JOC The Journal of Organic Chemistry

J. Org. Chem., 1996, 61(23), 8256-8263, DOI:10.1021/jo961076+

Charactarization data and experimental procedures of **1a**, **1d ~ 1j** and **2d ~ 2j** (8 page).

3-Benzyloxy-4-pentenylpropanedioic acid dimethyl ester (1a): To a solution of 3-benzyloxy-4-penten-1-ol[1] (2.05 g, 11 mmol) in CH_2Cl_2 was added Et_3N (1.9 mL, 14 mmol) and methanesulfonyl chloride (0.9 mL, 12 mmol) at 0 °C. After being stirred for 10 min at room temperature, the mixture was poured into 10 % HCl and extracted with ether. The ether extracts were evaporated to dryness. To a solution of NaH (60 % in oil, 0.5 g, 13 mmol) and dimethyl malonate (1.5 mL, 13 mmol) in THF (25 mL) was added the residue, then the reaction mixture was stirred at 140 °C for 3 days. The mixture was poured into 10 % HCl and extracted with ether. The ether extracts were dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (hexane / AcOEt = 9) to give **1a** (2.94 g, 90 %). **1a**: colorless oil; IR (neat) 2953, 1733 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.32 (5H, m), 5.72 (1H, ddd, J = 7.7, 10.6, 17.0 Hz), 5.21-5.27 (2H, m), 4.58 (1H, d, J = 11.8 Hz), 4.34 (1H, d, J = 11.8 Hz), 3.76 (1H, m), 3.72 (6H, s), 3.36 (1H, t, J = 7.5 Hz), 1.91-2.09 (2H, m), 1.50-1.70 (2H, m); ^{13}C-NMR ($CDCl_3$) δ: 169.7, 138.6, 138.4, 128.3, 127.7, 127.4, 117.5, 79.9, 70.1, 52.3, 51.5, 33.0, 24.8; MS (*m/z*) 307 (M^++H^+), 199 (M^+-OBn). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.61; H, 7.34.

3-Methoxymethoxy-4-pentenylpropanedioic acid dimethyl ester (1d): **1d** was prepared from 3-methoxymethoxy-4-penten-1-ol in accordance with the silimar procedure for **1a**. **1d**: colorless oil; IR (neat) 2955, 1756, 1737 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 5.65 (1H, ddd, J = 7.6, 10.4, 17.1 Hz), 5.22 (2H, m), 4.69 (1H, d, J = 6.7 Hz), 4.52 (1H, d, J = 6.7 Hz), 4.00 (1H, q, J = 6.8 Hz), 3.74 (6H, s), 3.40 (1H, t, J = 7.5 Hz), 3.37 (3H, s), 1.88 -2.11 (2H, m), 1.46-1.68 (2H, m); ^{13}C-NMR ($CDCl_3$) δ: 169.7, 169.7, 137.6, 117.8, 93.7, 76.6, 55.5, 52.5, 51.4, 32.8, 24.8; MS (m/z) 261 (M^++H^+), 228 (M^++H^+-OMe). Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.76. Found: C, 55.17; H, 7.81.

3-*tert*-Butyldimethylsiloxy-4-pentenylpropanedioic acid dimethyl ester (1e): **1e**

was prepared from 3-*tert*-butyldimethylsiloxy-4-penten-1-ol in accordance with the silimar procedure for **1a**. **1e**: colorless oil; IR (neat) 2931, 2858, 1757, 1740 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 5.77 (1H, ddd, *J* = 6.0, 10.4, 17.1 Hz), 5.16 (1H, td, *J* = 1.5, 17.1 Hz), 5.05 (1H, td, *J* = 1.5, 10.4 Hz), 4.13 (H, m), 3.73 (6H, s), 3.37 (1H, t, *J* = 7.9 Hz), 1.87 -2.02 (2H, m), 1.47-1.58 (2H, m), 0.89 (9H, s), 0.05 (3H, s), 0.03 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 169.8, 140.9, 114.3, 73.1, 52.4, 51.6, 35.3, 25.8, 24.5, 18.2, -4.4, -4.9; MS (m/z) 315 (M^+-Me), 299 (M^+-OMe). Anal. Calcd for $C_{16}H_{30}O_5Si$: C, 58.14; H, 9.15. Found: C, 58.09; H, 9.15.

3-Benzyloxy-4-methyl-4-pentenylpropanedioic acid dimethyl ester (1f): **1f** was prepared from 3-benzyloxy-4-methyl-4-penten-1-ol in accordance with the silimar procedure for **1a**. **1f**: colorless oil; IR (neat) 2953, 1735 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.24-7.38 (5H, m), 5.00 (1H, m), 4.95 (1H, m), 4.49 (1H, d, *J* = 11.8 Hz), 4.25 (1H, d, *J* = 11.8 Hz), 3.72 (6H, s), 3.72 (1H, m), 3.36 (1H, t, *J* =7.5 Hz), 1.82-2.04 (2H, m), 1.69 (3H, s), 1.68 (1H, m), 1.55 (1H, s); ^{13}C-NMR ($CDCl_3$) δ: 169.5, 165.7, 135.8, 133.0, 130.4, 129.7, 128.4, 117.3, 74.4, 52.5, 51.3, 31.8, 24.4; MS (*m/z*) 320 (M^+). Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.62; H, 7.54.

3-Methyl-4-pentenylpropanedioic acid dimethyl ester (1g): **1g** was prepared from 3-methyl-4-penten-1-ol[1] in accordance with the silimar procedure for **1a**. **1g**: colorless oil; IR (neat) 2980, 1737 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 5.64 (1H, ddd, *J* = 7.6, 10.2, 17.2 Hz), 4.90-5.01 (2H, m), 3.73 (6H, s), 3.33 (1H, t, *J* = 7.5 Hz), 2.12 (1H, m), 1.79-1.97 (2H, m), 1.25-1.32 (2H, m), 0.98 (3H, d, *J* = 6.7 Hz); ^{13}C-NMR ($CDCl_3$) δ: 169.8, 143.7, 113.3, 52.4, 51.7, 37.6, 34.0, 26.7, 20.1; MS (*m/z*) 214 (M^+); Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.67. Found: C, 61.49; H, 8.67.

2-Benzyloxy-4-pentenylpropanedioic acid dimethyl ester (1h): **1h** was prepared from 2-benzyloxy-4-penten-1-ol[2] in accordance with the silimar procedure for **1a**. **1h**: colorless oil; IR (neat) 2953, 1734 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.24-7.87 (5H, m), 5.82 (1H, tt, *J* =7.1, 10.2 Hz), 5.07-5.17 (2H, m), 4.58 (1H, d, *J* =11.3 Hz), 4.38 (1H, d, *J* =11.3 Hz), 3.67 (3H, s), 3.65 (3H, s),

3.64 (1H, dd, J=5.8, 9.0 Hz), 3.50 (1H, m), 2.27-2.47 (2H, m), 2.19 (1H, ddd, J=3.6, 9.0, 14.5 Hz), 2.07 (1H, ddd, J =5.8, 9.2, 14.5 Hz); ^{13}C-NMR ($CDCl_3$) δ: 170.0, 169.8, 138.2, 133.7, 128.3, 127.9, 127.6, 117.8, 75.9, 71.1, 52.4, 48.3, 38.0, 33.3; MS (*m/z*) 307 (M^++H^+), 199 (M^+-OBn). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.88; H, 7.35.

2-Methyl-4-pentenylpropanedioic acid dimethyl ester (1i): **1i** was prepared from 2-methyl-4-penten-1-ol[3] in accordance with the silimar procedure for **1a**. **1i**: colorless; IR (neat) 2957, 1757 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 5.74 (1H, dtd, J = 7.2, 9.7, 14.5 Hz), 4.98-5.04 (2H, m), 3.73 (6H, s), 3.48 (1H, dd, J = 6.7, 8.7 Hz), 1.88-2.18 (3H, m), 1.69 (1H, ddd, J = 6.7, 8.5, 13.9 Hz), 1.50 (1H, m), 0.89 (3H, d, J =6.7 Hz); ^{13}C-NMR ($CDCl_3$) δ: 170.1, 170.0, 136.4, 116.5, 52.5, 49.7, 41.0, 35.4, 30.7, 18.9; MS (*m/z*) 215 (M^++H^+), 183 (M^+-OMe); Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.67. Found: C, 61.37; H, 8.88.

2-*tert*-Butyl-4-pentenylpropanedioic acid dimethyl ester (1j): **1j** was prepared from 2-*tert*-butyl-4-penten-1-ol[4] in accordance with the silimar procedure for **1a**. **1j**: colorless; IR (neat) 2957, 1740 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 5.80 (1H, dddd, J = 6.1, 8.1, 10.1, 16.9 Hz), 4.95-5.07 (2H, m), 3.73 (3H, s), 3.71 (3H, s), 3.55 (1H, dd, J = 4.8, 10.6 Hz), 2.33 (1H, dddd, J = 1.6, 4.2, 8.1, 14.7 Hz), 2.16 (1H, ddd, J = 2.8, 10.6, 14.1 Hz), 1.89 (1H, td, J = 7.7, 14.7 Hz), 1.65 (1H, ddd, J = 4.8, 9.2, 14.1 Hz), 1.11 (1H, ddd, J = 2.8, 4.2, 7.2, 9.2 Hz), 0.89 (9H, s); ^{13}C-NMR ($CDCl_3$) δ: 170.2, 169.9, 138.7, 115.6, 52.4, 52.3, 51.2, 45.4, 35.5, 33.9, 30.2, 27.6; MS (*m/z*) 257 (M^++H^+), 225 (M^+-OMe). Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 64.92; H, 9.63.

General Procedure for Iodocarbocyclization Reactions. To a solution of the malonate (0.5 mmol) in dry CH_2Cl_2 (5 mL) was added Ti(O*t*-Bu)$_4$ (0.2 mL, 0.5 mmol). After the mixture was stirred for 10 min, I_2 (152 mg, 0.6 mmol) and CuO (48 mg, 0.6 mmol) were successively added, then the reaction mixture was stirred at room temperature for the indicated period (see Table 2,3). The mixture was poured into 10 % HCl and the products were extracted with ether.

The ether extracts were washed with aqueous $Na_2S_2O_3$ solution, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography and then MPLC to give the cyclic product as a diastereomeric mixture. The stereochemistries of diastereomers were determined on the basis of NOE experiments.

6-Methoxymethoxy-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2d). Compound **2d** was prepared from **1d** (130 mg, 0.5 mmol). Purification by column chromatography (hexane / AcOEt = 2) and then MPLC (hexane / AcOEt = 2) gave *trans*-**2d** (less polar, 10 mg, 8 %) and *cis*-**2d** (more polar, 105 mg, 86 %). *cis*-**2d**: colorless oil; IR (neat) 2957, 1773, 1741 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.67 (1H, d, *J* = 6.8 Hz), 4.61 (1H, d, *J* = 6.8 Hz), 4.58 (1H, dd, *J* =2.6, 9.4 Hz), 4.37 (1H, dd, *J* = 8.1, 9.4 Hz), 4.18 (1H, dt, *J* =5.1, 7.0 Hz), 3.78 (3H, s), 3.35 (3H, s), 3.21 (1H, dt, *J* =2.6, 7.7 Hz), 2.39 (1H, ddd, *J* =7.3, 8.8, 13.7 Hz), 2.28 (1H, ddd, *J* =5.7, 6.8, 13.7 Hz), 1.99 (1H, tdd, *J* =5.4, 7.3, 12.9 Hz), 1.77 (1H, tdd, *J* =7.0, 8.7, 13.3 Hz); ^{13}C-NMR ($CDCl_3$) δ: 176.1, 170.3, 96.1, 79.1, 66.3, 59.7, 55.8, 53.2, 48.4, 31.6, 30.4; MS (*m/z*) 245 (M^++H^+), 213 (M^+-OMe). Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.12; H, 6.56. *trans*-**2d**: colorless oil; IR (neat) 2956, 1774, 1743 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.65 (1H, d, *J* = 7.0 Hz), 4.62 (1H, d, *J* = 7.3Hz), 4.58 (1H, dd, *J* = 8.4, 9.6 Hz), 4.17 (1H, dd, *J* = 2.8, 9.6 Hz), 3.99(1H, m), 3.79 (3H, s), 3.35 (3H, s), 3.14 (1H, m), 2.65 (1H, ddd, *J* =7.3, 10.1, 13.6 Hz), 2.232 (1H, ddd, *J* =4.6, 7.1, 13.6 Hz), 1.97 (1H, m), 1.77 (1H, dddd, *J* = 5.0, 7.1, 10.1, 13.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 175.9, 169.8, 95.5, 83.9, 70.2, 59.9, 55.5, 53.2, 52.0, 31.8, 31.4; MS (*m/z*) 245 (M^++H^+), 199 (M^+-$MeOCH_2$). Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.20; H, 6.53.

6-*tert*-Butyldimethylsiloxy-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2e). Compound **2e** was prepared from **1e** (165 mg, 0.5 mmol). Purification by column chromatography (hexane / AcOEt = 9) and then MPLC (hexane / AcOEt = 9) gave *cis*-**2e** (142 mg, 90 %) and *trans*-**2e**. *cis*-**2e**: colorless oil; IR (neat) 2956, 2931, 1777, 1742

cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.53 (1H, dd, *J* =2.1, 9.2 Hz), 4.34 (1H, dd, *J* = 7.7, 9.2 Hz), 4.31 (1H, m), 3.78 (3H, s), 3.03 (1H, m), 2.42 (1H, ddd, *J* =7.0, 7.5, 13.6 Hz), 2.29 (1H, td, *J* = 7.0, 13.6 Hz), 1.88 (1H, dtd, *J* =4.5, 7.5, 12.8 Hz), 1.69 (1H, dtd, *J* =5.6, 7.0, 12.8 Hz), 0.87 (9H, s), 0.06 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 176.1, 170.5, 74.4, 66.2, 59.6, 53.0, 50.5, 35.0, 30.2, 25.5, 17.7, -4.7, -5.3; MS (*m/z*) 315 (M^++H^+), 299 (M^+-Me), 283 (M^+-OMe). Anal. Calcd for $C_{15}H_{26}O_5Si$: C, 57.31; H, 8.34. Found: C, 57.25; H, 8.30. *trans*-**2e**: colorless oil; IR (neat) 2956, 2931, 1780, 1747 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.55 (1H, dd, *J* = 8.3, 9.6 Hz), 4.08 (1H, dd, *J* = 3.0, 9.6 Hz), 4.06 (1H, m), 3.78 (3H, s), 3.00 (1H, dt, *J* =3.0, 8.3 Hz), 2.71 (1H, ddd, *J* =7.4, 9.6, 13.5 Hz), 2.17 (1H, ddd, *J* = 4.7, 7.1, 13.5 Hz), 1.66-1.86 (2H, m), 0.86 (9H, s), 0.05 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 176.2, 169.8, 78.9, 69.9, 59.6, 54.7, 53.1, 34.5, 31.1, 25.6, 17.8, -4.7, -4.9; MS (*m/z*) 314 (M^+). Anal. Calcd for $C_{15}H_{26}O_5Si$: C, 57.31; H, 8.34. Found: C, 57.51; H, 8.30.

6-Benzyloxy-6a-methyl-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2f). Compound **2f** was prepared from **1f** (149 mg, 0.47 mmol). Purification by column chromatography (hexane / AcOEt = 5) and then MPLC (hexane / AcOEt = 5) gave *trans*-**2f** (less polar, 2 mg, 1.4 %) and *cis*-**2f** (more polar, 114 mg, 80 %). *cis*-**2f**: white solid; mp 42 °C; IR ($CHCl_3$) 2957, 2360, 1775, 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.27-7.37 (5H, m), 4.75 (1H, d, *J* =9.1 Hz), 4.64 (1H, d, *J* =12.0 Hz), 4.44 (1H, d, *J* =12.0 Hz), 3.92 (1H, *J* =9.1 Hz), 3.77 (3H, s), 3.64 (1H, dd, *J* =5.2, 7.2 Hz), 2.44 (1H, ddd, *J* =7.7, 9.7, 13.7 Hz), 2.26 (1H, ddd, *J* =4.7, 7.1, 13.7 Hz), 2.07 (1H, dddd, *J* =4.7, 5.2, 7.7, 13.0 Hz), 1.65 (1H, dddd, *J* =7.1, 7.2, 9.7, 13.0 Hz), 1.10 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 176.8, 169.3, 137.9, 128.5, 127.8, 127.3, 86.7, 72.5, 71.7, 63.5, 53.5, 52.7, 29.4, 29.4, 20.7; MS (*m/z*) 304 (M^+), 273 (M^+-OMe). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.06; H, 6.65. *trans*-**2f**: colorless oil; IR (neat) 2956, 2360, 1778, 1745 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.28-7.37 (5H, m), 4.63 (1H, d, *J* =11.9 Hz), 4.44 (1H, d, *J* =11.9 Hz), 4.18 (1H, d, *J* =9.1 Hz), 4.05 (1H, *J* =9.1 Hz), 3.78 (3H, s), 3.70 (1H, dd, *J*

=6.0, 9.2 Hz), 2.73 (1H, m), 1.97-2.11 (2H, m), 1.77-1.88 (1H, m), 1.07 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 177.1, 168.9, 138.1, 128.5, 127.9, 127.5, 84.5, 75.3, 72.3, 62.2, 54.5, 52.8, 28.5, 27.4, 13.5; MS (*m/z*) 304 (M^+). HRMS: calcd for $C_{17}H_{20}O_5$ *m/z* 304.1311 (M^+). Found : 304.1311.

6-Methyl-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2g). Compound **2g** was prepared from **1g** (107 mg, 0.5 mmol). Purification by column chromatography (hexane / AcOEt = 3) and then MPLC (hexane / AcOEt = 6) gave *trans*-**2g** (less polar, 24 mg, 25 %) and *cis*-**2g** (more polar, 54 mg, 55 %). *cis*-**2g**: white solid; mp 57 °C; IR ($CHCl_3$) 2970, 2892, 1778, 1734 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.38 (1H, dd, *J* =8.1, 9.7 Hz), 4.30 (1H, dd, *J* =3.5, 9.7 Hz), 3.78 (3H, s), 3.10 (1H, td, *J* =3.5, 8.3 Hz), 2.25-2.41 (3H, m), 1.92 (1H, dtd, *J* =2.4, 6.41, 12.8 Hz), 1.25 (1H, qd, *J* =7.0, 12.2 Hz), 1.05 (3H, d, *J* =7.0 Hz); ^{13}C-NMR ($CDCl_3$) δ: 176.5, 170.5, 67.0, 61.6, 53.0, 48.5, 37.5, 33.8, 33.4, 14.5; MS (*m/z*) 199 (M^++H^+), 167 (M^+-OMe). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.54; H, 7.06. *trans*-**2g**: colorless oil; IR (neat) 2958, 2873, 1773, 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.51 (1H, dd, *J* =6.7, 9.2 Hz), 4.14 (1H, dd, *J* =1.6, 9.2 Hz), 3.77 (3H, s), 2.62 (1H, ddd, *J* =4.3, 8.2, 13.9 Hz), 2.55 (1H, dt, *J* =1.6, 7.1 Hz), 2.14 (1H, ddd, *J* =7.1, 8.6, 13.9 Hz), 1.40-1.50 (2H, m), 1.08 (3H, d, *J* =6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ: 176.6, 170.6, 71.0, 61.5, 54.3, 53.1, 41.8, 34.6, 32.8, 18.3; MS (*m/z*) 199 (M^++H^+), 167 (M^+-OMe). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.59; H, 7.06 .

5-Benzyloxy-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2h). Compound **2h** was prepared from **1h** (153 mg, 0.5 mmol). Purification by column chromatography (hexane / AcOEt = 3) and then MPLC (hexane / AcOEt = 4) gave *trans*-**2h** (less polar, 16 mg, 11 %) and *cis*-**2h** (more polar, 104 mg, 72 %). *cis*-**2h**: colorless oil; IR ($CHCl_3$) 2953, 2914, 1770, 1740 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.25-7.36 (5H, m), 4.59 (1H, t, *J* =8.8 Hz), 4.54 (1H, d, *J* =11.8 Hz), 4.28 (1H, d, *J* =11.8 Hz), 4.19 (1H, dd, *J* =2.9, 8.8 Hz), 4.12 (1H,

m), 3.79 (3H, s), 3.17 (1H, m), 2.75 (1H, m), 2.31 (1H, dd, J=3.7, 14. 2Hz), 2.15 (1H, ddd, J =4.3, 9.6, 14.2 Hz), 1.98 (1H, m); ^{13}C-NMR ($CDCl_3$) δ: 175.8, 170.5, 137.8, 128.3, 127.5, 79.8, 73.4, 70.2, 60.1, 53.1, 43.2, 40.3, 38.8; MS (*m/z*) 290 (M^+), 259 (M^+-OMe). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.09; H, 6.19. *trans*-**2h:** colorless oil; IR ($CHCl_3$) 2954, 2914, 1773, 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.26-7.36 (5H, m), 4.58 (1H, dd, J =6.8, 9.2 Hz), 4.56 (1H, d, J =11.7 Hz), 4.42 (1H, d, J =11.7 Hz), 4.13 (1H, dd, J =1.6, 9.2 Hz), 4.08 (1H, m), 3.79 (3H, s), 3.35 (1H, m), 2.80 (1H, ddd, J =2.1, 3.7, 14.4 Hz), 2.35 (1H, dd, J =4.9, 14.4 Hz), 2.30 (1H, dddd, J =2.1, 3.6, 8.3, 13.5 Hz), 1.72 (1H, ddd, J =4.9, 8.5, 13.5 Hz); ^{13}C-NMR ($CDCl_3$) δ: 176.0, 169.6, 138.0, 128.4, 127.7, 127.6, 79.6, 72.0, 70.8, 59.8, 53.2, 44.3, 39.4, 38.9; MS (*m/z*) 291 (M^++H^+), 184 (M^++H^+-BnO). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.12; H, 6.26.

5-Methyl-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2i). Compound **2i** was prepared from **1i** (107 mg, 0.5 mmol). Purification by column chromatography (hexane / AcOEt = 3) and then MPLC (hexane / AcOEt = 6) gave *trans*-**2i** (less polar, 12 mg, 12 %) and *cis*-**2i** (more polar, 74 mg, 75 %). *cis*-**2i**: colorless oil; IR ($CHCl_3$) 2958, 1773, 1743 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.49 (1H, dd, J = 6.8, 9.2 Hz), 4.15 (1H, dd, J = 1.6, 9.2 Hz), 3.76 (3H, s), 3.05 (1H, dt, J = 1.6, 7.1 Hz), 2.74 (1H, ddd, J = 1.9, 7.4, 13.8 Hz), 2.09-2.24 (2H, m), 1.65 (1H, dd, J = 10.3, 13.8 Hz), 1.20 (1H, q, J = 11.3 Hz), 1.04 (3H, d, J =6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ: 176.6, 170.6, 71.5, 61.1, 53.0, 47.5, 41.8, 41.4, 36.4, 18.6; MS (*m/z*) 199 (M^++H^+), 167 (M^+-OMe). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.38; H, 7.29. *trans*-**2i**: colorless oil; IR (neat) 2958, 2873, 1773, 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.56 (1H, dd, J = 8.2, 9.2 Hz), 4.04 (1H, dd, J = 2.6, 9.2 Hz), 3.77 (3H, s), 3.16 (1H, tt, J =2.5, 8.5 Hz), 2.39 (1H, m), 1.98 (1H, m), 1.95 (1H, t, J = 11.9 Hz), 1.81 (1H, m), 1.67 (1H, ddd, J = 9.1, 10.8, 13.2 Hz), 1.05 (3H, d, J = 6.0 Hz); ^{13}C-NMR ($CDCl_3$) δ: 176.3, 170.4, 73.7, 61.6, 53.0, 44.5,

42.5, 42.4, 33.7, 18.5; MS (*m/z*) 199 (M^++H^+), 167 (M^+-OMe). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.71; H, 7.19 .

5-*tert*-Butyl-3-oxo-tetrahydro-1*H*-cyclopenta[*c*]furan-3a(3*H*)-carboxylic acid methyl ester (2j). Compound **2j** was prepared from **1j** (128 mg, 0.5 mmol). Purification by column chromatography (hexane / AcOEt = 5) and then MPLC (hexane / AcOEt = 5) gave the mixture of *cis*-**2j** and *trans*-**2j** (109 mg, 91 %, *cis* / *trans* = 8). *cis*-**2j**: colorless oil; IR ($CHCl_3$) 2959, 1777, 1742 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 4.49 (1H, dd, *J* = 6.3, 9.2 Hz), 4.16 (1H, dd, *J* = 1.3, 9.2 Hz), 3.77 (3H, s), 3.02 (1H, m), 2.57 (1H, ddd, *J* = 1.8, 7.3, 13.1 Hz), 1.79-2.11 (3H, m), 1.28 (1H, q, *J* = 118 Hz), 0.88 (9H, s); ^{13}C-NMR ($CDCl_3$) δ: 176.6, 170.6, 74.1, 71.2, 60.4, 53.0, 52.3, 47.1, 34.6, 34.5, 27.5; MS (*m/z*) 241 (M^++H^+), 225 (M^+-Me). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.99; H, 8.39.

References

1. Reitz, A. B.; Nortey, S. O.; Maryanoff, B. E. *J. Org. Chem.* **1987**, *52*, 4191.
2. Mulzer, J.; Angermann, A. *Tetrahedron Lett.* **1983**, *24*, 2843.
3. Hasrami, M. E.; Lavergne, J. P.; Viallefont, P.; Itto, M. Y. A.; Hasnaoui, A. *Tetrahedron Lett.* **1991**, *32*, 3985.
4. Montaudon, E.; Lubeigt, X.; Maillard, B. *J. Chem. Soc. Perkin Trans. I* **1991**, 1531.