Supporting Information

Studies Towards the Total Synthesis of Mumbaistatin, a Highly Potent Glucose-6-phosphate Translocase Inhibitor. Synthesis of a Mumbaistatin Analog

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1. Experimental Procedures and Data for Compounds **15**, **18**, **19**, **22**, **23**:

2-Bromo-5-hydroxybenzaldehyde (15). In a 500 ml three-necked flask equipped with a dropping funnel 7.327 g (60 mmol) of 3-hydroxybenzaldehyde (**14**) was dissolved in 300 ml of chloroform and 30 ml of acetonitrile, before 3.25 ml (63 mmol) of bromine in 30 ml of chloroform was added slowly over a period of 30 min. The reaction mixture was further

stirred for 3 h until the reaction was quenched by addition of 50 ml of saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution. The layers were separated, and the aqueous layer was extracted with dichloromethane (3x100 ml). The combined organic layers were washed with brine and dried over MgSO_4 . Most of the solvent was evaporated. The resulting solution was filtrated through a short pad of silica and eluated with ethyl acetate. Removal of the solvent under reduced pressure gave a brown solid which was purified by recrystallization (2x) from hexane/ethyl acetate to give 9.410 g. (46.8 mmol, 78 %) of **15** as a yellow crystalline solid. MP: 131 °C (Lit.: 134 °C). - TLC (cyclohexane/ethyl acetate 3:1) R_f = 0.25. - IR (ATR): $\tilde{\nu}$ = 3210 (br, s), 1667 (s), 1598 (s), 1470 (w), 1441 (s), 1396 (m), 1302 (s), 1234 (m), 1174 (m), 1109 (w), 1027 (w), 974 (w), 880 (w), 830 (w), 760 (w), 684 (w). - ^1H NMR (250 MHz, CDCl_3): δ = 5.75 (br. s, 1 H, OH), 7.00 (dd, 1 H, 4J = 3 Hz, 3J = 8.5, H at C4), 7.42 (d, 1 H, 4J = 3 Hz, H at C6), 7.50 (d, 1 H, 3J = 8.5 Hz, H at C3), 10.27 (s, H at C7). - ^{13}C NMR (63 MHz, CDCl_3): δ = 115.7 (d, C4 or C6), 117.8 (s, C2), 123.4 (d, C4 or C6), 134.0 (s, C1), 134.9 (d, C3), 155.6 (s, C5), 192.2 (d, C7). - GC-MS (Optima 1 MS, 10 psi, $50^\circ_2 \xrightarrow{25^\circ\text{C}/\text{min}} 300^\circ_5$): t_{Ret} = 7.8 min, 100 % pure. MS(EI): 202 (90), 201 (96), 200 (100), 199 (90), 173 (23), 171 (19), 145 (14), 143 (14), 120 (21), 92 (31), 78 (39), 65 (29), 63 (53), 39 (23). - HRMS (EI): calcd 199.9473 for $\text{C}_7\text{H}_5\text{BrO}_2$, found 199.947.

7-Methoxy-3H-isobenzofuran-1-one (18). In a 500 ml argon-flushed three-necked flask equipped with reflux condenser 4.97 ml (40 mmol) of 3-methoxybenzylic alcohol was dissolved in 250 ml of anhydrous hexane. 75 ml of $n\text{BuLi}$ (1.6 M in hexane) was added. The mixture was refluxed for 1.5 h before being cooled to -20°C . – In a 500 ml flask a handful of dry ice was placed in 200 ml of THF. The orange aryllithium suspension was slowly added via transfer syringe. The yellow suspension was stirred for 3 h until the mixture had reached rt. Most of the solvent was evaporated under reduced pressure. The residue was poured into 100 ml of 2 M HCl solution and stirred for 30 min. The mixture was extracted with ethyl

acetate (3x150 ml). The combined organic layers were washed with water and brine and dried over MgSO_4 . The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (200 g silica, cyclohexane/ethyl acetate 3:1) to give 4.068 g (24.8 mmol, 62 %) of **18** as a white crystalline solid. MP: 105 °C. – TLC (cyclohexane/ethyl acetate 3:1) R_f = 0.25 - IR (ATR): $\tilde{\nu}$ = 2356 (m), 2339 (w), 1744 (s), 1601 (s), 1487 (s), 1455 (m), 1367 (w), 1317 (s), 1285 (s), 1200 (s), 1066 (s), 1027 (s), 1015 (s), 784 (s). - ^1H NMR (300 MHz, CDCl_3): δ = 3.98 (s, 3 H, CH_3 of C7-OMe), 5.22 (s, 2 H), 6.91 (d, 1 H, J = 8.5 Hz), 7.00 (d, 1 H, J = 8.5 Hz), 7.59 (t, 1 H, J = 8.5 Hz, H on C5). - ^{13}C NMR (75 MHz, CDCl_3): δ = 56.0, 68.7, 110.5, 113.6, 113.7, 136.2, 158.8. – GC-MS (Optima 1 MS, 10 psi, 50 °C $\xrightarrow{25^\circ/\text{min}}$ 300 °C): t_{Ret} = 8.2 min, 99 % pure; MS: 164 (50, $[\text{M}]^+$), 146 (54), 135 (77), 118 (100), 105 (35), 91 (31), 77 (63), 63 (35), 51 (38). - HRMS (EI): calcd 164.0473 for $\text{C}_9\text{H}_8\text{O}_3$, found 164.047.

1-Cyano-4-methoxy-1(3)isobenzofuranone (19). In a 250 ml argon-flushed three neck flask 8.292 g (40 mmol) of 1-Methoxy-*N,N*-diethylbenzamide was solved in 100 ml of dry THF. At –78 °C 7.2 ml (48 mmol) of TMEDA was added, followed by 37.0 ml (48 mmol) of *sec*-BuLi (1.3 M in cyclohexane) 5 min later. The intensive yellow solution was stirred for 1.5 h upon which the temperature was allowed to rise up to –30 °C. At –78 °C 4.65 ml (60 mmol) of anhydrous DMF was added slowly. The reaction mixture was stirred overnight while being allowed to slowly come to rt. After being quenched with 100 ml of saturated NH_4Cl solution, the phases were separated and the aqueous phase was extracted with ethyl acetate (3x100 ml). The combined organic layers were washed with brine and dried over MgSO_4 . After evaporation of the solvent under reduced pressure, the residue was purified by flash-chromatography (400 g silica, cyclohexane/ethyl acetate 1:3) to give 6.681 g (28.4 mmol, 71 %) of 2-formyl-6-methoxy-*N,N*-diethylbenzamide as a pale yellow oil.

TLC (cyclohexane/ethyl acetate 1:3) $R_f = 0.24$ - GC-MS (Optima 1, 10 psi, $50^\circ_2 \xrightarrow{10^\circ/\text{min}}$ 300°_5): $t_{\text{Ret}} = 19.0$ min, 98 % pure, MS: 235 (1, $[\text{M}]^+$), 221 (2), 206 (92, $[\text{M}-\text{C}_2\text{H}_5]^+$), 190 (5), 178 (69, 163 (100, $[\text{M}-\text{NEt}_2]^+$), 149 (25), 135 (35, $[\text{M}-\text{C}(\text{O})\text{NEt}_2]^+$), 119 (12), 105 (7), 92 (12), 72 (42), 58 (16).

In a 100 ml argon-flushed Schlenk flask 6.112 g (26 mmol) of 2-formyl-6-methoxy-*N,N*-diethylbenzamide was dissolved in 60 ml of dry dichloromethane. At 0°C 4.9 ml (39 mmol) of TMSCN and the catalyst (52 mg of KCN and 160 mg of 18-crown -6 in 6 ml of dry THF) was added. The solution was stirred for 1.5 h at 0°C and for 30 min at rt before the solvent was evaporated under reduced pressure. The resulting yellow oil was dissolved in 30 ml of glacial acetic acid and stirred overnight at rt. After addition of 30 ml of 1 N NaOH, the mixture was transferred into a separatory funnel with each 100 ml of 1 N NaOH solution and ethyl acetate. After separation of the phases the aqueous layer was extracted with ethyl acetate (3x100 ml). The combined organic phases were washed with brine and dried over MgSO_4 . The solution was concentrated in vacuo to give the crude product as crystalline solid. Recrystallization from chloroform/hexane gave 4.124 g (21.8 mmol, 84 %) of isobenzofuranone **19** as a white crystalline solid. Mp 151°C (lit. $154\text{--}156^\circ\text{C}$) - TLC (cyclohexane/ethyl acetate 4:1) $R_f = 0.13$. - IR (ATR): $\tilde{\nu} = 2942$ (w), 2843 (w), 2358 (m), 2340 (m), 1782 (s), 1683 (w), 1634 (w), 1612 (s), 1600 (s), 1558 (w), 1487 (s), 1436 (m), 1290 (s), 1234 (m), 1196 (s), 1069 (m), 1014 (s), 971 (m), 912 (w), 789 (m), 758 (m), 687 (m), 667 (w). - ^1H NMR (250 MHz, CDCl_3): $\delta = 4.00$ (s, 3 H, CH_3 of C4-OMe), 5.99 (s, 1 H, H on C1), 7.06 (d, 1 H, $^3J = 8.5$ Hz, H on C5), 7.20 (td, 1 H, $^3J = 7.5$ Hz, $^4J = 0.5$ Hz, H on C7), 7.74 (dd, 1 H, $^3J = 8.5$ Hz, $^3J = 7.5$ Hz, H on C6). - ^{13}C NMR (63 MHz, CDCl_3): $\delta = 56.3$ (q, CH_3 of C4-OMe), 64.8 (d, C1), 111.7 (s, C1a or C3a), 113.0 (d, C5 or C7), 114.0 (s, C1a or C3a), 114.1 (d, C5 or C7), 137.9 (d, C6), 144.1 (s, C8), 159.1 (s, C4), 165.4 (s, C3). - GC-MS (Optima 1 MS, 10 psi, $50^\circ_2 \xrightarrow{10^\circ/\text{min}}$ 300°_5): $t_{\text{Ret}} = 17.6$ min, 98 % pure; MS: 189

(82, $[M]^+$), 171 (100), 158 (73), 143 (95), 130 (59), 115 (90), 104 (64), 92 (25), 76 (98), 63 (44), 50 (32), 37 (20). - HRMS (EI): calcd 189.0426 for $C_{10}H_{17}NO_3$, found 189.043.

6-tert-Butyldimethylsiloxyhexan-1-ol. An argon-flushed 250 ml three-necked flask was charged with 2.000 g of sodium hydride (60 % oil dispersion; 1.200 g, 50 mmol of sodium hydride). After being washed twice with hexane, the sodium hydride was suspended in 60 ml of dry THF. At 0 °C 5.909 g (50 mmol) of 1,6-hexanediol dissolved in 40 ml of dry THF was added slowly via syringe and the solution was stirred for 30 min at rt. The now white suspension was treated slowly with a solution of 7.536 g of TBDMSCl dissolved in 20 ml of dry THF. After being stirred for 60 min, the reaction mixture was poured on crushed ice and extracted three times with 100 ml of MTBE. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue, a pale liquid was purified by flash chromatography (400 g of silica, cyclohexane/ethyl acetate 3:1) to give 7.418 g (32 mmol, 64 %) of the mono-protected alcohol as colorless liquid. TLC (cyclohexane/ethyl acetate 3:1) R_f = 0.25. - IR (ATR): $\tilde{\nu}$ = 3343 (br, m), 2896 (m), 2826 (m), 2355 (w), 1682 (m), 1585 (m), 1566 (m), 1459 (s), 1402 (w), 1253 (s), 1202 (m), 1151 (s), 1084 (m), 1009 (s), 920 (m), 775 (m), 713 (w), 652 (w). - 1H NMR (250 MHz, $CDCl_3$): δ = 0.02 (s, 6 H, CH_3 of Si-Me), 0.87 (s, 9 H, CH_3 of Si-*t*Bu), 1.2-1.7 (m, 9 H, H at C2, C3, C4, C5 and OH), 3.61 (t, 2 H, J = 6.5 Hz, C1 or C6), 3.65 (t, 2 H, J = 6.5 Hz, C1 or C6). - ^{13}C NMR (63 MHz, $CDCl_3$): δ = -5.3 (q), 18.3 (s), 25.5 (t), 25.6 (t), 25.9 (q), 32.7 (t), 32.8 (t), 62.9 (t), 63.1 (t). - GC-MS (Optima 1 MS, 10 psi, 50 °C $\xrightarrow{25^\circ/min}$ 300 °C): t_{Ret} = 8.6 min, 99 % pure, MS: 175 (5, $[M-C(CH_3)_3]^+$), 129 (4), 105 (40), 102 (13), 94 (14), 89 (6), 83 (55), 75 (100), 55 (95), 41 (18).

6-tert-Butyldimethylsiloxyhexanal (22). In a argon-flushed 100 ml three-necked flask 2.312 g (10 mmol) of 6-tert-Butyldimethyl-siloxyhexan-1-ol was dissolved in 60 ml of anhydrous

CH₂Cl₂. The solution was cooled to -78 °C, and 1.56 ml (22 mmol) of dry DMSO followed by 0.93 ml (11 mmol) of oxalylchloride was added slowly via syringe. The milky white solution was stirred at -78 °C for 45 min before 6.93 ml (50 mmol) of triethylamine was added via syringe. After 10 min the cooling bath was removed and the solution was allowed to come to rt. After stirring at rt for 30 min, the reaction was quenched by addition of water. The layers were separated and the aqueous layer was extracted with MTBE (3x 100 ml). The combined organic layers were washed with brine and dried over MgSO₄. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (80 g of silica, cyclohexane/ethyl acetate 10:1) to afford 2.185 g (9.5 mmol, 95 %) of the aldehyde 22 as pale yellow oil. TLC (cyclohexane/ethyl acetate 10:1) R_f = 0.25 - IR (ATR): $\tilde{\nu}$ = 2700 (s), 1722 (m), 1465 (s), 1454 (s), 1378 (s), 1349 (m) - ¹H NMR (250 MHz, CDCl₃): δ = 0.024 (s, 6 H, CH₃ of Si-Me₂), 0.87 (s, 9 H, CH₃ of Si-*t*Bu), 1.33-1.41 (m, 2 H, H at C3 or C5), 1.49-1.54 (m, 2 H, H at C4), 1.54-1.66 (m, 2 H, H at C3 or C5), 2.41 (dt, 2 H, ³J = 2 Hz, ³J = 7 Hz, H at C2), 3.59 (t, 2 H, ³J = 6.5 Hz, H at C6), 9.75 (t, 1 H, ³J = 2 Hz, H at C1). - ¹³C NMR (63 MHz, CDCl₃): δ = -5.4 (each q, CH₃ of Si-Me₂), 18.2 (s, C of Si-*t*Bu), 21.8 (t, C4), 25.4 (t, C3), 25.9 (q, CH₃ of Si-*t*Bu), 32.4 (t, C5), 43.8 (t, C2), 62.7 (t, C6), 202.5 (d, C1). - GC-MS (Optima 1 MS, 10 psi, 50 °C $\xrightarrow{25^\circ/\text{min}}$ 300 °C): t_{Ret} = 8.2 min, 99 % pure, MS(EI): 173 (26, [M - C(CH₃)₃]⁺), 143 (3), 131 (72), 115 (3), 101 (11), 81 (9), 75 (100), 73 (14), 59 (9), 41 (13).

3-Methoxymethoxyphenylbromide (23). A 500 ml argon-flushed three-necked flask was charged with 4.80 g (120 mmol) of a 60 % sodium hydride oil dispersion. The sodium hydride was washed two times with 30 ml of heptane before 180 ml of anhydrous DMF was added. The suspension was cooled to 0 °C and a solution of 17.302 g (100 mmol) of 3-bromophenol in 50 ml of dry DMF was added slowly. After the generation of hydrogen stopped the yellow solution was stirred at rt for 45 min. 9.1 ml (120 mmol) of MOMCl in 20 ml of DMF was

added slowly via syringe to the cooled solution (0 °C), and the reaction mixture was stirred for 60 min at rt. After addition of 100 ml of ice water and additional stirring for 5 min the mixture was transferred into a separator funnel. The mixture was extracted with MTBE (3x200 ml). The combined organic layers were washed with 200 ml of sat. NaHCO₃ solution, water and brine and dried over MgSO₄. After filtration through a short pad of silica, the solvent was removed under reduced pressure to give 21.5 g (99 %) of **23** as a pale oil, which did not need further purification (GC and ¹H-NMR). TLC (cyclohexane/ethyl acetate 5:1) R_f = 0.4 - IR (ATR): $\tilde{\nu}$ = 2952 (w), 2822 (w), 2724 (w), 1698 (s), 1583 (m), 1481 (m), 1452 (m), 1388 (w), 1319 (w), 1278 (w), 1251 (s), 1232 (m), 1205 (m), 1152 (s), 1077 (s), 1010 (s), 988 (s), 920 (m), 788 (m), 770 (m), 680 (m). - ¹H NMR (250 MHz, CDCl₃): δ = 3.46 (s, 3 H, CH₃ of OMOM), 5.14 (s, 2 H, CH₂ of OMOM), 7.18-7.22 (m, 1 H), 7.34-7.51 (m, 3 H), 9.90 (s, 1 H, H at C7). - ¹³C NMR (63 MHz, CDCl₃): δ = 55.9 (q, CH₃ of OMOM), 94.2 (t, CH₂ of OMOM), 115.7 (d), 122.6 (d), 123.6 (d), 129.9 (d), 137.7 (s, C1), 157.6 (s, C3), 191.6 (s, C7). - GC-MS (Optima 1 MS, 10 psi, 50 °C $\xrightarrow{25^\circ/\text{min}}$ 300 °C): t_{Ret} = 6.5 min, 98 % pure; MS(EI): 218, 216 (20, 19, [M]⁺), 188 (5), 157 (8), 143 (6), 117 (3), 92 (4), 76 (5), 63 (18), 45 (100).

2. Alternative approach towards compound **24**

As an alternative to the pathway described in Scheme 4, **24** may also derive from the reaction of a metallated C₅ sidechain with 3-methoxymethoxybenzaldehyde (Scheme S1):

The sequence started from the known bromide **29**, which was prepared in two steps from tetrahydropyran by ether cleavage with borontribromide to give **28** and subsequent TBS-protection of the primary OH function. Reaction of the *Grignard* reagent prepared from **29** with the MOM-protected benzaldehyde **30** gave **24** only in moderate yield of 49%. Attempts to improve the yield by using an excess of either the grignard reagent or the aldehyde were

not successful. Also, the lithum species derived from **30** by treatment with *t*BuLi did not lead to an improvement. So, we turned to the procedure described in Scheme 4.

Scheme S1^a

^aKey: (a) BBr₃, CH₂Cl₂, reflux, then methanol, reflux, 82 %; (b) TBS-Cl, NEt₃, cat. DMAP, CH₂Cl₂, rt, 85 %; (c) CH₂(OCH₃)₂ P₂O₅, CH₂Cl₂, rt, 84 %; (d) **30**, Mg, THF, 1 h reflux, then **29**, THF, 0 °C to rt, 49 %.

5-Bromopentan-1-ol (28). An argon-flushed 250 ml three-necked flask equipped with dropping funnel and reflux condenser was charged with 60 ml of a BBr₃ solution (1 M in CH₂Cl₂). At 0 °C 17.7 ml (180 mmol) of tetrahydropyran in 50 ml anhydrous CH₂Cl₂ was added slowly before the solution was refluxed for 90 min. Afterwards the solvent was evaporated under reduced pressure. The residue was dissolved in 50 ml of dry methanol and refluxed for 60 min. The methanol and the trimethoxyborate was evaporated under reduced pressure. The residue, a black liquid, was dissolved in ethyl acetate and filtered through a pad of silica. After removal of the solvent the residue was purified by distillation under reduced pressure to give 25.551 g (153 mmol, 85 %) 5-bromopentan-1-ol **28** as a pale liquid. B.p.: 106 °C (23 mbar) - TLC (cyclohexane/ethyl acetate 5:1) R_f = 0.3 - IR (ATR): $\tilde{\nu}$ = 3323 (Br, s), 2933 (s), 2860 (s), 2358 (w), 1643 (m), 1453 (m), 1429 (m), 1269 (m), 1245 (m), 1055 (s), 1013 (s), 984 (m), 732 (s). - ¹H NMR (250 MHz, CDCl₃): δ = 1.48-1.64 (m, 4 H), 1.72 (s, 1 H), 1.92 (qn, 2 H, *J* = 8 Hz), 3.42 (t, 2 H, *J* = 8 Hz), 3.70 (t, 2 H, *J* = 8 Hz).

1-Bromo-5-(tert-butyldimethylsilyloxy)pentane (29). A 500 ml argon flushed flask was charged with 16.704 g (100 mmol) of 5-bromopentan-1-ol **28** in 250 ml of dry CH₂Cl₂. After addition of 27.9 ml (200 mmol) of triethylamine, 19.595 g (130 mmol) of TBDMSCl and 0.611 g (5 mmol) of DMAP the solution was stirred for 24 h at rt. After addition of 100 ml of saturated NH₄Cl-solution the phases were separated and the aqueous layer was extracted three times with 100 ml portions of CH₂Cl₂. The combined organic layers were washed with brine and dried over MgSO₄. After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography (500 g silica, cyclohexane/ethyl acetat 30:1) to give 23.886 g (85 mmol, 85%) of **29** as a colorless liquid. TLC (cyclohexane/ethyl acetat 30:1) R_f = 0.6. - IR (ATR): $\tilde{\nu}$ = 2926 (s), 2889 (s), 2854 (s), 2735 (s), 1691 (w), 1551 (w), 1469 (s), 1461 (s), 1435 (m), 1386 (m), 1359 (m), 1276 (m), 1252 (s), 1100 (s), 1004 (s), 976 (m), 937 (m), 902 (m), 833 (s), 812 (s), 772 (s), 710 (m), 660 (m). - ¹H NMR (250 MHz, CDCl₃): δ = 0.03 (s, 6 H), 0.87 (s, 9 H), 1.38-1.56 (m, 4 H), 1.80-1.92 (ψquin, 2 H), 3.39 (t, 2 H, ³J = 7 Hz), 3.59 (t, 2 H, ³J = 6 Hz). - ¹³C NMR (63 MHz, CDCl₃): δ = -5.3 (q), 18.3 (s), 24.6 (t), 25.9 (q), 31.9 (t), 32.6 (t), 33.8 (t), 62.8 (t). - GC-MS (Optima 1 MS, 10 psi, 50°₂ $\xrightarrow{25^\circ/\text{min}}$ 300°₅): t_{Ret} = 7.2 min, 96 % pure, MS(EI): 225/223 (2, [M]⁺), 169/167 (25), 139 (24), 137 (22), 115 (4), 101 (5), 89 (6), 75 (29), 69 (100), 41 (40).

3-Methoxymethoxybenzaldehyde (30). A 500 ml three-necked flask equipped with mechanical stirrer was charged with 6.106 g (50 mmol) of 3-hydroxybenzaldehyde and 88.25 ml (1000 mmol) of dimethoxymethane in 150 ml of anhydrous CH₂Cl₂. 21.250 g (150 mmol) of phosphorpentoxide was added under strong stirring over a period of 30 min. The brown suspension was stirred at rt for 90 min. After the solution was poured off and collected, the solid residue in the flask was washed twice by addition of 100 ml CH₂Cl₂, stirring for 30 min and collection of the solution. The combined organic layers were washed with water, saturated KHCO₃ solution and brine and were dried over MgSO₄. After filtration through a

pad of silica, the solvent was evaporated under reduced pressure. The residue was purified by distillation under reduced pressure to give 6.980 g (42 mmol, 84 %) 3-methoxymethoxybenzaldehyde **30** as colorless oil. B.p.: 92 °C (oilpump-vacuum). - TLC (cyclohexane/ethyl acetate 7:1) R_f = 0.25 - IR (ATR): $\tilde{\nu}$ = 2953 (w), 2898 (w), 1587 (s), 1571 (s), 1474 (s), 1439 (w), 1399 (w), 1306 (w), 1272 (w), 1232 (m), 1223 (m), 1196 (s), 1150 (s), 1079 (s), 997 (s), 921 (m), 832 (m), 771 (m), 680 (m). - ^1H NMR (250 MHz, CDCl_3): δ = 3.46 (s, 3 H, CH_3 of C3-OMOM), 5.13 (s, 2 H, CH_2 of C3-OMOM), 6.93-6.98 (m, 1 H), 7.11-7.13 (m, 2 H), 7.20-7.22 (m, 1 H). - ^{13}C NMR (63 MHz, CDCl_3): δ = 55.9 (q, CH_3 of C3-OMOM), 94.3 (t, CH_2 of C3-OMOM), 114.3 (d), 119.5 (d), 122.6 (s, C1), 124.8 (d), 130.4 (d), 157.9 (s, C3). - GC-MS (Optima 1 MS, 10 psi, $50^\circ_2 \xrightarrow{25^\circ/\text{min}} 300^\circ_5$): t_{Ret} = 6.8 min, 99 % pure; MS(ED): 166 (30, $[\text{M}]^+$), 135 (10), 122 (6), 105 (5), 93 (4), 77 (15), 63 (15), 45 (100), 39 (6).

6-(tert-Butyldimethylsilanoxy)-1'-(3'-methoxymethoxyphenyl)-hexan-1-ol (24). A 100 ml argon-flushed three-necked flask equipped with reflux condenser and dropping funnel was charged with 362 mg (15 mmol) magnesia tunings. The magnesia was activated by stirring overnight in an argon atmosphere together with some iodine crystals. 5 ml of dry THF was added. After addition of two drops of 1-bromo-5-(tert-butyldimethylsilyloxy)pentane **29** the reaction started and 3.360 g (12 mmol) of 1-bromo-5-(tert-butyldimethylsilyloxy)pentane in 15 ml of THF was added dropwise. After complete addition the mixture was refluxed for 1 h and cooled to rt. – A 100 ml argon-flushed three-necked flask equipped with dropping funnel was charged with 1.662 g (10 mmol) of 3-methoxymethoxybenzaldehyde **30** in 50 ml of dry THF. The solution was cooled to -78°C . The grignard reagent was transferred into the dropping funnel via syringe. Then the grignard solution was added slowly to the benzaldehyde solution. The reaction mixture was stirred at -78°C for 1 h. Then the cooling bath was removed and the mixture was allowed to come to rt and further stirred for 2 h. After

quenching with 50 ml of saturated NH_4Cl solution the mixture was transferred into a separatory funnel. After phase separation the aqueous layer was extracted with CH_2Cl_2 (3x100 ml). The combined organic layers were washed with brine and dried over MgSO_4 . After filtration and removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (150 g of silica, cyclohexane/ethyl acetate 6:1) to give 1.806 g (4.9 mmol, 49 %) of **24** as colorless oil. TLC (cyclohexane/ethyl acetate 6:1) $R_f = 0.18$. - IR (ATR): $\tilde{\nu} = 3430$ (br,w), 2928 (s), 2854 (s), 1584 (m), 1485 (m), 1470 (m), 1461 (m), 1402 (w), 1387 (w), 1359 (w), 1315 (m), 1248 (s), 1206 (w), 1149 (s), 1079 (s), 1017 (s), 993 (s), 923 (m), 833 (s), 813 (w), 774 (s), 699 (m), 660 (w). - ^1H NMR (300 MHz, CDCl_3): $\delta = 0.01$ (s, 6 H, CH_3 of TBS), 0.86 (s, 9 H, $t\text{Bu}$ of TBS), 1.33-1.51 (m, 6 H, H at C3, C4, C5 or C2), 1.69-1.75 (m, 2 H, H at C5 or C2), 3.46 (s, 3 H, CH_3 of OMOM), 3.56 (t, 2 H, $^3J = 6.5$ Hz, H at C6), 4.61 (br. s, 1 H, H at C1), 5.15 (s, 2 H, CH_2 of OMOM), 6.90–7.02 (m, 3 H, H on C2', C4', C6'), 7.24 (t, 1 H, $J = 8$ Hz, H on C5'). - ^{13}C NMR (75 MHz, CDCl_3): $\delta = -5.3$ (s, 2 CH_3 of Me_2Si), 18.3 (s, C of $t\text{BuSi}$), 25.6 (t, C3 or C4), 25.7 (t, C3 or C4), 25.9 (q, 3 CH_3 of $t\text{BuSi}$), 32.7 (t, C5), 39.0 (t, C2), 56.0 (q, CH_3 of OMOM), 63.1 (t, C6), 74.4 (d, C1), 94.4 (t, CH_2 of OMOM), 113.8, 115.1 (each d, C2', C4'), 119.4 (d, C6'), 129.4 (d, C5'), 146.7 (s, C1'), 157.4 (s, C3'). - GC-MS (Optima 1, 10 psi, $150^\circ\text{C}_2 \xrightarrow{10^\circ/\text{min}} 300^\circ\text{C}_5$): $t_{\text{Ret}} = 11.6$ min, 98 % pure, MS: 311 (1, $[\text{M}-t\text{Bu}]^+$), 309 (7), 294 (3), 279 (13, $[\text{M}-t\text{Bu}-2 \text{ Me}]^+$), 263 (96), 250 (33), 231 (40), 207 (65), 187 (95), 182 (31), 168 (29), 165 (15), 152 (817), 145 (51), 121 (36), 106 (12), 91 (25), 75 (100), 73 (37), 45 (95). - HRMS (EI): calcd 311.1678 for $\text{C}_{16}\text{H}_{27}\text{SiO}_4$ ($\text{M}-t\text{Bu}^+$), found 311.168.

3. X-ray crystal structure analysis of compound 20

Figure S1. Structure of **20** in the crystalline state

Crystallographic data for compound **20**.

Table S1. Crystal data and structure refinement for **20**.

Identification code	20
Empirical formula	C ₂₁ H ₂₀ O ₇
Formula weight	384.37
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 4.884 (1) Å alpha = 90 deg. b = 17.477 (1) Å beta = 92.94 (1) deg. c = 20.841 (1) Å gamma = 90 deg.
Volume	1776.6 (4) Å ³
Z	4
Density (calculated)	1.437 g/cm ³
Absorption coefficient	0.108 mm ⁻¹
F(000)	808
Crystal size	0.10 x 0.10 x 0.05 mm
Theta range for data collection	1.52 to 25.00 deg.
Index ranges	0 ≤ h ≤ 5, 0 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	3112

Independent reflections	3112
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3112 / 0 / 334
Goodness-of-fit on F^2	1.090
Final R indices [$I > 2\sigma(I)$]	R1 = 0.1012, wR2 = 0.2174
Reflection observed [$I > 2\sigma(I)$]	1673
R indices (all data)	R1 = 0.1835, wR2 = 0.2662
Largest diff. peak and hole	0.306 and -0.313 e. $\text{\AA}^{-3}$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **20**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	5962(9)	3144(2)	3231(2)	56(1)
O(2)	7885(10)	1980(2)	3534(2)	57(1)
O(3)	12570(10)	4879(3)	4210(2)	63(1)
O(4)	6512(10)	1747(3)	4841(2)	62(1)
O(5)	11078(10)	5071(3)	3132(2)	61(1)
O(6)	7908(10)	464(2)	5446(2)	58(1)
O(7)	14710(13)	3214(3)	6074(3)	87(2)
C(8)	10304(12)	1635(3)	5596(3)	40(1)
C(9)	11850(13)	3145(4)	5133(3)	44(2)
C(10)	12349(13)	2051(3)	5933(3)	44(2)
C(11)	9781(13)	874(4)	5791(3)	44(2)
C(12)	9809(12)	2735(3)	4784(3)	39(1)
C(13)	8708(12)	3053(3)	4201(3)	42(2)
C(14)	12759(14)	3861(4)	4934(3)	48(2)
C(15)	8721(13)	2002(3)	5051(3)	44(2)
C(16)	6660(14)	2648(3)	3758(3)	43(2)
C(17)	9639(13)	3771(4)	4008(3)	46(2)
C(18)	13085(14)	2833(4)	5742(3)	49(2)
C(19)	11610(14)	4166(3)	4374(3)	49(2)
C(20)	3927(17)	2804(5)	2798(4)	64(2)
C(21)	11261(15)	579(4)	6324(3)	56(2)
C(22)	13782(15)	1740(4)	6469(3)	54(2)
C(23)	10913(19)	5324(5)	3762(4)	62(2)
C(24)	5890(20)	1565(5)	3122(4)	68(2)
C(25)	13213(16)	1008(4)	6657(4)	61(2)
C(26)	13780(20)	5121(7)	2893(5)	79(3)
C(27)	5000(20)	2059(5)	2558(4)	71(2)
C(28)	7400(20)	-317(4)	5651(5)	70(2)

Table S3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **20**.

O(1)-C(16)	1.427(7)
O(1)-C(20)	1.437(8)
O(2)-C(16)	1.404(7)
O(2)-C(24)	1.459(8)
O(3)-C(19)	1.381(7)
O(3)-C(23)	1.435(8)
O(4)-C(15)	1.227(7)
O(5)-C(23)	1.392(9)
O(5)-C(26)	1.436(10)
O(6)-C(11)	1.341(7)
O(6)-C(28)	1.455(8)
O(7)-C(18)	1.223(7)
C(8)-C(10)	1.396(8)
C(8)-C(11)	1.418(8)
C(8)-C(15)	1.486(8)
C(9)-C(14)	1.398(8)
C(9)-C(12)	1.401(8)
C(9)-C(18)	1.481(8)
C(10)-C(22)	1.398(9)
C(10)-C(18)	1.474(9)
C(11)-C(21)	1.393(9)
C(12)-C(13)	1.418(8)
C(12)-C(15)	1.504(8)
C(13)-C(17)	1.399(8)
C(13)-C(16)	1.502(8)
C(14)-C(19)	1.375(9)
C(17)-C(19)	1.382(8)
C(20)-C(27)	1.500(12)
C(21)-C(25)	1.372(10)
C(22)-C(25)	1.371(10)
C(24)-C(27)	1.503(11)
C(16)-O(1)-C(20)	111.3(5)
C(16)-O(2)-C(24)	109.0(6)
C(19)-O(3)-C(23)	117.6(5)
C(23)-O(5)-C(26)	114.0(7)
C(11)-O(6)-C(28)	117.9(6)
C(10)-C(8)-C(11)	118.6(5)
C(10)-C(8)-C(15)	119.4(5)
C(11)-C(8)-C(15)	122.0(5)
C(14)-C(9)-C(12)	122.2(6)
C(14)-C(9)-C(18)	117.5(5)
C(12)-C(9)-C(18)	120.3(6)
C(22)-C(10)-C(8)	121.1(6)
C(22)-C(10)-C(18)	117.3(6)
C(8)-C(10)-C(18)	121.7(5)
O(6)-C(11)-C(21)	122.7(6)
O(6)-C(11)-C(8)	118.4(5)
C(21)-C(11)-C(8)	118.9(6)
C(9)-C(12)-C(13)	118.2(5)
C(9)-C(12)-C(15)	120.0(5)
C(13)-C(12)-C(15)	121.7(5)
C(17)-C(13)-C(12)	118.9(5)
C(17)-C(13)-C(16)	117.5(5)
C(12)-C(13)-C(16)	123.5(5)
C(19)-C(14)-C(9)	118.4(6)
O(4)-C(15)-C(8)	122.0(6)
O(4)-C(15)-C(12)	119.9(5)
C(8)-C(15)-C(12)	118.0(5)
O(2)-C(16)-O(1)	109.8(5)
O(2)-C(16)-C(13)	108.4(5)

O (1) -C (16) -C (13)	108.2 (5)
C (19) -C (17) -C (13)	121.1 (6)
O (7) -C (18) -C (10)	120.8 (6)
O (7) -C (18) -C (9)	120.6 (6)
C (10) -C (18) -C (9)	118.6 (5)
C (14) -C (19) -C (17)	121.1 (6)
C (14) -C (19) -O (3)	115.5 (6)
C (17) -C (19) -O (3)	123.4 (6)
O (1) -C (20) -C (27)	109.1 (7)
C (25) -C (21) -C (11)	121.3 (7)
C (25) -C (22) -C (10)	119.4 (7)
O (5) -C (23) -O (3)	112.6 (6)
O (2) -C (24) -C (27)	109.5 (6)
C (21) -C (25) -C (22)	120.7 (7)
C (20) -C (27) -C (24)	109.3 (7)

4. Full analytical data for all compounds including NMR assignments based on two-dimensional NMR experiments or correlations

General Experimental

Melting points (MP) were determined in open capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on 250, 300 or 500 MHz instruments and are referenced to the non-deuterated impurities of the used solvents (CDCl_3 , CD_2Cl_2 , CD_3OD , d_6 -DMSO) as internal standard. The spectra are reported in ppm using the following abbreviations to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; b = broad. ^{13}C chemical shifts were determined using ^1H -decouplet spectra, the number of protons bound directly was determined employing the DEPT sequence (q = CH_3 ; t = CH_2 ; d = CH; s = quaternary carbon) Some of the assignments are based on 2-dimensional spectra. IR-spectra were recorded on a FT-IR spectrometer using the ATR-technique. Gas chromatography (GC) and low-resolution mass spectra (EI, 70 eV) were recorded on an GC-MS system using an Optima 1 MS column with H_2 as carrier-gas (flow 10 psi). Temperature programs are

presented as following: starting temperature length of stay [min] $\xrightarrow{\text{heatingrate}[\text{°C/min}]}$ end temperature length of stay [min]. Given are the retention times and the purities calculated from the uncorrected FID-integrations. High resolution mass spectra (HRMS) were recorded in EI or ESI mode. Analytical thin-layer chromatography (TLC) was performed on silica coated alumina plates containing fluorescent indicator, visualized by UV light or by staining with a cerium reagent (prepared by dissolving 2 g of phosphomolybdic acid and 1 g of cerium(IV)-sulfate in a mixture of 10 ml of conc. H₂SO₄ and 90 ml of water) followed by heating. Flash chromatography was performed on Merck silica gel 60 (230-400 mesh). A silica gel/crude product ratio of 25-100:1 by weight and flow rates of 10-20 ml/sec were normally employed for flash chromatography. Reagents were used without further purification unless otherwise noted. THF and toluene were freshly distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH₂. Other solvents (acetonitrile, benzene, hexane, DMF, DMSO) were purchased in HPLC-pure quality and stored under argon over molecular sieves. Bulk solvents for chromatography and extraction were distilled prior to use. All reactions with organometallic reagents were carried out under a positive atmosphere of dry argon in oven-dried glassware by using Schlenk techniques. Solvents and solutions were added with syringes through rubber septa. Organometallic reagents (*n*-, *sec*-, *t*-BuLi, PheLi) were titrated with menthol in THF in the presence of 1,10-phenanthroline prior to use.

4-Bromo-3-[1',3']-dioxan-2'-ylphenol (16). MP: 78-79 °C – TLC (cyclohexane/ethyl acetate 4:1): $R_f = 0.25$ – ¹H NMR (250 MHz, CDCl₃): $\delta = 1.44$ (dtt, 1 H, $J = 13.5$ Hz, H_{eq} at C5'), 2.12-2.28 (m, 1 H, H_{ax} at C5'), 2.98 (br s, 1 H, OH), 4.01 (dt, 2 H, $J = 12.5$ Hz, each 1 H_{ax} at C4', C6'), 4.22-4.28 (vdd, 2 H, each 1 H_{eq} at C4', C6'), 5.70 (s, 1 H, H at C2'), 6.61 (dd, 1 H, $^3J = 8.5$ Hz, $^4J = 3$ Hz, H at C6), 7.15 (d, 1 H, $^4J = 3$ Hz, H at C2), 7.30 (d, 1 H, $^3J = 8.5$ Hz, H at C5). – ¹³C NMR (63 MHz, CDCl₃): $\delta = 25.6$ (t, C5'), 67.6 (t, 2 C, C4', C6'), 100.8 (d, C2'), 111.9 (s, C4), 115.2 (d, C2 or C6), 118.0 (d, C2 or C6), 133.4 (d, C5), 137.7

(s, C3), 155.6 (s, C1). - GC-MS (Optima 1 MS, 10 psi, 50°₂ $\xrightarrow{25^\circ/\text{min}}$ 300°₅): t_{Ret} = 9.4 min, 98 % pure; MS(EI): 258/260 (30/31, [M]⁺), 243 (12), 201 (50), 179 (28), 143 (8), 122 (37), 107 (48), 87 (100), 78 (24), 63 (28), 39 (31). - HRMS (EI): calcd for C₁₀H₁₁BrO₃ 257.9891, found 257.988.

2'-(2-Bromo-5-methoxymethoxyphenyl)-[1',3']-dioxane (17). MP: 68 °C - TLC (cyclohexane/ethyl acetate 5:1) R_f = 0.25 - IR (ATR): $\tilde{\nu}$ = 2951 (w), 2851 (w), 1593 (w), 1573 (w), 1557 (w), 1473 (m), 1419 (w), 1387 (s), 1307 (w), 1267 (m), 1227 (m), 1206 (w), 1170 (m), 1146 (s), 1098 (s), 1078 (s), 1039 (m), 1002 (s), 987 (s), 956 (s), 920 (m), 880 (m), 856 (m), 815 (m). - ¹H NMR (250 MHz, CDCl₃): δ = 1.40 (d, 1 H, J = 13.5, H_{eq}. at C5'), 2.17-2.24 (m, 1 H, H_{ax}. at C5'), 3.41 (s, 3 H, CH₃ of C3-OMOM), 4.03-3.92 (m, 2 H, each 1 H_{ax}. at C4', C6'), 4.19-4.26 (m, 2 H, each 1 H_{eq}. at C4', C6'), 5.12 (s, 2 H, CH₂ of C3-OMOM), 5.66 (s, 1 H, H at C2'), 6.86 (dd, 1 H, ⁴J = 3 Hz, ³J = 9 Hz, H at C4), 7.34 (d, 1 H, ⁴J = 3 Hz, H at C6), 7.38 (d, 1 H, ³J = 9 Hz, H at C3). - ¹³C NMR (63 MHz, CDCl₃): δ = 25.5 (t, C5'), 56.0 (q, CH₃ of OMOM), 67.4 (t, 2 C, C4', C6'), 94.3 (t, CH₂ of OMOM), 100.6 (d, C2'), 113.8 (s, C2), 115.6, 118.3 (each d, C4, C6), 133.2 (d, C3), 138.3 (s, C1), 156.6 (s, C5). - GC-MS (Optima 1 MS, 10 psi, 50°₂ $\xrightarrow{10^\circ/\text{min}}$ 300°₅): t_{Ret} = 20.1 min, 97 % pure; MS(EI): 304 (3, [M]⁺), 302 (3, [M]⁺), 281 (6), 223 (3, [M-Br]⁺), 207 (18, [M-Br-CH₃-H]⁺), 191 (5), 165 (6), 152 (13), 122 (20), 108 (70), 107 (90), 91 (50), 79 (45), 77 (45), 63 (20), 45 (100), 40 (48). - HRMS (EI): calcd for C₁₂H₁₅BrO₄ 302.016, found 302.016.

1-[1',3']Dioxan-2'-yl-8-methoxy-3-(methoxymethoxy)anthraquinone (20). MP: 112 °C - TLC (cyclohexane/ethyl acetate 1:2) R_f = 0.15 - IR (ATR): $\tilde{\nu}$ = 3471 (br, w), 2957 (m), 2848 (m), 1729 (m), 1668 (s), 1595 (s), 1467 (s), 1413 (m), 1377 (s), 1354 (s), 1258 (s), 1148 (s), 1103 (s), 1076 (s), 1032 (s), 983 (s), 923 (s), 889 (s), 829 (w), 776 (m), 753 (m), 732 (s), 699 (m), 665 (w). - ¹H NMR (250 MHz, CDCl₃): δ = 1.44 (br d, 1 H, J = 13.5 Hz, H_{eq} at C5'),

2.11-2.31 (m, 1 H, H_{ax} at C5'), 3.44 (s, 3 H, CH_3 of C3-OMOM), 3.98 (s, 3 H, CH_3 of C8-OMe), 4.09 (m, 2 H, each 1 H_{ax} at C4', C6'), 4.20 (m, 2 H, each 1 H_{eq} at C4', C6'), 5.28 (s, 2 H, CH_2 of C3-OMOM), 6.65 (s, 1 H, H at C2'), 7.27 (dd, 1 H, $^3J = 7.5$ Hz, $J = 1$ Hz), 7.59 (t, 1 H, $^3J = 8$ Hz), 7.84 (m, 3 H). - ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 25.8$ (t, C5'), 56.4, 56.6 (each q, 2 CH_3 of OMOM, OMe), 67.5, 67.6 (each t, C4', C6'), 93.9 (t, CH_2 of C3-OMOM), 97.6 (d, C2'), 113.3 (d), 118.2 (d), 119.8 (d), 121.2 (d), 123.2 (s, C8a), 126.5 (s, C9a), 134.1 (d, C6), 134.7, 135.5 (each s, C4a, C5a), 159.7 (s, C8), 160.2 (s, C3), 183.3, 183.6 (each s, C9, C10). - GC-MS (Optima 1, 10 psi, $150^\circ \xrightarrow{10^\circ/min} 300^\circ$): $t_{Ret} = 18.4$ min, 97 % pure; MS(EI): 384 (12, $[M]^+$), 356 (3), 340 (4), 325 (36), 312 (12), 295 (29), 281 (11), 267 (4), 253 (6), 236 (5), 197 (4), 139 (7), 109 (3), 87 (4), 45 (100). - HRMS(EI): calcd. 384.121 for $C_{21}H_{20}O_7$, found 384.121.

2'-(8,9,10-Trimethoxy-3-(methoxymethoxy)anthracen-1-yl)-[1',3']dioxane (21) TLC (cyclohexane/ethyl acetate 2:1) $R_f = 0.25$ - IR (ATR): $\tilde{\nu} = 2951$ (m), 2840 (m), 1728 (m), 1665 (w), 1621 (s), 1567 (m), 1537 (m), 1451 (s), 1431 (s), 1397 (s), 1383 (s), 1355 (s), 1328 (s), 1290 (m), 1260 (s), 1231 (s), 1141 (s), 1102 (s), 1078 (s), 1030 (s), 986 (s), 921 (m), 863 (m). - 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.49$ (d, 1 H, $J = 13.5$ Hz, H_{eq} at C5'), 2.31 (m, 1 H, H_{ax} at C5'), 3.50 (s, 3 H, H of C3-OMOM), 3.85 (s, 3 H, H of C10-OMe), 3.98 (s, 3 H, H of C9-OMe), 4.06 (s, 3 H, H of C8-OMe), 4.15 (br d, 2 H, $J = 11.5$ Hz, each 1 H_{ax} at C4', C6'), 4.29 (ψ dd, 2 H, each 1 H_{eq} at C4', C6'), 5.33 (s, 2 H, H at C11), 6.74 (dd, 1 H, $J = 7.5$ Hz, $J = 1$ Hz, H at C7), 6.94 (s, 1 H, H at C3'), 7.35 (dd, 1 H, $J = 8.5$ Hz, $J = 7.5$ Hz, H at C6), 7.70 (d, 1 H, $J = 2.5$ Hz, H at C4), 7.81 (dd, 1 H, $J = 8.5$ Hz, $J = 1$ Hz, H at C5), 7.83 (d, 1 H, $J = 2.5$ Hz, H at C2). - ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 26.0$ (t, C5'), 56.14 (q, 2 C: CH_3 of C3-OMOM, C8-OMe), 62.1 (q, CH_3 of C9-OMe), 63.7 (q, CH_3 of C10-OMe), 67.7 (t, 2 C: C4', C6'), 94.2 (t, C11), 99.8 (d, C3'), 103.2 (d, C4), 103.4 (d, C7), 114.7 (d, C5), 117.3 (s, C8a), 120.2 (s, C9a), 120.6 (d, C2), 125.5 (d, C6), 127.3 (s, C5a), 127.5 (s, C4a), 137.5 (s, C1),

146.8 (s, C10), 150.7 (s, C9), 154.4 (s, C3), 156.4 (s, C8). - GC-MS (Optima 1, 10 psi, 150° $\xrightarrow{10^\circ/\text{min}}$ 300°₅): t_{Ret} = 18.6 min, 96 % pure; MS(EI): 414 (84, [M]⁺), 399 (24, [M-CH₃]⁺), 383 (5, [M-OCH₃]⁺), 369 (20, [M-CH₂OCH₃]⁺), 355 (3, [M-OCH₂OCH₃]⁺), 341 (37), 327 (34), 311 (49), 297 (20), 281 (17), 267 (23), 253 (16), 238 (13), 223 (13), 207 (15), 165 (12), 151 (11), 87 (7), 45 (100). - HRMS(EI): calcd 414.168 for C₂₃H₂₆O₇, found 414.168.

8,9,10-Trimethoxy-3-(methoxymethoxy)anthracene-1-carbaldehyde (13). MP: 94 °C – TLC (cyclohexane/ethyl acetate 2:1) R_f = 0.35 – IR (ATR): $\tilde{\nu}$ = 3290 (s, br), 2128 (w, br), 1681 (s), 1612 (s), 1558 (m), 1533 (m), 1455 (m), 1397 (m), 1358 (s), 1231 (m), 1152 (m), 1135 (m), 1066 (s), 1018 (s), 987 (m). – ¹H NMR (250 MHz, CDCl₃): δ = 3.52 (s, 3 H, CH₃ of C3-OMOM), 3.76 (s, 3 H, CH₃ of C9-OMe), 4.03 (s, 3 H, CH₃ of C10-OMe), 4.07 (s, 3 H, CH₃ of C8-OMe), 5.35 (s, 2 H, CH₂ of C3-OMOM), 6.79 (d, 1 H, J = 8.5 Hz, H at C7), 7.38 (ψt, 1 H, H at C6), 7.44 (d, 1 H, J = 2.5 Hz, H at C2), 7.80-7.85 (m, 2 H, H at C4, C5), 10.92 (s, 1 H, H at C11). – ¹³C NMR (63 MHz, CDCl₃): δ = 56.1 (q, CH₃ of C8-OMe), 56.3 (q, CH₃ of C3-OMOM), 62.5 (q, CH₃ of C10-OMe), 63.2 (q, CH₃ of C9-OMe), 94.5 (t, CH₂ of C3-OMOM), 103.9 (d, C7), 106.4 (d, C4), 114.8 (d, C5), 117.5 (s, C8a), 120.3 (s, C9a), 121.4 (d, C2), 126.2 (d, C6), 126.6 (s, C4a), 128.2 (s, C5a), 138.4 (s, C1), 147.4 (s, C9), 149.7 (s, C10), 154.2 (s, C3), 156.3 (s, C8), 194.4 (d, C11). – GC-MS (Optima 1, 10 psi, 150° $\xrightarrow{10^\circ/\text{min}}$ 300°₅): t_{Ret} = 12.8 min, 99 % pure; MS(EI): 356 (81, [M]⁺), 341 (50, [M-CH₃]⁺), 327 (5), 326 (5), 311 (50, [M-CH₂OCH₃]⁺), 296 (10), 281 (11), 266 (9), 253 (9), 237 (10), 222 (8), 209 (7), 181 (5), 165 (8), 139 (10), 45 (100). – HRMS(EI): calcd 356.1259 for C₂₀H₂₀O₆, found 356.126.

6-(tert-Butyldimethylsilanoxy)-1'-(3'-methoxymethoxyphenyl)-hexan-1-ol (24). TLC (cyclohexane/ethyl acetate 6:1) R_f = 0.18. - IR (ATR): $\tilde{\nu}$ = 3430 (br,w), 2928 (s), 2854 (s), 1584 (m), 1485 (m), 1470 (m), 1461 (m), 1402 (w), 1387 (w), 1359 (w), 1315 (m), 1248 (s),

1206 (w), 1149 (s), 1079 (s), 1017 (s), 993 (s), 923 (m), 833 (s), 813 (w), 774 (s), 699 (m), 660 (w). - ^1H NMR (300 MHz, CDCl_3): δ = 0.01 (s, 6 H, CH_3 of TBS), 0.86 (s, 9 H, *t*Bu of TBS), 1.33-1.51 (m, 6 H, H at C3, C4, C5 or C2), 1.69-1.75 (m, 2 H, H at C5 or C2), 3.46 (s, 3 H, CH_3 of OMOM), 3.56 (t, 2 H, 3J = 6.5 Hz, H at C6), 4.61 (br. s, 1 H, H at C1), 5.15 (s, 2 H, CH_2 of OMOM), 6.90–7.02 (m, 3 H, H on C2', C4', C6'), 7.24 (t, 1 H, J = 7.9 Hz, H on C5'). - ^{13}C NMR (75 MHz, CDCl_3): δ = -5.3 (s, 2 CH_3 of Me_2Si), 18.3 (s, C of *t*BuSi), 25.6 (t, C3 or C4), 25.7 (t, C3 or C4), 25.9 (q, 3 CH_3 of *t*BuSi), 32.7 (t, C5), 39.0 (t, C2), 56.0 (q, CH_3 of OMOM), 63.1 (t, C6), 74.4 (d, C1), 94.4 (t, CH_2 of OMOM), 113.8, 115.1 (each d, C2', C4'), 119.4 (d, C6'), 129.4 (d, C5'), 146.7 (s, C1'), 157.4 (s, C3'). - GC-MS (Optima 1, 10 psi, $150^\circ\text{C} \xrightarrow{10^\circ/\text{min}} 300^\circ\text{C}$): t_{Ret} = 11.6 min, 98 % pure, MS: 311 (1, $[\text{M}-t\text{Bu}]^+$), 309 (7), 294 (3), 279 (13, $[\text{M}-t\text{Bu}-2\text{ Me}]^+$), 263 (96), 250 (33), 231 (40), 207 (65), 187 (95), 182 (31), 168 (29), 165 (15), 152 (817), 145 (51), 121 (36), 106 (12), 91 (25), 75 (100), 73 (37), 45 (95). - HRMS (EI): calcd 311.1678 for $\text{C}_{16}\text{H}_{27}\text{SiO}_4$ ($\text{M}-t\text{Bu}^+$), found 311.168.

1-(2'-Bromo-3'-methoxymethoxyphenyl)-6-(tertbutyldimethylsilanyloxy)-hexan-1-ol

(**25**). TLC (cyclohexane/ethyl acetate 7:1) R_f = 0.2 - IR (ATR): $\tilde{\nu}$ = 3419 (br, w), 2927 (s), 2854 (s), 1592 (w), 1569 (w), 1462 (s), 1437 (m), 1387 (w), 1359 (w), 1307 (w), 1255 (s), 1203 (m), 1153 (s), 1086 (s), 1019 (s), 923 (m), 833 (s), 774 (s), 718 (m), 661 (w). - ^1H NMR (250 MHz, CDCl_3): δ = 0.01 (s, 6 H, CH_3 of Me_2Si), 0.86 (s, 9 H, CH_3 of *t*BuSi), 1.34-1.70 (m, 8 H, H at C2, C3, C4, C5), 2.15 (d, 1 H, 3J = 3.5 Hz, OH), 3.49 (s, 3 H, CH_3 of OMOM), 3.57 (t, 2 H, 3J = 6.5 Hz at C6), 5.09 (quin, 1 H, J = 4 Hz, H at C1), 5.22 (s, 2 H, CH_2 of OMOM), 7.02 (dd, 1 H, 4J = 2.5 Hz, 3J = 7.5 Hz, H at C4'), 7.17-7.23 (m, 2 H, H at C5', C6'). - ^{13}C NMR (63 MHz, CDCl_3): δ = -5.3 (q, 2 CH_3 of Me_2Si), 18.3 (s, C of *t*BuSi), 25.6 (t, C3 or C4), 25.9 (q, 2 CH_3 of *t*BuSi), 26.9 (t, C3 or C4), 32.7 (t, C5), 37.5 (t, C2), 56.4 (q, CH_3 of OMOM), 63.2 (t, C6), 72.9 (d, C1), 95.1 (t, CH_2 of OMOM), 112.7 (s, C2'), 114.6 (d, C4'), 120.3 (d, C6'), 128.1 (d, C5'), 145.8 (s, C1'), 153.4 (s, C3'). - GC-MS (Optima 1, 10

psi, 150°₂ $\xrightarrow{10^\circ/\text{min}}$ 300°₅): t_{Ret} = 13.6 min, 97 % pure, MS(EI): 389 (>1, [M-*t*Bu]⁺), 373 (1, [M-*t*Bu-O]⁺), 359 (7), 343 / 341 (6), 329 / 327 (5), 311/309 (19), 283 / 285 (7), 267 (19), 248 (13), 231 / 229 (19), 201 (8), 186 (9), 174 (13), 159 (7), 145 (21), 131 (11), 116 (10), 105 (15), 89 (12), 75 (62), 73 (20), 59 (8), 45 (100). - HRMS (EI): 389.0783 for C₁₆H₂₆BrSiO₄ (M-*t*Bu)⁺, found 389.078

2'-Bromo-1'-[6-(tertbutyldimethylsilanyloxy)-1-triethylsilanyloxyhexyl]-3'-methoxy-methoxybenzene (26). TLC (cyclohexane/ethyl acetate 30:1) R_f = 0.2 - IR (ATR): $\tilde{\nu}$ = 3066 (w), 2928 (s), 2872 (s), 2853 (s), 2731 /w), 1919 (w), 1714 (w), 1591 (m), 1569 (m), 1461 (s), 1435 (s), 1410 (m), 1385 (m), 1358 (m), 1305 (m), 1255 (s), 1203 (m), 1153 (s), 1097 (s), 999 (s), 938 (m), 923 (s), 832 (s), 774 (s), 724 (s), 663 (m). - ¹H NMR (250 MHz, CDCl₃): δ = 0.02 (s, 6 H, 2 CH₃ of C6-OTBS), 0.53 (t, 6 H, ³*J* = 7.5 Hz, 3 CH₂ of C1-OTES), 0.87 (s, 9 H, 3 CH₃ of C6-OTBS), 0.83-0.94 (m, 9 H, 3 CH₃ of C1-OTES), 1.30-1.62 (m, 8 H, H at C2, C3, C4, C5), 3.51 (s, 3 H, CH₃ of OMOM), 3.57 (t, 2 H, ³*J* = 6.5 Hz, H at C6), 5.07 (dd, 1 H, ⁴*J* = 4 Hz, ³*J* = 7.5 Hz, H at C1), 5.21, 5.23 (each d, AB system, 1 H, ²*J* = 6.5 Hz, CH₂ of OMOM), 6.99 (dd, 1 H, ³*J* = 5.5 Hz, ⁴*J* = 4 Hz, H at C4'), 7.16-7.23 (m, 2 H, H an C5', C6'). - ¹³C NMR (63 MHz, CDCl₃): δ = -5.3 (q, 2 CH₃ of C6-OTBS), 4.7 (t, 2 CH₂ of C1-OTES), 6.7 (q, 3 CH₃ of C1-OTES), 18.4 (s, C of C6-OTBS), 25.5, 25.7 (each t, C3, C4), 26.0 (q, 3 CH₃ of C6-OTBS), 32.8 (t, C5), 39.2 (t, C2), 56.4 (q, CH₃ of OMOM), 63.2 (t, C6), 73.3 (d, C1), 95.4 (t, CH₂ of OMOM), 111.9 (s, C2'), 114.1 (d, C4'), 121.3 (d, C6'), 127.7 (d, C5'), 146.9 (s, C1'), 153.1 (s, C3'). - GC-MS (Optima 1 MS, 10 psi, 150°₂ $\xrightarrow{10^\circ/\text{min}}$ 300°₅): t_{Ret} = 14.9 min, 98 % pure, MS(EI): 503 (1, [M-*t*Bu]⁺), 473 (5, [M-Et₃]⁺), 451 (5), 429 (5), 379 (5), 361 / 359 (35), 341 (7), 329 (22), 327 (24), 311 / 309 (65), 287 (23), 285 (28), 267 (38), 265 (40), 248 (55), 229 (25), 213 (25), 189 (30), 173 (43), 161 (48), 145 (52), 117 (85), 115 (98), 89 (37), 87 (100), 75 (88), 59 (37). - HRMS (EI): calcd 503.1648 for C₂₂H₄₀Si₂O₄Br (M-*t*Bu)⁺, found 503.165.

6-(*tert*-Butyldimethylsilanoxy)-1-{2-[hydroxy-(8,9,10-trimethoxy-3-methoxymethoxy-anthracen-1-yl)-methyl]-3-methoxymethoxyphenyl}-hexan-1-ol (11). The product was obtained as a 1.38:1 mixture of diastereomeres (determined by HPLC), the following presents the analytical data for the mixture: TLC (cyclohexane/ethyl acetate 2:1) $R_f = 0.2$ - IR (ATR): $\tilde{\nu} = 3322$ (br, s), 2929 (s), 2852 (m), 2177 (br, w), 1622 (s), 1537 (m), 1461 (m), 1429 (m), 1398 (s), 1354 (s), 1291 (m), 1245 (m), 1222 (m), 1203 (m), 1151 (s), 1132 (m), 1081 (s), 1066 (s), 1005 (s), 833 (s). - ^1H NMR (300 MHz, CDCl_3 , 54 °C): $\delta = 0.00/0.06$ (s, 6 H, $(\text{CH}_3)_2\text{Si}$ of C1-OTBS), 0.81/0.86 (s, 9 H, $(\text{CH}_3)_3\text{CSi}$ of C1-OTBS), 1.10-1.55 (m, 4 H, H on C3, C4), 1.25-1.61 (m, 2 H, H on C2), 1.67-1.92 (m, 2 H, H on C5), 3.28/3.30 (s, 3 H, CH_3 of C11-OMOM), 3.40/3.44 (s, 3 H, CH_3 of C16-OMOM), 3.46/3.52 (t, 2 H, $J = 6.5$ Hz, H on C2), 3.99/4.03 (s, 3 H, CH_3 of C26-OMe), 4.03/4.04 (s, 3 H, CH_3 of C24-OMe), 4.03/4.03 (s, 3 H, CH_3 of C19-OMe), 4.91/5.10 (t, 1 H, $J = 7.5$ Hz, H on C6), 5.03/5.10 (br d, 2 H, CH_2 of C11-OMOM), 5.09/5.22 (d, 2 H, CH_2 of C16-OMOM), 6.79/6.80 (d, 1 H, $J = 7$ Hz, H on C23), 6.84/6.84 (d, 1 H, $J = 2.5$ Hz, H on C15), 7.03/7.06 (m, 1 H, H on C10), 7.33/7.37 (m, 1 H, H on C9), 7.32/7.39 (s, 1 H, H on C13), 7.35/7.40 (m, 1 H, H on C22), 7.32/7.41 (m, 1 H, H on C8), 7.65/7.67 (d, 1 H, $J = 2.5$ Hz, H on C17), 7.84/7.85 (dd, 1 H, $J_o = 8.5$ Hz, $J_m = 1$ Hz, H on C21). - ^{13}C NMR (75 MHz, CDCl_3 , 54 °C): $\delta = -5.28/-5.35$ (q, 2 C, $(\text{CH}_3)_2\text{Si}$ of C1-OTBS), 18.28/18.31 (s, $(\text{Me})_3\text{CSi}$ of C1-OTBS), 25.94/25.98 (s, 3 C, $(\text{CH}_3)_3\text{CSi}$ of C1-OTBS), 25.98/26.0 (t, C3), 26.31/26.37 (t, C4), 32.87/32.91 (t, C2), 35.08 (br)/38.86 (t, C5), 55.97/56.05 (q, CH_3 of C11-OMOM), 56.05/56.07 (q, CH_3 of C16-OMOM), 56.31/56.35 (q, CH_3 of C24-OMe), 62.20/62.25 (q, CH_3 of C19-OMe), 63.25/63.31 (t, C1), 64.45/64.67 (q, CH_3 of C26-OMe), 68.58/69.17 (d, C13), 69.95/71.83 (d, C6), 94.38/94.44 (t, CH_2 of C16-OMOM), 95.10/95.15 (t, CH_2 of C11-OMOM), 102.27/104.28 (d, C17), 104.60/104.65 (d, C23), 113.19/113.61 (d, C10), 114.91/114.91 (d, C21), 117.84/118.05 (s, C25), 120.29/121.61 (d, C15), 120.74/121.02 (s, C27), 121.12/121.82 (d, C8), 125.82/125.82 (d, C22),

127.81/128.08 (s, C20), 128.18/128.26 (s, C18), 128.18/129.85 (s, C12), 128.76/129.00 (d, C9), 141.62 (br)/142.17 (s, C14), 145.97/148.54 (br) (s, C7), 147.89/147.92 (s, C19), 149.29/149.74 (s, C26), 153.67/153.92 (s, C16), 154.42/154.85 (s, C11), 156.59/156.71 (s, C24). - HPLC-purity: 95 %. - MS (EI, 70 eV): 724 (3, $[M]^+$), 705 (30), 682 (22), 661 (8), 615 (5), 570 (2), 513 (5), 477 (5), 355 (7), 341 (12), 331 (18), 311 (16), 281 (15), 271 (25), 171 (15), 125 (19), 89 (30), 75 (94), 73 (100). - HRMS (EI): calcd 724.3643 for $C_{40}H_{56}SiO_{10}$, found 724.364.

6-[3-Methoxymethoxy-2-(8-methoxy-3-methoxymethoxy-9,10-anthraquinone-1-carbonyl)-phenyl]-6-oxo-hexanoic acid (27) TLC (cyclohexane/ethyl acetate/acetic acid 33:66:1) R_f = 0.2. The NMR spectra showed that **27** was received as a mixture of the bis-MOM protected diketoacid and a partial deprotected mono-MOM-diketoacid. - HRMS (ESI): calcd 613.1686 for $C_{32}H_{30}O_{11}Na$, found 613.169.

6-[3-hydroxy-2-(3-hydroxy-8-methoxy-9,10-anthraquinone-1-carbonyl)phenyl]-6-oxo-hexanoic acid (10). TLC (cyclohexane/ethyl acetate/acetic acid 25:75:1) R_f = 0.17 - IR (ATR): $\tilde{\nu}$ = 3335 (br, s), 2122 (br, w), 1644 (s), 1583 (s), 1463 (m), 1350 (s), 1256 (s), 1169 (m), 1135 (m), 1069 (m), 1022 (m), 937 (m). - 1H NMR (250 MHz, CD_2Cl_2): δ = 1.64 (m, 4 H, H at C3, C4), 2.24 (br t, 2 H, J = 7 Hz, H at C2 or C5), 2.31 (s, 1 H, OH), 2.82 (br t, 2 H, J = 7 Hz, H at C2 or C5), 3.86 (s, 3 H, CH_3 of C24-OMe), 6.77 (dd, 1 H; J = 7.5 Hz, J = 1 Hz), 6.88 (dd, 1 H, J = 8 Hz, J = 1.0 Hz), 6.93 (d, 1 H, J = 2.5 Hz), 7.09-7.23 (m, 1 H), 7.43-7.47 (m, 1 H), 7.54 (d, 1 H, J = 2.5 Hz), 7.72 (t, 1 H, J = 7.5 Hz), 7.84 (dd, 1 H, J = 8 Hz, J = 1 Hz). - ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 25.1, 26.1 (each t, C3, C4), 36.1, 43.7 (each t, C2, C5), 56.9 (q, CH_3 of C24-OMe), 113.3 (d), 118.5 (d), 119.7 (d), 119.9 (d), 120.0 (d), 120.6 (d), 121.9 (s), 126.3 (s), 127.4 (s), 135.7 (d), 136.3 (s), 136.3 (d), 136.6 (s), 147.4 (s), 148.2 (s), 160.9, 161.7, 163.7 (each s, C11-OH, C16-OH, C24-OMe), 179.1 (s, C1), 182.9, 184.2

(each s, C19, C26), 197.9 (s, C6), 209.6 (s, C13). – MS(EI, 20 eV): 502 (25, $[M]^+$), 484 (10, $[M-CH_3-3 H]^+$), 438 (12), 415 (20), 401 (100, $[M-(CH_2)_4COOH]^+$), 341 (7), 325 (6), 281 (21), 253 (15), 136 (25), 121 (62), 93 (15), 73 (11), 57 (18), 55 (26). – HRMS (EI): calcd 502.1263 for $C_{28}H_{22}O_9$, found 502.126.