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Direct (Het)Arylation of Fluorinated Benzothiadiazoles and Benzotriazole with (Het)Aryl Iodides

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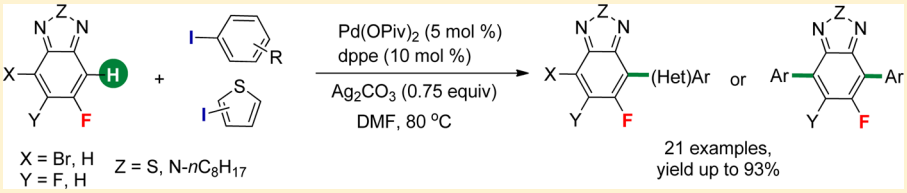
Supporting Information



ABSTRACT: A new and controllable method for the preparation of unsymmetrical and symmetrical fluorinated benzothiadiazole (FBT)−arene structures that can be applied in organic optoelectronic materials has been developed. The reaction proceeds under mild reaction conditions with high efficiency and shows excellent functional group compatibility, even toward bromide. Fluorinated benzotriazoles also take part in the reaction.

INTRODUCTION

Donor (D)/acceptor (A) moieties play an important role in advanced functional materials, particularly in organic solar cells.[1] In this context, many electron-poor aromatic units, such as benzothiadiazole (BT),[2] thiazolothiazole (TzTz),[3] thienopyrroledione (TPD),[4] diketopyrrolopyrrole (DPP),[5] and isoindigo (IID)[6] have been developed to meet the increasing demand in the development of high-performance organic electronic and optoelectronic materials. Among them, fluorinated benzothiadiazoles (FBTs), including 5-fluoro-BT (MFBT) and 5,6-difluoro-BT (DFBT), have gained great attention recently[7] and show great advantage over their nonfluorinated counterparts because of the strong electronegativity of the fluorine atom(s), which brings about a great improvement in device performance, such as photovoltaic performance.[8] Generally, FBTs have been introduced into organic materials through Stille cross-coupling.[9] Although it is reliable, such a process suffers from the use of toxic stannanes that require additional steps for preparation and are difficult to handle. Moreover, the preparation of FBT derivatives via such a strategy often generates symmetrical disubstituted FBTs,[7] in which sometimes an unstable 4,7-diiodo-DFBT[10] has to be used. To date, it remains challenging to access unsymmetrical FBTs. To address these issues, herein we demonstrate an efficient and straightforward method for the preparation of unsymmetrical and symmetrical arylated FBTs via C−H bond functionalization of FBTs with aryl iodides. The reaction proceeds under mild reaction conditions with high efficiency and shows excellent functional group tolerance, even toward bromide. During the preparation of our manuscript, a palladium-catalyzed direct C−H functionalization of FBTs with aryl bromides was reported.[11] The two methods are complementary to each other and provide facile access to unsymmetrical FBTs.

RESULTS AND DISCUSSION

We began this study by choosing 4-bromo-DFBT (**1**)[12] as the starting material on the consideration that if the selective direct arylation of **1** with aryl halides via C−H activation were feasible, the resulting arylated DFBT **3** could serve as a versatile building block through transformation of the bromide. Accordingly, compound **1** and 1-iodo-4-methylbenzene (**2a**) were chosen as the model substrates (Table 1). Initially, a negative result was obtained for the reaction of **1** with **2a** in the presence of $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), and K_2CO_3 (0.75 equiv) in DMF at 80 °C (entry 1). Inspired by our recent work,[13] we examined Ag_2CO_3 instead of K_2CO_3, as Ag_2CO_3 was previously supposed to abstract halide anions from the palladium complex, thus making it more electrophilic.[14] To our delight, a 25% yield of **3a** was obtained with intact bromide (entry 2). To improve the reaction efficiency further, different phosphane ligands and palladium sources were tested (for details, see the Supporting Information). It turned out that the bidentate ligand dppe was the optimal choice, providing **3a** in 56% yield (entry 3). Among the tested palladium salts (entries 4−7), $Pd(PPh_3)_4$ showed a beneficial effect on the reaction efficiency, affording a 74% yield of **3a** (entry 5). The counteranion of the palladium salt also had a profound influence on the reaction efficiency. Trifluoroacetate was

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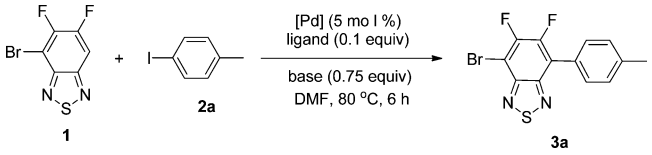
Table 1. Representative Results for Optimization of the Direct Arylation of DFBT 1 with 2a[a]



entry	[Pd]	ligand	base	yield of **3a** (%)[b]
1	$Pd(OAc)_2$	PPh_3	K_2CO_3	NR
2	$Pd(OAc)_2$	PPh_3	Ag_2CO_3	25
3	$Pd(OAc)_2$	dppe	Ag_2CO_3	56
4	$Pd_2(dba)_3$	dppe	Ag_2CO_3	30
5	$Pd(PPh_3)_4$	dppe	Ag_2CO_3	74
6	$Pd(TFA)_2$	dppe	Ag_2CO_3	60
7	$Pd(OPiv)_2$	dppe	Ag_2CO_3	85 (82)
8[c]	$Pd(OPiv)_2$	dppe	Ag_2CO_3	63
9	$PdCl_2$	dppe	Ag_2CO_3	15
10	$Pd(OPiv)_2$	dppe	Ag_2O	26
11[d]	$Pd(OPiv)_2$	dppe	AgOAc	20
12[e]	$Pd(OPiv)_2$	dppe	Ag_2CO_3	(91)
13[f]	$Pd(OPiv)_2$	dppe	Ag_2CO_3	(74)
14[g]	$Pd(OPiv)_2$	dppe	Ag_2CO_3	33
15	$Pd(OPiv)_2$	dppe	none	8
16	none	dppe	Ag_2CO_3	NR
17	$Pd(OPiv)_2$	none	none	NR

[a]Reaction conditions (unless otherwise specified): **1** (1.5 equiv), **2a** (0.2 mmol), base (0.75 equiv), DMF (1.5 mL), 6 h. [b]NMR yields as determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard (isolated yields are shown in parentheses). [c]0.05 equiv of dppe was used. [d]1.5 equiv of AgOAc was used. [e]The reaction was conducted for 12 h. [f]0.4 mmol scale, $Pd(OPiv)_2$ (2.5 mol %), dppe (5 mol %), DMF (1.5 mL), 12 h. [g]$Pd(OPiv)_2$ (1 mol %), dppe (2 mol %) in DMF (1.5 mL), 12 h.

comparable with acetate (entry 6), but the use of $PivO^-$ dramatically improved the yield to 82% (entry 7). We supposed that $PivO^-$ may function as a proton shuttle during the C−H cleavage step in FBT **1**.[15,16] The choice of the silver salt was also found to be crucial for the reaction efficiency, as Ag_2O and AgOAc both showed little effect (entries 10 and 11). The reaction is not so sensitive to the nature of the solvent, as the polar solvent DMSO, the nonpolar solvent toluene, and other solvents (dioxane and dichloroethane) were all suitable reaction media, leading to **3a** in slightly lower yields (see the Supporting Information). Finally, an optimal yield (91%) of **3a** was obtained by prolonging the reaction time to 12 h (entry 12). It is noteworthy that even when the $Pd(OPiv)_2$ loading was reduced to 2.5 mol %, a good yield of **3a** was still obtained (entry 13). The control experiments showed that palladium, phosphane ligand, and silver salt are essential for the reaction (entries 15−17), demonstrating that a Pd(0/II) redox catalytic cycle is involved in the reaction.

With the optimized conditions in hand (Table 1, entry 12), a variety of (hetero)aryl iodides **2** were investigated (Scheme 1). An excellent yield was obtained when 1-iodo-3-methylbenzene was used (**3b**). However, the steric effect dramatically influenced the reaction efficiency, and moderate yields were obtained when sterically hindered substrates were employed, such as 1-iodo-2-methylbenzene and 1-iodonaphthalene (**3c**, **3d**). Upon further optimization of the reaction conditions by increasing the reaction temperature to 100 °C, the yield of **3c** improved to 64%. Versatile functional groups such as an ester, a methyl ketone, and a nitrile were compatible with the reaction system, providing their corresponding products in good to excellent yields (**3e**−**g**). Remarkably, the successful formation of dibromide-substituted compounds **3h** and **3i** provides good opportunities for further transformation or polymerization. It should be mentioned that even when DFBT **1** was treated with 1-bromo-4-iodobenzene at 140 °C, the aryl bromide still tolerated the reaction conditions and the byproduct resulting from the coupling of aryl bromide with **1** was not observed. However, the yield of **3i** dramatically decreased to 45% (as determined by ^{19}F NMR analysis) because of the formation of some homocoupling product from the aryl iodide. 2-Iodothiophene and 3-iodothiophene also reacted smoothly, and moderate yields were obtained (**3k**, **3l**). This is noteworthy because the FBT−thiophene structure is a key structrual unit in the development of high-performance optoelectronic materials, in particular in bulk heterojunction (BHJ) solar cells.[7] The reaction was not restricted to FBTs, as difluorinated benzotriazole (DFTAZ) **4**,[12] an important structural motif in the development of optoelectronic materials,[7c] was also a suitable substrate, providing **3m** in good yield.

To probe the applicability of this method further, the selective direct monoarylation of DFBT (**5**) with aryl iodides was also tested (Scheme 2). In general, good yields of monoarylated FBTs **6a**−**d** were obtained with the use of 3 equiv of **5**, albeit with the formation of small amounts of the corresponding diarylated compounds **7**. Importantly, monothienylation of **5** still afforded the key structural motif FBT-thiophene **6e** in synthetically useful yield (**6e**). In addition, DFTAZ **9**[17] was also a competent coupling partner, providing **6f** in 62% yield. However, MFBT (**8**)[18] showed less reactivity than its difluorinated counterpart **5**, and only a moderate yield of **6g** was obtained, probably because of the low acidity of the C−H that was to be activated.[19] To our delight, the formation of symmetrical diarylated FBT **7b** also proceeded smoothly when the reaction temperature and the loading of aryl iodide were increased, thus demonstrating the controllability of this method.

To demonstrate the utility of this method, the unsymmetrical diarylated DFBT **11**, which can be used in organic optoelectronic materials, was prepared in an efficient manner through Suzuki−Miyaura coupling between **3a** and arylboronic acid **10** (Scheme 3a). Furthermore, the coupling of **6c** with aryl iodide **2g** also proceeded smoothly, providing unsymmetrical diarylated DFBT **12** in high yield (Scheme 3b). However, a one-pot strategy to prepare compound **12** through sequential C−H bond arylation failed as a result of deactivation of the palladium catalyst in the second coupling.

■ CONCLUSION

An efficient and controllable method for the preparation of arylated FBTs has been developed. The notable advantages of this protocol are its synthetic simplicity, high efficiency, mild reaction conditions, and excellent functional group compatibility. Thus, this protocol provides facile access to symmetrical and unsymmetrical FBT derivatives that can be applied in organic optoelectronic materials.

■ EXPERIMENTAL SECTION

General Procedure for the Selective Arylation of FBT 1 with Aryl Iodides. To a 25 mL Schlenk tube were added $Pd(OPiv)_2$ (5 mol %), dppe (8.0 mg, 0.1 equiv), aryl iodide (0.2 mmol, 1.0 equiv), Ag_2CO_3 (41.7 mg, 0.75 equiv), and FBT **1** (75 mg, 1.5 equiv) under

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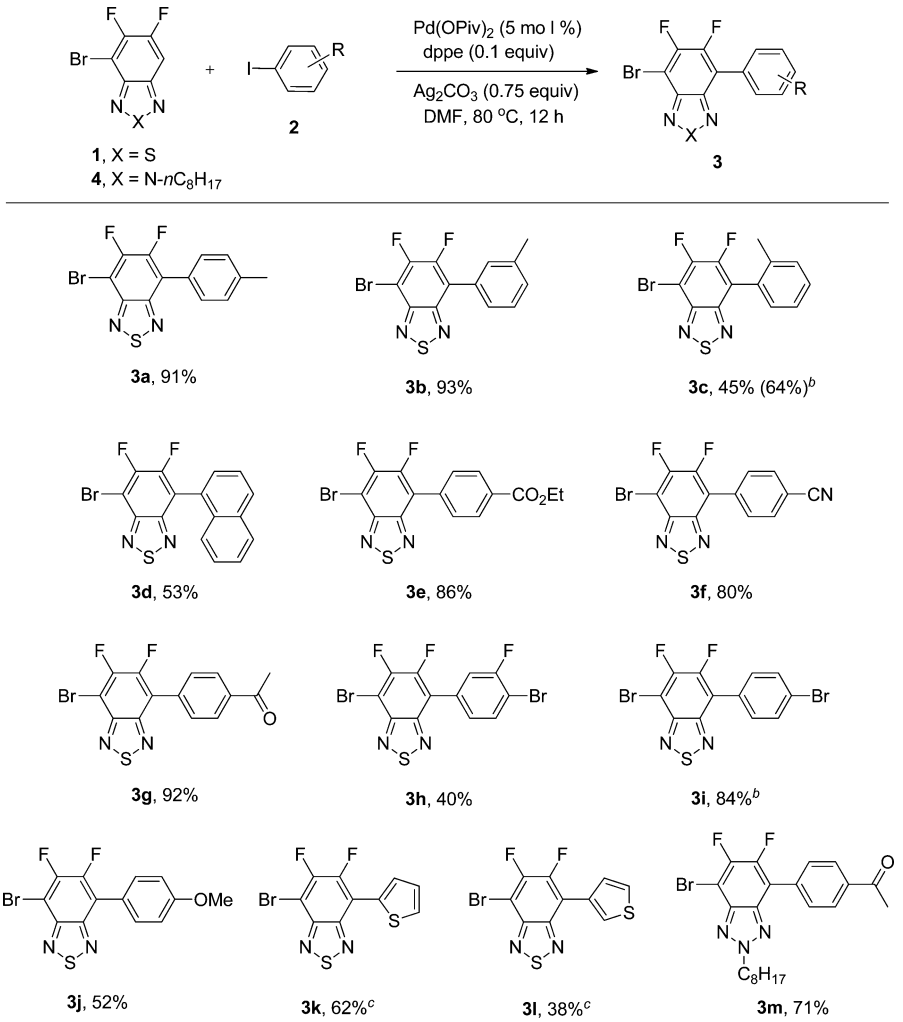
Scheme 1. Direct Arylation of DFBT 1 and DFTAZ 4 with Aryl Iodides[a]



[a]Reaction conditions (unless otherwise specified): **1** (1.5 equiv), **2** (0.2 mmol), DMF (1.5 mL). All of the reported yields are isolated yields. [b]The reaction was conducted at 100 °C. [c]$Pd(PPh_3)_4$ (5 mol %), (oxidi-2,1 phenylene)bis(diphenylphosphine) (0.1 equiv), DMF (1.5 mL).

N_2, followed by DMF (1.5 mL) with stirring. The reaction mixture was stirred at 80 °C (oil bath). After 12 h of stirring, the reaction mixture was cooled to room temperature, diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel chromatography to provide the pure product.

4-Bromo-5,6-difluoro-7-(p-tolyl)benzo[c][1,2,5]thiadiazole (**3a**). The product (62 mg, 91% yield) was purified by silica gel chromatography (PE/DCM = 50:1) as a yellow solid. Mp: 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.2 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 2.46 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.0 (d, J = 19.7 Hz, 1F), −132.0 (d, J = 19.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3 (dd, J = 256.4 Hz, 20.4 Hz), 149.9 (d, J = 5.3 Hz), 149.8 (dd, J = 257.6 Hz, 18.4 Hz), 149.5 (d, J = 7.8 Hz), 139.6, 130.2 (d, J = 2.8 Hz), 129.3, 126.6 (m), 119.5 (d, J = 13.9 Hz), 97.8 (d, J = 19.2 Hz), 21.4. MS (EI-quadrupole): m/z (%) 342 (M^+, 100), 340 (M^+, 100), 329, 327, 261, 241. HRMS (EI-TOF): calcd for $C_{13}H_7N_2F_2SBr$, 339.9481; found, 339.9485.

4-Bromo-5,6-difluoro-7-(m-tolyl)benzo[c][1,2,5]thiadiazole (**3b**). The product (63 mg, 93% yield) was purified by silica gel chromatography (PE/DCM = 50:1) as a yellow solid. Mp: 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 2.47 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.0 (d, J = 20.5 Hz, 1F), −131.5 (d, J = 20.5 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.3 (dd, J = 256.4 Hz, 20.1 Hz), 149.88 (d, J = 5.2 Hz), 149.87 (dd, J = 257.9 Hz, 18.4 Hz), 148.8 (d, J = 18.2 Hz), 138.3, 130.9 (d, J = 2.5 Hz), 130.2, 129.4 (m), 128.5, 127.4 (d, J = 2.6 Hz), 119.7 (d, J = 14.1 Hz), 97.4 (dd, J = 21.5 Hz, 2.0 Hz), 21.5. MS (EI-quadrupole): m/z (%) 342 (M^+, 100), 340 (M^+, 100), 329, 327, 261, 246. HRMS (EI-TOF): calcd for $C_{13}H_7N_2F_2SBr$, 339.9481; found, 339.9480.

4-Bromo-5,6-difluoro-7-(o-tolyl)benzo[c][1,2,5]thiadiazole (**3c**). The product (31 mg, 45% yield at 80 °C; 44 mg, 64% yield at 100 °C) was purified by silica gel chromatography (PE/DCM = 50:1) as a white solid. Mp: 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.39 (m, 2H), 7.39−7.30 (m, 2H), 2.17 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.0 (d, J = 21.2 Hz, 1F), −127.6 (d, J = 21.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1 (dd, J = 257.4 Hz, 20.4 Hz), 150.0 (dd, J = 257.0 Hz, 18.2 Hz), 149.8 (d, J = 8.3 Hz), 149.6 (d, J = 4.9 Hz), 137.1, 130.6, 130.3, 129.6, 129.0, 125.9, 119.6 (d, J = 17.4 Hz), 98.6 (d, J = 21.7 Hz), 20.0. MS (EI-quadrupole): m/z (%) 342 (M^+, 100), 340 (M^+, 100), 322, 320, 261, 241. HRMS (EI-TOF): calcd for $C_{13}H_7N_2F_2SBr$, 339.9481; found, 339.9478.

4-Bromo-5,6-difluoro-7-(naphthalen-1-yl)benzo[c][1,2,5]-thiadiazole (**3d**). The product (40 mg, 53%) was purified by silica gel chromatography (PE/DCM = 50:1) as a pale-yellow solid. Mp: 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.4 Hz, 1H), 7.60 (dd, J = 6.8 Hz, 0.8 Hz, 1H), 7.54 (m, 1H), 7.42 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.9 (d, J = 20.5 Hz, 1F), −126.0 (d, J = 20.5 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1 (dd, J = 257.4 Hz, 20.1 Hz), 150.6 (dd, J

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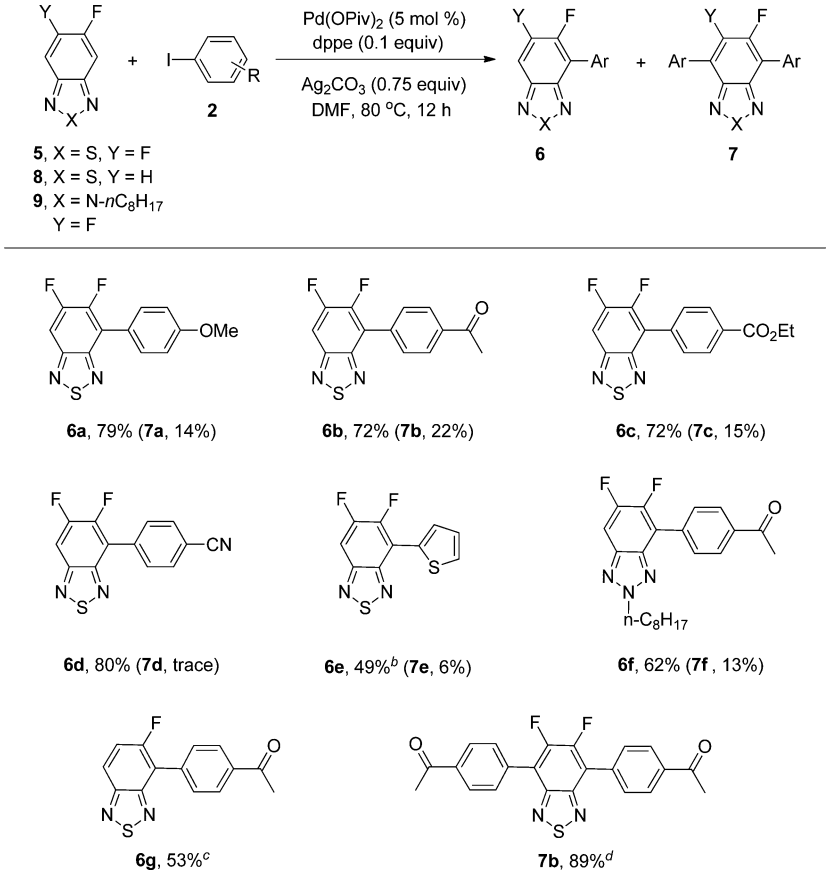
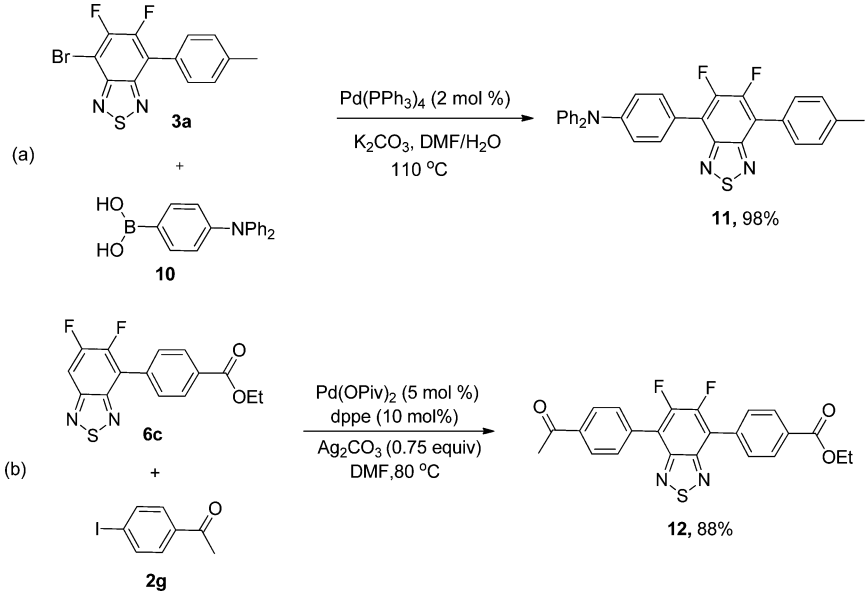
Scheme 2. Selective Arylation of FBTs and DFTAZ with Aryl Iodides[a]



[a]Reaction conditions (unless otherwise specified): **5**, **8**, or **9** (3 equiv), **2** (0.2 mmol), DMF (1.5 mL), 12 h. All of the reported yields of **6** are isolated yields; the numbers in the parentheses are the NMR yields of **7** determined by ^{19}F NMR spectroscopy. [b]$Pd(PPh_3)_4$ (5 mol %), (oxidi-2,1-phenylene)bis(diphenylphosphine) (0.1 equiv), DMF (1.5 mL). [c]The reaction was performed on a 0.4 mmol scale in 1.5 mL of DMF. [d]**5** (0.2 mmol), **2** (3 equiv), $Pd(OPiv)_2$ (5 mol %), dppe (0.1 equiv), Ag_2CO_3 (1.5 equiv), DMF (1.5 mL), 100 °C, 12 h.

Scheme 3. Syntheses of Unsymmetrical Diarylated FBTs 11 and 12



= 258.2 Hz, 18.1 Hz), 150.2 (d, J = 7.9 Hz), 149.7 (d, J = 5.1 Hz), 133.7, 131.3, 130.1, 128.8, 128.7, 127.0 (d, J = 2.2 Hz), 126.7, 126.3, 125.2, 125.0, 118.5 (d, J = 16.2 Hz), 99.1 (d, J = 21.2 Hz). MS (EI-quadrupole): m/z (%) 378 (M^+), 376 (M^+), 377 (M^+, 100), 375 (M^+, 100). HRMS (EI-TOF): calcd for $C_{16}H_7N_2F_2SBr$, 375.9481; found, 375.9479.

*Ethyl 4-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-benzoate (**3e**).* The product (69 mg, 86% yield) was purified by

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silica chromatography (PE/DCM = 5:1) as a white solid. Mp: 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H), 7.85 (dd, J = 8.2 Hz, 1.4 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.8 (d, J = 20.3 Hz, 1F), −130.7 (d, J = 20.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 153.3 (dd, J = 256.8 Hz, 20.1 Hz), 150.2 (dd, J = 259.6 Hz, 18.6 Hz), 149.9 (d, J = 5.0 Hz), 149.0 (d, J = 7.6 Hz), 133.9 (m), 131.2, 130.4 (d, J = 2.9 Hz), 129.7, 118.4 (d, J = 13.7 Hz), 99.2 (d, J = 21.5 Hz), 61.2, 14.3. MS (MALDI-TOF): m/z (%) 401 (M^+), 399 (M^+), 397 (M^+). HRMS (MALDI-FTMS): calcd for $C_{15}H_{10}N_2O_2F_2SBr$, 398.9609; found, 398.9619.

*4-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-benzonitrile (**3f**).* The product (56 mg, 80% yield) was purified by silica chromatography (PE/DCM = 5:1) as a white solid. Mp: 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.7 (d, J = 19.0 Hz, 1F), −130.3 (d, J = 19.0 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8 (dd, J = 256.9 Hz, 19.8 Hz), 149.9 (dd, J = 260.5 Hz, 18.8 Hz), 149.88 (d, J = 5.0 Hz), 148.5 (d, J = 7.5 Hz), 134.1, 132.2, 131.1 (d, J = 3.0 Hz), 118.2, 117.2 (d, J = 13.2 Hz), 113.0, 100.0 (dd, J = 21.2 Hz, 2.1 Hz). MS (EI-quadrupole): m/z (%) 353 (M^+, 100), 351 (M^+, 98), 273. HRMS (EI-TOF): calcd for $C_{13}H_4BrF_2N_3S$, 350.9277; found, 350.9276.

*1-(4-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)phenyl)-ethanone (**3g**).* The product (68 mg, 92% yield) was purified by silica gel chromatography (PE/DCM = 5:1) as a white solid. Mp: 159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 2.68 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.8 (d, J = 19.9 Hz, 1F), −130.6 (d, J = 19.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 152.1 (dd, J = 256.8 Hz, 20.1 Hz), 150.0 (dd, J = 259.8 Hz, 18.8 Hz), 149.9 (d, J = 5.2 Hz), 148.9 (d, J = 7.0 Hz), 137.4, 134.2, 130.7, 128.4, 118.2 (d, J = 13.5 Hz), 99.3 (d, J = 21.4 Hz), 26.7. MS (EI-quadrupole): m/z (%) 370 (M^+), 368 (M^+), 355 (98), 353 (100). HRMS (EI-TOF): calcd for $C_{14}H_7F_2N_2BrSO$, 367.9431; found, 367.9433.

*4-Bromo-7-(4-bromo-3-fluorophenyl)-5,6-difluorobenzo[c]-[1,2,5]thiadiazole (**3h**).* The product (34 mg, 40% yield) was purified by silica gel chromatography (PE/DCM = 50:1) as a white solid. Mp: 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 14.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −106.1 (apparent t, J = 8.3 Hz, 1F), −119.7 (d, J = 19.7 Hz, 1F), −130.5 (d, J = 19.7 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9 (d, J = 246.5 Hz), 152.0 (dd, J = 256.8 Hz, 20.0 Hz), 150.1 (dd, J = 260.0 Hz, 18.6 Hz), 149.9 (d, J = 5.1 Hz), 148.6 (d, J = 7.5 Hz), 133.6, 130.4 (dm, J = 8.9 Hz), 127.2 (t, J = 3.6 Hz), 118.5 (dd, J = 24.1 Hz, 3.1 Hz), 117.0 (dm, J = 13.2 Hz), 110.5 (d, J = 20.8 Hz), 99.4 (dd, J = 21.4 Hz, 2.1 Hz). MS (EI-quadrupole): m/z (%) 426 (M^+), 425 (M^+), 424 (M^+, 100), 345, 343. HRMS (EI-TOF): calcd for $C_{12}H_3Br_2F_3N_2S$, 421.8336; found, 421.8337.

*4-Bromo-7-(4-bromophenyl)-5,6-difluorobenzo[c][1,2,5]-thiadiazole (**3i**).* The product (68 mg, 84% yield at 100 °C) was purified by silica gel chromatography (PE/DCM = 50:1) as a white solid. Mp: 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.8 (d, J = 19.7 Hz, 1F), −131.2 (d, J = 19.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 (dd, J = 256.5 Hz, 20.1 Hz), 149.94 (dd, J = 258.8 Hz, 18.4 Hz), 149.9 (d, J = 5.1 Hz), 149.0 (d, J = 7.6 Hz), 131.9 (d, J = 2.8 Hz), 131.86, 128.4, 123.9, 118.2 (d, J = 13.8 Hz), 98.8 (d, J = 21.5 Hz). MS (EI-quadrupole): m/z (%) 408 (M^+), 406 (M^+, 100), 404 (M^+), 327, 325. HRMS (EI-TOF): calcd for $C_{12}H_4N_2Br_2F_2S$, 403.8430; found, 403.8424.

*4-Bromo-5,6-difluoro-7-(4-methoxyphenyl)benzo[c][1,2,5]-thiadiazole (**3j**).* The product (37 mg, 52% yield) was purified by silica gel chromatography (PE/DCM = 30:1) as a yellow solid. Mp: 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.1 (d, J = 20.5 Hz, 1F), −132.5 (d, J = 20.5 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 152.4 (dd, J = 256.2 Hz, 20.3 Hz), 149.9 (d, J = 5.2 Hz), 149.6 (d, J = 7.9 Hz), 149.5 (dd, J = 257.0 Hz, 18.2 Hz), 131.8 (d, J = 2.7 Hz), 121.8, 119.2 (d, J = 14.1 Hz), 114.1, 97.4 (d, J = 19.2 Hz), 55.4. MS (MALDI-TOF): m/z (%) 358 (M^+), 356 (M^+), 355 (M^+). HRMS (MALDI-FTMS): calcd for $C_{13}H_7N_2OSF_2Br$, 355.9425; found, 355.9439.

*4-Bromo-5,6-difluoro-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**3k**).* The reaction was carried out with $Pd(PPh_3)_4$ (0.05 mol %) and (oxidi-2,1-phenylene)bis(diphenylphosphine) (0.1 equiv) in DMF (1.5 mL). The product (41 mg, 62% yield) was purified by silica gel chromatography (PE/DCM = 30:1) as an orange solid. Mp: 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 3.2 Hz, 1H), 7.63 (d, J = 5.2 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.2 (d, J = 18.4 Hz, 1F), −126.8 (d, J = 18.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4 (dd, J = 255.5 Hz, 20.0 Hz), 149.8 (d, J = 5.4 Hz), 149.2 (dd, J = 261.2 Hz, 19.2 Hz), 147.8 (d, J = 11.2 Hz), 131.3 (d, J = 8.4 Hz), 130.7 (m), 129.4 (d, J = 6.6 Hz), 127.5, 113.3 (d, J = 9.3 Hz), 97.0 (d, J = 21.9 Hz). MS (EI-quadrupole): m/z (%) 334 (M^+, 100), 332 (M^+, 97), 288, 253. HRMS (EI-TOF): calcd for $C_{10}H_3N_2F_2S_2Br$, 331.8889; found, 331.8884.

*4-Bromo-5,6-difluoro-7-(thiophen-3-yl)benzo[c][1,2,5]thiadiazole (**3l**).* The reaction was carried out with $Pd(PPh_3)_4$ (0.05 mol %) and (oxidi-2,1-phenylene)bis(diphenylphosphine) (0.1 equiv) in DMF (1.5 mL). The product (25 mg, 38% yield) was purified by silica gel chromatography (PE/DCM = 30:1) as a yellow solid. Mp: 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 2.8 Hz, 1H), 7.88 (ddd, J = 4.8 Hz, 2.0 Hz, 1.2 Hz, 1H), 7.51 (dd, J = 5.0 Hz, 3.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −120.0 (d, J = 19.0 Hz, 1F), −129.2 (d, J = 19.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4 (dd, J = 255.7 Hz, 20.4 Hz), 149.9 (d, J = 5.3 Hz), 149.7 (dd, J = 259.2 Hz, 18.7 Hz), 148.6 (d, J = 8.6 Hz), 129.4 (t, J = 3.0 Hz), 128.64 (d, J = 5.6 Hz), 128.58 (d, J = 4.6 Hz), 114.1 (d, J = 12.7 Hz), 97.4 (dd, J = 21.5 Hz, 2.1 Hz). MS (EI-quadrupole): m/z (%) 334 (M^+, 100), 332 (M^+, 97), 253, 220. HRMS (EI-TOF): calcd for $C_{10}H_3N_2F_2S_2Br$, 331.8889; found, 331.8887.

*1-(4-(7-Bromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)phenyl)ethanone (**3m**).* The reaction was carried out with DFTAZ **4** instead of FBT **1**. The product (66 mg, 71% yield) was purified by silica gel chromatography (PE/DCM = 5:1) as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 4.71 (t, J = 7.2 Hz, 2H), 2.65 (s, 3H), 2.10 (m, 2H), 1.45−1.20 (m, 10H), 0.85 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.2 (d, J = 19.7 Hz, 1F), −137.0 (d, J = 19.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 149.4 (dd, J = 248.9 Hz, 19.2 Hz), 147.6 (dd, J = 253.2 Hz, 17.8 Hz), 139.8 (d, J = 5.1 Hz), 138.0 (d, J = 7.7 Hz), 136.9, 134.8, 130.3 (d, J = 3.5 Hz), 128.4, 116.1 (d, J = 13.7 Hz), 96.1 (d, J = 22.0 Hz), 57.2, 31.6, 30.0, 29.0, 28.8, 26.6, 26.4, 22.5, 14.0. MS (MALDI-TOF): m/z (%) 464 (M^+), 462 (M^+). HRMS (MALDI-FTMS): calcd for $C_{22}H_{24}N_3F_2OBr$, 462.0987; found, 462.0996.

General Procedure for the Preparation of Compounds 6a−d and 6f. To a 25 mL Schlenk tube were added $Pd(OPiv)_2$ (5 mol %), dppe (8.0 mg, 0.1 equiv), aryl iodide (0.2 mmol, 1.0 equiv), Ag_2CO_3 (41.7 mg, 0.75 equiv), and FBT **5** or DFTAZ **9** (3.0 equiv) under N_2, followed by DMF (1.5 mL) with stirring. The reaction mixture was stirred at 80 °C (oil bath). After 12 h of stirring, the reaction mixture was cooled to room temperature, diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel chromatography to provide the pure product.

*5,6-Difluoro-4-(4-methoxyphenyl)benzo[c][1,2,5]thiadiazole (**6a**).* The product (44 mg, 79%) was purified by silica gel chromatography (PE/DCM = 30:1) as a yellow solid. Mp: 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.68 (apparent t, J = 8.4 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −127.1 (dd, J = 19.0 Hz, 9.6 Hz, 1F), −134.8 (dd, J = 18.4 Hz, 7.5 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, 154.4 (dd, J = 256.8 Hz, 19.3 Hz), 150.8 (d, J = 7.5 Hz), 150.6 (d, J = 12.2 Hz), 149.4 (dd, J = 255.1 Hz, 18.4 Hz), 131.8 (d, J = 3.0 Hz), 122.3, 120.0 (d, J = 11.8 Hz), 114.0, 104.1 (d, J = 20.0 Hz), 55.3. MS (EI-quadrupole): m/z (%) 278 (M^+), 263, 235. HRMS (EI-TOF): calcd for $C_{13}H_8N_2OF_2S$, 278.0325; found, 278.0327.

*1-(4-(5,6-Difluorobenzo[c][1,2,5]thiadiazol-4-yl)phenyl)ethanone (**6b**).* The product (42 mg, 72% yield) was purified by silica gel

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chromatography (PE/DCM = 5:1) as a white solid. Mp: 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.78 (dd, J = 9.4 Hz, 7.4 Hz, 1H), 2.68 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.9 (dd, J = 17.9 Hz, 9.6 Hz, 1F), −132.8 (dd, J = 17.7 Hz, 8.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 154.1 (dd, J = 257.7 Hz, 19.0 Hz), 150.5 (d, J = 12.1 Hz), 150.2 (d, J = 7.3 Hz), 150.1 (dd, J = 258.2 Hz, 18.7 Hz), 137.2, 134.7, 130.7 (d, J = 2.8 Hz), 128.4, 119.0 (d, J = 11.6 Hz), 105.5 (d, J = 19.9 Hz), 26.7. MS (EI-quadrupole): m/z (%) 290 (M^+), 275 (100), 247. HRMS (EI-TOF): calcd for $C_{14}H_8N_2F_2SO$, 290.0325; found, 290.0323.

*Ethyl 4-(5,6-Difluorobenzo[c][1,2,5]thiadiazol-4-yl)benzoate (**6c**).* The product (46 mg, 72%) was purified by silica gel chromatography (PE/DCM = 5:1) as a white solid. Mp: 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.77 (dd, J = 9.6 Hz, 7.6 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.9 (dd, J = 18.4 Hz, 9.0 Hz, 1F), −132.9 (dd, J = 17.7 Hz, 6.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 154.1 (dd, J = 257.6 Hz, 19.0 Hz), 150.5 (d, J = 12.1 Hz), 150.3 (d, J = 7.5 Hz), 150.1 (dd, J = 258.1 Hz, 18.6 Hz), 134.4 (m), 131.0, 130.4 (d, J = 2.8 Hz), 129.6, 119.2 (d, J = 14.7 Hz), 105.4 (d, J = 18.5 Hz), 61.2, 14.3. MS (EI-quadrupole): m/z (%) 320 (M^+), 292, 275 (100). HRMS (EI-TOF): calcd for $C_{15}H_{10}N_2O_2F_2S$, 320.0431; found, 320.0429.

*4-(5,6-Difluorobenzo[c][1,2,5]thiadiazol-4-yl)benzonitrile (**6d**).* The product (44 mg, 80% yield) was purified by silica gel chromatography (PE/DCM = 5:1) as a white solid. Mp: 163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.81 (dd, J = 8.8 Hz, 7.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.7 (dd, J = 19.6 Hz, 8.6 Hz, 1F), −132.5 (dd, J = 18.4 Hz, 7.5 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9 (dd, J = 257.9 Hz, 18.9 Hz), 150.5 (d, J = 11.9 Hz), 150.2 (dd, J = 259.0 Hz, 18.8 Hz), 149.8 (d, J = 7.1 Hz), 134.7 (m), 132.2, 131.2 (d, J = 3.1 Hz), 118.4, 118.1 (dd, J = 12.9 Hz, 1.8 Hz), 112.9, 106.1 (dd, J = 19.8 Hz, 1.6 Hz). MS (EI-quadrupole): m/z (%) 273 (M^+, 100), 254, 227. HRMS (EI-TOF): calcd for $C_{13}H_5N_3SF_2$, 273.0172; found, 273.0170.

*5,6-Difluoro-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**6e**).* The reaction was carried out with $Pd(PPh_3)_4$ (5 mol %) and (oxidi-2,1-phenylene)bis(diphenylphosphine) (0.1 equiv) in DMF (1.5 mL). The product (25 mg, 49% yield) was purified by silica gel chromatography (PE/DCM = 30:1) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 4.0 Hz, 1H), 7.61 (apparent t, J = 8.2 Hz, 1H), 7.60 (d, J = 4.8 Hz, 1H), 7.24 (t, J = 5.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −127.2 (dd, J = 17.1 Hz, 8.8 Hz, 1F), −128.7 (dd, J = 16.5 Hz, 6.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3 (dd, J = 256.1 Hz, 19.0 Hz), 150.5 (d, J = 12.5 Hz), 149.1 (d, J = 7.9 Hz), 149.0 (dd, J = 259.5 Hz, 19.1 Hz), 131.2 (m), 131.1 (d, J = 8.3 Hz), 129.0 (d, J = 6.5 Hz), 127.3, 114.0 (d, J = 11.7 Hz), 103.6 (d, J = 20.2 Hz). MS (EI-quadrupole): m/z (%) 254 (M^+, 100), 210. HRMS (EI-TOF): calcd for $C_{10}H_4N_2F_2S_2$, 253.9784; found, 253.9782.

*1-(4-(5,6-Difluoro-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)phenyl)-ethanone (**6f**).* The product (48 mg, 62% yield) was purified by silica gel chromatography (PE/DCM = 5:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 7.59 (dd, J = 9.2 Hz, 6.8 Hz, 1H), 4.68 (t, J = 7.2 Hz, 2H), 2.66 (s, 3H), 2.08 (m, 2H), 1.40−1.20 (m, 10H), 0.85 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −133.1 (dd, J = 17.9 Hz, 9.6 Hz, 1F), −139.5 (dd, J = 17.7 Hz, 6.8 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 151.5 (dd, J = 249.0 Hz, 18.2 Hz), 147.6 (dd, J = 251.1 Hz, 17.7 Hz), 139.6 (d, J = 12.2 Hz), 139.2 (d, J = 7.4 Hz), 136.8, 135.4, 130.4 (d, J = 3.4 Hz), 128.3, 116.8 (d, J = 13.3 Hz), 103.1 (d, J = 21.0 Hz), 56.9, 31.6, 29.9, 29.0, 28.9, 26.6, 26.4, 22.5, 14.0. MS (MALDI-TOF): m/z (%) 387 (M^+), 386 (M^+). HRMS (MALDI-FTMS): calcd for $C_{22}H_{26}N_3OF_2$, 386.2038; found, 386.2052.

*1-(4-(5-Fluorobenzo[c][1,2,5]thiadiazol-4-yl)phenyl)ethanone (**6g**).* The reaction was performed on a 0.4 mmol scale in 1.5 mL of DMF. The product (58 mg, 53% yield) was purified by silica gel chromatography (PE/DCM = 5:1) as a white solid. Mp: 156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.0 Hz, 2H), 8.02 (dd, J = 9.4 Hz, 4.6 Hz, 1H), 7.89 (d, J = 6.8 Hz, 2H), 7.57 (t, J = 9.6 Hz, 1H), 2.67 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −113.7 (dd, J = 9.4 Hz, 4.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 159.4 (d, J = 253.1 Hz), 154.0 (d, J = 9.5 Hz), 152.2, 136.7, 135.8, 130.7 (d, J = 2.6 Hz), 128.2, 122.0 (d, J = 11.1 Hz), 121.7 (d, J = 30.8 Hz), 117.6 (d, J = 16.5 Hz), 26.7. MS (EI-quadrupole): m/z (%) 272 (M^+), 257 (100), 229. HRMS (EI-TOF): calcd for $C_{14}H_9N_2FSO$, 272.0420; found, 272.0425.

*1,1′-((5,6-Difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(4,1-phenylene))diethanone (**7b**).* The reaction was carried out with **5** (0.2 mmol, 1 equiv), Ag_2CO_3 (1.5 equiv), 1-(4-iodophenyl)ethanone (3 equiv), $Pd(OPiv)_2$ (5 mol %), and dppe (0.1 equiv) in DMF (1.5 mL) at 100 °C. The product (73 mg, 89% yield) was purified by silica gel chromatography (PE/EA = 5:1) as a white solid. Mp: 242 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.4 Hz, 4H), 7.95 (d, J = 8.4 Hz, 4H), 2.69 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −131.9 (s, 2F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 150.5 (dd, J = 259.1 Hz, 20.2 Hz), 150.0 (t, J = 3.6 Hz), 137.3, 134.6, 130.8, 128.4, 118.4 (dd, J = 10.4 Hz, 4.5 Hz), 26.7. MS (EI-quadrupole): m/z (%) 408 (M^+), 393 (100), 322, 189. HRMS (EI-TOF): calcd for $C_{22}H_{14}N_2F_2SO_2$, 408.0744; found, 408.0741.

*4-(4-(Diphenylamino)phenyl)-5,6-difluoro-7-(p-tolyl)benzo[c]-[1,2,5]thiadiazole (**11**).* To a 25 mL Schlenk tube were added **3a** (0.4 mmol, 1.0 equiv), (4-(diphenylamino)phenyl)boronic acid (231 mg, 2 equiv), $Pd(PPh_3)_4$ (2 mol %), and K_2CO_3 (220 mg, 4.0 equiv) under N_2, followed by DMF (5 mL) and H_2O (1 mL) with stirring. The reaction mixture was stirred at 110 °C (oil bath). After 10 h of stirring, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The product (199 mg, 98% yield) was purified by silica gel chromatography (PE/DCM = 5:1) as a green yellow solid. Mp: 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (t, J = 6.0 Hz, 4H), 7.36 (d, J = 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 4H), 7.19 (d, J = 8.0 Hz, 6H), 7.07 (t, J = 7.2 Hz, 2H), 2.44 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −133.5 (d, J = 17.7 Hz, 1F), −133.8 (d, J = 17.7 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6 (d, J = 8.5 Hz), 150.43 (d, J = 8.2 Hz), 150.4 (dd, J = 257.8 Hz, 21.8 Hz), 150.1 (dd, J = 252.2 Hz, 16.4 Hz), 148.4, 147.2, 139.0, 131.3 (d, J = 3.1 Hz), 130.3 (d, J = 2.5 Hz), 129.4, 129.2, 127.4, 125.2, 123.6, 123.1, 121.7, 118.1 (dd, J = 19.4 Hz, 13.4 Hz), 21.4. MS (EI-quadrupole): m/z (%) 505 (M^+), 245, 91 (100). HRMS (EI-TOF): calcd for $C_{31}H_{21}N_3F_2S$, 505.1424; found, 505.1420.

*Ethyl 4-(7-(4-Acetylphenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)benzoate (**12**).* To a 25 mL Schlenk tube were added **6c** (0.26 mmol, 1.3 equiv), 1-(4-iodophenyl)ethanone (49.2 mg, 1.0 equiv), $Pd(OPiv)_2$ (5 mol %), dppe (10 mol %), and Ag_2CO_3 (42 mg, 0.75 equiv) under N_2, followed by DMF (1.5 mL) with stirring. The reaction mixture was stirred at 80 °C (oil bath). After 12 h of stirring, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The product (77 mg, 88% yield) was purified by silica gel chromatography (PE/EA = 20:1) as a yellow solid. Mp: 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (t, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 2.69 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −131.96 (d, J = 17.7 Hz, 1F), −132.04 (d, J = 17.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 166.0, 150.5 (dd, J = 259.3 Hz, 20.2 Hz), 150.1 (dd, J = 259.0 Hz, 20.4 Hz), 150.06 (d, J = 4.8 Hz), 150.0 (d, J = 4.8 Hz), 137.2, 134.7, 134.3, 131.0, 130.8 (d, J = 2.0 Hz), 130.5 (d, J = 1.9 Hz), 129.6, 128.4, 118.6 (d, J = 12.8 Hz), 118.3 (dd, J = 11.9 Hz, 3.1 Hz), 61.2, 26.7, 14.3. MS (EI-quadrupole): m/z (%) 438 (M^+), 423 (100), 322, 189. HRMS (EI-TOF): calcd for $C_{23}H_{16}N_2F_2SO_3$, 438.0850; found, 438.0848.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Representative results for optimization of direct arylation of DFBT **1** with **2a** and copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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