APT spectrum δ syn conformer 10.8 (CH_3), 25.5 (CH_2 of C_2H_5 group), 36.5 (C-6), 54.2 (C-3), 56.8 (C-2), 59.8 (C-7), 134.1 and 137.3 (ipso carbons attached to C-2 and C-6), 172.8 (carbonyl carbon); anti conformer 11.0 (CH_3), 26.1 (CH_2 of C_2H_5 group, 36.5 (C-6), 48.4 (C-7), 55.0 (C-3), 70.2 (C-2), 135.2 and 135.9 (ipso carbons attached to C-2 and C-6), 173.0 (carbonyl carbon), 126.0, 126.2, 127.0, 127.7, 127.8, 127.9, 128.0, 128.2, 128.4 and 128.5 (aromatic carbon signals other than ipso carbons for both syn and anti conformers); MS *m/z* (relative intensity 323 (M^+), 305 (2.0), 295 (1.9), 294 (17.4), 293 (71.3), 132 (100). Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.56; H, 6.54; N, 12.99. Found: C, 70.63; H, 6.61; N, 12.92.

***t*-3-Isopropyl-1-nitroso-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one (19).** The same procedure as that for **17** was followed using **14** (2.1 g, 6.82 mmol) which was converted to colorless needles of **19** (yield 75%): mp 215–218 °C; IR (KBr) 3220 (CO*NH*), 1675 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ syn conformer 0.94 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.01 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.79 (d sep, *J* = 3.4 and 6.8 Hz, 1 H, C*H*Me_2), 3.23 (ddd, *J* = 1.5, 7.8, and 13.5 Hz, 1 H, H-6_{eq}), 3.75 (dd, *J* = 12.0 and 13.4 Hz, 1 H, H-6_{ax}), 4.17 (m, *J* = 3.4, 6.6 and 10.7 Hz, 1 H, H-3_{ax}), 5.72 (bs, NH), 6.42 (d, *J* = 10.7 Hz, 1 H, H-2_{ax}), 6.52 (dd, *J* = 7.8 and 11.8 Hz, 1 H, H-7_{ax}); anti conformer 1.06 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.08 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.96 (d sep, *J* = 3.7 and 6.9 Hz, 1 H, C*H*Me_2), 2.98 (ddd, *J* = 1.5, 6.7 and 13.2 Hz, 1 H, H-6_{eq}), 3.55 (dd, *J* = 12.9 and 12.7 Hz, 1 H, H-6_{ax}), 4.36 (m, *J* = 3.7, 5.9 and 10.0 Hz, 1 H, H-3_{ax}), 5.95 (bs, NH), 6.14 (d, *J* = 10.0 Hz, 1 H, H-2_{ax}), 6.69 (dd, *J* = 6.7 and 12.4 Hz, 1 H, H-7_{ax}), 6.8–7.4 (aromatic protons corresponding to both syn and anti conformers); ^{13}C NMR ($CDCl_3$) APT Spectrum δ syn conformer 15.9 and 20.6 (methyl groups), 29.0 ($CHMe_2$), 36.5 (C-6), 53.8 (C-2), 57.1 (C-3), 59.9 (C-7), 134.1 and 137.4 (ipso carbons at C-2 and C-7), 172.6 (carbonyl carbon); anti conformer 15.4 and 20.6 (methyl groups), 28.3 ($CHMe_2$), 36.4 (C-6), 48.6 (C-7), 57.7 (C-3), 67.7 (C-2), 135.3 and 136.0 (ipso carbons at C-2 and C-7), 172.6 (carbonyl carbon), 126.0, 126.1, 127.1, 127.7, 127.8, 127.9, 128.1, 128.5 and 128.6 (aromatic carbons other than ipso carbons corresponding to both syn and anti conformers); MS *m/z* (relative intensity) 337 (M^+), 307 (50.74), 293 (15.3), 250 (5.8), 132 (100). Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45. Found: C, 70.93; H, 6.83; N, 12.37.

***t*-3,*t*-6-Dimethyl-1-nitroso-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one (20).** The same procedure as for **16** was followed. Powdered crystals of **15** (2.0 g, 6.80 mmol) were converted to colorless needles of **20** (yield 85%): mp 217–218 °C; IR (KBr) 3200 (CO*NH*), 1675 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ syn conformer 1.23 (d, *J* = 6.4 Hz, 3 H, CH_3 at C-6), 1.42 (d, *J* = 6.4 Hz, 3 H, CH_3 at C-3), 3.98 (m, *J* = 6.4 and 10.6 Hz, 1 H, H-6_{ax}), 4.47 (m, *J* = 6.5, 10.9, and 4.5 Hz, 1 H, H-3_{ax}), 5.96 (d, *J* = 11.2 Hz, 1 H, H-2_{ax}), 6.02 (d, *J* = 10.4 Hz, 1 H, H-7_{ax}), 6.28 (NH); anti conformer 1.21 (d, *J* = 6.4 Hz, 3 H, CH_3 at C-6), 1.46 (d, *J* = 6.4 Hz, 3 H, CH_3 at C-3), 3.75 (m, *J* = 6.4 and 11.3 Hz, 1 H, H-6_{ax}), 4.72 (m, *J* = 6.4, 4.6 and 10.7 Hz, 1 H, H-3_{ax}), 5.77 (d, *J* = 10.6 Hz, 1 H, H-2_{ax}), 6.34 (d, *J* = 11.0 Hz, 1 H, H-7_{ax}), 6.22 (NH), 6.8–7.3 (aromatic protons corresponding to both syn and anti conformers); ^{13}C NMR ($CDCl_3$) δ syn conformer 14.8 (CH_3 at C-6), 18.4 (CH_3 at C-3), 37.5 (C-6), 46.5 (C-3), 58.6 (C-2), 67.0 (C-7), 134.2 and 135.4 (ipso carbons attached to C-2 and C-7), 173.9 (carbonyl carbon); anti conformer 14.2 (CH_3 at C-6), 18.9 (CH_3 at C-3), 37.4 (C-6), 46.9 (C-3), 53.6 (C-7), 70.5 (C-2), 134.7 and 134.9 (ipso carbons attached to C-2 and C-7), 174.1 (carbonyl carbon), 127.3, 127.5, 127.5, 127.6, 128.0, 128.1, 128.2, 128.3 and 128.5 (aromatic signals other than ipso carbons corresponding to both the syn and anti conformers); MS *m/z* (relative intensity) 323 (M^+), 293 (20.8), 279 (6.5), 264 (5), 250 (17.9), 132 (100), 127 (95). Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.57; H, 6.55; N, 12.99. Found: C, 70.34; H, 6.82; N, 12.69.

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N-Substituted 2,2,2-Trifluoroethanimidic Acid 1-Methylethylidene Hydrazides as Synthetic Blocks for Trifluoromethylated Nitrogen Heterocycles: Syntheses and Oxidative Cyclizations

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N-Substituted 2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazides have been prepared and allowed to react wtih *tert*-butyl hypochlorite in CH_2Cl_2. N-Aryl-, N-alkyl-, and *N*-(methoxycarbonyl)amidrazones **2–4** undergo three types of cyclizations via the initially formed *N*-chloro intermediates leading to 3-(trifluoromethyl)-1,2,4-benzotriazines **5**, 3-(trifluoromethyl)-5-alkyltriazoles **8** and **9**, and 3-chloro-3-(trifluoromethyl)-4-*N*-(methoxycarbonyl)-5,5-dimethyltriazoline (**11**), respectively. Reaction mechanisms for the cyclizations are discussed.

Trifluoromethylated compounds have received an increasing amount of attention because of their unique nature for biological activities and high-performance material science.[1] Functionalized trifluoromethylated building blocks are subjects of active investigation.[2] Among them, trifluoromethylated C_2 blocks such as trifluoroacetonitrile,[3] 2,2,2-trifluoroethyl tosylate,[4] trifluoroacetaldehyde ethyl

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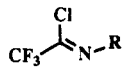
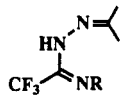
Chart I



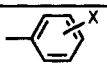
1



2: R= Aryl
3: R= Alkyl
4: R= Methoxycarbonyl

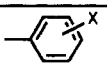
hemiacetal,[5] 1-chloro[6] or 1-methoxy-2,2,2-trifluoroethyl phenyl sulfide,[7] (2,2,2-trifluoroethyl)phenyliodonium triflate,[8] and 1,1,1-trichloro-2,2,2-trifluoroethane[9] have been derived from trifluoroacetic acid derivatives and employed for syntheses of a variety of trifluoromethylated compounds via further elongations. *N*-Hydroxytrifluoroacetimidoyl bromide[10] and N-aryltrifluoroacetimidoyl chlorides[11] are useful for the syntheses of trifluoromethylated heterocycles. We have shown nucleophilic substitutions of N-substituted acetimidoyl chlorides (1) with carbon and nitrogen nucleophiles[12] and palladium-catalyzed alkenylation and alkynylation of 1[13] and have demonstrated transformations of 1 to trifluoromethylated nitrogen heterocycles. The imidoyl chlorides 1 are stable, easily handled, and thus useful as the starting compounds for syntheses of trifluoromethylated compounds. N-Substituted 2,2,2-trifluoroethanimidic acid N-substituted hydrazides [N^1,N^3-substituted 2,2,2-trifluoroacetamidrazones[14]] **2–4** which would be prepared from 1 are of interest as novel trifluoromethylated synthetic blocks. Amidrazones are known as precursors for 1,2,4-triazoles and 1,2,4-triazines.[14] But there are only a few reports of the chemistry of N-substituted 2,2,2-trifluoroethanimidic acid hydrazides.[15] Here, we describe preparations and oxidative cyclizations of N-aryl-, N-alkyl-, and *N*-(methoxycarbonyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazides **2–4**.

Table I. Preparation of Amidrazones 2 from Imidoyl Chlorides 1[a]

entry		R	time (h)	2 yield (%)
				
1	**1a**	X = 4-CH_3O	5	81
2	**1b**	X = 4-CH_3	5	80
3	**1c**	X = 4-Cl	0.5	75
4	**1d**	X = 3-Cl	0.5	73
5	**1e**	X = 2-CH_3O	5	67[d]
6	**1f**	X = 3,4-Cl	0.5	75
7	**1g**	X = 3-CH_3O	2	65
8[b]	**1h**	X = 2,6-CH_3	5	77
9	**1i**	naphthyl	3	72
10[b]	**1j**	*n*-hexyl	5	89
11[b]	**1k**	phenethyl	5	79
12[c]	**1l**	CO_2Me		13

[a] 5 equiv of acetone azine and 1 equiv of hydrazine monohydrate were used in the reaction. The reactions were carried out in DMF and water at room temperature. [b] Same conditions except 5 equiv of hydrazine monohydrate was used. [c] Amidrazone **2l** was prepared from the corresponding ethanamide; see Experimental Section. [d] Two isomers exist; see Experimental Section.

Table II. Preparation of 3-(Trifluoromethyl)-1,2,4-benzotriazines[a]

entry		Ar	5 product	yield (%)
				
1	**2a**	X = 4-CH_3O	Y = 7-CH_3O	81
2	**2b**	X = 4-CH_3	Y = 7-CH_3	64
3	**2c**	X = 4-Cl	Y = 7-Cl	47
4	**2d**	X = 3-Cl	Y = 6-Cl	51
5	**2e**	X = 2-CH_3O	Y = 5-CH_3O	36
6	**2f**	X = 3,4-Cl	Y = 6,7-Cl, 7,8-Cl	75[b]
7	**2i**			76[c]

[a] 2.2 equiv of *tert*-butyl hypochlorite was used in all reactions. The reactions were carried in CH_2Cl_2 at −70 °C and then at room temperature. [b] Yields of 6,7-dichloro and 7,8-dichloro products are 45 and 30%, respectively. [c] Product is **7**.

Results and Discussion

N-Substituted ethanimidic acid hydrazides have been prepared by the reactions of N-substituted ethanimidic acid ester with hydrazines,[16] imidamides with isocyanate,[17] and *S*-methylthioamidium iodides with hydrazines.[18] In this study, reaction of **1** with acetone hydrazone generated in situ was chosen for the preparation of the amidrazones **2–4**. The imidoyl chloride **1a** was added to a solution of acetone azine[19] and hydrazine monohydrate in a mixture of DMF and water, and the mixture was stirred for 5 h at room temperature to give **2a** in 81% yield. The results of reactions with other imidoyl chlorides are summarized in Table I. N-Aryl compounds are obtained in reasonable yields. A chlorine atom on the aromatic ring enhanced the reaction rate (entries 3, 4, and 6). N-Alkyl and 2,6-dimethylphenyl compounds reacted slowly with the azine under the above conditions, but the reaction proceeded smoothly in the presence of 5 equiv of acetone azine and hydrazine monohydrate (entries 8, 10, and 11). It is well-known that alkanoimidoyl and benzoimidoyl halides [PhC(Cl)=NR] are very susceptible to hydrolysis.[20] However, it is noteworthy that the chlorides **1** are not hydrolyzed to the corresponding amides in the aqueous

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(14) We adopt the nomenclature recommended for systems capable of tautomerism according to $R^1C(NHR^2)=NNR^3{}_2R^1C(=NR^2{}_3)NHNR^3{}_2$ and refer to them as amidrazones: Neilson, D. G.; Roger, R.; Heatlie, J. M. W.; Newlands, L. R. *Chem. Rev.* **1970**, *70*, 151.
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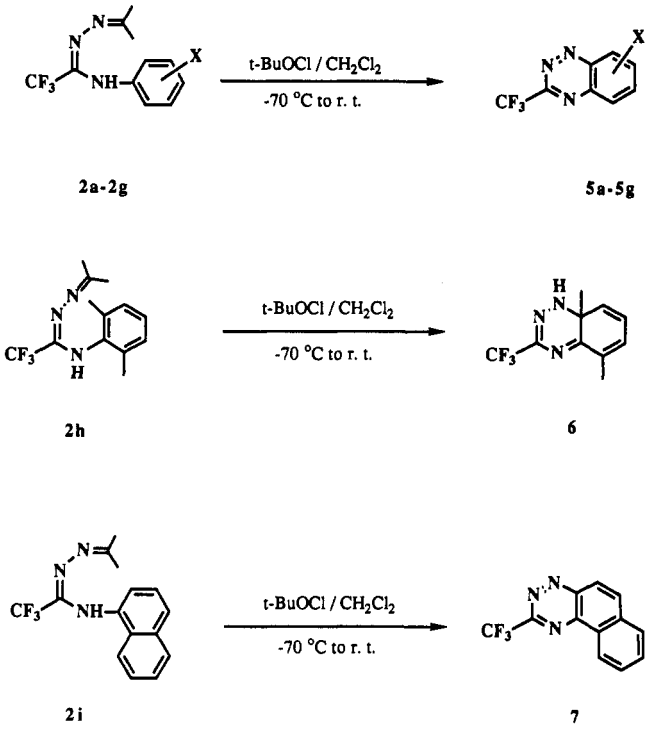
Scheme I



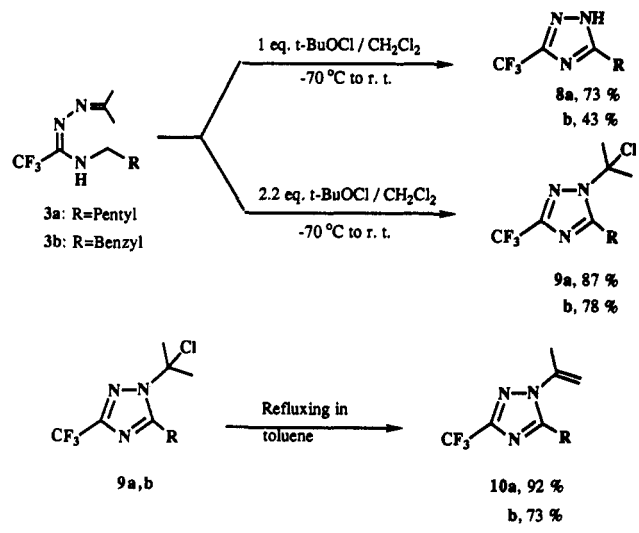
solution employed and react preferentially with acetone hydrazone. *N*-Methoxycarbonyl compound **4** was obtained from the corresponding ethanamide (**1**, R = CO_2Me) in 13% yield.

The amidrazone **2a** was allowed to react with 2.2 equiv of *tert*-butyl hypochlorite in CH_2Cl_2 at −70 °C, providing an orange solution which was slowly warmed to room temperature. On stirring for 4 h, 7-methoxy-3-(trifluoromethyl)-1,2,4-benzotriazine (**5a**) was obtained (81%). The amount of *tert*-butyl hypochlorite affected the yield of **5**. The yield increased gradually (27%, 76%, and 81%) by increasing the amount of *t*-BuOCl (0.55, 1.1, and 2.2 equiv). The ^{1}H-NMR of **2a** revealed three aromatic protons δ 7.77 (d, J = 2.7 Hz), 7.82 (dd, J_1 = 9.1 Hz, J_2 = 2.7 Hz), and 8.11 (d, J = 9.1 Hz) and no methyl group and suggested a 1,2,4-substituted benzene ring. ^{13}C-NMR showed two quartets δ 118.9 (J = 276.6 Hz) and δ 145.2 (J = 31.9 Hz) due to $CF_3C(NHR)$=NR moiety. The MS spectrum of **5a** showed m/z = 229 (M^+) and 201 ($M^+ - N_2$).

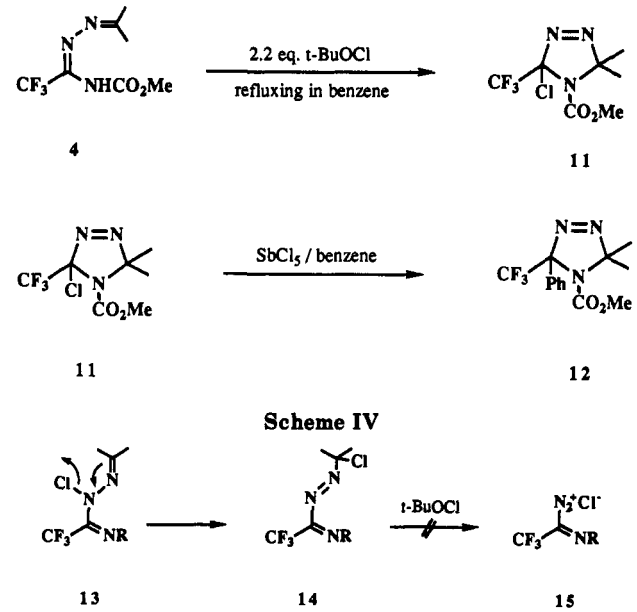
The results of the cyclization of **2** are summarized in Table II. The unsymmetrically substituted aromatic derivative **2f** afforded two isomers (entry 6). Similarly, the amidrazone **2i** was transformed into **7** (76%). 2,6-Substituted aromatics **2h** provided the nonaromatized compound **6** (34%).

In contrast to N-arylamidrazones, N-alkyl compounds underwent triazole formation. On treating the amidrazones **3a** and **3b** with 1 equiv of *t*-BuOCl in CH_2Cl_2 at −70 °C and raising the reaction temperature to room temperature slowly, the triazoles **8a** and **8b** were obtained in 73% and 43% yields, respectively. The ^{13}C- and ^{1}H-NMR and MS spectra of both **8a** and **8b** revealed no isopropyl moiety. On the other hand, upon treatment with 2.2 equiv of the chlorite, *N*-(1-chloro-1-methylethyl)triazoles **9a** and **9b** were obtained in 87% and 78% yields, respectively. The triazoles **9a** and **9b** were converted to **10a** (92%) and **10b** (73%) on refluxing in toluene. Both ^{13}C- and ^{1}H-NMR spectra of **10a** and **10b** showed clearly signals of olefinic methylene groups of isopropenyl groups at δ 112.7 and 113.3 for ^{13}C, and 5.14 and 5.34, 5.06 and 5.28 for ^{1}H, respectively.

Scheme II



Scheme III



Scheme IV

N-(Methoxycarbonyl)amidrazone **4** reacted more slowly than the corresponding N-aryl compounds and was transformed into the chloride **11** (44%) on reaction with *tert*-butyl hypochlorite in refluxing benzene. On treating **11** with antimony pentachloride in benzene, **12** was obtained in 32% yield.

Reaction Mechanism

One of the plausible mechanisms of the formation of **5** from **2** would be a sequence of formation of (trifluoromethyl)iminodiazonium ion **15** and intramolecular diazo coupling. Bulow reported that *m*-nitroanilinoformaldehyde 2,4-dichlorophenylhydrazone reacted with molecular chlorine to give 2,4-dichlorophenyldiazonium salt, which was subsequently trapped by 2-naphthol.[21] When **2**, **3**, and **4** were treated with *t*-BuOCl in the presence of anisole, no intramolecularly diazo-coupled products were obtained. They underwent intramolecular cyclizations preferentially as shown in schemes I–III.

Moon reported that chlorination of 1,2,3-indantrione 2-phenylhydrazone with chlorine led to 2,2-dichloro-1,3-indandione and benzenediazonium chloride, while its re-

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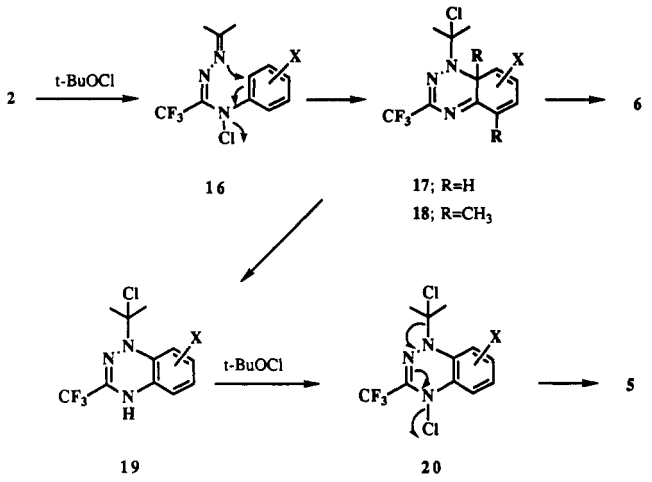
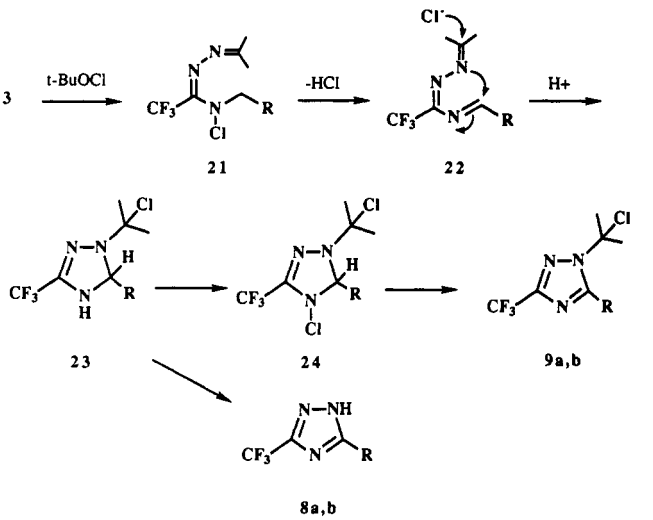
Scheme V



Scheme VI



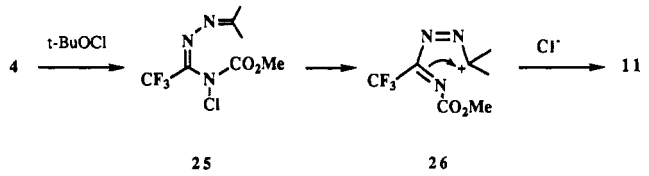
action with *tert*-butyl hypochlorite afforded 2-chloro-2-(phenylazo)-1,3-indandione.[22] Analogously, a sequence of N-chlorination of **2** with *t*-BuOCl and dechlorinative cyclization would result in the formation of intermediate **17** (R = H), which would undergo aromatization to **19** via prototropy (Scheme V). Oxidation of **19** with another mole of *t*-BuOCl provides **5** via **20**. Autoxidation of **19** by air during workup would be an alternative pathway to **5** since 1.1 equiv of *t*-BuOCl provided **5** in 76% yield. The methylated intermediate **18** from **2h** does not undergo aromatization and instead suffers acid-catalyzed C–N bond cleavage leading to **6** as a final product.

A proposed mechanism for the transformation of N-alkyl compounds **3a** and **3b** to **8a,b** and **9a,b** is shown in Scheme VI. In contrast to N-aryl intermediate **16**, the initial intermediate **21** releases hydrogen chloride to give **22** which undergoes acid-catalyzed ring closure to **23**. In the presence of an excess amount of *t*-BuOCl, N-chlorination of **23** followed by dehydrochlorination of **24** results in **9a** and **9b** as a final product. Acid-catalyzed C–N bond cleavage from the chloroisopropyl moiety of **23** followed by autoxidation during workup would provide **8a** and **8b** in the reaction with 1 equiv of *t*-BuOCl.

In the case of the *N*-methoxycarbonyl compound **4**, elimination of chloride from **25** and addition of chloride ion to **26** would produce **11** as a final product. On adding *t*-BuOCl to **4**, a pair of methyl singlets of **4** in ^{1}H-NMR

(22) Moon, M. W. *J. Org. Chem.* **1972**, *37*, 386.

Scheme VII



(δ 2.04 and 2.02) disappeared immediately and a new set of singlets (δ 2.10 and 2.12) of a possible intermediate **25** appeared. The downfield shift of the methyl signals suggests that N-chlorination occurs although the position of chlorine can not be fixed unequivocally. The intensity of the two singlets decreased gradually while those of methyl signals of **11** (δ 1.80 and 1.78) increased.

In conclusion, N-substituted amidrazones **2–4** react with *t*-BuOCl to give *N*-chloro intermediates which undergo three types of cyclizations depending on the N substituents. In the case of N-aryl compounds, dechlorinative ring closure occurs between the aromatic ring and nitrogen of acetone hydrazone, leading to 3-(trifluoromethyl)-1,2,4-benzotriazines **5**. While in the case of N-alkyl compounds, dehydrochlorination of the *N*-chloro intermediate proceeds preferentially on the N-alkyl group, and subsequent acid-catalyzed cyclization results in the formation of triazoles **8** and **9**. *N*-Methoxycarbonyl compound **4** provides another type of triazoline **11** because it cannot undergo either dehydrochlorination or aryl participation.

Experimental Section

The ^{1}H, ^{13}C, and ^{19}F-NMR spectra were measured using TMS as an internal standard for ^{1}H and ^{13}C-NMR and C_6F_6 for ^{19}F-NMR. Both electron impact and high-resolution mass spectra (HRMS) were obtained at 20 and 70 eV. Melting points and boiling points are uncorrected. Boiling points are indicated as an air-bath temperature. *tert*-Butyl hypochlorite was prepared by the reaction of *t*-BuOH with NaOCl and was dried over $CaCl_2$.[23]

***N*-*p*-Anisyl-2,2,2-trifluoroethanimidic Acid 1-Methylethylidene Hydrazide (2a).** To a solution of acetone azine (470 mg, 4.2 mmol) and hydrazine monohydrate (146 mg, 2.92 mmol) in DMF (4 mL)/H_2O (2 mL) was added *N*-*p*-anisyl-2,2,2-trifluoroethanimidoyl chloride (**1a**, 0.84 mmol) at rt, and the mixture was stirred for 5 h. The residue was extracted with ethyl acetate and hexane (1:1). The organic layer was washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The crude product was chromatographed on silica gel (hexane–AcOEt (2:1)) to give **2a** (81%) as white crystals. In a case of the N-alkyl compounds, hydrazine monohydrate (700 mg, 14.6 mmol) was used: mp 54–58 °C; IR (Nujol) 3284 (NH), 1632 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.11 (s, 3 H), 3.81 (s, 3 H), 6.85 (d, 2 H, J = 8.9 Hz), 7.14 (d, 2 H, J = 8.9 Hz), 7.40–7.55 (br, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.3 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 10.4, 25.2, 55.2, 113.9 (2 C), 118.9 (q, J_{C-F} = 276.6 Hz, CF_3), 128.3 (2 C), 130.2, 145.2 (q, J_{C-C-F} = 31.9 Hz), 158.3, 167.4; MS m/z (relative intensity) 273 (M^+, 18), 259 (40), 258 (100), 202 (14), 147 (24), 122 (21), 108 (14), 77 (8), 56 (62), 41 (6); HRMS calcd for $C_{12}H_{14}F_3N_3O$ [M^+] 273.1088, found 273.1100.

***N*-*p*-Tolyl-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2b):** yield 80%; white crystals; mp 37–38 °C; IR (neat) 3324 (NH), 1642 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.07 (s, 3 H), 2.10 (s, 3 H), 2.34 (s, 3 H), 7.07 (d, J = 8.6 Hz, 2 H), 7.13 (d, J = 8.6 Hz, 2 H), 7.50–7.60 (br, 1 H); ^{19}F-NMR (187.7 MHz, $CDCl_3$) δ 96.5 (s, 3 F). Anal. Calcd for $C_{12}H_{14}F_3N_3$: C, 56.03; H, 5.49; N, 16.33. Found: C, 55.93; H, 5.65; N, 16.20.

***N*-(4-Chlorophenyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2c):** yield 75%; white crystals;

(23) Mintz, M. J.; Walling, C. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 184.

(24) 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 and the SC-NMR Laboratory of Okayama University for the 500-MHz NMR analysis.

mp 61–62 °C; IR (Nujol) 3172 (NH), 1632 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.09 (s, 3 H), 2.12 (s, 3 H), 2.27 (s, 3 H), 7.11 (d, J = 8.8 Hz, 2 H), 7.30 (d, J = 8.8 Hz, 2 H), 7.55–7.65 (br, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.5 (s, 3 F). Anal. Calcd for $C_{11}H_{11}F_3N_3Cl$: C, 47.58; H, 3.99; N, 15.13. Found: C, 47.63; H, 3.94; N, 15.18.

***N*-(3-Chlorophenyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2d)**: yield 73%; a viscous oil; bp 116–118 °C (3 mmHg); IR (neat) 3296 (NH), 1646 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.12 (s, 3 H), 7.00–7.40 (m, 4 H), 7.60–7.75 (br, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.4 (s, 3 F). Anal. Calcd for $C_{11}H_{11}F_3N_3Cl$: C, 47.58; H, 3.99; N, 15.13. Found: C, 47.59; H, 3.79; N, 15.03.

***N*-(3-Methoxyphenyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2g)**: yield 65%; a viscous oil; bp 102 °C (4 mmHg); IR (Nujol) 3320 (NH), 1636, 1604 cm^{-1}, ^1H-NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.11 (s, 3 H), 3.79 (s, 3 H), 6.19–6.81 (m, 3 H), 7.22 (t, J = 7.8 Hz, 1 H), 7.56 (br s, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.5 (s, 3 F). Anal. Calcd for $C_{12}H_{14}F_3N_3O$: C, 52.75; H, 5.16; N, 15.38. Found: C, 52.47; H, 5.29; N, 15.04.

***N*-(2-Methoxyphenyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2e and 2e′)**: yield 67% as a mixture of **2e** and **2e′** (2:1); a viscous oil; bp 133–134 °C (4 mmHg); IR (neat) 3328 (NH), 1644, 1618, 1602 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.09 (s, 3 H), 3.84 (s, 3 H, OCH_3 of **2e**), 3.92 (s, 3 H, OCH_3 of **2e′**), 6.85–7.21 (m, 4 H), 7.39 (br, 1 H, NH of **2e**), 7.59 (br, 1 H, NH of **2e′**); ^{19}F-NMR (187.7 MHz, $CDCl_3$) δ 95.2 (s, 3 F, CF_3 of **2e**, 96.6 (s, 3 F, CF_3 of **2e′**). Anal. Calcd for $C_{12}H_{14}F_3N_3O$: C, 52.75; H, 5.16; N, 15.38. Found: C, 52.82; H, 5.25; N, 14.98.

***N*-(3,4-Dichlorophenyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2f)**: yield 75%; a viscous oil; bp 130–132 °C (4 mmHg); IR (neat) 3304 (NH), 1640, 1594 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.11 (s, 3 H), 7.01 (d, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1 H), 7.26 (br s, 1 H), 7.39 (d, J = 8.5 Hz, 1 H), 7.58 (br, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.3 (s, 3 F). Anal. Calcd for $C_{11}H_{10}F_3N_3Cl_2$: C, 42.33; H, 3.22; N, 13.46. Found: C, 42.15; H, 3.07; N, 13.26.

***N*-(2,6-Dimethylphenyl)-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2h)**: yield 77%; white crystals; mp 94–95 °C; IR (Nujol) 3296 (NH), 1640, 1612 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.05 (s, 3 H), 2.11 (s, 3 H), 2.27 (s, 6 H), 7.02–7.16 (m, 4 H); ^{19}F-NMR ($CDCl_3$) δ 93.0 (s, 3 F). Anal. Calcd for $C_{13}H_{16}F_3N_3$: C, 57.56; H, 5.94; N, 15.49. Found: C, 57.41; H, 6.18; N, 15.59.

***N*-1-Naphthyl-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (2i)**: yield 72%; white crystals; mp 66–69 °C; IR (Nujol) 3308 (NH), 1640, 1618 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.14 (s, 3 H), 7.39–8.10 (m, 8 H); ^{19}F-NMR ($CDCl_3$) δ 95.8 (s, 3 F). Anal. Calcd for $C_{12}H_6F_3N_3$: C, 61.43; H, 4.81; N, 14.33. Found: C, 61.56; H, 4.93; N, 14.06.

***N*-*n*-Hexyl-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (3a)**: yield 89%; a viscous oil; bp 95–97 °C (5 mmHg); IR (neat) 3368 (NH), 2936, 1642 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.89 (t, J = 6.6 Hz, 3 H), 1.20–1.45 (m, 6 H), 1.45–1.65 (m, 2 H), 2.03 (s, 3 H), 2.04 (s, 3 H), 3.27 (q, J = 6.8 Hz, 2 H), 5.68 (br, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.7 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 13.9, 18.2, 22.5, 25.2, 26.2, 30.7, 31.3, 43.2, 119.1 (q, J_{C-F} = 276.1 Hz, CF_3), 146.4 (q, J_{C-C-F} = 32.3 Hz), 166.2; MS m/z (relative intensity) 251 (M^+, 100), 236 (24), 195 (17), 180 (93), 152 (100), 126 (55), 100 (34), 72 (20), 58 (100), 43 (100). Anal. Calcd for $C_{11}H_{20}F_3N_3$: C, 52.58; H, 8.02; N, 16.72. Found: C, 52.93; H, 8.30; N, 16.64.

***N*-Phenethyl-2,2,2-trifluoroethanimidic acid 1-methylethylidene hydrazide (3b)**: yield 79%; a viscous oil; bp 106 °C (6 mmHg); IR (neat) 3360 (NH), 2920, 1644 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.00 (s, 3 H), 2.01 (s, 3 H), 2.85 (t, J = 7.1 Hz, 2 H), 3.52 (dt, J = 7.1 Hz, 2 H), 5.65–5.75 (br, 1 H), 7.18–7.36 (m, 5 H); ^{19}F-NMR ($CDCl_3$) δ 93.7 (s, 3 F). Anal. Calcd for $C_{13}H_{16}F_3N_3$: C, 57.56; H, 5.94; N, 15.49. Found: C, 57.59; H, 6.09; N, 15.49.

***N*-(Methoxycarbonyl)-2,2,2-trifluoroethanimidic Acid 1-Methylethylidene Hydrazide (4)**. A mixture of *N*-(methoxycarbonyl)-2,2,2-trifluoroethanamide (5.0 g, 0.029 mol) and phosphorus pentachloride (6.3 g, 0.035 mol) was heated at 130 °C for 4 h. After being cooled, the mixture was distilled at 100–130 °C at atmospheric pressure. The distillate was added to a solution of acetone azines (9.81 g, 0.088 mol) and hydrazine monohydrate (1.46 g, 0.029 mol) in THF at −70 °C, and the solution was stirred at rt 3 h. After filtration of the mixture, the filtrate was concentrated and extracted with AcOEt. The extracts were washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–AcOEt) to give a white solid, which was recrystallized from hexane, affording **2l** (0.884 g, 13%) as white crystals: mp 64–71 °C; IR (Nujol) 3136 (NH), 1752, 1596 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.02 (s, 3 H), 2.04 (s, 3 H), 3.71 (s, 3 H), 8.00–8.30 (br s, 1 H); ^{19}F-NMR ($CDCl_3$) δ 94.4 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 19.1, 25.4, 53.2, 118.1 (q, J_{C-F} = 274.4 Hz, CF_3), 139.7 (q, J_{C-C-F}, J = 37.7 Hz), 150.4, 171.8; MS m/z (relative intensity) 225 (M^+, 28), 210 (20), 193 (100), 166 (62), 146 (12), 124 (30), 105 (10), 76 (5), 56 (52); HRMS calcd for $C_7H_{10}F_3N_3O_2$ [M^+] 225.0724, found 225.0756.

3-(Trifluoromethyl)-7-methoxy-1,2,4-benzotriazine (5a). To a solution of **2a** (100.4 mg, 0.37 mmol) in CH_2Cl_2 (1 mL) was added dropwise *t*-BuOCl (87.9 mg, 0.81 mmol) in CH_2Cl_2 (0.5 mL) at −70 °C. The orange solution was stirred at rt for 4 h. After aqueous $Na_2S_2O_4$ was added, the reaction mixture was extracted several times with ethyl acetate. The extracts were washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–AcOEt) to give **5a** (72.5 mg, 81%) as yellow crystals: mp 121–122 °C; IR (Nujol) 1616 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 4.11 (s, 3 H), 7.77 (d, J = 2.7 Hz, 1 H), 7.82 (dd, J_1 = 9.1 Hz, J_2 = 2.7 Hz, 1 H), 8.11 (d, J = 9.1 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.4 (s, 3 F); MS m/z (relative intensity) 229 (M^+, 60), 201 (83), 106 (100), 63 (100). Anal. Calcd for $C_9H_6F_3N_3O$: C, 47.17; H, 2.64; N, 18.34. Found: C, 47.30; H, 2.43 N, 18.43.

3-(Trifluoromethyl)-7-methyl-1,2,4-benzotriazine (5b): yield 64%; yellow crystals; mp 108–109 °C; IR (Nujol) 1624, 842, 718 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.73 (s, 3 H), 7.99 (dd, J_1 = 8.8 Hz, J_2 = 1.8 Hz, 1 H), 8.13 (d, J = 8.8 Hz, 1 H), 8.40 (d, J = 1.8 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.3 (s, 3 F); MS m/z (relative intensity) 213 (M^+, 25), 185 (62), 135 (4), 116 (4), 90 (100), 89 (80), 64 (12), 51 (4), 39 (4). Anal. Calcd for $C_9H_6F_3N_3$: C, 50.71; H, 2.84; N, 19.71. Found: C, 51.10; H, 2.79; N, 19.71.

3-(Trifluoromethyl)-7-chloro-1,2,4-benzotriazine (5c): 47% yield; yellow crystals; mp 78–80 °C; IR (Nujol) 1600, 902, 848, 800 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 8.10 (dd, J_1 = 9.1 Hz, J_2 = 2.2 Hz, 1 H), 8.22 (d, J = 9.1 Hz, 1 H), 8.70 (d, J = 2.2 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.2 (s, 3 F): MS m/z (relative intensity) 233 (M^+, 25), 205 (78), 155 (5), 110 (100), 75 (80), 50 (10). Anal. Calcd for $C_8H_3F_3N_3Cl$: C, 41.14; H, 1.29; N, 17.99. Found: C, 41.06; H, 1.08; N, 17.95.

3-(Trifluoromethyl)-6-chloro-1,2,4-benzotriazine (5d): 51% yield from **2d**; yellow crystals; mp 73–74 °C; IR (Nujol) 1596, 876, 764 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 8.03 (dd, J_1 = 9.1 Hz, J_2 = 2.2 Hz, 1 H), 8.25 (d, J = 2.2 Hz, 1 H), 8.65 (d, J = 9.1 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.1 (s, 3 F); MS m/z (relative intensity) 235 (M^+, 20), 233 (M^+, 50), 207 (50), 205 (10), 233 (30), 207 (15), 205 (50), 112 (30), 110 (100), 75 (55). Anal. Calcd for $C_8H_3F_3N_3Cl$: C, 41.14; H, 1.29; N, 17.99. Found: C, 41.05; H, 1.03 N, 17.94.

3-(Trifluoromethyl)-5-methoxy-1,2,4-benzotriazine (5e): 36% yield from **2e**; yellow crystals; mp 152–154 °C; IR (Nujol) 1606, 776, 752, 722 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 4.16 (s, 3 H), 7.41 (d, J = 8.2 Hz, 1 H), 8.01 (t, J = 8.2 Hz, 1 H), 8.27 (d, J = 8.2 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.6 (s, 3 F); MS m/z (relative intensity) 229 (M^+, 20), 201 (30), 106 (30), 76 (100), 63 (2), 50 (6). Anal. Calcd for $C_9H_6F_3N_3O$: C, 47.17; H, 2.64; N, 18.34. Found: C, 46.81; H, 2.37; N, 18.25.

3-(Trifluoromethyl)-6,7-dichloro-1,2,4-benzotriazine (5f): 45% yield from **2f**; yellow crystals; mp 73–74 °C; IR (Nujol) 1598, 888, 812 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 8.40 (s, 1 H), 8.84 (s, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.0 (s, 3 F); MS m/z (relative intensity) 271 (M^+, 2), 269 (M^+, 13), 267 (M^+, 20), 241 (30), 239 (45), 148 (10), 146 (60), 144 (100), 109 (25), 84 (10). Anal. Calcd for $C_8H_2F_3N_3Cl_2$: C, 35.85; H, 0.75; N, 15.68. Found: C, 36.07; H, 0.65; N, 15.69.

3-(Trifluoromethyl)-7,8-dichloro-1,2,4-benzotriazine (5f′): 30% yield from **2f**; yellow crystals; mp 162–163 °C; IR (Nujol) 1592, 932, 856 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 8.13 (d, J = 8.8 Hz, 1 H), 8.20 (d, J = 8.2 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.2 (s, 3 F); MS m/z (relative intensity) 271 (M^+, 7), 269 (M^+, 15), 267 (M^+, 20), 241 (35), 239 (60), 146 (60), 144 (100), 109 (50), 74 (15). Anal. Calcd for $C_8H_2F_3N_3Cl_2$: C, 35.85; H, 0.75; N, 15.68. Found: C, 36.07; H, 0.64 N, 15.85.

3-(Trifluoromethyl)naphtho-1,2,4-triazine (7): 76%; yellow crystals: mp 141–142 °C; IR (Nujol) 1602, 904, 854, 814, 772 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 7.88–8.07 (m, 3 H), 8.26 (d, J = 9.3 Hz, 1 H), 8.37 (d, J = 9.3 Hz, 1 H), 9.37 (d, J = 7.9 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 93.5 (s, 3 F); MS m/z (relative intensity) 249 (M^+, 30), 221 (30), 202 (5), 152 (5), 126 (100). Anal. Calcd for $C_{12}H_6F_3N_3$: C, 57.84; H, 2.43; N, 16.86. Found: C, 58.06; H, 2.25; N, 17.11.

5,8a-Dimethyl-3-(trifluoromethyl)-1,8a-dihydro-1,2,4-benzotriazine (6): 34%; yellow crystals; mp 93–95 °C; IR (Nujol) 3345 (NH) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.70 (s, 3 H), 2.17 (s, 3 H), 5.91 (d, J = 9.3 Hz, 1 H), 6.36 (dd, J_1 = 9.3 Hz, J_2 = 6.1 Hz, 1 H), 6.38 (br s, 1 H), 6.47 (d, J = 6.1 Hz, 1 H); ^{19}F-NMR ($CDCl_3$) δ 92.3 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 16.6, 18.1, 29.7, 48.7, 120.2 (q, J_{C-F} = 270.4 Hz, CF_3), 123.3, 130.6, 133.8, 138.8 (q, J_{C-C-F} = 36.9 Hz), 156.1; MS m/z (relative intensity) 229 (M^+, 4), 214 (100), 200 (25), 180 (3), 131 (15), 116 (4), 105 (30), 79 (12), 65 (4); HRMS calcd for $C_{10}H_{10}F_3N_3$ [M^+] 229.0826, found 229.0776.

3-(Trifluoromethyl)-5-pentyl-1,2,4-triazole (8a). To a solution of amidrazones **3a** (61.3 mg, 0.24 mmol) in CH_2Cl_2 (1 mL) was added dropwise t-BuOCl (0.24 mmol) in CH_2Cl_2 (0.5 mL) at −70 °C. The orange solution was stirred at rt for 7 h. After aqueous $Na_2S_2O_4$ was added, the reaction mixture was extracted several times with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–AcOEt (2:1)) to give **8a** (36.3 mg, 73%) as white crystals: mp 99–101 °C; IR (Nujol) 3156 (NH) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3 H), 1.20–1.50 (m, 6 H), 1.70–1.90 (m, 2 H), 2.86 (t, J = 7.8 Hz, 2 H); ^{19}F-NMR ($CDCl_3$) δ 96.4 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 13.7, 22.1, 26.2, 27.5, 31.1, 119.2 (q, J_{C-F} = 270.3 Hz, CF_3), 153.6 (q, J_{C-C-F} = 38.7 Hz), 159.7; MS m/z (relative intensity) 207 (M^+, 20), 206 (18), 188 (5), 178 (25), 164 (58), 151 (100), 131 (10). Anal. Calcd for $C_8H_{12}F_3N_3$: C, 46.37; H, 5.84; N, 20.28. Found: C, 46.22; H, 5.82; N, 20.23.

3-(Trifluoromethyl)-5-benzyl-1,2,4-triazole (8b): yield 44%; white crystals; mp 145–146 °C; IR (Nujol) 3140 (NH) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 4.22 (s, 2 H), 7.20–7.45 (m, 5 H), 9.00–12.00 (br s, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.4 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 31.1, 118.4 (q, J_{C-F} = 270.1 Hz, CF_3), 125.8, 127.4 (4 C), 134.6, 151.9 (q, J_{C-C-F} = 36.7 Hz), 156.0. Anal. Calcd for $C_{10}H_8F_3N_3$: C, 52.87; H, 3.55; N, 18.50. Found: C, 53.05; H, 3.38; N, 18.47.

1-(1-Chloro-1-methylethyl)-3-(trifluoromethyl)-5-pentyl-1,2,4-triazole (9a): 87%; a viscous oil; IR (neat) 2964, 1534, 1428, 1262, 1198, 1148, 804 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.92 (t, J = 7.0 Hz, 3 H), 1.30–1.50 (m, 6 H), 1.80–2.00 (m, 2 H), 2.27 (s, 6 H), 3.09 (t, J = 7.9 Hz, 2 H); ^{19}F-NMR ($CDCl_3$) δ 96.3 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 13.9, 22.3, 27.3, 28.8, 31.5, 33.7 (2 C), 80.9, 119.2 (q, J_{C-F} = 270.1 Hz, CF_3), 150.6 (q, J_{C-C-F} = 39.5 Hz), 159.3; MS m/z (relative intensity) 283 (M^+, 15), 248 (32), 227 (14), 207 (15), 192 (46), 178 (50), 164 (56), 151 (100), 77 (20), 56 (40), 41 (10); HRMS calcd for $C_{11}H_{17}F_3N_3Cl$ [M^+] 283.1062, found 283.1038.

1-(1-Chloro-1-methylethyl)-3-(trifluoromethyl)-5-benzyl-1,2,4-triazole (9b): yield 78%; white crystals; mp 37–39 °C; IR (neat) 1608, 752 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.19 (s, 6 H), 4.58 (s, 2 H), 7.20–7.38 (m, 5 H); ^{19}F-NMR ($CDCl_3$) δ 96.4 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 33.8 (2 C), 34.3, 81.3, 119.1 (q, J_{C-F} = 270.7 Hz, CF_3), 127.2, 128.5 (2 C), 128.8 (2 C), 134.9, 150.9 (q, J_{C-C-F} = 39.7 Hz), 156.9; HRMS calcd for $C_{13}H_{13}F_3N_3Cl$ [M^+] 288.0639, found 288.0597.

1-(1-Methylethenyl)-3-(trifluoromethyl)-5-pentyl-1,2,4-triazole (10a). A solution of **9a** (195.8 mg, 0.69 mmol) in toluene (3 mL) was heated at reflux for 20 h. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with AcOEt. Th extracts were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–AcOEt (2:1) to give **10a** (135.6 mg, 92%) as a colorless oil; bp 120 °C (3 mmHg); IR (neat) 2968, 1732, 1668, 1430, 1208 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.90 (t, J = 6.2 Hz, 3 H), 1.30–1.45 (m, 4 H), 1.70–1.90 (m, 2 H), 2.23 (s, 3 H), 2.82 (t, J = 7.9 Hz, 2 H), 5.14 (s, 1 H), 5.34 (s, 1 H); ^{19}F-NMR ($CDCl_3$) δ 96.3 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 13.7, 21.2, 22.1, 26.5, 27.3, 31.3, 112.7, 119.2 (q, J_{C-F} = 270.1 Hz, CF_3), 140.0, 152.6 (q, J_{C-C-F} = 39.2 Hz), 157.7; MS m/z (relative intensity) 247 (M^+, 5), 232 (100), 218 (16), 204 (68), 191 (75), 165 (15), 152 (16), 136 (6), 122 (30), 96 (52), 83 (10), 69 (6), 55 (84), 42 (18); HRMS calcd for $C_{11}H_{16}F_3N_3$ [M^+] 247.1295, found 247.1314.

1-(1-Methylethenyl)-3-(trifluoromethyl)-5-benzyl-1,2,4-triazole (10b): yield 73%; colorless oil; bp 120–124 °C (6 mmHg); IR (neat) 1668 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.08 (s, 3 H), 4.26 (s, 2 H), 5.06 (s, 1 H), 5.28 (s, 1 H), 7.15–7.38 (m, 5 H); ^{19}F-NMR ($CDCl_3$) δ 96.4 (s, 3 F); ^{13}C-NMR ($CDCl_3$) δ 21.0, 32.5, 113.3, 119.2 (q, J_{C-F} = 270.0 Hz, CF_3), 127.2, 128.4 (2 C), 128.9 (2 C), 135.0, 140.1, 152.9 (q, J_{C-C-F} = 39.4 Hz), 155.6; HRMS calcd for $C_{13}H_{12}F_3N_3$ [M^+] 267.0983, found 267.0996.

3-Chloro-4-(methoxycarbonyl)-5,5-dimethyl-3-(trifluoromethyl)-Δ^1-1,2,4-triazoline (11). To a solution of 4 (138.5 mg, 0.62 mol) in benzene (3 mL) was added dropwise t-BuOCl (147.0 mg, 1.34 mmol), and the mixture was heated at reflux for 2 h. The usual workup gave 11 (65.0 mg, 41%) as a viscous oil: IR (neat) 1748 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.78 (s, 3 H), 1.80 (s, 3 H), 3.86 (s, 3 H); ^{19}F-NMR ($CDCl_3$) δ 88.5 (s, 3 F); ^{13}C-NMR (DMSO-d_6) δ 21.9, 23.6, 54.2, 104.8 (q, J_{C-C-F} = 36.3 Hz, CF_3), 110.3, 119.5 (q, J_{C-F} = 286.5 Hz), 149.4; MS m/z (relative intensity) 233 (M^+ − 1, 1), 231 (M^+ − 28, 3), 216 (12), 202 (1), 200 (3), 174 (70), 172 (100), 152 (32), 137 (66), 118 (12), 101 (6), 82 (68), 59 (65), 41 (88); HRMS calcd for $C_7H_9N_3O_3Cl$ [M^+] 259.0335, found 259.0342.

4-(Methoxycarbonyl)-5,5-dimethyl-3-phenyl-3-(trifluoromethyl)-Δ^1-1,2,4-triazoline (12). Antimony pentachloride (0.16 mL, 0.77 mmol) was added to a solution of 11 (201.4 mg, 0.77 mmol) in benzene (2 mL) at 0 °C. After being stirred for 5 h at room temperature, the reaction mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with AcOEt. The extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–AcOEt) to give 12 (74.7 mg, 32%) as a viscous oil: IR (neat) 1726, 946, 756 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.86 (s, 6 H), 3.64 (s, 3 H), 7.44 (s, 5 H); ^{19}F-NMR ($CDCl_3$) δ 93.5 (s, 3 F); MS m/z (relative intensity) 273 (M^+ − 28), 242 (24), 214 (100), 198 (4), 173 (4), 145 (8), 104 (20), 59 (6), 41 (26); ^{13}C-NMR ($CDCl_3$) δ 23.5, 23.7, 52.7, 106.6 (q, J_{C-C-F} = 29.9 Hz), 108.5, 122.5 (q, J_{C-F} = 289.4 Hz, CF_3), 126.8, 128.7 (2 C), 129.7 (2 C), 131.4, 151.6; HRMS calcd for $C_{13}H_{14}F_3N_3O_2$ [M^+] 273.0975, found 273.0998.