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Short Communication

Direct palladium-catalyzed desulfitative C–C coupling of polyfluoroarenes with arylsulfinate salts: Water-accelerated reactions

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ABSTRACT

A new approach to the synthesis of fluorinated biaryl compounds from easily available starting materials is described. This protocol is based on the direct palladium-catalyzed desulfitative cross-coupling of polyfluoroarenes with various arylsulfinate salts via C–H bond activation, accelerated by trace amount of water. The method allows the synthesis of various fluorinated biaryl products in moderate to good yields, and tolerated a variety of functional groups, including alkyl, phenyl, methoxy, fluoro, and chloro groups.

1. Introduction

Perfluoroarene structures represent a promising class of molecules which have been widely used as pharmaceuticals and functional materials [1–4]. Accordingly, methods able to synthesize such molecules are highly desired [5–11]. Different synthetic strategies utilized in the construction this structural motif have been reported in literature [12–16]. Among the existent protocols, the use of transition metal-catalysis to effect direct functionalization of C–H bonds of polyfluoroarenes must be regarded to be particularly promising because this method offers an effective and straightforward conversion of simple starting materials into more complex molecules by C–C bond formation.

Several metal-catalyzed direct arylation of electron-poor fluorinated arenes have been developed involving coupling either with aryl halides [17–21], aryl triflates [22], arylboronic acids [23], or arenediazonium tetrafluoroborates [24], even with simple arenes [23,25,26]. However, these precedents are still restricted in generality and selectivity: for example, addition of a base or an acid is required for the reactions and in some reactions low regioselectivity is observed. Therefore, further developments of this transformation, using more robust starting materials under milder reaction conditions are still quite desirable.

Arylsulfinate salts are attractive and useful synthetic reagents in organic chemistry owing to their remarkable stability and ease of reagent handling [27–32]. For example, sodium arenesulfinates have been successfully used as powerful sulfonylation reagents [33–37]. Furthermore, arylsulfinate salts could also serve as one ideal arylating reagents for C–C bond-forming reactions through release of SO_2, despite this transformation is rare [27–29,31].

As part of our ongoing research into synthesis of fluorine-containing compounds [38,39], we were interested in the possibility of developing an efficient, direct palladium-catalyzed C–C coupling of polyfluoroarenes with arylsulfinate salts via desulfitation. Such a reaction would represent a powerful new and direct C–C bond forming method for the formation of fluorinated polyaryls [40]. Herein we report the details of our preliminary findings.

2. Results and discussion

For optimization of the reaction conditions, pentafluorobenzene (**1**) and sodium 4-methylbenzenesulfinate (**2a**) were chosen as model substrates. Different palladium catalysts, ligands, and additives were screened in the transformation of **1** and **2a** into coupling product 1,2,4,5-tetrafluoro-3-(*p*-tolyloxy)benzene (**3a**) in

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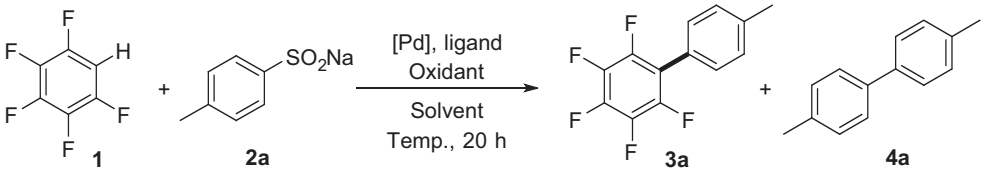
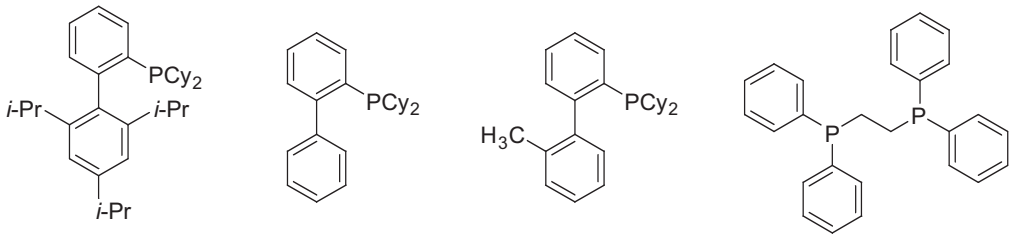
DMF for 20 h (Table 1). After exploring these reaction parameters, we found that the reaction of **1** and **2a**, using $[PdCl(allyl)]_2$ (20 mol%)/Xphos (20 mol%) as catalyst and Ag_2O (2 equiv) as an additive, in wet DMF (containing 1 vol% of H_2O) at 110 °C for 20 h afforded the desired coupling product **3a** in 72% yield (Table 1, entry 1). However, when the reaction was tested in anhydrous DMF, a predominant amount of the homocoupling product **4a** (74% yield) and only traces of the cross-coupled product **3a** was observed (Table 1, entry 2). This observation suggested that a trace amount of water present in DMF was highly beneficial for the cross-coupling. This acceleration might possibly be a result of formation of a more active catalyst [41,42]. In the absence of $[PdCl(allyl)]_2$ and Xphos, only 5% yield of cross-coupling product **3a** was observed, which proved that the present reaction is indeed catalyzed by palladium catalyst (Table 1, entry 3). At lower palladium complex loading (10 mol%), traces of **3a** and a significant amount of homocoupling product **4a** (50% yield) could be detected in the crude mixture (Table 1, entry 4). Almost no reaction occurred in the absence of an additive, Ag_2O, after a reaction time of 20 h (Table 1, entry 5). Furthermore, both 1 equiv and 3 equiv of Ag_2O offered the desired product **3a** in a low yield (Table 1, entries 6 and 7). Therefore, a combination of $[PdCl(allyl)]_2$ (20 mol%)/Xphos (20 mol%) and Ag_2O (2 equiv) turned out to be essential for obtaining the cross-coupled product **3a** in good yield (Table 1, entry 1). Replacing Ag_2O with other additives such as Ag_2CO_3, AgOAc, AgF, $AgNO_3$, air, $Cu(OTf)_2$, and $Cu(OAc)_2$ resulted in a much lower reaction efficiency (Table 1, entries 8–14). Subsequently, a series of other palladium complexes, including $Pd(OAc)_2$, $Pd(TFA)_2$, and $Pd_2(dba)_3$, were examined, and they exhibited very poor catalytic activity for the reaction (Table 1, entries 15–17). Reactions conducted with other mono- or bidentate phosphine ligands, such as Cy-John-Phos, Mephos, $P(Cy)_3$, and dppe, unfortunately provided unsatisfactory results (Table 1, entries 18–21). The temperature effects on the reaction were also examined. The cross-couplings were significantly retarded by decreasing the temperature to 80 °C or increasing the temperature to 140 °C (Table 1, entries 22 and 23).

Table 1
Optimization of direct Pd-catalyzed desulfitative cross-coupling of pentafluorobenzene with sodium 4-methylbenzenesulfinate.[a]

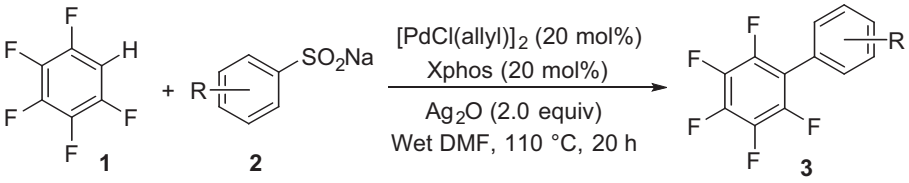


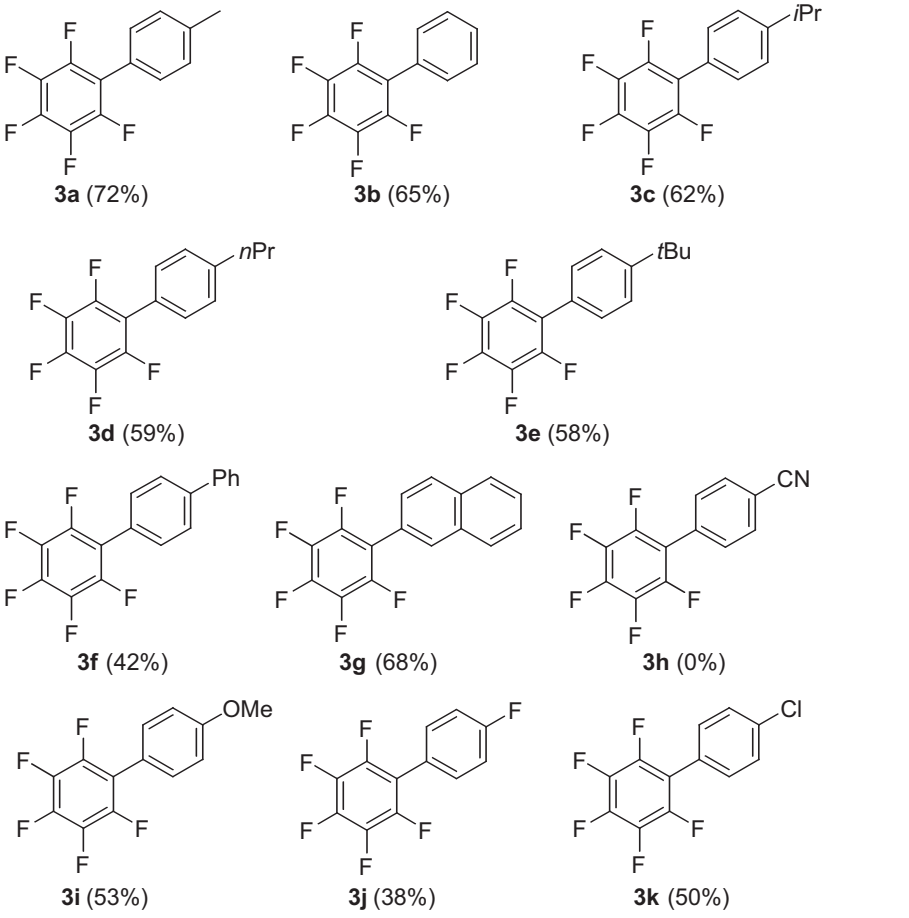
Entry	Pd catalyst (mol %)	Ligand (mol %)	Additive (equiv.)	Solvent[b]	Temp. (°C)	Yield of **3a** (%)	Yield of **4a** (%)[e]
1	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2O (2)	DMF	110	72[c]	2
2	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2O (2)	Anhydrous DMF	110	4[d]	74
3	–	–	Ag_2O (2)	DMF	110	5[d]	9
4	$[PdCl(allyl)]_2$ (10)	Xphos (20)	Ag_2O (2)	DMF	110	2[d]	50
5	$[PdCl(allyl)]_2$ (20)	Xphos (20)	–	DMF	110	3[d]	5
6	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2O (1)	DMF	110	30[d]	19
7	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2O (3)	DMF	110	47[c]	14
8	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2CO_3 (2)	DMF	110	15[d]	64
9	$[PdCl(allyl)]_2$ (20)	Xphos (20)	AgOAc (2)	DMF	110	9[d]	58
10	$[PdCl(allyl)]_2$ (20)	Xphos (20)	AgF (2)	DMF	110	6[d]	44
11	$[PdCl(allyl)]_2$ (20)	Xphos (20)	$AgNO_3$ (2)	DMF	110	8[d]	72
12	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Air	DMF	110	10[d]	32
13	$[PdCl(allyl)]_2$ (20)	Xphos (20)	$Cu(OTf)_2$ (2)	DMF	110	3[d]	67
14	$[PdCl(allyl)]_2$ (20)	Xphos (20)	$Cu(OAc)_2$ (2)	DMF	110	5[d]	53
15	$Pd(OAc)_2$ (20)	Xphos (20)	Ag_2O (2)	DMF	110	4[d]	82
16	$Pd(TFA)_2$ (20)	Xphos (20)	Ag_2O (2)	DMF	110	6[d]	78
17	$Pd_2(dba)_3$ (20)	Xphos (20)	Ag_2O (2)	DMF	110	9[d]	53
18	$[PdCl(allyl)]_2$ (20)	Cy-John-Phos (20)	Ag_2O (2)	DMF	110	36[c]	0
19	$[PdCl(allyl)]_2$ (20)	Mephos (20)	Ag_2O (2)	DMF	110	31[c]	0
20	$[PdCl(allyl)]_2$ (20)	$P(Cy)_3$ (20)	Ag_2O (2)	DMF	110	58[c]	0
21	$[PdCl(allyl)]_2$ (20)	dppe (20)	Ag_2O (2)	DMF	110	44[c]	0
22	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2O (2)	DMF	80	2[d]	12
23	$[PdCl(allyl)]_2$ (20)	Xphos (20)	Ag_2O (2)	DMF	140	4[d]	3



[a] Reaction conditions: pentafluorobenzene **1** (0.20 mmol), **2a** (0.10 mmol), solvents (1.0 mL), DMF = *N*,*N*-dimethylformamide.
[b] Containing 1 vol% of H_2O, based on the amount of DMF.
[c] Isolated yield.
[d] Detected by ^{19}F NMR.
[e] Yields were determined by GC–MS analysis of the crude reaction mixture.

Table 2
Direct Pd-catalyzed desulfitative cross-coupling of pentafluorobenzene with various arylsulfinate salts.[a,b]



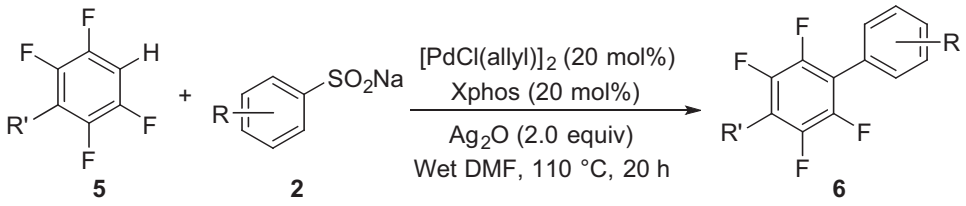


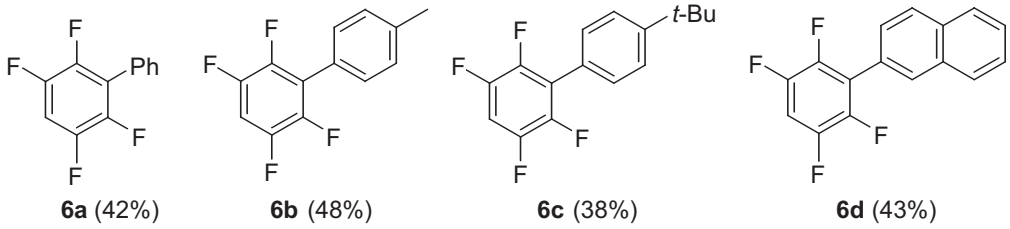
[a] Reaction conditions: pentafluorobenzene **1** (1.0 mmol), arylsulfinate salts **2** (0.5 mmol), $[PdCl(allyl)]_2$ (0.10 mmol), Xphos (0.10 mmol), Ag_2O (1.0 mmol), wet DMF (5.0 mL) containing 1 vol% of H_2O, 110 °C, 20 h.
[b] Isolated yield.

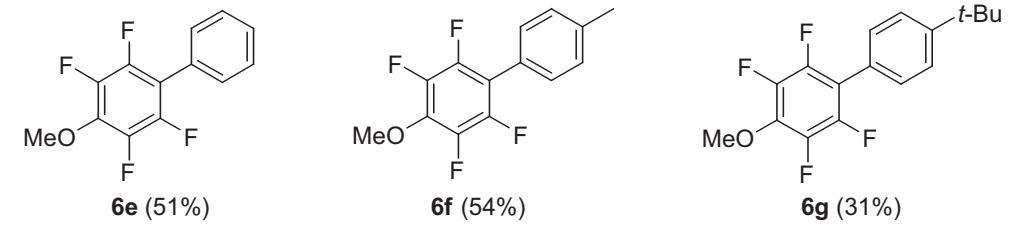
Having obtained the optimized reaction conditions, we studied the scope of the direct palladium-catalyzed desulfitative cross-coupling of pentafluorobenzene **1** with various arylsulfinate salts **2** leading to fluorinated biaryls **3**. As shown in Table 2, for sodium arylsulfinate bearing *para*-substituted alkyl or phenyl groups, the desired cross-coupled products **3a**, **3c**–**f** were obtained in moderate to good yields (42–72%). When sodium benzenesulfinate and sodium naphthalene-2-sulfinate were used to couple with pentafluorobenzene, **3b** and **3g** were isolated in 65 and 68% yields, respectively. Surprisingly, no desired product **3h** was obtained when sodium arylsulfinate having a strong electron-withdrawing *para*-CN group on the phenyl moiety was employed under the standard reaction conditions. The presence of electron-donating group, like a *para*-OMe group on the phenyl moiety of sulfinate, also provided the desired product **3i** in a 53% yield. Remarkably, the reaction tolerates fluoride and chloride in the substrates. For example, reactions with 4-fluoro- or chloro-substituted sodium benzenesulfinate led to the desired products **3j** and **3k** in 38 and 50% yields, respectively. The halogen substituents were well tolerated in this reaction, making it possible to further functionalize the products.

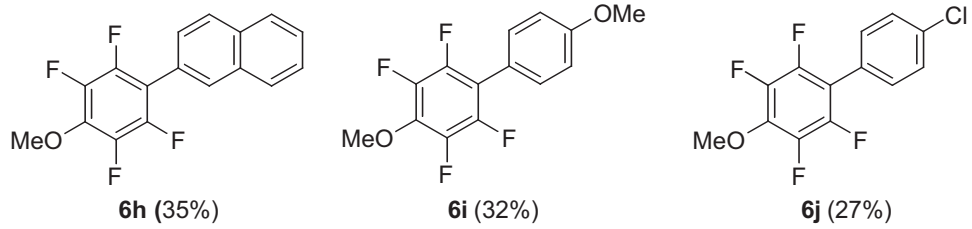
To further demonstrate the versatility of this method, we also explored various cross-coupling reactions of tetrafluoroarenes **5** with arylsulfinate salts **2** (Table 3). Reactions of 1,2,4,5-tetrafluorobenzene with sodium benzenesulfinate and sodium 4-methyl- and 4-*tert*-butyl-benzenesulfinates, or sodium naphthalene-2-sulfinate furnished the corresponding mono-arylation products **6a**–**d** in yields ranging from 38% to 48%. Furthermore, 1,2,4,5-tetrafluoro-3-methoxybenzene also smoothly reacted with sodium arylsulfinate to give the corresponding cross-coupled products **6e**–**j** in moderate yields (ranging from 27% to 54%). In contrast, 1,3-difluorobenzene failed to give the cross-coupled products under similar conditions.

Table 3
Direct Pd-catalyzed desulfitative cross-coupling of tetrafluoroarenes with various arylsulfinate salts.[a,b]









[a] Reaction conditions: tetrafluoroarenes **5** (1.0 mmol), arylsulfinate salts **2** (0.50 mmol), $[PdCl(allyl)]_2$ (0.10 mmol), Xphos (0.10 mmol), Ag_2O (1.0 mmol), wet DMF (5.0 mL) containing 1 vol% of H_2O, 110 °C, 20 h.
[b] Isolated yield.

3. Conclusions

In summary, a direct palladium-catalyzed desulfitative cross-coupling of fluorinated arenes with various arylsulfinate salts via C–H bond activation has been developed. The reaction was accelerated by trace amount of water to afford the corresponding cross-coupled products in moderate to good yields. Several functional groups, including alkyl, phenyl, methoxy, fluoro, and chloro groups, are tolerated. This reaction offers a new and convenient synthetic route to fluorinated biaryl compounds from easily available arylsulfinate salts. Work toward further development of relevant reactions is underway in our laboratories.

4. Experimental

4.1. General description of materials and methods

^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using a Bruker AVIII 400 spectrometer. ^1H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peaks were used as an internal reference: ^1H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Arylsulfinate salts were prepared according to literature procedures [29]. Other reagents were received from commercial sources. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60. Compounds **3a–k**, **6a–b**, **6e–f**, **6i–j** [39], and **6c** [43] have been previously reported in literature.

4.2. General procedure for direct Pd-catalyzed cross-coupling of polyfluoroarenes with sodium arylsulfinate

$[PdCl(allyl)]_2$ (36.6 mg, 0.10 mmol), Xphos (47.6 mg, 0.10 mmol), Ag_2O (236.0 mg, 1.0 mmol) and sodium arylsulfinate (0.50 mmol) were added to a Schlenk tube that was equipped with a stirring bar. Wet DMF (5.0 mL, containing 1 vol% of H_2O) was added into this tube, polyfluoroarene (1.0 mmol) were added in turn to the Schlenk tube through the rubber septum via syringe. The tube was capped with a septum and taken out. The reaction mixture was stirred at 110 °C for 20 h. After cooling down, the reaction mixture was

diluted with 10 mL of ethyl ether, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (10 mL). The filtrate was washed with water (3× 10 mL). The organic phase was dried over $MgSO_4$, filtered, concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

*4.2.1. 2-(2,3,5,6-Tetrafluorophenyl)naphthalene (**6d**)*

Following the general procedure, using petroleum ether as the eluent afforded a white solid (43% yield). mp: 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.89 (m, 4H), 7.65–7.51 (m, 3H), 7.19–7.07 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −138.9 to −139.2 (m), −143.6 to −143.8 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7–147.4 (m), 145.4–144.9 (m), 142.9–142.6 (m), 133.3 (s), 133.1 (s), 130.1 (t, J = 2.1 Hz), 128.4 (s), 128.3 (s), 127.8 (s), 127.1 (s), 126.6 (s), 124.9 (m), 121.6 (t, J = 16.2 Hz), 104.9 (t, J = 22.7 Hz). IR (KBr): ν 3068, 2921, 1510, 1486, 1169, 935, 828 cm^{-1}. GC–MS m/z 276 (M^+). HRMS (EI): calcd. for $C_{16}H_8F_4$ [M^+] 276.0564; found 276.0562.

*4.2.2. 4′-tert-Butyl-2,3,5,6-tetrafluoro-4-methoxybiphenyl (**6g**)*

Following the general procedure, using petroleum ether as the eluent afforded a white solid (31% yield). mp: 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 4.14 (s, 3H), 1.39 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.2 (dd, J = 22.2, 8.7 Hz, 2F), −158.3 (dd, J = 22.2, 8.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8–145.4 (m), 143.3–142.9 (m), 142.3–142.8 (m), 142.6–142.3 (m), 140.2–139.8 (m), 137.5–137.0 (m), 129.8 (t, J = 2.1 Hz), 125.6 (s), 124.4–124.3 (m), 114.5–114.2 (t, J = 17.2 Hz), 62.2 (t, J = 3.7 Hz), 34.7 (s), 31.3 (s). IR (KBr): ν 2961, 1648, 1487, 1397, 1082, 982, 838 cm^{-1}. GC–MS m/z 312 (M^+). HRMS (EI): calcd. for $C_{17}H_{16}F_4O$ [M^+] 312.1137; found 312.1135.

*4.2.3. 2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)naphthalene (**6h**)*

Following the general procedure, using petroleum ether as the eluent afforded a white solid (35% yield). mp: 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 4H), 7.61–7.45 (m, 3H), 4.14 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.0 (dd, J = 22.1, 8.7 Hz, 2F), −158.1 (dd, J = 22.1, 8.6 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8–145.6 (m), 143.4–143.2 (m), 142.6–142.4 (m), 140.1–139.9 (m), 137.8–137.5 (m), 133.1 (d, J = 10.8 Hz), 130.0 (t, J = 8.0 Hz), 128.3 (s), 128.2 (d, J = 11.2 Hz), 127.7 (s), 127.3 (t, J = 8.0 Hz), 126.9 (s), 126.5 (s), 124.7 (s), 114.3 (t, J = 68.4 Hz), 62.2 (t, J = 4.0 Hz). IR (KBr): ν 3053, 2958, 1649, 1484, 1207, 1085, 980, 826 cm^{-1}. GC–MS m/z 306 (M^+). HRMS (EI): calcd. for $C_{17}H_{10}F_4O$ [M^+] 306.0668; found 306.0667.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.06.017.

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