

Boron sulfonic acid (BSA) catalyzed selective synthesis of aryl-bis(2-hydroxynaphth-1-yl)methanes and 14-alkyl- and 14-aryl-14H-dibenzoxanthenes under solvent-free condition

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CHRONICLE

Article history:

Received January 21, 2015
Received in revised form
March 29, 2015
Accepted 9 April 2015
Available online
9 April 2015

Keywords:

Aryl-bis(2-hydroxy-1-naphthyl)methanes
Dibenzoxanthenes
B(HSO₄)₃
Reusable solid acid
Neat condition

ABSTRACT

This study investigated the selective synthesis of aryl-bis(2-hydroxy-1-naphthyl)methane for the first time under microwave irradiation in solvent-free medium within 5 min using 10 mol % of B(HSO₄)₃ (BSA) as reusable solid acid catalyst. The same reaction could also be conducted at 90-100 °C in neat for the formation of alkyl or aryl 14H-dibenzoxanthenes in presence of BSA catalyst with excellent yields.

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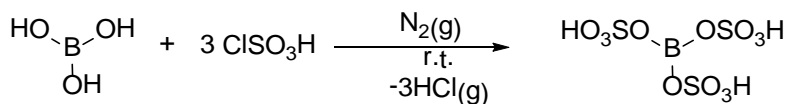
1. Introduction

The efficient applications of solid acid catalyst in organic synthesis have encouraged the chemists to devise new reagents and methods that are innocuous to the environment.¹ Most of these solid acids are safe, non-corrosive, easy separation via filtration, recyclable, cheaper, chemo selective and product selective in various reaction conditions.² Boron sulfonic acid (BSA) is a versatile solid acid which was first introduced by Kiasat *et al* that makes reaction processes convenient, more economic, and environmentally benign (Scheme 1).³ Owing to the numerous advantages associated with this cheap and non-hazardous reagent, BSA has been explored as a powerful catalyst for various organic transformations under mild conditions.⁴ In continuation of our research work on solid acid catalysed organic transformations,⁵⁻⁶ we have the opportunity to explore the catalytic activity of BSA for the selective generation of 14-alkyl or aryl 14H-dibenzoxanthenes and its precursors aryl or alkyl-bis(2-hydroxy-1-naphthyl)methane from the acid catalysed reaction of 2-naphthol with aldehydes (Scheme

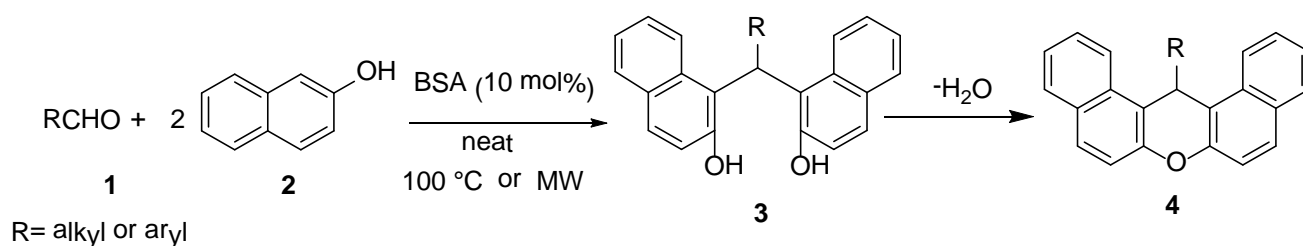
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2). Both dibenzoxanthene **4** and bisnaphthol **3** derivatives have wide range of applications in medicinal chemistry as antiviral, antibacterial, and anti-inflammatory activities, anticancer, and anti-analgesic activity.⁷⁻⁸ In material science, dibenzoxanthene can be used as dyes, in laser technology, pH-sensitive fluorescent materials for the visualization of biomolecular assemblies⁹⁻¹⁰ and in photodynamic therapy.¹¹⁻¹² Similarly bisnaphthol derivatives are applicable as non-linear optical materials, ion-selective electrodes or sensors, chiral ligands in organometallic chemistry, synthetic precursors for the formation of spirans and sometimes, as high-performance liquid chromatography stationary phases with some modifications.¹³⁻¹⁴



Scheme 1. Preparation of boron sulfonic acid catalyst.



Scheme 2. Synthesis of bisnaphthol (**3**) and dibenzoxanthene (**4**) derivatives.

A large number of acid catalysts have been reported in literature for the synthesis of dibenzoxanthenes which include traditional Brønsted/Lewis acids along with reusable heterogeneous acids.¹⁵ Some of the examples of solid acids are Amberlyst-15,² silica sulfuric acid,¹⁶ HClO₄/SiO₂,¹⁷ heteropoly acid,¹⁸ Yb(OTf)₃,¹⁹ montmorillonite K-10²⁰ and cellulose sulfuric acid.²¹ Most of the acid catalysed synthesis of dibenzoxanthene (Scheme 2) described the selective formation of required product without the intermediary of aryl or alkyl di-(2-hydroxy-1-naphthyl)methanes under solvent-free thermal treatment or in microwave irradiation. The literature survey shows few reports on the synthesis of aryl or alkyl di-(2-hydroxy-1-naphthyl) methane from aldehydes and 2-naphthol.²²⁻²⁴ The preparations of bisnaphthols were described as lower yields from the mixture of 2-naphthol and benzaldehyde in AcOH using conc. HCl for 50 h in refrigerator.²² Alizadeh *et al* introduced H₃[P(Mo₃O₁₀)₄].nH₂O as reusable heteropolyacids catalyst in refluxing dichloromethane.²³ Similarly the condensation of phenols with aromatic aldehydes in ethanol utilized 3 kbar pressure in 24 hours at 60 °C in presence of TfOH catalyst to produce good to excellent yields of bisnaphthols.²⁴ All these studies reveal that there is a scope to study the selective synthesis of both compounds (**3** & **4**) in presence of reactive BSA as reusable solid catalyst under thermal and microwave energies with the incorporation of more number of greener components. It is well established that the combination of microwave energy with solvent-free medium reduces the reaction time and thus make the reaction path cleaner by single product formation.²⁵ By considering the multifaceted advantages of microwave assisted organic synthesis we decided to investigate the BSA catalyzed reaction of 2-naphthol and aldehydes under microwave irradiation and compare the results with thermal energy to identify the exact conditions for selective synthesis of **3** and **4**.

2. Results and Discussion

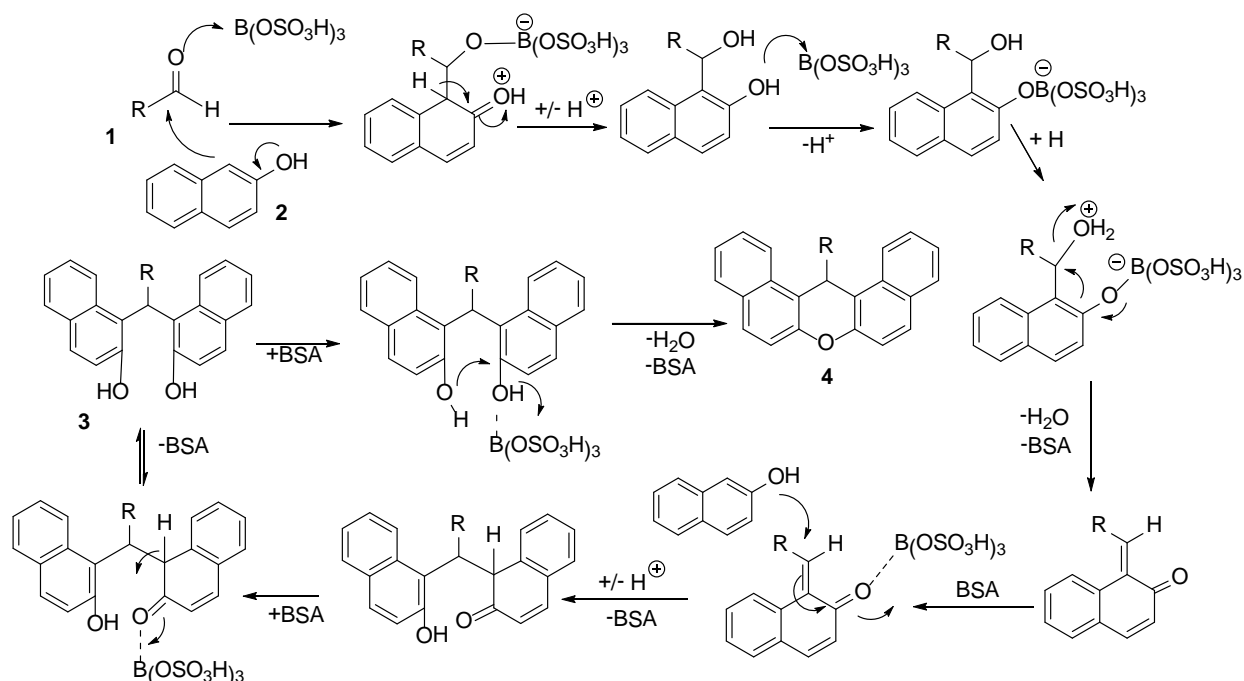
Initially, we optimized the amount of BSA catalyst with the model reaction of benzaldehyde (1 mmol) and 2-naphthol (2 mmol) (Table 1) in solvent-free medium under thermal as well as microwave energies to study the appropriate conditions for the selective synthesis of aryl-bis (2-hydroxy-1-naphthyl) methane **3a** and dibenzoxanthene derivatives **4a**. All the reactions were monitored by thin layer chromatography using 1: 5 ethyl acetate and hexane as solvent system.

Table 1. Standardization of the amount of catalyst using BSA catalyst

| Entry | BSA (mol %) | Time ^a (min) | | MW Power Method B (W) | Product Yields (%) | |
|-------|-------------|-------------------------|---|-----------------------|--------------------|---------|
| | | A | B | | 3 (A/B) | 4 (A/B) |
| 1 | 1 | 60 | 5 | 500 | 10/10 | 50/10 |
| 2 | 5 | 15 | 5 | 500 | 10/25 | 68/10 |
| 3 | 10 | 15 | 5 | 500 | -/80 | 96/15 |
| 4 | 10 | - | 5 | 625 | -/- | -/95 |
| 5 | 25 | 10 | 5 | 250 | -/- | 97/96 |

^aMethods A: solvent-free thermal method at 100°C; B: microwave irradiation in neat condition

These studies clearly identified two optimized conditions for selective formation of **3a** and **4a** under microwave and thermal energies with 10 mol% of BSA catalyst (Table 1, entry 3). The thermal treatment needed 100 °C to give 96% yield of dibenzoxanthene **4a** during 15 min reaction time (Table 1, entry 3) whereas it was 80% yield of bisnaphthol **3a** within 5 min with 500W microwave power irradiation (Table 1, entry 3). The reaction mixture was found with unreacted 2-naphthol at 80 °C in neat condition. It was observed that at 500W microwave power, the reaction produced only 15% of dibenzoxanthene **4a** and major amount of bisnaphthol **3a** in the presence of 10 mol% of BSA catalyst (Table 1, entry 3). Interestingly, the conversion of bisnaphthol **3a** to dibenzoxanthene **4a** became faster upon increasing the MW power to 25% with 10 mol % of BSA for 5 min irradiation (Table 1, entry 4). The use of 25 mol% of BSA produced dibenzoxanthene **4a** as sole product in both methods within 10 min at 100 °C in thermal treatment and at 50% lower microwave power than the power of bisnaphthol **3a** synthesis under optimized condition (Table 1, entry 5). This observation showed the product selectivity of BSA catalyst against its variations of amounts under thermal and microwave conditions. From this study, we selected 10 mol% and 25 mol% of BSA as the optimized amounts for the selective formation of bisnaphthol **3a** and dibenzoxanthene derivatives **4a** in thermal method at 100 °C and different microwave energies in solvent-free conditions. The model reaction was not efficient to produce good yields of products in water, dichloromethane, chloroform and ethanol under reflux in solution as compared to neat environment. The results were unacceptable both in terms of yield of the product and time for the completion of the reaction as compared to the solvent-free system.

**Scheme 3.** Plausible mechanism of BSA catalyzed synthesis of **3a** and **4a**.

By considering the above optimization studies, we extended the synthesis of alkyl or aryl-bis (2-hydroxy-1-naphthyl) methane **3** and their dehydration product dibenzoxanthene **4** with different aldehydes in solvent-free medium using both energy sources with 10 mol % and 25 mol % of BSA catalysts. All these observations were included in Table 2. The plausible mechanism of BSA catalyzed synthesis of dibenzoxanthene **4a** and bisnaphthol **3a** can be expressed according to Scheme 3.^{29,30}

The results in Table 2 showed selective behaviour of BSA catalyst for the formation of dibenzoxanthene **4** at 100°C with 10 mol% of catalyst from aliphatic or aromatic aldehydes except 4-nitrobenzaldehyde (Table 2, entry 2). The same amount of catalyst generated bisnaphthol **3** as major product from aromatic aldehydes (75-96 %) under microwave in short time excluding *p*-tolualdehyde (Table 2, entry 5).

Table 2. Formation of **3** and **4** with different aldehydes using BSA catalyst in solvent-free methods

| Entry | Aldehyde, R- | MW Power (W) (Method B) | BSA (mol %) | Time (min) (Method A/B) ^a | Yield (%) 3 ^{24,27} (Method A/B) | Yield (%) 4 ^{17,26,27,28} (Method A/B) |
|-------|---|-------------------------------|----------------|--|--|--|
| 1 | 1a Ph | 500 | 10 | 15(A)/5(B) | -/80(B) | 96(A)/5(B) |
| | | 625 | 10 | 5(B) | - | 87(B) |
| | | 250 | 25 | 10(A)/5(B) | - | 97(A)/92(B) |
| 2 | 1b 4-NO ₂ C ₆ H ₄ | 625 | 10 | 15(A)/3(B) | 95(A)/96(B) | - |
| | | 625 | 25 | 60(A)/5(B) | 72(A)/75(B) | 24(A)/15(B) |
| 3 | 1c 4-CH ₃ OC ₆ H ₄ | 250 | 10 | 45(A)/5(B) | -/75(B) | 70(A)/- |
| | | 500 | 25 | 5(B) | 65(B) | 25(B) |
| 4 | 1d 4-ClC ₆ H ₄ | 625 | 10 | 15(A)/3(B) | -/92(B) | 90(A)/- |
| | | 750 | 25 | 3(B) | 70(B) | 22(B) |
| 5 | 1e 4-CH ₃ C ₆ H ₄ | 375 | 10 | 30(A)/5(B) | - | 80(A)/85(B) |
| | | 625 | 25 | 2(B) | - | 96(B) |
| 6 | 1f CH ₃ (CH ₂) ₂ | 250 | 10 | 40(A)/5(B) | - | 75(A)/10(B) |
| 7 | 1g fur-2-yl | 500 | 10 | 15(A)/5(B) | Polymeric products | - |
| 8 | 1h naphth-2-yl | 500 | 10 | 40(A)/5(B) | 30(A)/85(B) | 65(A)/- |
| | | 625 | 25 | 60(A)/3(B) | -/60(B) | 85(A)/30(B) |
| 9 | 1i PhCH=CH | 250 | 10 | 15(A)/5(B) | - | 95(A)/90(B) |

^a Methods A: solvent-free thermal method at 100°C; B : microwave irradiation in neat condition ; ^b Isolated products; ^c All the isolated products are known and characterized by comparing their melting point, ¹H NMR, ¹³C NMR and elemental analysis data with reported literature.^{24,17,26-28}

Cinnamaldehyde produced dibenzoxanthene **4i** as single product under microwave and thermal energies (Table 2, entry 9). Butanal formed dibenzoxanthene as major product in thermal method at 90°C with 10 mol% of BSA (Table 2, entry 6). The BSA catalyst lost its selectivity with 25 mol% under microwave irradiation for the formation of bisnaphthol derivatives while benzaldehyde and *p*-tolualdehyde yielded dibenzoxanthene as major product (Table 2, entries 1, 5).

The recyclability of the catalyst was tested by conducting the model reaction of benzaldehyde and 2-naphthol with 10 mol % of BSA at 100 °C for the preparation of dibenzoxanthene **3a** for four cycles. The results obtained were depicted in Fig. 1.

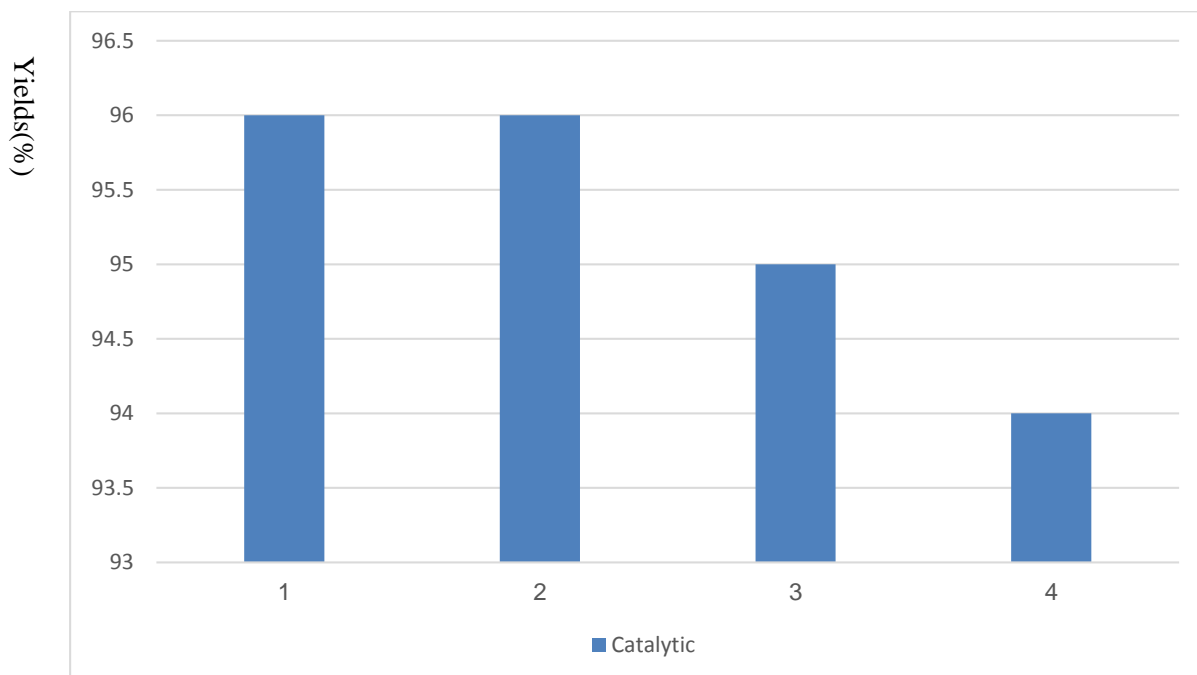


Fig. 1. Recycling of BSA catalyst for the preparation of **3a** at 100 °C.

3. Conclusions

This study explored the catalytic activities of boron sulfonic acid as reusable solid acid in neat conditions for the selective preparation of dibenzoxanthene and its precursor intermediate bisnaphthol under thermal and microwave energies in an efficient way. We observed different selectivity of BSA catalyst towards the synthesis of dibenzoxanthene in thermal and microwave conditions with variation of the amount of catalysts under optimized conditions. The catalyst was found to be recyclable for four runs for the synthesis of dibenzoxanthene and thus making it quite attractive in terms of green chemistry. Moreover, this is the first method for the selective synthesis of aryl-bis (2-hydroxy-1-naphthyl)methane under microwave irradiation in presence of a heterogeneous catalyst with excellent yields of product. In both conditions the selective syntheses of bisnaphthol and dibenzoxanthene derivatives were possible within 5-60 min reaction time.

Acknowledgements

The authors are thankful to Sophisticated Instrument Facility and Department of Chemical Sciences, Tezpur University for analysis of various samples for this work. The co-author of the paper expresses her acknowledgement to University Grants Commission, New Delhi for financial assistance under BSR scheme.

4. Experimental

4.1. Materials and Methods

All chemicals were purchased from chemical supplier and were used without purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM ECS- 400 MHz FT-NMR spectrometer in CDCl_3 solution using TMS as internal standard. J -values were given in Hertz. IR spectra were recorded on a Nicolet Impact-410 spectrometer. The products were identified by comparison of their FT-IR, ^1H and ^{13}C NMR

spectroscopic data with those of authentic compounds and literature reported data.^{17, 24, 26-28} The elemental analysis were performed on Perkin Elmer 20-analyzer. Melting points were recorded in a Buchi B-540 melting point apparatus and were uncorrected.

4.2 Preparation of Boron Sulfonic Acid (BSA)

The boron sulfonic acid (BSA) catalyst was prepared via the reaction of boric acid with chlorosulfonic acid by following the procedure reported by Kiasat et al in 2008.³ A 50 mL suction flask fitted with a constant pressure dropping funnel was connected to a vacuum system through water and an alkali trap. To the flask, 12 mmol of boric acid was introduced and after that, 36 mmol of chlorosulfonic acid was added drop wise over a period of an hour at ambient temperature with the help of pressure dropping funnel. The immediately evolved HCl generated was trapped by the water and alkali solutions through suction. Once the addition was completed, the resulting mixture was shaken for an hour. The solid residue was washed with diethyl ether to remove the unreacted chlorosulfonic acid. Finally, the product was collected as grey solid with 94% yield.

4.3 Typical Procedure for the Preparation of 14-Alkyl or Aryl -14H-Dibenzoxanthenes **4** under Solvent-free Thermal Energy

A mixture of aldehyde (1 mmol) and β -naphthol (2 mmol) along with BSA (10 mol%) was grounded in mortar into a fine powder and was introduced in a 50 ml round bottomed flask fitted with a reflux condenser to a preheated oil bath at 100°C for the specified time. After completion of the reaction as indicated by TLC, the mixture was diluted with ethyl acetate (5 ml) and filtered to isolate the solid catalyst for recycling. The crude filtrate was washed with dilute aqueous sodium hydroxide solution to remove the unreacted 2-naphthol. The organic extract was dried over anhydrous Na₂SO₄ and distilled under reduced pressure to furnish the crude product. The crude product was further purified by preparative TLC (thin layer chromatography) with ethyl acetate and hexane as solvent system to isolate the analytically pure product.

4.4 Typical Procedure for the Preparation of Aryl-bis (2-hydroxy-1-naphthyl)methanes **3** and 14-Alkyl or aryl -14H-dibenzoxanthenes **4** under microwave energy

A mixture of finely grounded aldehyde (1 mmol), 2-naphthol (2 mmol) and BSA (10 mol% or 25 mol%) was irradiated at different power level in a microwave reactor (Catalyst System) for the specified time as mentioned in the table 2. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature and ethyl acetate was added in order to recover the insoluble catalyst by filtration. The filtrate was washed with dilute aqueous sodium hydroxide solution to remove the unreacted 2-naphthol. The organic extract was dried over anhydrous Na₂SO₄ and distilled under reduced pressure to furnish the crude product. The crude product was purified by preparative chromatography using ethyl acetate and hexane as solvent system to get analytically pure product.

4.5. Selected Spectral Data of Aryl-bis (2-hydroxy-1-naphthyl)Methanes **3** and Dibenzoxanthene Derivatives **4**:

4.5.1. Phenyl-bis(2-hydroxy-1-naphthyl) methane (**3a**) (table 2, entry 1). M.p. 203-205°C. IR: 3422, 2926, 2378, 1953, 1618, 1505, 1436, 1358, 1257, 1210, 1146, 1031, 957, 813, 749, 699 cm⁻¹. ¹H NMR: 6.3 (s, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.20-7.39 (m, 9H), 7.7 (d, *J* = 9.1 Hz, 2H), 7.8 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H). ¹³C NMR: 42.7, 118.6, 119.9, 122.6, 123.6, 127.5, 128.4, 129, 129.7, 129.9, 130.1, 133.6, 140.6, 152.9. CHN analysis: Calcd. for C₂₇H₂₀O₂ (%): C 86.17, H 5.31, Found: C 86.21, H 5.35.

4.5.2. 14-(4-Methylphenyl)-14H-dibenzo[*a,j*]xanthenes **4e** (table 2, entry 5). M.p. 229.1°C. IR: 3068, 2917, 1626, 1597, 1515, 1466, 1437, 1404, 1258, 1125, 1087, 967, 840, 815, 785, 745 cm⁻¹. ¹H NMR: 2.3 (s, 3H), 6.14 (s, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 7.13-7.16 (m, 6H), 7.27 (t, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 3H), 7.69-7.78 (m, 3H). ¹³C NMR: 21.1, 62.7, 111.8, 116.5, 121.4,

122.8, 126.8, 127.9, 128.9, 129.1, 129.4, 129.9, 130, 138.4, 146.5, 156, 199.9. CHN analysis: Calcd. for C₂₈H₂₀O (%): C 90.32, H 5.37, Found C 90.37, H 5.40.

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