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Protocol status: Working
 We use this protocol and it's working

Created: Mar 07, 2023

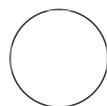
Synthetic Procedure of 3,3'-dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol

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DISCLAIMER

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ABSTRACT

A direct understanding of the degradation reaction pathways of lignin polymers in biomass is difficult due to the complexity of lignin's structure. To overcome the difficulty, simple lignin dimeric and trimeric model compounds which include typical lignin interunit linkages are useful to clarify reaction mechanisms. The following protocol describes the synthetic procedure of a 5-5' dimeric lignin model compound: 3,3'-Dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol. Lignin model compounds are useful for screening the effectiveness of catalysts and microorganisms. As well as determining the effect of a treatment on the lignin fraction, in particular the effect on the degree of depolymerization in the lignin polymer.

Last Modified: Sep 12, 2023

PROTOCOL integer ID: 78284

Keywords: lignin model compounds, dimers, nuclear magnetic resonance, lignin, synthesis, 5-5 linkage

MATERIALS

⊗ 2-methoxy-4-propylphenol Merck MilliporeSigma (Sigma-Aldrich) Catalog #W359807

Step 1.1

⊗ Acetone VWR International Catalog #BDH2002 Step 1.1

⊗ Sodium Acetate Merck MilliporeSigma (Sigma-Aldrich) Catalog #241245

Step 1.1 [see Note 1]

⊗ Acetic Acid Merck MilliporeSigma (Sigma-Aldrich) Catalog #695092

Step 1.1

[see Note 1]

⊗ Laccase Merck MilliporeSigma (Sigma-Aldrich) Catalog #38429

Step 1.1

⊗ Oxygen compressed gas Contributed by users Catalog #G2182101

Step 1.1

⊗ Silica gel Supelco Catalog #60737 Step 2.1

⊗ Hexane mixture of isomers Merck MilliporeSigma (Sigma-Aldrich) Catalog #178918

Step 2.1

⊗ Ethyl acetate Fisher Scientific Catalog #E145 Step 2.1

⊗ Chloroform-D Cambridge Isotope Laboratories, Inc. Catalog #DLM-7-100

Step 3.1

SAFETY WARNINGS



Almost all chemicals used for this procedure are hazardous. Read the Safety Data Sheet (SDS) for all chemicals and follow all applicable chemical handling and waste disposal procedures.

BEFORE START INSTRUCTIONS

All glassware is dried in an oven set to 105°C then cooled in a desiccator prior to use.

Synthetic Procedure

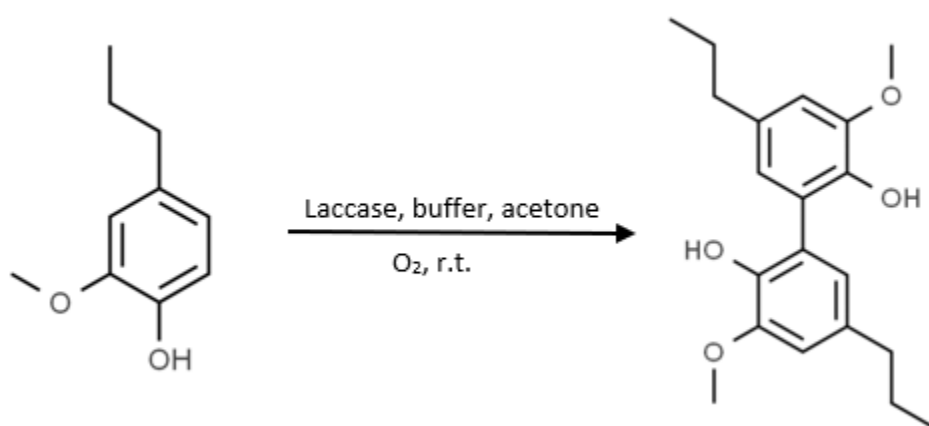


Figure 1. Reaction scheme for the synthesis of 3,3'-dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol (5-5' dimer).

- 1.1 4-propylguaiacol (5.00 g , 0.03 mol) was dissolved in acetone (75 mL) then diluted with 500 mL of acetic acid buffer (pH 5) [see Note 1]. Oxygen gas (O₂) was bubbled through the buffer solution for 30 minutes. 75 mg of laccase (>0.5 U/mg) was then added to the solution. The reaction was stirred at room temperature for four hours while the product precipitated.¹ The precipitated material was then collected via vacuum filtration using a Büchner funnel. The crude product was purified via flash chromatography to yield 3,3'-dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol (1.5452g, 31.3%).

Note

Note 1. Preparation of acetic acid buffer: 5.52 g of sodium acetate and 1.961 g of acetic acid are added to 1 L of deionized (D.I.) water. Stir until materials are completely dissolved. Check pH is close to 5.

[1]

CITATION

Maarit Lahtinen, Kristiina Kruus, Petri Heinonen, and Jussi Sipilä (2009). On the Reactions of Two Fungal Laccases Differing in Their Redox Potential with Lignin Model Compounds: Products and Their Rate of Formation. *J. Agric. Food Chem.*

LINK

<https://doi.org/10.1021/jf901511k>

Purification

- 2 Flash chromatography was performed using a Teledyne Isco Combiflash® NextGen 300+. Collected fractions were determined using a UV detector with wavelengths set at 254 and 280 nm. Samples were prepared by dissolving the crude material in the smallest amount of compatible solvent. Silica gel (mesh size 70-230) was then added to adsorb the material. Excess solvent was vacuum evaporated and the sample was loaded into a RediSep® R_f 25 g sample cartridge (catalog # 69-3873-240).
- 2.1 3,3'-Dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol was purified via flash chromatography. Column used was a RediSep® Silver 80 g silica gel flash column (catalog # 69-2203-380). Solvent system was hexane (Solvent A) and ethyl acetate (Solvent B). 3,3'-Dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol was separated from impurities using a ratio of 1:4 ethyl acetate:hexane for ten minutes then a ratio of 1:2 ethyl acetate: hexane.

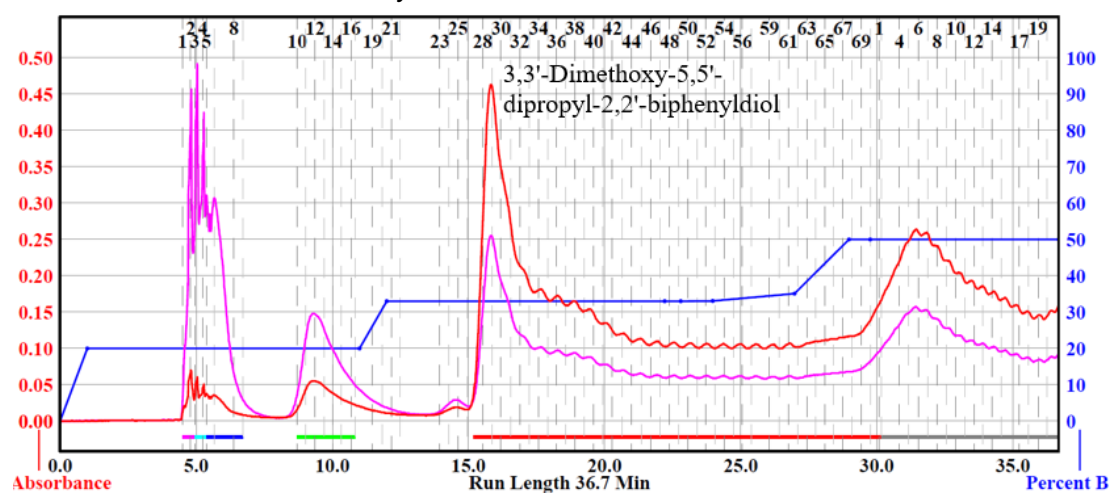


Figure 2. Run program from Combiflash® NextGen 300+ of 3,3'-dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol separation.

- 3 Nuclear magnetic resonance (NMR) spectra are acquired in a suitable deuterated NMR solvent at 25°C on a Bruker AVANCE 400 MHz spectrometer equipped with a 5 mm BBO probe. Chemical shifts (δ) are reported in ppm. ^1H -NMR spectra are recorded with a relaxation delay of 1.0 s and an acquisition time of 4.09 s. The acquisition parameters for ^{13}C -NMR include a 90° pulse width, a relaxation delay of 1.0 s, and an acquisition time of 1.36 s. Tetramethylsilane is used as a reference.

3.1

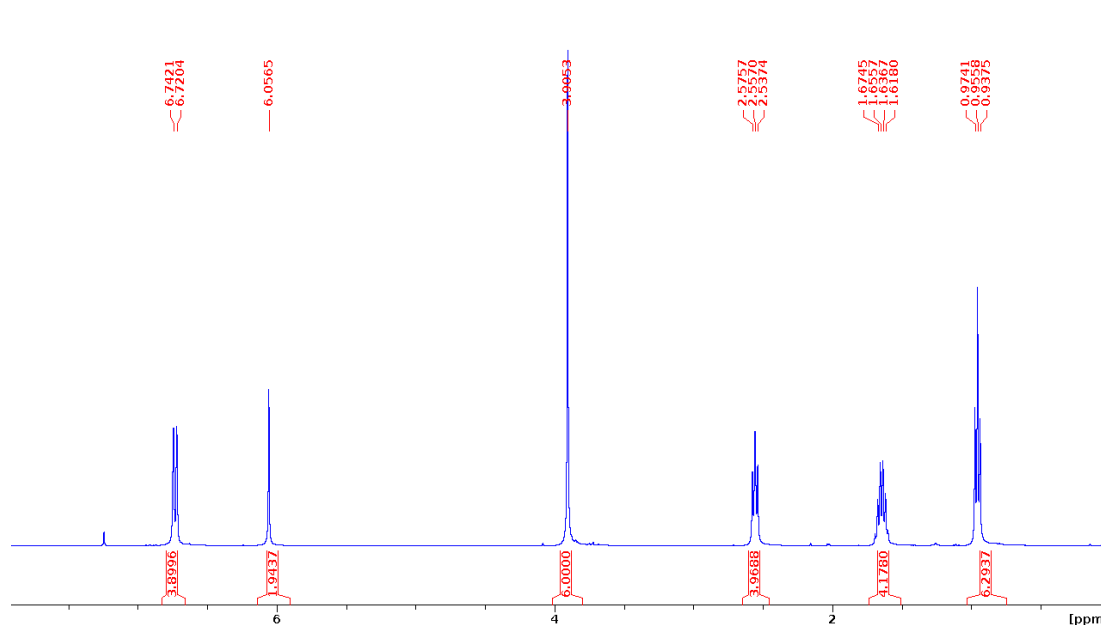


Figure 3. ^1H NMR spectrum of 3,3'-dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol.

^1H NMR (400 MHz, CDCl_3) δ 6.74 (d, $J=8.7$ Hz, 4H, 2&6), 6.06 (s, 2H, OH), 3.91 (s, 6H, OMe), 2.58 (t, $J=7.5$ Hz, 4H, α), 1.67 (q, $J=7.5$ Hz, 4H, β), 0.974 (t, $J=7.3$ Hz, 6H, γ).

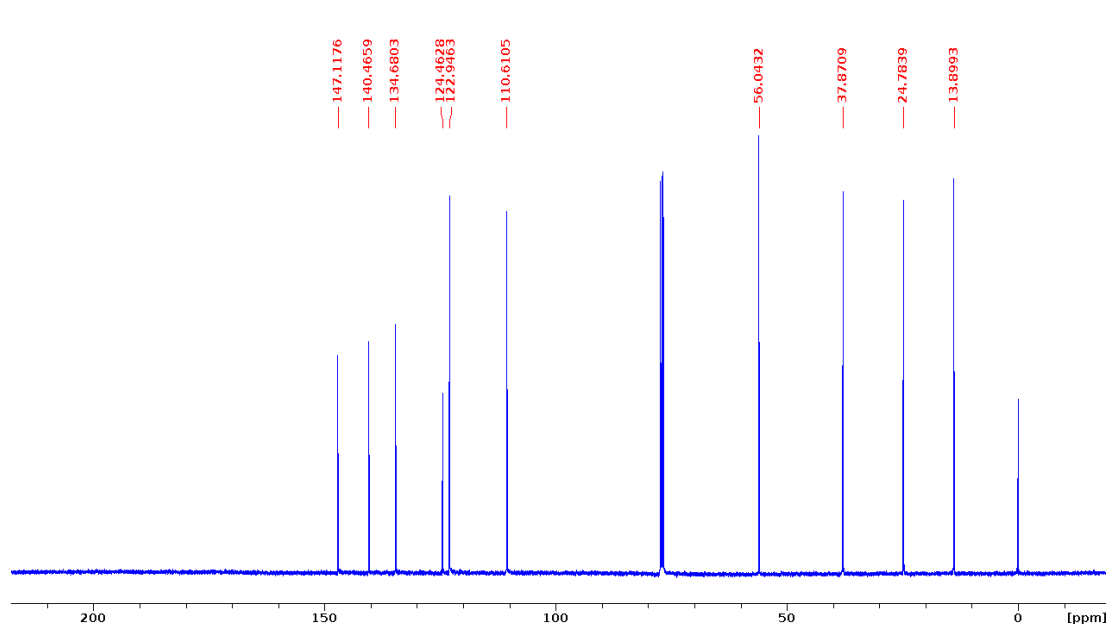


Figure 4. ^{13}C NMR spectrum of 3,3'-dimethoxy-5,5'-dipropyl-2,2'-biphenyldiol.

^{13}C NMR (100 MHz, CDCl_3) δ 147.12 (3), 140.47 (4), 134.68 (1), 124.46 (5), 122.95 (6), 110.61 (2), 56.04 (OMe), 37.87 (α), 24.78 (β), 13.90 (γ).