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Palladium-Catalyzed C−H Homocoupling of Furans and Thiophenes Using Oxygen as the Oxidant

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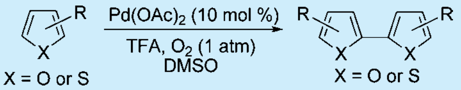
Ⓢ *Supporting Information*

ABSTRACT: A general and efficient palladium-catalyzed intermolecular direct C−H homocoupling of furans and thiophenes has been developed. The reaction is characterized by using molecular oxygen as the sole oxidant and complete C5-position regioselectivity. Both C2- and C3-substituted furans or thiophenes are appropriate substrates. The approach provides a straightforward, facile, and economical route to bifurans and bithiophenes under mild reaction conditions.

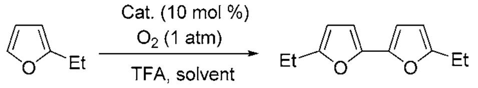


Bi(hetero)aryls are important structural components in natural products, pharmaceuticals, and functional materials.[1,2] Typically, the components are synthesized by the cross-coupling of an (hetero)aryl halide or a pseudohalide with an organometallic reagent, an organoboron reagent, or an electron-rich (hetero)arene (e.g., Stille, Negishi, and Suzuki reaction),[3] or by the homocoupling of two organometallic reagents or two (hetero)aryl halides (e.g., Wurtz and Ullmann reaction).[4] Alternatively, direct oxidative homocoupling of two unactivated (hetero)arenes using a C−H activation strategy through the cleavage of two C−H bonds represents an environmentally and economically more attractive method.[5] In the past decade, direct catalytic homocoupling has been successfully applied in many (hetero)arenes, such as arenes,[6] thiophenes,[7] indoles,[8] indolizines,[9] azoles,[10] and pyridines.[11] Nevertheless, to the best of our knowledge, the efficient catalytic homocoupling of furans with a direct C−H functionalization strategy has not been documented,[12] despite furans being very important heteroarenes and bifurans being important building blocks for synthesizing poly- and oligofurans. Furthermore, recently Bendikov et al. reported that oligofurans have higher fluorescence, tighter herringbone solid-state packing, and greater rigidity and solubility than the workhorse compound—oligothiophenes in the field of organic electronic materials.[13] In addition, furan-based materials should be biodegradable.[13]

Herein, we report the first efficient synthesis of bifurans by the direct catalytic C−H homocoupling of furans with a C−H activation strategy. The reaction is catalyzed by palladium(II) using oxygen as the sole oxidant and has complete C5-position regioselectivity. Also thiophenes are suitable substrates for the reaction.

Initially, we investigated the homocoupling reaction of 2-ethyl furan (**1a**) with 10 mol % $Pd(OAc)_2$ as the catalyst and oxygen as the oxidant in DMSO at room temperature (Table 1). The reaction was found to proceed in low conversion (<10%) (entry 1). Considering trifluoroacetic acid (TFA) and $Pd(OAc)_2$ can facilitate the generation of more electropositive $[Pd(II)O_2CCF_3]^+$ species, which compared with $[PdOAc]^+$ is easier to form σ-furan-Pd complexes through electrophilic substitution of C−H bonds,[14] 1 equiv of TFA was added to the reaction system. To our delight, the reaction gave the bifuran product (**2a**) in 82% yield with complete C5 regioselectivity (entry 2). Changing the amount of TFA could not improve the yield (entries 2−6). After careful solvent screening, DMSO proved to be the best (entry 7). By using other palladium sources, $Pd(TFA)_2$ was observed to be an acceptable catalyst for the reaction while $Pd(OH)_2$ and $PdCl_2$ could not promote the reaction (entries 8−10). It is noteworthy that the reaction rate and the yield were obviously reduced when air was used as

Table 1. Optimization of Reaction Conditions[a]



entry	cat.	acid (equiv)	temp (°C)	time (h)	yield (%)[b]
1[c]	$Pd(OAc)_2$	–	rt	72	<10
2	$Pd(OAc)_2$	TFA (1.0)	rt	24	82
3	$Pd(OAc)_2$	TFA (0.1)	rt	24	10
4	$Pd(OAc)_2$	TFA (0.5)	rt	24	30
5	$Pd(OAc)_2$	TFA (2.0)	rt	24	60
6	$Pd(OAc)_2$	TFA (4.0)	rt	24	35
7[d]	$Pd(OAc)_2$	TFA (1.0)	rt	24	≤45
8	$Pd(TFA)_2$	TFA (1.0)	rt	36	75
9	$Pd(OH)_2$	TFA (1.0)	rt	24	0
10	$PdCl_2$	TFA (1.0)	rt	4.5	0
11[e]	$Pd(OAc)_2$	TFA (1.0)	rt	24	65
12[f]	$Pd(OAc)_2$	TFA (1.0)	rt	48	66[g]

[a] Reaction conditions: **1a** (1 mmol), catalyst (0.1 mmol), O_2 (1 atm), and TFA (1 mmol) in DMSO (1.5 mL) at room temperature. [b] Isolated yield. [c] No acid. [d] Solvents: EtOAc, DMF, THF, *n*-hexane, toluene, acetone, CH_3CN, dioxane, Et_2O, CH_2Cl_2, $CHCl_3$, CH_3NO_2, EtOH. [e] Using air as the oxidant. [f] $Pd(OAc)_2$ (5 mol %) was used. [g] The conversion was 72%.

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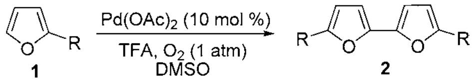
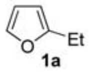
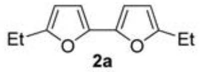
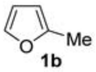
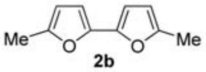
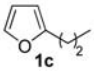
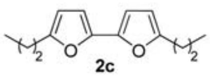
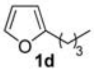
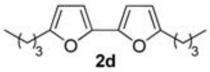
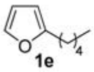
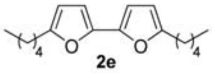
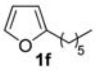
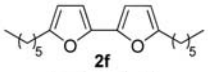
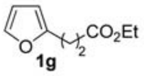
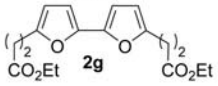
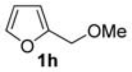
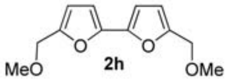
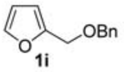
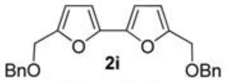
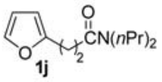
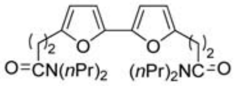
the oxidant instead of oxygen (entry 11). When the loading of $Pd(OAc)_2$ was lowered, e.g., to 5 mol %, the reaction was slow and would proceed incompletely (entry 12). Accordingly, the reaction conditions were optimized as follows: $Pd(OAc)_2$ (10 mol %), TFA (1 equiv) under an oxygen atmosphere in DMSO.

With the optimal reaction conditions in hand, we moved on to explore the scope of the homocoupling reaction. The results were summarized in Table 2. Furans substituted by various alkyl groups at the C2-position smoothly underwent the homocoupling reaction to give corresponding bifuran products in 78−86% yields (entries 1−6). Furans bearing an ester, ether, or amide functional group were also reacted successfully and provided the coupling products in good yields with the functional group intact (entries 7−10). These groups could be further transformed into other functionalities. It is worth mentioning that all reactions proceeded with complete C5-position regioselectivity of the furans. The product of another position could not be detected by analyzing the reaction mixtures. Additionally, the reaction could readily be enlarged to gram scale with a slightly higher yield (entry 1).

Table 2. Palladium-Catalyzed Homocoupling of 2-Substituted Furans[a]



entry	substrate	product	yield (%)[c]
1[b]	 1a	 2a	82 (88)[d]
2[b]	 1b	 2b	86
3	 1c	 2c	83
4	 1d	 2d	80
5	 1e	 2e	78
6	 1f	 2f	84
7	 1g	 2g	81
8	 1h	 2h	65
9	 1i	 2i	85
10	 1j	 2j	81

[a] Reaction conditions: **1** (1 mmol), catalyst (0.1 mmol), O_2 (1 atm), and TFA (1 mmol) in DMSO (1.5 mL) at 50 °C for 20−48 h. [b] The reaction proceeded at room temperature. [c] Isolated yield. [d] 10 mmol of 2-ethyl furan were used.

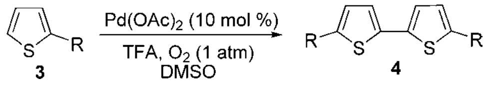
Next, we turned our focus toward thiophene substrates. Currently, oligothiophenes have been extensively studied and applied in the field of organic semiconductors due to their superior electronic properties.[13,15] In 2004, Mori et al. first reported the palladium-catalyzed C−H homocoupling of thiophenes.[7a] In the approach, 1 equiv of AgF was employed as an activator so that stoichiometric hydrogen fluoride was generated as a byproduct; therefore the reaction should be carried out in a well-ventilated hood with gloves throughout the procedure. Later, they developed another cheap activator system, $AgNO_3$/KF, to take the place of AgF.[16] In 2008, Tse et al. reported an efficient gold-catalyzed oxidative homocoupling of arenes using $PhI(OAc)_2$ as the oxidant.[6a,17] With this reaction they also examined the homocoupling of 2-methylthiophene, but the yield was only 31%. It is significant that this protocol did not need any silver salt to improve the reactivity.

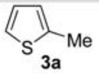
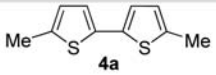
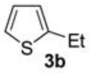
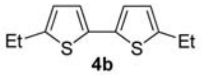
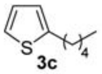
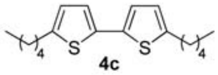
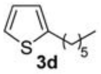
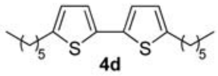
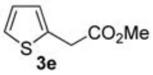
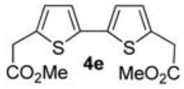
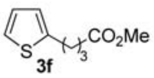
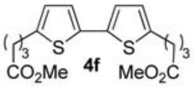
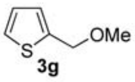
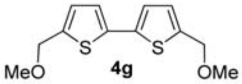
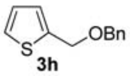
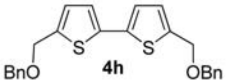
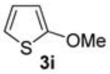
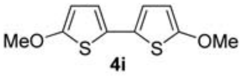
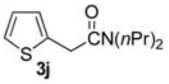
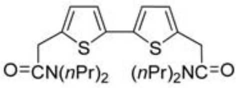
Under our above optimal reaction conditions, a variety of 2-substituted thiophenes were checked. Pleasingly, they all successfully gave the desired homocoupling products in good to excellent yields (Table 3). Moreover, the products were of complete C5-position regioselectivity, and no product of another position can be detected. Valuable advantages of the method included operational simplicity using oxygen as the oxidant without the requirement of special equipment.

Oligo-(3-alkyl)furans and oligo-(3-alkyl)thiophenes have received considerable attention recently due to their application in thin-film transistors (TFTs),[18] light-emitting devices (LEDs),[19] and photovoltaics.[20] Nevertheless, the homocoupling of 3-alkylfurans or 3-alkylthiophenes were very limited in the literature.[12a,21] Moreover, the substrates of the homocoupling reaction were confined to 3-substituted thiophenes. Because of the high nucleophilicity of the C2 position of the 3-substituted thiophenes, the reaction exclusively provided head-to-tail (H−T) products and head-to-head (H−H) products, with no tail-to-tail (T−T) products reported (Scheme 1). Furthermore, the homocoupling of 3-alkylfurans has not been shown previously to our knowledge. Thus, we investigated the homocoupling reaction of 3-alkylfurans and 3-alkylthiophenes with our above-mentioned homocoupling conditions. Delightedly, both 3-alkylfurans and 3-alkylthiophenes reacted smoothly under similar conditions to afford homocoupling products in moderate yield, albeit without complete conversion (Table 4). Interestingly, the reaction exhibited complete tail-to-tail (T−T) regioselectivity. The great C5-position regioselectivity is probably attributed to the steric hindrance of the 3-position substituent group that limits the palladation of the C2-position.

To gain insight into the reaction mechanism, a kinetic isotope effect (KIE) competition experiment was carried out by using the reaction of **1d** and its derivative deuterated at the C5 position ([D]-**1d**) (Supportig Information). The KIE value was 2.17, indicating that the C−H bond breaking was involved in the rate-determining step in the overall catalytic cycle. Our current understanding of the mechanism of the reaction is shown in Scheme 2. $Pd(OAc)_2$ is treated with TFA to obtain active $Pd(O_2CCF_3)^+$,[14,22] which affords the C2-palladated species **I** through electrophilic addition of furan and following rearomatization. Then the electrophilic palladation with the second furan leads to bis-furanylpalladium species **II**.[7a,8c] The following reductive elimination generates the bifuran product,

Table 3. Palladium-Catalyzed Homocoupling of 2-Substituted Thiophenes[a]



entry	substrate	product	yield (%)[c]
1[b]	 3a	 4a	85
2[b]	 3b	 4b	78
3	 3c	 4c	76
4	 3d	 4d	88
5	 3e	 4e	85
6	 3f	 4f	89
7	 3g	 4g	81
8	 3h	 4h	87
9	 3i	 4i	78
10	 3j	 4j	82

[a]Reaction conditions: **3** (1 mmol), catalyst (0.1 mmol), O$_2$ (1 atm), and TFA (1 mmol) in DMSO (1.5 mL) at 50 °C for 24−48 h. [b]The reaction proceeded at room temperature. [c]Isolated yield.

Scheme 1. Homocoupling of 3-Substituted Thiophene

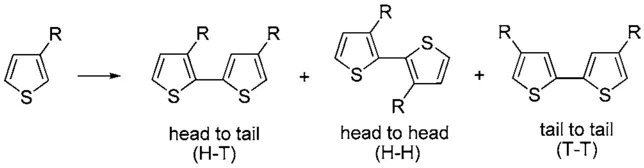
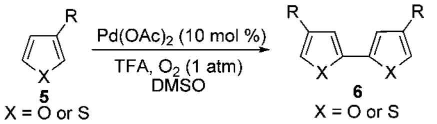
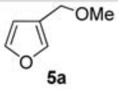
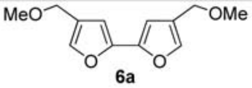
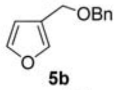
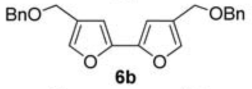
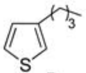
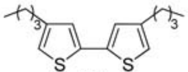
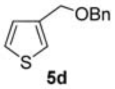
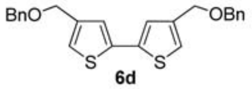
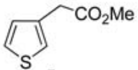
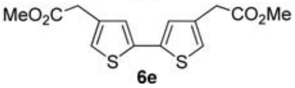


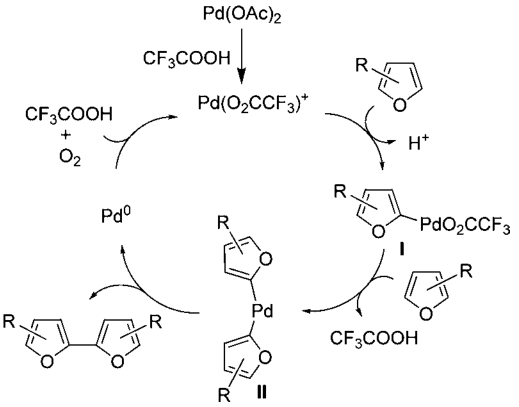
Table 4. Palladium-Catalyzed Homocoupling of 3-Substituted Furans and Thiophenes[a]



entry	substrate	product	yield (%)[b,c]
1	 5a	 6a	53 (84)
2	 5b	 6b	57 (88)
3	 5c	 6c	53 (85)
4	 5d	 6d	42 (73)
5	 5e	 6e	55 (86)

[a]Reaction conditions: **5** (1 mmol), catalyst (0.1 mmol), O$_2$ (1 atm), and TFA (1 mmol) in DMSO (1.5 mL) at 50 °C for 36−48 h. [b]Isolated yield. [c]Yield in parentheses based on recovered starting material.

Scheme 2. Plausible Mechanism for the Homecoupling



and the Pd^0 can be reoxidized to Pd(O$_2$CCF$_3$)$^+$ by O$_2$ in the presence of TFA to complete the catalytic cycle.[23]

In summary, we have developed an efficient C−H homocoupling of furans and thiophenes with the C−H activation strategy. The reaction is catalyzed by palladium(II), in which oxygen is used as the sole oxidant. Both C2- and C3-substituted furans or thiophenes are appropriate substrates. The reaction proceeds with complete C5-position regioselectivity. The approach provides a straightforward, facile, and economical route to bifurans and bithiophenes under mild reaction conditions. The method should have many applications in organic and material chemistry. Detailed mechanistic investigations and the applications of the reaction are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures including spectroscopic and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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