SUPPORTING INFORMATION

Facile Syntheses of 2,2-Dimethyl-6-(2-oxoalkyl)-1,3-dioxin-4-ones and the Corresponding 6-Substituted 4-hydroxy-2-pyrones

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General Procedure for the Preparation of 2,2-Dimethyl-6-(2-oxoalkyl)-1,3-dioxin-4-ones 5a-l, Byproduct b1 and N,N-Diisopropylacetamides 10m-n. To a solution of diisopropylamine (99%, 0.77 g, 7.5 mmol) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (1.6 M, 5.16 mL, 8.25 mmol) dropwise over ca. 30 min. A solution of 2,2,6-trimethyl-1,3-dioxin-4-one **4** (95%, 0.85 g, 5.68 mmol) in THF (20 mL) was then added dropwise at $-78\text{ }^{\circ}\text{C}$ for 10–15 min. After stirring for 1.5 h, a solution of 1-acylbenzotriazole **9a-n** (5 mmol) in THF (20 mL) was added at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ and allowed to warm to room temperature overnight. Saturated aqueous ammonium chloride solution (2 mL) was added to quench the reaction, and the reaction mixture was concentrated under reduced pressure. Water (100 mL) was added to the residue, and the solution was extracted with ethyl acetate (3 x 50 mL). The combined organic phase was washed with saturated aqueous sodium carbonate solution (100 mL), and dried over anhyd. MgSO_4 . After evaporation of the solvent, the residue was purified by column chromatography on silica gel to give 2,2-dimethyl-6-(2-oxoalkyl)-1,3-dioxin-4-ones **5a-l**, byproduct **b1** and *N,N*-diisopropylacetamides **10m-n**.

The ^1H NMR spectra of **5a-l** show a new set of singlets at 3.32–4.04 ppm assigned to the methylene group attached to position 6 of the resultant 1,3-dioxin-4-one rings. The ^{13}C NMR spectra of **5a-l** show characteristic carbonyl signals for ketones at 181.6 to 208.6 ppm and the absence of signals for the benzotriazole group on 1-acylbenzotriazoles **9a-l**.

2,2-Dimethyl-6-(2-oxo-2-phenylethyl)-4H-1,3-dioxin-4-one (5a): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (9/1, v/v); mp 105–107 $^{\circ}\text{C}$ [lit.⁸ mp 110.0–112.0 $^{\circ}\text{C}$]; yield 65%; ^1H NMR (CDCl_3) δ 1.71 (s, 6H), 3.91 (s, 2H), 5.43 (s, 1H), 7.46–7.54 (m, 2H), 7.60–7.66 (m, 1H), 7.91–7.96 (m, 2H); ^{13}C NMR (CDCl_3) δ 24.9 (2C), 43.2, 96.9, 107.3, 128.3 (2C), 128.9 (2C), 134.0, 135.8, 160.7, 165.1, 193.0. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4$: C, 68.28; H, 5.73. Found: C, 68.40; H, 5.80.

2,2-Dimethyl-6-[2-(4-methylphenyl)-2-oxoethyl]-4H-1,3-dioxin-4-one (5b): colorless needles after chromatography on silica gel using hexanes/chloroform as eluant (6/1→3/1, v/v); mp 87.0–88.0 $^{\circ}\text{C}$;

yield 58%; ^1H NMR (CDCl_3) δ 1.70 (s, 6H), 2.43 (s, 3H), 3.88 (s, 2H), 5.41 (s, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CDCl_3) δ 21.6, 24.9 (2C), 43.1, 96.7, 107.1, 128.3 (2C), 129.5 (2C), 133.3, 145.0, 160.7, 165.3, 192.6. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4$: C, 69.21; H, 6.21. Found: C, 69.18; H, 6.30.

6-[2-(4-chlorophenyl)-2-oxoethyl]-2,2-dimethyl-4H-1,3-dioxin-4-one (5c): colorless needles after chromatography on silica gel using hexanes/chloroform as eluant (6/1 $\rightarrow$ 3/1, v/v); mp 117–119 $^\circ\text{C}$; yield 61%; ^1H NMR (CDCl_3) δ 1.71 (s, 6H), 5.42 (s, 1H), 3.88 (s, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H); ^{13}C NMR (CDCl_3) δ 25.0 (2C), 43.2, 97.1, 107.3, 129.2 (2C), 129.79 (2C), 134.1, 140.6, 160.6, 164.7, 191.8. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}_4$: C, 59.90; H, 4.68. Found: C, 59.68; H, 4.57.

2,2-Dimethyl-6-(2-oxo-3,3-diphenylpropyl)-4H-1,3-dioxin-4-one (5d): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1 $\rightarrow$ 6/1, v/v); mp 87–89 $^\circ\text{C}$; yield 58%; ^1H NMR (CDCl_3) δ 1.68 (s, 6H), 3.43 (s, 2H), 5.16 (s, 1H), 5.26 (s, 1H), 7.18–7.24 (m, 4H), 7.28–7.39 (m, 6H); ^{13}C NMR (CDCl_3) δ 25.0 (2C), 46.5, 64.5, 96.7, 107.2, 127.7 (2C), 128.9 (8C), 37.0 (2C), 160.6, 164.4, 201.2. HRMS (EI) Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4$: m/z 336.1362. Found: 336.1353.

2,2-Dimethyl-6-[2-(2-naphthyl)-2-oxoethyl]-4H-1,3-dioxin-4-one (5e): yellowish prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 4/1, v/v); mp 103–105 $^\circ\text{C}$; yield 65%; ^1H NMR (CDCl_3) δ 1.72 (s, 6H), 4.04 (s, 2H), 5.48 (s, 1H), 7.56–7.67 (m, 2H), 7.88–8.01 (m, 4H), 8.45 (s, 1H); ^{13}C NMR (CDCl_3) δ 25.0 (2C), 43.3, 97.0, 107.3, 123.5, 127.2, 127.8, 128.9, 129.1, 129.6, 130.4, 132.3, 133.1, 135.9, 160.8, 165.2, 192.9. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4$: C, 72.96; H, 5.44. Found: C, 72.84; H, 5.63.

2,2-Dimethyl-6-(2-oxooctyl)-4H-1,3-dioxin-4-one (5f): colorless oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 5/1, v/v); yield 53%; ^1H NMR (CDCl_3) δ 0.89 (t, J = 6.4 Hz, 3H), 1.22–1.35 (m, 6H), 1.52–1.65 (m, 2H), 1.72 (s, 6H), 2.50 (t, J = 7.3 Hz, 2H), 3.33 (s, 2H),

5.34 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 22.4, 23.4, 25.0 (2C), 28.6, 31.5, 43.1, 47.0, 96.6, 107.1, 160.6, 164.6, 203.3. Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4$: C, 66.12; H, 8.72. Found: C, 66.28; H, 8.95.

6-(3,3-Dimethyl-2-oxobutyl)-2,2-dimethyl-4H-1,3-dioxin-4-one (5g): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 6/1, v/v); mp 76.0–78.0 $^{\circ}\text{C}$; yield 52%; ^1H NMR (CDCl_3) δ 1.19 (s, 9H), 1.71 (s, 6H), 3.43 (s, 2H), 5.32 (s, 1H); ^{13}C NMR (CDCl_3) δ 24.9 (2C), 26.0 (3C), 41.1, 44.8, 96.7, 107.1, 160.8, 165.6, 208.6. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4$: C, 63.70; H, 8.02. Found: C, 63.87; H, 8.26.

2,2-Dimethyl-6-(3-methyl-2-oxobutyl)-4H-1,3-dioxin-4-one (5h): colorless oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 6/1, v/v); yield 51%; ^1H NMR (CDCl_3) δ 1.15 (d, $J = 7.0$ Hz, 6H), 1.71 (s, 6H), 2.68 (septet, $J = 7.0$ Hz, 1H), 3.38 (s, 2H), 5.33 (s, 1H); ^{13}C NMR (CDCl_3) δ 17.8 (2C), 24.9 (2C), 41.3, 44.6, 96.6, 107.1, 160.7, 164.9, 207.0. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$: C, 62.25; H, 7.60. Found: C, 62.30; H, 7.82.

2,2-Dimethyl-6-(2-oxo-11-dodecenyl)-4H-1,3-dioxin-4-one (5i): yellow oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 8/1, v/v); yield 51%; ^1H NMR (CDCl_3) δ 1.28–1.42 (m, 10H), 1.52–1.65 (m, 2H), 1.71 (s, 6H), 2.04 (q, $J = 6.9$ Hz, 2H), 2.50 (t, $J = 7.4$ Hz, 2H), 3.32 (s, 2H), 4.91–5.02 (m, 2H), 5.34 (s, 1H), 5.74–5.87 (m, 1H); ^{13}C NMR (CDCl_3) δ 23.3, 25.0 (2C), 28.8, 28.9, 29.0, 29.1, 29.2, 33.7, 43.1, 47.0, 96.6, 107.1, 114.1, 139.0, 160.7, 164.6, 203.4. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4$: C, 70.10; H, 9.15. Found: C, 70.11; H, 9.52.

N,N-diisopropyl-3-phenyl-3-(2,2,6-trimethyl-4-oxo-4H-1,3-dioxin-5-yl)propanamide (b1): sticky oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (50/1 $\rightarrow$ 3/1, v/v, the second fraction); yield 21%; ^1H NMR (CDCl_3) δ 1.11 (d, $J = 6.7$ Hz, 3H), 1.17 (d, $J = 6.6$ Hz, 3H), 1.34 (d, $J = 6.3$ Hz, 3H), 1.36 (d, $J = 5.8$ Hz, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 2.08 (s, 3H), 2.76 (dd, $J = 15.7, 5.0$ Hz, 1H), 3.34–3.53 (m, 1H), 3.65 (dd, $J = 15.7, 10.1$ Hz, 1H), 4.08 (septet, $J = 6.7$ Hz, 1H), 4.31 (dd, $J = 15.7, 5.0$ Hz, 1H), 7.25–7.35 (m, 5H). Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{N}_2\text{O}_4$: C, 75.84; H, 8.92; N, 5.24. Found: C, 75.84; H, 8.92; N, 5.24.

= 10.1, 5.0 Hz, 1H), 7.15–7.23 (m, 1H), 7.24–7.32 (m, 2H), 7.33–7.40 (m, 2H); ^{13}C NMR (CDCl_3) δ 18.0, 20.7 (2C), 20.8 (2C), 23.9, 26.0, 38.4, 39.5, 45.6, 48.4, 104.7, 107.1, 126.3, 127.7 (2C), 128.4 (2C), 143.5, 161.7, 165.9, 170.4. Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_4$: C, 70.75; H, 8.37; N, 3.75. Found: C, 70.72; H, 8.54; N, 3.50.

2,2-Dimethyl-6-[(E)-2-oxo-4-phenyl-3-butenyl]-4H-1,3-dioxin-4-one (5j): colorless prisms^{10a} after chromatography on silica gel using hexanes/ethyl acetate as eluant (50/1→3/1, v/v, the third fraction); mp 101–102 °C; yield 37%; ^1H NMR (CDCl_3) δ 1.72 (s, 6H), 3.60 (s, 2H), 5.43 (s, 1H), 6.77 (d, J = 16.1 Hz, 1H), 7.38–7.46 (m, 3H), 7.52–7.58 (m, 2H), 7.62 (d, J = 16.1 Hz, 1H); ^{13}C NMR (CDCl_3) δ 24.9 (2C), 45.3, 96.6, 107.1, 124.6, 128.4 (2C), 129.0 (2C), 131.1, 133.7, 144.7, 160.6, 164.9, 192.3. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$: C, 70.58; H, 5.92. Found: C, 70.59; H, 5.99.

6-[2-(2-Furyl)-2-oxoethyl]-2,2-dimethyl-4H-1,3-dioxin-4-one (5k): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1→3/1, v/v); mp 72–74 °C; yield 66%; ^1H NMR (CDCl_3) δ 1.70 (s, 6H), 3.77 (s, 2H), 5.44 (s, 1H), 6.60 (dd, J = 3.6, 1.7 Hz, 1H), 7.28 (dd, J = 3.6, 0.6 Hz, 1H), 7.64 (dd, J = 1.7, 0.6 Hz, 1H); ^{13}C NMR (CDCl_3) δ 24.8 (2C), 42.9, 96.8, 107.3, 112.8, 118.4, 147.2, 151.6, 160.8, 164.5, 181.6. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_5$: C, 61.02; H, 5.13. Found: C, 61.15; H, 5.06.

2,2-Dimethyl-6-[2-oxo-2-(2-thienyl)ethyl]-4H-1,3-dioxin-4-one (5l): yellow prisms after chromatography on silica gel using hexanes/chloroform as eluant (5/1→3/1, v/v); mp 70–72 °C; yield 60%; ^1H NMR (CDCl_3) δ 1.71 (s, 6H), 3.84 (s, 2H), 5.45 (s, 1H), 7.18 (dd, J = 4.8, 3.9 Hz, 1H), 7.72–7.76 (m, 2H); ^{13}C NMR (CDCl_3) δ 24.9 (2C), 43.8, 96.9, 107.3, 128.4, 133.0, 135.1, 142.8, 160.7, 164.5, 185.5. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{S}$: C, 57.12; H, 4.80. Found: C, 56.95; H, 4.69.

General Procedure for the Preparation of 4-Hydroxy-6-substituted-2-pyrones 3a-l, Byproduct b2, 5-Alkyl-4-hydroxy-6-phenyl-2H-pyran-2-one 13a–c and Byproducts b3–4. A solution of each

2,2-dimethyl-6-(2-oxoalkyl)-1,3-dioxin-4-one (**5a-l**) or 2,2-dimethyl-6-(1-alkyl-2-oxo-2-phenylethyl)-1,3-dioxin-4-one (**12a-c**) (3.0 mmol) in toluene (30 mL) was heated under reflux for 20-30 min. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel to give 4-hydroxy-6-substituted-2-pyrones **3a-l**, byproduct **b2**, 5-alkyl-2-pyrones **13a-c** and byproducts **b3-4**.

The ^1H NMR spectra of **3a-l** show two sets of doublets for H^3 at 5.27–5.59 ppm and H^5 at 5.76–6.93 ppm, respectively, with typical meta coupling between H^3 and H^5 of 2-pyrone rings in the range 1.4–2.1 Hz. The ^{13}C NMR spectra of **3a-l** display the existence of two ring methine carbons: C-3 at 88.8–90.0 ppm, C-5 at 96.5–102.1 ppm.

4-Hydroxy-6-phenyl-2H-pyran-2-one (3a): off-white microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1→2/1, v/v); mp 250–251 °C [lit.⁸ mp 246 °C]; yield 82%; ^1H NMR ($\text{DMSO-}d_6$) δ 5.41 (d, J = 1.8 Hz, 1H), 6.77 (d, J = 1.8 Hz, 1H), 7.47–7.56 (m, 3H), 7.81–7.90 (m, 2H), 11.87 (br s, 1H); ^{13}C NMR ($\text{DMSO-}d_6$) δ 89.6, 98.4, 125.4 (2C), 129.0 (2C), 130.9, 131.0, 160.0, 163.0, 170.5.

4-Hydroxy-6-(4-methylphenyl)-2H-pyran-2-one (3b): yellowish microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1→1/1, v/v); mp 206–208 °C [lit.¹⁹ mp 212–213 °C]; yield 77%; ^1H NMR ($\text{DMSO-}d_6$) δ 2.37 (s, 3H), 5.37 (d, J = 2.0 Hz, 1H), 6.71 (d, J = 2.0 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 11.83 (br s, 1H); ^{13}C NMR ($\text{DMSO-}d_6$) δ 20.9, 89.3, 97.6, 125.4 (2C), 128.3, 129.6 (2C), 141.0, 160.2, 163.1, 170.6. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_3$: C, 71.28; H, 4.98. Found: C, 71.03; H, 5.01.

6-(4-Chlorophenyl)-4-hydroxy-2H-pyran-2-one (3c): yellowish microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (3/1→1/1, v/v); mp 228–230 °C [lit.²⁰ mp 250–252 °C for the monohydrate]; yield 75%; ^1H NMR ($\text{DMSO-}d_6$) δ 5.41 (d, J = 1.8 Hz, 1H), 6.81 (d, J = 1.8

Hz, 1H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.88 (d, $J = 8.6$ Hz, 2H), 11.92 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 89.9, 98.9, 127.3 (2C), 129.1 (2C), 129.9, 135.6, 158.8, 162.8, 170.5. Anal. Calcd for $\text{C}_{11}\text{H}_7\text{ClO}_3$: C, 59.35; H, 3.18. Found: C, 59.10; H, 3.23.

6-Benzhydryl-4-hydroxy-2H-pyran-2-one (3d): colorless microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1 $\rightarrow$ 1/1, v/v); mp 186–187 °C; yield 85%; ^1H NMR (DMSO- d_6) δ 5.27 (d, $J = 1.9$ Hz, 1H), 5.44 (s, 1H), 5.76 (d, $J = 1.9$ Hz, 1H), 7.20–7.41 (m, 10H), 11.73 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 53.9, 88.8, 102.1, 127.2 (2C), 128.7 (4C), 128.8 (4C), 139.5 (2C), 163.5, 166.5, 170.0. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3$: C, 77.68; H, 5.07. Found: C, 77.79; H, 5.10.

(Z)-4-Hydroxy-4-(2-naphthyl)-3-buten-2-one (b2): yellow prisms after chromatography on silica gel using hexanes/ethyl acetate as eluan (50/1 $\rightarrow$ 40/1, v/v, the first fraction); mp 72–74 °C [lit.²¹ mp 78–79 °C]; yield 14%; ^1H NMR (CDCl_3) δ 2.15 (s, 3H), 6.23 (s, 1H), 7.41–7.51 (m, 2H), 7.75–7.86 (m, 4H), 8.34 (s, 1H), 16.16 (br s, 1H); ^{13}C NMR (CDCl_3) δ 25.9, 97.0, 123.1, 126.7, 127.7, 128.0, 128.1, 128.4, 129.2, 132.1, 132.7, 135.2, 183.1, 193.8. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$: C, 79.22; H, 5.70. Found: C, 78.94; H, 5.85.

4-Hydroxy-6-(2-naphthyl)-2H-pyran-2-one (3e): off-white microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1 $\rightarrow$ 1/1, v/v, the last fraction); mp 235–236 °C; yield 66%; ^1H NMR (DMSO- d_6) δ 5.46 (d, $J = 1.7$ Hz, 1H), 6.93 (d, $J = 1.7$ Hz, 1H), 7.58–7.68 (m, 2H), 7.94–8.12 (m, 4H), 8.48 (s, 1H), 11.97 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 89.8, 98.9, 122.3, 125.5, 127.0, 127.6, 127.8, 128.3, 128.7, 129.0, 132.6, 133.8, 159.9, 163.1, 170.6. Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_3$: C, 75.62; H, 4.23. Found: C, 75.38; H, 4.16.

6-Hexyl-4-hydroxy-2H-pyran-2-one (3f): yellowish microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 2/1, v/v); mp 56–57 °C; yield 70%; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.20–1.40 (m, 6H), 1.58–1.70 (m, 2H), 2.48 (t, $J = 7.6$ Hz, 2H), 5.57 (d, $J =$

1.9 Hz, 1H), 5.97 (d, $J = 1.9$ Hz, 1H), 10.7 (br s, 1H); ^{13}C NMR (CDCl_3) δ 14.0, 22.4, 26.6, 28.6, 31.4, 33.6, 89.8, 101.3, 167.4, 168.4, 172.6. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_3$: C, 67.32; H, 8.22. Found: C, 67.22; H, 8.23.

6-(*tert*-Butyl)-4-hydroxy-2*H*-pyran-2-one (3g): yellowish prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 2/1, v/v); mp 131–133 °C; yield 86%; ^1H NMR (CDCl_3) δ 1.26 (s, 9H), 5.59 (d, $J = 1.8$ Hz, 1H), 6.06 (d, $J = 1.8$ Hz, 1H), 11.13 (br s, 1H); ^{13}C NMR (CDCl_3) δ 27.7 (3C), 36.1, 89.7, 98.3, 168.2, 172.8, 174.0. Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_3$: C, 64.27; H, 7.19. Found: C, 64.29; H, 7.26.

4-Hydroxy-6-isopropyl-2*H*-pyran-2-one (3h): yellowish microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1 $\rightarrow$ 2/1, v/v); mp 82–84 °C; yield 53%; ^1H NMR (CDCl_3) δ 1.23 (d, $J = 6.9$ Hz, 6H), 2.74 (septet, $J = 6.9$ Hz, 1H), 5.59 (d, $J = 2.0$ Hz, 1H), 5.99 (d, $J = 2.0$ Hz, 1H), 10.95 (br s, 1H); ^{13}C NMR (CDCl_3) δ 19.9 (2C), 32.6, 89.8, 99.2, 168.3, 171.8, 172.8. Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}_3$: C, 62.33; H, 6.54. Found: C, 62.45; H, 6.56.

6-(9-Decenyl)-4-hydroxy-2*H*-pyran-2-one (3i): yellowish prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (5/1 $\rightarrow$ 2/1, v/v); mp 62–64 °C; yield 64%; ^1H NMR (CDCl_3) δ 1.22–1.43 (m, 10H), 1.63 (br quintet, $J = 6.9$ Hz, 2H), 2.03 (q, $J = 7.0$ Hz, 2H), 2.48 (t, $J = 7.6$ Hz, 2H), 4.91–5.02 (m, 2H), 5.58 (d, $J = 1.7$ Hz, 1H), 5.73–5.88 (m, 1H), 5.98 (d, $J = 1.7$ Hz, 1H), 11.28 (br s, 1H); ^{13}C NMR (CDCl_3) δ 26.6, 28.8, 28.9, 29.0, 29.1, 29.2, 33.6, 33.7, 89.7, 101.3, 114.2, 139.1, 167.4, 168.4, 172.7. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$: C, 71.97; H, 8.86. Found: C, 71.89; H, 9.17.

4-Hydroxy-6-[(*E*)-2-phenylethenyl]-2*H*-pyran-2-one (3j): yellowish prisms^{10a} after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1 $\rightarrow$ 1/2, v/v); mp 234–236 °C; yield 73%; ^1H NMR ($\text{DMSO}-d_6$) δ 5.35 (d, $J = 1.5$ Hz, 1H), 6.25 (d, $J = 1.5$ Hz, 1H), 7.05 (d, $J = 16.1$ Hz, 1H), 7.31 (d, $J = 16.1$ Hz, 1H), 7.35–7.46 (m, 3H), 7.78 (d, $J = 7.3$ Hz, 2H), 11.8 (s, 1H); ^{13}C NMR

(DMSO- d_6) δ 90.0, 101.9, 119.9, 127.5, 128.8, 129.3, 133.9, 135.2, 159.0, 162.8, 170.1. Anal. Calcd for C₁₃H₁₀O₃: C, 72.89; H, 4.71. Found: C, 72.71; H, 4.94.

6-(2-Furyl)-4-hydroxy-2H-pyran-2-one (3k): yellowish microcrystals^{10a} after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1→1/1, v/v); mp 202–204 °C; yield 61%; ¹H NMR (DMSO- d_6) δ 5.27 (d, J = 2.1 Hz, 1H), 6.39 (d, J = 2.1 Hz, 1H), 6.71 (dd, J = 3.4, 1.4 Hz, 1H), 7.08 (d, J = 3.4 Hz, 1H), 7.92 (d, J = 1.4 Hz, 1H), 11.40 (br s, 1H); ¹³C NMR (DMSO- d_6) δ 89.1, 96.5, 111.9, 112.7, 145.7, 146.0, 152.1, 162.4, 170.8. HRMS (EI) Calcd for C₉H₆O₄: m/z 178.0266. Found: 178.0261.

4-Hydroxy-6-(2-thienyl)-2H-pyran-2-one (3l): yellowish microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1→1/1, v/v); mp 214–216 °C; yield 82%; ¹H NMR (DMSO- d_6) δ 5.33 (d, J = 1.4 Hz, 1H), 6.64 (d, J = 1.4 Hz, 1H), 7.22 (dd, J = 4.8, 3.7 Hz, 1H), 7.78 (d, J = 3.7 Hz, 1H), 7.83 (d, J = 4.8 Hz, 1H), 11.88 (br s, 1H); ¹³C NMR (DMSO- d_6) δ 89.0, 96.8, 127.7, 128.8, 130.2, 134.5, 156.1, 162.4, 170.5. Anal. Calcd for C₉H₆O₃S: C, 55.66; H, 3.11. Found: C, 55.72; H, 3.05.

2-[1,1'-Biphenyl]-4-yl-N,N-diisopropylacetamide (10m): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1→8/1, v/v); mp 116–118 °C; yield 37%; ¹H NMR (CDCl₃) δ 1.05 (d, J = 6.6 Hz, 6H), 1.43 (d, J = 6.7 Hz, 6H), 3.40 (br septet, 1H), 3.72 (s, 2H), 4.00 (septet, J = 6.7 Hz, 1H), 7.28–7.36 (m, 3H), 7.38–7.47 (m, 2H), 7.52–7.62 (m, 4H); ¹³C NMR (CDCl₃) δ 20.5 (2C), 20.7 (2C), 42.9, 45.8, 49.4, 127.0 (2C), 127.1, 127.3 (2C), 128.7 (2C), 129.0 (2C), 134.9, 139.4, 140.9, 169.8. Anal. Calcd for C₂₀H₂₅NO: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.09; H, 8.61; N, 4.38.

N,N-Diisopropyl-2-(phenylsulfanyl)acetamide (10n): yellow oil²² after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1→8/1, v/v); yield 41%; ¹H NMR (CDCl₃) δ 1.22 (d, J =

6.6 Hz, 6H), 1.37 (d, $J = 6.7$ Hz, 6H), 3.41 (br septet, $J = 6.6$ Hz, 1H), 3.74 (s, 2H), 3.99 (septet, $J = 6.7$ Hz, 1H), 7.17–7.24 (m, 1H), 7.25–7.33 (m, 2H), 7.41–7.48 (m, 2H); ^{13}C NMR (CDCl_3) δ 20.3 (2C), 20.8 (2C), 39.2, 46.1, 49.8, 126.6, 128.9 (2C), 130.0 (2C), 135.5, 166.9. Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{NOS}$: C, 66.89; H, 8.42; N, 5.57. Found: C, 66.74; H, 8.51; 5.77.

General Procedure for the Preparation of 2,2-Dimethyl-6-(1-alkyl-2-oxo-2-phenylethyl)-1,3-dioxin-4-one **12a–c.** Sodium hydride (60%, 3.25 mmol) was added to a stirred solution of 2,2-dimethyl-6-(2-oxo-2-phenylethyl)-1,3-dioxin-4-one **5a** (2.36 mmol) in THF (20 mL) at room temperature and stirring was continued for 40 min. A solution of alkyl iodide (EtI for **12a**, n-BuI for **12b**, n- $\text{C}_5\text{H}_{11}\text{I}$ for **12c**, 2.38 mmol) in THF (20 mL) was then added dropwise and the mixture was stirred for 15 days at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of hexanes and ethyl acetate as eluant (100/1→6/1, v/v) to give dioxinones **12a–c**.

Analysis of **12a–c** by ^1H NMR revealed the presence of two triplets at 0.87–1.01 and 4.07–4.17 ppm, corresponding to new methyl and methine groups respectively. The two multiplets of each of **12a–c** at 1.77–1.96 and 1.97–2.17 ppm are due to the two protons of the methylene group, which are not magnetically equivalent as they attach to the carbon adjacent to a new chiral center. The ^1H NMR of **13a–c** show singlets for H^3 at 5.48–5.49 ppm, appearance of alkyl groups and absence of H^5 as compared with **3a–l**. Interestingly, all hydrogens in the phenyl groups of **13a–c** resonate as apparent singlets at 7.51–7.52 ppm. The ^{13}C NMR of **13a–c** display C-3 at 90.0 ppm, but C-5 at 112.5–113.6 ppm, downfield from that of unsubstituted **3a–l** at 96.5–102.1 ppm.

6-(1-Benzoylpropyl)-2,2-dimethyl-4H-1,3-dioxin-4-one (12a**):** colorless needles after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1→6/1, v/v); mp 73–74 °C; yield 62%; ^1H NMR (CDCl_3) δ 1.01 (t, $J = 7.4$ Hz, 3H), 1.53 (s, 3H), 1.58 (s, 3H), 1.80–1.96 (m, 1H), 2.01–2.17 (m, 1H), 4.07 (t, $J = 7.1$ Hz, 1H), 5.42 (s, 1H), 7.45–7.53 (m, 2H), 7.57–7.64 (m, 1H), 7.91–7.98 (m, 2H); ^{13}C NMR (CDCl_3) δ 12.0, 22.6, 24.7, 24.8, 53.1, 95.3, 106.8, 128.4 (2C), 128.8 (2C),

133.7, 136.3, 160.7, 168.4, 195.6. Anal. Calcd for C₁₆H₁₈O₄: C, 70.06; H, 6.61. Found: C, 70.15; H, 6.79.

6-(1-Benzoylpentyl)-2,2-dimethyl-4H-1,3-dioxin-4-one (12b): yellow oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1→4/1, v/v); yield 52%; ¹H NMR (CDCl₃) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.25–1.42 (m, 4H), 1.54 (s, 3H), 1.58 (s, 3H), 1.77–1.90 (m, 1H), 1.97–2.09 (m, 1H), 4.15 (t, *J* = 7.2 Hz, 1H), 5.41 (s, 1H), 7.46–7.52 (m, 2H), 7.58–7.64 (m, 1H), 7.92–7.96 (m, 2H); ¹³C NMR (CDCl₃) δ 13.8, 22.5, 24.6, 24.8, 28.9, 29.5, 51.4, 95.1, 106.8, 128.4 (2C), 128.8 (2C), 133.7, 136.1, 160.8, 168.6, 195.6. Anal. Calcd for C₁₈H₂₂O₄: C, 71.50; H, 7.33. Found: C, 71.79; H, 7.56.

6-(1-Benzoylhexyl)-2,2-dimethyl-4H-1,3-dioxin-4-one (12c): yellow oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1→4/1, v/v); yield 51%; ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 6.3 Hz, 3H), 1.23–1.42 (m, 6H), 1.54 (s, 3H), 1.58 (s, 3H), 1.77–1.89 (m, 1H), 1.97–2.09 (m, 1H), 4.17 (t, *J* = 7.2 Hz, 1H), 5.42 (s, 1H), 7.46–7.52 (m, 2H), 7.58–7.64 (m, 1H), 7.93–7.96 (m, 2H); ¹³C NMR (CDCl₃) δ 13.8, 22.2, 24.6, 24.7, 27.0, 29.1, 31.4, 51.4, 95.0, 106.8, 128.3 (2C), 128.7 (2C), 133.7, 136.1, 160.7, 168.6, 195.6. Anal. Calcd for C₁₉H₂₄O₄: C, 72.13; H, 7.65. Found: C, 72.42; H, 7.96.

5-Ethyl-4-hydroxy-6-phenyl-2H-pyran-2-one (13a): off-white microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (20/1→2/1, v/v); mp 212–214 °C; yield 74%; ¹H NMR (DMSO-*d*₆) δ 1.08 (t, *J* = 7.3 Hz, 3H), 2.31 (q, *J* = 7.3 Hz, 2H), 5.48 (s, 1H), 7.52 (s, 5H), 12.05 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 14.2, 18.2, 90.0, 113.6, 128.3 (2C), 128.6 (2C), 129.9, 132.6, 158.0, 162.7, 170.3. Anal. Calcd for C₁₃H₁₂O₃: C, 72.21; H, 5.59. Found: C, 71.89; H, 5.58.

2-Butyl-1-phenyl-1,3-butanedione (b3): colorless oil²³ after chromatography on silica gel using hexanes/ethyl acetate as eluant (50/1→20/1, v/v, the first fraction); yield 15%; ¹H NMR (CDCl₃) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.22–1.41 (m, 4H), 1.89–2.10 (m, 2H), 2.15 (s, 3H), 4.43 (t, *J* = 7.1 Hz, 1H), 7.47–

7.52 (m, 2H), 7.58–7.63 (m, 1H), 7.98–8.01 (m, 2H); ^{13}C NMR (CDCl_3) δ 13.8, 22.6, 27.8, 28.8, 29.8, 63.5, 128.6 (2C), 128.8 (2C), 133.7, 136.4, 196.4, 204.6. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: C, 77.03; H, 8.31. Found: C, 77.38; H, 8.65.

5-Butyl-4-hydroxy-6-phenyl-2H-pyran-2-one (13b): colorless microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (8/1→1/1, v/v, the last fraction); mp 169–170 °C; yield 26%; ^1H NMR ($\text{DMSO}-d_6$) δ 0.77 (t, $J = 7.3$ Hz, 3H), 1.20 (sextet, $J = 7.4$ Hz, 2H), 1.39–1.50 (m, 2H), 2.27–2.33 (m, 2H), 5.49 (s, 1H), 7.52 (s, 5H), 12.08 (br s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 13.6, 22.0, 24.3, 31.2, 90.0, 112.5, 128.4 (2C), 128.6 (2C), 129.9, 132.7, 158.2, 162.8, 170.4. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: C, 73.75; H, 6.60. Found: C, 73.50; H, 6.90

2-Pentyl-1-phenyl-1,3-butanedione (b4): colorless oil²⁴ after chromatography on silica gel using hexanes/ethyl acetate as eluant (50/1→30/1, v/v, the first fraction); yield 22%; ^1H NMR (CDCl_3) δ 0.86 (t, $J = 6.3$ Hz, 3H), 1.20–1.42 (m, 6H), 1.88–2.10 (m, 2H), 2.15 (s, 3H), 4.44 (t, $J = 7.1$ Hz, 1H), 7.47–7.52 (m, 2H), 7.58–7.63 (m, 1H), 7.98–8.01 (m, 2H); ^{13}C NMR (CDCl_3) δ 13.9, 22.3, 27.4, 27.8, 29.0, 31.6, 63.6, 128.6 (2C), 128.8 (2C), 133.6, 136.4, 196.4, 204.6. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.55; H, 8.68. Found: C, 77.58; H, 9.06.

4-Hydroxy-5-pentyl-6-phenyl-2H-pyran-2-one (13c): colorless microcrystals after chromatography on silica gel using hexanes/ethyl acetate as eluant (8/1→1/1, v/v, the last fraction); mp 160–162 °C; yield 27%; ^1H NMR ($\text{DMSO}-d_6$) δ 0.79 (t, $J = 6.6$ Hz, 3H), 1.09–1.25 (m, 4H), 1.39–1.53 (m, 2H), 2.24–2.34 (m, 2H), 5.49 (s, 1H), 7.51 (s, 5H), 12.06 (br s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 13.8, 21.6, 24.4, 28.6, 31.0, 90.0, 112.5, 128.4 (2C), 128.6 (2C), 129.9, 132.7, 158.3, 162.8, 170.4. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$: C, 74.39; H, 7.04. Found: C, 74.00; H, 7.45.