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Total Synthesis of Angucyclines. 9 [1]

An Alternative Biomimetic-Type Synthesis of 8-Deoxytetrangomycin

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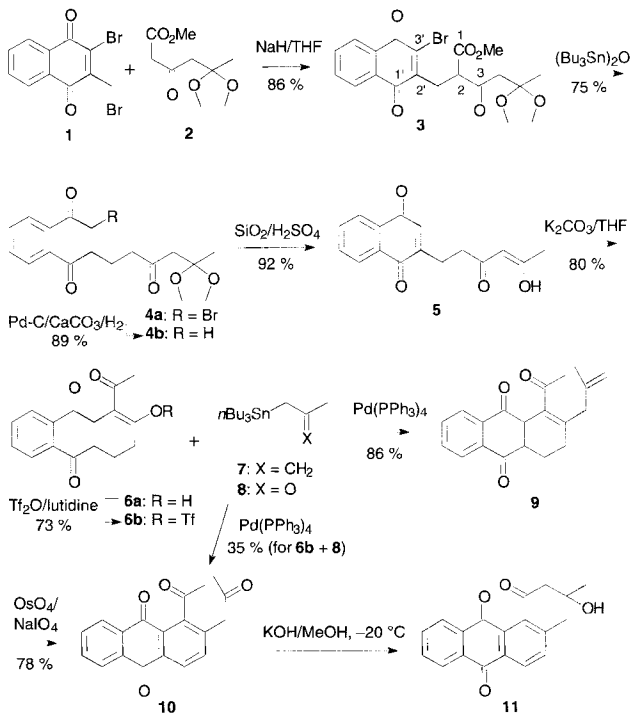
Abstract. Base-catalyzed cyclization of the naphthoquinone **5** afforded the 1,2-dihydroanthraquinone **6a**. The bisalkylation products **9** and **10** were obtained by Stille-type chain elongation of the corresponding triflate **6b** with the stannanes **7** or **8**. The dihydroanthraquinone **9** is a potential precursor for the SS-228 Y-type angucyclinones, where as the diketone **10** can be converted to 8-deoxytetrangomycin (**11**).

In a preceeding communication we have described the biomimetic-type synthesis of rabelomycin, tetrangomycin, and other related ring B aromatic angucyclinones such as 4-deoxy-tetrangomycin (**11**) [1]. The synthesis relied on the successive cyclization of short ketide side chains which were vicinally attached to a naphthoquinone core. This close connection on two neighboring sp^2-carbon atoms restricted the number of theoretically possible aldol condensations and assured the formation of the angularly condensed six-membered rings. On the other hand, the attachement of the two different chemically reactive side chains presented some synthetic problems and only one good solution using a Stille reaction emerged from the extensive search for possible side chain building blocks [2].

We now disclose an alternative approach which is – while still using ketide fragments – less analogous to the biosynthesis. However, the chemical access to the target compounds is much easier and the dihydroanthraquinone intermediate **9** is a promising precursor for the synthesis of the important non-aromatic angucyclines yet unavailable by synthesis (for reviews see [3, 4]; approaches to hydroaromatic angucyclines [5, 6]).

The brominated quinone ester **3**, prepared in a simple alkylation of the β-ketoester **2** with the bromide **1** [2], served as the starting material (Scheme 1). In a previous study this ketoester was debrominated and cyclized to an anthraquinone ester [2]. However, demethoxycarbonylation of **3** under mild neutral conditions using bis(tributyltin) oxide [7] to **4a** followed by hydrogenative debromination to yield the ketoacetal **4b** proved to be the better reaction sequence (Scheme 1). The acetal **4b** was easily cleaved using wet acidic silica gel [8] to afford the diketone that existed as the enol form **5** (ca. 85% in $CDCl_3$ solution) as shown by NMR studies.



Scheme 1

This open chain naphthoquinone derivative underwent facile cyclization to the dihydroanthraquinone **6a** under extremely mild basic conditions (K_2CO_3/18-crown-6) in THF solution. It is particularly noteworthy that only traces of the corresponding aromatic anthraquinone could be detected by

TLC under carefully controlled conditions. It is well known that 1,2-dihydroanthraquinones of type **6a** undergo very rapid dehydrogenative aromatization under basic conditions by deprotonation of the acidic benzylic position and subsequent irreversible tautomerization to the 9,10-dihydroanthraquinone, followed by air-oxidation. The cyclization product **6a** existed exclusively in the keto–enol form and our synthetic scheme anticipated the conversion to the corresponding triflate **6b** for attachement of side chains at this position using the Stille reaction. We were pleased to note that the conversion of **6a** to the triflate **6b** using triflate anhydride also proceeded in good yield with only very little concurrent aromatization (ca. 5%). The crucial step in the synthesis was the subsequent Stille reaction with either the allyl stannane **7** or the corresponding 1-tributylstannyl-2-propanone (**8**).

Gratifyingly, the attachment of the methallyl side chain to **9** proceeded also without aromatization in 86% yield. In the reaction with the less reactive oxoalkylstannane **8** the fully aromatized dioxoalkyl-9,10 anthraquinone **10** was the major product (35%). This compound was indentical with a sample prepared by a different route [1] and could also be obtained by Lemieux-Johnson [9] cleavage of the side chain double bond in **9**.

Interestingly, a complete dehydrogenation of **9** to the anthraquinone **10** was observed under these oxidative conditions in addition to double bond cleavage, demonstrating the instability of 1,2-dihydroanthraquinone intermediates such as **9**. However, oxygenation (epoxidation or *cis*-hydroxylation) of the internal double bond of **9** might be a key step in the synthesis of the large group of the non-aromatic angucyclinones of the SS-228 Y-type (for classification see [3]). In addition, the procedure outlined in Scheme 1 also describes an improved access to aromatic precursors such as **10** that could be converted with KOH in methanol to the non-naturally occurring 8-deoxytetrangomycin (**11**) as described previously [1].

Experimental

For general methods and instrumentation see [10].

2-Bromo-3-[4-(2-methyl-[1,3]dioxolan-2-yl)-3-oxobutyl]-[1,4]naphthoquinone (**4a**)

A solution of methyl ester **3** [2] (500 mg, 1.1 mmol) and bis(tributyltin) oxide (1.31 g, 2.2 mmol) in dry toluene (10 ml) was heated under nitrogen for 24 h at 80 °C (TLC control). The mixture was diluted with diethyl ether (15 ml) and acidified with HCl (1N, 15 ml). The organic phase was separated and the aqueous phase extracted twice with diethyl ether. The organic phases were combined, dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (1. petroleum ether, 2. petroleum ether/ethyl acetate) to afford the ketone **4a** (325 mg, 75%) as yellow needles. *m.p.* 109 °C. – IR (KBr): ν/cm^{-1} = 2984, 2932, 1701 (aliph. CO), 1673 (quinone CO), 1590 (arom. C=C), 1279 (C–Br). – UV (methanol): λ_{max}/nm (lg ε) = 205 (4.10), 246 (4.05), 252 (4.04), 280 (3.98), 334 (3.37). – ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm = 1.42 (s, 3H, dioxolane-CH_3), 2.81 (s, 2H, 4'-H), 2.80–2.85 (m, 2 H, 2'-H), 3.07–3.12 (m, 2H, 1'-H), 3.97 (s, 4H, OCH_2CH_2O), 7.62–7.80 (m, 2H, 6-H, 7-H), 8.08–8.19 (m, 2H, 5-H, 8-H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm = 24.60 (q, dioxolane-CH_3), 25.99 (t, C-1'), 41.24 (t, C-2'), 51.66 (t, C-4'), 64.69 (t, OCH_2CH_2O), 107.86 (s, dioxolane-OCO), 127.16 (d, C-5, C-8), 127.55 (d, C-5, C-8), 131.13 (s, C-4a, C-8a), 131.55 (s, C-4a, C-8a), 134.00 (d, C-6, C-7), 134.21 (d, C-6, C-7), 139.12 (s, C-2), 150.97 (s, C-3), 177.51 (s, C-1, C-4), 181.56 (s, C-1, C-4), 205.33 (s, C-3'). – MS (EI/90 °C): *m/z* (%) = 396/394 (< 1), 380/378 (< 0.1) [$M^+ + 1 - CH_3$], 379/377 (<0.1) [$M^+ - CH_3$], 337/335 (2), 291/293 (12) [$M^+ - CH_3C(OCH_2CH_2O)CH_2$], 265/263 (20) [$M^+ - CH_3C(OCH_2CH_2O)CH_2CO$], 87 (100) [$CH_3C(OCH_2CH_2O)^+$].

$C_{18}H_{17}BrO_5$	calcd.:	C 54.98	H 4.36
(393.23)	found:	C 54.88	H 4.36.

2-[4-(2-Methyl-[1,3]-dioxolan-2-yl)-3-oxobutyl]-[1,4]naphthoquinone (**4b**)

A solution of bromide **4a** (100 mg, 0.254 mmol) in dry methanol (5 ml) was hydrogenated with Pd/C (5%,46 mg) as the catalyst in presence of $CaCO_3$ (254 mg, 2.54 mmol) for 5 h at 20 °C. The debrominated naphthohydroquinone was reoxidi- zed by addition of dichlorodicyanobenzoquinone (DDQ, 63.2 mg, 0.279 mmol). The mixture was filtered, the solvent removed under reduced pressure, and the residue purified by chromatography on silica gel (CH_2Cl_2/MeOH: 100/2) to yield the quinone **4b** as an orange oil (70 mg, 89 %). – IR (KBr): ν/cm^{-1} = 2932 , 1711 (aliph. CO), 1663 (quinone CO), 1595 (arom. C=C), 1302, 1049, 781. – UV (methanol): λ_{max}/nm (lg ε) = 205 (4.47), 269 (3.69), 318 (3.13), 337 (3.01). – ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm = 1.39 (s, 3H, dioxola- ne-CH_3), 2.78 (s, 2H, 4'-H), 2.85 (m, 4H, 1'-H, 2'-H), 3.95 (s, 4H, OCH_2CH_2O), 6.82 (s, 1H, 3-H), 7.61–7.75 (m, 2H, 5-H, 8-H), 8.03–8.13 (m, 2H, 6-H, 7-H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm = 23.93 (t, C-1'), 24.49 (q, dioxolane-CH_3), 42.07 (t, C-2'), 51.78 (t, C-4'), 64.63 (t, OCH_2CH_2O), 107.92 (s, dioxolane-OCO), 126.09 (d, C-5, C-8), 126.58 (d, C-5, C-8), 132.12 (s, C-4a, C-8a), 132.30 (s, C-4a, C-8a), 133.66 (d, C-6, C-7), 133.74 (d, C-6, C-7), 135.38 (d, C-3), 150.43 (s, C-2), 185.00 (s, C-1, C-4), 185.09 (s, C-1, C-4), 205.55 (s, C-3'). – MS (EI/60 °C): *m/z* (%) = 314 (<0.1) [M^+], 299 (16) [$M^+ - CH_3$], 228 (48) [$M^+ + 1 - CH_3C(OCH_2CH_2O)$], 213 (60) [$M^+ - CH_3C(OCH_2CH_2O)CH_2$], 212 (78), 186 (78), 184 (74), 184 (34), 128 (28), 157 (22) [$M^+ - CH_3C(OCH_2CH_2O)\ CH_2COCH_2CH_2$], 87 (100) [$CH_3C(OCH_2CH_2O)^+$].

$C_{18}H_{17}O_5$	calcd.:	C 68.78	H 5.77
(314.34)	found:	C 68.59	H 5.58.

2-(3,5-Dioxohexyl)-[1,4]naphthoquinone (**5**)

A suspension of silica gel (7 g) in dichloromethane (15 ml) was treated with sulfuric acid (740 mg, 15%) and the mixture was stirred until the aqueous phase disappeared. A solution of the ketal **4b** (600 mg, 1.9 mmol) in CH_2Cl_2 (5 ml) was then added and the suspension was stirred for 1 h at 20 °C (TLC control). The suspension was filtered, the filtrate was washed with aqueous $NaHCO_3$ solution and dried (Na_2SO_4). The solvent was removed under reduced pressure, the residue purified by filtration over a short column of silica gel (CH_2Cl_2), and crystallized from diethyl ether to afford the diketone **5**

(474 mg, 92%) as yellow crystals. *m.p.* 88 °C. – UV (methanol): λ_{max}/nm (lg ε) = 208 (3.80), 246 (3.85), 410 (1.97). – IR (KBr): ν/cm^{-1} = 3075 (C-H), 2950 (C-H), 1660 (aliph. CO), 1631 (quinone CO), 1620 (quinone CO), 1593 (arom. C=C). – ^{1}H NMR (200 MHz, $CDCl_3$ only enol form): δ/ppm = 2.05 (s, 3 H, 6'-H), 2.65 (t, 2H, 2'-H) 2.95 (t, 2H, 1'-H), 5.54 (s, 1H, 4'-H), 6.84 (s, 1H, 3-H), 7.71–7.82 (m, 2H, 6-H and 7-H), 8.03–8.18 (m, 2H, 5-H and 8-H), 15.40 (chelat. OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 24.89 (q, C-6'), 25.78 (t, C-2'), 36.82 (t, C-1'), 100.4 (d, C-4'), 126.55 (d, C-5, C-8), 127.04 (d, C-5, C-8), 132.46 (s, C-4a, C-8a), 132.56 (s, C-4a, C-8a), 134.17 (d, C-6, C-7), 134.25 (d, C-6, C-7), 135.79 (d, C-3), 150.30 (s, C-2), 185.27 (s, C-1, C-4), 185.34 (s, C-1, C-4), 190.38 (s, C-3'), 193.46 (s, C-5'). – MS (EI/70 °C): *m/z* (%) = 270 (30) [M$^+$], 252/253 (30) [M$^+$ – H_2O], 229 (10) [M$^+$ +1–$COCH_3$], 228 (62) [M$^+$ – $COCH_3$], 212 (92) [M$^+$ – $(H_3C)_2CO^+$] 186 (100) [M$^+$ +1 – $CH_3COCH_2CO^+$], 185 (46) [M$^+$ – $CH_3COCH_2CO^+$], 184 (42), 157 (20), 128 (32), 129 (26), 115 (18), 105 (12), 85 (50) [$CH_3COCH_2CO^+$], 76 (21), 43 (48) [CH_3CO^+].

$C_{16}H_{14}O_4$ (270.28) calcd.: C 71.09 H 5.22 found: C 69.92 H 4.62.

4-Acetyl-3-hydroxy-1,2-dihydroanthraquinone (**6a**)

Naphthoquinone **5** (330 mg, 1.221 mmol) was added under argon to a suspension of potassium carbonate (1.34 g, 9.77 mmol) and 18-crown-6 (40 mg, 159 µmol) in THF (15 ml). The mixture was stirred at 20 °C until the starting material was converted (TLC-control, ca. 1 h). The suspension was filtered and the filtrate then acidified by addition of 1N HCl (ca. 5 ml, change of color from violet to orange). The mixture was extracted twice with dichloromethane (60 ml) and the combined organic phases were dried (Na_2SO_4), concentrated under reduced pressure (ca. 1 ml), and the product crystallized by addition of diethyl ether (2 ml) to yield orange crystals (262 mg, 80 %). *m.p.* 141 °C. – UV (methanol): λ_{max}/nm (lg ε) = 206 (4.09), 252 (4.11), 298 (3.91), 410 (3.16), 530 (2.76). – IR (KBr): ν/cm^{-1} = 2975 (C-H), 2925 (C-H), 2850 (C-H), 1662 (aliph. CO), 1601 (aliph. CO) , 1595 (quinone CO), 1572 (quinone CO), 1593 (arom. C=C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 2.10 (s, 3H, $COCH_3$), 2.57 (t, 2H, 2-H), 2.95 (t, 2H, 1-H), 7.68–7.84 (m, 2H, 6-H and 7-H), 7.98–8.22 (m, 2H, 5-H and 8-H), 16.00 (chelat. OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 20.10 (t, C-2), 26.10 (q, C-2'), 32.68 (t, C-1), 106.5 (s, C-4), 126.65 (d, C-5, C-8), 126.97 (d, C-5, C-8), 132.27 (s, C-4a, C-9a) 133.12 (s, C-4a, C-9a), 133.93 (d, C-6, C-7), 134.20 (d, C-6, C-7), 139.13 (s, C-8a, C-10a), 141.86 (s, C-8a, C-10a), 183.26 (s, C-9, C-10), 183.81 (s, C-9, C-10), 191.36 (s, C-3), 197.63 (s, C-1'). – MS (EI/75 °C): *m/z* (%) = 268 (100) [M$^+$], 253/254 (34) [M$^+$ – CH_3], 240 (12) [M$^+$ – CO], 227 (16), 226 (96) [M$^+$ +1 – CH_3CO^+], 225 (30) [M$^+$ – CH_3CO^+], 197 (39), 181 (9), 141 (12), 105 (8), 43 (18) [CH_3CO^+].

$C_{16}H_{12}O_4$ (268.23) calcd.: C 71.64 H 4.51 found: C 71.37 H 4.38.

Trifluoromethansulfonic acid-1-acetyl-9,10-dioxo-3,4,9,10-tetrahydroanthracen-2-yl-ester (**6b**)

A solution of 1,2-dihydroanthraquinone (**6a**) (100 mg, 0.37 mmol) and 2,6-lutidine (0.2 mg) in dry dichloromethane (2 ml) was treated with triflate anhydride (209 mg, 0.74 mmol). The mixture was stirred for 2 h at 20 °C (TLC control), diluted with CH_2Cl_2 (10 ml), and washed with HCl (1N, 5 ml). The solution is washed with brine (2 ml), dried ($MgSO_4$), filtered, and the filtrate was evaporated at reduced pressure. The residue was purified by filtration through a short column of silica gel (CH_2Cl_2) to afford the triflate **6b** (110 mg, 73 %). *m.p.* 123 °C. – UV (methanol): λ_{max} (lg ε) = 207 nm (4.13), 253 (4.10), 295 (3.92). – IR (KBr): ν/cm^{-1} = 3075 (C-H), 2925 (C-H), 2860 (C-H), 1714 (aliph. CO), 1677 (quinone CO), 1662 (quinone CO), 1593 (arom. C=C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 2.54 (s, 3H, C-2'), 2.78 (t, 2H, 3-H), 3.14 (t, 2H, 4-H), 7.72–7.84 (m, 2H, 6-H and 7-H), 8.03–8.20 (m, 2H, 5-H and 8-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 22.10 (t, C-3), 25.24 (t, C-4), 31.61 (q, C-2'), 115.15 (s, CF_3) 127.12 (d, C-5, C-8), 127.32 (d, C-5, C-8), 131.03 (s, C-4a, C-9a), 132.69 (s, C-4a, C-9a), 134.59 (d, C-6, C-7), 134.84 (d, C-6, C-7), 138.87 (s, C-8a, C-10a), 141.30 (s, C-8a, C-10a), 149.89 (s, C-2), 181.86 (s, C-9, C-10), 183.27 (s, C-9, C-10), 198.00 (s, C-1'). – MS (EI/75 °C): *m/z* (%) = 400 (10) [M$^+$], 385 (12) [M$^+$ – CH_3], 383 (22), 252 (14) [M$^+$ + 1 – $CF_3O_3S^+$], 250 (12), 211 (10), 168 (8), 139 (10), 105 (8), 76 (26), 69 (65) [CF_3^+], 64 (32) [SO_2], 48 (24), 43 (100) [$COCH_3^+$].

$C_{17}H_{11}O_6SF_3$ (400.02) calcd.: C 51.00 H 2.77 found: C 51.56 H 2.54.

4-Acetyl-3-(2-methylallyl)-1,2-dihydro-anthraquinone (**9**)

A solution of the triflate **6b** (130 mg, 325 µmol), tributyl-(2-methylallyl)-stannane (**7**) [11] (270 mg, 782 µmol), and $Pd(PPh_3)_4$ (30 mg, 26 µmol) in dry 1,4-dioxane (5 ml) was heated for 1 h under argon at 40 °C (TLC control). The solvent was removed under reduced pressure and the residue was purified by filtration through a short column of silica gel (first petroleum ether, then CH_2Cl_2) to yield the alkylation product **9** (86 mg, 86%) as yellow crystals, *m.p.* 100 °C immediately subjected to the next reaction (conversion to **10**, procedure B). – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 1.70 (s, 3H, Allyl-CH_3), 2.35 (s, 3H, 2"-H), 2.25–2.43 (t, 2H, 3-H and 4-H), 2.70–2.85 (t, 2H, 3-H and 4-H), 3.08 (s, 2H, 1'-H), 4.79 (s, 1H, 3'-H), 4.89 (s, 1H, 3'-H), 7.63–7.77 (m, 2H, 6-H and 7-H), 8.03–8.16 (m, 2H, 5-H and 8-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 20.63 (t, C-2), 23.13 (q, C-2"), 26.55 (t, C-1), 32.12 (q, allyl-CH_3), 42.32 (t, C-1'), 113.75 (t, C-3'), 126.61 (d, C-5, C-8), 127.12, (d, C-5, C-8), 131.80 (s, C-4a, C-9a), 132.46 (s, C-4a, C-9a), 134.13 (d, C-6, C-7), 134.40 (d, C-6, C-7), 134.81 (s, C-2'), 139.78 (s, C-8a, C-10a), 141.17 (s, C-8a, C-10a), 142.36 (s, C-4), 146.10 (s, C-3), 183.50 (s, C-9, C-10), 184.42 (s, C-9, C-10), 203.82 (s, C-1").

$C_{20}H_{18}O$ (306.2) calcd.: C 78.44 H 5.87 found: C 78.34 H 5.74.

1-Acetyl-2-(2-oxopropyl)-anthraquinone (**10**)

Procedure A

A solution of triflate **6b** (90 mg, 225 µmol), 1-tributylstannyl-propan-2-one (**8**) [12] (131 mg, 450 µmol), $Pd(PPh_3)_4$ (20 mg, 17 µmol) and CuBr (8 mg, 57 µmol) in dry toluene (3 ml) was stirred for 30 min at 20 °C and then for 3 h at 60 °C (TLC control). The solvent was removed under reduced pressure

and the residue purified by chromatography on silica gel (petroleum ether/AcOEt : 1/1) to yield the diketone **10** (25 mg, 36%) as a yellow solid. *m.p.* 185 °C (ref. [1] *m.p.* 185 °C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 2.31 (s, 3H, 3''-H), 2.48 (s, 3H, 2'-H), 3.89 (s, 2H, 1'-H), 7.67 (d, J = 8.0 Hz, 1H, 3-H), 7.84–7.88 (m, 2H, 6-H and 7-H), 8.26–8.33 (m, 2H, 5-H and 8-H), 8.38 (d, J = 8.0 Hz, 1H, 4-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 30.55 (q, C-3''), 32.09 (q, C-2'), 47.52 (t, C-1''), 127.74 (d, C-4, C-5, C-8), 127.95 (d, C-4, C-5, C-8), 128.37 (d, C-4, C-5, C-8), 131.01 (s, C-8a, C-10a), 133.22 (s, C-8a, C-10a), 133.38 (2 s, C-4a, C-9a), 134.89 (d, C-6, C-7), 135.09 (d, C-6, C-7), 137.22 (d, C-1, C-2), 137.57 (d, C-3), 143.81 (s, C-1, C-2), 182.68 (s, C-9, C-10), 183.77 (s, C-9, C-10), 204.5 (s, C-2''), 206.88 (s, C-1').

Procedure B

A solution of olefin **9** (200 mg, 0.52 mmol) and $NaIO_4$ (123 mg, 0.58 mmol) in 1,4-dioxane (60 mL) and water (50 mL) was treated with a solution of OsO_4 (0.1 mL of a 0.13M solution in water) until the starting material was completely converted (ca. 5 h, TLC control). Additional $NaIO_4$ (139 mg, 0.65 mmol) was added and the mixture was stirred again (5 h, TLC control). The mixture was poured into water, extracted with Et_2O (5 × each 50 ml), the combined organic phases were dried (Na_2SO_4), filtered, and the solvent was removed under reduced pressure at 40 °C. The residue was purified by column chromatography on silica gel (petroleum ether/AcOEt: 1/1) to afford **10** (157 mg, 78%) as yellow crystals.

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