


Short Note

# *N,N*-Bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)thiophen-2-amine

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**Abstract:** *N,N*-Diarylthiophen-2-amine units are of great interest for the synthesis of optoelectronic devices. In this communication, *N,N*-bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)thiophen-2-amine was obtained by means of a Buchwald–Hartwig cross-coupling reaction of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine and 2-bromothiophene in the presence of tris(dibenzylideneacetone)dipalladium(0), tri-*tert*-butyl phosphine and sodium *tert*-butanolate. The structure of newly synthesized compounds was established by means of elemental analysis, high-resolution mass spectrometry, <sup>1</sup>H, <sup>13</sup>C NMR, IR and UV spectroscopy and mass-spectrometry.

**Keywords:** donor building blocks; Buchwald–Hartwig cross-coupling reaction; triarylamines; biphenyls; 2-bromothiophene



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## 1. Introduction

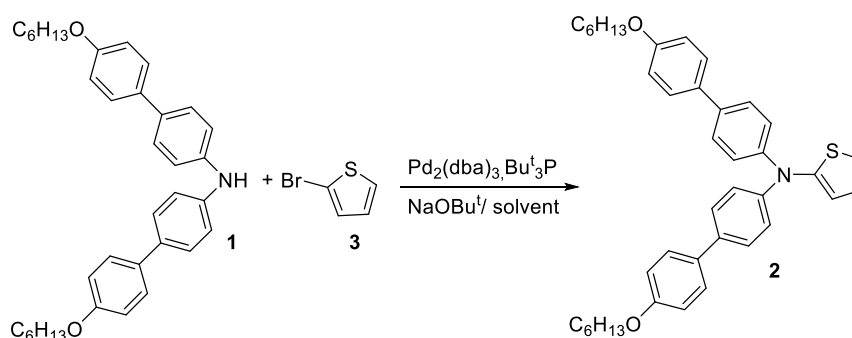
The triarylamine donor is one of the most investigated in recent years for the synthesis of components organic solar cells (OSCs), organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and others [1,2]. In some cases, replacing the triarylamine unit with an *N,N*-diarylthiophen-2-amine can lead to better electron-donating ability, a higher short-circuit current density, and broadening the absorption range [3]. Based on this fragment, a number of compounds with a hole-transporting ability for applications in optoelectronic devices [4] and for designing small molecule donors for future optoelectronics [5], highly fluorescent luminogens [6] and advanced photosensitizer-based immunogenic cell death (ICD) inducers [7] were obtained.

However, among the previously synthesized derivatives of *N,N*-diarylthiophen-2-amine, there were no derivatives where Ar = biphenyl. It is known that the use of a biphenyl group in triarylamine-containing donors can significantly increase the photovoltaic characteristics of dyes [8,9]. Previously, we synthesized bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **1** [10], which can be used as a precursor for the preparation of *N,N*-bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)thiophen-2-amine **2**. Herein, we report the synthesis of this compound by Buchwald–Hartwig cross-coupling of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **1**.

## 2. Results and Discussion

We conducted a study of the Buchwald–Hartwig cross-coupling reaction of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **1** with 2-bromothiophene **3** with the most frequently used *N,N*-bis(aryl)thiophen-2-amine and 2-bromothiophene catalysts—tris(dibenzylideneacetone)dipalladium(0), tri-*tert*-butyl phosphine and sodium *tert*-butanolate (Scheme 1, Table 1) [11–13]. The search for optimal reaction conditions was carried out by varying the nature of solvents and the temperature of chemical reactions. It was shown that when the reaction was carried out in boiling benzene, the yield of the reaction product **2** did not exceed 10% (Table 1, Entry 1). Replacement of benzene with a higher boiling toluene led to the introduction of a thienyl fragment into the amine **1** molecule within 24 h to obtain

product **2**, with a yield of 30% (Table 1, Entry 2). When using xylene as a solvent and heating the reaction mixture to 120 °C, the yield of the target product **2** reached to 45% (Table 1, Entry 3). A further increase in the reaction temperature to 130 °C did not lead to an improvement in the yield of compound **2** (Table 1, Entry 4).



**Scheme 1.** Synthesis of *N,N*-bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)thiophen-2-amine **2**.

**Table 1.** Reaction of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **1** with 2-bromothiophene **3**.

Entry	Solvent	Temperature, °C	Time, h	Yield, of 2%
1	Benzene	78	24	10
2	Toluene	110	24	30
3	Xylene	120	24	45
4	Xylene	130	24	44

The structure of *N,N*-bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)thiophen-2-amine **2** was confirmed by means of elemental analysis, high-resolution mass spectrometry, <sup>1</sup>H, <sup>13</sup>C NMR, IR and UV spectroscopy, and mass spectrometry.

### 3. Materials and Methods

Bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **1** was prepared according to the published method [10]. 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. <sup>1</sup>H and <sup>13</sup>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<sub>3</sub> solution, with TMS as the standard. J values are given 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 KBr pellet. The high-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization. The solution's UV-visible absorption spectra were recorded using a OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer controlled with SF-2000 software. The sample was measured in a 1 cm quartz cell at room temperature with 4.8 × 10<sup>-5</sup> mol/mL concentration in CH<sub>2</sub>Cl<sub>2</sub>.

Synthesis of *N,N*-bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)thiophen-2-amine **2** (Supplementary Materials).

A mixture of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **1** (60 mg, 0.11 mmol), 2-bromothiophene **3** (28 mg, 0.17 mmol), NaOBu<sup>t</sup> (16 mg, 0.17 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (2 mg, 2 mmol %) in xylene (5 mL) was degassed by argon and heated to 120 °C under argon for 20 h. On completion, the mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic phases were washed with brine (2 × 5 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel Merck 60, eluent hexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1, *v/v*). Yield 30 mg (45%), yellow oil, R<sub>f</sub> = 0.3 (hexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1, *v/v*). IR spectrum,  $\nu$ , cm<sup>-1</sup>:

2953, 2928 and 2858 (all C–H), 1608, 1496, 1471, 1274, 1250, 1177, 820, 674, 516.  $^1\text{H}$  NMR (ppm):  $\delta$  7.53–7.47 (8H, m), 7.22 (d,  $J = 8.6$ , 4H), 7.05 (d,  $J = 4.8$ , 1H), 6.99–6.93 (5H, m), 6.81 (d,  $J = 3.5$ , 1H), 4.02 (t,  $J = 6.6$ , 4H), 1.83 (p,  $J = 6.7$ , 4H), 1.56–1.46 (m, 4), 1.42–1.37 (8H, m), 0.97–0.92 (6H, m).  $^{13}\text{C}$  NMR (ppm):  $\delta$  158.5, 151.3, 146.6, 135.4, 133.0, 127.7, 127.3, 126.0, 122.5, 121.5, 120.8, 114.8, 68.1, 31.6, 29.3, 25.7, 22.6, 14.0. HRMS (ESI-TOF),  $m/z$ : calcd for  $\text{C}_{40}\text{H}_{46}\text{NO}_2\text{S}$   $[\text{M} + \text{H}]^+$ , 604.3244, found, 604.3228. MS (EI, 70eV),  $m/z$  ( $I$ , %): 606 ( $[\text{M} + 3]^+$ , 3), 605 ( $[\text{M} + 2]^+$ , 9), 604 ( $[\text{M} + 1]^+$ , 60), 603 ( $[\text{M}]^+$ , 100), 518 (12), 43 (5). UV-Vis spectra (in  $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$ : 267 nm ( $\epsilon = 17,850 \text{ M}^{-1} \text{ cm}^{-1}$ ), 331 nm ( $\epsilon = 22,402 \text{ M}^{-1} \text{ cm}^{-1}$ ). Anal. calcd. For  $\text{C}_{40}\text{H}_{45}\text{NO}_2\text{S}$  (603.8568): C, 79.56; H, 7.51; N, 2.32. Found: C, 79.85; H, 7.72; N, 2.49%.

**Supplementary Materials:** The followings are available online: copies of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, UV-Vis and mass-spectra for the compound 2.

**Author Contributions:** Conceptualization, O.A.R. and T.N.C.; methodology, O.A.R.; software, T.N.C.; validation, O.A.R.; formal analysis, T.N.C.; investigation, T.N.C.; resources, O.A.R.; data curation, O.A.R.; writing—Original draft preparation, O.A.R.; writing—Review and editing, O.A.R.; visualization, O.A.R.; supervision, O.A.R.; project administration, O.A.R.; funding acquisition, O.A.R. All authors have read and agreed to the published version of the manuscript.

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