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C−H-Activated Direct Arylation of Strong Benzothiadiazole and Quinoxaline-Based Electron Acceptors

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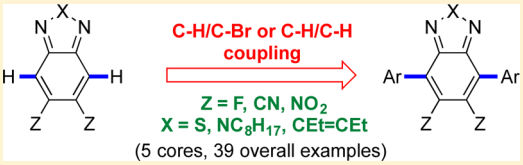
Supporting Information

ABSTRACT: Electron acceptors are important components of π-conjugated materials, but the strong electron-withdrawing properties of the required synthetic intermediates often make them poor substrates in synthetic schemes designed around conventional organometallic cross-coupling. Here, strong benzodiimine-based acceptors, including 5,6-difluoro[2,1,3]benzothiadiazole, 5,6-dicyano[2,1,3]benzothiadiazole, 5,6-dicyanobenzo[*d*][1,2,3]triazole, 6,7-dicyanoquinoxaline, and 6,7-dinitroquinoxaline, are shown to undergo facile palladium-catalyzed C−H direct arylation with a variety of bromoarenes in moderate to high yields. The electrochemical characteristics of di-2-thienyl derivatives synthesized using this methodology are compared and suggest that, in an electron-transfer sense, 5,6-dicyano[2,1,3]benzothiadiazole is a comparably strong acceptor to benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole. The synthetic results suggest that high electron-withdrawing ability, which has traditionally limited reaction yields and structural variety in organic electronic materials, may be advantageous when employing C−H activated direct arylation in certain circumstances.



INTRODUCTION

Electron acceptors can affect ground- and excited-state characteristics of materials including the wavelengths of light absorption and emission, electron affinity (EA), and ionization energy (IE) of organic π-conjugated materials, properties that are important for applications including nonlinear optics (NLO), organic photovoltaics (OPV), and organic field-effect transistors (OFET).[1−6] However, incorporation of strong π-acceptors into new materials, which is typically achieved via Stille or Suzuki cross couplings, can be problematic; many electron-poor precursors are resistant to electrophilic halogenation or require harsh conditions for these reactions, which can lead to low yield, while electron-poor lithiated precursors to Stille and Suzuki reagents are often unstable. Additionally, even *if* the corresponding Stille or Suzuki reagents can be synthesized, the strong electron-withdrawing ability of the acceptor moieties may result in reduced nucleophilicity, which presumably translates to reduced reactivity,[7,8] and, in the case of electron-poor boronic acids, significant air-instability and/or instability to the reaction conditions of the organometallic coupling.[9] One method that has been used to circumvent these challenges is the incorporation of relatively electron-donating synthetic "handles", such as thiophene groups, onto the core of an electron-acceptor unit to increase both the overall reactivity in electrophilic reactions, such as halogenation, and the nucleophilicity of metalated coupling derivatives; however, inclusion of such synthetic handles may limit the structural variation achievable and hence may limit the extent to which electronic properties may be varied.

C−H bond functionalization has been applied to a wide variety of syntheses in pharmaceuticals and natural products,[10−13] and is increasingly becoming a useful tool for the synthesis of π-conjugated materials, particularly for relatively electron-rich thiophene C−H active substrates.[14−16] More recently, direct C−H activation of relatively electron-poor imide-containing substrates has been reported.[17−20] In competition experiments by Fagnou et al., more strongly electron-accepting substrates have shown preferential C−H activated direct arylation in ratios up to 20:1 over less electron accepting substrates.[21] In separate work by Fagnou et al., more highly fluorinated aryl substrates underwent C−H activated direct arylation most efficiently and in the highest yields, which was attributed to greater acidity of the C−H bond in the more highly fluorinated arenes.[22] Although more recent computational studies of the mechanism of C−H activated direct arylation suggest the role of C−H bond acidity is less significant, a higher reactivity for electron-accepting substrates in certain cases was confirmed.[23,24] These experimental studies and theoretical insights raise the interesting possibility that electron-accepting building blocks—often a synthetic challenge to incorporate in π-conjugated materials due to resistance to electrophilic substitution and poor nucleophilicity—may actually be advantageous substrates for C−H activated direct arylation in some cases.

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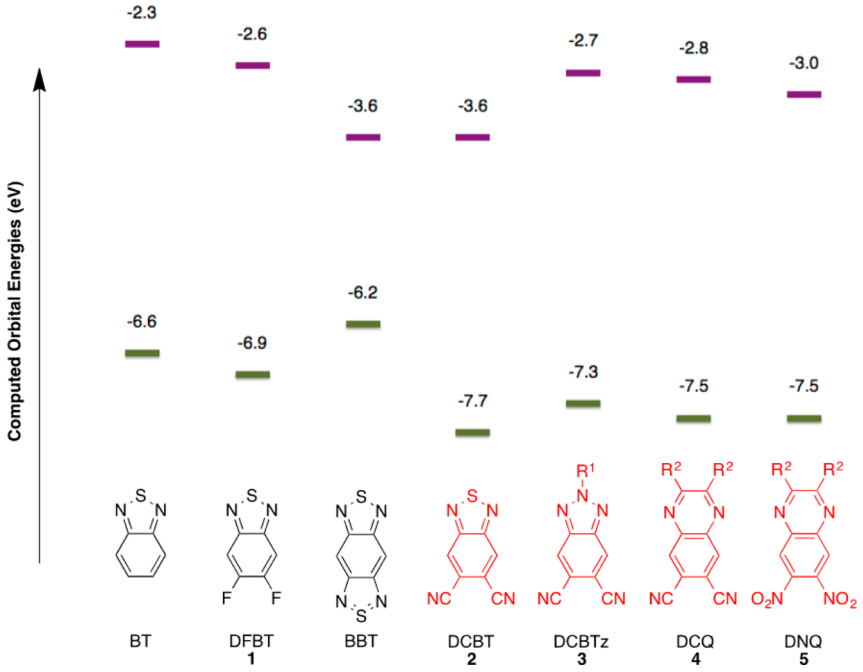

Figure 1. | [B3LYP/6-31G**]-computed HOMO (green) and LUMO (purple) energies for benzodiimine acceptors. For calculations, $R^1 = -CH_3$; $R^2 = H$.

o-Benzodiimine-based heterocycles, i.e., fused-ring quinoidal heterocycles derived, at least conceptually, from *o*-phenylenediamines and including [2,1,3]benzothiadiazole (BT) and derivatives,[25−27] benzo[*d*][1,2,3]triazole (BTz),[27,28] quinoxaline,[29] and benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole (BBT),[30,31] have been widely used as acceptors in π-conjugated organic materials. Given this widespread use, *o*-benzodiimine-based acceptors represent a materials-relevant class of compounds on which to examine the efficacy of C−H activated direct arylation on strong electron acceptors. Figure 1 shows potential C−H active substrates with higher electron-accepting potential than BT, as suggested by their [B3LYP/6-31G**]-calculated frontier molecular orbital energies, including 5,6-difluoro[2,1,3]-benzothiadiazole (DFBT, **1**), 5,6-dicyano[2,1,3]-benzothiadiazole (DCBT, **2**), 5,6-dicyanobenzo[*d*][1,2,3]-triazole (DCBTz, **3**), 6,7-dicyanoquinoxaline (DCQ, **4**), and 6,7-dinitroquinoxaline (DNQ, **5**). All of these *o*-benzodiimine acceptors **1**−**5** have lowest unoccupied molecular orbitals (LUMOs) and highest unoccupied molecular orbitals (HOMOs) that are lower in energy than those of the widely used acceptor BT. In particular, the low-lying LUMO of DCBT suggests it should have an acceptor strength comparable to that of BBT; however, the calculated HOMO of DCBT is much lower in energy (∼1.5 eV) than that of BBT, which may help address some of the deleterious effects that the relatively high HOMO energy of BBT has on BBT-containing OPV materials.[31]

DFBT derivatives have been used as electron-acceptor moieties with increased open-circuit voltage (V_{oc}) and power-conversion efficiency (PCE) in polymer solar cells.[26,32−34] However, synthesizing appropriate halogenated intermediates for including DFBT moieties into materials may require several steps[35] and/or harsh conditions. For example, 4,7-dibromination of DFBT (40% yield) has been reported to require Br_2/fuming H_2SO_4 at 60 °C for 24 h[34] and diiodination was achieved using I_2/fuming H_2SO_4 at 60 °C for 12 h, although no yield was reported,[33] perhaps due to the reported instability of 4,7-diiodo-DFBT under these conditions.[36] More recently, DCBT was incorporated into donor−acceptor (D−A) polymers[37] that were found to function as electron-transport materials in OFETs, in contrast to DFBT analogues that functioned as hole-transport materials in similar device architectures; this observation is consistent with the deeper LUMO calculated for DCBT (Figure 1). The DCBT-containing monomer was synthesized using a 3-fold excess of KCN to nucleophilically substitute the fluoro substituents of 5,6-difluoro-4,7-di-2-thienyl[2,1,3]benzothiadiazole, followed by bromination with a 3-fold excess of Br_2 over 3 days at 50 °C. These reagents, along with the harsh conditions required to halogenate DFBT, underscore the motivation to develop alternative potentially less toxic and hazardous methods, such as C−H direction arylation, for the incorporation of electron-acceptor moieties into π-conjugated materials.

We have recently reported that DFBT can be efficiently diarylated by aryl and heteroaryl bromides using direct Pd-catalyzed C−H functionalization.[38] DFBT can be also monoarylated and the isolated monocoupled product submitted to another direct arylation to obtain differentially substituted DFBT;[38] this chemistry has been exploited to incorporate DFBT into push−pull dyes that have shown power conversion efficiencies of up to 9.1% in dye-sensitized solar cells.[39] The direct diarylation of DFBT has also been applied to the synthesis of conjugated polymers.[40] Here, we extend our study of DFBT diarylation to functionalization of other benzodiimine-based acceptors, DCBT, DCBTz, DCQ, and DNQ, with a range of aryl and heteroaryl groups. We also compare the optical and electrochemical properties of dithienyl derivatives of these acceptors.

■ RESULTS AND DISCUSSION

Coupling conditions attempted on DCBT were based on those optimized for coupling to DFBT, described previously,[38] and are summarized in Table 1. As with DFBT, direct arylations of

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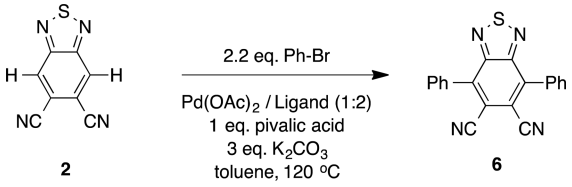
Table 1. Optimization of Direct Arylation of 5,6-Dicyanobenzothiadiazole[a]



2 **6**

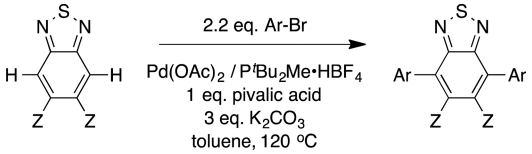
entry	Pd (mol %)[b]	ligand[c]	additive	yield (%)
1	$Pd(OAc)_2$ (10)	$P^tBu_2Me{\cdot}HBF_4$	pivalic acid	90
2	$Pd(OAc)_2$ (5)	$P^tBu_2Me{\cdot}HBF_4$	pivalic acid	99
3	$Pd(OAc)_2$ (2)	$P^tBu_2Me{\cdot}HBF_4$	pivalic acid	89
4	$Pd(OAc)_2$ (5)	$P^tBu_2Me{\cdot}HBF_4$		26
5	$Pd(OAc)_2$ (5)		pivalic acid	trace
6	Pd_2dba_3 (10)	$P^tBu_2Me{\cdot}HBF_4$	pivalic acid	58

[a]Reaction concentrations ~0.3 M. [b]Based on moles of benzodiimine. [c]2× the mol % of Pd.

DCBT in toluene with pivalic acid and K_2CO_3 at 120 °C provided a high yield of the corresponding product **6** (entry 1). Variation of the catalyst loading[41] down to 2 mol % of Pd did not significantly affect the yields (entries 1−3). However, the presence of pivalic acid[42] is critical to efficient diarylation in DCBT as it was to that of DFBT;[38] in the absence of pivalic acid, the reaction of DCBT is very sluggish and **6** is obtained in only 26% (entry 4), along with a significant amount of monoarylated product. Based on the seemingly critical presence of pivalic acid, it is likely this coupling proceeds via a concerted metalation−deprotonation pathway.[23,24] The presence of the phosphine ligand appears to be critical in the case of DCBT, with essentially no reaction observed in the absence of phosphine (entry 5). $Pd(OAc)_2$ seems to be preferred over Pd_2dba_3 in the current conditions (entry 6). As summarized in Table S1, entries 1−3, dimethylacetamide (DMAc) was also employed as a solvent for DCBT coupling using both $P^tBu_2Me{\cdot}HBF_4$ and 1,2-bis(dicyclohexylphosphino)ethane (dcpe), as well as with no phosphine ligand; the coupling results were inferior to those seen in toluene, as was previously seen in coupling to DFBT.[38] Finally initial attempts at C−H/C−I direct arylation on DCBT under the conditions previously developed for the *ortho*-arylation of benzonitriles with aryl iodides[43] gave no appreciable conversion of DCBT (Table S1, entry 4).

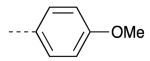
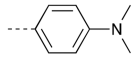
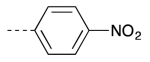
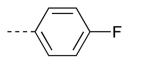
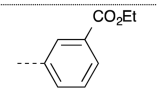
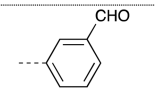
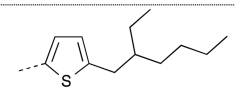
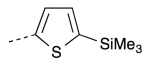
Scope of Diarylation of DFBT and DCBT. To test the applicability of the optimized reaction conditions for C−H/C−Br cross-couplings, DCBT was coupled with a variety of aryl and heteroaryl bromides. Table 2 compares the results of these tests with previously reported results for DFBT.[38] The reaction is reasonably general in scope and in most cases gives high to essentially quantitative yields of the diaryl DCBT product (**8a**−**j**). In general, the yield of the DCBT product is higher than the yield of DFBT product with the same aryl bromide, although the reactions were not performed under precisely the same conditions (e.g., lower catalyst loading for DCBT). The coupling tolerates functional groups such as dialkylamino (entry 3), ester (entry 6), and aldehyde (entry 7), proceeding in moderate to high yield in each case. The yield of products with aryl bromides having electron-withdrawing groups *p*-F and *p*-NO_2 (entries 4 and 5) and electron-donating groups *p*-OMe and *p*-NMe_2 (entries 2 and 3) were very similar. The most marked limitation of the coupling conditions herein is low

Table 2. Yields of Direct Diarylation of DFBT and DCBT Acceptors[a]



1: Z = F
2: Z = CN

7: Z = F
8: Z = CN

Entry	Z	Ar	Product (Yield)
1	F		**7a** (96%)
	CN		**8a** (98%)
2	F		**7b** (71%)
	CN		**8b** (89%)
3	F		**7c** (85%)
	CN		**8c** (99%)
4	F		**7d** (-)[b]
	CN		**8d** (81%)
5	F		**7e** (84%)
	CN		**8e** (86%)
6	F		**7f** (85%)
	CN		**8f** (93%)
7	F		**7g** (65%)
	CN		**8g** (75%)
8	F		**7h** (70%)
	CN		**8h** (99%)
9	F		**7i** (34%)[c]
	CN		**8i** (72%)
10	F		**7j** (72%)
	CN		**8j** (76%)

[a]For DCBT: $Pd(OAc)_2$ (5 mol %), $P^tBu_2Me{\cdot}HBF_4$ (10 mol %) based on DCBT. For DFBT: $Pd(OAc)_2$ (10 mol %), $P^tBu_2Me{\cdot}HBF_4$ (20 mol %) based on DFBT. For both: 1 equiv of pivalic acid, 3 equiv of K_2CO_3, and 2.2 equiv of aryl bromide unless otherwise noted. [b]Reactions occurred, but product was insoluble in common organic solvents. [c]3 equiv of aryl bromide.

yields obtained with some bromothiophenes. In particular, coupling of 2-bromothiophene to DFBT gives only 31% of corresponding diarylated product with a significant amount of side-product formation. Such side products may result from the direct arylation of the α-C−H of thiophene either before or after coupling to DFBT and/or oligothiophene formation by coupling in both the α- and β-positions, which has been seen for the Pd-catalyzed C−H activation of thiophenes in the synthesis of hyperbranched polythiophene.[44] However, yields of dithienyl coupling products can be improved substantially by

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blocking the α-thiophene C−H position on the bromothiophene, for example, with an alkyl group (entry 9) or a silyl group (entry 10). The silyl group can, in turn, potentially be removed by protodesilylation with acid[45] or with tetrabutylammonium fluoride,[46] offering an alternative route to 4,7-dithieno-DCBT, which was previously obtained from the reaction of KCN with 4,7-dithieno-DFBT.[37]

The single-crystal structures of 4,7-bis(5-trimethylsilyl-2-thienyl)-DCBT (**8j**) and 4,7-di(5-methyl-2-thienyl)-DCBT (**9**, Figure 2, obtained by direct arylation of DCBT with 2-bromo-5-methylthiophene) have been determined (Figure 2). Computational work suggests that the lowest energy conformation of bis(2-thienyl) derivatives of DFBT is approximately planar, with the thiophene sulfur atoms pointing in the opposite direction to the sulfur of the BT core, whereas for DCBT derivatives, the optimum structure is a little less planar and the thiophene sulfur atoms point in the same direction as the BT sulfur atom.[37] These predictions are born out by the conformations seen in the structure of **9**. However, in the crystal structure of **8j** and the previously reported structure of its DFBT analogue, **7j**,[38] the two thiophenes are oriented in opposite directions, suggesting intermolecular interactions can influence the solid-state conformational preferences, consistent with the relatively small energy differences (≤ca. 5 kJ mol^{-1}) seen in the calculations.[37] Further details of the crystal structures of **8j** and **9**, including the crystal packing, are discussed in the Supporting Information.

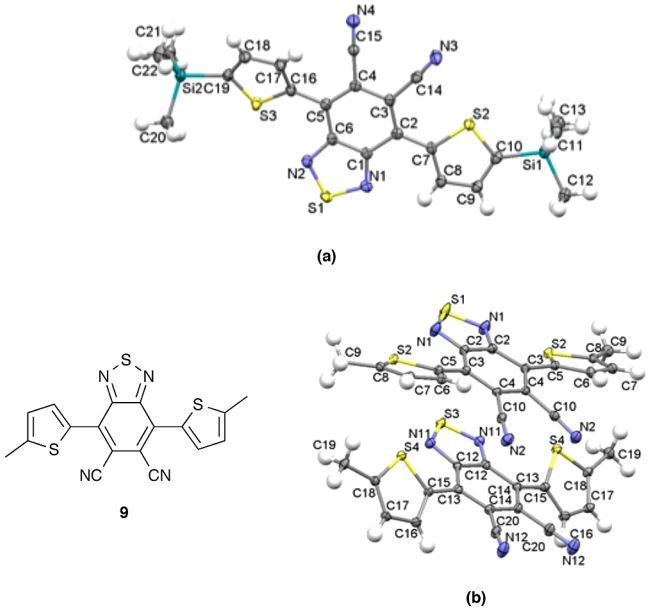
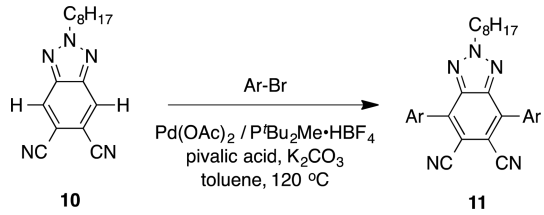
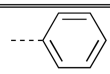
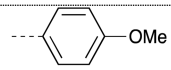
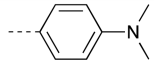
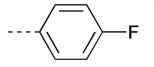
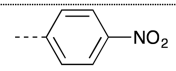
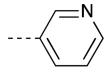
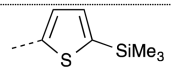


Figure 2. Views of (a) the molecular structures of 4,7-bis(5-trimethylsilyl-2-thienyl)-DCBT (**8j**) and (b) 4,7-bis(5-methyl-2-thienyl)-DCBT (two crystallographically inequivalent molecules (**9**)), determined by single-crystal X-ray diffraction.

Direct Arylation of DCBTz. Direct arylation was also attempted on 5,6-dicyano-2-*n*-octylbenzo[*d*][1,2,3]triazole (**10**) to further test the scope of C−H activation on the acceptor moieties. Recently, 2-alkyl-4,7-dithienyl-DCBTz derivatives have been synthesized by condensation of succinonitrile with a 4,5-di(2-thienylketo)-substituted, 2-alkyl-substituted 1,2,3-triazole in 37% yield.[47] An obvious advantage of the benzo[*d*][1,2,3]triazoles is that the nitrogen atom in the 2-position can be functionalized with a variety of groups, for example, in order to increase the solubility of materials into which the acceptor is incorporated. On the other hand, the parent heterocycle, benzo[*d*][1,2,3]triazole, is, according to DFT orbital-energy calculations and electrochemical data for di-2-thienyl derivatives, a weaker acceptor than BT.[48] However, as shown in Figure 1, the cyano substituents in DCBTz are calculated to more than outweigh the effects of the substitution of S with NR, resulting in both HOMO and LUMO energies (−7.3 and −2.7 eV, respectively) being significantly lower in energy than those of BT (−6.6 and −2.3 eV, respectively) and closer to those of DFBT. DCBTz **10** was prepared by alkylation of 5,6-dicyano-1*H*-benzo[*d*][1,2,3]triazole,[49] albeit in a low yield of 30%. Reaction conditions similar to those applied to the diarylation of DFBT and DCBT gave the results shown in Table 3. Good to high yields of diarylated derivatives (**11a−g**) were obtained, with yields comparable to those reported for diarylation of DFBT and DCBT in Table 2.

Table 3. Yields of Direct Diarylation of Dicyanobenzotriazoles (DCBTz)[a]



Entry	Ar	Product (Yield)
1		**11a** (90%)
2		**11b** (81%)
3		**11c** (74%)[b]
4		**11d** (72%)
5		**11e** (65%)[b]
6		**11f** (68%)
7[c]		**11g** (62%)

[a]$Pd(OAc)_2$ (10 mol %), $P^tBu_2Me{\cdot}HBF_4$ (20 mol %), 1 equiv of pivalic acid, 3 equiv of K_2CO_3 (3 equiv), and 2.2 equiv of aryl bromide unless otherwise noted. [b]Yields were determined by ^1H NMR spectroscopy using 1,4-dimethoxybenzene as the standard. [c]3 equiv of aryl bromide.

Diarylation of DCQ and DNQ. Quinoxaline-based acceptors constitute another class of benzodiimine acceptors and are possible substrates for direct arylation by C−H activation at the 5 and 8 positions (analogous to the 4,7-positions of BT and BTz heterocycles). Quinoxalines generally have been incorporated as acceptors into π-conjugated small molecules via Pd-catalyzed couplings of 5,8-dibromoquinoxalines to stannyl or boryl reagents[50−52] and most often into polymers through the

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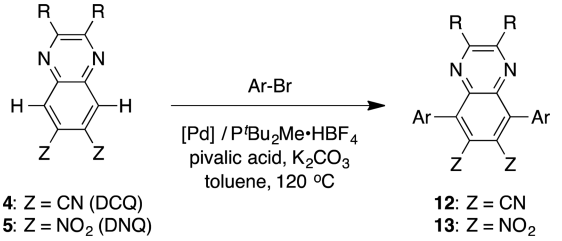
use of 5,8-di(2-thienyl)quinoxaline monomers, which are themselves obtained from Stille or Suzuki couplings with 5,8-dibromoquinoxalines,[53−57] although direct polymerizations of 5,8-dibromoquinoxalines and ditin derivatives have also been reported.[58] Consistent with the rest of this work, 6,7-dicyanoquinoxaline (DCQ) and 6,7-nitroquinoxaline (DNQ) were chosen as test substrates based on their frontier orbital energies, which, as shown in Figure 1, are calculated to be lower than those of BT, suggesting their incorporation into materials will lead to both higher EA and higher IE than those of analogous BT materials. In addition, these heterocycles are presumably more resistant to electrophilic substitution than BT and parent quinoxalines. As with DCBTz, DCQ, and DNQ building blocks can be used to introduce solubilizing alkyl groups as well as acceptor character to a material, in the case of the quinoxalines, at the 2,3-positions. Although several derivatives of DCQ[59] and DNQ[60]—including DNQ-containing porphyrins,[61] bisphenazines,[62] azaacenes,[63] and dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligands[64]—have been reported, to our knowledge, DCQ and DNQ have not been functionalized in the 5- and 8-positions. In the present study, 2,3-diethyl-substituted DCQ and DNQ cores were used in most cases to enhance the solubility and to eliminate the possibility of side products arising from coupling of bromoarenes to C−H groups at the 2,3-positions (although as shown by experiments with unsubstituted DNQ, vide infra, these side reactions do not appear to be a significant issue). As shown in Table 4, both DCQ (**4**) and DNQ (**5**) substrates undergo direct arylation to give corresponding products **12a−f** and **13a−d,f**, respectively; however, DNQ required slightly modified catalytic conditions for optimal coupling. Conditions for DNQ optimization included six Pd catalysts and six bases (summarized in Tables S2 and S3); the Pd_2dba_3 catalyst and K_3PO_4 generally gave good yields of diaryl DNQ derivatives. In some cases, the determined yields were lower than those reported for DFBT, DCBT, and DCBTz with similar substrates, this being likely attributable to poor solubility of the final product in common organic solvents, especially in the case of entry 5. In these cases, the C−H and aryl bromide starting materials were consumed, and the formation of side products was not observed, suggesting that the main limitation for yields using electron-acceptor to electron-donor aryl bromides for coupling to DCQ and DNQ results from limited solubility of the products, a limitation that could presumably be addressed through use of varying the 2,3-substituents.

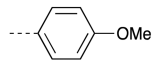
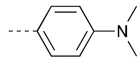
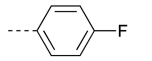
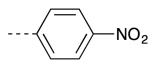
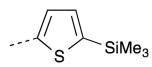
Experimental Comparison of Acceptor Strength. The acceptor properties of DCBT, DCBTz, and DCQ were evaluated by comparing optical and electrochemical data for di(2-thienyl) derivatives to data for analogous derivatives of the known acceptors BT, DFBT, and BBT (Table 5). In each case, alkyl or trialkylsilyl substituents were used in the 5-position of the 2-thienyl substituents to ensure reversible oxidation waves (the oxidations of dithienyl BT, BBT, and BTz derivatives examined in a previous study were irreversible, presumably owing to dimerization of radical cation species through the unprotected 5-position of the thienyl groups[48]). The di[5-(2-ethylhexyl-2-thienyl)]derivatives of BT (**14**) and BBT (**15**) were synthesized by conventional organometallic coupling chemistry, as shown in Figure 3. In all cases, reversible one-electron oxidation and reduction processes were observed. In comparing the di[5-(2-ethylhexyl-2-thienyl)] derivatives (entries 1−4), the reduction potentials ($E_{1/2}^{0/-}$) shown in Table 5 suggest that the DCBT **8i** is a stronger acceptor, at least in an electron-transfer sense, than BT **14** or DFBT **7i** and comparable in strength to BBT **15**. The oxidation potential ($E_{1/2}^{+/0}$) of DCBT **8i** indicates it to be less readily oxidized than its BT **14** and DFBT **7i** analogues and substantially less easily oxidized than BBT **15**. These data suggest that the DCBT acceptor may impart high EA in derivatives comparable to that of the BBT acceptor, while having significantly high IE, and are consistent with the DFT-predicted trends in orbital energies presented in Figure 1 and with the reported effects on OFET behavior of replacing DFBT with DCBT in polymers.[37] The trend in absorption maxima (or onsets, Figure 4) in entries 1−4 is also consistent with that in the electrochemical gap ($E_{1/2}^{+/0} - E_{1/2}^{0/-}$) and the DFT fundamental HOMO−LUMO gaps for the isolated cores (Figure 1). Table 5 also presents the optical and electrochemical data for the bis(5-trimethylsilyl-2-thienyl) derivatives of DCBT (**8j**), DCBTz (**11g**), and DCQ (**12f**) (entries 5−7) (comparison of **8i** and **8j** indicates that the choice of an alkyl or silyl substituent for the 5-thienyl position has little effect on the optical and electrochemical properties). $E_{1/2}^{0/-}$ values for DCBTz **11g** and DCQ **12f** are significantly more reducing than that for DCBT **8j**, while the oxidation potentials do not vary dramatically within the series; both of

Table 4. Yields of Direct Diarylation of Dicyano- and Dinitroquinoxalines[a]



4: Z = CN (DCQ)
5: Z = NO_2 (DNQ)

12: Z = CN
13: Z = NO_2

Entry	Z	R	Ar	Yield
1	CN	Et		**12a** (89%)
	NO_2	H		**13a** (38%)[b]
2	CN	Et		**12b** (65%)[b]
	NO_2	Et		**13b** (72%)
3	CN	Et		**12c** (80%)[b]
	NO_2	H		**13c** (48%)[b]
4	CN	Et		**12d** (55%)[b]
	NO_2	H		**13d** (72%)
5	CN	Et		**12e** (50%)[b]
	NO_2	H		**13e** (-)[c]
6	CN	Et		**12f** (46%)
	NO_2	Et		**13f** (68%)

[a]For DCQ (R = Et): $Pd(OAc)_2$ (10 mol %), P^{t}Bu$_2$Me·HBF_4 (20 mol %), pivalic acid (1 equiv), and K_2CO_3 (3 equiv). For DNQ (R = Et): Pd_2dba_3 (10 mol %), P^{t}Bu$_2$Me·HBF_4 (20 mol %), pivalic acid (0.5 equiv), and K_3PO_4 (2.2 equiv). [b]Yields were determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as the standard. [c]Reaction occurred, but product was insoluble in common organic solvents.

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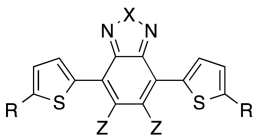
Table 5. Electrochemical and Optical Data for Dithienyl Derivatives of Benzodiimines with the Chemical Structures of Dithienyl Derivativs of BT, DFBT, and BBT Synthesized for Comparison to the DCBT Derivative



14: X = S; Z = H; R = 2-EtHex
7i: X = S; Z = F; R = 2-EtHex
8i: X = S; Z = CN; R = 2-EtHex
15: X = S; Z = –N=S=N–; R = 2-EtHex
8j: X = S; Z = CN; R = $SiMe_3$
11g: X = N-^{n}Oct; Z = CN; R = $SiMe_3$
12f: X = –CEt=CEt–; Z = CN; R = $SiMe_3$

entry	core	compd	λ_{max}[a]/nm ($\varepsilon_{max}/10^4$ M^{-1} cm^{-1})	E_{gap}^{opt}[b] (eV)	$E_{1/2}^{+/0}$[c] (V)	$E_{1/2}^{0/-}$[c] (V)	E_{gap}^{cv}[d] (eV)
1	BT	**14**	474 (1.5)	2.25	+0.65	−1.78	2.43
2	DFBT	**7i**	455 (1.7)	2.35	+0.86	−1.68	2.54
3	DCBT	**8i**	496 (1.8)	2.15	+1.14	−1.13	2.27
4	BBT	**15**	768 (1.7)	1.39	+0.36	−1.05	1.41
5	DCBT	**8j**	473 (1.6)	2.25	+1.25	−1.09	2.34
6	DCBTz	**11g**	410 (2.7)	2.64	+1.14	−1.60	2.74
7	DCQ	**12f**	416 (1.5)	2.53	+1.26	−1.46	2.72

[a]$CHCl_3$. [b]Estimated from the absorption onset in $CHCl_3$. [c]MeCN/0.1 Bu_4NPF_6 vs $FeCp_2^{+/0}$. [d]$E_{gap}^{cv} = e[E_{1/2}^{+/0} - E_{1/2}^{0/-}]$ where e is the electronic charge.

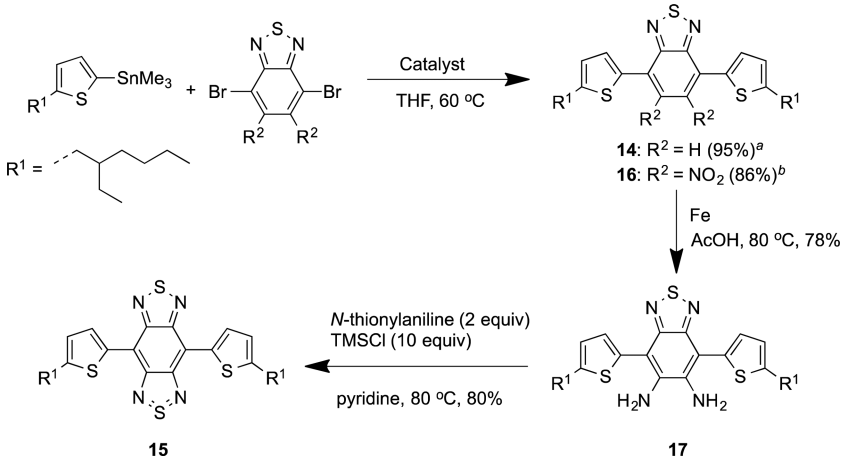


Figure 3. Synthesis of compounds **14** and **15**. (a) Catalyst = Pd_2dba_3 (10 mol %)/P(*o*-tol)$_3$ (40 mol %). (b) Catalyst = $Pd(PPh_3)_2Cl_2$ (7 mol %).

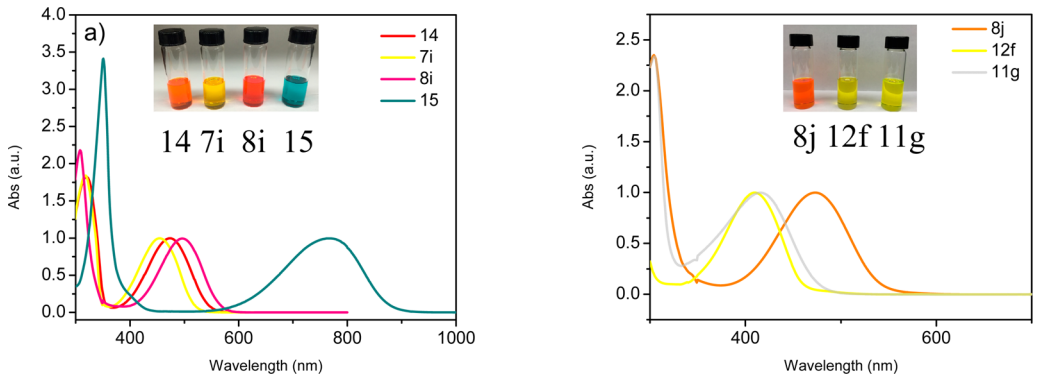


Figure 4. (a) Normalized solution absorption spectra of compounds **14**, **7i**, **8i**, and **15** in $CHCl_3$. (b) Normalized solution absorption spectra of compounds **8j**, **12f**, and **11g** in $CHCl_3$.

these trends are consistent with the HOMO and LUMO energies reported in Figure 1 for the parent acceptors and with previous computational work on BT, BTz, and Q derivatives without cyano substituents.[65,66] Additionally, the trends in absorption maxima within the series in entries 5−7 are consistent with those in $E_{1/2}^{0/+} - E_{1/2}^{0/-}$. Taken together, the experimental electrochemical data in Table 5 and the calculated data in Figure 1 suggest that, from an electron-transfer point of view, the acceptor strengths may be ordered as follows: BBT ∼ DCBT > DCQ > DCBTz > DFBT > BT.

In addition to direct arylation through the C−H/C−Br chemistry discussed above, we have also investigated the possibility of directly arylating DCBT using C−H/C−H oxidative coupling as shown in Figure 5. The best yield obtained for the oxidative C−H/C−H couplings of thiophene derivatives with DCBT **2** was for coupling with the 5-H of 2-bromo-3-hexylthiophene to give the dithienyl-DCBT derivative

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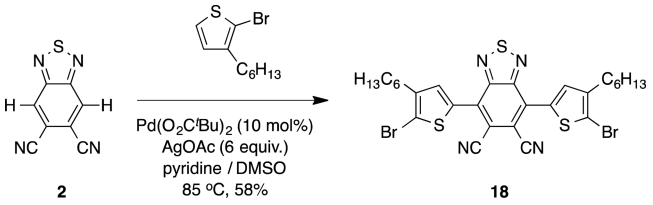

Figure 5. | Oxidative C−H/C−H diarylation of DCBT under optimized conditions.

18 in 58% yield using $Pd(O_2C^tBu)_2$ as a catalyst and AgOAc as an oxidant (Figure 5); these reaction optimizations are discussed in more detail in the Supporting Information.

■ CONCLUSION

The results described here for the diarylation of benzodiimine acceptors with both cyano and nitro substitution suggest that Pd-catalyzed C−H activation is a potentially useful general approach to the coupling of moderate to strong acceptor building blocks with bromoarenes in the synthesis of π-conjugated materials. Compared to conventional cross-coupling chemistry, its use can reduce the number of synthetic steps, reduce the need for toxic intermediates, and allow for the facile synthesis of materials that are otherwise difficult or impossible to obtain. One limitation is that other C−H positions, such as those in the α- or β-C−H positions of thiophenes or those in the cross-conjugated 5 and/or 6 positions of benzothiadiazole derivatives (such as in [2,1,3]benzothiadiazole and 5-fluoro-[2,1,3]benzothiadiazole), may react competitively with targeted C−H positions to reduce the yield of desired product and provide mixtures that are difficult to separate. However, in the cases examined here, employing cores with a range of acceptor strengths, the reactions generally proceed in good to high yields. Thus, the use of these C−H/C−Br couplings effectively turns the preparative *limitations* that strong benzodiimine acceptors such as DCBT pose for conventional cross-coupling chemistry into a *strength*; moreover, this principle may be more generally applicable to other electron-poor building blocks. In particular, the DCBT acceptor is a strong acceptor compared to most other benzothiadiazole acceptors investigated to date; a model compound exhibits a similar reduction potential to its BBT analogue, but very different oxidative and optical characteristics, potentially allowing for the development of benzodiimine-based materials with new combinations of properties. These properties, combined with the simplicity and versatility of the chemistry, may result in a greater range of acceptor building blocks that can be incorporated into π-conjugated small molecules and polymers.

■ EXPERIMENTAL SECTION

$Pd(OAc)_2$, $Pd(OPiv)_2$ [OPiv = pivalate, $^tBuCO_2$], and $Pd(CF_3COO)_2$, 4,5-dinitro-1,2-phenylenediamine, 3,4-hexadione, pivalic acid, and $P^tBu_2Me{\cdot}HBF_4$ were purchased and used as received. 4,5-Dibromo-1,2-benzenediamine,[41] 2-trimethylstannyl-5-(2-ethylhexyl)thiophene,[67] 5,6-dicyano-1*H*-benzotriazole,[49] and 5,6-dicyano[2,1,3]-benzothiadiazole (DCBT, **2**)[68] were prepared according to literature methods. Characterizing data for DFBT compounds have been reported previously.[38]

^1H and $^{13}C\{^1H\}$ NMR spectra were acquired in $CDCl_3$, and the signals were referenced using the solvent peak (7.27 ppm for ^1H NMR and 77.0 ppm for $^{13}C\{^1H\}$ NMR) or tetramethylsilane (TMS, 0.0 ppm) as an internal standard. ^{19}F NMR spectra were recorded using trifluorotoluene as an external standard (δ −63.73 ppm). Determination of yields by ^1H NMR spectroscopy is described in the Supporting Information. High-resolution mass spectrometric analysis was performed in electron impact (EI) ionization mode with a quadrupole mass analyzer.

General Procedure A for Pd(II)-Catalyzed Direct Diarylation of Benzodiimines DFBT, DCBT, DCBTz, and DCQ. To an oven-dried 5 mL collared tube containing a stirring bar were sequentially added $Pd(OAc)_2$, $P^tBu_2Me{\cdot}HBF_4$, pivalic acid, benzodiimine (0.125 mmol), K_2CO_3, and aryl bromide under a flow of N_2. Dry toluene was added, and a septum-cap was crimped on the vial to form a seal. The reaction mixture was heated in a 120 °C oil bath until the reaction was judged complete by examining aliquots with GC/MS or ^1H NMR spectroscopy. The resulting mixture was cooled to room temperature and filtered through a layer of Celite (5 mL) using dichloromethane (DCM). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (typical eluent: hexanes/DCM or DCM/ethyl acetate), affording the corresponding diarylated benzodiimine. For DCBT: catalyst loading was 5 mol % $Pd(OAc)_2$ and 10 mol % $P^tBu_2Me{\cdot}HBF_4$ based on DCBT. For DFBT, DCBTz, and DCQ: catalyst loading was 10 mol % $Pd(OAc)_2$ and 20 mol % $P^tBu_2Me{\cdot}HBF_4$ based on DFBT, DCBTz, or DCQ. For all benzodiimines: 1 equiv of pivalic acid, 3 equiv of K_2CO_3, 2.2 equiv of aryl bromide, and ca. 0.3 M reaction concentration were used unless otherwise noted.

General Procedure B for Pd(II)-Catalyzed Direct Diarylation of DNQ. To an oven-dried 5 mL collared tube containing a stirring bar were sequentially added Pd_2dba_3 (5.7 mg, 0.006 mmol), $P^tBu_2Me{\cdot}HBF_4$ (6.2 mg, 0.025 mmol), pivalic acid (6.3 mg, 0.063 mmol), DNQ (34.5 mg, 0.125 mmol), anhydrous K_3PO_4 (58 mg, 0.28 mmol), and aryl bromide (0.275 mmol) under a flow of N_2. Dry toluene (0.3 mL) was added, and a septum cap was crimped on the vial to form a seal. The reaction mixture was heated in a 120 °C oil bath for a certain amount of time until judged complete by examining aliquots with GC/MS or ^1H NMR spectroscopy. The resulting mixture was cooled to room temperature and filtered through a layer of Celite (5 mL) using dichloromethane (DCM). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexanes/DCM or DCM/ethyl acetate), affording the corresponding diarylated products.

*2-Octyl-5,6-dicyano-2H-benzo[d][1,2,3]triazole (**10**).* 5,6-Dicyano-1*H*-benzotriazole[49] (169 mg, 1.0 mmol), 1-bromooctane (195 mg, 1.0 mmol), potassium *tert*-butoxide (113 mg, 1 mmol), and methanol (5 mL) were mixed in a round-bottomed flask equipped with a condenser. The reaction mixture was refluxed overnight. The mixture was cooled to room temperature, and methanol was removed by rotary evaporator. The resulting mixture was then extracted with $CHCl_3$, and the organic phase was washed with water and dried over Na_2SO_4. The resulting off-white solid was purified by column chromatography (80 mg, 30%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 2H), 4.85 (t, J = 7 Hz, 2H), 2.20−2.15 (m, 2H), 1.39−1.26 (m, 10 H), 0.90 (t, J = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.9, 127.0, 115.4, 110.9, 57.9, 31.5, 29.7, 28.8, 28.7, 26.2, 22.4, 13.9; HRMS (EI) m/z calcd for $C_{16}H_{19}N_5$ (M^+) 281.1640, found 281.1647. Anal. Calcd for $C_{16}H_{19}N_5$: C, 68.30; H, 6.81; N, 24.89. Found: C, 68.40; H, 6.67; N, 24.99.

*2,3-Diethyl-6,7-dinitroquinoxaline (**5**).* 4,5-Dinitro-1,2-phenylenediamine (1000 mg, 5.0 mmol), 3,4-hexadione (685 mg, 6.0 mmol), and ethanol (50 mL) were mixed in a round-bottom flask equipped with a condenser. The reaction mixture was refluxed overnight. The mixture was cooled to room temperature, and ethanol was removed under vacuum. It was then extracted with $CHCl_3$, and the organic phase was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave the product as an off-white solid, which was purified by column chromatography (1000 mg, 72%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 2H), 3.15 (q, J = 8 Hz, 4H), 1.49 (t, J = 8 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.5, 141.7, 141.1, 126.6, 28.3, 11.1; HRMS (EI) m/z calcd for $C_{12}H_{12}N_4O_4$ (M^+) 276.0859, found, 276.0867. Anal. Calcd for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.43; H, 4.40; N, 20.18.

*4,7-Diphenylbenzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**6**).* Following general procedure A, **6** was obtained as a green solid (42 mg, 99%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.85−7.82 (m, 4H), 7.70−

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7.65 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.2, 141.6, 132.4, 130.7, 130.1, 128.8, 115.1, 112.6; HRMS (EI) m/z calcd for $C_{20}H_{10}N_4S$ (M^+) 338.0626, found 338.0620. Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56. Found: C, 70.99; H, 3.05; N, 16.23.

*4,7-Di-m-tolylbenzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8a**).* Following general procedure A, **8a** was obtained as a yellow solid (45 mg, 98%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.61−7.59 (m, 4H), 7.55 (t, J = 6 Hz, 2H), 7.46 (d, J = 6 Hz, 2H), 2.54 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.2, 141.8, 138.6, 132.4, 131.4, 130.5, 128.6, 127.1, 115.2, 112.5, 21.4; HRMS (EI) m/z calcd for $C_{22}H_{14}N_4S$ (M^+) 366.0939, found 366.0941. Anal. Calcd for $C_{22}H_{14}N_4S$: C, 72.11; H, 3.85; N, 15.29. Found: C, 71.98; H, 3.67; N, 15.15.

*4,7-Bis(4-methoxyphenyl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8b**).* Following general procedure A, **8b** was obtained as a yellow solid (44 mg, 89%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 9 Hz, 4H), 7.17 (d, J = 9 Hz, 4H), 3.96 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.4, 154.4, 140.8, 131.8, 124.7, 115.6, 114.2, 111.9, 55.3; HRMS (EI) m/z calcd for $C_{22}H_{14}N_4O_2S$ (M^+) 398.0837, found 398.0843. Anal. Calcd for $C_{22}H_{14}N_4O_2S$: C, 66.32; H, 3.54; N, 14.06. Found: C, 66.04; H, 3.67; N, 13.85.

*4,7-Bis(4-(dimethylamino)phenyl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8c**).* Following general procedure A, **8c** was obtained as a purple solid (53 mg, 99%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 9 Hz, 4H), 6.91 (d, J = 9 Hz, 4H), 3.12 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.7, 151.5, 140.3, 131.6, 119.8, 116.5, 111.5, 110.6, 39.9; HRMS (EI) m/z calcd for $C_{24}H_{20}N_6S$ (M^+) 424.1470, found 424.1478. Anal. Calcd for $(C_{24}H_{20}N_6S)$ $(CH_2Cl_2)_{0.25}$: C, 65.34; H, 4.64; N, 18.85. Found: C, 65.28; H, 4.85; N, 18.55. ^1H NMR spectroscopy also confirmed the presence of ca. 0.25 equiv of CH_2Cl_2.

*4,7-Bis(4-nitrophenyl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8d**).* Following general procedure A, **8d** was obtained as an off-white solid (43 mg, 81%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 9 Hz, 4H), 8.03 (d, J = 9 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.7, 149.2, 140.2, 138.1, 131.5, 124.2, 114.3, 113.4; HRMS (EI) m/z calcd for $C_{20}H_8N_6O_4S$ (M^+) 428.0328, found 428.0330. Anal. Calcd for $C_{20}H_8N_6O_4S$: C, 56.07; H, 1.88; N, 19.62. Found: C, 56.13; H, 2.03; N, 19.57.

*4,7-Bis(4-fluorophenyl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8e**).* Following general procedure A, **8e** was obtained as a yellow solid (40 mg, 86%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.87−7.81 (m, 4H), 7.36 (apparent t, J = 9 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.2 (d, J_{CF} = 251 Hz), 154.2, 140.8, 132.5 (d, J_{CF} = 8 Hz), 128.5 (d, J_{CF} = 4 Hz), 116.3 (d, J_{CF} = 22 Hz), 115.2, 112.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.38 (m); HRMS (EI) m/z calcd for $C_{20}H_8F_2N_4S$ (M^+) 374.0438, found 374.0438. Anal. Calcd for $C_{20}H_8F_2N_4S$: C, 64.17; H, 2.15; N, 14.97. Found: C, 64.04; H, 2.27; N, 14.79.

*Diethyl 3,3′-(5,6-Dicyanobenzo[c][1,2,5]thiadiazole-4,7-diyl)-dibenzoate (**8f**).* Following general procedure A, **8f** was obtained as a green solid (56 mg, 93%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 1 Hz, 2H), 8.34 (dt, J = 8, 1 Hz, 2H), 8.01 (dt, J = 8, 1 Hz, 2H), 7.76 (t, J = 8 Hz, 2H), 4.46 (q, J = 7 Hz, 4H), 1.45 (t, J = 7 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 154.1, 141.2, 134.1, 132.7, 131.8, 131.5, 131.4, 129.2, 114.9, 112.9, 61.5, 14.3; HRMS (EI) m/z calcd for $C_{26}H_{18}N_4O_4S$ (M^+) 482.1049, found 482.1045. Anal. Calcd for $(C_{26}H_{18}N_4O_4S)$ $(CH_2Cl_2)_{0.05}$: C, 64.28; H, 3.75; N, 11.51. Found: C, 64.17; H, 3.93; N, 11.25. ^1H NMR spectroscopy also confirmed the presence of ca. 5% CH_2Cl_2.

*4,7-Bis(3-formylphenyl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8g**).* Following general procedure A, **8g** was obtained as an off-white solid (37 mg, 75%): ^1H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 2H), 8.35 (s, 2H), 8.19 (d, J = 8 Hz, 2H), 8.11 (d, J = 8 Hz, 2H), 7.88 (t, J = 8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.1, 154.0, 140.8, 136.9, 135.7, 133.4, 131.9, 131.5, 129.9, 114.8, 113.1; HRMS (EI) m/z calcd for $C_{22}H_{10}N_4O_2S$ (M^+) 394.0524, found 394.0521. Anal. Calcd for $(C_{22}H_{10}N_4O_2S)(C_4H_8O_2)_{0.1}$: C, 66.72; H, 2.70; N, 13.89. Found: C, 66.34; H, 2.64; N, 14.11. ^1H NMR spectroscopy also confirmed the presence of a small quantity of EtOAc.

*4,7-Di(pyridin-3-yl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**8h**).* Following general procedure A, **8h** was obtained as an off-white solid (43 mg, 99%): ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, J = 2 Hz, 2H), 8.90 (dd, J = 5, 2 Hz, 2H), 8.20 (dt, J = 8, 2 Hz, 2H), 7.63 (dd, J = 8, 5 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.0, 151.8, 150.6, 139.1, 137.5, 128.7, 123.6, 114.7, 113.2; HRMS (EI) m/z calcd for $C_{18}H_8N_6S$ (M^+) 340.0531, found 340.0537. Anal. Calcd for $(C_{18}H_8N_6S)$ $(CH_2Cl_2)_{0.05}$: C, 62.91; H, 2.37; N, 24.39. Found: C, 62.79; H, 2.53; N, 24.32. ^1H NMR spectroscopy also confirmed the presence of a small quantity of CH_2Cl_2.

*4,7-Bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[c][1,2,5]-thiadiazole-5,6-dicarbonitrile (**8i**).* Following general procedure A, **8i** was obtained as a dark red solid from 3 equiv of 2-bromo-5-(2-ethylhexyl)thiophene (38 mg, 53%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 4 Hz, 2H), 6.98 (d, J = 4 Hz, 2H), 2.91 (d, J = 7 Hz, 4H), 1.75−1.71 (m, 2H), 1.49−1.30 (m, 16H), 0.95−0.85 (m, 12 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 152.9, 132.7, 132.6, 130.8, 126.3, 116.7, 109.8, 41.5, 34.4, 32.5, 28.9, 25.6, 23.0, 14.1, 10.8; HRMS (EI) m/z calcd for $C_{32}H_{38}N_4S_3$ (M^+) 574.2259, found 574.2255. Anal. Calcd for $C_{32}H_{38}N_4S_3$: C, 66.86; H, 6.66; N, 9.75. Found: C, 66.64; H, 6.71; N, 9.79.

*4,7-Bis(5-(trimethylsilyl)thiophene-2-yl)benzo[c][1,2,5]-thiadiazole-5,6-dicarbonitrile (**8j**).* Following general procedure A, **8j** was obtained as a red dark solid from 3 equiv of 2-bromo-5-trimethylsilylthiophene (50 mg, 76%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 4 Hz, 2H), 7.44 (d, J = 4 Hz, 2H), 0.45 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.4, 149.1, 137.8, 134.5, 133.4, 133.2, 116.3, 110.6, −0.1; HRMS (EI) m/z calcd for $C_{22}H_{22}N_4S_3Si_2$ (M^+), 494.0545, found 494.0553. Anal. Calcd for $C_{22}H_{22}N_4S_3Si_2$: C, 53.40; H, 4.48; N, 11.32. Found: C, 53.24; H, 4.44; N, 11.09.

*4,7-Bis(5-methylthiophene-2-yl)benzo[c][1,2,5]thiadiazole-5,6-dicarbonitrile (**9**).* Following general procedure A, **9** was obtained as a dark red solid from 3 equiv of 2-bromo-5-methylthiophene (33 mg, 70%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 4 Hz, 2H), 7.00 (dq, J = 4, 1 Hz, 2H), 2.67 (d, J = 1Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 147.9, 133.0, 132.8, 130.8, 126.6, 116.5, 110.1, 15.6; HRMS (EI) m/z calcd for $C_{18}H_{10}N_4S_3$ (M^+), 378.0068, found 378.0065. Anal. Calcd for $C_{18}H_{10}N_4S_3$: C, 57.12; H, 2.66; N, 14.80. Found: C, 56.96; H, 2.72; N, 14.55.

*2-Octyl-4,7-diphenyl-2H-benzo[d][1,2,3]triazole-5,6-dicarbonitrile (**11a**).* Following general procedure A, **11a** was obtained as a white solid (40 mg, 90%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 6, 1 Hz, 4H), 7.65−7.60 (m, 6H), 4.79 (t, J = 8 Hz, 2H), 2.15−2.05 (m, 2H), 1.38−1.20 (m, 10 H), 0.89 (t, J = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.1, 139.7, 132.5, 130.5, 130.1, 128.9, 116.1, 109.9, 57.9, 31.6, 30.0, 29.0, 28.8, 26.4, 22.6, 14.1; HRMS (EI) m/z calcd for $C_{28}H_{27}N_5$ (M^+) 433.2266, found 433.2274. Anal. Calcd for $C_{28}H_{27}N_5$: C, 77.57; H, 6.28; N, 16.15. Found: C, 77.44; H, 6.38; N, 15.79.

*4,7-Bis(4-methoxyphenyl)-2-octyl-2H-benzo[d][1,2,3]triazole-5,6-dicarbonitrile (**11b**).* Following general procedure A, **11b** was obtained as a white solid (40 mg, 81%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 9 Hz, 4H), 7.14 (d, J = 9 Hz, 4H), 4.79 (t, J = 7 Hz, 2H), 3.94 (s, 6H), 2.15−2.05 (m, 2H), 1.37−1.20 (m, 10 H), 0.89 (t, J = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 144.2, 138.9, 131.6, 124.8, 116.6, 114.4, 109.3, 57.8, 55.5, 31.7, 30.1, 29.1, 28.9, 26.4, 22.6, 14.1; HRMS (EI) m/z calcd for $C_{30}H_{31}N_5O_2$ (M^+) 493.2478, found 493.2473. Anal. Calcd for $C_{30}H_{31}N_5O_2$: C, 73.00; H, 6.33; N, 14.19. Found: C, 72.72; H, 6.22; N, 13.96.

*4,7-Bis(4-fluorophenyl)-2-octyl-2H-benzo[d][1,2,3]triazole-5,6-dicarbonitrile (**11d**).* Following general procedure A, **11d** was obtained as a white solid (34 mg, 72%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.90−7.85 (m, 4H), 7.35−7.28 (m, 4H), 4.80 (t, J = 8 Hz, 2H), 2.15−2.05 (m, 2H), 1.38−1.20 (m, 10 H), 0.89 (t, J = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0 (d, J_{CF} = 251 Hz), 144.1, 138.6, 132.2 (d, J_{CF} = 8 Hz), 128.4 (d, J_{CF} = 4 Hz), 116.2 (d, J_{CF} = 22 Hz), 115.9, 109.9, 57.9, 31.6, 30.0, 28.9, 28.8, 26.4, 22.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.20 (m); HRMS (EI) m/z calcd for $C_{28}H_{25}F_2N_5$ (M^+) 469.2078, found 469.2087. Anal. Calcd for $C_{28}H_{25}F_2N_5$: C, 71.62; H, 5.37; N, 14.92. Found: C, 71.77; H, 5.49; N, 14.88.

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*2-Octyl-4,7-di(pyridin-3-yl)-2H-benzo[d][1,2,3]triazole-5,6-dicarbonitrile (**11f**).* Following general procedure A, **11f** was obtained as a white solid (30 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, J = 2 Hz, 2H), 8.86 (dd, J = 5, 1 Hz, 2H), 8.23 (apparent dt, J = 7, 1 Hz, 2H), 7.60 (ddd, J = 8, 5 1 Hz, 2H), 4.81 (t, J = 7 Hz, 2H), 2.15−2.05 (m, 2H), 1.36−1.20 (m, 10 H), 0.88 (t, J = 7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.5, 150.6, 143.9, 137.2, 136.8, 128.5, 123.7, 115.4, 110.5, 58.2, 31.6, 29.9, 28.9, 28.8, 26.4, 22.6, 14.0; HRMS (EI) m/z calcd for $C_{26}H_{25}N_7$ (M^+) 435.2171, found 435.2175. Anal. Calcd for $C_{26}H_{25}N_7$: C, 71.70; H, 5.79; N, 22.51. Found: C, 71.56; H, 5.91; N, 22.23.

*2-Octyl-4,7-bis(5-(trimethylsilyl)thiophene-2-yl)-2H-benzo[d]-[1,2,3]triazole-5,6-dicarbonitrile (**11g**).* Following general procedure A, **11g** was obtained as an orange solid (37 mg, 62%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 4 Hz, 2H), 7.41 (d, J = 4 Hz, 2H), 4.88 (t, J = 7 Hz, 2H), 2.25−2.15 (m, 2H), 1.40−1.25 (m, 10 H), 0.89 (t, J = 7 Hz, 3H), 0.44 (s, 18H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.2, 142.8, 137.8, 134.4, 132.6, 131.0, 116.8, 107.7, 57.6, 31.5, 29.7, 28.9, 28.7, 26.3, 22.4, 13.9, −0.3; HRMS (EI) m/z calcd for $C_{30}H_{39}N_5S_2Si_2$ (M^+) 589.2185, found 589.2186. Anal. Calcd for $C_{30}H_{39}N_5S_2Si_2$: C, 61.07; H, 6.66; N, 11.87. Found: C, 60.98; H, 6.52; N, 11.67.

*2,3-Diethyl-5,8-diphenylquinoxaline-6,7-dicarbonitrile (**12a**).* Following general procedure A, **12a** was obtained as a white solid (38 mg, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68−7.60 (m, 4H), 7.60−7.55 (m, 6H), 3.01 (q, J = 7 Hz, 4H), 1.27 (t, J = 7 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.9, 147.3, 140.2, 133.4, 130.9, 129.3, 127.8, 115.6, 112.9, 27.9, 10.5; HRMS (EI) m/z calcd for $C_{26}H_{20}N_4$ (M^+) 388.1688, found 388.1686. Anal. Calcd for $(C_{26}H_{20}N_4)$ $(CH_2Cl_2)_{0.15}$: C, 78.28; H, 5.10; N, 13.96. Found: C, 78.31; H, 5.07; N, 13.77. ^{1}H NMR spectroscopy also confirmed the presence of ca. 15% CH_2Cl_2.

*2,3-Diethyl-5,8-bis(5-(trimethylsilyl)thiophen-2-yl)quinoxaline-6,7-dicarbonitrile (**12f**).* Following general procedure A, **12f** was obtained as a yellow solid (32 mg, 46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 4 Hz, 2H), 7.36 (d, J = 4 Hz, 2H), 3.11 (q, J = 7 Hz, 4H), 1.48 (t, J = 7 Hz, 6H), 0.40 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 147.8, 139.3, 138.3, 137.7, 133.3, 132.5, 116.8, 111.9, 28.4, 10.9, −0.1; HRMS (EI) m/z calcd for $C_{28}H_{32}N_4S_2Si_2$ (M^+), 544.1607, found 544.1609. Anal. Calcd for $C_{28}H_{32}N_4S_2Si_2$: C, 61.72; H, 5.92; N, 10.28. Found: C, 61.57; H, 5.96; N, 10.13.

*2,3-Diethyl-5,8-bis(4-methoxyphenyl)-6,7-dinitroquinoxaline (**13b**).* Following general procedure B, **13b** was obtained as a yellow solid (43 mg, 72%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 9 Hz, 4H), 7.05 (d, J = 9 Hz, 4H), 3.92 (s, 6H), 3.00 (q, J = 8 Hz, 4H), 1.27 (t, J = 8 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.1, 159.6, 141.7, 139.4, 134.0, 131.3, 123.2, 113.5, 55.1, 27.9, 10.7; HRMS (EI) m/z calcd for $C_{26}H_{24}N_4O_6$ (M^+) 488.1696, found 488.1695. Anal. Calcd for $C_{26}H_{24}N_4O_6$: C, 63.93; H, 4.95; N, 11.47. Found: C, 64.16; H, 5.29; N, 11.14.

*5,8-Bis(4-fluorophenyl)-6,7-dinitroquinoxaline (**13d**).* Note that this compound was synthesized from **4′** rather than **4**. Following general procedure B, **13d** was obtained as a yellow solid (36 mg, 72%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 2H), 7.49−7.45 (m, 4H), 7.29−7.22 (m, 4H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.4 (d, J_{CF} = 249 Hz), 147.4, 142.5, 141.8, 135.1, 131.7 (d, J_{CF} = 8 Hz), 126.1, (d, J_{CF} = 3 Hz), 115.8 (d, J_{CF} = 9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.65 (m); HRMS (EI) m/z calcd for $C_{20}H_{10}F_2N_4O_4$ (M^+) 408.0670, found 408.0676. Anal. Calcd for $(C_{20}H_{10}F_2N_4O_4)$ $(CH_2Cl_2)_{0.15}$: C, 57.48; H, 2.47; N, 13.31. Found: C, 57.27; H, 2.63; N, 13.18. ^{1}H NMR spectroscopy also confirmed the presence of ca. 15% CH_2Cl_2.

*2,3-Diethyl-6,7-dinitro-5,8-bis(5-(trimethylsilyl)thiophene-2-yl)-quinoxaline (**13f**).* Following general procedure B, **13f** was obtained as a yellow solid (50 mg, 68%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 4 Hz, 2H), 7.28 (d, J = 4 Hz, 2H), 3.10 (q, J = 7 Hz, 4H), 1.43 (t, J = 7 Hz, 6H), 0.41 (s, 18H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.71, 146.45, 141.09, 138.42, 134.62, 133.38, 130.66, 127.12, 28.01, 10.47, −0.27; HRMS (EI) m/z calcd for $C_{26}H_{32}N_4O_4S_2Si_2$ (M^+) 584.1404, found 584.1404. Anal. Calcd for $C_{26}H_{32}N_4O_4S_2Si_2$: C, 53.39; H, 5.51; N, 9.58. Found: C, 53.50; H, 5.63; N, 9.43.

*4,7-Bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[c][1,2,5]thiadiazole (**14**).* 2-Trimethylstannane-5-(2-ethylhexyl)thiophene[67] (108 mg, 0.3 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole[48] (29.3 mg, 0.10 mmol), Pd_2dba_3 (9.2 mg, 0.01 mmol), and tri(*o*-tolyl)phosphine (12.2 mg, 0.04 mmol) were added sequentially to a Schlenk flask with a magnetic stirring bar. The flask was sealed with a septum cap and evacuated and refilled with N_2 gas 3 times. Toluene (5 mL) was added, and the reaction was heated in a 90 °C oil bath. After 12 h, the reaction mixture was cooled to room temperature, diluted with DCM (50 mL), and filtered through Celite (10 mL). The filtrate was concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to provide **14** as an orange oil (50 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 4 Hz, 2H), 7.80 (s, 2H), 6.88 (d, J = 4 Hz, 2H), 2.85 (d, J = 7 Hz, 4H), 1.72−1.68 (m, 2H), 1.49−1.30 (m, 16H), 0.97−0.90 (m, 12 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7, 146.4, 137.1, 127.3, 126.3, 125.7, 125.2, 41.5, 34.3, 32.4, 28.9, 25.6, 23.0, 14.2, 10.9; HRMS (EI) m/z calcd for $C_{30}H_{40}N_2S_3$ (M^+) 524.2354, found 524.2352. Anal. Calcd for $C_{30}H_{40}N_2S_3$: C, 68.65; H, 7.68; N, 5.34. Found: C, 68.92; H, 7.71; N, 5.23.

*4,7-Bis(5-(2-ethylhexyl)thiophene-2-yl)-5,6-difluorobenzo[c]-[1,2,5]thiadiazole (**7i**).* Compound **7i** was synthesized according to the literature procedure:[38] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 4 Hz, 2H), 6.94 (s, 2H), 2.88 (d, J = 7 Hz, 4H), 1.75−1.68 (m, 2H), 1.49−1.30 (m, 16H), 0.97−0.90 (m, 12 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.5 (dd, J_{CF} = 258, 20 Hz), 148.9 (t, J_{CF} = 4 Hz), 148.6, 130.9 (t, J_{CF} = 4 Hz), 129.4, 125.8, 111.4 (dd, J_{CF} = 8, 3 Hz), 41.5, 34.1, 32.5, 28.9, 25.6, 23.0, 14.2, 10.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −128.99; HRMS (EI) m/z calcd for $C_{30}H_{38}F_2N_2S_3$ (M^+), 560.2165, found 560.2179. Anal. Calcd for $C_{30}H_{38}F_2N_2S_3$: C, 64.25; H, 6.83; N, 5.00. Found: C, 64.13; H, 6.89; N, 5.10.

*4,7-Bis(5-(2-ethylhexyl)thiophene-2-yl)-5,6-dinitrobenzo[c]-[1,2,5]thiadiazole (**16**).* 2-Trimethylstannyl-5-(2-ethylhexyl)-thiophene[67] (288 mg, 0.80 mmol), 4,7-dibromo-5,6-dinitrobenzo[c]-[1,2,5]thiadiazole[48] (76.8 mg, 0.20 mmol), and $Pd(PPh_3)_2Cl_2$ (9.8 mg, 0.014 mmol) were added sequentially to a Schlenk flask with a magnetic stirring bar. The flask was sealed with a septum cap and evacuated and refilled with N_2 gas three times. THF (2 mL) was added, and the reaction was heated in a 80 °C oil bath. After 3 h, the reaction mixture was cooled to room temperature, diluted with DCM (100 mL), and filtered through Celite (10 mL). The filtrate was concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to provide **16** as a dark red solid (105 mg, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 4 Hz, 2H), 6.91 (d, J = 4 Hz, 2H), 2.88 (d, J = 7 Hz, 4H), 1.71−1.68 (m, 2H), 1.43−1.30 (m, 16H), 0.97−0.90 (m, 12 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.9, 151.8, 141.2, 130.9, 127.1, 126.2, 120.7, 41.2, 34.1, 32.3, 28.7, 25.5, 22.8, 13.9, 10.6; HRMS (EI) m/z calcd for $C_{30}H_{38}N_4O_4S_3$ (M^+) 614.2055, found 614.2065. Anal. Calcd for $C_{30}H_{38}N_4O_4S_3$: C, 58.60; H, 6.23; N, 9.11. Found: C, 58.71; H, 6.34; N, 9.06.

*4,7-Bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[c][1,2,5]-thiadiazole-5,6-diamine (**17**).* Compound **16** (100 mg, 0.16 mmol) and iron powder (109 mg, 1.95 mmol) were added to a Schlenk flask with a magnetic stirring bar. Acetic acid (5 mL) was added, and the reaction was heated in a 80 °C oil bath. After 7 h, the reaction mixture was cooled to room temperature, diluted with diethyl ether (50 mL), and washed with brine (50 mL). The organic was concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to provide **17** as a dark brown oil (70 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 4 Hz, 2H), 6.91 (d, J = 4 Hz, 2H), 4.44 (s, 4H), 2.86 (d, J = 7 Hz, 4H), 1.71−1.68 (m, 2H), 1.48−1.30 (m, 16H), 0.97−0.90 (m, 12 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.9, 146.4, 139.1, 132.8, 128.3, 125.35, 107.5, 41.3, 34.3, 32.5, 28.9, 25.6, 23.0, 14.2, 10.9; HRMS (EI) m/z calcd for $C_{30}H_{42}N_4S_3$ (M^+) 554.2572, found 554.2578. Anal. Calcd for $C_{30}H_{42}N_4S_3$: C, 64.94; H, 7.63; N, 10.10. Found: C, 65.03; H, 7.48; N, 10.10.

*4,7-Bis[5-(2-ethylhexyl)thiophene-2-yl]-2$\lambda^4\delta^2$-benzo[1,2-c;4,5-c′]-bis[1,2,5]thiadiazole (**15**).* Compound **17** (200 mg, 0.34 mmol) was

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dissolved in pyridine (5 mL) in a Schlenk flask with a magnetic stirring bar. *N*-Thionylaniline (96 mg, 0.69 mmol) and trimethylsilyl chloride (374 mg, 3.43 mmol) were added in one portion, and the reaction was heated in a 80 °C oil bath. The reaction mixture turned blue in 5 min. After 24 h, the reaction mixture was cooled to room temperature, diluted with diethyl ether (100 mL), and washed with diluted HCl (100 mL, 3 M). The organic layer was concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to provide **15** as dark red solid (160 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, J = 4 Hz, 2H), 7.00 (d, J = 4 Hz, 2H), 2.92 (d, J = 7 Hz, 4H), 1.82−1.72 (m, 2H), 1.48−1.35 (m, 16H), 1.06−0.92 (m, 12 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 150.8, 150.7, 135.6, 132.5, 126.4, 113.0, 41.4, 34.3, 32.4, 28.7, 25.5, 22.9, 14.0, 10.7; HRMS (EI) m/z calcd for $C_{30}H_{38}N_4S_4$ (M^+) 582.1979, found 582.1974. Anal. Calcd for $C_{30}H_{38}N_4S_4$: C, 61.81; H, 6.57; N, 9.61. Found: C, 62.04; H, 6.45; N, 9.58.

*4,7-Bis(5-bromo-4-hexylthiophene-2-yl)benzo[c][1,2,5]-thiadiazole-5,6-dicarbonitrile (**18**).* To an oven-dried, 5 mL, collared tube containing a stirring bar were sequentially added $Pd(OPiv)_2$ (4.1 mg, 0.013 mmol), AgOAc (167 mg, 0.750 mmol), pyridine (9.9 mg, 0.125 mmol), **2** (23.3 mg, 0.125 mmol), and 2-bromo-3-hexylthiophene (123 mg, 0.500 mmol) under a flow of N_2. Dry DMSO (0.5 mL) was added, and a septum cap was crimped onto the vial to form a seal. The reaction mixture was heated in a 85 °C oil bath until judged complete by examining aliquots with GC/MS. The resulting mixture was cooled to room temperature and filtered through a layer of Celite (5 mL) using dichloromethane. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel, affording the diarylated product, **18**, as a dark red solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 2H), 2.70 (t, J = 8 Hz, 4H), 1.69 (q, J = 8 Hz, 4H), 1.46−1.32 (m, 12H), 0.92 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.9, 143.4, 133.2, 132.6, 131.8, 118.5, 116.2, 110.1, 31.6, 29.7, 29.6, 28.9, 22.6, 14.1; HRMS (EI) m/z calcd for $C_{28}H_{28}N_4S_3Br_2$ (M^+) 673.9843, found 673.9818. Anal. Calcd for $C_{28}H_{28}N_4S_3Br_2$: C, 49.71; H, 4.17; N, 8.28. Found: C, 49.99; H, 4.20; N, 7.98.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02551.

Reaction optimization tables, NMR spectra of new compounds, and analysis of crystallographic data of **8j** and **9** (PDF)

Crystallographic data of **8j** and **9** (CIF)

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Notes

The authors declare no competing financial interest.

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