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2,4-Diaryl-1,3-Chalcogen Azoles Bearing Pentafluorosulfanyl SF_5 Groups: A Synthetic and Structural Study

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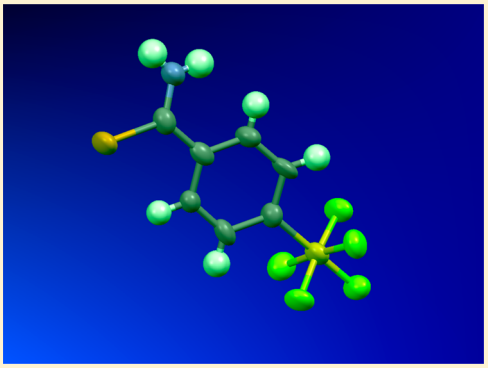
Supporting Information

ABSTRACT: A series of new 2,4-diaryl-1,3-chalcogen azoles having pentafluorosulfanyl SF_5 functional groups has been prepared by means of the two-component cyclization of the selenoamide or thioamide with α-bromoketones. The selenoamides or thioamides were obtained from the reaction of Woollins' reagent or Lawesson's reagent with 4-pentafluorosulfanylbenzonitrile, followed by hydrolysis with water. All new compounds were characterized by ^{1}H, ^{13}C, ^{77}Se, ^{19}F NMR spectroscopy, and accurate mass measurement. X-ray crystal structure analysis of the selenoamide, thioamide, and 2,4-diarylpentafluorosulfanyl-1,3-chalcogen azoles reveal that the selenoamide and thioamide have very similar structural features along with similar intermolecular interactions such as the $\pi-\pi$ stacking and the weak N−H···E (E = S or Se) hydrogen bonding. The 2,4-diarylpentafluorosulfanyl-1,3-chalcogen azoles show the newly formed five-membered N(1)−C(2)-E(3)-C(4)−C(5) ring is either perfectly planar (and coplanar with two peripheral aryl ring planes) or near-planar. The $\pi-\pi$ intermolecular interactions and the weak C−H···π and C−H···X (X = Br, F, O) hydrogen bonding are discussed in the cases of 2,4-diarylpentafluorosulfanyl-1,3-chalcogen azoles.



INTRODUCTION

Organic compounds bearing pentafluorosulfanyl (SF_5) are recognized as special organic derivatives of sulfur hexafluoride SF_6, because in both SF_6 and SF_5 derivatives, the sulfur atom is hypervalent and has a hexacoordinated state with an octahedral geometry. The pentafluorosulfanyl (SF_5) substituent, recently labeled as the "substituent of the future", occupies a special place due to its remarkable chemical stability and uniqueness. In recent years, organofluorine compounds bearing strongly electron-withdrawing and highly lipophilic pentafluorosulfanyl (SF_5) group have attracted much attention from synthetic organic and medicinal chemists because of its unique high electronegativity, substantial steric effect, low surface energy, significant hydrophobicity, and high chemical and metabolic stability.[1,2] The pentafluorosulfanyl SF_5 group has some resemblance to the trifluoromethyl CF_3, though it is even more electronegative and sterically demanding.[3] Thus, SF_5-containing compounds overtake the corresponding CF_3-containing compounds in altering molecular properties such as density, refractive index, dipole moment, lipophilicity, thermal and chemical stability, and they have a distinct impact on biological activity.[4] Since the first synthesis of pentafluorosulfanylbenzene was reported nearly 50 years ago,[5] a number of SF_5-group-containing compounds have become available so far,[1a,6] and consequently, wide applications such as superconductivity, metallic conductivity, semiconductivity,[7] herbicides,[8] enzyme inhibitors,[9] liquid crystals,[10] and energetic materials[11] have been explored. Recently, SF_5 functional aliphatic compounds were used as starting materials for surfactants,[12] and successful incorporation of SF_5 substituent into an antimalarial drug was developed.[13] In addition, selenium-containing heterocyclic compounds have gradually increased interest in recent years because of their diverse reactivity and pharmaceutical applications. In particular, the selenazole derivatives are of marked interest due to their antitumor, antibacterial and other notable activities.[14] Because distinctive properties can be found in both types of the compounds, we anticipate that the selenozoles combined with a SF_5 fragment have the potential to exhibit much better activity than any single type of the above-mentioned compounds. This expectation stimulated us to synthesize the new type of selenazoles and thiazoles. Herein, we report a very simple route to prepare a series of novel 1,3-selenazoles and 1,3-thiazoles incorporating a pentafluorosulfanyl-aryl $SF_5C_6H_4$ group and their single crystal X-ray structural profiles. To the best of our knowledge, this is the first report of a systematic synthesis and X-ray single crystal structures of 2,4-diaryl-1,3-chalcogen azoles bearing a pentafluorosulfanyl SF_5 group.

RESULTS AND DISCUSSION

Synthesis. Synthetic approaches to nitrogen- and sulfur-containing heterocyclic compounds have been extensively explored,[15] but methods for the synthesis of their selenium analogues have not been appreciably studied due mainly to the difficulty associated with the availability of the primary

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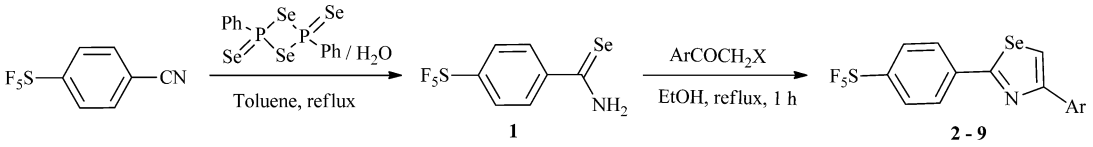
Scheme 1. Synthesis of Selenoamide 1 and 1,3-Selenazoles 2−9 (X and Ar Groups Defined in Table 1)



Scheme 2. Synthesis of Thioamide 10 and 1,3-Thiazoles 11−13 (X and Ar Groups Defined in Table 1)

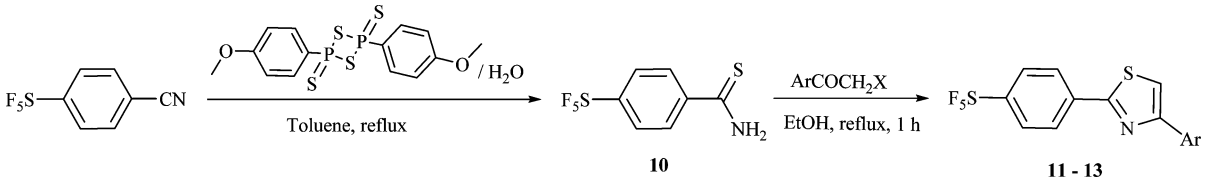


Table 1. Yields, ^{19}F and ^{77}Se NMR Data of Compounds 1−13

compd	X	Ar	yield (%)	^{19}F NMR (δ, ppm)	^{77}Se NMR (δ, ppm)
1			87	82.3 (pentet, ^2J = 150.4 Hz, 1F) 61.7 (d, ^2J = 149.7 Hz, 4F)	766.1
2	Br	4-ClC_6H_4	99	83.2 (pentet, ^2J = 152.3 Hz, 1F) 62.0 (d, ^2J = 149.5 Hz, 4F)	734.5
3	Br	3-$NO_2C_6H_4$	98	83.0 (pentet, ^2J = 153.3 Hz, 1F) 61.9 (d, ^2J = 149.8 Hz, 4F)	742.6
4	Br	4-$CH_3OC_6H_4$	95	84.3 (pentet, ^2J = 152.1 Hz, 1F) 62.0 (d, ^2J = 149.8 Hz, 4F)	725.8
5	Br	3,4-di-ClC_6H_3	90	83.1 (pentet, ^2J = 150.4 Hz, 1F) 62.0 (d, ^2J = 149.8 Hz, 4F)	739.9
6	Br	4-$CH_3C_6H_4$	94	83.3 (pentet, ^2J = 151.7 Hz, 1F) 62.0 (d, ^2J = 149.9 Hz, 4F)	727.0
7	Br	4-$NO_2C_6H_4$	97	83.0 (pentet, ^2J = 151.6 Hz, 1F) 61.9 (d, ^2J = 149.6 Hz, 4F)	746.7
8	Br	2,5-di-$CH_3OC_6H_3$	89	83.4 (pentet, ^2J = 149.0 Hz, 1F) 62.1 (d, ^2J = 149.8 Hz, 4F)	724.7
9	Cl	2,4-di-ClC_6H_3	97	83.1 (pentet, ^2J = 149.0 Hz, 1F) 62.0 (d, ^2J = 149.9 Hz, 4F)	734.6
10			61	82.3 (pentet, ^2J = 150.4 Hz, 1F) 61.7 (d, ^2J = 149.7 Hz, 4F)	
11	Br	4-$NO_2C_6H_4$	93	82.3 (pentet, ^2J = 153.3 Hz, 1F) 61.7 (d, ^2J = 149.7 Hz, 4F)	
12	Br	2,5-di-$CH_3OC_6H_3$	91	83.4 (pentet, ^2J = 150.5 Hz, 1F) 62.0 (d, ^2J = 149.6 Hz, 4F)	
13	Br	4-BrC_6H_4	99	83.2 (pentet, ^2J = 150.7 Hz, 1F) 61.9 (d, ^2J = 149.8 Hz, 4F)	

selenocarboxamides,[16] which are typically used as important precursors for the synthesis of the selenium−nitrogen rich heterocycles.[17,18] In general, the methods for the synthesis of selenoamides involve the reaction of nitrile with H_2Se, NaSeH,[16d] derived from $NaBH_4/Se$[16d,e,19], Se/CO,[20] or tris(trimethylsilyl)monoselenophosphate,[21] Another method involves the reaction of nitrile with Al_2Se_3 in the presence of Et_3N/pyridine/H_2O[22] or with P_2Se_5 in the presence of EtOH/H_2O.[17] These synthetic methods need toxic/not readily available reagents. We have previously reported a highly efficient approach for the preparation of a series of primary aryl-selenoamides from the reaction of arylnitriles with Woollins' reagent, followed by treatment with water.[23] Therefore, by using this documented method, 4-pentafluorosulfanylbenzoselenoamide **1** was prepared in 87% yield by the reaction of 4-pentafluorosulfanylbenzonitrile and Woollins' reagent, followed by hydrolysis with water. Then cyclization of selenoamide **1** with an equivalent of α-haloketones gave a series of 1,3-selenazoles **2−9** (Scheme 1) in excellent yields, as shown in Table 1. The lower yields of 1,3-selenazoles **5** (90%) and **8** (89%) could be attributed to the steric hindrance of the two substituents (methoxy groups) in one of the phenyl rings.

All new compounds **1−9** are yellow or white or purple crystalline solids which are soluble in common organic solvents. Compounds **1−9** were characterized by ^1H, ^{13}C, ^{19}F, and ^{77}Se NMR spectroscopy, IR spectroscopy, and mass spectrometry. All compounds showed the anticipated $[M + H]^+$ or $[M + Na]^+$ peak in their mass spectra and satisfactory accurate mass measurements. The IR spectra of compounds **2−9** show an absorption band between 1508−1606 cm^{-1} due to ν(C−N) stretch and an absorption band in the range of 593−584 cm^{-1}, which might be assigned to the ν(Se−C) vibration.[16f,24,25] The ^1H NMR spectra consist of a strong single peak of the sole azole proton in the range of 8.19−8.83 ppm and the ^{19}F NMR spectra comprise a quintet pattern for one F atom and a doublet pattern for the other four F atoms in SF_5 group (more details shown in the Experimental Section). The spectroscopic data for **2−9** provide support for the formulation of these compounds. It is worth noting that the ^{77}Se NMR chemical shift values are in the range of 724.5−746.7 ppm in 1,3-selenazoles **2−9** and are significantly lower than that in their starting material selenoamide **1** (766.1 ppm) (Table 1). In general, more electron-withdrawing groups result in higher ^{77}Se chemical shifts.

Similarly, four sulfur analogues, thioamide **10** and 1,3-thiazoles **11−13**, were also prepared following the same general procedure as the preparation of compounds **1−9**. 4-Pentafluorosulfanylbenzothioamide **10** was obtained in 61% yield by the reaction of 4-pentafluorosulfanylbenzonitrile and Lawesson's reagent, followed by treatment with water. Further treating thioamide **10** with an equivalent of α-haloketones afforded the corresponding 1,3-thiazoles **11−13** in excellent yields, as shown in Scheme 2 and Table 1. Once again, new compounds **10−13** are yellow or white crystalline solids, which are soluble in common organic solvents. In their mass spectra, we observed the anticipated $[M + H]^+$ or $[M + Na]^+$ peak, and satisfactory accurate mass measurements were found for all compounds. A strong single peak of the sole azole proton at the range of 7.49−8.02 ppm in the ^1H NMR spectra of compounds **11−13** was observed, and we note that the values are obviously

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Table 2. Details of the X-ray Data Collections and Refinements for Compounds 1−6

compound	1	2	3	4	5	6
formula	$C_7H_6F_5NSSe$	$C_{15}H_9ClF_5NSSe$	$C_{15}H_9F_5N_2O_2SSe$	$C_{16}H_{12}F_5NO_2SSe$	$C_{15}H_8Cl_2F_5NSSe$	$C_{16}H_{12}F_5NSSe$
M_w	310.14	444.71	455.26	440.29	479.15	424.29
crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	*Pnma*	*P*-1	*C*2/*c*	$P2_1/n$	$Pna2_1$
a/Å	17.608(10)	12.536(3)	7.911(11)	35.77(5)	15.288(8)	7.789(9)
b/Å	5.871(2)	6.791(4)	10.43(2)	6.207(8)	5.682(3)	33.34(4)
c/Å	10.079(4)	18.646(4)	11.61(2)	15.93(3)	19.113(10)	6.278(8)
α	90	90	109.181(3)	90	90	90
β	106.40(2)	90	109.09(12)	107.03(2)	101.98(11)	90
γ	90	90	100.490(13)	90	90	90
U/A^3	999.6(6)	1587.3(5)	808(2)	3381(8)	1624.1(15)	1630(4)
Z	4	4	2	8	4	4
μ/cm^{-1}	40.036	27.154	25.194	24.003	28.204	24.81
reflections collected	8097	15 600	10 284	20 519	11 719	17 000
independent reflections	1146	1972	5146	5631	2854	5227
R_{int}	0.1404	0.1126	0.0810	0.0717	0.1759	0.1299
*R*1	0.0621	0.0590	0.0599	0.0714	0.0718	0.0629
*wR*2 [$I > 2\sigma(I)$]	0.1745	0.1102	0.1479	0.2290	0.2210	0.1899

Table 3. Details of the X-ray Data Collections and Refinements for Compounds 7, 8, 10−13

compound	7	8	10	11	12	13
formula	$C_{15}H_9F_5N_2O_2SSe$	$C_{17}H_{14}F_5NO_2SSe$	$C_7H_6F_5NS_2$	$C_{15}H_9F_5N_2O_2S_2$	$C_{17}H_{14}F_5NO_2S_2$	$C_{15}H_9F_5BrNS_2$
M_w	455.26	470.32	263.24	408.36	423.42	442.26
crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	*P*-1	$P2_{1/c}$	*Pnma*	$P2_{1/c}$	*Pnma*
a/Å	6.761(5)	9.650(4)	17.361(6)	12.889(8)	12.075(10)	12.804(3)
b/Å	12.748(8)	12.717(6)	5.7603(16)	6.737(4)	9.345(7)	6.7729(16)
c/Å	18.642(12)	15.930(7)	9.950(3)	18.371(12)	16.111(13)	18.485(4)
α	90	77.557(13)	90	90	90	90
β	90	75.92(11)	106.615(7)	90	106.76(3)	90
γ	90	77.43(2)	90	90	90	90
U/A^3	1607(2)	1823(2)	953.4(5)	1595.1(18)	1741(3)	1603(6)
Z	4	4	4	4	4	4
μ/cm^{-1}	25.35	22.354	5.98	4.019	3.697	28.817
reflections collected	13 869	23 912	11 794	11 651	12 559	13 170
independent reflections	3765	11 731	1717	1528	3056	1536
R_{int}	0.0747	0.0478	0.1463	0.0782	0.1227	0.1718
*R*1	0.0544	0.0553	0.1210	0.0495	0.1192	0.0567
*wR*2 [$I > 2\sigma(I)$]	0.1681	0.1658	0.3179	0.1504	0.3828	0.1550

smaller than those (8.19−8.83 ppm) in compounds **2**−**9**. Not surprisingly, the ^{19}F NMR spectra comprise two typical patterns (a quintet pattern for one F atom and a doublet pattern for another four F atoms) for the SF_5 group in compounds **11**−**13**.

X-ray Single-Crystal Structures. Crystals of compounds **1**−**8** and **10**−**13** suitable for X-ray crystallographic analysis were grown by diffusion of a dichloromethane solution of the compound into hexane at room temperature in each case. All structures have a single molecule of the compound in the asymmetric unit, the exception being compound **8**, which contains two independent molecules with mirror symmetry. Crystal data and structure refinement for compounds **1**−**8** and **10**−**13** are summarized in Tables 2 and 3. Selected bond lengths and angles are listed in Tables 4−6.

The C═Se bond length in compound **1** (Figure 1) is 1.828(8) Å, which is within the range of ordinary C═Se bond distances in other selenoamides [1.81(5)−1.856(4) Å],[23,26−30] whereas the C−N bond distance [1.328(11) Å] is marginally longer than that in literature values [1.270(7)−1.324(8) Å].[30] The selenoamide functionality is not particularly coplanar with the aryl backbone, with the selenium atom lying 0.263 Å from the aryl ring plane and with the Se(1)−C(1)−N(1) mean plane inclining by 16.7° from the aryl ring plane in this case. In thioamide **10**, the conformation is quite similar to selenoamide **1**, and the bond distances for C═S and C−N are 1.679(7) and 1.321(9) Å, respectively, which are very close to the literature values for the thioamides.[31,32] The thioamide functionality is not coplanar with the phenyl backbone with the sulfur atom lying 0.274 Å from the phenyl ring plane and the S(1)−C(1)−N(1) plane inclined by 19.2° from the phenyl mean plane. However, it is interesting to note that in both **1** and **10**, the pentafluorosulfanyl SF_5 group is arranged with the equatorial S−F bonds essentially bisecting the aryl plane as previously proposed to be energetically favorable[33] and in accord with the strongly electron-withdrawing and highly lipophilic properties of the pentafluorosulfanyl (SF_5) group. The sulfur atom of the SF_5 group has octahedral coordination geometry for both

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Table 4. Selected Bond Distances [Å] and Angles [°] for Compounds 1 and 10 (* E = Se or S)

	1	10
E1*−C7	1.828(8)	1.679(7)
N1−C7	1.328(11)	1.321(9)
C4−C7	1.484(11)	1.492(12)
S1−F1	1.592(7)	1.587(4)
S1−F2	1.586(5)	1.604(4)
S1−F3	1.570(7)	1.587(4)
S1−F4	1.585(5)	1.564(4)
S1−F5	1.586(5)	1.570(5)
E1−C7-N1	119.7(6)	121.4(6)
E1−C7-C4	123.2(6)	121.5(5)
N1−C7−C4	117.0(7)	117.1(6)
F1−S1−F2	90.0(3)	89.8(2)
F1−S1−F3	176.4(3)	175.9(3)
F1−S1−F4	88.7(3)	90.3(2)
F1−S1−F5	88.1(3)	88.2(2)
F2−S1−F3	90.6(3)	89.5(2)
F2−S1−F4	175.4(3)	176.8(3)
F2−S1−F5	87.9(3)	88.0(3)
F3−S1−F4	90.5(3)	90.2(2)
F3−S1−F5	88.4(3)	87.8(2)
F4−S1−F5	87.7(3)	88.8(2)

compounds. In **10**, the bond distances of S−F_{ax} 1.570(5) Å; S−F_{eq} 1.587(4), 1.604(4), 1.587(4), 1.564(4) Å; the bond angles of F_{ax}−S−F_{eq} 88.2(2), 88.0(3), 87.8(2), 88.8(2)°; F_{eq}−S−F_{eq} 89.8(2), 90.3(2), 89.5(2), 90.2(2)° and the C−S bond distance of 1.679(7) Å are comparable to that in the analogous 3-pentafluorosulfanylbenzoic acid,[34] 3-acetamidopentafluorosulfanylbenzene, and 4-acetamidopentafluorosulfanylbenzene.[35]

In both **1** and **10**, there are hydrogen bond interactions between the primary amine hydrogen atoms of one molecule and the S or Se atom of another molecule resulting in a "infinite chain" framework built from the basic dimer unit as shown in Figure 2. The N−H···Se distance is 2.779 Å, and Se···N is 3.490 Å, and along with the angle N−H···Se 126.4°, these are the typical motifs for hydrogen bonding in primary selenoamides.[23,30] It is interesting to note that strong hydrogen bonding is observed in **10**, cf. **1**, in which the N−H···S distance is 2.615 Å and S···N 3.303(6) Å, with the N−H···S angle being 127.4°.

The supramolecular assemblies in **1** and **10**, forming three-dimensional networks, were built by the N−H···E (S or Se) hydrogen bonds and π-systems as shown in Figure 3. "Head-to-head" pairs of molecules are linked by paired N−H···E (S or Se) hydrogen bonds to form the centrosymmetric pair unit. The centrosymmetric pair unit is the key building block for the network conformation held together by strong $\pi-\pi$ stacking interaction leading to the three-dimensional network motifs. The SF_5 groups of molecules in adjacent tapes pack together, although there are no close contacts between the SF_5 group and the other surrounding functional groups.

The crystal characteristics of compounds **2**−**8** and **11**−**13**, despite their rather similar molecular formulas, are all somewhat different. Thus, compounds **2**, **5**, **6**, **7**, **8**, **11**, **12**, and **13** are assigned to seven different space groups (*Pnma*, *P*-1, *C*2/*c*, $P2_1/n$, $Pna2_1$, $P2_12_12_1$, and $P2^{1/c}$, respectively) belonging to three different space systems (monoclinic, orthorhombic, and triclinic space systems). Surprisingly, the structures **2**, **11**, and **13** show the newly formed five-membered N(1)−C(2)−E(3)−C(4)−C(5) rings being a perfectly planar arrangement, which is also coplanar with two peripheral aryl ring planes. The

Table 5. Selected Bond Distances [Å] and Angles [°] for Compounds 2−6

	2	3	4	5	6
N1−C2	1.295(7)	1.293(5)	1.308(5)	1.299(13)	1.310(9)
N1−C5	1.388(7)	1.385(6)	1.398(6)	1.398(15)	1.399(9)
C2−E3	1.890(6)	1.893(6)	1.905(5)	1.894(11)	1.918(8)
E3−C4	1.837(6)	1.839(4)	1.829(5)	1.830(11)	1.876(8)
C4−C5	1.346(8)	1.375(7)	1.388(7)	1.344(15)	1.381(10)
S1−F1	1.573(3)	1.576(5)	1.583(4)	1.574(7)	1.591(5)
S1−F2	1.572(4)	1.572(4)	1.592(5)	1.575(6)	1.602(6)
S1−F3	1.593(4)[a]	1.559(5)	1.589(5)	1.567(7)	1.587(5)
S1−F4	1.572(4)[a]	1.589(4)	1.591(4)	1.571(6)	1.587(5)
S1−F5	1.573(3)	1.585(4)	1.587(4)	1.579(7)	1.594(5)
N1−C2−E3	114.2(4)	114.2(4)	114.6(4)	113.1(8)	113.6(5)
C2-E3-C4	84.0(3)	84.8(2)	85.0(2)	84.4(5)	84.5(3)
E3−C4−C5	112.3(5)	110.9(4)	111.2(4)	113.1(9)	111.2(6)
C4−C5−N1	116.3(5)	116.7(3)	117.0(4)	114.9(4)	116.1(6)
C5−N1−C2	113.2(5)	113.5(4)	112.2(4)	114.4(9)	114.6(6)
F1−S1−F2	89.97(17)	89.5(2)	89.6(3)	89.8(4)	91.0(3)
F1−S1−F3	174.58(18)[a]	174.89(17)	175.59(18)	175.4(5)	175.5(3)
F1−S1−F4	88.95(17)[a]	89.2(2)	89.7(3)	89.4(4)	89.5(3)
F1−S1−F5	87.16(15)	87.32(18)	87.7(2)	87.6(4)	87.7(3)
F2−S1−F3	90.6(2)[a]	91.0(3)	90.3(3)	89.6(4)	89.2(3)
F2−S1−F4	174.58(18)[a]	175.4(2)	175.55(19)	175.2(4)	175.4(3)
F2−S1−F5	87.48(15)	87.76(19)	87.5(2)	87.8(4)	89.9(3)
F3−S1−F4	89.95(17)[a]	89.9(2)	90.1(3)	90.9(4)	87.8(3)
F3−S1−F5	87.48(15)[a]	87.61(18)	87.9(2)	87.9(4)	89.9(3)
F4−S1−F5	87.16(15)[a]	87.82(18)	88.1(2)	87.4(3)	87.8(3)

[a]E: Se or S; F2A and F1A in compound **2** correspond to the respective F3 and F4 in compounds **3**−**8**, **12**.

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Table 6. Selected Bond Distances [Å] and Angles [°] for Compounds 7, 8, 11−13

	7	8	11	12	13
N1−C2	1.310(7)	1.308(4)[1.304(5)]	1.299(5)	1.299(13)	1.295(12)
N1−C5	1.392(7)	1.390(6)[1.393(5)]	1.378(6)	1.391(14)	1.361(10)
C2−E3	1.875(6)	1.891(4)[1.889(3)]	1.728(4)	1.735(10)	1.723(9)
E3−C4	1.828(7)	1.851(4)[1.852(5)]	1.673(6)	1.701(11)	1.670(9)
C4−C5	1.375(8)	1.368(6)[1.377(5)]	1.376(7)	1.395(12)	1.386(13)
S1−F1	1.572(5)	1.571(3)[1.581(4)]	1.575(3)	1.588(6)	1.569(5)
S1−F2	1.579(5)	1.582(3)[1.579(4)]	1.575(3)[a]	1.608(5)	1.576(6)[a]
S1−F3	1.585(6)	1.592(3)[1.576(4)]	1.578(3)[a]	1.596(6)	1.576(6)
S1−F4	1.581(6)	1.577(3)[1.591(4)]	1.578(3)[a]	1.596(6)	1.569(5)[a]
S1−F5	1.584(4)	1.583(4)[1.585(3)]	1.585(3)	1.589(8)	1.588(6)
N1−C2−E3	113.2(4)	113.5(3)[114.3(3)]	113.3(3)	114.9(8)	113.8(7)
C2−E3−C4	85.9(3)	84.67(17)[84.56(15)]	90.1(2)	89.6(5)	90.3(5)
E3−C4−C5	111.0(5)	111.9(3)[111.7(3)]	111.4(4)	110.5(8)	110.1(7)
C4−C5−N1	115.9(5)	115.4(3)[115.4(4)]	112.9(4)	113.6(9)	114.3(8)
C5−N1−C2	114.0(5)	114.5(3)[114.1(3)]	112.3(4)	111.3(8)	111.5(8)
F1−S1−F2	90.2(3)	90.06(17)[90.0(2)]	90.57(17)[a]	89.6(3)	90.0(2)[a]
F1−S1−F3	174.3(3)	174.2(2)[175.30(18)]	174.78(14)	174.9(4)	174.1(3)
F1−S1−F4	89.7(3)	89.96(19)[89.4(2)]	89.73(14)[a]	90.9(3)	88.7(3)[a]
F1−S1−F5	86.9(3)	87.44(18)[87.3(2)]	87.70(13)	87.9(4)	86.8(2)
F2−S1−F3	88.9(3)	88.62(16)[90.5(2)]	89.73(14)[a]	89.6(3)	90.7(3)[a]
F2−S1−F4	174.9(3)	174.72(18)[175.36(16)]	174.78(14)[a]	175.2(4)	174.1(3)[a]
F2−S1−F5	86.9(3)	87.19(16)[87.92(19)]	87.6(2)[a]	87.0(4)	87.4(2)[a]
F3−S1−F4	90.7(3)	90.84(18)[89.7(2)]	89.3(3)[a]	89.5(3)	90.0(32)[a]
F3−S1−F5	87.4(3)	86.88(17)[88.03(19)]	87.1(2)	87.0(4)	87.4(2)
F4−S1−F5	88.0(3)	87.54(17)[87.45(19)	87.1(2)[a]	87.3(4)	86.8(2)[a]

[a]E: Se or S; F1A, F2A and F2 in compound **11** correspond to the respective F2, F3, and F4 in compounds **3**−**8**, **12**; F3A and F1A in compound **13** correspond to the respective F2 and F4 in compounds **3**−**8**, **12**.

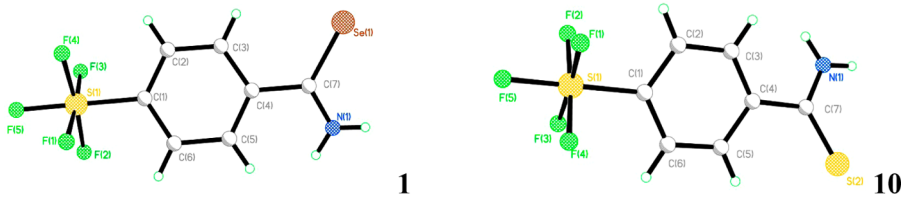

Figure 1. Single crystal X-ray structures of selenoamide **1** and thioamide **10**.

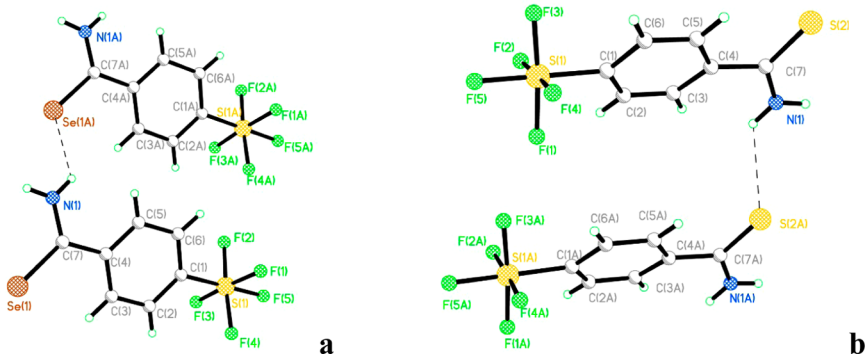

Figure 2. Molecular structures of **1** (a) and **10** (b) showing the atom-labeling scheme and the intermolecular N−H···Se and N−H···S hydrogen bonds (dashed line).

similar motifs could be seen in previously reported 1,3-selenazoles.[36] However, the newly formed five-membered N(1)−C(2)−E(3)−C(4)−C(5) rings in structures of **3**, **4**, **5**, **6**, **7**, **8** and **12** adopt the near-planar conformation with chalcogen (Se or S) atom being 0.006, 0.007, 0.009, 0.005, 0.005, 0.005[0.003], and 0.001 Å, respectively, out of the N(1)−C(2)−E(3)−C(4)−C(5) mean plane with the two peripheral aryl ring planes having dihedral angles of 16.48, 18.86, 11.61, 21.64, 6.19, 12.58(3.62), 11.52°, respectively. For all structures of **3**, **4**, **5**, **6**, **7**, **8**, and **12**, the dihedral angles between the newly formed five-membered ring N(1)−C(2)−E(3)−C(4)−C(5) mean planes and the SF_5-attaching aryl ring planes varying from 1.81 to 20.39° indicate the apparent effect of the peripheral aryl rings with different substituents.

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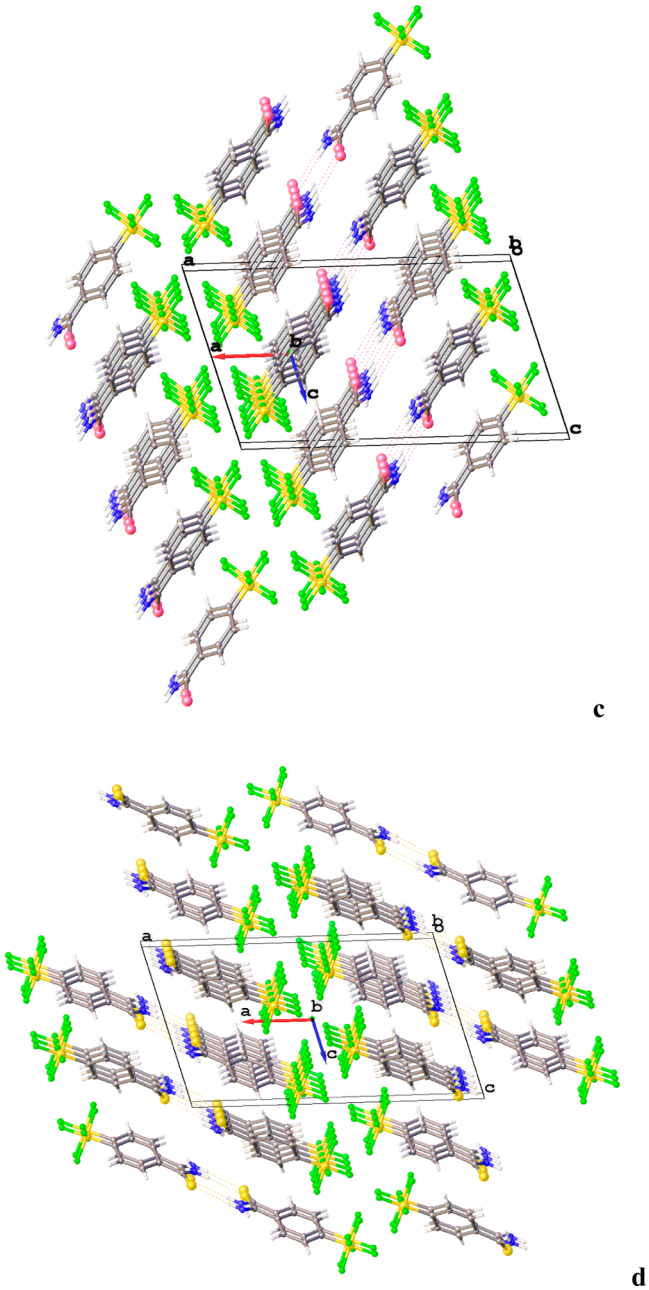

Figure 3. Views of the three-dimensional network in **1** (c) and **10** (d) formed by the combination of N−H···E (S or Se) hydrogen bonding and π-stacking.

The equatorial planes of the SF_5 group having an umbrella shape canting toward the fifth axial fluorine atom in all structures, as previously reported with the SF_5 group.[34] The F_{ax} and S atoms in structures of **2**, **3**, **7**, **11**, and **13** are coplanar with the adjacent aryl ring planes. Although the observed deviations of F_{ax} and S atoms out of the adjacent aryl ring planes in structures of **5**, **6**, **8** range from 0.020−0.179 Å, 0.015−0.097 Å, respectively. Two exceptions are structures of **4** and **12**, only the F_{ax} atom in structure of **4** is coplanar with the adjacent aryl ring plane with the S atom being 0.030 Å from the aryl ring plane. By contrast, the S atom in structure of **12** is coplanar with the adjacent aryl ring plane, and the F_{ax} atom is 0.030 Å out of this plane. The results may explain the relatively high dipole moment of the aromatic pentafluorosulfanyl group SF_5 resulting in an additional component to the overall dipole moment in the direction of the long molecular axis.[37]

The C−Se bond distances in structures of **2**−**8** differ from 1.828(7) to 1.918(8) Å, covering the range of C−Se bond lengths found in the reported 1,3,4-selenadiazoles [1.87−1.90 Å];[30,38−40] however, these values are marginally shorter than those expected for a typical C−Se single bond (ca. 1.92−1.94 Å). In addition, the C═N bond lengths in these structures differing from 1.293(5) to 1.310(9) Å and the C−N bond distances ranging from 1.385(6) to 1.399(9) Å are close to the reported 1,3-seleazoles [1.268(11) Å for the C═N bond and 1.384(11) Å for the C−N];[16f] however, these values are significantly shorter than the usual C−N single bond length of 1.47 Å,[36,41,42] indicating clearly that some degree of delocalization is present. The C−Se−C angles in structures of **2**−**8** [84.0(3)−85.9(3)°] are marginally wider than that in the reported similar structure [83.3(5)°].[16f] The results further support the assertion of a special effect of the peripheral SF_5 group within the molecules.

When compared to the above structures of **2**−**8**, their sulfur analogous structures of **11**−**13** have obvious differences in C−S and C−N bond lengths and C−S−C angles. The C−S bond distances ranging from 1.670(9) to 1.701(11) Å and the C═N and C−N bond lengths differing from 1.295(12) to 1.299(13) Å and 1.361(10) to 1.391(14) Å, respectively, are in good agreement with those observed in the similar structures.[43,44] However, the C−S bond lengths are considerately shorter, and the C−S−C angles altering from 89.6(5) to 90.3(5)° are much wider than that in their selenium counterparts (Figure 4).

Although the similarity of molecular geometries and types of intramolecular interactions might lead to similar packing motifs, this is not found in each case. The intermolecular interactions, namely, π−π interactions and weak C−H···O hydrogen bonding and C−H···F hydrogen bonding and C−H···Br close contacts, combined in a different way, give a variety of packing networks. In **4**, the layer-like network consists of the crossed-layer-like "three molecules group" and the "two molecules group", which are built up by the π−π interaction, the weak C−H···O hydrogen bonding, and the weak C−H···F hydrogen bonding, leading to the three-dimensional motif network. The situation in the case of **13** is somewhat different. The sheet network comprises a "single molecule sheet", which is linked together by the weak C−H···Br hydrogen bonding and the weak C−H···F hydrogen bonding, C−H···π interaction, and π−π interaction, resulting in the different three-dimensional motif network (Figures 5 and 6).

In summary, Woollins' reagent or Lawesson's reagent reacts with an equivalent of 4-pentafluorosulfanylbenzonitrile, and when followed by treatment with water, the reaction led to the corresponding 4-pentafluorosulfanylbenzoselenoamide (**1**) and 4-pentafluorosulfanylbenzothioamide (**10**) in good yields. The cyclization of primary 4-pentafluorosulfanylbenzoselenoamide or 4-pentafluorosulfanylbenzothioamide with α-haloketones afforded a variety of new 2,4-diaryl-1,3-selenazoles **2**−**9** and 2,4-diaryl-1,3-thiazoles **11**−**13** in excellent yields. The structures of all new compounds have been elucidated by using ^{1}H, ^{13}C, ^{77}Se, ^{19}F NMR spectroscopy, and accurate mass measurement. Ten single-crystal structures were investigated. 4-Pentafluorosulfanylbenzoselenoamide (**1**) and 4-pentafluorosulfanylbenzothioamide (**10**) have very close structural similarity along with similar intermolecular interactions, with π−π stacking and the weak N−H···E (E = S or Se) hydrogen bonding. However, 1,3-selenazoles **2**−**9** and 1,3-thiazoles **11**−

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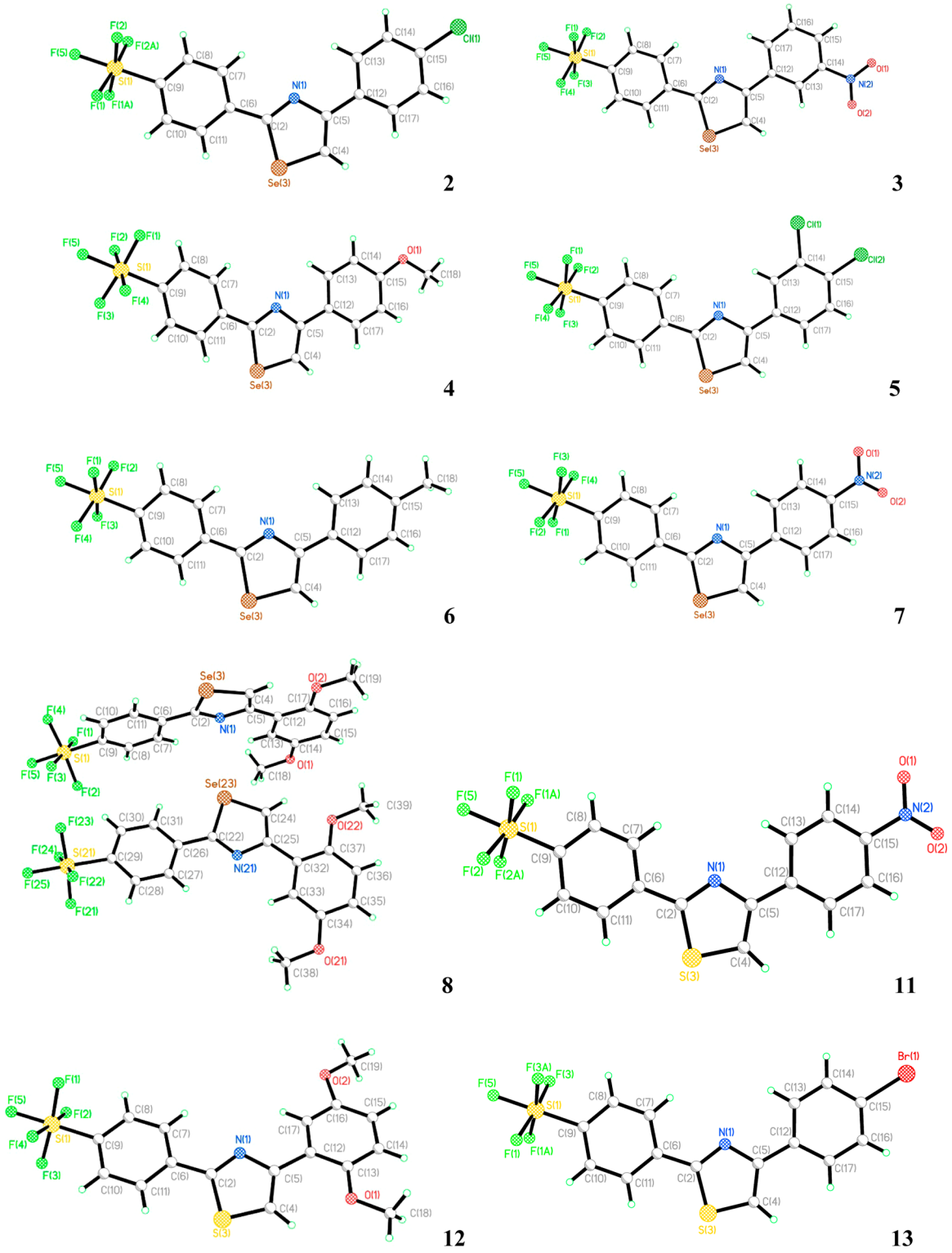

Figure 4. Single crystal X-ray structures of 1,3-selenazoles **2**–**8** and 1,3-thiazoles **11**–**13**.

13 display a diverse story of molecular configuration and intermolecular interaction information. The structures of **2**, **11**, and **13** show the newly formed five-membered N(1)–C(2)–E(3)–C(4)–C(5) rings being perfectly planar and also coplanar with two substituent aryl ring planes. However, near-planar conformations were observed for the newly formed five-membered N(1)–C(2)–E(3)–C(4)–C(5) rings in the other seven structures. Typical π–π intermolecular interactions and the weak C–H···π and C–H···X (X = Br, F, O) hydrogen bonding have been highlighted in two cases of **4** and **13** for their packing configurations.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using predried solvents and standard Schlenk techniques, and subsequent chromatographic and workup procedures

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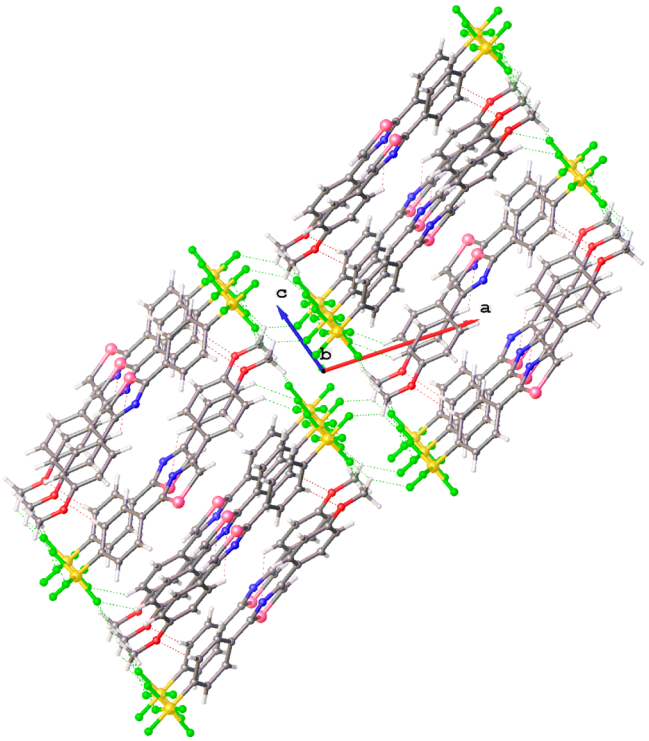

Figure 5. View of the three-dimensional network, which makes up the structure in **4**, formed by three sets of hydrogen bonds: C−H···O hydrogen bonding (shown as red dashed line), C−H···N hydrogen bonding (shown as orange dashed line), and C−H···F hydrogen bonding (shown as green dashed line), as well as the $\pi-\pi$ interaction which connects them into a three-dimensional network.

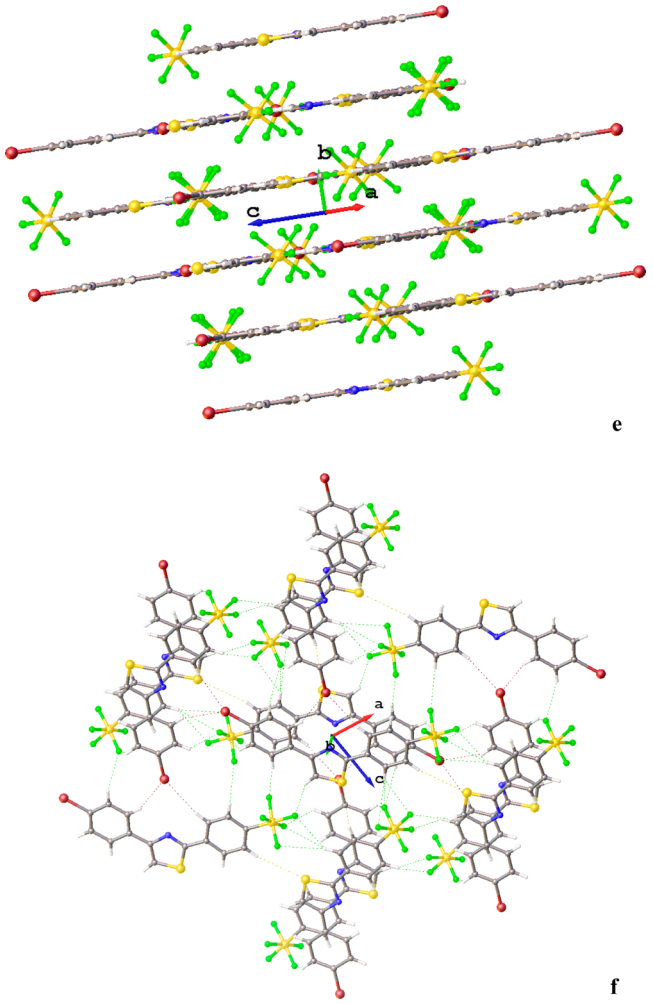

Figure 6. View of the three-dimensional network in **13**. (e) A view of a three-dimensional layer-like network. (f) A view of the network clearly displaying C−H···Br close contacts (shown as the red dashed line) and C−H···F (shown as the green dashed line) contacts, as well as the C−H···π interaction and $\pi-\pi$ interaction, which lead into the three-dimensional network.

were performed in air. ^{1}H (270 MHz), ^{13}C (67.9 MHz), and ^{77}Se-{^{1}H} (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise). ^{19}F NMR spectra were recorded at 25 °C (unless stated otherwise) and were referenced to $CFCl_3$ as the external standard. Chemical shifts are reported in parts per million (ppm), and coupling constants (J) are given in Hertz (Hz). IR spectra were recorded as KBr pellets in the range of 4000−250 cm^{-1}.

X-ray crystal structures were determined for compounds **1**−**8** and **10**−**13** at −148(1) °C[45] with SHINE optic using Mo Kα radiation (k = 0.71073 A). The data were corrected for Lorentz, polarization, and absorption. The data were collected and processed using CrystalClear.[46] The structures were solved by direct methods[47] and expanded using Fourier techniques.[48] Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[49] and SHELXL 97.[50] These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data center, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223−336−033; e-mail: deposit@ccdc.cam.ac.uk. CCDC **1** 992938, **2** 985909, **3** 989010, **4** 985911, **5** 992939, **6** 985913, **7** 985914, **8** 985915, **10** 992940, **11** 992941, **12** 985918, **13** 992942.

Synthesis of 4-Pentafluorosulfanylbenzoselenoamide (1).[23] A mixture of 4-pentafluorosulfanylbenzonitrile (0.458 g, 2.0 mmol) and Woollins' reagent (1.07 g, 2.0 mmol) in 20 mL of dry toluene was refluxed for 8 h. After the reaction mixture was cooled to 90 °C, 1.0 mL of water was added, and the reaction mixture was allowed to continue refluxing for another 1 h. After cooling the reaction mixture to room temperature, it was concentrated to ca. 5.0 mL in vacuo, extracted with dichloromethane (20 mL × 3), combined the dichloromethane solution, and dried over $MgSO_4$. After we filtered and dried the sample to remove the solvent, the organic residue was purified by a silica gel column (9:1 ethyl acetate/dichloromethane) to give the expected compounds **1** as a bright yellow solid (0.270 g) in 87% isolated yield: mp, 148−150 °C; selected IR (KBr, cm^{-1}) 1629(s), 1428(s), 1308(m), 1263(m), 1198(m), 1146(m), 1099(m), 891(s), 836(vs), 699(m), 669(m), 637(m), 601(s), 573(m); ^{1}H NMR (CD_2Cl_2, δ) 8.77 (s, 2H,), 7.92 (d, J(H,H) = 8.8 Hz, 2H,), 7.77 (d, J(H,H) = 8.8 Hz, 2H,) ppm; ^{13}C NMR (CD_2Cl_2, δ) 205.7, 127.0, 126.4, 126.3, 126.2 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 766.1 ppm; ^{19}F NMR (CD_2Cl_2, δ) 82.3 (quintet, ^{2}J(F,F) = 150.4 Hz, 1F), 61.7 (d, ^{2}J(F,F) = 149.7 Hz, 4F) ppm; MS (APCI^{+}, m/z) 312 [M + H]$^{+}$; accurate mass measurement (APCI^{+}, m/z): [M + H]$^{+}$ Calcd for $C_7H_6F_5SNSeH$ 311.9379; Found 311.9376.

General Procedure for the Synthesis of Compounds 2−9. A mixture of α-haloketones (1.0 mmol) in 20 mL of ethanol was added dropwise to a refluxing solution of 4-pentafluorosulfanylbenzoselenoamide (0.263 g, 1.0 mmol) in 20 mL of ethanol in the course of 1 h. The reaction mixture was then allowed to reflux for another 1 h. After the mixture was cooled to room temperature, it was concentrated by a rotary evaporator. The residue was neutralized with 5% aqueous ammonia (30 mL) and extracted with dichloromethane (30 mL × 3), combined the organic layers, washed with water (20 mL × 3), and dried over $MgSO_4$. After we filtered and dried the sample to remove solvent in vacuo, the organic residue was purified by a silica gel column (1:9 ethyl acetate/dichloromethane) to give the expected products **2**−**9**.

4-(4′-Chlorophenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (2). Purple solid (0.440 g) in 99% isolated yield; mp,

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170−172 °C; selected IR (KBr, cm^{-1}) 1595(m), 1508(m), 1481(s), 1402(m), 1284(m), 1091(s), 1043(m), 1012(m), 958(m), 821(vs), 738(m), 658(m), 587(s); ^1H NMR (CD_2Cl_2, δ) 8.24 (s, 1H), 8.06 (d, J(H,H) = 8.3 Hz, 2H), 7.94 (d, J(H,H) = 8.5 Hz, 2H), 7.83 (d, J(H,H) = 8.5 Hz, 2H), 7.41 (d, J(H,H) = 8.3 Hz, 2H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 171.4, 156.2, 139.0, 133.9, 133.6, 129.0, 128.0, 127.1, 126.8, 126.7, 120.8 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 734.5 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.2 (quintet, ^2J(F,F) = 152.3 Hz, 1F), 62.0 (d, ^2J(F,F) = 149.5 Hz, 4F) ppm; MS (APCI$^+$, m/z) 446 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_{15}H_9ClF_5NSSeH$ 445.9300; Found 445.9294.

4-(3′-Nitrophenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (3). Dark purple solid (0.446 g) in 98% isolated yield: mp, 138−140 °C; selected IR (KBr, cm^{-1}) 1600(m), 1527(s), 1482(m), 1403(m), 1347(s), 1278(m), 1099(m), 966(m), 851(vs), 822(vs), 741(m), 660(m), 598(m), 584(m); ^1H NMR (CD_2Cl_2, δ) 8.83 (s, 1H), 8.43 (s, 1H), 8.34−8.08 (m, 3H), 7.86 (d, J(H,H) = 8.8 Hz, 2H), 7.63 (d, J(H,H) = 8.8 Hz, 2H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 172.1, 154.9, 148.9, 138.8, 136.5, 132.4, 129.9, 127.2, 126.9, 126.8, 122.7, 122.6, 121.5 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 742.6 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.0 (quintet, ^2J(F,F) = 153.3 Hz, 1F), 61.9 (d, ^2J(F,F) = 149.8 Hz, 4F) ppm; MS (APCI$^+$, m/z) 457 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_{15}H_9F_5N_2O_2SSeH$ 456.9543; Found 456.9536.

4-(4′-Methoxyphenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (4). Pale yellow solid (0.420 g) in 95% isolated yield: mp, 106−108 °C; selected IR (KBr, cm^{-1}) 1604(s), 1525(m), 1511(m), 1483(m), 1461(m), 1402(m), 1302(m), 1254(s), 1175(m), 1028(m), 959(m), 844(vs), 745(m), 665(m), 640(m), 586(s); ^1H NMR (CD_2Cl_2, δ) 8.50 (s, 1H), 8.10 (d, J(H,H) = 8.5 Hz, 2H), 7.91 (d, J(H,H) = 8.5 Hz, 2H), 7.82 (d, J(H,H) = 7.2 Hz, 2H), 6.95 (d, J(H,H) = 7.2 Hz, 2H), 3.83 (s, 3H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 170.9, 159.8, 139.3, 131.2, 130.5, 128.0, 127.1, 126.7, 118.4, 114.1, 113.7, 55.4 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 725.8 ppm; ^{19}F NMR (CD_2Cl_2, δ) 84.3 (quintet, ^2J(F,F) = 152.1 Hz, 1F), 62.0 (d, ^2J(F,F) = 149.8 Hz, 4F) ppm; MS (APCI$^+$, m/z) 442 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_{16}H_{12}ONF_5SSeH$ 441.9798; Found 441.9787.

4-(3′,4′-Dichlorophenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (5). Pale purple solid (0.430 g) in 90% isolated yield: mp, 115−117 °C; selected IR (KBr, cm^{-1}) 1508(m), 1475(m), 1401(m), 1307(m), 1252(m), 1128(m), 1099(m), 1051(m), 964(m), 836(vs), 744(m), 729(m), 665(m)m 590(s); ^1H NMR (CD_2Cl_2, δ) 8.27 (s, 1H), 8.13 (s, 1H), 8.05 (d, J(H,H) = 9.1 Hz, 2H), 7.85−7.79 (m, 3H), 7.50 (d, J(H,H) = 8.5 Hz, 1H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 171.7, 154.9, 135.0, 132.9, 131.9, 130.8, 128.6, 127.2, 126.9, 126.8, 126.7, 125.9, 121.8 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 739.9 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.1 (quintet, ^2J(F,F) = 150.4 Hz, 1F), 62.0 (d, ^2J(F,F) = 149.8 Hz, 4F) ppm; MS (APCI$^+$, m/z) 480 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z) [M + H]$^+$ Calcd for $C_{15}H_9NCl_2F_5SSeH$ 479.8908; Found 479.8891.

4-(4′-Methylphenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (6). Pale purple solid (0.400 g) in 94% isolated yield: mp, 152−154 °C; selected IR (KBr, cm^{-1}) 1507 (m), 1480(s), 1448(m), 1400(m), 1296(m), 1227(m), 1098(m), 1041(m), 958(s), 838(vs), 824(vs), 742(s), 668(m), 588(s), 521(m); ^1H NMR (CD_2Cl_2, δ) 8.19 (s, 1H), 8.07 (d, J(H,H) = 8.3 Hz, 2H), 7.88 (d, J(H,H) = 8.3 Hz, 2H), 7.83 (d, J(H,H) = 8.8 Hz, 2H), 7.26 (d, J(H,H) = 8.8 Hz, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 171.0, 157.5, 139.3, 138.3, 132.3, 129.5, 129.1, 128.6, 127.1, 126.6, 119.6, 21.1 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 727.0 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.3 (quintet, ^2J(F,F) = 151.7 Hz, 1F), 62.0 (d, ^2J(F,F) = 149.9 Hz, 4F) ppm; MS (APCI$^+$, m/z) 426 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_{16}H_{12}NF_5SSeH$ 425.9848; Found 425.9835.

4-(4′-Nitrophenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (7). Pale yellow solid (0.440 g) in 97% isolated yield: mp, 195−197 °C; selected IR (KBr, cm^{-1}) 1597(s), 1519(s), 1483(m), 1402(m), 1343(s), 1187(m), 1109(m), 1092(m), 1045(m), 957(m), 821(vs), 731(m), 657(m), 587(s); ^1H NMR (CD_2Cl_2, δ) 8.49 (s, 1H), 8.28 (d, J(H,H) = 8.8 Hz, 2H), 8.17 (d, J(H,H) = 8.8 Hz, 2H), 8.08 (d, J(H,H) = 8.5 Hz, 2H), 7.85 (d, J(H,H) = 8.5 Hz, 2H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 172.1, 155.1, 147.3, 140.7, 138.7, 127.3, 127.2, 127.0, 126.9, 126.8, 124.2 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 746.7 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.0 (quintet, ^2J(F,F) = 151.6 Hz, 1F), 61.9 (d, ^2J(F,F) = 149.6 Hz, 4F) ppm; MS (APCI$^+$, m/z) 457 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z) [M + H]$^+$ Calcd for $C_{15}H_9O_2N_2F_5SSeH$ 456.9543; Found 456.9532.

4-(2′,5′-Dimethoxy)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (8). Off-white solid (0.417 g) in 89% isolated yield: mp, 104−106 °C; selected IR (KBr, cm^{-1}) 1606(m), 1501(s), 1462(m), 1439(m), 1403(m), 1315(m), 1261(m), 1214(m), 1181(m), 1158(m), 1096(m), 1048(s), 829(vs), 762(m), 723(m), 657(m), 593(s); ^1H NMR (CD_2Cl_2, δ) 8.72 (s, 1H), 8.05 (d, J(H,H) = 8.0 Hz, 2H), 7.95 (s, 1H), 7.79 (d, J(H,H) = 8.0 Hz, 2H), 6.94 (d, J(H,H) = 8.8 Hz, 1H), 6.87 (d, J(H,H) = 8.8 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 168.8, 153.8, 153.1, 151.5, 139.3, 127.1, 125.5, 124.4, 121.3, 119.8, 112.6, 56.0, 55.7 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 724.7 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.4 (quintet, ^2J(F,F) = 149.0 Hz, 1F), 62.1 (d, ^2J(F,F) = 149.8 Hz, 4F) ppm; MS (APCI$^+$, m/z) 472 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_{17}H_{14}F_5NO_2SSeH$ 471.9903; Found 471.9899.

4-(2′,4′-Dichloro)-2-(4″-pentafluorosulfanylphenyl)-1,3-selenazole (9). Pale yellow solid (0.467 g) in 97% isolated yield: mp, 94−96 °C; selected IR (KBr, cm^{-1}) 1587(m), 1481(m), 1449(m), 1403(m), 1261(m), 1107(m), 1029(m), 957(m), 849(vs), 821(vs), 658(m), 591(s); ^1H NMR (CD_2Cl_2, δ) 8.50 (s, 1H), 8.03 (d, J(H,H) = 8.3 Hz, 2H), 7.84 (s, 1H), 7.82 (d, J(H,H) = 8.3 Hz, 2H), 7.35 (d, J(H,H) = 8.8 Hz, 1H), 7.33 (d, J(H,H) = 8.8 Hz, 1H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 163.3, 153.0, 141.7, 132.8, 130.2, 127.3, 127.2, 126.9, 126.8, 126.7, 126.2 ppm; ^{77}Se NMR (CD_2Cl_2, δ) 734.6 ppm; ^{19}F NMR (CD_2Cl_2, δ) 83.1 (quintet, ^2J(F,F) = 149.0 Hz, 1F), 62.0 (d, ^2J(F,F) = 149.9 Hz, 4F) ppm; MS (APCI$^+$, m/z) 480 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_{15}H_8Cl_2F_5NSSeH$ 479.8908; Found 479.8899.

Synthesis of 4-Pentafluorosulfanylbenzothioamide (10). A mixture of 4-pentafluorosulfanylbenzonitrile (0.458 g, 2.0 mmol) and Lawesson's reagent (0.808 g, 2.0 mmol) in 20 mL of dry toluene was refluxed for 10 h. After the mixture was cooled to 90 °C, 1.0 mL of water was added, and the mixture was subjected to refluxing for another 1 h. After the reaction mixture was cooled to room temperature, it was concentrated to ca. 5.0 mL and extracted with dichloromethane (20 mL × 3), combined the dichloromethane solution, and dried over $MgSO_4$. After we filtered and dried the sample to remove solvent, the organic residue was purified by a silica gel column (9:1 ethyl acetate/dichloromethane) to give 0.341 g of the compounds **10** as greenish yellow solid (61%): mp, 136−137 °C; selected IR (KBr, cm^{-1}) 1632(s), 1423(s), 1323(m), 1276(m), 1145(m), 1099(m), 899(m), 836(vs), 728(m), 673(m), 641(m), 602(m), 576(m); ^1H NMR (CD_2Cl_2, δ) 7.91 (d, J(H,H) = 8.3 Hz, 2H), 7.75 (d, J(H,H) = 8.3 Hz, 2H), 7.30 (s, 2H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 200.5, 142.2, 129.2, 127.3, 126.2 ppm; ^{19}F NMR (CD_2Cl_2, δ) 82.3 (quintet, ^2J(F,F) = 150.4 Hz, 1F), 61.7 (d, ^2J(F,F) = 149.7 Hz, 4F) ppm; MS (APCI$^+$, m/z) 264 [M + H]$^+$; accurate mass measurement (APCI$^+$, m/z): [M + H]$^+$ Calcd for $C_7H_6F_5NS_2H$ 263.9935; Found 263.9936.

General Procedure for the Synthesis of Compounds 11−13. A mixture of α-haloketones (1.0 mmol) in 20 mL of ethanol was added dropwise to a refluxing solution of 4-pentafluorosulfanylbenzothioamide (0.263 g, 1.0 mmol) in 20 mL of ethanol in the course of 1 h. The reaction mixture was then refluxed for another 1 h. After the mixture was cooled to room temperature, it was concentrated by a rotary evaporator. The residue was neutralized with 5% aqueous ammonia (30 mL) and extracted with dichloromethane (30 mL × 3), combined organic layers, washed with water (20 mL × 3), and dried over $MgSO_4$. After we filtered and dried the sample to remove solvent, the organic residue was purified by a silica gel column (1:9 ethyl acetate/dichloromethane) to give the expected products **11−13**.

4-(4′-Nitrophenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-thiazole (11). Off-white solid (0.379 g) in 93% isolated yield: mp, 175−176 °C; selected IR (KBr, cm^{-1}) 1600(s), 1518(s), 1476(m),

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1403(m), 1343(s), 1093(m), 1060(m), 981(m), 823(vs), 737(m), 645(m), 593(m), 573(m); ^{1}H NMR (CD_2Cl_2, δ) 8.23 (d, J(H,H) = 8.8 Hz, 2H), 8.10 (d, J(H,H) = 8.5 Hz, 2H), 8.07 (d, J(H,H) = 8.5 Hz, 2H), 7.80 (d, J(H,H) = 8.8 Hz, 2H), 7.76 (s, 1H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 166.4, 154.7, 147.9, 140.2, 136.5, 129.6, 127.4, 127.2, 124.6, 124.2, 118.1 ppm; ^{19}F NMR (CD_2Cl_2, δ) 82.3 (quintet, ^2J(F,F) = 150.4 Hz, 1F), 61.7 (d, ^2J(F,F) = 149.7 Hz, 4F) ppm; MS (APCI$^+$, m/z) 409 $[M + H]^+$; accurate mass measurement (APCI$^+$, m/z): $[M + H]^+$ Calcd for $C_{15}H_9F_5N_2O_2S_2H$ 409.0098; Found 409.0099.

4-(2′,5′-Dimethoxy)-2-(4″-pentafluorosulfanylphenyl)-1,3-thiazole (12). Pale yellow solid (0.386 g) in 91% isolated yield: mp, 100−101 °C; selected IR (KBr, cm^{-1}) 1679(m), 1595(m), 1495(s), 1463(m), 1440(m), 1405(m), 1273(s), 1216(m), 1161(m), 1095(m), 1052(s), 1921(m), 829(vs), 729(m), 663(m), 593(m); ^{1}H NMR (CD_2Cl_2, δ), 8.05 (d, J(H,H) = 8.5 Hz, 2H), 8.02 (s, 1H), 7.89 (s, 1H), 7.76 (d, J(H,H) = 8.5 Hz, 2H), 6.88 (d, J(H,H) = 8.8 Hz, 1H), 6.80 (d, J(H,H) = 8.5 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H) ppm; ^{13}C NMR (CD_2Cl_2, δ), 163.3, 154.2, 152.8, 151.8, 137.1, 127.0, 123.7, 121.7, 120.2, 119.4, 115.8, 114.6, 112.8 ppm; ^{19}F NMR (CD_2Cl_2, δ), 83.4 (quintet, ^2J(F,F) = 150.5 Hz, 1F), 62.0 (d, ^2J(F,F) = 149.6 Hz, 4F) ppm; MS (APCI$^+$, m/z), 424 $[M + H]^+$; accurate mass measurement (APCI$^+$, m/z): $[M + H]^+$ Calcd for $C_{17}H_{14}F_5NO_2S_2H$ 424.0459; Found 424.0459.

4-(4′-Bromophenyl)-2-(4″-pentafluorosulfanylphenyl)-1,3-thiazole (13). Pale yellow solid (0.438 g) in 99% isolated yield: mp, 168−169 °C; selected IR (KBr, cm^{-1}) 1687(m), 1591(m), 1473(s), 1401(m), 1272(m), 1093(m), 1071(m), 1009(m), 982(m), 824(vs), 744(s), 643(m), 592(s), 573(m), 486(m); ^{1}H NMR (CD_2Cl_2, δ), 8.04 (d, J(H,H) = 8.5 Hz, 2H), 7.80 (d, J(H,H) = 8.7 Hz, 2H), 7.77(d, J(H,H) = 8.7 Hz, 2H), 7.52 (d, J(H,H) = 8.5 Hz, 2H), 7.49 (s, 1H, Azole-H) ppm; ^{13}C NMR (CD_2Cl_2, δ) 165.8, 156.0, 155.0, 136.8, 133.5, 132.3, 130.3, 128.4, 127.1, 122.8, 115.1 ppm; ^{19}F NMR (CD_2Cl_2, δ) 3.2 (quintet, ^2J(F,F) = 150.7 Hz, 1F), 61.9 (d, ^2J(F,F) = 149.8 Hz, 4F) ppm; MS (APCI$^+$, m/z) 442 and 444 $[M + H]^+$; accurate mass measurement (APCI$^+$, m/z): $[M + H]^+$ Calcd for $C_{15}H_9BrF_5NS_2H$ 441.9353 and 443.9331; Found 441.9353 and 443.9329 .

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, and ^{19}F NMR, IR, and mass spectra of compounds **1**−**13**. Thermal Ellipsoid plots of the crystal structures. This material is free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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