Synthesis of New Tetrafluorobenzo Heteroaromatic Compounds

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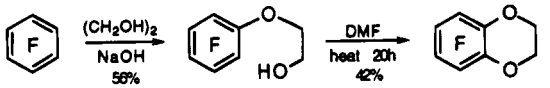
The cyclocondensation of pentafluorobenzoyl chloride with 2-mercaptobenzimidazole (**6**), 2-mercaptoimidazole (**10**), 2-imidazolidinethione (**12**), and perimidine-2-thione **15** gave tetrafluorobenzo heterocycles **7**, **11**, **13**, and **16**, respectively. In addition, the reaction of 2-mercaptobenzimidazole (**6**) with pentafluorobenzyl bromide followed by treatment with NaH gave tetrafluorobenzo heterocycle **22**.

Introduction

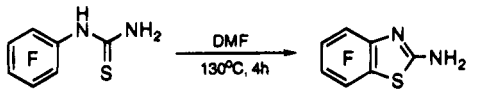
The electronic properties of an aromatic ring are profoundly changed by replacing the hydrogens with fluorines, and such a change can have a large effect on the properties of neighboring functional groups.[1] For example, pentafluorobenzoic acid is much more acidic than benzoic acid itself, due to the extremely strong electron-withdrawing ability of the fluorines. The pK_a of benzoic acid is 5.77, while the pK_a of pentafluorobenzoic acid is 3.07. Similarly, phenol has a pK_a of 9.9, compared to 5.5 for pentafluorophenol.

In addition, fluorinated aromatic compounds readily undergo nucleophilic aromatic substitution reactions. There are many such reactions in the literature, examples of which can be found in various reviews.[2] One example is the reaction of hexafluorobenzene (**1**) with ethylene glycol.[3] The ethylene glycol adduct **2** can undergo further cyclization by intramolecular nucleophilic aromatic substitution to give bicyclic structure **3**.



1 2 3

In this way, numerous bicyclic heterocycles have been synthesized.[2] An example of a fully aromatic bicyclic structure prepared by the intramolecular nucleophilic aromatic substitution reaction is the cyclization of the thiourea derivative **4** to give 2-amino-4,5,6,7-tetrafluorobenzothiazole **5** in 78% yield.[4]

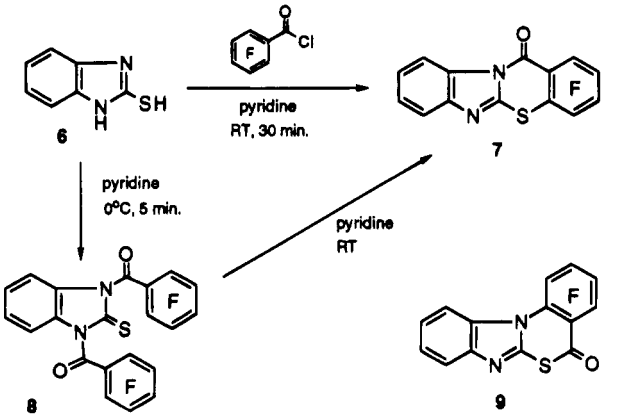


4 5

Many such bicyclic structures have been prepared, but tricyclic and higher polycyclic heterocycles with the tetrafluorobenzo ring structure are much rarer. Only a few examples are known.[5] Such compounds should be very interesting to study because their properties are expected to be very different from the hydrogen-substituted analogs. It was decided to try to find a reliable method for synthesizing such polycyclic heterocycles.

Results and Discussion

The reaction of 2-mercaptobenzimidazole (**6**) with pentafluorobenzoyl chloride was investigated. Attack could occur initially at sulfur or nitrogen. When this reaction was carried out in pyridine for 30 min at room temperature, the desired product **7** was obtained in 50% yield.



The product was characterized spectroscopically. The fluorine NMR spectrum revealed four contiguous, nonequivalent fluorines in the molecule. The mass spectrum gave a molecular ion of 324 as the base peak, and a good elemental analysis was obtained; however, there was concern about the possibility of an alternative product **9**, which would be obtained if the sulfur reacted first with the acid chloride. It was possible to grow very thin, platelike crystals from acetone, which gave the crystal structure shown in Figure 1. The structure corresponds to compound **7**. There are seven previous examples in the literature of this ring system.[6] The X-ray crystallographic structure of a compound similar to **7** has been reported.[6b]

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(3) Burdon, J; Damodaran, V. A.; Tatlow, J. C. *J. Chem. Soc.* **1964**, 763.

(4) Herkes, F. E. *J. Fluorine Chem.* **1978**, *12*, 1.

(5) (a) Brow, P. J. N.; Stephens, R.; Tatlow, J. C. *Tetrahedron* **1967**, *23*, 4041. (b) Jenkins, C. M.; Pedler, A. E.; and Tatlow, J. C. *Tetrahedron* **1971**, *27*, 2557. (c) Kolesnikova, I. V.; Petrova, T. D.; Platonov, V. E. *J. Fluorine Chem.* **1988**, *40* (2,3), 217. (d) Fokin, E. P.; Gerasimova, T. N.; Fomenko, T. V.; Semikolenova, N. V. *Zh. Org. Khim.* **1978**, *14*, 835. (e) Gerasimova, T. N.; and Kolchina, E. F. *J. Fluorine Chem.* **1994**, *66*, 69. (f) Koutonyuk, V. N.; and Kobrina, L. S. *J. Fluorine Chem.* **1994**, *66*, 219.

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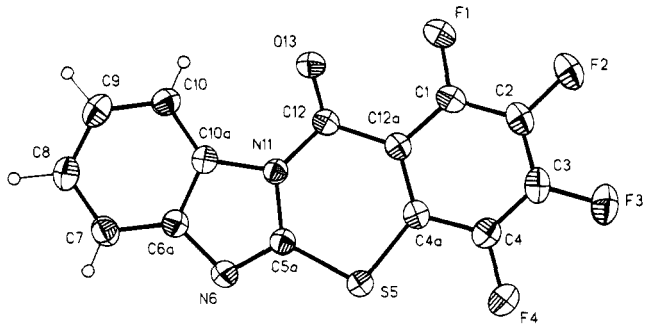


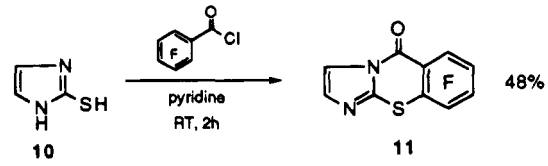
Figure 1. Molecular structure of **7** with 50% probability ellipsoids showing the atom numbering scheme.

Table 1. ^{19}F NMR Chemical Shifts (ppm) for Tetrafluorobenzo Heteroaromatics

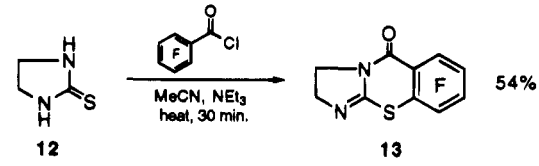
compd	F_1	F_2	F_3	F_4
7	−131.9	−136.1	−144.0	−154.5
13	−134.4	−137.3	−146.5	−155.8
11	−132.0	−136.0	−143.9	−155.0
16	−133.7	−139.5	−145.9	−155.8
22	−141.3	−141.9	−154.5	−158.2

During the course of the reaction, a yellow solid precipitated from solution and then redissolved to give a homogeneous solution. It was suspected that this yellow solid was an intermediate in the reaction leading to the product. In an attempt to isolate this transient, insoluble solid, the reaction was carried out for 5 min at 0 °C and then worked up by pouring the mixture containing the yellow solid into water and then filtering. The yellow solid proved to be the bis-benzoylated compound **8**. It was obvious from the molecular ion of 538 and the elemental analysis that **6** had reacted with two molecules of acid chloride even though the ratio of starting materials was 1:1. Apparently the monobenzoylated product is much more reactive with the acid chloride than the 2-mercaptobenzimidazole. The presence of only two resonances in the proton NMR and two CH carbons in the carbon NMR is consistent with structure **8** and not the alternative structure where one of the benzoylations has occurred at sulfur. When **8** was dissolved in pyridine and kept at room temperature, **7** was formed. From this evidence, it is concluded that compound **8** is initially formed and is then debenzoylated, followed by rapid cyclization to give **7**.

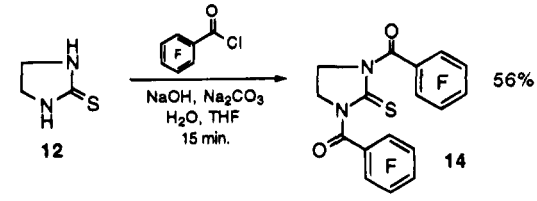
We then explored the scope and limitations of this cyclization reaction. Thus, 2-mercaptoimidazole **10** gave compound **11** in 48% yield. However, to get this yield it was necessary to use 2 equiv of acid chloride to 1 equiv of **10**. The mass spectrum gave a molecular ion of 274 as the base peak. Only two resonances were observed in the proton NMR, with a very small coupling of 1.7 Hz. The fluorine NMR conclusively showed the presence of four nonequivalent fluorines, consistent with structure **11**. A comparison of the chemical shifts of the fluorines in compound **11** to those in compound **7**, for which the X-ray structure is known, showed a very close correlation (see Table 1). Only one previous example of this ring system has been reported.[7]



The reaction of pentafluorobenzoyl chloride with 2-imidazolidinethione (**12**) was also investigated; however, the reaction in pyridine failed. After varying the experimental conditions, it was found that triethylamine in refluxing acetonitrile gave a 54% yield of the desired product **13**. Surprisingly, compound **13** exhibited only one signal in the proton NMR spectrum at 4.07 ppm. Apparently the hydrogens of the two methylene groups have extremely close chemical shifts. The carbon NMR spectrum did show two different resonances for the methylene carbons at 53.6 and 45.0 ppm. The mass spectrum showed a base peak at 276 for the molecular ion. As expected, there were four nonequivalent fluorines in the ^{19}F NMR spectrum. There is one previous example of this ring system in the literature;[7] however, this is the first example of a 2,3-dihydro system.



Compound **12** formed the bis-benzoylated product **14** under Schotten–Baumann conditions if THF was used as a cosolvent. The crude yield of **14** was quantitative. After recrystallization from chloroform/hexane, a 56% yield of pure **14** was obtained. The proton NMR showed only a singlet at 4.24 ppm and the carbon NMR showed a single CH_2 resonance at 44.2 ppm. As expected, treatment of a solution of **14** with triethylamine produced the cyclized product **13**.



Pentafluorobenzoyl chloride failed to afford the desired product with perimidine-2-thione (**15**) in pyridine or with triethylamine. A mixture of products was obtained in low yield. In this case a radically different procedure proved successful. The dianion of perimidine-2-thione (**15**) was generated with 2 equiv of n-butyllithium at 0 °C.[8] Reaction with pentafluorobenzoyl chloride afforded a 91% yield of product. The fluorine NMR and mass spectrum were consistent with structure **16**. This compound is the first example of the benzothiazinoperimidine

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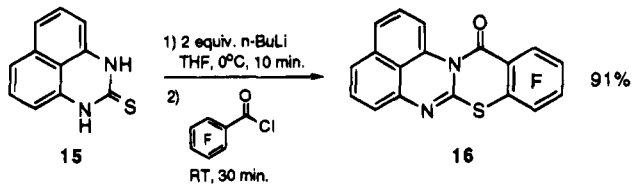
(7) Volovenko, Y. M.; Babichev, F. S.; Litvinenko, S. V.; Turov, A. V. U. S. S. R. SU 1,414,849, 26 Jan 1987; *Chem. Abstr.* **1989**, *110*, 8224m.

(8) Ibrahim, M. R.; Fataftah, Z. A.; Homed, O. A. *J. Chem. Eng. Data* **1987**, *32*, 128.

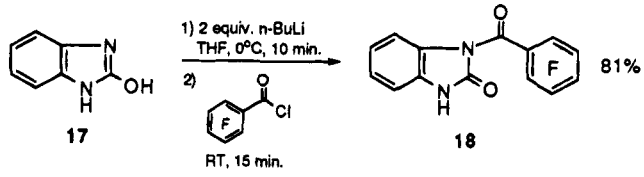
ring system. However, when this procedure was applied to **6**, a mixture of products was obtained.



15 16

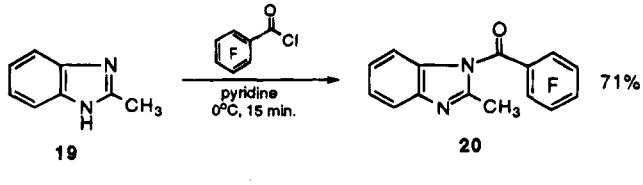
Although these procedures worked quite well for the starting materials so far presented, either no reaction occurred or a mixture of products was obtained with a number of other potential substrates. For example, 2-thiouracil, 2-thiohydantoin, 4,5-diphenyl-2-imidazolethiol, 1*H*-1,2,4-triazole-3-thiol, and 2-mercapto-4(3*H*)-quinazolinone all failed to give significant amounts of cyclized products.

Hydroxybenzimidazole (**17**) and pentafluorobenzoyl chloride failed to give a clean reaction in pyridine. Reaction of the dianion of **17** with pentafluorobenzoyl chloride gave an 81% yield of the uncyclized benzoyl adduct **18**. The proton NMR showed an exchangeable proton at 11.8 ppm and four nonequivalent aromatic protons. The carbon NMR showed four CH carbons.



17 18

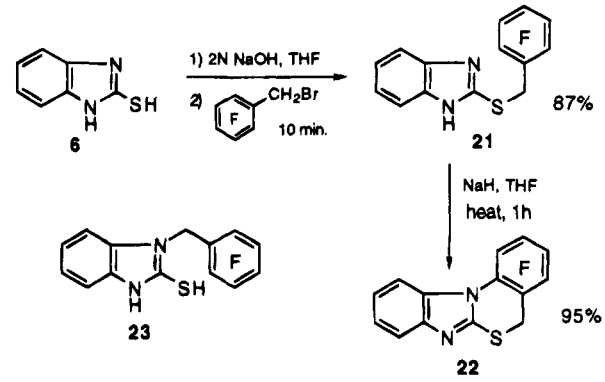
Reaction of 2-methylbenzimidazole (**19**) with pentafluorobenzoyl chloride in pyridine at 0 °C gave a 71% yield of benzoylated product **20**. No cyclized product was observed. This is undoubtedly due to the much weaker acidity of the methyl group compared to the SH of the thiol. Cyclization of compound **20** with an appropriate base would give a carbon analog of **7**, in which the sulfur has been replaced with a CH_2. The base would have to be strong enough to remove a proton from the methyl group so that cyclization could then occur. Unfortunately, it was found that a wide variety of bases failed to give a clean cyclization reaction. Reaction with n-butyllithium appeared to give addition to the pentafluorophenyl ring, while lithium diisopropylamide gave numerous products.



19 20

The same kind of cyclization reactions could, in principle, be carried out using pentafluorobenzyl bromide instead of pentafluorobenzoyl chloride; however, in this case, the product would have a methylene instead of a carbonyl moiety. It was possible to make the desired cyclized product in two steps from 2-mercaptobenzimidazole (**6**). Initially, the S-benzylated compound **21** was obtained in 87% yield. Compound **21** appears to exhibit partial tautomerization of the two nitrogen atoms. This was supported by the observation of a very broad resonance in the proton NMR at 7.48 ppm. Upon filtration of the NMR sample, this single broad resonance appeared as two well-resolved signals of equal integration at 7.55 and 7.40 ppm. Heating the sample in the NMR probe resulted in coalescence of the two signals at about 60°C and, after cooling the sample, the original spectrum was observed. It is thought that filtering the sample through a sintered glass funnel which had previously been washed with an acidic cleaning solution, removed traces of base which had catalyzed the tautomerization. The carbon NMR spectrum of compound **21** also showed two remarkably broad resonances at 142–135 ppm and 120–110 ppm. An alternative structure **23** was easily ruled out since it would have more resonances due to a lack of symmetry.

Next, attention was turned to the cyclization of **21**. The anion was made with sodium hydride in THF and it was found that cyclization was rather slow at room temperature. This is undoubtedly due to the absence of an activating carbonyl group. After allowing the solution of the anion to reflux for 1 h, a 95% crude yield of cyclized product **22** was obtained. This compound was characterized by NMR and mass spectrometry. The fluorine NMR (see Table 1) showed the presence of four nonequivalent fluorines; however, for this compound, the chemical shifts were significantly different from the other compounds previously prepared. The carbon NMR had an unusually large coupling of one of the fluorines to one of the CH aromatic carbons. The carbon at 112.7 ppm appears as a doublet with a coupling of 15.5 Hz. This is due to the close proximity of the internal fluorine to the internal hydrogen which allows coupling of the fluorine to one of the CH carbons in the carbon NMR. In fact, AM1 molecular orbital calculations showed that compound **22** is nonplanar due to the steric interaction of the internal fluorine and hydrogen. Compound **22** is the first example of the benzimidazobenzothiazine ring system.



6 21 23 22

It is possible to envisage a one-pot synthesis of compound **22** from 2-mercaptobenzimidazole (**6**); however, experiments to investigate this possibility have not yet been carried out. It is thought that the cyclization sequence with pentafluorobenzyl bromide has the potential for being more generally applicable than the pentafluorobenzoyl chloride reactions because cleavage of the amide bond would not be a competing side reaction. Moreover, nucleophilic substitution of the pentafluorophenyl ring by base should be substantially slower.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were measured at 300 MHz, and chemical shifts are reported in ppm downfield of internal $SiMe_4$. ^{19}F NMR spectra were measured

at 282 MHz and chemical shifts are reported in ppm upfield of internal $CFCl_3$. ^{13}C NMR spectra were measured at 75 MHz with all protons decoupled and the chemical shifts are reported in ppm downfield of internal $SiMe_4$. Mass spectra were recorded at 70 eV. IR spectra were recorded using a Fourier transform spectrometer.

All solvents were used without purification. Starting materials such as 2-mercaptobenzimidazole, 2-mercaptoimidazole, 2-imidazolidinethione, 2-hydroxybenzimidazole, 2-methylbenzimidazole, pentafluorobenzoyl chloride, and pentafluorobenzyl bromide are commercially available and were used without purification.

1,2,3,4-Tetrafluoro-12*H*-benzimidazo[2,1-*b*][1,3]-benzothiazin-12-one (7). A 25-mL, three-necked, round-bottom flask was equipped with a glass stopper, two rubber septa, and an egg-shaped stir bar. The system was flushed with nitrogen. To the flask were added 10 mL of pyridine (not dry) and 0.650 g (4.33 mmol) of 2-mercaptobenzimidazole, which dissolved giving a slightly cloudy, yellowish solution.

The flask was cooled in an ice–water bath for 30 min. Then 1.00 g (4.34 mmol) of pentafluorobenzoyl chloride were added over a period of 1 min. The ice bath was immediately removed and the cloudy, yellow mixture was allowed to stir as it came to room temperature. After a couple of minutes a large amount of insoluble, yellow solid was formed. The solid redissolved slowly as stirring was continued.

After 30 min, the slightly cloudy, amber solution was poured into 30 mL of water and the precipitated solid was collected by suction filtration after 0.5 min. The solid was washed with 5 mL of water and then dried under full vacuum (0.025 mm) for 2 h to give 0.700 g (50%) of a pale yellow solid, mp 175.8–179.0 °C. The crude product was recrystallized from acetone with a hot filtration (26 mL of acetone per gram of crude product with cooling in the freezer at −25 °C for 5 h). Pure compound **7** was obtained as pale yellowish flakes, mp 180.0–181.7 °C: ^1H NMR (300 MHz, $CDCl_3$) δ 8.55 (dm, 1H, J = 7.4 Hz), 7.79 (dm,1H, J = 7.2 Hz), 7.52 (quintet of d, 2H, J_q = 7.6 and J_d = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −131.94 (ddd, 1F, J = 19.6, 10.9, and 12.4 Hz), −136.12 (ddd, 1F, J = 21.3, 10.9, and 1.6 Hz), −144.02 (td, 1F, J_t = 21.1 and J_d = 12.4 Hz), −154.50 (td, 1F, J_t = 20.2 and J_d = 1.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3 (s, quat), 131.5 (s, quat), 126.5 (s, CH), 125.1 (s, CH), 118.9 (s, CH), 116.0 (s, CH); FTIR (KBr) 1706 s, 1637 w, 1516 m, 1458 s, 1357 m, 1269 m, 1173 w, 1129 m, 1070 w, 990 m, 799 m, 762 m cm^{-1}; MS (70 eV) 324 (M^+, 100%), 296 (9), 208 (7), 162 (10), 124 (2), 90 (3); HRMS calcd for $C_{14}H_4F_4N_2OS$ 323.9980, found 323.9969. Anal. Calcd for $C_{14}H_4F_4N_2OS$: C, 51.86; H, 1.23; N, 8.64. Found: C, 51.88; H, 1.22; N, 8.60.

X-ray experimental: $C_{14}H_4N_2OF_4S$, M_r = 324.25, monoclinic, $P2_1/n$, a = 8.137(1) Å, b = 5.768(1) Å, c = 25.488(5) Å, β = 97.28(1)°, V = 1186.6(3) Å^3, Z = 4, D_{calc} = 1.815 g cm^{-3}, Mo Kα (λ = 0.71073 Å), T = 298 K. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo K_α radiation (λ = 0.71073 Å), 40 reflections with 20.0° ≤ 2θ ≤ 22.0° were used to refine the cell parameters, and 3206 reflections were collected using the ω-scan method. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was <3%). Absorption corrections were applied based on measured crystal faces using *SHELXTL plus*;[9] absorption coefficient, μ = 0.33 mm^{-1}(min and max transmission factors are 0.852 and 0.988, respectively).

The structure was solved by the direct methods in *SHELXTL plus* from which the locations of all of the non-H atoms was obtained. The structure was refined in *SHELXTL plus* using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were refined isotropically without any constraints and 215 parameters were refined and $\sum w(|Fo| - |Fc|)^2$ was minimized: $w = 1/(\sigma|Fo|)^2$, $\sigma(Fo) = 0.5\ kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) = ($I_{peak} - I_{background}$)(scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$(scan rate),

Table 2. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-H Atoms of Compound 7

atom	x	y	z	U
S5	0.97557(8)	0.31328(11)	0.58138(2)	0.0396(2)
F1	0.7248(2)	−0.4125(3)	0.66262(6)	0.0593(6)
F2	0.8778(2)	−0.3050(3)	0.75620(6)	0.0719(7)
F3	1.0699(2)	0.0810(4)	0.77052(6)	0.0715(7)
F4	1.1029(2)	0.3596(3)	0.68766(6)	0.0604(6)
O13	0.6547(2)	−0.3171(3)	0.56239(7)	0.0483(6)
N6	0.8571(3)	0.2904(4)	0.48006(8)	0.0415(7)
N11	0.7683(2)	−0.0079(3)	0.52686(7)	0.0329(6)
C1	0.8172(3)	−0.2201(5)	0.66587(10)	0.04281(8)
C2	0.8972(3)	−0.1666(5)	0.71535(10)	0.0480(9)
C3	0.9931(3)	0.0276(5)	0.72244(10)	0.0486(9)
C4	1.0093(3)	0.1668(5)	0.68023(10)	0.0433(8)
C4a	0.9321(3)	0.1164(4)	0.62938(9)	0.0355(7)
C5a	0.8606(3)	0.1951(4)	0.52615(9)	0.0341(7)
C6a	0.7549(3)	0.1449(4)	0.44628(9)	0.0367(7)
C7	0.7113(3)	0.1647(5)	0.39222(11)	0.0454(9)
C8	0.6131(3)	−0.0064(5)	0.36662(11)	0.0490(9)
C9	0.5590(3)	−0.1937(5)	0.39503(11)	0.0482(9)
C10	0.5993(3)	−0.2146(5)	0.44865(11)	0.0410(8)
C10a	0.6989(3)	−0.0413(4)	0.47374(9)	0.0349(7)
C12	0.7433(3)	−0.1508(4)	0.56923(9)	0.0338(7)
C12a	0.8323(3)	−0.0817(4)	0.62165(9)	0.0348(7)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*\ a_j^*\ A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

where k is the correction due to decay and Lp effects, and 0.02 is a factor used to downweight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography*.[10] Scattering factors for non-hydrogen atoms were taken from Cromer & Mann[11] with anomalous-dispersion corrections from Cromer & Liberman,[12] while those of hydrogen atoms were from Stewart, Davidson & Simpson.[13]

1,3-Dihydro-1,3-bis(pentafluorobenzoyl)-2*H*-benzimidazole-2-thione (8). The above procedure for compound **7** was followed except that the reaction mixture was allowed to stir at 0 °C for 5 min. Then it was poured into 30 mL of water and the solid was collected by suction filtration. It was washed with 10 mL of water and dried under full vacuum (0.025 mm) for 3 h. A total of 979 mg (84%) of bright yellow solid were obtained, mp 148.5–150.5 °C. The crude product (829 mg) was recrystallized from 8 mL of chloroform and 22 mL of hexanes with a hot filtration. After cooling in an ice–water bath for 1 h, suction filtration gave 497 mg of a bright yellow solid, mp 178.0–180.5 °C (fairly rapid heating is necessary to get a sharp melting point), which was compound **8**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.48 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −141.3 (m, 4F), −148.0 (tt, 2F, J = 20.8 and 3.7 Hz), −160.2 (m, 4F); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 (s, quat), 158.0 (s, quat), 144.3 (dm, CF, J = 256 Hz), 144.0 (dm, CF, J = 256 Hz), 138.0 (dm, CF, J = 256 Hz), 129.5 (s, quat), 127.2 (s, CH), 114.2 (s, CH); FTIR (KBr) 1730 s, 1655 w, 1511 s, 1425 w, 1386 m, 1327 m, 1282 m, 1250 w, 1165 w, 1123 w, 993 s, 744 m cm^{-1}; MS (70 eV) 538 (M^+, 20%), 510 (5), 195 (100), 90 (5); HRMS calcd for $C_{21}H_4F_{10}N_2O_2S$ 537.9834, found 537.9830. Anal. Calcd for $C_{21}H_4F_{10}N_2O_2S$: C, 46.86; H, 0.75; N, 5.20. Found: C, 46.45; H, 0.72; N, 5.26.

6,7,8,9-Tetrafluoro-5*H*-imidazo[2,1-*b*][1,3]benzothiazin-5-one (11). A 25-mL, three-necked, round-bottom flask was

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Table 3. Bond Lengths (Å) and Angles (deg) for the Non-H Atoms of Compound 7

1	2	3	1–2	1–2–3
C4A	S5	C5A	1.738(2)	100.26(11)
C5A	S5		1.728(2)	
C1	F1		1.337(3)	
C2	F2		1.337(3)	
C3	F3		1.339(3)	
C4	F4		1.347(3)	
C12	O13		1.199(3)	
C5A	N6	C6A	1.294(3)	104.3(2)
C6A	N6		1.398(3)	
C5A	N11	C10A	1.393(3)	104.7(2)
C10A	N11	C12	1.412(3)	125.6(2)
C12	N11	C5A	1.394(3)	129.7(2)
C2	C1	C12A	1.379(4)	122.0(2)
C2	C1	F1		116.1(2)
C12A	C1	F1	1.399(4)	122.0(2)
C3	C2	F2	1.364(4)	120.6(2)
C3	C2	C1		120.1(3)
F2	C2	C1		119.3(2)
C4	C3	F3	1.362(4)	120.4(3)
C4	C3	C2		119.4(2)
F3	C3	C2		120.2(2)
C4A	C4	F4	1.397(3)	118.8(2)
C4A	C4	C3		122.2(2)
F4	C4	C3		119.0(2)
C12A	C4A	S5	1.401(3)	126.9(2)
C12A	C4A	C4		119.0(2)
S5	C4A	C4		114.1(2)
S5	C5A	N6		121.3(2)
S5	C5A	N11		123.9(2)
N6	C5A	N11		114.8(2)
C7	C6A	C10A	1.383(4)	120.4(2)
C7	C6A	N6		128.4(2)
C10A	C6A	N6	1.390(3)	111.2(2)
C8	C7	C6A	1.380(4)	118.2(3)
C9	C8	C7	1.402(4)	120.5(3)
C10	C9	C8	1.370(2)	122.2(3)
C10A	C10	C9	1.390(4)	116.6(3)
N11	C10A	C6A		105.1(2)
N11	C10A	C10		132.7(2)
C6A	C10A	C10		122.2(2)
C12A	C12	O13	1.491(3)	124.0(2)
C12A	C12	N11		115.7(2)
O13	C12	N11		120.3(2)
C1	C12A	C4A		117.4(2)
C1	C12A	C12		119.1(2)
C4A	C12A	C12		123.4(2)

Table 4. Bond Lengths (Å) and Angles (deg) of the H Atoms of Compound 7

1	2	3	1–2	1–2–3
C12	O13	1.199(3)		
H7	C7	C8	0.85(3)	124.0(2)
H7	C7	C6A		118.0(2)
H8	C8	C9	1.01(3)	122.0(2)
H8	C8	C7		117.0(2)
H9	C9	C10	0.96(3)	122.0(2)
H9	C9	C8		116.0(2)
H10	C10	C10A	0.86(3)	123.0(2)
H10	C10	C9		120.0(2)

equipped with an egg-shaped stir bar, two rubber septa, and a glass stopper. The system was flushed with nitrogen. To the flask were added 870 mg (8.69 mmol) of 2-mercaptoimidazole and 20 mL of pyridine (not dried). The solid dissolved giving a clear, pale yellow solution.

The flask was cooled in an ice–water bath for 30 min. Then 4.00 g (17.4 mmol) of pentafluorobenzoyl chloride was added over a period of 3 min. The ice bath was immediately removed and the mixture was allowed to stir for 2 h.

The mustard yellow, cloudy mixture was poured into 140 mL of water. After cooling in an ice–water bath for 30 min, suction filtration gave a solid which was washed with 20 mL of water. After drying under a full vacuum (0.025 mm) for 5.5 h, a total of 1.149 g (48%) of an off-white solid, mp 145.7–147.0 °C, were obtained. A 1.027 g sample of the crude product was recrystallized from 9.7 mL of 95% ethanol with cooling in an ice–water bath for 1 h. A total of 877 mg of amber crystals, mp 145.5–147.5 °C, were obtained. This was compound **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 1H, J = 1.7 Hz), 7.37 (d, 1H, J = 1.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −132.0 (dt, 1F, J_d = 19.6 and J_t = 11.5 Hz), −136.0 (dd, 1F, J = 21.0 and 10.9 Hz), −143.9 (td, 1F, J_t = 21.1 and J_d = 12.3 Hz), −155.0 (t, 1F, J = 20.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (br s, quat), 150.6 (dm, CF, J_{CF} = 272.8 Hz), 143.6 (dm, CF, J_{CF} = 265.9 Hz), 141.9 (dm, CF, J_{CF} = 248.6 Hz), 139.5 (dm, CF, J_{CF} = 255.9 Hz), 136.8 (d, quat, J_{CF} = 3.8 Hz), 132.0 (s, CH), 120.3 (d, quat, J = 15.1 Hz), 116.0 (s, CH), 107.4 (m, quat); FTIR (KBr) 3154 w, 3110 w, 1716 s, 1637 m, 1515 s, 1464 m, 1442 m, 1359 s, 1300 m, 1267 m, 1150 m, 1123 m, 1108 m, 1063 w, 986 m, 892 m cm^{-1}; MS (70 eV) 274 (M^+, 100%), 247 (47), 218 (5), 192 (39), 180 (6), 176 (6), 111 (6), 98 (5), 71 (7); HRMS calcd for $C_{10}H_2F_4N_2OS$ 273.9824, found 273.9807. Anal. Calcd for $C_{10}H_2F_4N_2OS$: C, 43.81; H, 0.74; N, 10.22. Found: C, 43.44; H, 0.73; N, 10.10.

6,7,8,9-Tetrafluoro-2,3-dihydro-5*H*-imidazo[2,1-*b*][1,3]-benzothiazin-5-one (13). A 100-mL, three-necked, round-bottom flask was equipped with a magnetic stirrer, a glass stopper, a rubber septum, and a condenser with a rubber septum at the top. The system was flushed with nitrogen. To the flask were added 890 mg (8.71 mmol) of 2-imidazolidinethione, 20 mL of acetonitrile (not dry), and 4.40 g (0.0435 mol) of triethylamine. The solid did not dissolve. To the rapidly stirred mixture was added 2.00 g (8.68 mmol) of pentafluorobenzoyl chloride over a period of 1 min. The flask became warm.

After stirring for 10 min, the mixture was heated at reflux for 30 min to give a clear, amber solution. Upon being allowed to cool to room temperature, an off-white solid crystallized from solution. The mixture, including the solid, was poured into 80 mL of water. The solid dissolved rapidly and a dark amber oil was formed. Cooling in an ice–water bath and scratching produced a solid. After 45 min in the ice bath, suction filtration gave a solid which was washed thoroughly with 20 mL of water. After drying under full vacuum (0.025 mm) for 11 h, a total of 1.29 g (54%) of a very pale amber solid were obtained, mp 109–115 °C.

The crude product was recrystallized from 2.6 mL of chloroform and 13 mL of hexanes with a hot filtration. After the solution cooled to room temperature, another filtration was performed. Crystallization occurred slowly at room temperature. After cooling in the freezer at −25 °C for 7 h, suction filtration gave 0.692 mg of a very pale amber solid, mp 107.5–109.6 °C (heating must be fairly rapid to get a sharp melting point), which was compound **13**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (m); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −134.4 (dt, 1F, J_d = 19.8 and J_t = 11.1 Hz), −137.3 (ddd, 1F, J = 21.4, 10.9, and 1.3 Hz), −146.5 (td, 1F, J_t = 21.0 and J_d = 11.3 Hz), −155.8 (td, 1F, J_t = 20.2 and J_d = 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8 (m, C=O), 149.9 (dddd, CF, J_{CF} = 270.5, 11.7, 3.7, and 2.7 Hz), 149.4 (d, NC=N, J_{CF} = 3.5 Hz), 143.4 (dddd, CF, J_{CF} = 263.8, 15.6, 13.2, and 3.7 Hz), 141.7 (dddd, CF, J_{CF} = 247.5, 12.4, 5.2, and 1.9 Hz), 139.8 (dddd, CF, J_{CF} = 255.2, 16.8, 12.2, and 3.2 Hz), 117.8 (ddd, quat, J_{CF} = 15.9, 4.3, and 1.1 Hz), 109.4 (t, quat, J_{CF} = 4.1 Hz), 53.6 (s, CH_2), 45.0 (s, CH_2); FTIR (KBr) 2974 w, 1689 s, 1599 s, 1512 m, 1462 s, 1378 s, 1244 m, 1131 w, 1076 m, 986 m, 940 w, 884 w, 800 w cm^{-1}; MS (70 eV) 276 (M^+, 100%), 248 (3), 208 (8), 180 (7), 111 (4), 68 (19); HRMS calcd for $C_{10}H_4F_4N_2OS$ 275.9980, found 275.9945. Anal. Calcd for $C_{10}H_4F_4N_2OS$: C, 43.49; H, 1.46; N, 10.14. Found: C, 43.64; H, 1.59; N, 9.82.

1,3-Bis(pentafluorobenzoyl)-2-imidazolidinethione (14). A 50-mL Erlenmeyer flask was equipped with a magnetic stirrer. To the flask were added 22.5 mL of 5% aqueous Na_2CO_3, 4.5 mL of 2 N aqueous NaOH, 918 mg (8.99 mmol) of 2-imidazolidinethione, and 4.2 mL of THF. To the slightly cloudy solution was added 3.36 g (14.6 mmol) of pentafluorobenzoyl chloride over a period of 1 min. After 15 min, a cloudy yellow oil had formed. Cooling in an ice–water bath and scratching produced a solid. After cooling for 15 min, suction filtration gave a solid which was washed with 15 mL of water and dried under full vacuum (0.025 mm) for 2 h. A total of

2.696 g (quantitative yield) of a bright yellow solid, mp 93–103 °C, were obtained.

Recrystallization of the crude solid from 15 mL of chloroform and 23 mL of hexanes was performed with a hot filtration. After coming to room temperature, the solution was decanted from a small amount of white solid which had formed. No crystallization occurred at room temperature. The solution was placed in the freezer at −25 °C for 4 h. Suction filtration gave 1.497 g (56%) of a bright yellow solid, mp 116.6–119.6 °C, which was compound **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24 (s); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −141.6 (m, 4F), −150.4 (tt, 2F, J = 20.7 and 2.6 Hz), −160.7 (m, 4F); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8 (s, quat), 158.7 (s, quat), 143.4 (dm, CF, J_d = 251.2 Hz), 143.2 (dm, CF, J_d = 258.7 Hz), 137.9 (dm, CF, J_d = 251.9 Hz), 111.4 (td, quat, J_t = 18.9 and J_d = 4.1 Hz), 44.2 (s, CH_2); FTIR (KBr) 3264 w, 1689 s, 1513 s, 1437 w, 1403 m, 1330 m, 1245 s, 1128 w, 995 s, 721 w cm^{-1}; MS (70 eV) 490 (M^+, 100%), 471 (5), 415 (6), 267 (14), 195 (150), 72 (3); HRMS calcd for $C_{17}H_4F_{10}N_2O_2S$ 489.9834, found 489.9842. Anal. Calcd for $C_{17}H_4F_{10}N_2O_2S$: C, 41.65; H, 0.82; N, 5.71. Found: C, 41.29; H, 0.81; N, 5.87.

Tetrafluorobenzothiazinoperimidinone (16). A 100-mL, three-necked, round-bottom flask was equipped with an egg-shaped stir bar, a glass stopper, and two rubber septa. The system was flushed with nitrogen and flame-dried. To the flask were added 1.74 g (8.69 mmol) of perimidine-2-thione[14] and 60 mL of THF (commercial anhydrous). The solid did not completely dissolve.

The flask was cooled in an ice–water bath for 30 min. Then, to the slightly cloudy, pale reddish-brown solution were added 7.3 mL (18.25 mmol) of 2.5 M n-butyllithium in hexanes over a period of 2 min. The clear, dark brown solution was allowed to stir at 0 °C for 10 min. Then 2.00 g (8.68 mmol) of pentafluorobenzoyl chloride was added over a period of 2 min. The ice bath was immediately removed and the solution was allowed to stir for 30 min.

The dark brown solution was poured into 180 mL of water. The mixture was extracted once with 100 mL of chloroform and twice with 50 mL of chloroform. An emulsion was broken by suction filtration. The combined chloroform extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation at reduced pressure to give 2.96 g (91%) of a brownish-orange solid, mp 187.0–189.0 °C. The crude solid was recrystallized from 37 mL of ethyl acetate with cooling in an ice–water bath for 30 min. A total of 1.85 g (57%) of an orange-brown solid, mp 189.0–191.5 °C, was obtained. When viewed under the microscope, the solid was seen to be composed of extremely small, amber, rod-shaped crystals. The solid was compound **16**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, 1H, J = 7.9 Hz), 7.5–7.3 (m, 4H), 7.04 (d, 1H, J = 7.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −133.7 (dt, 1F, J_d = 19.6 and J_t = 11.6 Hz), −139.5 (dd, 1F, J = 21.7 and 11.6 Hz), −145.9 (td, 1F, J_t = 21.1 and J_d = 11.6 Hz), −155.8 (t, 1F, J = 20.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0 (d, quat, J = 2.5 Hz), 137.5 (s, quat), 133.9 (s, quat), 131.3 (s, quat), 127.7 (s, CH), 127.0 (s, CH), 124.7 (s, CH), 124.5 (s, CH), 121.7 (s, quat), 119.2 (s, CH), 116.8 (s, CH); FTIR (KBr) 1706 s, 1629 m, 1572 s, 1514 m, 1501 m, 1460 s, 1363 s, 1311 m, 1282 m, 1260 m, 1175 m, 1154 m, 1067 m, 997 m, 824 m, 803 m, 765 m cm^{-1}; MS (70 eV) 374 (M^+, 100%), 346 (10), 208 (5), 180 (7), 166 (35), 139 (17); HRMS calcd for $C_{18}H_6F_4N_2OS$ 374.0137, found 374.0126. Anal. Calcd for $C_{18}H_6F_4N_2OS$: C, 57.76; H, 1.62; N, 7.48. Found: C, 57.82; H, 1.65; N, 7.46.

1,3-Dihydro-1-(pentafluorobenzoyl)-2*H*-benzimidazol-2-one (18). A 100–mL, three-necked, round-bottom flask was equipped with a magnetic stirrer, a glass stopper, and two rubber septa. The system was flushed with nitrogen and flame-dried. To the flask were added 1.16 g (8.65 mmol) of 2-hydroxybenzimidazole and 60 mL of THF (commercial anhydrous). The solid did not completely dissolve. The flask was cooled in an ice–water bath for 30 min.

To the rapidly stirred suspension at 0 °C was added 7.3 mL of 2.5 M n-butyllithium in hexanes over a period of 4 min. The solid dissolved giving a very slightly cloudy, pale yellowish-brown solution which was allowed to stir at 0 °C for 10 min. Then 2.00 g (8.68 mmol) of pentafluorobenzoyl chloride was added over a period of 3 min. The ice bath was immediately removed and the solution was allowed to stir for 15 min.

The reaction mixture was poured into 200 mL of water. The upper organic layer was separated and the aqueous layer was extracted three times with 50-mL portions of chloroform. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation to give 2.29 g (81%) of a pale amber-tinted solid, mp 170–193 °C (decomposes with gas evolution).

The crude product was recrystallized from 5.6 mL of 95% ethanol with cooling in an ice–water bath for 30 min. A total of 1.45 g (51%) of fine, off-white crystals, mp 198–203 °C (heating must be fairly rapid to get a good melting point), were obtained. This was compound **18**: ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.8 (br s, 1H), 8.03 (d, 1H, J = 7.9 Hz), 7.31 (tm, 1H, J = 7.7 Hz), 7.20 (tm, 1H, J = 7.8 Hz), 7.13 (dm, 1H, J = 7.7 Hz); ^{19}F NMR (282 ^{3}MHz, DMSO-d_6) ϕ −141.96 (m, 2F), −150.11 (t, 1F, J = 22.1 Hz), −160.86 (m, 2F); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.9 (s, quat), 151.1 (s, quat), 143.4 (dm, CF, J_{CF} = 249.6 Hz), 142.2 (dm, CF, J_{CF} = 255.2 Hz), 137.1 (dm, CF, J_{CF} = 248.2 Hz), 129.5 (s, quat), 126.1 (s, quat), 125.8 (s, CH), 122.2 (s, CH), 114.7 (s, CH), 111.1 (td, quat, J_t = 19.3 and J_d = 3.6 Hz), 110.0 (s, CH); FTIR (KBr) 3166 m, 3109 m, 1737 s, 1704 m, 1515 s, 1478 m, 1346 s, 1166 m, 1128 m, 993 m, 800 m, 760 m, 699 m cm^{-1}; MS (70 eV) 328 (M^+, 39%), 195 (100), 106 (5), 78 (3); HRMS calcd for $C_{14}H_5F_5N_2O_2$ 328.0271, found 328.0253. Anal. Calcd for $C_{14}H_5F_5N_2O_2$: C, 51.24; H, 1.54; N, 8.54. Found: C, 51.16; H, 1.57; N, 8.43.

1-(Pentafluorobenzoyl)-2-methyl-1*H*-benzimidazole (20). A 100-mL, three-necked, round-bottom flask was equipped with an egg-shaped stir bar, two rubber septa, and a glass stopper. The system was flushed with nitrogen. To the flask were added 1.15 g (8.70 mmol) of 2-methylbenzimidazole and 20 mL of pyridine (not dry). The solid dissolved readily giving a clear, colorless solution. The flask was cooled in an ice–water bath for 30 min and then 2.00 g (8.68 mmol) of pentafluorobenzoyl chloride were added over a period of 3 min.

After stirring for 15 min at 0 °C, the slightly cloudy, colorless solution was poured into 120 mL of ice–cold water. After 3 min in the ice bath, suction filtration gave a solid which was washed with 20 mL of water and dried under full vacuum (0.025 mm) for 11 h. A total of 2.02 g (71%) of a white solid, mp 94.6–96.6 °C, were obtained.

The crude product was recrystallized from 10 mL of hexanes with a hot filtration. After cooling in an ice–water bath for 1 h, suction filtration gave 1.49 g (53%) of fine white crystals, mp 95.7–97.3 °C, which was compound **20**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, 1H, J = 8.0 Hz), 7.12 (td, 1H, J_t = 7.7 and J_d = 1.0 Hz), 6.99 (td, 1H, J_t = 7.8 and J_d = 1.1 Hz), 6.73 (d, 1H, J = 8.3 Hz), 2.73 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −140.1 (m, 2F), −146.7 (tt, 1F, J = 20.8 and 3.7 Hz), −158.0 (m, 2F); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4 (s, quat), 152.4 (s, quat), 144.2 (dm, CF, J_{CF} = 258 Hz), 144.0 (dm, CF, J_{CF} = 258 Hz), 143.0 (s, quat), 138.3 (dm, CF, J_{CF} = 255 Hz), 132.5 (s, quat), 125.7 (s, CH), 125.3 (s, CH), 120.4 (s, CH), 112.7 (s, CH), 111.1 (td, quat, J_t = 19.0 and J_d = 4.2 Hz), 18.0 (s, CH_3); FTIR (KBr) 1702 s, 1655 m, 1608 m, 1558 m, 1499 s, 1456 m, 1365 s, 1312 m, 1274 m, 1174 m, 1126 m, 1101 w, 991 s, 797 m, 748 m cm^{-1}; MS (70 eV) 326 (M^+, 60%), 284 (39), 195 (100), 90 (8); HRMS calcd for $C_{15}H_7F_5N_2O$ 326.0479, found 326.0495. Anal. Calcd for $C_{15}H_7F_5N_2O$: C, 55.56; H, 2.16; N, 8.62. Found: C, 55.23; H, 2.14; N, 8.59.

2-[(Pentafluorophenyl)methyl]thio]-1*H*-benzimidazole (21). To a 25-mL, single-necked, round-bottom flask equipped with a magnetic stirrer were added 1.00 g (6.66 mmol) of 2-mercaptobenzimidazole and 10 mL of THF. To the rapidly stirred solution was added 3.4 mL (6.8 mmol) of 2 N aqueous NaOH. After 4 min, 1.74 g (6.67 mmol) of pentafluorobenzyl bromide was added over a period of 1.5 min. After 10 min, the solution was poured into 50 mL of water and a solid readily formed upon scratching. After 5 min, suction filtration gave a solid which was washed with 10 mL of water and dried under full vacuum to give 1.91 g (87%) of a white solid, mp 188.5–191.6 °C.

The crude product was recrystallized from 9.5 mL of 95% ethanol with cooling in an ice–water bath for 1 h. A total of 1.54 g (70%) of small, clear, colorless crystals, mp 191.5–195.3 °C, were obtained. This was compound **21**: ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.72 (br s, 1H), 7.48 (br s, 2H), 7.16 (m, 2H), 4.64 (s, 2H); ^{1}H NMR (300 MHz, DMSO-d_6, filtered) δ 12.72 (br s, 1H), 7.55 (m, 1H), 7.40 (m, 1H), 7.15 (m, 2H), 4.64 (s, 2H); ^{19}F NMR (282 MHz, DMSO-d_6) ϕ −141.3 (m, 2F), -155.0 (t, 1F, J = 22.3 Hz), −162.2 (m, 2F); ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.7 (s, quat), 144.9 (dm, CF, J_d = 247.8 Hz), 140.2 (dm, CF, J_d = 251.2 Hz), 137.1 (dm, CF, J_d = 246.5 Hz), 142–135 (extremely br s), 121.9 (s, CH), 120–110 (extremely br s), 112.1 (td, quat, J_t = 17.7 and J_d = 3.5 Hz), 23.4 (s, CH_2); FTIR (KBr) 3040–2500 br s, 1657 w, 1505 s, 1405 s, 1352 m, 1306 w, 1272 m, 1126 m, 989 s, 963 m, 750 m cm^{-1}; MS (70 eV) 330 (M^+, 100%), 297 (22), 149 (35), 122 (21); HRMS calcd for $C_{14}H_7F_5N_2S$ 330.0250, found 330.0221. Anal. Calcd for $C_{14}H_7F_5N_2S$: C, 50.91; H, 2.14; N, 8.48. Found: C, 50.89; H, 2.15; N, 8.48.

Tetrafluorobenzimidazobenzothiazine (22). A 50-mL, three-necked, round-bottom flask was equipped with a rubber septum, a magnetic stirrer, a glass stopper, and a spiral reflux condenser with a rubber septum. The system was flushed with nitrogen. To the flask were added 1.00 g (3.03 mmol) of 2-[(pentafluorophenyl)methyl]thio]-1*H*-benzimidazole (**21**) and 10 mL of THF (commercial anhydrous). To the clear, colorless solution was added 109 mg (4.54 mmol) of sodium hydride (dry, 97%) all at once. Reaction was rapid and vigorous, giving off a gas. After stirring for 5 min, the slightly cloudy, pale pink solution was heated at reflux for 1 h and then allowed to cool to room temperature.

The cloudy, mustard yellow mixture was poured into 30 mL of water and a solid formed. After 5 min, suction filtration gave a solid which was washed with 2 mL of water and dried under full vacuum (0.025 mm) for 1 h. A total of 805.4 mg of a white solid, mp 239.0–242.6 °C, was obtained.

The aqueous filtrate was extracted three times with 10-mL portions of chloroform. The combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation at reduced pressure to give a solid which was dried under full vacuum (0.025 mm) for 20 min. An additional 91.1 mg of an off-white solid, mp 229–239 °C, was obtained.

A combined yield of 896.5 mg (95%) of crude product were obtained. The combined crude material was recrystallized from 13.2 mL of chloroform and 8 mL of hexanes with cooling in an ice–water bath for 1 h. Suction filtration gave 574.6 mg (61%) of very fine, white crystals, mp 240.5–243.5 °C. When viewed with a microscope, they appeared as clear, colorless, rod-shaped crystals. This was compound **22**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (m, 1H), 7.47 (m, 1H), 7.34–7.39 (m, 2H), 4.08 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) ϕ −141.33 (m, 1F), −141.92 (ddm, 1F, J_d = 22.6 and 10.6 Hz), −154.46 (tm, 1F, J_t = 20.6 Hz), −158.15 (tm, 1F, J_t = 21.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3 (s, quat), 143.8 (dm, CF, J = 246.5 Hz), 143.3 (s, quat), 141.6 (dm, CF, J = 255.9 Hz), 139.9 (dm, CF, J = 256.6 Hz), 139.1 (dm, CF, J = 255.9 Hz), 133.0 (s, quat), 124.4 (s, CH), 123.9 (s, CH), 120.4 (m, quat), 119.9 (s, CH), 113.6 (d, quat, J = 16.8 Hz), 112.7 (d, CH, J = 15.5 Hz), 23.7 (s, CH_2); FTIR (KBr) 1604 w, 1507 s, 1478 m, 1451 m, 1329 m, 1262 m, 1200 m, 1114 m, 1025 m, 987 m, 914 m, 817 m, 760 m, 747 m cm^{-1}; MS (70 eV) 310 (M^+, 100%), 252 (76), 202 (10), 155 (M^{2+}, 2); HRMS calcd for $C_{14}H_6F_4N_2S$ 310.0188, found 310.017. Anal. Calcd for $C_{14}H_6F_4N_2S$: C, 54.20; H, 1.95; N, 9.03. Found: C, 54.27; H, 1.93; N, 9.02.