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Palladium-Catalyzed Cross-Coupling of Furfuryl Alcohols with Arylboronic Acids *via* Aromatization-Driven Carbon–Carbon Bond Cleavage to Synthesize 5-Arylfurfuryl Alcohols and 2,5-Diaryl Furans

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Abstract. Herein we report a protocol for novel palladium-catalyzed cross-coupling reactions of sustainably produced primary furfuryl alcohols with arylboronic acids to deliver 5-arylfurfuryl alcohols and 2,5-diaryl furans. Hammett plot analysis suggested that the reaction mechanism involved aromatization-driven cleavage of the carbon–carbon bond of a furan oxonium ion intermediate. This protocol provides a simple, practical way to transform 5-hydroxymethylfurfural into useful compounds.

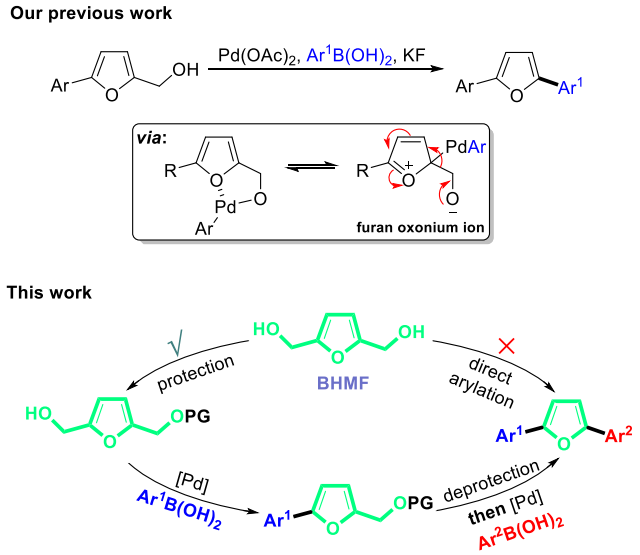
Keywords: C–C activation; Cleavage reactions; Cross-coupling; Primary alcohols; Synthetic methods

Introduction

Carbon–carbon bond cleavage reactions have attracted considerable attention owing to their utility in the synthesis of valuable chemicals.[1] For example, C–C bonds cleavage has been used to produce biomass-based fuels.[2] Attempts have been made to use homogeneous transition-metal complexes to catalyze C–C bond cleavage, but this process is challenging because of the high thermodynamic stability of such bonds.[3] One widely used strategy for cleaving C–C bonds is to take advantage of ring strain; that is, the energy required for dissociation of a C–C bond can be compensated for by the release of ring strain energy.[4] However, for unstrained molecules, some other driving force, such as the departure of a good leaving group or the presence of a chelation auxiliary to lower the energy of a reaction intermediate, is required for C–C bond cleavage. For example, ketones have been used as leaving groups in *β*-C cleavage reactions of tertiary alcohols,[5] and *N*-containing directing groups have been successfully used to accomplish C–C bond cleavage reactions of secondary alcohols.[6] In contrast, there have been only a few examples of direct catalytic C–C bond cleavage reactions of primary alcohols, because oxidation of the hydroxyl groups of such compounds to aldehydes occurs more readily than C–C bond cleavage. However, Shi and co-workers reported two examples of C–C bond cleavage reactions of primary alcohols, albeit with low yields.[6b,c] In addition, aromatization has proved to be a driving force for C–C bond cleavage, but only a few examples have been reported.[7] Therefore, development of novel C–C bond cleavage reactions that take advantage of aromatization would be highly desirable.

Arylfurans, including 2-arylfurans and 2,5-diaryl furans, which have interesting bioactivities[8] and physical properties,[9] are usually synthesized by construction of the furan ring from alkynes[10] or by cross-coupling reactions of environmentally unfriendly halides or organotin reagents.[11] Recently, Forgione and co-workers described palladium-catalyzed decarboxylative cross-coupling reactions of sustainably sourced 2,5-furandicarboxylic acid with aryl halides to access symmetric 2,5-diaryl furans, although the reaction conditions were harsh.[12] Very recently, we reported a method for synthesizing 2,5-diaryl furans by means of oxidative C–C bond cleavage reactions of primary alcohols (5-aryl furfuryl alcohols) driven by aromatization of a furan oxonium ion intermediate (Scheme 1).[13] However, the necessary 5-aryl furfuryl alcohol starting materials were obtained mainly by Suzuki coupling reactions, which lack atom- and step-economy and involve unreadily available starting materials. We envisioned that 5-aryl furfuryl alcohols **2** could be synthesized from 2,5-furandimethanol derivatives **1** by selective C–C bond cleavage and then used to

construct 2,5-diaryl furans **3**. 2,5-Furandimethanol derivatives **1** can be prepared easily from 5-hydroxymethylfurfural (HMF), which is produced on a large scale by hydrolysis of fructose.



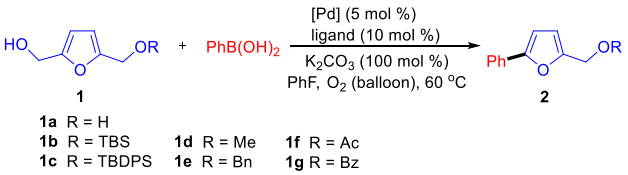
Scheme 1. Transition-metal-catalyzed C–C bond cleavage reactions of furfuryl alcohols.

Results and Discussion

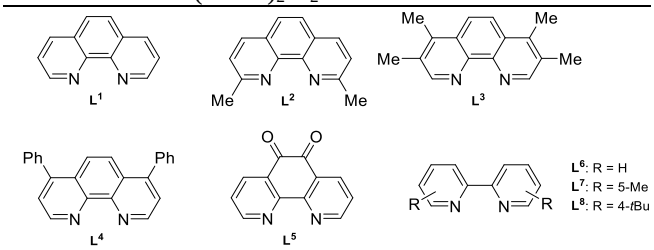
We began by evaluating conditions for reactions of 2,5-furandimethanol derivatives **1** with phenylboronic acid as a model system (Table 1). When **1a** (R = H, 100 mol %) and phenylboronic acid (350 mol %) were exposed to O_2 as the terminal oxidant in the presence of a catalyst assembled *in situ* from $Pd(PhCN)_2Cl_2$ (5 mol %) and 1,10-phenanthroline (10 mol %) in PhF (1.5 mL) containing K_2CO_3 (100 mol %) at 60 °C, only a trace of desired product **2aa** was observed, along with a highly complicated mixture of various by-products, including HMF and furan-2,5-dicarbaldehyde (entry 1). To suppress the side reactions, we introduced a series of mono-protecting groups (R) on **1a**. To our delight, when a substrate with a TBS ether protecting group (**1b**) was used, the reaction smoothly afforded desired product **2ba** in 55% isolated yield (entry 2). Increasing the size of the protecting group (R = TBDPS) decreased the yield (**2ca**, entry 3), as did the use of a smaller protecting group, such as Me or Bn (entries 4 and 5). When R was a good leaving group (Ac or Bz), a complex mixture containing only a trace of the 5-arylfurfuryl alcohol product (**2fa** or **2ga**, respectively) was detected (entries 6 and 7).

Next, we surveyed a number of bidentate nitrogen ligands in reactions of **1b** (Table 1, entries 8–14). 2,9-Dimethyl-1,10-phenanthroline ($\mathbf{L^2}$) and 1,10-phenanthroline-5,6-dione ($\mathbf{L^5}$) gave only traces of **2ba**, demonstrating that sterically hindered or electron-deficient ligands negatively affected the reaction (entries 8 and 11). Several commercially available palladium catalysts were screened and found to offer no improvement in the yield (entries 15–20). Increasing the $Pd(PhCN)_2Cl_2$ loading to 10 mol % also failed to improve the yield (entry 21). Gratifyingly, prolonging the reaction time to 20 h increased the yield to 61% (entry 22). When the K_2CO_3 additive was replaced with Na_2CO_3, Cs_2CO_3, $KHCO_3$, KOAc, or KOH, the yield dropped markedly (see SI for details). Moreover, control experiments revealed that the reaction did not proceed in the absence of the palladium catalyst, ligand, or additive (entries 23–25). On the basis of the above-described results, we concluded that the optimal conditions for this reaction involved the use of $Pd(PhCN)_2Cl_2$ (5 mol %) as the catalyst, $\mathbf{L^1}$ (10 mol %) as the ligand, K_2CO_3 (100 mol %) as the additive, PhF as the solvent, and 60 °C as the reaction temperature (entry 22).

Table 1. Optimization of reaction conditions.[a)]



Entry	1	[Pd]	Ligand	2	Yield (%)[b)]
1	**1a**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2aa**	trace
2	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ba**	55
3	**1c**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ca**	35
4	**1d**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2da**	40
5	**1e**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ea**	38
6	**1f**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2fa**	trace
7	**1g**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ga**	trace
8	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^2}$	**2ba**	trace
9	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^3}$	**2ba**	23
10	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^4}$	**2ba**	27
11	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^5}$	**2ba**	trace
12	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^6}$	**2ba**	28
13	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^7}$	**2ba**	27
14	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^8}$	**2ba**	25
15	**1b**	$Pd(OAc)_2$	$\mathbf{L^1}$	**2ba**	24
16	**1b**	$PdBr_2$	$\mathbf{L^1}$	**2ba**	31
17	**1b**	$PdCl_2$	$\mathbf{L^1}$	**2ba**	17
18	**1b**	$Pd(TFA)_2$	$\mathbf{L^1}$	**2ba**	trace
19	**1b**	$Pd(dppf)Cl_2$	$\mathbf{L^1}$	**2ba**	8
20	**1b**	$Pd(CH_3CN)_2Cl_2$	$\mathbf{L^1}$	**2ba**	28
21[c)]	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ba**	55
22[d)]	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ba**	61
23	**1b**	—	$\mathbf{L^1}$	**2ba**	ND
24	**1b**	$Pd(PhCN)_2Cl_2$	—	**2ba**	ND
25[e)]	**1b**	$Pd(PhCN)_2Cl_2$	$\mathbf{L^1}$	**2ba**	trace

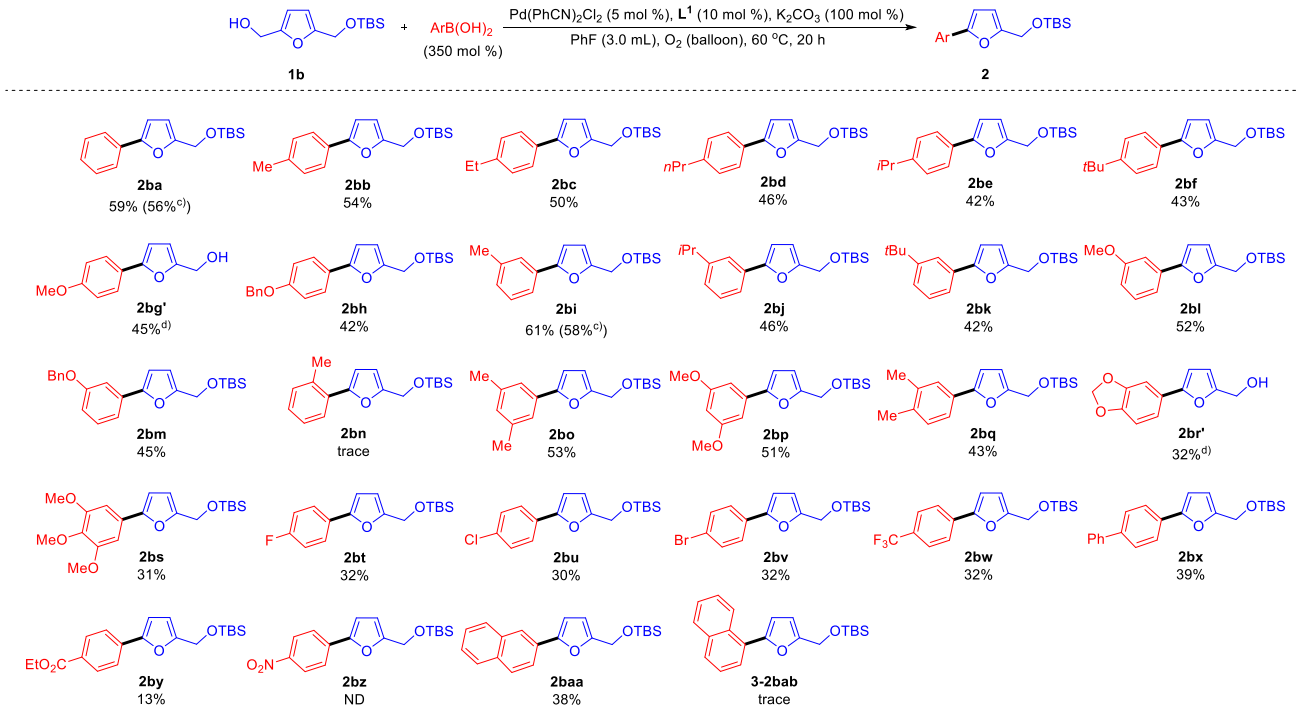


[a)] Reaction conditions, unless otherwise noted: **1** (0.25 mmol), $PhB(OH)_2$ (350 mol %), Pd catalyst (5 mol %), ligand (10 mol %), additive (100 mol %), O_2 (in a balloon),

PhF (1.5 mL), 60 °C, 15 h. [b] Isolated yields are given. ND = not detected. [c] 10 mol % Pd catalyst was used. [d] Reaction was carried out for 20 h. [e] Reaction was carried out without K_2CO_3.

With the optimized conditions in hand, we evaluated the scope of the transformation of TBS-protected substrate **1b** with a wide array of arylboronic acids (Table 2). Coupling of **1b** with phenylboronic acids bearing an electron-donating group at the *para*- or *meta*-position gave the corresponding products (**2bb**–**2bm**) in 42–61% isolated yields. Notably, commensurate yields were obtained when the scale of the reaction was increased from 0.5 to 5 mmol (**2ba**: 59% *vs* 56%; **2bi**: 61% *vs* 58%). An *ortho*-methyl-substituted phenylboronic acid gave only a trace of **2bn**, indicating that this reaction was sensitive to the steric bulk of the arylboronic acid. 3,5-Disubstituted phenylboronic acids were well tolerated, affording coupling products **2bo** and **2bp** in good yields. 3,4-Disubstituted and 3,4,5-trisubstituted phenylboronic acids produced the corresponding products (**2bq**–**2bs**), albeit in relatively low yields. In contrast, phenylboronic acids with an electron-withdrawing group (F, Cl, Br, CF_3, Ph, COOEt, or NO_2) at the *para*-position gave poor yields of coupling products **2bt**–**2bz**. Finally, evaluation of naphthylboronic acids confirmed the negative effect of steric bulk on this transformation. Specifically, the coupling of **1b** with 2-naphthylboronic acid provided **2baa** in moderate yield, whereas more hindered 1-naphthylboronic acid, gave only a trace of desired product **2bab**.

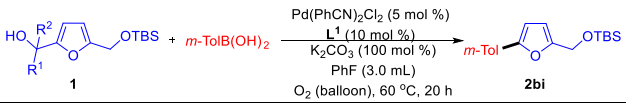
Table 2. Oxidative coupling reactions of primary alcohol **1b** with various arylboronic acids.[a]



[a] Reaction conditions: **1b** (0.5 mmol), $ArB(OH)_2$ (350 mol %), $Pd(PhCN)_2Cl_2$ (5 mol %), **L¹** (10 mol %), K_2CO_3 (100 mol %), O_2 (in a balloon), PhF (3.0 mL), 60 °C, 20 h. Isolated yields are provided. ND = not detected. [b] Reaction performed on a 5 mmol scale. [c] Isolated yields (over two steps from **1b**) of the corresponding alcohol after deprotection are provided.

In addition to the primary alcohol, secondary and tertiary alcohols were explored to determine their suitability for this transformation (Table 3). Secondary alcohols underwent coupling reactions with *m*-tolylboronic acid to give **2bi** in low yields, and increasing the steric hindrance around the hydroxyl group decreased the yield sharply (**1h** > **1i** > **1j** > **1k**). Tertiary alcohols (**1l** and **1m**) showed even lower reactivities under these conditions.

Table 3. Oxidative coupling reactions of furfuryl alcohols **1** with *m*-tolylboronic acid.[a]



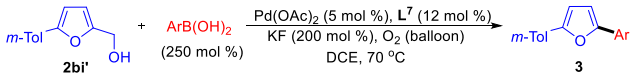
Entry	**1**	R^1	R^2	**2bi** (yield [%])[b]
1	**1b**	H	H	61
2	**1h**	Me	H	29
3	**1i**	Et	H	21
4	**1j**	*i*Pr	H	trace
5	**1k**	*t*Bu	H	ND
6	**1l**	Me	Me	trace
7	**1m**	Ph	Ph	ND

[a] Reaction conditions: **1** (0.50 mmol), *m*-TolB(OH)₂ (350 mol %), $Pd(PhCN)_2Cl_2$ (5 mol %), **L¹** (10 mol %), K_2CO_3

(100 mol %), O_2 (in a balloon), PhF (3.0 mL), 60 °C, 20 h. [b] Isolated yields are given. ND = not detected.

Because a number of compounds with 2,5-diaryl furan moieties have remarkable bioactivities and high luminescence efficiencies,[8,9] we explored the use of the above-described C–C bond cleavage reaction for the synthesis of 2,5-diaryl furans **3** from (5-(*m*-tolyl)furan-2-yl)methanol **2bi′**, which was obtained by deprotection of **2bi** (see SI for details). As shown in Table 4, the results of coupling reactions between primary furfuryl alcohol **2bi′** and arylboronic acids were similar to those shown in Table 2. That is, electron-rich phenylboronic acids with an alkyl or alkoxy group at the *meta*- or *para*-position delivered the corresponding products (**3b**–**3f**) in good isolated yields (Table 4, entries 2–6). In contrast, a sterically hindered *ortho*-methyl-substituted phenylboronic acid afforded **3g** in a low yield (entry 7). Coupling of **2bi′** with 3,5-dimethyl and 3,5-dimethoxyl phenylboronic acid proceeded smoothly to produce good yields of **3h** and **3i**, respectively (entries 8 and 9). Among the electron-deficient arylboronic acids that we tested, halogenated arylboronic acids were well tolerated, giving **3j**–**3l** in good yields (entries 10–12); however, extremely electron-deficient arylboronic acids afforded only very low yields of the corresponding products (**3m**–**3o**, entries 13–15). Finally, although 1-naphthylboronic acid gave only a 12% yield of desired product **3p**, the less sterically bulky 2-naphthylboronic acid provided **3q** in 55% yield (entries 16 and 17).

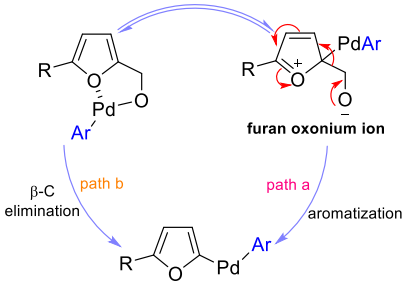
Table 4. Oxidative coupling reactions of **2bi′** with various arylboronic acids.[a]



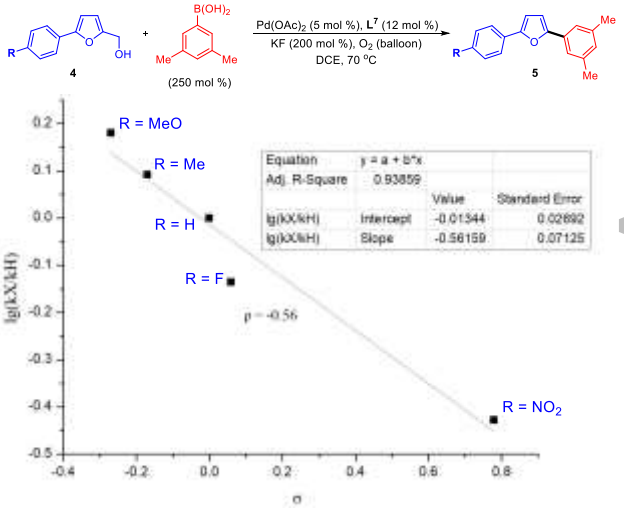
Entry	Ar	3	Yield (%)[b]
1	Ph	**3a**	74
2	3-MeC_6H_4	**3b**	69
3	4-MeC_6H_4	**3c**	65
4	3-MeOC_6H_4	**3d**	68
5	4-MeOC_6H_4	**3e**	62
6[c]	4-*t*BuC_6H_4	**3f**	60
7	2-MeC_6H_4	**3g**	23
8	3,5-diMeC_6H_3	**3h**	66
9	3,5-diMeOC_6H_3	**3i**	58
10	4-FC_6H_4	**3j**	61
11	4-BrC_6H_4	**3k**	52
12	4-ClC_6H_4	**3l**	45
13	4-COOEtC_6H_4	**3m**	17
14	4-$CF_3C_6H_4$	**3n**	17
15	4-$NO_2C_6H_4$	**3o**	Trace
16	1-Naphthyl	**3p**	12
17	2-Naphthyl	**3q**	55

[a] Reaction conditions, unless otherwise noted: **2bi′** (0.5 mmol), ArB(OH)$_2$ (1.25 mmol), Pd(OAc)$_2$ (5 mol %), **L**^{7} (12 mol %), KF (200 mol %), O_2 (in a balloon), DCE (1.5 mL), 70 °C, 15 h. [b] Isolated yields are given. [c] Reaction was carried out in 2.5 mL of DCE.

On the basis of our previous research on furan chemistry[14] and the known mechanism of palladium-catalyzed *β*-C elimination reactions of tertiary[5] and secondary alcohols[6], we propose two possible pathways for the C–C bond cleavage reactions reported herein (Scheme 2): (a) aromatization-driven cleavage of the C–C bond of a furan oxonium ion intermediate and (b) a direct *β*-C elimination reaction of an alcoholate. To evaluate the likelihood of these two possibilities, we performed a Hammett plot analysis (Scheme 3). When furfuryl alcohols bearing various substituted phenyl groups were employed as substrates under the optimal conditions, Hammett plot analysis clearly revealed that the rate of this transformation increased as the electron density of the C5-substituent of the furfuryl alcohol increased. The negative slope (ρ = −0.56) of the Hammett plot indicated the existence of a charged transition state, which is consistent with a furan oxonium ion intermediate (path a). In addition, arylation of sterically bulky secondary and tertiary alcohol substrates is disfavored, which is incompatible with the involvement of path b.



Scheme 2. Two possible pathways for cleavage of the C–C bonds of furfuryl alcohols.



Scheme 3. Hammett plot for cleavage of the C–C bond of furfuryl alcohols.

Conclusion

In summary, we have expanded the scope of the palladium-catalyzed oxidative coupling reaction between commercially available arylboronic acids and primary furfuryl alcohols for sustainable synthesis of 5-arylfurfuryl alcohols and 2,5-diaryl furans. The primary furfuryl alcohol substrates can be prepared readily from 5-hydroxymethylfurfural. Hammett plot analysis demonstrated that the C–C bond cleavage involved in this transformation was driven by aromatization of a furan oxonium ion intermediate. Taken together, our results indicate that this novel protocol offers a simple, practical route for transformation of sustainably produced 5-hydroxymethylfurfural into useful compounds.

Experimental Section

General procedure for the synthesis of arylfurans 2

1 (0.5 mmol) was added to a 25-mL dried Schlenk tube charged with arylboronic acids (1.75 mmol), $Pd(PhCN)_2Cl_2$ (5 mol %, 9.6 mg), 1,10-phenanthroline (**L**[1], 10 mol %, 10.0 mg), K_2CO_3 (0.5 mmol, 70.0 mg), and fluorobenzene (3.0 mL). The mixture was stirred at 60 °C for 20 h under O_2 atmosphere (in a balloon), and then was cooled to room temperature. The resultant mixture was evaporated in vacuum and further isolated by flash chromatography on silica gel with petroleum ether to give the pure product **2**.

General procedure for the synthesis of 5-aryl furfuryl alcohols 2'

Before being isolated by flash chromatography, the resultant mixture of **2** was dissolved in THF (5 mL), then tetrabutylammonium fluoride (1 M solution in THF, 150 mol % based on **1b**) was added. After being stirred for 1 h, H_2O (15 mL) was added and the mixture was concentrated in vacuo to remove the THF. The remaining aqueous mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo, and then was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to give the corresponding alcohol **2'**.

General procedure for the synthesis of 2,5-diaryl furans 3

2bi' (0.5 mmol) was added to an 25-mL dried Schlenk tube charged with arylboronic acids (1.25 mmol), $Pd(OAc)_2$ (5 mol %, 5.6 mg), **L**[7] (12 mol %, 11.0 mg), KF (1.0 mmol, 58.0 mg), and 1,2-dichloroethane (1.5 mL). The mixture was stirred at 70 °C for 15 h under O_2 atmosphere (in a balloon), and then was cooled down to room temperature. The resultant mixture was evaporated in vacuum and further isolated by flash chromatography on silica gel with petroleum ether to give the pure product **3**.

Characterizing data for previously unreported molecules

***tert*-Butyldimethyl((5-phenylfuran-2-yl)methoxy)silane (2ba)**

Yellow oil (85.0 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.45 (s, 1H), 6.18 (s, 1H), 4.57 (s, 2H), 0.81 (s, 9H), -0.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 153.6, 131.1, 128.8, 127.3, 123.8, 109.6, 105.8, 58.5, 26.1, 18.6, -5.0. IR (film) 3062, 2955, 2931, 2858, 1549, 1468, 1255, 1078, 838, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{24}NaO_2Si$ [*M*+Na]$^+$: 311.1443, found: 311.1440.

***tert*-Butyldimethyl((5-(*p*-tolyl)furan-2-yl)methoxy)silane (2bb)**

Yellow oil (81.0 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 6.54 (s, 1H), 6.31 (s, 1H), 4.72 (s, 2H), 2.37 (s, 3H), 0.95 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 153.7, 137.1, 129.4, 128.4, 123.8, 109.5, 105.0, 58.5, 26.1, 21.4, 18.6, -5.0. IR (film) 3027, 2954, 2930, 2858, 1553, 1498, 1254, 1078, 838, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{26}KO_2Si$ [*M*+K]$^+$: 341.1339, found: 341.1337.

***tert*-Butyl((5-(4-ethylphenyl)furan-2-yl)methoxy)dimethylsilane (2bc)**

Yellow oil (79.0 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.55 (d, *J* = 3.1 Hz, 1H), 6.32 (d, *J* = 3.1 Hz, 1H), 4.72 (s, 2H), 2.68 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H), 0.96 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.7, 143.6, 128.7, 128.3, 123.9, 109.5, 105.1, 58.5, 28.8, 26.1, 18.6, 15.6, -5.0. IR (film) 3028, 2959, 2931, 2858, 1551, 1498, 1254, 1078, 836, 779 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{28}KO_2Si$ [*M*+K]$^+$: 355.1496, found: 355.1493.

***tert*-Butyldimethyl((5-(4-propylphenyl)furan-2-yl)methoxy)silane (2bd)**

Yellow oil (76.0 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.54 (d, *J* = 3.1 Hz, 1H), 6.31 (d, *J* = 3.1 Hz, 1H), 4.71 (s, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.61 (m, 2H), 0.99 – 0.93 (m, 12H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.7, 142.0, 128.9, 128.7, 123.8, 109.5, 105.1, 58.5, 38.0, 26.1, 24.6, 18.6, 13.9, -5.0. IR (film) 3026, 2957, 2930, 2858, 1498, 1465, 1255, 1078, 838, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{30}KO_2Si$ [*M*+K]$^+$: 369.1652, found: 369.1648.

***tert*-Butyl((5-(4-isopropylphenyl)furan-2-yl)methoxy)dimethylsilane (2be)**

Yellow oil (69.3 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.39 (d, *J* = 2.1 Hz, 1H), 6.16 (d, *J* = 2.1 Hz, 1H), 4.57 (s, 2H), 2.84 – 2.69 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 6H), 0.81 (s, 9H), -0.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.7, 148.2, 128.8, 126.8, 123.9, 109.5, 105.1, 58.5, 34.0, 26.1, 24.0, 18.6, -5.0. IR (film) 3026, 2958, 2931, 2859, 1498, 1465, 1255, 1075, 836, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{30}KO_2Si$ [*M*+K]$^+$: 369.1652, found: 369.1646.

***tert*-Butyl((5-(4-(*tert*-butyl)phenyl)furan-2-yl)methoxy)dimethylsilane (2bf)**

Yellow oil (74.0 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 6.56 (s, 1H), 6.33 (s, 1H), 4.73 (s, 2H), 1.37 (s, 9H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 153.7, 150.4, 128.4, 125.7, 123.6, 109.5, 105.2, 58.5, 34.7, 31.4, 26.1, 18.6, -5.0. IR (film) 3027, 2958, 2931, 2859, 1553, 1495, 1256, 1080, 837, 781 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{32}KO_2Si$ [*M*+K]$^+$: 383.1809, found: 383.1805.

(5-(4-Methoxyphenyl)furan-2-yl)methanol (2bg')[15]

White solid (46.0 mg, 45% over two steps from **1b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 3.2 Hz, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 4.63 (s, 2H), 3.82 (s, 3H), 2.11 (br, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 159.2, 154.2, 153.0, 125.4, 123.9, 114.2, 110.1, 104.2, 57.7, 55.4.

((5-(4-(Benzyloxy)phenyl)furan-2-yl)methoxy)(*tert*-butyl)dimethylsilane (2bh)

White solid (82.8 mg, 42%), mp: 57-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.33 (m, 5H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.48 (s, 1H), 6.32 (s, 1H), 5.11 (s, 2H), 4.72 (s, 2H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 153.6, 153.4, 137.0, 128.7, 128.1, 127.6, 125.2, 124.4, 115.2, 109.5, 104.2, 70.2, 58.4, 26.1, 18.6, -5.0. IR (film) 3036, 2954, 2930, 2857, 1497, 1462, 1248, 1076, 835, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{24}H_{30}KO_3Si$ [*M*+K]$^+$: 433.1601, found: 433.1597.

***tert*-Butyldimethyl((5-(*m*-tolyl)furan-2-yl)methoxy)silane (2bi)**

Yellow oil (92.2 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.30 – 7.25 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 6.34 (s, 1H), 4.74 (s, 2H), 2.42 (s, 3H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.7, 138.3, 131.0, 128.7, 128.2, 124.5, 121.0, 109.5, 105.6, 58.5, 26.0, 21.6, 18.6, -5.0. IR (film) 3049, 2955, 2930, 2858, 1498, 1468, 1255, 1075, 838, 778 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{26}KO_2Si$ [*M*+K]$^+$: 341.1339, found: 341.1335.

***tert*-Butyl((5-(3-isopropylphenyl)furan-2-yl)methoxy)dimethylsilane (2bj)**

Yellow oil (75.8 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 2.6 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 4.74 (s, 2H), 3.03 – 2.89 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 6H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.9, 149.4, 131.1, 128.8, 125.6, 121.9, 121.5, 109.5, 105.6, 58.5, 34.3, 26.1, 24.1, 18.6, -5.0. IR (film) 3026, 2959, 2932, 2860, 1550, 1467, 1257, 1080, 838, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{30}KO_2Si$ [*M*+K]$^+$: 369.1652, found: 369.1648.

***tert*-Butyl((5-(3-(*tert*-butyl)phenyl)furan-2-yl)methoxy)dimethylsilane (2bk)**

Yellow oil (71.4 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.50 (d, *J* = 6.3 Hz, 1H), 7.38 – 7.29 (m, 2H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.34 (d, *J* = 2.8 Hz, 1H), 4.75 (s, 2H), 1.39 (s, 9H), 0.98 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 153.8, 151.6, 130.8, 128.5, 124.5, 121.2, 120.8, 109.5, 105.5, 58.5, 34.9, 31.5, 26.1, 18.6, -5.0. IR (film) 3028, 2958, 2932, 2859, 1546, 1468, 1254, 1076, 838, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{32}KO_2Si$ [*M*+K]$^+$: 383.1809, found: 383.1807.

***tert*-Butyl((5-(3-methoxyphenyl)furan-2-yl)methoxy)dimethylsilane (2bl)**

Yellow oil (82.3 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 4.74 (s, 2H), 3.88 (s, 3H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 154.1, 153.4, 132.4, 129.8, 116.5, 113.3, 109.6, 109.1, 106.1, 58.5, 55.4, 26.1, 18.6, -5.0. IR (film) 3028, 2956, 2929, 2857, 1539, 1467, 1258, 1081, 838, 778 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{26}KO_3Si$ [*M*+K]$^+$: 357.1288, found: 357.1285.

((5-(3-(Benzyloxy)phenyl)furan-2-yl)methoxy)(*tert*-butyl)dimethylsilane (2bm)

Yellow oil (91.3 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.40 – 7.29 (m, 4H), 6.90 (d, *J* = 6.0 Hz, 1H), 6.61 (s, 1H), 6.34 (s, 1H), 5.14 (s, 2H), 4.73 (s, 2H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 154.1, 153.3, 137.1, 132.4, 129.9, 128.7, 128.1, 127.7, 116.7, 114.0, 110.2, 109.6, 106.2, 70.2, 58.5, 26.1, 18.6, -5.0. IR (film) 3028, 2954, 2929, 2857, 1539, 1453, 1257, 1071, 837, 776 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{24}H_{30}KO_3Si$ [*M*+K]$^+$: 433.1601, found: 433.1598.

***tert*-Butyl((5-(3,5-dimethylphenyl)furan-2-yl)methoxy)dimethylsilane (2bo)**

Yellow oil (82.8 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 6.93 (s, 1H), 6.58 (d, *J* = 3.0 Hz, 1H), 6.33 (d, *J* = 3.0 Hz, 1H), 4.74 (s, 2H), 2.37 (s, 6H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.8, 138.2, 130.9, 129.1, 121.7, 109.4, 105.5, 58.5, 26.1, 21.5, 18.6, -5.0. IR (film) 3028, 2954, 2929, 2857, 1545, 1465, 1254, 1076, 838, 779 cm^{-1}. HRMS (ESI) *m/z* Calcd for $C_{19}H_{28}KO_2Si$ [*M*+K]$^+$: 355.1496, found: 355.1494.

***tert*-Butyl((5-(3,5-dimethoxyphenyl)furan-2-yl)methoxy)dimethylsilane (2bp)**

Yellow oil (88.6 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 6.60 (d, *J* = 3.1 Hz, 1H), 6.41 (s, 1H), 6.34 (d, *J* = 3.1 Hz, 1H), 4.73 (s, 2H), 3.86 (s, 6H), 0.96 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 154.1, 153.4, 132.8, 109.5, 106.3, 102.0, 99.9, 58.5, 55.6, 26.0, 18.6, -5.0. IR (film) 3001, 2954, 2932, 2857, 1549, 1463, 1254, 1202, 1156, 1069, 838, 781 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{28}KO_4Si$ [*M*+K]$^+$: 387.1394, found: 387.1390.

***tert*-Butyl((5-(3,4-dimethylphenyl)furan-2-yl)methoxy)dimethylsilane (2bq)**

Yellow oil (68.0 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 2.9 Hz, 1H), 6.32 (d, *J* = 2.9 Hz, 1H), 4.73 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 0.97 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.6, 136.9, 135.9, 130.0, 128.8, 125.1, 121.4, 109.5, 104.9, 58.5, 26.1, 20.0, 19.7, 18.6, -5.0. IR (film) 3018, 2954, 2930, 2858, 1550, 1458, 1255, 1076, 838, 780 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{28}KO_2Si$ [*M*+K]$^+$: 355.1496, found: 355.1496.

(5-(Benzo[*d*][1,3]dioxol-5-yl)furan-2-yl)methanol (2br')

Yellow solid (34.5 mg, 32% over two steps from **1b**), mp: 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 3.2 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 5.96 (s, 2H), 4.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 153.2, 148.1, 147.2, 125.3, 117.9, 110.1, 108.7, 104.7, 104.7, 101.3, 57.7. IR (film) 3338, 3021, 2980, 2900, 1550, 1450, 1285, 1255, 1034, 928, 862, 798 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{10}NaO_4$ [*M*+Na]$^+$: 241.0477, found: 241.0472.

***tert*-Butyldimethyl((5-(3,4,5-trimethoxyphenyl)furan-2-yl)methoxy)silane (2bs)**

Colorless solid (59.2 mg, 31%), mp: 49-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.54 (d, *J* = 3.2 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 4.73 (s, 2H), 3.94 (s, 6H), 3.89 (s, 3H), 0.96 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.6, 153.4, 137.8, 126.8, 109.6, 105.4, 101.2, 61.1, 58.4, 56.3, 26.0, 18.6, -5.0. IR (film) 3018, 2932, 2857, 1550, 1497, 1245, 1129, 1077, 837, 778 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{30}NaO_5Si$ [*M*+Na]$^+$: 401.1760, found: 401.1756.

***tert*-Butyl((5-(4-fluorophenyl)furan-2-yl)methoxy)dimethylsilane (2bt)**

Yellow oil (48.2 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.13 – 7.02 (m, 2H), 6.52 (d, *J* = 3.2 Hz, 1H), 6.31 (d, *J* = 3.2 Hz, 1H), 4.70 (s, 2H), 0.94 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.0, 153.4 (d, *J* = 135.2 Hz), 127.5 (d, *J* = 3.3 Hz), 125.5 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.9 Hz), 109.6, 105.4, 58.4, 26.0, 18.6, -5.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.52. IR (film) 3122, 2954, 2930, 2857, 1552, 1495, 1231, 1077, 835, 778 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{23}FNaO_2Si$ [*M*+Na]$^+$: 329.1349, found: 329.1346.

tert-Butyl((5-(4-chlorophenyl)furan-2-yl)methoxy)dimethylsilane (2bu)

Yellow oil (50.3 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 4.70 (s, 2H), 0.94 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 152.5, 133.0, 129.6, 129.0, 125.0, 109.6, 106.3, 58.4, 26.0, 18.6, -5.0. IR (film) 3123, 2954, 2930, 2857, 1542, 1481, 1255, 1092, 836, 781 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}ClO_2Si$ [*M*-H]$^-$: 321.1078, found: 321.1071.

((5-(4-Bromophenyl)furan-2-yl)methoxy)(*tert*-butyl)dimethylsilane (2bv)

Yellow oil (58.5 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 4H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 4.70 (s, 2H), 0.94 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 152.5, 131.9, 130.0, 125.3, 121.1, 109.6, 106.4, 58.4, 26.0, 18.6, -5.0. IR (film) 3123, 2954, 2930, 2857, 1545, 1476, 1255, 1074, 837, 781 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}BrO_2Si$ [*M*-H]$^-$: 365.0573, found: 365.0566.

tert-Butyldimethyl((5-(4-(trifluoromethyl)phenyl)furan-2-yl)methoxy)silane (2bw)

Yellow oil (56.3 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 6.70 (s, 1H), 6.36 (s, 1H), 4.72 (s, 2H), 0.94 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 152.1, 134.2, 129.0 (q, *J* = 32.6 Hz), 125.8 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 270.0 Hz),123.74, 109.7, 107.8, 58.4, 26.0, 18.6, -5.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51. IR (film) 3125, 2957, 2930, 2861, 1551, 1468, 1325, 1258, 1074, 838, 752 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{23}F_3NaO_2Si$ [*M*+Na]$^+$: 379.1317, found: 379.1316.

((5-([1,1'-Biphenyl]-4-yl)furan-2-yl)methoxy)(*tert*-butyl)dimethylsilane (2bx)

White solid (70.7 mg, 39%), mp: 73-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 4H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 6.38 (s, 1H), 4.76 (s, 2H), 1.00 (s, 9H), 0.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 153.3, 140.8, 140.0, 130.0, 128.9, 127.4, 127.0, 124.2, 109.7, 106.0, 58.5, 26.1, 18.6, -5.0. One of the peaks of ^{13}C NMR may be overlapped by others. IR (film) 3055, 2954, 2930, 2857, 1566, 1465, 1254, 1109, 838, 764 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{23}H_{28}NaO_2Si$ [*M*+Na]$^+$: 387.1756, found: 387.1752.

Ethyl 4-(5-(((*tert*-butyldimethylsilyl)oxy)methyl)furan-2-yl)benzoate (2by)

Yellow oil (22.8 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.35 (d, *J* = 3.0 Hz, 1H), 4.72 (s, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 155.3, 152.5, 134.9, 130.2, 128.9, 123.3, 109.8, 108.0, 61.1, 58.5, 26.0, 18.6, 14.5, -5.0. IR (film) 3123, 2955, 2931, 2858, 1716, 1611, 1571, 1274, 1105, 838, 772 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{28}NaO_4Si$ [*M*+Na]$^+$: 383.1655, found: 383.1650.

tert-Butyldimethyl((5-(naphthalen-2-yl)furan-2-yl)methoxy)silane (2baa)

Yellow solid (65.5 mg, 38%), mp: 46-47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.91 – 7.75 (m, 4H), 7.54 – 7.43 (m, 2H), 6.73 (s, 1H), 6.40 (s, 1H), 4.79 (s, 2H), 1.00 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 153.6, 133.7, 132.8, 128.4, 128.4, 128.3, 127.9, 126.6, 126.0, 122.4, 122.1, 109.7, 106.4, 58.5, 26.1, 18.6, -5.0. IR (film) 3057, 2953, 2930, 2857, 1542, 1464, 1254, 1075, 836, 779, 746 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{26}KO_2Si$ [*M*+K]$^+$: 377.1339, found: 377.1334.

(5-(*m*-Tolyl)furan-2-yl)methanol (2bi')

Yellow solid (0.52 g, 56% over two steps from **1b**), mp: 48-49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 6.34 (d, *J* = 3.1 Hz, 1H), 4.63 (s, 2H), 2.37 (s, 3H), 2.08 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 153.6, 138.4, 130.7, 128.7, 128.4, 124.5, 121.1, 110.0, 105.7, 57.7, 21.6. IR (film) 3287, 3126, 2923, 2867, 1547, 1481, 1206, 1017, 780, 694 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{12}H_{12}NaO_2$ [*M*+Na]$^+$: 211.0735, found: 211.0729.

2-Phenyl-5-(*m*-tolyl)furan (3a)

White solid (85.2 mg, 74%), mp: 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.21 (m, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.77 – 6.64 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 153.4, 138.4, 131.0, 130.8, 128.8, 128.7, 128.3, 127.4, 124.5, 123.8, 121.0, 107.3, 107.2, 21.6. IR (film) 3046, 2959, 1602, 1533, 1478, 1271, 1022, 772 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}O$ [*M*+H]$^+$: 235.1123, found: 235.1115.

2,5-Di-*m*-tolylfuran (3b)

White solid (85.0 mg, 69%), mp: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.58 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.79 (s, 2H), 2.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 138.4, 130.9, 128.7, 128.2, 124.4 121.0, 107.2, 21.6. IR (film) 3023, 2920, 1589, 1534, 1479, 1287, 1025, 782 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}O$ [*M*+H]$^+$: 249.1279, found: 249.1268.

2-(*m*-Tolyl)-5-(*p*-tolyl)furan (3c)

White solid (79.8 mg, 65%), mp: 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.63 (d, *J* = 3.4 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 153.3, 138.4, 137.2, 130.9, 129.5, 128.7, 128.3, 128.2, 124.4, 123.8, 121.0, 107.2, 106.6, 21.6, 21.4. IR (film) 3123, 2922, 1591, 1537, 1494, 1280, 1020, 778 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}O$ [*M*+H]$^+$: 249.1279, found: 249.1270.

2-(3-Methoxyphenyl)-5-(*m*-tolyl)furan (3d)

White solid (88.1 mg, 68%), mp: 81-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.44 – 7.32 (m, 4H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.81 – 6.73 (m, 2H), 3.91 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 153.7, 153.1, 138.4, 132.2, 130.7, 129.9, 128.7, 128.3, 124.4, 121.1, 116.5, 112.8, 109.4, 107.7, 107.2, 55.3, 21.6. IR (film) 3055, 2955, 1591, 1537, 1484, 1288, 1217, 1025, 774 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}O_2$ [*M*+H]$^+$: 265.1229, found: 265.1223.

2-(4-Methoxyphenyl)-5-(*m*-tolyl)furan (3e)

White solid (82.4 mg, 62%), mp: 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 3.4 Hz, 1H), 6.62 (d, *J* = 3.4 Hz, 1H), 3.86 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 153.5, 153.0, 138.4, 131.0, 128.7, 128.1, 125.3, 124.3, 124.1, 120.9, 114.3, 107.2, 105.8, 55.4, 21.6. IR (film) 3023, 2968, 1566, 1497, 1468, 1293, 1024, 774 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{16}O_2$ [*M*]$^+$: 264.1150, found: 264.1142.

2-(4-(*tert*-Butyl)phenyl)-5-(*m*-tolyl)furan (3f)

White solid (87.0 mg, 60%), mp: 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.74 (d, *J* = 3.4 Hz, 1H), 2.49 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 153.3, 150.5, 138.4, 131.0, 128.7, 128.3, 128.2, 125.7, 124.4, 123.7, 121.0, 107.2, 106.8, 34.7, 31.4, 21.6. IR (film) 3034, 2962, 1611, 1586, 1493, 1268, 1023, 779 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{23}O$ [*M*+H]$^+$: 291.1749, found: 291.1739.

2-(*m*-Tolyl)-5-(*o*-tolyl)furan (3g)

White solid (28.1 mg, 23%), mp: 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.31 – 7.18 (m, 4H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 3.4 Hz, 1H), 6.61 (d, *J* = 3.4 Hz, 1H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 153.1, 138.4, 134.6, 131.4, 130.9, 130.3, 128.8, 128.3, 127.5, 127.0, 126.2, 124.5, 121.1, 110.8, 106.9, 22.2, 21.7. IR (film) 3061, 2922, 1602, 1536, 1481, 1276, 1025, 776 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}O$ [*M*+H]$^+$: 249.1279, found: 249.1270.

2-(3,5-Dimethylphenyl)-5-(*m*-tolyl)furan (3h)

White solid (85.6 mg, 66%), mp: 88-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.45 (s, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.79 – 6.73 (m, 2H), 2.48 (s, 3H), 2.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 153.4, 138.4, 138.3, 130.9, 130.8, 129.2, 128.7, 128.2, 124.4, 121.7, 121.0, 107.2, 107.1, 21.6, 21.5. IR (film) 3021, 2919, 1605, 1534, 1478, 1288, 1026, 783 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{19}O$ [*M*+H]$^+$: 263.1436, found: 263.1426.

2-(3,5-Dimethoxyphenyl)-5-(*m*-tolyl)furan (3i)

White solid (85.8 mg, 58%), mp: 77-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 2H), 6.78 – 6.69 (m, 2H), 6.43 (t, *J* = 2.2 Hz, 1H), 3.88 (s, 6H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 153.7, 153.1, 138.4, 132.7, 130.7, 128.7, 128.4, 124.5, 121.1, 107.9, 107.2, 102.2, 99.6, 55.5, 21.6. IR (film) 3021, 2938, 1597, 1537, 1460, 1203, 1155, 1025, 779 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{19}O_3$ [*M*+H]$^+$: 295.1334, found: 295.1329.

2-(4-Fluorophenyl)-5-(*m*-tolyl)furan (3j)

White solid (76.7 mg, 61%), mp: 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 2H), 7.64 – 7.54 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.09 (m, 3H), 6.73 (s, 1H), 6.67 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.9 Hz), 153.6, 152.5, 138.4, 130.7, 128.7, 128.3, 127.3 (d, *J* = 3.3 Hz), 125.50 (d, *J* = 8.0 Hz), 124.4, 121.0, 115.8 (d, *J* = 21.9 Hz), 107.2, 107.0, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.16. IR (film) 3021, 2923, 1571, 1538, 1492, 1297, 1022, 781 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{13}FO$ [*M*]$^+$: 252.0950, found: 252.0938.

2-(4-Bromophenyl)-5-(*m*-tolyl)furan (3k)

White solid (80.5 mg, 52%), mp: 118-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.48 (m, 6H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.72 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 152.2, 138.5, 131.9, 130.6, 129.8, 128.8, 128.5, 125.2, 124.5, 121.1, 121.0, 107.9, 107.3, 21.6. IR (film) 3021, 2917, 1606, 1531, 1476, 1282, 1023, 782 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{14}BrO$ [*M*+H]$^+$: 313.0228, found: 313.0218.

2-(4-Chlorophenyl)-5-(*m*-tolyl)furan (3l)

White solid (60.7 mg, 45%), mp: 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.72 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 152.2, 138.5, 132.9, 130.6, 129.4, 129.0, 128.8, 128.5, 125.0, 124.5, 121.1, 107.8, 107.3, 21.6. IR (film) 3022, 2921, 1606, 1531, 1476, 1282, 1023, 782 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{13}ClO$ [*M*]$^+$: 268.0655, found: 268.0641.

Ethyl 4-(5-(*m*-tolyl)furan-2-yl)benzoate (3m)

White solid (25.0 mg, 17%), mp: 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 6.75 (s, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 154.8, 152.3, 138.5, 134.7, 130.4, 130.2, 128.9, 128.8, 128.8, 124.7, 123.3, 121.3, 109.6, 107.6, 61.1, 21.7, 14.5. IR (film) 3023, 2982, 1711, 1608, 1535, 1471, 1272, 1026, 773 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}O_3$ [*M*+H]$^+$: 307.1334, found: 307.1331.

2-(*m*-Tolyl)-5-(4-(trifluoromethyl)phenyl)furan (3n)

White solid (25.2 mg, 17%), mp: 129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.75 (d *J* = 3.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 151.8, 138.6, 134.1 (d, *J* = 1.4 Hz), 130.5, 129.0 (q, *J* = 32.2 Hz), 128.9, 128.8, 125.9 (q, *J* = 3.9 Hz), 124.7, 124.4 (q, *J* = 270.0 Hz), 123.8, 121.3, 109.4, 107.5, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47. IR (film) 3019, 2934, 1581, 1538, 1495, 1291, 1165, 1113, 1024, 783 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{13}F_3KO$ [*M*+K]$^+$: 341.0556, found: 341.0762.

2-(Naphthalen-1-yl)-5-(*m*-tolyl)furan (3p)

Yellow oil (17.0 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 6.8 Hz, 2H), 7.65 – 7.52 (m, 5H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 3.4 Hz, 1H), 6.83 (d, *J* = 3.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 153.0, 138.5, 134.2, 130.9, 130.5, 128.8, 128.7, 128.7, 128.7, 128.4, 126.8, 126.2, 126.1, 125.7, 125.5, 124.6, 121.2, 111.6, 107.0, 21.7. IR (film) 3053, 2922, 1528, 1478, 1277, 1022, 772 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{17}O$ [*M*+H]$^+$: 285.1279, found: 285.1271.

2-(Naphthalen-2-yl)-5-(*m*-tolyl)furan (3q)

White solid (77.7 mg, 55%), mp: 122-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.81 (m, 3H), 7.69 – 7.62 (m, 2H), 7.56 – 7.45 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 3.5 Hz, 1H), 6.79 (d, *J* = 3.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 153.5, 138.5, 133.8, 132.8, 130.8, 128.8, 128.5, 128.4, 128.3, 127.9, 126.6, 126.0, 124.6, 122.4, 122.1, 121.2, 108.0, 107.4, 21.7. One of the peaks of ^{13}C NMR may be overlapped by others. IR (film) 3056, 2924, 1534, 1454, 1266, 1024, 781 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{17}O$ [*M*+H]$^+$: 285.1279, found: 285.1268.

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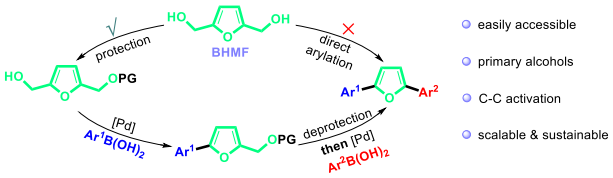
FULL PAPER

Palladium-Catalyzed Cross-Coupling of Furfuryl Alcohols with Arylboronic Acids *via* Aromatization-Driven Carbon–Carbon Bond Cleavage to Synthesize 5-Arylfurfuryl Alcohols and 2,5-Diaryl Furans



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