EurJOC
European Journal of Organic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Synthesis of 4,7-dibromo derivative of ultrahigh electron-deficient [1,2,5]thiadiazolo[3,4-d]pyridazine heterocycle and its cross-coupling reactions

Authors: Timofey Chmovzh, Ekaterina Knyazeva, Ludmila Mikhalchenko, Ivan Golovanov, Stanislav Amelichev, and Oleg A Rakitin

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201800961

Link to VoR: http://dx.doi.org/10.1002/ejoc.201800961

Supported by ACES Asian Chemical Editorial Society

WILEY-VCH

10.1002/ejoc.201800961

WILEY-VCH

FULL PAPER

Synthesis of 4,7-dibromo derivative of ultrahigh electron-deficient [1,2,5]thiadiazolo[3,4-*d*]pyridazine heterocycle and its cross-coupling reactions

Timofey N. Chmovzh,[a] Ekaterina A. Knyazeva,[a],[b] Ludmila V. Mikhalchenko,[a] Ivan S. Golovanov,[a] Stanislav A. Amelichev,[a] and Oleg A. Rakitin*[a],[b]

Abstract: An efficient synthesis of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine is reported. For the first time, palladium-catalysed cross-couplings chemistry for a dihalo derivative was found to be a powerful tool for the selective formation of various mono- and bis-derivatives of strong electron accepting heterocycles. Suzuki-Miyaura coupling can be successfully employed for the preparation of mono-arylated derivatives, whereas Stille coupling is useful for both mono- and di-aryl(hetaryl)ated heterocycles. The cyclic voltammogram showed that 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine can be easily oxidized to form a stable anion radical. The calculated values of E_{LUMO} confirmed that [1,2,5]thiadiazolo[3,4-*d*]pyridazine is one of the strongest electron acceptor system.

Introduction

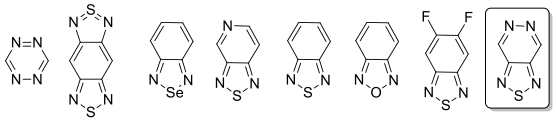
Electron-acceptor building blocks have been widely used in the synthesis of various photovoltaic materials including dye sensitized solar cells,[1] organic near-infrared molecules,[2] organic light emitting diodes (OLEDs),[3] charge transfer materials,[4] bioimaging[5] and others. Their presence in a π-conjugated organic molecule is important to tune such properties as light absorption, light emission and charge carrier mobility in the materials. The energies of the frontier orbitals: the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), as well as the difference between these energies (E_g), are fundamental properties of molecules and are crucial for high performance of the materials based on these molecules. Electron-acceptor building blocks (A) can be used in π-conjugated small molecules where such a block is linked with an electron donor (D) either directly, or more favorably, through a π-conjugated bridge (π). The important feature of the acceptor part is the electron affinity which is related to the energies of the lowest unoccupied molecular orbital (E_{LUMO}). The electron-acceptor building blocks with high electron deficiency may be used in the construction of compounds for such devices as light absorption materials in bulk heterojunction solar cells (BHJ),[6] donor-acceptor dyes with near infrared absorption and emissions,[7] and n-type organic field-effect transistors.[8] Moreover, polymeric molecules with an electron-deficient moiety in the structure, $(\text{-D-A-})_n$ or $(\text{-D-π-A-})_n$, have been successfully used as electrochromic materials.[9] Several different structural motifs have been intensely studied in the past few decades: more simple D-A, D-π-A, D-A-D or A-D-A, or more complex ones where different acceptors or donors were used: D-A^1-π-A^2, A- π-D-π-A, etc.[1c] Recently, heterocycles with high electron affinity as electron-acceptor central blocks have been given a great attention.[10] Although 2,1,3-benzothiadiazole has proven as an exceptional electron-accepting building block,[11] there is a strong demand to design a building block with ultrahigh electron deficiency in order to increase light absorption in the near infrared region, and therefore to use the solar light more efficiently in organic photovoltaics with the main purpose of replacing the currently used and expensive fullerene derivatives. Another purpose is to construct efficient air-stable electron-transport materials.[9b] The first idea on how to increase the electron-accepting ability of 2,1,3-benzothiadiazole was to attach strong electron-withdrawing groups at the 5- and 6-positions. In fact, 5,6-difluoro-2,1,3-benzothiadiazole has been employed in a variety of materials including small molecules in DSSCs chromophore, white and color light emitters, polymer molecules in OLEDs, OFETs, and OPVs.[9b] Another way to increase the electron-accepting strength of the 2,1,3-benzothiadiazole core was the heteroannulation at the 5- and 6-positions to afford acceptors such as [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (TDQ)[12] and benzo[1,2-*c*:4,5-*c*´]bis[1,2,5]thiadiazole (benzo-bis-thiadiazole, BBT).[13] The third way is to change carbon atoms in 5- or/and 6-positions to electronegative nitrogen atoms. 4,7-Dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine was effectively used for the preparation of DSSCs and other materials.[14] To complete this way, it is necessary to incorporate [1,2,5]thiadiazolo[3,4-*d*]pyridazine core in the design and preparation of photovoltaic materials.

In order to reveal the electronic nature of the [1,2,5]thiadiazolo[3,4-*d*]pyridazine block, the energy levels of the frontier orbitals along with other properties have been calculated and compared with the same properties of some relevant acceptors. Thiadiazolopyridazine has the lowest LUMO energy level among the compounds shown in Figure 1, excluding benzobis(thiadiazole). Hence, thiadiazolopyridazine possesses an ultrahigh electron deficiency. It may lead to unusual and even extreme physicochemical properties, and development of its chemistry requires special attention. As previously noted, the value of E_{gap} is also an important characteristic of the constituent parts of molecules for photoelectronic materials. We calculated the optical energy gap of the same molecules in the first excited electronic state in chloroform solution. It was found that the [1,2,5]thiadiazolo[3,4-*d*]pyridazine block had the maximum difference between E_{HOMO} and E_{LUMO}, which should ensure high

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospekt, 119991 Moscow, Russia. e-mail: orakitin@ioc.ac.ru; fax (+)7-499-1355327: tel. (+)7-499-1355328
[b] Nanotechnology Education and Research Center, South Ural State University, 454080 Chelyabinsk, Russia

Supporting information for this article is given via a link at the end of the document.

stability of the molecules in excited state and, as a result, high electron conductivity.



E_g, eV	2.134	2.255	3.307	3.563	3.573	3.636	3.690	4.106
E_{LUMO}, eV	- 3.495	- 3.853	- 2.767	- 3.140	- 2.680	- 2.800	- 2.999	- 3.591
E_{HOMO}, eV	- 5.629	- 6.108	- 6.074	- 6.703	- 6.253	- 6.436	- 6.689	- 7.697

Figure 1. Calculated LUMO and HOMO energy levels and optical energy gaps of relevant acceptors.

para-Dihalogenated (most often dibromo) representatives of the electron acceptor heterocycles shown in Figure 1 are used for the synthesis of various photovoltaic materials.[1c,11b] Although dibromo derivatives of all heterocyclic acceptors shown in Figure 1, are known, their substitution chemistry has been studied fragmentally, and the possibility of synthesizing photovoltaic materials from them is unclear. For example, the heterocycle with the strongest electron accepting properties – 3,7-dibromobenzo[1,2-c;4,5-c′]bis[1,2,5]thiadiazole – was studied in Stille reactions only.[15] The chemistry of 3,6-dibromo-1,2,5,6-tetrazine is unknown,[16] while the 3,6-dichloro derivative was slightly studied in Stille coupling.[17] In general, careful studies of cross-coupling displacement of halogen atoms in extremely electron-poor heteroarenes are very rare and still remain a challenge.

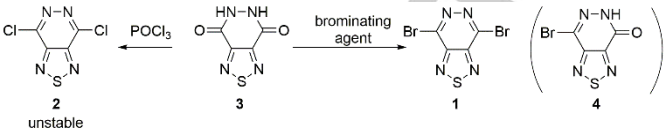
Herein, we describe the synthesis of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine and their S_NAr and cross-coupling reactions as a basis for the preparation of compounds which are of interest as photovoltaic materials.

Results and Discussion

Synthesis of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine 1

[1,2,5]Thiadiazolo[3,4-*d*]pyridazines are a well known class of heterocycles. To the best of our knowledge, about 50 compounds were described in the literature according to SciFinder and Reaxys search. As concerns 4,7-dihalo[1,2,5]thiadiazolo[3,4-*d*]pyridazines, which are of interest for the preparation of various photovoltaic materials, dichloro derivative **2** is the only known compound.[18] This derivative has been prepared by the reaction of 5,6-dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione[19] (**3**) with $POCl_3$. Unfortunately neither spectral or analytical data, nor reactions which could confirm this structure, have been given. We repeated this reaction and confirmed that dichloro derivative **2** was very unstable and could not be purified or involved in substitution reactions. On the other hand, it is known that bromo derivatives can react in substitution reactions (especially cross-couplings) much more successfully than the corresponding chloro derivatives. In order to obtain 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1**, the reaction of 5,6-dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione **3** with brominating agents ($POBr_3$, PBr_5, PBr_3) was investigated. The results are summarized in Table 1.

Table 1. Bromination of 5,6-dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione **3**.



2 unstable **3** **1** **4**

Entry	Reagent	Temp. (°C)	Time (h)	Yields (%)		
				3	**1**	**4**
1	PBr_3	25	4	90	1	5
2	PBr_3	60	4	80	2	6
3	PBr_3	80	4	75	3	10
4	PBr_3	110	4	70	4	12
5	$POBr_3$	25	4	88	5	4
6	$POBr_3$	60	4	70	6	10
7	$POBr_3$	60	8	50	7	20
8	$POBr_3$	80	4	55	8	10
9	$POBr_3$	80	8	40	9	11
10	$POBr_3$	110	4	45	10	8
11	$POBr_3$	110	8	30	11	20
12	$POBr_3$	110	9	25	12	22
13	$POBr_3$	130	9	10	13	25
14	$POBr_3$ + DMF	110	6	20	14	40
15	$POBr_3$ + C_6H_6	110	6	15	15	35
16	PBr_5	25	4	78	16	8
17	PBr_5	60	4	60	17	20
18	PBr_5	60	8	45	18	25
19	PBr_5	80	4	35	19	20
20	PBr_5	80	8	25	20	28
21	PBr_5	105	4	25	21	20
22	PBr_5	105	8	5	22	15
23	**PBr_5**	**105**	**9**	**0**	**75**	**8**

It has been found that the nature of the brominating reagent and the reaction temperature affect the yield of the target dibromo product **1** significantly. At room temperature, none of the reagents used reacted with compound **3**. PBr_3 did not convert dione **3** into bromo derivatives at higher temperatures either. Traces of dibromo compound **1** were isolated after heating at 110 °C for four hours (Entry 4, Table 1). Better results were obtained using $POBr_3$. Prolonged heating of the reaction mixture at 110 °C gave the target dibromo derivative in moderate yield (Entry 12, Table 1); significant amounts of mono- and diones (**4** and **3**) were isolated from the reaction mixture. The use of organic solvents (benzene or DMF) did not afford any significant success; the yields of the target compound remained practically the same (Entries 14, 15, Table 1). The best yield of **1** was achieved using PBr_5 as the most powerful brominating reagent. Careful investigation of the reaction conditions allowed us to reach the yield of 75% by heating the reaction mixture at 105 °C for 9 h (entry 23, Table 1). Small amounts of mono- and diones (**4** and **3**) were isolated. This fact can be explained by partial hydrolysis of the target compound **1** during work-up of the reaction mixture.

4,7-Dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** is a high-melting yellow solid with mp 199-200 °C. It is fairly 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 proved by NMR, mass and IR spectroscopy.

In order to reveal the possibility to construct various photovoltaic materials from dibromo derivative **1**, its reactivity in aromatic nucleophilic substitution and cross-coupling palladium catalyzed reactions was studied. In these sections we aimed at finding conditions for the substitution of one or two bromine atoms to expand the number of structures.

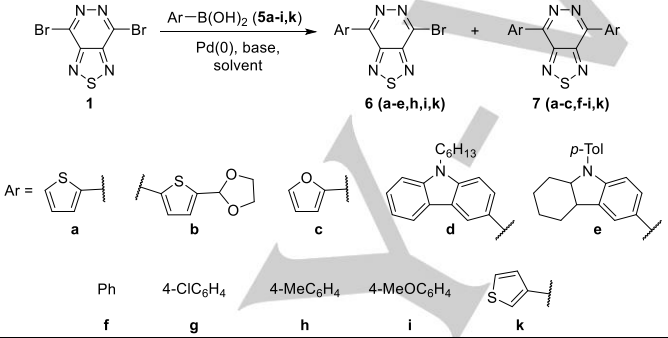
Cross-coupling reactions of 4,7-bromo[1,2,5]thiadiazolo[3,4-*d*]pyridazines

Dibromothiadiazolopyridazine **1** has been investigated in the palladium-catalyzed Suzuki-Miyamura and Stille coupling reactions in order to obtain mono- and bis-aryl(hetaryl)thiadiazolopyridazines.

The behavior of dibromothiadiazolopyridazine **1** under Suzuki-Miyaura cross-coupling conditions was studied. The nearest analog of this derivative - 4,7-dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine - reacted readily with aryl-[20] and heteroaryl-[14b,21] boronic acids or their cyclic esters to give the corresponding 4-aryl(hetaryl) derivatives in moderate yields. Treatment of dibromothiadiazolopyridazine **1** with phenylboronic acid, $Pd(PPh_3)_4$ and K_2CO_3 in water-dioxane solutions led to hydrolysis to give 7-bromo[1,2,5]thiadiazolo[3,4-*d*]pyridazin-4(5H)-one **4** in good yield. So, it is necessary to focus on nonaqueous protocols in order to limit the base-catalyzed hydrolysis of starting dibromide **1**. Similar anhydrous protocols were successfully used for Suzuki-Miyamura cross-couplings of highly reactive 3,5-dichloroisothiazole-4-carbonitrile.[22]

Suzuki-Miyaura coupling

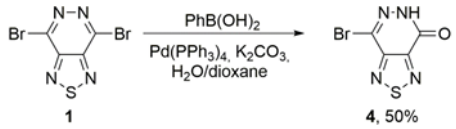
Table 2. Suzuki-Miyaura coupling of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** with aryl- and heteroaryl-boronic acids.



Entry	$ArB(OH)_2$ (equiv.)	Solvent	Catalyst	Base	Temp. (°C)	Time (h)	Yields (%)		
							6	**7**	**1**
1	**5a** (1)	THF	$Pd(PPh_3)_4$	K_2CO_3	66	8	0	0	60
2	**5a** (1)	dioxane	$Pd(PPh_3)_4$	K_2CO_3	101	8	15	0	40
3	**5a** (1)	toluene	$Pd(PPh_3)_4$	K_2CO_3	110	8	20	0	30
4	**5a** (1)	THF	$Pd(PPh_3)_4$	Cs_2CO_3	66	8	20	0	34
5	**5a** (1)	dioxane	$Pd(PPh_3)_4$	Cs_2CO_3	101	8	36	0	17
6	**5a** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	6	50	0	15
7	**5a** (1)	toluene	$Pd(PPh_3)_4$	K_2CO_3	110[a]	0.17	5	0	8
8	**5a** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	60	18	30	0	0
9	**5a** (1)	toluene	$Pd_2(dba)_3$	Cs_2CO_3	110	12	0	0	0
10	**5a** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	8	60	8	0
11	**5a** (2)	toluene	$Pd(OAc)_2$	Cs_2CO_3	110	8	15	0	8
12	**5a** (2)	toluene	$Pd(OAc)_2$, BINAP	Cs_2CO_3	110	8	35	0	0
13	**5a** (2)	toluene	$Pd(OAc)_2$, dppf	Cs_2CO_3	110	8	45	0	0
14	**5a** (2)	toluene	$Pd(OAc)_2$, $P(Cy)_3$	Cs_2CO_3	110	8	0	0	0
15	**5a** (2)	toluene	$Pd(OAc)_2$, XPhos	Cs_2CO_3	110	8	5	0	0
16	**5b** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	6	34	n.d.[b]	30
17	**5b** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	8	58	4	0
18	**5c** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	6	29	n.d.	25
19	**5c** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	9	53	n.d.	0
20	**5d** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	6	23	n.d.	28
21	**5d** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	8	45	n.d.	0
22	**5e** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	12	40	n.d.	0
23	**5e** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	8	60	n.d.	0
24	**5f (1)**	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	12	0	18	32
25	**5f** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	18	0	35	0
26	**5g** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	60	12	0	0	30
27	**5g** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	12	0	20	0
28	**5h** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	60	48	41	4	0
29	**5h** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	14	0	50	0
30	**5i** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	60	24	49	3	0
31	**5i** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	8	0	65	0
32	**5k** (1)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	60	4	54	9	0
33	**5k** (2)	toluene	$Pd(PPh_3)_4$	Cs_2CO_3	110	8	0	35	0

[a] In microwave oven at MW=150 W

[b] Not detected



Scheme 1. Partial hydrolysis of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** under Suzuki-Miyaura coupling conditions

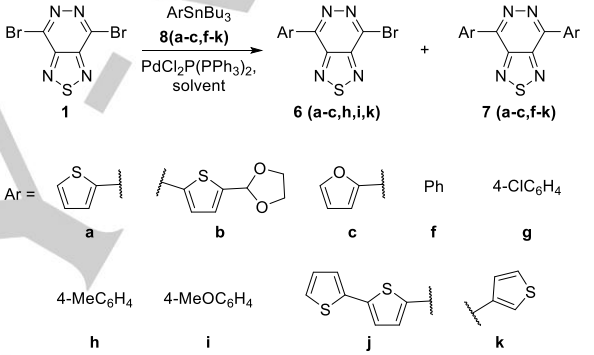
The investigation of Suzuki reaction conditions for the arylation of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** with thiopheneboronic acid **5a** under anhydrous conditions included varying the base, solvent, and reaction temperature. Potassium carbonate was found to be less effective than cesium carbonate, apparently due to its lower solubility (compare Entries 1-3 and Entries 4-6, Table 2). Using palladium catalysts other than $Pd(PPh_3)_4$ ($Pd_2(dba)_3$ and $Pd(OAc)_2$) led to partial of full decomposition of the starting dibromide **1** with low yields of arylated products (Entries 9, 11-15, Table 2). Of the solvents screened, toluene gave the better yields of arylated products, followed by dioxane or THF (Entries 4-6, Table 2). Surprisingly, employment of two equivalents of thienylboronic acid **5a** gave traces of bis-thienylated derivative **7a**, while the yield of mono-thienylated product **6a** increased (Entry 10 in Table 2, Procedure A). Yield of the bis-product **7a** was not risen by the increasing of the reaction time or boronic acid **5a** quantity because of decomposition of mono-substituted compound **6a** by further heating. Apparently, compound **6a** is much less reactive than starting dibromide **1** and decomposed more quickly than formed bis-substituted product **7a**. The scope of Suzuki coupling was then studied. Hetarylboronic acids **5(a-e)** yielded mono-adducts **6(a-e)** in moderate to high yields by heating at reflux in toluene with one equivalent of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** in the presence of $Pd(PPh_3)_4$ and Cs_2CO_3 according to Procedure A (Entries 17, 19, 21, 23, Table 2). In contrast to these results, arylboronic acids (**f-i**) and thiophen-3-ylboronic acid (**k**) under Procedure A conditions afforded bis-arylated products **7f-l,k** in moderate to low yields, mono-arylated compounds were detected in the reaction mixtures in trace amounts only (Entries 25, 27, 29, 31, 33, Table 2). It was found that in the cases of *p*-tolyl-(**h**), 4-methoxyphenyl(**i**)-boronic acids and thiophen-3-ylboronic acid (**k**), the reaction path can be directed to the selective formation of mono-arylated adducts **6(h, i, k)** by heating the reaction mixtures at 60 °C in toluene with one equivalent of the corresponding arylboronic acids according to Procedure B (Entries 28, 30, 32, Table 2).

So, Suzuki-Miayura coupling of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** led mainly to mono-aryl(hetaryl) thiadiazolopyridines **6** in moderate yields.

Stille coupling

In order to obtain both mono-aryl and diaryl[1,2,5]thiadiazolo[3,4-*d*]pyridazines, the palladium catalyzed Stille coupling was investigated. Treatment of thienyltributyl stannane **8a** with dibromo derivative **1** in the presence of $PdCl_2(PPh_3)_2$ showed that mono- **6** and diaryl **7** derivatives were formed depending on the conditions used. The quantities of the stannane, the nature of the solvent and the reaction temperature affected the results significantly (Table 3). The reaction with **8a** in dioxane under reflux conditions cannot be stopped at the formation of the mono-aryl derivative, even if one equivalent of stannane **8a** is employed (Entry 1, Table 3); if two equivalents of stannane **8a** were used, dithienylthiadiazolopyridazine **7a** was formed in a moderate yield (Entry 2, Table 3). Better results were obtained in toluene as the solvent (Entries 3-5, Table 3), and diaryl derivative was isolated in a high yield according to Procedure D. Careful temperature control in THF permitted us to find the best conditions for the synthesis of mono-aryl derivative **6a**, namely, heating the reaction mixture at 55 °C for 8 h according to Procedure C (Entry 7, Table 3). The conditions found for the synthesis of mono- and bis-thienyl derivatives were explored further. In general, this protocol worked well for aryltributylstannanes bearing electron donating groups, and less successfully for stannanes with electron accepting substituents such as furyl- or 4-chlorophenyl groups (Entries 12, 13 and 16, 17, Table 3).

Table 3. Stille coupling of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** with aryl- and heteroaryl-tributylstannates



Entry	ArSnBu3 (eqv.)	Solvent	Temp. (°C)	Time (h)	Yields (%)		
					1	**6**	**7**
1	**8a** (1)	dioxane	101	9	35	0	25
2	**8a** (2)	dioxane	101	9	0	0	45
3	**8a** (1)	toluene	55	8	18	40	8
4	**8a** (1)	toluene	110	9	40	0	40
5	**8a** (2)	toluene	110	9	0	0	80
6	**8a** (1)	THF	66	8	0	50	30
7	**8a** (1)	THF	55	8	0	75	10
8	**8a** (1)	THF	45	8	20	30	8
9	**8a** (1)	THF	45	12	0	40	12
10	**8b** (1)	THF	55	8	0	70	8
11	**8b** (2)	toluene	110	10	0	0	74
12	**8c** (1)	THF	55	8	0	64	0
13	**8c** (2)	toluene	110	8	0	0	57
14	**8f** (1)	THF	55	9	36	0	0
15	**8f** (2)	toluene	110	16	0	0	32
16	**8g** (1)	THF	55	18	28	0	0
17	**8g** (2)	toluene	110	12	0	0	24
18	**8h** (1)	THF	55	18	0	40	0
19	**8h** (2)	toluene	110	12	0	0	55
20	**8i** (1)	THF	55	18	0	52	0
21	**8i** (2)	toluene	110	12	0	0	67
22	**8j** (2)	toluene	110	8	0	0	65
23	**8k** (1)	THF	55	8	0	68	12
24	**8k** (2)	toluene	110	9	0	0	76

Cyclic voltammetry of fused 1,2,5-thiadiazoles

In order to evaluate the energy of frontier orbitals in dibromo derivative **1** and compare them with the corresponding values of pyrido- and benzothiadiazolo counterparts **9**, **10**, their formal reduction potentials were measured by the cyclic voltammetry

method. The cyclic voltammograms of compounds **1**, **9** and **10** are given in Figure 2.

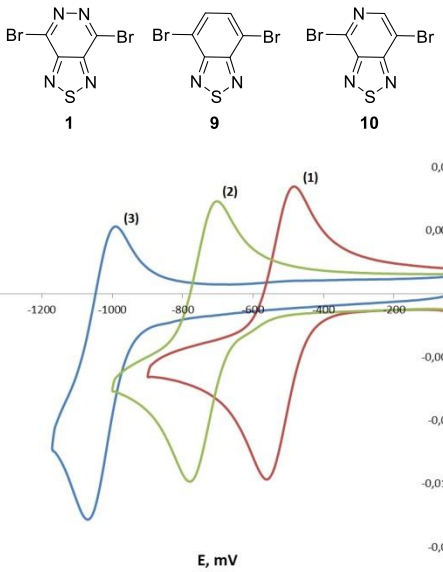


Figure 2. Cyclic voltammograms: (1) compound **1** ($2.0 \cdot 10^{-3}$ M); (2) compound **10** ($1.9 \cdot 10^{-3}$ M) and (3) compound **9** ($2.0 \cdot 10^{-3}$ M) on a platinum electrode at a potential scan rate of 0.1 $V \cdot s^{-1}$ in DMF containing 0.1 M Bu_4NClO_4 as the background electrolyte.

The first reduction stage of **1** (Fig. 2, curve 1) is reversible and corresponds to the transfer of one electron to the molecule. The ratio of the anodic peak of anion-radical (AR) oxidation to the cathodic peak of its formation is close to one at low potential sweep rates of 100 $mV \cdot s^{-1}$. Therefore, the resulting AR**1** seems to be quite stable. The stability of AR**1** can be explained by delocalization of the electron density of the unpaired electron due to the electron-acceptor effect of the thiadiazole ring and nitrogen atoms in the six-membered ring. For comparison, the reduction potential of **1** is only slightly more negative than the potential of benzo[1,2-*c*;4,5-*c'*]bis[1,2,5]thiadiazole **11** (-0.35 V)[13a], which has two thiadiazole rings in the structure and forms a stable AR by electroreduction.

The electroreduction of heterocycles **10** and **9** (Table 4 and Fig. 2) occurs at more negative potentials than that of **1**. The presence of electronegative nitrogen atoms in the six-membered ring leads to a positive shift in the reduction potentials in the sequence **9** → **10** → **1**. It is curious that the electrochemical behavior of pyridine derivative **10** is similar to that of pyridazine **1**. CV curves of benzothiadiazole **9** at low potential sweep rates ($v \leq 100$ mV^{-1}) showed that the ratio of the oxidation current of AR **9** to the cathodic current of its formation becomes less than one. In addition, electroreduction peaks were observed at more negative potentials than the potential of AR **9** formation; they disappear with an increase in v to 1 Vs^{-1}. The same pattern in v changes was observed at recordings of CV curves in acetonitrile. As it was shown before[23] the first reduction stage for compound **9** is irreversible at very low potential sweep rate (16 Vs^{-1}). These facts suggest that AR **9** participates in slow chemical reactions leading to the formation of electrochemically active products. The data obtained indicate that AR **9** is the least stable in the series of compounds **1, 10** and **9**.

The energy of the lowest unoccupied molecular orbital E_{LUMO} for **1** was estimated from the value of the formal potential of the first reversible stage of **1** ER in DMF and acetonitrile using platinum and glass-carbon electrodes. The formal reduction potentials (Table 4) were determined as the average values of peak potentials for direct and reverse scanning of the respective redox system: $E^{red} = (E_{cathode} + E_{anode})/2$. For conversion to the absolute scale of potentials, the values of E^{red} were determined relative to the reversible oxidation potential of ferrocene ($E_{Fc/Fc+}$), which was used as the internal reference. Taking into account the value of absolute oxidation potential of ferrocene, which is equal to 5.1 V,[24] the energy values of E_{LUMO} was calculated according to the equation:

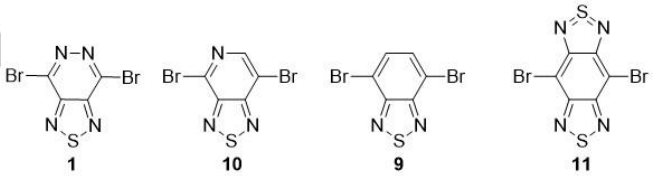
$$E_{LUMO} = - |e|(E_{Fc/Fc+}{}^{red} + 5.1)\ (eV)$$

Table 4. Determination of E_{LUMO} from CV curves of **1** on platinum (Pt) and glassy carbon (GC) electrodes in DMF and acetonitrile, v =0.1Vs^{-1}.

Solvent	Electrode	$E_{SCE}{}^{red}$, V	$E_{Fc/Fc+}{}^{red}$, V	E_{LUMO}, eV
DMF	Pt	-0.521	-1.008	-4.092
	GC	-0.522	-1.011	-4.089
CH_3CN	Pt	-0.597	-0.987	-4.113
	GC	-0.598	-0.994	-4.106

As follows from the data obtained (Table 4), the E_{LUMO} value remained almost invariable regardless of changes in the nature of the electrode or solvent. The E_{LUMO} values for **23** and **24** were calculated from the CV in DMF on a platinum electrode (Table 5).

Table 5. Cyclic voltammetry data for 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1**, 4,7-dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine **10**, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole **9** and benzo[1,2-*c*;4,5-*c'*]bis[1,2,5]thiadiazole **11** in DMF (0.1 M Bu_4NClO_4) on a platinum electrode at a potential scan rate of 0.1 $V \cdot s^{-1}$.



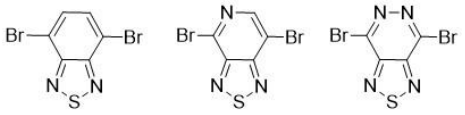
Compound	$E_{SCE}{}^{red}$, V[a]	$E_{Fc}{}^{red}$, V[a]	E_{LUMO}, eV[b]
1	-0.52	-1.01	-4.09
10	-0.72	-1.22	-3.87
9	-1.00	-1.52	-3.58
11[12a]	-0.35	-	-4.26[c]

[a] $E_{SCE}{}^{red}$ and $E_{Fc}{}^{red}$ - formal potentials of reduction peaks for the compounds relative to saturated calomel electrode (SCE) and to the reversible oxidation potential of ferrocene ($E_{Fc/Fc+}$ = 0.48 V relative to SCE) respectively. [b] E_{LUMO} was calculated from $E_{Fc}{}^{red}$ according to the equation $E_{LUMO} = - |e|(E_{Fc/Fc+}{}^{red} + 5.1)$ (eV). [c] The value E_{LUMO} was calculated taking into account the experimentally determined potential $E_{Fc/Fc+}$ = 0.49 V relative to SCE in CH_2Cl_2

The E_{LUMO} values obtained confirm that [1,2,5]thiadiazolo[3,4-*d*]pyridazine is one of the strongest electron-acceptor system that is slightly weaker than benzo[1,2-*c*;4,5-*c'*]bis[1,2,5]thiadiazole **11**. The E_{LUMO} values of electron-acceptor molecules in the ground state are proportional to the values of electron affinity (EA), which

is a fundamental molecular property and is crucial for determination of the prospects of their application in materials chemistry. The values of the electron affinity calculated by electron propagator theory[25] showed that replacement of carbon atoms by nitrogen atoms in fused 2,1,3-benzothiadiazoles results in a decrease in these values and, as a consequence, to an increase in the stability of the resulting anion radicals (Figure 3).

Figure 3. Calculated electron affinities of the dibromo derivatives



1, **9**, **10**.

The calculated patterns and experimental results obtained characterize an increased reactivity of [1,2,5]thiadiazolo[3,4-*d*]pyridazine in orbital-controlled ionic and radical reactions of nucleophilic nature and in donor-acceptor interactions as well.

Conclusions

4,7-Dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine was synthesized in good yield by treatment of 5,6-dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione with PBr_5. Nucleophilic aromatic substitution and palladium catalyzed cross-coupling reactions in 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine were successfully used for the selective synthesis of various mono- and bis-substituted derivatives, including functional and aryl(hetaryl) substituents. Oxygen and nitrogen nucleophiles could selectively form both mono- and bis-substituted derivatives. In the case of thiols, the reaction cannot be stopped at the stage of mono-thiols, and bis-thiols were isolated in high yields regardless of the reaction conditions. Cross-coupling reactions should be performed under anhydrous conditions due to the high hydrolytic ability of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine. Suzuki-Miyaura coupling was found to be useful for the preparation of mono-aryl(hetaryl)thiadiazolopyridazines, whereas the Stille reaction allowed us to prepare both mono- and bis-derivatives. The electron-acceptor properties of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine were confirmed by cyclic voltammetry, based on its high reduction potential and E_{LUMO} and calculated electron affinities.

Experimental Section

General Information. The reagents were purchased from commercial sources and used as received. 5,6-Dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione (**3**)[19] (for details see Supporting Information), (5-(1,3-dioxolan-2-yl)thiophen-2-yl)boronic acid (**5b**),[26] (9-hexyl-9H-carbazol-3-yl)boronic acid (**5d**),[27] (4-(diphenylamino)phenyl)boronic acid (**5l**),[28] (4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)boronic acid (**5m**),[29] (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane (**8b**),[30] [2,2'-bithiophen]-5-yltributylstannane (**8j**),[31] tributyl(thiophen-3-yl)stannane (**8k**),[32] tributyl(4-methoxyphenyl)stannane (**8i**),[33] tributyl(p-tolyl)stannane (**8h**)[34] were prepared according to the published methods and characterized by NMR spectra. All synthetic operations were performed under a dry argon atmosphere. Solvents were purified by distillation from the appropriate drying agents.

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were taken with a Bruker AM-300 machine (at frequencies of 300.1 and 75.5 MHz) in $CDCl_3$ or DMSO-d_6 solutions, 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. High-resolution MS spectra were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurement was performed in a positive ion mode (interface capillary voltage –4500 V) or in a negative ion mode (3200 V); mass range was from m/z 50 to m/z 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). Syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 □L/min^{-1}). Nitrogen was applied as a dry gas; interface temperature was set at 180°C. IR spectra were measured with a Bruker "Alpha-T" instrument in KBr pellets.

Cyclic voltammetry measurements were carried out in a dry argon atmosphere using an IPC Pro potentiostat/galvanostat and a three-electrode electrochemical cell. A three-electrode system consisting of platinum or glass carbon as the working electrode, platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode was employed. The reduction and oxidation potentials were determined in DMF and CH_3CN, using 0.1 M tetrabutylammonium perchlorate (n-Bu_4NClO_4) as the supporting electrolyte. The first reduction potentials are referenced to the internal standard redox couple Fc/Fc^+. Ferrocene was added to each sample solution at the end of the experiment, and employed for calibration.

4,7-Dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine (**1**). 5,6-Dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione **3** (650 mg, 3.82 mmol) was added to PBr_5 formed by addition of bromine (1.18 ml, 22.92 mmol) to PBr_3 (2.16 ml, 22.92 mmol) at 0 °C. The mixture was stirred for 9 h at 105 °C. The resulting mixture was cooled to the room temperature, poured into ice, washed with CCl_4, extracted with $CHCl_3$ (3×40ml) and dried over $MgSO_4$. The $CHCl_3$ was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel Merck 60, CH_2Cl_2) to give the title compound **1**. Yield 845 mg (75%), yellow solid. Mp = 199 – 200 °C. (R_f = 0.5, CH_2Cl_2 IR ν_{max} (KBr, cm^{-1}): 1369, 1361, 1343, 1257, 959, 863, 504. ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 149.6. HRMS (ESI-TOF), *m/z*: calcd for $C_4{}^{81}Br_2HN_4S$ $[M+H]^+$, 296.8262, found, 296.8269. MS, *m/z* (%): 298 ($[M+2]^+$, 22), 296 (M^+, 49), 294 ($[M-2]^+$, 28), 217 (27), 215 (28), 136 (52), 84 (67), 32 (100)

The organic layer was extracted with EtOAc (2×25ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel Merck 60, EtOAc) to give 7-bromo[1,2,5]thiadiazolo[3,4-d]pyridazin-4(5H)-one **4**. Yield 71 mg (8%), orange solid. Mp = 222 – 224 °C. IR ν_{max} (KBr, cm^{-1}): 3189, 3147, 3073, 3030, 1691, 1669, 1450, 1419, 1289, 1157, 975, 859, 844, 675, 614, 508. (R_f = 0.12, CH_2Cl_2). ^1H NMR (300 MHz, DMSO-d_6): δ 13.22 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 123.6, 150.5, 153.8, 156.8. HRMS (ESI-TOF), *m/z*: calcd for $C_4H^{79}BrN_4OSNa$ $[M + Na]^+$, 254.8947, found, 254.8939. MS (EI, 70eV), *m/z* (*I*, %): 235 ($[M+2]^+$, 4), 234 ($[M+1]^+$, 100), 233 (M^+, 3), 232 ($[M-1]^+$, 96), 177 (15), 125 (8), 46 (40).

7-Bromo[1,2,5]thiadiazolo[3,4-d]pyridazin-4(5H)-one (**4**). 5,6-Dihydro[1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-dione **3** (50 mg, 0.29 mmol) was added to $POBr_3$ (332 mg, 1.16 mmol) in 4 ml of dry DMF and the reaction mixture was stirred for 6 h at 80 °C. The resulting mixture was cooled to the room temperature, poured into ice, extracted with $CHCl_3$ (3×40ml) and dried over $MgSO_4$. The $CHCl_3$ was evaporated under reduced pressure. The residue was purified by column chromatography

(silica gel Merck 60, CH_2Cl_2) to give the title compound **1**. Yield 25 mg (30%), yellow solid. Then the water layer was extracted with EtOAc (2×25ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel Merck 60, EtOAc) to give the title compound **4**. Yield 27 mg (40%). The water layer was evaporated under reduced pressure to give compound **3**. Yield 10 mg (20%).

General procedure for the preparation of mono-substituted products 6 and bis-substituted products 7 under Suzuki coupling conditions (Procedure A). A mixture of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** (60 mg, 0.2 mmol), boronic acid **5(a-i, k)** (0.4 mmol), Cs_2CO_3 (130 mg, 0.4 mmol), $Pd(PPh_3)_4$ (34 mg, 15% mmol) in dry toluene (4 ml) was degassed by argon and heated at 110 ºC in a sealed vial. On completion (monitored by TLC), the mixture was poured into water and extracted with CH_2Cl_2 (3×35ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

General procedure for the preparation of mono-substituted products 6 under Suzuki coupling conditions (Procedure B). A mixture of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** (60 mg, 0.2 mmol), boronic acid **5(a-c, h, i, k)** (0.2 mmol), Cs_2CO_3 (78 mg, 0.24 mmol), $Pd(PPh_3)_4$ (34 mg,15% mmol) in dry toluene (4 ml) was degassed by argon and heated at 60 ºC in a sealed vial. On completion (monitored by TLC), the mixture was poured into water and extracted with CH_2Cl_2 (3×35ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

General procedure for the preparation of mono-substituted products 6 under Stille coupling conditions (Procedure C). To a solution of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** (60 mg, 0.2 mmol) in anhydrous THF (4 ml) were added $PdCl_2(PPh_3)_2$ (21 mg, 15% mmol) and stannane **8(a-c, h, i, k)** (0.2 mmol). The resulting cloudy yellow mixture was stirred and degassed by argon in a sealed vial. The resulting yellow mixture was then stirred at 55 ºC for the desired time. On completion (monitored by TLC), the mixture was washed with water and the organic layer was extracted with CH_2Cl_2 (3×35ml), dried over $MgSO_4$ and then concentrated in vacuo. The crude product was purified by column chromatography.

General procedure for the preparation of bis-substituted products 17 under Stille coupling conditions (Procedure D). To a solution of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** (60 mg, 0.2 mmol) in anhydrous toluene (4 ml) were added $PdCl_2(PPh_3)_2$ (21 mg, 15% mmol) and stannane **8(a-c, f-k)** (0.4 mmol). The resulting cloudy yellow mixture was stirred and degassed by argon in a sealed vial. The resulting yellow mixture was then stirred at 110 ºC for the desired time. On completion (monitored by TLC), the mixture was washed with water and the organic layer was extracted with CH_2Cl_2 (3×35ml), dried over $MgSO_4$ and then concentrated in vacuo. The crude product was purified by column chromatography.

4-Bromo-7-(thiophen-2-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**6a**). Yellow solid, 36 mg (60%, procedure A) or 45 mg (75%, procedure C), R_f = 0.2 (CH_2Cl_2). Mp = 170 – 172 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 3036, 1691, 1670, 1561, 1528, 1411, 1386, 1338, 1289, 1257, 1158, 976, 861, 839, 508. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (dd, J = 5.2, 3.9 Hz, 1H), 7.70 (dd, J = 5.2 Hz, 1.0 Hz, 1H), 8.67 (dd, J = 3.9 Hz, 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.0, 132.6, 134.0, 136.5, 139.2, 147.2, 149.5, 149.8. HRMS (ESI-TOF), *m/z*: calcd for $C_8H_4{}^{79}BrN_4S_2$ [M + H]$^+$, 298.9055, found, 298.9060. MS (EI, 70eV), *m/z* (*I*, %): 301 ([M+2]$^+$, 16), 300([M+1]$^+$, 45), 299 (M$^+$, 15), 298 ([M-1]$^+$, 48), 219 (100), 39 (55).

4-(5-(1,3-Dioxolan-2-yl)thiophen-2-yl)-7-bromo[1,2,5]thiadiazolo[3,4-d]pyridazine (**6b**). Yellow solid, 43 mg (58%, procedure A) or 52 mg (70%, procedure C), R_f = 0.2 (CH_2Cl_2). Mp = 174 – 176 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2984, 2960, 2898, 2875, 1737, 1727, 1395, 1382, 1355, 1335, 1302, 1211, 1166, 1082, 1024, 967, 939, 865, 831, 788, 522. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 – 4.23 (m, 4H), 6.19 (s, 1H), 7.30 (d, J = 3.8 Hz, 1H), 8.56 (d, J = 3.8 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 65.5, 100.0, 127.5, 133.5, 133.8, 136.9, 139.5, 147.2, 149.5, 149.7. HRMS (ESI-TOF), *m/z*: calcd for $C_{11}H_8{}^{79}BrN_4O_2S_2$ [M + H]$^+$, 370.9267, found, 370.9260. MS (EI, 70eV), *m/z* (*I*, %): 372 ([M+1]$^+$, 15), 371 (M$^+$, 8), 370 ([M-1]$^+$, 12), 369 ([M-2]$^+$, 10), 291 (25), 262 (100), 183 (30).

4-Bromo-7-(furan-2-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**6c**). Yellow solid, 30 mg (53%, procedure A) or 36 mg (64%, procedure C), R_f = 0.2 (CH_2Cl_2). Mp = 169 – 171 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 3096, 1574, 1490, 1342, 1230, 1209, 1018, 972, 866, 790, 643, 591, 511. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.77 (dd, J = 3.6, 1.7 Hz, 1H), 7.88 (d, J = 1.7 Hz, 1H), 8.03 (d, J = 3.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.2, 119.4, 145.5, 147.0, 147.2, 147.7, 147.9, 148.9. HRMS (ESI-TOF), *m/z*: calcd for $C_8H_4{}^{79}BrN_4OS$ [M + H]$^+$, 282.9284, found, 282.9286. MS (EI, 70eV), *m/z* (*I*, %): 285 ([M+2]$^+$, 10), 284 ([M+1]$^+$, 70), 283 (M$^+$, 8), 282 ([M-1]$^+$, 67), 238 (100), 203(55).

4-Bromo-7-(9-hexyl-9H-carbazol-3-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**6d**): Orange solid, 42 mg (45 %, procedure A), R_f = 0.4 (CH_2Cl_2). Mp = 129 – 131 °C. Eluent – CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2954, 2923, 2853, 1594, 1466, 1440, 1399, 1356, 1355, 1314, 1272, 1152, 960, 875, 810, 788, 745, 729, 661, 507. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 6.9 Hz, 3H), 1.31 – 1.45 (m, 6H), 1.89 – 1.99 (m, 2H), 4.37 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 8.23 (d, J = 7.7 Hz, 1H), 8.85 (dd, J = 8.8 Hz, 1.5 Hz, 1H), 9.50 (d, J = 1.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.6, 27.0, 29.0, 31.6, 43.4, 109.2, 109.3, 119.9, 120.8, 123.2, 123.4, 123.5, 123.6, 126.4, 127.7, 139.2, 141.0, 142.6, 148.9, 150.7, 154.6. HRMS (ESI-TOF), *m/z*: calcd for $C_{22}H_{21}{}^{79}BrN_5S$ [M + H]$^+$, 466.0696, found, 466.0684. MS (EI, 70eV), *m/z* (*I*, %): 468 ([M+2]$^+$, 5), 467 ([M+1]$^+$, 53), 466 (M$^+$, 6), 465 ([M-1]$^+$, 51), 396 (74), 205 (80), 179 (100).

4-Bromo-7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)-[1,2,5]thiadiazolo[3,4-d]pyridazine (**6e**). Violet solid, 57 mg (60%, procedure A), R_f = 0.4 (CH_2Cl_2). Mp = 53 – 55 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2926, 2863, 1603, 1513, 1460, 1395, 1329, 1297, 1270, 1137, 1117, 1035, 873, 811, 794, 732, 509. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 – 1.61 (m, 4H), 1.73 – 1.77 (m, 2H), 1.82 – 1.87 (m, 1H), 1.93 – 1.95 (m, 1H), 2.40 (s, 3H), 3.36 – 3.43 (m, 1H), 4.21 – 4.27 (m, 1H), 6.85 (d, J = 8.5 Hz, 1H), 7.21(d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 8.51 (s, 1H), 8.54 (dd, J = 8.5, 1.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.02, 21.05, 22.4, 25.8, 27.8, 40.1, 64.9, 108.4, 122.9, 123.5, 124.7, 130.0, 131.4, 134.4, 135.5, 137.9, 139.1, 148.8, 150.5, 152.7, 153.7. HRMS (ESI-TOF), *m/z*: calcd for $C_{23}H_{21}{}^{79}BrN_5S$ [M + H]$^+$, 478.0696, found, 478.0679. MS (EI, 70eV), m/z (*I*, %): 480 ([M+2]$^+$, 25), 479 ([M+1]$^+$, 98), 478 (M$^+$, 28), 477 ([M-1]$^+$, 100), 434 (75), 267 (45).

4-Bromo-7-(p-tolyl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**6h**). Yellow solid, 25 mg (41%, procedure B) or 25 mg (40%, procedure C), R_f = 0.35 (CH_2Cl_2). Mp = 139 – 141 °C. Eluent - CH_2Cl_2/hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2955, 2854, 1466, 1415, 1395, 1327, 1283, 1192, 966, 877, 830, 790, 663, 574, 519. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3H), 7.43 (d, J = 8.1 Hz, 2H), 8.55 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 129.8, 130.1, 130.2, 140.4, 142.6, 148.8, 150.7, 154.3. HRMS (ESI-TOF), *m/z*: calcd for $C_{11}H_8{}^{79}BrN_4S$ [M + H]$^+$, 306.9648, found, 306.9646. MS (EI, 70eV), m/z (*I*, %): 309 ([M+2]$^+$, 5), 308 ([M+1]$^+$, 25), 307 (M$^+$, 6), 306 ([M-1]$^+$, 20), 227 (100), 143 (60), 69 (98).

4-Bromo-7-(4-methoxyphenyl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**6i**). Yellow solid, 32 mg (49%, procedure B) or 34 mg (52%, procedure C), R_f

= 0.25 (CH_2Cl_2). Mp = 158 – 160 °C. Eluent - CH_2Cl_2. IR ν_{max} (KBr, cm^{-1}): 2963, 2925, 2840, 1603, 1515, 1461, 1397, 1332, 1266, 1191, 1098, 1022, 880, 844, 801, 589, 525. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 7.12 (d, J = 8.0 Hz, 2H), 8.67 (d, J = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 114.5, 125.4, 131.8, 131.9, 139.8, 148.7, 153.6, 162.8. HRMS (ESI-TOF), *m/z*: calcd for $C_{11}H_8{}^{79}BrN_4OS$ [M + H]$^+$, 322.9597, found, 322.9603. MS (EI, 70eV), m/z (*I*, %): 325 ([M+2]$^+$, 6), 324 ([M+1]$^+$, 10), 323 (M$^+$, 8), 322 ([M-1]$^+$, 11), 243 (100), 159 (72), 92 (55), 77 (98).

4-Bromo-7-(thiophen-3-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**6k**). Yellow solid, 21 mg (54%, procedure B) or 41 mg (68%, procedure C), R_f = 0.2 (CH_2Cl_2). Mp = 135 – 137 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 1515, 1455, 1433, 1262, 1100, 1029, 801.683, 509. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (dd, J = 5.2, 2.9 Hz, 1H), 8.31 (dd, J = 5.2, 1.3 Hz, 1H), 8.99 (dd, J = 3.0, 1.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.6, 127.6, 132.1, 134.9, 139.7, 143.1, 148.3, 150.0. HRMS (ESI-TOF), *m/z*: calcd for $C_8H_4{}^{79}BrN_4S_2$ [M + H]$^+$, 298.9055, found, 298.9062. MS (EI, 70eV), *m/z* (*I*, %): 301 ([M+2]$^+$, 10), 300 ([M+1]$^+$, 100), 299 (M$^+$, 8), 298 ([M-1]$^+$, 98), 219 (65), 135 (6), 28 (5).

4,7-Di(thiophen-2-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7a**). Red solid, 48 mg (80%, procedure D) or 5 mg (8%, procedure A), R_f = 0.3 (CH_2Cl_2). Mp = 193 – 195 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v).). IR ν_{max} (KBr, cm^{-1}): 3065, 1528, 1435, 1419, 1400, 1228, 1044, 847, 733, 718, 676, 652, 520. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (dd, J = 4.9, 3.6 Hz, 2H), 7.65 (d, J = 4.9 Hz, 2H), 8.67 (d, J = 3.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.5, 131.3, 132.5, 138.1, 147.8, 148.2. HRMS (ESI-TOF), *m/z*: calcd for $C_{12}H_7N_4S_3$ [M + H]$^+$, 302.9827, found, 302.9831. MS (EI, 70eV), *m/z* (*I*, %): 304 ([M+2]$^+$, 12), 303 ([M+1]$^+$, 15), 302 (M$^+$, 100), 109 (26), 45 (48).

4,7-Bis(5-(1,3-dioxolan-2-yl)thiophen-2-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7b**). Orange solid, 66 mg (74%, procedure D) or 3 mg (4%, procedure A), R_f = 0.1 (CH_2Cl_2). Mp = 168 – 170 °C. Eluent - CH_2Cl_2:EtOAc, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2955, 2924, 2854, 1662, 1542, 1525, 1476, 1459, 1402, 1387, 1329, 1298, 1206, 1151, 1082, 1067, 1034, 970, 940, 882, 864, 855, 819, 800, 678, 656, 525. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.04 – 4.24 (m, 8H), 6.22 (s, 2H), 7.31 (d, J = 3.9 Hz, 2H), 8.57 (d, J = 3.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.4, 100.2, 127.3, 132.5, 138.5, 147.9, 148.3, 148.3. HRMS (ESI-TOF), *m/z*: calcd for $C_{18}H_{15}N_4O_4S_3$ [M + H]$^+$, 447.0250, found, 447.0252. MS (EI, 70eV), *m/z* (*I*, %): 447 ([M+1]$^+$, 5), 446 (M$^+$, 25), 445 ([M-1]$^+$, 3), 120 (35), 73 (55), 45 (100).

4,7-Di(furan-2-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7c**). Orange solid, 31 mg (57%, procedure D), R_f = 0.1 (CH_2Cl_2). Mp = 112 – 114 °C. Eluent - CH_2Cl_2:EtOAc, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 3102, 1578, 1486, 1460, 1389, 1267, 1058, 1017, 976, 870, 594, 515. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.76 (dd, J = 3.6, 1.7 Hz, 2H), 7.87 (d, J = 1.7 Hz, 2H), 7.99 (d, J = 3.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.9, 118.0, 144.3, 146.6, 147.3, 148.3. HRMS (ESI-TOF) , *m/z*: calcd for $C_{12}H_7N_4O_2S$ [M + H]$^+$, 271.0284, found, 271.0280. MS (EI, 70eV), *m/z* (*I*, %): 272 ([M+2]$^+$, 10), 271 ([M+1]$^+$, 25), 270 (M$^+$, 100), 149 (12), 57 (8).

4,7-Diphenyl[1,2,5]thiadiazolo[3,4-d]pyridazine (**7f**). Yellow solid, 20 mg (35%, procedure A) or 19 mg (32%, procedure D), R_f = 0.35 (CH_2Cl_2). Mp = 207 – 208 °C. Eluent - CH_2Cl_2/hexane, 1:1 (v/v). The spectral data correspond to the literature.[35] HRMS (ESI-TOF), *m/z*: calcd. for $C_{16}H_{11}N_4S$ 291.0699 [M + H]$^+$, found 291.0697.

4,7-Bis(4-chlorophenyl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7g**). Yellow solid, 14 mg (20%, procedure A) or 17 mg (24%, procedure D), R_f = 0.4 (CH_2Cl_2). Mp > 260 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 3039, 1588, 1412, 1090, 1013, 833, 826, 721, 525. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.72 (d, J = 8.3 Hz, 4H), 8.67 (d, J = 8.3 Hz, 4H). HRMS (ESI-TOF), *m/z*: calcd for $C_{16}H_9{}^{35}Cl_2N_4S$ [M + H]$^+$, 358.9919, found, 358.9928. MS (EI, 70eV), *m/z* (*I*, %): 360 ([M+1]$^+$, 80), 359 (M$^+$, 20), 358 ([M-1]$^+$, 100), 277 (10).

4,7-Di-p-tolyl[1,2,5]thiadiazolo[3,4-d]pyridazine (**7h**). Yellow solid, 32 mg (50%, procedure A) or 35 mg (55%, procedure D), R_f = 0.3 (CH_2Cl_2). Mp = 193 – 195 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2956, 2853, 1415, 1400, 1188, 886, 825, 721, 662, 609, 523. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51 (s, 6H), 7.44 (d, J = 8.1 Hz, 4H), 8.65 (d, J = 8.1 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 129.5, 129.7, 131.3, 141.5, 149.7, 152.8. HRMS (EI-MS): calcd. for $C_{18}H_{15}N_4S$ 319.1012 [M + H]$^+$, found 319.1008. MS, m/z (%): 320 ([M+2]$^+$, 6), 319 ([M+1]$^+$, 25), 318 (M$^+$, 100), 168 (26), 91 (16).

4,7-Bis(4-methoxyphenyl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7i**). Orange solid, 46 mg (65%, procedure A) or 47 mg (67%, procedure D), R_f = 0.1 (CH_2Cl_2). Mp = 210 – 212 °C. Eluent - CH_2Cl_2. The spectral data correspond to the literature.[33] ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 6H), 7.15 (d, J = 8.9 Hz, 4H), 8.78 (d, J = 8.9 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 114.3, 126.9, 131.5, 149.8, 152.0, 162.2. HRMS (ESI-TOF), *m/z*: calcd for $C_{18}H_{15}N_4O_2S$ [M + H]$^+$, 351.0910, found, 351.0910. MS (EI, 70eV), m/z (*I*, %): 351, ([M+1]$^+$, 22), 350 (M$^+$, 100), 184 (48), 90 (30).

4,7-Di([2,2'-bithiophen]-5-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7j**). Red solid, 61 mg (65%, procedure D), R_f = 0.4 (CH_2Cl_2). Mp = 178 – 180 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v). IR ν_{max} (KBr, cm^{-1}): 2923, 1510, 1447, 1366, 1346, 1335, 1295, 1268, 1257, 1227, 1162, 1062, 991, 963, 884, 864, 846, 836, 814, 787, 728, 709, 637, 534, 506. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (dd, J = 3.9, 3.5 Hz, 2H), 7.36 (d, J = 3.5 Hz, 2H), 7.37 (d, J = 3.9 Hz, 2H), 7.42 (d, J = 3.5 Hz, 2H), 8.63 (d, J = 3.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.7, 122.2, 122.5, 123.9, 124.1, 132.4, 135.5, 136.8, 139.7, 151.1. HRMS (ESI-TOF), *m/z*: calcd for $C_{20}H_{11}N_4S_5$ [M + H]$^+$, 466.9582, found, 466.9578.

4,7-Di(thiophen-3-yl)[1,2,5]thiadiazolo[3,4-d]pyridazine (**7k**). Orange solid, 11 mg (35%, procedure A) or 46 mg (76%, procedure D), R_f = 0.35 (CH_2Cl_2). Mp = 186 – 188 °C. Eluent - CH_2Cl_2:hexane, 1:1 (v/v).). IR ν_{max} (KBr, cm^{-1}): 3081, 1853, 1508, 1441, 1234, 1109, 1078, 951, 864, 798, 690, 617, 512. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (dd, J = 5.1, 3.0 Hz, 2H), 8.41 (d, J = 5.1 Hz, 2H), 9.01 (d, J = 3.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.1, 127.4, 130.7, 136.0, 148.5, 149.0. HRMS (ESI-TOF), *m/z*: calcd for $C_{12}H_7N_4S_3$ [M + H]$^+$, 302.9827, found, 302.9822. MS (EI, 70eV), *m/z* (*I*, %): 302 (M$^+$, 100), 301 ([M+1]$^+$, 15), 302 ([M+2]$^+$, 8), 185 (20), 149 (12)..

Acknowledgements

We gratefully acknowledge financial support from the Russian Science Foundation (grant no. 15-13-10022). Authors are grateful to Dr. E. A. Chulanova for conducting preliminary calculations, and to Professor A. S. Mendkovich for valuable advices.

Keywords: [1,2,5]thiadiazolo[3,4-*d*]pyridazine; cross-coupling; palladium

[1] a) S. Chaurasia, J. T. Lin, *Chem. Rec.*, **2016**, *16*, 1311-1336; b) C.-P. Lee, C.-T. Li, K.-C. Ho, *Materials Today*, **2017**, *20*, 267-283; c) E. A. Knyazeva, O. A. Rakitin, *Russ. Chem. Rev*., **2016**, *85*, 1146-1183; d) W. Chen, Q. Zhang, *J. Mater. Chem. C*, **2017**, *5*, 1275-1304; e) H.-L. Cheng, Z.-S. Huang, L. Wang, H. Meier, D. Cao, *Dyes Pigm*., **2017**, *137*, 143-151; f) X. Zhang, M. Grätzel, J. Hua, *Front. Optoelectron*., **2016**, *9*, 3-37.

[2] a) J. Qi, W. Qiao, Z. Y. Wang, *Chem. Rec*., **2016**, *16*, 1531-1548; b) A. L. Antaris, H. Chen, K. Cheng, Y. Sun, G. Hong, C. Qu, S. Diao, Z. Deng, X. Hu, B. Zhang, X. Zhang, O. K. Yaghi, Z. R. Alamparambil, X. Hong, Z. Cheng, H. Dai, *Nat. Mater*., **2016**, *15*, 235-242; c) L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, *Chem. Rev*., **2015**, *115*, 12633-12665.

[3] F. Ni, Z. Wu, Z. Zhu, T. Chen, K. Wu, C. Zhong, K. An, D. Wei, D. Ma, C. Yang, *J. Mater. Chem. C*, **2017**, *5*, 1363-1368.

[4] a) P. Y. Gu, N. Wang, C. Wang, Y. Zhou, G. Long, M. Tian, W. Chen, X. W. Sun, M. G. Kanatzidis, Q. Zhang, *J. Mater. Chem. A* **2017**, *5*, 7339-7344; b) C. Chenga, H. Geng, Y. Yi, Z. Shuai, *J. Mater. Chem. C* **2017**, *5*, 3247-3253.

[5] a) F. Z. Chen, J. Zhang, W. Qu, X. Zhong, H. Liu, J. Ren, H. He, X. Zhang, S. Wang, *Sensors Actuators B*, **2018**, *266*, 528-533; b) D. L. Crossley, L. Urbano, R. Neumann, S. Bourke, J. Jones, L. A. Dailey, M. Green, M. J. Humphries, S. M. King, M. L. Turner, M. J. Ingleson, *ACS Appl. Mater. Inter*. **2017**, *9*, 28243-28249; c) A. A. R. Mota, J. R. Correa, P. H. P. R. Carvalho, N. M. P. de Sousa, H. C. B. de Oliveira, C. C. Gatto, D. A. da Silva, A. L. de Oliveira, B. A. D. Neto, *J. Org. Chem.* **2016**, 81, 2958-2965.

[6] a) C. Duan, F. Huang, Y. Cao, *J. Mater. Chem*. **2012**, *22*, 10416-10434; b) A. Pron, M. Leclerc, *Prog. Polym. Sci.* **2013**, *38*, 1815-1831.

[7] a) Y. Zhang, J. Zou, C.-C. Cheuh, H.-L. Yip A., K.-Y. Jen, *Macromolecules* **2012**, *45*, 5427-5435; b) A. C. Stuart, J. R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade, W. You, *J. Am. Chem. Soc.* **2013**, *135*, 1806-1815.

[8] a) Y. Zhao, Y. Guo, Y. Liu, *Adv. Mater.* **2013**, *25*, 5372-5391; b) X. Guo, A. Facchetti, T. J. Marks, *Chem. Rev.* **2014**, *114*, 8943-9021.

[9] a) H. A. M. van Mullekom, J. Vekemans, E. E. Havinga, E. W. Meijer, *Mater. Sci. Eng. R* **2001**, *32*, 1-40; b) J. Roncali, *Macromol. Rapid Commun*. **2007**, *28*, 1761-1775; c) T. C. Parker, D. G. (Dan) Patel, K. Moudgil, S. Barlow, C. Risko, J.-L. Brédas, J. R. Reynolds, S. R. Marder, *Mater. Horiz*. **2015**, *2*, 22-36.

[10] Y. Wu, W.-H. Zhu, S. M. Zakeeruddin, M. Grätzel, *ACS Appl. Mater. Inter*. **2015**, *7*, 9307-9318.

[11] a) B. A. D. Neto, A. A. M. Lapis, E. N. da Silva and J. Júnior Dupont, *Eur. J. Org. Chem.* **2013**, *2*, 228-255; b) L. S. Konstantinova, E. A. Knyazeva, O. A. Rakitin, *Org. Prep. Proc. Int.* **2014**, *46*, 475-544.

[12] a) Y. Tsubata, T. Suzuki, Y. Yamashita, T. Mukai, T. Miyashi, *Heterocycles* **1992**, *33*, 337-348; b) K. Susumu, T. V. Duncan, M. J. Therien, *J. Amer. Chem. Soc*. **2005**, *127*, 5186-5195; c) G. Zhang, Y. Fu, Q. Zhang, Z. Xie, *Polymer* **2010**, *51*, 2313-2319.

[13] a) Y. Yamashita, K. Ono, M. Tomura, S. Tanaka, *Tetrahedron* **1997**, *53*, 10169-10178; b) T. L. Tam, H. Li, F. Wei, K. J. Tan, C. Kloc, Y. M. Lam, S. G. Mhaisalkar, A. C. Grimsdale, *Org. Lett*. **2010**, *12*, 3340-3343.

[14] a) L. Ying, B. B. Y. Hsu, H. Zhan, G. C. Welch, P. Zalar, L. A. Perez, E. J. Kramer, T.-Q. Nguyen, A. J. Heeger, W.-Y. Wong, G. C. Bazan, *J. Amer. Chem. Soc*. **2011**, *133*, 18538-18541; b) G. C. Welch, L. A. Perez, C. V. Hoven, Y. Zhang, X.-D. Dang, A. Sharenko, M. F. Toney, E. J. Kramer, T.-Q. Nguyen, G. C. Bazan, *J. Mater. Chem*. **2011**, *21*, 12700-12709; c) Z. B. Henson, G. C. Welch, T. Van Der Poll, G. C. Bazan, *J. Amer. Chem. Soc*. **2012**, *134*, 3766-3779.

[15] a) M. Abdulrazzaq, M. I. Ozkut, G. Gokce, S. Ertan, E. Tutuncu, A. Cihaner, *Electrochim. Acta* **2017**, *249*, 189-197; b) Y. Liu, H. Phan, T. S. Herng, T. Y. Gopalakrishna, J. Ding, J. Wu, *Chem. Asian J.* **2017**, *12*, 2177-2182; c) B. Wang, G. Feng, M. Seifrid, M. Wang, B. Liu, G. C. Bazan, *Angew. Chem., Inter. Ed*. **2017**, *56*, 16063-16066; d) C. Zhang, Z. Chen, W. Zeng, G. Yu; C. Yang, *Dyes Pigm*. **2016**, *130*, 291-297; e) S. Huang, R. K. Kannadorai, Y. Chen, Q. Liu, M. Wang, *Chem. Commun*. **2015**, *51*, 4223-4226; f) G. Qian, Z. Y. Wang, *Can. J. Chem*. **2010**, *88*, 192-206; g) T. Kono, D. Kumaki, J. Nishida, S. Tokito, Y. Yamashita, *Chem. Commun*. **2010**, *46*, 3265-3267; h) G. Qian, X. Li, Z. Y. Wang, *J. Mater. Chem*. **2009**, *19*, 522-530.

[16] M. Abdo, S. P. Brown, J. R. Courter, M. J. Tucker, R. M. Hochstrasser, A. B. Smith, *Org. Lett*. **2012**, 14, 3518-3521.

[17] Pop, F.; Ding, J.; Daku, L. M. L.; Hauser, A.; Avarvari, N., *RSC Adv*. **2013**, *3*, 3218-3221.

[18] J. Marn, B. Stanovnik, M. Tishler, *Croatica Chem. Acta* **1971**, *43*, 101-105.

[19] I. Sekikawa, *Bull. Chem. Soc. Japan* **1960**, *33*, 1229-1231.

[20] a) B. Wang, M. Wang, A. Mikhailovsky, S. Wang, G. C. Bazan, *Angew. Chem., Int. Ed*. **2017**, *56*, 5031-5034; b) Y. Hua, J. He, C. Zhang, C. Qin, L. Han, J. Zhao, T. Chen, W.-Y. Wong, W.-K. Wong, X. Zhu, *J. Mater. Chem. A* **2015**, *3*, 3103-3112.

[21] a) Y. Adachi, Y. Ooyama, N. Shibayama, J. Ohshita, *Dalton Trans*. **2016**, *45*, 13817-13826; b) Y. Hua, H. Wang, X. Zhu, A. Islam, L. Han, C. Qin, W.-Y. Wong, W.-K. Wong, *Dyes Pigm*. **2014**, *102*, 196-203.

[22] I. C. Christoforou, P. A. Koutentis, C. W. Rees, *Org. Biomol. Chem*. **2003**, *1*, 2900-2907.

[23] E. O. Sherman, Jr., S. M. Lambert, K.Pilgram, *J. Heterocycl. Chem*. **1974**, *11*, 763-769.

[24] a) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.* **2011**, *23*, 2367-2371; b) P. Bujak, I. Kulszewicz-Bajer, M. Zagorska, V. Maurel, I. Wielgus, A. Pron, *Chem. Soc. Rev.* **2013**, *42*, 8895-8999.

[25] O. Dolgounitcheva, M. Díaz-Tinoco, V. G. Zakrzewski, R. M. Richard, N. Marom, C. D. Sherrill, J. V. Ortiz, *J. Chem. Theory Comput*. **2016**, *12*, 627-637.

[26] B. Mátravölgyi, T. Hergert, A. Thurner, V. Bálint, N. Sangiorgi, R. Bendoni, L. Zani, G. Reginato, M. Calamante, A. Sinicropi, A. Sanson, F. Faigl, A. Mordini, *Eur. J. Org. Chem.* **2017**, 1843-1854.

[27] G.-L. Feng, S.-J. Ji, W.-Y. Lai, W. Huang, *Synlett*, **2006**, *17*, 2841-2845.

[28] Wu, W.; Cheng, C.; Wu, W.; Guo, H.; Ji, S.; Song, P.; Han, K.; Zhao, J.; Zhang, X.; Wu, Y.; Du, G. *Eur. J. Inorg. Chem.* **2010**, *29*, 4683.

[29] D. Wang, W. Ying, X. Zhang, Y. Hu, W. Wu, J. Hua, *Dyes Pigm.* **2015**, *112*, 327-334.

[30] D. Prim, A. Auffrant, Z. F. Plyta, J.-P. Tranchier, F. Rose-Munch, E. Rose, *J. Organomet. Chem.* **2001**, *624*, 124-130.

[31] T. Kitagawa, H. Matsubara, T. Okazaki, K. Komatsu, *Molecules*, **2014**, *19*, 15298-15313.

[32] A. Leliège, C.-H. L. Régent, M. Allain, P. Blanchard, J. Roncali, *Chem. Commun.* **2012**, *48*, 8907-8909.

[33] A. Oikawa, G. Kindaichi, Y. Shimotori, M. Okimoto, M. Hoshi, *Tetrahedron,* **2015**, *71*, 1705-1711.

[34] P. J. Dunn, C. W. Rees, *J. Chem. Soc., Perkin Trans. 1* **1987**, 1579-1584.

[35] M. Shuntaro, M. Osamu, L.W. Hua, T. Masashi, T. Kazufumi, T. Akiyoshi, *J. Het. Chem*. **1992**, *29*, 87-92.

FULL PAPER

Introduction

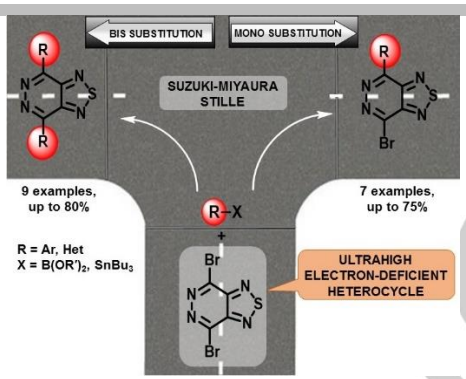
Results and discussion

Conclusions

Experimental section

Acknowledgments

References



[1,2,5]Thiadiazolo[3,4-*d*]pyridazine

*Timofey N. Chmovzh, Ekaterina A. Knyazeva, Ludmila V. Mikhalchenko, Ivan S. Golovanov, Stanislav A. Amelichev, Oleg A. Rakitin**

Page No. – Page No.

Synthesis of 4,7-dibromo derivative of ultrahigh electron-deficient [1,2,5]thiadiazolo[3,4-*d*]pyridazine heterocycle and its cross-coupling reactions