Synthesis of 2-(Perfluoroalkyl)- and 2-(Perfluoroaryl)benzimidazoles by Oxidative Intramolecular Cyclization of Perfluoroalkyl and Aryl Imidamides

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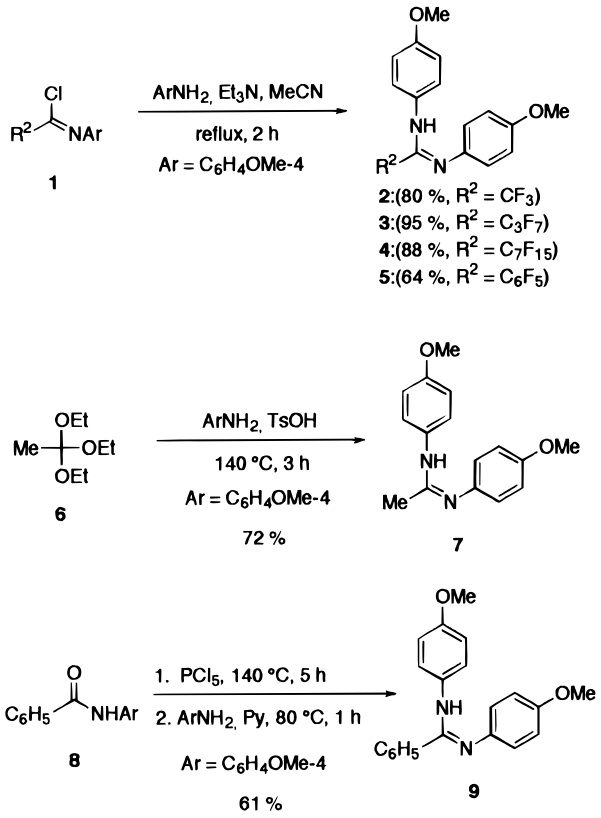
Because of the synthetic importance of fluoro-functionalized heterocycles,[1] a variety of approaches to the syntheses of fluorinated heterocycles have been studied. Fluorinated benzimidazoles show insecticidal and herbicidal activities.[2] The general procedure for the synthesis of the fluorinated benzimidazoles involves the direct trifluoromethylation[3] or perfluoroalkylation[4] of benzimidazoles and condensation of *o*-phenylenediamine or *o*-nitroaniline with trifluoroacetic acid or perfluoroalkanoic acid.[5] Since trifluoroethanimidamide derivatives **2**[6] and perfluoroalkyl and aryl imidamides **3**−**5** are easily available, these fluoro-functionalized imidamides would be converted to the corresponding fluorinated benzimidazoles by intramolecular carbon−nitrogen bond formation. Photoinduced[7] and oxidative intramolecular cyclizations by sodium hypochlorite[8] and lead(IV) acetate[9] have been demonstrated.

We have previously reported the preparation of 2-(trifluoromethyl)benzimidazoles by electrochemical oxidative cyclization of **2**[10] and Lewis acid-promoted cyclization of the electrochemically prepared *p*-benzoquinone imine derivatives **11**.[11] In this note, we describe a detailed study on the electrochemical and the oxidant-promoted reactions of perfluoroalkyl and aryl imidamides and related imidamides.

Perfluoroalkyl and aryl imidamides **3**, **4**, and **5** (R^2 = C_3F_7, C_7F_{15}, and C_6F_5, respectively) were easily prepared from *N*-aryl perfluoroalkyl and aryl imidoyl chlorides **1**[12] in reasonable yields as shown in Scheme 1. The imidamide **7** was prepared by the reaction of ethyl orthoacetate **6** with *p*-anisidine.[13] The preparation of **9** was achieved by the reaction of *p*-anisidine with the benzimidoyl chloride which was prepared by the reaction of benzamide **8** with PCl_5.[14]

Scheme 1



The electrooxidation of **2** in dry acetonitrile gave the desired benzimidazole **10** quantitatively (Table 1, entry 1). On the other hand, electrooxidation in MeOH provided quinone imine acetal **12** selectively (entry 2). This result suggests that intermolecular nucleophilic attack of methanol on an electron-deficient cationic aromatic ring is faster than intramolecular attack by an imine nitrogen. Oxidation of **2** by CAN in acetonitrile provided the desired benzimidazole **10** in 86% yield (entry 3). In contrast, oxidation by DDQ gave a very poor yield (22%) of **10** along with recovered **2** (50%) (entry 4). However, oxidation of **2** by *tert*-butyl hypochlorite or NCS resulted in predominant formation of the chlorinated compound **13**[15] (entries 5 and 6). This result also demonstrates that intermolecular nucleophilic reaction of chloride ion with the electron-deficient aromatic ring of **14** is faster than intramolecular carbon−nitrogen bond formation. Interestingly, reaction with lead(IV) acetate gave a mixture of benzimidazole **10** (20%), the *p*-benzoquinone imine derivative **11** (33%), and its methyl acetal **12** (13%) (Scheme 2). Compound **11** could arise via **15a** by hydrolysis of the intermediate **15c**. Replacement of acetoxy group of **15c** with methanol or water would produce **12** which may be more stable than **15c** (Scheme 3) and is thus isolable. When the same reaction was conducted in the presence of an equimolar amount of methanol, the methanol adduct **12** was formed preferentially (entry 8). Similarly, **11** became a major product

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(15) The hydrolysis of **13** followed by trifluoroacetylation and methylation gave the corresponding *N*-(2-chloro-4-methoxyphenyl)-*N*-methyl-2,2,2-trifluoroacetamide whose spectroscopic data (IR and ^{1}H NMR) are superimposable with those of an authentic sample.

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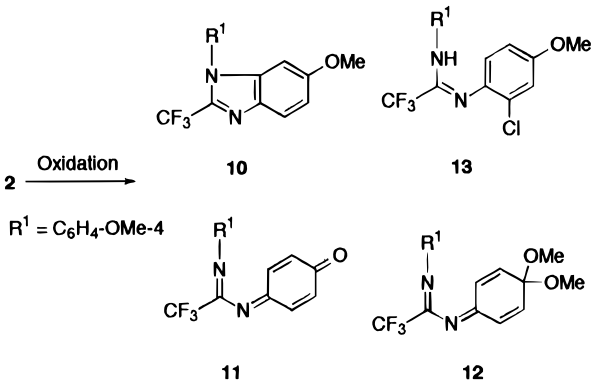
Table 1. Oxidation of Imidamide 2

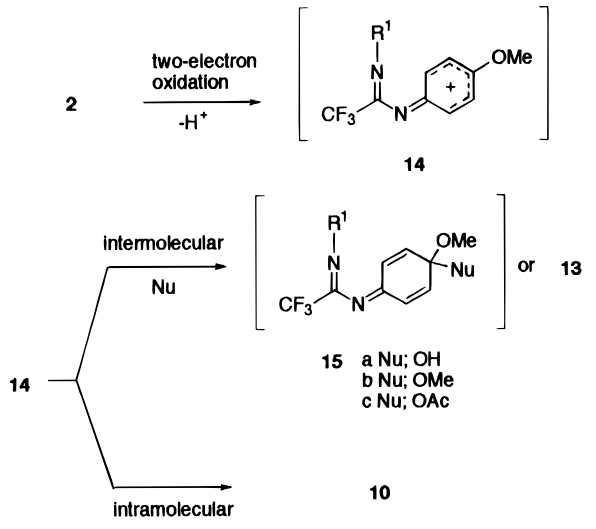
			yield (%)			
entry	reagents	solvent	**10**	**11**	**12**	**13**
1[a]	electrooxidation	MeCN	100			
2[b]	electrooxidation	MeOH			81	
3[c]	CAN	MeCN	86			
4[d]	DDQ	dioxane	22[e]			
5[f]	*t*-BuOCl	DMF				82
6[g]	NCS	DMF				80
7[h]	$Pb(OAc)_4$	CH_2Cl_2	20	33	13	
8[i]	$Pb(OAc)_4$	CH_2Cl_2/MeOH	5	trace	91	
9[j]	$Pb(OAc)_4$	CH_2Cl_2/H_2O	13	75	11	

[a] **2** (4 mmol); MeCN (35 mL); $NaClO_4$ (1 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm^2; 60 °C; 2.2 F/mol; undivided cell. [b] **2** (0.25 mmol); MeOH (8 mL); $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm^2; 60 °C; 2.2 F/mol; undivided cell. [c] **2** (0.5 mmol); CAN (2.2 equiv); MeCN (5 mL); rt; 5 min. [d] **2** (0.25 mmol), DDQ (1.5 equiv); 1,4-dioxane (4 mL); reflux; 12 h. [e] Recovery of **2** (50%). [f] **2** (0.5 mmol); *t*-BuOCl (2.2 equiv); DMF (5 mL); rt; 2 h. [g] **2** (0.5 mmol); NCS (2.2 equiv); DMF (5 mL); rt; 2 h. [h] **2** (0.25 mmol); $Pb(OAc)_4$ (1.2 equiv); CH_2Cl_2 (5 mL); rt; 2 h. [i] **2** (0.25 mmol); $Pb(OAc)_4$ (1.2 equiv); CH_2Cl_2 (5 mL); MeOH (0.25 mmol); rt; 5 min. [j] **2** (0.25 mmol); $Pb(OAc)_4$ (1.2 equiv); CH_2Cl_2 (5 mL); H_2O (2.0 mmol); rt; 2 h.

Scheme 2



Scheme 3



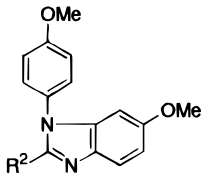
on reacting **2** with lead(IV) acetate in a wet dichloromethane (75%, entry 9).

Cationic intermediate **14** could undergo competitive electrophilic reaction inter- and intramolecularly. Nucleophiles such as nitrate, used in CAN oxidation, and perchlorate in electrooxidation are too weak to attack to the aromatic nucleus, so that intramolecular cyclization leading to **10** becomes preferred, while stronger nucleophiles such as water, methanol, and chloride ion predominantly promote nucleophilic attack on the aromatic ring. The acetate formed in lead(IV) acetate oxidation is intermediate, providing a mixture of **10**, **11**, and **12**. The electrochemical method for the preparation of **10** was found to be more advantageous than any other chemical oxidation so far examined. Not only the trifluoromethyl imidamide **2** but also perfluoroalkyl **3** and **4** and perfluoroaryl **5** imidamides were readily converted to the corresponding benzimidazoles in excellent yields (Table 2). Of particular interest is the fact that electrooxidation of the non-fluorinated imidamides **7** and **9** in a MeCN−$NaClO_4$−(C)−(Pt) system also provided the desired benzimidazoles **19** and **20**, in good yields.

Table 2. Electrochemical Preparation[a] of Benzimidazole Derivatives

imidamide	R^2	the first oxidation wave E^1 (V) vs Ag/AgCl[b]	yield (%)
2	CF_3	1.08	**10** (100)
3	C_3F_7	1.14	**16** (95)
4	C_7F_{15}	1.23	**17** (95)
5	C_6F_5	0.94	**18** (77)
7	CH_3	0.76	**19** (92)
9	C_6H_5	0.76	**20** (60)

[a] Imidamides (0.5 mmol); MeCN (7 mL); $NaClO_4$ (0.4 mmol); anode, glassy carbon; cathode, platinum foil; 5 mA/cm^2; 60 °C; 2.2 F/mol; undivided cell. [b] Imidamides (3.3×10^{-3} mol L^{-1}); MeCN (15 mL); $NaClO_4$ (0.1 mol L^{-1}); Pt wire electrodes; Ag/AgCl electrode for the reference electrode; scan rate, 0.2 V s^{-1}.



10:($R^2 = CF_3$)
16:($R^2 = C_3F_7$)
17:($R^2 = C_7F_{15}$)
18:($R^2 = C_6F_5$)
19:($R^2 = CH_3$)
20:($R^2 = C_6H_5$)

Cyclic voltammetry of trifluoromethylated imidamide **2** shows an irreversible wave which suggests deprotonation occurs soon after one-electron oxidation. The first oxidation wave E^1 appeared at about 1.08 V (vs Ag/AgCl) while non-fluorinated imidamide **7** had the corresponding oxidation wave at about 0.76 V (vs Ag/AgCl). The value of E^1 increased proportionally to the perfluoroalkyl chain length [1.08, 1.14, and 1.23 V (vs Ag/AgCl) for **2** ($R^2 = CF_3$), **3** ($R^2 = C_3F_7$), and **4** ($R^2 = C_7F_{15}$), respectively]. The comparison of oxidation potentials of compounds **5** ($R^2 = C_6F_5$) and **9** ($R^2 = C_6H_5$) clearly revealed the fluorinated phenyl compound **5** was less oxidizable. The electrochemical cyclization of both fluorinated and non-fluorinated imidamides occurred smoothly independently on the oxidizability of the substrates.

Experimental Section

Preparations of Imidamide Derivatives. Method A (2,[10] 3, 4, and 5). A mixture of *N*-arylimidoyl chloride (5 mmol) and *p*-anisidine (12 mmol) containing Et_3N (10 mmol) in acetonitrile (10 mL) was stirred at the reflux (80 °C) for 2 h. The reaction mixture was extracted with AcOEt (100 mL × 3) and 1% HCl (100 mL) and then washed with brine (50 mL). The organic layer was dried over anhydrous $MgSO_4$ followed by the filtration through activated carbon and then condensed. The residue was recrystallized from benzene−hexane.

***N,N′*-Bis(4-methoxyphenyl)-2,2,3,3,4,4,4-heptafluorobutanimidamide (3):** Colorless crystals (95%), mp 63−64 °C; IR ($CHCl_3$) 3444, 3044, 2844, 1670, 1166 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.65 (s, 6 H), 6.51 (d, 4 H, J = 9.1 Hz), 6.60 (d, 4 H, J = 9.1 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 36.1 (m, 2 F),

45.4−46.2 (br, 2 F), 81.8 (t, 3 F, J = 8.5 Hz); GCMS (m/z) 424 (M^+, 3), 302 (8), 255 ($M^+ - C_3F_7$, 14), 122 (65), 77 (100). Anal. Calcd for $C_{18}H_{15}F_7N_2O_2$ (424.32): C, 50.95; H, 3.56; N, 6.60. Found: C, 51.22; H, 3.28; N, 6.59.

***N,N′*-Bis(4-methoxyphenyl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanimidamide (4):** Colorless crystals (88%); mp 42−43 °C; IR 3444, 3000, 2840, 1668, 1150 ($CHCl_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.68 (s, 6 H), 6.53 (d, 4 H, J = 9.1 Hz), 6.62 (d, 4 H, J = 9.1 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 35.7 (m, 2 F), 38.9−40.8 (br, 8 F), 43.3−43.8 (br, 2 F), 81.1 (t, 3 F, J = 9.7 Hz); GCMS (m/z) 502 ($M^+ - NHC_6H_4OCH_3$, 25) 255 ($M^+ - C_7F_{15}$, 100), 122 (95). Anal. Calcd for $C_{22}H_{15}F_{15}N_2O_2$ (624.34): C, 42.32; H, 2.42; N, 4.49. Found: C, 42.72; H, 2.03; N, 4.24.

***N,N′*-Bis(4-methoxyphenyl)pentafluorobenzimidamide (5):** Colorless crystals (88%); mp 65−66 °C; IR ($CHCl_3$) 3460, 3400, 3068, 2844, 1640, 1198 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.73 (s, 6 H), 6.60−7.05 (br, 8 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 0.5−2.0 (m, 2 F), 9.5−11.0 (br, 1 F), 23.5−25.1 (br, 2 F); GCMS (m/z) 422 (M^+, 20), 300 ($M^+ - NHC_6H_4OCH_3$, 100). Anal. Calcd for $C_{21}H_{15}F_5N_2O_2$ (422.35): C, 59.72; H, 3.58; N, 6.63. Found: C, 59.78; H, 3.38; N, 6.78.

Method B (7). A mixture of ethyl orthoacetate (**6**) (10 mmol) and *p*-anisidine (50 mmol) containing TsOH (1 mmol) was stirred at 140 °C for 3 h. When most of the ethanol was distilled out, the reaction mixture was poured into ice water (20 mL) and extracted with AcOEt (20 mL × 3). The extracts were then washed with brine (20 mL) and were dried over anhydrous $MgSO_4$. The condensed residue was chromatographed on silica gel (50% AcOEt−hexane).

***N,N′*-Bis(4-methoxyphenyl)ethanimidamide (7):** Colorless crystals (72%); mp 102−103 °C; IR ($CHCl_3$) 3472, 3400, 3056, 2844, 1644 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.86−2.08 (br, 3 H), 3.79 (s, 6 H), 6.1−6.2 (br, 1 H), 6.8−7.2 (br, 8 H); GCMS (m/z) 270 (M^+, 14), 148 ($M^+ - NHC_6H_4OCH_3$, 100). Anal. Calcd for $C_{16}H_{18}N_2O_2$ (270.33); C, 71.09; H, 6.71; N, 10.36. Found: C, 70.82; H, 6.94; N, 10.32.

Method C (9). A mixture of *N*-(4-methoxyphenyl)benzamide (**8**) (10 mmol) and PCl_5 (12 mol) was stirred at 140 °C for 5 h. When the generation of HCl stopped, pyridine (12 mmol) and *p*-anisidine (15 mmol) were slowly added and the mixture was stirred at 80 °C for 1 h. Distillation gave **9**.

***N,N′*-Bis(4-methoxyphenyl)benzimidamide (9):** Colorless crystals (61%); mp 115−116 °C; IR ($CHCl_3$) 3460, 3396, 2962, 2844, 1626 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.74 (s, 6 H), 6.6−7.9 (br, 13 H); GCMS (m/z) 332 (M^+, 14), 210 ($M^+ - NHC_6H_4OCH_3$, 100). Anal. Calcd for $C_{21}H_{20}N_2O_2$ (332.10): C, 75.88; H, 6.06; N, 8.43. Found: C, 76.01; H, 6.04; N, 8.38.

CAN Oxidation of 2. A mixture of **2** (0.5 mmol) and CAN (1.2 mmol) was dissolved in MeCN (5 mL) and stirred at rt. After 5 min the solvent was evaporated under reduced pressure, and the residue was extracted with AcOEt (5 mL × 5) and washed with water (2 mL) and with brine (2 mL). The organic layer was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel (10% AcOEt−hexane). Recrystallization of the major portion from benzene−hexane, afforded benzimidazole **10**[10] in 86% yield.

Oxidation of 2 with *t*-BuOCl or NCS. The imidamide **2** (0.5 mmol) was dissolved in DMF (3 mL) and stirred at 70 °C. *t*-BuOCl (1.2 mmol) [or a DMF (2 mL) solution of NCS (1.2 mmol)] was added dropwise to the solution by syringe. After 2 h the solvent was evaporated under reduced pressure, and the residue was extracted with AcOEt (5 mL × 5). The extracts were washed with aqueous $Na_2S_2O_3$ (2 mL), then with water (2 mL), and finally with brine (2 mL). The organic layer was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel (5% AcOEt−hexane) to give **13** in 82% or 93% yield for *t*-BuOCl or NCS, respectively.

***N*-(2-Chloro-4-methoxyphenyl)-*N′*-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (13):** Colorless oil (93%); bp 270 °C (0.4 Torr); IR (neat) 3440, 3012, 2844, 1676, 1158 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.74 (s, 3 H), 3.76 (s, 3 H), 6.55−7.30 (br, 7 H); ^{19}F NMR (188 MHz, $CDCl_3$) δ 90.0−98.0 (br, 3 F); GCMS (m/z) 360 (M^+, 15), 358 (M^+, 40), 323 (M^+ − Cl, 100). Anal. Calcd for $C_{16}H_{14}ClF_3N_2O_2$ (358.75): C, 53.57; H, 3.93; N, 7.81. Found: C, 53.23; H, 3.72; N, 7.91.

Oxidation of 2 with Lead(IV) Acetate. Into **2** (0.5 mmol) dissolved in CH_2Cl_2 (3 mL) was added dropwise by syringe, a solution of lead(IV) acetate (1.2 mmol) in CH_2Cl_2 (2 mL). After 2 h the solvent was evaporated under reduced pressure, and the residue was extracted with AcOEt (5 mL × 5) and washed with aqueous Na_2CO_3 (2 mL) and with brine (2 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (5% AcOEt−hexane), affording **10**,[10] **11**,[10] and **12** in 20%, 33%, and 13% yields, respectively.

***N*¹-(4,4-Dimethoxy-2,5-cyclohexadien-1-ylidene)-*N*²-(4-methoxyphenyl)-2,2,2-trifluoroethanimidamide (12):** Orange oil (13 %), bp 250−251 °C (2.5 Torr); IR (neat) 2952, 2840, 1648, 1150 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.18 (s, 6 H), 3.77 (s, 3 H), 6.15−6.60 (br, 4 H), 6.77 (d, 2 H, J = 9.0 Hz), 6.97 (d, 2 H, J = 9.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 90.3 (s, 3 F); GCMS (m/z) 354 (M^+, 80) 339 ($M^+ - CH_3$, 60) 323 ($M^+ - OCH_3$, 75) 202 ($M^+ - NHC_6H_4OCH_3$, 100). Anal. Calcd for $C_{17}H_{17}F_3N_2O_3$ (354.33): C, 57.63; H, 4.83; N, 7.91. Found: C, 57.62; H, 5.04; N, 8.26.

Cyclic Voltammetry of Imidamides. Imidamide (0.05 mmol) and $NaClO_4$ (1.5 mmol) was dissolved in MeCN (15 mL) and N_2 was bubbled for 30 min. After the bubbling, the cyclic voltammogram was measured at a scan rate of 0.2 V s^{-1}; Pt wire electrodes and Ag/AgCl electrode as a reference electrode were employed.

Electrosynthesis of Benzimidazoles. Imidamide (4 mmol) was dissolved in MeCN (40 mL) containing $NaClO_4$ (1 mmol) and electrooxidized at 60 °C in an undivided beaker type cell (20 cm tall and 3 cm in diameter) with the use of a glassy carbon (Toyo carbon FE-4, 4.0 × 1.5 × 0.3 cm) anode and a platinum foil (2.0 × 1.5 cm) cathode under a constant current of 5 mA/cm^2 for 2.1 F/mol. After the electrolysis, the solvent was evaporated under reduced pressure, and the residue was extracted with AcOEt (20 mL × 3) and washed with water (20 mL) and with brine (20 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated, and chromatographed on silica gel (10 % AcOEt−hexane).

1-(4-Methoxyphenyl)-2-(1,1,2,2,3,3,3-heptafluoropropyl)-6-methoxybenzimidazole (16): Colorless crystals (95%); mp 107−108 °C; IR ($CHCl_3$) 3060, 2844, 1168 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 3 H), 3.92 (s, 3 H), 6.43 (d, 1 H, J = 2.5 Hz), 7.03 (dd, 1 H, J = 2.5 Hz, J = 9.0 Hz), 7.06 (d, 2 H, J = 9.0 Hz), 7.30 (d, 2 H, J = 9.0 Hz), 7.81 (d, 1 H, J = 9.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 37.1 (s, 2 F), 55.5 (q, 2 F, J = 9.9 Hz), 81.8 (t, 3 F, J = 9.9 Hz); GCMS (m/z) 422 (M^+, 100), 303 (80). Anal. Calcd for $C_{18}H_{13}F_7N_2O_2$ (422.30): C, 51.20; H, 3.10; N, 6.63. Found: C, 51.35; H, 3.02; N, 6.34.

1-(4-Methoxyphenyl)-2-(1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoroheptyl)-6-methoxybenzimidazole (17): Colorless crystals (95%); mp 76−77 °C; IR ($CHCl_3$) 2992, 2844, 1152 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 3.92 (s, 3 H), 6.42 (d, 1 H, J = 2.3 Hz), 7.02 (dd, 1 H, J = 2.3 Hz, J = 8.8 Hz), 7.06 (d, 2 H, J = 8.9 Hz), 7.30 (d, 2 H, J = 8.9 Hz), 7.81 (d, 1 H, J = 8.8 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 35.7 (s, 2 F), 39.2 (s, 2 F), 39.9 (s, 2 F), 40.6 (s, 2 F), 41.6 (s, 2 F), 56.2 (q, 2 F, J = 9.7 Hz), 81.0 (t, 3 F, J = 9.7 Hz); GCMS (m/z) 303 ($M^+ - C_6F_{13}$, 100). Anal. Calcd for $C_{22}H_{13}F_{15}N_2O_2$ (622.32): C, 42.40; H, 2.11; N, 4.50. Found: C, 42.73; H, 2.10; N, 4.35.

1-(4-Methoxyphenyl)-2-(pentafluorophenyl)-6-methoxybenzimidazole (18): Colorless crystals (77%); mp 132−133 °C; IR ($CHCl_3$) 2972, 2844, 1158 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 3 H), 3.84 (s, 3 H), 6.67 (d, 1 H, J = 2.2 Hz), 6.96 (d, 2 H, J = 8.8 Hz), 6.99 (dd, 1 H, J = 2.2 Hz, J = 8.8 Hz), 7.19 (d, 2 H, J = 8.8 Hz), 7.76 (d, 1 H, J = 8.8 Hz); ^{19}F NMR (188 MHz, $CDCl_3$) δ 0.81−1.08 (m, 2 F), 11.5 (t, 1 F, J = 21 Hz), 24.1−24.2 (m, 2 F); GCMS (m/z) 420 (M^+, 100), 405 (M^+ − Me, 100), 300 ($M^+ - NHC_6H_4OMe$, 30). Anal. Calcd for $C_{21}H_{13}F_5N_2O_2$ (420.34): C, 60.01; H, 3.12; N, 6.66. Found: C, 60.21; H, 3.04; N, 6.58.

1-(4-Methoxyphenyl)-2-methyl-6-methoxybenzimidazole (19): Colorless crystals (92%); mp 75−79 °C; IR ($CHCl_3$) 3048, 2964, 2844 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 3 H), 3.70 (s, 3 H), 3.85 (s, 3 H), 6.51 (d, 1 H, J = 2.4 Hz), 6.83 (dd, 1 H, J = 2.4 Hz, J = 8.7 Hz), 7.02 (d, 2 H, J = 8.9 Hz), 7.22 (d, 2 H, J = 8.9 Hz), 7.55 (d, 1 H, J = 8.7 Hz); GCMS (m/z) 268 (M^+, 100), 253 ($M^+ - CH_3$, 98). Anal. Calcd for $C_{16}H_{16}N_2O_2$ (268.32): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.49; H, 5.92; N, 10.70.

1-(4-Methoxyphenyl)-2-phenyl-6-methoxybenzimidazole (20): Colorless crystals (60%); mp 151−152 °C; IR ($CHCl_3$) 3048, 2968, 2844 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 3 H), 3.87 (s, 3 H), 6.64 (d, 1 H, $J = 2.2$ Hz), 6.95 (dd, 1 H, $J = 2.2$ Hz, $J = 8.8$ Hz), 7.00 (d, 2 H, $J = 8.8$ Hz), 7.22 (d, 2 H, $J = 8.8$ Hz), 7.24−7.32 (m, 3 H), 7.51−7.58 (m, 2 H), 7.74 (d, 1 H, $J_2 = 8.8$ Hz); GCMS (m/z) 330 (M^+, 100) 315 ($M^+ - CH_3$, 70). Anal. Calcd for $C_{21}H_{18}N_2O_2$ (330.39): C, 76.34; H, 5.49; N, 8.48. Found: C, 76.06; H, 5.38; N, 8.17.

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