SUPPORTING INFORMATION

Synthesis of Dihydrofurocoumarins via Palladium-Catalyzed Annulation of 1,3-Dienes with *o*-Iodoacetoxycoumarins

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General. All ^1H and ^{13}C 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, 4-hydroxycoumarin, 7-hydroxy-4-methylcoumarin, 1,3-cyclohexadiene, 2,3-dimethyl-1,3-butadiene, isoprene, and 2,4-hexadiene were purchased from Aldrich Chemical Co., Inc. 2-Methyl-1,3-pentadiene was purchased from Lancaster Co., Inc. 1-Phenyl-1,3-butadiene and 1,5,5-trimethyl-3-methylenecyclohexene were prepared by Wittig condensation according to the 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 Pechman condensation.³

Synthesis of *o*-iodoacetoxycoumarins

General procedure. Compounds **4**, **13**, **15** and **17** were prepared by acylation of the corresponding *o*-iodohydroxycoumarins, which in turn were prepared by iodination of the corresponding hydroxycoumarins,⁴ as indicated below. Iodine (5.0 mmol) dissolved in 50 mL of aq KI solution was slowly added to a solution of the corresponding hydroxycoumarin (5.0 mmol) in the minimal amount of aq ammonia solution at 0-5 °C. The resulting reaction mixture was stirred for 2 h, left overnight in the refrigerator, and then acidified by 20% aq HCl to pH = 4-5. The precipitated *o*-iodohydroxycoumarin was filtered, washed with water and dried in the open air. The resulting white solid was dissolved in 20 mL of acetyl chloride (a minimal amount of DMF can be used as a co-solvent) in the presence of 1 mL of pyridine and stirred for 48 h at room temperature. Then the reaction mixture was quenched with chilled water (caution, heat evolution!) and extracted by CH_2Cl_2 . The organic extract was washed with water and aq NH_4Cl solution, and dried over anhydrous MgSO_4 for 4 h. After evaporation of the CH_2Cl_2 , the resulting white solid was purified by column chromatography using silica gel as a stationary phase and 5:1 hexanes-ethyl acetate as the eluent. The following compounds were prepared using this procedure.

7-Acetoxy-8-iodo-4-methylcoumarin (4). Obtained in a 90% overall yield from 7-hydroxy-4-methylcoumarin, recrystallized from 1:1 ethanol-water: white solid, mp 173-175 °C; ^1H NMR (CDCl_3) δ 2.43 (s, 3H), 2.45 (d, J = 0.8 Hz, 3H), 6.28 (d, J = 0.8 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H); ^{13}C NMR (CDCl_3) δ 19.0, 21.5, 82.8, 115.2, 118.6, 119.7, 125.5, 151.9, 154.4, 154.6, 159.9, 168.4; IR (neat) 1760, 1729 cm^{-1} ; HRMS m/z 343.9550 (calcd for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{I}$, 343.9546).

7-Acetoxy-4,8-dimethyl-6-iodocoumarin (13). Obtained in a 92% overall yield from 7-hydroxy-4,8-dimethylcoumarin, recrystallized from 1:1 ethanol-water: white solid, mp 176-178 °C; ¹H NMR (CDCl₃) • 2.32 (s, 3H), 2.42 (d, *J* = 1.2 Hz, 3H), 2.44 (s, 3H), 6.28 (d, *J* = 1.2 Hz, 1H), 7.90 (s, 1H); ¹³C NMR (CDCl₃) δ 10.6, 19.0, 21.2, 85.5, 115.2, 120.0, 121.5, 131.9, 151.3, 152.0, 152.7, 160.1, 167.9; IR (neat) 1767, 1703 cm⁻¹; HRMS *m/z* 357.9707 (calcd for C₁₃H₁₁O₄I, 357.9702).

5-Acetoxy-6-iodo-4-methylcoumarin (15). Obtained in an 85% overall yield from 5-hydroxy-4-methylcoumarin, purified by column chromatography using 4:1 hexanes-ethyl acetate: white solid, mp 144-150 °C; ¹H NMR (CDCl₃) • 2.46 (s, 3H), 2.47 (d, *J* = 1.2 Hz, 3H), 6.27 (d, *J* = 1.2 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 22.2, 22.8, 87.6, 115.8, 117.4, 117.9, 118.4, 141.0, 150.4, 155.1, 159.3, 168.6; IR (neat) 1754, 1733 cm⁻¹; HRMS *m/z* 343.9551 (calcd for C₁₁H₇IO₄, 343.9546).

4-Acetoxy-3-iodocoumarin (17). Obtained in a 40% overall yield from 4-hydroxycoumarin, purified by column chromatography using 4:1 hexanes-ethyl acetate: white solid, mp 166-168 °C; ¹H NMR (CDCl₃) • 2.53 (s, 3H), 7.33 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 21.4, 82.8, 116.2, 117.2, 122.9, 125.1, 133.6, 153.1, 159.0, 162.6, 165.8; IR (neat) 1779, 1717 cm⁻¹; HRMS *m/z* 329.9396 (calcd for C₁₁H₇IO₄, 329.9389).

General procedure for the Pd-catalyzed annulation of 1,3-dienes by *o*-iodoacetoxy coumarins.

0.25 mmol of *o*-iodoacetoxy coumarin, 0.0125 mmol (5 mol %) of Pd(dba)₂, 0.0125 mmol (5 mol %) of dppe, 0.5 mmol of Ag₂CO₃ and 4 mL of 1,3-dioxane were stirred in a capped vial for 5 min, then 1 mL of water and 1.0 mmol of 1,3-diene were added. The resulted 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 1:1 hexanes-ethyl acetate as an eluent giving the final product in the form of a white solid. The white solid obtained was recrystallized from 1:1 ethanol-water. The following compounds were prepared using this procedure.

7a,10,11,11a-Tetrahydro-4-methylbenzo[*b*]-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (2). Obtained in a 63% yield: white solid, mp 164-165 °C; ¹H NMR (CDCl₃) • 1.43-2.32 (m, 4H), 2.40 (d, *J* = 1.2 Hz, 3H), 3.67 (m, 1H), 5.07 (m, 1H), 6.04 (m, 1H), 6.11 (d, *J* = 1.2 Hz, 1H), 6.21 (m, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 19.2, 23.3, 24.2, 38.4, 80.6, 107.2, 111.4, 114.3, 118.6, 123.3, 125.6, 134.8, 151.3, 153.4, 161.4, 163.1; IR (neat) 1733, 1615 cm⁻¹; HRMS *m/z* 254.0946 (calcd for C₁₆H₁₄O₃, 254.0943).

8,9-Dihydro-4-methyl-8-(*E*-2-phenylethenyl)-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (7). Obtained in an 80% yield: white solid mp 145-148 °C; ¹H NMR (CDCl₃) • 2.32 (d, *J* = 0.8 Hz, 3H), 3.16 (dd, *J* = 16.1, 7.5 Hz, 1H), 3.55 (dd, *J* = 16.1, 9.4 Hz, 1H), 5.49 (dddd, *J* = 9.4, 7.5, 7.4, 1.0 Hz, 1H), 6.03 (d, *J* = 0.8 Hz, 1H), 6.28 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.67 (dd, *J* = 15.8, 1.0 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 7.17-7.36 (m, 5H), 7.35 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) • 19.24, 33.28, 85.90, 106.77, 111.50, 113.69, 114.34, 125.76, 126.97, 127.33, 128.51, 128.85, 133.32, 136.02, 151.10, 153.26, 161.28, 163.44; IR (neat) 1727, 1615 cm⁻¹; HRMS *m/z* 304.1104 (calcd for C₂₀H₁₆O₃, 304.1099).

8,9-Dihydro-4,8-dimethyl-8-*E*-propenyl-2*H*-furo[2,3-*h*]-1-benzopyran-2-one (8). Obtained in a 78% yield: white solid, mp 91-93 °C; ¹H NMR (CDCl₃) • 1.59 (s, 3H), 1.72 (d, *J* = 5.6 Hz, 3H), 2.39 (d, *J* = 0.8 Hz, 3H), 3.17 (d, *J* = 15.9 Hz, 1H), 3.32 (d, *J* = 15.9 Hz, 1H), 5.71 (d, *J* = 15.7 Hz, 1H), 5.80 (dq, *J* = 15.7, 5.6 Hz, 1H), 6.09 (d, *J* = 0.8 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) 18.0, 19.3, 26.7, 39.2, 90.8, 106.2, 111.3, 113.7, 114.1, 125.3, 125.6, 134.1, 151.3, 153.4, 161.5, 162.9; IR (neat) 1735, 1615 cm⁻¹; HRMS *m/z* 256.1102 (calcd for C₁₆H₁₆O₃, 256.1099).

Dihydrofurocoumarin 9. Obtained in a 61% yield: white solid mp 70-74 °C; ¹H NMR (CDCl₃) • 1.02 (s, 3H), 1.09 (s, 3H), 1.70-2.20 (m, 4H), 1.78 (d, *J* = 1.2 Hz, 3H), 2.39 (d, *J* = 1.2 Hz, 3H), 3.24 (s, 2H), 5.92 (q, *J* = 1.2 Hz, 1H), 6.03 (d, *J* = 1.2 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) • 19.2, 24.1, 29.1, 29.5, 31.0, 40.5, 44.3, 48.2, 90.2, 106.9, 111.0, 113.7, 113.8, 122.6, 125.5, 138.4, 151.1, 153.4, 161.6, 162.8; IR (neat) 1732, 1615 cm⁻¹; HRMS *m/z* 310.1572 (calcd for C₂₀H₂₂O₃ 310.1569).

8,9-Dihydro-4,8-dimethyl-8-(2-propenyl)-2H-furo[2,3-*h*]-1-benzopyran-2-one (10). Obtained in a 75% yield: white solid, mp 101-103 °C; ¹H NMR (CDCl₃) • 1.61 (s, 3H), 1.83 (d, *J* = 0.8 Hz, 3H), 2.39 (d, *J* = 1.2 Hz, 3H), 3.18 (d, *J* = 16.0 Hz, 1H), 3.39 (d, *J* = 16.0, 1H), 4.88 (q, *J* = 0.8 Hz, 1H), 5.10 (q, *J* = 0.8 Hz, 1H), 6.09 (d, *J* = 1.2 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H); ¹³C (CDCl₃) δ 18.9, 19.2, 26.4, 38.4, 93.1, 106.8, 110.7, 111.3, 113.6, 114.1, 125.7, 146.9, 151.3, 153.4, 161.4, 163.0; IR (neat) 1728, 1615 cm⁻¹; HRMS *m/z* 256.1102 (calcd for C₁₆H₁₆O₃, 256.1099).

8,9-Dihydro-4-methyl-8-(2-propenyl)-2H-furo[2,3-*h*]-1-benzopyran-2-one (11a) and 8,9-dihydro-8-ethenyl-4,8-dimethyl-2H-furo[2,3-*h*]-1-benzopyran-2-one (11b) were isolated as a 3:2 inseparable mixture of regioisomers in a 73% overall yield. The ratio of regioisomers was confirmed by ¹H NMR spectroscopy and HPLC. **11a:** ¹H NMR (CDCl₃) • 1.77 (s, 3H), 2.40 (s, 3H), 3.19 (dd, *J* = 16.0, 9.6 Hz, 1H), 3.53 (dd, *J* = 16.0, 9.6 Hz, 1H), 4.96 (s, 1H), 5.11 (s, 1H), 5.35 (dd, *J* = 16.0, 9.6 Hz, 1H), 5.35 (t, *J* = 9.6 Hz, 1H), 6.10 (s, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H). **11b:** ¹H NMR (CDCl₃) • 1.61 (s, 3H), 2.40 (s, 3H), 3.20 (d, *J* = 15.6 Hz, 1H), 3.35 (d, *J* = 15.6 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 5.34 (d, *J* = 17.3 Hz, 1H), 6.06 (dd, *J* = 17.3, 10.8 Hz, 1H), 6.10 (s, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H). The following ¹³C NMR, IR and HRMS data were obtained on the mixture of isomers: ¹³C NMR (CDCl₃) • 17.3, 19.3, 19.3, 26.5, 31.7, 38.9, 88.0, 90.8, 106.6, 106.9, 111.4, 111.5, 113.0, 113.5, 113.7, 114.2, 114.3, 115.6, 125.7, 125.8, 140.9, 143.2, 151.1, 153.3, 153.4, 161.3, 161.4, 162.9, 163.9; IR (neat) 1731, 1614 cm⁻¹; HRMS, 242.0946 (calcd for C₁₅H₁₄O₃ 242.0943).

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) (12a and 12b). Obtained as a white solid in a 73% overall yield. *trans*-Isomer (**12a**): ¹H NMR (CDCl₃) • 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). *cis*-Isomer (**12b**): 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) δ 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).

2,3-Dihydro-2,5,9-trimethyl-2-(2-propenyl)-7H-furo[3,2-*g*][1]-benzopyran-7-one (14). Obtained in a 70% yield: white solid, mp 142-144 °C; ¹H NMR (CDCl₃) • 1.60 (s, 3H), 1.83 (s, 3H), 2.31 (s, 3H), 2.37 (d, *J* = 1.2 Hz, 3H), 3.08 (dd, *J* = 15.6, 1.0 Hz, 1H), 3.31 (dd, *J* = 15.6, 0.9 Hz, 1H), 4.87 (t, *J* = 1.4 Hz, 1H), 5.08 (s, 1H), 6.09 (d, *J* = 1.2 Hz, 1H), 7.21 (s, 1H); ¹³C NMR (CDCl₃) δ 8.7, 18.9, 19.3, 26.4, 41.2, 91.9, 108.0, 110.6, 110.9, 113.7, 117.6, 123.2, 147.2, 153.2, 153.4, 161.0, 162.1; IR (neat) 1705, 1618 cm⁻¹; HRMS *m/z* 270.1262 (calcd for C₁₇H₁₈O₃, 270.1256).

2,3-Dihydro-2,9-dimethyl-8-(2-propenyl)-7H-furo[2,3-*f*]-1-benzopyran-7-one (16). Obtained in a 55% yield: white solid, mp 73-76 °C; ¹H NMR (CDCl₃) • 1.59 (s, 3H), 1.85 (q, *J* = 0.6 Hz, 3H), 2.57 (d, *J* = 1.2 Hz, 3H), 3.03 (dd, *J* = 15.4, 0.8 Hz, 1H), 3.26 (dd, *J* = 15.4, 0.8 Hz, 1H), 4.88 (t, *J* = 1.6 Hz, 1H), 5.08 (s, 1H), 6.10 (d, *J* = 1.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 19.1, 22.7, 26.6, 40.6, 93.0, 106.6, 108.8, 110.5, 113.7, 122.3, 127.5, 147.4, 153.3, 154.1, 156.5, 161.4; IR (neat) 1725, 1615 cm⁻¹; HRMS *m/z* 256.1102 (calcd for C₁₆H₁₆O₃, 256.1099).

1a,5,6,6a-Tetrahydrobenzo[*b*]-4*H*-furo[3,2-*c*][1]-benzopyran-4-one (18). Obtained in a 48% yield: white solid, mp 140-144 °C; ¹H NMR (CDCl₃) • 1.55-1.67 (m, 1H), 1.92-2.06 (m, 1H), 2.13-2.27 (m, 2H), 3.54 (ddd, *J* = 10.0, 8.7, 4.7 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 6.06 (d, *J* = 10.2 Hz, 1H), 6.26-6.33 (m, 1H), 7.28 (ddd, *J* = 7.6, 7.5, 1.0 Hz, 1H), 7.38 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.5, 1.5 Hz, 1H), 7.67 (dd, *J* = 7.6, 1.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 22.5, 23.6, 38.0, 82.5, 106.3, 112.9, 116.9, 122.6, 122.8, 123.8, 132.2, 135.7, 154.9, 160.7, 166.4; IR (neat) 1718, 1640 cm⁻¹; HRMS *m/z* 240.0791 (calcd for C₁₅H₁₂O₃, 240.0786).

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Table 1, Compound 4

Table 1, Compound 7

Table 1, Compound **10**