Supporting Information

Ruthenium-Catalyzed Carbonylative Cycloaddition of α -Keto Lactones with Alkenes or Alkynes: The Participation of an Ester-Carbonyl Group in Cycloaddition Reactions as the Two-Atom Assembling Unit

Naoto Chatani,* Katsuya Amako, Mamoru Tobisu, Taku Asaumi, Yoshiya Fukumoto,
and Shinji Murai

*Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Suita, Osaka 565-0871, Japan*

Table of Contents

- S2-7 General Information, materials, characterization data for **1b-c**, typical procedure, and
characterization data for **2a-c**, **3a-b**, **3d**, **4**, **5**, **6**, **7**, and **8**.

General Information. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, quint = quintet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)). Preparative high performance liquid chromatography (HPLC) was performed on a Japan Analytical Industry LC-908 instrument, equipped with an RI absorbance detector.

Materials. Toluene was distilled over CaH_2 prior to use. $\text{Ru}_3(\text{CO})_{12}$ was prepared according to the literature procedure¹ and used after recrystallization from hexane. $\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3$ was purchased from Strem Chemicals Inc. and used without further purification. Cyclic keto esters, **1a**², **1b**, **1c**, and **1d**³ were obtained by the literature procedure.³

4,6-Dimethoxy-benzofuran-2,3-dione (1b). Yellow solid; mp 189-190 °C (EtOAc); R_f 0.69 (EtOAc); ^1H NMR (CDCl_3) δ 3.95 (s, 3H, 4-OMe or 6-OMe), 3.98 (s, 3H, 4-OMe or 6-OMe), 6.17 (d, J = 2.0 Hz, 1H, 5-H or 7-H), 6.30 (d, J = 2.0 Hz, 1H, 5-H or 7-H); ^{13}C NMR (CDCl_3) δ 56.62 (4-OMe or 6-OMe), 56.65 (4-OMe or 6-OMe), 91.24 (5-C or 7-C), 94.18 (5-C or 7-C), 103.74 (3a-C), 157.76 (4-C or 6-C or 7a-C), 160.80 (4-C or 6-C or 7a-C), 165.53 (4-C or 6-C or 7a-C), 170.93 (2-C), 171.64 (3-C); IR (KBr) 3608 w, 3416 w, 3108 m, 2996 w, 2952 w, 2848 w, 2716 w, 2172 w, 1850 m, 1820 s, 1722 s, 1632 s, 1580 s, 1516 s, 1470 s, 1430 s, 1338 s, 1226 s, 1198 s, 1162 s, 1042 s, 972 m, 932 s, 842 s; MS, m/z (relative intensity, %) 208 (M^+ , 4.4), 181 (14), 180 (100), 152 (33), 137 (38). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_5$: C, 57.70; H, 3.87. Found: C, 57.61; H, 3.81.

4,6-Bis(1,1-dimethylethyl)-benzofuran-2,3-dione (1c). Yellow solid; mp 99-100 °C; R_f 0.36 (hexane/EtOAc = 3/1); ^1H NMR (CDCl_3) δ 1.37 (s, 9H, 4- t Bu or 6- t Bu), 1.42 (s, 9H, 4- t Bu or 6- t Bu), 7.06 (d, J = 1.6 Hz, 1H, 5-H or 7-H), 7.28 (d, J = 1.6 Hz, 1H, 5-H or 7-H); ^{13}C NMR (CDCl_3) δ 28.90 (4- $\text{C}(\text{CH}_3)_3$ or 6- $\text{C}(\text{CH}_3)_3$), 30.76 (4- $\text{C}(\text{CH}_3)_3$ or 6- $\text{C}(\text{CH}_3)_3$), 36.37 (4- $\text{C}(\text{CH}_3)_3$ or 6- $\text{C}(\text{CH}_3)_3$), 36.75 (4- $\text{C}(\text{CH}_3)_3$ or 6- $\text{C}(\text{CH}_3)_3$), 108.50 (5-C or 7-C), 114.73 (3a-C), 119.89 (5-C or 7-C), 154.73 (4-C or 6-C or 7a-C), 156.25 (4-C or 6-C or 7a-C), 165.88 (4-C or 6-C or 7a-C), 166.09 (2-C), 175.43 (3-C); IR (KBr) 3436 w, 2968 s, 1828 s, 1738 s, 1620 s, 1568 s, 1480 m, 1398 m, 1368 m, 1324 m, 1298 w, 1264 w, 1242 w, 1212 m, 1168 w, 1108 m, 1026 w, 978 m, 932 w, 894 w, 868 w; MS, m/z (relative intensity, %) 260 (M^+ , 14), 233 (17), 232 (100), 217 (13), 190 (21), 189 (93), 131 (10), 115 (13), 105 (12), 91 (24), 79 (13), 77 (20), 73 (17), 65 (18), 63 (12), 59 (11), 58 (16), 57 (43), 55 (13), 53 (18), 51 (25). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.82; H, 7.74. Found: C, 73.80; H, 7.90.

Typical Procedure for the Cyclocoupling of Esters, Ethylene, and CO. A 50-mL stainless

autoclave was charged with 4,6-dimethyl-benzofuran-2,3-dione (**1a**) (1 mmol, 176 mg), toluene (3 mL), $\text{Ru}_3(\text{CO})_{12}$ (0.025 mmol, 16 mg), and $\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3$ (0.075 mmol, 35 mg). After the system was flushed with 10 atm of ethylene three times, it was pressurized with ethylene to 3 atm and then with carbon monoxide to an additional 5 atm. The autoclave was then immersed in an oil bath at 160 °C. After 20 hours had elapsed, it was removed from the oil bath, allowed to cool for ca. 1 h and the gases were then released. The contents were transferred to a round-bottomed flask with toluene, and the volatiles were removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 11/1) to give 4,6-dimethyl-3',4'-dihydro-spiro[benzofuran-2,2'-furan]-3,5'-dione (**2a**) (71 mg) and 4,6-dimethyl-3',4'-dihydro-spiro[benzofuran-3,2'-furan]-2,5'-dione (**3a**) (127 mg) (85 % total yield, 36/64 isomeric ratio) as colorless solid.

4,6-Dimethyl-3',4'-dihydro-spiro[benzofuran-2,2'-furan]-3,5'-dione (2a). White solid; mp 98-100 °C (hexane/EtOAc); R_f 0.26 (hexane/EtOAc = 3/1); ^1H NMR (CDCl_3) δ 2.28-2.42 (m, 1H, 3'-H or 4'-H), 2.40 (s, 3H, 4-Me or 6-Me), 2.55 (s, 3H, 4-Me or 6-Me), 2.61-2.98 (c, 3H, 3', 4'-H), 6.69 (s, 1H, 5-H or 7-H), 6.74 (s, 1H, 5-H or 7-H); ^{13}C NMR (CDCl_3) δ 17.88 (4-Me or 6-Me), 22.71 (4-Me or 6-Me), 27.52 (3'-C or 4'-C), 28.79 (3'-C or 4'-C), 106.65 (2-C or 3a-C), 110.40 (5-C or 7-C), 114.26 (2-C or 3a-C), 125.96 (5-C or 7-C), 140.39 (4-C or 6-C), 151.28 (4-C or 6-C), 170.71 (7a-C or 5'-C), 174.04 (7a-C or 5'-C), 193.36 (3-C); IR (KBr) 2948 m, 1808 s, 1730 s, 1630 s, 1600 s, 1498 w, 1450 m, 1414 m, 1380 m, 1328 m, 1284 w, 1224 m, 1194 s, 1140 m, 1118 m, 1098 m, 1060 w, 1032 s, 960 m, 912 s, 844 m, 806 w; MS, m/z (relative intensity, %) 232 (M^+ , 33), 160 (29), 150 (10), 149 (100), 148 (16), 132 (23), 104 (14), 91 (30), 77 (18), 65 (14), 63 (11), 55 (45), 53 (11), 52 (10), 51 (28). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_4$: C, 67.22; H, 5.21. Found: C, 67.11; H, 5.43.

4,6-Dimethyl-3',4'-dihydro-spiro[benzofuran-3,2'-furan]-2,5'-dione (3a). White solid; mp 83-84 °C (hexane/EtOAc); R_f 0.20 (hexane/EtOAc = 3/1); ^1H NMR (CDCl_3) δ 2.33 (s, 3H, 4-Me or 6-Me), 2.37 (s, 3H, 4-Me or 6-Me), 2.54-2.86 (c, 3H, 3', 4'-H), 3.12-3.26 (m, 1H, 3'-H or 4'-H), 6.80 (s, 1H, 7-H), 6.83 (s, 1H, 5-H); ^{13}C NMR (CDCl_3) δ 17.28 (4-Me or 6-Me), 21.87 (4-Me or 6-Me), 27.61 (3'-C or 4'-C), 30.02 (3'-C or 4'-C), 81.55 (3-C), 109.57 (7-C), 118.76 (4-C or 6-C), 127.77 (5-C), 136.21 (4-C or 6-C), 142.71 (3a-C), 153.56 (7a-C), 174.04 (2-C or 5'-C), 174.91 (2-C or 5'-C); IR (KBr) 1806 s, 1636 m, 1602 w, 1458 w, 1412 w, 1294 w, 1248 w, 1224 w, 1160 m, 1148 m, 1124 m, 1052 s, 1034 s, 970 w, 888 w, 850 w; MS, m/z (relative intensity, %) 232 (M^+ , 12), 204 (14), 150 (10), 149 (100), 91 (16), 77 (11), 51 (19). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_4$: C, 67.22; H, 5.21. Found: C, 67.18; H, 5.00.

4,6-Dimethoxy-3',4'-dihydro-spiro[benzofuran-2,2'-furan]-3,5'-dione (2b). Colorless solid; mp 163-164 °C; R_f 0.26 (hexane/ Et_2O = 3/1); ^1H NMR (CDCl_3) δ 2.30-2.41 (m, 1H, 3'-H or 4'-H), 2.63-2.94 (c, 3H, 3', 4'-H), 3.89 (s, 3H, 4-OMe or 6-OMe), 3.93 (s, 3H, 4-OMe or 6-OMe), 6.06 (d, J = 2.0 Hz, 1H, 5-H or 7-H), 6.13 (d, J = 2.0 Hz, 1H, 5-H or 7-H); ^{13}C NMR (CDCl_3) δ 27.46 (3'-C or 4'-C), 28.85 (3'-C or 4'-C), 56.28 (4-OMe or 6-OMe), 56.31 (4-OMe or 6-OMe), 89.32 (5-C or 7-C), 93.74 (5-C or 7-C), 101.84 (2-C or 3a-C), 107.80 (2-C or 3a-C), 159.66 (4-C or 6-C or 7a-C or 5'-C), 171.03

(4-C or 6-C or 7a-C or 5'-C), 172.54 (4-C or 6-C or 7a-C or 5'-C), 174.04 (4-C or 6-C or 7a-C or 5'-C), 188.12 (3-C); IR (KBr) 2940 w, 1804 s, 1706 s, 1624 s, 1598 s, 1510 m, 1452 m, 1432 m, 1368 m, 1334 m, 1260 m, 1202 s, 1158 s, 1108 s, 1048 s, 952 s, 918 s, 856 w, 820 m; MS, m/z (relative intensity, %) 264 (M^+ , 38), 209 (10), 205 (15), 191 (15), 181 (100), 164 (19), 163 (54), 161 (16), 137 (22), 135 (11), 134 (14), 106 (32), 79 (11), 78 (12), 77 (10), 69 (42), 66 (15), 65 (12), 63 (24), 62 (17), 59 (23), 56 (11), 55 (72), 53 (40), 51 (19). Anal. Calcd for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 58.98; H, 4.47.

4,6-Dimethoxy-3',4'-dihydro-spiro[benzofuran-3,2'-furan]-2,5'-dione (3b). Colorless solid; mp 152-153 °C; R_f 0.43 (hexane/Et₂O = 3/1); 1H NMR (CDCl₃) δ 2.53-2.78 (c, 2H, 3', 4'-H), 2.83-3.05 (c, 2H, 3'-H or 4'-H), 3.83 (s, 3H, 4-OMe or 6-OMe), 3.85 (s, 3H, 4-OMe or 6-OMe), 6.24 (d, J = 2.0 Hz, 1H, 5-H), 6.32 (d, J = 2.0 Hz, 1H, 7-H); ^{13}C NMR (CDCl₃) δ 28.25 (3'-C or 4'-C), 29.18 (3'-C or 4'-C), 55.88 (4-OMe or 6-OMe), 55.95 (4-OMe or 6-OMe), 81.30 (3-C), 89.82 (5-C), 94.97 (7-C), 103.95 (3a-C), 155.25 (4-C or 6-C or 7a-C), 157.72 (4-C or 6-C or 7a-C), 164.11 (4-C or 6-C or 7a-C), 173.58 (2-C or 5'-C), 175.27 (2-C or 5'-C); IR (KBr) 3536 w, 3100 w, 2948 w, 2852 w, 2056 w, 1826 s, 1782 s, 1634 s, 1616 s, 1510 s, 1478 s, 1436 s, 1356 s, 1338 m, 1270 m, 1230 s, 1208 s, 1172 s, 1146 s, 1074 s, 1048 s, 1002 s, 946 w, 896 m, 818 s; MS, m/z (relative intensity, %) 264 (M^+ , 26), 220 (46), 209 (18), 207 (22), 192 (10), 191 (16), 182 (10), 181 (100), 177 (24), 165 (11), 163 (17), 149 (13), 137 (12), 91 (11), 89 (10), 79 (15), 78 (13), 77 (18), 76 (14), 69 (50), 66 (13), 65 (17), 63 (19), 62 (12), 59 (23), 55 (40), 53 (28), 52 (14), 51 (31), 50 (24). Anal. Calcd for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 58.94; H, 4.51.

4,6-Bis(1,1-dimethylethyl)-3',4'-dihydro-spiro[benzofuran-2,2'-furan]-3,5'-dione (2c). White solid; mp 144-146 °C (hexane/EtOAc); R_f 0.31 (hexane/EtOAc = 3/1); 1H NMR (CDCl₃) δ 1.34 (s, 9H, 4-^tBu or 6-^tBu), 1.42 (s, 9H, 4-^tBu or 6-^tBu), 2.33-2.43 (m, 1H, 3'-H or 4'-H), 2.62-2.98 (c, 3H, 3', 4'-H), 6.93 (d, J = 1.3 Hz, 1H, 7-H), 7.15 (d, J = 1.3 Hz, 1H, 5-H); ^{13}C NMR (CDCl₃) δ 27.62 (3'-C or 4'-C), 28.89 (3'-C or 4'-C), 29.17 (4-C(CH₃)₃ or 6-C(CH₃)₃), 30.76 (4-C(CH₃)₃ or 6-C(CH₃)₃), 36.01 (4-C(CH₃)₃ or 6-C(CH₃)₃), 36.15 (4-C(CH₃)₃ or 6-C(CH₃)₃), 106.10 (2-C or 3a-C), 107.89 (7-C), 113.06 (2-C or 3a-C), 117.88 (5-C), 153.40 (4-C or 6-C), 164.38 (4-C or 6-C), 172.84 (7a-C or 5'-C), 173.94 (7a-C or 5'-C), 192.61 (3-C); IR (KBr) 2968 m, 2876 m, 1810 s, 1724 s, 1616 s, 1574 s, 1474 m, 1450 m, 1424 w, 1402 m, 1366 m, 1336 m, 1302 m, 1216 s, 1196 s, 1162 s, 1132 m, 1096 s, 1052 s, 1028 m, 986 m, 960 s, 924 s, 904 s, 860 m, 818 w; MS, m/z (relative intensity, %) 317 (M^+ +1, 12), 316 (M^+ , 46), 301 (12), 257 (24), 255 (10), 233 (25), 229 (43), 202 (30), 201 (31), 189 (16), 187 (45), 173 (12), 159 (10), 131 (15), 129 (17), 128 (12), 116 (12), 115 (24), 105 (11), 91 (22), 79 (10), 77 (15), 65 (12), 57 (100), 56 (16), 55 (74), 53 (11), 51 (10). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 71.99; H, 7.67.

7-(1,1-Dimethylethyl)-3',4'-dihydro-spiro[benzofuran-3,2'-furan]-2,5'-dione (3d). White solid; mp 118-119 °C; R_f 0.29 (hexane/EtOAc = 3/1); 1H NMR (CDCl₃) δ 1.40 (s, 9H, ^tBu), 2.55 (ddd, J = 13.5, 10.9, 9.6 Hz, 1H, 3'-H), 2.71 (ddd, J = 13.5, 9.6, 3.0 Hz, 1H, 3'-H), 2.83 (ddd, J = 17.8, 9.6, 3.0 Hz, 1H, 4'-H), 3.16 (ddd, J = 17.8, 10.9, 9.6 Hz, 1H, 4'-H), 7.21 (dd, J = 7.6, 7.6 Hz, 1H, 5-H), 7.26 (dd, J = 7.6, 1.7 Hz, 1H, 4-H or 6-H), 7.41 (dd, J = 7.6, 1.7 Hz, 1H, 4-H or 6-H); ^{13}C NMR (CDCl₃) δ

27.91 (4'-C), 29.50 (C(CH₃)₃), 32.15 (3'-C), 34.33 (C(CH₃)₃), 80.40 (3-C), 121.90 (4-C or 6-C), 124.70 (3a-C), 125.16 (5-C), 129.29 (4-C or 6-C), 134.96 (7-C), 151.41 (7a-C), 173.37 (2-C or 5'-C), 174.71 (2-C or 5'-C); IR (KBr) 2964 m, 2872 m, 1811 s, 1619 m, 1599 m, 1487 s, 1431 s, 1416 m, 1396 m, 1366 m, 1329 m, 1285 s, 1223 s, 1156 s, 1100 s, 1051 s, 991 m, 928 s, 896 m, 864 s, 816 m; MS, *m/z* (relative intensity, %) 260 (M⁺, 18), 232 (24), 217 (13), 204 (38), 190 (30), 189 (100), 178 (11), 177 (80), 175 (36), 161 (29), 157 (12), 149 (15), 148 (83), 145 (13), 133 (17), 131 (12), 128 (14), 115 (27), 105 (14), 103 (12), 91 (22), 89 (11), 80 (10), 79 (26), 78 (12), 77 (38), 73 (23), 66 (11), 65 (25), 64 (15), 63 (23), 59 (15), 58 (10), 57 (19), 55 (77), 53 (24), 52 (14), 51 (47). Anal. Calcd for C₁₅H₁₆O₄: C, 69.22; H, 6.20. Found: C, 69.17; H, 6.16.

Typical Procedure for the Cyclocoupling of Esters, Substituted Olefins or Acetylenes, and CO. A 50-mL stainless autoclave was charged with 4,6-bis(1,1-dimethylethyl)-benzofuran-2,3-dione (**1c**) (1 mmol, 260 mg), cyclopentene (10 mmol, 681 mg), toluene (3 mL), Ru₃(CO)₁₂ (0.025 mmol, 16 mg), and P(4-CF₃C₆H₄)₃ (0.075 mmol, 35 mg). After the system was flushed with 10 atm of carbon monoxide three times, it was pressurized with carbon monoxide to 5 atm and the autoclave was then immersed in an oil bath at 160 °C. After 90 hours had elapsed, it was removed from the oil bath, allowed to cool for ca. 1 h and the gases were then released. The contents were transferred to a round-bottomed flask with toluene, and the volatiles were removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 5/1) to give 4,6-bis(1,1-dimethylethyl)-3',4'-diphenyl-spiro[benzofuran-2,2'-cyclopenta[c]furan]-3,6'-dione (**4**) (316 mg, 89 % yield, 88/12 stereoisomeric mixture) as a white solid. Purification by recrystallization from hexane and EtOAc afforded the analytically pure products.

4,6-Bis(1,1-dimethylethyl)-3',4'-diphenyl-spiro[benzofuran-2,2'-cyclopenta[c]furan]-3,6'-dione (4**).** Spectral data were obtained from a mixture of stereoisomers. white solid; mp 198-200 °C (hexane/EtOAc); *R_f* 0.46 (hexane/EtOAc = 3/1); ¹H NMR (CDCl₃) δ [1.34 (s, minor), 1.35 (s, major), 9H, 4-^tBu or 6-^tBu], [1.41 (s, major), 1.43 (s, minor), 9H, 4-^tBu or 6-^tBu], 1.58-1.82 (c, 3H, 3', 4', 5'-H), 1.91-2.08 (m, 1H, 3'-H or 4'-H or 5'-H), 2.09-2.28 (c, 2H, 3', 4', 5'-H), 3.00-3.20 (m, 1H, 2'a-H or 5'a-H), 3.37-3.52 (m, 1H, 2'a-H or 5'a-H), [6.91 (d, *J* = 1.7 Hz, minor), 6.98 (d, *J* = 1.3 Hz, major), 1H, 7-H], [7.13 (d, *J* = 1.7 Hz, minor), 7.15 (d, *J* = 1.3 Hz, major), 1H, 5-H]; ¹³C NMR (CDCl₃) δ [26.11 (minor), 26.22 (major), 3'-C or 4'-C or 5'-C], [27.39 (minor), 28.12 (major), 3'-C or 4'-C or 5'-C], [29.17 (major), 30.19 (minor), 3'-C or 4'-C or 5'-C], [30.78 (major), 31.35 (minor), 4-C(CH₃)₃ or 6-C(CH₃)₃], [30.81 (major), 31.53 (minor), 4-C(CH₃)₃ or 6-C(CH₃)₃], 35.99 (4-C(CH₃)₃ or 6-C(CH₃)₃), [36.11 (minor), 36.18 (major), 4-C(CH₃)₃ or 6-C(CH₃)₃], [44.43 (major), 45.00 (minor), 2'a-C or 5'a-C], [46.61 (major), 48.08 (minor), 2'a-C or 5'a-C], [106.06 (minor), 106.13 (major), 2-C or 3a-C], [107.78 (minor), 107.90 (major), 7-C], [112.89 (major), 114.10 (minor), 2-C or 3a-C], [117.63 (minor), 117.96 (major), 5-C], [153.15 (minor), 153.44 (major), 4-C or 6-C], [164.06 (minor), 164.25 (major), 4-C or 6-C], [172.21 (minor), 173.32 (major), 7a-C or 6'-C], [177.06 (major), 178.29 (minor), 7a-C or 6'-C], [192.01 (minor), 194.48 (major), 3-C]; IR (KBr) 2964 s, 2876 m, 1792 s, 1728 s, 1618 s, 1576 s, 1484 s, 1400 s, 1368 s, 1334 s, 1300 s, 1260 s, 1218 s, 1164 s, 1132 s, 1100 s, 1054 s, 1004 s, 984 s, 954 s, 910 s, 864 s; MS, *m/z* (relative intensity, %) [356

(M^+ , 15), 269 (18), 262 (41), 242 (19), 233 (38), 232 (24), 227 (13), 217 (10), 216 (11), 201 (21), 189 (26), 173 (10), 131 (13), 117 (10), 115 (15), 105 (12), 95 (31), 91 (19), 77 (14), 68 (24), 67 (68), 65 (16), 57 (100), 55 (34), 53 (19), major], [356 (M^+ , 14), 269 (18), 262 (49), 242 (20), 233 (37), 232 (26), 227 (14), 217 (11), 216 (12), 201 (22), 189 (31), 173 (11), 131 (14), 128 (10), 115 (14), 105 (13), 95 (33), 91 (19), 77 (14), 68 (28), 67 (72), 65 (17), 57 (100), 55 (34), 53 (21), minor]. Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.04; H, 7.93.

4,6-Bis(1,1-dimethylethyl)-3',4'-diphenyl-spiro[benzofuran-2,2'-cyclohexa[c]furan]-3,7'-dione (5). Spectral data were obtained from a mixture of stereoisomers. colorless solid; mp 159-160 °C (hexane/EtOH); R_f 0.51 (hexane/EtOAc = 3/1); 1H NMR ($CDCl_3$) δ [1.34 (s, minor), 1.35 (s, major), 9H, 4- t Bu or 6- t Bu], [1.41 (s, major), 1.42 (s, minor), 9H, 4- t Bu or 6- t Bu], 1.46-1.87 (c, 7H, 3', 4', 5', 6-H), [2.00-2.11 (m, minor), 2.00-2.12 (m, major), 1H, 3'-H or 4'-H or 5'-H or 6-H], [2.61-2.70 (m, minor), 2.83 (ddd, J = 7.6 Hz, 7.1 Hz, 7.1 Hz, major), 1H, 2'-a-H or 6'-a-H], [3.22-3.26 (m, minor), 3.33 (ddd, J = 6.8 Hz, 6.8 Hz, 6.3 Hz, major), 1H, 2'-a-H or 6'-a-H], [6.96 (d, J = 1.3 Hz, minor), 6.97 (d, J = 1.7 Hz, major), 1H, 7-H], [7.13 (d, J = 1.3 Hz, minor), 7.15 (d, J = 1.7 Hz, major), 1H, 5-H]; ^{13}C NMR ($CDCl_3$) δ [22.24 (minor), 22.66 (major), 3'-C or 4'-C or 5'-C or 6'-C], [22.57 (minor), 22.68 (major), 3'-C or 4'-C or 5'-C or 6'-C], [22.70 (major), 22.89 (minor), 3'-C or 4'-C or 5'-C or 6'-C], [23.50 (major), 23.60 (minor), 3'-C or 4'-C or 5'-C or 6'-C], 29.20 (4-C(CH_3)₃ or 6-C(CH_3)₃), [30.83 (major), 31.39 (minor), 4-C(CH_3)₃ or 6-C(CH_3)₃], [34.79 (minor), 36.03 (major), 4-C(CH_3)₃ or 6-C(CH_3)₃], [36.14 (minor), 36.22 major, 4-C(CH_3)₃ or 6-C(CH_3)₃], [38.46 (minor), 39.25 (major), 2'-a-C or 6'-a-C], [39.65 (major), 43.83 (minor), 2'-a-C or 6'-a-C], [105.18 (minor), 106.43 (major), 2-C or 3a-C], [107.87 (major), 109.59 (minor), 7-C], [113.29 (major), 114.24 (minor), 2-C or 3a-C], [117.66 (minor), 117.92 (major), 5-C], [153.19 (minor), 153.44 (major), 4-C or 6-C], [163.92 (minor), 164.28 (major), 4-C or 6-C], [172.04 (minor), 173.34 (major), 7a-C or 7'-C], [175.60 (major), 176.06 (minor), 7a-C or 7'-C], [191.30 (minor), 194.04 (major), 3-C]; IR (KBr) 2964 s, 2868 s, 1798 s, 1718 s, 1618 s, 1574 s, 1534 w, 1488 m, 1450 m, 1402 s, 1366 s, 1328 s, 1304 m, 1256 m, 1236 s, 1188 s, 1166 s, 1096 s, 1062 m, 1018 s, 976 s, 938 s, 912 s, 884 s, 864 s, 820 w, 802 w; MS, m/z (relative intensity, %) [370 (M^+ , 18), 262 (24), 261 (11), 233 (49), 232 (27), 216 (10), 201 (16), 189 (20), 109 (100), 91 (14), 81 (45), 79 (20), 77 (11), 67 (20), 57 (86), 55 (24), 54 (14), 53 (23), major], [370 (M^+ , 18), 262 (32), 261 (14), 233 (53), 232 (28), 216 (10), 201 (17), 189 (20), 109 (100), 91 (15), 81 (50), 79 (22), 77 (10), 67 (20), 57 (91), 55 (23), 54 (15), 53 (22), minor]. Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.48; H, 8.16.

4,6-Bis(1,1-dimethylethyl)-3',4'-diphenyl-spiro[benzofuran-2,2'-furan]-3,5'-dione (6). Colorless solid; mp 144-145 °C (hexane/EtOAc); R_f 0.51 (hexane/EtOAc = 3/1); 1H NMR ($CDCl_3$) δ 1.34 (s, 9H, 4- t Bu or 6- t Bu), 1.39 (s, 9H, 4- t Bu or 6- t Bu), 6.98 (d, J = 1.3 Hz, 1H, 5-H or 7-H or Ph), 7.14-7.24 (c, 5H, 5-H or 7-H or Ph), 7.27-7.39 (c, 4H, 5-H or 7-H or Ph), 7.46-7.52 (c, 2H, 5-H or 7-H or Ph); ^{13}C NMR ($CDCl_3$) δ 29.05 (4-C(CH_3)₃ or 6-C(CH_3)₃), 30.80 (4-C(CH_3)₃ or 6-C(CH_3)₃), 36.04 (4-C(CH_3)₃ or 6-C(CH_3)₃), 36.27 (4-C(CH_3)₃ or 6-C(CH_3)₃), 104.83 (2-C or 3a-C), 108.26 (7-C), 114.31 (2-C or 3a-C), 118.32 (5-C), 128.10 (Ph), 128.53 (Ph), 128.64 (Ph), 128.88 (Ph), 129.34 (Ph), 129.46 (Ph), 129.47 (Ph), 130.06 (Ph), 131.09 (4'-C),

152.05 (3'-C), 153.83 (4-C or 6-C), 164.78 (4-C or 6-C), 168.88 (7a-C or 5'-C), 174.05 (7a-C or 5'-C), 191.01 (3-C); IR (KBr) 2964 m, 1788 s, 1724 s, 1618 s, 1568 s, 1488 m, 1450 m, 1400 m, 1366 m, 1322 s, 1300 m, 1256 m, 1242 m, 1160 s, 1092 m, 1058 s, 1026 m, 998 m, 958 s, 912 m, 870 m, 832 w, 814 w; MS, m/z (relative intensity, %) 467 ($M^+ + 1$, 28), 466 (M^+ , 74), 423 (10), 422 (27), 407 (18), 379 (10), 235 (15), 234 (73), 233 (14), 232 (20), 189 (13), 179 (19), 178 (100). Anal. Calcd for $C_{31}H_{30}O_4$: C, 79.80; H, 6.48. Found: C, 79.65; H, 6.56.

4,6-Bis(1,1-dimethylethyl)-3'-methyl-4'-trimethylsilyl-spiro[benzofuran-2,2'-furan]-3,5'-dione (7). White solid; mp 127-128 °C (hexane/EtOAc); R_f 0.37 (hexane/EtOAc = 3/1); 1H NMR ($CDCl_3$) δ 0.34 (s, 9H, SiMe₃), 1.36 (s, 9H, 4-*t*Bu or 6-*t*Bu), 1.41 (s, 9H, 4-*t*Bu or 6-*t*Bu), 1.93 (s, 3H, 3'-Me), 7.00 (d, J = 1.5 Hz, 1H, 7-H), 7.16 (d, J = 1.5 Hz, 1H, 5-H); ^{13}C NMR ($CDCl_3$) δ -1.11 (SiMe₃), 12.73 (3'-Me), 29.21 (4-C(CH₃)₃ or 6-C(CH₃)₃), 30.85 (4-C(CH₃)₃ or 6-C(CH₃)₃), 36.10 (4-C(CH₃)₃ or 6-C(CH₃)₃), 36.29 (4-C(CH₃)₃ or 6-C(CH₃)₃), 106.46 (2-C or 3a-C), 108.09 (7-C), 114.20 (2-C or 3a-C), 118.08 (5-C), 131.24 (4'-C), 153.59 (3'-C), 164.53 (4-C or 6-C), 167.12 (4-C or 6-C), 172.45 (7a-C or 5'-C), 174.09 (7a-C or 5'-C), 191.14 (3-C); IR (KBr) 3532 w, 2968 s, 1894 w, 1776 s, 1720 s, 1616 s, 1572 s, 1540 w, 1486 m, 1400 m, 1366 m, 1334 m, 1298 m, 1250 s, 1200 s, 1156 m, 1098 s, 1072 m, 1006 m, 984 m, 948 s, 874 s, 848 s; MS, m/z (relative intensity, %) 400 (M^+ , 0), 385 (10), 306 (13), 305 (48), 189 (12), 169 (14), 168 (90), 141 (10), 140 (53), 112 (40), 98 (11), 97 (100), 75 (16), 73 (59), 67 (18), 57 (33), 55 (10). Anal. Calcd for $C_{23}H_{32}O_4Si$: C, 68.96; H, 8.05. Found: C, 68.87; H, 7.90.

4,6-Bis(1,1-dimethylethyl)-3'-phenyl-4'-trimethylsilyl-spiro[benzofuran-2,2'-furan]-3,5'-dione (8). Colorless solid; mp 169-170 °C (hexane/EtOAc); R_f 0.54 (hexane/EtOAc = 3/1); 1H NMR ($CDCl_3$) δ 0.11 (s, 9H, SiMe₃), 1.29 (s, 9H, 4-*t*Bu or 6-*t*Bu), 1.34 (s, 9H, 4-*t*Bu or 6-*t*Bu), 6.89 (d, J = 1.5 Hz, 1H, 7-H), 7.04 (d, J = 1.5 Hz, 1H, 5-H), 7.15-7.21 (c, 2H, 2'', 6''-H or 3'', 5''-H), 7.23-7.34 (c, 3H, 2'', 4'', 6''-H or 3'', 4'', 5''-H); ^{13}C NMR ($CDCl_3$) δ -1.32 (SiMe₃), 29.00 (4-C(CH₃)₃ or 6-C(CH₃)₃), 30.76 (4-C(CH₃)₃ or 6-C(CH₃)₃), 35.94 (4-C(CH₃)₃ or 6-C(CH₃)₃), 36.17 (4-C(CH₃)₃ or 6-C(CH₃)₃), 106.53 (2-C or 3a-C), 107.98 (7-C), 114.48 (2-C or 3a-C), 118.00 (5-C), 127.77 (2'', 6''-C or 3'', 5''-C), 128.22 (2'', 6''-C or 3'', 5''-C), 129.59 (4''-C), 131.04 (1''-C), 134.63 (4'-C), 153.49 (3'-C), 164.48 (4-C or 6-C), 168.59 (4-C or 6-C), 172.27 (7a-C or 5'-C), 174.14 (7a-C or 5'-C), 191.24 (3-C); IR (KBr) 3968 w, 3520 w, 3056 w, 2968 s, 2332 w, 1908 w, 1774 s, 1728 s, 1618 s, 1568 s, 1490 m, 1448 m, 1400 s, 1366 m, 1322 s, 1302 m, 1250 s, 1214 s, 1172 m, 1156 m, 1092 m, 1052 s, 1024 m, 994 w, 954 s, 908 w, 868 s, 842 s; MS, m/z (relative intensity, %) 463 ($M^+ + 1$, 16), 462 (M^+ , 44), 305 (32), 231 (11), 230 (50), 175 (17), 174 (100), 160 (15), 159 (95), 129 (23), 105 (10), 73 (39), 57 (33). Anal. Calcd for $C_{28}H_{34}O_4Si$: C, 72.69; H, 7.41. Found: C, 72.45; H, 7.28.

References

- 1) Bruce, M. I.; Jensen, C. M.; Jones, N. L. *Inorg. Synth.* **1989**, 26, 259.
- 2) Barbieri, W. L.; Bernardi, S.; Vigevani, A. *Tetrahedron Lett.* **1971**, 52, 4913.
- 3) Zwanenburg, D. J.; Reynen, W. A. P. *Synthesis* **1976**, 624.