Supplementary Information

Synthesis of 1,8-naphthalimides with inbuilt catechol and crown ether functionality

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S1. General Experimental and Synthesis of Compounds

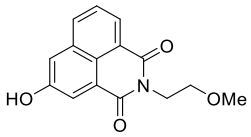
All general reagents and solvents were obtained from commercial sources and used as supplied.

All NMR spectra (^{1}H and ^{13}C) were obtained using either a Bruker Avance 400SB or Bruker Avance 500SB spectrometer as specified. Samples were dissolved in DMSO-d_6 or MeOD with the residual solvent signal used as the internal reference: 2.50 ppm (^{1}H) and 39.52 ppm (^{13}C). ^{1}H spectra are reported as: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constant *J* (Hz), integral, assignment. ^{13}C spectra are reported as: chemical shift δ (ppm), multiplicity, coupling constant *J* (Hz).

High Resolution Mass Spectra (HRMS) analysis was conducted and recorded on a Shimadzu LCMS-9030 Q-TOF mass spectrometer in a 95% MeOH in H_2O solvent system containing 0.1% formic acid. Analyte solutions were prepared in HPLC grade MeOH (conc. ~ 1 μg 1 mL^{-1}).

UV-Visible absorption spectra were collected on a Cary 60 Bio UV-Vis spectrophotometer and emission spectra were collected on a Cary Eclipse fluorescence spectrometer using a 1 cm quartz cuvette.

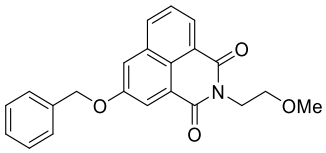
5-Hydroxy-2-(2-methoxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (5)



To a solution of 3-hydroxy-1,8-naphthalic anhydride (811 mg, 3.79 mmol) in EtOH (15 mL) was added 2-methoxyethylamine (370 μL, 4.26 mmol, 1.1 equiv.) and the resultant mixture heated using microwave irradiation at 100 °C for 60 mins. After cooling to ambient the solution was diluted with H_2O (10 mL) and cooled on ice, after which a precipitate formed that was collected by vacuum filtration to afford **5** (967 mg, 94%) as a pale yellow feathery crystals.

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.55 (br. s, 1H), 8.26–8.23 (m, 2H), 8.02 (d, *J* = 2.2, 1H), 7.76–7.72 (m, 1H), 7.65 (d, *J* = 2.2, 1H), 4.23 (t, *J* = 6.2, 2H), 3.57 (t, *J* = 6.2, 2H), 3.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.5, 163.2, 156.2, 133.3, 132.6, 127.4, 127.3, 123.3, 122.1, 121.9, 121.8, 115.8, 68.7, 58.0, 38.6. HRMS (ESI, *m/z*): calculated for $C_{15}H_{13}NO_4$ $[M+H]^+$ 272.0918, found 272.0925.

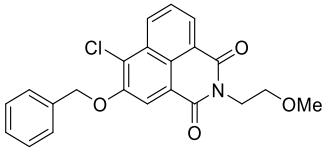
5-(Benzyloxy)-2-(2-methoxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6)



To a solution of **5** (2.33 g, 8.60 mmol) in MeCN (50 mL), was added K_2CO_3 (2.38 g, 17.2 mmol, 2.0 equiv.) and benzyl bromide (1.63 mL, 12.9 mmol, 1.5 equiv.), and the resultant mixture stirred at 40 °C for 24 h. After cooling to ambient temperature, the mixture was diluted with H_2O (30 mL) and a precipitate formed. Vacuum filtration afforded **6** (2.98 g, 96%) as a fluffy pale yellow powder.

^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.32–8.30 (m, 2H), 8.10 (d, *J* = 2.5, 1H), 8.02 (d, *J* = 2.5, 1H), 7.82–7.79 (m, 1H), 7.55–7.54 (m, 2H), 7.45–7.41 (m, 2H), 7.38–7.34 (m, 1H), 5.35 (s, 2H), 4.23 (t, *J* = 6.2, 2H), 3.58 (t, *J* = 6.2, 2H), 3.26 (s, 3H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 162.5, 163.1, 156.8, 136.4, 133.15, 133.11, 128.6 (2xC)^ 128.4, 128.2, 127.9 (2xC)^, 127.8, 123.6, 123.0, 122.1, 121.9, 114.7, 70.0, 68.7, 58.0, 38.7. HRMS (ESI, m/z): calculated for $C_{22}H_{19}NO_4$ $[M+H]^+$ 362.1387; found 362.1384. ^coincident signals confirmed using inverse gated ^{13}C experiment.

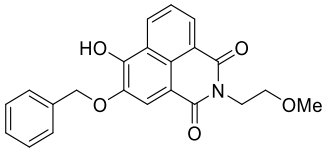
5-(Benzyloxy)-6-chloro-2-(methoxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7)



To a solution of **6** (2.09 g, 5.78 mmol) in MeCN (50 mL) was added *N*-chlorosuccinimide (1.54 g, 11.6 mmol, 2.0 equiv.) and the resultant mixture stirred at 40 °C for 22 h. After this time the mixture was cooled to ambient temperature and diluted with H_2O (20 mL). The resultant solid was collected using vacuum filtration, affording **7** (1.96 g, 86%) as a pale yellow powder.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.53 (dd, *J* = 1.0, 8.5, 1H), 8.43 (dd, *J* = 1.0, 7.3, 1H), 8.42 (s, 1H), 7.96 (dd, *J* = 7.3, 8.5, 1H), 7.57–7.55 (m, 2H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 1H), 5.56 (s, 2H), 4.24 (t, *J* = 6.1, 2H), 3.59 (t, *J* = 6.1, 2H), 3.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ 163.1, 162.7, 152.4, 136.2, 129.9, 129.4, 129.2, 129.0, 128.6 (2xC), 128.2, 127.6 (2xC), 123.3, 123.1, 122.4, 121.8, 118.5, 71.0, 68.6, 58.0, 29.6. HRMS (ESI, *m/z*): calculated for $C_{22}H_{18}ClNO_4$ $[M+H]^+$ 396.0997, found 396.0989. ^coincident signals confirmed using inverse gated ^{13}C experiment.

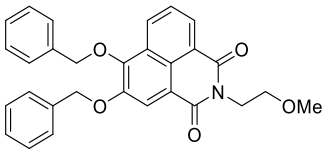
5-(Benzyloxy)-6-hydroxy-2-(2-methoxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (8)



To a solution of **7** (1.95 g, 4.93 mmol) in DMSO (50 mL) was added *N*-hydroxysuccinimide (624 mg, 5.43 mmol, 1.1 equiv.), and K_2CO_3 (2.25 mg, 16.3 mmol, 3.3 equiv.), and the resultant mixture heated at 80 °C for 24 h. After this time the mixture was cooled and diluted with H_2O (100 mL), then acidified to pH = 1 using 2M HCl. At this point a yellow precipitate formed in solution and was collected using vacuum filtration, affording **8** (1.45 g, 75%) as a yellow powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.09 (s, 1H), 8.50–8.48 (m, 1H), 8.33–8.32 (m, 1H), 8.22 (s, 1H), 7.72–7.68 (m, 1H), 7.58–7.56 (m, 2H), 7.42–7.40 (m, 2H), 7.34–7.30 (m, 1H), 5.23 (s, 2H), 4.19 (t, *J* = 6.1, 2H), 3.55 (t, *J* = 6.1, 2H), 3.24 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.7, 162.9, 148.4, 142.4, 136.8, 129.6, 128.5 (2xC)^, 128.4, 128.0, 127.7 (2xC)^, 125.8, 124.3, 123.0, 121.6, 119.8, 112.3, 70.9, 68.8, 58.0, 38.4. HRMS (ESI, *m/z*): calculated for $C_{22}H_{29}NO_5$ $[M+H]^+$ 378.1336, found 378.1340. ^coincident signals confirmed using inverse gated ^{13}C experiment.

5,6-Bis(benzyloxy)-2-(methoxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (9)

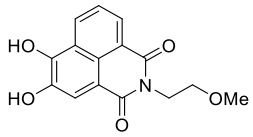


To a solution of **8** (1.80 mg, 4.76 mmol) in MeCN (50 mL) was added benzyl bromide (903 μL, 7.14 mmol, 1.5 equiv.) and K_2CO_3 (1.32 mg, 9.52 mmol, 2.0 equiv.), and the resultant mixture heated at 40 °C for 24 h. After this time the mixture was cooled to ambient temperature and the solvent removed under reduced pressure. The residue was then diluted with H_2O (40 mL) and the resultant solid collected using vacuum filtration, affording **9** (1.78 g, 80%) as a pale yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48–8.47 (m, 2H), 8.39 (dd, *J* = 8.5, 1.1, 1H), 7.63 (dd, *J* = 8.5, 7.2, 1H), 7.54–7.52 (m, 2H), 7.45–7.38 (m, 5H), 7.36–7.33 (m, 3H), 5.38 (s, 2H), 5.36 (s, 2H), 4.43 (t, *J* = 8.9, 2H), 3.72 (t, *J* = 8.9, 2H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6):

δ 163.5, 162.8, 148.2, 147.1, 136.7, 136.6, 129.3, 128.7 (2xC)^, 128.66 (2xC)^, 128.5 (2xC)^, 128.4, 128.24, 128.20, 128.0 (2xC)^, 127.3, 127.2, 123.7, 121.8, 120.3, 117.6, 75.2, 71.2, 68.7, 58.0, 38.6. HRMS (ESI, *m/z*): calculated for $C_{29}H_{25}NO_5$ $[M+H]^+$ 468.1806, found 468.1803. ^coincident signals confirmed using inverse gated ^{13}C experiment.

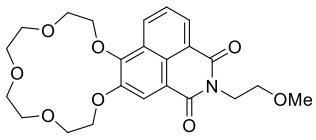
5,6-Dihydroxy-2-(methoxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (Nap-Cat)



To a flask flushed with N_2 was added $Pd(OH)_2/C$ 10% w/w (68 mg, 0.481 mmol, 0.5 equiv.) and MeOH (30 mL). The flask was then evacuated and backfilled with N_2 three times, then **9** (450 mg, 0.963 mmol) added to the flask. The flask was then evacuated and backfilled with N_2 twice, and then evacuated and backfilled with H_2 twice. The resultant mixture was allowed to stir at 21 °C for 8 h. After this time the flask was evacuated and backfilled with N_2, then diluted with 50 mL MeOH. The reaction mixture was then filtered through a bed of celite, washing with MeOH. The filtrate was transferred to a round bottom flask and the solvent removed *in vacuo* to afford **Nap-Cat** (214 mg, 77%) as a yellow powder.

^1H NMR (400 MHz, DMSO-d_6): δ 8.45–8.44 (m, 1H), 8.30–8.28 (m, 1H), 8.09 (s, 1H), 7.68–7.65 (m, 1H), 4.21 (t, J = 6.1, 2H), 3.55 (t, J = 6.1 Hz, 2H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 164.0, 163.0, 147.7, 141.8, 128.7, 128.3, 125.2, 123.9, 123.4, 121.6, 121.4, 111.3, 68.8, 58.0, 38.4. HRMS (ESI, m/z): calculated for $C_{15}H_{13}NO_5$¬ $[M+Na]^+$ 310.0686 found 310.0682.

5-(2-Methoxyethyl)-9,10,12,13,15,16,18,19-octahydro-4*H*-benzo[*de*][1,4,7,10,13]pentaoxacyclopentadecino[2,3-g]isoquinoline-4,6(5*H*)-dione (Nap-Crown)

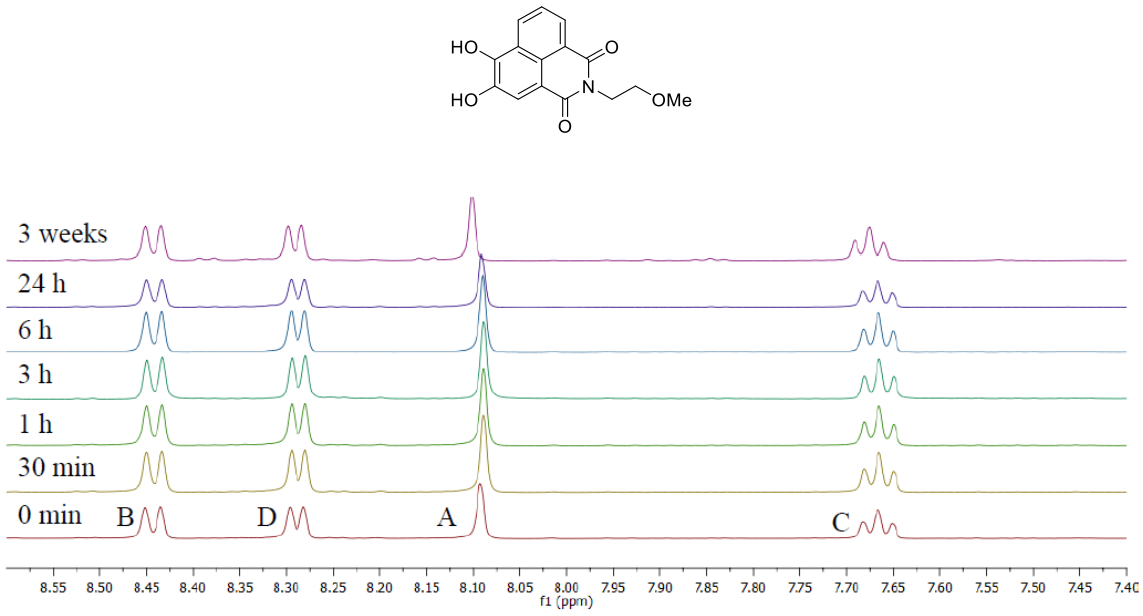


To a stirring solution of tetraethylene glycol di(*p*-toluenesulfonate) (2.25 g, 4.47 mmol, 2.0 equiv.) in acetone (50 mL) was added KI (1.71 g, 10.6 mmol, 4.8 equiv.) and the resultant mixture heated at 40 °C for 24 h. After this time the mixture was cooled and solvent removed under reduced pressure. The residue was then diluted with H_2O and extracted with 10% MeOH

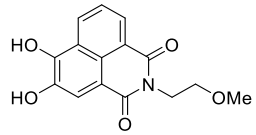
in CH_2Cl_2 (3 × 15 mL), the combined organics dried over $MgSO_4$, and solvent removed under reduced pressure to give a yellow oil. The crude material was immediately diluted with MeCN (15 mL) and **Nap-Cat** (635 mg, 2.21 mmol) and Cs_2CO_3 (3.18 g, 9.76 mmol, 4.4 equiv.) added, then the resultant mixture heated at 40 °C in a foil-wrapped flask for 48 h. The reaction mixture was then cooled, solvent removed under reduced pressure, then the residue diluted with H_2O and extracted with 10% MeOH in CH_2Cl_2 (3 × 5mL). The combined organics were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude solid was purified by flash column chromatography, using silica gel 60 (70–230 mesh) and 1% MeOH in CH_2Cl_2. The column was neutralised (before loading the crude product) by flushing with a dilute solution of Et_3N in CH_2Cl_2. Fractions containing the product were combined and the solvent removed to afford **Nap-Crown** as a yellow powder (5 mg, 1%).

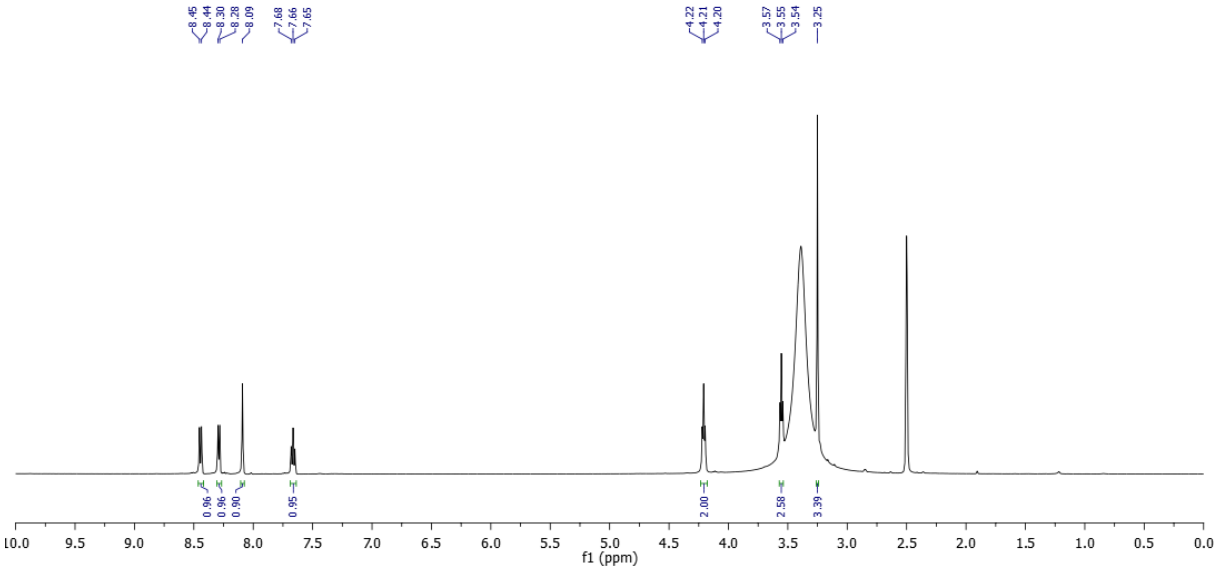
^{1}H NMR (400 MHz, MeOD): δ 8.34–8.32 (m, 1H), 8.28 (dd, *J* = 7.3, 0.9 Hz, 1H), 8.17 (s, 1H), 7.62 (dd, *J* = 8.4, 7.3 Hz, 1H), 4.49 (t, *J* = 5.6 Hz, 2H), 4.36-4.34 (m, 2H), 4.29 (t, *J* = 6.1 Hz, 2H), 4.04 (t, *J* = 5.6 Hz, 2H), 3.93–3.91 (m, 2H), 3.78–3.76 (m, 2H), 3.72-3.64 (m, 10H), 3.30 (s, 3H). ^{13}C NMR (101 MHz, MeOD): δ 165.9, 165.2, 149.6, 131.0, 129.7, 128.7, 128.2, 125.8, 123.6, 121.0, 118.9, 75.5, 73.4, 72.3, 72.1, 71.3, 71.0, 70.8, 70.4, 70.2, 59.2, 40.4. HRMS (ESI, *m/z*): calculated for $C_{23}H_{27}NO_8[M+Na]^+$ 468.1629, found 468.1644.

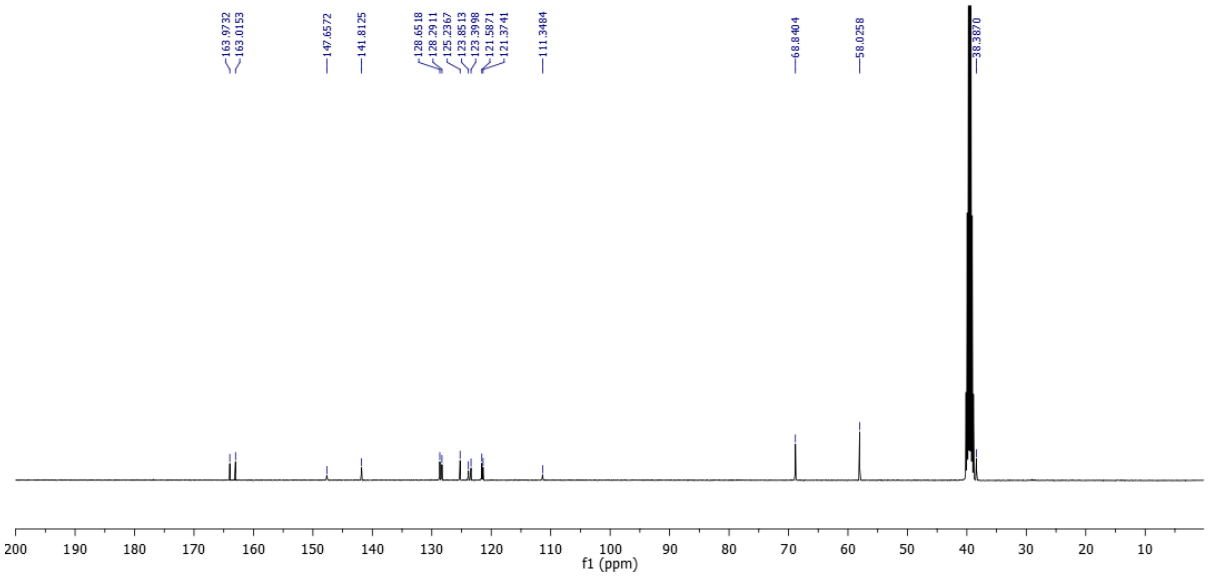
S2. ^{1}H NMR time study of Nap-Cat in DMSO-d_6 with excess H_2O_2

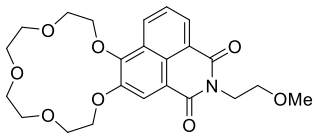


S3. ^{1}H and ^{13}C NMR Spectra of New Compounds in DMSO-d_6





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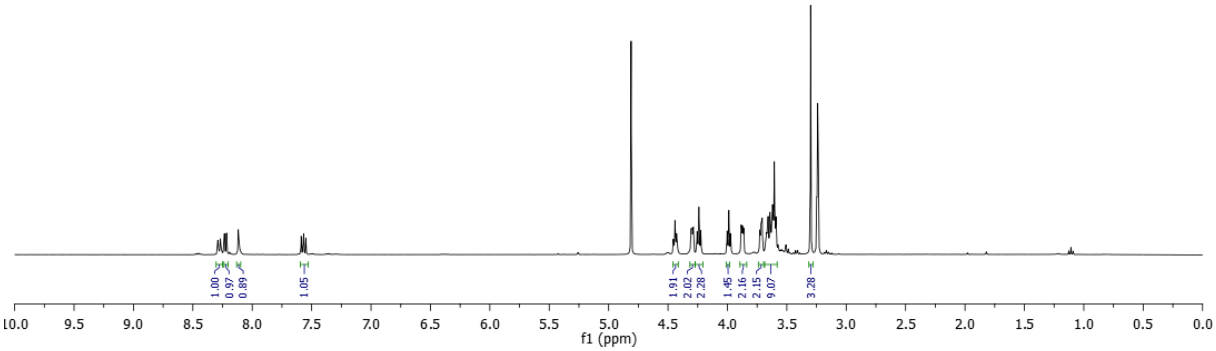
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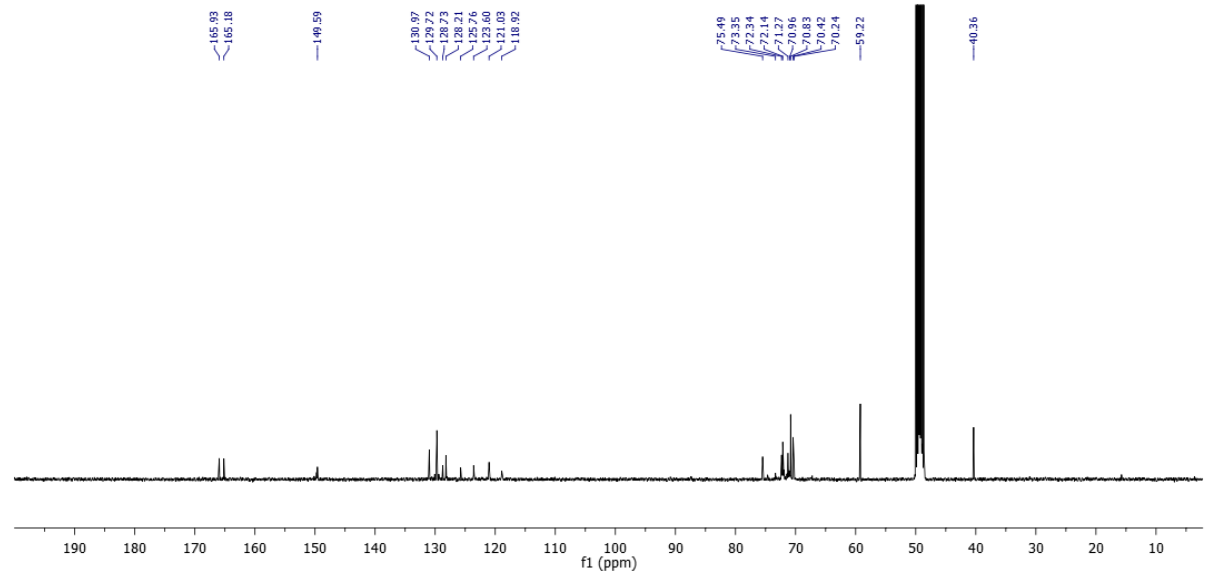
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70.42
70.24
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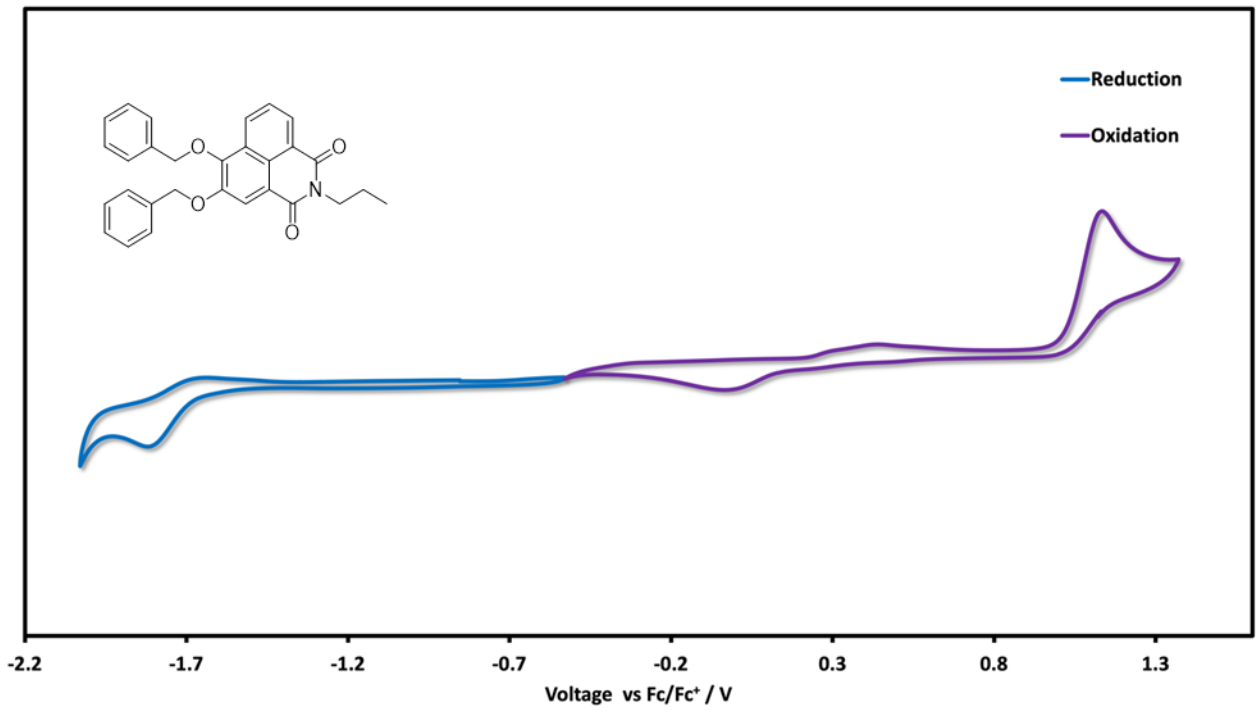
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

S4. Electrochemical Measurements

Cyclic voltammetry (CV) measurements were performed on a Bio-Logic Science Instrument VSP potentiostat with a PC controlled electrochemical workstation. Solutions for cyclic voltammetry were prepared in HPLC grade MeCN, which was dried using an in-house solvent purification system. A minimum volume of solvent (*ca*. 2–3 mL) was used. Pt wires were used as the pseudoreference electrode and the counter electrode, while a Pt disk electrode was used for the working electrode. Both before and after the experiments, the Pt disk electrode was cleaned by polishing the surface in an ethanol slurry of abrasive powder (gamma alumina powder, 0.05 micron, CH Instruments), before sonicating in ethanol, washing with acetone, water, and finally ethanol, and then drying. The electrochemical cell consisted of a glass vessel (ca. 40 mL) covered with a plastic lid and drilled with four holes: one for each electrode, and one for nitrogen purging. The vessel was sealed with parafilm to ensure minimal oxygen contamination. Tetra(n-butyl)ammoniumhexafluorophosphate ($TBAPF_6$; *ca*. 0.1 M in MeCN) was used as the supporting electrolyte, with the solution degassed by vigorous bubbling for about 10 min prior to scanning the blank sample to ensure a clean background. Small quantities of sample were then added in portions, and then the mixture degassed and scanned. This process was repeated until an adequate signal-to-background ratio became apparent. The measurements in the appropriate electrochemical windows were then carried out, at scan rates of 0.1 and 1 V s^{-1}. At the end of each experiment, ferrocene was added as an internal reference, and then the scans were repeated, again at 0.1 and 1 V s^{-1}. Estimated error: ±30 mV. The redox potentials are reported relative to the ferrocenium/ferrocene (Fc+ /Fc) redox couple.



Cyclic voltammogram of the propyl analogue of compound **9** in MeCN.