Supporting Information for
Rapid and Efficient Microwave-Assisted Copper(0)-Catalyzed
Ullmann Coupling Reaction: General Access to
Anilinoanthraquinone Derivatives

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Experimental

General: All materials were used as purchased (Sigma-Aldrich or Acros, Germany). Thin-layer chromatography was performed using TLC aluminum sheets silica gel 60 F₂₅₄, or TLC aluminum sheets RP silica gel 18 F₂₅₄ (Merck, Darmstadt, Germany). Colored compounds were visible at daylight; other compounds were visualized under UV light (254 nm). Flash chromatography was performed on a Büchi system using silica gel RP-18 (Merck, Darmstadt, Germany). ¹H- and ¹³C-NMR data were collected on a Bruker Avance 500 MHz NMR spectrometer at 500 MHz (¹H), or 126 MHz (¹³C), respectively. DMSO-d₆ was used as a solvent. Chemical shifts are reported in parts per million (ppm) relative to the deuterated solvent, i. e. DMSO, δ ¹H: 2.49 ppm, ¹³C: 39.7 ppm, coupling constants *J* are given in Hertz and spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The purities of isolated products were determined by ESI–mass spectra obtained on an LCMS instrument (Applied Biosystems API 2000 LCMS/MS, HPLC Agilent 1100) using the following procedure: the compounds were dissolved at a concentration of 0.5 mg/ml in H₂O : MeOH = 1 : 1, containing 2 mM NH₄CH₃COO. Then, 10 µl of the sample was injected into an HPLC column (Phenomenix Luna 3µ C18, 50 x 2.00 mm). Elution was performed with a gradient of water : methanol (containing 2 mM NH₄CH₃COO) from 90 : 10 to 0 : 100 for 30 min at a flow rate of 250 µl/min, starting the gradient after 10 min. UV absorption was detected from 200 to 950 nm using a diode array detector. Purity of the compounds was determined at 254 nm. For

microwave reactions a CEM FocusedTM Microwave Synthesis type Discover apparatus was used. A freeze dryer (CHRIST ALPHA 1-4 LSC) was used for lyophilization.

General procedures

The anilinoanthraquinone derivatives **3a-z** were synthesized by the Ullmann coupling reaction using six different protocols (standard heating procedures A, B, C, and microwave heating procedures A^{MW}, B^{MW}, C^{MW}).

General procedure A (copper(I) chloride as a catalyst).¹ Sodium 1-amino-4-bromo-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (bromaminic acid sodium salt, **1**) (0.808 g, 2.0 mmol) and the appropriate aniline derivative (**2a-g**, **2i-j**, 3.0 mmol) were added to a stirred solution of Na₂CO₃ (0.500 g) and Na₂SO₃ (0.400 g) in water (50 mL) at rt. CuCl (0.050 g) was added and the mixture was stirred for ca. 8 h. The progress of the reaction was monitored by reverse phase TLC using a mobile phase of methanol : water (2 : 3). After completion of the reaction the solution was filtered and the residue was washed with water (3 x 20 mL) and subsequently with methanol (3 x 20 mL). The combined filtrates were evaporated. The residue was purified by flash column chromatography on RP-18 silica gel using a mixture of methanol : water (1 : 3) as an eluent. Higher reaction temperatures (up to 120°C) as in the procedure described by Pearson et al.³ reduced the reaction times but also led to a reduction in the yields of the products along with the formation of higher amounts of by-products.

Microwave-assisted procedure A^{MW} (copper(I) chloride as a catalyst). To a 5 mL microwave reaction vial equipped with a magnetic stirring bar were added bromaminic acid sodium salt (**1**, 0.081 g, 0.20 mmol), *p*-hydroxyaniline (**2j**, 0.066 g, 0.60 mmol), Na₂CO₃ (0.050 g) and Na₂SO₃ (0.040 g) followed by 5 mL of water. A catalytic amount (ca. 0.003-0.005 g) of copper(I) chloride was added. The mixture was irradiated in a microwave oven under various conditions, at 40-100 W for 3-30 min at 80-120 °C. Then the reaction mixture was cooled to rt. RP-TLC did not show any blue spot for the product (**3j**), but indicated the formation of the degradation product **4** (1-amino-4-hydroxy-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate) of starting compound **1**. Since heating had never improved yields in the classical method

A, microwave (A^{MW}) was only applied in one example (**3j**) where it proved to be unsuccessful.

General procedure B (copper(II) sulfate as a catalyst).² Bromaminic acid sodium salt (**1**, 0.500 g, 1.25 mmol), Na_2CO_3 (0.175 g) and $CuSO_4$ (0.030 g) were dissolved in 10 mL of water. Then the appropriate aniline derivative (**2a-g**, **2i-j**, 5-10 mmol) was added and the reaction mixture was heated for 10-20 hours at 60-120°C. After completion of the reaction the solution was filtered and the residue was washed with 10 mL of water and subsequently with 200 mL of dichloromethane until the filtrate became colorless. The combined filtrates were evaporated under vacuum. The residue was purified by flash column chromatography on normal silica gel and subsequently on RP-18 silica gel using different solvents as eluents as described below. Some compounds were purified directly on RP-18 silica gel without prior normal phase silica gel chromatography.

Microwave-assisted procedure B^{MW} (copper(II) sulfate as a catalyst).

To a 5 mL microwave reaction vial equipped with a magnetic stirring bar were added bromaminic acid sodium salt (**1**, 0.081 mg, 0.20 mmol), the appropriate aniline derivative (0.60 mmol), Na_2CO_3 (0.0175 g) and $CuSO_4$ (0.005 g) followed by 5 mL of water. The mixture was irradiated in the microwave oven (40-100 W) for 3-30 min at 80-120 °C. After completion of the reaction the mixture was cooled to rt, filtered and the residue was washed with 200 mL of water, and subsequently extracted with chloroform (200 mL each) until the chloroform layer became colorless (2-3 times). The water layer was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel followed by chromatography on RP-18 silica gel using different solvents as eluents as described below. Some compounds were directly purified on RP-18 silica gel without prior normal phase silica gel chromatography. The water was removed using lyophilization to yield **3d-f**, **3i**, and **3j** (5-60%) as blue solids.

General procedure C (elemental copper powder (Cu^0) as a catalyst).³

Bromaminic acid sodium salt (**1**, 0.081 g, 0.20 mmol) and the appropriate aniline derivative (**2a-j** 0.40 mmol) were dissolved in 10 ml of a buffer solution prepared from 8 ml of a 0.2 M aq. Na_2HPO_4 solution (pH 9.6) and 2 ml of a 0.12 M NaH_2PO_4

(pH 4.2). The pH value of the resulting solution was adjusted to pH 6-7 either by the addition of Na_2HPO_4 or of NaH_2PO_4 solution. Then ca. 0.003 g of Cu^0 powder was added to the solution, and the reaction mixture was heated at 120 °C for ca. 2-15 h. After completion of the reaction the solution was filtered and the residue was washed with water. The combined filtrates were evaporated under vacuum. The residue was purified by flash column chromatography on normal silica gel and/or RP-18 silica gel.

Microwave-assisted procedure C^{MW} (elemental copper powder (Cu^0) as a catalyst).

To a 5 mL microwave reaction vial equipped with a magnetic stirring bar were added bromaminic acid sodium salt (**1**, 0.081 g, 0.20 mmol) and the appropriate aniline derivative (**2a-z**, 0.40 mmol), followed by a buffer solution of Na_2HPO_4 (pH 9.6) (4 mL) and NaH_2PO_4 (pH 4.2) (1 mL). A catalytic amount (ca. 0.002-0.003 g) of finely powdered elemental copper was added. The mixture was capped and irradiated in the microwave oven (40-100 W) for 2-20 min at 80-120 °C. Then the reaction mixture was cooled to rt, and the product was purified using the following procedure. The contents of the vial were filtered to remove the elemental copper. Then ca. 200 mL of water was added to the filtrate and the aqueous solution was extracted with chloroform (200 mL). The extraction procedure was repeated until the chloroform layer became colorless (2-3 times). Then the aqueous layer was reduced by rotary evaporation to a volume of 10-20 mL, which was subsequently submitted to flash column chromatography using RP-18 silica gel and water as an eluent. The polarity of the eluent was then gradually decreased by the addition of methanol in the following steps: 20, 40, 60, 80, and 100 %. Fractions containing blue product were collected. For some compounds the last step of purification (RP-18 flash chromatography) had to be repeated two to three times to obtain pure product ($\geq 95\%$ purity as determined by LC-MS). The pooled product-containing fractions were evaporated under vacuum to remove the methanol, and the remaining water was subsequently removed by lyophilization to yield **3a-z** (30-90%) as blue powders.

Spectral data of the synthesized compounds (3a-z):

Sodium 1-amino-4-(3-amino-5-carboxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3a):⁴

Reaction conditions: 20 min, 120 °C, 100 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. ¹H-NMR: δ 5.29 (bs, 2H, 3'-NH₂), 6.53 (dd, 1H, 6'-H), 7.03 (d, 1H, 2'-H), 7.08 (d, 1H, 4'-H), 7.83 (m, 2H, 6-H, 7-H), 7.96 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.13 (br, 2H, 1-NH₂), 12.04 (s, 1H, 4-NH). ¹³C-NMR: δ 109.05 (C-9a), 110.75 (C-4a), 110.93, 112.33, 112.51 (C-2', C-4', C-6'), 123.40 (C-3), 126.07 (C-5), 126.15 (C-8), 132.86 (C-6), 133.17 (C-7), 133.83 (C-10a), 134.29 (C-8a), 139.11 (C-1'), 142.12 (C-4), 142.94 (C-2, C-5'), 144.35 (C-1), 149.77 (C-3'), 172.50 (COOH), 181.78 (C-9), 182.14 (C-10). **LC-MS (m/z):** 471 [M-Na+NH₄⁺]⁺, 454 [M-Na]⁺, 452 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(3-carboxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3b):⁵

Reaction conditions: 20 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. ¹H-NMR: δ 7.38 (dd, 1H, 6'-H), 7.47 (dd, 1H, 5'-H), 7.76 (dd, 1H, 4'-H), 7.84 (m, 3H, 2'-H, 6-H, 7-H), 7.97 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.00 (br, 2H, 1-NH₂), 12.69 (s, 1H, 4-NH). ¹³C-NMR: δ

109.35 (C-9a), 111.72 (C-4a), 122.81 (C-3), 124.05 (C-2'), 125.45 (C-5), 125.62 (C-8), 126.11, 126.19 (C-4', C-6'), 129.38 (C-5'), 132.94 (C-6), 133.35 (C-7), 133.72 (C-10a), 134.30 (C-8a), 139.18 (C-1'), 140.95 (C-4), 142.91 (C-2), 144.51 (C-1), 145.21 (C-3'), 169.63 (COOH), 182.00 (C-9), 182.71 (C-10). **LC-MS (m/z):** 439 [M-Na]⁺, 437 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 96%.

Sodium 1-amino-4-(4-carboxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3c):⁶

Reaction conditions: 20 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.17 (d, 2H, 2'-H, 6'-H), 7.84 (m, 2H, 6-H, 7-H), 7.93 (d, 2H, 3'-H, 5'-H), 8.07 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.22 (br, 2H, 1-NH₂), 12.07 (s, 1H, 4-NH). **¹³C-NMR:** 109.28 (C-9a), 111.62 (C-4a), 121.43 (C-2', C-6'), 123.11 (C-3), 126.11 (C-5), 126.17 (C-8), 130.64 (C-3', C-5'), 132.91 (C-6), 133.29 (C-7), 133.74 (C-10a), 134.29 (C-8a), 136.59 (C-4'), 139.77 (C-1'), 140.78 (C-4), 142.85 (C-2), 144.53 (C-1), 169.78 (COOH), 181.93 (C-9), 182.56 (C-10). **LC-MS (m/z):** 439 [M-Na]⁺, 437 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 98%.

Sodium 1-amino-4-(2-aminophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3d):⁷

Reaction conditions: 20 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 5.02 (bs, 2H, 2'-NH₂), 6.62 (ddd, 1H, 4'-H), 6.84 (dd, 1H, 3'-H), 7.01 (m, 2H, 5'-H, 6'-H), 7.61 (s, 1H, 3-H), 7.83 (m, 2H, 6-H, 7-H), 8.27 (m, 2H, 5-H, 8-H), 10.15 (br, 2H, 1-NH₂), 11.67 (s, 1H, 4-NH). **¹³C-NMR:** 109.10 (C-9a), 110.58 (C-4a), 115.77, 116.72 (C-4', C-5'), 123.22 (C-3), 123.70, 126.01, 126.12, 126.64 (C-5, C-8, C-6', C-3'), 127.06 (C-1'), 132.71 (C-6), 132.93 (C-7), 133.96 (C-10a), 134.33 (C-8a), 143.08 (C-4), 143.66 (C-2), 144.26 (C-1), 144.28 (C-2'), 181.67 (C-9), 181.92 (C-10). **LC-MS (m/z):** 410 [M-Na]⁺, 408 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(3-aminophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3e):⁸

Reaction conditions: 2 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 5.28 (bs, 2H, 3'-NH₂), 6.42 (m, 3H, 2'-H, 4'-H, 6'-H), 7.06 (dd, 1H, 5'-H), 7.83 (m, 2H, 6-H, 7-H), 8.02 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.12 (br, 2H, 1-NH₂), 12.03 (s, 1H, 4-NH). **¹³C-NMR:** 108.69, 109.02, 110.76, 110.83, 110.95 (C-9a, C-4a, C-2', C-4', C-6'), 123.39 (C-3), 126.05 (C-5), 126.13 (C-8), 130.06 (C-5'), 132.79 (C-6), 133.10 (C-7), 133.82 (C-10a), 134.29 (C-8a), 139.76 (C-1'), 141.86 (C-4), 143.03 (C-2), 144.39 (C-1), 150.27 (C-3'), 181.74 (C-9), 182.11 (C-10). **LC-MS (m/z):** 410 [M-Na]⁺, 408 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(2-carboxy-4-chlorophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3f):⁹

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.13 (d, 1H, 6'-H), 7.29 (dd, 1H, 5'-H), 7.81 (m, 2H, 6-H, 7-H), 7.90 (d, 1H, 3'-H), 8.11 (s, 1H, 3-H), 8.22 (m, 2H, 5-H, 8-H), 9.97 (br, 2H, 1-NH₂), 12.72 (s, 1H, 4-NH). **¹³C-NMR:** δ 110.28 (C-9a), 115.81 (C-4a), 121.00 (C-3), 124.35, 126.08, 126.14 (C-2', C-4', C-6'), 125.43 (C-5, C-8), 129.50, 131.15 (C-5', C-3'), 32.92 (C-6), 133.23 (C-7), 133.93 (C-10a), 134.20 (C-8a), 136.71 (C-1'), 140.04 (C-4), 141.22 (C-2) 144.91 (C-1), signal for COOH not detectable (too broad and flat), 181.80 (C-9), 182.54 (C-10). **LC-MS (m/z):** 439 [M-Na]⁺, 437 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(2-carboxy-5-chlorophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3g):

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 6.92 (d, 1H, 6'-H), 7.05 (d, 1H, 4'-H), 7.70 (d, 1H, 3'-H), 7.80 (m, 2H, 6-H, 7-H), 8.12 (s, 1H, 3-H), 8.21 (m, 2H, 5-H, 8-H), 9.93 (br, 2H, 1-NH₂), 12.65 (s, 1H, 4-NH). **¹³C-NMR:** δ 110.58 (C-9a), 117.22, 117.50 (C-4a, C-2', C-4'), 120.02 (C-3), 125.90 (C-5'), 126.13, 126.19 (C-6', C-5, C-8) 132.91 (C-6), 133.48 (C-7), 133.78 (C-10a), 134.18 (C-8a), 135.05, 135.39

(C-3', C-1'), 141.01 (C-4), 143.26 (C-2), 145.21 (C-1), signal for COOH not detectable (too broad and flat), 182.36 (C-9), 182.69 (C-10). **LC-MS (m/z):** 473 [M-Na]⁺, 471 [M-Na]. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(2-carboxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3h):¹⁰

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. ¹**H-NMR:** 6.67 (dd, 1H, 4'-H), 7.13 (d, 1H, 6'-H), 7.30 (d, 1H, 5'-H), 7.80 (m, 2H, 6-H, 7-H), 8.15 (s, 1H, 3-H), 8.23 (m, 2H, 5-H, 8-H), 10.00 (br, 2H, 1-NH₂), 12.69 (s, 1H, 4-NH). ¹³**C-NMR:** 110.12 (C-9a), 115.18 (C-4a), 119.75 (C-2'), 121.24 (C-3), 125.31, 126.06, 126.21 (C-6', C-4', C-5, C-8), 130.73, 131.88 (C-5', C-3'), 132.76 (C-6), 133.20 (C-7), 133.91 (C-10a), 134.23 (C-8a), 137.34 (C-1'), 140.98 (C-4), 141.40 (C-2), 144.89 (C-1), signal for COOH not detectable (too broad and flat), 181.88 (C-9), 182.37 (C-10). **LC-MS (m/z):** 439 [M-Na]⁺, 437 [M-Na]. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(2-hydroxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3i):

Reaction conditions: 10 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. ¹H-NMR: δ 6.86 (ddd, 1H, 4'-H), 6.99 (dd, 1H, 6'-H), 7.04 (ddd, 1H, 5'-H), 7.21 (dd, H, 3'-H), 7.83 (m, 2H, 6-H, 7-H), 7.93 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 9.87 (br, 2H, 1-NH₂), 10.15 (br, 1H, 2'-OH), 11.92 (s, 1H, 4-NH). ¹³C-NMR: 109.19 (C-9a), 110.97 (C-4a), 116.30, 119.55, 123.24, 123.91, 125.60, 126.03, 126.12, 126.67 (C-1', C-3', C-4', C-5', C-6', C-3, C-5, C-8), 132.79 (C-6), 133.23 (C-7), 133.88 (C-10a), 134.28 (C-8a), 141.66 (C-4), 142.78 (C-2), 144.29 (C-1), 150.65 (C-2'), 181.81 (C-9), 181.99 (C-10). **LC-MS (m/z):** 411 [M-Na]⁺, 409 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 96%.

Sodium 1-amino-4-(4-hydroxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3j):¹¹

Reaction conditions: 10 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. ¹H-NMR: δ 6.82 (d, 2H, 2'-H, 6'-H), 7.08 (d, 2H, 3'-H, 5'-H), 7.81 (s, 1H, 3-H), 7.83 (m, 2H, 6-H, 7-H), 8.27 (m, 2H, 5-H, 8-H), 10.15 (br, 2H, 1-NH₂), 12.05 (s, 1H, 4-NH). ¹³C-NMR: δ 108.97 (C-9a), 110.03 (C-4a), 116.39 (C-2', C6'), 122.93 (C-3), 125.98 (C-5), 126.13 (C-8), 126.36 (C-3', C5'), 129.98 (C-1'), 132.75 (C-6), 132.96 (C-7), 133.90 (C-10a), 134.29 (C-8a), 143.22 (C-4), 143.25 (C-2), 144.19 (C-1), 155.52 (C-4'), 181.69 (C-9), 181.70 (C-10). **LC-MS (m/z):** 411 [M-Na]⁺, 409 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(4-aminophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3k):¹²

Reaction conditions: 5 min, 100 °C, 60 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 5.17 (bs, 2H, 4'-NH₂), 6.64 (d, 2H, 2'-H, 6'-H), 6.94 (d, 2H, 3'-H, 5'-H), 7.81 (s, 1H, 3-H), 7.82 (m, 2H, 6-H, 7-H), 8.27 (m, 2H, 5-H, 8-H), 10.17 (br, 2H, 1-NH₂), 12.09 (s, 1H, 4-NH). **¹³C-NMR:** δ 108.84 (C-9a), 109.52 (C-4a), 114.78 (C-2', C6'), 122.85 (C-3), 125.93 (C-5), 126.09 (C-8), 126.14, 126.82 (C-3', C5', C-1'), 132.65 (C-6), 132.75 (C-7), 133.99 (C-10a), 134.26 (C-8a), 143.24 (C-4), 143.88 (C-2), 144.15 (C-1), 147.08 (C-4'), 181.17 (C-9), 181.52 (C-10). **LC-MS (m/z):** 432 [M]⁺, 427 [M-Na+NH₄⁺]⁺, 410 [M-Na]⁺, 408 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-9,10-dioxo-4-phenylamino-9,10-dihydroanthracene 2-sulfonate (3l):¹³

Reaction conditions: 5 min, 80 °C, 40 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.20 (ddd, 1H, 4'-H), 7.28 (dd, 2H, 2'-H, 6'-H), 7.44 (ddd, 2H, 3'-H, 5'-H), 7.84 (m, 2H, 6-H, 7-H), 8.02 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 12.04 (s, 1H, 4-NH). **¹³C-NMR:** δ 109.30 (C-9a), 111.56 (C-4a), 122.82 (C-3), 123.20 (C-2', C6'), 124.58 (C-4'), 126.09 (C-5), 126.17 (C-8), 129.84 (C-3', C5'), 132.90 (C-6), 133.30 (C-7), 133.72

(C-10a), 134.29 (C-8a), 139.41 (C-1'), 140.93 (C-4), 142.95 (C-2), 144.50 (C-1), 181.94 (C-9), 182.62 (C-10). **LC-MS (m/z):** 395 [M-Na]⁺, 393 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 98%.

Sodium 1-amino-4-(4-chlorophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3m):⁷

Reaction conditions: 5 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.30 (d, 2H, 2'-H, 6'-H), 7.47 (d, 2H, 3'-H, 5'-H), 7.85 (m, 2H, 6-H, 7-H), 7.96 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.05 (br, 2H, 1-NH₂), 11.87 (s, 1H, 4-NH). **¹³C-NMR:** δ 109.46 (C-9a), 112.24 (C-4a), 122.79 (C-3), 124.61 (C-2', C6'), 126.08 (C-2'), 126.20 (C-5), 126.20 (C-8), 128.18 (C-4'), 129.70 (C-3' and C-5'), 133.00 (C-6), 133.47 (C-7), 133.63 (C-10a), 134.28 (C-8a), 138.66 (C-1'), 140.15 (C-4), 142.80 (C-2), 144.59 (C-1), 182.08 (C-9), 182.94 (C-10). **LC-MS (m/z):** 446 [M-Na+NH₄⁺]⁺, 429 [M-Na]⁺, 427 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 96%.

Sodium 1-amino-4-(4-carboxymethylphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3n):

Reaction conditions: 10 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 3.24 (s, 2H, CH₂), 7.12 (d, 2H, 2'-H, 6'-H), 7.30 (d, 2H, 3'-H, 5'-H), 7.84 (m, 2H, 6-H, 7-H), 7.99 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.12 (br, 2H, 1-NH₂), 12.12 (s, 1H, 4-NH). **¹³C-NMR:** δ 45.83 (CH₂), 109.11 (C-9a), 110.75 (C-4a), 122.78 (C-3), 122.99 (C-2', C6'), 126.05 (C-5), 126.15 (C-8), 130.49 (C-3', C-5'), 132.82 (C-6), 133.11 (C-7), 133.83 (C-10a), 134.30 (C-8a), 136.00, 137.11 (C-4', C-1'), 141.93 (C-4), 143.10 (C-2), 144.38 (C-1), 174.50 (COOH), 181.78 (C-9), 182.10 (C-10). **LC-MS (m/z):** 470 [M-Na+NH₄⁺]⁺, 453 [M-Na]⁺, 451 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-9,10-dioxo-4-(2,4,6-trimethylphenylamino)-9,10-dihydroanthracene 2-sulfonate (3o):¹⁴

Reaction conditions: 5 min, 120 °C, 100 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 2.10 (s, 6H, 2'-CH₃, 6'-CH₃), 2.30 (s, 3H, 4'-CH₃), 7.03 (s, 2H, 3'-H, 5'-H), 7.13 (s, 1H, 3-H), 7.84 (m, 2H, 6-H, 7-H), 8.29 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 11.73 (s, 1H, 4-NH). **¹³C-NMR:** δ 20.71 (C4'-CH₃), 18.10 (C2'-CH₃, C3'-CH₃), 109.20 (C-9a), 109.49 (C-4a), 121.92 (C-3), 126.04 (C-5), 126.16 (C-8), 129.38 (C-3' and C-5'), 132.77 (C-6), 133.02 (C-7), 133.43 (C-4'), 133.82 (C-10a), 134.32 (C-8a), 135.30 (C-2', C6'), 136.20 (C-1'), 143.59 (C-4), 143.86 (C-2), 144.08 (C-1), 181.77 (C-9), 182.18 (C-10). **LC-MS (m/z):** 454 [M-Na+NH₄⁺]⁺, 437 [M-Na]⁺, 435 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Sodium 1-amino-4-(2-methoxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3p):⁷

Reaction conditions: 5 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 3.86 (s, 3H, 3'-OCH₃), 7.01 (ddd, 1H, 4'-H), 7.17 (m, 2H, 5'-H, 6'-H), 7.29 (dd, 1H, 3'-H), 7.84 (m, 2H, 6-H, 7-H), 7.96 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 11.92 (s, 1H, 4-NH). **¹³C-NMR:** δ 55.93 (C3'-OCH₃), 109.31 (C-9a), 111.56 (C-4a), 112.38, 120.93, 122.88, 123.06 (C-3', C6', C-3 C-4'), 125.32 (C-5), 126.11 (C-8), 126.15 (C-5'), 128.07 (C-6), 132.86 (C-7), 133.20 (C-10a), 133.80 (C-8a), 134.29 (C-1'), 140.81 (C-4), 142.72 (C-2), 144.38 (C-1), 151.99 (C-2'), 181.92 (C-9), 182.37 (C-10). **LC-MS (m/z):** 442 [M-Na+NH₄⁺]⁺, 425 [M-Na]⁺, 423 [M-Na]⁻. Purity by **HPLC-UV (254 nm)**-ESI-MS: 98%.

Sodium 1-amino-4-(3-methoxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3q):¹⁵

Reaction conditions: 5 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 3.78 (s, 3H, 3'-OCH₃), 6.75 (dd, 1H, 4'-H), 6.85 (m, 2H, 2'-H, 6'-H), 7.33 (dd, 1H, 5'-H), 7.85 (m, 2H, 6-H, 7-H), 8.09 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 11.99 (s, 1H, 4-NH). **¹³C-NMR:** δ 55.33 (C3'-OCH₃), 108.41, 110.34, (C-2', C4'), 109.32 (C-9a), 111.77 (C-4a), 115.08 (C-6'), 123.23 (C-3), 126.10 (C-5), 126.18 (C-8), 130.54 (C-

5'), 132.93 (C-6), 133.35 (C-7), 133.69 (C-10a), 134.29 (C-8a), 140.61 (C-1'), 140.71 (C-4), 142.81 (C-2), 144.52 (C-1), 160.51 (C-3'), 181.97 (C-9), 182.69 (C-10). **LC-MS (m/z):** 442 [M-Na+NH₄⁺]⁺, 425 [M-Na]⁺, 423 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS: 100%**.

Sodium 1-amino-4-(4-methoxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3r):⁷

Reaction conditions: 5 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 3.80 (s, 3H, 4'-OCH₃), 7.03 (d, 2H, 2'-H, 6'-H), 7.22 (d, 2H, 3'-H, 5'-H), 7.83 (m, 2H, 6-H, 7-H), 7.84 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 12.04 (s, 1H, 4-NH). **¹³C-NMR:** δ 55.49 (C4'-OCH₃), 109.07 (C-9a), 110.43 (C-4a), 115.13 (C-2', C6'), 122.57 (C-3), 126.03, 126.15, (C-5, C-8, C-3', C-5'), 131.77 (C-6), 132.81 (C-7), 133.08 (C-10a), 133.84 (C-8a), 134.30 (C-1'), 142.71 (C-4), 143.19 (C-2), 144.26 (C-1), 157.05 (C-4') 181.77 (C-9), 181.99 (C-10). **LC-MS (m/z):** 442 [M-Na+NH₄⁺]⁺, 425 [M-Na]⁺, 423 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS: 100%**.

Sodium 1-amino-4-(4-fluorophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3s):

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.31 (m, 4H, 2'-H, 3'-H, 5'-H, 6'-H), 7.84 (m, 2H, 6-H, 7-H), 7.88 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.07 (br, 2H, 1-NH₂), 11.94 (s, 1H, 4-NH). **¹³C-NMR:** δ 109.26 (C-9a), 111.32 (C-4a), 116.48, 116.65 (d, *J* = 22.5 Hz, C-2', C6'), 122.47 (C-3), 125.85 (C-5), 125.92 (C-8), 126.07, 126.18 (d, *J* = 14.0 Hz, C-3', C-5'), 132.92 (C-6), 133.31 (C-7), 133.71 (C-10a), 134.30 (C-8a), 135.73 (C-1'), 141.50 (C-4), 143.06 (C-2), 144.40 (C-1), 158.46, 160.39 (d, *J* = 242.3 Hz, C-4') 181.96 (C-9), 182.58 (C-10). **LC-MS (m/z):** 430 [M-Na+NH₄⁺]⁺, 413 [M-Na]⁺, 411[M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

Sodium 1-amino-4-(3-bromophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3t):

Reaction conditions: 20 min, 120 °C, 100 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.27 (dd, 1H, 4'-H), 7.33 (dd, 1H, 6'-H), 7.35 (dd, 1H, 5'-H), 7.49 (dd, 1H, 2'-H), 7.85 (m, 2H, 6-H, 7-H), 8.00 (s, 1H, 3-H), 8.26 (m, 2H, 5-H, 8-H), 10.03 (br, 2H, 1-NH₂), 11.78 (s, 1H, 4-NH). **¹³C-NMR:** δ 109.58 (C-9a), 112.89 (C-4a), 121.36, 122.52 (C-2', C6'), 123.07 (C-3), 124.97 (C-4'), 126.15, 126.22, 126.67 (C-5, C-8, C-5'), 131.53 (C-6), 133.04 (C-7), 133.57 (C3', C-10a), 134.27 (C-8a), 139.37 (C-1'), 141.96 (C-4), 142.62 (C-2), 144.72 (C-1), 182.18 (C-9), 183.19 (C-10). **LC-MS (m/z):** 490 [M-Na+NH₄⁺]⁺, 473 [M-Na]⁺, 471 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

Sodium 1-amino-4-(3,5-dimethylphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3u):

Reaction conditions: 5 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 2.29 (s, 6H, 3'-CH₃, 5'-CH₃), 6.85 (s, 1H, 4'-H), 6.89 (s, 2H, 2'-H, 6'-H), 7.84 (m, 2H, 6-H, 7-H), 7.99 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 12.01 (s, 1H, 4-NH). **¹³C-NMR:** δ 21.07 (C3'-CH₃, C5'-CH₃), 109.18 (C-9a), 111.21 (C-4a), 121.18 (C-2', C6'), 123.11 (C-3), 126.07 (C-4'), 126.16, 126.42 (C-5, C-8), 132.87 (C-6), 133.23 (C-7), 133.76 (C-10a), 134.29 (C-8a), 139.05 (C-3' and C-5'), 139.16 (C-1'), 141.40 (C-4), 142.95 (C-2), 144.42 (C-1), 181.87 (C-9), 182.40 (C-10). **LC-MS (m/z):** 440 [M-Na+NH₄⁺]⁺, 422 [M-Na]⁺, 420 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

Sodium 1-amino-4-(3-chlorophenylamino)-9,10-dioxo-9,10-dihydro-anthracene 2-sulfonate (3v):⁷

Reaction conditions: 5 min, 100 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 7.20 (dd, 1H, 6'-H), 7.23 (dd, 1H, 4'-H), 7.35 (dd, 1H, 2'-H), 7.43 (dd, 1H, 5'-H), 7.85 (m, 2H, 6-H, 7-H), 8.00 (s, 1H, 3-H), 8.24 (m, 2H, 5-H, 8-H), 10.02 (br, 2H, 1-NH₂), 11.78 (s, 1H, 4-NH). **¹³C-NMR:** δ 109.59 (C-9a), 112.90 (C-4a), 120.96 (C-6'), 122.09 (C-3), 123.10,

123.77 (C-2', C-4'), 126.16 (C-5), 126.22 (C-8), 131.28 (C-6), 133.05 (C-7), 133.58 (C-3', C-5') 134.13 (C-10a), 134.28, (C-8a), 139.37 (C-1'), 141.56 (C-4), 142.62 (C-2), 144.72 (C-1), 182.19 (C-9), 183.20 (C-10). **LC-MS (m/z):** 439 [M-Na]⁺, 437 [M-Na]⁻. **LC-MS (m/z):** 446 [M-Na+NH₄⁺]⁺, 429 [M-Na]⁺, 427 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS: 95%**.

Sodium 1-amino-4-(3-amino-2-methylphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3w):¹⁶

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 1.99 (s, 3H, C2'-CH₃), 5.05 (bs, 2H, 3'-NH₂), 6.44 (d, 1H, 6'-H), 6.59 (d, 1H, 4'-H), 6.96 (dd, 1H, 5'-H), 7.66 (s, 1H, 3-H), 7.83 (m, 2H, 6-H, 7-H), 8.28 (m, 2H, 5-H, 8-H), 10.17 (br, 2H, 1-NH₂), 12.04 (s, 1H, 4-NH). **¹³C-NMR:** δ 11.84 (C2'-CH₃), 108.90 (C-9a), 109.96 (C-4a), 112.21 (C-6'), 113.66 (C-4'), 116.45 (C-2'), 123.14 (C-3), 126.03 (C-5), 126.13 (C-8), 126.65 (C-5'), 132.72 (C-6), 132.98 (C-7), 133.89 (C-10a), 134.33 (C-8a), 137.58 (C-1'), 143.22 (C-4), 143.44 (C-2), 144.16 (C-1), 148.27 (C-3'), 181.63 (C-9), 181.92 (C-10). **LC-MS (m/z):** 441 [M-Na+NH₄⁺]⁺, 424 [M-Na]⁺, 422 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS: 96%**.

Sodium 1-amino-4-(3-carboxy-4-hydroxyphenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3x):

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** δ 6.70 (d, 1H, 5'-H), 7.07 (dd, 1H, 6'-H), 7.53 (d, 1H, 2'-H), 7.75 (s, 1H, 3-H), 7.82 (m, 2H, 6-H, 7-H), 8.27 (m, 2H, 5-H, 8-H), 10.18 (br, 2H, 1-NH₂), 12.07 (s, 1H, 4-NH). **¹³C-NMR:** δ 108.86 (C-9a), 114.37 (C-4a), 116.96 (C-2'), 122.74 (C-3), 125.98 (C-5), 126.09 (C-8), 126.67 (C-6'), 128.87 (C-5'), 132.66 (C-6), 132.80 (C-7), 132.93 (C-3'), 133.59 (C-10a), 134.29 (C-8a), 134.62 (C-1'), 143.30 (C-4), 143.96 (C-2), 144.15 (C-1), 161.45 (C-4') 170.76 (COOH), 181.40 (C-9), 181.59 (C-10). **LC-MS (m/z):** 472 [M-Na+NH₄⁺]⁺, 455 [M-Na]⁺, 453 [M-Na]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

Disodium 1-amino-4-(2-sulfophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3y):^{1a}

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. **¹H-NMR:** 7.02 (ddd, 1H, 4'-H), 7.13 (dd, 1H, 6'-H), 7.28 (ddd, 1H, 5'-H), 7.75 (dd, 1H, 3'-H), 7.80 (m, 2H, 6-H, 7-H), 7.99 (s, 1H, 3-H), 8.23 (m, 2H, 5-H, 8-H), 10.03 (br, 2H, 1-NH₂), 11.78 (s, 1H, 4-NH). **¹³C-NMR:** 109.72 (C-9a), 113.42 (C-4a), 122.32 (C-4'), 122.69 (C-6'), 124.86 (C-3), 126.05 (C-5), 126.09 (C-8), 128.01 (C-3'), 129.45 (C-5'), 132.84 (C-6), 132.98 (C-7), 133.99 (C-10a), 134.24 (C-8a), 137.43 (C-1'), 139.14 (C-4), 139.59 (C-2'), 141.67 (C-2), 144.62 (C-1), 181.51 (C-9), 182.25 (C-10). **LC-MS (m/z):** 497 [M-Na]⁺, 495 [M-Na]⁻, 475 [M-2Na]⁺, 473 [M-2Na]⁻, 236 [M-2Na]²⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 98%.

Disodium 1-amino-4-(4-sulfophenylamino)-9,10-dioxo-9,10-dihydroanthracene 2-sulfonate (3z):^{1a}

Reaction conditions: 5 min, 120 °C, 80 W; pressure up to 10 bar.

Analytical data: mp > 300 °C, blue powder. ¹H-NMR: δ 7.19 (d, 2H, 2'-H, 6'-H), 7.62 (d, 2H, 3'-H, 5'-H), 7.84 (m, 2H, 6-H, 7-H), 8.04 (s, 1H, 3-H), 8.27 (m, 2H, 5-H, 8-H), 10.10 (br, 2H, 1-NH₂), 12.01 (s, 1H, 4-NH). ¹³C-NMR: 109.33 (C-9a), 111.87 (C-4a), 121.76 (C-2', C-6'), 122.98 (C-3), 126.12 (C-5), 126.17 (C-8), 127.14 (C-3', C-5'), 132.92 (C-6), 133.34 (C-7), 133.71 (C-10a), 134.29 (C-8a), 139.40 (C-1'), 140.45 (C-4), 142.86 (C-2), 144.56 (C-4'), 144.58 (C-1), 181.98 (C-9), 182.72 (C-10). **LC-MS (m/z):** 492 [M-Na+NH₄⁺]⁺, 473 [M-2Na]⁻, 236 [M-2Na]²⁻. Purity by **HPLC-UV (254 nm)**-ESI-MS: 96%.

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