Novel Fluorescent 2-(2-Aminofluorophenyl)benzoxazoles: Syntheses and Photophysical Properties

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2-(2-Amino-3,4,5,6-tetrafluorophenyl)benzoxazole (**2**) absorbs in long wavelength band (λ_{abs}^{max} = 346 nm in methanol) and in the normal wavelength band (λ_{abs}^{max} = 285.5 nm), and emits blue fluorescence. The emission intensity is highly affected by the solvent polarity and is large in a polar solvent such as methanol. 2-(2-Pentafluorobenzamido-3,4,5,6- tetrafluorophenyl)benzoxazole (**5**) emits green fluorescence along with the short wavelength emission around 380 nm and their relative intensity depends on the solvent polarity. Green fluorescence is enhanced in nonpolar solvents such as chloroform and toluene, resulting in the considerably large Stokes shift.

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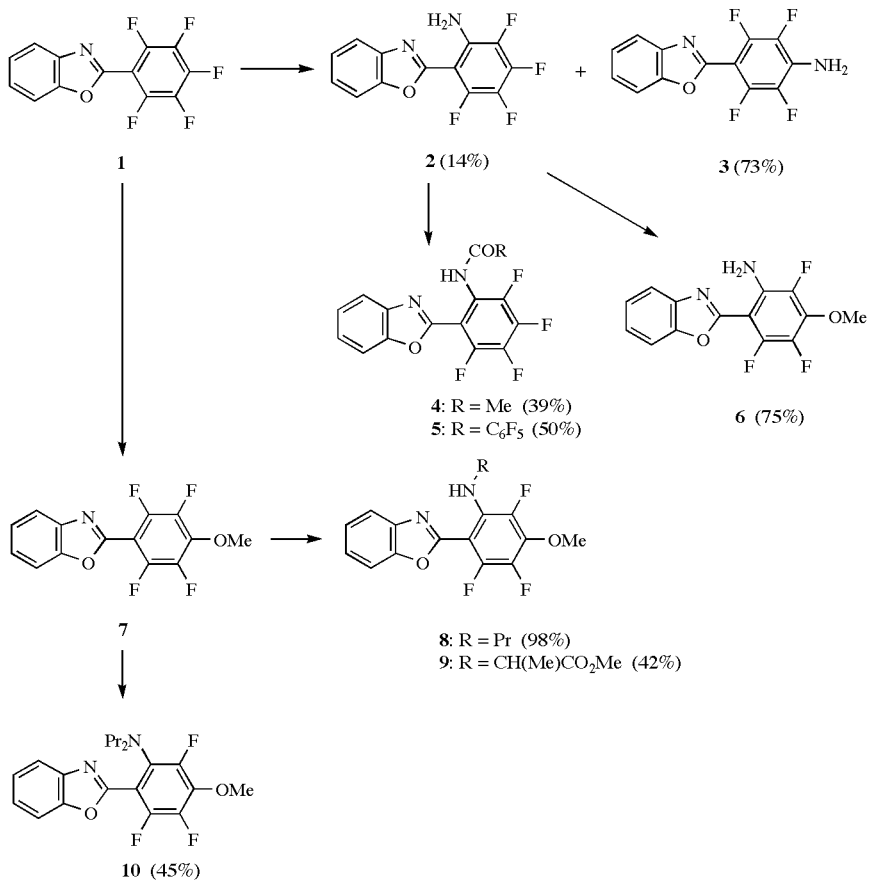
Photophysical properties of 2-(2-hydroxyphenyl)benzoxazole have been widely explored because of its dual fluorescence including the excited state intramolecular proton transfer (ESIPT)[1-7]. The excited state of the intramolecularly hydrogen bonded enol rapidly converts to the excited state of the keto-form, which emits fluorescence around 500 nm. Large Stokes shifted fluorescence through ESIPT process has been highly applied in the fields of lasing dyes, scintillators, and devices[8-10]. Photophysics of 2-aminophenyl analogue, 2-(2-aminophenyl)benzoxazole, has been also investigated and emission (415 nm in methanol) with large fluorescence quantum yield, which is not from ESIPT process, are clarified[11]. ESIPT process in 2-(2-aminophenyl)benzoxazoles is limited to a few cases where strongly electron-withdrawing group such as sufonyl group is attached to the amino group[12,13]. In a continuing research on the reactivity and the function of polyfluorobenzene derivatives[14,15], we have reported photophysical properties of 2-(2-hydroxy-3,4,5,6-tetrafluorophenyl)benzoxazole which emits not only the long wavelength fluorescence around 500 nm in nonpolar solvent *via* ESIPT process but also the intermediate wavelength fluorescence around 440 nm in polar solvent through the excited state of phenolate anion, the easy formation of which is explained by the strongly inductive fluorine atoms[16,17]. In this paper, we focus on fluorinated 2-amino analogues, 2-amino or amide substituted 2-(3,4,5,6-tetrafluorophenyl)benzoxazoles and describe their convenient syntheses and photophysical properties.

Since the preferential *ortho*-attack is reported in the substitution of pentafluoronitrobenzene with ammonia under mild conditions [18,19], the reaction of 2-(2,3,4,5,6-pentafluorophenyl)benzoxazole (**1**) with ammonia was carried out to obtain 2-(2-amino-3,4,5,6-tetrafluorophenyl)benzoxazole (**2**). Yield of the reaction was moderately good, but the product ratio of *ortho*-substituted benzoxazole **2** and *para*-analogue **3** was 13/87. The decrease in *ortho*-selectivity in the reaction of **1** seems to reflect the relatively weak interaction between the ammonium hydrogen atom and oxazole-nitrogen atom in the intermediate Meisenheimer complex, compared to the corresponding interaction in the case of pentafluoronitrobenzene[14]. It is interesting that the amino substituted benzoxazole **2** accepts the second nucleophilic substitution with methoxide at the *para*-position to produce the disubstitued benzoxazole **6**. Electrophilic substitution of **2** with acetic anhydride or pentafluorobenzoyl chloride takes place at the amino group to give the corresponding amide benzoxazole **4** or **5**. The selective introduction of the substituted amino group into the *ortho*-position is attained by the reaction with 2-(2,3,5,6-tetrafluoro-4-methoxyphenyl)benzoxazole (**7**), which is selectively obtained by the reaction of **1** with sodium methoxide in methanol. This strategy was applied to the preparation of **8**, **9**, and **10**.

The absorption spectra of **2** and **3** are essentially the same as those of the corresponding non-fluorinated 2-(2-aminophenyl)benzoxazole; that is, the absorption of **3** is notable at λ_{abs}^{max} = 305 nm in methanol whereas, in the case of **2**, a large red-shifted band at λ_{abs}^{max} = 346 nm in addition to the normal absorption band is observed. It is interesting that the red-shifted band observed in **2** is not present in **4**, *N*-acetyl substiuted **2**, which absorbs in the normal wavelength band. The fluorescent wavelength of **2** and **3** is comparable to the corresponding non-fluorinated (aminophenyl)benzoxazoles. Excitation of **2** in both normal and red-shifted absorption bands (λ_{ex} = 285.5 and 346 nm) gave rise to the same blue emission at 426 nm (Figure 1). It is noted that the excitation spectrum showed a correspondence between the blue emission and the long wavelength absorption. The shorter wavelength emission was observed in **3**, and its fluorescence quantum yield was evaluated to be very small (Φ= 0.002 in methanol)[20], which is in sharp contrast to almost unity of 2-(4-aminophenyl)benzoxazole. The small fluorescence quantum yield of **3** is ascribed to the fluorine atoms substituted at the *ortho*-positions of 2-phenyl group [16]. The fluorescence quantum yield of **2** is almost thirty times that of **3** but still smaller than that of 2-(2-aminophenyl)benzoxazole, the quantum yield of which is reported to be Φ= 0.75

Scheme 1



in methanol (Table 1)[11]. Large solvent-dependence of blue emission of **2** was noticed, although its absorption spectra in various solvents showed no significant change (Figure 2). It is clearly depicted that, in a polar solvent such as mehanol, the emission intensity is large and the wavelength is red-shifted, compared to those in nonpolar solvents such as toluene and ethyl acetate.

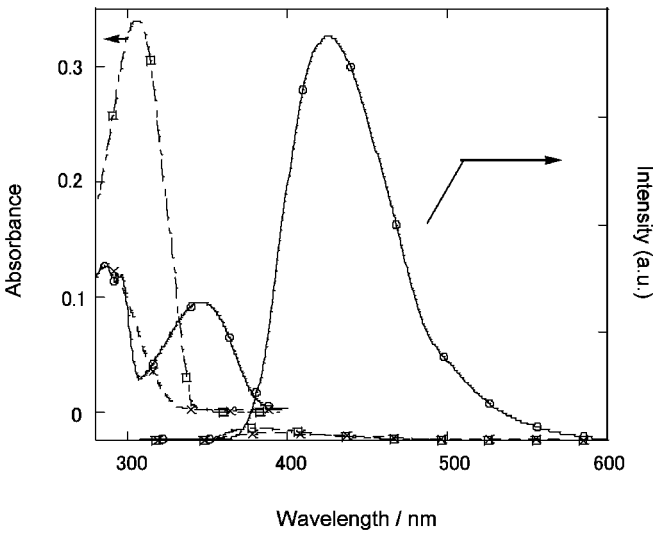


Figure 1. Absorption and Fluorescence Spectra of **2** (○), **3** (□), and **4** (x) in Methanol. [**2**] = [**3**] = [**4**] = $1x10^{-5}$ M, Excitation Wavelength; 285.5 nm (**2**), 305 nm (**3**), and 287 nm (**4**).

Effect of *N*-alkyl group on the absorption and fluorescence spectra was next investigated in the family of 2-(2-amino-3,5,6-trifluoro-4-methoxyphenyl)benzoxazole (**6**). The absorption and fluorescence behavior of **6** is similar to that of **2** except for the relatively large fluorescence quantum yield (Φ= 0.11 in methanol). The introduced propyl or L-alanyl group causes slight red-shifts of the normal and long wavelength absorption bands. However, the introduction of two propyl groups brings about the outstanding change in the absorption and, particularly, the long wavelength absorption band is almost disappeared and is shown as only a weak plateau. The similar red-shifts of the emissions, with the decrease in the fluorescence quantum yields, are caused by the introduction of propyl and L-alanyl groups. More appreciably red-shifted emission, appearing as green light, is observed in dipropylaminobenzoxazole **10** (Figure 3).

Table 1
Fluorescence Quantum Yields of Benzoxazoles [a]

Benzoxazole	**2**	**3**	**4**	**5**	**6**	**8**	**9**	**10**
Quantum Yield [b]	0.062	0.002	0.003 [c] (0.001 [d])	0.031 [c] (0.017 [d])	0.11	0.025	0.002	0.010

[a] Quantum yield was calculated on the basis of 2-phenylbenzoxazole in cyclohexane (φ = 0.78, λ_{ex} = 300 nm), see ref. 20; [b] Measured in methanol, unless otherwise noted; [c] Quantum yield as total emission in chloroform; [d] Quantum yield as total emission in toluene.

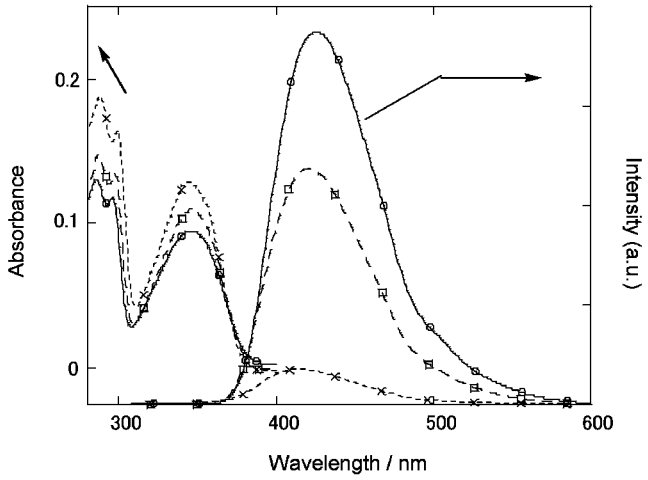


Figure 2. Absorption and Fluorescence Spectra of **2** in Methanol (○), Ethyl Acetate (□), and Toluene (x). [**2**] = 1x10^{-5} M, Excitation Wavelength; 285.5 nm (Methanol), 286 nm (Ethyl Acetate), and 288 nm (Toluene).

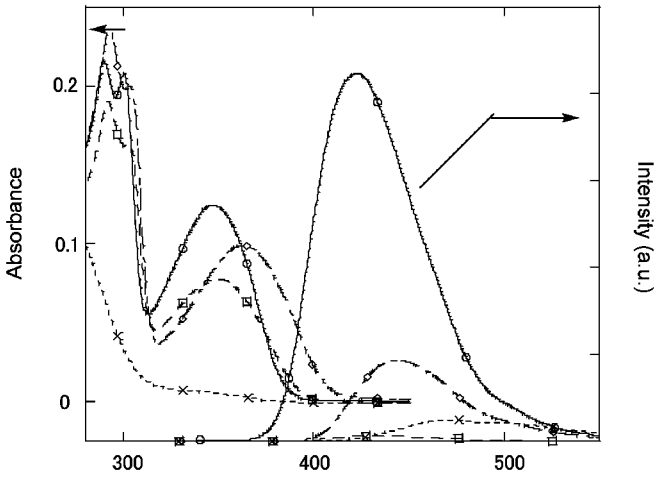


Figure 3. Absorption and Fluorescence Spectra of **6** (○), **8** (◇), **9** (□), and **10** (x) in Methanol. [**6**] = [**8**] = [**9**] = [**10**] = 1x10^{-5} M, Excitation Wavelength; 289.5 nm (**6**), 293.5 nm (**8**), 292.5 nm (**9**), and 248.5 nm (**10**).

The absorption spectrum of pentafluorobenzamidophenylbenzoxazole **5** shows only the normal absorption without a long wavelength one, which is a similar trend to that of acetamidophenylbenzoxazole **4**, and its absorption band is slightly red-shifted as the solvent polarity decreases. The fluorescence spectrum of **5** indicates the short wavelength emission at λ_{em} = 380.5 nm along with the long wavelength one at λ_{em} = 522.5 nm, the intensity of the former being larger than that of the latter in methanol. The relative intensity of the both emissions is found to be highly dependent on the solvent polarity. The long wavelength emission is enhanced and the short one is reversely quenched, with a decrease in the polarity of the solvent (Figure 4). The similar trend of the relative fluorescence intensity is observed in **4** but its change is quite small. The considerably large Stokes shift of **5** in the solvent with small polarity such as chloroform or toluene may come from the ESIPT process, which is accelerated by the strong intramolecular hydrogen-bonding of the amide hydrogen atom of **5** with the oxazole nitrogen atom in less polar solvent [21]. The fluorescence quantum yields as total emission of **4** and **5** are summarized in Table 1, and it is noted that **5** emits green light at the solid state, as observed with 2-(2-hydroxyphenyl)benzoxazoles.

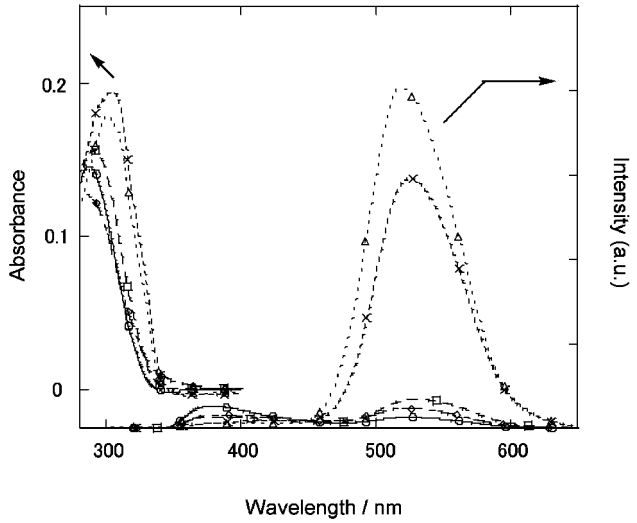


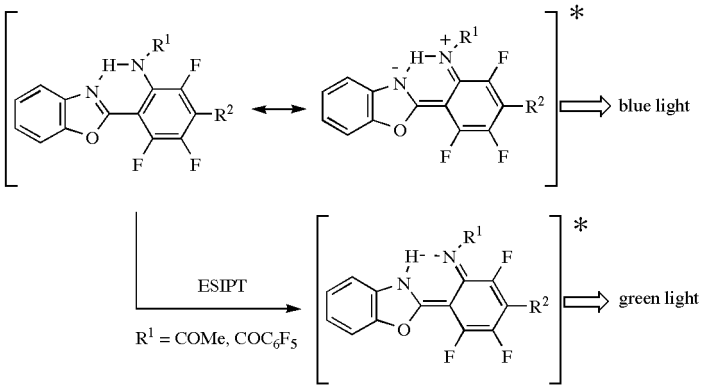
Figure 4. Absorption and Fluorescence Spectra of **5** in Methanol (○), Acetonitrile (◇), Ethyl Acetate (□), Toluene (x), and Chloroform (△). [**5**] = 1x10^{-5} M, Excitation Wavelength; 286.5 nm (Methanol), 290.5 nm (Ethyl Acetate), 283 nm (Acetonitrile), 304.5 nm (Toluene), and 300 nm (Chloroform).

Emission of 2-(2-aminophenyl)benzoxazole is reported to be sensitive to a pH change of surrounds and reveal a large blue-shift with considerable quenching in acidic conditions, which is due to the formation of its monocation [11]. So the effect of pH on the fluorescence spectra along with absorption spectra of **2** was investigated in

methanol/water (9:1) with the constant ionic strength (0.1 *M* NaCl). Observation was performed at pH 1 and pH 13 and, however, **2** showed no change in fluorescence and absorption, which pointed out its high acid and alkali resistance in fluorescence behavior.

In the case of **2**, a large red-shifted band at λ_{abs}^{max} = 346 nm along with the normal absorption band is observed. The similar red-shifted band at λ_{abs}^{max} = 354 nm (methanol) is reported in 2-(2-aminophenyl)benzoxazole and this is suggested by a result of intramolecular hydrogen-bonding formation between the amino hydrogen atom and the benzoxazole nitrogen atom [11]. This hydrogen-bonding is also supported by our results that the *N*-monosubstituted aminobenzoxazoles **8** and **9** have a similarl red-shifted band whereas the *N,N*- disubstituted aminobenzoxazole **10** has no such a band. Based on the consideration of the absence of a red-shifted band in amidobenzoxazoles **4** and **5**, where the strong intramolecular hydrogen-bonding formation is expected, a red-shifted band is limited to aminobenzoxazoles capable of both intramolecular hydrogen-bonding formation and polarization between two nitrogens, as depicted in Scheme 2. Blue emission is thought to come from the polarized excited state. On the other hand, the ESIPT process leading to green emission is caused by the strong intramolecular hydrogen-bonding formation of the amido hydrogen atom of **5**.

Scheme 2



In conclusion, a number of fluorinated (2-amino- and amidophenyl)benzoxazoles are synthesized through the nucleophilic substitutions of the pentafluorophenyl group and their photophysical properties are disclosed. Aminobenzoxazole **2** absorbs in long wavelength band (λ_{abs}^{max} = 346 nm in methanol) and emits blue fluorescence. The red-shifted absorption is ascribed to both the intramolecular hydrogen-bonding of the amino hydrogen atom with the benzoxazole nitrogen atom and the polarization between two nitrogen atoms, its blue emission being due to the polarized excited state. On the other hand, amidobenzoxazole **5** emits green fluorescence along with the short wavelength emission and green fluorescence is enhanced in nonpolar solvents, which supports that green emission comes from the ESIPT process caused by the strong intramolecular hydrogen-bonding formation. The ESIPT process along with the relatively short wavelength absorption of **5** gives rise to the considerably large Stokes shift.

EXPERIMENTAL

The ir spectra were recorded on a JASCO A-100 spectrometer and samples were run as pottasium bromide pellets, unless otherwise noted. The ^{1}H and ^{19}F nmr spectra were measured with a JEOL JNM-LA400 (400 MHz for ^{1}H nmr and 376 MHz for ^{19}F nmr) spectrometer for solutions of $CDCl_3$. The chemical shifts are given in δ/ppm downfield from tetramethylsilane as an internal standard for ^{1}H nmr and from trifluoroacetic acid as an external standard for ^{19}F nmr, respectively; *J* values are given in Hz. The uv-visible and fluorescence spectra were recorded with JASCO Ubest-50 and JASCO FP-777 spectrometers, respectively**.** Acetonitrile, ethyl acetate, cyclohexane, chloroform, and methanol for spectroscopy were the highest quality from KOKUSAN Chemical Co. and were used without further purification. Benzoxazole **1** was prepared by our previously reported method and **7** was obtained by the reaction of **1** with sodium methoxide in methanol [16,17].

Preparation of 2-(2-Amino-3,4,5,6-tetrafluorophenyl)benzoxazole (**2**) and Its 4-Aminophenyl Analogue **3**.

Ammonia gas was bubbled into a solution of **1** (4.0 g, 14.0 mmol) and triethylamine (10.0 g, 0.10 mol) in 50 cm^3 of dioxane at room temperature for 14 days. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine, dried over sodium sulfate, and evaporated to leave a residue. Chromatography on silica gel (hexane-ethyl acetate, 5/1) of the residue produced 0.55 g (14%) of **2** and 2.88 g (73%) of **3**. Each compound was then purified by recrystallization from hexane-ethyl acetate to give white crystals.

Compound **2** has mp 172-173 °C; ir: 3490, 3310 (NH_2), 1660 (C_6F_4), and 1250 cm^{-1} (CF); ^{1}H nmr: δ = 7.76 (1H, m), 7.64 (1H, m), 7.40(2H, m), and 6.50 (2H, br.s); ^{19}F nmr: δ = -61.2 (1F, ddd, *J*=20.3, 10.2, and 6.0 Hz), -74.8 (1F, td, *J*=20.3 and 6.0 Hz), -84.9 (1F, ddd, *J*=20.3, 10.2, and 7.1 Hz), and -92.8 (1F, td, J=20.3 and 7.1 Hz).

Anal. Calcd for $C_{13}H_6F_4N_2O$: C, 55.33; H, 2.14; N, 9.93. Found: C, 55.06; H, 1.91; N, 9.81.

Compound **3** has mp 195-196 °C; ir: 3460, 3400, 3320, 3200 (NH_2), 1670, 1650 (C_6F_4), and 1240 cm^{-1} (CF); ^{1}H nmr: δ = 7.85 (1H, m), 7.62 (1H, m), 7.35 (2H, m), and 4.44 (2H, br.s); ^{19}F nmr: δ = -62.3 (2F, A_2X_2) and -83.8 (2F, A_2X_2).

Anal. Calcd for $C_{13}H_6F_4N_2O$: C, 55.33; H, 2.14; N, 9.93. Found: C, 55.18; H, 1.83; N, 9.78.

Preparation of 2-(2-Acetamido-3,4,5,6-tetrafluorophenyl)benzoxazole (**4**).

A solution of **2** (0.20 g, 0.71 mmol) in 10 cm^3 of acetic anhydride was stirred at 80 °C for 20 hours. The mixture was extracted with ethyl acetate and the extracts were washed with water, 5%- aqueous solution of sodium hydrogencarbonate, and brine. After drying over sodium sulfate, the extracts were evaporated to leave a residue. A mixture of the residue in dioxane (20

cm^3) and 1%- aqueous solution of sodium hydrogencarbonate (25 cm^3) was stirred at room temperature for 2 days. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine. After drying over sodium sulfate, the extracts were evaporated to leave a residue which was chromatographed on silica gel (hexane-ethyl acetate, 5/1) to give **4** (0.09 g, 39%). The compound was purified by recrystallization from hexane-ethyl acetate to give white crystals of **4**: mp 158-159 °C; ir: 3260 (NH), 1680 (C_6F_4 and C=O), and 1250 cm^{-1} (CF); ^{1}H nmr: δ = 9.92 (1H, s), 7.82 (1H, m), 7.70 (1H, m), 7.48 (2H, m), and 2.27 (3H, s); ^{19}F nmr: δ = -58.6 (1F, m), -59.3 (1F, ddd, *J*=21.4, 8.6, and 5.6 Hz), -70.9 (1F, td, *J*=21.4 and 5.6 Hz), -81.0 (1F, t, *J*=21.4 Hz).

Anal. Calcd for $C_{15}H_8F_4N_2O_2$: C, 55.57; H, 2.49; N, 8.64. Found: C, 55.15; H, 2.50; N, 8.48.

Preparation of 2-(2-Pentafluorobenzamido-3,4,5,6-tetrafluorophenyl)benzoxazole (**5**).

A mixture of **2** (0.06 g, 0.21 mmol), pentafluorobenzoyl chloride (0.16 g, 0.70 mmol), and triethylamine (0.07 g, 0.69 mmol) in 10 cm^3 of ethyl acetate was stirred at room temperature for 5 days. The mixture was washed with water and brine, dried over sodium sulfate, and evaporated to leave a residue which was chromatographed on silica gel (hexane-ethyl acetate, 5/1) to give **5** (0.05 g, 50%). The compound was recrystallized from hexane-ethyl acetate to give white crystals of **5**: mp 204-205 °C; ir: 3250 (NH), 1680 (C_6F_4 and C=O), and 1240 cm^{-1} (CF); ^{1}H nmr: δ = 10.6 (1H, s), 7.73 (2H, m), and 7.48 (2H, m); ^{19}F nmr: δ = -56.2 (1F, m), -58.5 (1F, m), -61.2 (2F, m), -70.3 (1F, td, *J*=20.7 and 5.6 Hz), -70.7 (1F, m), -79.0 (1F, t, *J*=20.7 Hz), and -81.6 (2F, m).

Anal. Calcd for $C_{20}H_5F_9N_2O_2$: C, 50.44; H, 1.06; N, 5.88. Found: C, 50.30; H, 1.01; N, 5.87.

Preparation of 2-(2-Amino-3,5,6-trifluoro-4-methoxyphenyl)-benzoxazole (**6**).

A mixture of **2** (0.05 g, 0.18 mmol) and sodium methoxide (0.02 g, 0.37 mmol) in 30 cm^3 of methanol was stirred at room temperature for 6 days and then at 40 °C for 7 days. After the solvent was removed, the mixture was extracted with ethyl acetate and the extracts were washed with water and brine, dried over sodium sulfate, and evaporated to leave a residue. Chromatography on silica gel (hexane-ethyl acetate, 5/1) of the residue produced 0.04 g (75%) of **6**. The compound was then purified by recrystallization from hexane to give pale brown crystals of **6**: mp 126-127 °C; ir: 3480, 3300 (NH_2), 1650 (C_6F_3), and 1245 cm^{-1} (CF); ^{1}H nmr: δ = 7.74 (1H, m), 7.64 (1H, m), 7.38 (2H, m), 6.34 (2H, br.s), and 4.15 (3H, t, *J*=1.5 Hz); ^{19}F nmr: δ = -63.1 (1F, dd, *J*=20.7 and 10.5 Hz), -80.0 (1F, d, *J*=10.5 Hz), and -92.0 (1F, d, *J*=20.7 Hz).

Anal. Calcd for $C_{14}H_9F_3N_2O_2$: C, 57.15; H, 3.08; N, 9.52. Found: C, 56.93; H, 3.05; N, 9.46.

Preparation of 2-(3,5,6-Trifluoro-4-methoxy-2-propylamino-phenyl)benzoxazole (**8**).

A solution of **7** (0.20 g, 0.67 mmol) and propylamine (0.40 g, 6.8 mmol) in 25 cm^3 of dioxane was stirred at 50 °C for 5 hours and then at 80 °C for 20 hours. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine. After drying over sodium sulfate, the extracts were evaporated to leave a residue which was chromatographed on silica gel (hexane-ethyl acetate, 5/1) to give **8** (0.22 g, 98%). The compound was recrystallized from hexane to give pale yellow crystals of **8**: mp 61-62 °C; ir: 3250 (NH), 1650 (C_6F_3), and 1250 cm^{-1} (CF); ^{1}H nmr: δ = 8.20 (1H, br.s), 7.73 (1H, m), 7.61 (1H, m), 7.37 (2H, m), 4.12 (3H, t, *J*=1.2 Hz), 3.46 (2H, m), 1.68 (2H, qt, *J*=7.3 and 7.3 Hz), and 0.99 (3H, t, *J*=7.3 Hz); ^{19}F nmr: δ = -61.9 (1F, dd, *J*=21.4 and 10.1 Hz), -74.8 (1F, d, *J*=10.1 Hz), and -91.1 (1F, d, *J*=21.4 Hz).

Anal. Calcd for $C_{17}H_{15}F_3N_2O_2$: C, 60.71; H, 4.50; N, 8.33. Found: C, 60.66; H, 4.57; N, 8.33.

Preparation of 2-[3,5,6-Trifluoro-4-methoxy-2-(1-methoxycarbonylethyl)aminophenyl]benzoxazole (**9**).

A mixture of **7** (0.50 g, 1.7 mmol), L-alanine methyl ester hydrochloride (2.3 g, 16.6 mmol), and triethylamine (3 cm^3) in 25 cm^3 of dioxane was stirred at 50 °C for 5 days and then at 80 °C for 20 days. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine. After drying over sodium sulfate, the extracts were evaporated to leave a residue which was chromatographed on silica gel (hexane-ethyl acetate, 5/1) to give **9** (0.27 g, 42%). The compound was recrystallized from hexane-ethyl acetate to give white needles of **9**: mp 105-106 °C; ir: 3230 (NH), 1740 (C=O), 1640 (C_6F_3), and 1250 cm^{-1} (CF); ^{1}H nmr: δ = 8.59 (1H, d, *J*=7.6 Hz), 7.77 (1H, m), 7.63 (1H, m), 7.39 (2H, m), 4.58 (1H, qdd, *J*=7.6, 7.6, and 3.0 Hz), 4.11 (3H, t, *J*=1.5 Hz), 3.70 (3H, s), and 1.58 (3H, d, *J*=7.6 Hz); ^{19}F nmr: δ = -61.2 (1F, dd, *J*=21.8 and 8.6 Hz), -74.3 (1F, m), and -89.1 (1F, d, *J*=21.8 Hz).

Anal. Calcd for $C_{18}H_{15}F_3N_2O_4$: C, 56.85; H, 3.98; N, 7.37. Found: C, 56.96; H, 4.19; N, 7.28.

Preparation of 2-(3,5,6-Trifluoro-4-methoxy-2-dipropylamino-phenyl)benzoxazole (**10**).

A solution of **7** (0.30 g, 1.0 mmol) and dipropylamine (3.0 g, 29.7 mmol) in 25 cm^3 of dioxane was stirred at 50 °C for 20 hours and then at 80 °C for 30 hours. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine. After drying over sodium sulfate, the extracts were evaporated to leave a residue which was chromatographed on silica gel (hexane-ethyl acetate, 5/1) to give pale yellow oil (0.17 g, 45%) of **10**: ir (film): 1630 (C_6F_3) and 1240 cm^{-1} (CF); ^{1}H nmr: δ = 7.83 (1H, m), 7.59 (1H, m), 7.40 (2H, m), 4.13 (3H, t, *J*=1.2 Hz), 2.88 (4H, td, *J*=7.3 and 1.2 Hz), 1.38 (4H, qt, *J*=7.3 and 7.3 Hz), and 0.74 (6H, t, *J*=7.3 Hz); ^{19}F nmr: δ = -62.1 (1F, m), -62.4 (1F, dd, *J*=21.4 and 10.1 Hz), and -78.8 (1F, dd, *J*=21.4 and 4.5 Hz).

Anal. Calcd for $C_{20}H_{21}F_3N_2O_2$: C, 63.48; H, 5.59; N, 7.40. Found: C, 63.29; H, 5.60; N, 7.37.

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