Intramolecular Cyclization of N^1-(4-Oxo-2,5-cyclohexadien-1-ylidene)-N^2-substituted-2,2,2-trifluoroethanimidamides (*p*-Benzoquinone Imine Derivatives): Syntheses of Trifluoromethylated 6-Hydroxybenzimidazoles and Spiro Dienone Diazacarbocycles

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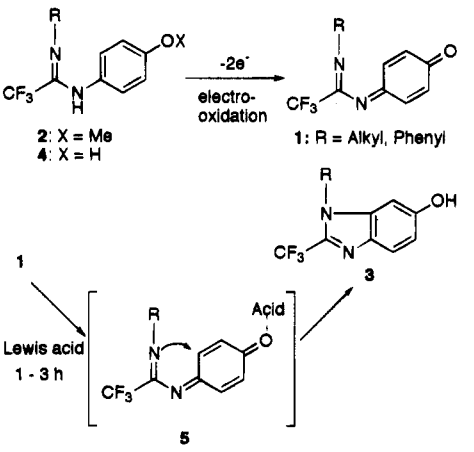
Lewis acid-catalyzed intramolecular cyclization of N^1-(4-oxo-2,5-cyclohexadien-1-ylidene)-N^2-substituted-2,2,2-trifluoroethanimidamides (*p*-benzoquinone imine derivatives, **1**) prepared by electrooxidation of *N*-(4-methoxyphenyl)-*N'*-substituted-2,2,2-trifluoroethanimidamides **2** occurred to give 1-substituted-2-(trifluoromethyl)-6-hydroxybenzimidazoles **3**. Alternatively, thermal cyclization of **1** gave spiro dienone diazacarbocycles **9** and **10**, which were converted into diazepine **12** via a dienone–phenol rearrangement.

Introduction

Organofluorine compounds have received a great deal of attention because of their bioactivity in the fields of medicine and agricultural chemistry.[1] Some 2-(trifluoromethyl)benzimidazoles, which are potentially bioactive,[2] are commonly prepared by one of the following methods: direct trifluoromethylation[3] of benzimidazoles by trifluoromethyl radicals and condensation of trifluoroacetic acid with *o*-phenylenediamines.[4] However, the first method is not very regioselective and the latter method requires the less readily available *N*-substituted-5-hydroxy-1,2-phenylenediamines.

We have previously reported the synthesis of 1-substituted-2-(trifluoromethyl)benzimidazoles by electrochemical oxidation of *N*-(4-methoxyphenyl)-*N'*-substituted-2,2,2-trifluoroethanimidamides **2** with a MeCN–$NaClO_4$–(C)–(Pt) system where the yield and selectivity of products formed were highly dependent upon substituents on the aromatic ring.[5] On the other hand, in a MeCN–H_2O–$NaClO_4$–(C)–(Pt) system the title compounds **1** (*p*-benzoquinone imine derivatives) were obtained selectively.[6,7] *p*-Benzoquinone imines **1** are promising trifluoromethylated synthons for nitrogen heterocycles.[8,9] In this paper, details of the cyclizations of **1** to **3** (Scheme 1) and **1** to **9** and **10** (Scheme 4) are described.

Scheme 1



Results and Discussions

Lewis Acid-Catalyzed Cyclizations of 1. Starting compounds **1** were prepared by the electrochemical oxidation of *N*-(4-methoxyphenyl) compounds **2** with a MeCN–H_2O–$NaClO_4$–(C)–(Pt) system.[5] *N*-(4-Hydroxyphenyl) analog **4** was also converted to **1**. The effects of acid catalysts and reaction conditions are summarized in Table 1. In the presence of BF_3·Et_2O, the desired **3a** was produced at 80 °C in excellent yield, in contrast to complete recovery of **1a** without BF_3·Et_2O. The yield of **3a** was proportional to the amount of BF_3·Et_2O used (55%, 82%, and 93% in the presence of 0.1, 0.5, and 1.0 molar equiv of BF_3·Et_2O, respectively). Stannic chloride provided **3a** cleanly in almost quantitative yield at 0 °C (entry 4). On the other hand, Lewis acids such as $AlCl_3$ and $ZnCl_2$ effected the cyclization but induced partial chlorination of the aromatic ring (Scheme 2), giving chlorinated 4-aminophenol derivative **6** as a side product

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(1) Filler, R.; Kobayashi, Y. *Biomedicinal Aspects of Fluorine Chemistry*; Kodansha Ltd.: Tokyo, 1982. Hudlicky, M. *Chemistry of Organic Fluorine Compounds*; Yew York, 1976.

(2) Joshi, K.; Jain, R.; Dandia, A.; Sharma, K. *J. Fluorine Chem.* **1992**, *56*, 1.

(3) Kimoto, H.; Fujii, S.; Cohen, L. *J. Org. Chem.* **1982**, *47*, 2667. Médebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 6872. Pinson, J.; Savéant, J.-M. *Tetrahedron Lett.* **1990**, *31*, 1279. Médebielle, M.; Pinson, J.; Savéant, J.-M. *Ibid.* **1992**, *33*, 7351. Chen, Q.; Qui, Z. *J. Fluorine Chem.* **1987**, *35*, 347.

(4) Belcher, R.; Sykes, A.; Tatlow, J. *J. Chem. Soc.* **1954**, 4159. Sykes, A.; Tatlow, J. *Ibid.* **1952**, 4078. Bishop, B.; Jones, A.; Tatlow, J. *Ibid.* **1964**, 3076.

(5) An electrochemical behavior of the imidamides **2** has been reported: Uneyama, K.; Kobayashi, M. *J. Org. Chem.* **1994**, *59*, 3003.

(6) Uneyama, K.; Kobayashi, M. *Tetrahedron Lett.* **1991**, *32*, 5981.

(7) Kobayashi, M.; Sadamune, K.; Mizukami, H.; Uneyama, K. *J. Org. Chem.* **1994**, *59*, 1909.

(8) Lewis acid-catalyzed cyclization of *p*-benzoquinone methides was reported; Angle, S. R.; Frutos, R. P. *J. Org. Chem.* **1993**, *58*, 5135.

(9) Kobayashi, M.; Uneyama, K.; Hamada, N.; Kashino, S. *Tetrahedron Lett.* **1994**, *35*, 5235.

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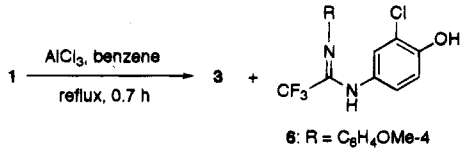
Table 1. Effect of Additives for the Reaction of 1a[a]

entry	additive (equiv)[b]	temp (°C)	time (h)	yield (%)
1	BF_3·Et_2O (1.0)	80	1.5	**3**(93)
2	BF_3·Et_2O (0.5)	80	2.0	**3**(82)
3	BF_3·Et_2O (0.1)	80	5.0	**3**(55), **1**(5)
4	$SnCl_4$ (1.0)	0[c]	0.1	**3** (quant)
5	$AlCl_3$ (1.0)	80	0.7	**3**(63), **6**[d] (31)
6	$ZnCl_2$ (1.0)	80	22	**3**(30), **6**(46)
7	TsOH·H_2O (1.0)	80	1.0	amide[e] (40)
8	TsOH (1.0)	80	22	many products
9	TFA (1.0)	40	0.5	**3**(50)

[a] **1a** (0.5 mmol), benzene (2 mL). [b] Molar equivalent to **1a**. [c] Toluene (2 mL) was employed as a solvent. [d] A structure of **6** is shown in Scheme 2. [e] *N*-(4-Methoxyphenyl)-2,2,2-trifluoroacetamide.

Scheme 2

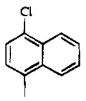


6: R = C_6H_4OMe-4

(entries 5 and 6 and Scheme 2).[10] The position of the chlorine atom on the aromatic ring of **6**[11,12] was unequivocally determined by comparison of its spectroscopic data with those of authentic samples synthesized by alternative methods.[13,14] The use of protic acids resulted in a poor yield of **3a**. *p*-Toluenesulfonic acid monohydrate (TsOH·H_2O) predominantly promoted hydrolysis of **1a** to *N*-(4-methoxyphenyl)-2,2,2-trifluoroacetamide. Alternatively, in the presence of anhydrous TsOH the reaction of **1a** was very slow and many inseparable byproducts were obtained. Use of the stronger acid TFA gave a moderate yield of **3a** (50%).

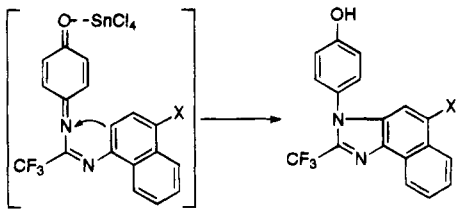
Not only 4-methoxyphenyl compound **1a** but also compounds **1b**–**k** easily cyclized to 1-substituted-2-(trifluoromethyl)-6-hydroxybenzimidazoles **3b**–**k** in good to excellent yields. The results of these experiments are summarized in Table 2. When an electron-withdrawing substituent such as a chlorine atom was attached to the *N*-aryl ring (compounds **1b** and **1f**), longer reaction times (3 h) were needed. Cyclization of 4-nitrophenyl compound **1d** proceeded only in refluxing toluene (110 °C, 77% of **3d**) because **1d** cyclized to **3d** very slowly in refluxing benzene. *N*-Alkyl compounds **1i**, **1j**, and **1k** also cyclized to the desired products **3i**, **3j**, and **3k** in 74%, 66%, and 60% yields, respectively, at a lower temperature (50 °C). Tetrahydronaphthyl compound **1h** gave a similar 6-hydroxybenzimidazole (**3h**) (54%). In contrast to the smooth BF_3-promoted cyclization of *N*-phenyl and *N*-alkyl derivatives **1a**–**k** to benzimidazoles **3**, the reaction of *N*-naphthyl derivatives **1m** and **1n** with BF_3·Et_2O

Table 2. BF_3·Et_2O-Catalyzed Cyclization[a] of 1

compd	R	temp (°C)	time (h)	**3** (%)
1a	4-$MeOC_6H_4$	80	1.5	93
1b	4-ClC_6H_4	80	3.0	91
1c	4-MeC_6H_4	80	1.5	99
1d	4-$NO_2C_6H_4$	110	1.5	57[b]
1e	4-HOC_6H_4	80	1.5	77
1f	3,4-$Cl_2C_6H_3$	80	3.0	91
1g	C_6H_5	80	1.5	80
1h		80	1.5	54
1i	*n*-C_6H_{13}	50	1.0	74
1j	CH_2=$CHCH_2$	50	1.0	66
1k	$C_6H_5CH_2$	50	1.0	60
1m		0	0.1	10[c,d]
1n		0	0.1	12[c,d]

[a] **1** (0.5 mmol), benzene (2 mL), refluxing in benzene. [b] Refluxing in toluene. [c] Overall yield from **2**. [d] Naphtho[2,1-*d*]imidazole (**7**).

Scheme 3



1m: X = H
1n: X = Cl

7m: X = H
7n: X = Cl

was somewhat different. Quinone imines **1m** and **1n** were too unstable to be isolated and were converted predominantly during the electrochemical reaction of **2m** and **2n**[5] to the spiro compounds **9m** and **9n**, which were isolated by chromatography. To obtain naphtho[2,1-*d*]-imidazole compounds **7**, lower reaction temperatures were required along with a stronger Lewis acid than BF_3·Et_2O. Therefore, the crude products (a mixture of **1m** and **9m**) obtained by electrolysis of **2m** were subjected to $SnCl_4$-promoted cyclization at 0 °C to give **7m** (10%),[15] along with many uncharacterizable compounds. Furthermore, the products were not benzimidazoles **3** (R = naphthyl), but instead naphtho[2,1-*d*]imidazoles **7** (Scheme 3). The ^1H NMR spectrum of product **7m** showed two doublets for the protons on the *N*-(4-hydroxyphenyl) ring at δ 7.12 (d, 2 H, J_1 = 8.7 Hz, ArH) and 7.46 (d, 2 H, J_1 = 8.7 Hz, ArH) and multiplets for the other six protons of the naphthyl ring.

Thermal Electrocyclic Reactions of 1. Since *N*-naphthyl compounds **1m** and **1n** underwent spirocyclization at room temperature, other *N*-aryl compounds (**1a**–**h**) were also expected to proceed via a [4 + 2] electrocyclic reaction. In fact, **1a** was transformed to a mixture of the corresponding spiro dienones **9a** and **10a** on heating. A typical reaction of **1** was conducted in DMSO solution at 120 °C for 2 h (Scheme 4). The product was an inseparable mixture of the two tautomers **9** and **10** in which the proton of the NH moiety in the pyrimidine ring was attached to different nitrogen atoms. ^{13}C NMR spectra

(10) Chlorine-containing Lewis acids such as $AlCl_3$, $FeCl_3$, and $TiCl_4$ sometimes promote chlorination of an aromatic ring. Stetter, H.; Krause, M.; Last, W.-D. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 894. Kovacic, P.; Brace, N. O. *J. Am. Chem. Soc.* **1954**, *76*, 5491. Chip, G. K.; Grossert, J. S. *Can. J. Chem.* **1972**, *50*, 1233.

(11) The hydrolysis of **6**[12] provided 4-amino-2-chlorophenol whose IR and ^1H NMR spectra were superimposable with those of an authentic sample.[13,14]

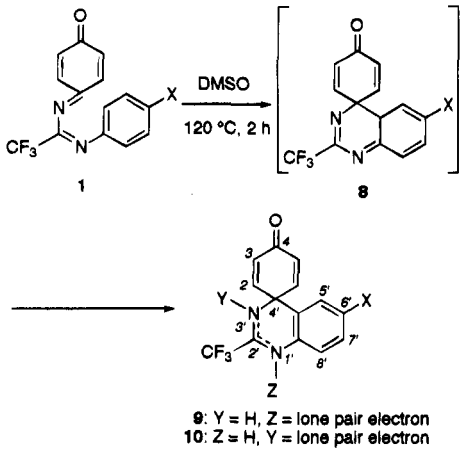
(12) The hydrolysis of **6** was effected by the usual procedure: Pearson, D. E.; Baxter, J. F.; Carter, K. N. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 154.

(13) 4-Amino-2-chlorophenol was prepared by chlorination of 4-nitrophenol followed by reduction with zinc. Ginsburg, D. *J. Am. Chem. Soc.* **1951**, *73*, 2723. Martin, E. L. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 501.

(14) 4-Amino-3-chlorophenol was prepared from 2-chloronitrobenzene. Tanaka, K.; Fujiwara, K.; Kimijima, J. *Jpn. Kokai Tokkyo Koho* JP 76 110,528 (C1 C07P3/14) 30 Sep 1976, 25 Mar 1975; 4pp.

(15) In our communication (ref 6), the structure of the major product isolated by silica gel chromatography from the electrochemically-produced crude mixture was assigned structure **7m**. However, an X-ray crystallographic study revealed that its structure is, in fact, **9m**.

Scheme 4



of the mixture of **9a** and **10a** revealed two signals for each carbonyl carbon (C4) at 184 and 185 ppm and two for each quaternary carbon (C4′) on the spiro ring at 55 and 58 ppm, respectively. These results are listed in Table 4. Judging from the relative intensities of each pair of the carbonyl carbons and quaternary carbons of **9a–h** and **10a–h**, one tautomer exhibits ^{13}C NMR chemical shifts at 184 and 55 ppm for the carbonyl carbons and quaternary carbons, respectively, while the corresponding peaks for the other tautomer appeared at 185 and 58 ppm, respectively. In contrast, the spiro dienone obtained from **2m** via **1m** was a single tautomer (**9m**), for which the peaks for the carbonyl carbon (C4) and quaternary carbon (C4′) appeared at 184.2 and 55.7 ppm, respectively. These results suggest that **9m** is the structure of the product.

Likewise, electrolysis of **2n** leads to **9n** as the sole product. According to the X-ray crystallographic analysis of the naphthyl derivative **9m** (Figure 1), the atomic distance between N(1′) and C(2′) is 1.25 Å and that between N(3′) and C(2′) is slightly longer (1.35 Å). This result suggests that the N(1′)–C(2′) bond is an imino double bond and, thus the proton is bonded to N(3′) shown in **9m**. Judging from both the X-ray crystallographic data and ^{13}C NMR chemical shift data for the spiro carbon of **9** shown in Table 4, it is assumed that the tautomer in which the spiro and carbonyl carbons showed signals at 55 and 184 ppm in the ^{13}C NMR spectrum, respectively, is **9m**, in which the proton on nitrogen is located on N(3′).

The cyclization of **1a** was greatly affected by the solvent as shown in Table 3. The reaction proceeded smoothly in neutral polar solvents such as DMSO, MeCN, *n*-BuOH, and EtOH. In particular, DMSO was an excellent reaction medium. In contrast, the use of acetic acid resulted in the formation of a mixture of spiro dienones **9** and **10** and benzimidazole **3**. In nonpolar solvents such as benzene, toluene, and *p*-xylene, however, none of the desired products were obtained, but rather a mixture of unidentified substances was formed.

The results of the thermal spirocyclization of **1** in DMSO are listed in Table 4. Compounds bearing either an electron-withdrawing or electron-donating substituent on the aromatic ring provided the spiro compounds in good to excellent yields. Not only compounds with an *N*-phenyl substituent but also those bearing *N*-naphthyl and *N*-5,6,7,8-tetrahydronaphthyl groups underwent the cyclization smoothly.

Treatment of the spiro dienone **9m** with $BF_3{\cdot}Et_2O$ (Scheme 5) provided 1,3-diazepine derivative **12m** (73%)

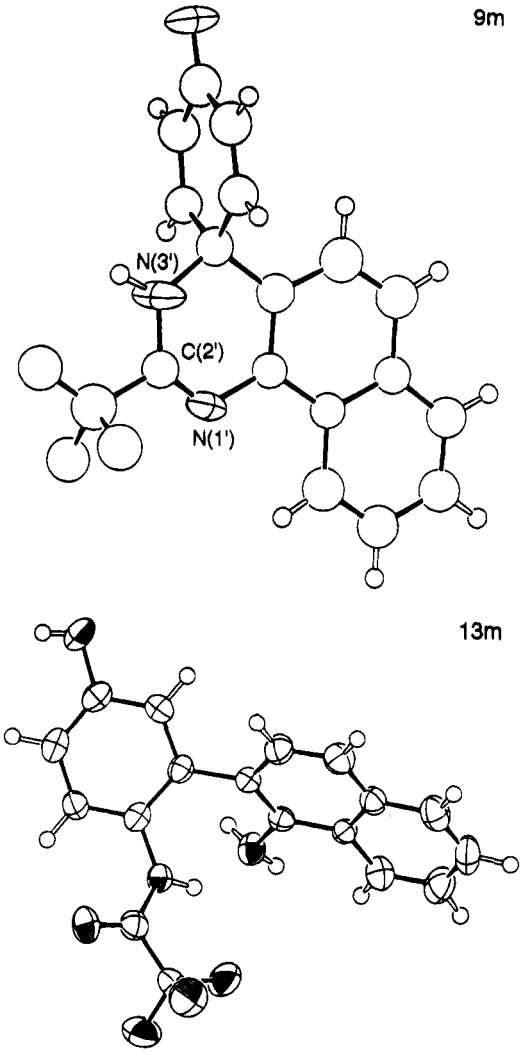


Figure 1. X-ray crystalographic data on **9m** and **13m**. Each atom distance of N(1′)–C(2′) or N(3′)–C(2′) in **9m** was 1.25 or 1.35 Å, respectively.

Table 3. Solvent Effect for Thermal Spirocyclization[a] of 1a

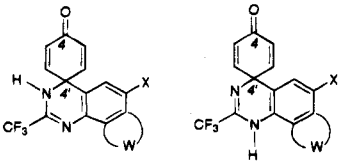
entry	solvent	temp (°C)	time (h)	**9a** and **10a** (% yield)
1	benzene	80	22.0	*b*
2	toluene	110	18.0	*c*
3	*p*-xylene	145	6.0	*c*
4	DMSO	120	2.0	97[d]
5	MeCN	80	21.0	91[d]
6	*n*-BuOH	117	2.0	83[d]
7	EtOH	78	4.0	88[d]
8	AcOH	118	2.0	32[d], 40[e]

[a] **1a** (0.5 mmol), solvent (2 mL). [b] Recovery of **1a** (88%). [c] A mixture of unidentified products. [d] A mixture of the two tautomers (**9a** and **10a**). [e] Yield of **3a**.

via a dienone–phenol rearrangement.[16] However, treatment of **9m** with commercial TFA resulted in quantitative formation of the corresponding 2-naphthylaminophenol **13m**, which may arise from hydrolysis of **12m**. X-ray analysis of **13m** revealed a 4-aminophenol derivative (Figure 1). This result suggests that the reaction

(16) Reviews on the dienone–phenol rearrangement: Collins, C. J.; Eastham, J. D. *Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience: New York, 1966; p 755. Miller, B. *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Interscience: New York, 1968: Vol. 1, p 275. Rishton, G. M.; Schwartz, M. A. *Tetrahedron Lett.* **1988**, *29*, 2643. Kita, Y.; Yakura, T.; Tohma, H.; Kikuchi, K.; Tamura, Y. *Tetrahedron Lett.* **1989**, *30*, 1119.

Table 4. Thermal Spirocyclization[a] of 1 in DMSO

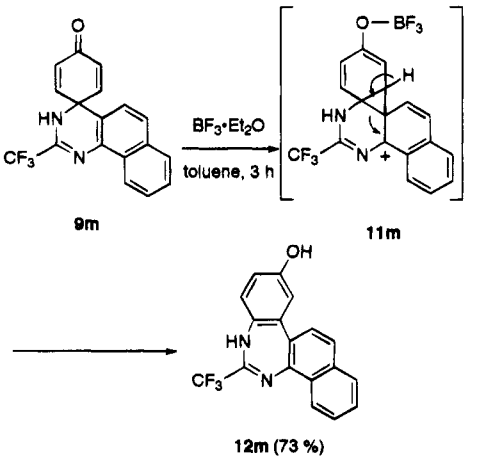


9 10

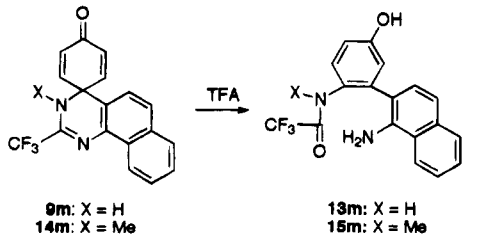
1	substit	yield (%)[b] of 9 and 10 ratio (9:10)[c]	chem shifts of ^{13}C NMR $C_{4'}$ (spiro)	C_4 (carbonyl)
a	X = MeO	97 (3:1)	**9** (55.1)	**9** (184.4)
			10 (58.8)	**10** (185.3)
b	X = Cl	97 (1:1)	**9** (54.9)	**9** (184.0)
			10 (58.4)	**10** (185.1)
c	X = Me	99 (1.2:1)	**9** (55.1)	**9** (184.5)
			10 (58.6)	**10** (185.5)
d	X = NO_2	66 (0.25:1)	**9** (55.5)	**9** (184.4)
			10 (58.1)	**10** (185.5)
g	X = H	92 (1:1)	**9** (55.3)	**9** (184.5)
			10 (58.7)	**10** (185.5)
h	X = H, W = $(CH_2)_4$	84 (0.5:1)	**9** (55.2)	**9** (184.4)
			10 (58.8)	**10** (185.2)
m	X = H, W = $(CH{=}CH)_2$	66[d,e] (1:0)	**9** (55.7)	**9** (184.7)
n	X = Cl, W = $(CH{=}CH)_2$	61[d,e] (1:0)	**9** (55.4)	**9** (184.5)

[a] Reaction conditions: **1** (1.0 mmol), DMSO (2 mL), 120 °C, 2 h. [b] A mixture of two tautomers (**9** and **10**). [c] By ^{13}C NMR analysis. [d] Only one tautomer (**9m**, **9n**) was formed. [e] Overall yield from **2m** and **2n**.

Scheme 5



Scheme 6



could proceed by a rearrangement via intermediate **12**, followed by hydrolysis, affording **13m** (Scheme 6). *N*-Methyl compound **14m** was also converted to 2-naphthyl aminophenol derivative **15m** quantitatively by treatment with either $BF_3{\cdot}Et_2O$ or TFA.

Experimental Section

General Methods. All commercial reagents and solvents were recrystallized or distilled by the usual methods. E. Merck silica gel (kieselgel 60, 230–400 mesh) was employed for the chromatography. Analytical thin layer chromatography (TLC) was performed with 0.2 mm coated commercial plates (E. Merck, kieselgel 60 F254). The ^1H, ^{13}C, and ^{19}F NMR were recorded using TMS for ^1H and C_6F_6 for ^{19}F as internal standards. Melting points are uncorrected.

Lewis Acid-Promoted Cyclization of 1. A mixture of **1a** (308 mg, 1 mmol) and boron trifluoride etherate (147 mg, 1 mmol) in benzene (5 mL) was stirred at reflux (80 °C) under N_2 for 0.5 h. After the reaction was quenched, the organic products were extracted with ethyl acetate (5 mL × 5) with dilute NH_4Cl solution (5 mL) and washed with brine (5 mL). The organic layer was dried with anhyd Na_2SO_4 and evaporated. The residue was recrystallized from hexane–ethyl acetate, affording **3a**.

1-(4′-Methoxyphenyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3a): colorless crystals (93%); mp 214–215 °C; IR ($CHCl_3$) 3620, 2900, 1244 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 3.92 (s, 3 H), 6.53 (d, 1 H, J = 2.3 Hz), 6.98 (dd, 1 H, J = 2.3, 8.8 Hz), 7.14 (d, 2 H, J = 8.8 Hz), 7.43 (d, 2 H, J = 8.8 Hz), 7.66 (d, 1 H, J = 8.8 Hz), 8.60 (s, 1 H); ^{19}F NMR (188 MHz, acetone-d_6) δ 102.7 (CF_3). Anal. Calcd for $C_{15}H_{11}F_3N_2O_2$: C, 58.44; H, 3.60; N, 9.09. Found: C, 58.33; H, 3.37; N, 9.18.

1-(4′-Chlorophenyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3b): colorless crystals (91%); mp 201–202 °C; IR ($CHCl_3$) 3624, 2980, 1232 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 6.48 (d, 1 H, J = 2.3 Hz), 6.93 (dd, 1 H, J = 2.3, 8.8 Hz), 7.42 (d, 2 H, J = 8.7 Hz), 7.57 (d, 2 H, J = 8.7 Hz), 7.61 (d, 1 H, J = 8.8 Hz), 8.40–8.60 (br, 1 H); ^{19}F NMR (188 MHz, acetone-d_6) δ 102.3 (CF_3). Anal. Calcd for $C_{14}H_8ClF_3N_2O$: C, 53.78; H, 2.58; N, 8.96. Found: C, 53.64; H, 2.51; N, 8.89.

1-(4′-Methylphenyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3c): colorless crystals (99%); mp 189–190 °C; IR ($CHCl_3$) 3624, 2980, 1230 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 2.49 (s, 3 H), 6.52 (d, 1 H, J = 2.4 Hz), 6.98 (dd, 1 H, J = 2.4, 8.8 Hz), 7.34 (d, 2 H, J = 8.5 Hz), 7.44 (d, 2 H, J = 8.5 Hz), 7.66 (d, 1 H, J = 8.8 Hz), 8.20–8.90 (br, 1 H); ^{19}F NMR (188 MHz, acetone-d_6) δ 102.6 (CF_3). Anal. Calcd for $C_{15}H_{11}F_3N_2O$: C, 61.65; H, 3.79; N, 9.58. Found: C, 61.91 H, 3.78 N, 9.36.

1-(4′-Nitrophenyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3d): yellow crystals (57%); mp 236–237 °C; IR ($CHCl_3$) 3624, 2904, 1236 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 6.60 (d, 1 H, J = 2.3 Hz), 7.03 (dd, 1 H, J = 2.3, 8.8 Hz), 7.70 (d, 1 H, J = 8.8 Hz), 7.88 (d, 2 H, J = 8.8 Hz), 8.54 (d, 2 H, J = 8.8 Hz), 8.68 (s, 1 H); ^{19}F NMR (188 MHz, acetone-d_6) δ 103.1 (CF_3). Anal. Calcd for $C_{14}H_8F_3N_3O_3$: C, 52.02; H, 2.49; N, 13.00. Found: C, 52.03; H, 2.38; N, 12.90.

1-(4′-Hydroxyphenyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3e): brown crystals (77%); mp 221–222 °C; IR (Nujol) 3372, 1184 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 6.42 (d, 1 H, J = 2.4 Hz), 6.88 (dd, 1 H, J = 2.4, 8.8 Hz), 6.96 (d, 2 H, J = 8.7 Hz), 7.27 (d, 2 H, J = 8.7 Hz), 7.62 (d, 1 H, J = 8.8 Hz), 9.25–9.47 (br, 1 H), 9.63–9.88 (br, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 103.1 (CF_3). Anal. Calcd for $C_{14}H_9F_3N_2O_2$: C, 57.15; H, 3.08; N, 9.52. Found: C, 57.06; H, 3.20; N, 9.30.

1-(3′,4′-Dichlorophenyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3f): colorless crystals (91%); mp 206–207 °C; IR ($CHCl_3$) 3604, 3048, 1172 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.48 (d, 1 H, J = 2.1 Hz), 6.93 (dd, 1 H, J = 2.1, 8.9 Hz), 7.62 (dd, 1 H, J = 2.5, 8.5 Hz), 7.69 (d, 1 H, J = 8.9 Hz), 7.91 (d, 1 H, J = 8.5 Hz), 8.01 (d, 1 H, J = 2.5 Hz), 9.76 (s, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 102.4 (CF_3). Anal. Calcd for $C_{14}H_7Cl_2F_3N_2O$: C, 48.44; H, 2.03; N, 8.07. Found: C, 48.65; H, 2.02; N, 7.82.

1-Phenyl-2-(trifluoromethyl)-6-hydroxybenzimidazole (3g): colorless crystals (80%); mp 171–176 °C; IR ($CHCl_3$) 3604, 3028, 1212 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.38–6.42 (br, 1 H), 6.86–6.92 (br, 1 H), 748–7.70 (br, 6 H), 9.62–9.73 (br, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 103.2 (CF_3). Anal. Calcd for $C_{14}H_9F_3N_2O$: C, 60.44; H, 3.26; N, 10.07. Found: C, 60.46; H, 3.29; N, 9.88.

1-(5′,6′,7′,8′-Tetrahydro-1′-naphthyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3h): colorless crystals (54%); mp 217–219 °C; IR ($CHCl_3$) 3664, 2940, 2844, 1144 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 1.60–1.72 (m, 4 H), 2.08 (t, 2 H, J = 5.7 Hz), 2.85 (t, 2 H, J = 6.0 Hz), 6.23 (d, 1 H, J = 2.3 Hz), 6.87 (dd, 1 H, J = 2.3, 8.9 Hz), 7.19–7.33 (m, 4 H), 7.65 (d, 1 H, J = 8.9 Hz), 9.60 (s, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 101.5 (CF_3). Anal. Calcd for $C_{18}H_{15}F_3N_2O$: C, 65.06; H, 4.55; N, 8.43. Found: C, 64.97; H, 4.44; N, 8.33.

1-(*n*-Hexyl)-2-(trifluoromethyl)-6-hydroxybenzimidazole (3i): colorless crystals (74%); mp 141–143 °C; IR ($CHCl_3$) 3604, 2960, 2864, 1166 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 0.87 (t, 3 H, J = 6.7 Hz), 1.20–1.85 (m, 8 H), 4.24 (t, 2 H, J = 7.8 Hz), 6.87 (dd, 1 H, J = 2.0, 8.8 Hz), 6.94 (d, 1 H, J = 2.0 Hz), 7.59 (d, 1 H, J = 8.8 Hz), 9.70 (s, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 101.6 (CF_3). Anal. Calcd for $C_{14}H_{17}F_3N_2O$: C, 58.74; H, 5.98; N, 9.78. Found: C, 58.73; H, 6.03; N, 9.70.

1-Allyl-2-(trifluoromethyl)-6-hydroxybenzimidazole (3j): colorless crystals (66%); mp 114–117 °C; IR ($CHCl_3$) 3688, 2906, 1136 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.84 (d, 2 H, J = 5.3 Hz), 5.11 (d, 1 H, J = 17 Hz), 5.26 (d, 1 H, J = 10.3 Hz), 5.82–6.02 (m, 1 H), 6.86 (d, 1 H, J = 2.3 Hz), 6.94 (dd, 1 H, J = 2.3, 8.8 Hz), 7.68 (d, 1 H, J = 8.8 Hz); ^{19}F NMR (188 MHz, DMSO-d_6) δ 99.9 (CF_3). Anal. Calcd for $C_{11}H_9F_3N_2O$: C, 54.55; H, 3.74; N, 11.57. Found: C, 54.41; H, 3.75; N, 11.38.

1-Benzyl-2-(trifluoromethyl)-6-hydroxybenzimidazole (3k): colorless crystals (60%); mp 148–149 °C; IR ($CHCl_3$) 3616, 3020, 2900, 1162 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.41 (s, 2 H), 6.73 (d, 1 H, J = 2.2 Hz), 6.93 (dd, 1 H, J = 2.2, 8.8 Hz), 7.05–7.10 (m, 3 H), 7.26–7.30 (m, 2 H), 7.64 (d, 1 H, J = 8.8 Hz), 7.70 (s, 1 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 100.4 (CF_3). Anal. Calcd for $C_{15}H_{11}F_3N_2O$: C, 61.65; H, 3.79; N, 9.59. Found: C, 61.60; H, 3.77; N, 9.45.

3-(4′-Hydroxyphenyl)-2-(trifluoromethyl)naphtho[2,1-*d*]imidazole (7m). Imidamide **2m** (172 mg, 0.5 mmol) was dissolved in a mixture of acetonitrile (9 mL) and water (1 mL) containing sodium perchlorate (49 mg, 0.4 mmol) and electrooxidized at 0 °C in an undivided cell using a glassy carbon anode and a platinum foil cathode at a constant current of 5 mA/cm^2 for 2.5 F/mol. 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). After drying over anhyd $MgSO_4$ and condensing, the residue was added to a toluene solution (5 mL) of $SnCl_4$ (0.5 mmol) and was stirred at 0 °C under an N_2 atmosphere for 0.5 h. The reaction was quenched with dilute $NaHCO_3$ solution (5 mL), and the organic products were extracted with ethyl acetate (5 mL × 5). The organic layer was washed with brine (5 mL), dried with anhyd Na_2SO_4, condensed, and chromatographed on silica gel (25% AcOEt–hexane) to give **7m**: colorless crystals (10%); mp 194–195 °C; IR ($CHCl_3$) 3600, 3056, 1146 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 7.12 (d, 2 H, J = 8.7 Hz), 7.29 (d, 1 H, J = 9.0 Hz), 7.46 (d, 2 H, J = 8.7 Hz), 7.59 (dt, 1 H, J = 1.5, 7.5 Hz), 7.73 (dt, 1 H, J = 1.5, 7.5 Hz), 7.88 (d, 1 H, J = 9.0 Hz), 8.04 (d, 1 H, J = 8.6 Hz), 8.64 (d, 1 H, J = 8.6 Hz), 9.07 (s, 1 H); ^{19}F NMR (188 MHz, acetone-d_6) δ 103.8 (CF_3). Anal. Calcd for $C_{18}H_{11}F_3N_2O$: C, 65.86; H, 3.38; N, 8.53. Found: C, 65.90; H, 3.32; N, 8.40.

3-(4′-Hydroxyphenyl)-2-(trifluoromethyl)-5-chloronaphtho[2,1-*d*]imidazole (7n): colorless crystals (12%); mp 256–258 °C; IR ($CHCl_3$) 3610, 3080, 1154 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 6.99 (d, 2 H, J = 8.6 Hz), 7.43 (s, 1 H), 7.44 (d, 2 H, J = 8.6 Hz), 7.70–7.90 (m, 2 H), 8.31 (d, 1 H, J = 8.2 Hz), 8.62 (d, 1 H, J = 7.8 Hz), 10.15 (s, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 103.4 (CF_3). Anal. Calcd for $C_{18}H_{10}ClF_3N_2O$: C, 59.60; H, 2.78; N, 7.72. Found: C, 59.77; H, 2.74; N, 7.38.

***N*-(2-Chloro-4-hydroxyphenyl)-*N*′-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (6).** A mixture of **1a** (308 mg, 1 mmol) and aluminum trichloride (134 mg, 1 mmol) in benzene (5 mL) was stirred at reflux (80 °C) under N_2 for 0.7 h. After the reaction was quenched, the organic products were extracted with ethyl acetate (5 mL × 5) and with dilute $NaHCO_3$ solution (5 mL) and washed with brine (5 mL). The organic layer was dried with anhyd Na_2SO_4, and condensed affording **3a** (63%) and **6**: colorless oil (31%); IR ($CHCl_3$) 3556, 3436, 2944, 2840, 1146 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 3 H), 5.20–5.50 (br, 1 H), 6.50–7.00 (br, 7 H); ^{19}F NMR (188 MHz, $CHCl_3$) δ 91.8 (CF_3), 98.0 (CF_3). Anal. Calcd for $C_{15}H_{12}ClF_3N_2O$: C, 52.27; H, 3.51; N, 8.13. Found: C, 51.98; H, 3.46; N, 7.96.

Preparation of Spiro Dienone Derivatives 9 and 10. The substrate **1a** (308 mg, 1 mmol) was dissolved in DMSO (2 mL) and stirred at 120 °C under N_2 for 2 h. The reaction mixture was extracted with ethyl acetate (5 mL × 5) and water (5 mL) followed by washing with brine (5 mL). The organic layer was dried with anhyd Na_2SO_4 and then condensed. The residue was recrystallized from hexane–benzene, affording a mixture of tautomers **9a** and **10a** (**9a/10a** = 3/1): yellow crystals (92%); mp 174–175 °C; IR ($CHCl_3$) 3440, 2848, 1676, 1190 cm^{-1}. Anal. Calcd for $C_{15}H_{11}F_3N_2O_2$: C, 58.45; H, 3.59; N, 9.09. Found: C, 57.78; H, 3.61; N, 9.22.

2′-(Trifluoromethyl)-6′-methoxyspiro[2,5-cyclohexadiene-1,4′-3′*H*-quinazolin]-4-one (9a): ^1H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 3 H), 5.60–5.67 (br, 1 H), 6.21 (d, 2 H, J = 10.0 Hz), 6.49 (d, 1 H, J = 2.5 Hz), 6.89 (dd, 1 H, J = 2.5, 8.8 Hz), 7.12 (d, 2 H, J = 10.0 Hz), 7.32 (d, 1 H, J = 8.8 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 89.2 (CF_3).

2′-(Trifluoromethyl)-6′-methoxyspiro[2,5-cyclohexadiene-1,4′-1′*H*-quinazolin]-4-one (10a): ^1H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 3 H), 6.24 (d, 2 H, J = 10.0 Hz), 6.51 (d, 1 H, J = 2.0 Hz), 6.81–6.82 (br, 2 H), 6.97 (d, 2 H, J = 10.0 Hz), 7.59–7.63 (br, 1 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 89.4 (CF_3).

2′-(Trifluoromethyl)-6′-chlorospiro[2,5-cyclohexadiene-1,4′-3′*H*-quinazolin]-4-one (9b) and 2′-(trifluoromethyl)-6′-chlorospiro[2,5-cyclohexadiene-1,4′-1′*H*-quinazolin]-4-one (10b) (9b/10b = 1/1): colorless crystals (97%); mp 172–173 °C; IR ($CHCl_3$) 3450, 1674, 1136 cm^{-1}. Anal. Calcd for $C_{14}H_8ClF_3N_2O$: C, 53.78; H, 2.58; N, 8.96. Found: C, 54.40; H, 2.63; N, 8.59.

Tautomer 9b: ^1H NMR (200 MHz, $CDCl_3$) δ 5.54–5.62 (br, 1 H), 6.26 (d, 2 H, J = 10.1 Hz), 6.79–6.97 (m, 2 H), 7.10 (d, 2 H, J = 10.1 Hz), 7.22–7.30 (m, 1 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 89.0 (CF_3).

Tautomer 10b: ^1H NMR (200 MHz, $CDCl_3$) δ 6.27 (d, 2 H, J = 10.1 Hz), 6.82 (d, 1 H, J = 8.5 Hz), 6.92 (d, 2 H, J = 10.1 Hz), 7.22–7.29 (m, 2 H), 7.39–7.43 (br, 1 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 89.0 (CF_3).

2′-(Trifluoromethyl)-6′-methylspiro[2,5-cyclohexadiene-1,4′-3′*H*-quinazolin]-4-one (9c) and 2′-(trifluoromethyl)-6′-methylspiro[2,5-cyclohexadiene-1,4′-1′*H*-quinazolin]-4-one (10c) (9c/10c = 1.2/1): colorless crystals (99%); mp 166–167 °C; IR ($CHCl_3$) 3440, 2984, 1676, 1158 cm^{-1}. Anal. Calcd for $C_{15}H_{11}F_3N_2O$: C, 61.65; H, 3.79; N, 9.59. Found: C, 61.63; H, 3.79; N, 9.62.

Tautomer 9c: ^1H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 3 H), 5.65–5.66 (br, 1 H), 6.22 (d, 2 H, J = 10.0 Hz), 6.75–6.78 (br, 1 H), 7.12 (d, 2 H, J = 10.0 Hz), 7.13–7.16 (m, 1 H), 7.26 (d, 1 H, J = 8.0 Hz); ^{19}F NMR (188 MHz, DMSO-d_6) δ 91.4 (CF_3).

Tautomer 10c: ^1H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 3 H), 6.25 (d, 2 H, J = 10.0 Hz), 6.78–6.80 (m, 2 H), 6.96 (d, 2 H, J = 10.0 Hz), 7.07–7.10 (m, 1 H), 7.54–7.64 (br, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 91.4 (CF_3).

2′-(Trifluoromethyl)-6′-nitrospiro[2,5-cyclohexadiene-1,4′-3′*H*-quinazolin]-4-one (9d) and 2′-(trifluoromethyl)-6′-nitrospiro[2,5-cyclohexadiene-1,4′-1′*H*-quinazolin]-4-one (10d) (9d/10d = 0.25/1): orange crystals (66%); mp 218–220 °C; IR ($CHCl_3$) 3420, 3080, 1676, 1132 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.24 (d, 2 H, J = 10.0 Hz), 7.18 (d, 2 H, J = 10.0 Hz), 7.33 (d, 1 H, J = 8.8 Hz), 7.61 (d, 1 H, J = 2.5 Hz), 8.18 (dd, 1 H, J = 8.8, 2.5 Hz), 11.4–11.6 (br, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 91.2 (CF_3). Anal. Calcd for $C_{14}H_8F_3N_3O_3$: C, 52.02; H, 2.49; N, 13.00. Found: C, 52.31; H, 2.58; N, 12.68.

2′-(Trifluoromethyl)spiro[2,5-cyclohexadiene-1,4′-3′*H*-quinazolin]-4-one (9g) and 2′-(trifluoromethyl)spiro[2,5-cyclohexadiene-1,4′-1′*H*-quinazolin]-4-one (10g) (a mixture of 9g and 10g, 9g/10g = 1/1): colorless crystals (92%); mp 205–206 °C; IR ($CHCl_3$) 1670, 1124 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.55–5.60 (br, 1 H), 6.19–6.27 (m, 2 H), 6.83–7.42 (m, 6 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 89.2 (CF_3).

Anal. Calcd for $C_{14}H_9F_3N_2O$: C, 60.44; H, 3.26; N, 10.07. Found: C, 60.40; H, 3.16; N, 9.88.

2′-(Trifluoromethyl)-7′,8′,9′,10′-tetrahydrospiro[2,5-cyclohexadiene-1,4′-3′*H*-benzo[*h*]quinazolin]-4-one (9h) and 2′-(trifluoromethyl)-7′,8′,9′,10′-tetrahydrospiro[2,5-cyclohexadiene-1,4′-1′*H*-benzo[*h*]quinazolin]-4-one (10h) (9c/10c = 1/2): yellow crystals (84%); mp 203−205 °C; IR ($CHCl_3$) 3464, 2940, 1674, 1152 cm^{-1}. Anal. Calcd for $C_{18}H_{15}F_3N_2O$: C, 65.06; H, 4.55; N, 8.43. Found: C, 65.08; H, 4.49; N, 8.43.

Tautomer 9h: ^1H NMR (500 MHz, $CDCl_3$) δ 1.90−1.96 (m, 4 H), 2.71−2.77 (m, 2 H), 2.95 (t, 2 H, J = 5.5 Hz), 5.50 (br, 1 H), 6.71 (d, 2 H, J = 10.0 Hz), 6.69 (d, 1 H, J = 8.0 Hz), 6.89 (d 1 H, J = 8.0 Hz), 7.09 (d, 2 H, J = 10.0 Hz); ^{19}F NMR (188 MHz, DMSO-d_6) δ 91.4 (CF_3).

Tautomer 10h: ^1H NMR (500 MHz, $CDCl_3$) δ 1.74−1.84 (m, 4 H), 2.56 (t, 2 H, J = 6.0 Hz), 2.71−2.77 (m, 2 H), 6.21 (d, 2 H, J = 10.0 Hz), 6.74 (d, 1 H, J = 8.0 Hz), 6.86 (d, 1 H, J = 8.0 Hz), 6.93 (d, 2 H, J = 10.0 Hz), 7.3−7.8 (br, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 91.4 (CF_3).

2′-(Trifluoromethyl)spiro[2,5-cyclohexadiene-1,4′-3′H-benzo[*h*]quinazolin]-4-one (9m). Imidamide **2m** (172 mg, 0.5 mmol) was dissolved in a mixture of acetonitrile (9 mL) and water (1 mL) containing $NaClO_4$ (49 mg, 0.4 mmol) and electrooxidized at 0 °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 F/mol. After the electrolysis, the reaction mixture was stirred at rt for 2 h. 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). After drying over anhyd Na_2SO_4 and condensing, the residue was chromatographed on silica gel column (25% AcOEt−hexane), affording **9m**: orange crystals (66%): mp 219−221 °C; IR ($CHCl_3$) 3432, 2992, 1676, 1150 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.17 (d, 2 H, J = 9.8 Hz), 6.99 (d, 1 H, J = 9.0 Hz), 7.32 (d, 2 H, J = 9.8 Hz), 7.54 (dd, 1 H, J = 8.0, 8.0 Hz), 7.56 (dd, 1 H, J 8.0, 8.0 Hz), 7.66 (d, 1 H, J = 8.0 Hz), 7.82 (d, 1 H, J = 8.0 Hz), 8.55 (d, 1 H, J = 8.0 Hz), 9.23−9.29 (br, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 90.1 (CF_3). Anal. Calcd for $C_{18}H_{11}F_3N_2O$: C, 65.86; H, 3.38; N, 8.53. Found: C, 65.68; H, 3.23; N, 8.44.

2′-(Trifluoromethyl)-6′-chlorospiro[2,5-cyclohexadiene-1,4′-3′*H*-benzo[*h*]quinazolin]-4-one (9n): yellow crystals (61%); mp 189−190 °C; IR ($CHCl_3$) 3428, 3056, 1676, 1146 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 6.19 (d, 2 H, J = 9.8 Hz), 7.08 (s, 1 H), 7.35 (d, 2 H, J = 9.8 Hz), 7.68−7.72 (m, 2 H), 8.06 (m, 1 H), 8.58−8.63 (m, 1 H), 9.45 (s, 1 H); ^{19}F NMR (188 MHz, DMSO-d_6) δ 91.4 (CF_3). Anal. Calcd for $C_{18}H_{10}ClF_3N_2O$: C, 59.60; H, 2.78; N, 7.72. Found: C, 59.54; H, 2.73; N, 7.49.

2′-(Trifluoromethyl)-5′-methylspiro[2,5-cyclohexadiene-1,4′-3′*H*-benzo[*h*]quinazolin]-4-one (14m). A mixture of spiro dienone **9m** (328 mg, 1 mmol), iodomethane (248 mg, 2 mmol), and K_2CO_3 (138 mg, 1 mmol) in acetone (2 mL) was stirred at rt for 2 d. The reaction mixture was neutralized with 10% aqueous HCl (5 mL), followed by extraction with ethyl acetate (5 mL × 5) and water (5 mL) and washing with brine (5 mL). The organic layer was dried with anhyd Na_2SO_4, condensed, and chromatographed with silica gel, affording **14m**: yellow crystals (60%); mp 160−161 °C; IR ($CHCl_3$) 1676, 1624, 1136 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.09 (q, 3 H, J = 1.4 Hz), 6.37 (d, 2 H, J = 10.2 Hz), 6.90 (d, 1 H, J = 8.6 Hz), 7.20 (d, 2 H, J = 10.2 Hz), 7.48−7.62 (m, 3 H), 7.72−7.78 (m, 1 H), 8.64−8.71 (m, 1 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 94.6 (CF_3). Anal. Calcd for $C_{19}H_{13}F_3N_2O$: C, 66.67; H, 3.83; N, 8.18. Found: C, 66.89; H, 3.73; N, 7.79.

2-(Trifluoromethyl)-3*H*-benzo[*d*]naphtho[2,1-*f*]-1,3-diazepine (12m). A mixture of **9m** (328 mg, 1 mmol) and boron trifluoride etherate (294 mg, 2 mmol) in toluene (5 mL) was stirred at reflux (110 °C) under N_2 for 3 h. The reaction mixture was extracted with ethyl acetate (5 mL × 5) and dilute $NaHCO_3$ solution (5 mL) followed by washing with brine (5 mL). The organic layer was dried with anhyd Na_2SO_4 and condensed. After silica gel column chromatography, **12m** was obtained as a yellow solid (73%): mp 35−36 °C; IR ($CHCl_3$) 3596, 3404, 1136 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 5.20−5.40 (br, 1 H), 6.56 (d, 1 H, J = 8.5 Hz), 6.63−6.65 (br, 1 H), 6.73 (dd, 1 H, J = 8.5, 3.0 Hz), 6.92 (d, 1 H, J = 3.0 Hz), 7.44 (d, 1 H, J = 9.0 Hz), 7.50−7.55 (m, 3 H), 7.74 (d, 1 H, J = 9.0 Hz), 7.78 (d, 1 H, J = 9.5 Hz); ^{19}F NMR (188 MHz, $CHCl_3$) δ 89.2 (CF_3). Anal. Calcd for $C_{18}H_{11}F_3N_2O$: C, 65.86; H, 3.38; N, 8.53. Found: C, 65.93; H, 3.61; N, 8.24.

3-(1′-Amino-2′-naphthyl)-4-[(*N*-trifluoroacetyl)amino]-phenol (13m). A mixture of **9m** (32.8 mg, 0.1 mmol) and TFA (28.8 mg, 0.2 mmol) in toluene (2 mL) was stirred at rt under N_2 for 0.5 h. The reaction mixture was extracted with ethyl acetate (5 mL × 5) and dilute $NaHCO_3$ solution (5 mL) followed by washing with brine (5 mL). The organic layer was dried with anhyd Na_2SO_4 and condensed. The residue was recrystallized from hexane−ethyl acetate, affording **13m** as colorless crystals (100%): mp 174−176 °C; IR ($CHCl_3$) 3640, 3404, 1726, 1186 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 4.80−5.40 (br, 2 H), 6.80−6.90 (m, 2 H), 7.04 (d, 1 H, J = 8.4 Hz), 7.19 (d, 1 H, J = 8.4 Hz), 7.29 (d, 1 H, J = 8.4 Hz), 7.35−7.47 (m, 2 H), 7.75−7.82 (m, 1 H), 8.15−8.22 (m, 1 H), 9.83 (s, 1 H), 10.52 (s, 1 H); ^{19}F NMR (188 MHz, DMSO-d) δ 88.1 (CF_3). Anal. Calcd for $C_{18}H_{13}F_3N_2O_2$: C, 62.43; H, 3.78; N, 8.08. Found: C, 62.43; H, 3.78; N, 8.09.

3-(1′-Amino-2′-naphthyl)-4-[(*N*-methyl-*N*-trifluoroacetyl)amino]phenol (15m): yellow solids (100%); mp 80−84 °C; IR ($CHCl_3$) 3592, 3356, 1728, 1156 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.75 (s, 3 H), 4.0−5.0 (br, 2 H), 6.64−6.80 (br, 3 H), 7.38 (d, 1 H, J = 8.5 Hz), 7.49−7.64 (m, 2 H), 7.77−7.92 (m, 3 H), 10.3−10.7 (s, 1 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 85.7 (CF_3). Anal. Calcd for $C_{19}H_{15}F_3N_2O_2$: C, 63.33; H, 4.19; N, 7.77. Found: C, 63.52; H, 4.54; N, 7.95.

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Supporting Information Available: Details of the X-ray data acquisition (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. The authors have deposited atomic coordinates, bond lengths, bond angles, thermal parameters, and structure factors for **9m** and **13m** with the Cambridge Crystallographic Data Centre. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre 12, Union Road, Cambridge, CB2 1EZ, U.K.

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