

## Supporting Information

### Mercury (II) Chloride Mediated Cyclization-Rearrangement of *O*-Propargylglycolaldehyde Dithioacetals to 3-Pyranone Dithioketals: An Expeditious Access to 3-Pyranones

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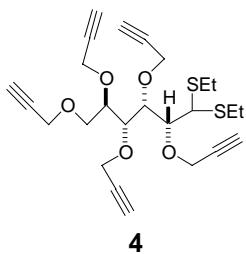
e-mail: [anupbh@hotmail.com](mailto:anupbh@hotmail.com)

### **Experimental Section**

**General procedure for Hg (II) chloride mediated cyclization:** The general procedure is illustrated by the reaction of **23** (entry 8, Table 1): A mixture of **23** (100 mg, 0.41 mmol) in 80% aq. CH<sub>3</sub>CN (10 mL), HgCl<sub>2</sub> (334 mg, 1.23 mmol) and CaCO<sub>3</sub> (164 mg, 1.64 mmol) was stirred at 25 °C for 4 h. After completion of the reaction as revealed by TLC, the resulting precipitate was filtered and washed with CH<sub>3</sub>CN. The combined filtrate and washings were evaporated under reduced pressure. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL) and the combined organic extracts were washed with water (2 x 10 mL) and dried. Removal of solvent yielded a yellow liquid, which on chromatography over silica gel (60-120 mesh) (EtOAc-petroleum ether, b.p. 60-80 °C, 1:20) afforded **33** (40 mg, 63%) as a colorless liquid.

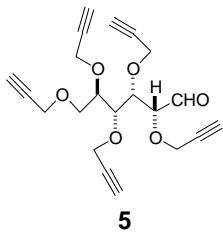
The same procedure using HgCl<sub>2</sub> (2.2 equiv.) and CaCO<sub>3</sub> (2.2 equiv.) afforded **33** (36%) and **34** (19%) as colorless liquids.

### **Spectroscopic Data**

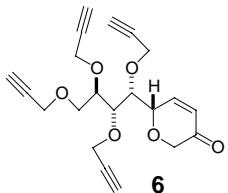


**4:**  $[\alpha]^{25}_D -12.0$  (c 0.76, CHCl<sub>3</sub>); IR (Neat): 3291, 2117, 1449 cm<sup>-1</sup>; MS (EI): *m/z* 476 (M), 415 (M - SEt); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.51 (t, 2H, *J* = 2.4 Hz), 4.49 (d, 2H, *J* = 2.1 Hz), 4.41 (d, 2H, *J* = 2.2 Hz), 4.36 (t, 2H, *J* = 2.4 Hz), 4.22-4.21 (m, 2H), 4.11 (t, 2H, *J* = 4.5 Hz),

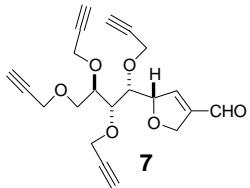
4.00-3.96 (m, 3H), 3.88 (t, 1H,  $J = 4.3$  Hz), 3.73 (dd, 1H,  $J = 11.3, 6.1$  Hz), 2.81-2.68 (m, 4H), 2.47-2.45 (m, 5H), 1.28 (t, 6H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  81.9 (CH), 80.0 (CH), 79.7 (CH), 79.6 (2 x CH), 79.3 (CH), 79.2 (CH), 78.2 (CH), 77.4 (CH), 74.8 (q), 74.6 (q), 74.5 (2 x q), 74.4 (q), 68.5 ( $\text{CH}_2$ ), 60.0 ( $\text{CH}_2$ ), 59.8 ( $\text{CH}_2$ ), 58.8 ( $\text{CH}_2$ ), 58.1 ( $\text{CH}_2$ ), 57.2 ( $\text{CH}_2$ ), 52.5 (CH), 25.1 ( $\text{CH}_2$ ), 24.8 ( $\text{CH}_2$ ), 14.2 ( $\text{CH}_3$ ), 14.1 ( $\text{CH}_3$ ).



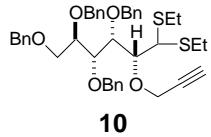
**5:** IR (Neat): 3290, 2119, 1727  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  341 (M - CHO);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.86 (s, 1H), 4.47-4.18 (m, 12H), 3.98-3.92 (m, 2H), 3.85-3.76 (m, 2H), 2.50 (t, 1H,  $J = 2.4$  Hz), 2.49-2.46 (m, 3H), 2.42 (t, 1H,  $J = 2.5$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.8 (CH), 79.8 (CH), 79.5 (CH), 79.4 (2 x CH), 79.2 (CH), 78.8 (CH), 78.7 (CH), 76.8 (CH), 75.9 (CH), 75.7 (q), 75.4 (q), 75.0 (2 x q), 74.4 (q), 66.6 ( $\text{CH}_2$ ), 59.3 (2 x  $\text{CH}_2$ ), 58.3 (2 x  $\text{CH}_2$ ), 56.5 ( $\text{CH}_2$ ).



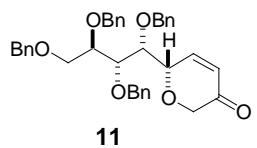
**6:** IR (Neat): 3287, 2118, 1688  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  370 (M), 340 (M - CO), 273;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43 (dd, 1H,  $J = 10.5, 1.4$  Hz), 6.21 (dd, 1H,  $J = 10.5, 2.3$  Hz), 4.72-4.70 (m, 1H), 4.43-4.31 (m, 5H), 4.27-4.11 (m, 5H), 4.08 (dd, 1H,  $J = 4.7, 4.0$  Hz), 4.00-3.90 (m, 3H), 3.75 (dd, 1H,  $J = 10.6, 3.8$  Hz), 2.49 (t, 1H,  $J = 2.2$  Hz), 2.47 (t, 1H,  $J = 2.2$  Hz), 2.46 (t, 1H,  $J = 2.2$  Hz), 2.41 (t, 1H,  $J = 2.2$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.5 (q), 150.2 (CH), 126.2 (CH), 79.8 (CH), 79.6 (CH), 79.5 (CH), 79.3 (CH), 78.3 (CH), 77.3 (CH), 76.7 (CH), 75.2 (q), 74.93 (q), 74.89 (q), 74.5 (q), 73.0 (CH), 72.0 ( $\text{CH}_2$ ), 67.3 ( $\text{CH}_2$ ), 59.5 ( $\text{CH}_2$ ), 59.4 ( $\text{CH}_2$ ), 58.4 ( $\text{CH}_2$ ), 56.9 ( $\text{CH}_2$ ).



**7:** IR (Neat): 3287, 2118, 1681 cm<sup>-1</sup>; MS (positive ion ESI): *m/z* 393 (M + Na); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.86 (s, 1H), 7.09 (d, 1H, *J* = 1.7 Hz), 5.35-5.31 (m, 1H), 4.89 (ddd, 1H, *J* = 12.7, 5.6, 1.7 Hz), 4.80 (ddd, 1H, *J* = 12.6, 3.9, 1.9 Hz), 4.44-4.14 (m, 8H), 3.97-3.89 (m, 3H), 3.83 (dd, 1H, *J* = 5.2, 3.5 Hz), 3.73 (dd, 1H, *J* = 10.6, 4.6 Hz), 2.50-2.41 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 186.9 (CH), 146.2 (CH), 142.7 (q), 86.8 (CH), 79.9 (CH), 79.7 (2 x CH), 79.3 (CH), 79.2 (CH), 77.6 (CH), 77.5 (CH), 74.9 (q), 74.8 (2 x q), 74.7 (q), 72.6 (CH<sub>2</sub>), 68.1 (CH<sub>2</sub>), 59.4 (CH<sub>2</sub>), 59.1 (CH<sub>2</sub>), 58.5 (CH<sub>2</sub>), 57.4 (CH<sub>2</sub>).

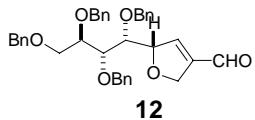


**10:** [α]<sup>25</sup><sub>D</sub> +1.0 (c 0.20, CHCl<sub>3</sub>); IR (Neat): 3289, 3062, 3031, 2120, 1603, 1495, 1452 cm<sup>-1</sup>; MS (FAB): *m/z* 685 (M + H), 623 (M - SEt), 577 (M - OBn); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.36-7.23 (m, 20H), 4.81 (d, 1H, *J* = 11.2 Hz), 4.76 (d, 1H, *J* = 11.3 Hz), 4.72 (d, 1H, *J* = 11.2 Hz), 4.68 (d, 1H, *J* = 11.2 Hz), 4.66 (d, 1H, *J* = 11.4 Hz), 4.55-4.51 (m, 3H), 4.47-4.45 (m, 2H), 4.20-4.17 (m, 1H), 3.96-3.87 (m, 5H), 3.76-3.70 (m, 1H), 2.64 (q, 2H, *J* = 7.4 Hz), 2.59-2.50 (m, 2H), 2.37 (t, 1H, *J* = 2.2 Hz), 1.20 (t, 3H, *J* = 7.4 Hz), 1.15 (t, 3H, *J* = 7.4 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 138.5 (2 x q), 138.2 (q), 138.1 (q), 128.2 (3 x CH), 128.1 (3 x CH), 128.0 (4 x CH), 127.9 (2 x CH), 127.5 (2 x CH), 127.4 (3 x CH), 127.3 (CH), 127.27 (CH), 127.2 (CH), 82.0 (CH), 80.2 (CH), 80.0 (CH), 79.2 (CH), 78.8 (CH), 75.1 (CH<sub>2</sub>), 74.5 (q), 73.6 (CH<sub>2</sub>), 73.1 (CH<sub>2</sub>), 71.8 (CH<sub>2</sub>), 69.8 (CH<sub>2</sub>), 59.5 (CH<sub>2</sub>), 52.8 (CH), 25.1 (CH<sub>2</sub>), 24.7 (CH<sub>2</sub>), 14.3 (CH<sub>3</sub>), 14.1 (CH<sub>3</sub>).

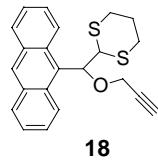


**11:** IR (Neat): 3062, 3032, 1696, 1604 cm<sup>-1</sup>; MS (FAB): *m/z* 601 (M + Na), 579 (M + H), 471 (M - OBn); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.31-7.25 (m, 20 H), 7.03 (d, 1H, *J* = 10.5 Hz), 5.97 (d, 1H, *J* = 10.5 Hz), 4.71-4.65 (m, 3H), 4.57-4.47 (m, 5H), 4.40-4.39 (m, 1H), 4.32 (d, 1H, *J* = 16.3 Hz), 4.07-3.97 (m, 3H), 3.89-3.87 (m, 2H), 3.70 (dd, 1H, *J* = 11.4, 5.6 Hz); <sup>13</sup>C

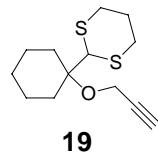
NMR (75 MHz, CDCl<sub>3</sub>): δ 194.8 (q), 150.6 (CH), 138.3 (q), 138.2 (q), 138.0 (q), 137.8 (q), 128.3-127.4 (CH), 125.9 (CH), 79.3 (CH), 78.1 (CH), 77.9 (CH), 74.3 (CH<sub>2</sub>), 73.9 (CH<sub>2</sub>), 73.3 (CH<sub>2</sub>), 73.0 (CH), 71.8 (CH<sub>2</sub>), 71.6 (CH<sub>2</sub>), 68.5 (CH<sub>2</sub>).



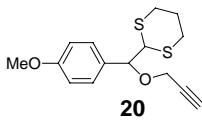
**12:** IR (Neat): 3062, 3031, 1682, 1605 cm<sup>-1</sup>; MS (FAB): *m/z* 579 (M + H); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.50 (s, 1H), 7.32-7.26 (m, 20H), 6.38 (d, 1H, *J* = 1.4 Hz), 5.13-5.12 (m, 1H), 4.83 (dd, 1H, *J* = 12.7, 5.9 Hz), 4.76-4.47 (m, 9H), 3.91-3.89 (m, 3H), 3.79-3.71 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 186.9 (CH), 146.6 (CH), 142.5 (q), 138.4 (q), 138.3 (q), 138.2 (q), 129.7-127.0 (CH), 87.3 (CH), 80.5 (CH), 78.8 (CH), 78.7 (CH), 74.3 (CH<sub>2</sub>), 73.5 (CH<sub>2</sub>), 73.4 (CH<sub>2</sub>), 72.4 (CH<sub>2</sub>), 72.2 (CH<sub>2</sub>), 69.3 (CH<sub>2</sub>).



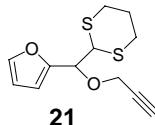
**18:** IR (KBr): 3285, 2119 cm<sup>-1</sup>; MS (EI): *m/z* 365 (M + H), 245, 119; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.95 (d, 1H, *J* = 8.5 Hz), 8.49 (d, 1H, *J* = 8.5 Hz), 8.47 (s, 1H), 8.03-8.00 (m, 2H), 7.58-7.44 (m, 4H), 6.36 (d, 1H, *J* = 9.8 Hz), 5.19 (d, 1H, *J* = 9.8 Hz), 4.25 (dd, 1H, *J* = 16.0, 2.3 Hz), 3.83 (dd, 1H, *J* = 16.0, 2.2 Hz), 3.00-2.86 (m, 2H), 2.63-2.54 (m, 2H), 2.47 (t, 1H, *J* = 2.2 Hz), 2.07-2.02 (m, 1H), 1.96-1.85 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 132.2 (q), 131.6 (q), 130.8 (q), 130.0 (q), 129.5 (CH), 129.3 (2 x CH), 127.1 (q), 126.3 (CH), 125.8 (CH), 125.7 (CH), 125.0 (CH), 124.8 (CH), 123.3 (CH), 79.3 (CH), 77.1 (CH), 75.4 (q), 56.1 (CH<sub>2</sub>), 52.0 (CH), 30.2 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>).



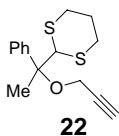
**19:** IR (Neat): 3288, 2120 cm<sup>-1</sup>; MS (EI): *m/z* 256 (M); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.30 (s, 1H), 4.22 (d, 2H, *J* = 2.3 Hz), 2.93-2.80 (m, 4H), 2.41 (t, 1H, *J* = 2.3 Hz), 2.13-2.06 (m, 1H), 1.92-1.75 (m, 3H), 1.72-1.51 (m, 7H), 1.23-1.21 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 80.3 (CH), 78.1 (q), 72.9 (q), 56.9 (CH), 49.6 (CH<sub>2</sub>), 31.7 (2 x CH<sub>2</sub>), 30.9 (2 x CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 21.2 (2 x CH<sub>2</sub>).



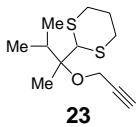
**20:** IR (KBr): 3252, 2109, 1615 cm<sup>-1</sup>; MS (EI): *m/z* 294 (M), 175, 119; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.31 (d, 2H, *J* = 8.6 Hz), 6.91 (d, 2H, *J* = 8.6 Hz), 4.73 (d, 1H, *J* = 7.2 Hz), 4.36 (d, 1H, *J* = 7.2 Hz), 4.22 (dd, 1H, *J* = 15.9, 2.3 Hz), 3.88 (dd, 1H, *J* = 15.9, 2.3 Hz), 3.81 (s, 3H), 2.92-2.73 (m, 4H), 2.43 (t, 1H, *J* = 2.3 Hz), 2.11-2.02 (m, 1H), 1.94-1.80 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 159.5 (q), 128.5 (q), 128.5 (2 × CH), 113.3 (2 × CH), 81.2 (CH), 78.7 (CH), 74.7 (q), 55.4 (CH<sub>2</sub>), 54.8 (CH<sub>3</sub>), 52.2 (CH), 29.7 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 25.4 (CH<sub>2</sub>).



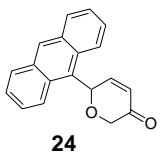
**21:** IR (KBr): 3280, 3104, 2119 cm<sup>-1</sup>; MS (EI): *m/z* 254 (M), 135, 119; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.47 (s, 1H), 6.49 (d, 1H, *J* = 3.0 Hz), 6.39 (dd, 1H, *J* = 3.0, 1.7 Hz), 4.85 (d, 1H, *J* = 7.9 Hz), 4.52 (d, 1H, *J* = 7.9 Hz), 4.27 (dd, 1H, *J* = 16.0, 2.3 Hz), 3.97 (dd, 1H, *J* = 16.0, 2.2 Hz), 2.96-2.77 (m, 4H), 2.46 (t, 1H, *J* = 2.2 Hz), 2.15-2.06 (m, 1H), 1.98-1.86 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 149.2 (q), 142.5 (CH), 110.4 (CH), 109.7 (CH), 78.4 (CH), 74.9 (q), 74.6 (CH), 55.6 (CH<sub>2</sub>), 48.6 (CH), 28.9 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>).



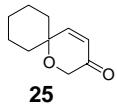
**22:** IR (KBr): 3286, 2120 cm<sup>-1</sup>; MS (EI): *m/z* 278 (M), 159, 119; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.48-7.33 (m, 5H), 4.38 (s, 1H), 3.95 (dd, 1H, *J* = 15.3, 2.4 Hz), 3.89 (dd, 1H, *J* = 15.3, 2.4 Hz), 2.91-2.81 (m, 2H), 2.79-2.68 (m, 2H), 2.38 (t, 1H, *J* = 2.4 Hz), 2.06-1.98 (m, 1H), 1.86 (s, 3H), 1.83-1.75 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 140.3 (q), 127.3 (2 × CH), 127.2 (CH), 126.1 (2 × CH), 81.8 (q), 79.8 (CH), 73.2 (q), 58.5 (CH), 51.2 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 19.7 (CH<sub>3</sub>).



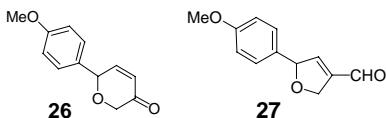
**23:** IR (Neat): 3290, 2120 cm<sup>-1</sup>; MS (EI): *m/z* 244 (M), 201 (M – isopropyl); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.48 (dd, 1H, *J* = 15.0, 2.4 Hz), 4.32 (dd, 1H, *J* = 15.0, 2.4 Hz), 4.32 (s, 1H), 2.91-2.79 (m, 4H), 2.40 (t, 1H, *J* = 2.4 Hz), 2.24 (septet, 1H, *J* = 6.8 Hz), 2.15-2.05 (m, 1H), 1.93-1.80 (m, 1H), 1.32 (s, 3H), 1.00 (d, 3H, *J* = 6.0 Hz), 0.98 (d, 3H, *J* = 6.5 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 81.8 (q), 80.7 (CH), 72.8 (q), 58.2 (CH), 52.1 (CH<sub>2</sub>), 32.0 (CH), 31.6 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 17.7 (CH<sub>3</sub>), 17.5 (CH<sub>3</sub>), 16.4 (CH<sub>3</sub>).



**24:** IR (Neat): 3054, 3021, 1682, 1596 cm<sup>-1</sup>; MS (EI): *m/z* 274 (M); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.54 (s, 1H), 8.49 (d, 2H, *J* = 8.5 Hz), 8.05 (d, 2H, *J* = 8.5 Hz), 7.57-7.47 (m, 4H), 7.35 (dd, 1H, *J* = 10.4, 1.6 Hz), 6.82-6.81 (m, 1H), 6.45 (dd, 1H, *J* = 10.4, 2.8 Hz), 4.66 (d, 1H, *J* = 16.4 Hz), 4.57 (dd, 1H, *J* = 16.4, 1.9 Hz).

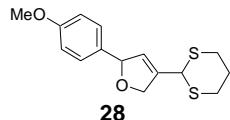


**25:** IR (Neat): 1692 cm<sup>-1</sup>; MS (EI): *m/z* 166 (M), 136 (M – CO); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.92 (d, 1H, *J* = 10.5 Hz), 6.00 (d, 1H, *J* = 10.5 Hz), 4.20 (s, 2H), 1.89-1.85 (m, 2H), 1.69-1.47 (m, 7H), 1.35-1.30 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 195.2 (q), 156.0 (CH), 124.6 (CH), 72.9 (q), 66.5 (CH<sub>2</sub>), 33.2 (2 x CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 21.2 (2 x CH<sub>2</sub>).

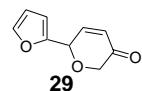


Mixture of pyranone **26** and dihydrofuran **27**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.88 (s, 1H, dihydrofuran), 7.30 (d, 2H, *J* = 8.6 Hz, pyranone), 7.22 (d, 2H, *J* = 8.6 Hz, dihydrofuran), 7.10 (dd, 1H, *J* = 10.4, 2.2 Hz, pyranone), 6.93 (dd, 2H, *J* = 8.6 Hz, pyranone), 6.90 (d, 2H, *J* = 8.5 Hz, dihydrofuran), 6.86-6.83 (m, 1H, dihydrofuran), 6.26 (dd, 1H, *J* = 10.4, 2.1 Hz, pyranone), 5.97-5.94 (m, 1H, dihydrofuran), 5.34-5.33 (m, 1H, pyranone), 5.04 (ddd, 1H, *J* =

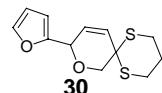
12.8, 5.6, 1.8 Hz, dihydrofuran), 4.90 (ddd, 1H,  $J = 12.8, 3.8, 2.2$  Hz, dihydrofuran), 4.29 (d, 1H,  $J = 16.3$  Hz, pyranone), 4.19 (dd, 1H,  $J = 16.3, 1.1$  Hz, pyranone), 3.81 (s, 3H, pyranone), 3.80 (s, 3H, dihydrofuran);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.4 (q, pyranone), 187.0 (CH, dihydrofuran), 159.9 (q, pyranone), 159.8 (q, dihydrofuran), 150.7 (CH, pyranone), 147.1 (CH, dihydrofuran), 142.3 (q, dihydrofuran), 131.5 (q, dihydrofuran), 129.7 (q, pyranone), 128.9 (2 x CH, pyranone), 127.8 (2 x CH, dihydrofuran), 126.8 (CH, pyranone), 114.2 (CH), 87.8 (CH, dihydrofuran), 75.3 (CH, pyranone), 72.7 (CH<sub>2</sub>, dihydrofuran), 70.6 (CH<sub>2</sub>, pyranone), 55.2 (CH<sub>3</sub>).



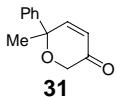
**28:** IR (Neat): 1609 cm<sup>-1</sup>; MS (positive ion ESI):  $m/z$  295 (M + H);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22 (d, 2H,  $J = 8.6$  Hz), 6.87 (d, 2H,  $J = 8.7$  Hz), 5.95 (d, 1H,  $J = 1.4$  Hz), 4.89 (ddd, 1H,  $J = 12.4, 5.4, 1.3$  Hz), 5.79 (br s, 1H), 4.79-4.75 (m, 2H), 3.79 (s, 3H), 2.99-2.87 (m, 4H), 2.17-2.10 (m, 1H), 1.99-1.88 (m, 1H).



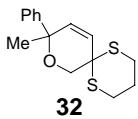
**29:** IR (Neat): 1677 cm<sup>-1</sup>; MS (EI):  $m/z$  164 (M), 134 (M - CO);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (s, 1H), 7.16 (dd, 1H,  $J = 10.5, 3.2$  Hz), 6.39 (s, 2H), 6.30 (dd, 1H,  $J = 10.5, 2.0$  Hz), 5.49 (br s, 1H), 4.28 (d, 1H,  $J = 16.6$  Hz), 4.18 (d, 1H,  $J = 16.6$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.6 (q), 155.5 (CH), 149.0 (q), 142.2 (CH), 124.9 (CH), 110.7 (CH), 109.9 (CH), 76.3 (CH), 66.7 (CH<sub>2</sub>).



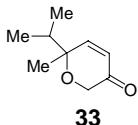
**30:** IR (Neat): 3038 cm<sup>-1</sup>; MS (positive ion ESI):  $m/z$  255 (M + H);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43 (s, 1H), 6.35-6.31 (m, 2H), 6.03 (d, 1H,  $J = 10.1$  Hz), 5.98 (dd, 1H,  $J = 10.1, 2.1$  Hz), 5.30 (s, 1H), 4.15 (d, 1H,  $J = 11.8$  Hz), 4.08 (d, 1H,  $J = 11.9$  Hz), 3.02-2.90 (m, 2H), 2.78-2.69 (m, 2H), 2.13-2.04 (m, 1H), 1.99-1.86 (m, 1H).



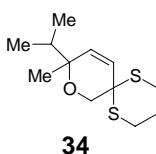
**31:** IR (Neat): 3059, 2979, 1696 cm<sup>-1</sup>; MS (EI): *m/z* 188 (M), 173 (M - CH<sub>3</sub>), 158 (M - CO), 111 (M - Ph); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.41-7.33 (m, 6H), 6.20 (d, 1H, *J* = 10.4 Hz), 4.15 (d, 1H, *J* = 16.8 Hz), 3.99 (d, 1H, *J* = 16.8 Hz), 1.70 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 194.2 (q), 154.1 (CH), 141.2 (q), 128.4 (2 x CH), 127.9 (CH), 125.9 (2 x CH), 125.4 (CH), 75.6 (q), 67.6 (CH<sub>2</sub>), 29.0 (CH<sub>3</sub>).



**32:** IR (Neat): 3056, 3029, 1600 cm<sup>-1</sup>; MS (EI): *m/z* 278 (M), 263 (M-CH<sub>3</sub>), 248 (M- CO); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.46-7.24 (m, 5H), 6.21 (d, 1H, *J* = 10.2 Hz), 5.89 (d, 1H, *J* = 10.1 Hz), 4.20 (d, 1H, *J* = 11.9 Hz), 3.77 (d, 1H, *J* = 11.8 Hz), 3.02-2.71 (m, 4H), 2.08-2.05 (m, 1H), 1.92-1.87 (m, 1H), 1.60 (s, 3H).

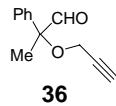


**33:** IR (Neat): 1691 cm<sup>-1</sup>; MS (EI): *m/z* 154 (M), 139 (M - CH<sub>3</sub>), 124 (M - CO), 111 (M - isopropyl); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.98 (d, 1H, *J* = 10.6 Hz), 6.05 (d, 1H, *J* = 10.6 Hz), 4.26 (d, 1H, *J* = 17.2 Hz), 4.18 (d, 1H, *J* = 17.2 Hz), 1.97 (septet, 1H, *J* = 6.8 Hz), 1.32 (s, 3H), 0.99 (d, 3H, *J* = 6.8 Hz), 0.98 (d, 3H, *J* = 6.7 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 194.6 (q), 155.5 (CH), 124.9 (CH), 76.3 (q), 66.7 (CH<sub>2</sub>), 35.7 (CH), 18.8 (CH<sub>3</sub>), 17.1 (CH<sub>3</sub>), 16.8 (CH<sub>3</sub>).

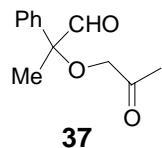


**34:** IR (Neat): 3031 cm<sup>-1</sup>; MS (EI): *m/z* 244 (M), 214 (M - CO), 201 (M - isopropyl); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.79 (d, 1H, *J* = 10.3 Hz), 5.74 (d, 1H, *J* = 10.3 Hz), 4.16 (d, 1H, *J* = 11.9 Hz), 4.01 (d, 1H, *J* = 11.9 Hz), 3.02-2.90 (m, 2H), 2.75-2.65 (m, 2H), 2.11-2.02 (m,

1H), 1.96-1.87 (m, 1H), 1.82 (septet, 1H,  $J = 6.9$  Hz), 1.20 (s, 3H), 0.95 (d, 6H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.7 (CH), 126.3 (CH), 76.8 (q), 67.1 ( $\text{CH}_2$ ), 45.6 (q), 35.9 (CH), 26.5 ( $\text{CH}_2$ ), 26.2 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_2$ ), 20.7 ( $\text{CH}_3$ ), 17.3 ( $\text{CH}_3$ ), 17.2 ( $\text{CH}_3$ ); HRMS (positive ion ESI): Calcd for  $\text{C}_{12}\text{H}_{20}\text{OS}_2$  ( $\text{M} + \text{Na}^+$ ) 267.0853, found 267.0850.



**36:** IR (Neat): 3290, 2123, 1736  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  159 (M - CHO);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.60 (s, 1H), 7.45-7.31 (m, 5H), 4.18 (dd, 1H,  $J = 15.5, 2.3$  Hz), 4.12 (dd, 1H,  $J = 15.5, 2.4$  Hz), 2.47 (t, 1H,  $J = 2.4$  Hz), 1.74 (s, 3H).



**37:** IR (Neat): 1734 (broad)  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  177 (M - CHO);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.62 (s, 1H), 7.43-7.34 (m, 5H), 4.02 (d, 1H,  $J = 16.7$  Hz), 3.96 (d, 1H,  $J = 16.7$  Hz), 2.24 (s, 3H), 1.71 (s, 3H).