

Palladium-Catalyzed C2-Selective Oxidative Olefination of Benzo[*b*]thiophene 1,1-Dioxides with Styrenes and Acrylates

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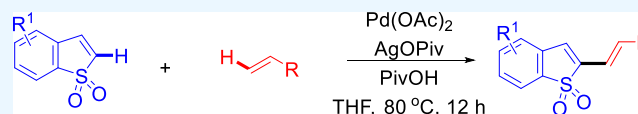


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ABSTRACT: Here, we disclose a novel Pd(II)-catalyzed oxidative Heck reaction of benzo[*b*]thiophene 1,1-dioxides with styrenes and acrylates. This transformation features broad functional group tolerance and high C2 selectivity. Furthermore, the photoluminescence properties of C-2 alkenylated products have been characterized, which illustrates the potential usefulness of our protocol in constructing π -conjugated fluorescent molecules.



INTRODUCTION

Thiophenes are the most popular structural motifs of luminescent materials for optoelectronic devices due to the rich π -electrons and high aromaticity.¹ Thiophene 1,1-dioxide is a good electron-withdrawing group, which has been introduced into thiophene-based materials to improve photo-physical properties.² For example, Barbarella and co-workers first demonstrated that oxidizing conjugated oligothiophenes to thiophene 1,1-dioxides will reduce the highest occupied molecular orbital–least unoccupied molecular orbital (HOMO–LUMO) band gap value and enhance photoluminescence efficiency.^{3,4} Dibenzothiophene 1,1-dioxide unit was incorporated into the chain of oligofluorenes, showing high luminescence efficiency,^{5a} strong solvatochromism,^{5b} and dual fluorescence.^{5c} 2,3-Diaryl-substituted benzo[*b*]thiophene 1,1-dioxides represented a new aggregation-induced emission platform.⁶ Thus, the synthesis and modification of various thiophene 1,1-dioxides have attracted significant attention of synthetic chemists.

Traditional methods for the synthesis of thiophene 1,1-dioxides contain oxidation of thiophenes,^{6,7} Diels–Alder reactions,⁸ and C–X/C–M (M = Sn and B) cross-couplings.⁹ Recently, transition-metal-catalyzed oxidative C–H activation has been one of the most powerful tools in organic synthesis.¹⁰ However, catalytic functionalization of thiophene 1,1-dioxides via C–H activation strategy is highly rare. Nelson¹¹ and Farinola¹² reported Cu- and Pd-catalyzed C–H activation/arylation of benzodithiophene *S,S*-tetraoxides with aryl iodides for the preparation of extended heteroaromatic conjugated molecules, respectively (Scheme 1a). In 2019, *N*-chelator-directed diastereoselective oxidative annulation of benzo[*b*]thiophene 1,1-dioxides with amino quinolinamides via double C–H activation was developed by Nicholls and co-workers (Scheme 1b).¹³ Very recently, Parthasarathy achieved *N*-pyridinyl-assisted oxidative cross-dehydrogenative coupling of *N*-pyridinylindoles with benzo[*b*]thiophene 1,1-dioxides (Scheme 1c).¹⁴ Herein, we would like to report a novel

palladium-catalyzed C2-selective oxidative olefination of benzo[*b*]thiophene 1,1-dioxides with alkenes (Scheme 1d).

RESULTS AND DISCUSSION

Our study commenced with the oxidative Heck reaction of benzo[*b*]thiophene 1,1-dioxide **1a** with styrene **2a** as the model reaction to optimize the reaction conditions. Initially, (*E*)-2-styrylbenzo[*b*]thiophene 1,1-dioxide **3a** was generated in 37% yield in the presence of 5 mol % of Pd(OAc)₂ and 3.0 equiv of AgOAc using 1.0 mL of AcOH as the solvent at 100 °C for 24 h (Table S1, entry 1). At the same time, a trace amount of homo-coupling product from benzo[*b*]thiophene 1,1-dioxide **1a** and nonisolated complex mixture was obtained as byproducts. Compound **3a** was further testified by X-ray crystallographic analysis.¹⁵ Other Pd(II) catalysts such as PdCl₂ and Pd(TFA)₂ gave lower yields (Table S1, entries 2 and 3). Among various oxidants including Ag(I) salts, Cu(OAc)₂, K₂S₂O₈, and BQ examined, AgOAc was the most effective (Table S1, entries 4–8). Using PivOH instead of AcOH, the yield of **3a** was increased to 71% (Table S1, entries 9–11). Further screenings showed that **3a** can be obtained in 87% yield in the presence of 2 mL of PivOH as solvent at 80 °C (Table S1, entries 12–17). The addition of a great quantity of acid brought trouble to post-processing. To our delight, the oxidative Heck reaction could occur with 5 equiv of PivOH in some common solvents (Table 1). Among various solvents examined, tetrahydrofuran (THF) was superior to toluene, 1,2-dichloroethane, 1,4-dioxane, DMSO, DMF, isopropanol, and methyl *tert*-butyl ether (Table 1, entries 1–8). This transformation afforded **3a** in 88% yield when AgOAc was changed

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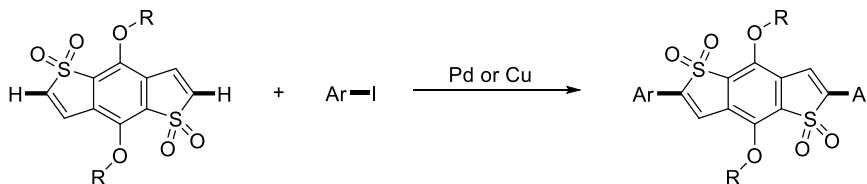
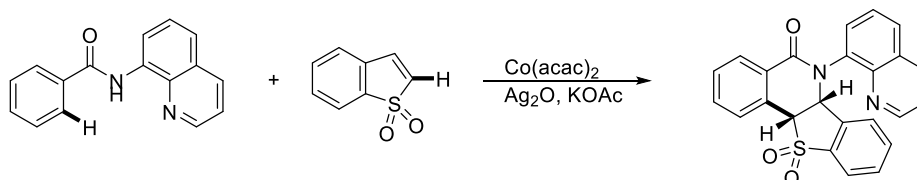
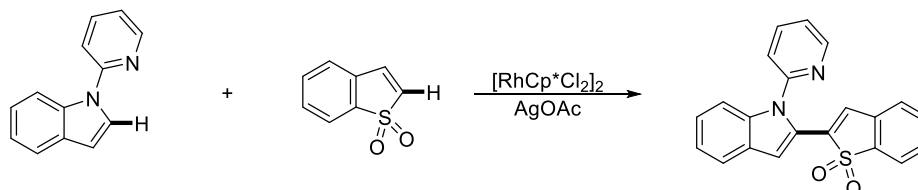
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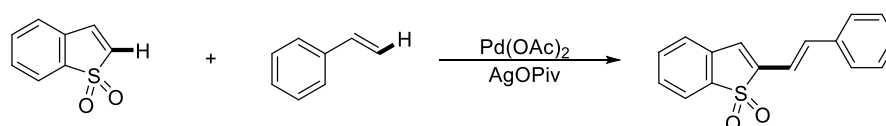
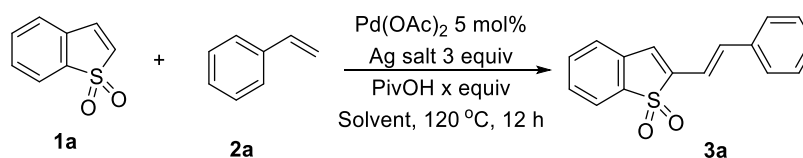


Scheme 1. Evolution of Transition-Metal-Catalyzed C–H Activation/Functionalization of Thiophene 1,1-Dioxides

Previous work:

(a) Pd or Cu-catalyzed arylation of benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxides with aryl iodides(b) Co-catalyzed diastereoselective oxidative annulation of benzo[*b*]thiophene 1,1-dioxides(c) Rh(III)-catalyzed coupling of *N*-pyridinylindoles with benzo[*b*]thiophene 1,1-dioxides

This work:

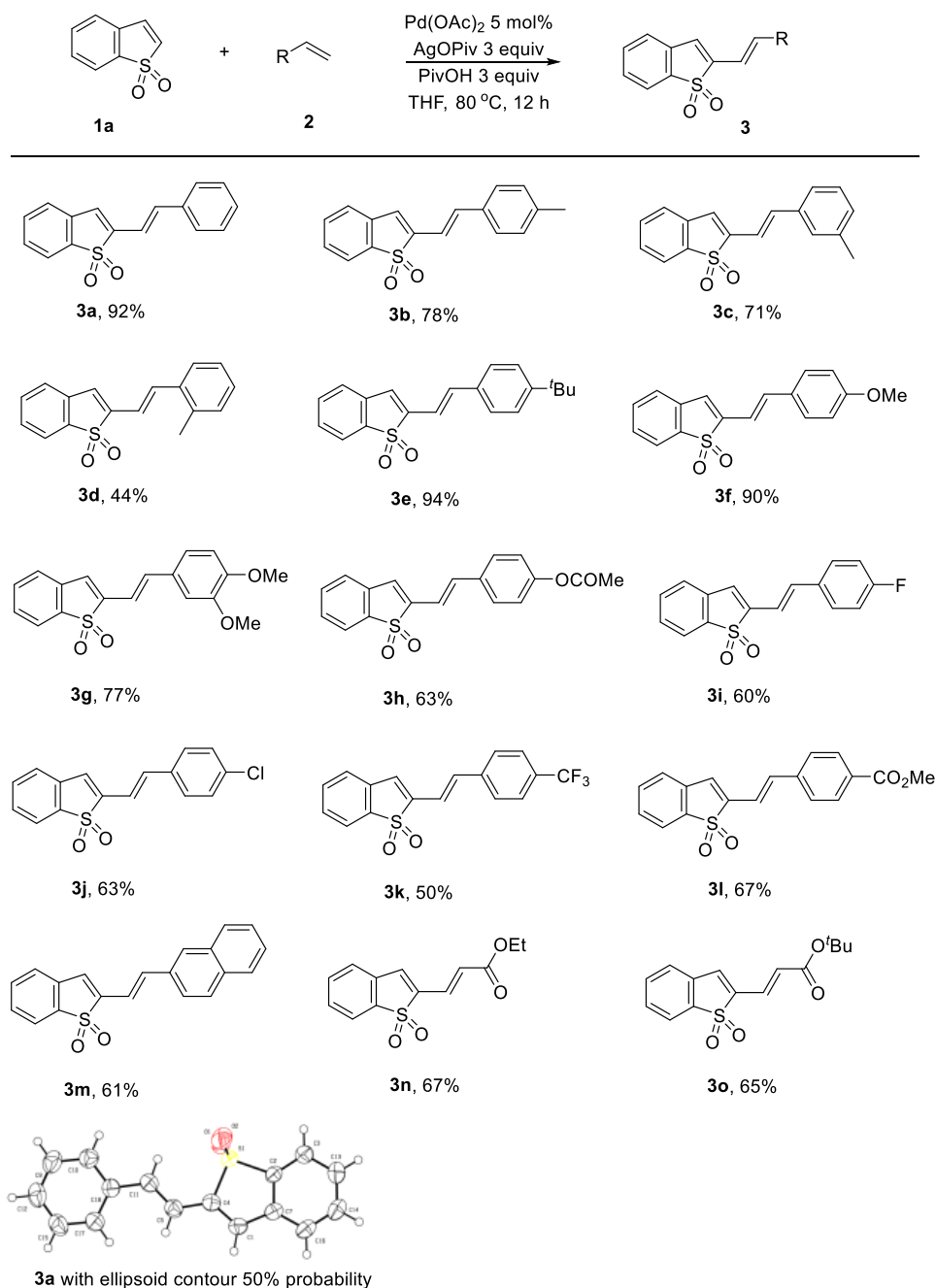
(d) Pd-catalyzed oxidative olefination of benzo[*b*]thiophene 1,1-dioxides with alkenesTable 1. Optimization of Pd(II)-Catalyzed Oxidative Heck Reaction^a

entry	Ag salt	solvent	<i>x</i>	yield (%) ^b
1	AgOAc	toluene	5.0	45
2	AgOAc	DCE	5.0	71
3	AgOAc	1,4-dioxane	5.0	63
4	AgOAc	DMSO	5.0	nr
5	AgOAc	IPA	5.0	nr
6	AgOAc	DMF	5.0	34
7	AgOAc	THF	5.0	78
8	AgOAc	MTBE	5.0	22
9	AgOPiv	THF	5.0	88
10	AgOPiv	THF	3.0	92
11 ^c	AgOPiv	THF	3.0	95
12	AgOPiv	THF	1.0	65

^aReaction conditions: **1a** (0.1 mmol), styrene **2a** (0.15 mmol, 1.5 equiv), Pd(OAc)₂ (5 mol %), Ag salt (3.0 equiv), and PivOH (*x* equiv) in solvent (0.6 mL) at 120 °C for 12 h. ^bGC yields. ^cAt 80 °C. DCE = 1,2-dichloroethane, DMSO = dimethyl sulfoxide, IPA = isopropanol, DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran, MTBE = methyl *tert*-butyl ether.

to AgOPiv (Table 1, entry 9). Further optimization decreased the amount of PivOH to 3.0 equiv with a lower temperature (Table 1, entries 10 and 11). When the amount of PivOH was

further decreased to 1.0 equiv, only 65% yield of **3a** was obtained (Table 1, entry 12). The result indicated that redundant AgOPiv might assist in accelerating the metalation

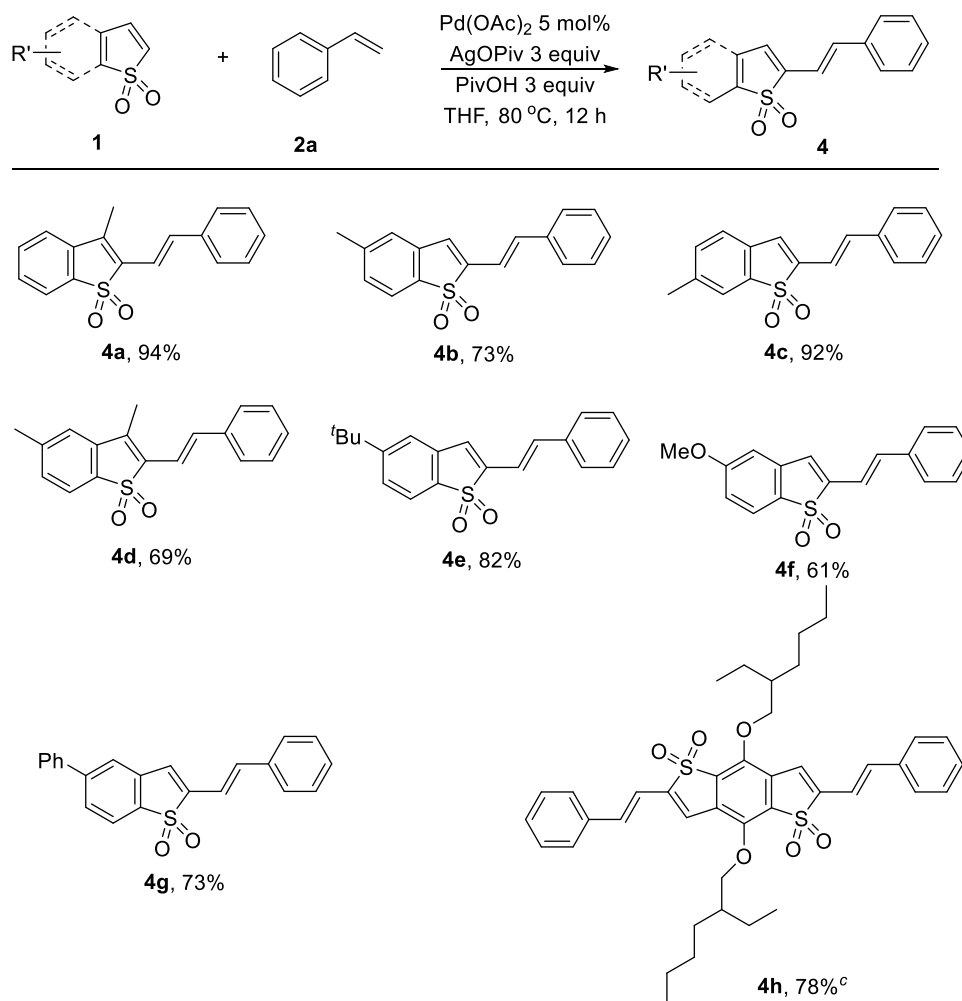
Scheme 2. Scope of Alkenes^{a,b}

^aReactions were performed with benzo[*b*]thiophene 1,1-dioxide **1a** (0.20 mmol), and alkenes **2** (0.30 mmol) in 1.2 mL of THF. ^bYields of isolated products.

process.^{10d} In addition, 15% yield of **3a** was obtained, when benzo[*b*]thiophene 1,1-dioxide **1a** reacted with styrene **2a** under the reported condition of the Heck reaction of thiophenes.¹⁶ Finally, the yield of **3a** can reach 95% under the optimized reaction condition comprising Pd(OAc)₂ (5 mol %), AgOPiv (3.0 equiv), and PivOH (3.0 equiv) in THF solution at 80 °C for 12 h.

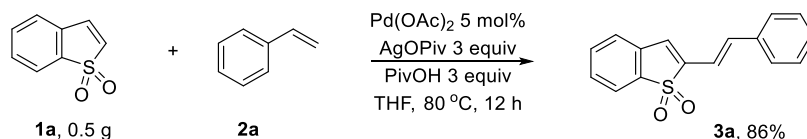
With the optimal conditions in hand, we next investigated the scope of this oxidative Heck reaction. As summarized in Scheme 2, various styrene derivatives possessing electron-donating groups such as methyl, methoxy, *tert*-butyl, and acetoxyl on the aryl moiety smoothly coupled with benzo[*b*]thiophene 1,1-dioxide **1a**, affording the desired products in

good to excellent yields (**3b–3h**). 1-Methyl-2-vinylbenzene reacted with **1a** to give the corresponding alkenylated products in only 44% yield (**3d**), which implied that steric effect diminishes the reactivity of styrenes. Styrenes with electron-withdrawing substituents (halide, trifluoromethyl, and ester groups) can be also tolerated in the oxidative Heck reaction, but only moderate yields were obtained (**3i–3l**). Moreover, 2-vinylnaphthalene underwent this transformation in 61% yield (**3m**). Acrylates were investigated under standard conditions, and the desired products were obtained in moderate yields (**3n** and **3o**). It is worth noting that aliphatic olefins, cyclic alkenes, and α - or β -substituted styrenes were limited in the oxidative

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

^aReactions were performed with benzo[*b*]thiophene 1,1-dioxides **1** (0.20 mmol), and styrene **2a** (0.30 mmol) in 1.2 mL of THF. ^bYields of isolated products. ^c**2a** (0.6 mmol) was used.

Scheme 4. Gram-Scale Reaction



Heck transformation, and extremely complex mixtures were obtained as a result.

Subsequently, the scope of benzo[*b*]thiophene 1,1-dioxide derivatives was examined. Benzo[*b*]thiophene 1,1-dioxides with various substituents were compatible with this palladium-catalyzed oxidative Heck reaction in good to excellent yields (Scheme 3). 3-Methylbenzo[*b*]thiophene 1,1-dioxide reacted with **2a** to afford the desired product in satisfactory yields, which revealed that steric effect had no obvious influence on the reactivity of the benzo[*b*]thiophene 1,1-dioxides (**4a** and **4d**). Bis sulfone substrate was investigated with 3.0 equiv of styrene **2a**, and bis alkenylated product **4h** was obtained in 78% yield. This result showed a positive outlook of this oxidative Heck reaction in the synthesis of new functional materials because both the bis thiophenes and bis sulfones are core skeletons in numerous photoelectric material molecules. A great deal of effort tried to realize the olefination

of thiophene 1,1-dioxide. However, thiophene 1,1-dioxides were instable even at <−40 °C and can be easily transformed to dimers along with the liberation of SO₂.¹⁷

Next, the gram-scale reaction of benzo[*b*]thiophene 1,1-dioxide **1a** with styrene **2a** was carried out under standard conditions to assess the practical synthetic utility of this oxidative olefination method (Scheme 4). The desired product **3a** was isolated in up to 86% yield from the scale-up reaction.

To evaluate the potential usefulness of our protocol in constructing thiophene 1,1-dioxides-alkenes-type π -conjugated skeletons for the screening of fluorescent molecules, we characterized the photophysical properties of several alkenylated products. As shown in Figure 1a, ultraviolet–visible (UV–vis) spectra of **3a**, **3f**, and **3g** in dichloromethane solutions gave the absorption maxima from 363 to 389 nm. The absorption spectra of bis alkenylated product **4h** are red-shifted obviously due to the expansion of π -conjugated system

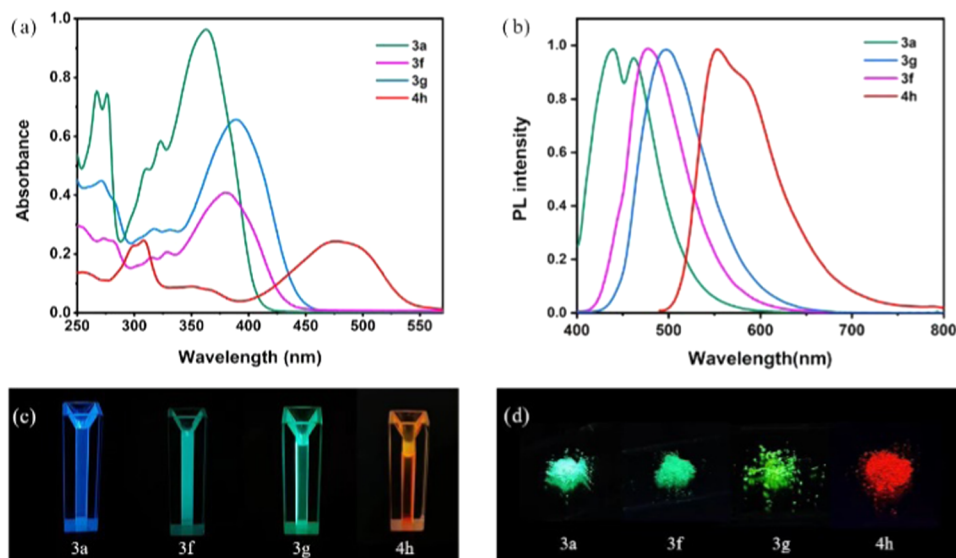
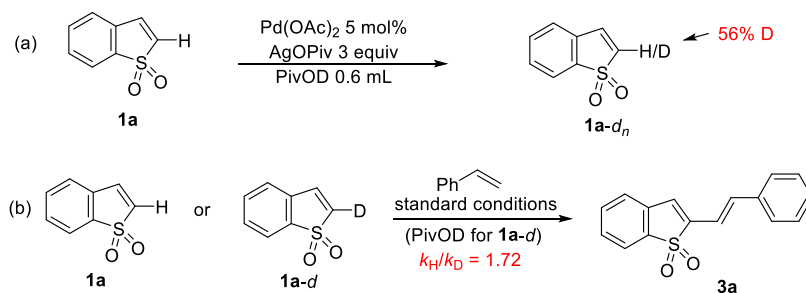


Figure 1. (a, b) Absorption and emission spectra, respectively. (c, d) Fluorescence images in DCM (CH_2Cl_2) under UV light ($\lambda_{\text{exc}} = 365 \text{ nm}$) and in the solid state, respectively.

Scheme 5. Deuterium-Labeling Experiments^a



^a(a) Hydrogen/deuterium exchange experiment. (b) Kinetic isotopic experiment.

and the introduction of electron-donating alkoxy group. In addition, all of the products exhibited significant fluorescence emission in both DCM solution and the solid state (Figure 1b–d).

To gain preliminary insight into the mechanism of the oxidative Heck reaction, we carried out some deuterium-labeling experiments (Scheme 5). The hydrogen/deuterium exchange experiment indicated that the C2 position of C–H bond cleavage was a reversible process (Scheme 5a). The parallel competition reactions between **1a** and **1a-d** with styrene **2a** resulted in a primary kinetic isotopic effect ($k_{\text{H}}/k_{\text{D}} = 1.72$) (Scheme 5b), exhibiting that the C–H bond cleavage might be related to the rate-determining step.¹⁸

Based on the above experiments and reported Pd(II)-catalyzed C–H bond oxidative Heck reaction,¹⁹ a plausible mechanism was proposed (Scheme 6). First, reversible C–H activation of benzo[*b*]thiophene 1,1-dioxide **1a** with Pd(II) afforded the intermediate **IM1**. Next, **IM1** coordinated with styrene **2a** to form **IM2**, which was transformed to intermediate **IM3** via a migratory insertion process. **IM3** underwent β -hydride elimination to release the desired product **3a** and Pd(II)H species. Finally, a reductive elimination of Pd(II)H species resulted in Pd(0) species, which then was reoxidized to active Pd(II) catalyst by AgOPiv to complete the catalytic cycle.

CONCLUSIONS

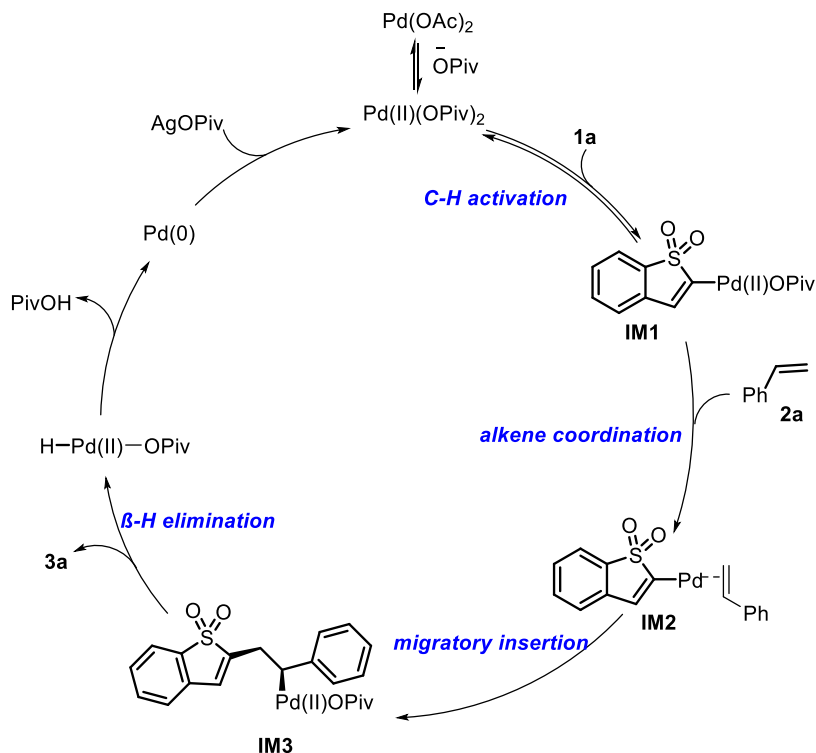
In conclusion, we have disclosed the first Pd(II)-catalyzed C2-selective oxidative alkenylation of benzo[*b*]thiophene 1,1-dioxides and with alkenes via direct C–H bond activation strategy. This oxidative cross-coupling tolerates various benzo[*b*]thiophene 1,1-dioxides and benzodithiophene *S,S*-tetraoxides substrates with broad functional group tolerance. In addition, the photophysical properties of several alkenylated products were investigated, which indicate the potential usefulness of our protocol in constructing thiophene 1,1-dioxide-alkene-type π -conjugated skeletons.

EXPERIMENTAL SECTION

General. NMR spectra were obtained on Bruker AV-400 MHz and AV-600 MHz spectrometers. The ¹H NMR chemical shifts were measured relative to CDCl_3 or $\text{DMSO-}d_6$ as the internal reference (CDCl_3 : $\delta = 7.26 \text{ ppm}$; $\text{DMSO-}d_6$: $\delta = 2.50 \text{ ppm}$). The ¹³C NMR chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : $\delta = 77.16 \text{ ppm}$; $\text{DMSO-}d_6$: $\delta = 39.52 \text{ ppm}$). 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.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. PivOD (>95% deuterium incorporation by ¹H NMR

Scheme 6. Plausible Mechanistic Pathway



analysis)²⁰ and 2-deuterated benzo[*b*]thiophene (>95% deuterium incorporation by ¹H NMR analysis)²¹ were prepared according to the literature procedures. Ultradry solvents including *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropanol (IPA), 1,2-dichloroethane (DCE), and 1,4-dioxane were purchased from J&K Scientific. Tetrahydrofuran (THF) and methyl *tert*-butyl ether (MTBE) were dried by refluxing over Na and freshly distilled prior to use.

General Procedure for the Preparation of Benzo[*b*]thiophene 1,1-Dioxides.²² H₂O₂ (30%, 6.5 equiv) was slowly added to the solution of benzo[*b*]thiophene (10 mmol) in 11 mL of AcOH. The mixture was stirred at 100 °C for 1.5 h. After cooling to room temperature, the reaction mixture was treated with saturated aqueous NaHCO₃ solution, and the pH was adjusted to 7. The resulting mixture was extracted with DCM (20 mL × 3), washed with brine, and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give the corresponding product.

3-Methylbenzo[*b*]thiophene 1,1-Dioxide (1b). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a white solid. 68% yield. Mp: 115–116 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.73–7.70 (m, 1H), 7.62–7.52 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 6.47 (q, *J* = 1.6 Hz, 1H), 2.28 (d, *J* = 1.6 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 143.0, 137.7, 133.6, 133.3, 130.6, 125.9, 122.4, 121.1, 14.0 ppm. IR (cm⁻¹): 3082, 2921, 2851, 1593, 1440, 1286, 1177, 1106, 832, 765, 606. HRMS (ESI): calcd for C₉H₉O₂S [M + H]⁺ 181.0323, found 181.0313.

5-Methylbenzo[*b*]thiophene 1,1-Dioxide (1c). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a white solid. 74% yield. Mp: 118–119 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, *J* = 7.6 Hz, 1H), 7.32

(d, *J* = 7.6 Hz, 1H), 7.17–7.16 (m, 2H), 6.69 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 144.8, 134.1, 132.5, 131.7, 131.3, 131.1, 126.2, 121.4, 21.8 ppm. IR (cm⁻¹): 3092, 1557, 1288, 1168, 1134, 852, 820, 763, 696, 622. HRMS (ESI): calcd for C₉H₉O₂S [M + H]⁺ 181.0323, found 181.0317.

6-Methylbenzo[*b*]thiophene 1,1-Dioxide (1d). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a white solid. 70% yield. Mp: 123–125 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 6.8 Hz, 1H), 2.44 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 141.9, 137.0, 134.2, 132.5, 129.9, 128.7, 125.2, 122.2, 21.6 ppm. IR (cm⁻¹): 3078, 2923, 2849, 1543, 1282, 1199, 1144, 1063, 819, 742, 632. HRMS (ESI): calcd for C₉H₉O₂S [M + H]⁺ 181.0323, found 181.0328.

3,5-Dimethylbenzo[*b*]thiophene 1,1-Dioxide (1e). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a white solid. 65% yield. Mp: 138–140 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.54 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 6.41 (d, *J* = 2.0 Hz, 1H), 2.42 (s, 3H), 2.21 (d, *J* = 1.6 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 144.5, 143.0, 134.8, 133.4, 130.7, 126.1, 123.1, 120.7, 21.8, 13.8 ppm. IR (cm⁻¹): 3082, 2920, 2851, 1578, 1285, 1177, 1107, 832, 765, 606. HRMS (ESI): calcd for C₁₀H₁₁O₂S [M + H]⁺ 195.0480, found 195.0488.

5-(*tert*-Butyl)benzo[*b*]thiophene 1,1-Dioxide (1f). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a white solid. 60% yield. Mp: 76–77 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.36 (s, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 6.8 Hz, 1H), 1.34 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 158.1, 134.1, 132.8, 131.6, 131.0, 127.8, 122.9, 121.3, 35.5, 31.2 ppm. IR (cm⁻¹): 3086, 2962, 2362, 1552, 1323, 1294, 1190, 1138, 854, 697, 608. HRMS

(ESI): calcd for $C_{12}H_{15}O_2S$ $[M + H]^+$ 223.0793, found 223.0790.

5-Methoxybenzo[b]thiophene 1,1-Dioxide (1g). The product was isolated by flash chromatography (petroleum ether/EtOAc = 4:1, v/v) as a white solid. 55% yield. Mp: 125–126 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.25 (m, 2H), 7.17 (dd, J = 6.8, 0.8 Hz, 1H), 7.02 (dd, J = 8.4, 2.4 Hz, 1H), 6.61 (d, J = 6.8 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 138.6, 132.6, 129.0, 126.4, 123.4, 118.9, 107.7, 56.2 ppm. IR (cm^{-1}): 3077, 2960, 2360, 1589, 1280, 1251, 1183, 1146, 771, 760, 635. HRMS (ESI): calcd for $C_9H_9O_3S$ $[M + H]^+$ 197.0272, found 197.0260.

5-Phenylbenzo[b]thiophene 1,1-Dioxide (1h). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a white solid. 80% yield. Mp: 148–150 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.58–7.55 (m, 3H), 7.51–7.44 (m, 3H), 7.27 (d, J = 6.8 Hz, 1H), 6.76 (d, J = 6.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.3, 139.1, 135.3, 132.4, 132.2, 131.4, 129.5, 129.3, 128.9, 127.4, 124.3, 121.9 ppm. IR (cm^{-1}): 3067, 2961, 2361, 1603, 1280, 1163, 1101, 782, 768, 743, 630. HRMS (ESI): calcd for $C_{14}H_{11}O_2S$ $[M + H]^+$ 243.0480, found 243.0471.

Preparation of 4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene 1,1,5,5-Tetraoxide (1i). H_2O_2 (30%, 13 equiv) was slowly added to the solution of 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (5 mmol) in 6 mL of AcOH. The mixture was stirred at 100 °C for 1.5 h. After cooling to room temperature, the reaction mixture was treated with saturated aqueous $NaHCO_3$ solution, and the pH was adjusted to 7. The resulting mixture was extracted with DCM (20 mL \times 3), washed with brine, and dried over anhydrous Na_2SO_4 . Solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 2:1, v/v) on silica gel to give the corresponding product **1i** (54%). Mp: 153–155 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 6.8 Hz, 2H), 6.70 (d, J = 7.8 Hz, 2H), 4.36 (d, J = 5.6 Hz, 4H), 1.82–1.76 (m, 2H), 1.57–1.31 (m, 16H), 0.98–0.89 (m, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 131.3, 130.8, 128.3, 127.2, 79.0, 40.4, 30.3, 29.1, 23.8, 23.1, 14.2, 11.3 ppm. IR (cm^{-1}): 3096, 2958, 2928, 2859, 1577, 1446, 1310, 1135, 999, 837, 748, 637. HRMS (ESI): calcd for $C_{26}H_{39}O_6S_2$ $[M + H]^+$ 511.2188, found 511.2168.

General Procedure for the C–H Olefination of Thiophene 1,1-Dioxides. In a nitrogen-filled glovebox, thiophene 1,1-dioxide derivative **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.2 mg, 5 mol %), $AgOPiv$ (125 mg, 0.6 mmol, 3.0 equiv), $PivOH$ (61 mg, 0.6 mmol, 3.0 equiv), and THF (1.2 mL) were added to a 10 mL Schlenk tube. The reaction mixture was stirred at 80 °C for 12 h. The solution was filtered through a celite pad and washed with 10 mL of dichloromethane. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to provide the desired product.

(E)-2-Styrylbenzo[b]thiophene 1,1-Dioxide (3a). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 92% yield. Mp: 172–174 °C. 1H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.8 Hz, 1H), 7.55–7.53 (m, 3H), 7.47 (t, J = 7.2 Hz, 1H), 7.41–7.32 (m, 5H), 6.94 (s, 1H), 6.89 (t, J = 16.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.8, 137.5, 136.3, 135.9, 133.9, 132.0, 129.8, 129.4, 129.0, 127.4, 125.1, 124.9, 121.5, 114.9

ppm. IR (cm^{-1}): 3024, 2921, 2360, 1559, 1445, 1300, 1145, 1118, 962, 888, 752, 690. HRMS (ESI): calcd for $C_{16}H_{13}O_2S$ $[M + H]^+$ 269.0636, found 269.0623.

(E)-2-(4-Methylstyryl)benzo[b]thiophene 1,1-Dioxide (3b). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 78% yield. Mp: 187–189 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.6 Hz, 1H), 7.54 (td, J = 7.6, 1.2 Hz, 1H), 7.48–7.33 (m, 5H), 7.18 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 6.85 (d, J = 16.4 Hz, 1H), 2.37 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1, 139.7, 137.5, 136.4, 133.9, 133.2, 132.1, 129.7, 129.7, 127.4, 124.9, 124.2, 121.6, 113.9, 21.6 ppm. IR (cm^{-1}): 3025, 2920, 2360, 1584, 1458, 1301, 1149, 1117, 963, 889, 758, 591. HRMS (ESI): calcd for $C_{17}H_{14}NaO_2S$ $[M + Na]^+$ 305.0612, found 305.0606.

(E)-2-(3-Methylstyryl)benzo[b]thiophene 1,1-Dioxide (3c). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 71% yield. Mp: 133–135 °C. 1H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 16.2 Hz, 1H), 7.56–7.52 (m, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.24–7.19 (m, 3H), 6.93 (s, 1H), 6.80 (d, J = 16.2 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.1, 137.5, 137.3, 134.9, 134.2, 133.9, 132.0, 130.1, 129.8, 129.3, 126.4, 125.3, 125.0, 124.7, 121.5, 115.8, 19.9 ppm. IR (cm^{-1}): 3057, 2924, 2361, 1589, 1459, 1295, 1147, 1056, 956, 889, 751, 732, 592. HRMS (ESI): calcd for $C_{17}H_{14}NaO_2S$ $[M + Na]^+$ 305.0612, found 305.0602.

(E)-2-(2-Methylstyryl)benzo[b]thiophene 1,1-Dioxide (3d). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 44% yield. Mp: 150–151 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 16.4 Hz, 1H), 7.57–7.53 (m, 2H), 7.47 (td, J = 7.6, 1.2 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.25–7.19 (m, 3H), 6.94 (s, 1H), 6.80 (d, J = 16.4 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.2, 137.6, 137.3, 135.0, 134.3, 133.9, 132.0, 130.9, 129.8, 129.3, 126.4, 125.4, 125.0, 124.6, 121.6, 115.8, 19.9 ppm. IR (cm^{-1}): 3056, 2924, 2360, 1588, 1459, 1296, 1146, 1116, 955, 886, 749, 731, 591. HRMS (ESI): calcd for $C_{17}H_{15}O_2S$ $[M + H]^+$ 283.0793, found 283.0780.

(E)-2-(4-(tert-Butyl)styryl)benzo[b]thiophene 1,1-Dioxide (3e). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a green solid. 94% yield. Mp: 182–185 °C. 1H NMR (400 MHz, $DMSO-d_6$): δ = 7.89 (d, J = 7.6 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.60–7.56 (m, 3H), 7.46–7.44 (m, 3H), 7.20 (s, 2H), 1.30 (s, 9H) ppm. ^{13}C NMR (101 MHz, $DMSO-d_6$): δ 152.2, 140.8, 136.7, 134.4, 134.1, 132.9, 131.4, 130.2, 127.0, 125.9, 125.8, 125.8, 121.3, 115.1, 34.6, 31.0 ppm. IR (cm^{-1}): 2960, 2869, 2336, 1586, 1460, 1303, 1149, 1115, 958, 846, 756, 742, 594. HRMS (ESI): calcd for $C_{20}H_{21}O_2S$ $[M + H]^+$ 325.1262, found 325.1249.

(E)-2-(4-Methoxystyryl)benzo[b]thiophene 1,1-Dioxide (3f). The product was isolated by flash chromatography (petroleum ether/EtOAc = 4:1, v/v) as a green solid. 90% yield. Mp: 196–199 °C. 1H NMR (400 MHz, $DMSO-d_6$): δ = 7.88 (d, J = 7.2 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.63–7.54 (m, 4H), 7.38 (s, 1H), 7.18 (d, J = 16.8 Hz, 1H), 7.10 (d, J = 16.8 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H) ppm. ^{13}C NMR (101 MHz, $DMSO-d_6$): δ 160.3, 141.0, 136.6, 134.3, 134.1, 131.6, 129.9, 128.7, 128.2, 125.6, 124.8, 121.2, 114.5, 113.5, 55.3 ppm. IR (cm^{-1}): 3055, 2361, 2341, 1588, 1507,

1458, 1293, 1142, 1056, 958, 746, 728, 631. HRMS (ESI): calcd for $C_{17}H_{15}O_3S$ [$M + H$]⁺ 299.0742, found 299.0726.

(*E*)-2-(3,4-Dimethoxystyryl)benzo[*b*]thiophene 1,1-Dioxide (**3g**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 3:1, v/v) as a green solid. 77% yield. Mp: 227–229 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.73 (d, *J* = 7.2 Hz, 1H), 7.52 (td, *J* = 7.6, 0.8 Hz, 1H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.37–7.30 (m, 2H), 7.12 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.87–6.85 (m, 2H), 6.76 (d, *J* = 16.4 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 150.4, 149.3, 142.0, 137.3, 136.1, 133.9, 132.2, 129.5, 129.0, 124.9, 123.6, 121.5, 121.1, 112.9, 111.3, 109.6, 56.1, 56.0 ppm. IR (cm⁻¹): 3054, 2926, 2360, 1588, 1460, 1298, 1149, 1056, 960, 752, 734, 635. HRMS (ESI): calcd for $C_{18}H_{17}O_4S$ [$M + H$]⁺ 329.0848, found 329.0859.

(*E*)-4-(2-(1,1-Dioxidobenzo[*b*]thiophen-2-yl)vinyl)phenyl Acetate (**3h**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 3:1, v/v) as a yellow solid. 63% yield. Mp: 183–184 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, *J* = 7.6 Hz, 1H), 7.56–7.52 (m, 3H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.39 (d, *J* = 16.4 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.13–7.10 (m, 2H), 6.94 (d, *J* = 0.8 Hz, 1H), 6.83 (dd, *J* = 16.4, 0.8 Hz, 1H), 2.31 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 169.4, 151.5, 141.7, 137.5, 135.1, 133.9, 133.7, 131.9, 129.9, 128.4, 125.1, 122.2, 121.6, 115.1, 21.3 ppm. IR (cm⁻¹): 3064, 2360, 1756, 1580, 1504, 1372, 1295, 1188, 1163, 909, 849, 760. HRMS (ESI): calcd for $C_{18}H_{15}O_4S$ [$M + H$]⁺ 327.0691, found 327.0671.

(*E*)-2-(4-Fluorostyryl)benzo[*b*]thiophene 1,1-Dioxide (**3i**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6/1, v/v) as a green solid. 60% yield. Mp: 162–164 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.73 (d, *J* = 7.2 Hz, 1H), 7.54–7.45 (m, 4H), 7.36 (d, *J* = 16.8 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 8.4 Hz, 2H), 6.92 (s, 1H), 6.79 (d, *J* = 16.2 Hz, 1H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 164.2, 162.6, 141.6, 137.4, 134.9, 133.9, 132.2, 132.1, 131.9, 129.9, 129.10, 129.05, 125.1, 125.0, 121.6, 116.1, 116.0, 114.7, 114.7 ppm. ¹⁹F NMR (377 MHz, CDCl₃): δ = -111.1 ppm. IR (cm⁻¹): 3057, 2924, 2361, 1588, 1490, 1295, 1144, 1138, 1086, 957, 810, 752. HRMS (ESI): calcd for $C_{16}H_{12}FO_2S$ [$M + H$]⁺ 287.0542, found 287.0531.

(*E*)-2-(4-Chlorostyryl)benzo[*b*]thiophene 1,1-Dioxide (**3j**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a green solid. 63% yield. Mp: 174–175 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 7.2 Hz, 1H), 7.55 (td, *J* = 7.6, 1.2 Hz, 1H), 7.50–7.45 (m, 3H), 7.38–7.33 (m, 4H), 6.95 (s, 1H), 6.86 (d, *J* = 16.4 Hz, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 141.6, 137.5, 135.2, 134.8, 134.4, 134.0, 131.9, 130.0, 129.2, 128.5, 125.4, 125.2, 121.6, 115.5 ppm. IR (cm⁻¹): 3058, 2923, 2360, 1586, 1489, 1458, 1297, 1147, 1090, 1056, 956, 843, 808, 753. HRMS (ESI): calcd for $C_{16}H_{12}ClO_2S$ [$M + H$]⁺ 303.0247, found 303.0243.

(*E*)-2-(4-(Trifluoromethyl)styryl)benzo[*b*]thiophene 1,1-Dioxide (**3k**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a green solid. 50% yield. Mp: 185–187 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.76 (d, *J* = 7.2 Hz, 1H), 7.63–7.62 (m, 4H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 16.2 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 6.96 (d, *J* = 16.8 Hz, 1H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 141.3, 139.3, 137.6, 134.4, 134.0, 131.7, 130.3, 127.5, 126.5, 126.0, 125.92, 125.90, 125.4, 121.7, 117.3 ppm. ¹⁹F NMR (377 MHz,

CDCl₃): δ = -62.7 ppm. IR (cm⁻¹): 3058, 2358, 1610, 1416, 1322, 1294, 1148, 1107, 956, 872, 753, 738. HRMS (ESI): calcd for $C_{17}H_{11}F_3NaO_2S$ [$M + Na$]⁺ 359.0330, found 359.0303.

Methyl (*E*)-4-(2-(1,1-dioxidobenzo[*b*]thiophen-2-yl)vinyl)benzoate (**3l**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 2:1, v/v) as a green solid. 67% yield. Mp: 204–207 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.03 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.59–7.47 (m, 4H), 7.42 (d, *J* = 16.8 Hz, 1H), 7.36 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.00 (s, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 3.93 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 166.7, 141.4, 140.2, 137.6, 134.9, 134.0, 131.7, 130.5, 130.2, 127.2, 126.3, 125.3, 121.7, 117.2, 52.4 ppm. IR (cm⁻¹): 3056, 2361, 1757, 1585, 1447, 1290, 1126, 962, 815, 787, 645. HRMS (ESI): calcd for $C_{18}H_{15}O_4S$ [$M + H$]⁺ 327.0691, found 327.0669.

(*E*)-2-(2-(Naphthalen-2-yl)vinyl)benzo[*b*]thiophene 1,1-Dioxide (**3m**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a yellow solid. 61% yield. Mp: 210–212 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (s, 1H), 7.86–7.80 (m, 3H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.50–7.45 (m, 3H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.03–6.97 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 142.0, 137.5, 136.4, 133.93, 133.90, 133.6, 133.4, 132.1, 129.8, 129.0, 128.7, 128.6, 127.9, 127.0, 126.8, 125.1, 124.8, 123.1, 121.6, 115.1 ppm. IR (cm⁻¹): 3056, 2923, 2360, 1590, 1462, 1295, 1146, 958, 790, 752, 736. HRMS (ESI): calcd for $C_{20}H_{15}O_2S$ [$M + H$]⁺ 319.0793, found 319.0781.

Ethyl (*E*)-3-(1,1-dioxidobenzo[*b*]thiophen-2-yl)acrylate (**3n**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 2:1, v/v) as a green oil. 67% yield. ¹H NMR (600 MHz, CDCl₃): δ = 7.77 (d, *J* = 7.2 Hz, 1H), 7.62–7.56 (m, 2H), 7.45–7.41 (m, 2H), 7.22 (s, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 165.8, 139.6, 138.0, 134.1, 131.7, 131.4, 130.8, 129.2, 126.2, 124.9, 121.8, 61.3, 14.3 ppm. IR (cm⁻¹): 3062, 2360, 1747, 1590, 1445, 1272, 1108, 943, 832, 777. HRMS (ESI): calcd for $C_{13}H_{13}O_4S$ [$M + H$]⁺ 265.0535, found 265.0530.

tert-Butyl (*E*)-3-(1,1-dioxidobenzo[*b*]thiophen-2-yl)acrylate (**3o**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 2:1, v/v) as a green oil. 65% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 7.2 Hz, 1H), 7.61–7.53 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 16.4 Hz, 1H), 7.19 (s, 1H), 6.64 (d, *J* = 16.4 Hz, 1H), 1.51 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 165.0, 139.8, 137.9, 134.1, 131.3, 131.2, 130.9, 128.2, 126.9, 126.1, 121.8, 81.6, 28.2 ppm. IR (cm⁻¹): 3060, 2361, 1752, 1592, 1448, 1297, 1122, 959, 847, 760, 624. HRMS (ESI): calcd for $C_{15}H_{17}O_4S$ [$M + H$]⁺ 293.0848, found 293.0844.

(*E*)-3-Methyl-2-styrylbenzo[*b*]thiophene 1,1-Dioxide (**4a**). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 94% yield. Mp: 198–200 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 7.6 Hz, 1H), 7.62–7.55 (m, 3H), 7.52–7.43 (m, 3H), 7.40–7.32 (m, 3H), 6.95 (d, *J* = 16.4 Hz, 1H), 2.33 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 136.7, 136.4, 135.9, 135.1, 133.9, 133.8, 133.5, 129.8, 129.2, 128.9, 127.2, 122.3, 121.1, 113.4, 11.48. IR (cm⁻¹): 3057, 2359, 1587, 1461, 1291, 1150, 1118, 950, 760, 686. HRMS (ESI): calcd for $C_{17}H_{15}O_2S$ [$M + H$]⁺ 283.0793, found 283.0785.

(E)-5-Methyl-2-styrylbenzo[b]thiophene 1,1-Dioxide (4b).

The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 73% yield. Mp: 199–201 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (d, *J* = 7.6 Hz, 1H), 7.53–7.50 (m, 2H), 7.43–7.30 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 6.89–6.85 (m, 2H), 2.41 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 144.9, 142.1, 136.1, 136.0, 134.8, 132.3, 130.3, 129.4, 128.9, 127.3, 125.8, 125.0, 121.4, 115.0, 21.9 ppm. IR (cm⁻¹): 3041, 2361, 1583, 1444, 1284, 1145, 1118, 944, 762, 743, 616. HRMS (ESI): calcd for C₁₇H₁₅O₂S [M + H]⁺ 283.0793, found 283.0774.

(E)-4-Methyl-2-styrylbenzo[b]thiophene 1,1-Dioxide (4c).

The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 88% yield. Mp: 202–203 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 7.6 Hz, 1H), 7.62–7.55 (m, 3H), 7.52–7.44 (m, 3H), 7.40–7.32 (m, 2H), 7.34–7.30 (m, 1H), 6.95 (d, *J* = 16.4 Hz, 1H), 2.33 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 136.8, 136.4, 136.0, 135.1, 133.9, 133.8, 133.5, 129.8, 129.2, 128.9, 127.3, 122.3, 121.1, 113.5 ppm. IR (cm⁻¹): 3057, 2921, 1581, 1448, 1300, 1140, 955, 752, 690. HRMS (ESI): calcd for C₁₇H₁₅O₂S [M + H]⁺ 283.0793, found 283.0782.

(E)-3,5-Dimethyl-2-styrylbenzo[b]thiophene 1,1-Dioxide (4d). The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a green solid. 69% yield. M.p.: 206–208 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.64 (d, *J* = 8.0 Hz, 1H), 7.56–7.54 (m, 2H), 7.46–7.28 (m, 5H), 7.22 (s, 1H), 6.94 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 2.30 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 144.7, 136.4, 136.1, 134.8, 134.1, 134.0, 133.7, 130.3, 129.1, 128.9, 127.2, 123.0, 121.0, 113.5, 22.1, 11.4. IR (cm⁻¹): 3056, 2920, 2360, 1591, 1447, 1281, 1146, 1126, 949, 813, 746. HRMS (ESI): calcd for C₁₈H₁₇O₂S [M + H]⁺ 297.0949, found 297.0930.

(E)-5-(tert-Butyl)-2-styrylbenzo[b]thiophene 1,1-Dioxide (4e). The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a green solid. 82% yield. Mp: 205–207 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43–7.32 (m, 5H), 6.93–6.87 (m, 2H), 1.35 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 158.2, 142.0, 136.01, 135.97, 134.7, 132.1, 129.3, 128.9, 127.4, 126.9, 125.4, 122.4, 121.3, 115.0, 35.5, 31.2 ppm. IR (cm⁻¹): 2961, 2869, 2360, 1587, 1460, 1300, 1149, 1116, 959, 846, 756, 742. HRMS (ESI): calcd for C₂₀H₂₁O₂S [M + H]⁺ 325.1262, found 325.1256.

(E)-5-Methoxy-2-styrylbenzo[b]thiophene 1,1-Dioxide (4f). The product was isolated by flash chromatography (petroleum ether/EtOAc = 4:1, v/v) as a green solid. 61% yield. Mp: 197–199 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (d, *J* = 5.6 Hz, 2H), 7.38–7.27 (m, 6H), 7.04 (dd, *J* = 5.6 Hz, 1.6 Hz, 1H), 6.90–6.85 (m, 2H), 3.89 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 161.5, 140.5, 139.2, 136.1, 134.8, 129.2, 128.9, 127.2, 126.1, 125.1, 124.2, 119.6, 115.1, 107.4, 56.2. IR (cm⁻¹): 2360, 2342, 1489, 1295, 1231, 1144, 1045, 962, 879, 753, 699. HRMS (ESI): calcd for C₁₇H₁₅O₃S [M + H]⁺ 299.0742, found 299.0732.

(E)-5-Phenyl-2-styrylbenzo[b]thiophene 1,1-Dioxide (4g).

The product was isolated by flash chromatography (petroleum ether/EtOAc = 6:1, v/v) as a green solid. 73% yield. Mp: 218–221 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.60–7.35 (m, 12H), 6.99–6.90 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 147.4, 142.5, 139.3, 136.5, 136.0, 135.9, 132.8, 129.5, 129.3,

129.0, 128.9, 128.5, 127.43, 127.41, 124.8, 123.8, 121.9, 114.9. IR (cm⁻¹): 3057, 2923, 2360, 1591, 1462, 1296, 1150, 960, 887, 763, 742. HRMS (ESI): calcd for C₂₂H₁₇O₂S [M + H]⁺ 345.0949, found 345.0931

4,8-Bis((2-ethylhexyl)oxy)-2,6-di((E)-styryl)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-Tetraoxide (4h). Styrene 2a (0.6 mmol, 3.0 equiv) was used. The product was isolated by flash chromatography (petroleum ether/EtOAc = 5:1, v/v) as a yellow solid. 78% yield. Mp: 218–220 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.55 (d, *J* = 7.2 Hz, 4H), 7.44–7.36 (m, 8H), 7.07 (s, 2H), 6.91 (d, *J* = 16.2 Hz, 2H), 4.40 (dd, *J* = 5.4 Hz, 1.2 Hz, 4H), 1.88–1.84 (m, 2H), 1.65–1.59 (m, 2H), 1.58–1.47 (m, 6H), 1.42–1.36 (m, 8H), 1.02 (t, *J* = 7.2 Hz, 6H), 0.95 (t, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 145.3, 141.8, 137.1, 135.8, 131.8, 129.8, 129.1, 128.1, 127.5, 119.5, 114.9, 79.1, 40.6, 30.4, 29.2, 23.8, 23.2, 14.3, 11.32. IR (cm⁻¹): 2956, 2928, 2361, 1445, 1376, 1304, 1242, 1138, 1035, 943, 871, 686. HRMS (ESI): calcd for C₄₂H₅₁O₆S₂ [M + H]⁺ 715.3127, found 715.3133.

■ ASSOCIATED CONTENT**SI Supporting Information**

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07427>.

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

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Notes

The authors declare no competing financial interest.

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