

Palladium-Catalyzed C2-Selective Direct Arylation of Benzo[*b*]thiophene 1,1-Dioxides with Arylboronic Acids

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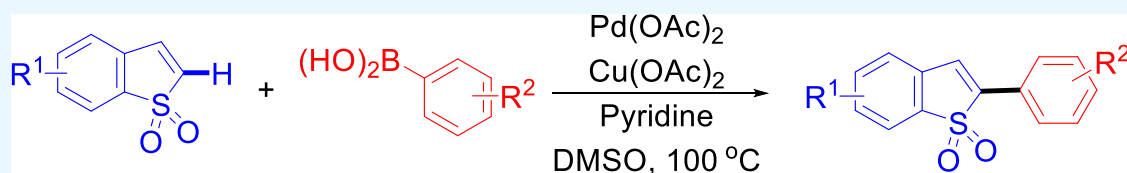
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ABSTRACT: A novel oxidative cross-coupling of benzo[*b*]thiophene 1,1-dioxides with arylboronic acids was reported. The efficient reaction occurred at the C2-position via C–H activation, followed by Pd(II)-catalyzed arylation. Furthermore, a series of C2-arylated products with significant photoluminescence properties have been synthesized and characterized, which illustrates the potential applications of our method in the aggregation-induced emission field.

INTRODUCTION

Since Barbarella and co-workers first reported that oxidizing oligothiophenes and ring-fused oligothiophenes to thiophene 1,1-dioxides can reduce the HOMO–LUMO band gap value and improve their photoluminescence efficiencies,^{1,2} electron-withdrawing thiophene 1,1-dioxide group has been commonly introduced into thiophene-based organic functional materials to improve photophysical properties.³ For example, Tang⁴ and Liou⁵ demonstrated that aryl-substituted benzo[*b*]thiophene 1,1-dioxides showed obvious aggregation-induced emission (AIE) characteristics. Polymer light-emitting diodes based on copolymers containing thiophene 1,1-dioxide units were reported by various groups.^{6,7} Incorporation of the dibenzo-thiophene 1,1-dioxide unit into the chain of oligofluorenes showed strong solvatochromism^{7b} and dual-fluorescence^{7c} with high luminescence efficiency. Thus, there are important significances to develop new methods for the synthesis and modification of thiophene 1,1-dioxide compounds.

Traditional approaches to thiophene 1,1-dioxides include oxidation of thiophenes by peroxides,^{4,8} Diels–Alder reactions,⁹ and C–X/C–M cross-couplings (Stille coupling, Suzuki–Miyaura coupling, etc.).¹⁰ Over the past decade, transition metal-catalyzed direct C–H activation and functionalization reactions have evolved into one of the most attractive tools in organic synthesis owing to abundant C–H bonds, high atom- and step-economy, and environmental friendliness.¹¹ However, only limited examples on functionalization of thiophene 1,1-dioxides involved in transition metal-catalyzed C–H activation have been reported so far. Nelson¹² and Farinola¹³ developed Cu(I)- and Pd(0)-catalyzed C–H/C–I cross-coupling of benzodithiophene *S,S*-tetraoxides with aryl

iodides, respectively (Scheme 1a). Afterward, the N-chelator-assisted C–H/C–H dehydrogenative coupling strategy was used in the formation of extended heteroaromatic conjugated molecules (Scheme 1b).¹⁴ Very recently, we reported the Pd(II)-catalyzed oxidative olefination reaction of benzo[*b*]thiophene 1,1-dioxides with alkenes based on the C–H activation pathway (Scheme 1c).¹⁵ Following our continued interest in the transformation of thiophene 1,1-dioxide compounds, we herein disclose a novel Pd(II)-catalyzed direct arylation of benzo[*b*]thiophene 1,1-dioxides with arylboronic acids for the synthesis of aryl-substituted benzo[*b*]thiophene 1,1-dioxides. The efficient reaction took place at the C2-position via C–H activation, followed by a Pd(II)-catalyzed direct arylation process (Scheme 1d).

RESULTS AND DISCUSSION

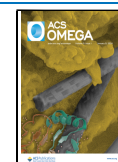
Benzo[*b*]thiophene 1,1-dioxide **1a** and phenylboronic acid **2a** were chosen as starting materials to optimize the reaction conditions. 2-Phenylbenzo[*b*]thiophene 1,1-dioxide **3a** was successfully obtained in 39% yield in the presence of 10 mol % of Pd(OAc)₂, 2.0 equiv of Cu(OAc)₂, and 3.0 equiv of pyridine by using 1,4-dioxane as the solvent at 100 °C for 20 h (Table 1, entry 1). Meanwhile, trace amounts of homocoupling products such as 1,1'-biphenyl and [2,2'-bibenzo[*b*]thiophene]

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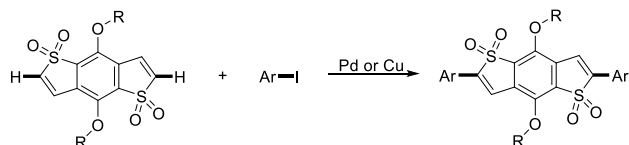
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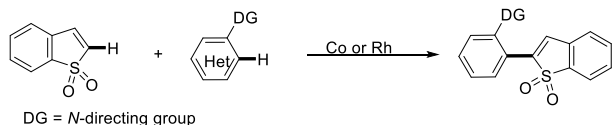
Scheme 1. Evolution of Catalytic C–H Activation/Functionalization of Thiophene 1,1-Dioxides

Previous work:

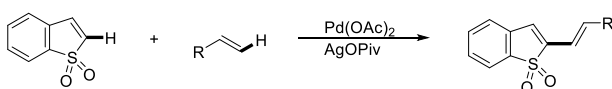
(a) Pd or Cu-catalyzed C-H/C-I cross-coupling



(b) Co or Rh-catalyzed *N*-chelator-assisted C-H/C-H cross-coupling



(c) Pd-catalyzed oxidative Heck cross-coupling



This work:

(d) Pd-catalyzed direct arylation

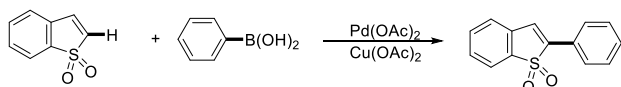
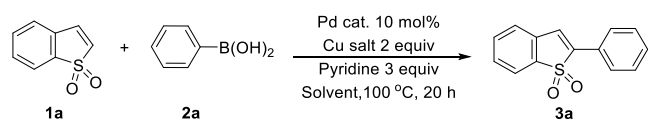


Table 1. Optimization of Pd(II)-Catalyzed Direct Arylation^a



entry	Pd cat.	Cu salt	solvent	conv. of 1a (%) ^b	yield (%) ^b
1	Pd(OAc) ₂	Cu(OAc) ₂	dioxane	55	39
2	Pd(OAc) ₂	Cu(OAc) ₂	toluene	42	27
3	Pd(OAc) ₂	Cu(OAc) ₂	DCE	48	33
4	Pd(OAc) ₂	Cu(OAc) ₂	DMSO	92	74
5	Pd(OAc) ₂	Cu(OAc) ₂	DMF	55	37
6	PdCl ₂	Cu(OAc) ₂	DMSO	62	44
7	Pd(MeCN) ₂ Cl ₂	Cu(OAc) ₂	DMSO	70	50
8	Pd(OAc) ₂	Cu(OAc) ₂	DMSO	10	0
9	Pd(OAc) ₂	Cu(acac) ₂	DMSO	32	18
10	Pd(OAc) ₂	CuBr ₂	DMSO	25	0
11	Pd(OAc) ₂	Cu(OTf) ₂	DMSO	82	60
12	Pd(OAc) ₂	AgOAc	DMSO	68	35
13 ^c	Pd(OAc) ₂	Cu(OAc) ₂	DMSO	100	80
14 ^d	Pd(OAc) ₂	Cu(OAc) ₂	DMSO	100	87
15 ^e	Pd(OAc) ₂	Cu(OAc) ₂	DMSO	65	41
16 ^f	Pd(OAc) ₂	Cu(OAc) ₂	DMSO	45	32

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol, 3.0 equiv), Pd cat. (10 mol %), Cu salt (2.0 equiv), and pyridine (3.0 equiv) in solvent (1.0 mL) at 100 °C for 20 h. ^bConversion and yield data were detected by GC. ^cCu(OAc)₂ (3.0 equiv). ^dCu(OAc)₂ (4.0 equiv). ^eCu(OAc)₂ (50 mol %) under an O₂ atmosphere. ^fCu(OAc)₂ (20 mol %) under an O₂ atmosphere. Dioxane = 1,4-dioxane, DCE = 1,2-dichloroethane, DMSO = dimethyl sulfoxide, and DMF = *N,N*-dimethylformamide.

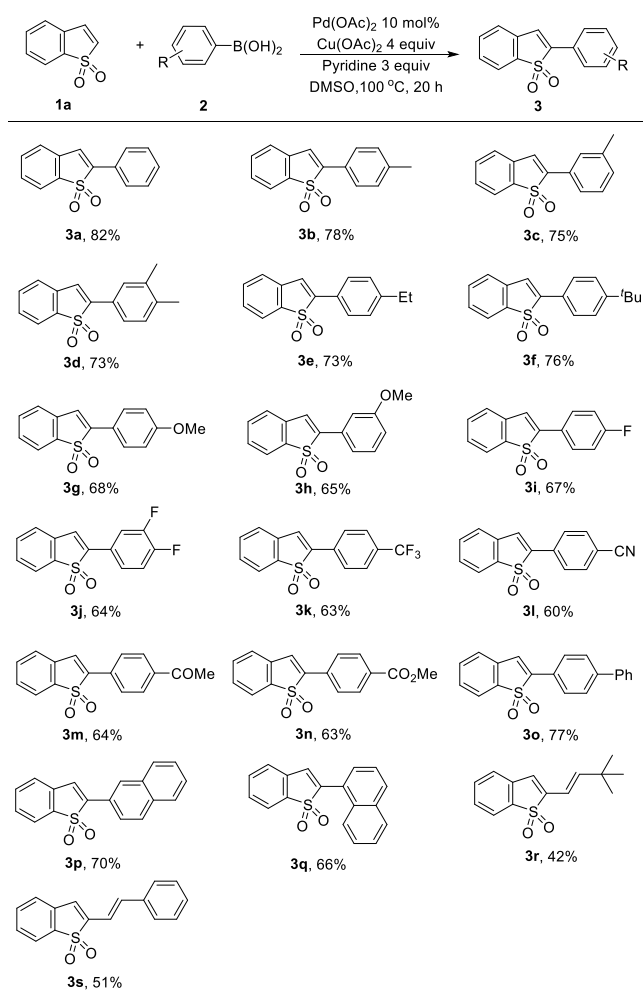
1,1,1',1'-tetraoxide were generated as byproducts. It was noted that no C3-position-arylated benzothiophene 1,1-dioxide

product was generated. Other solvents such as toluene, 1,2-dichloroethane (DCE), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) were examined, and DMSO was the most effective (Table 1, entries 2–5). Among the various Pd(II) catalysts examined, Pd(OAc)₂ was superior to PdCl₂ and Pd(MeCN)₂Cl₂ (Table 1, entries 4 and 6–7). The oxidative cross-coupling did not proceed in the absence of the Pd(II) catalyst, indicating that the Pd(II) catalyst might play an important role in the C–H activation process (Table 1, entry 8). We further screened other oxidants, including Cu(II) salts and AgOAc. As a result, Cu(OAc)₂ showed the highest activity (Table 1, entries 4 and 9–12). Further experiments indicated that a better yield (87%) of the desired product was gained when the loading of Cu(OAc)₂ was increased to 4.0 equiv (Table 1, entries 13 and 14). When using O₂ as the terminal oxidant and a catalytic amount of Cu(OAc)₂ as the co-oxidant, only low yields of **3a** can be obtained (Table 1, entries 15 and 16). Moreover, various inorganic bases (NaO^tBu, NaOH, K₃PO₄, Cs₂CO₃, NaOAc, and KF) and organic bases (pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, triethylamine, and *N,N*-diisopropylethylamine) were examined, and as a result, pyridine was superior to other bases (Table S1 in Supporting Information). Finally, the optimized reaction conditions comprising Pd(OAc)₂ (10 mol %), Cu(OAc)₂ (4.0 equiv), and pyridine (3.0 equiv) in DMSO solution at 100 °C for 20 h were established.

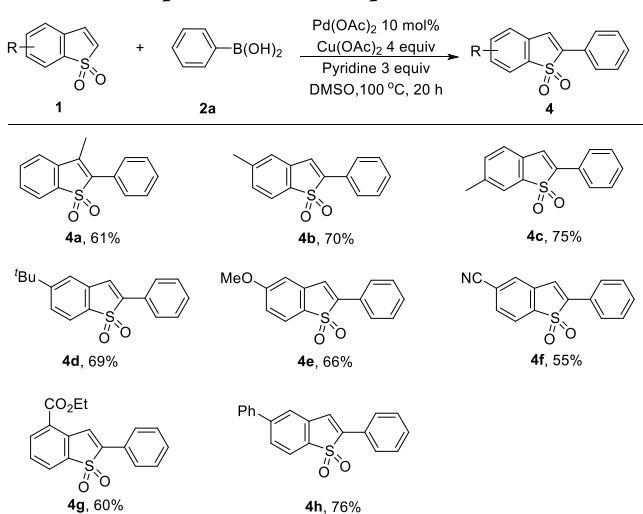
With the optimal conditions in hand, the scope of the arylation reaction was investigated. As shown in Scheme 2, various arylboronic acids containing electron-donating groups, such as methyl, ethyl, and *tert*-butyl, and methoxy groups on the phenyl moiety reacted smoothly with **1a** to give the corresponding products in good yields (**3a–3h**). Arylboronic acids with electron-withdrawing groups (fluoride, trifluoromethyl, cyano, acyl, and ester groups) can also undergo this transformation, but only moderate yields were obtained (**3i–3n**). [1,1'-Biphenyl]-4-ylboronic acid coupled with **1a**, affording the desired **3o** in a 77% yield. Both 1- and 2-naphthyl boronic acids were compatible under the optimal conditions, and the corresponding products were obtained in good yields (**3p** and **3q**). Moreover, alkenyl boronic acids such as (*E*)-styrylboronic acid and (*E*)-(3,3-dimethylbut-1-en-1-yl)boronic acid were compatible with this protocol, leading to the corresponding products in lower yields (**3r** and **3s**).

Next, we examined the scope of benzo[*b*]thiophene 1,1-dioxide derivatives. As illustrated in Scheme 3, benzo[*b*]thiophene 1,1-dioxides with various substituents could undergo palladium-catalyzed direct arylation. In comparison with 5- and 6-methyl-substituted benzo[*b*]thiophene 1,1-dioxides, 3-methylbenzo[*b*]thiophene 1,1-dioxide led to a lower yield due to the steric effect (**4a–4c**). Both typical electron-donating *tert*-butyl (**4d**), methoxy (**4e**), and electron-withdrawing cyano (**4f**) and ester (**4g**) groups on the aryl ring of benzo[*b*]thiophene 1,1-dioxides were compatible with this protocol, affording the desired products in good yields. When 5-phenylbenzo[*b*]thiophene 1,1-dioxide was used as substrate, a 2-arylated product **4h** was obtained in 76% yield. It is notable that thiophene 1,1-dioxide was limited under the standard conditions since thiophene 1,1-dioxide can easily undergo desulfonylative transformation to afford a dimer even at <40 °C.¹⁶

Arylated benzo[*b*]thiophene 1,1-dioxide derivatives were demonstrated as novel organic functional material molecules exhibiting obvious AIE characteristics.^{4,5} The application of

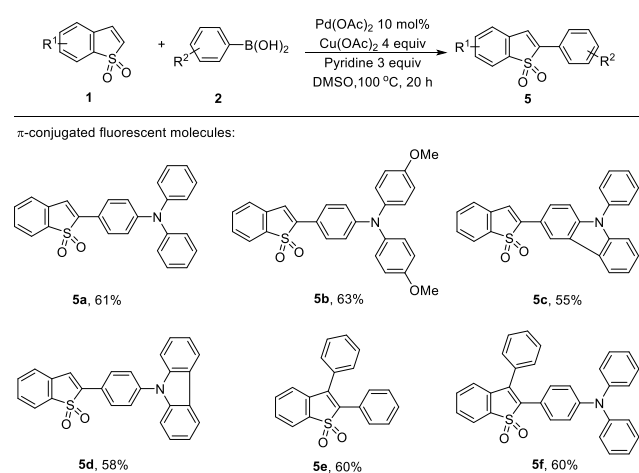
Scheme 2. Scope of Arylboronic Acids^{a,b}

^aReactions were performed with 1a (0.20 mmol) and arylboronic acid 2 (0.60 mmol, 3.0 equiv) in DMSO. ^bYields of isolated products.

Scheme 3. Scope of Benzo[*b*]thiophene 1,1-Dioxides^{a,b}

^aReactions were performed with 1 (0.20 mmol) and phenylboronic acid 2a (0.60 mmol, 3.0 equiv) in DMSO. ^bYields of isolated products.

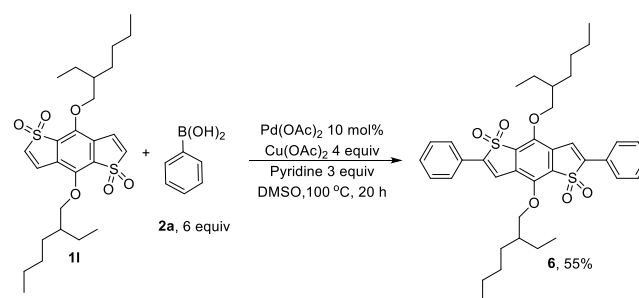
new synthetic methodologies to rapidly and directly construct novel π -conjugated fluorescent core skeletons has been attracting extra attention.¹⁷ Using the Pd(II)-catalyzed C–H oxidative Suzuki coupling strategy, a series of π -conjugated arylated benzo[*b*]thiophene 1,1-dioxides with the AIE effect were synthesized and characterized, and arylated benzo[*b*]thiophene 1,1-dioxide products with triaryl amino groups were obtained in acceptable yields (Scheme 4, 5a–5d). 3-

Scheme 4. Synthesis of π -Conjugated Fluorescent Molecules^{a,b}

^aReactions were performed with 1 (0.20 mmol) and arylboronic acid 2 (0.60 mmol, 3.0 equiv) in DMSO. ^bYields of isolated products.

Phenylbenzo[*b*]thiophene 1,1-dioxide reacted with arylboronic acids successfully to afford 2,3-diaryl-substituted products (Scheme 4, 5e–5f). Moreover, when bis-sulfone substrate 11 was used as a starting material with 6.0 equiv of phenylboronic acid 2a, bis-arylated product 6 was obtained in 55% yield (Scheme 5).

Scheme 5. Reaction of Bis-Sulfone 11 with Phenylboronic Acid 2a



The UV–vis spectra of 5a and 5c–5f in DCM solutions afforded the absorption maxima from 336 to 419 nm (Figure 1a). Compound 5b displayed a greater absorption λ_{max} value in 430 nm due to the introduction of the electron-donating –OMe group. As the π -conjugated system expanded, the absorption λ_{max} value of bis-arylated product 6 was further red-shifted. In addition, all the compounds 5a–5f and 6 displayed obvious fluorescence emission properties in both the solution and the solid state (Figure 1b,c).

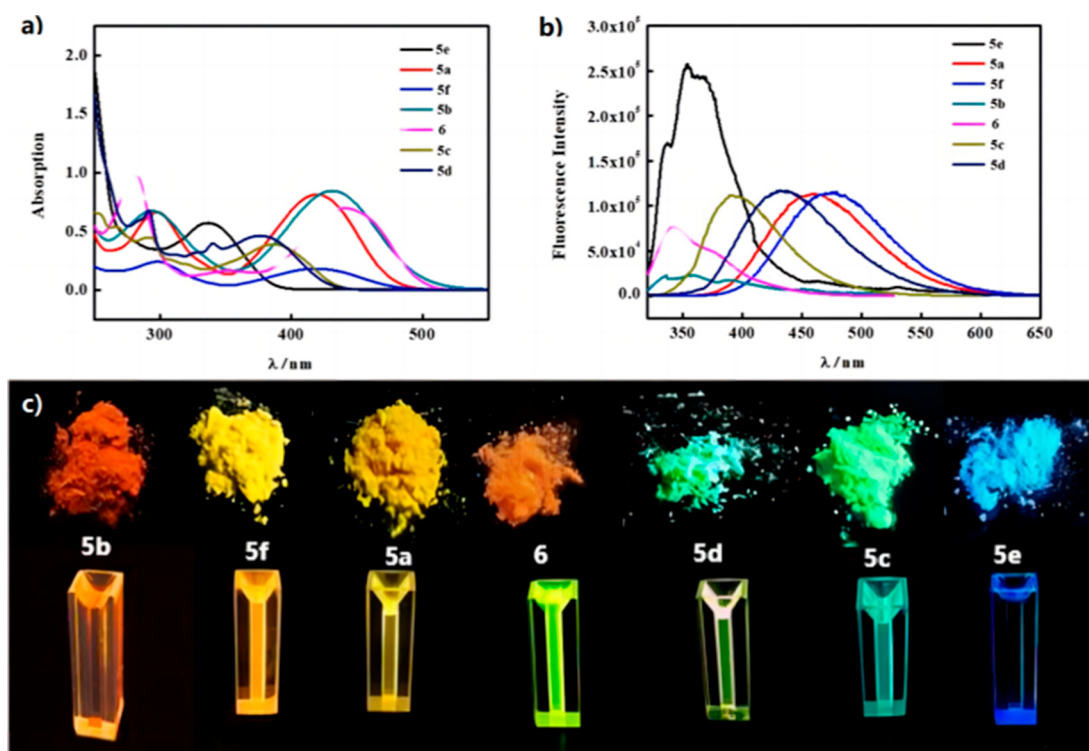
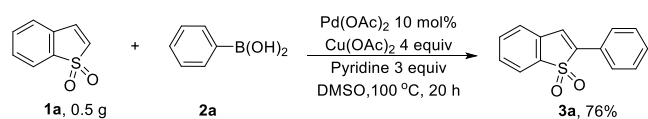


Figure 1. (a,b) Absorption and emission spectra, respectively. (c) Fluorescence images in DCM (CH_2Cl_2) under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) and in the solid state.

To illustrate the practical synthetic utility, the gram-scale reaction of **1a** with phenylboronic acid **2a** was next carried out under the optimal conditions (Scheme 6). The desired 2-phenylbenzo[*b*]thiophene 1,1-dioxide **3a** was obtained in 76% yield from the scale-up reaction.

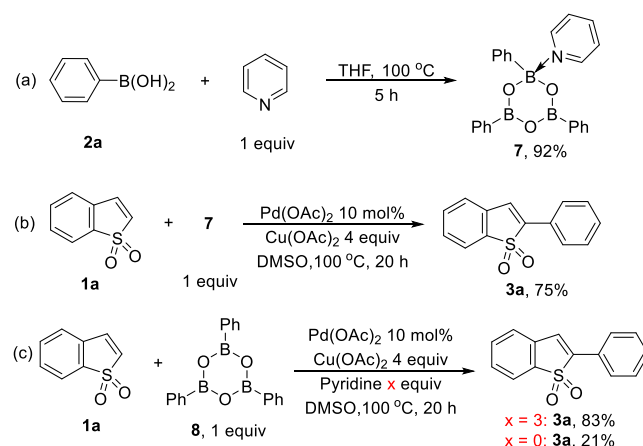
Scheme 6. Gram-Scale Reaction



To gain insight into the mechanism of arylation, the following parallel experiments were carried out. Triphenylboroxine pyridine complex **7** was obtained from the reaction of phenylboronic acid **2a** with pyridine (Scheme 7a).¹⁸ The catalytic reaction of **1a** with **7** in the absence of base gave product **3a** in 75% yield (Scheme 7b). In addition, triphenylboroxine **8** can also undergo Pd(II)-catalyzed cross-coupling in the presence of pyridine (Scheme 7c). All the results indicated that triphenylboroxine pyridine complex **7** was the active arylation reagent in the arylation process.^{18c}

Finally, a plausible mechanism for the Pd(II)-catalyzed C–H bond oxidative cross-coupling was proposed (Scheme 8).^{15,19} First, the cyclopalladium intermediate **IM1** was obtained via the C–H activation of benzo[*b*]thiophene 1,1-dioxide **1a**. Next, phenylboronic acid **2a** is coordinated with pyridine to give the triphenylboroxine pyridine complex **7**. Complex **7** underwent transmetalation with **IM1** to form **IM2**. A reductive elimination process of **IM2** led to the desired product **3a** with the release of Pd(0) species. Finally, the Pd(0) species was reoxidized to the Pd(II) catalyst by $\text{Cu}(\text{OAc})_2$ for the next cycle.

Scheme 7. Mechanistic Study



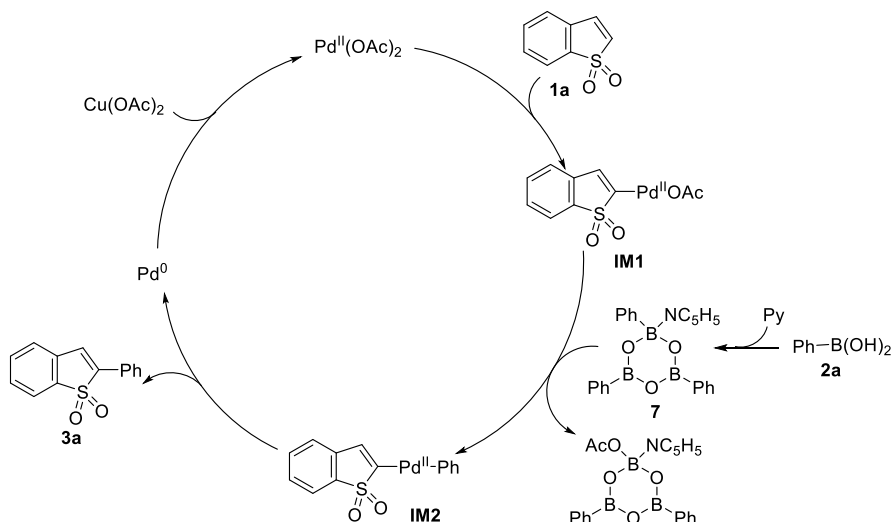
CONCLUSIONS

In conclusion, we have reported a novel Pd(II)-catalyzed oxidative cross-coupling of benzo[*b*]thiophene 1,1-dioxides with arylboronic acids via direct C–H bond activation. This oxidative transformation features high C2 selectivity, good substrate scope, and broad functional group tolerance. Moreover, a series of C2-arylated products with significant photoluminescence properties have been synthesized and characterized, which illustrates the potential applications of our method in constructing thiophene 1,1-dioxide-arenes-type π -conjugated frameworks.

EXPERIMENTAL SECTION

General. NMR spectra were obtained on Bruker AV-400 and AV-600 MHz spectrometers. The ^1H NMR chemical shifts were measured relative to CDCl_3 or $\text{DMSO}-d_6$ as the internal

Scheme 8. Plausible Mechanistic Pathway



reference (CDCl_3 : $\delta = 7.26$ ppm; $\text{DMSO}-d_6$: $\delta = 2.50$ ppm). The ^{13}C NMR chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : $\delta = 77.16$ ppm; $\text{DMSO}-d_6$: $\delta = 39.52$ ppm). Melting points were determined with XRC-1 and uncorrected. High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI).

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Thiophene 1,1-dioxide derivatives were prepared according to the literature procedures.¹⁵ Arylboronic acids were purchased from Energy Chemical. DCE, DMF, and DMSO were dried by refluxing over CaH_2 . Toluene and 1,4-dioxane were dried by refluxing over Na and freshly distilled prior to use.

General Procedure for Oxidative Cross-Coupling of Thiophene 1,1-Dioxides. A 10 mL-Schlenk tube was charged with thiophene 1,1-dioxide derivative **1** (0.2 mmol, 1.0 equiv), arylboronic acid **2** (0.6 mmol, 3.0 equiv), $\text{Pd}(\text{OAc})_2$ (4.4 mg, 10 mol %), $\text{Cu}(\text{OAc})_2$ (145 mg, 0.8 mmol, 4.0 equiv), pyridine (48 μL , 0.6 mmol, 3.0 equiv), and DMSO (1.0 mL) under a N_2 atmosphere. The resulting mixture was stirred at 100 $^\circ\text{C}$ for 20 h. Upon completion, the reaction mixture was diluted with 10 mL of H_2O and extracted with EtOAc (3 \times). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product.

2-Phenylbenzo[*b*]thiophene 1,1-Dioxide (3a).²⁰ The product was isolated by flash chromatography (petroleum ether/ $\text{EtOAc} = 5/1$, v/v) as a white solid, 82% yield. mp: 124–125 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): δ 7.85–7.83 (m, 2H), 7.77 (d, $J = 7.2$ Hz, 1H), 7.57 (td, $J = 7.8, 1.2$ Hz, 1H), 7.51–7.44 (m, 4H), 7.41 (d, $J = 7.2$ Hz, 1H), 7.30 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3): δ 142.7, 137.2, 133.9, 131.3, 130.5, 130.1, 129.4, 127.3, 126.7, 125.2, 123.8, 121.7. HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{11}\text{O}_2\text{S}$ [$\text{M} + \text{H}^+$], 243.0480; found, 243.0477.

2-(*p*-Tolyl)benzo[*b*]thiophene 1,1-Dioxide (3b).²¹ The product was isolated by flash chromatography (petroleum ether/ $\text{EtOAc} = 5/1$, v/v) as a white solid, 78% yield. mp: 150–151 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.75–7.70 (m, 3H), 7.57–7.53 (m, 1H), 7.49–7.45 (m, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.28 (s, 1H), 7.23 (d, $J = 10.8$ Hz, 2H), 2.39 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 142.8, 141.0, 137.2,

133.9, 131.5, 130.1, 129.8, 126.6, 125.0, 124.4, 122.7, 121.6, 21.7 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}^+$], 279.0456; found, 279.0455.

2-(*m*-Tolyl)benzo[*b*]thiophene 1,1-Dioxide (3c).²¹ The product was isolated by flash chromatography (petroleum ether/ $\text{EtOAc} = 5/1$, v/v) as a white solid, 75% yield. mp: 134–135 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): δ 7.76 (d, $J = 7.8$ Hz, 1H), 7.65 (s, 1H), 7.63 (d, $J = 7.8$ Hz, 1H), 7.57–7.53 (m, 1H), 7.52–7.47 (m, 1H), 7.40–7.35 (m, 2H), 7.27 (d, $J = 2.4$ Hz, 2H), 2.42 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 142.8, 139.1, 137.2, 133.8, 131.33, 131.31, 129.9, 129.2, 127.1, 125.1, 123.8, 123.6, 121.6, 21.6 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}^+$], 279.0456; found, 279.0450.

2-(3,4-Dimethylphenyl)benzo[*b*]thiophene 1,1-Dioxide (3d). The product was isolated by flash chromatography (petroleum ether/ $\text{EtOAc} = 5/1$, v/v) as a white solid, 73% yield. mp: 154–156 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): δ 7.74 (d, $J = 7.8$ Hz, 1H), 7.59 (s, 1H), 7.57–7.52 (m, 2H), 7.46 (td, $J = 7.2, 0.6$ Hz, 1H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.22–7.21 (m, 2H), 2.31 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 142.9, 139.7, 137.8, 137.2, 133.8, 131.5, 130.6, 129.7, 127.6, 124.9, 124.7, 124.2, 122.6, 121.5, 20.0 ppm. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{NaO}_2\text{S}$ [$\text{M} + \text{H}^+$], 293.0612; found, 293.0602.

2-(4-Ethylphenyl)benzo[*b*]thiophene 1,1-Dioxide (3e). The product was isolated by flash chromatography (petroleum ether/ $\text{EtOAc} = 5/1$, v/v) as a white solid, 73% yield. mp: 148–150 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 6.8$ Hz, 3H), 7.57–7.53 (m, 1H), 7.49–7.46 (m, 1H), 7.39 (d, $J = 7.2$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.24 (s, 1H), 2.70 (q, $J = 7.6$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 147.2, 142.8, 137.1, 133.9, 131.5, 129.8, 128.9, 126.7, 125.0, 124.6, 122.8, 121.6, 29.0, 15.5 ppm. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{S}$ [$\text{M} + \text{H}^+$], 271.0793; found, 271.0791.

2-(4-(*tert*-Butyl)phenyl)benzo[*b*]thiophene 1,1-Dioxide (3f).²¹ The product was isolated by flash chromatography (petroleum ether/ $\text{EtOAc} = 5/1$, v/v) as a white solid, 76% yield. mp: 186–187 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): δ 7.78 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 7.2$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.50–7.45 (m, 3H), 7.38 (d, $J = 7.8$ Hz, 1H), 7.25 (s, 1H), 1.34 (s, 9H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ

154.0, 142.7, 137.1, 133.8, 131.5, 129.8, 126.44, 126.38, 125.0, 124.4, 122.8, 121.5, 35.0, 31.2 ppm. HRMS (ESI): calcd for $C_{18}H_{19}O_2S$ $[M + H]^+$, 299.1106; found, 299.1112.

2-(4-Methoxyphenyl)benzo[b]thiophene 1,1-Dioxide (3g).²⁰ The product was isolated by flash chromatography (petroleum ether/EtOAc = 4/1, v/v) as a white solid, 68% yield. mp: 131–132 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.79–7.73 (m, 3H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.14 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 161.4, 142.5, 136.9, 133.9, 131.7, 129.5, 128.3, 124.8, 121.5, 121.4, 119.7, 114.9, 55.6 ppm. HRMS (ESI): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$, 273.0585; found, 273.0581.

2-(3-Methoxyphenyl)benzo[b]thiophene 1,1-Dioxide (3h). The product was isolated by flash chromatography (petroleum ether/EtOAc = 4/1, v/v) as a white solid, 65% yield. mp: 123–124 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.44–7.36 (m, 3H), 7.34 (s, 1H), 7.27 (s, 1H), 7.00–6.99 (m, 1H), 3.86 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 160.1, 142.6, 137.2, 133.9, 131.2, 130.5, 130.1, 128.5, 125.2, 124.2, 121.6, 119.2, 116.5, 111.8, 55.5 ppm. HRMS (ESI): calcd for $C_{15}H_{13}O_3S$ $[M + H]^+$, 273.0585; found, 273.0580.

2-(4-Fluorophenyl)benzo[b]thiophene 1,1-Dioxide (3i).²¹ The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 67% yield. mp: 164–165 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.22 (s, 1H), 7.16 (t, *J* = 8.4 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 163.9 (d, *J*_{C–F} = 253.2 Hz), 141.7, 136.9, 134.0, 131.2, 130.1, 128.8 (d, *J*_{C–F} = 8.7 Hz), 125.2, 123.7 (d, *J*_{C–F} = 2.0 Hz), 123.5 (d, *J*_{C–F} = 3.4 Hz), 121.7, 116.7 (d, *J*_{C–F} = 22.4 Hz) ppm. ¹⁹F NMR (377 MHz, CDCl₃): δ –108.7 ppm. HRMS (ESI): calcd for $C_{14}H_{10}FO_2S$ $[M + H]^+$, 261.0386; found, 261.0381.

2-(3,4-Difluorophenyl)benzo[b]thiophene 1,1-Dioxide (3j). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6/1, v/v) as a white solid, 64% yield. mp: 159–160 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.67–7.64 (m, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.30–7.27 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 152.1 (d, *J*_{C–F} = 132.6 Hz), 150.4 (d, *J*_{C–F} = 128.8 Hz), 140.7, 136.9, 134.1, 130.8, 130.5, 125.4, 124.9 (d, *J*_{C–F} = 1.7 Hz), 123.5 (d, *J*_{C–F} = 3.6 Hz), 123.4 (d, *J*_{C–F} = 3.8 Hz), 121.8, 118.5 (d, *J*_{C–F} = 18.0 Hz), 115.9 (d, *J*_{C–F} = 19.0 Hz) ppm. ¹⁹F NMR (565 MHz, CDCl₃): δ –133.3 (d, *J* = 21.5 Hz), –135.2 (d, *J* = 20.9 Hz) ppm. HRMS (ESI): calcd for $C_{14}H_9F_2O_2S$ $[M + H]^+$, 279.0291; found, 279.0286.

2-(4-(Trifluoromethyl)phenyl)benzo[b]thiophene 1,1-Dioxide (3k). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 63% yield. mp: 181–182 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 6.4 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 2H), 7.57 (m, 2H), 7.44 (d, *J* = 6.4 Hz, 1H), 7.40 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 141.3, 137.2, 134.1, 132.0 (q, *J*_{C–F} = 32.9 Hz), 130.7 (q, *J*_{C–F} = 2.1 Hz), 127.0, 126.3 (q, *J*_{C–F} = 3.7 Hz), 126.0, 125.6, 123.8 (q, *J*_{C–F} = 273.4 Hz), 121.8 ppm. ¹⁹F NMR (377 MHz, CDCl₃): δ –63.0 ppm. HRMS (ESI): calcd for $C_{15}H_{10}F_3O_2S$ $[M + H]^+$, 311.0354; found, 311.0348.

4-(1,1-Dioxidobenzo[b]thiophen-2-yl)benzotrinitrile (3l). The product was isolated by flash chromatography (petroleum

ether/EtOAc = 4/1, v/v) as a white solid, 60% yield. mp: 217–218 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.78 (m, 3H), 7.65–7.56 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.44 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 140.9, 137.2, 134.2, 133.0, 131.6, 131.1, 130.5, 127.1, 126.8, 125.8, 121.9, 118.3, 113.7, 29.8 ppm. HRMS (ESI): calcd for $C_{15}H_{10}NO_2S$ $[M + H]^+$, 268.0432; found, 268.0428.

1-(4-(1,1-Dioxidobenzo[b]thiophen-2-yl)phenyl)ethan-1-one (3m). The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid, 64% yield. mp: 160–161 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.43 (s, 1H), 2.64 (s, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 197.3, 141.7, 138.0, 137.3, 134.1, 131.5, 130.8, 129.2, 128.3, 126.8, 125.9, 125.6, 121.8, 26.9 ppm. HRMS (ESI): calcd for $C_{16}H_{13}O_3S$ $[M + H]^+$, 285.0585; found, 285.0578.

Methyl 4-(1,1-dioxidobenzo[b]thiophen-2-yl)benzoate (3n). The product was isolated by flash chromatography (petroleum ether/EtOAc = 3/1, v/v) as a white solid, 63% yield. mp: 187–188 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41–7.39 (m, 2H), 3.94 (s, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 166.3, 141.6, 137.2, 134.0, 131.5, 131.4, 130.8, 130.6, 130.4, 126.5, 125.8, 125.6, 121.7, 52.5 ppm. HRMS (ESI): calcd for $C_{16}H_{13}O_4S$ $[M + H]^+$, 301.0535; found, 301.0530.

[[1,1'-Biphenyl]-4-yl]benzo[b]thiophene 1,1-Dioxide (3o). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 77% yield. mp: 212–214 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.93–7.91 (m, 2H), 7.80–7.78 (m, 1H), 7.72–7.70 (m, 2H), 7.64–7.56 (m, 3H), 7.53–7.38 (m, 5H), 7.33 (s, 1H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 143.2, 142.5, 140.1, 137.2, 133.9, 131.4, 130.0, 129.1, 128.1, 128.0, 127.2, 127.1, 126.1, 125.2, 123.5, 121.7 ppm. HRMS (ESI): calcd for $C_{20}H_{15}O_2S$ $[M + H]^+$, 319.0793; found, 319.0787.

2-(Naphthalen-2-yl)benzo[b]thiophene 1,1-Dioxide (3p).²⁰ The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 70% yield. mp: 210–211 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.42 (s, 1H), 7.94 (m, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.82 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.74 (m, 1H), 7.55–7.52 (m, 3H), 7.49–7.47 (m, 1H), 7.38 (d, *J* = 7.2 Hz, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 142.6, 137.2, 133.9, 133.2, 131.3, 130.0, 129.3, 129.1, 127.9, 127.7, 127.1, 126.8, 125.2, 124.4, 123.8, 123.2, 121.6 ppm. HRMS (ESI): calcd for $C_{18}H_{12}NaO_2S$ $[M + Na]^+$, 315.0456; found, 315.0450.

2-(Naphthalen-1-yl)benzo[b]thiophene 1,1-Dioxide (3q). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 66% yield. mp: 204–205 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.16–8.12 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.94–7.89 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.61 (m, 1H), 7.58–7.53 (m, 4H), 7.46–7.44 (m, 1H), 7.23 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 141.8, 136.7, 134.0, 133.9, 132.3, 131.1, 130.8, 130.4, 129.7, 128.8, 128.0, 127.3, 126.6, 125.34, 125.29, 125.0, 124.6, 121.9 ppm. HRMS (ESI): calcd for $C_{18}H_{12}NaO_2S$ $[M + Na]^+$, 315.0456; found, 315.0455.

(E)-2-(3,3-Dimethylbut-1-en-1-yl)benzo[b]thiophene 1,1-Dioxide (3r). The product was isolated by flash chromatog-

raphy (petroleum ether/EtOAc = 5/1, v/v) as a colorless oil, 42% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.71 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.54–7.50 (m, 1H), 7.46–7.41 (m, 1H), 7.31–7.29 (m, 1H), 7.61 (m, 1H), 6.78–6.77 (m, 1H), 6.66 (dd, $J = 16.4$, 0.8 Hz, 1H), 6.14 (dd, $J = 16.4$, 0.8 Hz, 1H), 1.14 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 150.7, 142.1, 137.6, 133.7, 132.0, 129.5, 124.7, 123.4, 121.5, 112.4, 34.6, 29.2 ppm. HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 249.0949; found, 249.0942.

(*E*)-2-Styrylbenzo[*b*]thiophene 1,1-Dioxide (3s). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a colorless oil, 51% yield. ^1H NMR (600 MHz, CDCl_3): δ 7.75 (d, $J = 7.8$ Hz, 1H), 7.56–7.53 (m, 3H), 7.49–7.46 (m, 1H), 7.42 (d, $J = 16.2$ Hz, 1H), 7.40–7.32 (m, 4H), 6.95 (m, 1H), 6.90 (dd, $J = 16.8$, 0.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 141.9, 137.5, 136.3, 135.9, 133.9, 132.0, 129.8, 129.5, 129.0, 127.4, 125.1, 124.9, 121.6, 114.9 ppm. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$, 291.0456; found, 291.0453.

3-Methyl-2-phenylbenzo[*b*]thiophene 1,1-Dioxide (4a).²² The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 61% yield. mp: 150–151 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.78 (d, $J = 7.2$ Hz, 1H), 7.66–7.61 (m, 3H), 7.54–7.52 (m, 1H), 7.51–7.46 (m, 4H), 2.28 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 133.7, 136.3, 135.5, 133.7, 133.6, 129.9, 129.5, 129.1, 127.2, 122.4, 121.2, 12.2 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$, 279.0456; found, 279.0451.

5-Methyl-2-phenylbenzo[*b*]thiophene 1,1-Dioxide (4b).²³ The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 70% yield. mp: 164–167 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.83 (d, $J = 6.6$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.49–7.43 (m, 3H), 7.29 (d, $J = 7.8$ Hz, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 2.44 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 144.9, 143.0, 134.5, 131.6, 130.5, 130.4, 129.3, 127.4, 126.7, 125.9, 123.9, 121.5, 21.9 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$, 279.0456; found, 279.0450.

6-Methyl-2-phenylbenzo[*b*]thiophene 1,1-Dioxide (4c). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 75% yield. mp: 185–187 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.83–7.81 (m, 2H), 7.58 (s, 1H), 7.48–7.42 (m, 3H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.26 (s, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 141.9, 141.0, 137.4, 134.4, 130.2, 129.3, 128.6, 127.5, 126.6, 124.9, 123.9, 122.2, 21.7 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$, 279.0456; found, 279.0455.

5-(*tert*-Butyl)-2-phenylbenzo[*b*]thiophene 1,1-Dioxide (4d).²³ The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 69% yield. mp: 181–182 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 8.4$ Hz, 1H), 7.39–7.33 (m, 4H), 7.23 (t, $J = 7.2$ Hz, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 5.89 (s, 1H), 1.26 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 157.5, 136.8, 132.5, 129.4, 128.9, 128.8, 128.4, 127.7, 126.6, 122.2, 121.5, 35.14, 31.2 ppm. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 299.1106; found, 299.1102.

5-Methoxy-2-phenylbenzo[*b*]thiophene 1,1-Dioxide (4e). The product was isolated by flash chromatography (petroleum ether/EtOAc = 4/1, v/v) as a white solid, 66% yield. mp: 157–158 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.81–7.78 (m, 2H), 7.49–7.40 (m, 3H), 7.32 (m, 2H), 7.25 (s, 1H), 7.05 (m, 1H),

3.90 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 161.6, 141.3, 138.9, 130.0, 129.3, 127.6, 126.4, 126.2, 124.0, 123.5, 119.5, 107.5, 56.2 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$, 273.0585; found, 273.0581.

2-Phenylbenzo[*b*]thiophene-5-carbonitrile 1,1-Dioxide (4f). The product was isolated by flash chromatography (petroleum ether/EtOAc = 4/1, v/v) as a white solid, 55% yield. mp: 206–207 °C. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 8.24 (d, $J = 8.4$ Hz, 1H), 8.15 (d, $J = 7.2$ Hz, 2H), 8.04 (s, 1H), 7.89–7.87 (m, 2H), 7.62–7.56 (m, 3H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ 142.0, 139.6, 134.8, 131.7, 130.9, 129.5, 129.2, 126.4, 126.3, 123.8, 122.4, 117.4, 116.8, 99.5 ppm. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{10}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 268.0432; found, 268.0427.

Ethyl 2-phenylbenzo[*b*]thiophene-4-carboxylate 1,1-Dioxide (4g). The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as a white solid, 60% yield. mp: 187–188 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.39 (s, 1H), 8.21 (d, $J = 7.8$ Hz, 1H), 7.92 (d, $J = 7.2$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.50–7.49 (m, 3H), 4.46 (q, $J = 7.2$ Hz, 2H), 1.46 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 165.0, 143.8, 138.5, 135.2, 132.4, 130.9, 129.6, 129.4, 127.2, 127.0, 125.9, 125.0, 123.1, 62.0, 14.4 ppm. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{15}\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$, 315.0691; found, 315.0694.

2,5-Diphenylbenzo[*b*]thiophene 1,1-Dioxide (4h). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 76% yield. mp: 147–148 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.87–7.84 (m, 2H), 7.82 (d, $J = 8$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.61–7.58 (m, 3H), 7.52–7.42 (m, 6H), 7.34 (s, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 147.3, 143.4, 139.3, 135.7, 132.1, 130.5, 129.4, 129.3, 128.9, 128.7, 127.4, 127.3, 126.8, 123.9, 123.7, 122.0 ppm. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{15}\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 319.0793; found, 319.0781.

2-(4-(Diphenylamino)phenyl)benzo[*b*]thiophene 1,1-Dioxide (5a).²⁴ The product was isolated by flash chromatography (petroleum ether/EtOAc = 10/1, v/v) as a yellow solid, 61% yield. mp: 198–199 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.74 (d, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 8.8$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 4H), 7.16–7.08 (m, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 149.9, 146.9, 142.6, 137.0, 133.8, 131.9, 129.7, 129.4, 127.6, 125.6, 124.7, 124.3, 122.0, 121.6, 120.7, 119.8 ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{19}\text{NNaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$, 432.1034; found, 432.1031.

3-(4-(Bis(4-methoxyphenyl)amino)phenyl)benzo[*b*]thiophene 1,1-Dioxide (5b). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6/1, v/v) as a yellow solid, 63% yield. mp: 216–218 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.11–7.06 (m, 5H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 4H), 3.81 (s, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 156.8, 136.9, 133.8, 132.1, 129.1, 127.5, 124.5, 121.5, 119.6, 119.1, 115.0, 55.6 ppm. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{24}\text{NO}_4\text{S}$ [$\text{M} + \text{H}$] $^+$, 470.1426; found, 470.1421.

2-(9-Phenyl-9H-carbazol-3-yl)benzo[*b*]thiophene 1,1-Dioxide (5c). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 55% yield. mp: 210 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.65 (d, $J = 1.6$ Hz, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.79 (d, $J = 7.2$ Hz, 1H), 7.65–7.61 (m, 2H), 7.57–7.43 (m,

7H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.36–7.32 (m, 1H), 7.29 (s, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 143.6, 141.9, 141.6, 137.2, 137.0, 133.8, 132.0, 130.2, 129.4, 128.1, 127.2, 126.9, 124.7, 124.67, 124.1, 123.2, 121.6, 121.4, 120.97, 120.86, 119.2, 119.1, 110.8, 110.3 ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{17}\text{NNaO}_2\text{S} [\text{M} + \text{Na}]^+$, 430.0878; found, 430.0872.

2-(4-(9H-Carbazol-9-yl)phenyl)benzo[*b*]thiophene 1,1-Dioxide (5d).²⁵ The product was isolated by flash chromatography (petroleum ether/EtOAc = 6/1, v/v) as a green solid, 58% yield. mp: 194–196 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.16 (d, $J = 7.2$ Hz, 2H), 8.09 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 7.2$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.50–7.43 (m, 5H), 7.39 (s, 1H), 7.32 (t, $J = 7.4$ Hz, 2H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 142.0, 140.5, 139.7, 137.2, 134.1, 131.2, 130.3, 128.3, 127.6, 126.3, 126.0, 125.3, 124.2, 123.9, 121.8, 120.60, 120.56, 109.9 ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{17}\text{NNaO}_2\text{S} [\text{M} + \text{Na}]^+$, 430.0878; found, 430.0867.

2,3-Diphenylbenzo[*b*]thiophene 1,1-Dioxide (5e).⁴ The product was isolated by flash chromatography (petroleum ether/EtOAc = 5/1, v/v) as a white solid, 60% yield. mp: 147 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.88–7.84 (m, 1H), 7.57–7.52 (m, 2H), 7.50–7.41 (m, 5H), 7.36–7.27 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 138.2, 137.6, 136.5, 133.6, 133.4, 131.0, 130.2, 129.8, 129.6, 129.5, 129.3, 129.2, 128.9, 127.2, 124.3, 121.7 ppm. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{15}\text{O}_2\text{S} [\text{M} + \text{H}]^+$, 319.0793; found, 319.0787.

(4-(Diphenylamino)phenyl)-3-phenylbenzo[*b*]thiophene 1,1-Dioxide (5f). The product was isolated by flash chromatography (petroleum ether/EtOAc = 15/1, v/v) as a yellow solid, 60% yield. mp: 216–218 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.84–7.82 (m, 1H), 7.53–7.42 (m, 5H), 7.38–7.31 (m, 4H), 7.28–7.24 (m, 4H), 7.22–7.20 (m, 1H), 7.11–7.05 (m, 6H), 6.88 (d, $J = 8.4$ Hz, 2H) ppm. ^{13}C NMR (151 MHz, CDCl_3): δ 149.1, 146.9, 137.4, 136.2, 135.5, 134.0, 133.6, 131.8, 130.0, 129.59, 129.56, 129.4, 129.1, 125.7, 124.2, 123.9, 121.5, 121.2, 119.5 ppm. HRMS (ESI): calcd for $\text{C}_{32}\text{H}_{24}\text{NO}_2\text{S} [\text{M} + \text{H}]^+$, 486.1528; found, 486.1522.

Procedure for Oxidative Cross-Coupling of Bis-Sulfone 1l with Phenylboronic Acid 2a. A 10 mL-Schlenk tube was charged with 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide **1l** (102 mg, 0.2 mmol, 1.0 equiv), phenylboronic acid **2a** (146 mg, 1.2 mmol, 6.0 equiv), $\text{Pd}(\text{OAc})_2$ (4.4 mg, 10 mol %), $\text{Cu}(\text{OAc})_2$ (145 mg, 0.8 mmol, 4.0 equiv), pyridine (48 μL , 0.6 mmol, 3.0 equiv), and DMSO (2.0 mL) under a N_2 atmosphere. The resulting mixture was stirred at 100 °C for 20 h. Upon completion, the reaction mixture was diluted with 10 mL of H_2O and extracted with EtOAc (3 \times). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) to provide the desired 4,8-bis((2-ethylhexyl)oxy)-2,6-diphenylbenzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide **6** in 55% yield. mp: 231–232 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.84–7.81 (m, 4H), 7.53–7.49 (m, 6H), 7.44 (s, 2H), 7.26 (s, 2H), 4.44 (d, $J = 5.6$ Hz, 4H), 1.91–1.85 (m, 2H), 1.69–1.46 (m, 9H), 1.41–1.36 (m, 7H), 1.02 (t, $J = 7.6$ Hz, 6H), 0.94 (t, $J = 7.2$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 145.3, 142.8, 131.7, 130.9, 129.5, 127.6, 127.0, 126.9, 118.4, 40.6, 30.4, 29.2, 23.9, 23.2, 14.2, 11.3 ppm. HRMS (ESI): calcd for $\text{C}_{38}\text{H}_{47}\text{O}_6\text{S}_2 [\text{M} + \text{H}]^+$, 663.2814; found, 663.2808.

Procedure for the Synthesis of Triphenylboroxine Pyridine Complex 7.^{18a,b} To a solution of $\text{PhB}(\text{OH})_2$ (1.22 g, 10 mmol) in THF (30 mL) was added pyridine (0.80 mL, 10 mmol) at room temperature. The mixture was stirred at 100 °C for 5 h before the THF was removed by distillation under reduced pressure. The crude product was purified via recrystallization (hexane– CH_2Cl_2), providing product **7** in 92% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.08–9.06 (m, 2H), 8.11–8.09 (m, 6H), 7.99–7.95 (m, 1H), 7.61–7.57 (m, 2H), 7.44–7.41 (m, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 143.9, 140.9, 133.8, 129.8, 127.68, 125.7 ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{24}\text{B}_3\text{N}_2\text{O}_3 [\text{M} + \text{NH}_4]^+$, 409.2066; found, 409.2081.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c08334>.

Experimental procedures, characterization data, X-ray data, and copies of NMR (PDF)

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Notes

The authors declare no competing financial interest.

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