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Palladium-Catalyzed Direct C−H Arylation of 3-(Methylsulfinyl)thiophenes

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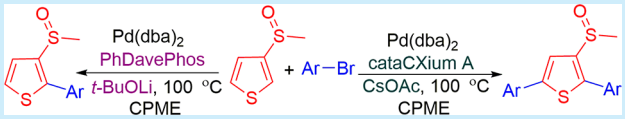
Supporting Information

ABSTRACT: A palladium-catalyzed direct arylation of (3-thiophene)S(O)Me derivatives has been developed. This protocol is effective for the selective synthesis of 2-arylated and 2,5-diarylated sulfinylthiophene derivatives with as low as 0.5 mol % catalyst loading. Various functional groups are well tolerated. A method to install two different aryl groups on 3-(methylsulfinyl)thiophenes is also introduced.



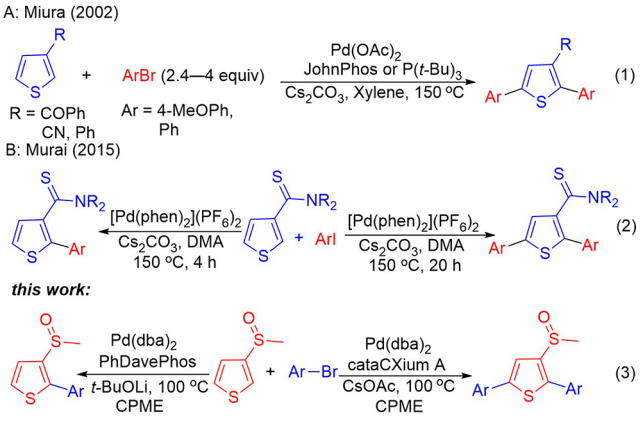
Thiophenes are prominent scaffolds in modern organic functional materials due to their unique optoelectronic[1] and biological properties.[2] Multisubstituted thiophenes containing sulfinyl groups are also important pharmacophores.[3] Thus, the development of effective methods for regioselective functionalization of thiophenes has received much attention.[4] In recent years, direct C−H arylation of thiophenes has emerged as a powerful approach to synthesize functionalized molecules, and directed transformations have been reported.[5] Since the pioneering work of Ohta,[6] a variety of functionalized thiophenes have been explored in palladium-catalyzed direct *mono*arylations, including alkyl,[7] halide,[8] carboxyl,[5a,9] and acetyl,[5a,9b,10] among others.[9−11]

Although direct functionalization of 3-substituted thiophenes to generate C2- or C5-arylated derivatives is known,[5a,8c,10,11h] only a few examples of the selective diarylation have been described. In 2002, Miura and co-workers reported a method for diarylation of thiophenes in the presence of $Pd(OAc)_2$ and either JohnPhos or $P(t\text{-}Bu)_3$ (Scheme 1, eq 1).[12] In 2015, Murai and Shibahara developed a direct C−H arylation method for thiophenes bearing thioamides with aryl iodides (Scheme 1, eq 2).[13] This reaction selectively afforded C2-monoarylated products, while 2,5-diarylated products were obtained by increasing the catalyst loading from 10 to 15 mol % and extending reaction times to 20 h (three examples). From a structural diversity viewpoint, thiophenes bearing two different (hetero)aryl groups are more attractive scaffolds in medicinal chemistry yet have rarely been prepared.[5d,11b,i]

Despite advances in palladium-catalyzed arylation of thiophenes, the direct selective sequential diarylation remains difficult. Herein, we report a palladium-catalyzed selective mono- and diarylation of 3-(methylsulfinyl)thiophene to afford either 2-arylated or 2,5-diarylated thiophenes.

As part of our interest in the α-arylation of methyl sulfoxides[14] and related reactions,[15] we found the arylation of 3-(methylsulfinyl)thiophene **1a** with bromobenzene **2a** catalyzed by $Pd(OAc)_2$/Kwong's indole ligand (**L1**, Figure 1) in the presence of *t*-BuOLi formed 2-arylated **3a** (20% yield) with no

Scheme 1. Selective Multiarylation of 3-Substituted Thiophenes



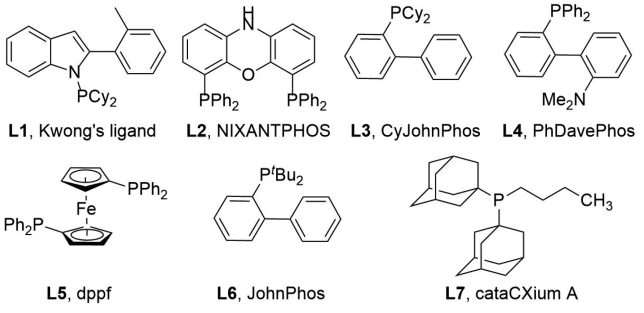


Figure 1. Ligand structures.

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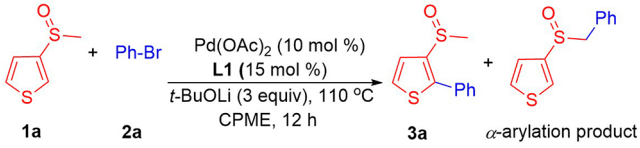
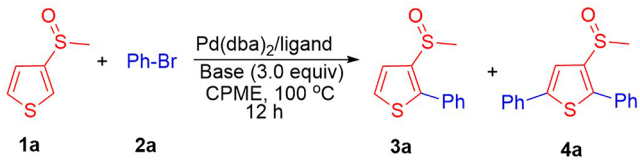
desired α-arylation product detected (Scheme 2). Considering the importance of sulfinylthiophenes in medicinal chemistry, we decided to optimize this reaction.

Scheme 2. Discovery of Direct Arylation of 3-(Methylsulfinyl)thiophene



We initiated optimization with a search for an efficient catalyst for this transformation. Two common palladium sources [$Pd(OAc)_2$, and $Pd(dba)_2$] and four ligands [NIXANTPHOS **L2**, CyJohnPhos **L3**, PhDavePhos **L4** and dppf **L5** see Figure 1 for ligand structures] were screened as well as six bases [*t*-BuOLi, *t*-BuONa, *t*-BuOK, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, and $KN(SiMe_3)_2$] in CPME (cyclopentyl methyl ether) at 100 °C (see Table S1 for details). The base *t*-BuOLi and $Pd(dba)_2$ were the best combination. We next examined 24 sterically and electronically diverse mono- and bidentate ligands using $Pd(dba)_2$ and *t*-BuOLi, in CPME at 100 °C on microscale (see Table S2 for details). The ligands PhDavePhos **L4** and JohnPhos **L6** were the best performing. With 10 mol % of $Pd(dba)_2$ and 20 mol % of ligand loading (**L4** and **L6**), the microscale reactions were translated to laboratory scale (0.1 mmol scale, Table 1, entries 1 and 2). The leading hit was obtained using $Pd(dba)_2$, PhDavePhos **L4**, and *t*-BuOLi, rendering **3a** in 93% assay yield (AY, determined by ^{1}H NMR) and with 90% isolated yield after purification. Attempts to decrease the temperature, catalyst loading, and equivalents of aryl bromide **2a** or *t*-BuOLi led to a diminished AY of **3a** (entry 1 vs 3−6).

Table 1. Optimization of the Reaction Conditions for the Arylation Reaction between 1a and 2a



entry	ligand	[Pd]/ligand (mol %)	base	**3a** (yield, %)[a]	**4a** (yield, %)[a]
1	**L4**	10:20	*t*-BuOLi	93 (90[b])	5
2	**L6**	10:20	*t*-BuOLi	88	8
3	**L4**	5:10	*t*-BuOLi	77	3
4[c]	**L4**	10:20	*t*-BuOLi	<5	0
5[d]	**L4**	10:20	*t*-BuOLi	75	0
6[e]	**L4**	10:20	*t*-BuOLi	69	0
7	**L4**	10:20	CsOAc	33	65
8	**L7**	10:20	CsOAc	0	99
9	**L7**	5:10	CsOAc	0	98
10	**L7**	0.5:1	CsOAc	0	98
11	**L7**	0.1:0.2	CsOAc	0	78
12[c]	**L7**	0.5:1	CsOAc	0	<5
13[f]	**L7**	0.5:1	CsOAc	0	58
14[g]	**L7**	0.5:1	CsOAc	0	98 (95[b])

[a]Assay yields determined by ^{1}H NMR using 0.1 mmol (7 μL) of CH_2Br_2 as internal standard; for product **3a**, 2 equiv **2a**; for product **4a**, 4 equiv **2a**. [b]Isolated yield. [c]50 °C. [d]1.5 equiv of **2a**. [e]2.0 equiv of *t*-BuOLi. [f]2.0 equiv of CsOAc. [g]3.0 equiv of **2a**.

In the optimization of reaction conditions for the C2-arylation of thiophene **1a**, we also noticed the generation of the 2,5-diarylated compound **4a**. To optimize formation of **4a**, we screened 12 bases (*t*-BuOLi, *t*-BuONa, *t*-BuOK, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, LiOAc, LiH, NaH, K_3PO_4, CsOAc, and Cs_2CO_3) and eight solvents [toluene, 2-Me-THF, DME (dimethoxyethane), DMF (dimethylformamide), CPME, 1,4-dioxane, DMAc (dimethylacetamide), and MeCN] using PhDavePhos **L4** and $Pd(dba)_2$ (see Table S3 for details). The base CsOAc and solvent CPME were the best, with 2,5-bisarylated product **4a** generated in 65% yield, and the C2-arylated **3a** afforded in 33% yield (entry 7).

Using CsOAc as base and CPME as solvent, we then examined 24 ligands with $Pd(dba)_2$ and found that cataCXiumA **L7** was the most promising hit (see Table S4 for details). With 10 mol % of $Pd(dba)_2$ and 20 mol % of **L7**, the product **4a** was generated in 99% AY (entry 8). The ligand cataCXium A **L7** was used for the duration of these studies. When the palladium loading was reduced from 10 mol % to 0.5 mol %, we obtained the diarylated product **4a** in nearly quantitative AY (entries 8−10). Attempts to decrease the catalyst loading to 0.1 mol %, lower the temperature, or reduce the equivalents of CsOAc led to a diminished AY of **4a** (entry 10 vs 11−13). Decreasing the dosage of the aryl bromide **2a** from 4 equiv to 3 equiv did not affect the AY (98%) with 95% isolated yield after purification (entry 14).

With the optimized conditions in hand, we investigated the substrate scope of aryl bromides **2** with 3-(methylsulfinyl)-thiophene **1a** under monoarylation conditions (Scheme 3). Generally, a broad range of functional groups on the aryl bromides, including halogens, trifluoromethyl, amine, and nitrile, as well as heteroaryl groups, were well tolerated (60−92% yields). The parent 3-(methylsulfinyl)-2-phenylthiophene **3a** was generated from bromobenzene **2a** in 90% yield. 1-Bromo-4-chlorobenzene **2b** provided product **3b** in 92% yield. Aryl bromides bearing electron-withdrawing groups, such as 4-F (**2c**), 4-CF_3 (**2d**), and 4-CN (**2e**), furnished products **3c−e** in 60−91% yield. Electron-donating groups on the aryl bromides also exhibited good reactivity. 4-Bromo-*N*,*N*-dimethylaniline **2f**, 1-bromo-4-*tert*-butylbenzene **2g**, and 4-bromoanisole **2h** provided the desired products in 67−89% yield. 3-Bromoanisole **2i**, 3-bromotoluene **2j**, and 1-bromo-3-fluorobenzene **2k** were also suitable coupling partners, furnishing **3i−k** in 80−85% yields. Sterically hindered aryl bromides, such as 1-bromonaphthalene **2l**, 2-bromotoluene **2m**, 2-bromoanisole **2n**, and 1-bromo-2-fluorobenzene **2o**, successfully afforded the products **3l−o** in 78−86% yield. To demonstrate the scalability of this approach, we performed the coupling of 3-(methylsulfinyl)thiophene **1a** (2 mmol) with 4-chlorobromobenzene **2b** (4 mmol) to generate **3b** in 84% yield.

Heterocyclic thiophenes exhibit a broad range of biological activities and, thus, are very important synthetic targets. To our delight, the heteroaryl bromides also exhibited good compatibilities under our optimal conditions. Thus, 2-bromothiophene **2p**, 3-bromothiophene **2q**, 2-bromopyridine **2r**, and 5-bromoquinoline **2s** afforded products **3p−s** in 63−80% yields. It is noteworthy that **3r** is a key structural motif with bioactivity against hepatitis C.[3b]

We next examined the scope of aryl bromides **2** to generate the 2,5-diarylated products **4**. A variety of aryl bromides reacted

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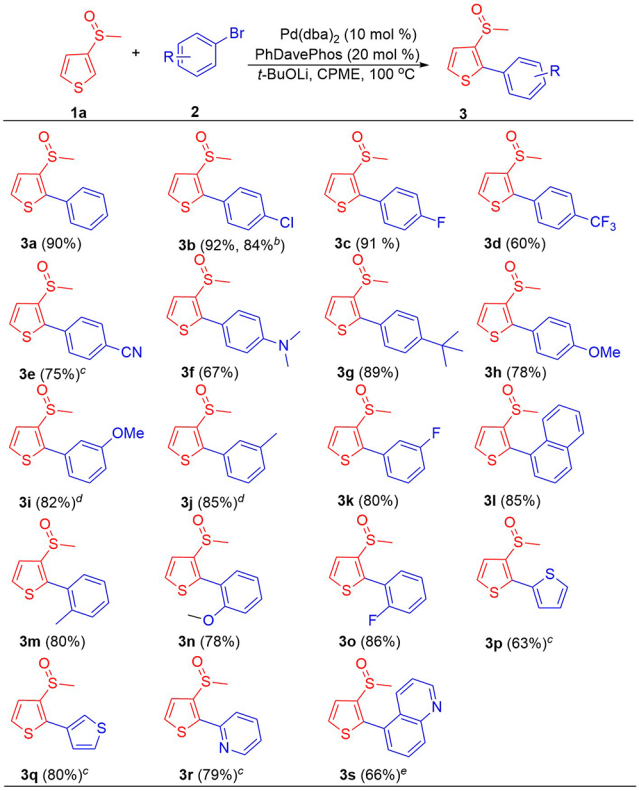
Scheme 3. Substrate Scope of Aryl Bromides in Palladium-Catalyzed Monoarylation of Thiophene 1a[a]



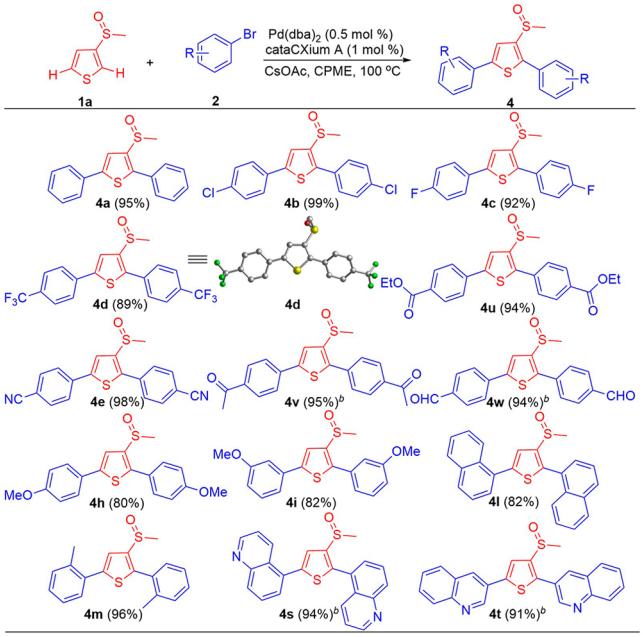
[a]Reaction conditions: **1a** (0.1 mmol), **2a**–**s** (0.2 mmol), *t*-BuOLi (0.3 mmol), $Pd(dba)_2$ (0.01 mmol), PhDavePhos (0.02 mmol), CPME (1 mL), 100 °C, 12 h. [b]**1a** (2 mmol), **2b** (4 mmol), *t*-BuOLi (6 mmol), $Pd(dba)_2$ (0.2 mmol), PhDavePhos (0.4 mmol), CPME (20 mL), 100 °C, 16 h. [c]36 h. [d]16 h. [e]24 h.

smoothly with **1a** to produce the corresponding diarylated products **4** in good to excellent yields (Scheme 4). Both electron-donating and electron-withdrawing aryl bromides were well tolerated. 3-(Methylsulfinyl)thiophene **1a** coupled with bromobenzene **2a** to give the parent 3-(methylsulfinyl)-2,5-diphenylthiophene **4a** in 95% yield. 1-Bromo-4-chlorobenzene **2b** provided **4b** in 99% yield. Aryl bromides bearing electron-withdrawing groups, such as 4-F (**2c**), 4-CF_3 (**2d**), 4-COOEt (**2u**), 4-CN (**2e**), 4-$COCH_3$ (**2v**), and 4-CHO (**2w**), were successfully utilized as coupling partners, providing the products in 89–98% yield. The structure of **4d** was confirmed by X-ray crystallography. Electron-donating 4-bromoanisole **2h** generated product **4h** in 80% yield, while 3-bromoanisole **2i** gave the product **4i** in 82% yield. Sterically hindered 1-naphthyl **2l** and 2-tolyl **2m** bromides provided the desired products in 82 and 96% yield, respectively. Heterocyclic 5-bromoquinoline **2s** and 3-bromoquinoline **2t** afforded **4s** and **4t** in 94 and 91% yield, respectively.

The next goal was to perform the arylation of 2-aryl 3-(methylsulfinyl)thiophenes to prepare sulfinylthiophenes possessing two different aryl groups (Scheme 5, eq 1). When **3a** was coupled with 4-bromobenzonitrile **2e**, the arylation product **5a**, which was characterized by X-ray crystallography, was isolated in 78% yield (see the Supporting Information for details).

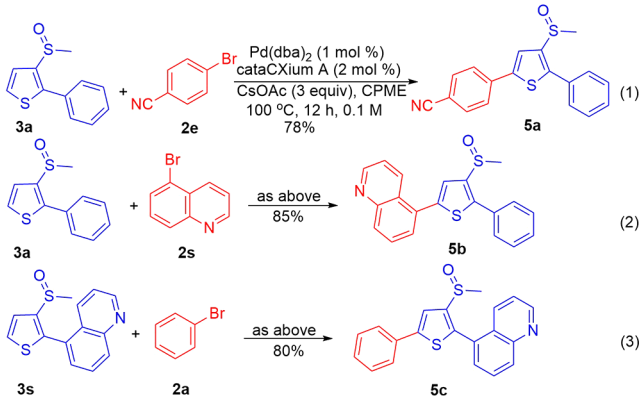
Heteroarylthiophenes are a class of important bioactive scaffolds, yet the synthesis of these molecules remains a

Scheme 4. Substrate Scope of Aryl Bromides in Palladium-Catalyzed 2,5-Bisarylation Thiophene 1a[a]



[a]Reaction conditions: **1a** (0.1 mmol), **2a**–**w** (0.3 mmol), CsOAc (0.3 mmol), $Pd(dba)_2$ (0.0005 mmol), cataCXium A (0.001 mmol), CPME (1 mL), 100 °C, 12 h. [b]$Pd(dba)_2$ (0.001 mmol), cataCXium A (0.002 mmol).

Scheme 5. Substrate Scope of Palladium-Catalyzed 2-Monoarylated Thiophenes with Aryl Bromides



challenge. We were pleased to find that the sequential arylation strategy could be successfully applied to the synthesis of constitutional isomeric heteroaryl thiophenes. Simply swapping the order of aryl bromide addition in the cross-coupling reactions enabled the synthesis of isomers **5b** and **5c** under the same conditions in 85 and 80% yield, respectively (Scheme 5, eq 2 and 3).

In conclusion, we have developed a versatile palladium-catalyzed direct C–H functionalization of thiophenes bearing sulfinyl groups with excellent regioselectivities. This protocol is effective for the synthesis of either 2-arylated or 2,5-diarylated sulfinylthiophene derivatives. This method has potential applications in the preparation of sulfinylthiophenes for material science and medicinal chemistry.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00599.

Procedures and characterization data for all new compounds (PDF)

Accession Codes

CCDC 1817431−1817432 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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