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Chiron approach to the synthesis of yashabushidiol B, (3*S*,5*S*)-1-(4′-hydroxyphenyl)-7-phenylheptane-3,5-diol, and its 4′-methoxy analogue

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ABSTRACT

The total synthesis of yashabushidiol B **4**, a linear diarylheptanoid containing a 1,3-diol system and its analogues **5** and **6** has been achieved by utilizing intermediate **7**, which was derived from D-glucose. The Wittig reaction is the key step of our synthetic strategy.

1. Introduction

Diarylheptanoids constitute an important class of natural plant metabolites due to their interesting biological and pharmacological properties, such as antiiinflammatory, antioxidant, anticancer, inhibition of nitric oxide production, DPPH-radical scavenging activity.[1] The linear diarylheptanoids are characterized by a linear seven carbon chain flanked by two aromatic rings. More than 70 linear diarylheptanoids have been isolated from Nature.[2] In addition to the aforementioned biological activities, linear diarylheptanoids with a 1,3-diol system also exhibit hepatoprotective and antiemetic activities.[1i,3] Yashabushidiol, A **1** and B **2** (Fig. 1), linear diarylheptanoids containing a 1,3-diol system, were first isolated in 1986 from the male flowers of *Alnus sieboldiana*.[4]

Antiemetic compounds **3** and **6** were isolated by Takahashi et al.[5] from *Alpinia katsumadai* Hayata and from the rhizomes of *Alpinia officinarum*,[6] respectively. Recently, Narsimhulu et al.[7] have synthesized compounds **4** and **6**, which are the antipodes of the natural products, along with other isomers via alkynylation of the D-mannitol derivative 3-hydroxy-5-phenyl pentanal with substituted phenyl acetylenes and their anticancer activity was tested. Compound **6** showed potent anticancer activity with an IC_{50} of 12.82 μg/mL on a THP-1 leukemia cell line while negligible activity was observed for compound **4**.

Herein we report the first total synthesis of yashabushidiol B **4** and its analogues **5** and **6** from compound **7** (1,2-*O*-isopropylidene-3,5,6-trideoxy-6-phenyl-α-D-gulo-1,4-furanose), which has been synthesized from D-glucose.[8]

2. Results and discussion

Treatment of compound **7** with cat. H_2SO_4 at 65 °C afforded **8** as a 1:1 mixture of α,β-anomers (determined by ^{1}H NMR) which can be visualized as a masked aldehyde. We planned to utilize this masked aldehyde in a Wittig reaction to obtain the required heptanoid chain with a 1,3-diol functionality. For this reaction, we tested various temperatures (Scheme 1), but in all cases, we observed a complex reaction mixture. Varying the equivalents of base and Wittig salt, were also unsuccessful.

Although Wittig reactions with similar anomers were reported[9] with other reagents, our reaction was unsuccessful probably due to the free –OH group at the C2 position, which can interfere in betaine intermediate formation leading to a complex mixture. Therefore, we thought to protect the C2 hydroxyl group as a benzyl ether so that it could be deprotected during the reduction of the olefin after the Wittig reaction in a single step.

The synthesis of target molecules **4**, **5**, and **6** can be visualized as shown in the retrosynthesis (Scheme 2). The chiral 1,3-diol functionality in these diarylheptanoids can be seen in the anomers **13**. These C2 benzyl protected anomers can be extended to diarylheptanoids using suitable Wittig reagents. This anomeric mixture could be obtained by anomeric methyl deprotection of C2 benzylated compound **12**. This compound could be derived in two steps from **7**, which was synthesized from D-glucose.

To achieve the synthesis of C2 benzyl protected anomers **13**, compound **7** was treated with acidic resin in methanol at room temperature (Scheme 3) to afford methoxy protected **11** in quantitative yield as a mixture of anomers (α/β = 17:83) as evident from ^{1}H NMR spectrum. The C2 hydroxy group of this mixture was then protected as a benzyl ether using NaH and BnBr in THF with 93% yield to give **12**. The anomeric methoxy group was deprotected with an acidic resin in the presence of cat. H_2SO_4 under reflux conditions to give compound **13** in 71% yield. Our next task was to perform the Wittig olefination on compound **13**. We repeated the same reaction conditions for Wittig reaction as discussed in Scheme 1. This time, we observed the formation of Wittig products **14** and **15** only under reflux conditions in 76% and 79% yield, respectively, as a diastereomeric mixture of olefins. Reduction of the olefin and benzyl deprotection was carried out under hydrogenation conditions using 10% Pd/C in ethyl acetate at 80 psi; the yashabushidiol B **4** and methoxy derivative **5** were obtained in

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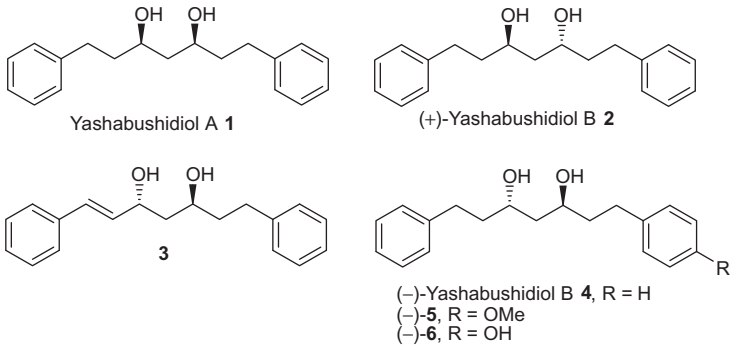
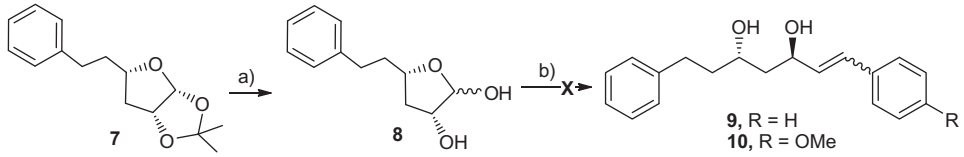
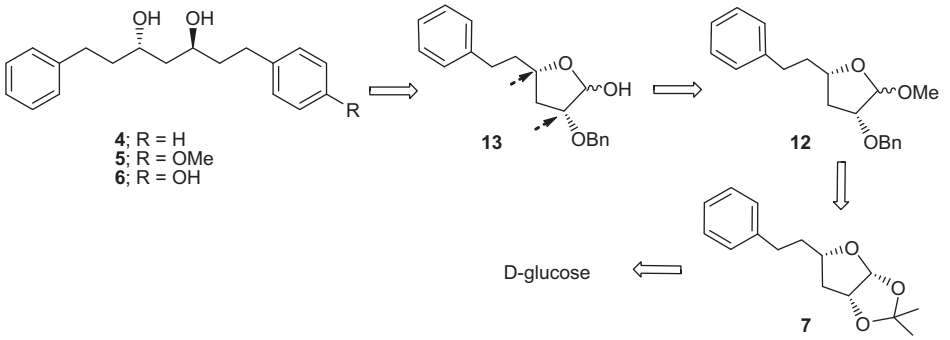


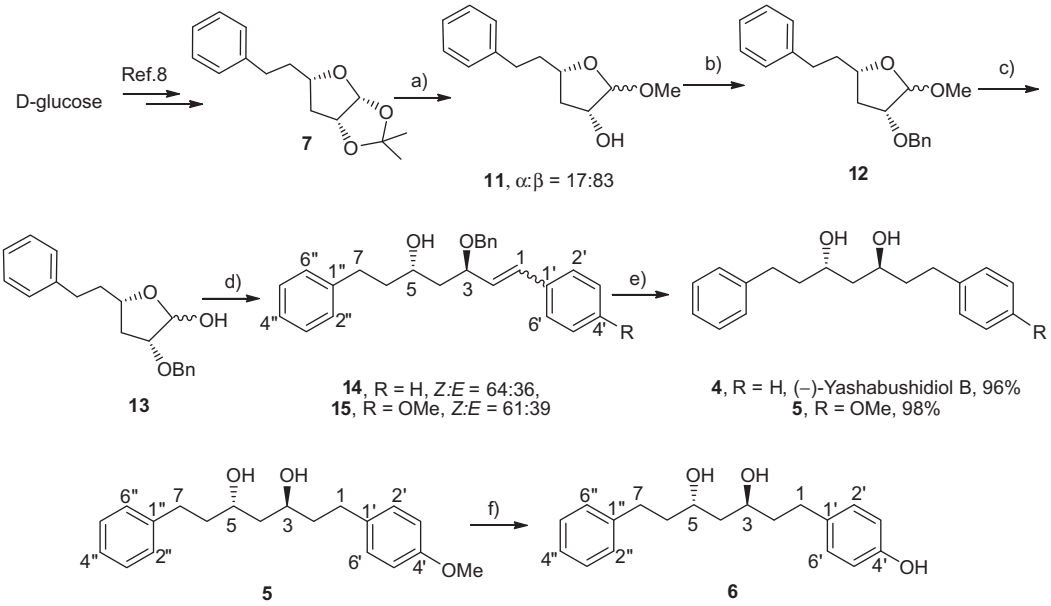
Figure 1. Yashabushidiol A, B, and other linear diarylheptanoids.



Scheme 1. Reagents and conditions: (a) cat. H_2SO_4, THF/H_2O (4:1), 65 °C, 2.5 h, 85%; (b) $Ph_3P^+CH_2Ph(4'\text{-}R)Br^-$, *n*-BuLi, THF. Temperature conditions: (i) −78 °C to rt; (ii) 0 °C to rt; (iii) 0 °C to reflux; (iv) rt to reflux.



Scheme 2. Retrosynthesis.



Scheme 3. Reagents and conditions: (a) Dowex® 50WX4-200 (H^+ form), MeOH, rt, 12 h, quant.; (b) NaH, BnBr, THF, 0 °C to rt, 2 h, 93%; (c) Dowex® 50WX4-200 (H^+ form), cat. H_2SO_4, reflux, 12 h, 71%; (d) $Ph_3P^+CH_2Ph(4'\text{-}R)Br^-$, *n*-BuLi, THF, 0 °C to reflux, 4 h; 76% for **14,** and 79% for **15**; (e) H_2, Pd/C, ethyl acetate, 80 psi, rt, 12 h; 96% for **4**, 98% for **5**; (f) $AlCl_3$, EtSH, 0 °C to rt, 1 h, 99%.

96% and 98% yield, respectively. Our initial attempts at the demethylation of compound **5** by using BBr_3 were unsuccessful, due to the interference of free 1,3-diol functionality. Therefore, demethylation was carried out using Fujita's protocol[10] with $AlCl_3$ in $EtSH/CH_2Cl_2$ (2.0:0.5, v/v) which afforded phenolic diarylheptanoid **6** in quantitative yield.

3. Conclusion

In conclusion, a new, efficient and straightforward total synthesis of (−)-yashabushidiol B **4** and other diarylheptanoids **5** and **6** has been demonstrated via a chiron approach from D-glucose derivative **7**. The target molecules **4** and **5** were obtained in five steps with 48% overall yield and compound **6** in six steps with 51% overall yield. It is noteworthy that there is only one known report[7] for the synthesis of compounds **4** and **6**, our strategy utilizes simple, non-hazardous reagents and high yielding steps. Further efforts are currently in progress for the synthesis of other diarylheptanoids by utilizing this methodology.

4. Experimental

4.1. General

Melting points were recorded with Thomas Hoover Capillary melting point apparatus and are uncorrected. IR spectra were recorded with Shimadzu FTIR-8400 as a thin film or using KBr pellets and are expressed in cm^{-1}. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded with a Varian Mercury instrument using $CDCl_3$ as a solvent. Chemical shifts were reported in δ unit (ppm) with reference to TMS as the internal standard and J values are given in hertz. ^1H–^1H COSY and decoupling experiments confirmed the assignments of the signals wherever required. Elemental analyses were carried out with Thermo-Electron Corporation CHNS analyzer Flash-EA 1112. Optical rotations were measured using Jasco P1020 polarimeter with sodium light (589.3 nm) at 25 °C. Thin layer chromatography was performed on pre-coated plates (0.25 mm, silica gel 60 F254). Visualization was made by absorption of UV light or by thermal development after spraying with 3.5% solution of 2,4-dinitrophenylhydrazine in methanol/H_2SO_4 or with basic aqueous potassium permanganate solution or with 10% solution of phosphomolybdic acid (PMA) in ethanol.

4.1.1. 1-*O*-Methyl-3,5,6-trideoxy-6-phenyl-D-gulo-1,4-furanose 11

To a solution of **7** (0.205 g, 0.826 mmol) in methanol (5 mL) was added DOWEX® 50WX4-200 (H^+ form, 0.5 g) at room temperature. After stirring for 12 h, the reaction mixture was filtered through a pad of Celite and washed with methanol (40 mL). The filtrate was concentrated in vacuo to give **11** (0.183 g, 99%) as a colorless oil. R_f: 0.23 (ethyl acetate/hexane = 3:7). ^1H NMR showed a mixture of anomers (α/β = 17:83). Further reactions were carried out on this anomeric mixture. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.44–1.52 (m, 1H, *H*-5a), 1.82–1.94 (m, 1H, *H*-5b), 1.98–2.10 (m, 1H, *H*-3a), 2.33–2.42 (m, 1H, *H*-3b), 2.59–2.75 (m, 2H, *H*-6, and 1H, –O*H*, D_2O Ex.), 3.29 (s, 3H, –OC*H*$_3$), 3.99–4.17 (m, 1H, *H*-4), 4.15 (dd, J = 2.7, 6.3 Hz, 1H, *H*-2), 4.81 (s, 1H, *H*-1), 7.11–7.26 (m, 5H, Ar*H*). Elem. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.51; H, 8.22.

4.1.2. 1-*O*-Methyl-2-*O*-benzyl-3,5,6-trideoxy-6-phenyl-D-gulo-1,4-furanose 12

To an ice cooled suspension of NaH (0.093 g, 3.87 mmol) in THF (15 mL), a solution of **11** (0.43 g, 1.93 mmol) in THF (10 mL) was added dropwise and stirred for 10 min. To this, benzyl bromide (0.46 mL, 3.87 mmol) was added. The reaction was quenched with a satd solution of NH_4Cl. The solvent was evaporated and the reaction mixture was extracted in ethyl acetate to give a mixture of C-2 benzylated methoxy anomers **12** as a thick liquid; (0.562 g, 93%). R_f: 0.70 (ethyl acetate/hexane = 3:7). Elem. Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.71; H, 7.52.

4.1.3. 2-*O*-Benzyl-3,5,6-trideoxy-6-phenyl-D-gulo-1,4-furanose 13

A solution of **12** (0.55 g, 1.76 mmol) in THF/H_2O (9:1; 10 mL) was refluxed in the presence of DOWEX® 50WX4-200 (H^+ form, 0.3 g) and cat. H_2SO_4 for 12 h. The reaction was cooled to rt, carefully neutralized with solid $NaHCO_3$. Next, the THF was evaporated under vacuum and the reaction mixture was extracted in ethyl acetate to give a mixture of anomers **13** as a thick liquid; (0.373 g, 71%). R_f: 0.46 (ethyl acetate/hexane = 4:6). Elem. Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.61; H, 7.62.

4.1.4. (3*R*,5*S*)-1-(4′-Methoxyphenyl)-3-benzyloxy-7-phenylhept-1-ene-5-ol 14

A suspension of Wittig salt (0.451 g, 1.039 mmol) and *n*-BuLi (0.65 ml, 1.039 mmol) in dry THF (10 mL) was cooled to 0 °C to give a clear, dark red solution. To this, a solution of **13** (0.16 g, 0.519 mmol) in THF (10 ml) was added slowly at the same temperature. The reaction mixture was refluxed for 5 h, cooled to rt, after which THF was vacuum evaporated. The ^1H NMR of crude product showed mixture of olefins. Column purification with hexane/ethyl acetate (9.5:0.5) on silica gel (100–200 mesh) afforded a mixture of **14** (0.152 g, 76%). R_f: 0.83 (ethyl acetate/hexane = 4:6). ^1H NMR (300 MHz, $CDCl_3$, δ): 1.64–1.96 (m, 4H, *H*-4, and *H*-6), 2.61–2.93 (m, 2H, *H*-7, and 1H, –OH, D_2O Ex.), 3.91–4.03 (m, 2H, *H*-3, and *H*-5), 4.15 (d, J = 11.7 Hz, 1H, –OC*H*H-Ph), 4.53 (d, J = 11.7 Hz, 1H, –OCH*H*-Ph), 5.75 (dd, J = 9.6, 11.7 Hz, 1H, *H*-2), 6.72 (d, J = 11.7 Hz, 1H, *H*-1), 7.17–7.41 (m, 15H, 3 × Ar*H*). Elem. Anal. Calcd for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.67; H, 7.62.

4.1.5. (3*R*,5*S*)-3-Benzyloxy-1,7-diphenylhept-1-ene-5-ol 15

The same procedure as used for **14**, was adopted for the synthesis of **15**; (0.171 g, 79%). R_f: 0.73 (ethyl acetate/hexane = 4:6).^1H NMR (300 MHz, $CDCl_3$, δ): 1.69–1.88 (m, 4H, *H*-4, and *H*-6), 2.58–2.82 (m, 2H, *H*-7, and 1H, –OH, D_2O Ex.), 3.76 (s, 3H, –OC*H*$_3$), 3.96–4.01 (m, 2H, *H*-3, and *H*-5), 4.13 (d, J = 11.6 Hz, 1H, –OC*H*H-Ph), 4.51 (d, J = 11.6 Hz, 1H, –OCH*H*-Ph), 5.69 (dd, J = 9.5, 11.8 Hz, 1H, *H*-2), 6.70 (d, J = 11.8 Hz, 1H, *H*-1), 6.82 (d, J = 8.4 Hz, 2H, *H*-3′, and *H*-5′), 7.11 (d, J = 8.4 Hz, 2H, *H*-2′, and *H*-6′), 7.15–7.31 (m, 10H, 2 × Ar*H*). Elem. Anal. Calcd for $C_{27}H_{30}O_3$: C, 80.56; H, 7.51. Found: C, 80.61; H, 7.82.

4.1.6. (3*S*,5*S*)-Yashabushidiol B 4

A solution of **14** (0.1 g, 0.3 mmol) in ethyl acetate (20 mL) and 10% Pd/C (0.03 g) was hydrogenated at 80 psi for 12 h at 25 °C. After completion of the reaction, it was filtered through a Celite pad, washed with ethyl acetate and concentrated on a rotavapor to give **4** as a white crystalline solid (0.073 g, 96%). Mp: 93–95 °C; R_f: 0.57 (ethyl acetate/hexane = 4:6); $[\alpha]_D^{25} = -7.3$ (*c* 1, $CHCl_3$), IR (KBr): 3374 (OH), 2934 (CH), 1048 (C–O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, δ): 1.68 (t, J = 5.4 Hz, 2H, *H*-4), 1.73–1.88 (m, 4H, *H*-2, and *H*-4), 2.64–2.81 (m, 4H, *H*-1, *H*-7, and 2H, 2 × –OH, D_2O Ex.), 3.97–4.01 (m, 2H, *H*-3, and *H*-5), 7.12 (m, 10H, 2 × Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 32.2 (*C*-1, *C*-7), 39.0 (*C*-2, *C*-6), 42.6 (*C*-4), 68.9 (*C*-3, *C*-5), 125.9, 128.4, 128.5, 141.8, Ar-*C*). Elem. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.31; H, 8.42.

4.1.7. (3*S*,5*S*)-1-(4′-Methoxyphenyl)-7-phenylheptane-3,5-diol 5

A solution of **15** (0.09 g, 0.23 mmol) in ethyl acetate (20 mL) and 10% Pd/C (0.03 g) was hydrogenated at 80 psi for 12 h at 25 °C. After completion of the reaction, it was filtered through a Celite pad, washed with ethyl acetate and concentrated on a rotavapor to give **5** as a white crystalline solid (0.068 g, 98%). Mp: 71–73 °C; R_f: 0.51 (ethyl acetate/hexane = 1:1); $[\alpha]_D^{25} = -7.7$ (*c* 0.7, $CHCl_3$); IR (KBr, disk, cm^{-1}): 3352 (OH), 2928 (CH), 1068 (C–O); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.65 (t, *J* = 5.4 Hz, 2H, *H*-4), 1.70–1.87 (m, 4H, *H*-2, and *H*-6), 2.59–2.78 (m, 4H, *H*-1, *H*-7, and 2H, 2 × –OH, D_2O Ex.), 3.77 (s, 3H, –O*CH*$_3$), 3.95–4.01 (m, 2H, *H*-3, and *H*-5), 6.82 (d, *J* = 8.4 Hz, 2H, *H*-3′, and *H*-5′), 7.10 (d, *J* = 8.4 Hz, 2H, *H*-2′, and *H*-6′), 7.17–7.30 (m, 5H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 31.2 (*C*-1), 32.2 (*C*-7), 39.0 (*C*-2), 39.2 (*C*-6), 42.4 (*C*-4), 55.3 (–OCH_3), 68.7 (*C*-3 and *C*-5), 113.9 (*C*-3′ and *C*-5′), 125.9 (*C*-4″), 128.4 (*C*-2″ and 3″), 128.5 (*C*-5″ and 6″), 129.3 (*C*-2′ and *C*-6′), 133.9 (*C*-1′), 141.9 (*C*-1″), 157.8 (*C*-4′). Elem. Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33. Found: C, 76.51; H, 8.22.

4.1.8. (3*S*,5*S*)-1-(4′-Hydroxyphenyl)-7-phenylheptane-3,5-diol 6

To a mixture of ethanethiol (0.2 mL) and dichloromethane (1 mL) was added $AlCl_3$ (0.064 g, 0.48 mmol) at 0 °C. A solution of **5** (0.05 g, 0.16 mmol) in CH_2Cl_2 (2 mL) was added at the same temperature and stirred for 1 h at rt. Excess $AlCl_3$ was quenched by methanol (2 mL). The solvent was evaporated to obtain thick residue, which was extracted in ethyl acetate. Column purification (ethyl acetate/hexane, 1:3) afforded demethylated product **6** as a thick liquid (0.047 g, 99%). R_f: 0.45 (ethyl acetate/hexane = 1:1); $[\alpha]_D^{25} = -8.4$ (*c* 1.5, $CHCl_3$); IR (KBr): 3352 (OH), 2928 (CH), 1068 (C–O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.65 (t, *J* = 5.3 Hz, 2H, *H*-4), 1.69–1.87 (m, 4H, *H*-2, and *H*-6), 2.57–2.79 (m, 4H, *H*-1, *H*-7, and 2H, 2 × –O*H*, D_2O Ex.), 3.94–4.00 (m, 2H, *H*-3, and *H*-5), 6.73 (d, *J* = 8.2 Hz, 2H, *H*-3′, and *H*-5′), 7.01 (d, *J* = 8.2 Hz, 2H, *H*-2′, and *H*-6′), 7.16–7.19 (m, 3H, Ar*H*), 7.25–2.31 (m, 2H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 31.2 (*C*-1), 32.1 (*C*-7), 39.0 (*C*-2), 39.1 (*C*-6), 42.4 (*C*-4), 68.9 (*C*-3), 69.0 (*C*-5), 115.3 (*C*-3′ and *C*-5′), 125.9 (*C*-4″), 128.3 (*C*-2″ and *C*-3″), 128.4 (*C*-5″ and *C*-6″), 129.4 (*C*-2′ and *C*-6′), 133.5 (*C*-1′), 141.8 (*C*-1″), 154.0 (*C*-4′). Elem. Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.78; H, 8.12.

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