A novel and efficient cross-coupling of tris(fluorinated phenyl)boroxins with disulfides catalyzed by CuI/1,10-phenanthroline

Chuanming Yu, Beibei Jin, Zhenyu Liu, and Weihui Zhong

Abstract: Under an oxygen atmosphere, the cross-coupling of tris(fluorinated phenyl)boroxins and disulfides catalyzed by CuI/1,10-phenanthroline were smoothly achieved to produce the corresponding asymmetric fluorinated arylsulfides in good-to-excellent yields.

Key words: disulfide, tris(fluorinated phenyl)boroxin, fluorinated arylsulfide, cross-coupling, cuprous iodide.

Résumé : On a effectué sans difficulté le couplage croisé de tris(flurophényl)boroxines et de disulfures, sous atmosphère d'oxygène et catalyse par du CuI/phénanthroline; on a pu isoler les arylsulfures fluorés asymétriques correspondants avec des rendements allant de bons à excellents.

Mots-clés : disulfure, tris(flurophényl)boroxine, arylsulfure fluoré, couplage croisé, iodure cuivreux.

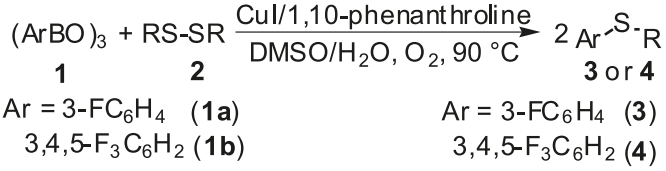
[Traduit par la Rédaction]

Introduction

Transition-metal-catalyzed aryl carbon–sulfur formation reaction is an indispensable tool in synthetic organic chemistry. Aryl sulfides and their derivatives are a common functional group in numerous pharmaceutical and biological active compounds.[1] However, compared with metal-catalyzed formation of aryl C–N or aryl C–O bonds, transition-metal-mediated carbon–sulfur bonds formation have not received particular interest, which brought about a further research area.[2] In the 1980s, Migita and co-workers[3] first reported C–S bond formation through $Pd(PPh_3)_4$ catalyzing the coupling reaction of aryl halides with thiols, but this method required considerable environmentally unfriendly PPh_3 as ligands. Later, various metal catalysts such as palladium,[4] nickel,[5] cobalt[6] and copper[7] have been developed among these reactions. While some synthetic difficulties must be addressed, for example, high temperatures, high catalyst loadings, and specially designed phosphine ligands,[8] it is gratifying to see that aryl triflates and organoboronic acids are sometimes used as good counterparts instead of aryl halides to overcome the disadvantages of the traditional reactions.[9] To the best of our knowledge, the preparation of asymmetric fluorinated arylsulfides via the cross-coupling of disulfide with tris(fluorinated phenyl)boroxin has not been reported.[10]

The arylation of tris(fluorinated phenyl)boroxins is of current interest because the unique properties conferred by the fluorine atoms might get some unexpected results and high biological activity compounds that are otherwise difficult to obtain.[11] Moreover, the analogous carbon–sulfur bond formation without aryl halides should be desirable from the viewpoint of atom economy and the waste treatment of hydrogen halides.[12] Herein, we wish to report an efficient cross-coupling of tris(fluorinated phenyl)boroxins with disulfides catalyzed by the CuI/1,10-phenanthroline complex under oxygen atmosphere to give the corresponding fluorinated arylsulfides in good to excellent yields (Scheme 1).

Scheme 1.



Results and discussion

Initially, the cross-coupling reaction of tris(3-fluorophenyl)boroxin (**1a**) with 1,2-di-*p*-tolyldisulfide (**2a**) was investigated under different conditions. Various factors including copper source and its amount, solvents, ligands, and reaction temperatures were screened. Firstly, this cross-coupling reaction was carried out in a mixture of DMSO and water (2:1) at 100 °C catalyzed by CuI in the presence of 2,2-bipyridyl,[10] the desired product (3-fluorophenyl)-4-tolylsulfide (**3a**) was obtained in only 26% yields (Table 1, entry 1) and most of **2a** was recovered. When we carried out the same reaction in an oxygen atmosphere, the yield of corresponding target product **3a** improved up to 68% (Table 1, entry 2),

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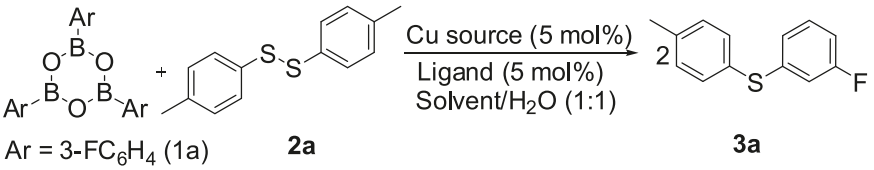
Table 1. Copper-catalyzed coupling of tris(3-fluorophenyl)boroxin with 1,2-di-*p*-tolyldisulfide.



Entry	[Cu]	Ligand	Solvent and ratios	Time (h)	*T* (°C)	Yield (%)[a]
1[b]	CuI	**L1**	DMSO/H_2O (2:1)	12	100	26
2	CuI	**L1**	DMSO/H_2O (2:1)	12	100	68
3[c]	CuI	**L1**	DMSO/H_2O (2:1)	12	90	ND
4	CuI	—	DMSO/H_2O (2:1)	24	120	ND
5	CuI	**L2**	DMSO/H_2O (2:1)	8	90	93
6	CuI	**L3**	DMSO/H_2O (2:1)	8	90	Trace
7	CuI	**L4**	DMSO/H_2O (2:1)	8	90	ND
8	CuI	**L2**	DMSO/H_2O (1:1)	8	90	94
9	CuI	**L2**	DMSO	8	90	93
10	CuI	**L2**	DMSO/H_2O (1:2)	8	90	88
11	CuI	**L2**	1,4-Dioxane	8	90	56
12	CuI	**L2**	DMF	8	90	68
13	CuI	**L2**	2-Methyltetrahydrofuran	8	90	54
14	—	**L2**	DMSO/H_2O (1:1)	8	90	ND
15	CuBr	**L2**	DMSO/H_2O (1:1)	8	90	Trace
16	CuCl	**L2**	DMSO/H_2O (1:1)	8	90	Trace
17	$CuCl_2$	**L2**	DMSO/H_2O (1:1)	8	90	Trace
18	$Cu(OAc)_2$	**L2**	DMSO/H_2O (1:1)	8	90	Trace

Note: Conditions: **1a** (1.5 mmol), **2a** (0.5 mmol), [Cu] (0.025 mmol), ligand (0.025 mmol) at 90 °C under oxygen atmosphere. ND = not determined.

[a]Isolated yields based on **2a**.

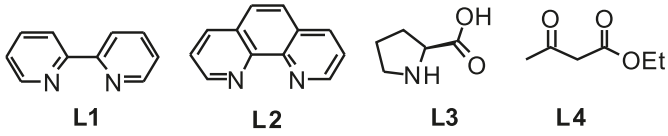
[b]Under air atmosphere.

[c]Under nitrogen atmosphere.

while no desired product was observed under nitrogen atmosphere (Table 1, entry 3). Secondly, the effect of ligands was investigated (Fig. 1). The coupling reaction did not proceed in the absence of ligand (Table 1, entry 4), even by prolonging the reaction time or increasing the temperature. To our delight, the yield of product **3a** increased up to 94% when 1,10-phenanthroline (**L2**) was employed as ligand (Table 1, entries 5–7). Then, 1,10-phenanthroline (**L2**) was employed under Taniguchi's[10] conditions, and the reactions showed that this ligand was less stable than 2,2-bipridyl (**L1**). Subsequently, we studied the effect of solvents, which have a negligible impact as compared to the reactions without additional water (Table 1, entries 5 and 8–9). A rate of DMSO and water of 1:1 was found not only to be an appropriate solvent for this reaction but also friendly to environment (Table 1, entries 5 and 8–13). Among these copper sources, CuI was the most effective (Table 1, entries 5 and 14–18). Therefore, the optimal conditions for the synthesis of fluorinated arylsulfides is by the treatment of disulfides and tri(fluorinated phenyl)boroxins in DMSO/H_2O (1:1), under oxygen atmosphere at 90 °C, in the presence of only 5 mol% of CuI/**L2** (1,10-phenanthroline).

With the optimal conditions in hand, we decided to assess the scope of this reaction. Tris(fluorinated phenyl)boroxins were first investigated to react with a series of disulfides (see Table 2). It was found that both electron-donating and electron-withdrawing substituted disulfides were tolerated

Fig. 1. Ligands employed for the C–S coupling reaction.

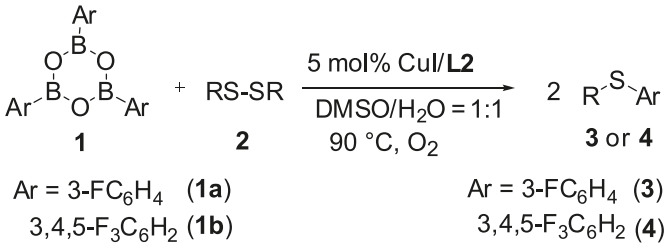


well under the optimal reactions (Table 2, entries 1–9). The present process was shown to work well in the coupling of tris(fluorinated phenyl)boroxins with disulfides containing free *para*-hydroxyl or *meta*-amino groups to provide the desired products **3j**, **4j** and **3k**, **4k** in good yields (Table 2, entries 10 and 11). These compounds are very important intermediates.

Unfortunately, as shown in Table 2, no expected product was detected when using benzothiazol-2-yl disulfide (**2l**) as substrate (Table 2, entry 12). The same result happened with **2m** (Table 2, entry 13). The possible reason was that the benzothiazol-2-yl group and carboxyl group had strong electron-donating effects and decreased the reactivities of corresponding disulfides.

Another interesting aspect of the reaction was when aliphatic of disulfides as substrates were employed (Table 2, entry 14). While 1,2-dibenzyldisulfide (**2n**) was found to give the corresponding products **3n** and **4n** only in yields of 23% and 29%, respectively, the main products were bis(4-fluorophenyl)sulfide (**5a**) and bis(3,4,5-trifluorophenyl)sul-

Table 2. CuI/1,10-phenanthroline-catalyzed coupling of tris(fluorinated phenyl)boroxins with disulfides.

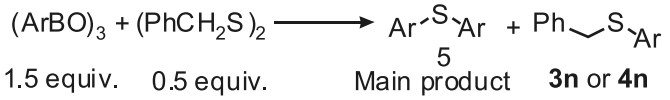


Entry	R	Ar	Time (h)	Product	Yield (%)[a]
1	4-$CH_3C_6H_4$	3-FC_6H_4	8	**3a**	90
		3,4,5-$F_3C_6H_2$	7	**4a**	95
2	4-BrC_6H_4	3-FC_6H_4	7	**3b**	99
		3,4,5-$F_3C_6H_2$	6.5	**4b**	99
3	4-ClC_6H_4	3-FC_6H_4	7	**3c**	99
		3,4,5-$F_3C_6H_2$	6.5	**4c**	99
4	4-FC_6H_4	3-FC_6H_4	7	**3d**	93
		3,4,5-$F_3C_6H_2$	6.5	**4d**	95
5	4-$O_2NC_6H_4$	3-FC_6H_4	7	**3e**	97
		3,4,5-$F_3C_6H_2$	6.5	**4e**	99
6	C_6H_5	3-FC_6H_4	7	**3f**	99
		3,4,5-$F_3C_6H_2$	6.5	**4f**	99
7	2,4-$(CH_3)_2C_6H_3$	3-FC_6H_4	8	**3g**	90
		3,4,5-$F_3C_6H_2$	7	**4g**	93
8	4-Isopropyl-C_6H_4	3-FC_6H_4	8	**3h**	93
		3,4,5-$F_3C_6H_2$	7	**4h**	93
9	2,3-$(Cl)_2C_6H_3$	3-FC_6H_4	7	**3i**	94
		3,4,5-$F_3C_6H_2$	6.5	**4i**	95
10	4-OHC_6H_4	3-FC_6H_4	8	**3j**	75
		3,4,5-$F_3C_6H_2$	7	**4j**	79
11	2-$NH_2C_6H_4$	3-FC_6H_4	8	**3k**	67
		3,4,5-$F_3C_6H_2$	7	**4k**	73
12	Benzothiazol-2-yl	3-FC_6H_4	24	**3l**	ND
		3,4,5-$F_3C_6H_2$	24	**4l**	ND
13	$HO_2CCH_2CH_2$	3-FC_6H_4	24	**3m**	ND
		3,4,5-$F_3C_6H_2$	24	**4m**	58
14	Bn	3-FC_6H_4	24	**3n**	28
		3,4,5-$F_3C_6H_2$	24	**4n**	29

Note: Conditions: **1** (1.5 mmol), **2** (0.5 mmol), CuI/**L2** (0.025 mmol/0.025 mmol), DMSO/H_2O (20 mL), O_2 (1.01×10^5 Pa). ND = not determined.

[a]Isolated yields based on disulfides.

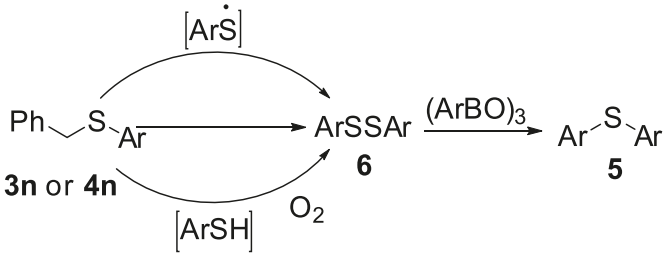
Scheme 2.



fide (**5b**) in satisfactory yields (Scheme 2). The mechanistic speculation was shown in Fig. 2; presumably, 1,2-dibenzyldisulfide underwent the expected cross-coupling reaction to form the alkylarylsulfides, followed by subsequent Cu-promoted S-dealkylation to generate arylthiols or radicals in situ and then were oxidated disulfides (**6**), which participated in a second cross-coupling with another tris(fluorinated phenyl)boroxins to afford diarylsulfides (**5**).[13]

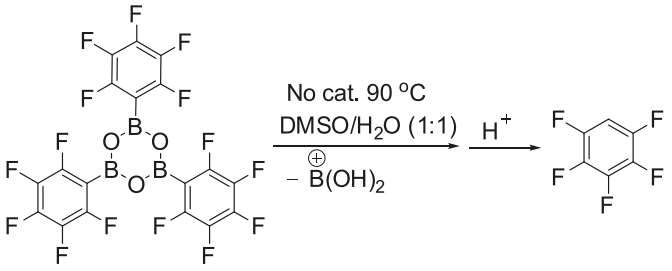
Only desired products **3a** and **4a** were observed after treating model disulfide **2a** with tris(fluorinated phenyl)boroxins in the same conditions. In this way, we demonstrate that only 1,2-dibenzyldisulfuide can be used as a surrogate for sulfides in symmetrical diarylation reactions.

Fig. 2. Plausible mechanism to produce **5** from $PhCH_2SAr$.



Nevertheless, tris(pentafluorophenyl)boroxin seems to be sensitive to the series of reaction conditions in Table 1. The

Scheme 3.



reasonable explanation was that the basic catalyst system, or even the light basic solvent DMSO at 90 °C, may be decomposing tris(pentafluorophenyl)-boroxin (Scheme 3).[14]

Conclusion

In summary, we have developed a practical protocol to asymmetric fluorinated arylsulfides via CuI catalyzed cross-coupling of tris(fluorinated phenyl)boroxins with disulfides in the presence of 1,10-phenanthroline under an oxygen atmosphere. The merits of our method are simple operation, short reaction times, good to excellent yields, and one-pot synthesis of asymmetric fluorinated phenylsulfides. Further studies on the application of fluorinated boronic acids are now in progress in our laboratory.

Experimental section

General method

All reagents are commercially available. Tris(4-fluorophenyl)boroxin, tris(3,4,5-trifluorophenyl)boroxin, and tris(pentafluorophenyl)boroxin were prepared from our own laboratory.[15] Melting points were measured on a digital melting-point apparatus WR-1B and were uncorrected. ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a Varian 400 MHz instrument using $CDCl_3$ as the solvent, and chemical shifts were expressed in parts per million (ppm) using TMS and trifluoroacetic acid as internal standards. Mass spectra were measured with a Trace Finnigan DSQ. High resolution mass spectra (HR-MS) analyse were measured on an Agilent 6210 TOF LC/MS using APCI (electrospray ionization) techniques. IR measurements were carried out with a Nicolet Aviatar-370 instrument. Elemental analysis was performed on a VarioEL-III instrument. All spectral data of the products were identical to authentic samples.

General procedure for the preparation of asymmetric fluorinated arylsulfides

To a solution of CuI (0.025 mmol) and 1,10-phenanthroline (**L2**, 0.025 mmol) in DMSO/H_2O (1:1, 20 mL) were added disulfides (0.5 mmol) and tri(3-fluorophenyl)boroxin (1.5 mmol). The mixture was stirred at 90 °C under O_2 atmosphere for a given time. Then the reaction was quenched with brine and extracted with ethyl acetate (3 × 15 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo and the crude product was purified by column chromatography on silica gel with petroleum ether as eluent to afford the desired product. All new compounds were identified by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HR-MS. Data of known compounds have been found to be identical to those reported.

(3-Fluorophenyl)-4-tolylsulfide (3a)

Colorless viscous oil. IR (KBr, cm^{-1}): 3072, 2917, 1599, 1492, 881, 810, 774. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 6.77–6.85 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 5.2 Hz, 3H), 7.34 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0 (d, *J* = 15.7 Hz, 1C), 112.7 (d, *J* = 21.2 Hz, 1C), 115.2 (d, *J* = 23.2 Hz, 1C), 123.9, 128.4, 129.3, 129.7, 130.0–130.3 (m, 1C), 130.5, 133.5, 138.6, 140.5 (d, *J* = 7.5 Hz, 1C), 163.0 (d, *J* = 246.6 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.72 (dd, *J* = 15.4, 9.4 Hz, 1F). MS (EI) *m/z* (%): 218 (M^+, 100), 203 (5). HR-MS calcd. for $C_{13}H_{11}FS$ [M^+]: 218.0565; found: 218.0553.

(4-Bromophenyl)-3-fluorophenylsulfide (3b)

Colorless viscous oil. Lit. value[16a] bp 360.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.89–6.97 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 15.2, 8.4 Hz, 3H), 7.45 (d, *J* = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –110.83 (dd, *J* = 3.0, 2.0 Hz, 1F).

(4-Chlorophenyl)-3-fluorophenylsulfide (3c)

Colorless viscous oil. IR (KBr, cm^{-1}): 3064, 2925, 2839, 1598, 1580, 1474, 881, 821, 776. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88–6.95 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 15.2, 7.2 Hz, 1H), 7.27–733 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 114.2 (d, *J* = 20.5 Hz, 1C), 117.0 (d, *J* = 22.6 Hz, 1C), 125.7, 130.0, 130.7 (d, *J* = 9.0 Hz, 2C), 133.0, 133.8 (2C), 134.4, 138.8 (d, *J* = 7.2 Hz, 1C), 163.3 (d, *J* = 247.3 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –110.95 ~ –111.01 (m, 1F). MS (EI) *m/z* (%): 238 (M^+, 100), 203 (45). HR-MS calcd. for $C_{12}H_8ClFS$ [M^+]: 238.0019; found: 238.0004.

(3-Fluorophenyl)-4-fluorophenylsulfide (3d)

Yellow oil. Lit. value[16b] bp 313.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 (td, *J* = 9.6, 2.0 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 3H), 7.45 (d, *J* = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –110.90 (dd, *J* = 15.1, 9.0 Hz, 2F).

(3-Fluorophenyl)-4-nitrophenylsulfide (3e)

Yellow solid. Mp (recrystallization in petroleum ether) 71.5–73.5 °C (lit. value[16c] mp 71.0 °C). 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13–7.14 (m, 1H), 7.21–7.27 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 5.6 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –110.63 ~ –110.69 (m, 1F).

(3-Fluorophenyl)phenylsulfide (3f)

Colorless viscous oil. Lit. value[16c] bp 302.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.86 (td, *J* = 8.4, 2.4 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 14.0, 8.0 Hz, 1H), 7.32 (dd, *J* = 15.6, 7.6 Hz, 3H), 7.41 (d, *J* = 7.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –111.51 (dd, *J* = 15.4, 9.4 Hz, 1F).

(3-Fluorophenyl)-2,4-dimethylphenylsulfide (3g)

Colorless viscous oil. IR (KBr, cm^{-1}): 3056, 2917, 1598, 1472, 880, 815, 773. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 6H), 6.68 (dt, *J* = 6.0, 2.0 Hz, 1H), 6.78 (td, *J* = 8.4,

1.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 3.6 Hz, 1H), 7.15 (dd, *J* = 14.0, 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 21.1, 112.2 (d, *J* = 21.3 Hz, 1C), 114.0 (d, *J* = 23.5 Hz, 1C), 122.8, 127.7, 127.8, 130.7 (d, *J* = 8.4 Hz, 1C), 131.8, 135.6, 139.6, 140.7 (d, *J* = 7.6 Hz, 1C), 141.7, 163.1 (d, *J* = 246.6 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.07 (dd, *J* = 24.9, 9.4 Hz, 1F). MS (EI) *m/z* (%): 127 (100), 137 (35), 232 (M^+, 5). HR-MS calcd. for $C_{14}H_{13}FS$ [M^+]: 232.0732; found: 232.0722.

(3-Fluorophenyl)-4-isopropylphenylsulfide (3h)

Colorless viscous oil. IR (KBr, cm^{-1}): 2962, 1598, 1473, 1426, 881, 828, 775, 678, 547. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24 (d, *J* = 6.8 Hz, 6H), 2.88 (dd, *J* = 13.6, 7.2 Hz, 1H), 6.80 (dd, *J* = 8.4, 8.4 Hz, 1H), 6.88 (d, *J* = 9.6 Hz, 1H), 6.97–7.04 (m, 1H), 7.12–7.21 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8 (2C), 33.8 (d, *J* = 11.4 Hz, 1C), 112.8 (d, *J* = 21.2 Hz, 1C), 115.4 (d, *J* = 22.8 Hz, 1C), 116.8, 122.7, 124.1 (2C), 127.2–128.1 (m, 1C), 129.7–130.4 (m, 1C), 133.4, 135.5 (d, *J* = 7.6 Hz, 1C), 149.4, 163.0 (d, *J* = 246.5 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –111.32 ~ –111.36 (m, 1F). MS (EI) *m/z* (%): 246 (M^+, 95), 231 (100). HR-MS calcd. for $C_{15}H_{15}FS$ [M^+]: 246.0878; found: 246.0843.

(3-Fluorophenyl)-2,3-dichlorophenylsulfide (3i)

Colorless viscous oil. IR (KBr, cm^{-1}): 1597, 1474, 1399, 1086, 881, 781, 678. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.89 (d, *J* = 8.0 Hz, 2H), 7.02–7.13 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.31–7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 116.0 (d, *J* = 20.8 Hz, 1C), 120.0 (d, *J* = 22.4 Hz, 1C), 127.9 (d, *J* = 28.1 Hz, 1C), 128.5–129.0 (m, 1C), 129.9, 130.6, 131.2 (d, *J* = 7.9 Hz, 1C), 131.7, 134.0, 134.8 (d, *J* = 7.5 Hz, 1C), 138.4, 163.2 (d, *J* = 248.3 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –110.03 (dd, *J* = 13.9, 9.4 Hz, 1F). MS (EI) *m/z* (%): 272 (M^+, 100), 202 (15). HR-MS calcd. for $C_{12}H_7Cl_2FS$ [M^+]: 271.9630; found: 271.9651.

(3-Fluorophenyl)-4- hydroxylphenylsuifide (3j)

Colorless viscous oil. IR (KBr, cm^{-1}): 3391, 2925, 1599, 1493, 878, 830, 774, 673. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.44 (s, 1H), 6.75–6.80 (m, 2H), 6.85–6.92 (m, 3H), 7.16 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.4 (d, *J* = 21.3 Hz, 1C), 114.1 (d, *J* = 23.5 Hz, 2C), 116.7, 122.8 (2C), 130.1 (d, *J* = 8.3 Hz, 2C), 136.5, 141.5, 156.4, 163.0 (d, *J* = 246.5 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –111.61 (dd, *J* = 15.4, 9.0 Hz, 1F). MS (EI) *m/z* (%): 220 (M^+, 100), 201 (25). HR-MS calcd. for $C_{12}H_9FOS$ [M^+]: 220.0358; found: 220.0347.

(3-Fluorophenyl)-2-aminophenylsulfide (3k)

Red viscous oil. IR (KBr, cm^{-1}): 3469, 3375, 1609, 1479, 879, 750, 673. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.24 (s, 2H), 6.70–6.79 (m, 4H), 6.85 (d, *J* = 8.0 Hz, 1 H), 7.15 (dd, *J* = 15.2, 7.2 Hz, 1H), 7.20 (td, *J* = 8.4, 1.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.2 (d, *J* = 21.2 Hz, 1C), 113.0 (d, *J* = 23.5 Hz, 2C), 115.4, 118.8, 121.7, 130.1 (d, *J* = 8.3 Hz, 1C), 131.6, 137.6, 139.5 (d, *J* = 6.8 Hz, 1C), 148.9, 163.1 (d, *J* = 246.4 Hz, 1C).^{19}F NMR (376 MHz, $CDCl_3$) δ: –111.37 (dd, *J* = 15.1, 9.0 Hz, 1F). MS (EI) *m/z* (%): 219 (M^+, 100), 186 (25). HR-MS calcd. for $C_{12}H_{10}FNS$ [M^+]: 219.0518; found: 219.0505.

(3-Fluorophenyl)benzylsulfide (3n)

White soild. Mp (recrystallization in petroleum ether) 30.5–31.4 °C. IR (KBr, cm^{-1}): 3060, 2921, 1599, 1495, 773, 713, 697, 678. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.13 (s, 2H), 6.86 (td, *J* = 8.4, 2.4 Hz, 1H), 7.03 (dd, *J* = 22.0, 7.6 Hz, 2H), 7.31–7.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 38.5, 110.4, 113.1 (t, *J* = 6.8 Hz, 2C), 115.7–116.0 (m, 1C), 118.8, 124.6 (2C), 127.4–128.8 (m, 2C), 130.0 (d, *J* = 8.4 Hz, 1C), 136.7, 161.5–164.0 (m, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –111.65 ~ –111.73 (m, 1F). MS (EI) *m/z* (%): 218 (M^+, 100), 91 (75). HR-MS calcd. for $C_{13}H_{11}FS$ [M^+]: 218.0565; found: 218.0554.

(3,4,5-Trifluorophenyl)-4-tolylsulfide (4a)

Colorless viscous oil. IR (KBr, cm^{-1}): 2925, 1599, 1515, 1425, 1046, 878, 829, 760. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 6.74 (dd, *J* = 8.0, 6.8 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2, 112.0 (dd, *J* = 16.7, 6.1 Hz, 2C), 128.3, 130.6 (2C), 134.0 (2C), 136.7, 139.5, 151.2 (d, *J* = 150.2 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –162.66 ~ –162.80 (m, 1F), –132.87 ~ –132.98 (m, 2F). MS (EI) *m/z* (%): 254 (M^+, 100), 239 (30). HR-MS calcd. for $C_{13}H_9FS$ [M^+]: 254.0377; found: 254.0357.

(3,4,5-Trifluorophenyl)-4-bromophenylsulfide (4b)

White soild. Mp (recrystallization in petroleum ether) 56.0–58.0 °C. IR (KBr, cm^{-1}): 3132, 1613 1518, 855, 811, 759. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.87 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 113.8 (dd, *J* = 16.7, 6.1 Hz, 2C), 123.0, 132.3 (d, *J* = 16.7 Hz, 1C), 132.9 (2C), 134.1 (2C), 137.5, 140.0, 151.3 (d, *J* = 247.3 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.11 ~ –132.19 (m, 2F), –160.92 ~ –161.07 (m, 1F). MS (EI) *m/z* (%): 318 (M^+, 100), 239 (10). HR-MS calcd. for $C_{12}H_6BrF_3S$ [M^+]: 317.9326; found: 317.9248.

(3,4,5-Trifluorophenyl)-4-chlorophenylsulfide (4c)

Colorless viscous oil. IR (KBr, cm^{-1}): 3134, 1614, 1516, 896, 841, 824, 759. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.83 (dd, *J* = 6.8, 6.8 Hz, 2H), 7.34 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 113.5 (dd, *J* = 16.7, 6.1 Hz, 2C), 120.1, 129.4 (d, *J* = 18.2 Hz, 1C), 129.9, 131.4, 132.5 (d, *J* = 50.8 Hz, 1C), 134.0, 135.0, 138.7 (d, *J* = 243.4 Hz, 1C), 151.3 (d, *J* = 247.2 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.11 ~ –132.19 (m, 2F), –160.92 ~ –161.07 (m, 1F). MS (EI) *m/z* (%): 274 (M^+, 100), 239 (40). HR-MS calcd. for $C_{12}H_6ClF_3S$ [M^+]: 273.981; found: 273.972.

(3,4,5-Trifluorophenyl)-4-fluorophenylsulfide (4d)

Colorless viscous oil. IR (KBr, cm^{-1}): 2964, 1614, 1517, 1425, 1047, 834, 759. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.76 (dd, *J* = 3.6, 3.6 Hz, 2H), 7.09 (dd, *J* = 11.6, 11.6 Hz, 2H), 7.76 (dd, *J* = 11.6, 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.3 (dd, *J* = 17.1, 6.2 Hz, 1C), 113.1 (d, *J* = 23.2 Hz, 1C), 116.1–117.1 (m, 1C), 125.2, 127.4, 132.8 (d, *J* = 264.4 Hz, 1C), 135.4, 136.0, 138.2 (d, *J* = 249.8 Hz, 1C), 151.3 (d, *J* = 251.5 Hz, 2C), 163.3 (d, *J* = 240.4 Hz,

1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –152.71 ~ –152.86 (m, 2F), –182.25 ~ –183.40 (m, 1F). MS (EI) *m/z* (%): 258 (M^+, 100), 238 (35). HR-MS calcd. for $C_{12}H_6F_3S$ [M^+]: 258.0126; found: 258.0114.

(3,4,5-Trifluorophenyl)-4-nitrophenylsulfide (4e)

Yellow solid. Mp (recrystallization in petroleum ether) 110.2–111.0 °C. IR (KBr, cm^{-1}): 3130, 1617, 1505, 1401, 1087, 854, 739. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (dd, *J* = 6.8, 6.8 Hz, 2H), 7.26–7.31 (m, 2H), 8.15 (dd, *J* = 9.6, 4.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 117.8–118.0 (m, 2C), 124.4 (2C), 128.4 (2C), 139.3, 141.8, 145.1, 146.4, 151.6 (d, *J* = 244.0 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –130.60 (dd, *J* = 22.6, 9.0 Hz, 2F), –156.68 ~ –156.78 (m, 1F). MS (EI) *m/z* (%): 285 (M^+, 100), 238 (50), 255 (25). HR-MS calcd. for $C_{12}H_6F_3NO_2S$ [M^+]: 285.0071; found: 285.0060.

(3,4,5-Trifluorophenyl)phenylsulfide (4f)

Colorless viscous oil. Lit. value[16d] bp 316.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.81–6.84 (m, 2H), 7.37–7.74 (m, 5H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –161.80 (t, *J* = 19.3 Hz, 1F), –132.62 (t, *J* = 12.0 Hz, 2F).

(3,4,5-Trifluorophenyl)-2,4-dimethylphenylsulfide (4g)

Cololress viscous oil. IR (KBr, cm^{-1}): 2917, 1613, 1515, 1424, 1317, 1046, 899, 875, 758. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (d, *J* = 9.2 Hz, 6H), 6.61 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.8 (d, *J* = 24.9 Hz, 1C), 22.7, 110.7 (dd, *J* = 17.1, 6.1 Hz, 2C), 126.6, 128.1, 132.1, 134.7, 136.1 (d, *J* = 27.3 Hz, 1C), 138.8, 140.4, 142.0, 151.4 (d, *J* = 250.4 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –153.34 (dd, *J* = 19.9, 16.9 Hz, 2F), –183.71 ~ –183.86 (m, 1F). MS (EI) *m/z* (%): 268 (M^+, 100), 91 (50), 218 (25). HR-MS calcd. for $C_{14}H_{11}F_3S$ [M^+]: 268.053; found: 268.133.

(3,4,5-Trifluorophenyl)-4-isopropylphenylsulfide (4h)

Colorless viscous oil. IR (KBr, cm^{-1}): 2963, 1613, 1516, 1425, 1317, 1233, 897, 831, 758. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, *J* = 7.6 Hz, 6H), 2.30 (t, *J* = 7.2 Hz, 1H), 6.77 (dd, *J* = 8.4, 6.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8 (2C), 33.9, 112.2 (dd, *J* = 17.1, 6.1 Hz, 2C), 127.5 (d, *J* = 33.1 Hz, 1C), 128.7, 133.7 (d, *J* = 28.7 Hz, 1C), 134.6 (d, *J* = 4.8 Hz, 1C), 136.0, 136.8, 139.3, 150.2, 151.3 (d, *J* = 247.7 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –153.17 ~ –153.28 (m, 2F), –182.87 ~ –183.00 (m, 1F). MS (EI) *m/z* (%): 282 (M^+, 100), 267 (95), 105 (35). HR-MS calcd. for $C_{15}H_{13}F_3S$ [M^+]: 282.0690; found: 282.0710.

(3,4,5-Trifluorophenyl)-2,3-dichlorophenylsulfide (4i)

Colorless solid. Mp (recrystallization in petroleum ether) 55.4–57.2 °C. IR (KBr, cm^{-1}): 3131, 1616, 1518, 1401, 796, 770. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.92–7.06 (m, 3H), 7.13 (dd, *J* = 16.0, 8.4 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.1 (d, *J* = 22.0 Hz, 1C), 116.5 (dd, *J* = 16.3, 6.0 Hz, 2C), 127.7, 129.3 (d, *J* = 26.2 Hz, 2C), 132.6, 134.2, 136.6, 140.0 (d, *J* = 245.0 Hz, 1C), 151.5 (d, *J* = 242.3 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –131.44 (dd, *J* = 24.4, 20.3 Hz, 2F), –158.49 (dd, *J* = 26.3, 20.3 Hz, 1F). MS (EI) *m/z* (%): 238 (100), 308 (M^+, 40). HR-MS calcd. for $C_{12}H_5Cl_2F_3S$ [M^+]: 307.9441; found: 307.9462.

(3,4,5-Trifluorophenyl)-4-hydroxylphenylsulfide (4j)

White solid. Mp (recrystallization in petroleum ether) 68.7–70.1 °C. IR (KBr, cm^{-1}): 3403, 3133, 1614, 1516, 1401, 1045, 832, 758, 619. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.07 (s, 1H), 6.69 (dd, *J* = 13.2, 13.2 Hz, 2H), 6.88 (d, *J* = 5.2 Hz, 2H), 7.40 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.0 (dd, *J* = 17.4, 6.1 Hz, 2C), 117.0 (2C), 122.1, 135.6, 136.2 (d, *J* = 31.90 Hz, 2C), 138.9, 151.3 (d, *J* = 250.3 Hz, 2C), 156.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –153.25 ~ –153.37 (m, 2F), –183.69 (dd, *J* = 25.9, 19.9 Hz, 1F). MS (EI) *m/z* (%): 256 (M^+, 100), 195 (25). HR-MS calcd. for $C_{12}H_7F_3OS$ [M^+]: 256.0170; found: 256.0159.

(3,4,5-Trifluorophenyl)-2-aminophenylsulfide (4k)

Light yellow solid. Mp (recrystallization in petroleum ether) 66.5–66.9 °C. IR (KBr, cm^{-1}): 3484, 3385, 3133, 1612, 1513, 1478, 1401, 832, 756, 607. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.27 (s, 2H), 6.45 (dd, *J* = 7.2, 7.2 Hz, 2H), 6.76–6.82 (m, 2 H), 7.25–7.30 (m, 1H), 7.41 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.1 (dd, *J* = 17.5, 6.1 Hz, 1C), 112.4, 115.7, 119.1, 132.2, 133.5, 136.4, 137.7, 138.9, 149.0, 151.4 (d, *J* = 252.2 Hz, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –152.36 (dd, *J* = 22. 6, 15.0 Hz, 2F), –179.93 (dd, *J* = 21.4, 12.4 Hz, 1F). MS (EI) *m/z* (%): 255 (M^+, 100), 80 (30). HR-MS calcd. for $C_{12}H_8F_3NS$ [M^+]: 255.0330; found: 255.0315.

(3,4,5-Trifluorophenylthio)-3-propanoic acid (4m)

Yellow solid. Mp (recrystallization in petroleum ether) 68.9–71.2 °C. IR (KBr, cm^{-1}): 3133, 1709, 1610, 1519, 1399, 1232, 1047, 810, 756, 656. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.68–2.72 (m, 2H), 3.15 (t, *J* = 7.2 Hz, 2H), 7.00 (dd, *J* = 7.6, 6.8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.6, 33.4, 112.3 (d, *J* = 22.8 Hz, 1C), 117.8 (d, *J* = 17.5 Hz, 1C), 133.3, 136.9 (d, *J* = 253.5 Hz, 1C), 150.4 (d, *J* = 254.8 Hz, 2C), 172.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.36 (dd, *J* = 24.4, 19.9 Hz, 2F), –161.00 ~ –161.13 (m, 1F). MS (EI) *m/z* (%): 236 (M^+, 100), 177 (45). HR-MS calcd. for $C_9H_7F_3O_2S$ [M^+]: 236.2109; found: 236.1989.

(3,4,5-Trifluorophenyl)benzylsulfide (4n)

White solid. Mp (recrystallization in petroleum ether) 50.0–50.9 °C. IR (KBr, cm^{-1}): 3414, 3132, 1613, 1519, 1505, 1401, 1049, 823, 719, 694. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.08 (s, 2H), 6.88 (dd, *J* = 7.2, 6.0 Hz, 2H), 7.21–7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.5, 110.7, 113.5, 114.1 (d, *J* = 17.1 Hz, 1C), 116.4, 119.2, 127.9, 129.0, 132.6, 136.5, 151.3 (d, *J* = 26.0 Hz, 2C), 163.0–161.7 (m, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.96 (m, 2F), –161.69 (d, *J* = 17.1 Hz, 1F). MS (EI) *m/z* (%): 254 (M^+, 100), 163 (15). HR-MS calcd. for $C_{13}H_9F_3S$ [M^+]: 254.0377; found: 254.0364.

Bis(3-fluorophenyl)sulfide (5a)

Yellow oil. IR (KBr, cm^{-1}): 3064, 1597, 1472, 881, 815, 777, 677. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05 (dd, *J* = 10.4, 8.4 Hz, 2H), 7.22–7.26 (m, 2H), 7.31–7.41 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.4, 111.2 (dd, *J* = 15.7,

6.1 Hz, 1C), 113.2, 116.0, 118.9, 134.2, 139.9 (d, J = 252.3 Hz, 2C), 151.6 (dd, J = 249.4, 6.1 Hz, 2C), 162.8–161.9 (m, 2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –117.87 (dd, J = 15.4, 9.0 Hz, 2F). MS (EI) m/z (%): 222 (M^+, 100), 203 (25). HR-MS calcd. for $C_{12}H_8F_6S$ [M^+]: 222.0315; found: 222.0322.

Bis(3,4,5-trifluorophenyl)sulfide (5b)

White solid. Mp (recrystallization in petroleum ether) 87.8–89.1 °C. IR (KBr, cm^{-1}): 3133, 1617, 1514, 1402, 1043, 690, 610, 478. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08–7.16 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.1 (dd, J = 16.1, 6.1 Hz, 4C), 134.3 (2C), 139.9 (d, J = 252.5 Hz, 2C), 151.6 (d, J = 249.80 Hz, 4C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –132.07 (t, J = 16.5 Hz, 4F), –159.54 ~ –159.69 (m, 2F). MS (EI) m/z (%): 294 (M^+, 100), 163 (95). HR-MS calcd. for $C_{12}H_4F_6S$ [M^+]: 293.9938; found: 293.9921.

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