4′,4‴,4‴‴-Nitrilotris(4-methoxy-[1,1′-biphenyl]-3-carbaldehyde)

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Abstract: Multipodal salicylaldehydes have attracted much scientific interest as scaffolds for the construction of multinuclear complexes, as well as metal and covalent organic frameworks. Herein, we report a preparation of 4′,4‴,4‴‴-nitrilotris(4-methoxy-[1,1′-biphenyl]-3-carbaldehyde), a direct precursor for the tripodal salicylaldehyde with triphenylamine core. The structure of the product was confirmed by molecular spectroscopy. The reported approach may be broadened over a variety of multipodal salicylaldehydes.

Keywords: salicylaldehyde; triphenylamine; metal organic framework; covalent organic framework

1. Introduction

Multipodal salicylaldehydes and their derivatives represent a popular scaffold for metalorganic catalysts [1–3], as well as metal and covalent organic frameworks [4–6]. In addition, they attract attention due to their luminescent properties, especially aggregation-induced luminescence [7], and liquid crystalline properties [8]. Of great interest are the multipodal salicylaldehydes with three or more salicylic fragments, which are able to form multinuclear complexes or 2D and 3D frameworks. For example, tetrapodal salicylaldehyde based on a tetraphenylmethane core was applied for the synthesis of the covalent organic frameworks to separate aromatic hydrocarbons [9,10].

Herein, we report the synthesis of the tripod O-methylsalicaldehyde, namely 4′,4‴,4‴‴-nitrilotris(4-methoxy-[1,1′-biphenyl]-3-carbaldehyde) 1, by the Suzuki coupling of the tris(4-bromophenyl)amine and 2-methoxy-5-(pinacolboronato)benzaldehyde. Due to the presence of a triphenylamine core, this scaffold has an inherent redox center, which may be interesting for the energy storage and other electrochemical applications. The obtained product was characterized with nuclear magnetic resonance (NMR), high resolution mass spectrometry (HRMS) and Fourier-transform infrared spectroscopy (FTIR) spectra.

2. Results

The desired product was obtained by Suzuki coupling of tris(4-bromophenyl)amine and 2-methoxy-5-(pinacolboronato)benzaldehyde (Scheme 1) using the Pd(PPh₃)₄ as a catalyst and K₂CO₃ as base in DMF/H₂O. The product was isolated in 82% yield after recrystallization from acetone.

The ¹H-NMR spectrum of product 1 (Figure S1) contains aldehyde and methoxy singlets at 10.52 and 3.98 ppm, respectively, three aryl signals of the outer phenyl rings at 8.07, 7.79 and 7.07 ppm, and two doublets from the inner phenyl rings at 7.50 and 7.21 ppm. The ¹³C-NMR spectrum (Figure S2) contains a complete set of signals attributed to the proposed structure of the product: carbonyl signal at 189.9 ppm, and 2-methoxy-5-(pinacolboronato)benzaldehyde. Due to the presence of a triphenylamine core, this scaffold has an inherent redox center, which may be interesting for the energy storage and other electrochemical applications. The obtained product was characterized with nuclear magnetic resonance (NMR), high resolution mass spectrometry (HRMS) and Fourier-transform infrared spectroscopy (FTIR) spectra.
tris(4-bromophenyl)amine (965 mg, 2 mmol) in DMF (20 mL) and H2O (4 mL) was loaded.

The 13C-NMR spectrum (Figure S2) contains a complete set of signals attributed to the following positions: 7.07, 7.79 and 8.07 ppm, and two doublets from the inner phenyl rings at 7.50 and 7.21 ppm. The 1H-NMR spectrum (Figure S2) contains a gplet at 10.52 and 3.98 ppm, respectively, three aryl signals of the outer phenyl rings at 7.07 ppm. The FTIR spectrum recorded in KBr (Figure S4) contains two strong peaks at 1678 and 1605 cm−1, accompanied by two weaker peaks, which is attributed to the vibration of three C=O fragments in the molecule of D3h.

We demonstrate the preparation of the tripodal 4′,4″,4"′"′-nitrilotris(4-methoxy-[1,1′-biphenyl]-3-carbaldehyde), a direct precursor of the tripodal salicylaldehyde with a redox-active triphenylamine core. An obtained product may be used as a scaffold for the synthesis of novel trinuclear metal complexes and 2D metal and covalent organic frameworks.

3. Materials and Methods

3.1. General Consideration

Reagents of “reagent grade” purity were purchased from Sigma-Aldrich (Darmstadt, Germany). The Fourier-transform infrared spectra were recorded on a Shimadzu IRaffinity-1 FTIR spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in KBr pellets. 1H and 13C-NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in CDCl3. The HRMS spectrum was recorded using electrospray ionization on a Bruker microTOF apparatus (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) in positive mode.

3.2. Synthesis of 4′,4″,4"′"′-Nitrilotris(4-Methoxy-[1,1′-biphenyl]-3-carbaldehyde)

A solution of 2-methoxy-5-(pinacolboronato)benzaldehyde (2.10 g, 8 mmol) and tris(4-bromophenyl)amine (965 mg, 2 mmol) in DMF (20 mL) and H2O (4 mL) was loaded Schlenk flask and degassed in vacuo with ultrasonication. The flask was refilled with Ar and then K2CO3 (1.1 g, 8 mmol), and Pd(PPh3)4 (230 mg, 0.2 mmol) was loaded in the Ar stream. The flask was sealed and heated to 80 °C for 48 h. The reaction mixture was cooled, diluted with H2O and filtered. The resulting precipitate was recrystallized from boiling acetone with hot filtration to render the desired product as a creamy powder (1.06 g, 1.64 mol, 82%).

1H-NMR (400 MHz, CDCl3) δ, ppm: 10.52 (s, 3H, CHO), 8.07 (d, J = 8.7, 2.6 Hz, 3H, Ar), 7.50 (d, J = 8.2 Hz, 6H, Ar), 7.21 (d, J = 8.1 Hz, 6H, Ar), 7.07 (d, J = 8.7 Hz, 3H, Ar), 3.98 (s, 9H, CH3O). 13C-NMR (101 MHz, CDCl3) δ, ppm: 189.9 (CHO), 161.2 (Ar), 146.9 (Ar), 134.2 (Ar), 134.0 (Ar), 133.4 (Ar), 127.7 (Ar), 126.5 (Ar), 125.1 (Ar), 124.6 (Ar), 112.3 (Ar), 56.0 (CH3O). FTIR (KBr) ν, cm−1: 2842 (C-H), 1678, 1605 (C=O). HRMS (ESI) m/z [M + Na]+ calcd. for C42H33NO6Na+ 670.2200, found 670.2200.

Supplementary Materials: The following are available online: 1H and 13C-NMR spectra, HRMS and FTIR data for 4′,4″,4"′"′-nitrilotris(4-methoxy-[1,1′-biphenyl]-3-carbaldehyde).

Author Contributions: Conceptualization: D.A.L. and O.V.L.; synthesis: D.A.L., A.A.V., A.Y.K. and J.V.N.; writing—original draft preparation: D.A.L.; writing—review and editing: D.A.L. and A.A.V.;
visualization: D.A.L. and A.A.V.; supervision: O.V.L.; funding acquisition: O.V.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Russian Foundation for Basic Research (RFBR), grant number 18-29-04058.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** We thank the Research Center for Magnetic Resonance, the Center for Chemical Analysis and Materials Research of Saint Petersburg State University Research Park for the measurements provided.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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