Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information-I

Multi-catalysis Reactions: Direct Organocatalytic Sequential One-pot Synthesis of Highly Functionalized Cyclopenta[b]chromen-1-ones

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Due to the keto-enol tautomerism in 2-alkyl or 2-aryl-cyclopentane-1,3-dione compounds, ^{13}C NMR shows some of carbons (2 x CH_2 and 2 x C=O) are poor resolution even after more scans.

Materials: All solvents and commercially available chemicals were used as received.

General Experimental Procedures for the Multi-catalysis Reactions:

Aniline-Catalyzed Cascade Olefination/Hydrogenation Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9 mmol of the aldehyde **2**, 0.3 mmol of CH-acid **1a** and 0.3 mmol of Hantzsch ester **3** was added 1.0 mL of dichloromethane, and then the catalyst aniline **4c** (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Tables 1 to 6. The crude reaction mixture was directly loaded onto a silica gel column with or without aqueous work-up, and pure cascade products **6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

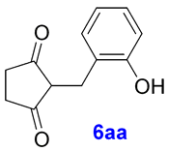
Acid-Catalyzed Cascade Oxy-Michael/Dehydration Reactions of 2-(2-Hydroxy-benzyl)-Cyclopentane-1,3-Diones 6: A solution of substituted 2-(2-hydroxy-benzyl)-cyclopentane-1,3-diones **6** (0.1 mmol) and *p*-TSA **9f** (0.03 mmol, 30 mol%) in dichloromethane (1.0 ml) was stirred at 45 °C for 9 to 18 h. After cooling, the reaction mixture washed with water and the aqueous layer was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Amino Acid or Aniline-/p-TSA-Catalyzed One-Pot Double Cascade Olefination/Hydrogenation/Oxy-Michael/Dehydration Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9

mmol of the aldehyde **2**, 0.3 mmol of CH-acid **1a** and 0.3 mmol of Hantzsch ester **3** was added 1.0 mL of dichloromethane, and then the catalyst amino acid **4a** or aniline **4c** (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Table 3. After evaporation of the solvent completely, to the crude reaction mixture added 1.0 mL of toluene solvent and *p*-TSA **9f** (0.09 mmol, 30 mol%) and the reaction mixture was stirred at 90 °C for 10 h. The crude reaction mixture was worked up with aqueous $NaHCO_3$ solution, and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Pure one-pot products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General Procedure for the Direct Organocatalytic One-Pot Synthesis of 2-(2-Hydroxy-benzyl)-3-Methoxy-Cyclopent-2-enones 11: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9 mmol of the aldehyde **2**, 0.3 mmol of CH-acid **1a** and 0.3 mmol of Hantzsch ester **3** was added 1.0 mL of dichloromethane, and then the catalyst aniline **4c** (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Table 6. After evaporation of the solvent completely, to the crude reaction mixture added 15 equivalents of an ethereal solution of diazomethane and the reaction mixture was stirred at room temperature for the 2 h. After evaporation of the solvent and excess diazomethane completely in fume hood, the crude reaction mixture was directly loaded onto a silica gel column with or without aqueous work-up and pure one-pot products **11** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

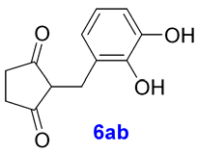
General Procedure for the Multi-catalysis Synthesis of 3,9-Dihydro-2H-Cyclopenta[b]chromen-1-ones 10: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9 mmol of the aldehyde **2**, 0.3 mmol of CH-acid **1a** and 0.3 mmol of Hantzsch ester **3** was added 1.0 mL of dichloromethane, and then the catalyst aniline **4c** (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Scheme 3. After evaporation of the solvent completely, to the crude reaction mixture added 15 equivalents of an ethereal solution of diazomethane and the reaction mixture was stirred at room temperature for the 2 h. After evaporation of the solvent and excess diazomethane completely in fume hood, to the crude reaction mixture added 3 equivalents of K_2CO_3 and solvent ethanol and the reaction mixture was stirred at room temperature for the 18 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Pure one-pot products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).



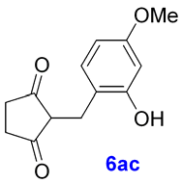
6aa

2-(2-Hydroxy-benzyl)-cyclopentane-1,3-dione (6aa): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 156 °C; IR (Neat): ν_{max} 3239, 2924, 1547, 1369, 1262, 1242, 1174, 1101 and 760 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 7.20 (1H, d, *J* = 7.2 Hz), 7.08 (1H, t, *J* = 7.6 Hz), 6.88 (1H, d, *J*

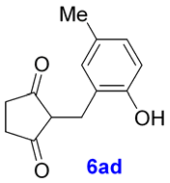
= 8.0 Hz), 6.81 (1H, t, *J* = 7.6 Hz) [Ar-H]; 3.43 (2H, s), 2.47 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135]** δ 153.7 (C, C-OH), 130.6 (CH), 127.7 (CH), 126.5 (C), 120.7 (CH), 117.9 (C), 116.6 (CH), 30.1 (2 x CH$_2$), 21.7 (CH$_2$); HRMS m/z 205.0842 (M + H$^+$), calcd for $C_{12}H_{12}O_3H$ 205.0864.



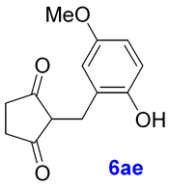
2-(2,3-Dihydroxy-benzyl)-cyclopentane-1,3-dione (6ab): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 168 °C; IR (Neat): ν$_{max}$ 3384, 2921, 1540, 1479, 1440, 1373, 1266, 1216, 1175, 1070 and 742 cm^{-1}; **^{1}H NMR [CDCl$_3$ + CD$_3$OD (three drops)]** δ 6.72 (3H, m) [Ar-H]; 3.41 (2H, s), 2.49 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135]** δ 146.1 (C, C-OH), 141.6 (C, C-OH), 127.3 (C), 121.2 (CH), 120.6 (CH), 118.1 (C), 113.0 (CH), 30.1 (2 x CH$_2$), 21.8 (CH$_2$); LRMS m/z 221.00 (M + H$^+$), calcd for $C_{12}H_{12}O_4H$ 221.0736; Anal. calcd for $C_{12}H_{12}O_4$ (220.0736): C, 65.45; H, 5.49. Found: C, 65.426; H, 5.457%.



2-(2-Hydroxy-4-methoxy-benzyl)-cyclopentane-1,3-dione (6ac): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; IR (Neat): ν$_{max}$ 3297, 2927, 1619, 1583, 1504, 1439, 1354, 1259, 1166, 1099, 1026, 957 and 824 cm^{-1}; **^{1}H NMR [CDCl$_3$ + CD$_3$OD (three drops)]** δ 7.09 (1H, d, *J* = 8.0 Hz), 6.48 (1H, d, *J* = 2.4 Hz), 6.39 (1H, dd, *J* = 8.4, 2.4 Hz) [Ar-H]; 3.74 (3H, s, OC*H*$_3$), 3.35 (2H, s), 2.47 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135]** δ 159.3 (C), 154.8 (C), 131.0 (CH), 119.0 (C), 118.2 (C), 106.2 (CH), 102.6 (CH), 55.1 (CH$_3$, O*C*H$_3$), 30.1 (2 x CH$_2$), 21.0 (CH$_2$); LRMS m/z 235.00 (M + H$^+$), calcd for $C_{13}H_{14}O_4H$ 235.0892; Anal. calcd for $C_{13}H_{14}O_4$ (234.0892): C, 66.66; H, 6.02. Found: C, 66.613; H, 6.030%.

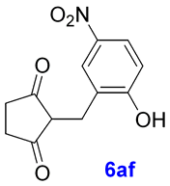


2-(2-Hydroxy-5-methyl-benzyl)-cyclopentane-1,3-dione (6ad): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; IR (Neat): ν$_{max}$ 2931, 2433, 1553, 1373, 1351, 1253, 1171, 843 and 754 cm^{-1}; **^{1}H NMR [CDCl$_3$ + CD$_3$OD (three drops)]** δ 7.01 (1H, d, *J* = 1.6 Hz), 6.88 (1H, dd, *J* = 8.0, 1.6 Hz), 6.78 (1H, d, *J* = 8.0 Hz) [Ar-H]; 3.39 (2H, s), 2.47 (4H, s, 2 x C*H*$_2$), 2.22 (3H, s, Ar-C*H*$_3$); **^{13}C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135]** δ 151.2 (C), 131.1 (CH), 129.9 (C), 128.1 (CH), 126.3 (C), 117.9 (C), 116.4 (CH), 30.0 (2 x CH$_2$), 21.6 (CH$_2$), 20.2 (CH$_3$, Ar-*C*H$_3$); LRMS m/z 219.00 (M + H$^+$), calcd for $C_{13}H_{14}O_3H$ 219.0943; Anal. calcd for $C_{13}H_{14}O_3$ (218.0943): C, 71.54; H, 6.47. Found: C, 71.627; H, 6.461%.

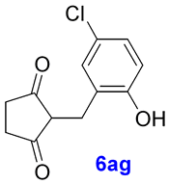


2-(2-Hydroxy-5-methoxy-benzyl)-cyclopentane-1,3-dione (6ae): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 153 °C; IR (Neat): ν$_{max}$ 3307, 2925, 1499, 1361, 1261, 1235, 1172, 1048 and 810 cm^{-1}; **^{1}H NMR [CDCl$_3$ + CD$_3$OD (three drops)]** δ 6.81 (1H, d, *J* = 8.8 Hz), 6.78 (1H, d, *J* = 1.6 Hz), 6.65 (1H, dd, *J* = 8.8, 2.8 Hz) [Ar-H]; 3.73 (3H, s, OC*H*$_3$), 3.40 (2H, s), 2.48 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135]** δ 153.4 (C), 147.5 (C), 127.7 (C), 117.6 (C), 117.4 (CH), 115.7 (CH), 112.8 (CH), 55.6 (CH$_3$, O*C*H$_3$), 30.1 (2 x CH$_2$), 21.9 (CH$_2$); LRMS m/z 235.00 (M +

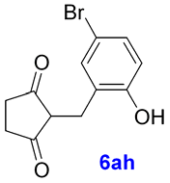
H^+), calcd for $C_{13}H_{14}O_4H$ 235.0892; Anal. calcd for $C_{13}H_{14}O_4$ (234.0892): C, 66.66; H, 6.02. Found: C, 66.683; H, 6.004%.



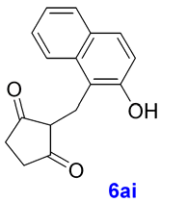
2-(2-Hydroxy-5-nitro-benzyl)-cyclopentane-1,3-dione (6af): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 168 °C; IR (Neat): ν_{max} 3118, 2925, 1588, 1521, 1489, 1338, 1285, 1207, 1084, 832 and 748 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 8.10 (1H, d, *J* = 2.4 Hz), 7.99 (1H, dd, *J* = 8.8, 2.8 Hz), 6.92 (1H, d, *J* = 9.2 Hz) [Ar-H]; 3.46 (2H, s), 2.55 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 161.4 (C), 140.5 (C), 127.0 (C), 126.4 (CH), 124.1 (CH), 117.4 (CH), 116.3 (C), 30.2 (2 x CH_2), 22.0 (CH_2); LRMS m/z 250.00 (M + H^+), calcd for $C_{12}H_{11}NO_5H$ 250.0637; Anal. calcd for $C_{12}H_{11}NO_5$ (249.0637): C, 57.83; H, 4.45; N, 5.62. Found: C, 57.879; H, 4.461; N, 5.692%.



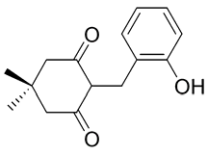
2-(5-Chloro-2-hydroxy-benzyl)-cyclopentane-1,3-dione (6ag): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 158 °C; IR (Neat): ν_{max} 3282, 2931, 1536, 1482, 1365, 1263, 1235, 1173, 1113, 1023 and 830 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 7.15 (1H, d, *J* = 2.4 Hz), 7.02 (1H, dd, *J* = 8.8, 2.8 Hz), 6.81 (1H, d, *J* = 8.4 Hz) [Ar-H]; 3.37 (2H, s), 2.50 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 152.8 (C), 129.9 (CH), 128.3 (C), 127.3 (CH), 124.8 (C), 118.2 (CH), 117.1 (C), 30.1 (2 x CH_2), 21.7 (CH_2); LRMS m/z 239.00 (M + H^+), calcd for $C_{12}H_{11}ClO_3H$ 239.0397; Anal. calcd for $C_{12}H_{11}ClO_3$ (238.0397): C, 60.39; H, 4.65. Found: C, 60.324; H, 4.637%.



2-(5-Bromo-2-hydroxy-benzyl)-cyclopentane-1,3-dione (6ah): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 157 °C; IR (Neat): ν_{max} 3283, 2930, 1536, 1482, 1367, 1284, 1235, 1173, 1114, 1023 and 830 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 7.29 (1H, d, *J* = 6.4 Hz), 7.16 (1H, dd, *J* = 8.8, 2.4 Hz), 6.76 (1H, d, *J* = 8.4 Hz) [Ar-H]; 3.37 (2H, s), 2.51 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 153.3 (C), 132.8 (CH), 130.3 (CH), 128.8 (C), 118.7 (CH), 117.1 (C), 112.1 (C), 30.0 (2 x CH_2), 21.6 (CH_2); LRMS m/z 283.65 (M + H^+), calcd for $C_{12}H_{11}BrO_3H$ 282.9892; Anal. calcd for $C_{12}H_{11}BrO_3$ (281.9892): C, 50.91; H, 3.92. Found: C, 50.887; H, 3.922%.

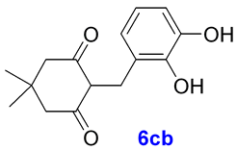


2-(2-Hydroxy-naphthalen-1-ylmethyl)-cyclopentane-1,3-dione (6ai): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 228 °C; IR (Neat): ν_{max} 3049, 2988, 2926, 1564, 1512, 1438, 1361, 1311, 1237, 814 and 754 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 8.39 (1H, d, *J* = 8.0 Hz), 7.73 (1H, d, *J* = 8.0 Hz), 7.64 (1H, d, *J* = 8.8 Hz), 7.48 (1H, t, *J* = 7.2 Hz), 7.31 (1H, t, *J* = 7.2 Hz), 7.19 (1H, d, *J* = 8.8 Hz) [Ar-H]; 3.87 (2H, s), 2.48 (4H, s, 2 x C*H*$_2$); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 151.3 (C), 133.1 (C), 129.3 (C), 128.02 (CH), 127.98 (CH), 126.1 (CH), 123.8 (CH), 123.0 (CH), 119.0 (C), 118.9 (CH), 117.7 (C), 17.0 (CH_2); LRMS m/z 255.00 (M + H^+), calcd for $C_{16}H_{14}O_3H$ 255.0943; Anal. calcd for $C_{16}H_{14}O_3$ (254.0943): C, 75.57; H, 5.55. Found: C, 75.646; H, 5.550%.



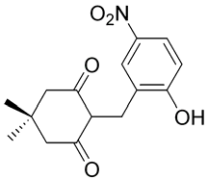
6ca

2-(2-Hydroxy-benzyl)-5,5-dimethyl-cyclohexane-1,3-dione (6ca): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 134 °C; IR (Neat): ν_{max} 3071, 2957, 1616, 1570, 1515, 1461, 1376, 1236, 1149, 1102, 1038 and 752 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 7.32 (1H, br d, *J* = 7.2 Hz), 7.03 (1H, m), 6.85-6.75 (2H, m) [Ar-H]; 3.57 (2H, s), 2.28 (4H, s, 2 x C*H*$_2$), 1.02 (6H, s, 2 x CH_3); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 153.6 (C), 131.2 (CH), 127.26 (CH), 127.22 (C), 120.1 (CH), 116.0 (CH), 114.2 (C), 41.5 (2 x CH_2), 31.7 (C), 28.0 (2 x CH_3), 22.0 (CH_2); LRMS m/z 247.12 (M + H^+), calcd for $C_{15}H_{18}O_3H$ 247.1334; Anal. calcd for $C_{15}H_{18}O_3$ (247.1256): C, 73.15; H, 7.37. Found: C, 73.175; H, 7.372%.



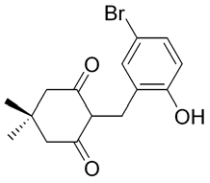
6cb

2-(2,3-Dihydroxy-benzyl)-5,5-dimethyl-cyclohexane-1,3-dione (6cb): Purified by column chromatography using EtOAc/hexane and isolated as a light yellowish solid. Mp 142 °C; IR (Neat): ν_{max} 3179, 2959, 2873, 1583, 1478, 1386, 1249, 1187, 1071, 753 and 646 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 6.79 (1H, dd, *J* = 9.2, 1.6 Hz), 6.68 (1H, dd, *J* = 9.6, 1.6 Hz), 6.62 (1H, t, *J* = 7.6 Hz) [Ar-*H*]; 3.52 (2H, s, C*H*$_2$Ar), 2.26 (4H, s, 2 x C*H*$_2$C=O), 0.98 (6H, s, 2 x CH_3); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 145.3 (C), 141.6 (C), 127.8 (C), 122.0 (CH), 120.1 (CH), 114.5 (C), 112.6 (CH), 46.4 (2 x CH_2), 31.9 (C), 28.1 (2 x CH_3), 22.2 (CH_2); LRMS m/z 263.00 (M + H^+), calcd for $C_{15}H_{18}O_4H$ 263.1205; Anal. calcd for $C_{15}H_{18}O_3$ (262.1205): C, 68.68; H, 6.92. Found: C, 68.724; H, 6.947%.



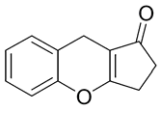
6cf

2-(2-Hydroxy-5-nitro-benzyl)-5,5-dimethyl-cyclohexane-1,3-dione (6cf): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. Mp 142 °C; IR (Neat): ν_{max} 2963, 2613, 1585, 1512, 1458, 1333, 1251, 1196, 1086, 1038 and 613 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 8.22 (1H, br s), 7.97 (1H, d, *J* = 8.0 Hz), 6.88 (1H, d, *J* = 8.0 Hz) [Ar-H]; 3.59 (2H, s, ArCH_2), 2.34 (4H, s, 2 x C*H*$_2$C=O), 1.05 (6H, s, 2 x C*H*$_3$); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 161.5 (C), 140.3 (C), 127.7 (C), 127.4 (CH), 124.0 (CH), 116.9 (CH), 113.1 (C), 32.1 (C), 28.2 (2 x CH_3), 22.8 (CH_2); LRMS m/z 292.00 (M + H^+), calcd for $C_{15}H_{17}NO_5$ 291.1107; Anal. calcd for $C_{15}H_{17}NO_5$ (291.1107): C, 61.85; H, 5.88; N, 4.81. Found: C, 61.832; H, 5.870; N, 4.824%.

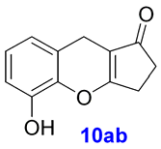


6ch

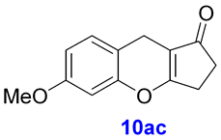
2-(5-Bromo-2-hydroxy-benzyl)-5,5-dimethyl-cyclohexane-1,3-dione (6ch): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 146 °C; IR (Neat): ν_{max} 3174, 2960, 2616, 1732, 1584, 1515, 1477, 1380, 1336, 1246, 1173, 1086, 1038 and 817 cm^{-1}; **^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)]** δ 7.42 (1H, d, *J* = 4.0 Hz), 7.14 (1H, dd, *J* = 8.0, 4.0 Hz), 6.72 (1H, d, *J* = 8.0 Hz) [Ar-H]; 3.51 (2H, s, ArCH_2), 2.29 (4H, s, 2 x C*H*$_2$C=O), 1.03 (6H, s, 2 x C*H*$_3$); **^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135]** δ 153.5 (C), 133.7 (CH), 130.2 (CH), 129.6 (C), 118.2 (CH), 113.9 (C), 111.8 (C), 32.0 (C), 28.2 (2 x CH_3), 22.3 (CH_2); LRMS m/z 325.00 (M + H^+), calcd for $C_{15}H_{17}BrO_3$ 324.0361; Anal. calcd for $C_{15}H_{17}BrO_3$ (324.0361): C, 55.40; H, 5.27. Found: C, 55.452; H, 5.291%.


10aa

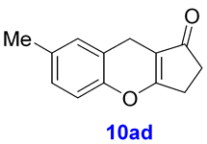
3,9-Dihydro-2H-cyclopenta[b]chromen-1-one (10aa): Purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 166 °C; IR (neat): ν_{max} 2921, 1656 (C=O), 1489, 1460, 1438, 1395, 1251, 1164, 1115, 761 and 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21 (1H, t, *J* = 7.6 Hz), 7.18 (1H, d, *J* = 6.8 Hz), 7.11 (1H, t, *J* = 7.2 Hz), 7.05 (1H, d, *J* = 8.0 Hz) [Ar-H]; 3.52 (2H, s, C*H*$_2$Ar), 2.73 (2H, m), 2.54 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.4 (C, *C*=O), 179.2 (C, O-*C*=C), 150.8 (C, *C*-O), 130.4 (CH), 128.0 (CH), 125.1 (CH), 119.6 (C), 117.2 (CH), 114.2 (C), 33.3 (CH_2), 25.8 (CH_2), 20.8 (CH_2); LRMS m/z 187.00 (M + H^+), calcd for $C_{12}H_{10}O_2H$ 187.0681; Anal. calcd for $C_{12}H_{10}O_2$ (186.0681): C, 77.40; H, 5.41. Found: C, 77.372; H, 5.416%.


10ab

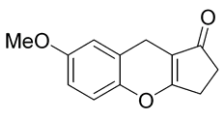
5-Hydroxy-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10ab): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 184 °C; IR (neat): ν_{max} 3159, 3115, 2925, 1640 (C=O), 1572, 1477, 1402, 1248, 1232, 1160, 1115, 782 and 714 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 6.97 (1H, t, *J* = 8.0 Hz), 6.82 (1H, d, *J* = 7.6 Hz), 6.69 (1H, d, *J* = 7.6 Hz) [Ar-H]; 3.78 (1H, br s, O-H), 3.51 (2H, s, C*H*$_2$Ar), 2.83 (2H, br s, C*H*$_2$), 2.59 (2H, br s, C*H*$_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 205.0 (C, *C*=O), 179.9 (C, O-*C*=C), 145.3 (C), 139.1 (C), 125.0 (CH), 120.4 (CH), 120.0 (C), 114.8 (CH), 114.0 (C), 33.0 (CH_2), 25.6 (CH_2), 20.3 (CH_2); LRMS m/z 203.00 (M + H^+), calcd for $C_{12}H_{10}O_3$ 202.0630; Anal. calcd for $C_{12}H_{10}O_3$ (202.0630): C, 71.28; H, 4.98. Found: C, 71.313; H, 5.026%.


10ac

6-Methoxy-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10ac): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 168 °C; IR (neat): ν_{max} 2922, 2852, 1656 (C=O), 1495, 1437, 1396, 1240, 1183, 1031, 813 and 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (1H, d, *J* = 8.4 Hz), 6.69 (1H, d, *J* = 8.4 Hz), 6.60 (1H, s) [Ar-H]; 3.80 (3H, s, OC*H*$_3$), 3.44 (2H, s, C*H*$_2$Ar), 2.71 (2H, m, C*H*$_2$), 2.53 (2H, m, C*H*$_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.6 (C, *C*=O), 179.2 (C, O-*C*=C), 159.4 (C), 151.4 (C), 130.8 (CH), 114.7 (C), 111.45 (CH), 111.35 (C), 102.6 (CH), 55.5 (CH_3, O*C*H$_3$), 33.4 (CH_2), 25.8 (CH_2), 20.1 (CH_2); LRMS m/z 217.00 (M + H^+), calcd for $C_{13}H_{12}O_3H$ 217.0786; Anal. calcd for $C_{13}H_{12}O_3$ (216.0786): C, 72.21; H, 5.59. Found: C, 72.221; H, 5.587%.

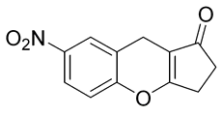

10ad

7-Methyl-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10ad): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 168 °C; IR (neat): ν_{max} 2920, 2852, 1658 (C=O), 1587, 1560, 1494, 1438, 1392, 1258, 1192, 811 and 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.01 – 6.98 (2H, br m), 6.93 (1H, d, *J* = 8.4 Hz) [Ar-H]; 3.47 (2H, s, C*H*$_2$Ar), 2.71 (2H, m, C*H*$_2$), 2.54 (2H, m, C*H*$_2$), 2.30 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.6 (C, *C*=O), 179.5 (C, O-*C*=C), 148.8 (C), 134.8 (C), 130.8 (CH), 128.6 (CH), 119.2 (C), 116.9 (CH), 114.1 (C), 33.3 (CH_2), 25.8 (CH_2), 20.8 (CH_2), 20.6 (CH_3); LRMS m/z 201.00 (M + H^+), calcd for $C_{13}H_{12}O_2$ 200.0837; Anal. calcd for $C_{13}H_{12}O_2$ (200.0837): C, 77.98; H, 6.04. Found: C, 78.013; H, 6.020%.



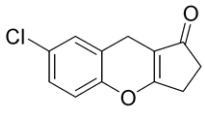
10ae

7-Methoxy-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10ae): Purified by column chromatography using EtOAc/hexane and isolated as a yellowish solid. Mp 174 °C; IR (neat): ν_{max} 2923, 2851, 1656 (C=O), 1651, 1494, 1444, 1396, 1239, 1182, 1030, 813 and 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.98 (1H, d, *J* = 8.8 Hz), 6.75 (1H, dd, *J* = 8.8, 2.8 Hz), 6.67 (1H, d, *J* = 2.4 Hz) [Ar-H]; 3.79 (3H, s, OCH_3), 3.49 (2H, s, CH_2Ar), 2.72–2.70 (2H, m, CH_2), 2.54–2.52 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.5 (C, *C*=O), 179.5 (C, O-*C*=C), 156.7 (C), 144.9 (C), 120.5 (C), 118.0 (CH), 114.5 (CH), 113.8 (CH), 113.5 (C), 55.7 (CH_3, OCH_3), 33.4 (CH_2), 25.8 (CH_2), 21.2 (CH_2); LRMS m/z 217.00 (M + H^+), calcd for $C_{13}H_{12}O_3H$ 217.0786; Anal. calcd for $C_{13}H_{12}O_3$ (216.0786): C, 72.21; H, 5.59. Found: C, 72.208; H, 5.566%.



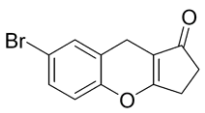
10af

7-Nitro-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10af): Purified by column chromatography using EtOAc/hexane and isolated as a light yellowish solid. Mp 160 °C; IR (neat): ν_{max} 2924, 2853, 1657 (C=O), 1522, 1437, 1389, 1342, 1236, 1168, 1084, 921, 839, 748 and 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.12 (1H, br s), 8.10 (1H, dd, *J* = 8.8, 2.8 Hz), 7.20 (1H, d, *J* = 9.2 Hz) [Ar-H]; 3.62 (2H, s, CH_2Ar), 2.80–2.77 (2H, m, CH_2), 2.62–2.58 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 202.7 (C, *C*=O), 178.3 (C, O-*C*=C), 155.1 (C), 144.6 (C), 126.3 (CH), 123.99 (CH), 121.2 (C), 118.2 (CH), 114.2 (C), 33.5 (CH_2), 25.6 (CH_2), 21.1 (CH_2); LRMS m/z 232.00 (M + H^+), calcd for $C_{12}H_9NO_4$ 231.0532; Anal. calcd for $C_{12}H_9NO_4$ (231.0532): C, 62.34; H, 3.92; N, 6.06. Found: C, 62.346; H, 3.920; N, 6.068%.



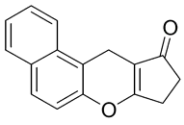
10ag

7-Chloro-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10ag): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 162 °C; IR (neat): ν_{max} 2959, 2930, 1661 (C=O), 1480, 1446, 1387, 1247, 1165, 1121, 818, 785 and 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (2H, br s), 6.99 (1H, d, *J* = 9.2 Hz) [Ar-H]; 3.49 (2H, s, CH_2Ar), 2.72 (2H, br s, CH_2), 2.55 (2H, br d, *J* = 2.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.1 (C, *C*=O), 179.0 (C, O-*C*=C), 149.4 (C), 130.1 (CH), 130.1 (C), 128.1 (CH), 121.4 (C), 118.5 (CH), 113.8 (C), 33.4 (CH_2), 25.7 (CH_2), 20.9 (CH_2); LRMS m/z 221.00 (M + H^+), calcd for $C_{12}H_9ClO_2$ 220.0291; Anal. calcd for $C_{12}H_9ClO_2$ (220.0291): C, 65.32; H, 4.11. Found: C, 65.364; H, 4.132%.



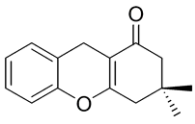
10ah

7-Bromo-3,9-dihydro-2H-cyclopenta[b]chromen-1-one (10ah): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 172 °C; IR (neat): ν_{max} 2925, 1656 (C=O), 1476, 1439, 1411, 1385, 1252, 1163, 1119, 815 and 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32–7.31 (2H, m), 6.93 (1H, d, *J* = 9.6 Hz) [Ar-H]; 3.50 (2H, s, CH_2Ar), 2.74–2.71 (2H, m, CH_2), 2.56–2.53 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.1 (C, *C*=O), 178.9 (C, O-*C*=C), 150.0 (C), 133.1 (CH), 131.1 (CH), 121.9 (C), 118.9 (CH), 117.6 (C), 113.9 (C), 33.4 (CH_2), 25.7 (CH_2), 20.8 (CH_2); LRMS m/z 265.00 (M + H^+), calcd for $C_{12}H_9BrO_2H$ 264.9786; Anal. calcd for $C_{12}H_9BrO_2$ (263.9786): C, 54.37; H, 3.42. Found: C, 54.402; H, 3.418%.



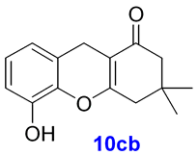
10ai

8,11-Dihydro-9H-7-oxa-cyclopenta[b]phenanthren-10-one (10ai): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 244 °C; IR (neat): ν_{max} 2927, 1658 (C=O), 1594, 1440, 1397, 1242, 1209, 1165, 810, 766 and 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (2H, br d, *J* = 8.4 Hz), 7.76 (1H, d, *J* = 8.8 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.50 (1H, t, *J* = 7.2 Hz), 7.25 (1H, d, *J* = 9.2 Hz) [Ar-H]; 3.79 (2H, s, C*H*$_2$Ar), 2.79–2.78 (2H, m, C*H*$_2$), 2.61–2.59 (2H, m, C*H*$_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 203.8 (C, *C*=O), 178.9 (C, O-*C*=C), 148.1 (C), 132.3 (C), 131.1 (C), 128.8 (CH), 128.3 (CH), 127.2 (CH), 125.3 (CH), 123.1 (CH), 117.5 (CH), 114.4 (C), 112.8 (C), 32.5 (CH_2), 25.8 (CH_2), 18.8 (CH_2); LRMS m/z 237.00 ($M + H^+$), calcd for $C_{16}H_{12}O_2H$ 237.0837; Anal. calcd for $C_{16}H_{12}O_2$ (236.0837): C, 81.34; H, 5.12. Found: C, 81.502; H, 5.145%.



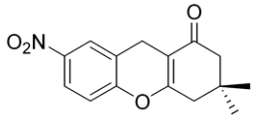
10ca

3,3-Dimethyl-2,3,4,9-tetrahydro-xanthen-1-one (10ca): Purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 80 °C; IR (neat): ν_{max} 2957, 2931, 1632 (C=O), 1578, 1491, 1462, 1389, 1239, 1230, 1180, 1147, 1121, 1016, 765 and 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (1H, t, *J* = 8.0 Hz), 7.15 (1H, d, *J* = 8.0 Hz), 7.05 (1H, t, *J* = 6.8 Hz), 6.95 (1H, d, *J* = 8.0 Hz) [Ar-H]; 3.52 (2H, s, C*H*$_2$Ar), 2.43 (2H, s, CH_2), 2.32 (2H, s, CH_2), 1.12 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.9 (C, *C*=O), 165.1 (C, O-*C*=C), 149.9 (C), 129.7 (CH), 127.6 (CH), 124.6 (CH), 120.8 (C), 116.4 (CH), 108.8 (C), 50.6 (CH_2), 41.5 (CH_2), 32.1 (C), 28.4 (2 x CH_3), 21.0 (CH_2); LRMS m/z 229.00 ($M + H^+$), calcd for $C_{15}H_{16}O_2$ 228.1150; Anal. calcd for $C_{15}H_{16}O_2$ (228.1150): C, 78.92; H, 7.06. Found: C, 78.975; H, 7.072%.



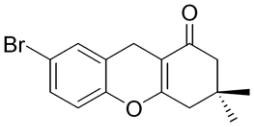
10cb

5-Hydroxy-3,3-dimethyl-2,3,4,9-tetrahydro-xanthen-1-one (10cb): Purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 194 °C. IR (neat): ν_{max} 3348 (O-H), 3120, 2960, 2892, 1612 (C=O), 1577, 1474, 1398, 1226, 1123, 1059, 764 and 654 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (1H, t, *J* = 7.6 Hz), 6.81 (1H, br d, *J* = 7.2 Hz), 6.70 (1H, d, *J* = 7.6 Hz) [Ar-H]; 5.42 (1H, s, O-*H*), 3.51 (2H, s, C*H*$_2$Ar), 2.48 (2H, s, C*H*$_2$), 2.34 (2H, s, C*H*$_2$), 1.14 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.8 (C, *C*=O), 163.9 (C, O-*C*=C), 143.9 (C), 137.7 (C), 124.8 (CH), 121.3 (C), 120.7 (CH), 114.0 (CH), 109.4 (C), 50.6 (CH_2), 41.4 (CH_2), 32.2 (C), 28.4 (2 x CH_3), 20.9 (CH_2); LRMS m/z 245.00 ($M + H^+$), calcd for $C_{15}H_{16}O_3H$ 245.1099; Anal. calcd for $C_{15}H_{16}O_3$ (244.1099): C, 73.75; H, 6.60. Found: C, 73.733; H, 6.602%.



10cf

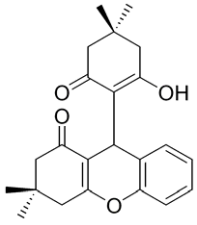
3,3-Dimethyl-7-nitro-2,3,4,9-tetrahydro-xanthen-1-one (10cf): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. Mp 116 °C; IR (neat): ν_{max} 2958, 1655, 1649 (C=O), 1583, 1523, 1340, 1234, 1188, 1084, 1023 and 747 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.08-8.05 (2H, m), 7.08 (1H, d, *J* = 8.0 Hz) [Ar-H]; 3.60 (2H, s, C*H*$_2$Ar), 2.47 (2H, s, C*H*$_2$), 2.35 (2H, s, C*H*$_2$), 1.15 (6H, s, 2 x C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.4 (C, *C*=O), 164.2 (C, O-*C*=C), 154.4 (C), 144.2 (C), 125.6 (CH), 123.6 (CH), 122.2 (C), 117.4 (CH), 108.6 (C), 50.5 (CH_2), 41.1 (CH_2), 32.2 (C), 28.4 (2 x CH_3), 21.2 (CH_2); LRMS m/z 274.10 ($M + H^+$), calcd for $C_{15}H_{15}NO_4$ 273.1001; Anal. calcd for $C_{15}H_{15}NO_4$ (273.1001): C, 65.92; H, 5.53; N, 5.13. Found: C, 65.970; H, 5.525; N, 5.151%.



10ch

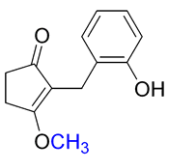
7-Bromo-3,3-dimethyl-2,3,4,9-tetrahydro-xanthen-1-one (10ch): Purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 118 °C; IR (neat): ν_{max} 2956, 1641 (C=O), 1479, 1415, 1385, 1239, 1180 and 814 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28-7.26 (2H, m), 6.84 (1H, d, *J* = 8.4 Hz) [Ar-H]; 3.49 (2H, s, CH_2Ar), 2.42 (2H, s, CH_2), 2.32 (2H, s, CH_2), 1.12 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.6 (C, *C*=O), 164.8 (C, O-*C*=C), 149.0 (C), 132.3 (CH), 130.6 (CH), 123.1 (C), 118.2 (CH), 116.9 (C), 108.4 (C), 50.6 (CH_2), 41.4 (CH_2), 32.1 (C), 28.4 (2 x CH_3), 21.0 (CH_2); LRMS m/z 307.00 (M + H^+), calcd for $C_{15}H_{15}BrO_2$ 306.0255; Anal. calcd for $C_{15}H_{15}BrO_2$ (306.0255): C, 58.65; H, 4.92. Found: C, 58.641; H, 4.964%.

9-(2-Hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-3,3-dimethyl-2,3,4,9-tetrahydro-xanthen-1-one (L-152,804): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid.



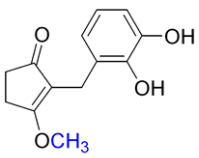
L-152,804

Mp 206 °C; IR (Neat): ν_{max} 3190 (O-*H*), 2956, 1641 (C=O), 1590, 1376, 1313, 1261, 1231, 1188, 1027 and 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.47 (1H, s, O-*H*), 7.20-7.10 (1H, m), 7.05-6.95 (3H, m) [Ar-H]; 4.67 (1H, s, C*H*), 2.54 (2H, ABq, *J* = 16.0 Hz), 2.40-2.20 (4H, m), 1.97 (2H, ABq, *J* = 16.0 Hz), 1.12 (3H, s, CH_3), 1.03 (3H, s, CH_3), 0.99 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.9 (C, C=O), 196.5 (C, C=O), 170.7 (C, O-C=C), 169.2 (C, O-C=C), 151.0 (C), 128.0 (CH), 127.5 (CH), 124.6 (CH), 124.3 (C), 118.3 (C), 115.7 (CH), 111.0 (C), 50.6 (CH_2), 49.9 (CH_2), 43.2 (CH_2), 41.5 (CH_2), 32.3 (C), 30.9 (C), 29.8 (CH), 29.1 (CH_3), 27.8 (CH_3), 27.2 (CH_3), 26.4 (CH_3); LRMS m/z 367.00 (M + H^+), calcd for $C_{23}H_{26}O_4$ 366.1831; Anal. calcd for $C_{23}H_{26}O_4$ (366.1831): C, 75.38; H, 7.15. Found: C, 75.466; H, 7.143%.



11aa

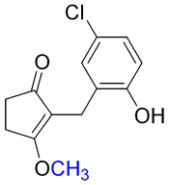
2-(2-Hydroxy-benzyl)-3-methoxy-cyclopent-2-enone (11aa): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 104 °C; IR (neat): ν_{max} 3071, 2953, 2737, 1584 (C=O), 1459, 1453, 1374, 1269, 1238, 1105, 824 and 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.93 (1H, s, O-*H*), 7.14–7.08 (2H, m), 6.92 (1H, d, *J* = 8.0 Hz), 6.79 (1H, t, *J* = 7.6 Hz) [Ar-H]; 4.02 (3H, s, OCH_3), 3.40 (2H, s, CH_2Ar), 2.71 (2H, m, CH_2), 2.49 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 207.6 (C, *C*=O), 186.6 (C, O-*C*=C), 155.3 (C), 130.5 (CH), 128.1 (CH), 126.1 (C), 120.7 (C), 120.0 (CH), 118.1 (CH), 57.0 (CH_3, O*C*H_3), 32.7 (CH_2), 25.2 (CH_2), 22.6 (CH_2); LRMS m/z 219.00 (M + H^+), calcd for $C_{13}H_{14}O_3$ 218.0943; Anal. calcd for $C_{13}H_{14}O_3$ (218.0943): C, 71.54; H, 6.47. Found: C, 71.541; H, 6.465%.



11ab

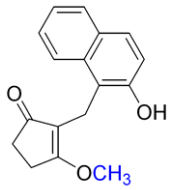
2-(2,3-Dihydroxy-benzyl)-3-methoxy-cyclopent-2-enone (11ab): Purified by column chromatography using EtOAc/hexane and isolated as a color less solid. Mp 142 °C; IR (neat): ν_{max} 3381, 2925, 1590 (C=O), 1476, 1369, 1261, 1189, 1087 and 734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.64 (1H, s, O-*H*), 6.77 (1H, br d, *J* = 8.0 Hz), 6.70 (1H, t, *J* = 8.0 Hz), 6.64 (1H, br d, *J* = 8.0 Hz) [Ar-H]; 6.0 (1H, br s, O-*H*), 4.03 (3H, s, OCH_3), 3.39 (2H, s, CH_2Ar), 2.72 (2H, m, CH_2), 2.49 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 208.3 (C, *C*=O), 187.2 (C, O-*C*=C), 146.8 (C), 142.0 (C), 126.7 (C), 121.1 (CH), 120.9 (C), 120.6 (CH), 112.8

(CH), 57.1 (CH_3, OCH_3), 32.6 (CH_2), 25.3 (CH_2), 22.4 (CH_2); LRMS m/z 235.00 (M + H^+), calcd for $C_{13}H_{14}O_4$ 234.0892; Anal. calcd for $C_{13}H_{14}O_4$ (234.0892): C, 66.66; H, 6.02. Found: C, 66.659; H, 6.020%.



11ag

2-(5-Chloro-2-hydroxy-benzyl)-3-methoxy-cyclopent-2-enone (11ag): Purified by column chromatography using EtOAc/hexane and isolated as a yellow solid. Mp 98 °C; IR (neat): ν_{max} 2923, 1610 (C=O), 1575, 1483, 1432, 1369, 1264, 1239, 1170, 1114, 817 and 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.10 (1H, s, O-*H*), 7.07 (1H, d, *J* = 2.4 Hz), 7.03 (1H, dd, *J* = 8.4, 2.4 Hz), 6.83 (1H, d, *J* = 8.8 Hz) [Ar-H]; 4.05 (3H, s, OCH_3), 3.34 (2H, s, CH_2Ar), 2.74 (2H, m, CH_2), 2.49 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 207.6 (C, *C*=O), 187.1 (C, O-*C*=C), 154.0 (C), 129.9 (CH), 127.8 (C), 127.7 (CH), 124.4 (C), 119.9 (C), 119.5 (CH), 57.2 (CH_3, OCH_3), 32.6 (CH_2), 25.2 (CH_2), 22.4 (CH_2); LRMS m/z 253.00 (M + H^+), calcd for $C_{13}H_{13}ClO_3$ 252.0553; Anal. calcd for $C_{13}H_{13}ClO_3$ (252.0553): C, 61.79; H, 5.19. Found: C, 61.814; H, 5.198%.



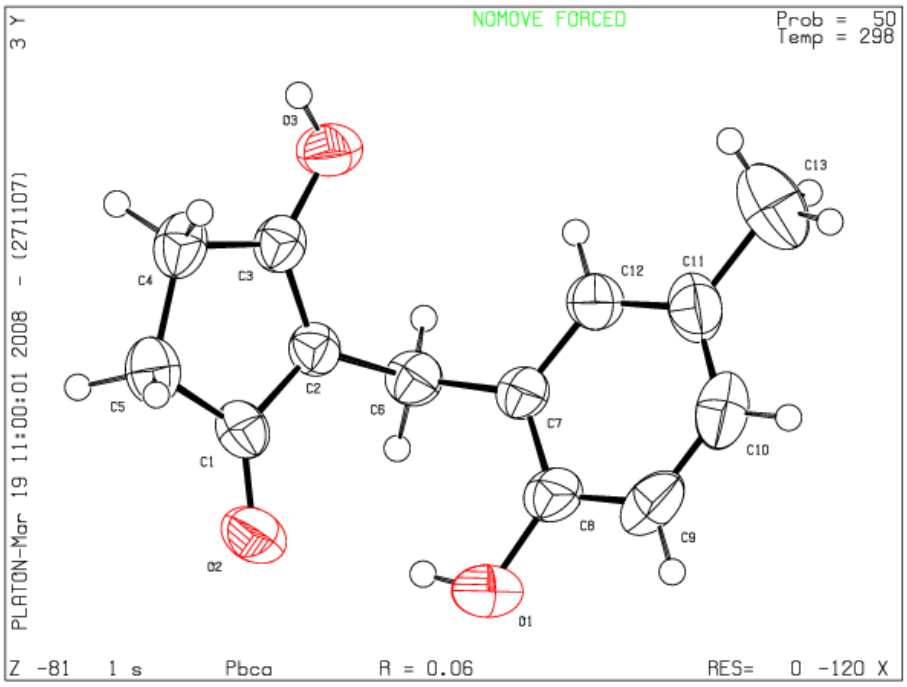
11ai

2-(2-Hydroxy-naphthalen-1-ylmethyl)-3-methoxy-cyclopent-2-enone (11ai): Purified by column chromatography using EtOAc/hexane and isolated as a light yellowish solid. Mp 154 °C; IR (neat): ν_{max} 2954, 2952, 1602 (C=O), 1588, 1466, 1400, 1368, 1262, 1239, 1091, 829 and 751 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.85 (1H, s, O-*H*), 8.21 (1H, d, *J* = 8.8 Hz), 7.72 (1H, d, *J* = 8.0 Hz), 7.62 (1H, d, *J* = 8.8 Hz), 7.44 (1H, dt, *J* = 6.8, 0.8 Hz), 7.28 (1H, t, *J* = 8.0 Hz), 7.22 (1H, d, *J* = 8.8 Hz) [Ar-H]; 4.06 (3H, s, OCH_3), 3.81 (2H, s, CH_2Ar), 2.66 (2H, m, CH_2), 2.41 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 208.3 (C, *C*=O), 186.0 (C, O-*C*=C), 153.4 (C), 133.2 (C), 129.3 (C), 128.4 (CH), 128.2 (CH), 125.8 (CH), 123.2 (CH), 122.7 (CH), 121.0 (CH), 120.6 (C), 118.4 (C), 57.0 (CH_3, OCH_3), 32.6 (CH_2), 25.1 (CH_2), 17.9 (CH_2); LRMS m/z 269.00 (M + H^+), calcd for $C_{17}H_{16}O_3$ 268.1099; Anal. calcd for $C_{17}H_{16}O_3$ (268.1099): C, 76.10; H, 6.01. Found: C, 76.169; H, 6.057%.

Datablock: dbr1_s (Product 6ad)

```
Bond precision:     C-C = 0.0036 A              Wavelength=0.71073
Cell:       a=12.869(2)    b=7.4613(14)   c=23.807(4)
            alpha=90       beta=90        gamma=90
Temperature: 298 K
                  Calculated                    Reported
Volume            2285.9(7)                     2285.9(7)
Space group       P b c a                       Pbca
Hall group        -P 2ac 2ab                    ?
Moiety formula    C13 H14 O3                    ?
Sum formula       C13 H14 O3                    C13 H14 O3
Mr                218.24                        218.24
Dx,g cm-3         1.268                         1.268
Z                 8                             8
Mu (mm-1)         0.090                         0.090
F000              928.0                         928.0
F000'             928.49
h,k,lmax          15,9,29                       15,9,29
Nref              2255                          2132
Tmin,Tmax         0.989,0.991                   0.963,0.991
Tmin'             0.963
Correction method= AbsCorr=MULTI-SCAN
Data completeness= Ratio =
0.945                          Theta(max)= 26.030
R(reflections)= 0.0639( 1668)     wR2(reflections)= 0.1522( 2132)
S = 1.137            Npar= 148
```

Datablock dbr1_s - ellipsoid plot



Datablock: dbr50_m (Product 10aa)

```
Bond precision:     C-C = 0.0021 A              Wavelength=0.71073
Cell:       a=6.589(3)     b=7.550(3)     c=9.691(4)
            alpha=97.609(6) beta=103.781(6) gamma=106.000(6)
Temperature: 298 K
                  Calculated                    Reported
Volume            439.8(3)                      439.9(3)
Space group       P -1                          P-1
Hall group        -P 1                          ?
Moiety formula    C12 H10 O2                    ?
Sum formula       C12 H10 O2                    C12 H10 O2
Mr                186.20                        186.20
Dx,g cm-3         1.406                         1.406
Z                 2                             2
Mu (mm-1)         0.095                         0.095
F000              196.0                         196.0
F000'             196.10
h,k,lmax          8,9,11                        8,9,11
Nref              1699                          1678
Tmin,Tmax         0.976,0.983                   0.961,0.983
Tmin'             0.961
Correction method= AbsCorr=MULTI-SCAN
Data completeness= Ratio =
0.988                          Theta(max)= 25.900
R(reflections)= 0.0399( 1394)     wR2(reflections)= 0.1102( 1678)
S = 1.071            Npar= 128
```

Datablock dbr50_m - ellipsoid plot