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PALLADIUM-CATALYZED HOMO-COUPLING OF HETEROARYLSULFONIUMS VIA BORYLATION/SUZUKI-MIYaura COUPLING SEQUENCE

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Abstract – Palladium-catalyzed homo-coupling of heteroaryldimethylsulfoniums proceeds in the presence of bis(pinacolato)diboron and a base to yield biheteroaryls. The homo-coupling involves palladium-catalyzed borylation and the subsequent Suzuki-Miyaura coupling. As the sulfoniums were able to be prepared *in situ* from the corresponding heteroaryl sulfides and methyl triflate, one-pot transformations of heteroaryl sulfides into the homo-coupling products were executed. Furthermore, a facile synthesis of a highly substituted 2,2'-bibenzofuran was accomplished with a combination of Pummerer-type synthesis of 2-benzofuryl sulfide and the present homo-coupling.

INTRODUCTION

Organosulfur compounds occupy a unique position in organic chemistry due to their intriguing properties, and are often found in bioactive molecules as well as functional materials.¹ Recently, in the cross-coupling arena, significant efforts have been devoted to develop cross-coupling of organosulfur compounds such as aryl sulfides as surrogates for organic halides.² Although robust C–S bonds and catalyst-poisonous metallophilic sulfur fragments often disturb the cross-coupling reaction, researchers have overcome these problems by means of sophisticated transition metal catalysts or external thiophilic additives.

As an alternative approach, use of arylsulfoniums instead of aryl sulfides can be considered. The electron-deficiency of arylsulfoniums would enhance C–S bond cleavage through oxidative addition, and the leaving neutral sulfides would be far less catalyst-poisonous than anionic thiolate species derived from aryl sulfides. As a pioneering work, in 1997, Liebeskind reported cross-coupling of arylsulfoniums with organoboron reagents under palladium catalysis.³ Although this seminal work

Dedicated to Prof. Dr. Kiyoshi Tomioka on the occasion of his 70th birthday

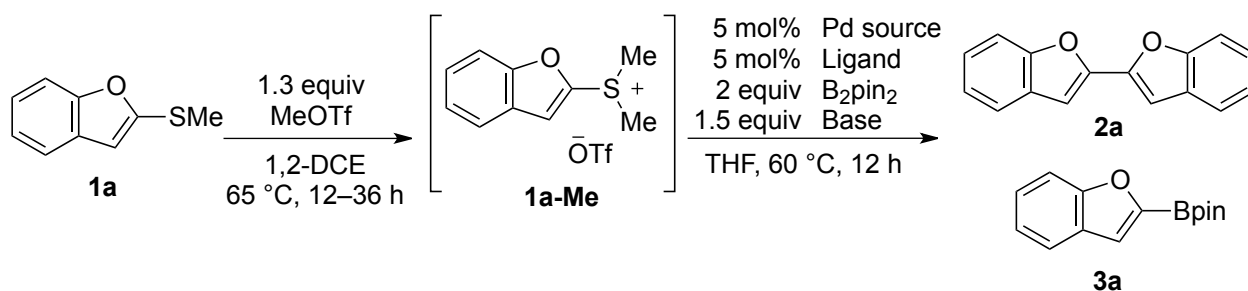
demonstrated the prospectivity of arylsulfoniums as aryl electrophiles, a limited number of cross-coupling of arylsulfoniums as aryl electrophiles have been developed.⁴

Recently, we reported palladium-catalyzed borylation of arylsulfoniums with a diboron reagent.⁵ Owing to the sufficient reactivity of arylsulfoniums, the borylation proceeded smoothly under mild reaction conditions with sufficient functional group compatibility. Moreover, since aryl dimethylsulfoniums could be prepared *in situ* from aryl methyl sulfides with methyl triflate (MeOTf), aryl methyl sulfides were able to be transformed into the corresponding arylboronates in a one-pot manner. During this investigation, we found that attempted one-pot borylation of heteroaryl sulfides afforded not only the borylated product but also the corresponding biheteroaryls, most likely via the expected borylation followed by Suzuki-Miyaura-type coupling in the same flask.⁶ Considering the prevalence of biaryl motifs in the field of organic chemistry, we further investigated this homo-coupling of heteroaryl sulfoniums via borylation, which is reported herein.

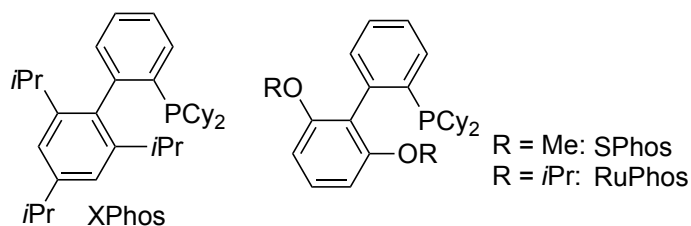
RESULTS AND DISCUSSION

First, we attempted the homo-coupling of 2-(methylsulfanyl)benzofuran (**1a**) under the optimal reaction conditions for our previous borylation.⁵ Treatment of **1a** with MeOTf in 1,2-dichloroethane (1,2-DCE) yielded the corresponding 2-benzofuryldimethylsulfonium **1a-Me**. After removal of all volatiles under a reduced pressure, the homo-coupling was conducted in a one-pot manner by adding 5 mol% of Pd(OAc)₂ and XPhos, 2 equivalents of B₂pin₂, 1.5 equivalents of K₃PO₄, and THF. The desired 2,2'-bibenzofuran (**2a**) was obtained in 50% yield, along with a 20% yield of 2-borylbenzofuran **3a** as the borylated product (Table 1, entry 1). The yield of **2a** was increased when RuPhos or SPhos was used as the ligand (entries 2 and 3). Since the combined yield of **2a** and **3a** in the reaction with SPhos was slightly higher than that with RuPhos, we chose SPhos as the optimal ligand. Other palladium sources such as Pd₂(dba)₃ and [Pd(allyl)Cl]₂ did not give better results (entries 4 and 5). The use of K₃PO₄·H₂O considerably increased the yield of **2a** to 87% yield (entry 6). We suppose that Suzuki-Miyaura-type coupling of **1a-Me** with *in situ* generated **3a** would be accelerated by H₂O.

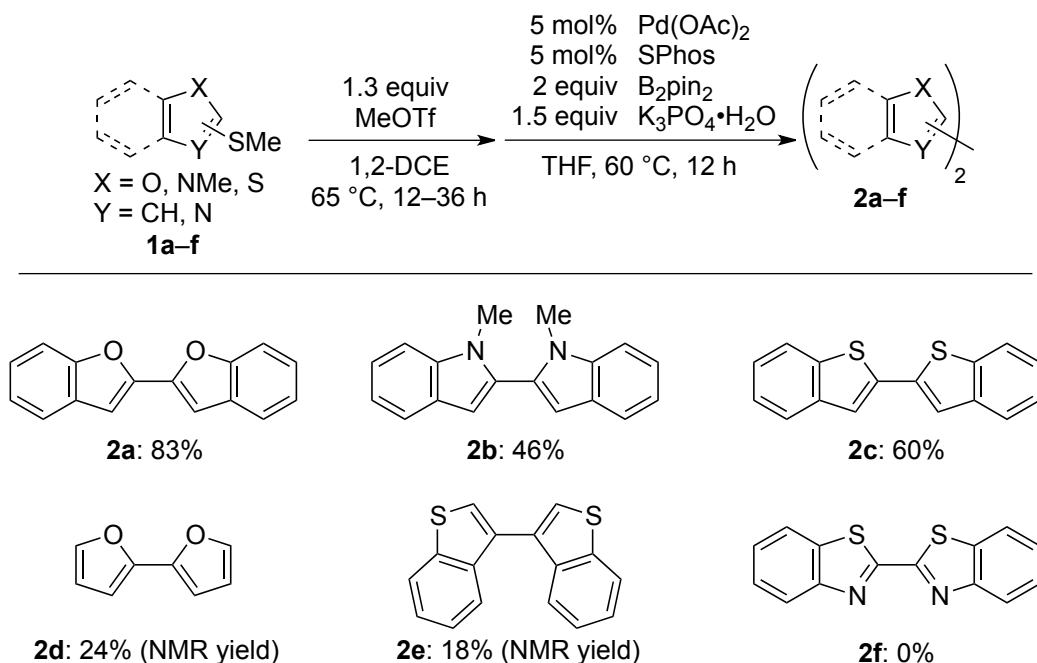
Table 1. Condition Screening



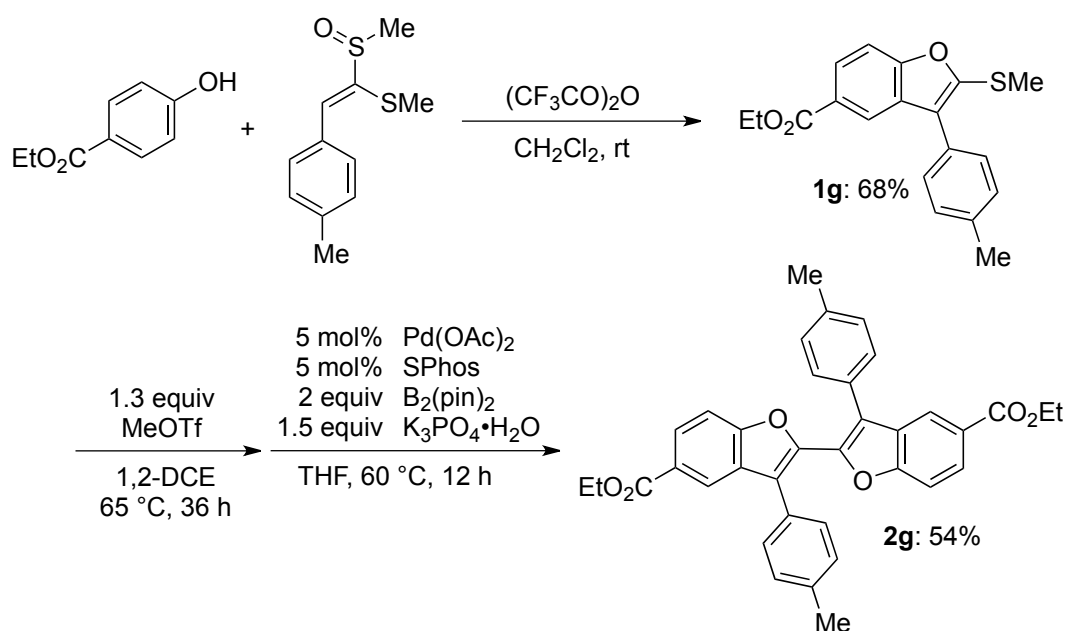
Entry	Pd source	Ligand	Base	NMR yield of 2a (%)	NMR yield of 3a (%)
1	Pd(OAc) ₂	XPhos	K ₃ PO ₄	50	20
2	Pd(OAc) ₂	RuPhos	K ₃ PO ₄	66	8
3	Pd(OAc) ₂	SPhos	K ₃ PO ₄	64	13
4	Pd ₂ (dba) ₃	SPhos	K ₃ PO ₄	60	<5
5	[Pd(allyl)Cl] ₂	SPhos	K ₃ PO ₄	67	<5
6	Pd(OAc) ₂	SPhos	K ₃ PO ₄ ·H ₂ O	87	<5



Under the optimized reaction conditions, **2a** was isolated in 83% yield (Scheme 1). As other heteroaryl sulfides, 1-methyl-2-(methylsulfanyl)indole (**1b**) and 2-(methylsulfanyl)benzothiophene (**1c**) were applicable to the homo-coupling to afford biaryls **2b** and **2c** in 46% and 60% yields, respectively. Although the homo-coupling of monocyclic 2-(methylsulfanyl)furan (**1d**) proceeded, the yield of 2,2'-bifuran (**2d**) was low. The position of the methylsulfanyl moiety was important; the homo-coupling of 3-(methylsulfanyl)benzothiophene (**1e**) gave the coupling product in low yield. In both unsuccessful cases, demethylation of the sulfonium intermediates predominated over the catalytic heteroaryl–sulfur bond cleavage to lower the yields of **2d** and **2e**. Indeed, for instance, a 31% of **1e** was recovered after the reaction. 2-(Methylsulfanyl)benzothiazole (**1f**) did not undergo the homo-coupling because *N*-methylation proceeded in the first step preferentially instead of the desired *S*-methylation.



Scheme 1. Scope of Heteroaryl Sulfides

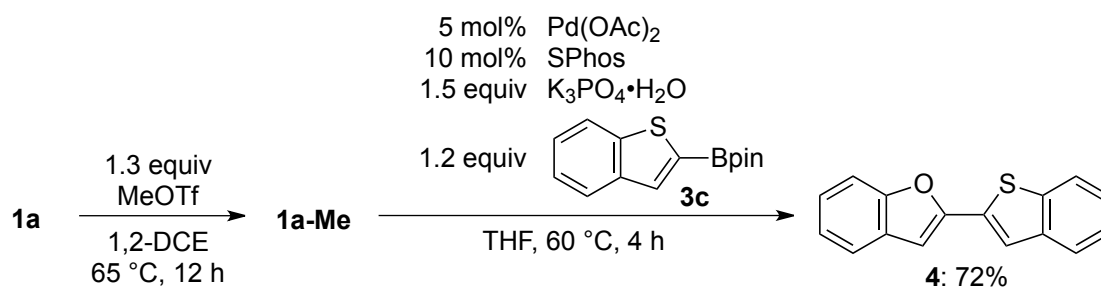


Scheme 2. Synthesis of Multi-Substituted 2,2'-Bibenzofuran

Next, we attempted to synthesize multi-functionalized 2,2'-bibenzofuran by means of a combination of Pummerer-type synthesis of benzofuran and the present homo-coupling (Scheme 2). We previously reported the formation of 2-(alkylsulfanyl)benzofurans from ketene dithioacetal monoxides (KDM) and phenols with the aid of Pummerer-type activation of KDM with acid anhydrides.⁷ According to this benzofuran synthesis, we prepared multi-substituted 2-(methylsulfanyl)benzofuran **1g**. Subsequent

homo-coupling of **1g** furnished the expected 2,2'-bibenzofuran **2g** in 54% yield. This two-pot three-step transformation should become a powerful method for the synthesis of highly substituted 2,2'-bibenzofurans from easily accessible KDM⁸ and phenols.

We assume that the homo-coupling of heteroarylsulfoniums proceeded through the borylation to yield heteroarylboronates, followed by Suzuki-Miyaura-type coupling of the remaining sulfoniums with the resulting boronates. To confirm our mechanistic hypothesis, we attempted the Suzuki-Miyaura-type cross-coupling of 2-benzofuryldimethylsulfonium (**1a-Me**) with 2-borylbenzothiophene **3c** (Scheme 3). As a result, the cross-coupling product **4** was obtained in 72% yield. Notably, none of 2,2'-bibenzofuran (**2a**) was naturally detected because of the absence of B₂pin₂. Probably in order to reduce the divalent palladium acetate, 2,2'-bibenzothiophene (**2c**) was formed in only 5% yield (calculated based on the molar amount of **3c**). These results are supportive of our hypothesis.⁹



Scheme 3. Cross-Coupling of **1a-Me** with **3c** to Confirm Intermediacy of Sulfonium and Boronate

In conclusion, we have developed palladium-catalyzed homo-coupling of heteroaryldimethylsulfoniums with the aid of B₂pin₂. As the sulfoniums were prepared *in situ* from heteroaryl methyl sulfides and MeOTf, one-pot transformations of heteroaryl sulfides into the corresponding homo-coupling products were accomplished. A facile synthesis of a highly substituted 2,2'-bibenzofuran was achieved with a combination of Pummerer-based benzofuran synthesis and the present homo-coupling.

EXPERIMENTAL

¹H NMR (600 MHz) and ¹³C NMR (151 MHz) spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts (δ) are reported in parts per million in CDCl₃ relative to residual CHCl₃ at 7.26 ppm for ¹H and relative to CDCl₃ at 77.16 ppm for ¹³C. Mass spectra were determined on a Bruker micrOTOF II-KR spectrometer. TLC analyses were performed on commercial aluminium sheets bearing a 0.25-mm layer of Merck silica gel 60F₂₅₄. Purification was done by column chromatography using silica gel (KANTO CHEMICAL CO., INC., 60N, 100–210 μm) or Florisil (nacalai tesque, 100–200 mesh). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI

LC-9260 II NEXT system with CHCl_3 as an eluent.

All reactions were performed under nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. B_2pin_2 was purchased from Ark Pharm. $\text{Pd}(\text{OAc})_2$ and MeOTf were purchased from Wako Pure Chemical Industries, Ltd. XPhos, RuPhos, and SPhos were purchased from Sigma-Aldrich. Dehydrated THF was purchased from KANTO CHEMICAL CO., INC. and stored under nitrogen atmosphere. Dehydrated 1,2-DCE was purchased from Sigma-Aldrich and stored under nitrogen atmosphere. Arylboronate **3c** was prepared according to the literature.¹⁰

Procedure for Synthesis of Aryl Sulfides **1a**, **1b**, **1c**, and **1d**

The synthesis of 2-(methylsulfanyl)benzofuran (**1a**) is representative. A 100-mL two-necked flask was charged with benzofuran (2.2 mL, 20 mmol) and THF (20 mL), and the resulting solution was cooled to 0 °C. BuLi (1.6 M in hexane, 13 mL, 21 mmol) was added slowly, and the resulting mixture was stirred for 1 h at 0 °C. Dimethyl disulfide (1.9 mL, 21 mmol) was added and the resulting solution was stirred for an additional 1 h at the same temperature. Then, saturated aqueous NaHCO_3 was added to the reaction mixture, and the resulting biphasic solution was extracted with EtOAc (30 mL \times 3). The combined organic layer was dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give **1a** (2.8 g, 17 mmol, 85%) as a colorless oil. All the resonances in the ^1H and ^{13}C NMR spectra of **1a** were consistent with the reported data.¹¹ Aryl sulfides **1b**, **1c**, and **1d** were also prepared through this procedure. All the resonances in the ^1H and ^{13}C NMR spectra of **1d** were consistent with the reported data.¹²

1-Methyl-2-(methylsulfanyl)indole (1b): ^1H NMR: δ 7.55 (d, $J = 7.9$ Hz, 1H), 7.29–7.26 (m, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 7.10 (t, $J = 7.9$ Hz, 1H), 6.57 (s, 1H), 3.79 (s, 3H), 2.45 (s, 3H); ^{13}C NMR: δ 138.3, 134.3, 127.8, 121.9, 120.0, 119.8, 109.3, 104.9, 30.0, 19.3. HRMS (APCI-MS, positive): $m/z = 177.0612$. calcd for $\text{C}_{10}\text{H}_{11}\text{NS}$: 177.0607 [M]⁺

2-(Methylsulfanyl)benzothiophene (1c): ^1H NMR: δ 7.73 (d, $J = 7.2$ Hz, 1H), 7.66 (d, $J = 7.2$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.21 (s, 1H), 2.60 (s, 3H); ^{13}C NMR: δ 140.9, 140.0, 139.7, 124.8, 124.6, 124.1, 122.8, 121.9, 20.3. HRMS (APCI-MS, positive): $m/z = 180.0057$. calcd for $\text{C}_9\text{H}_8\text{S}_2$: 180.0062 [M]⁺

Procedure for Synthesis of Aryl Sulfide **1e**

A 100-mL two-necked flask was charged with benzothiophene (1.6 g, 12 mmol), dimethyl sulfoxide (0.86 mL, 12 mmol), and CH_2Cl_2 (24 mL). The resulting solution was cooled to 0 °C, and Tf_2O (2.4 mL, 14 mmol) was added dropwise. The mixture was stirred for 1.5 h at 0 °C, allowed to warm to room temperature, and stirred for another 1.5 h. After addition of aqueous solution of K_2CO_3 (0.42 M, 20 mL) and NEt_3 (2.4 mL, 17 mmol), the resulting mixture was stirred for 12 h additionally. The

reaction mixture was extracted with CH₂Cl₂ (40 mL × 3). The combined organic layer was concentrated under a reduced pressure and purified by silica gel column chromatography to give **1e** (0.54 g, 3.0 mmol, 25%) as a pale yellow oil.

3-(Methylsulfonyl)benzothiophene (1e): ¹H NMR: δ 7.88–7.85 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.19 (s, 1H), 2.54 (s, 3H); ¹³C NMR: δ 140.0, 138.4, 129.4, 125.0, 124.5, 123.1, 122.4, 122.0, 17.4. HRMS (APCI-MS, positive): *m/z* = 180.0068. calcd for C₉H₈S₂: 180.0062 [*M*]⁺

Procedure for Synthesis of Aryl Sulfide **1g**

The synthesis of **1g** was conducted by a similar procedure in the previous report.⁷ A 100-mL two-necked flask was charged with *p*-tolyl-substituted KDM (0.83 g, 5.0 mmol) and ethyl 4-hydroxybenzoate (1.1 mL, 6.0 mmol), and CH₂Cl₂ (20 mL). Trifluoroacetic anhydride (0.85 mL, 6.0 mmol) was added at once to the flask at room temperature. The resulting mixture was stirred for 1 h. The mixture was filtered through pads of alumina and silica gel. The filtrate was then concentrated in vacuo, and purified by silica gel column chromatography to give **1g** (1.1 g, 3.4 mmol, 68%) as a pale yellow solid.

5-(Ethoxycarbonyl)-3-(4-methylphenyl)-2-(methylsulfonyl)benzofuran (1g): ¹H NMR: δ 8.32 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.51–7.48 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 2.44 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C NMR: δ 166.9, 158.1, 149.0, 137.9, 129.6, 129.1, 128.7, 128.2, 126.3, 125.9, 122.9, 122.3, 110.8, 61.1, 21.5, 17.0, 14.5. HRMS (APCI-MS, positive): *m/z* = 326.0984. calcd for C₁₉H₁₈O₃S: 326.0971 [*M*]⁺

Typical Procedure for Homo-Coupling (Scheme 1)

The synthesis of **2a** is representative. A Schlenk tube was charged with 2-(methylsulfonyl)benzofuran (**1a**, 68 μL, 0.50 mmol) and 1,2-DCE (2.0 mL). MeOTf (74 μL, 0.65 mmol) was added and the resulting mixture was stirred for 12 h at 65 °C. After the completion of the reaction as indicated by TLC, all volatiles were completely removed under a reduced pressure (ca. 1 Torr). B₂pin₂ (0.25 g, 1.0 mmol), Pd(OAc)₂ (5.6 mg, 0.025 mmol), SPhos (10 mg, 0.025 mmol), K₃PO₄·H₂O (0.17 g, 0.75 mmol), and THF (4.0 mL) were then added sequentially to the tube. The resulting mixture was stirred for 12 h at 60 °C. After the reaction, the mixture was passed through a pad of Florisil and purified by preparative recycling GPC to afford **2a** (48 mg, 0.21 mmol, 83%) as a white solid.

2,2'-Bibenzofuran (2a): ¹H NMR: δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.17 (s, 2H); ¹³C NMR: δ 155.3, 147.9, 128.7, 125.2, 123.5, 121.5, 111.4, 103.8. HRMS (APCI-MS, positive): *m/z* = 234.0669. calcd for C₁₆H₁₀O₂: 234.0675 [*M*]⁺

1,1'-Dimethyl-2,2'-biindole (2b): After the reaction, the mixture was passed through a pad of Florisil and purified by preparative recycling GPC to afford **2b** (30 mg, 0.11 mmol, 46%) as a white solid. ¹H

NMR: δ 7.70 (d, $J = 7.8$ Hz, 2H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.32 (t, $J = 7.8$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 2H), 6.68 (s, 2H), 3.73 (s, 6H); ^{13}C NMR: δ 138.1, 131.7, 127.8, 122.4, 120.9, 120.2, 109.8, 104.6, 31.0. HRMS (APCI-MS, positive): $m/z = 260.1315$. calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2$: 260.1308 [M] $^+$

2,2'-Bibenzothiophene (2c): After the reaction, the mixture was passed through a pad of Florisil and the filtrate was concentrated under a reduced pressure. Washing the residual solid with pentane and CHCl_3 sequentially afforded **2c** (40 mg, 0.15 mmol, 60%) as a white solid. ^1H NMR: δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 7.2$ Hz, 2H), 7.52 (s, 2H), 7.38–7.32 (m, 4H); ^{13}C NMR: δ 140.4, 139.6, 137.4, 125.1, 125.0, 123.9, 122.3, 121.6. HRMS (APCI-MS, positive): $m/z = 266.0223$. calcd for $\text{C}_{16}\text{H}_{10}\text{S}_2$: 266.0218 [M] $^+$

5,5'-Bis(ethoxycarbonyl)-3,3'-bis(4-methylphenyl)-2,2'-bibenzofuran (2g): After the reaction, the mixture was passed through a pad of Florisil and purified by preparative recycling GPC to afford **2g** (75 mg, 0.13 mmol, 54%) as a white solid. ^1H NMR: δ 8.32 (d, $J = 1.8$ Hz, 2H), 8.10 (dd, $J = 1.8, 9.0$ Hz, 2H), 7.52 (d, $J = 9.0$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 4H), 7.10 (d, $J = 7.8$ Hz, 4H), 4.39 (q, $J = 7.1$ Hz, 4H), 2.38 (s, 6H), 1.39 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR: δ 166.7, 157.5, 143.1, 137.8, 129.3, 129.2, 128.8, 127.8, 127.5, 126.2, 123.3, 122.7, 111.5, 61.2, 21.4, 14.5. HRMS (APCI-MS, positive): $m/z = 558.2045$. calcd for $\text{C}_{36}\text{H}_{30}\text{O}_6$: 558.2037 [M] $^+$

Procedure for Cross-Coupling of 1a-Me with 3c (Scheme 3)

A Schlenk tube was charged with 2-(methylsulfanyl)benzofuran (**1a**, 68 μL , 0.50 mmol) and 1,2-DCE (2.0 mL). MeOTf (74 μL , 0.65 mmol) was added and the resulting mixture was stirred for 12 h at 65 $^\circ\text{C}$. After the completion of the reaction as indicated by TLC, all volatiles were completely removed under a reduced pressure (ca. 1 Torr). Under nitrogen atmosphere, 2-(2-benzothieryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**, 0.15 g, 0.60 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol), SPhos (21 mg, 0.050 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (0.17 g, 0.75 mmol), and THF (4.0 mL) were then added to the tube. The resulting mixture was stirred for 12 h at 60 $^\circ\text{C}$. After the reaction, the mixture was passed through a pad of Florisil and the filtrate was concentrated under a reduced pressure. Washing the residual solid with pentane and CHCl_3 sequentially afforded a 98 mg of white solid containing **4** and **2c** (molar ratio of **4**:**2c** = 13:1). From these data, the yield of **4** was calculated. The compounds **4** and **2c** could not be further separated with any methods. All the resonances in the ^1H and ^{13}C NMR spectra of **4** were consistent with the reported data.¹³

ACKNOWLEDGEMENTS

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