Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of 2,3-Diaza-anthraquinones via Bidentate Lewis Acid Catalyzed Inverse Electron-Demand Diels-Alder (IEDDA) Reaction

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General Information:

All reagents and solvents were obtained from Sigma-Aldrich, Acros, TCI or Alfa Aesar and were used as received unless otherwise stated. Technical grade solvents for extraction and column chromatography were bulb-to-bulb distilled prior to usage. Air sensitive reactions were set up using dry glassware in glovebox, or just flushed by nitrogen or argon. ^{1}H- and ^{13}C-NMR experiments where performed at 25 ºC on a Bruker DPX-NMR (400 MHz) at 25 ºC. Chemical shifts are reported in parts per million (ppm) related to solvent peek or trimethylsilane (TMS), coupling constants (*J*) are reported in Hertz (Hz). NMR-solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The multiplicities are written as: s=singlet, d=doublet, t=triplet, m=multiplet and their combinations, such as dd=doublet of a doublet. Multiplets are reported as a span of their extent or their middle. Elementary analysis was performed on a Perkin-Elmer Analysator 240. Thin layer Chromatography (TLC) was carried out on silica gel 60 F254 glass plates with a 0.25 mm layer or Polygram® Alox N/UV254 with a 0.2 mm-coating and detected with a CAMAG UV Cabinet dual wavelength, 254/366 nm.

The bidentate bisborane Lewis acid catalyst, 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene, was prepared according to the method described in previous work.[1] 1,4-Naphthoquinones **1a**, **1c**, **1d** were purchased from Sigma-Aldrich and **1b**,[2] **1e**[3] have been prepared by standard literature procedures. 1,2,4,5-Tetrazine were prepared according to literature procedure[4] and has additionally been purified via sublimation. Dienophiles includes bis(trimethylsilyl)acetylene and 2,3-dihydrofuran were purchased from Sigma-Aldrich, while 1-cyclopentenylpyrrolidine and *N*,*N*-dimethyl(-2-phenylethynyl)amine were prepared and stored under N_2 before use. Catalytic IEDDA reactions have been carried out under nitrogen atmosphere with degased solvents, which were purchased from Sigma-Aldrich.

Synthesis of Substrates

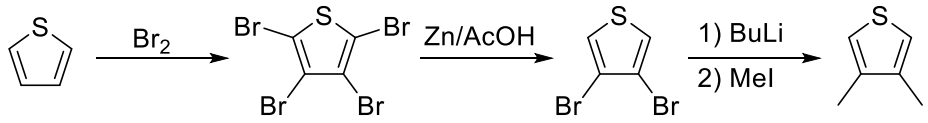
1. **The synthesis of 1,2,4,5-tetrazine (TZ)**[4]

   1,2,4,5-Tetrazine was prepared according to Domasevitch's method. An additional sublimation gave the pure product as red crystals, which was then stored in a refrigerator (–20 ºC) before use.

2. **The synthesis of 1,4-naphthoquinones**

   1,4-Naphthoquinone **1a**, **1c**, **1d** were purchased from Sigama-Aldrich and **1b**, **1e** have been prepared by the following procedures.

   6,7-Dimethyl-1,4-naphthoquinone (1b)[2]

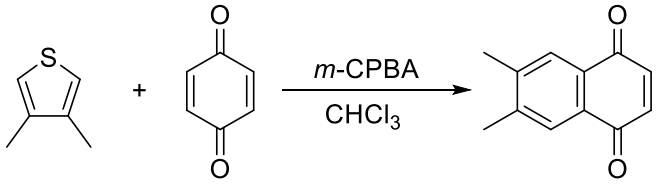


   Tetrabromothiophene: To a chloroform solution (20 mL) of thiophene (51.0 g, 0.600 mol, 1.00 equiv), a chloroform solution (40 mL) of bromine (215 mL, 4.20 mol, 7.00 equiv) was added dropwise within 4 h at 0 ºC. The reaction mixture was warmed to rt and was subsequently stirred under reflux for 3 h. Then, a saturated aqueous solution of NaOH was added and the mixture was stirred under reflux for 1 h to remove the bromine. The mixture was extracted with dichloromethane (DCM) three times and the combined organic portions were dried over magnesium sulfate. After filtration, the organic solution was condensed under reduced pressure. The crude solid was recrystallized from a 1:1(v/v) solution of chloroform and ethanol to give the pure product as colorless crystals (204 g, 85 % yield).

   3,4-Dibromothiophene: In a 500 mL flask with 180 mL glacial acetic acid/water (1:2, v/v) tetrabromothiophene (56.8 g, 0.142 mol, 1.00 equiv) and zinc powder (30.1 g, 0.460 mol, 3.29 equiv) were added alternately in several portions. The mixture was stirred for 1 h at rt, and then stirred under reflux for another 3 h. Then, the reaction mixture was cooled down to rt and filtered to remove the excess zinc powder. The filtrate was extracted with diethylether. And the combined organic portions were washed several

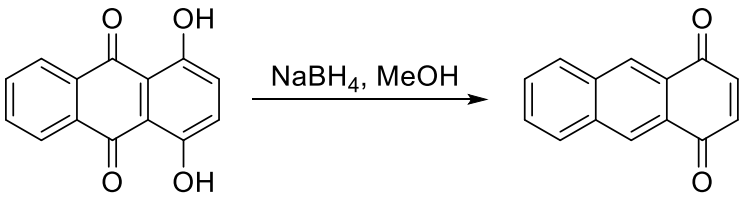
times with water and then dried over Na_2SO_4. The crude product, which remained after the removal of the solvent by evaporation, was distilled under reduced pressure and a colorless oil was obtained (21.0 g, 61% yield). Bp: 75–83 ºC/1.2 mbar.

3,4-Dimethylthiophene:[5] Under a dry N_2 atmosphere, a solution of 3,4-dibromothiophene (12.1 g, 50.0 mmol, 1.00 equiv) in anhydrous diethylether (100 mL) in a Schlenk tube was cooled to –70 ºC. To the vessel *n*-BuLi (1.0 M, 110 mL, 110 mmol, 2.20 equiv, obtained by diluting commercial 10 M *n*-BuLi in hexanes with anhydrous diethylether) was added dropwise, and the reaction mixture stirred thereafter at –70 ºC for 30 min. A solution of MeI (6.50 mL, 0.104 mol, 2.08 equiv) in diethylether was then slowly added in order to keep the temperature below –30 ºC. After the mixture was stirred overnight, 100 mL of ice water was added slowly to quench the reaction. The ether layer was then separated, the aqueous phase was extracted twice with diethylether, and the combined extracts were washed three times with water and dried over Na_2SO_4. The solvent was then removed under reduced pressure, and the residue was purified by vacuum distillation to obtain the 2,3-dimethylthiophene (4.12 g, 73 % yield).



6,7-Dimethyl-1,4-naphthoquinone (1b):[2] To a stirred solution of 2,3-dimethyl-thiophene (1.35 g, 12.0 mmol, 1.00 equiv) and benzoquinone (1.06 g, 9.80 mmol, 0.817 equiv) in $CHCl_3$ (40 mL) at 0 ºC was added *m*-CPBA (9.60 g 38.9 mmol, 3.24 equiv, technical grade, 70%) in small portions. After 2 h, the reaction was warmed to rt for 30 min and heated at reflux for 48 h. The mixture was allowed to cool to rt and then filtered to obtain a liquid. The liquid was neutralized with aq. saturated Na_2CO_3 solution. The mixture was extracted with chloroform (3 × 50 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography to give 6,7-dimethyl-1,4-naphthoquinone as a yellow solid (379 mg, 21% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 2H), 6.90 (s, 2H), 2.41 (s, 6H). Spectroscopic data for the title compound was consistent with the literature.

Anthracene-1,4-dione (1e)[3]

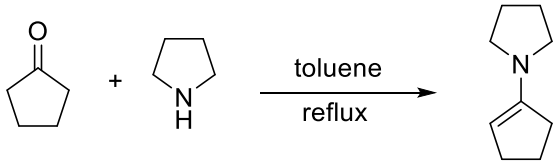


The reaction was carried out according to the literature for the synthesis of anthracene-1,4-dione, and an orange solid was obtained through column chromatography. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 2H), 8.05 (dd, J_1 = 2.9 Hz, J_2 = 9.5 Hz, 2H), 7.68 (dd, J_1 = 2.9 Hz, J_2 = 9.5 Hz, 2H), 7.06 (s, 2H). Spectroscopic data for the title compound was consistent with the literature.

3. The synthesis of dienophiles

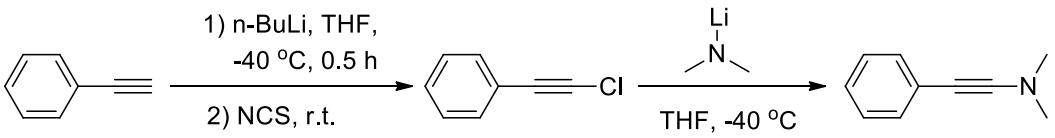
Dienophiles bis(trimethylsilyl)acetylene and 2,3-dihydrofuran were purchased from Sigma-Aldrich, 1-cyclopentenylpyrrolidine and *N*,*N*-dimethyl(2-phenylethynyl)amine were prepared and stored under N_2 before use.

Cyclopentenylpyrrolidine[6]



A mixture of cyclopentanone (8.41 g, 100 mmol, 1.00 equiv) and pyrrolidine (10.7 g, 150 mmol, 12.3 mL, 1.50 equiv) in anhydrous toluene (20 mL) was heated to reflux under Dean-Stark conditions for 3.5 h. Excess pyrrolidine and toluene were removed in vacuo and the crude residue was purified by Kugelrohr distillation (11.0 mbar, 140 ºC) to yield a pale yellow oil (9.61 g, 70%). The product was stored under N_2 before use; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.07 (s, 1H), 3.15 – 3.06 (m, 4H), 2.57 – 2.24 (m, 4H), 1.98 – 1.82 (m, 6H). Spectroscopic data for the title compound was consistent with the literature.

***N*,*N*-Dimethyl-(2-phenylethynyl)amine**



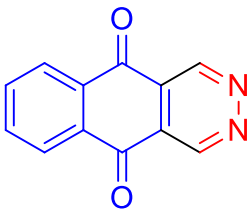
1-Chloro-2-phenylacetylene:[7] A flame-dried flask was charged with a stirring bar and the starting material phenylacetylene (1.02 g, 1.1 mL, 10.0 mmol, 1.00 equiv), followed by anhydrous THF (20 mL) under N_2 and cooled to –40 ºC. The solution was treated with *n*-butyllithium (1.6 M solution in hexanes, 7.5 mL, 12.0 mmol, 1.20 equiv) over 5 min at –40 ºC under N_2. The resulting suspension was stirred at –40 ºC for 30 min. Then, a solution of recrystallised *N*-chlorosuccinimide (1.47 g, 11.0 mmol, 1.10 equiv) in anhydrous THF (5 mL) was added in one portion. The reaction was allowed to warm to rt after 20 min and stirred for another 0.5 h. The reaction mixture was quenched with saturated NH_4Cl (100 mL), diluted with Et_2O (100 mL) and washed with brine. The aqueous layer was extracted with Et_2O (3 × 60 mL) and the organic layers were combined, dried over Na_2SO_4, filtered and concentrated under vacuum. Purification by distillation gave the title compound, which was subjected to the next reaction step. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.52 (m, 2H), 7.33 – 7.39 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.1, 128.7, 128.5, 122.3, 69.6, 68.2.

***N*,*N*-Dimethyl-(2-phenylethynyl)amine:** Liquefied dimethylamine (2.87 g, 1.52 mL, 63.6 mmol, 1.20 equiv) was dissolved in 25 mL of THF, cooled to –40 ºC. The mixture was added to a solution of *n*-butyllithium in hexanes (1.6 M, 33.1 mL, 53.0 mmol, 1.00 equiv) keeping the temperature between –20 and –40 ºC. Subsequently, 1-chloro-2-phenylacetylene (7.24 g, 6.4 mL, 53.0 mmol, 1.00 equiv) was added dropwise over 15 min keeping the temperature between –15 and –20 ºC. After warming to rt, the salt was filtered off on a (dry) sintered-glass funnel and rinsed well with dry Et_2O. The solution was concentrated in vacuo, and the product was distilled under 0.6 mbar through a 5 cm Vigreux column. The product was collected in a (single) receiver, cooled in a bath to a temperature of –20 ºC. During the distillation the temperature of the heating bath was gradually raised until the light yellow liquid begin to come out (about 120 ºC). Distillation

of the contents of the receiver gave the yneamine (2.68 g, 29 % yield), b.p. 67 ºC/0.6 mbar. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.26 (m, 2H), 7.17 – 7.21 (m, 2H), 7.07 – 7.11 (m, 1H), 2.75 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 129.8, 128.1, 125.6, 125.4, 98.2, 61.8, 43.8. **HRMS** (ESI) m/z calcd for $C_{10}H_{11}N$ $[M+Na]^+$ 168.0789, found: 168.0781.

IEDDA Reactions of 1,4-Naphthoquinones with 1,2,4,5-Tetrazine

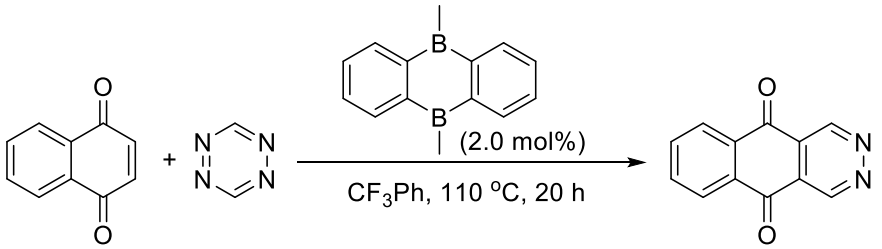
General procedure I: The catalyst, 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (25.0 μmol, 5.00 mol%) and tetrazine (2.50 mmol, 5.00 equiv) in CF_3Ph (2.5 mL) were thoroughly stirred for several minutes. 1,4-Naphthoquinone **1** (0.500 mmol, 1.00 equiv) was added, the reaction mixture was heated to 110 ºC for 20 h. The solvent, together with the excess of tetrazine were distilled off from the resulting mixture in vacuo. Then, the remaining residue was purified by column chromatography over SiO_2 (ethylacetate/cyclohexane 1:1) to obtain the product.



2,3-Diaza-9,10-anthracenedione (2a)

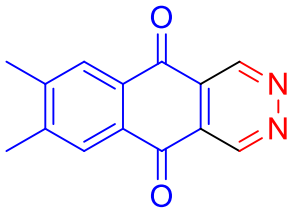
Naphthaquinone **1a** (31.6 mg, 0.200 mmol, 1.00 equiv), tetrazine (82.1 mg, 1.00 mmol, 5.00 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (2.0 mg, 10.0 μmol, 5.00 mol%) in CF_3Ph (1.0 mL) were reacted according to the general procedure I to yield the target compounds **2a** as a gray green solid (32.0 mg, 76 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 2H), 8.33 (dd, J_1 = 4 Hz, J_2 = 4 Hz, 2H), 7.94 (dd, J_1 = 4 Hz, J_2 = 4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.3, 147.2, 135.8, 132.5, 127.6, 125.4; **HRMS** (ESI) m/z calcd for $C_{12}H_6N_2O_2$ $[M+Na]^+$ 233.0327, found: 233.0324.

Gram-scale synthesis



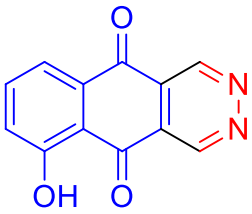
1a **TZ** **2a:** 71 %

The catalyst, 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (37.1 mg, 0.182 mmol, 2.00 mol%) and tetrazine (3.33 g, 40.6 mmol, 4.46 equiv) in CF_3Ph (18.0 mL) were thoroughly stirred for several minutes. 1,4-Naphthoquinone **1a** (1.48 g, 9.10 mmol, 1.00 equiv) was added, the reaction mixture was heated to 110 ºC for 20 h. The reaction mixture was filtrated to afford a block brown solid, which was then washed with aceton (3 × 50 mL) to yield the product (1.36 g, 71 %).



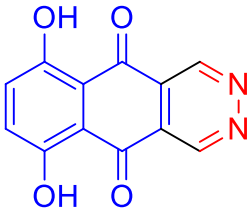
6,7-Dimethyl-2,3-diaza-9,10-anthracenedione (2b)

Naphthaquinone **1b** (93.1 mg, 0.500 mmol, 1.00 equiv), tetrazine (205 mg, 2.50 mmol, 5.00 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (5.10 mg, 25.0 μmol, 5.00 mol%) in CF_3Ph (2.5 mL) were reacted according to the general procedure I to yield the target compounds **2b** as a grayish yellow solid (95.3 mg, 80 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 2H), 8.04 (s, 2H), 2.48 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.4, 147.2, 146.2, 130.5, 128.4, 125.6, 20.6; **HRMS** (ESI) m/z calcd for $C_{14}H_{10}N_2O_2$ $[M+Na]^+$ 261.0640, found: 261.0632.



5-Hydroxy-2,3-diaza-9,10-anthracenedione (2c)

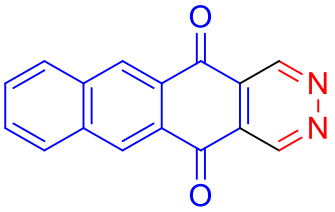
Naphthaquinone **1c** (87.1 mg, 0.500 mmol, 1.00 equiv), tetrazine (205 mg, 2.50 mmol, 5.00 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (5.10 mg, 25.0 μmol, 5.00 mol%) in CF_3Ph (2.5 mL) were reacted according to the general procedure I. Instead of purification by column chromatography, the reaction mixture was exacted by 1 M aq. HCl (2 × 15 mL) and then neutralized by aq. NaOH. Afterward, the aqueous solution was exacted with DCM (3 × 30 mL) and the organic layers were combined, dried over Na_2SO_4, filtered and concentrated under vacuum. Further purification by flash column chromatography gave the target compounds **2c** as a deep brown solid (13.7 mg, 12 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.07 (s, OH, 1H), 10.02 (d, J = 1.2 Hz, 1H), 9.98 (d, J = 1.3 Hz, 1H), 7.87 (dd, J_1 = 1.4 Hz, J_2 = 7.4 Hz, 1H), 7.80 – 7.84 (m, 1H), 7.45 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.4, 181.6, 162.9, 147.1, 146.7, 138.5, 132.1, 126.4, 125.8, 125.5, 120.4, 115.9; **HRMS** (ESI) m/z calcd for $C_{12}H_6N_2O_3$ $[M+Na]^+$ 249.0276, found: 249.0270.



5,8-Dihydroxy-2,3-diaza-9,10-anthracenedione (2d)[8]

Naphthaquinone **1d** (95.1 mg, 0.500 mmol, 1.00 equiv), tetrazine (205 mg, 2.50 mmol, 5.00 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (5.1 mg, 25.0 μmol, 5.00 mol%) in CF_3Ph (2.5 mL) were reacted according to the general procedure I. Instead of purification by column chromatography, the reaction mixture was exacted by 1 M aq. HCl (2 × 15 mL) and then neutralized by aq. NaOH. Afterward, the aqueous solution was exacted with DCM (3 × 30 mL) and the organic layers were combined, dried over Na_2SO_4,

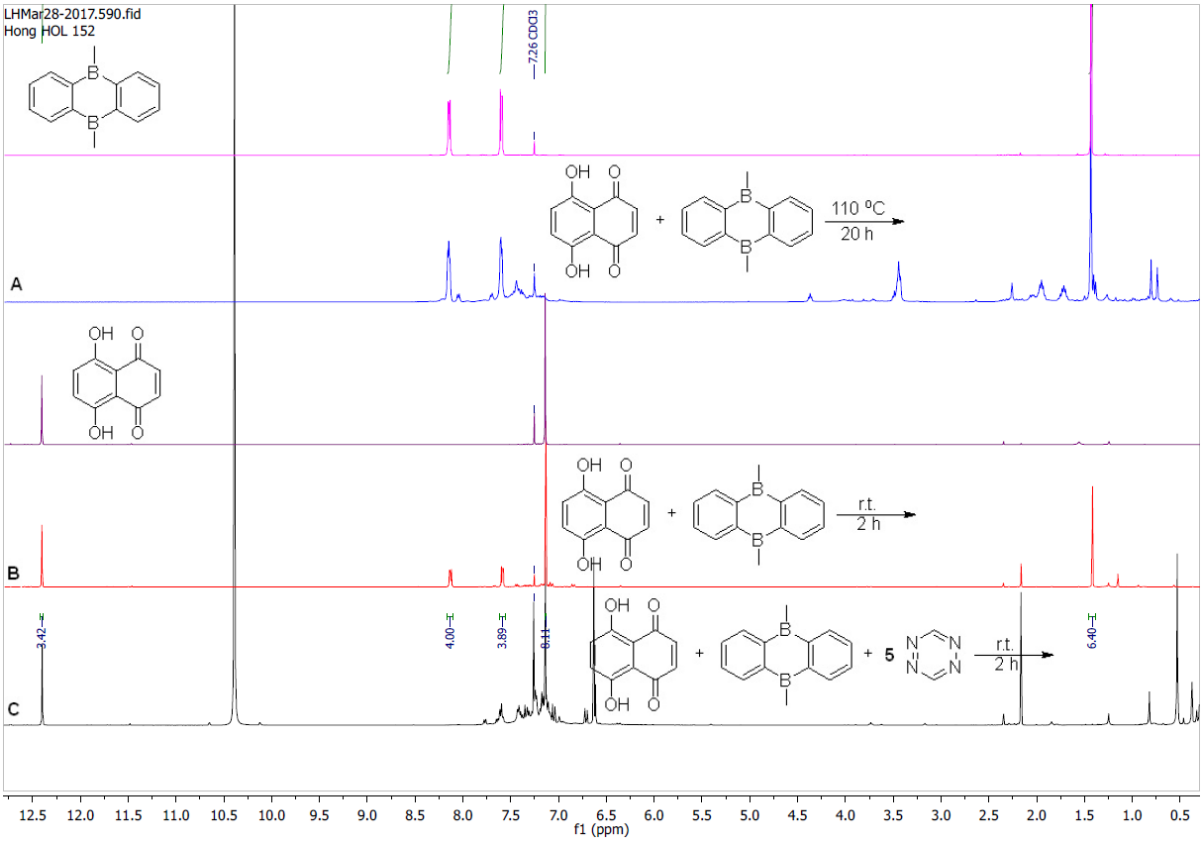
filtered and concentrated under vacuum. Further purification by flash column chromatography gave the target compounds **2d** as a dark red solid (17.0 mg, 14 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.26 (s, OH, 2H), 10.07 (s, 2H), 7.46 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 184.7, 159.3, 146.9, 131.9, 126.3, 112.5; **HRMS** (ESI) m/z calcd for $C_{12}H_6N_2O_4$ $[M+Na]^+$ 265.0226, found: 265.0218. Spectroscopic data for the title compound was consistent with the literature.



2,3-Diaza-5,12-naphthacenedione (2e)

Anthracene-1,4-dione **1e** (104 mg, 0.500 mmol, 1.00 equiv), tetrazine (205 mg, 2.50 mmol, 5.00 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (5.1 mg, 25.0 μmol, 5.00 mol%) in CF_3Ph (2.5 mL) were reacted according to the general procedure I. Instead of purification by column chromatography, the reaction mixture was filtered and the solid was washed with acetone twice and dried under vacuum to afford the target compounds **2e** as a yellow-green solid (102 mg, 79 % yield). **^{1}H NMR** (400 MHz, CF_3CO_2D) δ 10.26 (d, J = 2.6 Hz, 2H), 8.94 (d, J = 2.8 Hz, 2H), 8.11 – 8.14 (m, 2H), 7.78 – 7.81 (m, 2H); **^{13}C NMR** (100 MHz, CF_3CO_2D): δ 180.1, 151.5, 138.2, 137.4, 134.9, 134.3, 133.0, 129.3; **HRMS** (ESI) m/z calcd for $C_{16}H_8N_2O_2$ $[M+Na]^+$ 283.0484, found: 283.0476.

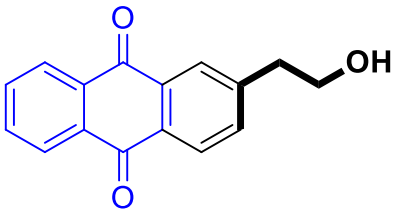
Complexation/stability tests with the dihydroxy-substituted naphthoquinone 1d



Several control experiments were carried out and monitored by proton NMR spectroscopy. As shown above, a 1:1 mixture of 5,8-dihydroxyl-1,4-naphthoquinone (**1d**) with the catalyst was heated at 110 °C for 20 h (**A**). At rt only small amounts of **1d** were transformed (**B**). The results show that the catalyst survives in the presence of **1d** even at a higher temperature for long time, but readily undergoes reaction with tetrazine (**C**).

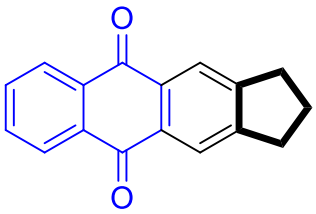
IEDDA Reactions for the synthesis of 9,10-anthraquinones

General procedure II: The catalyst, 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (25.0 μmol, 5.00 mol%) and 2,3-diaza-9,10-anthraquinone **2** (0.200 mmol, 1.00 equiv) in diglyme (1.00 mL) were thoroughly stirred for several minutes. The dienophile (0.300 mmol, 1.50 equiv) was added, the reaction mixture was heated to the given temperature. After the reaction finished, the solvent was distilled off. The remaining residue was purified by column chromatography over SiO_2 (ethylacetate/cyclohexane 1:6→1:3) to obtain the product.



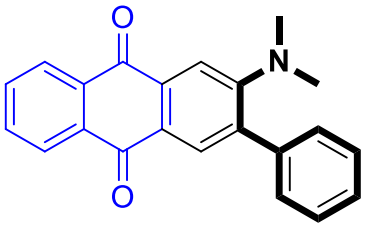
2-(2-Hydroxyethyl)-9,10-anthraquinone (3a)[9]

2,3-Diaza-anthraquinone **2a** (42.0 mg, 0.200 mmol, 1.00 equiv), 2,3-dihydrofuran (21.0 mg, 0.300 mmol, 1.50 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (2.0 mg, 10.00 μmol, 5.00 mol%) in diglyme (1.0 mL) were reacted according to the general procedure II to yield the target compounds **3a** as a pale yellow solid (5.1 mg, 10 % yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.19 – 8.22 (m, 2H), 8.13 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 1.5 Hz, 1H), 7.91 – 7.94 (m, 2H), 7.79 (dd, J_1 = 1.8 Hz, J_2 = 8.0 Hz, 1H), 4.76 (t, J = 5.2 Hz, 1H, OH), 3.69-3.74 (m, 2H), 2.94 (t, J = 6.5 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 182.7, 182.3, 147.5, 135.3, 134.53, 134.45, 133.07, 133.05, 132.8, 131.1, 127.1, 126.8, 126.74, 126.69, 71.3, 61.3; **HRMS** (ESI) m/z calcd for $C_{16}H_{12}O_3$ $[M+Na]^+$ 253.0859, found: 253.0851. Spectroscopic data for the title compound was consistent with the literature.



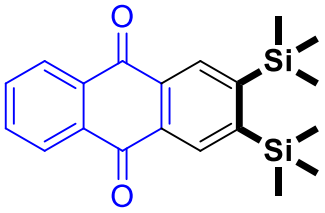
2,3-Dihydro-1*H*-cyclopenta[*b*]anthracene-5,10-dione (3b)[10]

2,3-Diaza-anthraquinone **2a** (42.0 mg, 0.200 mmol, 1.00 equiv), cyclopentenylpyrrolidine (41.2 mg, 0.300 mmol, 1.50 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (2.0 mg, 10.00 μmol, 5.00 mol%) in diglyme (1.0 mL) were reacted according to the general procedure II to yield the target compounds **3b** as a gray yellow solid (21.9 mg, 44 % yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (dd, J_1 = 3.4 Hz, J_2 = 5.8 Hz, 2H), 8.12 (s, 2H), 7.76 (dd, J_1 = 3.4 Hz, J_2 = 5.8 Hz, 2H), 3.06 (t, J = 7.5 Hz, 4H), 2.13 – 2.21 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.6, 151.7, 134.0, 133.8, 132.6, 127.2, 123.1, 33.2, 25.3. Spectroscopic data for the title compound was consistent with the literature.



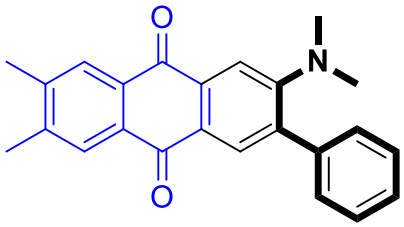
2-(Dimethylamino)-3-phenyl-9,10-anthraquinone (3c)

2,3-Diaza-anthraquinone **2a** (42.0 mg, 0.200 mmol, 1.00 equiv), *N*,*N*-dimethyl-(2-phenyl-ethynyl)amine (43.6 mg, 0.300 mmol, 1.50 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (2.0 mg, 10.00 μmol, 5.00 mol%) in diglyme (1.0 mL) were reacted according to the general procedure II to yield the target compounds **3c** as a red solid (21.0 mg, 320% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 – 8.29 (m, 2H), 8.11 (s, 1H), 7.72 – 7.79 (m, 3H), 7.56 (d, J = 7.1 Hz, 2H), 7.42 – 7.46 (m, 2H), 7.34 – 7.37 (m, 1H), 2.76 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.9, 182.2, 155.8, 141.0, 136.7, 134.3, 134.1, 133.9, 133.6, 133.5, 132.3, 128.9, 128.3, 127.8, 127.10, 127.11, 125.5, 114.1, 43.0; **HRMS** (ESI) m/z calcd for $C_{22}H_{17}NO_2$ $[M+Na]^+$ 350.1157, found: 350.1156.



2,3-Bis(trimethylsilyl)-9,10-anthraquinone (3d)[11]

2,3-Diaza-anthraquinone **2a** (42.0 mg, 0.200 mmol, 1.00 equiv), bis(trimethylsilyl)-acetylene (51.1 mg, 0.300 mmol, 1.50 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (2.0 mg, 10.00 μmol, 5.00 mol%) in diglyme (1.0 mL) were reacted according to the general procedure II to yield the target compounds **3d** as an orange solid (31.0 mg, 44 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 2H), 8.26 (dd, J_1 = 3.4 Hz, J_2 = 5.8 Hz, 2H), 7.76 (dd, J_1 = 3.4 Hz, J_2 = 5.8 Hz, 2H), 0.45 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.8, 155.0, 134.1, 133.6, 133.0, 131.1, 127.1, 1.8. Spectroscopic data for the title compound was consistent with the literature.



2-(Dimethylamino)-6,7-dimethyl-3-phenyl-9,10-anthraquinone (3e)

6,7-dimethyl-2,3-diaza-anthraquinone **2b** (47.7 mg, 0.200 mmol, 1.00 equiv), *N*,*N*-dimethyl-(2-phenylethynyl)amine (43.6 mg, 0.300 mmol, 1.50 equiv), 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene (2.0 mg, 10.00 μmol, 5.00 mol%) in diglyme (1.0 mL) were reacted according to the general procedure II to yield the target compounds **3e** as an orange solid (24.2 mg, 34 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.01 (s, 2H), 7.74 (s, 1H), 7.56 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 2.75 (s, 6H), 2.42 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 184.0, 182.5, 155.6, 143.9, 143.2, 141.1, 136.5, 133.7, 132.3, 132.1, 131.9, 128.8, 128.3, 128.14, 128.12, 127.6, 125.8, 114.1, 43.0, 20.33, 20.26; **HRMS** (ESI) m/z calcd for $C_{24}H_{21}NO_2$ $[M+Na]^+$ 378.1470, found: 378.1473.

X-Ray Crystallography

Some single crystals of **2b** ($2b \cdot H_2O$ = $C_{14}H_{12}N_2O_3$) were transferred into inert oil (Fomblin Y, 1600 cst, Sigma Aldrich GmbH, Steinheim, Germany). A suitable crystal was then mounted onto a micromount sample holder (MiTeGen, Dual-Thickness MicroMounts, 100 µm) and immediately placed into a stream of cold N_2 (100K) inside the diffractometer (Bruker D8 Venture, Bruker, Karlsruhe, Germany). Mo-Kα- radiation (λ = 71.073 pm) from an Incoatec microsource was used. After unit cell determination, the reflection intensities were collected. The software of the diffractometer (Bruker Apex III)[12] was used for data collection, unit cell determination and processing of the raw data. Absorption correction was applied using SADABS.[13] The structure was solved by intrinsic phasing using SHELXT,[14] full matrix least squares refinement on $|F^2|$ using SHELXL-2014/7[15] as implemented in the Olex2- program[16] was used for structure refinement.

All non-hydrogen atoms could be refined with anisotropic displacement parameters. All hydrogen atoms could be refined freely. The program Diamond was used for graphical representations.[17] The CCDC reference number is 1534878.

Table S1. Crystal data and structure refinement data of compound $C_{14}H_{12}N_2O_3$ for the X-Ray measurement at 100K.

Empirical formula	$C_{14}H_{12}N_2O_3H_{28}$
Formula weight	256.26 g/ mol
Temperature	100 K
Wavelength	71.073 pm
Crystal system	triclinic
Space group	*P*-1
Unit cell dimensions	*a* = 7.1026(3) Å
	b = 7.8866(3) Å

	c = 11.4159(5) Å
	α = 92.777(2)°
	β = 92.263(2)°
	γ = 114.968(1)°
Volume	V = 577.75(4) x 10^6 Å^3
No. of formula units	2
Density (calculated)	1.473 g/cm^3
F(000)	268
Theta range for data collection	2.86 to 45.35°
Index ranges	-11<=h<=11, -12<=k<=12, -18<=l<=18
R_{int} and R_σ	0.0415 and 0.0192
Reflections collected	52988
Independent reflections	5048
Crystal size	0.146 x 0.261 x 0.372 mm^3
Absorption coefficient	0.106 mm^{-1}
Absorption correction	numerical
Max. and min. transmission	0.985 and 0.962
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	5048 / 0 / 220
Goodness-of-fit on F²	1.084
Final R- indices (I>2sigma(I)	R_1 = 0.0450, wR_2 = 0.1174

R indices (all data)	R_1 = 0.0557, wR_2 = 0.1233
Largest diff. peak and hole	0.614 and -0.375 $e^-/Å^3$

Geometrical parameters of compound 2b (2b·H_2O = $C_{14}H_{12}N_2O_3$).

Table S2. Fractional atomic coordinates and equivalent isotropic displacement parameters (pm^2 x 10^{-1}) for the X-Ray measurement at 100K. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.74409 (9)	0.78889 (7)	0.37251 (5)	0.01393 (11)
O2	0.72866 (10)	0.17494 (8)	0.56792 (5)	0.01627 (12)
O3	0.46495 (11)	0.21827 (9)	-0.09024 (5)	0.02266 (15)
N2	0.62336 (10)	0.15629 (9)	0.20532 (5)	0.01229 (12)
N1	0.62407 (10)	0.30903 (9)	0.15641 (5)	0.01239 (12)
C6	0.78408 (10)	0.65194 (9)	0.54719 (5)	0.00790 (11)
C3	0.69695 (10)	0.31863 (9)	0.39628 (6)	0.00834 (11)
C2	0.70120 (10)	0.47602 (9)	0.34626 (6)	0.00792 (11)
C5	0.74431 (10)	0.65266 (9)	0.41883 (6)	0.00850 (12)
C7	0.77323 (10)	0.48961 (9)	0.59846 (6)	0.00829 (11)
C9	0.82908 (10)	0.81481 (9)	0.61857 (6)	0.00980 (12)
C1	0.66139 (11)	0.46374 (9)	0.22391 (6)	0.01039 (12)
C12	0.80401 (11)	0.49340 (10)	0.72038 (6)	0.01002 (12)
C4	0.65750 (11)	0.15964 (9)	0.32088 (6)	0.01047 (12)
C8	0.73206 (10)	0.31567 (9)	0.52605 (6)	0.00911 (12)
C11	0.84899 (11)	0.65538 (10)	0.79181 (6)	0.01034 (12)
C10	0.86253 (10)	0.81943 (9)	0.74015 (6)	0.01017 (12)
C14	0.88295 (13)	0.65539 (11)	0.92260 (6)	0.01523 (14)
C13	0.91200 (12)	0.99676 (10)	0.81520 (7)	0.01466 (14)
H12	0.789 (2)	0.3784 (18)	0.7544 (12)	0.026 (3)*
H1	0.650 (2)	0.5610 (18)	0.1836 (12)	0.024 (3)*
H9	0.836 (2)	0.9257 (19)	0.5851 (12)	0.030 (3)*
H4	0.654 (2)	0.0445 (19)	0.3519 (12)	0.027 (3)*
H14A	0.7835 (19)	0.6920 (18)	0.9629 (11)	0.024 (3)*
H13A	0.817 (2)	0.9729 (18)	0.8816 (11)	0.026 (3)*
H13B	1.054 (2)	1.0466 (18)	0.8489 (12)	0.027 (3)*

H14B	0.861 (2)	0.5288 (19)	0.9434 (12)	0.032 (3)*
H13C	0.897 (2)	1.0897 (19)	0.7673 (12)	0.028 (3)*
H3A	0.515 (2)	0.236 (2)	-0.0217 (15)	0.043 (4)*
H14C	1.023 (2)	0.7427 (19)	0.9465 (12)	0.029 (3)*
H3B	0.448 (2)	0.107 (2)	-0.1115 (14)	0.042 (4)*

Table S3. Anisotropic displacement parameters (Å²) for the X-Ray measurement at 100K. The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2\ a^{*\ 2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

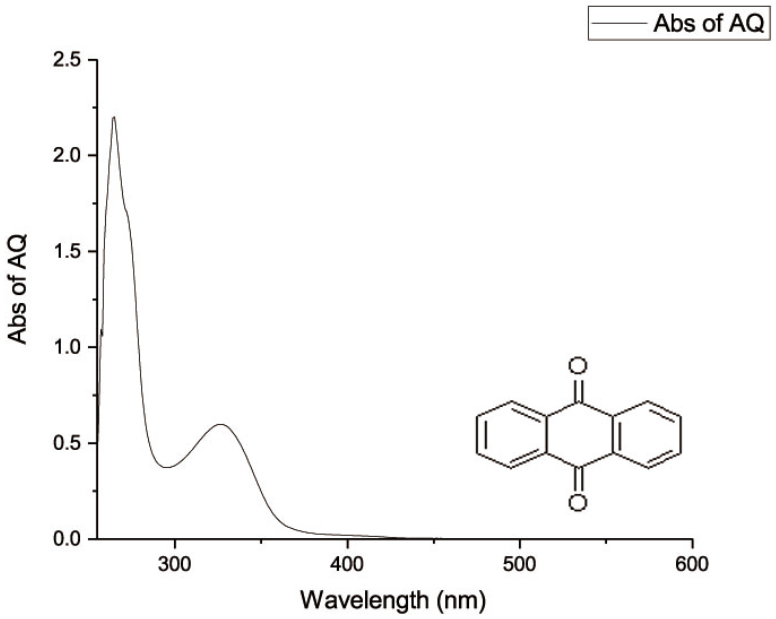
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0219 (3)	0.0087 (2)	0.0117 (2)	0.00722 (19)	-0.00199 (18)	0.00176 (16)
O2	0.0297 (3)	0.0114 (2)	0.0121 (2)	0.0127 (2)	0.0022 (2)	0.00323 (17)
O3	0.0380 (4)	0.0187 (3)	0.0133 (3)	0.0152 (3)	-0.0074 (2)	-0.0034 (2)
N2	0.0157 (3)	0.0111 (2)	0.0105 (2)	0.0065 (2)	-0.00071 (19)	-0.00152 (19)
N1	0.0162 (3)	0.0122 (3)	0.0095 (2)	0.0070 (2)	-0.00133 (19)	-0.00137 (19)
C6	0.0092 (3)	0.0070 (2)	0.0074 (2)	0.0035 (2)	-0.00021 (19)	-0.00007 (19)
C3	0.0093 (3)	0.0074 (2)	0.0084 (3)	0.0037 (2)	0.00052 (19)	0.00011 (19)
C2	0.0085 (2)	0.0074 (2)	0.0075 (2)	0.0032 (2)	-0.00034 (19)	-0.00007 (19)
C5	0.0092 (3)	0.0072 (2)	0.0088 (3)	0.0033 (2)	-0.00024 (19)	0.00063 (19)
C7	0.0098 (3)	0.0078 (2)	0.0077 (2)	0.0042 (2)	0.00052 (19)	0.00026 (19)
C9	0.0109 (3)	0.0079 (3)	0.0100 (3)	0.0037 (2)	-0.0006 (2)	-0.0009 (2)
C1	0.0133 (3)	0.0104 (3)	0.0076 (3)	0.0054 (2)	-0.0009 (2)	-0.0005 (2)
C12	0.0126 (3)	0.0106 (3)	0.0078 (3)	0.0057 (2)	0.0009 (2)	0.0012 (2)
C4	0.0130 (3)	0.0086 (3)	0.0100 (3)	0.0051 (2)	0.0004 (2)	-0.0010 (2)
C8	0.0117 (3)	0.0084 (3)	0.0085 (3)	0.0053 (2)	0.0013 (2)	0.00128 (19)
C11	0.0111 (3)	0.0122 (3)	0.0076 (3)	0.0049 (2)	0.00008 (19)	-0.0005 (2)
C10	0.0101 (3)	0.0097 (3)	0.0094 (3)	0.0033 (2)	-0.0006 (2)	-0.0020 (2)
C14	0.0201 (3)	0.0185 (3)	0.0073 (3)	0.0088 (3)	-0.0006 (2)	-0.0005 (2)
C13	0.0177 (3)	0.0113 (3)	0.0126 (3)	0.0046 (2)	-0.0013 (2)	-0.0046 (2)

Table S4. Experimental bond lengths [Å] and angles [°] for the X-Ray measurement at 100K.

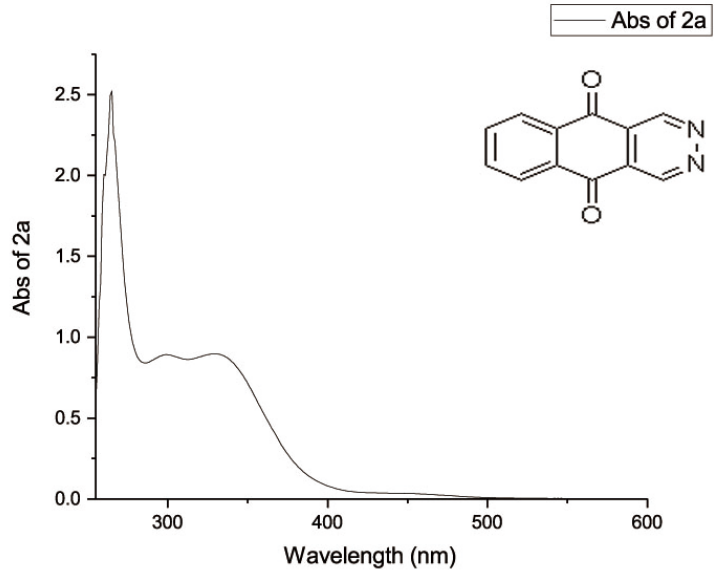
O1—C5	1.2207 (8)	C7—C8	1.4775 (9)
O2—C8	1.2209 (8)	C9—C10	1.3949 (9)
O3—H3A	0.827 (17)	C9—H9	0.955 (14)
O3—H3B	0.851 (16)	C1—H1	0.945 (13)
N2—C4	1.3288 (9)	C12—C11	1.3904 (10)

N2—N1	1.3502 (9)	C12—H12	0.969 (13)
N1—C1	1.3313 (9)	C4—H4	0.981 (13)
C6—C9	1.3955 (9)	C11—C10	1.4157 (10)
C6—C7	1.4073 (9)	C11—C14	1.5031 (10)
C6—C5	1.4821 (9)	C10—C13	1.5029 (10)
C3—C2	1.3807 (9)	C14—H14A	0.989 (13)
C3—C4	1.4041 (9)	C14—H14B	0.986 (14)
C3—C8	1.4955 (9)	C14—H14C	0.960 (14)
C2—C1	1.4045 (9)	C13—H13A	1.006 (13)
C2—C5	1.4929 (9)	C13—H13B	0.970 (13)
C7—C12	1.3971 (9)	C13—H13C	0.973 (13)
H3A—O3—H3B	104.6 (15)	C7—C12—H12	118.1 (8)
C4—N2—N1	120.03 (6)	N2—C4—C3	122.45 (6)
C1—N1—N2	119.94 (6)	N2—C4—H4	116.7 (8)
C9—C6—C7	119.54 (6)	C3—C4—H4	120.9 (8)
C9—C6—C5	119.11 (6)	O2—C8—C7	122.74 (6)
C7—C6—C5	121.34 (6)	O2—C8—C3	120.31 (6)
C2—C3—C4	117.62 (6)	C7—C8—C3	116.94 (6)
C2—C3—C8	121.66 (6)	C12—C11—C10	119.39 (6)
C4—C3—C8	120.72 (6)	C12—C11—C14	120.02 (6)
C3—C2—C1	117.48 (6)	C10—C11—C14	120.58 (6)
C3—C2—C5	121.66 (6)	C9—C10—C11	119.27 (6)
C1—C2—C5	120.86 (6)	C9—C10—C13	120.22 (6)
O1—C5—C6	122.79 (6)	C11—C10—C13	120.52 (6)
O1—C5—C2	120.29 (6)	C11—C14—H14A	109.8 (7)
C6—C5—C2	116.91 (5)	C11—C14—H14B	109.6 (8)
C12—C7—C6	119.34 (6)	H14A—C14—H14B	109.1 (11)
C12—C7—C8	119.24 (6)	C11—C14—H14C	108.9 (8)
C6—C7—C8	121.42 (6)	H14A—C14—H14C	110.0 (11)
C10—C9—C6	121.15 (6)	H14B—C14—H14C	109.5 (11)
C10—C9—H9	118.3 (8)	C10—C13—H13A	111.1 (7)
C6—C9—H9	120.5 (8)	C10—C13—H13B	110.0 (8)
N1—C1—C2	122.46 (6)	H13A—C13—H13B	108.0 (11)
N1—C1—H1	114.5 (8)	C10—C13—H13C	109.6 (8)
C2—C1—H1	122.9 (8)	H13A—C13—H13C	109.4 (10)
C11—C12—C7	121.30 (6)	H13B—C13—H13C	108.7 (11)
C11—C12—H12	120.6 (8)		

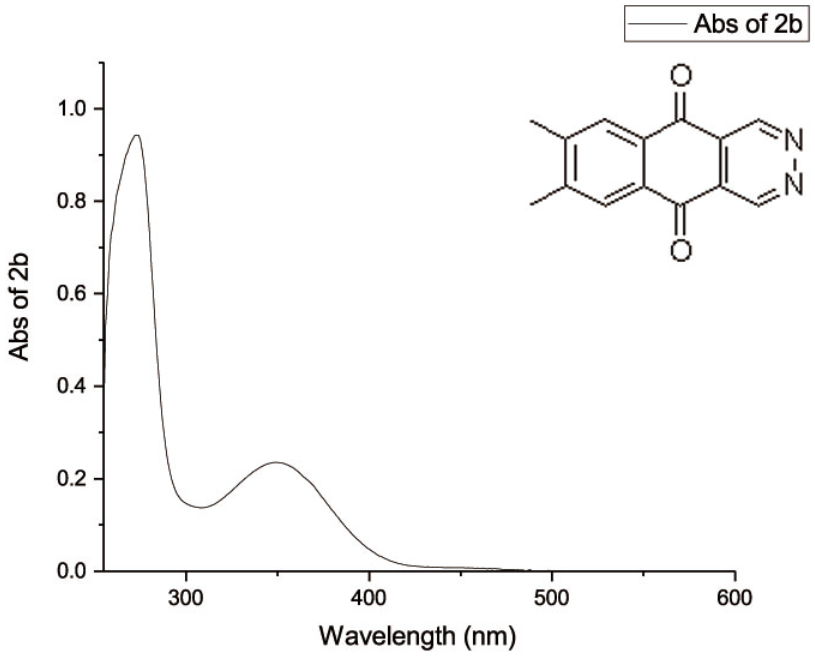
UV/Vis Spectra



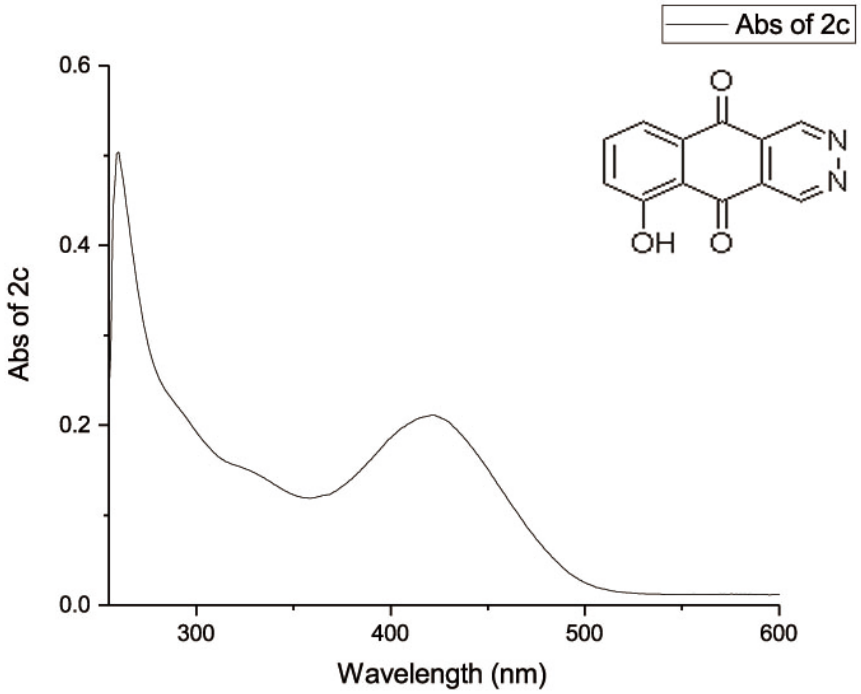
UV/Vis Spectra of 9,10-anthracenedione (**AQ**) in DMSO



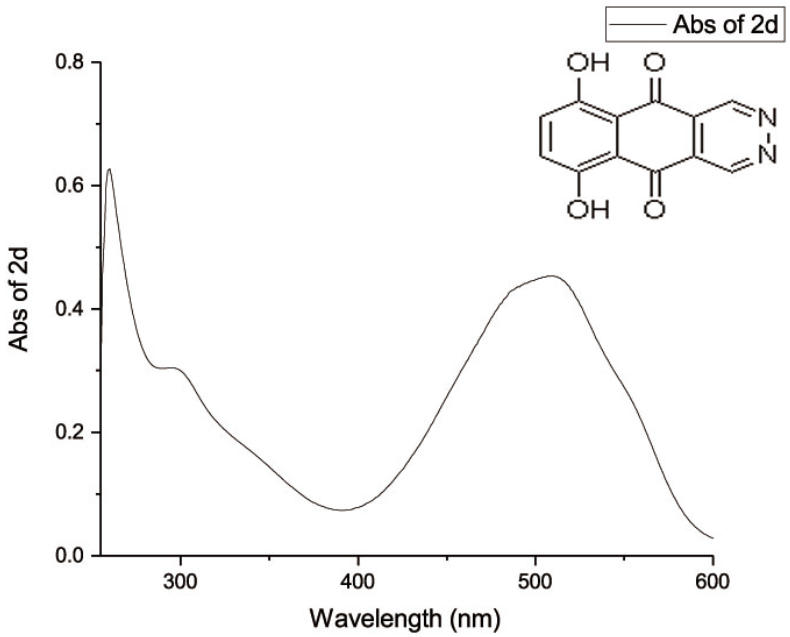
UV/Vis Spectra of 2,3-diaza-9,10-anthracenedione (**2a**) in DMSO



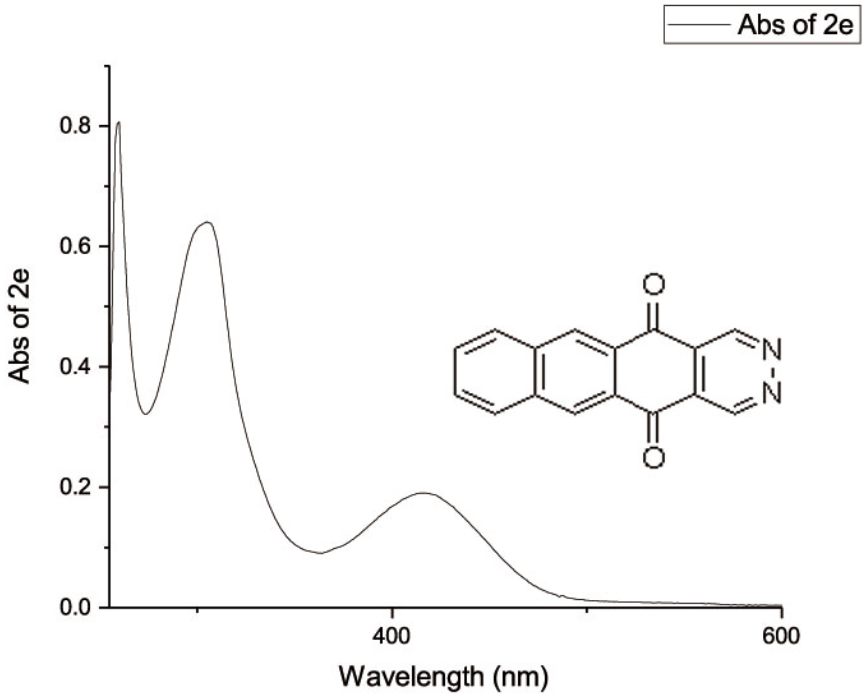
UV/Vis Spectra of 6,7-dimethyl-2,3-diaza-9,10-anthracenedione (**2b**) in DMSO



UV/Vis Spectra of 5-hydroxy-2,3-diaza-9,10-anthracenedione (**2c**) in DMSO

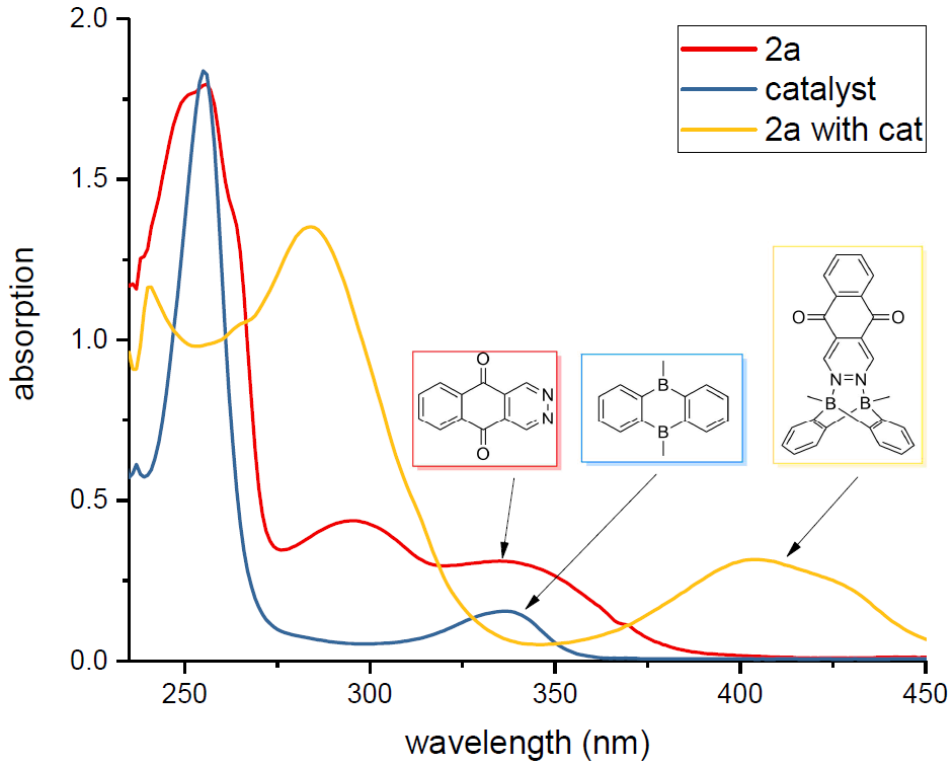


UV/Vis Spectra of 5,8-dihydroxy-2,3-diaza-9,10-anthracenedione (**2d**) in DMSO



UV/Vis Spectra of 2,3-diaza-5,12-naphthacenedione (**2e**) in DMSO

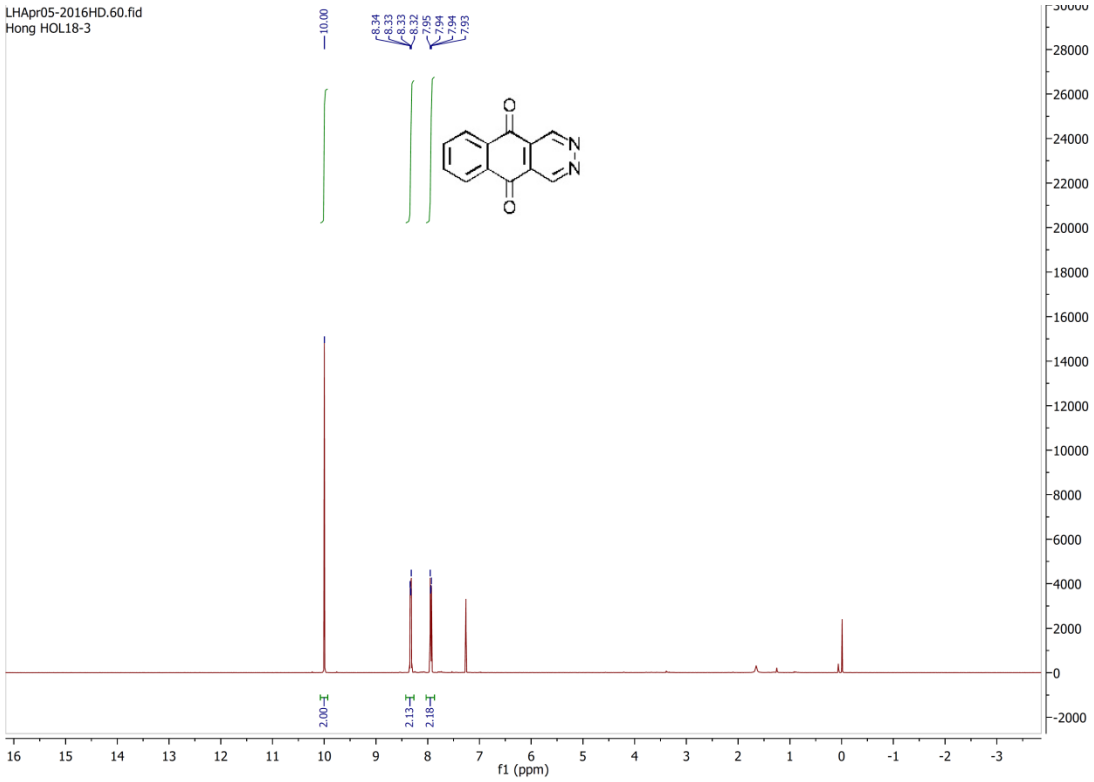
UV-spectrum of a 1:1 complex of catalyst with 2a



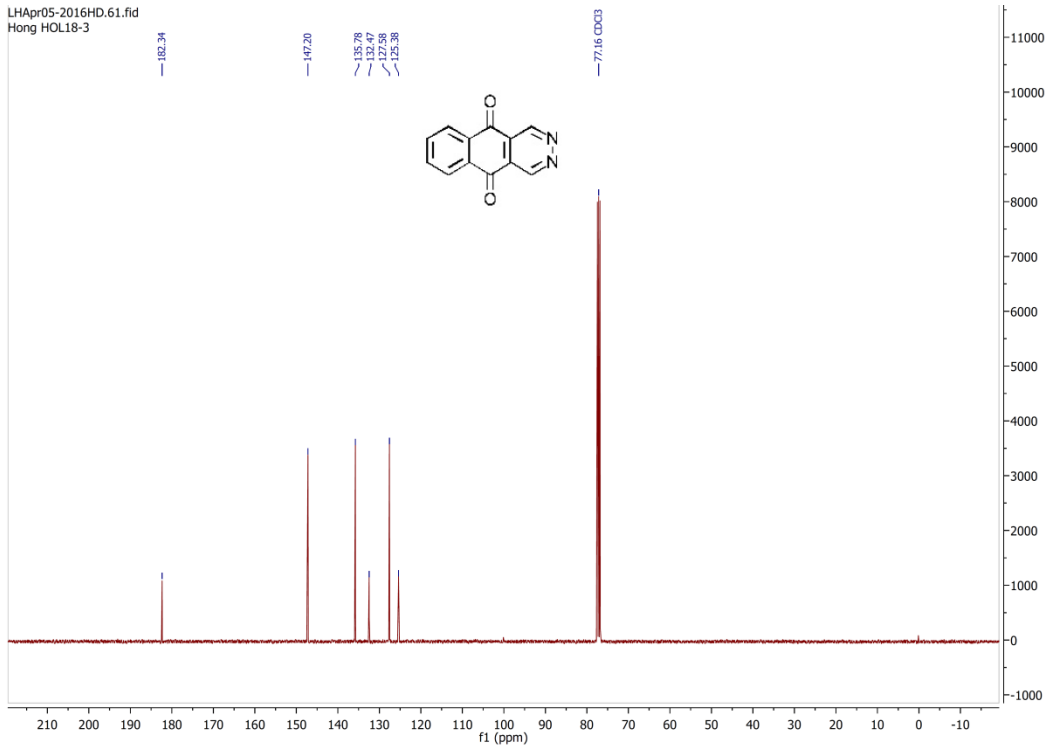
UV-spectrum of a 1:1 complex of catalyst with **2a** was measured in $CHCl_3$ under the protection of N_2 (Concentrations: **2a**: 5.12×10^{-5} mol/L, catalyst: 4.52×10^{-5} mol/L, complex of **2a**/catalyst: 4.52×10^{-5} mol/L).

^{1}H and ^{13}C NMR spectra of products

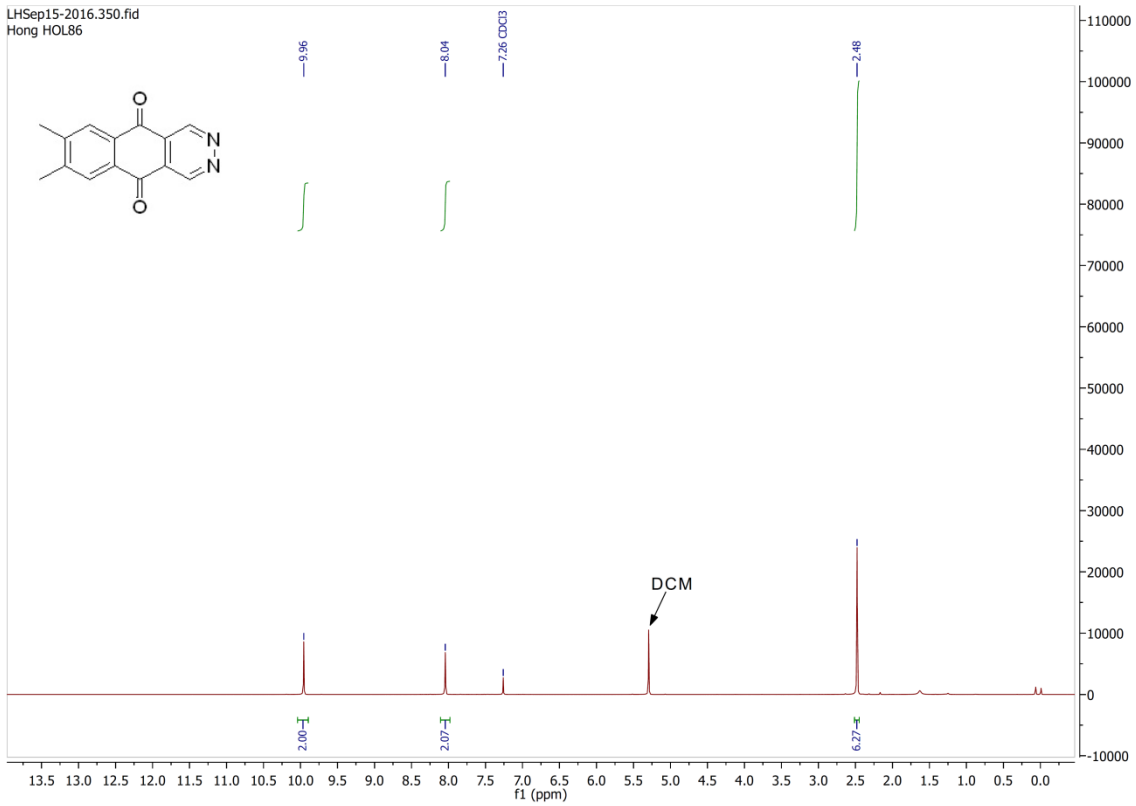
^{1}H NMR Spectrum of 2,3-diaza-9,10-anthracenedione (**2a**)



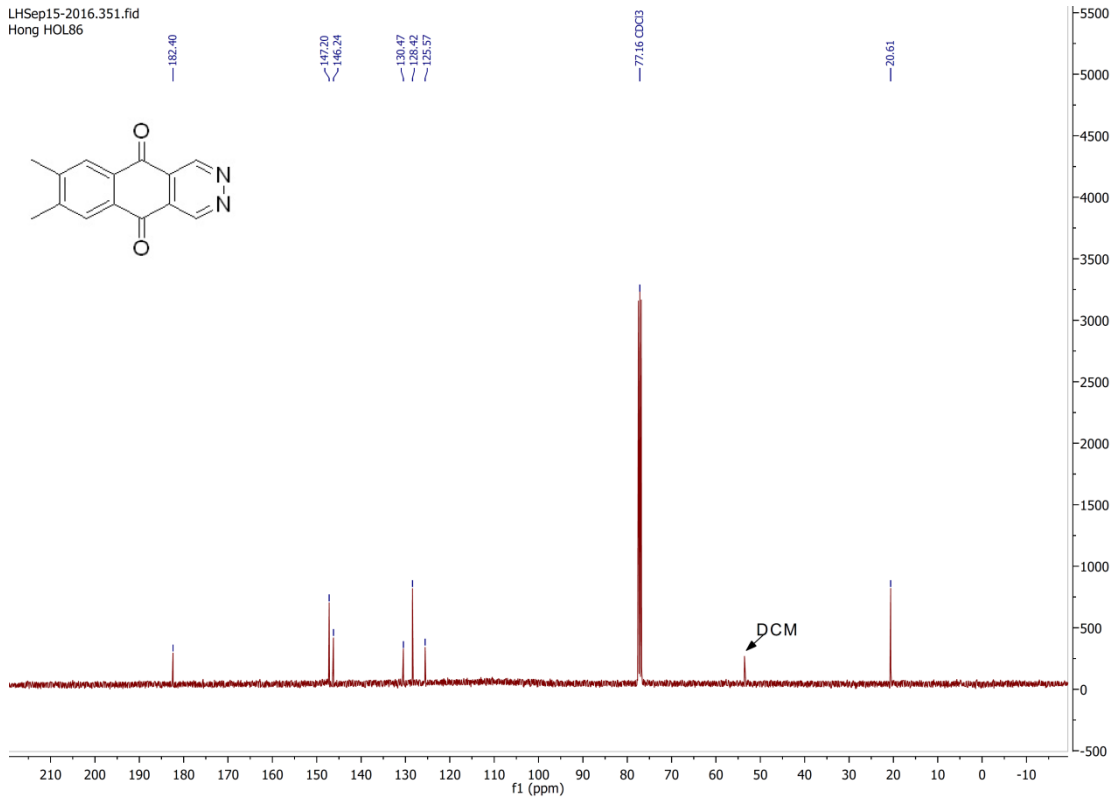
^{13}C NMR Spectrum of 2,3-diaza-9,10-anthracenedione (**2a**)



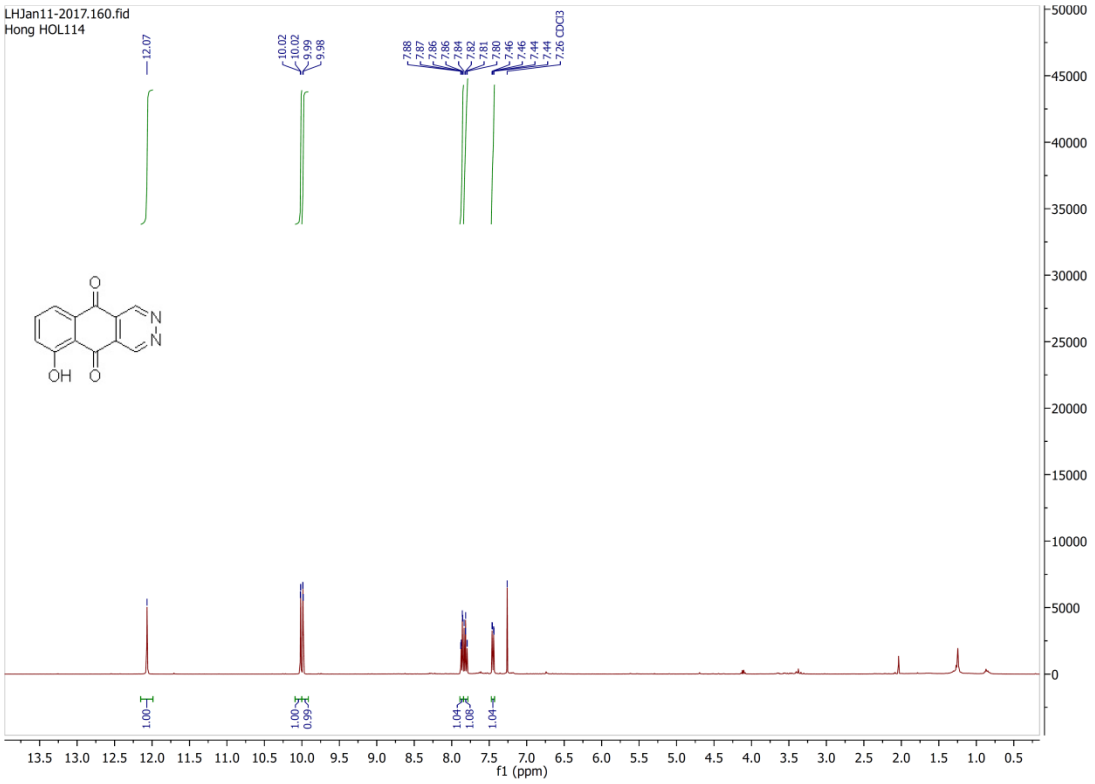
^{1}H NMR Spectrum of 6,7-dimethyl-2,3-diaza-9,10-anthracenedione (**2b**)



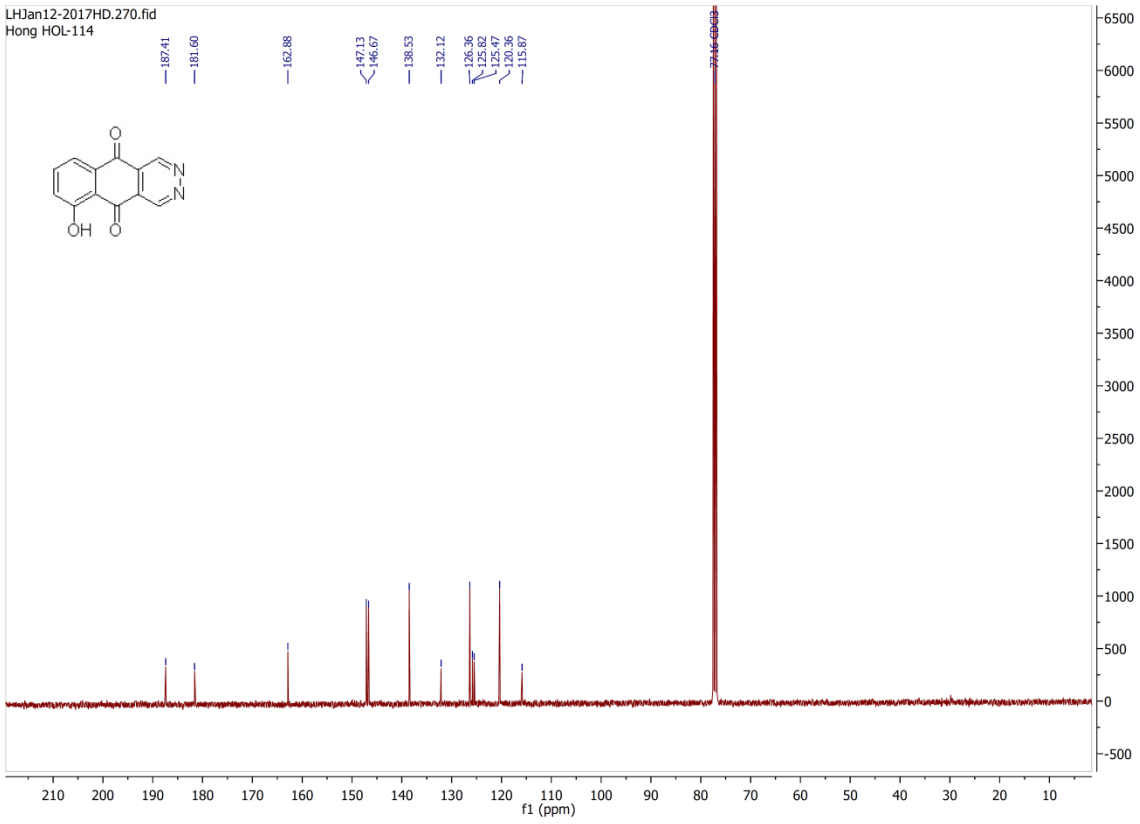
^{13}C NMR Spectrum of 6,7-dimethyl-2,3-diaza-9,10-anthracenedione (**2b**)



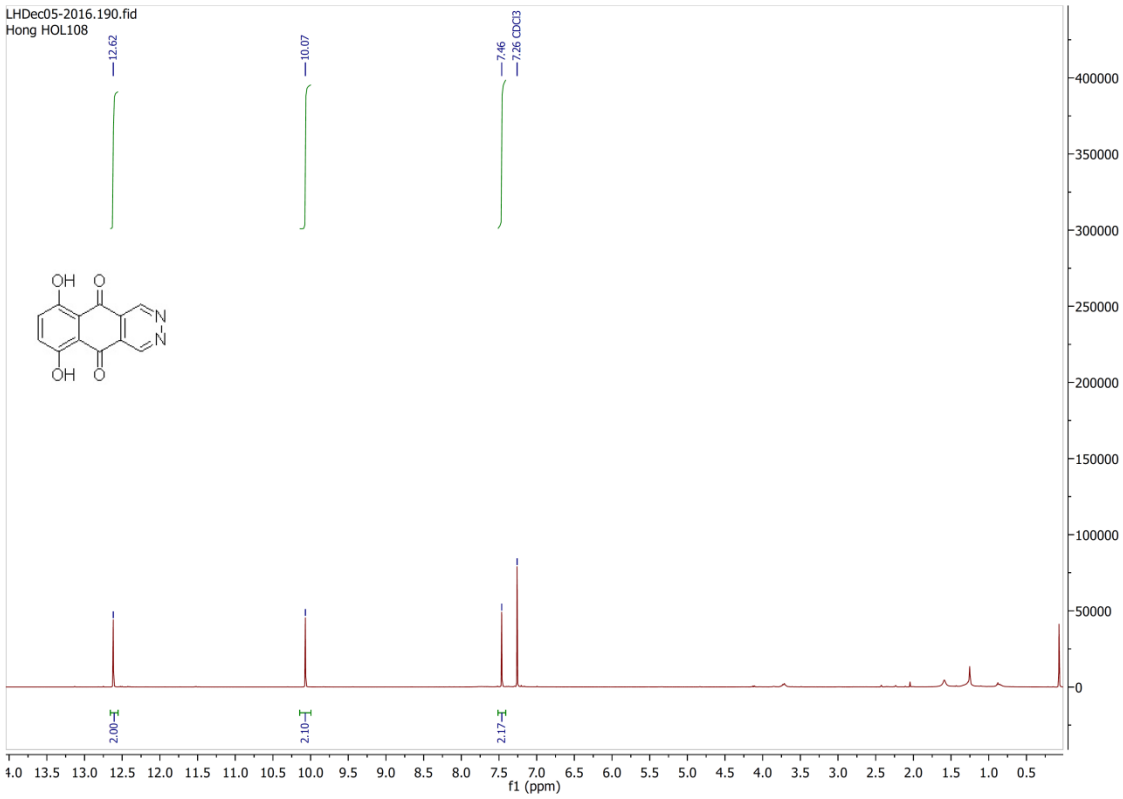
^{1}H NMR Spectrum of 5-hydroxy-2,3-diaza-9,10-anthracenedione (**2c**)



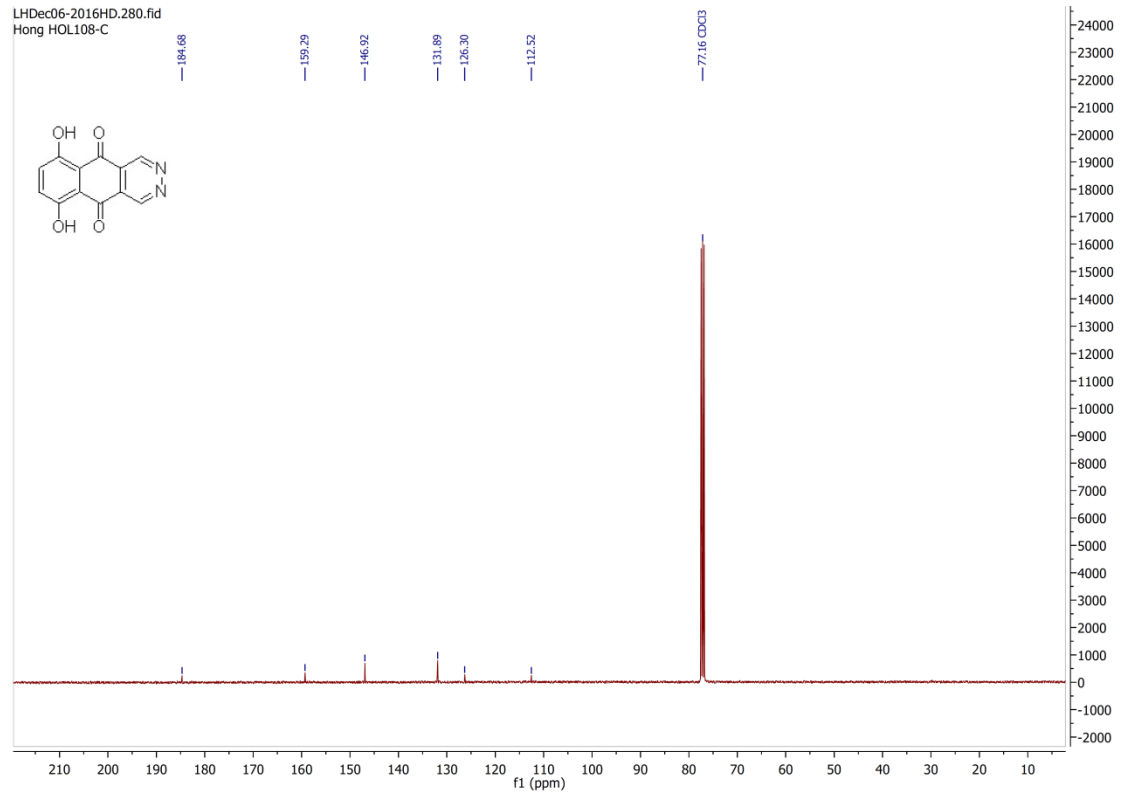
^{13}C NMR Spectrum of 5-hydroxy-2,3-diaza-9,10-anthracenedione (**2c**)



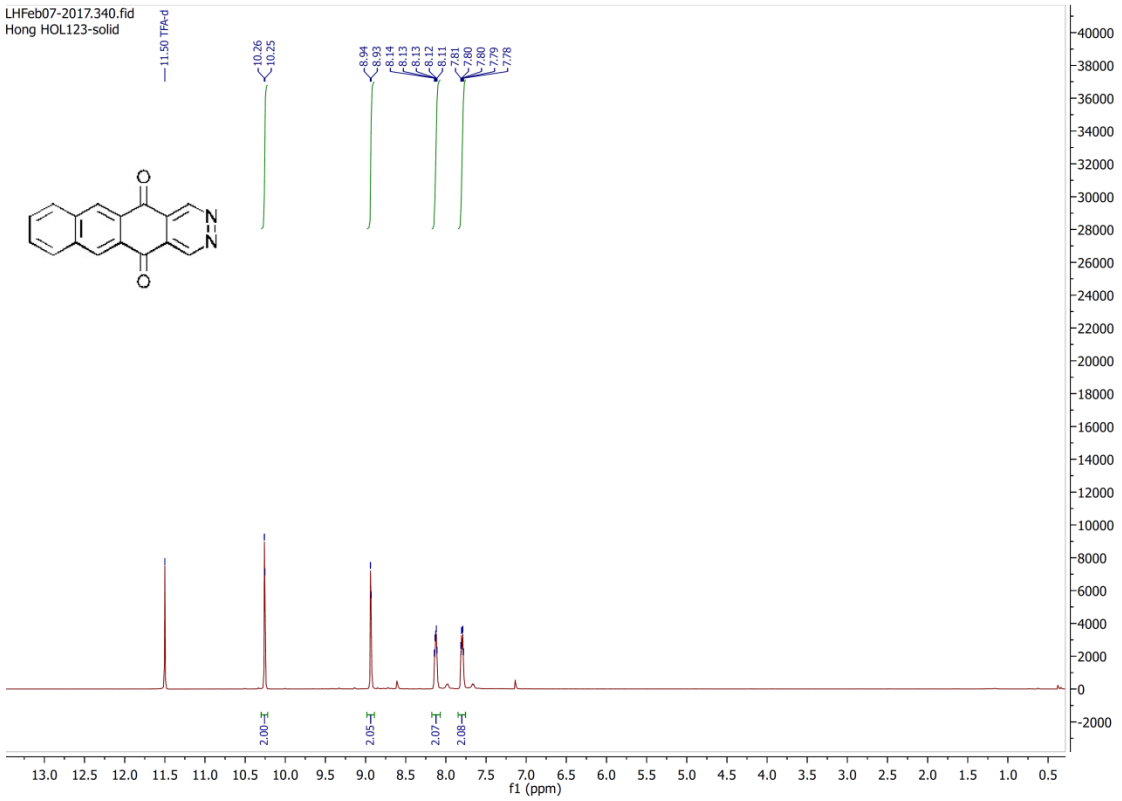
^{1}H NMR Spectrum of 5,8-dihydroxy-2,3-diaza-9,10-anthracenedione (**2d**)



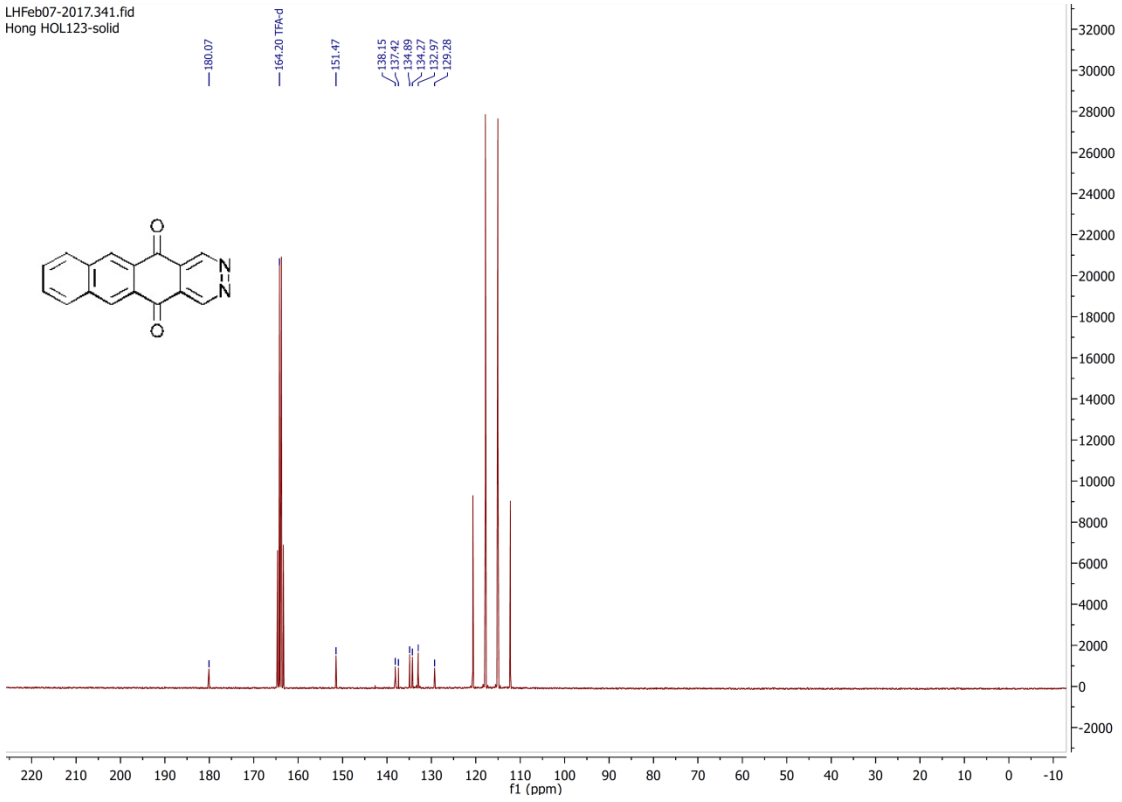
^{13}C NMR Spectrum of 5,8-dihydroxy-2,3-diaza-9,10-anthracenedione (**2d**)



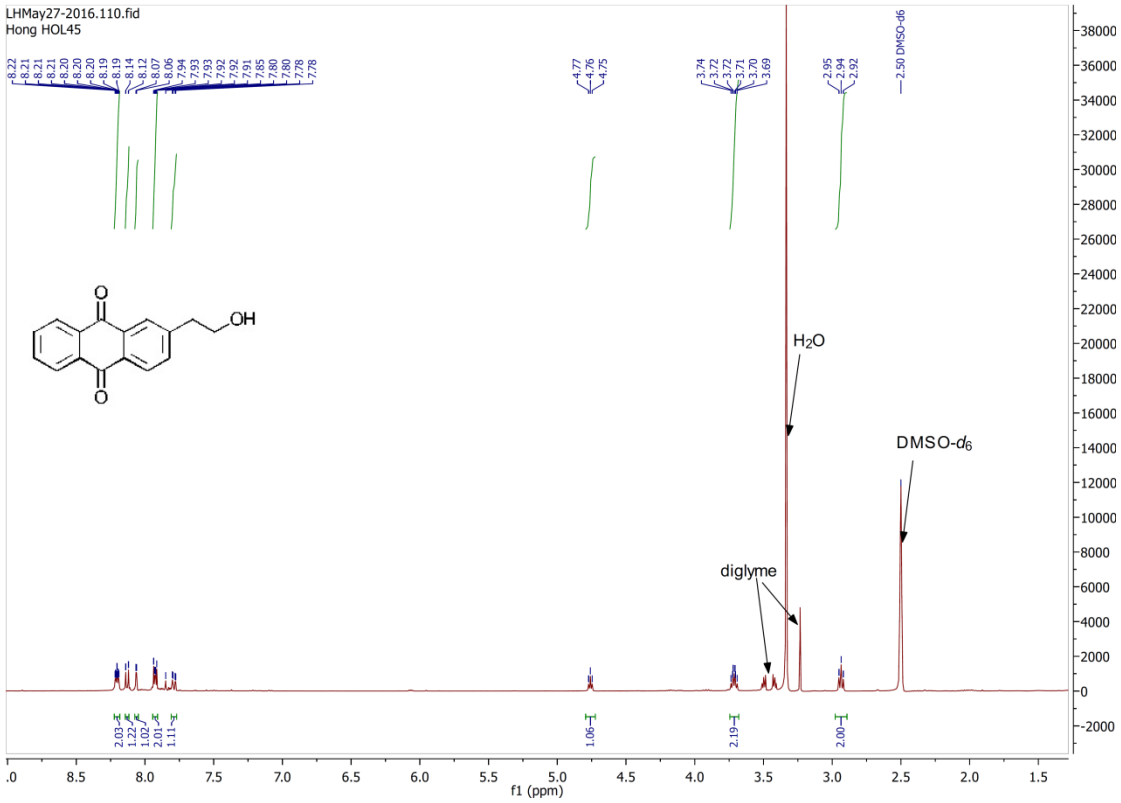
^{1}H NMR Spectrum of 2,3-diaza-5,12-naphthacenedione (**2e**)



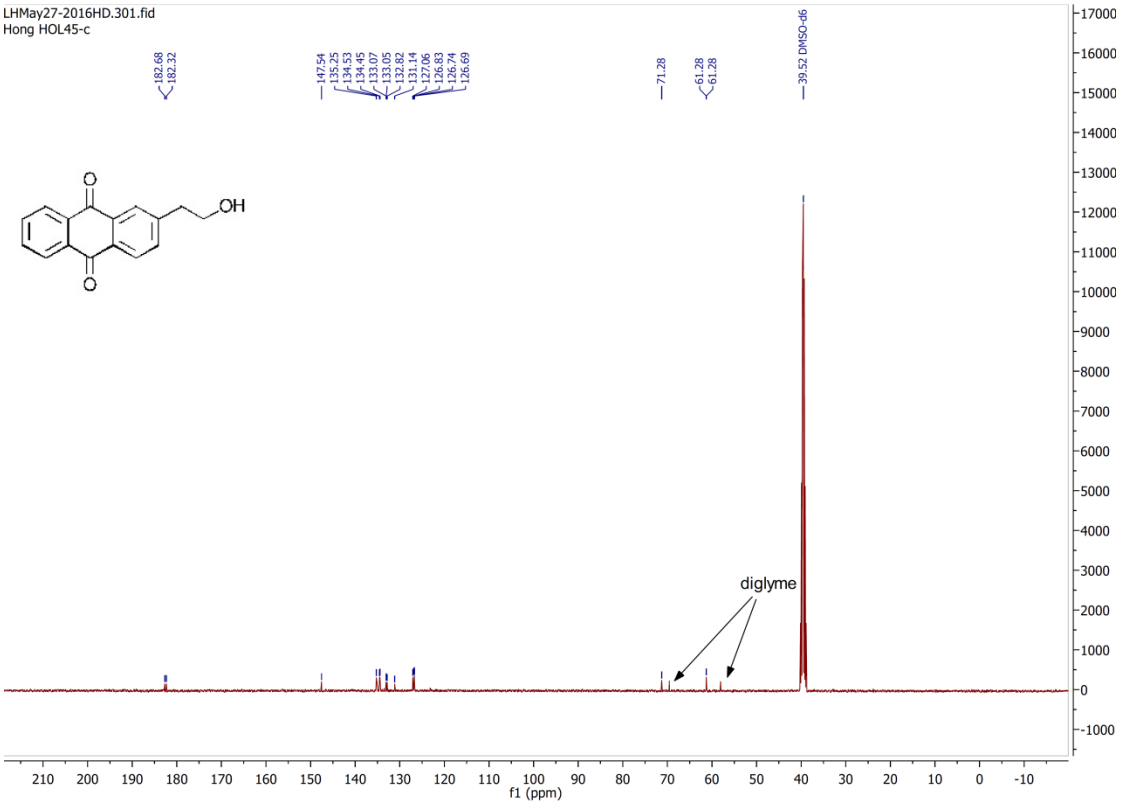
^{13}C NMR Spectrum of 2,3-diaza-5,12-naphthacenedione (**2e**)



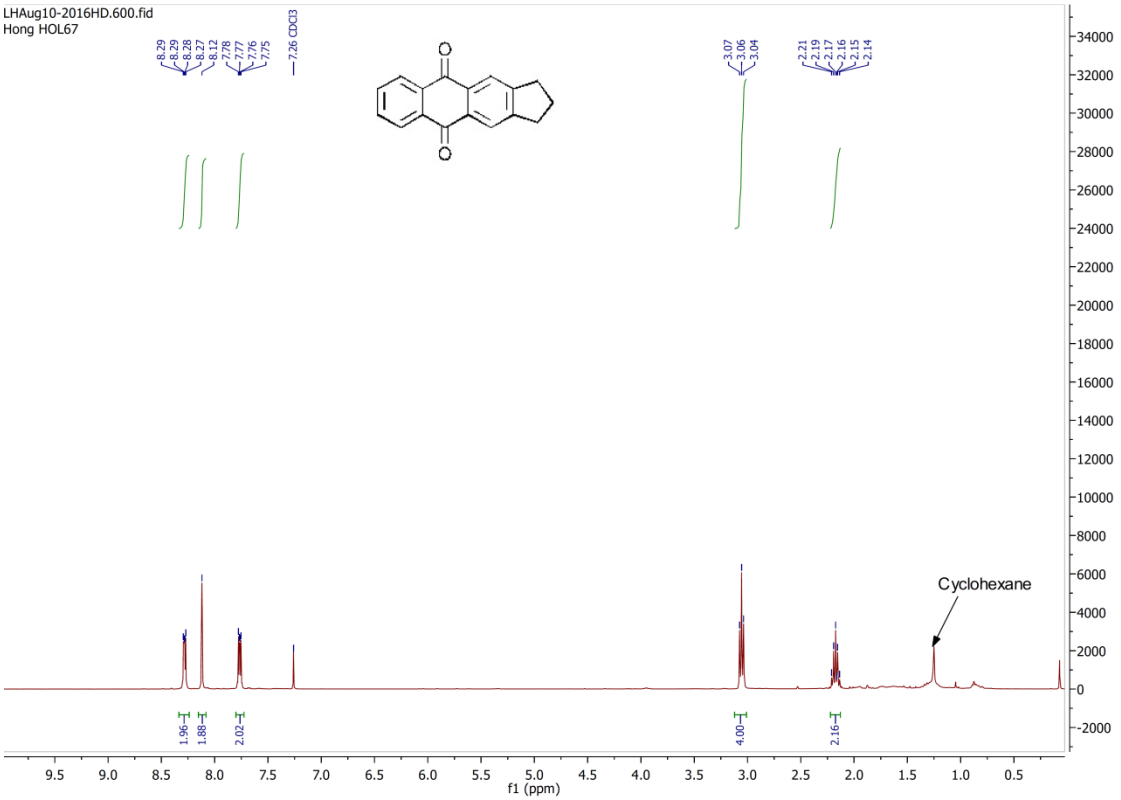
^{1}H NMR Spectrum of 2-(2-hydroxyethyl)-9,10-anthraquinone (**3a**)



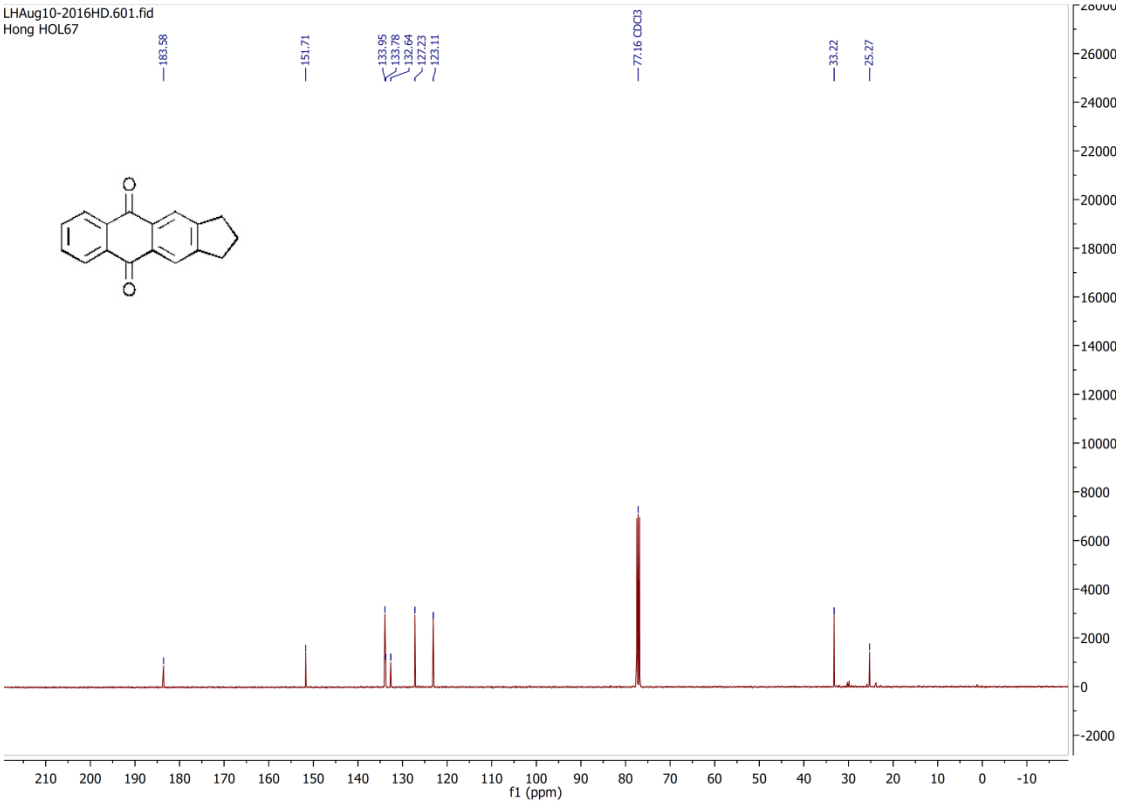
^{13}C NMR Spectrum of 2-(2-hydroxyethyl)-9,10-anthraquinone (**3a**)



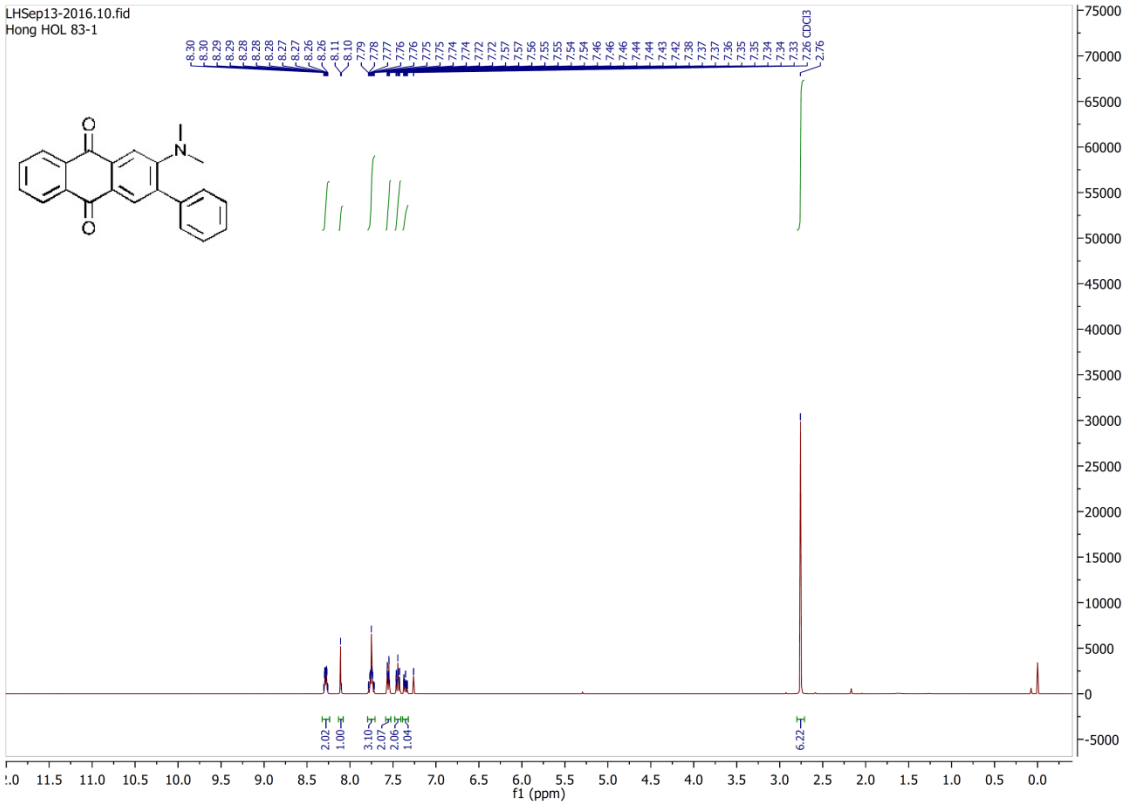
^{1}H NMR Spectrum of 2,3-dihydro-1*H*-cyclopenta[*b*]anthracene-5,10-dione (**3b**)



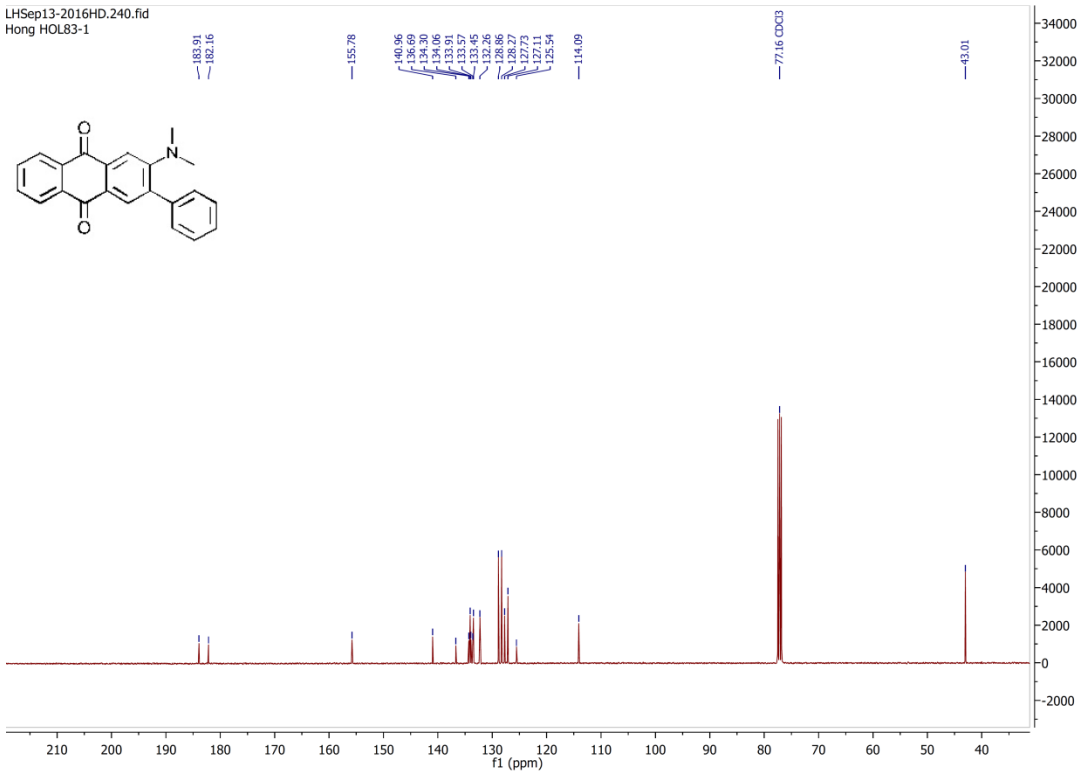
^{13}C NMR Spectrum of 2,3-dihydro-1*H*-cyclopenta[*b*]anthracene-5,10-dione (**3b**)



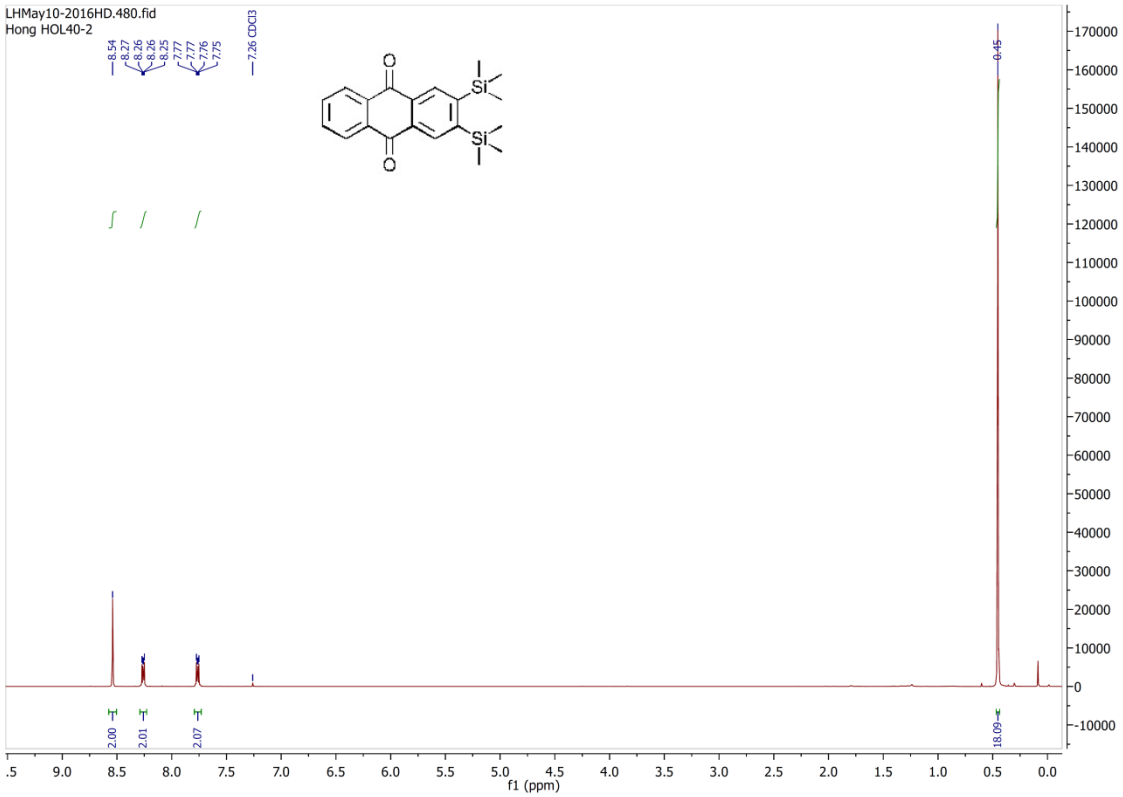
^{1}H NMR Spectrum of 2-(dimethylamino)-3-phenyl-9,10-anthraquinone (**3c**)



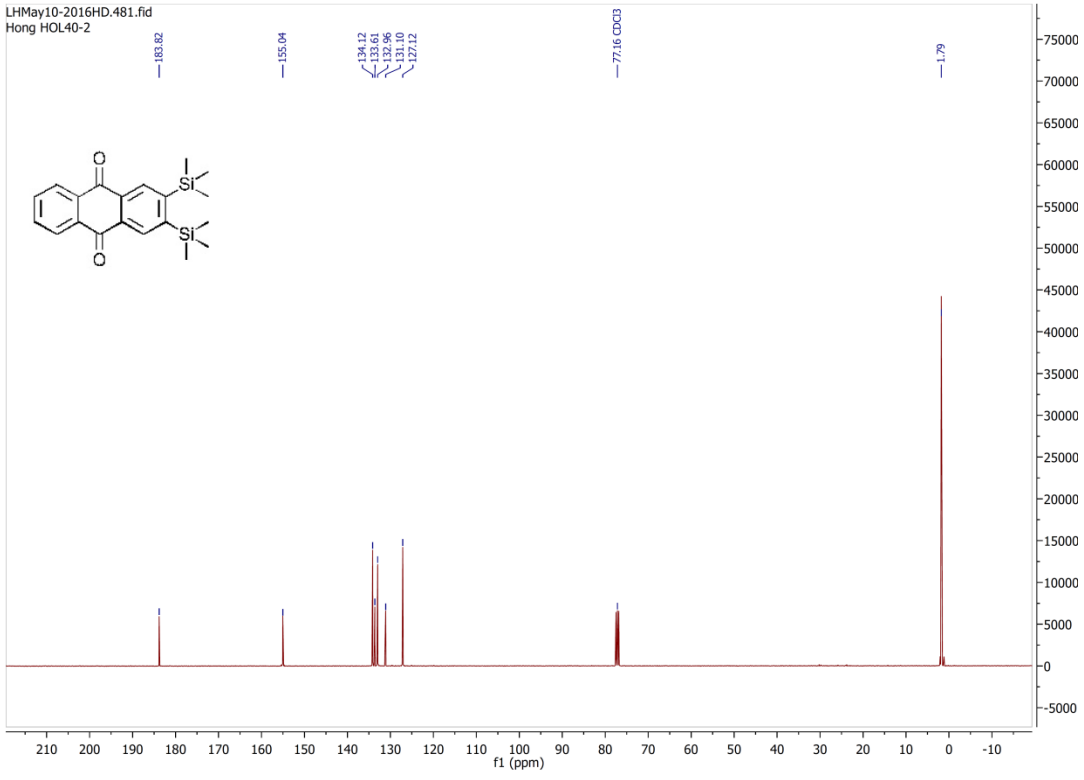
^{13}C NMR Spectrum of 2-(dimethylamino)-3-phenyl-9,10-anthraquinone (**3c**)



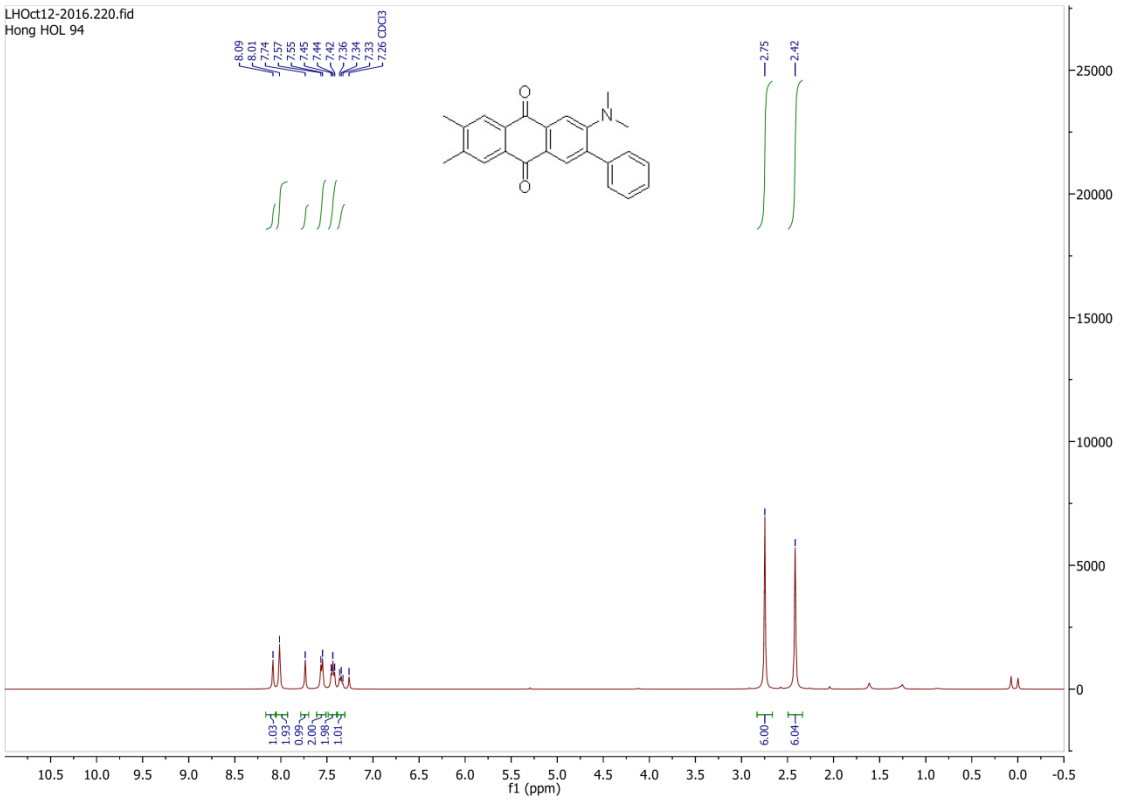
^{1}H NMR Spectrum of 2,3-bis(trimethylsilyl)-9,10-anthraquinone (**3d**)



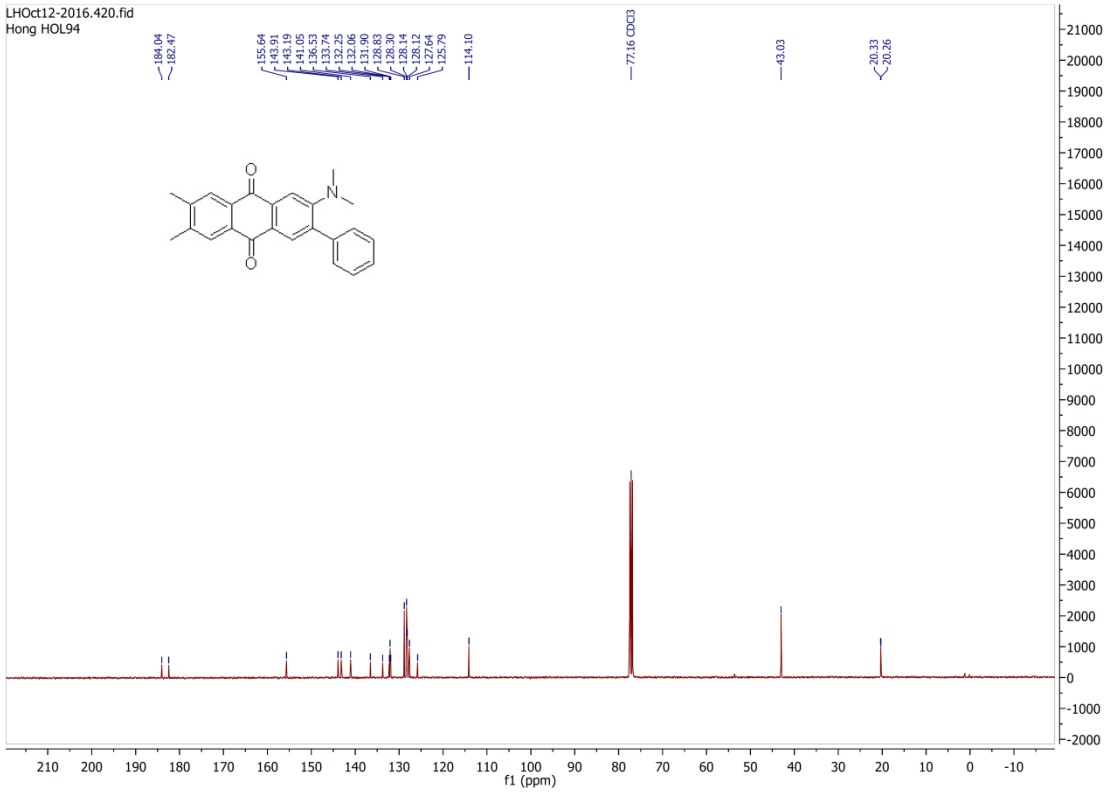
^{13}C NMR Spectrum of 2,3-bis(trimethylsilyl)-9,10-anthraquinone (**3d**)



^{1}H NMR Spectrum of 2-(dimethylamino)-6,7-dimethyl-3-phenyl-9,10-anthraquinone (**3e**)



^{13}C NMR Spectrum of 2-(dimethylamino)-6,7-dimethyl-3-phenyl-9,10-anthraquinone (**3e**)



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