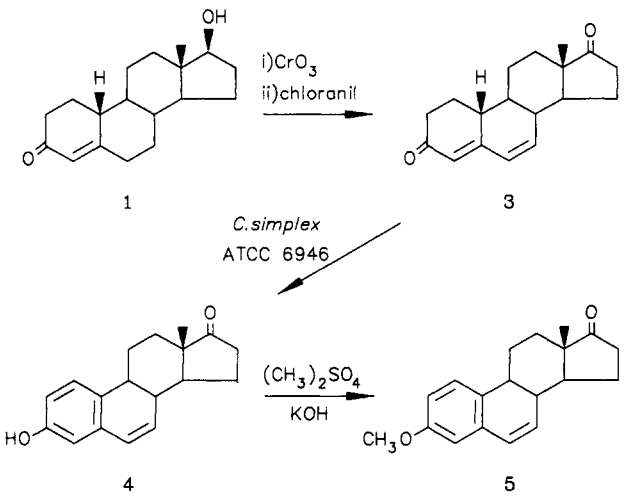
Scheme I



in pyridine, via the procedure reported by Alvarez and Watt,[6] gave **4** in only 3% yield.

Previous workers[7] had already shown that *Corynebacterium simplex* could be used to effect aromatization by the microbial dehydrogenation of certain 19-nor-Δ^4-3-ketosteroids. When **3** was submitted to this transformation, the phenol **4**, equal in all aspects to authentic sample, was isolated in 74% yield. Finally **4** was reacted to dimethyl sulfate and potassium hydroxide in aqueous methanol to give, after crystallization from ethanol, 90% of pure **5**.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 683 instrument. Ultraviolet spectra were measured in ethanol on a Hewlett-Packard 8450A spectrophotometer. ^{1}H NMR spectra were run at 80.131 MHz on a Bruker AC-80 spectrometer with $CDCl_3$ as a solvent. The chemical shifts are reported in δ values relative to tetramethylsilane, which was used as internal standard. Mass spectra were obtained through electron-impact ionization on a Hewlett-Packard 5995A instrument.

Analytical thin-layer chromatography (TLC) was performed on plates of Polygram Sil N-HR/UV_{254} (Macherey-Nagel) with a thickness of 0.20 mm silica gel.

Estr-4-ene-3,17-dione (2). To a solution of 17β-hydroxyestr-4-en-3-one (**1**) (6.17 g, 22.5 mmol) in acetic acid (300 mL) was added chromium(VI) oxide (1.70 g, 17.0 mmol) dissolved in acetic acid 96% (150 mL), and the solution was stirred at ambient temperature for 1 h. The reaction mixture was concentrated under vacuum to half of its initial volume, poured into 1 M hydrochloric acid (300 mL), and extracted with ethyl acetate (3 × 400 mL). The combined organic extracts were washed with saturated solution of $NaHCO_3$ and water and then dried over $MgSO_4$. Evaporation of solvent gave **2** (5.88 g, 96%), mp 165–168 °C (lit.[4] mp 169–171 °C).

Estra-4,6-diene-3,17-dione (3). A solution of **2** (4.10 g, 15.1 mmol) and chloranil (2.75 g, 11.2 mmol) in dry ethanol (400 mL) was stirred at 50 °C for 2 h and then evaporated under reduced pressure. The residue was triturated with chloroform (80 mL), and the mixture was allowed to stand overnight. The solid was removed by filtration, the filtrate was evaporated to dryness and redissolved in ethanol (400 mL), and the above procedure was repeated. The final residue from the evaporation of the chloroform was adsorbed onto basic alumina (100 g) and eluted with chloroform. Evaporation of the solvent afforded the crude dienone **3** (2.30 g), which was crystallized from acetone–petroleum ether to give a sample (1.75 g, 43%) of mp 177–180 °C (lit.[6] mp 180–182 °C).

3-Hydroxyestra-1,3,5(10),6-tetraen-17-one (4). *C. simplex* (ATCC 6946), conserved at 4 °C in agar slants, was grown for 24 h in a culture medium of distilled water (100 mL) containing yeast extract (0.3 g), KH_2PO_4 (0.5 g), and $Na_2HPO_4 \cdot 12H_2O$ (0.12 g). A sterile solution (100 mL) of this medium was inoculated with previous culture (10 mL), and, after 8 h of agitation on a rotatory shaker at 30 °C, **3** (50 mg, 0.185 mmol) in DMF (2 mL) was added and incubated for 46 h in the same conditions. Final pH (≈7) was brought to 3.5 by addition of 1 M HCl. Ten such experiments were combined, and, after adding CH_2Cl_2 (500 mL) with shaking, the mixture was filtered and the residue and the aqueous layer were extracted separately with CH_2Cl_2. The combined organic extracts (2 L) were washed with a saturated solution of $NaHCO_3$ and water and then dried over $MgSO_4$. Removal of the solvent in vacuo gave a residue (510 mg), which was crystallized from acetone–petroleum ether, affording **4** (365 mg, 74%), mp 258–261 °C (lit.[3b] mp 261–263 °C).

3-Methoxyestra-1,3,5(10),6-tetraen-17-one (5). To a well-stirred solution of **4** (500 mg, 1.86 mmol) in methanol (100 mL), at ambient temperature, were added dropwise and simultaneously a 6.2 M aqueous solution of potassium hydroxide (2 mL, 12.4 mmol) and dimethyl sulfate (1 mL, 1.3 g, 10.3 mmol) under N_2 atmosphere, and the mixture was stirred for 10 min. After two more dropwise additions of potassium hydroxide solution (1 mL) and dimethyl sulfate (1 mL), the alkaline solution was stirred for 12 h. Finally, a new addition of the two reagents (1 mL each) was made, and the resulting mixture was heated under reflux for 1 h. Most of the solvent was distilled under reduced pressure, and the residue was diluted with water (250 mL) and extracted with CH_2Cl_2 (3 × 250 mL). The combined organic extracts were washed with water (250 mL) and dried over $MgSO_4$. Evaporation of solvent gave a solid (535 mg), which was crystallized from methanol to give pure **5**; 474 mg (90%); mp 121–123 °C (lit.[8] mp 118–120 °C); IR (KBr) 1740, 1605, 1570, 1495, 1260, 1050 cm^{-1}; UV λ_{max} (ϵ) 222 (29 200), 262 (7400), 302 (2500); ^{1}H NMR δ 7.16 (d, J = 7.9 Hz, 1 H, 1-CH), 6.73 (dd, J = 7.9 Hz, J = 2.7 Hz, 1 H, 2-CH), 6.66 (d, J = 2.7 Hz, 1 H, 4-CH), 6.51 (d, J = 11.8 Hz, 1 H, 6-CH), 6.05 (d, J = 11.8 Hz, 1 H, 7-CH), 3.80 (s, 3 H, 3-CH_3O), 0.91 (s, 3 H, 18-CH_3); MS m/z (relative intensity) 282 (M^+, 100), 226 (11), 225 (20), 197 (48), 184 (69), 171 (67), 158 (63).

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Registry No. **1**, 434-22-0; **2**, 734-32-7; **3**, 13209-45-5; **4**, 2208-12-0; **5**, 17253-36-0.

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Acyl Anion Equivalents in the Synthesis of 2*H*-Pyran-2-ones: An Efficient Synthesis of Anibine†

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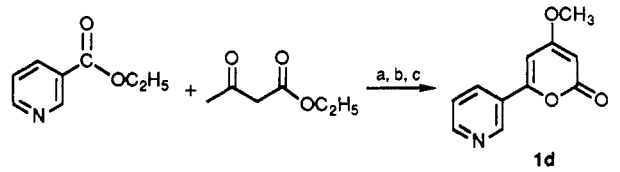
A number of 4-hydroxy-2*H*-pyran-2-ones and their methyl ethers have been isolated from natural sources.[1] Some of these, e.g. anibine (**1d**) and its analogues **1a** and **1b**, show interesting pharmacological properties.[1] Synthetic efforts toward construction of 2*H*-pyran-2-ones are

† Dedicated to Prof. N. S. Narasimhan on his 60th birthday.

0022-3263/89/1954-3985$01.50/0

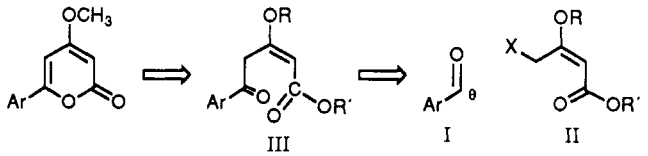
Scheme I[a]



[a] (a) LDA, THF; (b) 150 °C (3 mmHg); (c) CH_2N_2, ether.

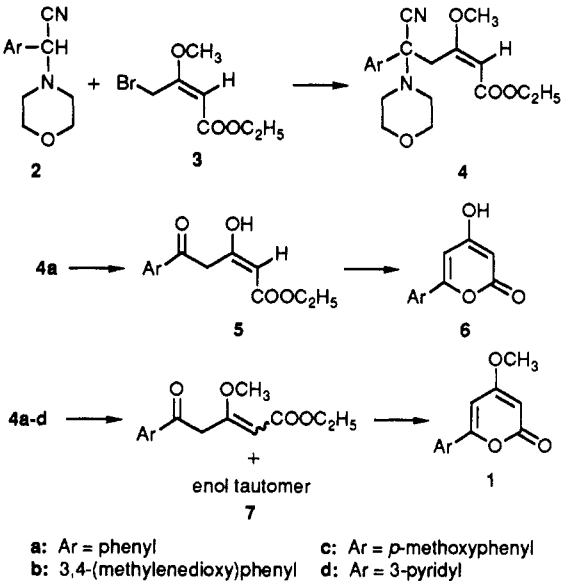
of current interest.[2] We report here a short, novel, general, and simple synthesis of this class of compounds. The key step in the synthesis is the alkylation of the masked acyl anion equivalent of type **2** (Scheme II), a methodology that, to the best of our knowledge, until now has been unexplored for the synthesis of 2*H*-pyran-2-ones.

The principal methods[2] used for the synthesis of 2*H*-pyran-2-ones are based on cyclization of intermediate δ-keto acids or esters. A recent synthesis of anibine (**1d**) reported from our laboratory by Narasimhan and Ammanamanchi[3] entailed Claisen type condensation of ethyl acetoacetate with ethyl nicotinate to give a β,δ-diketo ester, which, on thermal cyclization and subsequent methylation, gave **1d** (Scheme I). Our retrosynthetic analysis (eq 1) involves nucleophilic attack of an aromatic or heteroaromatic aldehyde (I) (umpolung of CO) to a suitably functionalized electrophile (II) to give β-substituted δ-keto ester (III), an immediate precursor of 4-methoxy(or hydroxy)-6-substituted-2*H*-pyran-2-ones.



The anions of α-(dialkylamino) nitriles derived from aromatic and heteroaromatic aldehydes have been adopted for their umpolung of CO reactivity.[4] In a preliminary study, α-aryl-α-(4-morpholino)acetonitrile (**2a**)[5] was deprotonated with 1.3 equiv of sodium hydride in *N*,*N*-dimethylformamide and reacted with ethyl (*E*)-4-bromo-3-methoxy-2-butenoate (**3**)[6] to give **4a** as white crystals in 86% yield (Scheme II). The ^{1}H NMR spectrum of **4a** showed it to be a single compound, and its *E* geometry indicated by the large downfield shift of the allylic methylene protons (two doublets at δ 4.08 and 3.25, respectively, with J = 14 Hz), suggesting a cis relationship with the ethoxycarbonyl functionality.[7] This assignment was

Scheme II



a: Ar = phenyl **c**: Ar = *p*-methoxyphenyl
b: 3,4-(methylenedioxy)phenyl **d**: Ar = 3-pyridyl

confirmed by NOE studies where spatial proximity of the methoxy group and the olefinic proton was demonstrated.[8]

Hydrolysis of **4a** with 70% aqueous acetic acid[5] gave **5** in which the vinyl methyl ether has been hydrolyzed. Thermal cyclization of **5** gave 4-hydroxy-6-aryl-2*H*-pyran-2-one (**6**), which on methylation with diazomethane afforded **1a**. When **4a** was subjected to milder hydrolysis conditions using copper sulfate in aqueous methanol as a cyanide sequestering agent,[9] **7a** was obtained in good yield with the vinyl methyl ether group intact. The ^{1}H NMR spectra of **7a** revealed it to be a mixture of keto enol, *E* and *Z* isomers[10] (Scheme II).

Our attempts to cyclize **7a** thermally under vacuum gave **1a** in low yield. Base-promoted cyclization with 1,8-diazabicyclo[5.4.0]undec-7-ene[11] in benzene under reflux for 30 h gave **1a** in better yield (Scheme II). After the successful synthesis of the analogue **1a**, the generality and the ease associated with the method was demonstrated by its application to the synthesis of 4-methoxyparacotoin (**1b**),[1a] a recently reported 4-methoxy-6-(*p*-methoxyphenyl)-2*H*-pyran-2-one (**1c**)[2a] and anibine (**1d**) (Tables I and II).

In conclusion, we have demonstrated the potentiality of acyl anion equivalent for the construction of an important ring system viz. 2*H*-pyran-2-one. The present synthesis has the advantages of readily preparable starting materials, use of simple reagents, and two efficient steps with easy workup and better overall yield, compared to the earlier reported methods.

Experimental Section

Melting points were determined on a Thomas-Hoover oil immersion capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 337 IR spectro-

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(8) In the NOE experiment, irradiation of the methoxy signal at δ 3.32 showed 18% increase in intensity for the olefinic proton at δ 4.68. The complementary NOE experiment would require irradiation of the methylene protons. However, these appear as an AB quartet in which the low-field proton (δ 4.08) is having close chemical shift with the olefinic proton (δ 4.68). In view of this such an NOE experiment could not be satisfactorily performed.

(9) Buchi, G.; Paul, H. L.; Wuest, H. *Tetrahedron Lett.* **1978**, 2763.

(10) The reaction medium during copper sulfate hydrolysis was acidic (pH ≅ 3.5), which may promote acid-catalyzed isomerization of double bond.

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Table I

2b–d → 4b–d

	Ar	mp, °C	yield, %
4b	3′,4′-(methylenedioxy)phenyl	137–139	84
4c	*p*-methoxyphenyl	72–74	85
4d	3′-pyridyl	118–120	84

photometer. ^{1}H NMR (90 MHz) were recorded on a JEOL FX-90Q spectrometer with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm on the δ scale.

General Procedures: (a) Alkylation. Sodium hydride (NaH) (80% in oil) was washed with dry hexane under nitrogen. To the hydride was added dry *N*,*N*-dimethylformamide (DMF) and α-aryl-α-(4-morpholino)acetonitrile in DMF at room temperature. After 1 h of stirring, the mixture was cooled to 0 °C, and ethyl (*E*)-4-bromo-3-methoxy-2-butenoate (**3**) in DMF was added slowly. The reaction mixture was allowed to warm to room temperature, stirred for 2 h, and poured into ice–water. The product was extracted with dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave a gummy product, which on flash chromatography with silica gel using 1:19 ethyl acetate–hexane (unless otherwise stated) followed by crystallization with petroleum ether (unless otherwise stated) afforded crystals of alkylated product.

(b) Hydrolysis. A suspension of alkylated product and copper sulfate ($CuSO_4 \cdot 5H_2O$) in 3:1 methanol–water was stirred for 10 h. Ether was added, the mixture was filtered, the residue was washed with ether, and combined filtrate was extracted with ether. Workup as above gave a gummy product, which was dried under vacuum for several hours and used without further purification for the next reaction.

(c) Cyclization. A mixture of hydrolyzed product and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry benzene was azeotropically refluxed for several hours. Evaporation of benzene followed by flash chromatography with silica gel and 1:9 ethyl acetate–hexane (unless otherwise stated) gave the 2*H*-pyran-2-one as a crystalline solids.

Ethyl (*E*)-δ-Cyano-δ-phenyl-β-methoxy-δ-(4-morpholino)pent-2-enoate (4a). Reaction of **2a** (1.0 g, 4.95 mmol), NaH (0.19 g, 6.43 mmol), and **3** (1.32 g, 5.94 mmol) in DMF (10 mL) gave 1.46 g (86%) of **4a** as a crystalline solid: mp 135 °C; IR (Nujol) 2220 (w), 1710, 1620, 1250, 1135, 1110, 1055, 847 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 2.2–2.9 (m, 4 H, $N(CH_2)_2$), 3.25 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 3.32 (s, 3 H, OCH_3), 3.55–3.8 (m, 4 H, $O(CH_2)_2$), 4.05 (q, *J* = 7 Hz, 2 H, OCH_2CH_3), 4.08 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 4.68 (s, 1 H, CH=), 7.1–7.6 (m, 5 H, Ph). Anal. Calcd for $C_{19}H_{24}N_2O_4$: C, 66.26; H, 7.02. Found: C, 66.18; H, 6.85.

Ethyl (*E*)-δ-Cyano-δ-(3′,4′-(methylenedioxy)phenyl)-β-methoxy-δ-(4-morpholino)pent-2-enoate (4b). Reaction of **2b** (1.0 g, 4.06 mmol), NaH (0.16 g, 5.28 mmol), and **3** (1.08 g, 4.88 mmol) in DMF (10 mL) gave 1.33 g (84%) of **4b** as a solid: mp 137–139 °C; IR (Nujol) 2240 (w), 1715, 1625, 1240, 1140, 1040, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 2.17–2.88 (m, 4 H, $N(CH_2)_2$), 3.2 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 3.37 (s, 3 H, OCH_3), 3.48–3.77 (m, 4 H, $O(CH_2)_2$), 3.94 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 4.0 (q, *J* = 7 Hz, 2 H, OCH_2CH_3), 4.65 (s, 1 H, CH=), 5.86 (b s, 2 H, OCH_2O), 6.6 (d, *J* = 8 Hz, 1 H, $H_{5'}$), 6.9–7.1 (m, 2 H, $H_{2'}$, $H_{6'}$). Anal. Calcd for $C_{20}H_{24}N_2O_6$: C, 61.84; H, 6.23. Found: C, 61.58; H, 6.14.

Ethyl (*E*)-δ-Cyano-δ-(*p*-methoxyphenyl)-β-methoxy-δ-(4-morpholino)pent-2-enoate (4c). Reaction of **2c** (1.0 g, 4.31 mmol), NaH (0.17 g, 5.6 mmol), and **3** (1.16 g, 5.2 mmol) in DMF (10 mL) gave 1.37 g (85%) of **4c** as a crystalline solid: mp 72–74 °C; IR (Nujol) 2235 (w), 1715, 1620, 1220, 1140, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 2.22–2.9 (m, 4 H, $N(CH_2)_2$), 3.29 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 3.4 (s, 3 H, OCH_3), 3.55–3.93 (m, 4 H, $O(CH_2)_2$), 3.81 (s, 3 H, OCH_3), 4.08 (q, *J* = 7 Hz, 2 H, OCH_2CH_3), 4.15 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 4.77 (s, 1 H, CH=), 6.84 (d, *J* = 9 Hz, 2 H, $H_{3'}$, $H_{5'}$), 7.49 (d, *J* = 9 Hz, 2 H, $H_{2'}$, $H_{6'}$). Anal. Calcd for $C_{20}H_{26}N_2O_5$: C, 64.15; H, 7.0. Found: C, 63.92; H, 7.06.

Ethyl (*E*)-δ-Cyano-δ-(3′-pyridyl)-β-methoxy-δ-(4-morpholino)pent-2-enoate (4d). Reaction of **2d** (1.0 g, 4.93 mmol), NaH (0.19 g, 6.4 mmol), and **3** (1.31 g, 5.91 mmol) in DMF (10 mL) followed by flash chromatography (1:6 ethyl acetate–hexane) and crystallization (1:9 benzene–petroleum ether) gave 1.43 g (84%) of **4d** as a crystalline pale yellow solid: mp 118–120 °C; IR (Nujol) 2240 (w), 1720, 1625, 1290, 1140, 1060, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 2.2–2.9 (m, 4 H, $N(CH_2)_2$), 3.34 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 3.35 (s, 3 H, OCH_3), 3.7 (m, 4 H, $O(CH_2)_2$), 4.0 (q, *J* = 7 Hz, 2 H, OCH_2CH_3), 4.08 (d, *J* = 14 Hz, 1 H, $=CCH_2$), 4.72 (s, 1 H, CH=), 7.21 (dd, *J* = 8 and 5 Hz, 1 H, $H_{5'}$), 7.88 (dt, *J* = 8 and 1.5 Hz, 1 H, $H_{4'}$), 8.52 (dd, *J* = 5 and 1.5 Hz, 1 H, $H_{6'}$), 8.77 (d, *J* = 1.5 Hz, 1 H, $H_{2'}$). Anal. Calcd for $C_{18}H_{23}N_3O_4$: C, 62.59; H, 6.71. Found: C, 62.85; H, 6.91.

Table II[a]

4b–d → 1b–d

	Ar	mp, °C	yield, %
1b	3′,4′-(methylenedioxy)phenyl	222–223	66
1c	*p*-methoxyphenyl	150–151	66
1d	3′-pyridyl	177–179	64

[a] Yields are for combined two steps: hydrolysis followed by cyclization.

4-Methoxy-6-phenyl-2*H*-pyran-2-one (1a). Reaction of **4a** (1.0 g, 2.9 mmol) and copper sulfate (0.94 g, 3.77 mmol) in methanol–water (10 mL) gave 0.6 g (84%) of **7a** as an oil. A mixture of **7a** (0.6 g, 2.42 mmol) and DBU (0.48 g, 3.15 mmol) in benzene (10 mL) was refluxed for 30 h. Flash chromatography gave 0.39 (80%) of **1a**: mp 129–130 °C (lit.[1c] mp 129.5–130.5 °C); IR (Nujol) 1720, 1650, 1575, 1270, 1220, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3 H, OCH_3), 5.45 (d, *J* = 2.5 Hz, 1 H, H_3), 6.42 (d, *J* = 2.5 Hz, 1 H, H_5), 7.3–7.55 (m, 3 H, $H_{3'}$, $H_{4'}$, $H_{5'}$), 7.65–7.9 (m, 2 H, $H_{2'}$, $H_{6'}$). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.39; H, 4.99. Found: C, 71.68; H, 4.97.

4-Methoxy-6-(3′,4′-(methylenedioxy)phenyl)-2*H*-pyran-2-one (1b). Reaction of **4b** (1.0 g, 2.56 mmol) and copper sulfate (0.83 g, 3.33 mmol) in methanol–water (10 mL) gave 0.61 g (82%) of **7b** as an oil. A mixture of **7b** (0.61 g, 2.1 mmol) and DBU (0.41 g, 2.78 mmol) in benzene (10 mL) was refluxed for 30 h. Flash chromatography gave 0.41 g (80%) of **1b**: mp 222–223 °C (lit.[1a] mp 222–224 °C); IR (Nujol) 1720, 1656, 1634, 1567 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 3 H, OCH_3), 5.25 (d, *J* = 2.5 Hz, 1 H, H_3), 5.82 (b s, 2 H, OCH_2O), 6.05 (d, *J* = 2.5 Hz, 1 H, H_5), 6.65 (d, *J* = 8 Hz, 1 H, $H_{5'}$), 6.95–7.25 (m, 2 H, $H_{2'}$, $H_{6'}$). Anal. Calcd for $C_{13}H_{10}O_5$: C, 63.41; H, 4.06. Found: C, 63.22; H, 3.96.

4-Methoxy-6-(*p*-methoxyphenyl)-2*H*-pyran-2-one (1c). Reaction of **4c** (1.0 g, 2.67 mmol) and copper sulfate (0.86 g, 3.5 mmol) in methanol–water (10 mL) gave 0.61 g (82%) of **7c** as an oil. A mixture of **7c** (0.61 g, 2.2 mmol) and DBU (0.43 g, 2.85 mmol) in benzene (10 mL) was refluxed for 30 h. Flash chromatography gave 0.41 g (80%) of **1c**: mp 150–152 °C (lit.[2a] mp 153 °C); IR (Nujol) 1725, 1630, 1500, 1490, 1400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 6 H, 2 OCH_3), 5.54 (d, *J* = 2.5 Hz, 1 H, H_3), 6.4 (d, *J* = 2.5 Hz, 1 H, H_5), 7.05 (d, *J* = 8 Hz, 2 H, $H_{3'}$, $H_{5'}$), 7.87 (d, *J* = 8 Hz, 2 H, $H_{2'}$, $H_{6'}$). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.52; H, 5.61.

4-Methoxy-6-(3′-pyridyl)-2*H*-pyran-2-one (1d). Reaction of **4d** (1.0 g, 2.9 mmol) and copper sulfate (0.94 g, 3.77 mmol) in methanol–water (10 mL) gave 0.58 g (80%) of **7d** as an oil. A mixture of **7d** (0.58 g, 2.32 mmol) and DBU (0.46 g, 3.01 mmol) in benzene (10 mL) was refluxed for 36 h. Flash chromatography with 2:8 ethyl acetate–hexane gave 0.38 g (80%) of **1d**: mp 177–179 °C (lit.[1a] mp 179–180 °C); IR (Nujol) 1720, 1640, 1570, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.0 (s, 3 H, OCH_3), 5.5 (d, *J* = 2.5 Hz, 1 H, H_3), 6.5 (d, *J* = 2.5 Hz, 1 H, H_5), 7.35 (dd, *J* = 8 and 5 Hz, 1 H, $H_{5'}$), 8.1 (m, 1 H, $H_{4'}$), 8.67 (dd, *J* = 5 and 1.5 Hz, 1 H, $H_{6'}$), 9.0 (d, *J* = 2.5 Hz, 1 H, $H_{2'}$). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.43. Found: C, 64.98; H, 4.21.

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