Effective synthesis of 4,5-dibromobenzo[1,2-*c*:3,4-*c'*]-bis([1,2,5]thiadiazole) by bromination of benzo[1,2-*c*:3,4-*c'*]-bis([1,2,5]thiadiazole)

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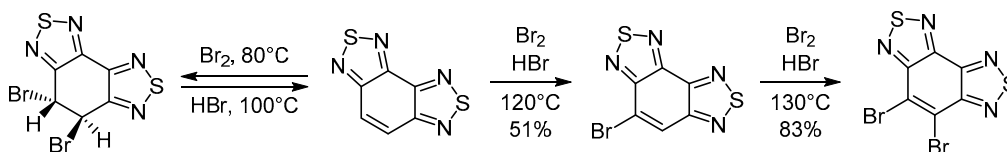
The bromination of benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) was studied. An efficient method has been developed for the synthesis of 4,5-dibromobenzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole), an important intermediate for the preparation of highly efficient photochromic diarylethenes for photosensitive and mechanoreactive materials that can be useful in a number of applications, including stress perception and information storage.

Keywords: benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole), bromination, cross-coupling reactions, IR and Raman spectroscopy.

The 1,2,5-benzothiadiazole core is one of the most commonly used moderately electron-deficient building blocks for constructing various optovoltaic devices.[1] Fused benzothiadiazoles are used to create electron transport materials for organic and polymer LEDs,[2] organic field-effect transmitters (OFETs),[3] Grätzel[4] and bulk heterojunction solar cells,[5] polymers for nonlinear optics and near-infrared radiation,[6] organic electron transport layers for perovskite solar cells.[7] Typically, the starting compounds for these types of materials are 4,7-dibromo derivatives of benzothiadiazoles and their analogs.[8] Dibromo derivatives of benzenes fused with two thiadiazole rings have also been studied well.[9] In particular, linear 4,8-dibromobenzo-[1,2-*c*:4,5-*c'*]bis([1,2,5]thiadiazole) (**1**) (Scheme 1) has been widely studied in Stille, Suzuki, and Sonogashira cross-coupling reactions for the synthesis of diaryl and other deriva-

tives with well-known optoelectronic properties.[9] Another isomer of bisthiadiazoles of this type, 4,5-dibromobenzo-[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) (**2**), is less available, although is used for preparation of photosensitive and

Scheme 1
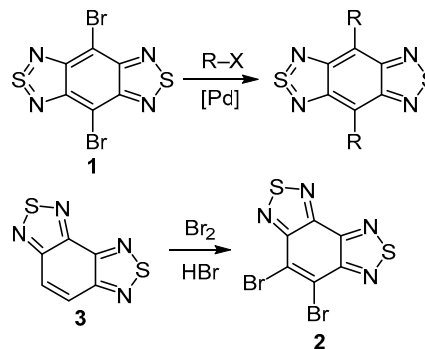
Scheme 2
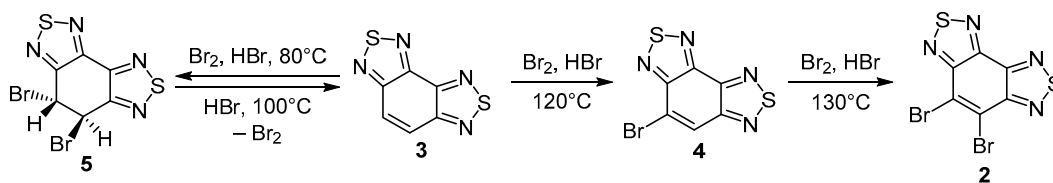
novel mechanoreactive materials that may be useful in a number of applications.[10–12] This is due to the lack of a well-developed methods for the synthesis of this compound – a single article describes a nonselective method for obtaining compound **2** by bromination of benzo[1,2-*c*:3,4-c']bis-([1,2,5]thiadiazole) (**3**) with Br_2 in HBr with a yield of 27% (Scheme 1).[13]

However, for a more active study of compound **2** in cross-coupling reactions and also as a new building block for constructing optovoltaic device components, it was necessary to develop its high-yielding, selective synthetic method. For this, we carried out a systematic study of the bromination of benzo[1,2-*c*:3,4-*c*']bis([1,2,5]thiadiazole) (**3**).

It was found that the reaction of benzo[1,2-*c*:3,4-*c*']bis-([1,2,5]thiadiazole) (**3**) with Br_2 in AcOH at 100°C for 4 h, or refluxing in $SOCl_2$ for 6 h and in PBr_3 at 125°C for 4 h did not proceed. The reaction of compound **3** with Br_2 in trifluoromethanesulfonic acid (TfOH) at 50°C for 5 h and in oleum of various concentrations at different temperatures leads to the formation of monobromo derivative **4** in low yields (7–23%). It is known that the most frequently used reagents for bromination of benzo-1,2,5-thiadiazoles are Br_2 in HBr and NBS in various solvents.[8] We studied these two methods in detail. Unfortunately, in a reaction of tricycle **3** with NBS in various acids (H_2SO_4, TfOH), and oleum at 20–80°C temperatures we observed the formation of monobrominated product **4** with yields not higher than 20%.

Our studies of the reaction with Br_2 in HBr have shown that the reaction temperature, the amount of Br_2 used, and the reaction time have a significant impact on the structure of the resulting product and its yield. The most important results of this study are given in Scheme 2 and Table 1.

Analysis of the products and reaction conditions showed that the formation of dibromo derivative **2** occurs stepwise. When the reaction is carried out at 80°C, the formation of compound **5** is observed, which is the product of the addition of a Br_2 molecule to the starting tricycle **3** (Table 1, entries 1, 2). It is interesting to note, that this reaction is reversible. It was proved by heating hydrogenated dibromide **5** in acidic conditions in the absence of brominating agents at 100°C, which led to a complete recovery of the starting tricycle **3**. A prolonged heating of compound **5** at 120°C with Br_2 in HBr gave monobromide **4** (Table 1, entries 3, 4) with HBr elimination. The possibility of such transformations is confirmed by the presence of an analogy in the bromination of phenanthrene, when the hydrocarbon form is capable of eliminating Br_2 with gentle heating, and the addition of Br_2 to the heated mixture leads to the loss of HBr, and an aromatic monobromo derivative is formed.[16] Increasing the amount of Br_2 and additional heating at 120°C leads to only a slight increase in the yield of monobromide

Table 1. Yields of the reaction of benzo[1,2-*c*:3,4-*c*']bis-([1,2,5]thiadiazole) **3** (1 mmol) with Br_2 in HBr (48%, 25 ml)

Entry	Br_2, mmol (reaction time, h)	Temperature, °C	Yields of compound, %		
			5	**4**	**2**
1	4 (10) + 2 (6)	80	80	Traces	0
2	4 (16) + 2 (8)	85	85	Traces	0
3	2 (16)	120	0	47	0
4	2 (74) + 2 (46)	120	0	51	0
5	4 (24)	130	0	18	3
6	4 (24) + 8 (24)	130	0	Traces	41
7	4 (72) + 8 (48)	130	0	0	52
8	4 (96) + 8 (48)	130	0	0	69
9	4 (120) + 8 (48)	130	0	0	83
10	4 (48)	140	0	0	0

4. These reaction conditions and the yield we obtained (47%, Table 1, entry 3) are very close to the reported conditions for the reaction producing monobromide **4** (54%).[14]

Under the above-mentioned conditions, the reaction does not lead to the formation of the target dibromide **2**. It is reported that this problem can be solved by heating the reaction mixture for four days at 120°C with addition of a twofold Br_2 excess, however, the reaction still did not reach completion, and the yield of dibromide **2** was only 27%.[13] Since we didn't detect formation of dibromide **2** under such conditions (Table 1, entries 3, 4) we decided to increase the reaction temperature to 130°C, and we observed that after 24 h of heating, the formation of dibromide **2** had started (Table 1, entry 5). A consistent increase of the reaction time to 120 h and the additional introduction of the excess of Br_2 and heating the reaction mixture for additional 48 h at the same temperature, allowed to increase the yield of dibromide **2** to 83% (Table 1, entries 6–9). Under these conditions, the reaction becomes selective – pure dibromide **2** was isolated by simple filtration without thorough washing with a solvent to remove impurities and intermediate products. A further increase in the reaction temperature to 140°C led to a decomposition of the reaction products (Table 1, entry 10). Thus, we have developed an effective and selective method for the synthesis of the target dibromide **2** in high yield.

Compounds **5** and **4** also were converted into dibromide **2** under prolonged heating at 130°C in HBr in presence of a large excess of Br_2 (conditions similar to those in Table 1, entry 9), with yields of 73 and 79%, respectively. Additionally we found that compound **5** forms monobromide **4** with a yield of 85%, when the reaction mixture is heated at 120°C

for 16 h with 2 equiv of Br_2. Apparently, the transformation of dibromide **5** proceeds through the formation of tricycle **3** followed by further bromination to aromatic derivatives **4** and **2**.

To confirm the structure of compounds **2–5** and to establish the isomerism of compound **5**, IR and Raman spectra of the solids (Figs. 1–4) were recorded and interpreted using normal coordinate analysis (NCA) at the TPSS/Def2-TZVP level. Since compounds **2**, **3**, and **4** have a C=C double bond in a six-membered ring, the reactivity of which is described above, the vibration involving it (Table 2, entry 1) appears as a weak band at 1563, 1642, and 1576 cm^{-1}, respectively. The most characteristic bands in the spectra of the whole series of compounds **2–5** are stretching νC=N vibrations of thiadiazole rings (Table 2), located in the range of 1300–1500 cm^{-1}. These vibrations obey the selection rules according to the C_{2v} symmetry of molecules **2** and **3**, C_s – compound **4**, and C_2 – compound **5**, and they are also mixed with C–C vibrations due to the cyclic structure. The νC=N stretchings can be categorized in pairs as antisymmetric (Table 2, entries 2 and 3) and symmetric (Table 2, entries 3 and 4) vibrations of the two C=N bonds in the thiadiazole ring, observed at ~1500 and 1400 cm^{-1}, respectively. Since the molecules have two heterocycles, each of their vibrations should interact, thus there are ν^{as}C=N and ν^sC=N modes in phase and counterphase of the two cycles. The νC=N frequencies can distinguish molecules **2–5** from each other. For the nonplanar compound **5**, it should be observed that the IR intensity of all νC=N vibrations in the 1400–1500 cm^{-1} range is weak. Other important vibrations in compounds **2–5** are two vibrations with preferential contribution of C(N)–C(N) bonds in the range of 1300–1370 cm^{-1} (Table 2, entry 5 (antisymmetric) and entry 6 (symmetric)). In planar molecules **2–4**, a significant frequency difference of 30–40 cm^{-1} is observed between modes (Table 2, entries 5 and 6), whereas in compound **5**, the difference is only 10 cm^{-1}. According to NCA results, this difference is characteristic for the *trans*-isomer of compound **5**, for the *cis*-isomer, it should be significantly larger (22 cm^{-1}), which is caused by the mechanics of vibrations, specifically a small participation of ρCH deformations. The *trans*-location of Br substituents in compound **5** is also confirmed by the νCH frequencies at 3002 and 3014 cm^{-1}, which, in the case of the *cis*-isomer, are calculated to differ by more than 50 cm^{-1}, taking into account all corrections. In the 800–900 cm^{-1} region, a series of vibrations are observed (Table 2, entries 10–13), manifested as characteristic bands in the IR and Raman spectra, in which the N–S stretching contributes. The presence of the Br substituent in compounds **2**, **4**, and **5** is not quite unambiguous, since the νC–Br stretching is not characteristic, it contributes to several vibrations. In the IR spectrum of compound **2**, there is a characteristic band at 911 cm^{-1}, which belongs to a complex mode (Table 2, entry 8) involving ν^{as}C–Br and C_6-ring deformations. A similar mode is present in compound **4**, it involves one C–Br coordinate and appears as an intense IR band at 862 cm^{-1}. In the nonplanar compound **5**, due to the saturated carbon atom, the ν^sC–Br vibrations are more
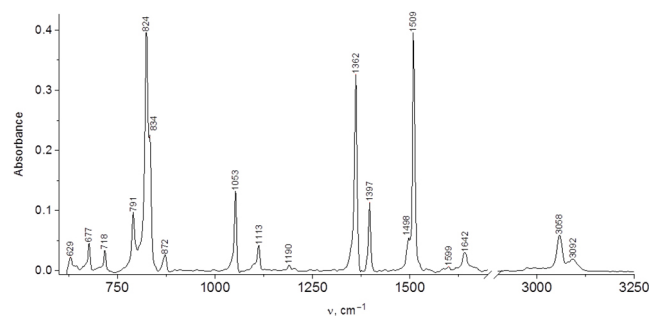

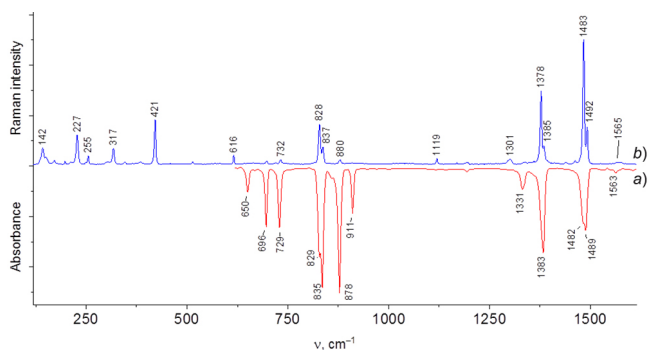**Figure 1**. The FTIR spectrum of compound **3**.

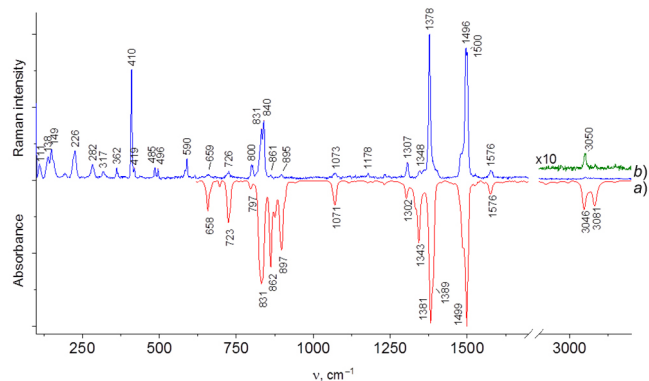**Figure 2**. *a*) The FTIR and *b*) Raman spectra of compound **2**.

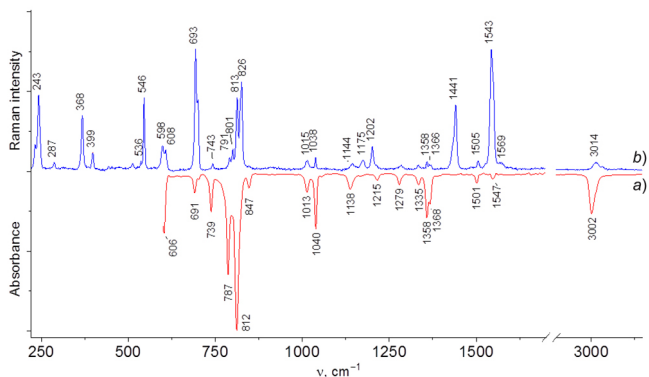**Figure 3**. *a*) The FTIR and *b*) Raman spectra of compound **4**.

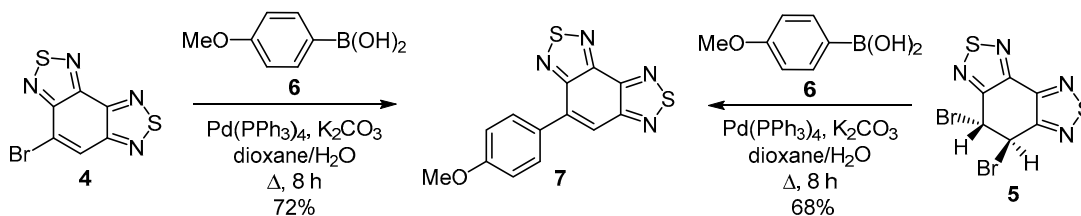**Figure 4**. The FTIR (*a*) and Raman (*b*) spectra of compound **5**.

characteristic, and the medium Raman line at 546 cm^{-1} can be attributed to ν^sC–Br.

Monobromo derivative **4**, as well as dibromide **2**, can be used in the synthesis of photosensitive materials by conversion to efficient mono- or diaryl-substituted derivatives in cross-coupling reactions. We have shown that under Suzuki

**Table 2**. The vibration modes (ν, cm^{-1}) and its assignment in the spectra of compounds **2**–**5**

Entry	2		3	4		5		Normal mode form
	IR	Raman	IR	IR	Raman	IR	Raman	
1	1563 w (A_1)	1565 vw (A_1)	1642 w (A_1)	1576 w (A')	1576 w (A')	–	–	νC=C
2	1487 s (B_1)	1492 m (B_1)	1509 vs (B_1)	1499 vs (A'')	1500 vs (A'')	1547 w (A)	1543 vs (A)	ν^{as}C=N + νC⋯C
3	1482 s (A_1)	1483 vs (A_1)	1498 w (A_1)		1496 sh (A')	1501 w (B)	1505 w (B)	ν^{as}C=N + νC⋯C
4	1383 s (B_1)	1385 w (B_1)	1397 m (B_1)	1388vs (A'')				ν^{s}C=N + νC⋯C
5		1378 s (A_1)		1382 vs (A')	1371 vs (A')		1441 s (A)	ν^{s}C=N + νC⋯C
6	1331 m (B_1)		1362 vs (B_1)	1343 m (A')	1348 vw (A')	1368 m (B)	1366 w (B)	νC⋯C – νC⋯C
7		1301 w (A_1)		1302 w (A'')	1307 w (A'')	1358 m (A)	1358 w (A)	νC⋯C + νC⋯C
8	911 m (B_1)			862 s (A'')	861 vw (A'')			νC–Br + δC=C
9			824 vs (B_1)	897 s	895 vw			Out-of-plane δC–H
10	878 vs	880w	872 w		840 s	847 w		ν^{as}S–N + δC$_6$-ring
11	835 vs	837 w	791 m	831 vs	831s		826 s	ν^{as}S–N + δC$_6$-ring
12	829 sh	828 m		797 w	800 w	812 vs	813s	ν^{as}S–N + δC$_6$-ring
13						787 vs	801/791 w	ν^{as}S–N + δC$_6$-ring
14	696 s (B_1)			723 m (A'')	726 vw (A'')	739 m (B)	743 w (B)	δC$_6$-ring + ν^{s}S–N
15	650 s (A_1)			658 m (A')	659 vw (A')	691 w (A)	693 s (A)	νC–Br + δC$_6$-ring + ν^{s}S–N
14							546 m	νC–Br

Scheme 3

reaction conditions, monobromide **4** with (4-methoxy-phenyl)boronic acid (**6**) gave a corresponding mono-substituted product **7** (Scheme 3). The same product **7** was isolated when hydrogenated dibromide **5** was used as the starting material under the same conditions. Apparently, when dibromide **5** is treated with a base under the given reaction conditions, *in situ* dehydrobromination occurs, followed by further cross-coupling reaction of the resulting monoderivative **4** with boronic acid **6**. The yields of the final product **7** were comparable in both cases, 72 and 68%, respectively. Since the synthesis of hydrogenated dibromide **5** proceeded under milder conditions and with a higher yield than synthesis of monobromide **4**, the involvement of synthon **5** in the Suzuki reaction to obtain monosubstitution products looked more promising.

To confirm the assumption of dehydrobromination process of hydrogenated dibromide **5**, we studied its behavior under alkaline conditions (Scheme 4), which resulted in the isolation of monobromide **4** in high yield (87%). Thus, the overall yield of compound **4** from tricycle **3** through the production of dibromide **5** was 74%, which is higher than in the one-step process of direct bromination of tricycle **3** (51%).

Dibromide **2** was also successfully converted into disubstituted product **8** in Suzuki reaction with boronic acid **6** in a good yield (Scheme 5).

Scheme 4
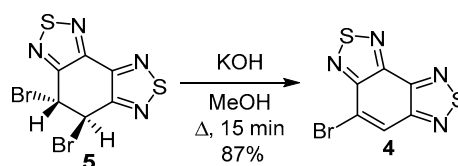
Scheme 5
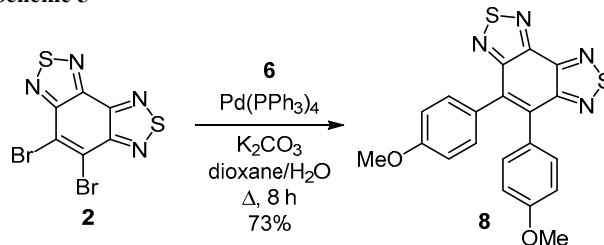
Dyes **7** and **8** have two pronounced absorption maxima (Table 3). The first absorption maximum corresponded to the π–π* electronic transition practically coincide for both compounds, which is explained by the use of the same donor fragment. The second absorption maximum corresponds to an intramolecular charge transfer (ICT) process between the donor and acceptor parts, and for the disubstituted derivative **8** is shifted to longer wavelengths by 10 nm, which may mean a more pronounced charge

Table 3. UV-Vis absorption data of compounds **7** and **8** in CH_2Cl_2 solutions (2×10^{-5} M)

Com-pound	λ_{max1}, nm	$\varepsilon_{max1} \times 10^3$, $M^{-1} \cdot cm^{-1}$	λ_{max2}, nm	$\varepsilon_{max2} \times 10^3$, $M^{-1} \cdot cm^{-1}$
7	280	24.8	350	12.5
8	283	23.2	360	7.9

separation caused by the presence of two donor substituents. It is likely that the absence of a bathochromic shift in the ICT maximum in comparison to the similar compounds with a linear structure[17] is due to the curved structure of the molecule, which disrupts the electron transfer between donor fragments and the acceptor cycle. Nevertheless, the intense absorption of light by the resulting compounds in the short-wavelength region with extinction coefficients of more than 100 $M^{-1} \cdot cm^{-1}$ indicates a promising use of the tricyclic block as an effective internal acceptor for various applications in materials chemistry.

In conclusion, the bromination of benzo[1,2-*c*:3,4-*c'*]bis-([1,2,5]thiadiazole) has been thoroughly investigated. Methods have been found for the selective synthesis of bromo derivatives with high yields. It has been established that bromo derivatives can transform into each other under various conditions. The IR and Raman spectra of compounds of the benzothiadiazole series were studied, and characteristic bands were assigned to the corresponding vibrations, which proved that (4*R*,5*R*)-4,5-dibromo-4,5-dihydrobenzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) is in the form of the *trans*-isomer. Suzuki cross-coupling reactions of bromides yielded aryl-substituted benzo[1,2-*c*:3,4-*c'*]bis-([1,2,5]thiadiazoles) that have potential for use in a variety of applications in the materials chemistry.

Experimental

IR spectra for solid microparticles deposited on polished stainless steel plate were recorded on an FTIR spectrometer Simex FT-801 equipped IR-microscope (15× lens) Micran-3 (Novosibirsk, Russia) and cooled MCT detector in the range of 4000–600 cm^{-1} at a spectral resolution of 4 cm^{-1} in trans-reflection mode with aperture 100 μm. Raman spectra for solids were recorded using a Raman spectrometer JY Horiba LabRam 300 with He-Ne excitation of 1 MW power. The Raman spectrum for compound **3** has not been registered due to a broadband luminescence. UV-visible absorption spectra were recorded using an OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer (Saint-Petersburg, Russia) controlled with SF-2000 software in the standard 10 mm photometric quartz cells in HPLC grade CH_2Cl_2 in concentration of 2×10^{-5} M. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75 MHz, respectively), in $CDCl_3$ or DMSO-d_6, internal standard TMS. Electrospray ionization (ESI) high-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF instrument in the positive ion mode (capillary voltage 4.5 kV) in the mass scan range from 50 to 3000 Da. Solutions were injected at a rate of 3 μl·min^{-1}, the nebulizer gas was nitrogen, and the interface temperature was 180°C. Mass

spectra were recorded on a Finnigan MAT INCOS 50 instrument with a direct inlet system (EI, 70 eV). Norman coordinate analysis (NCA) for compounds **2**–**5** and *cis*-isomer of compound **5** was performed in harmonic approximation at the TPSS/Def2-TZVP level using Gaussian 16 A.03 program. Melting points were measured on a Kofler heating stage with a heating rate at the melting point equal to 4 deg. min^{-1}, as well as on a Stuart SMP10 instrument. All the synthetic experiments were carried out under dry argon atmosphere. Reaction progress was monitored by thin-layer chromatography (TLC) on 10 × 15 cm plates (Merck, TLC Silica gel 60 F$_{254}$; eluents – petroleum ether, CH_2Cl_2, EtOAc, Et_2O, $CHCl_3$, CCl_4), visualized under UV light at 254 nm. Preparative separation of mixtures and purification of target products were carried out by column chromatography on Silica gel 60 (Merck) using eluents selected by TLC.

Solvents purchased from Sigma-Aldrich were purified by distillation over the corresponding drying agents following standard procedures, commercially available reagents from Sigma-Aldrich were used without additional purification. Benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) (**3**) was synthesized by a reported method.[18]

(4*R*,5*R*)-4,5-Dibromo-4,5-dihydrobenzo[1,2-*c*:3,4-*c'*]-bis([1,2,5]thiadiazole) (5). To a stirred mixture of benzo-[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) (**3**) (1.4 g, 7.2 mmol) in aq HBr (48%, 5 ml), Br_2 (4.9 g, 1.5 ml, 30 mmol) was added dropwise at room temperature. The reaction mixture was stirred at 85°C for 16 h. After cooling the reaction mixture to room temperature, additional amount of Br_2 (2.4 g, 0.75 ml, 15 mmol) was added, and mixture was stirred at 85°C for another 8 h. Then the mixture was poured into H_2O and extracted with CH_2Cl_2 (3×100 ml). Organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether – CH_2Cl_2, 3:1). Yield 2.48 g (85%), colorless solid, mp 135–137°C. R_f 0.6 (petroleum ether – CH_2Cl_2, 3:1). IR spectrum, ν, cm^{-1}: 3014, 1543, 1441, 1202, 826, 813, 693, 546. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.03 (2H, s, 2CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 157.8; 149.0; 40.8. Found, *m/z*: 376.7946 [M+Na]$^+$. $C_6H_2(^{81}Br)_2N_4NaS_2$. Calculated, *m/z*: 376.7958.

4-Bromobenzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) (4). Method A. To a stirred mixture of benzo[1,2-*c*:3,4-*c'*]bis-([1,2,5]thiadiazole) (**3**) (194 mg, 1 mmol) in aq HBr (48%, 4 ml), Br_2 (319 mg, 0.1 ml, 2 mmol) was added dropwise at room temperature. The reaction mixture was stirred at 120°C for 74 h. After cooling to room temperature, additional amount of Br_2 (319 mg, 0.1 ml, 2 mmol) was added, and the mixture was stirred at 120°C for another 46 h. Then the mixture was poured into H_2O, extracted with CH_2Cl_2 (3×20 ml). Organic layer was dried over Na_2SO_4 and then evaporated. The residue was purified by column chromato-graphy with petroleum ether – CH_2Cl_2, 3:1. Yield 0.140 g (51%), colorless solid, mp 203–205°C (mp 205°C).[28] R_f 0.55 (petroleum ether – CH_2Cl_2, 3:1). IR spectrum, ν, cm^{-1}: 3050, 1496, 1378, 1307, 840, 831, 590. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.03 (1H, s, CH). Found, *m/z*: 296.8686 [M+Na]$^+$. $C_6HBrN_4NaS_2$. Calculated, *m/z*: 296.8697.

Method B. To a solution of KOH (0.335 g, 6 mmol) in MeOH (5 ml), dibromide **5** (2.124 g, 6 mmol) was added in one portion, and the resulting mixture was refluxed for 30 min, then poured into H_2O and extracted with EtOAc (3×100 ml). Organic layer was washed with H_2O (3×100 ml), dried over Na_2SO_4, and then evaporated. The residue was purified by column chromatography with petroleum ether – CH_2Cl_2, 3:1. Yield 1.145 g (87%).

4,5-Dibromobenzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) (2). A mixture of benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thiadiazole) (**3**) (0.100 g, 0.5 mmol) and Br_2 (0.319 mg, 0.1 ml, 2 mmol) in aq HBr (48%, 2 ml) was heated in sealed vial at 130°C for 120 h. After cooling to room temperature, additional amount of Br_2 (0.638 g, 0.2 ml, 4 mmol) was added and the mixture was heated at 130°C for another 48 h. Then the mixture was poured into H_2O, precipitate was collected by filtration, and washed with CH_2Cl_2. Yield 0.146 g (83%), colorless solid, mp 250–252°C. R_f 0.50 (petroleum ether – CH_2Cl_2, 1:1). IR spectrum, ν, cm^{-1}: 1565, 1492, 1483, 1385, 1378, 828, 616. ^{13}C NMR spectrum (CDCl_3), δ, ppm: 154.9; 145.6; 122.3.

Suzuki coupling (General method). A solution of K_2CO_3 (1.55 g, 14.6 mmol) in H_2O (7.3 ml) was added to a stirred solution of bromo derivative **5**, **4**, or **2** (0.28 mmol) and (4-methoxyphenyl)boronic acid (**6**) (130 mg, 0.85 mmol) in dry 1,4-dioxane (10 ml). The mixture was degassed for 20 min with a stream of argon, then Pd(PPh_3)_4 (33 mg, 0.029 mmol) was added, and the resulting mixture was refluxed for 8 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (20 ml) and washed with H_2O (3 × 20 ml). Organic layer was dried over Na_2SO_4, and then evaporated. The residue was purified by column chromatography (petroleum ether – CH_2Cl_2).

4-(4-Methoxyphenyl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]thia-diazole) (7). Eluent for column chromatography petroleum ether – CH_2Cl_2, 4:1. Yield 57 mg (68%, from compound **5**), 61 mg (72%, from compound **4**), light-yellow solid, mp 163–165°C. R_f 0.4 (petroleum ether – CH_2Cl_2, 2:1). UV/Vis spectrum, $λ_{max}$, nm (ε, ×10^3 $M^{-1}·cm^{-1}$): 280 (24.8), 350 (12.5). ^1H NMR spectrum (CDCl_3), δ, ppm (*J*, Hz): 8.05 (1H, s, CH); 7.92 (2H, d, *J* = 8.4, H Ar); 7.11 (2H, d, *J* = 8.1, H Ar); 3.93 (3H, s, OCH_3). ^{13}C NMR spectrum (CDCl_3), δ, ppm: 160.7; 156.6; 155.9; 148.5; 147.6; 136.6; 130.6; 128.3; 123.8; 120.6; 114.2; 55.5. Found, *m/z*: 301.0211 [M+H]⁺. $C_{13}H_9N_4OS_2$. Calculated, *m/z*: 301.0212.

4,5-Bis(4-methoxyphenyl)benzo[1,2-*c*:3,4-*c'*]bis([1,2,5]-thiadiazole) (8). Eluent for column chromatography petroleum ether – CH_2Cl_2, 3:1. Yield 83 mg (73%), light-yellow solid, mp 239–241°C. R_f 0.3 (petroleum ether – CH_2Cl_2, 2:1). UV/Vis spectrum, $λ_{max}$, nm (ε, ×10^3 $M^{-1}·cm^{-1}$): 283 (23.2), 360 (7.9). ^1H NMR spectrum (CDCl_3), δ, ppm (*J*, Hz): 7.31 (4H, d, *J* = 8.7, H Ar); 6.91 (4H, d, *J* = 8.6, H Ar); 3.85 (6H, s, 2OCH_3). ^{13}C NMR spectrum (CDCl_3), δ, ppm: 159.3; 157.6; 147.4; 133.9; 132.3; 127.6; 113.6; 55.2. Found, *m/z*: 407.0620 [M+H]⁺. $C_{20}H_{15}N_4O_2S_2$. Calculated, *m/z*: 407.0631.

Supplementary information file containing ^{13}C NMR spectra of compound **2**, ^1H NMR spectrum and HRMS of compound **4**, ^1H, ^{13}C NMR spectra and HRMS of compound **5**, UV/Vis, ^1H, ^{13}C NMR spectra and HRMS of compounds **7**, **8** is available at the journal website http://link.springer.com/journal/10593.

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