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Short Note

(*E*)-4-(2-(7-Bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)vinyl)-*N*,*N*-diphenylaniline

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Abstract: (Diphenylamino)phenylethenyl group-containing chromophores are widely employed to design effective materials with useful electronic properties. In this communication, (*E*)-4-(2-(7-Bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)vinyl)-*N*,*N*-diphenylaniline was regioselectively obtained by the Heck reaction of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine with *N*,*N*-diphenyl-4-vinylaniline. The structure of the newly synthesized compound was established by means of elemental analysis, high resolution mass-spectrometry, ^{1}H, ^{13}C, NOESY NMR, IR and UV spectroscopy and mass-spectrometry.

Keywords: [1,2,5]thiadiazolo[3,4-*c*]pyridines; *N*,*N*-diphenyl-4-vinylaniline; Heck reaction; (diphenylamino)phenylethenyl derivatives

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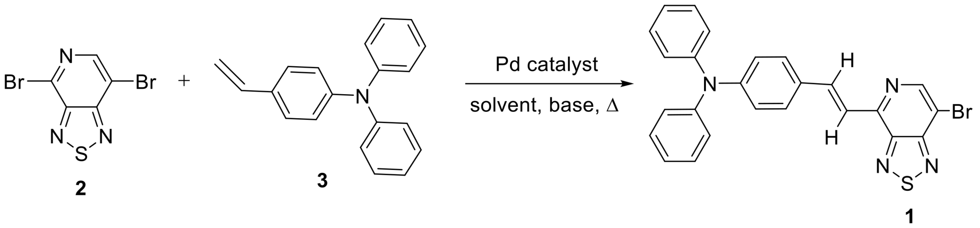
1. Introduction

2,1,3-Benzothiadiazole (BTD)-based dyes containing various combinations of donor (D), acceptor (A), and π-spacer building blocks are of considerable interest to chemists working in the synthesis of various electronic materials [1,2]. It was found that BTD chromophores containing a (diphenylamino)phenylethenyl group were treated as compounds with large two-photon absorption cross-sections and high fluorescent quantum yields in orange-red color [3], red-fluorescent dyes with enhanced two-photon absorption cross-sections [4], solution processable organic solar cells [5], and for the surface modification of a fragile organic 1D microstructure [6]. Mono(diphenylamino)phenylethenylbenzothiadiazoles have proven to be important precursors for the preparation of unsymmetrical BTD derivatives to create the desired materials [7]. To the best of our knowledge (diphenylamino)phenylethenyl group-containing 1,2,5-thiadiazolo[3,4-*c*]pyridines have not been described in the literature. Meanwhile, derivatives of this and similar heterocyclic systems can exhibit interesting physical properties [8–11]. Herein, we report the regioselective synthesis of (*E*)-4-(2-(7-bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)vinyl)-*N*,*N*-diphenylaniline **1** by the Heck reaction of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** with *N*,*N*-diphenyl-4-vinylaniline **3**.

2. Results and Discussion

We have studied the Heck cross-coupling reaction of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine **3** with of *N*,*N*-diphenyl-4-vinylaniline **3** (1 equiv) in the presence of a palladium catalyst (Scheme 1, Table 1). The search for optimal conditions for the selective introduction of a donor substituent was carried out by varying the nature of palladium catalysts, bases, solvents, temperature, and time of chemical transformations. When the reaction was carried out in the presence of palladium acetate ($Pd(OAc)_2$) in DMF and K_2CO_3 as a base at 80 °C, complete decomposition of the starting dibromide **2** was observed with the formation of a mixture of unidentifiable compounds (Table 1, entry 1). The replacement of palladium acetate with tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) in the same solvent was also unsuccessful (Entry 2). However, the use of toluene as a solvent made it possible to isolate the Heck cross-coupling reaction product 1 (Entry 3). The replacement of the inorganic base (K_2CO_3) by triethylamine (Et_3N) led to the formation of monocoupling product 1 in 38% yield (Entry 4). An increase in the reaction time led only to a slight increase in the yield of the target product up to 45% (Entry 5).

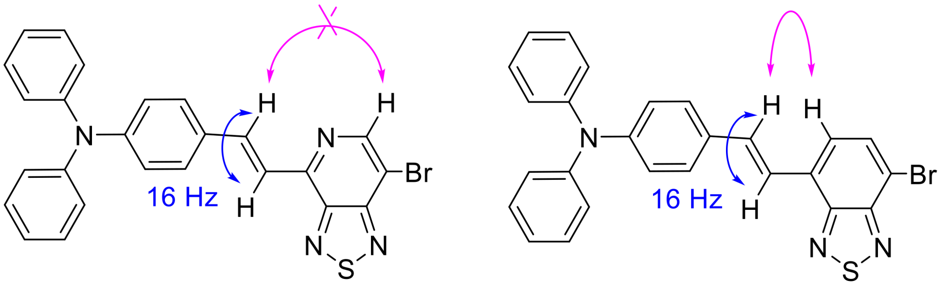


Scheme 1. Synthesis of (*E*)-4-(2-(7-bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)vinyl)-*N*,*N*-diphenylaniline **1**.

Table 1. Reaction of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** with *N*,*N*-diphenyl-4-vinylaniline **3**.

Entry	Catalyst	Base	Solvent	Temperature, °C	Time, h	Yield, of 3%
1	$Pd(OAc)_2$	K_2CO_3	DMF	80	8	0
2	$Pd(PPh_3)_4$	K_2CO_3	DMF	80	10	0
3	$Pd(PPh_3)_4$	K_2CO_3	Toluene	110	10	3
4	$Pd(PPh_3)_4$	Et_3N	Toluene	110	48	38
5	$Pd(PPh_3)_4$	Et_3N	Toluene	110	64	45

The evidence for the formation of the *E*-isomer was the presence of a large spin–spin constant of approximately 16 Hz between the protons of the ethylene fragment (see Experimental part) (compare with the data in [7]), which, for the *Z*-isomer, would be approximately 11 Hz [12]. It has been previously shown that cross-coupling reactions with 4,7-dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine occur preferentially over the electron-deficient position 4, closest to the pyridine nitrogen atom [13,14]. The selective introduction of a donor moiety in cross-coupling reactions has been proven by 2D NMR spectroscopy. In the two-dimensional proton–proton interaction (NOESY) spectrum of compound **1**, the pyridine ring proton did not cross-peak with the protons of the ethylene moiety (see Figure S6 in Supplementary Materials). When a bromine atom is replaced by an ethylene group at position 7 in the two-dimensional spectrum of proton–proton interaction (NOESY), the proton of the pyridine ring would have a cross-peak with the proton of the ethylene fragment, as in the case of 4-bromo-7-{2-[4-(diphenylamino)phenyl]ethenyl}-2,1,3-benzothiadiazole 4, as described in the literature [7] (see Figure 1 and Figure S7 in Supplementary Materials).



1 **4**

Figure 1. Cross-peak interactions in NOESY NMR spectra of compounds **1** and **4**.

The structure of (*E*)-4-(2-(7-bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)vinyl)-*N*,*N*-diphenylaniline 1 was confirmed by means of elemental analysis, high resolution mass-spectrometry, ^{1}H, ^{13}C, NOESY NMR, IR and UV spectroscopy, and mass-spectrometry. This compound may be used if the synthesis of unsymmetrical disubstituted [1,2,5]thiadiazolo[3,4-*c*]pyridines as chromophores in various optoelectronic devices.

3. Materials and Methods

4,7-Dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine **1** [15] and *N*,*N*-diphenyl-4-vinylaniline **2** [16] were prepared according to the published methods. The solvents and reagents were purchased from commercial sources and used as received. Elemental analysis was performed on a 2400 Elemental Analyzer (Perkin Elmer Inc., Waltham, MA, USA). The melting point was determined on a Kofler hot-stage apparatus and is uncorrected. ^{1}H and ^{13}C NMR spectra were taken with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA), at frequencies of 300 and 75 MHz, in $CDCl_3$ solution, with TMS as the standard. J values are given in Hz. The IR spectrum was measured with a Bruker "Alpha-T" instrument (Santa Barbara, CA, USA) in KBr pellet. The high-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). Solution UV–visible absorption spectra were recorded using an OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer (St. Petersburg, Russia) controlled with SF-2000 software (St. Petersburg, Russia). The sample was measured in a 1 cm quartz cell at room temperature with 2.8×10^{-5} mol/mL concentration in CH_2Cl_2.

The synthesis of (*E*)-4-(2-(7-bromo-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)vinyl)-*N*,*N*-diphenylaniline **1** (Supplementary Materials).

$Pd(PPh_3)_4$ (51 mg, 15 %mol), Et_3N (1 mL), and vinylaniline **3** (92 mg, 0.3 mmol) were added to a solution of 4,7-dibromo[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** (100 mg, 0.3 mmol) in anhydrous toluene (5 mL). The resulting mixture was degassed by argon in a sealed vial and then stirred at 110 °C for 64 h. On completion (monitored by TLC), water (30 mL) was added to reaction mixture and the organic layer was extracted with CH_2Cl_2 (3 × 35 mL), dried with $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH_2Cl_2, 2:1, *v*/*v*). Yield 65 mg (45%), red solid, R_f = 0.4 (hexane–CH_2Cl_2, 2:1, *v*/*v*). Mp = 28–30 °C. IR spectrum, ν, cm^{-1}: 2957, 2924, 2853, 1591, 1543, 1511, 1493, 1462, 1327, 1278, 1080, 956, 753, 697. ^{1}H-NMR (ppm): δ 8.69 (s, 1H), 8.35 (d, *J* = 16.1, ^{1}H), 7.76 (d, *J* = 16.0, 1H), 7.61 (d, *J* = 8.7, 2H), 7.35–7.28 (m, 4H), 7.19–7.07 (m, 8H). ^{13}C-NMR (ppm): δ 157.8, 147.7, 146.7, 145.2, 143.7, 133.0, 129.7, 129.2, 127.3, 127.0, 126.3, 124.2, 124.0, 122.7, 122.0. HRMS (ESI-TOF), *m*/*z*: calcd for $C_{25}H_{17}{}^{79}BrN_4S$ $[M]^+$, 484.0352, found, 484.0349. UV–Vis spectra (in CH_2Cl_2), λmax: 359 nm (ε 13,538 M^{-1} cm^{-1}), 501 nm (ε = 3533 M^{-1} cm^{-1}). Anal. calcd. for $C_{25}H_{17}{}^{79}BrN_4S$ (484.0352): C, 61.86; H, 3.53; N, 11.54. Found: C, 61.80; H, 3.45; N, 11.48%.

Supplementary Materials: The following supporting information can be downloaded online: copies of ^{1}H, ^{13}C NMR, IR, HMRS, UV–Vis, and NOESY spectra for the compound **1**.

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Sample Availability: Samples of the compounds **1**–**4** are available from the authors.

References

1. Rakitin, O.A. Recent Developments in the Synthesis of 1,2,5-Thiadiazoles and 2,1,3-Benzothiadiazoles. *Synthesis* **2019**, *51*, 4338–4347. [CrossRef]
2. Neto, B.A.D.; Lapis, A.A.M.; da Silva Júnior, E.N.; Dupont, J. 2,1,3-Benzothiadiazole and Derivatives: Synthesis, Properties, Reactions, and Applications in Light Technology of Small Molecules. *Eur. J. Org. Chem.* **2013**, *2013*, 228–255. [CrossRef]
3. Kato, S.; Matsumoto, T.; Ishi-i, T.; Thiemann, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Yamashita, Y.; Mataka, S. Strongly red-fluorescent novel donor–π-bridge–acceptor–π-bridge–donor (D–π–A–π–D) type 2,1,3-benzothiadiazoles with enhanced two-photon absorption cross-sections. *Chem. Commun.* **2004**, 2342–2343. [CrossRef]
4. Kato, S.; Matsumoto, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Ishi-i, T.; Mataka, S. Novel 2,1,3-Benzothiadiazole-Based Red-Fluorescent Dyes with Enhanced Two-Photon Absorption Cross-Sections. *Chem. -A Eur. J.* **2006**, *12*, 2303–2317. [CrossRef]
5. He, C.; He, Q.; Yi, Y.; Wu, G.; Bai, F.; Shuai, Z.; Li, Y. Improving the efficiency of solution processable organic photovoltaic devices by a star-shaped molecular geometry. *J. Mater. Chem.* **2008**, *18*, 4085. [CrossRef]
6. Wang, X.; Yan, J.; Zhou, Y.; Pei, J. Surface Modification of Self-Assembled One-Dimensional Organic Structures: White-Light Emission and Beyond. *J. Am. Chem. Soc.* **2010**, *132*, 15872–15874. [CrossRef]
7. Ishi-i, T.; Taguri, Y.; Kato, S.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Mataka, S. Singlet oxygen generation by two-photon excitation of porphyrin derivatives having two-photon-absorbing benzothiadiazole chromophores. *J. Mater. Chem.* **2007**, *17*, 3341. [CrossRef]
8. Rakitin, O.A. Fused 1,2,5-thia- and 1,2,5-selenadiazoles: Synthesis and application in materials chemistry. *Tetrahedron Lett.* **2020**, *61*, 152230. [CrossRef]
9. Chmovzh, T.N.; Kudryashev, T.A.; Rakitin, O.A. 4,7-Bis(dodecylthio)-[1,2,5]thiadiazolo[3,4-c]pyridine. *Molbank* **2021**, *2021*, M1291. [CrossRef]
10. Knyazeva, E.A.; Wu, W.; Chmovzh, T.N.; Robertson, N.; Woollins, J.D.; Rakitin, O.A. Dye-sensitized solar cells: Investigation of D-A-π-A organic sensitizers based on [1,2,5]selenadiazolo[3,4-c]pyridine. *Sol. Energy* **2017**, *144*, 134–143. [CrossRef]
11. Bolshakov, O.I.; Grishina, M.A.; Galushko, A.S.; Potemkin, V.A.; Rakitin, O.A. Design and theoretical study of D–A–π–A organic sensitizers with [1,2,5]thiadiazolo[3,4-c]pyridine, [1,2,5]selenadiazolo[3,4-c]pyridine, [1,2,5]oxadiazolo[3,4-c]pyridine π component. *J. Chem.* **2015**, *2015*, 467593. [CrossRef]
12. Goossen, L.J.; Rodríguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L.M. Biaryl Synthesis via Pd-Catalyzed Decarboxylative Coupling of Aromatic Carboxylates with Aryl Halides. *J. Am. Chem. Soc.* **2007**, *129*, 4824–4833. [CrossRef]
13. Welch, G.C.; Perez, L.A.; Hoven, C.V.; Zhang, Y.; Dang, X.-D.; Sharenko, A.; Toney, M.F.; Kramer, E.J.; Nguyen, T.-Q.; Bazan, G.C. A modular molecular framework for utility in small-molecule solution-processed organic photovoltaic devices. *J. Mater. Chem.* **2011**, *21*, 12700. [CrossRef]
14. Henson, Z.B.; Welch, G.C.; van der Poll, T.; Bazan, G.C. Pyridalthiadiazole-Based Narrow Band Gap Chromophores. *J. Am. Chem. Soc.* **2012**, *134*, 3766–3779. [CrossRef]
15. Sun, Y.; Chien, S.-C.; Yip, H.-L.; Zhang, Y.; Chen, K.-S.; Zeigler, D.F.; Chen, F.-C.; Lin, B.; Jen, A.K.-Y. High-mobility low-bandgap conjugated copolymers based on indacenodithiophene and thiadiazolo[3,4-c]pyridine units for thin film transistor and photovoltaic applications. *J. Mater. Chem.* **2011**, *21*, 13247–13255. [CrossRef]
16. McKeown, N.B.; Badriya, S.; Helliwell, M.; Shkunov, M. The synthesis of robust, polymeric hole-transport materials from oligoarylamine substituted styrenes. *J. Mater. Chem.* **2007**, *17*, 2088–2094. [CrossRef]