# Electrochemical Oxidation of N,N'-Disubstituted Trifluoroethanimidamides. An Approach to N-Substituted 2-(Trifluoromethyl)benzimidazoles

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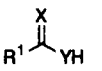
Electrochemical oxidation of N,N'-disubstituted trifluoroethanimidamides **11** in dry acetonitrile and in aqueous acetonitrile provided N-substituted 2-(trifluoromethyl)benzimidazoles **15** and $N^1$-(4-oxo-2,5-cyclohexadien-1-ylidene)-$N^2$-substituted-2,2,2-trifluoroethanimidamides (p-benzoquinone imine derivatives) **20**, respectively. In dry acetonitrile, electron-donating para substituents in the N,N'-diaryl derivatives strongly promoted the formation of benzimidazoles, whereas N-alkyl-N'-(4-methoxyphenyl) derivatives provided rather complex mixtures of **11**, **20**, and polymeric compounds. In wet acetonitrile, p-benzoquinone imines **20** were major products regardless of the substituents. An ECEC process via two-electron oxidation is proposed.

## Introduction

Electrochemical oxidation triggers electrophilic reactions of heteroatom compounds. A great number of electrochemically induced reactions of heteroatom compounds have been reported.[1] Compounds of general structure **1**, other than imidamides **1f**, are most frequently studied (Chart 1). Typical reactions of **1** are shown in Scheme 1. The electrochemical oxidation of alkanoic acids **1a** is the well-known Kolbe reaction, in which alkyl radicals are generated via one-electron oxidation followed by decarboxylation (Scheme 1, eq 2).[2] Oxidation of dithiocarboxylic acids **1b** causes a different kind of dimerization, one that proceeds via the corresponding dithiocarboxyl radicals generated by one-electron oxidation followed by deprotonation (eq 3).[3] The slower rate of dethiocarboxylation and the higher stability of dithiocarboxyl radicals make the reactivity of radical **3b** different from that of the acyloxyl radicals. Electrooxidation of acetamidine **1c** in liquid ammonia produces ethane **4** and cyanamide **6** (eq 4).[4] When subjected to electrooxidation, N-substituted amides **1d** undergo two reactions. One is replacement of hydrogen with nucleophiles on the carbon bearing the amide nitrogen atom to form **7**[5] via an ECEC mechanism[1] and the other is aromatic substitution[6,7] to form heterocycle **8** (eq 5). Bond cleavage between the amide nitrogen and the aryl carbon via a quinone iminium intermediate[6,7] to form p-benzoquinone[6] has been also observed in some N-aryl amides (eq 6).[5] N-Aryl thioamides **1e** cyclize to benzothiazoles **10** by two-electron oxidation (eq 7).[8]

However, the electrochemistry of nitrogen analogues **1f** is relatively unknown because they are unstable and difficult to synthesize.[9] Replacement of the alkyl or aryl group ($R^1$) of **1f** with the trifluoromethyl group, however, gives fluorinated imidamides **11** (Chart 2), which are stable under electrolysis reaction conditions and are easily prepared from trifluoroacetic acid and primary amines.[10,11] Therefore, imidamides **11** would be useful model compounds for the study of electrochemical oxidation of imidamides. The object of this study was to see whether radicals **3f** (X = $NR^1$, Y = $NR^2$) would undergo intermolecular N–N bond formation[12] leading to **12** (Scheme 2, eq 8), formation of carbodiimide **13** via detrifluoromethylation (eq 9),[4,13] or electrophilic intramolecular cyclization via further one-electron oxidation to give heterocycle **14** (eq 10).[14]

**Chart 1**



**1**

$R^1$ = Alkyl or Aryl

| | X | Y |
|---|---|---|
| **1a** | O | O |
| **1b** | S | S |
| **1c** | NH | NH |
| **1d** | O | $NR^2$ |
| **1e** | S | $NR^2$ |
| **1f** | $NR^2$ | $NR^3$ |

® Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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(3) Cauquis, G.; Deronzier, A. *J. Chem. Soc., Chem. Commun.* **1978**, 809.

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(8) Tabakovic, I.; Trkovnik, M.; Batusic, M.; Tabakovic, K. *Synthesis* **1979**, 590.

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(11) Trifluoromethylated imidamides were easily prepared from **19** and amines: Uneyama, K.; Yamashita, F.; Sugimoto, K.; Morimoto, O. *Tetrahedron Lett.* **1990**, *31*, 2717.

(12) N,N-Dialkylhydrazines undergo electrooxidative intermolecular N–N bond formation. Cauquis, G.; Chabaud, B.; Genies, M. *J. Electroanal. Chem.* **1970**, 2903.

(13) Trifluoroacetic acid **1b** ($R^1$ = $CF_3$, X = O, Y = OH) electrochemically decarboxylates almost quantitatively via one-electron oxidation. Uneyama, K. *Tetrahedron* **1991**, *47*, 555.

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**Scheme 1**

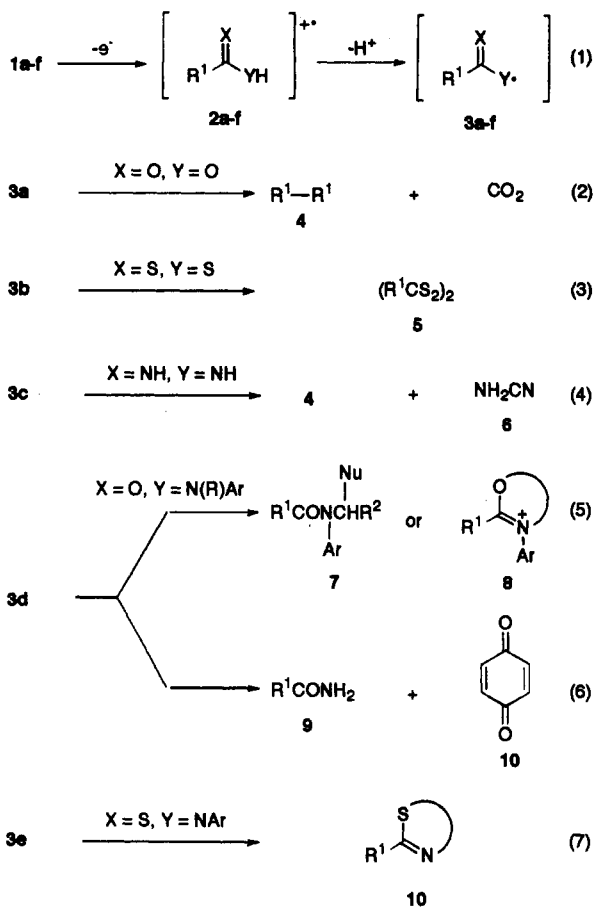
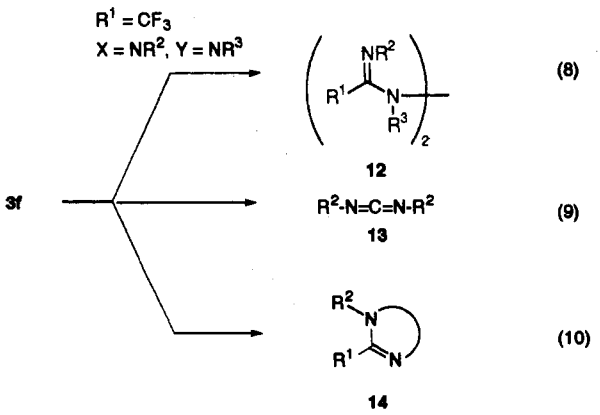


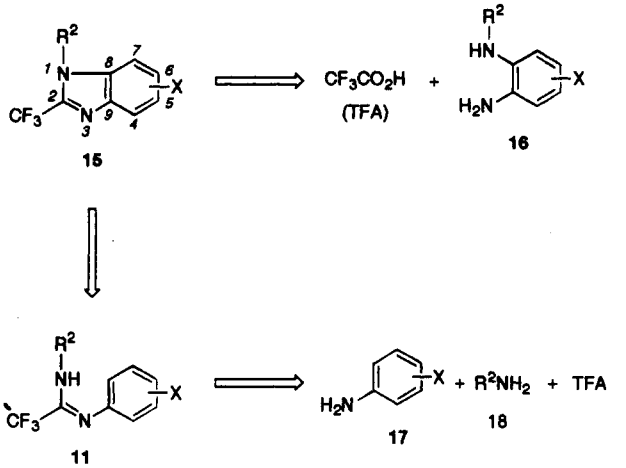
**Chart 2**

**Scheme 2**



Another object of this study was to find a general synthetic route to *N*-substituted 2-(trifluoromethyl)benzimidazoles **15**. Some 2-(trifluoromethyl)benzimidazoles **15** are bioactive as herbicides and insecticides.[15] 2-(Trifluoromethyl)benzimidazoles have been prepared by condensation of TFA with *o*-phenylenediamines **16** (Scheme 3).[16] However, the ring-substituted or *N*-substituted *o*-phenylenediamines **16** are not necessarily available. An alternative promising pathway to **15** would be a combination of two kinds of primary amines, **17** and **18**, with TFA. Stepwise formation of the C(2)–N(3) and C(2)–N(1) bonds leads to imidamides **11**, which can be cyclized to desired benzimidazoles **15** via oxidative bond formation between C(8) and N(1). An electrochemical oxidation would be promising for this purpose. We describe herein a detailed study of the electrochemical oxidation of **11** and transformations of **11** to 2-trifluoromethylated benzimidazoles **15**.

**Scheme 3**



## Results and Discussion

**Preparation of *N,N'*-Disubstituted Imidamides 11.** Unsubstituted or *N*-monosubstituted 2,2,2-trifluoroethanimidamides have been prepared from trifluoroacetonitrile and ammonia or aniline, respectively.[17] However, the chemistry of *N,N'*-disubstituted trifluoroethanimidamides **11** has been relatively unexplored. Some imidamides **11** have been prepared from imidoyl chlorides **19**[10] and amines. The chlorine atom of imidoyl chlorides is easily displaced with amines.[11]

In the case of symmetric imidamides **11** ($R^1 = R^2$, Scheme 4), the reaction proceeded smoothly in refluxing toluene, and the results are shown in Table 1. But preparation of unsymmetric imidamides **11** ($R^1 \neq R^2$) under the same conditions failed. The reaction of $R^2NH_2$ with **19** gave a mixture of the desired unsymmetric imidamide ($R^1$, $R^2$) and two symmetric imidamides (($R^1$, $R^1$) and ($R^2$, $R^2$)). For instance, the reaction of chloride **19a** ($R^1$ = 4-Me-$OC_6H_4$) with an excess of 4-aminophenol **17g** ($R^2$ = 4-$HOC_6H_4$) in refluxing toluene provided a mixture of three imidamides, **11aa** ($R^1$, $R^1$), **11ag** ($R^1$, $R^2$), and **11gg** ($R^2$, $R^2$), in yields of 14, 24, and 21%, respectively. This result suggests that *N*-aryl groups of **11** are easily exchangeable under the reaction conditions.[18] Therefore, activation of amines and use of milder reaction conditions are necessary. The desired unsymmetric imidamides **11** ($R^1 \neq R^2$) could

(14) *N*-Aryl imidamides were transformed to the corresponding nitrogen heterocycles with an oxidative reagent such as sodium hypochlorite[14a] or *tert*-butyl hypochlorite.[14b] (a) Grenda, V. J.; Jones, R. E.; Gal, G.; Sletzinger, M. *J. Org. Chem.* **1965**, *30*, 259. (b) Uneyama, K.; Sugimoto, K. *J. Org. Chem.* **1992**, *57*, 6014.

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**Scheme 4**

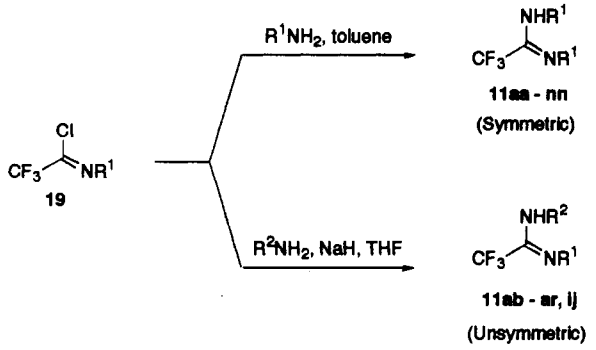
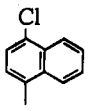



**Table 1. Preparation of Symmetric *N,N'*-Disubstituted Imidamides 11**

| 11 | $R^1$ | yield (%) |
|---|---|---|
| aa | 4-$MeOC_6H_4$ | 80[a] |
| bb | 4-$ClC_6H_4$ | 91[a] |
| cc | 4-*t*-$BuC_6H_4$ | 47[b] |
| dd | 4-*i*-$PrC_6H_4$ | 77[a] |
| ee | 4-$MeC_6H_4$ | 95[a] |
| ff | 4-$NO_2C_6H_4$ | 55[a] |
| gg | 4-$HOC_6H_4$ | 21[b] |
| hh | 3,4-$Cl_2C_6H_3$ | 82[a] |
| ii | 2-$MeOC_6H_4$ | 81[a] |
| jj | 3-$MeOC_6H_4$ | 90[a] |
| kk | Ph | 75[a] |
| mm |  | 60[a] |
| nn |  | 30[b] |

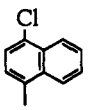
[a] The detailed preparations of the imidamides are summerized in the Experimental Section, see method A. [b] See method B.

be obtained in reasonable yields by sodium hydride-promoted reaction in THF at 68 °C (Scheme 4). The results are shown in Table 2.

The $^1H$ NMR spectra of *N,N'*-disubstituted 2,2,2-trifluoroethanimidamides 11 (DMSO-$d_6$, 25 °C) showed broad signals for the aromatic protons. The $^{19}F$ NMR spectra revealed a broad signal for the fluorine atoms of the trifluoromethyl group. Raising the temperature of the NMR probe, however, caused the $^{19}F$ NMR signal to converge into a sharp peak, and the broad $^1H$ NMR signals of the aromatic region also were sharpened. These results suggest the tautomerization[19] shown in Scheme 5. In fact, the $^1H$ NMR spectra of compounds **11ae** prepared from *N*-(4-methylphenyl)-2,2,2-trifluoroacetimidoyl chloride (**19e**) and *p*-anisidine (**17a**) and from *N*-(4-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (**19a**) and *p*-toluidine (**17e**), respectively, were superimposable.

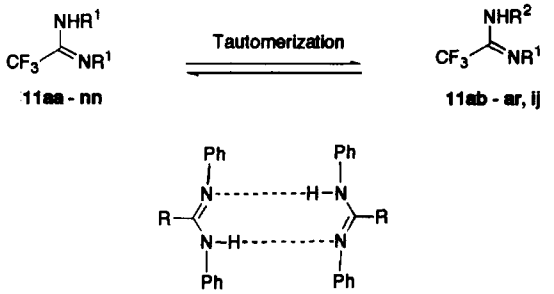
The IR spectrum of imidamide **11kk** in $CHCl_3$ showed a sharp N–H absorption at 3500 $cm^{-1}$. However, the spectrum of a neat sample of **11kk** showed a very broad N–H vibration band in the range of 3500–3200 $cm^{-1}$. This result indicates a compound with hydrogen bonding,[20] the structure (R = H,[21] Me,[22] and $CF_3$) of which would be as same as the dimeric structure of a carboxylic acid.

**Table 2. Preparation of Unsymmetric *N,N'*-Disubstituted Imidamides 11**

| 11 | $R^1$ | $R^2$ | yield (%) |
|---|---|---|---|
| ab | 4-$MeOC_6H_4$ | 4-$ClC_6H_4$ | 78[a] |
| ae | 4-$MeOC_6H_4$ | 4-$MeC_6H_4$ | 87[a] |
| af | 4-$MeOC_6H_4$ | 4-$NO_2C_6H_4$ | 95[a] |
| ag | 4-$MeOC_6H_4$ | 4-$HOC_6H_4$ | 24[b] |
| ah | 4-$MeOC_6H_4$ | 3,4-$Cl_2C_6H_3$ | 79[a] |
| ai | 4-$MeOC_6H_4$ | 2-$MeOC_6H_4$ | 82[a] |
| aj | 4-$MeOC_6H_4$ | 3-$MeOC_6H_4$ | 79[a] |
| ak | 4-$MeOC_6H_4$ | Ph | 81[a] |
| al | 4-$MeOC_6H_4$ |  | 67[a] |
| am | 4-$MeOC_6H_4$ |  | 87[a] |
| an | 4-$MeOC_6H_4$ | Cl  | 87[a] |
| ao | 4-$MeOC_6H_4$ | *n*-$C_6H_{13}$ | 62[c] |
| ap | 4-$MeOC_6H_4$ | $CH_2$=$CHCH_2$ | 66[c] |
| aq | 4-$MeOC_6H_4$ | $PhCH_2$ | 78[c] |
| ar | 4-$MeOC_6H_4$ | 4-$Ph_3COC_6H_4$ | 48[d] |
| ij | 2-$MeOC_6H_4$ | 3-$MeOC_6H_4$ | 74[a] |

[a] The detailed preparations of the imidamides are summerized in the Experimental Section, see method C. [b] See method B. [c] See method D. [d] See method E.

**Scheme 5**




**Electrochemical Oxidation of Imidamides 11.** The electrolysis was conducted under constant current density conditions rather than constant potential conditions so as to get products on a preparative scale. A glassy carbon anode and a platinum foil cathode were employed in an undivided cell.

Product selectivity in electrooxidations of 11 was strongly affected by the concentration of water in the solvent acetonitrile, the current density, the electrolysis temperature, the electronic nature, and the position of substituents on the *N*-aryl ring. Electrooxidation of **11aa** in dry acetonitrile provided intramolecularly cyclized benzimidazole **15aa** quantitatively (Scheme 6). The detrifluoromethylation[4] leading to *N*-aryl carbodiimide seen with acyloxy radicals was not observed. Intermolecular nitrogen–nitrogen coupling[5] was not observed although some nitrogen radicals undergo N–N coupling.[12] Intramolecular trapping of the amide radical with an aryl ring would be much faster than the intermolecular N–N

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(22) White, N. E.; Kilpatrick, M. *J. Phys. Chem.* **1955**, *59*, 1044.
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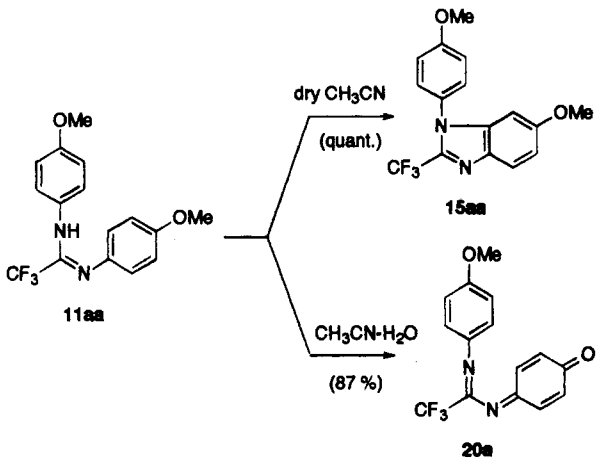
**Scheme 6**




coupling. Meanwhile, *p*-benzoquinone imine **20a** was produced exclusively in aqueous acetonitrile[23] (Scheme 6).

The formations from **11aa** of **15aa** in dry acetonitrile and **20a** in aqueous acetonitrile were highly dependent on current density as shown in Figure 1. The lower current density conditions increased the yields of **15aa** and **20a**. The effect of the concentration of water in acetonitrile was examined at both 60 °C and 0 °C, and the results are shown in Figure 2. At 60 °C, cyclization occurred cleanly in dry acetonitrile. But an increase of the water concentration sharply decreased the yield of **15aa**. Although formation of **15aa** (10%) was observed at the higher temperature even in 10% water, the yield of **20a** was poor, and a large amount (>40%) of starting substrate **11aa** was recovered after 2.0 F/mol (Figure 2, part a). In contrast, at 0 °C, *p*-benzoquinone imine **20a** formed in a reasonable yield, and the recovery of **11aa** was only 10% when 2 F/mol of electricity was passed through the solution (Figure 2, part b). These results indicate that the current efficiency for the consumption of **11aa** in the aqueous medium is highly dependent on the electrolysis temperature and suggest that electrooxidation of water is favored over oxidation of substrate **11aa** at the higher temperature.

**Substituent Effect on Benzimidazoles 15 in Dry Acetonitrile.** The results of electrooxidation of symmetric *N,N'*-diaryl imidamides are shown in Table 3. High reaction temperature favored the formation of benzimidazoles **15aa** (quantitatively (60 °C), 95% (25 °C), 79% (0 °C), and 58% (−20 °C)). When the temperature was decreased, recovery of starting substrate **11aa** increased. When *N*-aryl groups were para-substituted phenyl, desired benzimidazoles **15** were obtained in reasonable yields. Thus, 4-chlorophenyl compound **11bb** and 4-*tert*-butylphenyl compound **11cc** were transformed to the corresponding benzimidazoles **15bb** and **15cc** in 94 and 80% yields, respectively. 4-Isopropylphenyl compound **11dd** and 4-methylphenyl compound **11ee** provided desired products **15dd** and **15ee** in 51 and 33% yields, respectively. In these cases, substantial amounts of substrate **11** were recovered, and the mass balance was low after 4 F/mol of electricity was passed through. The yield of **15ee** did not increase even though an excess amount of electricity was passed. Taking into account the good yield (80%) of *tert*-butylphenyl compound (**11cc** → **15cc**), the low efficiency of the cyclizations of **11dd** and **11ee** may be due to the facile removal of a benzylic proton[24] from the initially formed cation radicals and subsequent oligomerization or polymerization.

Electrooxidation of 4-nitrophenyl compound **11ff** resulted in complete recovery of **11ff**. 4-Hydroxyphenyl compound **11gg** provided *p*-benzoquinone imine derivative **20g** (Scheme 7, $R^2$ = 4-hydroxyphenyl) in 80% yield. Deprotonation of the phenolic hydroxyl group of the initially formed cation radicals proceeds faster than the intramolecular cyclization. 3,4-Dichlorophenyl compound **11hh** gave a mixture of two regioisomers, 1,2,4,5-tetrasubstituted isomer **15hh** (40%) and 1,2,3,4-tetrasubstituted isomer **15hh'** (19%) (Chart 5 and Table 5). However, 2-methoxyphenyl compound **11ii** gave a very poor yield of desired product **15ii** (5% yield). Compound **11ii** (30%) and unidentified polymeric compounds were recovered. Similarly, 3-methoxyphenyl compound **11jj** provided no **15jj**. Unsubstituted compound **11kk** gave only a 12% yield of desired product **15kk**, and polymeric products were formed predominantly even under the conditions where **11kk** was almost consumed. In the case where the 4-position of the *N*-aryl group in **11ii**, **11jj**, and **11kk** was unsubstituted, an intermolecular reaction similar to the electrooxidative polymerization of aniline occurred predominantly.[25] A similar trend was obtained with *N*-naphthyl imidamides **11mm** and **11nn**. Unsubstituted *N*-naphthyl compound **11mm** provided only unidentified polymers, although starting material **11mm** was consumed almost completely. In contrast, 4-chloro-1-naphthyl compound **11nn** provided desired compound **15nn** in 57% yield, demonstrating again the importance of substitution at the 4-position.

Electrooxidation of unsymmetric imidamides (**11ab–ar** and **11ij**, Table 4) in dry acetonitrile resulted in the formation of complicated mixtures. Two isomeric benzimidazoles (**15** and **21**, Scheme 7) and *p*-benzoquinone imines **20** were produced in most cases.

The structural elucidation of compounds **15** and **21** was performed by $^1$H NMR analysis. Dimethoxy compound **15aa** provided the couplings and chemical shifts of aryl protons H(4) [$\delta$ 7.78 (d, $J$ = 9.0 Hz)], H(5) [$\delta$ 7.02 (dd, $J$ = 2.5 Hz, 9.0 Hz)], and H(7) [$\delta$ 6.51 (d, $J$ = 2.5 Hz)] of the 6-methoxybenzimidazole skeleton and H(2') [$\delta$ 7.34 (d, $J$ = 8.0 Hz)] and H(3') [$\delta$ 7.08 (d, $J$ = 8.0 Hz)] of the *N*-4-methoxyphenyl group. The $^1$H NMR of **15ae** shows protons at $\delta$ 7.81 (d, $J$ = 8.9 Hz), 7.04 (dd, $J$ = 2.3 Hz, 8.9 Hz), and 6.53 (d, $J$ = 2.3 Hz), which are similar to those of benzimidazole ring of **15aa**, and pair of doublets for H(2') and H(3') at $\delta$ 7.31 and 7.40, which are also similar to those of **15ee**. These data support the conclusion that **15ae** has a 6-methoxybenzimidazole skeleton and an *N*-4-methylphenyl group. On the other hand, the $^1$H NMR of **21ae** reveals three protons, at $\delta$ 7.79 (d, $J$ = 8.3 Hz), 7.21 (dd, $J$ = 8.3 Hz, 1.3 Hz), and 6.92 (d, $J$ = 1.3 Hz), that are almost similar to the H(4) [$\delta$ 7.80 (d, $J$ = 8.4 Hz)], H(5) [$\delta$ 7.22 (dd, $J$ = 8.4 Hz, 1.7 Hz)], and H(7) [$\delta$ 6.92 (d, $J$ = 1.7 Hz)] protons of **15ee**, suggesting **21ae** has a 6-methylbenzimidazole skeleton. The spectrum of **21ae** also shows two doublets at $\delta$ 7.33 and 7.08, which arise from the *N*-4-methoxyphenyl group. These NMR analyses provide strong evidence for the structure of **21ae**.

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(25) Desideri, P. G.; Lepri, L.; Heimler, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *43*, 387.

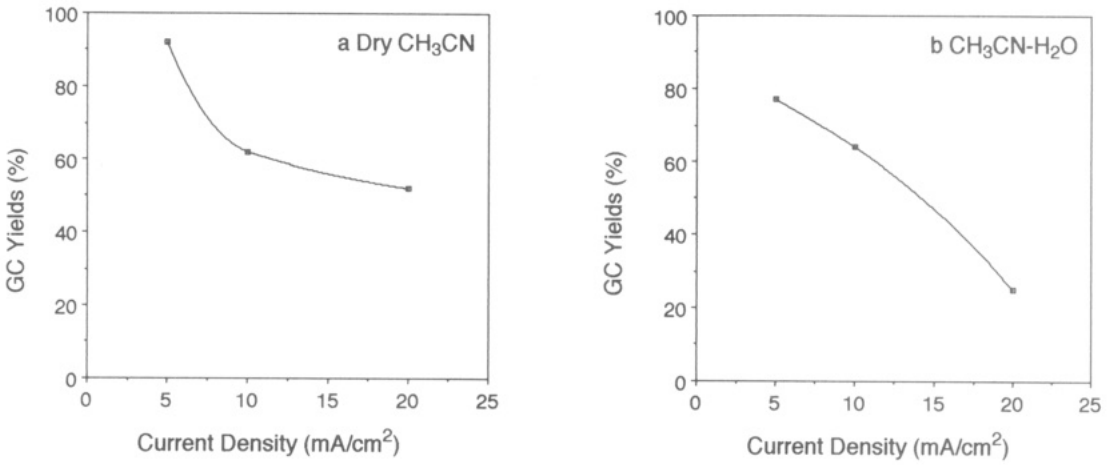



**Figure 1.** Effect of current density. (a) **11aa** (0.25 mmol), $CH_3CN$ (8 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 2.1 F/mol, undivided cell, 60 °C. (b) **11aa** (0.5 mmol), $CH_3CN$ (7 mL), $H_2O$ (1 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 2.1 F/mol, undivided cell, 0 °C.

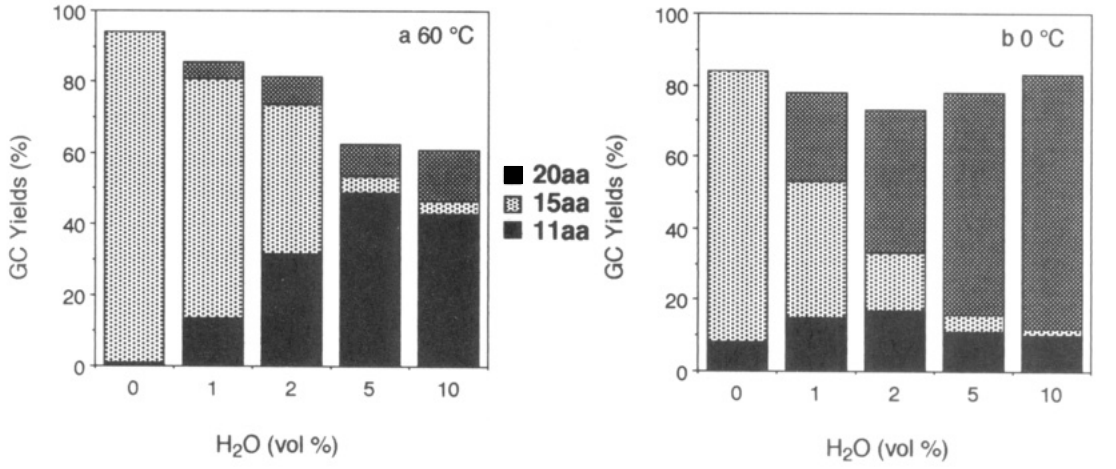



**Figure 2.** Effect of water concentration. (a) 60 °C, **11aa** (0.25 mmol), $CH_3CN$–$H_2O$ solution (10 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 2.0 F/mol, undivided cell. (b) 0 °C, **11aa** (0.25 mmol), $CH_3CN$–$H_2O$ solution (10 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 2.0 F/mol, undivided cell.

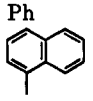
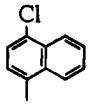
The product selectivity was again highly dependent on the electronic nature and the position of the substituent on the aryl ring. When $R^2$ of **11** was a 2-methoxyphenyl group, benzimidazole **15ai** was obtained in 54% yield as the sole isolable product, whereas 3-methoxyphenyl compound **11aj** provided not **15aj** but another type of benzimidazole, **21aj**, in 74% yield. A 2-methoxy group deactivates the C(6) position of the aryl ring ($R^2$), whereas a 3-methoxy group activates it to promote cyclization to **21**. Oxidation of both *N*-naphthyl compounds (**11am** and **11an**) led to exclusive formation of naphtho[2,1-*d*]-imidazoles **21am** and **21an** (Chart 3) in 42% and 94% yields, respectively, demonstrating again the importance of the 4-substituent. Taking into account the balance between the energy lost by destruction of the aromaticity in intermediate **A** (Chart 4) and the energy gained from the larger aromatic π-system in naphtho[2,1-*d*]imidazoles **21am** and **21an** when compared with that between **B** and **15am** ($R^2$ = 1-naphthyl) or **15an** ($R^2$ = 4-chloro-1-naphthyl), the formation of **21** rather than **15** is expected to be prefered in the cases of *N*-naphthyl compounds **11am** and **11an**.

Electrooxidation of 4-methylphenyl and phenyl compounds (**11ae**, and **11ak**) provided a mixture of **15**, **20**, and **21** (Scheme 7). Particularly noteworthy is the fact that the electron-withdrawing groups such as 4-nitro and 3,4-dichloro groups inhibited benzimidazole formation but markedly promoted *p*-benzoquinone imine formation. The weaker nucleophilicity of the nitrogen atom attached to the aryl ring bearing the electron-withdrawing group suppresses its nucleophilic attack on the electrooxidatively generated cationic carbon of the 4-methoxyphenyl moiety. Replacement of the *N*-aryl group with an *N*-alkyl group (**11ao**, **11ap**, and **11aq**) resulted in exclusive formation of *p*-benzoquinone imines (**20o**, **20p**, and **20q**, respectively), and the formation of **15** was completely suppressed.

Electrooxidation of 4-hydroxyphenyl compound **11ag** afforded *p*-benzoquinone imine **20a**. Deprotonation of the phenolic proton of the cation radical intermediate is much faster than intramolecular cyclization.

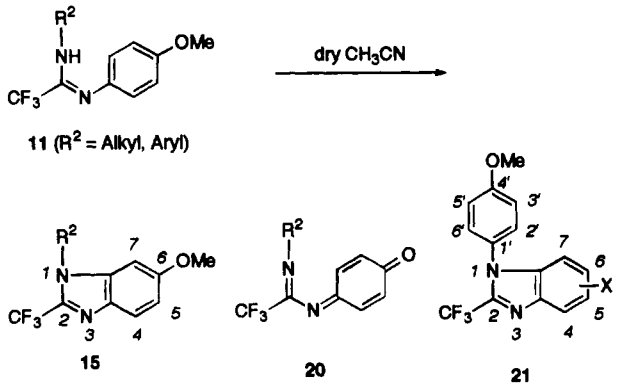
An overall two-electron process (ECEC process) leading from **11** to **15** is proposed (Scheme 8), although intramolecular cyclization at the stage of cation **22** and radical **23** cannot be ruled out. The question to be answered is the mechanism of *p*-benzoquinone imine formation in dry acetonitrile. There are two possible pathways. One involves demethylation of carbocation intermediate **24**, produced by two-electron oxidation of **11** (Scheme 9, path A). The other involves solvolysis of **22** with acetonitrile leading to iminium ion **25** and hydrolysis of **25** to **20** in the workup process (Scheme 9, path B). To check for the demethylation pathway, the methyl group was replaced

**Table 3. Electrooxidation[a] of Symmetric Imidamides 11 in Dry Acetonitrile**

| 11 | $R^1$ | yield (%) 15 |
|---|---|---|
| aa | 4-$MeOC_6H_4$ | quant. |
| bb | 4-$ClC_6H_4$ | 94 |
| cc | 4-*t*-$BuC_6H_4$ | 80 |
| dd | 4-*i*-$PrC_6H_4$ | 51[b] |
| ee | 4-$MeC_6H_4$ | 33[b] |
| ff | 4-$NO_2C_6H_4$ | *c* |
| gg | 4-$HOC_6H_4$ | 80[d] |
| hh | 3,4-$Cl_2C_6H_3$ | 40,[e,f] 19[f,g] |
| ii | 2-$MeOC_6H_4$ | 5[h] |
| jj | 3-$MeOC_6H_4$ | *h* |
| kk | Ph | 12[h] |
| mm |  | *h* |
| nn |  | 57[i,j] |

[a] Electrolysis conditions; 11 (0.25 mmol), $CH_3CN$ (10 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 60 °C, 2.1 F/mol, undivided cell. [b] An excess of electricity (4 F/mol) was passed. [c] Recovery of starting material 11. [d] The product was *p*-benzoquinone imine **20g**. [e] One of the regioisomers **15hh**. [f] The structure is listed in Chart 5 and Table 5. [g] Another of the regioisomers **15hh'**. [h] Polymeric products were obtained. [i] The product was naphtho[2,1-*d*]imidazole **21**. [j] The structure is shown in Chart 3.

**Scheme 7**

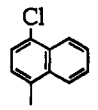



with a triphenylmethyl group, which was expected to enhance bond-breaking of the oxygen–carbon bond by leaving the more stable triphenylmethyl carbocation. If the carbon–oxygen bond-breaking proceeds via **24**, *N*-(triphenylmethyl)acetamide should be a major product. The electrooxidation of **11ar** resulted in the exclusive formation of **28** (82%) and **20a** (77%), and no amide **27** was detected. Taking into account the fact that the electrochemically generated triphenylmethyl carbocation can be trapped with acetonitrile and readily converted into amide **27**[26] and the fact that the *N*-(triphenylmethyl)-acetamide was not hydrolyzed to triphenylmethyl alcohol **28** under the electrolysis and the subsequent workup conditions, the present result suggests that the reaction proceeds by path B in Scheme 10. Nucleophilic attack of acetonitrile on the electrochemically oxidized aromatic ring has been reported in various electrooxidation processes of aromatic compounds.[27]

(26) Uneyama, K.; Torii, S. *Tetrahedron Lett.* **1971**, 329.

(27) An electrooxidation of anthracene[27a] or benzoic acid[27b] provided the corresponding acetamide compounds. (a) Hammerich, O.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1974**, 245. (b) Matsuda, Y.; Kimura, K.; Iwakura, C.; Tamura, H. *Bull. Soc. Chem. Jpn.* **1973**, *46*, 430.

**Table 4. Electrooxidation[a] of Unsymmetric Imidamides 11 ($R^1$ = 4-$MeOC_6H_4$) in Dry Acetonitrile**

| | | yield (%) | | |
|---|---|---|---|---|
| 11 | $R^2$ | 15 | 21 | 20 |
| ab | 4-$ClC_6H_4$ | 10[b] | | 57 |
| ae | 4-$MeC_6H_4$ | 9[b] | 48[b] | 16 |
| af | 4-$NO_2C_6H_4$ | | | 57 |
| ag | 4-$HOC_6H_4$ | | | 59[c] |
| ah | 3,4-$Cl_2C_6H_3$ | | | 62 |
| ai | 2-$MeOC_6H_4$ | 54[b] | | |
| aj | 3-$MeOC_6H_4$ | | 74[b] | |
| ak | Ph | 13[b] | 10[b] | 47 |
| am |  | | 42[d] | |
| an |  | | 94[d] | |
| ao | *n*-$C_6H_{13}$ | | | 60 |
| ap | $CH_2$=$CHCH_2$ | | | 20 |
| aq | $PhCH_2$ | | | 51 |
| ar | 4-$Ph_3COC_6H_4$ | | | 77[b,c] |
| ij | $R^1$ = 2-$MeOC_6H_4$, $R^2$ = 3-$MeOC_6H_4$ | | 18[b] | |

[a] Electrolysis conditions; 11 (0.25 mmol), $CH_3CN$ (10 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 60 °C, 2.1 F/mol, undivided cell. [b] Structures of **15** and **21** are listed in Chart 5 and Table 5. [c] The product was *p*-benzoquinone imine **20a**. [d] The product was naphtho[2,1-*d*]imidazole **21** (see Chart 3).

**Chart 3**

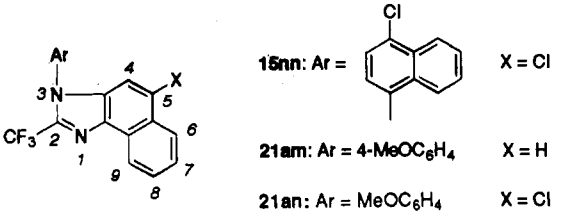



**Chart 4**

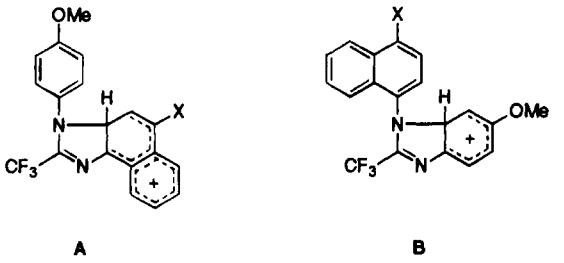
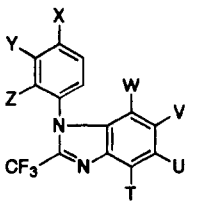



**Chart 5**




**Electrooxidation in Aqueous Acetonitrile.** In the electrooxidation of unsymmetric *N,N'*-diaryl imidamides such as **11ae** and **11ak** in dry acetonitrile, two intramolecular cyclizations, to benzimidazoles **15** and **21**, and formation of *p*-benzoquinone imine **20** were competitive. In contrast, the reaction pathway of the electrooxidation of **11** in aqueous acetonitrile was highly convergent. The formation of *p*-benzoquinone imines **20** was predominant

Scheme 8

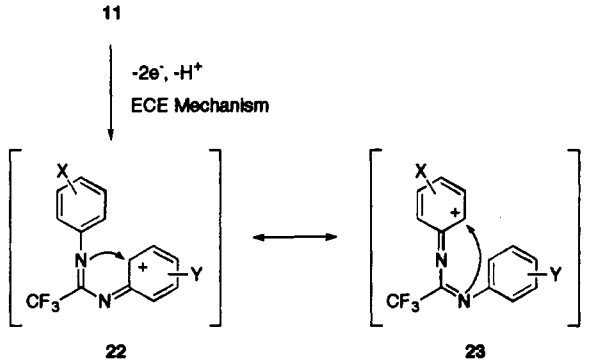
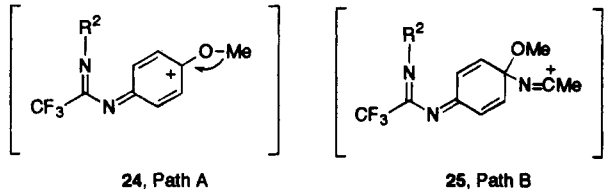


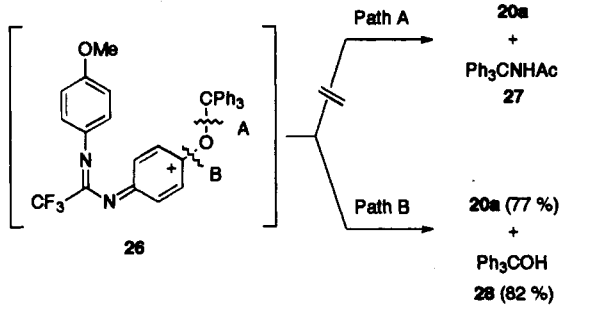

Table 5. Structure of Benzimidazole Derivatives 15 and 21

| compd | T | U | V | W | X | Y | Z |
|---|---|---|---|---|---|---|---|
| 15aa | H | H | MeO | H | MeO | H | H |
| 15bb | H | H | Cl | H | Cl | H | H |
| 15cc | H | H | *t*-Bu | H | *t*-Bu | H | H |
| 15dd | H | H | *i*-Pr | H | *i*-Pr | H | H |
| 15ee | H | H | Me | H | Me | H | H |
| 15hh | H | Cl | Cl | H | Cl | Cl | H |
| 15hh′ | H | H | Cl | Cl | Cl | Cl | H |
| 15ii | MeO | H | H | H | H | H | MeO |
| 15kk | H | H | H | H | H | H | H |
| 15ab | H | H | MeO | H | Cl | H | H |
| 15ae | H | H | MeO | H | Me | H | H |
| 15ai | H | H | MeO | H | H | H | MeO |
| 15ak | H | H | MeO | H | H | H | H |
| 21ae | H | H | Me | H | MeO | H | H |
| 21aj | H | MeO | H | H | MeO | H | H |
| 21ak | H | H | H | H | MeO | H | H |
| 21ij | H | MeO | H | H | H | H | MeO |

Scheme 9




Scheme 10




in almost all of the *N*-(4-methoxyphenyl)-*N*′-aryl imidamides **11** examined (Scheme 6). Noteworthy is the fact that regardless of the substituents electronic nature, *p*-benzoquinone imines **20** were produced in good to excellent yields (for instance, 87% for **20a** (4-MeO), 77% for **20f** (4-$NO_2$), and 85% for **20h** (3,4-$Cl_2$), Table 6). Even unsubstituted phenyl compound **11ak**, electrooxidation of which in dry acetonitrile resulted in polymerization, gave **20k** in a quite reasonable yield (91%). *N*-Alkyl compounds (**11ao**, **11ap**, and **11aq**) also provided **20** in excellent yields. The comparison between the quantitative formation of benzimidazole **15aa** from the 4-methoxy compound **11aa** in dry acetonitrile and lack of formation

Table 6. Preparation of *p*-Benzoquinone Imines 20 by Electrooxidation[a] of 11 in Aqueous Acetonitrile

| 11 | $R^2$ | yield (%) 20 |
|---|---|---|
| aa | 4-$MeOC_6H_4$ | 87 |
| ab | 4-$ClC_6H_4$ | 85 |
| ae | 4-$MeC_6H_4$ | 99 |
| af | 4-$NO_2C_6H_4$ | 77[b] |
| ag | 4-$HOC_6H_4$ | 60[c] |
| ah | 3,4-$Cl_2C_6H_3$ | 85 |
| ak | Ph | 91 |
| al |  | 61 |
| ao | *n*-$C_6H_{13}$ | 89 |
| ap | $CH_2$=$CHCH_2$ | 90 |
| aq | $PhCH_2$ | 94 |

[a] Electrolysis conditions; 11 (0.25 mmol), $CH_3CN$ (7 mL), $H_2O$ (1 mL), $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm², 0 °C, 2.1 F/mol, undivided cell. [b] A divided cell was used in order to suppress reaction of the *p*-benzoquinone imine **20f** at cathode. [c] The product was **20a**.

of **15aa** in aqueous acetonitrile is quite suggestive. Those results suggest that nucleophilic attack of water on the electrooxidatively generated aromatic cation (**24** → **20a**) is much faster than intramolecular cyclization (**22** → **15aa**).

## Experimental Section

**General Methods.** All commercial reagents were distilled or recrystallized before use. Acetonitrile was freshly distilled over phosphorus pentoxide. THF was distilled over sodium benzophenone prior to use. Benzene and toluene were distilled from calcium hydride. E. Merck silica gel (Kieselgel 60, 230–400 mesh) was employed for the chromatography. Analytical TLC was performed with 0.2-mm coated commercial plates (E. Merck, Kieselgel 60 F254). The $^1H$ and $^{19}F$ NMR were recorded on a Varian VXR-200 or 500 with TMS and $C_6F_6$ as internal standards. IR spectra were measured on a Hitachi 270-30 spectrometer. Analytical GC was performed on a Hitachi GC-3000 or a Shimazu GC-12A (25-m capillary column silicone OV-101, carrier gas $N_2$). GC-MS was performed on a Hewlett-Packard 5971 GC/MS workstation and a Hitachi M-80. Elemental analysis was performed on a Perkin-Elmer 2400 CHNS/O. Boiling points and melting points were uncorrected.

**Preparations of *N*,*N*′-Diaryl-2,2,2-trifluoroethanimidamides 11.** Imidamides **11** were prepared by the following five methods:

**Method A (Table 1, 11aa, 11bb, 11dd–ff, and 11hh–mm).** A mixture of *N*-aryl-2,2,2-trifluoroacetimidoyl chloride **19** (5 mmol) and arylamine (12 mmol) in toluene (10 mL) was stirred at the refluxing temperature (110 °C) for 2 h. The reaction mixture was extracted with ethyl acetate (100 mL × 3) and 1% hydrogen chloride (100 mL) and then washed with brine (50 mL). The organic layer was dried with anhyd magnesium sulfate, filtered, and concentrated. Then the residue was recrystallized from benzene–hexane.

**Method B (Table 1, 11cc, 11gg, 11nn, and 11ag).** A mixture of *N*-(4-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (**19a**) (5 mmol) and *p*-*tert*-butylaniline (20 mmol) in toluene (10 mL) was stirred at the refluxing temperature (110 °C) for 1 day. The reaction mixture was extracted with ethyl acetate (100 mL × 3). The extracts were washed with 1% aqueous hydrogen chloride (100 mL) and with brine (50 mL), dried over anhyd magnesium sulfate, filtered, and concentrated. Purification of the residue by silica gel column chromatography with ethyl acetate–hexane solution afforded **11cc**.

**Method C (Table 2, 11ab, 11ae, 11af, 11ah–an, and 11ij).** *N*-(4-Methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (**19a**) (5 mmol) in THF (5 mL) was poured into a mixture of arylamine (7.5 mmol) and sodium hydride (10 mmol) in THF (10 mL), and the mixture was stirred at 68 °C for 30 min. The mixture was extracted with ethyl acetate, and the extracts (100 mL × 3) were washed with 1% aqueous hydrogen chloride (100 mL) and with

brine (50 mL). The organic extract was dried over anhyd magnesium sulfate, filtered, and then recrystallized from benzene–hexane.

**Method D (11ao–aq).** A mixture of *N*-(4-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (**19a**) (5 mmol) and alkylamine (12 mmol) in benzene (10 mL) was stirred at rt for a few minutes under an $N_2$ atmosphere. The reaction mixture was extracted with ethyl acetate (100 mL × 3), and the extracts were washed with 1% aqueous hydrogen chloride (100 mL) and with brine (50 mL). The organic layer was dried over anhyd magnesium sulfate and filtered, and the concentrated residue was distilled to afford **11**.

**Method E (11ar).** A mixture of **11ag** (1 mmol) and triphenylmethyl chloride (trityl chloride) (1.6 mmol) in THF (10 mL) in the presence of sodium hydroxide (1.5 mmol) was stirred at 50 °C for 30 min under an $N_2$ atmosphere. The reaction mixture was extracted with ethyl acetate (20 mL × 3) and the extracts were washed with water (20 mL) and with brine (20 mL). The organic layer was dried over anhyd sodium sulfate and chromatographed on silica gel to give **11ar**.

***N,N'*-Bis(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11aa) (method A):** colorless crystals (80%); mp 110–113 °C; IR (neat) 3360, 3080, 2844, 1672, 1180 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 110 °C) δ 3.68 (s, 6 H, $OCH_3$) 6.57–6.73 (m, 6 H, Ar*H*), 7.05–7.19 (m, 2 H, Ar*H*), 8.85–9.05 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 96.3–96.5 (br, 3 F, $CF_3$); MS *m/z* 324 ($M^+$, 100) 202 ($M^+ - NHC_6H_4OMe$, 80). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2$ (324.30): C, 59.26; H, 4.66; N, 8.64. Found: C, 58.96; H, 4.57; N, 8.57.

***N,N'*-Bis(4-chlorophenyl)-2,2,2-trifluoroethanimidamide (11bb) (method A):** colorless crystals (91%); mp 64–66 °C; IR (neat) 3464, 3040, 1676, 1188 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.21–7.26 (br, 8 H, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 97.7–98.1 (br, 3 F, $CF_3$); MS *m/z* 336 ($M^+$, 10) 334 ($M^+$, 50) 332 ($M^+$, 80) 111 (100). Anal. Calcd for $C_{14}H_9Cl_2F_3N_2$ (333.14): C, 50.48; H, 2.72; N, 8.41. Found: C, 50.30; H, 2.69; N, 8.32.

***N,N'*-Bis(4-*tert*-butylphenyl)-2,2,2-trifluoroethanimidamide (11cc) (method B):** colorless crystals (47%); mp 27–28 °C; IR ($CHCl_3$) 3468, 3040, 2872, 1676, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 1.20 (s, 18 H, $ArC(CH_3)_3$), 6.60–7.13 (br, 8 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.3–96.5 (br, 3 F, $CF_3$); MS *m/z* 376 ($M^+$, 47) 361 ($M^+$ – Me, 100) 228 ($M^+ - NHC_6H_4C_4H_9$, 14). Anal. Calcd for $C_{22}H_{27}F_3N_2$ (376.45): C, 70.19; H, 7.23; N, 7.44. Found: C, 70.28; H, 7.31; N, 7.51.

***N,N'*-Bis(4-isopropylphenyl)-2,2,2-trifluoroethanimidamide (11dd) (method A):** colorless crystals (77%); mp 34–36 °C; IR ($CHCl_3$) 3440, 2956, 2876, 1676, 1148 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 1.13 (d, 12 H, *J* = 6.88 Hz, $ArCH(CH_3)_2$), 2.65–2.87 (m, 2 H, $ArCH(CH_3)_2$), 6.70–6.98 (br, 8 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.5–96.7 (br, 3 F, $CF_3$); MS *m/z* 348 ($M^+$, 80) 333 ($M^+$ – Me, 100), 214 ($M^+ - NHC_6H_4C_3H_7$, 30). Anal. Calcd for $C_{16}H_{15}F_3N_2$ (348.40): C, 68.95; H, 6.65; N, 8.04. Found: C, 69.09; H, 6.66; N, 8.14.

***N,N'*-Bis(4-methylphenyl)-2,2,2-trifluoroethanimidamide (11ee) (method A):** colorless crystals (95%); mp 66–68 °C; IR (neat) 3452, 3032, 2872, 1674, 1188 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 2.29 (s, 6 H, $ArCH_3$), 7.04–7.08 (br, 8 H, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 95.3–95.9 (br, 3 F, $CF_3$); MS *m/z* 292 ($M^+$, 100) 223 ($M^+ - CF_3$, 45) 186 ($M^+ - NHC_6H_4Me$, 50). Anal. Calcd for $C_{16}H_{15}F_3N_2$ (292.30): C, 65.75; H, 5.17; N, 9.58. Found: C, 65.73; H, 5.16; N, 9.41.

***N,N'*-Bis(4-nitrophenyl)-2,2,2-trifluoroethanimidamide (11ff) (method A):** yellow crystals (55%); mp 221–222 °C; IR (Nujol) 3332, 3108, 1696, 1176 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.92–7.11 (br, 2 H, Ar*H*), 7.68–7.91 (br, 2 H, Ar*H*), 8.05–8.17 (m, 4 H, Ar*H*), 10.30–10.47 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 98.2–98.4 (br, 3 F, $CF_3$); MS *m/z* 354 ($M^+$, 60) 285 ($M^+ - CF_3$, 20), 217 ($M^+ - NHC_6H_4NO_2$, 100). Anal. Calcd for $C_{14}H_9F_3N_4O_4$ (354.24): C, 47.47; H, 2.56; N, 15.81. Found: C, 47.07; H, 2.84; N, 16.03.

***N,N'*-Bis(4-hydroxyphenyl)-2,2,2-trifluoroethanimidamide (11gg) (method B):** colorless crystals (21%); mp 199–201 °C; IR (Nujol) 3280, 1640, 1220 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.20–7.05 (br, 8 H, Ar*H*), 8.41–9.01 (br, 3 H, O*H*, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.1–102.5 (br, 3 F, $CF_3$); MS *m/z* 296 ($M^+$, 90) 227 ($M^+ - CF_3$, 35), 188 ($M^+ - NHC_6H_4OH$, 100). Anal. Calcd for $C_{14}H_{11}F_3N_2O_2$ (296.24): C, 56.76; H, 3.74; N, 9.46. Found: C, 56.79; H, 3.67; N, 9.58.

***N,N'*-Bis(3,4-dichlorophenyl)-2,2,2-trifluoroethanimidamide (11hh) (method A):** colorless crystals (82%); mp 80–84 °C; IR (neat) 3444, 3108, 1680, 1182 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.64–6.78 (br, 1 H, Ar*H*), 6.86–6.95 (br, 1 H, Ar*H*), 7.28–7.45 (br, 3 H, Ar*H*), 7.52–7.68 (br, 1 H, Ar*H*), 9.70–10.10 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 99.9–100.1 (br, 3 F, $CF_3$); MS *m/z* 406 ($M^+$, 5), 404 ($M^+$, 20), 402 ($M^+$, 45), 400 ($M^+$, 30), 240 ($M^+ - NHC_6H_3Cl_2$, 100). Anal. Calcd for $C_{14}H_7Cl_4F_3N_2$ (402.03): C, 41.83; H, 1.76; N, 6.97. Found: C, 41.89; H, 1.81; N, 6.71.

***N,N'*-Bis(2-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ii) (method A):** colorless crystals (81%); mp 91–93 °C; IR (neat) 3452, 3012, 2844, 1682, 1186 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.68 (s, 6 H, $OCH_3$), 6.59–6.99 (br, 8 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 93.8–94.0 (br, 3 F, $CF_3$); MS *m/z* 324 ($M^+$, 40), 293 ($M^+$ – OMe, 100), 202 ($M^+ - NHC_6H_4OMe$, 20). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2$ (324.30): C, 59.26; H, 4.66; N, 8.64. Found: C, 59.06; H, 4.66; N, 8.48.

***N,N'*-Bis(3-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11jj) (method A):** colorless crystals (90%); mp 63–65 °C; IR (neat) 3352, 2948, 2840, 1680, 1216 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.65 (s, 6 H, $ArCH_3$), 6.50 (d, 4 H, *J* = 7.3 Hz, Ar*H*), 6.20–6.85 (br, 2 H, Ar*H*), 7.03 (t, 2 H, *J* = 7.3 Hz, Ar*H*), 9.02–9.42 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.7–96.9 (br, 3 F, $CF_3$); MS *m/z* 324 ($M^+$, 80), 323 ($M^+ - 1$, 100), 255 ($M^+ - CF_3$, 20), 202 ($M^+ - NHC_6H_4OMe$, 20). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2$ (324.30): C, 59.26; H, 4.66; N, 8.64. Found: C, 59.26; H, 4.65; N, 8.67.

***N,N'*-Diphenyl-2,2,2-trifluoroethanimidamide (11kk) (method A):** colorless crystals (75%); mp 73–74 °C; IR (neat) 3456, 3268, 3040, 1670, 1186 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.65–7.34 (br, 10 H, Ar*H*), 9.48–9.88 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.4–92.6 (br, 3 F, $CF_3$); MS *m/z* 264 ($M^+$, 90), 195 ($M^+ - CF_3$, 50), 172 ($M^+ - NHC_6H_5$, 50), 77 ($Ph^+$, 100). Anal. Calcd for $C_{14}H_{11}F_3N_2$ (264.26): C, 63.63; H, 4.19; N, 10.60. Found: C, 63.54; H, 4.10; N, 10.30.

***N,N'*-Bis(1-naphthyl)-2,2,2-trifluoroethanimidamide (11mm) (method A):** colorless crystals (60%); mp 123–125 °C; IR ($CHCl_3$) 3428, 3056, 1660, 1150 $cm^{-1}$; $^1HNMR$ (200 MHz, DMSO-$d_6$, 80 °C) δ 6.30–8.05 (br, 14 H, Ar*H*), 9.49–9.89 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 94.6–94.9 (br, 3 F, $CF_3$); MS *m/z* 364 ($M^+$, 100), 363 ($M^+ - 1$, 75), 295 ($M^+ - CF_3$, 25), 222 ($M^+ - NHC_{10}H_7$, 35). Anal. Calcd for $C_{22}H_{15}F_3N_2$ (364.36): C, 72.52; H, 4.15; N, 7.69. Found: C, 72.64; H, 4.10; N, 7.57.

***N,N'*-Bis(4-chloro-1-naphthyl)-2,2,2-trifluoroethanimidamide (11nn) (method B):** colorless crystals (30%); mp 107–111 °C; IR ($CHCl_3$) 3424, 3008, 1678, 1190 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.40–6.75 (br, 2 H, Ar*H*), 6.88–7.00 (br, 2 H, Ar*H*), 7.41–7.60 (m, 4 H, Ar*H*), 7.79–7.96 (m, 4 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 94.1–94.3 (br, 3 F, $CF_3$); MS *m/z* 436 ($M^+$, 16), 434 ($M^+$, 60), 432 ($M^+$, 100), 256 ($M^+ - NHC_{10}H_6Cl$, 72). Anal. Calcd for $C_{22}H_{13}Cl_2F_3N_2$ (433.26): C, 60.99; H, 3.02; N, 6.47. Found: C, 60.86; H, 3.04; N, 6.53.

***N*-(4-Chlorophenyl)-*N'*-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ab) (method C):** colorless crystals (78%, a mixture of two tautomers); mp 95–97 °C; IR (neat) 3368, 2970, 2870, 1672, 1186 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.68 (s, 3 H, $OCH_3$), 6.71 (d, 2 H, *J* = 8.5 Hz, Ar*H*), 6.70–7.21 (br, 4 H, Ar*H*), 7.11 (d, 2 H, *J* = 8.5 Hz, Ar*H*), 9.00–9.50 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.6–96.8 (br, 3 F, $CF_3$); MS *m/z* 330 ($M^+$, 35), 328 ($M^+$, 100), 208 ($M^+ - NHC_6H_4OMe$, 12), 206 ($M^+ - NHC_6H_4OMe$, 36), 202 ($M^+ - NHC_6H_4Cl$, 76). Anal. Calcd for $C_{15}H_{12}ClF_3N_2O$ (328.72): C, 54.81; H, 3.68; N, 8.52. Found: C, 54.52; H, 3.66; N, 8.38.

***N*-(4-Methoxyphenyl)-*N'*-(4-methylphenyl)-2,2,2-trifluoroethanimidamide (11ae) (method C):** colorless crystals (87%, a mixture of two tautomers); mp 109–110 °C; IR ($CHCl_3$) 3476, 2844, 1672, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 50 °C) δ 2.29 (s, 3 H, $ArCH_3$), 3.77 (s, 3 H, $OCH_3$), 6.76 (d, 2 H, $J_1$ = 8.5 Hz, Ar*H*), 6.90 (d, 2 H, $J_2$ = 8.4 Hz, Ar*H*), 6.99 (d, 2 H, $J_2$ = 8.4 Hz, Ar*H*), 7.03 (d, 2 H, $J_1$ = 8.5 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 50 °C) δ 95.2–95.4 (br, 3 F, $CF_3$); MS *m/z* 308 ($M^+$, 100), 307 ($M^+$

– 1, 95), 239 ($M^+ - CF_3$, 20), 202 ($M^+ - NHC_6H_4Me$, 40), 186 ($M^+ - NHC_6H_4OMe$, 40). Anal. Calcd for $C_{16}H_{15}F_3N_2O$ (308.30): C, 62.34; H, 4.90; N, 9.09. Found: C, 62.35; H, 4.84; N, 9.06.

***N*-(4-Methoxyphenyl)-*N*'-(4-nitrophenyl)-2,2,2-trifluoroethanimidamide (11af) (method C):** lemon yellow crystals (95%, a mixture of two tautomers); mp 99–101 °C; IR (neat) 3372, 3012, 2840, 1676, 1156 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.66 (s, 3 H, $OCH_3$), 6.73 (d, 2 H, $J$ = 8.9 Hz, Ar*H*), 6.81–7.20 (br, 4 H, Ar*H*), 7.95 (d, 2 H, $J$ = 8.9 Hz, Ar*H*), 9.42–9.82 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 95.9–96.1 (br, 3 F, $CF_3$); MS $m/z$ 339 ($M^+$, 85), 202 ($M^+ - NHC_6H_4NO_2$, 50), 122 ($C_6H_4NO_2^+$, 100). Anal. Calcd for $C_{15}H_{12}F_3N_3O_3$ (339.27): C, 53.10; H, 3.56; N, 12.39. Found: C, 53.18; H, 3.43; N, 12.17.

***N*-(4-Hydroxyphenyl)-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ag) (method B):** colorless crystals (24%, a mixture of two tautomers); mp 45–50 °C; IR ($CHCl_3$) 3680, 3472, 3032, 2844, 1664, 1152 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.67 (s, 3 H, $OCH_3$), 6.48–6.90 (br, 8 H, Ar*H*), 8.50–9.00 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 95.8–98.6 (br, 3 F, $CF_3$); MS $m/z$ 310 ($M^+$, 100), 241 ($M^+ - CF_3$, 25), 202 ($M^+ - NHC_6H_4OH$, 52), 189 (40). Anal. Calcd for $C_{15}H_{13}F_3N_2O_2$ (310.27): C, 58.07; H, 4.22; N, 9.03. Found: C, 58.21; H, 4.34; N, 8.64.

***N*-(3,4-Dichlorophenyl)-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ah) (method C):** colorless crystals (79%, a mixture of two tautomers); mp 103–104 °C; IR (neat) 3440, 3008, 2844, 1678, 1184 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.69 (s, 3 H, $OCH_3$), 6.68–7.30 (br, 7 H, Ar*H*), 9.23–9.63 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 95.7–96.1 (br, 3 F, $CF_3$); MS $m/z$ 366 ($M^+$, 5), 364 ($M^+$, 45), 362 ($M^+$, 68), 240 ($M^+ - NHC_6H_4OMe$, 22), 202 ($M^+ - NHC_6H_3Cl_2$, 100). Anal. Calcd for $C_{15}H_{11}Cl_2F_3N_2O$ (363.16): C, 49.61; H, 3.05; N, 7.71. Found: C, 49.88; H, 3.11; N, 7.60.

***N*-(2-Methoxyphenyl)-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ai) (method C):** colorless crystals (82%, a mixture of two tautomers); mp 70–72 °C; IR ($CHCl_3$) 3448, 2956, 2844, 1668, 1148 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.64 (s, 3 H, $OCH_3$), 3.66 (s, 3 H, $OCH_3$), 6.58–7.20 (br, 8 H, Ar*H*), 9.02–9.42 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 95.0–95.2 (br, 3 F, $CF_3$); MS $m/z$ 324 ($M^+$, 60), 293 ($M^+$ – Me, 100), 202 ($M^+ - NHC_6H_4OMe$, 40). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2$ (324.30): C, 59.26; H, 4.66; N, 8.64. Found: C, 59.52; H, 4.69; N, 8.75.

***N*-(3-Methoxyphenyl)-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11aj) (method C):** colorless crystals (79%, a mixture of two tautomers); mp 71–73 °C; IR ($CHCl_3$) 3480, 2995, 2852, 1682, 1158 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.65 (s, 3 H, $OCH_3$), 3.68 (s, 3 H, $OCH_3$), 6.20–7.15 (br, 8 H, Ar*H*), 8.85–9.25 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.5–96.7 (br, 3 F, $CF_3$); MS $m/z$ 324 ($M^+$, 80), 323 ($M^+$ – 1, 100), 255 ($M^+ - CF_3$, 20), 202 ($M^+ - NHC_6H_4OMe$, 20). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2$ (324.30): C, 59.26; H, 4.66; N, 8.64. Found: C, 59.06; H, 4.58; N, 8.56.

***N*-(4-Methoxyphenyl)-*N*'-phenyl-2,2,2-trifluoroethanimidamide (11ak) (method C):** colorless crystals (81%, a mixture of two tautomers); mp 80–81 °C; IR (neat) 3480, 3012, 2844, 1678, 1184 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.67 (s, 3 H, $OCH_3$), 6.51–7.31 (br, 9 H, Ar*H*), 9.09–9.49 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 97.4–97.6 (br, 3 F, $CF_3$); MS $m/z$ 294 ($M^+$, 90), 225 ($M^+ - CF_3$, 35), 202 ($M^+$ – NHPh, 35), 172 ($M^+ - NHC_6H_4OMe$, 35), 122 ($NHC_6H_4OMe^+$, 30), 77 ($Ph^+$, 100). Anal. Calcd for $C_{15}H_{13}F_3N_2O$ (294.27): C, 61.23; H, 4.45; N, 9.52. Found: C, 61.26; H, 4.44; N, 9.46.

***N*-(4-Methoxyphenyl)-*N*'-(5,6,7,8-tetrahydro-1-naphthyl)-2,2,2-trifluoroethanimidamide (11al) (method C):** colorless crystals (67%, a mixture of two tautomers); mp 70–73 °C; IR (neat) 3368, 3008, 2840, 1672, 1182 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 1.60–1.80 (m, 4 H, $CH_2(CH_2)_2CH_2$), 2.35–2.69 (m, 4 H, $CH_2(CH_2)_2CH_2$), 3.66 (s, 3 H, $OCH_3$), 6.35–7.26 (br, 7 H, Ar*H*), 8.95–9.35 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.4–96.6 (br, 3 F, $CF_3$); MS $m/z$ 348 ($M^+$, 30), 226 ($M^+ - NHC_6H_4OMe$, 15), 123 (100). Anal. Calcd for $C_{19}H_{19}F_3N_2O$ (348.36): C, 65.51; H, 5.49; N, 8.04. Found: C, 65.73; H, 5.65; N, 8.01.

***N*-(4-Methoxyphenyl)-*N*'-(1-naphthyl)-2,2,2-trifluoroethanimidamide (11am) (method C):** yellow oil (87%, a mixture of two tautomers): bp 185 °C (2 mmHg); IR (neat) 3352, 3008, 2840, 1676, 1182 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.62 (s, 3 H, $OCH_3$), 6.62 (d, 2 H, $J_1$ = 8.7 Hz, Ar*H*), 6.70 (d, 1 H, $J_2$ = 8.0 Hz, Ar*H*), 6.93–7.23 (br, 3 H, Ar*H*), 7.40–7.66 (m, 3 H, Ar*H*), 7.71–7.84 (m, 2 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 96.1–96.5 (br, 3 F, $CF_3$); MS $m/z$ 344 ($M^+$, 100), 275 ($M^+ - CF_3$, 20), 222 ($M^+ - NHC_6H_4OMe$, 15), 202 ($M^+ - NHC_{10}H_7$, 65). Anal. Calcd for $C_{19}H_{15}F_3N_2O$ (344.33): C, 66.28; H, 4.39; N, 8.14. Found: C, 65.91; H, 4.36; N, 8.09.

***N*-(4-Chloro-1-naphthyl)-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11an) (method C):** colorless crystals (87%, a mixture of two tautomers); mp 90–92 °C; IR (neat) 3476, 2980, 2855, 1674, 1182 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.61 (s, 3 H, $OCH_3$), 6.49 (d, 2 H, $J_1$ = 8.7 Hz, Ar*H*), 6.63 (d, 1 H, $J_2$ = 8.0 Hz, Ar*H*), 6.93–7.15 (br, 2 H, Ar*H*), 7.29 (d, 1 H, $J_2$ = 8.0 Hz, Ar*H*), 7.47–7.66 (m, 2 H, Ar*H*), 7.84–7.90 (m, 1 H, Ar*H*), 8.02–8.09 (m, 1 H, Ar*H*), 9.19–9.59 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 95.5–95.9 (br, 3 F, $CF_3$); MS $m/z$ 380 ($M^+$, 33), 378 ($M^+$, 100), 256 ($M^+ - NHC_6H_4OMe$, 13), 202 ($M^+ - NHC_{10}H_6Cl$, 100). Anal. Calcd for $C_{19}H_{14}ClF_3N_2O$ (378.78): C, 60.25; H, 3.72; N, 7.40. Found: C, 60.26; H, 3.93; N, 7.15.

***N*-*n*-Hexyl-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ao) (method D):** colorless oil (62%, a mixture of two tautomers); bp 142 °C (4 mmHg); IR ($CHCl_3$) 3484, 3024, 2936, 2864, 1664, 1136 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 0.85 (t, 3 H, $J_1$ = 6.8 Hz, $NCH_2(CH_2)_4CH_3$), 1.15–1.52 (br, 8 H, $NCH_2(CH_2)_4CH_3$), 2.94–3.09 (br, 2 H, $NCH_2(CH_2)_4CH_3$), 3.71 (s, 3 H, $OCH_3$), 6.65 (d, 2 H, $J_2$ = 8.8 Hz, Ar*H*), 6.80 (d, 2 H, $J_2$ = 8.8 Hz, Ar*H*), 6.88–7.28 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 97.4–97.9 (br, 3 F, $CF_3$); MS $m/z$ 302 ($M^+$, 100), 287 ($M^+ - CH_3$, 8), 217 ($M^+ - C_6H_{13}$, 75), 204 ($M^+ - NHC_6H_{13}$, 73), 180 ($M^+ - NHC_6H_4OMe$, 8). Anal. Calcd for $C_{15}H_{21}F_3N_2O$ (302.33): C, 59.61; H, 7.00; N, 9.27. Found: C, 59.57; H, 7.0; N, 9.43.

***N*-Allyl-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11ap) (method D):** colorless oil (66%, a mixture of two tautomers); bp 210 °C (28 mmHg); IR ($CHCl_3$) 3484, 3044, 2956, 2840, 1682, 1154 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.71 (s, 3 H, $OCH_3$), 3.62–3.75 (br, 2 H, $NCH_2CH{=}CH_2$), 5.03–5.17 (br, 2 H, $NCH_2CH{=}CH_2$), 5.68–5.88 (m, 1 H, $NCH_2CH{=}CH_2$), 6.65 (d, 2 H, $J$ = 8.7 Hz, Ar*H*), 6.81 (d, 2 H, $J$ = 8.7 Hz, Ar*H*), 7.18–7.58 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 98.1–98.3 (br, 3 F, $CF_3$); MS $m/z$ 258 ($M^+$, 60), 243 ($M^+ - CH_3$, 100), 202 ($M^+ - NHCH_2CH{=}CH_2$, 18), 189 ($M^+ - CF_3$, 16), 148 ($C(NH)NC_6H_4OMe^+$, 60). Anal. Calcd for $C_{12}H_{13}F_3N_2O$ (258.24): C, 55.81; H, 5.07; N, 10.85. Found: C, 55.81; H, 5.09; N, 11.02.

***N*-Benzyl-*N*'-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11aq) (method D):** colorless oil (78%, a mixture of two tautomers); bp 176–179 °C (4 mmHg); IR ($CHCl_3$) 3476, 2952, 2840, 1682, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.71 (s, 3 H, $OCH_3$), 4.33 (s, 2 H, $ArCH_2C_6H_5$), 6.59 (d, 2 H, $J$ = 8.8 Hz, Ar*H*), 6.77 (d, 2 H, $J$ = 8.8 Hz, Ar*H*), 7.16–7.34 (m, 5 H, $CH_2C_6H_5$), 7.58–7.98 (br, 1 H, N*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 98.1–98.3 (br, 3 F, $CF_3$); MS $m/z$ 308 ($M^+$, 50), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{16}H_{15}F_3N_2O$ (308.30): C, 62.33; H, 4.90; N, 9.09. Found: C; 62.09; H, 4.91; N, 9.26.

***N*-(4-Methoxyphenyl)-*N*'-(4-(triphenylmethoxy)phenyl)-2,2,2-trifluoroethanimidamide (11ar) (method E):** colorless crystals (48%, a mixture of two tautomers); mp 48–52 °C; IR ($CHCl_3$) 3468, 3048, 2844, 1668, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.78 (s, 3 H, $OCH_3$), 6.41–6.61 (br, 4 H, Ar*H*), 6.56–6.76 (br, 4 H, Ar*H*), 7.20–7.26 (br, 10 H, Ar*H*), 7.39–7.44 (br, 5 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.8–93.0 (br, 3 F, $CF_3$), 98.0–98.1 (br, 3 F, $CF_3$); MS $m/z$ 310 (45), 243 ($CPh_3^+$, 95), 202 ($M^+ - NHC_6H_4OCPh_3$, 35), 165 (100). Anal. Calcd for $C_{34}H_{27}F_3N_2O_2$ (552.59): C, 73.90; H, 4.92; N, 5.07. Found: C, 74.05; H, 5.10; N, 5.46.

***N*-(2-Methoxyphenyl)-*N*'-(3-methoxyphenyl)-2,2,2-trifluoroethanimidamide (11aj) (method B):** colorless oil (74%, a mixture of two tautomers); bp 145 °C (4 mmHg); IR ($CHCl_3$) 3450, 2948, 2849, 1680, 1158 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.64 (s, 3 H, $OCH_3$), 3.70 (s, 3 H, $OCH_3$), 6.40–7.02 (br, 8 H Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 95.0–95.5 (br, 3 F, $CF_3$); MS $m/z$ 324 ($M^+$, 30), 293 ($M^+$ – OMe, 100), 202

($M^+$ – $NHC_6H_4OMe$, 20). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2$ (324.30): C, 59.26; H, 4.66; N, 8.64. Found: C, 58.88; H, 4.60; N, 8.36.

**General Procedure of Electrolysis.** Imidamide 11 (0.5 mmol) was dissolved in acetonitrile (10 mL) containing sodium perchlorate (0.4 mmol) and electrooxidized at 60 °C in an undivided beaker type cell (10 cm tall and 1.5 cm in diameter) using a glassy carbon (Toyo carbon FE-4, 2.0 × 1.5 × 0.3 cm) anode and a platinum foil (2.0 × 1.5 cm) cathode in a constant current of 5 mA/cm² for 2.1 F/mol of electricity. After the electrolysis, the solvent was evaporated under reduced pressure, and the residue was extracted with ethyl acetate (5 mL × 5) and washed with water (5 mL) and with brine (5 mL). The organic layer was dried over anhyd sodium sulfate, concentrated, chromatographed on silica gel, and recrystallized from benzene–hexane, affording benzimidazoles 15.

**1-(4-Methoxyphenyl)-2-(trifluoromethyl)-6-methoxybenzimidazole (15aa):** colorless crystals (quantitatively); mp 97–98 °C; IR (neat) 2968, 2844, 1172 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C) δ 3.77 (s, 3 H, $OCH_3$), 3.91 (s, 3 H, $OCH_3$), 6.51 (d, 1 H, $J_1$ = 2.5 Hz, Ar*H*), 7.02 (dd, 1 H, $J_1$ = 2.5 Hz, $J_2$ = 9.0 Hz, Ar*H*), 7.08 (d, 2 H, $J_3$ = 8.0 Hz, Ar*H*), 7.34 (d, 2 H, $J_3$ = 8.0 Hz, Ar*H*), 7.78 (d, 1 H, $J_2$ = 9.0 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.1 (s, 3 F, $CF_3$); MS *m/z* 322 ($M^+$, 100), 307 ($M^+$ – $CH_3$, 20). Anal. Calcd for $C_{16}H_{13}F_3N_2O_2$ (322.29): C, 59.63; H, 4.07; N, 8.69. Found: C, 59.62; H, 4.06; N, 8.57.

**1-(4-Chlorophenyl)-2-(trifluoromethyl)-6-chlorobenzimidazole (15bb):** colorless crystals (94%); mp 98–100 °C; IR (neat) 3072, 1190 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.14 (d, 1 H, $J_1$ = 2.0 Hz, Ar*H*), 7.38 (dd, 1H, $J_1$ = 2.0 Hz, $J_2$ = 8.5 Hz, Ar*H*), 7.40 (d, 2 H, $J_3$ = 9.0 Hz, Ar*H*), 7.59 (d, 2 H, $J_3$ = 9.0 Hz, Ar*H*), 7.85 (d, 1 H, $J_2$ = 8.5 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.0 (s, 3 F, $CF_3$); MS *m/z* 334 ($M^+$, 10), 332 ($M^+$, 60), 330 ($M^+$, 100). Anal. Calcd for $C_{14}H_7Cl_2F_3N_2$ (322.29): C, 50.78; H, 2.13; N, 8.46. Found: C, 50.65; H, 2.14; N, 8.31.

**1-(4-*tert*-Butylphenyl)-2-(trifluoromethyl)-6-*tert*-butylbenzimidazole (15cc):** colorless crystals (80%); mp 159–161 °C; IR ($CHCl_3$) 2956, 2872, 1152 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 1.33 (s, 9 H, $C(CH_3)_3$), 1.43 (s, 9 H, $C(CH_3)_3$), 7.16 (d, 1 H, $J_1$ = 1.8 Hz, Ar*H*), 7.35 (d, 2 H, $J_2$ = 8.5 Hz, Ar*H*), 7.49 (dd, 1 H, $J_1$ = 1.8 Hz, $J_3$ = 8.8 Hz, Ar*H*), 7.59 (d, 2 H, $J_2$ = 8.5 Hz, Ar*H*), 7.85 (d, 1 H, $J_3$ = 8.8 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.3 (s, 3 F, $CF_3$); MS *m/z* 374 ($M^+$, 10), 359 ($M^+$ – Me, 100). Anal. Calcd for $C_{22}H_{25}F_3N_2$ (374.44): C, 70.57; H, 6.73; N, 7.48. Found: C, 70.75; H, 6.73; N, 7.63.

**1-(4-Isopropylphenyl)-2-(trifluoromethyl)-6-isopropylbenzimidazole (15dd):** colorless crystals (51%); mp 77–79 °C; IR ($CHCl_3$) 2964, 2876, 1174 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 1.25 (d, 6 H, $J_1$ = 6.8 Hz, $CH(CH_3)_2$), 1.36 (d, 6 H, $J_2$ = 6.8 Hz, $CH(CH_3)_2$), 2.89–3.12 (m, 2 H, $CH(CH_3)_2$), 6.93–6.99 (m, 1 H Ar*H*), 7.25–7.31 (m, 1 H, Ar*H*), 7.33 (d, 2 H, $J_3$ = 8.5 Hz, Ar*H*), 7.43 (d, 2 H, $J_3$ = 8.5 Hz, Ar*H*), 7.84 (d, 1 H, $J_4$ = 8.4 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.2 (s, 3 F, $CF_3$); MS *m/z* 346 ($M^+$, 30), 331 ($M^+$ – Me, 100). Anal. Calcd for $C_{20}H_{21}F_3N_2$ (346.39): C, 69.35; H, 6.11; N, 8.09. Found: C, 69.41; H, 6.05; N, 8.25.

**1-(4-Methylphenyl)-2-(trifluoromethyl)-6-methylbenzimidazole (15ee):** colorless crystals (33%); mp 94–95 °C; IR (neat) 3036, 2964, 1198 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 2.44 (s, 3 H, $ArCH_3$), 2.49 (s, 3 H, $ArCH_3$), 6.92 (d, 1 H, $J_1$ = 1.7 Hz, Ar*H*), 7.22 (dd, 1 H, $J_1$ = 1.7 Hz, $J_2$ = 8.4 Hz, Ar*H*), 7.29 (d, 2 H, $J_3$ = 8.7 Hz, Ar*H*), 7.38 (d, 2 H, $J_3$ = 8.7 Hz, Ar*H*), 7.80 (d, 1 H, $J_2$ = 8.4 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.2 (s, 3 F, $CF_3$); MS *m/z* 290 ($M^+$, 100), 221 ($M^+$ – $CF_3$, 10), 91 ($C_6H_4Me^+$, 10). Anal. Calcd for $C_{16}H_{13}F_3N_2$ (290.29): C, 66.20; H, 4.51; N, 9.65. Found: C, 66.01; H, 4.43; N, 9.58.

**1-(3,4-Dichlorophenyl)-2-(trifluoromethyl)-5,6-dichlorobenzimidazole (15hh):** colorless crystals (40%); mp 136–138 °C; IR ($CHCl_3$) 3004, 1156 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.29 (s, 1 H, Ar*H*), 7.30 (dd, 1 H, $J_1$ = 2.4 Hz, $J_2$ = 9.4 Hz, Ar*H*), 7.56 (d, 1 H, $J_1$ = 2.4 Hz, Ar*H*), 7.72 (d, 1 H, $J_2$ = 9.4 Hz, Ar*H*), 8.04 (s, 1 H, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 100.8 (s, 3 F, $CF_3$); MS *m/z* 404 ($M^+$, 10), 402 ($M^+$, 50), 400 ($M^+$, 100). Anal. Calcd for $C_{14}H_5Cl_4F_3N_2$ (400.01): C, 42.04; H, 1.26; N, 7.00. Found: C, 42.14; H, 1.21; N, 6.95.

**1-(3,4-Dichlorophenyl)-2-(trifluoromethyl)-6,7-dichlorobenzimidazole (15hh′):** colorless crystals (19%); mp 135–136 °C; IR ($CHCl_3$) 3002, 1128 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.29 (dd, 1 H, $J_1$ = 2.4 Hz, $J_2$ = 8.4 Hz, Ar*H*), 7.52 (d, 1 H, $J_3$ = 8.8 Hz, Ar*H*), 7.57 (d, 1 H, $J_1$ = 2.4 Hz, Ar*H*), 7.63 (d, 1 H, $J_2$ = 8.4 Hz, Ar*H*), 7.79 (d, 1 H, $J_3$ = 8.8 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.0 (s, 3 F, $CF_3$); MS *m/z* 406 ($M^+$, 1), 404 ($M^+$, 10), 402 ($M^+$, 50), 400 ($M^+$, 100). Anal. Calcd for $C_{14}H_5Cl_4F_3N_2$ (400.01): C, 42.04; H, 1.26; N, 7.00. Found: C, 41.75; H, 1.24; N, 6.68.

**1-(2-Methoxyphenyl)-2-(trifluoromethyl)-4-methoxybenzimidazole (15ii):** colorless oil (5%); bp 220 °C (4 mmHg); IR ($CHCl_3$) 3076, 2844, 1164 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.71 (s, 3 H, $OCH_3$), 4.07 (s, 3 H, $OCH_3$), 6.64 (d, 1 H, $J_1$ = 8.3 Hz, Ar*H*), 6.77 (d, 1 H, $J_2$ = 8.2 Hz, Ar*H*), 7.07–7.14 (m, 2 H, Ar*H*), 7.23–7.31 (m, 1 H, Ar*H*), 7.36 (dd, 1 H, $J_3$ = 7.5 Hz, $J_4$ = 8.1 Hz, Ar*H*), 7.50–7.58 (m, 1 H, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 99.7 (s, 3 F, $CF_3$); MS *m/z* 322 ($M^+$, 100), 307 ($M^+$ – Me, 62). Anal. Calcd for $C_{16}H_{13}F_3N_2O_2$ (322.29): C, 59.63; H, 4.07; N, 8.69. Found: C, 59.63; H, 4.01; N, 8.99.

**1-Phenyl-2-(trifluoromethyl)benzimidazole (15kk):** colorless oil (12%); bp 175 °C (2 mmHg); IR ($CHCl_3$) 2984, 1598, 1144 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.11–7.21 (m, 1 H, Ar*H*), 7.35–7.50 (m, 4 H, Ar*H*), 7.54–7.67 (m, 3 H, Ar*H*), 7.91–7.99 (m, 1 H, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.2 (s, 3 F, $CF_3$); MS *m/z* 262 ($M^+$, 100), 193 ($M^+$ – $CF_3$, 15), 77 ($Ph^+$, 18). Anal. Calcd for $C_{14}H_9F_3N_2$ (262.23): C, 64.13; H, 3.46; N, 10.68. Found: C, 64.51; H, 3.47; N, 10.32.

**3-(4-Chloro-1-naphthyl)-2-(trifluoromethyl)-5-chloronaphtho[2,1-*d*]imidazole (15nn):** colorless crystals (57%); mp 188–189 °C; IR (neat) 3064, 1172 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.07 (d, 1 H, $J_1$ = 8.3 Hz, Ar*H*), 7.08 (s, 1 H, Ar*H*), 7.48–7.52 (m, 1 H, Ar*H*), 7.58 (d, 1 H, $J_2$ = 7.8 Hz, Ar*H*), 7.68–7.84 (m, 4 H, Ar*H*), 8.38 (d, 1 H, $J_3$ = 7.8 Hz, Ar*H*), 8.46 (d, 1 H, $J_4$ = 8.3 Hz, Ar*H*), 8.83 (d, 1 H, $J_5$ = 7.0 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 100.9 (s, 3 F, $CF_3$); MS *m/z* 432 ($M^+$, 66), 430 ($M^+$, 100). Anal. Calcd for $C_{22}H_{11}Cl_2F_3N_2$ (431.24): C, 61.28; H, 2.57; N, 6.50. Found: C, 61.16; H, 2.52; N, 6.31.

**1-(4-Chlorophenyl)-2-(trifluoromethyl)-6-methoxybenzimidazole (15ab):** colorless crystals (10%); mp 152–154 °C; IR ($CHCl_3$) 2936, 1142 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.78 (s, 3 H, $OCH_3$), 6.49 (d, 1 H, $J_1$ = 2.3 Hz, Ar*H*), 7.04 (dd, 1 H, $J_1$ = 2.3 Hz, $J_2$ = 8.9 Hz, Ar*H*), 7.38 (d, 2 H, $J_3$ = 8.7 Hz, Ar*H*), 7.58 (d, 2 H, $J_3$ = 8.7 Hz, Ar*H*), 7.90 (d, 1 H, $J_2$ = 8.9 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.3 (s, 3 F, $CF_3$); MS *m/z* 328 ($M^+$, 35), 326 ($M^+$, 100), 313 ($M^+$ – Me, 13), 311 ($M^+$ – Me, 42), 113 ($C_6H_4Cl^+$, 8), 111 ($C_6H_4Cl^+$, 25). Anal. Calcd for $C_{15}H_{10}ClF_3N_2O$ (326.70): C, 55.15; H, 3.08; N, 8.57. Found: C, 55.18; H, 2.95; N, 8.63.

**1-(4-Methylphenyl)-2-(trifluoromethyl)-6-methoxybenzimidazole (15ae):** colorless crystals (9%); mp 89–91 °C; IR ($CHCl_3$) 2968, 1142 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 2.51 (s, 3 H, $ArCH_3$), 3.78 (s, 3 H, $OCH_3$), 6.53 (d, 1 H, $J_1$ = 2.3 Hz, Ar*H*), 7.04 (dd, 1 H, $J_1$ = 2.3 Hz, $J_2$ = 8.9 Hz, Ar*H*), 7.31 (d, 2 H, $J_3$ = 8.9 Hz, Ar*H*), 7.40 (d, 2 H, $J_3$ = 8.9 Hz, Ar*H*), 7.81 (d, 1 H, $J_2$ = 8.9 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.2 (s, 3 F, $CF_3$); MS *m/z* 306 ($M^+$, 100), 291 ($M^+$ – Me, 40), 91 ($C_6H_4Me^+$, 20). Anal. Calcd for $C_{16}H_{13}F_3N_2O$ (306.28): C, 62.74; H, 4.28; N, 9.15. Found: C, 62.88; H, 4.28; N, 9.12.

**1-(4-Methoxyphenyl)-2-(trifluoromethyl)-6-methylbenzimidazole (21ae):** colorless crystals (48%); mp 99–100 °C; IR ($CHCl_3$) 2964, 2844, 1144 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 2.44 (s, 3 H, Ar-$CH_3$), 3.81 (s, 3 H, $OCH_3$), 6.92 (d, 1 H, $J_1$ = 1.3 Hz, Ar*H*), 7.08 (d, 2 H, $J_2$ = 9.0 Hz, Ar*H*), 7.21 (dd, 1 H, $J_1$ = 1.3 Hz, $J_3$ = 8.3 Hz, Ar*H*), 7.33 (d, 2 H, $J_2$ = 9.0 Hz, Ar*H*), 7.79 (d, 1 H, $J_3$ = 8.3 Hz, Ar*H*); $^{19}$F NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.1 (s, 3 F, $CF_3$); MS *m/z* 306 ($M^+$, 100), 291 ($M^+$ – Me, 10). Anal. Calcd for $C_{16}H_{13}F_3N_2O$ (306.28): C, 62.74; H, 4.28; N, 9.15. Found: C, 62.73; H, 4.36; N, 9.26.

**1-(2-Methoxyphenyl)-2-(trifluoromethyl)-6-methoxybenzimidazole (15ai):** colorless crystals (54%); mp 84–86 °C; IR ($CHCl_3$) 2964, 2844, 1144 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.74 (s, 3 H, $OCH_3$), 3.76 (s, 3 H, $OCH_3$), 6.42 (d, 1 H, $J_1$ = 2.4 Hz, Ar*H*), 7.01 (dd, 1 H, $J_1$ = 2.4 Hz, $J_2$ = 8.9 Hz, Ar*H*), 7.10–7.17 (m, 2 H, Ar*H*), 7.34–7.39 (m, 1 H, Ar*H*), 7.51–7.60 (m, 1 H, Ar*H*), 7.79 (d, 1 H, $J_2$ = 8.9 Hz, Ar*H*); $^{19}$F NMR (188 MHz,

$CDCl_3$, 25 °C) δ 99.56 (s, 3 F, $CF_3$); MS *m/z* 322 ($M^+$, 100), 307 ($M^+$ – Me, 20), 253 ($M^+$ – $CF_3$, 25). Anal. Calcd for $C_{16}H_{13}F_3N_2O_2$ (322.29): C, 59.63; H, 4.07; N, 8.69. Found: C, 59.42; H, 4.03; N, 8.72.

**1-(4-Methoxyphenyl)-2-(trifluoromethyl)-5-methoxybenzimidazole (21aj):** colorless crystals (74%); mp 77–79 °C; IR ($CHCl_3$) 2912, 2844, 1142 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 50 °C) δ 3.87 (s, 3 H, $OCH_3$), 3.90 (s, 3 H, $OCH_3$), 7.05–7.08 (m, 2 H, Ar*H*), 7.15 (d, 2 H, $J_2$ = 8.9 Hz, Ar*H*), 7.38–7.39 (m, 1 H, Ar*H*), 7.49 (d, 2 H, $J_2$ = 8.9 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 50 °C) δ 101.1 (s, 3 F, $CF_3$); MS *m/z* 322 ($M^+$, 100), 307 ($M^+$ – Me, 68). Anal. Calcd for $C_{16}H_{13}F_3N_2O_2$ (322.29): C, 59.63; H, 4.07; N, 8.69. Found: C, 59.89; H, 4.06; N, 8.53.

**1-Phenyl-2-(trifluoromethyl)-6-methoxybenzimidazole (15ak):** colorless crystals (13%); mp 87–91 °C; IR ($CHCl_3$) 2960, 2840, 1142 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.76 (s, 3 H, $OCH_3$), 6.51 (d, 1 H, $J_1$ = 2.2 Hz, Ar*H*), 7.03 (dd, 1 H, $J_1$ = 2.2 Hz, $J_2$ = 9.0 Hz, Ar*H*), 7.36–7.48 (m, 2 H, Ar*H*), 7.52–7.63 (m, 3 H, Ar*H*), 7.80 (d, 1 H, $J_2$ = 9.0 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.3 (s, 3 F, $CF_3$); MS *m/z* 292 ($M^+$, 100), 277 ($M^+$ – Me, 50). Anal. Calcd for $C_{15}H_{11}F_3N_2O$ (292.26): C, 61.65; H, 3.79; N, 9.59. Found: C, 61.53; H, 3.74; N, 9.55.

**1-(4-Methoxyphenyl)-2-(trifluoromethyl)benzimidazole (21ak):** colorless crystals (10%); mp 84–88 °C; IR ($CHCl_3$) 2980, 2844, 1144 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.91 (s, 3 H, $OCH_3$), 7.07 (d, 2 H, $J_1$ = 9.0 Hz, Ar*H*), 7.34 (d, 1 H, $J_1$ = 9.0 Hz, Ar*H*), 7.10–7.43 (m, 3 H, Ar*H*), 7.89–7.95 (m, 1 H, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.0 (s, 3 F, $CF_3$); MS *m/z* 292 ($M^+$, 100), 277 ($M^+$ – Me, 15). Anal. Calcd for $C_{15}H_{11}F_3N_2O$ (292.26): C, 61.65; H, 3.79; N, 9.59. Found: C, 61.75; H, 3.81; N, 9.48.

**3-(4-Methoxyphenyl)-2-(trifluoromethyl)naphtho[2,1-*d*]imidazole (21am):** colorless crystals (42%); mp 115–116 °C; IR ($CHCl_3$) 2966, 2844, 1142 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.93 (s, 3 H, $OCH_3$), 7.10 (d, 2 H, $J_1$ = 9.0 Hz, Ar*H*), 7.21 (d, 1 H, $J_2$ = 9.0 Hz, Ar*H*), 7.39 (d, 2 H, $J_1$ = 9.0 Hz, Ar*H*), 7.53–7.72 (m, 2 H, Ar*H*), 7.78 (d, 1 H, $J_3$ = 8.9 Hz, Ar*H*), 7.96 (d, 1 H, $J_2$ = 9.0 Hz, Ar*H*), 8.75 (d, 1 H, $J_4$ = 8.7 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.9 (s, 3 F, $CF_3$); MS *m/z* 342 ($M^+$, 100), 327 ($M^+$ – Me, 8), 273 ($M^+$ – $CF_3$, 25). Anal. Calcd for $C_{19}H_{13}F_3N_2O$ (342.32): C, 66.67; H, 3.83; N, 8.18. Found: C, 66.46; H, 3.63; N, 7.98.

**3-(4-Methoxyphenyl)-2-(trifluoromethyl)-5-chloronaphtho[2,1-*d*]imidazole (21an):** colorless crystals (94%); mp 105–107 °C; IR ($CHCl_3$) 2940, 2844, 1144 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.94 (s, 3 H, $OCH_3$), 7.10 (d, 2 H, $J_1$ = 9.0 Hz, Ar*H*), 7.35 (s, 1 H, Ar*H*), 7.38 (d, 1 H, $J_1$ = 9.0 Hz, Ar*H*), 7.64–7.81 (m, 2 H, Ar*H*), 8.37 (d, 1 H, $J_2$ = 7.9 Hz, Ar*H*), 8.77 (d, 1 H, $J_3$ = 7.8 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 101.7 (s, 3 F, $CF_3$); MS *m/z* 378 ($M^+$, 33), 376 ($M^+$, 100). Anal. Calcd for $C_{19}H_{12}ClF_3N_2O$ (376.76): C, 60.57; H, 3.21; N, 7.44. Found: C, 60.53; H, 3.15; N, 7.29.

**1-(2-Methoxyphenyl)-2-(trifluoromethyl)-5-methoxybenzimidazole (21ij):** colorless oil (18%): bp 210 °C (1 mmHg); IR ($CHCl_3$) 3108, 2848, 1164 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 25 °C) δ 3.70 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 6.95 (d, 1 H, $J_1$ = 8.9 Hz, Ar*H*), 7.04 (dd, 1 H, $J_1$ = 8.9 Hz, $J_2$ = 2.2 Hz, Ar*H*), 7.12–7.20 (m, 1 H, Ar*H*), 7.30–7.34 (m, 1 H, Ar*H*), 7.38 (d, 1 H, $J_2$ = 2.2 Hz, Ar*H*), 7.51–7.65 (m, 2 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 25 °C) δ 101.4 (s, 3 F, $CF_3$); MS *m/z* 322 ($M^+$, 100), 307 ($M^+$ – $CH_3$, 70). Anal. Calcd for $C_{16}H_{13}F_3N_2O_2$ (322.29): C, 59.63; H, 4.07; N, 8.69. Found: C, 60.03; H, 4.07; N, 8.58.

**Electrochemical Preparation of *p*-Benzoquinone Imine 20.** Imidamide **11** (0.5 mmol) was dissolved in a mixture of acetonitrile (9 mL) and water (1 mL) containing sodium perchlorate (0.4 mmol) and electrooxidized at –10 °C in an undivided cell using a glassy carbon anode and a platinum foil cathode in the constant current of 5 mA/$cm^2$ for 2.5–3.0 F/mol of electricity.

The solvent was evaporated under reduced pressure, and the residue was extracted with ethyl acetate (5 mL × 5) and washed with water (5 mL) and brine (5 mL). The organic layer was dried over anhyd sodium sulfate, condensed, chromatographed on silica gel, and recrystallized from benzene–hexane to give *p*-benzoquinone imine derivative **20**.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (20a):** dark violet crystals (87%); mp 85–87 °C; IR (neat) 3040, 2840, 1660, 1196 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 50 °C) δ 3.76 (s, 3 H, $OCH_3$), 6.54 (d, 2 H, $J_1$ = 9.3 Hz, N=CC*H*=CH), 6.81 (d, 2 H, $J_2$ = 8.0 Hz, Ar*H*), 6.91 (d, 2 H, $J_1$ = 9.3 Hz, CH=C*H*C=O), 6.97 (d, 2 H, $J_2$ = 8.0 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 50 °C) δ 90.8 (s, 3 F, $CF_3$); MS *m/z* 308 ($M^+$, 100), 293 ($M^+$ – Me, 6), 280 ($M^+$ – CO, 26), 239 ($M^+$ – $CF_3$, 80), 202 ($M^+$ – $NC_6H_4O$, 20). Anal. Calcd for $C_{15}H_{11}F_3N_2O_2$ (308.26): C, 58.44; H, 3.60; N, 9.09. Found: C, 58.49; H, 3.57; N, 9.46.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-(4-chlorophenyl)-2,2,2-trifluoroethanimidamide (20b):** red crystals (85%); mp 87–92 °C; IR (neat) 3195, 1660, 1198 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 50 °C) δ 6.58 (d, 2 H, $J_1$ = 10.0 Hz, N=CC*H*=CH), 6.88 (d, 2 H, $J_1$ = 10.0 Hz, CH=C*H*C=O), 6.89 (d, 2 H, $J_2$ = 8.6 Hz, Ar-*H*), 7.25 (d, 2 H, $J_2$ = 8.6 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 50 °C) δ 91.9 (s, 3 F, $CF_3$); MS *m/z* 314 ($M^+$, 35), 312 ($M^+$, 65), 286 ($M^+$ – CO, 10), 284 ($M^+$ – CO, 28), 277 ($M^+$ – Cl, 32), 208 ($M^+$ – $NC_6H_4O$, 10), 206 ($M^+$ – $NC_6H_4O$, 30), 113 ($C_6H_4Cl^+$, 30), 111 ($C_6H_4Cl^+$, 100). Anal. Calcd for $C_{14}H_8ClF_3N_2O$ (312.68): C, 53.78; H, 2.58; N, 8.96. Found: C, 53.66; H, 2.52; N, 8.67.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-(4-methylphenyl)-2,2,2-trifluoroethanimidamide (20e):** red crystals (99%); mp 95–98 °C; IR (neat) 2988, 2876, 1644, 1196 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 2.28 (s, 3 H, $ArCH_3$), 6.52 (d, 2 H, $J_1$ = 10.5 Hz, N=CC*H*=CH), 6.83 (d, 2 H, $J_2$ = 8.1 Hz, Ar*H*), 6.88 (d, 2 H, $J_1$ = 10.5 Hz, CH=C*H*C=O), 7.05 (d, 2 H, $J_2$ = 8.1 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 90.8 (s, 3 F, $CF_3$); MS *m/z* 292 ($M^+$, 60), 264 ($M^+$ – CO, 20), 223 ($M^+$ – $CF_3$, 58), 186 ($M^+$ – $NC_6H_4O$, 18), 91 ($C_6H_4Me^+$, 100). Anal. Calcd for $C_{15}H_{11}F_3N_2O$ (292.26): C, 61.65; H, 3.79; N, 9.59. Found: C, 61.91; H, 3.72; N, 9.52.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-(4-nitrophenyl)-2,2,2-trifluoroethanimidamide (20f):** yellow crystals (77%); mp 137–140 °C; IR ($CHCl_3$) 2936, 1632, 1158 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.66 (d, 2 H, $J_1$ = 10.1 Hz, N=CC*H*=CH), 7.12 (d, 2 H, $J_1$ = 10.1 Hz, CH=C*H*C=O), 7.16 (d, 2 H, $J_2$ = 8.9 Hz, Ar*H*), 8.15 (d, 2 H, $J_2$ = 8.9 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.3 (s, 3 F, $CF_3$); MS *m/z* 323 ($M^+$, 95), 295 ($M^+$ – CO, 28), 277 ($M^+$ – $NO_2$, 12), 254 ($M^+$ – $CF_3$, 75), 76 (100). Anal. Calcd for $C_{14}H_8F_3N_3O_3$ (323.23): C, 52.02; H, 2.49; N, 13.00. Found: C, 51.97; H, 2.37; N, 12.85.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-(4-hydroxyphenyl)-2,2,2-trifluoroethanimidamide (20g):** dark violet crystals (80%); mp 136–140 °C; IR ($CHCl_3$) 3596, 3296, 1658, 1152 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.66 (d, 2 H, $J_1$ = 10.0 Hz, N=CC*H*=CH), 6.71 (d, 2 H, $J_2$ = 8.5 Hz, Ar*H*), 6.87 (d, 2 H, $J_1$ = 10.0 Hz, CH=C*H*C=O), 7.08 (d, 2 H, $J_2$ = 8.5 Hz, Ar*H*), 9.29–9.41 (br, 1 H, O*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 93.0 (s, 3 F, $CF_3$); MS *m/z* 294 ($M^+$, 100), 266 ($M^+$ – CO, 25), 225 ($M^+$ – $CF_3$, 95), 188 (100), 93 (60). Anal. Calcd for $C_{14}H_9F_3N_2O_2$ (294.23): C, 57.15; H, 3.08; N, 9.52. Found: C, 57.44; H, 2.98; N, 9.50.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-(3,4-dichlorophenyl)-2,2,2-trifluoroethanimidamide (20h):** orange crystals (85%); mp 127–129 °C; IR ($CHCl_3$) 3008, 1662, 1156 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.68 (d, 2 H, $J_1$ = 10.1 Hz, N=CC*H*=CH), 6.92 (dd, 1 H, $J_2$ = 8.6 Hz, $J_3$ = 2.4 Hz, Ar*H*), 7.12 (d, 2 H, $J_1$ = 10.1 Hz, CH=C*H*C=O), 7.20 (d, 1 H, $J_3$ = 2.4 Hz, Ar*H*), 7.51 (d, 1 H, $J_2$ = 8.6 Hz, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.3 (s, 3 F, $CF_3$); MS *m/z* 352 ($M^+$, 1), 350 ($M^+$, 16), 348 ($M^+$, 58), 346 ($M^+$, 74), 320 (33), 313 ($M^+$ – Cl, 24), 311 ($M^+$ – Cl, 75), 279 ($M^+$ – $CF_3$, 66), 277 ($M^+$ – $CF_3$, 95), 242 ($M^+$ – $NC_6H_4O$, 22), 240 ($M^+$ – $NC_6H_4O$, 36), 147 ($C_6H_3Cl_2^+$, 64), 145 ($C_6H_3Cl_2^+$, 100). Anal. Calcd for $C_{14}H_7Cl_2F_3N_2O$ (347.12): C, 48.44; H, 2.03; N, 8.07. Found: C, 48.05; H, 1.96; N, 7.99.

***N*¹-(4-Oxo-2,5-cyclohexadien-1-ylidene)-*N*²-phenyl-2,2,2-trifluoroethanimidamide (20k):** red crystals (91%); mp 75–77 °C; IR (neat) 3068, 1662, 1198 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 6.63 (d, 2 H, $J_1$ = 10.0 Hz, N=CC*H*=CH), 6.92 (d, 2 H, $J_1$ = 10.0 Hz, CH=C*H*C=O), 7.05–7.13 (m, 3 H, Ar*H*), 7.26–7.34 (m, 2 H, Ar*H*); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.5 (s, 3 F, $CF_3$); MS *m/z* 278 ($M^+$, 56), 250 ($M^+$ – CO, 24), 209 ($M^+$ – $CF_3$, 52), 172 ($M^+$ – $NC_6H_4O$, 18), 77 ($Ph^+$, 100). Anal.

Calcd for $C_{14}H_9F_3N_2O$ (278.23): C, 60.44; H, 3.26; N, 10.07. Found: C, 60.58; H, 3.19; N, 9.96.

**$N^1$-(4-Oxo-2,5-cyclohexadien-1-ylidene)-$N^2$-(5,6,7,8-tetrahydro-1-naphthyl)-2,2,2-trifluoroethanimidamide (20l):** brown oil (61%): bp 160 °C (2 mmHg); IR (neat) 3068, 2936, 2844, 1658, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C) δ 1.71–1.90 (br, 4 H, $CH_2CH_2CH_2CH_2$), 2.57–2.81 (br, 4 H, $CH_2CH_2CH_2CH_2$), 6.46–7.01 (m, 7 H, N=CCH=CH, ArH); $^{19}F$ NMR (188 MHz, $CDCl_3$, 25 °C) δ 90.7 (s, 3 F, $CF_3$); MS *m/z* 332 ($M^+$, 100), 263 ($M^+ - CF_3$, 30), 225 (35), 156 (65), 129 (50), 109 (60). Anal. Calcd for $C_{18}H_{15}F_3N_2O$ (332.32): C, 65.06; H, 4.55; N, 8.43. Found: C, 64.70; H, 4.88; N, 8.79.

**$N^1$-(4-Oxo-2,5-cyclohexadien-1-ylidene)-$N^2$-*n*-hexyl-2,2,2-trifluoroethanimidamide (20o):** yellow liquid (89%): bp 135 °C (6 mmHg); IR ($CHCl_3$) 2932, 1630, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 0.80–0.91 (br, 3 H, $CH_3$), 1.14–1.68 (br, 8 H, $NCH_2(CH_2)_4CH_3$), 3.00–3.12 (m, 2 H, N-$CH_2$), 6.75 (d, 2 H, *J* = 10.1 Hz, N=CCH=CH), 7.09 (d, 2 H, *J* = 10.1 Hz, CH=CHC=O); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.6 (s, 3 F, $CF_3$); MS *m/z* 286 ($M^+$, 10), 215 (35), 204 (25), 187 ($M^+ - NC_6H_{13}$, 55), 109 ($CF_3CN_2^+$, 50), 43 ($C_3H_7^+$, 100). Anal. Calcd for $C_{14}H_{17}F_3N_2O$ (286.29): C, 58.74; H, 5.98; N, 9.79. Found: C, 58.78; H, 5.95; N, 10.05.

**$N^1$-(4-Oxo-2,5-cyclohexadien-1-ylidene)-$N^2$-allyl-2,2,2-trifluoroethanimidamide (20p):** yellow liquid (90%): bp 125 °C (6 mmHg); IR ($CHCl_3$) 3032, 1634, 1148 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 3.72–3.79 (m, 2 H, $NCH_2$), 5.06–5.26 (m, 2 H, $NCH_2CH=CH_2$), 5.83–6.03 (m, 1 H, $NCH_2CH=CH_2$), 6.75 (d, 2 H, *J* = 10.1 Hz, N=CCH=CH), 7.09 (d, 2 H, *J* = 10.1 Hz, CH=CHC=O); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.6 (s, 3 F, $CF_3$); MS *m/z* 244 ($M^+$ + 2, 27), 242 ($M^+$, 36), 229 (45), 213 ($M^+$ – CO, 36), 187 ($M^+ - NCH_2CH=CH_2$, 100). Anal. Calcd for $C_{11}H_9F_3N_2O$ (242.20): C, 54.55; H, 3.74; N, 11.57. Found: C, 54.45; H, 3.56; N, 11.30.

**$N^1$-(4-Oxo-2,5-cyclohexadien-1-ylidene)-$N^2$-benzyl-2,2,2-trifluoroethanimidamide (20q):** yellow liquid (94%); bp 140 °C (6 mmHg); IR ($CHCl_3$) 2956, 2872, 1660, 1150 $cm^{-1}$; $^1H$ NMR (200 MHz, DMSO-$d_6$, 80 °C) δ 4.31–4.34 (m, 2 H, N-$CH_2$), 6.73 (d, 2 H, *J* = 10.0 Hz, N=CCH=CH), 7.10 (d, 2 H, *J* = 10.0 Hz, CH=CHC=O); $^{19}F$ NMR (188 MHz, DMSO-$d_6$, 80 °C) δ 92.6 (s, 3 F, $CF_3$); MS *m/z* 292 ($M^+$, 15), 91 ($C_6H_5CH_2^+$, 100). Anal. Calcd for $C_{15}H_{11}F_3N_2O$ (292.26): C, 61.65; H, 3.79; N, 9.59. Found: C, 61.43; H, 3.75; N, 9.94.

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