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Acid-Catalyzed Cyclization of Anthracenol Derivatives to Homotriptycenes

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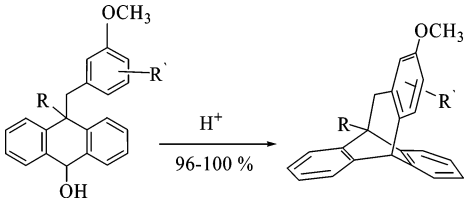

10-Benzyl-9,10-dihydroanthracen-9-ols, having high electron densities in the benzene ring, exhibit in the presence of acid a transannular ring closure to the corresponding homotriptycenes in almost quantitative yields. Since the starting compounds are easily accessible from 9(10*H*)-anthracenone, this process represents the most facile route to such pentacyclic systems. An electron-releasing methoxy group enables the intramolecular electrophilic substitution in its para position. In the absence of such an activation, a number of alternative processes can occur, namely the acid-catalyzed dehydration to anthracene derivatives with ($R \neq H$) or without ($R = H$) rearrangement or a disproportionation reaction of the secondary alcohol to the corresponding ketone and hydrocarbon.

Introduction

Triptycene and its derivatives attract great attention because of their rigid, aromatic 3D structure,[1−5] their unique electrochemical and photochemical properties,[6−10] their potential pharmaceutical properties,[11−13] and their applications in supramolecular chemistry and materials science.[6,8,14−18] However, there are only few examples of homotriptycenes which have been reported. Cristol and co-workers[19] synthesized homotriptycene and its derivatives by ring enlargement of 1-aminomethyltriptycene, but the route was lengthy and required a tedious separation from the concomitant isomers. Szeimies et al.[20] reported a unique route for the preparation of homotriptycenes using a thermal dehydrogenation of anellated dibenzohomobarrelene, but its application is limited because of the

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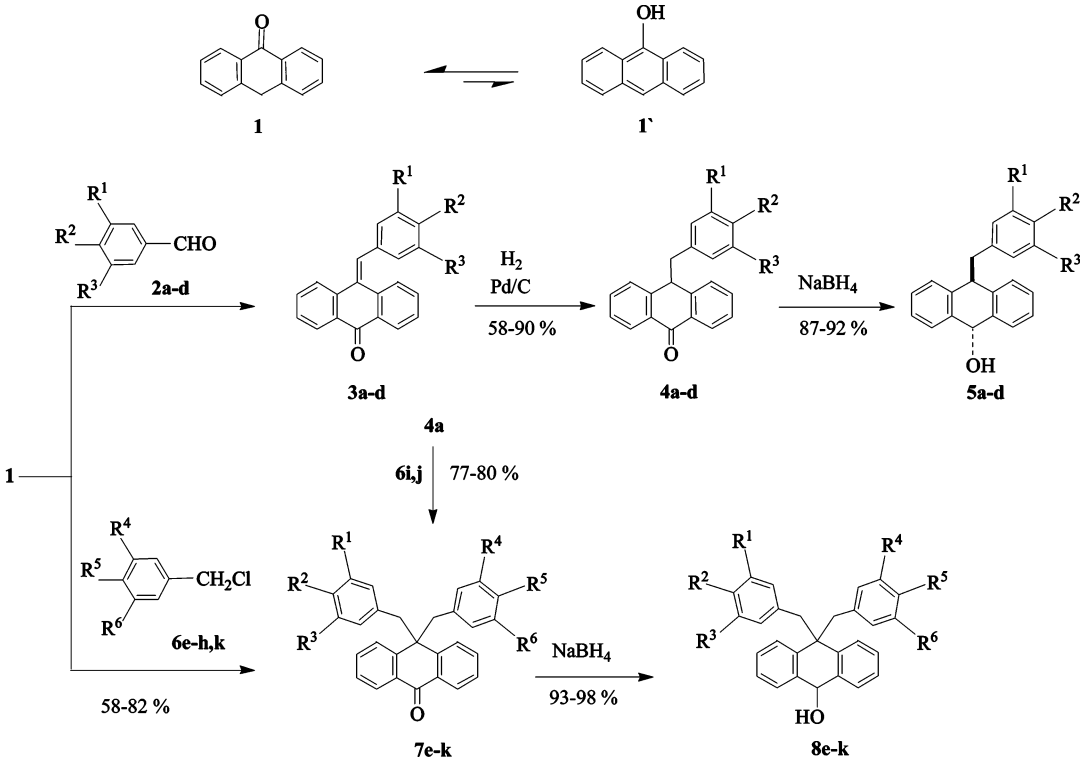
SCHEME 1. Preparation of the Anthracenol Derivatives 5a−d and 8e−k



2 - 8 a: $R^1 = R^3 = OMe$, $R^2 = H$

b: $R^1 = R^2 = R^3 = OMe$

c: $R^1 = R^3 = H$, $R^2 = OMe$

d: $R^1 = R^2 = R^3 = H$

e: $R^1 = R^3 = R^4 = R^6 = OBn$, $R^2 = R^5 = H$

f: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = OMe$

g: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = R^6 = OMe$

h: $R^1 = R^3 = R^4 = R^6 = H$, $R^2 = R^5 = OMe$

i: $R^1 = R^3 = R^4 = OMe$, $R^2 = R^5 = R^6 = H$

j: $R^1 = R^3 = OMe$, $R^2 = R^4 = R^5 = R^6 = H$

k: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$

multistep preparation of the starting propellane and the restricted possibility for substituent variations in the homotriptycene skeleton. Saito et al.[21] reported an alternative method using the cycloaddition of strained benzocyclopropene to anthracenes. We found now a simple novel route for the synthesis of homotriptycenes on the basis of anthracenol derivatives.[22]

Results and Discussion

Scheme 1 summarizes the preparation of the *trans*-10-benzyl-9,10-dihydroanthracen-9-ols **5a−d** and the 10,10-dibenzyl-9,10-dihydroanthracen-9-ols **8e−k** which were used as key compounds for the attempted preparation of homotriptycenes. 9-Anthracenol is a tautomeric system which exists predominantly in the more stable 9(10*H*)-anthracenone form (1 ⇌ 1'). The high electrophilicity in the 10-position enables the attack of benzaldehydes as well as benzyl halides. A mixture of **1** and **2a−d** in pyridine/piperidine yielded the 10-benzylidene-9(10*H*)-anthracenones **3a−d**.[23,24] Hydrogenation of **3a−d** on 5% palladium-on-carbon afforded **4a−d**,[23] and subsequent hydro-

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genation of the carbonyl group with $NaBH_4$ in diglyme gave **5a**−**d**. The *trans* configuration of **5a**−**d** was established by NOESY measurements. The proton 9-H shows a cross-peak to the enantiotopic protons of the benzylic CH_2 group, but not to the proton 10-H. 9,10-Dihydroanthracene derivatives exist in a boat conformation in which larger substituents such as benzyl groups are in a pseudoaxial position.[25] We explain the diastereoselective generation of the *trans*-configured compounds **5a**−**d** by a transition state in which H^- approaches from the less hindered "inner" side of the boat. The benzene rings condensed on the central ring shield the carbonyl face on the "inner" side of the boat conformation.

Reaction of **1** with the benzyl chlorides **6e**−**h**,**k** gave the 10,10-dibenzyl-9(10*H*)-anthracenons **7e**−**h**,**k**. The related compounds **7i**,**j** were obtained from **4a** by the reaction with **6i**,**j**. The latter method had the advantage that different benzyl substituents could be introduced in the 10-position of **1**. Compounds **7e**−**k** were then reduced to the 10,10-dibenzyl-9,10-dihydroanthracen-9-ols **8e**−**k** by the reaction with $NaBH_4$ in diglyme. The attack of H^- did not exhibit a diastereoselectivity for the reactions **7i** → **8i** and **7j** → **8j** which have different benzyl groups.

The 11 secondary alcohols **5a**−**d** and **8e**−**k** were subjected to the acid-catalyzed dehydration by applying acids, such as formic acid, oxalic acid, and acetic acid. The monobenzyl systems **5a**,**b** yielded homotriptycenes (**9a**,**b**) and anthracenes (**10a**,**b**), whereas **5c**,**d** gave quantitatively **10c**,**d**. Apparently, the OCH_3 substituents on the benzyl group affected the competition of 1,4- and 1,7-elimination of H_2O. We assume that protonation generates a secondary, resonance-stabilized carbenium ion (center on C-9), which forms **10a**−**d** by deprotonation on C-9. However, when the benzyl group on C-10 has a suitably activated position by an electron-donating group, an intramolecular aromatic electrophilic substitution can compete. The (transannular) 1,7-elimination of H_2O generates then a homotriptycene (pentacyclo[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]heneicosa-2,4,6,10,12,14,16,18,20-nonaene).

Treatment of the 10,10-dibenzyl-9,10-dihydroanthracen-9-ols **8e**−**g**,**i**,**j** with formic acid led in all cases to the quantitative formation of the corresponding homotriptycenes (**9e**−**g**,**i**,**j**). The reactions **8g** → **9g** and **8i** → **9i** deserve special interest. Compound **8g** contains two 3-methoxybenzyl groups. The electron-releasing OCH_3 substituent could activate its *para* and/or *ortho* position for the electrophilic attack. The obtained product **9g** reveals the regioselective ring closure in the para position. Compound **8i** contains a 3-methoxybenzyl and a 3,5-dimethoxybenzyl group. Altogether, three homotriptycenes are conceivable, but only **9i** was obtained. That means the electron richer 3,5-dimethoxybenzene ring reacts exclusively. Accordingly, the unsubstituted benzyl group of **8j** is not involved in the ring closure **8j** → **9j**.

Compounds **8h** and **8k** do not contain in the benzyl groups an activated position which is suitable for the ring closure to a homotriptycene. 1,4-Elimination of **8h** with 4-methoxybenzyl is a minor process (**8h** → **10h**); the major route is due to the rearrangement to 9,10-bis(4-methoxybenzyl)anthracene (**8h** → **11h**). Compound **8k** did not show any of the reactions mentioned above. It undergoes in the presence of formic acid a slow disproportionation to ketone **7k** and 9,10-dihydroanthracene **12k** (Scheme 2).

SCHEME 2. Acid-Catalyzed Reactions of the 10-Benzyl-9,10-dihydroanthracen-9-ols 5a−d and 8e−k

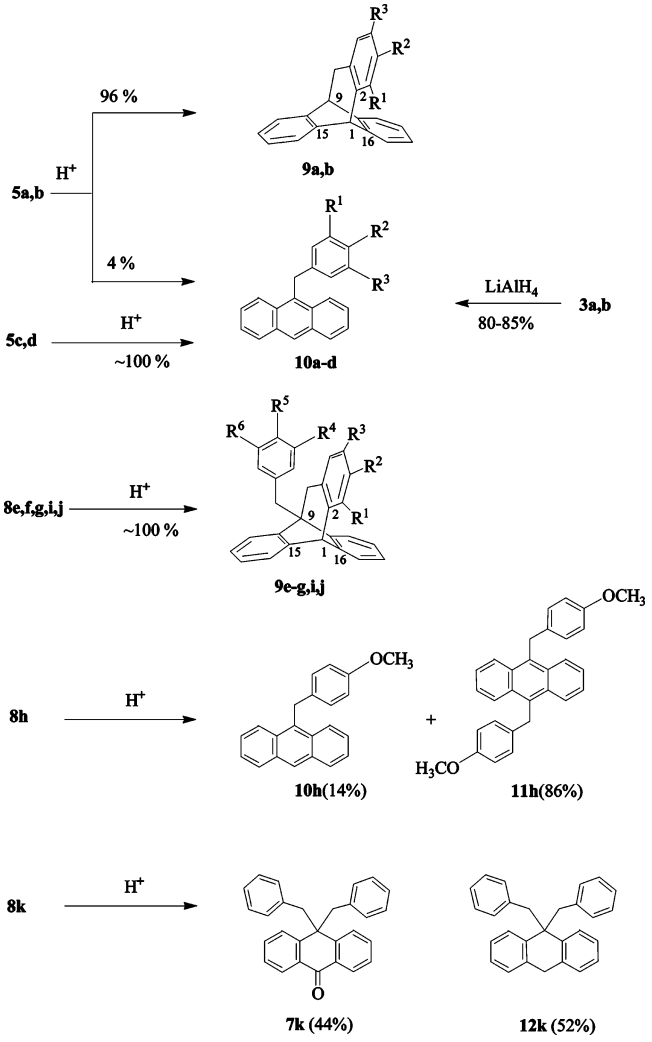

TABLE 1. Product Distribution of the Acid-catalyzed Dehydration of 5a in CH_2Cl_2 at Ambient Temperature

entry	molar ratio **5a**/HCOOH	reaction time (h)	conversion (%)	product distribution[a] **9a**/**10a**
1	1/56	0.5	100	96:4
2	1/12	0.5	100	92:8
3	1/2	2.0	100	67:33
4	3/2	2.0	100	64:36
5	trace of DCl[b]	36.0	53	55:45

[a] Determined by ^{1}H NMR spectroscopy (a) in 0.5 mL of $CDCl_3$ and (b) in 0.5 mL of $CDCl_3$.

Interestingly, the ratio **9**/**10** depends strongly on the acid concentration. Table 1 shows the results obtained for **5a** and decreasing amounts of HCOOH.

Anthracene **10a** is a minor side product when a high excess of HCOOH was used. Traces of DCl in $CDCl_3$, on the other hand, led to a mixture of **9a** and **10a**, which is close to 1:1. The higher the excess of acid is, the faster the 1,7-elimination; the elimination seems to be not or much less affected by the acid concentration.

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TABLE 2. Selected ^{1}H and ^{13}C NMR Data of 5a−d and 8e−k (δ Values in $CDCl_3$, TMS as Internal Standard)

compd	9-H d	C-9	10-H t	C-10	α-CH_2 d/s	α-CH_2 d/s	OH d
5a−d	4.77−5.03 ^3J = 10.8 Hz	66.7−66.9	4.22−4.28 ^3J = 6.3 Hz	47.9−48.5	2.88−2.94 ^3J = 6.3 Hz	44.8−46.2	1.95−2.03 ^3J = 10.8 Hz
8e−k	4.96−5.01 ^3J = 11.6 Hz	67.3−67.6		49.0−49.4	3.40−3.47 3.61−3.74	47.5−48.5 51.2−52.7	−0.14−0.32 ^3J = 11.6 Hz

TABLE 3. Selected ^{1}H and ^{13}C NMR Data of the Homotriptycenes 9a,b,e−g,i,j (δ Values in $CDCl_3$, TMS as Internal Standard)

compd	C-1	1-H s	C-9	9-H t	CH_2 d/s	CH_2 d/s
9a	41.9	5.69	45.6	4.19	37.4	3.21
9b	43.4	5.55	45.6	4.21	36.9	3.20
9e	44.7	5.84	46.9		40.1	3.03
					42.6	3.90
9f	39.9	5.63	44.8		43.7	3.05
					46.2	3.92
9g	40.0	4.85	44.7		46.8	3.09
					54.1	3.98
9i	40.0	5.75	44.7		42.4	3.05
					46.9	3.95
9j	39.9	5.77	44.6		42.3	3.07
					47.0	3.98

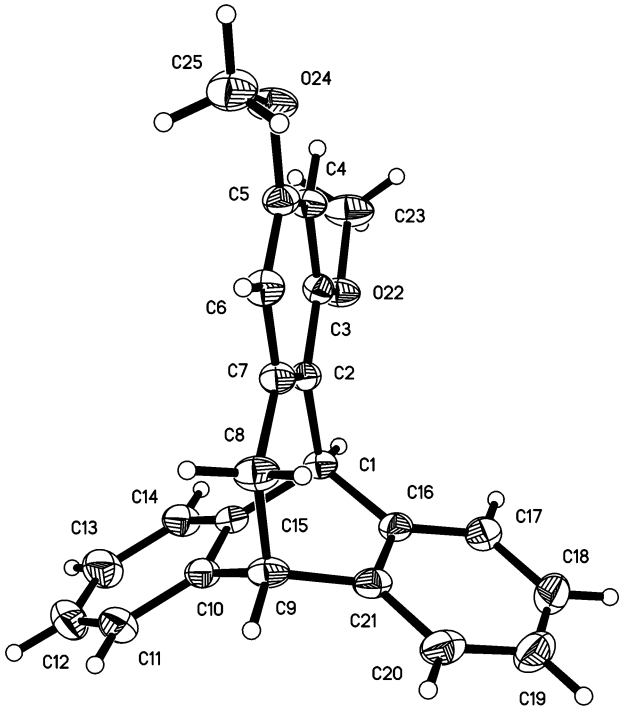
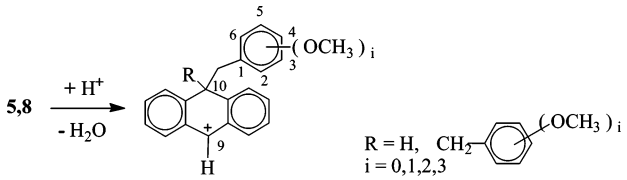


FIGURE 1. Crystal structure analysis (ORTEP plot) of homotriptycene **9a**, a bicyclo[3.2.2.]nona-2,6,8-triene scaffold condensed with three benzene rings (A−C).

The spectroscopic identification and characterization of the anthracene derivatives **4**, **5**, **7**, **8**, and **10**−**12** can be seen in the Experimental Section. Selected ^{1}H and ^{13}C NMR data of the compounds **5a**−**d** and **8e**−**k** and the homotriptycenes **9a**,**b**,**e**−**g**,**i**,**j** are listed in Tables 2 and 3, respectively. An ORTEP plot of a crystal structure analysis of **9a** is depicted in Figure 1. The bond lengths and bond angles are in the expected range. The most interesting feature of the X-ray study concerns the angles α between the three benzene ring planes: α(A,B) = 110.14°; α(B,C) = 109.08°; α(C,A) = 110.57°.

SCHEME 3. Initial Formation of the Carbocations 13 by Protonation of 5a−d and 8e−k



The molecule has in the crystalline state (as well as in solution) a de facto C_s symmetry.

Conclusions

With the exception of **8k**, all acid-catalyzed reactions of the 10-benzyl- and 10,10-dibenzyl-9,10-dihydroanthracen-9-ols **5** and **8** can be rationalized by the initial formation of resonance-stabilized carbenium ions **13** (Scheme 3).

The desired transannular ring closure of **13** to homotriptycenes requires a high nucleophilicity in position 2 of the substituted benzene ring. This can be effected by an electron-donating group such as methoxy in 5-position. In the absence of such an activating group **13** can eliminate a proton (R = H) or a benzyl group (R = 4-$H_3COC_6H_4CH_2$) and form a monosubstituted anthracene **10a**−**d**,**h**. Rearrangement and cleavage of the proton in 9-position of **13** yields the 9,10-disubstituted anthracene **11h**. Formally, the acid-catalyzed reactions **5**,**8** → **9** correspond to 1,7-eliminations, the process **5**,**8** → **10** to 1,4-eliminations, and the reaction **8** → **11** to a 1,1-elimination, which includes a rearrangement.

The disproportionation of the secondary alcohol **8k** to ketone **7k** and hydrocarbon **12k** is in the absence of a hydrogen-transfer catalyst a rather unusual process.[26] The related diphenylmethanol (benzhydrol) shows such a reaction in the presence of Raney nickel[27] or Pd/C.[28] Since much more benzophenone than diphenylmethane is formed in these cases, such reactions are not real disproportionations. A 1:1 mixture of benzophenone and diphenylmethane was obtained from benzhydrol under drastic conditions in supercritical water.[29]

The most useful preparative process, described here, is certainly the facile formation of homotriptycenes. This transannular ring closure is related to a reaction that was found in an addition product of anthranol with lignin model quinone methides.[30,31]

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Experimental Section

General Procedure for the Preparation of the 9(10*H*)-Anthracenones 4a−d. A mixture of **3a−d** (3.0 mmol) and 5% palladium-on-carbon (1.14 g) in ethyl acetate/methanol (3:1, 72 mL) was treated overnight with hydrogen at ambient temperature. The catalyst was removed by filtration through silica gel under nitrogen. The filtrate was evaporated under reduced pressure and the residue recrystallized from ethanol.

10-(3,5-Dimethoxybenzyl)-9(10*H*)-anthracenone (4a): yield 877 mg, 85%, lit.[23] 36%; colorless crystals; mp 98−99 °C, lit.[23] mp 99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (d, ^3J = 6.0 Hz, 2H), 3.49 (s, 6H), 4.51 (t, ^3J = 6.0 Hz, 1H), 5.54 (d, ^4J = 1.8 Hz, 2H), 6.18 (t, ^4J = 1.8 Hz, 1H), 7.35 (m, 2H), 7.40 (m, 2H), 7.54 (m, 2H), 8.16 (m, 2H).

General Procedure for the Preparation of the 10-Benzyl-9,10-dihydroanthracen-9-ols 5a−d. A solution of **4** (1.0 mmol) in diglyme (4 mL) was stirred under nitrogen for 15 min. $NaBH_4$ (120 mg, 3.1 mmol) was added. After 30 min, methanol (2 mL) was added dropwise. The mixture was stirred for another 10 min, and then $NaBH_4$ (60 mg, 1.5 mmol) was added. After 3−4 h, water was slowly added with rapid stirring in an ice−water bath. Colorless crystals were obtained by filtration.

***trans*-10-(3,5-Dimethoxybenzyl)-9,10-dihydroanthracen-9-ol (5a):** yield 315 mg, 91%; colorless crystals; mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (d, ^3J = 10.8 Hz, 1H), 2.87 (d, ^3J = 6.4 Hz, 2H), 3.53 (s, 6H), 4.25 (t, ^3J = 6.4 Hz, 1H), 5.03 (d, ^3J = 10.8 Hz, 1H), 5.69 (d, ^3J = 1.0 Hz, 2H), 6.23 ("s", 1H), 7.16 (m, 2H), 7.24 (m, 2H), 7.30 (m, 2H), 7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.9, 48.2, 55.1, 66.9, 99.0, 107.5, 124.6, 126.5, 127.1, 127.7, 137.0, 140.0, 140.3, 160.0; MS (EI) *m*/*z* 328 (M^+ − 18, 100.0). Anal. Calcd for $C_{23}H_{22}O_3$ (346.42): C, 79.74; H, 6.40. Found: C, 79.80; H, 6.38.

General Procedure for the Preparation of the 10,10-Dibenzyl-9(10*H*)-anthracenones 7e−h,k. A mixture of **1** (394 mg, 1.0 mmol), the corresponding benzyl chloride **6** (2.0 mmol), potassium hydroxide (143 mg, 2.1 mmol), 18-crown-6 (20 mg, 0.07 mmol), and potassium iodide (25 mg, 0.15 mmol) in dry acetone (8 mL) was heated at 60 °C and stirred vigorously under nitrogen for 1.5−2 h. The volatile parts were removed under reduced pressure and the residue treated with 10 mL of CH_2Cl_2 and 10 mL of H_2O. The separated water layer was extracted three times with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried with Na_2SO_4 and the products purified by column chromatography (40 × 3 cm SiO_2, petroleum ether (bp 40−70 °C)/ethyl acetate).

10,10-Bis(3,5-dibenzyloxybenzyl)-9(10*H*)-anthracenone (7e). Chromatography with the eluent of petroleum ether (bp 40−70 °C)/ethyl acetate 10:1): yield 520 mg, 65%; colorless crystals; mp 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 4H), 4.49 (s, 8H), 5.55 (d, ^4J = 2.2 Hz, 4H), 6.14 (t, ^4J = 2.2 Hz, 2H), 7.18−7.33(m, 20H), 7.38 (m, 2H), 7.69 (m, 2H), 7.92 (m, 2H), 8.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.9, 50.3, 69.7, 101.0, 108.8, 126.9, 127.3, 127.5, 127.5, 127.8, 128.4, 132.9, 132.9, 136.9, 138.2, 145.7, 158.9, 182.9; MS (FAB) *m*/*z* 799 (M^+, 6.0), 154 (100.0). Anal. Calcd for $C_{56}H_{46}O_5$ (798.96): C, 84.18; H, 5.80. Found: C, 83.85; H, 5.80.

General Procedure for the Preparation of the 10,10-Dibenzyl-9(10*H*)-anthracenones 7i,j. A mixture of **4a** (346 mg, 1.0 mmol), the corresponding benzyl chloride **6** (1.0 mmol), potassium hydroxide (68 mg, 1.0 mmol), 18-crown-6 (25 mg, 0.09 mmol), potassium iodide (50 mg, 0.30 mmol), and acetone (8 mL) was stirred vigorously for 1.5−2 h at 60 °C under nitrogen. The volatile parts were removed under reduced pressure, and the residue was treated with 10 mL of CH_2Cl_2 and 10 mL of H_2O. The separated water layer was extracted three times with 10 mL of CH_2Cl_2 each. The combined organic phases were dried with Na_2SO_4 and the products purified by column chromatography (40 × 2 cm SiO_2, petroleum ether (bp 40−70 °C)/ethyl acetate 20:1).

10-(3,5-Dimethoxybenzyl)-10-(3-methoxybenzyl)-9(10*H*)-anthracenone (7i): yield 357 mg, 77%; colorless crystals; mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (s, 6H), 3.32 (s, 3H), 3.65 (s, 2H), 3.68 (s, 2H), 5.45 (m, 2H), 5.79 (m, 1H), 5.92 (m, 1H), 5.97 (m, 1H), 6.42 (m, 1H), 6.67 (m, 1H), 7.38 (m, 2H), 7.73 (m, 2H), 7.96 (m, 2H), 8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.8, 50.1, 50.3, 54.7, 54.8, 99.1, 107.5, 112.5, 114.5, 122.1, 126.9, 127.4, 127.4, 128.2, 132.8, 132.8, 137.4, 138.2, 145.7, 158.5, 159.6, 182.9; MS (EI) *m*/*z* 464 (M^+, 40.8), 313 (100.0). Anal. Calcd for $C_{31}H_{28}O_4$ (464.55): C, 80.15; H, 6.08. Found: C, 79.88; H, 6.02.

General Procedure for the Preparation of the 10,10-Dibenzyl-9,10-dihydroanthracen-9-ols 8e−k. Compound **7** (1.0 mmol) in diglyme (4 mL) was stirred under nitrogen for 15 min before $NaBH_4$ (120 mg, 3.1 mmol) was added. After 30 min (the compounds **8f** and **8k** were hardly soluble in diglyme and needed about 4 h), methanol (2 mL) was added dropwise. The mixture was stirred for another 10 min, and then a second portion of $NaBH_4$ (60 mg, 1.5 mmol) was added. After 4 h, water was slowly added with rapid stirring in an ice−water bath. Colorless solid/crystals were obtained by filtration.

10,10-Bis[3,5-bis(benzyloxy)benzyl]-9,10-dihydroanthracen-9-ol (8e): yield 753 mg, 94%; colorless solid; mp 43−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32 (d, ^3J = 11.6 Hz, 1H), 3.40 (s, 2H), 3.61 (s, 2H), 4.50 (s, 4H), 4.52 (s, 4H), 5.01 (d, ^3J = 11.6 Hz, 1H), 5.50 (d, ^4J = 2.2 Hz, 2H), 5.71 (d, ^4J = 2.2 Hz, 2H), 6.14 (t, ^4J = 2.2 Hz, 1H), 6.19 (t, ^4J = 2.2 Hz, 1H), 7.19−7.39 (m, 26H), 7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.5, 49.0, 52.4, 67.5, 69.6, 69.8, 100.7, 101.1, 109.0, 109.1, 126.7, 126.9, 127.3, 127.3, 127.7, 127.8, 127.9, 128.4, 129.8, 129.8, 136.9, 137.0, 137.9, 138.4, 139.3, 139.5, 158.7, 158.7; MS (FAB) *m*/*z* 801 (M^+, 0.4), 154 (100.0). Anal. Calcd for $C_{56}H_{48}O_5$ (800.98): C, 83.97; H, 6.04. Found: C, 83.89; H, 5.97.

General Procedure for the Preparation of the Homotriptycenes 9a,b. Method A. Compound **5a**,**b** (0.1 mmol) was dissolved in dichloromethane (1 mL), and then formic acid (290 mg, 88%, 5.6 mmol) was added. The mixture was stirred for 30 min and then the solvent was evaporated to give **9a**,**b**. Further purification of **9a**,**b** by column chromatography (30 × 3 cm SiO_2, ethyl acetate/petroleum ether (bp 40−70 °C) 1/30) afforded white crystals.

Method B. Compound **5a**,**b** (0.1 mmol) was dissolved in diglyme (1 mL), and then $H_2C_2O_4 \cdot 2H_2O$ (705 mg, 5.6 mmol) was added. The mixture was stirred for 30 min, and water was slowly added with rapid stirring in an ice−water bath. Filtration and column chromatography afforded white crystals **5a**,**b**.

Method C. Compound **5a**,**b** (0.1 mmol) was dissolved in dichloromethane (1 mL), and then acetic acid (336 mg, 5.6 mmol) was added. The mixture was stirred for 30 min, and then the solvent was evaporated to give **9a**,**b**, which was purified by column chromatography.

3,5-Dimethoxypentacyclo[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]heneicosa-2,4,6,10,12,14,16,18,20-nonaene (9a): yield (method A) 96% (determined by ^{1}H NMR); isolated yield 30 mg, 91%; yield (method B) 92% (determined by ^{1}H NMR); isolated yield 87%; yield (method C) 92% (determined by ^{1}H NMR); isolated yield 87%; colorless crystals; mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.21 (d, ^3J = 3.6 Hz, 2H), 3.63 (s, 3H), 3.89 (s, 3H), 4.19 (t, ^3J = 3.6 Hz, 1H), 5.69 (s, 1H), 6.00 (d, ^4J = 1.8 Hz, 1H), 6.22 (d, ^4J = 1.8 Hz, 1H), 7.09−7.14 (m, 4H), 7.31−7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.4, 41.9, 45.6, 55.1, 56.1, 96.6, 107.5, 123.0, 125.1, 125.6, 126.2, 126.2, 136.6, 141.4, 144.7, 156.4, 158.5; MS (FD) *m*/*z* 328 (M^+, 100.0). Anal. Calcd for $C_{23}H_{20}O_2$ (328): C, 84.12; H, 6.14. Found: C, 84.15; H, 6.17.

3,4,5-Trimethoxypentacyclo[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]heneicosa-2,4,6,10,12,14,16,18,20-nonaene (9b): yield 96% (determined by ^{1}H NMR); isolated yield 33 mg, 91%; colorless crystals; mp 173−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (d, ^3J = 3.8 Hz, 2H), 3.67 (s, 3H), 3.81 (s, 3H), 4.02 (s, 3H), 4.21 (t, ^3J = 3.8 Hz, 1H),

5.55 (s, 1H), 6.18 (s, 1H), 7.10−7.16 (m, 4H), 7.32−7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.9, 43.4, 45.6, 55.8, 60.8, 61.5, 110.9, 125.2, 125.8, 126.4, 126.4, 127.8, 130.0, 140.2, 141.3, 144.4, 149.7, 151.8; MS (EI) *m*/*z* 358 (M^+, 100.0). Anal. Calcd for $C_{24}H_{22}O_3$ (358.43): C, 80.42; H, 6.19. Found: C, 80.45; H, 6.16.

General Procedure for the Preparation of the Homotriptycenes 9e−g,i,j. To a solution of **8e−g,i,j** (0.5 mmol) in 5 mL of dichloromethane was added formic acid (100 mg, 1.9 mmol). The mixture was stirred for 10 min. Colorless crystals/solid were obtained after evaporation of the solvent. The reaction was quantitative, and the isolated yield was about 100%.

3,5-Bis(benzyloxy)-9-[3,5-bis(benzyloxy)benzyl]pentacyclo-[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]heneicosa-2,4,6,10,12,14,16,18,20-nonaene (9e): yield 392 mg, 100%; colorless crystals; mp 197−198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (s, 2H), 3.90 (s, 2H), 4.65 (s, 4H), 4.83 (s, 2H), 5.11 (s, 2H), 5.84 (s, 1H), 6.04 (d, ^4J = 2.4 Hz, 1H), 6.17 (d, ^4J = 2.0 Hz, 2H), 6.34 (m, 2H), 7.00 (m, 2H), 7.08 (m, 2H), 7.16−7.40 (m, 20H), 7.47 (m, 2H), 7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 42.6, 44.7, 46.9, 69.8, 70.0, 70.7, 98.6, 99.7, 108.6, 109.6, 123.4, 125.3, 125.3, 126.0, 126.4, 127.2, 127.4, 127.4, 127.8, 127.9, 128.4, 128.5, 128.7, 136.9, 137.0, 137.3, 137.4, 140.1, 140.4, 143.5, 155.0, 157.7, 159.2 (one signal hidden by superposition); MS (FAB) *m*/*z* 783 (M^+, 9.8), 154 (100.0). Anal. Calcd for $C_{56}H_{46}O_4$ (782.96): C, 85.90; H, 5.92. Found: C, 85.64; H, 6.04.

3,4,5-Trimethoxy-9-(3,4,5-trimethoxybenzyl)pentacyclo-[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]heneicosa-2,4,6,10, 12,14,16,18,20-nonaene (9f): yield 269 mg, 100%; colorless crystals; mp 232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 2H), 3.39 (s, 6H), 3.66 (s, 3H), 3.75 (s, 3H), 3.80 (s, 3H), 3.92 (s, 2H), 4.03 (s, 3H), 5.63 (s, 1H), 6.06 (s, 2H), 6.14 (s, 1H), 7.05 (m, 2H), 7.11 (m, 2H), 7.22 (m, 2H), 7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 43.7, 44.8, 46.2, 55.6, 55.8, 60.8, 60.8, 61.5, 107.7, 110.5, 125.2, 125.6, 126.1, 126.5, 127.6, 130.4, 132.8, 135.5, 140.2, 140.4, 143.3, 149.4, 151.7, 152.3; MS (FAB) *m*/*z* 538 (M^+, 9.4), 154 (100.0). Anal. Calcd for $C_{34}H_{34}O_6$ (538.63): C, 75.82; H, 6.36. Found: C, 75.70; H, 6.12.

5-Methoxy-9-(3-methoxybenzyl)pentacyclo[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]-heneicosa-2,4,6,10,12,14,16,18, 20-nonaene (9g): yield 209 mg, 100%; colorless solid; mp 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 2H), 3.53 (s, 3H), 3.63 (s, 3H), 3.98 (s, 2H), 4.85 (s, 1H), 6.37 (m, 1H), 6.40 (m, 1H), 6.49 (m, 1H), 6.55−6.60 (m, 2H), 6.94 (m, 1H), 7.02 (m, 2H), 7.11 (m, 2H), 7.19−7.24 (m, 3H), 7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 44.7, 46.8, 54.1, 54.9, 55.1, 110.7, 111.4, 116.0, 116.9, 122.8, 124.9, 125.5, 126.2, 126.5, 127.6, 128.5, 133.6, 136.0, 139.1, 139.6, 143.3, 158.4, 158.9; MS (EI) *m*/*z* 418 (M^+, 100.0). Anal. Calcd for $C_{30}H_{26}O_2$ (418.53): C, 86.09; H, 6.26. Found: C, 86.54; H, 6.37.

3,5-Dimethoxy-9-(3-methoxybenzyl)pentacyclo-[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]heneicosa-2,4,6,10,12,14,16,18,20-nonaene (9i): yield 224 mg, 100%; colorless crystals; mp 245−246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 2H), 3.54 (s, 3H), 3.62 (s, 3H), 3.90 (s, 3H), 3.95 (s, 2H), 5.75 (s, 1H), 5.95 (d, ^4J = 2.3 Hz, 1H), 6.21 (d, ^4J = 2.3 Hz, 1H), 6.41 (m, 1H), 6.52 (m, 1H), 6.59 (m, 1H), 6.94 (m, 1H), 6.99 (m, 2H), 7.08 (m, 2H), 7.18 (m, 2H), 7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 42.4, 44.7, 46.9, 54.9, 55.1, 56.1, 96.6, 107.1, 110.6, 116.0, 122.9, 125.2, 125.3, 126.0, 126.3, 128.5, 137.2, 139.2, 140.4, 143.7, 156.1, 158.5, 158.9 (one signal hidden by superposition); MS (EI) *m*/*z* 448 (M^+, 100.0). Anal. Calcd for $C_{31}H_{28}O_3$ (448.55): C, 83.01; H, 6.29. Found: C, 82.76; H, 6.40.

9-Benzyl-3,5-dimethoxypentacyclo[7.6.6.0.^{2,7}0.^{10,15}0.^{16,21}]-heneicosa-2,4,6,10,12,14,16,18,20-nonaene (9j): yield 209 mg, 100%; colorless crystals; mp 213-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (s, 2H), 3.61 (s, 3H), 3.91 (s, 3H), 3.98 (s, 2H), 5.77 (s, 1H), 5.96 (d, ^4J = 2.4 Hz, 1H), 6.22 (d, ^4J = 2.4 Hz, 1H), 6.90 (m, 2H), 6.99−7.18 (m, 9H), 7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 42.3, 44.6, 47.0, 55.1, 56.1, 96.5, 107.1, 122.8, 125.2, 125.3, 126.0, 126.3, 127.6, 130.2, 137.2, 137.5, 140.4, 143.7, 156.0, 158.5 (one signal hidden by superposition); MS (FAB) *m*/*z* 418 (M^+, 18.9), 154 (100.0). Anal. Calcd for $C_{30}H_{26}O_2$ (418.53): C, 86.09; H, 6.26. Found: C, 85.69; H, 6.02.

Acid-Catalyzed Reaction of 8h. To a solution of **8h** (44 mg, 0.1 mmol) in 2 mL of dichloromethane was added formic acid (45 mg, 0.86 mmol). The mixture was stirred for 10 min and then evaporated. The products were purified by column chromatography (20 × 2 cm SiO_2, ethyl acetate/petroleum ether (bp 40−70 °C) 1/50). Light yellow crystals of **11h** (36 mg) were obtained in 86% yield, and light yellow crystals **10c (**4 mg) were obtained in 14% yield, respectively.

Acid-Catalyzed Reaction of 8k. Method A. To a solution of **8k** (120 mg, 0.32 mmol) in dichloromethane (5 mL) was added formic acid (1200 mg, 23 mmol). The mixture was stirred for 1.5 h and then the solvent evaporated. The products were purified by column chromatography (20 × 2 cm SiO_2, ethyl acetate/petroleum ether (bp 40−70 °C) 1/50). Colorless crystals **12k** (60 mg) were obtained in 52% yield and colorless crystals **7k** (52 mg) in 44% yield.

Method B. The mixture of **8k** (120 mg, 0.32 mmol), dichloromethane (5 mL), and *p*-tolylsulfonic acid (6 mg, 0.032 mmol) was stirred for 30 min and then the solvent evaporated. The ratio of **7k/12k** was 50/50 (determined by ^{1}H NMR). Chromatography gave **12k** (55 mg, 48%) and **7k** (57 mg, 48%).

Method C. To a solution of **8k** (120 mg, 0.32 mmol) in dichloromethane (5 mL) was added trifluoroacetic acid (24 mg, 0.21 mmol). The mixture was stirred for 30 min and then the solvent evaporated. The products were purified by column chromatography to give **12k** (53 mg, 46%) and **7k** (54 mg, 45%).

Method D. A solution of **8k** (120 mg, 0.32 mmol), dichloromethane (5 mL), and acetic acid (3.4 g, 56 mmol) was stirred for 2 weeks at room temperature; almost no reaction occurred.

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Supporting Information Available: Preparation and characterization of compounds **4b−d**, **5b−d**, **7f−h**, **7j**,**k**, **8f−k**, **10a−d**, **11h**, **12k**; X-ray experimental procedure for **9a**; spectra of ^{1}H and ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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