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Generation and Reactions of Trifluoroacetimidoyl Radicals

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N-Aryltrifluoroacetimidoyl radicals have been generated by three different methods: the tin-radical promoted deiodination and photochemical homolysis of imidoyl iodides and the thermal homolysis of imidoyl azo-compounds. *N*-[2-(1-alkynyl)phenyl]trifluoroacetimidoyl iodides have been converted to trifluoromethylated indoles by the tin-radical promoted homolysis of the carbon–iodine bond followed by intramolecular cyclization. The photolysis of trifluoroacetimidoyl iodides enabled both intra- and intermolecular cyclization to indoles and quinolines. Likewise, thermal reactions of *N*-(2,2,2-trifluoro-1-tritylazoethylidene)anilines provided trifluoromethylated quinolines and indoles.

Trifluoromethylated compounds have been receiving great interest in medicinal, agricultural, and material sciences.$^{1)}$ Among the various trifluoromethylations,$^{2)}$ the preparation and utilization of trifluoromethylated building blocks involve one of the useful approaches to the goal, and have currently been receiving interest in synthetic organofluorine chemistries.$^{3)}$

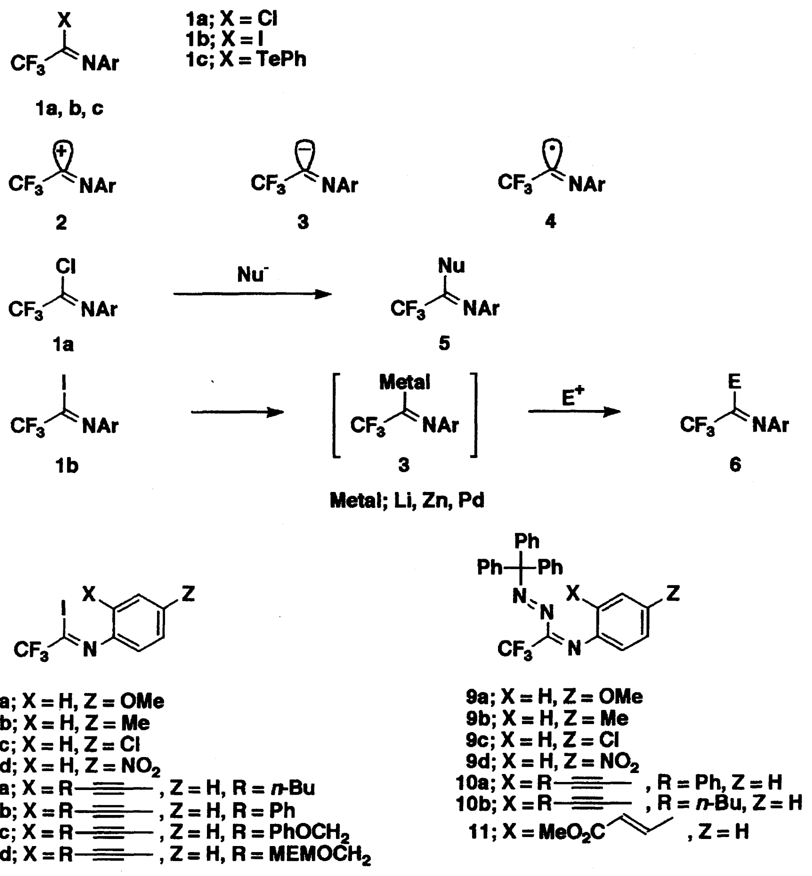
N-Aryltrifluoroacetimidoyl chlorides **1a** (X=Cl) are useful trifluoromethylated synthetic blocks, which are readily available from trifluoroacetic acid by a triphenylphosphine-promoted one-pot reaction.$^{4)}$ The corresponding iodides **1b** (X=I) and tellurides **1c** (X=TePh) are prepared by replacing chlorine by iodide and telluride anions. The halogens of **1** can be replaced by various nucleophiles to produce nitrogen heterocycles.$^{5)}$ The reactions of **1** with carbon and nitrogen nucleophiles have also been demonstrated by Tanaka$^{6)}$ and ourselves.$^{7)}$ In these reactions, compounds **1a** behaved as a trifluoroacetimidoyl carbocation equivalent **2**. On the other hand, *N*-aryltrifluoroacetimidoyl carbanions **3** were derived by metal–halogen exchange reactions of *N*-aryltrifluoroacetimidoyl iodides **1b**, and were allowed to react with various electrophiles.$^{8)}$ These reactions of **1a** and **1b** provided us with a new entry to the synthesis of trifluoromethylated nitrogen compounds.

Although trifluoroacetimidoyl radicals **4** would be another reactive intermediate for trifluoromethylated heterocycles, they have never been explored (Scheme 1). The generation and utilization of novel reactive radical intermediates have been current subjects for organic synthesis.$^{9)}$ The generation of nonfluorinated alkano- and benzoimidoyl radicals has already been demonstrated by intermolecular radical reactions of isocyanides,$^{10)}$ isocyanates,$^{11)}$ isothiocyanates,$^{11)}$ imines,$^{12)}$ imidoyl chlorides,$^{13)}$ thioimidates,$^{14)}$ and selenoimidates.$^{14)}$ Some of them are useful synthetic intermediates. Trifluoroacetyl radicals have also been demonstrated.$^{15)}$ However, none of the trifluoroacetimidoyl radicals **4** have been known. The trifluoroacetimidoyl radicals would be promising electrophilic reactive species, and would undergo an alternative carbon–carbon bond formation via radical pathways, leading to trifluoromethylated nitrogen heterocycles. In fact, we have communicated the generation of **4** by the photochemical homolysis of the carbon–tellurium bond of **1c**.$^{16)}$ Although the photolysis provided the first generation of **4** and a synthetic approach to 2-trifluoromethylindoles, it requires a toxic tellurium compound and an unnecessarily long reaction time of 3—4 d. The iodides and azo-compounds must be alternative starting materials. Concerning these bases, this paper describes the generation of a trifluoroacetimidoyl radicals by three different methods: the iodine abstraction of **7** with a tributyltin radical, the photochemical homolytic cleavage of a carbon-iodine bond of **7** and **8**, and the thermal homolysis of azo-compounds **9**, **10**, and **11**, and their synthetic utilizations.

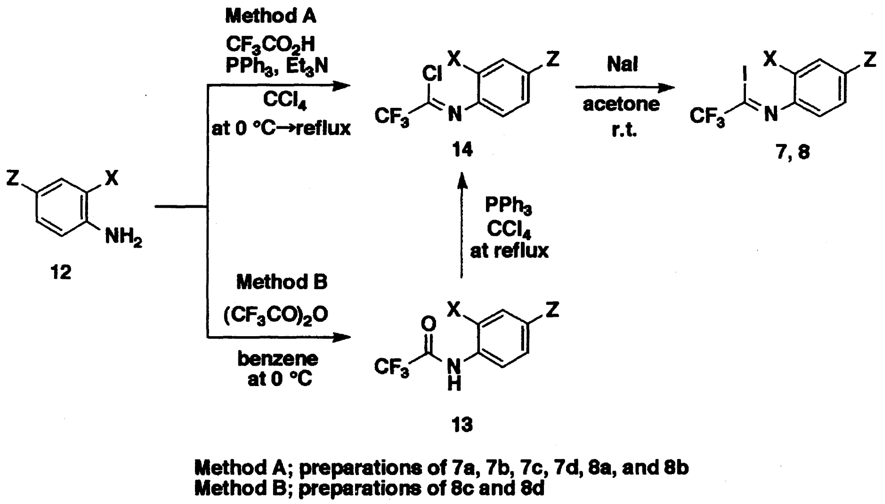
Results and Discussion

1. Preparation of the Imidoyl Iodides 7 and 8, and Azo-Compounds 9, 10, and 11.

N-Aryltrifluoroacetimidoyl iodides were prepared by a triphenylphosphine-promoted reaction$^{4)}$ of *o*- or *p*-substituted anilines **12**$^{17)}$ with trifluoroacetic acid, followed by a chlorine–iodine exchange reaction (Scheme 2). However, the yields were low in the triphenylphosphine-promoted reaction of trifluoroacetic acid with anilines **12** (X=$PhOCH_2C{\equiv}C$–, $MEMOCH_2C{\equiv}C$–). Thus, chlorides **14** were prepared by two-step reactions (Method B) via amides **13**.



Scheme 1.

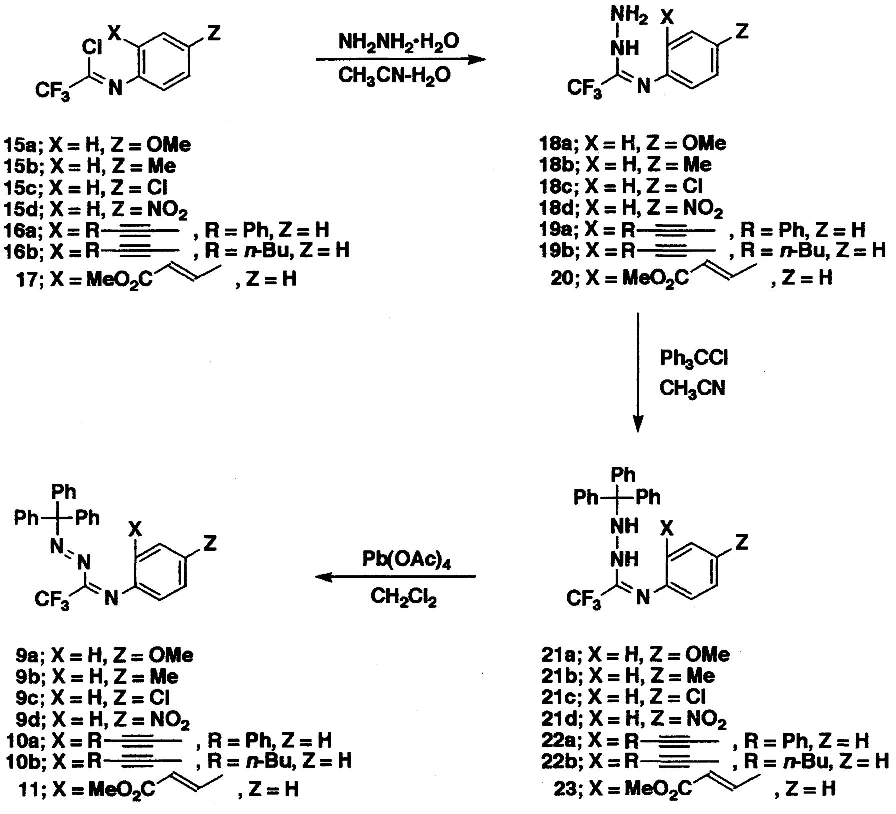


Scheme 2.

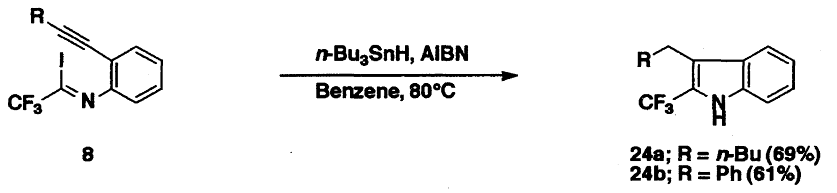
Azo-compounds **9**, **10**, and **11** were prepared from trifluoroacetimidoyl chlorides **15**, **16**, and **17** in three steps as follows: the reaction of *N*-aryltrifluoroacetimidoyl chlorides (**15**—**17**)[18] with $NH_2NH_2 \cdot H_2O$, and then with trityl chloride, followed by oxidation of the corresponding hydrazines (**21**—**23**) with $Pb(OAc)_4$ (Scheme 3).[19] Fortunately, a nucleophilic substitution reaction of the chlorides with hydrazine was faster than hydrolysis to the amides in an aqueous media. The azo-compounds are colored crystals, and are stable when stored in a refrigerator.

2. Generation of Radicals 4. At first, the tin-radical promoted generation of the imidoyl radicals **4** from *N*-aryltrifluoroacetimidoyl iodides was examined. The reaction of **8** was conducted under the conventional conditions of an AIBN-initiated reaction in an **8**–*n*-Bu_3SnH–AIBN–benzene system at 80 °C (Scheme 4).

Four compounds were subjected to the reaction. For R being *n*-Bu or Ph, desired products **24** were obtained in moderate yields. However, for R being $PhOCH_2$ or



Scheme 3.



Scheme 4.

MEMOCH$_2$, the yields of **24** were very poor. Because of the high reactivity of the methylene group attached to ethereal oxygen, the radical hydrogen abstraction reaction may cause the formation of a very complicated mixture. It is known that the radicals add to the double bond in an *exo*-fashion to produce a five-membered ring over a six-membered ring in the case of intramolecular cyclization via vinyl radicals.[20] The trifluoroacetimidoyl radicals also cyclized in an *exo* fashion.

The iodine abstraction of **8** with tributyltin radicals would lead to radical **25**, which would undergo intramolecular cyclization to radical **26**. Hydrogen abstraction of **26**, followed by reduction with tributyltin hydride, would provide 2-trifluoromethyl-3-substituted indoles **24** as final products (Scheme 5).

Intra- and intermolecular reactions, such as the photochemical homolysis of **7** and **8**, would be promising for suppressing any undesired side reactions presumably arising from intermolecular radical hydrogen abstraction.

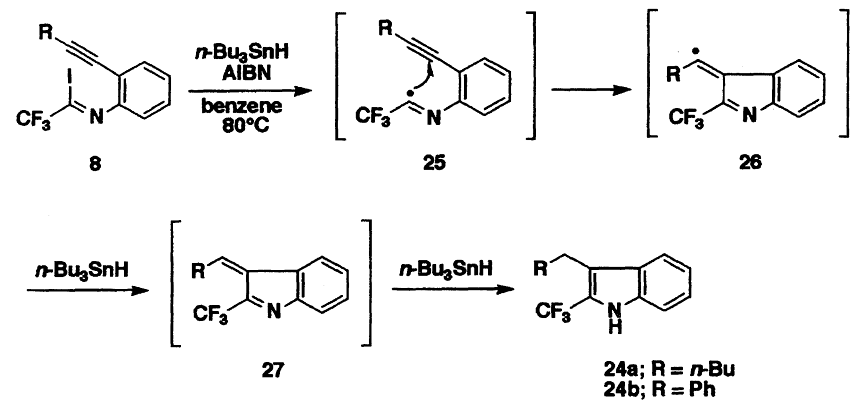
Next, the photochemical reaction of **8** was explored. We have already communicated the photochemical generation of radical **4** from the tellurides **1c**.[16] The carbon-iodine bond is also cleaved photochemically. Therefore, iodides **1b** will be more convenient alternative substrates for this photochemical reaction.

In a typical experimental procedure, a solution of **8** and a drop of water in dist. THF was irradiated with a 438-W high-pressure mercury lamp at ambient temperature for a few days (Scheme 6).

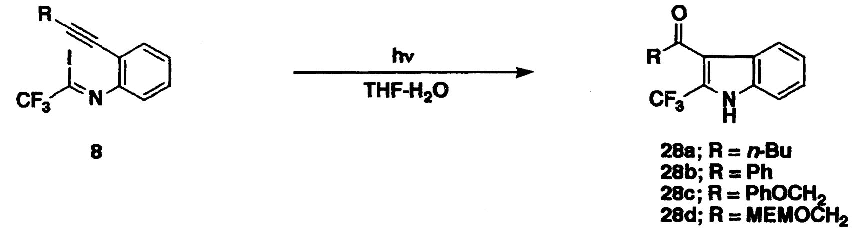
As shown in Table 1, these iodides **8** also intramolecularly cyclized to indoles **28**. In contrast to the formation of 3-alkylindoles from **8** by a tin-radical promoted reaction, the photochemical reaction provided 3-

Table 1. Photochemical Intramolecular Cyclization of the Iodides **8**

Compound 8	R	Time d	Yield (%) 28	 Recovery of 8
8a	*n*-Bu–	9	53	1
8b	Ph–	6	68	4
8c	PhOCH$_2$–	8	55	36
8d	MEMOCH$_2$–	9	30	27



Scheme 5.



Scheme 6.

acylindoles **28**. It is notable that products **28** were obtained even when substituents (R) in **8** were $PhOCH_2$ and $MEMOCH_2$. The use of a wet THF solution is a key point for this purpose. In these reactions, 3-acylindoles **28** were obtained in reasonable yields, although the reactions required long reaction times.

One of the possible pathway would be a radical route. After radicals **25** had attacked the triple bond, the vinyl radicals would have been trapped with iodine to form **29**, which would be hydrolyzed to the final products **28** (Scheme 7).

However, it was reported that the photolysis of vinyl and acyl halides sometimes produced vinyl-type cations by either the heterolysis of the carbon–halogen bond or an initial homolytic cleavage of the carbon–halogen bond to vinyl radicals, followed by an electron-transfer reaction.[21)] Trifluoroacetimidoyl carbocations **2** would generally be unstable due to the electron-withdrawing nature of the α-trifluoromethyl group. However, a cation pathway of the vinyl carbocation formation, followed by hydrolysis can not be ruled out at this stage.

Intermolecular cyclization would also be both possible and useful for heterocycle syntheses.

Thus, irradiation of substrate **7a** in the presence of phenylacetylene was examined (Scheme 8). The major products were regioisomers of quinolines **32a** and **33a**. These quinoline derivatives were characterized by a spectroscopic comparison with authentic samples, which were synthesized by a palladium-catalyzed Heck-type reaction of trifluoroacetimidoyl iodide **7a** and the corresponding 3-methoxyphenyl compound with styrene, followed by thermal cyclization.[8)]

The yields of **32a** and **33a** were slightly dependent on the concentration of phenylacetylene (Table 2). However, the use of a large excess amount of phenylacetylene is meaningless from a synthetic point of view. An examination of various solvents revealed that acetonitrile was a choice of solvents in which a yield of 56% was obtained by using 1.5 molar amounts of phenylacetylene.

Table 2. Photochemical Intermolecular Cyclization of **7a** with Phenylacetylene

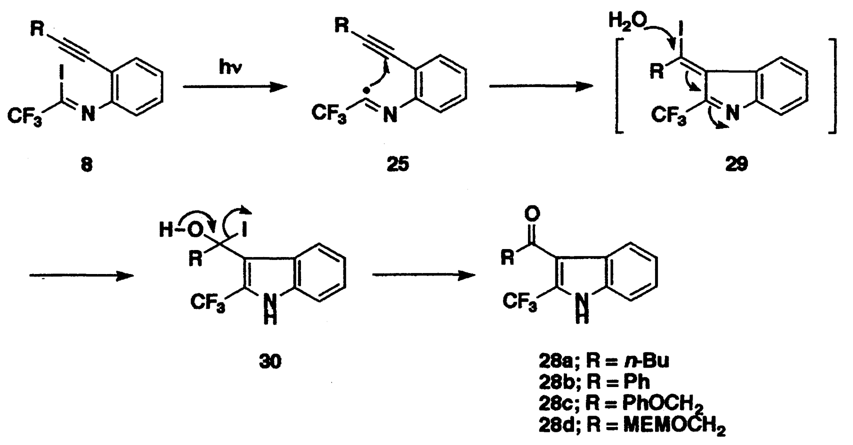
Entry	**31**[a)]	Sol.	Time/d	**32a**+**33a** Yield (%)[b)]
1	20	—	3	64
2	10	—	3	61
3	6	—	5	50
4	1.5	CH_3CN	4	56

a) Molar amounts of **31**. b) Regioisomer (6-OMe : 7-OMe)=7 : 1.

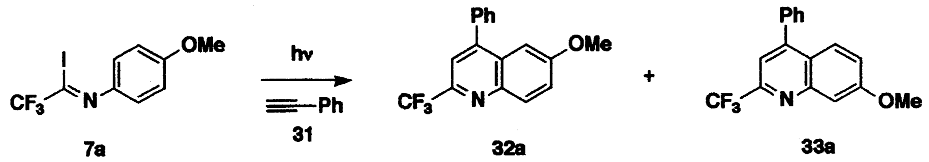
As demonstrated by Leardini,[12)] quinolines **32a** and **33a** would be formed from the spirohexadienyl radical intermediate **36**. The radical **34** attacks phenylacetylene to produce radical intermediate **35**, which undergoes spirocyclization to **36**. Migration of the carbon-carbon bond gives **32a**, while that of the carbon-nitrogen bond gives **33a**, respectively, as final products (Scheme 9).

Some types of photochemical intra- and intermolecular cyclizations of imidoyl radicals **25** and **34** have been examined. However, a long reaction time is a serious demerit for synthesis. Easily available and more reactive substrates are required from the point of organic synthesis.

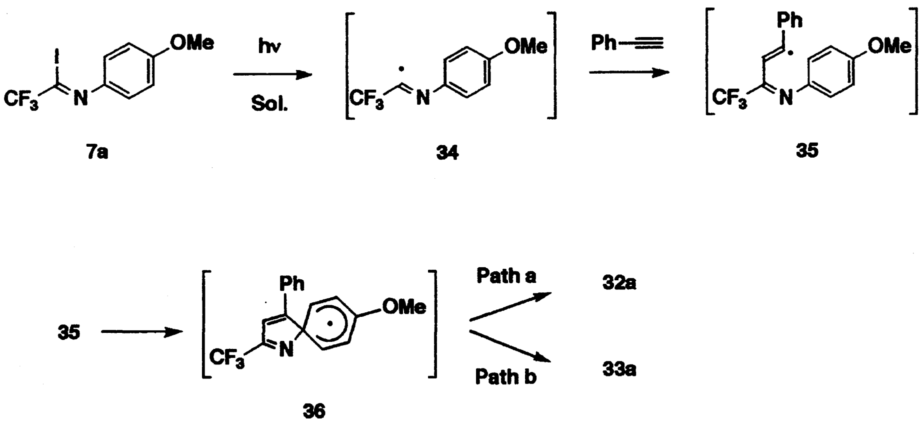
On this basis, the thermal generation of trifluoroacetimidoyl radicals from the azo-compounds **9** was examined. Heating of **9** in the presence of phenylacetylene produced quinolines **32** and **33**, the structures of which



Scheme 7.



Scheme 8.



Scheme 9.

Table 3. Thermal Intermolecular Cyclization

Compound **9**	Z	**32**+**33** Yield (%)	(**32**/**33**)
9a	OMe	51	2.8
9b	Me	47	2.0
9c	Cl	55	1.6
9d	NO_2	37	0.11

were also charactalyzed by a spectroscopic comparison with authentic samples (Scheme 10).

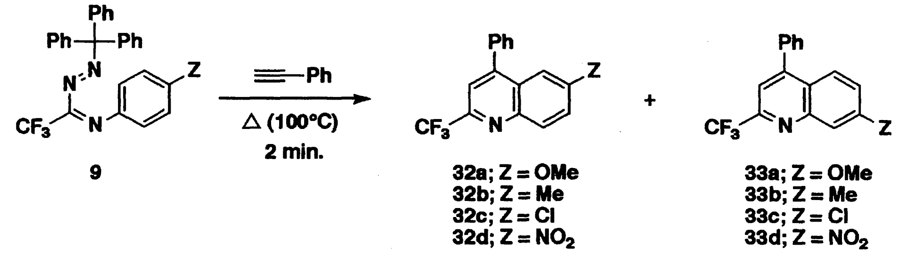
In contrast to the very slow photochemical reaction of **1b** and **1c**, the thermal reaction of **9** was so fast that it was completed at 80 °C within ten minutes, and at 100 °C within few minutes. As shown in Table 3, the electronic nature of substituent Z slightly affected the yields of the desired quinolines.

When the substituent was the methoxy group, the main product was **32a**. However, an increase in the electron-withdrawing nature of substituent Z resulted in an increase of isomer **33**.

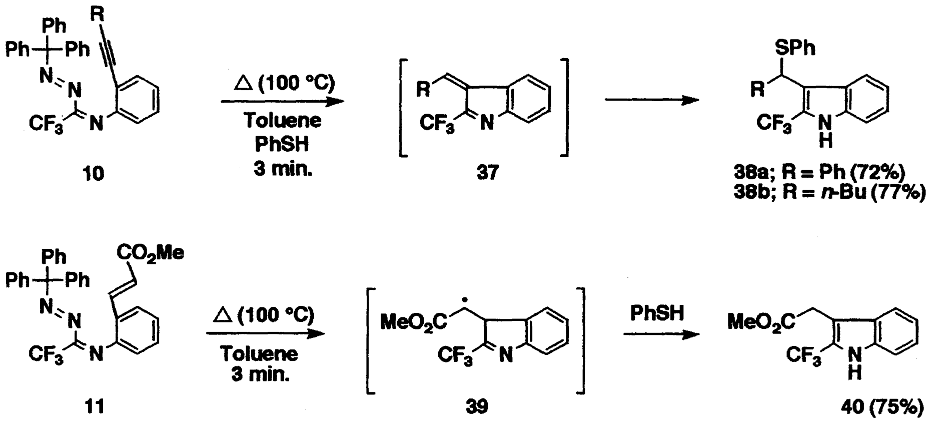
Thermal intramolecular reactions of **10** and **11** were also examined. In these reactions, indole derivatives **38** and **40** were produced in the presence of an excess amount of benzenethiol (Scheme 11).

The yields of **38** and **40** were 72—77% and 75%, respectively. The use of PhSH as a radical trapping agent was a key point for this purpose. The formation of **38** may arise by sequential reactions of an intramolecular *exo*-attack of the imidoyl radical **25**, hydrogen abstraction of the intermediate vinyl radical from PhSH, and the addition of PhSH to **37**. The formation of **40** may also arise through the same sequence of reactions. Taking into account the electrophilic nature of the imidoyl radicals, the intramolecular addition to an electron-deficient carbon–carbon double bond (**11** to **40** via **39**) is noteworthy.

In summary, some types of indole and quinoline derivatives were produced from the *N*-aryltrifluoroacetimidoyl radicals, which were useful intermediates for trifluoromethylated the nitrogen heterocycles, and were



Scheme 10.



Scheme 11.

generated by the tin-radical promoted reaction, the photochemical homolysis of the imidoyl iodides, and the thermal homolysis of imidoyl azo-compounds. In particular, the thermolysis of the azo-compounds **9**, **10**, and **11** proceeds quite smoothly, and can be used for trifluoromethylated indole synthesis.

Experimental

Infrared spectra were taken on a Hitachi 270-30 spectrometer. The ^{1}H and ^{19}F NMR spectra were measured on a Varian VXR-200 instrument using TMS for ^{1}H and C_6F_6 for ^{19}F NMR as internal standards and $CDCl_3$ as the solvent. An elemental analysis was performed on a Perkin–Elmer 2400 CHNS/O. The boiling points and melting point were uncorrected.

General Procedure for Preparations of *N*-Aryl-2,2,2-trifluoroacetimidoyl Iodides (7) and (8). A one-necked flask with a stir bar was charged with triphenylphosphine (6.489 g, 24.7 mmol), triethylamine (1.001 g, 9.8 mmol) and CCl_4 (12.68 g, 82.4 mmol); and then, trifluoroacetic acid (1.128 g, 9.8 mmol) was added dropwisely through a syringe at 0 °C. After stirring for 10 min, substituted aniline (1.428 g, 8.2 mmol) was added; the mixture was then heated for 5 h at 70 °C. The mixture was filtered through a short silica-gel column with ether, and concentrated by evaporation of the solvent. The residue was purified by silica-gel column chromatography with hexane to give *N*-aryl-2,2,2-trifluoroacetimidoyl chloride. A mixture of NaI (1.56 g, 10.4 mmol) and the imidoyl chloride (3.5 mmol) in acetone (15 ml) was stirred under an N_2-atmosphere at room temperature in the dark over night. 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 **7** or **8**.

2,2,2-Trifluoro-*N*-[2-(1-hexynyl)phenyl]acetimidoyl Iodide (8a). Yield: 68%; A yellow oil. IR (neat) 1696, 1480, 1446 cm^{-1}; ^{1}H NMR δ=0.92 (3H, t, J=6.9 Hz, CH_3), 1.42—1.54 (4H, m, CH_2CH_2), 2.38 (2H, t, J=6.8 Hz, CH_2), 6.72 (1H, dd, J_1=7.8 Hz, J_2=1.5 Hz, ArH), 7.22 (1H, td, J_1=7.4 Hz, J_2=3.6 Hz, ArH), 7.33 (1H, td, J_1=7.7 Hz, J_2=1.7 Hz, ArH), 7.46 (1H, dd, J_1=7.5 Hz, J_2=1.7 Hz, ArH); ^{19}F NMR δ=91.60 (3F, s, CF_3). Found: C, 44.59; H, 3.68; N, 3.80%. Calcd for $C_{14}H_{13}F_3IN$: C, 44.35; H, 3.46; N, 3.69%.

2,2,2-Trifluoro-*N*-[2-(2-phenylethynyl)phenyl]acetimidoyl Iodide (8b). Yield: 51%; A yellow oil. IR (Nujol) 1690, 1470, 1446 cm^{-1}; ^{1}H NMR δ=6.82 (1H, d, J=7.8 Hz, ArH), 7.30—7.88 (4H, m, ArH), 7.42—7.49 (3H, m, ArH), 7.62 (1H, d, J=7.5 Hz, ArH); ^{19}F NMR δ=91.74 (3F, s, CF_3). Found: C, 48.05; H, 2.56; N, 3.36%. Calcd for $C_{16}H_9F_3IN$: C, 48.15; H, 2.27; N, 3.51%.

2,2,2-Trifluoro-*N*-[2-(3-phenoxy-1-propynyl)phenyl]acetimidoyl Iodide (8c). Yield: 41%; A yellow oil. IR (neat) 1692, 1600, 1496, 1482 cm^{-1}; ^{1}H NMR δ=4.87 (2H, s, CH_2), 6.76 (1H, d, J=7.9 Hz, ArH), 6.95—7.01 (3H, m, ArH), 7.21—7.34 (3H, m, ArH), 7.40 (1H, td, J_1=7.7 Hz, J_2=1.5 Hz, ArH), 7.52 (1H, dd, J_1=7.6 Hz, J_2=1.5 Hz, ArH); ^{19}F NMR δ=91.63 (3F, s, CF_3). Found: C, 47.50; H, 2.85; N, 3.48%. Calcd for $C_{17}H_{11}F_3IN$: C, 49.42; H, 2.68; N, 3.39%.

2,2,2-Trifluoro-*N*-(2-{3-[(2-methoxyethoxy)methoxy]-1-propynyl}phenyl)acetimidoyl Iodide (8d). Yield: 72%; A yellow oil. IR (neat) 1692, 1482, 1446 cm^{-1}; ^{1}H NMR δ=3.40 (3H, s, CH_3), 3.55—3.60 (2H, m, OCH_2CH_2O), 3.71—3.76 (2H, m, OCH_2CH_2O), 4.43 (2H, s, CH_2), 4.83 (2H, s, OCH_2O), 6.78 (1H, d, J=7.9 Hz, ArH), 7.26 (1H, dt, J_1=7.6 Hz, J_2=1.4 Hz, ArH), 7.41 (1H, dt, J_1=7.6 Hz, J_2=1.6 Hz, ArH), 7.53 (1H, dd, J_1=7.7 Hz, J_2=1.5 Hz, ArH); ^{19}F NMR δ=91.59 (3F, s, CF_3). Found: C, 40.95; H, 3.56; N, 3.36%. Calcd for $C_{15}H_{15}F_3IN$: C, 45.82; H, 3.85; N, 3.56%.

General Procedure for Reaction of *N*-Aryl-2,2,2-trifluoroacetimidoyl Iodide (8) with *n*-Bu$_3$SnH. A two-necked flask fitted with a septam cap, a stir bar and a condenser topped with a nitrogen inlet was charged with AIBN (0.004 g, 0.013 mmol), *n*-Bu$_3$SnH (0.153 g, 0.93 mmol), and benzene (3 mL); then, *N*-aryl-2,2,2-trifluoroacetimidoyl iodide **8** (0.26 mmol) in benzene (2 mL) was added dropwisely through a syringe at 80 °C. The mixture was stirred for 1 h. After evaporation of the solvent, the residue was purified by silica-gel column chromatography to give **24**.

3-Pentyl-2-trifluoromethylindole (24a). Yield: 69%; A yellow oil. IR (neat) 3496, 3432, 1594, 1572, 1454 cm^{-1}; ^{1}H NMR δ=0.89 (3H, t, J=6.8 Hz, CH_3), 1.33—1.74 (4H, m, CH_2CH_2), 2.87 (2H, td, J_1=7.8 Hz, J_2=1.4 Hz, CH_2), 7.18 (1H, td, J_1=6.8 Hz, J_2=1.4 Hz, ArH), 7.31 (1H, td, J_1=6.8 Hz, J_2=1.2 Hz, ArH), 7.41 (1H, dd, J_1=8.8 Hz, J_2=1.1 Hz, ArH), 7.67 (1H, d, J=7.8 Hz, ArH), 8.18 (1H, br, NH); ^{19}F NMR δ=103.48 (3F, s, CF_3). Found: C, 66.04; H, 6.48; N, 5.21%. Calcd for $C_{14}H_{16}F_3N$: C, 65.87; H, 6.32; N, 5.49%.

3-Benzyl-2-trifluoromethylindole (24b). Yield: 61%; A white solid (recrystallization from hexane). Mp 97.5—98.5 °C. IR ($CHCl_3$) 3484, 3260, 2240, 1594, 1572, 1494, 1452 cm^{-1}; ^{1}H NMR δ=4.27 (2H, s, CH_2), 7.11 (1H, t, J=7.0 Hz, ArH), 7.15—7.33 (6H, m, ArH), 7.39 (1H, d, J=8.3 Hz, ArH), 7.51 (1H, d, J=8.1 Hz, ArH), 8.32 (1H, br, NH); ^{19}F NMR δ=103.74 (3F, s, CF_3). Found: C, 69.91; H, 4.43; N, 4.88%. Calcd for $C_{16}H_{12}F_3N$: C, 69.81; H, 4.39; N, 5.09%.

General Procedure for Photolysis of *N*-Aryl-2,2,2-trifluoroacetimidoyl Iodide (8). A solution of **8** (0.3 mmol) and a drop of water in dist. THF (3.0 ml) was irradiated with a 438-W high-pressure mercury lamp at ambient temperature for a few days. The usual workup provided **28**.

3-Pentanoyl-2-trifluoromethylindole (28a). Yield: 53%; A white solid (recrystallization from benzene). Mp 110—111 °C. IR (CCl_4) 3800, 3484 (NH), 2964, 1670 (C=O) cm^{-1}; ^{1}H NMR δ=0.95 (3H, t, J=7.2 Hz, CH_3), 1.43 (2H, sex, J=7.2 Hz, CH_2), 1.83 (2H, quint, J=7.2 Hz, CH_2), 3.04 (2H, t, J=7.2 Hz, CH_2CO), 7.21—7.65 (3H, m, ArH), 7.96—8.14 (1H, m, ArH); ^{19}F NMR δ=103.00 (3F, s, CF_3). Found: C, 62.68; H, 5.19; N, 5.36%. Calcd for $C_{14}H_{14}F_3NO$: C, 62.45; H, 5.24; N, 5.20%.

3-Benzoyl-2-trifluoromethylindole (28b). Yield: 68%; A white solid (recrystallization from benzene). Mp 138—139 °C. IR (CCl_4) 3480(NH), 1666 (C=O) cm^{-1}; ^{1}H NMR δ=7.09—7.67 (7H, m, ArH), 7.82—7.94 (2H, m, ArH), 9.62 (1H, br, NH); ^{19}F NMR δ=103.24 (3F, s, CF_3). Found: C, 66.56; H, 3.49; N, 4.59%. Calcd for $C_{16}H_{10}F_3NO$: C, 66.44; H, 3.48; N, 4.84%.

3-(2-Phenoxyethanoyl)-2-trifluoromethylindole (28c). Yield: 55%; A white solid (recrystallization from benzene). Mp 156.5—157.5 °C. IR (CCl_4) 3480 (NH), 1670 (C=O) cm^{-1}; ^{1}H NMR δ=5.25 (2H, s, CH_2), 6.93 (2H, d, J=9.0 Hz, ArH), 6.98 (1H, t, J=7.0 Hz, ArH), 7.28 (2H, t, J=7.5 Hz, ArH), 7.38 (1H, t, J=7.0 Hz, ArH), 7.43 (1H, t, J=8.0 Hz, ArH), 7.51 (1H, d, J=8.0 Hz, ArH), 8.15 (1H, d, J=8.0 Hz, ArH); ^{19}F NMR δ=102.76 (3F, s, CF_3). Found: C, 64.07; H, 3.80; N, 4.11%. Calcd for $C_{17}H_{12}F_3NO_2$: C, 63.95; H, 3.79; N, 4.39%.

3-{2-[(2-Methoxyethoxy)methoxy]ethanoyl}-2-trifluoromethylindole (28d). Yield: 30%; A yellow oil. IR (CCl_4) 3500, 3476 (NH), 1682 (C=O) cm^{-1}; ^{1}H NMR δ=3.39 (3H, s, CH_3), 3.55—3.67 (2H, m, CH_2), 3.76—3.84 (2H, m, CH_2), 4.88 (2H, s, CH_2), 4.92 (2H, s, CH_2), 7.32—7.54 (3H, m, ArH), 8.04—8.12 (1H, m, ArH), 9.27 (1H, br, NH); ^{19}F NMR δ=102.47 (3F, s, CF_3). Found: C, 54.15; H, 5.15; N, 4.50%. Calcd for $C_{15}H_{16}F_3NO_4$: C, 54.38; H, 4.87; N, 4.23%.

Photolysis of 2,2,2-Trifluoro-*N*-*p*-methoxyphenylacetimidoyl Iodide (7a). A solution of **7a** (98.7 mg, 0.3 mmol) and phenylacetylene **31** (0.049 ml, 0.45 mmol) in dist. CH_3CN (0.3 ml) was irradiated with a high-pressure mercury lamp (438 W) at ambient temperature for 4 d. The usual workup provided a mixture of **32a** and **33a** in 56% yields.

6-Methoxy-4-phenyl-2-trifluoromethylquinoline (32a). Yield: 56% (7 : 1 mixture of **32a** and **33a**); A white solid (recrystallization from ether–hexane). Mp 71.5—72.5 °C. IR ($CHCl_3$) 1624, 1592 cm^{-1}; ^{1}H NMR δ=3.81 (3H, s, OCH_3), 7.22 (1H, d, J=2.7 Hz, ArH), 7.48 (1H, dd, J_1=3.6 Hz, J_2=1.2 Hz, ArH), 7.52—7.60 (5H, m, PhH), 7.62 (1H, s, ArH), 8.19 (1H, d, J=9.3 Hz, ArH); ^{19}F NMR δ=94.58 (3F, s, CF_3). Found: C, 67.09; H, 3.80; N, 4.58%. Calcd for $C_{17}H_{12}NF_3O$: C, 67.33; H, 3.99; N, 4.62%.

7-Methoxy-4-phenyl-2-trifluoromethylquinoline (33a). A white solid (recrystallization from ether-hexane). Mp 85.5—86.5 °C. IR ($CHCl_3$) 1622, 1588 cm^{-1}; ^{1}H NMR δ=3.99 (3H, s, OCH_3), 7.26 (1H, dd, J_1=9.3 Hz, J_2=2.6 Hz, ArH), 7.50—7.55 (5H, m, ArH), 7.56 (1H, s, ArH), 7.60 (1H, d, J=2.6 Hz, ArH), 7.87 (1H, d, J=9.3 Hz, ArH); ^{19}F NMR δ=94.20 (3F, s, CF_3). Found: C, 67.15; H, 3.99; N, 4.61%. Calcd for $C_{17}H_{12}NF_3O$: C, 67.33; H, 3.99; N, 4.62%.

General Procedure for Preparation of Trifluoroacetohydrazide *N*-Arylimides (18), (19), and (20). Into a solution of *N*-aryl-2,2,2-trifluoroacetimidoyl chloride (12.6 mmol) in CH_3CN (8 ml) and H_2O (3 ml), $NH_2NH_2 \cdot H_2O$ (1.26 g, 25.2 mmol) was added; the mixture was stirred for a few minutes, and then extracted with AcOEt. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by recrystallization in hexane or silica-gel column chromatography to give trifluoroacetohydrazide *N*-arylimides **18**, **19**, or **20**.

Trifluoroacetohydrazide *N*-(*p*-Methoxyphenyl)imide (18a). Yield: 85%; A white solid (recrystallization from ether–hexane). Mp 87—88 °C. IR ($CHCl_3$) 3428 (NH), 3310 (NH), 1650, 1614, 1504 cm^{-1}; ^{1}H NMR δ=3.78 (3H, s, OCH_3), 5.33 (2H, br, NH_2), 5.50 (1H, br, NH), 6.65—6.75 (2H, m, ArH), 6.80—6.90 (2H, m, ArH); ^{19}F NMR δ=91.10 (3F, s, CF_3). Found: C, 46.54; H, 4.28; N, 17.98%. Calcd for $C_9H_{10}F_3N_3O$: C, 46.36; H, 4.32; N, 18.02%.

Trifluoroacetohydrazide *N*-(*p*-Tolyl)imide (18b). Yield: 80%; A white solid (recrystallization from ether–hexane). Mp 69—70 °C. IR ($CHCl_3$) 3424 (NH), 3308 (NH), 1642, 1614, 1354, 1308, 1282 cm^{-1}; ^{1}H NMR δ=2.29 (3H, s, CH_3), 5.48 (3H, br, $NHNH_2$), 6.56—6.66 (2H, m, ArH), 7.04—7.16 (2H, m, ArH); ^{19}F NMR δ=90.88 (3F, s, CF_3). Found: C, 50.08; H, 4.56; N, 19.12%. Calcd for $C_9H_{10}F_3N_3$: C, 49.77; H, 4.64; N, 19.35%.

Trifluoroacetohydrazide *N*-(*p*-Chlorophenyl)imide (18c). Yield: 94%; A white solid (recrystallization from ether–hexane). Mp 75—76 °C. IR ($CHCl_3$) 3424 (NH), 3304 (NH), 1644, 1600 cm^{-1}; ^{1}H NMR δ=5.52 (3H, br, $NHNH_2$), 6.55—6.63 (2H, m, ArH), 7.20—7.28 (2H, m, ArH); ^{19}F NMR δ=90.88 (3F, s, CF_3). Found: C, 40.70; H, 2.74; N, 17.63%. Calcd for $C_8H_7ClF_3N_3$: C, 40.44; H, 2.97; N, 17.68%.

Trifluoroacetohydrazide *N*-(*p*-Nitrophenyl)imide (18d). Yield: 83%; A yellow solid (recrystallization from ether–hexane). Mp 142—143 °C. IR ($CDCl_3$) 3480 (NH), 3420 (NH), 1600, 1524 (NO_2), 1342 (NO_2) cm^{-1}; ^{1}H NMR δ=5.82 (3H, br, $NHNH_2$), 6.64—6.69 (2H, m, ArH), 8.16—8.21 (2H, m, ArH); ^{19}F NMR δ=91.10 (3F, s, CF_3). Found: C, 38.75; H, 2.63; N, 22.74%. Calcd for $C_8H_7F_3N_4O_2$: C, 38.72; H, 2.84; N, 22.58%.

Trifluoroacetohydrazide *N*-[2-(Phenylethynyl)phenyl]imide (19a). Yield: 87%; A white solid (recrystallization from ether–hexane). Mp 115—116 °C. IR ($CDCl_3$) 3476—3392 ($NHNH_2$), 1600, 1578 cm^{-1}; ^{1}H NMR δ=5.70 (2H, br, $NHNH_2$), 6.15 (1H, br, NH), 6.44 (1H, dd, J_1=8.1 Hz, J_2=1.1 Hz, ArH), 6.94 (1H, td, J_1=7.6 Hz, J_2=1.1 Hz, ArH), 7.28 (1H, td, J_1=7.8 Hz, J_2=1.5 Hz, ArH), 7.34—7.60 (6H, m, ArH); ^{19}F NMR δ=90.88 (3F, s, CF_3). Found: C, 63.29; H, 4.22; N, 14.10%. Calcd for $C_{16}H_{12}F_3N_3$: C, 63.36; H, 3.99; N, 13.85%.

Trifluoroacetohydrazide *N*-[2-(1-Hexynyl)phenyl]imide (19b). Yield: 62%; A yellow oil. IR (neat) 3448—3208 ($NHNH_2$), 1606, 1580 cm^{-1}; ^{1}H NMR δ=0.97 (3H, t, J=7.3 Hz, CH_3), 1.40—1.72 (4H, m, CH_2CH_2), 2.51 (2H, t, J=6.9 Hz, CH_2), 5.65 (2H, br, NH_2), 6.11 (1H, br, NH), 6.37 (1H, dd, J_1=8.3 Hz, J_2=1.1 Hz, ArH), 6.87 (1H, td, J_1=7.5 Hz, J_2=1.1 Hz, ArH), 7.21 (1H, td, J_1=7.8 Hz, J_2=1.5 Hz, ArH), 7.36 (1H, dd, J_1=7.7 Hz, J_2=1.5 Hz, ArH); ^{19}F NMR δ=90.76 (3F, s, CF_3). Found: C, 59.09; H, 5.71; N, 15.10%. Calcd for $C_{14}H_{16}F_3N_3$: C, 59.36; H, 5.69; N, 14.83%.

Trifluoroacetohydrazide *N*-[2-(2-Methoxycarbonylvinyl)phenyl]imide (20). Yield: 94%; A white solid (recrystallization from ether–hexane). Mp 120.5—121.5 °C. IR ($CHCl_3$) 3470, 3424 ($NHNH_2$), 1714 (C=O) cm^{-1}; ^{1}H NMR δ=3.83 (3H, s, CH_3), 5.49 (2H, br, NH_2), 5.56 (1H, br, NH), 6.45 (1H, d, J=15.8 Hz, CH=CH), 6.55 (1H, d, J=8.1 Hz, CH_2), 7.05 (1H, t, J=7.6 Hz, ArH), 7.34 (1H, td, J_1=8.1 Hz, J_2=1.4 Hz, ArH), 7.52 (1H, dd, J_1=7.6 Hz, J_2=1.4 Hz, ArH), 7.92 (1H, d, J=15.8 Hz, CH=CH); ^{19}F NMR δ=91.19 (3F, s, CF_3). Found: C, 50.27; H, 4.13; N, 14.48%. Calcd for $C_{12}H_{12}F_3N_3O_2$: C, 50.18; H, 4.21; N, 14.63%.

General Procedure for Preparation of Trifluoroaceto-2′-tritylhydrazide *N*-Arylimides (21), (22), and (23). Into a solution of trifluoroacetohydrazide *N*-arylimide (3.74 mmol) in CH_3CN(10 ml), trityl chloride (1.042 g, 3.74 mmol) and Et_3N (0.26 ml, 1.87 mmol) were added; the mixture was stirred for few minutes, and extracted with AcOEt. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was recrystallized from hexane to give **21**, **22**, or **23**.

Trifluoroaceto-2′-tritylhydrazide *N*-(*p*-Methoxyphenyl)imide (21a). Yield: 94%; A brown solid (recrystallization from ether–hexane). Mp 113.5—114.5 °C. IR (neat) 3428 (NH), 3288 (NH), 1632, 1600 cm^{-1}; ^{1}H NMR δ=3.77 (3H, s, OCH_3), 5.46 (1H, br, NH), 5.90 (1H, br, NH), 6.58—6.68 (2H, m, ArH), 6.77—6.85 (2H, m, ArH), 7.13—7.45 (15H, m, ArH); ^{19}F NMR δ=91.65 (3F, s, CF_3). Found: C, 70.82; H, 5.16; N, 8.79%. Calcd for $C_{28}H_{24}F_3N_3O$: C, 70.73; H, 5.09; N, 8.84%.

Trifluoroaceto-2′-tritylhydrazide *N*-(*p*-Tolyl)imide (21b). Yield: 89%; A brown solid (recrystallization from ether–hexane). Mp 131—132 °C. IR ($CDCl_3$) 3416 (NH), 1614 cm^{-1}; ^{1}H NMR δ=2.31 (3H, s, CH_3), 5.44 (1H, br, NH), 6.01 (1H, br, NH), 6.51—6.60 (2H, m, ArH), 7.01—7.11 (2H, m, ArH), 7.11—7.43 (15H, m, ArH); ^{19}F NMR δ=91.63 (3F, s, CF_3). Found: C, 73.23; H, 5.33; N, 9.11%. Calcd for $C_{28}H_{24}F_3N_3$: C, 73.19; H, 5.26; N, 9.14%.

Trifluoroaceto-2′-tritylhydrazide *N*-(*p*-Chlorophenyl)imide (21c). Yield: 94%; A brown solid (recrystallization from ether–hexane). Mp 108—109 °C. IR (neat) 3428 (NH), 3272 (NH), 1600 cm^{-1}; ^{1}H NMR δ=5.48 (1H, br, NH), 6.10 (1H, br, NH), 6.49—6.61 (2H, m, ArH), 7.11—7.43 (17H, m, ArH); ^{19}F NMR δ=91.65 (3F, s, CF_3). Found: C, 67.67; H, 4.36; N, 8.78%. Calcd for $C_{27}H_{21}ClF_3N_3$: C, 67.57; H, 4.41; N, 8.76%.

Trifluoroaceto-2′-tritylhydrazide *N*-(*p*-Nitrophenyl)imide (21d). Yield: 97%; A yellow solid (recrystallization from ether–hexane). Mp 163—164 °C. IR ($CDCl_3$) 3416 (NH), 1600, 1520, 1504 (NO_2), 1342 (NO_2) cm^{-1}; ^{1}H NMR δ=5.79 (1H, br, NH), 6.40 (1H, br, NH), 6.53—6.63 (2H, m, ArH), 7.10—7.38 (17H, m, ArH), 8.08—8.18 (2H, m, ArH); ^{19}F NMR δ=91.91 (3F, s, CF_3). Found: C, 66.34; H, 4.34; N, 11.31%. Calcd for $C_{27}H_{21}F_3N_4O_2$: C, 66.12; H, 4.32; N, 11.42%.

General Procedure for Preparation of *N*-(2,2,2-Trifluoro-1-tritylazoethylidene)anilines (9), (10), and (11). A two-necked flask with a septam cap, a stir bar and a condenser topped with an N_2-inlet was charged with $Pb(OAc)_4$ (0.848 g, 1.91 mmol) and CH_2Cl_2 (8 ml). Then, trifluoroaceto-2′-tritylhydrazide *N*-arylimide (1.91 mmol) in CH_2Cl_2 was added through syringe at 0 °C. The mixture was stirred for 30 min and filtered through a florisil column (CH_2Cl_2). The mixture was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure, and then recrystallized from hexane to give **9**, **10**, or **11**.

***N*-(2,2,2-Trifluoro-1-tritylazoethylidene)-*p*-anisidine (9a).** Yield: 60%; A red solid (recrystallization from hexane). IR ($CDCl_3$) 1678, 1588, 1504, 1446 cm^{-1}; ^{1}H NMR δ=3.76 (3H, s, OCH_3), 6.62 (2H, d, J=9.1 Hz, ArH), 6.94 (2H, d, J=9.1 Hz, ArH), 7.00—7.37 (15H, m, ArH); ^{19}F NMR δ=95.10 (3F, s, CF_3). Found: C, 71.17; H, 4.73; N, 8.94%. Calcd for $C_{28}H_{22}F_3N_3O$: C, 71.03; H, 4.68; N, 8.87%.

***N*-(2,2,2-Trifluoro-1-tritylazoethylidene)-*p*-toluidine (9b).** Yield: 89%; A red solid (recrystallization from hexane). IR ($CDCl_3$) 1678, 1600, 1492, 1446 cm^{-1}; ^{1}H NMR δ=2.28 (3H, s, CH_3), 6.72—6.80 (2H, m, ArH), 6.88—7.35 (17H, m, ArH); ^{19}F NMR δ=94.11 (3F, s, CF_3). Found: C, 73.78; H, 5.01; N, 9.31%. Calcd for $C_{28}H_{22}F_3N_3$: C, 73.51; H, 4.85; N, 9.19%.

4-Chloro-*N*-(2,2,2-trifluoro-1-tritylazoethylidene)aniline (9c). Yield: 70%; A red solid (recrystallization from hexane). IR ($CHCl_3$) 1686, 1602, 1584, 1484, 1446 cm^{-1}; ^1H NMR δ=6.70—6.80 (2H, m, ArH), 6.87—7.00 (6H, m, ArH), 7.00—7.10 (2H, m, ArH), 7.17—7.35 (9H, m, PhH); ^{19}F NMR δ=93.83 (3F, s, CF_3). Found: C, 67.77; H, 4.04; N, 8.63%. Calcd for $C_{27}H_{19}ClF_3N_3$: C, 67.86; H, 4.01; N, 8.79%.

4-Nitro-*N*-(2,2,2-trifluoro-1-tritylazoethylidene)aniline (9d). Yield: 77%; A brown solid (recrystallization from hexane). IR ($CDCl_3$) 1692, 1606, 1594, 1522, 1348 cm^{-1}; ^1H NMR δ=6.78—6.91 (7H, m, ArH), 7.15—7.32 (10H, m, ArH), 7.90—8.00 (2H, m, ArH); ^{19}F NMR δ=93.15 (3F, s, CF_3). Found: C, 66.62; H, 3.90; N, 11.57%. Calcd for $C_{27}H_{19}F_3N_4O_2$: C, 66.39; H, 3.92; N, 11.47%.

2-(Phenylethynyl)-*N*-(2,2,2-trifluoro-1-tritylazoethylidene)aniline (10a). Yield: 56% from **19a**; A red solid (recrystallization from hexane). IR ($CDCl_3$) 1692, 1600, 1530, 1492, 1446 cm^{-1}; ^1H NMR δ=6.80—7.38 (24H, m, ArH); ^{19}F NMR δ=93.47 (3F, s, CF_3). Found: C, 77.35; H, 4.56; N, 7.44%. Calcd for $C_{35}H_{24}F_3N_3$: C, 77.33; H, 4.45; N, 7.73%.

2-(1-Hexynyl)-*N*-(2,2,2-trifluoro-1-tritylazoethylidene)aniline (10b). Yield: 57% from **19b**; A red solid (recrystallization from hexane). IR ($CHCl_3$) 1694, 1598, 1532, 1490, 1478, 1446 cm^{-1}; ^1H NMR δ=0.86 (3H, t, J=5.9 Hz, CH_3), 1.20—1.50 (4H, m, CH_2CH_2), 2.23 (2H, t, J=6.8 Hz, CH_2), 6.70—7.30 (19H, m, ArH); ^{19}F NMR δ=93.32 (3F, s, CF_3). Found: C, 75.41; H, 5.47; N, 7.97%. Calcd for $C_{33}H_{28}F_3N_3$: C, 75.70; H, 5.39; N, 8.03%.

2-(2-Methoxycarbonylvinyl)-*N*-(2,2,2-trifluoro-1-tritylazoethylidene)aniline (11). Yield: 73% from **20**; A brown solid (recrystallization from hexane). IR ($CHCl_3$) 1714 (C=O), 1636, 1600, 1598, 1492, 1448 cm^{-1}; ^1H NMR δ=3.79 (3H, s, CH_3), 6.28 (1H, d, J=16.1 Hz, CH=CH), 6.57 (1H, dd, J_1=7.2 Hz, J_2=1.9 Hz, ArH), 6.80—6.88 (5H, m, ArH), 7.03 (1H, td, J_1=7.4 Hz, J_2=1.8 Hz, ArH), 7.09 (1H, td, J_1=7.4 Hz, J_2=1.7 Hz, ArH), 7.16—7.32 (10H, m, ArH), 7.46 (1H, dd, J_1=7.5 Hz, J_2=2.1 Hz, ArH), 7.74 (1H, d, J=16.1 Hz, CH=CH); ^{19}F NMR δ=93.61 (3F, s, CF_3). Found: C, 70.59; H, 4.56; N, 7.71%. Calcd for $C_{31}H_{24}F_3N_3O_2$: C, 70.58; H, 4.59; N, 7.97%.

General Procedure for Thermal Reaction of *N*-(2,2,2-Trifluoro-1-tritylazoethylidene)anilines (9). A glass tube with a septam cap, a stirbar and N_2-inlet was charged with **9** (0.11 mmol) and phenylacetylene (0.05 ml, 0.46 mmol). Then, the mixture was heated at 100 °C for 2—3 min and concentrated under reduced pressure to provide a separable mixture of **32** and **33**.

6-Methoxy-4-phenyl-2-trifluoromethylquinoline (32a). Yield: 51% (2.8 : 1 mixture of **32a** and **33a**); A white solid (recrystallization from ether–hexane). Mp 71.5—72.5 °C. IR ($CHCl_3$) 1624, 1592 cm^{-1}; ^1H NMR δ=3.81 (3H, s, OCH_3), 7.22 (1H, d, J=2.7 Hz, ArH), 7.48 (1H, dd, J_1=3.6 Hz, J_2=1.2 Hz, ArH), 7.52—7.60 (5H, m, PhH), 7.62 (1H, s, ArH), 8.19 (1H, d, J=9.3 Hz, ArH); ^{19}F NMR δ=94.58 (3F, s, CF_3). Found: C, 67.09; H, 3.80; N, 4.58%. Calcd for $C_{17}H_{12}NF_3O$: C, 67.33; H, 3.99; N, 4.62%.

7-Methoxy-4-phenyl-2-trifluoromethylquinoline (33a). A white solid (recrystallization from ether–hexane). Mp 85.5—86.5 °C. IR ($CHCl_3$) 1622, 1588 cm^{-1}; ^1H NMR δ=3.99 (3H, s, OCH_3), 7.26 (1H, dd, J_1=9.3 Hz, J_2=2.6 Hz, ArH), 7.50—7.55 (5H, m, ArH), 7.56 (1H, s, ArH), 7.60 (1H, d, J=2.6 Hz, ArH), 7.87 (1H, d, J=9.3 Hz, ArH); ^{19}F NMR δ=94.20 (3F, s, CF_3). Found: C, 67.15; H, 3.99; N, 4.61%. Calcd for $C_{17}H_{12}NF_3O$: C, 67.33; H, 3.99; N, 4.62%.

6-Methyl-4-phenyl-2-trifluoromethylquinoline (32b). Yield: 47% (2 : 1 mixture of **32b** and **33b**); A yellow oil. IR (neat) 1624, 1590, 1578, 1568, 1506, 1496, 1474, 1448 cm^{-1}; ^1H NMR δ=2.51 (3H, s, CH_3), 7.46—7.60 (5H, m, ArH), 7.64 (1H, s, ArH), 7.66 (1H, dd, J_1=8.7 Hz, J_2=2.0 Hz, ArH), 7.72 (1H, m, ArH), 8.19 (1H, d, J=8.7 Hz, ArH); ^{19}F NMR δ=94.36 (3F, s, CF_3). Found: C, 71.05; H, 4.47; N, 4.89%. Calcd for $C_{17}H_{12}NF_3$: C, 71.07; H, 4.21; N, 4.88%.

7-Methyl-4-phenyl-2-trifluoromethylquinoline (33b). A slight red oil. IR (neat) 1628, 1590, 1578, 1514, 1452, 1434 cm^{-1}; ^1H NMR δ=2.60 (3H, s, CH_3), 7.46 (1H, dd, J_1=8.7 Hz, J_2=1.8 Hz, ArH), 7.53—7.56 (5H, m, ArH), 7.62 (1H, s, ArH), 7.88 (1H, d, J=8.7 Hz, ArH), 8.06—9.00 (1H, m, ArH); ^{19}F NMR δ=94.22 (3F, s, CF_3). Found: C, 70.91; H, 4.34; N, 4.83%. Calcd for $C_{17}H_{12}NF_3$: C, 71.07; H, 4.21; N, 4.88%.

6-Chloro-4-phenyl-2-trifluoromethylquinoline(32c). Yield: 55% (1.6 : 1 mixture of **32c** and **33c**); A white solid (recrystallization from ether–hexane). Mp 85.5—86.5 °C. IR ($CHCl_3$) 1612, 1592, 1490, 1458, 1386 cm^{-1}; ^1H NMR δ=7.48—7.62 (5H, m, ArH), 7.70 (1H, s, ArH), 7.77 (1H, dd, J_1=9.0 Hz, J_2=2.3 Hz, ArH), 7.96 (1H, d, J=2.2 Hz, ArH), 8.23 (1H, d, J=9.0 Hz, ArH); ^{19}F NMR δ=94.15 (3F, s, CF_3). Found: C, 62.42; H, 2.70; N, 4.49%. Calcd for $C_{16}H_9ClNF_3$: C, 62.46; H, 2.95; N, 4.55%.

7-Chloro-4-phenyl-2-trifluoromethylquinoline(33c). A white solid (recrystallization from ether–hexane). Mp 70—71 °C. IR ($CHCl_3$) 1610, 1590, 1492, 1448, 1384 cm^{-1}; ^1H NMR δ=7.47—7.62 (6H, m, ArH), 7.68 (1H, s, ArH), 7.94 (1H, d, J=9.1 Hz, ArH), 8.29 (1H, d, J=2.1 Hz, ArH); ^{19}F NMR δ=94.05 (3F, s, CF_3). Found: C, 62.51; H, 2.90; N, 4.58%. Calcd for $C_{16}H_9ClNF_3$: C, 62.46; H, 2.95; N, 4.55%.

6-Nitro-4-phenyl-2-trifluoromethylquinoline (32d). Yield: 37% (1 : 0.11 mixture of **32d** and **33d**); A white solid (recrystallization from ether–hexane). Mp 169—170 °C. IR ($CDCl_3$) 1624, 1596, 1538, 1492, 1464, 1386, 1348 cm^{-1}; ^1H NMR δ=7.50—7.70 (5H, m, ArH), 7.85 (1H, s, ArH), 8.45 (1H, d, J=9.2 Hz, ArH), 8.60 (1H, dd, J_1=9.2 Hz, J_2=2.5 Hz, ArH), 8.95 (1H, d, J=2.5 Hz, ArH); ^{19}F NMR δ=93.81 (3F, s, CF_3). Found: C, 60.26; H, 2.74; N, 8.63%. Calcd for $C_{16}H_9N_2F_3O_2$: C, 60.38; H, 2.85; N, 8.80%.

7-Nitro-4-phenyl-2-trifluoromethylquinoline (33d). A white solid (recrystallization from ether–hexane). Mp 107—108 °C. IR ($CDCl_3$) 1626, 1538, 1354 cm^{-1}; ^1H NMR δ=7.50—7.65 (5H, m, ArH), 7.85 (1H, s, ArH), 8.18 (1H, d, J=9.3 Hz, ArH), 8.39 (1H, dd, J_1=9.3 Hz, J_2=2.3 Hz, ArH), 9.20 (1H, d, J=2.3 Hz, ArH); ^{19}F NMR δ=93.91 (3F, s, CF_3). Found: C, 60.14; H, 2.72; N, 8.60%. Calcd for $C_{16}H_9N_2F_3O_2$: C, 60.38; H, 2.85; N, 8.80%.

General Procedure for Thermal Reaction of *N*-(2,2,2-Trifluoro-1-tritylazoethylidene)anilines (10) and (11). A glass tube with a septam cap, a stir bar and N_2-inlet was charged with *N*-(2,2,2-trifluoro-1-tritylazoethylidene)aniline (0.092 mmol), thiophenol (0.019 ml, 0.18 mmol) and toluene (0.25 ml). Then, the mixture was heated at 100 °C for 3 min. After evaporation of the solvent, the residue was chromatographed over silica-gel using hexane–AcOEt to give **38** or **40**.

3- (α- Phenylthiobenzyl)- 2- trifluoromethylindole (38a). Yield: 72%; A white solid (recrystallization from ether–hexane). Mp 85—86 °C. IR ($CDCl_3$) 3480 (NH), 1586, 1566 cm^{-1}; ^1H NMR $\delta=6.02$ (1H, s, CH), 7.10—7.41 (11H, m, ArH), 7.52—7.62 (2H, m, ArH), 8.04 (1H, d, $J=8.1$ Hz, ArH), 8.29 (1H, br, NH); ^{19}F NMR $\delta=104.07$ (3F, s, CF_3). Found: C, 68.61; H, 3.90; N, 3.53%. Calcd for $C_{22}H_{16}F_3NS$: C, 68.92; H, 4.21; N, 3.65%.

3- (1- Phenylthiopentyl)- 2- trifluoromethylindole (38b). Yield: 77%; A white solid (recrystallization from ether–hexane). Mp 78—79 °C. IR ($CDCl_3$) 3484 (NH), 1588, 1568 cm^{-1}; ^1H NMR $\delta=0.83$ (3H, t, $J=7.2$ Hz, CH_3), 1.12—1.46 (4H, m, CH_2CH_2), 2.05—2.35 (2H, m, CH_2), 4.64 (1H, dd, $J_1=9.2$ Hz, $J_2=6.0$ Hz, CH), 7.08—7.40 (8H, m, ArH), 8.14 (1H, d, $J=7.3$ Hz, ArH), 8.05—8.25 (1H, br, NH); ^{19}F NMR $\delta=104.23$ (3F, s, CF_3). Found: C, 66.17; H, 5.42; N, 3.77%. Calcd for $C_{20}H_{20}F_3NS$: C, 66.10; H, 5.55; N, 3.85%.

Methyl 2- Trifluoromethylindole- 3- acetate (40). Yield: 75%; A white solid (recrystallization from ether–hexane). Mp 55—57 °C. IR ($CDCl_3$) 3484 (NH), 1738 (C=O), 1600, 1576 cm^{-1}; ^1H NMR $\delta=3.69$ (3H, s, OCH_3), 3.93 (2H, s, CH_2), 7.21 (1H, td, $J_1=6.5$ Hz, $J_2=1.4$ Hz, ArH), 7.35 (1H, td, $J_1=6.5$ Hz, $J_2=1.2$ Hz, ArH), 7.42 (1H, d, $J=8.3$ Hz, ArH), 7.67 (1H, d, $J=8.3$ Hz, ArH), 8.38 (1H, br, NH); ^{19}F NMR $\delta=103.15$ (3F, s, CF_3). Found: C, 56.41; H, 4.10; H, 5.14%. Calcd for $C_{12}H_{10}F_3NO_2$: C, 56.04; H, 3.92; N, 5.45%.

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17) *o*-Substituted anilines were prepared by palladium-catalized Heck-type reaction of *o*-iodoaniline with alkynes or alkenes.

18) These chlorides were prepared as shown in Scheme 2.

19) Trifluoroaceto-2′-tritylhydrazide *N*-arylimides **22** and **23** were not isolated and used for preparation of azo-compounds **10** and **11** without further purification.

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