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# Halophilic reaction of *N*-sodium-substituted azoles with polyhaloperfluoroethanes containing different vicinal halogen atoms

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ABSTRACT

The reactions of *N*-sodium-substituted azoles with 2-chloro-1-iodo- tetrafluoroethane, 1,2-dichloro-1-iodotrifluoroethane, and 1,2-dibromo-1-chlorotrifluoroethane have been investigated. As shown for iodo derivatives, it is the chlorine rather than the iodine atom that is substituted by the heterocyclic residue, which is consistent with the halophilic reaction mechanism. In the case of indole, the products of simultaneous *N*-iodopolyfluoroalkylation and ring-iodination have been isolated. The reaction with 1,2-dibromo-1-chlorotrifluoroetane yields *N*-(2-bromo-2-chlorotrifluoroethyl)azoles accompanied by minor amounts of *N*-(2,2-dibromotrifluoroethyl) derivatives as by-products.



## 1. Introduction

The halophilic mechanism was proposed in 1973 to explain *trans*-stilbene formation in the reaction of 2-chloro-1-iododiphenylethane with various nucleophiles [1]. This mechanism postulates that nucleophilic agents, when reacted with a 1,2-dihalodiarylethane, directly attack the halogen atom rather than the halogen-bound carbon atom (contrary to what is observed in a normal $S_N2$ process), followed by elimination of the halogenide anion from the α-position and production of the olefin (see Scheme 1).

Such a reaction pathway accounts for increased reactivity towards nucleophiles of halogen atoms in 1,2-dichloro [2] and 1,2-dibromo [3] perfluoroalkanes ($CF_2ClCFCl_2$, $CF_2BrCF_2Br$, $CF_2BrCFBrCF_3$, etc.), as compared to their 1,1-dihalo and, especially, monohalo analogues. It is evident that the reaction of the vicinal dihalo compounds with nucleophiles, e.g., phenolate, thiophenolate, or dialkylamine anions, which proceeds by the above-discussed mechanism intermediately yields polyfluoroolefins as well as *O*-Hal, *S*-Hal or *N*-Hal species. Due to their high electrophilic reactivity, polyfluoroolefins *in situ* add to nucleophilic agents to form a combined anion which attacks the halogen atom in the starting molecule and in *O*-Hal, *S*-Hal, or *N*-Hal intermediates. The halophilic process is thus responsible for the formation of 2,2-dichlorotrifluoroethylthio derivatives as the only products of the reaction between $CF_2ClCFCl_2$ and thiophenolates [2], the formation of 2-bromo-2-chlorotrifluoroethoxy derivatives in the reaction between 1,2-dibromo-1-chlorotrifluoroethane and phenolates [4], and *C*-halogenation which occurs on using *C*-nucleophiles [5]. In all cases, the dihalopolyfluoroalkanes under study contained the same vicinal halogen atoms, so that competition between the attacked and leaving groups was ruled out. On the other hand, the reaction of bromochlorodifluoromethane with thiophenolates can be rationalized only in terms of the halophilic mechanism, as it leads to bromodifluoromethylthio derivatives thus suggesting that it is the chlorine and not the bromine atom which is substituted in spite of the much weaker C–Br than C–Cl bond strength [6].

Previously we investigated the reactions of various *N*-sodium-substituted azoles with $CF_2ClCFCl_2$ [7] and $CF_2BrCF_2Br$ [8] as well as the chemical behavior of the resulting *N*-(polyhaloperfluoroethyl)azoles and their derivatives [9]. In this work, we address the reactions of *N*-sodium derivatives of biologically and pharmaceutically relevant azoles (imidazole **1a**, benzimidazole **1b**, pyrazole **1c**, 3,5-dimethylpyrazole **1d**, and indole **1e**), with polyhalo tetra- and trifluoroethanes containing different vicinal halogen atoms (2-chloro-1-iodotetrafluoroethane, 1,2-dichloro-1-iodotrifluoroethane, and 1,2-dibromo-1-chlorotrifluoroethane). Of special interest is the reactivity of compounds bearing iodine and chlorine atoms at positions 1 and 2, with largely different C–Cl and C–I bond strengths.

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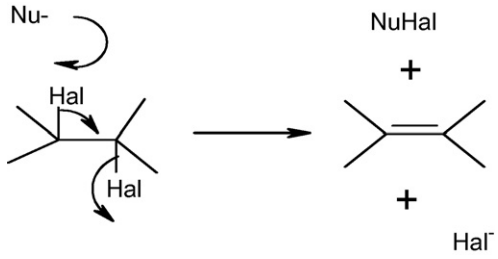



**Scheme 1.**

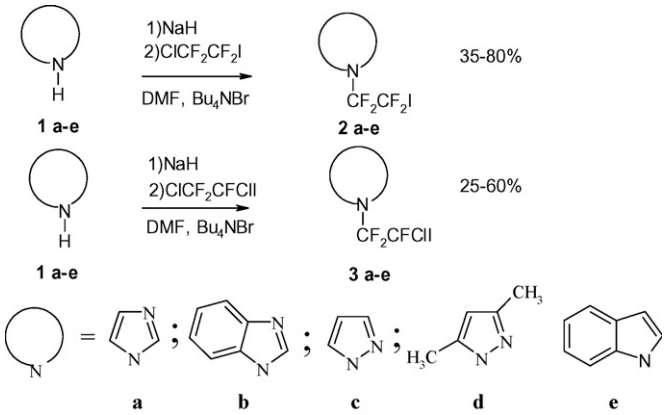
## 2. Results and discussion

*N*-Sodium-substituted azoles were reacted with (2-chloro-1-iodotetrafluoroethane and 1,2-dichloro-1-iodotrifluoroethane in DMF using tetrabutylammonium bromide as a catalyst. The reaction conditions were much the same as in the analogous reaction with $CF_2ClCFCl_2$ described by us before (heating the reaction mixture at 50–90 °C for 1–2 h) [7]. At the same time, the reaction proceeded much more vigorously in the present study (due to the presence of an iodine atom in the polyhaloperfluoroethanes concerned): it was complete after 10–15 min and required cooling to −10 to −15 °C because of the high exothermicity. In all cases, solely the chlorine atom was substituted by the heterocyclic residue, so that *N*-(2-iodotetrafluoroethyl) (**2a–e**) and *N*-(2-chloro-2-iodotrifluoroethyl) azole derivatives (**3a–e**) were obtained, without any evidence of iodine substitution (see Scheme 2). The reaction with indole also provided ring-iodinated products.

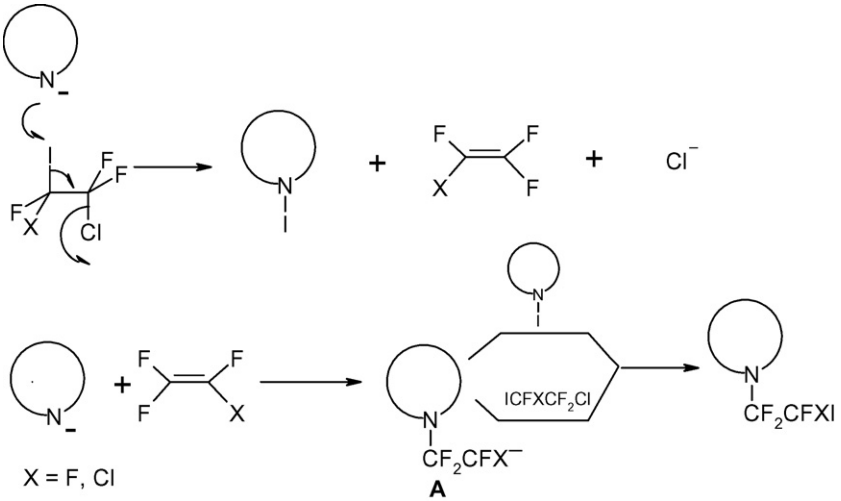
It should be noted that the iodine atom in 2-chloro-1-iodotetrafluoroethane can be substituted by treatment with phenolates to produce the corresponding 2-chlorotetrafluoroethyl derivatives, provided the reaction is performed in the presence of KF at 120 °C in DMSO [10]. Likewise, iodine substitution occurs via a radical process with dimethyl disulfide under UV irradiation [11].

In our case, another reaction pathway is due to the halophilic mechanism. The negatively charged heterocyclic nitrogen atom attacks the iodine atom (more reactive than the adjacent carbon atom) to form the N–I intermediate and polyfluoroolefin, with the chlorine atom eliminated as $Cl^-$. The polyfluoroolefin adds to another heterocyclic anion to produce the *N*-hetaryl(chloro)perfluoroethyl anion (**A**) which in turn attacks the iodine atom in the N–I intermediate or in the starting polyhaloperfluoroethane thus affording the azole with the 2-iodo-substituted (chloro)perfluoroethyl residue at the nitrogen atom (see Scheme 3). As seen, the reaction scenario starts with an abstraction of the iodine atom and ends with its return to the reaction product. Many compounds containing an N–I bond, as for instance, *N*-iodosuccinimide [12], are known to be efficient iodinating agents. This property probably plays a crucial role in the course of the reaction under study.

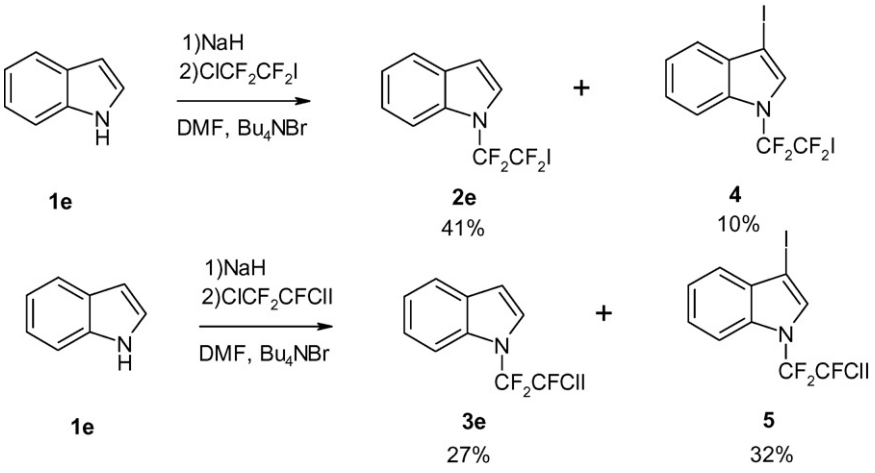
In the case of benzimidazole, pyrazole, and 3,5-dimethylpyrazole (**1b–d**) which are not very prone to ring halogenation, products **2**




**Scheme 2.**




**Scheme 3.**




**Scheme 4.**

and **3** are obtained in high yields (60–80%). Imidazole **1a** reacts to give target compounds **2a** and **3a** in yields no higher than 35%, and a large amount of by-products, which may be attributable to the high lability of *N*-iodoimidazole rearranging to *C*-iodinated derivatives. The reactions with indole **1e** also resulted in the product mixtures which were separated by column chromatography to give, in addition to *N*-(iodo(chloro)perfluoroethyl) indoles **2e** and **3e**, their ring-iodinated derivatives **4** and **5** (see Scheme 4). In the latter case, compound **5** obtained in 32% yield represented the main product (cf. to 27% yield of compound **3e**).

The formation of disubstituted products **4** and **5** is accounted for by the well-known fact that electrophiles attack both the N-1 and C-3 atoms of the indole molecule. Thus, indolyl sodium reacts with iodine-containing polyhaloperfluoroethanes to intermediately produce 1- and 3-iodoindoles, the latter undergoing further *N*-iodination. The terminal iodine atom in the polyhaloperfluoroethyl moiety of the compounds obtained makes them promising precursors in various fluoroorganic syntheses.

On studying the reactions of *N*-sodium-substituted azoles with 1,2-dibromo-1-chlorotrifluoroethane, we have prepared their hitherto unknown *N*-(2-bromo-2-chlorotrifluoroethyl) derivatives **6a–c**. The reaction conditions were similar to those used with iodopolyfluoroethanes, with the only difference that it was possible to run the reactions at room temperature, since much less heat was released. The desired products were obtained in high yields (80–90%) after preliminary distillation. However, they contained up to 10% of by-products which showed the $^{19}$F NMR triplet at −76 ppm and the doublet at −92 ppm thus suggesting the presence of the $CF_2CFX_2$ moiety. The elemental analysis of the crude products indicated a 2–3% higher Cl + Br content than calculated. Compounds **6a** and **6b** appearing as low-melting solids were purified by recrystallization from hexane. Liquid compound **6c** was purified by fraction distillation in vacuo. The higher-boiling residue as well as the concentrated mother liquor remaining after crystallization of **6a** and **6b** were analyzed by liquid chromatography/mass spectrometry to find that minor amounts of *N*-(2,2-dibromotrifluoroethyl)azoles **7a–c** were present among the reaction products in all cases (see Scheme 5). As previously revealed [4], the reaction of phenolates with 1,2-dibromo-1-chloroethane yields similar by-products, (2,2-dibromotrifluoroethoxy)benzenes.

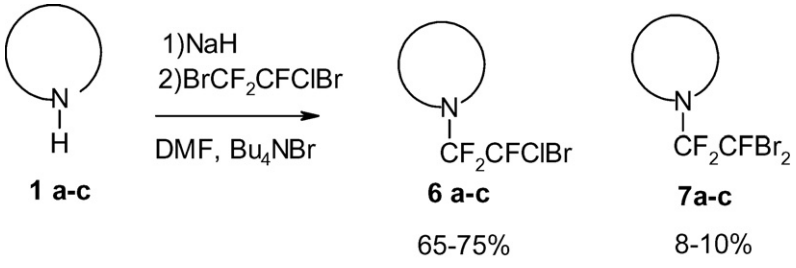
Formation of compounds **7** in parallel to **6** occurs because the initial halophilic abstraction of the bromine atom from dibromochlorotrifluoroethane can be followed by the elimination of the second bromine atom to finally yield the main products **6** or (to a minor extent, in view of a larger C–Cl bond energy) of the chlorine atom to produce by-products **7**. In the latter case, intermediately formed bromotrifluoroethylene adds to the *N*-nucleophile and the resulting anion **B** is further converted into the corresponding *N*-(2,2-dibromotrifluoroethyl) derivatives (see Scheme 6).

In conclusion, we have investigated the reactions of *N*-sodium-substituted azoles with polyhaloperfluoroethanes containing different vicinal halogen atoms and established that the main reaction pathway is governed by the halophilic mechanism. A synthetic method has been developed to obtain *N*-(polyhaloperfluoroethyl)azoles with a terminal iodine or bromine atom in the fluorinated moiety.

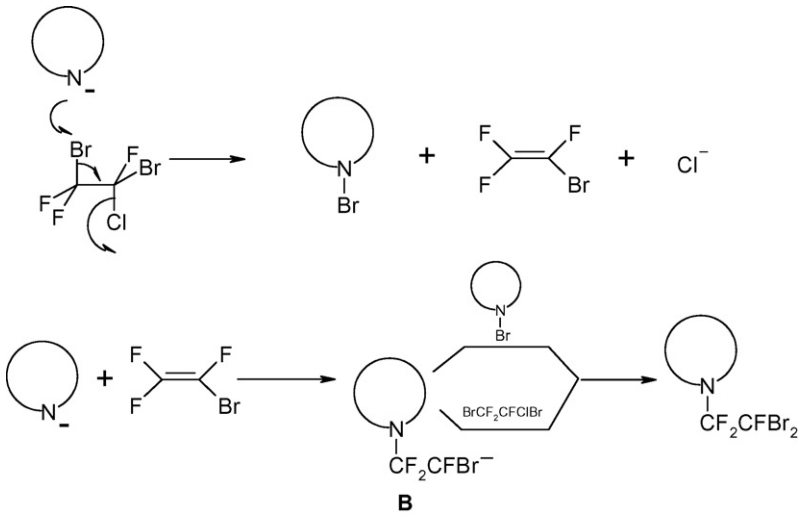
## 3. Experimental

### 3.1. General

Boiling and melting points are uncorrected. $^1$H NMR spectra were recorded in $CDCl_3$ on a Varian VXR-300 spectrometer (300 MHz) using TMS as an internal standard. $^{19}$F NMR spectra were recorded in




**Scheme 5.**




**Scheme 6.**

$CDCl_3$ on a Varian VXR-200 spectrometer (188 MHz) using $CCl_3F$ as an internal standard. LC/MC (APCI MS) spectra were recorded with a chromatography/mass spectrometric system based on an Agilent 1100/DAD/MSV VL G1965a instrument and a HEWLETT-PACKARD HP GC/MS 5890/5972 instrument (EI 70 eV), by GC inlet. All reactions were carried out under argon. DMF was dried over BaO and distilled off.

### 3.2. General procedure for preparation of N-(polyhaloperfluoroethyl)azoles (2a–e, 3a–e, 4, 5, 6a–c)

To a suspension of sodium hydride (0.024 mol, 20% excess) in anhydrous DMF (15 mL) in an inert dry atmosphere, a solution of the corresponding heterocycle **1a–e** (0.02 mol) in anhydrous DMF (15 mL) was added dropwise at 0 °C. After stirring for 40 min, tetrabutylammoniun bromide (0.05 g) was added and the reaction mixture was cooled to −15 °C under an argon stream. After stirring for 5 min at this temperature, the corresponding polyhalo tetra- or trifluoroethane (0.034 mol, 70% excess) was added in one portion. In the cases of 2-chloro-1-iodotetrafluoroethane and 1,2-dichloro-1-iodotrifluoroethane, the reaction mixture self-heated to +45 to 50 °C. The reaction with 1,2-dibromo-1-chlorotrifluoroethane was less exothermic, so that a rapid self-heating to room temperature was observed. After stirring for 15 min, the reaction mixture was poured into water (100 mL) and the oil (or the mixture of crystals and oil) was extracted with hexane (3 mL × 50 mL) and washed with water (3 mL × 100 mL). The extract was dried over $MgSO_4$. After removal of the solvent, products **2a,c,d**; **3a,c,d**; and **6a–c** were distilled in vacuo. Compounds **2b** and **3b** were crystallized from hexane, and the mixture of resulting indole derivatives (**2e, 3e, 4**, and **5**) was separated by column chromatography on $SiO_2$ (Kieselgel MN-60).

#### 3.2.1. 1-(2-iodo-1,1,2,2-tetrafluoroethyl)-1H-imidazole (2a)

Yield 32%; bp 76–78 °C (15 Torr); mp 53–54 °C (hexane). $^{19}$F NMR $\delta$ −93.18 (s, 2F), −63.51 (s, 2F). $^1$H NMR $\delta$ 7.15 (s, 1H), 7.17 (s, 1H), 7.80 (s, 1H). Anal. Calcd. for $C_5H_3F_4IN_2$: I, 43.17. Found: I, 43.30.

#### 3.2.2. 1-(2-iodo-1,1,2,2-tetrafluoroethyl)-1H-benzimidazole (2b)

Yield 71%; mp 78–79 °C (hexane). $^{19}$ F NMR $\delta$ −93.14 (s, 2F). −62.52 (s, 2F); $^1$H NMR $\delta$ 7.35 (m, 2H), 7.53 (m, 1H), 7.82 (m, 1H), 8.08 (s, 1H). Anal. Calcd. for $C_9H_5F_4IN_2$: Anal. Calcd. for $C_9H_5F_4IN_2$: I, 36.89. Found: I, 37.18.

#### 3.2.3. 1-(2-iodo-1,1,2,2-tetrafluoroethyl)-1H-pyrazole (2c)

Yield 70%; bp 77–78 °C (15 Torr). $^{19}$F NMR −95.14 (s, 2F), −61.71 (s, 2F). $^1$H NMR δ 6.43 (dd, 1H, $J$ = 2 Hz), 7.71 (d, 1H, $J$ = 2 Hz), 7.77 (d, 1H, $J$ = 2 Hz). Anal. Calcd. for $C_5H_3F_4IN_2$: I, 43.17. Found: I, 43.41.

#### 3.2.4. 1-(2-iodo-1,1,2,2-tetrafluoroethyl)-3,5-dimethyl-1H-pyrazole (2d)

Yield 76%; bp 37–38 °C (0.5 Torr). $^{19}$F NMR −94.11 (s, 2F). −61.98 (s, 2F). $^1$H NMR δ 2.21 (s, 3H), 2.35 (s, 3H), 5.94 (s, 1H). Anal. Calcd. for $C_7H_7F_4IN_2$: I, 39.41; Found: I, 39.40.

#### 3.2.5. 1-(2-iodo-1,1,2,2-tetrafluoroethyl)-1H-indole (2e)

Yield 41%; bp 77–79 °C (0.5 Torr); $R_f$ = 0.5 (hexane). $^{19}$F NMR $\delta$ −92.66 (s, 2F). −61.74 (s, 2F). $^1$H NMR $\delta$ 6.90 (d, $J$ = 3.5 Hz, 1H), 7.40–7.55 (m, 3H), 7.78–7.85 (m, 2H). Anal. Calcd. for $C_{10}H_6F_4IN$: I, 36.99; Found: I, 37.38.

#### 3.2.6. 1-(2-chloro-2-iodo-1,1,2-trifluoroethyl)-1H-imidazole (3a)

Yield 29%; bp 48–50 °C (0.5 Torr); mp 54–55 °C (hexane). $^{19}$F NMR $\delta$ −91.57 (dd, 1F, $^2J$ = 209 Hz, $^3J$ = 14 Hz), −88.55 (dd, 1F, $^2J$ = 209 Hz, $^3J$ = 14 Hz), −77.95 (t, 1F, $J$ = 14 Hz). $^1$H NMR $\delta$ 7.15 (s, 1H), 7.17 (s, 1H), 7.83 (s, 1H). Anal. Calcd. for $C_5H_3ClF_3IN_2$: I, 40.88; Cl, 11.42; Found: I, 40.92; Cl, 11.58.

#### 3.2.7. 1-(2-chloro-2-iodo-1,1,2-trifluoroethyl)-1H-benzimidazole (3b)

Yield 73%; mp 67–69 °C (hexane). $^{19}$F NMR $\delta$ −90.72 (dd, 1F, $^2J$ = 219 Hz, $^3J$ = 11 Hz), −86.58 (dd, 1F, $^2J$ = 219 Hz, $^3J$ = 11Hz), −75.71 (t, 1F, $J$ = 14 Hz). $^1$H NMR $\delta$ 7.35 (m, 2H), 7.57 (m, 1H), 7.82 (m, 1H), 8.12 (s, 1H). Anal. Calcd. for $C_9H_5ClF_3N_2$: I, 35.20; Cl, 9.83; Found: I, 35.45; Cl, 9.61.

#### 3.2.8. 1-(2-chloro-2-iodo-1,1,2-trifluoroethyl)-1H-pyrazole (3c)

Yield 66%; bp 85–86 °C (15 Torr). $^{19}$F NMR $\delta$ −92.82 (dd, 1F, $^2J$ = 207 Hz, $^3J$ = 13 Hz), −90.55 (dd, 1F, $^2J$ = 207 Hz, $^3J$ = 13 Hz), −75.18 (t, 1F, $J$ = 13 Hz). $^1$H NMR $\delta$ 6.47 (dd, $J$ = 2 Hz, 1H), 7.76 (d, $J$ = 2 Hz, 1H), 7.83 (d, $J$ = 2 Hz, 1H). Anal. Calcd. for $C_5H_3ClF_3IN_2$: I, 40.88; Cl, 11.42; Found: I, 40.79; Cl, 11.27.

#### 3.2.9. 1-(2-chloro-2-iodo-1,1,2-trifluoroethyl)-3,5-dimethyl-1H-pyrazole (3d)

Yield 52%; bp 95–98 °C (15 Torr). $^{19}$F NMR $\delta$ −92.77 (dd, 1F, $^2J$ = 213 Hz, $^3J$ = 15 Hz), −89.72 (dd, 1F, $^2J$ = 213 Hz, $^3J$ = 15Hz),

−75.33 (t, 1F, $J$ = 15 Hz). $^1$H NMR $\delta$ 2.21 (s, 3H), 2.35 (s, 3H), 5.94 (s, 1H). Anal. Calcd. for $C_7H_7ClF_3IN_2$: I, 37.49; Cl, 10.47; Found: I, 37.72; Cl, 10.33.

*3.2.10. 1-(2-chloro-2-iodo-1,1,2-trifluoroethyl)-1H-indole* ***(3e)***

Yield 27%; bp 87–88 °C (0.5 Torr); $R_f$ = 0.4 (hexane). $^{19}$F NMR $\delta$ −92.42 (dd, 1F, $^2J$ = 217 Hz, $^3J$ = 12 Hz), −88.76 (dd, 1F, $^2J$ = 217 Hz, $^3J$ = 12Hz), −75.19 (t, 1F, $J$ = 12 Hz). $^1$H NMR $\delta$ 6.90 (d, $J$ = 3.5 Hz, 1H), 7.40–7.55 (m, 3H), 7.78–7.85 (m, 2H). Anal. Calcd. for $C_{10}H_6ClF_3IN$: I, 35.30; Cl, 9.86; Found: I, 35.72; Cl, 10.13.

*3.2.11. 1-(2-iodo-1,1,2,2-tetrafluoroethyl)-3-iodo-1H-indole (4)*

Yield 10%; bp 110–112 °C (0.5 Torr); $R_f$ = 0.65 (hexane). $^{19}$F NMR $\delta$ −91.87 (s, 2F). −61.15 (s, 2F). $^1$H NMR $\delta$ 7.35–7.55 (m, 3H), 7.69–7.73 (m, 1H), 7.78–7.85 (m, 1H). Anal. Calcd. for $C_{10}H_5F_4I_2N$: I, 54.12; Found: I, 53.49. Mass spectra, $m/z$ (EI): 469 ($M^+$, 10), 342 ($M^+$−I, 12), 166 (30), 116 (100%).

*3.2.12. 1-(2-chloro-2-iodo-1,1,2-trifluoroethyl)-3-iodo-1H-indole* **(5)**

Yield 32%; mp 50–51 °C (hexane); $R_f$ = 0.55 (hexane). $^{19}$F NMR $\delta$ −89.54 (dd, 1F, $^2J$ = 200 Hz, $^3J$ = 12 Hz), −84.56 (dd, 1F, $^2J$ = 200 Hz, $^3J$ = 12 Hz), −73.73 (t, 1F, $J$ = 12 Hz). $^1$H NMR $\delta$, 7.28–7.35 (m, 2H), 7.41 (s, 1H) 7.53–7.56 (m, 1H), 7.63–7.69 (m, 1H). Anal. Calcd. for $C_{10}H_5ClF_3I_2N$: I, 52.29; Cl, 7.30; Found: I, 52.38; Cl, 7.37. Mass spectra, $m/z$ (EI): 485 ($M^+$, 8), 443 ($M^+$−Cl, 10) 358 ($M^+$−I, 15), 166 (35), 116 (100%).

*3.2.13. 1-(2-bromo-2-chloro-1,1,2-trifluoroethyl)-1H-imidazole* ***(6a)***

Yield 65%; bp 75–77 °C (15 Torr); mp 39–40 °C (hexane). $^{19}$F NMR $\delta$ −91.72 (dd, 1F, $^2J$ = 209 Hz, $^3J$ = 14 Hz), −88.55 (dd, 1F, $^2J$ = 209 Hz, $^3J$ = 14 Hz), −74.76 (t, 1F, $J$ = 14 Hz). $^1$H NMR $\delta$ 7.13 (s, 1H), 7.17 (s, 1H), 7.81 (s, 1H). Anal. Calcd. for $C_5H_3BrClF_3N_2$: C, 22.80; H, 1.15; Cl + Br, 43.79; Found: C, 22.29; H, 1.25; Cl + Br, 43.25. Mass spectra, $m/z$ (EI): 263 ($M^+$, 15), 228 ($M^+$−Cl, 10) 183 ($M^+$−Br, 15), 117 (55), 67 (100%).

*3.2.14. 1-(2-bromo-2-chloro-1,1,2-trifluoroethyl)-1H-benzimidazole* ***(6b)***

Yield 67%; bp 78–80 °C (0.2 Torr); mp 31–33 °C (hexane). $^{19}$F NMR $\delta$ −92.12 (dd, 1F, $^2J$ = 211 Hz, $^3J$ = 12 Hz), −89.36 (dd, 1F, $^2J$ = 211 Hz, $^3J$ = 12 Hz), −74.23 (t, 1F, $J$ = 14 Hz). $^1$H NMR $\delta$ 7.35–7.39 (m, 2H), 7.59–7.62 (m, 1H), 7.81–7.84 (m, 1H), 8.13 (s, 1H). Anal. Calcd. for $C_9H_5BrClF_3N_2$: C, 34.48; H, 1.61; Cl + Br, 36.80; Found: C, 34.57; H, 1.58; Cl + Br, 36.40. Mass spectra, $m/z$ (EI): 313 ($M^+$, 12), 288 ($M^+$−Cl, 10) 133 ($M^+$−Br, 12), 167 (53), 117 (100%).

*3.2.15. 1-(2-bromo-2-chloro-1,1,2-trifluoroethyl)-1H-pyrazole* ***(6c)***

Yield 60%; bp 57–60 °C (10 Torr). $^{19}$F NMR $\delta$ −92.75 (dd, 1F, $^2J$ = 218 Hz, $^3J$ = 14 Hz), −89.36 (dd, 1F, $^2J$ = 218 Hz, $^3J$ = 14 Hz), −72.69 (t, 1F, $J$ = 14 Hz). $^1$H NMR $\delta$ 6.47 (dd, $J$ = 2 Hz, 1H), 7.76 (d, $J$ = 2 Hz, 1H), 7.83 (d, $J$ = 2 Hz, 1H). Anal. Calcd. for $C_5H_3BrClF_3N_2$: C, 22.80; H, 1.15; Cl + Br, 43.79; Found: C, 23.21; H, 1.28; Cl + Br, 42.87. Mass spectra, $m/z$ (EI): 263 ($M^+$, 13), 228 ($M^+$−Cl, 9) 183 ($M^+$−Br, 12), 117 (42), 67 (100%).

*3.2.16. 1-(2,2-dibromo-1,1,2-trifluoroethyl)-1H-imidazole* ***(7a)***

$^{19}$F NMR $\delta$ −90.75 (d, 2F, $J$ = 14 Hz), −75.73 (t, 1F, $J$ = 14 Hz). Mass spectra, $m/z$ (EI): 308 ($M^+$, 12), 228 ($M^+$−Br, 10) 148 ($M^+$−2Br, 20), 117 (45), 67 (100%).

*3.2.17. 1-(2,2-dibromo-1,1,2-trifluoroethyl)-1H-benzimidazole (7b)*

$^{19}$F NMR $\delta$ −90.52 (d, 2F, $J$ = 12 Hz), −75.18 (t, 1F, $J$ = 12 Hz). Mass spectra, $m/z$ (EI): 358 ($M^+$, 12), 278 ($M^+$−Br, 10) 198 ($M^+$−2Br, 20), 167 (45), 117 (100%).

*3.2.18. 1-(2,2-dibromo-1,1,2-trifluoroethyl)-1H-pyrazole* ***(7c)***

$^{19}$F NMR $\delta$ −93.17 (d, 2F, $J$ = 12 Hz), −73.43 (t, 1F, $J$ = 12 Hz). Mass spectra, $m/z$ (EI): 308 ($M^+$, 14), 228 ($M^+$−Br, 14) 148 ($M^+$−2Br, 26), 117 (39), 67 (100%).

## References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