

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

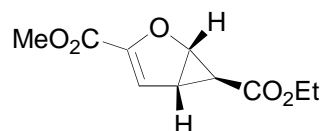
Supporting Information

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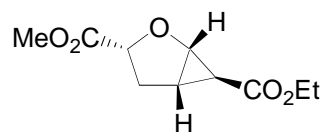
(1*S*,5*S*,6*S*)-6-ethyl 3-methyl 2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (9)



Fp: 42 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 6.32 (d, ³*J* = 2.8 Hz, 1 H, H-4), 4.90 (dd, ³*J* = 5.4 Hz, ³*J* = 1.1 Hz, 1 H, H-1), 4.08 (q, ³*J* = 7.1 Hz, 2 H, CH₂), 3.74 (s, 3 H, -OCH₃), 2.80 (ddd, ³*J* = 5.4 Hz, ³*J* = 2.8 Hz, ³*J* = 2.7 Hz, 1 H, H-5), 1.20 (t, ³*J* = 7.1 Hz, 3 H, CH₂CH₃), 1.09 (dd, ³*J* = 2.7 Hz, ³*J* = 1.1 Hz, 1 H, H-6). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 171.77 (C_q, CO₂Et), 159.54 (C_q, CO₂Me), 149.16 (C_q, C-3), 116.18 (+, C-4), 67.54 (+, C-1), 61.07 (-, CH₂), 52.25 (+, OCH₃), 31.97 (+, C-5), 21.46 (+, C-6), 14.20 (+, CH₂CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 1.0) = -272. **MS** (EI-MS): *m/z* (%) = 212.3 (10) [M⁺], 153.4 (12), [M⁺ΔCO₂Me], 139.4 (100) [M⁺ΔCO₂Et], 125.4 (19), 97.3 (23). C₁₀H₁₂O₅ (212.2): calcd. C 56.60, H 5.70; found C 56.51, H 5.73.

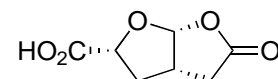
(1*S*,3*R*,5*S*,6*S*)-6-ethyl 3-methyl 2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (10)



Fp: 69 °C.

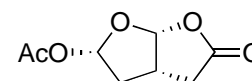
¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 4.74 (dd, ³J = 10.7 Hz, ³J = 4.3 Hz, 1 H, H-3), 4.28 (dd, ³J = 5.7 Hz, ³J = 0.9 Hz, 1 H, H-1), 4.06 (dq, ²J = 10.8 Hz, ³J = 7.1 Hz, 1 H, CHHCH₃), 4.02 (dq, ²J = 10.8 Hz, ³J = 7.1 Hz, 1 H, CHHCH₃), 3.71 (s, 3 H, OCH₃), 2.60 (ddd, ²J = 13.4 Hz, ³J = 10.7 Hz, ³J = 6.0 Hz, 1 H, H-4_{exo}), 2.23 (dd, ²J = 13.4 Hz, ³J = 4.3 Hz, 1 H, H-4_{endo}), 2.13 (ddd, ³J = 6.0 Hz, ³J = 5.7 Hz, ³J = 4.0 Hz, 1 H, H-5), 1.83 (dd, ³J = 4.0 Hz, ³J = 0.9 Hz, 1 H, H-6), 1.18 (dd, ³J = 7.1 Hz, ³J = 7.1 Hz, 3 H, CH₂CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 173.33 (C_q, C=O), 170.40 (C_q, C=O), 79.11 (+, C-3), 67.46 (+, C-1), 60.55 (-, CH₂CH₃), 52.48 (+, OCH₃), 32.02 (-, CH₂CH), 28.20 (+, C-6), 25.58 (+, C-5), 14.22 (+, CH₂CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 1.4) = + 27. **MS** (EI-MS): *m/z* (%) = 214.1 (4) [M⁺], 169.1 (17) [M⁺ΔOEt], 168.1 (41) [M⁺ΔEtOH], 155.1 (25) [M⁺ΔCO₂Me], 141.1 (28) [M⁺ΔCO₂Et], 136.1 (38), 113.1 (49), 109.1 (56), 81.1 (100), 55.1 (39), 53.1 (39), 29.2 (43) [Et⁺]. **HRMS** (EI-MS): für C₁₀H₁₄O₅ (M⁺) calcd. 214.0841, found 214.0841.

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

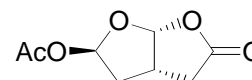


Fp: 103 °C.

¹H-NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 12.89 (s, br, 1 H, CO₂H), 6.07 (d, ³J = 5.7 Hz, 1 H, H-6a), 4.66 (dd, ³J = 8.9 Hz, ³J = 4.2 Hz, 1 H, H-2), 3.17 (dddd, ³J = 10.1 Hz, ³J = 9.6 Hz, ³J = 5.7 Hz, ³J = 4.3 Hz, ³J = 3.4 Hz, 1 H, H-3a), 2.82 (dd, ²J = 18.3 Hz, ³J = 10.1 Hz, 1 H, H-4_{exo}), 2.46 (ddd, ²J = 13.3 Hz, ³J = 9.6 Hz, ³J = 8.9 Hz, 1H, H-3_{exo}), 2.35 (dd, ²J = 18.3 Hz, ³J = 3.4 Hz, 1H, H-4_{endo}), 1.98 (ddd, ²J = 13.3 Hz, ³J = 4.3 Hz, ³J = 4.2 Hz, 1H, H-3_{endo}). **¹³C-NMR** (100 MHz, DMSO-*d*₆): δ (ppm) = 175.04 (C_q, C-5), 172.87 (C_q, CO₂H), 108.65 (+, C-6a), 78.32 (+, C-2), 37.93 (+, C-3a), 34.68 (-, C-4), 33.95 (-, C-3). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (MeOH, c = 1.9) = -77. **MS** (CI-MS): *m/z* (%) = 190.0 (100) [M+NH₄⁺]. **HRMS** (EI-MS): für C₇H₈O₅ (M⁺) calcd. 172.0372, found 172.0376. **C₇H₈O₅**: calcd. C 48.84, H 4.68, found C 48.76, H 4.79.

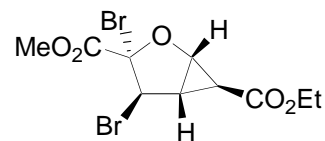
(2*S*,3*aS*,6*aR*)-5-oxohexahydrofuro[2,3-*b*]furan-2-yl acetate (13)**Fp:** 65 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 6.45 (d, ³*J* = 4.9 Hz, 1 H, H-2), 6.19 (d, ³*J* = 6.1 Hz, 1 H, H-6a), 3.27 (dddd, ³*J* = 11.2 Hz, ³*J* = 9.6 Hz, ³*J* = 6.1 Hz, ³*J* = 4.2 Hz, ³*J* = 1.2 Hz, H-3a), 2.91 (dd, ²*J* = 18.6 Hz, ³*J* = 11.2 Hz, 1 H, H-4_{exo}), 2.62 (dd, ²*J* = 18.6 Hz, ³*J* = 4.2 Hz, 1 H, H-4_{endo}), 2.40 (ddd, ²*J* = 14.0 Hz, ³*J* = 9.6 Hz, ³*J* = 4.9 Hz, 1 H, H-3_{exo}), 2.07 (dd, ²*J* = 14.0 Hz, ³*J* = 1.2 Hz, 1 H, H-3_{endo}), 2.05 (s, 3 H, CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 174.04 (C_q, C-5), 168.52 (C_q, C=O), 107.41 (+, C-6a), 97.42 (+, C-2), 37.27 (-, C-3), 35.18 (+, C-3a), 34.47 (-, C-4), 20.20 (+, CH₃). **IR** (KBr): ν (cm⁻¹) = 2985, 2959, 2928, 1783, 1722, 1381, 1359, 1260, 1242, 1179, 1112, 1067, 1024, 975, 933, 919, 866, 833, 792, 773, 685. **[α]_D²⁰** (CH₂Cl₂, c = 1.1) = -152. **MS** (CI-MS): *m/z* (%) = 204.0 (100) [M+NH₄⁺]. **C₈H₁₀O₅**: 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.

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 6.49 (ddd, ³*J* = 5.2 Hz, ³*J* = 1.1 Hz, ⁴*J* = 0.5 Hz, 1 H, H-2), 6.10 (d, ³*J* = 5.5 Hz, 1 H, H-6a), 3.25 (dddd, ³*J* = 9.4 Hz, ³*J* = 8.7 Hz, ³*J* = 8.7 Hz, ³*J* = 5.5 Hz, ³*J* = 1.9 Hz, ⁴*J* = 0.5 Hz, 1 H, H-3a), 2.86 (dd, ²*J* = 18.1 Hz, ³*J* = 8.7 Hz, 1 H, H-4_{exo}), 2.52 (dd, ²*J* = 18.1 Hz, ³*J* = 1.9 Hz, 1 H, H-4_{endo}), 2.40 (ddd, ²*J* = 13.9 Hz, ³*J* = 8.7 Hz, ³*J* = 1.1 Hz, 1 H, H-3_{exo}), 2.07 (s, 3 H, CH₃), 1.97 (ddd, ²*J* = 13.9 Hz, ³*J* = 9.4 Hz, ³*J* = 5.2 Hz, 1 H, H-3_{endo}). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 173.56 (C_q, C-5), 169.57 (C_q, C=O), 107.59 (+, C-6a), 98.76 (+, C-2), 36.81 (-, C-3), 36.71 (+, C-3a), 34.78 (-, C-4), 21.08 (+, CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 0.9) = + 18. **MS** (CI-MS): *m/z* (%) = 127.0 (66) [M⁺ΔOAc], 109.0 (15), 99.0 (18) [M⁺ΔOAcΔCO], 82.0 (28), 70.0 (23), 43.0 (100) [CH₃CO⁺], 42.0 (17), 41.0 (12). **C₈H₁₀O₅**: calcd. C 51.61, H 5.41, found C 51.35, H 5.34.

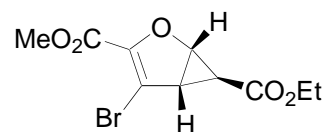
(1R,3S,4R,5S,6S)-6-ethyl 3-methyl 3,4-dibromo-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (14)



Fp: 97 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 5.11 (s, 1 H, H-4), 4.89 (dd, ³J = 5.3 Hz, ³J = 1.1 Hz, 1 H, H-1), 4.15 (q, ³J = 7.1 Hz, 2 H, CH₂), 3.88 (s, 3 H, OCH₃), 3.66 (dd, ³J = 4.0 Hz, ³J = 1.1 Hz, 1 H, H-6), 2.82 (dd, ³J = 5.3 Hz, ³J = 4.0 Hz, 1 H, H-5), 1.28 (t, ³J = 7.1 Hz, 3 H, CH₂CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 168.58 (C_q, C=O₂Et), 163.82 (C_q, C=O₂Me), 95.98 (C_q, C-3), 68.03 (+, C-1), 61.51 (-, CH₂), 54.31 (+, C-4), 53.52 (+, OCH₃), 31.00 (+, C-5), 24.94 (+, C-6), 14.14 (+, CH₂CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 1.4) = -298. **MS** (CI-MS): *m/z* (%) = 392.1 (5) [M(⁸¹Br)₂+NH₄⁺], 390.1 (10) [M(⁸¹Br⁷⁹Br)+NH₄⁺], 388.1 (5) [M(⁷⁹Br)₂+NH₄⁺], 310.1 (7) [M(⁸¹Br)+NH₄⁺ΔBr], 308.1 (7) [M(⁷⁹Br)+NH₄⁺ΔBr], 230.1 (100) [M+NH₄⁺Δ2Br], 213.2 (14) [MH⁺Δ2Br]. **C₁₀H₁₂Br₂O₅**: calcd. C 32.29, H 3.25, found C 32.54, H 3.26.

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

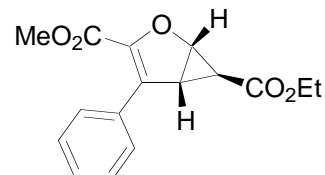


Fp: 39 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 4.88 (dd, ³J = 5.6 Hz, ³J = 1.2 Hz, 1 H, H-1), 4.15 (q, ³J = 7.1 Hz, 2 H, CH₂), 3.82 (s, 3 H, OCH₃), 3.03 (dd, ³J = 5.6 Hz, ³J = 2.6 Hz, 1 H, H-5), 1.36 (dd, ³J = 2.6 Hz, ³J = 1.2 Hz, 1 H, H-6), 1.26 (t, ³J = 7.1 Hz, 3 H, CH₂CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 170.83 (C_q, C=O₂Et), 158.82 (C_q, C=O₂Me), 143.51 (C_q, C-3), 108.14 (C_q, C-4), 66.16 (+, C-1), 61.42 (-, CH₂), 52.40 (+, OCH₃), 37.54 (+, C-5), 21.34 (+, C-6), 14.17 (+, CH₂CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 1.6) =

-154. **MS** (EI-MS): m/z (%) = 292.0 (15) [$M(^{81}\text{Br})^+$], 290.0 (15) [$M(^{79}\text{Br})^+$], 247.0 (4) [$M(^{81}\text{Br})^+\Delta\text{OEt}$], 245.0 (4) [$M(^{79}\text{Br})^+\Delta\text{OEt}$], 218.9 (99) [$M(^{81}\text{Br})^+\Delta\text{CO}_2\text{Et}$], 216.9 (100) [$M(^{79}\text{Br})^+\Delta\text{CO}_2\text{Et}$], 211.0 (17) [$M^+\Delta\text{Br}$]. $\text{C}_{10}\text{H}_{11}\text{BrO}_5$: calcd. C 41.26, H 3.81, Br 27.45, found C: 41.42, H 3.78, Br 27.09.

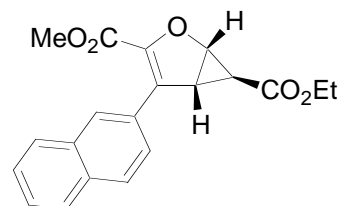
(1S,5R,6S)-6-ethyl 3-methyl 4-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (16)



Fp: 68 °C.

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ (ppm) = 7.61 (m, 2 H, H_{arom}), 7.37 (m, 3 H, H_{arom}), 4.94 (dd, $^3J = 5.4$ Hz, $^3J = 1.1$ Hz, 1 H, H-1), 4.21 (dq, $^2J = 10.8$ Hz, $^3J = 7.2$ Hz, 1 H, CHH-CH_3), 4.17 (dq, $^2J = 10.8$ Hz, $^3J = 7.1$ Hz, 1 H, CHH-CH_3), 3.78 (s, 3H, OCH_3), 3.11 (dd, $^3J = 5.4$ Hz, $^3J = 2.7$ Hz, 1H, H-5), 1.41(dd, $^3J = 2.7$ Hz, $^3J = 1.1$ Hz, 1H, H-6), 1.29 (dd, $^3J = 7.2$ Hz, $^3J = 7.1$ Hz, 3 H, CH_2CH_3). **$^{13}\text{C-NMR}$** (151 MHz, CDCl_3): δ (ppm) = 171.75 (C_q , CO_2Et), 160.11 (C_q , CO_2Me), 140.28 (C_q , C-3), 131.23 (C_q , C-4), 131.19 (C_q , C_{arom}), 129.04 (+, 2 C, C_{arom}), 128.87 (+, C_{arom}), 128.06 (+, 2 C, C_{arom}), 64.73 (+, C-1), 61.20 (-, CH_2), 52.10 (+, OCH_3), 36.37 (+, C-5), 21.68 (+, C-6), 14.24 (+, CH_2CH_3). **IR** (KBr): ν (cm^{-1}) = 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. $[\alpha]_{\text{D}}^{20}$ (CH_2Cl_2 , $c = 1.3$) = -103. **MS** (EI-MS): m/z (%) = 288.0 (1) [M^+], 243.0 (5) [$M^+\Delta\text{OEt}$], 215.0 (63) [$M^+\Delta\text{CO}_2\text{Et}$], 201.0 (100) [$M^+\Delta\text{CH}_2\text{CO}_2\text{Et}$], 173.0 (52) [$M^+\Delta\text{CH}_2\text{CO}_2\text{Et}\Delta\text{CO}$], 155.0 (15), 128.0 (19), 127.0 (19), 115.0 (10), 102.0 (11), 77.0 (6) [Ph^+]. $\text{C}_{16}\text{H}_{16}\text{O}_5$: calcd. C 66.66, H 5.59, found C 66.53, H 5.41.

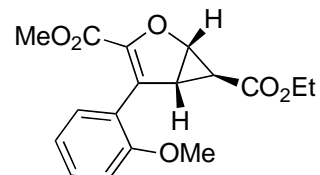
(1*S*,5*R*,6*S*)-6-ethyl 3-methyl 4-(naphthalen-2-yl)-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (17)



Fp: 115 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.08 – 8.06 (m, 1 H, H_{arom}), 7.90 – 7.79 (m, 3 H, H_{arom}), 7.71 (dd, ³*J* = 8.6 Hz, ⁴*J* = 1.8 Hz, 1 H, H_{arom}), 7.53 – 7.46 (m, 2 H, H_{arom}), 4.98 (dd, ³*J* = 5.4 Hz, ³*J* = 1.1 Hz, 1 H, H-1), 4.24 (dq, ²*J* = 10.8 Hz, ³*J* = 7.1 Hz, 1 H, CHHCH₃), 4.20 (dq, ²*J* = 10.8 Hz, ³*J* = 7.1 Hz, 1 H, CHHCH₃), 3.79 (s, 3 H, CO₂CH₃), 3.21 (dd, ³*J* = 5.4 Hz, ³*J* = 2.7 Hz, 1 H, H-5), 1.49 (dd, ³*J* = 2.7 Hz, ³*J* = 1.1 Hz, 1 H, H-6), 1.31 (dd, ³*J* = 7.1 Hz, ³*J* = 7.1 Hz, 3 H, CH₂CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 171.86 (C_q, CO₂Et), 160.19 (C_q, CO₂Me), 140.48 (C_q, C-3), 133.30 (C_q), 132.89 (C_q), 131.30 (C_q), 128.69 (C_q), 128.64 (+, C_{arom}), 128.35 (+, C_{arom}), 127.68 (+, C_{arom}), 127.51 (+, C_{arom}), 126.82 (+, C_{arom}), 126.63 (+, C_{arom}), 126.44 (+, C_{arom}), 64.82 (+, C-1), 61.47 (-, CH₂CH₃), 52.20 (+, CO₂CH₃), 36.41 (+, C-5), 21.83 (+, C-6), 14.29 (+, CH₂CH₃). **IR** (KBr): ν (cm⁻¹) = 3067, 2988, 2950, 2905, 1713, 1611, 1437, 1399, 1377, 1343, 1302, 1269, 1171, 1137, 1094, 1077, 1040, 995, 935, 857, 840, 816, 746. **[α]_D²⁰** (CH₂Cl₂, c = 0.3) = -24. **MS** (EI-MS): *m/z* (%): 338.2 (9) [M⁺], 265.2 (73) [M⁺ΔCO₂Et], 251.2 (100) [M⁺ΔCH₂CO₂Et], 223.2 (60) [M⁺ΔCH₂CO₂EtΔCO], 205.2 (38), 178.2 (22), 155.1 (27), 152.1 (21), 127.1 (5) [C₁₀H₇⁺], 95.1 (8). **C₂₀H₁₈O₅**: 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)

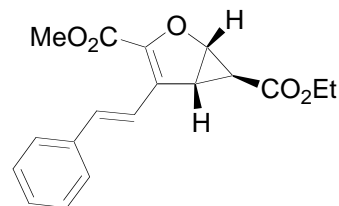


Fp: 76 °C.

¹H-NMR (300 MHz, Aceton-d₆): δ (ppm) = 7.38 – 7.31 (m, 2 H, H_{arom}), 7.06 – 6.93 (m, 2 H, H_{arom}), 4.97 (dd, ³*J* = 5.3 Hz, ³*J* = 1.1 Hz, 1 H, H-1), 4.16 (dq, ²*J* = 10.9 Hz, ³*J* = 7.1 Hz, 1 H, CHHCH₃), 4.12 (dq, ²*J* = 10.9 Hz, ³*J* = 7.1 Hz, 1 H, CHHCH₃), 3.84 (s, 3 H, CO₂CH₃), 3.63 (s, 3 H, Ar-OCH₃), 3.04 (dd, ³*J* = 5.3 Hz, ³*J* = 2.6 Hz, 1 H, H-5), 1.35 (dd, ³*J* = 2.6 Hz, ³*J* =

1.1 Hz, 1 H, H-6), 1.24 (dd, $^3J = 7.1$ Hz, $^3J = 7.1$ Hz, 3 H, CH_2CH_3). $^{13}\text{C-NMR}$ (75 MHz, Aceton- d_6): δ (ppm) = 172.19 (C_q , CO_2Et), 160.15 (C_q , CO_2Me), 157.14 (C_q , $\text{C}_{\text{arom}}\text{OMe}$), 142.02 (C_q , C-3), 130.95 (+, CH_{arom}), 130.07 (+, CH_{arom}), 128.37 (C_q , C-4), 120.81 (C_q , C_{arom} -C-4), 120.11 (+, CH_{arom}), 110.68 (+, CH_{arom}), 66.01 (+, C-1), 60.96 (-, CH_2), 55.43 (+, Ar-OCH_3), 51.95 (+, CO_2CH_3), 36.92 (+, C-5), 22.06 (+, C-6), 14.30 (+, CH_2CH_3). **IR** (KBr): ν (cm^{-1}) = 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_2Cl_2 , $c = 0.5$) = -102 . **MS** (EI-MS): m/z (%) = 318.1 (1) $[\text{M}^+]$, 287.1 (2) $[\text{M}^+\Delta\text{OMe}]$, 245.1 (51) $[\text{M}^+\Delta\text{CO}_2\text{Et}]$, 231.1 (100) $[\text{M}^+\Delta\text{CH}_2\text{CO}_2\text{Et}]$, 203.1 (35) $[\text{M}^+\Delta\text{CH}_2\text{CO}_2\text{Et}\Delta\text{CO}]$, 135.0 (87), 114.9 (22). **HRMS** (EI-MS): für $\text{C}_{17}\text{H}_{18}\text{O}_6$ (M^+) calcd. 318.1103, found 318.1100. $\text{C}_{17}\text{H}_{18}\text{O}_6$: calcd. C 64.14, H 5.70, found C 64.15, H 5.73.

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

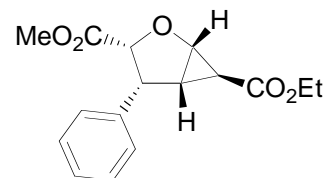


Fp: 85-88 °C.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.72 (d, $^3J = 16.2$ Hz, 1 H, CHPh), 7.54 – 7.49 (m, 2 H, H_{arom}), 7.39 – 7.25 (m, 3 H, H_{arom}), 6.91 (d, $^3J = 16.2$ Hz, 1 H, $\text{CH}=\text{CHPh}$), 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_3), 4.19 (dq, $^2J = 10.8$ Hz, $^3J = 7.2$ Hz, 1 H, CHHCH_3), 3.88 (s, 3 H, CO_2CH_3), 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_2CH_3). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 171.88 (C_q , CO_2Et), 160.36 (C_q , CO_2Me), 141.84 (C_q , C-3), 136.61 (C_q , C_{arom}), 134.44 (+, CHPh), 131.32 (C_q , C-4), 128.80 (+, 2 C, C_{arom}), 128.53 (+, C_{arom}), 127.03 (+, 2 C, C_{arom}), 119.59 (+, $\text{CH}=\text{CHPh}$), 65.66 (+, C-1), 61.29 (-, CH_2CH_3), 52.16 (+, CO_2CH_3), 31.31 (+, C-5), 22.18 (+, C-6), 14.24 (+, CH_2CH_3). **IR** (KBr): ν (cm^{-1}) = 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_2Cl_2 , $c = 1.0$) = -30 . **MS** (EI-MS): m/z (%) = 314.1 $[\text{M}^+]$ (23), 241.1 $[\text{M}^+\Delta\text{CO}_2\text{Et}]$ (78), 227.1 (67)

[M⁺ΔCH₂CO₂Et], 181.1 (100), 153.1 (64). C₁₈H₁₈O₅: calcd. C 68.78, H 5.77, found C 68.85, H 5.52.

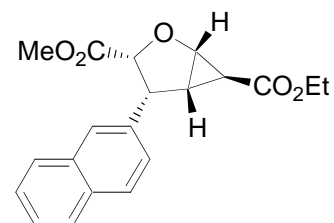
(1S,3R,4R,5S,6S)-6-ethyl 3-methyl 4-phenyl-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate (20)



Fp: 67 – 69 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.39-7.19 (m, 5 H, H_{arom}), 5.01 (dd, ³J = 11.0 Hz, ⁴J = 0.4 Hz, 1 H, H-3), 4.40 (ddd, ³J = 5.6 Hz, ³J = 1.0 Hz, ⁴J = 0.4 Hz, 1 H, H-1), 4.35 (dd, ³J = 11.0 Hz, ³J = 5.2 Hz, 1 H, H-4), 4.17 (dd, ²J = 10.8 Hz, ³J = 7.1 Hz, 1 H, CHHCH₃), 4.11 (dd, ²J = 10.8 Hz, ³J = 7.1 Hz, 1 H, CHHCH₃), 3.13 (s, 3 H, OCH₃), 3.13 (dd, ³J = 4.5 Hz, ³J = 1.0 Hz, 1 H, H-6), 2.42 (ddd, ³J = 5.6 Hz, ³J = 5.2 Hz, ³J = 4.5 Hz, 1 H, H-5), 1.28 (dd, ³J = 7.1 Hz, ³J = 7.1 Hz, 3 H, CH₂CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 170.84 (C_q, C=O₂Me), 169.61 (C_q, C=O₂Et), 134.73 (C_q, C_{arom}), 127.35 (+, 2 C, CH_{arom}), 127.30 (+, 2 C, CH_{arom}), 126.60 (+, CH_{arom}), 81.36 (+, C-3), 64.71 (+, C-1), 59.68 (-, CH₂CH₃), 50.39 (+, OCH₃), 47.33 (+, C-4), 28.47 (+, C-5), 25.12 (+, C-6), 13.24 (+, CH₂CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 1.0) = -54. **MS** (EI-MS): *m/z* (%) = 290.0 (1) [M⁺], 162.0 (100), 131.9 (45), 129.0 (26). C₁₆H₁₈O₅: 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)

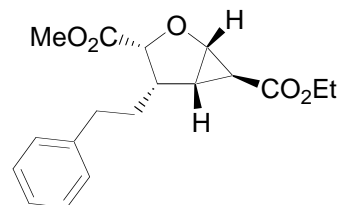


Fp: 69 - 70 °C.

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 7.84 (d, ⁴J = 1.7 Hz, 1 H, H_{arom}), 7.82 - 7.79 (m, 2 H, H_{arom}), 7.78 (d, ³J = 8.5 Hz, 1 H, H_{arom}), 7.50 - 7.46 (m, 2 H, H_{arom}), 7.40 (dd, ³J = 8.5 Hz, ⁴J =

1.7 Hz, 1 H, H_{arom}), 5.12 (d, $^3J = 11.0$ Hz, 1 H, H-3), 4.53 (dd, $^3J = 11.0$ Hz, $^3J = 5.2$ Hz, 1 H, H-4), 4.47 (dd, $^3J = 5.6$ Hz, $^3J = 1.0$ Hz, 1 H, H-1), 4.22 (dq, $^2J = 10.8$ Hz, $^3J = 7.2$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}_3$), 4.16 (dq, $^2J = 10.8$ Hz, $^3J = 7.1$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}_3$), 3.22 (dd, $^3J = 4.4$ Hz, $^3J = 1.0$ Hz, 1 H, H-6), 3.04 (s, 3 H, CO_2CH_3), 2.52 (ddd, $^3J = 5.6$ Hz, $^3J = 5.2$ Hz, $^3J = 4.4$ Hz, 1 H, H-5), 1.32 (dd, $^3J = 7.2$ Hz, $^3J = 7.1$ Hz, 3 H, $\text{CH}_2\underline{\text{C}}\underline{\text{H}}_3$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 171.86 (C_q , $\underline{\text{C}}\underline{\text{O}}_2\underline{\text{M}}\underline{\text{e}}$), 170.69 (C_q , $\underline{\text{C}}\underline{\text{O}}_2\underline{\text{E}}\underline{\text{t}}$), 133.29 (C_q , C_{arom}), 133.14 (C_q , C_{arom}), 132.69 (C_q , C_{arom}), 127.96 (+, C_{arom}), 127.78 (+, C_{arom}), 127.56 (+, C_{arom}), 126.99 (+, C_{arom}), 126.71 (+, C_{arom}), 126.28 (+, C_{arom}), 126.11 (+, C_{arom}), 82.36 (+, C-3), 65.83 (+, C-1), 60.78 (-, $\underline{\text{C}}\underline{\text{H}}_2\underline{\text{C}}\underline{\text{H}}_3$), 51.46 (+, $\text{CO}_2\underline{\text{C}}\underline{\text{H}}_3$), 48.59 (+, C-4), 29.65 (+, C-5), 26.29 (+, C-6), 14.33 (+, $\underline{\text{C}}\underline{\text{H}}_2\underline{\text{C}}\underline{\text{H}}_3$). **IR** (KBr): ν (cm^{-1}) = 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. $[\alpha]_{\text{D}}^{20}$ (CH_2Cl_2 , $c = 0.6$) = -60. **MS** (EI-MS): m/z (%) = 340.2 (9) [M^+], 212.1 (100) [$\text{C}_{10}\text{H}_7\text{-CH=CH-CO}_2\text{Me}^+$], 181.1 (34) [$\text{C}_{10}\text{H}_7\text{-CH=CH-CO}^+$], 179.1 (38), 178.1 (30), 165.1 (18), 153.1 (15) [$\text{C}_{10}\text{H}_7\text{-CH=CH}^+$], 152.1 (21), 141.1 (13), 128.1 (7), 127.1 (5) [$\text{C}_{10}\text{H}_7^+$]. $\text{C}_{20}\text{H}_{20}\text{O}_5$: calcd. C 70.57, H 5.92, found C 70.58, H 5.86.

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

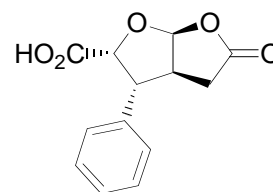


Fp: 67 – 71 °C.

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ (ppm) = 7.29 (dd, $^3J = 7.7$ Hz, $^3J = 7.4$ Hz, 2 H, $H_{\text{arom-meta}}$), 7.20 (t, $^3J = 7.4$ Hz, 1 H, $H_{\text{arom-para}}$), 7.18 (d, $^3J = 7.7$ Hz, 2 H, $H_{\text{arom-ortho}}$), 4.78 (d, $^3J = 10.4$ Hz, 1 H, H-3), 4.30 (dd, $^3J = 5.7$ Hz, $^3J = 1.1$ Hz, 1 H, H-1), 4.14 (dq, $^2J = 10.8$ Hz, $^3J = 7.1$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}_3$), 4.08 (dq, $^2J = 10.8$ Hz, $^3J = 7.1$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}_3$), 3.71 (s, 3 H, CO_2CH_3), 3.01 (dddd, $^3J = 11.3$ Hz, $^3J = 10.4$ Hz, $^3J = 5.6$ Hz, $^3J = 4.4$ Hz, 1 H, H-4), 2.80 (ddd, $^2J = 13.9$ Hz, $^3J = 8.9$ Hz, $^3J = 5.6$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{P}}\underline{\text{h}}$), 2.65 (ddd, $^2J = 13.9$ Hz, $^3J = 8.6$ Hz, $^3J = 7.2$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{P}}\underline{\text{h}}$), 2.34 (dd, $^3J = 4.3$ Hz, $^3J = 1.1$ Hz, 1 H, H-6), 2.28 (ddd, $^3J = 5.7$ Hz, $^3J = 5.6$ Hz, $^3J = 4.3$ Hz, 1 H, H-5), 1.85 (dddd, $^2J = 13.3$ Hz, $^3J = 8.9$ Hz, $^3J = 7.2$ Hz, $^3J = 4.4$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}_2\underline{\text{P}}\underline{\text{h}}$), 1.51 (dddd, $^2J = 13.3$ Hz, $^3J = 11.3$ Hz, $^3J = 8.6$ Hz, $^3J = 5.6$ Hz, 1 H, $\underline{\text{C}}\underline{\text{H}}\underline{\text{H}}\underline{\text{C}}\underline{\text{H}}_2\underline{\text{P}}\underline{\text{h}}$), 1.26 (dd, $^3J = 7.1$ Hz, $^3J = 7.1$ Hz, 3 H, $\text{CH}_2\underline{\text{C}}\underline{\text{H}}_3$). $^{13}\text{C-NMR}$ (75 MHz,

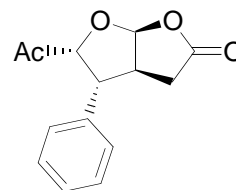
CDCl₃): δ (ppm) = 172.17 (C_q, CO₂Me), 170.61 (C_q, CO₂Et), 140.94 (C_q, C_{arom}), 128.53 (+, 2 C, C_{arom-meta}), 128.37 (+, 2 C, C_{arom-ortho}), 126.18 (+, C_{arom-para}), 82.24 (+, C-3), 66.99 (+, C-1), 60.58 (-, CH₂CH₃), 51.98 (+, CO₂CH₃), 42.33 (+, C-4), 34.64 (-, CH₂Ph), 29.93 (+, C-5), 29.48 (-, CH₂CH₂Ph), 25.21 (+, C-6), 14.24 (+, CH₂CH₃). **IR** (KBr): ν (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. $[\alpha]_D^{20}$ (CH₂Cl₂, c = 1.6) = + 10.8. **MS** (EI-MS): m/z (%) = 318.1 (1) [M⁺], 229.1 (56), 213.1 (15), 185.1 (25), 129.1 (23), 104.0 (51), 91.0 (100) [PhCH₂⁺]. **HRMS** (EI-MS): für C₁₈H₂₂O₅ (M⁺) calcd. 318.1467, found 318.1465.

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

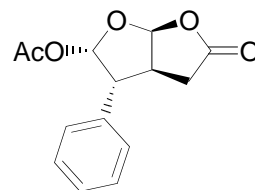


Fp: 164 °C.

¹H-NMR (300 MHz, CD₃OD): δ (ppm) = 7.35-7.21 (m, 5 H, H_{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, CO₂H), 3.63 (dd, ³J = 6.4 Hz, ³J = 3.5 Hz, 1 H, H-3), 3.43 (dddd, 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_{exo}), 2.70 (dd, ²J = 18.9 Hz, ³J = 3.9 Hz, 1 H, H-4_{endo}). **¹³C-NMR** (75 MHz, CD₃OD): δ (ppm) = 177.32 (C_q, C-5), 172.01 (C_q, CO₂H), 139.67 (C_q, C_{arom}), 129.58 (+, 2 C, C_{arom}), 129.31 (+, 2 C, C_{arom}), 128.61 (+, C_{arom}), 109.95 (+, C-6a), 82.33 (+, C-2), 55.27 (+, C-3), 47.56 (+, C-3a), 35.13 (-, C-4). **IR** (KBr): ν (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. $[\alpha]_D^{20}$ (MeOH, c = 0.8) = - 66. **MS** (CI-MS): m/z (%) = 266.1 (100) [M+NH₄⁺]. **HRMS** (CI-MS): für C₁₃H₁₃O₅ (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.

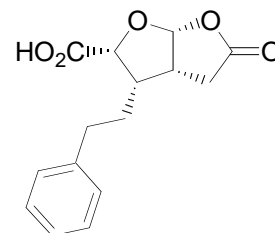
¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.36 – 7.24 (m, 3 H, H_{arom}), 7.13 – 7.04 (m, 2 H, H_{arom}), 6.49 (d, ³*J* = 5.6 Hz, 1 H, H-6a), 4.84 (d, ³*J* = 6.1 Hz, 1 H, H-2), 3.52 (dd, ³*J* = 6.1 Hz, ³*J* = 2.6 Hz, 1 H, H-3), 3.42 (dddd, ³*J* = 10.6 Hz, ³*J* = 5.6 Hz, ³*J* = 4.1 Hz, ³*J* = 2.6 Hz, 1 H, H-3a), 3.03 (dd, ²*J* = 18.9 Hz, ³*J* = 10.6 Hz, 1 H, H-4_{exo}), 2.63 (dd, ²*J* = 18.9 Hz, ³*J* = 4.1 Hz, 1 H, H-4_{endo}), 1.72 (s, 3 H, CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 205.54 (C_q, C=O), 174.13 (C_q, C-5), 137.25 (C_q, C_{arom}), 129.04 (+, 2 C, C_{arom}), 128.07 (+, C_{arom}), 127.86 (+, 2 C, C_{arom}), 107.87 (+, C-6a), 86.26 (+, C-2), 54.77 (+, C-3), 46.00 (+, C-3a), 34.50 (-, C-4), 27.83 (+, CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰** (CH₂Cl₂, c = 0.5) = -5.1. **MS** (EI-MS): *m/z* (%): 246.1 (7) [M⁺], 218.1 (31) [M⁺ΔCO], 203.1 (86) [M⁺ΔCOCH₃], 157.1 (100), 129.1 (77), 115.1 (33), 91.1 (81), 85.1 (26), 77.0 (23) [Ph⁺], 57.1 (14), 43.0 (57) [CH₃CO⁺]. **C₁₄H₁₄O₄**: 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.

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 7.40 – 7.24 (m, 5 H, H_{arom}), 6.59 (d, ³*J* = 4.7 Hz, 1 H, H-2), 6.22 (d, ³*J* = 5.4 Hz, 1 H, H-6a), 3.49 (dddd, ³*J* = 11.1 Hz, ³*J* = 8.3 Hz, ³*J* = 5.4 Hz, ³*J* = 1.1 Hz, 1 H, H-3a), 3.32 (dd, ³*J* = 11.1 Hz, ³*J* = 4.7 Hz, 1 H, H-3), 2.86 (dd, ²*J* = 18.2 Hz, ³*J* = 8.3 Hz, 1 H, H-4_{exo}), 2.55 (dd, ²*J* = 18.2 Hz, ³*J* = 1.1 Hz, 1 H, H-4_{endo}), 1.90 (s, 3 H, CH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 172.99 (C_q, C-5), 168.89 (C_q, C=O), 132.65 (C_q, C_{arom}), 128.98 (+, 2 C, C_{arom}), 128.81 (+, 2 C, C_{arom}), 128.31 (+, C_{arom}), 107.02 (+,

C-6a), 98.87 (+, C-2), 53.36 (+, C-3), 42.36 (+, C-3a), 34.18 (-, C-4), 20.84 (+, CH₃). **IR** (KBr): ν (cm⁻¹) = 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]_D²⁰ (CH₂Cl₂, c = 1.4) = -90. **MS** (EI-MS): m/z (%): 262.2 [M⁺] (2), 203.1 [M⁺ Δ OAc] (21), 175.1 (16), 174.1 (100) [M⁺ Δ HOAc Δ CO], 158.1 (13), 157.1 (19), 146.1 (17), 145.1 (96), 132.1 (79), 131.1 (74) [Ph-CH=CCHCO⁺], 129.1 (28), 117.1 (36), 91.1 (42) [PhCH₂⁺], 77.1 (12) [Ph⁺], 43.0 (64) [CH₃CO⁺]. **HRMS** (EI-MS): für C₁₄H₁₄O₅ (M⁺) calcd. 262.0841, found 262.0838.

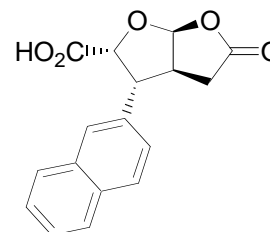
(2R,3S,3aR,6aR)-5-oxo-3-phenethylhexahydrofuro[2,3-b]furan-2-carboxylic acid (31)



Fp: 146 °C.

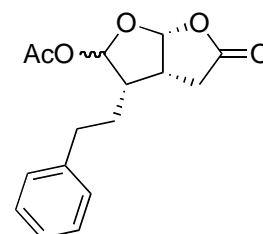
¹H-NMR (400 MHz, CD₃OD): δ (ppm) = 7.30 – 7.15 (m, 5 H, H_{arom}), 6.12 (d, ³J = 6.0 Hz, 1 H, H-6a), 4.90 (s, br, 1 H, CO₂H), 4.62 (d, ³J = 8.8 Hz, 1 H, H-2), 3.29 (dddd, ³J = 11.5 Hz, ³J = 8.4 Hz, ³J = 6.5 Hz, ³J = 6.0 Hz, 1 H, H-3a), 2.79 – 2.65 (m, 2 H, CH₂Ph), 2.78 (dd, ³J = 8.8 Hz, ³J = 8.4 Hz, 1 H, H-3), 2.56 (dd, ²J = 18.8 Hz, ³J = 6.5 Hz, 1 H, H-4_{endo}), 2.45 (dd, ²J = 18.8 Hz, ³J = 11.5 Hz, 1 H, H-4_{exo}), 1.96 – 1.90 (m, 1 H, CHHCH₂Ph), 1.76 – 1.70 (m, 1 H, CHHCH₂Ph). **¹³C-NMR** (75 MHz, CD₃OD): δ (ppm) = 179.28 (C_q, C-5), 174.62 (C_q, CO₂H), 142.81 (C_q, C_{arom}), 129.61 (+, 2 C, C_{arom}), 129.46 (+, 2 C, C_{arom}), 127.24 (+, C_{arom}), 110.68 (+, C-6a), 82.76 (+, C-2), 44.58 (+, C-3), 42.33 (+, C-3a), 35.36 (-, CH₂Ph), 29.87 (-, CH₂CH₂Ph), 29.43 (-, C-4). **IR** (KBr): ν (cm⁻¹) = 3422, 3022, 2926, 2857, 1773, 1385, 1202, 1111, 1088, 1017, 993, 975, 751, 737, 700, 627. [α]_D²⁰ (MeOH, c = 0.6) = - 47. **MS** (EI-MS): m/z (%) = 258.1 (2) [M⁺ Δ H₂O], 230.1 (11) [M⁺ Δ H₂O Δ CO], 201.1 (37), 129.1 (27), 105.1 (14) [Ph(CH₂)₂⁺], 104.1 (66) [PhCH=CH₂⁺], 91.1 (100) [PhCH₂⁺]. **C₁₅H₁₆O₅**: calcd. C 65.21, H 5.84, found C 65.13, H 5.84.

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



¹H-NMR (400 MHz, CD₃OD): δ (ppm) = 7.84 – 7.76 (m, 3 H, H_{arom}), 7.72 (m, 1 H, H_{arom}), 7.48 – 7.40 (m, 2 H, H_{arom}), 7.38 – 7.35 (m, 1 H, H_{arom}), 6.52 (d, ³*J* = 5.6 Hz, 1 H, H-6a), 5.13 (d, ³*J* = 6.5 Hz, 1 H, H-2), 4.84 (s, br, 1 H, CO₂H), 3.82 (dd, ³*J* = 6.5 Hz, ³*J* = 3.7 Hz, 1H, H-3), 3.57 (dddd, ³*J* = 10.3 Hz, ³*J* = 5.6 Hz, ³*J* = 3.8 Hz, ³*J* = 3.7 Hz, 1 H, H-3a), 3.07 (dd, ²*J* = 18.8 Hz, ³*J* = 10.3 Hz, 1 H-4_{exo}), 2.77 (dd, ²*J* = 18.8 Hz, ³*J* = 3.8 Hz, 1 H, H-4_{endo}). **¹³C-NMR** (75 MHz, CD₃OD): δ (ppm) = 177.30 (C_q, C-5), 172.12 (C_q, CO₂H), 137.11 (C_q, C_{arom}), 134.77 (C_q, C_{arom}), 134.26 (C_q, C_{arom}), 129.21 (+, CH_{arom}), 128.96 (+, CH_{arom}), 128.58 (+, CH_{arom}), 128.09 (+, CH_{arom}), 127.37 (+, CH_{arom}), 127.28 (+, CH_{arom}), 127.10 (+, CH_{arom}), 110.04 (+, C-6a), 82.46 (+, C-2), 55.39 (+, C-3), 47.53 (+, C-3a), 35.20 (-, C-4). **IR** (KBr): ν (cm⁻¹) = 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⁺], 252.1 (15) [M⁺ΔH₂OΔCO], 224.1 (15) [M⁺ΔH₂OΔ2CO], 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) [C₁₀H₇⁺], 115.1 (13). **HRMS** (EI-MS): für C₁₇H₁₄O₅ (M⁺): calcd. 298.0841, found 298.0839.

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



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

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 7.34-7.30 (m, 2 H, H_{arom-ortho}), 7.26-7.22 (m, 1 H, H_{arom-para}), 7.20-7.16 (m, 2 H, H_{arom-meta}), 6.21 (d, ³*J* = 5.0 Hz, 1 H, H-2), 6.09 (d, ³*J* = 5.4 Hz, 1 H, H-6a), 3.21 (dddd, ³*J* = 9.1 Hz, ³*J* = 8.1 Hz, ³*J* = 7.0 Hz, ³*J* = 5.4 Hz, 1 H, H-3a), 2.76 (ddd, ²*J* = 14.3 Hz, ³*J* = 8.7 Hz, ³*J* = 6.0 Hz, 1H, CHHPh), 2.64 (ddd, ²*J* = 14.3 Hz, ³*J* = 8.3

Hz, $^3J = 7.1$ Hz, 1 H, $\underline{\text{CHHPh}}$), 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, CH_3), 1.86 (dddd, $^2J = 14.0$ Hz, $^3J = 8.3$ Hz, $^3J = 8.1$ Hz, $^3J = 6.0$ Hz, 1 H, $\underline{\text{CHHCH}_2\text{Ph}}$), 1.76 (dddd, $^2J = 14.0$ Hz, $^3J = 8.7$ Hz, $^3J = 7.3$ Hz, $^3J = 7.1$ Hz, 1 H, $-\underline{\text{CHHCH}_2\text{Ph}}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 174.61 (C_q , C-5), 169.74 (C_q , $\underline{\text{COCH}_3}$), 140.42 (C_q , C_{arom}), 128.69 (+, 2 C, CH_{arom}), 128.37 (+, 2 C, CH_{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 (+, CH_3).

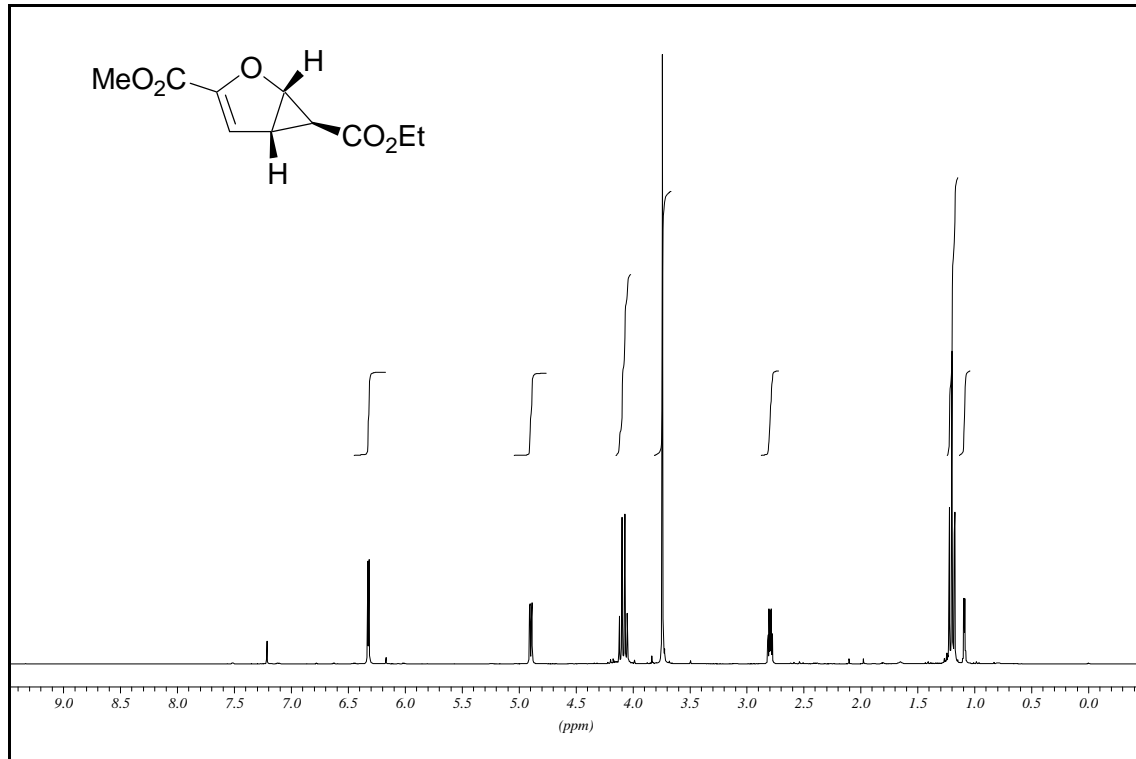
NMR-data for the 2S-Isomer:

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ (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, $\underline{\text{CHHPh}}$), 2.76 (dd, $^2J = 18.4$ Hz, $^3J = 5.1$ Hz, 1 H, H-4), 2.69 - 2.65 (m, 1 H, $\underline{\text{CHHPh}}$), 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, CH_3), 1.96-1.90 (m, 1 H, $\underline{\text{CHHCH}_2\text{Ph}}$), 1.84-1.76 (m, 1 H, $\underline{\text{CHHCH}_2\text{Ph}}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 175.37 (C_q , C-5), 169.49 (C_q , $\underline{\text{COCH}_3}$), 140.59 (C_q , C_{arom}), 128.74 (+, 2 C, CH_{arom}), 128.28 (+, 2 C, CH_{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 (+, 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) [$\text{PhCH}=\text{CH}_2^+$], 91.0 (59) [PhCH_2^+]. **HRMS** (LSI-MS): für $\text{C}_{16}\text{H}_{19}\text{O}_5$ (MH^+) calcd. 291.1232, found 291.1232.

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

¹H-NMR (300 MHz, CDCl₃)



¹³C-NMR (75.5 MHz, CDCl₃)

