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Copper-Catalyzed Direct Thiolation of Pentafluorobenzene with Diaryl Disulfides or Aryl Thiols by C–H and C–F Bond Activation

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A Cu-catalyzed cross-coupling reaction of diaryl disulfides or aryl thiols with pentafluorobenzene using CuBr as the catalyst, *t*BuOLi or *t*BuOK as the base in DMSO at 60 °C under an O_2 atmosphere was investigated. The corresponding bisarylthiolation products were obtained in moderate to good yields by C–H bond and C–F bond activation. When 1,10-phenanthroline·H_2O and DDQ were added to the above system, monoarylthiolation products, with/without bisarylthiolation products, could be isolated in moderate yields. A plausible mechanism for these transformations was given. Thus, it represents a method for the synthesis of polyfluorinated diaryl sulfides and polyfluorinated triarylbisulfides through C–H bond and C–F bond activation.

Introduction

Transition-metal-catalyzed carbon–carbon and carbon–heteroatom bond formation has become a powerful tool to construct organic molecules. The construction of carbon–sulfur bonds and the direct functionalization of a C–H bond are central themes in organic synthesis.[1] Diaryl sulfides are common functionalities found in numerous pharmaceutically active compounds and medicinally important natural products.[2] Organic molecules containing a polyfluorinated aromatic structure have found applications in medicinal chemistry and material science.[3] Pentafluorobenzene (C_6F_5H) is a representative example of such fluoroorganic molecule, and thus, the development of efficient methods for its introduction has been an important strategy for synthetic chemists. The key C–H bond functionalization step occurs through a concerted arene metalation and carbon–hydrogen bond cleaving process, the accessibility of which depends directly on the acidity of the C–H bond being cleaved.[4] Recently, the direct arylation, alkenylation, alkylation, decarboxylation, and olefination of perfluoroarenes through C–H activation were reported by Fagnou,[4] Daugulis,[5] Nakao and Hiyama,[6] Miura,[7] Zhao,[8] Su,[9] Shi,[10] Zhang,[11] and Liu.[12] Pu and Wu have reported a copper(I)-catalyzed tandem reaction of 2-(2,2-dibromovinyl)phenol with polyfluoroarene recently.[13]

Synthetically useful routes for the generation of fluoroorganics by transition-metal-mediated conversions of aromatic C–F bonds have now also been observed. Several excellent reviews and articles on the structural and synthetic aspects of C–F bond activation by metal complexes have been published.[14] Selective C–F activation of pentafluorobenzene derivatives were also reported by Radius,[15a] Sandford,[15b] and Zhu and Xu.[15c]

A rhodium-catalyzed substitution reaction of aryl fluorides with disulfides containing a notable mode of C–F activation by a transition-metal catalyst was reported by Yamaguchi.[16] The direct thiolation of azoles through copper-catalyzed C–H functionalization with thiols or disulfides has been reported,[17] but the copper-catalyzed direct thiolation of electron-deficient pentafluorobenzene through C–H and C–F bond activation with diaryl disulfides or aryl thiols has not been reported to date; this still poses a great synthetic challenge because of the difficulties in controlling the selectivity in the activation of the C–H and C–F bonds.

To the best of our knowledge, this is the first copper-catalyzed direct thiolation of pentafluorobenzene and provides a new method for the construction of C–S bonds. Herein we report the preliminary results of the direct thiolation with pentafluorobenzene.

Results and Discussion

We started with the coupling reaction of pentafluorobenzene (**1**) with 1,2-bis(*p*-tolyl)disulfane (**2a**) to assess the catalyst activity and to determine the optimum reaction conditions. These results are shown in Table 1. To our surprise, we could obtain bisarylthiolation products **4a** in a high yield (85%) when using CuBr (30 mol-%) and *t*BuOLi (2 equiv.) in DMSO at 60 °C under an atmosphere of O_2 (1 atm) but desired monoarylthiolation products **3a** were not detected (Table 1, Entry 1). We speculated that the C–

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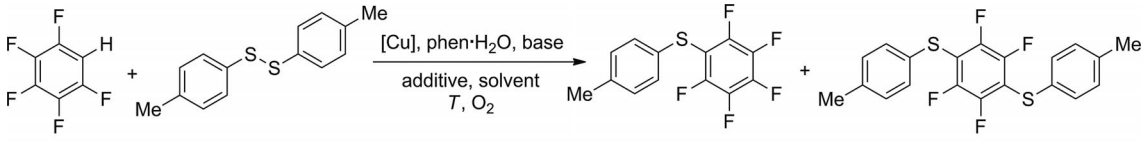
F bond, which is in the *para* position to the C–H bond, can easily be activated.[15a,15c] Secondly, when 1,10-phenanthroline (phen)·H_2O (30 mol-%) was added, we were excited to find that products **3a** were obtained in low yield (16%; Table 1, Entry 2). Because DDQ may serve as an electron-transfer mediator for activating the C–H bond, we were pleased to find that the introduction of DDQ (30 mol-%) improved the yield of **3a** (68%; Table 1, Entry 3). Subsequently, the amounts (20 and 40 mol-%) of DDQ were also examined (Table 1, Entries 4 and 5), indicating that introduction of DDQ (30 mol-%) was very important. Under otherwise identical conditions, the replacement of *t*BuOLi (2 equiv.) with weaker bases such as *t*BuOLi (1 equiv.) and K_2CO_3 (2 equiv.) led to lower yields of **3a** and no formation of **4a** (Table 1, Entries 6 and 7), indicating that the base additive plays an important role in the cleavage of the C–H and C–F bonds. CuBr proved to be more active than other Cu sources, furnishing **3a** in 68% yield (Table 1, Entries 11–16). Monoarylthiolation product **3a** was obtained in the highest yield when the reaction was performed at 60 °C. Both 40 and 120 °C gave **3a** in slightly lower yields. Product **4a** was also formed in low yield (50 and 69%, respectively; Table 1, Entries 17 and 19). We speculated that monoarylthiolation product **3a** could be obtained in the highest yield in the absence of DDQ at a specific temperature, and it could be transformed into **4a** by increasing the temperature. Further screening of the solvents revealed that DMSO was the optimal solvent (Table 1, Entries 20 and 21). Performing the reaction under an atmosphere of oxygen was critical for the reaction, whereas the reaction performed under an atmosphere of nitrogen (in the absence of oxygen) produced **3a** a low yield (12%; Table 1, Entry 22). Along with reducing the amount of catalyst to 20 or 10 mol-%, the yields of **3a** and **4a** decreased (Table 1, Entries 23 and 24).

Having delineated the optimum reaction conditions for the thiolation of pentafluorobenzene with disulfides to obtain the bisarylthiolation products through C–H and C–F bond activation (Table 1, Entry 1), we then applied them to a variety of substrates to determine the scope and limitations of the method. As depicted in Table 2, electron-donating groups on the phenyl ring of ArSSAr were beneficial to the reaction (78–90% yield; Table 2, Entries 1–6).

Disulfides with electron-withdrawing functionalities had limited reactivity with pentafluorobenzene. A possible reason is that electron-withdrawing groups decrease the reactivities of the corresponding disulfides. For example, substrate **2g** delivered 50% yield of **4g**, **2h** delivered 55% yield of **4h**, and **2i** delivered 31% yield of **4i**. Unfortunately, the

Table 1. Optimization of the reaction condition.[a]

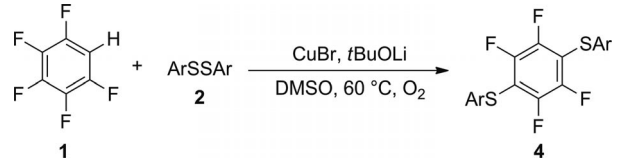


1 **2a** **3a** **4a**

Entry	[Cu] (30 mol-%)	phen·H_2O	Base (2 equiv.)	Additive (30 mol-%)	Solvent	*t* [h]	*T* [°C]	Yield [%][b] **3a**	**4a**
1	CuBr	–	*t*BuOLi	–	DMSO	4	60	–	85
2	CuBr	30	*t*BuOLi	–	DMSO	4	60	16	75
3	CuBr	30	*t*BuOLi	DDQ	DMSO	4	60	68	31
4[c]	CuBr	30	*t*BuOLi	DDQ	DMSO	4	60	49	29
5[d]	CuBr	30	*t*BuOLi	DDQ	DMSO	4	60	39	36
6[e]	CuBr	30	*t*BuOLi	DDQ	DMSO	8	60	20	–
7	CuBr	30	K_2CO_3	DDQ	DMSO	8	60	10	–
8	CuBr	30	Cs_2CO_3	DDQ	DMSO	8	60	27	48
9	CuBr	30	*t*BuONa	DDQ	DMSO	8	60	45	30
10	CuBr	30	*t*BuOK	DDQ	DMSO	8	60	21	22
11	CuI	30	*t*BuOLi	DDQ	DMSO	4	60	57	32
12	CuCl	30	*t*BuOLi	DDQ	DMSO	4	60	12	65
13	$CuCl_2·2H_2O$	30	*t*BuOLi	DDQ	DMSO	5	60	40	19
14	$Cu(OAc)_2·H_2O$	30	*t*BuOLi	DDQ	DMSO	6	60	21	43
15	$Cu(OTf)_2$	30	*t*BuOLi	DDQ	DMSO	4	60	48	44
16	CuO	30	*t*BuOLi	DDQ	DMSO	8	60	–	trace
17	CuBr	30	*t*BuOLi	DDQ	DMSO	5	40	25	50
18	CuBr	30	*t*BuOLi	DDQ	DMSO	5	80	40	51
19	CuBr	30	*t*BuOLi	DDQ	DMSO	5	120	18	69
20	CuBr	30	*t*BuOLi	DDQ	DMF	8	60	33	40
21	CuBr	30	*t*BuOLi	DDQ	NMP	8	60	21	32
22[f]	CuBr	30	*t*BuOLi	DDQ	DMSO	8	60	12	50
23[g]	CuBr	20	*t*BuOLi	DDQ	DMSO	8	60	35	45
24[h]	CuBr	10	*t*BuOLi	DDQ	DMSO	8	60	21	40
25	CuBr	30	–	DDQ	DMSO	8	60	–	–

[a] Reaction conditions: **2a** (1 mmol), **1** (5 equiv.). [b] Isolated yield. [c] DDQ (20 mol-%). [d] DDQ (40 mol-%). [e] *t*BuOLi (1 equiv.). [f] The reaction was carried out under a N_2 atmosphere. [g] CuBr (20 mol-%). [h] CuBr (10 mol-%).

Table 2. Scope of the thiolation of pentafluorobenzene with diaryl disulfides.[a]



1 4

Entry	Ar	Product	Yield [%][b]
1	4-$CH_3C_6H_4$ (**2a**)	**4a**	85
2	C_6H_5 (**2b**)	**4b**	83
3	3-$CH_3C_6H_4$ (**2c**)	**4c**	78
4	2-$CH_3C_6H_4$ (**2d**)	**4d**	84
5	2,4-$(CH_3)_2C_6H_3$ (**2e**)	**4e**	90
6	4-$OCH_3C_6H_4$ (**2f**)	**4f**	86
7	4-FC_6H_4 (**2g**)	**4g**	50
8	3-FC_6H_4 (**2h**)	**4h**	55
9[c]	4-ClC_6H_4 (**2i**)	**4i**	31
10[c]	4-$NO_2C_6H_4$ (**2j**)	**4j**	–
11[c]	benzothiazol-2-yl (**2k**)	**4k**	–

[a] Reaction conditions: **2** (1 mmol), **1** (5 equiv.), CuBr (30 mol-%), *t*BuOLi (2 equiv.), DMSO (5 mL), 4 h. [b] Isolated yield. [c] *t*BuOK (2 equiv.).

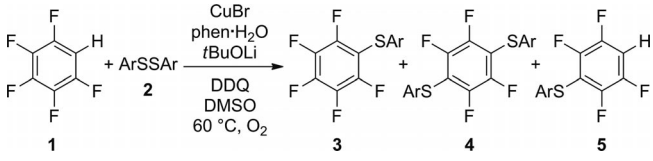
expected products were not detected when using bis(*p*-nitrophenyl)disulfide (**2j**) and benzothiazol-2-yl disulfide (**2k**) as substrates (Table 2, Entries 10 and 11).

With the optimal conditions in hand to obtain the monoarylthiolation product by C–H bond activation (Table 1, Entry 3), we next examined the substrate scope with respect to the pentafluorobenzene. As depicted in Table 3, a series of electron-donating groups on the phenyl ring of disulfides, such as *p*-methyl, *m*-methyl, *o*-methyl, and *p*-methoxy, afforded the corresponding monoarylthiolation products **3b**–**f** in moderate to good yields (Table 3, Entries 1, 3–6), and for the *m*-methyl substrate, monoarylthiolation product **3c** was obtained in a lower yield (42%) probably due to the decreased electron density at the *meta* position of such a substrate.

Unfortunately, as shown in Table 3, no monoarylthiolation products were detected, but bisarylthiolation products **4g**, **4h**, and **4i** were found in a yield of 41, 50, and 29%, respectively, when using a series of electron-withdrawing groups on the phenyl ring of the disulfides (Table 3, Entries 7–10). One possible reason for this decreased reactivity is that the electron-withdrawing groups decreased the reactivities of the corresponding disulfides. Bis(*p*-nitrophenyl) disulfide, containing the strong NO_2 electron-withdrawing group on the phenyl ring, was utilized as a substrate and it did not give **3j** and **4j** (Table 3, Entry 10). Interestingly, under these conditions another monoarylthiolation product, which results from C–F bond activation, was obtained (Table 3, Entries 8, 10, 11).

In comparison to diaryl disulfides, aryl thiols are prone to undergo C–S coupling reactions and would perform better as thiolating agents. Thus, we examined the potential for aryl thiols to undergo this direct thiolation reaction. These results are summarized in Table 4. The reactions of **6a**, **6b**, and **6c** with pentafluorobenzene were carried out by using the same reaction conditions as those used for the diaryl disulfides and the corresponding thioethers **3a**–**c** were afforded in moderate yields (50–60%; Table 4, Entries 1–3). Aryl thiol **6i** containing an electron-withdrawing group on the phenyl ring was treated with **1**, in the absence of DDQ, to give bisarylthiolation product **4i** in 36% yield and monoarylthiolation product **5i** in 33% yield (Table 4, Entry 5). For *p*-nitrophenyl thiol (**6j**), thioether **5j** was obtained in moderate yield (49%) with *t*BuOK (2 equiv.) and a longer reaction time (Table 4, Entry 7), whereas benzo[*d*]-thiazole-2-thiol (**6k**) gave **5k** in low yield (35%; Table 4, Entry 8).

Table 3. Scope of the thiolation of pentafluorobenzene with diaryl disulfides.[a]

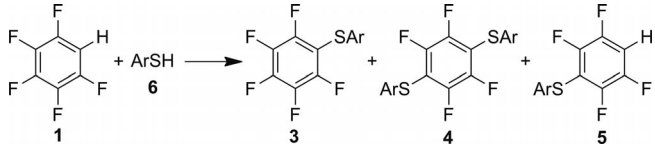


1 3 4 5

Entry	Ar	Product, yield [%][b]		
1	4-$CH_3C_6H_4$ (**2a**)	**3a**, 68	**4a**, 31	–
2	C_6H_5 (**2b**)	**3b**, 56	**4b**, 42	–
3	3-$CH_3C_6H_4$ (**2c**)	**3c**, 42	**4c**, 45	–
4	2-$CH_3C_6H_4$ (**2d**)	**3d**, 63	**4d**, 27	–
5	2,4-$(CH_3)_2C_6H_3$ (**2e**)	**3e**, 68	**4e**, 30	–
6	4-$OCH_3C_6H_4$ (**2f**)	**3f**, 70	**4f**, 23	–
7	4-FC_6H_4 (**2g**)	–	**4g**, 41	–
8	3-FC_6H_4 (**2h**)	–	**4h**, 50	–
9	4-ClC_6H_4 (**2i**)	–	**4i**, 29	**5i**, 24
10	4-$NO_2C_6H_4$ (**2j**)	–	–	**5j**, 45
11	benzothiazol-2-yl (**2k**)	–	–	**5k**, 26

[a] Reaction conditions: **2a** (1 mmol), **1** (5 equiv.), CuBr (30 mol-%), phen·H_2O (30 mol-%), *t*BuOLi (2 equiv.), DDQ(30 mol-%), DMSO (5 mL), 4–8 h. [b] Isolated yield.

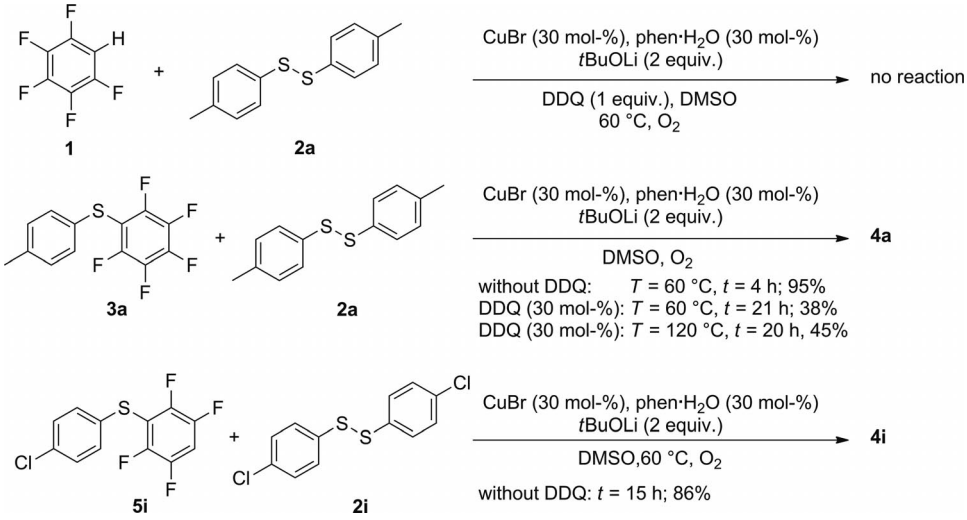
Table 4. Scope of the thiolation of pentafluorobenzene with thiols.[a]



1 3 4 5

Entry	Ar	Product, yield [%][b]		
1	4-$CH_3C_6H_4$ (**6a**)	**3a**, 60	**4a**, 32	–
2	C_6H_5 (**6b**)	**3b**, 50	**4b**, 40	–
3	3-$CH_3C_6H_4$ (**6c**)	**3c**, 55	**4c**, 35	–
4	4-ClC_6H_4 (**6i**)	–	**4i**, 26	**5i**, 23
5[c]	4-ClC_6H_4 (**6i**)	–	**4i**, 36	**5i**, 33
6	4-$NO_2C_6H_4$ (**6j**)	–	–	**5j**, 39
7[d]	4-$NO_2C_6H_4$ (**6j**)	–	–	**5j**, 49
8[d]	benzothiazol-2-yl (**6k**)	–	–	**5k**, 35

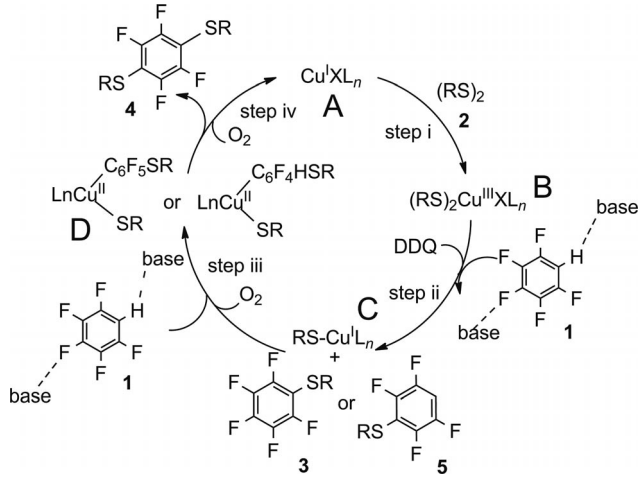
[a] Reaction conditions: **6** (1 mmol), **1** (2.5 equiv.), CuBr (30 mol-%), phen·H_2O (30 mol-%), *t*BuOLi (2 equiv.), DDQ(30 mol-%), DMSO (5 mL), 60 °C, 1 atm of O_2. [b] Isolated yield. [c] Without DDQ. [d] Without DDQ, and *t*BuOK(2 equiv.) was used instead of *t*BuOLi.



Scheme 1. Preliminary mechanistic study.

More experiments were carried out to gain preliminary insight into the mechanism of the catalytic reaction. As shown in Scheme 1, when we carried out the reaction of pentafluorobenzene (**1**) with 1,2-bis(*p*-tolyl)disulfane (**2a**) in the presence of CuBr (30 mol-%), phen·H_2O (30 mol-%), *t*BuOLi (2 equiv.), and DDQ (1 equiv.) at 60 °C under an atmosphere of oxygen, no reaction occurred. Furthermore, in the absence of DDQ, product **4a** was isolated in high yield (95%). In the presence of 30 mol-% of DDQ at 60 °C for 21 h, **4a** was obtained in only 38% yield, and when the temperature was increased to 120 °C, **4a** was obtained in 45% yield. Otherwise, under the same reaction conditions, CuBr (30 mol-%), phen·H_2O (30 mol-%), *t*BuOLi (2 equiv.) but without of DDQ, **4i** could be obtained in the presence of **5i** and **2i**. These results indicated that bisarylthiolation products could be formed from monoarylthiolation products, DDQ may serve an important role in the reaction, diaryl disulfides were very stable in the presence of 1 equiv. of DDQ, and the monoarylthiolation products could be obtained with an appropriate amount of DDQ.[9b]

It is known that pentafluorophenylcopper phenanthroline complex can be synthesized.[5b] The cooper-catalyzed method may contain a notable mode of C–H and C–F activation by a transition-metal catalyst.[5a] On the basis of the experimental results, it is reasonable to assume a plausible pathway for the thiolation reaction of diaryl disulfides with pentafluorobenzene, as shown in Scheme 2. In step i, complex **A** reacts with the diaryl disulfides to provide intermediate **B**. In step ii, deprotonation of pentafluorobenzene (Ar-H) is promoted by base or DDQ followed by cupration through transmetalation, and activation of the C–F bond at the C-4 position is promoted by base. In this step, DDQ may serve an important role, and **3** is formed as the main product with DDQ. This substrate has a strong influence on the reaction product and the exclusive formation of **5** can be obtained only in certain cases. Then, in step iii, complex **C** reacts with pentafluorobenzene and monoarylthiolation product **3** or **5** under the promotion of a base and under an atmosphere of O_2 to generate intermediate **D**. Finally, reductive elimination of Cu^{II} complex **D** affords products **4** and Cu^{I}**A**, which is oxidized to Cu^{I} by oxygen.



Scheme 2. Plausible mechanism.

Conclusions

In conclusion, we have demonstrated a novel Cu-catalyzed reaction of pentafluorobenzene with diaryl disulfides or aryl thiols by C–H bond and C–F bond activation. This reaction proceeds under mild conditions and tolerates some functional groups, and substrates are strongly influential on the reaction products. Moreover, this is new methodology for the construction of polyfluorinated diaryl sulfides and polyfluorinated triaryl bisulfides. Ongoing work seeks to develop related C–H and C–F bond-cleavage processes under oxidative copper–oxygen catalysis.

Experimental Section

General Information: All reagents unless otherwise noted were obtained from commercial sources (purity >99%) and used without further purification. The reactions were carried out under an oxygen atmosphere, and the products were isolated by column chromatography on silica gel (200–300 mesh or 300–400 mesh) by using petroleum ether (60–90 °C) and ethyl acetate as eluents. Melting points were determined using a Büchi B-540 capillary melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded with Varian (400 MHz) instrument by using $CDCl_3$ as the solvent, and chemical shifts are expressed in parts per million (ppm) by using TMS as an internal standard. Mass spectra were measured with a Finnigan Trace DSQ instrument or a GCT Premier mass spectrometer. High-resolution mass spectral (HRMS) analyses were measured with an APEX (Bruker) mass III spectrometer or GC Premier mass spectrometer by using ESI or EI techniques. Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Lt. All yields described herein are the isolated yields after column chromatography.

General Procedure for the Reaction of Pentafluorobenzene and Diaryl Disulfides: To a solution of CuBr (30 mol-%), 1,10-phenanthroline·H_2O (30 mol-%), DDQ (30 mol-%), *t*BuOLi (2 equiv.), and DMSO (5 mL) was added the disulfide (1 mmol). The mixture was stirred for 2–3 h at room temperature. Then the reaction flask was evacuated and refilled with O_2 three times. Subsequently, pentafluorobenzene (5 equiv.) was added under an oxygen flow. The mixture was stirred at the indicated temperature under an atmosphere of oxygen for a given time and cooled to room temperature. Upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), filtered through a pad of silica gel, followed by washing the silica gel pad with ethyl acetate (30 mL). The filtrate was washed with brine. The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the corresponding product.

General Procedure for the Reaction of Pentafluorobenzene and Aryl Thiols: To a solution of CuBr (30 mol-%), 1,10-phenanthroline·H_2O (30 mol-%), DDQ (30 mol-%), *t*BuOLi (2 equiv.), and DMSO (5 mL) was added aryl thiol (1 mmol). Subsequently, pentafluorobenzene **1** (5 equiv.) was added under an O_2 atmosphere. The mixture was stirred under an O_2 atmosphere at the indicated temperature for a given time and then cooled to room temperature. Upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), filtered through a pad of silica gel, followed by washing the silica gel pad with ethyl acetate (30 mL). The filtrate was washed with brine. The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the corresponding product.

General Procedure for the Reaction of (Perfluorophenyl)(*p*-tolyl)sulfane (3a) with 1,2-Bis(*p*-tolyl)disulfane (2a): To a solution of CuBr (30 mol-%), 1,10-phenanthroline·H_2O (30 mol-%), *t*BuOLi (2 equiv.), and DMSO (5 mL) was added **2a** (1 mmol). The mixture was stirred for 2 h at room temperature. Then, the reaction flask was evacuated and refilled with O_2 three times. Subsequently, **3a** (1 equiv.) was added under an oxygen flow. The mixture was stirred under an O_2 atmosphere at the indicated temperature for a given time and then cooled to room temperature. Upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), filtered through a pad of silica gel, followed by washing the silica gel pad with ethyl acetate (30 mL). The filtrate was washed with brine. The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether) to provide the corresponding product.

General Procedure for the Reaction of (4-Chlorophenyl)(2,3,5,6-tetrafluorophenyl)sulfane (5i) and 1,1′-Disulfanediyl[bis(4-chlorobenzene)] (2i): To a solution of CuBr (30 mol-%), 1,10-phenanthroline·H_2O (30 mol-%), *t*BuOLi (2 equiv.), and DMSO (5 mL) was added **2i** (1 mmol). The mixture was stirred for 2 h at room temperature. Then, the reaction flask was evacuated and refilled with O_2 three times. Subsequently, **5i** (1 equiv.) was added under an oxygen flow. The mixture was stirred under an O_2 atmosphere at the indicated temperature for a given time and then cooled to room temperature. Upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), filtered through a pad of silica gel, followed by washing the silica gel pad with ethyl acetate (30 mL). The filtrate was washed with brine. The organic phase was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether) to provide the corresponding product.

(Perfluorophenyl)(*p*-tolyl)sulfane (3a): Colorless oil. CAS: 16495-78-6.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.0 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.45 (m), 145.99 (m), 142.93 (m), 140.45 (m), 138.81 (m), 138.36, 136.38 (m), 131.32, 130.00, 129.03, 109.72 (m), 21.20 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.16 to –132.28 (m, 2 F), –151.87 (m, 1 F), –160.42 to –160.62 (m, 2 F) ppm. MS (EI): m/z = 290 $[M]^+$.

(Perfluorophenyl)(phenyl)sulfane (3b): Colorless oil. CAS: 16496-09-6.[20a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 2 H), 7.27 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.58 (m), 146.12 (m), 143.19 (m), 140.61 (m), 138.90 (m), 136.39 (m), 132.78, 130.42, 129.25, 127.83, 108.90 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –131.28 (m, 2 F), –151.25 (m, 1 F), –160.26 (m, 2 F) ppm. GC–MS (EI): m/z = 276 $[M]^+$.

(Perfluorophenyl)(*m*-tolyl)sulfane (3c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.11 (m, 3 H), 7.06 (d, J = 8.0 Hz, 1 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.59 (m), 146.14 (m), 143.07 (m), 140.49 (m), 138.83 (m), 136.36 (m), 132.45, 130.98, 129.05, 128.72, 127.47, 109.13 (m), 21.36 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –131.85 (m, 2 F), –151.41 (m, 1 F), –160.25 to –160.42 (m, 2 F) ppm. GC–MS (EI): m/z = 290 $[M]^+$. HRMS (EI): calcd. for $C_{13}H_7F_5S$ $[M]^+$ 290.0189; found 290.0175.

(Perfluorophenyl)(*o*-tolyl)sulfane (3d): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.12 (m, 3 H), 7.09 (m, 1 H), 2.47 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.51 (m), 146.06 (m), 142.87 (m), 140.36 (m), 139.01 (m), 138.76, 136.39 (m), 131.73, 130.89, 130.59, 127.98, 126.74, 108.84 (m), 20.53 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –131.98 (m, 2 F), –151.69 (m, 1 F), –160.35 (m, 2 F) ppm. GC–MS (EI): m/z = 290 $[M]^+$. HRMS (EI): calcd. for $C_{13}H_7F_5S$ $[M]^+$ 290.0189; found 290.0238.

(2,4-Dimethylphenyl)(perfluorophenyl)sulfane (3e): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, J = 8.0 Hz, 1 H), 7.02 (s, 1 H), 6.93–6.88 (m, 1 H), 2.43 (s, 3 H), 2.28 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.37 (m), 145.91 (m), 142.62 (m), 140.08 (m), 139.40, 138.84 (m), 138.58, 136.33 (m), 132.28, 131.44, 127.93, 127.51, 109.72 (m), 21.05, 20.51 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.37 to –132.49 (m, 2 F), –152.42 (m, 1 F), –160.54 to –160.72 (m, 2 F) ppm. GC–MS (EI): m/z = 304 $[M]^+$. HRMS (EI): calcd. for $C_{14}H_9F_5S$ $[M]^+$ 304.0345; found 304.0342.

(4-Methoxyphenyl)(perfluorophenyl)sulfane (3f): Colorless oil. CAS: 57517-98-3.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.0 Hz, 2 H), 6.84–6.78 (m, 2 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.02, 148.25 (m), 145.81 (m), 142.73 (m), 140.16 (m), 138.79 (m), 136.25 (m), 134.48, 122.66, 114.80, 110.60 (m), 55.34 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.83 (m, 2 F), –152.32 (m, 1 F), –160.55 to –160.73 (m, 2 F) ppm. GC–MS (EI): m/z = 306 $[M]^+$.

1,4-Bis(*p*-tolylthio)-2,3,5,6-tetrafluorobenzene (4a): White solid, m.p. 119–120 °C, CAS: 55677-92-4.[20b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.0 Hz, 4 H), 7.08 (d, J = 8.0 Hz, 4 H), 2.31 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.90 (m), 145.44 (m), 138.40, 131.64, 130.01, 128.74, 115.59 (m), 21.28 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.75 (s, 4 F) ppm. MS(EI): m/z = 394 $[M]^+$.

1,4-Bis(phenylthio)-2,3,5,6-tetrafluorobenzene (4b): White solid, m.p. 104–106 °C, CAS: 2712-34-7.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.34 (m, 4 H), 7.31–7.24 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.97 (m), 145.51 (m), 132.36, 130.78, 129.20, 127.89, 115.10 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.17 (s, 4 F) ppm. GC–MS (EI): m/z = 366 $[M]^+$

1,4-Bis(*m*-tolylthio)-2,3,5,6-tetrafluorobenzene (4c): White solid, m.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.13 (m, 6 H), 7.06 (m, 2 H), 2.30 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.04 (m), 145.56 (m), 139.15, 132.14, 131.39, 129.01, 128.80, 127.88, 115.26 (m), 21.35 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.25 (s, 4 F) ppm. GC–MS (EI): m/z = 394 $[M]^+$. HRMS (EI): calcd. for $C_{20}H_{14}F_4S_2$ $[M]^+$ 394.0473; found 394.0472.

1,4-Bis(*o*-tolylthio)-2,3,5,6-tetrafluorobenzene (4d): White solid, m.p. 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, J = 4.0 Hz, 2 H), 7.18 (m, 4 H), 7.12–7.06 (m, 2 H), 2.46 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.90 (m), 145.44 (m), 139.13, 131.55, 131.35, 130.57, 128.15, 126.70, 114.79 (m), 20.65 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.73 (s, 4 F) ppm. GC–MS (EI): m/z = 394 $[M]^+$. HRMS (EI): calcd. for $C_{20}H_{14}F_4S_2$ $[M]^+$ 394.0473; found 394.0493.

1,4-Bis(2,4-dimethylphenylthio)-2,3,5,6-tetrafluorobenzene (4e): White solid, m.p. 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, J = 8.0 Hz, 2 H), 7.01 (s, 2 H), 6.91 (d, J = 8.0 Hz, 2 H), 2.41 (s, 6 H), 2.28 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.75 (m), 145.29 (m), 139.63, 138.61, 132.70, 131.41, 127.63, 127.47, 115.11 (m), 21.12, 20.63 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –133.35 (s, 4 F) ppm. GC–MS (EI): m/z = 422 $[M]^+$. HRMS (EI): calcd. for $C_{22}H_{18}F_4S_2$ $[M]^+$ 422.0786; found 422.0782.

1,4-Bis(4-methoxyphenylthio)-2,3,5,6-tetrafluorobenzene (4f): White solid, m.p. 109–111 °C, CAS: 1173915-06-4.[20b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.0 Hz, 4 H), 6.80 (m, 4 H), 3.77 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.96, 147.66 (m), 145.18 (m), 134.67, 122.34, 116.13 (m), 114.77, 55.41 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –133.52 (s, 4 F) ppm. GC–MS (EI): m/z = 426 $[M]^+$.

1,4-Bis(4-fluorophenylthio)-2,3,5,6-tetrafluorobenzene (4g): White solid, m.p. 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 4 H), 7.02–6.96 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.89, 161.41, 147.77 (m), 145.30 (m), 134.19 (d, J = 8.0 Hz), 127.11, 116.58, 116.36, 115.66 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.27 to –112.36 (m, 2 F), –132.63 (s, 4 F) ppm. GC–MS (EI): m/z = 402 $[M]^+$. HRMS (EI): calcd. for $C_{18}H_8F_6S_2$ $[M]^+$ 401.9972; found 401.9950.

1,4-Bis(3-fluorophenylthio)-2,3,5,6-tetrafluorobenzene (4h): White solid, m.p. 74–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 6.98 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.77, 161.29, 148.05 (m), 145.58 (m), 134.35 (d, J = 7.0 Hz), 130.53 (d, J = 8.0 Hz), 125.94 (d, J = 2.0 Hz), 117.30 (d, J = 23.0 Hz), 115.06 (d, J = 21.0 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.32 (m, 2 F), –131.40 (s, 4 F) ppm. GC–MS (EI): m/z = 402 $[M]^+$. HRMS (EI): calcd. for $C_{18}H_8F_6S_2$ $[M]^+$ 401.9972; found 401.9972.

1,4-Bis(4-chlorophenylthio)-2,3,5,6-tetrafluorobenzene (4i): White solid, m.p. 164–166 °C, CAS: 122127-55-3.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 4 H), 7.26 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.88 (m), 145.40 (m), 134.43, 132.48, 131.47, 129.46, 115.15 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –131.96 (s, 4 F) ppm. MS (EI): m/z = 434 $[M]^+$.

(4-Chlorophenyl)(2,3,5,6-tetrafluorophenyl)sulfane (5i): White solid, m.p. 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.22 (m, 4 H), 7.15–7.04 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.86 (d, J = 13.0 Hz), 147.14 (m), 145.40 (d, J = 13.0 Hz), 144.68 (m), 134.06, 132.82, 131.91, 129.36, 114.44 (m), 107.12 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.85 (m, 2 F), –137.26 to –137.45 (m, 2 F) ppm. GC–MS (EI): m/z = 292 $[M]^+$. HRMS (EI): calcd. for $C_{12}H_5F_4SCl$ $[M]^+$ 291.9737; found 291.9724.

(4-Nitrophenyl)(2,3,5,6-tetrafluorophenyl)sulfane (5j): Yellow solid, m.p. 93.7–95.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14–8.10 (m, 2 H), 7.29 (m, 2 H), 7.27–7.21 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.01 (d, J = 11.0 Hz), 147.26 (m), 146.19, 145.55 (m), 144.76 (m), 142.45, 127.60, 124.19, 111.15 (m), 108.54 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –131.50 (m, 2 F), –136.05 to –136.24 (m, 2 F) ppm. MS (EI): m/z = 303 $[M]^+$. HRMS (EI): calcd. for $C_{12}H_5NO_2F_4S$ $[M]^+$ 302.9977; found 302.9986.

2-(2,3,5,6-Tetrafluorophenylthio)benzo[d]thiazole (5k): Yellow solid, m.p. 74.2–75.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (m, 1 H), 7.74–7.70 (m, 1 H), 7.45–7.39 (m, 1 H), 7.35–7.25 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.04, 152.94, 148.13 (m), 147.18 (m), 145.63 (m), 144.68 (m), 135.52, 126.29, 124.94, 122.26, 120.86, 109.96 (m), 109.11 (m) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –130.64 (m, 2 F), –136.31 to –136.46 (m, 2 F) ppm. MS (ESI): m/z = 316 $[M]^+$. HRMS (EI): calcd. for $C_{13}H_5NF_4S_2$ $[M]^+$ 314.9800; found 314.9794.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra.

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