

Short Note

5-(9-(*p*-Tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde

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Abstract: Donor- π spacer-acceptor (D- π -A) dyes are among the most attractive structures for the design of organic dye-sensitized solar cells (DSSCs). Typically, the key intermediates for these sensitizers are D- π compounds containing an aldehyde group to which an anchor acceptor group is attached via the Knoevenagel reaction. In this communication, 5-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde was prepared via the Suzuki cross-coupling reaction. The structure of the newly synthesized compound was established by means of high-resolution mass spectrometry, ^1H NMR, ^{13}C NMR, IR, and UV-Vis spectroscopy. The title compound would be used in the synthesis of sensitizers for DSSCs.

Keywords: donor-acceptor dyes; Suzuki cross-coupling reaction; aldehydes; boronic esters; 2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole



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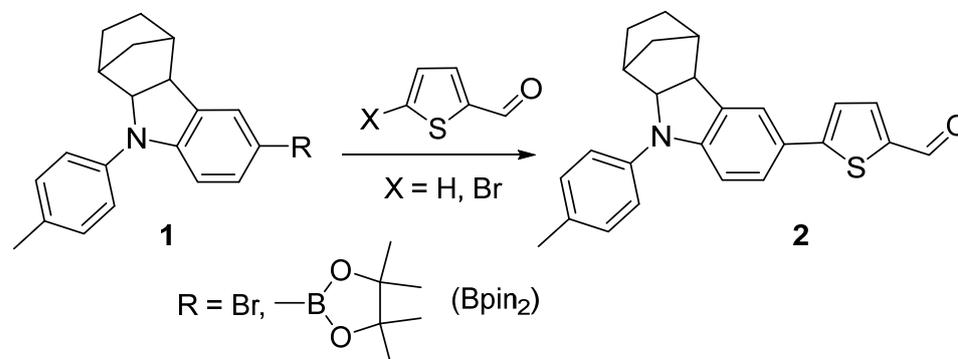
1. Introduction

In recent years, solar-to-electricity converters such as organic solar cells have gained significant interest, not only theoretically but also in practice [1,2]. Using organic materials instead of traditional inorganic ones offers many advantages, such as ease of device manufacture, low cost, universal molecular design, and ease of control over the physical properties of materials [3,4]. Dye-sensitized solar cells (DSSCs) based on organic dyes are one of the most promising devices for the transformation of solar energy [5,6]. However, industrial applications of organic solar cells are hampered by issues related to cost, synthesis scalability, and the stability of organic dyes [2,7,8]. Organic sensitizers for DSSCs, as a rule, have a D- π -A-type donor-acceptor structure, in which the acceptor also acts as an anchor during adsorption on the surface of nanocrystalline TiO_2 [9,10]. In this case, the donor (D) and acceptor (A) parts are connected to each other through a π bridge, designed to expand the conjugation chain and increase the distance traveled by the electron during excitation [11]. Typically, in the synthesis of D- π -A dyes, the last step is the well-known Knoevenagel reaction of D- π -aldehyde with cyanoacrylic acid [12,13], and Suzuki cross-couplings are most often employed for the preparation of a D- π -aldehyde-type molecule [14,15]. Therefore, aldehyde synthesis is a key step in the preparation of the sensitizer. Herein, we report the synthesis of 5-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde **2** as a precursor for the preparation of DSSCs components.

2. Results and Discussion

To synthesize the target 5-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde **2**, we studied the direct C-H activation reactions between 6-bromo-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **1** (R = Br) [15] and thiophene-2-carbaldehyde (X = H) under the conditions previously described in the literature for similar transformations (Scheme 1) [16]. However, under the conditions studied, the

reaction did not occur, and the starting compounds were recovered in almost quantitative yield (Table 1, entries 1–2). The Suzuki reaction of 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **1** (R = Bpin₂) [15] with 5-bromothiophene-2-carbaldehyde (X = Br) resulted in compound **2** in moderate yield (Table 1, entry 3).



Scheme 1. Synthesis of 5-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde **2**.

Table 1. Reaction of 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazoles **1** with thiophene-2-carbaldehydes.

Entry	R	X	Catalyst	Solvent	Base	Conditions	Yield of 2 , %
1	Br	H	Pd(PPh ₃) ₂ Cl ₂	Toluene	K ₂ CO ₃ /PivOH	110 °C, 16 h	0
2	Br	H	Pd(OAc) ₂	Toluene	K ₂ CO ₃ /PivOH P ^t Bu ₃ ·HBF ₄	110 °C, 16 h	0
3	Bpin ₂	Br	Pd(PPh ₃) ₄	THF/H ₂ O	K ₂ CO ₃ /PivOH	66 °C, 8 h	63

The structure of 5-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde **2** was confirmed by means high-resolution mass spectrometry, ¹H NMR, ¹³C NMR, and IR spectroscopy. For compound **2**, the UV–Vis absorption spectrum was recorded in a solution in DCM, which showed the presence of two absorption maxima. In this case, the far-wave absorption maximum, responsible for the charge transfer from the donor to the acceptor (intramolecular charge transfer, CT band) [17], had a value of 432 nm. The obtained results suggest that further functionalization of compound **2** at the aldehyde group may result in a bathochromic shift of the CT band, which may lead to D–π–A-type dyes with a wide spectral range overlap.

3. Materials and Methods

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **1** (R = Bpin₂) was prepared according to the published method [15]. The solvents and reagents were purchased from commercial sources and used as received. ¹H and ¹³C 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 CDCl₃ solutions, with TMS as the standard. *J* values are presented in Hz. The MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Hazlet, NJ, USA). The IR spectrum was measured with a Bruker “Alpha-T” instrument in the KBr pellet. High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). The UV–Vis absorption spectrum was recorded using an OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer (Saint Petersburg, Russia), controlled with SF-2000 software in standard 10 mm photometric quartz cells using HPLC-grade DCM in a concentration of 2 × 10^{−5} M.

The spectra for 5-(9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazol-6-yl)thiophene-2-carbaldehyde **2** are provided in Supplementary Materials.

In a 50 mL round-bottom flask, 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanocarbazole **1** (317 mg, 0.79 mmol) and 5-bromothiophene-2-carbaldehyde (189 mg, 0.99 mmol) were dissolved in THF (20 mL), and a solution of K₂CO₃ (109 mg, 0.79 mmol) in water (5 mL) was added. The mixture was degassed for 20 min with a stream of argon, and Pd(PPh₃)₄ (45 mg, 0.040 mmol) was added. After refluxing for 8 h, the reaction mixture was diluted using EtOAc (25 mL) and washed with water (3 × 30 mL). The organic layer was dried using Na₂SO₄ and then evaporated. The residue was purified via column chromatography on silica gel (Silica gel Merck 60, with eluent a mixture of petroleum ether (40–60 °C) and EtOAc, 100:1, *v/v*). Yield 191 mg (63%, 0.496 mmol), orange solid, mp 205–206 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 9.82 (s, 1H), 7.67 (d, *J* = 3.9, 1H), 7.42–7.13 (m, 7H), 6.76 (d, *J* = 8.3, 1H), 4.31 (d, *J* = 8.1, 1H), 3.32 (d, *J* = 8.3, 1H), 2.52–2.38 (m, 2H), 2.35 (s, 3H), 1.59–1.35 (m, 4H), 1.31–1.16 (m, 2H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 182.4, 156.3, 151.2, 140.0, 139.8, 138.1, 134.4, 132.9, 130.0, 126.6, 123.1, 122.9, 121.5, 121.3, 107.1, 71.9, 50.0, 43.7, 40.9, 32.4, 28.6, 25.3, 20.9. HRMS-ESI (*m/z*): [M+H]⁺ calcd for (C₂₅H₂₃NOS) 386.1528, found 386.1535. UV-Vis (CH₂Cl₂, λ_{max}, nm/logε): 297/4.05, 432/4.40. IR, ν, cm⁻¹: 2950, 2916, 2865, 1729, 1646, 1600, 1513, 1450, 1434, 1372, 1272, 1235, 1059, 800. R_f = 0.33 (petroleum ether/EtOAc—10:1).

Supplementary Materials: The following are available online: copies of ¹H, ¹³C NMR, IR, UV, and HR mass spectra for compound **2**.

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