A Triflate Hydrodeoxygenation Route to Resveratrol from Syringaldehyde

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OPPI BRIEF

A Triflate Hydrodeoxygenation Route to Resveratrol from Syringaldehyde

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When a starting material is being contemplated for the synthesis of an active pharmaceutical ingredient or a building block for polymers, natural products are the green alternatives to petroleum feedstocks.1,2 Plant metabolites are an excellent source for aromatic compounds but are invariably oxygenated.3–5 In certain cases, the hydroxy groups of the natural products are ideally located and can be simply built upon or protected to allow for chemical modification elsewhere in the molecule. More often, the natural product has too many hydroxy groups or it would be preferable to replace one or more of them with some other group. This paper describes an investigation in the hydrodeoxygenation of some phenolic compounds (Ph-OH to Ph-H) by reduction of the corresponding trifluoromethanesulfonates (triflates)6–10 in an effort to synthesize the natural polyphenol resveratrol (trans-3,4′,5-trihydroxystilbene), a compound which may have biological activity in mammals.11,12

The spent liquor from paper processing mills contains variable amounts of aromatic aldehydes vanillin (3-methoxy-4-hydroxybenzaldehyde, 1a) and syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde, 1b) depending on the source of wood (conifer or deciduous).13,14 Syringaldehyde is very close in structure to one of the typical starting materials for the synthesis of resveratrol, namely 3,5-dimethoxybenzaldehyde (3b).15–18 The triflates of vanillin (2a)18,19 and syringaldehyde (2b)20,21 were obtained by reaction with trifluoromethanesulfonic anhydride using pyridine as base in methylene chloride in high yields (Scheme 1). Triflate 2a was isolated as an oil and yet even after distillation gave unsatisfactory combustion analysis. The reduction procedure employed was based on the homogeneous method established by Cacchi et al.,22 using palladium acetate and a phosphine ligand along with a reducing agent in dimethylformamide as solvent. However, with the formic acid salt of triethylamine as the hydrogen donor and triphenylphosphine...
as ligand, only starting material was recovered after the reaction. The careful studies of Cabri et al.\textsuperscript{23} later established the critical role bidentate phosphine ligands plays in the reaction.\textsuperscript{24,25} The reduction proceeded very smoothly to give the aldehydes 3a and 3b in high yield using 1,1′-bis(diphenylphosphino)ferrocene (DPPF) all else being the same. The selectivity in reduction of triflate 2a is noteworthy since Clauss and Jensen\textsuperscript{26} only obtained 3-methoxybenzyl alcohol by reduction of the mesylate of vanillin, although under rather different conditions (H\textsubscript{2}/palladium on charcoal/MeOH/triethylamine).

Although expensive due to the price of Tf\textsubscript{2}O, this rapid preparation of aldehyde 3b may be attractive for laboratory scale natural product synthesis. Otherwise, the compound is made by a five-step route starting from benzoic acid, the last step of which is a stoichiometric, heavy metal-mediated oxidation to the carboxaldehyde which can be capricious.\textsuperscript{27–29} Rather than repeat the conversion of 3b to resveratrol, an attempt was made to expand the scope of this triflate reduction (Scheme 2). Perkin condensation\textsuperscript{30} of syringaldehyde (1b) with 4-methoxyphenyl-acetic acid (4) gave, after hydrolysis of the intermediate
acetate ester, a good yield of the previously unreported 2-arylcinnamic acid 5. Because the alkene hydrogen of 5 appeared downfield (δ 7.66), it was believed to be the trans regioisomer, a fact confirmed by X-ray crystallographic analysis. Rather than the conventional method of copper and quinoline for the decarboxylation of 5, the interesting conditions using ionic liquids reported by Sharma et al. were adopted. Microwave irradiation, however, was not necessary and simple heating of 5 to ~130°C in the melt of the protic ionic liquid, 1-methylimidazolium p-toluenesulfonate, gave an excellent yield of stilbene 6, mp. 110–112°C. Incidentally, Sharma et al. described the preparation of 6 by the Heck reaction between 2,6-dimethoxy-4-vinylphenol and 4-iodoanisole. They indicated the trans geometry for their product melting at 96–98°C, although the 3J coupling constant of the alkene protons could not be observed due to overlapping signals. Using DMSO as NMR solvent for 6, the alkene vicinal coupling of 16 Hz is clearly visible which is typical for trans geometry. So these conditions not only brought about decarboxylation but, fortuitously, isomerized the stilbene to the thermodynamically favored trans isomer presumably by way of a quinone-type resonance contributor.

The hydrodeoxygenation of 6 was carried out in the same manner as previously described for 1a and 1b. Triflate 7 underwent reduction to the stilbene 8 (resveratrol trimethyl ether) without concomitant reduction of the double bond. This result was surprising since several groups have reduced stilbenes to bibenzyls by catalytic transfer hydrogenation using formate salts and homogeneous or heterogeneous palladium catalyst. However, Brunel did report the failure of alkene reduction when bidentate phosphine ligands were employed. The synthesis of resveratrol was completed by refluxing a mixture of 8 in the molten salt pyridine hydrochloride. Although this reagent is convenient to work with, the yield of the dealkylation was poor which, based on other work, is most likely caused by oligomerization and there are better reagents to accomplish this step cleanly (such as BBr3 or BCl3). Since 6 (DMU-291) is the putative active metabolite of the anticancer compound DMU-212 (9), the latter was prepared by simple methylation of 6, using potassium tert-butoxide and iodomethane (Scheme 3), and the product was fully characterized adding further value to the synthetic pathway described here.

In conclusion, the triflates of hydroxybenzaldehydes undergo palladium-catalyzed deoxygenation without reduction of the carbonyl group. Syringaldehyde, which can be obtained from the spent liquor of paper processing, was converted into resveratrol in five steps in 12% overall yield (unoptimized).
Experimental Section

The melting points were acquired on a Meltemp II electrothermal capillary melting point apparatus (Laboratory Devices, Holliston, MA) and are not corrected. All NMR data were obtained on a Bruker Avance II 300 MHz spectrometer (1H at 300 MHz, 13C at 75 MHz, 19F at 282 MHz). NMR data (free induction decay signals) were processed using NUTS software from Acorn NMR (Livermore, CA). All 1H, 13C and 19F spectra are referenced to solvent, tetramethylsilane or fluorotrichloromethane. In all cases, thin-layer chromatography (TLC) was carried out on aluminum foil backed, silica gel plates eluting with a mixture of hexanes/EtOAc. Trifluoromethanesulfonic anhydride (Tf2O), syringaldehyde (1b), vanillin (1a), 4-methoxyphenylacetic acid (4), anhydrous N,N-dimethylformamide (DMF), 1,1′-bis(diphenylphosphino)ferrocene (DPPF) and all other reagents were obtained commercially.

3-Methoxy-4-(trifluoromethanesulfonyloxy)benzaldehyde (2a)

To a round-bottomed flask equipped with magnetic stir bar was charged 1a (3.0 g, 20 mmol), pyridine (4.7 g, 59 mmol, 3 equiv) and CH2Cl2 (25 mL). The mixture was cooled in a Dry Ice-acetone bath and Tf2O (6.6 mL, 11.1 g, 39 mmol, 2 equiv) was added dropwise over 30 min. Afterwards, the mixture was stirred at rt for 2 h. The reaction mixture was washed with H2O (25 mL × 2) followed by brine (25 mL). The organic phase was separated, dried over anhydrous MgSO4 and evaporated in vacuo leaving a brownish oil (5.12 g, 90%). Although the crude material could be further purified by short-path distillation at reduced pressure (0.1 torr) to give the product as colorless oil, it appears to be heat sensitive as there was a significant decomposition residue in the distillation pot. 1H NMR (CDCl3): δ 9.98 (s, 1H), 7.56 (d, J = 1.7 Hz, 1H), 7.51 (dd, J = 8.2 and 1.8 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 3.99 (s, 3H); 13C NMR (CDCl3): δ 190.53, 152.49, 142.97, 137.06, 124.27, 123.45, 121.06, 118.92 (q, JCF = 321.5 Hz), 112.06, 56.75; 19F {13C} NMR (CDCl3): δ -74.2. The product was used in the synthesis of compound 3a without purification.

3,5-Dimethoxy-4-(trifluoromethanesulfonyloxy)benzaldehyde (2b)

To a round-bottomed flask (100 mL) equipped with magnetic stir bar and addition funnel (10 mL) was added 1b (3.0 g, 16.5 mmol), CH2Cl2 (50 mL) and triethylamine (3.3 g, 33 mmol, 2 equiv). The mixture was cooled to 0°C in an ice bath. The funnel was charged with Tf2O (6.9 g, 4.18 mL, 24.8 mmol, 1.5 equiv) which was added dropwise over 1 h. After several hours at 0°C, the mixture was allowed to warm up to rt and washed with H2O. The organic phase was washed with brine (25 mL), separated and dried over anhydrous MgSO4. The organic phase was treated with decolorizing charcoal, filtered and evaporated in vacuo. Compound 2b was obtained as colorless crystals by recrystallization from hexanes (4.5 g, 87%), mp. 105–107°C, lit.21 108–110°C. 1H NMR (CDCl3): δ 9.95 (s, 1H), 7.17 (s, 2H), 3.99 (s, 6H); 13C NMR (CDCl3): δ 190.65, 153.45, 136.13, 132.25, 118.85 (q, JCF = 321.2 Hz), 106.15, 56.89; 19F {13C} NMR (CDCl3): δ -74.08.

3-Methoxybenzaldehyde (3a)

To a round-bottomed flask equipped with magnetic stirring bar charged with DMF (5 mL) and triethylamine (2.81 g, 27.8 mmol), 98% formic acid (1.28 g, 27.8 mmol) was added dropwise over 1 min. Then, 2a (1 g, 3.5 mmol) was added followed by Pd(OAc)$_2$ (30 mg, 0.13 mmol) and DPPF (150 mg, 0.27 mmol); all the solids dissolved to give a clear orange solution. It was then heated to 80$^\circ$C and after about 15 min a yellow solid precipitated. The mixture was cooled to rt and filtered to remove the solid. The filtrate was partitioned between Et$_2$O (25 mL) and H$_2$O (25 mL). The organic layer was further washed with H$_2$O (25 mL) followed by brine. The organic phase was dried over anhydrous MgSO$_4$ and evaporated in vacuo to a brown oil. Distillation under reduced pressure (0.1 torr) gave 3a a colorless, mobile liquid (400 mg, 85%), lit.$^5$ bp. 121$^\circ$C / 1 4 torr. $^1$HNMR (CDCl$_3$): $\delta$ 9.97 (s, 1H), 7.47–7.42 (m, 2H), 7.39–7.37 (m, 1H), 7.20–7.14 (m, 1H), 3.86 (s, 3H); $^{13}$CNMR (CDCl$_3$): $\delta$ 192.29, 160.38, 138.03, 130.22, 123.71, 121.70, 112.28, 55.67.

**Anal.** Calcd for C$_8$H$_8$O$_2$: C, 70.57; H, 5.92. Found: C, 70.27; H, 5.95.

3,5-Dimethoxybenzaldehyde (3b)

To a round-bottomed flask (100 mL) equipped with magnetic stir bar and reflux condenser charged with DMF (3 mL) and triethylamine (1.29 g, 13 mmol), was added dropwise 98% formic acid (0.588 g, 13 mmol). Then, 2b (500 mg, 1.6 mmol) was added followed by Pd(OAc)$_2$ (35 mg, 0.15 mmol) and DPPF (177 mg, 0.3 mmol). All the solids dissolved resulting in a clear orange solution. The solution was heated to 80$^\circ$C under an N$_2$ atmosphere; shortly after heating began, a yellow solid precipitated. After 1 h, the reaction mixture was cooled to rt and filtered through medium filter paper to remove the solid. The filtrate was partitioned between Et$_2$O (50 mL) and H$_2$O (50 mL). The organic layer was separated and washed with H$_2$O (25 mL) followed by brine (25 mL). The organic phase was separated and dried over anhydrous MgSO$_4$ and evaporated in vacuo leaving a yellowish solid which was essentially pure 3b (260 mg, 90%), mp. 42–44$^\circ$C, lit.$^5$ 45–46$^\circ$C. $^1$HNMR (CDCl$_3$): $\delta$ 9.92 (s, 1H), 7.02 (d, $J = 2.2$ Hz, 2H), 6.71 (t, $J = 2.2$ Hz, 1H), 3.85 (s, 6H); $^{13}$CNMR (CDCl$_3$): $\delta$ 192.14, 161.49, 138.64, 107.41, 107.36, 55.88.


trans-2-(4-Methoxyphenyl)-3-(3,5-dimethoxy-4-hydroxyphenyl)acrylic Acid (5)

To a round-bottomed flask (500 mL) equipped with magnetic stir bar and reflux condenser was added 1b (9.1 g, 50 mmol), 4 (8.3 g, 50 mmol), Ac$_2$O (50 mL) and, lastly, triethylamine (10 g, 100 mmol, 2 equiv). The mixture was refluxed for 18 h. and then the hot reaction mixture was poured into vigorously stirred H$_2$O (300 mL). The precipitate formed was collected on a coarse porosity fritted glass filter was dissolved in 0.83 M NaOH (300 mL, 5 equiv). The solution was filtered through a medium glass frit to remove a small amount of brown insoluble matter. The filtrate was then stirred and slowly acidified to pH 5 with conc. HCl. The tan precipitate formed was collected and dried in vacuo (10 torr, 40$^\circ$C) to give compound 5 as a tan powder (13.19 g, 79%) which upon crystallization from ethanol gave pale yellow plates, mp. 228–230$^\circ$C. $^1$HNMR (DMSO): $\delta$ 12.43 (bs, CO$_2$H), 8.83 (bs, OH), 7.66 (s, 1H), 7.11 (d, $J = 8.6$ Hz, 2H), 6.99 (d, $J = 8.6$ Hz, 2H), 6.39 (s, 2H), 3.76 (s,
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$^3$H), 3.47 (s, 6H); $^{13}$C NMR (DMSO): $\delta$ 168.78, 158.66, 147.32, 139.69, 137.03, 130.94, 129.82, 129.07, 124.56, 114.12, 108.37, 55.41, 55.19.

**Anal. Calcd for C$_{18}$H$_{18}$O$_6$: C, 65.45; H, 5.49. Found: C, 65.18; H, 5.60.**

**1-Methylimidazolium p-Toluenesulfonate**

To a round-bottomed flask (50 mL) equipped with magnetic stir bar was added p-toluenesulfonic acid monohydrate (4.3 g, 23 mmol) followed by 1-methylimidazole (1.86 g, 23 mmol, 1 equiv); the mixture became warm as all the solids dissolved. After dissolution, water was removed in vacuo (10 torr to 1 torr, 60°C) to give a crude white solid which upon recrystallization from EtOAc/MeCN, gave the salt as a white microcrystalline powder (4.0 g, 69%), mp. 83–85°C, *lit.*$^{41}$ 90–91°C. $^1$H NMR (CDCl$_3$): $\delta$ 9.09 (s, 1H), 7.76 (d, $J$ = 8.3 Hz, 2H), 7.31 (s, 1H), 7.20 (s, 1H), 7.15 (d, $J$ = 7.9 Hz, 2H), 3.88 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 142.73, 140.24, 136.24, 129.05, 125.92, 122.92, 120.36, 36.05, 21.41.

**Anal. Calcd for C$_{11}$H$_{14}$N$_2$O$_3$S · 1/2 H$_2$O: C, 50.18; H, 5.74; N, 10.64. Found: C, 50.16; H, 5.52; N, 11.06.**

**trans-3,4′,5-Trimethoxy-4-hydroxystilbene (6)**

To a round-bottomed flask (500 mL) equipped with magnetic stir bar and reflux condenser was added 1-methylimidazolium p-toluenesulfonate (34.8 g, 137 mmol, 5 equiv.) and 5 (9.1 g, 27.6 mmol). The mixture was stirred and heated to 130°C (internal temperature) using a heating mantle. As the mixture reached 130°C, the solids dissolved to a brownish colored solution with concurrent gas evolution (CO$_2$). At 10 min intervals, a small aliquot of the reaction mixture was removed, dissolved in H$_2$O and extracted with Et$_2$O for TLC analysis. After heating for ~30 min, the mixture had a purplish color and TLC showed the reaction was complete. The mixture was cooled to ~90°C and diluted with H$_2$O (300 mL) whereupon a pinkish-tan colored solid precipitated. The precipitate was collected on a medium porosity fritted glass filter (7.57 g, 95%) and was purified by recrystallization from MeOH to afford compound 6 as rose colored needles, mp. 110–112°C, *lit.*$^{42}$ 96–98°C. $^1$H NMR (CDCl$_3$): $\delta$ 7.43 (d, $J$ = 8.7 Hz, 2H), 6.93–6.86 (m, 4H), 6.73 (s, 2H), 5.56 (bs, OH), 3.94 (s, 6H), 3.82 (s, 3H); $^1$H NMR (DMSO): $\delta$ 8.47 (s, OH), 7.49 (d, $J$ = 8.8 Hz, 2H), 7.07 (d, $J$ = 16.5 Hz, 1H), 6.97 (d, $J$ = 16.4 Hz, 1H), 6.93 (d, $J$ = 8.6 Hz, 2H), 6.85 (s, 2H), 3.81 (s, 6H), 3.76 (s, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 159.18, 147.38, 134.69, 130.37, 129.37, 127.56, 126.88, 126.48, 114.25, 103.28, 56.39, 55.41; $^{13}$C NMR (DMSO): $\delta$ 158.55, 148.12, 135.40, 130.14, 127.92, 127.27, 126.78, 125.39, 114.15, 103.92, 55.98, 55.09.

**Anal. Calcd for C$_{17}$H$_{18}$O$_4$: C, 71.31; H, 6.34. Found: C, 71.11; H, 6.17.**

**trans-3,4′,5-Trimethoxy-4-(trifluoromethanesulfonyloxy)stilbene (7)**

To a round-bottomed flask (50 mL) equipped with magnetic stir bar and N$_2$ bubbler was added 6 (600 mg, 2 mmol), pyridine (332 mg, 4 mmol, 2 equiv) and CH$_2$Cl$_2$ (20 mL).
The mixture was cooled in an ice bath before Tf₂O (888 mg, 3 mmol, 1.5 equiv) was added dropwise over 20 min, during which time the color changed from deep red to pale orange. Afterwards, the ice bath was removed and the reaction mixture was stirred at rt overnight. A work-up similar to that used in the preparation of 1a and 2a gave an oil that slowly crystallized during drying in vacuo (790 mg, 90%). Recrystallization from heptanes/EtOAc gave compound 7 as clear, tan needles, mp. 104–106°C (dec.). 

\[ \text{H NMR (CDCl₃): } \delta 7.46 (d, J = 8.7 Hz, 2H), 7.03 (d, J_{ab} = 16.1 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 6.89 (d, J_{ab} = 16.3 Hz, 1H), 6.72 (s, 2H), 3.93 (s, 6H), 3.84 (s, 3H); \text{C NMR (CDCl₃): } 160.00, 152.69, 138.64, 130.35, 129.59, 128.21, 125.75, 118.92 (q, J_{CF} = 321.3 Hz), 114.49, 102.94, 56.49, 55.58; \text{F NMR (CDCl₃): } –74.11. \]


**trans-3,4′,5-Trimethoxystilbene (8)**

To a round-bottomed flask (100 mL) equipped with magnetic stir bar charged with anhydrous DMF (6 mL) and triethylamine (960 mg, 9.5 mmol, 5 equiv), was added dropwise, 98% formic acid (437 mg, 9.5 mmol, 5 equiv) was added over 10 min. (exotherm). After the mixture was allowed to cool to rt, a solution of 7 (790 mg, 2 mmol) in anhydrous DMF (3 mL) was added in one portion followed by Pd(OAc)₂ (21 mg, 0.09 mmol) and DPPF (105 mg, 0.18 mmol). A reflux condenser was attached and the reaction mixture was heated under N₂ to an internal temperature of 80°C. After 20 min., the reaction mixture had become dark and was complete as indicated by TLC analysis. The mixture was cooled to rt and partitioned between H₂O (50 mL) and Et₂O (50 mL). A rag layer formed and the mixture was filtered through medium filter paper. The organic layer was separated and washed with H₂O (50 mL) and then brine (50 mL). After drying over anhydrous MgSO₄, the organic phase was evaporated in vacuo to give a pale brown oil that slowly crystallized (470 mg, 91%), mp. 55–57°C, lit. 56–57°C. 

\[ \text{H NMR (CDCl₃): } \delta 7.45 (d, J = 8.9 Hz, 2H), 7.05 (d, J = 16 Hz, 1H), 6.90 (d, J = 16 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 2.2 Hz, 2H), 6.38 (t, J = 2.5 Hz, 1H), 3.83 (s, 9H); \text{C NMR (CDCl₃): } 161.20, 139.93, 130.16, 128.96, 128.02, 126.81, 114.37, 104.57, 99.86, 55.57, 55.53. \]


**trans-3,4′,5-Trihydroxystilbene (Resveratrol)**

To a 250 mL round-bottom flask equipped with a magnetic stir bar was added 8 (2.7 g, 10 mmol) and pyridine hydrochloride (10.4 g, 90 mmol, 9 equiv). A reflux condenser was attached and the reaction mixture was refluxed for 2 h under an N₂ atmosphere. Afterwards, the mixture was allowed to cool to ~90°C and quenched into H₂O (200 mL) whereupon a purplish colored solid precipitated; the mixture (including the solid) was extracted with EtOAc (50 mL × 3). The combined extracts were diluted with hexanes (100 mL) and then filtered through a thin pad of silica gel to remove insoluble dark colored, polar impurities. The filtrate was evaporated in vacuo leaving an off-white solid. The crude product was slurried with HOAc and collected to give resveratrol as a tan microcrystalline powder.
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(450 mg, 20%), mp. 258–261°C, lit.\(^\text{16}\) 261°C, \(^1\)H NMR (DMSO): \(\delta 9.59\) (s, OH), \(9.23\) (s, 2OH), \(7.41\) (d, \(J = 8.9\) Hz, 2H), \(6.95\) (d, \(J_{ab} = 16.3\) Hz, 1H), \(6.82\) (d, \(J_{ab} = 16.3\) Hz, 1H), \(6.76\) (d, \(J = 8.9\) Hz, 2H), \(6.39\) (d, \(J = 2.0\) Hz, 2H), \(6.13\) (t, \(J = 2.1\) Hz, 1H); \(^{13}\)C NMR (DMSO): \(\delta 158.58, 157.28, 139.36, 128.15, 127.96, 127.92, 125.74, 115.61, 104.41, 101.87.

Anal. Calcd for C\(_{14}\)H\(_{12}\)O\(_3\): C, 73.67; H, 5.30. Found: C, 73.40; H, 5.44.

trans-3,4,4',5-Tetramethoxystilbene (9, DMU-212)

To a round-bottom flask (100 mL) equipped with a magnetic stir bar and reflux condenser was added 6 (1.16 g, 4.1 mmol) and anhydrous DMF (15 mL). The mixture was stirred until all the solids had dissolved to give a red solution and then followed by addition of KO\(_2\)Bu (690 mg, 6.2 mmol, 1.5 equiv) in one portion. The color changed to fluorescent yellow-green and shortly thereafter copious solids precipitated (potassium salt of 6). Then iodomethane (1.16 g, 8.2 mmol, 2 equiv) was added to the suspension and the mixture was heated to 80°C. After 1 h, all the solids had dissolved and the color of the solution had changed to pale yellow. The mixture was cooled to rt and diluted with H\(_2\)O (50 mL) whereupon a white solid precipitated. The solid was collected on a medium porosity fritted glass filter. The off-white filter cake was air dried on the frit (1.10 g, 89%) and recrystallized from heptanes/1,2-dichloroethane to afford compound 9 as colorless plates, mp. 148–150°C, lit.\(^\text{55}\) 152–153°C, \(^1\)H NMR (DMSO): \(\delta 7.53\) (d, \(J = 8.5\) Hz, 2H), \(7.17\) (d, \(J_{ab} = 16.1\) Hz, 1H), \(7.02\) (d, \(J_{ab} = 16.3\) Hz, 1H), \(6.95\) (d, \(J = 8.5\) Hz, 2H), \(6.89\) (s, 2H), \(3.83\) (s, 6H), \(3.78\) (s, 3H), \(3.67\) (s, 3H); \(^{13}\)C NMR (DMSO): \(\delta 158.87, 153.04, 137.05, 133.12, 129.76, 127.59, 127.44, 126.29, 114.19, 103.61, 60.05, 55.86, 55.12.

Anal. Calcd for C\(_{18}\)H\(_{20}\)O\(_4\): C, 71.98; H, 6.71. Found: C, 71.84; H, 6.61.

Acknowledgments

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References


37. Crystallographic data (without structure factors) for compound 5 has been deposited with Cambridge Crystallographic Data Centre as supplementary publication CCDC 888230.