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Deoxygenation of Hydroquinones as a General Route to Norbornane-Fused Aromatic Systems: An Entry into Substituted and Functionalized Dimethano- and Methanoanthracenes

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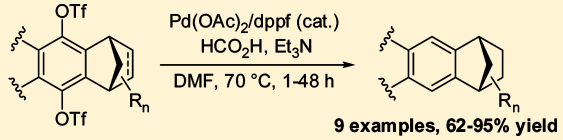
Supporting Information

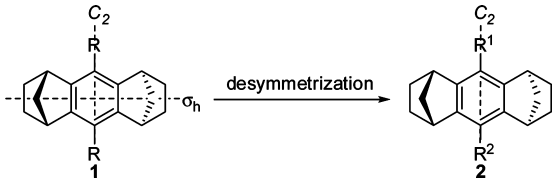
ABSTRACT: A high-yielding route to substituted and functionalized dimethanoanthracenes by the Pd-catalyzed deoxyenation of the corresponding hydroquinone precursors is described. Attempts were made to deoxygenate the 9,10-dimesylate, ditosylate, and ditriflate derivatives of *anti*-dimethanoanthracene **1a**, and it was found that under the studied conditions only the ditriflate **8a** gave the corresponding deoxygenated aromatic scaffold. Optimization of the reaction conditions identified the $Pd(OAc)_2$/dppf tandem as a suitable catalytic system for this transformation. The presented strategy was further extended to a novel and efficient synthetic route to methanoanthracenes employing a one-pot Pd-catalyzed deoxygenation/hydrogenation sequence.



INTRODUCTION

Dimethanoanthracenes have been utilized as rigid building blocks for molecular tweezers and clips,[1] rigid cavitands,[2] and highly robust radical-cations.[3] Notably, the removal of the σ_h plane in C_{2h}-symmetrical *anti*-dimethanoathracenes **1** by the desymmetrization of the 9 and 10 positions, for instance, leads to C_2-symmetrical compounds that have found application as catalyst precursors in a number of asymmetric catalytic processes (Scheme 1).[4−8]

Scheme 1. Chiral *anti*-Dimethanoanthracenes 2 ($R^1 \neq R^2$) from the Desymmetrization of 1

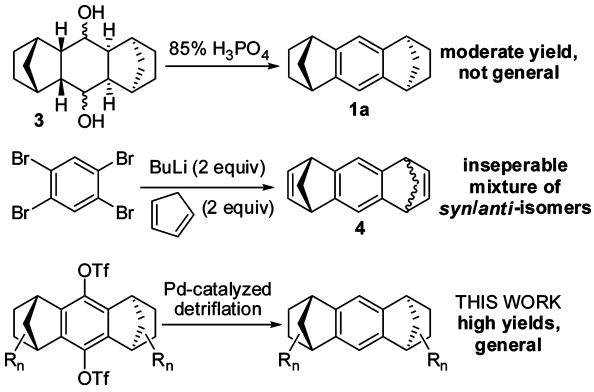


D_4-symmetrical metalloporphyrin catalysts derived from resolved 9-acyl-*anti*-dimethanoanthracenes of type **2** have been employed successfully in a number of asymmetric transformations, including asymmetric epoxidation,[4] asymmetric cyclopropanation,[4f,5] asymmetric aziridination,[6] asymmetric C−H activation,[7] and asymmetric Diels−Alder (DA) reactions.[4b,8]

In ongoing projects in our laboratory exploiting nonracemic *anti*-dimethanoanthracenes of type **2** in asymmetric transformations, we required multigram quantities of sterically engineered analogues of **1**.

A literature survey revealed several approaches to this class of arenes, which are summarized in Scheme 2. Halterman reported that the dehydration of diol **3** with 85% H_3PO_4 leads to *anti*-dimethanoanthracene **1a** (R = H) in a moderate yield.[9] However, the harsh reaction conditions (85% H_3PO_4, 110 °C, 16 h) are incompatible with the synthesis of other substituted, functionalized, and acid-sensitive analogues. Other approaches, including the double DA reaction of 1,3-cyclopentadiene with "dibenzyne", generated formally from 1,2,4,5-tetrabromobenzene and *n*-butyllithium, gave diene **4** as an inseparable mixture of *syn*/*anti*-isomers.[10]

Scheme 2. Synthetic Strategies to *anti*-Dimethanoanthracenes



We report here on a general route to dimethanoanthracenes by the Pd-catalyzed deoxygenation of readily accessible hydroquinone precursors via the corresponding ditriflates and extend this methodology to a novel and efficient synthetic route to methanoanthracenes.

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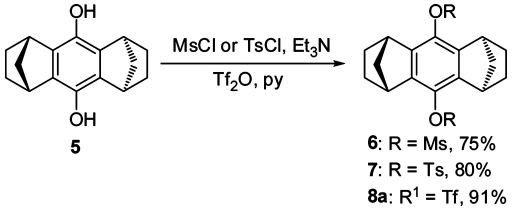
RESULTS AND DISCUSSION

Efforts to deoxygenate hydroquinone **5**[3] were made by converting it to the dimesylate **6**, ditosylate **7**, and ditriflate **8a** in good yields (Scheme 3). Attempts to deoxygenate

Scheme 3. Synthesis of *anti*-Dimethanoanthracene-Derived Disulfonates from Hydroquinone 5



disulfonates **6**, **7**, and **8a** under the Sajiki deoxygenation conditions using Mg metal in the presence of NH_4OAc in MeOH under Pd/C catalysis,[11] as well as the Ni-catalyzed hydrogenolysis of **7** with $NaBH_4$,[12] failed or gave **1a** in trace amounts. Furthermore, attempts to deoxygenate **6** by Sajiki's Pd/C-catalyzed hydrogenolysis under hydrogen atmosphere employing diethylamine as a SET agent also failed to give 1a.[13]

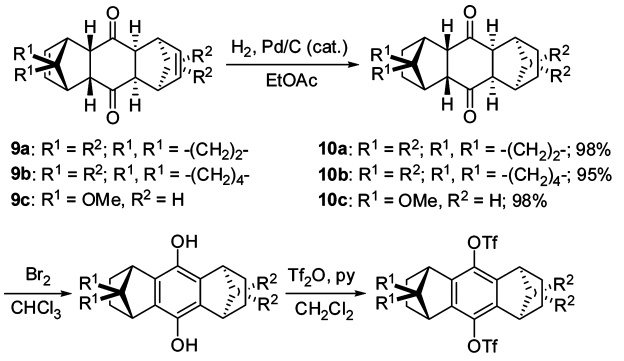
We then focused on the deoxygenation of ditriflate **8a**, as the Pd-catalyzed detriflation of aryl and vinyl triflates has been documented.[14] Our initial detriflation was carried out using reaction conditions similar to those reported by Snieckus, consisting of the $Pd(OAc)_2/PPh_3$ catalytic system in conjunction with the HCO_2H/Et_3N tandem as the reducing agent.[15]

Using a higher $Pd(OAc)_2$ loading of 16 mol % and an excess in the reducing agent, we were pleased to find that arene **1a** was formed in 76% yield after 24 h (Table 1, entry 1). However, efforts to lower the high catalyst loading to 10 mol % in palladium resulted in a tripling of the reaction time (entry 2). We then examined other phosphine ligands and found that 1,1′-bis(diphenylphosphino)ferrocene (dppf) greatly accelerated the reaction (Table 1, entries 3 and 4).[16] Moreover, we were able to lower the Pd loading even further to 1 mol % and observed in 1 h a complete conversion to the product, which was isolated in an excellent yield of 95% (entry 5). Efforts to further reduce the amount of the reducing agent resulted in a sluggish conversion (entries 6 and 7).

The deoxygenation of **8a** was scaled up to 10 mmol without problems, and **1a** was obtained in 91% yield (Table 2, entry 1).[17]

We then proceeded to test other substituted and functionalized dimethanoanthracene ditriflates **8b–f**, which were synthesized according to Schemes 4 and 5, and results from these investigations are summarized in Table 2.

Scheme 4. Synthesis of Ditriflates 8b–d



Scheme 5. Synthesis of Ditriflates 8e–i from the Corresponding Enedione Precursors 12e–i

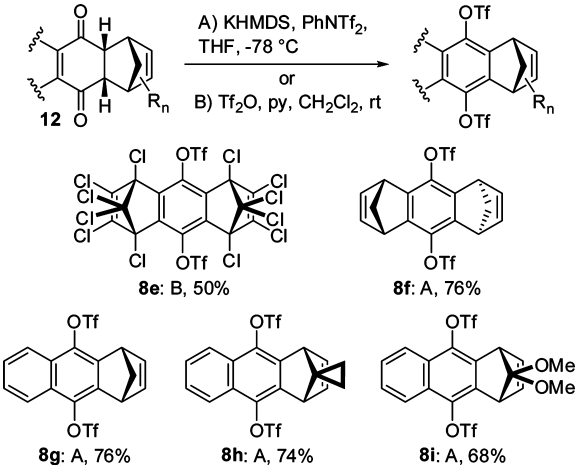
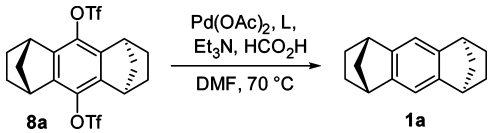


Table 1. Pd-Catalyzed Hydrogenolysis of Ditriflate 8a



entry	$Pd(OAc)_2$ (mol %)	L (loading) (mol %)	HCO_2H/Et_3N (equiv)	time (h)	yield[a] (%)
1	16.0	PPh_3 (32.0)	16.0/24.0	24	76 (≥98)
2	10.0	PPh_3 (20.0)	16.0/24.0	72	78 (≥98)
3	4.0	dppf (4.0)	16.0/24.0	0.5	86 (≥98)
4	2.0	dppf (2.0)	16.0/24.0	1	87 (≥98)
5	1.0	dppf (1.0)	16.0/24.0	1	95 (≥98)
6	1.0	dppf (1.0)	8.0/12.0	32	91 (≥98)
7	1.0	dppf (1.0)	4.0/6.0	60	92 (≥98)

[a]Yield of isolated product after short-pad column chromatography; conversion, determined by ^1H NMR of the crude product, is given in parentheses.

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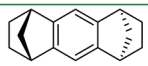
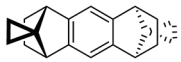
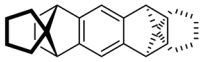
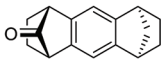
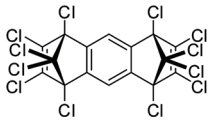
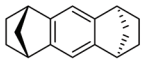
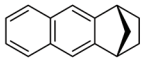
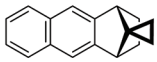
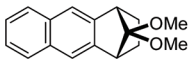
Table 2. Pd-Catalyzed Deoxygenation of $Ar(OTf)_2$[a]

entry	$Ar(OTf)_2$	cat. (mol %)	time (h)	product		yield (%)
1	**8a**	1.0	1		**1a**	91
2	**8b**	5.0	28		**1b**	72
3	**8c**	5.0	48		**1c**	95
4	**8d**	2.0	2		**1d**	67
5	**8e**	2.0	1		**1e**	66
6	**8f**	2.0	28		**1a**	72
7	**8g**	5.0	24		**1g**	78
8	**8h**	5.0	24		**1h**	82
9	**8i**	5.0	24		**1i**	62

[a]Reaction conditions: $Pd(OAc)_2$/dppf (cat.), HCO_2H (16 equiv), Et_3N (24 equiv), DMF, 70 °C.

The sterically congested bis(spirocyclopropane) ditriflate **8b** and bis(spirocyclopentane) ditriflate **8c** were prepared according to a route identical to that used for ditriflate **8a** in high overall yields (Scheme 4).

In analogy, the synthesis of keto ditriflate **8d** involved first the DA reaction of *p*-benzoquinone with 5,5-dimethoxycyclopentadiene,[18] followed by a second DA reaction of the obtained *endo*-9,9-dimethoxy-1,4-methanonaphthalene with cyclopentadiene, which proceeded to give exclusively the *endo*,*anti*,*endo*-bis-DA adduct **9c**. Subsequent hydrogenation and treatment with bromine gave, due to the acidic conditions in the latter reaction, the hydrolyzed keto hydroquinone **11c**, which upon triflation furnished the keto ditriflate **8d** in a good yield (Scheme 4).

The deoxygenation of sterically hindered ditriflates **8b** and **8c** using the $Pd(OAc)_2$/dppf catalytic system required a higher catalyst loading of 5 mol %, and longer reaction times were needed to obtain arenes **1b** and **1c** in 72% and 95% yields, respectively (Table 2, entries 2 and 3).

Treatment of **8d** with 2 mol % of $Pd(OAc)_2$/dppf gave after 2 h the detriflated keto *anti*-dimethanoanthracene **1d** in 67% yield (Table 2, entry 4). We were able to obtain crystals suitable for X-ray analysis, and the structure of **1d** is shown in Figure 1.

The synthesis of ketone **1d** clearly demonstrates that our approach is general, providing for the first time access to functionalized *anti*-dimethanoanthracenes.

In order to demonstrate that our approach is also applicable to *syn*-dimethanoanthracenes, we chose to subject the dodecachloro ditriflate **8e** to our deoxygenation conditions. Ditriflate **8e** was prepared by the triflation of the literature-known enedione precursor **12e**[19] using the Tf_2O/py triflation conditions (method B, Scheme 5). Subjecting **8e** to our deoxygenation conditions using 2.0 mol % of catalyst gave the detriflated dodecachloro arene **1e** in 66% yield (Table 2, entry 5).

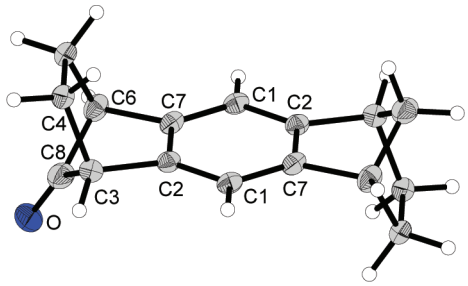


Figure 1. Crystal structure of ketone **1d** drawn with 50% thermal ellipsoids.

The hydroquinone precursor of diene ditriflate **8f** has been used as a bis-dienophile in supramolecular chemistry, and we were interested in examining if **8f** could be deoxygenated under our conditions.[2b] Monitoring this reaction by TLC analysis, we observed the formation of several spots which converged into one spot after 28 h. Examination of the crude ^1H NMR spectrum revealed that detriflation had taken place; however, this was accompanied by the hydrogenation of the double bonds to give **1a** in 72% isolated yield (Table 2, entry 6).[20]

The fact that the detriflation of **8f** occurred with concomitant alkene hydrogenation encouraged us to exploit this detriflation/hydrogenation sequence in a short and efficient synthetic route to methanoanthracenes starting from commercially available naphthoquinone.[21] Thus, DA reactions of cyclopentadiene and spirocyclopropane-annulated and 5,5-dimethoxy analogues to naphthoquinone gave enediones **12g–i**, which were converted to the corresponding ditriflates **8g–i** using the KHMDS/$PhNTf_2$ triflation conditions (method A, Scheme 5).[22]

A subsequent Pd-catalyzed one-pot detriflation/hydrogenation sequence using 5 mol % of $Pd(OAc)_2$/dppf furnished methanoanthracenes **1g–i** in good yields (Table 2, entries 7–9).

The observed Pd-catalyzed hydrogenation of the double bonds proceeds presumably under transfer-hydrogenation conditions.[23] However, it is not clear at present if this reduction is occurring in parallel or after the detriflation event and if it is proceeding under homogeneous or heterogeneous catalytic conditions.[24]

■ CONCLUSION

In summary, we have described a general and efficient procedure for the synthesis of norbornane-fused aromatic systems utilizing an initial DA reaction between cyclopentadienes and readily available quinones to install the carbon skeleton, followed by an aromatization/triflation/deoxygenation sequence. This unified approach allowed the preparation of substituted and functionalized dimethanoanthracenes in high overall yields and provided a novel and efficient route to methanoanthracene utilizing, to best of our knowledge, an unexploited Pd-catalyzed deoxygenation/hydrogenation sequence. Current investigations are focused on the desymmetrative asymmetric hydrogenolysis of the reported ditriflates, and results from these studies will be reported in due course.

■ EXPERIMENTAL SECTION

General Remarks. All air- and moisture-sensitive reactions were conducted under a dry nitrogen atmosphere in oven-dried glassware,

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using standard syringe/cannula transfer techniques. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Freshly distilled cyclopentadienes were used in DA reactions. Pyridine was purified by distillation over KOH, and triethylamine was stored over KOH for 24 h prior to use. DMF was purified by distillation over CaH_2. Dichloromethane, THF, and diethyl ether were obtained from a solvent purification system, and the remaining solvents were used as received. Thin-layer chromatography was performed on aluminum sheets (silica gel 60 F_{254}). Detection was by UV and by coloration with ceric ammonium molybdate (CAM) or vanillin. Flash column chromatography was performed using silica gel 60 (230−400 mesh). The following compounds were prepared according to literature procedures: spiro[2.4]hepta-4,6-diene,[25] spiro[4.4]nona-1,3-diene,[26] 5,5-dimethoxycyclopenta-1,3-diene,[18] **5**,[3a] **9b**,[4c] **12e**,[19] **12f**,[27] **12g**,[28] and **12h**.[29]

NMR spectra were recorded on 300, 400, and 500 MHz FT spectrometers at room temperature. All NMR spectra are referenced relative to the solvent residual peak. NMR peak assignments are based on 2D NMR experiments (gCOSY, HSQC). The relative stereochemistry of DA adduct **9c** was assigned on the basis of a 1D NOSEY experiment. Melting points were recorded in open capillaries and are uncorrected. Infrared spectra were recorded at room temperature on KBr plates. High-resolution mass spectra were obtained by electrospray ionization (ESI) or electron impact (EI) in positive ion mode. Elemental analyses are expressed as percentage values.

*9,10-Bis(methanesulfonyloxy)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-anti-dimethanoanthracene (**6**).* Hydroquinone **5** (2.42 g, 10.0 mmol) was placed in an oven-dried Schlenk tube, and then Et_3N (2.4 g, 24.0 mmol) and dry CH_2Cl_2 (20 mL) were added via a syringe. To this stirred suspension was added dropwise CH_3SO_2Cl (2.7 g, 24.0 mmol) at 0 °C over 10 min, and the resulting reaction mixture was stirred at room temperature for 2 h. The precipitate formed was filtered off, and the filtrate was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (2 × 20 mL). The organic layer was evaporated under reduced pressure to give the crude product, which was triturated with methanol (10 mL) to give the title compound as a white solid (2.96 g, 75%). Mp: 230−235 °C. IR (KBr, cm^{-1}): 2962, 1465, 1301. ^1H NMR (300 MHz, $CDCl_3$): δ 1.27−1.30 (m, 4 H, C*H*H), 1.51−1.54 (m, 2 H, C*H*H bridge), 1.77−1.80 (m, 2 H, CH*H* bridge), 1.89−1.92 (m, 4 H, CH*H*), 3.26 (s, 6 H, CH_3), 3.62 (s, 4 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2, 38.4, 42.0, 49.4, 135.0, 140.8. HRMS (ESI): $C_{18}H_{22}O_6S_2$ $[M + Na]^+$ calcd, 421.0756; found, 421.0768. Anal. Calcd for $C_{18}H_{22}O_6S_2$ (398.49): C, 54.25; H, 5.56. Found: C, 54.52; H, 5.51.

*9,10-Bis(p-toluenesulfonyloxy)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-anti-dimethanoanthracene (**7**).* Hydroquinone **5** (2.42 g, 10.0 mmol) was placed in a Schlenk tube, and then Et_3N (2.4 g, 24.0 mmol) and dry CH_2Cl_2 (20 mL) were added via a syringe. To this stirred suspension was added portion wise TsCl (4.7 g, 24.0 mmol) at 0 °C over 10 min, and the reaction mixture was stirred at room temperature for 2 h. The precipitate formed was filtered, and the filtrate was diluted with CH_2Cl_2 (20 mL). The filtrate was washed with water (2 × 20 mL) and evaporated under reduced pressure to give the crude product, which was triturated with methanol (10 mL) to give the title compound as a white solid (4.40 g, 80%). Mp: 220−226 °C. IR (KBr, cm^{-1}): 2926, 1593, 1333. ^1H NMR (300 MHz, $CDCl_3$): δ 1.10−1.12 (m, 4 H, C*H*H), 1.25−1.28 (m, 2 H, C*H*H bridge), 1.38−1.41 (m, 2 H, CH*H* bridge), 1.68−1.70 (m, 4 H, CH*H*), 2.47 (s, 6 H, CH_3), 3.18 (bs, 4 H, CH), 7.35 (d, J = 8.0 Hz, 4 H, ArH), 7.82 (d, J = 8.0 Hz, 4 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 26.0, 41.9, 49.2, 128.4, 129.7, 133.5, 135.5, 140.8, 145.2. HRMS (ESI): $C_{30}H_{30}O_6S_2$ $[M + Na]^+$ calcd, 573.1382; found, 573.1384. Anal. Calcd for $C_{30}H_{30}O_6S_2$ (550.08): C, 65.43; H, 5.49. Found: C, 65.29; H, 5.40.

*endo,anti,endo-11,12-Bis[spiro(cyclopropyl)]-1,4,4a,5,8,8a,9a,10a-octahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**9a**).* To a stirred suspension of *p*-benzoquinone (3.0 g, 27.0 mmol) in benzene (30 mL) was added freshly distilled spiro[2.4]hepta-4,6-diene (7.6 g, 81.0 mmol) at 0 °C via a syringe over 10 min. The resulting reaction mixture was refluxed for 24 h and evaporated under reduced pressure to give the crude product, which was recrystallized from hot benzene (10 mL) to afford the title compound as a cream crystalline solid (6.0 g, 74%). Mp: 203−208 °C. IR (KBr, cm^{-1}): 3070, 1697, 1628, 1292. ^1H NMR (400 MHz, $CDCl_3$): δ 0.40 (dd, J = 9.2, 6.0 Hz, 4 H, CH_2 cyclopropyl), 0.56 (dd, J = 9.2, 6.0 Hz, 4 H, CH_2 cyclopropyl), 2.73 (s, 4 H, C*H*CHCO), 3.07 (s, 4 H, CHCO), 6.29 (s, 4 H, CH═CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.7, 8.2, 45.2, 53.2, 54.1, 136.4, 212.4. MS (ESI): $[M - H]^+$ 291.4. Anal. Calcd for $C_{20}H_{20}O_2$ (292.14): C, 82.16; H, 6.89. Found: C, 82.13; H, 6.84.

endo-9,9-Dimethoxy-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione. To a stirred suspension of *p*-benzoquinone (0.5 g, 4.6 mmol) in toluene (5 mL) at 0 °C was added a solution of 5,5-dimethoxycyclopentadiene (1.75 g, 13.8 mmol) in toluene (2 mL), and the reaction mixture was stirred at 70 °C for 12 h. The reaction mixture was evaporated under reduced pressure to give the crude product, which was recrystallized from hot isopropanol (5 mL) to afford the title compound as a white crystalline solid (810 mg, 76%). Mp: 78−82 °C. IR (KBr, cm^{-1}): 2955, 1687, 1620, 1485, 1265, 1142. ^1H NMR (400 MHz, $CDCl_3$): δ 3.13 (s, 3 H, OCH_3), 3.24 (s, 3 H, OCH_3), 3.42 (d, J = 1.5 Hz, 2 H, CHCO), 3.48 (d, J = 1.8 Hz, 2 H, C*H*CHCO), 6.08 (virtual t, J = 2.2 Hz, 2 H, CH═CH), 6.61 (s, 2 H, CH═CHCO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.9, 50.0, 50.1, 52.2, 117.0, 133.2, 142.6, 198.7. HRMS (EI): $C_{13}H_{14}O_4$ $[M + H]^+$ calcd, 234.0892; found, 234.0882.

*endo,anti,endo-11,11-Dimethoxy-1,4,4a,5,8,8a,9a,10a-octahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**9c**).* To a suspension of *endo*-9,9-dimethoxy-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (1.0 g, 4.2 mmol) in toluene at 0 °C was added freshly distilled cyclopentadiene (415 mg, 6.3 mmol). The reaction mixture was heated at 70 °C for 3 h, allowed to cool to room temperature, and then stirred at 0 °C for 1 h. The precipitate formed was filtered and washed with chilled toluene (2 mL) to give the title compound as a white crystalline solid (982 mg, 85%). Mp: 154−158 °C. IR (KBr, cm^{-1}): 2965, 1678, 1635, 1427, 1290. ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (d, J = 8.6 Hz, 1 H, CH*H* bridge), 1.52 (d, J = 8.6 Hz, 1 H, C*H*H bridge), 2.93 (s, 2 H, CHCO), 3.04 (s, 2 H, CHCO), 3.10 (s, 3 H, OCH_3), 3.18 (s, 3 H, OCH_3), 3.28−3.33 (m, 2 H, C*H*CHCO), 3.33−3.38 (m, 2 H, C*H*CHCO), 6.14 (virtual t, J = 2.2 Hz, 2 H, CH═CH), 6.29 (virtual t, J = 1.8 Hz, 2 H, CH═CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.9, 49.5, 50.0, 51.7, 52.2, 53.5, 116.9, 134.5, 136.0, 212.1. MS (ESI): $[M + H]^+$ 301.4. Anal. Calcd for $C_{18}H_{20}O_4$ (300.34): C, 71.98; H, 6.71. Found: C, 71.90; H, 6.73.

*endo-11,11-Dimethoxy-1,4,4a,9a-tetrahydro-1,4-methanoanthracene-9,10-dione (**12i**).* To a solution of 1,4-naphthoquinone (316 mg, 2.0 mmol) in CH_2Cl_2 at 0 °C was added freshly prepared 5,5-dimethoxycyclopentadiene (504 mg, 4.0 mmol). The reaction mixture was stirred at room temperature for 12 h and evaporated under reduced pressure to give the crude product, which was purified by flash column chromatography (SiO_2; pentane/EtOAc, 90:10) to obtain the title compound as a white solid (369 mg, 65%). Mp: 137−140 °C. IR (KBr, cm^{-1}): 2971, 1673, 1641. ^1H NMR (400 MHz, $CDCl_3$): δ 3.19 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 3.62−3.65 (m, 2 H, C*H*CHCO), 3.66−3.68 (m, 2 H, CHCO), 6.07 (t, J = 2.1 Hz, 2 H, CH═CH), 7.70 (dd, J = 5.8, 3.4 Hz, 2 H, ArH), 8.03 (dd, J = 5.8, 3.4 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.1, 50.2, 50.5, 52.3, 117.2, 126.9, 133.6, 134.1, 136.2, 197.2. HRMS (ESI): $C_{17}H_{16}O_4$ $[M]^+$ calcd, 285.1127; found, 285.1140. Anal. Calcd for $C_{17}H_{16}O_4$ (284.31): C, 71.82; H, 5.67. Found: C, 71.62; H, 5.67.

General Procedure for the Hydrogenation of Diels−Alder Adducts (GP I). A Schlenk tube containing a suspension of DA adducts **9a−c**, 5% Pd/C (5 mol %) or 10% Pd/C (10 mol %), and EtOAc was connected to a 5 gallon balloon containing H_2, equipped with a three-way tap. The reaction mixture was degassed by three vacuum/hydrogen cycles and stirred under H_2 atmosphere for 24−48 h. The hydrogenated products were obtained by filtration of the reaction mixture through a short pad of silica gel using chloroform as the eluent.

endo,anti,endo-11,12-Bis[spiro(cyclopropyl)]-1,2,3,4,4a,5,6,7,8,8a,9a,10a-dodecahydro-1,4:5,8-dimethanoan-

*thracene-9,10-dione (**10a**).* According to GP I, DA adduct **9a** (3.9 g, 13.4 mmol), EtOAc (10 mL), and 5% Pd/C (71 mg, 0.67 mmol) were stirred under H_2 atmosphere for 24 h. The title compound was isolated as a white solid (3.74 g, 98%). Mp: 221−224 °C. IR (KBr, cm^{-1}); 2966, 1679, 1225. ^1H NMR (400 MHz, $CDCl_3$): δ 0.58 (s, 8 H, CH_2 cyclopropyl), 1.38−1.45 (m, 4 H, CH*H*), 1.74−1.78 (m, 4 H, *CH*H), 2.08 (s, 4 H, *CH*CHCO), 3.10 (s, 4 H, COCH). ^{13}C NMR (100.0 MHz, $CDCl_3$): δ 5.9, 6.5, 25.3, 35.2, 48.5, 54.0, 214.5. HRMS (EI): $C_{20}H_{24}O_2$ $[M]^+$ calcd, 296.1776; found, 296.1773. Anal. Calcd for $C_{20}H_{24}O_2$ (296.40): C, 81.04; H, 8.16. Found: C, 80.98; H, 8.13.

*endo,anti,endo-11,12-Bis[spiro(cyclopentyl)]-1,2,3,4,4a,5,6,7,8,8a,9a,10a-dodecahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**10b**).* According to GP I, DA adduct **9b** (400 mg, 1.1 mmol), EtOAc (3 mL), and 10% Pd/C (12 mg, 0.11 mmol) were stirred under H_2 atmosphere for 48 h. The title compound was isolated as a white solid (385 mg, 95%). Mp: 279−281 °C. IR (KBr, cm^{-1}): 2958, 1698, 1254. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27−1.29 (m, 4 H, CH_2), 1.48−1.77 (m, 20 H, CH_2), 2.30 (s, 4 H, *CH*CHCO), 2.98 (s, 4 H, CHCO). ^{13}C NMR (100 MHz, $CDCl_3$): 24.8, 25.9, 26.0, 29.9, 30.8, 50.3, 53.5, 58.2, 216.0. HRMS (ESI): $C_{24}H_{32}O_2$ $[M]^+$ calcd, 353.2481; found, 353.2497. Anal. Calcd for $C_{24}H_{32}O_2$ (352.51): C, 81.77; H, 9.15. Found: C, 81.66; H, 9.03.

*endo,anti,endo-11,11-Dimethoxy-1,2,3,4,4a,5,6,7,8,8a,9a,10a-dodecahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**10c**).* According to GP I, DA adduct **9c** (1.0 g, 3.3 mmol), EtOAc (5 mL), and 10% Pd/C (34 mg, 0.33 mmol) were stirred under H_2 atmosphere for 24 h. The title compound was isolated as a white solid (0.95 g, 98%). Mp: 157−161 °C. IR (KBr, cm^{-1}): 2931, 1687, 1243. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23−1.31 (m, 2 H, CH_2), 1.32−1.42 (m, 2 H, CH_2), 1.42−1.45 (m, 2 H, CH_2 bridge), 1.55−1.58 (m, 2 H, CH_2), 1.76 (d, J = 10.5 Hz, 2 H, CHH), 2.66 (s, 2 H, *CH*CHCO), 2.84 (s, 2 H, *CH*CHCO), 2.86 (s, 2 H, CHCO), 3.11 (s, 2 H, CHCO), 3.27 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8, 25.1, 39.8, 43.8, 44.2, 50.6, 50.8, 51.6, 53.8, 111.8, 214.0. MS (ESI): $[M + H]^+$ 305.2. Anal. Calcd for $C_{18}H_{24}O_4$ (304.16): C, 71.03; H, 7.95. Found: C, 71.28; H, 7.98.

General Procedure for the Preparation of Hydroquinones (GP II). Diones **10a−c** and $CHCl_3$ were placed in an oven-dried Schlenk tube under N_2, and the reaction mixture was cooled to 0 °C. To this stirred suspension was added dropwise a solution of Br_2 (1 equiv) in $CHCl_3$ (2 −20 mL) over 10 min. The reaction mixture was stirred at room temperature for 2 h, and the HBr produced in the reaction was blown off by bubbling N_2 through the reaction mixture for 10 min. The resulting suspension was stirred at −10 °C for 1 h. The precipitate formed was filtered and washed with chilled $CHCl_3$ to give hydroquinones **11a−c**.

*9,10-Dihydroxy-11,12-bis[spiro(cyclopropyl)]-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-anti-dimethanoanthracene (**11a**).* According to GP II, dione **10a** (3.0 g, 10 mmol) was reacted with Br_2 (1.6 g, 10 mmol) in $CHCl_3$ (30 mL). The title compound was isolated as a pale yellow solid (2.86 g, 96%). Mp: 292−296 °C. IR (KBr, cm^{-1}): 3406, 3032, 1508. ^1H NMR (300 MHz, CD_3OD): δ 0.04−0.09 (m, 8 H, CH_2 cyclopropyl), 0.81−0.83 (m, 4 H, CH*H*), 1.61−1.64 (m, 4 H, *CH*H), 2.39 (s, 4 H, CH). ^{13}C NMR (100 MHz, CD_3OD): δ 5.6, 6.6, 26.5, 44.1, 45.3, 132.7, 136.9. HRMS (EI): $C_{20}H_{22}O_2$ $[M + H]^+$ calcd, 295.1698; found, 295.1684. Anal. Calcd for $C_{20}H_{22}O_2$ (294.38): C, 81.60; H, 7.53. Found C, 81.52; H, 7.51.

*9,10-Dihydroxy-11,12-bis[spiro(cyclopentyl)]-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-anti-dimethanoanthracene (**11b**).* According to GP II, dione **10b** (400 mg, 1.13 mmol) in $CHCl_3$ (4 mL) was reacted with Br_2 (180 mg, 1.13 mmol). The title compound was isolated as a pale yellow solid (388 mg, 97%). Mp: 328−330 °C. IR (KBr, cm^{-1}): 3455, 2971, 1602. ^1H NMR (300 MHz, CD_3OD): δ 1.05−1.14 (m, 4 H, CH_2 cyclopentyl), 1.26 (virtual t, J = 7.2 Hz, 4 H, CH_2 cyclopentyl), 1.43−1.53 (m, 8 H, CH_2 cyclopentyl), 1.56−1.69 (m, 4 H, CH*H*), 1.93 (d, J = 8.1 Hz, 4 H, C*H*H), 2.98 (bs, 4 H, CH). ^{13}C NMR (75 MHz, CD_3OD): 25.1, 25.7, 25.8, 31.4, 32.2, 47.8, 67.8, 133.2, 138.1. HRMS (ESI): $C_{24}H_{30}O_2$ $[M + H]^+$ calcd, 351.2324; found, 351.2329.

*9,10-Dihydroxy-11-keto-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-anti-dimethanoanthracene (**11c**).* According to GP II, dione **10c** (500 mg, 1.6 mmol) in $CHCl_3$ (5 mL) was reacted with Br_2 (260 mg, 1.6 mmol). The title compound was isolated as a pale yellow solid (357 mg, 74%). Mp: 294−298 °C. IR (KBr, cm^{-1}): 3350, 3032, 1516. ^1H NMR (300 MHz, CD_3OD): δ 1.12−1.17 (m, 2 H, CH_2), 1.27−1.32 (m, 2 H, CH_2), 1.45 (d, J = 8.8 Hz, 1 H, C*H*H bridge), 1.58 (d, J = 8.8 Hz, 1 H, CH*H* bridge), 1.84−1.87 (m, 2 H, CH_2), 2.07−2.10 (m, 2 H, CH_2), 3.41 (s, 2 H, CH), 3.56 (s, 2 H, CH). ^{13}C NMR (75 MHz, CD_3OD): δ 21.8, 26.1, 40.0, 43.8, 48.4, 125.5, 133.5, 137.2, 205.0. HRMS (ESI): $C_{16}H_{16}O_3$ $[M - H]^+$ calcd, 255.1029; found, 255.1021.

General Procedure for the Preparation of Ditriflates from Hydroquinones (GP III). In an oven-dried Schlenk tube were placed hydroquinone **11a−11d**, anhydrous pyridine (3−6 equiv), and dry CH_2Cl_2 under N_2, and the reaction mixture was cooled to −10 °C using an ice−acetone bath. To this stirred suspension was added a solution of Tf_2O (2.4 equiv) in dry CH_2Cl_2 over 15 min via a syringe. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Water was added to the reaction mixture and extracted with CH_2Cl_2. The combined organic layers were washed with 10% aqueous HCl and water, dried over Na_2SO_4, and evaporated under reduced pressure to afford the crude product, which was carried to the next step without further purification.

*9,10-Bis(trifluoromethanesulfonyloxy)-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-anti- dimethanoanthracene (**8a**).* According to GP III, hydroquinone **5** (2.42 g, 10 mmol) and pyridine (2.37 g, 30 mmol) in CH_2Cl_2 (50 mL) were reacted with Tf_2O (6.7 g, 24 mmol). The title compound was isolated as a pale yellow solid (4.6 g, 91%). Mp: 229−232 °C. IR (KBr, cm^{-1}): 2962, 1612, 1213. ^1H NMR 400 MHz, $CDCl_3$): δ 1.25−1.28 (m, 4 H, CH_2), 1.56−1.59 (m, 2 H, C*H*H bridge), 1.81−1.84 (m, 2 H, CH*H* bridge), 1.94−1.97 (m, 4 H, CH_2), 3.63 (s, 4 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.8, 41.9, 49.5, 120.4 (q, J = 320 Hz), 135.7, 140.7. MS (ESI): $[M + H]^+$ 507.1. Anal. Calcd for $C_{18}H_{16}F_6O_6S_2$ (506.02): C, 42.69; H, 3.18. Found: C, 42.71; H, 3.17.

*9,10-Bis(trifluoromethanesulfonyloxy)-11,12-di[spiro-(cyclopropyl)]-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-anti-dimethanoanthracene (**8b**).* According to GP III, hydroquinone **11a** (2.0 g, 6.8 mmol) and pyridine (3.2 g, 40.8 mmol) in CH_2Cl_2 were reacted with Tf_2O (4.6 g, 16.3 mmol). The title compound was isolated as a pale yellow solid (3.53 g, 93%). Mp: 232−234 °C. IR (KBr, cm^{-1}): 2983, 1426, 1209. ^1H NMR (400 MHz, $CDCl_3$): δ 0.51−0.60 (m, 8 H, CH_2 cyclopropyl), 1.38−1.42 (m, 4 H, CH*H*), 2.13−2.15 (m, 4 H, C*H*H), 2.92 (s, 4 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.3, 7.4, 26.2, 45.8, 47.2, 120.2 (q, J = 309.4 Hz), 135.8, 140.5. HRMS (ESI): calcd, 559.0684; found, 559.0671. Anal. Calcd for $C_{22}H_{20}F_6O_6S_2$ (558.06): C, 47.31; H, 3.61. Found: C, 47.40; H, 3.73.

*9,10-Bis(trifluoromethanesulfonyloxy)-11,12-di[spiro-(cyclopentane)]-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-anti-dimethanoanthracene (**8c**).* According to GP III, hydroquinone **11b** (350 mg, 1.0 mmol) and pyridine (474 mg, 6.0 mmol) in CH_2Cl_2 were reacted with Tf_2O (676 mg, 2.4 mmol). The title compound was isolated as a pale yellow solid (583 mg, 95%). Mp: 231−234 °C. IR (KBr, cm^{-1}): 2958, 1520, 1201. ^1H NMR (400 MHz, $CDCl_3$): δ 1.22−1.30 (m, 8 H, CH_2 cyclopentyl), 1.43−1.57 (m, 8 H, CH_2 cyclopentyl), 1.58−1.62 (m, 4 H, C*H*H), 1.97−2.12 (m, 4 H, CH*H*), 3.12 (bs, 4 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4, 25.5, 25.9, 31.4, 32.1, 49.6, 69.8, 120.2 (q, J = 320 Hz), 137.0, 141.1. HRMS (ESI): $C_{26}H_{28}F_6O_6S_2$ $[M + Na]^+$ calcd, 637.1129; found, 637.1159.

*9,10-Bis(trifluoromethanesulfonyloxy)-11-keto-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-anti-dimethanoanthracene (**8d**).* According to GP III, hydroquinone **11c** (281 mg, 1.1 mmol) and pyridine (522 mg, 6.6 mmol) in CH_2Cl_2 (5 mL) were reacted with Tf_2O (744 mg, 2.64 mmol). The title compound was isolated as a pale yellow solid (388 mg, 68%). Mp: 212−215 °C. IR (KBr, cm^{-1}): 2987, 1685, 1535. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27−1.34 (m, 2 H, CH*H*), 1.51−1.55 (m, 2 H, C*H*H), 1.66 (d, J = 9.3, 1 H, C*H*H bridge), 1.90 (d, J = 9.4 Hz, 1 H, CH*H* bridge), 1.96−2.07 (m, 2 H, C*H*H), 2.21−2.33 (m, 2 H, CH*H*), 3.62 (s, 2 H, CH), 3.71 (s, 2 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 25.8, 42.0, 45.5, 49.3, 120.3 (q, J = 344 Hz), 133.1, 135.6, 141.2, 200.1. HRMS (ESI): $C_{18}H_{14}F_6O_7S_2$ $[M + Na]^+$ calcd, 542.9982; found, 542.9976.

*9,10-Bis(trifluoromethanesulfonyloxy)perchloro-1,4:5,8-syn-dimethanoanthracene (**8e**).* According to GP III, enedione **12e** (300

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mg, 0.4 mmol) and pyridine (220 mg, 2.7 mmol) in CH_2Cl_2 (5 mL) were reacted with Tf_2O (314 mg, 1.1 mmol). The title compound was isolated as a pale yellow solid (212 mg, 50%). Mp: >300 °C. IR (KBr, cm^{-1}): 2837, 1612, 1409, 1219. ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.0, 113.5, 120.1 (q, J = 321 Hz), 137.3, 138.4, 140.1. MS (ESI): $[M + H]^+$ 916.4. Anal. Calcd for $C_{18}Cl_{12}F_6O_6S_2$ (915.74): C, 23.61. Found: C, 23.70.

General Procedure for the Preparation of Ditriflates from Enediones (GP IV). In an oven-dried Schlenk tube were placed enedione (**12f–i**), anhydrous THF (10–20 mL), and $PhNTf_2$ (2.4 equiv) under N_2. The reaction mixture was cooled to −78 °C, KHMDS (0.5 M in THF, 2.5 equiv) was added via a syringe dropwise over 10 min, and the resulting mixture was stirred at −78 °C for 2 h. The reaction mixture was poured into water and extracted with Et_2O (2×). The combined organic layers were washed with 1 N aqueous NaOH solution and water, dried over Na_2SO_4, and evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography.

*9,10-Bis(trifluoromethanesulfonyloxy)-1,4,5,8-tetrahydro-1,4:5,8-anti-dimethanoanthracene (**8f**).* According to GP IV, enedione **12f** (240 mg, 1.0 mmol) was treated with $PhNTf_2$ (900 mg, 7.92 mmol), and KHMDS (0.5 M in THF, 4.7 mL, 2.5 mmol) in anhydrous THF (20 mL). The title compound was obtained after purification by flash column chromatography (SiO_2; pentane/Et_2O, 99:1) as a white solid (480 mg, 76%). Mp: 182–186 °C. IR: 2938, 1630, 1225. ^1H NMR (400 MHz, $CDCl_3$): δ 2.28–2.35 (m, 4 H, CH_2), 4.09–4.11 (m, 4 H, CH), 6.77–6.85 (m, 4 H, CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.7, 70.0, 120.3 (q, J = 320 Hz), 137.4, 142.9, 145.0. MS (ESI): $[M + H]^+$ 503.14. Anal. Calcd for $C_{18}H_{12}F_6O_6S_2$ (502.40): C, 43.03; H, 2.41. Found: C, 43.32; H, 2.39.

*9,10-Bis(trifluoromethanesulfonyloxy)-1,4-methanoanthracene (**8g**).* According to GP IV, enedione **12g** (448 mg, 2.0 mmol) was treated with $PhNTf_2$ (1.71 g, 4.8 mmol) and KHMDS (0.5 M in THF, 10 mL, 5 mmol) in anhydrous THF (20 mL). The title compound was obtained after purification by flash column chromatography (SiO_2; pentane/Et_2O, 99:1) as a white solid (740 mg, 76%). Mp: 85–89 °C. IR (KBr, cm^{-1}): 2444, 2294, 1406, 1337. ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (d, J = 8.2 Hz, 1 H, C*H*H), 2.39 (dt, J = 8.2, 1.4 Hz, 1 H, CH*H*), 4.25–4.44 (m, 2 H, CH), 6.85 (virtual t, J = 1.7 Hz, 2 H, CH=CH), 7.65 (dd, J = 6.4, 3.2 Hz, 2 H, ArH), 7.96 (dd, J = 6.4, 3.2 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.5, 64.9, 120.3 (q, J = 320 Hz), 121.4, 126.6, 128.1, 136.6, 141.9, 141.93. HRMS (ESI): $C_{17}H_{10}O_6F_6S_2$ $[M + Na]^+$ calcd, 510.9721; found, 510.9708.

*9,10-Bis(trifluoromethanesulfonyloxy)-11-[spiro(cyclopropyl)]-1,4-methanoanthracene (**8h**).* According to GP IV, enedione **12h** (250 mg, 1.0 mmol) was treated with $PhNTf_2$ (0.86 g, 2.4 mmol) and KHMDS (0.5 M in THF, 5 mL, 2.5 mmol) in THF (10 mL). The title compound was obtained after purification by flash column chromatography (SiO_2; pentane/Et_2O, 99:1) as a white solid (369 mg, 72%). Mp: 102–106 °C. IR (KBr, cm^{-1}): 2988, 2306, 1422, 1265. ^1H NMR (400 MHz, $CDCl_3$): δ 0.60 (dd, J = 9.4, 6.6 Hz, 2 H, C*H*H cyclopropyl), 0.79 (dd, J = 9.5, 6.5 Hz, 2 H, CH*H* cyclopropyl), 3.81 (virtual t, J = 1.7 Hz, 2 H, CH), 6.88 (virtual t, J = 1.9 Hz, 2 H, CH=CH), 7.65 (dd, J = 6.4, 3.2 Hz, 2 H, ArH), 7.97 (dd, J = 6.4, 3.2 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.2, 8.5, 53.7, 61.4, 120.3 (q, J = 320 Hz), 121.5, 126.5, 128.1, 136.3, 141.1, 141.8. HRMS (ESI): $C_{19}H_{12}O_6F_6S_2$ $[M + Na]^+$ calcd, 536.9877; found, 536.9868.

*9,10-Bis(trifluoromethanesulfonyloxy)-11,11-dimethoxy-1,4-methanoanthracene (**8i**).* According to GP IV, enedione **12i** (284 mg, 1.0 mmol) was treated with $PhNTf_2$ (0.86 g, 2.4 mmol) and KHMDS (0.5 M in THF, 5 mL, 2.5 mmol) in THF (10 mL). The title compound was obtained after purification by flash column chromatography (SiO_2; pentane/Et_2O, 99:1) as a white solid (372 mg, 68%). Mp: 93–96 °C. IR (KBr, cm^{-1}): 2837, 2254, 1409, 1219. ^1H NMR (400 MHz, $CDCl_3$): δ 3.09 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3), 4.46 (t, J = 2.1 Hz, 2 H, CH), 6.63–6.85 (m, 2 H, CH=CH), 7.68 (dd, J = 6.4, 3.2 Hz, 2 H, ArH), 8.01 (dd, J = 6.4, 3.2 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.2, 52.3, 52.4, 120.3 (q, J = 320 Hz), 121.4, 126.5, 126.7, 128.2, 137.1, 138.0, 138.3. HRMS (ESI): $C_{19}H_{14}O_8F_6S_2$ $[M + Na]^+$ calcd, 570.9932; found, 570.9911.

General Procedure for the Deoxygenation of Ditriflates (GP V). In an oven-dried Schlenk tube were placed ditriflate **8a–i**, HCO_2H (16 equiv), dry Et_3N (24 equiv), and anhydrous DMF under N_2. The reaction mixture was degassed by three vacuum/nitrogen cycles, followed by the addition of $Pd(OAc)_2$ (1–5 mol %) and dppf (1–5 mol %). The resulting mixture was stirred at 70 °C for 1–48 h, cooled to room temperature, diluted with brine, and extracted with EtOAc (3 × 10–100 mL). The combined organic layers were washed with brine and evaporated under reduced pressure to give the crude product, which was purified either by filtration through a short pad of silica gel using pentane as the eluent or by flash column chromatography to afford arenes **1a–i**.

*1,2,3,4,5,6,7,8-Octahydro-1:4,5:8-anti-dimethanoanthracene[4b] (**1a**).* According to GP V, ditriflate **8a** (5.06 g, 10.0 mmol), HCO_2H (7.36 g, 6.0 mL, 160 mmol), dry Et_3N (24.29 g, 33.5 mL, 240 mmol), anhydrous DMF (50 mL), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol, 1 mol %), and dppf (55.4 mg, 0.1 mmol, 1 mol %) were stirred at 70 °C for 1 h. The title compound was isolated as a white solid (1.91 g, 91%).

*11,12-Bis[spiro(cyclopropyl)]-1,2,3,4,5,6,7,8–octahydro-1:4,5:8-anti-dimethanoanthracene (**1b**).* According to GP V, ditriflate **8b** (558 mg, 1.0 mmol), HCO_2H (736 mg, 0.60 mL, 16 mmol), dry Et_3N (2.43 g, 3.35 mL, 24 mmol), anhydrous DMF (5 mL), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 5 mol %), and dppf (27.7 mg, 0.05 mmol, 5 mol %) were stirred at 70 °C for 28 h. The title compound was isolated as a white solid (190 mg, 72%). Mp: 162–164 °C. IR (KBr, cm^{-1}): 2996, 1639, 1412. ^1H NMR (300 MHz, $CDCl_3$): δ 0.34–0.44 (m, 4 H, CH_2 cyclopropyl), 0.45–0.54 (m, 4 H, CH_2 cyclopropyl), 1.04–1.33 (m, 4 H, C*H*H), 1.88–2.12 (m, 4 H, CH*H*), 2.53 (s, 4 H, CH), 6.90 (s, 2 H, Ar-H). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ 5.5, 6.3, 26.6, 28.7, 44.1, 112.5, 144.0. HRMS (ESI): $C_{20}H_{22}$ $[M]^+$ calcd, 262.1722; found, 262.1734.

*11,12-Bis[spiro(cyclopentyl)]-1,2,3,4,5,6,7,8-octahydro-1:4,5:8-anti-dimethanoanthracene[4c] (**1c**).* According to GP V, ditriflate **8c** (500 mg, 0.81 mmol), HCO_2H (597 mg, 0.49 mL, 12.9 mmol), dry Et_3N (1.97 g, 2.70 mL, 19.4 mmol), anhydrous DMF (5 mL), $Pd(OAc)_2$ (9.1 mg, 0.041 mmol, 5 mol %), and dppf (22.5 mg, 0.041 mmol, 5 mol %) were stirred at 70 °C for 48 h. The title compound was isolated as a white solid (240 mg, 95%).

*1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-anti-dimethanoanthracene-11-one (**1d**).* According to GP V, ditriflate **8d** (250 mg, 0.48 mmol), HCO_2H (353 mg, 0.29 mL, 7.7 mmol), dry Et_3N (1.16 g, 1.60 mL, 11.5 mmol), anhydrous DMF (2 mL), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 2 mol %), and dppf (5.3 mg, 0.01 mmol, 2 mol %) were stirred at 70 °C for 2 h. The title compound was isolated as a white solid (72 mg, 67%). Mp: 172–176 °C. IR (KBr, cm^{-1}): 2968, 2870, 1790, 1606. ^1H NMR (400 MHz, $CDCl_3$): δ 1.08–1.15 (m, 2 H, CH_2), 1.25–1.37 (m, 2 H, CH_2), 1.43–1.53 (m, 1 H, C*H*H bridge), 1.63–1.76 (m, 1 H, C*H*H bridge), 1.79–1.95 (m, 2 H, CH_2), 2.05–2.22 (m, 2 H, CH_2), 3.24–3.29 (m, 2 H, CH), 3.32–3.34 (m, 2 H, CH), 7.08 (s, 2 H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.7, 27.1, 43.8, 47.7, 49.1, 114.4, 137.8, 147.0, 205.3. HRMS (EI): $C_{16}H_{16}O$ $[M]^+$ calcd, 224.1201; found, 224.1198.

*1,2,3,4,5,6,7,8,11,11,12,12-Dodecachloro-1,4:5,8-syn-dimethanoanthracene (**1e**).* According to GP V, ditriflate **8e** (200 mg, 0.23 mmol), HCO_2H (169 mg, 0.14 mL, 3.7 mmol), dry Et_3N (558 mg, 0.77 mL, 5.5 mmol), anhydrous DMF (2 mL), $Pd(OAc)_2$ (1.0 mg, 0.005 mmol, 2 mol %), and dppf (2.6 mg, 0.005 mmol, 2 mol %) were stirred at 70 °C for 1 h. The title compound was isolated as a white solid (94 mg, 66%). Mp: >300 °C. IR (KBr, cm^{-1}): 2918, 1620, 1350, 1226. ^1H NMR (300 MHz, $CDCl_3$): δ 6.25 (s, 2 H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.2, 112.0, 128.5, 138.2, 143.5. HRMS (EI): $C_{16}H_2Cl_{12}$ $[M]^+$ calcd, 613.6419; found, 613.6419.

*1,2,3,4,5,6,7,8-Octahydro-1:4,5:8-anti-dimethanoanthracene[4b] from **8f** (**1a**).* According to GP V, ditriflate **8f** (400 mg, 0.8 mmol), HCO_2H (588 mg, 0.48 mL, 12.8 mmol), dry Et_3N (1.93 g, 2.7 mL, 19.2 mmol), anhydrous DMF (5 mL), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol, 2 mol %), and dppf (8.9 mg, 0.016 mmol, 2 mol %) were stirred at 70 °C for 28 h. The title compound was isolated as a white solid (120 mg, 72%).

*1,2,3,4-Tetrahydro-1,4-methanoanthracene[21a] (**1g**).* According to GP V, ditriflate **8g** (200 mg, 0.41 mmol), HCO_2H (301 mg, 0.24

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mL, 6.5 mmol), dry Et_3N (995 mg, 1.37 mL, 9.8 mmol), anhydrous DMF (2 mL), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol %), and dppf (11.4 mg, 0.02 mmol, 5 mol %) were stirred at 70 °C for 24 h. The title compound was isolated by flash column chromatography (SiO_2; pentane) as a white solid (62 mg, 78%).

*11-[Spiro(cyclopropyl)]-1,2,3,4-tetrahydro-1,4-methanoanthracene (**1h**).* According to GP V, ditriflate **8h** (250 mg, 0.48 mmol), HCO_2H (354 mg, 0.29 mL 7.7 mmol), dry Et_3N (1.17 g, 1.61 mL, 11.5 mmol), anhydrous DMF (2 mL), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol, 5 mol %), and dppf (13.3 mg, 0.024 mmol, 5 mol %) were stirred at 70 °C for 24 h. The title compound was isolated by flash column chromatography (SiO_2; pentane) as a white solid (87 mg, 82%). Mp: 177−181 °C. IR (KBr, cm^{-1}): 2253, 1636, 1403, 1096. ^1H NMR (400 MHz, $CDCl_3$): δ 0.43−0.66 (m, 4 H, CH_2 cyclopropyl), 1.36−1.40 (m, 2 H, C*H*H), 1.98−2.27 (m, 2 H, CH*H*), 2.61−2.83 (m, 2 H, CH), 7.37 (dd, J = 6.2, 3.3 Hz, 2 H, Ar-H), 7.55 (s, 2 H, Ar-H), 7.76 (dd, J = 6.2, 3.3 Hz, 2 H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.1, 7.0, 27.9, 44.2, 48.8, 118.1, 124.7, 127.6, 132.7, 147.3. MS (ESI): $[M + H]^+$ 221.4. Anal. Calcd for $C_{17}H_{16}$ (220.1): C, 92.68; H, 7.32. Found: C, 92.39; H, 7.66.

*11,11-Dimethoxy-1,2,3,4-tetrahydro-1,4-methanoanthracene (**1i**).* According to GP V, ditriflate **8i** (200 mg, 0.36 mmol), HCO_2H (268 mg, 0.22 mL, 5.8 mmol), dry Et_3N (880 mg, 1.21 mL, 8.7 mmol), anhydrous DMF (2 mL), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), and dppf (10.0 mg, 0.018 mmol) were stirred at 70 °C for 24 h. The title compound was isolated by flash column chromatography (SiO_2; pentane/Et_2O, 95:5) as a white solid (61 mg, 62%). Mp: 182−185 °C. IR (KBr, cm^{-1}): 3054, 2411, 1231. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23−1.26 (m, 2 H, C*H*H), 2.15−2.24 (m, 2 H, CH*H*), 3.11 (s, 3 H, CH_3), 3.36 (s, 3 H, CH_3), 3.40−3.46 (m, 2 H, CH), 7.39 (dd, J = 6.2, 3.3 Hz, 2 H, Ar-H), 7.58 (s, 2 H, Ar-H), 7.77 (dd, J = 6.2, 3.3 Hz, 2 H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 46.2, 50.0, 51.5, 117.8, 119.1, 124.8, 127.6, 132.9, 144.13. HRMS (ESI): $C_{17}H_{18}O_2$ $[M + Na]^+$ calcd, 277.1204; found, 277.1208.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR and ^{13}C NMR spectra of all compounds in the Experimental Section, and X-ray data for compound **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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