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Supporting Information

Direct access to polycyclic peripheral-diepoxy-*meso*-quinone derivatives from acene catalytic oxidation

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1. Experimental procedures

1.1 General information

All the reagents and solvents were used as received: tetracene (Aldrich, 98%), pentacene (Aldrich), urea-hydrogen peroxide addition compound (UHP, Aldrich, 97%), hydrogen peroxide solution in water, 30% wt with inhibitor (Aldrich) and ammonium acetate (Merck, 98%), acetonitrile (Fluka, HPLC grade), chloroform (Fluka, *p.a.*), chloroform-*d* (Euriso-top, H_2O<0,01%) and acetone (Fisher, *p.a.*). Preparative thin layer chromatography (TLC), was performed on plates of silica gel 60 F254 (Merck) and examined under UV-light irradiation (254 and 365 nm). For small silica columns was used silica gel 60 (40-63 μm, Merck).

NMR spectra were recorded on Brucker Advance III spectrometer at a frequency of 400 MHz and room temperature. All spectra were recorded in $CDCl_3$ at 22ºC unless otherwise specified. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Mass spectra were performed at Unidad de Masas, Universidade de Santiago de Compustela, with positive electronic impact ionization (EI^+) at 70 eV. Electronic spectra were recorded on a range cell Cary 50 BIO spectrometer.

The catalyst [Mn(TDCPP)Cl] (chloro [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinate] manganese(III)) was synthesized by previously described procedures.[1-3]

1.2 Catalytic oxidation of acenes

1.2.1 Conditions A

In a round bottom flash under light protection, 0.15 mmol of substrate (tetracene or pentacene) were added to 250 mL of acetonitrile and sonicated until total dissolution (2h). To this solution the metalloporphyrin catalyst was added at the chosen ratio substrate/catalyst (S/C) and 1g of ammonium acetate as the co-catalyst, was added. The reaction was carried out at room temperature and magnetic stirring through progressive addition of hydrogen peroxide at a rate of 2 mmol h^{-1} during 4h (8 molar equivalents relative to substrate, Table 1, conditions **A**). The hydrogen peroxide was added in two forms: *i*) through a syringe pump as aqueous solution 30 wt % [$HP_{(aq)}$] diluted in acetonitrile (1:9) – conditions **A1** or *ii*) Urea-hydrogen peroxide addition compound (UHP) – conditions **A2**. The reaction was followed by UV-Vis spectroscopy, to control substrate consumption (see page S22, for UV-Vis spectrum of the total reaction mixture). At the reaction end, when no more substrate consumption is observed, the reaction mixture was concentrated to near 50 mL by solvent

(1) R. A. W. Johnstone, M. L. P. G. Nunes, M. M. Pereira, A. M. d'A. R. Gonsalves, A. C. Serra, *Heterocycles* **1996**, *43*, 635-640.
(2) A. D. Adler, F. R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
(3) S. L. H. Rebelo, M. M. Pereira, M. M. Q. Simoes, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *J. Catal.* **2005**, *234*, 76-87.

evaporation under vacuum at low temperature and passed through filter paper to separate non reacted insoluble substrate and the solid was washed with dichloromethane to assure removal of oxidation products, and the filtrate set aside. Non reacted substrate was further washed with ethanol to remove remaining urea or hydrogen peroxide, dried and weighted. Then the filtrate containing the reaction mixture was passed through a small column of silica gel, to remove the catalyst and excess of UHP or H_2O_2; the small column was washed with a mixture of acetone (5%):chloroform and the eluate evaporated to dryness and weighted. The residue of the final reaction mixture was analyzed by ^{1}H NMR or re-dissolved in dichloromethane for product isolation by preparative TLC using a mixture of acetone (5%):chloroform. Isolated products were weighted and characterized. Substrate conversion was based on the sum of isolated yields and was confirmed by the non reacted substrate. Product yields were based ^{1}H NMR spectra of the final reaction mixture and conversion percentage.

1.2.2 Conditions B

In a round bottom flask, 5 mL of acetonitrile were deaerated with argon flow for 15 minutes. To the flask were added 0.15 mmol of substrate (tetracene or pentacene) and the catalyst [Mn(TDCPP)Cl] in a ratio substrate/catalyst (S/C) of 150. To this mixture were added 20 mg of ammonium acetate and the urea hydrogen peroxide addition compound (UHP) was progressively added at a rate of 10 molar equivalents.h^{-1} during 5h (8 equiv. totally added at reaction beginning or 25 equivalents in five additions); then, the mixture was kept under stirring, in inert atmosphere and light protection for (4h or 24 h) at room temperature (20ºC) or at 45ºC.

The resulting mixture was filtered to remove solid non reacted substrate that was washed with dichloromethane, the filtrate was set aside and the solid further washed with ethanol, dried and weighted. The filtered solution containing the reaction mixture was passed through a small plug of silica and eluted with acetone (5%):chloroform to remove the catalyst and excess of UHP. The collected solution was evaporated to dryness, weighted and the obtained total reaction mixture residue was analysed by ^{1}H NMR. For products isolation, the mixture was re-dissolved on dichloromethane and fractionated by preparative TLC using a mixture of acetone (5%):chloroform for both substrates. Isolated products were weighted and characterized. Alternatively, the compounds were separated by a silica column with initial elution with chloroform to separate remaining substrate and quinone **1d** and then with chloroform/acetone (5%) to separate other oxidation products. Substrate conversion was based on the sum of isolated yields and was confirmed by the non reacted substrate. Product yields were based ^{1}H NMR spectra of the final reaction mixture and conversion percentage.

2. Characterization of isolated products

The characterization of the products was made by mono- and bi-dimensional NMR techniques, ^{1}H, ^{13}C, COSY, APT, HSQC and HMBC and by Mass Spectrometry.

2.1 Spectroscopic data for *anti*-diepoxyquinones

anti-7,8:9,10-diepoxy-7,8,9,10-tetrahydrotetracene-5,12-dione (***1b***)

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=3.90-3.93 (m, 2H, H-7,10), 4.08-4.12 (m, 2H, H-8,9), 7.81-7.87 (m, 2H, H-2,3), 8.30-8.36 (m, 2H, H-1,4), 8.37 (s, 2H, H-6,11). ^{13}C NMR: δ=51.3 (C-7,10), 55.2 (C-8,9), 127.5 (C-1,4), 130.2 (C-6,11), 133.3 (C-4a,12a), 133,9 (C5a,11a), 134.6 (C-2,3), 138.3 (C6a,10a), 182.4 (C-5,12).

MS (EI^+) *m/z* (rel. Int. %) = 290 ($[M]^{+\bullet}$, 41), 274 (17), 261 (100), 245 (32), 233 (18). HRMS (EI^+) *m/z* calculated for $C_{18}H_{10}O_4$ ($M^{+\bullet}$) 290.0579, found 290.0582.

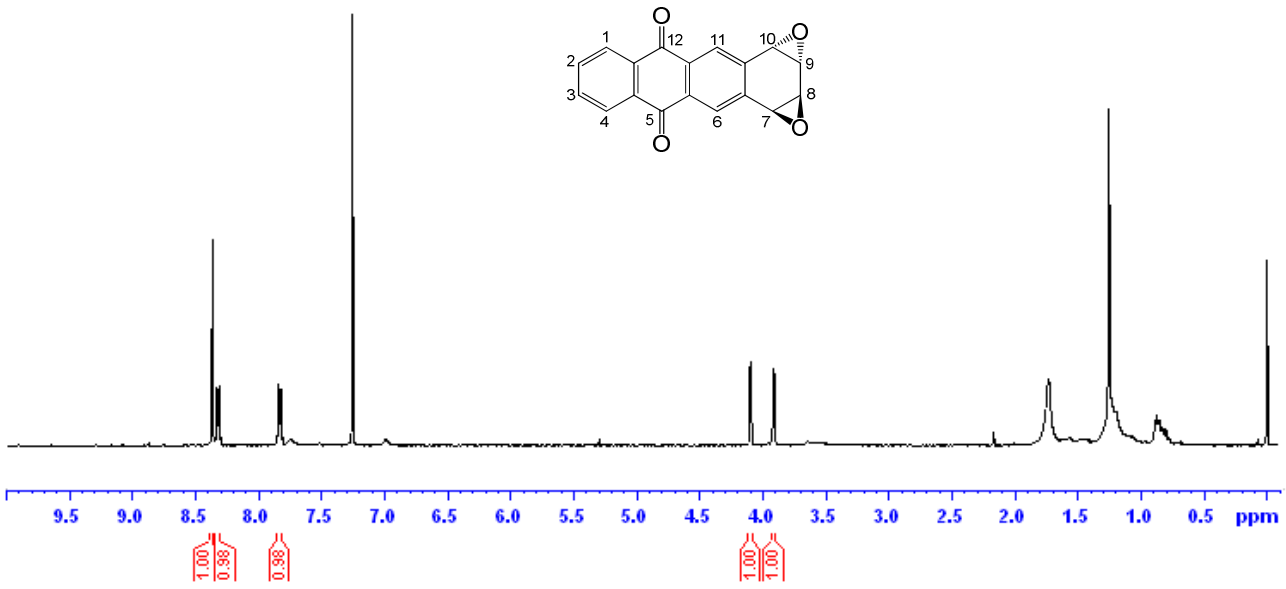

Figure S1. ^{1}H NMR spectrum of compound **1b**.

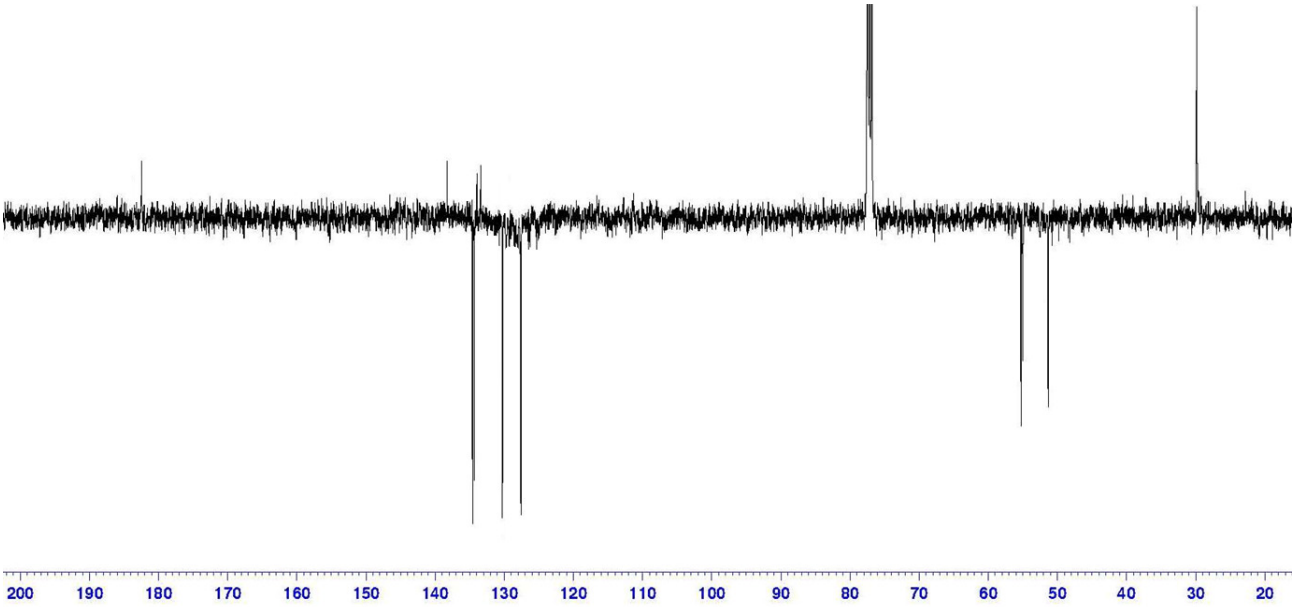

Figure S2. APT NMR spectrum of compound **1b**

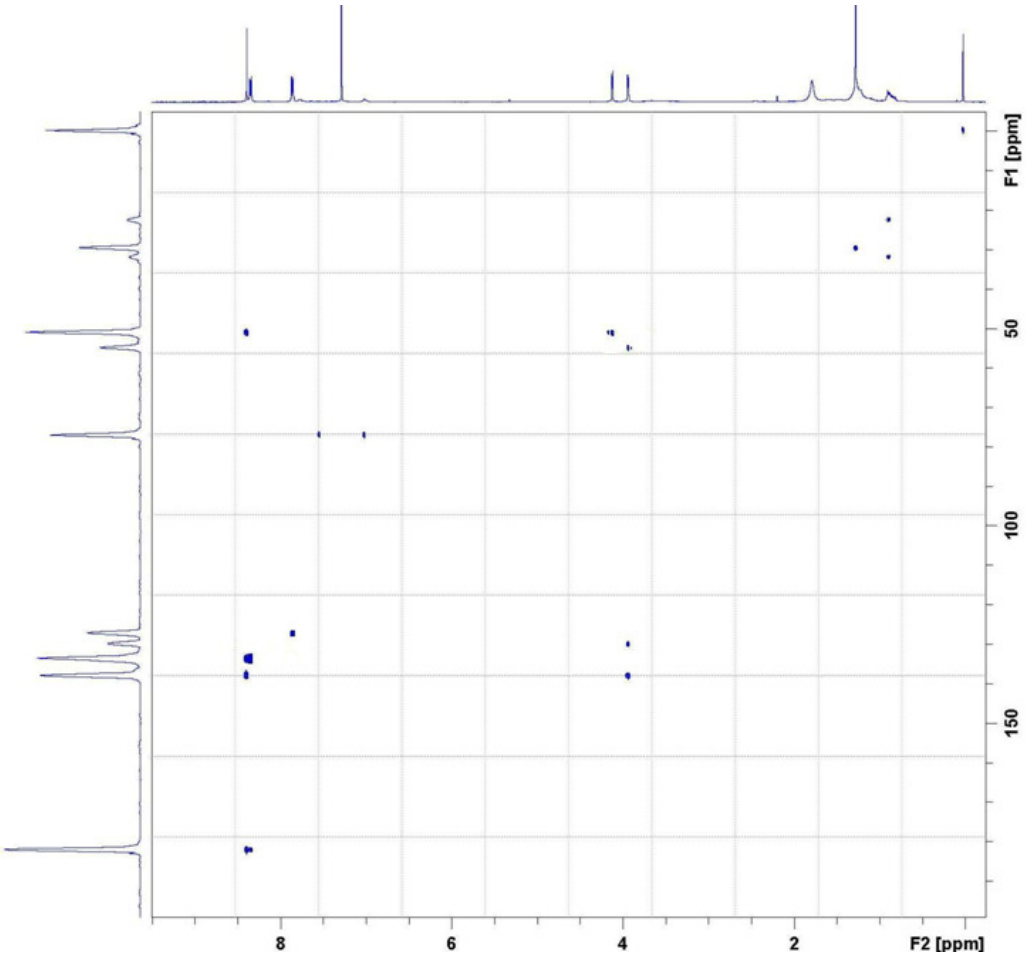

Figure S3. NMR (^{1}H-^{13}C HMBC) spectrum of compound **1b**.

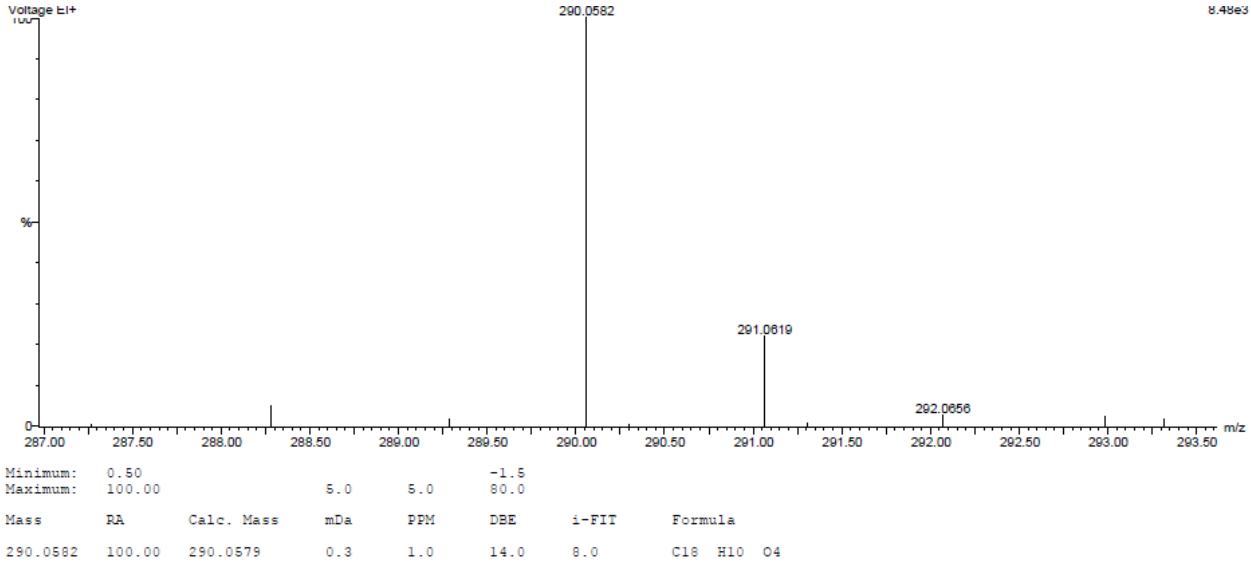

Figure S4. High resolution mass spectrum (EI^+) of compound **1b**. Predicted isotopic pattern: *m/z* 290,0579 (100,0%), 291,0613 (19,5%), 292,0646 (1,8%).

*Anti-1,2:3,4-diepoxy-1,2,3,4-tetrahydropentacene-6,13-dione (**2a**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=3.93-3.95 (m, 2H, H-1,4), 4.10-4.12 (m, 2H, H-2,3), 7.71-7.75 (m, 2H; H-9,10), 8.11-8.15 (m, 2H, H-8,11), 8.46 (s, 2H, H-5,14), 8.88 (s, 2H, H-7,12).

MS (EI^+) *m/z* (rel. Int. %) = 340 ($[M]^{+\bullet}$, 93), 324 (61), 311($[M\text{-}CHO]^+$, 100), 296 (13), 283 ($[M\text{-}CHO\text{-}CO]^+$, 26), 268 (8), 255 ($[M\text{-}CHO\text{-}(CO)_2]^+$, 16), 239 (34), 226 (45). HRMS (EI^+) *m/z* calculated for $C_{22}H_{12}O_4$ ($M^{+\bullet}$) 340.0736, found 340.0735.

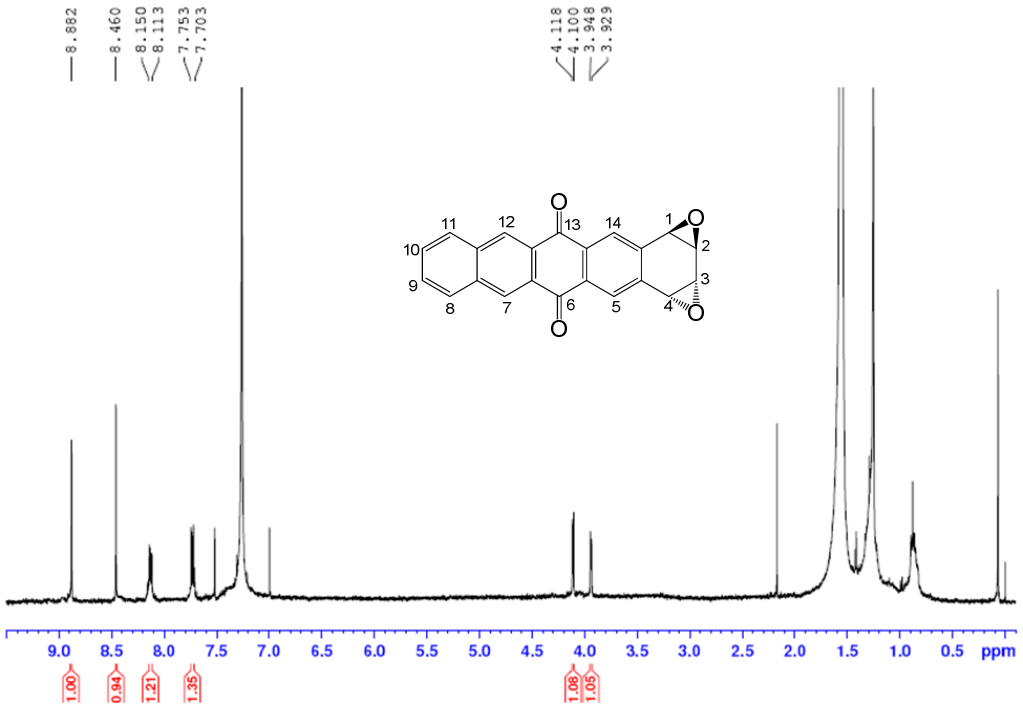

Figure S5. ^{1}H NMR spectrum for compound **2a**.

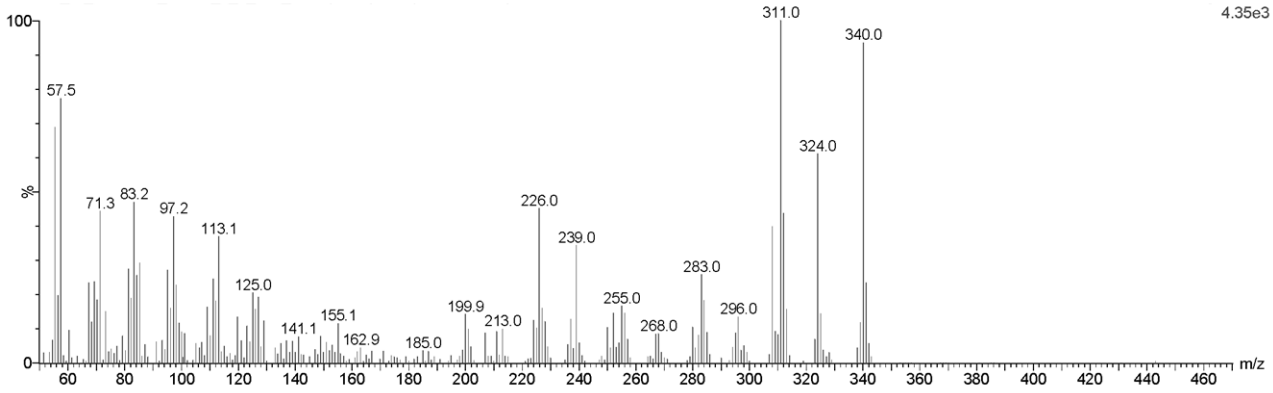

Figure S6. Mass spectrum (EI^+) of compound **2a**.

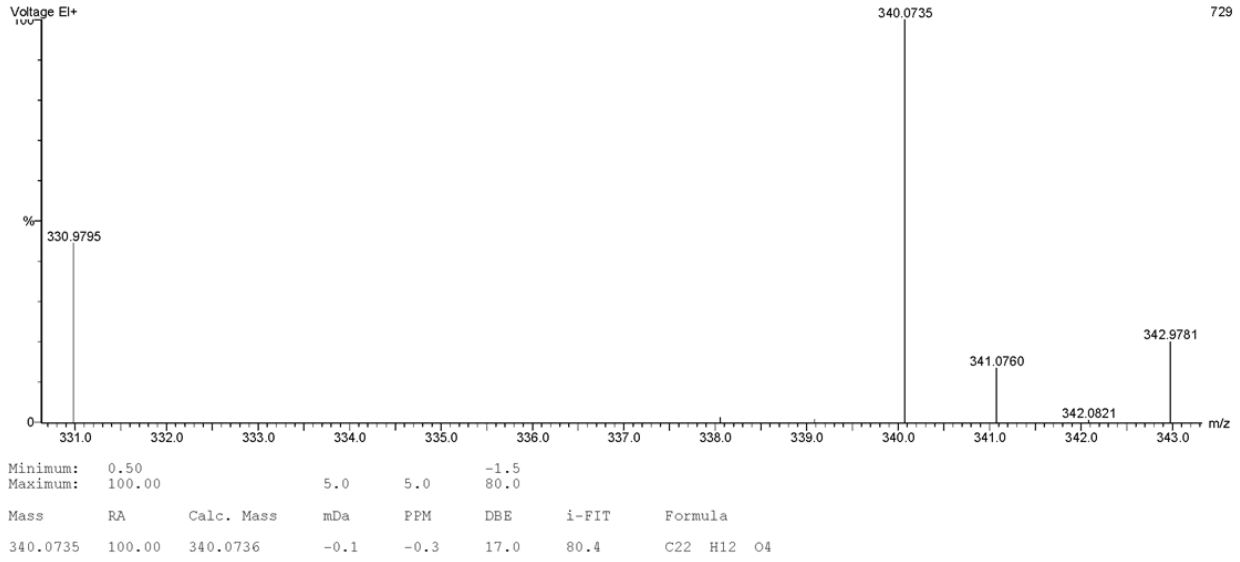

Figure S7. High resolution mass spectrum (EI^+) of compound **2a**.

2.2 Spectroscopic data for *meso*-quinones

*Tetracene-5,12-dione (**1d**)*[4]

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=7.68-7.73 (m, 2H, H-8,9), 7.80-7.86 (m, 2H, H-2,3), 8.08-8.14 (m, 2H, H-7,10), 8.38-8.43 (m, 2H; H-1,4), 8.87 (s, 2H; H-6,11). ^{13}C NMR: δ=127.6 (C-1,4), 129.6 (C-6,11), 129.7 (C-8,9), 129.9 (C-5a,11a), 130.3 (C-7,10), 134.3 (C-2,3), 134.6 (C-4a,12a), 135.3 (C-6a,10a), 183.04 (C-5,12).

MS (EI^+) *m/z* (rel. Int. %) = 258 ($[M]^{+\bullet}$, 100), 230 ($[M-CO]^+$, 63), 202 ($[M-(CO)_2]^+$, 89), 101 (31).

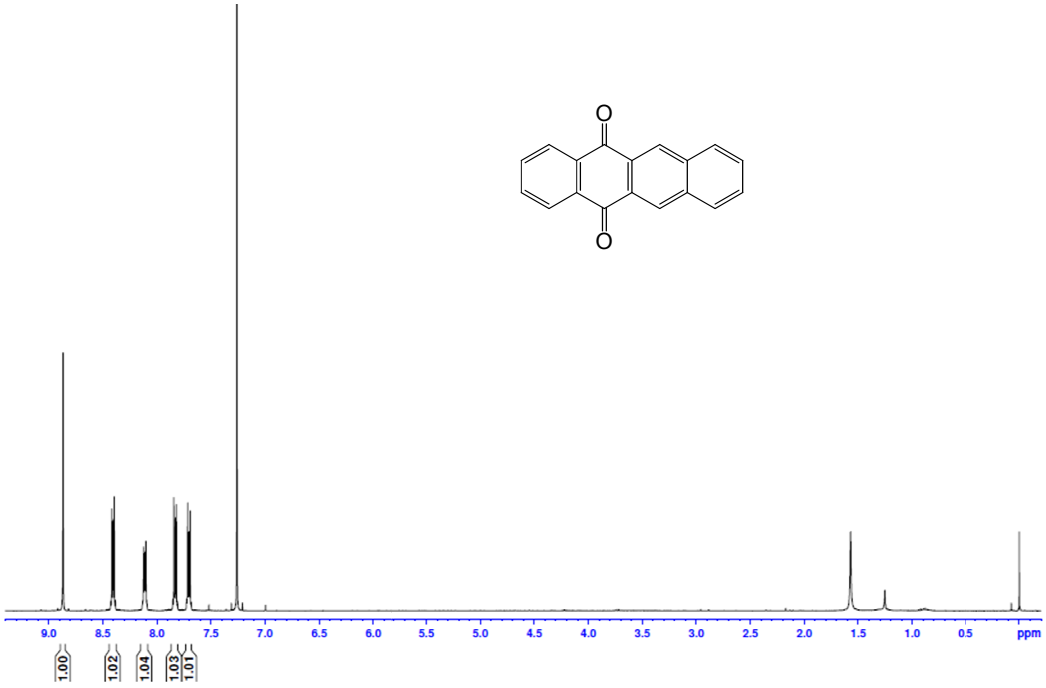

Figure S8. ^{1}H NMR spectrum of compound **1d**.

(4) R. Dabestani, M. Nelson, M.E. Sigman, *Photochem. Photobiol.* **1996**, *64*, 80-86.

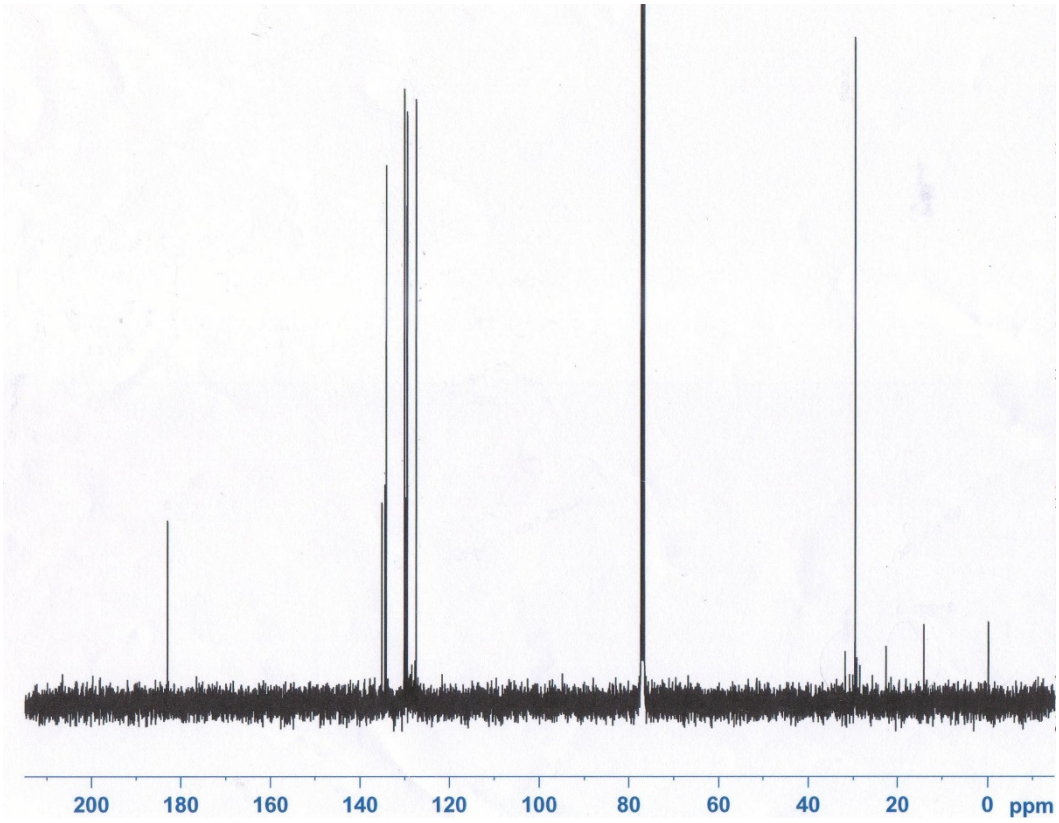

Figure S9. ^{13}C NMR spectrum of compound **1d**.

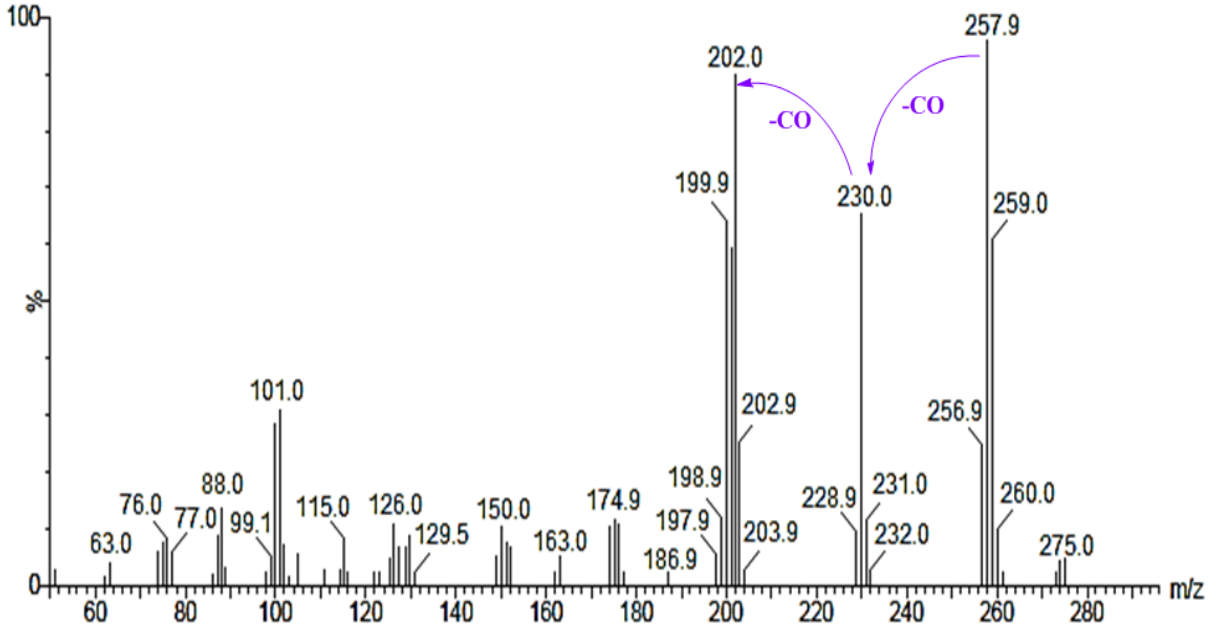

Figure S10. Mass spectrum EI$^+$ compound **1d**.

*Pentacene-6,13-dione (**2c**)*[5]

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=7.71-7.74 (m, 4H, H-2,3,9,10), 8.13-8.16 (m, 4H, H-1,4,8,11), 8.97 (s, 4H; H-5,7,12,14). ^{13}C NMR: δ= 129.5 (C-5,7,12,14), 129.8 (C-2,3,9,10), 130.2 (C-1,4,8,11), 130.6 (5a,6a,12a,13a), 135.3 (C-4a,7a,11a,14a), 183.06 (C-6,13).

MS (EI^+) *m/z* (rel. Int. %) = 308 ($[M]^{+\bullet}$, 100), 280 ($[M\text{-}CO]^+$, 27), 252 ($[M\text{-}(CO)_2]^+$, 41), 126 (18).

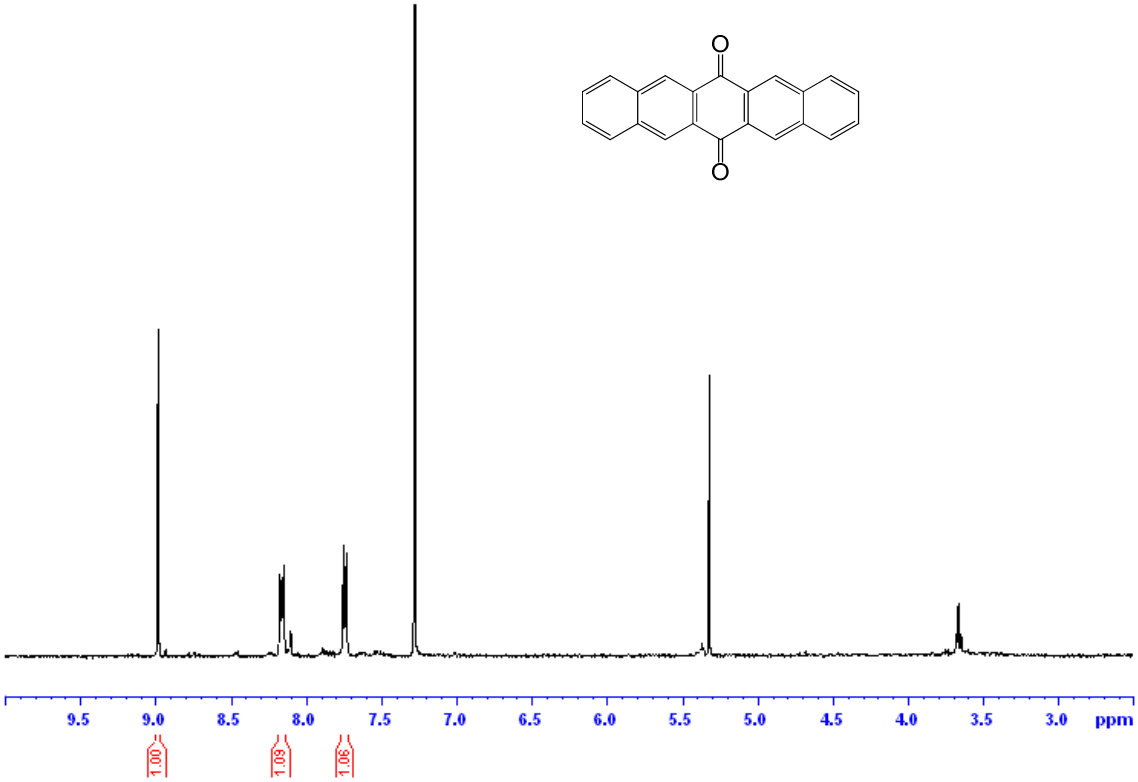

Figure S11. ^{1}H NMR spectrum of compound **2c**.

(5) H. Yamada, Y. Yamashita, M. Kikuchi, H. Watanabe, T. Okujima, H. Uno, T. Ogawa, K. Ohara, N. Ono, *Chem. Eur. J.* **2005,** *11*, 6212-6220.

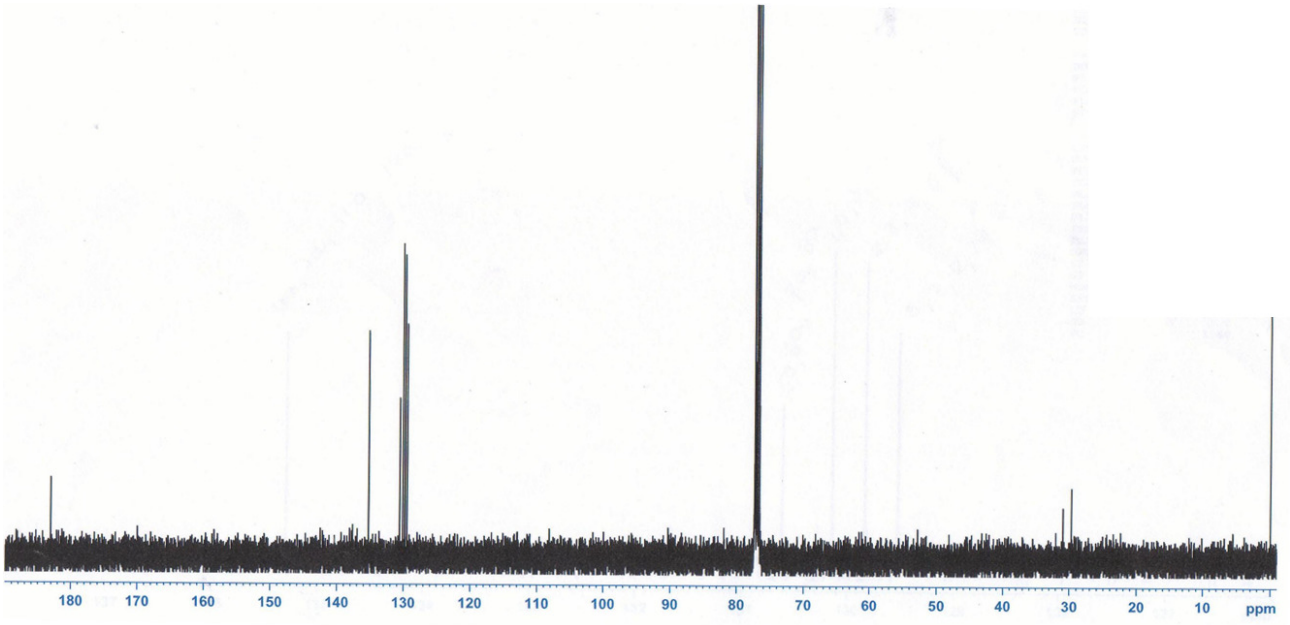

Figure S12. ^{13}C NMR spectrum of compound **2c**.

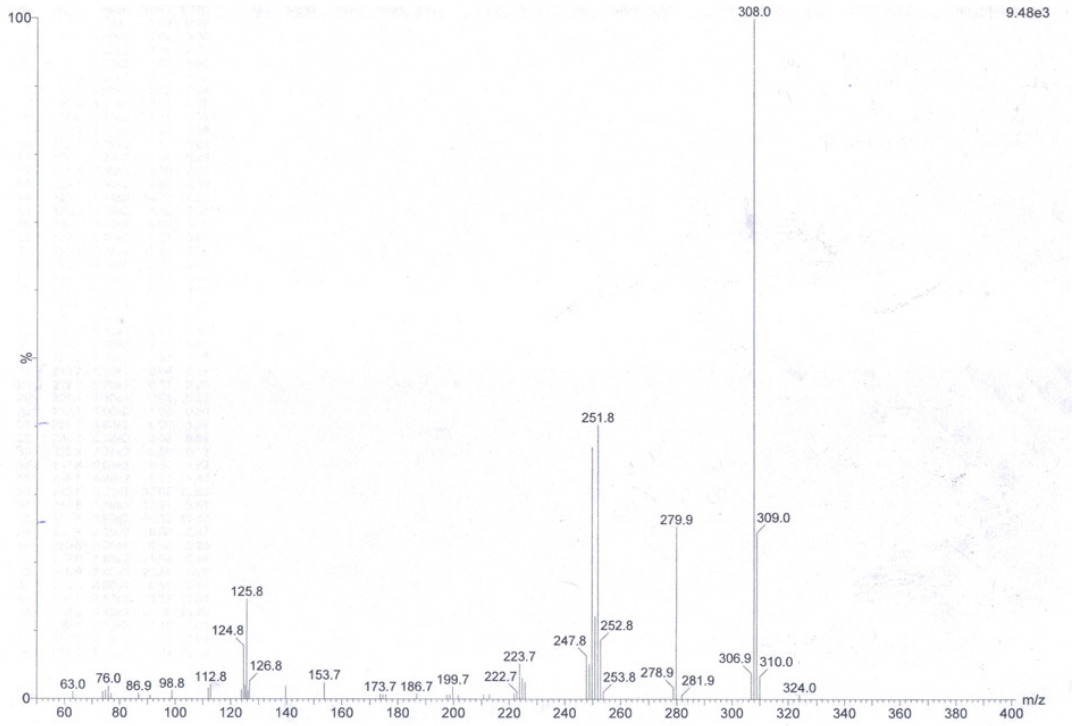

Figure S13. Mass spectrum EI$^+$ compound **2c**.

*Pentacene-5,7,12,14-tetraone (**2d**)*[6]

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=7.85-7.92 (m, 4H, H-2,3,8,11), 8.38-8.42 (m, 4H, H-1,4,9,10), 9.26 (s, 2H; H-6,13).

MS (EI^+) *m/z* (rel. Int. %) = 338 ($[M]^{+\bullet}$, 66), 310 ($[M\text{-}CO]^+$, 33), 282 ($[M\text{-}(CO)_2]^+$, 20), 254 (16), 226 (20), 224 (24).

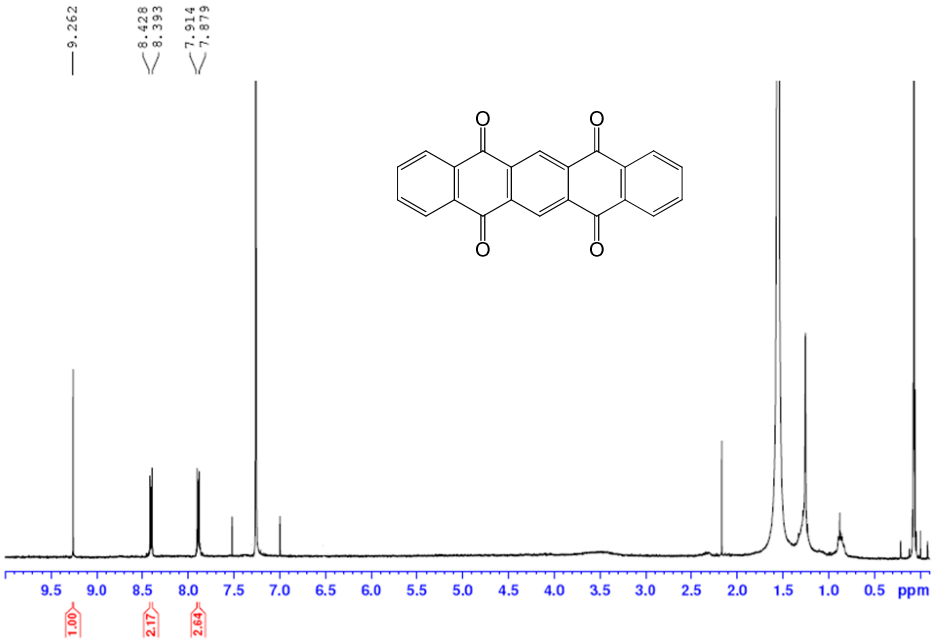

Figure S14. ^{1}H NMR spectrum of **2d**.

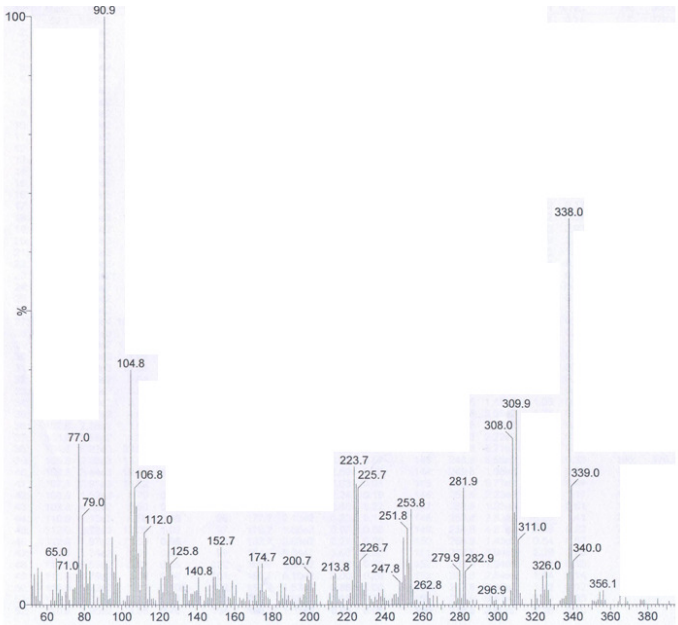

Figure S15. Mass spectrum EI^+ of compound **2d**.

(6) Aldrich R174017.

*Tetracene-5,6,11,12-tetraone (**1f**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=7.80-7.85 (m, 4H, H-2,3,8,9), 8.38-8.43 (m, 4H, H-1,4,7,10).

2.3 Spectroscopic data for *syn*-diepoxyquinones

*syn-7,8:9,10-diepoxy-7,8,9,10-tetrahydrotetracene-5,12-dione (**1c**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=4.02-4.05 (m, 2H, H-7,10), 4.17-4.20 (m, 2H, H-8,9), 7.83-7.87 (m, 2H, H-2,3), 8.33-8.36 (m, 2H, H-1,4), 8.61 (s, 2H, H-6,11). ^{13}C NMR: δ=48.2 (C-7,10), 50.8 (C-8,9), 130.3 (C-1,4), 131.3 (C-6,11), 133.5 (C-4a,12a,5a,11a), 134.6 (C-2,3),182.5 (C-5,12). MS (EI^+) *m/z* (rel. Int. %) = 290 ($[M]^{+\bullet}$, 43), 274 (18), 261 ($[M\text{-}CHO]^+$, 100), 233 (18).

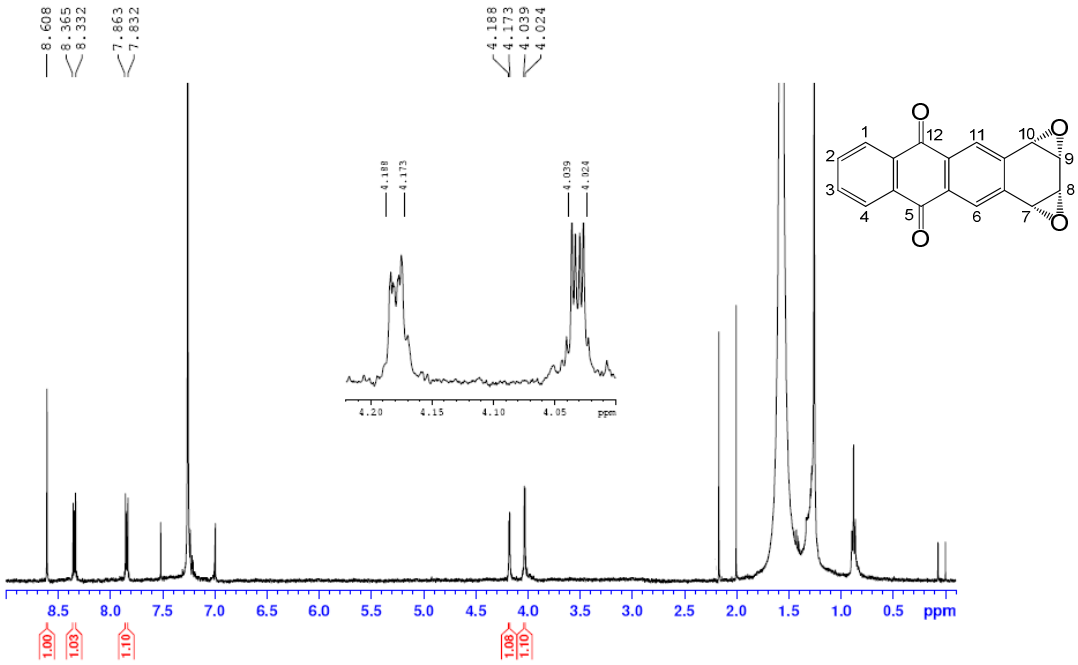

Figure S16. ^{1}H NMR spectrum of compound **1c**.

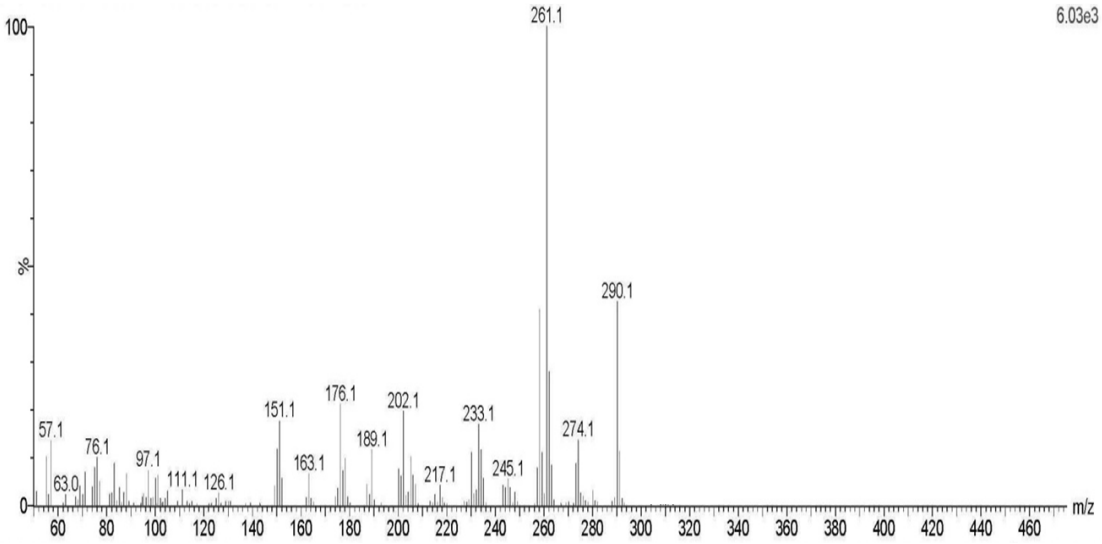

Figure S17 Mass spectrum EI^+ for compound **1c**.

*Syn-1,2:3,4-diepoxy-1,2,3,4-tetrahydropentacene-6,13-dione (**2b**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=3.98-4.01 (m, 2H, H-1,4), 4.13-4.15 (m, 2H, H-2,3), 7.83-7.87 (m, 2H, H-9,10), 8.39-8.43 (m, 2H, H-8,11), 8.17 (s, 2H, H-5,14), 8.84 (s, 2H, H-7,12).

MS (EI$^+$) *m/z* (rel. Int. %) = 340 ([M]$^{+\bullet}$, 80), 324 (45), 311 (100), 282 (51).

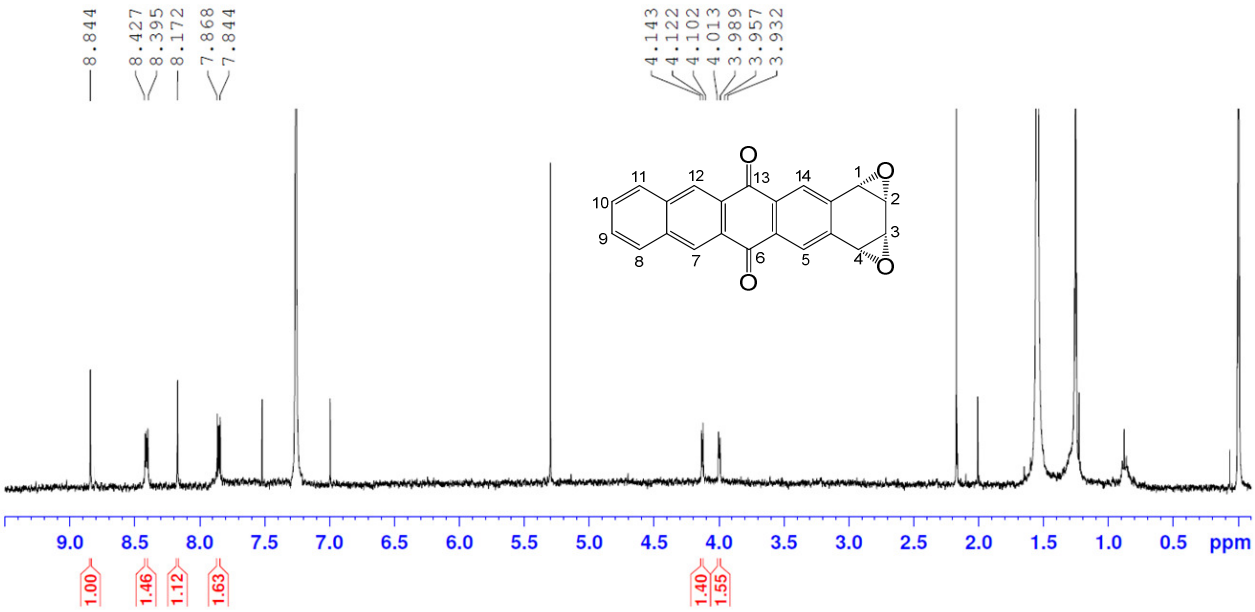

Figure S18. ^{1}H NMR spectrum of compound **2b**.

2.4 Spectroscopic data for monoepoxytetracenedione and its derivatives

*7,8-epoxy-7,8-dihydrotetracene-5,12-dione (**1a**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=4.20 (dt, *J*=3.7 and 1.6 Hz, 1H, H-8), 4.66 (d, *J*=3.7 Hz, 1H, H-7), 6.70 (dd, *J*=9.6 and 1.6 Hz, 1H, H-9), 6,98 (d, *J*=9.6 Hz, 1H, H-10), 7.81-7.86 (m, 2H, H-2,3), 8.31-8.36 (m, 2H, H-1,4), 8.24 (s, 1H, H-6), 8.58 (s, 1H, H-11).

MS (EI$^+$) *m/z* (rel. Int. %) = 274 ([M]$^{+\bullet}$, 24), 244 (100), 215 (74).

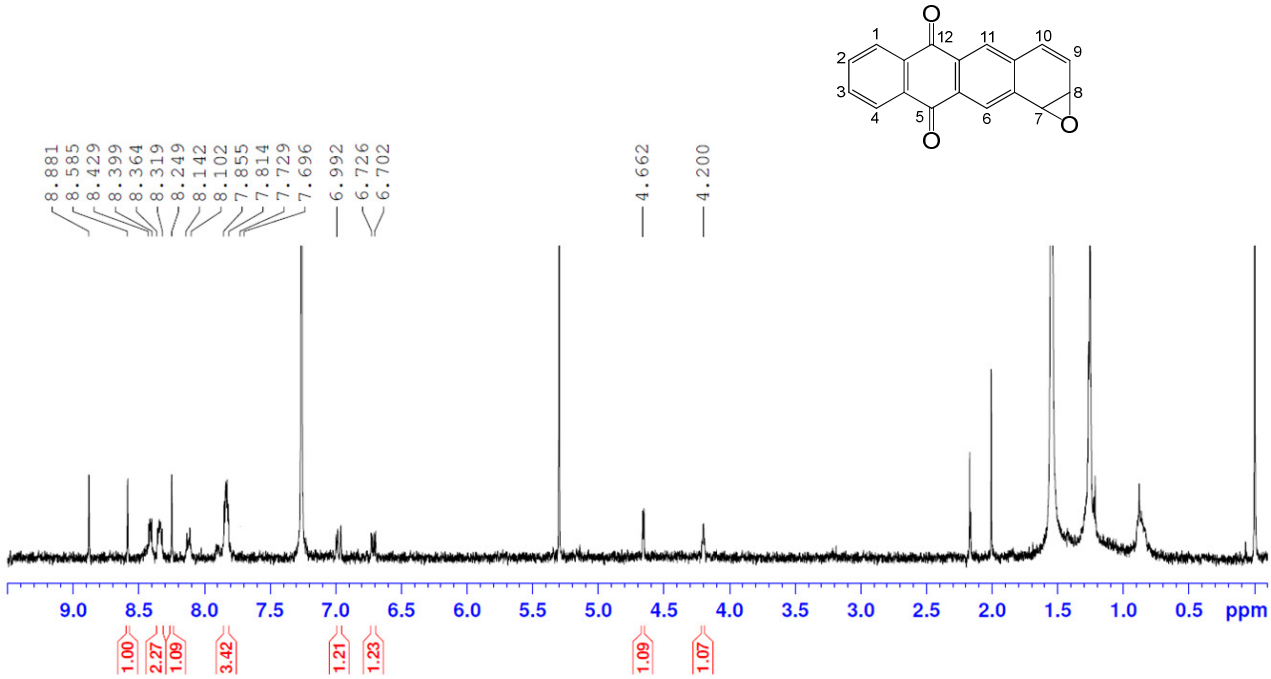

Figure S19. ^{1}H NMR spectrum of compound **1a** in a mixture with *meso*-quinone **1d**.

*7-hydroxytetracene-6,11-dione (**1g**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=5.88 (s-broad, 1H, OH), 7.03 (d, *J*=8.0 Hz, 1H, H-8), 7.55 (t, *J*=8.0 Hz, 1H, H-9), 7.60 (d, J=8.0 Hz, 1H, H-10), 7.81-7.86 (m, 2H, H-2,3), 8.39-8.45 (m, 2H, H-1,4), 8.82 (s, 1H, H-11), 9.26 (s, 1H, H-6).

MS (EI^+) *m/z* (rel. Int. %) = 274 ($[M]^{+\bullet}$, 100), 246 ($[M\text{-}CO]^+$, 19), 245 ($[M\text{-}CHO]^+$, 19), 217 (24), 189 (81).

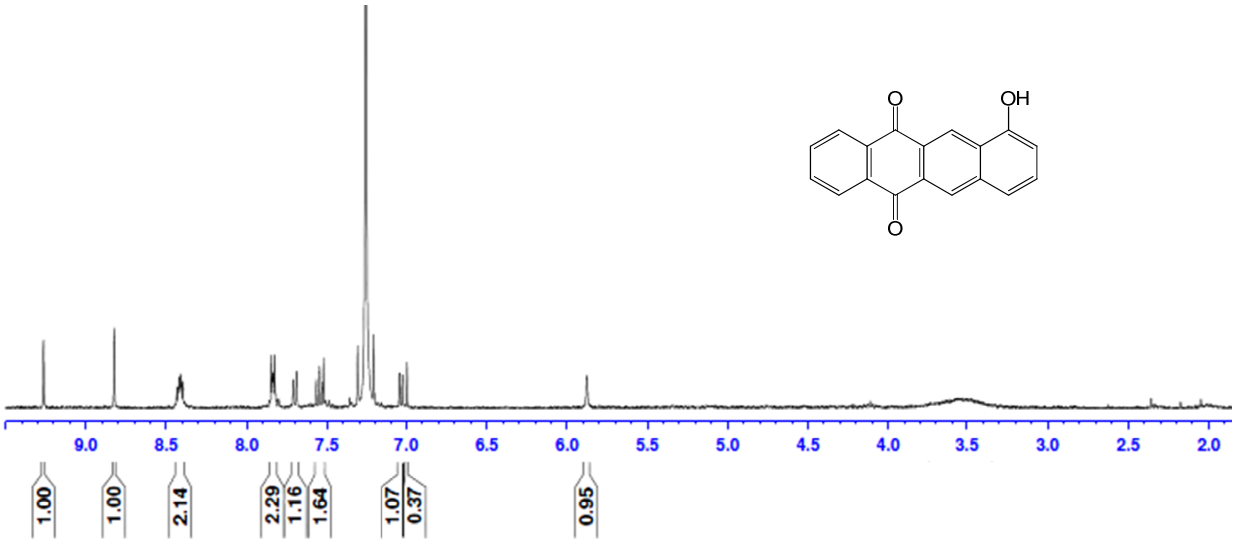

Figure S20. ^{1}H NMR spectrum of compound **1g**.

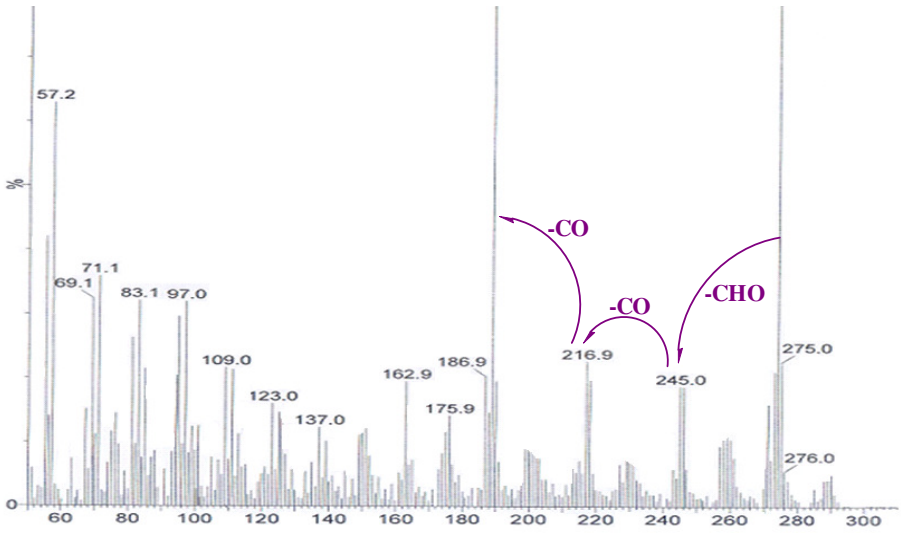

Figure S21. Mass spectrum EI^+ of compound **1g**.

*Tetracene-1,4,6,11-tetraone (**1h**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=7.15 (s, 2H, H-2,3), 7.87-7.90 (m, 2H, H-8,9), 8.34-8.40 (m, 2H, H-7,10), 9.04 (s, 2H, H-5,12).

MS (EI^+) *m/z* (rel. Int. %) = 288 ($[M]^{+\bullet}$, 39), 258 (68), 243 (100), 215 (70).

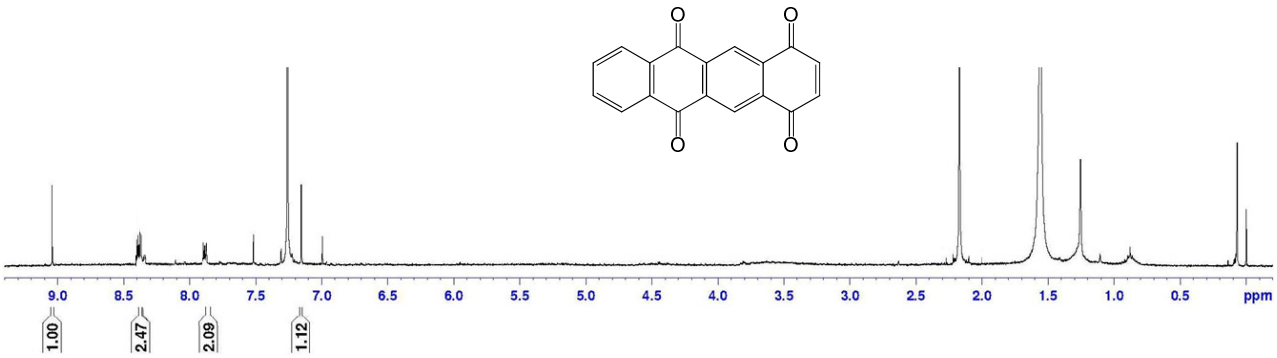

Figure S22. ^{1}H NMR spectrum of compound **1h**.

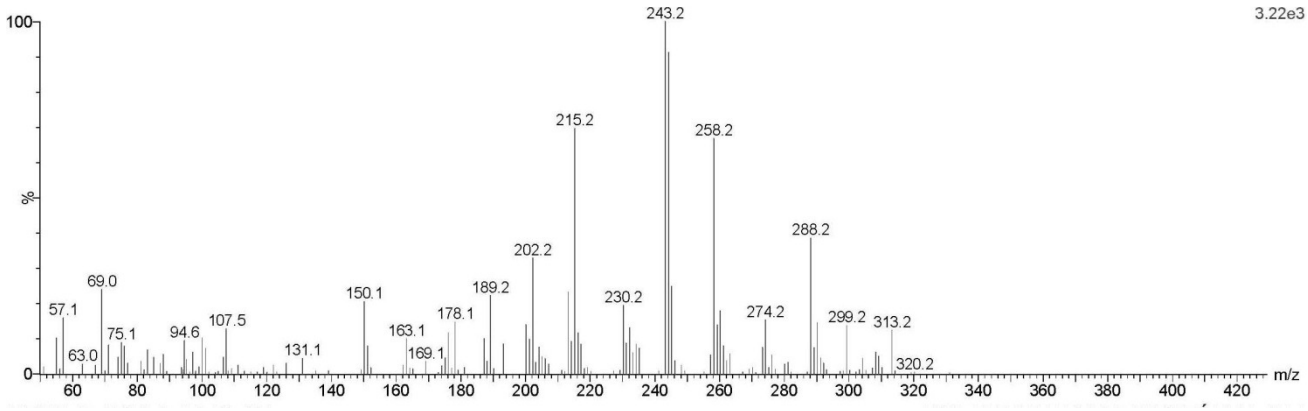

Figure S23. Mass spectrum EI^+ of compound **1h**.

2.4 Tetracene and tetracene-5,12-endoperoxide

*Tetracene (**1**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=7.37-7.42 (m, 4H, H-Ar), 7.98-8.02 (m, 4H, H-Ar), 8.67 (s, 4H, H-5,6,11,12).

*Tetracene-5,12-endoperoxide (**1e**)*

^{1}H NMR (400 MHz, $CDCl_3$, 22°C, TMS): δ=6.15 (s, 2H, H-5,12); 7.29-7.35 (m, 2H, H-Ar), 7.44-7.48 (m, 2H, H-Ar), 7.48-7.52 (m, 2H, H-Ar), 7.81-7.86 (m, 2H, H-Ar), 7.84 (s, 2H, H-Ar).

3. Spectra of total reaction mixtures

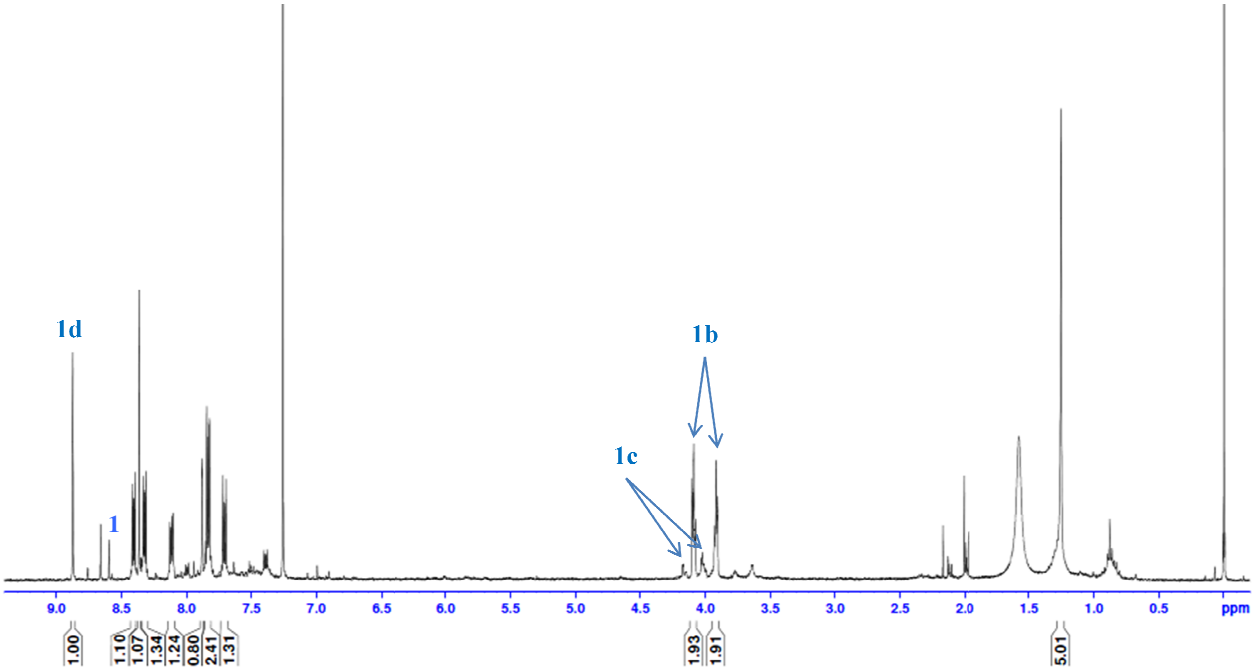

Figure S24. ^{1}H NMR spectrum of the total reaction mixture at the end of the oxidation reaction of tetracene (**1**) in conditions B2.

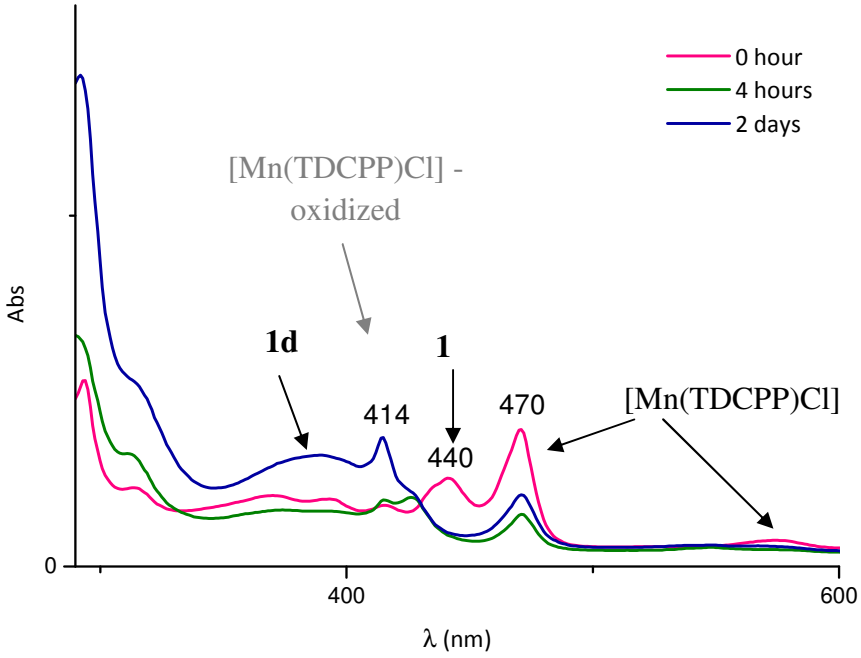

Figure S25. UV-vis spectrum of reaction mixture of tetracene oxidation at different reaction times in conditions of A1.