Synthesis A. Sasmal et al. Paper

Reactivity of 3-Bromofuran in Pd-Catalyzed C–H Bond Arylation toward the Synthesis of 2,3,5-Triarylfurans

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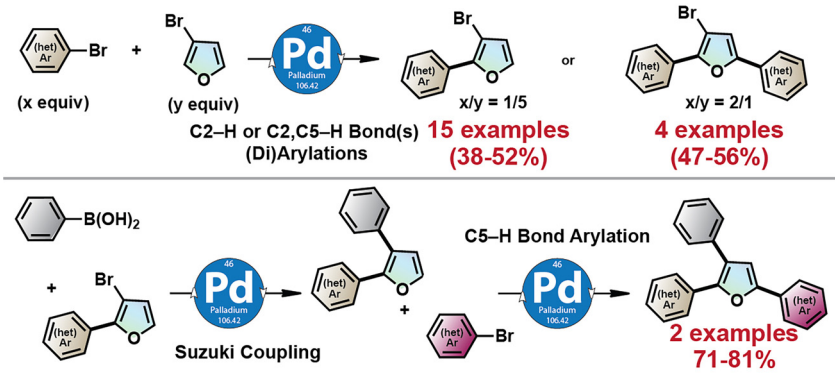

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Abstract Arylation of the C–H bond at the C2 position of 3-bromofuran is achieved using aryl bromides as coupling partners in the presence of phosphine-free $Pd(OAc)_2$/KOAc in DMA. This procedure gives C2,C5-di- and even C2,C4,C5-triarylated 3-bromofuran derivatives when larger amounts of aryl bromides are employed. In addition, C2,C3,C5-triarylated furans—containing three different aryl groups—are synthesized via a C2–H bond arylation/Suzuki reaction/C5–H bond arylation sequence.

Key words palladium, furans, C–H bond arylation, aryl bromides

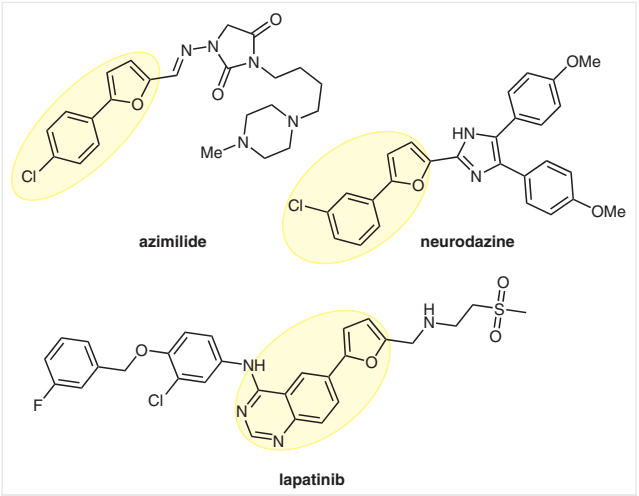
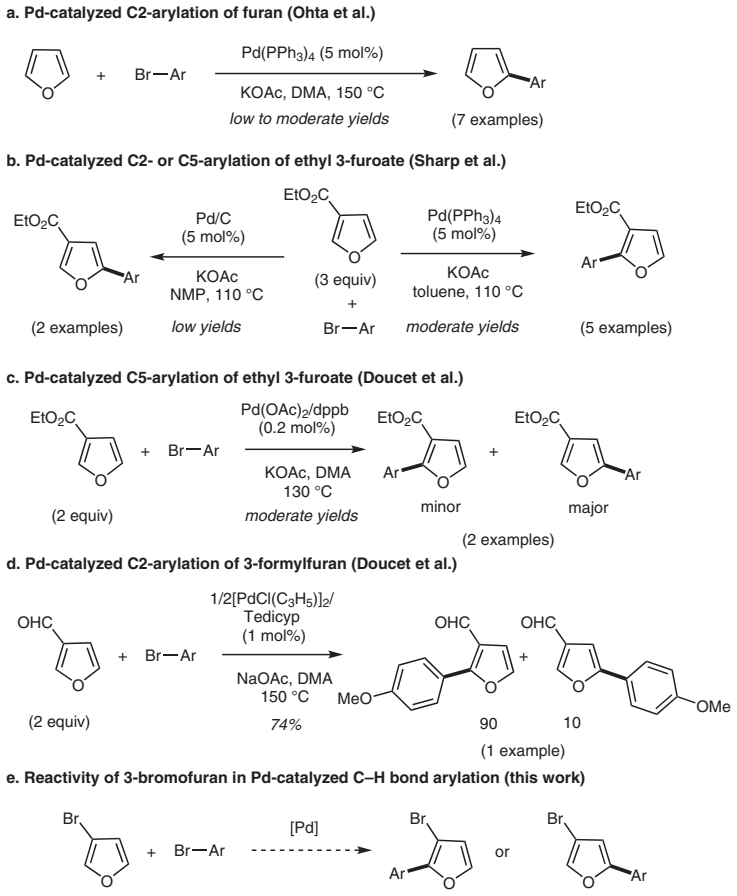


Figure 1 Examples of drugs containing a 2-arylfuran motif

Substituted furans are omnipresent in natural products,[1] pharmaceuticals,[2] (bio-sourced) polymeric materials,[3] and other functional molecules.[4] They are also useful synthetic intermediates.[5] Arylated furans are important frameworks embedded in many important pharmaceuticals drugs. As examples, azimilide® is a class III antiarrhythmic drug, neurodazine® affects neuronal cell differentiation and lapatinib® is an orally active drug for breast cancer and other solid tumors (Figure 1).

Therefore, the development of efficient and regioselective synthetic pathways for the preparation of multisubstituted furans is an important research area in heterocyclic chemistry. Besides the traditional approaches involving cyclocondensation, cycloisomerization or multistep synthesis,[6] the direct functionalization of furan rings via palladium-catalyzed C–H bond arylation is a modular approach to access polyarylated furans.[7] The first example of Pd-catalyzed C2–H bond arylation of furan with activated aryl bromides was reported in 1990 by Ohta and co-workers using 5 mol% of $Pd(PPh_3)_4$ associated with KOAc in DMA at 150 °C (Scheme 1a).[8] However, low to moderate yields in favor of the C2-arylated furans were often obtained due to the high reactivity of the C5–H bond of C2-arylated furans leading to the formation of C2,C5-diarylated furans.[9] On the other hand, the reactivity of C3-substituted furans has attracted less attention. Controlling the regioselectivity of the C–H bond arylation of ethyl 3-furoate depends on the reaction conditions. In 2003, Sharp and co-workers reported C2 arylation with electron-deficient aryl bromides using 5 mol% of $Pd(PPh_3)_4$ associated with KOAc in non-polar solvents such as toluene at 110 °C (Scheme 1b, right).[10] In contrast, they reported two examples of the C5-arylation of ethyl 3-furoate using polar solvents, such as NMP, with Pd/C as the catalyst (Scheme 1b, left).[10] Later, Doucet and co-workers also investigated the regioselectivity of the C–H bond arylation of ethyl 3-furoate and observed that using 0.2 mol% of $Pd(OAc)_2$/dppb in the presence of KOAc in DMA resulted in C5-arylated furans being obtained as the major products

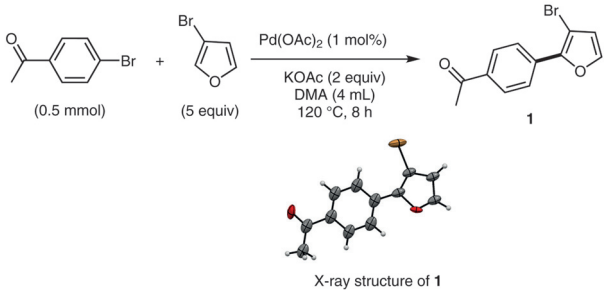


Scheme 1 Reactivity of (substituted) furan derivatives in Pd-catalyzed C–H bond arylation

along with the formation of C2-arylated furans as minor products (Scheme 1c).[11] Doucet and co-workers also reported one example of the C2-arylation of 3-formylfuran using a similar catalytic system (Scheme 1d).[12] Conversely, the chemoselective C–H bond arylations of thiophenes or pyrazoles, possessing bromo substituents at C3 or C4, with aryl halides allowed the construction of polyarylated heteroaromatics.[13] To the best of our knowledge, the reactivity of 3-bromofuran in direct arylation has not been reported previously. Herein, we report our investigations on the coupling of 3-bromofuran with electron-deficient aryl bromides and on their polyarylation to construct triarylated furans (Scheme 1e).

We selected 4-bromoacetophenone as the coupling partner to investigate the chemoselectivity of the coupling with 3-bromofuran. During development of the reaction, we determined that the best conditions to regioselectively obtain C2-arylated 3-bromofuran **1** in 47% yield were 1 mol% of $Pd(OAc)_2$ as the catalyst and 2 equivalents of KOAc as the base in DMA at 120 °C over 8 hours (Table 1, entry 1). The regioselectivity of the arylation at the C2 position was confirmed by X-ray crystal structure analysis of **1**.[14,15] The amount of 3-bromofuran (5 equiv) was critical to isolate **1** in a good yield due to oligomerization as major side reaction (Table 1, entries 1 and 2). The reaction time was also a very important factor for this coupling, as shorter (4 h) or longer reaction times (16 h) resulted in lower yields (Table 1, entries 3 and 4). A higher temperature of 150 °C led to oligomerization, while at 80 °C a partial conversion of 4-bromoacetophenone was observed (Table 1, entries 5 and 6). Palladium sources other than $Pd(OAc)_2$ and different catalyst loadings gave lower yields of **1** (Table 1, entries 7–11). Reactions performed in other solvents such as cyclopentyl methyl ether (CPME), 1,4-dioxane or pentan-1-ol failed to afford the arylated furan **1** (Table 1, entries 12–14). The concentration plays a major role in avoiding the oligomerization. Indeed, a concentration of 0.125 molar was determined to be the best choice; a concentration of 0.25 molar afforded more oligomers, and when the reaction was performed at 0.1 molar, only partial conversion was observed (Table 1, entries 15 and 16). Finally, our attempts to inhibit the degradation of 3-bromofuran by addition of TEMPO or catechol were unsuccessful (Table 1, entries 17 and 18).

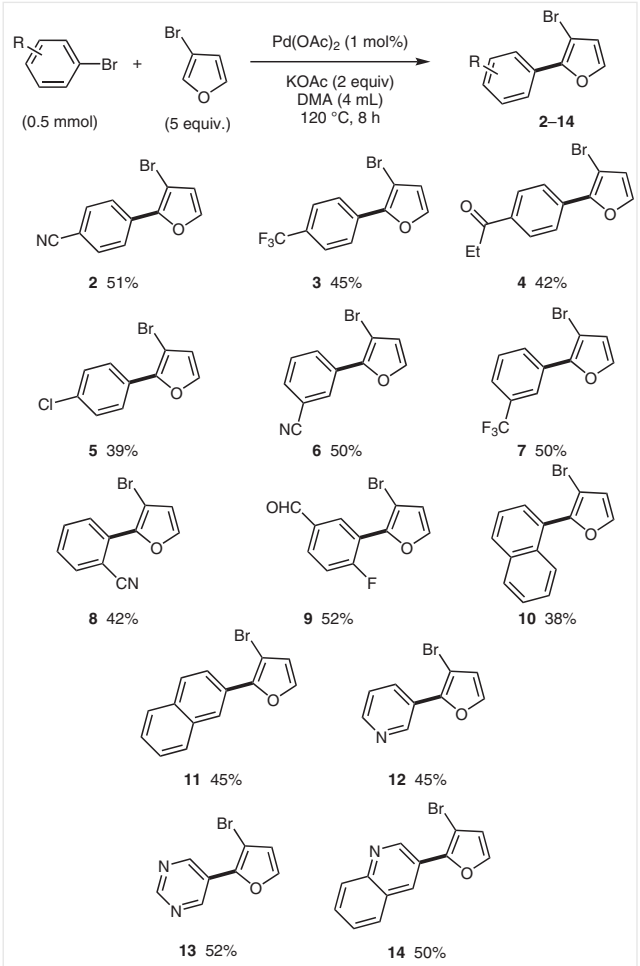
Table 1 Reaction Development



Entry	Variation from standard conditions	Yield of **1** (%)[a]
1	–	52 (47)
2	3 equiv of 3-bromofuran	26
3	4 h	32
4	16 h	49
5	150 °C	traces
6	80 °C	22
7	$PdCl_2$ (1 mol%)	48
8	$PdCl_2(CH_3CN)_2$ (1 mol%)	42
9	$PdCl(C_3H_5)$(dppb) (1 mol%)	25
10	$Pd(OAc)_2$ (2 mol%)	49
11	$Pd(OAc)_2$ (0.5 mol%)	42
12	cyclopentyl methyl ether (CPME)	traces
13	1,4-dioxane	traces
14	pentan-1-ol	traces
15	DMA (2 mL)	29
16	DMA (5 mL)	42
17	TEMPO (0.2 equiv) as additive	45
18	catechol (0.2 equiv) as additive	41

[a] Determined by GC-MS analysis using *n*-dodecane as the internal standard. Yield of isolated product is shown in parentheses.

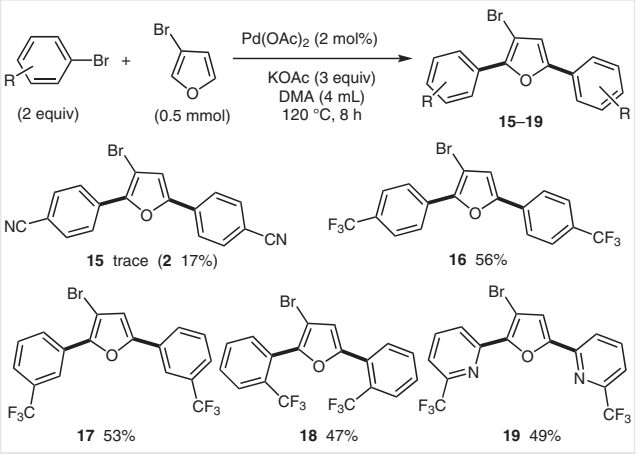
Having determined the best conditions to selectively arylate the C–H bond at the C2 position of 3-bromofuran without cleavage of the C–Br bond on the furan ring, we turned our attention to the scope of the aryl bromides (Scheme 2). Firstly, the reactivity of a set of *para*-substituted aryl bromides was investigated. The reaction proceeded smoothly using aryl bromides bearing an electron-withdrawing group such as cyano, trifluoromethyl, propionyl, or chloro, affording the C2-arylated 3-bromofurans **2**–**5** in moderate yields. Notably, when non-activated aryl bromides were employed (e.g., bromobenzene or 4-bromoanisole), the corresponding C2-arylated 3-bromofurans were not obtained due to the oligomerization of 3-bromofuran. *meta*-Substituted aryl bromides such as 3-bromobenzonitrile and 3-bromobenzotrifluoride were chemoselectively coupled with 3-bromofuran to give the arylated compounds **6** and **7** in 50% yields, again without formation of diarylated products. The reaction was slightly sensitive to steric hindrance, as from 2-bromobenzonitrile the coupling product **8** was isolated in only 42% yield. From less bulky and activated 3-bromo-2-fluorobenzaldehyde, Pd-catalyzed C2 arylation led to the furan derivative **9** in 52% yield. Due to steric factors, 2-bromonaphthalene displayed a higher reactivity than 1-bromonaphthalene in the Pd-catalyzed C2 arylation with 3-bromofuran. 3-Bromopyridine was also successfully coupled with 3-bromofuran to afford **12** in good yield. Other *N*-heteroaryl bromides such as 5-bromopyrimidine and 3-bromoquinoline gave the C2-heteroarylated 3-bromofuran derivatives **13** and **14** in 52% and 50% yields, respectively.



Scheme 2 Scope of the (hetero)aryl bromides in Pd-catalyzed direct C2-arylation of 3-bromofuran

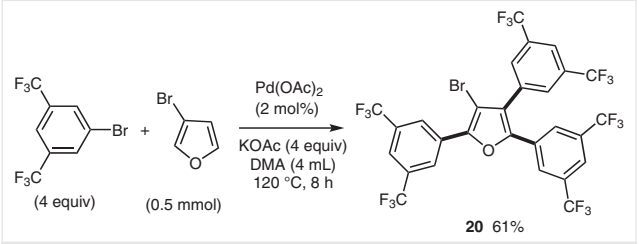
The C–H bond arylation of furan using palladium catalysis often occurred at the C2 and C5 positions.[8] We thus decided to employ an excess amount of the aryl bromides to have access to C2,C5-diarylated 3-bromofurans in one step (Scheme 3). The reaction of 2 equivalents of 4-bromobenzonitrile and 3-bromofuran in the presence of 2 mol% of

$Pd(OAc)_2$ and 3 equivalents of KOAc did not afford the desired diarylated product **15**; only the mono-arylated furan **2** was obtained, albeit in a poor yield. Surprisingly, in the presence of 2 equivalents of 4-bromobenzotrifluoride, 3-bromofuran was diarylated at the C2 and C5 positions to give the furan **16** in 56% yield. This reactivity was also observed with 2- and 3-bromobenzotrifluorides and 2-bromo-6-(trifluoromethyl)pyridine, leading to the diarylated furans **17**–**19** being selectively obtained in 47–53% yields. It is noteworthy to mention that in all cases the formation of mono-arylated 3-bromofurans was also observed in 5–10% yields. The reason behind the outperformance of aryl bromides bearing a trifluoromethyl group in multi-C–H bond arylations remains unclear. However, similar phenomena have been previously observed in the Pd-catalyzed multiple C–H bond arylations of other heterocycles (e.g., thiophenes, pyrroles, imidazoles and benzofuran).[16]



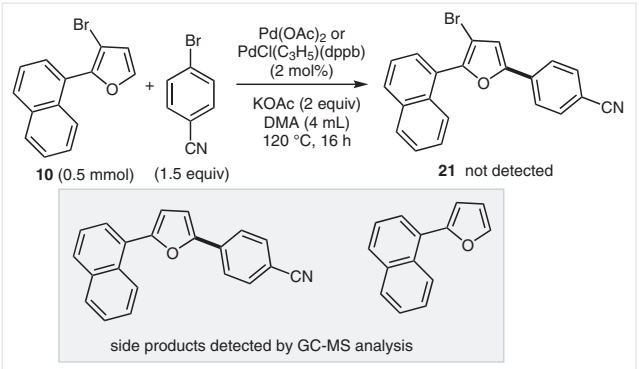
Scheme 3 Scope of the (hetero)aryl bromides in Pd-catalyzed direct C2,C5-diarylation of 3-bromofuran

We also performed the multiple C–H bond arylation of 3-bromofuran with 1-bromo-3,5-bis(trifluoromethyl)benzene using 2 mol% of $Pd(OAc)_2$ as the catalyst in DMA (Scheme 4). In the presence of 2 equivalents of this aryl bromide with 3 equivalents of base, the formation of triarylated furan **20** as well as the formation of a diarylated furan were observed. Notably, we were not able to separate them by flash chromatography. Furthermore, we setup the reaction using 4 equivalents of 1-bromo-3,5-bis(trifluoromethyl)benzene to obtain selectively the triarylated furan **20** in a good 61% yield.



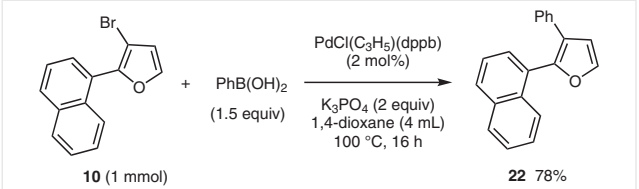
Scheme 4 Pd-catalyzed direct C2,C4,C5-triarylation of 3-bromofuran with 1-bromo-3,5-bis(trifluoromethyl)benzene

We also tried to prepare 2,5-diarylated 3-bromofurans with two different aryl units by iterative C–H bond arylations (Scheme 5). However, our attempts to selectively arylate the C5–H bond of 3-bromo-2-(naphthalen-1-yl)furan (**10**) with 4-bromobenzonitrile remained unsuccessful, even in the presence of the highly active diphosphine-palladium complex [$PdCl(C_3H_5)$(dppb)]. Instead, a complex mixture of side products was observed by GC-MS analysis, which included debrominated products.



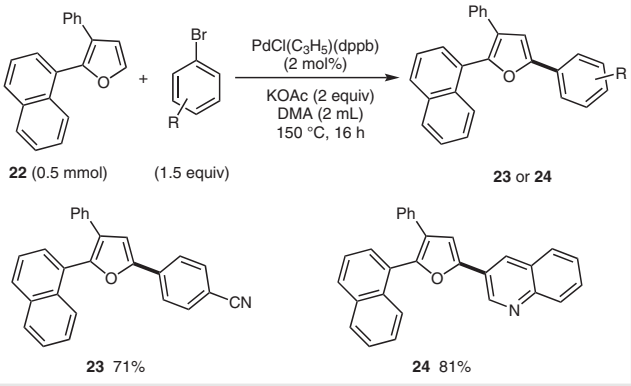
Scheme 5 Reactivity of 3-bromo-2-(naphthalen-1-yl)furan (**10**)in a Pd-catalyzed direct C5-arylation

Therefore, we decided to transform the C–Br bond into a less reactive C–Ph bond to later investigate the reactivity of the C5–H bond. From a mixture of 3-bromo-2-(naphthalen-1-yl)furan (**10**) and phenylboronic acid (1.5 equiv) in the presence of 2 mol% of a diphosphine-palladium catalyst and 2 equivalents of K_3PO_4 in dioxane at 100 °C over 16 hours, the 2,3-diarylfuran **22** was obtained in 78% yield (Scheme 6).



Scheme 6 Reactivity of the C–Br bond of 3-bromo-2-(naphthalen-1-yl)furan (**10**) in a Pd-catalyzed Suzuki reaction

Only a few methods are reported to prepare 2,3,5-triarylfurans containing three different aryl groups and they involve cyclization reactions.[17] To the best of our knowledge, there is no example of the direct arylation of 2,3-diarylfurans. Therefore, we further demonstrated the potential of this methodology with the introduction of a third aryl group, by the sequential synthesis of 2,3,5-triarylfuran derivatives containing three different aryl units (Scheme 7). From a mixture of 2-naphthyl-3-phenylfuran (**22**) and 4-bromobenzonitrile (1.5 equiv) in the presence of Pd-Cl(C_3H_5)(dppb) (2 mol%) and KOAc as the base in DMA at 150 °C, the arylated product **23** was obtained in 71% yield. The arylation took place at the most acidic C–H bond, namely the C5 position. Similarly, the reaction with 3-bromoquinoline afforded the 2,3,5-triarylfuran **24** in 81% yield.



Scheme 7 Reactivity of 2-naphthyl-3-phenylfuran (**22**) in Pd-catalyzed direct C5-arylation

In summary, we have demonstrated that 3-bromofuran is an attractive platform for the synthesis of polyarylated furans. Firstly, conditions for the regioselective C2–H bond arylation of 3-bromofuran with activated aryl bromides were developed using phosphine-free $Pd(OAc)_2$ as the catalyst. Interestingly, the reaction was very chemoselective. There was no formation of products resulting from the activation of the C–Br bond on the furan ring and this C–Br bond remained untouched after the C2-arylation if the aryl bromide contained an electron-withdrawing group. The use of a larger amount of aryl bromide coupling partners allowed access to C2,C5-diarylfurans, and even a C2,C4,C5-triarylfuran in the case of 3,5-bis(trifluoromethyl)bromobenzene. Moreover, C2,C3,C5-triarylfurans containing three different aryl units have been prepared in good yields via a C2–H bond arylation/Suzuki cross-coupling/C5–H bond arylation sequence.

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. DMA was purchased from Acros Organics and was not purified before use. All reagents were weighed and handled in air. Column chromatography was performed with MACHEREY-NAGEL silica gel (0.04–0.063 nm). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV III 400 MHz NMR spectrometer equipped with a BBFO probehead. Chemical shifts (δ) are reported in parts per million relative to residual chloroform (7.28 ppm for ^1H; 77.23 ppm for ^{13}C); coupling constants (*J*) are reported in Hertz. ^1H NMR assignment abbreviations are as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). Elemental analyses were recorded using a Thermo Fisher FLASH 1112 instrument.

C2-Arylation of 3-Bromofuran; General Procedure

Reaction of the aryl bromide (0.5 mmol), 3-bromofuran (2.5 mmol, 5 equiv, 367 mg) and KOAc (1 mmol, 2 equiv, 98 mg) at 120 °C for 8 h in DMA (4 mL) in the presence of $Pd(OAc)_2$ (1 mol%, 0.005 mmol, 1.12 mg) (see Table 1 and Scheme 2) under argon afforded the arylation product after evaporation of the solvent and purification on silica gel.

1-[4-(3-Bromofuran-2-yl)phenyl]ethan-1-one (1)

From 4-bromoacetophenone (100 mg, 0.5 mmol) and 3-bromofuran (2.5 mmol, 5 equiv, 367 mg), product **1** was obtained in 47% (62 mg) yield.

^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.11 (d, *J* = 8.7 Hz, 2 H), 8.04 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 2.0 Hz, 1 H), 6.61 (d, *J* = 2.0 Hz, 1 H), 2.65 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 197.6, 148.0, 142.9, 136.1, 134.0, 128.8, 125.3, 117.0, 98.5, 26.8.

Anal. Calcd for $C_{12}H_9BrO_2$ (265.11): C, 54.37; H, 3.42. Found: C, 54.59; H, 3.21.

4-(3-Bromofuran-2-yl)benzonitrile (2)

From 4-bromobenzonitrile (91 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **2** was obtained in 51% (63 mg) yield.

^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.09 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 1.7 Hz, 1 H), 6.59 (d, *J* = 1.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.0, 143.3, 133.8, 132.5, 125.6, 118.9, 117.1, 111.2, 99.3.

Anal. Calcd for $C_{11}H_6BrNO$ (248.08): C, 53.26; H, 2.44. Found: C, 53.09; H, 2.23.

3-Bromo-2-[4-(trifluoromethyl)phenyl]furan (3)

From 4-bromobenzotrifluoride (113 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **3** was obtained in 45% (65 mg) yield.

^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.12 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 1.9 Hz, 1 H), 6.61 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.5, 142.6, 132.9, 128.4, 125.5 (q, *J* = 4.1 Hz), 125.4, 124.0 (q, *J* = 274.2 Hz), 116.6, 98.0.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –62.7 (s).

Anal. Calcd for $C_{11}H_6BrF_3O$ (291.07): C, 45.39; H, 2.08. Found: C, 45.51; H, 2.34.

1-[4-(3-Bromofuran-2-yl)phenyl]propan-1-one (4)

From 4-bromopropiophenone (107 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **4** was obtained in 42% (59 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (d, *J* = 8.8 Hz, 2 H), 8.02 (d, *J* = 8.9 Hz, 2 H), 7.47 (d, *J* = 1.9 Hz, 1 H), 6.58 (d, *J* = 1.9 Hz, 1 H), 3.02 (q, *J* = 7.2 Hz, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 200.3, 148.0, 142.9, 135.9, 133.8, 128.4, 125.4, 116.9, 98.4, 32.0, 8.4.

Anal. Calcd for $C_{13}H_{11}BrO_2$ (279.13): C, 55.94; H, 3.97. Found: C, 56.11; H, 4.05.

3-Bromo-2-(4-chlorophenyl)furan (5)

From 1-bromo-4-chlorobenzene (96 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **5** was obtained in 39% (50 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.90 (d, *J* = 8.7 Hz, 2 H), 7.42 (d, *J* = 1.9 Hz, 1 H), 7.39 (d, *J* = 8.7 Hz, 2 H), 6.54 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 148.1, 142.1, 133.9, 128.9, 128.4, 126.9, 116.5, 96.6.

Anal. Calcd for $C_{10}H_6BrClO$ (257.51): C, 46.64; H, 2.35. Found: C, 46.36; H, 2.57.

3-(3-Bromofuran-2-yl)benzonitrile (6)

From 3-bromobenzonitrile (91 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **6** was obtained in 50% (62 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.26 (t, *J* = 1.3 Hz, 1 H), 8.20 (td, *J* = 1.3, 7.7 Hz, 1 H), 7.60 (td, *J* = 1.3, 7.7 Hz, 1 H), 7.53 (t, *J* = 7.7 Hz, 1 H), 7.47 (d, *J* = 1.9 Hz, 1 H), 6.58 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.7, 142.9, 131.2, 131.1, 129.6, 129.4, 128.9, 118.7, 116.8, 113.1, 98.2.

Anal. Calcd for $C_{11}H_6BrNO$ (248.08): C, 53.26; H, 2.44. Found: C, 53.41; H, 2.36.

3-Bromo-2-[3-(trifluoromethyl)phenyl]furan (7)

From 3-bromobenzotrifluoride (113 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **7** was obtained in 50% (73 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.22 (s, 1 H), 8.17 (d, *J* = 7.8 Hz, 1 H), 7.63–7.51 (m, 2 H), 7.46 (d, *J* = 2.0 Hz, 1 H), 6.57 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.6, 142.6, 131.4, 130.6, 129.2, 128.5, 124.6 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 274.1 Hz), 122.3 (q, *J* = 4.0 Hz), 116.7, 97.5.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –62.9 (s).

Anal. Calcd for $C_{11}H_6BrF_3O$ (291.07): C, 45.39; H, 2.08. Found: C, 45.56; H, 2.21.

2-(3-Bromofuran-2-yl)benzonitrile (8)

From 2-bromobenzonitrile (91 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **8** was obtained in 42% (52 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.92 (d, *J* = 7.4 Hz, 1 H), 7.77 (d, *J* = 7.9 Hz, 1 H), 7.65 (td, *J* = 1.3, 7.9 Hz, 1 H), 7.57 (d, *J* = 1.9 Hz, 1 H), 7.46 (td, *J* = 1.3, 7.7 Hz, 1 H), 6.61 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.7, 143.7, 134.5, 132.5, 132.3, 129.4, 128.8, 118.2, 116.2, 111.0, 99.8.

Anal. Calcd for $C_{11}H_6BrNO$ (248.08): C, 53.26; H, 2.44. Found: C, 53.20; H, 2.49.

3-(3-Bromofuran-2-yl)-4-fluorobenzaldehyde (9)

From 4-bromo-2-fluorobenzaldehyde (102 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **9** was obtained in 52% (70 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.00 (s, 1 H), 8.24 (dd, *J* = 2.1, 6.9 Hz, 1 H), 7.93 (ddd, *J* = 2.2, 4.8, 8.5 Hz, 1 H), 7.53 (d, *J* = 1.9 Hz, 1 H), 7.40–7.24 (m, 1 H), 6.60 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 190.2, 163.0 (d, *J* = 263.4 Hz), 144.6 (d, *J* = 2.3 Hz), 143.8, 132.9 (d, *J* = 3.1 Hz), 132.8 (d, *J* = 4.6 Hz), 131.7 (d, *J* = 9.9 Hz), 118.9 (d, *J* = 14.7 Hz), 117.7 (d, *J* = 23.0 Hz), 115.8, 100.2.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –100.9 (s)

Anal. Calcd for $C_{11}H_6BrFO_2$ (269.07): C, 49.10; H, 2.25. Found: C, 49.38; H, 2.44.

3-Bromo-2-(naphthalen-1-yl)furan (10)

From 1-bromonaphthalene (103 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **10** was obtained in 38% (52 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.98–7.90 (m, 3 H), 7.73 (dd, *J* = 1.3, 7.1 Hz, 1 H), 7.61 (d, *J* = 2.0 Hz, 1 H), 7.59–7.53 (m, 3 H), 6.68 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.5, 142.8, 133.9, 131.7, 130.0, 129.0, 128.5, 126.8, 126.3, 126.1, 125.1, 115.3, 99.1.

Anal. Calcd for $C_{14}H_9BrO$ (273.13): C, 61.57; H, 3.32. Found: C, 61.46; H, 3.28.

3-Bromo-2-(naphthalen-2-yl)furan (11)

From 2-bromonaphthalene (103 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **11** was obtained in 45% (61 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.45 (s, 1 H), 8.08 (dd, *J* = 1.8, 8.7 Hz, 1 H), 7.94–7.86 (m, 2 H), 7.86–7.81 (m, 1 H), 7.54–7.45 (m, 3 H), 6.59 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.2, 142.1, 133.3, 132.9, 128.6, 128.3, 127.8, 127.3, 126.6, 126.6, 124.9, 123.4, 116.6, 96.6.

Anal. Calcd for $C_{14}H_9BrO$ (273.13): C, 61.57; H, 3.32. Found: C, 61.79; H, 3.51.

3-(3-Bromofuran-2-yl)pyridine (12)

From 3-bromopyridine (79 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **12** was obtained in 45% (50 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.23 (br s, 1 H), 8.57 (br s, 1 H), 8.38–8.11 (m, 1 H), 7.47 (d, *J* = 2.0 Hz, 1 H), 7.36 (dd, *J* = 4.8, 8.2 Hz, 1 H), 6.57 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 148.8, 146.8, 146.5, 142.9, 132.5, 123.5, 116.6, 97.8.

Anal. Calcd for C_9H_6BrNO (224.06): C, 48.25; H, 2.70. Found: C, 48.21; H, 2.83.

5-(3-Bromofuran-2-yl)pyrimidine (13)

From 5-bromopyrimidine (79 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **13** was obtained in 52% (58 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.34 (s, 2 H), 9.18 (s, 1 H), 7.53 (d, *J* = 2.0 Hz, 1 H), 6.62 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.3, 153.0, 144.0, 143.9, 124.6, 116.8, 99.5.

Anal. Calcd for $C_8H_5BrN_2O$ (225.05): C, 42.70; H, 2.24. Found: C, 42.96; H, 2.37.

3-(3-Bromofuran-2-yl)quinoline (14)

From 3-bromoquinoline (104 mg, 0.5 mmol) and 3-bromofuran (367 mg, 2.5 mmol, 5 equiv), product **14** was obtained in 50% (69 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.50 (d, *J* = 2.3 Hz, 1 H), 8.69 (d, *J* = 2.3 Hz, 1 H), 8.11 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.1 Hz, 1 H), 7.73 (t, *J* = 6.8 Hz, 1 H), 7.57 (t, *J* = 7.9 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 6.61 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.7, 147.2, 146.9, 143.0, 131.8, 130.0, 129.4, 128.3, 127.6, 127.4, 123.3, 116.7, 98.0.

Anal. Calcd for $C_{13}H_8BrNO$ (274.12): C, 56.96; H, 2.94. Found: C, 57.08; H, 2.69.

C2,C5-Diarylation of 3-Bromofuran; General Procedure

Reaction of the aryl bromide (1 mmol), 3-bromofuran (0.5 mmol, 1 equiv, 73 mg) and KOAc (1.5 mmol, 3 equiv, 147 mg) at 120 °C for 8 h in DMA (2 mL) in the presence of $Pd(OAc)_2$ (2 mol%, 0.01 mmol, 2.24 mg,) (see Table 1 or Scheme 3) under argon afforded the diarylation product after evaporation of the solvent and purification on silica gel.

3-Bromo-2,5-bis[4-(trifluoromethyl)phenyl]furan (16)

From 4-bromobenzotrifluoride (223 mg, 1 mmol, 2 equiv) and 3-bromofuran (73 mg, 0.5 mmol, 1 equiv), product **16** was obtained in 56% (122 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.17 (d, *J* = 8.8 Hz, 2 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.75–7.66 (m, 4 H), 6.93 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.0, 147.7, 132.5, 132.4, 130.2 (q, *J* = 29.3 Hz), 129.9 (q, *J* = 28.4 Hz), 126.0 (q, *J* = 3.9 Hz), 125.6 (q, *J* = 3.9 Hz), 125.5, 124.1, 124.0 (q, *J* = 273.5 Hz), 123.9 (q, *J* = 273.5 Hz), 113.4, 100.0.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –62.7 (s), –62.7 (s).

Anal. Calcd for $C_{18}H_9BrF_6O$ (435.16): C, 49.68; H, 2.08. Found: C, 49.67; H, 2.00.

3-Bromo-2,5-bis[3-(trifluoromethyl)phenyl]furan (17)

From 3-bromobenzotrifluoride (223 mg, 1 mmol, 2 equiv) and 3-bromofuran (73 mg, 0.5 mmol, 1 equiv), product **17** was obtained in 53% (115 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.30 (s, 1 H), 8.26–8.19 (m, 1 H), 7.92 (s, 1 H), 7.87 (dt, *J* = 2.0, 5.8 Hz, 1 H), 7.66–7.52 (m, 4 H), 6.90 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.0, 147.6, 131.7 (q, *J* = 25.4 Hz), 131.3 (d, *J* = 25.3 Hz), 130.2, 130.2, 129.7, 129.3, 128.6 (m), 127.2 (m), 125.1 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 273.2 Hz), 124.0 (q, *J* = 273.2 Hz), 122.3 (q, *J* = 4.0 Hz), 120.9 (d, *J* = 3.9 Hz), 112.9, 99.6.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –62.9 (s), –62,9 (s).

Anal. Calcd for $C_{18}H_9BrF_6O$ (435.16): C, 49.68; H, 2.08. Found: C, 49.89; H, 1.97.

3-Bromo-2,5-bis[2-(trifluoromethyl)phenyl]furan (18)

From 2-bromobenzotrifluoride (223 mg, 1 mmol, 2 equiv) and 3-bromofuran (73 mg, 0.5 mmol, 1 equiv), product **18** was obtained in 47% (102 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.89–7.81 (m, 2 H), 7.80–7.73 (m, 2 H), 7.70–7.53 (m, 3 H), 7.50–7.41 (m, 1 H), 6.93 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.4, 148.2, 132.5, 132.1, 131.7, 130.0, 129.7, 129.6 (q, *J* = 31.5 Hz), 128.6, 127.1 (q, *J* = 5.4 Hz), 126.7 (q, *J* = 5.9 Hz), 126.7 (q, *J* = 31.2 Hz), 123.9 (q, *J* = 271.6 Hz), 123.8 (q, *J* = 271.6 Hz), 115.2 (q, *J* = 4.7 Hz), 100.5.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –59.6, –60.0.

Anal. Calcd for $C_{18}H_9BrF_6O$ (435.16): C, 49.68; H, 2.08. Found: C, 49.58; H, 2.34.

6,6′-(3-Bromofuran-2,5-diyl)bis[2-(trifluoromethyl)pyridine] (19)

From 2-bromo-6-trifluoromethylpyridine (192 mg, 1 mmol, 2 equiv) and 3-bromofuran (73 mg, 0.5 mmol, 1 equiv), product **19** was obtained in 49% (107 mg) yield.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.19 (d, *J* = 8.1 Hz, 1 H), 8.05–7.93 (m, 3 H), 7.67–7.59 (m, 2 H), 7.44 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.6, 148.5, 148.5 (q, *J* = 25.3 Hz), 148.2, 148.2 (q, *J* = 25.9 Hz), 147.6, 138.3, 138.0, 122.8, 121.3, 121.3 (q, *J* = 274.5 Hz), 121.2 (q, *J* = 274.5 Hz), 119.3 (t, *J* = 2.9 Hz), 119.0 (q, *J* = 2.7 Hz), 116.9, 103.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –68.2 (s), –68.3 (s).

Anal. Calcd for $C_{16}H_7BrF_6N_2O$ (437.14): C, 43.96; H, 1.61. Found: C, 44.09; H, 1.98.

2,3,5-Tris[3,5-bis(trifluoromethyl)phenyl)]-4-bromofuran (20)

The reaction of 1-bromo-3,5-bis(trifluoromethyl)benzene (586 mg, 2 mmol, 4 equiv), 3-bromofuran (73 mg, 0.5 mmol, 1 equiv) and KOAc (180 mg, 3 mmol, 4 equiv) at 120 °C for 8 h in DMA (2 mL) in the presence of $Pd(OAc)_2$ (2.24 mg, 0.01 mmol, 2 mol%) under argon afforded, after evaporation of the solvent and purification, product **20** in 61% (239 mg) yield.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.52 (s, 2 H), 8.05 (s, 1 H), 7.95 (s, 1 H), 7.89 (s, 2 H), 7.84 (s, 1 H), 7.82 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.6, 147.5, 133.2 (q, *J* = 34.7 Hz), 132.9 (q, *J* = 35.1 Hz), 132.8 (q, *J* = 35.2 Hz), 132.6, 130.5, 130.5 (m), 130.4, 126.0 (m), 125.8 (m) 125.2, 123.2 (q, *J* = 273.1 Hz), 123.2 (m), 123.0 (q, *J* = 273.1 Hz), 122.8 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 273.1 Hz), 103.0.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = –63.0 (s), –63.1 (s), –63.5 (s).

Anal. Calcd for $C_{28}H_9BrF_{18}O$ (783.25): C, 42.94; H, 1.16. Found: C, 42.75; H, 1.01.

2-(Naphthalen-1-yl)-3-phenylfuran (22)

The reaction of 3-bromo-2-(naphthalen-1-yl)furan (**10**) (271 mg, 1 mmol), phenylboronic acid (180 mg, 1.5 mmol) and K_3PO_4 (424 mg, 2 mmol) at 80 °C over 16 h in 1,4-dioxane (4 mL) in the presence of Pd-Cl(C_3H_5)(dppb) (12 mg, 0.02 mmol) under argon afforded, after evaporation of the solvent and purification on silica gel, product **22** in 78% (211 mg) yield.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.94–7.88 (m, 2 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.64 (d, *J* = 1.9 Hz, 1 H), 7.54–7.45 (m, 2 H), 7.45–7.37 (m, 2 H), 7.24–7.18 (m, 2 H), 7.18–7.12 (m, 3 H), 6.82 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 148.5, 142.4, 133.9, 133.4, 132.0, 129.3, 129.1, 128.9, 128.4, 128.3, 127.6, 126.6, 126.5, 126.1, 125.3, 123.8, 111.7.

Anal. Calcd for $C_{20}H_{14}O$ (270.33): C, 88.86; H, 5.22. Found: C, 88.96; H, 5.35.

C5-Arylation of 2-(Naphthalen-1-yl)-3-phenylfuran (22); General Procedure

Reaction of the aryl bromide (0.75 mmol), 2-(naphthalen-1-yl)-3-phenylfuran (**22**) (0.5 mmol, 1 equiv) and KOAc (1 mmol, 2 equiv, 98 mg) at 120 °C for 16 h in DMA (2 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12 mg, 0.02 mmol) (see Scheme 7) under argon afforded the arylation product after evaporation of the solvent and purification on silica gel.

4-[5-(Naphthalen-1-yl)-4-phenylfuran-2-yl]benzonitrile (23)

From 4-bromobenzonitrile (137 mg, 0.75 mmol, 1.5 equiv) and 2-(naphthalen-1-yl)-3-phenylfuran (**22**) (135 mg, 0.5 mmol, 1 equiv), product **23** was obtained in 71% (132 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.00–7.92 (m, 3 H), 7.86 (d, *J* = 8.5 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.59 (ddd, *J* = 1.3, 7.6, 8.1 Hz, 1 H), 7.56–7.50 (m, 2 H), 7.50–7.42 (m, 1 H), 7.32–7.20 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 151.6, 149.9, 134.5, 134.1, 132.8, 132.8, 131.8, 130.0, 129.2, 128.7, 128.6, 128.4, 127.7, 127.3, 126.9, 126.6, 126.4, 126.0, 125.4, 124.1, 119.1, 110.5, 110.3.

Anal. Calcd for $C_{27}H_{17}NO$ (371.44): C, 87.31; H, 4.61. Found: C, 87.45; H, 4.81.

3-[5-(Naphthalen-1-yl)-4-phenylfuran-2-yl]quinoline (24)

From 3-bromoquinoline (156 mg, 0.75 mmol, 1.5 equiv) and 2-(naphthalen-1-yl)-3-phenylfuran (**22**) (135 mg, 0.5 mmol, 1 equiv), product **24** was obtained in 81% (161 mg) yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.38 (d, *J* = 2.1 Hz, 1 H), 8.48 (s, 1 H), 8.17 (d, *J* = 9.1 Hz, 1 H), 8.04 (d, *J* = 8.5 Hz, 1 H), 7.97 (t, *J* = 7.1 Hz, 2 H), 7.85 (d, *J* = 8.2 Hz, 1 H), 7.77–7.64 (m, 2 H), 7.58–7.51 (m, 4 H), 7.35 (d, *J* = 7.5 Hz, 3 H), 7.31–7.20 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.9, 149.2, 146.9, 146.9, 134.0, 132.8, 131.8, 129.7, 129.5, 129.3, 129.2, 129.1, 128.6, 128.5, 128.4, 128.0, 128.0, 127.6, 127.4, 127.4, 127.1, 126.7, 126.2, 126.0, 125.4, 123.9, 108.8.

Anal. Calcd for $C_{29}H_{19}NO$ (397.48): C, 87.63; H, 4.82. Found: C, 87.89; H, 5.01.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611819.

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