

Short Note

# *tert*-Butyl Bis(4'-(Hexyloxy)-[1,1'-biphenyl]-4-yl)carbamate

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**Abstract:** New donor building blocks, i.e., triaryl amino derivatives, are of great interest for the production of organic photovoltaic materials. In this communication, bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine was synthesized in a two-step process via hydrolysis of its *tert*-butyl carbamate derivative. *tert*-Butyl bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)carbamate was obtained by Suzuki cross-coupling reaction of *tert*-butyl bis(4-bromophenyl)carbamate and (4-(hexyloxy)phenyl)boronic acid in the presence of tetrakis(triphenylphosphine)palladium(0). 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; Suzuki cross-coupling reaction; triaryl amines; bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine



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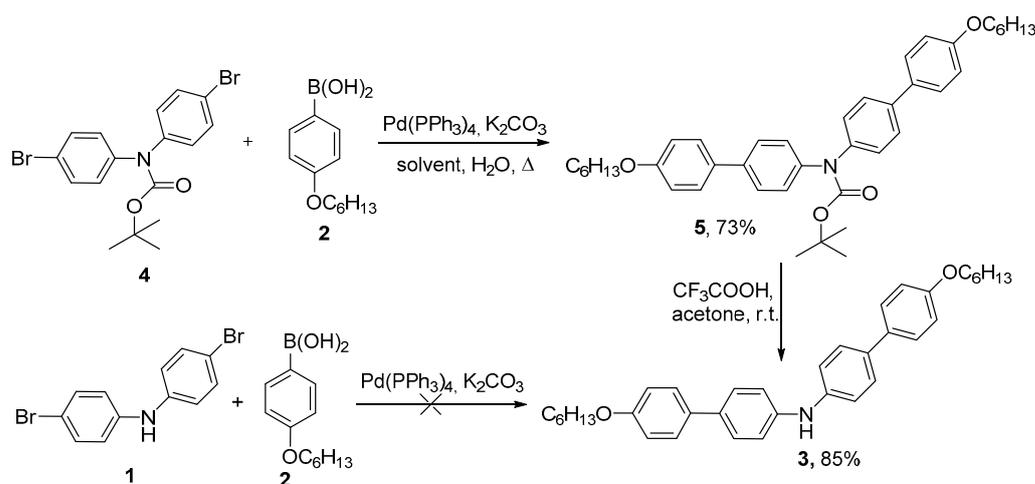
## 1. Introduction

Over the past ten years, small molecules used in photovoltaic devices have evolved from the simplest ones with the structure of D-A, D- $\pi$ -A, D-A-D, or A-D-A, to more complex ones containing several different donor and acceptor fragments (for example, D-A1- $\pi$ -A2, A- $\pi$ -D- $\pi$ -A). The donor fragment plays a significant role in the formation of the properties of small molecules, as well as polymeric materials. Introduction of electron-rich fragment on the donor segment helps to broaden the absorption spectra, and attachment of energy delocalizing chromophores causes prolongation of excited state lifetime and facilitates the electron injection into the conduction band of TiO<sub>2</sub> [1]. Synthesis of new effective donor blocks (D), the use of which in various combinations with acceptors and  $\pi$ -bridges will lead to the production of new photovoltaic materials, i.e., organic solar cells (OSCs), organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), and others, is of great interest [2–7]. A family of triaryl amino derivatives, including bis ([1,1'-biphenyl]-4-yl)aminophenyl derivatives, is desirable for organic sensitizers [8,9]. Bis ([1,1'-biphenyl]-4-yl) amines are the most convenient precursors for the synthesis of these donor building blocks [10]. Surprisingly, bis(4'-(alkyloxy)-[1,1'-biphenyl]-4-yl)amine, according to the Reaxys and SciFinder search, is not described in the literature. Herein, we report the synthesis of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **2** via its carbamate derivative.

## 2. Results and Discussion

We have shown that the Suzuki cross-coupling reaction between bis(4-bromophenyl) amine **1** and (4-(hexyloxy)phenyl) boronic acid **2** in the presence of tetrakis (triphenylphosphine) palladium and potassium carbonate proceeded non-selectively with the formation of a series of side products, probably due to the poor solubility of compound **1**. To increase the solubility of amine **1** and protect the NH group, a protective *tert*-butoxycarbonyl group (Boc-group) was introduced into the bis(4-bromophenyl) amine [10]. *tert*-Butyl bis (4-bromophenyl) carbamate **4** was studied in the Suzuki cross-coupling reaction with (4-(hexyloxy)phenyl) boronic acid **2** in the presence of tetrakis(triphenylphosphine)palladium(0)

and potassium carbonate (Scheme 1, Table 1). The search for optimal conditions for the selective introduction of phenyl substituents was carried out by varying the nature of solvents, temperature, and reaction time. It was shown that when the reaction was carried out in boiling THF, the yield of the bis-coupling product **5** did not exceed 15% (Table 1, entry 1). Replacing THF with a higher boiling dioxane resulted in the replacement of both bromine atoms with phenyl group within 50 h to obtain the bis-coupling product **5** in 65% yield (Table 1, entry 2). An even higher yield (73%) was obtained using toluene as the solvent (Table 1, entry 3). The use of Pd(OAc)<sub>2</sub> together with triphenylphosphine in toluene at the same temperature resulted in a lower yield of compound **5** (58%). The Boc-protection was removed by the action of trifluoroacetic acid in acetone at room temperature. The reaction gave amine **3** in high yield.



**Scheme 1.** Synthesis of *tert*-butyl bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)carbamate **5**.

**Table 1.** Reaction of *tert*-butyl bis(4-bromophenyl) carbamate **4** with boronic acid **2**.

Entry	Solvent	Temperature, °C	Time, h	Yield, of 5%
1	THF	78	24	15
2	Dioxane	81	50	65
3	Toluene	110	50	73

The structure of *tert*-butyl bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)carbamate **5** 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. Since amine **3** was extremely poorly soluble in organic solvents, it was characterized by elemental analysis, high resolution mass-spectrometry, IR spectroscopy, and mass-spectrometry.

### 3. Materials and Methods

Bis(4-Bromophenyl) amine **1**, *tert*-butyl bis(4-bromophenyl)carbamate **4**, and 4-(hexyloxy)phenylboronic acid **2** were prepared according to the published method [11,12]. 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). 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. MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Finnigan, Hazlet, NJ, USA). IR spectrum was measured with a Bruker "Alpha-T" instrument in KBr pellet. High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) 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). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. Solution UV-visible absorption spectra were recorded using a OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer controlled with SF-2000 software. All samples were measured in a 1 cm quartz cell at room temperature with  $3.7 \times 10^{-5}$  mol/mL concentration in  $\text{CH}_2\text{Cl}_2$ .

Synthesis of *tert*-butyl bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)carbamate **5** (Supplementary Materials).

A mixture of *tert*-butyl bis(4-bromophenyl)carbamate **4** (845 mg, 1.97 mmol), boronic acid **2** (1098 mg, 4.94 mmol), solution of 2M  $\text{K}_2\text{CO}_3$  (2.5 mL) and  $\text{Pd}(\text{PPh}_3)_4$  (3 mmol %) in toluene (25 mL) was degassed by argon and refluxed under argon for 50 h. On completion, the mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic phases were washed with brine ( $2 \times 50$  mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane– $\text{CH}_2\text{Cl}_2$ , 5:1,  $v/v$ ). Yield 900 mg (73%), white solid, m.p. = 85–87 °C,  $R_f$  = 0.2 ( $\text{CH}_2\text{Cl}_2$ , 5:1,  $v/v$ ). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2952, 2932, 2868, 1715, 1607, 1497, 1474, 1329, 1295, 1246, 1176, 1160, 1059, 1034, 1016, 823, 754, 564, 526.  $^1\text{H}$ -NMR (ppm):  $\delta$  7.51 (8H, d,  $J$  = 8.1), 7.29 (4H, d,  $J$  = 8.5), 6.97 (4H, d,  $J$  = 8.4), 4.00 (4H, t,  $J$  = 6.5), 1.89–1.74 (4H, m), 1.50 (9H, s), 1.44–1.27 (12H, m), 0.96–0.89 (6H, m).  $^{13}\text{C}$ -NMR (ppm):  $\delta$  158.8, 153.9, 141.7, 138.2, 132.8, 128.0, 127.2, 126.9, 114.8, 81.3, 68.1, 31.6, 29.3, 28.3, 25.7, 22.6, 14.0. HRMS (ESI-TOF),  $m/z$ : calcd for  $\text{C}_{41}\text{H}_{52}\text{NO}_4$  [ $\text{M} + \text{H}$ ] $^+$ , 622.3891, found, 622.3888. MS (EI, 70 eV),  $m/z$  ( $I$ , %): 621 ([ $\text{M}$ ] $^+$ , 40), 565 (75), 521 (100), 436 (20), 389 (25), 345 (20), 57 (50). UV-Vis spectra (in  $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$ : 219 nm ( $\epsilon$  = 20,836  $\text{M}^{-1} \text{cm}^{-1}$ ), 284 nm ( $\epsilon$  = 54,041  $\text{M}^{-1} \text{cm}^{-1}$ ). Anal. calcd. for  $\text{C}_{41}\text{H}_{52}\text{NO}_4$  (621.85): C, 79.19; H, 8.27; N, 2.25. Found: C, 79.36; H, 8.32; N, 2.52%.

Synthesis of bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amine **3** (Supplementary Materials).

*tert*-Butyl bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)carbamate **5** (50 mg, 0.08 mmol) was dissolved in acetone (5 mL) under nitrogen. Trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ , 0.25 mL, 3 mmol) was added drop by drop, and the solution was stirred at room temperature overnight. The precipitated product was filtered and dried under reduced pressure. Yield 35 mg (85%), white solid, m.p. = > 250 °C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2955, 2935, 2862, 1610, 1506, 1476, 1282, 1254, 1234, 1180, 1127, 1034, 996, 813, 727, 510. HRMS (ESI-TOF),  $m/z$ : calcd for  $\text{C}_{36}\text{H}_{44}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$ , 522.3367, found, 522.3345. MS (EI, 70 eV),  $m/z$  ( $I$ , %): 522 ([ $\text{M} + 1$ ] $^+$ , 40), 521 ([ $\text{M}$ ] $^+$ , 100), 436 (15), 352 (8), 69 (9), 43 (8), 28 (45). Anal. calcd. for  $\text{C}_{36}\text{H}_{44}\text{NO}_2$  (521.73): C, 82.87; H, 8.31; N, 2.68. Found: C, 83.03; H, 8.45; N, 2.78%.

**Supplementary Materials:** The following are available online: copies of  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR, IR, HRMS, UV, and mass-spectra for the compound **3** and **5**.

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