April, 1988] © 1988 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 61, 1221—1224 (1988) 1221

One-Pot Ortho Hydroxylations of 2-(1-Hydroxyalkyl)-naphthalenes and (1-Hydroxyalkyl)benzenes[1]

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(Received August 20, 1987)

Hydroxylations of 2-(1-hydroxyalkyl)-1,4,5,8(or 1,4,5,6,8)-tetra(or penta)methoxynaphthalenes and 2-(1-hydroxyalkyl)-1,4-dimethoxybenzenes at the 3-position were accomplished by a one-pot procedure. The same procedure has been found to be applicable to 2-(1-hydroxyalkyl)naphthalenes and (1-hydroxyalkyl)benzenes having no methoxyl substituent.

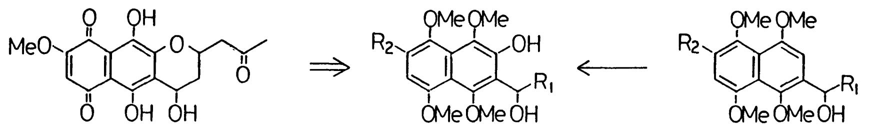
Our synthetic route of Erythrostominone (**1**)[2] requires a polymethoxynaphtol **2** which has a possibility of being converted into **1** by using our method.[3] During synthetic studies involving naphthoquinone derivatives, we have found a new one-pot procedure that introduces a phenolic hydroxyl group into type-**3** compounds at the ortho position of the hydroxyalkyl to give type-**2** compounds in good yields.

Usually, the hydroxylations of aromatic rings by the oxidation of the corresponding Grignard or organolithium compounds required two steps,[4] except for the synthesis of 2,2′-dimethoxy-3,3′-dihydroxybiphenyl from 2,2′-dimethoxybiphenyl by Gilman et al.[5] That is to say, the first step should be a halogenation of the starting aromatic compounds and the second an oxidative hydroxylation of the Grignard or lithium compounds obtained from the halides.

The lithiation of aromatic rings having both methoxyl and hydroxymethyl groups at 1- and 3-positions has already been reported.[6] Also, aromatics bearing either a methoxyl or hydroxymethyl group could be ortho lithiated.[7] However, no information has been found in the literature concerning one-pot hydroxylation at the 2-position of aromatic rings having methoxyl and hydroxyalkyl groups at both the 1- and 3-positions, or about one-pot ortho hydroxylation of aromatics bearing only one hydroxyalkyl. In this paper, we report one-pot ortho hydroxylations of 2-(1-hydroxyalkyl)naphthalenes and (1-hydroxyalkyl)benzenes.

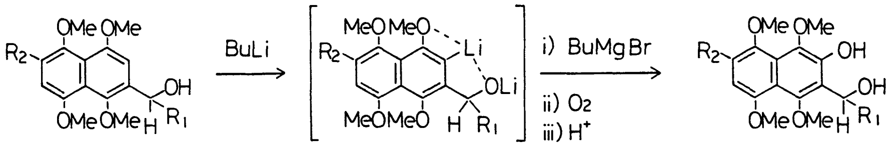
Results and Discussion

The substrates **3a**—**3f** in THF were first treated with butyllithium, then with butylmagnesium bromide and at last oxidized by dry oxygen. A decomposition of the system by an addition of dil HCl or aq NH_4Cl resulted in the formation of naphthols **2a**—**2f** (Table 1).



1 2 3

Table 1. Hydroxylation of 2-(1-Hydroxyalkyl)-1,4,5,8(or 1,4,5,6,8)-tetra(or penta)methoxynaphthalene

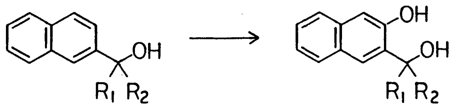


3a~3f 2a~2f

Substrate	Product	Yield/%
3a: $R_1=R_2=H$	**2a**	36[53][a]
3b: $R_1=H$, $R_2=OMe$	**2b**	59
3c: $R_1=C_4H_9$, $R_2=H$	**2c**	39[46][a]
3d: $R_1=C_4H_9$, $R_2=OMe$	**2d**	73
3e: $R_1=CH_2CH=CH_2$, $R_2=H$	**2e**	45
3f: $R_1=CH_2CH=CH_2$, $R_2=OMe$	**2f**	78

a) Conversion yield.

Table 2. Hydroxylation of 2-(1-Hydroxyalkyl)naphthalene

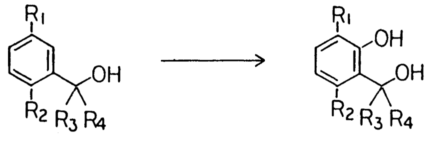


4a, b 5a, b

Substrate	Product	Yield/%
4a: R_1=R_2=H	**5a**	15[76]$^{a)}$
4b: R_1=H, R_2=C_4H_9	**5b**	22[69]$^{a)}$

a) Conversion yield.

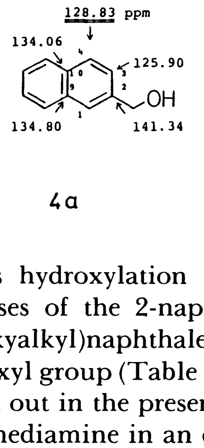
Table 3. Hydroxylation of 2-(1-Hydroxyalkyl)benzene



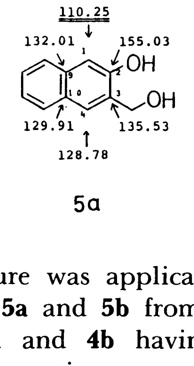
6a~6f 7b~7f

Substrate	Product	Yield/%
6a: R_1=R_2=OMe, R_3=R_4=H	**7a**	51[68]$^{a)}$
6b: R_1=R_2=OMe, R_3=H, R_4=C_4H_9	**7b**	58[98]$^{a)}$
6c: R_1=OMe, R_2=R_3=R_4=H	**7c**	19[73]$^{a)}$
6d: R_1=OMe, R_2=R_3=H, R_4=C_4H_9	**7d**	22[72]$^{a)}$
6e: R_1=R_2=R_3=R_4=H	**7e**	26[66]$^{a)}$
6f: R_1=R_2=R_3=H, R_4=C_4H_9	**7f**	19[93]$^{a)}$

a) Conversion Yield.



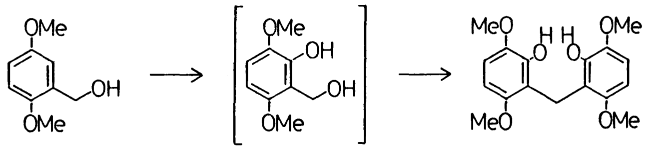
4a



5a

This hydroxylation procedure was applicable to syntheses of the 2-naphthols **5a** and **5b** from 2-(1-hydroxyalkyl)naphthalenes **4a** and **4b** having no methoxyl group (Table 2). The reactions were usually carried out in the presence of *N,N,N′,N′*-tetramethylethylenediamine in an ether solvent. Even if a large excess of *n*-BuLi was used for the reactions, a part of the starting materials was always recovered.

It was clearly proved by ^{13}C NMR that the newly introduced hydroxyl group had occupied the 3-position in the substrats **4a** and **4b**. It is well-known that the ^{13}C-chemical shift of the ortho positional carbon atom adjacent to the carbon atom bearing the hydroxyl group in an aromatic ring moves upfield to an appreciable extent.[8] The chemical shift of C_1 (δ 110.25) in product **5a** was observed more upfield than that of C_4 (δ 128.83) in 2-hydroxymethylnaphthalene (**4a**). Since this C_1 peak (δ 110.25) of the singlet changed into a doublet upon a proton off-resonace decoupling operation, this carbon atom must be a tertiary one of C_1. Therefore, the newly introduced hydroxyl group occupied the 2-position in **5a**.



6a 7a

In the similar fashion, the benzenes **6a**—**6f** were also ortho-hydroxylated to give phenols **7a**—**7f** (Table 3).

A product from **6a** was concluded to have the structure **7a** and the formation process might be as shown in the following chart. This is one of the typical Bakelite formation reactions. Martin,[9] for example, has reported that the formation of his diphenylmethanes could be explained best by a loss of one mole of water and one mole of formaldehyde between two moles of hydroxymethylphenols; he confirmed a loss of formaldehyde in this experiment. These kinds of condensations were easily carried out in the presence of lithium hydroxide.[10] Dean et al.[11] also reported that a change of 1-hydroxymethyl-2-naphthol into 1,1′-methylenedi-2-naphthol occured at 25 °C in ethanol containing of HCl during 1 min, along with an elimination of formaldehyde.

Experimental

^{1}H and ^{13}C NMR spectra were taken on a JEOL JNM-60. MS was obtained with a JEOL DX-300, IR with a Hitachi 260-30. Column chromatography was carried out on silica gel (Wakogel C-200) or alumina gel (Sumitomo, KCG-30) with chloroform as eluent. Melting points were determined with a Yanagimoto micromelting point apparatus and uncorrected. High-performance liquid chromatography (HPLC) was performed with a EYELA PLC-10 using TC-ODS 1171.

Materials. The substrates **3a**—**3f** were prepared by reductions or by Grignard reactions of 2-formyl-1,4,5,8-tetramethoxynaphthalene (see Ref. 12) and of 2-formyl-1,4,5,6,8-pentamethoxynaphthalene (see Ref. 3).

3a: A cream-colored solid (99% yield); mp 104—105 °C (from hexane-benzene); IR (KBr) 3520 (OH) and 1060 cm^{-1} (OCH_3, OH); ^{1}H NMR ($CDCl_3$) δ=2.42 (s, 1H, OH), 3.76, 3.88, 3.90, 3.92 (each s, 3H, OCH_3), 4.84 (s, 2H, CH_2), 6.80 (s, 2H, ArH), and 6.91 (s, 1H, ArH); MS, *m/z* 278 (M^+), 263, and 245. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52%. Found: C, 64.39; H, 6.57%.

3b: It was prepared as shown in Ref. 12.

3c: Colorless viscous oil (99% yield); IR (neat) 3450 (OH), 1600, and 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.6 Hz, 3H, CH_3), 1.1—1.9 (m, 6H, CH_2), 2.42 (broad, 1H, OH), 3.74, 3.88 (each s, 3H, OCH_3), 3.92 (s, 6H, OCH_3), 5.22 (t, *J*=6.0 Hz, 1H, CH), 6.80 (s, 2H, ArH), and 6.97 (s, 1H, ArH); MS, *m/z* 334 (M^+), 316 (M^+ $-H_2O$), 301, 270, 231, and 137; HRMS, Calcd for $C_{19}H_{26}O_5$: M, 334.1781. Found: *m/z* 334.1784.

3d: Colorless viscous oil (89% yield); IR (neat) 3450 (OH), 1600, 1360, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, *J*=6.0 Hz, 3H, CH_3), 1.1—1.9 (m, 6H, CH_2), 2.18 (broad, 1H, OH), 3.74, 3.81, 3.94 (each s, 3H, OCH_3), 3.97 (s, 6H, OCH_3), 5.22 (t, *J*=6.9 Hz, 1H, CH), 6.73 (s, 1H, ArH), and 6.92 (s, 1H, ArH);

MS, *m/z* 364 (M^+), 346 ($M^+ -H_2O$), 331, and 152; HRMS, Calcd for $C_{20}H_{28}O_6$: M, 364.1862. Found: *m/z* 364.1885.

3e: Colorless viscous oil (97% yield); IR (neat) 3470 (OH), 1640 (C=C), 1605, 1070, 995 (vinyl), and 915 cm^{-1} (vinyl); ^{1}H NMR ($CDCl_3$) δ=2.20 (broad, 1H, OH), 2.57 (t, *J*=6.9 Hz, 2H, CH_2), 3.75, 3.88 (each s, 3H, OCH_3), 3.92 (s, 6H, OCH_3), 4.9—5.4 (m, 3H, CH, =CH_2), 5.9 (m, 1H, -CH=), 6.81(s, 2H, ArH), and 7.00 (s, 1H, ArH); MS, *m/z* 318 (M^+), 300 ($M^+ -H_2O$), 285, 277, and 262; HRMS, Calcd for $C_{18}H_{22}O_5$: M, 318.1467. Found: *m/z* 318.1472.

3f: Cream-colored crystals (98% yield); mp 90—91 °C (from hexane); IR (KBr) 3460 (OH), 1640 (C=C), 1600, 1070, 995 (vinyl), and 915 cm^{-1} (vinyl); ^{1}H NMR ($CDCl_3$) δ=2.20 (broad, 1H, OH), 2.56 (t, *J*=6.8 Hz, 2H, CH_2), 3.75, 3.81, 3.95 (each s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.9—5.4 (m, 3H, CH, =CH_2), 5.9 (m, 1H, -CH=), 6.73, 6.95 (each s, 1H, ArH); MS, *m/z* 348 (M^+), 330 ($M^+ -H_2O$), 315, and 269. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94%. Found: C, 65.25; H, 7.01%.

Substrates **4a** and **4b** were obtained by a treatment of 2-formylnaphthalene with $NaBH_4$ or with butylmagnesium bromide.

4a: White crystals; mp 82—83 °C (lit,[13a]) mp 81—82 °C); ^{13}C NMR ($CDCl_3$) δ=125.90 (C_3), 126.48, 126.68, 127.17, 128.98 (C_4, C_5, C_8), 134.06 (s, C_{10}), 134.80 (s, C_9), 141.34 (s, C_2).

4b: A white solid (96% yield); mp 50—51 °C; IR (KBr) 3300 (OH), 1600, 1050, and 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=5.1 Hz, 3H, CH_3), 1.1—2.1 (m, 7H, OH, CH_2), 4.82 (t, *J*=7.1 Hz, 1H, CH), and 7.3—7.9 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$) δ=124.19 (C_3), 124.63, 125.70, 126.05, 127.71, 127.95, 128.19 (C_4), 132.99 (s, C_{10}), 133.28 (s, C_9), 142.32 (s, C_2); MS, *m/z* 214 (M^+), 196 ($M^+ -H_2O$), 157, and 129. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%. Found: C, 83.55; H, 8.54%.

Substrates **6a** and **6e** were commercially available, and **6b**, **6c**, **6d**, and **6f** were prepared by reductions of Grignard reactions of the corresponding aldehydes.

6b: White crystals (92% yield); mp 52—53 °C (from hexane); IR (KBr) 3360 (OH), 1600, 1220, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=5.3 Hz, 3H, CH_3), 1.1—1.9 (m, 7H, OH, CH_2), 2.57 (d, *J*=5.9 Hz, 1H, OH), 3.76, 3.80 (each s, 3H, OCH_3), 4.82 (q, *J*=5.9 Hz, 1H, CH), and 6.7—7.0 (m, 3H, ArH); MS, *m/z* 224 (M^+), 206 ($M^+ -H_2O$), 177, and 167. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%. Found: C, 69.65; H, 9.06%.

6c: Colorless viscous oil (99% yield); IR (neat) 3300 (OH), 1600, 1260, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.60 (t, *J*=5.2 Hz, 1H, OH), 3.76 (s, 3H, OCH_3), 4.59 (d, *J*=5.2 Hz, 2H, CH_2), and 6.6—7.3 (m, 4H, ArH); MS, *m/z* 138 (M^+), 109, and 77; HRMS, Calcd for $C_8H_{10}O_2$: M, 138.0682. Found: *m/z* 138.0696.

6d: Colorless viscous oil (98% yield); IR (neat) 3350 (OH), 1600, 1265, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=5.3 Hz, 3H, CH_3), 1.0—2.0 (m, 7H, OH, CH_2), 3.80 (s, 3H, OCH_3), 4.62 (t, *J*=6.6 Hz, 1H, CH), and 6.7—7.3 (m, 4H, ArH); MS, *m/z* 194 (M^+), 176 ($M^+ -H_2O$), 137, and 109; HRMS, Calcd for $C_{12}H_{18}O_2$: M, 194.1306. Found: *m/z* 194.1301.

6f: Colorless viscous oil (93% yield); IR (neat) 3380 (OH), 1500, 1455, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=5.1 Hz,3H, CH_3), 1.0—1.9 (m, 6H, CH_2), 2.11 (broad, 1H, OH), 4.62 (t, *J*=5.6 Hz, 1H, CH), and 7.30 (s, 5H, ArH); MS, *m/z* 164 (M^+), 163, 107, and 79; HRMS, Calcd for $C_{11}H_{16}O$: M, 164.1200. Found: *m/z* 164.1196.

General Procedure for Hydroxylations of the Substrates 3a—3f. A solution of a substrate (1 mmol) in THF (10 ml) was cooled to −15 °C in an ice bath, then allowed to react with *n*-BuLi (7 mmol, 10 w/v% in hexane), stirred at −15 °C for 2 h. To the system, a dark red solution, was added a solution of butylmagnesium bromide in THF (Mg: 8 mmol; BuBr: 8 mmol; THF: 10 ml) at −15 °C. After 1 h, dry oxygen was bubbled into the system for 1 h at such a rate as to keep the temperature below 0 °C. The reaction mixture was decomposed upon the addition of dil HCl or aq NH_4Cl, extracted with chloroform, washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude products by silica-gel chromatography with chloroform as eluent gave the hydroxylated products **2a—2f**. The purity of the oily products isolated by chromatography was determined by HPLC.

General Procedure for Hydroxylations of 4a, 4b, and 6a—6f. *n*-BuLi (7.5 mmol) was added under cooling to −15 °C to a solution of a substrate (3 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (7.5 mmol) in ether (15 ml) and stirred at room temperature for 3 h. To the system was added a solution of butylmagnesium bromide (9 mmol) in THF (15 ml) at −10 °C. Oxidation, decomposition, and purification procedures were carried out in the same manner as the above mentioned general procedure.

2a: Viscous oil (contained ca. 20% of **3a**); IR (neat) 3400 (OH), 1605, 1370, 1075, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.38 (broad, 2H, OH), 3.74, 3.77, 3.90, 3.92 (each s, 3H, OCH_3), 4.84 (s, 2H, CH_2), 6.68 (d, *J*=5.7 Hz, 1H, ArH), and 6.76 (d, *J*=5.7 Hz, 1H, ArH); MS, *m/z* 294 (M^+), 279, and 233; HRMS, Calcd for $C_{15}H_{18}O_6$: M, 294.1102. Found: *m/z* 294.1093.

2b: Viscous oil (a pure); IR (neat) 3400 (OH), 1600, 1355, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.21 (broad, 2H, OH), 3.79, 3.85, 3.86, 3.97, 4.06 (each s, 3H, OCH_3), 4.85 (s, 2H, CH_2), and 6.74 (s, 1H, ArH); MS, *m/z* 324 (M^+), 309, 291, 279, and 263; HRMS, Calcd for $C_{16}H_{20}O_7$: M, 324.1208. Found: *m/z* 324.1206.

2c: Viscous oil (contained ca. 20% of **3c**); IR (neat) 3400 (OH), 1603, 1365, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, *J*=6.0 Hz, 3H, CH_3), 1.1—1.9 (m, 6H, CH_2), 2.28 (broad, 2H, OH), 3.72, 3.76, 3.89, 3.93 (each s, 3H, OCH_3), 5.21 (t, *J*=6.0 Hz, 1H, CH), 6.69 (d, *J*=6.3 Hz, 1H, ArH), and 6.78 (d, *J*=6.3 Hz, 1H, ArH); MS, *m/z* 350 (M^+), 332 ($M^+ -H_2O$), 317, and 301; HRMS, Calcd for $C_{19}H_{26}O_6$: M, 350.1730. Found: *m/z* 350.1755.

2d: Viscous oil (a pure); IR (neat) 3400 (OH), 1600, 1355, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (t, *J*=6.0 Hz, 3H, CH_3), 1.1—1.9 (m, 6H, CH_2), 2.22 (broad, 1H, OH), 3.75, 3.83, 3.86, 3.97, 4.04 (each s, 3H, OCH_3), 5.23 (t, *J*=7.2 Hz, 1H, CH), 6.22 (broad, 1H, OH), and 6.77 (s, 1H, ArH); MS, *m/z* 380 (M^+), 362 ($M^+ -H_2O$), 347, and 309; HRMS, Calcd for $C_{20}H_{28}O_7$: M, 380.1835. Found: *m/z* 380.1847.

2e: Viscous oil (contained ca. 10% of **3e**); IR (neat) 3430 (OH), 1640 (C=C), 1605, 1370, 1050, 995 (C=C), and 920 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.22 (broad, 2H, OH), 2.58 (t, *J*=6.7 Hz, CH_2), 3.75, 3.76, 3.89, 3.93 (each s, 3H, OCH_3), 4.9—5.5 (m, 3H, CH, =CH_2), 5.9 (m, 1H,-CH=), 6.73 (d, *J*=11.0 Hz, 1H, ArH), and 6.91 (d, *J*=11.0 Hz, 1H, ArH); MS, *m/z* 334 (M^+), 316 ($M^+ -H_2O$), 300, and 277; HRMS, Calcd for $C_{18}H_{22}O_6$: 334.1417. Found: *m/z* 334.1429.

2f: Viscous oil (a pure); IR (neat) 3400 (OH), 1640 (C=C), 1600, 1355, 1050, 990 (C=C), 915 cm^{-1} (C=C); ^{1}H NMR

($CDCl_3$) δ=2.30 (broad, 1H, OH), 2.58 (t, J=6.8 Hz, 2H, CH_2), 3.76, 3.83, 3.86, 3.97, 4.04 (each s, 3H, OCH_3), 4.9—5.5 (m, 3H, CH, =CH_2), 5.9 (m, 1H, -CH=), 6.30 (broad, 1H, OH), and 6.81 (s, 1H, ArH); MS, m/z 364 (M^+), 346 (M^+ $-H_2O$), 331, and 323; HRMS, Calcd for $C_{19}H_{24}O_7$: M, 364.1523. Found: m/z 364.1538.

5a: Cream-colored crystals; mp 191—192 °C (from hexane-ethanol); IR (KBr) 3430 (OH), 3150 (OH), 1630, 1600, 1245, and 870 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ=4.45 (q, J=4.9 Hz, 1H, OH), 4.89 (d, J=4.9 Hz, 2H, CH_2), 7.0—8.0 (m, 6H, ArH), and 8.75 (s, 1H, OH); ^{13}C NMR ($(CD_3)_2CO$) δ=62.24 (CH_2OH), 110.25 (d, C_1), 124.29 (C_6), 126.93 (C_8), 127.07 (C_5), 127.36 (C_7), 128.78 (C_4), 129.91 (s, C_{10}) 132.01 (s, C_9), 135.53 (C_3), and 155.03 (C_2); MS, m/z 174 (M^+), 156, and 128. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%. Found: C, 75.41; H, 5.86%.

5b: Cream-colored crystals; mp 81—82 °C (from hexane); IR (KBr) 3450 (OH), 3100 (OH), 1630, 1600, 1230, 1170, 875, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=5.0 Hz, 3H, CH_3), 1.1—2.1 (m, 6H, CH_2), 2.72 (broad, 1H, OH), 4.96 (t, J=6.9 Hz, 1H, CH), 7.1—7.9 (m, 6H, ArH), and 7.98 (s, 1H, OH); ^{13}C NMR ($CDCl_3$) δ=14.08, 22.59, 28.11, 36.91, 76.42, 111.67 (d, C_1), 123.65 (C_6), 126.34 (C_5, C_7, C_8), 127.61 (C_4), 128.19 (s, C_{10}), 129.95 (s, C_9), 134.26 (C_3), and 153.66 (C_2); MS, m/z 230 (M^+), 212 (M^+ $-H_2O$), 183, and 157. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%. Found: C, 77.69; H, 7.87%.

7a: White crystals; mp 209.5—210.5 °C (from hexane-ethanol); IR (KBr) 3370 (OH), 1600, 1230, and 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.75, 3.76 (each s, 6H, OCH_3), 3.80 (s, 2H, CH_2), 5.49 (s, 2H, OH), 6.56, 6.61 (each s, 2H, ArH); ^{13}C NMR ($(CD_3)_2NCDO$) δ=29.04 (CH_2), 56.13 (C_3-OMe), 57.30 (C_6-OMe), 101.06 (C_5), 116.37 (C_4), 120.03 (C_1), 141.99 (C_3), 146.68 (C_2), and 152.64 (C_6); MS, m/z 320 (M^+), 305, 289, and 153. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29%. Found: C, 63.36; H, 6.45%.

7b: Viscous oil (contained ca. 16% of **6b**); IR (neat) 3550 (OH), 3430 (OH), 1610, 1200, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=5.4 Hz, 3H, CH_3), 1.1—2.0 (m, 7H, OH, CH_2), 3.74, 3.84 (each s, 3H, OCH_3), 4.62 (t, J=6.5 Hz, 1H, CH), 5.64 (s, 1H, ArOH), 6.53 and 6.92 (each s, 1H, ArH); MS, m/z 240 (M^+), 239, 222 (M^+ $-H_2O$), 193, and 161; HRMS, Calcd for $C_{13}H_{20}O_4$: 240.1362. Found: m/z 240.1396.

7c: White crystals; mp 115—116 °C (from hexane); IR (KBr) 3440 (OH), 3150 (OH), 1600, 1265, 1235, 1030, and 995 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.57 (s, 1H, OH), 3.90 (s, 3H, OCH_3), 4.61 (s, 2H, CH_2), 5.60 (s, 1H, ArOH), and 6.87 (m, 3H, ArH); MS, m/z 154 (M^+), 137, 93, and 65. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54%. Found: C, 62.37; H, 6.66%.

7d: A semisolid; IR (neat) 3400 (OH), 1600, 1270, and 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (t, J=5.4 Hz, 3H, CH_3), 1.1—1.9 (m, 6H, CH_2), 2.35 (broad, 1H, OH), 3.85 (s, 3H, OCH_3), 4.62 (t, J=4.4 Hz, 1H, CH), 5.80 (broad, 1H, ArOH), and 6.80 (m, 3H, ArH); MS, m/z 210 (M^+), 153, 125, and 93; HRMS, Calcd for $C_{12}H_{18}O_3$: M, 210.1257. Found: m/z 210.1278.

7e: White crystals, mp 82.5—83.5 °C (from hexane-ethanol) (lit,[13b] mp 80 °C).

7f: Viscous oil (a pure); IR (neat) 3300 (OH), 1590, 1240, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=5.9 Hz, 3H, CH_3), 1.1—2.0 (m, 6H, CH_2), 2.53 (broad, 1H, OH), 4.82 (t, J=5.6 Hz, 1H, CH), 6.7—7.4 (m, 4H, ArH), and 7.93 (s, 1H, ArOH); MS, m/z 180 (M^+), 162 (M^+ $-H_2O$), 133, and 77; HRMS, Calcd for $C_{11}H_{16}O_2$: 180.1150. Found: 180.1119.

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