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Efficient Synthesis of 4,8-Dibromo Derivative of Strong Electron-Deficient Benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole and Its S_NAr and Cross-Coupling Reactions

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Abstract: An efficient synthesis of hydrolytically and thermally stable 4,8-dibromobenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole by the bromination of its parent heterocycle is reported. The structure of 4,8-dibromobenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole was confirmed by X-ray analysis. The conditions for the selective aromatic nucleophilic substitution of one bromine atom in this heterocyclic system by nitrogen nucleophiles are found, whereas thiols formed the bis-derivatives only. Suzuki–Miyaura cross-coupling reactions were found to be an effective method for the selective formation of various mono- and di(het)arylated derivatives of strong electron-deficient benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole, and Stille coupling can be employed for the preparation of bis-arylated heterocycles, which can be considered as useful building blocks for the synthesis of DSSCs and OLEDs components.

Keywords: sulfur–nitrogen heterocycles; benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole; aromatic nucleophilic substitution; Suzuki and Stille cross-coupling reactions; X-ray analysis

1. Introduction

Organic photovoltaics is a developing technology with a unique set of properties, such as low-cost solution processing with nontoxic materials, the possibility of using small amounts of materials due to ultrathin absorber films, and the ease of varying the most important characteristics of materials [1]. The chromophores, both polymeric and low-molecular weight, used in these devices, consisting of a combination of electron-donating (D) and electron-withdrawing (A) groups linked either directly or, preferably, through a π-conjugated bridges (π), have been extensively studied. The electron-deficient π-conjugated building blocks play an essential role in achieving the most important characteristics, such as light absorption, light emission and charge carrier mobility in materials by reducing the bandgap by promoting intramolecular charge transfer (ICT) [2,3]. The most important property of the acceptor is the electron affinity, which is related to the energy of the lowest unoccupied molecular orbital (LUMO). The choice of acceptor is crucial to achieving high performance in materials such as bulk heterojunction solar cells (BHJ) [4,5], dye-sensitized solar cells (DSSCs) [4,6,7], n-type organic field-effect transistors [8,9], near-infrared absorption and emissions materials [10,11], and electrochromic materials [12,13]. Although many heterocyclic acceptor building blocks are known [14], 2,1,3-benzothiadiazole (BTD) occupies an exceptional place among them [15,16]. Nevertheless, there is a strong demand to create ultra-high electron-deficient building blocks based on it to improve the special characteristics of photovoltaic materials [17,18]. Several attempts have been made. The attachment of strong electron-withdrawing groups (i.e., fluorine) at positions 5 and 6 has produced many different materials derived from 5,6-difluoro-2,1,3-
benzothiadiazole [13]. Recently, the synthesis of an ultra-high electron-deficient [1,2,5]thiadiazolof[3,4-d]pyridazine system with the formal replacement of carbon atoms in the 5- and/or 6-positions by electronegative atoms nitrogen has been reported [19]; it has been shown to be an important intermediate for the synthesis of dyes with various possible applications [18,20,21]. A third way to increase the electron-withdrawing strength of the benzothiadiazole ring is heteroannelation at positions 5 and 6 to create an acceptor, such as benzo[1,2-c,4,5-c’]bis[1,2,5]thiadiazole (benzo-thiadiazole, BBT), a sulfur–nitrogen heterocycle with the lowest LUMO energy [19]. The synthesis and functionalization of benzo[1,2-c,4,5-c’]bis[1,2,5]thiadiazole derivatives has been well investigated [22]. On the other hand, the possibilities of its bis(isothiadiazole) isomer, benzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) (isoBTD), have been largely unexplored. Meanwhile, it has been shown that the replacement of the 1,2,5-thiadiazole ring in 2,1,3-benzothiadiazole (BTD) by the 1,2,3-thiadiazole ring leads to benzo[d][1,2,3]thiadiazole (isoBTD) compounds with properties similar to those of BTD, but with higher values of $E_{\text{LUMO}}$ and the band gap ($E_g$), which indicates a high electronic conductivity due to the high stability of the molecule in the excited state. The careful selection of components in the design of appropriate compounds with benzo[d][1,2,3]thiadiazole as an internal acceptor can lead to promising photovoltaic materials [23]. In this regard, it becomes relevant to study the BBT isomer, benzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) (isoBTD), which differs in the order of atoms in two five-membered heterocyclic rings. Figure 1 shows the boundary orbital energies ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) for 2,1,3-benzothiadiazole, as well as its derivatives and isomers.

![Figure 1. HOMO–LUMO energy levels and energy gap values for electron-deficient heterocycles for 2,1,3-benzothiadiazole, as well as its derivatives and isomers.](image)

The data in Table 1 show that the fusion of a benzothiadiazole with another electron-withdrawing ring is the preferred method for increasing the electron-withdrawing capacity of the heterocyclic system, because it reduces the most important characteristic for photovoltaic materials, the energy band gap ($E_g$). Nevertheless, $E_g$ for isoBTD compounds is much higher than for BTD derivatives, which determines the stability of the molecule in the excited state, and as a result the high electron conductivity, and requires a careful selection of donor moieties in the dye by designing photovoltaic components.

Dihalogenated (usually dibrominated) derivatives of the electron-deficient heterocycles shown in Figure 1 are most often employed to prepare components of various photovoltaic materials [22,24,25]. 4,8-Dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 was described as a minor component of an inseparable mixture of three compounds, with tricycle 2 and its mono-derivative 3 obtained by the nitrosation of 2,5-diaminobenzene-1,4-dithiol dihydrochloride 4 in HBr (Scheme 1) [26]. Neither the yield of compound 1 nor its spectral and analytical data are given in the paper.
Scheme 1. Nitrosation of 2,5-diaminobenzene-1,4-dithiol dihydrochloride 4.

Herein, we describe the synthesis of 4,8-dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1, its spectral and analytical data, S\textsubscript{N}Ar and cross-coupling reactions as a basis for the preparation of compounds that are of interest as photovoltaic materials.

Table 1. Bromination of benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Brominating Agent</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Yields (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>NBS</td>
<td>AcOH</td>
<td>25 °C, 12 h</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>NBS</td>
<td>CHCl\textsubscript{3}</td>
<td>25 °C, 24 h</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>NBS</td>
<td>DMF</td>
<td>25 °C, 24 h</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>NBS</td>
<td>CHCl\textsubscript{3}</td>
<td>61 °C, 12 h</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>NBS</td>
<td>DMF</td>
<td>110 °C, 12 h</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>Br\textsubscript{2}</td>
<td>dioxane</td>
<td>25 °C, 12 h</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>HBr</td>
<td>HBr</td>
<td>80 °C, 12 h</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>Br\textsubscript{2}</td>
<td>HBr</td>
<td>80 °C, 12 h</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>Br\textsubscript{2}</td>
<td>HBr</td>
<td>110 °C, 12 h</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Br\textsubscript{2}</td>
<td>HBr</td>
<td>120 °C, 12 h</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>Br\textsubscript{2}</td>
<td>HBr</td>
<td>120 °C, 18 h</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>Br\textsubscript{2}</td>
<td>HBr</td>
<td>130 °C, 18 h</td>
<td>0</td>
</tr>
</tbody>
</table>

2. Results and Discussion

2.1. Synthesis of 4,8-Dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1

Taking into account the failures in the synthesis of compound 1 from 2,5-diaminobenzene-1,4-dithiol dihydrochloride 4, we decided to synthesize this compound from unsubstituted tricycle 2, which is easily formed from dithiol 4 in almost quantitative yields upon nitrosation in hydrochloric acid [27]. We recently found that the bromination of tricycle 2 in hydrobromic acid can selectively give 4-bromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 3 in good yields [28]. In a continuation of this study, the bromination of benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 2 was carried out by varying the nature of the brominating agent (NBS and bromine), the solvent, and the reaction temperature. The results are summarized in Table 1.

The use of N-bromosuccinimide in a solvent (AcOH, CHCl\textsubscript{3}, DMF) or molecular bromine (Br\textsubscript{2}) in dioxane as brominating agents at room temperature did not lead to mono-3 and di-bromides 1; only starting compound 2 was isolated from the reaction mixture (Table 1, entries 1–6), which can be explained by the high electron-withdrawing character of
tricycle 2, which slows down the reaction of electrophilic bromination. Carrying out the reaction in hydrobromic acid with heating in the absence of molecular bromine also led to a low conversion of compound 2, and 4-bromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 3 was isolated in a 20% yield, while the yield of 4,8-dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 did not exceed 5% (Entry 7). This result is similar to the formation of the mixture of compounds 1, 2, and 3, which was obtained by the nitrosation of 2,5-diaminobenzene-1,4-dithiol dihydrochloride 4 in HBr (Scheme 1). Carrying out the reaction when heated to 80 °C in hydrobromic acid in the presence of molecular bromine made it possible to increase the yield of 4-bromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 3 to 60%. However, trace amounts of 4,8-dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 were detected in the reaction mixture (Entry 8). Increasing both the reaction temperature to 120 °C and the amount of bromine made it possible to increase the yield of the target 4,8-dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 up to 38%, while the yield of monobromo derivative 3 was only 5% (Entry 10). The longer heating of the reaction mixture (18 h) led to the target dibromide in a 40% yield (Entry 11). A further increase in the temperature of the reaction medium to 130 °C gave a slight decrease in the yield of the target compound (Entry 12). Thus, we have developed a method for the selective preparation of 4,8-dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 in moderate yield. Unfortunately, the reactivity of the parent ultra-high electron-withdrawing heterocycles, such as benzoc[1,2-c:4,5-c’]bis[1,2,3]thiadiazole (BBT) or benzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 2, has not been previously studied. We assume that for such compounds, the reactions of the electrophilic substitution of the hydrogen atom are difficult, and it is necessary to apply the conditions of radical reactions (for example, bromine in hydrobromic acid). The reactivity of the unsubstituted tricycle 2 will be reported in more detail in our next publication.

4,8-Dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 is a high-melting yellow solid with mp > 250 °C (Supplementary Materials). It is stable to hydrolysis at room temperature and can be kept in a freezer under argon for a few months without noticeable changes. Its structure was fully proven by NMR, mass and IR spectroscopy, and finally established by single-crystal X-ray diffraction study (Figure 2).

![Figure 2](image)

**Figure 2.** The general view of 4,8-dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 in a representation of atoms by thermal ellipsoids (p = 50%).

2.2. Aromatic Nucleophilic Substitution of 4,8-Dibromobenzoc[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1

The nucleophilic substitution in 1,2,5-thiadiazoles and 1,2,3-thiadiazoles fused with benzene or strong electron-withdrawing heterocycles has been poorly investigated. Two examples of nucleophilic substitution with morpholine and piperidine are known for 4,7-dibromobenzoc[c]1,2,5-thiadiazole 5 [29,30], one reaction with morpholine for 4,7-dibromobenzoc[d]1,2,3-thiadiazole 6 [31] and two procedures with morpholine and thiophenol
for benzo[1,2-c:4,5-c′]bis[1,2,5]thiadiazole 7 [32]. The formation of mono-substituted derivatives 8,9 in the first two cases and bis-derivative 10 for the more activated tricycle 7 was observed (Scheme 2).

Scheme 2. Nucleophilic substitution in fused 1,2,5-thiadiazoles and 1,2,3-dithiazoles.

Aromatic nucleophilic substitution in 4,7-dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine 11 was recently investigated [14], and selective conditions were found for the substitution of one or two bromine atoms by oxygen and nitrogen nucleophiles, whereas thiols formed only bis-derivatives (Scheme 3).

Scheme 3. Nucleophilic substitution in 4,7-dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine 11.

In order to find selective conditions for the formation of mono- and bis-substituted products in 4,8-dibromobenzo[1,2-d:4,5-d′]bis[[1,2,3]thiadiazole] 1, its reactions with nitrogen, sulfur- and oxygen-containing nucleophiles were systematically studied.

The treatment of 4,8-dibromobenzo[1,2-d:4,5-d′]bis[[1,2,3]thiadiazole] 1 with morpholine gave mono- and bis-substituted derivatives, depending on the reaction conditions. Carrying out the reaction at room temperature, regardless of the solvent used (DCM, MeCN, DMF) and the amount of morpholine, resulted in the mono-substitution product 12a in low to moderate yields (Table 2, entries 1–6). Refluxing of the reaction mixture in MeCN for 24 h with two morpholine equivalents gave a mono-substituted product 12a with the best yield of 78% (Entry 7). Heating in DMF under similar conditions did not improve the yield of 12a (70%, entry 8). The formation of bis-substituted product 13a in a moderate yield was achieved by the prolonged heating of dibromide 1, with an excess of
morpholine at 130 °C (Entry 9). Thus, optimal conditions were found for the synthesis of an asymmetric compound 12a and a disubstituted product 13a.

**Table 2.** Nucleophilic substitution of 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 with morpholine.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Morpholine (Eqv.)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yields (%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12a</td>
</tr>
<tr>
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<td>2</td>
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<td>25</td>
<td>6</td>
<td>15</td>
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<tr>
<td>2</td>
<td>4</td>
<td>DCM</td>
<td>25</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>MeCN</td>
<td>25</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>MeCN</td>
<td>25</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>DMF</td>
<td>25</td>
<td>8</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>DMF</td>
<td>25</td>
<td>8</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>MeCN</td>
<td>80</td>
<td>18</td>
<td>78</td>
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<tr>
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<td>2</td>
<td>DMF</td>
<td>80</td>
<td>12</td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>DMF</td>
<td>130</td>
<td>24</td>
<td>0</td>
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</table>

We applied the conditions found for nucleophilic substitution reactions to other primary and secondary amines. Piperidine 14b was found to react similarly to morpholine, forming mono-12b and bis-13b derivatives with moderate yields (Table 3, entries 1 and 2). A somewhat unexpected result was obtained for pyrrolidine 14c, which was converted into a mono-derivative 12c both when carrying out the reaction in acetonitrile and when heated at 130 °C in DMF; in the second case, the yield of the mono-product 12c decreased apparently due to its partial decomposition at elevated temperatures (Entries 3, 4). With the cyclopentaindoline derivative 14d and aniline 14e, dibromide 1 reacted when heated to 100–130 °C in DMF with an excess of amine, to form only mono-substitution products 12d, e in moderate yields (Entries 6–9). However, with more basic aliphatic primary amines, such as cyclohexylamine 14f and tert-butylamine 14g, no nucleophilic aromatic substitution reaction products were isolated, and only the partial decomposition of the starting dibromide 1 occurred when heated to 100–130 °C in DMF (Entries 10–16). When mono-adduct 12a and cyclohexylamine were heated in DMF at 130 °C, the latter decomposed within 12 h to form a mixture of products, from which it was not possible to isolate identifiable compounds.

It was shown that carbazole and diphenylamine did not react with 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 under the studied conditions. Our attempts to carry out reactions using sodium salts of these amines (obtained in situ from carbazole or diphenylamine and NaH) were also unsuccessful—dibromide 1 decomposed when reacted with sodium carbazolate or sodium diphenylamide in THF or DMF for 3 h, and heated at a temperature of 60 °C.

Thus, we have successfully developed effective methods for introducing aromatic and aliphatic amines into the 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) mole-
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The selective formation of mono-12 and bis-13 substitution products (Supplemental Materials). Nucleophilic aromatic substitution reactions under mild conditions led to the formation of the mono-substitution product 12. The introduction of a donor fragment into the dibromide molecule leads to a decrease in the reactivity of position 4 or 7 of the benzene ring. Therefore, to replace the second bromine atom, it is necessary to apply severe conditions, namely, to heat the reaction mixture in DMF to 130 °C.

Table 3. The nucleophilic substitution of 4,8-dibromobenzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) 1 with aromatic and aliphatic amines.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine (Eqv.)</th>
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<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yields (%)</th>
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<tr>
<td>1</td>
<td>14b (2)</td>
<td>MeCN</td>
<td>80</td>
<td>18</td>
<td>12b (70)</td>
</tr>
<tr>
<td>2</td>
<td>14b (6)</td>
<td>DMF</td>
<td>130</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>14c (2)</td>
<td>MeCN</td>
<td>80</td>
<td>18</td>
<td>12c (72)</td>
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<tr>
<td>4</td>
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<td>DMF</td>
<td>130</td>
<td>24</td>
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</tr>
<tr>
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The reactions of 4,8-dibromobenzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) 1 with such S-nucleophiles as thiophenol, hexylthiol, and dodecanethiol were studied. It was shown that when dibromide 1 was treated with thiophenol at room temperature in THF or DMF, the formation of only trace amounts of dimercapto derivative 15a was observed, even when using less than a two-fold equivalent of thiol (Table 4, entries 1,2). The use of one equivalent of base and thiophenol resulted in a mixture of disubstituted derivative 15a and starting dibromide 1, and our attempts to isolate the mono-substituted derivative were unsuccessful. The reaction with two equivalents of sodium thiophenolate led to an increase in the yield of bis(phenylthio) derivative 15a to 80% (Entry 3). The optimal conditions for the preparation of 15a were extended to hexanethiol and dodecanethiol, which resulted in the preparation of bis-thiols 15b,c in high yields (Supplemental Materials).
Table 4. Reaction of 4,8-dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 with S-nucleophiles.

<table>
<thead>
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<th>Entry</th>
<th>RSH (Equiv.)</th>
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<th>Base (Equiv.)</th>
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<th>Yield (%)</th>
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<td>-</td>
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<td>15a (8)*</td>
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<td>NaH (2)</td>
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<tr>
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<td>THF</td>
<td>NaH (2)</td>
<td>6</td>
<td>15b (78)</td>
</tr>
<tr>
<td>5</td>
<td>c (2)</td>
<td>THF</td>
<td>NaH (2)</td>
<td>6</td>
<td>15c (75)</td>
</tr>
</tbody>
</table>

* Dibromide 1 was isolated in 51–53% yields.

Dibromo derivative 1 proved to be sufficiently resistant to hydrolysis. Our study of the reaction of dibromide with various O-nucleophiles, such as alcohols (water, methanol, ethanol, n-butanol, tert-butanol, phenol) and corresponding alcohohalates, showed that 4,8-dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 did not react with them in both THF and DMF. The heating of the reaction mixtures also did not lead to the nucleophilic substitution of bromine atoms, and starting compound 1 was isolated in all cases.

2.3. Cross-Coupling Reactions of 4,8-Dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1

4,8-Dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 was investigated in palladium-catalyzed Suzuki–Miyaura and Stille coupling reactions in order to obtain mono- and bis-aryl(hetaryl)thiadiazolopyridazines. The mono-arylation of dibromo derivatives of strong electron-deficient heterocycles is the most challenging task, and requires special attention to achieve the best yields [15,19,25].

2.3.1. Suzuki–Miyaura Coupling

The behavior of 4,8-dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 in the palladium-catalyzed Suzuki–Miyaura reactions was investigated in order to find the best conditions for the preparation of mono- and bis-aryl derivatives. In the reaction of dibromo derivative 1 with thiophen-2-yl-pinacolate ester 16a and boronic acid 17a, the base, solvent, and reaction temperature were varied. The results of this study are summarized in Table 5. We have shown that the nature of the reagents, solvents, and the temperature of the reaction medium significantly affect the course of chemical transformations. The tetrakis(triphenylphosphine)palladium complex (Pd(PPh₃)₄) most widely used in these transformations was employed as a catalyst. It was shown that when the reaction with pinacolate ester 16a (1 eqv) was carried out at 110 °C in toluene for 24 h, the formation of the mono-coupling product 18a was observed in 72% yield (Table 6, entry 1). The presence of water to dissolve inorganic salts reduced the yield of product 18a to 50%, which is apparently associated to side reactions (Entry 2). We have shown that when using 2-thiopheneboronic acid 17a, the mono-coupling product 18a was isolated in almost the same yield (70%) as thiophen-2-pinacolate ester 16a (cf. entries 1, 3). Since the use of 2-thiopheneboronic acid 17a did not lead to an increase in the yield of the target product 18a, and also because to the lower stability of 2-thiopheneboronic acids 17, pinacolate esters of boronic acids 16 were employed in further studies. Carrying out the reaction in xylene at 130 °C with two eqv. of pinacolate ester 16a resulted in the bis-coupling product 19a with a
65% yield (Entry 4). The best conditions for the synthesis of mono-18a and bis-19a products were extended to other pinacolate esters 16b–h. In all cases, mono-coupling products 18b–h and bis-products 19b–h were selectively formed by refluxing the reaction mixtures in toluene with one equiv. 16 (18b–h) or in xylene with two equiv. 17 (19b–h) in moderate yields (50–72%) (Entries 5–18).

Table 5. Suzuki–Miyaura cross-coupling of 4,8-dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) 1 with pinacolate esters 16a–h and boronic acid 17a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>B(OR)2 (equiv)</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Yields (%)</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16a (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>72</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>16a (1)</td>
<td>toluene/H2O</td>
<td>110 °C, 20 h</td>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>17a (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>70</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>16a (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>16b (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>70</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>16b (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>63</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>16c (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>65</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>16c (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>16d (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>16d (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>16e (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>70</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>16e (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>16f (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>16f (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>55</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>16g (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>16g (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>16h (1)</td>
<td>toluene</td>
<td>110 °C, 18 h</td>
<td>72</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>16h (2)</td>
<td>xylene</td>
<td>130 °C, 24 h</td>
<td>0</td>
<td>67</td>
<td>0</td>
</tr>
</tbody>
</table>

Thus, it was found that the Suzuki reaction between 4,8-dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) 1 and pinacolate esters 16 requires the use of anhydrous solvents, and mono-18 and bis-19 coupling products can be selectively obtained by changing the reaction temperature (Supplementary Materials).

Table 6. Stille cross-coupling of 4,8-dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) 1 with aryl- and heteroaryl-tributylstannanes 20a.
2.3.2. Stille Coupling

We studied the Stille reaction of 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 with various aromatic and heteroaromatic stannyl derivatives 20a–h to synthesize both mono- and bis-coupling products. Optimal conditions were developed for the reaction with thienyltributyl stannate 20a in toluene in the presence of PdCl₂(PPh₃)₂ as the most widely used catalyst in these transformations. When refluxing in toluene, the reaction could not be stopped at the stage of the mono-aryl derivative’s formation, even when one equivalent of stannate 20a was used (Table 6, entry 1). By employing two equivalents of stannate 20a, the bis-coupling product 19a was isolated in high yields (Entry 2). Careful temperature control allowed us to find the best conditions for the synthesis of the mono-aryl derivative 18a by heating the reaction mixture at 60 °C for 16 h, although we could not avoid the formation of the bis-product in small amounts (Entry 3). An increase in the reaction temperature to 80 °C led to a decrease in the selectivity of the formation of the mono-coupling product 18a, and a decrease in the reaction to 40 °C led to a decrease in...
the yield of the product $18a$ (Entries 4,5). The conditions found for the formation of bis-$19a$ and mono-$18a$ adducts (Entries 2,3) were applied to other aryl(hetaryl) stannates $20$. As a result, a series of mono- $18a$–$h$ and bis-substitution products $19a$–$h$ were isolated in moderate to high yields (Entries 6–19).

Thus, we have shown that the Stille reactions, compared with the Suzuki reactions, proceeded faster and with similar yields, but less selectively in the case of the formation of mono-coupling products $18$.

3. Experimental Section

3.1. Materials and Reagents

The chemicals were purchased from commercial sources (Sigma-Aldrich, St. Louis, MO, USA) and used as received. Benzo[1,2-$d$:4,5-$d'$]bis(1,2,3)thiadiazole $2$ [27], 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane $16a$ [33], 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane $16b$ [34], 2-[(2,2'-bithiophen)-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane $16c$ [35], (4-diphenylamino)phenyl)boronic acid $17h$ [36], tributyl(4-hexyl-2-thienyl)stannane $20b$ [37], [2,2'-bithiophen]-5-yltributylstannane $20c$ [38], tributyl(5-(2-ethylhexyl)thiophen-2-yl)stannane $20d$ [39], tributyl(p-tolyl)stannane $20f$ [40], tributyl(4-methoxyphenyl)stannane $20g$ [40], and diphenyl-(4-tributylstannanyl-phenyl)-amine $20h$ [41] were prepared according to the published methods and characterized by NMR spectra. All synthetic operations were performed under a dry argon atmosphere. The solvents were purified by distillation over the appropriate drying agents.

3.2. Analytical Instruments

The melting points were determined on a Kofler hot-stage apparatus and were uncorrected. $1^H$ and $13^C$ NMR spectra were taken with a Bruker AM-300 machine (Bruker Ltd., Moscow, Russia) with TMS as the standard. $J$ values are given in Hz. MS spectra (EI, 70 eV) were obtained with a Finnigan MAT INCOS 50 instrument (Thermo Finnigan LLC, San Jose, CA, USA). High-resolution MS spectra were measured on a Bruker microTOF II instrument using electrospray ionization (ESI). IR spectra were measured with a Bruker “Alpha-T” instrument (Bruker, Billerica, MA, USA) in KBr pellets. The HOMO–LUMO energies were calculated using the Gaussian 16 Rev C.01 program M11 DFT functional with a 6-31+g(d) basis.

3.3. X-ray Analysis

X-ray diffraction data were collected at 100 K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless omega-scan technique), using graphite mono-chromatized Cu $K\alpha$-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program (Austin, TX, USA, accessed on 1 September 2022) [42]. The structure was solved by direct methods using SHELXT and refined on $F^2$ using SHELXL-2018 [43] in the OLEX2 program [44]. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. The Cambridge Crystallographic Data Centre holds the supplementary crystallographic data for this paper (Table 7), No. CCDC 2210625 (compound $1$). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, accessed on 1 September 2022 (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 7. Crystal data and structural refinement for compound $1$.
Formula weight 352.04
Temperature 100.00(10) K
Wavelength 0.71073 Å
Crystal system monoclinic
Space group P121/n1
Unit cell dimensions
\[a = 16.1779(4) \text{ Å}, \quad b = 3.88730(10) \text{ Å}, \quad c = 16.1804(4) \text{ Å}, \]
\[\alpha = 90^\circ, \quad \beta = 119.312(3)^\circ, \quad \gamma = 90^\circ. \]
Volume 887.28(4) Å³
Z 4
Density (calculated) 2.635 Mg/m³
Absorption coefficient 9.562 mm⁻¹
F(000) 664
Crystal size 0.56 × 0.3 × 0.2 mm³
Theta range for data collection 2.492 to 26.996°
Index ranges
\[-20 \leq h \leq 20, -4 \leq k \leq 4, -20 \leq l \leq 20. \]
Reflections collected 28,713
Independent reflections 1924 [R(int) = 0.0815]
Completeness to theta = 25.242° 99.9%
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.12670
Refinement method Full-matrix least-squares on F²
Data/restraints/parameters 1924/0/92

3.4. 4,8-. Dibromobenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (1)

Bromine (2.5 mL, 48.55 mmol) was added dropwise to a solution of compound 2 (650 mg, 3.35 mmol) in HBr (18 mL) at 80 °C. The reaction mixture was stirred for 18 h at 120 °C, cooled to room temperature, poured onto ice, washed with NaHSO₃, extracted with EtOAc and dried over MgSO₄. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel Merck 60, CH₂Cl₂) to give the title compound 1. Yield 471 mg (40%), yellow solid. Eluent—CH₂Cl₂/hexane, 1:2 (v/v). Mp > 250 °C. (Rf = 0.3, CH₂Cl₂). IR νmax (KBr, cm⁻¹): 2925, 2853, 1300, 1287, 1191, 1160, 1082, 968, 890, 811, 547, 511. ¹³C NMR (75 MHz, CDCl₃): δ 153.3, 143.4, 105.0. HRMS (ESI-MS), m/z: calcld for C₆H₇Br₂N₄S₂ [M+Ag]+, 456.6977, found, 456.6977. MS, m/z (%): 353 ([M+1]+, 60), 352 (M+, 80), 351 ([M−1]+, 58), 296 (100), 217 (62), 173 (70), 149 (85), 136 (68), 92 (86), 68 (75), 44 (10), 28 (5).

3.5. General Procedure for the Preparation of Mono-Aminated Products 12a–c

Amine 14a–c (0.29 mmol) was added to a solution of 4,8-dibromobenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole 1 (50 mg, 0.14 mmol) in dry MeCN (10 mL) at room temperature and the mixture was stirred at reflux for 18 h, poured into water (20 mL) and extracted with CH₂Cl₂ (3 × 35 mL). The combined organic layers were washed with brine, dried over
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3.5.1. 4-(8-Bromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole)-4-yl)morpholine (12a)

Orange solid, 39 mg (78%), eluent—CH2Cl2/hexane, 2:1 (v/v). Rf = 0.1 (CH2Cl2/hexane, 1:1, (v/v)). Mp = 150–153 °C. IR νmax (KBr, cm−1): 2960, 2920, 2857, 1640, 1531, 1458, 1432, 1376, 1361, 1313, 1277, 1249, 1187, 1113, 1029, 984, 874, 815, 631, 511. 1H NMR (300 MHz, CDCl3): δ 4.04–4.01 (m, 4H), 3.99–3.95 (m, 4H). 13C NMR (75 MHz, CDCl3): δ 157.5, 148.4, 145.9, 138.9, 131.2, 94.7, 67.4, 52.3. HRMS (ESI-TOF), m/z: calcd for C24H19BrN2O4S2: [M + H]+, 537.9426, found, 537.9417. MS (EI, 70 eV), m/z (I, %): 359 ([M+1]+, 12), 358 ([M]+, 11), 331 (14), 245 (30), 149 (31), 43 (35), 28 (100).

3.5.2. 4-Bromo-8-(piperidin-1-yl)benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole (12b)

Orange solid, 37 mg (75%), eluent—CH2Cl2/hexane, 1:1 (v/v). Rf = 0.4 (CH2Cl2/hexane, 1:1, (v/v)). Mp = 143–145 °C. IR νmax (KBr, cm−1): 2936, 2864, 1641, 1531, 1442, 1376, 1344, 1315, 1264, 1238, 1188, 1153, 1099, 1019, 979, 890, 865, 847, 817, 603, 539. 1H NMR (300 MHz, CDCl3): δ 3.97–3.94 (m, 4H), 1.94–1.84 (m, 6H). 13C NMR (75 MHz, CDCl3): δ 157.5, 148.1, 145.9, 140.0, 131.0, 92.57, 53.5, 26.8, 24.4. HRMS (ESI-TOF), m/z: calcd for C19H18BrN2O4S2: [M+H]+, 354.9556, found, 354.9563. MS (EI, 70 eV), m/z (I, %): 357 ([M+1]+, 5), 356 ([M]+, 4), 329 (27), 317 (24), 212 (80), 105 (78), 77 (45), 55 (40), 41 (100), 28 (78).

3.5.3. 4-Benzyl-8-(pyrrolidin-1-yl)benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole (12c)

Orange solid, 36 mg (77%), eluent—CH2Cl2/hexane, 1:2 (v/v). Rf = 0.3 (CH2Cl2/hexane, 1:1, (v/v)). Mp = 153–155 °C. IR νmax (KBr, cm−1): 2955, 2921, 1854, 1638, 1540, 1447, 1373, 1354, 1323, 1303, 1260, 1236, 1177, 1119, 991, 893, 870, 816, 739, 667, 515. 1H NMR (300 MHz, CDCl3): δ 4.30 (t, J = 6.5, 4H), 2.23–2.19 (m, 4H). 13C NMR (75 MHz, CDCl3): δ 157.6, 146.6, 144.7, 138.3, 127.1, 87.0, 53.8, 29.8. HRMS (ESI-TOF), m/z: calcd for C21H19BrN2O4S2: [M+1]+, 341.9477, found, 341.9475. MS (EI, 70 eV), m/z (I, %): 344 ([M+2]+, 3), 343 ([M+1]+, 50), 342 ([M]+, 4), 341 ([M]+, 46), 315 (55), 285 (25), 256 (23), 206 (40), 191 (35), 178 (37), 149 (86), 96 (48), 69 (50), 57 (100), 41 (95), 27 (47), 18 (84).

3.6. General Procedure for the Preparation of Mono-Aminated Products 12d,e

Aniline 14d,14e (27 mg, 0.29 mmol) was added to a solution of 4,8-dibromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 2 (50 mg, 0.14 mmol) in dry DMF (10 mL), and the mixture was stirred at 100–130 °C for 18 h, poured into water and extracted with CH2Cl2 (3 × 35 mL). The combined organic layers were washed with water and brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel Merck 60).

3.6.1. 4-Bromo-8-(2,3,3a,8b-tetrahydrocyclopenta[b]indol-4(1H)-yl)benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole (12d)

Violet solid, yield 36 mg (60%), eluent—CH2Cl2/hexane, 1:2 (v/v). Rf = 0.4 (CH2Cl2/hexane, 1:1 (v/v)). Mp = 178–180 °C. IR νmax (KBr, cm−1): 2957, 2924, 2853, 1597, 1523, 1480, 1444, 1366, 1306, 1259, 1187, 1080, 1023, 968, 881, 813, 749, 695, 535, 523. 1H NMR (300 MHz, CDCl3): δ 7.32–7.26 (m, 2H), 7.11 (t, J = 7.7, 1H), 6.99 (t, J = 7.4, 1H), 6.36–6.30 (m, 1H), 4.03–3.97 (m, 1H), 2.12–1.94 (m, 2H), 1.74–1.45 (m, 4H). 13C NMR (75 MHz, CDCl3): δ 157.7, 150.5, 145.3, 144.5, 136.4, 126.8, 125.6, 124.5, 124.1, 122.2, 111.0, 97.6, 72.8, 46.8, 35.2, 33.7, 24.8. HRMS (ESI-TOF), m/z: calcd for C26H20BrN2O4S2: [M]+, 428.9712, found, 428.9708. MS (EI, 70 eV), m/z (I, %): 432 ([M+2]+, 4), 431 ([M+1]+, 39), 430 ([M]+, 3), 429 ([M]+, 41), 403 (58), 375 (26), 346 (53), 147 (30), 115 (28), 67 (50), 57 (47), 41 (100), 27 (80).

3.6.2. 8-Bromo-N-phenylbenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole-4-amine (12e)
Red solid, yield 50 mg (55%), eluent—CH₂Cl₂/hexane, 1:1 (v/v). Rf = 0.3 (CH₂Cl₂/hexane, 1:1 (v/v)). Mp = 157–160 °C. IR ʋmax (KBr, cm⁻¹): 2958, 2924, 2853, 1729, 1495, 1465, 1450, 1425, 1323, 1287, 1262, 1099, 1078, 1022, 967, 868, 810, 743, 717, 696, 533. ¹H NMR (300 MHz, CDCl₃): δ 8.28 (s, 1H), 7.56–7.50 (m, 3H), 7.32 (dd, ʋ = 7.5, 1.5, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 158.3, 144.8, 144.4, 136.6, 134.1, 129.8, 128.2, 127.0, 123.4, 91.3. HRMS (ESI-TOF), m/z: calcd for C₁₂H₇CLN₅S₂ [M + H]+, 363.9321, found, 363.9321. MS (EI, 70 eV), m/z (%): 364 ([M]+, 4), 363 ([M-1]+, 3), 337 (20), 228 (40), 184 (45), 149 (20), 125 (35), 77 (98), 51 (100), 28 (23).

3.7. General Procedure for the Preparation of Bis-Aminated Products 13a,b

Amine 14 (0.84 mmol) was added to a solution of 4,8-dibromobenzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) 1 (50 mg, 0.14 mmol) in dry DMF (10 mL) at room temperature and the mixture was stirred at 130 °C for 24 h, poured into water (20 mL) and extracted with CH₂Cl₂ (3 × 35 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel Merck 60).

3.7.1. 4,8-Dimorpholinobenzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) (13a)

Red solid, 20 mg (40%), eluent—CH₂Cl₂. Rf = 0.1 (CH₂Cl₂). Mp > 250 °C. IR ʋmax (KBr, cm⁻¹): 2968, 2947, 2918, 2849, 1827, 1637, 1539, 1480, 1442, 1371, 1327, 1298, 1272, 1251, 1108, 1068, 992, 922, 887, 824, 632, 514. ¹H NMR (300 MHz, CDCl₃): δ 4.01–3.98 (m, 8H), 3.77–3.74 (m, 8H). ¹³C NMR (75 MHz, CDCl₃): δ 153.0, 135.7, 133.2, 67.7, 52.6. HRMS (ESI-TOF), m/z: calcd for C₁₄H₁₆N₆O₂S₂ [M]+, 364.0771, found, 364.0769. MS (EI, 70 eV), m/z (%): 364 ([M]+, 12), 192 (20), 45 (21), 28 (100).

3.7.2. 4,8-Di(piperidin-1-yl)benzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) (13b)

Red solid, 20 mg (50%), eluent—CH₂Cl₂/hexane, 1:2 (v/v). Rf = 0.6 (CH₂Cl₂:hexane, 1:1 (v/v)). Mp = 158–160 °C. IR ʋmax (KBr, cm⁻¹): 2928, 2847, 2804, 1637, 1479, 1446, 1372, 1327, 1313, 1268, 1241, 1202, 1112, 1072, 1056, 980, 855, 823, 737, 701, 614, 515. ¹H NMR (300 MHz, CDCl₃): δ 3.68–3.64 (m, 8H), 1.87–1.73 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 153.0, 135.8, 134.0, 53.7, 27.0, 24.5. HRMS (ESI-TOF), m/z: calcd for C₁₆H₂₀N₆S₂ [M]+, 360.1185, found, 360.1183. MS (EI, 70 eV), m/z (%): 360 ([M]+, 20), 303 (21), 275 (14), 247 (19), 219 (22), 192 (15), 96 (35), 55 (40), 41 (100), 29 (20).

3.8. General Procedure for the Reaction of 4,8-Dibromobenzo[1,2-d:4,5-d']Bis([1,2,3]Thiadiazole) 1 with Thiols

Sodium hydride (6 mg, 0.28 mmol) was added to a solution of thiol (0.28 mmol) in dry THF (15 mL) at 0 °C with stirring. The reaction mixture was stirred at 0 °C for 30 min, then 4,8-dibromobenzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) 1 (50 mg, 0.14 mmol) was added. The mixture was stirred for 6 h at room temperature. On completion (monitored by TLC), the mixture was poured into water (20 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

3.8.1. 4,8-Bis(phenylthio)benzo[1,2-d:4,5-d']bis([1,2,3]thiadiazole) (15a)

Orange solid, 45 mg (80%), Mp = 168–172 °C, eluent—CH₂Cl₂/hexane, 1:2 (v/v). Rf = 0.4 (CH₂Cl₂/hexane, 1:1 (v/v)). IR ʋmax (KBr, cm⁻¹): 1574, 1492, 1468, 1438, 1397, 1371, 1310, 1265, 1231, 1155, 1065, 1020, 1000, 907, 815, 748, 688, 566, 500. ¹H NMR (300 MHz, CDCl₃): δ 7.66–7.58 (m, 4H), 7.54–7.40 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 156.3, 141.4, 135.7, 135.0, 130.2, 130.0, 123.8. HRMS (ESI-TOF), m/z: calcd for C₁₈H₁₁N₄S₄ [M + H]+, 410.9861, found, 410.9849. MS (EI, 70 eV), m/z (%): 410 ([M]+, 100), 320 (80), 290 (35), 277 (37), 201 (15), 177 (16), 169 (13), 136 (13), 77 (50), 51 (15).
3.8.2. 4,8-Bis(hexylthio)benzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) (15b)

Yellow solid, 46 mg (78%), eluent—CH₂Cl₂/hexane, 1:4 (v/v). Rᵣ = 0.7 (CH₂Cl₂/hexane, 1:1 (v/v)). Mp = 78–80 °C. IR νmax (KBr, cm⁻¹): 2957, 2924, 2853, 1637, 1461, 1412, 1375, 1315, 1280, 1239, 1179, 906, 811, 723, 515. ¹H NMR (300 MHz, CDCl₃): δ 3.62 (t, J = 7.4, 4H), 1.66 (p, J = 7.3, 4H), 1.48–1.39 (m, 4H), 1.27–1.21 (m, 8H), 0.84 (t, J = 7.0, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 155.7, 145.3, 122.5, 36.9, 31.2, 30.0, 28.2, 22.4, 13.9. HRMS (ESI-TOF), m/z: calcd for C₁₈H₂₇N₄S₄ [M + H]+, 427.1113, found, 427.1108. MS (EI, 70 eV), m/z (I, %): 426 ([M]+, 4), 314 (M⁺, 3), 215 (4), 136 (5), 101 (7), 55 (25), 43 (100), 29 (95).

3.8.3. 4,8-Bis(dodecylthio)benzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) (15c)

Yellow solid, 46 mg (78%), eluent—CH₂Cl₂/hexane, 1:2 (v/v). Rᵣ = 0.9 (CH₂Cl₂). Mp = 78–80 °C. IR νmax (KBr, cm⁻¹): 2955, 2922, 2851, 1642, 1469, 1414, 1375, 1312, 1262, 1238, 1177, 1084, 1026, 903, 806, 719, 517. ¹H NMR (300 MHz, CDCl₃): δ 3.62 (t, J = 7.3, 4H), 1.65 (p, J = 7.3, 4H), 1.47–1.38 (m, 4H), 1.32–1.21 (m, 32H), 0.87 (t, J = 6.6, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 155.7, 145.3, 122.5, 36.9, 31.9, 30.0, 29.7, 29.6, 29.58, 29.51, 29.4, 29.0, 28.5, 22.7, 14.1. HRMS (ESI-TOF), m/z: calcd for C₃₀H₅₀N₄S₄Ag [M]+, 701.1964, found, 701.1954. MS (EI, 70 eV), m/z (I, %): 595 ([M]+, 12), 215 (8), 97 (3), 83 (5), 69 (18), 57 (50), 43 (100), 29 (35).

3.9. General Procedure for the Preparation of Mono-Substituted Products 18 under Suzuki Coupling Conditions (Procedure A)

A mixture of 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 (50 mg, 0.14 mmol), boronic ether 16a–h or its acid 17a (0.14 mmol), K₂CO₃ (19 mg, 0.14 mmol), and Pd(PPh₃)₄ (24 mg, 15% mmol) in dry toluene (8 mL) was degassed by argon and heated at 110 °C in a sealed vial. On completion (monitored by TLC), the mixture was poured into water and extracted with CH₂Cl₂ (3 × 35 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

3.10. General Procedure for the Preparation of Bis-Substituted Products 19 under Suzuki Coupling Conditions (Procedure B)

A mixture of 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 (50 mg, 0.14 mmol), boronic ether 16a–h or its acid 17a (0.28 mmol), K₂CO₃ (38 mg, 0.28 mmol), and Pd(PPh₃)₄ (24 mg, 15% mmol) in dry xylene (8 mL) was degassed by argon and heated at 130 °C in a sealed vial. On completion (monitored by TLC), the mixture was poured into water and extracted with CH₂Cl₂ (3 × 35 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

3.11. General Procedure for the Preparation of Mono-Substituted Products 18 under Stille Coupling Conditions (Procedure C)

PdCl₂(PPh₃)₂ (14 mg, 15% mmol) and stannane 20a–h (0.14 mmol) were added to a solution of 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 (50 mg, 0.14 mmol) in anhydrous toluene (4 mL). The resulting cloudy yellow mixture was stirred and degassed by argon in a sealed vial. The resulting yellow mixture was then stirred at 60 °C for the desired time. On completion (monitored by TLC), the mixture was washed with water and the organic layer was extracted with CH₂Cl₂ (3 × 35 mL). The combined organic layers were washed with brine, dried over MgSO₄ and then concentrated in vacuo. The products were isolated by column chromatography.

3.12. General Procedure for the Preparation of Bis-Substituted Products 19 under Stille Coupling Conditions (Procedure D)

PdCl₂(PPh₃)₂ (14 mg, 15% mmol) and stannane 20a–h (0.28 mmol) were added to a solution of 4,8-dibromobenzo[1,2-d:4,5-d’]bis([1,2,3]thiadiazole) 1 (50 mg, 0.14 mmol) in anhydrous toluene (4 mL). The resulting cloudy yellow mixture was stirred and degassed...
by argon in a sealed vial. The resulting yellow mixture was then stirred at 110 °C for the desired time. On completion (monitored by TLC), the mixture was washed with water and the organic layer was extracted with CH₂Cl₂ (3 × 35 mL), dried over MgSO₄ and then concentrated in vacuo. The products were isolated by column chromatography.

### 3.12.1. 4-Bromo-8-(thiophen-2-yl)benzo[1,2-d:4,5-d′]bis[1,2,3]thiadiazole (18a)

Yellow solid, 35 mg (72%, procedure A) or 34 mg (70%, procedure C), eluent—CH₂Cl₂:hexane, 1:1 (v/v). Rₜ = 0.4 (CH₂Cl₂). Mp = 198–200 °C. IR ʋmax (KBr, cm⁻¹): 1738, 1641, 1494, 1464, 1413, 1262, 1186, 1081, 1023, 809, 701, 544. ¹H NMR (300 MHz, CDCl₃): δ 8.20 (d, J = 3.9, 1H), 7.76 (d, J = 5.2, 1H), 7.36 (t, J = 4.5, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 156.1, 152.2, 139.2, 139.1, 137.0, 131.7, 128.8, 122.4, 104.4. HRMS (ESI-TOF), m/z: calc for C₁₀H₄₇⁹BrN₄S₃ [M + H]+: 354.8776, found, 354.8772.

### 3.12.2. 4-Bromo-8-(4-hexylthiophen-2-yl)benzo[1,2-d:4,5-d′]bis[1,2,3]thiadiazole (18b)

Yellow solid, 43 mg (70%, procedure A) or 44 mg (73%, procedure C), eluent—CH₂Cl₂:hexane, 1:2 (v/v). Rₜ = 0.6 (CH₂Cl₂:hexane, 1:1). Mp = 67–69 °C. IR ʋmax (KBr, cm⁻¹): 2954, 2924, 2852, 1642, 1449, 1397, 1371, 1327, 1306, 1263, 1237, 1109, 1089, 892, 812, 727, 581, 537. ¹H NMR (300 MHz, CDCl₃): δ 8.09 (s, 1H), 7.35 (s, 1H), 2.76 (t, J = 7.7, 2H), 1.73 (p, J = 7.2, 2H), 1.42–1.31 (m, 6H), 0.91 (t, J = 6.9, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 155.9, 152.0, 145.4, 144.7, 138.8, 136.4, 133.3, 125.6, 122.5, 103.8, 31.6, 30.5, 30.4, 28.9, 22.6, 14.1. HRMS (ESI-TOF), m/z: calc for C₁₄H₆₇⁹BrN₄S₄ [M + H]+: 343.9715, found, 343.9730.

### 3.12.3. 4-[[2,2'-Bithiophen]-5-yl]-8-bromobenzol[1,2-d:4,5-d′]bis[1,2,3]thiadiazole (18c)

Red solid, 39 mg (65%, procedure A) or 41 mg (67%, procedure C), eluent—CH₂Cl₂:hexane, 1:1 (v/v). Rₜ = 0.4 (CH₂Cl₂:hexane, 1:1 (v/v)). Mp = 130–132 °C. IR ʋmax (KBr, cm⁻¹): 1639, 1445, 1423, 1375, 1308, 1268, 1123, 892, 812, 689, 537. ¹H NMR (300 MHz, CDCl₃): δ 8.09 (d, J = 4.0, 1H), 7.40–7.34 (m, 3H), 7.14–7.07 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 156.3, 151.9, 144.9, 143.5, 138.4, 136.2, 135.2, 132.6, 128.4, 126.3, 125.4, 125.0, 122.0, 103.9. HRMS (ESI-TOF), m/z: calc for C₁₄H₆₇⁹BrN₄S₄ [M + H]+: 436.8653, found, 436.8642.

### 3.12.4. 4-Bromo-8-(5-(2-ethylhexylthiophen-2-yl)benzo[1,2-d:4,5-d′]bis[1,2,3]thiadiazole (18d)

Yellow solid, 44 mg (68%, procedure A) or 45 mg (69%, procedure C), eluent—CH₂Cl₂:hexane, 1:1 (v/v). Rₜ = 0.6 (CH₂Cl₂). Mp = 57–60 °C. IR ʋmax (KBr, cm⁻¹): 2955, 2922, 2853, 1639, 1455, 1421, 1376, 1307, 1266, 1213, 1104, 892, 813, 544. ¹H NMR (300 MHz, CDCl₃): δ 8.06 (d, J = 3.8, 1H), 7.01 (d, J = 3.8, 1H), 2.90 (d, J = 6.8, 2H), 1.77–1.69 (m, 1H), 1.45–1.31 (m, 8H), 0.97–0.89 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 156.0, 151.8, 151.6, 144.7, 138.3, 134.4, 131.8, 126.9, 122.7, 103.1, 41.5, 34.4, 32.4, 29.7, 25.6, 23.0, 14.1. HRMS (ESI-TOF), m/z: calc for C₂₄H₆₇⁹BrN₄S₄ [M + H]+: 476.0028, found, 476.0019. MS (EI, 70 eV), m/z (l, %): 470 ([M+2]+, 1), 469 ([M+1]+, 2), 468 ([M]+, 11), 467 ([M−1]+, 2), 466 ([M−2]+, 9), 440 (6), 369 (3), 341 (5), 326 (4), 232 (5), 188 (10), 105 (30), 83 (35), 71 (60), 57 (100), 43 (95), 29 (15).

### 3.12.5. 4-Bromo-8-phenylbenzo[1,2-d:4,5-d′]bis[1,2,3]thiadiazole (18e)

Yellow solid, 34 mg (70%, procedure A) or 32 mg (67%, procedure C), eluent—CH₂Cl₂:hexane, 1:1 (v/v). Rₜ = 0.4 (CH₂Cl₂). Mp = 163–165 °C. IR ʋmax (KBr, cm⁻¹): 1725, 1445, 1398, 1371, 1343, 1316, 1275, 1211, 1188, 1155, 1078, 1025, 924, 898, 823, 766, 698, 538. ¹H
NMR (300 MHz, CDCl3): δ 7.97−7.93 (m, 2H), 7.68−7.61 (m, 3H). 13C NMR (75 MHz, CDCl3): δ 155.8, 153.9, 144.6, 141.6, 136.3, 130.5, 129.5, 129.4, 128.9, 105.3. HRMS (ESI-TOF), m/z: calcd for C24H14I2N5S2 [M + H]+, 514.9874. MS (EI, 70 eV), m/z (I, %): 363 ([M]+, 3), 362 ([M−1]+, 1), 361 ([M−2]+, 5), 360 ([M−3]+, 5), 359 ([M−4]+, 2), 318 (98), 303 (15), 285 (16), 159 (98), 115 (97), 93 (50), 69 (85), 57 (100), 43 (96).

3.12.6. 4-Bromo-8-(p-toly1)benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (18f)

Yellow solid, 34 mg (67%, procedure A) or 35 mg (68%, procedure C), eluent—CH2Cl2:hexane, 1:1 (v/v), Rr = 0.5 (CH2Cl2). Mp = 135−137 °C. IR νmax (KBr, cm−1): 2958, 2924, 2854, 1729, 1493, 1461, 1401, 1385, 1283, 1187, 1081, 1023, 969, 894, 812, 723, 491. 1H NMR (300 MHz, CDCl3): δ 7.90 (d, J = 7.9, 2H), 7.46 (d, J = 7.9, 2H), 2.52 (s, 3H). 13C NMR (75 MHz, CDCl3): δ 155.8, 153.8, 147.2, 144.6, 141.0, 133.4, 130.2, 129.4, 128.1, 104.8, 21.6. HRMS (ESI-TOF), m/z: calcd for C24H19BrN5Si [M + H]+, 362.9368, found, 362.9370. MS (EI, 70 eV), m/z (I, %): 363 ([M]+, 3), 362 ([M−1]+, 1), 361 ([M−2]+, 5), 360 ([M−3]+, 5), 359 ([M−4]+, 2), 318 (98), 303 (15), 285 (16), 159 (98), 115 (97), 93 (50), 69 (85), 57 (100), 43 (96).

3.12.7. 4-Bromo-8-(4-methoxyphenyl)benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (18g)

Yellow solid, 32 mg (60%, procedure A) or 26 mg (50%, procedure C), eluent—CH2Cl2:hexane, 1:1 (v/v), Rr = 0.2 (CH2Cl2). Mp = 125−127 °C. IR νmax (KBr, cm−1): 2957, 2925, 2854, 1641, 1609, 1460, 1429, 1376, 1301, 1264, 1179, 1081, 1029, 967, 885, 829, 815, 702, 614, 534. 1H NMR (300 MHz, CDCl3): δ 7.92 (d, J = 8.7, 2H), 7.16 (d, J = 8.7, 2H), 3.94 (s, 3H). 13C NMR (75 MHz, CDCl3): δ 161.3, 155.8, 153.8, 146.4, 141.3, 131.1, 128.9, 128.5, 114.9, 104.3, 55.6. HRMS (ESI-TOF), m/z: calcd for C25H18BrN5O2 [M + H]+, 378.9317, found, 378.9314. MS (EI, 70 eV), m/z (I, %): 380 ([M]+, 7), 379 ([M]+, 5), 350 (20), 271 (80), 199 (90), 175 (100), 132 (55), 28 (9).

3.12.8. 4-(8-Bromobenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole)-4-yl)-N,N-diphenylaniline (18h)

Red solid, 52 mg (72%, procedure A) or 46 mg (64%, procedure C), eluent—CH2Cl2:hexane, 1:2 (v/v), Rr = 0.5 (CH2Cl2:hexane, 1:1 (v/v)). Mp = 165−168 °C. IR νmax (KBr, cm−1): 1588, 1468, 1432, 1331, 1315, 1274, 1193, 1075, 1026, 814, 753, 695, 618, 512. 1H NMR (300 MHz, CDCl3): δ 7.83 (d, J = 8.7, 2H), 7.35 (t, J = 7.7, 4H), 7.24−7.08 (m, 8H). 13C NMR (75 MHz, CDCl3): δ 155.9, 153.7, 153.7, 146.8, 144.7, 141.0, 130.6, 129.1, 128.1, 125.4, 124.5, 121.4, 103.8. HRMS (ESI-TOF), m/z: calcd for C25H18BrN5O2 [M + H]+, 514.9869, found, 514.9874. MS (EI, 70 eV), m/z (I, %): 159 ([M]+, 5), 158 ([M]+, 10), 517 ([M]+, 75), 516 ([M]+, 11), 515 ([M]+, 70), 489 (8), 459 (6), 408 (50), 380 (35), 336 (100), 312 (65), 167 (12), 149 (15), 77 (20), 51 (11).

3.12.9. 4,8-Di(thiophen-2-yl)benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (19a)

Red solid, 32 mg (65%, procedure B) or 33 mg (67%, procedure D), eluent—CH2Cl2:hexane, 1:2 (v/v), Rr = 0.5 (CH2Cl2:hexane, 1:1 (v/v)). Mp > 250 °C. IR νmax (KBr, cm−1): 1637, 1513, 1442, 1412, 1376, 1341, 1315, 1267, 1064, 819, 797, 700, 549. 1H NMR (300 MHz, CDCl3): δ 8.20 (dd, J = 3.8, 1.2, 2H), 7.74 (dd, J = 5.1, 1.2, 2H), 7.37 (dd, J = 5.1, 3.8, 2H). 13C NMR (75 MHz, CDCl3): δ 154.1, 139.6, 137.7, 131.1, 130.2, 128.4, 120.2. HRMS (ESI-TOF), m/z: calcd for C19H18N2O2 [M + H]+, 358.9548, found, 358.9544. MS (EI, 70 eV), m/z (I, %): 360 ([M]+, 21), 359 ([M]+, 22), 358 ([M]+, 96), 330 (45), 302 (98), 270 (30), 226 (28), 151 (50), 69 (48), 57 (85), 43 (100), 29 (99), 17 (98).

3.12.10. 4,8-Bis(4-hexylthiophen-2-yl)benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (19b)

Red solid, 46 mg (63%, procedure B) or 47 mg (57%, procedure D), eluent—CH2Cl2:hexane, 1:3 (v/v), Rr = 0.7 (CH2Cl2:hexane, 1:1 (v/v)). Mp = 134−136 °C. IR νmax (KBr, cm−1): 2961, 2928, 2851, 1645, 1461, 1180, 1071, 925, 761, 555, 459. 1H NMR (300 MHz, CDCl3): δ 8.09 (d, J = 1.3, 2H), 7.32 (d, J = 1.3, 2H), 2.77 (t, J = 7.7, 4H), 1.75 (p, J = 7.6, 4H),
1.45–1.33 (m, 12H), 0.94–0.89 (m, 6H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) 154.0, 145.0, 139.4, 137.4, 132.7, 125.0, 120.8, 31.6, 30.5, 30.4, 29.0, 22.6, 14.1. HRMS (ESI-TOF), \(m/z\): calcld for C\(_{22}\)H\(_{11}\)N\(_4\)S\(_6\) [M+H]+, 528.9927, found, 528.9925. MS (EI, 70 eV), \(m/z\) (I, %): 528 ([M+2]+, 98), 527 ([M]+, 100), 466 (90), 434 (35), 421 (32), 389 (30), 233 (80), 201 (50), 177 (45), 127 (30), 18 (60).

3.12.12. 4,8-Bis(5-(2-ethylhexyl)thien-2-yl)benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (19d)

Red solid, 55 mg (68%, procedure B) or 58 mg (72%, procedure D), eluent—CHCl\(_3\):hexane, 1:2 (v/v). \(R_t\) = 0.5 (CHCl\(_3\):hexane, 1:1 (v/v)). Mp > 250 °C. IR \(v_{\text{max}}\) (KBr, cm\(^{-1}\)): 1728, 1632, 1504, 1456, 1373, 1319, 1276, 1225, 1165, 1122, 1093, 1052, 824, 783, 701, 643, 548, 485. \(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.07 (d, \(J = 3.2\) Hz, 2H), 7.39 (d, \(J = 3.2\) Hz, 3H), 7.37 (d, \(J = 5.1\) Hz, 2H), 7.12–7.09 (m, 3H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) 132.1, 129.8, 125.8, 125.0, 114.2, 109.3, 105.2, 98.2, 97.1, 87.6, 81.6, 80.0, 77.8, 70.1, 63.9, 54.5, 50.8. HRMS (ESI-TOF), \(m/z\): calcld for C\(_{22}\)H\(_{11}\)N\(_4\)S\(_6\) [M+H]+, 528.9927, 528.0205, found, 528.0204. MS (EI, 70 eV), \(m/z\) (I, %): 528 ([M+2]+, 4), 583 ([M]+, 6), 582 ([M]+, 27), 525 (2), 497 (3), 483 (6), 427 (8), 343 (6), 328 (7), 252 (4), 177 (12), 164 (8), 121 (6), 57 (100), 41 (97), 29 (60).

3.12.13. 4,8-Diphenylbenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (19e)

Yellow solid, 24 mg (50%, procedure B) or 31 mg (65%, procedure D), eluent—CHCl\(_3\):hexane, 1:4 (v/v). \(R_t\) = 0.7 (CHCl\(_3\):hexane). Mp > 250 °C. IR \(v_{\text{max}}\) (KBr, cm\(^{-1}\)): 2957, 2924, 2855, 1664, 1376, 1313, 1272, 1245, 1139, 1088, 1013, 871, 816, 782, 703, 642, 545, 508. \(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.01 (d, \(J = 3.8\) Hz, 2H), 7.00 (d, \(J = 3.8\) Hz, 2H), 2.90 (d, \(J = 6.8\) Hz, 4H), 1.73 (p, \(J = 5.8\), 2H), 14.6–1.30 (m, 16H), 0.94–0.90 (m, 2H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) 153.7, 150.5, 138.6, 135.3, 131.1, 126.8, 120.3, 41.5, 34.4, 32.5, 28.9, 25.7, 23.0, 14.2, 10.9. HRMS (ESI-TOF), \(m/z\): calcld for C\(_{32}\)H\(_{25}\)N\(_6\)S\(_6\) [M+H]+, 583.0205, found, 583.0204. MS (EI, 70 eV), \(m/z\) (I, %): 584 ([M+2]+, 4), 583 ([M]+, 6), 582 ([M]+, 27), 525 (2), 497 (3), 483 (6), 427 (8), 343 (6), 328 (7), 252 (4), 177 (12), 164 (8), 121 (6), 57 (100), 41 (97), 29 (60).

3.12.14. 4,8-Di-p-tolylbenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (19f)

Yellow solid, 28 mg (55%, procedure B) or 34 mg (65%, procedure D), eluent—CHCl\(_3\):hexane, 1:2 (v/v). \(R_t\) = 0.4 (CHCl\(_3\):hexane, 1:1 (v/v)). Mp > 250 °C. IR \(v_{\text{max}}\) (KBr, cm\(^{-1}\)): 1572, 1491, 1445, 1374, 1317, 1275, 1210, 1186, 1153, 1077, 1024, 978, 923, 898, 832, 766, 743, 696, 643, 539, 476. \(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.90 (d, \(J = 7.9\) Hz, 4H), 7.39 (d, \(J = 7.9\) Hz, 4H), 2.52 (s, 6H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) 155.5, 141.7, 140.4, 134.3, 130.0, 129.6, 127.9, 21.6. HRMS (ESI-TOF), \(m/z\): calcld for C\(_{32}\)H\(_{25}\)N\(_6\)S\(_6\) [M+H]+, 384.0474, found, 384.0473. MS (EI, 70 eV), \(m/z\) (I, %): 374 ([M]+, 8), 318 (70), 303 (5), 285 (3), 159 (100), 115 (97), 93 (25), 63 (14), 39 (30).

3.12.15. 4,8-Bis(4-methoxyphenyl)benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole (19g)

Orange solid, 32 mg (60%, procedure B) or 26 mg (50%, procedure D), eluent—CHCl\(_3\):hexane, 1:1 (v/v). \(R_t\) = 0.2 (CHCl\(_3\):hexane, 1:1 (v/v)). Mp > 250 °C. IR \(v_{\text{max}}\) (KBr, cm\(^{-1}\)): 1605, 1519, 1450, 1371, 1316, 1302, 1282, 1256, 1178, 1026, 816, 718, 546, 515. \(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 8.3\) Hz, 4H), 7.17 (d, \(J = 8.3\) Hz, 4H), 3.95 (s, 6H). HRMS (ESI-TOF),
m/z: calcd for C_{20}H_{15}N_4O_2S_2 [M + H]^+, 407.0631, found, 407.0626. MS (EI, 70 eV), m/z (I, %): 407 ([M+1]^+, 1), 406 ([M]^+, 10), 335 (100), 307 (25), 265 (8), 175 (20), 160 (21), 132 (98), 93 (6), 15 (70).

3.12.16. 4,4′-(Benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole)-4,8-diyl)bis(N,N-diphenylaniline) (19h)

Red solid, 63 mg (67%, procedure B) or 65 mg (69%, procedure D), eluent—CH_2Cl_2:hexane, 1:2 (v/v). Rf = 0.5 (CH_2Cl_2:hexane, 1:1(v/v)). Mp > 250 °C. IR ν max (KBr, cm⁻¹): 1587, 1514, 1489, 1444, 1329, 1315, 1277, 1192, 1176, 841, 817, 753, 734, 695, 653, 620, 509. ^1H NMR (300 MHz, CDCl₃): δ 7.85 (d, J = 8.2, 4H), 7.35–7.30 (m, 8H), 7.24–7.08 (m, 16H). ^13C NMR (75 MHz, CDCl₃): δ 155.4, 149.4, 147.0, 141.2, 130.5, 129.6, 129.5, 127.0, 124.0, 121.6. HRMS (ESI-TOF), m/z: calcd for C_{42}H_{29}N_6S_2 [M+H]^+, 681.1890, found, 681.1901.

4. Conclusions

4,8-Dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) was successfully prepared in a moderate yield by the heating of a parent heterocycle with bromine in hydrobromic acid. Its structure was finally confirmed by single-crystal X-ray diffraction study. Aromatic nucleophilic substitution and palladium-catalyzed cross-coupling reactions were found to be powerful tools for the selective synthesis of various mono- and bis-derivatives. It was found that 4,8-dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) is resistant to the action of water, alcohols and corresponding alcoholates; when using aromatic nucleophilic substitution (SnAr), mono- and bis-aminated derivatives were successfully obtained, while thiols formed only bis-derivatives, and the reaction could not be stopped at the stage of the formation of mono-thiols. The Stille coupling of 4,8-dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) is useful for the synthesis of bis-arylated heterocycles, while Suzuki–Miyaura coupling can be successfully employed for the selective formation of various mono- and di-(het)arylated derivatives of benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole). The obtained compounds can represent an effective basis for the design and construction of components of organic light-emitting diodes and solar cells.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/molecules27217372/s1, Characterization data including ^1H, ^13C NMR and HRMS spectra for compounds 1, 12, 13, 15, 18, 19 and quantum chemical calculations data.

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References


