# Benzenesulfonyl Chlorides: Alternative Coupling Partners for Regiocontrolled Palladium-Catalyzed Direct Desulfitative 5-Arylation of Furans

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**Abstract:** The reactivity of furan derivatives in palladium-catalyzed desulfitative arylation was studied. Alkyl-substituted furan derivatives were successfully coupled with a variety of benzenesulfonyl chlorides using a phosphine-free catalyst; regioselective arylation at C5 of the furan was observed in all cases. This reaction tolerates a wide variety of substituents on the benzenesulfonyl derivative. It should be noted that even bromo- and iodobenzenesulfonyl chlorides were successfully coupled with furan derivatives without cleavage of the C–Br or C–I bonds, thus allowing further transformations. The use of these reactants demonstrates the potential of benzenesulfonyl chlorides as coupling partners to access to functionalized 5-arylfurans.

**Key words:** palladium, C–H bond activation, furans, benzenesulfonyl chlorides, arylation

The synthesis of arylated furans is an important field of research in organic chemistry due to the biological properties of these derivatives. For example, dantrolene is a muscle relaxant and lapatinib is used in the treatment of breast cancer (Figure 1).

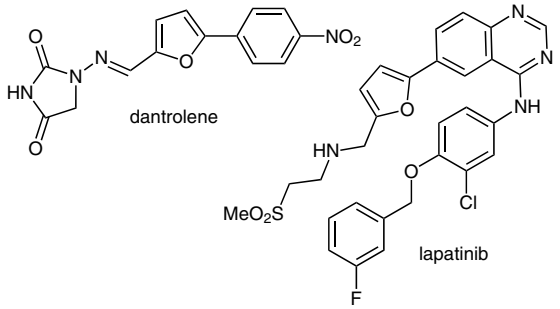
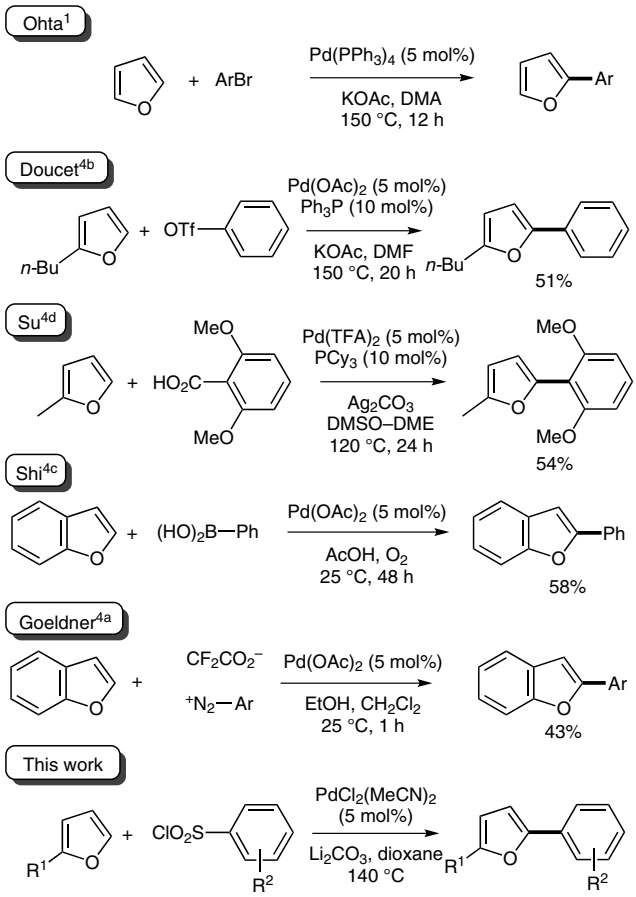



**Figure 1** Examples of bioactive arylfurans

In 1990, Ohta and co-workers reported the 2- or 5-arylation of several heteroaromatics with aryl halides as coupling partners via a C–H bond activation using $Pd(PPh_3)_4$ as the catalyst.[1] Since these exciting results, the palladium-catalyzed so-called direct arylation of heteroaryl derivatives has proved to be a very powerful method for the synthesis of a wide variety of arylated heterocycles.[2] The first example of palladium-catalyzed direct arylation of a furan was reported by Ohta who obtained a low yield of 23% for its coupling with bromobenzene (Scheme 1).[1] Several groups have since developed more effective conditions allowing the formation of arylfurans in high yields.[3] On the other hand, relatively little effort has been expended toward developing alternative coupling partners to aryl halides for the direct arylation of furans.[4] Using arenediazonium salts[4a] or aryl triflates[4b] in the presence of




**Scheme 1** Reported coupling partners for the palladium-catalyzed direct arylation of (benzo)furans

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5 mol% of a palladium catalyst gives the aryl-substituted (benzo)furans in moderate yields (Scheme 1).

Recently, benzoic acids[4d] or arylboronic acids,[4c] using (benzo)furans as the coupling partner and 5 mol% palladium catalyst under oxidative conditions also afforded aryl-substituted (benzo)furans (Scheme 1). It should be noted that two of these procedures were not extended to benzofuran derivatives. The synthesis of 5-arylfurans under metal-catalyzed oxidative coupling conditions[5] has also been reported.

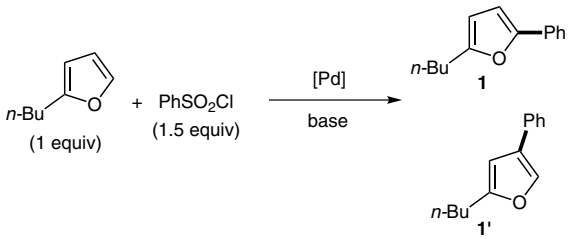
Aryl halides and benzoic acids are generally attractive couplings partners in terms of cost and availability; the use of aryl triflates, arylboronic acids or diazonium salts is less attractive. Therefore, the discovery of new easily available coupling partners for the regioselective intermolecular direct arylation of furan derivatives especially using a simple catalyst, base, and substrate would be a considerable advantage.

Dong and co-workers recently reported the palladium-catalyzed coupling of 2-phenylpyridine with benzenesulfonyl chlorides for the preparation of sulfones.[6] In this study, in one case they also observed a desulfitative direct arylation of a quinoline derivative. In 2011, Cheng et al. extended the use of benzenesulfonyl chlorides[7–10] as the reaction partners for the desulfitative palladium-catalyzed direct 2-arylation of benzoxazoles derivatives.[11a] We have also recently reported the first palladium-catalyzed desulfitative β-arylation of thiophenes and α-arylation of benzofurans.[12] It should be noted that Deng, Luo, and co-workers recently reported that benzenesulfinic acid sodium salts can also be employed for palladium-catalyzed direct arylation of azoles and indoles under oxidative conditions.[11b,c] On the other hand, to our knowledge, the desulfitative direct arylation of furans with benzenesulfonyl chlorides has not yet been described.[11] As the use of benzenesulfonyl chlorides as coupling partners instead of aryl halides drastically modifies the regioselectivity of the palladium-catalyzed direct arylations,[12a] their behavior in the presence of furans needed to be investigated.

Herein, we describe regioselective access to C5-arylated furans using desulfitative palladium-catalyzed C–H bond functionalization of furans with benzenesulfonyl chlorides as the coupling partners (Table 1). The influence of both the benzenesulfonyl chloride and furan substituents are reported.

We first examined the influence of several reaction conditions on the product formation based on our previous results on palladium-catalyzed desulfitative coupling with thiophene derivatives[12a] (Table 1). The reaction of 2-butylfuran (1 equiv) and benzenesulfonyl chloride (1.5 equiv) in the presence of 5 mol% $PdCl_2(MeCN)_2$ catalyst with lithium carbonate as the base at 140 °C for 20 hours gave regioselectively the C5 arylation product **1** in 40% yield (entry 1). A partial conversion of 2-butylfuran was observed under these conditions. It should be noted that the formation of C3- or C4-arylation products or diaryla-

**Table 1** Influence of the Reaction Conditions on the Palladium-Catalyzed Direct Arylation of 2-Butylfuran with Benzenesulfonyl Chloride[a]




| Entry | Catalyst (mol%) | Solvent | Base | Time (h) | Conv. (%) | Yield (%) of **1** |
|---|---|---|---|---|---|---|
| 1 | $PdCl_2(MeCN)_2$ (5) | dioxane | $Li_2CO_3$ | 20 | 45 | 40 |
| 2 | $Pd(OAc)_2$ (5) | dioxane | $Li_2CO_3$ | 45 | 38 | 25 |
| 3 | $PdCl_2$ (5) | dioxane | $Li_2CO_3$ | 20 | 21 | 17 |
| 4 | $PdCl_2(MeCN)_2$ (5) | dioxane | $Li_2CO_3$ | 20 | 41 | 36[b] |
| 5 | $PdCl_2(MeCN)_2$ (5) | dioxane | $Li_2CO_3$ | 72 | 44 | 41 |
| 6 | $PdCl_2(MeCN)_2$ (5) | dioxane | $Na_2CO_3$ | 45 | 16 | 13 |
| 7 | $PdCl_2(MeCN)_2$ (5) | dioxane | $K_2CO_3$ | 45 | 10 | 9 |
| 8 | $PdCl_2(MeCN)_2$ (5) | dioxane | KOAc | 45 | 19 | 17 |
| 9 | $PdCl_2(MeCN)_2$ (5) | dioxane | $K_3PO_4$ | 45 | 17 | 13 |
| 10 | $PdCl_2(MeCN)_2$ (5) | ethylbenzene | $Li_2CO_3$ | 20 | 8 | 6 |

[a] Conditions: 2-butylfuran (1 equiv), benzenesulfonyl chloride (1.5 equiv), base (3 equiv), 140 °C, conversion of 2-butylfuran.
[b] Benzenesulfonyl chloride (2 equiv).

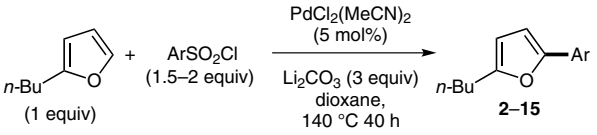
 

tion products was not detected by GC/MS and $^1$H NMR of the crude mixture. Then, we examined the influence of the palladium catalyst. The use of 5 mol% palladium(II) acetate or chloride as the catalyst afforded a lower yield of **1** (entries 2 and 3). A larger excess of benzenesulfonyl chloride or a longer reaction time did not improve the yield of **1** (entries 4 and 5). The influence of the nature of the base was also examined. The use of sodium carbonate, potassium carbonate, potassium acetate, or tripotassium phosphate led to lower conversions of 2-butylfuran and to lower yields of **1** than with lithium carbonate (entries 6–9). The influence of an alternative solvent was then examined. Ethylbenzene afforded **1** in 6% yield due to a very low conversion of 2-butylfuran (entry 10).

Next, the influence of the substituents on benzenesulfonyl chloride in the coupling with 2-butylfuran was examined using 5 mol% $PdCl_2(MeCN)_2$ as the catalyst, lithium carbonate as the base in dioxane at 140 °C (Table 2). We first employed several 4-substituted benzenesulfonyl chloride derivatives. In the presence of 4-nitro, 4-cyano, and 4-(trifluoromethyl)-substituted benzenesulfonyl chlorides the C5-arylated furans **2**–**4** were obtained regioselectively in 79–89% yields (entries 1–3); using 4-chlorobenzenesulfonyl chloride gave **5** in a lower yield of 50% (entry 4). Then, we examined the reactivity of 4-iodobenzenesulfonyl chloride as the C–I bond on the benzene ring is known to be very reactive in the presence of palladium catalysts. The reaction proceeds nicely without cleavage of the C–I bond to afford **6** in 70% yield, allowing further transformations (entry 5). From slightly electron-deficient 4-fluorobenzenesulfonyl chloride, a poor 32% yield of **7** was obtained due to a low conversion of 2-butylfuran (entry 6), and in the presence of the electron-rich 4-methoxybenzenesulfonyl chloride the formation of **8** was not observed by GC/MS analysis of the crude mixture and 2-butylfuran was recovered (entry 8). We also examined the reactivity of some *meta*-substituted benzenesulfonyl derivatives for this coupling. *meta*-Substituents have a small influence on the reactivity of the benzenesulfonyl chlorides. 3-(Trifluoromethyl)benzenesulfonyl chloride and 3-chlorobenzenesulfonyl chloride afforded **9** and **10** in 62% and 73% yields, respectively (entries 9 and 10). A moderate yield of **11** was obtained from a di-*meta*-substituted benzenesulfonyl chloride (entry 11). From the *ortho*-substituted 2-cyanobenzenesulfonyl chloride and 2-fluorobenzenesulfonyl chloride **12** and **13** were also obtained in good yields of 83% and 89% (entries 12 and 13); whereas the use of naphthalene-1-sulfonyl chloride afforded **14** in only 44% yield (entry 14). The detrimental effect of an *ortho*-methyl substituent on benzenesulfonyl chloride was observed as only a trace amount the desired product **15** was detected by GC/MS analysis (entry 15).

To gain more insight into the electronic effect of the substituent on the benzenesulfonyl chloride, a competition reaction using an equimolar mixture of benzenesulfonyl chloride and 4-(trifluoromethyl)benzenesulfonyl chloride in the presence of 2-butylfuran was performed (Scheme 2). A mixture of products **1** and **4** was obtained in a 23:77 ratio, which confirms the higher reactivity of electron-deficient benzenesulfonyl chlorides for such couplings.

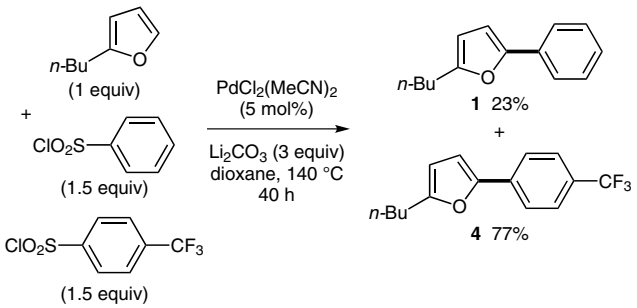
**Table 2** Influence of the Benzenesulfonyl Chloride Substituents on the Palladium-Catalyzed Direct C5-Arylation of 2-Butylfuran[a]




| Entry | Ar | Product | Yield (%) |
|---|---|---|---|
| 1 | 4-$O_2NC_6H_4$ | **2** | 88 |
| 2 | 4-$NCC_6H_4$ | **3** | 89 |
| 3 | 4-$F_3CC_6H_4$ | **4** | 79 |
| 4 | 4-$ClC_6H_4$ | **5** | 50 |
| 5 | 4-$IC_6H_4$ | **6** | 70 |
| 6 | 4-$FC_6H_4$ | **7** | 32 |
| 7 | | | 31[b] |
| 8 | 4-$MeOC_6H_4$ | **8** | <5 |
| 9 | 3-$F_3CC_6H_4$ | **9** | 62 |
| 10 | 3-$ClC_6H_4$ | **10** | 73 |
| 11 | 3,5-$(F_3C)_2C_6H_3$ | **11** | 75 |
| 12 | 2-$NCC_6H_4$ | **12** | 83 |
| 13 | 2-$FC_6H_4$ | **13** | 89 |
| 14 | 1-naphthyl | **14** | 44 |
| 15 | 2-$MeC_6H_4$ | **15** | <5 |

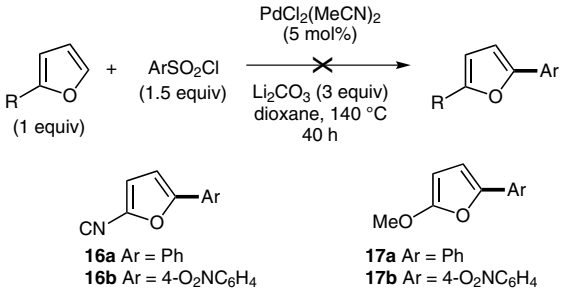
[a] Conditions: $PdCl_2(MeCN)_2$ (0.05 equiv), 2-butylfuran (1 equiv), benzenesulfonyl chloride derivative (1.5 equiv), $Li_2CO_3$ (3 equiv), dioxane, 140 °C, 40 h, isolated yields.
[b] Benzenesulfonyl chloride derivative (2 equiv).

The influence of electron-withdrawing and electron-donating substituents on the furan derivative was also investigated (Scheme 3). In the presence of furan-2-carbonitrile and benzenesulfonyl chloride or 4-nitrobenzenesulfonyl chloride as the coupling partners the formation of **16a** or **16b** was not observed and the furan derivative was recovered unreacted. The presence of an electron-donating sub-




**Scheme 2** Competitive palladium-catalyzed direct arylations using an equimolar mixture of benzenesulfonyl chloride derivatives

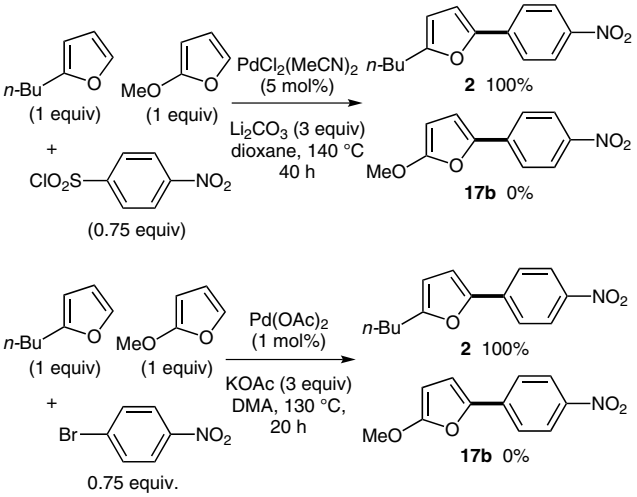
stituent was also not tolerated, as no trace of coupling products **17a** or **17b** was detected in the presence of 2-methoxyfuran.




**Scheme 3** Influence of the furan C2-substituent on palladium-catalyzed direct arylation with benzenesulfonyl chloride derivatives

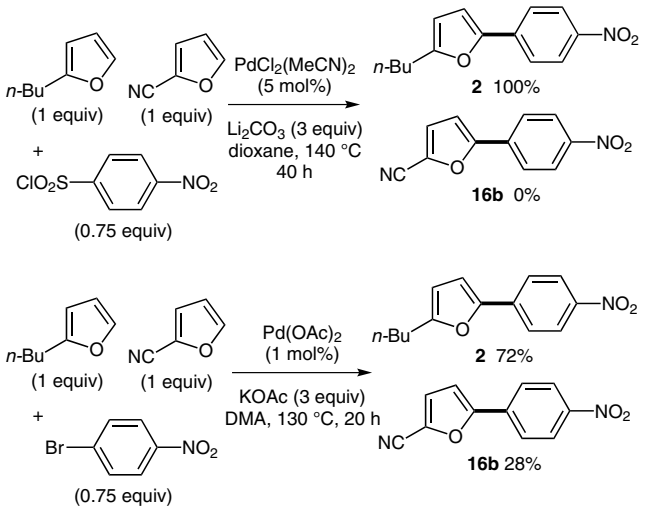
In order to gain more insight into the influence of furan substituents, we also performed competition reactions to probe the substituent preference of this catalyst system for such couplings (Schemes 4 and 5). From an equimolar mixture of 2-butylfuran and furan-2-carbonitrile using 4-nitrobenzenesulfonyl chloride as the coupling partner, in the presence of 5 mol% $PdCl_2(MeCN)_2$ catalyst, the exclusive formation of **2** from coupling with 2-butylfuran was observed (Scheme 4). This result indicates that an electron-withdrawing substituent at the C2-position of furan is strongly deactivating, but has no poisoning effect on the palladium catalyst. In order to compare the selectivity of this arylation procedure with direct arylation using aryl halides, a competition experiment using again an equimolar mixture of 2-butylfuran and furan-2-carbonitrile, but with 1-bromo-4-nitrobenzene as the coupling partner was performed (Schemes 4). A mixture of C5-arylated furans **2** and **16b** was obtained in a 72:28 ratio; revealing that the direct arylations with aryl bromides are less sensitive to electron-withdrawing substituents on the furan than reactions employing benzenesulfonyl chlorides. The different behavior of these two catalytic systems might allow a simpler control of the regioselectivity for direct arylations of polyheteroaromatic substrates.

A similar competition reaction was performed using an equimolar mixture of 2-butylfuran and 2-methoxyfuran in the presence of 4-nitrobenzenesulfonyl chloride or 1-bromo-4-nitrobenzene (Scheme 5). In both cases, only the formation of **2** was observed by GC/MS and $^1$H NMR analysis of the crude mixture.

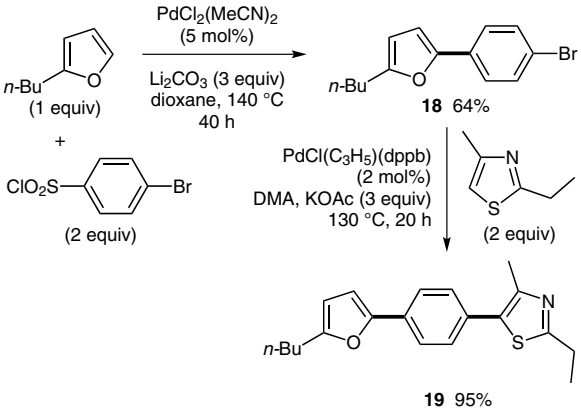



**Scheme 5** Competitive palladium-catalyzed direct arylations using an equimolar mixture of furans

We also studied consecutive palladium-catalyzed direct arylations employing 4-bromobenzenesulfonyl chloride as the central unit (Scheme 6). Using $PdCl_2(MeCN)_2$ catalyst in the presence of lithium carbonate in dioxane, this reactant was coupled at C5 of 2-butylfuran without cleavage of the C–Br bond to afford **18** in 64% yield. Then, from **18** and 2-ethyl-4-methylthiazole as the coupling partner, using $PdCl(C_3H_5)(dppb)$ catalyst[13] with potassium acetate as the base in *N*,*N*-dimethylacetamide (DMA), the desired product **19** was obtained in 95% yield.




**Scheme 4** Competitive palladium-catalyzed direct arylations using an equimolar mixture of furans



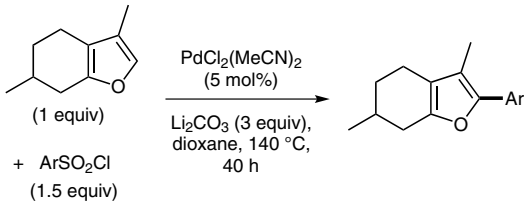

**Scheme 6** Consecutive palladium-catalyzed direct arylations using 4-bromobenzenesulfonyl chloride



Finally, we examined the reactivity of menthofuran, which is naturally present in mint oil, for direct arylation using a set of benzenesulfonyl chlorides as coupling partners (Table 3). This 2,3,4-trisubstituted furan was also found to be very reactive in the direct arylation using electron-deficient benzenesulfonyl chlorides. From 1.5 equivalents of benzenesulfonyl chlorides and 5 mol% $PdCl_2(MeCN)_2$ catalyst in the presence of lithium carbonate in dioxane, the desired coupling products **21**–**31** were obtained in 63–88% yields. Again, using both 4-bromobenzenesulfonyl chloride and 4-iodobenzenesulfonyl chloride cleavage of the C–Br and C–I bonds was not observed to afford **25** and **26** in 76% and 65% yields, respectively, allowing further transformations. A slightly lower yield of 61% for **20** was obtained in the presence of benzenesulfonyl chloride due to a partial conversion of menthofuran.

**Table 3** Palladium-Catalyzed Direct Arylations of Menthofuran with Benzenesulfonyl Chloride Derivatives[a]




| Entry | Ar | Product | Yield (%) |
|---|---|---|---|
| 1 | Ph | **20** | 61 |
| 2 | 4-$O_2NC_6H_4$ | **21** | 80 |
| 3 | 4-$NCC_6H_4$ | **22** | 82 |
| 4 | 4-$F_3CC_6H_4$ | **23** | 78 |
| 5 | 4-$ClC_6H_4$ | **24** | 63 |
| 6 | 4-$BrC_6H_4$ | **25** | 76 |
| 7 | 4-$IC_6H_4$ | **26** | 65 |
| 8 | 4-$FC_6H_4$ | **27** | 70 |
| 9 | 3-$ClC_6H_4$ | **28** | 68 |
| 10 | 3,5-$(F_3C)_2C_6H_3$ | **29** | 79 |
| 11 | 2-$NCC_6H_4$ | **30** | 83 |
| 12 | 2-$FC_6H_4$ | **31** | 88 |

[a] Conditions: $PdCl_2(MeCN)_2$ (0.05 equiv), menthofuran (1 equiv), benzenesulfonyl chloride derivative (1.5 equiv), $Li_2CO_3$ (3 equiv), dioxane, 140 °C, 40 h, isolated yields.

Although the mechanism has not yet been elucidated, the reactions with 4-bromo- or 4-iodobenzenesulfonyl chlorides, which afford the coupling products without cleavage of the C–Br or C–I bonds, seem to reveal that the first step of the catalytic cycle is the oxidative addition of the benzenesulfonyl chloride to Pd(II) to afford an $ArSO_2$–Pd(IV)Cl intermediate. The oxidative addition of benzenesulfonyl chloride to Pd(II) has been reported to proceed even at room temperature.[6b] Then, after elimination of $SO_2$ and coordination of furan to palladium, a migration of the aryl group to C5 of furan followed by proton abstraction assisted by the base gives the 5-arylfurans and regenerates the Pd(II) species.

In summary, we report here the first palladium-catalyzed desulfitative arylations of furan derivatives. The reaction proceeds with easily accessible ligand-free $PdCl_2(MeCN)_2$ catalyst and lithium carbonate as base, and affords very selectively the C5-arylated furans. Moreover, this procedure tolerates a wide variety of substituents on the benzenesulfonyl chloride such as nitro, cyano, trifluoromethyl, fluoro, chloro, bromo, or even iodo. As several benzenesulfonyl chlorides with diverse functionalities are available at an affordable cost, such simple reaction conditions (no expensive base and ligand) should be very attractive to synthetic chemists to access to 5-arylfurans. Moreover, from 4-bromobenzenesulfonyl chloride, the 5-arylfuran was obtained without cleavage of the C–Br bond allowing a second palladium-catalyzed C–H bond functionalization with another heteroarene to afford the 1,4-di(heteroaryl)benzene with two different heteroaryl groups.

All reactions were carried out under argon atmosphere with standard Schlenk techniques. HPLC grade 1,4-dioxane was used and stored under argon without further purification. $^1H$ NMR spectra were recorded on a Bruker GPX (400 MHz) spectrometer relative to residual $CHCl_3$ ($\delta = 7.26$ for $^1H$; 77.0 for $^{13}C$). $^{13}C$ NMR spectra were recorded at 100 MHz on the same spectrometer. All reagents were weighed and handled in air.

**Preparation of $PdCl(C_3H_5)(dppb)$**[13]

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar under argon, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). Anhyd $CH_2Cl_2$ (10 mL) was added, and the solution was stirred at r.t. for 20 min. The solvent was removed under vacuum. The yellow powder was used without purification.

$^{31}P$ NMR (81 MHz, $CDCl_3$): $\delta = 19.3$ (s).

**C5-Arylated Furans; General Procedure**

To a 25-mL oven-dried Schlenk tube, arenesulfonyl chloride (1.5–2 mmol), furan derivative (1 mmol), $Li_2CO_3$ (0.222 g, 3 mmol), 1,4-dioxane (2 mL) and $PdCl_2(MeCN)_2$ (12.9 mg, 0.05 mmol) were added successively. The mixture was evacuated by vacuum-argon cycles (5 ×) and stirred at 140 °C (oil bath temperature) for 20–72 h (see tables and schemes). After cooling the reaction at r.t. and concentration, the crude mixture was purified by column chromatography (silica gel) to afford the C5-arylated furans.

**2-Butyl-5-phenylfuran (1)**[14]

2-Butylfuran (0.124 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol) afforded **1** (0.082 g, 41%) as a colorless oil.

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (d, $J = 8.0$ Hz, 2 H), 7.27 (t, $J = 8.0$ Hz, 2 H), 7.13 (t, $J = 8.0$ Hz, 1 H), 6.46 (d, $J = 3.2$ Hz, 1 H), 5.98 (d, $J = 3.2$ Hz, 1 H), 2.61 (t, $J = 7.3$ Hz, 2 H), 1.59 (quint, $J = 7.3$ Hz, 2 H), 1.33 (sext, $J = 7.3$ Hz, 2 H), 0.87 (t, $J = 7.3$ Hz, 3 H).

**2-Butyl-5-(4-nitrophenyl)furan (2)**[14]

2-Butylfuran (0.124 g, 1 mmol) and 4-nitrobenzenesulfonyl chloride (0.332 g, 1.5 mmol) afforded **2** (0.216 g, 88%) as a yellow solid; mp 65–68 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.6 Hz, 2 H), 7.61 (d, *J* = 8.6 Hz, 2 H), 6.68 (d, *J* = 3.2 Hz, 1 H), 6.05 (d, *J* = 3.2 Hz, 1 H), 2.61 (t, *J* = 7.4 Hz, 2 H), 1.58 (quint, *J* = 7.4 Hz, 2 H), 1.34 (sext, *J* = 7.4 Hz, 2 H), 0.87 (t, *J* = 7.4 Hz, 3 H).

**2-Butyl-5-(4-cyanophenyl)furan (3)**[14]
2-Butylfuran (0.124 g, 1 mmol) and 4-cyanobenzenesulfonyl chloride (0.303 g, 1.5 mmol) afforded **3** (0.200 g, 89%) as a yellow solid; mp 80–84 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.6 Hz, 2 H), 7.51 (d, *J* = 8.6 Hz, 2 H), 6.61 (d, *J* = 3.2 Hz, 1 H), 6.02 (d, *J* = 3.2 Hz, 1 H), 2.60 (t, *J* = 7.4 Hz, 2 H), 1.59 (quint, *J* = 7.4 Hz, 2 H), 1.33 (sext, *J* = 7.4 Hz, 2 H), 0.87 (t, *J* = 7.4 Hz, 3 H).

**2-Butyl-5-[4-(trifluoromethyl)phenyl]furan (4)**[14]
2-Butylfuran (0.124 g, 1 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (0.367 g, 1.5 mmol) afforded **4** (0.212 g, 79%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.6 Hz, 2 H), 7.59 (d, *J* = 8.6 Hz, 2 H), 6.67 (d, *J* = 3.2 Hz, 1 H), 6.10 (d, *J* = 3.2 Hz, 1 H), 2.70 (t, *J* = 7.4 Hz, 2 H), 1.69 (quint, *J* = 7.4 Hz, 2 H), 1.45 (sext, *J* = 7.4 Hz, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H).

**2-Butyl-5-(4-chlorophenyl)furan (5)**
2-Butylfuran (0.124 g, 1 mmol) and 4-chlorobenzenesulfonyl chloride (0.317 g, 1.5 mmol) afforded **5** (0.117 g, 50%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.6 Hz, 2 H), 7.20 (d, *J* = 8.6 Hz, 2 H), 6.42 (d, *J* = 3.2 Hz, 1 H), 5.95 (d, *J* = 3.2 Hz, 1 H), 2.58 (t, *J* = 7.4 Hz, 2 H), 1.56 (quint, *J* = 7.4 Hz, 2 H), 1.33 (sext, *J* = 7.4 Hz, 2 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.1, 151.3, 132.5, 130.0, 129.0, 124.8, 107.2, 106.4, 30.4, 28.1, 22.5, 14.1.

MS: *m*/*z* = 234 ($M^+$).

Anal. Calcd for $C_{14}H_{15}ClO$ (234.72): C, 71.64; H, 6.44; found: C, 71.55; H, 6.51.

**2-Butyl-5-(4-iodophenyl)furan (6)**
2-Butylfuran (0.124 g, 1 mmol) and 4-iodobenzenesulfonyl chloride (0.453 g, 1.5 mmol) afforded **6** (0.228 g, 70%) as a yellow solid; mp 45–48 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.6 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 2 H), 6.46 (d, *J* = 3.2 Hz, 1 H), 5.97 (d, *J* = 3.2 Hz, 1 H), 2.58 (t, *J* = 7.4 Hz, 2 H), 1.56 (quint, *J* = 7.4 Hz, 2 H), 1.32 (sext, *J* = 7.4 Hz, 2 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.2, 151.3, 137.8, 130.9, 125.2, 107.3, 106.7, 91.7, 30.4, 28.1, 22.5, 14.1.

MS: *m*/*z* = 326 ($M^+$).

Anal. Calcd for $C_{14}H_{15}IO$ (326.17): C, 51.55; H, 4.64; found: C, 51.47; H, 4.73.

**2-Butyl-5-(4-fluorophenyl)furan (7)**[14]
2-Butylfuran (0.124 g, 1 mmol) and 4-fluorobenzenesulfonyl chloride (0.343 g, 1.5 mmol) afforded **7** (0.070 g, 32%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 8.6, 5.5 Hz, 2 H), 7.06 (t, *J* = 8.6 Hz, 2 H), 6.48 (d, *J* = 3.2 Hz, 1 H), 6.05 (d, *J* = 3.2 Hz, 1 H), 2.68 (t, *J* = 7.4 Hz, 2 H), 1.70 (quint, *J* = 7.4 Hz, 2 H), 1.42 (sext, *J* = 7.4 Hz, 2 H), 0.95 (t, *J* = 7.4 Hz, 3 H).

**2-Butyl-5-[3-(trifluoromethyl)phenyl]furan (9)**
2-Butylfuran (0.124 g, 1 mmol) and 3-(trifluoromethyl)benzenesulfonyl chloride (0.367 g, 1.5 mmol) afforded **9** (0.166 g, 62%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.77 (s, 1 H), 7.69 (m, 1 H), 7.40–7.33 (m, 2 H), 6.54 (d, *J* = 3.2 Hz, 1 H), 6.00 (d, *J* = 3.2 Hz, 1 H), 2.61 (t, *J* = 7.4 Hz, 2 H), 1.60 (quint, *J* = 7.4 Hz, 2 H), 1.35 (sext, *J* = 7.4 Hz, 2 H), 0.88 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.4, 150.6, 131.9, 131.0 (q, *J* = 31.8 Hz), 129.0, 126.2, 124.1 (q, *J* = 272.6 Hz), 123.2 (q, *J* = 4.0 Hz), 119.9 (q, *J* = 4.0 Hz), 107.1, 107.0, 30.2, 27.9, 22.3, 13.8.

MS: *m*/*z* = 268 ($M^+$).

Anal. Calcd for $C_{15}H_{15}F_3O$ (268.27): C, 67.16; H, 5.64; found: C, 67.01; H, 5.79.

**2-Butyl-5-(3-chlorophenyl)furan (10)**
2-Butylfuran (0.124 g, 1 mmol) and 3-chlorobenzenesulfonyl chloride (0.317 g, 1.5 mmol) afforded **10** (0.171 g, 73%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 1 H), 7.36 (d, *J* = 8.6 Hz, 1 H), 7.13 (t, *J* = 8.6 Hz, 1 H), 7.03 (d, *J* = 8.6 Hz, 1 H), 6.44 (d, *J* = 3.2 Hz, 1 H), 5.93 (d, *J* = 3.2 Hz, 1 H), 2.55 (t, *J* = 7.4 Hz, 2 H), 1.54 (quint, *J* = 7.4 Hz, 2 H), 1.29 (sext, *J* = 7.4 Hz, 2 H), 0.82 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.4, 150.9, 134.9, 133.1, 130.1, 126.8, 123.5, 121.6, 107.3, 107.1, 30.4, 28.1, 22.5, 14.1.

MS: *m*/*z* = 234 ($M^+$).

Anal. Calcd for $C_{14}H_{15}ClO$ (234.72): C, 71.64; H, 6.44; found: C, 71.79; H, 6.30.

**2-[3,5-Bis(trifluoromethyl)phenyl]-5-butylfuran (11)**
2-Butylfuran (0.124 g, 1 mmol) and 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (0.469 g, 1.5 mmol) afforded **11** (0.252 g, 75%) as a yellow solid; mp 38–40 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 2 H), 7.68 (s, 1 H), 6.74 (d, *J* = 3.3 Hz, 1 H), 6.14 (d, *J* = 3.3 Hz, 1 H), 2.72 (t, *J* = 7.4 Hz, 2 H), 1.71 (quint, *J* = 7.4 Hz, 2 H), 1.43 (sext, *J* = 7.4 Hz, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.2, 148.8, 132.6, 131.7 (q, *J* = 33.3 Hz), 123.0 (q, *J* = 272.7 Hz), 122.5 (m), 119.3 (quint, *J* = 3.8 Hz), 108.4, 107.2, 29.8, 27.5, 22.0, 13.4.

MS: *m*/*z* = 326 ($M^+$).

Anal. Calcd for $C_{16}H_{14}F_6O$ (336.27): C, 57.15; H, 4.20; found: C, 57.31; H, 4.14.

**2-Butyl-5-(2-cyanophenyl)furan (12)**[14]
2-Butylfuran (0.124 g, 1 mmol) and 2-cyanobenzenesulfonyl chloride (0.303 g, 1.5 mmol) afforded **12** (0.187 g, 83%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.59 (t, *J* = 7.8 Hz, 1 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 7.23 (d, *J* = 3.3 Hz, 1 H), 6.18 (d, *J* = 3.3 Hz, 1 H), 2.74 (t, *J* = 7.4 Hz, 2 H), 1.73 (quint, *J* = 7.4 Hz, 2 H), 1.42 (sext, *J* = 7.4 Hz, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H).

**2-Butyl-5-(2-fluorophenyl)furan (13)**
2-Butylfuran (0.124 g, 1 mmol) and 2-fluorobenzenesulfonyl chloride (0.343 g, 1.5 mmol) afforded **13** (0.194 g, 89%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.70 (m, 1 H), 7.10–6.95 (m, 3 H), 6.66 (d, *J* = 3.3 Hz, 1 H), 6.02 (d, *J* = 3.3 Hz, 1 H), 2.60 (t, *J* = 7.4 Hz, 2 H), 1.58 (quint, *J* = 7.4 Hz, 2 H), 1.34 (sext, *J* = 7.4 Hz, 2 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.4 (d, *J* = 248.7 Hz), 156.4, 146.1 (d, *J* = 3.0 Hz), 127.5 (d, *J* = 8.1 Hz), 125.6 (d, *J* = 3.3 Hz), 124.1 (d, *J* = 3.3 Hz), 119.5 (d, *J* = 12.1 Hz), 115.8 (d, *J* = 21.5 Hz), 111.0 (d, *J* = 11.8 Hz), 107.2, 30.2, 27.8, 22.3, 13.8.

MS: *m*/*z* = 218 ($M^+$).

Anal. Calcd for $C_{14}H_{15}FO$ (218.27): C, 77.04; H, 6.93; found: C, 77.10; H, 7.07.

**2-Butyl-5-naphthalen-1-ylfuran (14)**[15]
2-Butylfuran (0.124 g, 1 mmol) and 1-naphthalenesulfonyl chloride (0.340 g, 1.5 mmol) afforded **14** (0.110 g, 44%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.2 Hz, 1 H), 7.88 (d, *J* = 8.1 Hz, 1 H), 7.80 (d, *J* = 8.2 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.55–7.45 (m, 3 H), 6.63 (d, *J* = 3.2 Hz, 1 H), 6.18 (d, *J* = 3.2 Hz, 1 H), 2.77 (t, *J* = 7.4 Hz, 2 H), 1.76 (quint, *J* = 7.4 Hz, 2 H), 1.48 (sext, *J* = 7.4 Hz, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

**2-Butyl-5-(4-bromophenyl)furan (18)**[16]
2-Butylfuran (0.124 g, 1 mmol) and 4-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol) afforded **18** (0.179 g, 64%) as a yellow solid; mp 50–54 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 6.44 (d, *J* = 3.2 Hz, 1 H), 5.95 (d, *J* = 3.2 Hz, 1 H), 2.57 (t, *J* = 7.4 Hz, 2 H), 1.56 (quint, *J* = 7.4 Hz, 2 H), 1.32 (sext, *J* = 7.4 Hz, 2 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.2, 151.3, 131.9, 130.4, 125.0, 120.5, 107.3, 106.5, 30.4, 28.1, 22.5, 14.1.

**5-[4-(5-Butylfuran-2-yl)phenyl]-2-ethyl-4-methylthiazole (19)**
Compound **18** (0.140 g, 0.5 mmol), 2-ethyl-4-methylthiazole (0.127 g, 1 mmol), and AcOK (0.147 g, 1.5 mmol) was reacted at 130 °C during 20 h in DMA (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) complex (6.1 mg, 0.01 mmol) under argon; evaporation of the solvent and filtration (silica gel, pentane–$Et_2O$) (0.154 g, 95%) afforded **19** as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.6 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 6.47 (d, *J* = 3.2 Hz, 1 H), 5.97 (d, *J* = 3.2 Hz, 1 H), 2.90 (q, *J* = 7.4 Hz, 2 H), 2.59 (t, *J* = 7.4 Hz, 2 H), 2.39 (s, 3 H), 1.59 (quint, *J* = 7.4 Hz, 2 H), 1.32 (sext, *J* = 7.4 Hz, 2 H), 1.29 (t, *J* = 7.4 Hz, 3 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 170.1, 156.9, 151.6, 147.0, 130.9, 130.7, 130.4, 129.3, 123.5, 107.1, 106.3, 30.3, 28.0, 27.0, 22.4, 16.3, 14.4, 13.9.

MS: *m*/*z* = 325 ($M^+$).

Anal. Calcd for $C_{20}H_{23}NOS$ (325.47): C, 73.81; H, 7.12; found: C, 73.99; H, 7.20.

**3,6-Dimethyl-2-phenyl-4,5,6,7-tetrahydrobenzofuran (20)**
Menthofuran (0.150 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol) afforded **20** (0.138 g, 61%) as a yellow solid; mp 85–88 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 2.70–2.60 (m, 1 H), 2.40–2.10 (m, 3 H), 2.08 (s, 3 H), 1.90–1.70 (m, 2 H), 1.40–1.20 (m, 1 H), 1.01 (d, *J* = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 149.7, 146.9, 132.7, 128.6, 126.2, 125.2, 120.0, 116.3, 31.6, 31.5, 29.9, 21.7, 20.3, 10.0.

MS: *m*/*z* = 226 ($M^+$).

Anal. Calcd for $C_{16}H_{18}O$ (226.31): C, 84.91; H, 8.02; found: C, 84.99; H, 7.89.

**2-(4-Nitrophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (21)**
Menthofuran (0.150 g, 1 mmol) and 4-nitrobenzenesulfonyl chloride (0.332 g, 1.5 mmol) afforded **21** (0.217 g, 80%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.6 Hz, 2 H), 7.71 (d, *J* = 8.6 Hz, 2 H), 2.80–2.60 (m, 1 H), 2.50–2.24 (m, 3 H), 2.23 (s, 3 H), 2.00–1.80 (m, 2 H), 1.50–1.30 (m, 1 H), 1.12 (d, *J* = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 152.4, 145.1, 145.0, 138.4, 124.3, 124.2, 121.2, 121.1, 31.6, 31.2, 29.2, 21.5, 120.0, 10.5.

MS: *m*/*z* = 271 ($M^+$).

Anal. Calcd for $C_{16}H_{17}NO_3$ (271.31): C, 70.83; H, 6.32; found: C, 70.99; H, 6.48.

**4-(3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)benzonitrile (22)**[14]
Menthofuran (0.150 g, 1 mmol) and 4-cyanobenzenesulfonyl chloride (0.303 g, 1.5 mmol) afforded **22** (0.206 g, 82%) as a yellow solid; mp 137–141 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.6 Hz, 2 H), 7.52 (d, *J* = 8.6 Hz, 2 H), 2.70–2.60 (m, 1 H), 2.40–2.10 (m, 3 H), 2.10 (s, 3 H), 1.90–1.70 (m, 2 H), 1.40–1.10 (m, 1 H), 1.02 (d, *J* = 7.5 Hz, 3 H).

**3,6-Dimethyl-2-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydrobenzofuran (23)**
Menthofuran (0.150 g, 1 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (0.367 g, 1.5 mmol) afforded **23** (0.229 g, 78%) as a yellow solid; mp 75–78 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.6 Hz, 2 H), 7.51 (d, *J* = 8.6 Hz, 2 H), 2.70–2.60 (m, 1 H), 2.40–2.10 (m, 3 H), 2.09 (s, 3 H), 1.90–1.70 (m, 2 H), 1.40–1.20 (m, 1 H), 1.02 (d, *J* = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 150.7, 145.4, 135.6, 127.3 (q, *J* = 32.5 Hz), 125.4 (q, *J* = 3.9 Hz), 124.4, 124.3 (q, *J* = 271.8 Hz), 120.3, 118.4, 31.4, 31.2, 29.6, 21.4, 19.9, 10.0.

MS: *m*/*z* = 294 ($M^+$).

Anal. Calcd for $C_{17}H_{17}F_3O$ (294.31): C, 69.38; H, 5.82; found: C, 69.37; H, 5.90.

**2-(4-Chlorophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (24)**
Menthofuran (0.150 g, 1 mmol) and 4-chlorobenzenesulfonyl chloride (0.317 g, 1.5 mmol) afforded **24** (0.164 g, 63%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.6 Hz, 2 H), 7.24 (d, *J* = 8.6 Hz, 2 H), 2.70–2.58 (m, 1 H), 2.40–2.10 (m, 3 H), 2.05 (s, 3 H), 1.90–1.70 (m, 2 H), 1.40–1.20 (m, 1 H), 1.01 (d, *J* = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 150.0, 145.9, 131.7, 131.1, 128.8, 126.2, 120.2, 116.8, 31.6, 31.5, 29.9, 21.7, 20.2, 10.1.

MS: *m*/*z* = 260 ($M^+$).

Anal. Calcd for $C_{16}H_{17}ClO$ (260.76): C, 73.70; H, 6.57; found: C, 73.61; H, 6.66.

**2-(4-Bromophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (25)**
Menthofuran (0.150 g, 1 mmol) and 4-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol) afforded **25** (0.232 g, 76%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 2.70–2.60 (m, 1 H), 2.40–2.10 (m, 3 H), 2.05 (s, 3 H), 2.00–1.75 (m, 2 H), 1.40–1.25 (m, 1 H), 1.02 (d, *J* = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 150.1, 145.9, 131.7, 131.5, 126.5, 120.2, 119.7, 117.0, 31.6, 31.4, 29.8, 21.7, 20.2, 10.1.

MS: *m*/*z* = 304 ($M^+$).

Anal. Calcd for $C_{16}H_{17}BrO$ (305.21): C, 62.96; H, 5.61; found: C, 63.07; H, 5.48.

**2-(4-Iodophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (26)**
Menthofuran (0.150 g, 1 mmol) and 4-iodobenzenesulfonyl chloride (0.453 g, 1.5 mmol) afforded **26** (0.229 g, 65%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.6 Hz, 2 H), 7.23 (d, *J* = 8.6 Hz, 2 H), 2.65–2.55 (m, 1 H), 2.35–2.05 (m, 3 H), 2.03 (s, 3 H), 1.90–1.70 (m, 2 H), 1.35–1.20 (m, 1 H), 1.00 (d, *J* = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 150.2, 145.9, 137.7, 132.1, 126.7, 120.3, 117.2, 91.0, 31.6, 31.4, 29.9, 21.7, 20.2, 10.1.

MS: $m/z$ = 352 ($M^+$).

Anal. Calcd for $C_{16}H_{17}IO$ (352.21): C, 54.56; H, 4.86; found: C, 54.60; H, 5.00.

**2-(4-Fluorophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (27)**[14]
Menthofuran (0.150 g, 1 mmol) and 4-fluorobenzenesulfonyl chloride (0.343 g, 1.5 mmol) afforded **27** (0.171 g, 70%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, $J$ = 8.6, 5.3 Hz, 2 H), 6.99 (t, $J$ = 8.6 Hz, 2 H), 2.70–2.60 (m, 1 H), 2.40–2.10 (m, 3 H), 2.05 (s, 3 H), 2.00–1.75 (m, 2 H), 1.40–1.25 (m, 1 H), 1.02 (d, $J$ = 7.5 Hz, 3 H).

**2-(3-Chlorophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (28)**
Menthofuran (0.150 g, 1 mmol) and 3-chlorobenzenesulfonyl chloride (0.317 g, 1.5 mmol) afforded **28** (0.177 g, 68%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 1 H), 7.37 (d, $J$ = 8.2 Hz, 1 H), 7.19 (t, $J$ = 8.2 Hz, 1 H), 7.06 (d, $J$ = 8.2 Hz, 1 H), 2.70–2.58 (m, 1 H), 2.40–2.10 (m, 3 H), 2.06 (s, 3 H), 1.90–1.70 (m, 2 H), 1.40–1.20 (m, 1 H), 1.01 (d, $J$ = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 150.4, 145.5, 134.7, 134.3, 129.9, 126.0, 124.9, 122.9, 120.3, 117.6, 31.6, 31.4, 29.9, 21.7, 20.2, 10.1.

MS: $m/z$ = 260 ($M^+$).

Anal. Calcd for $C_{16}H_{17}ClO$ (260.76): C, 73.70; H, 6.57; found: C, 73.64; H, 6.41.

**2-[3,5-Bis(trifluoromethyl)phenyl]-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (29)**
Menthofuran (0.150 g, 1 mmol) and 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (0.469 g, 1.5 mmol) afforded **29** (0.286 g, 79%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 2 H), 7.58 (s, 1 H), 2.75–2.65 (m, 1 H), 2.45–2.15 (m, 3 H), 2.13 (s, 3 H), 1.95–1.70 (m, 2 H), 1.40–1.12 (m, 1 H), 1.04 (d, $J$ = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 151.7, 144.2, 134.4, 131.9 (q, $J$ = 33.3 Hz), 124.2 (m), 123.9 (q, J = 272.7 Hz), 120.8, 119.6, 119.0 (quint, $J$ = 3.8 Hz), 31.6, 31.3, 29.8, 21.6, 20.1, 10.2.

MS: $m/z$ = 362 ($M^+$).

Anal. Calcd for $C_{18}H_{16}F_6O$ (362.31): C, 59.67; H, 4.45; found: C, 59.80; H, 4.28.

**2-(2-Cyanophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (30)**
Menthofuran (0.150 g, 1 mmol) and 2-cyanobenzenesulfonyl chloride (0.303 g, 1.5 mmol) afforded **30** (0.208 g, 83%) as a yellow solid; mp 137–140 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, $J$ = 8.0 Hz, 1 H), 7.45 (t, $J$ = 8.0 Hz, 1 H), 7.41 (d, $J$ = 8.0 Hz, 1 H), 7.19 (t, $J$ = 8.0 Hz, 1 H), 2.80–2.60 (m, 1 H), 2.40–2.00 (m, 3 H), 1.97 (s, 3 H), 1.80–1.70 (m, 2 H), 1.40–1.20 (m, 1 H), 0.97 (d, $J$ = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 151.6, 143.8, 135.1, 133.9, 132.3, 128.6, 126.8, 119.9, 119.8, 118.8, 109.9, 31.3, 31.1, 29.5, 21.4, 20.0, 10.1.

MS: $m/z$ = 251 ($M^+$).

Anal. Calcd for $C_{17}H_{17}NO$ (251.32): C, 81.24; H, 6.82; found: C, 81.44; H, 6.89.

**2-(2-Fluorophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (31)**
Menthofuran (0.150 g, 1 mmol) and 2-fluorobenzenesulfonyl chloride (0.343 g, 1.5 mmol) afforded **31** (0.215 g, 88%) as a yellow oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, $J$ = 7.8 Hz, 1 H), 7.15–7.07 (m, 1 H), 7.03 (t, $J$ = 7.8 Hz, 1 H), 6.98 (dd, $J$ = 8.0, 7.8 Hz, 1 H), 2.70–2.55 (m, 1 H), 2.40–2.20 (m, 3 H), 1.88 (s, 3 H), 1.85–1.70 (m, 2 H), 1.40–1.20 (m, 1 H), 0.97 (d, $J$ = 7.5 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.9 (d, $J$ = 248.8 Hz), 150.6, 141.9, 129.6 (d, $J$ = 3.2 Hz), 128.5 (d, $J$ = 7.9 Hz), 123.9 (d, $J$ = 4.0 Hz), 120.1 (d, $J$ = 14.3 Hz), 119.3, 118.5, 116.0 (d, $J$ = 22.2 Hz), 31.4, 31.2, 29.6, 21.5, 20.1, 9.1 (d, $J$ = 7.2 Hz).

MS: $m/z$ = 244 ($M^+$).

Anal. Calcd for $C_{16}H_{17}FO$ (244.30): C, 78.66; H, 7.01; found: C, 78.47; H, 7.11.

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