An Efficient Approach to Dihydrofurocoumarins via Palladium-Catalyzed Annulation of 1,3-Dienes by *o*- Iodoacetoxycoumarins

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General. All ¹H and ¹³C NMR spectra were recorded at 400 and 100.5 MHz respectively. All melting points are uncorrected. Low resolution mass spectra were recorded on a Finnigan TSQ700

triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA). High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV.

Reagents. Iodine, acetic anhydride, pyridine, mercury(II) acetate, trimethylamine *N*-oxide, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, osmium tetroxide, 4-hydroxycoumarin, 7-hydroxy-4-methylcoumarin, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, *E*-1,3-hexadiene, 2,3-dimethoxy-1,3-butadiene, 1-methoxy-1,3-cyclohexadiene, 3-methyl-1,3-pentadiene (a mixture of isomers), 2,4-dimethyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, isoprene, 2,4-hexadiene (a mixture of isomers) and 2,3-diphenyl-1,3-butadiene were obtained from commercial sources. *E*-2-Methyl-1,3-pentadiene was purchased from Lancaster Co., Inc. *trans,trans*-2,4-Hexadiene (95% pure) was purchased from ChemSamp Co., Inc. *E*-1-Phenyl-1,3-butadiene and 1,5,5-trimethyl-3-methylenecyclohexene were prepared by Wittig condensation according to a literature procedure.¹ 5-Hydroxy-4-methylcoumarin and 6-hydroxycoumarin were prepared as described by Harayama *et al.*² 4,8-Dimethyl-7-hydroxycoumarin was synthesized by a Pechman condensation.³ The preparation and characterization data for compounds **11**, **27**, **35** and **37** can be found in the Supporting Information for our earlier communication.⁴

General procedure for the Pd-catalyzed annulation of 1,3-dienes by *o*-iodoacetoxycoumarins. The *o*-iodoacetoxycoumarin (0.25 mmol), Pd(dba)₂ (5 mol %, 0.0125 mmol), dppe (5 mol %, 0.0125 mmol), Ag₂CO₃ (0.5 mmol) and 1,4-dioxane (4 mL) were stirred in a capped vial for 5 min, and then water (1 mL) and the 1,3-diene (1.0 mmol) were added. The resulting reaction mixture was stirred at 100 °C for 24 h, cooled to room temperature, filtered and the filtrate was concentrated to give a yellow residue. The resulting residue was purified by column chromatography using silica gel as a solid phase and 4:1 hexanes/ethyl acetate as the eluent to afford after solvent removal the final product. Solid products were then recrystallized from 1:1 ethanol/water. Characterization data for compounds

9, 16, 17, 21, 23, 24, 32, 36 and **38** can be found in the Supporting Information for our earlier communication.⁴ The following new compounds were prepared using this procedure.

7a,10,11,12,12a-Pentahydro-4-methylcyclohepta[*b*]-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (14).

Obtained in a 25% yield: white solid, mp 154-158 °C; ¹H NMR (CDCl₃) 1.53-2.34 (m, 6H), 2.39 (d, *J* = 1.2 Hz, 3H), 3.77 (ddd, *J* = 10.3, 9.1, 2.8 Hz, 1H), 5.60 (dd, *J* = 9.1, 1.8 Hz, 1H), 5.80-5.84 (m, 2H), 6.10 (d, *J* = 1.2 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H); ¹³C NMR (CDCl₃) 19.3, 22.4, 26.7, 26.8, 42.3, 87.2, 106.8, 111.4, 114.3, 118.7, 125.7, 127.1, 129.9, 151.1, 153.4, 161.4, 162.4; ; IR (neat) 1725, 1605 cm⁻¹; HRMS *m/z* 268.1102 (calcd for C₁₇H₁₆O₃, 268.1099).

7a,10,11,12,13,13a-Hexahydro-4-methylcycloocta[*b*]-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (15).

Obtained in a 28% yield: white solid, mp 126-130 °C; ¹H NMR (CDCl₃) 1.18-2.30 (m, 8H), 2.38 (d, *J* = 1.2 Hz, 3H), 2.78 (m, 1H), 3.85 (dt, *J* = 10.1, 2.3 Hz, 1H), 5.40 (ddt, *J* = 11.8, 5.1, 1.4 Hz, 1H), 5.75-5.95 (m, 2H), 6.09 (d, *J* = 1.2 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) 19.4, 25.6, 26.4, 29.7, 30.4, 47.9, 86.0, 107.1, 111.4, 114.5, 117.1, 125.7, 127.9, 134.1, 152.0, 153.4, 161.2, 162.9; IR (neat) 1733, 1607 cm⁻¹; HRMS *m/z* 282.1259 (calcd for C₁₈H₁₈O₃, 282.1256).

8-(*E*-1-Butenyl)-8,9-dihydro-4-methyl-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (18). Obtained in an 80% yield: white solid, mp 142-146 °C; ¹H NMR (CDCl₃) 1.04 (t, *J* = 7.6 Hz, 3H), 2.08-2.18 (m, 2H), 2.39 (s, 3H), 3.11 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.52 (dd, *J* = 16.0, 9.4 Hz, 1H), 5.33 (q, *J* = 7.8 Hz, 1H), 5.66 (ddq, *J* = 15.2, 7.8, 1.4 Hz, 1H), 5.93 (dt, *J* = 15.2, 6.3 Hz, 1H), 6.09 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 1H); 7.41 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) 13.3, 19.2, 21.4, 33.1, 86.4, 106.7, 111.3, 113.9, 114.2, 125.6, 127.3, 137.6, 151.0, 153.3, 161.4, 163.5; IR (neat) 1732, 1613 cm⁻¹; HRMS *m/z* 256.1103 (calcd for C₁₆H₁₆O₃, 256.1099).

8,9-Dihydro-4-methyl-8-(2-methyl-1-propenyl)-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (19).

Obtained in a 78% yield: white solid, mp 140-146 °C; ¹H NMR (CDCl₃) 1.81 (d, *J* = 1.2 Hz, 3H),

1.82 (d, $J = 1.4$ Hz, 3H), 2.39 (d, $J = 1.2$ Hz, 3H), 3.04 (dd, $J = 16.0, 8.8$ Hz, 1H), 3.53 (dd, $J = 16.0, 8.8$ Hz, 1H), 5.45 (dt, $J = 8.8, 1.2$ Hz, 1H), 5.65 (q, $J = 8.8$ Hz, 1H), 6.09 (d, $J = 1.2$ Hz, 1H), 6.73 (d, $J = 8.4$ Hz, 1H); 7.40 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3) 18.6, 19.2, 26.0, 33.5, 82.3, 106.7, 111.3, 114.0, 114.1, 123.9, 125.6, 139.6, 151.0, 153.3, 161.4, 163.6; IR (neat) 1727, 1610 cm^{-1} ; HRMS m/z 256.1103 (calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$, 256.1099).

8-(*E*-2-Butenyl)-8,9-dihydro-4-methyl-2H-furo[2,3-*h*]-1-benzopyran-2-one (20). Obtained in an 83% yield: white solid, mp 140-144 °C; ^1H NMR (CDCl_3) 1.64 (s, 3H), 1.68 (d, $J = 6.8$ Hz, 3H), 2.40 (s, 3H), 3.18 (dd, $J = 16.4, 8.0$ Hz, 1H), 3.45 (dd, $J = 16.4, 9.6$ Hz, 1H), 5.33 (t, $J = 9.0$ Hz, 1H), 5.68 (q, $J = 6.8$ Hz, 1H), 6.10 (s, 1H), 6.76 (d, $J = 8.4$ Hz, 1H); 7.41 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3) 10.8, 13.4, 19.2, 31.2, 90.5, 106.5, 111.3, 114.1, 124.0, 125.6, 133.8, 151.0, 153.3, 161.4, 164.0; IR (neat) 1728, 1613 cm^{-1} ; HRMS m/z 256.11025 (calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$, 256.10994).

8,9-Dihydro-4,8-dimethyl-8-(2-methyl-1-propenyl)-2H-furo[2,3-*h*]-1-benzopyran-2-one (22). Obtained in a 75% yield: white solid, mp 78-80 °C; ^1H NMR (CDCl_3) 1.56 (s, 3H), 1.72 (s, 3H), 1.76 (s, 3H), 2.39 (s, 3H), 3.30 (d, $J = 15.8$ Hz, 1H), 3.40 (d, $J = 15.8$ Hz, 1H), 5.57 (s, 1H), 6.09 (s, 1H), 6.74 (d, $J = 8.5$ Hz, 1H), 7.41 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (CDCl_3) 19.3, 19.5, 26.9, 28.7, 40.8, 91.1, 106.9, 111.2, 113.9, 114.0, 125.7, 129.6, 136.2, 151.2, 153.4, 161.5, 162.6; IR (neat) 1728, 1614 cm^{-1} ; HRMS m/z 270.1262 (calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$, 270.1256).

8,9-Dihydro-4,9-dimethyl-8-(*E*-1-propenyl)-2H-furo[2,3-*h*]-1-benzopyran-2-one (3:2 mixture of *trans*- and *cis*-isomers **25a** and **25b** respectively). Obtained as a white solid in a 60% overall yield when a commercially available 3:2 mixture of *trans,trans*- and *cis,cis*-2,4-hexadienes was used. *trans,trans*-2,4-Hexadiene (95% pure) gave a 20:1 ratio of **25a** and **25b** in a 70% yield. *trans*-Isomer (**25a**): ^1H NMR (CDCl_3) 1.27 (d, $J = 7.2$ Hz, 3H), 1.82 (dd, $J = 7.0, 1.5$ Hz, 3H), 2.39 (s, 3H), 3.74 (p, $J = 7.7$ Hz, 1H), 5.52 (t, $J = 8.4$ Hz, 1H), 5.73 (ddq, $J = 15.2, 8.4, 1.5$ Hz, 1H), 5.88-6.01 (m, 1H), 6.10 (s, 1H), 6.75 (d, $J = 8.6$ Hz, 1H); 7.40 (d, $J = 8.6$ Hz, 1H); ^{13}C NMR (CDCl_3) 15.1, 18.3, 19.3, 38.3, 89.7, 107.0, 111.5, 114.4, 119.9, 125.6, 125.6, 132.7, 151.1, 153.4, 161.4, 162.7; IR (neat) 1720,

1605 cm⁻¹. *cis*-Isomer (**25b**): ¹H NMR (CDCl₃) 1.50 (d, *J* = 7.0 Hz, 3H), 1.77 (dd, *J* = 6.6, 1.5 Hz, 3H), 2.39 (s, 3H), 3.49 (p, *J* = 7.2 Hz, 1H), 4.76 (t, *J* = 7.3 Hz, 1H), 5.64 (ddq, *J* = 15.4, 7.7, 1.5 Hz, 1H), 5.82-5.91 (m, 1H), 6.10 (s, 1H), 6.74 (d, *J* = 8.6 Hz, 1H); 7.40 (d, *J* = 8.6 Hz, 1H). The following ¹³C NMR, IR and HRMS data were obtained on the mixture of stereoisomers: ¹³C NMR (CDCl₃) 15.1, 18.0, 18.1, 18.2, 19.3, 38.0, 38.3, 41.5, 89.7, 93.7, 106.9, 107.0, 111.4, 111.5, 114.3, 114.4, 118.3, 119.9, 125.6, 125.7, 125.8, 129.0, 131.0, 132.7, 151.1, 151.4, 153.3, 153.4, 161.2, 161.3, 162.7, 163.0; IR (neat) 1729, 1613 cm⁻¹; HRMS *m/z* 256.1105 (calcd for C₁₆H₁₆O₃, 256.1099).

8,9-Dihydro-4-methyl-8-phenyl-8-(1-phenylethenyl)-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (26).

Obtained in a 10% yield: white solid, mp 60-64 °C; ¹H NMR (CDCl₃) 2.38 (d, *J* = 1.2 Hz, 3H), 3.81 (d, *J* = 15.8 Hz, 1H), 3.83 (d, *J* = 15.8 Hz, 1H), 5.43 (d, *J* = 0.8 Hz, 1H), 5.60 (d, *J* = 0.8 Hz, 1H), 6.08 (d, *J* = 1.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 7.05-7.34 (m, 10H), 7.31 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (CDCl₃) 19.2, 38.7, 95.9, 106.9, 111.6, 113.6, 114.5, 116.8, 125.8, 126.4, 127.8, 128.1, 128.3, 128.6, 128.7, 139.4, 142.6, 150.9, 151.0, 153.3, 161.2, 162.3; IR (neat) 1727, 1612 cm⁻¹; HRMS *m/z* 380.1419 (calcd for C₂₆H₂₀O₃, 380.1412).

Dihydrofurocoumarin 28. Obtained in a 72% yield: white solid, mp 180-184 °C; ¹H NMR (CDCl₃) 1.00 (s, 3H), 1.11 (s, 3H), 1.66 (d, *J* = 13.8 Hz, 1H), 1.74 (s, 3H), 1.81 (d, *J* = 17.6 Hz, 1H), 1.90 (d, *J* = 17.6 Hz, 1H), 1.99 (d, *J* = 13.8 Hz, 1H), 2.25 (s, 3H), 2.37 (d, *J* = 1.2 Hz, 3H), 3.12 (d, *J* = 16.0 Hz, 1H), 3.14 (d, *J* = 16.0 Hz, 1H), 5.51 (s, 1H), 6.07 (d, *J* = 1.2 Hz, 1H), 7.20 (s, 1H); ¹³C NMR (CDCl₃) 8.8, 19.3, 24.2, 28.6, 30.2, 31.0, 43.4, 44.4, 48.1, 89.5, 107.9, 110.7, 113.4, 117.4, 122.9, 123.7, 138.6, 153.3, 153.4, 160.9, 162.2; IR (neat) 1720, 1616 cm⁻¹; HRMS *m/z* 324.1731 (calcd for C₂₁H₂₄O₃, 324.1725).

2,3-Dihydro-5,9-dimethyl-2-(*E*-2-phenylethenyl)-7*H*-furo[3,2-*g*][1]-benzopyran-7-one (29).

Obtained in a 73% yield: white solid, mp 140-144 °C; ¹H NMR (CDCl₃) 2.32 (s, 3H), 2.39 (d, *J* = 1.0 Hz, 3H), 3.16 (dd, *J* = 15.6, 7.7 Hz, 1H), 3.52 (dd, *J* = 15.6, 9.2 Hz, 1H), 5.49 (dt, *J* = 9.2, 7.7 Hz, 1H), 6.11 (q, *J* = 1.0 Hz, 1H), 6.36 (dd, *J* = 15.8, 7.7 Hz, 1H), 6.73 (d, *J* = 15.8 Hz, 1H), 7.27-7.48 (m, 6H);

^{13}C NMR (CDCl_3) 8.8, 19.3, 36.2, 85.2, 108.2, 111.2, 113.9, 117.5, 119.2, 123.1, 126.8, 127.8, 128.5, 129.0, 132.3, 133.2, 136.1, 153.2, 153.4, 161.4, 170.0; IR (neat) 1714, 1616, 1585 cm^{-1} ; HRMS m/z 318.1263 (calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3$, 318.1256).

2-(*E*-1-Butenyl)-2,3-dihydro-5,9-dimethyl-7*H*-furo[3,2-*g*][1]-benzopyran-7-one (30). Obtained in a 75% yield: white solid, mp 127-129 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) 1.04 (t, $J = 7.6$ Hz, 3H), 2.19 (m, 2H), 2.29 (s, 3H), 2.38 (d, $J = 1.2$ Hz, 3H), 3.04 (ddd, $J = 15.6, 8.1, 1.2$ Hz, 1H), 3.40 (ddd, $J = 15.6, 9.0, 1.0$ Hz, 1H), 5.27 (q, $J = 8.2$ Hz, 1H), 5.65 (ddt, $J = 15.3, 7.8, 1.7$ Hz, 1H), 5.92 (dtd, $J = 15.3, 6.2, 0.8$ Hz, 1H), 6.09 (d, $J = 1.2$ Hz, 1H), 7.22 (s, 1H); ^{13}C NMR (CDCl_3) 8.8, 13.3, 19.3, 25.4, 36.0, 85.6, 108.0, 111.0, 113.7, 117.4, 123.5, 127.7, 137.2, 153.2, 153.3, 161.5, 162.1; IR (neat) 1713, 1614 cm^{-1} ; HRMS m/z 270.1262 (calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$, 270.1256).

2,3-Dihydro-5,9-dimethyl-2-(2-methyl-1-propenyl)-7*H*-furo[3,2-*g*][1]benzopyran-7-one (31). Obtained in a 79% yield: white solid, mp 176-180 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) 1.81 (d, $J = 1.2$ Hz, 3H), 2.28 (s, 3H), 2.38 (d, $J = 1.0$ Hz, 3H), 2.98 (ddd, $J = 15.5, 8.6, 1.3$ Hz, 1H), 3.39 (ddd, $J = 15.5, 8.7, 1.0$ Hz, 1H), 5.44 (dt, $J = 9.1, 1.1$ Hz, 1H), 5.57 (q, $J = 8.6$ Hz, 1H), 6.09 (d, $J = 1.2$ Hz, 1H), 7.22 (s, 1H); ^{13}C NMR (CDCl_3) 8.6, 18.4, 19.1, 25.9, 36.2, 81.4, 107.7, 110.7, 113.4, 117.0, 123.5, 124.0, 138.7, 152.9, 153.1, 161.4, 161.8; IR (neat) 1704, 1622 cm^{-1} ; HRMS m/z 270.1262 (calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$, 270.1256).

2-(*E*-2-Butenyl)-2,3-dihydro-5,9-dimethyl-7*H*-furo[3,2-*g*][1]-benzopyran-7-one (33). Obtained in a 75% yield: white solid, mp 180-186 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) 1.82 (d, $J = 1.2$ Hz, 3H), 2.28 (s, 3H), 2.38 (d, $J = 1.2$ Hz, 3H), 2.97 (ddd, $J = 15.6, 7.5, 0.9$ Hz, 1H), 3.39 (ddd, $J = 15.6, 8.8, 0.8$ Hz, 1H), 5.44 (dt, $J = 9.2, 1.2$ Hz, 1H), 5.57 (q, $J = 8.8$ Hz, 1H), 6.09 (d, $J = 1.2$ Hz, 1H), 7.22 (s, 1H); ^{13}C NMR (CDCl_3) 8.8, 18.7, 19.3, 26.1, 36.4, 81.7, 108.0, 111.0, 113.6, 117.3, 123.8, 124.3, 139.0, 153.2, 153.4, 161.6, 162.1; IR (neat) 1698, 1613 cm^{-1} ; HRMS m/z 270.1262 (calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$, 270.1256).

2,3-Dihydro-3,5,9-trimethyl-8-(*E*-1-propenyl)-7*H*-furo[3,2-*g*][1]-benzopyran-7-one (3:2 mixture of *trans*- and *cis*-isomers **34a** and **34b** respectively). Obtained as a white solid in a 60% overall yield when a commercially available 3:2 mixture of *trans,trans*- and *cis,cis*-2,4-hexadienes was used. *trans,trans*-2,4-Hexadiene (95% pure) gave a 20:1 ratio of **34a** and **34b** in a 70% yield. *trans*-Isomer (**34a**): $^1\text{H NMR}$ (CDCl_3) 1.20 (d, $J = 7.2$ Hz, 3H), 1.80 (dd, $J = 6.5, 1.5$ Hz, 3H), 2.29 (s, 3H), 2.40 (s, 3H), 3.54 (p, $J = 7.4$ Hz, 1H), 5.21 (t, $J = 8.5$ Hz, 1H), 5.57-5.75 (m, 1H), 5.80-6.00 (s, 1H), 6.10 (s, 1H), 7.17 (s, 1H). *cis*-Isomer (**34b**): $^1\text{H NMR}$ (CDCl_3) 1.36 (d, $J = 6.9$ Hz, 3H), 1.80 (dd, $J = 6.5, 1.5$ Hz, 3H), 2.28 (s, 3H), 2.40 (s, 3H), 3.25 (p, $J = 7.2$ Hz, 1H), 4.65 (t, $J = 8.3$ Hz, 1H), 5.57-5.75 (m, 1H), 5.80-6.00 (m, 1H), 6.10 (s, 1H), 7.14 (s, 1H). The following $^{13}\text{C NMR}$, IR and HRMS data were obtained on the mixture of stereoisomers: $^{13}\text{C NMR}$ (CDCl_3) 8.8, 16.5, 17.7, 18.3, 19.4, 39.9, 42.6, 89.0, 93.5, 108.1, 111.0, 111.1, 113.9, 116.2, 116.7, 126.2, 129.29, 129.7, 131.6, 131.9, 153.3, 153.4, 160.8, 162.0; IR (neat) 1714, 1620 cm^{-1} ; HRMS m/z 270.1262 (calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$, 270.1256).

Derivatization of the Dihydrofurocoumarins

Preparation of dihydrofurocoumarin 39. A modified solvomercuration procedure was used.⁵ Coumarin **23** (0.25 mmol, 64 mg) and $\text{Hg}(\text{OAc})_2$ (0.5 mmol, 163 mg) were dissolved in 2 mL of a 1:1 ether/water solution and 2 drops of 48% HClO_4 was added to dissolve the precipitated mercury(II) oxide. The reaction mixture was stirred at room temperature for 24 h, then quenched with a solution of NaBH_4 (0.3 mmol, 11.4 mg) in 5 % aq NaOH (0.5 mL). The resulting reaction mixture was stirred for 10 min, gently acidified with 10 mL of satd NH_4Cl (use of HCl results in only a 10% yield of the product **39**), and extracted with diethyl ether. Then the ether extract was dried over anhydrous MgSO_4 and concentrated. The resulting residue was purified by column chromatography using silica gel as a solid phase and 4:1 hexanes/ethyl acetate as the eluent to afford the final product after solvent removal.

8,9-Dihydro-8-(1-hydroxy-1-methylethyl)-4,8-dimethyl-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (39). Obtained in a 65% yield: white solid, mp 118-120 $^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3) 1.26 (s, 3H), 1.39 (s, 3H),

1.47 (s, 3H), 2.39 (d, $J = 1.2$ Hz, 3H), 2.98 (d, $J = 16.0$ Hz, 1H), 3.59 (d, $J = 16.0$, 1H), 6.11 (d, $J = 1.2$ Hz, 1H), 6.75 (d, $J = 8.4$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3) 19.3, 23.0, 24.5, 24.9, 34.9, 74.5, 97.1, 106.8, 111.4, 114.2, 114.3, 125.6, 151.3, 153.3, 161.4, 162.8; IR (neat) 3469, 1727, 1614 cm^{-1} ; HRMS m/z 274.1212 (calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$, 274.1205).

Preparation of the diol 40. A modified dihydroxylation procedure was used.⁶ A solution of coumarin **23** (0.25 mmol, 64 mg) and NMO dihydrate (0.55 mmol, 61 mg) in 8:1 acetone-water (2 mL) was treated with 1 mL of 5 % OsO_4 solution in ethanol (0.02 mmol, 5 mg). The reaction was stirred at 70 °C for 2 h, then diluted with 10 % aq NaHCO_3 (2 mL) and extracted with ethyl acetate. The organic extract was washed with water and aq NH_4Cl solution, dried over anhydrous MgSO_4 for 4 h and concentrated. The resulting residue was purified by column chromatography using silica gel as a solid phase and 4:1 hexanes/ethyl acetate as the eluent to afford the final product after solvent removal.

8,9-Dihydro-4,8-dimethyl-8-(1,2-dihydroxy-1-methylethyl)-2H-furo[2,3-*h*]-1-benzopyran-2-one (40). Obtained as a pair of diastereomers in a 96% yield: white solid, mp 163-173 °C; ^1H NMR (CDCl_3) 1.26 (s, 3H), 1.37 (s, 3H), 1.47 (s, 6H), 2.39 (d, $J = 0.8$ Hz, 6H), 2.70-4.40 (m, 8H), 6.11 (q, $J = 0.8$ Hz, 1H), 6.70-6.77 (m, 2H), 7.41 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) 19.3, 20.2, 20.5, 23.1, 23.3, 35.0, 35.2, 66.4, 66.9, 75.3, 76.2, 95.9, 97.4, 106.8, 106.9, 111.5, 111.7, 113.8, 114.0, 114.4, 14.5, 125.6, 125.7, 151.2, 151.3, 153.2, 153.3, 161.2, 161.3, 162.2, 162.3; IR (neat) 3406, 1709, 1608 cm^{-1} ; HRMS m/z 290.1160 (calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5$, 290.1154).

Preparation of the coumarin 41. A standard dehydrogenation procedure was used.⁷ A solution of coumarin **9** (0.25 mmol, 64 mg) and DDQ (0.50 mmol, 60 mg) in 1 mL of toluene was stirred at 100 °C for 24 h. Then the resulting reaction mixture was cooled to room temperature, filtered and the filtrate was concentrated. The resulting residue was purified by column chromatography using silica gel as a stationary phase and 8:1 hexanes/ethyl acetate as the eluent to afford the final product after solvent removal.

4-Methylbenzo[*b*]-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (41). Obtained in a 90% yield: white solid, mp 216-219 °C; ¹H NMR (CDCl₃) 2.53 (d, *J* = 1.2 Hz, 3H), 6.07 (d, *J* = 1.2 Hz, 1H), 7.45 (td, *J* = 7.3, 1.0 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.53 (td, *J* = 7.6, 1.2 Hz, 1H), 7.60 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 8.42 (ddd, *J* = 7.6, 1.2, 0.8 Hz, 1H); ¹³C NMR (CDCl₃) 19.6, 108.5, 111.7, 111.7, 113.2, 115.2, 122.1, 123.4, 123.8, 124.0, 128.0, 149.7, 153.5, 156.3, 158.5, 160.8; IR (neat) cm⁻¹; HRMS *m/z* 250.0635 (calcd for C₁₆H₁₄O₃, 250.0630).

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Table 2, Compound **15**