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N-Substituted trifluoroacetimidoyl halides: synthesis and properties

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N-Substituted trifluoroacetimidoyl halides in ionic-type transformations readily undergo nucleophilic substitution and dehydrofluorination rather than 1,3-dehydrohalogenation to give nitrile ylides.

Key words: trifluoroacetimidoyl halides, nucleophilic substitution, dehydrofluorination, dihydropyrimidine.

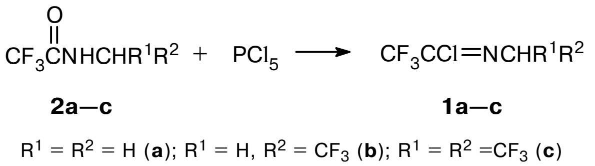
The chemistry of fluorinated imidoyl fluorides is peculiar differing markedly from the chemistry of their hydrocarbon analogs.[1] Functionalized fluorinated imidoyl chlorides, bromides, and iodides have been synthesized.[2—4] *N*-Benzyltrifluoroacetimidoyl chloride was studied as a source of trifluoroacetonitrile phenylmethylide, which underwent *in situ* [2+3] cycloaddition[5] with alkenes to give dihydropyrrole derivatives.

In the present work, the reactions of *N*-substituted trifluoroacetimidoyl halides $CF_3CHal{=}NCHR^1R^2$ (**1a—c**, **a**: $R^1 = R^2 = H$; **b**: $R^1 = H$, $R^2 = CF_3$; **c**: $R^1 = R^2 = CF_3$) with nucleophilic agents were studied.

Results and Discussion

Imidoyl chlorides **1a—c** were prepared by the conventional method involving the reaction of the corresponding amides **2a—c** with PCl_5 (Scheme 1) in 26, 54, and 60% yields, respectively.

Scheme 1



$$CF_3\overset{O}{\overset{\|}{C}}NHCHR^1R^2 + PCl_5 \longrightarrow CF_3CCl{=}NCHR^1R^2$$

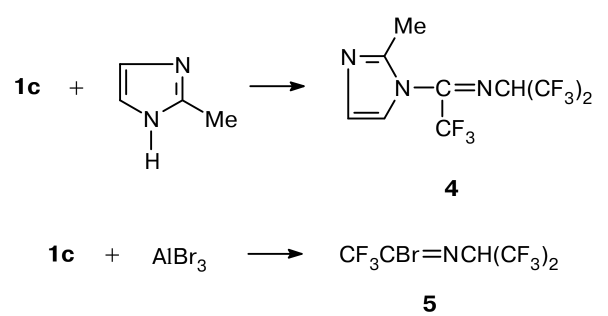
2a—c **1a—c**

$R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = CF_3$ (**b**); $R^1 = R^2 = CF_3$ (**c**)

The yield of the known compound **1a**[6] could not be increased either by varying the reaction conditions or by using another chlorinating agent because of easy cleavage of the amide bond.[6] The synthesis of *N*-(α-hydrohexafluoroisopropyl)trifluoroacetimidoyl chloride **1c** should be carried out in $POCl_3$ as a solvent. Compounds **1b,c** are highly hydrophobic and withstand low-temperature aqueous work-up for purification.

Imidoyl chlorides **1a—c** are easily involved in nucleophilic substitution reactions: they are hydrolyzed to the starting amides **2a—c** under homogeneous conditions and react with secondary amines to form the corresponding amidines **3a,b** and **4** (Scheme 2). The chlorine atom in **1c** is also rather active with respect to electrophilic substitution and can be replaced by bromine in the reaction with aluminum tribromide in acetyl bromide.

Scheme 2



In attempts to generate nitrile ylides **1′a—c** from imidoyl halides **1a—c** and **5,** we treated them with triethylamine (pyridine). The reactions were carried out in the presence of various dipolarophiles (styrene, ethyl

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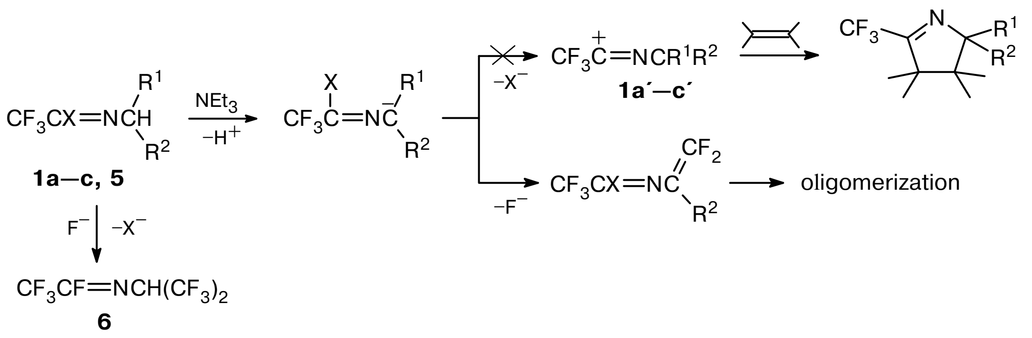
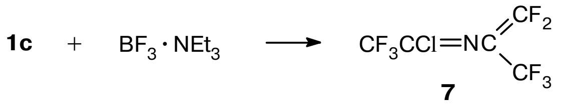
Scheme 3



vinyl ether, and norbornene) at different temperatures and reagent concentrations as described earlier.[5] It turned out that these compounds are not 1,3-dehydrohalogenated under the conditions employed, and no dihydropyrroles—[2+3] cycloaddition products—are formed. Instead, unidentified oligomers were detected; in the case of **1c** and **5**, imidoyl fluoride **6** was isolated. Thus, no 1,3-dehydrohalogenation of imidoyl halides **1c** and **5** occurs, probably, because of easy 1,2-dehydrofluorination so that the resulting fluoride ion replaces halogens to give compound **6** (Scheme 3).

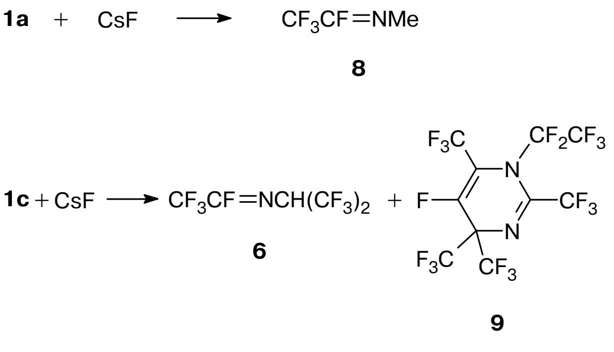
Imidoyl chloride **1c** was easily 1,2-dehydrofluorinated in a special experiment[7] by treatment with the known dehydrofluorinating reagent, $BF_3 \cdot NEt_3$, to give azadiene **7** in 70% yield (Scheme 4).

Scheme 4



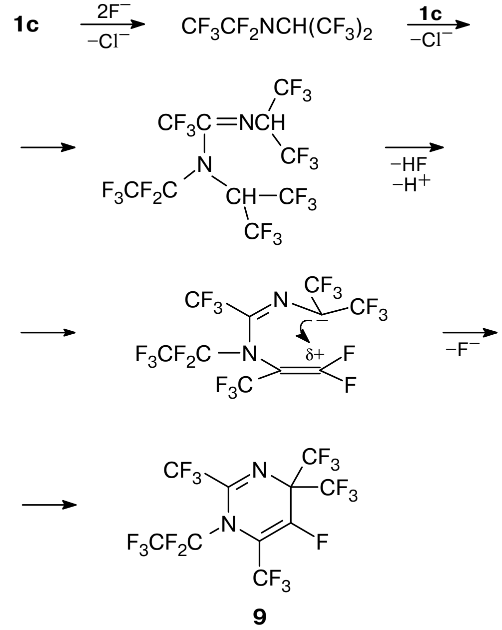
The Cl atom in imidoyl chlorides **1a,c** can also be replaced easily by fluorine under the action of CsF in sulfolane. In the case of **1c**, the reaction is complicated by side dehydrofluorination and cyclization resulting in dihydropyrimidine **9** (Scheme 5).

Scheme 5

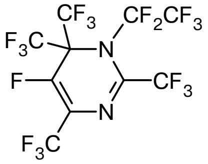


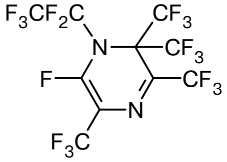
A prolonged reaction at elevated temperature gave dihydropyrimidine **9** as the sole product, which is probably formed according to Scheme 6.

Scheme 6



There are several other alternative structures (*e.g.*, those shown below), which could result from the nucleophilic processes.





However, ^{19}F and ^{13}C NMR data, two-dimensional correlation experiment (COSY, HETCOR, and HMQC), homonuclear ($^{19}F/^{19}F$) double resonance spectroscopic data, and analysis of signal multiplicities are in favor of structure **9**. A signal at δ 143.2 in the ^{13}C NMR spectrum was unambiguously assigned to C(5) in the F—C=C—CF_3 fragment owing to two greatly differing spin-spin coupling constants in the correlation $^{13}C/^{19}F$ spectrum (J_d = 376.0 Hz and J_q = 46.6 Hz) (Table 1). A signal for C(2) at δ 167.9 (J_q = 41.0 Hz) was also undoubtedly assigned to the carbon atom bearing a CF_3 group. The absence of additional splittings indicates that the C—CF_3 fragment is located between two heteroatoms. Signals for C(4) and C(6) at δ 83.3 and 77.0 were also assigned from their multiplicity. A septet at δ 83.3 (*J* = 31.0 Hz) and a quartet at δ 77.0 (*J* = 33.0 Hz) correspond to the C atoms bearing two and one CF_3 group, respectively. A slight additional splitting is probably due to a long-range coupling constant in the CF_3—C=CF—C$(CF_3)_2$ fragment.

Signals for the pentafluoroethyl group were identified from the correlation $^{19}F/^{19}F$ COSY, $^{13}C/^{19}F$ HETCOR, and $^{13}C/^{19}F$ DEPT-135 spectra. The signals at δ 28.0 and 33.5 for nonequivalent F atoms in the ^{19}F NMR spectrum (^2J = 290.0 Hz) and a signal at δ 120.6 with negative polarity for the carbon atom bearing two F atoms in the DEPT spectrum were assigned to difluoromethylene fragment **D** (see Table 1). A signal for the trifluoromethyl group **E** at δ −5.8(^{19}F)/119.5(^{13}C) of the CF_3CF_2 fragment was identified from the COSY spectrum containing two correlation peaks with the CF_2 group and from the HETCOR spectrum also showing the corresponding correlation peak.

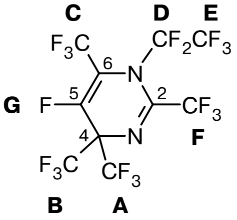
Signals for the other trifluoromethyl groups were assigned using homonuclear ($^{19}F/^{19}F$) double resonance experiments. Preirradiation of the signal **B**(**A**) at δ −5.8 causes narrowing of a signal at δ −0.5 and *vice versa*, which allows the assignment of these two signals to the CF_3—C—CF_3 fragment. Unfortunately, stereospecific identification is impossible at this stage.

Table 1. NMR, IR, and elemental analysis data, physicochemical parameters, and yields of the compounds synthesized

Compound	B.p. /°C (*p*/Torr)	m.p. /°C	n_D^{20}	Yield (%)	Found / Calculated (%)			^{1}H, ^{19}F NMR, δ (*J*/Hz)	IR, ν/cm^{-1}
					C	H	N		
2c	93 (15)	65	—	41	22.95 22.81	0.81 0.76	5.46 5.32	^{1}H: 5.2 (sept, 1 H, CH$(CF_3)_2$, *J* = 7.5); 9.4 (br.s, 1 H, HN); ^{19}F: −6.8 (d, 6 F, $(CF_3)_2$CH); −2.8 (s, 3 F, CF_3)	—
1a	48	—	1.340	26	24.86 24.74	2.16 2.06	9.92 9.62	—	—
1b	73	—	1.331	54	22.65 22.48	1.07 0.94	6.80 6.56	^{1}H: 4.1 (q, 2 H, CH_2CF_3, *J* = 8.8); ^{19}F: −5.7 (s, 3 F, CF_3); −4.3 (t, 3 F, CF_3CH_2)	1700 (C=N)
1c	62	—	1.306	60	21.10 21.31	0.30 0.36	5.20 4.97	^{1}H: 5.0 (sept, 1 H, CH$(CF_3)_2$, *J* = 6.1); ^{19}F: −7.6 (d, 6 F, $(CF_3)_2$CH); −5.0 (s, 3 F, CF_3)	1690 (C=N)
3a	76 (10)	—	1.402	54	36.28 36.36	3.67 3.79	10.53 10.61	^{1}H: 3.5 (s, 4 H, $(CH)_2$N); 3.7 (s, 4 H, $(CH)_2$O); 4.0 (br.q, 2 H, CH_2CF_3); ^{19}F: −4.0 (s, 3 F, CF_3); −1.5 (t, 3 F, CF_3CH_2, *J* = 9.9)	1661 (C=N)
3b	80 (18)	—	1.318	47	32.35 32.53	2.96 2.71	8.20 8.43	^{1}H: 3.3 (m, 4 H, $(CH)_2$N); 3.5 (m, 4 H, $(CH)_2$O); 4.8 (sept, 1 H, CH$(CF_3)_2$, *J* = 5.8); ^{19}F: −3.6 (d, 6 F, $(CF_3)_2$CH, *J* = 5.9); 16.1 (s, 3 F, CF_3)	1640 (C=N)
4	—	80	—	41	33.35 33.03	1.93 1.83	12.61 12.84	^{1}H: 2.4 (s, 3 H, CH_3); 4.3 (sept, 1 H, CH$(CF_3)_2$, *J* = 5.6); 6.8 (s, 1 H, HC=); 7.2 (s, 1 H, HC=); ^{19}F: −8.0 (d, 6 F, 2CF_3); −5.5 (s, 3 F, CF_3)	—
5	78	—	1.318	75	18.50 18.40	0.20 0.31	4.11 4.29	^{1}H: 4.8 (sept, 1 H, CH$(CF_3)_2$, *J* = 6.0); ^{19}F: −5.8 (d, 6 F, $(CF_3)_2$CH); −4.7 (s, 3 F, CF_3)	1720 (C=N)
6	43	—	1.266	41	22.70 22.64	0.62 0.38	5.55 5.28	^{1}H: 4.9 (sept, 1 H, CH$(CF_3)_2$, *J* = 6.5); ^{19}F: −5.1 (d, 6 F, $(CF_3)_2$CH); −3.0 (br.s, 3 F, CF_3); 34.3 (br.s, 1 F, CF)	1770 (C=N)

(*to be continued*)

Table 1 (*continued*)

Compound	B.p. /°C (p/Torr)	m.p. /°C	n_D^{20}	Yield (%)	Found/Calculated (%)			^{1}H, ^{19}F NMR, δ (J/Hz)	IR, ν/cm^{-1}
					C	H	N		
7	71	—	1.352	80	23.05 22.94	—	5.20 5.36	^{19}F: −14.2 (dd, 3 F, CF_3, J = 9.8, 22.9); −5.1 (s, 3 F, CF_3); −1.8 (dq, 1 F, CF_2, J = 9.8); 9.7 (dq, 1 F, CF_2, J = 9.8, 22.9)	—
8	20	—	—	78	28.35 27.91	2.04 2.33	10.37 10.85	^{1}H: 3.2 (s, 1 H, CH_3); ^{19}F: −3.2 (br.s, 3 F, CF_3); −23.0 (m, 1 F, CF)	—
9  	120	—	1.306	53	24.70 24.49	—	5.49 5.71	^{13}C: **A*** 114.1** (q, CF_3, J = 285.0); **B** 116.9** (q, CF_3, J = 282.0); **C** 119.7 (q, CF_3, J = 275.0); **D** 120.6 (t, CF_2, J = 267.0); **E** 119.5 (q, CF_3, J = 277.0); **F** 119.8 (q, CF_3, J = 277.0); C(4) 83.3 (sept, $\underline{C}(CF_3)_2$, J = 31.0); C(5) 143.2 (dq, CF, J = 46.6, J = 376.0); C(6) 77.0 (q, $\underline{C}CF_3$, J = 33.0); C(2) 167.9 (q, N—$\underline{C}(CF_3)$=N, J = 41.0); ^{19}F: **A** −0.5** (d, 3 F, CF_3, J = 2.2) **B** −5.8** (sept, 3 F, CF_3, J = 7.3); **C** −5.6 (m, 3 F, CF_3); **D** 28.0$_A$ (dq, 1 F, CF_2, ^3J = 22.0); **D** 33.5$_B$ (dsept, 1 F, CF_2, ^3J = 22.0, ^2J = 290.0) **E** −5.8 (m, 3 F, CF_3); **F** −4.3 (m, 3 F, CF_3); **G** −47.0 (m, 1 F, =CF)	1720 (C=N); 1620 (C=C)
10	60 (17)	—	1.344	28	24.66 24.59	0.28 0.20	5.91 5.74	^{1}H: 7.0 (br.s, 1 H, OH); ^{19}F: −10.4 (m, 3 F, CF_3); −9.6 (m, 6 F, CF_3); −8.7 (m, 3 F, CF_3); −2.6 (m, 3 F, CF_3); 23.7$_A$ (dq, 1 F, CF_2, J = 21.0); 32.2$_B$ (dm, 1 F, CF_2), J_{AB} = 262.2	2930 (OH); 1700 (C=N); 1610 (C=C)
11	115 (1)	—	—	45	45.03 44.88	2.87 2.63	7.34 7.76	^{1}H: 2.5 (s, 4 H, CH_2); 3.6 (s, 4 H, CH_2); 4.3 (s, 1 H, HC); 7.2 (br.s, 2 H, HC=); 7.3 (br.s, 4 H, HC=); 7.5 (br.s, 4 H, HC=); ^{19}F: −11.9 (m, 3 F, CF_3); −9.0 (m, 3 F, CF_3); −7.2 (m, 6 F, CF_3); −6.7 (m, 3 F, CF_3); 22.4$_A$ (dm, 1 F, CF_2); 36.2$_B$ (dm, 1 F, CF_2), J_{AB} = 248.8	—
12	138 (1)	—	—	40	43.68 43.99	1.82 2.20	4.37 4.11	^{1}H: 1.7 (br.s, 6 H, CH_3); 6.9 (d, 2 H, HC=, J = 10.5); 7.8 (m, 7 H, HC=); ^{19}F: −7.9 (m, 3 F, CF_3); −9.9 (m, 6 F, CF_3); −10.4 (m, 3 F, CF_3); −13.0 (s, 3 F, CF_3); 24.0$_A$ (dq, 1 F, CF_2, J = 23.5); 32.0$_B$ (dm, 1 F, CF_2), J_{AB} = 244.9	—

* The signals for the groups **A—F** have more complex multiplicities due to long-range splittings.

** The assignments may be interchanged.

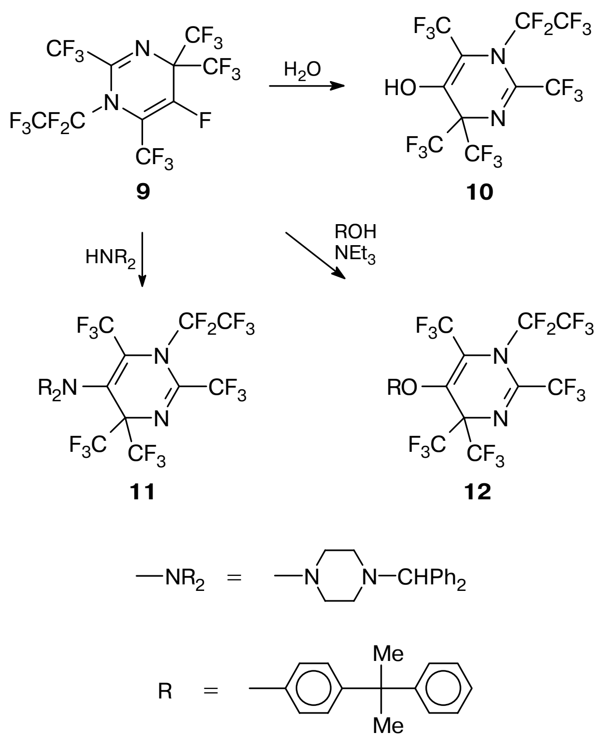
Narrowing of a signal at δ −5.6 upon irradiation of the signal **G** at δ −47.0 and the presence of a cross-peak with a signal for CF_2 (**D**) at δ 28.0 in the $^{19}F/^{19}F$ COSY spectrum allow assigning the signal **C**.

The corresponding ^{13}C signals were identified from the $^{13}C/^{19}F$ HETCOR data.

Mass spectrometry data do not contradict the proposed structure. The mass spectrum contains a molecular ion peak with *m/z* 490 and the fragmentation ions due to elimination of F, CF_3, *etc.*

Dihydropyrimidine **9** reacts with nucleophilic reagents such as water, phenols, and amines with the replacement of the vinylic F atom (Scheme 7). The reaction with water yields product **10**, which exists in the enol form (NMR data).

Scheme 7



Thus, unlike the previously described compound,[5] the imidoyl halides studied are not precursors of nitrile ylides. The heterocyclic compounds synthesized exhibit antibacterial activities and are promising for further investigation.

Experimental

^1H and ^{19}F NMR spectra were recorded on Bruker AC-300 (300 MHz) and Bruker WP-200 SY (188.31 MHz) spectrometers with Me_4Si and CF_3COOH as the external standards, respectively. The ^{19}F and ^{13}C NMR spectra of compound **9** were recorded for neat liquid at 313 K on a Bruker DRX-500 instrument (470 and 125 MHz, respectively) with CF_3COOH ($\delta_F = 0.0$) and acetone-d_6 ($\delta_C = 29.5$) as the external standards. A DUAL $^{19}F/^1H$ probehead was used in homonuclear $^{19}F/^{19}F$ experiments. $^{13}C/^{19}F$ HETCOR, $^{13}C\{^{19}F\}$, $^{13}C/^{19}F$ DEPT, and $^{19}F/^{13}C$ HMQC studies were carried out with a $^1H\{^{13}C,X\}$ triple resonance probehead with a proton channel tuned for ^{19}F observation. Two-dimensional correlation $^{19}F/^{19}F$ (COSY) and $^{19}F/^{13}C$ (HMQC and HETCOR) spectra were recorded using modified pulse programs to control the QNP H/F/X unit of the spectrometer. $^{13}C\{^{19}F\}$ and DEPT $^{13}C\{^{19}F\}$ spectra were also recorded using modified pulse programs. Heteronuclear $^{13}C\{^{19}F\}$ decoupling was performed with the WURST[8] sequence on an effective band >60 kHz. Mass spectra were obtained on a GS/MS instrument based on an HP 5890 II Series gas chromatograph with an HP 5972A MSD mass-selective detector. IR spectra (ν/cm^{-1}, thin film) were recorded on a UR-20 spectrometer. Physicochemical parameters, spectroscopic (^1H, ^{13}C, and ^{19}F NMR and IR) and elemental analysis data, and yields are given in Table 1. Commercial reagents were used as purchased, and solvents were purified according to the known recommendations.[10]

***N*-Methyltrifluoroacetimidoyl chloride[6] (1a).** *N*-Methyltrifluoroacetamide[6] (0.413 mol) was added to PCl_5 (0.413 mol) at 10—15 °C. After the exothermic reaction was completed, the reaction mixture was heated for ~3 h with simultaneous distillation of a fraction with b.p. < 65 °C, which was refractionated.

***N*-(2,2,2-Trifluoroethyl)trifluoroacetimidoyl chloride (1b).** *N*-(2,2,2-Trifluoroethyl)trifluoroacetamide[9] (0.410 mol) was added to PCl_5 (0.820 mol) at 10—15 °C, and the reaction mixture was heated for ~3 h with simultaneous distillation of a fraction with b.p. ≤ 90 °C. The distillate was mixed with ice (~200 g), kept for 2 h with periodical stirring, washed with water (3×50 mL), dried with $MgSO_4$, and distilled to give **1b**.

***N*-(α-Hydrohexafluoroisopropyl)trifluoroacetimidoyl chloride (1c).** *N*-(α-Hydrohexafluoroisopropyl)trifluoroacetamide[7] (0.32 mol) and $POCl_3$ (40 g) were added to PCl_5 (0.640 mol) at 20 °C. The reaction mixture was slowly heated for ~4 h with simultaneous distillation of a fraction with b.p. ≤ 85 °C, which then was worked up as described for **1b**.

Hydrolysis of trifluoroacetimidoyl chlorides 1a—c (general procedure). Water (7 mmol) was added to a cooled (water + ice) solution of the corresponding imidoyl chloride (14 mmol) in diethyl ether (5 mL) over 10 min. The reaction mixture was stirred for 2 h and concentrated to dryness at 20 Torr, and the residue was dried over P_2O_5 to give amides **2a—c** in 50, 60, and 55% yields, respectively. Their physicochemical properties and spectral parameters correspond to the literature data.[6,9]

1,1,1,5,5,5-Hexafluoro-2-morpholino-3-azapent-2-ene (3a). A solution of morpholine (14 mmol) in diethyl ether (2 mL) was added at −20 °C over 30 min to a solution of imidoyl chloride **1b** (7 mmol) in diethyl ether (10 mL). The reaction mixture was warmed to ~20 °C and filtered. Distillation of the filtrate gave amidine **3a**. **1,1,1,5,5,5-Hexafluoro-2-morpholino-4-trifluoromethyl-3-azapent-2-ene (3b)** was obtained analogously from imidoyl chloride **1c** at 0 °C.

1,1,1,5,5,5-Hexafluoro-2-(2-methylimidazol-1-yl)-4-trifluoromethyl-3-azapent-2-ene (4). A solution of **1c** (2.5 mmol) in diethyl ether (2 mL) was added at 5 °C over 15 min to a solution of 2-methylimidazole (5 mmol) in diethyl ether (3 mL). The reaction mixture was warmed to ~20 °C, and 2-methylimidazole hydrochloride was filtered off. Fractional sublimation at 78—98 °C (14 Torr) followed by recrystallization from *n*-hexane gave amidine **4**.

***N*-(α-Hydrohexafluoroisopropyl)trifluoroacetimidoyl bromide (5).** A mixture of $AlBr_3$ (0.036 mol), imidoyl chloride **1c** (0.036 mol), and AcBr (5.0 mL) were kept at ~20 °C for 4 h with periodical stirring, and then the reaction mixture was poured into ice (~100 g), washed with cold water (3×15 mL), dried with $MgSO_4$, and distilled to give imidoyl bromide **5**.

Dehydrohalogenation of imidoyl bromide 5 in the presence of triethylamine. *N*-(α-Hydrohexafluoroisopropyl)trifluoroacetimidoyl fluoride (6). Triethylamine (6 mmol) was added with stirring at 10 °C to a mixture of **5** (6 mmol) and norbornene (12 mmol) in dry diethyl ether (15 mL). The reaction mixture was stirred for ~4 h and kept at ~20 °C for 10 h. The precipitate of triethylamine hydrobromide was filtered off and washed with dry ether (5 mL). Distillation of the filtrate gave imidoyl fluoride **6** as a mixture with diethyl ether (1 : 1), b.p. 38—40 °C.

Reaction of imidoyl chloride 1c with CsF. *A*. Imidoyl chloride **1c** (0.06 mol) was added with stirring at 20 °C over 10 min to a suspension of dry CsF (0.17 mol) in sulfolane (10 mL); the reaction proceeded exothermically (~35 °C). Fractionation gave imidoyl fluoride **6** and **5-fluoro-1-perfluoroethyl-2,4,4,6-tetrakis(trifluoromethyl)-1,4-dihydropyrimidine 9**.

***B*.** Imidoyl chloride **1c** (0.05 mol) was added at 35 °C over 30 min to a suspension of CsF (0.27 mol) in sulfolane (10 mL). The reaction mixture was heated to boiling and kept with stirring for 3 h. Fractionation gave dihydropyrimidine **9**.

MS (EI, 70 eV), *m/z* (I_{rel} (%)): 490 $[M]^+$ (4), 471 $[M - F]^+$ (21), 421 $[M - CF_3]^+$ (12), 333 $[M - CF_3 - CF_3]^+$ (5), 245 $[M - CF_2 - C_2N]^+$ (80), 226 (5), 195 (10), 69 $[CF_3]^+$ (100), 28 (12).

***N*-(Perfluoroisopropenyl)trifluoroacetimidoyl chloride (7).** A mixture of imidoyl chloride **1c** (12 mmol), $BF_3 \cdot NEt_3$ (18 mmol), and dry dioxane (3 mL) was heated in a sealed tube at 110—120 °C for 50 min. Double fractionation gave compound **7**, which may contain 5—10 % of the starting imidoyl chloride **1c** since they have close physicochemical properties and are difficult to separate by distillation. The properties of compound **7** are given for a high-purity sample (98%) obtained in one of the experiments.

***N*-Methyltrifluoroacetimidoyl fluoride (8).** Imidoyl chloride **1a** (0.128 mol) was added with stirring at 40 °C over 50 min to a suspension of CsF (0.256 mol) in dry sulfolane (15 mL) with trapping of volatile products at −78 °C. Fractionation gave imidoyl fluoride **8**.

1-Perfluoroethyl-2,4,4,6-tetrakis(trifluoromethyl)-1,4-dihydropyrimidin-5-ol (10). Water (11 mmol) and dioxane (2 mL) were added to compound **9** (1.8 mmol). The reaction mixture was kept at ~20 °C for 14 days and, after the addition of Freon 113 (5 mL), washed with water (5×2 mL). The aqueous phase was extracted with Freon (3×1.5 mL). The combined organic phase and Freon extracts were dried with Na_2SO_4 for 24 h. Fractionation gave compound **10**.

5-[4-(Diphenylmethyl)piperazin-1-yl]-1-perfluoroethyl-2,4,4,6-tetrakis(trifluoromethyl)-1,4-dihydropyrimidine (11). A solution of *N*-diphenylmethylpiperazine (6 mmol) in diethyl ether (2 mL) was added to a solution of compound **9** (3 mmol) in ether (5 mL). The reaction mixture was kept at ~20 °C for 3 days with periodical stirring, and then water (3 mL) and CH_2Cl_2 (3 mL) were added. The organic layer was separated, dried with Na_2SO_4, and distilled to give compound **11**.

1-Perfluoroethyl-5-[4-(2-phenylpropan-2-yl)phenyl]-2,4,4,6-tetrakis(trifluoromethyl)-1,4-dihydropyrimidine (12). A solution of 4-(2-phenylpropan-2-yl)phenol (3 mmol) and triethylamine (3 mmol) in diethyl ether (2 mL) was added to a solution of compound **9** (3 mmol) in ether (2 mL). The reaction mixture was kept at ~20 °C for 3 days with periodical stirring, and then water (2 mL) and CH_2Cl_2 (2 mL) were added. The organic layer was separated, dried with Na_2SO_4, and distilled to give ether **12**.

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