Supporting Information to:

Elaboration of D-(-)-Ribose into a Tricyclic, Natural Product-Like Scaffold.

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General experimental methods

Chemicals, solvents and reagents for reactions were the highest quality available. Solvents for extraction and chromatography were of technical grade and distilled prior to use. TLC Sil G-25 UV_{254} glass plates; visualisation by UV and or *A*) by dipping in a soln. of H_2SO_4/H_2O/EtOH 14:4:1 or *B*) cerium(IV)sulfate-hydrate/phosphomolybdic acid hydrate/H_2SO_4/H_2O , followed by heating. Flash column chromatography was performed on silica gel 60 (40-63 µm, 230-400 mesh,) at low pressure. ^{1}H- and ^{13}C-NMR: δ values in ppm (solvents signals as internal standard), *J* [Hz]; EI-MS:*)* ionisation energy 70eV; only selected peaks; LSI-MS: Cs^+ ion gun. ESI-MS: *VG Platform* single quadrupole ESI-Mass spectrometer.

Abbreviations used: sat. = saturated; min. = minutes; h = hour; DMAP = 4-N;N-dimethylaminopyridine; RT = room temperature; R_f = retension factor; TLC = thin layer chromatography; HV = high vacuum

Carboxylic acids 2a-h

(E)-4-Oxo-pent-2-enoic acid *(2a).* To a solution of glyoxylic acid monohydrate (50 g, 0.53 mol) in 500 ml aceton, morpholine.HCl (66.4 g, 0.54 mol) were added and stirring was applied for one hour. The now clear solution was refluxed for three days. At –10°C, morpholine.HCl was crystallised and filtered off over Hyflo®, which is rinsed with 200 ml of acetone. After evaporation of the solvents, the obtained brown oil was washed with 200 ml of water and extracted 5 times with 160 ml of diethylether. The org. Phases were dried over Na_2SO_4 and solvents evaporated. The obtained solid was stirred with 155 ml EtOAc and filtered off after 10 min. This yielded 39.3 g (0.344 mol, 65 %) of a yellow solid. ^{1}H–NMR (300 MHz, CD_3OD): 6.94 (d, J = 16.2 Hz, 1H), 6.69 (d, J = 16.2 Hz, 1H), 2.36 (s, 3H); ^{13}C-NMR (75 MHz, CD_3OD): 200.7, 169.1, 141.7, 134.0, 28.5; IR (KBr): 3066s, 2930s, 2704m, 2584m, 2518m, 1670s, 1644s, 1623s, 1439s, 1409s, 1361s, 1304s, 1294s, 1277s, 1258s, 1236s, 1217s, 1104w, 1026m, 1005s, 930m, 894m

(E)-4-Oxo-4-phenyl-but-2-enoic acid *(2b)*
commercially available

(E)-4-(4-Bromo-phenyl)-4-oxo-but-2-enoic acid *(2c).* 4-Bromo-acetophenon (5,65 g, 27.8 mmol) were suspended in 50 ml acetic acid and 5ml HCl conc. After addition of glyoxylic acid monohydrate (2.65 g, 27.8 mmol) the mixture was refluxed for 15 h. Solvents were removed from the orange solution, the solid yellow residue was taken up in EtOAc and filtered. After evaporation of the EtOAc the procedure was repeated once. Drying afforded 2.52 g ((9.89 mmol, 35,7 %) of a pale yellow solid. ^{1}H-NMR (300MHz, CDCl3) 7.95 (d, J=15.5, 1H), 7.88 (d, J=8.5, 2H), 7.68 (d, J=8.5, 2H), 6.90 (d, J=15.5, 2H); 13C-NMR: (75 MHz CDCl3) 188.1, 170.1, 137.7, 135.1, 132.4, 131.8, 130.3, 129.6; IR: (KBr) 3038 (s, br), 2678 (m), 2579 (m), 1693 (s), 1668 (s), 1634 (s), 1584 (s), 1568 (m), 1486 (m), 1417 (s), 1398 (s), 1297 (s), 1193 (s), 1106 (m), 1071 (s), 1007 (s), 979 (s), 916 (m), 837 (s), 763 (s), 717 (m), 654 (s).

(E)-4-(3-Nitro-phenyl)-4-oxo-but-2-enoic acid *(2d).* 3-nitro-acetophenon (16.85 g, 0.1 mol) was suspended in 30 ml of acetic acid. After adding glyoxylic acid monohydrate (9.49 g, 0.1 mol) under stirring, the mixture was refluxed for 15 h. The solution was cooled to RT and the obtained yellow brown solid was filtered. The filtrate was washed with ethanol to obtain 10.57 g (47.8 mmol, 47.8%) product which was used without further purification. 1H-NMR (300MHz, DMSO) 8.68-8.61 (m, 1H), 8.53-8.40 (m, 2H), 7.90 (d, J=15.4, 1H), 7.89-7.81 (m, 1H), 6.73 (d, J= 15.8, 1H); 13C-NMR: (75MHz, DMSO) 188.5, 166.4, 148.3, 137.5, 135.9, 135.1, 134.1, 131.0, 128.2, 123.3; IR: (KBr) 3081 (m, br), 2680 (m, br), 1683 (s), 1615 (s), 1580 (m), 1532 (s), 1480 (m), 1418 (s), 1347 (s), 1306 (s), 1199 (m), 1091 (m), 1037 (m), 980 (m), 942 (m), 809 (m), 775 (m), 730 (s), 666 (s), 634 (s).

(E)-4-(4-Nitro-phenyl)-4-oxo-but-2-enoic acid *(2e).* 4-nitro-acetophenon (36.5 g, 0.21 mol) was dissolved in 300 ml of toluene. After adding glyoxylic acid monohydrate (22.4 g, 0.243 mol) and p-toluenesulfonic acid (841

mg, 4.4 mmol) under stirring, the mixture was refluxed for 4.5 h in an apparatus with $CaCl_2$-tube and water separator. The

solution was cooled to 50°C and 400 ml of 5% aq. Na_2CO_3 solution was added. The toluene phase was separated

and washed once more with water. Under stirring the water phases were slowly treated with 30 ml of 36% HCl. The so obtained precipitation was filtered off and washed three times with water. After drying 22.9 g (47%) whitish crystals are obtained. Recrystalization from first $CHCl_3$, then $CHCl_3$/1,2-dichloroethane 3/5, and last 1,2-dichloroethane gave 20.8 g (42,5%) of **2e** as yellow crystals. 1H-NMR (300MHz, DMSO) 8.35 (d, J=8.8, 2H), 8.24 (d, J=8.8, 2H), 7.85 (d, J=15.4, 1H), 6.70 (d, J=15.4, 1H); ^{13}C-NMR (75MHz, DMSO) 189.2, 166.4, 150.4, 141.0, 136.0, 134.1, 130.5, 124.2; IR (KBr) 2982 (m, br), 2868 (m, br), 2678 (m), 2580 (m), 1696 (s), 1672 (s), 1606 (s), 1532 (s), 1420 (s), 1351 (s), 1316 (s), 1191 (s), 1113 (m), 1009 (m), 981 (s), 944 (m), 857 (s), 826 (m), 782 (m), 733 (s), 687 (m), 656 (m).

(E)-3-Benzyl-4-oxo-pent-2-enoic acid *(2f).* To a solution of glyoxylic acid monohydrate (3.31 g, 36 mmol) in 4-phenyl-2-butanon (9.46 ml, 63 mmol) 3 ml of orthophosphoric acid (85%) was poured. The mixture was first heated for 4h at 90°C and then just stirred at room temperature for 18 more hours. The reaction mixture was extracted three times with 10-15 ml of CH_2Cl_2:ether = 1:1. The organic phases were washed with 20 ml of brine. After drying (Na_2SO_4), evaporating the solvents and distilling at 165°C (0.29 Torr) 2.37g (11 mmol, 32%) of **2f** as a colorless oil was obtained. ^{1}H-NMR (300MHz, $CDCl_3$): 7.37-7.11 (5H, m), 6.66 (1H, s), 2.34 (3H, s); ^{13}C-NMR (75MHz, $CDCl_3$): 199.4, 170.6, 155.1, 137.7, 128. 9, 128,5, 126.5, 125.0, 32.1, 27.0; IR: 3062, 3029, 1679, 1628, 1604, 1495, 1453, 1418, 1369, 1258, 1233, 1186, 1076, 1030, 1015, 934, 905, 782, 739, 694, 667; EI-MS: 204 (M^+), 187, 186, 172, 171, 159

(E)-3-Acetyl-oct-2-enoic acid *(2g).* To a solution of glyoxylic acid monohydrate (3.31 g, 36 mmol) in 4-phenyl-2-butanone (9.86 ml, 63 mmol) 3 ml of orthophosphoric acid (85%) was poured. The mixture was first heated for 4h at 90°C and then just stirred at room temperature for 18 more hours. The reaction mixture was extracted three times with 10-15 ml of CH_2Cl_2:ether = 1:1. The organic phases were washed with 20 ml of brine. After drying (Na_2SO_4), evaporating the solvents and distilling at 40°C (0.1 Torr) 3.462g (18.8 mmol, 28%) of **2g** as a colorless oil was obtained. ^{1}H-NMR (300MHz, $CDCl_3$): 6.51 (1H, s), 2.79-2.74 (2H, m), 3.18 (3H, s), 1.40-1.28 (6H, m), 0.90- 0.86 (3H, m); ^{13}C-NMR (75MHz, $CDCl_3$): 200, 170.9, 157.9, 124.5, 31.9, 28.9, 26.8, 26.7, 22.3, 13.9; IR: 2957, 2929, 2860, 1686, 1636, 1415, 1359, 1245, 1181, 1126, 878, 737; EI-MS: 184 (M^+), 169, 167,166, 137, 138, 124

3-Acetyl-4-oxo-pent-2-enoic acid *(2h).* To a solution of glyoxylic acid monohydrate (5 g, 54.3 mmol) in 50 ml acetic acid, acetylaceton (5.6 ml, 54.3 mmol) were added. The mixture was heated to 80°C for 5h or until no more acetylaceton was detectable by TLC. Acetic acid and the water formed were evaporated and fully removed by destilation of the remaining acetic acid at 0.1 mbar and 155°C for two days. ^{1}H-NMR (300MHz, $CDCl_3$: 6.55 (1H, s), 2.52 (3H, s), 1.84 (3H, s); ^{13}C-NMR (75MHz, CDCl3): 193.4, 169.0, 159.4, 126.7, 106.7, 28.7, 24.6; IR:

3104, 3004, 1748, 1685, 1419, 1370, 1324, 1211, 1131, 1085, 1022, 930, 860, 741, 678, 658, 614; EI-MS: 156 (M^+), 141, 138, 114

Esters 3a-g

(4R,5R)-5-Methoxy-4-((E)-4-oxo-pent-2-enoyloxy)-4,5-dihydro-furan-2-carboxylic acid methyl ester (*3a).*
To a suspension of **2a** (2.28 g, 20 mmol) in 1,2-dichloroethane, triethylamine (3.1 ml, 22 mmol) was added at 0°C. The addition of pivaloyl chloride (2.65 g, 22 mmol) was followed by dihydrofuranoside **1** (3.48 g, 20 mmol). After 3 h DMAP (310 mg, 2.5 mmol) was added and thus all remaining starting material converted. The reaction mixture was washed with 200 ml of sat. aq. $NaHCO_3$ and extracted three times with 200 ml EtOAc. After drying (Na_2SO_4), evaporating the solvent and separation of the crude on 200 g of silicagel (ethylacetate/hexane 3:7) 3.27 g (12.1 mmol, 60.5%) of **3a** as a white solid was obtained. TLC (EtOAc/hexane 3:7): R_f 0.24. ^{1}H-NMR (300MHz, $CDCl_3$): 7.04 (1H, d, *J* = 15.8), 6.63 (1H, d, *J* = 16.2), 6.06 (1H, d, *J* = 2.9), 5.66 (1H, dd, *J* = 1.3, *J* = 2.8), 5.44 (1H, d, *J* = 1.5), 3.86 (3H, s), 3.59 (3H, s), 2.36 (3H, s,); ^{13}C-NMR (75MHz, CDCl3): 197, 164, 160, 152, 141, 130, 110, 107, 81, 57, 52, 28; IR (KBr): 3064m, 3041w, 3004w, 2954m, 2844w, 1732s, 1716s, 1677s, 1648m, 1626m, 1456m, 1440s, 1373s, 1331s, 1312s, 1272s, 1256s, 1228s, 1202s, 1165m, 1135s, 1107s, 1074m, 1023s, 1008s, 980m, 969m, 921s, 906s, 896s; EI-MS: 270 (M+), 238 , 211;

(4R,5R)-5-Methoxy-4-((E)-4-oxo-4-phenyl-but-2-enoyloxy)-4,5-dihydro-furan-2-carboxylic acid methyl ester *(3b).* In an absolute three-neck flask **2b** (1.2 g, 6.6 mmol) was suspended in 9ml of absolute 1,2-dichloroethane under argon. The suspension was cooled to 0°C before triethylamine (0.95 ml, 6.9 mmol) was added. To the now yellow solution pivaloyl chloride (0.78 ml, 6.3 mmol) was added slowly in 2 ml 1,2-dichloroethane and after stirring for some minutes **1 (**1 g, 5.7 mmol) was added in another 4ml of 1,2-dichloroethane. After adding DMAP (140 mg, 1.15 mmol) and warming to RT the mixture was stirred for 3 h. The red turbid mixture was washed with 100 ml sat. aq. $NaHCO_3$ and extracted with diethylether. The solvents were evaporated and the crude was purified on silicagel (EtOAc:hexane 9:1, 6:1, 3:1). This yielded 1.308 g (3.9 mmol, 68.6%) of **3b** as a yellow oil. TLC: 0.59 (hexane:EtOAc 3:2). ^{1}H-NMR: (300MHz, $CDCl_3$) 8.02-7.95 (m, 2H), 7.91 (d, J=15.8, 1H), 7.68-7.59 (m, 1H), 7.55-7.48 (m, 2H), 6.85 (d, J=15.8, 1H), 6.08 (d, J=2.6, 1H), 5.69 (dd, J=2.9, 1.5, 1H), 5.47 (d, J=1.1, 1H), 3.86 (s, 3H), 3.59 (s, 3H); ^{13}C-NMR: (75MHz, $CDCl_3$) 189.0, 164.4, 159.9, 152.0, 137.5, 136.3, 134.0, 131.2, 128.8, 109.7, 107.3, 81.3, 57.0, 52.6; IR: (Film on NaCl) 3128 (w), 3064 (w), 3006 (w), 2956 (m), 2849 (w), 1732 (s), 1674 (s), 1633 (s), 1598 (m), 1581 (m), 1449 (s), 1370 (s), 1291 (s), 1252 (s), 1222 (s), 1164 (s), 1109 (s), 1005 (s), 923 (s), 899 (s), 792 (w), 758 (s), 731 (s), 690 (m).

(4R,5R)-4-[(E)-4-(4-Bromo-phenyl)-4-oxo-but-2-enoyloxy]-5-methoxy-4,5-dihydro-furan-2-carboxylic acid methyl ester *(3c).* In a three neck flask **2c** (0.79 g, 3.1 mmol, 1.1 eq) was suspended in 10 ml of absolute 1,2-dichloroethane. The suspension was cooled to 0°C before triethylamine (0.45 ml, 3.2 mmol) was added. To the thus obtained yellow brown solution pivaloyl chloride (0.38 ml, 3.1 mmol) was added slowly in 3 ml 1,2-

dichloroethane and the mixture was stirred at RT for 1h. After cooling again to 0°C **1** (0.49 g, 28 mmol) in 3 ml 1,2-dichloroethane was added dropwise. Shortly after, DMAP (68 mg, 0.56 mmol) was added and the cooling bath was removed. After 4 h the mixture was washed with 50 ml sat. aq. $NaHCO_3$ and extracted three times with diethylether. After drying over Na_2SO_4 and evaporation of the solvents the orange crude was purified on silicagel

(hexane:EtOAc 9:1, 6:1). This yielded 0.78 g (1.89 mmol, 67.2%) of **3c** as a yellow solid. TLC: 0.68-0.71 (hexane:EtOAc 3:2). ^{1}H-NMR: (300 MHz, $CDCl_3$) 7.87 (d, J=15.8, 1H), 7.85 (d, J=8.8, 2H), 7.66 (d, J=8.5, 2H), 6.86 (d, J=15.8, 1H), 6.08 (d, J=2.6, 1H), 5.69 (dd, J=2.9, 1.5, 1H), 5.47 (d, J=1.5, 1H), 3.86 (s, 3H), 3.59 (s, 3H); ^{13}C-NMR: (75 MHz, CDCl3) 188.0, 164.3, 159.9, 152.1, 136.9, 135.1, 132.3, 131.7, 130.3, 129.5, 109.7, 107.2, 81.4, 57.1, 52.6; IR: (KBr) 3127 (w), 3081 (w), 2958 (w), 2851 (w), 1729 (s), 1673 (s), 1630 (s), 1580 (s), 1440 (s), 1400 (s), 1370 (s), 1328 (s), 1308 (s), 1291 (s), 1667 (s), 1220 (s), 1155 (s), 1108 (s), 1071 (s), 998 (s), 975 (s), 933 (s), 927 (s), 895 (s), 846 (s), 760 (s), 751 (s).

(4R,5R)-5-Methoxy-4-[(E)-4-(3-nitro-phenyl)-4-oxo-but-2-enoyloxy]-4,5-dihydro-furan-2-carboxylic acid methyl ester (*3d).* In a three neck flask **2d** (3.5 g, 15.8 mmol) was suspended in 43 ml of absolute 1,2-dichloroethane. The suspension was cooled to 0°C before triethylamine (2.3 ml, 16.4 mmol) was added during 5 min. To the thus obtained yellow brown solution pivaloyl chloride (1.9 ml, 15.4 mmol) was added within 10 min in 1.8 ml 1,2-dichloroethane. The mixture was stirred at 0°-15°C for 40 min. After cooling again to 5°C **1 (**1.22 g, 7 mmol) in 4 ml 1,2-chloroethane was added dropwise. Shortly after, DMAP (0.222 g, 1.82 mmol) of were added and the cooling bath was removed. After 4 h the mixture was washed with sat. aq. $NaHCO_3$ and extracted three times with diethylether. After drying over Na_2SO_4 and evaporation of the solvents the orange crude was purified on silicagel (hexane:EtOAc 6:1 -> 2:1). This yielded 1.67 g (4.4 mmol, 63%) of **3d** as a yellow oil. TLC: 0.34 (hexane:EtOAc 3:2) ^{1}H-NMR: (30MHz, $CDCl_3$) 8.83-8.78 (m, 1H), 8.55-8.45 (m, 1H), 8.35-8.28 (m, 1H), 7.92 (d, J=15.4, 1H), 7.75 (t, J= 7.9, 1H), 6.94 (d, J=15.4, 1H), 6.09 (d, J=2.6, 1H), 5.70 (dd, J=2.9, 1.5, 1H), 5.49 (d, J=1.1, 1H), 3.87 (s, 3,H), 3.60 (s, 3H); ^{13}C-NMR: (75MHz, CDCl3) 187.0; 164.0; 159.9, 152.1, 148.6, 137.6, 135.9, 134.2, 132.9, 130.3, 128.1, 123.6, 109.6, 107.1, 81.6, 57.1, 52.6; IR: (Film on NaCl) 3088 (w), 2958 (m), 2850 (w), 1733 (s), 1679 (s), 1634 (m), 1615 (m), 1535 (s), 1480 (m), 1440 (s), 1352 (s), 1309 (s), 1291 (s), 1252 (s), 1222 (s), 1165 (s), 1108 (s), 1006 (s), 976 (m), 924 (m), 900 (m), 814 (m), 758 (m), 727 (m), 677 (m).

(4R,5R)-5-Methoxy-4-[(E)-4-(4-nitro-phenyl)-4-oxo-but-2-enoyloxy]-4,5-dihydro-furan-2-carboxylic acid methyl ester *(3e).* In a three-neck flask **2e** (3.0 g, 13.6 mmol) was suspended in 38 ml of absolute 1,2-dichloroethane. The suspension was cooled to 0°C before triethylamine (1.9 ml, 14.0 mmol) was added within 8 min. To the thus obtained yellow brown solution pivaloyl chloride (1.6 ml, 13.2 mmol) was added during 10 min in 1.5 ml 1,2-dichloroethane and the mixture was stirred at 0°C for 30 min. Then **1 (**1.57 g, 9.04 mmol) in 5 ml 1,2-dichloroethane and, shortly after, DMAP (0.188 g, 1.54 mmol) of was added. Stirring was contioued at 0°C for 2.5 h. The mixture was poured on sat. aq. $NaHCO_3$ and extracted twice with diethylether. After drying over Na_2SO_4 and evaporation of the solvents the brown crude was purified on silicagel (EtOAc/hexane 1:3). This yielded 2.65 g (7.0mmol, 78%) of **3e** as a yellow oil. TLC: 0.52 (hexane:EtOAc 3:2). ^{1}H-NMR: (300 MHz, $CDCl_3$) 8.37 (d, J= 8.8, 2H), 8.14 (d, J= 8.8, 2H), 7.89 (d, J=15.5, 1H), 6.92 (d, J=15.5, 1H), 6.08 (d, J= 2.9, 1H), 5.70

(dd, J=2.9, 1.5, 1H), 5.48 (d, J=1.1, 1H), 3.87 (s, 3H), 3.60 (s, 3H); ^{13}C-NMR: (75 MHz, $CDCl_3$) 187.7, 164.0, 159.9, 152.2, 150.7, 140.8, 136.2, 132.9, 129.8, 124.1, 109.7, 107.1, 81.6, 57.1, 52.7; IR (KBr): 3114 (w), 3080 (w), 2956 (m), 2851 (w), 1732 (s), 1678 (s), 1633 (m), 1604 (m), 1529 (s), 1441 (m), 1349 (s), 1320 (s), 1289 (s), 1252 (s), 1222 (s), 1165 (s), 1108 (s), 1006 (s), 977 (m), 923 (m), 898 (m), 858 (m), 841 (w), 757 (m), 731 (m).

(4R,5R)-4-((E)-3-Benzyl-4-oxo-pent-2-enoyloxy)-5-methoxy-4,5-dihydro-furan-2-carboxylic acid methyl ester *(3f).* Under an argon atmosphere **2f** (834 mg, 4.08 mmol) was dissolved in 13 ml 1,2-dichlorethane. At 0°C Et_3N (0.59 ml, 4.22 mmol) was added dropwise to the solution within 3 min. Then still at 0°C pivaloyl chloride (0.49 ml, 4.0 mmol) was added in 0.61 ml 1,2-dichlorethane within 5 min. After stirring for 45 min dihydrofuranoside **1** (474 mg, 2.7 mmol) in 1.6 ml of 1,2-dichloroethane and DMAP (57mg, 0.46 mmol) were added. The reaction was left to warm from 0 to 18°C within 1 h 50 min then the mixture was washed with cold sat. $NaHCO_3$ and extracted twice with ether. The organic phases were washed once more with brine. After drying (Na_2SO_4), evaporating the solvents and separation of the black crude on silicagel (EtOAc/hexane 1:4) 735 mg (2.04 mmol, 75%) of a yellow oil was obtained. TLC (EtOAc/hexane = 2:8): R_f 0.24 ^{1}H-NMR (300MHz, $CDCl_3$): 7.23-7.18 (5H, m), 6.60 (1H, s), 6.07 (1H, d, j = 3.01), 5.59 (1H, dd, J = 1.31 and 2.83), 5.41 (1H, d, J = 1.31), 4.19 (2H, s), 3.87 (3H, s), 3.58 (3H, s), 2.32 (3H, s); ^{13}C-NMR (75MHz, $CDCl_3$): 199.2, 164.8, 159.9, 154.4, 151.9, 137.9, 128.8, 128.5, 126.4, 125.0, 109.7, 107.4, 81.0, 57.1, 52.6, 31.9, 26.8; IR: 2954, 2359, 1730, 1684, 1632, 1602, 1495, 1439, 1370,1310, 1247, 1220, 1202, 1158, 1104, 1007, 917, 897; ESI-MS: 383 ($M+Na^+$), 361 (M^+), 329, 313, 311, 227, 209

(4R,5R)-4-((E)-3-Acetyl-oct-2-enoyloxy)-5-methoxy-4,5-dihydro-furan-2-carboxylic acid methyl ester *(3g).* Under an argon atmosphere **2g** (600 mg, 3.26 mmol) was dissolved in 9.6 ml 1,2-dichlorethane. At 0°C Et_3N (0.47 ml, 3.4 mmol) was added dropwise to the solution within 3 min. Then pivaloyl chloride (0.39 ml, 3.17 mmol) was added in 0.49 ml 1,2-dichlorethane at –10°C within 5 min. After stirring for 30 min dihydrofuranoside **1** (378 mg, 2.17 mmol) in 1.3 ml 1,2-dichloroethane and DMAP (45 mg, 0.37 mmol) were added The reaction was left to warm from 0 to 18°C within 2 h 10 min then the mixture was washed with cold sat. aq. $NaHCO_3$ and extracted twice with diethylether. The organic phases were washed once more with brine. After drying (Na_2SO_4), evaporating the solvents and separation of the black crude on silicagel (EtOAc/hexane 1:4) 443 mg (1.3 mmol, 60%) of a yellow oil was obtained. TLC (EtOAc/hexane = 2:8): R_f 0.24 ^{1}H-NMR (300MHz, $CDCl_3$): 6,46 (1H, s), 6.08 (1H, d, J = 2.82), 5.65 (1H, dd, J = 1.31 and 2.82), 5.44 (1H, d, J = 1.13), 3.86 (3H, s), 3.60 (3H, s), 2.77-2.72 (2H, m), 2.38 (3H, s), 1.40-1.24 (6H, m), 0.91-0.86 (3H, m); ^{13}C-NMR (75MHz, $CDCl_3$): 199.6, 164.7, 160.0, 157.2, 151.9, 124.3, 109.8, 107.6, 80.7, 57.0, 52.6, 32.0, 29.0, 26.9, 26.6, 22.4, 14.0; IR: 2957, 2931, 2859, 1730, 1685, 1631, 1439, 1366, 1309, 1244, 1204, 1163, 1104, 1064, 1009, 919, 897, 756; ESI-MS: 363 ($M+Na^+$), 3341 (M^+), 309, 281

Tricycles 4a-h

(2R,2aR,4aR,7aS,7bS)-2-Methoxy-6-methyl-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxa-cyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4a).* A solution of **3a** (5 g, 18.5 mmol) in 500 ml o-xylene was heated to reflux for 17 h. Evaporation of the solvent and recrystalisation from methanol/H_2O 9:1 gave 2.66 g (9.83 mmol, 53%) of white crystals. TLC (EtOAc/hexane 4:6): R_f 0.47; ^{1}H-NMR (300MHz, $CDCl_3$): 5.08 (1H, m), 5.06 (1H, s), 4.98 (1H, d, *J* = 7.7), 4.03 (1H, dd, *J* = 7.4 and 11.8), 3.87 (3H, s), 3.42 (3H, s), 3.29 (1H, dm, *J* = 11.5), 1.89 (3H, m); ^{13}C-NMR (75MHz, $CDCl_3$): 175, 168, 148, 106, 103, 93, 85, 56, 53, 36, 34, 20; IR (KBr): 3039, 2963, 2943, 2847, 1789, 1745, 1707, 1432, 1380, 1334, 1307, 1291, 1269, 1237, 1200, 1186, 1163, 1126, 1099, 1069, 1042, 1013, 985, 949, 930, 886, 829, 810; EI-MS: 271 (50, M^+), 239 (45), 211 (60);

(2R,2aR,4aR,7aS,7bS)-2-Methoxy-4-oxo-6-phenyl-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxacyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4b).* A solution of **3b** (1.28 g, 3.88 mmol) in 38 ml of o-xylene was stirred at 150°C for 5 h. The obtained solution was cooled to 70°C and the solvent was evaporated. After drying on the HV a yellow crystalline product was obtained which was further purified by recrystallization from methanol. Thus 0.94 g (2.83 mmol, 72.9 %) of a pale yellow product was obtained. TLC: (Toluol:EtOAc 5:1) Rf 0.45; ^{1}H-NMR: (300 MHz, $CDCl_3$) 7.67-7.58 (m, 2H), 7.42-7.32 (m, 3H), 5.86 (d, J=4.4, 1H), 5.11 (s, 1H), 5.04 (d, J=7.7, 1H), 4.17 (dd, J=11.6, 7.5, 1H), 3.90 (s, 3H), 3.52 (dd, J=11.6, 4.6, 1H), 3.44 (s, 3H); ^{13}C-NMR: (75 MHz, $CDCl_3$) 175.0, 168.1, 148.6, 133.1, 129.3, 128.4, 125.0, 106.7, 103.4, 94.1, 85.0, 56.0, 53.3, 37.5, 35.0; IR: (KBr) 3090, 3008, 2967, 2938, 2844, 1971, 1794, 1742, 1676, 1580, 1498, 1444, 1374, 1319, 1279, 1235, 1164, 1108, 1075, 1018, 985, 924, 858, 826, 806, 773, 747, 721, 693; MS: 332 (M+, 34), 301, 273, 229, 215, 201, 187, 185, 159, 157, 131, 127, 115, 105, 85, 77, 59, 45.

(2R,2aR,4aR,7aS,7bS)-6-(4-Bromo-phenyl)-2-methoxy-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxa-cyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4c).* In a round bottom flask equipped with a reflux condensor, **3c** (1.0 g, 2.43 mmol) was dissolved in 24 ml of o-xylene and stirred at 150°C for 18 h. The obtained solution was cooled to 70°C and the solvent was evaporated. After purification on silicagel (hexane:EtOAc 5:1, 3:1, 1:1) and drying on the HV, 0.447 g (1.1 mmol, 45%) of a yellow oil were obtained. TLC: 0.33 (hexane:EtOAc 2:1). ^{1}H-NMR: (300 MHz, $CDCl_3$) 7.49 (s, 4H), 5.87 (d, J=4.8, 1H), 5.11 (s, 1H), 5.04 (d, J=7.7, 1H), 4.17 (dd, J=11.6, 7.5, 1H), 3.91 (s, 3H), 3.51 (dd, J=11.6, 4.2, 1H), 3.45 (s, 3H). ^{13}C-NMR: (75MHz, $CDCl_3$) 174.8, 167.9, 147.7, 132.0, 131.6, 126.5, 123.5, 106.7, 103.4, 94.7, 85.0, 56.0, 53.4, 37.5, 35.0; IR: (Film on NaCl) 2954, 2847, 1790, 1752, 1677, 1589, 1490, 1439, 1399, 1376, 1282, 1242, 1174, 1106, 1073, 1008, 981, 927, 823, 808, 788, 730; MS: 412 (M+, 36), 410, 381, 379, 353, 351, 339, 337, 309, 307, 295, 293, 281, 279, 267, 265, 239, 237, 235, 211, 209, 185, 183, 157, 155;

(2R,2aR,4aR,7aS,7bS)-2-Methoxy-6-(3-nitro-phenyl)-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxacyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4d).* In a round bottom flask equipped with a reflux condensor, **3d** (2.5 g, 6.63 mmol) was dissolved in 45 ml of toluene and stirred at reflux for 20 h. The obtained solution was cooled to 70°C and the solvent was evaporated. After drying on the HV 2.41g (6.38 mmol, 96%) of a brown solid was obtained which was used without further purification. TLC: 0.39 (toluene:EtOAc 5:1). 1H-NMR: (300 MHz, $CDCl_3$) 8.48 (s, 1H), 8.21 (dd, J=8.3, 1.3, 1H), 7.94 (d, J=8.1, 1H),

7.56 (t, J=8.0, 1H), 6.04 (d, J=4.4, 1H), 5.13 (s, 1H), 5.06 (d, J=7.7, 1H), 4.20 (dd, J=11.8, 7.7, 1H), 3.93 (s, 3H), 3.58 (dd, J=11.6, 4.6, 1H), 3.46 (s, 3H); ^{13}C-NMR: (75 MHz, $CDCl_3$) 174.4, 167.7, 148.4, 146.6, 134.8, 130.7, 129.5, 123.9, 120.0, 106.8, 103.5, 96.9, 85.0, 56.1, 53.5, 37.7, 35.0; IR: (Film on NaCl) 3091, 2956, 1790, 1752, 1616, 1532, 1439, 1351, 1275, 1243, 1174, 1106, 1077, 1025, 981, 930, 789, 741, 724; MS: 377 (M+, 22), 346, 318,304, 290, 274, 260, 246, 232, 214, 204, 176, 150, 138, 106, 104, 91, 84, 59;

(2R,2aR,4aR,7aS,7bS)-2-Methoxy-6-(4-nitro-phenyl)-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxacyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4e).* In a round bottom flask equipped with a reflux condensor, **3e** (1.0 g, 2.65 mmol) was dissolved in 12 ml of o-xylene and stirred at reflux for 3 h. After evaporation of the solvents 990 mg (2.62 mmol, 99%) of crude material was obtained, which was used without further purification. TLC: 0.52 (hexane:EtOAc 3:2). ^{1}H-NMR: (300 MHz, $CDCl_3$) 8.23 (d, J=9.2, 2H), 7.79 (d, J=9.2, 2H), 6.08 (d, J=4.8, 1H), 5.12 (s, 1H), 5.06 (d, J=7.4, 1H), 4.20 (dd, J=11.6, 7.5, 1H), 3.92 (s, 3H), 3.58 (dd, J=11.4, 4.8, 1H), 3.45 (s, 3H); ^{13}C-NMR: (75 MHz, $CDCl_3$) 174.2, 167.7, 148.1, 146.8, 138.9, 125.8, 123.8, 106.9, 103.5, 98.3, 85.0, 56.1, 53.5, 37.6, 35.2; IR: 3104, 3006, 2962, 2926, 2855, 1791, 1747, 1683, 1599, 1516, 1451, 1429, 1379, 1349, 1323, 1289, 1245, 1223, 1183, 1099, 1072, 1041, 1019, 982, 969, 928, 858, 848, 806, 743, 721; MS: 377 (M^+, 22), 346, 318, 307, 274, 260, 246, 230, 214, 204, 176, 150, 139, 127, 104, 85, 76, 59, 45;

(2R,2aR,4aS,7aS,7bS)-5-Benzyl-2-methoxy-6-methyl-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxa-cyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4f*). A solution of **3f** (168 mg, 0.46 mmol) in 15 ml of toluene was heated in a autoclave at 180°C for over 3 h. After evaporation of the solvent and separation on 15 g silicagel (EtOAc/hexane 1:9 to 2:8) **4f** (40 mg, 0.11 mmol, 24%) was obtained as a yellow oil. TLC (EtoAc/Hex = 2:8): R_f: 0.33 ^{1}H-NMR (300MHz, $CDCl_3$): 7.37-7.19 (5H,m), 5.18 (1H,s), 4.82 (1H,d, J = 6.98), 3.86 (3H,s), 3.78 (1H,dd, J = 7.53 and 11,21), 3.75 (1H,d,J = 4.77), 3.44 (3H,s), 3.09 (1H,dd,J = 10.66 and 1.1), 2.04 (3H,s); ^{13}C-NMR (75MHz, $CDCl_3$): 174.5, 168.3, 145.34, 128.9, 128.7, 128.6, 128.5, 126.6, 106.8, 105.4, 103.7, 83.5, 56.0, 53.2, 41.0, 3.2, 34.6, 16.6; IR: 2952, 2844, 2359, 1747, 1697, 1494, 1453, 1436, 1382, 1250, 1197, 1151, 1107, 1065, 1040, 972, 910, 728, 700; ES-MS: 360 (M^+), 301, 269, 243, 217, 186; HR-MS: Calcd. for $C_{19}H_{20}O_7$: 360.12090; measured: 360.12088.

(2R,2aR,4aS,7aS,7bS)-2-Methoxy-6-methyl-4-oxo-5-pentyl-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxa-cyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4g*). A solution of **3g** (300 mg, 0.88 mmol) in 30 ml of toluene was heated in a autoclave at 180°C for 5 h. After evaporation of the solvent and separation on silicagel (EtOAc/Hex 2:8) 88 mg (0.26 mmol, 30%) of a colorless oil was obtained which was further purified by crystallization from hexane for analytical purposes. TLC (EtOAc/hexane = 2:8): R_f 0.34 ^{1}H-NMR (300MHz, $CDCl_3$): 5.22 (1H,s), 4.87 (1H, d, J = 6.78), 3.94 (1H, dd, J = 6.97 and 10.36), 3.83 (3H, s), 3.44 (3H, s), 3.29 (1H, dd, J = 10.45 and 1.03), 2.45-2.37 (1H, m), 2.23-2.13 (1H, m), 1.87 (3H, s), 1.55-1.23 (6H, m), 0.92-0.87 (3H, m); ^{13}C-NMR (75MHz, $CDCl_3$): 174.5, 168.4, 144.7, 107.4, 107.1, 104.3, 83.4, 55.9, 53.1, 42.3, 37.5, 31.4, 29.2, 27.4, 22.5, 16.2, 14.1; IR: 2955, 2932, 2857, 2365, 2256, 1747, 1439, 1378, 1248,1201, 1152, 1108, 1061,

973, 910, 729, 647; ES-MS: 340 (M^+), 283, 281, 253, 223, 197, 195; HR-MS: Calcd. for $C_{17}H_{24}O_7$: 340.15220; measured: 340.15213.

(2R,2aR,4aS,7aS,7bS)-5-Acetyl-2-methoxy-6-methyl-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxa-cyclopenta[cd]indene-7a-carboxylic acid methyl ester *(4h).* Under an argon atmosphere, **2h** (1.49 g, 9.5 mmol) was suspended in 60 ml 1,2-dichloroethane. At 0°C Et_3N (1.39 ml, 9.9mmol) was added dropwise within 3 min. Over 15 min. pivaloyl chloride (1.14 ml, 9.3 mmol) was added in 12.8 ml 1,2-dichloroethane and stirring was

continued for an other 20 min. During 15 min dihydrofuranoside **1** (1.108 g, 6.4 mmol) was given to the mix in 13 ml 1,2-dichloroethane. Shortly after cooling to –20°C DMAP (116 mg, 0.95 mmol) was added. After stirring 3 hours at 0°C the rection was left to warm to RT over night (total 20h reaction time). The reaction mixture was washed with sat. aq. $NaHCO_3$ and extracted twice with ether and once with CH_2Cl_2. After drying (Na_2SO_4), evaporating the solvents and separation of the black crude on silicagel (hexane/EtOAc 6:4 -> 1:1) 1.0 g (3.2 mmol, 51% from **1**) of a yellow solid were obtained. TLC (CH_2Cl_2/ether 9:1): R_f 0.38 ^{1}H-NMR (300MHz, $CDCl_3$): 5.32 (1H, s), 4.97 (1H, d, J = 6.3), 4.23 (1H, d, = 10.3), 3.87 (1H, dd, J = 10.5 and 6.8), 3.84 (3H, s), 3.49 (3H, s), 2.46 (3H, s), 2.32 (3H, s); ^{13}C-NMR (75MHz, $CDCl_3$):196.2, 173.7, 167.5, 162.2, 112.3, 107.5, 105.5, 83.1, 56.0, 53.6, 43.8, 36.3, 30.2, 20.5; IR: 2927, 2848, 1787, 1734, 1686, 1629, 1604, 1439, 1374, 1236, 1151, 1107, 1059, 1017, 970, 930; EI-MS: 312 (M^+), 253, 211, 207, 195; HR-MS: Calcd. for $C_{14}H_{16}O_8$: 312.08451; measured: 312.08472.

General procedure for the synthesis of 5a and 5b

In an absolute 3 neck flask with two cocks (for vacuum and H_2) 500 mg **4a** or **b** was dissolved in 50 ml MeOH. Under argon and stirring 250 mg Pd/C 10% was added. The flask was evacuated and filled with hydrogen (twice). Stirring is continued for 2.5 – 4 h. The reaction was quenched with argon and filtered through MeOH-soaked Celite. The celite was washed twice more with MeOH. After evaporation of the solvents the crude product was used without further purification.

General procedure for the synthesis of 6a-e and 7a-e.

Under absolute conditions 100 mg (0.286mmol, 1 eq.) of **5a** or **5b** were dissolved in 5ml pyridine. The corresponding acid chloride (0.344 mmol, 1.2 eq.) and DMAP (0.2 eq) were added at 0°C. After stirring for 20 h at RT, the reaction mixture was washed with sat. aq. $NaHCO_3$ and extracted twice with EtOAc. The organic phase was washed once more with brine. After evaporation of the solvents and column chromatography, the products were isolated in the yields (over three steps, starting from **3d** and **3e**) given in the following Table.

compound #	formula	yield (%)	calculated mass:	HR-MS found:
6a	$C_{24}H_{29}NO_8$	53	459.189317	459.189420
6b	$C_{20}H_{23}NO_9$	51	421.137282	421.137540
6c	$C_{25}H_{25}NO_9$	46	483.152932	483.152500
6d	$C_{24}H_{22}N_2O_{10}$	43	498.127445	498.127590
6e	$C_{30}H_{27}NO_8$	64	529.173667	529.174130
7a	$C_{24}H_{29}NO_8$	54	459.189317	459.189150
7b	$C_{20}H_{23}NO_9$	43	421.137282	421.137150
7c	$C_{25}H_{25}NO_9$	38	483.152932	483.152560
7d	$C_{24}H_{22}N_2O_{10}$	30	498.127445	498.127410
7e	$C_{30}H_{27}NO_8$	45	529.173667	529.173520

The structure of derivative **6e** was established by COSY and ROESY experiments.

(2R,2aR,4aR,7aS,7bS)-6-(3-Amino-phenyl)-2-methoxy-4-oxo-2a,4,4a,7b-tetrahydro-2H-1,3,7-trioxa-cyclopenta[cd]indene-7a-carboxylic acid methyl ester (*8*). In a dried two-neck flask **4d** (0.48 g, 1.27 mmol) and Pd/C (80 mg, 75 mmol) was suspended in dry methanol (9 ml). After stirring at RT for 30 min ammonium formate (0.373 g, 5.9 mmol) were added in portions and stirring was continued for 5 more hours. The mixture was then filtered and the filtercake was washed with methanol. The dark yellow solution was washed with 75 ml of sat. aq. $NaHCO_3$ and extracted with diethylether. After purification on silicagel with hexane:EtOAc 1:1 and evaporation of the solvents 0.221 g (0.637 mmol, 50%) of a viscose oil was obtained. TLC: 0.37 (hexane:EtOAc 1:1). ^{1}H-NMR: (300 MHz, $CDCl_3$) 7.14 (m, 1H), 7.03-7.00 (m, 1H), 6.96-6.94 (m, 1H), 6.69-6.66 (m, 1H), 5.82 (d, J=4.4, 1H), 5.11 (s, 1H), 5.03 (d, J=7.4, 1H), 4.16 (dd, J=11.4, 7.7, 1H), 3.90 (s, 3H), 3.50 (dd, J=11.8, 4.4, 1H),

3.45 (s, 3H). ^{13}C-NMR: (75 MHz, $CDCl_3$) 175.0 (s), 167.9 (s), 148.3 (s), 146.5 (s), 133.9 (s), 129.1 (d), 115.8 (d), 114.9 (d), 111.2 (d), 106.4 (d), 103.2 (s), 93.9 (d), 84.8 (d), 55.7 (q), 53.1 (q), 37.4 (d), 34.7 (d). IR: (KBr) 3468 (m), 3379 (m), 3005 (w), 2955 (m), 2845 (w), 1788 (s), 1750 (s), 1678 (w), 1625 (m), 1605 (m), 1495 (m), 1458 (m), 1376 (m), 1325 (s), 1255 (s), 1175 (s), 1106 (s), 1078 (s), 982 (s), 780 (m), 727 (m). MS: 347 (M+, 80), 316 (6), 288 (27), 260 (3), 244 (15), 230 (87), 212 (8), 202 (10), 184 (7), 174 (13), 146 (11), 120 (100), 92 (34), 84 (29), 65 (20), 59 (11), 45 (43).

General procedure for *9a and 9b*

Under absolute conditions **8a** or **8b** (100 mg, 0.29mmol) were dissolved in 3 ml pyridine. At 0°C 0.349 mmol of the corresponding acid chloride was added and, shortly after, 0.2 eq DMAP. After stirring for 5 h at RT the reaction mixture was washed with sat. aq. $NaHCO_3$ and extracted twice with EtOAc. The organic phase was washed once more with brine. After evaporation of the solvents and column chromatography the product was obtained (for **9a** 98 mg, 0.22 mmol, 75%; for **9b** 114mg, 0.23 mmol, 71%).

Data for **9a**: TLC: 0.66 (EtOAc:hexane 2:1).^{1}H-NMR: ($CDCl_3$) 7.91-7.85 (m, 3H), 7.72-7.70 (m, 1H), 7.60-7.55 (m, 1H), 7.55-7.49 (m, 2H), 7.45-7.38 (m, 2H), 5.92 (d, J=4.8, 1H), 5.12 (s, 1H), 5.04 (d, J=7.7, 1H), 4.18 (dd, J=11.6, 7.5, 1H), 3.92 (s, 3H), 3.54 (dd, J=11.6, 4.6, 1H), 3.46 (s, 3H); ^{13}C-NMR:($CDCl_3$) 174.8, 168.0, 165.7, 148.0, 138.1, 134.8, 134.0, 132.0, 129.3, 128.8, 127.0, 121.2, 116.5, 106.8, 103.5, 94.8, 85.0, 56.0, 53.4, 37.6, 35.0; IR: (KBr) 3335, 2927, 2855, 1797, 1763, 1652, 1581, 1530, 1486, 1437, 1376, 1303, 1250, 1195, 1107, 1077, 1049, 982; MS: 451 (M+, 18), 392, 369, 348, 334, 243, 224, 155, 105, 97, 83, 69, 57, 43;
Data for **9b**: TLC: 0.69 (EtOAc:hexane 2:1); ^{1}H-NMR: ($CDCl_3$) 8.41-8.33, 8.03-7.87, 7.81-7.70, 7.63-7.48, 7.48-7.37 (m, 11H), 5.92 (d, J=4.4, 1H), 5.09 (s, 1H), 5.03 (d, J=7.7, 1H), 4.17 (dd, J=11.8, 7.7, 1H), 3.89 (s, 3H), 3.52 (dd, J=11.6, 4.6, 1H), 3.43 (s, 3H); ^{13}C-NMR: ($CDCl_3$) 174.8, 168.0, 147.9, 138.3, 134.0, 133.7, 131.1, 130.0, 129.4, 128.4, 127.4, 126.6, 125.2, 125.1, 124.7, 121.2, 120.9, 116.3, 106.7, 103.4, 94.9, 85.0, 56.0, 53.4, 37.6, 34.9; IR:(KBr) 3304, 3062, 2928, 2853, 1790, 1770, 1670, 1609, 1593, 1540, 1489, 1437, 1374, 1320, 1248, 1172, 1106, 1077, 1046, 981, 783, 725, 690; **MS:** 501 (M^+, 53), 442, 384, 318, 274, 230, 205, 172, 155, 127, 97, 70, 57, 43;

Crystal Structures

X-ray crystallography of 4a

Suitable crystals of ***4a*** were grown from MeOH/H_2O as colourless rods. Intensity data were collected at 153K on a Stoe Image Plate Diffraction system using MoKα graphite monochromated radiation. Image plate distance 70mm, ϕ oscillation scans 0 - 200°, step $\Delta\phi$ = 1.5°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97 [1]. The refinement and all further calculations were carried out using SHELXL-97 [2]. The H-atoms located from Fourier difference maps and

refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

The bond distances and angles are normal within experimental error.

It was not possible to determine the absolute structure of the molecule in the crystal by crystallographic means.

X-ray crystallography of 4b

Suitable crystals of **4b** were obtained as colourless rods by slow evaporation of a methanol solution. The intensity data were collected at room tempeature on a Stoe Image Plate Diffraction System [1] using MoKα graphite monochromated radiation. Image plate distance 70mm, ϕ oscillation scans 0 - 200°, step Δϕ = 1.5°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97 [2]. The refinement and all further calculations were carried out using SHELXL-97 [3].

The H-atoms were located from Fourier difference maps and refined isotropically.

The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

It was not possible to determine crystallographically the absolute strutue of the molecule in the crystal.

X-ray crystallography of 4g

Suitable crystals of **4g** were obtained as colourles rods from hexane. The intensity data were collected at 153K (-120°C) on a Stoe Mark II-Image Plate Diffraction System [1] equiped with a two-circle goniometer and using MoKα graphite monochromated radiation. Image plate distance 100mm, ω rotation scans 0 - 148° at ϕ 0°, step Δω = 1.2°, 2θ range 3.2 – 51.0°, d_{min} – d_{max} = 12.91 - 0.83 Å.

The structure was solved by Direct methods using the programme SHELXS-97 [2]. The refinement and all further calculations were carried out using SHELXL-97 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

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2 G. M. Sheldrick, (1999) "SHELXL-97", Universität Göttingen, Göttingen, Germany.

3 A. L. Spek, (1990) "PLATON/PLUTON version Jan. 1999", *Acta Crystallogr*., **A46,** C34.