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Synthesis of Heterocyclic Homotriptycenes

Hong Zhang,[†,‡] Derong Cao,[*,†] Wenjie Liu,[‡] Huanfeng Jiang,[†] and Herbert Meier[*,§]

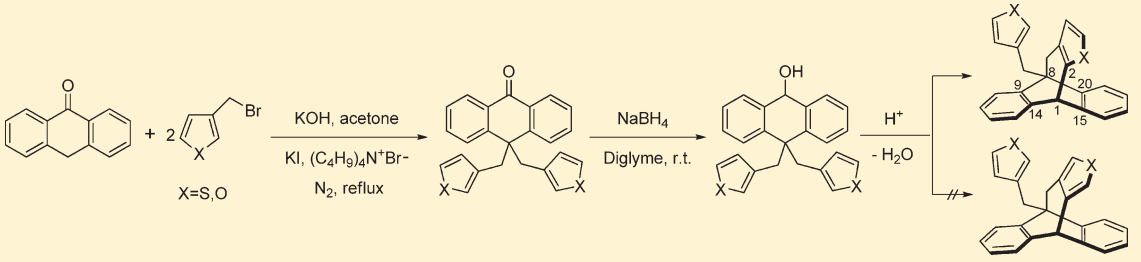
[†]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

[‡]School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Guangzhou 510006, China

[§]Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

Supporting Information

ABSTRACT:



A series of novel heterocyclic homotriptycenes bearing furan, thiophene, and pyridine rings, **7a**−**f**, were synthesized by intramolecular dehydration reactions of 10,10-dihetarylmethyl-9,10-dihydroanthracen-9-ols **6a**−**f**. In the presence of acids, the secondary alcohols **6a**−**f** show different reactions which depend on the electron densities of the attached heterocyclic rings. The initially formed carbenium ions react in an electrophilic substitution with electron-rich heterocycles. The formation of a transannular bridge (1,7-elimination) leads to homotriptycenes in high yields. When the heterocyclic ring has a moderate electron density, two competitive reactions exist, which afford 9-monosubstituted anthracenes by 1,4-elimination or 9,10-disubstituted anthracenes by a rearrangement, respectively. Electron-deficient heterocycles undergo a disproportionation to give hydrocarbons and ketones.

INTRODUCTION

Barrelene (bicyclo[2.2.2]octa-2,5,7-triene) **1** condensed with three benzene rings (Figure 1) represents the well-known triptycene **1′**, whose derivatives have been widely used in various fields, such as molecular machines,[1] supramolecular chemistry,[2] liquid crystals,[3] host−guest complexes,[4] pharmaceutical agents,[5] and polymers.[6,3b] The rigid, aromatic 3D structure conveys the triptycenes' unique properties.[7] Recently, MacLachlan and Chong reviewed the application of the bigger class of iptycenes in supramolecular chemistry and materials science.[8a] Yang and Yan reported the progress in pentiptycene chemistry.[8b] Chen reviewed his own work about novel triptycene-derived hosts: synthesis and their applications in supramolecular chemistry.[8c] However, there are few references about homotriptycenes **2′**, the analogous 3-fold condensation products of bicyclo[3.2.2]nona-2,6,8-triene **2** (Figure 1). Synthetic difficulties,[9] such as multistep preparations and/or moderate yields, limited the development of the homotriptycene chemistry. We published recently a simple route to homotriptycenes by an acid-catalyzed intramolecular electrophilic dehydration of 10,10-dibenzyl-9,10-dihydroanthrancen-9-ols.[10] A high electron density in the benzyl groups proved to be the key factor for the desired transannular ring closure.

In the present paper we report on heterocyclic homotriptycenes. In addition to two anelated benzene rings in the 6,7- and 8,9-position of **2**, the central bicyclic scaffold is condensed in the 2,3-position to heterocycles such as thiophene, furan, or pyridine. Until now, very few heterocyclic homotriptycenes have been discussed in the literature. In an early paper, Cioranescu et al. reported on [2,3-*b*] condensed systems **2** with pyridine or pyrylium rings.[11] Margomedov et al. described a [2,3-*b*] condensed system with indole.[12] Recently, Ivanova et al. published a

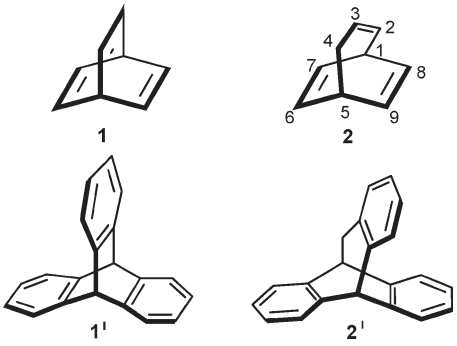


Figure 1. Barrelene (**1**) and homobarrelene (**2**) as central scaffolds for triptycenes (**1′**) and homotriptycenes (**2′**).

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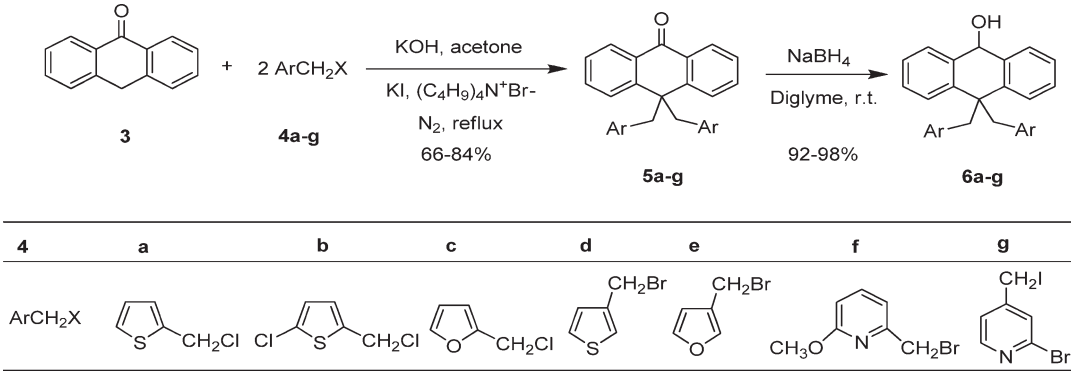
Scheme 1. Preparation of the 9-Anthracenol Derivatives 6a−g



[3,2-*b*] condensed system with thiophene.[13] All these compounds have benzene rings in the 6,7- and 8,9-position of **2**.

RESULTS AND DISCUSSION

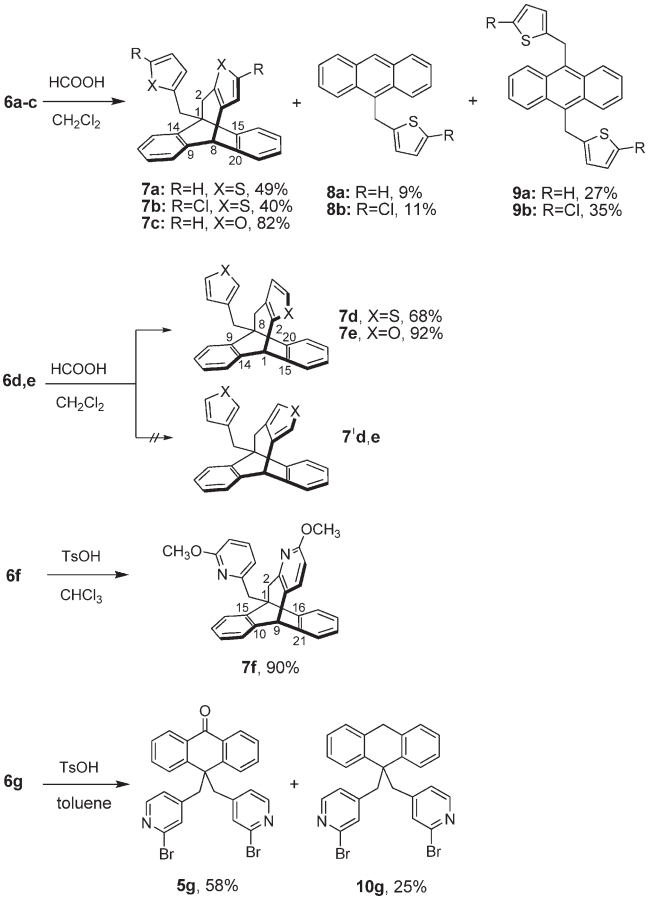
Our synthetic concept is based on the preparation of 10,10-dihetarylmethyl-9,10-dihydroanthracen-9-ols **6a**−**g** (Scheme 1). The dialkylation of anthracen-9-one **3** was obtained by the reaction of **3** and the chloro-, bromo-, or iodomethyl compounds **4a**−**g**. According to the literature, the 10,10-dialkylation of **3** depends on the utilized base. The yield was low when K_2CO_3 served as catalyst[14a] and could be improved to 58−65% by NaH or $LiOC(CH_3)_3$.[14b,c] Several years ago our group utilized KOH and 18-crown-6 in acetone to obtain 10,10-dibenzyl anthracenone (58−82%).[10a,b] Now, our experimental results revealed that the reaction rate and the selectivity of C,C-dialkylation can be improved by KOH and *n*-$Bu_4N^+Br^-$. The yields of **5a**−**g** reached 66−84%. The 9-anthracenol derivatives **6a**−**g** as key compounds for the preparation of the heterocyclic homotriptycenes were then synthesized in high yield (92−98%) by the reduction of **5a**−**g** with $NaBH_4$ in diglyme (Scheme 1).

There are three competitive reactions when the secondary alcohols **6a**−**g** are treated with acids (Scheme 2). The reactions depend on the electron density in the attached heterocyclic groups and the stability of the heterocyclic rings of the alcohols, as well as the reaction conditions. In this study, we chose $HCOOH/CH_2Cl_2$ as reaction medium for **6a**−**e**, *p*-TsOH/$CHCl_3$ for **6f**, and *p*-TsOH/toluene for **6g** (Scheme 2).

When **6a**,**b** were treated with an excess amount of formic acid (Scheme 2), three reaction products were obtained: the desired homotriptycenes **7a**,**b** (by 1,7-elimination of H_2O), the anthracene derivatives **8a**,**b** (by 1,4-elimination of the corresponding thiophen-2-ylmethanol), and the anthracene derivatives **9a**,**b** (by elimination of H_2O and rearrangement). Table 1 shows for **6a** that the product distribution depends on the molar ratio **6a**:HCOOH. The reaction rate increases by an increasing excess of acid. The portion of homotriptycene **7a** reaches a maximum and the portion of **9a** a minimum for entry 3 in Table 1. When trifluoroacetic acid was used instead of formic acid, the reaction became very fast, and the rearrangement product **9a** was the major component. Alcohol **6b** behaved in a similar way. Note that the furan system **6c** yielded selectively the homotriptycene **7c** (82%).

In contrast to **6a**−**c**, the heterocyclic rings in **6d** and **6e** are linked in their β-position. Consequently, two options exist for

Scheme 2. Acid-Catalyzed Reactions of the Anthracenol Derivatives 6a−g



the transannular ring closure. It turned out that the α-positions reacted exclusively to yield **7d**,**e**.

The competing reaction routes are rationalized in Scheme 3. Protonation of the secondary alcohol and dehydration **6**→**11** are always the initial steps. When a resonance-stabilized cation, such as **11a**−**e**, encounters a suitable nucleophilic center in the attached hetarylmethyl group, an intramolecular electrophilic substitution can occur **11a**−**e** → **12a**−**e** → **7a**−**e**. This process corresponds to the formation of a transannular bridge by a 1,7-elimination of H_2O. The reactivity of the thiophene and furan

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ring systems **6c**, **6d**, and **6e** is so high that this route represents the single observed reaction (Schemes 2 and 3).

Interestingly, **6d,e** react in the α-position of the heterocyclic ring, although the β-position has a higher electron density in the ground state. We assume a kinetically controlled process via a transition state, which is close to the resonance-stabilized cation **12d,e**. The resonance stabilization of the alternative cation **12′d,e** is lower. This result is in accordance to the reactivity of thiophenes and furans, which preferentially show electrophilic substitution reactions in α-position.[15]

The compounds **6a,b** underwent two further reaction routes. Either a thenyl cation migration or a rearrangement occurs. The bridged carbenium ion **11′a,b** can be responsible for both processes **11′a,b** → **8a,b** and **11′a,b** → **9a,b**. Crossover experiments, in which the mixtures of **6a** and **6b** were treated with formic acid, reveal that no crossover products **9ab** were obtained, showing no migration of the free anions.

Anthracen-9-ols with electron-rich pyridine rings, such as **6f** with an electron-releasing methoxy group, behave like **6c**, even though it reacts very slowly in $HCOOH/CH_2Cl_2$ but reacts fast under somewhat severer conditions to **7f** (90%, refluxing for 1 h in *p*-TsOH/$CHCl_3$). However, anthracen-9-ols such as **6g**, which has in the 10-position an electron-deficient substituent, do not show any of these reactions in $HCOOH/CH_2Cl_2$. They exhibit a kind of disproportionation on heating with *p*-toluenesulfonic acid. However, the oxidation process **6g** → **5g** has a much higher yield than the reduction **6g** → **10g**, even though the reaction was carried out under nitrogen. Therefore, another oxidizing agent (for example, *p*-toluenesulfonic acid) must be involved. In addition, **6g** was refluxed for 2 h in *p*-TsOH/$CHCl_3$ to give the corresponding 9-ethoxyanthracenes as major product, because EtOH in $CHCl_3$ (about 0.3−1% as stabilizer) was involved in the reaction.

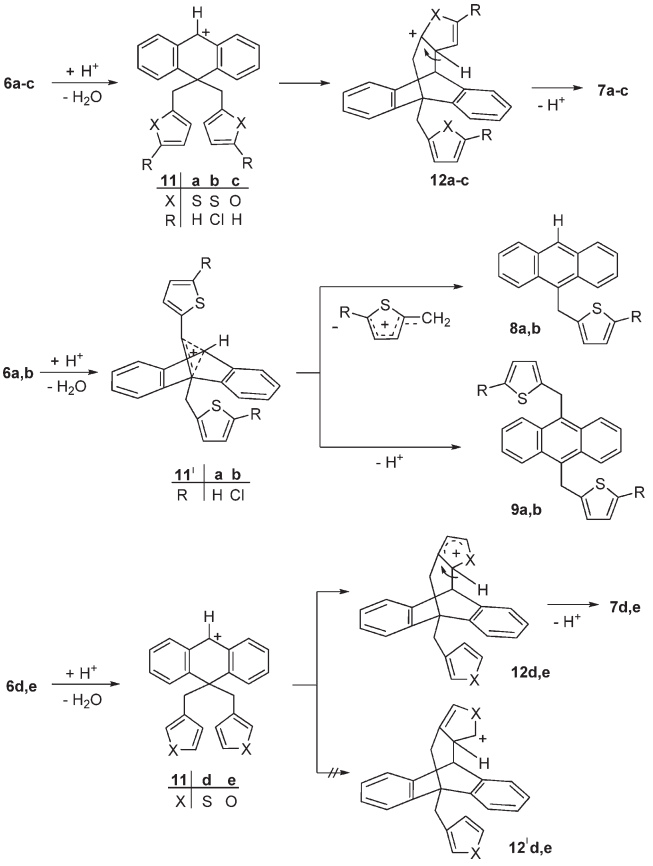
The structure determinations of **5**−**10** were based on NMR and MS measurements (see Experimental Section). Figure 2 shows the decision between **7e** and the alternative **7′e**. An AB spin pattern of 4-H and 5-H with a small vicinal coupling ^3J = 1.8 Hz was found in the 500 MHz ^{1}H NMR spectrum of the furan ring which has reacted. The chemical shifts δ (α-H, or 4-H) = 7.02 and δ (β-H, or 5-H) = 5.92 correspond to an enol ether moiety. The ^{13}C NMR spectrum of **7e** reveals the presence of a new quaternary C-atom (2-C, δ = 151.5) formed by the electrophilic substitution. If the product was **7′e**, owing to the

Table 1. Product Distribution of the Acid-Catalyzed Reaction of 6a in CH_2Cl_2 at Room Temperature

				relative product distribution[a]		
entry	acid	molar ratio **6a**:acid	reaction time	**7a** (%)	**8a** (%)	**9a** (%)
1	HCOOH	1:05	10 h	37	14	49
2	HCOOH	1:10	5 h	58	10	32
3	HCOOH	1:22	2 h	62	7	31
4	HCOOH	1:44	0.5 h	34	10	56
5	CF_3COOH	1:20	1 min	16	14	70

[a] Determined by ^{1}H NMR spectroscopy according to the CH_2 peaks of three compounds with an error of the ^{1}H NMR measurement of ±3%.

Scheme 3. Mechanistic Rationalization of the Competing Reactions



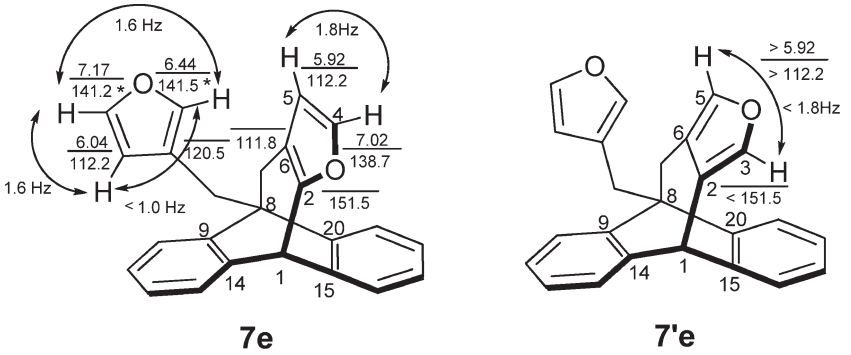


Figure 2. ^{1}H and ^{13}C NMR data (upper and lower values) of the furan substructures in **7e** and **7′e**.

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enol ether structure, the new quaternary C-atom (2-C, δ <151.5) would have a δ value at much higher field and δ values of 3-H or 5-H (δ > 5.92), 3-C or 5-C (δ > 112.2) would be at much lower field. These results indicate that the product is in accordance with the structure **7e** but not **7′e**.

CONCLUSIONS

In summary, a series of novel heterocyclic homotriptycenes **7a**−**f** have been synthesized by the intramolecular electrophilic dehydration of 10,10-dihetarylmethyl-9,10-dihydroanthracen-9-ols **6a**−**f**. The electron density in the heterocyclic ring (thiophene, furan, pyridine) is a key factor of the acid-catalyzed reaction. When groups of moderate nucleophilicity, such as 2-thenyl or 5-chloro-2-thenyl are linked in 10-position (compounds **6a**,**b**), two competitive side reactions exist, namely the 1,4-elimination to monosubstituted anthracenes **8a**,**b** and the rearrangement to 9,10-disubstituted anthracenes **9a**,**b**. The selectivity of the homotriptycene formation depends strongly in these cases on the amount and the strength of the acid.

If the initially generated carbenium ion has two options for the formation of the transannular bridge, the α-position in thiophene or furan is preferred in comparison to the β-position.

The electron-deficient pyridine compound **6g** did not yield a homotriptycene. It underwent a disproportionation to the ketone **5g** and the 9,10-dihydroanthracene **10g**.[16] However, when an OCH_3 group as electron-donating group was introduced into the pyridine ring, the transannular ring closure to the corresponding homotriptycene **7f** took place.

The newly found reaction route to heterocyclic homotriptycenes opens the door to further studies of the biological or pharmacological properties of these rigid 3D aromatic compounds and to possible applications in materials science.

EXPERIMENTAL SECTION

9(10*H*)-Anthracenone **3** and the compounds **4a**, **4b** were commercially available. **4c**,[17] **4d**,[18] **4e**,[19] **4f**,[20] and **4g**[14b,c] were synthesized by ourselves according to the literature. These halomethyl heterocyclic compounds **4a**,**c**−**e**,**g** are all very active, unstable, and irritative, leaving deposits of black resinous material sometimes. **4d** and **4f** are very powerful lachrymators, and some individuals may develop extensive irritation of the skin upon exposure to their vapors. Caution! The preparation should be run in a well-ventilated hood. 2-Bromo-4-iodomethylpyridine was prepared by chlorination and iodination from 2-bromo-4-methylpyridine.[14b,c]

General Procedure for the Preparation of the Anthracenones 5a−g. A mixture of 9(10*H*)-anthracenone (**3**) (1.943 g, 10.0 mmol), the corresponding heterocyclic halomethyl compounds **4a**−**g** (21.0 mmol), *n*-$Bu_4N^+Br^-$ (322 mg, 1.0 mmol), potassium iodide (250 mg, 1.5 mmol), and potassium hydroxide (1.434 g, 21.0 mmol, 82%) in dry acetone (80 mL) was heated at 60 °C and stirred vigorously under nitrogen for 2 h. After cooling to room temperature, the solvent was evaporated in vacuo and the residue was treated with 50 mL of CH_2Cl_2 and 50 mL of H_2O. The separated water layer was extracted three times with CH_2Cl_2 (3 × 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the products were purified by 200−300 mesh silica gel column chromatography [petroleum ether (bp 60−90 °C)/CH_2Cl_2 or petroleum ether (bp 60−90 °C)/ethyl acetate] and recrystallized from CH_2Cl_2/petroleum ether (bp 60−90 °C) to give **5a**−**f** as colorless crystals.

*10,10-Bis(2-thenyl)-9(10H)-anthracenone (**5a**).* Yield: 3.24 g (84%), colorless needles; mp 278−280 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 4H, CH_2), 5.99 (d, ^3J = 3.6 Hz, 2H, 3-H, thiophene), 6.46 (dd, ^3J = 3.6 Hz, ^3J = 4.8 Hz, 2H, 4-H, thiophene), 6.71 (d, ^3J = 4.8 Hz, 2H, 5-H, thiophene), 7.43 (m, 2H, benzene), 7.73 (m, 2H, benzene), 7.89 (m, 2H, benzene), 8.15 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.6 (CH_2), 49.0 (C-10), 124.0, 125.7, 126.5, 126.6, 127.3, 127.5, 133.4 (CH, benzene and thiophene), 133.3, 137.7, 144.8 (C_q, benzene and thiophene), 183.0 (C-9); MS (APCI): *m*/*z*(%) 387.0 ([M + H]$^+$, 100); elemental analysis calcd (%) for $C_{24}H_{18}OS_2$ (386.53): C 74.58, H 4.69, S 16.59; found: C 74.42, H 4.68, S 16.74.

*10,10-Bis(5-chloro-2-thenyl)-9(10H)-anthracenone (**5b**).* Yield: 3.32 g (73%), colorless plates; mp 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 4H, CH_2), 5.80 (d, ^3J = 3.8 Hz, 2H, 3-H, thiophene), 6.27 (d, ^3J = 3.8 Hz, 2H, 4-H, thiophene), 7.47 (m, 2H, benzene), 7.72−7.80 (m, 4H, benzene), 8.22 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.2 (CH_2), 48.4 (C-10), 124.8, 126.0, 126.2, 127.8, 127.9, 133.6 (CH, benzene and thiophene), 127.9, 133.3, 136.4, 144.0 (C_q, benzene and thiophene), 182.7 (C-9) ; MS (APCI): *m*/*z*(%) 455.1 ([M + H]$^+$, 100); elemental analysis calcd (%) for $C_{24}H_{16}Cl_2OS_2$ (455.42): C 63.29, H 3.54, S 14.08; found: C 63.26, H 3.45, S 14.20.

*10,10-Bis(2-furfuryl)-9(10H)-anthracenone (**5c**).* Yield: 2.34 g (66%), colorless crystals; mp 202−203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 4H, CH_2), 5.09 (d, ^3J = 3.2 Hz, 2H, 3-H, furan), 5.87 (dd, ^3J = 3.2 Hz, ^3J = 2.0 Hz, 2H, 4-H furan), 6.89 (d, ^3J = 2.0 Hz, 2H, 5-H, furan), 7.40 (m, 2H, benzene), 7.63−7.71 (m, 4H, benzene), 8.21 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.2 (CH_2), 46.5 (C-10), 107.5, 109.9 (C-3, C-4, furan), 126.6, 127.0, 127.3, 133.1 (CH, benzene), 132.1 (C_q, benzene), 140.9 (C-5, furan), 145.3 (C_q, benzene), 150.8 (C-2, furan), 183.3 (C-9); MS (APCI): *m*/*z*(%) 355.0 ([M + H]$^+$, 100); elemental analysis calcd (%) for $C_{24}H_{18}O_3$ (354.41): C 81.34, H 5.12; found: C 81.30, H 5.15.

*10,10-Bis(3-thenyl)-9(10H)-anthracenone (**5d**).* Yield: 2.63 g (68%), colorless crystals; mp 267−269 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 4H, CH_2), 5.90 (d, ^3J = 5.2 Hz, 2H, 4-H, thiophene), 6.07 (d, ^4J = 2.8 Hz, 2H, 2-H, thiophene), 6.72 (dd, ^4J = 2.8 Hz, ^3J = 5.2 Hz, 2H, 5-H, thiophene), 7.39 (m, 2H, benzene), 7.71 (m, 2H, benzene), 7.92 (m, 2H, benzene), 8.12 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.8 (CH_2), 48.4 (C-10), 122.5, 124.0, 126.7, 127.0, 127.4, 128.4, 133.0 (CH, benzene, thiophene), 132.7, 136.2, 145.9 (C_q, benzene, thiophene), 182.9 (C-9); MS (APCI): *m*/*z*(%) 387.0 ([M + H]$^+$, 100); elemental analysis calcd (%) for $C_{24}H_{18}OS_2$ (386.53): C 74.58, H 4.69, S 16.59; found: C 74.48, H 4.63, S 16.55.

*10,10-Bis(3-furfuryl)-9(10H)-anthracenone (**5e**).* Yield: 2.51 g (71%), colorless needles; mp 179−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (s, 4H, CH_2), 5.11 (d, ^3J = 1.0 Hz, 2H, 4-H, furan), 6.37 (br. s, 2H, 2-H, furan), 6.82 (m, ^3J = ^4J ≈ 1.0 Hz, 2H, 5-H, furan), 7.40 (m, 2H, benzene), 7.70 (m, 2H, benzene), 7.82 (m, 2H, benzene), 8.18 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.1 (CH_2), 47.7 (C-10), 110.9 (C-4, furan), 119.3 (C-3, furan), 126.4, 127.0, 127.4, 133.1 (CH, benzene), 132.9, 145.0 (C_q, benzene), 140.0, 141.7 (C-2, C-5, furan), 183.1 (C-9); MS (APCI): *m*/*z*(%) 355.0 ([M + H]$^+$, 100); elemental analysis calcd (%) for $C_{24}H_{18}O_3$ (354.41): C 81.34, H 5.12; found: C 81.29, H 5.09.

*10,10-Bis(6-methoxypyridin-2-ylmethyl)-9(10H)-anthracenone (**5f**).* Yield: 3.31 g (76%), colorless needles; mp 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.22 (s, 6H, OCH_3), 3.81 (s, 4H, CH_2), 5.90 (d, ^3J = 7.6 Hz, 2H, 5-H, pyridine), 6.21 (d, ^3J = 8.2 Hz, 2H, 3-H, pyridine), 7.01 (dd, ^3J = 7.6 Hz, ^3J = 8.2 Hz, 2H, 4-H, pyridine), 7.31 (m, 2H, benzene), 7.62 (m, 2H, benzene), 7.90 (m, 2H, benzene), 8.09 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.4 (C-10), 51.6, 52.6 (CH_2, OCH_3), 108.1, 116.4, 126.3, 127.0, 127.7, 132.6, 137.7 (CH, benzene, pyridine), 132.2, 146.4, 154.1, 162.6 (C_q, benzene, pyridine), 183.5 (C-9); MS (APCI): *m*/*z*(%) 437.3 ([M + H]$^+$, 100); elemental analysis calcd (%)

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for $C_{28}H_{24}N_2O_3$ (436.51): C 77.04, H 5.54, N 6.42; found: C 76.91, H 5.61, N 6.37.

*10,10-Bis(2-bromopyridin-4-ylmethyl)-9(10H)-anthracenone (**5g**).* Yield: 3.74 g (70%), colorless crystals; mp 190−192 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.67 (s, 4H, CH_2), 6.08 (dd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 2H, 5-H, pyridine), 6.42 (d, ^4J = 1.2 Hz, 2H, 3-H, pyridine), 7.52 (m, 2H, benzene), 7.76 (d, ^3J = 5.0 Hz, 2H, 6-H, pyridine), 7.85 (m, 2H, benzene), 7.93 (m, 2H, benzene), 8.19 (m, 2H, benzene); ^{13}C NMR (125 MHz, $CDCl_3$): δ 47.7 (C-10), 48.9 (CH_2), 123.3, 126.5, 128.2, 128.3, 128.9, 133.6, 149.1 (CH, benzene, pyridine), 132.6, 141.5, 142.8, 147.4 (C_q, benzene, pyridine), 181.5 (C-9); MS (APCI): m/z(%) 534.9 ([M + H]$^+$, Br_2 isotope pattern, 100); elemental analysis calcd (%) for $C_{26}H_{18}Br_2N_2O$ (534.25): C 58.45, H 3.40.; N 5.24; found: C 58.54, H 3.321, N 5.271.

General Procedure for the Preparation of the 9,10-Dihydroanthracen-9-ols 6a−g. Compound **5** (3.0 mmol) was dissolved in diglyme (12 mL) before $NaBH_4$ (360 mg, 96%, 9.1 mmol) was added. After stirring for 30 min at room temperature, methanol (6 mL) was added dropwise. The mixture was stirred for another 10 min, and then a second portion of $NaBH_4$ (180 mg, 96%, 4.5 mmol) was added. The reaction was monitored by TLC. After about 4 h (**5g** needed 1day at 40 °C), water was slowly added under vigorous stirring in an ice−water bath (quenching of the reaction). Product **6** was obtained by filtration as colorless crystals.

*10,10-Bis(2-thenyl)-9,10-dihydroanthracen-9-ol (**6a**).* Yield: 1.14 g (98%), colorless plates; mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.42 (d, ^3J = 11.6 Hz, 1H, OH), 3.65 (s, 2H, CH_2), 3.87 (s, 2H, CH_2), 5.12 (d, ^3J = 11.6 Hz, 1H, 9-H), 5.90 (m, ^3J = 3.2 Hz, 1H, 3-H, thiophene), 6.13 (m, ^3J = 3.2 Hz, 1H, 3-H, thiophene), 6.49 (dd, ^3J = 3.2 Hz, ^3J = 5.2 Hz, 1H, 4-H, thiophene), 6.57 (dd, ^3J = 3.2 Hz, ^3J = 5.2 Hz, 1H, 4-H, thiophene), 6.70 (dd, ^3J = 5.2 Hz, ^4J = 1.2 Hz, 1H, 5-H, thiophene), 6.79 (dd, ^3J = 5.2 Hz, ^4J = 1.2 Hz, 1H, 5-H, thiophene), 7.32 (m, 2H, benzene), 7.41 (m, 2H, benzene), 7.47 (m, 2H, benzene), 7.74 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.3, 46.5 (CH_2), 49.2 (C-10), 67.6 (C-9), 123.6, 124.0, 125.5, 125.8, 126.1, 126.5, 126.5, 127.2, 128.4, 129.8 (CH, benzene, thiophene), 137.8, 138.3, 139.1, 139.3 (C_q, benzene, thiophene); MS (APCI): m/z(%) 387.0 ([M − H]$^+$, 8), 371.0 ([M − OH]$^+$, 100), 286.8 (73), 190.7 (43); elemental analysis calcd (%) for $C_{24}H_{20}OS_2$ (388.54): C 74.19, H 5.19, S 16.51; found: C 74.06, H 5.27, S 16.61.

*10,10-Bis(5-chloro-2-thenyl)-9,10-dihydroanthracen-9-ol (**6b**).* Yield: 1.28 g (95%), colorless crystals; mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (d, ^3J = 11.2 Hz, 1H, OH), 3.55 (s, 2H, CH_2), 3.66 (s, 2H, CH_2), 5.21 (d, ^3J = 11.2 Hz, 1H, 9-H), 5.77 (d, ^3J = 3.6 Hz, 1H, 3-H, thiophene), 5.89 (d, ^3J = 4.0 Hz, 1H, 3-H, thiophene), 6.30 (d, ^3J = 4.0 Hz, 1H, 4-H, thiophene), 6.37 (d, ^3J = 3.6 Hz, 1H, 4-H, thiophene), 7.34 (m, 2H, benzene), 7.44 (m, 2H, benzene), 7.51 (m, 2H, benzene), 7.61 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.6, 46.3 (CH_2), 48.6 (C-10), 67.3 (C-9), 124.6, 124.9, 125.8, 125.9, 126.1, 126.8, 127.1, 127.6, 128.6, 129.9, 136.8, 137.8, 138.0, 138.5 (CH and C_q, benzene, thiophene); MS (APCI): m/z(%) 457.0 ([M + H]$^+$, 13), 455.0 ([M − H]$^+$, 18), 439.1 ([M−OH]$^+$, 36), 320.9 (100), 190.7 (58); elemental analysis calcd (%) for $C_{24}H_{18}Cl_2OS_2$ (457.43): C 63.02, H 3.97, S 14.02; found: C 62.95, H 3.90, S 14.14.

*10,10-Bis(2-furfuryl)-9,10-dihydroanthracen-9-ol (**6c**).* Yield: 0.99 g (93%), colorless crystals; mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, ^3J = 10.1 Hz, 1H, OH), 3.50 (s, 2H, CH_2), 3.61 (s, 2H, CH_2), 4.99 (d, ^3J = 3.1 Hz, 1H, 3-H, furan), 5.15 (d, ^3J = 3.1 Hz, 1H, 3-H, furan), 5.32 (d, ^3J = 10.1 Hz, 1H, 9-H), 5.86 (dd, ^3J = 3.2 Hz, ^3J = 1.8 Hz, 1H, 4-H, furan), 5.97 (dd, ^3J = 1.9 Hz, ^3J = 3.1 Hz, 1H, 4-H, furan), 6.94 (d, ^3J = 1.6 Hz, 1H, 5-H, furan), 6.97 (d, ^3J = 1.7 Hz, 1H, 5-H, furan), 7.30 (m, 2H, benzene), 7.37 (m, 2H, benzene), 7.50 (m, 2H, benzene), 7.57 (m, 2H, benzene); ^{13}C NMR (125 MHz, CD_3SOCD_3): δ 38.1, 41.4 (CH_2), 46.0 (C-10), 65.4 (C-9), 107.4, 107.5, 109.9, 110.1 (C-3, C-4, furan), 125.8, 126.0, 126.6, 126.7 (aromat. CH), 138.1, 139.3, 140.5, 141.1 (C_q, benzene, C-5, furan), 151.8, 152.4 (C-2, furan); MS (APCI): m/z(%) 355.0 ([M − H]$^+$, 6), 339.0 ([M−OH]$^+$, 100), 270.9 (17.5), 256.9 (19.1), 190.7 (76.6); elemental analysis calcd (%) for $C_{24}H_{20}O_3$ (356.42): C 80.88, H 5.66; found: C 80.79, H 5.72.

*10,10-Bis(3-thenyl)-9,10-dihydroanthracen-9-ol (**6d**).* Yield: 1.12 g (96%), colorless crystals; mp 148−150 °C; ^{1}H NMR (500 MHz, CD_3SOCD_3): δ 3.24 (s, 2H, CH_2), 3.80 (s, 2H, CH_2), 4.54 (br. s, 1H, 9-H), 5.78 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1H, 4-H, thiophene), 6.10 (d, ^4J = 2.8 Hz 1H, 2-H, thiophene), 6.31 (dd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 1H, 4-H, thiophene), 6.42 (d, ^4J = 2.8 Hz, 1H, 2-H, thiophene), 7.01 (dd, ^3J = 4.9 Hz, ^4J = 2.9 Hz, 1H, 5-H, thiophene), 7.04 (dd, ^3J = 4.9 Hz, ^4J = 2.9 Hz, 1H, 5-H, thiophene), 7.25 (m, 2H, benzene), 7.30 (m, 2H, benzene), 7.52 (m, 2H, benzene), 7.69 (m, 2H, benzene); ^{13}C NMR (125 MHz, CD_3SOCD_3): δ 40.3, 45.8, 47.4 (CH_2, C-10), 64.7 (C-9), 122.1, 122.3, 123.8, 123.9, 126.0, 126.2, 126.7, 126.8, 129.0, 129.3 (CH, benzene, thiophene), 137.5, 138.0, 138.5, 139.7 (C_q, benzene, thiophene); MS (APCI): m/z(%) 388.0 (M^+, 5), 387.0 ([M − H]$^+$, 14), 371.0 ([M−OH]$^+$, 100), 286.9 (19), 272.8 (28), 190.7 (31); elemental analysis calcd (%) for $C_{24}H_{20}OS_2$ (388.54): C 74.19, H 5.19,S 16.51; found: C 74.06, H 5.24, S 16.65.

*10,10-Bis(3-furfuryl)-9,10-dihydroanthracen-9-ol (**6e**).* Yield: 0.98 g (92%), colorless crystals; mp 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 1H, ^3J = 11.3 Hz, OH), 3.27 (s, 2H, CH_2), 3.39 (s, 2H, CH_2), 5.17 (d, ^3J = 11.3 Hz, 1H, 9-H), 5.20 (br. s, 1H, 4-H, furan), 5.22 (br. s, 1H, 4-H, furan), 6.38 (br. s, 1H, 2-H, furan), 6.45 (br. s, 1H, 2-H, furan), 6.85 (br. s, 1H, 5-H, furan), 6.95 (br. s, 1H, 5-H, furan), 7.29 (m, 2H, benzene), 7.41−7.47 (m, 4H, benzene), 7.66 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.7, 40.8 (CH_2), 47.3 (C-10), 67.1 (C-9), 110.9, 111.3 (C-4, furan), 119.7, 120.0 (C-3, furan), 125.5, 126.4, 127.7, 129.0 (CH, benzene), 137.5, 138.3, 139.7, 140.3, 140.8, 141.0 (C-2, C-5, furan and C_q, benzene); MS (APCI): m/z(%) 356.0 (M^+, 11), 355.0 ([M − H]$^+$, 50), 339.1 ([M−OH]$^+$, 100), 271.0 (6), 257.0 (16), 191.0 (21); elemental analysis calcd (%) for $C_{24}H_{20}O_3$ (356.42): C 80.88, H 5.66; found: C 80.75, H 5.70.

*10,10-Bis(6-methoxypyridin-2-ylmethyl)-9,10-dihydroanthracen-9-ol (**6f**).* Yield: 1.27 g (97%), colorless crystals; mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (d, ^3J = 9.6 Hz, 1H, OH), 3.36 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.61 (s, 2H, CH_2), 3.79 (s, 2H, CH_2), 5.15 (d, ^3J = 9.6 Hz, 1H, 9-H), 5.90 (d, ^3J = 7.2 Hz, 1H, 5-H, pyridine), 5.97 (d, ^3J = 7.2 Hz, 1H, 5-H, pyridine), 6.22 (d, ^3J = 8.0 Hz, 1H, 3-H, pyridine), 6.29 (d, ^3J = 8.0 Hz, 1H, 3-H, pyridine), 6.98 (dd, ^3J = 7.2 Hz, ^3J = 8.0 Hz, 1H, 4-H, pyridine), 7.09 (dd, ^3J = 7.2 Hz, ^3J = 8.0 Hz, 1H, 4-H, pyridine), 7.20 (m, 2H, benzene), 7.27 (m, 2H, benzene), 7.39 (m, 2H, benzene), 7.65 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.6 (C-10), 49.6, 52.7, 52.9, 53.2 (CH_2, OCH_3), 68.4 (C-9), 107.4, 107.9, 116.6, 116.9, 126.4, 127.3, 127.6, 128.8, 137.2, 137.6, 137.7, 139.3, 155.3, 155.6, 162.5, 162.7 (CH and C_q, benzene, pyridine); MS (APCI): m/z(%) 438.2 (M^+, 1), 437.3 ([M − H]$^+$, 5), 421.3 ([M−OH]$^+$, 100) ; elemental analysis calcd (%) for $C_{28}H_{26}N_2O_3$(438.53): C 76.69, H 5.98, N 6.39; found: C 76.58, H 6.05, N 6.43.

*10,10-Bis(2-bromopyridin-4-ylmethyl)-9,10-dihydroanthracen-9-ol (**6g**).* Yield: 1.51 g (94%), colorless crystals; mp 189−190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (br. s, 1H, OH), 3.47 (s, 2H, CH_2), 3.57 (s, 2H, CH_2), 5.00 (br. s, 1H, 9-H), 6.07 (d, ^3J = 5.2 Hz, 1H, 5-H, pyridine), 6.21 (d, ^3J = 5.1 Hz, 1H, 5-H, pyridine), 6.37 (s, 1H, 3-H, pyridine), 6.53 (s, 1H, 3-H, pyridine), 7.35 (m, 2H, benzene), 7.48 (m, 4H, benzene), 7.64 (m, 2H, benzene), 7.73 (d, ^3J = 5.2 Hz, 1H, 6-H, pyridine), 7.78 (d, ^3J = 5.2 Hz, 1H, 6-H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.9 (C-10), 48.8, 48.9 (CH_2), 66.4 (C-9), 123.8, 124.0, 126.1, 128.0, 128.6, 129.2, 129.4, 129.6, 135.7, 137.9, 141.3, 141.5, 148.6, 148.8, 148.9, 149.0 (CH and C_q, benzene, pyridine); MS (APCI): m/z (%) 537.0 ([M + H]$^+$, Br_2 isotope pattern, 100) elemental analysis calcd (%) for $C_{26}H_{20}Br_2N_2O$ (536.27): C 58.23, H 3.76.; N 5.22; found: C 58.43, H 3.772, N 5.23.

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Gnenral Procedure for the Preparation of the Heterocyclic Homotriptycenes 7a−e. To the anthracenol derivative **6a−e** (1.0 mmol), dissolved in CH_2Cl_2 (20 mL), formic acid (518 mg, 88%, 10.0 mmol) was added. The mixture was stirred for 2−18 h and the reaction was controlled by TLC (SiO_2, CH_2Cl_2). The solvent was evaporated and the crude products **7c−e** were purified by 200−300 mesh silica gel column chromatography eluted by petroleum ether (bp 60 − 90 °C)/ CH_2Cl_2. The homotriptycenes **7a,b** and the byproduct **8a, b** and **9a,b** were purified by 300−400 mesh silica gel column chromatography (3 × 80 cm SiO_2). The first fraction contained monosubstituted anthracenes **8a,b**, the second fraction contained the 9,10-disubstituted anthracenes **9a,b**, and the third fraction contained the homotriptycenes **7a,b**, respectively. The column chromatography should be repeated three times for the full separation of them. The homotriptycenes **7a−e** were recrystallized from CH_2Cl_2/petroleum ether (bp 60−90 °C).

*1-(2-Thenyl)-4-thiapentacyclo[6.6.6.0^{3,7}.0^{9,14}.0^{15,20}]icosa-3(7),5,-9,11,13,15,17,19-octaene (**7a**).* Reaction time 5 h, yield: 181 mg (49%), colorless crystals; mp 188−190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (s, 2H, CH_2), 4.14 (s, 2H, CH_2), 4.96 (s, 1H, 8-H, bridge-head), 6.25 (m, 1H, 3-H, thiophene), 6.65 (dd, ^3J = 3.6 Hz, ^3J = 5.0 Hz, 1H, 4-H, thiophene), 6.90/6.92 (AB, ^3J = 5.1 Hz, 2H, 5-H, 6-H), 6.97 (d, ^3J = 5.0 Hz, 1H, 5-H, thiophene), 7.08 (m, 2H, benzene), 7.13 (m, 2H, benzene), 7.30 (m, 2H, benzene), 7.40 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.7, 43.1, 48.6 (C-2, C-8, CH_2), 46.6 (C-1), 121.9, 123.0, 124.5, 125.9, 126.1, 126.2, 126.3, 126.6, 127.5 (C-5, C-6, CH, benzene, thiophene), 133.1, 138.7, 138.8, 140.1, 144.8 (C-3, C-7, C_q, benzene, thiophene); MS (APCI): m/z(%) 371.0 ([M + H]$^+$, 4), 159.8 (100); elemental analysis calcd (%) for $C_{24}H_{18}S_2$ (370.53): C 77.80, H 4.90, S 17.31; found: C 77.84, H 4.990, S 17.34.

*5-Chloro-1-(5-chloro-2-thenyl)-4-thiapentacyclo[6.6.6.0^{3,7}.0^{9,14}.0^{15,20}]-icosa-3(7),5,9,11,13,15,17,19-octaene (**7b**).* Reaction time 18 h, yield: 175 mg (40%), colorless crystals; mp 290−292 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (s, 2H, CH_2), 3.99 (s, 2H, CH_2), 4.80 (s, 1H, 8-H, bridge-head), 6.07/6.46 (AB, ^3J = 3.6 Hz, 2H, 3-H, 4-H, thiophene), 6.71 (s, 1H, 6-H), 7.12−7.18 (m, 4H, benzene), 7.28 (m, 2H, benzene), 7.39 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.0, 42.3, 46.4, 48.4 (C-1, C-2, C-8, CH_2), 124.6, 125.1, 125.2, 125.7, 126.5, 126.6, 126.9, 127.0, 127.2, 131.6, 138.3, 138.6, 144.3 (C-3, C-5, C-7, CH and C_q, benzene, thiophene, partly superimposed); 440.4 (M^+, Cl_2, isotope pattern, 76) elemental analysis calcd (%) for $C_{24}H_{16}Cl_2S_2$ (439.42): C 65.60, H 3.67, S 14.59 ; found: C 65.73, H 3.682, S 14.47.

*1-(2-Furfuryl)-4-oxapentacyclo[6.6.6.0^{3,7}.0^{9,14}.0^{15,20}]icosa-3(7),5,9,-11,13,15,17,19-octaene (**7c**).* Reaction time 3 h, yield: 277 mg (82%), colorless crystals; mp 161−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 2H, CH_2), 3.97 (s, 2H, CH_2), 4.72 (s, 1H, 8-H, bridge-head), 5.16 (m, 1H, 3-H, furan), 6.00 (dd, ^3J = 1.8 Hz, ^3J = 3.1 Hz, 1H, 4-H, furan), 6.30 (d, ^3J = 1.8 Hz, 1H, 6-H), 7.02 (d, ^3J = 1.6 Hz, 1H, 5-H, furan), 7.07−7.15 (m, 4H, benzene), 7.27 (m, 2H, benzene), 7.29 (d, ^3J = 1.8 Hz, 1H, 5-H), 7.37 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.5, 42.5, 44.7 (C-2, C-8, CH_2), 45.2 (C-1), 108.7, 108.8, 110.2 (C-6 and C-3, C-4, furan), 123.3, 124.1, 125.7, 125.9, 126.5 (C-7 and CH, benzene), 139.4, 140.1 (C-5 and C-5 of furan), 139.1, 145.8, 146.5, 151.9 (C-3 and C_q, benzene and furan); MS (APCI): m/z(%) 338.5 (M^+, 100) elemental analysis calcd (%) for $C_{24}H_{18}O_2$ (338.41): C 85.18, H 5.36; found: C 85.23, H 5.352.

*8-(3-Thenyl)-3-thiapentacyclo[6.6.6.0^{2,6}.0^{9,14}.0^{15,20}]icosa-2(6),4,9,-11,13,15,17,19-octaene (**7d**).* Reaction time 4 h, yield: 252 mg (68%), colorless crystals; mp 235−236 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.01 (s, 2H, CH_2), 3.97 (s, 2H, CH_2), 4.95 (s, 1H, 1-H, bridge-head), 6.26 (dd, ^4J = 1.3 Hz, ^4J = 2.8 Hz, 1H, 2-H, thiophene), 6.50 (d, ^3J = 5.1 Hz, 1H, 5-H), 6.77 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, 4-H, thiophene), 6.78 (d, ^3J = 5.1 Hz, 1H, 4-H), 7.07 (m, 2H, benzene), 7.09 (m, ^3J = 5.1 Hz, ^4J = 2.9 Hz, 1H, 5-H, thiophene), 7.14 (m, 2H, benzene), 7.29 (m, 2H, benzene), 7.33 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.3, 44.4, 47.1 (C-1, C-7, CH_2), 45.6 (C-8), 119.7, 123.1, 124.0, 124.5, 126.1, 126.3, 126.4, 129.5, 130.1 (C-4, C-5 and CH, benzene, thiophene), 131.5, 137.3, 137.4, 139.7, 143.9 (C-2, C-6 and C_q, benzene, thiophene); MS (APCI): m/z(%) 370.5 (M^+, 56), 281.7 (100); elemental analysis calcd (%) for $C_{24}H_{18}S_2$ (370.53): C 77.80, H 4.90, S 17.31; found: C 77.69, H 4.90, S 17.27.

*8-(3-Furfuryl)-3-oxapentacyclo[6.6.6.0^{3,7}.0^{9,14}.0^{15,20}]icosa-2(6),4,9,-11,13,15,17,19-octaene (**7e**).* Reaction time 2 h, yield: 311 mg (92%), colorless crystals; mp 158−159 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.81 (s, 2H, CH_2), 3.75 (s, 2H, CH_2), 4.91 (s, 1H, 1-H, bridge-head), 5.92 (d, ^3J = 1.8 Hz, 1H, 5-H), 6.04 (br. s, 1H, 4-H, furan), 6.44 (br. s, 1H, 2-H, furan), 7.02 (d, ^3J = 1.8 Hz, 1H, 4-H), 7.11 (m, 2H, benzene), 7.14 (m, 2H, benzene), 7.17 (t, ^3J = ^4J = 1.6 Hz, 1H, 5-H, furan), 7.32 (m, 2H, benzene), 7.37 (m, 2H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.0, 41.6, 46.2, 46.3 (C-1, C-7, C-8, CH_2), 111.8, 112.1, 112.2, 120.5, 124.1, 126.2, 126.3, 126.3, 138.7, 139.8, 141.2, 141.5, 143.8, 151.5 (CH, C_q); MS (APCI): m/z(%) 339.1 ([M + H]$^+$, 100); elemental analysis calcd (%)for $C_{24}H_{18}O_2$ (338.41): C 85.18, H 5.36; found: C 85.25, H 5.348.

*5-Methoxy-1-(6-methoxypyridin-2-ylmethyl)-4-azapentacyclo-[7.6.6.0^{3,8}.0^{10,15}.0^{16,21}]henicosa-3,5,7,10,12,14,16,18,20-nonaene (**7f**).* To anthracenol **6f** (439 mg, 1.0 mmol), dissolved in $CHCl_3$ (20 mL), anhydrous *p*-toluenesulfonic acid (86 mg, 0.5 mmol) was added. The mixture was refluxed for about 1 h and controlled by TLC (SiO_2, CH_2Cl_2). After cooling, 10% aqueous NaOH solution was added slowly in an ice−water bath to regulate pH 7−8. The organic phase was washed with water and the solvent evaporated in vacuo. The product was purified by column chromatography (3 × 40 cm SiO_2) with petroleum ether (bp 60−90 °C)/ethyl acetate and recrystallized from CH_2Cl_2/petroleum ether (bp 60−90 °C) to give **7f** as colorless crystals. Yield: 378 mg (90%), mp 160−161 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.17 (s, 2H, CH_2), 3.60 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 4.11 (s, 2H, CH_2), 4.82 (s, 1H, 9-H, bridge-head), 6.12 (d, ^3J = 7.4 Hz, 1H, 5-H, pyridine), 6.40 (d, ^3J = 8.1 Hz, 1H, 6-H), 6.42 (d, ^3J = 8.2 Hz, 1H, 3-H, pyridine), 7.05 (m, 2H, benzene), 7.13 (m, 2H, benzene), 7.15 (m, 1H, 4-H, pyridine), 7.25 (m, 2H, benzene), 7.32 (m, 2H, benzene), 7.48 (d, ^3J = 8.0 Hz, 1H, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.3, 44.5, 49.8, 52.4, 53.0, 53.2 (C-1, C-2, C-9, CH_2, OCH_3), 107.1, 107.7, 117.7, 124.6, 125.5, 126.3, 130.4, 137.5, 138.0, 140.2, 142.7, 152.2, 155.4, 162.4, 162.9 (CH and Cq, partly superimposed); MS (APCI): m/z(%) 421.1 ([M + H]$^+$, 100); elemental analysis calcd (%) for $C_{28}H_{24}N_2O_2$ (420.51): C 79.98, H 5.75, N 6.66; found: C 79.84, H 5.69, N 6.63.

*By-products **8a**,**b** and **9a**,**b**.* The compounds **8a,b** and **9a,b** were byproducts of the homotriptycenes **7a,b** which were obtained by 300−400 mesh silica gel column chromatography (3 × 80 cm SiO_2, see above). All of them were recrystallized from CH_2Cl_2/petroleum ether (bp 60−90 °C).

*9-(2-Thenyl)anthracene (**8a**).* Yield: 25 mg (9%), colorless needles; mp 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (s, 2H, CH_2), 6.61 (dd, ^3J = 3.6 Hz, ^4J = 1.0 Hz, 1H, 3-H, thiophene), 6.80 (dd, ^3J = 3.6 Hz, ^3J = 5.2 Hz, 1H, 4-H, thiophene), 7.05 (dd, ^3J = 5.2 Hz, ^4J = 1.0 Hz, 1H, 5-H, thiophene), 7.44−7.51 (m, 4H, anthracene), 8.01 (m, 2H, anthracene), 8.30 (m, 2H, anthracene), 8.42 (s, 1H, anthracene, 10-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3 (CH_2), 123.3, 124.5, 124.8, 125.0, 126.0, 126.8, 126.9, 129.1 (CH), 130.0, 131.5, 131.7, 143.9 (C_q); HRMS (EI) calcd for $C_{19}H_{14}S$ 274.0816, found 274.0810.

*9,10-Bis(2-thenyl)anthracene (**9a**).* Yield: 100 mg (27%), light yellow plates; mp 224−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14 (s, 4H, CH_2), 6.61 (dd, ^3J = 3.6 Hz, ^4J = 1.0 Hz, 2H, 3-H, thiophene), 6.81 (dd, ^3J = 3.6 Hz, ^3J = 5.2 Hz, 2H, 4-H, thiophene), 7.07 (dd, ^3J = 5.2 Hz, ^4J = 1.0 Hz, 2H, 5-H, thiophene), 7.49 (m, 4H, anthracene), 8.33

(m, 4H, anthracene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.6 (CH_2), 123.4, 124.9, 125.3, 125.7, 126.8 (CH), 130.0, 131.6, 143.9 (C_q); HRMS (EI) calcd for $C_{24}H_{18}S_2$ 370.0849, found 370.0841.

*9-(5-Chloro-2-thenyl)anthracene (**8b**).* Yield: 34 mg (11%), light yellow crystals; mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (s, 2H, CH_2), 6.37 (m, ^3J = 4.0 Hz, 1H, 3-H, thiophene), 6.59 (d, ^3J = 4.0 Hz, 1H, 4-H, thiophene), 7.44−7.52 (m, 4H, anthracene), 8.00 (m, 2H, anthracene), 8.21 (m, 2H, anthracene), 8.42 (s, 1H, anthracene, 10-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5 (CH_2), 124.1, 124.2, 125.0, 125.7, 126.2, 127.2, 127.3, 129.2, 130.0, 130.3, 131.6, 142.6 (CH and C_q); HRMS (EI) calcd for $C_{19}H_{13}ClS$ 308.0426, found 308.0426.

*9,10-Bis(5-chloro-2-thenyl)anthracene (**9b**).* Yield: 153 mg (35%), light yellow-green crystals; mp 208−210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.03 (s, 4H, CH_2), 6.38 (d, ^3J = 3.6 Hz, 2H, 3-H, thiophene), 6.61 (d, ^3J = 3.6 Hz, 2H, 4-H, thiophene), 7.50 (m, 4H, benzene), 8.27 (m, 4H, benzene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.9 (CH_2), 124.2, 125.1, 125.8, 125.9 (CH), 127.4, 130.0, 130.8, 142.5 (C_q); HRMS (EI) calcd for $C_{24}H_{16}Cl_2S_2$ 438.0070, found 438.0062.

Acid-Catalyzed Disproportionation Reaction of Anthracenol 6g to 5g and 10g. To a solution of anthracenol **6g** (536 mg, 1.0 mmol) in 30 mL of toluene was added *p*-TsOH (86 mg, 0.5 mmol). The mixture was heated at reflux for 2 h and then cooled to room temperature. A 10% NaOH solution was added slowly to the mixture to pH 7−8 in an ice−water bath. The separated water layer was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, and the products were purified by column chromatography on SiO_2 to give **10g** in the first fraction eluted by petroleum ether (bp 60−90 °C): ethyl acetate = 1: 8 (V: V) and **5g** in the second fraction eluted by ethyl acetate. Recrystallization from CH_2Cl_2/petroleum ether (bp 60−90 °C) gave **5g** and **10g** as colorless crystals.

*10,10-Bis(2-bromopyridin-4-ylmethyl)-9(10H)-anthracenone (**5g**).* Yield: 309 mg(58%); mp 190−192 °C. The ^{1}H NMR was in accord with the alkylation product **5g** described above.

*9,9-Bis(2-bromopyridin-4-ylmethyl)-9,10-dihydroanthracene (**10g**).* Yield: 130 mg (25%); mp 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 2H, 10-H), 3.48(s, 4H, CH_2), 6.22 (d, ^3J = 5.2 Hz, 2H, 5-H, pyridine), 6.53 (s, 2H, 3-H, pyridine), 7.05 (m, 2H, anthracene), 7.24 (m, 2H, anthracene), 7.32 (m, 2H, anthracene), 7.57 (m, 2H, anthracene), 7.81 (d, ^3J = 5.2 Hz, 2H, 6-H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.8 (C-10), 48.0 (C-9), 48.7 (CH_2), 124.1, 126.4, 126.8, 127.3, 128.7, 129.5, 148.8 (CH), 135.3, 135.8, 141.3, 149.4 (C_q); MS (APCI): m/z(%) 520.9 ($[M + H]^+$, Br_2 isotope pattern, 100); elemental analysis calcd (%) for $C_{26}H_{20}Br_2N_2$ (520.27): C 60.02, H 3.87, N 5.38; found: C 60.08, H 3.89, N 5.37.

■ ASSOCIATED CONTENT

Supporting Information. General experimental information; copies of ^{1}H NMR and ^{13}CNMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: drcao@scut.edu.cn (D.C.); hmeier@uni-mainz.de (H.M.).

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