

Short Note

# 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



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## 1. Introduction

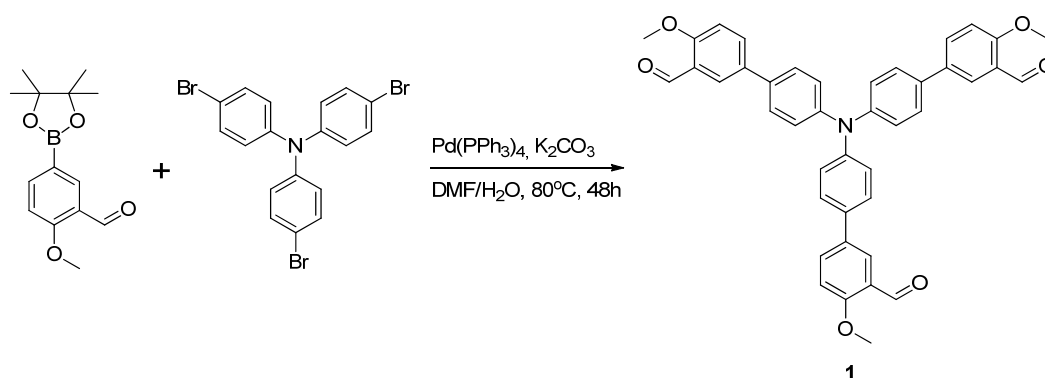
Multipodal salicylaldehydes and their derivatives represent a popular scaffold for metalorganic catalysts [1–3], as well as metal and covalent organic frameworks [4–6]. In addition, they attract attention due to their luminescent properties, especially aggregation-induced luminescence [7], and liquid 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*-methylsalicylaldehyde, 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(PPh<sub>3</sub>)<sub>4</sub> as a catalyst and K<sub>2</sub>CO<sub>3</sub> as base in DMF/H<sub>2</sub>O. The product was isolated in 82% yield after recrystallization from acetone.

The <sup>1</sup>H-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 <sup>13</sup>C-NMR spectrum (Figure S2) contains a complete set of signals attributed to the proposed structure of the product: carbonyl signal at 189.9 ppm, 10 aryl signals at 161.2, 146.9, 134.2, 134.0, 133.4, 127.7, 126.5, 125.1, 124.6, and 112.3 ppm and a methoxy signal at 56.0 ppm.



**Scheme 1.** Reaction conditions for the synthesis of **1**.

The exact mass of  $[M + Na]^+$  ion, determined by ESI-HRMS (Figure S3), was found to be 670.2200 (670.2200 as calcd. for  $C_{42}H_{33}NO_6Na^+$ ). 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 **D<sub>3</sub>h**.

We demonstrate the preparation of the tripodal 4',4''',4''''-nitritotris(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  $^{13}C$ -NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in  $CDCl_3$ . 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''''-Nitritotris(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  $H_2O$  (4 mL) was loaded Schlenk flask and degassed in vacuo with ultrasonication. The flask was refilled with Ar and then  $K_2CO_3$  (1.1 g, 8 mmol), and  $Pd(PPh_3)_4$  (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  $H_2O$  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,  $CDCl_3$ )  $\delta$ , ppm: 10.52 (s, 3H, CHO), 8.07 (d,  $J = 2.5$  Hz, 3H, Ar), 7.79 (dd,  $J = 8.7, 2.6$  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,  $CH_3O$ ).  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ )  $\delta$ , 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 ( $CH_3O$ ). FTIR (KBr)  $\tilde{\nu}$ ,  $cm^{-1}$ : 2842 (C-H), 1678, 1605 (C=O). HRMS (ESI)  $m/z$   $[M + Na]^+$  calcd. for  $C_{42}H_{33}NO_6Na^+$  670.2200, found 670.2200.

**Supplementary Materials:** The following are available online:  $^1H$  and  $^{13}C$ -NMR spectra, HRMS and FTIR data for 4',4''',4''''-nitritotris(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.

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