

Short Note

6,6'-(1*E*,1'*E*)-((1*R*,2*R*)-1,2-Diphenylethane-1,2-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-*tert*-butyl-4-((trimethylsilyl)ethynyl)phenol)

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Abstract: Functionalizable salen derivative, 6,6'-(1*E*,1'*E*)-((1*R*,2*R*)-1,2-diphenylethane-1,2-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-*tert*-butyl-4-((trimethylsilyl)ethyn-yl)phenol) (**3**), was synthesized by condensation between (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (**2**) and 3-*tert*-butyl-2-hydroxy-5-((trimethylsilyl)ethynyl)benzaldehyde (**1**) under refluxing conditions. The title compound was characterized by ¹H-NMR, ¹³C-NMR, FT-IR, high-resolution mass spectrometry, optical rotation and melting point determination.

Keywords: salen ligands; chiral 1,2-diamines; alkynes; nucleophilic addition

Introduction

N,N'-Bis(salicylidene)ethylidenediamines, more commonly referred to as salen molecules, constitute one of the most popular and useful ligands for catalysts used in asymmetric synthesis [1]. Since the first metallated salen ligand reported independently by Jacobsen [2] and Katsuki [3], which continues being the most efficient catalyst for a wide variety of organic reactions [1], a plethora of different chiral salen ligands has been comprehensively studied. Indeed, the facile and modular

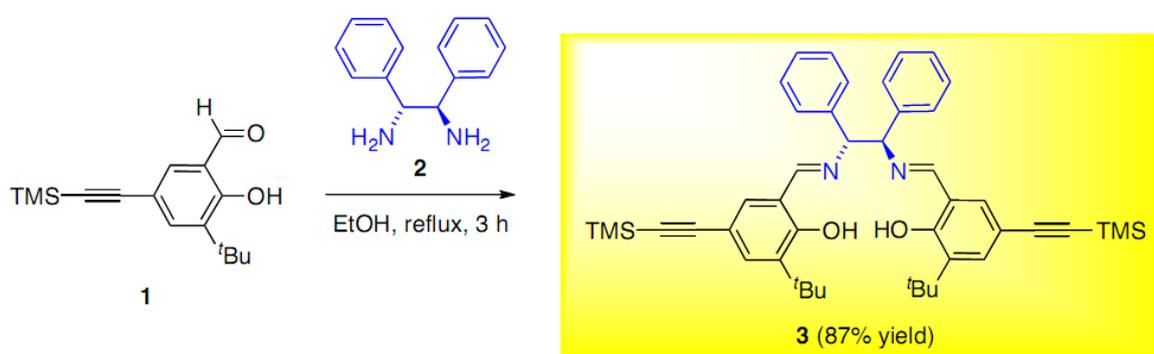
synthesis of salens from diamines and salicylaldehydes has allowed researchers to control the activity of many by finely tuning its steric and electronic properties [4]. On the other hand, a number of approaches have been also described to immobilize salen ligands (e.g., polymer- or zeolite-immobilized salens) in order to take advantage of the heterogeneous catalysis [5,6]. In this sense, incorporation of functionalizable organic units into salen ligand frameworks constitutes one of the platforms of choice to expand their versatility. In this sense, acetylenes have been proven to be one of the most valuable functional groups in organic synthesis and materials chemistry [7,8], mainly due to (1) their facile incorporation into organic compounds, and (2) their numerous characteristic reactions including, among others, electrophilic additions, metathesis, hydroboration, oxidative cleavage, C–C coupling and cycloadditions [8,9].

Herein, we report the synthesis and full characterization of a chiral salen ligand derived from (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine and bearing TMS-protected terminal alkynes (TMS = trimethylsilyl), which are available for further modifications. To the best of our knowledge, the isolation and characterization of this compound have not been reported elsewhere.

Results and Discussion

The title compound **3** was obtained in 87% yield via the nucleophilic addition of (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (**2**) to 5-(trimethylsilyl)ethynyl-3-*tert*-butyl-2-hydroxybenzaldehyde (**1**), which was previously synthesized following the method reported by Seebach and co-workers [10]. The reaction was carried out in refluxing ethanol during 3 h (Scheme 1), affording the desired compound as a yellow solid after a simple filtration-washing protocol of the so-formed precipitate (see Experimental Section and Supporting Information).

Scheme 1. Synthesis of title compound **3**.



Regarding the importance of this structural moiety, it is worth to mention that condensation of **2** with disalicylaldehydes based on 1,4-dialkoxy-2,6-diethynylbenzene has been reported to form chiral linear polymers that catalyze the Et₂Zn addition to aldehydes with good enantioselectivity [11]. In addition, alkene analogues of **3** have been prepared for radical grafting of salen structures onto controlled-pore glass silica gel [6]. In our case, preliminary experiments also indicated the conversion of **3** in the presence of hydrophilic 3-mercaptopropyl silica gel and AIBN as a radical initiator [12], upon deprotection of TMS groups. Reaction was confirmed by disappearance of **3** in the TLC analysis and Ellman's SH test [13], which indicated reaction of ca. 85% of SH groups (see Supporting Information). Similarly, other orthogonal reactions such as the 1,3-dipolar cycloaddition between

alkynes and azides may constitute an alternative and versatile method for the synthesis of **3**-based polymers, immobilization of **3** on solid supports or preparation of new chiral salen molecules after reaction with either multivalent or monovalent azides.

Experimental

General: ^1H - and ^{13}C -NMR spectra were recorded at 25 °C on Bruker Avance 300 spectrometer in CDCl_3 as solvent. Chemical shifts are reported in parts per million relative to internal TMS (0.00 ppm). High-resolution mass spectrum was recorded with a Bruker Microtof-Q spectrometer. Elemental analysis was performed on a PerkinElmer 2400 Series II CHNS/O elemental analyzer. Infrared spectrum was recorded using a Nicolet Avatar 360 FTIR spectrophotometer. Melting point (mp) was measured with a Gallenkamp apparatus and is uncorrected. UV-vis measurements were performed on a UNICAM UV-vis spectrometer. Optical rotation was determined in a JASCO P-1020 polarimeter. Thin-layer chromatography was carried out on Merck aluminium sheets coated with silica gel 60 F₂₅₄. Compounds were visualized by use of 254 nm UV light and phosphomolybdic acid solution in ethanol with heating. All solvents used during this work were of p.a. grade or purified by standard techniques [14]. Anhydrous sodium sulfate was used for drying solutions. Alkynyl derivative **1** was obtained by Sonogashira cross-coupling of trimethylsilyl acetylene with 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde, affording the desired product as a yellow oil that displayed identical spectroscopic data to those reported in the literature [10]. Chiral 1,2-diamine **2** was purchased from Aldrich and used as received.

*Synthetic procedure and characterization data of 6,6'-((1*E*,1'*E*)-(((1*R*,2*R*)-1,2-diphenylethane-1,2-diyl)bis(azanilylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-((trimethylsilyl)ethynyl)phenol) (**3**):* A stirred yellow solution of 5-(trimethylsilyl)ethynyl-3-*tert*-butyl-2-hydroxybenzaldehyde (**1**) (1.37 g, 5.0 mmol) and (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (**2**) (0.52 g, 2.46 mmol) in anhydrous EtOH (20 mL) was heated under reflux for 3 h. During this time, copious amount of precipitate was observed and TLC analysis of the supernatant indicated complete conversion of **1**. The reaction mixture was allowed to cool down to room temperature and the resulting yellow precipitate was filtered over a Buchner funnel, washed thoroughly with EtOH (3 × 20 mL) and dried under vacuum. The residue was finally purified by flash column chromatography on silica gel (eluent EtOAc/hexanes 1:9 → 3:7 v/v) affording Schiff base ligand **3** (1.55 g, 87% yield) as a yellow solid: TLC R_f (EtOAc/hexanes 1:9 v/v) 0.75; $[\alpha]_D^{20} = -50.9 \pm 1^\circ$ (c 0.14, CHCl_3); mp = $107 \pm 3^\circ\text{C}$; ^1H -NMR (300 MHz, CDCl_3) δ /ppm = 0.20 (s, 18H), 1.40 (s, 18H), 4.67 (s, 2H), 7.10 (s, 2H), 7.14–7.22 (m, 10H), 7.33 (s, 2H), 8.20 (s, 2H), 14.01 (s, 2H); ^{13}C -NMR (75 MHz, CDCl_3) δ /ppm = 0.0 (6C), 29.1 (6C), 34.8 (2C), 79.9 (2C), 91.5 (2C), 105.2 (2C), 112.3 (2C), 118.1 (2C), 127.7 (2C), 127.9 (4C), 128.4 (4C), 133.3 (2C), 133.9 (2C), 137.6 (2C), 138.8 (2C), 160.7 (2C), 166.2 (2C); FT-IR (KBr) ν_{max} (cm^{-1}) 3444, 2959, 1634, 1464, 1440, 1391, 1361, 1271, 1249, 1209, 1156, 1120, 1052, 1030, 938, 857; HRMS (ESI) m/z calculated for $\text{C}_{46}\text{H}_{57}\text{N}_2\text{O}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 725.3953; found 725.3947.

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