

# Enantioselective synthesis of furo[2,3-b]furans, a spongiane diterpenoid substructure

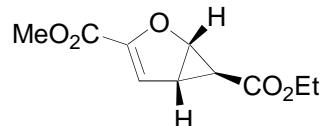
## Supporting Information

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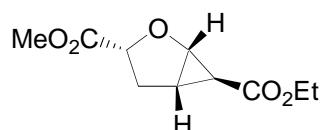
### (1S,5S,6S)-6-ethyl 3-methyl 2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (9)



Fp: 42 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.32 (d, <sup>3</sup>J = 2.8 Hz, 1 H, H-4), 4.90 (dd, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-1), 4.08 (q, <sup>3</sup>J = 7.1 Hz, 2 H, CH<sub>2</sub>), 3.74 (s, 3 H, -OCH<sub>3</sub>), 2.80 (ddd, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 2.8 Hz, <sup>3</sup>J = 2.7 Hz, 1 H, H-5), 1.20 (t, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.09 (dd, <sup>3</sup>J = 2.7 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-6). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 171.77 (C<sub>q</sub>, CO<sub>2</sub>Et), 159.54 (C<sub>q</sub>, CO<sub>2</sub>Me), 149.16 (C<sub>q</sub>, C-3), 116.18 (+, C-4), 67.54 (+, C-1), 61.07 (-, CH<sub>2</sub>), 52.25 (+, OCH<sub>3</sub>), 31.97 (+, C-5), 21.46 (+, C-6), 14.20 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3139, 3067, 2992, 2958, 2908, 2851, 1715, 1625, 1439, 1399, 1382, 1343, 1301, 1217, 1183, 1113, 1085, 1040, 1009, 988, 970, 932, 878, 831, 795, 733. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.0) = -272. **MS** (EI-MS): *m/z* (%) = 212.3 (10) [M<sup>+</sup>], 153.4 (12), [M<sup>+</sup>ΔCO<sub>2</sub>Me], 139.4 (100) [M<sup>+</sup>ΔCO<sub>2</sub>Et], 125.4 (19), 97.3 (23). C<sub>10</sub>H<sub>12</sub>O<sub>5</sub> (212.2): calcd. C 56.60, H 5.70; found C 56.51, H 5.73.

### (1S,3R,5S,6S)-6-ethyl 3-methyl 2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (10)

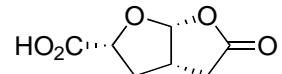


Fp: 69 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 4.74 (dd, <sup>3</sup>J = 10.7 Hz, <sup>3</sup>J = 4.3 Hz, 1 H, H-3), 4.28 (dd, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J = 0.9 Hz, 1 H, H-1), 4.06 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 4.02 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 3.71 (s, 3 H, OCH<sub>3</sub>), 2.60 (ddd, <sup>2</sup>J = 13.4 Hz, <sup>3</sup>J = 10.7 Hz, <sup>3</sup>J = 6.0 Hz, 1 H, H-4<sub>exo</sub>), 2.23 (dd, <sup>2</sup>J = 13.4 Hz, <sup>3</sup>J = 4.3 Hz, 1 H, H-4<sub>endo</sub>), 2.13 (ddd, <sup>3</sup>J = 6.0 Hz, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J = 4.0 Hz, 1 H, H-5), 1.83 (dd, <sup>3</sup>J = 4.0 Hz, <sup>3</sup>J = 0.9 Hz, 1 H, H-6), 1.18 (dd, <sup>3</sup>J = 7.1 Hz, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 173.33 (C<sub>q</sub>, C=O), 170.40 (C<sub>q</sub>, C=O), 79.11 (+, C-3), 67.46 (+, C-1), 60.55 (-, CH<sub>2</sub>CH<sub>3</sub>), 52.48 (+, OCH<sub>3</sub>), 32.02 (-, CH<sub>2</sub>CH), 28.20 (+, C-6), 25.58 (+, C-5), 14.22 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3070, 2986, 2943, 2905, 1744, 1713, 1457, 1435, 1416, 1357, 1328, 1298, 1279, 1211, 1196, 1171, 1115, 1084, 1048, 1029, 981, 963, 929, 905, 878, 845, 809, 737, 718, 702, 674, 653, 474, 417. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.4) = + 27. **MS** (EI-MS): m/z (%) = 214.1 (4) [M<sup>+</sup>], 169.1 (17) [M<sup>+</sup>ΔOEt], 168.1 (41) [M<sup>+</sup>ΔEtOH], 155.1 (25) [M<sup>+</sup>ΔCO<sub>2</sub>Me], 141.1 (28) [M<sup>+</sup>ΔCO<sub>2</sub>Et], 136.1 (38), 113.1 (49), 109.1 (56), 81.1 (100), 55.1 (39), 53.1 (39), 29.2 (43) [Et<sup>+</sup>]. **HRMS** (EI-MS): für C<sub>10</sub>H<sub>14</sub>O<sub>5</sub> (M<sup>+</sup>) calcd. 214.0841, found 214.0841.

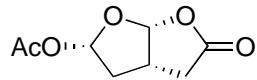
### (2*R*,3*aS*,6*aR*)-5-oxohexahydrofuro[2,3-*b*]furan-2-carboxylic acid (11)

Fp: 103 °C.



**<sup>1</sup>H-NMR** (400 MHz, DMSO-d<sub>6</sub>): δ (ppm) = 12.89 (s, br, 1 H, CO<sub>2</sub>H), 6.07 (d, <sup>3</sup>J = 5.7 Hz, 1 H, H-6a), 4.66 (dd, <sup>3</sup>J = 8.9 Hz, <sup>3</sup>J = 4.2 Hz, 1 H, H-2), 3.17 (ddddd, <sup>3</sup>J = 10.1 Hz, <sup>3</sup>J = 9.6 Hz, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J = 4.3 Hz, <sup>3</sup>J = 3.4 Hz, 1 H, H-3a), 2.82 (dd, <sup>2</sup>J = 18.3 Hz, <sup>3</sup>J = 10.1 Hz, 1 H, H-4<sub>exo</sub>), 2.46 (ddd, <sup>2</sup>J = 13.3 Hz, <sup>3</sup>J = 9.6 Hz, <sup>3</sup>J = 8.9 Hz, 1 H, H-3<sub>exo</sub>), 2.35 (dd, <sup>2</sup>J = 18.3 Hz, <sup>3</sup>J = 3.4 Hz, 1 H, H-4<sub>endo</sub>), 1.98 (ddd, <sup>2</sup>J = 13.3 Hz, <sup>3</sup>J = 4.3 Hz, <sup>3</sup>J = 4.2 Hz, 1 H, H-3<sub>endo</sub>). **<sup>13</sup>C-NMR** (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) = 175.04 (C<sub>q</sub>, C-5), 172.87 (C<sub>q</sub>, CO<sub>2</sub>H), 108.65 (+, C-6a), 78.32 (+, C-2), 37.93 (+, C-3a), 34.68 (-, C-4), 33.95 (-, C-3). **IR** (KBr): ν (cm<sup>-1</sup>) = 3436, 2983, 2955, 1762, 1731, 1715, 1462, 1421, 1414, 1394, 1356, 1328, 1307, 1292, 1265, 1240, 1220, 1186, 1100, 1060, 1011, 970, 928, 880, 870, 829, 778, 693, 668. [α]<sub>D</sub><sup>20</sup> (MeOH, c = 1.9) = -77. **MS** (CI-MS): m/z (%) = 190.0 (100) [M+NH<sub>4</sub><sup>+</sup>]. **HRMS** (EI-MS): für C<sub>7</sub>H<sub>8</sub>O<sub>5</sub> (M<sup>+</sup>) calcd. 172.0372, found 172.0376. **C<sub>7</sub>H<sub>8</sub>O<sub>5</sub>**: calcd. C 48.84, H 4.68, found C 48.76, H 4.79.

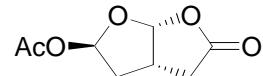
**(2*S*,3*aS*,6*aR*)-5-oxohexahydrofuro[2,3-*b*]furan-2-yl acetate (13)**



**Fp:** 65 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.45 (d, <sup>3</sup>J = 4.9 Hz, 1 H, H-2), 6.19 (d, <sup>3</sup>J = 6.1 Hz, 1 H, H-6a), 3.27 (ddddd, <sup>3</sup>J = 11.2 Hz, <sup>3</sup>J = 9.6 Hz, <sup>3</sup>J = 6.1 Hz, <sup>3</sup>J = 4.2 Hz, <sup>3</sup>J = 1.2 Hz, H-3a), 2.91 (dd, <sup>2</sup>J = 18.6 Hz, <sup>3</sup>J = 11.2 Hz, 1 H, H-4<sub>exo</sub>), 2.62 (dd, <sup>2</sup>J = 18.6 Hz, <sup>3</sup>J = 4.2 Hz, 1 H, H-4<sub>endo</sub>), 2.40 (ddd, <sup>2</sup>J = 14.0 Hz, <sup>3</sup>J = 9.6 Hz, <sup>3</sup>J = 4.9 Hz, 1 H, H-3<sub>exo</sub>), 2.07 (dd, <sup>2</sup>J = 14.0 Hz, <sup>3</sup>J = 1.2 Hz, 1 H, H-3<sub>endo</sub>), 2.05 (s, 3 H, CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 174.04 (C<sub>q</sub>, C-5), 168.52 (C<sub>q</sub>, COCH<sub>3</sub>), 107.41 (+, C-6a), 97.42 (+, C-2), 37.27 (-, C-3), 35.18 (+, C-3a), 34.47 (-, C-4), 20.20 (+, CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 2985, 2959, 2928, 1783, 1722, 1381, 1359, 1260, 1242, 1179, 1112, 1067, 1024, 975, 933, 919, 866, 833, 792, 773, 685. **[α]<sub>D</sub><sup>20</sup>** (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.1) = -152. **MS** (CI-MS): *m/z* (%) = 204.0 (100) [M+NH<sub>4</sub><sup>+</sup>]. **C<sub>8</sub>H<sub>10</sub>O<sub>5</sub>**: calcd. C 51.61, H 5.41, found C 51.76, H 5.60.

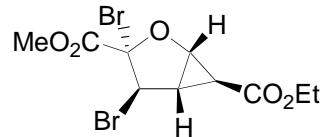
**(2*R*,3*aS*,6*aR*)-5-oxohexahydrofuro[2,3-*b*]furan-2-yl acetate (epi-13)**



**Fp:** = 116 – 118 °C.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.49 (ddd, <sup>3</sup>J = 5.2 Hz, <sup>3</sup>J = 1.1 Hz, <sup>4</sup>J = 0.5 Hz, 1 H, H-2), 6.10 (d, <sup>3</sup>J = 5.5 Hz, 1 H, H-6a), 3.25 (ddddd, <sup>3</sup>J = 9.4 Hz, <sup>3</sup>J = 8.7 Hz, <sup>3</sup>J = 8.7 Hz, <sup>3</sup>J = 5.5 Hz, <sup>3</sup>J = 1.9 Hz, <sup>4</sup>J = 0.5 Hz, 1 H, H-3a), 2.86 (dd, <sup>2</sup>J = 18.1 Hz, <sup>3</sup>J = 8.7 Hz, 1 H, H-4<sub>exo</sub>), 2.52 (dd, <sup>2</sup>J = 18.1 Hz, <sup>3</sup>J = 1.9 Hz, 1 H, H-4<sub>endo</sub>), 2.40 (ddd, <sup>2</sup>J = 13.9 Hz, <sup>3</sup>J = 8.7 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-3<sub>exo</sub>), 2.07 (s, 3 H, CH<sub>3</sub>), 1.97 (ddd, <sup>2</sup>J = 13.9 Hz, <sup>3</sup>J = 9.4 Hz, <sup>3</sup>J = 5.2 Hz, 1 H, H-3<sub>endo</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 173.56 (C<sub>q</sub>, C-5), 169.57 (C<sub>q</sub>, COCH<sub>3</sub>), 107.59 (+, C-6a), 98.76 (+, C-2), 36.81 (-, C-3), 36.71 (+, C-3a), 34.78 (-, C-4), 21.08 (+, CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 2975, 1786, 1739, 1443, 1420, 1374, 1355, 1332, 1296, 1241, 1219, 1184, 1165, 1103, 1088, 1048, 1009, 974, 952, 928, 860, 829, 780, 660, 642, 605. **[α]<sub>D</sub><sup>20</sup>** (CH<sub>2</sub>Cl<sub>2</sub>, c = 0.9) = + 18. **MS** (CI-MS): *m/z* (%) = 127.0 (66) [M<sup>+</sup>ΔOAc], 109.0 (15), 99.0 (18) [M<sup>+</sup>ΔOAcΔCO], 82.0 (28), 70.0 (23), 43.0 (100) [CH<sub>3</sub>CO<sup>+</sup>], 42.0 (17), 41.0 (12). **C<sub>8</sub>H<sub>10</sub>O<sub>5</sub>**: calcd. C 51.61, H 5.41, found C 51.35, H 5.34.

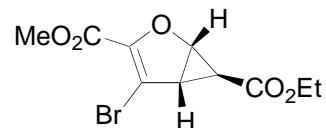
**(1*R*,3*S*,4*R*,5*S*,6*S*)-6-ethyl 3-methyl 3,4-dibromo-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (14)**



Fp: 97 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 5.11 (s, 1 H, H-4), 4.89 (dd, <sup>3</sup>J = 5.3 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-1), 4.15 (q, <sup>3</sup>J = 7.1 Hz, 2 H, CH<sub>2</sub>), 3.88 (s, 3 H, OCH<sub>3</sub>), 3.66 (dd, <sup>3</sup>J = 4.0 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-6), 2.82 (dd, <sup>3</sup>J = 5.3 Hz, <sup>3</sup>J = 4.0 Hz, 1 H, H-5), 1.28 (t, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 168.58 (C<sub>q</sub>, CO<sub>2</sub>Et), 163.82 (C<sub>q</sub>, CO<sub>2</sub>Me), 95.98 (C<sub>q</sub>, C-3), 68.03 (+, C-1), 61.51 (-, CH<sub>2</sub>), 54.31 (+, C-4), 53.52 (+, OCH<sub>3</sub>), 31.00 (+, C-5), 24.94 (+, C-6), 14.14 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3089, 3039, 2990, 2976, 2958, 2908, 1769, 1753, 1709, 1474, 1440, 1409, 1388, 1315, 1294, 1184, 1128, 1115, 1089, 1066, 1039, 1022, 1002, 979, 947, 885, 840, 803, 785, 748, 731, 715, 690, 610. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.4) = -298. **MS** (CI-MS): m/z (%) = 392.1 (5) [M(<sup>81</sup>Br)<sub>2</sub>+NH<sub>4</sub><sup>+</sup>], 390.1 (10) [M(<sup>81</sup>Br<sup>79</sup>Br)+NH<sub>4</sub><sup>+</sup>], 388.1 (5) [M(<sup>79</sup>Br)<sub>2</sub>+NH<sub>4</sub><sup>+</sup>], 310.1 (7) [M(<sup>81</sup>Br)+NH<sub>4</sub><sup>+</sup>ΔBr], 308.1 (7) [M(<sup>79</sup>Br)+NH<sub>4</sub><sup>+</sup>ΔBr], 230.1 (100) [M+NH<sub>4</sub><sup>+</sup>Δ2Br], 213.2 (14) [MH<sup>+</sup>Δ2Br]. **C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>O<sub>5</sub>**: calcd. C 32.29, H 3.25, found C 32.54, H 3.26.

**(1*R*,5*S*,6*S*)-6-ethyl 3-methyl 4-bromo-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (15)**

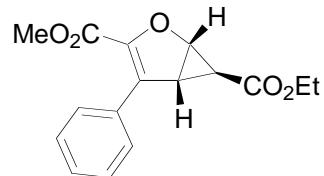


Fp: 39 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 4.88 (dd, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 1.2 Hz, 1 H, H-1), 4.15 (q, <sup>3</sup>J = 7.1 Hz, 2 H, CH<sub>2</sub>), 3.82 (s, 3 H, OCH<sub>3</sub>), 3.03 (dd, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 2.6 Hz, 1 H, H-5), 1.36 (dd, <sup>3</sup>J = 2.6 Hz, <sup>3</sup>J = 1.2 Hz, 1 H, H-6), 1.26 (t, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 170.83 (C<sub>q</sub>, CO<sub>2</sub>Et), 158.82 (C<sub>q</sub>, CO<sub>2</sub>Me), 143.51 (C<sub>q</sub>, C-3), 108.14 (C<sub>q</sub>, C-4), 66.16 (+, C-1), 61.42 (-, CH<sub>2</sub>), 52.40 (+, OCH<sub>3</sub>), 37.54 (+, C-5), 21.34 (+, C-6), 14.17 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3097, 3063, 3036, 2999, 2985, 2913, 2870, 2845, 1728, 1606, 1483, 1437, 1403, 1378, 1354, 1326, 1298, 1271, 1180, 1171, 1139, 1103, 1075, 1029, 991, 910, 895, 870, 829, 801, 772, 729, 581, 523, 454. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.6) =

–154. **MS** (EI-MS):  $m/z$  (%) = 292.0 (15) [ $M(^{81}Br)^+$ ], 290.0 (15) [ $M(^{79}Br)^+$ ], 247.0 (4) [ $M(^{81}Br)^+\Delta OEt$ ], 245.0 (4) [ $M(^{79}Br)^+\Delta OEt$ ], 218.9 (99) [ $M(^{81}Br)^+\Delta CO_2Et$ ], 216.9 (100) [ $M(^{79}Br)^+\Delta CO_2Et$ ], 211.0 (17) [ $M^+\Delta Br$ ]. **C<sub>10</sub>H<sub>11</sub>BrO<sub>5</sub>**: calcd. C 41.26, H 3.81, Br 27.45, found C: 41.42, H 3.78, Br 27.09.

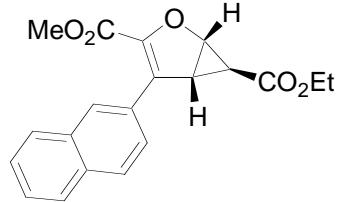
**(1*S*,5*R*,6*S*)-6-ethyl 3-methyl 4-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (16)**



**Fp:** 68 °C.

**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.61 (m, 2 H, H<sub>arom</sub>), 7.37 (m, 3 H, H<sub>arom</sub>), 4.94 (dd, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-1), 4.21 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.2 Hz, 1 H, CHH-CH<sub>3</sub>), 4.17 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHH-CH<sub>3</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 3.11 (dd, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 2.7 Hz, 1H, H-5), 1.41(dd, <sup>3</sup>J = 2.7 Hz, <sup>3</sup>J = 1.1 Hz, 1H, H-6), 1.29 (dd, <sup>3</sup>J = 7.2 Hz, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (151 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 171.75 (C<sub>q</sub>, CO<sub>2</sub>Et), 160.11 (C<sub>q</sub>, CO<sub>2</sub>Me), 140.28 (C<sub>q</sub>, C-3), 131.23 (C<sub>q</sub>, C-4), 131.19 (C<sub>q</sub>, C<sub>arom</sub>), 129.04 (+, 2 C, C<sub>arom</sub>), 128.87 (+, C<sub>arom</sub>), 128.06 (+, 2 C, C<sub>arom</sub>), 64.73 (+, C-1), 61.20 (-, CH<sub>2</sub>), 52.10 (+, OCH<sub>3</sub>), 36.37 (+, C-5), 21.68 (+, C-6), 14.24 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr):  $\nu$  (cm<sup>-1</sup>) = 3064, 2984, 2956, 2906, 1712, 1616, 1495, 1437, 1400, 1381, 1354, 1304, 1263, 1173, 1138, 1096, 1082, 1041, 998, 986, 936, 878, 843, 807, 763, 743, 691, 667, 642, 613. **[ $\alpha$ ]<sub>D</sub><sup>20</sup>** (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.3) = –103. **MS** (EI-MS):  $m/z$  (%) = 288.0 (1) [M<sup>+</sup>], 243.0 (5) [M<sup>+</sup>ΔOEt], 215.0 (63) [M<sup>+</sup>ΔCO<sub>2</sub>Et], 201.0 (100) [M<sup>+</sup>ΔCH<sub>2</sub>CO<sub>2</sub>Et], 173.0 (52) [M<sup>+</sup>ΔCH<sub>2</sub>CO<sub>2</sub>EtΔCO], 155.0 (15), 128.0 (19), 127.0 (19), 115.0 (10), 102.0 (11), 77.0 (6) [Ph<sup>+</sup>]. **C<sub>16</sub>H<sub>16</sub>O<sub>5</sub>**: calcd. C 66.66, H 5.59, found C 66.53, H 5.41.

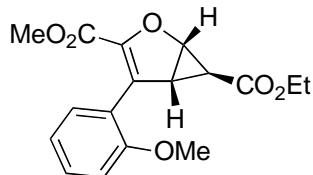
**(1*S*,5*R*,6*S*)-6-ethyl 3-methyl 4-(naphthalen-2-yl)-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (17)**



**Fp:** 115 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.08 – 8.06 (m, 1 H, H<sub>arom</sub>), 7.90 – 7.79 (m, 3 H, H<sub>arom</sub>), 7.71 (dd, <sup>3</sup>J = 8.6 Hz, <sup>4</sup>J = 1.8 Hz, 1 H, H<sub>arom</sub>), 7.53 – 7.46 (m, 2 H, H<sub>arom</sub>), 4.98 (dd, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-1), 4.24 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 4.20 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 3.79 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 3.21 (dd, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 2.7 Hz, 1 H, H-5), 1.49 (dd, <sup>3</sup>J = 2.7 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-6), 1.31 (dd, <sup>3</sup>J = 7.1 Hz, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 171.86 (C<sub>q</sub>, CO<sub>2</sub>Et), 160.19 (C<sub>q</sub>, CO<sub>2</sub>Me), 140.48 (C<sub>q</sub>, C-3), 133.30 (C<sub>q</sub>), 132.89 (C<sub>q</sub>), 131.30 (C<sub>q</sub>), 128.69 (C<sub>q</sub>), 128.64 (+, C<sub>arom</sub>), 128.35 (+, C<sub>arom</sub>), 127.68 (+, C<sub>arom</sub>), 127.51 (+, C<sub>arom</sub>), 126.82 (+, C<sub>arom</sub>), 126.63 (+, C<sub>arom</sub>), 126.44 (+, C<sub>arom</sub>), 64.82 (+, C-1), 61.47 (-, CH<sub>2</sub>CH<sub>3</sub>), 52.20 (+, CO<sub>2</sub>CH<sub>3</sub>), 36.41 (+, C-5), 21.83 (+, C-6), 14.29 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3067, 2988, 2950, 2905, 1713, 1611, 1437, 1399, 1377, 1343, 1302, 1269, 1171, 1137, 1094, 1077, 1040, 995, 935, 857, 840, 816, 746. **[α]<sub>D</sub><sup>20</sup>** (CH<sub>2</sub>Cl<sub>2</sub>, c = 0.3) = -24. **MS** (EI-MS): *m/z* (%): 338.2 (9) [M<sup>+</sup>], 265.2 (73) [M<sup>+</sup>ΔCO<sub>2</sub>Et], 251.2 (100) [M<sup>+</sup>ΔCH<sub>2</sub>CO<sub>2</sub>Et], 223.2 (60) [M<sup>+</sup>ΔCH<sub>2</sub>CO<sub>2</sub>EtΔCO], 205.2 (38), 178.2 (22), 155.1 (27), 152.1 (21), 127.1 (5) [C<sub>10</sub>H<sub>7</sub><sup>+</sup>], 95.1 (8). **C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>**: calcd. C 70.99, H 5.36, found C 70.66, H 5.33.

**(1*S*,5*R*,6*S*)-6-ethyl 3-methyl 4-(2-methoxyphenyl)-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (18)**

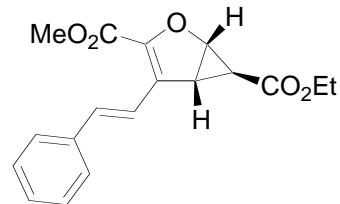


**Fp:** 76 °C.

**<sup>1</sup>H-NMR** (300 MHz, Aceton-d<sub>6</sub>): δ (ppm) = 7.38 – 7.31 (m, 2 H, H<sub>arom</sub>), 7.06 – 6.93 (m, 2 H, H<sub>arom</sub>), 4.97 (dd, <sup>3</sup>J = 5.3 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-1), 4.16 (dq, <sup>2</sup>J = 10.9 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 4.12 (dq, <sup>2</sup>J = 10.9 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 3.84 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 3.63 (s, 3 H, Ar-OCH<sub>3</sub>), 3.04 (dd, <sup>3</sup>J = 5.3 Hz, <sup>3</sup>J = 2.6 Hz, 1 H, H-5), 1.35 (dd, <sup>3</sup>J = 2.6 Hz, <sup>3</sup>J =

1.1 Hz, 1 H, H-6), 1.24 (dd,  $^3J = 7.1$  Hz,  $^3J = 7.1$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ).  **$^{13}\text{C-NMR}$**  (75 MHz, Aceton-d<sub>6</sub>):  $\delta$  (ppm) = 172.19 (C<sub>q</sub>, CO<sub>2</sub>Et), 160.15 (C<sub>q</sub>, CO<sub>2</sub>Me), 157.14 (C<sub>q</sub>, C<sub>arom</sub>OMe), 142.02 (C<sub>q</sub>, C-3), 130.95 (+, CH<sub>arom</sub>), 130.07 (+, CH<sub>arom</sub>), 128.37 (C<sub>q</sub>, C-4), 120.81 (C<sub>q</sub>, C<sub>arom</sub>-C-4), 120.11 (+, CH<sub>arom</sub>), 110.68 (+, CH<sub>arom</sub>), 66.01 (+, C-1), 60.96 (-, CH<sub>2</sub>), 55.43 (+, Ar-OCH<sub>3</sub>), 51.95 (+, CO<sub>2</sub>CH<sub>3</sub>), 36.92 (+, C-5), 22.06 (+, C-6), 14.30 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr):  $\nu$  (cm<sup>-1</sup>) = 3067, 3008, 2985, 2964, 2946, 2877, 1719, 1707, 1617, 1598, 1493, 1462, 1444, 1402, 1381, 1356, 1305, 1258, 1200, 1179, 1138, 1098, 1078, 1034, 993, 940, 908, 876, 840, 811, 792, 781, 753, 650.  $[\alpha]_D^{20}$  (CH<sub>2</sub>Cl<sub>2</sub>, c = 0.5) = -102. **MS** (EI-MS):  $m/z$  (%) = 318.1 (1) [M<sup>+</sup>], 287.1 (2) [M<sup>+</sup>ΔOMe], 245.1 (51) [M<sup>+</sup>ΔCO<sub>2</sub>Et], 231.1 (100) [M<sup>+</sup>ΔCH<sub>2</sub>CO<sub>2</sub>Et], 203.1 (35) [M<sup>+</sup>ΔCH<sub>2</sub>CO<sub>2</sub>EtΔCO], 135.0 (87), 114.9 (22). **HRMS** (EI-MS): für C<sub>17</sub>H<sub>18</sub>O<sub>6</sub> (M<sup>+</sup>) calcd. 318.1103, found 318.1100. **C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>**: calcd. C 64.14, H 5.70, found C 64.15, H 5.73.

**(1S,5R,6S)-6-ethyl 3-methyl 4-(E)-styryl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (19)**

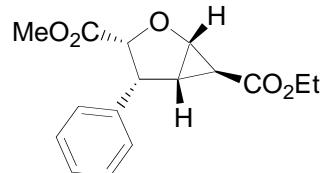


**Fp:** 85-88 °C.

**$^1\text{H-NMR}$**  (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.72 (d,  $^3J = 16.2$  Hz, 1 H, CHPh), 7.54 – 7.49 (m, 2 H, H<sub>arom</sub>), 7.39 – 7.25 (m, 3 H, H<sub>arom</sub>), 6.91 (d,  $^3J = 16.2$  Hz, 1 H, CH=CHPh), 4.92 (dd,  $^3J = 5.5$  Hz,  $^3J = 1.0$  Hz, 1 H, H-1), 4.23 (dq,  $^2J = 10.8$  Hz,  $^3J = 7.1$  Hz, 1 H, CHHCH<sub>3</sub>), 4.19 (dq,  $^2J = 10.8$  Hz,  $^3J = 7.2$  Hz, 1 H, CHHCH<sub>3</sub>), 3.88 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 3.19 (dd,  $^3J = 5.5$  Hz,  $^3J = 2.9$  Hz, 1 H, H-5), 1.34 (dd,  $^3J = 2.9$  Hz,  $^3J = 1.0$  Hz, 1 H, H-6), 1.31 (dd,  $^3J = 7.2$  Hz,  $^3J = 7.1$  Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>).  **$^{13}\text{C-NMR}$**  (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 171.88 (C<sub>q</sub>, CO<sub>2</sub>Et), 160.36 (C<sub>q</sub>, CO<sub>2</sub>Me), 141.84 (C<sub>q</sub>, C-3), 136.61 (C<sub>q</sub>, C<sub>arom</sub>), 134.44 (+, CHPh), 131.32 (C<sub>q</sub>, C-4), 128.80 (+, 2 C, C<sub>arom</sub>), 128.53 (+, C<sub>arom</sub>), 127.03 (+, 2 C, C<sub>arom</sub>), 119.59 (+, CH=CHPh), 65.66 (+, C-1), 61.29 (-, CH<sub>2</sub>CH<sub>3</sub>), 52.16 (+, CO<sub>2</sub>CH<sub>3</sub>), 31.31 (+, C-5), 22.18 (+, C-6), 14.24 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr):  $\nu$  (cm<sup>-1</sup>) = 3062, 3026, 2986, 2945, 2904, 2871, 2846, 1713, 1618, 1582, 1496, 1476, 1448, 1436, 1402, 1377, 1308, 1290, 1259, 1230, 1184, 1165, 1131, 1089, 1067, 1039, 996, 987, 944, 926, 895, 879, 839, 814, 778, 763, 751, 690, 622.  $[\alpha]_D^{20}$  (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.0) = -30. **MS** (EI-MS):  $m/z$  (%) = 314.1 [M<sup>+</sup>] (23), 241.1 [M<sup>+</sup>ΔCO<sub>2</sub>Et] (78), 227.1 (67)

$[M^+\Delta CH_2CO_2Et]$ , 181.1 (100), 153.1 (64). **C<sub>18</sub>H<sub>18</sub>O<sub>5</sub>**: calcd. C 68.78, H 5.77, found C 68.85, H 5.52.

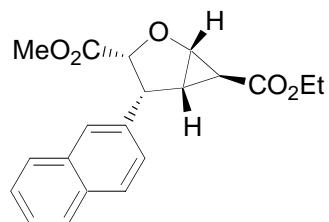
**(1S,3R,4R,5S,6S)-6-ethyl 3-methyl 4-phenyl-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (20)**



**Fp:** 67 – 69 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.39-7.19 (m, 5 H, H<sub>arom</sub>), 5.01 (dd, <sup>3</sup>J = 11.0 Hz, <sup>4</sup>J = 0.4 Hz, 1 H, H-3), 4.40 (ddd, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 1.0 Hz, <sup>4</sup>J = 0.4 Hz, 1 H, H-1), 4.35 (dd, <sup>3</sup>J = 11.0 Hz, <sup>3</sup>J = 5.2 Hz, 1 H, H-4), 4.17 (dd, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 4.11 (dd, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CHHCH<sub>3</sub>), 3.13 (s, 3 H, OCH<sub>3</sub>), 3.13 (dd, <sup>3</sup>J = 4.5 Hz, <sup>3</sup>J = 1.0 Hz, 1 H, H-6), 2.42 (ddd, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 5.2 Hz, <sup>3</sup>J = 4.5 Hz, 1 H, H-5), 1.28 (dd, <sup>3</sup>J = 7.1 Hz, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 170.84 (C<sub>q</sub>, CO<sub>2</sub>Me), 169.61 (C<sub>q</sub>, CO<sub>2</sub>E<sub>t</sub>), 134.73 (C<sub>q</sub>, C<sub>arom</sub>), 127.35 (+, 2 C, CH<sub>arom</sub>), 127.30 (+, 2 C, CH<sub>arom</sub>), 126.60 (+, CH<sub>arom</sub>), 81.36 (+, C-3), 64.71 (+, C-1), 59.68 (-, CH<sub>2</sub>CH<sub>3</sub>), 50.39 (+, OCH<sub>3</sub>), 47.33 (+, C-4), 28.47 (+, C-5), 25.12 (+, C-6), 13.24 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3083, 3066, 3035, 3003, 2985, 2975, 2948, 2932, 2911, 1749, 1713, 1497, 1476, 1456, 1434, 1410, 1376, 1351, 1321, 1293, 1281, 1215, 1197, 1173, 1121, 1091, 1076, 1065, 1046, 1030, 999, 967, 937, 904, 888, 875, 848, 812, 759, 704. **[α]<sub>D</sub><sup>20</sup>** (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.0) = -54. **MS** (EI-MS): m/z (%) = 290.0 (1) [M<sup>+</sup>], 162.0 (100), 131.9 (45), 129.0 (26). **C<sub>16</sub>H<sub>18</sub>O<sub>5</sub>**: calcd. C 66.19, H 6.25, found C 66.08, H 6.17.

**(1S,3R,4R,5S,6S)-6-ethyl 3-methyl 4-(naphthalen-2-yl)-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (21)**

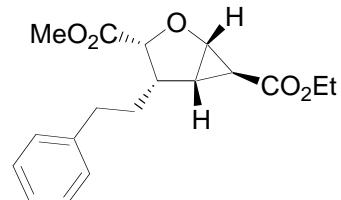


**Fp:** 69 - 70 °C.

**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.84 (d, <sup>4</sup>J = 1.7 Hz, 1 H, H<sub>arom</sub>), 7.82 - 7.79 (m, 2 H, H<sub>arom</sub>), 7.78 (d, <sup>3</sup>J = 8.5 Hz, 1 H, H<sub>arom</sub>), 7.50 - 7.46 (m, 2 H, H<sub>arom</sub>), 7.40 (dd, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J =

1.7 Hz, 1 H, H<sub>arom</sub>), 5.12 (d, <sup>3</sup>J = 11.0 Hz, 1 H, H-3), 4.53 (dd, <sup>3</sup>J = 11.0 Hz, <sup>3</sup>J = 5.2 Hz, 1 H, H-4), 4.47 (dd, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 1.0 Hz, 1 H, H-1), 4.22 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.2 Hz, 1 H, CH<sub>2</sub>HCH<sub>3</sub>), 4.16 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CH<sub>2</sub>HCH<sub>3</sub>), 3.22 (dd, <sup>3</sup>J = 4.4 Hz, <sup>3</sup>J = 1.0 Hz, 1 H, H-6), 3.04 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 2.52 (ddd, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 5.2 Hz, <sup>3</sup>J = 4.4 Hz, 1 H, H-5), 1.32 (dd, <sup>3</sup>J = 7.2 Hz, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 171.86 (C<sub>q</sub>, CO<sub>2</sub>Me), 170.69 (C<sub>q</sub>, CO<sub>2</sub>Et), 133.29 (C<sub>q</sub>, C<sub>arom</sub>), 133.14 (C<sub>q</sub>, C<sub>arom</sub>), 132.69 (C<sub>q</sub>, C<sub>arom</sub>), 127.96 (+, C<sub>arom</sub>), 127.78 (+, C<sub>arom</sub>), 127.56 (+, C<sub>arom</sub>), 126.99 (+, C<sub>arom</sub>), 126.71 (+, C<sub>arom</sub>), 126.28 (+, C<sub>arom</sub>), 126.11 (+, C<sub>arom</sub>), 82.36 (+, C-3), 65.83 (+, C-1), 60.78 (-, CH<sub>2</sub>CH<sub>3</sub>), 51.46 (+, CO<sub>2</sub>CH<sub>3</sub>), 48.59 (+, C-4), 29.65 (+, C-5), 26.29 (+, C-6), 14.33 (+, CH<sub>2</sub>CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3079, 3051, 2992, 2950, 1746, 1717, 1509, 1436, 1417, 1366, 1324, 1287, 1271, 1215, 1185, 1117, 1078, 1066, 1049, 1033, 1013, 973, 935, 893, 854, 827, 798, 745, 699. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 0.6) = -60. **MS** (EI-MS): m/z (%) = 340.2 (9) [M<sup>+</sup>], 212.1 (100) [C<sub>10</sub>H<sub>7</sub>-CH=CH-CO<sub>2</sub>Me<sup>+</sup>], 181.1 (34) [C<sub>10</sub>H<sub>7</sub>-CH=CH-CO<sup>+</sup>], 179.1 (38), 178.1 (30), 165.1 (18), 153.1 (15) [C<sub>10</sub>H<sub>7</sub>-CH=CH<sup>+</sup>], 152.1 (21), 141.1 (13), 128.1 (7), 127.1 (5) [C<sub>10</sub>H<sub>7</sub><sup>+</sup>]. **C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>**: calcd. C 70.57, H 5.92, found C 70.58, H 5.86.

**(1S,3R,4S,5S,6S)-6-ethyl 3-methyl 4-phenethyl-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (22)**

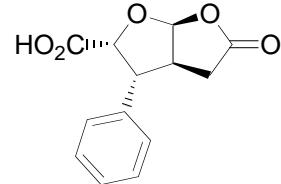


**Fp:** 67 – 71 °C.

**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.29 (dd, <sup>3</sup>J = 7.7 Hz, <sup>3</sup>J = 7.4 Hz, 2 H, H<sub>arom-meta</sub>), 7.20 (t, <sup>3</sup>J = 7.4 Hz, 1 H, H<sub>arom-para</sub>), 7.18 (d, <sup>3</sup>J = 7.7 Hz, 2 H, H<sub>arom-ortho</sub>), 4.78 (d, <sup>3</sup>J = 10.4 Hz, 1 H, H-3), 4.30 (dd, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-1), 4.14 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CH<sub>2</sub>HCH<sub>3</sub>), 4.08 (dq, <sup>2</sup>J = 10.8 Hz, <sup>3</sup>J = 7.1 Hz, 1 H, CH<sub>2</sub>HCH<sub>3</sub>), 3.71 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 3.01 (dd, <sup>3</sup>J = 11.3 Hz, <sup>3</sup>J = 10.4 Hz, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 4.4 Hz, 1 H, H-4), 2.80 (dd, <sup>2</sup>J = 13.9 Hz, <sup>3</sup>J = 8.9 Hz, <sup>3</sup>J = 5.6 Hz, 1 H, CH<sub>2</sub>HPh), 2.65 (dd, <sup>2</sup>J = 13.9 Hz, <sup>3</sup>J = 8.6 Hz, <sup>3</sup>J = 7.2 Hz, 1 H, CH<sub>2</sub>HPh), 2.34 (dd, <sup>3</sup>J = 4.3 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-6), 2.28 (dd, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 4.3 Hz, 1 H, H-5), 1.85 (dd, <sup>3</sup>J = 13.3 Hz, <sup>3</sup>J = 8.9 Hz, <sup>3</sup>J = 7.2 Hz, <sup>3</sup>J = 4.4 Hz, 1 H, CH<sub>2</sub>H<sub>2</sub>Ph), 1.51 (dd, <sup>3</sup>J = 13.3 Hz, <sup>3</sup>J = 11.3 Hz, <sup>3</sup>J = 8.6 Hz, <sup>3</sup>J = 5.6 Hz, 1 H, CH<sub>2</sub>H<sub>2</sub>Ph), 1.26 (dd, <sup>3</sup>J = 7.1 Hz, <sup>3</sup>J = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz,

$\text{CDCl}_3$ ):  $\delta$  (ppm) = 172.17 ( $\text{C}_\text{q}$ ,  $\underline{\text{CO}_2\text{Me}}$ ), 170.61 ( $\text{C}_\text{q}$ ,  $\underline{\text{CO}_2\text{Et}}$ ), 140.94 ( $\text{C}_\text{q}$ ,  $\text{C}_\text{arom}$ ), 128.53 (+, 2 C,  $\text{C}_\text{arom-meta}$ ), 128.37 (+, 2 C,  $\text{C}_\text{arom-ortho}$ ), 126.18 (+,  $\text{C}_\text{arom-para}$ ), 82.24 (+, C-3), 66.99 (+, C-1), 60.58 (-,  $\underline{\text{CH}_2\text{CH}_3}$ ), 51.98 (+,  $\text{CO}_2\underline{\text{CH}_3}$ ), 42.33 (+, C-4), 34.64 (-,  $\underline{\text{CH}_2\text{Ph}}$ ), 29.93 (+, C-5), 29.48 (-,  $\underline{\text{CH}_2\text{CH}_2\text{Ph}}$ ), 25.21 (+, C-6), 14.24 (+,  $\text{CH}_2\underline{\text{CH}_3}$ ). **IR** (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3063, 3027, 2982, 2951, 2909, 2865, 1750, 1716, 1496, 1455, 1413, 1370, 1304, 1263, 1205, 1186, 1070, 1031, 990, 924, 874, 854, 749, 701.  $[\alpha]_D^{20}$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 1.6$ ) = + 10.8. **MS** (EI-MS):  $m/z$  (%) = 318.1 (1) [ $\text{M}^+$ ], 229.1 (56), 213.1 (15), 185.1 (25), 129.1 (23), 104.0 (51), 91.0 (100) [ $\text{PhCH}_2^+$ ]. **HRMS** (EI-MS): für  $\text{C}_{18}\text{H}_{22}\text{O}_5$  ( $\text{M}^+$ ) calcd. 318.1467, found 318.1465.

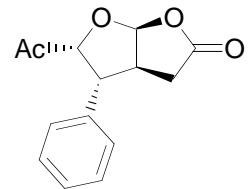
### (2*R*,3*R*,3*aS*,6*aS*)-5-oxo-3-phenylhexahydrofuro[2,3-*b*]furan-2-carboxylic acid (23)



**Fp:** 164 °C.

**<sup>1</sup>H-NMR** (300 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm) = 7.35-7.21 (m, 5 H,  $\text{H}_\text{arom}$ ), 6.43 (d,  ${}^3J = 5.7$  Hz, 1 H, H-6a), 5.05 (d,  ${}^3J = 6.4$  Hz, 1 H, H-2), 4.91 (s, br, 1 H,  $\text{CO}_2\text{H}$ ), 3.63 (dd,  ${}^3J = 6.4$  Hz,  ${}^3J = 3.5$  Hz, 1 H, H-3), 3.43 (dd,  ${}^3J = 10.4$  Hz,  ${}^3J = 5.7$  Hz,  ${}^3J = 3.9$  Hz,  ${}^3J = 3.5$  Hz, 1 H, H-3a), 3.02 (dd,  ${}^2J = 18.9$  Hz,  ${}^3J = 10.4$  Hz, 1 H-4<sub>exo</sub>), 2.70 (dd,  ${}^2J = 18.9$  Hz,  ${}^3J = 3.9$  Hz, 1 H, H-4<sub>endo</sub>). **<sup>13</sup>C-NMR** (75 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm) = 177.32 ( $\text{C}_\text{q}$ , C-5), 172.01 ( $\text{C}_\text{q}$ ,  $\text{CO}_2\text{H}$ ), 139.67 ( $\text{C}_\text{q}$ ,  $\text{C}_\text{arom}$ ), 129.58 (+, 2 C,  $\text{C}_\text{arom}$ ), 129.31 (+, 2 C,  $\text{C}_\text{arom}$ ), 128.61 (+,  $\text{C}_\text{arom}$ ), 109.95 (+, C-6a), 82.33 (+, C-2), 55.27 (+, C-3), 47.56 (+, C-3a), 35.13 (-, C-4). **IR** (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3446, 3063, 3034, 2926, 2855, 1787, 1763, 1630, 1495, 1456, 1417, 1377, 1339, 1300, 1255, 1192, 1104, 985, 906, 866, 830, 807, 775, 749, 703, 677, 651, 583, 519.  $[\alpha]_D^{20}$  ( $\text{MeOH}$ ,  $c = 0.8$ ) = -66. **MS** (CI-MS):  $m/z$  (%) = 266.1 (100) [ $\text{M}+\text{NH}_4^+$ ]. **HRMS** (CI-MS): für  $\text{C}_{13}\text{H}_{13}\text{O}_5$  ( $\text{MH}^+$ ) calcd. 249.0763, found 249.0769.

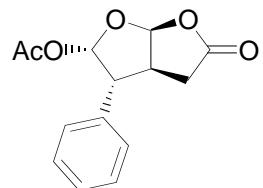
**(3a*S*,4*R*,5*R*,6a*S*)-5-acetyl-4-phenyltetrahydrofuro[2,3-*b*]furan-2(6a*H*)-one (29)**



**Fp:** 189 °C.

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.36 – 7.24 (m, 3 H, H<sub>arom</sub>), 7.13 – 7.04 (m, 2 H, H<sub>arom</sub>), 6.49 (d, <sup>3</sup>J = 5.6 Hz, 1 H, H-6a), 4.84 (d, <sup>3</sup>J = 6.1 Hz, 1 H, H-2), 3.52 (dd, <sup>3</sup>J = 6.1 Hz, <sup>3</sup>J = 2.6 Hz, 1 H, H-3), 3.42 (dd, <sup>3</sup>J = 10.6 Hz, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 4.1 Hz, <sup>3</sup>J = 2.6 Hz, 1 H, H-3a), 3.03 (dd, <sup>2</sup>J = 18.9 Hz, <sup>3</sup>J = 10.6 Hz, 1 H, H-4<sub>exo</sub>), 2.63 (dd, <sup>2</sup>J = 18.9 Hz, <sup>3</sup>J = 4.1 Hz, 1 H, H-4<sub>endo</sub>), 1.72 (s, 3 H, CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 205.54 (C<sub>q</sub>, COCH<sub>3</sub>), 174.13 (C<sub>q</sub>, C-5), 137.25 (C<sub>q</sub>, C<sub>arom</sub>), 129.04 (+, 2 C, C<sub>arom</sub>), 128.07 (+, C<sub>arom</sub>), 127.86 (+, 2 C, C<sub>arom</sub>), 107.87 (+, C-6a), 86.26 (+, C-2), 54.77 (+, C-3), 46.00 (+, C-3a), 34.50 (-, C-4), 27.83 (+, CH<sub>3</sub>). **IR** (KBr): ν (cm<sup>-1</sup>) = 3091, 3068, 3038, 3013, 2991, 2976, 2944, 2927, 2889, 2854, 1784, 1719, 1500, 1490, 1457, 1411, 1360, 1333, 1294, 1245, 1228, 1191, 1176, 1096, 1058, 1020, 994, 971, 920, 910, 881, 867, 834, 808, 798, 760, 718, 696, 641, 604. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 0.5) = -5.1. **MS** (EI-MS): *m/z* (%): 246.1 (7) [M<sup>+</sup>], 218.1 (31) [M<sup>+</sup>ΔCO], 203.1 (86) [M<sup>+</sup>ΔCOCH<sub>3</sub>], 157.1 (100), 129.1 (77), 115.1 (33), 91.1 (81), 85.1 (26), 77.0 (23) [Ph<sup>+</sup>], 57.1 (14), 43.0 (57) [CH<sub>3</sub>CO<sup>+</sup>]. **C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>:** calcd. C 68.28, H 5.73, found C 68.12, H 5.67.

**(2*S*,3*R*,3a*S*,6a*S*)-5-oxo-3-phenylhexahydrofuro[2,3-*b*]furan-2-yl acetate (30)**

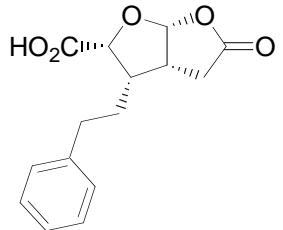


**Fp:** 149 °C.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.40 – 7.24 (m, 5 H, H<sub>arom</sub>), 6.59 (d, <sup>3</sup>J = 4.7 Hz, 1 H, H-2), 6.22 (d, <sup>3</sup>J = 5.4 Hz, 1 H, H-6a), 3.49 (dd, <sup>3</sup>J = 11.1 Hz, <sup>3</sup>J = 8.3 Hz, <sup>3</sup>J = 5.4 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-3a), 3.32 (dd, <sup>3</sup>J = 11.1 Hz, <sup>3</sup>J = 4.7 Hz, 1 H, H-3), 2.86 (dd, <sup>2</sup>J = 18.2 Hz, <sup>3</sup>J = 8.3 Hz, 1 H, H-4<sub>exo</sub>), 2.55 (dd, <sup>2</sup>J = 18.2 Hz, <sup>3</sup>J = 1.1 Hz, 1 H, H-4<sub>endo</sub>), 1.90 (s, 3 H, CH<sub>3</sub>). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) = 172.99 (C<sub>q</sub>, C-5), 168.89 (C<sub>q</sub>, CO<sub>2</sub>CH<sub>3</sub>), 132.65 (C<sub>q</sub>, C<sub>arom</sub>), 128.98 (+, 2 C, C<sub>arom</sub>), 128.81 (+, 2 C, C<sub>arom</sub>), 128.31 (+, C<sub>arom</sub>), 107.02 (+,

C-6a), 98.87 (+, C-2), 53.36 (+, C-3), 42.36 (+, C-3a), 34.18 (-, C-4), 20.84 (+, CH<sub>3</sub>). **IR** (KBr):  $\nu$  (cm<sup>-1</sup>) = 3056, 3034, 3016, 2994, 2977, 2941, 2926, 2856, 1786, 1735, 1498, 1457, 1432, 1381, 1352, 1322, 1293, 1260, 1235, 1160, 1112, 1092, 1030, 1008, 992, 928, 915, 900, 871, 775, 731, 704, 674, 663, 633, 610. [α]<sub>D</sub><sup>20</sup> (CH<sub>2</sub>Cl<sub>2</sub>, c = 1.4) = -90. **MS** (EI-MS): *m/z* (%): 262.2 [M<sup>+</sup>] (2), 203.1 [M<sup>+</sup>ΔOAc] (21), 175.1 (16), 174.1 (100) [M<sup>+</sup>ΔHOAcΔCO], 158.1 (13), 157.1 (19), 146.1 (17), 145.1 (96), 132.1 (79), 131.1 (74) [Ph-CH=CCHCO<sup>+</sup>], 129.1 (28), 117.1 (36), 91.1 (42) [PhCH<sub>2</sub><sup>+</sup>], 77.1 (12) [Ph<sup>+</sup>], 43.0 (64) [CH<sub>3</sub>CO<sup>+</sup>]. **HRMS** (EI-MS): für C<sub>14</sub>H<sub>14</sub>O<sub>5</sub> (M<sup>+</sup>) calcd. 262.0841, found 262.0838.

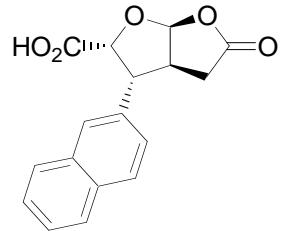
### (2*R*,3*S*,3a*R*,6a*R*)-5-oxo-3-phenethylhexahydrofuro[2,3-*b*]furan-2-carboxylic acid (31)



**Fp:** 146 °C.

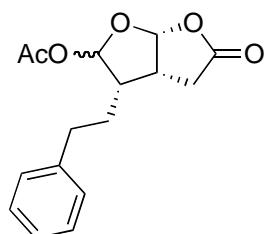
**<sup>1</sup>H-NMR** (400 MHz, CD<sub>3</sub>OD): δ (ppm) = 7.30 – 7.15 (m, 5 H, H<sub>arom</sub>), 6.12 (d, <sup>3</sup>J = 6.0 Hz, 1 H, H-6a), 4.90 (s, br, 1 H, CO<sub>2</sub>H), 4.62 (d, <sup>3</sup>J = 8.8 Hz, 1 H, H-2), 3.29 (dd, <sup>3</sup>J = 11.5 Hz, <sup>3</sup>J = 8.4 Hz, <sup>3</sup>J = 6.5 Hz, <sup>3</sup>J = 6.0 Hz, 1 H, H-3a), 2.79 – 2.65 (m, 2 H, CH<sub>2</sub>Ph), 2.78 (dd, <sup>3</sup>J = 8.8 Hz, <sup>3</sup>J = 8.4 Hz, 1 H, H-3), 2.56 (dd, <sup>2</sup>J = 18.8 Hz, <sup>3</sup>J = 6.5 Hz, 1 H, H-4<sub>endo</sub>), 2.45 (dd, <sup>2</sup>J = 18.8 Hz, <sup>3</sup>J = 11.5 Hz, 1 H, H-4<sub>exo</sub>), 1.96 – 1.90 (m, 1 H, CHHCH<sub>2</sub>Ph), 1.76 – 1.70 (m, 1 H, CHHCH<sub>2</sub>Ph). **<sup>13</sup>C-NMR** (75 MHz, CD<sub>3</sub>OD): δ (ppm) = 179.28 (C<sub>q</sub>, C-5), 174.62 (C<sub>q</sub>, CO<sub>2</sub>H), 142.81 (C<sub>q</sub>, C<sub>arom</sub>), 129.61 (+, 2 C, C<sub>arom</sub>), 129.46 (+, 2 C, C<sub>arom</sub>), 127.24 (+, C<sub>arom</sub>), 110.68 (+, C-6a), 82.76 (+, C-2), 44.58 (+, C-3), 42.33 (+, C-3a), 35.36 (-, CH<sub>2</sub>Ph), 29.87 (-, CH<sub>2</sub>CH<sub>2</sub>Ph), 29.43 (-, C-4). **IR** (KBr):  $\nu$  (cm<sup>-1</sup>) = 3422, 3022, 2926, 2857, 1773, 1385, 1202, 1111, 1088, 1017, 993, 975, 751, 737, 700, 627. [α]<sub>D</sub><sup>20</sup> (MeOH, c = 0.6) = -47. **MS** (EI-MS): *m/z* (%) = 258.1 (2) [M<sup>+</sup>ΔH<sub>2</sub>O], 230.1 (11) [M<sup>+</sup>ΔH<sub>2</sub>OΔCO], 201.1 (37), 129.1 (27), 105.1 (14) [Ph(CH<sub>2</sub>)<sub>2</sub><sup>+</sup>], 104.1 (66) [PhCH=CH<sub>2</sub><sup>+</sup>], 91.1 (100) [PhCH<sub>2</sub><sup>+</sup>]. **C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>**: calcd. C 65.21, H 5.84, found C 65.13, H 5.84.

**(2*R*,3*R*,3a*S*,6a*S*)-3-(naphthalen-2-yl)-5-oxohexahydrofuro[2,3-*b*]furan-2-carboxylic acid (32)**



**<sup>1</sup>H-NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) = 7.84 – 7.76 (m, 3 H, H<sub>arom</sub>), 7.72 (m, 1 H, H<sub>arom</sub>), 7.48 – 7.40 (m, 2 H, H<sub>arom</sub>), 7.38 – 7.35 (m, 1 H, H<sub>arom</sub>), 6.52 (d, <sup>3</sup>J = 5.6 Hz, 1 H, H-6a), 5.13 (d, <sup>3</sup>J = 6.5 Hz, 1 H, H-2), 4.84 (s, br, 1 H, CO<sub>2</sub>H), 3.82 (dd, <sup>3</sup>J = 6.5 Hz, <sup>3</sup>J = 3.7 Hz, 1 H, H-3), 3.57 (dddd, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 5.6 Hz, <sup>3</sup>J = 3.8 Hz, <sup>3</sup>J = 3.7 Hz, 1 H, H-3a), 3.07 (dd, <sup>2</sup>J = 18.8 Hz, <sup>3</sup>J = 10.3 Hz, 1 H-4<sub>exo</sub>), 2.77 (dd, <sup>2</sup>J = 18.8 Hz, <sup>3</sup>J = 3.8 Hz, 1 H, H-4<sub>endo</sub>). **<sup>13</sup>C-NMR** (75 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm) = 177.30 (C<sub>q</sub>, C-5), 172.12 (C<sub>q</sub>, CO<sub>2</sub>H), 137.11 (C<sub>q</sub>, C<sub>arom</sub>), 134.77 (C<sub>q</sub>, C<sub>arom</sub>), 134.26 (C<sub>q</sub>, C<sub>arom</sub>), 129.21 (+, CH<sub>arom</sub>), 128.96 (+, CH<sub>arom</sub>), 128.58 (+, CH<sub>arom</sub>), 128.09 (+, CH<sub>arom</sub>), 127.37 (+, CH<sub>arom</sub>), 127.28 (+, CH<sub>arom</sub>), 127.10 (+, CH<sub>arom</sub>), 110.04 (+, C-6a), 82.46 (+, C-2), 55.39 (+, C-3), 47.53 (+, C-3a), 35.20 (-, C-4). **IR** (KBr):  $\nu$  (cm<sup>-1</sup>) = 3233, 3053, 3018, 2936, 1757, 1373, 1317, 1252, 1195, 1099, 1024, 996, 984, 901, 870, 813, 752, 708, 632. **MS** (EI-MS): *m/z* (%) = 298.1 (100) [M<sup>+</sup>], 252.1 (15) [M<sup>+</sup>ΔH<sub>2</sub>OΔCO], 224.1 (15) [M<sup>+</sup>ΔH<sub>2</sub>OΔ2CO], 207.1 (21), 195.1 (42), 182.1 (51), 181.1 (44), 165.1 (45), 152.1 (35), 141.1 (32), 128.1 (18), 127.1 (7) [C<sub>10</sub>H<sub>7</sub><sup>+</sup>], 115.1 (13). **HRMS** (EI-MS): für C<sub>17</sub>H<sub>14</sub>O<sub>5</sub> (M<sup>+</sup>): calcd. 298.0841, found 298.0839.

**(2*R/S*,3*S*,3a*R*,6a*R*)-5-oxo-3-phenethylhexahydrofuro[2,3-*b*]furan-2-yl acetate (33)**



NMR-data for the 2*R*-Isomer:

**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.34-7.30 (m, 2 H, H<sub>arom-ortho</sub>), 7.26-7.22 (m, 1 H, H<sub>arom-para</sub>), 7.20-7.16 (m, 2 H, H<sub>arom-meta</sub>), 6.21 (d, <sup>3</sup>J = 5.0 Hz, 1 H, H-2), 6.09 (d, <sup>3</sup>J = 5.4 Hz, 1 H, H-6a), 3.21 (dddd, <sup>3</sup>J = 9.1 Hz, <sup>3</sup>J = 8.1 Hz, <sup>3</sup>J = 7.0 Hz, <sup>3</sup>J = 5.4 Hz, 1 H, H-3a), 2.76 (ddd, <sup>2</sup>J = 14.3 Hz, <sup>3</sup>J = 8.7 Hz, <sup>3</sup>J = 6.0 Hz, 1H, CH<sub>HPh</sub>), 2.64 (ddd, <sup>2</sup>J = 14.3 Hz, <sup>3</sup>J = 8.3

Hz,  $^3J = 7.1$  Hz, 1 H,  $\underline{\text{CH}}\text{HPh}$ ), 2.55 (dd,  $^2J = 18.4$  Hz,  $^3J = 7.0$  Hz, 1 H, H-4), 2.52 (dd,  $^2J = 18.4$  Hz,  $^3J = 9.1$  Hz, 1 H, H-4), 2.42 (dddd,  $^3J = 8.1$  Hz,  $^3J = 8.1$  Hz,  $^3J = 7.3$  Hz,  $^3J = 5.0$  Hz, 1 H, H-3), 2.12 (s, 3 H,  $\text{CH}_3$ ), 1.86 (dddd,  $^2J = 14.0$  Hz,  $^3J = 8.3$  Hz,  $^3J = 8.1$  Hz,  $^3J = 6.0$  Hz, 1 H,  $\underline{\text{CH}}\text{HCH}_2\text{Ph}$ ), 1.76 (dddd,  $^2J = 14.0$  Hz,  $^3J = 8.7$  Hz,  $^3J = 7.3$  Hz,  $^3J = 7.1$  Hz, 1 H, - $\text{CH}\underline{\text{HCH}}_2\text{Ph}$ ).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 174.61 ( $\text{C}_q$ , C-5), 169.74 ( $\text{C}_q$ ,  $\underline{\text{COCH}}_3$ ), 140.42 ( $\text{C}_q$ ,  $\text{C}_{\text{arom}}$ ), 128.69 (+, 2 C,  $\text{CH}_{\text{arom}}$ ), 128.37 (+, 2 C,  $\text{CH}_{\text{arom}}$ ), 126.49 (+,  $\text{C}_{\text{arom-para}}$ ), 106.33 (+, C-6a), 100.84 (+, C-2), 44.75 (+, C-3), 40.44 (+, C-3a), 34.12 (-,  $\underline{\text{CH}}_2\text{Ph}$ ), 28.71 (-,  $\underline{\text{CH}}_2\text{CH}_2\text{Ph}$ ), 28.51 (-, C-4), 21.09 (+,  $\text{CH}_3$ ).

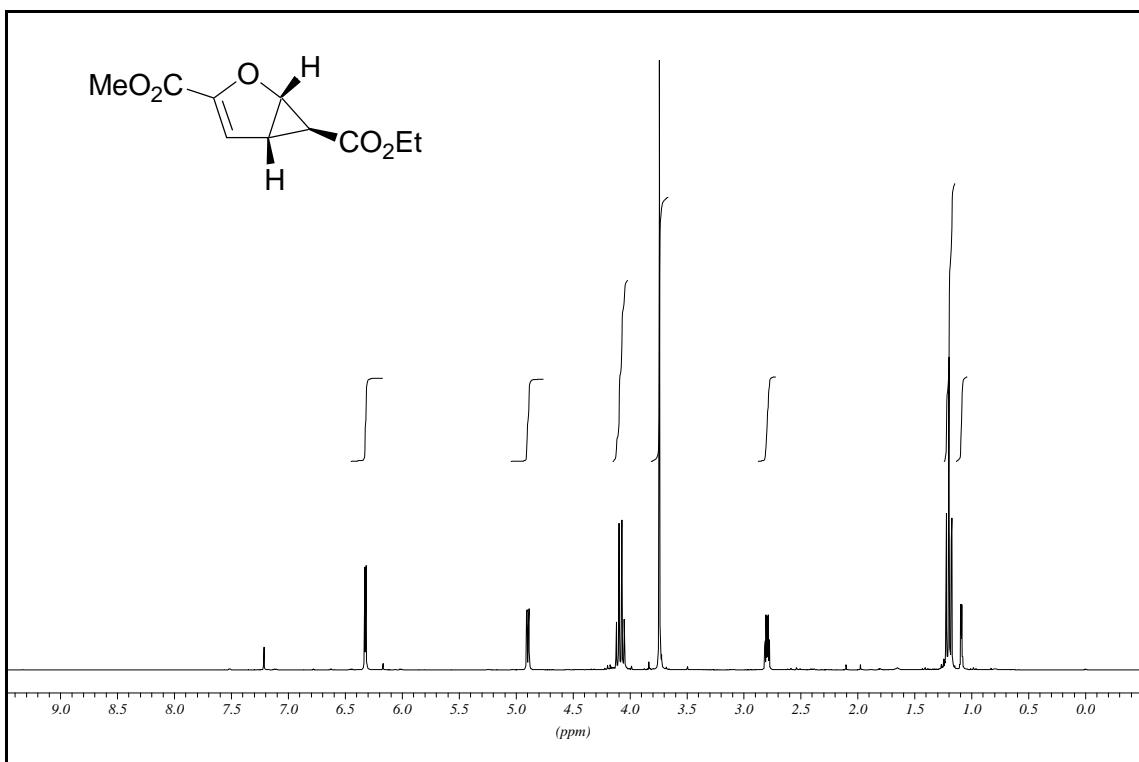
**NMR-data for the 2S-Isomer:**

**$^1\text{H-NMR}$**  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.34 - 7.30 (m, 2 H,  $\text{H}_{\text{arom-ortho}}$ ), 7.26 - 7.22 (m, 1 H,  $\text{H}_{\text{arom-para}}$ ), 7.20 - 7.16 (m, 2 H,  $\text{H}_{\text{arom-meta}}$ ), 6.28 (d,  $^3J = 4.4$  Hz, 1 H, H-2), 6.11 (d,  $^3J = 6.1$  Hz, 1 H, H-6a), 3.17 (dddd,  $^3J = 11.4$  Hz,  $^3J = 8.6$  Hz,  $^3J = 6.1$  Hz,  $^3J = 5.1$  Hz 1 H, H-3a), 2.78 - 2.73 (m , 1 H,  $\underline{\text{CH}}\text{HPh}$ ), 2.76 (dd,  $^2J = 18.4$  Hz,  $^3J = 5.1$  Hz, 1 H, H-4), 2.69 - 2.65 (m, 1 H,  $\underline{\text{CH}}\text{HPh}$ ), 2.52 (dd,  $^2J = 18.4$  Hz,  $^3J = 11.4$  Hz, 1 H, H-4), 2.46-2.40 (m, 1 H, H-3), 2.05 (s, 3 H,  $\text{CH}_3$ ), 1.96-1.90 (m, 1 H,  $\underline{\text{CH}}\text{HCH}_2\text{Ph}$ ), 1.84-1.76 (m, 1 H,  $\underline{\text{CH}}\text{HCH}_2\text{Ph}$ ).  **$^{13}\text{C-NMR}$**  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 175.37 ( $\text{C}_q$ , C-5), 169.49 ( $\text{C}_q$ ,  $\underline{\text{COCH}}_3$ ), 140.59 ( $\text{C}_q$ ,  $\text{C}_{\text{arom}}$ ), 128.74 (+, 2 C,  $\text{CH}_{\text{arom}}$ ), 128.28 (+, 2 C,  $\text{CH}_{\text{arom}}$ ), 126.54 (+,  $\text{C}_{\text{arom-para}}$ ), 107.86 (+, C-6a), 98.00 (+, C-2), 44.32 (+, C-3), 38.96 (+, C-3a), 33.96 (-,  $\underline{\text{CH}}_2\text{Ph}$ ), 28.86 (-, C-4), 26.83 (-,  $\underline{\text{CH}}_2\text{CH}_2\text{Ph}$ ), 21.17 (+,  $\text{CH}_3$ ).

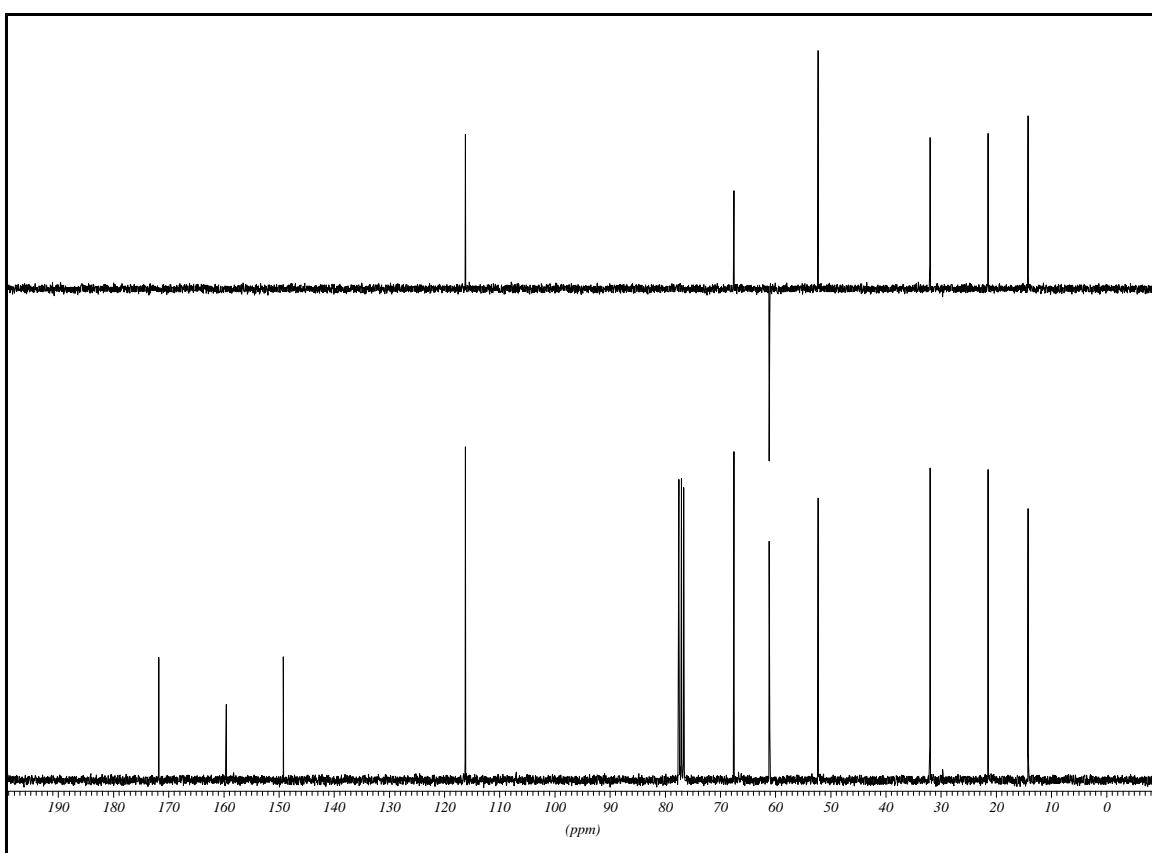
**MS** (PI-EI-MS):  $m/z$  (%): 231.0 (3) [ $\text{M}^+\Delta\text{OAc}$ ] 230.0 (9) [ $\text{M}^+\Delta\text{HOAc}$ ], 213.0 (13), 129.0 (19), 128.0 (37), 104.0 (100) [ $\text{PhCH=CH}_2^+$ ], 91.0 (59) [ $\text{PhCH}_2^+$ ]. **HRMS** (LSI-MS): für  $\text{C}_{16}\text{H}_{19}\text{O}_5$  ( $\text{MH}^+$ ) calcd. 291.1232, found 291.1232.

**(1S,5S,6S)-(-)-2-Oxa-bicyclo[3.1.0]hex-3-en-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )**

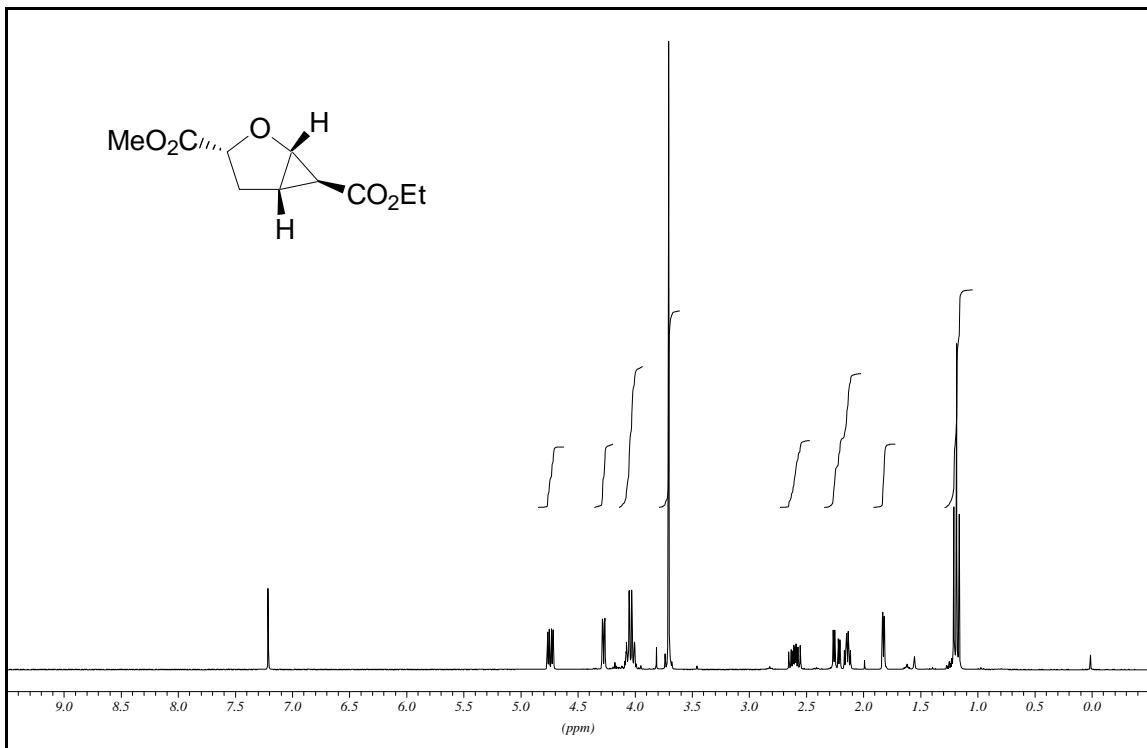


**$^{13}\text{C-NMR}$  (75.5 MHz,  $\text{CDCl}_3$ )**

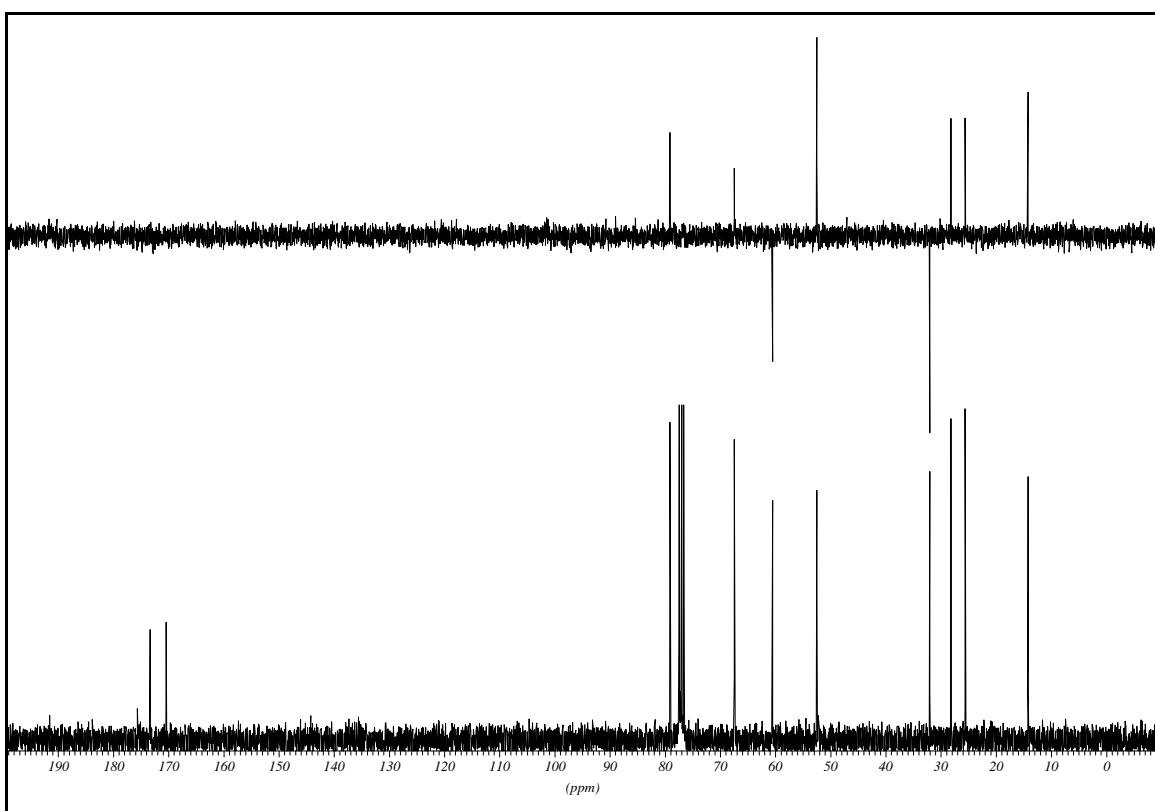


**(1*S*,3*R*,5*S*,6*S*)-(+)-2-Oxa-bicyclo[3.1.0]hexan-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )**

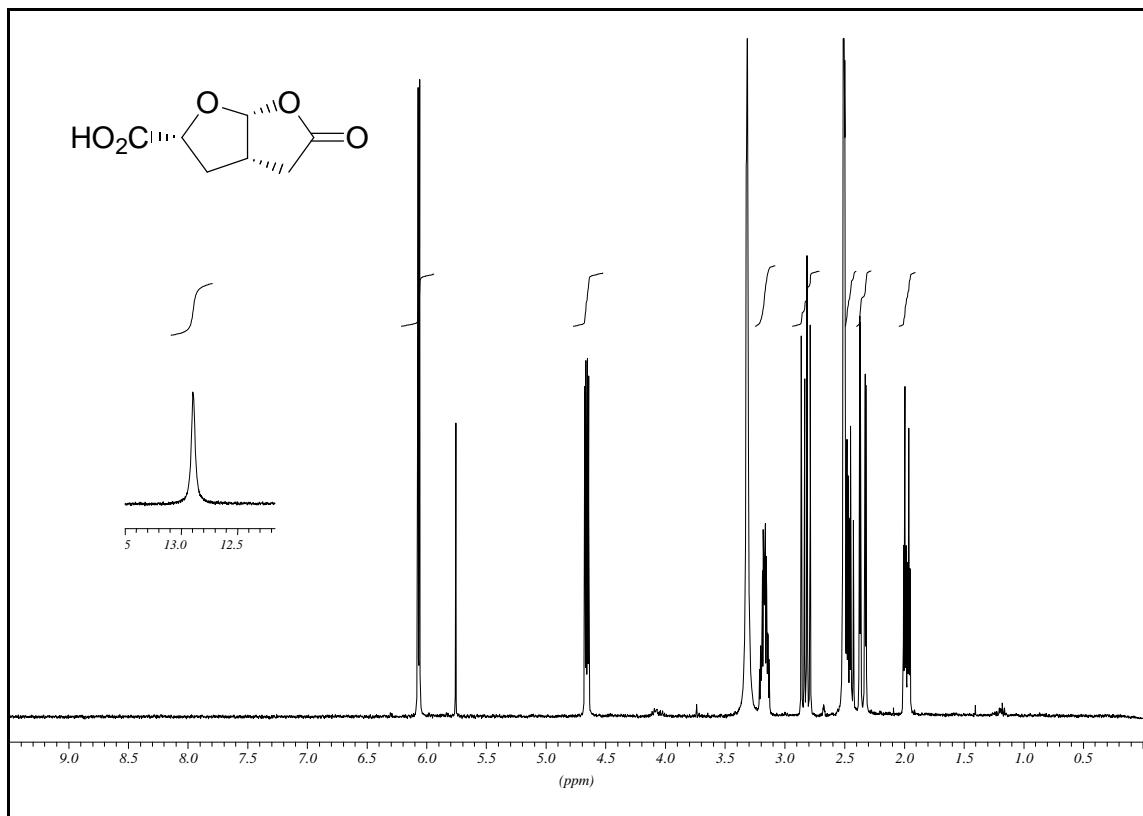


**$^{13}\text{C}$ -NMR (75.5 MHz,  $\text{CDCl}_3$ )**

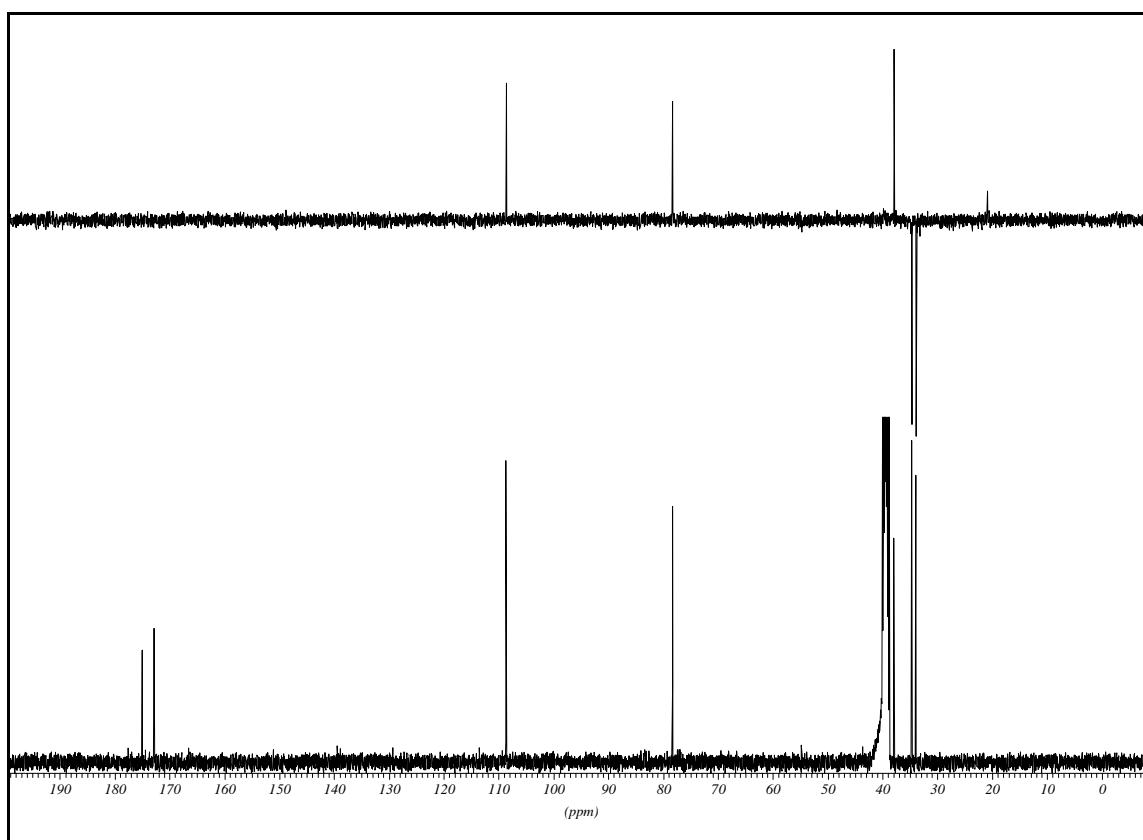


**(2*R*,3*aS*,6*aR*)-(-)-5-Oxo-hexahydrofuro[2,3-*b*]furan-2-carbonsäure**

**$^1\text{H-NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>)**

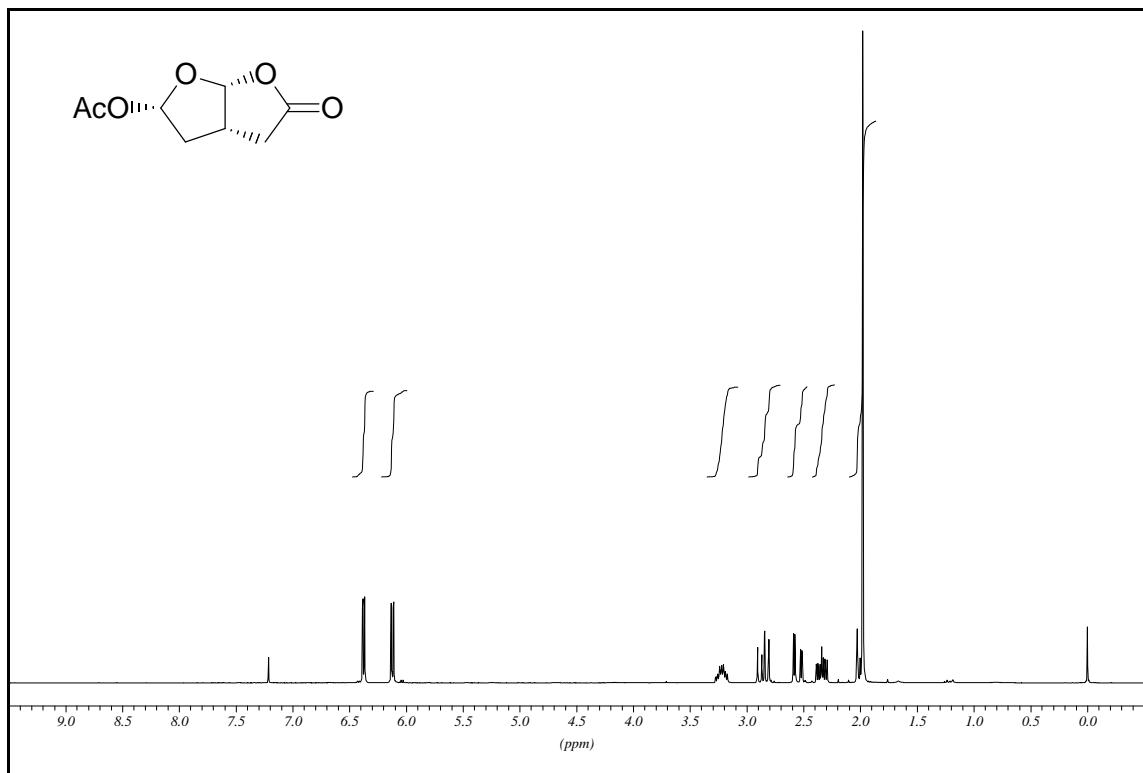


**$^{13}\text{C-NMR}$  (100.6 MHz, DMSO-*d*<sub>6</sub>)**

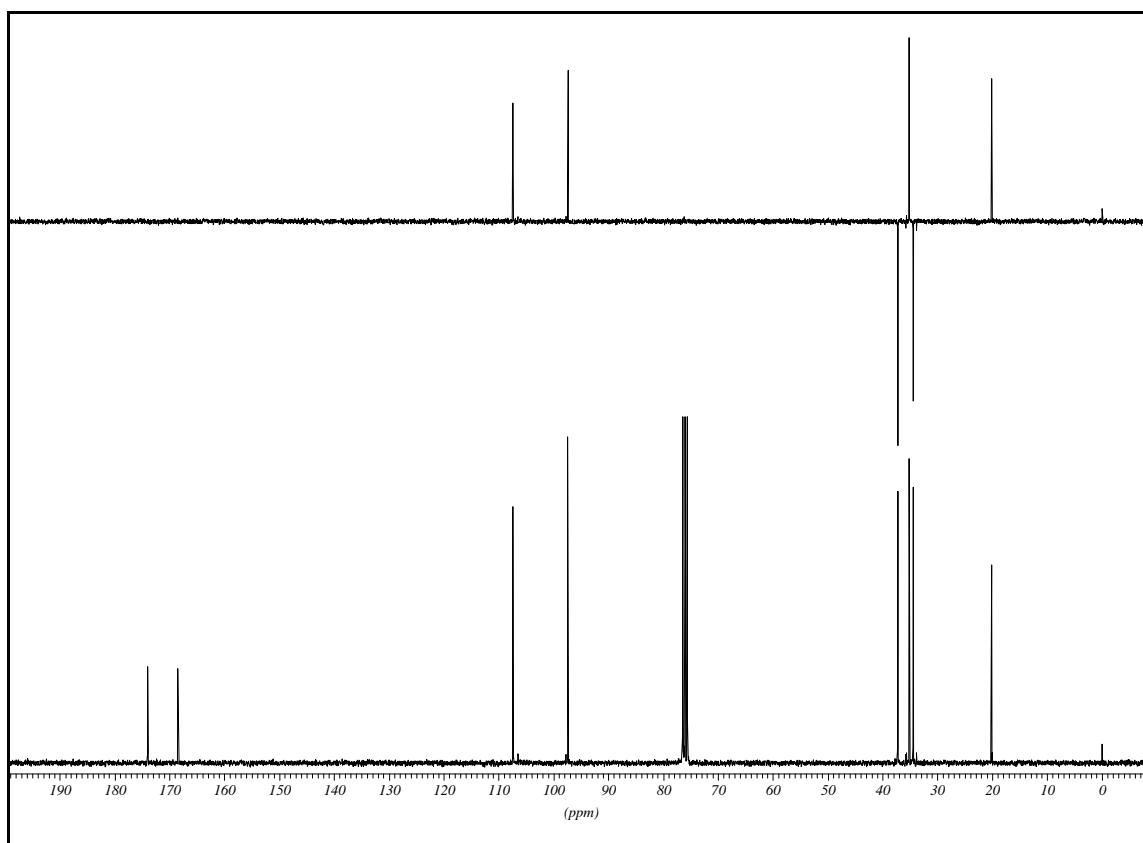


**(2*S*,3*a**S*,6*a**R*)-(−)-Essigsäure-5-oxo-hexahydrofuro[2,3-*b*]furan-2-yl-ester**

**$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )**

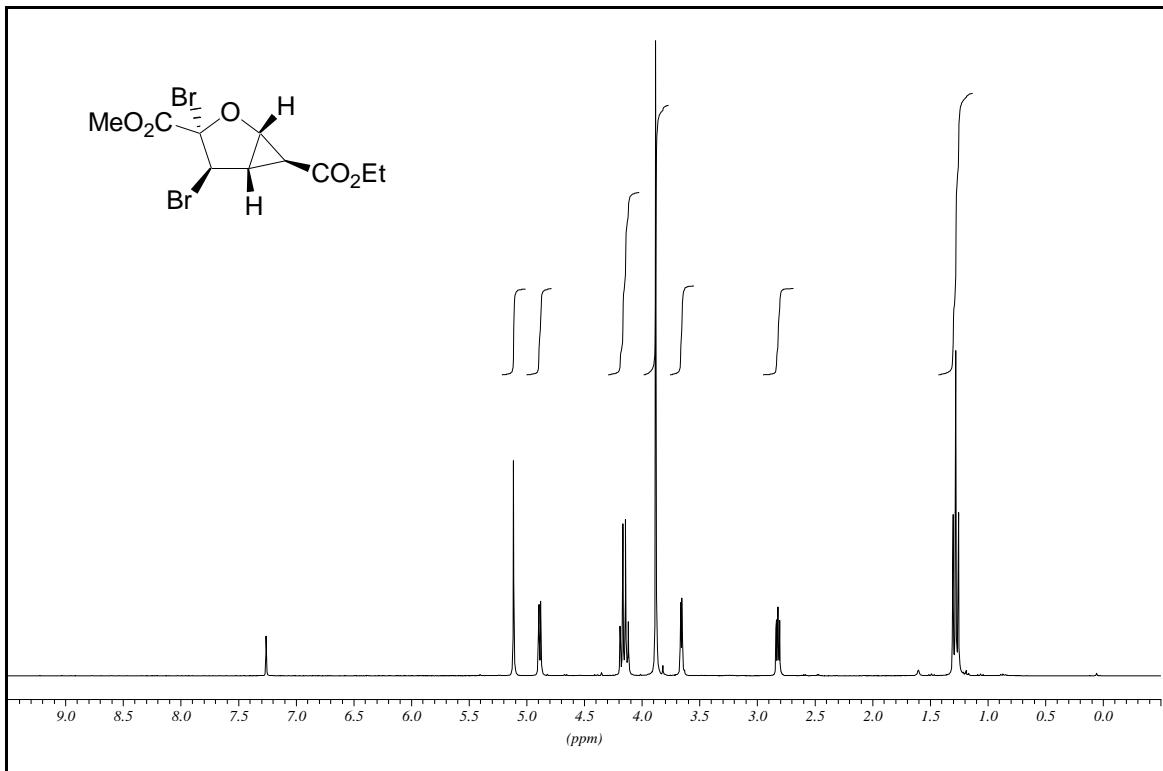


**$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )**

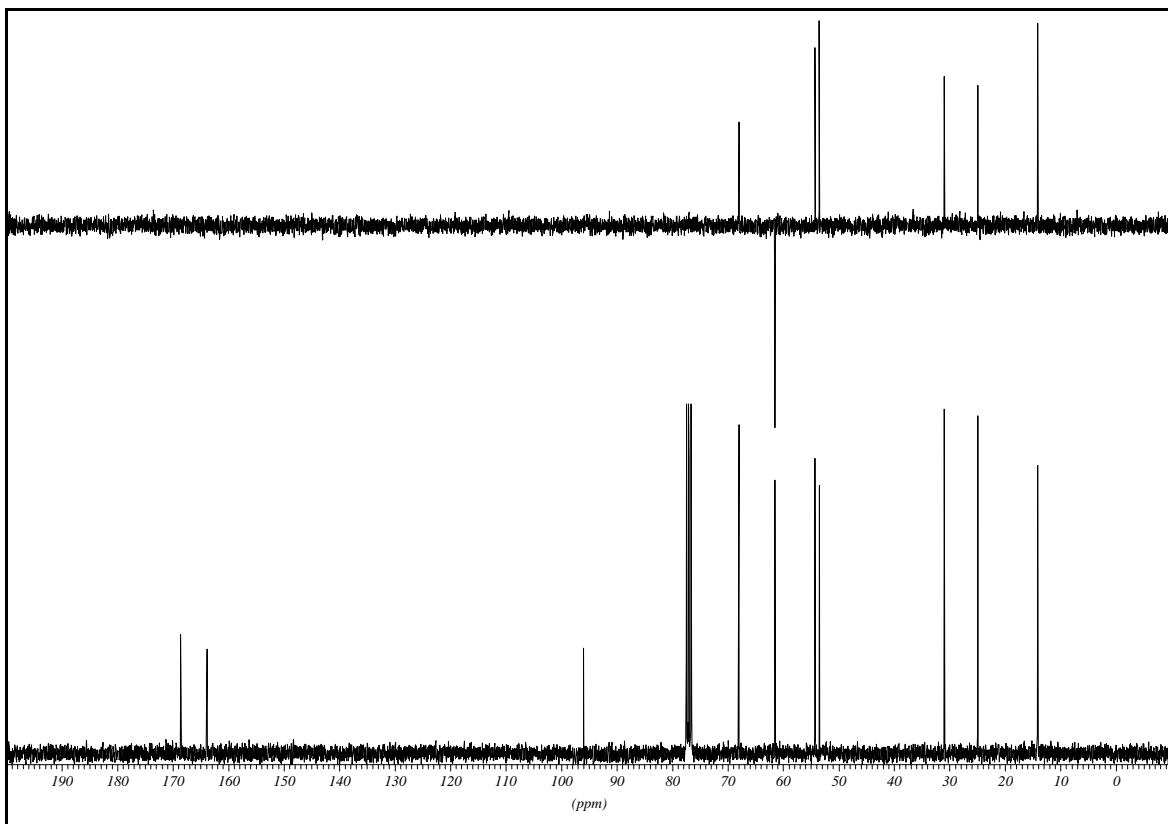


**(1*R*,3*S*,4*S*,5*S*,6*S*)-(−)-3,4-Dibrom-2-oxa-bicyclo[3.1.0]hexan-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )**

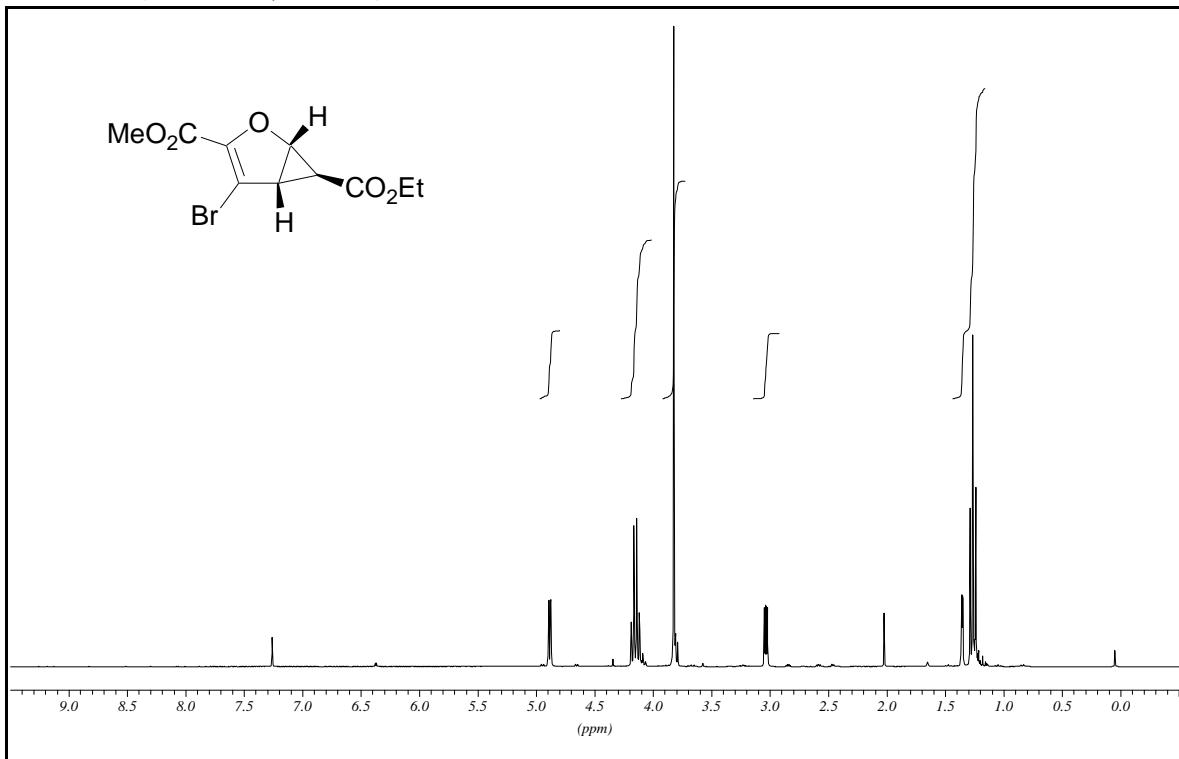


**$^{13}\text{C}$ -NMR (75.5 MHz,  $\text{CDCl}_3$ )**

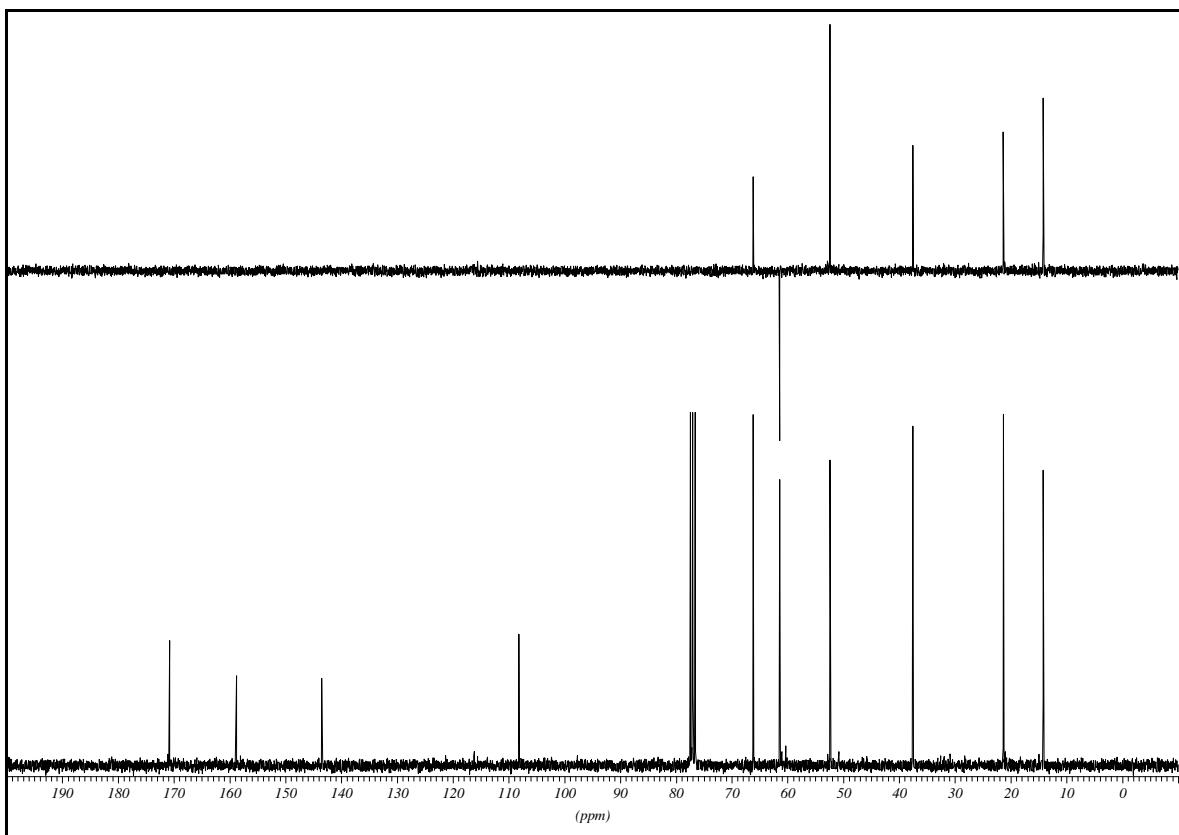


**(1*R*,5*S*,6*S*)-(−)-4-Brom-2-oxa-bicyclo[3.1.0]hex-3-en-3,6-dicarbonsäure-6-ethylester-3-methylester**

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)

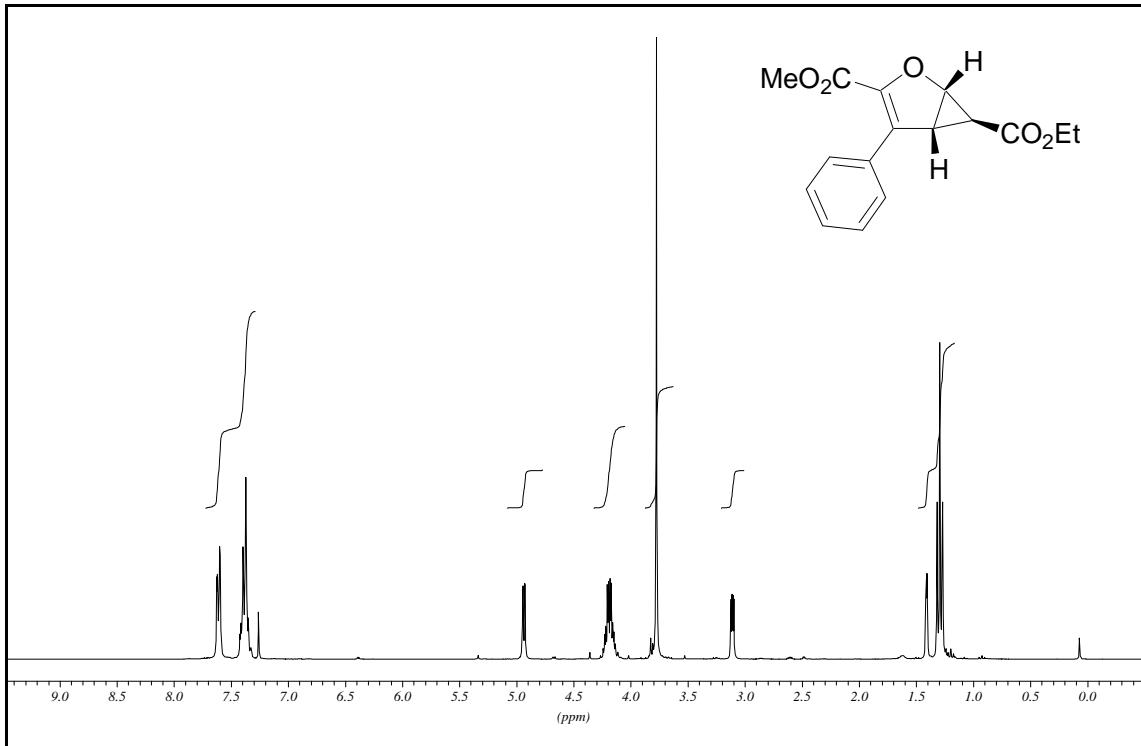


<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)

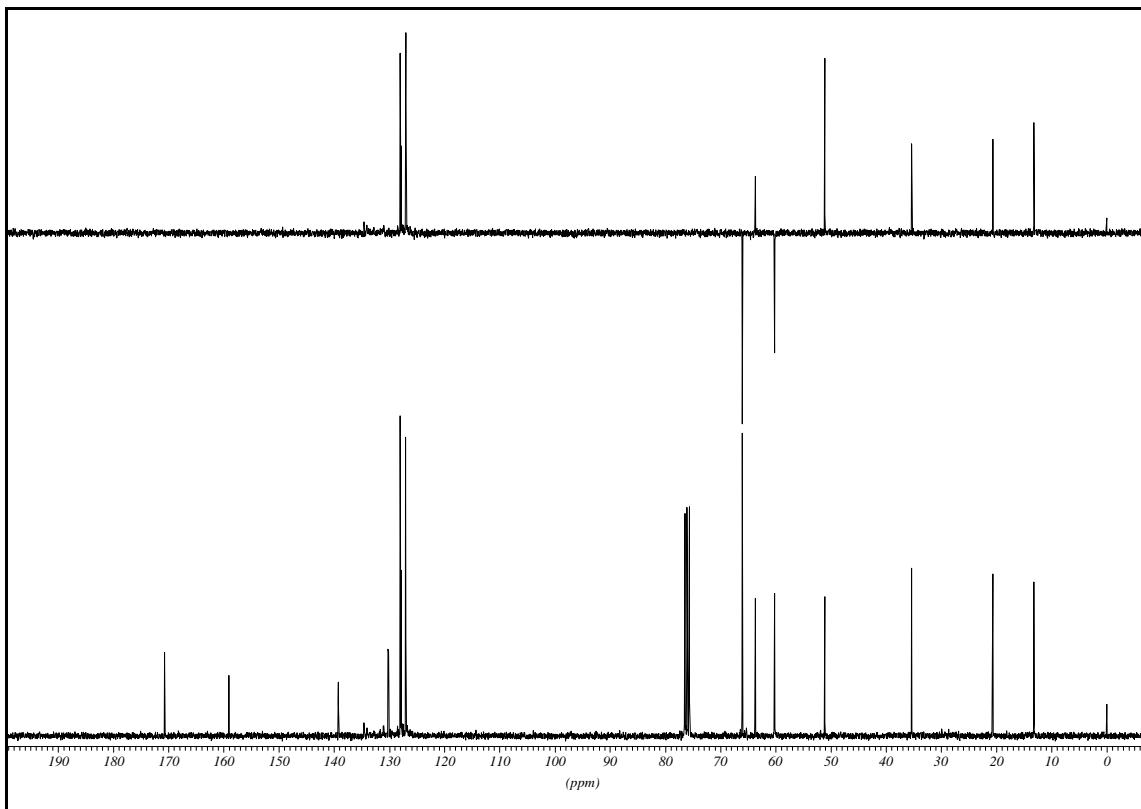


**(1*S*,5*R*,6*S*)-(−)-4-Phenyl-2-oxa-bicyclo[3.1.0]hex-3-en-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )**

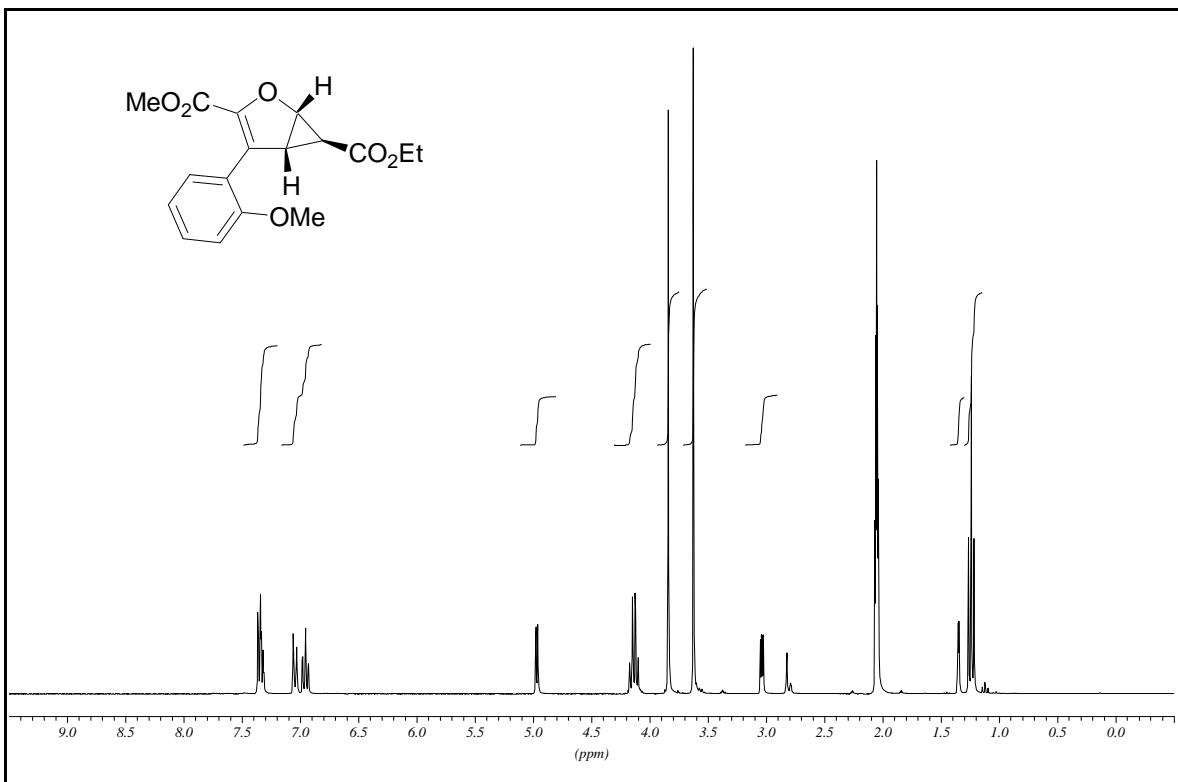


**$^{13}\text{C-NMR}$  (75.5 MHz,  $\text{CDCl}_3$ )**

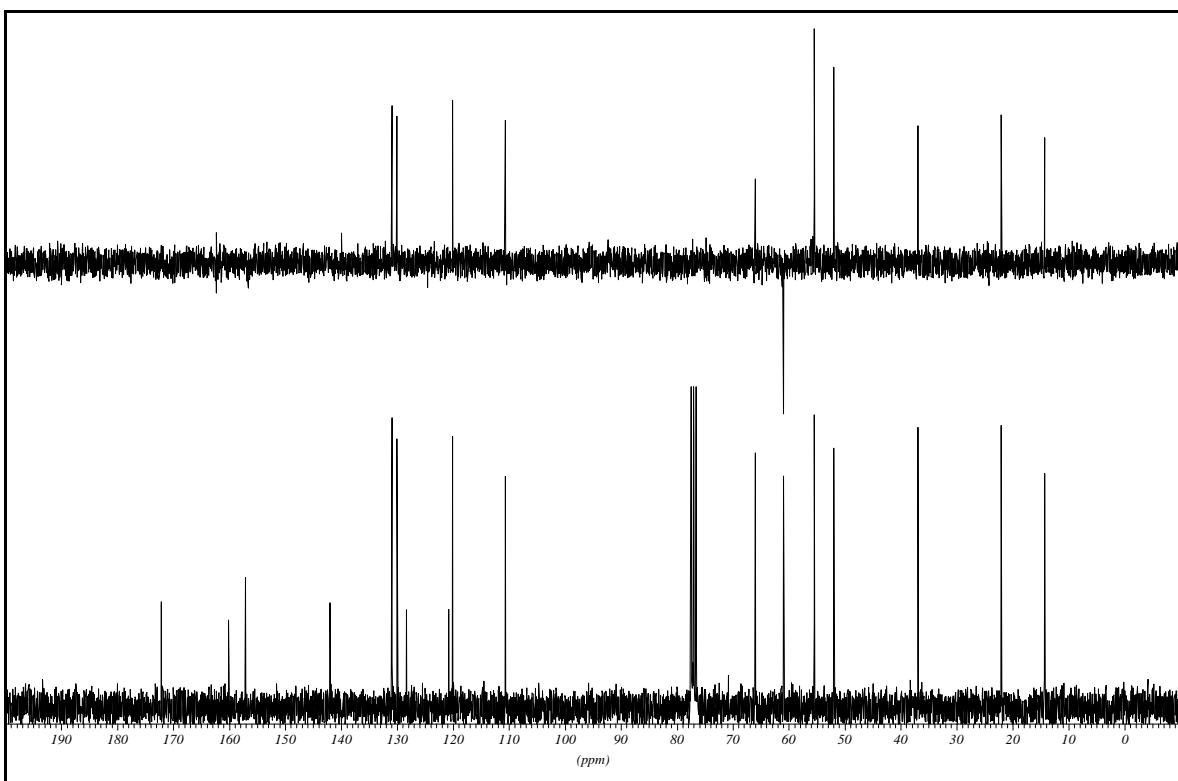


**(1*S*,5*R*,6*S*)-(−)-4-(2-Methoxyphenyl)-2-oxa-bicyclo[3.1.0]hex-3-en-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )**

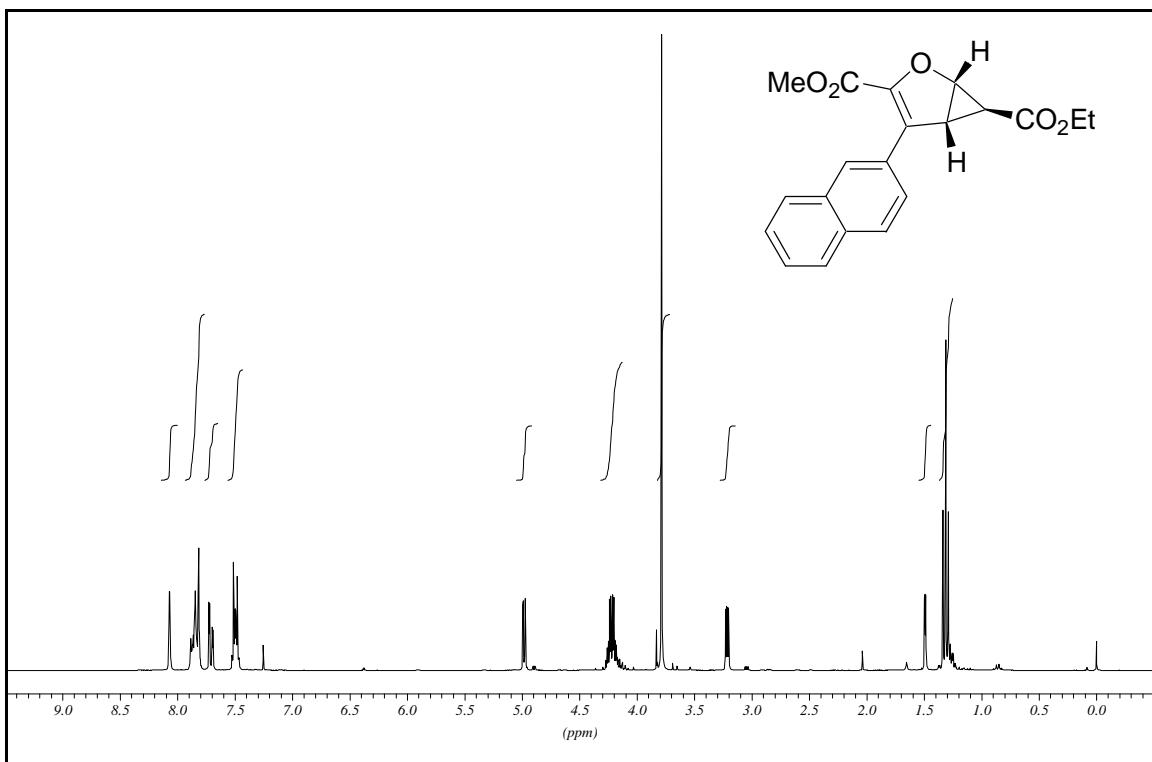


**$^{13}\text{C-NMR}$  (75.5 MHz,  $\text{CDCl}_3$ )**

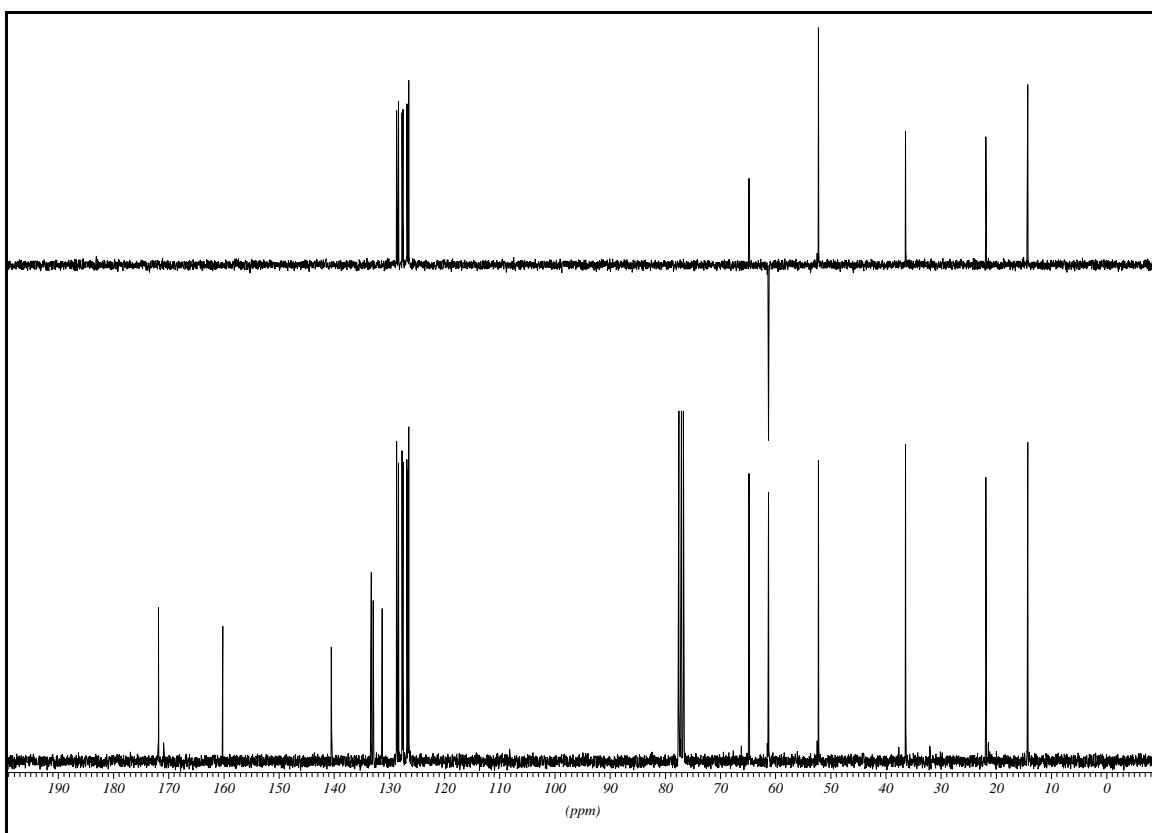


**(1S,5R,6S)-(-)-4-Naphthalin-2-yl-2-oxa-bicyclo[3.1.0]hex-3-en-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )**

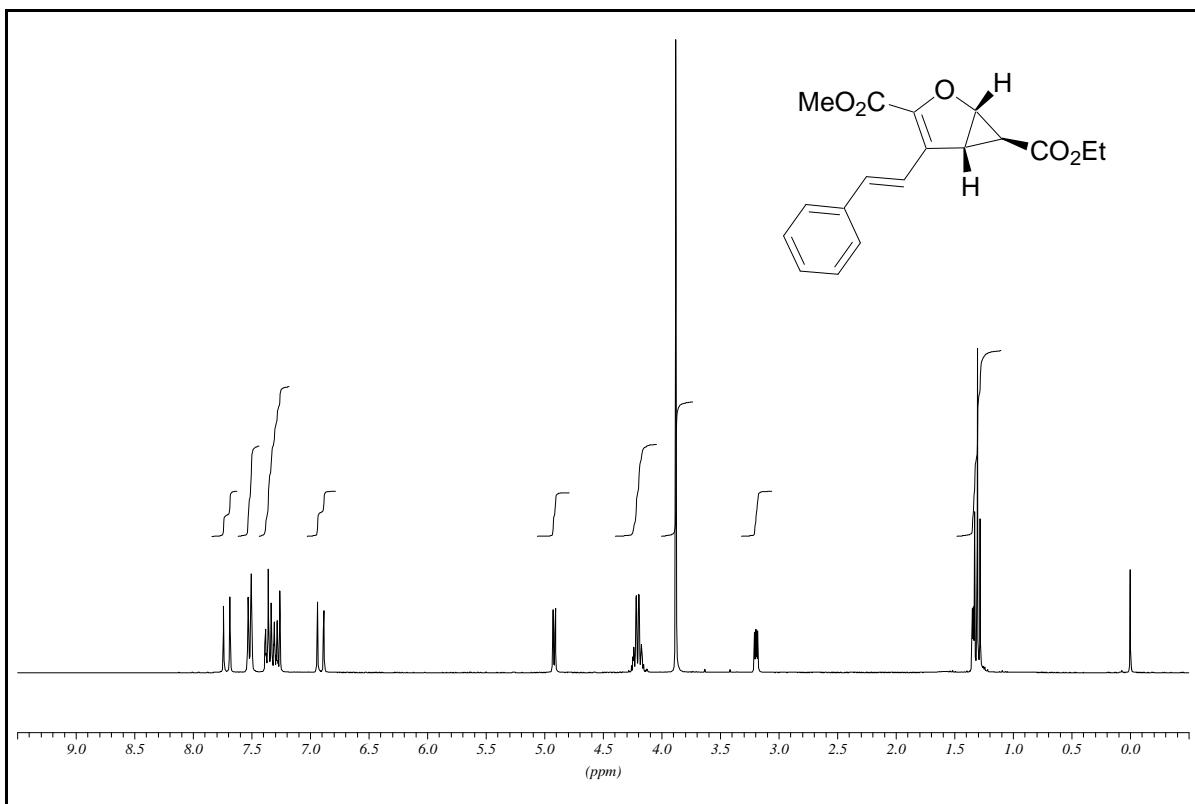


**$^{13}\text{C}$ -NMR (75.5 MHz,  $\text{CDCl}_3$ )**

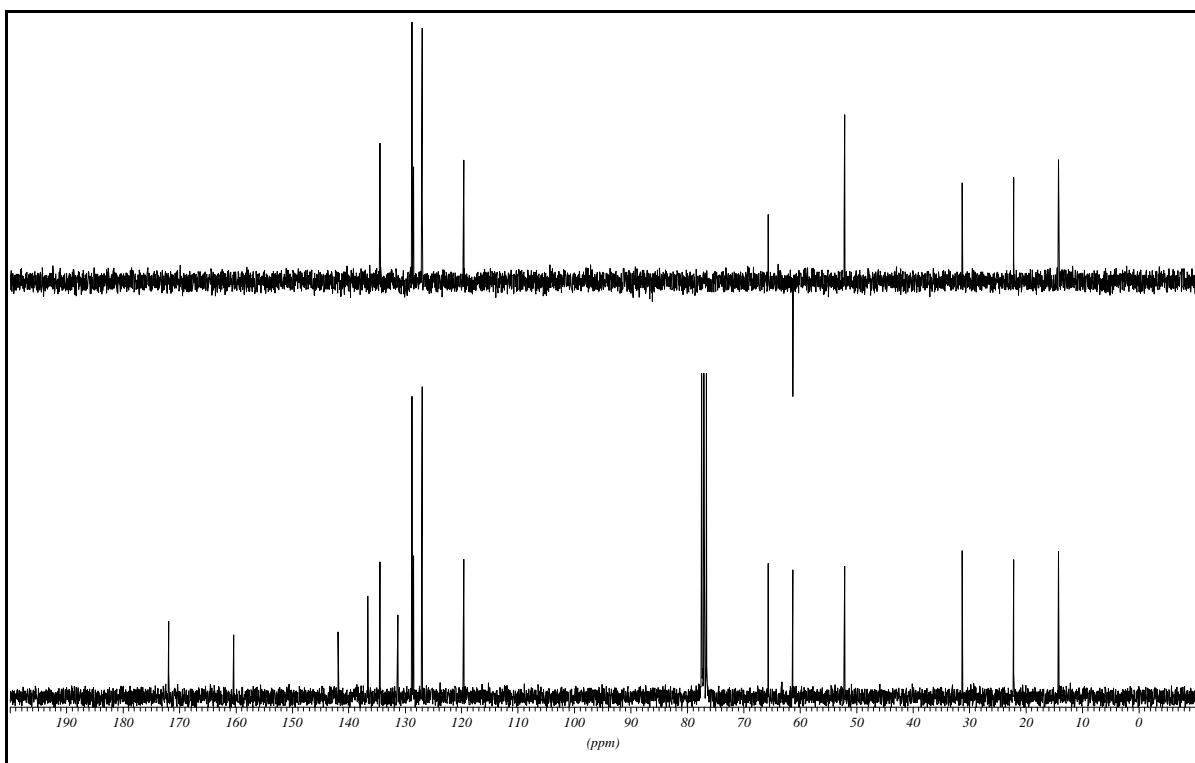


*trans*-(1*S*,5*R*,6*S*)-(-)-4-Styryl-2-oxa-bicyclo[3.1.0]hex-3-ene-3,6-dicarbonsäure-6-ethylester-3-methylester

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)

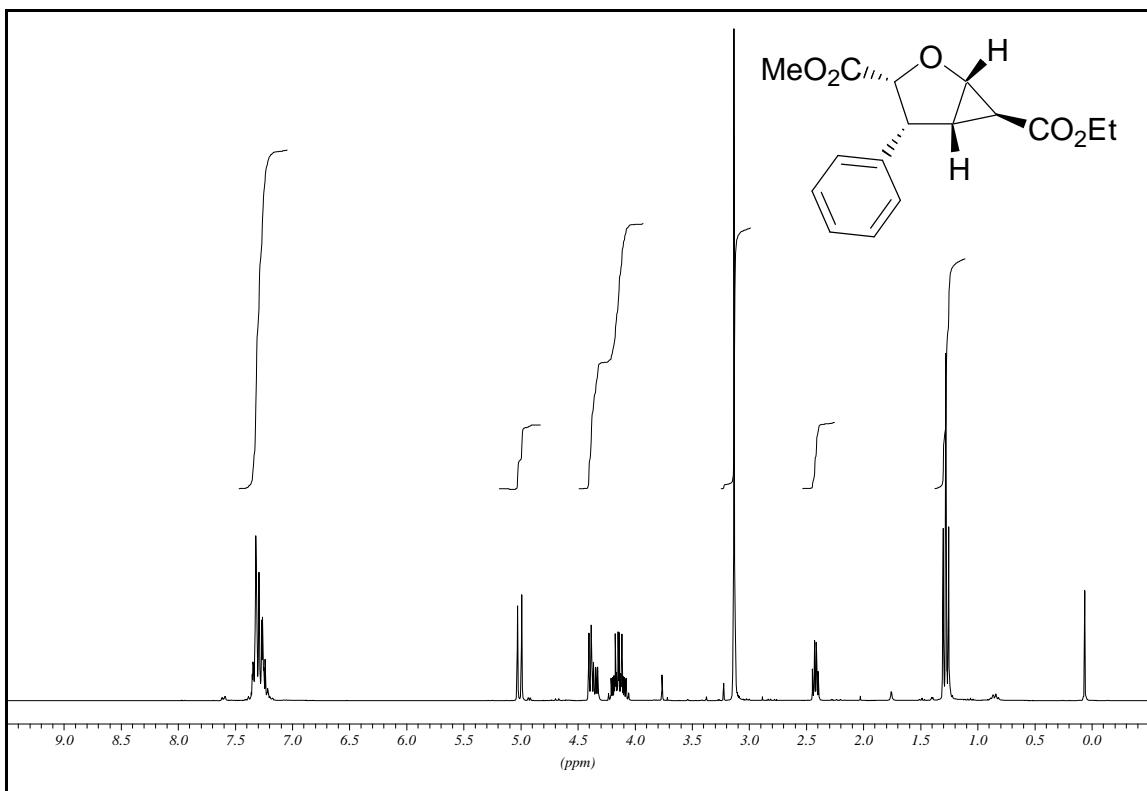


<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)

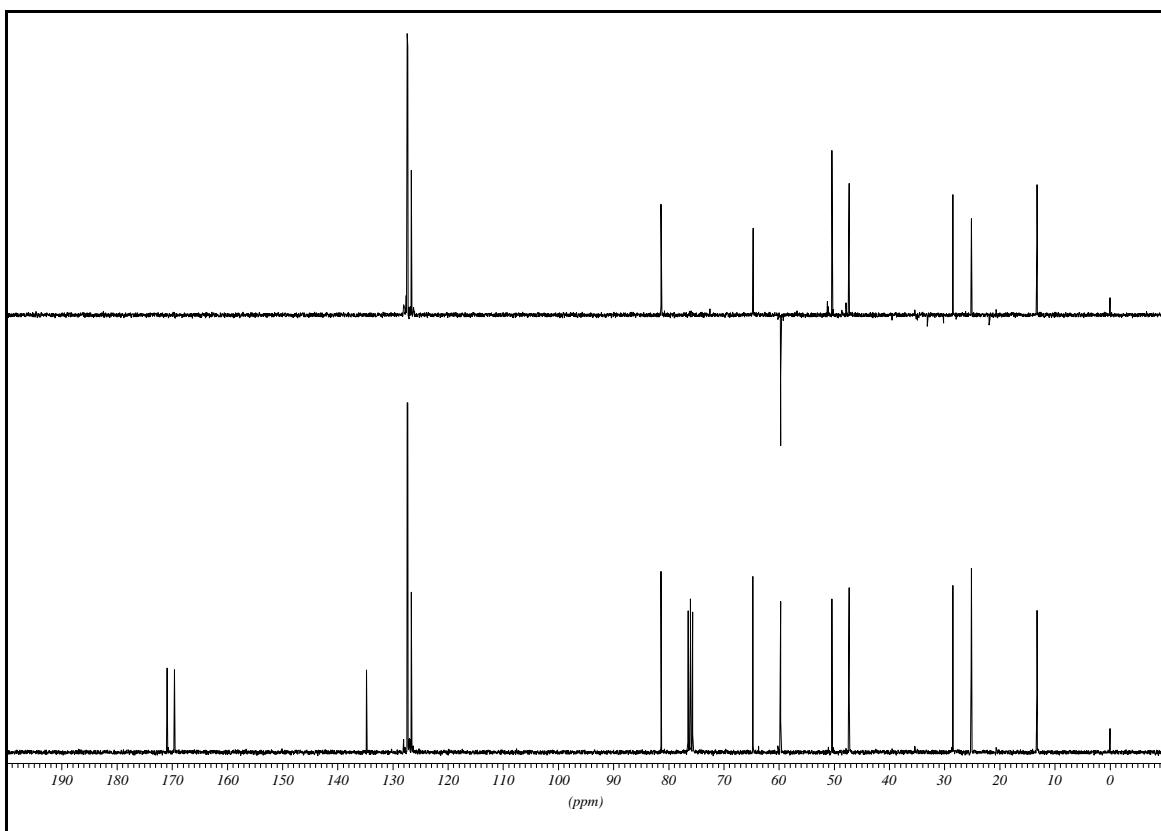


**(1*S*,3*R*,4*R*,5*S*,6*S*)-(−)-4-Phenyl-2-oxa-bicyclo[3.1.0]hexan-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )**

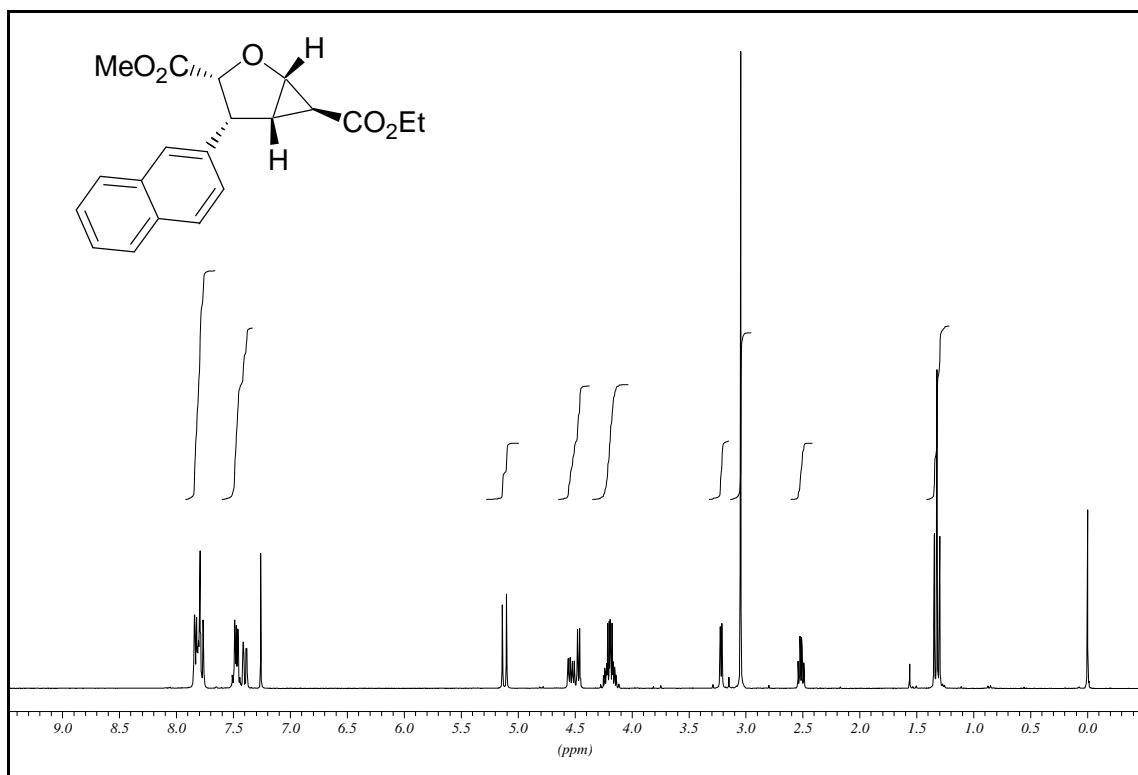


**$^{13}\text{C}$ -NMR (75.5 MHz,  $\text{CDCl}_3$ )**

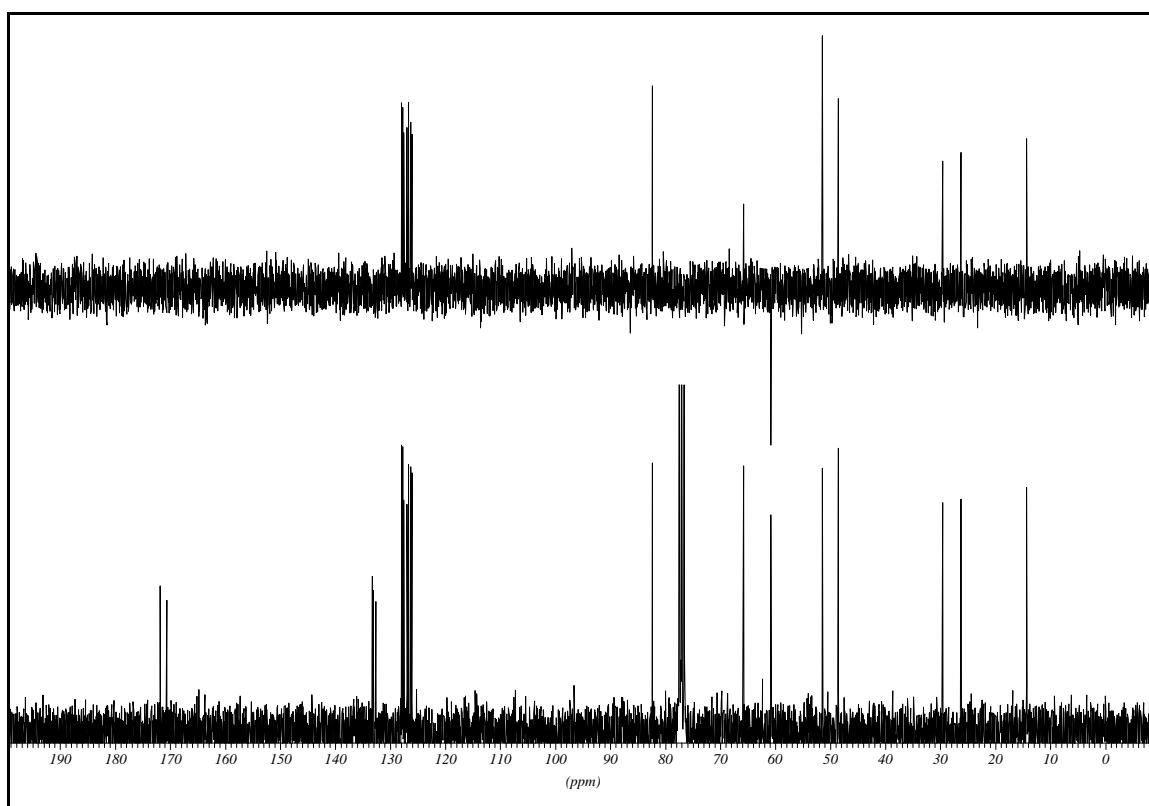


**(1*S*,3*R*,4*R*,5*S*,6*S*)-(−)-4-Naphthalin-2-yl-2-oxa-bicyclo[3.1.0]hexan-3,6-dicarbonsäure-6-ethylester-3-methylester**

**$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )**

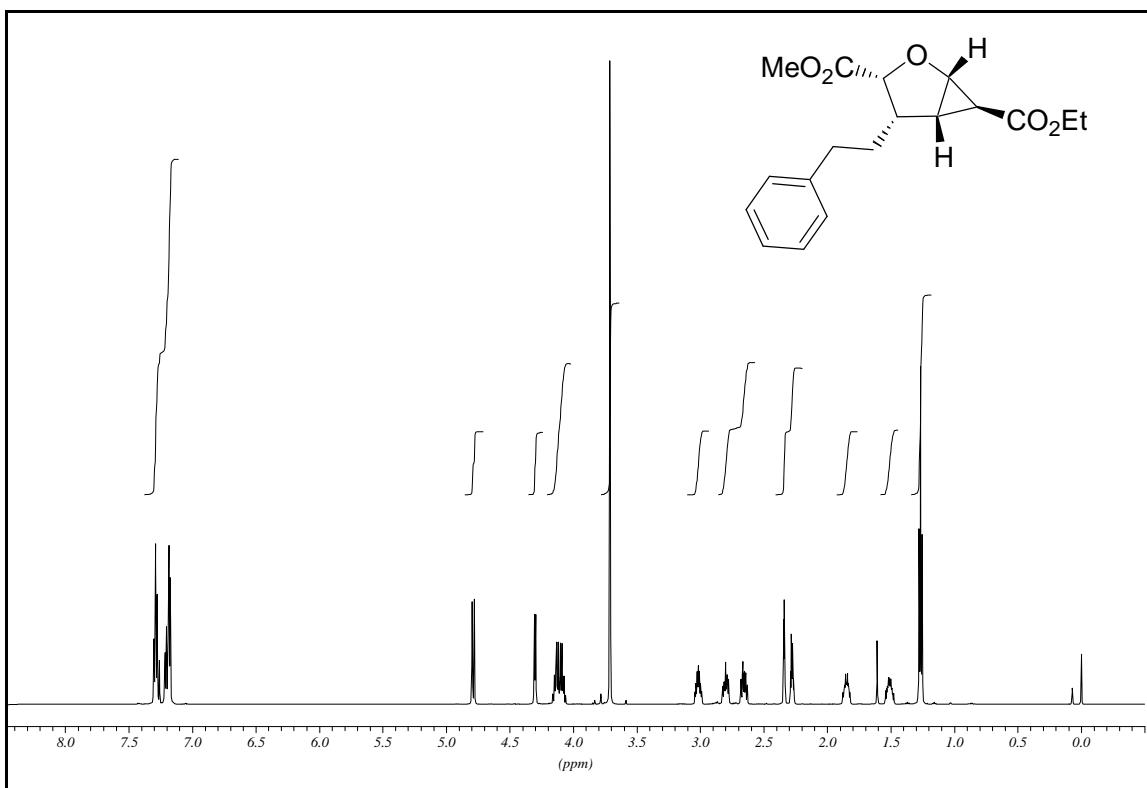


**$^{13}\text{C}$ -NMR (75.5 MHz,  $\text{CDCl}_3$ )**

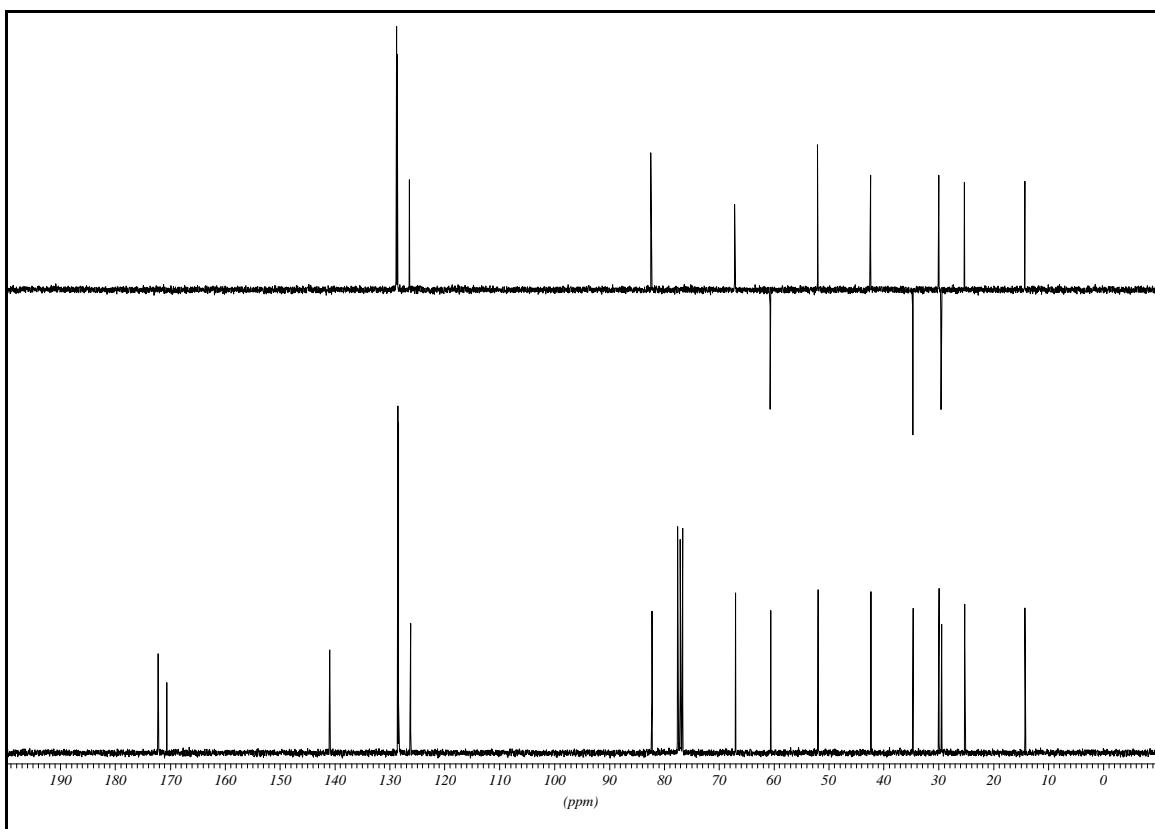


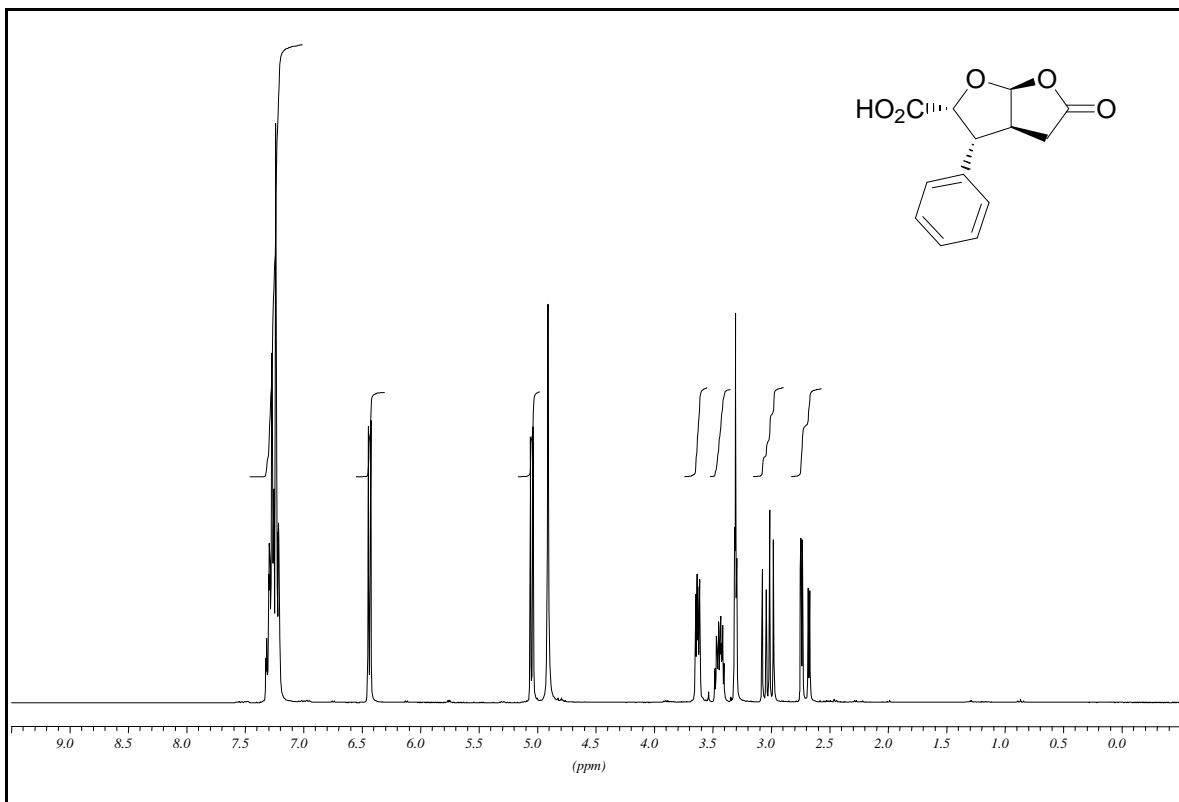
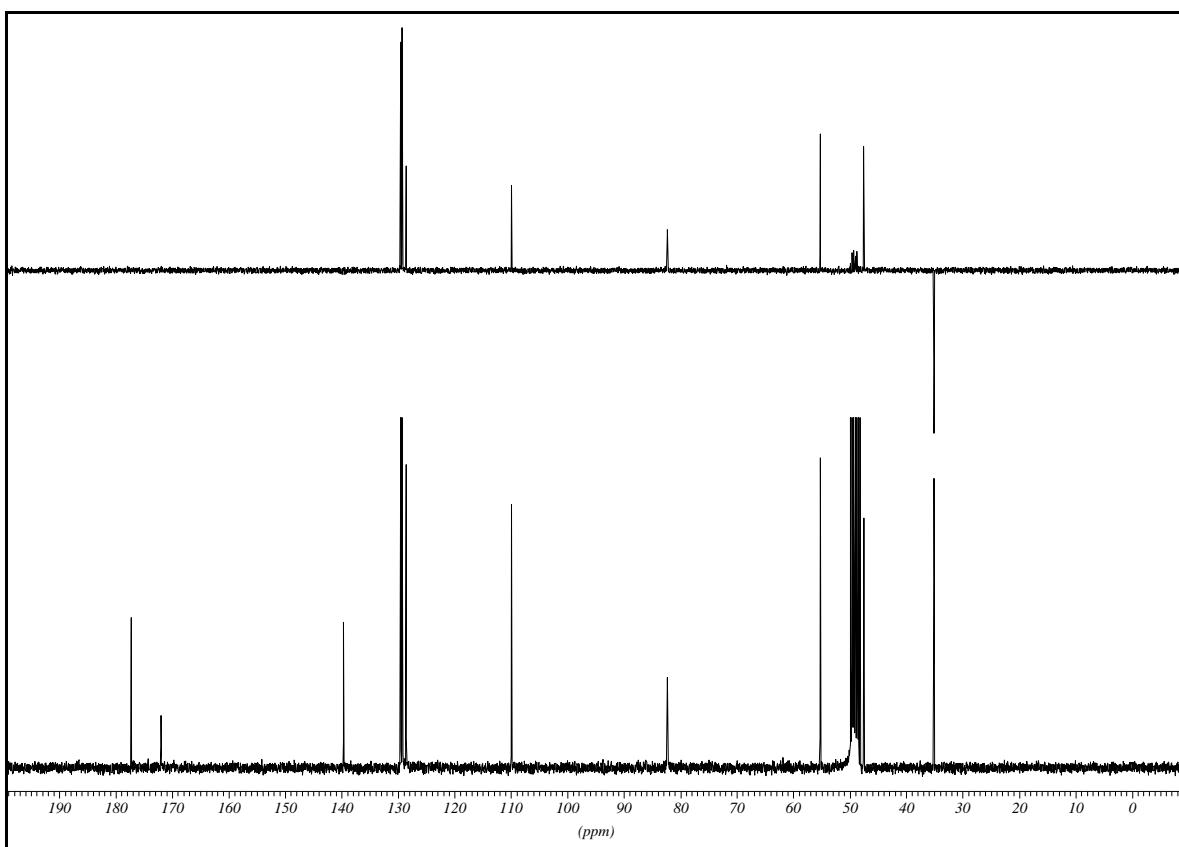
**(1*S*,3*R*,4*S*,5*S*,6*S*)-(+)-4-Phenethyl-2-oxa-bicyclo[3.1.0]hexan-3,6-dicarbonsäure-6-ethylester-3-methylester**

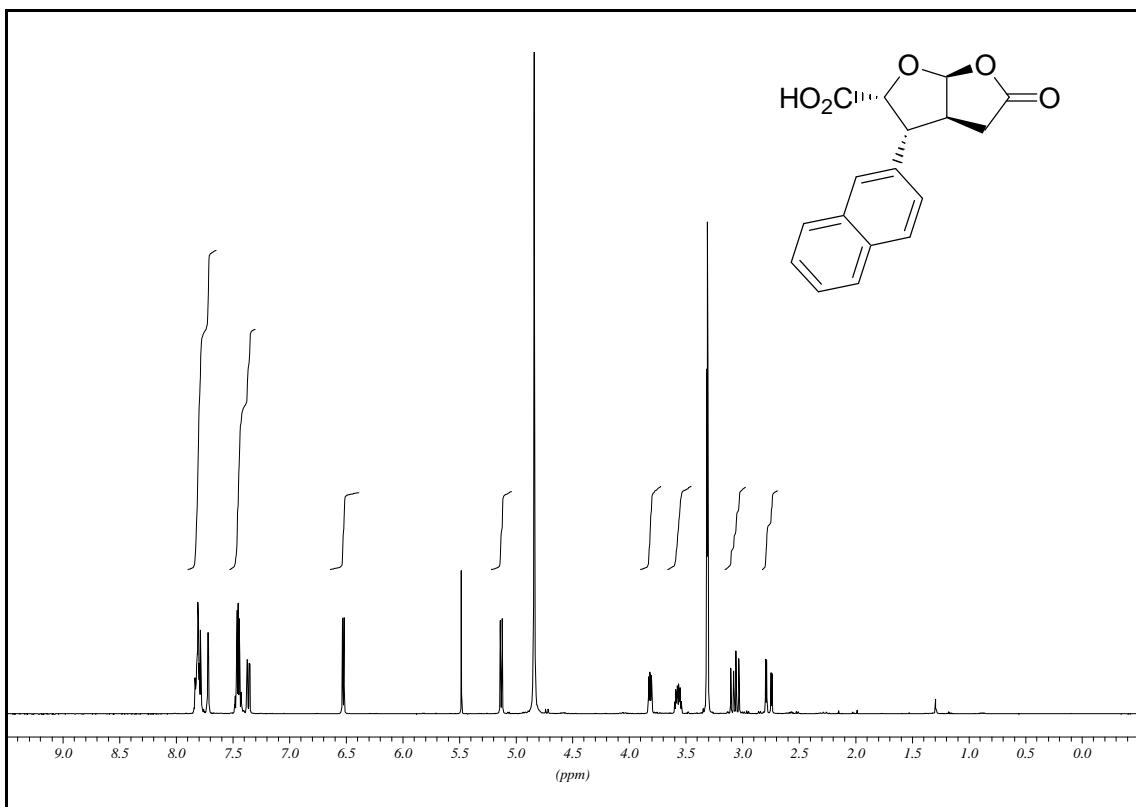
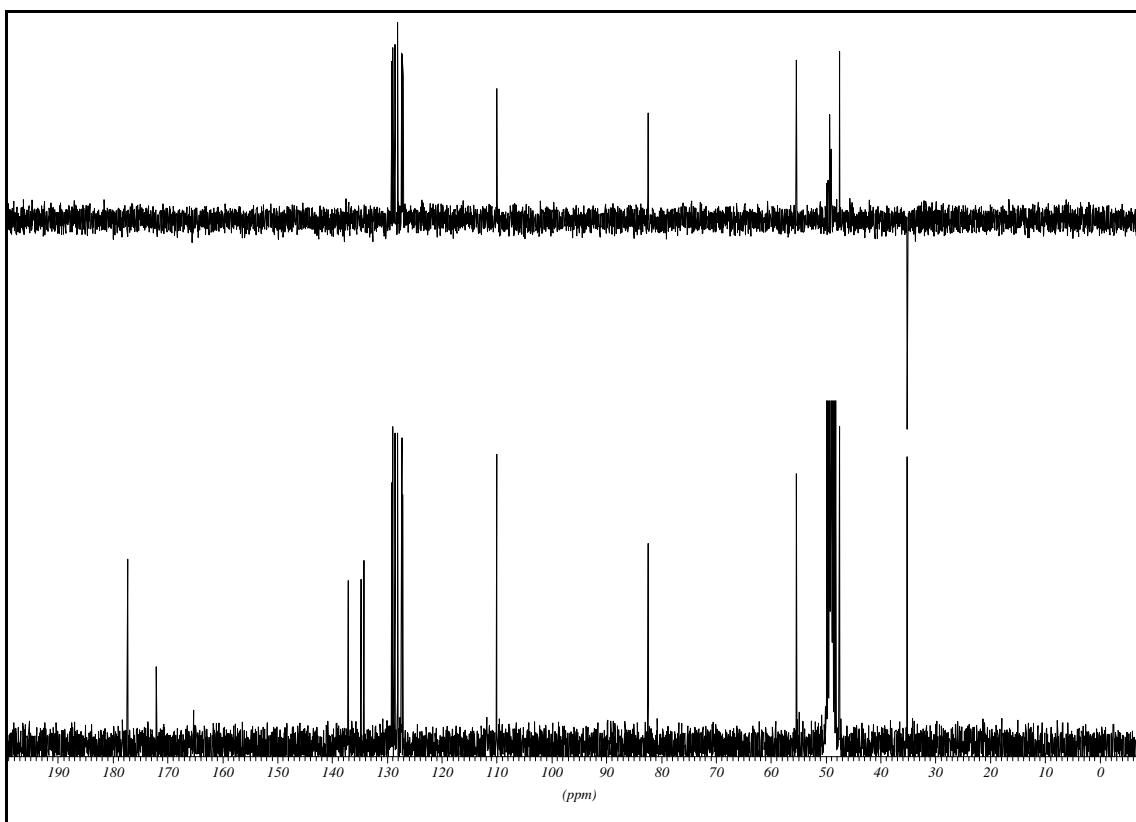
**$^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ )**



**$^{13}\text{C}$ -NMR (75.5 MHz,  $\text{CDCl}_3$ )**

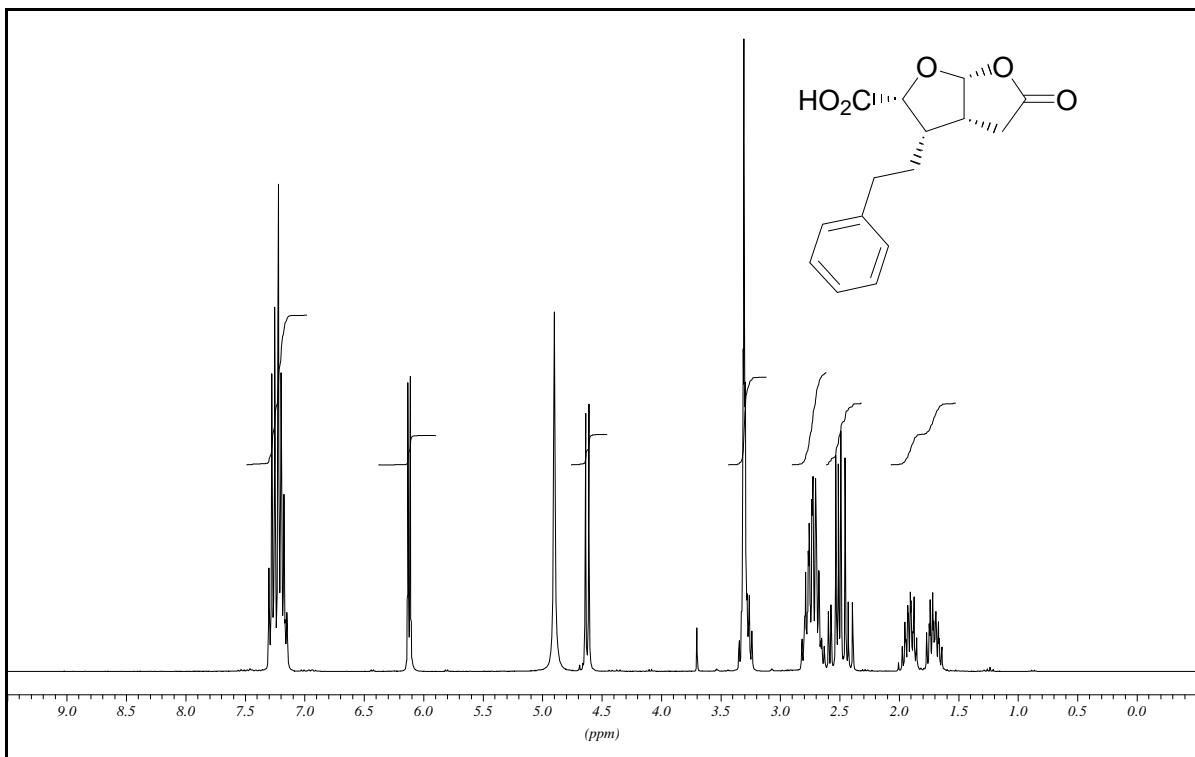


(2*R*,3*R*,3*aS*,6*aS*)-(−)-5-Oxo-3-phenyl-hexahydrofuro[2,3-*b*]furan-2-carbonsäure<sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>OD)<sup>13</sup>C-NMR (75.5 MHz, CD<sub>3</sub>OD)

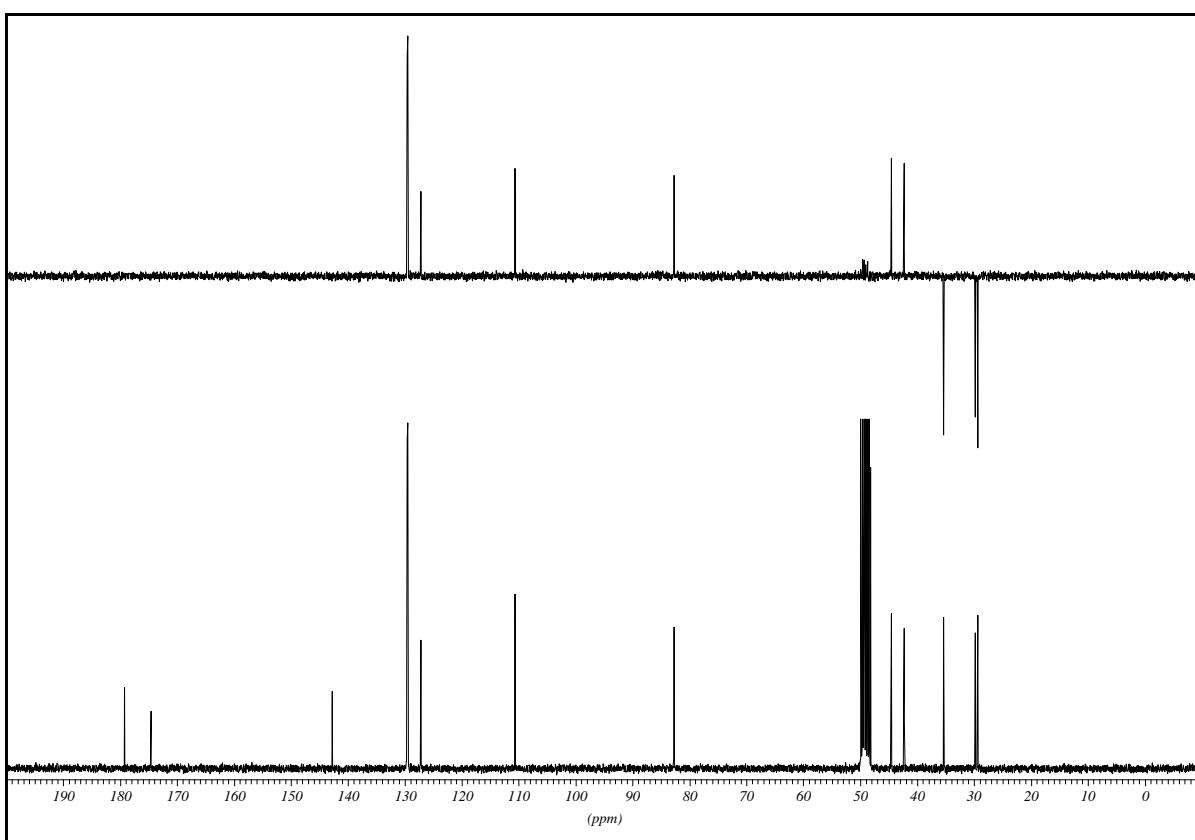
(2*R*,3*R*,3a*S*,6a*S*)-3-Naphthalen-2-yl-5-oxo-hexahydrofuro[2,3-*b*]furan-2-carbonsäure<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD)<sup>13</sup>C-NMR (75.5 MHz, CD<sub>3</sub>OD)

**(2*R*,3*S*,3*aR*,6*aR*)-(−)-5-Oxo-3-phenethyl-hexahydrofuro[2,3-*b*]furan-2-carbonsäure**

**<sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>OD)**

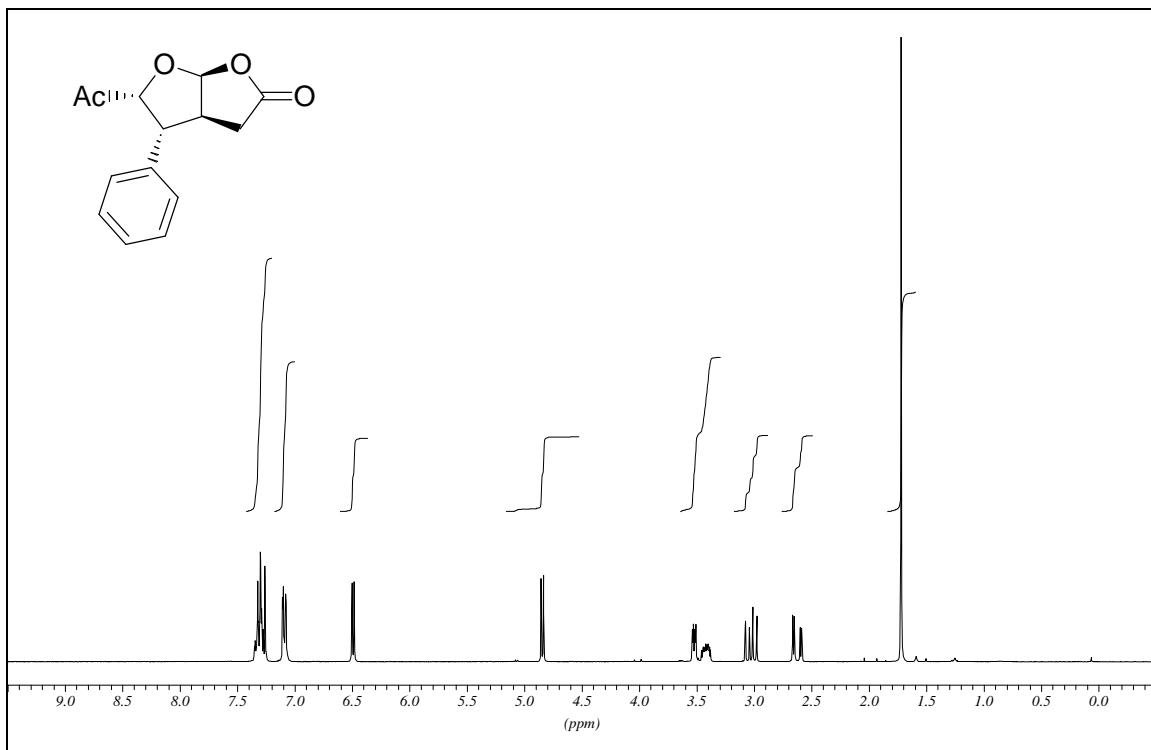


**<sup>13</sup>C-NMR (75.5 MHz, CD<sub>3</sub>OD)**

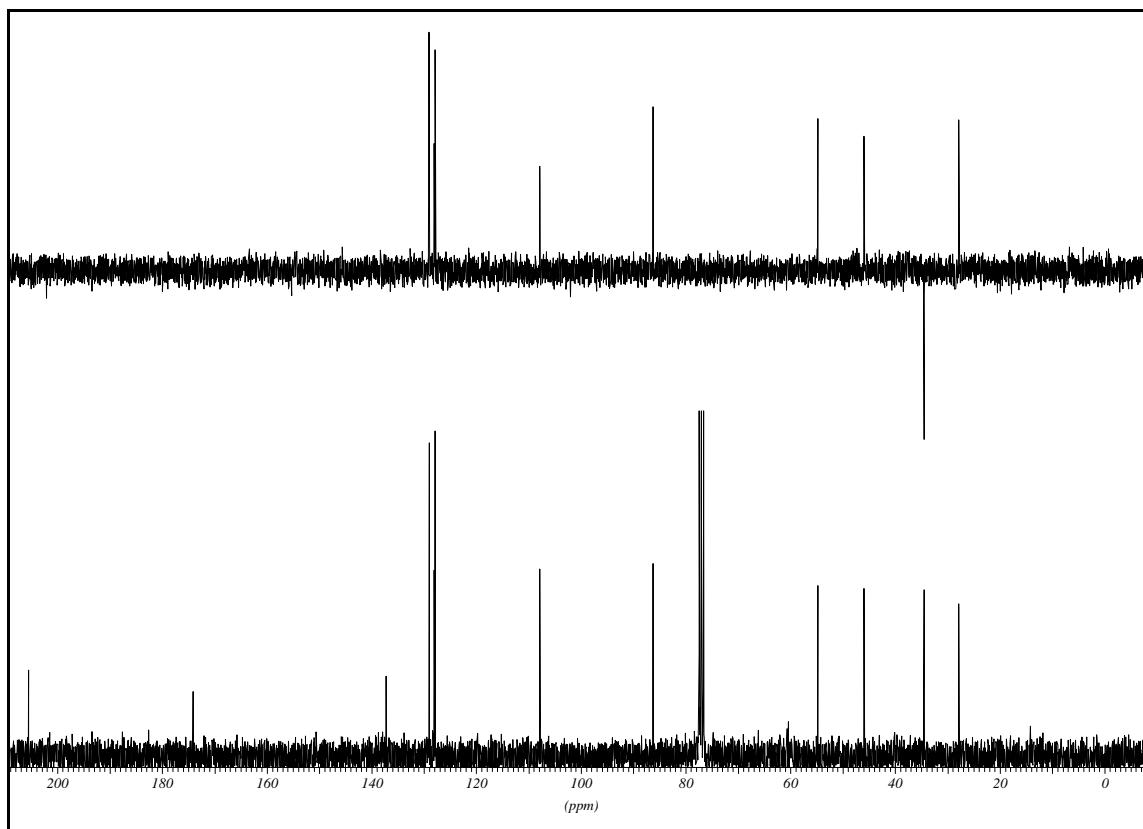


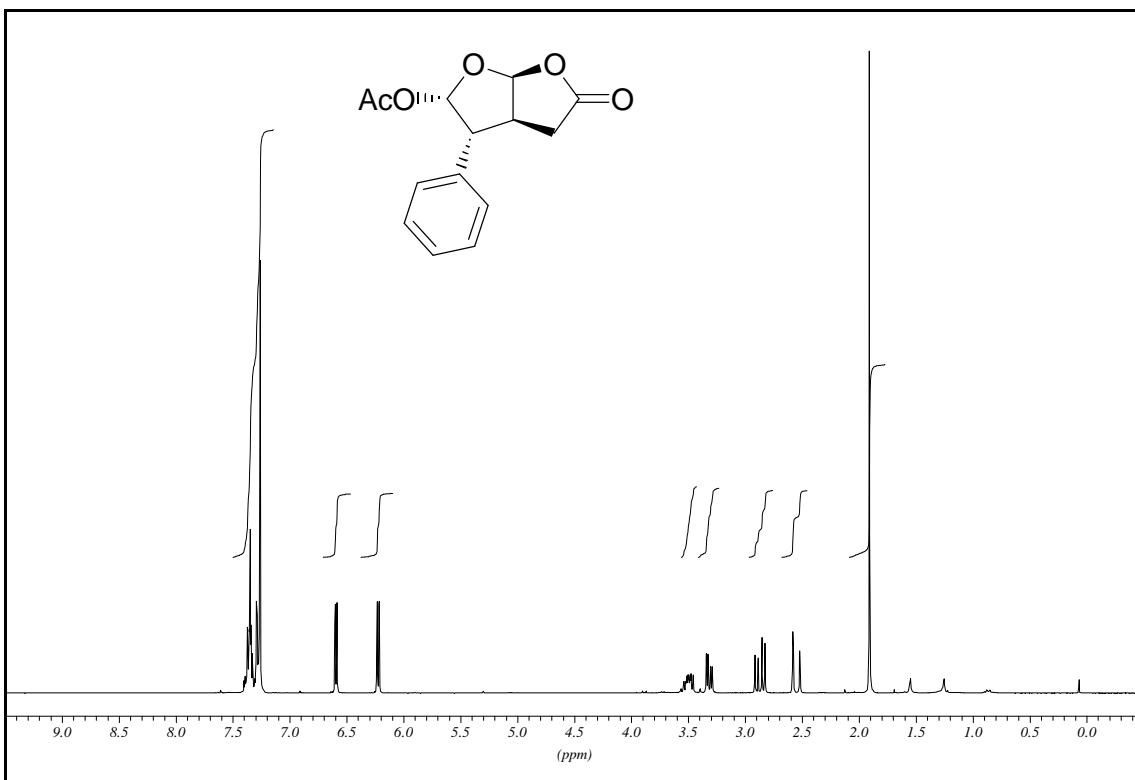
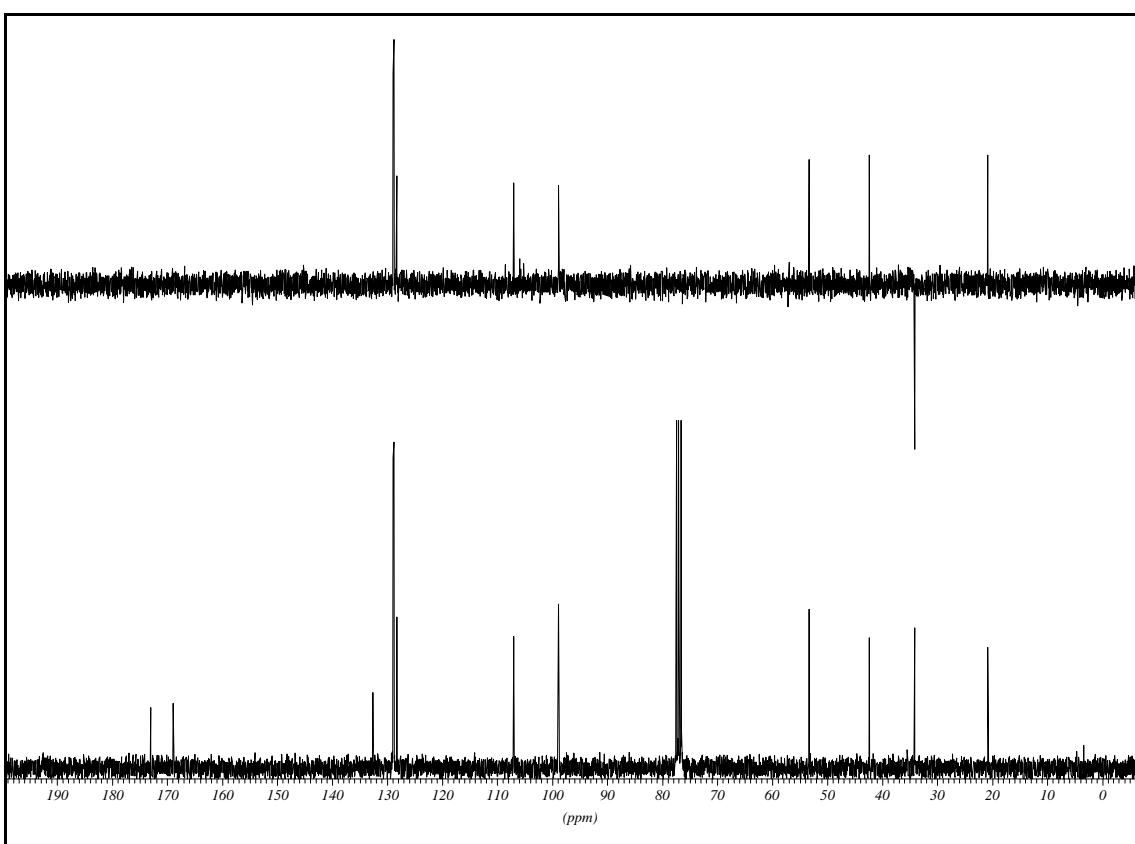
**(2*R*,3*R*,3*aS*,6*aS*)-(−)-5-Acetyl-4-phenyl-tetrahydrofuro[2,3-*b*]furan-2-on**

**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)**



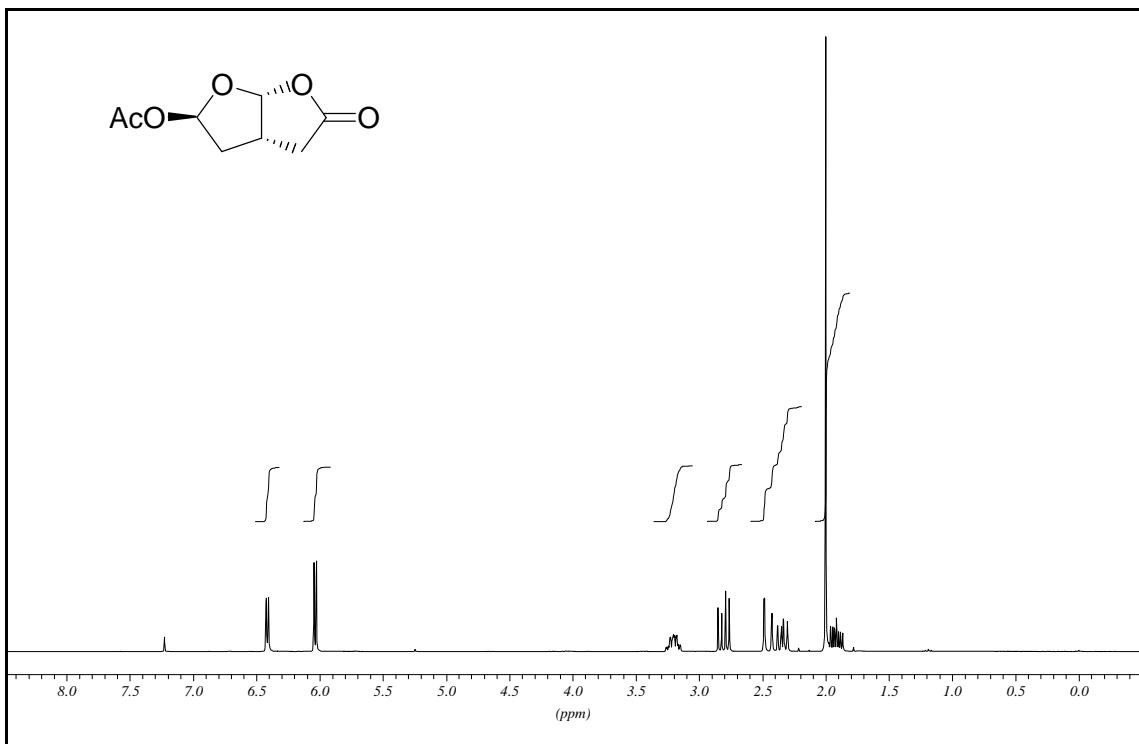
**<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)**



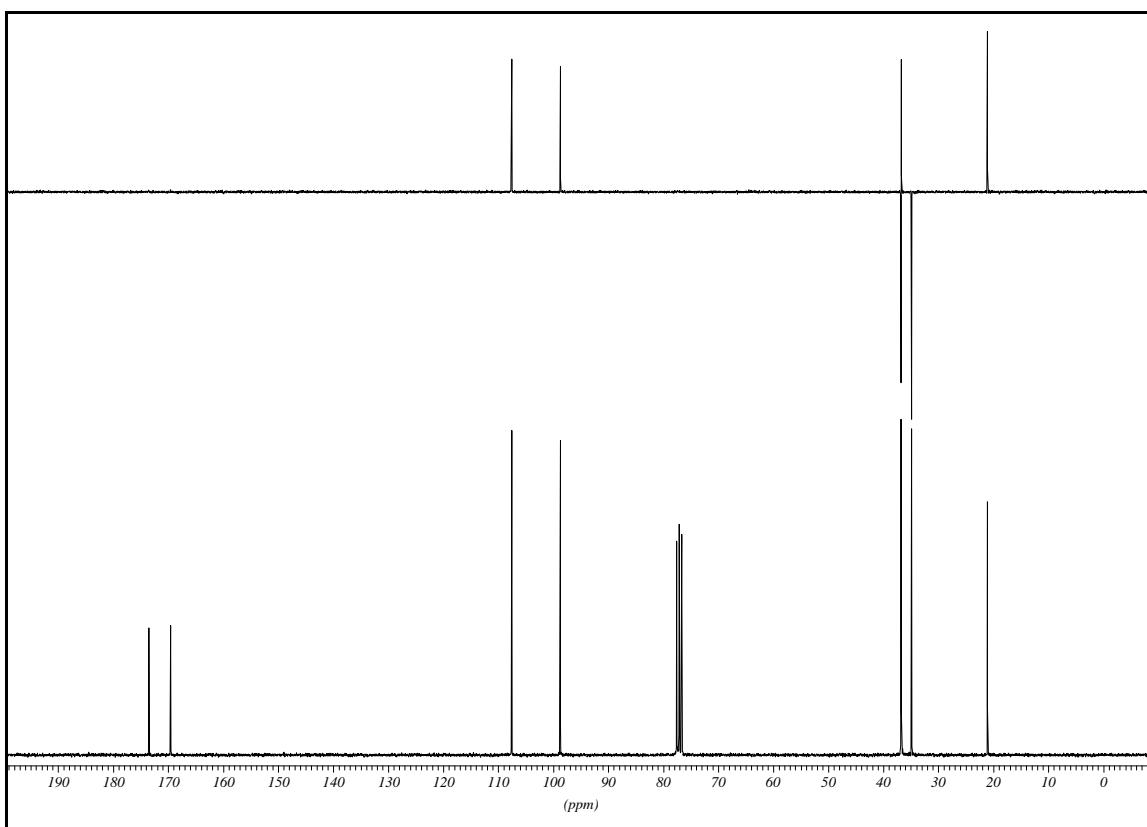
(2*S*,3*R*,3*aS*,6*aS*)-(-)-Essigsäure-5-oxo-3-phenyl-hexahydrofuro[2,3-*b*]furan-2-ylester<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)

### (2*R*,3*aS*,6*aR*)-(+)-Essigsäure-5-oxo-hexahydrofuro[2,3-*b*]furan-2-yl-ester

**$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )**

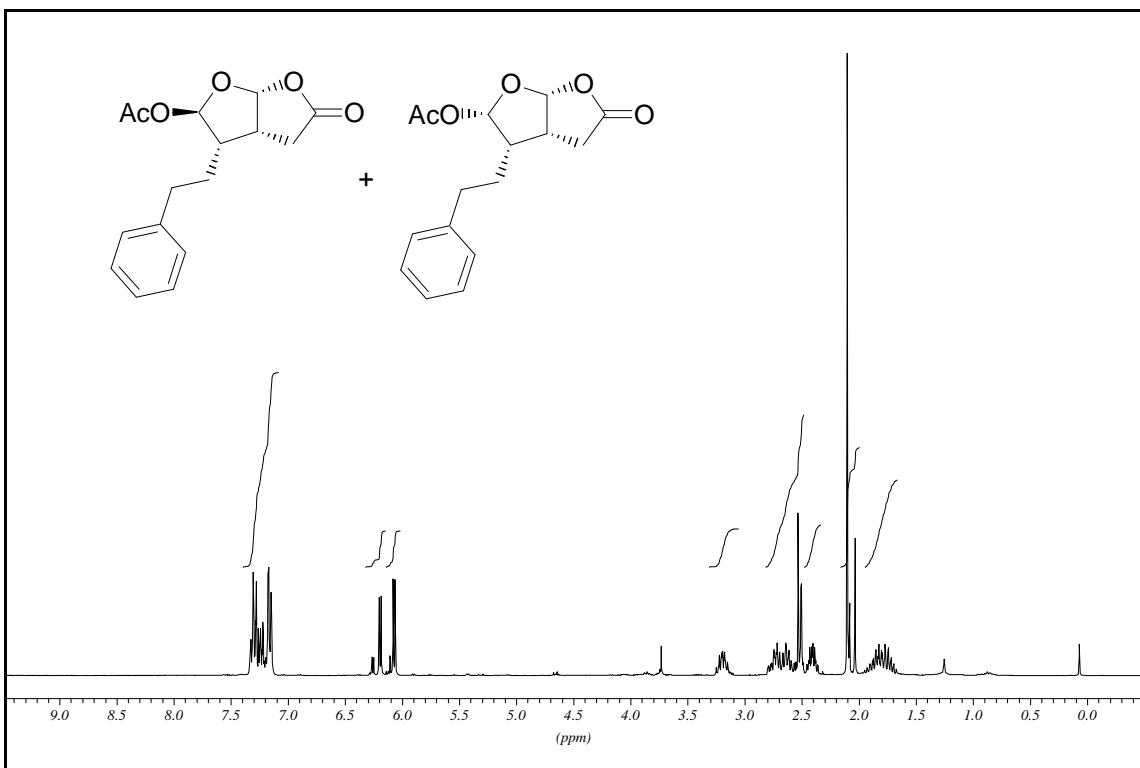


**<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)**



**(2*R/S*,3*S*,3*aR*,6*aR*)-Essigsäure-5-oxo-3-phenethyl-hexahydrofuro[2,3-*b*]furan-2-yl-ester**

**$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )**



**$^{13}\text{C-NMR}$  (75.5 MHz,  $\text{CDCl}_3$ )**

