

Supporting Information

Synthesis and near infrared electrochromic properties of novel anthraquinone imide derivatives

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General method: ¹H NMR spectra were measured on a Bruker ARX400 (400 MHz) spectrometer at the ambient temperature with CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal standard. ¹³C NMR spectra were recorded on Bruker ARX400 (125 MHz) spectrometer at the ambient temperature with CDCl₃ as the solvent. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (CDCl₃ at 77 ppm). Mass spectra were recorded on a Micromass Finnigan MAT ZAB-HS mass spectrometer. Elemental analyses were performed on an Elementar Vario EL instrument. Melting points were determined by differential scanning calorimetry (TA Q100) at a heating rate of 10 °C/min under N₂ atmosphere. Cyclic voltammetry was carried out on a CHI 630C electrochemical workstation. The solutions were made in CH₂Cl₂ containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and were degassed with nitrogen prior to electrochemical work. Platinum working and counter electrodes were employed together with a silver pseudoreference electrode. All the electrochemical measurements were referenced to Ag/Ag⁺. The pseudo-reference was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc⁺). Spectroelectrochemical data were performed on a Shimadzu UV 3100 UV-Visible-NIR spectrophotometer connected to a computer in an optical transparent thin layer (OTTLE) cell.

Preparation of 6-nitro-2,3-dimethylanthraquinone (6NO₂-DMAQ).

Aluminum(III) chloride (88.0 g, 0.66 mol) was added to a suspension of 4-bromophthalic anhydride 1 (57.9g, 0.30 mol) in *o*-xylene (400 mL). The mixture was refluxed for 4 h then cooled to room temperature, and 400 mL cooled 2M HCl was added. The resulting mixture was stirred for 2 h and taken up in ether, and extracted with 2 M NaOH. The aqueous solution was washed with ether and acidified to pH ~2 with cold concentrated HCl. The solid thus precipitated was filtered, washed with dilute HCl and water successively. After dried, 57.6 g of white solids were obtained in 64% yield.

15.0 g of above obtained solid was dissolved in concentrated sulfuric acid (100 mL). The solution was warmed gradually to 110 °C over 30 min, kept at this temperature for 1 h, and then poured onto ice (400 g). The precipitated gray powder was collected

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by filtration, washed with water, dried, and purified by silica gel chromatography (CH_2Cl_2) to afford a yellow powder containing isomers. Three times of recrystallization from toluene resulted in a mixture of needle-like and grain-like crystals. The needle-like crystals had a much better solubility in dichloromethane than the other grain-like crystals. Thus, the crystalline mixture was further treated with dichloromethane, followed by removal of solvent and recrystallization from toluene, to yield pure **6NO₂-2,3-DMAQ** in yield of 10 % (not including the recovered product).

m.p. 220.8~222.0 °C. m/z 281. ¹H NMR(400 MHz, CDCl_3) δ 2.46 (s, 6H, CH_3), 8.03 (s, 1H, ArH), 8.05 (s, 1H, ArH), 8.43 (d, 1H, $J=8.1$ Hz, $m\text{-ArH}$ to NO_2), 8.53 (dd, 1H, $J=2.3$ and 8.4 Hz, $o\text{-ArH}$ to NO_2), 9.03 (d, 1H, $J=2.3$ Hz, $o\text{-ArH}$ to NO_2). ¹³C NMR(125 MHz, CDCl_3) δ 20.30, 122.38, 127.68, 128.50, 128.54, 128.91, 131.04, 131.16, 134.73, 137.08, 145.12, 145.16, 151.07, 181.04, 181.49. Anal.Calcd for $\text{C}_{16}\text{H}_{11}\text{NO}_4$: C, 68.32; H, 3.94; N, 4.98. Found: C, 68.32; H, 4.00; N, 4.98.

Preparation of 6-bromo-2,3-dimethylantraquinone (6Br-DMAQ).

Aluminum(III) chloride (88.0 g, 0.66 mol) was added to a suspension of 4-bromophthalic anhydride 1 (68.1g, 0.30 mol) in *o*-xylene (400 mL). The mixture was refluxed for 4 h then cooled to room temperature, and 400 mL cooled 2M HCl was added. The resulting mixture was stirred for 2 h and taken up in ether, and extracted with 2 M NaOH. The aqueous solution was washed with ether and acidified to pH ~2 with cold concentrated HCl. The solid thus precipitated was filtered, washed with dilute HCl and water successively. After dried, obtained 89.6 g white solid in 90% yield.

30.0 g of above obtained solid was dissolved in concentrated sulfuric acid (200 mL). The solution was warmed gradually to 110 °C over 30 min, kept at this temperature for 1 h, and then poured onto ice (800 g). The precipitated gray powder was collected by filtration, washed with water, dried, and purified by silica gel chromatography (CH_2Cl_2) to afford a yellow powder containing a small amount of isomers. The isomers were separated by recrystallization with acetic acid/petroleum ether (V/V=1/1) three to four times to afford isomerically pure 2, 3-dimethyl-6-bromoanthraquinone as a light yellow powder (12 g, yield 42%).

m.p. 194.8~196.0 °C. m/z 314. ¹H NMR(400 MHz, CDCl_3) δ 2.43 (s, 6H, CH_3), 7.86 (dd, 1H, $J=2.1$ and 8.4 Hz, $o\text{-ArH}$ to Br), 8.01 (s, 2H, $o\text{-ArH}$ to CH_3), 8.21 (d, 1H, $J=8.3$ Hz, $m\text{-ArH}$ to Br), 8.38 (d, 1H, $J=2.0$ Hz, $o\text{-ArH}$ to Br). ¹³C NMR(125 MHz, CDCl_3) δ 20.23, 20.26, 128.24, 128.28, 128.84, 129.39, 130.04, 131.12, 131.24, 132.21, 134.69, 136.81, 144.36, 144.51, 182.08, 182.46. Anal.Calcd for $\text{C}_{16}\text{H}_{11}\text{BrO}_2$: C, 60.98; H, 3.52. Found: C, 60.75; H, 3.55.

Preparation of 6-nitro-anthraquinone-2,3-dicarboxylic acid (6NO₂-AQA).

6NO₂-DMAQ (2.0 g, 7.1 mmol) was dissolved in 20 mL concentrated sulfuric acid. The mixture was slowly added in 100 mL H₂O. The resulting mixture was heated to 90 °C, then added 14.22 g (90 mmol) of KMnO_4 as several portion during 4 h. The resulting mixture was heated for another 1 h, then cooled to room temperature and excessive oxalic acid was added until the color was changed from black to light yellow. The solid was filtrated and washed with water, then added into 50 mL

ammonia water. The mixture was filtrated and the solution was acidified with dilute HCl to pH ~2. The precipitate thus formed was filtrated and washed with water and dried to afford a light yellow powder (1.4 g, yield 58%).

The characteristics of its dimethyl ester: m.p. 233.0~234.8 °C. m/z 369. ^1H NMR (400MHz, CDCl_3) δ 4.01 (s, 3H, CH_3), 4.02 (s, 3H, CH_3), 8.55 (d, 1H, $J=8.4$ Hz, $m\text{-ArH}$ to NO_2), 8.64 (dd, 1H, $J=2.3$ and 8.5 Hz, $o\text{-ArH}$ to NO_2), 8.67 (s, 1H, $o\text{-ArH}$ to C-C=O), 8.69 (s, 1H, $o\text{-ArH}$ to C-C=O), 9.15 (d, 1H, $J=2.3$ Hz, $o\text{-ArH}$ to NO_2). Anal.Calcd for $\text{C}_{18}\text{H}_{11}\text{NO}_8$: C, 58.54; H, 3.00; N, 3.79. Found: C, 58.68; H, 3.13; N, 3.74.

Preparation of 6-bromo-anthraquinone-2,3-dicarboxylic acid (6Br-AQA).

6Br-AQA was synthesized with the similar method as 6NO₂-AQA in 31% yield.

The characteristics of its dimethyl ester: m.p. 177.7~178.8 °C. m/z 402. ^1H NMR (400 MHz, CDCl_3) δ 4.00 (s, 6H, CH_3), 7.96 (dd, 1H, $J=2.2$ and 8.4 Hz, $o\text{-ArH}$ to Br), 8.19 (d, 1H, $J=8.3$ Hz, $o\text{-ArH}$ to Br), 8.46 (d, 1H, $J=2.0$ Hz, $m\text{-ArH}$ to Br), 8.622 (s, 1H, $o\text{-ArH}$ to C-C=O), 8.624 (s, 1H, $o\text{-ArH}$ to C-C=O). ^{13}C NMR(125 MHz, CDCl_3) δ 53.20, 128.19, 128.25, 129.27, 130.45, 130.54, 131.81, 134.20, 134.34, 134.51, 136.70, 136.88, 137.73, 166.28, 166.33, 180.52, 180.83. Anal.Calcd for $\text{C}_{18}\text{H}_{11}\text{BrO}_6$: C, 53.62; H, 2.75. Found: C, 53.62; H, 2.91.

Preparation of N-butyl-6-nitroanthraquinone-2,3-dicarboxylic imide (6NO₂-AQI).

2.49 g of 6NO₂-AQA and 60 mL acetic anhydride were added into a 100 mL round bottom flask. The mixture was heated to reflux for 12 h then cooled to room temperature and green-yellow crystalline solid was produced. The solid was filtrated and washed with petroleum ether. After dried, 6-nitroanthraquinone-2,3-dicarboxylic anhydride was obtained(1.92 g, yield: 81%).

n-butyl amine (0.27 g, 3.6 mmol) and anhydrous DMF (15 mL) were added into a 50 mL three necked flask. Under Ar atmosphere, 6-nitroanthraquinone-2,3-dicarboxylic anhydride (0.97g, 3.0 mmol) was added. After was stirred for 1 h at room temperature, the mixture was heated to reflux. After 12 h, the mixture was allowed to cool to room temperature, the solid thus produced was filtrated and washed with methanol. After dried, the product was purified by silica gel chromatography (CH_2Cl_2) to afford 6NO₂-AQI (0.63 g) in 55% yield.

m.p. 327.2~328.3 °C. m/z 378. ^1H NMR (400 MHz, CDCl_3) δ 0.95~0.99 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.37~1.43 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.57~1.75 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.77~3.81 (t, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 8.58 (d, 1H, $J=8.5$ Hz, $m\text{-ArH}$ to NO_2), 8.67 (dd, 1H, $J=2.3$ and 8.5 Hz, $o\text{-ArH}$ to NO_2), 8.83 (s, 1H, $o\text{-ArH}$ to C=O), 8.85 (s, 1H, $o\text{-ArH}$ to C=O), 9.18 (d, 1H, $J=2.2$ Hz, $o\text{-ArH}$ to NO_2). Anal.Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_6$: C, 63.49; H, 3.73; N, 7.40. Found: C, 63.57; H, 3.93; N, 7.45.

Preparation of N-butyl-6-bromoanthraquinone-2,3-dicarboxylic imide (6Br-AQI).

6Br-AQI was synthesized with the similar method as 6NO₂-AQI in 78% yield.

m.p. 283.1~284.1 °C. m/z 411. ^1H NMR (400 MHz, CDCl_3) δ 0.95~0.99 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.35~1.44 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.57~1.75 (m, 2H,

CH₃CH₂CH₂CH₂N), 3.76~3.79 (t, 2H, CH₃CH₂CH₂CH₂N), 7.99 (dd, 1H, *J*=1.9 and 8.3 Hz, *o*-ArH to Br), 8.22 (d, 1H, *J*=8.3 Hz, *m*-ArH to Br), 8.49 (d, 1H, *J*=1.8 Hz, *o*-ArH to Br), 8.768 (s, 1H, *o*-ArH to C=O), 8.773 (s, 1H, *o*-ArH to C=O). ¹³C NMR(125 MHz, CDCl₃) δ 13.60, 20.10, 30.47, 38.54, 122.57, 122.60, 129.42, 130.72, 131.64, 134.02, 136.11, 136.22, 137.62, 137.81, 137.99, 166.45, 166.47, 180.57, 180.86. Anal.Calcd for C₂₀H₁₄BrNO₄: C, 58.27; H, 3.42; N, 3.40. Found: C, 58.31; H, 3.59; N, 3.38.

Preparation of *N*-butyl-6-(4-methoxyphenoxy)anthraquinone- 2,3-dicarboxylic imide (CH₃OPh-O-AQI)

0.27 g (0.6 mmol) **6NO₂-AQI** was added to 30 mL of anhydrous DMSO. The mixture was heated to 120 °C under Ar atmosphere. Then, 0.088 g (0.6 mmol) sodium 4-methoxyphenolate was added. After stirred for 15 min at 120 °C, the solution was allowed to cool to room temperature and poured into 100 mL dilute HCl. The precipitate was collected by filtration and washed with water. After dried *in vacuo*, the product was purified by column chromatography (silica gel, CH₂Cl₂) to give **CH₃OPh-O-AQI** as a yellow solid in 34% yield.

m.p. 222.2~223.3 °C. *m/z* 455. ¹H NMR (400 MHz, CDCl₃) δ 0.95~0.98 (t, 3H, CH₃CH₂CH₂CH₂N), 1.34~1.44 (m, 2H, CH₃CH₂CH₂CH₂N), 1.66~1.74 (m, 2H, CH₃CH₂CH₂CH₂N), 3.74~3.78 (t, 2H, CH₃CH₂CH₂CH₂N), 3.86 (s, 3H, CH₃O), 6.97~6.70 (m, 2H, *o*-ArH to -O-), 7.05~7.08 (m, 2H, *o*-ArH to CH₃O-), 7.36 (dd, 1H, *J*=2.6 and 8.8 Hz, *o*-ArH to -O-Ph-OCH₃), 7.71 (d, 1H, *J*=2.6 Hz, *o*-ArH to O-Ph-OCH₃), 8.31 (d, 1H, *J*=8.7 Hz, *m*-ArH to -O-Ph-OCH₃), 8.71 (s, 1H, *o*-ArH to C=O), 8.76 (s, 1H, *o*-ArH to C=O). ¹³C NMR(125 MHz, CDCl₃) δ 13.59, 20.08, 30.46, 38.44, 55.69, 113.79, 115.44, 121.87, 122.35, 122.44, 122.95, 127.37, 130.53, 135.17, 135.63, 135.97, 137.98, 138.17, 147.57, 157.31, 164.60, 166.62, 166.65, 180.33, 181.37. Anal.Calcd for C₂₇H₂₁NO₆: C, 71.20; H, 4.65; N, 3.08. Found: C, 71.43; H, 4.46; N, 3.22.

Preparation of *N*-butyl-6-(4-hexyloxyphenyl)anthraquinone- 2,3-dicarboxylic imide (C₆H₁₃OPh-O-AQI).

To a 50 mL three-necked round bottom flask fitted with a magnetic stirring bar and a condenser was added 0.21 g (0.5 mmol) **6Br-AQI**, 0.22 g (1.0 mmol) 4-(hexyloxy)phenylboronic acid, 0.21 g (2.0 mmol) Na₂CO₃ and 23.1 mg (0.02 mmol) (PPh₃)₄Pd(0). After degassed three times by alternately connecting to vacuum and Ar, 20 mL benzene, 2 mL EtOH and 2 mL H₂O were added under Ar atmosphere. Then, the contents were heated to reflux for 30 min. After cooling, the reaction mixture was poured into 20 mL water and extracted with CH₂Cl₂ (3×50 mL). The combined organic layer was washed successively with water and brine and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, CH₂Cl₂) to give **C₆H₁₃OPh -AQI** as a golden solid in 98% yield.

m.p. 248.7~249.8 °C; clear point 275.7~276.5 °C. *m/z* 509. ¹H NMR (400 MHz, CDCl₃) δ 0.91~0.99 (m, 6H, CH₃CH₂CH₂CH₂N and CH₃CH₂CH₂CH₂CH₂CH₂O), 1.35~1.50 (m, 8H, CH₃CH₂CH₂CH₂N and CH₃CH₂CH₂CH₂CH₂CH₂O), 1.69~1.73 (m, 2H, CH₃CH₂CH₂CH₂N), 1.81~1.86(m, 2H, CH₃CH₂CH₂CH₂CH₂CH₂O), 3.75~3.79 (t,

2H, CH₃CH₂CH₂CH₂N), 4.02~4.05(t, 2H, CH₃CH₂CH₂CH₂CH₂CH₂O), 7.02~7.04(m, 2H, *o*-ArH to OC₆H₁₃), 7.67~7.69(m, 2H, *m*-ArH to OC₆H₁₃), 8.02 (dd, 1H, *J*=1.9 and 8.1, Hz, *o*-ArH to -Ph-OC₆H₁₃), 8.36 (d, 1H, *J*=8.2 Hz, *m*-ArH to -Ph-OC₆H₁₃), 8.51 (d, 1H, *J*=1.8 Hz, *o*-ArH to O-Ph-OCH₃), 8.77 (s, 1H, *o*-ArH to C=O) , 8.78 (s, 1H, *o*-ArH to C=O). ¹³C NMR(125 MHz, CDCl₃) δ 13.59, 14.03, 20.09, 22.60, 25.70, 29.17, 30.47, 31.57, 38.45, 68.23, 115.21, 122.41, 122.44, 125.06, 128.50, 128.53, 130.40, 130.93, 132.24, 133.41, 135.75, 135.90, 138.06, 138.22, 147.26, 160, 32, 166.65, 181.14, 181.79. Anal.Calcd for C₃₂H₃₁NO₅: C, 75.42; H, 6.13; N, 2.75. Found: C, 75.63; H, 6.47; N, 2.94.

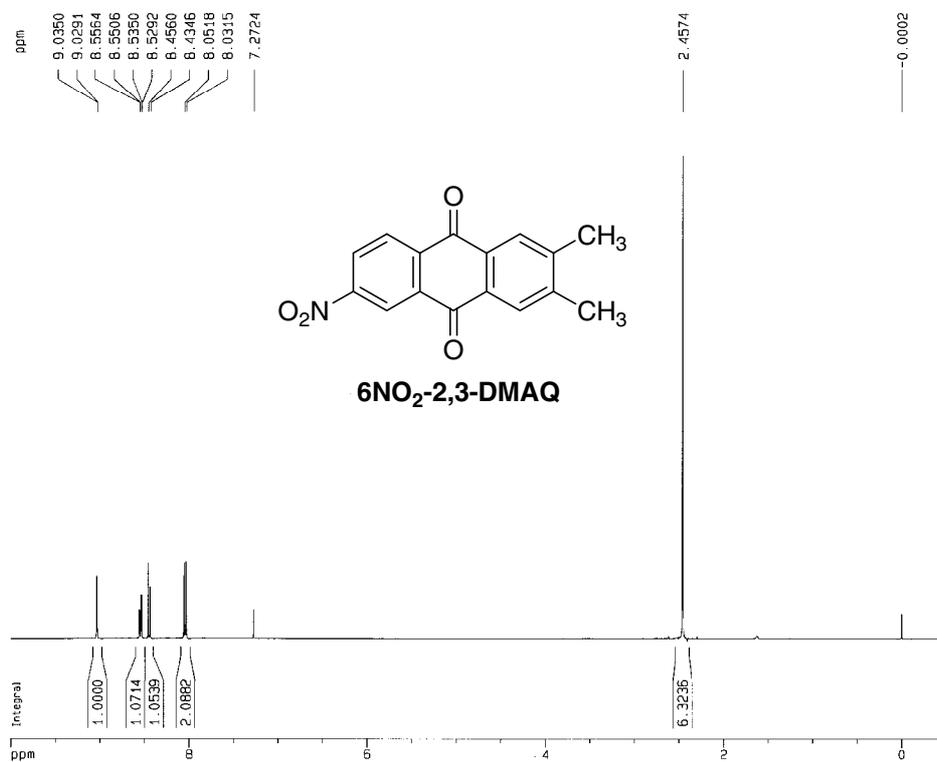


Figure S1 ¹H NMR spectrum of **6NO₂-2,3-DMAQ** in CDCl₃

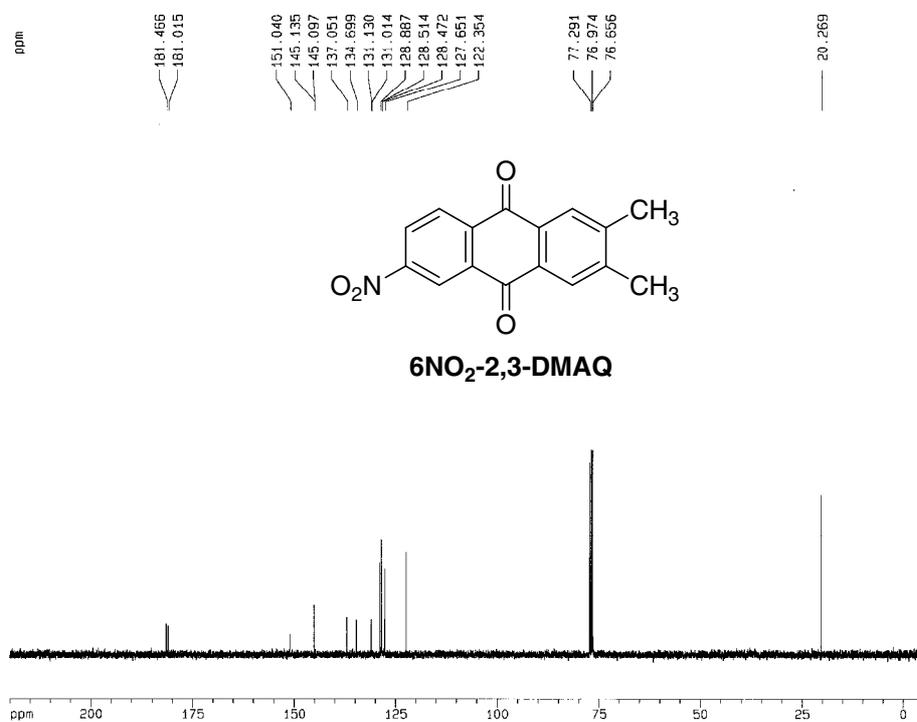


Figure S2 ¹³C NMR spectrum of **6NO₂-2,3-DMAQ** in CDCl₃

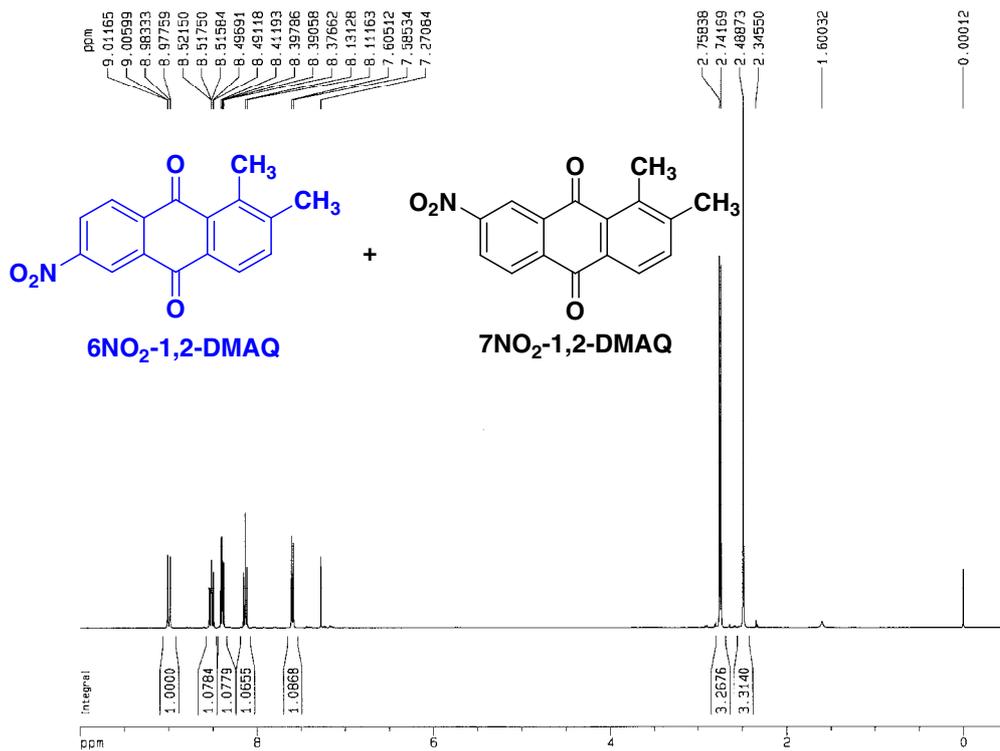


Figure S3 ¹H NMR spectrum of isomers containing **6NO₂-1,2-DMAQ** and **7NO₂-1,2-DMAQ** in CDCl₃

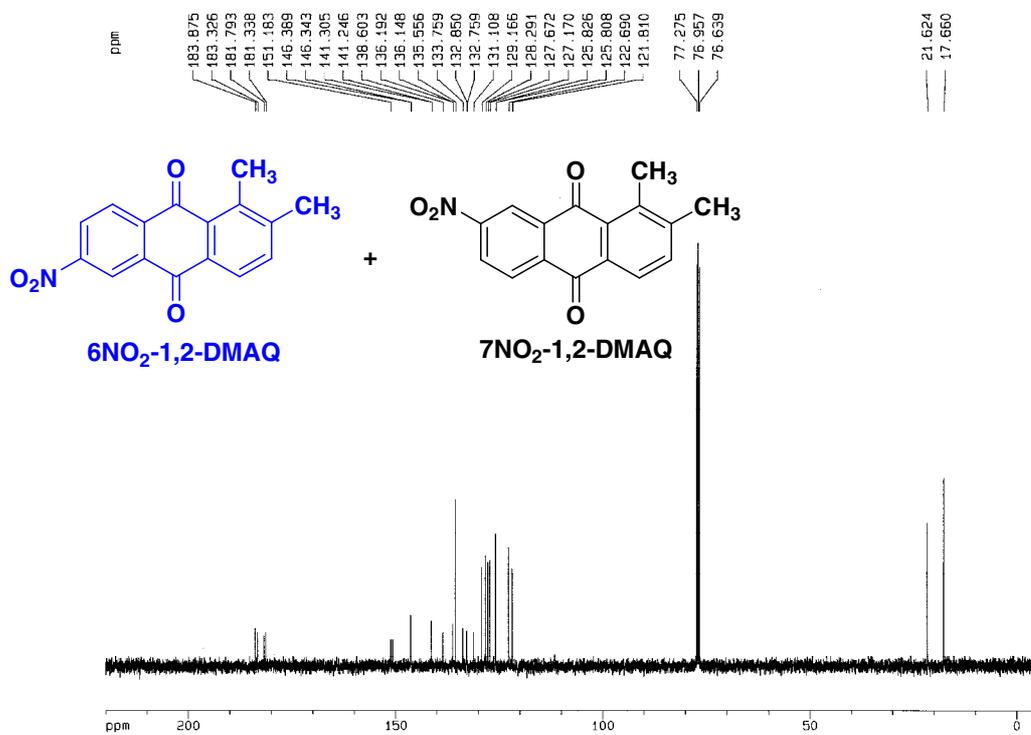


Figure S4 ¹³C NMR spectrum of isomers containing **6NO₂-1,2-DMAQ** and **7NO₂-1,2-DMAQ** in CDCl₃

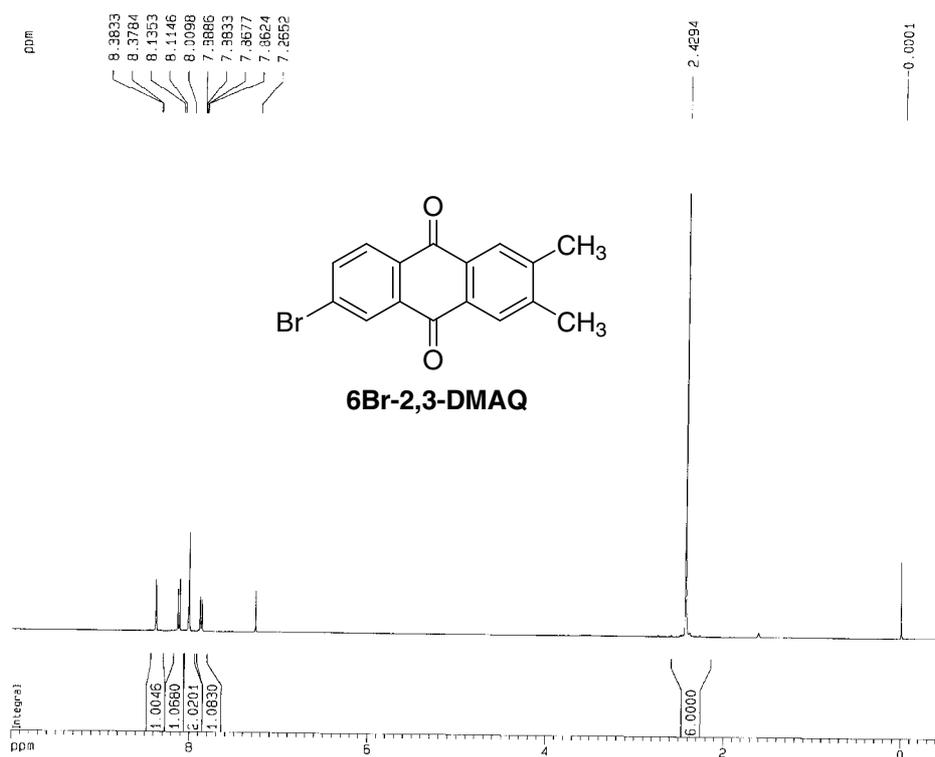


Figure S5 ¹H NMR spectrum of **6Br-2,3-DMAQ** in CDCl₃

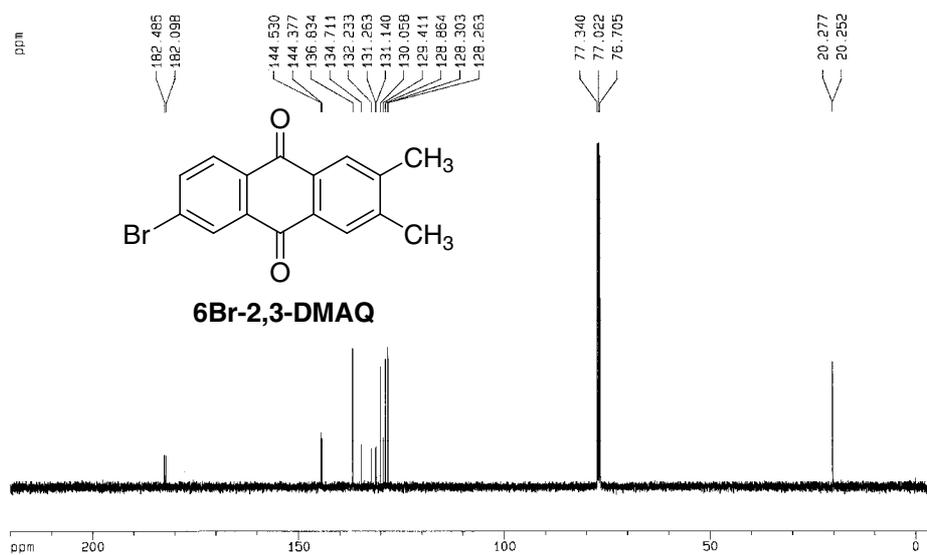


Figure S6 ¹³C NMR spectrum of **6Br-2,3-DMAQ** in CDCl₃

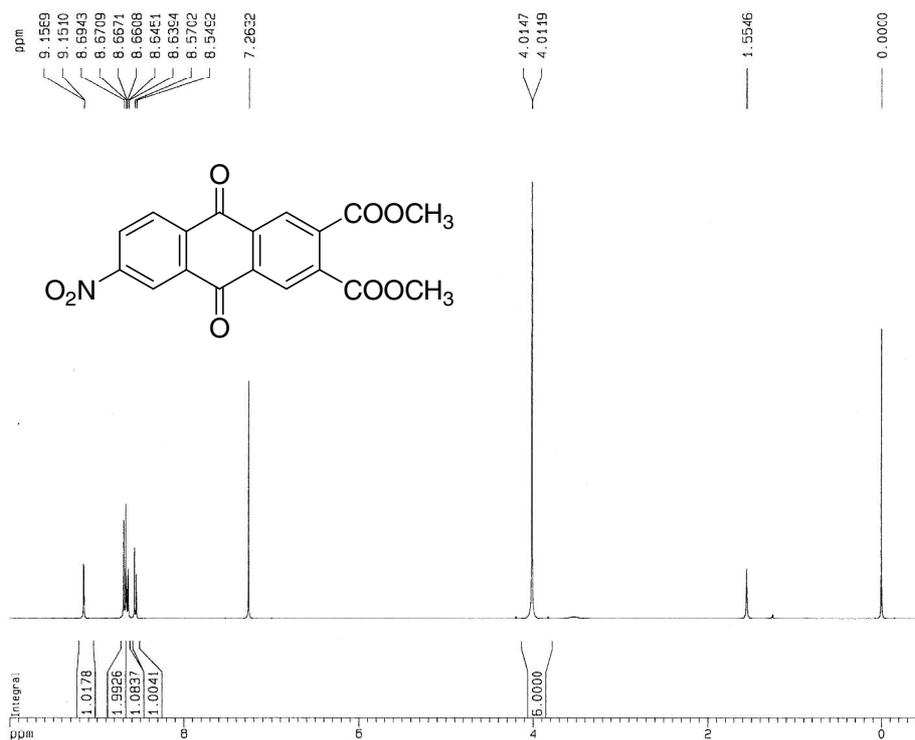


Figure S7 ^1H NMR spectrum of dimethyl 6-nitroanthraquinone-2, 3- dicarboxylate in CDCl_3



Figure S8 ^1H NMR spectrum of dimethyl 6-bromoanthraquinone-2, 3- dicarboxylate in CDCl_3

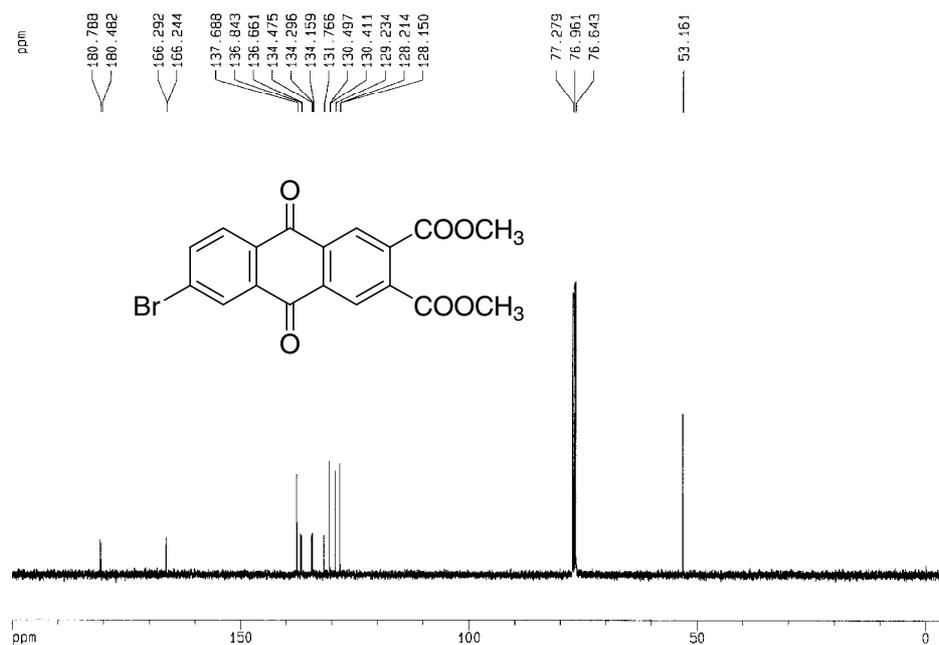


Figure S9 ¹³C NMR spectrum of dimethyl 6-bromoanthraquinone-2, 3- dicarboxylate in CDCl₃

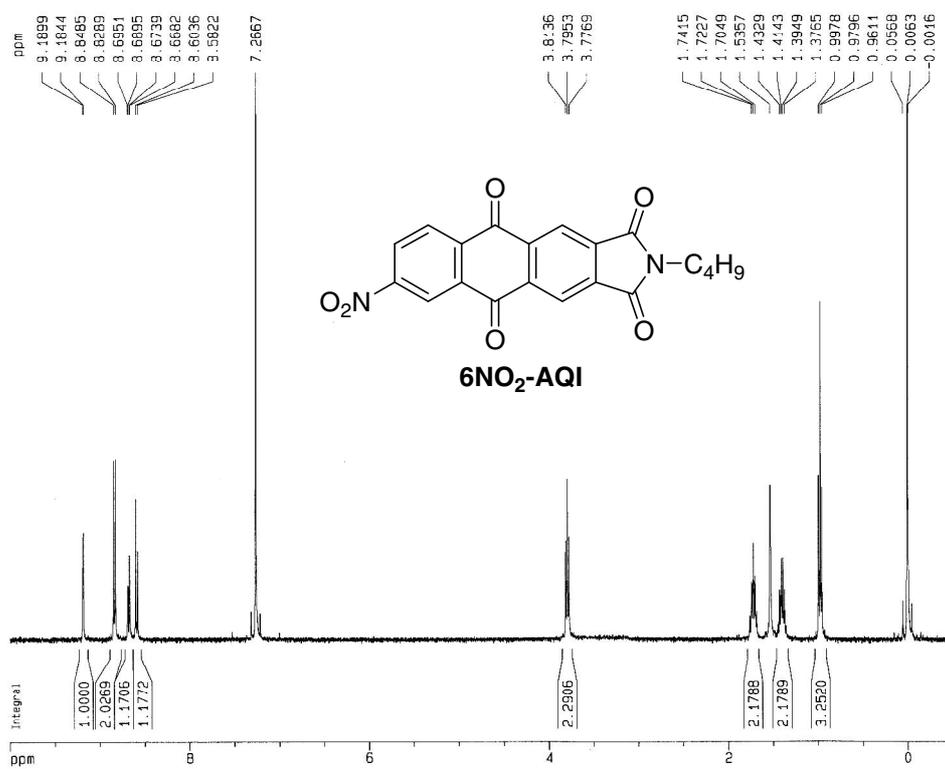


Figure S10 ¹H NMR spectrum of 6NO₂-AQI in CDCl₃

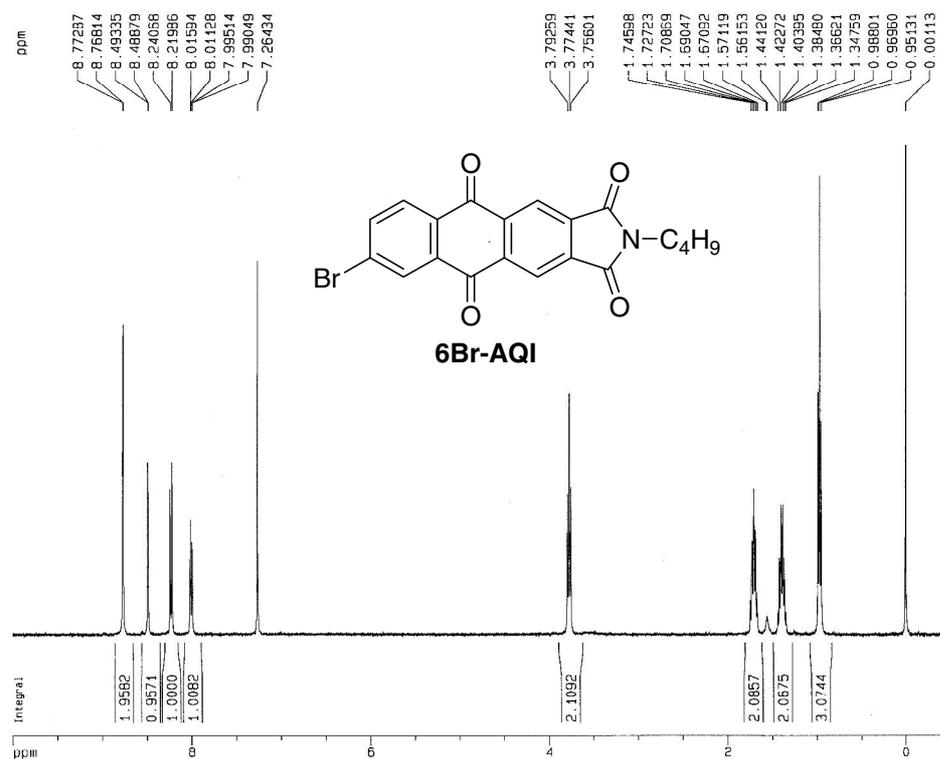


Figure S11 ¹H NMR spectrum of 6Br-AQI in CDCl₃

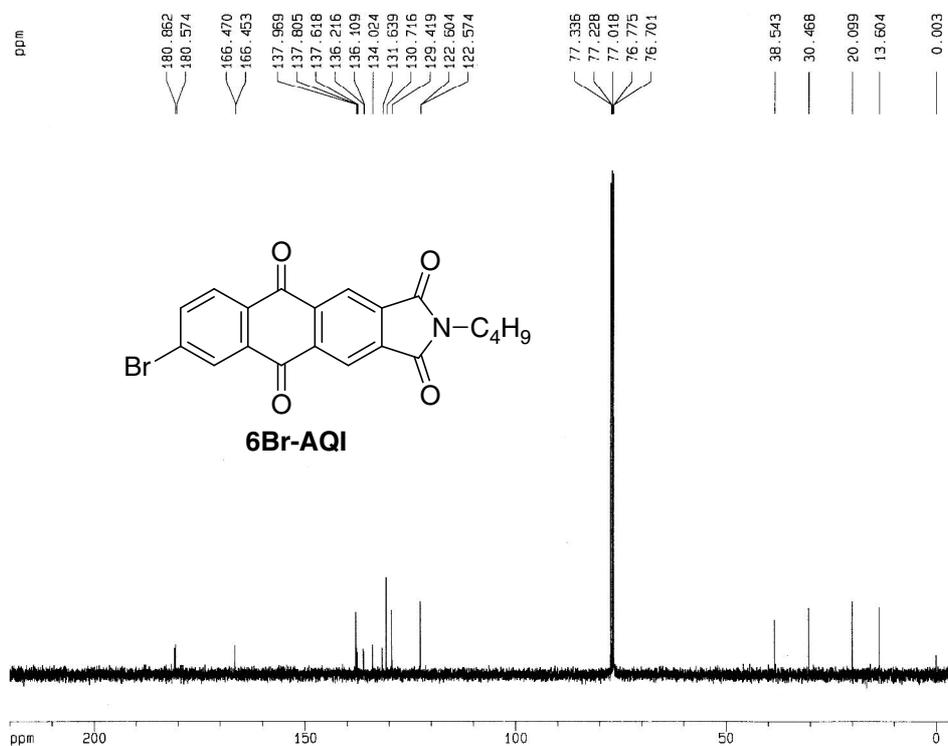


Figure S12 ¹³C NMR spectrum of 6Br-AQI in CDCl₃

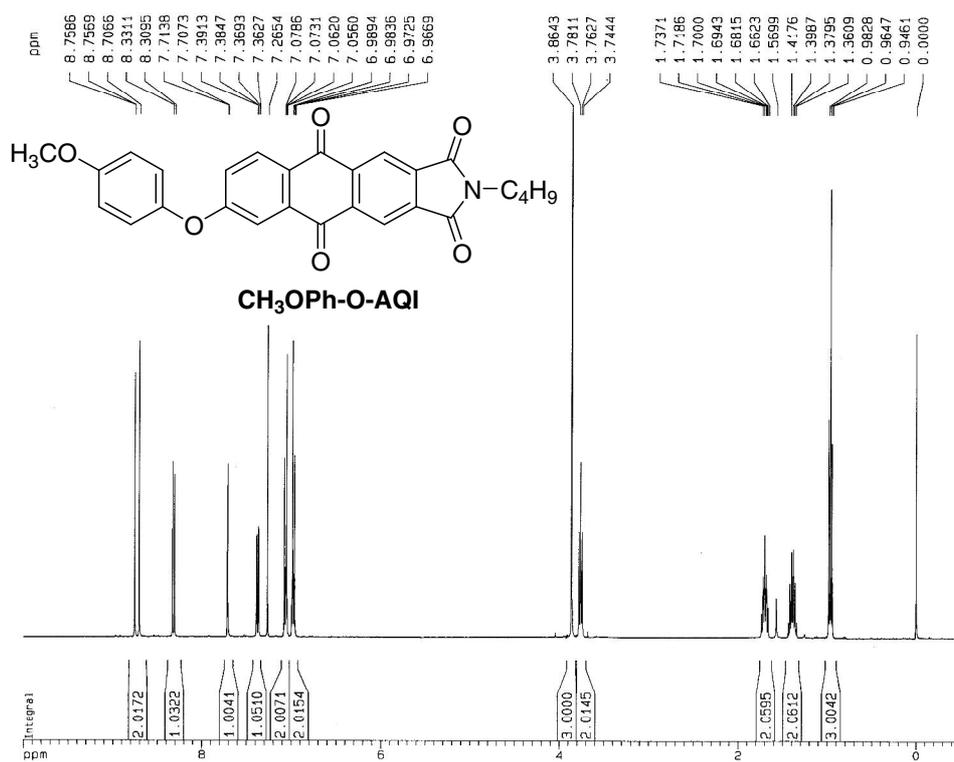


Figure S13 ¹H NMR spectrum of **CH₃OPh-O-AQI** in CDCl₃

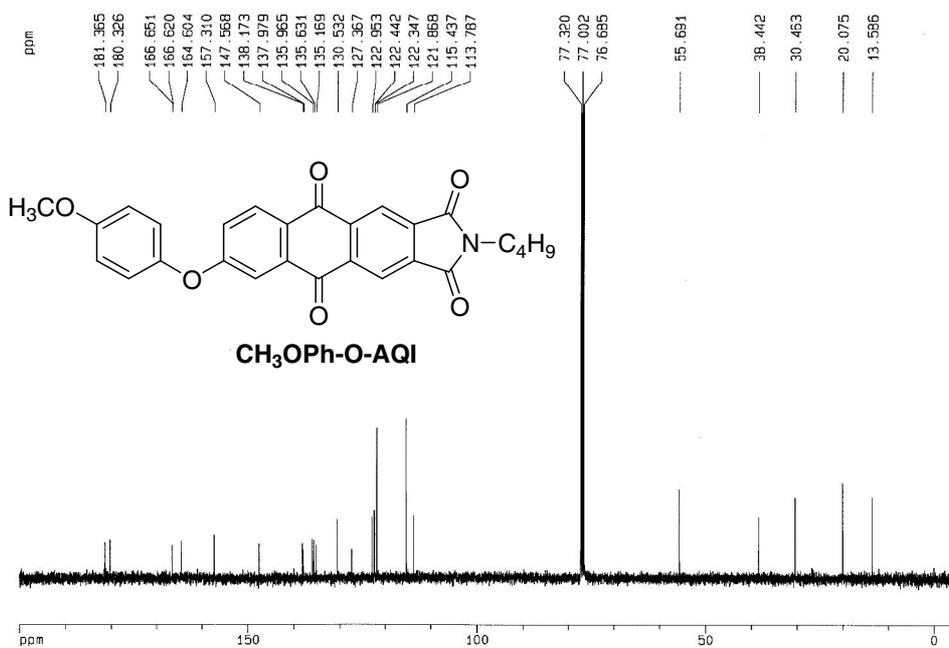


Figure S14 ¹³C NMR spectrum of **CH₃OPh-O-AQI** in CDCl₃

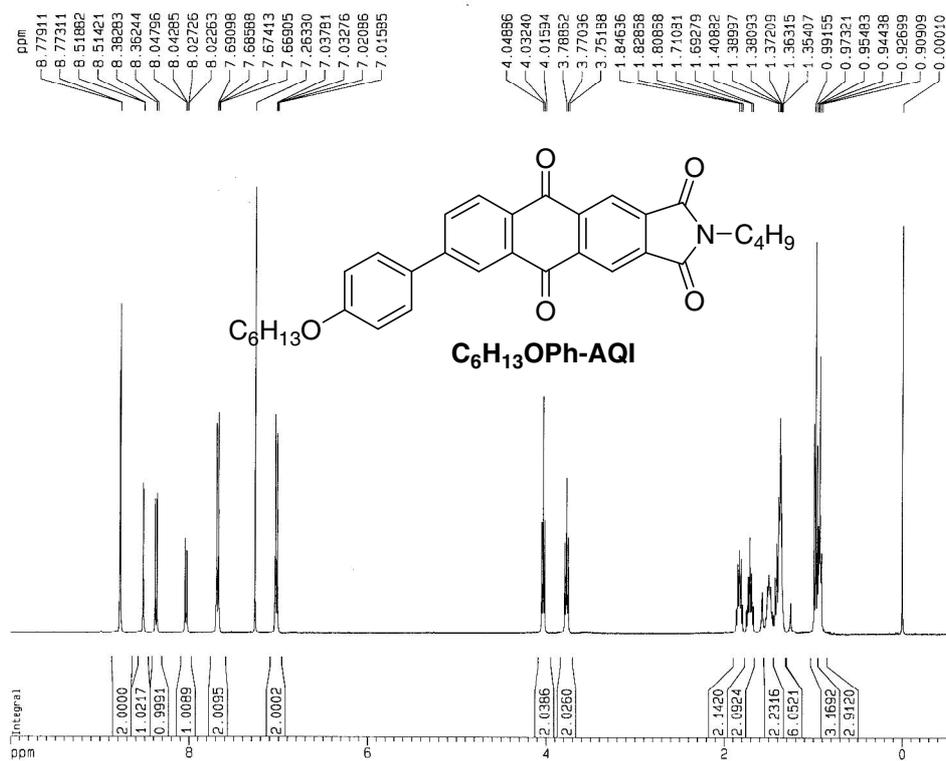


Figure S15 1H NMR spectrum of $C_6H_{13}OPh-AQI$ in $CDCl_3$

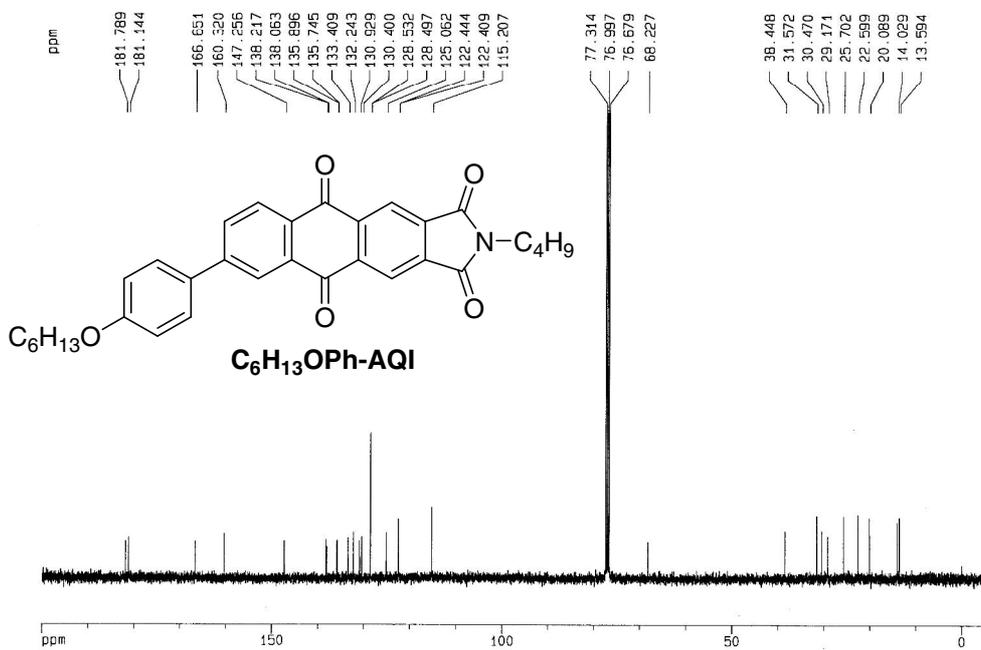


Figure S16 ^{13}C NMR spectrum of $C_6H_{13}OPh-AQI$ in $CDCl_3$

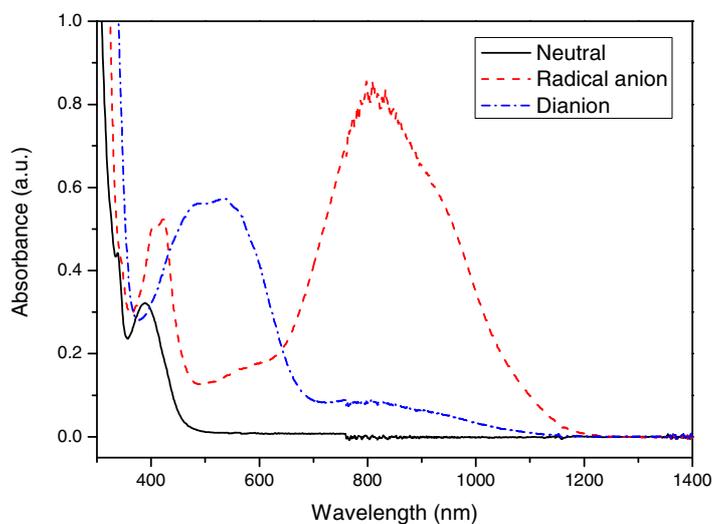


Figure S17. UV/vis/NIR absorption spectra of $\text{CH}_3\text{OPh-O-AQI}$ (10^{-3} M containing 0.1 M TBAP) and its electrochemically generated radical anion and dianion in CH_2Cl_2 .

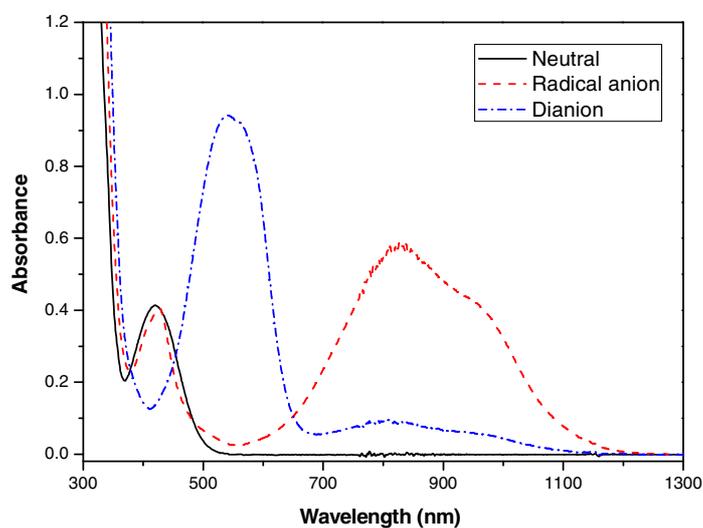


Figure S18. UV/vis/NIR absorption spectra of $\text{C}_6\text{H}_{13}\text{OPh-AQI}$ (10^{-3} M containing 0.1 M TBAP) and its electrochemically generated radical anion and dianion in CH_2Cl_2 .