Regioselective C-S Bond Formation Accomplished by Regioselective C-F Substitution of Polyfluoroarenes with Substituted Thiophenols

Qizhong Zhou*[,1], Bin Zhang[1,2], Haining Gu[3], Aiguo Zhong[1], Tieqi Du[2], Qiong Zhou[1], Yuyuan Ye[1], Zhengneng Jin[1], Huajiang Jiang*[,1] and Rener Chen*[,1]

[1]*Department of Chemistry, Taizhou University, Taizhou 317000, P.R. China*

[2]*College of Pharmacy, Zhejiang University of Technology, Hangzhou 310014, P.R. China*

[3]*Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China*

Received July 23, 2011: Revised October 24, 2011: Accepted December 16, 2011

Abstract: The nucleophilic aromatic substitution reaction of pentafluorobenzene, methyl 2,3,4,5-tetrafluorobenzoic acid ester and 1,2,4,5-tetrafluorobenzene with substituted thiophenols showed good regioselectivity while pentafluorobenzene gave high yields. The computational results suggest that the specificity difference between polyfluorobenzenes originates from their electronic properties.

Keywords: Polyfluorobenzene, thiophenol, S_NAr, selective substution.

1. INTRODUCTION

Polyfluorobenzene derivatives are very useful compounds. Perfluoroazides were employed to modify CNT forests [1]. Polyfluorobenzene functionalized acenes can make ambipolar OFETs with high mobilities and good on/off ratios [2]. 1,2,3,4,5,6,7,8-Octafluoroanthracene was a potential n-type organic semiconductor [3]. 2,7-Substituted hexafluoroheterofluorenes were potential building blocks for the electron transporting materials [4]. Perfluoro[2.2] paracyclophane has been the subject of much interest as a potential parylene precursor [5]. 9,10-Diaryloctafluoroanthracenes and 9,10-dialkynyloctafluoroanthracenes were potential high-performance n-type organic materials [6]. Tetrakis(pentafluorophenyl)porphyrin was an ideal platform for the rapid formation of porphyrin conjugates for drugs and photonic materials [7]. 2,5,8,11,14,17-Hexafluoro-hexaperihexabenzocoronene could be used for n-type organic field-effect transistors [8].

Polyfluorobenzene attracts much indetest in modern organic synthesis. Keith Fagnou firstly developed direct intermolecular arylation of perfluorobenzene with aryl halides catalyzed by $Pd(OAc)_2$ in the presence of S-Phos or P^tBu_2Me-HBF_4 [9,10]. Olafs Daugulis demonstrated copper-catalyzed arylation and alkenylation of polyfluoroarene C-H bonds [11]. Tamejiro Hiyama established nickel-catalyzed alkenylation and alkylation of fluoroarenes *via* the activation of C-H Bond over C-F Bond [12]. Su developed direct arylation of electron deficient polyfluoroarenes with arylboronic acids catalyzed by $Pd(OAc)_2$ [13], oxidative C-H/C-H cross coupling of electron deficient polyfluoroarenes with simple arenes catalyzed by $Pd(OAc)_2$ [14], direct alkynylation of electron deficient polyfluoroarenes with terminal alkynes using O_2 as an oxidant catalyzed by $CuCl_2$ [15] and decarboxylative cross coupling of aromatic carboxylic acids with electron deficient polyfluoroarenes catalyzed by $Pd(OTFA)_2$ in the presence of PCy_3 [16]. Zhang confirmed olefination of electron deficient polyfluoroarenes with catalysis of $Pd(OAc)_2$ [17] and oxidative cross coupling of polyfluoroarenes with aromatic heterocycles by catalysis of $Pd(OAc)_2$ [18]. Shi proved cross coupling of polyfluoroarenes with simple arenes catalyzed by $Pd(OAc)_2$ using Ag_2CO_3 as an oxidant [19]. Miura *et al*. demonstrated the direct sulfoximination of azoles and polyfluoroarenes catalyzed by $Cu(OAc)_2$ [20] and the direct amination of electron deficient polyfluoroarenes with benzyl protected hydroxylamines catalyzed by $Cu(OAc)_2$ [21].

Perutz reported that fluorinated organic derivatives could be synthesized by nickel mediated C–F activation of heteroaromatics [22]. Radius reported that C-F bond could be efficiently activated by a novel N-heterocyclic carbene–nickel(0) complex [23]. In 2006, Radius reported the catalytic C-C bond formation in mild to high yield (44-83%) was accomplished by the selective C-F activation of polyfluoroarenes using N-heterocyclic carbene-stabilized nickel complex $[Ni_2(iPr_2Im)_4(COD)]$ as catalyst [24].

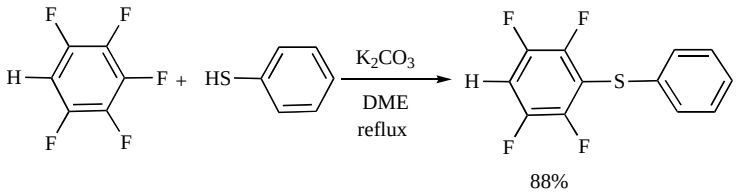
In this paper, we describe the direct regioselective C-S bond formation in mild to high yields accomplished by regioselective C-F substitution of polyfluoroarenes with substituted thiophenols.

2. RESULTS AND DISCUSSION

It was reported decades ago that several fluorine atoms of hexafluorobenzene could be replaced by thiophenol through nucleophilic aromatic substitution (S_NAr) which showed no regioselectivity [25-29]. It was also reported decades ago that several fluorine atoms of pentafluorobenzene could be

*Address correspondence to these authors at the Department of Chemistry, Taizhou University, Taizhou 317000, P.R. China; Tel: 86-571-85137169; Fax: 86-571-85137182; E-mails: cre@tzc.edu.cn; jhj@tzc.edu.cn; qizhongchou@yahoo.com

1875-6255/12 $58.00+.00



Scheme 1. Direct C-S bond formation by regioselective C-F substitution from pentafluorobenzene and thiophenol.

replaced by thiophenol through S_NAr in a non-regioselective way [26,30]. However, the reaction gave monothiolation products in very low yield. Meanwhile, the reaction of substituted tetrafluorobenzene with thiophenol was not reported before.

Pentafluorobenzene (1 mmol) and thiophenol (1 mmol) and potassium carbonate (2 mmol) was placed in dimethoxyethane (DME) (5 mL). The reaction was stirred at reflux under nitrogen atmosphere for 12 hours. After work up, we obtained compound 3a in 88% yield (see Scheme **1** and entry 1, Table **2**). Compound 3a was confirmed by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MS (EI) and HRMS.

We screened various kinds of bases and solvents (see Table **1**). We found that potassium carbonate was the best base and dry DME was the best solvent (see entry 10, Table **1**).

On the basis of these results, the optimal reaction condition involved the following parameters: potassium carbonate as a base, DME as a solvent, and reaction temperature at 86 °C under nitrogen atmosphere.

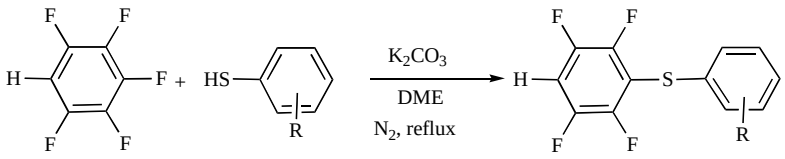
Under the optimal reaction condition in hand, a study on the substrate scope was carried out, and the results were summarized in Table **2** (see Scheme **2** and Table **2**).

When pentafluorobenzene and substituted thiophenols bearing electron donating group as well as electron withdrawing group were used as starting materials, all products were obtained in high yields (85-97%, see Table **2**, entry 1-8) and in good regioselectivity. Substituted thiophenols suffered a great functional group tolerance. All the substituted thiophenols bearing electron donating group as well as electron withdrawing group replaced the third F atom of pentafluorobenzene and showed similar reactivity to

Table 1. Optimization of the Reaction Conditions

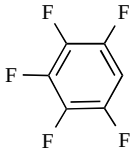
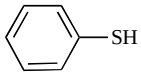
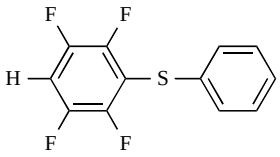
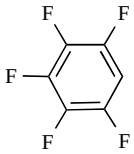
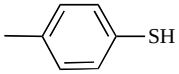
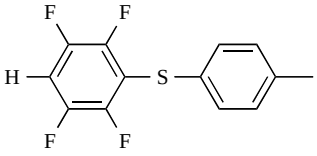
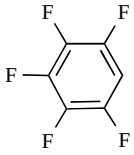
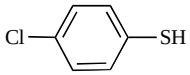
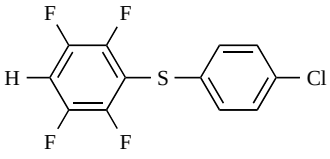
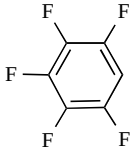
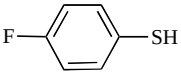
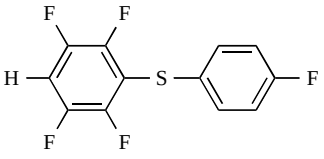
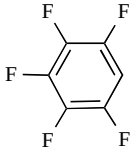
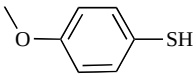
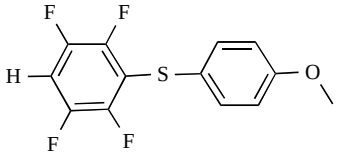
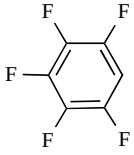
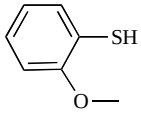
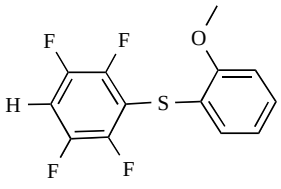
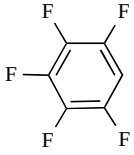
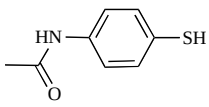
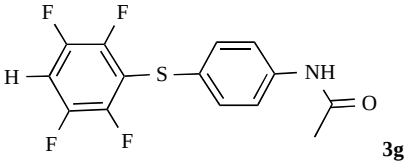
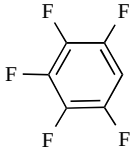
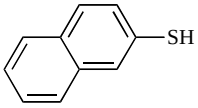
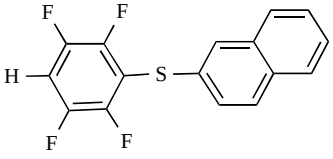
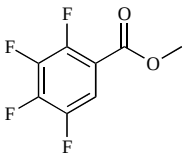
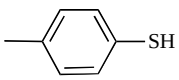
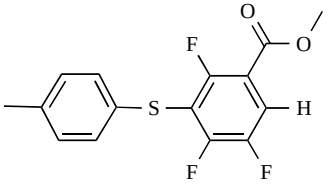
entry	base	solvent	Temp.	Yield%
1	K_2CO_3	$CHCl_3$	reflux	5
2	K_2CO_3	MeOH	reflux	5
3	K_2CO_3	THF	reflux	35
4	K_2CO_3	CH_3CN	reflux	85
5	K_2CO_3	$ClCH_2CH_2Cl$	reflux	75
6	K_2CO_3	dioxane	reflux	83
7	K_2CO_3	PhMe	reflux	26
8	K_2CO_3	DMF	110 °C	73
9	K_2CO_3	DMSO	110°C	17
10	K_2CO_3	DME	reflux	93[a]
11	K_2CO_3	DME	reflux	88[b]
12	K_3PO_4	DME	reflux	91[a]
13	KOAc	DME	reflux	47[b]
14	Na_2CO_3	DME	reflux	37[b]
15	Cs_2CO_3	DME	reflux	81[b]

[a]DME (anhydrous) was distilled from sodium on benzophenone; [b]DME (chemical purity) was used without purification and [c]other solvents were used without purification.

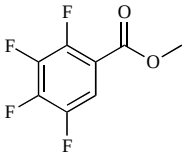
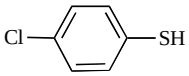
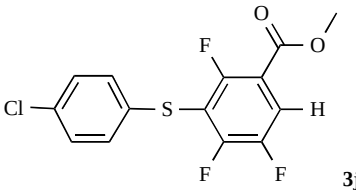
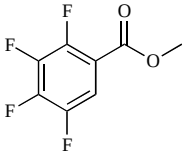
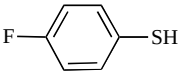
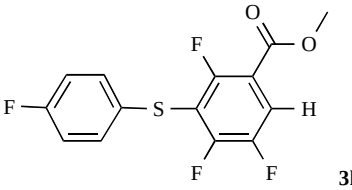
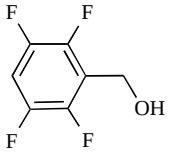
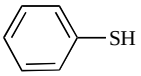
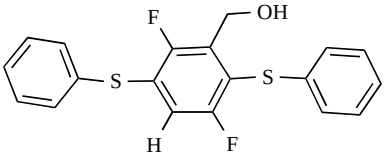
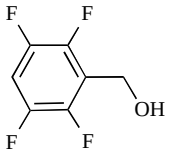
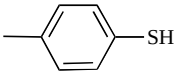
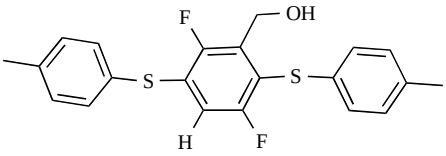
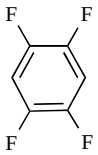
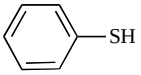
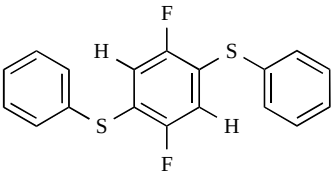
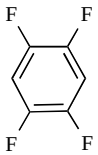
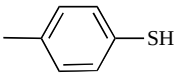
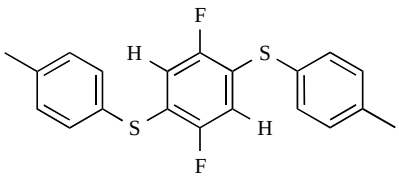
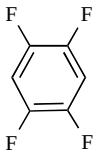
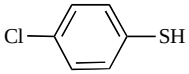
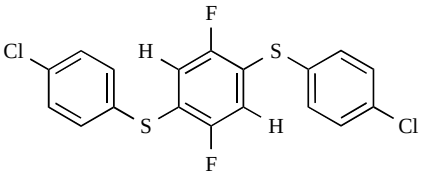
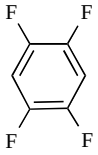
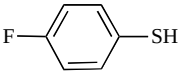
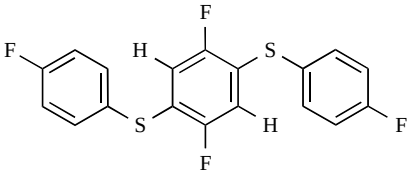
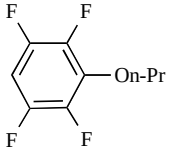
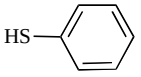


Scheme 2. Synthesis of various polyfluoroaryl aryl thioethers.

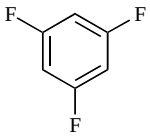
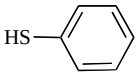
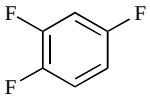
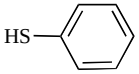
Table 2. Synthesis of Various Polyfluoroaryl Aryl Thioethers

entry	polyfluoroarene	Thiophenol	product	Yield(%)
1			 **3a**	94
2			 **3b**	97
3			 **3c**	89
4			 **3d**	94
5			 **3e**	91
6			 **3f**	85
7			 **3g**	87
8			 **3h**	88
9			 **3i**	58

(Table 2). Contd…..

entry	polyfluoroarene	Thiophenol	product	Yield(%)
10			 **3j**	54
11			 **3k**	71
12			 **3l**	45
13			 **3m**	48
14			 **3n**	40
15			 **3o**	49
16			 **3p**	46
17			 **3q**	42
18				0

(Table 2). Contd…..

entry	polyfluoroarene	Thiophenol	product	Yield(%)
19				0
20				0

generate the corresponding product in high yields. The reaction showed good regioselectivity. Substituted thiophenols also replaced the third F atom of methyl 2,3,4,5-tetrafluorobenzoic acid ester in mild yields, which showed good regioselectivity (see Table **2**, entry 9-11). When 2,3,5,6-tetrafluorobenzyl alcohol was used as a starting material, two substituted thiophenols replaced the second and the fifth F atoms of 2,3,5,6-tetrafluorobenzyl alcohol, which gave mild yields (see Table **2**, entry 12-13). Substituted thiophenols replaced the first and the forth F atoms of 1,2,4,5-tetrafluorobenzene in mild yields, which showed regioselectivity (see Table **2**, entry 14-17). n-propyl 2,3,5,6-tetrafluoropheny ether and trifluorobenzenes did not react with thiophenol (see Table **2**, entry 18-20).

Computational Details

In our present work, we explored the polyfluorobenzene bindings' selectivity and specicity from the perspective of structure and reactivity properties. The ultimate question we wanted to answer is the following: What are the structural, electronic, or stereoelectronic factors that govern Polyfluorobenzene specific binding capability? To describe regioselectivity tendencies of individual atoms in molecules, local descriptors were employed.

We first performed computational chemistry studies to predict the most electrophilic (nucleophilic) site of the pentafluorobenzene and 1,2,4,5-tetrafluorobene model systems. This was done through the dual descriptor in conceptual density functional theory (CDFT).[31-33] In CDFT, the dual descriptor is defined as [34,35]

$$f^2(r)=(\partial^2\rho(r)/\partial^2 N(r))_{\upsilon} \quad (1)$$

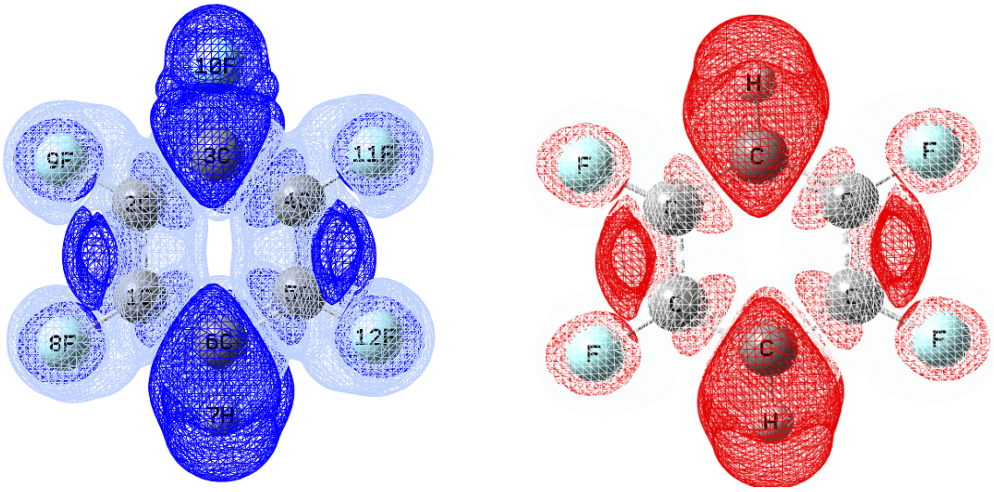
where N is the total number of electrons, $\rho(r)$ is the electron density, and $v(r)$ is the external potential, the framework formed by all atomic nuclei of the system. Within the frozen orbital approximation

$$f^2(r) \approx \rho_{LUMO}(r) - \rho_{HOMO}(r), \quad (2)$$

the $\rho_{HOMO}(r)$ and $\rho_{LUMO}(r)$ are the highest occupied molecular orbital(HOMO) density and the lowest unoccupied molecular orbital(LUMO) density, respectively.

In CDFT, it is known that $f^{(2)}(r)$ will be positive in the electrophilic regions as $\rho_{LUMO}(r)$ is large, and negative in the nucleophilic regions as $\rho_{HOMO}(r)$ dominates these regions. The dual descriptor contour surface of the polyfluorobenzene model systems are shown at the DFT B3LYP/6-311+G(*d*) level of theory in Fig. (**1**).

In Fig. (**1**), it clearly shows that the 3C-10F bond is the most nucleophilic(blue in color, negative in the dual



(a) $f^2(r)<0$ for pentafluorobenzene (b) $f^2(r)>0$ for 1,2,4,5-tetrafluorobene

Fig. (1). Predicted (**a**) nucleophilic aromatic substation(blue region, the C-F bond) and (**b**) electrophilic aromatic substation(red region, the C-H bond) site, from the dual descriptor, $f^{(2)}(r)$, of conceptual density functional theory for polyfluorobenzene systems.

descriptor quantity, Fig. **1a**) within the pentafluorobenzene system. But the C-H bond is the most electrophilic(red in color, positive in the dual descriptor quantity, Fig. **1b**) within the 1,2,4,5-tetrafluorobene system. This verified experimentally. These results suggest that the specicity difference between polyfluorobenzenes originates from their electronic properties.

3. CONCLUSIONS

The regioselective S_NAr reaction of pentafluorobenzene, methyl 2,3,4,5-tetrafluorobenzoic acid ester and 1,2,4,5-tetrafluorobene with substituted thiophenols showed good regioselectivity while pentafluorobenzene gave high yields. Herein, we develop a novel method in a regioselective way to prepare polyfluoroaryl aryl thioether from polyfluoroarenes and substituted thiophenes. These computational results suggest that the specicity difference between polyfluorobenzenes originates from their electronic properties. The transition metal catalyzed cross coupling reactivity of polyfluoroarene *via* C-H functionalized way was on the progress.

4. EXPERIMENTAL

Pentafluorobenzene (0.168 g, 1 mmol), thiophenol (0.11 g, 1 mmol), and potassium carbonate (0.276 g, 2 mmol) was placed in dry dimethoxyethane (DME) (5 mL). The reaction was refluxed under nitrogen atmosphere for 12 hours. Till cooled, the reaction mixture was filtered. The organic solvent was evaporated. The mixture was dissolved with dichloromethane (10 mL). Then the mixture was washed with 10% NaOH (10 mL). The organic phase was dried over sodium sulphate. After evaporation of the solvent, the mixture was subjected to column chromatography with petroleum ether as eluent.

3a:colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.51-7.22 (m, 5H), 7.11-7.07 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.0 (dm, J = 79.2 Hz), 145.5 (dm, J = 84.7 Hz), 137.4, 133.3, 130.9, 129.6, 129.3, 128.1, 127.9, 127.5, 115.2 (t, J = 21.0 Hz), 107.3 (t, J = 22.6 Hz); ^{19}F NMR ($CDCl_3$, 300 MHz): -133.1 (m, 2F), -137.9 (m, 2F); MS (EI): 258 (M^+); HRMS calcd for $C_{12}H_6F_4S$: 258.0126, found: 258.0123.

3b: colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.32-7.25 (m, 2H), 7.11-7.03 (m, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.0 (dm, J = 69.0 Hz), 145.5 (dm, J = 70.6 Hz), 138.6, 131.7, 130.4, 130.1, 129.6, 128.9, 116.0 (t, J = 19.5 Hz), 106.9 (t, J = 23.0 Hz), 21.4; ^{19}F NMR ($CDCl_3$, 300 MHz): -62.5 (m, 2F), -67.2 (m, 2F); MS (EI): 272 (M^+); HRMS calcd for $C_{13}H_8F_4S$: 272.0283, found: 272.0281.

3c: white solid; m.p. 60-62°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.32-7.25 (m, 4H), 7.13-7.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.0 (dm, J = 75.3 Hz), 145.5 (dm, J = 76.8 Hz), 134.5, 132.4, 131.7, 129.8, 114.9 (t, J = 20.1 Hz), 107.5 (t, J = 22.4 Hz); ^{19}F NMR ($CDCl_3$, 300 MHz): -62.2 (m, 2F), -66.8 (m, 2F); MS (EI): 292 (M^+); HRMS calcd for $C_{12}H_5ClF_4S$: 291.9737, found: 291.9734.

3d: white solid; m.p. 56-58°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.46-7.42 (m, 2H), 7.12-6.98 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.3, 161.8, 147.9 (dm, J = 67.7 Hz), 145.4 (dm, J = 70.5 Hz), 134.2 (d, J = 7.9 Hz), 131.6 (d, J = 8.4 Hz), 128.1, 116.8 (d, J = 21.6 Hz), 115.8 (t, J = 20.4 Hz), 107.2 (t, J = 22.6 Hz); ^{19}F NMR ($CDCl_3$, 300 MHz): -62.8 (m, 2F), -67.1 (m, 2F), -87.9 (m, 1F); MS (EI): 276 (M^+); HRMS calcd for $C_{12}H_5F_5S$: 276.0032, found: 276.0036.

3e: colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.44 (d, J = 8.8 Hz, 2H), 6.97-7.05 (m, 1H), 6.82 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 160.4, 147.8 (dm, J = 44.7 Hz), 145.2 (dm, J = 76.2 Hz), 134.8, 123.1, 116.9 (t, J = 19.2 Hz), 115.2, 106.6 (t, J = 22.4 Hz), 55.6; ^{19}F NMR ($CDCl_3$, 300 MHz): -61.4 (m, 2F), -65.7 (m, 2F); MS (EI): 288 (M^+); HRMS calcd for $C_{13}H_8F_4OS$: 288.0232, found: 288.0234.

3f: white solid; m.p. 44-45°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.22-7.26 (m, 1H), 7.04-7.11 (m, 2H), 6.85-6.88 (m, 2H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.8, 148.0 (dm, J = 105.7 Hz), 145.5 (dm, J = 107.6 Hz), 130.9, 129.3, 121.5, 121.3, 114.4 (t, J = 19.2 Hz), 111.4, 106.8 (t, J = 21.9 Hz), 56.2; ^{19}F NMR ($CDCl_3$, 300 MHz): -62.2 (m, 2F), -67.4 (m, 2F); MS (EI): 288 (M^+); HRMS calcd for $C_{13}H_8F_4OS$: 288.0232, found: 288.0231.

3g: white solid; m.p. 139-140°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.68 (br, s, 1H), 7.41 (dd, J_1 = 8.4 Hz, J_2 = 8.8 Hz, 4H), 7.04-7.09 (m, 1H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 168.9, 147.9 (dm, J = 67.8 Hz), 145.4 (dm, J = 71.1 Hz), 138.4, 132.8, 127.7, 120.8, 115.8 (t, J = 18.9 Hz), 107.0 (t, J = 22.5 Hz), 24.7; ^{19}F NMR ($CDCl_3$, 300 MHz): -62.6 (m, 2F), -67.1 (m, 2F); MS (EI): 315 (M^+); HRMS calcd for $C_{14}H_9F_4NOS$: 315.0341, found: 315.0340.

3h: white solid; m.p. 72-73°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.71-7.86 (m, 4H), 7.37-7.48 (m, 3H), 7.02-7.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 148.0 (dm, J = 87.4 Hz), 145.5 (dm, J = 89.7 Hz), 133.9, 132.8, 130.4, 130.1, 129.4, 128.0, 127.7, 127.1, 126.9, 115.2 (t, J = 19.7 Hz), 107.3 (t, J = 22.7 Hz); ^{19}F NMR ($CDCl_3$, 300 MHz): -62.8 (d, J = 10.2 Hz, 2F), -67.6 (d, J = 6.6 Hz, 2F); MS (EI): 308 (M^+); HRMS calcd for $C_{18}H_8F_4S$: 308.0283, found: 308.0281.

3i: white solid; m.p. 58-59°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.47-7.43 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 3.94 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.1 (d, J = 1.8 Hz), 158.4 (t, J = 3.2 Hz), 155.9 (t, J = 3.2 Hz), 152.7 (dd, J_1 = 5.3 Hz, J_2 = 5.0 Hz), 150.2 (dd, J_1 = 3.9 Hz, J_2 = 4.0 Hz), 148.8 (dd, J_1 = 4.1 Hz, J_2 = 4.6 Hz), 146.2 (dd, J_1 = 4.2 Hz, J_2 = 3.9 Hz), 138.7, 131.8, 130.4, 129.0, 120.0 (m), 112.7 (dd, J_1 = 4.2 Hz, J_2 = 4.1 Hz), 53.2, 21.4; ^{19}F NMR ($CDCl_3$, 300 MHz): -62.6 (d, J = 16.5 Hz, 1F), -74.8 (d, J = 22.2 Hz, 1F), -90.5 (d, J = 6.6 Hz, 1F); MS (EI): 312 (M^+); HRMS calcd for $C_{15}H_{11}F_3O_2S$: 312.0432, found: 312.0428.

3j: colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.50-7.46 (m, 1H), 7.33-7.25 (m, 4H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 162.9 (d, J = 2.8 Hz), 158.4 (t, J = 2.8 Hz), 155.9 (t, J = 1.5 Hz), 152.8 (dd, J_1 = 4.3 Hz, J_2 = 4.1 Hz), 150.3 (dd, J_1 = 4.2 Hz, J_2 = 4.1 Hz), 148.8 (dd, J_1 = 4.0 Hz, J_2 = 3.0 Hz), 146.2 (dd, J_1 = 3.9 Hz, J_2 = 4.2 Hz), 134.6, 132.5, 131.2, 129.8, 119.6 (dm, J = 204.6 Hz), 112.9 (dd, J_1 = 3.1 Hz, J_2 = 4.4 Hz), 53.2; ^{19}F NMR ($CDCl_3$, 300 MHz): -64.0

(m, 1F), -76.2 (m, 1F), -91.7 (m, 1F); MS (EI): 332 (M^+); HRMS calcd for $C_{14}H_8ClF_3O_2S$: 331.9886 found:331.9889.

3k: white solid; m.p. 63-64°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.50-7.46 (m, 1H), 7.38-7.28 (m, 4H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.1 (t, J = 2.0 Hz), 158.5 (t, J = 3.9 Hz), 156.1 (t, J = 3.3 Hz), 152.9 (m), 150.4 (dd, J_1 = 4.6 Hz, J_2 = 5.0 Hz), 148.8 (m), 146.2 (dd, J_1 = 4.5 Hz, J_2 = 2.0 Hz), 132.9, 131.1, 129.6, 128.3, 119.8 (dm, J = 122.2 Hz), 112.8 (dd, J_1 = 4.0 Hz, J_2 = 3.9 Hz), 53.2; ^{19}F NMR ($CDCl_3$, 300 MHz): -110.0 (dd, J_1 = 21.9 Hz, J_2= 22.5 Hz, 1F), -112.6 (m, 1F), -125.6 (d, J = 23.4 Hz, 1F), -137.6 (m, 1F); MS (EI): 316 (M^+); HRMS calcd for $C_{14}H_8F_4O_2S$: 316.0181, found: 316.0184.

3l: colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.53-7.41 (m, 5H), 7.24-7.13 (m, 5H), 6.60 (q, J = 6.4 Hz, 1H), 4.90 (d, J = 2.0 Hz, 2H), 2.16 (br, s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.0 (d, J = 3.0 Hz), 158.5 (d, J = 2.1 Hz), 155.1, 152.6, 135.9, 134.8, 132.6, 132.4, 130.9 (dd, J_1 = 7.1 Hz, J_2 = 7.9 Hz), 130.2, 130.0, 129.8, 129.5, 128.1, 126.8, 118.4 (d, J = 20.7 Hz), 115.6 (d, J = 28.5 Hz), 57.2 (q, J = 2.2 Hz); ^{19}F NMR ($CDCl_3$, 300 MHz): -81.7 (m, 1F), -92.8 (q, J = 9.3 Hz, 1F); MS (EI): 360 (M^+); HRMS calcd for $C_{19}H_{14}F_2OS_2$: 360.0454, found: 360.0449.

3m: colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.41 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.05 (q, J = 8.0 Hz, 4H), 6.52 (q, J = 6.8 Hz, 1H), 4.89 (d, J = 2.0 Hz, 2H), 2.39 (s, 3H), 2.27 (s, 3H), 2.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.0 (d, J = 2.6 Hz), 158.5 (d, J = 2.8 Hz), 154.7, 152.3, 140.3, 137.0, 135.3, 132.3, 132.1, 131.1, 130.3, 128.7, 126.0, 118.6 (d, J = 20.0 Hz), 115.0 (d, J = 29.5 Hz), 57.2 (q, J = 2.2 Hz), 21.5, 21.2; ^{19}F NMR ($CDCl_3$, 300 MHz): -80.6 (d, J = 16.2 Hz, 1F), -92.0 (m, 1F); MS (EI): 388 (M^+); HRMS calcd for $C_{21}H_{18}F_2OS_2$: 380.0767, found: 380.0766.

3n: colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.42-7.33 (m, 10H), 6.78 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.5, 155.1 (d, J = 3.6 Hz), 132.6, 132.0, 129.7, 128.5, 124.4 (dd, J_1 = 12.2 Hz, J_2 = 12.6 Hz), 117.8 (m); ^{19}F NMR ($CDCl_3$, 300 MHz): -85.4 (t, J = 7.2 Hz, 2F); MS (EI): 330 (M^+); HRMS calcd for $C_{18}H_{12}F_2S_2$: 330.0349, found: 330.0347.

3o: white solid; m.p. 162-164°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.33 (d, J = 8.0 Hz, 4H), 7.17 (d, J = 8.0 Hz, 4H), 6.68 (t, J = 7.6 Hz, 2H), 2.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.4 (d, J = 2.8 Hz), 155.0 (d, J = 2.7 Hz), 139.2, 133.6, 130.8, 128.2, 125.0 (dd, J_1 = 12.6 Hz, J_2 = 11.4 Hz), 117.2 (m), 21.5; ^{19}F NMR ($CDCl_3$, 300 MHz): -84.3 (t, J = 9.6 Hz, 2F); MS (EI): 358 (M^+); HRMS calcd for $C_{20}H_{16}F_2S_2$: 358.0662, found: 358.0662.

3p: colorless gel; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.33 (s, 8H), 6.80 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.8 (d, J = 3.1 Hz), 155.4 (d, J = 3.6 Hz), 135.1, 134.0, 130.8, 130.2, 124.5 (dd, J_1 = 12.5 Hz, J_2 = 12.2 Hz), 118.3 (m); ^{19}F NMR ($CDCl_3$, 300 MHz): -86.0 (t, J = 7.5 Hz, 2F); MS (EI): 398 (M^+); HRMS calcd for $C_{18}H_{10}Cl_2F_2S_2$: 397.9569, found: 397.9566.

3q: white solid; m.p. 143-145°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.45-7.42 (m, 4H), 7.08 (t, J = 8.4 Hz, 4H), 6.69 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.6, 162.2, 157.4, 155.0 (d, J = 2.9 Hz), 135.7 (d, J = 8.1 Hz), 127.0, 125.0 (dd, J_1 = 11.7 Hz, J_2 = 11.8 Hz), 117.4 (m); ^{19}F NMR ($CDCl_3$, 300 MHz): -112.1 (s, 2F), -115.9 (s, 2F); MS (EI): 366 (M^+); HRMS calcd for $C_{18}H_{10}F_4S_2$: 366.0160, found:366.0158.

ACKNOWLEDGEMENTS

We thank the National Natural Science Foundation of China (No. 21172166) and Natural Science Foundation of Zhejiang Province (Y4100783) for financial support.

REFERENCES

[1] Pastine, S. J.; Okawa, D.; Kessler, B.; Rolandi, M.; Llorente, M.; Zettl, A.; Fréchet, J. M. J. A facile and patternable method for the surface modification of carbon nanotube forests using perfluoroarylazides. *J. Am. Chem. Soc.*, **2008**, *130*, 4238-4239.

[2] Tang, M.; Reichardt, A. D.; Miyaki, N.; Stoltenberg, R. M.; Bao, Z. Ambipolar, high performance, acene-based organic thin film transistors. *J. Am. Chem. Soc.*, **2008**, *130*, 6064-6065.

[3] Tannaci, J. F.; Noji, M.; McBee, J.; Tilley, T. D. 9,10-Dichlorooctafluoroanthracene as a building block for n-type organic semiconductors. *J. Org. Chem.*, **2007**, *72*, 5567-5573.

[4] Geramita, K.; McBee, J.; Tilley, T. D. 2,7-Substituted hexafluoroheterofluorenes as potential building blocks for electron transporting materials. *J. Org. Chem.*, **2009**, *74*, 820-829.

[5] Dolbier, W. R., Jr.; Xie, P.; Zhang, L.; Xu, W.; Chang, Y.; Abboud. K. A. Synthesis of perfluoro[2.2]paracyclophane. *J. Org. Chem.*, **2008**, *73*, 2469-2472.

[6] Tannaci, J. F.; Noji, M.; McBee, J.; Tilley, T. D. 9,10-Disubstituted octafluoroanthracene derivatives *via* palladium-catalyzed cross-coupling. *J. Org. Chem.*, **2008**, *73*, 7895-7900.

[7] Samaroo, D.; Soll, C. E.; Todaro, L. J.; Drain, C. M. Efficient microwave-assisted synthesis of amine-substituted tetrakis(pentafluorophenyl)porphyrin. *Org. Lett.*, **2006**, *8*, 4985-4988.

[8] Kikuzawa, Y.; Mori, T.; Takeuchi, H. Synthesis of 2,5,8,11,14,17-hexafluoro-hexa-peri- hexabenzocoronene for n-type organic field-effect transistors. *Org. Lett.*, **2007**, *9*, 4817-4820.

[9] Lafrance, M.; Shore, D.; Fagnou, K. Mild and general conditions for the cross-coupling of aryl halides with pentafluorobenzene and other perfluoroaromatics. *Org. Lett.*, **2006**, *8*, 5097-5100.

[10] Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. Catalytic intermolecular direct arylation of perfluorobenzenes. *J. Am. Chem. Soc.*, **2006**, *128*, 8754-8756.

[11] Do H.; Daugulis O. Copper-catalyzed arylation and alkenylation of polyfluoroarene C-H bonds. *J. Am. Chem. Soc.*, **2008**, *130*, 1128-1129.

[12] Nakao, Y.; Kashihara, N.; Kanyiva, K. S.; Hiyama T. Nickel-catalyzed alkenylation and alkylation of fluoroarenes *via* activation of C-H bond over C-F bond. *J. Am. Chem. Soc.*, **2008**, *130*, 16170-16171.

[13] Wei, Y.; Kan, J.; Wang, M.; Su, W.; Hong, M. Palladium-catalyzed direct arylation of electron-deficient polyfluoroarenes with arylboronic acids. *Org. Lett.*, **2009**, *11*, 3346-3349.

[14] Wei, Y.; Su, W. $Pd(OAc)_2$-catalyzed oxidative C-H/C-H cross-coupling of electron-deficient polyfluoroarenes with simple arenes. *J. Am. Chem. Soc.*, **2010**, *132*, 16377-16379.

[15] Wei, Y.; Zhao, H.; Kan, J.; Su, W.; Hong, M. Copper-catalyzed direct alkynylation of electron-deficient polyfluoroarenes with terminal alkynes using O_2 as an oxidant. *J. Am. Chem. Soc.*, **2010**, *132*, 2522-2523.

[16] Zhao, H.; Wei, Y.; Xu, J.; Kan, J.; Su, W.; Hong, M. Pd/PR_3-catalyzed cross-coupling of aromatic carboxylic acids with electron-deficient polyfluoroarenes *via* combination of decarboxylation with sp^2 C-H cleavage. *J. Org. Chem.*, **2011**, *76*, 882-893.

[17] Zhang, X.; Fan, S.; He, C.; Wan, X.; Min, Q.; Yang, J.; Jiang, Z. $Pd(OAc)_2$ catalyzed olefination of highly electron-deficient perfluoroarenes. *J. Am. Chem. Soc.*, **2010**, *132*, 4506-4507.

[18] He, C.; Fan, S.; Zhang, X. Pd-catalyzed oxidative cross-coupling of perfluoroarenes with aromatic heterocycles. *J. Am. Chem. Soc.*, **2010**, *132*, 12850-12852.

[19] Li, H.; Liu, J.; Sun, C.; Li, B.; Shi, Z. Palladium-catalyzed cross-coupling of polyfluoroarenes with simple arenes. *Org. Lett.*, **2011**, *13*, 276-279.

[20] Miyasaka, M. ; Hirano, K. ; Satoh, T. ; Kowalczyk, R. ; Bolm, C. ; Miura, M. Copper-catalyzed direct sulfoximination of azoles and polyfluoroarenes under ambient conditions. *Org. Lett.*, **2011**, *13*, 359-361.

[21] Matsuda, N. ; Hirano, K.; Satoh, T.; Miura, M. Copper-catalyzed direct amination of electron-deficient arenes with hydroxylamines. *Org. Lett.*, **2011**, *13*, 2860-2863.

[22] Braun, T.; Perutz, R. N. Routes to fluorinated organic derivatives by nickel mediated C–F activation of heteroaromatics. *Chem. Commun.*, **2002**, *38*, 2749-2757.

[23] Schaub, T.; Radius, Udo. Efficient C-F and C-C activation by a novel N-heterocyclic carbene–nickel(0) complex. *Chem. Eur. J.*, **2005**, *11*, 5024-5030.

[24] Schaub, T.; Backes, M.; Radius, U. Catalytic C-C bond formation accomplished by selective C-F activation of perfluorinated arenes. *J. Am. Chem. Soc.*, **2006**, *128*, 15964-15965.

[25] Hynes, R. C.; Peach, M. E. The thiolate anion as a nucleophile. Part XIII. Reactions of some tin(II) aromatic thiolates. *J. Fluorine Chem.*, **1986**, *31*, 129-133.

[26] MacDougall, C. T.; Peach, M. E. Nickel arenethiolates as synthetic reagents. *Sulfur Lett.*, **1987**, *7*, 15-17.

[27] Jesudason, J. J.; Peach, M. E. The thiolate anion as a nucleophile Part XIV. further reactions of tin(II) arenethiolates. *J. Fluorine Chem.*, **1988**, *41*, 357-362.

[28] Mayor, M.; Lehn, J. M. Potassium cryptate of a macrobicyclic ligand featuring a reducible hexakis(phenylthio)benzene electron-acceptor site. *Helv. Chim. Acta.*, **1997**, *80*, 2277-2285.

[29] Du, N.; Robertson, G. P.; Pinnau I.; Guiver, M. D. Polymers of intrinsic microporosity derived from novel disulfone-based monomers. *Macromolecules*, **2009**, *42*, 6023-6030.

[30] Peach, M. E.; Smith, K. C. The thiolate anion as a nucleophile. Part XII. Reactions of lead(II) benzenethiolate. *J. Fluorine Chem.*, **1985**, *27*, 105-114.

[31] Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U. K., **1989**.

[32] Liu, S. Conceptual Density Functional Theory and some recent developments. *Acta Phys.Chim. Sin.*, **2009**, *25*, 590-600.

[33] Huang, Y.; Zhong, A. G.; Rong, C.Y.; Xiao, X. M.; Liu, S. B. Structure, spectroscopy, and reactivity properties of porphyrin pincers: A conceptual density functional theory and time-dependent density functional theory study. *J. Phys. Chem. A*, **2008**, *112*, 305-311;

[34] Feng, X. T.; Yu, J. G.; Lei, M.; Fang, W. H.; Liu, S. B. Toward understanding metal-binding specificity of porphyrin: A conceptual density functional theory study. *J. Phys. Chem. B*, **2009**, *113*, 13381-13389.

[35] Geerlings, P.; DeProft, F. Conceptual DFT: the chemical relevance of higher response functions. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3028-3042.