Supplementary Materials

for

Diels-Alder Reactions and Electrophilic Substitutions with Atypical Regioselectivity Enable Functionalization of Terminal Rings of Anthracene

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1. Supplementary Methods

1.1. General Information

All moisture sensitive reactions were performed in flame-dried glassware under nitrogen atmosphere. All reactions were performed in pressure tube apparatus. Commercially available chemicals were purchased in high quality and used without any further purification. DCM, ethyl acetate and hexanes (petroleum ether, PE (60/40)) were distilled prior to use. Anhydrous solvents were prepared according to standard procedures. All the reactions were monitored by TLC and visualized by a dual short (254 nm) / long (366 nm) wavelength UV lamp and staining was performed with vanillin or potassium permanganate solutions followed by heating. Analytical thin layer chromatography was performed on Merck TLC aluminium sheets silica gel 60 F 254. Column chromatographic purifications were performed using Merck flash silica gel 60 (0.040–0.063 mm). \(^1\)H- and \(^13\)C-NMR spectra were recorded on BRUKER Avance III 400 Nanobay (400 MHz) and BRUKER Avance 300 (300 MHz) spectrometers at ambient temperature. Chemical shifts are reported as \(\delta\) (ppm) relative to the signal of the solvent. Characterization of the signals: s = singlet, d = doublet, t = triplet, quin = quintet, m = multiplet, br s= broad singlet, dd = doublet of a doublet, ddd = doublet of doublet of doublet, dt = doublet of a triplet, dq = doublet of a quartet, td = triplet of a doublet, qt = quartet of a triplet. Integration is determined as the relative number of atoms, and the coupling constants \((J)\) are given in Hertz (Hz). FT-IR spectroscopy was carried out on a Cary 630 spectrometer, equipped with a Diamond Single Reflection ATR-System and compounds were measured neatly, and wave numbers are reported in \(\text{cm}^{-1}\). Mass spectrometry was performed in the Central Analytical Department of the University of Regensburg on a Jeol AccuTOF GCX, Agilent Q-TOF 6540 UHD, Finnigan MAT SSQ 710 A or a ThermoQuest Finnigan TSQ 7000 and are reported in \(m/z\). The melting points were measured on an SRS MPA 100 OptiMelt in a silicon oil bath and are reported uncorrected. Single crystal X-ray analyses were performed on Agilent Technologies SuperNova, Agilent Technologies Gemini R Ultra or Stoe IPDS I.
1.2. Synthetic Procedures and Spectral Data of Starting Materials

1,5-Dimethoxy-9,10-anthraquinone

To a stirred solution of 1,5-dihydroxy-9,10-anthraquinone (9.61 g, 40.0 mmol, 1.0 equiv) and K₂CO₃ (15.8 g, 114 mmol, 2.9 equiv) in acetone (50.0 mL) dimethyl sulfate (8.27 mL, 87.2 mmol, 2.2 equiv) was added. The reaction mixture was refluxed for 48 h. After being cooled to room temperature, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (DCM) and 1,5-dimethoxy-9,10-anthraquinone was obtained as yellow needles in 79% yield (8.43 g, 31.4 mmol). The spectroscopic data is in accordance with the literature¹.

¹H NMR (300 MHz, CDCl₃) δ 8.01–7.78 (m, 2H), 7.77–7.51 (m, 2H), 7.38–7.09 (m, 2H), 4.13–3.82 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 182.8, 159.8, 137.5, 135.1, 120.9, 119.8, 116.8, 56.6.

1,5-Bis(dimethoxy)anthracene (1b)

This compound 1b was synthesized from 1,5-dimethoxy-9,10-anthraquinone following the literature procedure² in 64% yield (1.48 g, 6.21 mmol). The spectroscopic data is in accordance with the literature.

¹H NMR (300 MHz, CDCl₃) δ 8.79 (s, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 7.3 Hz, 2H), 4.08 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 155.5, 132.3, 125.3, 121.3, 120.6, 102.1, 55.7.

1,5-Diaminoanthracene

1,5-Diaminoanthracene was synthesized from 1,5-diamino-9,10-anthraquinone following the literature procedure³ in 78% yield (4.50 g, 21.6 mmol). The spectroscopic data is in accordance with the literature.

¹H NMR (300 MHz, DMSO-d₆) δ 8.57 (s, 2H), 7.40–6.97 (m, 4H), 6.61 (d, J = 6.9 Hz, 2H), 5.83 (s, 4H); ¹³C NMR (75 MHz, DMSO-d₆) δ 144.2, 131.3, 125.8, 123.0, 120.5, 116.0, 104.7.
1,5-Bis(N,N-dimethylamino)anthracene (1c)

1,5-Diaminoanthracene (4.00 g, 19.2 mmol, 1.0 equiv) and methyl iodide (12.0 mL, 192 mmol, 10 equiv) were dissolved in dry THF (200 mL) under a nitrogen atmosphere. The mixture was cooled to 0 °C and a 60% dispersion of NaH in mineral oil (7.68 g, 192 mmol, 10 equiv) was added portionwise. The reaction mixture was stirred at room temperature for 12 h and then refluxed for additional 12 h. The mixture was cooled with an ice/water bath and water was slowly added to it. After the removal of THF under reduced pressure, the resulting mixture was extracted with DCM (3 × 40 mL). The combined extracts were washed with brine, dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The black crude reaction mixture was purified by flash column chromatography (hexanes:DCM = 3:1) to afford the pure product 1c as bright yellow solid in 64% yield (3.20 g, 12.1 mmol).

Mp.: 144–145 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.78 (d, J = 3.5 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.39 (dd, J = 10.4, 5.2 Hz, 2H), 7.02 (d, J = 7.2 Hz, 2H), 3.01 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 150.6, 132.8, 127.5, 125.2, 123.6, 112.6, 45.3; IR (ν/cm⁻¹): 3049, 2981, 2944, 2862, 2832, 2788, 1610, 1543, 1453, 1349, 1189, 1140, 1077, 916, 793, 730; HRMS (ESI-TOF) m/z calculated for C₁₈H₂₁N₂ [MH⁺]: 265.1699 found: 265.1702.

1,5-Bis(dipyrrolidin-1-yl)anthracene (1d)

To a suspension of 1,5-diaminoanthracene (2.00 g, 9.60 mmol, 1.0 equiv) and K₂CO₃ (5.31 g, 38.4 mmol, 4.0 equiv) in dioxane/water (1:1 v/v, 40.0 mL) 1,4-dibromobutane (3.49 mL, 28.8 mmol, 3.0 equiv) was added at room temperature. After heating the mixture under refluxing condition for 24 h, additional 1,4-dibromobutane (3.49 mL, 28.8 mmol, 3.0 equiv) was added. The mixture was refluxed again for 24 h before it was allowed to cool down to room temperature. Cold water was added and the aqueous phase was extracted with DCM (3 × 25 mL). The combined organic phases were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to give rise to a black crude reaction mixture which was purified by flash column chromatography (hexanes:DCM = 7:3 to 1:1) affording the pure product 1d as bright yellow solid in 51% yield. (1.55 g, 4.90 mmol).

Mp.: 194–195 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.74 (s, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.45–7.28 (m, 2H), 6.91 (d, J = 7.3 Hz, 2H), 3.50 (t, J = 6.4 Hz, 8H), 2.27–1.91 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 147.3, 132.4, 127.1, 125.1, 123.9, 122.1, 109.7, 52.8, 25.0;
IR (ν/cm⁻¹): 3067, 2948, 2873, 2821, 1610, 1539, 1453, 1353, 1110, 920, 793, 730; HRMS (ESI-TOF) m/z calculated for C₂₂H₂₅N₂ [MH⁺]: 317.2012, found: 317.2013.

1-Aminoanthracene

![1-Aminoanthracene](image)

1-Aminoanthracene was synthesized from 1-amino-9,10-anthraquinone following the literature procedure in 69% yield (11.3 g, 58.5 mmol). The spectroscopic data is in accordance with the literature.

¹H NMR (300 MHz, CDCl₃) δ 8.40 (s, 2H), 8.06 – 7.95 (m, 2H), 7.52 (dd, J = 8.5, 1.0 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.31 (dd, J = 8.5, 7.1 Hz, 1H), 6.76 (dd, J = 7.1, 1.0 Hz, 1H), 4.29 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 141.9, 132.6, 131.7, 131.0, 128.5, 128.0, 126.7, 125.9, 125.6, 125.2, 123.9, 119.7, 119.4, 107.7.

1-(Pyrrolidine-1-yl)anthracene (1e)

![1-(Pyrrolidine-1-yl)anthracene](image)

To a suspension of 1-aminoanthracene (9.79 g, 50.7 mmol, 1.0 equiv) and K₂CO₃ (14.0 g, 101.3 mmol, 2.0 equiv) in dioxane/water (1:1 v/v, 212 mL) 1,4-dibromobutane (8.97 mL, 76.0 mmol, 1.5 equiv) was added at room temperature. After heating the mixture under reflux condition for 24 h, additional 1,4-dibromobutane (8.97 mL, 76.0 mmol, 1.5 equiv) was added. The mixture was refluxed again for 24 h before it was allowed to cool down to room temperature. Cold water was added and the aqueous phase was extracted with DCM (3 × 40 mL). The combined organic phases were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to give a black crude reaction mixture which was purified by flash column chromatography (hexanes:DCM = 7:3 to 1:1) to afford the pure product 1e as bright yellow solid in 57% yield (7.14 g, 28.9 mmol).

M.p.: 60–61 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.85 (s, 1H), 8.41 (s, 1H), 8.13–7.96 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.54–7.45 (m, 2H), 7.39 (dd, J = 8.4, 7.3 Hz, 1H), 6.95 (d, J = 7.3 Hz, 1H), 3.56–3.44 (m, 4H), 2.17–2.06 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 133.3, 131.4, 130.8, 128.8, 127.7, 126.3, 125.5, 125.0, 123.7, 121.7, 109.9, 52.9, 24.9; IR (ν/cm⁻¹): 3049, 2996, 2967, 2870, 2810, 1613, 1535, 1453, 1394, 1349, 1230, 1129, 887, 749; HRMS (EI-TOF) m/z calculated for C₁₈H₁₇N [M⁺]: 247.1355, found: 247.1350.
2. Supplementary Table 1. Diels-Alder reactions between substituted anthracenes 1b-1e and dienophiles A-C.

![Diagram of Diels-Alder reaction]

| entry[^a] | anthracene | dienophile | product[^b] |
|-----------|------------|------------|-------------|
| 1         | 1b         |            |             |
| 2         | 1c         |            |             |
| 3         | 1d         |            |             |
| 4         | 1e         |            |             |
| 5         | 1b         |            |             |
| 6         | 1c         |            |             |
| 7         | 1d         |            |             |
| 8         | 1e         |            |             |

[^a] anthracene (1b,c, 1.0 equiv) and dienophile (A-C, 1.1 equiv) in toluene (0.5 M) in a sealed tube at 150°C (for details see SI),[^b] Isolated yield,[^c] determined by ^1^H-NMR,[^d] also _exo_-product with _R^1_ = N(CH_2)_4, _R^2_ = H obtained (ratio _endo_/exo = 67:33).
3. Spectral Data of Products

**Dimethyl 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (2aD)**

Following the general procedure, reaction of anthracene (1a) (200 mg, 1.12 mmol, 1.0 equiv) and DMAD (D) (175 mg, 1.23 mmol, 1.1 equiv) afforded after 24 h **2aD** as white solid in 87% yield (314 mg, 0.98 mmol) after purification by flash column chromatography (hexanes:DCM = 1:1). The spectroscopic data is in accordance with the literature.

**1H NMR** (300 MHz, CDCl₃) δ 7.48–7.32 (m, 4H), 7.10–6.94 (m, 4H), 5.48 (s, 2H), 3.79 (s, 6H).

**Syn-dimethyl-1,5-dimethoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (syn-2bA)**

Following the general procedure, reaction of 1,5-bis(dimethoxy)anthracene (1b) (80.0 mg, 0.34 mmol, 1.0 equiv) and dimethyl fumarate (A) (53.0 mg, 0.37 mmol, 1.1 equiv) afforded after 24 h **syn-2bA** as white solid in 95% yield (122 mg, 0.32 mmol) after purification by flash column chromatography (DCM to DCM:EA = 99:1).

**syn-2bA**: Mp.: 162–163 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.10–6.99 (m, 3H), 6.91 (d, J = 7.3 Hz, 1H), 6.68 (d, J = 8.2 Hz, 2H), 5.22–5.17 (m, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.64 (s, 3H), 3.63 (s, 3H), 3.37 (dt, J = 5.5, 1.3 Hz, 2H); **13C NMR** (101 MHz, CDCl₃) δ 173.18, 173.15, 155.1, 154.0, 144.2, 142.5, 129.9, 128.2, 127.2, 127.0, 117.5, 116.6, 109.1, 108.9, 55.7, 55.5, 52.2, 52.1, 47.5, 47.4, 40.0, 39.5; **IR (ν/cm⁻¹)**: 3000, 2952, 2840, 1729, 1587, 1483, 1438, 1263, 1200, 1095, 1021, 909, 782, 730; **HRMS (ESI-TOF) m/z** calculated for C₂₂H₂₂O₆ [MH⁺]: 383.1489, found: 383.1490.

**1,5-Dimethoxy-9,10-dihydro-9,10-[3,4]furanoanthracene-12,14-dione (2bB)**

Following the general procedure, reaction of 1,5-bis(dimethoxy)anthracene (1b) (80.0 mg, 0.34 mmol, 1.0 equiv) and maleic anhydride (B) (36.0 mg, 0.37 mmol, 1.1 equiv) afforded after 2 h **2bB** as white solid in 97% yield (109 mg, 0.32 mmol) after purification by recrystallization from DCM.
Mp.: 263–264 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (ddd, J = 8.3, 7.4, 4.2 Hz, 2H), 7.03 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.75 (ddd, J = 8.4, 0.9 Hz, 2H), 5.33 (dd, J = 17.1, 3.0 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.50–3.41 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 170.6, 155.0, 154.6, 142.8, 128.6, 128.5, 127.6, 127.1, 126.4, 117.9, 117.0, 109.5, 55.9, 55.6, 47.8, 47.7, 38.5, 38.4; IR (v/cm⁻¹): 3011, 2959, 2922, 2840, 1863, 1781, 1587, 1483, 1267, 1215, 1099, 939, 786, 726; HRMS (EI-TOF) m/z calculated for C₂₀H₁₆O₅ [M⁺]: 336.0992, found: 336.0998.

1,5-Dimethoxy-13-phenyl-9,10-dihydro-9,10-[3,4]epipyrraloanthracene-12,14-dione (2bC)

Following the general procedure, reaction of 1,5-bis(dimethoxy)anthracene (1b) (80.0 mg, 0.34 mmol, 1.0 equiv) and N-phenylmaleimide (C) (64.0 mg, 0.37 mmol, 1.1 equiv) afforded 2bC in 2 h as white solid in 99% yield (137 mg, 0.33 mmol) after purification by flash column chromatography (DCM:EA = 99:1).

Mp.: 274–275 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.27 (m, 3H), 7.16 (ddd, J = 8.1, 7.3, 4.6 Hz, 2H), 7.08 (d, J = 7.3 Hz, 1H), 7.01 (d, J = 7.3 Hz, 1H), 6.77 (ddd, J = 8.2, 0.9 Hz, 2H), 6.60–6.52 (m, 2H), 5.42 (d, J = 3.3 Hz, 1H), 5.38 (d, J = 3.3 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.32 (dq, J = 8.4, 3.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 176.3, 176.1, 155.1, 154.6, 143.5, 140.8, 131.7, 129.3, 129.1, 128.7, 127.8, 127.5, 127.1, 126.6, 118.0, 117.0, 109.8, 109.2, 56.1, 55.6, 46.9, 46.7, 38.8; IR (v/cm⁻¹): 3067, 2996, 2937, 2899, 2836, 2255, 1777, 1707, 1479, 1382, 1263, 1095, 909, 723; HRMS (ESI-TOF) m/z calculated for C₂₆H₂₁NO₄ [MH⁺]: 412.1543, found: 412.1547.

Dimethyl 1,5-dimethoxy-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (2bD)

Following the general procedure, reaction of 1,5-bis(dimethoxy)anthracene (1b) (300 mg, 1.26 mmol, 1.0 equiv) and DMAD (D) (197 mg, 1.38 mmol, 1.1 equiv) afforded after 48 h 2bD as white solid in 73% yield (351 mg, 0.92 mmol) and 3bD as white solid in 6% yield (29.0 mg, 0.08 mmol) after purification by flash column chromatography (hexanes:DCM = 1:1).

2bD: Mp.: 238–239 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.07 (d, J = 7.2 Hz, 2H), 7.02–6.91 (m, 2H), 6.60 (d, J = 8.0 Hz, 2H), 5.93 (s, 2H), 3.83 (s, 6H), 3.79 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 166.1, 154.6, 147.8, 146.3, 131.9, 126.3, 116.8, 108.7, 55.8, 52.4, 45.9; IR (v/cm⁻¹):
HRMS (ESI-TOF) m/z calculated for C_{22}H_{21}O_6 [MH^+] : 381.1333, found: 381.1337.

3bD: Mp.: 143–144 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 8.09 (s, 1H), 7.81 (s, 1H), 7.45–7.29 (m, 2H), 7.16 (d, \( J = 7.5, 1.6 \) Hz, 1H), 7.02 (dd, \( J = 7.4, 6.1 \) Hz, 1H), 6.81 (dd, \( J = 5.9, 2.8 \) Hz, 1H), 5.44 (dd, \( J = 6.1, 1.4 \) Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 3.83 (s, 3H), 3.73 (s, 3H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 166.5, 163.3, 155.2, 141.7, 139.0, 138.2, 135.6, 132.0, 126.1, 122.8, 120.5, 119.1, 115.6, 104.7, 89.3, 55.6, 52.5, 46.9; IR (\( \nu/cm^-1 \)) : 3075, 3008, 2952, 2840, 1736, 1640, 1595, 1431, 1259, 1103, 902, 793, 708; HRMS (ESI-TOF) m/z calculated for C_{22}H_{21}O_6 [MH^+] : 381.1338.

Syn-dimethyl 1,5-bis(dimethylamino)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (syn-2cA)

Anti-dimethyl 1,5-bis(dimethylamino)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (anti-2cA)

Following the general procedure, reaction of 1,5-bis(N,N-dimethylamino)anthracene (1c) (200 mg, 0.76 mmol, 1.0 equiv) and dimethyl fumarate (A) (118 mg, 0.83 mmol, 1.1 equiv) afforded after 24 h syn-2cA as white solid in 40% yield (125 mg, 0.31 mmol) and anti-2cA as white solid in 28% yield (87.0 mg, 0.21 mmol) after purification by flash column chromatography (hexanes:EA = 4:1).

syn-2cA: Mp.: 159–160 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.19–6.96 (m, 4H), 6.96–6.68 (m, 2H), 5.21 (s, 2H), 3.60 (s, 6H), 3.38 (s, 2H), 2.73 (s, 12H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 173.1, 150.4, 143.0, 134.7, 126.8, 118.5, 116.5, 52.0, 47.5, 45.1, 42.6; IR (\( \nu/cm^-1 \)) : 2981, 2940, 2858, 2776, 1729, 1479, 1435, 1304, 1174, 1010, 883, 793, 745; HRMS (ESI-TOF) m/z calculated for C_{24}H_{29}N_{2}O_{4} [MH^+] : 409.2122, found: 409.2125.

anti-2cA: Mp.: 139–140 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.15–6.96 (m, 4H), 6.87 (d, \( J = 7.6 \) Hz, 2H), 5.18 (s, 2H), 3.67 (s, 6H), 3.39 (s, 2H), 2.79 (s, 12H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 173.2, 149.2, 141.5, 135.9, 126.5, 119.4, 116.1, 52.2, 47.5, 45.0, 42.1; IR (\( \nu/cm^-1 \)) : 3056, 2985, 2948, 2825, 2780, 1729, 1584, 1479, 1435, 1304, 1174, 1010, 883, 793, 749; HRMS (ESI-TOF) m/z calculated for C_{24}H_{29}N_{2}O_{4} [MH^+] : 409.2122, found: 409.2127.

1,5-Bis(dimethylamino)-9,10-dihydro-9,10-[3,4]furanoanthracene-12,14-dione (2cB)

Following the general procedure, reaction of 1,5-bis(N,N-dimethylamino)anthracene (1c) (100 mg, 0.38 mmol, 1.0 equiv) and maleic anhydride (B) (41.0 mg, 0.42 mmol, 1.1 equiv)
afforded after 0.5 h \(2cB\) as white solid in 88% yield (120 mg, 0.33 mmol) after purification by recrystallization from DCM.

**Mp.**: 265–266 °C; \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.21–7.00 (m, 4H), 7.00–6.84 (m, 2H), 5.37 (d, \(J = 3.0\) Hz, 1H), 5.25 (d, \(J = 2.8\) Hz, 1H), 3.57–3.30 (m, 2H), 2.77 (s, 6H), 2.74 (s, 6H); \(^13C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.9, 170.4, 150.5, 150.1, 141.8, 138.8, 134.6, 132.9, 128.0, 127.3, 119.8, 118.6, 117.9, 116.9, 47.8, 45.0, 44.9, 41.2, 40.8; IR (\(\nu/cm\^-1\)): 2993, 2862, 2832, 2784, 1863, 1777, 1580, 1483, 1319, 1140, 1080, 924, 756; HRMS (EI-TOF) \(m/z\) calculated for C\(_{22}\)H\(_{22}\)N\(_2\)O\(_3\) [\(M^+\)]: 362.1630, found: 362.1627.

**1,5-Bis(dimethylamino)-13-phenyl-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (2cC)**

Following the general procedure, reaction of 1,5-bis(N,N-dimethylamino)anthracene (1c) (132 mg, 0.50 mmol, 1.0 equiv) and N-phenylmaleimide (C) (95.2 mg, 0.55 mmol, 1.1 equiv) afforded 2cC in 0.5 h as white solid in 98% yield (219 mg, 0.49 mmol) after purification by flash column chromatography (DCM:EA = 99:1).

**Mp.**: 209–210 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43–7.37 (m, 3H), 7.25 (dd, \(J = 7.0, 3.2\) Hz, 3H), 7.17 (dd, \(J = 7.3, 1.1\) Hz, 1H), 7.07 (dd, \(J = 8.1, 1.1\) Hz, 1H), 7.03 (dd, \(J = 6.4, 2.8\) Hz, 1H), 6.68–6.60 (m, 2H), 5.54 (d, \(J = 3.1\) Hz, 1H), 5.41 (d, \(J = 3.0\) Hz, 1H), 3.45–3.37 (m, 2H), 2.90 (s, 6H), 2.84 (s, 6H); \(^13C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.3, 175.9, 150.6, 150.1, 142.6, 139.6, 135.2, 133.5, 131.7, 129.0, 128.6, 127.3, 126.9, 126.6, 119.8, 118.6, 117.2, 116.5, 47.0, 46.8, 45.1, 44.9, 41.5, 41.2; IR (\(\nu/cm\^-1\)): 3063, 2985, 2944, 2862, 2784, 2251, 1777, 1710, 1584, 1483, 1382, 1319, 1189, 909, 790, 726; HRMS (ESI-TOF) \(m/z\) calculated for C\(_{28}\)H\(_{27}\)N\(_3\)O\(_2\) [\(MH^+\)]: 438.2176, found: 438.2181.

**Dimethyl 1,5-bis(dimethylamino)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (2cD)**

Following the general procedure, reaction of 1,5-bis(N,N-dimethylamino)anthracene (1c) (200 mg, 0.76 mmol, 1.0 equiv) and DMAD (D) (118 mg, 0.83 mmol, 1.1 equiv) afforded after 24 h \(2cD\) as white solid in 20% yield (61 mg, 0.15 mmol) and \(3cD\) as white solid in 58% yield (178 mg, 0.44 mmol) after purification by flash column chromatography (DCM:EA = 24:1).
2cD: Mp.: 182–183 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.14 (d, J = 7.1 Hz, 2H), 6.95 (t, J = 7.7 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 5.95 (s, 2H), 3.79 (s, 6H), 2.77 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 166.4, 150.0, 147.8, 145.3, 137.8, 125.8, 118.8, 115.8, 52.4, 48.5, 45.1; IR (v/cm⁻¹): 3056, 2989, 2940, 2870, 2836, 2791, 1736, 1714, 1636, 1587, 1476, 1438, 1271, 1066, 939, 782; HRMS (ESI-TOF) m/z calculated for C₂₄H₂₇N₂O₄ [MH⁺]: 407.1965, found: 407.1966.

3cD: Mp.: 155–156 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.03 (s, 1H), 7.86 (s, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.08–7.04 (m, 3H), 5.40 (t, J = 3.9 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 2.90 (s, 6H), 2.87 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 168.5, 163.7, 154.2, 150.5, 142.7, 142.1, 141.7, 139.0, 136.5, 132.2, 126.0, 123.5, 122.74, 117.6, 114.8, 78.6, 52.5, 47.7, 45.3, 42.4; IR (v/cm⁻¹): 2996, 2940, 2899, 2829, 1714, 1632, 1587, 1435, 1326, 1259, 1215, 1058, 902, 745, 715; HRMS (ESI-TOF) m/z calculated for C₂₄H₂₇N₂O₄ [MH⁺]: 407.1965, found: 407.1966.

**Syn**-dimethyl 1,5-di(pyrrrolidin-1-yl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (**syn-2dA**)

*Anti*-dimethyl 1,5-di(pyrrrolidin-1-yl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (**anti-2dA**)

Following the general procedure, reaction of 1,5-bis(dipyrrrolidin-1-yl)anthracene (**1d**) (200 mg, 0.63 mmol, 1.0 equiv) and dimethyl fumarate (**A**) (99.0 mg, 0.70 mmol, 1.1 equiv) afforded after 24 h **syn-2dA** as white solid in 55% yield (160 mg, 0.35 mmol) and **anti-2dA** as white solid in 31% yield (89.0 mg, 0.19 mmol) after purification by flash column chromatography (DCM:EA = 9:1).

**syn-2dA**: Mp.: 188–189 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.03 (t, J = 7.7 Hz, 2H), 6.91 (d, J = 7.0 Hz, 2H), 6.63 (d, J = 8.2 Hz, 2H), 5.29 (s, 2H), 3.71–3.47 (m, 10H), 3.42 (s, 2H), 3.23–3.21 (brs, 4H), 2.06–2.05 (brs, 4H), 1.93–1.89 (brs, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 173.3, 146.3, 144.2, 128.6, 126.8, 114.9, 113.4, 51.8, 51.8, 47.5, 44.2, 25.7; IR (v/cm⁻¹): 2959, 2866, 1729, 1587, 1476, 1304, 1177, 1088, 1013, 879, 786; HRMS (ESI-TOF) m/z calculated for C₂₈H₃₃N₂O₄ [MH⁺]: 461.2435, found: 461.2441.

**anti-2dA**: Mp.: 208–209 °C; ¹H NMR (300 MHz, CDCl₃) δ 6.98 (t, J = 7.7 Hz, 2H), 6.83 (d, J = 7.0 Hz, 2H), 6.68 (d, J = 8.0 Hz, 2H), 5.18 (s, 2H), 3.66 (s, 6H), 3.53–3.17 (m, 10H), 2.00–2.00 (brs, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 173.3, 145.9, 142.3, 131.3, 126.3, 116.6, 113.6, 52.2, 52.0, 47.7, 43.6, 25.5; IR (v/cm⁻¹): 3060, 3004, 2948, 2851, 1729, 1580, 1476, 1345, 1185, 1092, 775; HRMS (ESI-TOF) m/z calculated for C₂₈H₃₃N₂O₄ [MH⁺]: 461.2435, found: 461.2437.
Following the general procedure, reaction of 1,5-bis(dipyrrolidin-1-yl)anthracene (1d) (100 mg, 0.32 mmol, 1.0 equiv) and maleic anhydride (B) (34.0 mg, 0.35 mmol, 1.5 equiv) afforded after 0.5 h 2dB as white solid in 75% yield (98.0 mg, 0.24 mmol) after purification by recrystallization from DCM.

Mp.: 220–221 °C; 1H NMR (400 MHz, DMSO-d6) δ 7.03–6.97 (m, 3H), 6.75 (d, J = 7.0 Hz, 1H), 6.69 (dd, J = 6.4, 3.0 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 5.31 (d, J = 3.1 Hz, 1H), 5.01 (d, J = 2.7 Hz, 1H), 3.64–3.53 (m, 2H), 3.51–3.39 (m, 2H), 3.36–3.28 (m, 2H), 3.28–3.12 (m, 4H), 2.03–1.78 (m, 8H); 13C NMR (101 MHz, DMSO-d6) δ 171.8, 171.7, 146.1, 145.8, 143.3, 140.6, 129.2, 127.2, 126.8, 126.1, 115.8, 115.4, 114.0, 113.8, 51.6, 51.3, 48.0, 47.7, 42.2, 41.4, 25.2, 25.0; IR (ν/cm⁻¹): 2955, 2862, 1707, 1584, 1476, 1423, 1312, 1222, 1088, 920, 849; HRMS (EI-TOF) m/z calculated for C26H26N2O3 [M⁺]: 414.1943, found: 414.1939.

13-Phenyl-1,5-di(pyrrolidin-1-yl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (2dC)

Following the general procedure, reaction of 1,5-bis(dipyrrolidin-1-yl)anthracene (1d) (158 mg, 0.50 mmol, 1.0 equiv) and N-phenylmaleimide (C) (95.2 mg, 0.55 mmol, 1.1 equiv) afforded after 0.5 h 2dC as brownish solid in 92% yield (223 mg, 0.46 mmol) after purification by flash column chromatography (DCM:EA = 99:1).

Mp.: 225–226 °C; 1H NMR (400 MHz, CDCl3) δ 7.27 (m, 3H), 7.03 (dt, J = 9.5, 7.6 Hz, 2H), 6.94 (d, J = 7.2 Hz, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.64 (d, J = 8.3 Hz, 1H), 6.60–6.51 (m, 2H), 5.44 (d, J = 2.7 Hz, 1H), 5.22 (d, J = 2.3 Hz, 1H), 3.52 (q, J = 7.8 Hz, 2H), 3.46–3.38 (m, 2H), 3.31–3.17 (m, 6H), 1.97 (m, 6H), 1.90–1.77 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 176.6, 176.4, 146.7, 146.4, 143.7, 140.5, 131.8, 130.4, 129.0, 128.5, 127.2, 126.8, 126.69, 126.65, 115.8, 115.6, 113.94, 113.91, 52.0, 51.8, 47.1, 47.0, 43.2, 42.8, 25.6, 25.4; IR (ν/cm⁻¹): 3063, 2967, 2870, 2825, 2825, 2251, 1774, 1710, 1580, 1476, 1382, 1356, 1185, 909, 726; HRMS (ESI-TOF) m/z calculated for C32H31N3O2 [MH⁺]: 490.2489, found: 490.2496.
Dimethyl 1,5-di(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3dD)

Following the general procedure, reaction of 1,5-bis(dipyrrolidin-1-yl)anthracene (1d) (200 mg, 0.63 mmol, 1.0 equiv) and DMAD (D) (99.0 mg, 0.70 mmol, 1.1 equiv) afforded after 24 h 3dD as white solid in 78% yield (226 mg, 0.49 mmol) after purification by flash column chromatography (DCM:EA = 19:1).

Mp.: 199–200 °C; 1H NMR (300 MHz, CDCl₃) δ 7.98 (s, 1H), 7.87 (s, 1H), 7.39–7.28 (m, 2H), 7.08–7.04 (m, 1H), 7.01–6.93 (m, 2H), 5.40 (dd, J = 6.0, 1.6 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.53–3.29 (m, 6H), 3.29–3.16 (m, 2H), 2.03 (brs, 8H); 13C NMR (75 MHz, CDCl₃) δ 168.1, 163.8, 154.9, 147.4, 142.3, 142.0, 140.6, 139.3, 132.4, 125.9, 125.5, 122.6, 122.1, 118.1, 112.7, 79.0, 52.8, 52.7, 52.4, 51.4, 47.8, 26.3, 24.7; IR (ν/cm⁻¹): 2952, 2870, 2840, 1729, 1625, 1591, 1453, 1319, 1252, 1107, 1062, 749; HRMS (ESI-TOF) m/z calculated for C₂₈H₃₁N₂O₄ [MH⁺]: 459.2278, found: 459.2280.

Methyl 1,5-di(pyrrolidin-1-yl)-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate (2dE)

Methyl 1,5-di(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethenoanthracene-2-carboxylate (3dE)

Following the general procedure, reaction of 1,5-bis(dipyrrolidin-1-yl)anthracene (1d) (200 mg, 0.63 mmol, 1.0 equiv) and methyl propiolate (E) (62.0 µL, 0.70 mmol, 1.1 equiv) afforded after 24 h 2dE as white solid in 14% yield (35.0 mg, 0.09 mmol) and 3cE as white solid in 56% yield (142 mg, 0.35 mmol) after purification by flash column chromatography (DCM:EA = 19:1 to 3:2).

2dE: Mp.: 118–119 °C; 1H NMR (400 MHz, CDCl₃) δ 7.87 (dd, J = 6.3, 1.9 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.91–6.83 (m, 3H), 6.55 (dd, J = 8.3, 1.0 Hz, 1H), 6.51 (d, J = 8.2 Hz, 1H), 6.20 (d, J = 1.9 Hz, 1H), 5.69 (d, J = 6.4 Hz, 1H), 3.70 (s, 3H), 3.49–3.38 (m, 6H), 3.31–3.24 (m, 2H), 2.03–1.95 (m, 8H); 13C NMR (101 MHz, CDCl₃) δ 165.5, 150.8, 147.7, 146.6, 146.2, 146.0, 144.9, 133.58 132.9, 125.4, 125.3, 116.0, 114.9, 112.7, 52.8, 52.7, 52.4, 51.4, 47.8, 26.3, 24.7; IR (ν/cm⁻¹): 3034, 2944, 2866, 1710, 1625, 1580, 1461, 1330, 1237, 1092, 730; HRMS (ESI-TOF) m/z calculated for C₂₆H₂₈N₂O₂ [MH⁺]: 401.2224, found: 401.2230.

3dE: Mp.: 201–202 °C; 1H NMR (400 MHz, CDCl₃) δ 7.89 (s, 2H), 7.43 (d, J = 6.3 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 3.8 Hz, 2H), 6.96 (d, J = 7.5 Hz, 1H), 4.90 (dt, J = 7.2, 3.9 Hz, 1H), 3.70 (s, 3H), 3.37–3.21 (m, 8H), 2.08–1.98 (m, 8H); 13C NMR (101 MHz, CDCl₃) δ 166.7, 148.7, 147.4, 146.0, 143.8, 141.2, 139.6, 138.5, 132.5,
125.7, 125.4, 122.2, 121.7, 117.5, 112.5, 52.8, 52.0, 51.3, 48.0, 26.0, 24.7; IR (v/cm\(^{-1}\)):
2948, 2866, 2817, 1714, 1621, 1580, 1457, 1364, 1289, 1230, 1073, 894, 738; HRMS (ESI-TOF) m/z calculated for C\(_{26}H_{38}N_2O_2\) [MH\(^+\)]: 401.2224, found: 401.2232.

**Methyl 12-phenyl-1,5-di(pyrrrolidin-1-yl)-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate (2dF)**

![Image of 2dF](image_url)

Following the general procedure, reaction of 1,5-bis(dipyrrolidin-1-yl)anthracene (1d) (200 mg, 0.63 mmol, 1.0 equiv) and methyl phenylpropionate (F) (506 mg, 3.16 mmol, 5.0 equiv) afforded after 72 h 2dF as white solid in 23% yield (69.0 mg, 0.14 mmol) after purification by flash column chromatography (hexanes:DCM = 2:3).

**Mp.**: 188–189 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.32 (d, \(J = 5.3\) Hz, 5H), 7.04 (d, \(J = 6.5\) Hz, 1H), 6.68–6.76 (m, 3H), 6.58 (d, \(J = 8.0\) Hz, 2H), 6.34 (s, 1H), 5.81 (s, 1H), 3.70–3.42 (m, 7H), 3.42–3.03 (m, 4H), 2.59–1.53 (m, 8H); \(^1^C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.5, 162.1, 147.6, 146.6, 146.2, 145.8, 138.8, 136.9, 133.0, 132.3, 127.9, 127.7 (2C), 125.6, 125.5, 115.4, 114.5, 112.6, 112.5, 57.6, 52.1, 51.8, 51.4, 49.6, 25.9, 25.6; IR (v/cm\(^{-1}\)):
3049, 2948, 2836, 1714, 1621, 1584, 1476, 1334, 1192, 1088, 775; HRMS (ESI-TOF) m/z calculated for C\(_{32}H_{53}N_2O_2\) [MH\(^+\)] 477.2537, found: 477.2538.

**Syn-dimethyl 1-(pyrrrolidin-1-yl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (syn-2eA)**

**Anti-dimethyl 1-(pyrrrolidin-1-yl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (anti-2eA)**

Following the general procedure, reaction of 1-(pyrrolidine-1-yl)anthracene (1e) (200 mg, 0.81 mmol, 1.0 equiv) and dimethyl fumarate (A) (128 mg, 0.89 mmol, 1.1 equiv) afforded after 24 h syn-2eA as white solid in 46% yield (147 mg, 0.37 mmol) and anti-2eA as white solid in 50% yield (157 mg, 0.40 mmol) after purification by flash column chromatography (DCM to DCM:EA = 19:1).

**syn-2eA: Mp.**: 138–139 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.52–7.47 (m, 1H), 7.42–7.39 (m, 1H), 7.31–7.22 (m, 2H), 7.16 (dd, \(J = 8.2, 7.2\) Hz, 1H), 7.03 (d, \(J = 7.1\) Hz, 1H), 6.78 (dd, \(J = 8.3, 1.0\) Hz, 1H), 5.46 (d, \(J = 2.9\) Hz, 1H), 4.84 (d, \(J = 2.8\) Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.69–3.60 (m, 3H), 3.51 (dd, \(J = 4.7, 2.9\) Hz, 1H), 3.32 (td, \(J = 8.0, 4.6\) Hz, 2H), 2.25–2.13 (m, 2H), 2.10–1.98 (m, 2H); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 173.1, 173.0, 146.3, 142.5, 140.8, 128.6, 126.9, 126.3, 126.2, 124.7, 123.2, 115.5, 113.7, 52.2, 51.9, 51.8, 47.8, 47.6, 47.4, 43.5,
25.7; **IR** (v/cm\(^{-1}\)): 3052, 3022, 2952, 2870, 1729, 1580, 1479, 1435, 1356, 1259, 1192, 1006, 868, 771; **HRMS** (ESI-TOF) \(m/z\) calculated for \(C_{24}H_{25}NO_4\) [\(MH^+\)]: 392.1856, found: 392.1858.

**anti-2eA**: **Mp.**: 106–107 °C; **\(^{1}H\) NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.51–7.46 (m, 1H), 7.44–7.41 (m, 1H), 7.30–7.22 (m, 2H), 7.13 (dd, \(J = 8.2, 7.2\) Hz, 1H), 6.96 (d, \(J = 7.1\) Hz, 1H), 6.84 (dd, \(J = 8.3, 1.0\) Hz, 1H), 5.37 (d, \(J = 2.6\) Hz, 1H), 4.85 (d, \(J = 2.6\) Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.61 (dd, \(J = 5.0, 2.6\) Hz, 1H), 3.58–3.43 (m, 5H), 2.21–2.09 (m, 4H); **\(^{13}C\) NMR** (101 MHz, CDCl\(_3\)) \(\delta\) 173.0, 172.9, 146.0, 142.6, 141.8, 140.7, 130.9, 126.4, 126.2, 126.1, 124.3, 123.6, 116.8, 113.8, 52.2, 52.0, 47.9, 47.6, 47.3, 42.9, 25.4; **IR** (v/cm\(^{-1}\)): 3019, 2955, 2577, 2814, 1729, 1587, 1476, 1435, 1304, 1177, 1010, 872, 782, 738; **HRMS** (ESI-TOF) \(m/z\) calculated for \(C_{24}H_{25}NO_4\) [\(MH^+\)]: 392.1856, found: 392.1863.

**Exo-1-(pyrrolidin-1-yl)-9,10-dihydro-9,10-[3,4]furoanthracene-12,14-dione (exo-2eB)***

**Endo-1-(pyrrolidin-1-yl)-9,10-dihydro-9,10-[3,4]furoanthracene-12,14-dione (endo-2eB)**

Following the general procedure, reaction of 1-(pyrrolidine-1-yl)anthracene (1e) (200 mg, 0.81 mmol, 1.0 equiv) and maleic anhydride (B) (128 mg, 0.89 mmol, 1.1 equiv) afforded after 0.5 h a crude mixture of *exo-2eB* and *endo-2eB* (NMR yield > 99%, ratio *endo-2eB*/*exo-2eB* = 67:33) as white solid. During purification by flash column chromatography (DCM to DCM:EA = 19:1) decomposition of both products was observed and only *endo-2eB* could be isolated as white solid in 34% yield (94.0 mg, 0.27 mmol).

**endo-2eB**: **Mp.**: 218–219 °C; **\(^{1}H\) NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (dt, \(J = 8.5, 4.0\) Hz, 2H), 7.06 (t, \(J = 7.7\) Hz, 1H), 6.93 (d, \(J = 7.2\) Hz, 1H), 6.74 (d, \(J = 8.2\) Hz, 1H), 5.29 (d, \(J = 3.1\) Hz, 1H), 4.77 (d, \(J = 3.2\) Hz, 1H), 3.57–3.37 (m, 4H), 3.26 (dt, \(J = 8.6, 5.1\) Hz, 2H), 2.08–1.92 (m, 4H); **\(^{13}C\) NMR** (101 MHz, CDCl\(_3\)) \(\delta\) 170.9, 170.8, 146.7, 142.4, 138.6, 129.3, 127.6, 127.4, 125.2, 124.8, 116.3, 114.6, 52.2, 48.1, 48.0, 46.1, 42.1, 25.5; **IR** (v/cm\(^{-1}\)): 3026, 2970, 2825, 1859, 1774, 1580, 1476, 1356, 1222, 1077, 928, 756; **HRMS** (EI-TOF) \(m/z\) calculated for \(C_{22}H_{19}NO_3\) [\(M^+\)]: 345.1359, found: 345.1353.
Exo-13-phenyl-4-(pyrrolidin-1-yl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (exo-2eC)

Endo-13-phenyl-4-(pyrrolidin-1-yl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (endo-2eC)

Following the general procedure, reaction of 1-(pyrrolidine-1-yl)anthracene (1e) (200 mg, 0.81 mmol, 1.0 equiv) and N-phenylmaleimide (C) (154 mg, 0.89 mmol, 1.1 equiv) afforded after 0.5 h a mixture of exo-2eC and endo-2eC (ratio endo-2eC/exo-2eC = 67:33) as white solid after purification by flash column chromatography (DCM:EA = 99:1) in 95% yield (324 mg, 0.77 mmol).

Characteristic signals of minor compound exo-2eC are marked in the proton NMR.

exo-2eC and endo-2eC: Mp.: 177–178 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50–7.13 (m, 13H), 7.05 (q, $J$ = 7.5 Hz, 2H), 6.96 (d, $J$ = 7.2 Hz, 1H), 6.81$^{\text{minor}}$ (t, $J$ = 3.7 Hz, 2H), 6.74 (d, $J$ = 8.2 Hz, 1H), 6.67$^{\text{minor}}$ (d, $J$ = 8.3 Hz, 1H), 6.64–6.54 (m, 1H), 6.49 (dd, $J$ = 7.0, 2.7 Hz, 2H), 5.51$^{\text{minor}}$ (d, $J$ = 3.2 Hz, 1H), 5.32 (d, $J$ = 3.1 Hz, 1H), 4.82 (d, $J$ = 3.3 Hz, 1H), 4.80$^{\text{minor}}$ (d, $J$ = 3.1 Hz, 1H), 3.54 (q, $J$ = 7.8 Hz, 1H), 3.44 (q, $J$ = 6.9 Hz, 2H), 3.40–3.15 (m, 6H), 2.06–1.92 (m, 5H), 1.87 (td, $J$ = 10.6, 8.3, 5.7 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.47, 176.42, 176.3, 176.1, 146.7, 146.5, 143.1, 141.9, 140.0, 139.1, 134.2, 131.7, 131.5, 130.0, 129.1, 129.09, 129.05, 128.7, 128.6, 127.9, 127.3, 127.05, 127.00, 126.66, 126.60, 126.5, 126.4, 126.0, 125.1, 124.7, 124.3, 123.6, 116.3, 116.2, 114.5, 114.1, 52.1, 51.8, 47.2, 47.1, 47.0, 46.5, 46.4, 42.4, 42.1, 25.6, 25.4; IR (ν/cm$^{-1}$): 3067, 2967, 2870, 2825, 2251, 1774, 1707, 1587, 1498, 1382, 1185, 909, 723; HRMS (ESI-TOF) m/z calculated for C$_{28}$H$_{24}$N$_2$O$_2$ [MH$^+$]: 421.1911, found: 421.1913 and 421.1916.

Dimethyl 1-(pyrrolidine-1-yl)-1,4-dihydro-1,4-ethanoanthracene-2,3-dicarboxylate (3eD)

Following the general procedure, reaction of 1-(pyrrolidine-1-yl)anthracene (1e) (282 mg, 1.14 mmol, 1.0 equiv) and DMAD (D) (178 mg, 1.25 mmol, 1.1 equiv) afforded after 24 h 3eD as white solid in 90% yield (403 mg, 1.03 mmol) after purification by flash column chromatography (DCM:EA = 19:1).

Mp.: 159–160 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (s, 1H), 7.77–7.68 (m, 2H), 7.63 (s, 1H), 7.45–7.39 (m, 2H), 7.07–6.99 (m, 2H), 5.38 (dd, $J$ = 5.9, 1.9 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.39 (dt, $J$ = 10.1, 6.2, 3.0 Hz, 4H), 2.06–1.98 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.1, 163.8, 155.2, 142.6, 142.0, 141.8, 139.5, 139.0, 131.05, 131.02, 128.3, 127.2, 126.2, 125.9,
Methyl 4-(pyrrolidin-1-yl)-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate (syn-2eE)

Following the general procedure, reaction of 1-(pyrrolidine-1-yl)anthracene (1e) (200 mg, 0.81 mmol, 1.0 equiv) and methyl propiolate (E) (79.0 µL, 0.89 mmol, 1.1 equiv) afforded after 24 h a mixture of syn-2eE and anti-2eE (ratio: syn-2eE/anti-2eE = 55:45) as a white solid in 25% yield (67.0 mg, 0.20 mmol) and 3eE as a white solid in 72% yield (193 mg, 0.58 mmol) after purification by flash column chromatography (DCM:EA = 19:1 to 3:2).

Characteristic signals of minor compound anti-2eE are marked in the proton NMR.

**syn-2eE and anti-2eE: Mp.:** 64–65 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (dd, $J = 6.2, 1.8$ Hz, 1H), 7.87$^{\text{minor}}$ (dd, $J = 6.3, 1.8$ Hz, 1H), 7.42–7.31 (m, 4H), 7.00 (qd, $J = 5.3, 4.7, 2.3$ Hz, 5H), 6.94–6.86 (m, 3H), 6.60$^{\text{minor}}$ (d, $J = 8.1$ Hz, 1H), 6.54 (quin, $J = 3.5$ Hz, 1H), 6.27 (d, $J = 1.8$ Hz, 1H), 5.77$^{\text{minor}}$ (d, $J = 6.3$ Hz, 1H), 5.66$^{\text{minor}}$ (d, $J = 1.9$ Hz, 1H), 5.21 (d, $J = 6.2$ Hz, 1H), 3.74 (d, $J = 1.5$ Hz, 6H), 3.51–3.46 (m, 4H), 3.45–3.38$^{\text{minor}}$ (m, 2H), 3.29$^{\text{minor}}$ (dq, $J = 9.1, 5.4, 4.2$ Hz, 2H), 2.01 (qt, $J = 7.2, 3.4$ Hz, 8H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.5, 165.3, 150.4, 149.7, 147.2, 146.4, 146.3, 146.04, 146.02, 145.7, 145.14, 145.13, 144.5, 144.3, 134.7, 133.0, 132.4, 131.3, 125.58, 125.51, 124.95, 124.94, 124.8, 124.7, 123.7, 123.4, 123.3, 123.1, 116.4, 115.3, 112.9, 112.7, 52.6, 52.1, 51.9, 51.84, 51.82, 51.1, 48.1, 47.1, 25.7, 25.4; IR (v/cm$^{-1}$): 3063, 2948, 2870, 1701, 1617, 1587, 1435, 1330, 1244, 1214, 1066, 946, 745; HRMS (ESI-TOF) m/z calculated for C$_{22}$H$_{21}$NO$_2$ [MH$^+$]: 332.1645, found: 332.1651 and 332.1649.

**3eE: Mp.:** 84–85 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1H), 7.78–7.73 (m, 1H), 7.69–7.64 (m, 1H), 7.52 (s, 1H), 7.44–7.38 (m, 3H), 7.03–6.97 (m, 2H), 4.88 (dt, $J = 6.4, 3.8$ Hz, 1H), 3.71 (s, 3H), 3.38–3.23 (m, 4H), 2.04 (dt, $J = 12.9, 7.6$, 6.7, 3.2 Hz, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.7, 148.4, 146.1, 144.1, 142.2, 139.6, 138.4, 131.1, 130.8, 128.2, 127.1, 125.9, 125.8, 121.2, 120.5, 52.0, 51.4, 47.5, 26.0; IR (v/cm$^{-1}$): 3056, 2948, 2866, 1714, 1621, 1580, 1431, 1289, 1226, 1196, 1077, 883, 745; HRMS (ESI-TOF) m/z calculated for C$_{22}$H$_{21}$NO$_2$ [MH$^+$]: 332.1645, found: 332.1650.
1-Phenyl-3-(4-(pyrrolidin-1-yl)anthracen-1-yl)pyrrolidine-2,5-dione (8)

A sealed tube was charged with 1-(pyrrolidine-1-yl)anthracene (1e) (100 mg, 0.40 mmol, 1.0 equiv), N-phenylmaleimide (C) (77.0 mg, 0.44 mmol, 1.1 equiv), AlCl₃ (162 mg, 1.21 mmol, 3.0 equiv) and CHCl₃ (5.00 mL). The mixture was dispersed in an ultrasonic bath for 1 min and afterwards stirred at room temperature for 3 h. The reaction was quenched with water (10 mL) and the aqueous phase was extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. After purification by flash column chromatography (hexanes:DCM = 1:2 to DCM) product 8 was obtained as a brown solid in 62% yield (106 mg, 0.25 mmol).

Mp.: 94–95 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.88 (s, 1H), 8.33 (s, 1H), 8.06–7.96 (m, 2H), 7.56–7.44 (m, 7H), 7.28 (d, J = 7.7 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 4.95 (dd, J = 9.7, 4.8 Hz, 1H), 3.59 (dd, J = 18.5, 9.7 Hz, 1H), 3.46 (td, J = 9.4, 7.0, 3.0 Hz, 4H), 3.04 (dd, J = 18.5, 4.9 Hz, 1H), 2.11–2.05 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 177.6, 175.4, 148.6, 132.2, 131.6, 130.9, 130.5, 129.4, 128.8, 128.6, 128.0, 127.9, 126.6, 126.2, 125.9, 125.3, 125.5, 125.3, 121.4, 108.7, 52.9, 43.5, 37.9, 25.0; IR (ν/cm⁻¹): 3049, 2963, 2870, 2817, 1777, 1707, 1561, 1498, 1375, 1170, 745, 693; HRMS (ESI-TOF) m/z calculated for C₂₈H₂₄N₂O₂ [MH⁺]: 421.1911, found: 421.1918.

4-Methyl-1-(4-(pyrrolidin-1-yl)anthracen-1-yl)-1,2,4-triazolidine-3,5-dione (9)

Under a nitrogen atmosphere 1-(pyrrolidine-1-yl)anthracene (1e) (247 mg, 1.00 mmol, 2.0 equiv), NEt₃ (279 µL, 2.00 mmol, 4.0 equiv) and MTAD (57.0 mg, 0.50 mmol, 1.0 equiv) were dissolved in degassed acetone (5.00 mL) and stirred under irradiation with a green LED (λ = 530 nm) at −78 °C for 5 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (DCM to DCM:MeOH = 19:1) to afford product 9 as a brown solid in 60% yield (107 mg, 0.30 mmol).

Mp.: 191–192 °C; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.79 (s, 1H), 8.24 (s, 1H), 8.00–7.98 (m, 1H), 7.92–7.88 (m, 1H), 7.48–7.43 (m, 2H), 7.21 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H),
3.51 – 3.45 (m, 4H), 3.12 (s, 3H), 2.07–2.01 (m, 4H); $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) δ 155.3, 153.3, 149.9, 132.1, 130.9, 129.1, 127.1, 126.9, 126.6, 126.0, 125.6, 123.8, 121.3, 107.1, 53.4, 25.7; IR (ν/cm$^{-1}$): 3049, 2952, 2866, 1766, 1692, 1617, 1453, 1386, 1323, 1148, 1021, 875, 741; HRMS (ESI-TOF) m/z calculated for C$_{21}$H$_{20}$N$_4$O$_2$ [MH$^+$]: 361.1659, found: 361.1666.

1-(2,4-Dibromoanthracen-1-yl)pyrrolidine (10)

![Diagram](image)

1-(pyrrolidine-1-yl)anthracene (1e) (200 mg, 0.81 mmol, 1.0 equiv) and NEt$_3$ (676 µL, 4.85 mmol, 6.0 equiv) were dissolved in DCM (10.0 mL) and the resulting solution was cooled to 0 °C. Then NBS (864 mg, 4.85 mmol, 6.0 equiv) was added portionwise over a period of 15 min and the reaction mixture was stirred at 0 °C for 5 h. The mixture was washed with saturated K$_2$CO$_3$ solution (15 mL) and the aqueous phase was extracted with DCM (3 × 10 mL). The combined organic phases were dried over anhydrous K$_2$CO$_3$ and the solvent was removed under reduced pressure. The black crude product was purified by flash column chromatography (hexanes) and product 10 was obtained as a bright yellow solid in 58% yield (191 mg, 0.47 mmol).

Mp.: 138–139 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.80 (s, 1H), 8.73 (s, 1H), 8.09–8.03 (m, 2H), 7.92 (s, 1H), 7.57–7.50 (m, 2H), 3.53–3.48 (m, 4H), 2.23–2.18 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.9, 133.6, 133.4, 132.4, 132.3, 130.1, 128.6, 128.5, 127.1, 126.6, 126.4, 124.2, 120.2, 119.0, 50.8, 27.0; IR (ν/cm$^{-1}$): 3052, 2967, 2862, 2814, 2668, 1677, 1595, 1558, 1442, 1293, 1140, 939, 838, 872, 715; HRMS (EI-TOF) m/z calculated for C$_{18}$H$_{15}$NBr$_2$ [M$^+$]: 402.9565, found: 402.9555.

Dimethyl (1R,4S)-1-(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethanoanthracene-2,3-dicarboxylate (11)

![Diagram](image)

Dimethyl (1R,4S)-1-(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethanoanthracene-2,3-dicarboxylate (3eD) (50 mg, 128 µmol, 1.0 equiv) and ammonium formate (163 mg, 2.57 mmol, 20.0 equiv) were dissolved in dry methanol (5 mL) and Pd/C (13.7 mg, 10 w%, 12.8 µmol, 0.1 equiv) was added. The reaction mixture was stirred for one hour until complete conversion of the starting material was observed. The mixture was filtered over celite and washed with ethyl acetate. The organic phase was washed two times with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure. The pure product was obtained as a yellowish oil (49 mg, 125 µmol, 98%).
Rf (PE:EA = 1:1): 0.64; 1H NMR (400 MHz, CDCl3) δ 7.83–7.77 (m, 4H), 7.70 (s, 1H), 7.48–7.40 (m, 2H), 4.57 (t, J = 2.7 Hz, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 3.59–3.49 (m, 2H), 3.27–3.22 (m, 2H), 2.23–2.16 (m, 1H), 2.08–1.90 (m, 4H), 1.89–1.78 (m, 2H), 1.67–1.60 (m, 1H); 13C NMR (101 MHz, CDCl3) δ 168.9, 163.7, 152.6, 139.7, 135.9, 132.0, 131.9, 128.2, 127.3, 125.8, 125.4, 121.5, 121.2, 69.8, 52.3, 52.3, 48.9, 39.4, 32.9, 27.3, 26.2; IR (ν/cm–1): 3056, 2948, 2870, 2255, 1714, 1621, 1502, 1435, 1334, 1308, 1248, 1196, 1133, 1069, 954, 909, 805, 730; HRMS (ESI-TOF) m/z calculated for C24H26NO4 [MH⁺]: 392.1862 found: 392.1860.

4. Optimization Studies for 1,3-Dipolar Cycloaddition

| entry | temperature [°C] | time [h] | yield 13 [%] | yield 14 [%] |
|-------|------------------|----------|--------------|--------------|
| 1     | 25 to reflux     | 24       | -            | 41           |
| 2     | 25               | 17       | 45           | 14           |
| 3     | reflux           | 17       | -            | 76           |
| 4     | 25               | 5        | 60           | 21           |
| 5     | 0                | 4        | 47           | 22           |
| 6     | 0                | 6        | 74           | 21           |

**Method.** Dimethyl (1R,4S)-1-(pyrrolin-1-yl)-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3eD) (50 mg, 128 µmol, 1.0 equiv) was dissolved in dry toluene (1 mL) and triethylamine (0.5 mL) was added. The solution was cooled down to 0 °C and N-hydroxybenzimidoyl chloride (40 mg, 257 µmol, 2.0 equiv) was added slowly over one hour. The reaction mixture was stirred at 0 °C for six hours. Then, toluene was added. The organic phase was washed three times with distilled water and dried over anhydrous NaSO4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (PE:EA = 95:5, 10% NEt3). Dimethyl 1-(pyrrolin-1-yl)anthracene-2,3-dicarboxylate (14) was isolated as a red oil (9.7 mg, 26.7 µmol, 21%). Dimethyl-3-phenyl-11-(pyrrolin-1-yl)-3a,4,11,11a-tetrahydro-4,11-ethenoanthra[2,3-d]isoxazole-12,13-dicarboxylate (13) was isolated as a yellow oil as a mixture of isomers (48.2 mg, 94.8 µmol, 74%). The major isomer was separated partially by column chromatography (CH2Cl2:acetone = 95:5, 10% NEt3).
Dimethyl (4S,11R,11aS)-3-phenyl-11-(pyrrolidin-1-yl)-3a,4,11,11a-tetrahydro-4,11-ethenoantra[2,3-d]isoxazole-12,13-dicarboxylate (major isomer, 13)

|R_f (PE:EA = 1:1)| 0.64; |H NMR (400 MHz, CDCl3) δ 7.88 (s, 1H), 7.83 (dt, J = 7.6, 4.6 Hz, 2H), 7.79 (s, 1H), 7.71 (dd, J = 6.6, 3.0 Hz, 2H), 7.52–7.48 (m, 2H), 7.44 (dd, J = 5.0, 1.9 Hz, 3H), 5.19 (d, J = 9.8 Hz, 1H), 4.93 (d, J = 2.9 Hz, 1H), 4.19 (dd, J = 9.8, 2.9 Hz, 1H), 3.84 (s, 3H), 3.65 (dd, J = 9.1, 5.5 Hz, 2H), 3.35 (s, 1H), 3.35–3.30 (m, 4H), 2.14–1.99 (m, 4H); |C NMR (101 MHz, CDCl3) δ 167.5, 162.6, 155.7, 151.1, 137.5, 135.1, 133.1, 132.3, 131.9, 130.1, 128.8, 128.5, 128.4, 127.3, 126.9, 126.7, 126.2, 124.5, 122.4, 88.1, 73.1, 58.3, 52.7, 51.9, 49.3, 40.7, 26.2; IR (ν/cm⁻¹): 3056, 2952, 2855, 2251, 1722, 1625, 1498, 1435, 1334, 1252, 1211, 1140, 1058, 957, 909, 849, 816, 760, 730, 693; HRMS (ESI-TOF) m/z calculated for C₃₁H₂₉N₂O₅ [MH⁺]: 509.2076 found: 509.2078; |R_f (DCM:acetone = 95:5): major: 0.43, minor: 0.62.

Dimethyl 1-(pyrrolidin-1-yl)anthracene-2,3-dicarboxylate (14)

|R_f (PE:EA = 1:1)| 0.72; |H NMR (400 MHz, CDCl3) δ 8.61 (s, 1H), 8.57 (s, 1H), 8.54 (s, 1H), 8.03 (ddd, J = 7.3, 5.2, 2.1 Hz, 2H), 7.59–7.47 (m, 2H), 3.98 (s, 3H), 3.96 (s, 3H), 3.51–3.42 (m, 4H), 2.18–2.13 (m, 4H); |C NMR (101 MHz, CDCl3) δ 169.9, 166.2, 144.4, 133.0, 132.2, 131.6, 130.9, 130.7, 130.4, 129.9, 128.8, 128.3, 126.9, 126.4, 124.7, 123.5, 52.5, 52.5, 52.4, 26.6. IR (ν/cm⁻¹): 3049, 2948, 2847, 2363, 2255, 1718, 1438, 1364, 1326, 1285, 1196, 1196, 1095, 1051, 984, 946, 913, 790, 730; HRMS (ESI-TOF) m/z calculated for C₂₂H₂₂NO₄ [MH⁺]: 364.1549 found: 364.1552.

Dimethyl (6R,12S)-12-bromo-9-oxo-9,10-dihydro-6H-6,10-methanocyclohepta[b]naphthalene-7,8-dicarboxylate (15)
Dimethyl (1R,4S)-1-(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3eD) (100 mg, 257 µmol, 1.0 equiv) was dissolved in H₂O/acetone (1:3, 4 mL) and cooled down to 0 °C. NBS (183 mg, 1.03 mmol, 4.0 equiv) was added at portions. The mixture was allowed to warm up to room temperature and was stirred for 16 h. Then, saturated aqueous solution of Na₂S₂O₅ was added. The aqueous layer was extracted with Et₂O and the combined organic phases were washed with water and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (PE:EA = 95:5) and 15 was obtained as a yellow solid (81 mg, 194 µmol, 76%).

Mp.: 180–182 °C; Rf (PE:EA = 1:1): 0.56; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 1H), 7.80 (s, 1H), 7.80–7.75 (m, 2H), 7.54–7.47 (m, 2H), 5.04 (t, J = 4.5 Hz, 1H), 4.67 (dd, J = 4.6, 1.1 Hz, 1H), 4.29 (dd, J = 4.5, 1.1 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 189.9, 164.4, 164.2, 142.6, 140.2, 133.4, 133.3, 133.2, 132.7, 128.3, 128.1, 127.3, 127.0, 125.4, 123.2, 61.8, 54.4, 53.5, 52.7, 48.0; IR (v/cm⁻¹): 3004, 2952, 2922, 2851, 2363, 2258, 1722, 1625, 1505, 1435, 1341, 1263, 1166, 1043, 961, 909, 797, 726; HRMS (ESI-TOF) m/z calculated for C₂₀H₁₅BrO₅ [MH⁺]: 415.0181 found: 415.0184.
5. NMR Spectra

**Supplementary Figure 1.** $^1$H NMR of 1,5-dihydroxy-9,10-anthraquinone (300 MHz, CDCl$_3$)

**Supplementary Figure 2.** $^{13}$C NMR of 1,5-dihydroxy-9,10-anthraquinone (75 MHz, CDCl$_3$)
Supplementary Figure 3. $^1$H NMR of 1b (300 MHz, CDCl$_3$)

Supplementary Figure 4. $^{13}$C NMR of 1b (75 MHz, CDCl$_3$)
Supplementary Figure 5. $^1$H NMR of 1,5-diaminoanthracene (300 MHz, CDCl$_3$)

Supplementary Figure 6. $^{13}$C NMR of 1,5-diaminoanthracene (75 MHz, CDCl$_3$)
Supplementary Figure 7. $^1$H NMR of 1c (300 MHz, CDCl$_3$)

Supplementary Figure 8. $^{13}$C NMR of 1c (75 MHz, CDCl$_3$)
Supplementary Figure 9. $^1$H NMR of 1d (300 MHz, CDCl$_3$)

Supplementary Figure 10. $^{13}$C NMR of 1d (75 MHz, CDCl$_3$)
Supplementary Figure 11. $^1$H NMR of 1-aminoanthracene (300 MHz, CDCl$_3$)

Supplementary Figure 12. $^{13}$C NMR of 1-aminoanthracene (75 MHz, CDCl$_3$)
Supplementary Figure 13. $^1$H NMR of 1e (400 MHz, CDCl$_3$)

Supplementary Figure 14. $^{13}$C NMR of 1e (101 MHz, CDCl$_3$)
Supplementary Figure 15. $^1$H NMR of 2aD (300 MHz, CDCl$_3$)
Supplementary Figure 16. $^1$H NMR of syn-2bA (400 MHz, CDCl$_3$)

Supplementary Figure 17. $^{13}$C NMR of syn-2bA (101 MHz, CDCl$_3$)
Supplementary Figure 18. $^1$H NMR of 2bB (400 MHz, CDCl$_3$)

Supplementary Figure 19. $^{13}$C NMR of 2bB (101 MHz, CDCl$_3$)
**Supplementary Figure 20.** $^1$H NMR of 2bC (400 MHz, CDCl$_3$)

**Supplementary Figure 21.** $^{13}$C NMR of 2bC (101 MHz, CDCl$_3$)
Supplementary Figure 22. $^1$H NMR of 2bD (300 MHz, CDCl$_3$)

Supplementary Figure 23. $^{13}$C NMR of 2bD (75 MHz, CDCl$_3$)
Supplementary Figure 24. $^1$H NMR of 3bD (300 MHz, CDCl$_3$)

Supplementary Figure 25. $^{13}$C NMR of 3bD (75 MHz, CDCl$_3$)
Supplementary Figure 26. \(^1\)H NMR of \textit{syn-2cA} (300 MHz, CDCl\(_3\))

Supplementary Figure 27. \(^13\)C NMR of \textit{syn-2cA} (75 MHz, CDCl\(_3\))
Supplementary Figure 28. $^1$H NMR of anti-2cA (300 MHz, CDCl$_3$)

Supplementary Figure 29. $^{13}$C NMR of anti-2cA (75 MHz, CDCl$_3$)
Supplementary Figure 30. $^1$H NMR of 2cB (300 MHz, CDCl$_3$)

Supplementary Figure 31. $^{13}$C NMR of 2cB (75 MHz, CDCl$_3$)
Supplementary Figure 32. $^1$H NMR of 2cC (400 MHz, CDCl$_3$)

Supplementary Figure 33. $^{13}$C NMR of 2cC (101 MHz, CDCl$_3$)
Supplementary Figure 34. $^1$H NMR of 2cD (300 MHz, CDCl$_3$)

Supplementary Figure 35. $^{13}$C NMR of 2cD (75 MHz, CDCl$_3$)
Supplementary Figure 36. $^1$H NMR of 3cD (300 MHz, CDCl$_3$)

Supplementary Figure 37. $^{13}$C NMR of 3cD (75 MHz, CDCl$_3$)
Supplementary Figure 38. $^1$H NMR of syn-2dA (300 MHz, CDCl$_3$)

Supplementary Figure 39. $^{13}$C NMR of syn-2dA (75 MHz, CDCl$_3$)
Supplementary Figure 40. $^1$H NMR of anti-2dA (300 MHz, CDCl$_3$)

Supplementary Figure 41. $^{13}$C NMR of anti-2dA (75 MHz, CDCl$_3$)
Supplementary Figure 42. $^1$H NMR of 2dB (400 MHz, CDCl$_3$)

Supplementary Figure 43. $^{13}$C NMR of 2dB (101 MHz, CDCl$_3$)
Supplementary Figure 44. $^1$H NMR of 2dC (400 MHz, CDCl$_3$)

Supplementary Figure 45. $^{13}$C NMR of 2dC (101 MHz, CDCl$_3$)
Supplementary Figure 46. $^1$H NMR of 3dD (300 MHz, CDCl$_3$)

Supplementary Figure 47. $^{13}$C NMR of 3dD (75 MHz, CDCl$_3$)
Supplementary Figure 48. $^1$H NMR of 2dE (400 MHz, CDCl$_3$)

Supplementary Figure 49. $^{13}$C NMR of 2dE (101 MHz, CDCl$_3$)
Supplementary Figure 50. $^1$H NMR of 3dE (400 MHz, CDCl$_3$)

Supplementary Figure 51. $^{13}$C NMR of 3dE (101 MHz, CDCl$_3$)
Supplementary Figure 52. $^1$H NMR of 2dF (300 MHz, CDCl$_3$)

Supplementary Figure 53. $^{13}$C NMR of 2dF (75 MHz, CDCl$_3$)
Supplementary Figure 54. $^1$H NMR of syn-2eA (400 MHz, CDCl$_3$)

Supplementary Figure 55. $^{13}$C NMR of syn-2eA (101 MHz, CDCl$_3$)
Supplementary Figure 56. $^1$H NMR of anti-2eA (400 MHz, CDCl$_3$)

Supplementary Figure 57. $^{13}$C NMR of anti-2eA (101 MHz, CDCl$_3$)
Supplementary Figure 58. $^1$H NMR of endo-2eB (400 MHz, CDCl$_3$)

Supplementary Figure 59. $^{13}$C NMR of endo-2eB (101 MHz, CDCl$_3$)
Supplementary Figure 60. $^1$H NMR of exo/endo-2eC (400 MHz, CDCl$_3$)

Supplementary Figure 61. $^{13}$C NMR of exo/endo-2eC (101 MHz, CDCl$_3$)
Supplementary Figure 62. $^1$H NMR of 3eD (400 MHz, CDCl$_3$)

Supplementary Figure 63. $^{13}$C NMR of 3eD (101 MHz, CDCl$_3$)
Supplementary Figure 64. $^1$H NMR of *anti*-2eE (400 MHz, CDCl$_3$)

Supplementary Figure 65. $^{13}$C NMR of *anti*-2eE (101 MHz, CDCl$_3$)
Supplementary Figure 66. $^1$H NMR of 3eE (300 MHz, CDCl$_3$)

Supplementary Figure 67. $^{13}$C NMR of 3eE (101 MHz, CDCl$_3$)
Supplementary Figure 68. $^1$H NMR of 8 (400 MHz, CDCl$_3$)

Supplementary Figure 69. $^{13}$C NMR of 8 (101 MHz, CDCl$_3$)
Supplementary Figure 70. $^1$H NMR of 9 (400 MHz, CDCl$_3$)

Supplementary Figure 71. $^{13}$C NMR of 9 (101 MHz, CDCl$_3$)
Supplementary Figure 72. DEPT-135 of 9 (101 MHz, CDCl₃)
Supplementary Figure 73. $^1$H NMR of 10 (400 MHz, CDCl$_3$)

Supplementary Figure 74. $^{13}$C NMR of 10 (75 MHz, CDCl$_3$)
Supplementary Figure 75. $^1$H NMR of 11 (400 MHz, CDCl$_3$)

Supplementary Figure 76. $^{13}$C NMR of 11 (101 MHz, CDCl$_3$)
Supplementary Figure 77. DEPT-135 of 11 (101 MHz, CDCl₃)
Supplementary Figure 78. $^1$H NMR of 13 (major isomer, 400 MHz, CDCl$_3$)

Supplementary Figure 79. $^{13}$C NMR of 13 (101 MHz, CDCl$_3$)
Supplementary Figure 80. DEPT-135 of 13 (101 MHz, CDCl₃)

Supplementary Figure 81. HSQC of 13 (400 MHz, CDCl₃)
Supplementary Figure 8. COSY of 13 (400 MHz, CDCl₃)
Supplementary Figure 83. $^1$H NMR of 14 (400 MHz, CDCl$_3$)

Supplementary Figure 84. $^{13}$C NMR of 14 (101 MHz, CDCl$_3$)
Supplementary Figure 85. DEPT-135 of 14 (101 MHz, CDCl₃)

Supplementary Figure 86. HSQC of 14 (400 MHz, CDCl₃)
Supplementary Figure 87. $^1$H NMR of 15 (400 MHz, CDCl$_3$)

Supplementary Figure 88. $^{13}$C NMR of 15 (101 MHz, CDCl$_3$)
Supplementary Figure 89. DEPT-135 of 15 (101 MHz, CDCl₃)
6. X-Ray Crystallographic Studies

Dimethyl 1,5-dimethoxy-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3bD)

**Compound**

| Parameter                  | Value                  |
|----------------------------|------------------------|
| Compound                   | N095                   |
| CCDC                       | 1979830                |
| Formula                    | C_{22}H_{20}O_{6}       |
| D_{calc}/g cm\(^{-3}\)     | 1.388                  |
| \(\mu/\text{mm}^\text{1}\) | 0.838                  |
| Formula Weight             | 380.38                 |
| Colour                     | yellowish colourless   |
| Shape                      | block                  |
| Size/mm\(^{3}\)           | 0.26\times0.11\times0.07|
| T/K                        | 124(1)                 |
| Crystal System             | triclinic              |
| Space Group                | P-1                    |
| a/Å                        | 9.0753(2)              |
| b/Å                        | 9.76091(19)            |
| c/Å                        | 10.8610(2)             |
| \(\alpha^\circ\)          | 91.7335(16)            |
| \(\beta^\circ\)           | 108.5566(19)           |
| \(\gamma^\circ\)          | 92.3162(17)            |
| V/Å\(^{3}\)               | 910.40(3)              |
| Z                          | 2                      |
| Z'                         | 1                      |
| Wavelength/Å               | 1.54184                |
| Radiation type             | Cu K\(_{\alpha}\)     |
| \(\Theta_{\text{min}}^\circ\) | 4.298                 |
| \(\Theta_{\text{max}}^\circ\) | 66.030                |
| Measured Refl's.           | 10461                  |
| Ind't Refl's               | 3154                   |
| Refl's with I > 2(I)       | 2892                   |
| \(R_{\text{int}}\)        | 0.0202                 |
| Parameters                | 257                    |
| Restraints                | 0                      |
| Largest Peak               | 0.278                  |
| Deepest Hole              | -0.250                 |
| Goof                       | 1.038                  |
| \(wR_2\) (all data)       | 0.1032                 |
| \(wR_2\)                   | 0.1004                 |
| \(R_1\) (all data)        | 0.0399                 |
| \(R_1\)                    | 0.0372                 |
Dimethyl 1,5-bis(dimethylamino)-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3cD)

| Compound | L086 |
|----------|------|
| CCDC     | 1979832 |
| Formula  | C_{48}H_{52}N_{4}O_{8} |
| D_{calc} / g cm\(^{-3}\) | 1.309 |
| \(\mu\) / mm\(^{-1}\) | 0.724 |
| Formula Weight | 812.93 |
| Colour    | light yellow |
| Shape     | prism |
| Size/mm\(^3\) | 0.08×0.05×0.04 |
| T/K       | 123.00(10) |
| Crystal System | monoclinic |
| Space Group | C2/c |
| a/Å       | 19.2416(13) |
| b/Å       | 19.8451(8) |
| c/Å       | 12.2391(8) |
| \(\alpha\)/° | 90 |
| \(\beta\)/° | 117.999(9) |
| \(\gamma\)/° | 90 |
| V/Å\(^3\) | 4126.5(5) |
| Z         | 4 |
| Z’        | 0.5 |
| Wavelength/Å | 1.54184 |
| Radiation type | Cu K\(_\alpha\) |
| \(\Theta_{\min}\)/° | 3.425 |
| \(\Theta_{\max}\)/° | 63.070 |
| Measured Refl's. | 9176 |
| Ind't Refl's | 3208 |
| Refl's with \(I > 2(I)\) | 2767 |
| \(R_{int}\) | 0.0235 |
| Parameters | 275 |
| Restraints | 0 |
| Largest Peak | 0.272 |
| Deepest Hole | -0.197 |
| GooF | 1.048 |
| \(wR_{2}\) (all data) | 0.1191 |
| \(wR_{2}\) | 0.1135 |
| \(R_{1}\) (all data) | 0.0483 |
| \(R_{1}\) | 0.0413 |
Dimethyl 1,5-di(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3dD)

| Compound | N077 |
|----------|------|
| CCDC     | 1979833 |
| Formula  | C_{28}H_{30}N_{2}O_{4} |
| D_{calc} | 1.344 g cm^{-3} |
| μ/mm^{-1} | 0.724 |
| Formula Weight | 458.54 |
| Colour   | colourless |
| Shape    | prism |
| Size/mm³ | 0.24×0.11×0.08 |
| T/K      | 123.01(10) |
| Crystal System | orthorhombic |
| Flack Parameter | 0.22(5) |
| Hooft Parameter | 0.25(5) |
| Space Group | P2_12_12_1 |
| a/Å     | 9.08860(17) |
| b/Å     | 9.11769(15) |
| c/Å     | 27.3374(4) |
| α°      | 90 |
| β°      | 90 |
| γ°      | 90 |
| V/Å³    | 2265.37(7) |
| Z       | 4 |
| Z'      | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | Cu Kα |
| θ_{min}° | 5.114 |
| θ_{max}° | 74.063 |
| Measured Refl's. | 35025 |
| Ind't Refl's | 4539 |
| Refl's with I > 2(I) | 4444 |
| R_{int} | 0.0436 |
| Parameters | 343 |
| Restraints | 36 |
| Largest Peak | 0.284 |
| Deepest Hole | -0.164 |
| GooF    | 1.057 |
| wR² (all data) | 0.0879 |
| wR²     | 0.0871 |
| R_{I} (all data) | 0.0335 |
| R_{I}   | 0.0329 |
### Dimethyl 1-(pyrrolidin-1-yl)-1,4-dihydro-1,4-ethenoanthracene-2,3-dicarboxylate (3eD)

| Compound | R040 |
|----------|------|
| CCDC     | 1979834 |
| Formula  | C$_{24}$H$_{23}$NO$_4$ |
| $D_{\text{calc}}$ g cm$^{-3}$ | 1.347 |
| $\mu$/mm$^{-1}$ | 0.742 |
| Formula Weight | 389.43 |
| Colour    | clear yellow |
| Shape     | block |
| Size/mm$^3$ | 0.30×0.27×0.20 |
| $T$/K     | 122.9(2) |
| Crystal System | orthorhombic |
| Flack Parameter | -0.06(5) |
| Hooft Parameter | -0.05(5) |
| Space Group | $P2_12_12_1$ |
| $a$/Å     | 6.74420(10) |
| $b$/Å     | 7.90290(10) |
| $c$/Å     | 36.0260(3) |
| $\alpha^\circ$ | 90 |
| $\beta^\circ$ | 90 |
| $\gamma^\circ$ | 90 |
| $V$/Å$^3$ | 1920.14(4) |
| $Z$       | 4 |
| $Z'$      | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | CuK$_\alpha$ |
| $\theta_{\text{min}}$/° | 4.910 |
| $\theta_{\text{max}}$/° | 74.780 |
| Measured Refl. | 22748 |
| Independent Refl. | 3901 |
| Reflections Used | 3824 |
| $R_{\text{int}}$ | 0.0300 |
| Parameters | 264 |
| Restraints | 0 |
| Largest Peak | 0.155 |
| Deepest Hole | -0.245 |
| GooF | 1.049 |
| $wR_2$ (all data) | 0.0771 |
| $wR_2$ | 0.0765 |
| $R_1$ (all data) | 0.0291 |
| $R_1$ | 0.0285 |
### Dimethyl (6R,12S)-12-bromo-9-oxo-9,10-dihydro-6H-6,10-methanocyclohepta-[b]naphthalene-7,8-dicarboxylate (15)

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Compound                                      | T086                                       |
| CCDC                                          | 2017368                                   |
| Formula                                       | C_{20}H_{15}BrO_{5}                        |
| \(D_{\text{calc.}} \)  g cm\(^{-3}\)         | 1.587                                     |
| \(\mu/\text{mm}^{-1}\)                       | 3.482                                     |
| Formula Weight                                | 415.23                                    |
| Colour                                        | clear yellow                              |
| Shape                                         | irregular                                 |
| Size/mm\(^3\)                                | 0.24×0.13×0.08                            |
| \(T/K\)                                       | 123.01(10)                                |
| Crystal System                               | monoclinic                                |
| Space Group                                   | \(P2_1/n\)                                |
| \(a/\text{Å}\)                               | 7.79240(10)                               |
| \(b/\text{Å}\)                               | 11.7162(2)                                |
| \(c/\text{Å}\)                               | 19.1249(3)                                |
| \(\alpha/^\circ\)                            | 90                                        |
| \(\beta/^\circ\)                             | 95.530(2)                                 |
| \(\gamma/^\circ\)                            | 90                                        |
| \(V/\text{Å}^3\)                             | 1737.93(5)                                |
| \(Z\)                                        | 4                                         |
| \(Z'\)                                       | 1                                         |
| Wavelength/Å                                  | 1.54184                                   |
| Radiation type                               | Cu K\(\alpha\)                           |
| \(\Theta_{\text{min}}/^\circ\)               | 4.431                                     |
| \(\Theta_{\text{max}}/^\circ\)               | 72.612                                    |
| Measured Refl's.                             | 23376                                     |
| Indep't Refl's.                              | 3442                                      |
| Refl's I≥2 σ(I)                              | 3136                                      |
| \(R_{\text{int}}\)                          | 0.0461                                    |
| Parameters                                   | 237                                       |
| Restraints                                   | 0                                         |
| Largest Peak                                 | 0.700                                     |
| Deepest Hole                                 | -0.975                                    |
| GoF                                           | 1.053                                     |
| \(wR_2\) (all data)                         | 0.0750                                    |
| \(wR_2\)                                     | 0.0721                                    |
| \(R_1\) (all data)                          | 0.0338                                    |
| \(R_1\)                                      | 0.0301                                    |
7. Computational Studies

All calculations have been conducted with the Gaussian09 E.01 suite of programs. The calculations were carried out at the B3LYP-D3/6-31G** level of theory with Grimme’s D3 dispersion correction accounting for long-range dispersion interactions. Stationary points were confirmed as ground or transition states with the computation of the harmonic vibrational frequencies and evaluating the number of imaginary frequencies (0 for ground state, 1 for transition state). IRC calculations were conducted to classify the transition states as the correct one and also to find potential hints of step-wise processes by analyzing the RMS gradient. Population analyses according to Mulliken and NBO were employed to derive FMO information and provide access to partial charges.
8. Calculated Thermodynamic Data

Supplementary Table 2: Thermodynamic data for the reaction of anthracenes with DMAD D.

| # | parent anthracene | 9,10 addition | 1,4 addition |
|---|-------------------|---------------|--------------|
|   |                   | DG (kcal mol⁻¹) | DH (kcal mol⁻¹) | DrG (kcal mol⁻¹) | DrH (kcal mol⁻¹) | DG (kcal mol⁻¹) | DH (kcal mol⁻¹) | DrG (kcal mol⁻¹) | DrH (kcal mol⁻¹) |
| 1 | 1a                | 25.7          | 13.5          | −24.6          | −39.6          | 31.9          | 19.5          | −12.4          | −27.2          |
| 2 | 1b                | 26.7          | 13.6          | −22.7          | −38.0          | 28.1          | 14.3          | −6.9           | −22.7          |
| 3 | 1c                | 25.0          | 11.9          | −25.6          | −41.4          | 25.0          | 10.2          | −5.1           | −21.7          |
| 4 | 1d                | 24.4          | 8.2           | −26.8          | −42.9          | 21.6          | 5.4           | −5.0           | −21.0          |
| 5 | 1e                | 29.1          | 14.8          | −24.8          | −40.9          | 23.1          | 7.0           | −19.7          | −2.3           |

* Values (in kcal mol⁻¹) for 5,8 addition: DG = 36.1 ; DH = 22.0 ; DrG = -10.8 ; DrH = -42.3

Supplementary Table 3: Thermodynamic data for the reaction of anthracenes with maleic anhydride B.

| # | parent anthracene | 9,10 addition | 1,4 addition (endo) |
|---|-------------------|---------------|---------------------|
|   |                   | DG (kcal mol⁻¹) | DH (kcal mol⁻¹) | DrG (kcal mol⁻¹) | DrH (kcal mol⁻¹) | DG (kcal mol⁻¹) | DH (kcal mol⁻¹) | DrG (kcal mol⁻¹) | DrH (kcal mol⁻¹) |
| 1 | 1a                | 23.2          | 9.8              | −8.6            | −22.6          | 31.0          | 17.5          | 4.1            | −9.9           |
| 2 | 1b                | 22.8          | 8.9              | −7.4            | −21.9          | 33.4          | 19.5          | 11.4           | −3.4           |
| 3 | 1c                | 22.1          | 8.0              | −8.5            | −23.4          | 24.8          | 10.6          | 14.3           | −0.8           |
| 4 | 1d                | 19.8          | 6.1              | −10.1           | −24.5          | 17.1          | 1.2           | 8.1            | −7.5           |
| 5 | 1e                | 28.5          | 14.1             | −7.3            | −21.9          | 19.5          | 4.3           | 7.9            | −7.5           |

* Values (in kcal mol⁻¹) for 5,8 addition: DG = 31.0 ; DH = 17.0 ; DrG = 4.4 ; DrH = -10.1 ;
* Values for 9,10 addition for endo pathway

Supplementary Table 4: Thermodynamic data for the reaction of anthracenes with maleic anhydride B.

| # | parent anthracene | 9,10 addition | 1,4 addition (exo) |
|---|-------------------|---------------|---------------------|
|   |                   | DG (kcal mol⁻¹) | DH (kcal mol⁻¹) | DrG (kcal mol⁻¹) | DrH (kcal mol⁻¹) | DG (kcal mol⁻¹) | DH (kcal mol⁻¹) | DrG (kcal mol⁻¹) | DrH (kcal mol⁻¹) |
| 1 | 1a                | 23.2          | 9.8              | −8.6            | −22.6          | 30.6          | 17.3          | 3.9            | −10.0          |
| 2 | 1b                | 22.8          | 8.9              | −7.4            | −21.9          | 29.9          | 16.2          | 10.1           | −4.8           |
| 3 | 1c                | 22.1          | 8.0              | −8.5            | −23.4          | 22.6          | 7.8           | 12.7           | −2.5           |
| 4 | 1d                | 19.8          | 6.1              | −10.1           | −24.5          | 17.9          | 2.5           | 11.5           | −3.6           |
| 5 | 1e                | 22.7          | 9.0              | −7.3            | −22.6          | 17.4          | 2.3           | 10.9           | −3.5           |

* Values (in kcal mol⁻¹) for 5,8 addition: DG = 30.4 ; DH = 16.6 ; DrG = 4.2 ; DrH = −10.3 ;
* Values for 9,10 addition for exo pathway
9. Calculation of Bond Orders

The bond orders have been calculated with Pauling’s equation (equation 1) with 0.6 as a fitting factor for transition states.\textsuperscript{17,18} As reference, the according product structures were used.

\[
BO = n_0 \times e^{\frac{r_0 - r x}{c}}
\]  

(1)

With \(n_0\) being the reference bond order, \(r_0\) being the reference bond length in Å, \(r_x\) being the examined bond length in Å and \(c\) a factor with 0.3 for ground states and 0.6 for transition states.

Supplementary Table 5: Bond lengths in the product structures for 2a-eB and 3a-eB.

| #  | parent anthracene | 1,4-Addition \(\text{exo}\)  | 1,4-Addition \(\text{endo}\)  | 9,10-Addition |
|----|-------------------|----------------|----------------|----------------|
|    |                   | C1 – CA (Å)    | C4 – CB (Å)    | C9-C9 (Å)      |
| 1  | 1a                | 1.57           | 1.57           | 1.57           |
| 2  | 1b                | 1.58           | 1.58           | 1.57           |
| 3  | 1c                | 1.59           | 1.58           | 1.59           |
| 4  | 1d                | 1.59           | 1.57           | 1.59           |
| 5a | 1e                | 1.60           | 1.57           | 1.57           |

\(^a\) for 5,8 addition \(\text{endo}\) product: C5 – CA = 1.57, C8 – CB = 1.57; \(^b\) for 5,8 addition \(\text{exo}\) product: C5 – CA = 1.57, C8 – CB = 1.57; \(^c\) values in table for \(\text{exo}\) transition state. Values for \(\text{endo}\) transition state: C9 – CA = 1.57, C10 – CB = 1.57

Supplementary Table 6: Bond lengths in the transition state structures for 2a-eB and 3a-eB.

| #  | parent anthracene | 1,4-Addition \(\text{exo}\)  | 1,4-Addition \(\text{endo}\)  | 9,10-Addition |
|----|-------------------|----------------|----------------|----------------|
|    |                   | C1 – CA (Å)    | C4 – CB (Å)    | C9-C9 (Å)      |
| 1  | 1a                | 2.13           | 2.13           | 2.19           |
| 2  | 1b                | 2.46           | 1.86           | 2.17           |
| 3  | 1c                | 2.66           | 1.85           | 2.15           |
| 4  | 1d                | 2.76           | 1.86           | 2.16           |
| 5a | 1e                | 2.75           | 1.86           | 2.20           |

\(^a\) for 5,8 addition \(\text{endo}\) product: C5 – CA = 2.13, C8 – CB = 2.13; \(^b\) for 5,8 addition \(\text{exo}\) product: C5 – CA = 2.14, C8 – CB = 2.14; \(^c\) values in table for \(\text{exo}\) transition state. Values for \(\text{endo}\) transition state: C9 – CA = 2.28, C10 – CB = 2.12.
Supplementary Table 7: Bond orders after Pauling, calculated after equation 1 for structures 2a-eB and 3a-eB.

| # | parent anthracene | 1,4-Addition exo C1 – CA (Å) | 1,4-Addition endo C1 – CA (Å) | 9,10-Addition C9-CA C10-CB (Å) |
|---|-------------------|-------------------------------|-------------------------------|-------------------------------|
| 1 | 1a                | 0.39                          | 0.39                          | 0.36                          |
| 2 | 1b                | 0.23                          | 0.63                          | 0.25                          |
| 3 | 1c                | 0.17                          | 0.64                          | 0.16                          |
| 4 | 1d                | 0.14                          | 0.62                          | 0.14                          |
| 5a,b,c | 1e            | 0.15                          | 0.62                          | 0.14                          |

* for 5,8 addition endo: C5 – CA = 0.39, C8 – CB = 0.39; *b* for 5,8 addition exo product: C5 – CA = 0.39, C8 – CB = 0.39; *c* values in table for exo addition transition state. Values for endo transition state: C9 – CA = 0.31, C10 – CB = 0.40.

Supplementary Figure 90: Assignment of the carbon atoms for the calculation of the bond orders.

Supplementary Table 8: Computed bond lengths in product structures for 2a-eD and 3a-eD.

| # | parent anthracene | 1,4-Addition C1 – CA (Å) | 1,4-Addition C4 – CB (Å) | 9,10-Addition C9-CA C10-CB (Å) |
|---|------------------|--------------------------|--------------------------|-------------------------------|
| 1 | 1a               | 1.54                     | 1.53                     | 1.54                          |
| 2 | 1b               | 1.56                     | 1.56                     | 1.53                          |
| 3 | 1c               | 1.55                     | 1.53                     | 1.54                          |
| 4 | 1d               | 1.56                     | 1.55                     | 1.53                          |
| 5a | 1e             | 1.56                     | 1.53                     | 1.54                          |

* for 5,8 addition, values are: C5-CA = 1.53, C8 – CB = 1.54
Supplementary Table 9: Computed bond lengths in transition state structures for 2a-eD and 3a-eD.

| #  | parent anthracene | 1,4-Addition | 9,10-Addition |
|----|-------------------|--------------|--------------|
|    |                   | C1 – CA (Å)  | C4 – CB (Å)  | C9-CA (Å) | C10-CB (Å) |
| 1  | 1a                | 2.40         | 2.04         | 2.50       | 2.05       |
| 2  | 1b                | 2.76         | 1.91         | 2.61       | 2.03       |
| 3  | 1c                | 3.08         | 1.96         | 2.26       | 2.15       |
| 4  | 1d                | 3.35         | 1.94         | 3.50       | 1.86       |
| 5a | 1e                | 3.18         | 1.95         | 2.20       | 2.31       |

*a for 5,8 addition, values are: C5-CA = 2.20, C8 – CB = 2.20

Supplementary Table 10: Calculated bond orders in transition state structures for 2a-eD and 3a-eD.

| #  | parent anthracene | 1,4-Addition | 9,10-Addition |
|----|-------------------|--------------|--------------|
|    |                   | C1 – CA (Å)  | C4 – CB (Å)  | C9-CA (Å) | C10-CB (Å) |
| 1  | 1a                | 0.24         | 0.43         | 0.20       | 0.42       |
| 2  | 1b                | 0.13         | 0.56         | 0.17       | 0.44       |
| 3  | 1c                | 0.08         | 0.51         | 0.30       | 0.36       |
| 4  | 1d                | 0.05         | 0.52         | 0.04       | 0.58       |
| 5a | 1e                | 0.07         | 0.50         | 0.33       | 0.28       |

*a for 5,8 addition, values are: C5-CA = 0.33, C8 – CB = 0.33
10. Marcus Analysis

The data for the intrinsic barrier were calculated after the following equation 2\textsuperscript{19,20}:

\[
\Delta G^\ddagger = \Delta G^\ddagger_0 + 0.5 \Delta R G^+ \frac{\Delta R G^2}{16 \Delta G^\ddagger_0} \tag{2}
\]

With \(\Delta G^\ddagger\) being the activation barrier, \(\Delta G^\ddagger_0\) being the intrinsic barrier and \(\Delta R G\) being the driving force.

Supplementary Table 11: Calculated intrinsic barriers for the reaction of anthracenes with DMAD D.

| # | cmpd | R, R' | \(\Delta G^\ddagger_{9,10}^a\) | \(\Delta R G_{9,10}^a\) | \(\Delta G^\ddagger_{9,10}^a\) | \(\Delta G^\ddagger_{1,4}^a\) | \(\Delta R G_{1,4}^a\) | \(\Delta G^\ddagger_{1,4}^a\) |
|---|------|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1 | 1a   | H    | 25.7            | -24.6           | 37.0            | 31.9            | -12.4           | 37.9            |
| 2 | 1b   | OMe  | 26.7            | -22.7           | 37.2            | 28.1            | -6.9            | 31.5            |
| 3 | 1c   | NMe₂ | 25.0            | -25.6           | 35.7            | 25.0            | -5.1            | 27.5            |
| 4 | 1d   | N(CH\textsubscript{2})₄ | 23.1 | -26.8           | 36.6            | 21.6            | -5.0            | 24.0            |
| 5 | 1e\textsuperscript{b} | H, N(CH\textsubscript{2})₄ | 29.1 | -24.8           | 40.6            | 23.1            | -2.3            | 24.2            |

\textsuperscript{a} (kcal mol\textsuperscript{-1}), \textsuperscript{b} values for 5,8 position: \(\Delta G^\ddagger_{5,8} = 36.1\); \(\Delta R G_{5,8} = -10.8\), \(\Delta G^\ddagger_{5,8} = 41.3\).

Supplementary Table 12: Calculated intrinsic barriers for the reaction of anthracenes with maleic anhydride B (endo path for 1,4-addition process).

| # | cmpd | R, R' | \(\Delta G^\ddagger_{9,10}^a\) | \(\Delta R G_{9,10}^a\) | \(\Delta G^\ddagger_{9,10}^a\) | \(\Delta G^\ddagger_{1,4}^a\) | \(\Delta R G_{1,4}^a\) | \(\Delta G^\ddagger_{1,4}^a\) |
|---|------|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1 | 1a   | H    | 23.2            | -8.6            | 27.3            | 31.0            | 4.1             | 28.9            |
| 2 | 1b   | OMe  | 22.8            | -7.4            | 26.4            | 33.4            | 11.4            | 27.4            |
| 3 | 1c   | NMe₂ | 22.1            | -8.5            | 26.2            | 24.8            | 14.3            | 16.9            |
| 4 | 1d   | N(CH\textsubscript{2})₄ | 19.8 | -10.1           | 24.6            | 17.1            | 8.1             | 12.7            |
| 5 | 1e\textsuperscript{b} | H, N(CH\textsubscript{2})₄ | 28.5 | -7.3            | 33.0            | 19.5            | 7.9             | 15.3            |

\textsuperscript{a} (kcal mol\textsuperscript{-1}), \textsuperscript{b} values for 5,8 position: \(\Delta G^\ddagger_{5,8} = 31.0\); \(\Delta R G_{5,8} = 4.4\), \(\Delta G^\ddagger_{5,8} = 28.8\).

Supplementary Table 13: Calculated intrinsic barriers for the 1,4-addition process of anthracenes with maleic anhydride, exo pathway.

| # | cmpd | R, R' | \(\Delta G^\ddagger_{9,10}^a\) | \(\Delta R G_{9,10}^a\) | \(\Delta G^\ddagger_{9,10}^a\) | \(\Delta G^\ddagger_{1,4}^a\) | \(\Delta R G_{1,4}^a\) | \(\Delta G^\ddagger_{1,4}^a\) |
|---|------|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1 | 1a   | H    | 23.2            | -8.6            | 27.3            | 30.6            | 3.9             | 28.6            |
| 2 | 1b   | OMe  | 22.8            | -7.4            | 26.4            | 29.9            | 10.1            | 24.6            |
| 3 | 1c   | NMe₂ | 22.1            | -8.5            | 26.2            | 22.6            | 12.7            | 15.6            |
| 4 | 1d   | N(CH\textsubscript{2})₄ | 19.8 | -10.1           | 24.6            | 17.9            | 11.5            | 11.4            |
| 5 | 1e\textsuperscript{b} | H, N(CH\textsubscript{2})₄ | 22.7 | -7.3            | 26.2            | 17.4            | 10.9            | 11.3            |
11. FMO Analysis

The computed orbital energies from the Mulliken analysis were used for the calculation of the HOMO-LUMO gap.

Supplementary Table 14: FMO Analysis for anthracenes 1a-e with DMAD D.

| # | parent anthracene | normal electron demand | inverse electron demand |
|---|-------------------|------------------------|------------------------|
|   |                   | $\varepsilon_{\text{HOMO}}$ (D) (eV) | $\varepsilon_{\text{LUMO}}$ (DP) (eV) | $D_{\text{HOMO-LUMO}}$ (eV) |
| 1 | 1a                | -5.23                  | 3.74                   | 3.74                    |
| 2 | 1b                | -4.82                  | 3.33                   | -1.65                   | 6.24        |
| 3 | 1c                | -4.81                  | 3.32                   | -7.89                   | -1.40       | 6.49        |
| 4 | 1d                | -4.37                  | 2.88                   | -1.12                   | 6.77        |
| 5 | 1e                | -4.68                  | 3.19                   | -1.38                   | 6.51        |

Supplementary Table 15: FMO Analysis for anthracenes 1a-e with maleic anhydride B.

| # | parent anthracene | normal electron demand | inverse electron demand |
|---|-------------------|------------------------|------------------------|
|   |                   | $\varepsilon_{\text{HOMO}}$ (D) (eV) | $\varepsilon_{\text{LUMO}}$ (DP) (eV) | $D_{\text{HOMO-LUMO}}$ (eV) |
| 1 | 1a                | -5.23                  | 2.04                   | 3.19                    |
| 2 | 1b                | -4.82                  | 1.63                   | -8.14                   | -1.27       | 6.87        |
| 3 | 1c                | -4.81                  | 1.62                   | -8.14                   | -1.40       | 6.74        |
| 4 | 1d                | -4.37                  | 1.18                   | -1.12                   | 7.02        |
| 5 | 1e                | -4.68                  | 1.49                   | -1.38                   | 6.76        |
12. NBO Analysis (Partial Charges)

The partial charges were taken from the NBO analysis. In all cases, the charge from the neighbouring hydrogen atom was added to the charge of the carbon centre.

Supplementary Table 16: Partial charges at the reaction centres for the reaction of anthracenes with DMAD D.

| # | Cmpd | R = R’ = | 1,4-addition | 9,10-addition |
|---|------|----------|--------------|--------------|
|   |      |          | CA  | CB  | C1  | C4  | CA  | CB  | C9  | C10 |
| 1 | 1a   | H        | -0.023 | -0.130 | 0.049 | 0.076 | -0.132 | -0.013 | 0.074 | 0.102 |
| 2 | 1b   | OMe      | -0.025 | -0.153 | 0.410 | 0.005 | -0.130 | -0.022 | 0.083 | 0.119 |
| 3 | 1c   | NMe₂     | -0.060 | -0.131 | 0.269 | -0.012 | -0.103 | -0.052 | 0.077 | 0.091 |
| 4 | 1d   | N(CH₂)₄ | -0.058 | -0.148 | 0.283 | -0.022 | -0.173 | -0.047 | 0.019 | 0.125 |
| 5 | 1eᵇ  | H, N(CH₂)₄ | -0.103 | -0.138 | 0.282 | -0.032 | -0.123 | -0.086 | 0.068 | 0.096 |

ᵃ Values for 5,8-addition: CA = -0.106, CB = -0.110, C5 = 0.074, C8 = 0.056.

Supplementary Table 17: Partial charges at the reaction centers for the reaction of anthracenes with maleic anhydride B.

| # | Cmpd | R = R’ = | 1,4-addition endo | 9,10-addition |
|---|------|----------|-------------------|--------------|
|   |      |          | CA  | CB  | C1  | C4  | CA  | CB  | C9  | C10 |
| 1 | 1a   | H        | -0.086 | -0.086 | 0.075 | 0.075 | -0.083 | -0.083 | 0.102 | 0.102 |
| 2 | 1b   | OMe      | -0.150 | -0.076 | 0.403 | 0.030 | -0.087 | -0.087 | 0.118 | 0.117 |
| 3 | 1c   | NMe₂     | -0.201 | -0.070 | 0.273 | 0.004 | -0.083 | -0.096 | 0.107 | 0.112 |
| 4 | 1d   | N(CH₂)₄ | -0.222 | -0.057 | 0.293 | -0.003 | -0.084 | -0.084 | 0.106 | 0.101 |
| 5 | 1eᵇ  | H, N(CH₂)₄ | -0.214 | -0.065 | 0.287 | -0.004 | -0.094 | -0.078 | 0.104 | 0.093 |

ᵃ Values for 5,8-addition endo: CA = -0.089, CB = -0.087, C5 = 0.074, C8 = 0.074.
ᵇ Values for 9,10-addition are for endo case. Values for 9,10-addition exo: CA = -0.093, CB = -0.084, C9 = 0.112, C10 = 0.088.
Supplementary Table 18: Partial charges at the reaction centres for the reaction of anthracenes with maleic anhydride B.

| #  | Cmpd | R = R' = | 1,4-addition exo |
|----|------|---------|------------------|
|    |      |         | CA   | CB   | C1   | C4   |
| 1  | 1a   | H       | -0.079 | -0.079 | 0.074 | 0.074 |
| 2  | 1b   | OMe     | -0.142 | -0.066 | 0.414 | 0.020 |
| 3  | 1c   | NMe₂    | -0.185 | -0.060 | 0.272 | 0.005 |
| 4  | 1d   | N(CH₂)₄ | -0.201 | -0.059 | 0.284 | -0.003 |
| 5  | 1e   | H, N(CH₂)₄ | -0.200 | -0.057 | 0.282 | -0.002 |

* Values for 5,8-addition exo: CA = -0.079, CB = -0.080, C5 = 0.073, C8 = 0.074

Supplementary Figure 91: Assignment of the carbon atoms for the calculation of the bond orders.
13. All Obtained IRC Plots

IRC Plots with DMAD D as Dienophile

The SCF Energy was plotted against the longer critical bond length in the transition state

(a) IRCs for $R = R' = H$

**Supplementary Figure 92**

IRC Path 1,4 Addition

**Supplementary Figure 93**

IRC Path 9,10 Addition
(b) IRCs for R = R' = OMe

Supplementary Figure 94
IRC Path 1,4 Addition

Supplementary Figure 95
IRC Path 9,10 Addition
(c) IRCs for $R = R' = \text{NMe}_2$

**Supplementary Figure 96**

IRC Path 1,4 Addition

**Supplementary Figure 97**

IRC Path 9,10 Addition
IRC plots with maleic anhydride B as dienophile
(a) Plots for $R = R' = H$

Supplementary Figure 98

IRC Path 9,10 addition

Supplementary Figure 99

IRC path 1,4 addition
(b) Plots for $R = R' = \text{OMe}$

**Supplementary Figure 100**

![IRC 9,10 addition](image)

**Supplementary Figure 101**

![IRC 1,4 addition](image)
(c) Plots for $R = R' = \text{NMe}_2$

**Supplementary Figure 102**

**IRC 1,4 addition**

- SCF Energy (kcal mol$^{-1}$)
- RMS Gradient (Hartree Bohr$^{-1}$)

**Supplementary Figure 103**
(d) Plots for $R = R' =$ Pyrrolidine

![Supplementary Figure 104](image-url)
(e) Plots for $R = H$ ; $R’ = $ Pyrrolidine

**Supplementary Figure 105**

IRC 9,10 addition

![Graph showing bond length C9-CA vs. SCF Energy and RMS Gradient.](image1)

**Supplementary Figure 106**

IRC 1,4 addition

![Graph showing bond length C1-CA vs. SCF Energy and RMS Gradient.](image2)
Supplementary Figure 107

IRC 5,8 addition

**SCF Energy (kcal mol\(^{-1}\))**

**Bond length C5-CA [Å]**

*TS*

*exo-5,8 product*

*1e + B*
14. Supplementary References

1. Carreno, M. C., Ruano, J. L. & Urbanoy, A. Asymmetric Diels-Alder reactions of (S)-2-(p-tolylsulfinyl)-1,4-naphthoquinones. *J. Org. Chem.* **57**, 6870–6876 (1992).

2. Tius, M. A., Gomez-Galeno, J. & Zaidi, J. H. A Bifunctional Anthraquinone Synthon. *Tetrahedron Lett.* **29**, 6909–6912 (1988).

3. Klanderman, B. H. Novel Products from the Reaction of Benzyne with Anthracenes. *J. Am. Chem. Soc.* **87**, 4649–4651 (1965); 10.1021/ja00948a049.

4. Verma, S. M. & Singh, M. D. Structural elucidation with nuclear magnetic resonance spectroscopy. Diels-Alder adducts of 1-aminoanthracene and maleic anhydride: restricted rotation about the aryl C(1)-N bond and intrinsic asymmetry about the imide (Nsp2-Csp3) system. *J. Org. Chem.* **42**, 3736–3740 (1977).

5. Bouffard, J., Eaton, R. F., Müller, P. & Swager, T. M. Iptycene-derived pyridazines and phthalazines. *J. Org. Chem.* **72**, 10166–10180 (2007); 10.1021/jo702000d.

6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. *Gaussian 09, Revision E.01* (Gaussian, Inc., Wallingford CT, 2013).

7. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).

8. Krishnan, R., Binkley, J. S., Seeger, R. & Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **72**, 650–654 (1980); 10.1063/1.438955.

9. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993); 10.1063/1.464913.

10. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Phys. Chem. B* **132**, 154104 (2010); 10.1063/1.3382344.

11. Mulliken, R. S. Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I. *J. Chem. Phys.* **23**, 1833–1840 (1955); 10.1063/1.1740588.

12. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold as implemented in Gaussian09.E01.
13. Foster, J. P. & Weinhold, F. Natural hybrid orbitals. *J. Am. Chem. Soc.* **102**, 7211–7218 (1980).

14. Reed, A. E., Weinstock, R. B. & Weinhold, F. Natural population analysis. *J. Chem. Phys.* **83**, 735–746 (1985); 10.1063/1.449486.

15. Reed, A. E. & Weinhold, F. Natural localized molecular orbitals. *J. Chem. Phys.* **83**, 1736–1740 (1985); 10.1063/1.449360.

16. Reed, A. E., Curtiss, L. A. & Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **88**, 899–926 (1988).

17. Pauling, L. Atomic Radii and Interatomic Distances in Metals. *J. Am. Chem. Soc.* **69**, 543–553 (1947).

18. Houk, K. N., Gustafson, S. M. & Black, K. A. Theoretical secondary kinetic isotope effects and the interpretation of transition state geometries. 1. The Cope rearrangement. *J. Am. Chem. Soc.* **114**, 8565–8572 (1992).

19. Marcus, R. A. Theoretical relations among rate constants, barriers, and Broensted slopes of chemical reactions. *J. Phys. Chem.* **72**, 891–899 (1968).

20. Follet, E., Mayer, P. & Mayr, H. Lewis Acidities of Indol-3-ylmethylium Ions and Intrinsic Barriers of Their Reactions with Phosphines and Pyridines. *Eur. J. Org. Chem.* **2016**, 4050–4058 (2016); 10.1002/ejoc.201600572.