One-Pot Synthesis of Trifluoroacetimidoyl Halides

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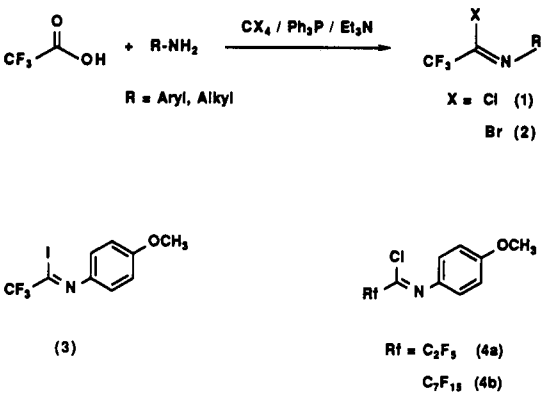
Trifluoroacetimidoyl chlorides 1 were obtained in 80–90% yields when a mixture of trifluoroacetic acid and a primary amine was heated in carbon tetrachloride in the presence of triphenylphosphine and triethylamine. The corresponding bromides 2 were obtained when carbon tetrabromide was used instead of carbon tetrachloride. Imidoyl iodides 3 were prepared by substitution of the chloro group of 1 by iodide ion in acetone.

Trifluoromethylation, which has been recently reviewed,[1] has received increasing attention because of the unique properties of the trifluoromethylated heterocycles and the related organofluorine compounds in the fields of medicinal and agricultural chemistry[2] and material science.[3] Development and effective use of the trifluoromethylated synthetic building blocks would be useful for the syntheses of many target trifluoromethylated compounds.

N-aryltrifluoroacetimidoyl chlorides, which appeared in a French patent,[4] are examples of some of the promising building blocks, and they have been recently employed for the syntheses of trifluoromethylated nitrogen heterocycles.[5] However, because of the limited availability of 1, very little is known about the physical constants, spectral data, and chemical properties. They have been prepared by two different procedures. The first is the reaction of N-substituted trifluoroacetamides with phosphorus pentachloride.[6] The second is the thermal or copper-catalyzed addition of perfluoroalkyl iodide to isocyanides.[7] The former route suffers from poor yields (30–50%), troublesome experimental procedures because of the evolution of hydrochloric acid and trichlorophosphine oxide, and severe reaction conditions (150 °C for 4 h). In the latter case, the limited availability of trifluoromethyl iodide and isocyanides make the method impractical.

Imidoyl halides of nonfluorinated carboxylic acids have been obtained from N-monosubstituted carboxamides and triphenylphosphine in carbon tetrachloride.[8] These mild conditions make it possible to synthesize imidoyl chlorides not available by the other methods. The same system provides the corresponding carboxamides from acetic or benzoic acids and primary amines.[9] Therefore, combining these two systems should, in principle, provide a straightforward conversion of carboxylic acids to the corresponding imidoyl halides in a one-pot procedure. However, no practical one-pot synthesis has appeared in the literature. Imidoyl halides 1 are in general so susceptible to water and other nucleophiles that a primary amine in the reaction mixture would react spontaneously with 1 to form amidines.[10] Successful conversion would be dependent on the carboxamidation step (equation 3 in Scheme III) being much faster than chlorination step (eq 5) and on the stability of the imidoyl halides to the reaction conditions.

Scheme I



We now describe a one-pot synthesis of imidoyl halides 1, 2, and 4, which consists of refluxing a mixture of trifluoroacetic acid (or perfluoroalkanoic acid) and a primary amine in carbon tetrachloride (or carbon tetrabromide) in the presence of triethylamine and triphenylphosphine. A mixture of triphenylphosphine (3 equiv), trifluoroacetic acid (1 equiv), and triethylamine (1.2 equiv) was refluxed in carbon tetrachloride for 3 h. Workup and distillation provided the desired imidoyl chlorides in good to excellent yields as listed in Table I. The yields have not been affected by the electronic effects of substituents in the cases examined so far. There is little difference in the yields of 1 obtained from *o*-, *m*-, and *p*-methoxyanilines (entries 3, 2, 1). Naphthylamine gave a reasonable yield (entry 12), and the sterically hindered amine 2,6-dimethylaniline reacted smoothly (entry 5). Particularly noteworthy is the fact that *o*-methoxy aniline (entry 3) gave a good yield of 1c (87%) under these conditions, in contrast to the very poor yield (less than 5%) obtained from the chlorination of the corresponding amide with

(1) Uneyama, K. *J. Synth. Org. Chem. Jpn.* **1991**, *49*, 612.
(2) Miesel, J. L. U.S. 4,000,295 (Cl, 424-273; AOIN9/22), 28 Dec 1976, Appl. 833,685, 16 Jun 1969, 23 pp; *Chem. Abstr.* **1977**, *86*, 140050s. Kitazume, T.; Lin, J. T.; Yamamoto, T.; Yamazaki, T. *J. Am. Chem. Soc.* **1991**, *113*, 2123. Kitazume, T.; Lin, J. T.; Yamazaki, T. *J. Am. Chem. Soc.* **1991**, *113*, 8573.
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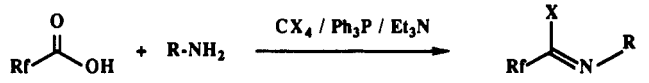
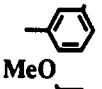
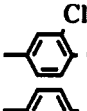
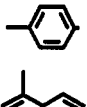
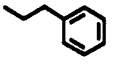
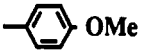
(7) Tordeux, M.; Wakselman, C. *Tetrahedron* **1981**, *37*, 315.
(8) Appel, R.; Warning, K.; Ziehn, K.-D. *Chem. Ber.* **1973**, *106*, 2093 and 3450. Appel, R.; Warning, K.; Ziehn, K.-D. *Chem. Ber.* **1974**, *107*, 698. Appel, R.; Warning, K.; Ziehn, K.-D. *German Pat. Appl.* 23331104 (Le A 15116), 1975.
(9) Barstow, L. E.; Hruby, V. J. *J. Org. Chem.* **1971**, *36*, 1305. Duncia, J. V.; Pierce, M. E.; Santella, J. B., III. *J. Org. Chem.* **1991**, *56*, 2395.
(10) Uneyama, K.; Kobayashi, M. *Tetrahedron Lett.* **1991**, *32*, 5981.

0022-3263/93/1958-0032$04.00/0

Table I. Yields and ^{19}F- and ^{13}C-NMR Chemical Shifts of Imidoyl Halides 1-4[a]



entry	X	R	Rf	yield (%)	^{19}F (δ)[b]	^{13}C CF_3[c]	^{13}C $CF_3C(X)=N$[d]
1	Cl		CF_3	1a (91)	-71.8	117.0 (276.6)	127.9 (43.1)
2				1b (90)	-72.2	116.8 (277.2)	132.2 (43.1)
3				1c (87)	-72.0	116.8 (277.1)	133.9 (42.8)
4				1d (86)	-72.1	117.0 (277.0)	130.5 (42.9)
5				1e (84)	-71.8	116.7 (277.7)	134.4 (43.0)
6				1f (73)	-72.2	116.9 (277.0)	131.9 (43.0)
7				1g (91)	-72.2	116.8 (277.2)	132.6 (43.3)
8				1h (87)	-72.3	116.8 (277.4)	133.7 (43.3)
9				1i (95)	-72.2	116.6 (277.6)	134.1 (43.7)
10				1j (77)	-72.1	116.9 (277.1)	131.6 (43.0)
11				1k (77)	-72.2	116.5 (278.2)	135.7 (43.8)
12				1l (88)	-71.7	117.0 (277.5)	132.8 (42.9)
13				1m (94)	-72.2	116.6 (276.9)	132.5 (42.8)
14				1n (77)	-72.2	116.6 (276.4)	131.5 (42.9)
15				8 (87)[e]	-71.6[e]	124.5[e] (276.7)	-
16	Br			2 (84)	-70.9	116.6 (277.2)	121.4 (43.2)
17	I			3 (-)[f]	-70.3	115.2 (278.2)	111.8 (41.7)
18	Cl		C_2F_5	4a (96)	-[f]	-[f]	-[f]
19			C_7F_{15}	4b (70)	-[f]	-[f]	-[f]

[a] For structures, see Scheme I. [b] ^{19}F-NMR chemical shift of CF_3. [c] ^{13}C-NMR chemical shift of CF_3 (q, J_{C-F} (Hz)). [d] ^{13}C-NMR chemical shift of imino carbon (q, J_{C-C-F} (Hz)). [e] The product was *N*-(2,2,2-trifluoroethyl)benzoimidoyl chloride (8), see Scheme III. [f] See Experimental Section.

PCl_5.[11] Alkylamines such as phenethyl and hexylamines provided good yields (entries 13, 14).

However, when the reaction was carried out with benzylamine under the same reaction conditions, *N*-(2,2,2-trifluoroethyl)benzoimidoyl chloride (8) was obtained in 87% yield. Compound 8 must arise from a rearrangement of the chlorine atom (entry 15). Both ^1H-NMR (δ 4.18, quartet, J = 9.3 Hz) and ^{19}F-NMR (δ -71.6, triplet, J = 9.2 Hz) reveal the existence of a CF_3CH_2 moiety in 8. ^{13}C-NMR shows two quartets (δ 124.5, J = 276.7 Hz, and δ 55.0, J = 33.1 Hz), also supporting the structure of 8. Because the benzylimino moiety of 5 is less stable than the benzimino moiety in 6, the imidoyl chloride 5 generated in situ rearranges to 6. Nucleophilic S_N2' reaction of 6 with a chloride ion and subsequent prototropy in 7 led to 8 (Scheme II).[12]

Each step of the overall transformation of trifluoroacetic acid to 1 is shown in Scheme III. The present one-pot

(11) On treatment of *N*-(*o*-methoxyphenyl)-2,2,2-trifluoroacetamide with PCl_5,[6] the reaction mixture was solidified. Very little 1c (less than 5%) was distilled out, and the residue was undistillable and polymeric.

(12) Tanaka, K.; Daikaku, H.; Mitsuhashi, K. *Chem. Lett.* **1983**, 1463.

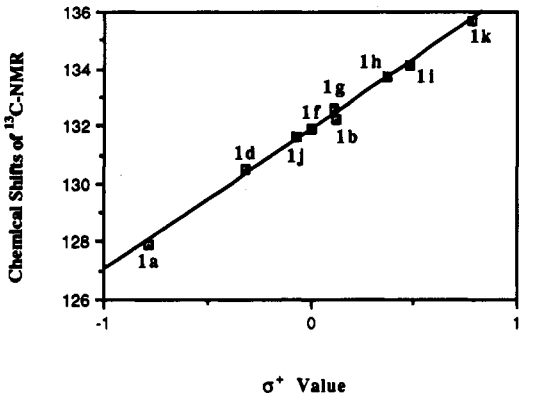


Figure 1. Plot of ^{13}C-NMR chemical shifts of the imino carbons of 1 vs Brown–Okamoto σ^+ values of the N-aryl substituent.

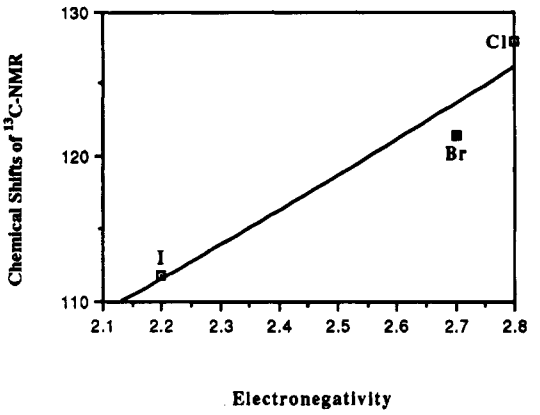
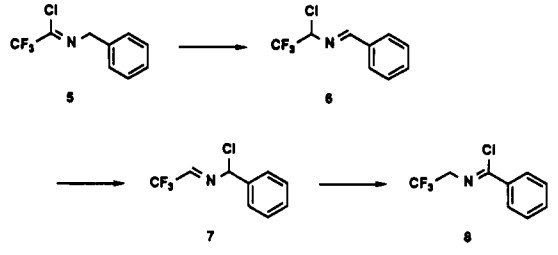
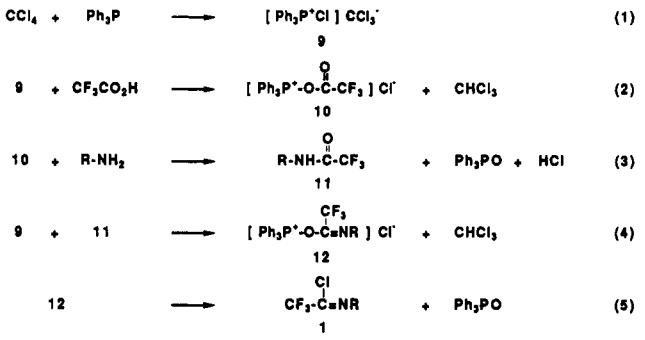


Figure 2. Plot of ^{13}C-NMR chemical shifts of the imino carbons of **1a**, **2**, and **3** vs electronegativity of halogen.

Scheme II



Scheme III



synthesis of 1 is successful because of the fast reaction of primary amines in step 3 and the slower subsequent steps 4 and 5. No primary amine is present at stage 5; otherwise, the primary amine would react with 1 to form the corresponding amidines.[10]

The present method is generally applicable to perfluoroalkanoic acids. Both perfluoropropanoic and octanoic acids were transformed to the corresponding imidoyl chlorides (entries 18, 19). Imidoyl bromide **2** (R = *p*-methoxyphenyl) can be prepared similarly from carbon tetrabromide (entry 16) instead of carbon tetrachloride. Imidoyl iodide **3** (R = *p*-methoxyphenyl) is prepared almost quantitatively by displacement of the chloro group of **1a** with iodine in a NaI–acetone system (entry 17).

Chemical shifts in the ^{19}F- and ^{13}C-NMR of the trifluoromethyl group and the ^{13}C-NMR of the imino sp^2 carbon are listed in Table I. Although the ^{19}F and ^{13}C chemical shifts of the trifluoromethyl group of **1** are not affected by ring substituents, the ^{13}C-NMR chemical shifts of the imino sp^2 carbon are altered significantly by the substituents. The chemical shifts are plotted against Brown–Okamoto σ^+ values, affording a clean straight line as shown in Figure 1. The good correlation of the chemical shifts with the σ^+ values suggests that the electronic effect of the ring substituents is transmitted through resonance to the imino carbon. The chemical shifts were also affected by halogens attached to the imino carbon of **1** (X = Cl), **2** (X = Br), and **3** (X = I). A plot of the chemical shifts against electronegativity of X is shown in Figure 2.

Imidoyl chlorides **1** are rather stable thermally and not as moisture-sensitive as nonfluorinated imidoyl chlorides.[13,14] In fact, when **1a** (R = *p*-methoxyphenyl) was stirred in aqueous acetone at room temperature for 1 day, only 10% of **1a** was hydrolyzed to the corresponding amide, whereas the nonfluorinated acetimidoyl chloride is known to be hydrolyzed instantaneously.[13]

Experimental Section

^{1}H-, ^{13}C-, and ^{19}F-NMR spectra were obtained in $CDCl_3$ on instruments operating at 200, 50, and 188 MHz, respectively. Chemical shifts for ^{1}H- and ^{13}C-NMR spectra are reported in ppm downfield from TMS. ^{19}F-NMR spectra were obtained using C_6F_6 as internal standard (−162.3 ppm) but are reported as chemical shifts upfield from $CFCl_3$.

***N*-(*p*-Anisyl)-2,2,2-trifluoroacetimidoyl Chloride (1a).** A 200-mL two-necked flask equipped with a septum cap, a condenser, and a Teflon-coated magnetic stir bar was charged with Ph_3P (34.5 g, 132 mmol), Et_3N (7.3 mL, 53 mmol), CCl_4 (21.1 mL, 220 mmol), and TFA (3.4 mL, 44 mmol). After the solution was stirred for about 10 min (ice bath), *p*-anisidine (6.48 g, 53 mmol) dissolved in CCl_4 (21.1 mL, 220 mmol) was added. The mixture was then refluxed under stirring (3 h). Solvents were removed under reduced pressure, and the residue was diluted with hexane and filtered. Residual solid Ph_3PO, Ph_3P, and Et_3N–HCl were washed with hexane several times. The filtrate was concentrated under reduced pressure, and the residue was distilled to afford **1a** (9.5 g) in 91% yield as a yellow oil. Bp: 97–98 °C (14 Torr). IR (neat): 1682 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.85 (s, 3 H, OMe), 6.93–7.02 (m, 2 H, Ar), 7.30–7.37 (m, 2 H, Ar). ^{13}C-NMR ($CDCl_3$): δ 55.2, 114.2 (2 C), 117.0 (q, J_{C-F} = 276.6 Hz, CF_3), 124.4 (2 C), 127.9 (q, J_{C-C-F} = 43.1 Hz), 135.3, 159.6. ^{19}F-NMR ($CDCl_3$): δ −71.8 (s). HRMS: calcd for $C_9H_7NOF_3Cl$ 237.0165, found 237.0141.

***N*-(*m*-Anisyl)-2,2,2-trifluoroacetimidoyl Chloride (1b).** Bp: 94–95 °C (11 Torr). IR (neat): 1692 cm^{-1}. ^{1}H-NMR: δ 3.83 (s, 3 H, OMe), 6.61 (dd, 1 H, J_1 = 2.4 Hz, J_2 = 1.8 Hz, Ar), 6.64–7.00 (m, 1 H, Ar), 6.84 (ddd, 1 H, J_1 = 2.4 Hz, J_2 = 1.0 Hz, J_3 = 8.3 Hz, Ar), 7.34 (dd, 1 H, J_1 = 7.8 Hz, J_2 = 8.3 Hz, Ar). ^{13}C-NMR: δ 55.2, 106.2, 112.5, 113.0, 116.8 (q, J_{C-F} = 277.2 Hz,

(13) Ugi, I.; Beck, F.; Fetzer, U. *Chem. Ber.* **1962**, *95*, 126.

(14) The imidoyl chlorides can be stored in a refrigerator but are rather unstable at room temperature. HRMS data were reported instead of elemental analysis.

(15) The authors are grateful to the Ministry of Education, Culture, and Science of Japan (a Grant-in-Aid, No. 04453101 and No. 04555204) for financial support, the SC-NMR Laboratory of Okayama University for ^{19}F-NMR analysis, and Mr. M. Ishihara, Shiono Koryo Kaisha Ltd, for HRMS spectra analysis.

CF_3), 123.0, 132.2 (q, J_{C-C-F} = 43.1 Hz), 114.6, 160.3. ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_9H_7NOF_3Cl$ 237.0165, found 237.0138.

***N*-(*o*-Anisyl)-2,2,2-trifluoroacetimidoyl Chloride (1c).** Bp: 88–89 °C (13 Torr). IR (neat): 1698 cm^{-1}. ^{1}H-NMR: δ 3.85 (s, 3 H, OMe), 6.92–7.05 (m, 3 H, Ar), 7.20–7.30 (m, 1 H, Ar). ^{13}C-NMR: δ 55.5, 111.8, 116.8 (q, J_{C-F} = 277.1 Hz, CF_3), 120.2, 120.5, 127.9, 133.1, 133.9 (q, J_{C-C-F} = 42.8 Hz), 149.2. ^{19}F-NMR: δ −72.0 (s). HRMS: calcd for $C_9H_7NOF_3Cl$ 237.0165, found 237.0144.

***N*-(*p*-Tolyl)-2,2,2-trifluoroacetimidoyl Chloride (1d).** Bp: 90 °C (15 Torr). IR (neat): 1696 cm^{-1}. ^{1}H-NMR: δ 2.37 (s, 3 H, Me), 7.03–7.10 (m, 2 H, Ar), 7.20–7.27 (m, 2 H, Ar). ^{13}C-NMR: δ 20.9, 117.0 (q, J_{C-F} = 277.0 Hz, CF_3), 121.3 (2 C), 129.7 (2 C), 130.5 (q, J_{C-C-F} = 42.9 Hz), 137.9, 140.6. ^{19}F-NMR: δ −72.1 (s). HRMS: calcd for $C_9H_7NF_3Cl$ 221.0218, found 221.0222.

***N*-(2,6-Xylyl)-2,2,2-trifluoroacetimidoyl Chloride (1e).** Bp: 64–65 °C (12 Torr). IR (neat): 1690 cm^{-1}. ^{1}H-NMR: δ 2.06 (s, 6 H, Me_2), 7.05–7.10 (m, 3 H, Ar). ^{13}C-NMR: δ 17.3 (2 C), 116.7 (q, J_{C-F} = 277.4 Hz, CF_3), 125.4 (2 C), 125.7, 128.2 (2 C), 134.4 (q, J_{C-C-F} = 43.0 Hz), 142.9. ^{19}F-NMR: δ −71.8 (s). HR-MS: calcd for $C_{10}H_9NF_3Cl$ 235.0374, found 235.0364.

***N*-Phenyl-2,2,2-trifluoroacetimidoyl Chloride (1f).** Bp: 55–56 °C (11 Torr). IR (neat): 1700 cm^{-1}. ^{1}H-NMR: δ 7.08–7.12 (m, 2 H, Ph), 7.26–7.49 (m, 3 H, Ph). ^{13}C-NMR: δ 116.9 (q, J_{C-F} = 277.0 Hz, CF_3), 120.7, 127.4 (2 C), 129.1 (2 C), 131.9 (q, J_{C-C-F} = 43.0 Hz), 143.5. ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_8H_5NF_3{}^{37}Cl$ 209.0032, found 209.0030.

***N*-(*p*-Chlorophenyl)-2,2,2-trifluoroacetimidoyl Chloride (1g).** Bp: 82–83 °C (10 Torr). IR (neat): 1702 cm^{-1}. ^{1}H-NMR: δ 7.03–7.11 (m, 2 H, Ar), 7.38–7.46 (m, 2 H, Ar). ^{13}C-NMR: δ 116.8 (q, J_{C-F} = 277.2 Hz, CF_3), 122.3 (2 C), 129.3 (2 C), 132.6 (q, J_{C-C-F} = 43.3 Hz), 133.3, 141.7. ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_8H_4NF_3Cl_2$ 240.9673, found 240.9713.

***N*-(*m*-Chlorophenyl)-2,2,2-trifluoroacetimidoyl Chloride (1h).** Bp: 79–80 °C (13 Torr). IR (neat): 1706 cm^{-1}. ^{1}H-NMR: δ 6.96 (ddd, 1 H, J_1 = 8.0 Hz, J_2 = 2.0 Hz, J_3 = 1.3 Hz, Ar), 7.09 (dd, 1 H, J_1 = 2.0 Hz, J_2 = 2.0 Hz, Ar), 7.28 (ddd, 1 H, J_1 = 1.3 Hz, J_2 = 2.0 Hz, J_3 = 8.0 Hz, Ar), 7.38 (t, 1 H, J = 8.2 Hz, Ar). ^{13}C-NMR: δ 116.8 (q, J_{C-F} = 277.4 Hz, CF_3), 118.6, 120.7, 127.3, 130.3, 133.7 (q, J_{C-C-F} = 43.3 Hz), 135.0, 144.6. ^{19}F-NMR: δ −72.3 (s). HRMS: calcd for $C_8H_4NF_3Cl_2$ 240.9673, found 240.9630.

***N*-(3,4-Dichlorophenyl)-2,2,2-trifluoroacetimidoyl Chloride (1i).** Bp: 108–109 °C (13 Torr). IR (neat): 1710, 1690 cm^{-1}. ^{1}H-NMR: δ 6.97 (dd, 1 H, J_1 = 8.6 Hz, J_2 = 2.4 Hz, Ar), 7.24 (d, 1 H, J = 2.4 Hz, Ar), 7.53 (d, 1 H, J = 8.6 Hz, Ar). ^{13}C-NMR: δ 116.6 (q, J_{C-F} = 277.6 Hz, CF_3), 120.1, 122.6, 130.9, 131.4, 133.3, 134.1 (q, J_{C-C-F} = 43.7 Hz), 142.5. ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_8H_3NF_3Cl_3$ 274.9282, found 274.9271.

***N*-(*p*-Fluorophenyl)-2,2,2-trifluoroacetimidoyl Chloride (1j).** Bp: 53–54 °C (10 Torr). IR (neat): 1694 cm^{-1}. ^{1}H-NMR: δ 7.07–7.24 (m, 4 H, Ar). ^{13}C-NMR: δ 116.1 (d, 2 C, J = 22.9 Hz), 116.9 (q, 1 C, J_{C-F} = 277.1 Hz, CF_3), 123.4 (d, 2 C, J = 8.5 Hz), 131.6 (q, 1 C, J_{C-C-F} = 43.0 Hz), 139.2 (d, 1 C, J = 3.0 Hz), 161.8 (d, 1 C, J = 248.7 Hz). ^{19}F-NMR: δ −72.1 (s, 3 F), −113.9 (m, 1 F); HRMS: calcd for $C_8H_4NF_4{}^{37}Cl$ 226.9939, found 226.9996 (ER +5.7).

***N*-(*p*-Nitrophenyl)-2,2,2-trifluoroacetimidoyl Chloride (1k).** Bp: 129–130 °C (10 Torr). IR (Nujol): 1706 cm^{-1}. ^{1}H-NMR: δ 7.10–7.13 (m, 2 H, Ar), 8.25–8.34 (m, 2 H, Ar). ^{13}C-NMR: δ 116.5 (q, J_{C-F} = 278.2 Hz, CF_3), 120.4 (2 C), 125.0 (2 C), 135.7 (q, J_{C-C-F} = 43.8 Hz), 146.2, 149.0. ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_8H_4N_2O_2F_3Cl$ 251.9912, found 251.9864.

***N*-Naphthyl-2,2,2-trifluoroacetimidoyl Chloride (1l).** Bp: 130 °C (13 Torr). IR (neat): 1688 cm^{-1}. ^{1}H-NMR: δ 7.22 (d, 1 H, J = 7.4 Hz), 7.45–7.60 (m, 3 H, Ar), 7.77–7.92 (m, 3 H, Ar). ^{13}C-NMR: δ 115.1, 117.0 (q, J_{C-F} = 277.5 Hz, CF_3), 122.7, 125.1, 126.3, 126.7, 126.8, 127.7, 128.0, 132.8 (q, J_{C-C-F} = 42.9 Hz), 134.0, 139.6. ^{19}F-NMR: δ −71.7 (s). HRMS: calcd for $C_{12}H_7NF_3Cl$ 257.0218, found 257.0204.

***N*-Phenethyl-2,2,2-trifluoroacetimidoyl Chloride (1m).** Bp: 86–87 °C (12 Torr). IR (neat): 1704 cm^{-1}. ^{1}H-NMR: δ 3.01 (t, 2 H, J = 7.4 Hz), 3.82–3.90 (m, 2 H), 7.18–7.38 (m, 5 H, Ph). ^{13}C-NMR: δ 35.3, 54.9, 116.6 (q, J_{C-F} = 276.9 Hz, CF_3), 126.7, 128.6 (2 C), 128.9 (2 C), 132.5 (q, J_{C-C-F} = 42.8 Hz), 138.5. ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_{10}H_9NF_3Cl$ 235.0374, found 235.0401.

***N*-(*n*-Hexyl)-2,2,2-trifluoroacetimidoyl Chloride (1n).** Bp: 49–50 °C (13 Torr). IR (neat): 1706 cm^{-1}. ^{1}H-NMR: δ 0.90 (t, 3 H, J = 6.5 Hz), 1.25–1.45 (m, 6 H), 1.60–1.80 (m, 2 H), 3.57–3.68 (m, 2 H). ^{13}C-NMR: δ 13.9, 22.6, 26.9, 28.9, 31.5, 53.6, 116.6 (q, J_{C-F} = 276.4 Hz, CF_3), 131.5 (q, J_{C-C-F} = 42.9 Hz). ^{19}F-NMR: δ −72.2 (s). HRMS: calcd for $C_8H_{13}NF_3Cl$ (M^+ − Cl) 180.1000, found 180.1033.

***N*-(2,2,2-Trifluoroethyl)benzimidoyl Chloride (8).** Bp: 84–85 °C (13 Torr). IR (neat): 1668 cm^{-1}. ^{1}H-NMR: δ 4.18 (q, 2 H, J = 9.3 Hz, CF_3CH_2), 7.38–7.58 (m, 3 H, Ph), 8.02–8.09 (m, 2 H, Ph). ^{13}C-NMR: δ 55.0 (q, J_{C-C-F} = 33.1 Hz), 124.5 (q, J_{C-F} = 276.7 Hz, CF_3), 128.4 (2 C), 129.1 (2 C), 132.2, 134.8, 148.2. ^{19}F-NMR: δ −71.6 (t, J = 9.2 Hz). HRMS: calcd for $C_9H_7NF_3Cl$ 221.0218, found 221.0243.

***N*-(*p*-Anisyl)-2,2,2-trifluoroacetimidoyl Bromide (2).** To a solution of CBr_4 (3.8 g, 11.4 mmol) in dry CH_2Cl_2 (15 mL) at 0 °C was added a mixture of Ph_3P (4.1 g, 15.6 mmol), Et_3N (0.86 mL, 6.2 mmol), and TFA (0.4 mL, 5.2 mmol) dropwise. Subsequently, *p*-anisidine (0.76 g, 6.2 mmol) was added. The mixture was stirred for 6.5 h at ambient temperature in the dark. The reaction mixture was distilled under reduced pressure, and the distillate was purified by silica gel column chromatography with hexane to afford **2** (1.23 g, 84%) as a yellow oil. Bp: 80–90 °C (14 Torr). IR (neat): 1696 cm^{-1}. ^{1}H-NMR: δ 3.81 (s, 3 H, OMe), 6.94–7.02 (m, 2 H, Ar), 7.21–7.30 (m, Ar). ^{13}C-NMR: δ 55.2, 114.1 (2 C), 116.6 (q, J_{C-F} = 277.2 Hz, CF_3), 121.4 (q, J_{C-C-F} = 43.2 Hz), 122.9 (2 C), 136.7, 159.5. ^{19}F-NMR: δ −70.9 (s). HRMS: calcd for $C_9H_7NOF_3Br$ (M^+ − Br) 202.0479, found 202.0478.

***N*-(*p*-Anisyl)-2,2,2-trifluoroacetimidoyl Iodide (3).** A mixture of NaI (1.9 g, 12.7 mmol) and **4** (1.0 g, 4.2 mmol) in acetone (10 mL) was stirred under a N_2 atmosphere at room temperature in the dark overnight. The mixture was washed with aqueous $Na_2S_2O_3$ and extracted with AcOEt. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane to give **3** quantitatively. IR (neat); 1682 cm^{-1}. ^{1}H-NMR: δ 3.85 (s, 3 H, OMe), 6.94–7.08 (m, 4 H, Ar). ^{13}C-NMR: δ 55.3, 111.8 (q, J_{C-C-F} = 41.7 Hz), 114.4 (2 C), 115.2 (q, J_{C-F} = 278.2 Hz, CF_3), 120.6 (2 C), 141.0, 159.1. ^{19}F-NMR: δ −70.3 (s). HRMS: calcd for $C_9H_7NOF_3I$ 328.9524, found 328.9496.

***N*-(*p*-Anisyl)-2,2,3,3,3-pentafluoropropanimidoyl Chloride (4a).** A two-necked flask with a septum cap, a Teflon-coated magnetic stir bar, and a condenser was charged with pentafluoropropanoic acid (1.0 g, 6.1 mmol), Ph_3P (6.4 g, 24.4 mmol), and CCl_4 (5.9 mL, 61 mmol). Then, Et_3N (1.0 mL, 7.3 mmol) was added dropwise to the mixture at ice-bath temperature. Subsequently, *p*-anisidine (0.9 g, 7.3 mmol) was added. The mixture was refluxed for 12 h and filtered through a silica gel column with ether. After evaporation of the solvent, the residue was purified by silica gel column chromatography with hexane to give **4a** (1.68 g, 96%) as a liquid. IR (neat): 1682 cm^{-1}. ^{1}H-NMR: δ 3.86 (s, 3 H, OMe), 6.94–7.02 (m, 2 H, Ar), 7.33–7.42 (m, 2 H, Ar). ^{13}C-NMR: δ 55.4, 108.1 (tq, J_1 = 259.4 Hz, J_2 = 37.6 Hz, CF_3), 114.2, 118.2 (qt, J_1 = 286.7 Hz, J_2 = 35.4 Hz, CF_2), 124.7, 128.0 (t, J = 33.5 Hz, C=N), 135.3, 159.8. ^{19}F-NMR: δ −81.7, −114.0. HRMS: calcd for $C_{10}H_7NOF_5Cl$ 287.0135, found 287.0107.

***N*-(*p*-Anisyl)perfluorooctanoimidoyl Chloride (4b).** Colorless crystals. Mp: 35–37 °C. IR (Nujol): 1668 cm^{-1}. ^{1}H-NMR: δ 3.85 (s, 3 H, OMe), 6.91–7.00 (m, 2 H, Ar), 7.30–7.37 (m, 2 H, Ar). ^{13}C-NMR: δ 55.3, 114.2 (2 C), 124.6 (2 C), 128.6 (t, J_{C-F} = 32.2 Hz, CF_3), 135.7, 159.9. ^{19}F-NMR: δ −81.4, −110.3, −121.1, −121.5, −122.6, −123.3, −126.7. HRMS: calcd for $C_{15}H_7NOF_{15}Cl$ 536.9975, found 536.9959.

Supplementary Material Available: ^{1}H- and ^{19}F-NMR spectra of compounds **1a–1n**, **2**, **3**, **8**, **4a**, and **4b** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS. Ordering information is given on any current masthead page.