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The Cobalt Way to Angucyclinones: Asymmetric Total Synthesis of the Antibiotics (+)-Rubiginone B_2, (−)-Tetrangomycin, and (−)-8-*O*-Methyltetrangomycin

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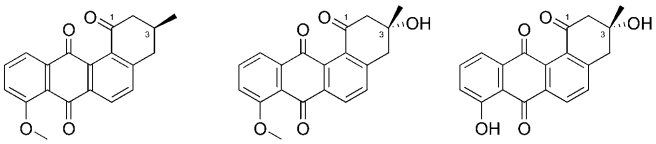
Abstract: A cobalt(I)-mediated convergent and asymmetric total synthesis of angucyclinones with an aromatic B ring has been developed. In the course of our research, we synthesized three naturally occurring anguclinone derivatives, namely, (+)-rubiginone B_2 (**1**), (−)-8-*O*-methyltetrangomycin (**2**), and (−)-tetrangomycin (**3**). By combining 3-hydroxybenzoic acid, 3-methoxybenzoic acid, citronellal, and geraniol as starting materials in a convergent way, we were able to synthesize chiral triyne chains, which were cyclized with $[CpCo(C_2H_4)_2]$ (Cp = cyclopentadienyl) by means of an intramolecular [2+2+2] cycloaddition to their corresponding tetrahydrobenzo[*a*]anthracenes. Successive oxidation and deprotection steps led to the above-mentioned natural products **1**–**3**.

Keywords: angucyclinone · catalysis · cobalt · cycloaddition · natural products

Introduction

Angucycline antibiotics have stimulated great interest because of their wide range of biological properties such as antitumor, antibiotic, and anti-HIV activity.[1,2] The angucyclinones represent a group of angucyclines that show the same angular, quinoide aglycon, but differ in their sugar moieties. A characteristic feature of the angucyclines is the existence of at least one *O*-glycosidic bonded sugar, whereas the angucyclinones usually have none or so-called 'noncleavable' *C*-glycosidic bonded sugars. Among this simpler group are, for example, the tetrangomycins **2** and **3**, and the rubiginones such as **1**. The rubiginones A_1, A_2, B_1, B_2, C_1, and C_2, which were isolated by Oka et al.,[3] are secondary microbial metabolites produced by the strain *Streptomyces griseorubiginosus* Q144-2. All of these antibiotics have been shown to potentiate the cytotoxicity of the chemotherapeutic agent vincristine against vincristine resistent P 388 leukaemia and human Moser cells in vitro as well as in vivo. The most active member of this group is rubiginone B_1, which can easily be obtained from rubiginone B_2 (**1**). Its mode of action was studied by Hamagishi et al.,[4,5] who found that the effect was synergistic. Furthermore, he concluded that, in combination with cytotoxic agents, rubiginone B_1 and congeners could serve as efflux blockers (like verapamil) in cancer therapy for the treatment of a variety of protein-involved multi-drug-resistant tumor cells. Moreover, it was found that the rubiginones can potentiate the cytotoxicity of colchicine against colchicine resistant cancer kB cell lines in vitro.[6] However, the naturally occurring rubiginones show no potentiation effect on doxorubicin.

From the synthetical point of view, the stereogenic center in the C3 position of the aglyca in the nonaromatic A ring, which is a widespread feature of the angucyclines, is one of the major challenges. In addition to our approach, other



(+)-Rubiginone B_2 (**1**) (-)-8-*O*-Methyltetrangomycin (**2**) (-)-Tetrangomycin (**3**)

methods have already successfully been applied for the total synthesis of angucyclinones to yield the natural products in moderate to excellent optical purity. Therefore it is necessary to mention the groups of Krohn,[7–11] Suzuki,[12,13] Larsen,[14–17] and Sulikowski,[18–21] all of whom considerably

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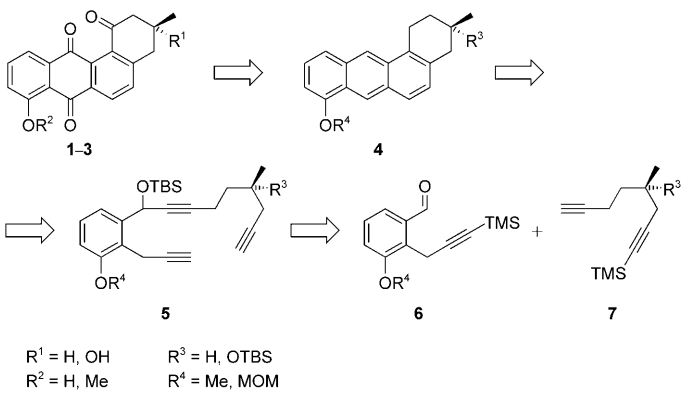
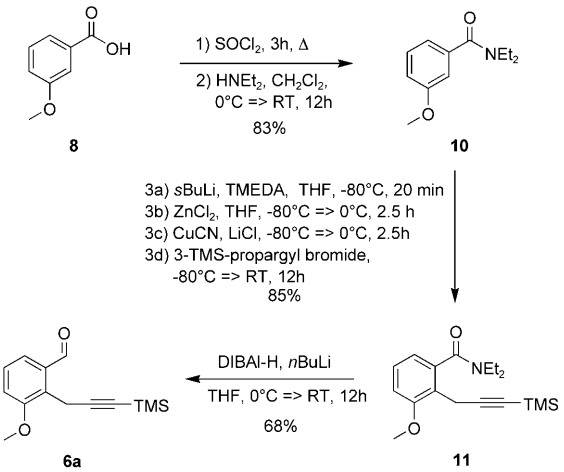
contributed to the research work done in the field of natural product synthesis. Whereas all of these groups focused their research on creating building blocks for an intermolecular Diels–Alder reaction, we decided to choose another approach. Our synthetic approach towards enantiomerically pure (+)-rubiginone B_2 (**1**), (−)-8-*O*-methyltetrangomycin (**2**), and (−)-tetrangomycin (**3**) is demonstrated in the following retrosynthetic analysis (Scheme 1).



Scheme 1. Retrosynthetic analysis of (+)-rubiginone (**1**), (−)-8-*O*-methyltetrangomycin **2**, and (−)-tetrangomycin **3**.

boxylic acid **8** with thionyl chloride (Scheme 2) followed by transfer into the respective amide **10** with diethylamine. This amide was alkylated by *ortho* metalation with *sec*-butyllithium and a twofold transmetalation into a so-called 'Knochel-cuprate',[23] which was reacted with 3-trimethylsilylpropargyl bromide. Without transmetalation of the lithiated



Scheme 2. Synthesis of benzaldehyde **6a**.

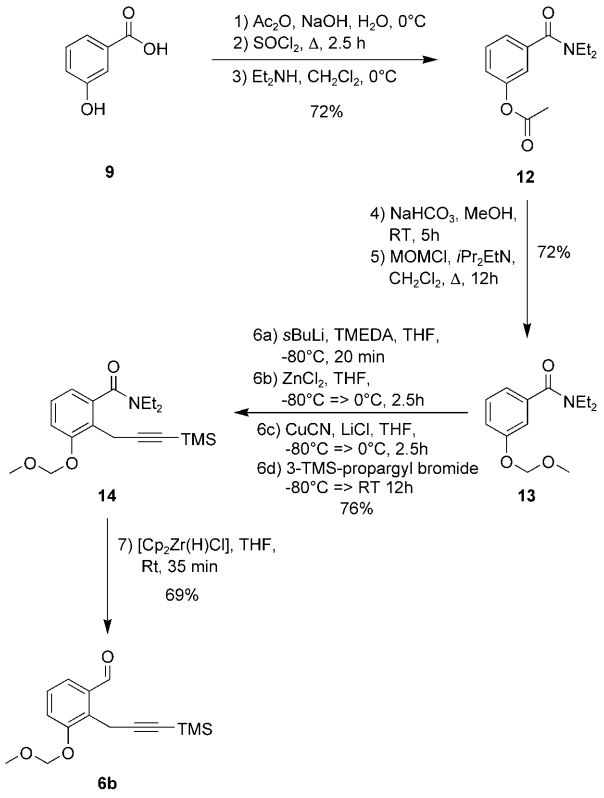
This highly convergent synthetic strategy is based on an intramolecular catalytic [2+2+2] cycloaddition[22] of a triyne following an A→ABCD approach.[22i,l] The A-ring building block **6** and the side chain **7** were synthesized independently and connected with each other during a very late stage of the synthesis to triyne **5**. Cobalt-catalyzed [2+2+2] cycloaddition to **4**, spontaneous aromatization, anthracene oxidation, and finally photooxidation at C1 should afford (+)-rubiginone B_2 (**1**), (−)-8-*O*-methyltetrangomycin (**2**), and (−)-tetrangomycin (**3**).

The major advantages of our methodology are 1) the complete regioselectivity during the [2+2+2] cycloaddition as a result of the intramolecular mode of the reaction, 2) the configurative stability of the asymmetric center under the conditions of a cobalt(I)-mediated reaction, and 3) a high tolerance of functional groups inside the triyne as long as the reactivity of the acetylene groups are not affected. By employing this method, we are able to synthesize natural products of the angucyclinone family with an exceptionally high enantiomeric purity regarding the C3 center of the A ring.

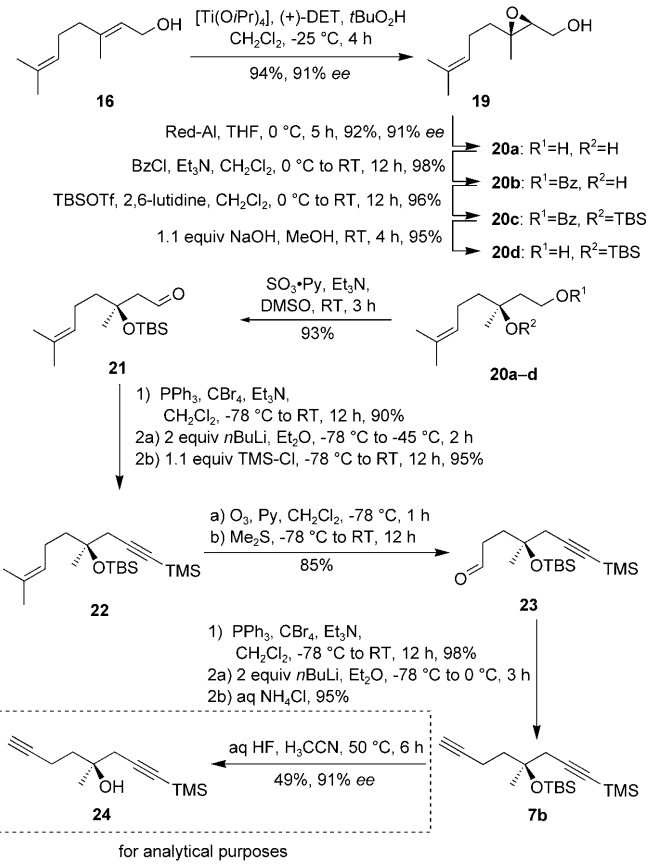
Results and Discussion

Preparation of 2,3-disubstituted benzaldehydes 6a and 6b: The main starting material for the synthesis of the benzaldehydes **6a** and **6b** was 3-methoxybenzoic acid (**8**) or 3-hydroxybenzoic acid (**9**), respectively, in the case of the (−)-tetrangomycin synthesis. The synthesis of the methoxy derivative **6a** (R^4 = Me) was conducted by chlorination of the carbenzamide into its cuprate, it was impossible to isolate any desired product. The resulting alkylated amide **11** was reduced to the respective benzaldehyde **6a** following a one-pot procedure developed by Kim et al.[24] (Scheme 2). Therefore, the 'ate'-complex was used; it was obtained by mixing diisobutylaluminum hydride (DIBAl-H) with equimolar amounts of *n*-butyllithium in THF at 0 °C, thus leading to benzaldehyde **6a**, a main building block for the synthesis of (+)-rubiginone B_2 (**1**) and (−)-8-*O*-methyltetrangomycin (**2**).

For the second benzaldehyde, **6b** (R^4 = methoxymethyl ether (MOM)), the synthesis had to be changed to introduce the MOM protecting group (Scheme 3). Starting with 3-hydroxybenzoic acid (**9**), the phenolic hydroxy group was protected with acetic acid anhydride, which first led to 3-acetoxybenzoic acid.[25] After chlorination and further conversion into the corresponding amide with diethylamine, *N,N*-3-acetoxydiethyl amide (**12**) was isolated. Deprotection of the phenolic hydroxy group with sodium bicarbonate in methanol afforded the 3-hydroxybenzamide, which was converted into the MOM acetale **13** by reaction with MOM-Cl and diisopropylethylamine in dichloromethane heated at reflux. The resulting benzamide **13** was alkylated following the procedure described before for the synthesis of **11**. Unfortunately, the subsequent reduction of the alkylated amide **14** by applying the 'ate'-complex led to no measurable amount of aldehyde **6b**. Thus, several reduction methods for benzamides were tested, whereby the use of the Schwartz reagent $[Cp_2Zr(H)Cl]$[26,27] (Cp = cyclopentadienyl) showed the highest yields under comparably mild conditions. Reduction with the Schwartz reagent was performed at room tem-



Scheme 3. Synthesis of benzaldehyde **6b**.

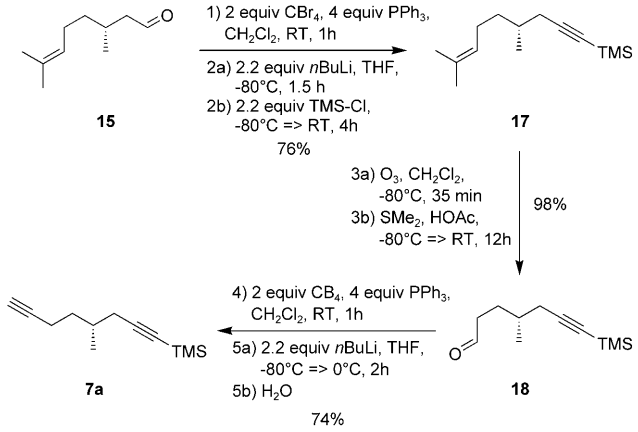


Scheme 5. Preparation of **7b**.

perature in THF and showed relatively short reaction times of about 35–40 min also in scaled-up experiments. After a short-column filtration, the analytically pure benzaldehyde **6b** was obtained in a yield of 69% (Scheme 3).

Preparation of the diynes 7a and 7b: Diynes **7a** and **7b**—the second building blocks—were prepared starting from the natural products citronellal (**15**) (Scheme 4) and geraniol (**16**) (Scheme 5), respectively.

For the synthesis of diyne **7a** (R^3=H), we started from the commercially available natural product citronellal (**15**), which can be isolated from rose oil in its natural form. The enantiomeric excess of the starting material was confirmed to be 94% *ee* by comparison of the measured values with the values known from literature.[28,29] Starting with the synthesis of **7a** (Scheme 4), we employed the Corey–Fuchs reaction[30] to transform aldehyde **15** into its geminal dibromide. Elimination with a surplus of *n*-butyllithium in THF led to a lithiated alkyne, which was quenched with trimethylsilyl chloride, thereby leading to the trimethylsilyl (TMS)-protected enyne **17**. Subsequent ozonolysis of **17** in dichloromethane at −80°C yielded aldehyde **18** after acidic workup with dimethylsulfide and acetic acid. A final Corey–Fuchs reaction followed by an elimination reaction with *n*-butyllithium and final aqueous workup led to the desired diyne **7a**.



Scheme 4. Preparation of the diyne **7a**.

For the synthesis of diyne **7b** (R^3=OTBS (TBS=*tert*-butyldimethylsilyl)), we had to follow a more complicated route to achieve our desired side chain. Therefore, we started from the natural product geraniol (**16**) (Scheme 5), which is also a part of rose oil. With geraniol as the starting material, we began the synthesis with a catalytic asymmetric epoxidation following the original literature of Sharpless et al.,[31] which yielded epoxy alcohol **19** in 94% yield and with an enantiomeric excess of 91% *ee*. During our work on the synthesis of diyne **7b**, it could be shown that raising the amount of the catalytically active titanium complex from 5

to 10% led to more reproducible results with regards to the enantiomeric excess without an influence on the chemical yield. The second step in our synthetic pathway to **7b** was a reductive ring opening with sodium bis(methoxyethoxy)aluminumhydride (Red-Al). This reaction was conducted according to another procedure published by Sharpless et al.,[32] whereby diole **20a** was isolated after aqueous workup. Due to the fact that three different rotation values for compound **20** exist in the literature, we measured its enantiomeric excess by means of gas chromatography with the aid of a chiral GC column. Afterwards, diole **20a** was subjected to a three-step protection/deprotection sequence to get the mono-protected diole **20d**. The primary hydroxy function was thereby esterified with benzoyl chloride in dichloromethane first, followed by silylation of the tertiary hydroxy function with TBS triflate and 2,6-lutidine in dichloromethane. The third and last step of the sequence was the cleavage of the ester function with sodium hydroxide in methanol at room temperature. The mono-protected diole **20d** was then transformed into the respective aldehyde **21** by a so-called Parikh–Doering oxidation,[33,34] a Swern-analogue reaction with a sulfur trioxide–pyridine complex and dimethylsulfoxide as reagents. With aldehyde **21** in hand, we had a compound comparable to citronellal (**15**; Scheme 4), which was suitable for the synthesis of diyne **7b**. Unfortunately, we noticed that with the introduction of R^2=OTBS the reactivity of aldehyde **21** changed tremendously. By applying standard Corey–Fuchs conditions as we used for the synthesis of **7a**, it was not possible to convert aldehyde **21** into its geminal dibromide. The addition of triethylamine and conduction of the reaction at −80°C enabled us to transfer the aldehyde into the dibromide. Elimination with a small excess amount of *n*-butyllithium in THF and quenching with TMS-Cl led to the TMS-protected enyne **22**. Ozonolysis of enyne **22** under basic conditions with pyridine as cosolvent afforded aldehyde **23** after workup with dimethylsulfide. It is remarkable to note that in the case of the ozonolysis due to the OTBS group under standard conditions without pyridine, the yield of **23** was much lower. By the addition of pyridine, we were able to increase the yield up to 85%. Under modified Corey–Fuchs conditions with Et_3N as described before and an elimination reaction with *n*-butyllithium, aldehyde **23** was converted into the substituted octadiyne **7b**.

After optimization of this sequence, we were able to synthesize octadiyne **7b** in an overall yield of 49% over 11 linear steps. To ensure the enantiomeric purity, we decided to cleave the tertiary TBS group (Scheme 5) to measure the enantiomeric excess of the monoprotected octadiyne **24** by means of chiral gas chromatography in comparison with the racemic octadiyne *rac*-**24**, which was synthesized from 5-hexynone and a Grignard reagent prepared from 3-TMS-propargyl bromide. As a result of this comparative measurement, we could show that the enantiomeric excess was unchanged and remained at 91% *ee*.

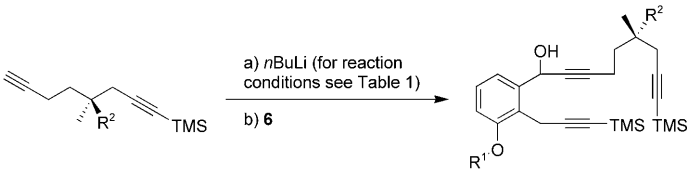
Preparation of the triynes 5: With benzaldehydes **6** and octadiynes **7** in hand, we could now combine benzaldehyde **6a** with both diynes **7a** and **b** and benzaldehyde **6b** with octadiyne **7b**. By combining these building blocks, we were able to accomplish the total syntheses of three different naturally occurring antibiotics: (+)-rubiginone B_2 (**1**), (−)-8-*O*-methyltetrangomycin (**2**), and (−)-tetrangomycin (**3**).

We started with the addition of the lithiated octadiyne **7a** to benzaldehyde **6a**. For this addition reaction, octadiyne **7a** was dissolved in THF, cooled to −80°C, and then treated with *n*-butyllithium. The deprotonated octadiyne was then stirred for 50 min, whereby the temperature increased slightly to −40°C. After cooling the solution again to −80°C, it was transferred into another flask containing a solution of the aldehyde **6a** in THF at −80°C. The combined solutions were stirred for 2 h until the solution reached a temperature of 0°C, whereupon an aqueous workup followed. When the same reaction was conducted with **6a** and **7b**, the yield was much lower. This problem was solved by adding boron trifluoride etherate to the solution of the aldehyde to increase the reactivity of the carbonyl group. When benzaldehyde **6b** and octadiyne **7b** were finally brought to reaction, we again had the problem of very poor yields. Due to the fact that the addition of strong Lewis acids to acetals is often problematic, we decided to search for another solution. The best way to increase the reactivity without adding a Lewis acid was to raise the reaction temperature. By conducting the addition reaction at −15°C we were able to achieve a yield of 93% for this coupling reaction (Table 1).

Through this method, we could build up the terminally protected triynes **25** (Scheme 6). However, these were not suitable for the cobalt-mediated [2+2+2] cycloaddition in this form. Therefore, we had to deprotect the terminal ace-

Table 1. Reaction conditions for the addition of octadiynes **7** to aldehydes **6.**

Entry	Octadiyne	Aldehyde	Reaction conditions	Yield [%]
1	**7a** (R^2=H)	**6a** (R^1=Me)	a) *n*BuLi, THF, −80°C→−30°C, 1 h b) **6a**, THF, −80°C→RT, 4 h	98
2	**7b** (R^2=OTBS)	**6a** (R^1=Me)	a) *n*BuLi, Et_2O, −80°C→−30°C, 1 h b) **6a**, BF_3•Et_2O, Et_2O, −80°C→RT, 2 h	70
3	**7b** (R^2=OTBS)	**6b** (R^1=MOM)	a) *n*BuLi, THF, −80°C→−30°C, 1 h b) **6b**, Et_2O, −15°C, 1 h	93

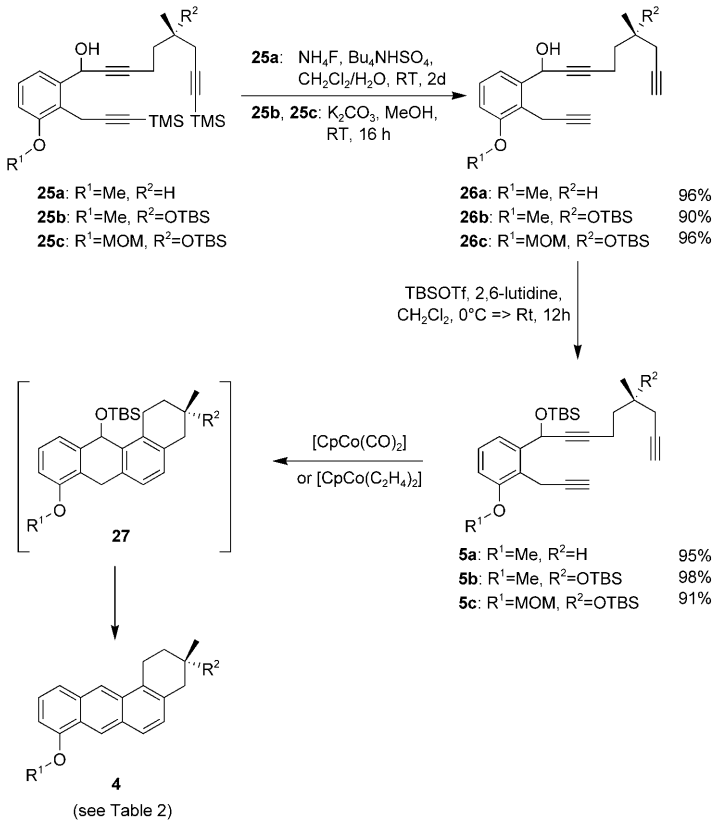


7 **25**

R^1 = Me, MOM
R^2 = H, OTBS

Scheme 6. Addition of octadiynes **7** to aldehydes **6**.

tylenes and to protect the free hydroxy functionality (Scheme 7). Thus, we first removed the trimethylsilyl groups from the acetylenic groups. In the case of the rubiginone B_2



Scheme 7. Preparation of the tetrahydrobenzo[*a*]anthracenes **4**.

precursor **25a**, we used ammonium fluoride in a two-phase system of water and dichloromethane for this reaction. In the cases in which a TBS-protected tertiary alcohol was present (**25b** and **c**) we used potassium carbonate in methanol to remove the terminal TMS groups without affecting the TBS group.

The second step to accomplish the precursor synthesis was to protect the secondary alcohol with *tert*-butyldimethylsilyltrifluoromethanesulfonate (OTBSTf). For this reaction, the triynes **26** were dissolved in dichloromethane together with 2,6-lutidine, cooled to 0 °C, and OTBSTf was slowly added with a syringe. After aqueous workup and column chromatography, we obtained analytically pure triynes **5**, the starting material for the [2+2+2] cycloaddition.

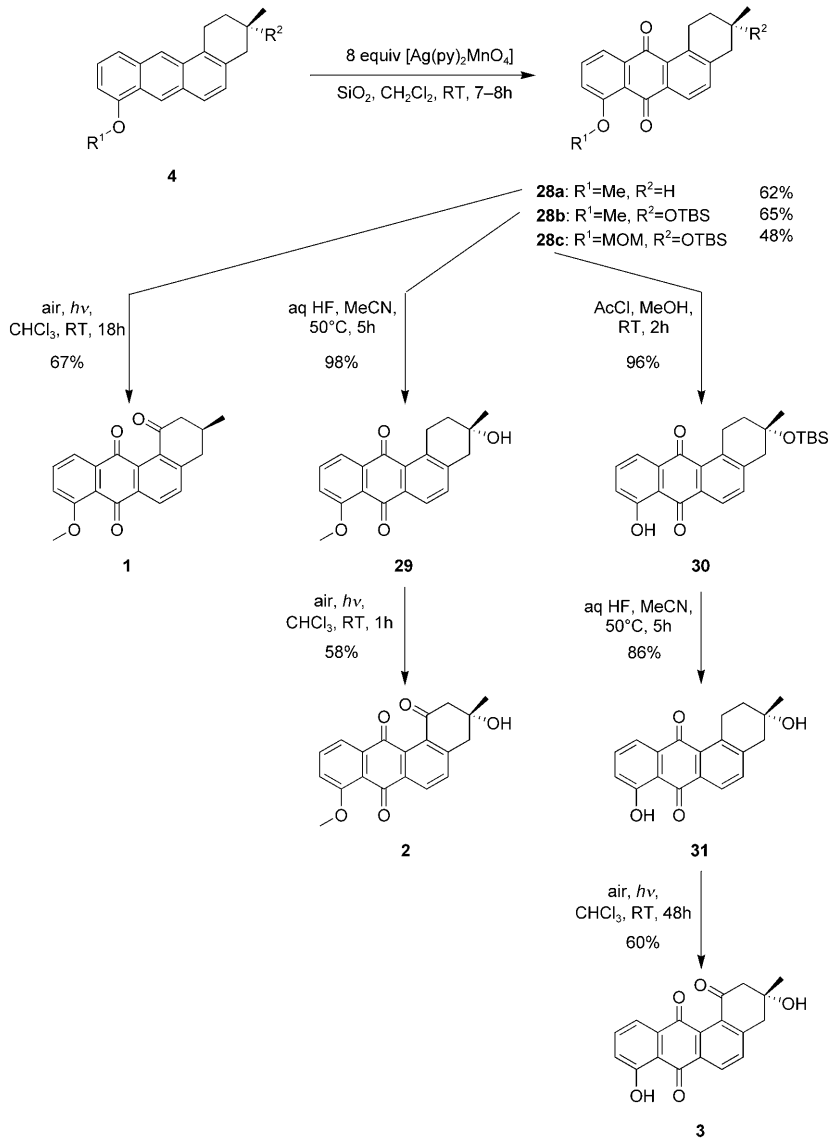
The cobalt-mediated [2+2+2] cycloaddition of triynes **5a–c** was tested and performed under various conditions using $[CpCo(CO)_2]$ and $[CpCo(C_2H_4)]$ as catalysts (Table 2). Whereas the cycloaddition of **5a** with catalytic amounts of either the carbonyl complex or the ethene complex gave excellent yields, triyne **5b** afforded only low yields under these conditions. In the case of **5b** and **5c**, only stoichiometric amounts of the cobalt–ethene yielded the tetrahydrobenzo[*a*]anthracene in good yields. We observed that, under the

Table 2. Cobalt-mediated [2+2+2]-cycloaddition of triynes **5**.

Entry	Triyne	Catalyst Type	Amount [mol %]	Reaction conditions	Yield [%]
1	**5a**	$[CpCo(CO)_2]$	5	*hν*, toluene, reflux, 4 h	61
2	**5a**	$[CpCo(CO)_2]$	10	*hν*, toluene, reflux, 4 h	74
3	**5a**	$[CpCo(C_2H_4)_2]$	5	Et_2O, −80 °C→0 °C, 4 h	76
4	**5b**	$[CpCo(CO)_2]$	10	slow addition of the catalyst, *hν*, toluene, reflux, 40 h	23
5	**5b**	$[CpCo(CO)_2]$	20	slow addition of the catalyst, *hν*, toluene, reflux, 8 h	44
6	**5b**	$[CpCo(CO)_2]$	20	*hν*, toluene, reflux, 4 h	31
7	**5b**	$[CpCo(CO)_2]$	40	*hν*, toluene, reflux, 4 h	38
8	**5b**	$[CpCo(CO)_2]$	100	*hν*, toluene, reflux, 4 h	58
9	**5b**	$[CpCo(C_2H_4)_2]$	40	Et_2O, −80 °C→0 °C, 4 h acidic workup	45
10	**5b**	$[CpCo(C_2H_4)_2]$	100	Et_2O, −80 °C→0 °C, 4 h acidic workup	80
11	**5c**	$[CpCo(CO)_2$	100	*hν*, toluene, reflux, 4 h	38
12	**5c**	$[CpCo(C_2H_4)_2]$	100	Et_2O, −60 °C→0 °C, 4 h	93

reaction conditions given for the cyclization with the biscarbonyl complex, we could only isolate the aromatic tetrahydrobenzo[*a*]anthracenes **4**. In contrast, after cyclization with the bis-ethene complex, we isolated a mixture of the aromatic products **4** and the direct cyclization products **27** with a OTBS group situated at the C12 position. By choosing an acidic workup with acetic acid, we were able to convert the primer cyclization products **27** into the desired aromatic tetrahydrobenzo[*a*]anthracenes **4**.[22i]

Afterwards, the aromatic systems were oxidized with a silver permanganate complex to their corresponding tetrahydrobenzo[*a*]anthraquinones.[35] The oxidation was accomplished in dichloromethane at room temperature with a huge excess amount of oxidant mixed thoroughly with silica gel prior to use. As a typical workup, the brown suspension was filtered, whereby an intensive yellow solution was obtained. This solution was concentrated in vacuo and the resulting solid was purified by means of flash column chromatography over silica gel to give the pure compounds **28** in 48–65 % yield. At this stage, the reaction pathway split (Scheme 8). Whereas the rubiginone B_2 precursor **28a** was directly converted into the natural product **1** by photooxidation with light and air,[36] compounds **28b** and **28c** had to be deprotected before they could be oxidized to their corresponding natural products. Compound **28b** was deprotected with hydrofluoric acid in acetonitrile to lead to compound **29**, which was subsequently oxidized to **2** following the procedure given for the photooxidation to **1**. For the synthesis of **3** from compound **28c**, two different deprotection steps



Scheme 8. Synthesis of the antibiotics (+)-rubiginone B_2 (**1**), (−)-8-*O*-methyl-tetrangomycin (**2**), and (−)-tetrangomycin (**3**).

were necessary. At first we removed the MOM group in position C8 with acetyl chloride in dry methanol for an excellent yield of 96%. The resulting monoprotected compound **30** was treated with hydrofluoric acid in acetonitrile at elevated temperatures to remove the TBS group. By this means, we obtained **31** as precursor for the synthesis of the natural product **3**. Successful photooxidation in chloroform with a tungsten lamp in air afforded natural product **3** in a yield of 60% and with an enantiomeric excess of 91% *ee*. Noticeable are the differences in reaction time for the photooxidation between the different natural products. Whereas oxidation of **29** needed only 1 h, oxidation of **28a** took 18 h, and oxidation of **31** even 48 h, whereas the yields of the different photooxidations are in the same range.

Conclusion

In the end, we were able to complete the synthesis of three representative members of the angucyclinone natural product class. (+)-rubiginone B_2 (**1**) has been synthesized in 15 steps (longest linear synthesis sequence was 11 steps) with an overall yield of 15% and an enantiomeric excess of 92% *ee*. (−)-8-*O*-methyltetrangomycin (**2**) was synthesized in 22 steps, whereby the longest linear sequence had 18 steps, in 9% overall yield and an enantiomeric excess of 91% *ee*. And, finally, (−)-tetrangomycin (**3**) has been obtained by a synthesis containing 26 steps (19 linear steps); it afforded the product in 9% overall yield and with an enantiomeric excess of 90% *ee*.

Experimental Section

General remarks: Infrared (IR) spectra were obtained using a Perkin–Elmer 1600 spectrometer. NMR spectra were obtained using a JEOL 400 GX JNM or a Bruker Advance DRX 600 spectrometer for ^{1}H and ^{13}C NMR spectroscopy. Chemical shifts are given in parts per million (δ) using tetramethylsilane as internal standard for ^{1}H and ^{13}C NMR spectroscopy. Mass spectra were recorded using a Varian MAT 312 spectrometer. GC–MS analyses were recorded using an HP-6890 GC system with an HP 5973 MSD. HPLC analyses were performed using a MERCK/HITACHI L4000 HPLC system with UV detection at 254 nm. Optical rotations were measured using a Perkin–Elmer Mod. 241 MC polarimeter. The melting points were measured in open capillary tubes using a Gallenkamp melting-point apparatus and are not corrected. TLC analyses were performed using Polygram Sil G/UV_{254} silica gel plates (Macherey & Nagel). Merck silica gel 60 (0.040–0.063 mm, 230–400 mesh) was used for flash chromatography. Combustion analyses were carried out by the microanalytical laboratory of the University of Konstanz. All reactions were carried out under an argon atmosphere except those involving hydrolysis. All reagents were purified and dried if necessary before use.

***N,N*-Diethyl-3-methoxybenzamide (10)**: 3-Methoxybenzoic acid (31.4 g, 0.206 mol) was heated to reflux in thionyl chloride (65 mL) for 3 h. Completion of the reaction was controlled by TLC. The excess amount of thionyl chloride was removed by distillation. The residue was dissolved in dichloromethane (100 mL). Diethylamine (40.4 mL, 0.392 mol) in dichloromethane (150 mL) was added dropwise to this solution and was stirred overnight at room temperature. For workup, the solution was di-

luted with dichloromethane (250 mL) and poured into an aqueous $NaHCO_3$ solution (300 mL). Phases were separated, the organic layer was washed with HCl (1 M, 300 mL) and water (300 mL), dried over $MgSO_4$, and concentrated in vacuo, thereby providing **10** (35.8 g, 0.173 mol, 84 %). B.p. 123 °C (1 mbar); R_f = 0.18 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (m, 3H; $-CH_3$), 1.25 (m, 3H; $-CH_3$), 3.25 (m, 2H; $-CH_2-$), 3.54 (m, 2H; $-CH_2-$), 3.82 (s, 3H; $-OCH_3$), 6.92 (m, 3H; H2, H3, H5), 7.30 ppm (t, ^3J(H,H) = 8.2 Hz, 1H; H4); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8 and 14.1 (2×$-CH_3$), 39.0 and 43.1 (2×$-CH_2-$), 55.2 ($-OCH_3$), 111.5, 114.8, 118.2, 129.4 (CH arom.), 138.4 (C1), 159.4 (C3), 170.8 ppm (C=O).

3-Acetoxybenzoic acid: 3-Hydroxybenzoic acid (100.0 g, 0.724 mol) was dissolved in a solution of sodium hydroxide (96.1 g, 0.796 mol) in distilled water (400 mL) at room temperature. After the acid had been dissolved completely, ice (500 g) was added and stirred vigorously for 10 min. Acetic anhydride (88 mL, 0.94 mol) was quickly added in one portion to this water/ice mixture, and the reaction mixture stirred overnight at ambient temperature. The aqueous solution was extracted with diethyl ether (3×250 mL). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo to provide colorless crystals (97.4 g, 0.541 mol, 75 %). M.p. 114 °C; R_f = 0.35 (petroleum ether/diethyl ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H; CH_3), 7.38 (d, ^3J(H,H) = 7.8 Hz, 1H; H4), 7.53 (t, ^3J(H,H) = 7.8 Hz, 1H; H5), 7.66 (s, 1H; H2), 7.82 ppm (d, ^3J(H,H) = 7.8 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 ($-CH_3$), 122.8 (C2), 126.5 (C4), 126.8 (C6), 129.9 (C5), 132.3 (C1), 150.6 (C3), 166.6 ($-CO_2H$), 169.3 ppm ($-COCH_3$); IR (CCl_4): $\tilde{\nu}$ = 3711.5 (w), 3608.9 (w), 3538.4 (w), 3079.7 (m), 3018.7 (m), 2888.1 (m), 2674.3 (m), 2559.2 (m), 1773.9 (s), 1745.3 (m), 1700.4 (s), 1589.1 (s), 1489.2 (m), 1452.7 (s), 1414.3 (m), 1369.6 (s), 1302.2 (s), 1288.1 (s), 1269.7 (s), 1200.0 (s), 1106.8 (w), 1076.8 (w), 1012.7 (m), 942.1 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 180 (11.4) [M^+], 163 (0.8), 140 (1), 139 (8), 138 (100) [M^+-Ac], 122 (3), 121 (42) [M^+-OAc], 110 (1), 93 (8), 81 (3), 66 (1), 65 (7), 63 (7), 53 (3), 50 (1); elemental analysis calcd (%) for $C_9H_8O_4$: C 60.00, H 4.48; found: C 59.11, H 4.68.

***N,N*-Diethyl-3-acetoxybenzamide (12)**: A suspension of 3-acetoxybenzoic acid (97.4 g, 0.541 mol) in thionyl chloride (180 mL) was heated at reflux for 4.5 h to give a colorless solution. Distillation (110 °C, 0.5 mbar) of the solution provided a colorless oil (105.3 g, 0.530 mol, 98 %). The benzoyl chloride was dissolved in absolute dichloromethane (500 mL), cooled to 0 °C, and treated dropwise with diethylamine (120 mL, 1.16 mol). The reaction mixture was stirred overnight while slowly warming to ambient temperature. The mixture was diluted with water (300 mL) and made acidic with hydrochloric acid (450 mL, 2 M). Phases were separated, and the aqueous layer was extracted with dichloromethane (2×300 mL). The combined organic layers were washed with brine (300 mL), dried over $MgSO_4$, and concentrated in vacuo. Drying the orange oil in vacuum (<0.1 mbar) provided pure **12** (122.0 g, 0.519 mol, 98 %). R_f = 0.15 (petroleum ether/diethyl ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (brs, 3H; $-CH_3$), 1.25 (brs, 3H; $-CH_3$), 2.30 (s, 3H; $-CH_3$), 3.28 (brs, 2H; $-NCH_2-$), 4.64 (brs, 2H; $-NCH_2-$), 7.15 (m, 2H; H2 and H4), 7.25 (d, ^3J(H,H) = 7.8 Hz, 1H; H6), 7.41 ppm (t, ^3J(H,H) = 7.8 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 ($-CH_3$), 14.0 ($-CH_3$), 21.0 ($-CH_3$), 39.2 and 43.2 (2×$-NCH_2-$), 119.7 (C2), 122.2 (C4), 123.5 (C6), 129.4 (C5), 138.3 (C1), 150.3 (C3), 169.0 ($-CONEt_2$), 169.9 ppm ($-COCH_3$); IR (CCl_4): $\tilde{\nu}$ = 3264.8 (w), 3073.1 (w), 2977.3 (s), 2936.9 (s), 2876.1 (m), 2360.8 (w), 1772.1 (s), 1635.6 (s), 1585.8 (s), 1490.1 (s), 1470.2 (s), 1456.7 (s), 1425.9 (s), 1382.7 (s), 1368.5 (s), 1348.8 (m), 1314.9 (s), 1290.4 (s), 1203.6 (s), 1157.1 (s), 1097.8 (s), 1079.0 (m), 1045.7 (w), 1015.0 (m), 1002.6 (m), 949.3 (m), 934.5 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 235 (48) [M^+], 234 (51), 220 (2), 206 (1), 194 (4), 193 (33), 192 (63) [M^+-Ac], 178 (1), 176 (2) [M^+-OAc], 165 (5), 164 (19), 163 (54) [M^+-NEt_2], 150 (3), 136 (1), 122 (13), 121 (100) [163−Ac], 120 (9), 107 (3), 94 (3), 93 (22), 92 (15), 76 (2), 72 (4), 65 (11), 64 (7), 63 (5), 56 (2); elemental analysis calcd (%) for $C_{13}H_{17}NO_3$: C 66.36, H 7.28, N 5.95; found: C 65.25, H 7.73, N 6.79.

***N,N*-Diethyl-3-hydroxybenzamide**: A saturated $NaHCO_3$ solution (250 mL) was added to a solution of **12** (46.4 g, 0.197 mol) in methanol (400 mL) and stirred for 5 h at room temperature until no starting material was detected by TLC. The reaction mixture was extracted with diethyl ether (3×300 mL). The combined organic layers were washed with brine (300 mL), dried over $MgSO_4$, and concentrated in vacuo. The viscous brown oil was dissolved in boiling ethyl acetate (100 mL) and cooled overnight in a refrigerator to provide colorless crystals (27.8 g, 0.144 mol, 73 %). M.p. 84 °C; R_f = 0.09 (petroleum ether/diethyl ether 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (t, ^3J(H,H) = 6.6 Hz, 3H; $-CH_3$), 1.23 (t, ^3J(H,H) = 6.6 Hz, 3H; $-CH_3$), 3.25 (q, ^3J(H,H) = 6.6 Hz, 2H; $-NCH_2-$), 3.53 (q, ^3J(H,H) = 6.6 Hz, 2H; $-NCH_2-$), 6.76 (m, 2H; H4 and H6), 6.85 (s, 1H; H2), 7.13 (t, ^3J(H,H) = 7.8 Hz, 1H; H5), 8.76 ppm (brs, 1H; Ar−OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 ($-CH_3$), 14.0 ($-CH_3$), 39.5 ($-NCH_2-$), 43.5 ($-NCH_2-$), 114.0 (C2), 116.8 (C4), 117.1 (C6), 129.4 (C5), 137.0 (C1), 157.1 (C3), 172.1 ppm (*C*ONEt$_2$); IR (CCl_4): $\tilde{\nu}$ = 3606.6 (w), 3237.2 (br m), 3072.0 (m), 2979.0 (m), 2937.7 (m), 2876.3 (m), 1613.1 (s), 1592.0 (s), 1509.6 (m), 1506.5 (m), 1475.4 (s), 1446.7 (s), 1383.1 (m), 1366.1 (m), 1349.1 (m), 1314.8 (s), 1294.4 (s), 1262.2 (m), 1232.2 (m), 1219.5 (m), 1177.8 (m), 1158.8 (m), 1102.1 (m), 1079.8 (w), 1070.2 (w), 1012.6 (w), 998.9 (w), 949.7 (w), 927.1 cm^{-1} (w); MS (GC–MS): *m*/*z* (%): 194 (4), 193 (30) [M^+], 192 (53), 164 (6), 122 (9), 121 (100) [M^+-NEt_2], 120 (3), 107 (1), 94 (2), 93 (19) [121−CO], 92 (3), 72 (3), 66 (1), 65 (11), 64 (2), 63 (2), 56 (1), 53 (1); elemental analysis calcd (%) for $C_{11}H_{15}NO_2$: C 68.37, H 7.82, N 7.25; found: C 67.93, H 7.76, N 7.13.

***N,N*-Diethyl-3-methoxymethoxybenzamide (13)**: Diisopropylethylamine (44 mL, 0.263 mol) and MOM-Cl (14.4 mL, 0.193 mol) were added consecutively to a solution of *N,N*-diethyl-3-hydroxybenzamide (33.9 g, 0.175 mol) in absolute dichloromethane (500 mL) by means of a dropping funnel at room temperature. The reaction mixture was left at reflux for 12 h whereupon the colorless solution turned orange. The reaction was quenched by the addition of a half-concentrated $NaHCO_3$ solution (300 mL) and vigorous stirring for 3 min. Phases were separated, and the aqueous layer was extracted with dichloromethane (2×50 mL). The combined organic layers were washed with brine (300 mL), dried over $MgSO_4$, and concentrated in vacuum. Chromatography (petroleum ether/diethyl ether 1:2) of the residue, an orange oil, provided a colorless oil (40.7 g, 0.172 mol, 98 %). R_f = 0.32 (petroleum ether/diethyl ether 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (brs, 3H; $-CH_3$), 1.08 (brs, 3H; $-CH_3$), 3.09 (brs, 2H; $-NCH_2-$), 3.30 (s, 3H; $-OCH_3$), 3.36 (brs, 2H; $-NCH_2$), 5.02 (s, 2H; $-OCH_2-OCH_3$), 6.83 (d, ^3J(H,H) = 7.4 Hz, 1H; H4), 6.89 (m, 2H; H2 and H6), 7.14 ppm (t, ^3J(H,H) = 7.4 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 ($-CH_3$), 14.0 ($-CH_3$), 39.0 ($-NCH_2$), 43.1($-NCH_2-$), 55.8 ($-OCH_3$), 94.2 ($-OCH_2-OCH_3$), 114.0 (C2), 116.7 (C4), 119.4 (C6), 129.4 (C5), 138.4 (C1), 157.0 (C3), 170.6 ppm ($-CONEt_2$); IR (CCl_4): $\tilde{\nu}$ = 3263.2 (w), 3070.5 (m), 2974.1 (s), 2935.5 (s), 2900.5 (s), 2845.8 (m), 2837.3 (m), 2786.6 (w), 2360.7 (w), 2336.6 (w), 2073.8 (w), 2000.8 (w), 1930.8 (w), 1856.5 (w), 1771.8 (w), 1647.7 (s), 1609.4 (s), 1581.0 (s), 1489.4 (s), 1456.9 (s), 1382.2 (s), 1365.7 (s), 1348.7 (m), 1315.6 (s), 1289.9 (s), 1239.8 (s), 1220.7 (s), 1206.7 (s), 1151.9 (s), 1100.6 (s), 1982.7 (s), 1015.1 (s), 979.1 (m), 925.8 cm^{-1} (s); MS (GC–MS): *m*/*z* (%): 238 (8), 237 (54) [M^+], 236 (34), 208 (1), 207 (3), 206 (7), 193 (9), 192 (71) [$M^+-C_2H_5O$], 190 (1), 178 (2), 176 (3) [M^+ −OMOM], 166 (12), 165 (100) [M^+-NEt_2], 164 (20), 151 (1), 149 (3), 137 (4) [165−CO], 136 (2), 135 (12), 133 (3), 121 (16) [165−C_2H_5O], 120 (10), 107 (7), 105 (3), 104 (3), 93 (9) [137−C_2H_5O], 92 (15), 77 (6), 76 (7) [$C_6H_4^+$], 72 (5) [NEt_2^+], 65 (5), 64 (6), 63 (4), 45 (45); elemental analysis calcd (%) for $C_{13}H_{19}NO_3$: C 65.80, H 8.07, N 5.90; found: C 65.31, H 8.13, N 6.03.

General procedure for the synthesis of the alkylated benzamides 11 and 14: A solution of *sec*-BuLi (100.0 mL, 0.140 mmol, 1.4 M in cyclohexane) was added dropwise at −80 °C to a solution of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 19.0 mL, 0.126 mol) in THF (100 mL). After 30 min of stirring, a solution of the *N,N*-diethylbenzamide (0.120 mol) in THF (70 mL) was added dropwise at −80 C. After 90 min of stirring at −80 °C, a solution of $ZnCl_2$ (18.0 g, 0.132 mol) in THF (100 mL) was added through a cannula and the resulting mixture was allowed to warm to 0 °C under stirring. The reaction was again cooled to −80 °C and a solution of CuCN (11.8 g, 0.132 mol) and LiCl (11.2 g, 0.264 mol) in THF (150 mL) was added through a cannula. The mixture was allowed to warm to 0 °C, stirred for 10 min and cooled again to −80 °C. Then 3-tri-

methylsilylpropargyl bromide (25.2 g, 0.132 mol) was added dropwise, and the resulting mixture was slowly allowed to warm to room temperature over 18 h. Then the mixture was poured into half-saturated aqueous NH_4Cl (1 L). The organic layer was separated, and the aqueous phase was extracted with diethyl ether (5×350 mL). The combined organic layers were washed with brine (1 L), dried over $MgSO_4$, and concentrated in vacuum. Chromatography on silica gel (diethyl ether/petroleum ether 1:1) provided the alkylated benzamide as a yellow solid.

***N,N*-Diethyl-3-methoxy-2-(3-trimethylsilyl-prop-2-ynyl)benzamide (11)**: M.p. 73 °C; R_f=0.3 (diethyl ether/petroleum ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.09 (s, 9H; −TMS), 1.08 (t, ^3J(H,H)=7.8 Hz, 3H; $-CH_3$), 1.28 (t, ^3J(H,H)=7.8 Hz, 3H; $-CH_3$), 3.1–3.3 (m, 4H; 2×$-CH_2-$), 3.46 and 3.75 (2×d, ^2J(H,H)=16.8 Hz, 2H; H2′), 3.87 (s, 3H; $-OCH_3$), 6.80 (d, ^3J(H,H)=7.8 Hz, 1H; H4), 6.89 (d, ^3J(H,H)=7.8 Hz, 1H; H6), 7.24 ppm (t, ^3J(H,H)=7.8 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.01 (TMS), 12.5 and 13.8 ($-CH_3$), 17.1 (C1′), 38.6 and 43.2 (2×$-N$-CH_2-), 55.7 ($-OCH_3$), 83.3 (C3′), 104.2 (C2′), 111.0 (C4), 117.5 (C6), 121.6 (C2), 128.0 (C5), 138.2 (C1), 157.4 (C3), 169.8 ppm (C=O); IR (CCl_4): $\tilde{\nu}$=2172 (C≡C−Si), 1636 cm^{-1} (C=O); MS (EI, 70 eV): *m*/*z* (%): 317 (100) [M^+], 302 (67) [M^+-CH_3], 288 (36) [$M^+-C_2H_5$], 243 (61) [M^+−TMS], 229 (92) [$M^+-C_5H_{13}O$], 215 (18); elemental analysis calcd (%) for $C_{18}H_{27}NO_2Si$: C 68.09, H 8.57, N 4.41; found: C 68.13, H 8.71, N 4.41.

***N,N*-Diethyl-3-methoxymethoxy-2-(3-trimethylsilyl-prop-2-ynyl)benzamide (14)**: M.p. 60 °C (petroleum ether/diethyl ether); R_f=0.32 (petroleum ether/diethyl ether 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.05 (s, 9H; −TMS), 1.05 (t, ^3J(H,H)=7.4 Hz, 3H; $-CH_3$), 1.25 (t, ^3J(H,H)=7.4 Hz, 3H; $-CH_3$), 3.1–3.85 (m, 6H; 2×N$-CH_2-$ and H1′), 3.48 (s, 3H; $-OCH_3$), 5.19–5.26 (m, 2H; $-OCH_2-$OMe), 6.82 (d, ^3J(H,H)=7.4 Hz, 1H; H4), 7.07 (d, ^3J(H,H)=7.4 Hz, 1H; H6), 7.19 ppm (t, ^3J(H,H)=7.4 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$): δ=−0.06 (−TMS), 12.6 ($-CH_3$), 13.9 ($-CH_3$), 17.6 (C1′), 38.6 (N$-CH_2-$), 43.3 (N$-CH_2-$), 56.0 ($-OCH_3$), 83.6 (C3′), 94.0 ($-OCH_2-$OMe), 104.3 (C2′), 114.2 (C4), 118.6 (C6), 122.4 (C2), 128.0 (C5), 138.4 (C1), 155.0 (C3), 169.7 ($-C$ONEt$_2$); IR (CCl_4): $\tilde{\nu}$=2172.9 (−C≡C−Si), 1635.9 cm^{-1} (C=O); MS (GC-MS): *m*/*z* (%): 347 (93) [M^+], 332 (24) [M^+−Me], 316 (85) [M^+−OMe], 302 (49) [$M^+-C_2H_5O$], 286 (4) [M^+−OMOM], 275 (6) [M^+−NEt$_2$], 274 (25) [M^+−TMS], 246 (15) [M^+−CONEt$_2$], 243 (100) [274−MeOH], 215 (13) [286−NEt$_2$], 187 (11) [246−OMOM], 73 (26) [TMS$^+$]; elemental analysis calcd (%) for $C_{19}H_{29}NO_3Si$: C 65.67, H 8.41, N 4.03; found: C 65.41, H 8.34, N 3.98.

3-Methoxy-2-(3-trimethylsilyl-prop-2-ynyl)benzaldehyde (6a): A solution of *n*BuLi (5.1 mL, 8.14 mmol, 1.6 M in hexane) was added dropwise to a solution of diisobutylaluminum (DIBAL; 1.2 g, 8.14 mmol) in THF (30 mL) at 0 °C. After 30 min, a solution of amide **11** (2.6 g, 8.14 mmol) in THF (25 mL) was added with a cannula, and the resulting mixture was allowed to warm up slowly to room temperature over 18 h. The mixture was then poured into aqueous hydrochloric acid (0.5 M, 50 mL). The organic layer was separated and the aqueous phase was extracted with diethyl ether (3×100 mL). The combined organic layers were then extracted with brine (0.5 L), dried over $MgSO_4$, and concentrated in vacuo. Chromatography on silica gel (diethyl ether/petroleum ether 1:10) provided benzaldehyde **6a** (1.36 g, 5.54 mmol, 68%) as a yellow solid. M.p.=53 °C; R_f=0.55 (petroleum ether/diethyl ether 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.10 (s, 9H; −TMS), 3.90 (s, 3H; $-OCH_3$), 4.04 (s, 2H; H1′), 7.13 (d, ^3J(H,H)=8.2 Hz, 1H; H4), 7.38 (t, ^3J(H,H)=8.2 Hz, 1H; H5), 7.5 (d, ^3J(H,H)=8.2 Hz, 1H; H6), 10.46 ppm (s, 1H; −CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.01 (−TMS), 15.1 (C1′), 56.2 ($-OCH_3$), 85.0 (C3′), 104.6 (C2′), 116.6 (C4), 122.2 (C6), 127.51 (C2), 128.1 (C5), 134.80 (C1), 157.09 (C3), 191.91 ppm (−CHO); IR (CCl_4): $\tilde{\nu}$=2838 (m, $-OCH_3$), 2174 (m, −C≡C−Si), 1708 cm^{-1} (s, C=O); MS (EI, 70 eV): *m*/*z* (%): 246 (22) [M^+], 231 (58) [M^+-CH_3], 216 (24) [$M^+-C_2H_6$], 201 (18) [$M^+-C_3H_9$], 73 (100) [TMS$^+$]; elemental analysis calcd (%) for $C_{14}H_{18}O_2Si$: C 68.25, H 7.36; found: C 68.18, H 7.62.

3-Methoxymethoxy-2-(3-trimethylsilylprop-2-ynyl)benzaldehyde (6b): In a flame-dried Schlenk flask, the Schwartz complex ([CpZr(H)Cl]) (2.6 g, 10.1 mmol) was suspended under a nitrogen atmosphere in absolute THF (25 mL). A solution of the benzamide **14** (2.33 g, 6.7 mmol) in absolute THF (70 mL) was added quickly to this white suspension and stirred for 30–35 min until the white suspension turned into a clear yellow solution. The volume of the solution was then reduced to 5% of its original volume. The concentrated solution was transferred onto a prepacked column (silica gel) and purified with a mixture of petroleum ether/diethyl ether (3:1) as eluent to give a bright-brown oil (1.28 g, 4.6 mmol, 69% yield). R_f=0.63 (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.15 (s, 9H; −TMS), 3.57 (s, 3H; $-OCH_3$), 4.13 (s, 2H; H1′), 5.33 (s, 2H; $-OCH_2-$OMe), 7.42 (m, 2H; H4 and H6), 7.58 (t, ^3J(H,H)=4.4 Hz, 1H; H5), 10.43 ppm (s, 1H; −CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ=−0.1 (−TMS), 15.4 (C1′), 56.2 ($-OCH_3$), 84.8 (C3′), 94.7 ($-OCH_2-$OMe), 104.5 (C2′), 120.0 (C4), 124.3 (C6), 128.1 (C2), 128.4 (C5), 134.8 (C1), 155.0 (C3), 191.8 ppm (−CHO); IR (CCl_4): $\tilde{\nu}$=2175.0 (−C≡C−Si), 1707.8 cm^{-1} (−CHO); MS (GC–MS): *m*/*z* (%): 276 (29) [M^+], 246 (11) [M^+-H_2CO], 245 (29) [M^+−OMe], 244 (100) [M^+−MeOH], 231 (24) [$M^+-C_2H_5O$], 217 (7) [246−OMe], 215 (8) [M^+−OMOM], 203 (14) [M^+−TMS], 185 (32) [285−H_2CO], 175 (10) [203−H_2CO], 73 (93) [TMS$^+$]; elemental analysis calcd (%) for $C_{15}H_{20}O_3Si$: C 65.18, H 7.29; found: C 65.08, H 7.21.

(−)-[4*R*]-2,6-Dimethyl-9-trimethylsilylnon-2-ene-8-yne (17): CBr_4 (21.5 g, 65.0 mmol) was added slowly to a solution of PPh_3 (34.0 g, 0.13 mol) in CH_2Cl_2 (500 mL) at 0 °C and stirring was continued for 30 min. A solution of (+)-citronellal (**15**) (5.0 g, 32.4 mmol) in CH_2Cl_2 (20 mL) was added dropwise at the same temperature and stirring was continued at room temperature for 2 h. The reaction mixture was filtered through a silica gel column with diethyl ether. The solvent was removed in vacuum and the residue—crude dibromo alkene—was dissolved in THF (100 mL). The solution was cooled to −80 °C, a solution of *n*BuLi (2.7 M in heptane, 24 mL, 64.8 mmol) was added slowly, and stirring was continued for 1 h. Chlorotrimethylsilane (7.0 g, 64.9 mmol) was added with a cannula, and the resulting mixture was allowed to warm to room temperature within 18 h. The mixture was poured then into saturated aqueous NH_4Cl (150 mL). The organic layer was separated and the aqueous phase extracted with diethyl ether (3×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (diethyl ether/petroleum ether 1:10) provided the enyne **17** (5.47 g, 25.0 mmol, 76%) as a colorless liquid. $[\alpha]_D^{23}$=−7.9 (*c*=1.0 in $CHCl_3$); R_f=0.26 (diethyl ether/petroleum ether 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.12 (s, 9H; −TMS), 0.95 (d, ^3J(H,H)=6.6 Hz, 3H; C4-CH_3), 1.19–1.39 (m, 2H), 1.58 and 1.67 (2×s, 6H; 2×$-CH_3$), 1.93–2.20 (m, 4H), 5.08 ppm (t, ^3J(H,H)=6.1 Hz, 1H; H7); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.17 (−TMS), 17.65, 19.39, 25.51, 25.71, 27.07, 32.15, 36.11, 85.35 and 86.44 (C≡C), 124.46 and 131.40 ppm (C=C); IR (CCl_4): $\tilde{\nu}$=2173 cm^{-1} (C≡C−Si); MS (GC–MS): *m*/*z* (%): 222 (2) [M^+], 207 (20) [M^+-CH_3], 149 (18) [$M^+-Si(CH_3)_3$], 148 (20) [$M^+-Si(CH_3)_3-H$], 133 (28) [$M^+-Si(CH_3)_3-CH_4$], 73 (100) [$Si(CH_3)_3^+$].

(−)-[4*R*]-4-Methyl-7-trimethylsilyl-hept-6-yneal (18): A solution of enyne **17** (2.0 g, 9.01 mmol) in CH_2Cl_2/MeOH (10:1, 20 mL) was cooled to −78 °C and an ozone/oxygene stream was bubbled through this solution until the solution stayed dark blue for more than 10 s. This indicates an excess of ozone. The excess of ozone was removed with an oxygen stream and then dimethyl sulfide (1.12 g, 18.00 mmol) and acetic acid (7 drops) were added at −78 °C and the solution was stirred at room temperature for 18 h. The solvent was removed in vacuo and crude aldehyde **18** (1.86 g, 9.49 mmol, 105%) was obtained, which was used directly for the next reaction step without any further purification. A small sample of **18** was purified by column chromatography (diethyl ether/petroleum ether 1:20) for analytical purposes. $[\alpha]_D^{22}$=−1.54 (*c*=1.17 in $CHCl_3$); R_f=0.21 (diethyl ether/petroleum ether 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.12 (s, 9H; $Si(CH_3)_3$), 0.97 (d, ^3J(H,H)=6.6 Hz, 3H; 4-CH_3), 1.57 (m, 1H), 1.75 (m, 2H), 2.18 (m, 2H), 2.49 (m, 2H), 9.79 ppm (s, 1H; CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.10 ($Si(CH_3)_3$), 19.25, 26.89, 27.89, 31.99, 41.59 (CH, CH_2, CH_3), 86.05 and 105.313 (C≡C), 202.44 ppm (C=O); IR (CCl_4): $\tilde{\nu}$=2173 (C≡C−Si), 1713 cm^{-1} (C=O); MS (GC–MS) *m*/*z* (%): 195 (3) [M^+−H], 181 (69) [M^+-CH_3], 163 (19) [$M^+-CH_3-H_2O$], 123 (18) [$M^+-Si(CH_3)_3$], 73 (100) [$Si(CH_3)_3^+$].

(−)-[4*R*]-4-Methyl-1-trimethylsilylocta-1,7-diyne (7a): CBr_4 (15.43 g, 47 mmol) was added slowly to a solution of PPh_3 (24.41 g, 93 mmol) in

CH_2Cl_2 (300 mL) at 0 °C with stirring, and this stirring was continued for 30 min. A solution of aldehyde **18** (4.56 g, 23 mmol) in CH_2Cl_2 (20 mL) was added dropwise at the same temperature and stirring was continued at room temperature for 2 h. The reaction mixture was filtered through a silica gel column with diethyl ether. The solvent was removed in vacuum and the residue—crude dibromo alkene (6.96 g, 20 mmol)—was dissolved in THF (100 mL). The solution was cooled down to −78 °C, a solution of *n*BuLi in heptane (2.7 N, 17 mL, 47 mmol) was added dropwise, and stirring was continued for 1 h. H_2O (2 mL, 0.11 mol) was added dropwise with a cannula, and the resulting mixture was allowed to warm up to room temperature over 10 min. Then the mixture was poured into saturated aqueous NH_4Cl (100 mL). The organic layer was separated and the aqueous phase was extracted with diethyl ether (3×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuum. Distillation in vacuo afforded the octa-1,7-diyne **7a** (3.19 g, 17.00 mmol, 74 %) as a colorless liquid. B.p. = 80 °C (12 mbar); $[\alpha]_D^{26} = -9.4$ ($c = 1.17$, $CHCl_3$); $R_f = 0.35$ (diethyl ether/petroleum ether 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.12$ (s, 9H; $Si(CH_3)_3$), 0.97 (d, ^3J(H,H) = 6.7 Hz, 3H; 4-CH_3), 1.43–1.82 (m, 4H), 1.92 (t, ^4J(H,H) = 2.7 Hz, 1H; C≡C–H), 2.11–2.26 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 0.21 ($Si(CH_3)_3$), 16.26, 26.84, 34.52 (3×CH_2), 19.08, 31.43 (CH and 4-CH_3), 68.38 (C≡C–H), 84.22, 85.83, 105.57 ppm (C_{quart}, 3×C≡C); IR (CCl_4): $\tilde{\nu} = 3311$ (C≡C–H), 2172 cm^{-1} (C≡C–Si); MS (EI, 70 eV): *m*/*z* (%): 177 (6) [$M^+ - CH_3$], 73 (100) [$Si(CH_3)_3^+$].

(2*S*,3*S*)-3,7-Dimethyl-2,3-epoxy-6-octenol (19): L-(+)-Tartaric acid (5.1 mL, 29.9 mmol) was added to a stirred suspension of 4 Å molecular sieves (5.4 g) in absolute dichloromethane (150 mL) at 0 °C, followed by titanium isopropoxide (5.8 mL, 19.5 mmol). The reaction mixture was cooled to −20 °C using a cryostat, whereupon a solution of *tert*-butyl hydroperoxide (54.5 mL, 0.292 mol, 5.5 M in CH_2Cl_2) was added slowly. The resulting suspension was stirred for 35 min at −20 °C before cooling to −25 °C. At this temperature, a solution of geraniol **16** (30 g, 0.195 mol, 50 % in dichloromethane) was slowly added with a syringe and stirred for 2.5 h at −25 °C until complete conversion of the starting material was observed by TLC. The reaction mixture was slowly warmed to 0 °C, diluted with water (100 mL), and stirred at ambient temperature until the reaction mixture had also reached room temperature. NaOH (30 mL, 30 % in water saturated with NaCl) was added and the mixture stirred for 20 min until phase separation was observed. The solution was filtered, phases were separated, and the aqueous layer was extracted with dichloromethane (3×100 mL). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Distillation of the residue using a Kugelrohr (150 °C, 7×10^{-2} mbar) provided a colorless oil (29.8 g, 0.174 mol, 90 %). B.p. 115–120 °C (0.5×10^{-2} mbar) Kugelrohr distillation; $[\alpha]_D^{20} = -5.0°$ ($c = 3$ in $CHCl_3$); $R_f = 0.23$ (petroleum ether/diethyl ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.24$ (s, 3H; C3-CH_3), 1.43 (m, 1H; H4), 1.55 (s, 3H; C7-CH_3), 1.59 (m, 1H; H4), 1.62 (s, 3H; C7-CH_3), 2.02 (q, ^3J(H,H) = 7.8 Hz, 2H; H5), 2.71 (t, ^3J(H,H) = 4.7 Hz, 1H; C1-OH), 2.93 (dd, ^3J(H,H) = 6.8 Hz, 1H; H2), 3.61 (m, 1H; H1), 3.75 (m, 1H; H1), 5.02 ppm (t, ^3J(H,H) = 7.4 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.6$ (C7-CH_3), 17.5 (C3-CH_3), 23.6 (C5), 25.6 (C7-CH_3), 38.4 (C4), 61.2 (C3), 61.3 (C1), 63.1 (C2), 123.2 (C6), 132.0 ppm (C7); IR (CCl_4): $\tilde{\nu} = 3484.6$ (m), 2968.5 (s), 2929.5 (s), 2858.2 (s), 1739.8 (w), 1672.7 (w), 1451.5 (s), 1383.9 (s), 1342.7 (m), 1247.4 (m), 1199.1 (m), 1152.0 (w), 1093.8 (m), 1076.6 (m), 1027.9 (s), 1009.0 (m), 986.0 (w), 951.0 cm^{-1} (w); MS (GC–MS): *m*/*z* (%): 155 (<1) [$M^+ - CH_3$], 152 (<1) [$M^+ - H_2O$], 139 (3), 121 (7), 111 (11), 110 (37), 109 (98) [$C_8H_{13}^+$], 101 (<1), 97 (8), 95 (39), 93 (13), 91 (8), 88 (8), 83 (28), 82 (46), 81 (33), 79 (18), 77 (8), 71 (26), 69 (87), 67 (81), 61 (34), 55 (41), 53 (19), 43 (86), 41 (100) [$C_3H_5^+$]; elemental analysis calcd (%) for $C_{10}H_{18}O_2$: C 70.55, H 10.66; found: C 70.75, H 10.83.

(3*S*)-3,7-Dimethyloct-6-ene-1,3-diol (20a): At 0 °C, a solution of Red-Al (35.5 g, 0.176 mol, 70 % in toluene) was added dropwise to a solution of epoxide **19** (28.5 g, 0.167 mol) in absolute tetrahydrofuran (500 mL) in such a way that only slow evolution of gas was observed. After complete addition of Red-Al, the reaction mixture was stirred for 5 h at ambient temperature. The mixture was diluted with diethyl ether (200 mL) and the reaction carefully quenched with water (200 mL) to result in a white precipitate. The precipitate was dissolved using aqueous HCl (100 mL, 2 M). After phase separation, the aqueous phase was extracted with diethyl ether (3×250 mL), the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Distillation using Kugelrohr (170–180 °C, 10^{-1} mbar) yielded a colorless oil (26.5 g, 0.154 mol, 92 %, 91 % *ee*). B.p. 170–180 °C (10^{-1} mbar) Kugelrohr distillation; $[\alpha]_D^{20} = +3.1°$ ($c = 3$ in $CHCl_3$); $R_f = 0.05$ (petroleum ether/diethyl ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.18$ (s, 3H; C3-CH_3), 1.45–1.60 (m, 2H; H4), 1.56 (s, 3H; C7-CH_3), 1.6–1.75 (m, 2H; H2), 1.62 (s, 3H; C7-CH_3), 1.97 (qi, ^3J-(H,H) = 7.2 Hz, 2H; H5), 3.33 (br s, 1H; −OH), 3.75 (br s, 1H; −OH), 3.78 (m, 2H; H1), 5.06 ppm (t, ^3J(H,H) = 7.0 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.5$ (C7-CH_3), 22.6 (C5), 25.6 (C7-CH_3), 26.4 (C3-CH_3), 41.3 (C4), 42.2 (C2), 59.5 (C1), 73.7 (C3), 124.1 (C6), 131.6 ppm (C7); IR (CCl_4): $\tilde{\nu} = 3536.2$ (m), 3382.9 (m), 2969.3 (s), 2928.8 (s), 2883.4 (s), 1557.3 (m), 1451.3 (m), 1376.3 (s), 1342.5 (m), 1216.9 (m), 1116.0 (s), 1067.6 cm^{-1} (s); MS (GC–MS): *m*/*z* (%): 155 (4) [$M^+ - OH$], 154 (31) [$M^+ - H_2O$], 139 (9), 123 (9), 122 (7), 121 (74), 112 (6), 111 (15), 110 (16), 109 (100) [$M^+ - EtOH - H_2O$], 95 (23), 93 (17), 89 (20) [$C_4H_9O_2^+$], 84 (9), 83 (8), 81 (20), 79 (8), 71 (39), 69 (67) [$C_5H_9^+$], 68 (12), 67 (28), 57 (5), 56 (8), 55 (20), 53 (11); elemental analysis calcd (%) for $C_{10}H_{20}O_2$: C 69.72, H 11.70; found: C 69.07, H 10.92.

(3*S*)-3-Hydroxy-3,7-dimethyl-oct-6-enyl benzoate (20b): After addition of absolute triethylamine (31.0 mL, 0.222 mol) to a solution of **20a** (25.5 g, 0.148 mol) in absolute dichloromethane (500 mL), the solution was cooled to 0 °C. Then benzoyl chloride (21.0 mL, 0.178 mol) was added dropwise. After addition was completed, the reaction mixture was stirred for 12 h at ambient temperature. The reaction was quenched by the addition of water (300 mL) and aqueous HCl (75 mL, 2 M) and vigorous stirring for 3 min. Phases were separated, and the aqueous layer was extracted with dichloromethane (3×150 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was subjected to chromatography (petroleum ether/ethyl acetate 6:1) to provide a pale yellow oil (40.0 g, 0.145 mol, 98 %). $[\alpha]_D^{20} = -1.4°$ ($c = 3$ in $CHCl_3$); $R_f = 0.14$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (s, 3H; C3′-CH_3), 1.59 (m, 2H; H4′), 1.62 (s, 3H; C7′-CH_3), 1.68 (s, 3H; C7′-CH_3), 1.98 (dt, ^3J(H,H) = 7.0, 2.4 Hz, 2H; H5′), 2.08 (d, ^3J(H,H) = 7.4 Hz, 1H; H2′), 2.12 (d, ^3J(H,H) = 7.4 Hz, 1H; H2′), 2.27 (br s, 1H; −OH), 4.50 (t, ^3J(H,H) = 7.0 Hz, 2H; H1′), 5.12 (t, ^3J-(H,H) = 7.0 Hz, 1H; H6′), 7.42 (t, ^3J(H,H) = 7.8 Hz, 2H; H3 and H5), 7.55 (t, ^3J(H,H) = 7.4 Hz, 1H; H4), 8.03 ppm (d, ^3J(H,H) = 8.0 Hz, 2H; H2 and H6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.7$ (C7′-CH_3), 22.7 (C5′), 25.7 (C7′-CH_3), 27.0 (C3′-CH_3), 39.9 (C2′), 42.3 (C4′), 61.8 (C1′), 71.9 (C3′), 124.1 (C6′), 128.4 (C3 and C5), 129.6 (C2 and C6), 130.2 (C1), 132.0 (C7′), 133.0 (C4), 166.7 ppm (C=O); IR (CCl_4): $\tilde{\nu} = 3544.4$ (m), 3091.0 (w), 3063.6 (m), 3033.7 (m), 2969.3 (s), 2928.3 (s), 2856.2 (m), 2730.1 (w), 2361.5 (w), 2336.0 (w), 1961.6 (w), 1907.5 (w), 1722.4 (ss), 1602.8 (m), 1585.0 (m), 1490.6 (m), 1451.1 (s), 1376.9 (s), 1314.8 (s), 1272.2 (ss), 1248.3 (s), 1175.9 (s), 1110.9 (s), 1097.2 (s), 1069.9 (s), 1026.8 (s), 981.9 (m), 963.7 (m), 933.2 (m), 914.3 (w), 909.1 (w), 906.4 (w), 900.2 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 258 (<1) [$M^+ - H_2O$], 139 (2), 137 (2), 136 (18), 123 (4), 122 (16), 121 (100) [$C_7H_5O_2^+$], 109 (9), 105 (73) [$C_7H_5O^+$], 93 (15), 91 (2), 81 (3), 77 (25) [$C_6H_5^+$], 71 (8), 69 (12), 68 (5), 67 (5), 55 (5), 51 (5); elemental analysis calcd (%) for $C_{17}H_{24}O_3$: C 73.88, H 8.75; found: C 73.98, H 8.75.

(3*S*)-3-(*tert*-Butyldimethylsilyloxy)-3,7-dimethyl-oct-6-enyl benzoate (20c): Absolute 2,6-lutidin (23.3 mL, 0.2 mol) was added to a solution of **20b** (27.6 g, 99.0 mmol) in dichloromethane (500 mL) and the mixture was stirred for 5 min at room temperature before being cooled to 0 °C. At this temperature, OTBSTf (25.0 mL, 0.109 mol) was added slowly with a dropping funnel. The reaction mixture was stirred overnight while it was allowed to warm to room temperature. The reaction was quenched by addition of water (500 mL) and vigorous stirring for 10 min until the color of the organic layer changed from brown to orange. Phases were separated, and the aqueous layer was extracted with dichloromethane (3×300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The brown residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide a colorless oil (37.0 g, 94.7 mmol, 96 %). $[\alpha]_D^{20} = -2.3°$ ($c = 3$ in $CHCl_3$); $R_f = 0.66$ (petroleum ether/diethyl ether 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.11$ (s, 6H; −Si*t*Bu(CH_3)$_2$), 0.86 (s, 9H; −SiMe$_2$C(CH_3)$_3$), 1.30 (s, 3H; C3′-CH_3),

1.54 (m, 2H; H4′), 1.60 (s, 3H; C7′-CH_3), 1.67 (s, 3H; C7′-CH_3), 1.94 (m, 2H; H5′), 2.05 (m, 2H; H2′), 4.44 (t, ^3J(H,H) = 7.0 Hz, 2H; H1′), 5.08 (t, ^3J(H,H) = 7.0 Hz, 1H; H6′), 7.41 (t, ^3J(H,H) = 7.6 Hz, 2H; H3 and H5), 7.53 (t, ^3J(H,H) = 7.6 Hz, 1H; H4), 8.03 ppm (d, ^3J(H,H) = 7.4 Hz, 2H; H2 and H6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −3.0 (−Si*t*Bu(CH_3)$_2$), −2.0 (−Si*t*Bu(CH_3)$_2$), 17.6 (C7′-CH_3), 18.1 (−$SiMe_2CMe_3$), 18.2 (C6′), 23.0 (C7′-CH_3), 25.9 ($SiMe_2$*t*Bu), 27.9 (C3′-CH_3), 40.5 (C4′), 43.0 (C2′), 62.0 (C1′), 74.6 (C3′), 124.3 (C6′), 128.3 (C3 and C5), 129.5 (C2 and C6), 130.4 (C1), 131.3 (C7′), 132.7 (C4), 166.6 ppm (C=O); IR (CCl_4): $\tilde{\nu}$ = 2955.3 (s), 2928.4 (s), 2855.9 (s), 1722.3 (s), 1471.2 (m), 1462.1 (m), 1451.2 (m), 1387.3 (w), 1376.1 (w), 1360.1 (w), 1314.8 (m), 1274.0 (s), 1253.3 (s), 1175.9 (m), 1143.8 (m), 1111.8 (m), 1097.2 (m), 1069.7 (s), 1048.9 (s), 1026.9 (m), 1005.3 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 333 (<1) [M^+ −*t*Bu], 258 (1), 253 (2), 241 (7), 221 (<1), 197 (2), 185 (12), 179 (47) [$C_{10}H_{11}O_3^+$], 145 (2), 137 (14), 136 (5), 135 (4), 121 (16) [Ph^+−CO_2], 106 (8), 105 (100) [Ph^+−CO], 95 (5), 81 (13), 77 (11) [$C_6H_5^+$], 75 (13), 73 (12), 69 (9) [$C_5H_9^+$], 55 (2); elemental analysis calcd (%) for $C_{23}H_{34}O_3Si$: C 70.72, H 9.81; found: C 70.56, H 9.70.

(3*S*)-3-(*tert*-Butyl-dimethylsilyloxy)-3,7-dimethyloct-6-en-1-ol (20d): NaOH (4.1 g, 0.103 mol) dissolved in absolute MeOH (250 mL) was slowly added with a dropping funnel to a solution of **20c** (35.6 g, 91.0 mmol) in absolute MeOH (250 mL) at room temperature, whereupon the reaction mixture slowly turned yellow. After stirring for 5 h at ambient temperature no starting material was observed by TLC. The reaction was quenched by addition of water (1.5 L) and 5 min vigorous stirring. The aqueous phase was extracted with diethyl ether (3×600 mL). The combined organic layers were washed with brine (350 mL), dried over $MgSO_4$, and concentrated in vacuum. The yellow oil was subjected to chromatography (petroleum ether/ethyl acetate 5:1) to yield a colorless oil (24.8 g, 86.5 mmol, 95%) . $[\alpha]_D^{20}$ = +8.9° (*c* = 3 in $CHCl_3$); R_f = 0.21 (petroleum ether/diethyl ether 5:1); ^{1}H NMR (400 MHz, CDCl3): δ = 0.08 (s, 6H; −Si*t*Bu(CH_3)$_2$), 0.83 (s, 9H; −$SiMe_2CMe_3$), 2.95 (s, 3H; C3-CH_3), 1.45 (m, 2H; H4), 1.56 (s, 3H; C7-CH_3), 1.64 (s, 3H; C7-CH_3), 1.71 (m, 2H; H2), 1.93 (q, ^3J(H,H) = 8.0 Hz, 2H; H5), 2.80 (brs, 1H; −OH), 3.74 (t, ^3J(H,H) = 6.2 Hz, 2H; H1), 5.04 ppm (t, ^3J(H,H) = 7.0 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.91 (−Si*t*Bu(CH_3)$_2$), −1.89 (−Si*t*Bu(CH_3)$_2$), 17.6 (C7-CH_3), 18.0 (−$SiMe_2CMe_3$), 23.2 (C5), 25.6 (C7-CH_3), 25.8 (−$SiMe_2$*t*Bu), 27.6 (C3-CH_3), 42.6 (C4), 42.8 (C2), 59.6 (C1), 78.0 (C3), 124.1 (C6), 131.4 ppm (C7); IR (CCl_4): $\tilde{\nu}$ = 3527.7 (m), 2956.1 (s), 2929.1 (s), 2856.8 (s), 2734.9 (w), 2361.9 (w), 1471.7 (m), 1462.3 (m), 1408.4 (m), 1387.7 (m), 1375.7 (m), 1360.1 (m), 1339.9 (m), 1305.6 (w), 1254.7 (s), 1215.8 (m), 1158.2 (m), 1114.8 (s), 1094.4 (s), 1072.6 (m), 1027.9 cm^{-1} (s); MS (GC–MS): *m*/*z* (%): 271 (<1) [M^+−CH_3], 242 (3), 241 (13), 203 (5) [M^+−C_6H_{11}], 187 (2), 173 (5), 161 (2), 154 (7) [M^+−OTBSH], 145 (8), 137 (22) [154−H_2O], 133 (10), 121 (10), 115 (7) [TBS^+], 111 (7) [$C_8H_{15}^+$], 109 (13), 105 (27), 95 (28), 89 (13), 81 (50), 75 (88), 73 (29), 70 (6), 69 (100) [$C_5H_9^+$], 67 (9), 57 (6) [*t*Bu$^+$], 55 (8). 45 (6); elemental analysis calcd (%) for $C_{16}H_{34}O_2Si$: C 67.07, H 11.96; found: C 66.83, H 11.34.

(+)-[3*S*]-3-(*tert*-Butyldimethylsilanyloxy)-3,7-dimethyl-oct-6-enal (21): Dry triethylamine (96.8 mL, 0.7 mol, 8 equiv) was added at room temperature to a solution of the alcohol **20d** (25 g, 87.3 mmol) in methyl sulfoxide (500 mL). Afterwards, the sulfurtrioxidepyridine complex (55.6 g, 0.35 mol, 4 equiv) was added portionwise, and the brownish solution was then stirred for 3 h at room temperature under TLC control. After complete conversion, the reaction solution was diluted with water (around 1.5 L; exothermic reaction) and extracted 4 times with diethyl ether (300 mL portions). The combined organic phases were then dried over magnesium sulfate, and the solvent was evaporated to give a brown oil (with an intense odor). The oily residue was purified then by means of column chromatography over silica gel with petroleum ether/diethyl ether (20:1) to give a colorless oil (23.0 g, 93% yield). $[\alpha]_D^{20}$ = +8.32 (*c* = 3 in $CHCl_3$); R_f = 0.6 (petroleum ether/diethyl ether = 5:1); ^{1}H NMR (400 MHz, CDCl3): δ = 0.08 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.09 (s, 3H; −Si*t*Bu-(CH_3)$_2$), 0.84 (s, 9H; −$SiMe_2C(CH_3)_3$), 1.32 (s, 3H; C3-CH_3), 1.55 (m, 2H; H4), 1.57 (s, 3H; H8), 1.65 (s, 3H; C7-CH_3), 2.03 (m, 2H; H5), 2.45 (dd, ^2J(H,H) = 14.6 Hz, ^3J(H,H) = 3.1 Hz, 2H; H2), 5.04 (t, ^3J(H,H) = 7.2 Hz, 1H; H6), 9.84 ppm (t, ^3J(H,H) = 3.1 Hz, 1H; H1); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.0 and −1.9 (−Si*t*Bu(CH_3)$_2$), 17.6 (C5), 18.2 (−$SiMe_2C$(Me)$_3$), 22.9 (C7-CH_3), 25.7 (−$SiMe_2C(CH_3)_3$), 26.9 (C7-CH_3), 28.3 (C3-CH_3), 43.5 (C4), 55.0 (C2), 74.8 (C3), 123.7 (C6), 131.9 (C7), 203.4 ppm (C1); IR (CCl_4): $\tilde{\nu}$ = 2956.4 (s), 2929.2 (s), 2856.7 (s), 2734.2 (w), 1723.6 (s), 1471.6 (m), 1462.1 (m), 1376.4 (m), 1360.1 (w), 1254.6 (s), 1171.0 (w), 1136.6 (m), 1120.5 (m), 1098.8 (w), 1050.7 (s), 1005.5 (m), 982.9 cm^{-1} (w); MS (GC–MS): *m*/*z* (%): 269 (<1) [M^+−CH_3], 241 (5), 227 (10), 209 (2), 201 (7), 185 (2), 171 (6), 159 (11), 152 (3), 151 (5), 145 (53), 135 (49), 123 (4), 115 (20), 107 (23), 101 (19), 93 (18), 84 (3), 77 (6), 75 (48), 73 (19), 69 (100), 59 (13), 45 (6).

(1*S*)-*tert*-Butyl-[1-(3,3-dibromoallyl)-1,5-dimethylhex-4-enyloxy]dimethyl-silane: Tetrabromocarbon (53.6 g, 0.162 mol, 2 equiv) was carefully added portionwise (in large-scale preparation, the reaction is very exothermic) at room temperature to a solution of triphenylphosphane (85 g, 0.324 mol, 4 equiv) in dry dichloromethane (500 mL), which gave a deep orange solution after stirring for 30 min at room temperature. Then dry triethylamine (90 mL, 0.648 mol, 8 equiv) was added slowly at RT, followed by cooling the solution to −80 °C (isopropanol/liquid nitrogen), whereupon a 50 vol% solution of the aldehyde **21** (23 g, 81 mmol, 1 equiv) in dichloromethane was added with a syringe to the reaction solution. The reaction was then stirred in a cooling bath overnight under warming to room temperature. On the next day, silica gel (300 g) was added to the solution, followed by evaporation of the solvent with a rotary evaporator. The resulting yellow solid was pounded in a mortar and the yellow powder was put onto the top of an already packed column (1 kg of silica gel, petroleum ether/diethyl ether 10:1) and purified by means of column chromatography with petroleum ether/diethyl ether (10:1), which gave a colorless oil (32.1 g, 72.9 mmol, 90% yield). $[\alpha]_D^{20}$ = −4.38 (*c* = 3 in $CHCl_3$); R_f = 0.84 (petroleum ether/diethyl ether = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.075 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.078 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.86 (s, 9H; −$SiMe_2C(CH_3)_3$), 1.21 (s, 3H; C1-CH_3), 1.44 (m, 2H; H2), 1.60 (s, 3H; C5-CH_3), 1.67 (s, 3H; C5-CH_3), 1.98 (q, ^3J(H,H) = 8.2 Hz, 2H; H3), 2.24 (dd, ^2J(H,H) = 15.2 Hz, ^3J-(H,H) = 6.7 Hz, 2H; H1′), 5.7 (t, ^3J(H,H) = 7.0 Hz, 1H; H4), 6.48 ppm (t, ^3J(H,H) = 6.7 Hz, 1H; H2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.0 (−Si*t*Bu(CH_3)$_2$), 17.6 (C3), 18.2 (−$SiMe_2C$(Me)$_3$), 22.9 (C5-CH_3), 25.7 (C5-CH_3), 25.9 (−$SiMe_2C(CH_3)_3$), 27.4 (C1-CH_3), 42.7 (C1′), 45.8 (C2), 75.1 (C1), 89.2 (C3′), 124.3 (C4), 131.5 (C5), 136.0 ppm (C2′); IR (CCl_4): $\tilde{\nu}$ = 2956.1 (s), 2928.5 (s), 2856.3 (s), 2359.7 (w), 1471.7 (m), 1462.0 (m), 1375.6 (m), 1360.1 (w), 1339.3 (w), 1316.8 (w), 1254.1 (s), 1216.0 (w), 1144.9 (m), 1117.3 (m), 1066.6 (m), 1043.1 (m), 1006.0 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 425 (2), 385 (18), 383 (35), 381 (17), 367 (5), 365 (8), 363 (5), 359 (4), 357 (8), 355 (4), 343 (2), 325 (1), 303 (2), 301 (4), 299 (2), 285 (1), 273 (2), 259 (7), 257 (10), 255 (7), 241 (100), 225 (<1), 205 (7), 203 (14), 201 (7), 185 (2), 173 (9), 139 (12), 115 (12), 109 (30), 75 (96), 73 (56), 69 (53), 57 (6), 45 (5).

(4*S*)-4-(*tert*-Butyldimethylsilanyloxy)-4,8-dimethyl-1-trimethylsilanylnon-7-en-1-yne (22): *n*BuLi (100 mL, 0.161 mol, 2.2 equiv, 1.6 M in hexane) was added dropwise with a dropping funnel at −80 °C to a solution of (1*S*)-*tert*-butyl-[1-(3,3-dibromoallyl)-1,5-dimethylhex-4-enyloxy]dimethyl-silane (32.0 g, 72.7 mmol, 1 equiv) in dry THF (500 mL), and the solution was then stirred for 45 min in a cooling bath under warming to −40 °C, whereupon the cooling bath was removed and the solution was stirred for 1 h at room temperature; the color of the solution turned black. After cooling the solution to −80 °C again, TMS-Cl (10.2 mL, 80 mmol, 1.1 equiv) was added dropwise with a syringe. The solution was then stirred in a cooling bath overnight under warming to room temperature. The next morning, water (500 mL) was added to the reaction solution, and after the phase separation the aqueous phase was extracted 3 times with diethyl ether (300 mL portions). The combined organic phases were then dried over magnesium sulfate, and the solvent was evaporated to give a brown oil. Column chromatography of the oil with petroleum ether/diethyl ether (50:1) gave a colorless oil (24.4 g, 69.1 mmol, 95% yield). $[\alpha]_D^{20}$ = −9.84 (*c* = 3 in $CHCl_3$); R_f = 0.93 (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.068 (s, 3H; −Si*t*Bu-(CH_3)$_2$), 0.074 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.12 (s, 9H; −Si(CH_3)$_3$), 0.85 (s, 9H; −$SiMe_2C(CH_3)_3$), 1.27 (s, 3H; C4-CH_3), 1.53 (m, 2H; H5), 1.60 (s, 3H; H9), 1.67 (s, 3H; C8-CH_3), 2.01 (q, ^3J(H,H) = 7.4 Hz, 2H; H6), 2.35 (dd, ^2J(H,H) = 16.6 Hz, ^4J(H,H) = 19.3 Hz, 2H; H3), 5.10 ppm (t, ^3J(H,H) = 7.4 Hz, 1H; H7); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.0 and

−1.9 (−Si*t*Bu-(CH_3)$_2$), 0.1 (−Si(CH_3)$_3$), 17.6 (C6), 18.2 (−SiMe$_2$-*C*(CH_3)$_3$), 22.7 (C8-CH_3), 25.7 (C8-*C*H$_3$), 25.8 (−SiMe$_2$-C(*C*H$_3$)$_3$), 27.4 (C4-*C*H$_3$), 33.8 (C3), 42.0 (C5), 75.0 (C4), 86.3 (C1), 104.8 (C2), 124.5 (C7), 131.3 ppm (C8); IR (CCl_4): $\tilde{\nu}$ = 2957.7 (s), 2928.6 (s), 2855.5 (s), 2359.9 (w), 2336.0 (w), 2174.5 (m), 1471.6 (m), 1461.8 (m), 1374.9 (m), 1359.6 (m), 1310.1 (w), 1250.1 (ss), 1215.9 (w), 1188.2 (w), 1168.0 (m), 1128.7 (m), 1114.3 (m), 1096.6 (m), 1050.2 (s), 1005.0 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 337 (2), 297 (6), 296 (16), 295 (62), 269 (6), 241 (100), 221 (3), 207 (6), 197 (2), 183 (5), 170 (18), 169 (89), 157 (5), 147 (21), 139 (4), 127 (4), 115 (9), 109 (22), 97 (6), 83 (4), 75 (24), 73 (56), 69 (36), 59 (8), 45 (2).

(4*S*)-4-(*tert*-Butyldimethylsilanyloxy)-4-methyl-7-trimethylsilanylhept-6-ynal (23): Ozone was introduced at −80 °C for 30 min into a solution of enyne **22** (22.0 g, 62.4 mmol, 1 equiv) and pyridine (11.1 g, 0.14 mol, 2.25 equiv) in dry dichloromethane (1 L) until the color of the solution turned purple. A TLC analysis showed that enyne **22** reacted completely, so dimethyl sulfide (66 mL) was added at −80 °C to the solution, which was stirred overnight under warming to room temperature. The next day, silica gel (around 200 g) was added to the orange solution, and the solvent was evaporated. The orange solid was then purified by means of column chromatography with petroleum ether/diethyl ether (20:1→10:1) to give a yellow oil (17.3 g, 53.1 mmol, 85% yield). $[\alpha]_D^{20} = -5.6$ (c = 3, $CHCl_3$); R_f = 0.42 (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.07 (s, 3H; −Si*t*Bu-(CH_3)$_2$), 0.10 (s, 9H; −Si(CH_3)$_3$), 0.82 (s, 9H; −SiMe$_2$C(CH_3)$_3$), 1.29 (s, 3H; C4-CH_3), 1.88 (m, 2H; H3), 2.35 (s, 2H; H5), 2.50 (dt, ^3J = 7.7, 1.6 Hz, 2H; H2), 9.76 ppm (t, ^3J = 1.6 Hz, 1H; H1). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.2 and −2.16 (−Si*t*Bu(CH_3)$_2$), −0.04 (−Si(*C*H$_3$)$_3$), 18.2 (−SiMe$_2$*C*(CH_3)$_3$), 25.8 (−SiMe$_2$C(*C*H$_3$)$_3$), 27.3 (C4-*C*H$_3$), 33.9 (C2), 34.0 (C3), 39.1 (C5), 74.3 (C4), 87.1 (C7), 103.7 (C6), 202.5 ppm (C1). MS (GC–MS): *m*/*z* (%): 311 (<1%), 269 (15.0), 216 (12.8), 215 (100.0), 195 (6.4), 179 (4.9), 169 (10.8), 157 (32.8), 147 (27.9), 133 (6.4), 123 (2.0), 115 (5.4), 105 (12.7), 97 (2.9), 83 (5.9), 75 (28.9), 73 (62.7), 59 (5.9), 45 (2.9). IR (CCl_4): $\tilde{\nu}$ = 3534.7 (w), 2956.8 (s), 2929.3 (s), 2898.0 (s), 2856.2 (s), 2711.3 (m), 2175.0 (s), 1756.2 (m), 1728.23 (s), 1711.3 (ss), 1471.5 (m), 1462.1 (m), 1412.8 (m), 1388.3 (m), 1376.1 (m), 1360.1 (m), 1304.3 (m), 1250.3 (s), 1170.5 (m), 1112.6 (s), 1042.8 (s), 1005.6 cm^{-1} (m).

(5*S*)-1,1-Dibromo-5-(*tert*-butyldimethylsilanyloxy)-5-methyl-8-trimethylsilanyl-oct-1-en-7-yne: Tetrabromocarbon (34.2 g, 0.103 mol, 2 equiv) was carefully (exothermic reaction!) added portionwise to a solution of triphenylphosphane (54.0 g, 0.206 mol, 4 equiv) in dry dichloromethane (500 mL) and then stirred for 30 min at room temperature. After adding dry triethylamine (57 mL, 0.411 mol, 8 equiv), the solution was cooled to −80 °C in a cooling bath (isopropanol/liquid nitrogen). After reaching −80 °C a 50 vol% solution of aldehyde **23** (16.8 g, 51.4 mmol, 1 equiv) in dichloromethane was added with a syringe to the reaction mixture. The solution was then stirred in a cooling bath overnight under warming to room temperature. The next day, silica gel (≈250 g) was added to the solution, whereby the solvent was then removed with a rotary evaporator. The orange solid was then pounded in a mortar followed by purification by means of column chromatography over a prepacked column with silica gel (0.75 kg) with petroleum ether/diethyl ether (75:1) to give a colorless oil (24.2 g, 50.2 mmol, 98% yield) . Please note: The dibromide tends toward decomposition, even under an inert gas in a freezer (−25 °C), so the elimination to the acetylenic compound **7b** was done on the same day as the column chromatography. R_f = 0.88 (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.509 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.517 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.56 (s, 9H; −Si(CH_3)$_3$), 1.28 (s, 9H; −SiMe$_2$C(CH_3)$_3$), 1.72 (s, 3H; C5-CH_3), 2.07 (m, 2H; H4), 2.60 (q, ^3J(H,H) = 7.4 Hz, 2H; H3), 2.80 (d, ^2J(H,H) = 18.3 Hz, 2H; H6), 6.82 ppm (t, ^3J(H,H) = 7.4 Hz, 1H; H2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.12 and −2.09 (−Si*t*Bu(*C*H$_3$)$_2$), 0.05 (−Si(*C*H$_3$)$_3$), 18.2 (−SiMe$_2$-*C*-(CH_3)$_3$), 25.8 (−SiMe$_2$-C(*C*H$_3$)$_3$), 27.2 (C3), 28.0 (C5-*C*H$_3$), 33.9 (C6), 39.5 (C4), 74.6 (C5), 86.9 (C8), 88.6 (C1), 104.1 (C7), 138.7 ppm (C2); IR (CCl_4): $\tilde{\nu}$ = 2957.0 (s), 2929.3 (s), 2897.4 (m), 2856.1 (s), 2174.7 (m), 1628.1 (w), 1471.4 (m), 1462.1 (m), 1435.7 (m), 1407.5 (m), 1388.2 (m), 1375.5 (m), 1360.0 (m), 1312.0 (m), 1295.3 (m), 1170.9 (m), 1139.2 (s), 1119.5 (s), 1063.71 (s), 1041.5 (s), 1004.9 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 469 (<1), 467 (1), 465 (<1), 427 (19), 425 (35), 423 (13), 373 (36), 371 (70), 369 (35), 269 (4), 226 (3), 211 (4), 170 (20), 169 (100), 155 (4), 147 (11), 139 (11), 115 (7), 97 (4), 75 (21), 73 (59), 59 (4), 45 (2).

(4*S*)-4-(*tert*-Butyldimethylsilanyloxy)-4-methyl-1-trimethylsilanyl-octa-1,7-diyne (7b): *n*BuLi (70 mL, 0.110 mmol, 2.2 equiv, 1.6 M in hexane) was added with a dropping funnel to a solution of (5*S*)-1,1-dibromo-5-(*tert*-butyldimethylsilanyloxy)-5-methyl-8-trimethylsilanyl-oct-1-en-7-yne (24.0 g, 50 mmol, 1 equiv) in dry THF (500 mL) at −80 °C. The brownish solution was then stirred for 2 h under warming to room temperature, followed by cooling the solution again to 0 °C. After quenching the solution with saturated NH_4Cl solution (100 mL), additional H_2O (400 mL) was added, and the resulting solution was then stirred for 5 min at 0 °C. After phase separation, the aqueous phase was extracted 3 times with diethyl ether (200 mL portions), and the combined organic phases were then dried over magnesium sulfate. Evaporation of the solvent gave a brown oil, which was purified by means of column chromatography with petroleum ether/diethyl ether (50:1) to give a yellowish oil (15.3 g, 47.5 mmol, 95% yield). $[\alpha]_D^{20} = -5.3$ (c = 3 in $CHCl_3$); R_f = 0.84 (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.069 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.077 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.12 (s, 9H; −Si(CH_3)$_3$), 0.84 (s, 3H; C4-CH_3), 1.82 (m, 2H; H5), 1.90 (t, ^4J(H,H) = 2.7 Hz, 1H; H8), 2.25 (dt, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.7 Hz, 2H; H6), 2.34 ppm (s, 2H; H3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.17 and −2.22 (−Si*t*Bu-(CH_3)$_2$), 0.02 (−Si(CH_3)$_3$), 13.2 (C6), 18.2 (−SiMe$_2$C(CH_3)$_3$), 25.8 (−SiMe$_2$C(CH_3)$_3$), 27.0 (C4-CH_3), 33.9 (C3), 41.0 (C5), 67.8 (C8), 74.4 (C4), 84.9 (C7), 87.1 (C1), 104.0 ppm (C2); IR (CCl_4): $\tilde{\nu}$ = 3313.4 (m), 2956.8 (s), 2929.3 (s), 2897.3 (m), 2856.1 (m), 2175.1 (m), 1471.5 (m), 1462.1 (m), 1375.5 (w), 1359.9 (w), 1250.4 (s), 1171.5 (w), 1133.3 (m), 1112.2 (s), 1046.8 (s), 1019.8 (m), 1006.0 cm^{-1} (w); MS (GC–MS): *m*/*z* (%): 307 (1), 269 (5), 265 (14), 249 (<1), 235 (<1) 221 (2), 212 (20), 211 (100), 191 (4), 177 (3), 170 (10). 169 (52), 157 (4), 147 (22), 133 (15), 115 (6), 97 (4), 83 (4), 75 (18), 73 (54), 59 (5), 45 (2).

(4*S*)-4-Methyl-1-trimethylsilanylocta-1,7-diyn-4-ol (24): *Caution! Concentrated hydrofluoric acid is toxic and harmful in addition to its corrosive properties toward glassware. Personal safety equipment is an absolute necessity as well as a good working fume hood. We decided to use polytetrafluoroethylene (PTFE) flasks for this reaction.* Hydrofluoric acid (3 mL, 70 mmol, 40% in H_2O, p.a.) was added dropwise with a plastic pipette to a solution of the substituted octadiyne **7b** (0.48 g, 1.5 mmol, 1 equiv) in HPLC-grade acetonitrile (60 mL). The reaction mixture was then stirred under TLC control for 6 h at 50 °C. During the reaction, the color of the originally colorless solution turned yellow. For workup, the reaction solution was poured into a saturated $CaCl_2$ solution (200 mL) and stirred for 5 min at room temperature. The aqueous phase was then extracted 3 times with diethyl ether (150 mL portions). $NaHCO_3$ (1 g) was added to the combined organic phases, followed by magnesium sulfate. After filtering and evaporation of the solvent, the brown oily residue was purified by column chromatography with petroleum ether/diethyl ether (5:1) to give a colorless oil (0.15 g, 0.73 mmol, 49% yield). $[\alpha]_D^{20} = +5.3$ (c = 1 in $CHCl_3$); R_f = 0.06 (petroleum ether/diethyl ether 10:1), 0.17 (petroleum ether/diethyl ether 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 9H; −Si(CH_3)$_3$), 1.40 (s, 3H; C4-CH_3), 1.96 (m, 2H; H5), 2.10 (t, ^4J(H,H) = 2.7 Hz, 1H; H8), 2.21 (brs, 1H; C4-OH), 2.45 (dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 2.7 Hz, 1H; H6), 2.55 ppm (d, ^2J(H,H) = 19.3 Hz, 1H; H3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.02 (−Si(*C*H$_3$)$_3$), 13.3 (C6), 26.2 (C4-*C*H$_3$), 33.9 (C3), 39.4 (C5), 68.6 (C8), 71.3 (C4), 84.5 (C7), 88.3 (C1), 102.7 (C2); IR (CCl_4): $\tilde{\nu}$ = 3614.7 (m), 3568.1 (m), 3312.5 (ss), 2961.5 (ss), 2930.2 (s), 2902.6 (s), 2172.9 (ss), 2120.5 (m), 1740.9 (m), 1722.7 (m), 1451.2 (m), 1431.71 (m), 1420.5 (m), 1408.0 (m), 1390.4 (m), 1374.3 (s), 1250.1 (ss), 1198.5 (m), 1160.2 (m), 1116.1 (s), 1034.7 (s), 985.3 (m), 974.9 (m), 915.0 (s), 904.7 cm^{-1} (m); MS (GC–MS): *m*/*z* (%): 208 (1), 193 (2), 175 (2), 170 (9), 169 (57), 135 (4), 119 (3), 112 (22), 97 (78), 91 (2), 83 (12), 75 (29), 73 (100), 69 (9), 67 (6), 59 (5), 53 (9), 45 (8).

(6*R*)-1-[3-Methoxy-2-(3-trimethylsilylprop-2-ynyl)-phenyl]-6-methyl-9-trimethylsilylnona-2,8-diyn-1-ol (25a): *n*BuLi (3.2 mL, 8.54 mmol, 2.7 M in hexanes) was added dropwise at −80 °C to a solution of **7a** (1.72 g, 8.94 mmol) in THF (10 mL). At this temperature the solution was stirred for 1 h before it was added with a cannula to a solution of **6a** (2.00 g, 8.13 mmol) in THF (20 mL) cooled to −80 °C. The reaction mixture was

stirred for 4 h and allowed to warm to −30 °C until no further starting material could be detected by TLC. The mixture was poured into an ice-cold NH_4Cl solution (20 mL). The aqueous phase was extracted thrice with diethyl ether (10 mL), the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography (petroleum ether/diethyl ether 1:5) to provide the alcohol as a colorless oil (3.53 g, 8.04 mmol, 94 %). $[\alpha]_D^{22} = -5.11$ ($c = 0.705$ in $CHCl_3$); $R_f = 0.56$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.11$ and 0.15 (s, 18H; 2×Si-$(CH_3)_3$), 1.01 (d, ^3J(H,H) = 6.6 Hz, 3H; 3-CH_3), 1.49–1.83 and 2.20–2.32 (m, 7H; 3×CH_2 and H-3), 2.72 (d, ^3J(H,H) = 4.9 Hz, 1H; OH, D_2O exchangeable), 3.72 and 4.00 (2×d, AB signal, J(A,B) = 17.13 Hz, 2H; Ar-CH_2-C≡C), 3.87 (s, 3H; OCH_3), 5.87 (dt, ^3J(H,H) = 5.0 Hz, ^5J(H,H) = 2 Hz, 1H; Ar-CH-OH), 6.90 and 7.39 (d, J_0 = 7.8 Hz, 2H; H-arom.), 7.30 ppm (t, J_0 = 7.8 Hz, 1H; H-5); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.08, 0.21 (2×Si$(CH_3)_3$), 15.44, 16.56, 26.59, 34.39 (4×CH_2), 18.79, 31.49, 56.02, 62.26 (C-3, 3-CH_3, OCH_3, ArCHO), 79.54, 84.83, 85.83, 86.92, 105.62, 105.75 (6×C-alkyne), 111.09, 120.00, 128.26 (CH-arom.), 123.17, 140.78, 156.85 ppm (C_{quart}-arom.); IR (CCl_4): $\tilde{\nu}$ = 3602–3513 (OH), 2172 (C≡C–Si),1263 and 1250 cm^{-1} (C–O); MS (EIMS, 70 eV): m/z (%): 438 (3) [M^+], 423 (6) [M^+−CH_3], 408 (4) [M^+−2CH_3], 365 (69) [M^+−Si$(CH_3)_3$], 350 (11) [365−CH_3]; elemental analysis calcd (%) for $C_{26}H_{38}O_2Si_2$: C 71.17, H 8.73; found: C 70.92, H 8.97.

(6*S*)-6-(*tert*-Butyldimethylsilyloxy)-1-[3-methoxy-2-(3-trimethylsilylprop-2-ynyl)phenyl]-6-methyl-9-trimethylsilylnona-2,8-diyn-1-ol (25b): *n*BuLi (9.0 mL, 14.4 mmol, 1.6 M in hexanes) was added dropwise with a syringe at −80 °C to a solution of **7b** (4.4 g, 13.7 mmol) in absolute diethyl ether (120 mL). The mixture was stirred for 30 min at this temperature, then for a further 30 min at room temperature. After cooling to −80 °C again, the reaction mixture was added with a cannula to a solution of **6a** (3.1 g, 12.5 mmol) and BF_3·Et_2O (1.7 mL, 13.1 mmol) in absolute diethyl ether (120 mL). The reaction mixture was stirred for 3 h at ambient temperature, diluted with distilled water (250 mL), and stirred vigorously for a further 3 min. Phases were separated, and the aqueous layer was extracted with diethyl ether (3×200 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography (petroleum ether/diethyl ether 10:1) provided the asymmetric product (5.0 g, 8.8 mmol, 70 %). $[\alpha]_D^{20} = -3.8°$ ($c = 2$ in $CHCl_3$); $R_f = 0.17$ (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.09$ (s, 3H; −Si*t*Bu$(CH_3)_2$), 0.10 (s, 3H; −Si*t*Bu$(CH_3)_2$), 0.12 (s, 9H; −TMS), 0.15 (s, 9H; −TMS), 0.86 (s, 9H; −SiMe_2*t*Bu), 1.30 (s, 3H; C6-CH_3), 1.86 (m, 2H; H5), 2.36 (m, 2H; H4), 2.38 (s, 2H; H7), 2.71 (d, ^3J(H,H) = 5.8 Hz, 1H; C1-OH), 3.70 and 3.98 (d, ^2J(H,H) = 17.6 Hz, 1H; H1″), 3.85 (s, 3H; C3′-OMe), 5.87 (m, 1H; H1), 6.87 (d, ^3J(H,H) = 8.2 Hz, 1H; H4′), 7.28 (t, ^3J(H,H) = 8.2 Hz, 1H; H5′), 7.38 ppm (d, ^3J(H,H) = 8.2 Hz, 1H; H6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.17 and −2.14 (−Si*t*Bu$(CH_3)_2$), 0.02 and 0.03 (−Si$(CH_3)_3$), 13.7 (C4), 15.5 (C1″), 18.2 (−Si$Me_2C(CH_3)_3$), 25.8 (−SiMe_2*t*Bu), 26.9 (C6-CH_3), 34.0 (C7), 41.0 (C5), 56.0 (C3′-OCH_3), 62.3 (C1), 74.5 (C6), 79.1 (C2), 84.8 (C3), 87.0 (C3″), 87.5 (C9), 104.1 (C2″), 105.7 (C8), 111.0 (C4′), 123.2 (C2′), 128.1 (C6′), 136.1 (C5′), 140.8 (C1′), 156.9 ppm (C3′); IR (CCl_4): $\tilde{\nu}$ = 3516.0 (w), 3313.4 (w), 2957.2 (s), 2929.5 (s), 2898.2 (m), 2855.8 (m), 2172.1 (s), 1587.3 (m), 1471.8 (s), 1461.8 (m), 1439.4 (m), 1407.4 (w), 1375.5 (m), 1359.8 (m), 1321.3 (w), 1262.3 (ss), 1250.4 (ss), 1212.9 (w), 1171.5 (m), 1111.01 (s), 1074.7 (m), 1045.6 (s), 1016.6 (s), 1005.1 (s), 981.3 (m), 976.1 (m), 939.0 (w), 908.1 cm^{-1} (s); MS (EIMS, 70 eV): m/z (%): 569 (<1) [M^+], 553 (<1) [M^+−Me], 535 (<1) [M^+ vMeOH], 511 (6) [M^+−*t*Bu], 496 (7) [M^+−TMS], 482 (<1), 457 (13) [M^+−C_6H_{11}Si], 439 (100) [496−*t*Bu], 419 (8), 404 (20), 347 (21), 345 (14), 331 (28), 316 (14), 291 (12), 275 (20), 269 (22) [M^+−$C_{14}H_{29}$OSi], 247 (9), 235 (10), 231 (9), 209 (10), 195 (20), 171.0 (12), 169 (34), 149 (41), 147 (56), 133 (13) [OTBSH$^+$], 115 (17) [TBS$^+$], 75 (64) 74 (30) [$C_6H_3^+$], 74 (12), 73 (99) [TMS$^+$]; elemental analysis calcd (%) for $C_{32}H_{54}O_3Si_3$: C 67.55, H 9.21; found: C 67.33, H 9.15.

(6*S*)-6-(*tert*-Butyldimethylsilyloxy)-1-[3-methoxymethoxy-2-(3-trimethylsilylprop-2-ynyl)phenyl]-6-methyl-9-trimethylsilylnona-2,8-diyn-1-ol (25c): At 0 °C, *n*BuLi (25.0 mL, 39.5 mmol, 1.6 M in hexanes) was quickly added to a solution of **7b** (10.63 g, 32.9 mmol) in absolute tetrahydrofuran (200 mL) with a syringe. The solution was stirred for 1 h and allowed to warm slowly to −30 °C. After cooling to −80 °C again, the reaction mixture was added with a cannula to a solution of **6b** (8.7 g, 31.5 mmol) in diethyl ether (200 mL) cooled to −15 °C. The solution was stirred for 1 h at −15 °C until TLC showed complete conversion of the starting material. At room temperature the reaction was quenched with water (250 mL). After phase separation, the aqueous layer was extracted with diethyl ether (3×250 mL). The combined organic layers were washed with brine (300 mL), dried over $MgSO_4$, and concentrated in vacuo to give an orange viscous oil, which was purified by column chromatography (petroleum ether/ethyl acetate 4:1). Thus, a yellow oil (18.1 g, 30.2 mmol, 96 %) could be isolated. $[\alpha]_D^{20} = -4.3°$ ($c = 1.1$ in $CHCl_3$); $R_f = 0.63$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.08$ (s, 3H; −Si*t*Bu$(CH_3)_2$) 0.10 (s, 12H; −TMS and −Si*t*Bu$(CH_3)_2$), 0.14 (s, 9H; −TMS), 0.85 (s, 9H; −SiMe_2*t*Bu), 1.29 (s, 3H; C6-CH_3), 1.85 (m, 2H; H5), 2.37 (m, 4H; H4 and H7), 3.49 (s, 3H; −OCH_3), 3.73 (d, ^2J(H,H) = 17.2 Hz, 1H; H1″), 3.96 (d, ^2J(H,H) = 17.2 Hz, 1H; H1″), 5.22 (s, 2H; −OCH_2O−), 5.82 (s, 1H; H1), 7.08 (d, ^3J(H,H) = 8.2 Hz, 1H; H4′), 7.25 (t, ^3J(H,H) = 8.2 Hz, 1H; H5′), 7.42 ppm (d, ^3J(H,H) = 8.2 Hz, 1H; H6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.21 (−Si*t*Bu$(CH_3)_2$), −2.17 (−Si*t*Bu-$(CH_3)_2$), −0.05 (−TMS), −0.01 (−TMS), 13.7 (C4), 16.0 (−SiMe_2CMe$_3$), 18.2 (C1″), 25.8 (−SiMe_2*t*Bu), 27.0 (C6-*C*H_3), 33.9 (C7), 40.9 (C5), 56.0 (−OCH_3), 62.4 (C1), 74.4 (C6), 79.0 (C2), 84.7 (C3), 87.0 (C3″), 87.6 (C9), 94.5 (−OCH_2O−), 104.1 (C8), 105.3 (C2″), 114.5 (C4′), 121.1 (C6′), 124.1 (C2′), 128.0 (C5′), 140.6 (C1′), 154.5 ppm (C3′); IR (CCl_4): $\tilde{\nu}$ = 3603.3 (w), 2958.7 (s), 2931.1 (m), 2899.5 (m), 2857.5 (m), 2173.4 (m), 1587.9 (w), 1471.7 (m), 1376.1 (m), 1360.4 (w), 1311.1 (w), 1250.9 (ss), 1205.5 (w), 1155.0 (s), 1111.2 (m), 1089.7 (m), 1044.1 (s), 1017.5 cm^{-1} (s); MS (EIMS, 70 eV): m/z (%): 599 (0.1) [M^+], 566 (0.2), 542 (0.9) [M^+−*t*Bu], 526 (0.6), 512 (0.3), 497 (0.7) [541−C_2H_5O], 488 (2), 469 (17), 437 (4), 429 (1), 417 (2), 404 (3), 397 (1), 389 (1), 377 (4), 365 (1), 345 (7), 340 (4), 305 (9), 269 (5), 253 (3), 229 (3), 185 (3), 169 (17), 155 (3), 149 (5), 147 (12), 133 (3), 115 (7), 89 (7), 77 (3), 75 (23), 74 (11), 73 (100) [TMS$^+$], 59 (5), 45 (40) [$C_2H_5O^+$], 41 (1); elemental analysis calcd (%) for $C_{33}H_{54}O_4Si_3$: C 66.16, H 9.09; found: C 66.14, H 8.96.

(6*R*)-1-(3-Methoxy-2-prop-2-ynylphenyl)-6-methylnona-2,8-diyn-1-ol (26a): The alcohol **25a** (3.01 g, 6.86 mmol) was dissolved in dichloromethane (50 mL). Tetrabutylammonium hydrogensulfate (1.17 g, 3.43 mmol) and ammonium fluoride solution (60 mL, 45 % in water) were added, and the mixture was stirred intensively for 24 h at ambient temperature. Additional ammonium fluoride solution (20 mL, 45 % in water) was added and the solution was stirred for another 24 h. Phases were separated, the aqueous layer was extracted thrice with dichloromethane (100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/diethyl ether 3:1) to yield a colorless oil (1.94 g, 6.60 mmol, 96 %). $[\alpha]_D^{23} = -3.47$ ($c = 0.98$ in $CHCl_3$); $R_f = 0.31$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.98$ (d, ^3J(H,H) = 6.6 Hz, 3H; 3-CH_3), 1.41–1.81 and 2.14–2.25 (m, 8H; 3×CH_2, H-3 and OH, D_2O-exchangeable), 1.94 (t, ^4J(H,H) = 2.3 Hz; C≡C–H), 1.97 (t, ^4J(H,H) = 2.8 Hz, 1H; C≡C–H), 3.70 and 3.82 (2×dd, AB signal, J(A,B) = 17.13 Hz, ^4J(H,H) = 2.8 Hz, 2H; Ar–CH_2–C≡C), 3.87 (s, 3H; OCH_3), 5.87 (dt, ^3J(H,H) = 5.0 Hz, ^5J(H,H) = 2 Hz, 1H; Ar–CH–OH), 6.86 and 7.29 (d, J_0 = 7.8 Hz, 2H; H-arom.), 7.25 ppm (t, J_0 = 7.8 Hz, 1H; H-5); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.41, 16.60, 25.21, 34.08 (4×CH_2), 18.90, 31.70, 55.82, 62.38 (C-3, 3-CH_3, OCH_3, ArCHO), 67.97, 69.55 (2×C≡C–H), 79.64, 82.61, 82.90, 87.21 (4x C-alkyne), 110.93, 119.52, 128.13 (CH-arom.), 122.93, 140.28, 157.03 ppm (C_{quart}- arom.); IR (CCl_4): $\tilde{\nu}$ = 3601–3510 (OH), 3312 cm^{-1} (C≡C–H); MS (EIMS, 70 eV): m/z (%): 294 (7) [M^+], 251 (7) [M^+−CH_2C≡CH−H_2O], 237 (11) [251−CH_2]; elemental analysis calcd (%) for $C_{21}H_{24}O_2$: C 81.60, H 7.53; found: C 79.42, H 7.47.

(6*S*)-6-(*tert*-Butyldimethylsilyloxy)-1-(3-methoxy-2-prop-2-ynylphenyl)-6-methylnona-2,8-diyn-1-ol (26b): A solution of **25b** (7.1 g, 12.5 mmol) in absolute methanol (150 mL) was stirred with dried potassium carbonate (3.5 g, 25.0 mmol) for 6.5 h at room temperature until no further starting material could be detected by TLC. The reaction mixture was diluted with diethyl ether (150 mL) and distilled water (400 mL). Phases were separated, and the aqueous layer was extracted thrice with diethyl ether (250 mL). The combined organic layers were dried over $MgSO_4$ and con-

centrated in vacuo. The remaining yellow oil was subjected to chromatography (petroleum ether/diethyl ether 10:1) to yield a pale yellow oil (4.8 g, 11.3 mmol, 90%). $[\alpha]_D^{20} = -5.9°$ ($c = 2$ in $CHCl_3$); $R_f = 0.28$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.09$ (s, 3H; $-SitBu(CH_3)_2$), 0.10 (s, 3H; $-SitBu(CH_3)_2$), 0.86 (s, 9H; $-SiMe_2tBu$), 1.32 (s, 3H; C6-CH_3), 1.87 (m, 2H; H5), 1.99 (t, ^4J(H,H) = 2.8 Hz, 1H; H9), 2.0 (t, ^4J(H,H) = 2.8 Hz, 1H; H3″), 2.36 (m, 4H; H4 and H7), 3.72 and 3.85 (dd, ^2J(H,H) = 16.0 Hz, ^4J(H,H) = 2.8 Hz, 2H; H1″), 3.87 (s, 3H; C3′-OCH_3), 5.79 (m, 1H; H1), 6.88 (d, ^3J(H,H) = 7.4 Hz, 1H; H4′), 7.27 (t, ^3J(H,H) = 7.4 Hz, 1H; H5′), 7.33 ppm (d, ^3J(H,H) = 7.4 Hz, 1H; H6′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.21$ and -2.17 ($-SitBu(CH_3)_2$), 13.6 (C4), 14.4 (C1″), 18.1 ($-SiMe_2C(CH_3)_3$), 25.7 ($-SiMe_2tBu$), 27.0 (C6-CH_3), 32.4 (C7), 40.5 (C5), 56.0 (C3′-OCH_3), 67.9 (C1), 70.6 (C3″), 74.3 (C9), 79.2 (C2″), 81.3 (C2), 82.9 (C8), 87.7 (C3), 111.0 (C4′), 119.5 (C2′), 123.0 (C6′), 128.1 (C5′), 140.3 (C1′), 157.1 ppm (C3′); IR (CCl_4): $\tilde{\nu} =$ 3516.0 (w), 3312.2 (s), 2955.6 (s), 2929.5 (s), 2894.8 (m), 2856.1 (m), 2836.8 (w), 2231.0 (w), 2119.1 (w), 1588.2 (m), 1472.0 (s), 1462.0 (s), 1439.7 (m), 1375.9 (m), 1360.0 (m), 1312.2 (w), 1264.2 (ss), 1213.5 (w), 1171.7 (m), 1133.0 (m), 1111.8 (s), 1085.6 (m), 1074.8 (m), 1043.7 cm^{-1} (s); MS (EIMS, 70 eV): m/z (%): 424 (1) [M^+], 385 (17) [$M^+ - C_3H_3$], 367 (30) [$M^+ - t$Bu], 349 (7), 328 (8) [$367 - C_3H_3$], 313 (7), 293 (6) [M^+−OTBS], 275 (50), 260 (40), 245 (51), 235 (54), 231 (18), 215 (23), 195 (46), 171 (17), 165 (28), 153 (19), 152 (19), 145 (16) [$C_{10}H_9O^+$], 115 (34), 97 (59), 77 (16), 75 (100) [$C_6H_3^+$], 73 (93), 69 (12); elemental analysis calcd (%) for $C_{26}H_{36}O_3Si$: C 73.54, H 8.54; found: C 73.58, H 8.49.

(6*S*)-6-(*tert*-Butyldimethylsilyloxy)-1-(3-methoxymethoxy-2-prop-2-ynylphenyl)-6-methylnona-2,8-diyn-1-ol (26c): Compound **25c** (17.84 g, 29.8 mmol) was dissolved in absolute methanol (500 mL). After the addition of dry potassium carbonate (9.23 g, 66.8 mmol), the mixture was stirred for 5 h at room temperature until TLC showed complete conversion. The solvent was evaporated and the residue dissolved in distilled water (250 mL) and diethyl ether (250 mL). Phases were separated, and the aqueous layer was extracted with diethyl ether (3×200 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The remaining orange oil was subjected to chromatography (petroleum ether/ethyl acetate 3:1) to provide a yellow oil (12.97 g, 28.5 mmol, 96%). $[\alpha]_D^{20} = -5.4°$ ($c = 1.08$ in $CHCl_3$); $R_f = 0.43$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.09$ (s, 3H; $-SitBu(CH_3)_2$), 0.10 (s, 3H; $-SitBu(CH_3)_2$), 0.85 (s, 9H; $-SiMe_2tBu$), 1.32 (s, 3H; C6-CH_3), 1.81 and 1.93 (m, 2H; H5), 2.00 (t, ^4J(H,H) = 2.7 Hz, 2H; H9 and H3″), 2.24 (s, 1H; −OH), 2.36 (m, 4H; H4 and H7), 3.50 (s, 3H; $-OCH_3$), 3.75 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.7 Hz, 1H; H1″), 3.86 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.7 Hz, 1H; H1″), 5.24 (s, 2H; $-OCH_2O-$), 5.78 (s, 1H; H1), 7.09 (d, ^3J(H,H) = 7.8 Hz, 1H; H4′), 7.25 (t, ^3J(H,H) = 7.8 Hz, 1H; H5′), 7.37 ppm (d, ^3J(H,H) = 7.8 Hz, 1H; H6′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.03$ ($-SitBu(CH_3)_2$), −1.99 ($-SitBu(CH_3)_2$), 13.8 (C4), 15.0 ($-SiMe_2CMe_3$), 18.3 (C1″), 25.9 ($-SiMe_2tBu$), 27.2 (C6-CH_3), 32.6 (C7), 40.7 (C5), 56.3 ($-OCH_3$), 62.7 (C1), 68.3 (C3″), 74.5 (C9), 79.3 (C2), 81.5 (C2″), 82.9 (C8), 88.1 (C3), 94.7 ($-OCH_2O-$), 114.7 (C4′), 120.9 (C6′), 124.0 (C2′), 128.3 (C5′), 140.5 (C1′), 155.0 ppm (C3′); IR (CCl_4): $\tilde{\nu} =$ 3604.0 (w), 3313.9 (s), 2957.4 (s), 2931.0 (s), 2898.3 (m), 2857.8 (m), 2827.4 (w), 2120.3 (w), 1588.0 (m), 1471.9 (s), 1442.2 (m), 1404.2 (w), 1376.7 (m), 1360.6 (m), 1312.3 (m), 1253.1 (s), 1205.0 (m), 1172.9 (m), 1155.1 (s), 1133.2 (m), 1113.3 (s), 1088.8 (m), 1042.9 (s), 1015.2 (s), 1006.0 cm^{-1} (s); MS (EIMS, 70 eV): m/z (%): 454 (0.02) [M^+], 415 (7), 397 (11) [$M^+ - t$Bu], 379 (2) [$397 - H_2O$], 366 (1), 365 (2), 335 (2) [397−OMOM], 325 (1), 307 (1), 306 (2), 305 (7), 273 (14), 261 (8), 258 (10), 251 (4), 245 (12), 243 (9), 233 (19), 229 (8), 219 (9), 215 (10), 205 (9), 197 (10), 181 (12), 165 (12), 152 (8), 115 (14) [TBS$^+$], 97 (31), 77 (11), 75 (68) [$C_6H_3^+$], 73 (69), 45 (100) [$C_2H_5O^+$], 43 (20), 41 (3); elemental analysis calcd (%) for $C_{27}H_{38}O_4Si$: C 71.32, H 8.42; found: C 71.23, H 8.34.

General procedure for the synthesis of the TBS ether of the triynes (5a–c): 2,6-Lutidine (2.9 g, 27.1 mmol) was added at room temperature to a solution of the alcohol **26** (11.3 mmol) in absolute dichloromethane (150 mL). After cooling the solution to 0°C, OTBSTf (3.6 g, 13.6 mmol) was added dropwise. The reaction mixture was stirred and allowed to warm to room temperature slowly until no starting material could be detected by TLC. The reaction was quenched by the addition of water (200 mL) and vigorous stirring for 3 min. After phase separation, the aqueous layer was extracted thrice with dichloromethane (150 mL). The combined organic layers were washed with brine (250 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography of the residue provided the product as a colorless to pale yellow oil.

(6′*R*)-1-[1′-(*tert*-Butyldimethylsilyloxy)-6′-methylnona-2′,8′-diynyl]-3-methoxy-2-prop-2-ynyl benzene (5a): $[\alpha]_D^{22} = -1.36$ ($c = 0.59$ in $CHCl_3$); $R_f =$ 0.28 (petroleum ether/diethyl ether 40:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.13$ and 0.15 (2×s, 6H; $Si(CH_3)_2$), 1.00 (d, ^3J(H,H) = 6.6 Hz, 3H; 3-CH_3), 1.45–1.82 and 2.13 to 2.29 (m, 7H; 3×CH_2, H-3), 1.93 (t, ^4J(H,H) = 2.3 Hz, 1H; C≡C−H), 1.96 (t, ^4J(H,H) = 2.8 Hz, 1H; C≡C−H), 3.76 and 3.82 (2×dd, AB signal, J(A,B) = 17.13 Hz, ^4J(H,H) = 2.8 Hz, 2H; Ar−CH_2−C≡C), 3.88 (s, 3H; OCH_3), 5.87 (t, ^5J(H,H) = 2 Hz, 1H; Ar−CH−OTBDMS), 6.85 (m, 1H; H-arom.), 7.26 ppm (m, 2H; H-arom.); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.89$, -4.61 ($Si(CH_3)_2$), 14.50, 16.66, 25.24, 34.19 (4×CH_2), 18.90, 31.27, 55.82, 62.64 (C-3, 3 CH_3, OCH_3, ArCHO), 67.35, 69.39 (2×C≡C−H), 80.66, 82.64, 82.66, 85.52 (4×C-alkyne), 110.15, 118.53, 127.71 (CH-arom.), 121.89, 141.85, 156.96 ppm (C_{quart}-arom.); IR (CCl_4): $\tilde{\nu} = 3312$ cm^{-1} (C≡C−H); MS (EIMS, 70 eV): m/z (%): 408 (0.2) [M^+], 351 (26) [$M^+ - t$Bu], 336 (28) [351−CH_3], 335 (6) [336−H]; elemental analysis calcd (%) for $C_{27}H_{38}O_2Si$: C 76.42, H 8.88; found: C 75.56, H 8.77.

(6′*S*)-1-[1′,6′-Bis-(*tert*-butyldimethylsilyloxy)-6′-methylnona-2′,8′-diynyl]-3-methoxy-2-prop-2-ynyl benzene (5b): $[\alpha]_D^{20} = -5.2°$ ($c = 2$ in $CHCl_3$); $R_f = 0.65$ (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.07$ (s, 3H; $-SitBu(CH_3)_2$), 0.08 (s, 3H; $-SitBu(CH_3)_2$), 0.12 (s, 3H; $-SitBu(CH_3)_2$), 0.15 (s, 3H; $-SitBu(CH_3)_2$), 0.84 ($-SiMe_2tBu$), 0.92 ($-SiMe_2tBu$), 1.29 (s, 3H; C6′-CH_3), 1.81 (m, 2H; H5′), 1.93 (t, ^4J(H,H) = 2.7 Hz, 1H; H9′), 1.97 (t, ^4J(H,H) = 2.7 Hz, 1H; H3″), 2.28 (m, 4H; H4′ and H7′), 3.70 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.7 Hz, 1H; H2″), 3.82 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.7 Hz, 1H; H2″), 3.86 (s, 3H; C3-OCH_3), 5.76 (m, 1H; H1′), 6.84 (t, ^3J(H,H) = 5.4 Hz, 1H; H5), 7.25 ppm (m, 2H; H4 and H6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.53$ and -4.24 ($-SitBu(CH_3)_2$), -1.89 and -1.84 ($-SitBu(CH_3)_2$), 14.0 (C4′), 14.9 (C1″), 18.5 and 18.6 ($-SiMe_2C(CH_3)_3$), 26.1 and 26.2 ($-SiMe_2tBu$), 27.3 (C6′-CH_3, 32.8 (C7′), 40.8 (C5′), 56.2 (C3-OCH_3, 63.0 (C1′), 67.7 (C6′), 70.8 (C3″), 74.7 (C9′), 80.5 (C2″), 81.6 (C8′), 83.0 (C2′), 86.5 (C3′), 110.5 (C4), 119.0 (C2), 122.3 (C6), 128.1 (C5), 142.2 (C1), 157.3 ppm (C3); IR (CCl_4): $\tilde{\nu} =$ 3312.6 (s), 2955.7 (s), 2929.1 (s), 2894.8 (m), 2856.3 (s), 2360.8 (w), 2224.8 (w), 2118.8 (w), 1588.7 (m), 1471.6 (s), 1462.3 (s), 1439.4 (m), 1406.5 (w), 1388.4 (m), 1376.1 (m), 1360.8 (m), 1257.1 (s) 1215.4 (m), 1199.8 (m), 1170.6 (m), 1132.7 (s), 1111.7 (s), 1058.2 (s), 1004.9 (s), 938.5 (m), 906.1 cm^{-1} (m); MS (EIMS, 70 eV): m/z (%): 538 (<1) [M^+], 523 (3) [M^+−Me], 499 (17) [$M^+ - C_3H_3$], 482 (59), 481 (86) [$M^+ - t$Bu], 407 (22) [M^+−OTBS], 368 (18), 367 (54), 350 (27) [480−OTBS], 349 (70), 334 (33), 327 (33), 309 (28), 294 (22), 289 (53) [$C_{17}H_{23}OSi^+$], 275 (89), 269 (31), 260 (27), 259 (17), 247 (47), 235 (53) [$C_{14}H_{23}OSi^+$], 231 (56), 211 (17), 209 (20), 195 (47), 181 (17), 165 (31), 153 (38), 149 (22), 147 (72), 141 (26), 115 (55) [TBS$^+$], 97 (69), 75 (90) [$C_6H_3^+$], 74 (48), 73 (100), 59 (32); elemental analysis calcd (%) for $C_{32}H_{50}O_3Si_2$: C 71.32, H 9.35; found: C 71.04, H 8.76.

(6′*S*)-1-[1′,6′-Bis(*tert*-butyldimethylsilyloxy)-6′-methylnona-2′,8′-diynyl]-3-methoxymethoxy-2-prop-2-ynyl benzene (5c): $[\alpha]_D^{20} = -4.8°$ ($c = 1.16$, $CHCl_3$); $R_f = 0.75$ (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.08$ (s, 3H; $-SitBu(CH_3)_2$), 0.09 (s, 3H; $-SitBu(CH_3)_2$), 0.13 (s, 3H; $-SitBu(CH_3)_2$), 0.16 (s, 3H; $-SitBu(CH_3)_2$), 0.85 (s, 9H; $-SiMe_2tBu$), 0.93 (s, 9H; $-SiMe_2tBu$), 1.30 (s, 3H; C6-CH_3), 1.77 (m, 1H; H5), 1.87 (m, 1H; H5), 1.94 (t, ^4J(H,H) = 2.3 Hz, 1H; H9), 1.98 (t, ^4J(H,H) = 2.7 Hz, 1H; H3″), 2.31 (m, 4H; H4 and H7), 3.51 (s, 3H; $-OCH_3$), 3.74 (dd, ^2J(H,H) = 17.0 Hz, ^4J(H,H) = 2.7 Hz, 1H; H1″), 3.83 (dd, ^2J(H,H) = 17.0 Hz, ^4J(H,H) = 2.7 Hz, 1H; H1″), 5.24 (s, 2H; $-OCH_2O-$), 5.74 (s, 1H; H1), 7.05 (d, ^3J(H,H) = 7.6 Hz, 1H; H4′), 7.22 (t, ^3J(H,H) = 7.6 Hz, 1H; H5′), 7.27 ppm (d, ^3J(H,H) = 7.6 Hz, 1H; H6′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.9$ ($-SitBu(CH_3)_2$), -4.6 ($-SitBu(CH_3)_2$), -2.23 ($-SitBu(CH_3)_2$), -2.17 ($-SitBu(CH_3)_2$), 13.6 (C4), 14.9 (C1″), 18.1 ($-SiMe_2CMe_3$), 18.3 ($-SiMe_2CMe_3$), 25.8 ($-SiMe_2tBu$), 25.9 ($-SiMe_2tBu$), 27.0 (C6-CH_3), 32.4 (C7), 40.5 (C5), 56.1 ($-OCH_3$), 62.8 (C1), 67.5 (C6), 70.4 (C3″), 74.3 (C9), 80.1 (C2″), 81.3 (C8), 82.6 (C2),

86.4 (C3), 94.6 (−O*C*H$_2$O−), 113.7 (C4′), 119.9 (C6′), 122.9 (C2′), 127.8 (C5′), 141.8 (C1′), 154.7 ppm (C3′); IR (CCl_4): $\tilde{\nu}$ = 3314.0 (s), 2957.3 (s), 2930.4 (s), 2897.3 (m), 2857.7 (s), 2827.1 (w), 2336.6 (w), 2120.1 (w), 1588.1 (m), 1472.0 (s), 1463.4 (m), 1442.1 (m), 1404.6 (w), 1389.4 (m), 1376.8 (m), 1361.3 (m), 1312.9 (m), 1253.0 (s), 1211.1 (m), 1155.1 (s), 1133.4 (m), 1112.3 (m), 1090.2 (m), 1029.9 cm^{-1} (s); MS (EIMS, 70 eV): *m*/*z* (%): 569 (0.1) [M^+], 554 (1) [M^+−Me], 530 (6), 512 (45) [M^+−*t*Bu], 479 (5), 451 (1), 437 (4) [M^+−OTBS], 421 (2), 409 (1), 405 (5), 397 (8), 379 (11) [512−OTBSH], 347 (15), 325 (6), 319 (13) [$C_{18}H_{27}O_3Si^+$], 305 (11), 299 (8), 287 (6), 273 (27), 251 (7), 245 (16), 233 (10), 229 (8), 217 (5), 197 (7), 193 (7) [$C_{11}H_{16}OSi^+$], 181 (7), 165 (8), 153 (8), 147 (15), 115 (14) [TBS$^+$], 99 (6), 97 (36), 89 (21), 75 (41) [$C_6H_3^+$], 74 (12), 73 (100), 59 (9), 45 (61) [$C_2H_5O^+$], 43 (6); elemental analysis calcd (%) for $C_{33}H_{52}O_4Si_2$: C 69.67, H 9.21; found: C 69.66, H 9.12.

General procedure for the cycloaddition to 4a–c with [CpCo(CO)$_2$]: For reaction details, see Table 2. A solution of the catalyst in toluene was added with a cannula to a solution of the triynes in dry and degassed toluene. The mixture was heated to reflux while being irradiated with a tungsten lamp (Osram Vitalux 300 W) for the time indicated in Table 2. The solvent was evaporated and the residue was purified by column chromatography.

General procedure for the cycloaddition to 4a–c with [CpCo(C$_2$H$_4$)] as catalyst: For reaction details, see Table 2. The catalyst in toluene at −80 °C was added to a solution of the triynes in dry and degassed toluene. This solution was stirred for 4 h and allowed to warm slowly to 0 °C. The solvent was evaporated, and the residue was dissolved in glacial acetic acid and stirred for several minutes. The solvent was removed in vacuo and the residue was purified by column chromatography.

(+)-(3*R*)-8-Methoxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene (4a): M.p. 136 °C; $[\alpha]_D^{22}$ = +86.43 (*c* = 0.14 in $CHCl_3$); R_f = 0.31 (petroleum ether/diethyl ether 100:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, ^3J(H,H) = 6.6 Hz, 3H; 3-CH$_3$), 1.58 (m, 1H; H-2), 2.00 (m, 1H; H-3), 2.14 (m, 1H; H-2), 2.60 (dd, ^2J(H,H) = 16.5 Hz, ^3J(H,H) = 10.5 Hz, 1H; H-4), 2.95 (dd, ^2J(H,H) = 16.5 Hz, ^3J(H,H) = 3.9 Hz, 1H; H-4), 3.14 (m, 1H; H-1), 3.40 (d, ^2J(H,H) = 16.5 Hz, 1H; H-1), 4.09 (s, 3H; OCH$_3$), 6.73 (d, J_0 = 8.0 Hz, 1H; H-9), 7.18 (d, J_0 = 8.6 Hz, 1H; H-5), 7.37 (t, J_0 = 8.0 Hz, 1H; H-10), 7.62 (d, J_0 = 8.0 Hz, 1H; H-11), 7.82 (d, J_0 = 8.6 Hz, 1H; H-6), 8.44 (s, 1H; H-12), 8.78 ppm (s, 1H; H-7); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.79 (3-CH$_3$), 25.83 (C-1), 28.88 (C-3), 31.35 (C-2), 39.14 (C-4), 55.45 (OCH$_3$), 101.34 (C-9), 120.75 (C-12), 120.83 (C-11), 121.35 (C-7), 125.06 (C-10), 126.58 (C-6), 128.05 (C-5), 124.09, 130.34, 131.42, 132.64, 133.57, 155.38 ppm (C$_{quart}$-arom.); IR (CCl_4): $\tilde{\nu}$ = 2935–2810 cm^{-1} (C−H of OCH$_3$); MS (EIMS, 70 eV): *m*/*z* (%): 276 (100) [M^+], 261 (15) [M^+−CH$_3$], 246 (7) [261−CH$_3$], 233 (77) [261−C$_2$H$_4$].

(3*S*)-3-(*tert*-Butyldimethylsilyloxy)-8-methoxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene (4b): $[\alpha]_D^{20}$ = −49.1° (*c* = 0.75 in $CHCl_3$); R_f = 0.80 (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.06 (s, 3H; −Si*t*Bu(CH$_3$)$_2$), 0.12 (s, 3H; −Si*t*Bu(CH$_3$)$_2$), 0.72 (s, 9H; −SiMe$_2$*t*Bu), 1.40 (s, 3H; C3-CH$_3$), 2.00 (m, 2H; H2), 2.95 (d, ^2J(H,H) = 25 Hz, 1H; H4), 2.99 (d, ^2J(H,H) = 25 Hz, 1H; H4), 3.29 (m, 2H; H1), 4.06 (s, 3H; C8-OCH$_3$), 6.70 (d, ^3J(H,H) = 8.2 Hz, 1H; H9), 7.10 (d, ^3J(H,H) = 9.2 Hz, 1H; H5), 7.34 (t, ^3J(H,H) = 8.2 Hz, 1H; H10), 7.60 (d, ^3J(H,H) = 9.2 Hz, 1H; H6), 7.81 (d, ^3J(H,H) = 8.2 Hz, 1H; H9), 8.43 (s, 1H; H12), 8.75 ppm (s, 1H; H7); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.7 and −2.3 (−Si*t*Bu(CH$_3$)$_2$), 18.0 (−SiMe$_2$*C*Me$_3$), 24.3 (C1), 25.7 (−SiMe$_2$*t*Bu), 28.8 (C3-CH$_3$), 36.8 (C2), 45.2 (C4), 55.5 (C8-OCH$_3$), 71.5 (C3), 101.4 (C9), 120.9 (C7a), 121.4 (C11 and C12), 124.2 (C7), 125.2 (C6a), 126.9 (C6), 128.0 (C10), 129.7 (C5), 130.4 (C11a), 131.3 (C12a), 132.2 (C12b), 132.7 (C4a), 155.5 ppm (C8); IR (CCl_4): $\tilde{\nu}$ = 3056.7 (w), 2956.6 (s), 2929.0 (s), 2855.6 (m), 1625.6 (w), 1585.2 (w), 1542.9 (m), 1471.9 (s), 1471.9 (m), 1462.6 (m), 1430.7 (w), 1405.6 (m), 1387.8 (w), 1373.0 (m), 1351.1 (m), 1328.6 (w), 1290.8 (w), 1260.3 (ss), 1223.9 (m), 1205.5 (m), 1187.1 (w), 1107.2 (s), 1071.6 (m), 1045.1 (s), 1023.9 cm^{-1} (s); MS (EIMS, 70 eV): *m*/*z* (%): 406 (81) [M^+], 392 (6) [M^+−Me], 365 (11), 350 (23), 349 (66) [M^+−*t*Bu], 334 (9), 290 (6) [M^+−TBS], 289 (6), 277 (10), 276 (11), 275 (63) [M^+−OTBS], 274 (100), 273 (44), 261 (6), 260 (17) [391−OTBS], 259 (28), 258 (8), 246 (8), 245 (11), 235 (8), 234 (23) [$C_7H_{14}O^+$], 231 (11), 228 (7), 219 (8), 217 (8), 216 (10), 215 (13), 203 (8), 202 (9), 191 (14), 153 (8), 136 (4), 107 (8), 89 (10), 77 (22), 76 (9), 75 (96), 73 (37), 59 (6), 57 (12) [*t*Bu$^+$], 52 (7), 44 (8); elemental analysis calcd (%) for $C_{26}H_{34}O_2Si$: C 76.80, H 8.43; found: C 76.54, H 8.44.

(3*S*)-3-(*tert*-Butyldimethylsilyloxy)-8-methoxymethoxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene (4c): M.p. 126 °C (from petroleum ether/diethyl ether); $[\alpha]_D^{20}$ = −42.5° (*c* = 1.4 in $CHCl_3$); R_f = 0.53 (petroleum ether/diethyl ether 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.05 (s, 3H; −Si*t*Bu(CH$_3$)$_2$), 0.13 (s, 3H; −Si*t*Bu(CH$_3$)$_2$), 0.74 (s, 9H; −SiMe$_2$*t*Bu), 1.42 (s, 3H; C3-CH$_3$), 1.93 and 2.09 (m, 2H; H2), 2.97 and 3.00 (d, ^2J(H,H) = 23.0 Hz, 2H; H4), 3.25 and 3.36 (m, 2H; H1), 3.60 (s, 3H; −OCH$_3$), 5.48 (s, 2H; −OCH$_2$O−), 7.02 (d, ^3J(H,H) = 7.8 Hz, 1H; H9), 7.12 (d, ^3J(H,H) = 7.8 Hz, 1H; H11), 7.35 (t, ^3J(H,H) = 7.8 Hz, 1H; H10), 7.68 (d, ^3J(H,H) = 8.4 Hz, 1H; H5), 7.84 (d, ^3J(H,H) = 8.4 Hz, 1H; H6), 8.47 (s, 1H; H12), 8.78 ppm (s, 1H; H7); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.4 (−Si*t*Bu(CH$_3$)$_2$), −2.0 (−Si*t*Bu(CH$_3$)$_2$), 18.0 (−SiMe$_2$*C*Me$_3$), 24.2 (C1), 25.7 (−SiMe$_2$*t*Bu), 28.8 (C3-CH$_3$), 36.9 (C2), 45.1 (C4), 56.3 (−OCH$_3$), 71.4 (C3), 94.7 (−OCH$_2$O−), 105.3 (C9), 121.0 (C12), 121.2 (C7a), 121.9 (C11), 124.3 (C6a), 125.1 (C7), 126.7 (C6), 128.2 (C10), 129.7 (C5), 130.5 (C11a), 131.1 (C12a), 132.1 (C12b), 132.7 (C4a), 152.8 ppm (C8); IR (CCl_4): $\tilde{\nu}$ = 3059.2 (w), 2956.9 (s), 2929.8 (s), 2897.8 (m), 2856.9 (s), 2827.2 (w), 1626.7 (m), 1563.5 (m), 1472.6 (s), 1462.9 (m), 1431.8 (w), 1399.7 (m), 1374.0 (m), 1350.0 (m), 1328.9 (w), 1292.6 (w), 1258.4 (s), 1222.7 (m), 1194.9 (s), 1170.0 (m), 1153.0 (s), 1137.2 (m), 1114.1 (s), 1078.2 (s), 1050.6 (s), 1024.27 (s), 1005.8 (m), 984.6 (s), 944.4 (w), 926.9 cm^{-1} (m); MS (EIMS, 70 eV): *m*/*z* (%): 436 (100) [M^+], 380 (16), 379 (51) [M^+−*t*Bu], 348 (11), 347 (36), 335 (20), 334 (67) [379−C$_2$H$_5$O], 305 (35) [M^+−OTBS], 304 (41) [M^+−OTBSH], 273 (22), 260 (17), 259 (23) [M^+−C$_2$H$_5$O], 245 (11) [305−OMOM], 231 (19), 216 (9), 215 (9), 203 (8), 107 (16), 89 (14), 77 (24), 75 (48) [$C_6H_3^+$], 73 (17), 57 (14) [*t*Bu$^+$], 51 (6), 45 (65) [$C_2H_5O^+$]; elemental analysis calcd (%) for $C_{27}H_{36}O_3Si$: C 74.27, H 8.31; found: C 74.17, H 8.32.

General method for the oxidation to the benzo[*a*]anthracenediones 28a–c: A well-ground mixture of [Ag(py)$_2$MnO$_4$] (3.8 g, 9.89 mmol) and silica gel (5.0 g) was added in one portion at room temperature to a solution of **4** (1.24 mmol) in absolute dichloromethane (100 mL). Excluding light, the reaction mixture was stirred until the conversion of the starting material was completed. The suspension was filtered over Celite and the filtrate was concentrated after addition of silica gel (25.0 g). The residue was purified by column chromatography.

(+)-(3*R*)-8-Methoxy-3-methyl-1,2,3,4-tetrahydrobenz[*a*]anthracen-7,12-dione (28a): M.p. 170 °C; $[\alpha]_D^{23}$ = +64.00 (*c* = 0.14 in $CHCl_3$); R_f = 0.28 (petroleum ether/diethyl ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, ^3J(H,H) = 6.7 Hz, 3H; 3-CH$_3$), 1.30 (m, 1H; H-2), 1.84 (m, 1H; H-3), 1.94 (m, 1H; H-2), 2.44 (dd, ^2J(H,H) = 16.5 Hz, ^3J(H,H) = 10.5 Hz, 1H; H-4), 2.86 (dd, ^2J(H,H) = 16.5 Hz, ^3J(H,H) = 3.9 Hz, 1H; H-4), 3.15 (m, 1H; H-1), 3.45 (m 1H; H-1), 3.97 (s, 3H; OCH$_3$), 7.20 (d, J_0 = 8.2 Hz, 1H; H-arom.), 7.36 (d, J_0 = 7.8 Hz, 1H; H-arom.), 7.61 (t, J_0 = 8.2, 7.8 Hz, 1H; H-10), 7.77 (d, J_0 = 7.8 Hz, 1H; H-arom.), 8.01 ppm (d, J_0 = 7.8 Hz, 1H; H-arom.); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.62 (3-CH$_3$), 27.91 (C-3), 29.22, 31.73, 39.82 (3 × CH$_2$), 56.75 (OCH$_3$), 116.72, 119.64, 124.97, 134.86 (CH-arom.), 120.96, 130.35, 134.73, 137.61, 139.99, 159.55 (C$_{quart}$-arom.), 183.22, 185.85 ppm (C=O); IR (CCl_4): $\tilde{\nu}$ = 1671, 1722 cm^{-1} (C=O); MS (EIMS, 70 eV): *m*/*z* (%): 306 (13) [M^+], 291 (10) [M^+−CH$_3$], 277 (25) [M^+−CHO].

(3*S*)-3-*tert*-Butyldimethylsilyloxy-8-methoxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene-7,12-dione (28b): M.p. 115 °C; $[\alpha]_D^{20}$ = −61.1° (*c* = 1 in MeOH); R_f = 0.17 (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.05 (s, 3H; −Si*t*Bu(CH$_3$)$_2$), 0.08 (s, 3H; −Si*t*Bu(CH$_3$)$_2$), 0.68 (s, 9H; −SiMe$_2$*t*Bu), 1.35 (s, 3H; C3-CH$_3$), 1.71 (m, 1H; H2), 1.96 (m, 1H; H2), 2.87 (d, ^2J(H,H) = 27.3 Hz, 1H; H4), 2.91 (d, ^2J(H,H) = 27.3 Hz, 1H; H4), 3.37 (m, 2H; H1), 4.01 (s, 3H; C8-OCH$_3$), 7.25 (d, ^3J(H,H) = 8.6 Hz, 1H; H5), 7.37 (d, ^3J(H,H) = 7.6 Hz, 1H; H9), 7.67 (t, ^3J(H,H) = 7.6 Hz, 1H; H10), 7.84 (d, ^3J(H,H) = 7.6 Hz, 1H; H11), 8.07 ppm (d, ^3J(H,H) = 8.6 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.4 and −2.3 (−Si*t*Bu(CH$_3$)$_2$), 18.0 (−SiMe$_2$*C*Me$_3$), 25.5 (−SiMe$_2$*t*Bu), 26.7 (C1), 28.8 (C3-*C*H$_3$), 36.7 (C2), 45.5 (C4), 56.3 (C8-OCH$_3$), 70.2 (C3), 116.7 (C11), 119.6 (C7a), 120.7 (C9), 125.1 (C6), 129.7 (C6a), 134.8 (C10 and C11a), 134.9 (C12a), 137.4 (C5), 139.4 (C12b), 143.2 (C4a),

159.5 (C8), 183.3 (C12), 185.6 ppm (C7); IR (CCl_4): $\tilde{\nu}$ = 3546.2 (w), 2955.8 (m), 2929.2 (m), 2895.1 (w), 2856.1 (m), 1670.1 (s), 1588.1 (s), 1571.7 (m), 1470.9 (m), 1447.3 (m), 1435.6 (w), 1417.9 (m), 1374.8 (m), 1359.8 (w), 1270.2 (ss), 1216.0 (m), 1186.0 (w), 1160.1 (m), 1133.6 (m), 1117.0 (m), 1098.6 (m), 1075.8 (m), 1050.8 (m), 1029.9 (s), 1005.0 (w), 989.6 cm^{-1} (m); MS (EIMS, 70 eV): *m/z* (%): 436 (0.6) [M^+], 421 (3) [M^+−Me], 393 (6), 382 (5), 381 (23), 380 (64), 379 (100) [M^+−*t*Bu], 361 (4), 348 (6), 347 (14), 346 (40), 331 (3), 305 (11) [M^+−OTBS], 304 (6), 289 (9), 288 (10), 287 (31), 259 (3), 121 (4), 119 (12), 117 (13), 77 (7), 75 (47), 73 (18), 61 (25), 47 (4), 44 (32); elemental analysis calcd (%) for $C_{26}H_{32}O_4Si$: C 71.52, H 7.39; found: C 71.44, H 7.45.

(3*S*)-3-*tert*-Butyldimethylsilyloxy-8-methoxymethoxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene-7,12-dione (28c): M.p. 105 °C (from petroleum ether/diethyl ether); $[\alpha]_D^{20}$ = −37.5° (*c* = 0.6 in $CHCl_3$); R_f = 0.49 (petroleum ether/diethyl ether 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.03 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.10 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.70 (−SiMe$_2$*t*Bu), 1.37 (s, 3H; C3-CH_3), 1.75 and 1.97 (m, 2H; H2), 2.88 and 2.96 (d, ^2J(H,H) = 17.0 Hz, 2H; H4), 3.43 (m, 2H; H1), 3.57 (s, 3H; −OCH_3), 5.39 (s, 2H; −OCH_2O−), 7.40 (d, ^3J(H,H) = 7.8 Hz, 1H; H9), 7.50 (d, ^3J(H,H) = 7.8 Hz, 1H; H11), 7.65 (t, ^3J(H,H) = 7.8 Hz, 1H; H10), 7.92 (d, ^3J(H,H) = 8.4 Hz, 1H; H5), 8.08 ppm (d, ^3J(H,H) = 8.4 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.3 (−Si*t*Bu(CH_3)$_2$), −2.2 (−Si*t*Bu-(CH_3)$_2$), 18.0 (−SiMe$_2$*C*Me$_3$), 25.6 (−SiMe$_2$*t*Bu), 26.8 (C1), 28.9 (C3-*C*H_3), 36.8 (C2), 45.6 (C4), 56.6 (−OCH_3), 70.3 (C3), 95.2 (−OCH_2O−), 121.1 (C9), 121.3 (C11), 122.0 (C7a), 125.1 (C6), 129.9 (C6a), 134.5 (C11a), 134.9 (C10), 135.0 (C5), 137.4 (C12a), 139.6 (C12b), 143.3 (C4a), 157.0 (C8), 183.1 (C12), 185.5 ppm (C7); IR (CCl_4): $\tilde{\nu}$ = 3684.4 (s), 3620.4 (s), 3473.4 (m), 3018.8 (ss), 2435.0 (s), 1668.8 (m), 1517.5 (s), 1476.3 (s), 1424.0 (s), 1334.4 (m), 1218.1 (ss), 1047.7 (s), 928.0 cm^{-1} (s); MS (EIMS, 70 eV): *m/z* (%): 466 (0.4) [M^+], 451 (2) [M^+−Me], 423 (4), 411 (10), 410 (35), 409 (100) [M^+−*t*Bu], 365 (6), 348 (10), 347 (29), 332 (9), 321 (2), 305 (3), 303 (4), 289 (3), 273 (7), 245 (3), 234 (2), 215 (1), 202 (2), 189 (1), 153 (2), 107 (4), 89 (4), 77 (7), 75 (38), 73 (17), 57 (5) [*t*Bu$^+$], 45 (50) [$C_2H_5O^+$]; elemental analysis calcd (%) for $C_{27}H_{34}O_5Si$: C 69.49, H 7.34; found: C 69.24, H 7.32.

(3*S*)-3-(*tert*-Butyldimethylsilyloxy)-8-hydroxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene-7,12-dione (30): Acetyl chloride (0.3 mL, 4.2 mmol) was added dropwise to a solution of **28c** (0.25 g, 0.59 mmol) in absolute methanol (75 mL) and stirred for 2 h at ambient temperature, until no further starting material was detected by TLC. The solvent was evaporated, and the residue was purified by column chromatography (petroleum ether/diethyl ether 2:1) to yield an orange solid (0.24 g, 0.57 mmol, 96%). M.p. 133 °C (from petroleum ether/diethyl ether); $[\alpha]_D^{20}$ = −56.7° (*c* = 0.3 in $CHCl_3$); R_f = 0.82 (petroleum ether/diethyl ether 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.03 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.10 (s, 3H; −Si*t*Bu(CH_3)$_2$), 0.69 (s, 9H; −SiMe$_2$*t*Bu), 1.38 (C3-*C*H_3), 1.74 and 1.98 (m, 2H; H2), 2.88 and 2.93 (d, ^2J(H,H) = 17.6 Hz, 2H; H4), 3.46 (m, 2H; H1), 7.21 (d, ^3J(H,H) = 8.2 Hz, 1H; H9), 7.40 (d, ^3J(H,H) = 8.0 Hz, 1H; H5), 7.61 (t, ^3J(H,H) = 8.2 Hz, 1H; H10), 7.70 (d, ^3J(H,H) = 8.2 Hz, 1H; H11), 8.11 (d, ^3J(H,H) = 8.0 Hz, 1H; H6), 12.53 ppm (s, 1H; −OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.3 (−Si*t*Bu(CH_3)$_2$), −2.2 (−Si*t*Bu-(CH_3)$_2$), 18.0 (−SiMe$_2$*C*Me$_3$), 25.6 (−SiMe$_2$*t*Bu), 27.0 (C1), 28.9 (C3-*C*H_3), 36.6 (C2), 45.6 (C4), 70.1 (C3), 115.5 (C7a), 119.2 (C9), 122.9 (C11), 124.8 (C6), 130.7 (C6a), 132.8 (C11a), 134.9 (C10), 135.0 (C12a), 136.4 (C5), 141.0 (C12b), 145.2 (C4a), 161.7 (C8), 184.7 (C12), 188.8 ppm (C7); IR (CCl_4): $\tilde{\nu}$ = 3735.8 (w), 2957.7 (m), 2929.6 (m), 2857.4 (m), 2363.4 (w), 1700.4 (m), 1684.4 (m), 1669.3 (m), 1653.2 (s), 1638.0 (s), 1472.2 (m), 1456.9 (m), 1419.4 (m), 1369.1 (m), 1363.2 (m), 1319.4 (w), 1269.3 (s), 1244.6 (m), 1159.7 (m), 1135.3 (w), 1118.2 (m), 1073.7 (m), 1049.8 (w), 1029.1 (w), 1012.3 cm^{-1} (m); MS (EIMS, 70 eV): *m/z* (%): 422 (0.3) [M^+], 407 (1), 389 (1), 381 (1), 379 (5), 367 (8), 366 (32), 365 (100) [M^+−*t*Bu], 348 (16), 347 (43), 330 (14), 319 (1), 310 (5), 303 (3), 290 (14) [M^+−OTBSH], 275 (10), 250 (4), 247 (4), 219 (2), 205 (2), 202 (3), 189 (3), 165 (2), 153 (2), 107 (3), 77 (10), 75 (72), 73 (27), 57 (8) [*t*Bu$^+$], 51 (3), 43 (2), 41 (4); elemental analysis calcd (%) for $C_{25}H_{30}O_4Si$: C 71.05, H 7.16; found: C 70.93, H 7.16.

General procedure for the deprotection of 3-TBS ether to 29 and 31: Concentrated hydrofluoric acid (5.0 mL, 45% in water, p.a.) was added to a solution of **28b** or **30** (0.69 mmol), respectively, in acetonitrile (75 mL) at room temperature. The reaction mixture was stirred for 6 h at 50 °C until complete conversion was observed by TLC. The yellow solution was poured into a half-concentrated $CaCl_2$ solution (200 mL) and stirred for 5 min at ambient temperature. Phases were separated, and the aqueous layer was extracted thrice with diethyl ether (200 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (150 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was subjected to chromatography to provide a yellow solid.

(3*S*)-3-Hydroxy-8-methoxy-3-methyl-1,2,3.4-tetrahydrobenzo[*a*]anthracene-7,12-dione (29): M.p. 190 °C; $[\alpha]_D^{20}$ = −65.7° (*c* = 1 in $CHCl_3$); R_f = 0.2 (diethyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 3H; C3-CH_3), 1.80 (m, 1H; H2), 1.94 (m, 1H; H2), 2.92 (s, 2H; H4), 3.44 (m, 2H; H1), 4.00 (s, 3H; C8-OCH_3), 7.24 (d, ^3J(H,H) = 7.6 Hz, 1H; H9), 7.38 (d, ^3J(H,H) = 7.4 Hz, 1H; H5), 7.65 (t, ^3J(H,H) = 7.6 Hz, 1H; H10), 7.79 (d, ^3J(H,H) = 7.6 Hz, 1H; H11), 8.04 ppm (d, ^3J(H,H) = 7.4 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.3 (C1), 28.6 (C3-CH_3), 35.7 (C2), 44.6 (C4), 56.4 (C8-OCH_3), 68.2 (C3), 116.8 (C11), 119.7 (C7a), 120.7 (C9), 125.4 (C6), 130.1 (C6a), 134.9 (C10), 135.1 (C11a), 135.2 (C12a), 137.4 (C5), 138.6 (C12b), 142.3 (C4a), 159.6 (C8), 183.1 (C12), 185.7 ppm (C7); IR (CCl_4): $\tilde{\nu}$ = 3708.0 (w), 3611.6 (w), 3546.6 (w), 2961.1 (w), 2927.9 (w), 2335.8 (w), 1670.0 (s), 1588.4 (s), 1571.4 (m), 1466.3 (m), 1447.2 (m), 1435.3 (w), 1419.9 (w), 1376.2 (w), 1322.1 (m), 1270.6 (ss), 1216.0 (m), 1185.8 (w), 1159.2 (w), 1109.9 (m), 1096.7 (m), 1028.5 (m), 994.9 (m), 985.0 cm^{-1} (m); MS (EIMS, 70 eV): *m/z* (%): 323 (34) [M^++H], 322 (100) [M^+], 318 (7), 307 (7), 305 (14), 304 (27) [M^+−H_2O], 293 (9), 290 (10) [M^+−MeOH], 289 (30), 280 (23), 279 (48), 277 (9), 266 (12), 265 (40), 264 (42), 247 (21), 235 (11), 219 (7), 202 (8), 189 (13), 178 (12), 167 (15), 165 (12), 149 (33), 71 (10), 58 (14), 44 (27); elemental analysis calcd (%) for $C_{20}H_{18}O$: C 74.52, H 5.63; found: C 74.47, H 5.44.

(3*S*)-3,8-Dihydroxy-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]anthracene-7,12-dione (31): M.p. = 195 °C (decomposition, from petroleum ether/diethyl ether); $[\alpha]_D^{20}$ = −9.6° (*c* = 0.28 in $CHCl_3$); R_f = 0.55 (diethyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (s, 3H; C3-CH_3), 1.70 and 1.84 (m, 2H; H2), 2.89 (s, 2H; H4), 3.35 (m, 2H; H1), 7.34 (d, ^3J(H,H) = 7.8 Hz, 1H; H9), 7.59 (d, ^3J(H,H) = 8.5 Hz, 1H; H5), 7.65 (d, ^3J(H,H) = 7.8 Hz, 1H; H11), 7.8 (t, ^3J(H,H) = 7.8 Hz, 1H; H10), 8.06 (d, ^3J(H,H) = 8.5 Hz, 1H; H6), 12.38 ppm (s, 1H; C8-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.3 (C1), 29.0 (C3-CH_3), 35.0 (C2), 44.3 (C4), 65.6 (C3), 115.2 (C7a), 119.0 (C11), 122.7 (C9), 124.4 (C6), 130.3 (C9a), 132.2 (C11a), 134.8 (C12a), 135.2 (C5), 137.0 (C10), 140.2 (C12b), 145.6 (C4a), 160.5 (C8), 184.2 (C12), 188.2 ppm (C7); IR (CCl_4): $\tilde{\nu}$ = 3612.1 (w), 2961.2 (w), 2927.7 (w), 2845.8 (w), 2360.8 (w), 2336.4 (w), 1670.7 (m), 1639.1 (s), 1577.0 (m), 1456.5 (m), 1418.6 (w), 1367.0 (m), 1321.7 (w), 1269.3 (s), 1245.5 (m), 1159.7 (m), 1111.4 (w), 1072.7 (m), 1053.6 cm^{-1} (w); MS (EIMS, 70 eV): *m/z* (%): 308 (100) [M^+], 291 (23), 290 (87) [M^+−H_2O], 275 (26), 272 (11), 266 (42), 265 (61), 263 (16), 251 (60), 245 (55), 247 (16), 237 (14), 202 (14), 194 (13), 189 (26), 165 (29), 153 (24), 152 (19), 139 (12), 136 (13), 115 (21), 107 (39), 97 (10), 89 (24), 81 (12), 78 (10), 77 (81), 73 (10), 69 (41), 60 (12), 57 (21), 55 (19), 51 (16), 45 (14), 43 (67), 41 (9); elemental analysis calcd (%) for $C_{19}H_{16}O_4$: C 74.01, H 5.23; found: C 74.17, H 5.30.

General procedure for the oxidation to the benzo[*a*]anthracene-1,7,12-triones (1–3): Compound **28a**, **29**, or **31** (0.31 mmol) was dissolved in chloroform (150 mL). During irradiation with a tungsten lamp (Osram Vitalux 300 W), the solution was stirred at room temperature in an open round-bottomed flask until the conversion of starting material was completed. The solvent was evaporated and the residue was purified by column chromatography.

(+)-Rubiginone B_2 (1): M.p. > 262 °C (decomposition); $[\alpha]_D^{25}$ = +71.64 (*c* = 0.275 in $CHCl_3$); R_f = 0.14 (petroleum ether/diethyl ether 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, ^3J(H,H) = 6.4 Hz, 3H; 3-CH_3), 2.45 (m, 1H; H-3), 2.55 (dd, ^2J(H,H) = 15.6 Hz, ^3J(H,H) = 11 Hz, 1H; H-2), 2.67 (dd, ^2J(H,H) = 16.4 Hz, ^3J(H,H) = 11 Hz, 1H; H-4), 2.98 (m, 2H; H-2 and H-4), 4.04 (s, 3H; OCH_3), 7.24 (d, J_0 = 8.2 Hz, 1H; H-9), 7.45 (d, J_0 = 8.0 Hz, 1H; H-5), 7.65 (dd, J_0 = 8.2, 7.8 Hz, 1H; H-10), 7.71 (d, J_0 = 7.8 Hz, 1H; H-11), 8.20 ppm (d, J_0 = 8.0 Hz, 1H; H-6); ^{13}C NMR

(100 MHz, $CDCl_3$): $\delta = 21.43$ (3-CH_3), 30.82 (C-3), 38.33 (C-4), 47.55 (C-2), 56.50 (OCH_3), 117.15 (C-9), 119.68 (C-11), 129.60 (C-6), 132.99 (C-5), 135.34 (C-10), 120.56, 134.98, 135.07, 137.67, 149.13, 159.81 (C_{quart}-arom.), 181.59, 184.51, 198.89 ppm (C=O); IR (CCl_4): $\tilde{\nu} = 1673$, 1677, 1708 cm^{-1} (C=O); MS (EIMS, 70 eV): *m/z* (%): 320 (100) [M^+], 305 (15) [$M^+ - CH_3$], 292 (35) [$M^+ - CO$], 291 (15) [$M^+ - HCO$], 261 (27) [292 − OCH_3], 233 (24) [261 − CO].

(−)-8-*O*-Methyltetrangomycin (2): M.p. 169 °C; $[\alpha]_D^{20} = -89.2°$ ($c = 1$ in MeOH); $R_f = 0.05$ (diethylether); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.49$ (s, 3H; C3-CH_3), 1.81 (br s, 1H; C3-OH), 2.97 (d, ^2J(H,H) = 15.0 Hz, 1H; H2), 3.08 (d, ^2J(H,H) = 15.0 Hz, 1H; H2), 3.15 (s, 2H; H4), 4.02 (s, 3H; C8-OCH_3), 7.28 (d, ^3J(H,H) = 8.2 Hz, 1H; H9), 7.50 (d, ^3J(H,H) = 7.8 Hz, 1H; H5), 7.69 (t, ^3J(H,H) = 8.2 Hz, 1H; H10), 7.74 (d, ^3J(H,H) = 8.2 Hz, 1H; H11), 8.27 ppm (d, ^3J(H,H) = 7.8 Hz, 1H; H6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.9$ (C3-CH_3), 44.0 (C4), 53.8 (C2), 56.5 (C8-OCH_3), 72.6 (C3), 117.1 (C9), 119.6 (C11), 120.5 (C7a), 130.0 (C6), 133.8 (C5), 134.3 (C6a), 135.1 (C12a), 135.2 (C10), 135.4 (C11a), 137.8 (C12b), 146.3 (C4a), 159.7 (C8), 181.5 (C12), 184.7 (C7), 196.9 ppm (C1); IR (CCl_4): $\tilde{\nu} = 3709.2$ (w), 3607.2 (w), 2963.0 (m), 2928.3 (w), 2855.0 (w), 1709.7 (m), 1674.2 (s), 1588.4 (s), 1470.9 (m), 1444.0 (m), 1436.0 (m), 1299.9 (m), 1269.8 (ss), 1216.1 (m), 1154.0 (m), 1101.3 (m), 1074.0 (m), 1025.7 cm^{-1} (m); MS (EIMS, 70 eV): *m/z* (%): 336 (4) [M^+], 320 (5), 319 (33), 318 (100) [$M^+ - H_2O$], 301 (10), 290 (4), 289 (8), 273 (8), 272 (9), 245 (7), 244 (14), 231 (9), 216 (7), 215 (9), 203 (8), 202 (14), 190 (5), 189 (16), 153 (4), 107 (4), 89 (5), 77 (10), 58 (5), 45 (7), 44 (5); elemental analysis calcd (%) for $C_{20}H_{16}O_5$: C 71.42, H 4.79; found: C 71.32, H 4.71.

(−)-Tetrangomycin (3): $[\alpha]_D^{20} = -89.6$ ($c = 0.2$ in MeOH); literature: $[\alpha]_D^{20} = -100°$ ($c = 0.2$ in MeOH) for 99% *ee*; $R_f = 0.18$ (diethyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.52$ (s, 3H; C3-CH_3), 1.74 (br s, 1H; C3-OH), 3.02 and 3.13 (d, ^2J(H,H) = 14.6 Hz, 2H; H2), 3.49 (s, 2H; H4), 7.28 (d, ^3J(H,H) = 7.4 Hz, 1H; H9), 7.56 (d, ^3J(H,H) = 8.5 Hz, 1H; H5), 7.67 (m, 2H; H10 and H11), 8.31 (d, ^3J(H,H) = 8.5 Hz, 1H; H6), 12.26 ppm (s, 1H; C8-OH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.2$ (C3-CH_3), 44.0 (C4), 53.9 (C2), 72.6 (C3), 115.3 (C7a), 119.6 (C11), 123.7 (C9), 129.4 (C6), 133.6 (C12a), 133.8 (C10), 135.1 (C6a), 135.7 (C12b), 136.1 (C11a), 137.1 (C5), 147.6 (C4a), 162.0 (C8), 183.1 (C12), 187.4 (C7), 197.0 ppm (C1); H,H COSY correlation ($CDCl_3$): $\delta = 3.03$ (H2)–3.13 (H2), 7.08 (H9)–7.67 (H10 and H11), 7.56 (H5)–8.31 (H6); IR (CCl_4): $\tilde{\nu} = 3706.7$ (w), 3606.6 (w), 2957.5 (m), 2927.6 (s), 2855.3 (m), 2361.2 (w), 2334.3 (w), 1712.9 (m), 1682.2 (m), 1639.9 (s), 1593.4 (m), 1456.5 (s), 1362.1 (m), 1269.4 (s), 1216.8 (m), 1158.9 (m), 1075.3 (m), 1051.0 cm^{-1} (m); MS (EIMS, 70 eV): *m/z* (%): 322.2 (31) [M^+], 305.1 (6), 304.1 (27) [$M^+ - H_2O$], 278.9 (16), 264.9 (20), 263.9 (100) [$M^+ - C_2H_4O$], 235.9 (7), 208.0 (10), 189.0 (4), 179.9 (6), 165.0 (7), 152.1 (31), 151.0 (12), 126.2 (7), 116.2 (11), 107.2 (3), 89.2 (4), 77.1 (6), 57.1 (4), 55.1 (3), 43.1 (18); elemental analysis calcd (%) for $C_{19}H_{14}O_5$: C 74.80, H 4.38; found: C 74.55, H 4.49.

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