Note: The version of SI posted April 24, 2003 contained errors.

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Efficient Synthesis of Bi-butenolides Derivatives through Oxidative Dimeric Cyclization-Coupling Reaction of 2,3-Allenoic Acids

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Supporting Information

2,2'-Diphenyl-4,4'-dipropyl-2H,2'H-[3,3']bifuranyl-5,5'-dione (3a): (R*,S*)-isomer (less polar): solid, M.p. 143-145 ^{o}C (ethyl acetate and petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.33 (m, 6 H), 6.95-6.88 (m, 4 H), 5.21 (s, 2 H), 2.02-1.80 (m, 4 H), 1.56-1.39 (m, 2 H), 1.21-1.05 (m, 2 H), 0.84 (t, *J* = 7.35 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.16, 20.86, 26.60, 83.39, 126.43, 129.09, 129.82, 132.27, 133.10, 151.81, 172.01; EIMS *m/z* 402 (M^+, 11.02), 105 (100); IR(neat) 1758, 1456 cm^{-1}; (R*,R*)-isomer (more polar): solid, M.p. 185-187 ^{o}C (ethyl acetate and petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.27 (m, 6 H), 7.15-7.08 (m, 4 H), 5.85 (s, 2 H), 2.20-2.08 (m, 2 H), 1.97-1.85 (m, 2 H), 1.48-1.33 (m, 2 H), 1.03-0.93 (m, 2 H), 0.74 (t, *J* = 7.35 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.02, 20.43, 27.19, 82.77, 126.24, 129.18, 129.73, 132.51,

133.20, 150.73, 171.98; EIMS *m/z* 402 (M^+, 19.33), 105 (100); IR(neat) 1747, 1456 cm^{-1}; Anal. calcd. for $C_{26}H_{26}O_4$: (%) C 77.59, H 6.51. Found: C 77.27, H 6.36.

4,4'-Dimethyl-2,2'-diphenyl-2H,2'H-[3,3']bifuranyl-5,5'-dione (3b): A solution of 2-methyl-4-phenyl-2,3-butadienoic acids (**1b**) (87 mg, 0.5 mmol), propyl iodide (**2a**) (0.26 ml, 447 mg, 2.63 mmol) and $PdCl_2$ (4 mg, 0.022 mmol) in DMA (4 ml) was stirred at 80 ^oC for 4 hours. Then the mixture was diluted with ether (50 ml), washed by water (2 x 10 ml) and dried by $MgSO_4$. After evaporation, the residues were purified via flash chromatography on silica gel with CH_2Cl_2 as the eluent to afford 55 mg (64%) of **3b** (R*S* : R*R* = 1 : 1.62). (R*,S*)-isomer (more polar): solid, M.p. 160-162 ^oC (ethyl acetate and petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.27 (m, 6 H), 6.87-6.82 (m, 4 H), 5.34 (q, *J* = 2.03 Hz, 2 H), 1.69 (d, *J* = 2.03 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.61, 83.23, 126.64, 128.72, 129.01, 129.83, 132.92, 151.52, 172.39; EIMS *m/z* 346 (M^+, 11.22), 105 (100); IR(neat) 1755, 1646 cm^{-1}; (R*,R*)-isomer (less polar): solid, M.p. 224-226 ^oC (ethyl acetate and petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.24 (m, 6 H), 7.06-6.99 (m, 4 H), 5.70 (q, *J* = 1.88 Hz, 2 H), 1.79 (d, *J* = 1.88 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.63, 82.81, 126.76, 129.19, 129.29, 130.00, 132.99, 150.37, 172.39; EIMS *m/z* 346 (M^+, 20.82), 105 (100); IR(neat) 1756, 1647, 1603 cm^{-1};Anal. calcd. for $C_{22}H_{18}O_4$: (%) C 76.29, H 5.24. Found: C 76.19, H 5.37.

4,4'-Dibenzyl-2,2'-diphenyl-2H,2'H-[3,3']bifuranyl-5,5'-dione (3c): A solution of 2-benzyl-4-phenyl-2,3-butadienoic acids (**1c**) (125 mg, 0.5 mmol), propyl iodide (**2a**) (0.26 ml, 447 mg, 2.63 mmol) and $PdCl_2$ (4 mg, 0.022 mmol) in DMA (4 ml) was stirred at 80 ^oC for 11.5 hours. Then the mixture was diluted with ether (50 ml), washed by water (2 x 10 ml) and dried by $MgSO_4$. After evaporation, the residues were purified via flash

chromatography on silica gel with CH_2Cl_2/petroleum ether (5:1) as the eluent to afford 93 mg (75%) of **3c** (R*S* : R*R* = 1 : 1.53). (R*,S*)-isomer (less polar): solid, M.p. 170-172 ^oC (ethyl acetate and petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.43-7.18 (m, 12 H), 6.94-6.82 (m, 8 H), 4.55 (d, *J* = 1.65 Hz, 2 H), 3.44 (d, *J* = 15.00 Hz, 2 H), 2.37 (dd, *J* = 1.65, 15.00 Hz, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.30, 82.91, 126.03, 127.22, 128.51, 128.89, 129.19, 129.86, 131.35, 132.94, 137.02, 153.19, 172.21; EIMS *m/z* 498 (M^+, 13.34), 105 (100); IR(neat) 1754, 1496, 1454 cm^{-1}; (R*,R*)-isomer (more polarity): solid, M.p. 228-230 ^oC (ethyl acetate and petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.14 (m, 12 H), 6.94-6.81 (m, 8 H), 5.88 (s, 2 H), 3.61 (s, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.92, 83.12, 126.50, 127.03, 128.27, 128.77, 129.31, 129.79, 131.75, 132.55, 135.72, 151.31, 171.74; EIMS *m/z* 498 (M^+, 11.65), 105 (100); IR(neat) 1769, 1752, 1495, 1454 cm^{-1}; Anal. calcd. for $C_{34}H_{26}O_4$: (%) C 81.91, H 5.26. Found: C 81.82, H 5.37.

2,2'-Dinaphthyl-4,4'-dimethyl-2H,2'H-[3,3']bifuranyl-5,5'-dione (3d): A solution of 2-methyl-4-naphthyl-2,3-butadienoic acids (**1d**) (112 mg, 0.5 mmol), propyl iodide (**2a**) (0.26 ml, 447 mg, 2.63 mmol) and $PdCl_2$ (4 mg, 0.022 mmol) in DMA (4 ml) was stirred at 80 ^oC for 4 hours. Then the mixture was diluted with ether (50 ml), washed by water (2 x 10 ml) and dried by $MgSO_4$. After evaporation, the residues were purified via flash chromatography on silica gel with ethyl acetate/petroleum ether (1:2) as the eluent to afford 79 mg (71%) of **3d** (R*S* : R*R* = 1 : 1.28). (R*,S*)-isomer (more polar): solid, M.p. 206-208 ^oC (ethyl acetate and petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.40 Hz, 2 H), 7.49 (d, *J* = 8.10 Hz, 2 H), 7.40 (t, *J* = 7.80 Hz, 2 H), 7.25 (t, *J* = 7.65 Hz, 2 H), 7.12 (d, *J* = 8.40 Hz, 2 H), 7.01 (t, *J* = 7.65 Hz, 2 H), 6.78 (d, *J* = 7.80 Hz,

2 H), 6.11 (s, 2 H), 1.96 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.82, 79.58, 121.51, 124.49, 125.11, 125.99, 126.77, 128.30, 128.90, 129.98, 130.05, 130.50, 133.58, 151.25, 172.39; EIMS *m/z* 446 (M^+, 61.83), 155 (100); IR(neat) 1744, 1647, 1597 cm^{-1}; (R*,R*)-isomer (less polar): solid, M.p. 149-151 ^oC (ethyl acetate and petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.10 Hz, 4 H), 7.77 (d, *J* = 8.10 Hz, 2 H), 7.61-7.40 (m, 6 H), 7.15 (d, *J* = 8.10 Hz, 2 H), 6.30 (s, 2 H), 2.06 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.39, 79.11, 122.05, 125.17, 125.78, 126.53, 127.37, 128.65, 129.31, 130.32, 131.10, 131.39, 134.08, 150.67, 172.30; EIMS *m/z* 446 (M^+, 68.03), 155 (100); IR(neat) 1748, 1646 cm^{-1}; Anal. calcd. for $C_{30}H_{22}O_4$: (%) C 80.70, H 4.97. Found: C 80.73, H 5.16.

2,2'-Dinaphthyl-4,4'-dipropyl-2H,2'H-[3,3']bifuranyl-5,5'-dione (3e): A solution of 4-naphthyl-2-propyl-2,3-butadienoic acids (**1e**) (63 mg, 0.25 mmol), propyl iodide (**2a**) (0.13 ml, 224 mg, 1.32 mmol) and $PdCl_2$ (2 mg, 0.011 mmol) in DMA (2 ml) was stirred at 80 ^oC for 4.5 hours. Then the mixture was diluted with ether (50 ml), washed by water (2 x 10 ml) and dried by $MgSO_4$. After evaporation, the residues were purified via flash chromatography on silica gel with CH_2Cl_2/petroleum ether (5:1) as the eluent to afford 40 mg (64%) of **3e** (R*S* : R*R* = 1 : 1.43). (R*,S*)-isomer (more polar): solid, M.p. 198-200 ^oC (ethyl acetate and petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.40 Hz, 2 H), 7.73 (d, *J* = 8.10 Hz, 2 H), 7.45 (t, *J* = 7.95 Hz, 2 H), 7.32 (t, *J* = 8.40 Hz, 2 H), 7.22 (d, *J* = 8.10 Hz, 2 H), 7.14 (d, *J* = 8.40 Hz, 2 H), 6.86 (d, *J* = 6.90 Hz, 2 H), 5.93 (s, 2 H), 2.12 (t, *J* = 8.70 Hz, 4 H), 1.70-1.54 (m, 2 H), 1.25-1.09 (m, 2 H), 0.85 (t, *J* = 7.35 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.22, 20.70, 27.24, 80.37, 121.64, 124.83, 125.30, 126.19, 126.85, 128.45, 129.09, 130.23, 130.46, 133.25, 133.71, 151.77, 171.93; EIMS *m/z* 502 (M^+, 50.81), 155 (100); IR(neat) 1744, 1598 cm^{-1}; (R*,R*)-isomer

(less polar): solid, M.p. 203-205 ^{o}C (ethyl acetate and petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.93 (m, 4 H), 7.93-7.82 (m, 2 H), 7.63-7.51 (m, 4 H), 7.44 (t, *J* = 7.50 Hz, 2 H), 7.23 (d, J = 6.75 Hz, 2 H), 6.38 (s, 2 H), 2.37-2.28 (m, 2 H), 2.22-2.12 (m, 2 H), 1.64-1.52 (m, 2 H), 1.30-1.15 (m, 2 H), 0.88 (t, *J* = 7.35 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.33, 20.36, 27.99, 79.42, 121.90, 125.09, 125.88, 126.45, 127.29, 128.58, 129.39, 130.94, 131.21, 133.78, 134.06, 150.56, 171.83; EIMS *m/z* 502 (M^+, 59.62), 155 (100); IR(neat) 1755, 1512 cm^{-1}; Anal. calcd. for $C_{34}H_{30}O_4$: (%) C 81.25, H 6.02. Found: C 81.14, H 6.20.

4,4'-Dibenzyl-2,2'-dimethyl-2H,2'H-[3,3']bifuranyl-5,5'-dione (3f): A solution of 2-benzyl-4-methyl-2,3-butadienoic acids (**1f**) (94 mg, 0.5 mmol), propyl iodide (**2a**) (0.26 ml, 447 mg, 2.63 mmol) and $PdCl_2$ (4 mg, 0.022 mmol) in DMA (4 ml) was stirred at 80 ^{o}C for 3.5 hours. Then the mixture was diluted with ether (50 ml), washed by water (2 x 10 ml) and dried by $MgSO_4$. After evaporation, the residues were purified via flash chromatography on silica gel with ethyl acetate/petroleum ether (2:1) as the eluent to afford 67 mg (72%) of **3f** (R*S* : R*R* = 1.04 : 1). solid, M.p. 156-160 ^{o}C (ethyl acetate and petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.15 (m, 6 H), 7.13-7.02 (m, 4 H), [5.03 (q, *J* = 6.45 Hz), 4.68 (q, *J* = 6.75 Hz), 2 H], [3.72 (d, *J* = 15.00 Hz), 3.58 (d, *J* = 15.15 Hz), 2 H], [3.55 (d, *J* = 15.15 Hz), 3.31 (d, *J* = 15.00 Hz), 2 H], [1.29 (d, *J* = 6.90 Hz), 1.14 (d, *J* = 6.90 Hz), 6 H]; EIMS *m/z* 374 (M^+, 23.37), 91 (100); IR(neat) 1746, 1639, 1602, 1497 cm^{-1}; Anal. calcd. for $C_{24}H_{22}O_4$: (%) C 76.99, H 5.92. Found: C 76.80, H 6.00.