2H), 5.85–5.94 (m, ¹H), 7.34–7.51 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ 44.1 (t, J = 27.8 Hz), 81.4(t, J = 40.6 Hz), 87.3 (t, J = 6.7 Hz),114.0 (t, J = 234 Hz), 120.2, 121.1, 128.5, 129.9, 132.1; ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 79.1 (t, J = 15.5 Hz, 2F); HRMS (EI) *m*/*z* Calcd. for C₁₀H₁₀F₂, 192.0751. Found, 192.0744.

3.13. Fluoride ion promoted alkylation of **2a** with benzyl halide

A solution of **1a** (224 mg, 1.0 mmol), benzylbromide (513 mg, 3.0 mmol), KF (70 mg, 1.2 mmol), and CuI (286 mg, 1.5 mmol) in DMF (1.5 mL) under an argon atmosphere was stirred for 8 h at 70 °C. The usual workup procedure of the mixture provided the crude product. The crude mixture was chromatographed on silica gel (hexane) to give **4** (87 mg, 36%) as a colorless oil.

3.14. 3,3-Difluoro-1,4-diphenylbutyne (4)

IR (neat) 2244 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.44 (t, J = 14.0 Hz, 2H), 7.33–7.42 (m, 10H); ¹³C NMR (126 MHz, CDCl₃) δ 45.8 (t, J = 27.0 Hz), 81.4 (t, J = 40.3 Hz) 88.0 (t, J = 6.7 Hz), 114.2 (t, J = 235 Hz), 120.2, 127.7, 128.3, 128.4, 129.8, 130.7, 132.0, 132.1; ¹⁹F NMR (470 MHz, CDCl₃, C₆F₆ as an internal standard) δ 79.9 (t, J = 14.0 Hz, 2F); HRMS (EI) m/z Calcd. for C₁₀H₁₂F₂, 242.0907. Found, 242.0905.

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- [11] A similar $[M 19]^+$ ion was observed in the case of CF₃-C(=N-PMP)tol. This might indicate that the HF loss under CI conditions is a prevalent occurrence on fluorinated carbons attached to unsaturated systems. *Note*: PMP = *p*-methoxyphenyl, tol = *p*-methylphenyl.