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Synthesis of Benzothiadiazole Derivatives by Applying C−C Cross-Couplings

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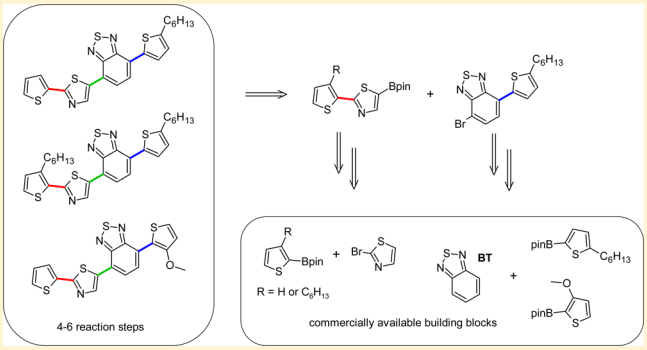
Supporting Information

ABSTRACT: The benzothiadiazole moiety has been extensively exploited as a building block in the syntheses of efficient organic semiconducting materials during the past decade. In this paper, parallel synthetic routes to benzothiadiazole derivatives, inspired by previous computational findings, are reported. The results presented here show that various C−C cross-couplings of benzothiadiazole, thiophene, and thiazole derivatives can be efficiently performed by applying Xantphos as a ligand of the catalyst system. Moreover, improved and convenient methods to synthesize important chemical building blocks, e.g., 4,7-dibromo-2,1,3-benzothiadiazole, in good to quantitative yields are presented. Additionally, the feasibility of Suzuki−Miyaura and direct coupling methods are compared in the synthesis of target benzothiadiazole derivatives. The computational characterization of the prepared benzothiadiazole derivatives shows that these compounds have planar molecular backbones and the possibility of intramolecular charge transfer upon excitation. The experimental electrochemical and spectroscopic studies reveal that although the compounds have similar electronic and optical properties in solution, they behave differently in solid state due to the different alkyl side-group substitutions in the molecular backbone. These benzothiadiazole derivatives can be potentially used as building blocks in the construction of more advanced small molecule organic semiconductors with acceptor−donor−acceptor motifs.



INTRODUCTION

Benzothiadiazole (BT) has become a highly important building block that has been extensively exploited in efficient semiconducting materials.[1] The BT unit also has one of the top frequencies of occurrence among the leading candidate structures in The Harvard Clean Energy Project.[2] This project computationally assessed candidate structures for organic electronic materials and particularly for organic photovoltaics (OPVs). Two example structures are presented in Scheme 1.

OPV devices with the theoretical compounds of Scheme 1 as donor components were predicted to produce power conversion efficiencies of 8.0 and 9.1%.[3] In addition, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were also reported. Inspired by these results, we were interested in investigating the possibility of synthesizing close analogues of these theoretical compounds. The plan for the synthetic pathway to the target molecules is presented in Scheme 1. The framework of the target molecule was planned so that it can be constructed from widely commercially available chemical building blocks by connecting them using palladium-catalyzed cross-coupling reactions.

Cross-coupling reactions are efficient tools in the syntheses of semiconducting organic materials that have a modular structure.[4] Stille and Suzuki−Miyaura have been the most extensively used methods to connect different building blocks, but within the last two decades, many researchers have started to favor direct coupling instead. The major drawback of both the Stille and Suzuki−Miyaura methods is the necessity of preparing the organostannane or boron reagent, which increases the number of reaction steps and thus, in most cases, the cost of the method. The Suzuki−Miyaura method has some important advantages compared to Stille coupling: (1) boron reagents are safer to use compared to the toxic organostannanes, and (2) there is a wide variety of boron reagents available commercially for different applications of Suzuki−Miyaura couplings.[5] Pd-catalyzed direct coupling mechanistically resembles other cross-coupling reactions.[6] The main advantage of the method is that the C−H bond is directly converted to the C−C bond without preceding halogenation or other conversions, thus reducing previous reaction steps before the actual coupling reaction. However, the direct coupling method also has disadvantages of its own. In some cases, higher yields of the target compound have only been achieved by using a large excess of another direct coupling

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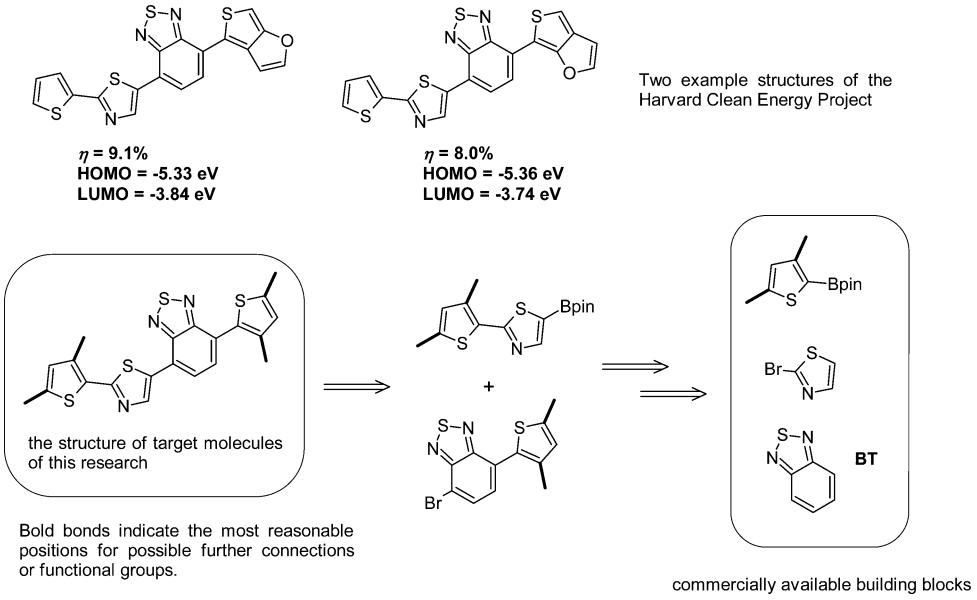
Scheme 1. Model Compounds of the Harvard Clean Energy Project[2,3] and the Proposed Synthetic Pathway to the Target Molecules



Scheme 2. Syntheses of 2-(Thiophen-2-yl)thiazole Derivatives

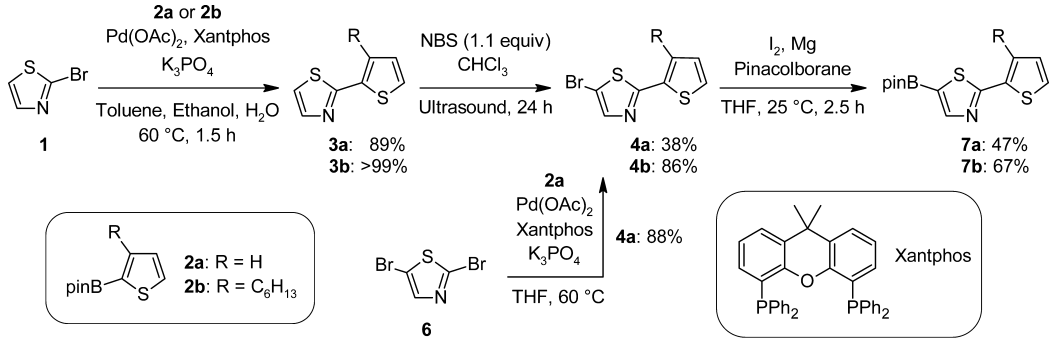


Table 1. Optimization of Suzuki–Miyaura Cross-Coupling of 2-Bromothiazole (1) with Compounds 2a and 2b

entry	catalyst	ligand	base	temperature	reaction time	yield[a] (%)
1	$Pd(PPh_3)_4$[b]		Cs_2CO_3[c]	110 °C	3 h	**3a** 62
2	$Pd_2(dba)_3$[d]	$P(t\text{-}Bu_3)\cdot HBF_4$[e]	Cs_2CO_3[c]	110 °C	3 h	**3a** 87
3	$Pd(OAc)_2$[d]	Xantphos[d]	K_3PO_4[f]	60 °C	3 h	**3a** 89
4	$Pd(PPh_3)_4$[b]		Cs_2CO_3[c]	110 °C	1.5 h	**3b** 69
5	$Pd(OAc)_2$[d]	Xantphos[d]	K_3PO_4[f]	60 °C	1.5 h	**3b** >99

[a]Isolated yield. [b]With 5 mol %. [c]With 2.5 equiv. [d]With 2.5 mol %. [e]With 10 mol %. [f]With 3.0 equiv.

partner.[7] The regioselectivity of the coupling may be an issue with the compounds that have more than one C–H bond available. At least partially, that problem can be solved with a careful choice of the catalyst system and the reaction conditions.[8] On the other hand, the availability of two or more reactive C–H bonds in the same compound can be a desired property in polymer synthesis using the direct arylation approach.[9]

In this paper, we present various parallel synthetic routes to BT derivatives. Particularly, improved and convenient methods to synthesize important chemical building blocks, e.g., 4,7-dibromo-2,1,3-benzothiadiazole, in good to quantitative yields are presented. Moreover, the results of this paper show that various couplings of BT, thiophene, and thiazole derivatives can be efficiently done by applying Xantphos as a ligand of the catalyst system in particular cases. Additionally, the feasibility of Suzuki–Miyaura and direct coupling methods are compared in the synthesis of target BT derivatives. The optical and electronic properties of the prepared compounds, which have been determined both experimentally and computationally, are also reported. These BT derivatives can potentially be applied as building blocks in the construction of more advanced acceptor–donor–acceptor-type organic semiconductors.

RESULTS AND DISCUSSION

Synthesis. The first target compounds of the synthetic scheme, **3a** and **3b**, were synthesized using Suzuki–Miyaura cross-coupling between commercial 2-bromothiazole (**1**) and pinacolboronic ester reagents **2a** and **2b** (Scheme 2). Previous efforts to synthesize compound **3a** using the Suzuki–Miyaura

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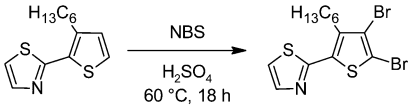
method have afforded the product in 36−43% yields.[10] The cross-coupling reaction between compound **1** and thienyl aluminum reagent have been reported to produce product **3a** in 87% yield,[11] whereas Stille coupling has given product **3a** in 99% yield.[12] In our hands, the Suzuki−Miyaura cross-coupling reaction with $Pd(PPh_3)_4$ as a catalyst gave products **3a** and **3b** in 62 and 69% yields, respectively (Table 1, entries 1 and 4). The use of $Pd_2(dba)_3$ with $P(t\text{-}Bu)_3{\cdot}HBF_4$ as a catalyst system raised the yield of compound **3a** to 87% (entry 2). The bidentate phosphine ligand Xantphos together with air stable palladium source $Pd(OAc)_2$ was shown to be very efficient and gave compounds **3a** and **3b** in 89% and quantitative yields, respectively (entries 3 and 5).

Recently, our and other groups have demonstrated that ultrasound-assisted bromination is an efficient method to produce brominated thiophene derivatives.[13] However, bromination of 2-(thiophen-2-yl)thiazole (**3a**) with NBS in $CHCl_3$ gave the desired monobrominated regioisomer **4a** only in low 38% yield. TLC and MS analyses revealed that the reaction mixture contained mono- and dibrominated products together with the unreacted starting material. The reactions in toluene and DMF gave product **4a** in lower yields (12 and 29%, respectively).

The hexyl side-chain analogue 2-(3-hexylthiophen-2-yl)-1,3-thiazole **3b** showed completely different reactivity in bromination with NBS in $CHCl_3$ compared with compound **3a**. Compound **3b** could be monobrominated with high regioselectivity affording compound **4b** in 86% yield (Scheme 2). Formation of a small amount of dibrominated product of **3b** was also observed during the reaction. Interestingly, the reaction of compound **3b** with NBS in concentrated H_2SO_4 instead of $CHCl_3$ gave solely 2-(4,5-dibromo-3-hexylthiophen-2-yl)-1,3-thiazole (**5**) (Scheme 3) without any traces of desired

Scheme 3. Bromination of Compound 3b with NBS in Concentrated H_2SO_4



3b **5**

product **4b** or byproducts. Apparently, the protonation of thiazole nitrogen in concentrated H_2SO_4 prevents bromination at the thiazole site of compound **3b**, thereby directing bromination to the otherwise more inactive thiophene sites and giving dibrominated product **5**.

Because of the problems with bromination of compound **3a**, we looked for an alternative route to synthesize compounds **4a** and **4b**. The study of Strotman et al. demonstrated that Suzuki−Miyaura cross-couplings of commercially available 2,5-dibromothiazole (**6**) with various arylboronic acids can be conducted regioselectively by applying a suitable phosphine ligand.[14] Our experiments revealed that compound **4a** can be efficiently synthesized by cross-coupling compound **6** with pinacolboronic ester reagent **2a** (Scheme 2). Product **4a** was isolated in good 88% yield after a chromatographic separation. In the case of **4b**, this reaction approach gave the full conversion of the starting material. However, formation of the undesired dicoupling product was also observed. Furthermore, the 1:9 mixture of dicoupling product and the desired monocoupling product **4b** were shown to be inseparable in our hands. Thus, this reaction route to produce compound **4b** was unsatisfactory.

Singaram et al. have demonstrated that various bromo aryl, alkyl, and thiophene derivatives react with pinacolborane under Barbier-type conditions, producing corresponding aryl, alkyl, and thiophene pinacolboronic esters, respectively.[15] This approach gave the desired pinacolboronic ester derivatives **7a** and **7b** in moderate 47 and 67% yields, respectively (Scheme 2). As a comparison, a trial of Pd-catalyzed borylation of compound **4b** using $Pd_2(dba)_3$ together with SPhos as a catalyst system and reaction conditions presented by Buchwald et al.[16] gave only trace amounts of compound **7b**. Furthermore, the common borylation using *n*-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[17] failed to give compound **7b**.

4,7-Dibromo-2,1,3-benzothiadiazole (**9**) is an important heterocyclic starting material that is usually prepared from 2,1,3-benzothiadiazole (**8**) by using elemental Br_2 in HBr.[18] This approach has been reported to give compound **9** at up to 95% yield. However, the synthetic procedure and workup are somewhat time-consuming and laborious. Previously, compound **9** was also synthesized from compound **8** by using NBS in anhydrous THF.[19] After 24 h of reaction time, product **9** was isolated in 50% yield. Our experiments showed that compound **9** can be prepared easily and highly efficiently from compound **8** by using a slight excess of NBS (2.05 equiv) in concentrated H_2SO_4 (Scheme 4). Compound **9** was isolated after a 3 h reaction and simple workup procedure as an off-white powder in a quantitative yield (>99%). The product was used without further purification in the next reaction step.

Compound **9** was applied as a starting material in the synthesis of compound **10** (Scheme 4). The monocoupling product **10** has been previously synthesized from compound **9** via both the Stille and the Suzuki−Miyaura cross-coupling reactions in 59−60% yields.[20] Following similar reaction conditions as presented in the literature, our first Suzuki−Miyaura coupling trial with a standard $Pd(PPh_3)_4$ catalyst gave product **10** in 56% yield (Table 2, entry 1). The yield could be improved to 61% by increasing the excess of compound **9** in the reaction system (entry 2). The use of $Pd_2(dba)_3$ with $P(t\text{-}Bu)_3{\cdot}HBF_4$ as a catalyst instead of $Pd(PPh_3)_4$ raised the yield to 66% (entry 3). TLC and MS analyses revealed that product **10** undergoes consequent cross-coupling with the pinacolboronic ester reagent, producing an undesired dicoupling byproduct. Naturally, this side reaction decreases the yield of compound **10**. In the literature, compound **9** has been cross-coupled with various organostannanes using the Stille coupling approach and $Pd(PPh_3)_4$ as a catalyst. The resulting monocoupling products have been isolated in 66−70% yields.[21] Respectively, Suzuki−Miyaura cross-coupling reactions with $Pd(PPh_3)_4$ as a catalyst have produced the monoarylation products in 30−78%[22] yields. In some cases, the reaction outcome has been an inseparable mixture of mono- and dicoupling products.[23] The Dupont's palladacyclic catalyst[24] has produced monoarylated Suzuki−Miyaura coupling products of compound **9** in somewhat higher yields (71−85%).[25] However, restricted commercial availability of Dupont's catalyst makes its utilization difficult in cross-coupling reactions. Our studies showed that bidentate Xantphos ligand together with $Pd(OAc)_2$ is capable of producing the desired monocoupling product **10** in 78% yield (Table 2, entry 4) which could be further improved up to 80% after solvent, base, and reaction temperature optimizations (entries 5−8).

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Scheme 4. Syntheses of BT Derivatives

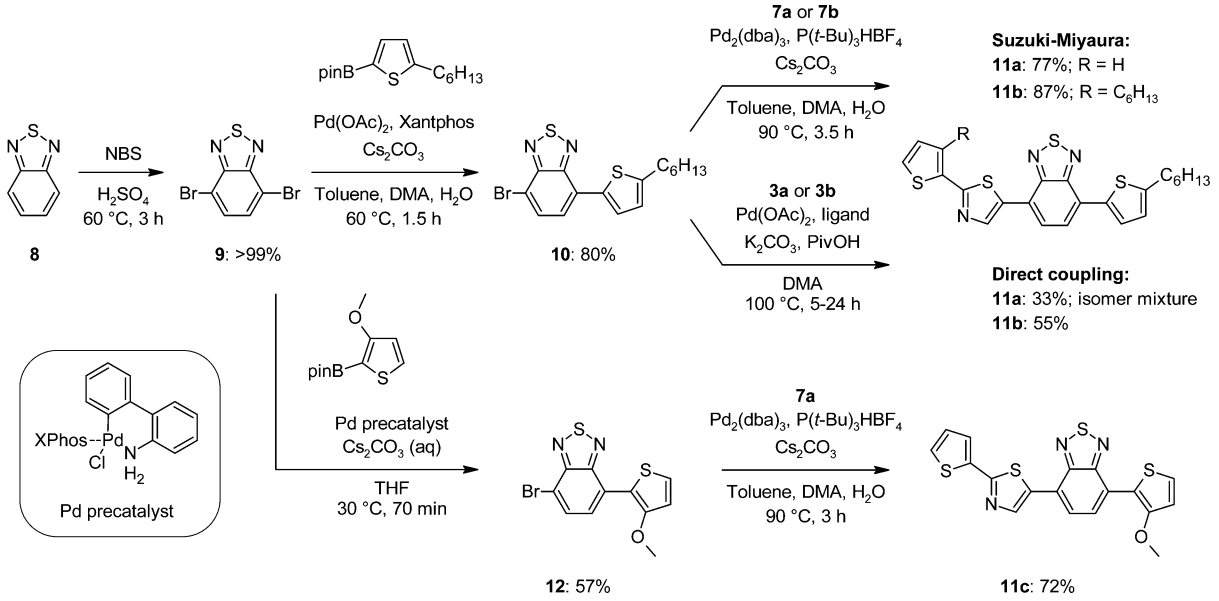

Table 2. Optimization of Suzuki–Miyaura Cross-Coupling of Compound 9 with 5-Hexyl-2-thiopheneboronic Acid Pinacol Ester

entry	catalyst	ligand	temperature	reaction time	yield[a] of compound **10** (%)
1	$Pd(PPh_3)_4$[b]		85 °C	3 h	56[c]
2	$Pd(PPh_3)_4$[b]		85 °C	3 h	61
3	$Pd_2(dba)_3$[d]	$P(t\text{-}Bu)_3{\cdot}HBF_4$[e]	85 °C	1.5 h	66
4	$Pd(OAc)_2$[b]	Xantphos[b]	85 °C	1.5 h	78
5	$Pd(OAc)_2$[b]	Xantphos[b]	60 °C	1.5 h	80[f]
6	$Pd(OAc)_2$[b]	Xantphos[b]	50 °C	1.5 h	58
7	$Pd(OAc)_2$[b]	Xantphos[b]	60 °C	1.5 h	79[g]
8	$Pd(OAc)_2$[b]	Xantphos[b]	60 °C	1.5 h	63[h]

Reaction conditions: 5-hexyl-2-thiopheneboronic acid pinacol ester (50 mg), compound **9** (1.5 equiv), Cs_2CO_3 (2.5 equiv), solvents: toluene (2 mL), DMA (2 mL), and H_2O (0.4 mL). [a]Isolated yield. [b]With 5 mol %. [c]With 1.1 equiv of compound **9**. [d]With 2.5 mol %. [e]With 10 mol %. [f]Average of two runs. [g]Solvents: 1,4-dioxane (4 mL) and H_2O (0.4 mL). [h]Base: K_3PO_4 (2.5 equiv).

To synthesize a structurally closer analogue of the model compounds of the Harvard Clean Energy Project from the easily available starting materials, we were interested in cross-coupling compound **9** with 3-methoxythiophene-2-boronic acid pinacol ester (Scheme 4). However, the use of the optimized cross-coupling reaction conditions described above gave desired Suzuki–Miyaura reaction product **12** only in 7% yield. Obviously, the quick protodeboronation of pinacol ester reagent occurred,[26] which could be observed by TLC analysis as quick disappearance of the reagent from the reaction medium. The solution to the problem was to use XPhos-containing palladium precatalyst (Scheme 4), which forms the catalytically active XphosPd(0) rapidly even at room temperature and efficiently catalyzes various Suzuki–Miyaura cross-couplings of unstable boronic reagents.[26,27] This approach gave compound **12** in 55% yield. Similarly to the synthesis of compound **10**, the yield of product **12** was limited by the formation of the undesired dicoupling product. By replacing K_3PO_4(aq) with Cs_2CO_3(aq) as a base, the yield could be slightly improved to 57%.

The final target compounds **11a** and **11b** were synthesized from compound **10** and pinacolboronic ester reagents **7a** and **7b** using Suzuki–Miyaura cross-coupling (Scheme 4). Respectively, the third target molecule of this study, compound **11c**, was synthesized from compound **12** and pinacolboronic ester reagent **7a**. The standard $Pd(PPh_3)_4$ catalyst gave compound **11b** in only very low 16% yield. Furthermore, the otherwise superior $Pd(OAc)_2$/Xantphos catalyst combination gave only partial conversion of starting materials within 21 h in this case. The $Pd_2(dba)_3/P(t\text{-}Bu)_3{\cdot}HBF_4$ catalyst system gave all of the desired products in good 77% (**11a**), 87% (**11b**), and 72% (**11c**) yields.

A drawback of the Suzuki–Miyaura approach is the necessity of preparing the borylated compounds **7a** and **7b**, which in terms of atom economy and synthesis time is a waste of resources. Potentially, the other possibility to produce the final target compounds **11a–c** is to couple compounds **10** and **12** with compounds **3a** and **3b** directly. In the literature, compound **9** has been coupled directly with cyclopentadithiophene derivatives to form polymeric materials and with thiophene derivatives to form oligomeric products.[7b,28] Specifically, the drawback of the ligand-free direct coupling approach is the requirement of a large excess of thiophene (15–20 equiv).[7b] Direct arylation of thiazole has been researched somewhat more.[8a,b,29] After comparing the most promising results of these studies, we carried out the optimization studies of the direct coupling of compound **10** with compound **3b**. The optimized reaction conditions were also tested in direct coupling reaction of compound **10** with compound **3a**. The results are presented in Table 3.

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Table 3. Optimization of Direct Coupling of Compound 10 with Compounds 3a and 3b

entry	ligand	base	additive	amount of 3b/3a	reaction time	yield[a] (%)
1	Xantphos[b]	Cs_2CO_3	PivOH[c]	1.0 equiv	24 h	**11b** 21
2	Xantphos[b]	K_2CO_3	PivOH[c]	1.0 equiv	24 h	**11b** 45
3	Xantphos[b]	K_2CO_3	CuI[d]	1.0 equiv	24 h	**11b** 28
4	P(*t*-Bu)$_3$·HBF$_4$[d]	K_2CO_3	PivOH[c]	1.0 equiv	6 days	**11b** 29
5	PCy$_3$·HBF$_4$[d]	K_2CO_3	PivOH[c]	1.0 equiv	24 h	**11b** 43
6	P(*t*-Bu)$_2$Me·HBF$_4$[d]	K_2CO_3	PivOH[c]	1.0 equiv	24 h	**11b** 52
7	P(*t*-Bu)$_2$Me·HBF$_4$[d]	K_2CO_3	PivOH[c]	1.5 equiv	24 h	**11b** 55
8	Xantphos[b]	K_2CO_3	PivOH[c]	1.5 equiv	5 h	**11b** 55
9	Xantphos[b]	K_2CO_3	PivOH[c]	1.5 equiv	5 h	**11a** trace
10	P(*t*-Bu)$_2$Me·HBF$_4$[d]	K_2CO_3	PivOH[c]	1.5 equiv	5 h	**11a** 33[e]

Reaction conditions: compound **10** (30 mg), Pd(OAc)$_2$ 5 mol %, base (2.5 equiv), DMA (1 mL), 100 °C. [a]Isolated yield. [b]With 5 mol %. [c]With 60 mol %. [d]With 10 mol %. [e]Mixture of structural isomers.

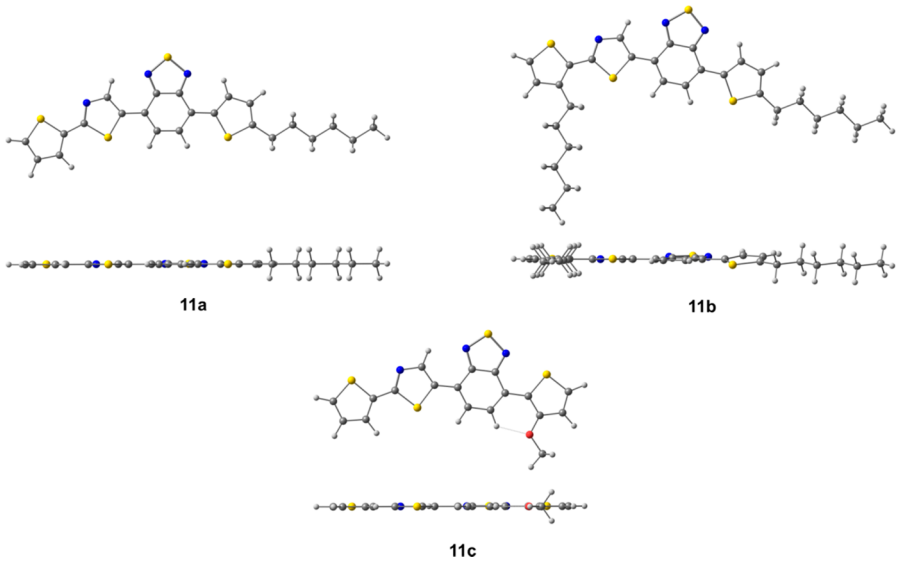

Figure 1. Molecular ground-state geometries of compounds **11a–c** optimized in $CHCl_3$ at the B3LYP/6-311++G(d) level of theory.

In the presence of Cs_2CO_3 base, the direct coupling gave desired compound **11b** in low yield (Table 3, entry 1), and the formation of an unidentified byproduct was observed that was not present in other reactions. The use of K_2CO_3 as a base improved the yield up to 45% (entry 2). The replacement of pivalic acid additive with CuI led to decreased yield of compound **11b** (entries 2 and 3). The screening of the ligand effect for this particular coupling revealed that the decrease of the steric size of the monodentate ligand improves the yield of the direct coupling product **11b** (entries 4–6). P(*t*-Bu)$_2$Me·HBF$_4$ ligand showed improved and the best performance compared with other monodentate ligands and, moreover, bidentate Xantphos. The yield of direct coupling product **11b** could be slightly improved by increasing the amount of coupling partner **3b** from 1.0 to 1.5 equiv (entries 6 and 7). Surprisingly, the use of Xantphos as a ligand and 1.5 equiv of compound **3b** gave compound **11b** in the same 55% yield as P(*t*-Bu)$_2$Me·HBF$_4$ ligand (entries 7 and 8). Interestingly, the conversion rate of starting material **10** was much higher for the reaction with Xantphos ligand. The reaction was finished just after 5 h.

Direct coupling of **3a** with compound **10** showed a major difference compared to the reaction of **3b** with compound **10**. The reaction in the presence of Xantphos ligand gave only trace amounts of product **11a** (Table 3, entry 9). P(*t*-Bu)$_2$Me·HBF$_4$ ligand gave full conversion of starting material **10** within 5 h, and the product was isolated in 33% yield (entry 10). However, ^{1}H NMR and HPLC-HRMS analyses revealed that the product was a mixture of desired product **11a** and its structural isomer in a 9:1 ratio (see Supporting Information). This mixture of two isomers was shown to be inseparable in our hands. These experiments reflect the fact that the problems in both reactivity and selectivity may cause serious limitations to exploit the direct coupling reaction as an effective synthetic tool.

■ COMPUTATIONAL STUDIES

The optimized ground-state molecular geometries presented in Figure 1 (see also Figure S1, Table S1, and the coordinates in the Supporting Information), the total energies (Table S2), the energies of the HOMO and LUMO, and the HOMO–LUMO gaps (Table 4) of compounds **11a–c** were computed using density functional theory (DFT). The final optimized geometries (Figure 1) were confirmed at the same level of theory to be the minimum energy structures by the absence of the imaginary frequency. The energetically most favorable conformations of compounds **11a–c** (Figure S2, Table S2) are almost planar both in vacuum and in $CHCl_3$. The second hexyl side-chain of compound **11b** causes small torsional twists of the molecular backbone compared to the totally planar structure of compound **11a**. The hexyl side-chain at the end position is

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Table 4. Experimental and Computational Values of HOMO, LUMO, and Band Gap (E_g) Energies of Compounds 11a–c in Electron Volts (eV)

compound	HOMO[a,b]	LUMO[a,b]	$E_{HOMO-LUMO}$[a,b]	HOMO[a,c]	LUMO[a,c]	$E_{HOMO-LUMO}$[a,c]	HOMO[d]	LUMO[d]	E_g[d]
11a	−5.52	−3.00	2.52	−5.59	−3.04	2.55	−5.70	−3.36	2.34
11b	−5.43	−2.94	2.50	−5.53	−3.00	2.53	−5.49	−3.13	2.36
11c	−5.39	−2.88	2.51	−5.47	−2.95	2.52	−5.47	−3.31	2.16

[a]Calculated at the B3LYP/6-311++G(d,p) level of theory. [b]In vacuum. [c]In $CHCl_3$. [d]Experimentally measured by DPV.

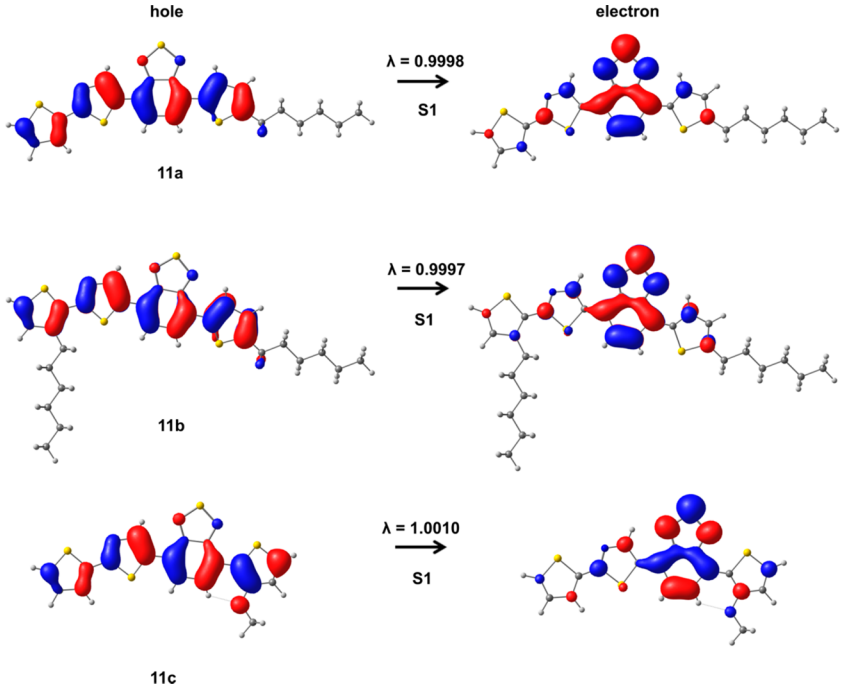

Figure 2. Natural transition orbitals (NTOs) presenting the hole (left) and electron (right) of the $S_0 \rightarrow S_1$ transitions of compounds **11a–c** calculated at the TDDFT/B3LYP/6-311++G(d,p) level of theory in $CHCl_3$ (isodensity contour = 0.030). The eigenvalue λ is the fraction of the hole–electron contribution to the given excitation which in all of these is 100%.

present in both **11a** and **11b**, but due to its parallel positioning with the backbone, it has only a small effect on the dihedral angles of compound **11a**. In the energetically less favorable conformation of compound **11c**, the oxygen atom of the methoxy substituent is repelled by the nitrogen atom of the BT unit, which makes the structure nonplanar. On the other hand, in the most favorable conformation of **11c**, the distance between the methoxy oxygen and a hydrogen atom of the BT unit is 2.12 Å, implying hydrogen bonding, which stabilizes the structure and makes it nearly planar. These kinds of highly planar backbones are important starting points for effective conjugation.

Natural transition orbitals (NTO)[30] were used to study the nature of the electronic transitions. The NTOs provide a compact description for the electronic transition density matrix and simplify the analysis of the excited states consisting of mixed electronic configurations, which are usually difficult to characterize with MOs. The NTOs reduce the description of an excited-state transition into a single hole-particle excitation whose fraction to the given transition is given by an eigenvalue λ, which is $0 \leq \lambda \leq 1$. The NTOs of compounds **11a–c** for the $S_0 \rightarrow S_1$ transition are illustrated in Figure 2. The $S_0 \rightarrow S_1$ transitions are mostly HOMO → LUMO in character (Table S3), and thus the corresponding NTOs are almost identical to the frontier molecular orbitals (not shown here). In the $S_0 \rightarrow S_1$ transitions, the hole is delocalized along the conjugated backbone of **11a–c**, whereas the electron is mainly localized on the central BT acceptor unit. Thus, the lowest singlet excitation of compounds **11a–c** has a clear charge transfer character.

Electrochemical and Spectroscopic Studies. The HOMO/LUMO energy levels of compounds **11a–c**, calculated from differential pulse voltammetry (DPV) experiments, and the HOMO–LUMO gap energies (E_g) are presented in Table 4 together with the computational values. The voltammograms (change in current–voltage curves, where voltages are given with respect to the ferrocene couple) are shown in the Supporting Information.

Compound **11a** undergoes a three-step reduction and a two-step oxidation. The reduction peaks are detected at −2.2, −1.6, and −1.5 V, whereas the oxidation peaks appear at +0.9 and +1.0 V. Compound **11b** shows a two-step oxidation and reduction. The reductions occur at −1.7 and −2.3 V, whereas the oxidations occur at +0.7 and +0.9 V. Compound **11c** has oxidation peaks at +0.67, + 0.87, and +1.18 V and reduction peaks at −1.49, −1.69, and −2.21 V. The slightly higher reduction potential of **11b** suggests that it is the strongest electron donor among the studied compounds. However, all three compounds, **11a–c**, present similar electrochemical properties, as shown in Table 4. These experimental findings are supported by the computed HOMO/LUMO levels and HOMO–LUMO gap values, which show only minor differ-

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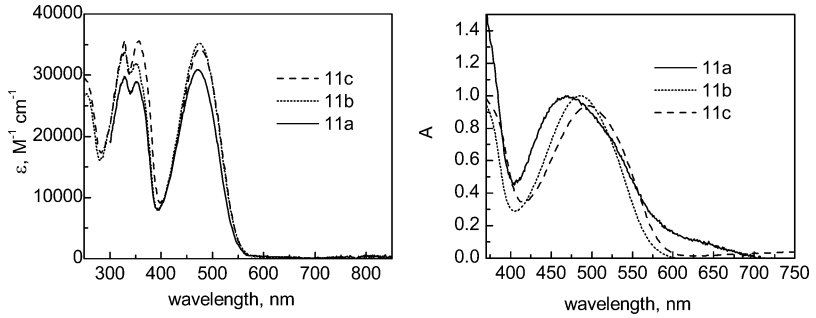

Figure 3. Molar absorptivity (ε) of compounds **11a–c** in $CHCl_3$ solution (left); normalized absorption spectra of **11a–c** in solid films (right).

Table 5. Absorption and Fluorescence Emission Maxima and Stokes Shifts of Compounds 11a–c

compound	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{em}{}^{a}$ (nm)	Stokes shift[a] (nm)	$\varepsilon^{a,b}$ (cm^{-1} mol^{-1} dm^3)	$\lambda_{abs}{}^{c}$ (nm)	$\lambda_{em}{}^{c}$ (nm)	Stokes shift[c] (nm)
11a	472	593	121	30900	471	626	155
11b	475	597	122	35300	486	677	191
11c	475	618	143	34300	496	683	187

[a]In $CHCl_3$ solution. [b]Molar extinction coefficient at absorption maxima. [c]In solid film.

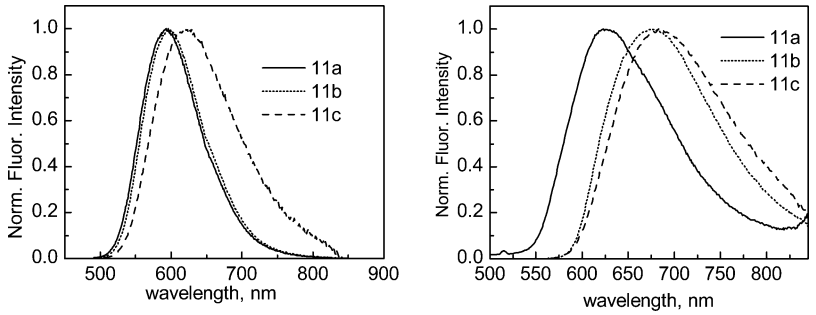

Figure 4. Normalized fluorescence emission spectra of compounds **11a–c** in solution (left) and solid films (right).

ences between the compounds. However, compound **11c**, the structurally closest analogue of the theoretical Harvard Clean Energy Project molecules (presented in Scheme 1), has the closest experimentally determined HOMO level and HOMO–LUMO gap relative to the theoretical compounds of Scheme 1. Compared to the HOMO/LUMO levels of the theoretical molecules, the LUMO levels of compounds **11a–b** and also **11c** are higher and the HOMO–LUMO gap wider. This is logical because the fused furan structure of the theoretical molecules extends the conjugation and thus lowers the LUMO level and simultaneously decreases the HOMO–LUMO gap.

Absorption spectra (on molar absorptivity (ε) scale) of compounds **11a–c** in $CHCl_3$ solution and absorption spectra in solid films normalized at the Q-transition (S0–S1) absorption maximum are depicted in Figure 3. The non-normalized spectra are presented in the Supporting Information. The summary of optical data is shown in Table 5. The absorption spectra of compounds **11a–c** in solution are almost identical with a 3 nm red-shift (in the Q-band absorption) for the spectra of compounds **11b** and **11c** with respect to **11a**. The absorption spectra of **11b** and **11c** in solid films are instead bathochromically (red) shifted 15 and 20 nm, respectively, compared to that of **11a**. It can be further noted that for compound **11a** there is a very small hypsochromic (blue) shift between the absorption maximum in solid films (λ^{b}_{abs}) compared to the maximum in solution (λ^{a}_{abs}), whereas for **11b** and **11c** there are 11 and 21 nm red-shifts, respectively, in the absorption maxima peaks in solution and solid films. This suggests the possibility for different types of aggregation in solid films of compounds **11a** (H-aggregates)[31] and **11b** and **11c** (J-aggregates).[32]

In Figure 4, the normalized fluorescence emission spectra of **11a–c** in solution and films are presented, whereas in the Supporting Information, the non-normalized emission spectra (Figure S5) together with the fluorescence measurements setup are reported. In $CHCl_3$ solution, the emission spectra of **11a** and **11b** approximately overlap, and the spectrum of compound **11c** has red-shifted 21 nm with respect to **11b**. Whereas the emission spectra of **11b** and **11c** show similar spectral features and are considered red-shifted with respect to that of **11a** in solid films. Interestingly, these compounds or their derivatives may also find potential future applications as coloring substances. For example, compound **11a**, which has the smallest full width at half-maximum of emission in solution (95 nm), shows high color purity (98%) of a yellowish-orange hue with CIE 1931 chromaticity coordinates of (0.54, 0.45).

In organic materials, the emission peak from an electronic state is red-shifted with respect to the absorption peak by the Stokes shift. The Stokes shifts for **11a** and **11b** are nearly the same in $CHCl_3$ solution and considerably smaller in comparison to that of **11c** (Table 5). In solid films, compounds **11b** and **11c** have a larger Stokes shifts (191 and 187 nm, respectively) compared to **11a** (155 nm). A large Stokes shift typically indicates a change in geometry from the ground state to the excited state. It can be expected that the energy losses due to reorganization upon excitation are larger for **11b** and **11c** than for **11a** because of the extra hexyl side-chain (**11b**)

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and methoxy substituent (**11c**).[13d] Hence, there is a larger dipole moment change from the ground state to the excited state in **11b** and **11c** compared to **11a** in solid films.[33] The larger Stokes shift of **11c** in $CHCl_3$ is attributed to the methoxy substituent providing greater reorganization energy loss upon light absorption.

CONCLUSIONS

Various reaction routes involving 4−6 reaction steps for the synthesis of three BT derivatives, compounds **11a−c**, are presented. Our synthetic findings show in particular that the use of bidentate Xantphos ligand as a part catalyst system in cross-couplings is an effective way to synthesize various thiophene-thiazole, thiophene-BT, and thiazole-BT coupling products. For instance, monocoupling product 4-bromo-7-(5-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (**10**) can be synthesized in good 80% yield by applying the Xantphos ligand in Suzuki−Miyaura cross-coupling to overcome the competing dicoupling. In the final reaction step, Suzuki−Miyaura cross-coupling was a more powerful tool compared to the direct coupling method and, in particular, the only way to produce compound **11a**. However, the overall yields of compound **11b** were 39% via the Suzuki−Miyaura pathway (6 reaction steps) and 43% via the direct coupling pathway (4 reaction steps). This means that the direct coupling method may offer a good alternative for Suzuki−Miyaura coupling in particular cases: (i) the yield of boron reagent, which is needed in Suzuki−Miyaura cross-coupling, is low, and (ii) the direct coupling does not suffer regioselectivity problems.

The prepared target molecules **11a−c** closely structurally resemble the selected molecules (Scheme 1) presented by the Harvard Clean Energy Project.[2] Computational studies showed that compounds **11a−c** have nearly planar molecular backbones, which offer prerequisites for effective conjugation and intramolecular charge transfer. Electronic and optical properties of the compounds resemble each other, nevertheless, **11b** and **11c** exhibit stronger red-shift in absorption and emission in film with respect to those in **11a**. In addition, compound **11c** shows more pronounced red-shift in emission also in solution in comparison to **11a** and **11b**. Larger Stokes shifts for **11b** and **11c** are assigned to a larger dipole moment change upon light excitation due to extra hexyl side-chain of **11b** and methoxy substituent of **11c**. This is consistent with our previous observation that the nature of the solubility increasing alkyl side-chains may notably change the solid state properties.[13d] Compounds **11a−c** can be potentially applied as building blocks in the construction of more advanced acceptor−donor−acceptor-type organic semiconductors in which the compounds act as the acceptor units. This strategy allows for free variation of the central donor unit. Our current work continues with that subject.

EXPERIMENTAL SECTION

Characterization. All new compounds were purified using flash chromatography (SiO_2). Only fractions that showed a single spot on TLC were collected. The chemical structures of new compounds were characterized using ^1H NMR, ^{13}C NMR, and HRMS techniques. ESI-MS/MS studies were carried out for compounds **11a−c**. ^1H NMR spectra assignments are presented in the Supporting Information. A heat-flux differential scanning calorimeter was used for measuring the melting points (reported as onset values) of crystalline compounds **4b**, **5**, **7b**, **11a**, **11c**, and **12**. A heating rate of 20 °C min^{-1}, temperature scans from 5 to 300 °C, and a nitrogen flow of 60 mL min^{-1} were used in the measurements. Samples of 0.34−3.16 mg were placed in 40 μL Al crucibles, which were sealed with pierced lids.

*Synthesis of 2-(Thiophen-2-yl)thiazole (**3a**).* Toluene (2.5 mL), ethanol (0.8 mL), distilled water (0.8 mL), and 2-bromothiazole (**1**) (99.0 mg, 0.60 mmol) were deoxygenated with argon for 15 min in a reaction tube with a magnetic stirring bar. Ground K_3PO_4 (3 equiv, 389.5 mg, 1.83 mmol), 2-thiopheneboronic acid pinacol ester (**2a**) (1.03 equiv, 130.4 mg, 0.62 mmol), $Pd(OAc)_2$ (2.6 mol %, 3.5 mg, 15.6 μmol), and Xantphos (2.6 mol %, 9.0 mg, 15.6 μmol) were added. The sealed tube was evacuated and backfilled with argon five times, and finally the tube was flushed with argon for 5 min. The reaction mixture was stirred and heated in an oil bath (60 °C) for 3 h. The reaction mixture was filtered through a thin pad of silica gel, rinsed with toluene, and evaporated under reduced pressure. The product was purified by using flash chromatography (SiO_2, toluene). Isolated product **3a** was collected as a viscous oil (89.7 mg) in 89% yield. The spectral data correspond with that in a previous report.[12] ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ 7.09 (dd, J = 5.1, 3.6 Hz, 1H), 7.29 (d, J = 3.3 Hz, 1H), 7.41 (dd, J = 5.1, 1.1 Hz, 1H), 7.53 (dd, J = 3.6, 1.1 Hz, 1H), 7.75 (d, J = 3.3 Hz, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, ppm): δ 118.8, 127.1, 128.1, 128.4, 138.0, 143.7, 162.3. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_7H_6NS_2$, 167.9942; found, 167.9934.

*2-(3-Hexylthiophen-2-yl)thiazole (**3b**).* Compound **3b** was prepared by using the same synthetic procedure as described above for compound **3a**. The specific amounts of reagents used were toluene (3.75 mL), ethanol (1.2 mL), distilled water (1.2 mL), compound **1** (146.6 mg, 0.89 mmol), K_3PO_4 (3 equiv, 582.4 mg, 2.74 mmol), 3-hexyl-2-thiopheneboronic acid pinacol ester (**2b**) (1.04 equiv, 274.6 mg, 0.93 mmol), $Pd(OAc)_2$ (2.6 mol %, 5.1 mg, 22.7 μmol), and Xantphos (2.6 mol %, 13.4 mg, 23.2 μmol). Pure compound **3b** was isolated as a viscous oil (223.2 mg) in >99% yield. ^1H NMR (200 MHz, CD_2Cl_2, ppm): δ 0.90 (t, J = 6.8 Hz, 3H), 1.28−1.50 (m, 6H), 1.62−1.77 (m, 2H), 2.93 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 5.2 Hz, 1H), 7.30 (d, J = 5.2 Hz, 1H), 7.35 (d, J = 3.3 Hz, 1H), 7.79 (d, J = 3.3 Hz, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, ppm): δ 14.0, 22.5, 29.2, 29.8 (2C), 31.5, 118.0, 126.2, 130.3, 131.4, 142.0, 142.5, 160.9. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NS_2$, 252.0881; found, 252.0893.

*Synthesis of 5-Bromo-2-(thiophen-2-yl)thiazole (**4a**) from **3a**.* Compound **3a** (61.9 mg, 0.37 mmol) was dissolved in $CHCl_3$ (5.5 mL), and NBS (1.1 equiv, 73.7 mg, 0.41 mmol) was added. The reaction mixture was irradiated with ultrasound (42 kHz, 100 W) for 24 h. The solvent was evaporated, and the crude product was subjected to flash chromatography (SiO_2, toluene). Pure compound **4a** was isolated as an off-white solid (34.7 mg) in 38% yield. ^1H NMR (400 MHz, $CHCl_3$, ppm): δ 7.07−7.10 (m, 1H), 7.42 (d, J = 5.1 Hz, 1H), 7.45 (d, J = 3.7 Hz, 1H), 7.65 (s, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 107.6, 126.8, 127.9, 128.2, 136.7, 144.4, 163.2. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_7H_5NS_2Br$, 245.9047; found, 245.9036. HRMS (ESI+, TOF) m/z of dibrominated byproduct: $[M + H]^+$ calcd for $C_7H_4NS_2Br_2$, 323.8152; found, 323.8161. HRMS (ESI+, TOF) m/z of monobrominated byproduct: $[M + H]^+$ calcd for $C_7H_5NS_2Br$, 245.9047; found, 245.9039.

*5-Bromo-2-(3-hexylthiophen-2-yl)thiazole (**4b**).* Compound **4b** was prepared by using the same synthetic procedure as described above for compound **4a**. The specific amounts of reagents used were compound **3b** (97.2 mg, 0.39 mmol), NBS (1.1 equiv, 76.5 mg, 0.43 mmol), and $CHCl_3$ (6 mL). Pure compound **4b** was isolated as a solid (110.3 mg) in 86% yield; mp 44 °C. ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ 0.90 (t, J = 7.0 Hz, 3H), 1.30−1.44 (m, 6H), 1.64−1.71 (m, 2H), 2.86 (t, J = 7.8 Hz, 2H), 6.98 (d, J = 5.3 Hz, 1H), 7.32 (d, J = 5.3 Hz, 1H), 7.67 (s, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, ppm): δ 14.4, 23.2, 29.8, 30.4, 30.5, 32.2, 108.2, 127.4, 131.1, 131.7, 143.4, 144.3, 162.8. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}NS_2Br$, 329.9986; found, 329.9986. HRMS (ESI+, TOF) m/z of dibrominated byproduct: $[M + H]^+$ calcd for $C_{13}H_{16}NS_2Br_2$, 407.9091; found, 407.9094.

*Synthesis of Compound **4a** Using Compound **6** as a Starting Material.* 2,5-Dibromothiazole (**6**) (72.8 mg, 0.30 mmol), 2-thiopheneboronic acid pinacol ester (**2a**) (1.07 equiv, 68.0 mg, 0.32

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mmol), $Pd(OAc)_2$ (3.3 mol %, 2.3 mg, 10 μmol), Xantphos (2.5 mol %, 4.3 mg, 7.4 μmol), and K_3PO_4 (3 equiv, 199.3 mg, 0.94 mmol) were placed in a reaction tube with a magnetic stirring bar. The sealed tube was evacuated and backfilled with argon five times. Deoxygenated dry THF (1.5 mL) was added with a syringe. The reaction mixture was stirred in oil bath (60 °C) for 5 h. The reaction mixture was filtered through a thin pad of silica gel, rinsed with toluene, and evaporated under reduced pressure. The product was purified using flash chromatography (SiO_2, toluene). Isolated product **4a** was collected as an off-white solid (65.2 mg) in 88% yield. Dicoupling byproduct of the coupling reaction between compounds **2b** and **6**: HRMS (ESI+, TOF) m/z of dicoupling byproduct: $[M + H]^+$ calcd for $C_{23}H_{32}NS_3$, 418.1697; found, 418.1679.

*Synthesis of 2-(4,5-Dibromo-3-hexylthiophen-2-yl)-1,3-thiazole (**5**).* Compound **3b** (11.6 mg, 46 μmol) was dissolved in concentrated H_2SO_4 (0.5 mL) in a round-bottom flask with a magnetic stirring bar. The reaction mixture was stirred and heated in an oil bath (60 °C). NBS (1.0 equiv, 8.3 mg, 47 μmol) was dissolved in concentrated H_2SO_4 (0.5 mL). The prepared solution was added dropwise to the reaction mixture. After an 18 h reaction time, the cooled reaction mixture was added dropwise in the mixture of aqueous NaOH (1M, 5 mL) and toluene (5 mL). The pH of the aqueous layer was adjusted to >7 with solid NaOH. The mixture was extracted with toluene (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 for 10 min. The solution was filtered and evaporated under reduced pressure. The crude product was purified with flash chromatography (SiO_2, toluene). Pure product **5** was isolated as a solid (5.4 mg); mp 34 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ 0.88−0.92 (m, 3H), 1.32−1.37 (m, 4H), 1.44−1.51 (m, 2H), 1.56−1.64 (m, 2H), 2.97−3.01 (m, 2H), 7.42 (d, J = 3.3 Hz, 1H), 7.80 (d, J = 3.3 Hz, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, ppm): δ 14.4, 23.2, 29.1, 29.9, 31.4, 32.0, 113.8, 118.8, 119.7, 133.7, 141.1, 143.3, 159.7. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}NS_2Br_2$, 407.9091; found, 407.9094.

*Synthesis of 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)thiazole (**7a**).* Magnesium powder (1.3 equiv, 22.3 mg, 0.92 mmol) and an iodine crystal were added in a reaction tube with a magnetic stirring bar. The sealed reaction system was heated until iodine sublimed. The reaction system was allowed to cool to 25 °C after which the system was purged with argon for 5 min. Compound **4a** (170.8 mg, 0.70 mmol) was dissolved in dry THF (2 mL) and added through the septum in the reaction system. Under constant stirring, pinacolborane (1.1 equiv, 0.11 mL, 0.76 mmol) was added dropwise through the septum. The reaction mixture was stirred at 25 °C for 2.5 h. The reaction mixture was cooled in an ice bath; 2 M aqueous HCl (5 mL) was added dropwise, and the mixture was stirred for 15 min. During that period, the released H_2 gas escaped from the reaction system through the open needle. The reaction mixture was extracted with toluene (4 × 5 mL). The combined organic layers were dried with Na_2SO_4, filtered, and evaporated to dryness. The product was isolated using flash chromatography (SiO_2). The column was eluated with toluene until the impurities ran out. In the second stage, the column was eluated with acetone to isolate the desired product. Compound **7a** was collected as a solid (96.5 mg) in 47% yield. ^{1}H NMR (400 MHz, $CHCl_3$, ppm): δ 1.37 (s, 12H), 7.09−7.11 (m, 1H), 7.42 (d, J = 4.9 Hz, 1H), 7.58 (d, J = 3.7 Hz, 1H), 8.16 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 24.7, 84.5, 127.3, 128.0, 128.2, 137.2, 152.6, 167.1. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}NO_2S_2B$, 293.0830; found, 293.0839.

*2-(3-Hexylthiophen-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (**7b**).* Compound **7b** was prepared using the same synthetic procedure as described above for compound **7a**. The specific amounts of reagents used were compound **4b** (222.0 mg, 0.67 mmol), Mg (1.2 equiv, 20.0 mg, 0.82 mmol), pinacolborane (1.1 equiv, 0.11 mL, 0.76 mmol), and THF (6 mL). Pure compound **7b** was isolated as a solid (161.1 mg) in 67% yield; mp 103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.90 (t, J = 7.1 Hz, 3H), 1.33−1.45 (m, 18H), 1.71 (quin, J = 7.6 Hz, 2H), 2.95 (t, J = 7.8 Hz, 2H), 6.98 (d, J = 5.1 Hz, 1H), 7.32 (d, J = 5.1 Hz, 1H), 8.21 (s, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, ppm): δ 14.1, 22.6, 24.8, 29.2, 29.7, 30.0, 31.7, 84.5, 126.9, 130.4, 131.7, 143.0, 152.0, 166.3. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{29}NO_2S_2B$, 377.1769; found, 377.1774.

*Synthesis of 4,7-Dibromo-2,1,3-benzothiadiazole (**9**).* 2,1,3-Benzothiadiazole (**8**) (501.1 mg, 3.68 mmol) and NBS (2.1 equiv, 1.354 g, 7.61 mmol) were placed in a round-bottom reaction flask. Concentrated H_2SO_4 (97%; 5 mL) was added, and the reaction mixture was stirred in an oil bath (60 °C) for 3 h. The cooled reaction flask was transferred to an ice bath. Distilled water (25 mL) was added dropwise. The product was extracted with 3 × 30 mL of toluene. The combined organic layers were dried with anhydrous Na_2SO_4 for 10 min, filtered, and evaporated under reduced pressure. The procedure gave compound **9** as an off-white powder (1.08 g) in >99% yield. The spectral data corresponds with a previous report.[18a] ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 7.74 (s, 2H). HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_6H_3N_2SBr_2$, 292.8384; found, 292.8393.

*Synthesis of 4-Bromo-7-(5-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (**10**).* Toluene (2 mL), DMA (2 mL), distilled water (0.5 mL), and 5-hexyl-2-thiopheneboronic acid pinacol ester (49.2 mg, 0.17 mmol) were deoxygenated with argon for 15 min in a reaction tube with a magnetic stirring bar. Compound **9** (1.5 equiv, 75.1 mg, 0.26 mmol), Cs_2CO_3 (2.5 equiv, 138.6 mg, 0.43 mmol), $Pd(OAc)_2$ (5 mol %, 1.9 mg, 8.46 μmol), and Xantphos (5 mol %, 5.1 mg, 8.81 μmol) were added. The sealed tube was evacuated and backfilled with argon five times, and finally the tube was flushed with argon for 5 min. The reaction mixture was stirred and heated in an oil bath (60 °C) for 1.5 h. The reaction mixture was filtered through a thin pad of silica gel, rinsed with toluene, and evaporated under reduced pressure. The product was purified using flash chromatography (SiO_2, toluene 1:1 *n*-heptane). Isolated product **10** was collected as a yellow solid (51.1 mg) in 80% yield. The spectral data corresponds with previous reports.[20] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.91 (t, J = 7.0 Hz, 3H), 1.31−1.36 (m, 4H), 1.39−1.44 (m, 2H), 1.75 (quin, J = 7.6 Hz, 2H), 2.88 (t, J = 7.7 Hz, 2H), 6.87 (d, J = 3.5 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 3.5 Hz, 1H). HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}N_2S_2Br$, 381.0095; found, 381.0094. HRMS (ESI+, TOF) m/z of dicoupling byproduct: $[M + H]^+$ calcd for $C_{26}H_{33}N_2S_3$, 469.1806; found, 469.1811.

General Method for the Syntheses of Compounds 11a−c Using Suzuki−Miyaura Cross-Coupling. Toluene, DMA, and distilled water were deoxygenated with argon for 15 min in a reaction tube with a magnetic stirring bar. Compound **10** or **12**, compound **7a** or **7b**, Cs_2CO_3, *t*-$Bu_3P{\cdot}HBF_4$, and $Pd_2(dba)_3$ were added. The sealed tube was evacuated and backfilled with argon five times, and finally the tube was flushed with argon for 5 min. The reaction mixture was stirred and heated in an oil bath (90 °C) for 2−3.5 h. The reaction mixture was filtered through a thin pad of silica gel, rinsed with toluene, and evaporated under reduced pressure. The product was purified using flash chromatography (SiO_2, toluene).

*4-(5-Hexylthiophen-2-yl)-7-(2-(thiophen-2-yl)thiazol-5-yl)benzo[c][1,2,5]thiadiazole (**11a**).* Compound **11a** was prepared by using the general method described above. The specific amounts of reagents used were toluene (1.5 mL), DMA (1.5 mL), distilled water (0.3 mL), compound **10** (49.9 mg, 0.13 mmol), compound **7a** (1.4 equiv, 53.0 mg, 0.18 mmol), Cs_2CO_3 (3.3 equiv, 138.5 mg; 0.43 mmol), *t*-$Bu_3P{\cdot}HBF_4$ (15 mol %, 5.8 mg; 20.0 μmol), and $Pd_2(dba)_3$ (3.9 mol %, 4.7 mg, 5.1 μmol). Isolated product **11a** was collected as a red solid (47.3 mg) in 77% yield; mp 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.92 (t, J = 6.9 Hz, 3H), 1.32−1.37 (m, 4H), 1.40−1.47 (m, 2H), 1.77 (quin, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 6.90 (d, J = 3.7 Hz, 1H), 7.14 (dd, J = 5.1, 3.7 Hz, 1H), 7.45 (dd, J = 5.1, 1.1 Hz, 1H), 7.63 (dd, J = 3.7, 1.1 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.99 (d, J = 3.7 Hz, 1H), 8.65 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 14.1, 22.6, 28.8, 30.3, 31.5, 31.6, 122.2, 124.6, 125.3, 126.3, 126.7, 127.0, 127.9, 128.0, 128.0, 133.7, 136.3, 137.4, 142.1, 148.5, 152.1, 152.3, 162.0. HRMS (ESI+, TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}N_3S_4$, 468.0697; found, 468.0680.

*4-(5-Hexylthiophen-2-yl)-7-(2-(3-hexylthiophen-2-yl)thiazol-5-yl)benzo[c][1,2,5]thiadiazole (**11b**).* Compound **11b** was prepared using the general method described above. The specific amounts of reagents used were toluene (1 mL), DMA (1 mL), distilled H_2O (0.2 mL),

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compound **10** (36.0 mg, 94.4 μmol), compound **7b** (1.1 equiv, 38.4 mg, 0.10 mmol), Cs_2CO_3 (2.5 equiv, 79.2 mg, 0.24 mmol), P(*t*-Bu)$_3$·HBF_4 (13 mol %, 3.5 mg, 12.1 μmol), and $Pd_2(dba)_3$ (3 mol %, 2.7 mg, 2.9 μmol). Pure compound **11b** was isolated as a dark red solid (45.2 mg) in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.90−0.94 (m, 6H), 1.32−1.44 (m, 12H), 1.73−1.81 (m, 4H), 2.90 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 3.7 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 7.35 (d, *J* = 5.1 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 3.7 Hz, 1H), 8.74 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 14.1, 14.1, 22.6, 22.6, 28.8, 29.3, 29.9, 30.1, 30.3, 31.5, 31.6, 31.7, 122.4, 124.6, 125.3, 126.2, 126.7, 126.8, 127.9, 130.5, 131.8, 133.7, 136.4, 141.7, 142.6, 148.4, 152.2, 152.3, 161.2. HRMS (ESI+, TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{34}N_3S_4$, 552.1636; found, 552.1622.

*4-(3-Methoxythiophen-2-yl)-7-(2-(thiophen-2-yl)thiazol-5-yl)-benzo[c][1,2,5]thiadiazole (**11c**).* Compound **11c** was prepared using the general method described above. The specific amounts of reagents used were toluene (1 mL), DMA (1 mL), distilled H_2O (0.2 mL), compound **12** (34.2 mg, 105 μmol), compound **7a** (1.07 equiv, 32.9 mg, 112 μmol), Cs_2CO_3 (2.5 equiv, 85.5 mg, 0.26 mmol), P(*t*-Bu)$_3$·HBF_4 (12 mol %, 3.8 mg, 13.1 μmol), and $Pd_2(dba)_3$ (3 mol %, 2.9 mg, 3.2 μmol). Pure compound **11c** was isolated as a red solid (31.1 mg) in 72% yield; mp 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.04 (s, 3H), 7.03 (d, *J* = 5.6 Hz, 1H), 7.13 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.43−7.45 (m, 2H), 7.63 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 8.66 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 58.7, 115.4, 115.8, 121.7, 126.3, 126.3, 126.7, 126.8, 126.8, 127.8, 128.0, 134.1, 137.6, 142.1, 152.1, 152.8, 157.2, 161.9. HRMS (ESI+, TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{12}N_3OS_4$, 413.9863; found, 413.9859.

Synthesis of Compound 11a Using Direct Coupling. DMA (1 mL) and compound **3a** (1.5 equiv, 20.1 mg, 0.12 mmol) were deoxygenated with argon for 15 min in the reaction tube with a magnetic stirring bar. Compound **10** (30.3 mg, 79 μmol), $Pd(OAc)_2$ (5 mol %, 0.9 mg, 4.0 μmol), P(*t*-Bu)$_2$Me·HBF_4 (10 mol %, 1.9 mg, 7.7 μmol), K_2CO_3 (2.5 equiv, 27.7 mg, 0.20 mmol), and PivOH (60 mol %, 5.1 mg, 49.9 μmol) were added. The sealed tube was evacuated and backfilled with argon five times, and finally the tube was flushed with argon for 5 min. The reaction mixture was stirred and heated in an oil bath (100 °C) for 5 h. The reaction mixture was filtered through a thin pad of silica gel, rinsed with toluene, and evaporated under reduced pressure. The product was purified using flash chromatography (SiO_2, toluene). Product **11a**, with its structural isomer, were collected (12.3 mg) in 33% yield.[34]

Compound 11b. Compound **11b** was prepared using the same synthetic procedure as described above for compound **11a**. The specific amounts of reagents used were DMA (1 mL), compound **10** (30.1 mg, 78.9 μmol), compound **3b** (1.5 equiv, 30.2 mg, 0.12 mmol), $Pd(OAc)_2$ (5 mol %, 0.9 mg, 4.0 μmol), Xantphos (5 mol %, 2.5 mg, 4.3 μmol), K_2CO_3 (2.5 equiv, 27.7 mg, 0.20 mmol), and PivOH (74 mol %, 6.0 mg, 58.7 μmol). Isolated product **11b** was collected (24.1 mg) in 55% yield.

*Synthesis of 4-Bromo-7-(3-methoxythiophen-2-yl)-2,1,3-benzothiadiazole (**12**).* 3-Methoxythiophene-2-boronic acid pinacol ester (48.9 mg, 0.20 mmol), compound **9** (1.5 equiv, 89.2 mg, 0.30 mmol), and Pd precatalyst (3 mol %, 4.6 mg, 5.8 μmol) were dissolved in deoxygenated THF (2 mL). The sealed tube was evacuated and backfilled with argon five times. Deoxygenated 1 M Cs_2CO_3 (aq) (5 equiv, 1 mL, 1 mmol) was added via syringe. The reaction mixture was stirred and heated in an oil bath (30 °C) for 70 min. At this point, toluene (10 mL) and distilled water (3 mL) were added to the reaction mixture. The aqueous phase was extracted with toluene (3 × 5 mL). The combined organic layers were dried with Na_2SO_4 for 10 min, filtered, and evaporated under reduced pressure. The product was purified by using flash chromatography (SiO_2, toluene 2:3 *n*-heptane). Isolated product **12** was collected as a yellow solid (37.7 mg) in 57% yield; mp 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.02 (s, 3H), 7.02 (d, *J* = 5.6 Hz, 1H), 7.45 (d, *J* = 5.6 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 58.7, 110.5, 114.4, 115.7, 126.2, 126.7, 126.8, 132.6, 152.2, 153.4, 156.9. HRMS (ESI+, TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_8N_2OS_2Br$, 326.9261; found, 326.9263. HRMS (ESI+, TOF) *m*/*z* of dicoupling byproduct: $[M + H]^+$ calcd for $C_{16}H_{13}N_2O_2S_3$, 361.0139; found, 361.0125.

Computational Methods. The DFT and the time-dependent DFT (TDDFT) methods were applied using the Gaussian 09 (revision D.01) suite of programs.[35] The ground-state geometries were optimized and the electronic properties calculated both in vacuum and $CHCl_3$ using the B3LYP approximation, i.e., the combination of the hybrid Becke's three-parameter exchange functional[36] and the Lee−Yang−Parr correlation functional.[37] The suitable level of theory was verified with the polarized split-valence basis sets 6-31G(d), 6-31G(d,p), 6-311+G(d,p), and 6-311++G(d,p) with the latter two also including the diffuse functions. Solvation effects were taken into account by means of the integral equation formalism of the polarizable continuum model.[38] The energies of the vertical transitions to the lowest singlet (S) excited states, the oscillator strengths, and the electronic configurations were determined with TDDFT for the first 10 excited states both in vacuum and in $CHCl_3$ at the B3LYP/6-311++G(d,p) level of theory. In the TDDFT solvent calculations, the ground state geometries optimized with DFT in $CHCl_3$ were employed in the TDDFT single-point calculations using the same solvent. The electronic transitions were qualitatively described using NTOs as a representation for the transition density matrix.[30] Pictorial data for the geometries and NTOs were generated using Chemcraft 1.7. The figures of the molecular geometries and NTOs were edited with the Inkscape version 0.91.

Spectroscopic Measurements. The steady-state absorption spectra were measured with a UV-3600 Shimadzu UV−vis−NIR spectrophotometer, and emission spectra were recorded using a Yobin Yvon-SPEX Fluorolog spectrofluorometer. Absorption and emission spectra were measured in $CHCl_3$ solution and in films. The excitation wavelengths were 475 and 470 nm for solution and solid samples, respectively. The solid films were deposited by spin-coating in WS-400B-6NPP/LITE spin-coater from Laurell Technologies from $CHCl_3$ solution (1700 rpm, 1 min). The concentrations of the spin-coating solutions are reported in the Supporting Information.

Electrochemical Measurements. To determine the HOMO and LUMO energy levels of the synthesized target compounds, DPV measurements were realized by employing a potentiostat (Compact-Stat, Ivium Technologies) and a three-electrode cell configuration. The DPV experiments were carried out using 0.1 M dry tetrabutylammonium tetrafluoroborate in dichloromethane (DCM) as a supporting electrolyte, glass platinum electrode as a working electrode, platinum wire as a counter electrode, and Ag/AgCl wire as a pseudo-reference electrode. Ferrocene/ferrocenium (Fc/Fc+) couple was used as an internal standard reference to scale the measured potentials against the vacuum level.[39]

For each sample, the background was initially measured for 2.5 mL of the electrolyte solution after 20 min deoxygenation with N_2; 100 μL of 0.5 mM sample in DCM was then inserted into the electrolyte solution and, after the system was stabilized by purging N_2, the voltammogram was recorded. Finally, 20 μL of ferrocene (3 mM in DCM) was added to the "electrolyte + sample" solution, and a new voltammogram was recorded.

Each measurement was carried out between −2.4 and 1.6 V, scanning in both directions with 2.5 mV steps. The HOMO and LUMO energy levels were calculated from the oxidation and reduction potentials observed from the DPV curves according to the equations

$$E_{HOMO}(eV) = -(E_{ox} - E_{Fc/Fc+}) - 4.80eV$$

$$E_{LUMO}(eV) = (E_{red} - E_{Fc/Fc+}) - 4.80eV$$

where E_{ox} and E_{red} are the oxidation and reduction potentials of the sample and $E_{Fc/Fc+}$ the potential of ferrocene. E_{ox}, E_{red}, and $E_{Fc/Fc+}$ are all referred against the Ag/AgCl reference electrode. The value −4.80 eV is the energy level of ferrocene against vacuum.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02689.

NMR spectra of synthesized compounds, ESI-MS/MS spectra of compounds **11a−c**, and computational and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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