Electronic Supplementary Material (ESI) for ChemComm.

A General Strategy for Visible-Light Decaging Based on the Quinone Cis-Alkenyl Lock

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Supporting Information:

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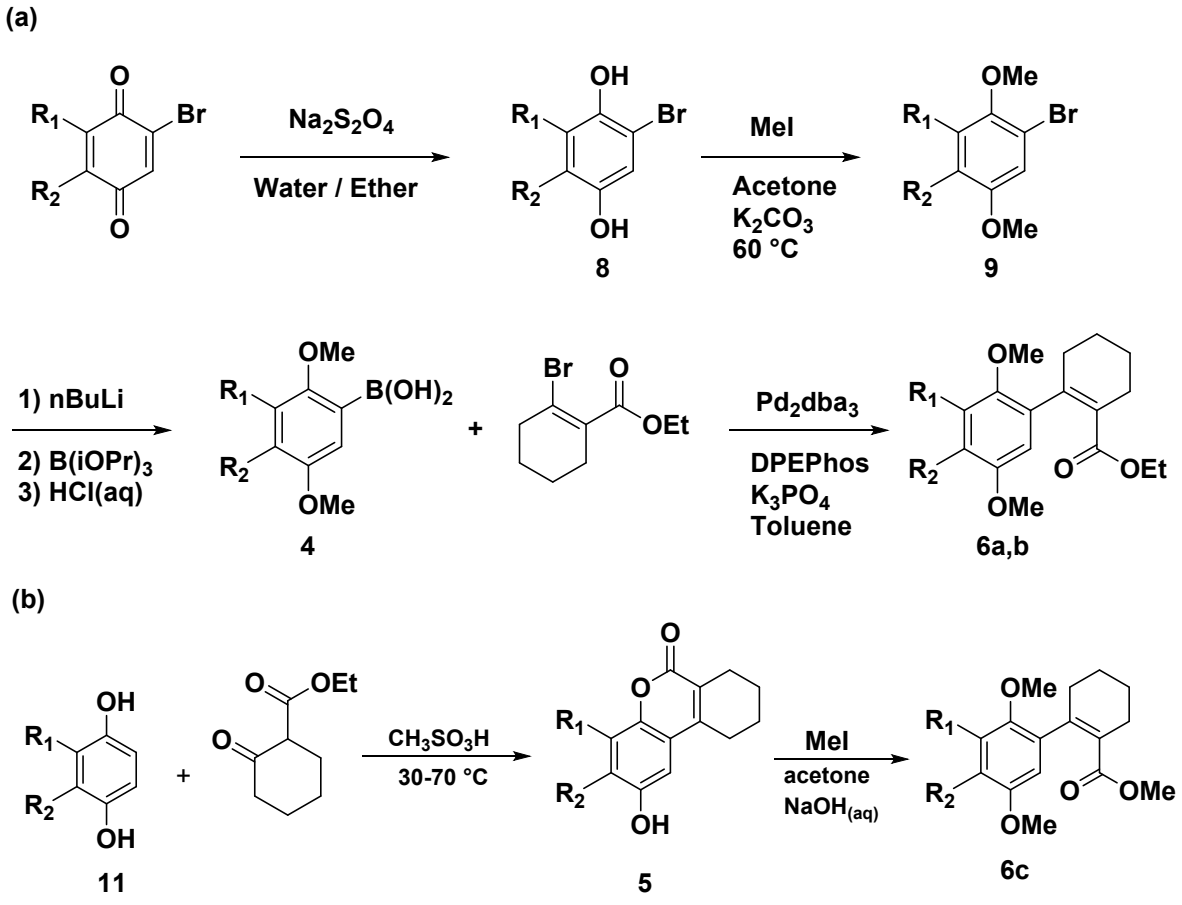
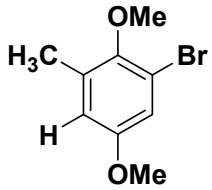
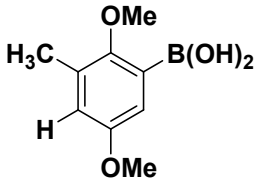
Materials and Methods. Unless otherwise stated, reactions were carried out in air-equilibrated solvents under ambient conditions. Commercially available reagents were used as received from Sigma Aldrich, AK Scientific, Alfa Aesar, or Acros Organics. Photolysis and UV-vis solvents were EMD Millipore (OmniSolv®) grade. When necessary, solvents were dried by elution through activated alumina or with molecular sieves where noted. Reactions were monitored by thin-layer chromatography with Sigma Aldrich silica gel coated plates with fluorescent indicator (0.25 mm). Silica gel chromatography procedures were as described by Still et al. (W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923), with silica gel purchased from AK Scientific (60 Å, 230-400 mesh). NMR spectra were recorded on Bruker (400 MHz) or Varian (300, 400, 500, or 600 MHz) spectrometers. HRMS (ESI) was obtained with an Agilent 6200 Series TOF. UV-vis spectra were recorded on a Cary 60 spectrometer.



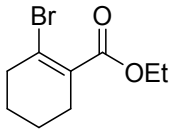
Scheme S1: preparation of dimethoxyarenes **6a-c**.



1-bromo-2,5-dimethoxy-3-methylbenzene (9): To a vigorously stirred mixture of 2-bromo-6-methyl-1,4-benzoquinone (5.692 g, 28 mmol) in ether, methanol, and water (2:1:2) was added sodium borohydride (5.3 g, 140 mmol). After stirring 15 minutes, the mixture was extracted with ether (3x100 mL). The combined organic phase was washed with brine and dried ($MgSO_4$) before removing solvent. The crude hydroquinone was immediately dissolved in acetone. To the resulting solution was added cesium carbonate (18.45 g, 57 mmol) and methyl iodide (4.4 mL, 57 mmol), and the mixture was refluxed under argon. Once conversion was complete by TLC, the mixture was cooled, filtered, and concentrated to yield 4.6466 g of 1-bromo-2,5-dimethoxy-3-methylbenzene (71% yield over two steps). An analytically pure sample was prepared by flash chromatography. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.90 (dd, *J* = 3.1, 0.6 Hz, 1H), 6.66 (dq, *J* = 3.1, 0.7 Hz, 1H), 3.75 (d, *J* = 5.1 Hz, 6H), 2.30 (t, *J* = 0.7 Hz, 3H).

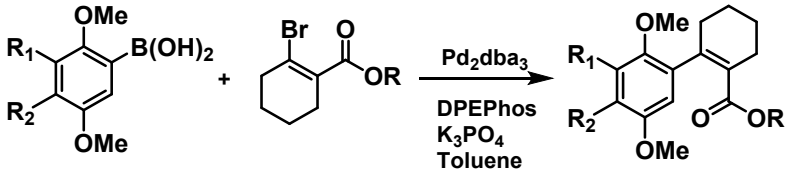


(2,5-Dimethoxy-3-methylphenyl)boronic acid (4). To a solution of aryl bromide (3.5 g, 15 mmol) in 60 mL of dry THF at -76 °C was added dropwise 6.7 mL of *n*-butyl lithium (2.5 M in hexanes). The resulting mixture was stirred at -76 °C under argon for 1 hour before 9 mL of triisopropyl borate was added. After 30 minutes, the mixture was allowed to warm to ambient temperature. The crude borate ester was hydrolyzed with aqueous HCl, then extracted into ether, washed with brine and dried ($MgSO_4$). The solvent was removed and the crude was recrystallized to yield 2.1339 g of the boronic acid in 72% yield as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 3.1 Hz, 1H), 6.84 (dq, *J* = 3.4, 0.7 Hz, 1H), 6.16 (s, 2H), 3.77 (d, *J* = 20.1 Hz, 6H), 2.29 (d, *J* = 0.6 Hz, 3H).



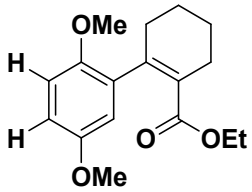
ethyl 2-bromocyclohex-1-ene-1-carboxylate. To a solution of bromocyclohex-1-ene-1-carboxylic acid (1.1025 g, 5.4 mmol) in dichloromethane was added excess oxalyl chloride (1.5 mL), followed by a drop of DMF. The mixture was stirred until bubbling ceased, then the solvent was removed to give the acid chloride as a yellow solid. The solid was dissolved in absolute ethanol, then 5 mg DMAP and 1 equivalent triethyl amine was added. The solvent was removed with heating. The resulting oil was dissolved in dichloromethane and washed with dilute HCl $_{(aq)}$, $NaHCO_{3(aq)}$, and brine before drying ($MgSO_4$). Evaporation of the organic layer yielded ethyl bromocyclohex-1-ene-1-carboxylate as a colorless oil (1.085 g, 86%) without further purification. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.24 (q, *J* = 7.1 Hz, 2H), 2.68 – 2.48 (m, 2H), 2.48 – 2.31 (m, 2H), 1.80 – 1.63 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 167.98, 131.21, 125.35, 61.02, 36.95, 28.75, 23.98, 21.32, 21.31, 14.14.

ethyl 2-bromocyclohex-1-ene-1-carboxylate (alternative preparation). To a solution of 2-bromocyclohex-1-ene-1-carboxylic acid (1.9215 g, 9.3 mmol) in dichloromethane was added 10 mL ethanol, followed by EDCI·HCl (2.2 g, 11.5 mmol), DMAP (176 mg, 1.5 mmol). The solution was stirred until conversion was complete by TLC (less than 1 hour). The solvent was removed, and the crude was taken up in CH_2Cl_2 and loaded onto a column with an equal volume of hexanes, then flashed (10% Ethyl acetate / hexanes) to yield 1.003 g of a colorless oil (46% yield).

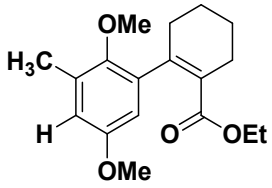


General conditions for coupling reaction:

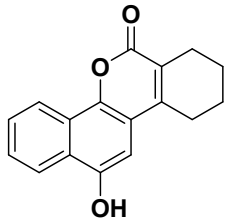
Suzuki couplings were carried out according to the published procedure[1] for derivatives of **4**. To a flask under argon is added 2 equivalents of boronic acid, 3 equivalents powdered K_3PO_4, 10 % Pd_2dba_3, 10% DPEPhos. 1 equivalent of vinyl bromide is then added with toluene and 3 Å molecular sieves. The resulting mixture is refluxed over night or until TLC indicates completion.



ethyl 2',5'-dimethoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (6a). Prepared in 23% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.78 (d, *J* = 8.9 Hz, 1H), 6.74 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.55 (d, *J* = 2.9 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 2H), 2.39 (d, *J* = 52.9 Hz, 4H), 1.73 (t, *J* = 4.1 Hz, 4H), 0.84 (t, *J* = 7.1 Hz, 3H).

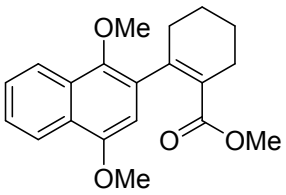


Ethyl 2',5'-dimethoxy-3'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (6b). To a solution of ethyl 2-bromocyclohex-1-ene-1-carboxylate (360 mg) and (2,5-Dimethoxy-3-methylphenyl)boronic acid (660 mg) in degassed toluene (25 mL), was added K_3PO_4 (1.04 g), Pd_2dba_3 (200 mg), and DPEPhos (100 mg). The resulting mixture was heated overnight at 80 °C, then diluted with ether and filtered through celite before purification by flash chromatography (10% ethyl acetate / hexanes) to give 320 mg (38%) of a yellow oil (1:1 mixture of dba and product) which was carried on to the next step. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.64 (dq, *J* = 3.2, 0.7 Hz, 1H), 6.39 (dd, *J* = 3.2, 0.6 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.67 (s, 3H), 2.70 – 2.31 (m, 4H), 2.27 (s, 3H), 1.76 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).



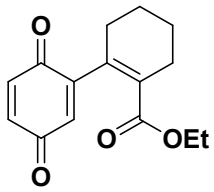
12-hydroxy-7,8,9,10-tetrahydro-6H-dibenzo[c,h]chromen-6-one (5). Prepared in 40% yield according to literature procedures[2,3] with 1,4-naphthalene diol and ethyl 2-oxocyclohexane-1-carboxylate in methanesulfonic acid at 70 °C for 3 days. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.37

(s, 1H), 8.28 (ddd, *J* = 8.3, 1.4, 0.7 Hz, 1H), 8.18 (ddd, *J* = 8.2, 1.4, 0.7 Hz, 1H), 7.68 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.64 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 6.97 (s, 1H), 2.82 – 2.71 (m, 2H), 2.49 – 2.38 (m, 2H), 1.89 – 1.77 (m, 2H), 1.77 – 1.70 (m, 2H).

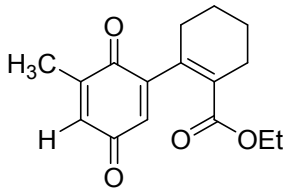


methyl 2-(1,4-dimethoxynaphthalen-2-yl)cyclohex-1-ene-1-carboxylate (6c): To a suspension of **5** (613 mg, 2.2 mmol) in 50% aqueous acetone was added NaOH (12 g, 300 mmol). Catalytic tetrabutylammonium bromide was added and the mixture was violently stirred at reflux until all solids dissolved. The solution was cooled to 60 °C, and methyl iodide (1 mL) was added. Heating and hourly addition of methyl iodide (1 mL) was continued until NMR aliquots showed complete conversion to **6c** (4 h, 4 mL total MeI). The reaction was cooled, diluted with water, and extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated to give the pure **6c** (95% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (ddd, *J* = 8.3, 1.3, 0.7 Hz, 1H), 8.06 (ddd, *J* = 8.4, 1.3, 0.7 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.45 (s, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 3.40 (s, 3H), 2.88 – 2.19 (m, 4H), 1.80 (t, *J* = 3.6 Hz, 4H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 169.56, 151.39, 145.11, 145.06, 131.37, 128.74, 128.25, 126.40, 125.69, 125.13, 122.14, 121.98, 104.53, 61.53, 55.69, 51.24, 31.94, 26.58, 22.56, 22.14.

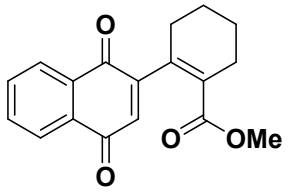
Procedure for ceric (IV) ammonium nitrate oxidations: A 1 mM solution of quinone (1 equivalent) in degassed 30% aqueous acetonitrile then cooled to 0 °C under argon. A degassed solution of CAN in 30% aqueous acetonitrile is added slowly with rapid stirring. After 15 min, the yellow solution that formed was diluted with water and extracted with ethyl acetate (3 x 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography, collecting the yellow band, afforded the quinone **7**. A common contaminant requiring additional purification was dibenzylideneacetone from the coupling.



ethyl 3',6'-dioxo-[1,1'-bi(cyclohexane)]-1,1',4'-triene-2-carboxylate (**7a**). Prepared in 85% isolated yield from **6a**. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.81 (d, *J* = 10.1 Hz, 1H), 6.75 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.43 (tt, *J* = 3.8, 2.0 Hz, 2H), 2.29 – 2.20 (m, 2H), 1.73 (h, *J* = 3.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 187.43, 185.18, 166.83, 152.22, 141.51, 137.01, 136.47, 130.15, 128.96, 60.69, 32.48, 25.43, 21.71, 21.62, 14.10.

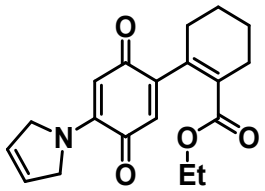


ethyl 5'-methyl-3',6'-dioxo-[1,1'-bi(cyclohexane)]-1,1',4'-triene-2-carboxylate (7b). To a degassed solution of ethyl 2',5'-dimethoxy-3'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (311.4 mg) in 30 mL of acetonitrile / water (2:1) at 0 °C was added 1.4734 g CAN as a solution in 10 mL of acetonitrile/water (1:1). After TLC indicated the reaction was complete (15 min), water was added, and the mixture was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. Purification by flash chromatography gave the product as a yellow oil (73 mg, 26% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.59 (dq, *J* = 3.1, 1.6 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 3.61 (s, 3H), 2.49 – 2.33 (m, 2H), 2.30 – 2.19 (m, 2H), 2.09 (d, *J* = 1.6 Hz, 3H), 1.79 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.44, 185.82, 167.27, 152.31, 146.33, 142.68, 133.27, 129.39, 128.81, 51.72, 32.55, 25.39, 21.69, 21.65, 16.15.

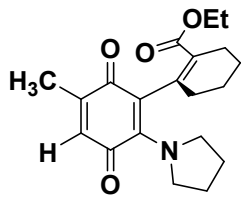


Ethyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)cyclohex-1-ene-1-carboxylate (7c). Prepared in 41% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 7.98 (m, 2H), 7.89 – 7.64 (m, 2H), 6.62 (s, 1H), 3.56 (s, 3H), 2.47 (dd, *J* = 4.4, 2.2 Hz, 2H), 2.39 – 2.20 (m, 2H), 1.93 – 1.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.02, 183.27, 167.26, 154.26, 142.77, 133.67, 133.64, 132.46, 132.18, 131.26, 129.49, 126.81, 126.08, 51.71, 32.61, 25.43, 21.75, 21.70.

General conditions for amine addition to quinones 7. 2.2 equivalents of amine are added to a solution of quinone **7** in dry acetonitrile at 0 °C under air. Dichloromethane and benzene are also suitable solvents, but methanol gives the coumarin product (cyclization is faster than aerobic aminoquinone oxidation in methanol). The solution is stirred, protected from light, until TLC indicates complete conversion (1-48 h). If a large excess of amine is used, starting material is not recovered and yields do not improve. Removal of solvent and purification by column chromatography (SiO_2, 5-30% EtOAc / hexanes), and collecting the red or red-purple bands gave the product. Further purification by prep-HPLC was required for **1a,b**.

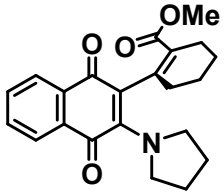


ethyl 4'-(2,5-dihydro-1H-pyrrol-1-yl)-3',6'-dioxo-[1,1'-bi(cyclohexane)]-1,1',4'-triene-2-carboxylate (1a). Prepared from **7a** (143 mg, 0.55 mmol) and pyrroline by the general procedure to yield **1a** (29.3 mg, 16%). An analytically pure sample was obtained by preparatory HPLC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.21 (s, 1H), 5.92 (s, 2H), 5.51 (s, 1H), 4.63-4.11 (broad coalescing peaks) 4H, 4.09 (q, 2H), 4.37 2.54 – 2.32 (m, 2H), 2.34 – 2.12 (m, 3H), 1.72 (m, Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 3H).



ethyl 5'-methyl-3',6'-dioxo-2'-(pyrrolidin-1-yl)-[1,1'-bi(cyclohexane)]-1,1',4'-triene-2-carboxylate (1b). To a solution of quinone **7b** (34.7 mg, 0.13 mmol) in acetonitrile was added excess pyrrolidine (2-4 equivalents) until a purple band was noted by TLC. The solution was

diluted with dilute HCl and extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography gave the product as a purple solid (10.4 mg, 24%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.30 (q, *J* = 1.5 Hz, 1H), 4.03 (qd, *J* = 7.2, 1.1 Hz, 2H), 3.76 – 3.61 (m, 2H), 3.58 – 3.43 (m, 2H), 2.66 – 2.46 (m, 1H), 2.45 – 2.24 (m, 2H), 2.03 (s, 1H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.94 – 1.48 (m, 8H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.87, 183.08, 168.56, 147.32, 145.29, 142.38, 130.27, 129.84, 118.11, 59.99, 52.24, 32.80, 26.21, 25.73, 21.92, 21.82, 16.17, 14.11.



methyl 2-(1,4-dioxo-3-(pyrrolidin-1-yl)-1,4-dihydronaphthalen-2-yl)cyclohex-1-ene-1-carboxylate (1c). (7% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.90 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 3.92 – 3.72 (m, 2H), 3.69 – 3.59 (m, 2H), 3.58 (s, 3H), 2.73 – 2.61 (m, 1H), 2.44 – 2.24 (m, 2H), 2.22 – 2.05 (m, 1H), 2.03 – 1.68 (m, 7H), 1.68 – 1.60 (m, 1H).

NMR spectra of 1a-c.

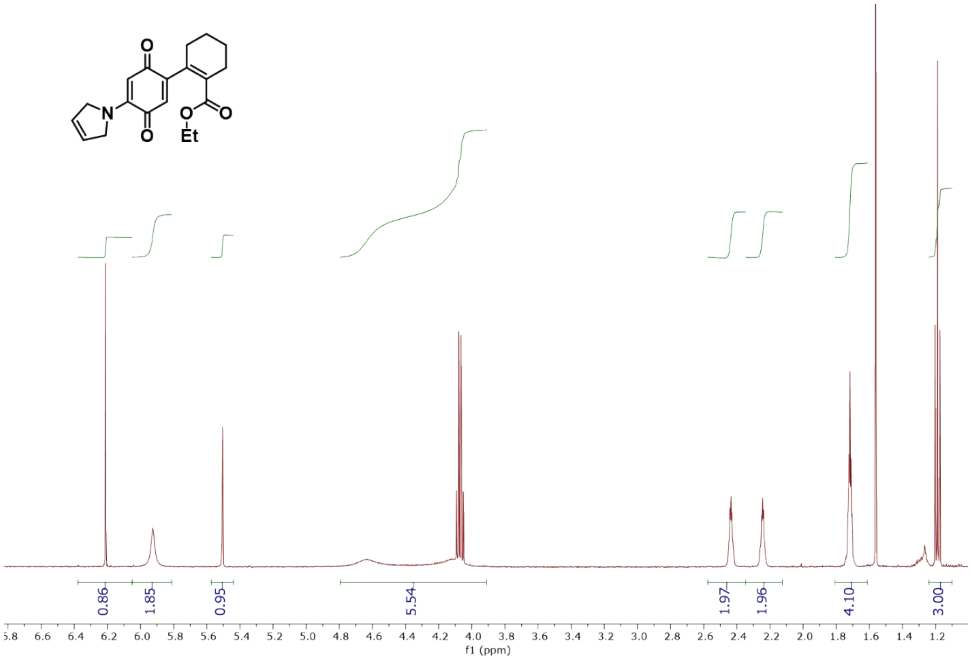


Figure S1. ^{1}H NMR of **1a** in chloroform-d.

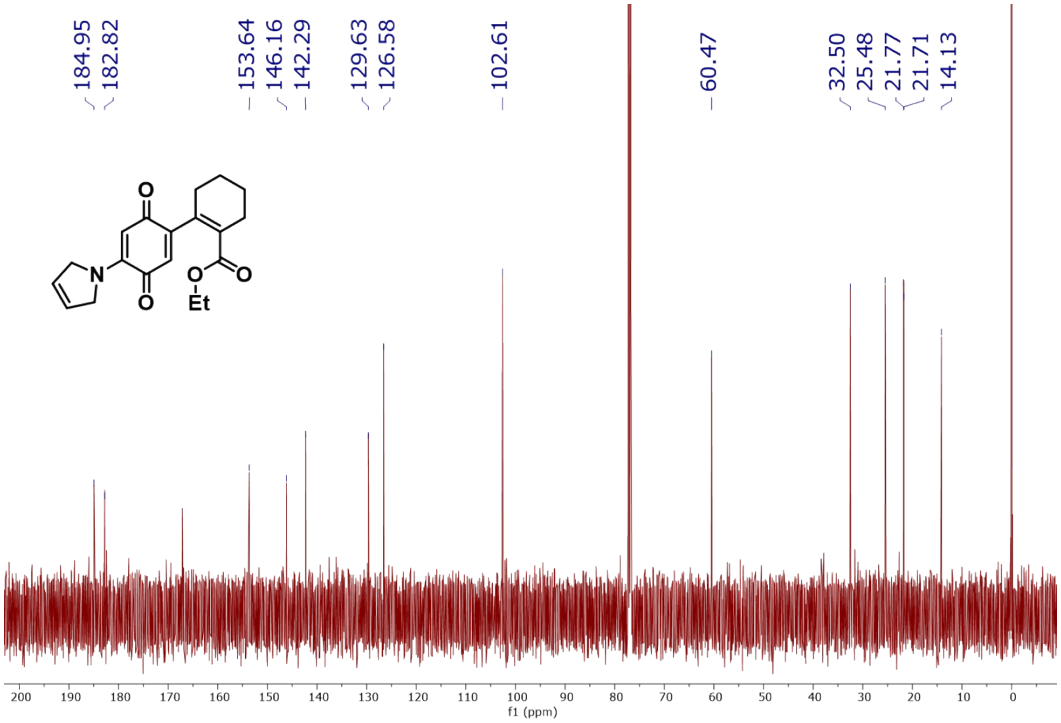


Figure S2. ^{13}C NMR of **1a** in chloroform-d.

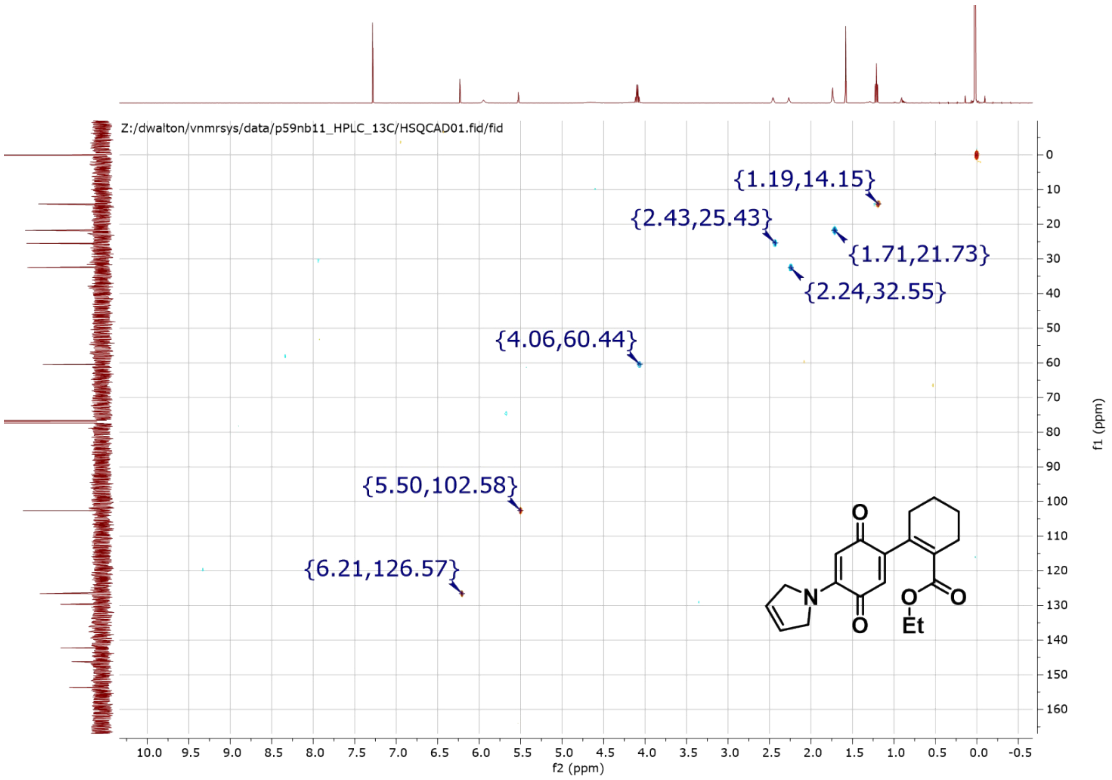


Figure S3. HSQC of **1a** in chloroform-d.

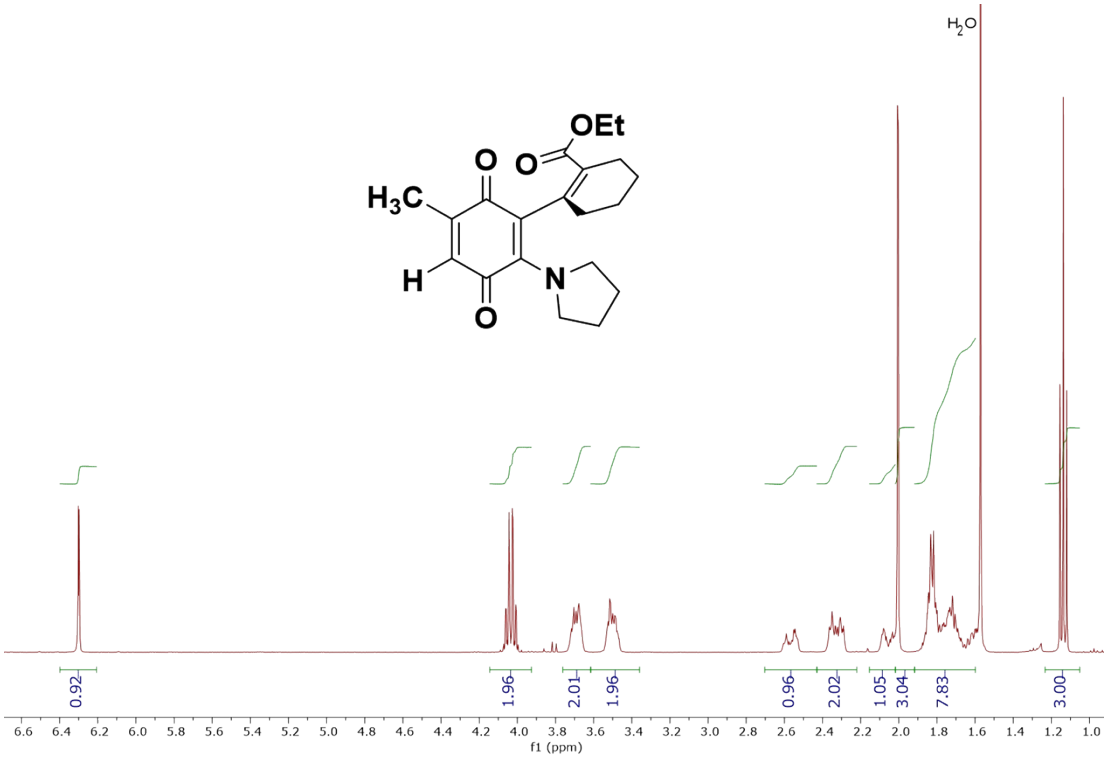


Figure S4. ^{1}H NMR of **1b** in chloroform-d.

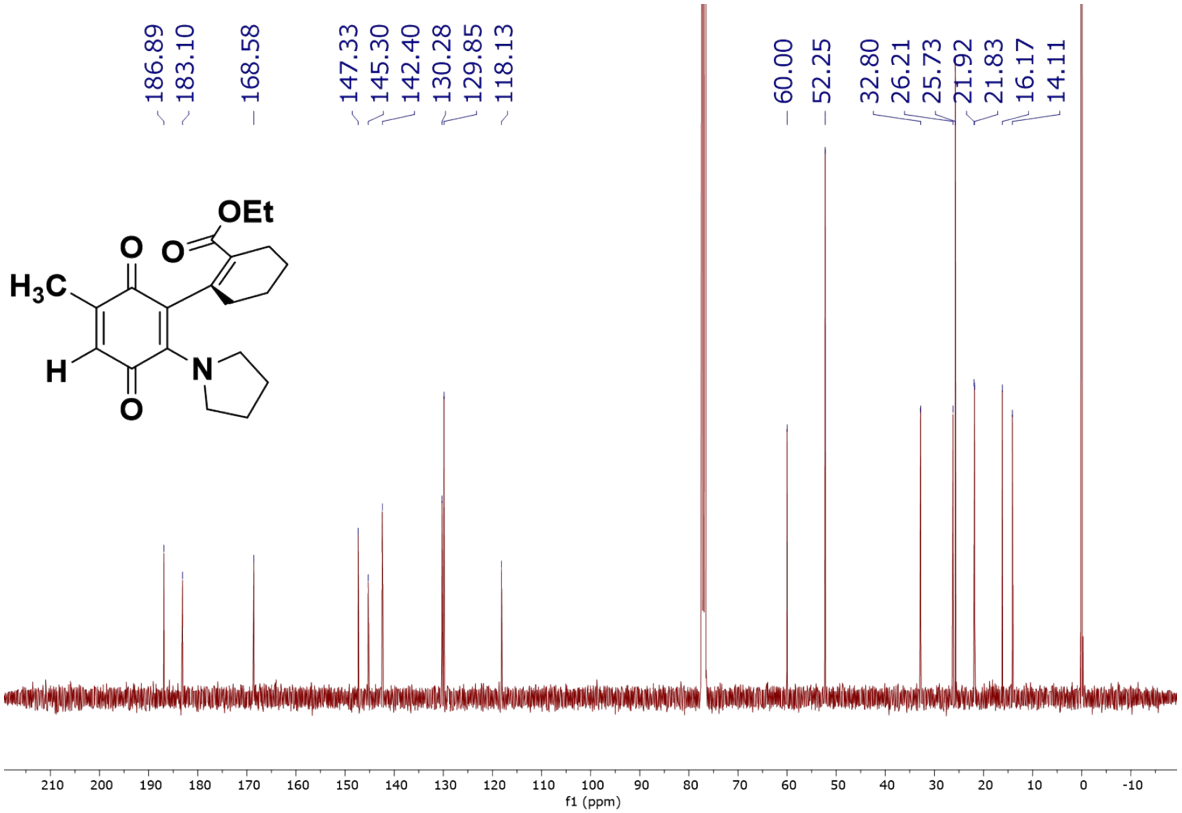


Figure S5. ^{13}C NMR of **1b** in chloroform-d.

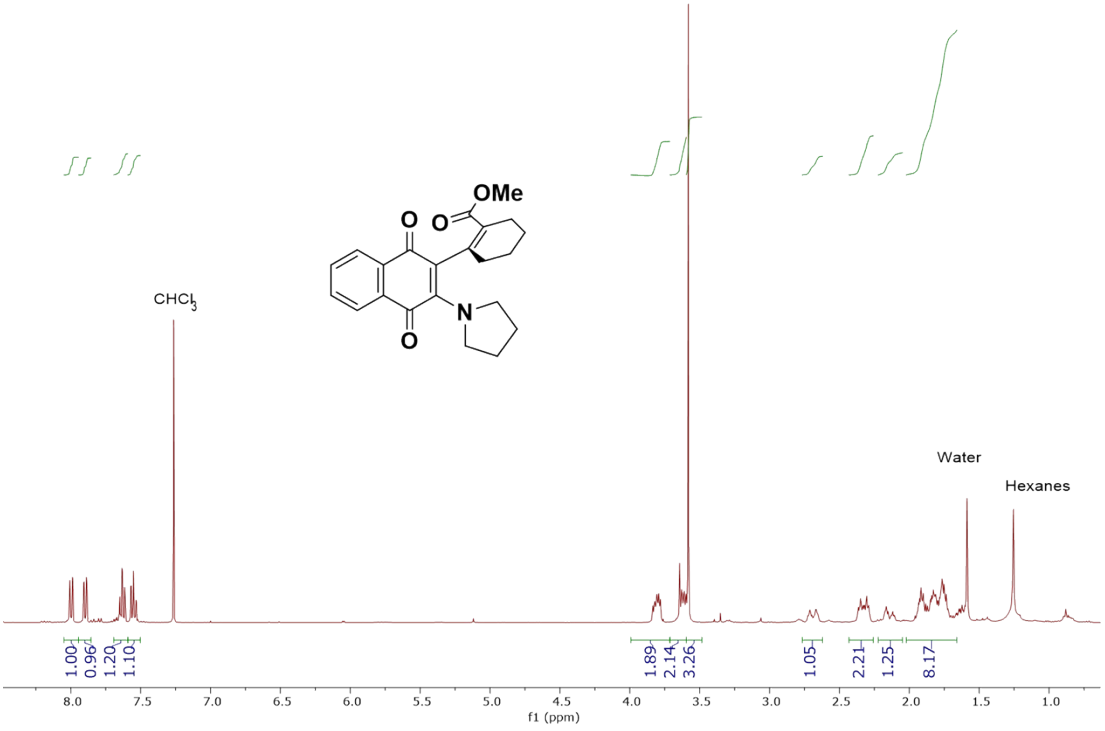


Figure S6. ^{1}H NMR of **1c** in chloroform-d.

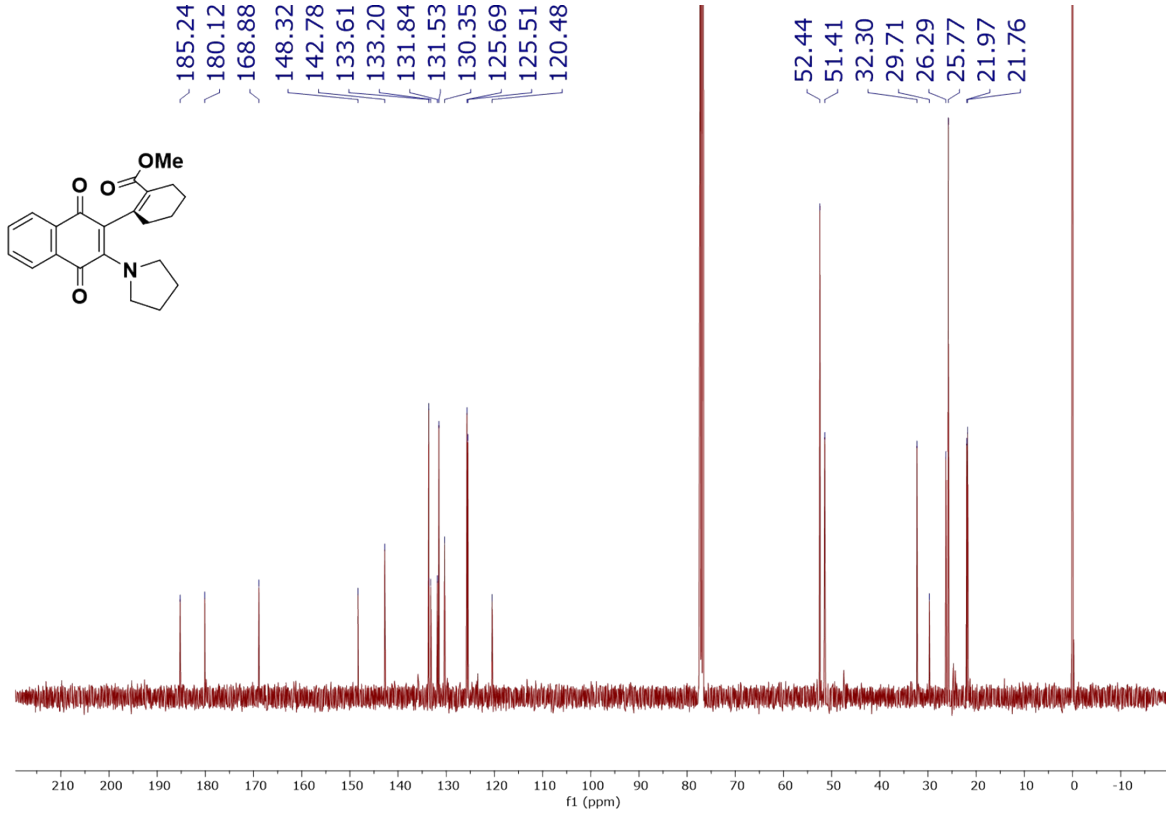
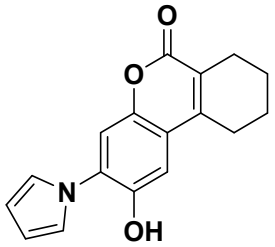
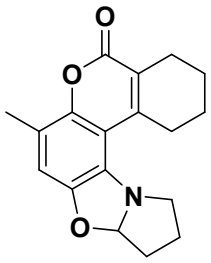


Figure S7. ^{13}C NMR of **1c** in chloroform-d.

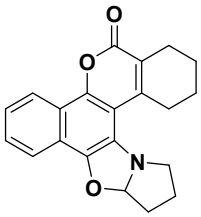
Photolysis: Samples were irradiated with a M565L3 (565 nm, 880 mW) mounted LED purchased from Thor Labs. Timecourse photolysis was conducted inside the UV-vis spectrometer cavity in a 3 mL cuvette with air-equilibrated methanol.



2-hydroxy-3-(1H-pyrrol-1-yl)-7,8,9,10-tetrahydro-6H-benzo[c]chromen-6-one (3a). Photolysis gave >95% yield by NMR. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (s, 1H), 7.20 (s, 1H), 6.93 (t, *J* = 2.1 Hz, 2H), 6.45 (t, *J* = 2.1 Hz, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 2.68 – 2.52 (m, 2H), 1.98 – 1.76 (m, 4H). HRMS (ESI) calculated 282.1125 for $C_{17}H_{16}NO_3$ $[M+H]^+$, found: 282.1127.



7-methyl-1,2,3,4,9a,10,11,12-octahydro-5H-benzo[3,4]chromeno[5,6-d]pyrrolo[2,1-b]oxazol-5-one (3b). Photolysis gave >95% yield by NMR. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.74 (s, 1H), 5.82 (d, *J* = 4.2 Hz, 1H), 3.55 – 3.40 (m, 1H), 3.40 – 3.30 (m, 1H), 2.95 (ddd, *J* = 10.3, 7.6, 2.6 Hz, 1H), 2.83 – 2.64 (m, 2H), 2.53 – 2.42 (m, 1H), 2.42 – 2.37 (m, 1H), 2.36 (s, 3H), 2.29 – 2.18 (m, 1H), 2.08 – 1.83 (m, 3H), 1.71 – 1.56 (m, 1H). LCMS (ESI+): 298.



1,2,3,4,11a,12,13,14-octahydro-5H-dibenzo[3,4:7,8]chromeno[5,6-d]pyrrolo[2,1-b]-oxazol-5-one (3c). Photolysis gave >95% yield by NMR. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.49 (ddd, *J* = 8.5, 1.2, 0.8 Hz, 1H), 7.82 (ddd, *J* = 8.3, 1.3, 0.7 Hz, 1H), 7.54 (ddd, *J* = 8.2, 6.8, 1.2

Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 6.05 (d, *J* = 4.1 Hz, 1H), 3.59 (d, *J* = 19.2 Hz, 1H), 3.37 (td, *J* = 10.2, 6.6 Hz, 1H), 2.99 (ddd, *J* = 10.4, 7.9, 2.8 Hz, 1H), 2.93 – 2.71 (m, 1H), 2.62 (s, 2H), 2.59 – 2.47 (m, 2H), 2.42 (s, 2H), 2.34 (dtd, *J* = 14.1, 7.4, 3.7 Hz, 1H), 2.17 – 1.82 (m, 4H), 1.69 – 1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.62, 148.05, 144.56, 143.60, 130.62, 127.67, 125.51, 123.32, 122.90, 120.99, 120.76, 119.87, 104.09, 59.09, 31.97, 29.71, 27.38, 24.46, 23.61, 21.94, 21.52. HRMS (ESI) calculated 334.1438 for $C_{21}H_{20}NO_3$ $[M+H]^+$, found: 334.1441.

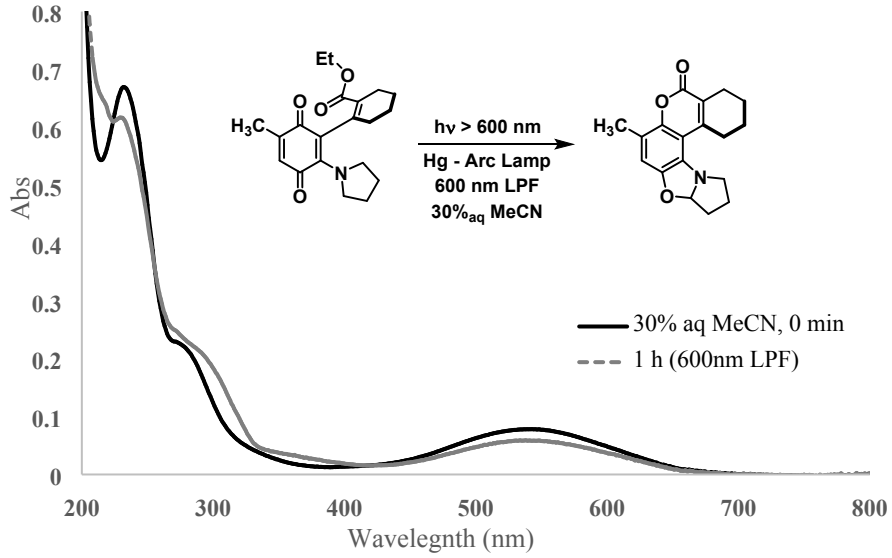


Figure S8. Aqueous decaging of **1b** at >600 nm (long-pass filter) in 30% $_{aq}$ acetonitrile. UV-vis spectra before and after 1 h of photolysis indicates partial decaging.

Evidence for Hydroquinone Intermediates: For compound **1a**, cyclization was rapid in methanol. To observe hydroquinone intermediate **2a**, photolysis was conducted in aerated $CDCl_3$ with a 565 nm LED (**Figure S9**).

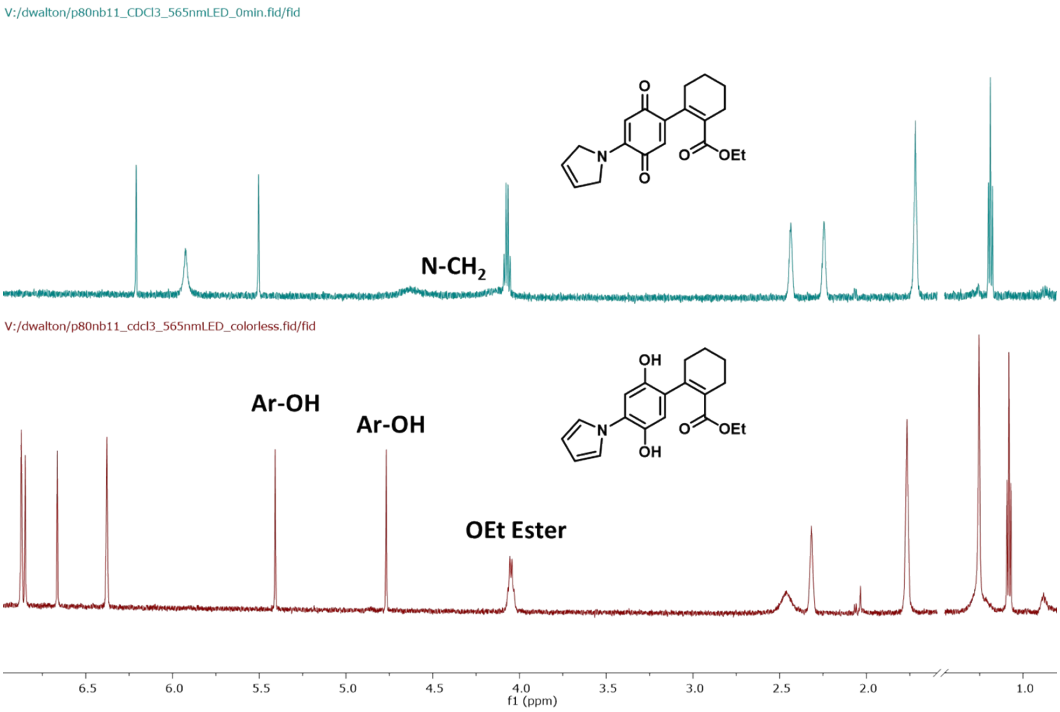


Figure S9. Photolysis of **1a** in $CDCl_3$ to give hydroquione **2a**. The large water peak at 1.56 ppm of the dilute sample was removed for clarity.

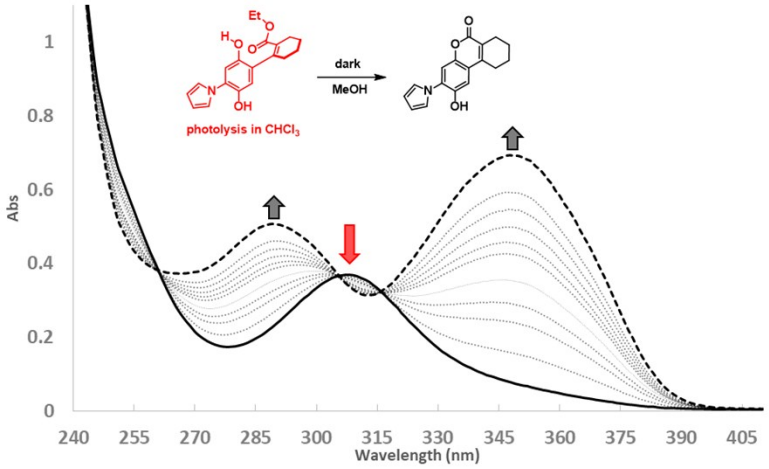


Figure S10. Conversion of **2a** to **3a** after addition of methanol to photolyzed chloroform solution of **1a**.

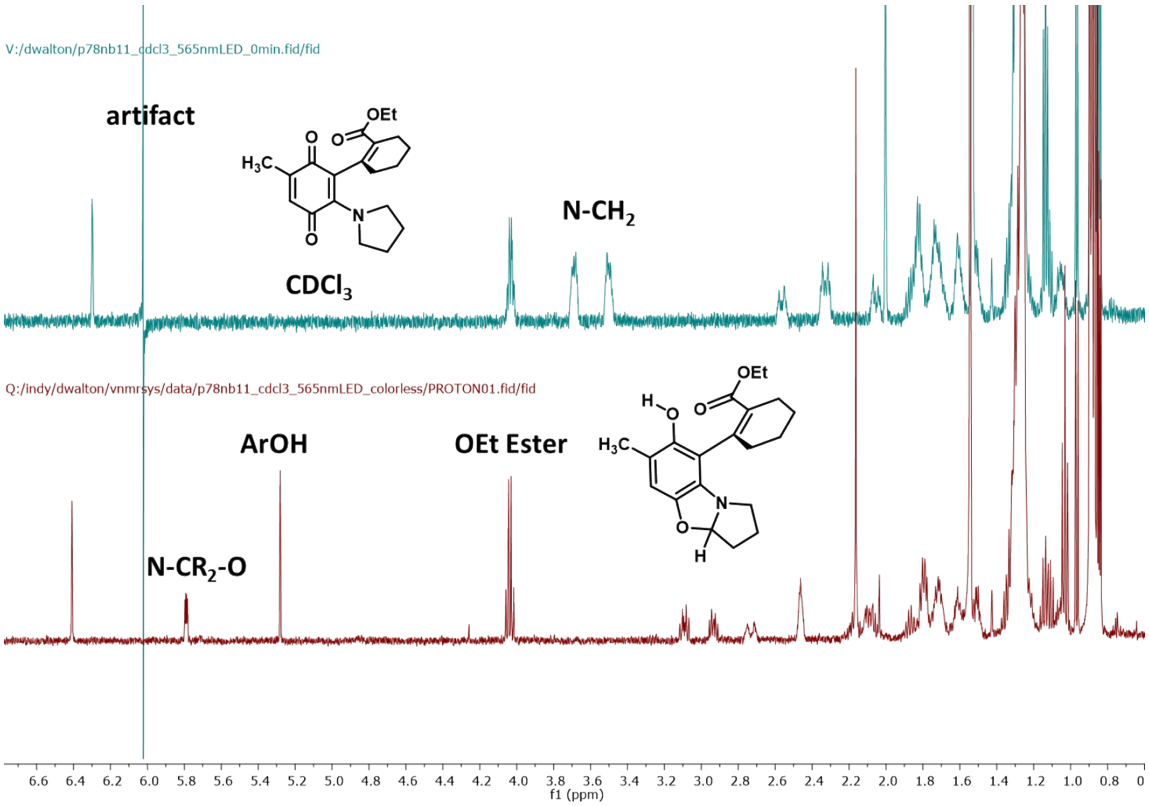


Figure S1. Photolysis of **1b** in chloroform-*d*. Hydroquinone **2b** is formed based on characteristic ester, phenol, and oxaline N-C**H**R-O peaks.

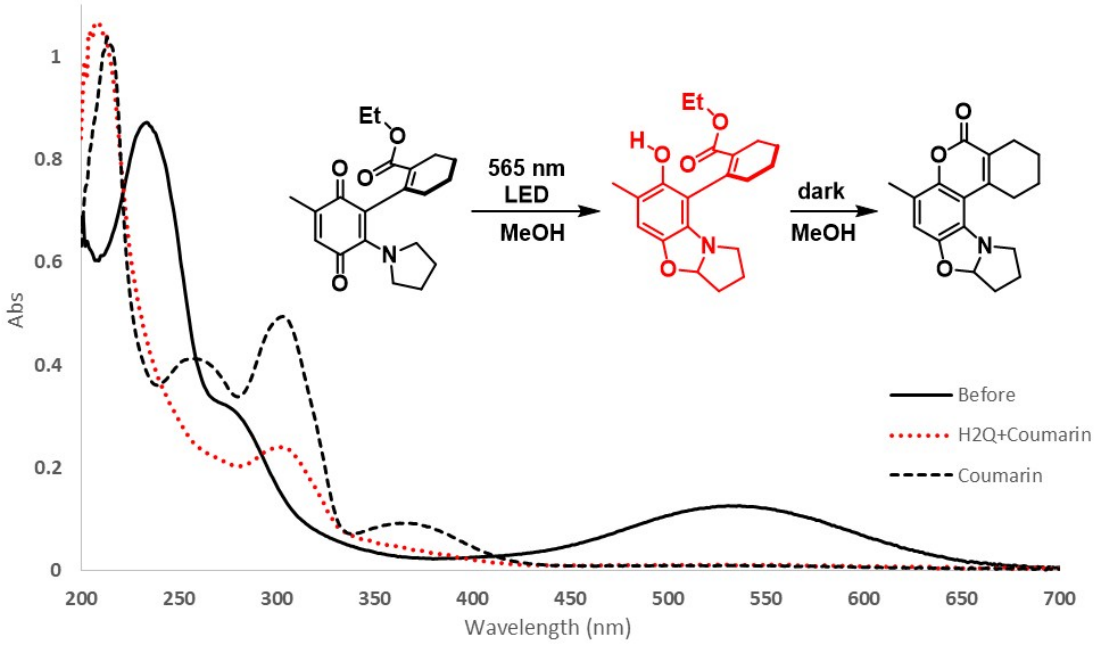


Figure S12. Timecourse photolysis of **1b** in methanol before photolysis, after photolysis, and after completion of the dark lactonization step.

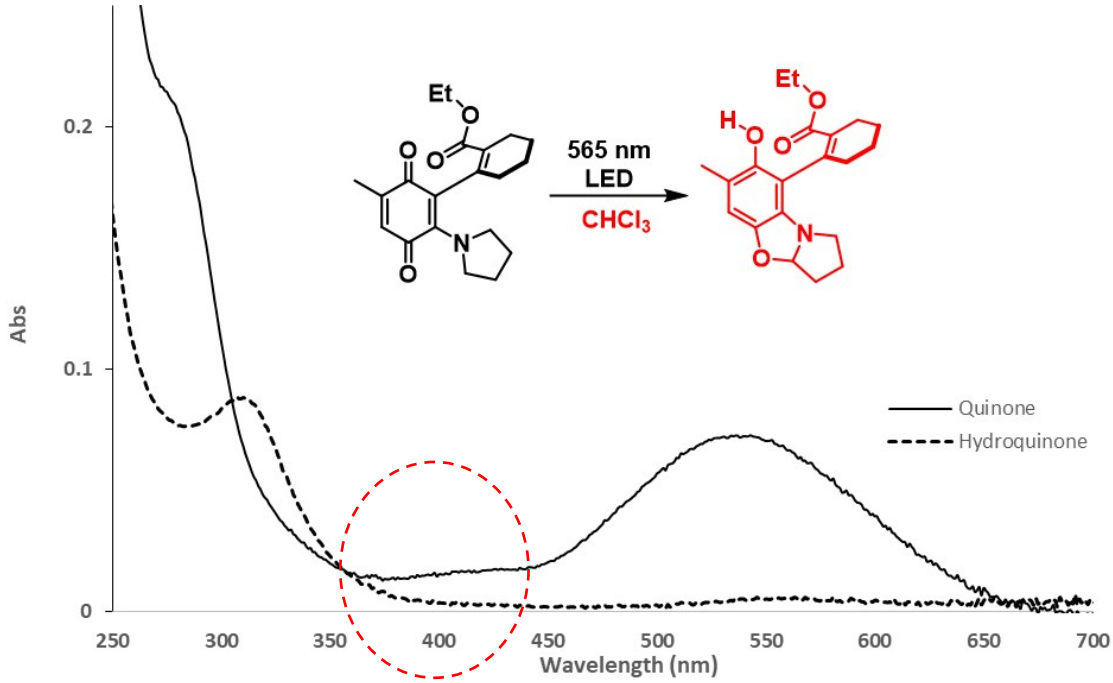


Figure S13. Photolysis of **1b** in chloroform. Hydroquinone **2b** notably lacks the coumarin absorbance of **3b** at 370 nm.

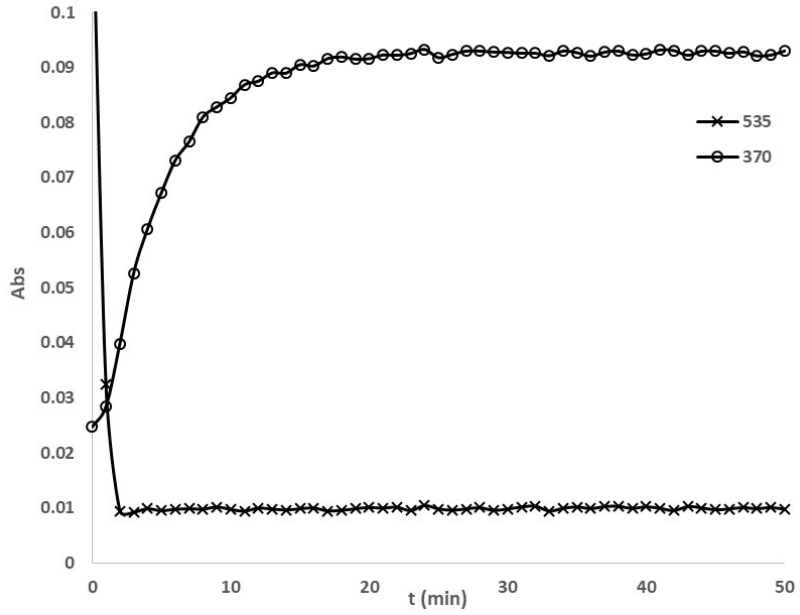


Figure S14. Photolysis of **1b** in methanol, monitoring absorbance at 535 nm (**1b**) and 370 nm (**3b**). In 2 minutes, the quinone absorbance (535 nm) reaches a minimum while the coumarin absorbance (370 nm) continues to grow in over 20 minutes.

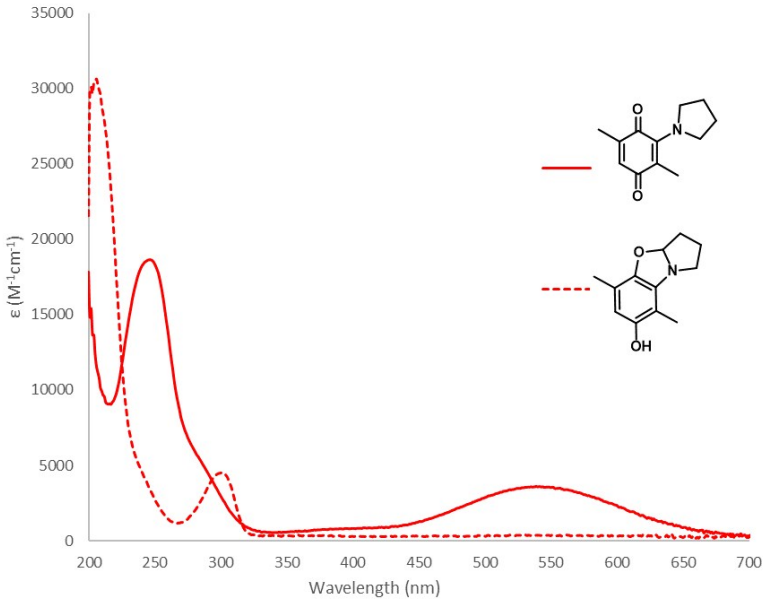


Figure S15. Photolysis of 2,5-dimethyl-3-pyrrolidino-1,4-benzoquinone in methanol for comparison to **2b** and **3b**.

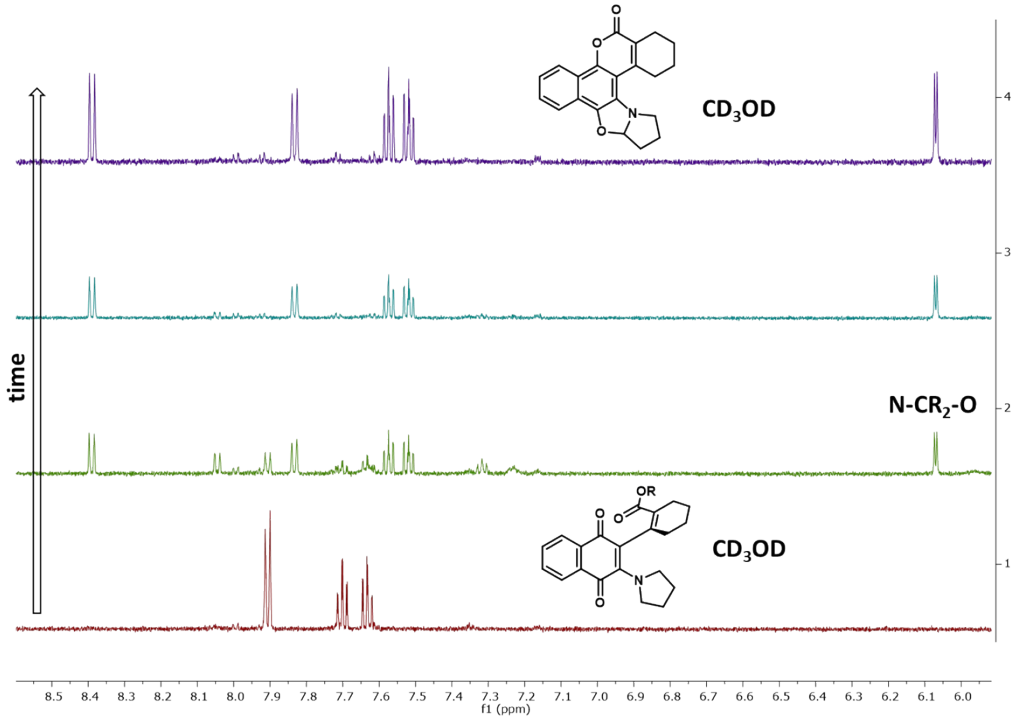
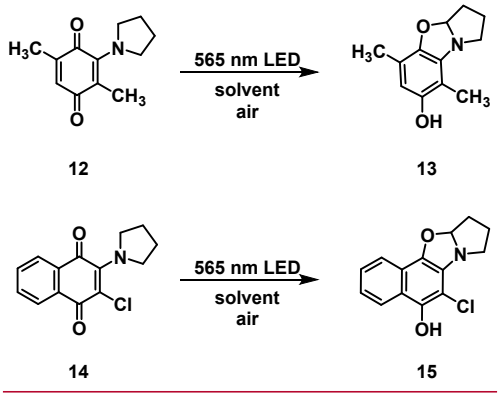


Figure S16. Partial ^{1}H NMR timecourse photolysis of **1c** in CD_3OD monitored over time.

Relative Quantum yields: A dilute solution of quinone ($A_0 < 0.1$) in air equilibrated methanol was irradiated side on with an unfocused, 880 mW, 565 nm LED beside the appropriate reference compound. The change in absorbance for each compound at $\lambda_{max,vis}$ was recorded after 5 min of irradiation. Results (n = 2-6) were averaged, and the quantum yields were calculated relative to previously reported quantum yields[4,5] based on percent conversion. Reference compounds were chosen due to closely matched UV-vis spectra to ensure similar absorption of light at each wavelength, namely 2-chloro-3-pyrrolidino-1,4-naphthoquinone ($\Phi = 0.19$ in PhMe) for **1a,c** and 2,5-dimethyl-3-pyrrolidino-1,4-benzoquinone for compound **1b** ($\Phi = 0.09$ in CH_2Cl_2) (**Figure S17-18**). Due to the lack of actinometers at suitable wavelenghts, we sought to compare the quinones to compounds that underwent the same photolysis reaction and had similar absorption spectra and known quantum yields. The following considerations make this an acceptable approach for these compounds. First, photolysis of amine substituted quinones has previously been determined to be independent of the wavelength of photolysis. Second, for dilute solutions ($A_0 < 0.1$), photolysis follows a near-linear relation to irradiation time.[6] The photoproducts are transparent at the excitation wavelength, therefore only starting material absorbs light over time. Finally, when comparing the two known quinones against each other in various solvents, literature results[4,5] were reproducible within the error expected of a quantum yield.



12 13 14 15

Scheme S2. Reference photolysis reactions for relative quantum yields

Table S1. Quantum yield vs. solvent for reference quinones

quinone	$\lambda_{max,\ vis}$ (nm)	ε ($M^{-1}cm^{-1}$)	Φ_{decomp}	Solvent
12[5]	540	3,380	0.09	CH_2Cl_2
12	540	3,590	0.06	MeOH
12[5]	540	--	0.03	MeCN
13[4]	495	4,900	0.19	PhMe
13	495		0.05	MeOH

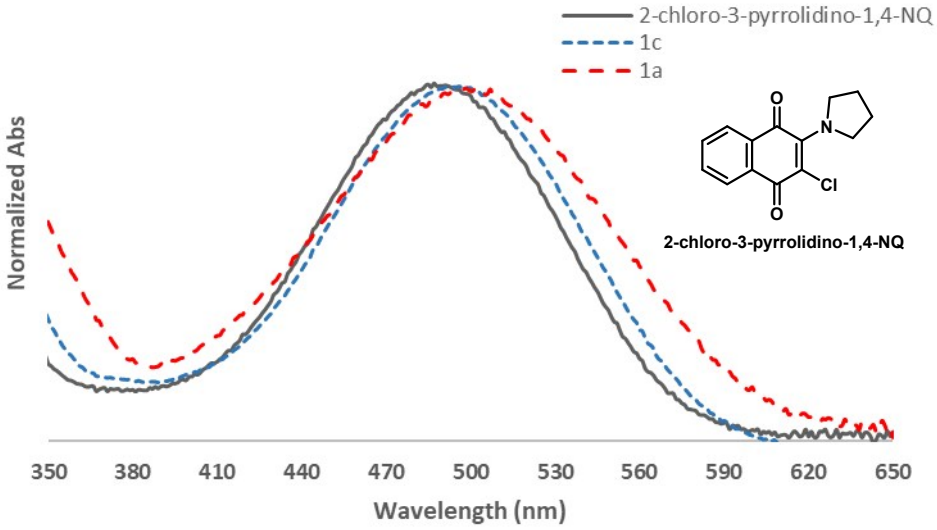


Figure S17. Normalized absorption spectra for reference quinone and **1a,c** in methanol.

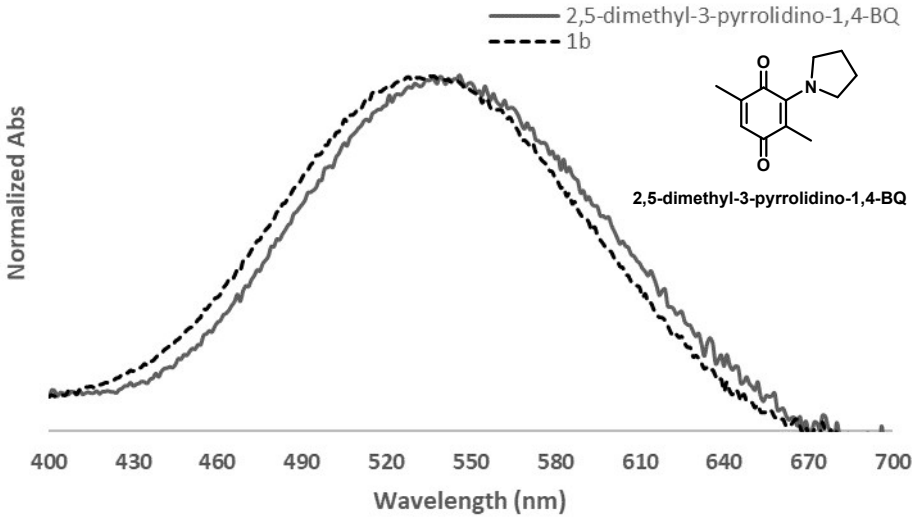


Figure S18. Normalized absorption spectra for reference quinone and **1b** in methanol.

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