Efficient Synthesis of α-Benzylidene-γ-methyl-γ-butyrolactones

by **Raghao S. Mali***[1]) and **Kantipudi N. Babu**

Garware Research Centre, Department of Chemistry, University of Pune, Pune – 411 007, India

Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

A concise synthesis of α-benzylidene-γ-methyl-γ-butyrolactones **5a** – **g** from substituted benzaldehydes is described. Compounds **1a** – **g** on reaction with phosphorane **2**, provide the pentenoates **3a** – **g**, which can be hydrolyzed to the acids **4a** – **g**. The latter are cyclized to the corresponding butyrolactones **5a** – **g** in excellent yields. The pentenoates **3a** – **g**, on acid catalyzed cyclization, also provide **5a** – **g** in very high yields.

1. Introduction. – Alkylidene-γ-butyrolactones (substituted dihydrofuran-2(3*H*)-ones) are important compounds, since this subunit is found in a variety of natural products [1], especially in sesquiterpene lactones and lignans [2]. They serve as valuable building blocks for the synthesis of various types of natural products and biologically active substances [3]. A few alkylidene-γ-butyrolactones are reported to possess interesting pharmacological, fungicidal, and plant-growth regulatory activities [4]. In view of their biological importance, numerous methods have been reported for their synthesis [5 – 8].

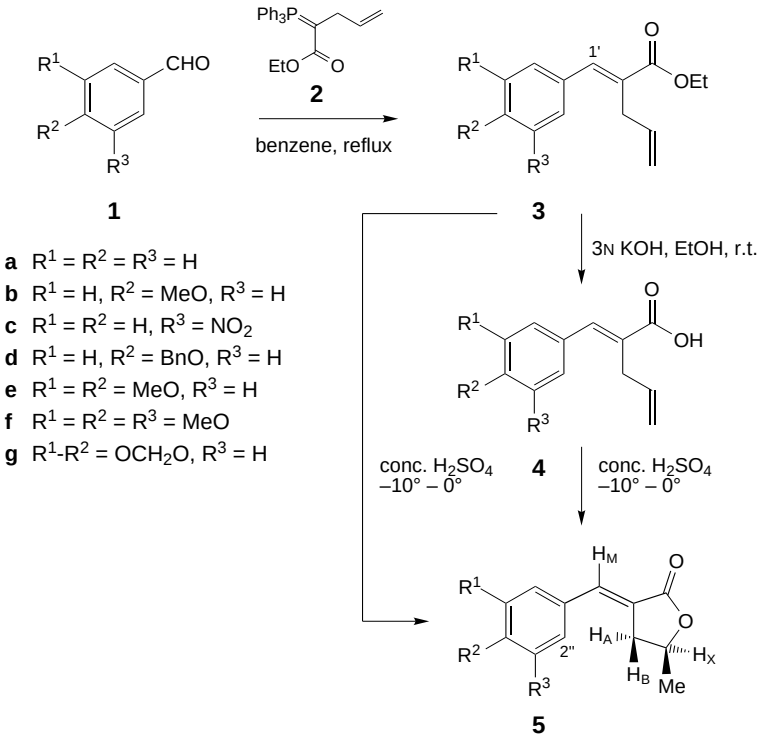
Standard methods for the synthesis of alkylidene-γ-butyrolactones from aldehydes include base-catalyzed condensation of γ-butyrolactones [5], *Wittig* reaction of α-[γ-butyrolactonylidene]triphenylphosphorane [6], or *Wittig – Horner* reaction of α-diethylphospho-γ-butyrolactones [7]. Unfortunately, the yields are sometimes modest and mixtures of (*E*)- and (*Z*)-isomers are obtained.

2. Results and Discussion. – We wish to report an efficient and simple method for the preparation of α-benzylidene-γ-butyrolactones. *Wittig* olefination of benzaldehydes **1a** – **g** with ethyl 2-(triphenyl-λ^5-phosphanylidene)pent-4-enoate (**2**) [9] in refluxing benzene provided the pentenoates **3a** – **g** in 84 – 94% yield (*Scheme 1*). In the ^{1}H-NMR spectra of **3a** – **g**, H – C(1′) resonances appear as *singlets* at 7.83 – 8.08 ppm. These chemical shifts are closer to the calculated [10] value for the (*E*)-isomer (7.53 ppm) rather than that for the (*Z*)-isomer (6.96 ppm). Therefore, the pentenoates **3a** – **g** are most likely (*E*)-configured. Hydrolysis of **3a** – **g** under basic conditions (KOH in EtOH) provided the pentenoic acids **4a** – **g** in 89 – 93% yield, which were cyclized in the presence of H_2SO_4 at $-10°$ to $0°$ to the corresponding benzylidene-γ-butyrolactones **5a** – **g** in 84 – 94% yield. These products were found to be the (*E*)-isomers on the basis of the ^{1}H-NMR chemical shifts (7.43 – 8.22 ppm) of H – C(1′), which are in agreement

[1]) Present Address: North Maharashtra University, Jalgaon – 425 001, India (fax: +(91) 0257-252183; e-mail: rsmali@rediffmail.com).

with the reported [8] chemical shifts (7.20–7.69 ppm). The (*E*)-configuration was further confirmed by NOESY experiments. The aromatic proton, H–C(2″) was found in close proximity to H_A and H_B of the γ-lactone ring.

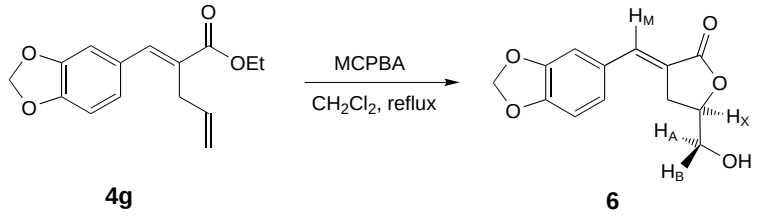
Scheme 1



To improve the overall yields, the hydrolysis step was eliminated, and the pentenoates **3a**–**g** were directly reacted with H_2SO_4 to provide the lactones **5a**–**g** in 82–94% yield.

A CH_2OH group in γ-position of the lactone ring is required for the synthesis of some natural products [11]. We, therefore, also prepared compound **6** from **4g** in 55% yield by reacting it with *m*-chloroperbenzoic acid (MCPBA) in refluxing CH_2Cl_2 (*Scheme 2*).

Scheme 2



In an alternative approach to the synthesis of lactones **5a**–**g**, the *Wittig* reaction was carried out under microwave irradiation, a technique now widely used in organic synthesis [12]. The pentenoates **3a**–**g** were obtained in nearly quantitative yields when a mixture of the aldehyde **1** and reagent **2** was irradiated with silica gel (SiO_2) as a solid support in a commercial microwave oven[2]) for 1–10 min. The lactonization was also carried out by microwave irradiation (3–8 min) with *Montmorillonite K-10*[3]) as a solid support.

3. Conclusions. – A stereolective synthesis has been developed for (*E*)-configured α-benzylidene-γ-butyrolactones based on a *Wittig* reaction followed by lactone formation (cyclization). Both classical and microwave-irradiation approaches have been used. The present method is very efficient and provides the title compounds in excellent yields.

Experimental Part

General. Melting points are uncorrected. IR spectra (nujol) were recorded on a *Perkin-Elmer FTIR-1615* spectrophotometer, ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) on a *Jeol FX 90Q* (90 MHz) spectrometer. Chemical shifts are expressed in δ (ppm) relative to Me_4Si as an internal standard, coupling constants *J* in Hz. Elemental analyses were performed on *Hosli*'s rapid carbon-hydrogen analyser.

*Ethyl (*E*)-2-Benzylidenepent-4-enoates* **3a**–**g**. *General Procedure 1* (*GP1*): **1a**–**g** (10 mmol) in anh. benzene (20 ml) reagent **2** (4 g, 10.3 mmol) was added and the mixture was refluxed for 3–11 h. The solvent was removed *in vacuo*, and the residue was chromatographed (SiO_2; hexane/AcOEt 9:1) to yield **3a**–**g** as viscous liquids. For anal. details, *cf. Table 1*.

General Procedure 2 (*GP2*): Silica gel (3 g) was added to a soln. of **1a**–**g** (1 mmol) and **2** (1.2 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred for 2 min. The solvent was removed, and the residual powder was dried *in vacuo*. The mixture, spread in a *Petri* dish, was irradiated in a microwave oven [13] for 1–10 min and chromatographed (SiO_2; hexane/AcOEt 9:1) to yield **3a**–**g**.

*(*E*)-2-Benzylidenepent-4-enoic Acids* **4a**–**g**. *General Procedure*: Aq. KOH (3N, 3 ml) was added to a soln. of the appropriate pentenoate **3** (1 mmol) in EtOH (5 ml). The mixture was stirred at r.t. for 6 h (3 h in case of **3c**). Then, the EtOH was removed, H_2O (5 ml) was added, and the mixture was acidified with ice-cold HCl (1:1). The precipitated solid was filtered off, washed with H_2O, and dried to provide **4a**–**g**. For anal. details, *cf. Table 2* and *4*.

*(*E*)-α-Benzylidene-γ-methyl-γ-butyrolactones* **5a**–**g**. *General Procedure 3* (*GP3*): The pentenoic acid **4** (0.50 mmol) was added to well-cooled conc. H_2SO_4 (2 ml). The mixture was stirred at $-10°$ for 1 h before allowed to warm to 0° over 30 min. The mixture was poured on crushed ice, and the solid obtained was extracted with $CHCl_3$ (2 × 15 ml). The combined org. extract were washed successively with aq. $NaHCO_3$ soln. and H_2O and dried (Na_2SO_4). The crude products obtained after removing the solvent were recrystallized from CH_2Cl_2/hexane to furnish **5a**–**g**. For analytical data, *cf. Table 3* and *4*.

General Procedure 4 (*GP4*): Ice-cold conc. H_2SO_4 (2 ml) was added to the well-cooled pentenoate **3**. The mixture was stirred at $-10°$ for 1 h and allowed to warm to 0° over 30 min. The mixture was poured on crushed ice, and the solid obtained was extracted with $CHCl_3$ (2 × 15 ml). The combined org. extracts were washed successively with aq. $NaHCO_3$ soln. and H_2O and dried (Na_2SO_4). The solvent was removed, and the remainder was recrystallized from CH_2Cl_2/hexane to furnish **5a**–**g**, which were analytically identical to authentic samples prepared by the above procedure.

General Procedure 5 (*GP5*): Pentenoate **3** (0.25 mmol) in CH_2Cl_2 (3 ml) was adsorbed on *Montmorillonite K-10* (2 g) [14], and the mixture was stirred for 2 min. After removal of the solvent, the mixture was spread in a *Petri* dish and irradiated in a microwave oven for 3–8 min (monitored by TLC). The mixture was dissolved in CH_2Cl_2 (10 ml), filtered, washed with CH_2Cl_2 (20 ml), and concentrated to yield **5a**–**g**.

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2) *Kelvinator T37*, 2450 MHz (700 W).

3) *Fluka*, activated by microwave irradiation for 10 min.

Table 1. *Selected Experimental Data for Compounds* **3a**–**g** (*cf. Scheme 1*). For elemental analyses, *cf. Table 4*.

Product	*GP*: reaction time	Yield [%]	IR (nujol) ν [cm^{-1}]	^{1}H-NMR ($CDCl_3$) δ [ppm], J [Hz]	^{13}C-NMR ($CDCl_3$) δ [ppm]
3a	*GP1*: 11 h *GP2*: 10 min	92 98	1720	1.45 (*t*, *J* = 7.5, Me); 3.30 (br. *d*, *J* = 6.0, 2 H–C(3)); 4.29 (*q*, *J* = 7.5, CH_2O); 4.80–5.18 (*m*, 2 H–C(5)); 5.66–6.22 (*m*, H–C(4)); 7.44 (*s*, 5 arom. H); 7.83 (*s*, H–C(1′))	14.05; 31.38; 60.58; 115.35; 128.29; 129.00; 130.0; 135.34; 139.89; 144.23; 146.18; 167.74
3b	*GP1*: 6 h *GP2*: 6 min	94 94	1720	1.37 (*t*, *J* = 7.5, Me); 3.42 (br. *d*, *J* = 6.0, 2 H–C(3)); 3.94 (*s*, MeO); 4.42 (*q*, *J* = 7.5, CH_2O); 5.41–5.45 (*m*, 2 H–C(5)); 6.08–6.48 (*m*, H–C(4)); 7.17 (*d*, *J* = 8.0, 2 arom. H); 7.68 (*d*, *J* = 8.0, 2 arom. H); 8.08 (*s*, H–C(1′))	14.10; 31.49; 54.89; 60.53; 113.62; 113.83; 126.45; 126.88; 127.92; 130.84; 135.56; 139.62; 144.01; 159.94; 168.06
3c	*GP1*: 10 h *GP2*: 1 min	94 95	1720, 1540	1.31 (*t*, *J* = 7.5, Me); 3.30 (br. *d*, *J* = 6.0, 2 H–C(3)); 4.29 (*q*, *J* = 7.5, CH_2O); 4.92–5.27 (*m*, 2 H–C(5)); 5.66–6.22 (*m*, H–C(4)), 7.51–8.38 (*m*, 5 arom. H)	14.05; 31.60; 61.01; 116.11; 122.88; 123.69; 129.33; 133.50; 134.80; 136.91; 141.41; 148.34; 166.98
3d	*GP1*: 12 h *GP2*: 7 min	85 96	1720	1.34 (*t*, *J* = 7.5, Me); 3.42 (br. *d*, *J* = 6.0, 2 H–C(3)); 4.45 (*q*, *J* = 7.5, CH_2O); 5.20–5.51 (*m*, 4 H, 2 H–C(5), PhCH_2O); 6.02–6.54 (*m*, H–C(4)); 7.28 (*d*, *J* = 8.0, 2 arom. H); 7.60–7.85 (*m*, 7 arom. H); 8.11 (*s*, H–C(1′))	14.21; 31.54; 60.58; 70.06; 114.92; 115.46; 127.32; 127.92; 128.51; 131.01; 135.67; 136.80; 139.67; 159.23; 168.12
3e	*GP1*: 10 h *GP2*: 2 min	90 92	1710	1.37 (*t*, *J* = 7.5, Me); 3.42 (br. *d*, *J* = 6.0, 2 H–C(3)); 4.0 (*s*, 2 MeO); 4.42 (*q*, *J* = 7.5, CH_2O); 5.14–5.42 (*m*, 2 H–C(5)); 6.02–6.48 (*m*, H–C(4)); 7.05–7.40 (*m*, 3 arom. H); 8.05 (*s*, H–C(1′))	14.16; 31.65; 55.87; 60.53; 111.40; 112.80; 115.30; 122.83; 128.35; 128.51; 135.77; 139.89; 148.94; 149.81; 167.95
3f	*GP1*: 7 h *GP2*: 3 min	93 93	1720	1.37 (*t*, *J* = 7.5, Me); 3.40 (br. *d*, *J* = 6.0, 2 H–C(3)); 3.97 (*s*, 3 MeO); 4.34 (*q*, *J* = 7.5, CH_2O); 5.17–5.45 (*m*, 2 H–C(5)); 6.02–6.51 (*m*, H–C(4)); 6.85 (*s*, 2 arom. H); 8.02 (*s*, H–C(1′))	14.10; 37.71; 55.98; 60.58; 106.68; 115.30; 129.44; 130.68;135.77; 138.65; 140.11; 152.95; 167.74
3g	*GP1*: 7 h *GP2*: 2 min	84 95	1720	1.34 (*t*, *J* = 7.5, Me); 3.42 (br. *d*, *J* = 6.0, 2 H–C(3)); 4.40 (*q*, *J* = 7.5, CH_2O); 5.05–5.42 (*m*, 2 H–C(5)); 5.91–6.31 (*m*, OCH_2O and H–C(4)); 6.91–7.31 (*m*, 3 arom. H); 8.02 (*s*, H–C(1′))	14.16; 31.54; 60.53; 101.16; 108.20; 109.12; 115.46; 124.18; 128.95; 129.54; 135.50; 139.67; 144.28; 147.96; 167.98

*(3*E,5R*)-3-[(1,3-Benzodioxol-5-yl)methylidene]-4,5-dihydro-5-(hydroxymethyl)furan-2(3*H*)-one* (**6**). A soln. of **4g** (0.116 g, 0.5 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a suspension of *m*-chloroperbenzoic acid (0.172 g, 1 mmol) in CH_2Cl_2 (10 ml). The mixture was refluxed for 10 h, cooled, and washed thoroughly with aqu. $NaHSO_3$ soln., aqu. $NaHCO_3$ soln., brine, and H_2O, and was dried (Na_2SO_4). The solvent was removed *in vacuo* to yield a crude product that was chromatographed (SiO_2; hexane/AcOEt 9 :1) and recrystallized from CH_2Cl_2/hexane to provide **6** (0.068 g, 55%) as a white solid. M.p. 129°. IR (nujol): 3300, 1730. ^{1}H-NMR ($CDCl_3$):

Table 2. *Selected Experimental Data for Compounds* **4a**–**g** (*cf. Scheme 1*). For elemental analyses, *cf. Table 4*.

Product	Yield [%]	M.p. [°]	IR (nujol) ν [cm^{-1}]	^{1}H-NMR ($CDCl_3$) δ [ppm], J [Hz]
4a	90	90–91	3300, 1670	3.42 (br. *d*, J = 6.0, 2 H–C(3)); 5.14–5.51 (*m*, 2 H–C(5)); 6.05–6.51 (*m*, H–C(4)); 7.74 (*s*, 5 arom. H); 8.28 (*s*, H–C(1′))
4b	93	95–96	3300, 1670	3.42 (br. *d*, J = 6.0, 2 H–C(3)); 3.97 (*s*, MeO); 5.20–5.57 (*m*, 2 H–C(5)); 6.05–6.62 (*m*, H–C(4)); 7.20 (*d*, J = 9.0, 2 arom. H); 7.74 (*d*, J = 9.0, 2 arom. H); 8.22 (*s*, H–C(1′))
4c	92	113–115	3250, 1690, 1540	3.40 (br. *d*, J = 6.0, 2 H–C(3)); 5.22–5.57 (*m*, 2 H–C(5)); 6.05–6.57 (*m*, H–C(4)), 7.82–8.80 (*m*, 4 arom. H and H–C(1′))
4d	91	130–132	3300, 1700	3.42 (br. *d*, J = 6.0, 2 H–C(3)); 5.20–5.51 (*m*, 4 H, 2 H–C(5) and PhCH_2O); 6.02–6.51 (*m*, H–C(4)); 7.28 (*d*, J = 8.5, 2 arom. H); 7.60–7.84 (*m*, 7 arom. H).
4e	89	120	3250, 1680	3.48 (br. *d*, J = 6.0, 2 H–C(3)); 4.00, 4.05 (2*s*, 2 MeO); 5.22–5.54 (*m*, 2 H–C(5)); 6.05–6.57 (*m*, H–C(4)); 7.11–7.48 (*m*, 3 arom. H); 8.25 (*s*, H–C(1′))
4f	89	95–97	3250, 1690	3.45 (br. *d*, J = 6.0, 2 H–C(3)); 3.94 (*s*, 2 MeO); 4.02 (*s*, MeO); 5.22–5.54 (*m*, 2 H–C(5)); 6.11–6.68 (*m*, H–C(4)); 7.00 (*s*, 2 arom. H); 8.20 (*s*, H–C(1′))
4g	92	108–110	3300, 1680	3.42 (br. *d*, J = 6.0, 2 H–C(3)); 5.17–5.45 (*m*, 2 H–C(5)); 6.00–6.61 (*m*, OCH_2O and H–C(4)); 7.00–7.37 (*m*, 3 arom. H); 8.14 (*s*, H–C(1′))

Table 3. *Selected Experimental Data for Compounds* **5a**–**g** (*cf. Scheme 1*). For elemental analyses, *cf. Table 4*.

Product	*GP*: yield [%]	M.p. [°]	IR (nujol) ν [cm^{-1}]	^{1}H-NMR ($CDCl_3$) δ [ppm], J [Hz]	^{13}C-NMR ($CDCl_3$) δ [ppm]
5a	*GP3*: 84 *GP4*: 94 *GP5*: 92	58 (lit. 48° [8b])	1750	1.48 (*d*, J = 6.5, Me); 2.90 (*ddd*, J_{AB} = 18, J_{BX} = 5.6, J_{BM} = 2.5, H_B); 3.40 (*ddd*, J_{AB} = 18, J_{AX} = 7.9, J_{AM} = 2.5, H_A); 4.90 (br. *sext.*, H_X); 7.65–7.91 (*m*, 5 arom. H and H_M)	22.27; 35.19; 74.07; 125.09; 128.87; 129.72; 129.90; 134.64; 136.28; 171.95
5b	*GP3*: 84 *GP4*: 82 *GP5*: 90	76–77 (lit. 76° [8b])	1740	1.48 (*d*, J = 6.5, Me); 2.80 (*ddd*, J_{AB} = 18, J_{BX} = 6.0, J_{BM} = 2.5, H_B); 3.51 (*ddd*, J_{AB} = 18, J_{AX} = 7.7, J_{AM} = 2.5, H_A); 3.97 (*s*, MeO); 4.90 (br. *sext.*, H_X); 7.22 (*d*, J = 8.5, 2 arom. H); 7.54–7.85 (*m*, 2 arom. H and H_M)	22.56; 35.42; 55.54; 74.04; 114.58; 122.29; 127.69; 131.89; 136.36; 161.03; 172.50
5c	*GP3*: 94 *GP4*: 92 *GP5*: 99	100–103	1750	1.54 (*d*, J = 6.5, Me); 2.90 (*ddd*, J_{AB} = 18, J_{BX} = 5.9, J_{BM} = 2.5, H_B); 3.60 (*ddd*, J_{AB} = 18, J_{AX} = 7.7, J_{AM} = 2.5, H_A); 4.97 (br. *sext.*, H_X); 7.85–8.22 (*m*, 2 arom. H); 8.54–8.74 (*m*, 2 arom. H and H_M)	22.06; 35.07;73.80; 123.48; 123.69; 128.84; 129.76; 133.12; 135.12; 136.48; 148.83; 170.39
5d	*GP3*: 92 *GP4*: 93 *GP5*: 88	117–120	1740	1.40 (*d*, J = 6.5, Me); 2.80 (*ddd*, J_{AB} = 18, J_{BX} = 6.0, J_{BM} = 2.5, H_B); 3.45 (*ddd*, J_{AB} = 18, J_{AX} = 7.7, J_{AM} = 2.5, H_A); 5.02 (br. *sext.*, H_X); 5.40 (*s*, PhCH_2O); 7.28 (*d*, J = 8.0, 2 arom. H); 7.60–7.95 (*m*, 5 arom. H and H_M)	21.63; 34.20; 34.96; 72.93; 115.00; 120.17; 125.32; 127.54; 128.24; 129.06; 131.93; 135.88; 139.84; 156.47;171.58
5e	*GP3*: 92 *GP4*: 90 *GP5*: 94	98–99	1740	1.54 (*d*, J = 6.5, Me); 2.82 (*ddd*, J_{AB} = 18, J_{BX} = 5.6, J_{BM} = 2.5, H_B); 3.51 (*ddd*, J_{AB} = 18, J_{AX} = 7.7, J_{AM} = 2.5, H_A); 4.05 (*s*, 2 MeO); 4.94 (br. *sext.*, H_X); 7.11–7.57 (*m*, 3 arom. H); 7.80 (br. *s*, H_M)	22.06; 35.12; 55.76; 73.64; 115.50; 113.18; 122.34; 123.53; 127.70; 136.26; 149.10; 150.60; 171.85
5f	*GP3*: 88 *GP4*: 91 *GP5*: 90	103–105	1740	1.48 (*d*, J = 6.5, Me); 2.80 (*ddd*, J_{AB} = 18, J_{BX} = 5.6, J_{BM} = 2.5,H_B); 3.40 (*ddd*, J_{AB} = 18, J_{AX} = 7.7, J_{AM} = 2.5, H_A); 3.90 (*s*, 3 MeO); 4.74 (br. *sext.*, H_X); 7.70 (*m*, 2 arom. H); 7.43 (*t*, J = 2.5, H_M)	22.06; 35.17; 56.63; 60.58; 73.53; 108.96; 124.24; 130.25; 136.21; 141.19; 153.65; 171.20
5g	*GP3*: 88 *GP4*: 90 *GP5*: 91	98–99	1760	1.48 (*d*, J = 6.5, Me); 2.82 (*ddd*, J_{AB} = 18, J_{BX} = 5.6, $_{BM}$ = 2.5, H_B); 3.51 (*ddd*, J_{AB} = 18, J_{AX} = 7.7, J_{AM} = 2.5, H_A); 5.02 (br. *sext.*, H_X); 6.28 (*s*, OCH_2O); 7.07–7.42 (*m*, 3 arom. H); 7.80 (*t*, J = 2.5, H_M)	22.21; 35.04; 73.86; 101.61; 108.56; 108.80; 122.55; 125.71; 128.84; 135.93; 148.09; 148.87; 172.05

Table 4. *Elemental Analyses of Compounds* **3**–**5**.

Product	Formula	Mol. weight	Calc.		Found	
			C	H	C	H
3a	$C_{14}H_{16}O_2$	216.268	77.75	7.76	77.70	7.61
3b	$C_{15}H_{18}O_3$	246.294	73.14	7.73	73.31	7.58
3c	$C_{14}H_{15}NO_4$	261.270	64.36	5.79	64.50	5.85
3d	$C_{21}H_{22}O_3$	322.386	78.23	6.88	78.37	6.89
3e	$C_{16}H_{20}O_4$	276.320	69.54	7.30	69.72	7.42
3f	$C_{17}H_{22}O_5$	306.346	66.65	7.24	66.75	7.32
3g	$C_{15}H_{16}O_4$	260.278	69.21	6.20	69.02	6.28
4a	$C_{12}H_{12}O_2$	188.216	76.57	6.43	76.50	6.43
4b	$C_{13}H_{14}O_3$	218.242	71.57	6.47	71.77	6.46
4c	$C_{12}H_{11}NO_4$	233.218	61.80	4.75	61.63	4.82
4d	$C_{19}H_{18}O_3$	294.334	77.53	6.16	77.66	6.16
4e	$C_{14}H_{16}O_4$	248.268	67.73	6.50	67.52	6.57
4f	$C_{15}H_{18}O_5$	278.294	64.73	6.52	64.87	6.38
4g	$C_{13}H_{12}O_4$	232.226	67.23	5.21	67.14	5.20
5a	$C_{12}H_{12}O_2$	188.216	76.57	6.43	76.68	6.35
5b	$C_{13}H_{14}O_3$	218.242	71.54	6.47	71.36	6.75
5c	$C_{12}H_{11}NO_4$	233.218	61.80	4.75	61.94	4.89
5d	$C_{19}H_{18}O_3$	294.334	77.53	6.16	77.65	6.34
5e	$C_{14}H_{16}O_4$	248.268	67.73	6.50	67.99	6.74
5f	$C_{15}H_{18}O_5$	278.294	64.73	6.52	68.82	6.60
5g	$C_{13}H_{12}O_4$	232.226	67.23	5.21	67.05	5.32

2.25 (br. *s*, OH); 3.08–3.41 (*m*, 2 H–C(4)); 3.60 (*dd*, $J_{AB} = 12.5$, $J_{AX} = 5.0$, H_A); 4.10 (*dd*, $J_{AB} = 12.5$, $J_{BX} = 2.5$, H_B); 4.72–5.05 (*m*, H_X); 6.25 (*s*, OCH_2O); 7.00–7.44 (*m*, 3 arom. H); 7.75 (br. *s*, H_M). ^{13}C-NMR ($CDCl_3$/(D_6)DMSO): 28.60; 62.78; 77.01; 101.01; 108.03; 108.29; 122.11; 125.23; 128.25; 134.86; 147.25; 148.69; 171.69. Anal. calc. for $C_{13}H_{12}O_5$ (248.226): C 62.90, H 4.97; found: C 63.07, H 5.13.

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