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Facile Synthesis of 1,3,7-Trihydroxyxanthone and Its Regioselective Coupling Reactions with Prenal: Simple and Efficient Access to Osajaxanthone and Nigrolineaxanthone F†

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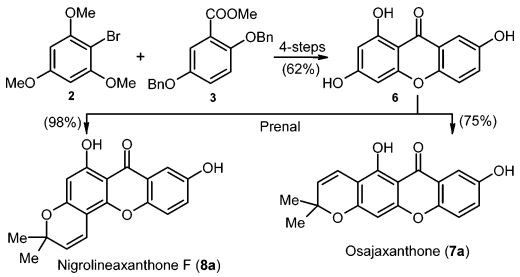

A facile five-step synthesis of naturally occurring 1,3,7-trihydroxyxanthone has been described starting from 1,3,5-trimethoxybenzene via NBS-induced nuclear bromination, lithiation followed by an in situ benzoylation with methyl 2,5-dibenzyloxybenzoate, selective deprotection of the two benzyl groups, base-catalyzed intramolecular cyclization, and demethylations pathway with 62% overall yield. The regioselective coupling reactions of 1,3,7-trihydroxyxanthone with prenal in the presence of calcium hydroxide at room temperature and under thermal conditions at 140−150 °C have been demonstrated to exclusively obtain the natural products osajaxanthone in 75% yield and nigrolineaxanthone F in 98% yield, respectively.

The natural and unnatural xanthones are an important class of compounds.[1] Several hydroxy and multiple-hydroxy-substituted xanthones exist in nature.[2] Nature very smartly explores all the available sites on these hydroxy-substituted xanthones for remarkable regioselective coupling reactions with the naturally occurring prenal, citral, and farnesal to design a vast array of corresponding pyranoxanthones and also to generate their complex structural architectures with the help of further intramolecular cyclizations.[1−4] The 1,3,7-trihydroxyxanthone (**6**) has been isolated from *Athyrium mesosorum*, and it possesses xanthine oxidase inhibitor activity.[5] The xanthone **6** has been synthesized earlier in good yield using the intramolecular oxidative coupling reaction of suitably substituted benzophenone derivatives.[6] In nature, xanthone **6** produces two structural analogues, osajaxanthone (**7a**) and nigrolineaxanthone F (**8a**), via two different regioselective coupling reactions with prenal. Osajaxanthone (**7a**) has been isolated from *Calophyllum enervosum*, and it possesses antimicrobial and antifish poison activities.[3] Nigrolineaxanthone F (**8a**) has been isolated from the *Garcinia nigrolineata* species.[4] Two multistep total syntheses of osajaxanthone (**7a**) have been reported using two different synthetic strategies.[7] To date, exclusive synthesis of Nigrolineaxanthone F is not known in the literature. All the reported attempts to condense xanthone **6** with prenal have resulted in the formation of a mixture of xanthones **7a** and **8a**.[8] Now we herein report a short and efficient synthesis of xanthone **6** and the regioselective coupling reactions of **6** with prenal to exclusively design osajaxanthone (**7a**) and nigrolineaxanthone F (**8a**) in high yield (Scheme 1).

1,3,5-Trimethoxybenzene (**1**) on treatment with NBS (1.0 equiv) in refluxing CCl_4 furnished 2-bromo-1,3,5-trimethoxybenzene (**2**) in quantitative yield. Bromobenzene **2** on *n*-BuLi (1.0 equiv) induced lithiation, followed by the benzoylation of the lithiated species with methyl 2,5-dibenzyloxybenzoate gave the corresponding dibenzyloxytrimethoxybenzophenone **3** in 75% yield. The benzophenone **3**, when subjected to catalytic hydrogenation, yielded the desired dihydroxytrimethoxybenzophenone **4** in nearly 100% yield. The benzophenone **4** on base-catalyzed intramolecular cyclization[9] via the oxa-Michael addition, followed by the elimination pathway, furnished the dimethoxyhydroxyxanthone **5** in quantitative yield. The BBr_3 (6.0 equiv) induced demethylations of xanthone **5** gave the naturally occurring 1,3,7-trihydroxyxanthone (**6**) in 82% yield. Starting from the symmetrical trimethoxybenzene **1**, the xanthone **6** was obtained in five steps with 62% overall yield. The analytical and spectral data obtained for xanthone **6** was in

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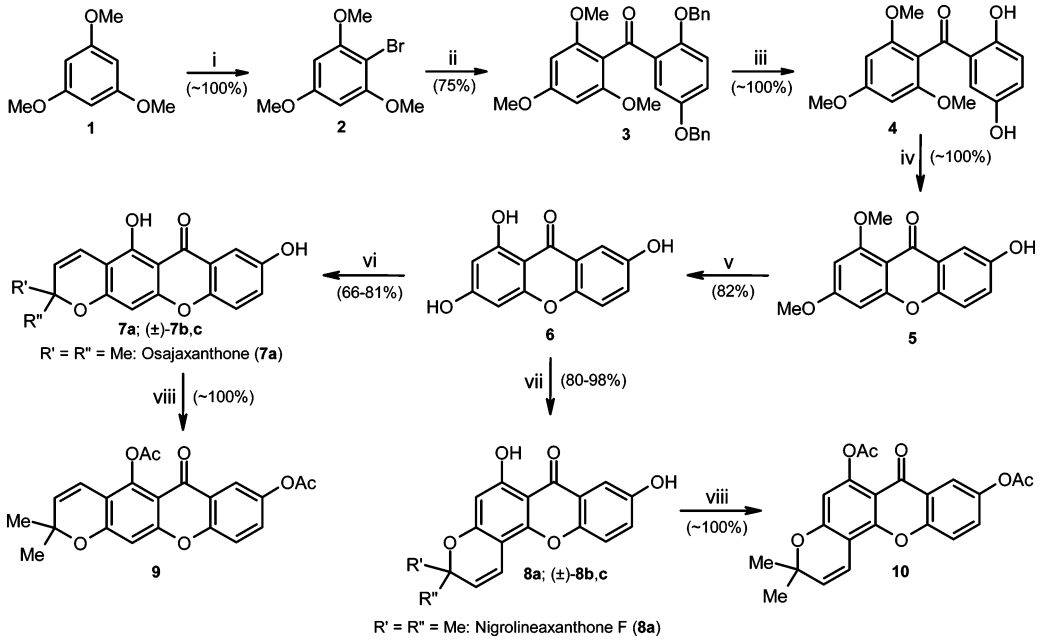
SCHEME 1 [a]



[a] Key: (i) CCl_4, NBS (1.0 equiv), reflux, 6 h (~100%); (ii) THF, −78 °C, *n*-BuLi (1.0 equiv), 45 min, methyl 2,5-dibenzyloxybenzoate, 30 min (75%); (iii) H_2, 10% Pd−C, methanol, rt, 6 h (~100%); (iv) (a) KOH (5.0 equiv), MeOH, reflux, 12 h, (b) H^+/2 N HCl (~100%); (v) DCM, BBr_3 (6.0 equiv), −78 °C to room temperature, 36 h (82%); (vi) prenal/crotonaldehyde/citral (5 equiv), $Ca(OH)_2$ (2.0 equiv), methanol, rt, 36 h (**7a**, 75%; **7b**, 66%; **7c**, 81%); (vii) prenal/crotonaldehyde/citral (10.0 equiv), 140−150 °C, 6 h (**8a**, 98%; **8b**, 86%; **8c**, 80%); (viii) pyridine, Ac_2O, rt, 12 h (~100%).

complete agreement with the reported data.[5,6] We feel that our present simple and efficient approach to xanthone **6** using two different protecting groups, selective deprotections, and intramolecular cyclization is noteworthy.

Theoretically, the xanthone **6** can undergo coupling reactions with the α,β-unsaturated aldehydes at the 2-, 4-, 6-, and 8-position to generate the corresponding benzopyrans via an aldol-type condensation, followed by S_N2'-dehydrative ring-closure reactions. The order of thermodynamic stability for these in situ-generated carbanions will be 4 > 2 > 8 > 6 as a result of the flanking of the 4-position carbanion between carbonyl and α,β-unsaturated carbonyl, flanking of the 2-position carbanion between 1,3-dicarbonyl system (on conversion of enol to keto form), electron-withdrawing inductive effect of xanthone carbonyl on the 8-position carbanion, and formation of simple α-carbanion at the 6-position. Because, in xanthone **6**, the ring A is doubly activated, the regioselective coupling reactions of xanthone **6** at the 2- and 4-position with the α,β-unsaturated aldehydes to exclusively generate, respectively, the linear and angular pyranoxanthones under kinetic and thermodynamic conditions is a practical and challenging task of current interest. The DBU-induced generation of kinetic carbanion on 3,5-dihydroxyphthalide[10a] and $Ca(OH)_2$-induced generation of kinetic carbanion on methyl 2,4-dihydroxybenzoate[10b] and their condensation with α,β-unsaturated aldehydes are known in the literature.[10] The DBU-induced coupling of xanthone **6** with prenal in acetonitrile at room temperature was slow and gave **7a** in only 11% yield after a 72 h reaction time. The same reaction on heating lost its selectivity and furnished a mixture of **7a** and **8a** in good yield. However, the $Ca(OH)_2$-induced regioselective generation of the kinetic carbanion at the 2-position of xanthone **6** and its condensation with prenal at room temperature exclusively furnished the osajaxanthone (**7a**) in 75% yield. We surmise that the complexation of the Ca^{2+} ion with xanthone could be responsible for the present observed selectivity. The reaction of xanthone **6** with prenal under thermodynamic conditions (heat, 140−150 °C), with the generation of a stable carbanion at the 4-position, exclusively furnished the nigrolineaxanthone F (**8a**) in 98% yield. The osajaxanthone (**7a**) and nigrolineaxanthone F (**8a**) were further characterized as their respective diacetyl derivatives **9**[3b] and **10**. The analytical and spectral data obtained for xanthones **7a** and **8a** were in complete agreement with the reported data.[3,4,7,8] As expected, the linear product osajaxanthone (**7a**) had a higher melting point than the corresponding angular nigrolineaxanthone F (**8a**), but the confirmatory structural discrimination of these two natural products on the basis of ^1H and ^{13}C NMR data was a difficult task. Finally, the structures of these nice yellow crystalline linear and angular pyranoxanthones **7a** and **8a** were confirmed by using X-ray crystallographic data.[11] The X-ray data revealed that the intramolecular O−H···O hydrogen bonding is seen for the compound **7a** in addition to intermolecular O−H···O hydrogen bondings. The molecules of **7a** pack in a zigzag manner when viewed down the "a" axis (Figure 1). Compound **8a** initially forms a dimer by intramolecular O−H···O hydrogen bonding and intermolecular O−H···O hydrogen bondings in the packing of the molecules when viewed down the "c" axis (Figure 2).

The present approach to these xanthones is general in nature, and we could also very selectively condense crotonaldehyde and citral with xanthone **6** to obtain the compounds **7b**,**c** and **8b**,**c** in very good yields.

In summary, we have demonstrated a facile access to 1,3,7-trihydroxyxanthone and its two different regioselective cou-

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(11) For all the details related to X-ray crystallographic data, please see the Supporting Information.

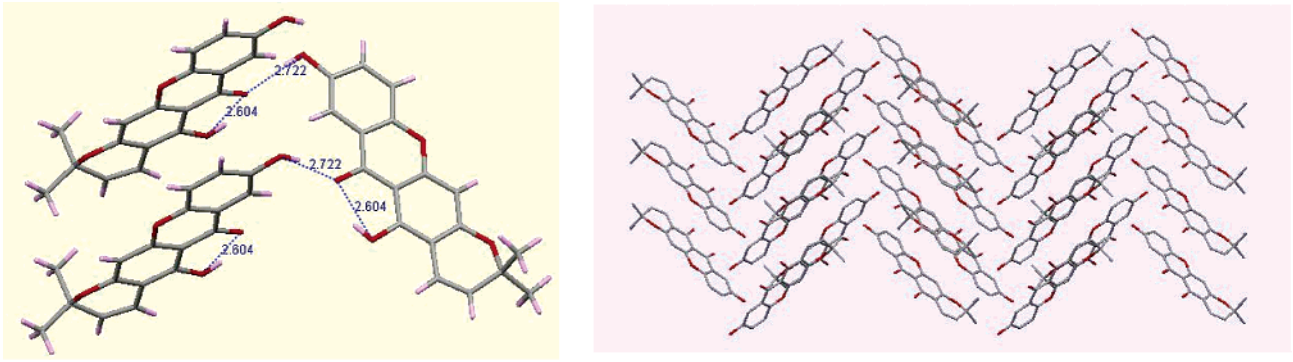

FIGURE 1. Intra- and intermolecular hydrogen bonding in **7a** and packing of **7a** in a zigzag manner when viewed down the "a" axis.

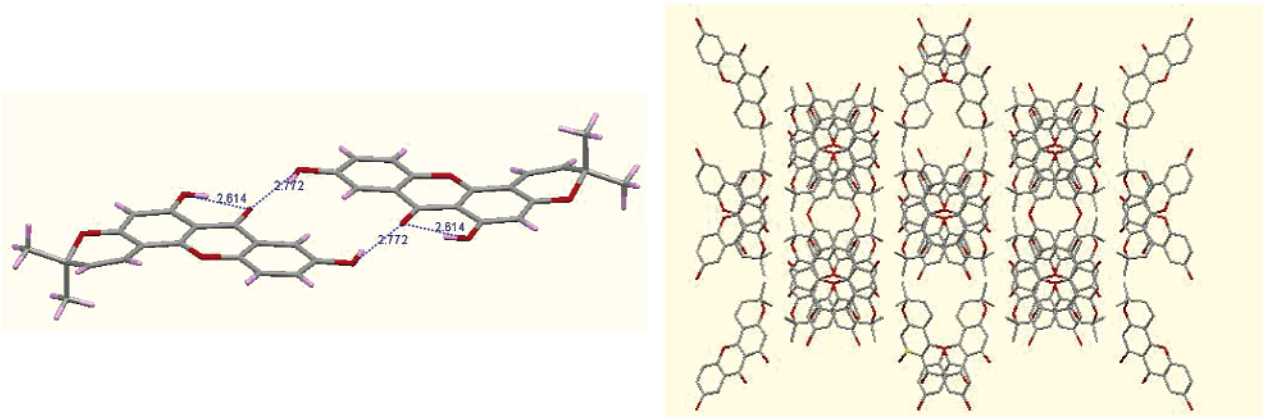

FIGURE 2. Dimeric **8a** with intra- and intermolecular hydrogen bonding and packing of **8a** when viewed down the "c" axis.

pling reactions with prenal to obtain osajaxanthone and nigrolineaxanthone F. Our present approach to these three natural products has several advantages over other known approaches in the literature.

Experimental Section

Methyl 2,5-Dibenzyloxybenzoate. To a stirring mixture of methyl 2,5-dihydroxybenzoate (10.00 g, 59.52 mmol) and anhydrous potassium carbonate (41.10 g, 297.62 mmol) in acetone (100 mL) was added benzylbromide (17.70 mL, 148.80 mmol), and the reaction mixture was refluxed for 6 h. After cooling, the reaction mixture was filtered, and concentration of the filtrate under vacuum followed by silica gel column chromatographic purification of the residue using 15% ethyl acetate in petroleum ether afforded methyl 2,5-dibenzyloxybenzoate (20.23 g, 98%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.90 (s, 3H), 5.03 (s, 2H), 5.12 (s, 2H), 6.94 (d, J = 9.1 Hz, 1H), 7.05 (dd, J = 9.1 and 3.2 Hz, 1H), 7.25−7.55 (m, 11H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 51.7, 70.2, 71.3, 115.9, 117.0, 119.9, 121.3, 126.7−128.2 (7 carbons) 136.5, 136.8, 152.3, 166.0; MS (*m*/*z*) 387, 371, 349, 317, 281, 257, 224, 181, 143; IR (Nujol) 1722, 1504 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 76.02; H, 5.67.

2-Bromo-1,3,5-trimethoxybenzene (2). To a solution of **1** (10.00 g, 59.46 mmol) in CCl_4 (100 mL) was added NBS (10.58 g, 59.46 mmol), and the reaction mixture was refluxed gently for 3 h. After cooling, the reaction mixture was filtered, and concentration of the filtrate under vacuum followed by silica gel column chromatographic purification of the residue using 25% ethyl acetate in petroleum ether gave **2**[12] (14.6 g, ∼100%) as a white solid. Mp 84−86 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.79 (s, 3H), 3.85 (s, 6H), 6.14 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.3, 56.1, 91.4, 91.6, 157.2, 160.3; MS (*m*/*z*) 271, 269, 249, 247, 224, 119; IR (Nujol) 1589, 1574, 1462, 1377, 1346, 1229, 1207, 1155, 1128 cm^{-1}. Anal. Calcd for $C_9H_{11}BrO_3$: C, 43.75; H, 4.49; Br, 32.34. Found: C, 43.69; H, 4.53; Br, 32.59.

2,5-Dibenzyloxyphenyl 2′,4′,6′-Trimethoxyphenyl Methanone (3). To a stirring solution of **2** (10.00 g, 40.45 mmol) in THF (60 mL) at −78 °C was added *n*-BuLi (27.00 mL, 40.45 mmol) dropwise. After stirring at −78 °C for 45 min, this reaction mixture was added slowly to a stirring solution of methyl 2,5-dibenzyloxybenzoate (16.90 g, 48.55 mmol) in THF (80 mL) at −78 °C and stirred for an additional 30 min. A saturated solution of NH_4Cl was then added to the reaction mixture at −78 °C, and the reaction mixture was allowed to reach room temperature. THF was removed in vacuo. To the reaction mixture was added ethyl acetate (150 mL), and the organic layer was washed with water and brine and dried over Na_2SO_4. Removal of the solvent in vacuo followed by silica gel column chromatographic purification of the residue using 30% ethyl acetate in petroleum ether afforded **3** (14.6 g, 75%) as a white solid. Mp 123−125 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.57 (s, 6H), 3.77 (s, 3H), 4.86 (s, 2H), 5.04 (s, 2H), 5.97 (s, 2H), 6.88 (d, J = 9.0 Hz, 1H), 7.00−7.15 (m, 2H), 7.20−7.45 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.1, 55.7, 70.5, 71.3, 90.7, 114.5, 115.0, 116.3, 120.1, 127.2, 127.4, 127.5, 127.8, 128.0, 128.4, 130.8, 136.7, 136.9, 152.5, 152.6, 158.7, 162.0, 192.9; MS (*m*/*z*) 485, 391, 317, 261, 185; IR (Nujol) 1643, 1605, 1585, 1491, 1462, 1416, 1377 cm^{-1}. Anal. Calcd for $C_{30}H_{28}O_6$: C, 74.36; H, 5.82. Found: C, 74.29; H, 5.90.

2,5-Dihydroxyphenyl 2′,4′,6′-Trimethoxyphenyl Methanone (4). To a stirring solution of **3** (10.00 g, 20.66 mmol) in methanol (100 mL) at room temperature was added 10% Pd/C (500 mg), and the reaction mixture was subjected to hydrogenation at 65-psi hydrogen pressure for 24 h. The reaction mixture was filtered

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through Celite, and the filtrate was concentrated in vacuo. Silica gel column chromatographic purification of the residue using 40% ethyl acetate in petroleum ether furnished **4** (6.20 g, ~100%) as a yellow solid. Mp 232−234 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 3.69 (s, 6H), 3.85 (s, 3H), 6.34 (s, 2H), 6.66 (d, J = 2.9 Hz, 1H), 6.83 (d, J = 8.8 Hz, 1H), 7.00 (dd, J = 9.0 and 3.0 Hz, 1H), 9.10 (s, 1H), 11.45 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 56.1, 91.2, 109.1, 116.8, 118.4, 120.9, 125.4, 149.6, 154.8, 157.8, 162.6, 200.6; MS (*m*/*z*) 305, 279, 187, 155, 109; IR (Nujol) 3234, 1611, 1582, 1568, 1483, 1458 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.19; H, 5.42.

7-Hydroxy-1,3-dimethoxy-xanthen-9-one (5). To an ice-cooled stirring solution of **4** (5.00 g, 16.45 mmol) in methanol (30 mL), a solution of KOH (4.60 g, 82.24 mmol) in methanol (30 mL) was added slowly. The reaction mixture was refluxed gently for 12 h. After cooling to 0 °C, the reaction mixture was acidified with 2 N HCl, and the solid compound obtained was filtered, washed with cold water, and dried to provide **5** (4.40 g, ~100%) as a faint yellow solid. Mp 290−292 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 3.83 (s, 3H), 3.84 (s, 3H), 6.39 (d, J = 2.3 Hz, 1H), 6.54 (d, J = 2.3 Hz, 1H), 7.16 (dd, J = 9.0 and 2.9 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.38 (d, J = 2.9 Hz, 1H), 9.82 (s, 1H); ^{13}C NMR (DMSO-d_6, 50 MHz) δ 56.1, 56.3, 93.0, 95.2, 106.1, 109.2, 118.5, 123.1, 123.3, 148.1, 153.9, 159.3, 161.6, 164.7, 173.7; MS (*m*/*z*) 273, 253, 205, 185, 155, 149, 125, 114, 109; IR (Nujol) 3391, 1638, 1632, 1593, 1460 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_5$: C, 66.17; H, 4.44. Found: C, 65.98; H, 4.58.

1,3,7-Trihydroxyxanthen-9-one (6). To a stirring suspension of **5** (4.00 g, 14.71 mmol) in dichloromethane (80 mL) at −78 °C was added borontribromide (8.40 mL, 88.24 mmol) quickly, and the reaction mixture was allowed to attain room temperature slowly. After stirring for 36 h at room temperature, the reaction mixture was cooled to 0 °C and very slowly quenched with water. Dichloromethane was removed in vacuo, and ethyl acetate (100 mL) was added to the reaction mixture. The organic layer was washed with water and brine and dried over Na_2SO_4. Removal of the solvent under vacuo followed by silica gel column chromatographic purification of the residue using 30% ethyl acetate in petroleum ether afforded **6** (3.65 g, 82%) as a yellow solid. Mp 318−319 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 6.18 (d, J = 2.1 Hz, 1H), 6.35 (d, J = 1.9 Hz, 1H), 7.27 (dd, J = 9.0 and 3.0 Hz, 1H), 7.40 (d, J = 2.9 Hz, 1H), 7.45 (d, J = 9.1 Hz, 1H), 10.00 (s, 1H), 11.04 (s, 1H), 12.88 (s, 1H); ^{13}C NMR (DMSO-d_6, 50 MHz) δ 93.9, 98.0, 102.1, 108.2, 119.1, 120.6, 124.6, 149.2, 154.1, 157.7, 162.7, 163.0, 179.9; MS (*m*/*z*) 291, 267, 259, 245, 224, 204, 191, 161, 127; IR (Nujol) 3368, 3207, 1651, 1614, 1582, 1464 cm^{-1}. Anal. Calcd for $C_{13}H_8O_5$: C, 63.94; H, 3.30. Found: C, 64.06; H, 3.35.

5,8-Dihydroxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one (7a). To a stirring mixture of **6** (250 mg, 1.02 mmol) and $Ca(OH)_2$ (15 mg, 2.05 mmol) in methanol (10 mL) at room temperature was added 3-methyl-2-butenal (prenal; 0.5 mL, 5.12 mmol). After stirring for 36 h at room temperature, methanol was removed at room temperature under vacuo, and the reaction mixture was diluted with ethyl acetate (30 mL). The organic layer was washed with 2 N HCl, water, and brine and dried over Na_2SO_4. Removal of the solvent under vacuo followed by silica gel column chromatographic purification of the residue using 12% ethyl acetate in petroleum ether gave **7a** (235 mg, 75%) as a yellow solid. Mp 266−268 °C (MeOH/EtOH = 1:1); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.43 (s, 6H), 5.77 (d, J = 10.1 Hz, 1H), 6.40 (s, 1H), 6.60 (d, J = 9.9 Hz, 1H), 7.29 (dd, J = 9.0 and 2.8 Hz, 1H), 7.40 (d, J = 2.6 Hz, 1H), 7.47 (d, J = 9.1 Hz, 1H), 10.07 (s, 1H), 13.26 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 28.3, 78.8, 94.9, 103.1, 104.0, 108.2, 114.7, 119.5, 120.6, 125.2, 128.8, 149.4, 154.4, 157.0 (2 carbons), 160.4, 180.5; MS (*m*/*z*) 311, 301, 268, 239, 204, 188, 172, 126; IR (Nujol) 3227, 1651, 1632, 1609 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_5$: C, 69.67; H, 4.55. Found: C, 69.55; H, 4.73.

6,9-Dihydroxy-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]xanthen-7-one (8a). A stirring mixture of **6** (250 mg, 1.02 mmol) and 3-methyl-2-butenal (prenal; 1.00 mL, 10.24 mmol) was heated at 140−150 °C for a period of 6 h. After cooling, the obtained residue on silica gel column chromatographic purification using 15% ethyl acetate in petroleum ether gave **8a** (310 mg, 98%) as a yellow solid. Mp 244−245 °C (EtOH); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.43 (s, 6H), 5.77 (d, J = 10.2 Hz, 1H), 6.19 (s, 1H), 6.79 (d, J = 10.1 Hz, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.39 (s, 1H), 7.53 (d, J = 9.0 Hz, 1H), 10.06 (s, 1H), 12.98 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 28.1, 78.6, 98.4, 100.7, 103.0, 108.1, 114.5, 119.4, 120.5, 125.0, 127.8, 149.2, 151.6, 154.4, 160.3, 162.4, 180.4; MS (*m*/*z*) 311, 229, 167; IR (Nujol) 3381, 1645, 1466 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_5$: C, 69.67; H, 4.55. Found: C, 69.58; H, 4.49.

5,8-Diacetoxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one (9). To a stirring solution of **7a** (100 mg, 0.32 mmol) in pyridine (5 mL) was added acetic anhydride (5 mL), and the reaction mixture was kept in the dark at room temperature for 24 h. The reaction mixture was poured into ice-cold water and extracted with ethyl acetate (15 mL × 5). The combined organic layer was washed with 10% aq $CuSO_4$ solution, water, and brine and dried over Na_2SO_4. Concentration of the organic layer under vacuum followed by silica gel column chromatographic purification of the residue using 25% ethyl acetate in petroleum ether gave **9** (125 mg, ~100%) as a white solid. Mp 197−199 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (s, 6H), 2.31 (s, 3H), 2.50 (s, 3H), 5.75 (d, J = 10.1 Hz, 1H), 6.50 (d, J = 10.0 Hz, 1H), 6.73 (s, 1H), 7.35−7.45 (m, 2H), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 21.0, 28.5, 78.4, 102.1, 108.7, 112.1, 115.0, 118.5, 118.6, 122.7, 128.2, 131.5, 145.5, 146.6, 152.7, 158.0, 159.0, 169.2 (2 carbons), 174.2; MS (*m*/*z*) 395, 375, 353, 300, 239; IR (Nujol) 1759, 1749, 1659, 1643, 1614, 1470 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_7$: C, 67.00; H, 4.60. Found: C, 67.15; H, 4.52.

6,9-Diacetoxy-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]xanthen-7-one (10). Compound **10** was prepared from **8a** using the same procedure described for **9**. **10:** White solid (126 mg, ~100% yield); mp 185−187 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (s, 6H), 2.31 (s, 3H), 2.46 (s, 3H), 5.70 (d, J = 10.0 Hz, 1H), 6.47 (s, 1H), 6.88 (d, J = 10.3 Hz, 1H), 7.40 (dd, J = 8.8 and 2.7 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 21.2, 28.4, 78.5, 107.3, 108.5, 108.6, 114.9, 118.5, 118.6, 122.6, 128.3, 129.4, 146.7, 150.7, 152.5, 152.9, 158.4, 169.2, 169.6, 174.2; MS (*m*/*z*) 395, 353, 301, 282, 260, 204, 149; IR (Nujol) 1763, 1751, 1653, 1464 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_7$: C, 67.00; H, 4.60. Found: C, 66.89; H, 4.66.

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Supporting Information Available: ^{1}H NMR spectra of **3**−**6**, **7a**−**c**, and **8a**−**c** and ^{13}C NMR spectra of **4**−**6**, **7a**−**c**, and **8a**. X-ray crystallographic data in CIF format and ORTEP diagrams for compounds **7a** and **8a**. Preparation details and tabulated analytical and spectral data of compounds **7b**, **7c**, **8b**, and **8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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