Supporting Information

1,10-Pyrene-monoimides: A new class of electron acceptors and excimer-forming fluorescent dyes.

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Materials and Methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker 400MHz spectrometer. IR measurements were taken on a Thermo Scientific Nicolet iS50 FTIR infrared spectrophotometer using attenuated total reflectance (ATR). High-resolution mass spectra were collected on a Waters Xevo G2-S QToF with ESI source. UV-vis spectra were measured with a Jasco V-700 series spectrophotometer in a 1-cm quartz cell. Fluorescence emission spectra were recorded with a Jasco FP-8000 Spectrofluorometer at room temperature in degassed solvents. Quantum yield measurements were carried out using the comparative method vs. anthracene (Φ = 0.30 in ethanol, recrystallized from ethanol) and 9,10-diphenylanthracene ((Φ = 0.95 in ethanol, recrystallized from m-xylene).

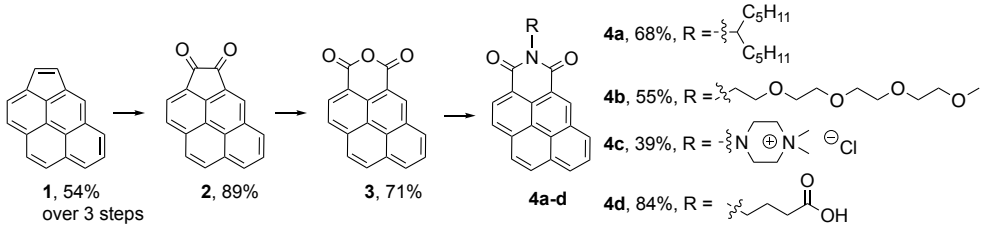
Time-correlated single photon counting (TCSPC) measurements were carried out on a FLS1000 Photoluminescence Spectrometer by Edinburgh Instruments using a picosecond LED 280 nm excitation source. Decay curves were analyzed by non-linear least-squares fitting using the Fluoracle® software package following the equation: $I(t) = A + \beta \exp\left(\frac{-x}{\tau}\right)$

Cyclic voltammetry (CV) was performed with a Pine Research WaveNow potentiostat. Measurements were carried out in 0.2 M tetrabutylammonium hexafluorophosphate in dry, degassed dichloromethane, at room temperature, under a blanket of argon, using flame-cleaned platinum wires as the working and counter electrodes and Ag/AgCl wire as a reference electrode. The Ag/AgCl wire was immersed in bleach for 15 minutes prior to the experiment. Scanning began at an initial potential of 0 V and compounds gave identical profiles with both oxidative and reductive sweep directions. A ferrocene-ferrocenium (Fc/Fc+) redox couple was used as an internal standard and its redox potential assumed to be –4.80 eV below vacuum level. All potentials are reported versus the $E_{1/2}$ of Fc/Fc+ at 0V. Estimated LUMO levels were calculated using the equation: $E_{LUMO} = -(E_{1/2} red\ vs.\ Fc + 4.8) eV$.

Geometry optimizations and frequency DFT calculations were performed at the B3PW91/6-31G(d) level of theory using the Gaussian Engine in the WebMO software. (Polik, WF, Schmidt, JR. WebMO: Web-based computational chemistry calculations in education and research. *WIREs Comput Mol Sci.* 2021;e1554. https://doi.org/10.1002/wcms.1554) The reorganization energies were calculated based on the four-point scheme neglecting the outer-sphere contributions: ($\lambda_i^- =$

$(E_C^0 - E_N^0) + (E_N^{-1} - E_C^{-1})$, where E_C^0 is the energy of the neutral species at the optimized minimum geometry of the anion and E_N^{-1} is the energy of the anionic species at the optimized minimum geometry of the neutral molecule. Calculated electron affinities were approximated from the equation: $EA = (E_C^{-1} - E_N^0)$.

Synthetic Details



Scheme S1. Synthesis of of 1,10-pyreneimide derivatives **4a-d** from cyclopenta[cd]pyrene **1**.

Cyclopenta[cd]pyrene **1** was synthesized according to the following literature procedure: M. Sarobe, J.W. Zwikker, J.D. Snoeijer, U.E. Wiersum, L.W. Jenneskens. Preparative flash vacuum thermolysis. A short synthesis of cyclopenta[c,d]pyrene. *J. Chem. Soc., Chem. Commun.* **1994**, No. 1, 89–90. In brief, the three steps consist of a Friedel-Crafts acylation to form 1-acetylpyrene, followed by phosphorus pentachloride to give 1-(1-chloroethenyl)pyrene. This undergoes cyclization to cyclopenta[cd]pyrene **1** under flash vacuum pyrolysis at 1,000ºC. In our hands we achieved an overall percent yield of 54% starting from 4.00 grams of pyrene. NMR analytical data matched literature reports: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62 (t, *J* = 3.7 Hz, 2H), 8.47 (d, *J* = 7.7 Hz, 1H), 8.23-8.15 (m, 5H), 7.52 (d, *J* = 5.1 Hz, 1H), 7.35 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (101 MHz; DMSO-d_6): δ 138.6, 135.3, 133.8, 131.6, 130.5, 129.2, 128.2, 127.4, 127.2, 127.08, 126.7, 124.7, 123.3, 121.4, 120.1.

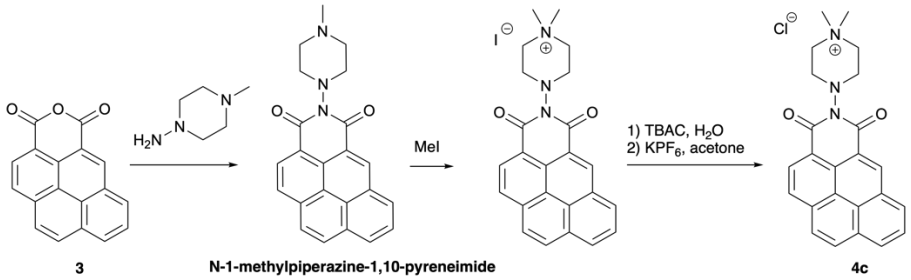
Synthesis of cyclopenta[cd]pyrene-3,4-dione (2): To cyclopenta[cd]pyrene **1** (0.2188 g, 0.9669 mmol, 1 eq) in chlorobenzene (60 mL) was added benzeneseleninic anhydride (0.4603 g, 1.278 mmol, 1.32 eq). The reaction mixture was heated to 100°C in a sand bath and left stirring overnight. The reaction mixture was allowed to cool to room temperature and excess solvent was removed under reduced pressure. The resulting dark solids were taken up in aqueous saturated $NaHCO_3$ and vacuum filtered. The solids were rinsed in sequence with DI water, methanol, and hexane to afford **2** as an insoluble black powder (0.22124 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.58 (d, J = 7.8 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.41 (d, J = 9.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.26-8.23 (m, 2H). Sample was not sufficiently soluble for ^{13}CNMR analysis. FTIR ν_{max}/cm^{-1}: 3052.4, 1743.2, 1712.6, 1629.2, 1608.2. FTMS (ESI): [M]+ Calculated for $C_{18}H_8O_2Na$, 279.04220; found, 279.04132.

Synthesis of 1,10-pyrene anhydride (3): In a 50 mL round bottom flask was combined cyclopenta[cd]pyrene-3,4-dione **2** (0.5734 g, 2.238 mmol, 1 eq) and 2N aqueous sodium hydroxide

(24 mL, 48 mmol, 21 eq). A condenser was attached, and the brown turbid reaction mixture was brought to reflux in a sand bath. Hydrogen peroxide (30%, 24 mL) was added slowly dropwise through the condenser causing the evolution of foamy bubbles. Once the addition was complete, the reaction mixture stirred under refluxed for one hour. The reaction mixture was then allowed to cool to room temperature and diluted with DI water (25 mL). HCl (1N) was added until the pH was 1 (~7 mL). The mixture was vacuum filtered and rinsed with DI water (3x), affording a dark brown powder that was left to dry overnight. The solids were transferred to a 125 mL Erlenmeyer flask with acetic anhydride (40 mL). The mixture was stirred and heated to boiling for two hours. After cooling the solution to room temperature, the insoluble solids were vacuum filtered through Teflon and rinsed with methanol, yielding a dark brown powder (0.4303g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.90 (d, J = 8.1 Hz, 1H), 8.60 (d, J = 7.5 Hz, 1H), 8.56 (d, J = 7.5 Hz, 1H), 8.41 (d, J = 8.2 Hz, 1H), 8.38 (d, J = 9.0 Hz, 1H), 8.27-8.24 (m, 2H). Sample was not sufficiently soluble for ^{13}CNMR analysis. FTIR ν_{max}/cm^{-1}: 3052.4, 1759.7, 1731.6, 1627.2, 1601.0. FTMS (ESI): [M]+ Calculated for $C_{18}H_8O_3Na$, 295.03712; found, 295.03613.

Synthesis of N-C(C_5H_{11})$_2$-1,10-pyreneimide 4a: To an oven-dried 25 mL long-neck Schlenk flask was loaded anhydride **3** (0.0505 g, 0.185 mmol) and the flask was degassed by evacuating and refilling with argon 3 times. Dry dimethylformamide (DMF) (5mL) and undecamine (0.1535 g, 0.896 mmol, 4.8 eq) were syringed in and the reaction mixture was heated to 130ºC in a sand bath while stirring vigorously. After 18 hours, the reaction was cooled to room temperature and transferred to a 250 mL round bottom flask, rinsing with dichloromethane. The DMF residue was mostly removed under reduced pressure via rotary evaporation, yielding a brown, crude oil. The crude product was passed through a silica plug with dichloromethane, and the main fraction concentrated via rotary evaporation. The product was purified by prep-TLC using a 2:1 hexane:dichloromethane (DCM) mixture as eluent. The pure product was an orange powder (53.9 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 16.0 Hz, 1H), 9.04 (br, dd, *J* = 14.9, 7.7 Hz, 1H), 8.48 (d, *J* = 7.7 Hz, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 8.9 Hz, 1H), 8.16-8.11 (m, 2H), 5.34-5.27 (m, 1H), 2.38-2.29 (m, 2H), 1.96-1.88 (m, 2H), 1.36-1.23 (m, 12H), 0.82 (t, *J* = 7.04 Hz, 6H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 165.0, 164.7, 135.3, 134.7, 134.4, 130.7, 130.1, 129.9, 129.7, 127.7, 127.3, 127.2, 127.0, 126.8, 125.5, 125.1, 122.4, 54.6, 32.5, 31.9, 26.7, 22.6, 14.0. FTMS (ESI): [M]+ Calculated for $C_{29}H_{31}NO_2Na$, 448.22525; found, 448.22437.

Synthesis of N-PEG4-1,10-pyreneimide 4b: Following the same procedure as for **4a**, anhydride **3** (0.0494g, 0.181 mmol) was reacted with m-PEG4-amine (0.1486g, 0.7169 mmol, 4.0 eq). The crude product was passed through a silica plug with dichloromethane, and the main fraction concentrated via rotary evaporation to afford a dark orange oil. The product was then purified by column chromatography on basic alumina, eluting with 9:1 DCM:acetone. The pure product was a reddish-orange oil (0.0459 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.91 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 8.22-8.17 (m, 2H), 4.56 (t, *J* = 6.2 Hz, 2H), 3.91 (t, *J* = 6.2 Hz, 2H), 3.75 (t, *J* = 4.4 Hz, 2H), 3.66-3.60 (m, 4H), 3.54 (dd, *J* = 5.0, 2.8 Hz, 4H), 3.48-3.45 (m, 2H), 3.32 (s, 3H). ^{13}CNMR (101 MHz; CDCl3): δ 164.4, 164.1, 134.58, 134.43, 130.4, 129.99, 129.86, 128.9, 127.17, 127.11, 126.92, 126.1, 125.3, 124.6, 121.9, 121.1, 118.6, 71.8, 70.65, 70.58, 70.54, 70.42, 70.2, 68.0, 59.0, 39.2. FTMS (ESI): [M]+ Calculated for $C_{27}H_{27}NO_6Na$, 484.17361; found, 484.17250.



Synthesis of N-1,1-dimethylpiperazinium-1,10-pyreneimide chloride 4c: To an oven-dried 25 mL long-neck Schlenk flask was loaded anhydride **3** (0.0749g, 0.275 mmol) and purged under a stream of argon for 1.5 hours before adding dry DMF (5mL) and 4-methylpiperazin-1-amine (184.7 mg, 1.604 mmol, 5.8 eq) via syringe. The reaction was stirred at 120°C under argon for 18 hours. The reaction mixture was then cooled to room temperature and transferred to a 100mL round bottom flask, rinsing with DCM. Most of the DMF residue was removed via rotary evaporation to yield a brown, mud-like crude solid. The product was first purified by column chromatography on silica, eluting with 9:1 to 5:1 DCM:methanol. As a piperazine by-product eluted along with the product, the product was further purified by dissolving it in 25mL ethyl acetate and washing with 25mL saturated $NaHCO_3$(aq) followed by 25mL H_2O. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo to afford an orange solid **N-1-methylpiperazine-1,10-pyreneimide** (0.0449 g, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.85 (d, *J* = 8.1 Hz, 1H), 8.48 (d, *J* = 7.7 Hz, 1H), 8.42 (d, *J* = 7.5 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 9.0 Hz,

1H), 8.16-8.12 (m, 2H), 3.67 (br, 4H), 2.82 (s, 4H), 2.47 (s, 3H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 164.4, 164.2, 135.1, 134.9, 130.7, 130.2, 130.0, 129.3, 127.38, 127.37, 127.3, 126.4, 125.7, 125.1, 122.5, 119.7, 55.4, 50.4, 45.8. FTMS (ESI): [M]+ Calculated for $C_{23}H_{20}N_3O_2$, 370.15555; found, 370.15529.

N-1-methylpiperazine-1,10-pyreneimide (0.0278 g, 0.0753 mmol) was loaded into a 100mL round bottom flask and dissolved in 10 mL ACN to produce a clear orange solution. Methyl iodide (14.7 μL, 0.0253 mmol, 3.1 eq) was added by micropipette and the reaction stirred at room temperature for 18 hours. The resulting turbid solution is concentrated in vacuo to afford dull orange solids. The solids were transferred to a centrifuge tube and washed with 8 mL DCM, and then 2x 8mL ethyl acetate. With each wash the solids were sonicated for 5 minutes, centrifuged for 15 minutes and the supernatant decanted. The iodide salt of the product was an orange solid (0.0281 g, 97% yield.)

The iodide salt was then purified by anion exchange: The iodide salt of the desired product (0.0195g, 0.0381 mmol) was dissolved in 20 mL H_2O and KPF_6 (0.0471 g, 0.256 mmol) was added, and the solution left to stir overnight. The solution was then centrifuged, and the water removed. The solids were rinsed with 2x20 mL fractions of H_2O and centrifuged each time. The product was then lyophilized to remove trace water. The dry orange solids were dissolved in 20 mL acetone and tetrabutylammonium chloride (TBAC) (0.0755 g, 0.272 mmol) was added to immediately afford orange precipitate. The reaction was stirred for 3 hours, and the solids collected via centrifuge. The solids were rinsed with 2x20 mL fractions of acetone and centrifuged to afford pure **4c** as flaky orange solids (0.0148 g, 92% yield). ^{1}H NMR (400 MHz, MeOD) δ 9.41 (s, 1H), 8.91 (d, J = 8.0 Hz, 1H), 8.72 (d, J = 7.5 Hz, 1H), 8.64 (d, J = 7.1 Hz, 1H), 8.51 (d, J = 8.3 Hz, 1H), 8.44 (s, 1H), 8.34 (d, J = 9.0 Hz, 1H), 8.29 (t, J = 7.7 Hz, 1H), 3.94 (s, 4H), 3.81 (t, J = 5.1 Hz, 4H), 3.37 (s, 6H). ^{13}C NMR (101 MHz; D_2O): δ 163.9, 163.3, 133.6, 133.0, 130.6, 130.3, 129.2, 128.1, 126.9, 125.7, 125.0, 124.4, 122.3, 121.04, 120.98, 117.9, 116.8, 114.7, 61.6, 51.1, 43.9. FTMS (ESI): [M]+ Calculated for $C_{24}H_{22}N_3O_2$, 384.17120; found, 384.17041.

Synthesis of N-butanoic acid-1,10-pyreneimide 4d: Following the same procedure as for **4a**, anhydride **3** (0.0482 g, 0.177 mmol) was reacted with 4-aminobutanoic acid (0.0763 g, 0.740 mmol, 4.2 eq) in dry DMF at 110ºC for 18 hours. The cooled reaction mixture was then poured into 150 mL of chilled water and stirred vigorously, while adding ~0.5 mL of concentrated HCl. The resulting precipitate was filtered, rinsed with water, and air-dried. The product was then purified by

column chromatography on silica, eluting with 9:1 DCM:methanol. The pure product was an orange powder (53.0 mg, 84%). ^{1}H-NMR (400 MHz; DMSO-d_6): δ 12.01 (br, s, 1H), 9.09 (br, s, 1H), 8.64 (br, s, 2H), 8.56 (br, s, 1H), 8.37 (br, s, 2H), 8.23 (br, s, 2H), 4.18-4.15 (m, 2H), 2.37 (t, J = 7.3 Hz, 2H), 1.97 (quintet, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz; DMSO-d_6): δ 174.5, 164.3, 163.9, 134.8, 134.6, 130.8, 130.7, 130.6, 129.1, 128.0, 127.6, 127.0, 126.3, 126.0, 124.4, 121.9, 121.5, 118.8, 31.9, 23.6. (one signal of butanoic moiety overlapped by DMSO signal at ~40 ppm) FTMS (ESI): [M]+ Calculated for $C_{22}H_{15}NO_4Na$, 380.08988; found, 380.08823.

IR Spectra

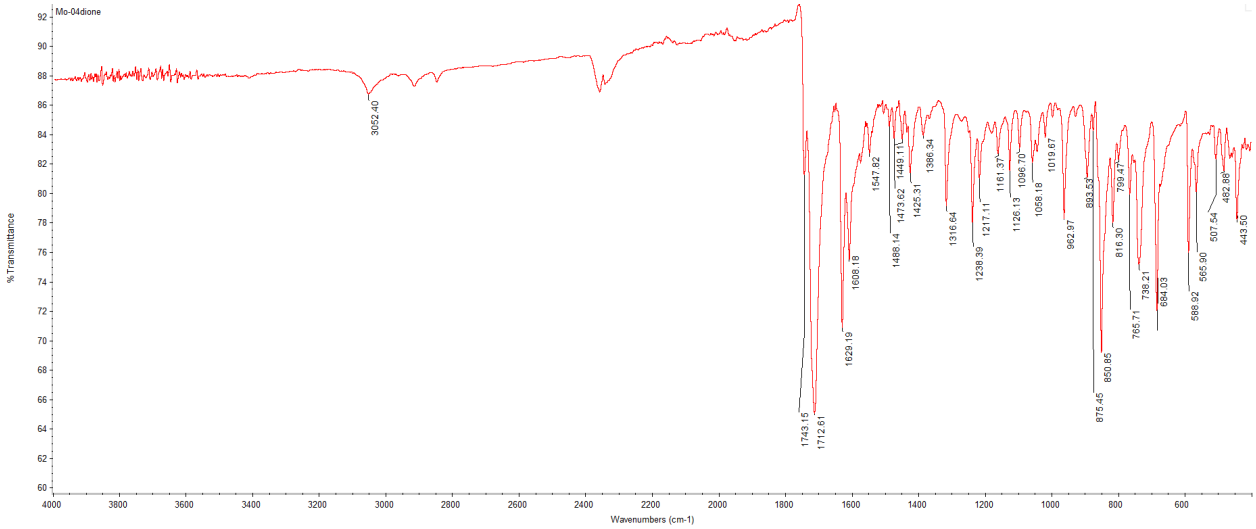


Figure S1. FTIR spectrum, neat, of **2**

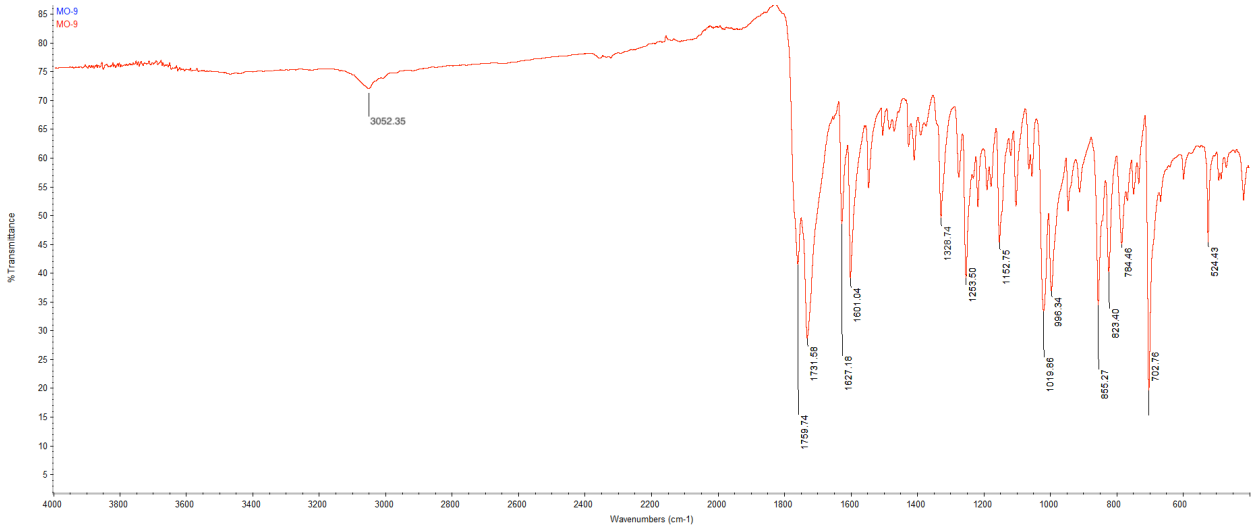


Figure S2. FTIR spectrum, neat, of **3**

NMR Spectra

(Solvent peaks referenced in red and expanded portions of the spectra bordered in black.)

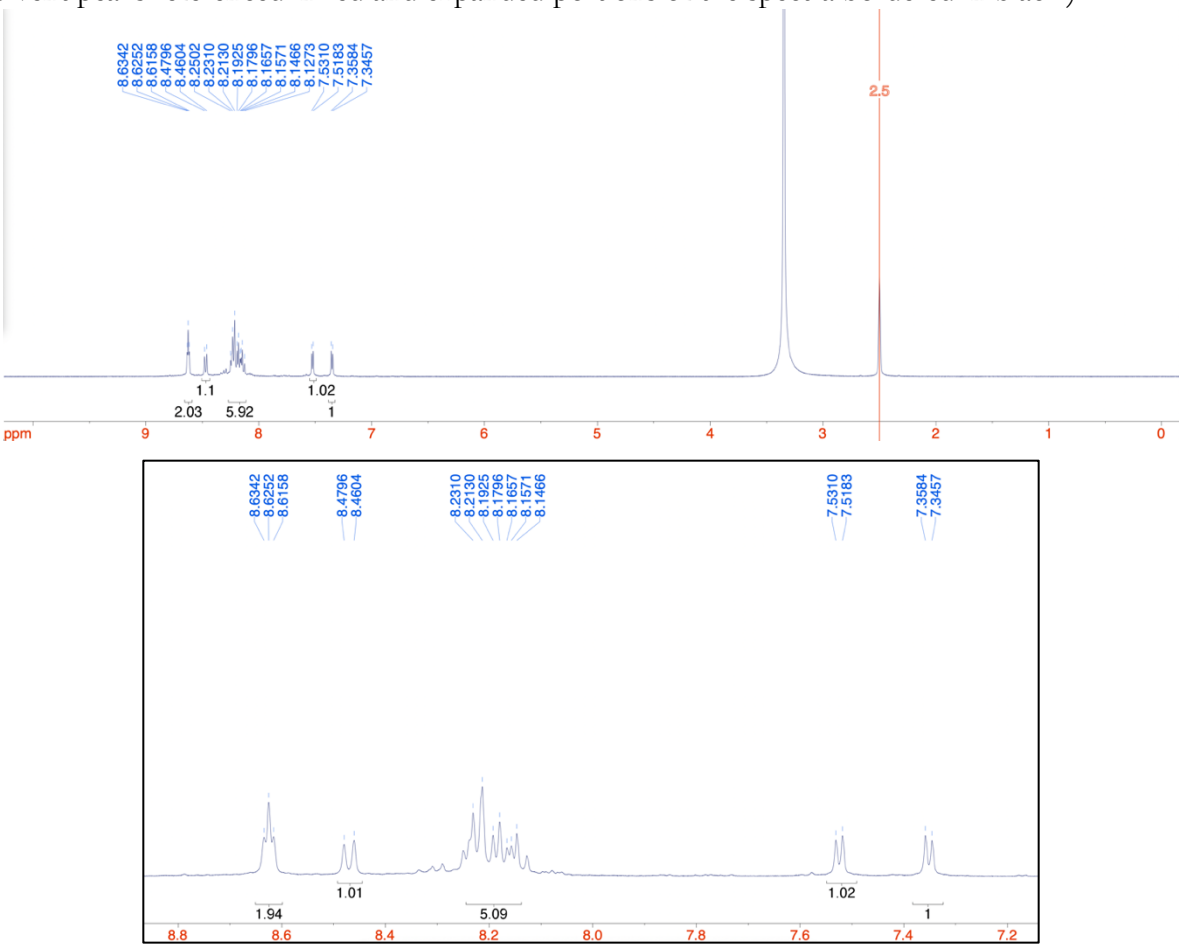


Figure S3. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of cyclopenta[cd]pyrene **1**.

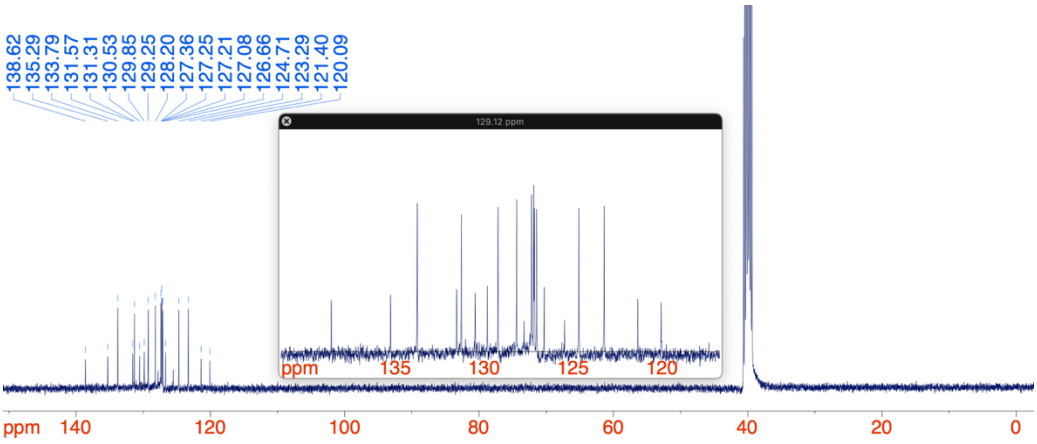


Figure S4. ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of cyclopenta[cd]pyrene **1**.

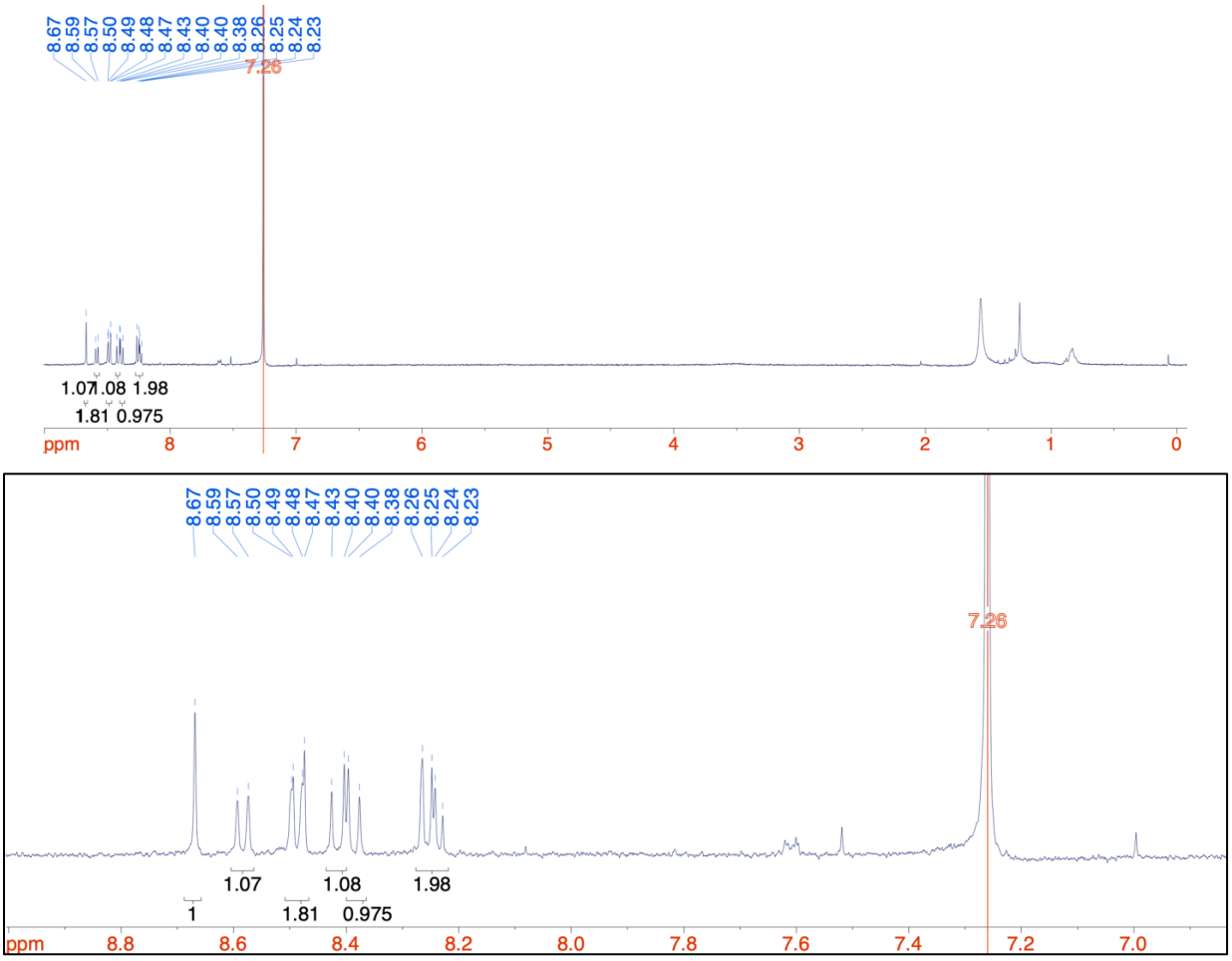


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.

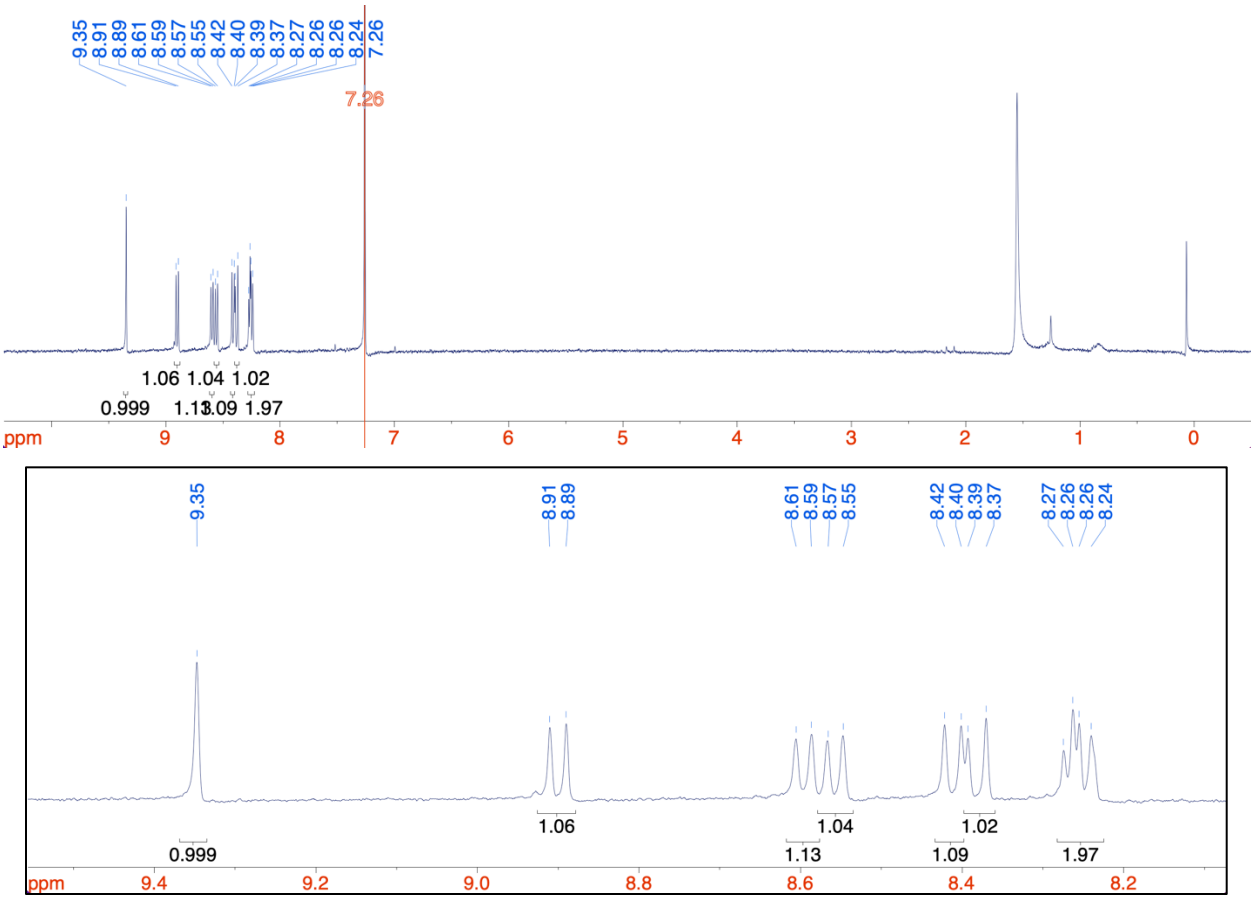


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.

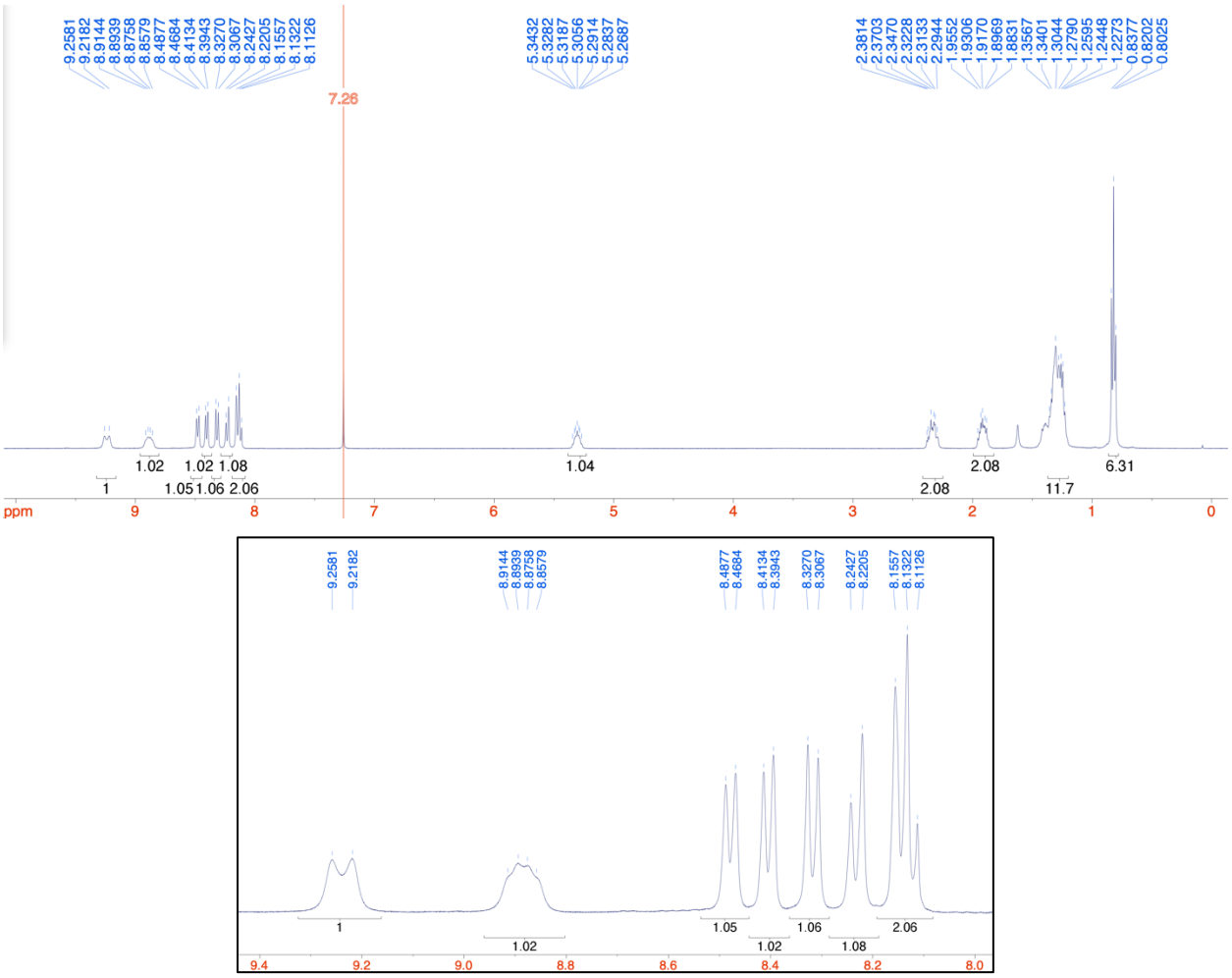


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**.

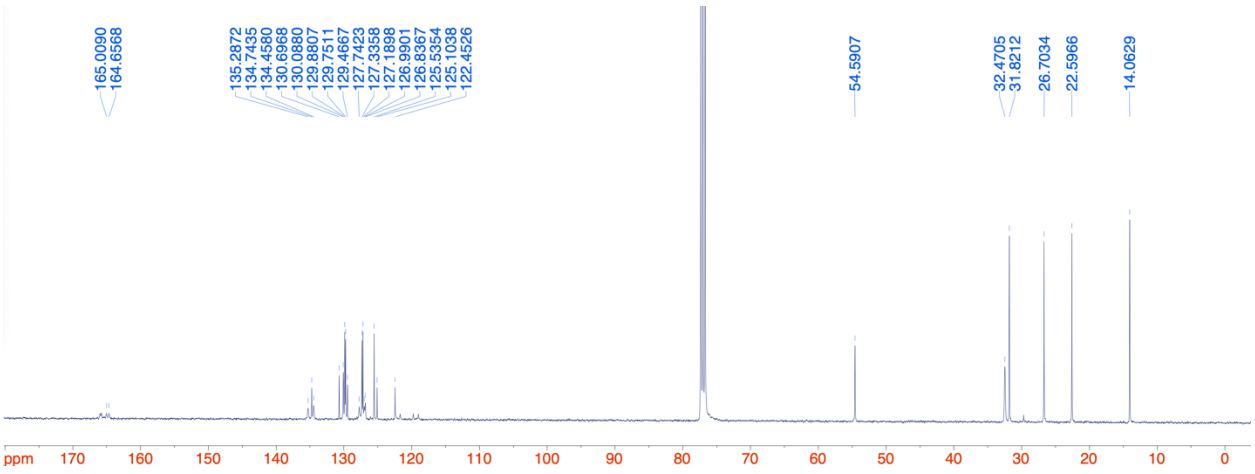


Figure S7. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4a**.

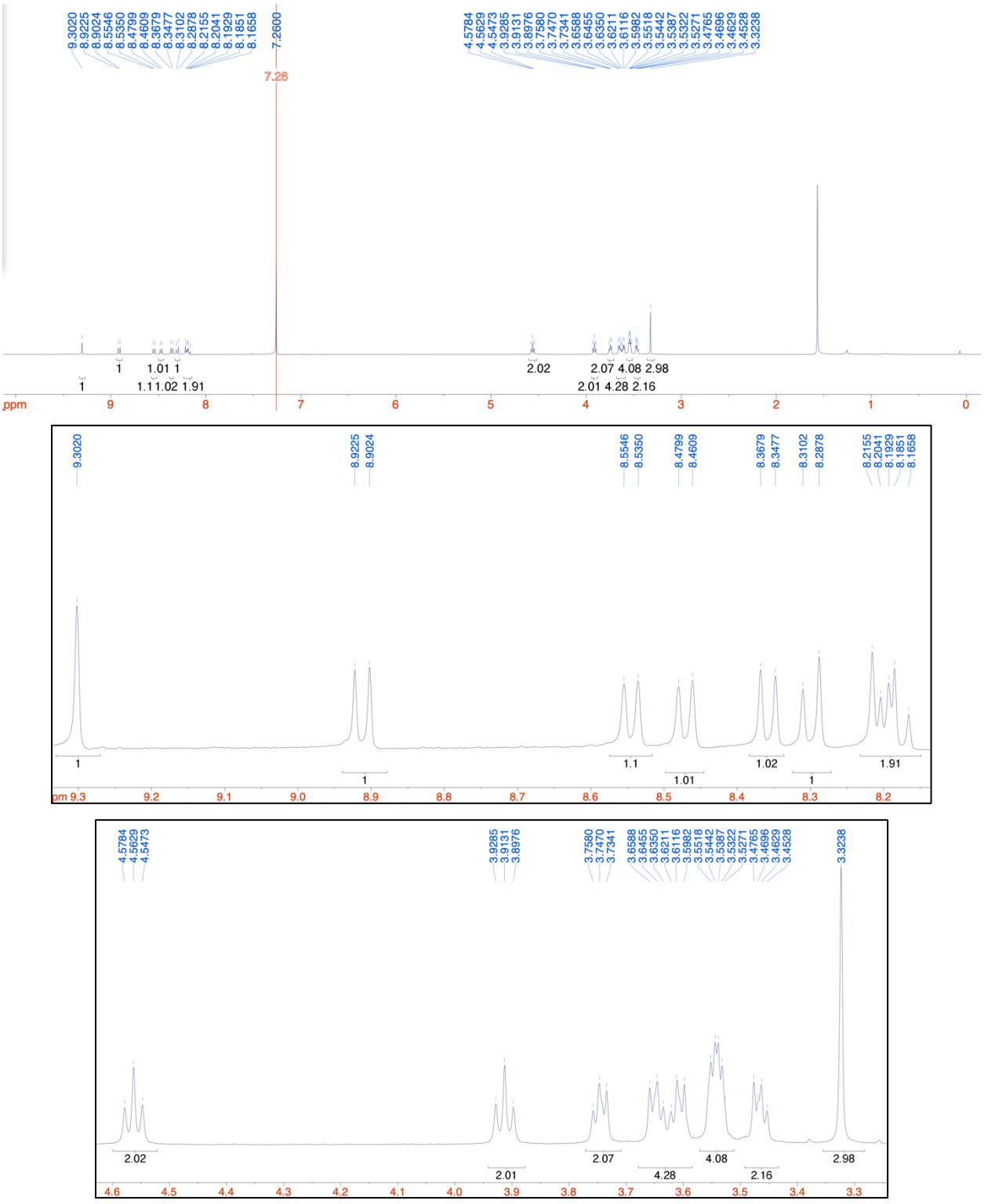


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**.

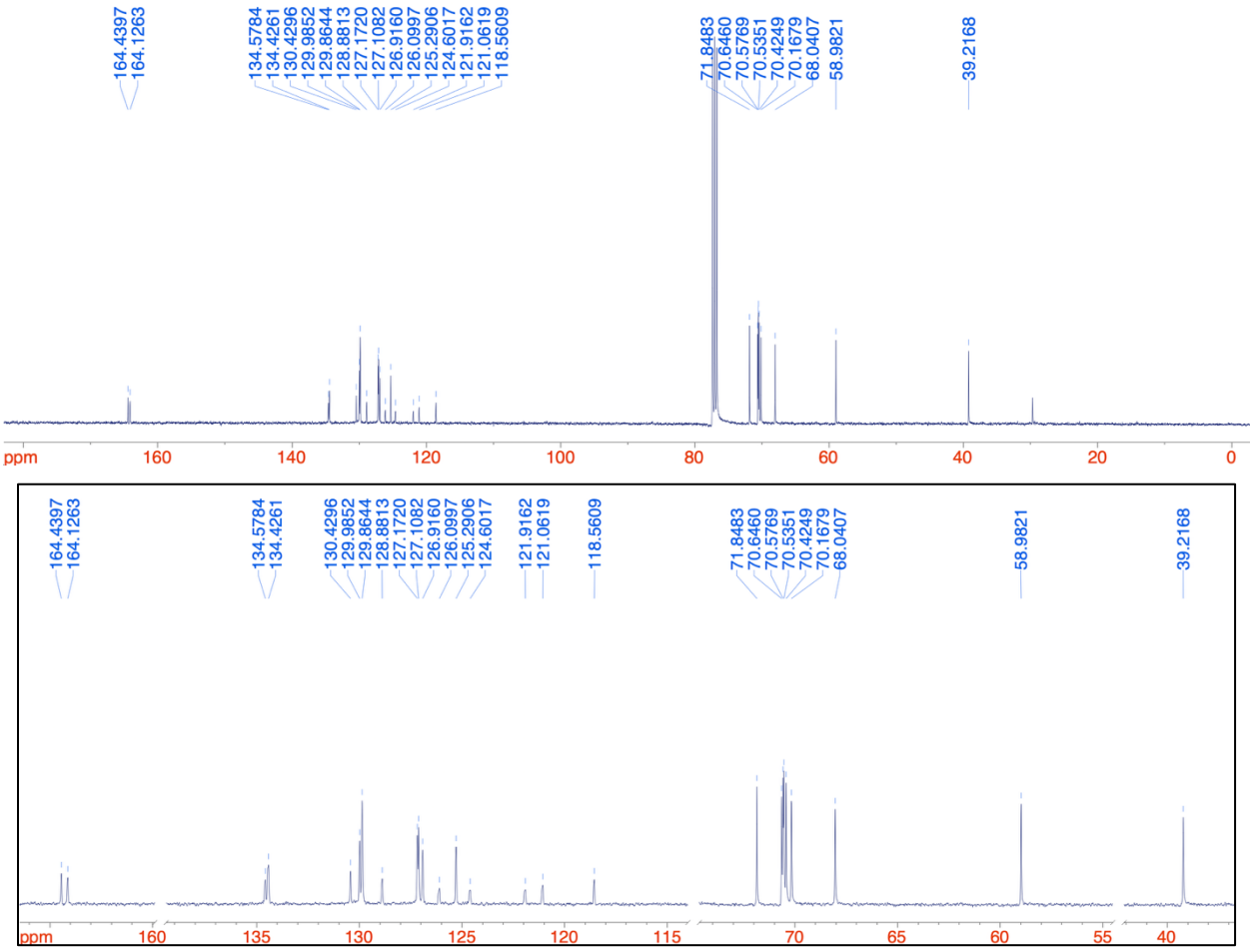


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4b**.

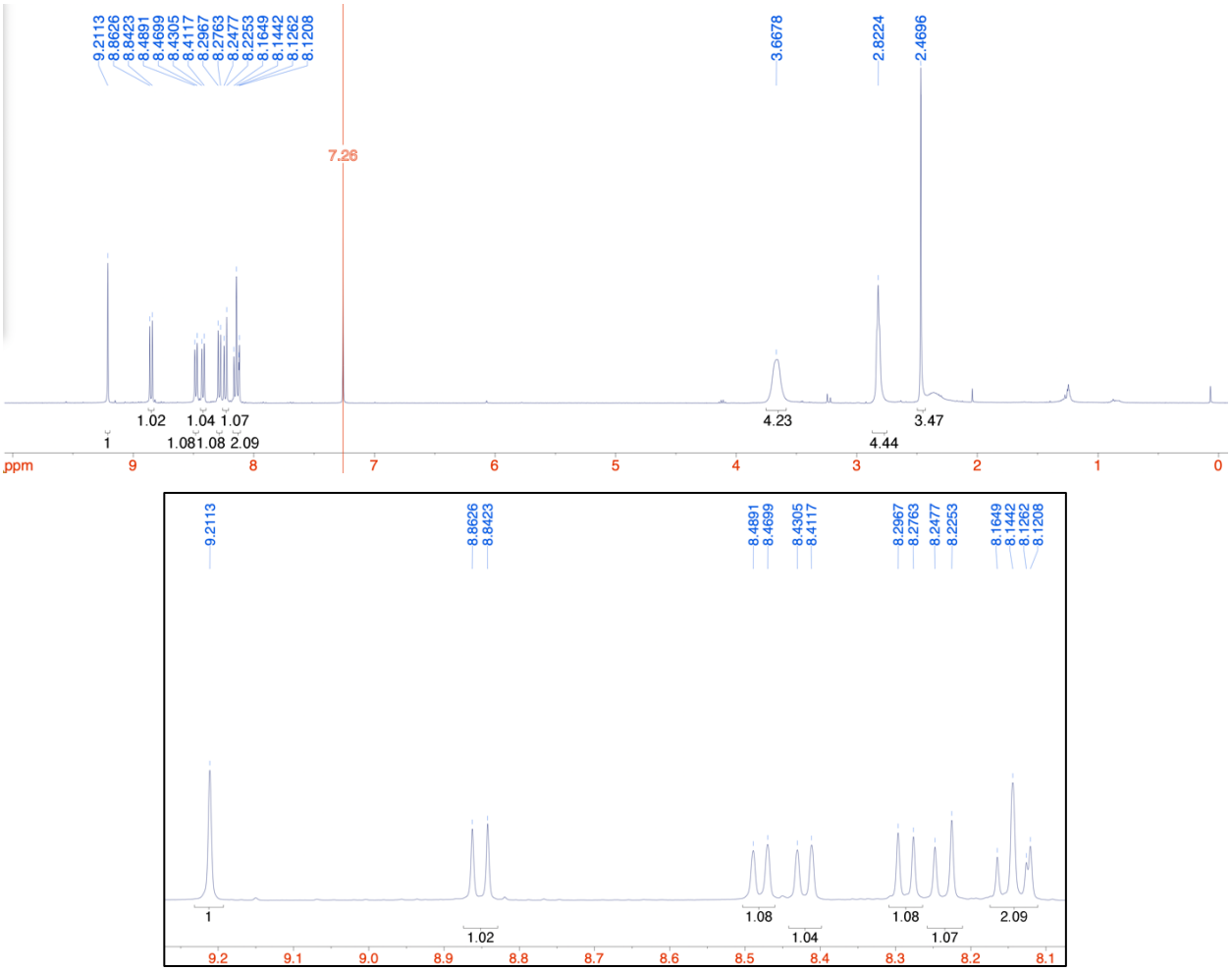


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **N-1-methylpiperazine-1,10-pyreneimide**.

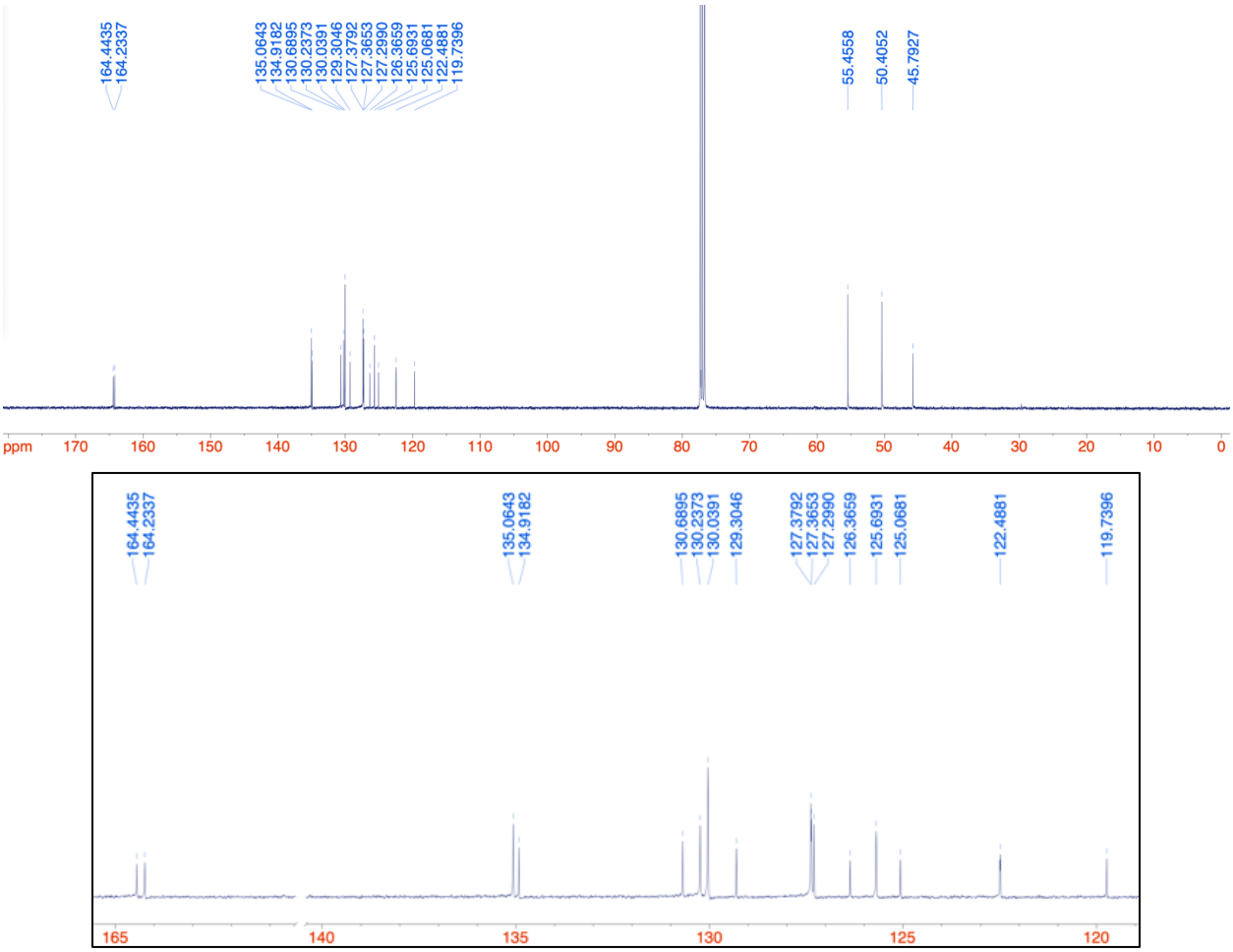


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **N-1-methylpiperazine-1,10-pyreneimide**.

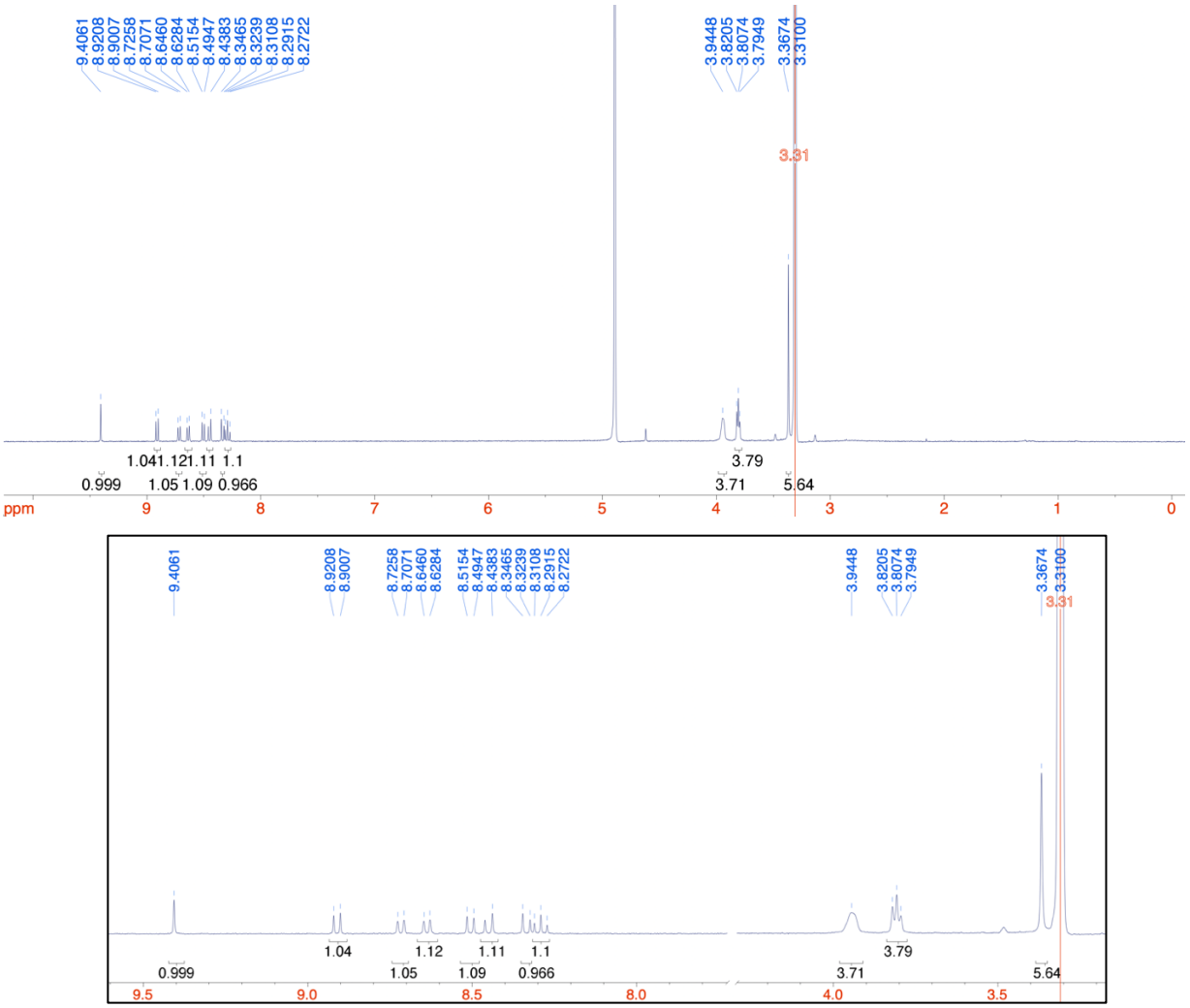


Figure S12. [1]H NMR (400 MHz, MeOD) spectrum of **4c**.

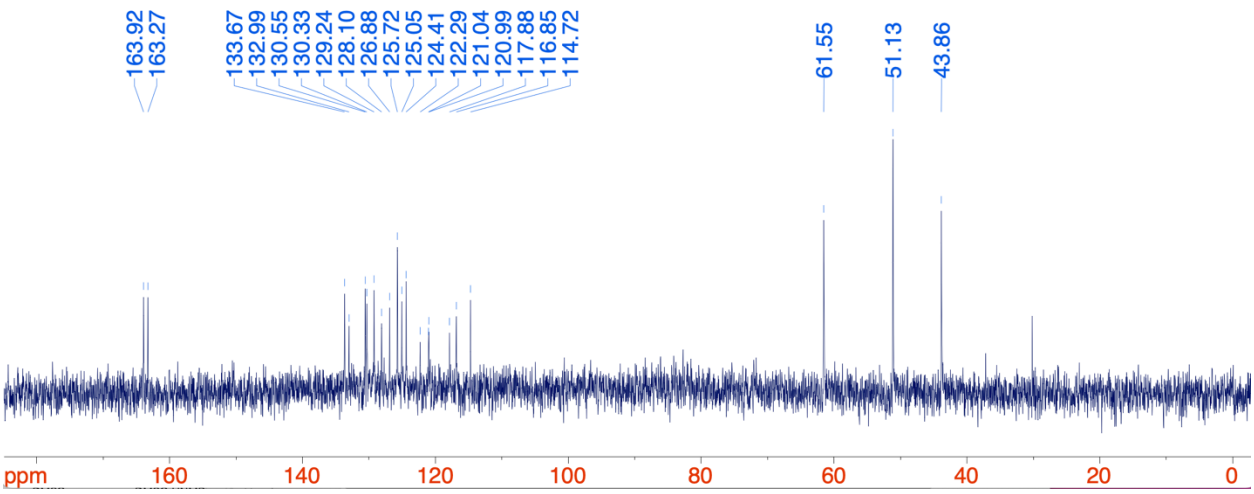


Figure S13. [13]C NMR (101 MHz, D_2O) spectrum of **4c**.

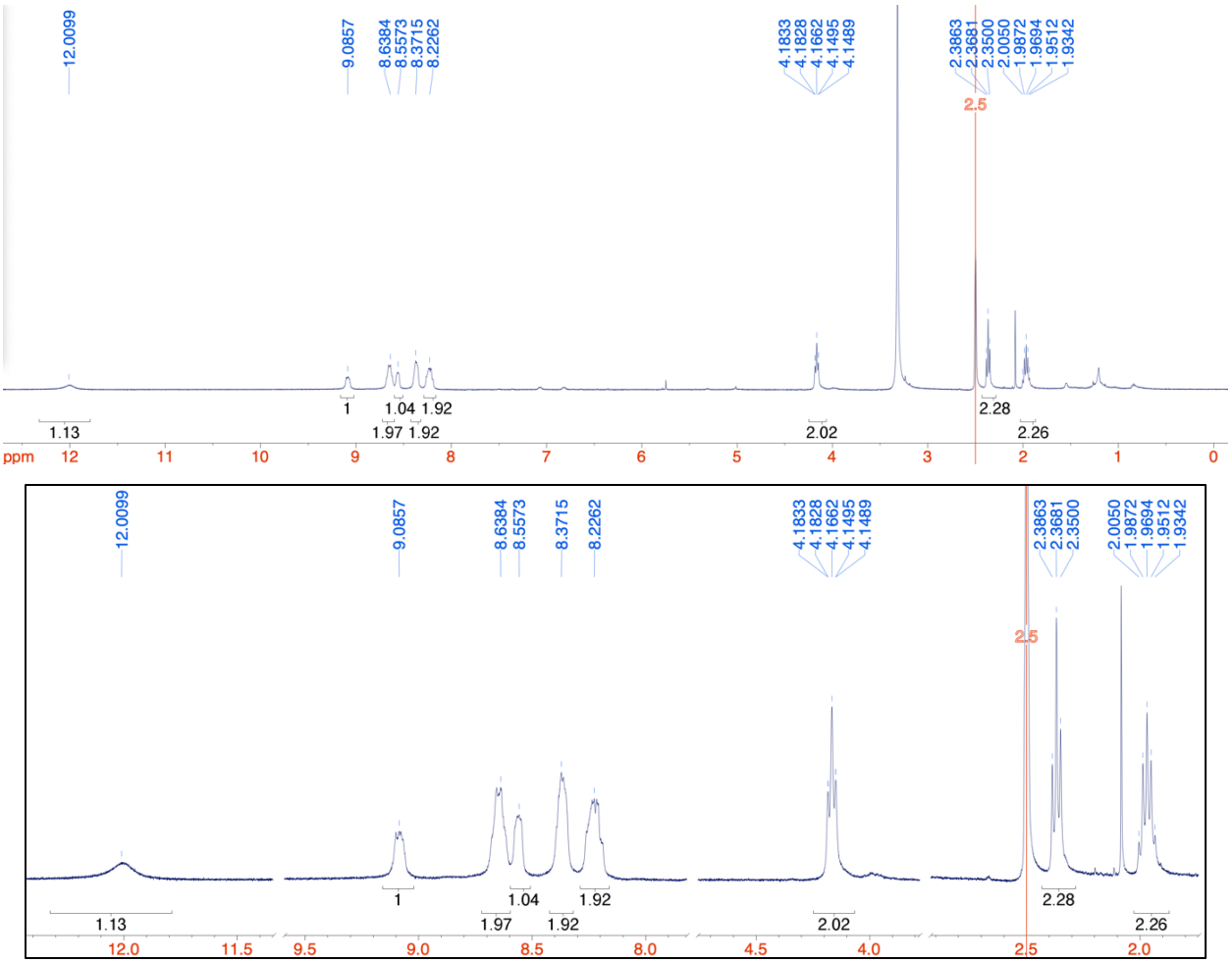


Figure S14. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **4d**.

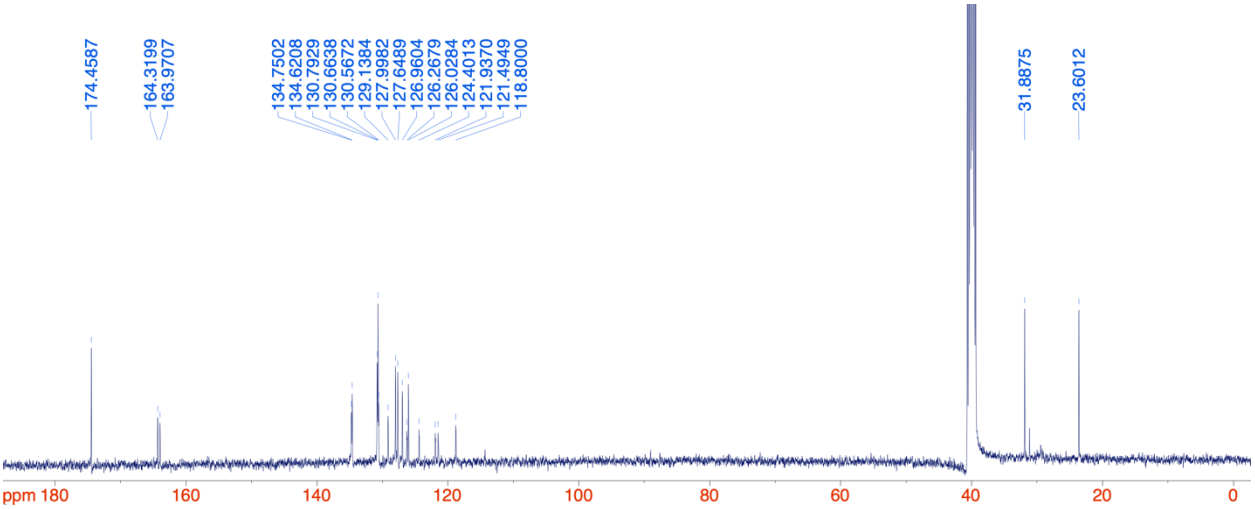


Figure S15. ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **4d**.

Table S1: Optical properties of pyrene monoimides **4a-d** and calculated HOMO/LUMO levels (B3PW91/6-31G(d)).

Compound (solvent used for measurements)	λ_{max}^{abs}	λ_{max}^{em}	λ_{max}^{em} solid	λ_{max}^{em} excimer	PLQY monomer	HOMO (eV)	LUMO (eV)	Eg (eV)
4a (DCM)	412 nm	429 nm	583 nm	562-575 nm	0.93	-6.05[a]	-2.66[a]	3.39
4b (DCM)	412 nm	430 nm	593 nm (film)	566 nm	0.94	-6.09[a]	-2.71[a]	3.38
4c (DCM)	380, 417 nm	439 nm	626 nm			-2.43	-0.23	2.20
4c (H_2O)	386, 421 nm	476 nm		625 nm	0.06			
4d (DCM)	413 nm	431 nm	601 nm		0.98	-6.11	-2.74	3.37
4d (10mM aq Et3N)	385, 419 nm	476 nm						
4d (DMSO/H2O)		445 nm		627 nm				

a) Calculated on model with truncated sidechain.

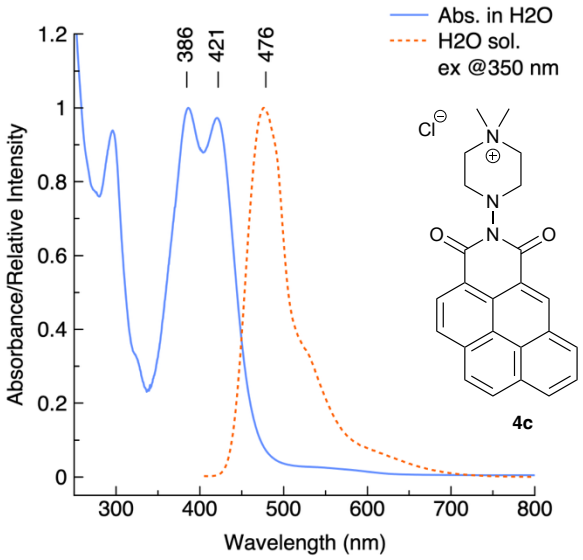


Figure S16. Normalized UV−vis absorption (solid blue) and emission spectra (dashed red) of **4c** in water.

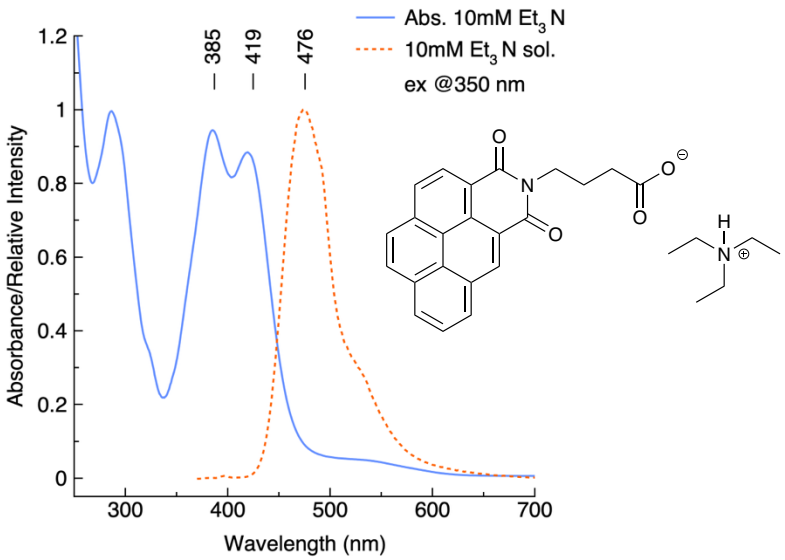


Figure S17. Normalized UV−vis absorption (solid blue) and emission spectra (dashed red) of **4d** in the presence of base in water (10mM Et_3N).

a) b)

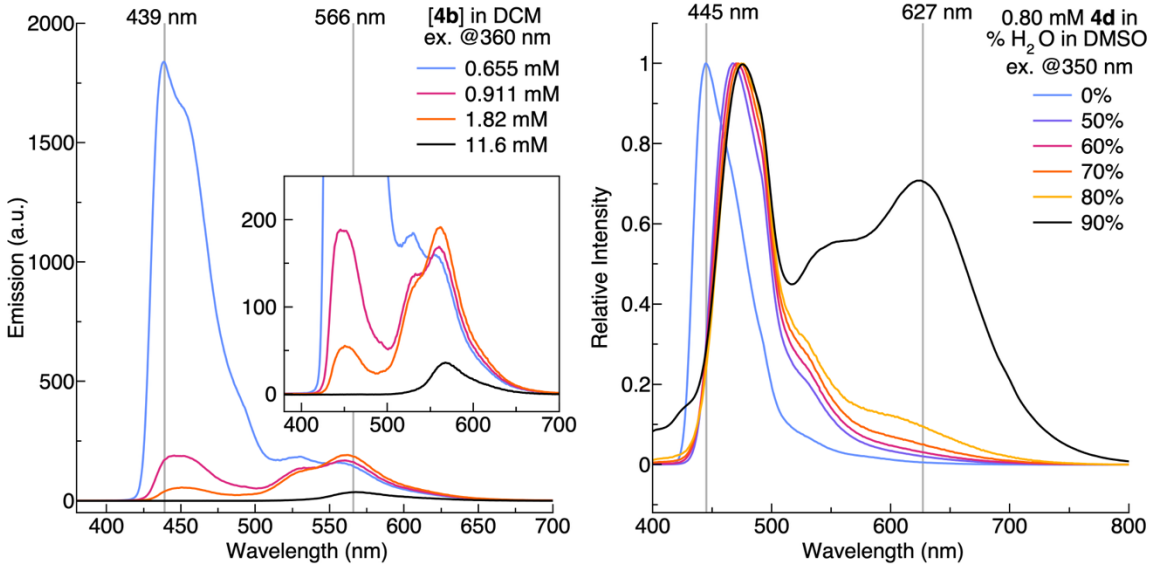


Figure S18. Excimer formation in solutions of (a) **4b** in increasing v/v fractions of water in acetonitrile and (b) 4d in increasing v/v fractions of water in dimethyl sulfoxide (normalized).

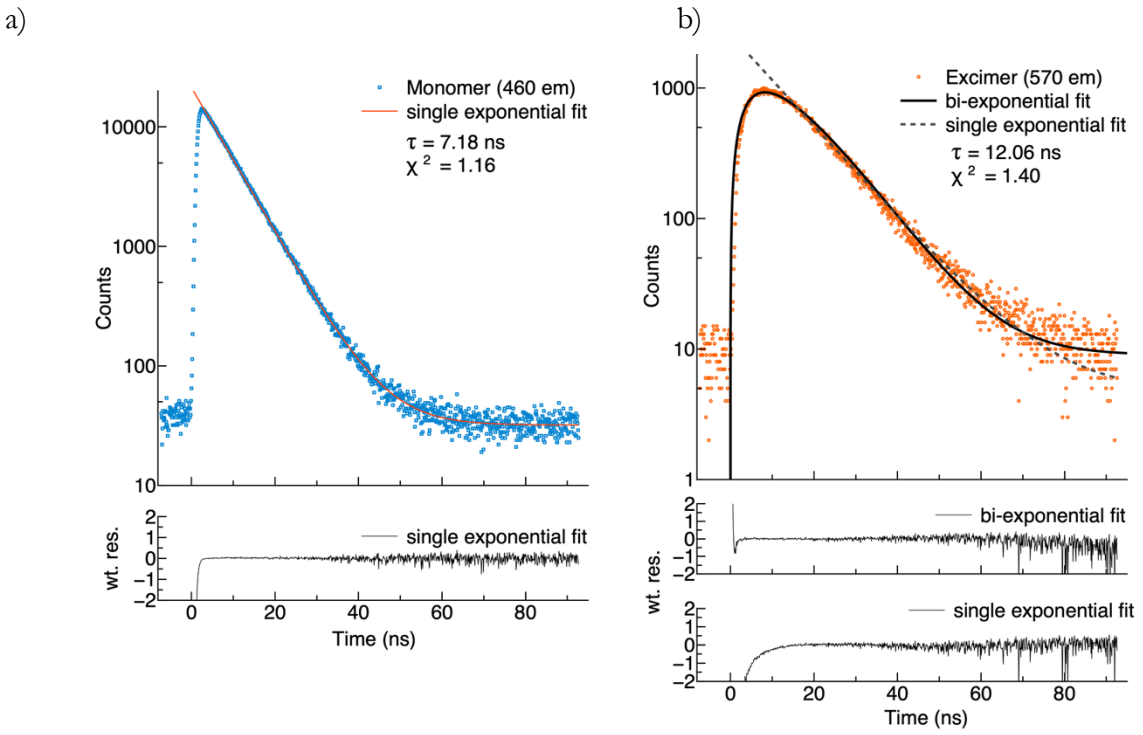


Figure S19. Fluorescence decay profiles (λex = 280 nm) of **4a** in (a) DCM at λem = 460 nm, and (b) λem = 570 nm, right. TCSPC data is overlaid with exponential fits and weighted residuals are plotted below.

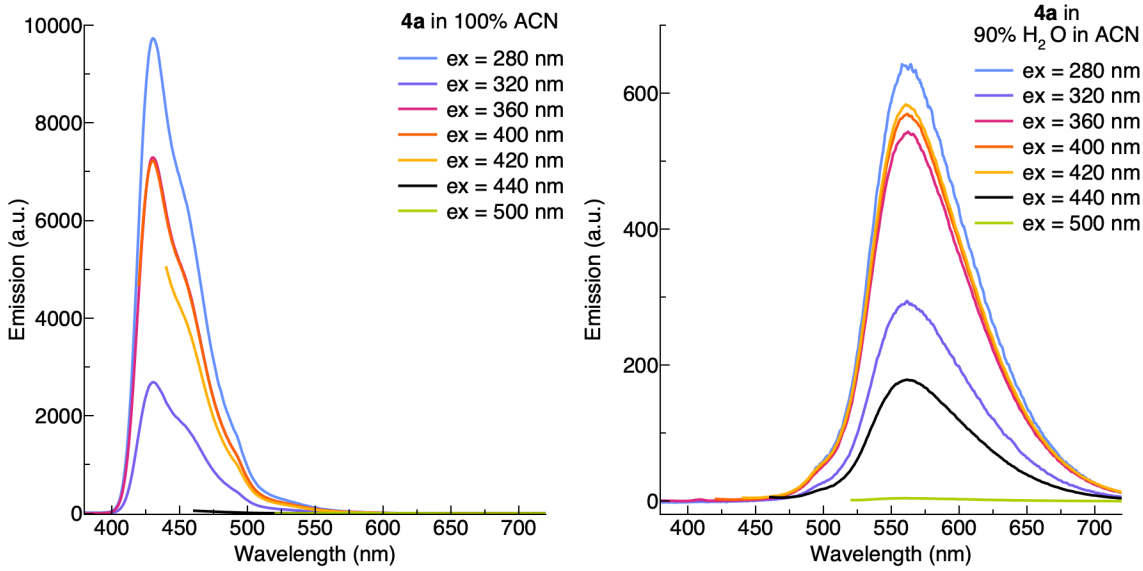


Figure S20. Emission spectra at different excitation wavelengths of **4a** in (left) ACN and (right) 90% v/v H_2O/ACN. The emission spectra are excitation wavelength independent for both monomer emission (left) and excimer emission (right).

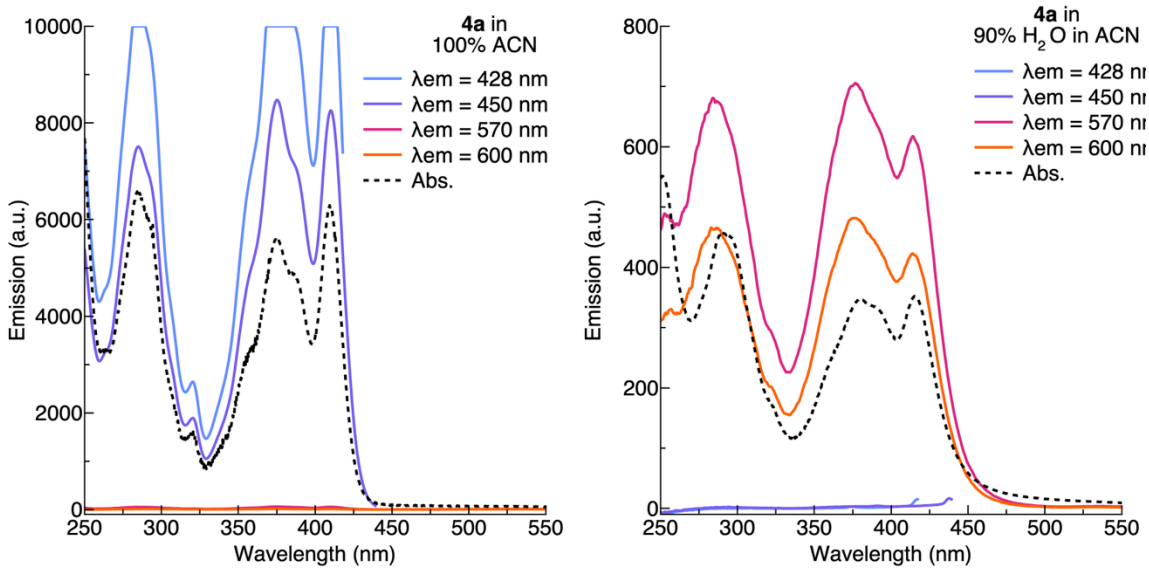


Figure S21. Excitation spectra of **4a** in (left) ACN where only monomer emission is observed and in (right) 90% v/v H_2O/ACN where only excimer emission is observed. In both, the excitation spectra agree with the absorption spectra of the respective solutions (dotted black line).

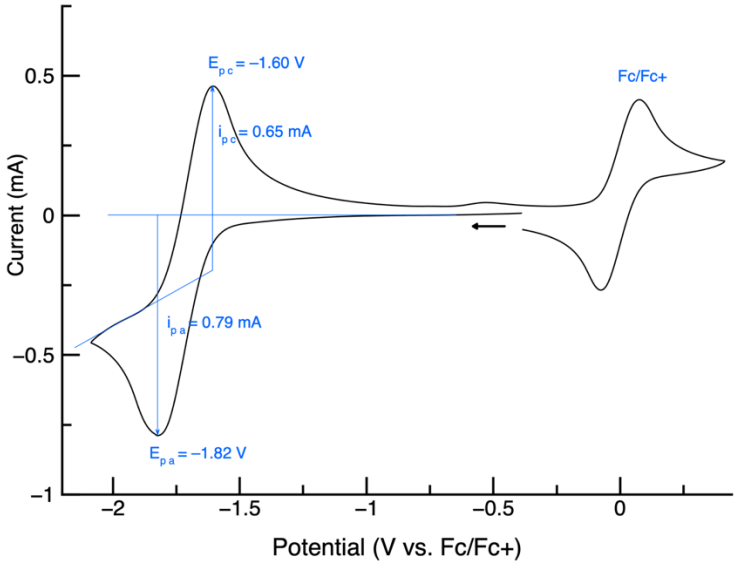
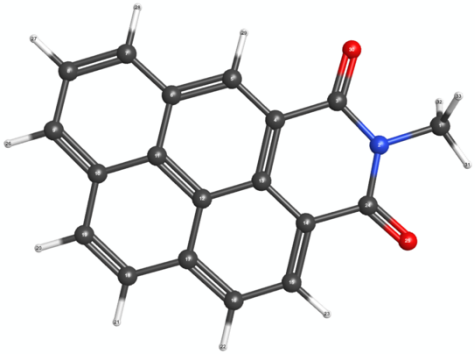
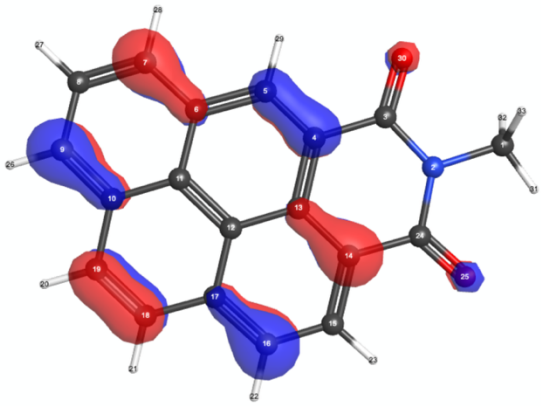


Figure S22. Cyclic voltammogram of compound **4a**. Voltammograms were recorded in 0.20 M $[NBu_4][PF_6]$ CH_2Cl_2 solutions at a scan rate of 100 mV per second and plotted using IUPAC convention. Scans start at 0V and follow the direction shown by the arrow. The potential is referenced with respect to the $E_{1/2}$ of the ferrocene/ferrocenium redox couple.

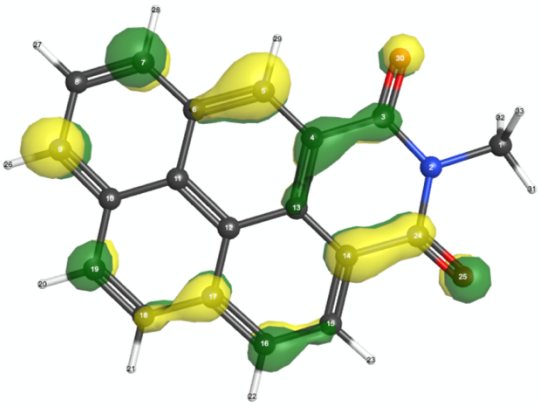


Computational data for 1,10-pyrene monoimide, R = CH_3

SCF total energy = -935.588855496 Hartree
E_g = 3.39 eV
Reorganization energy (λ) = 0.2416 eV
$\lambda_i^- = (E_C^0 - E_N^0) + (E_N^{-1} - E_C^{-1})$
$\lambda_i^- = (-935.584441924 - -935.588855496) + (-935.633110975 - -935.637576510)$
$\lambda_i^- =$ 0.008879107 hartrees



HOMO = – 6.05 eV



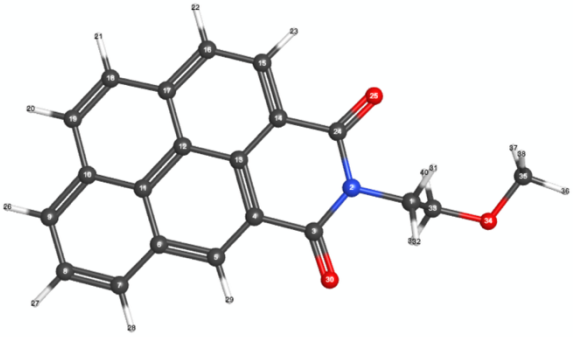
LUMO = – 2.66 eV

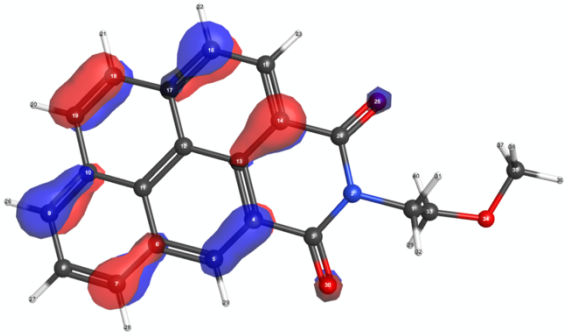
	Coordinates (Angstroms)		
Atom	X	Y	Z
1	3.197018	3.447702	0
2	2.098127	2.487188	0
3	2.46103	1.139013	0
4	1.357125	0.152376	0
5	1.64823	-1.184302	0
6	0.613769	-2.168665	0
7	0.891239	-3.545006	0
8	-0.142399	-4.476302	0
9	-1.471642	-4.059525	0
10	-1.799034	-2.695577	0
11	-0.746207	-1.737706	0
12	-1.05167	-0.350298	0
13	0	0.602554	0
14	-0.298434	1.970557	0
15	-1.631629	2.396832	0
16	-2.666584	1.474804	0
17	-2.40488	0.092455	0
18	-3.44422	-0.894265	0
19	-3.154169	-2.225202	0
20	-3.955737	-2.96026	0
21	-4.478131	-0.557529	0
22	-3.698343	1.817801	0
23	-1.82818	3.464358	0
24	0.782889	2.977804	0
25	0.558942	4.179086	0
26	-2.27167	-4.796331	0
27	0.088694	-5.537992	0
28	1.926675	-3.876517	0
29	2.691226	-1.490064	0
30	3.640318	0.818283	0
31	2.762706	4.44555	0
32	3.819594	3.299121	0.885836
33	3.819594	3.299121	-0.885836

Computational data for 1,10-pyrene monoimide, R = $CH_2CH_2OCH_3$

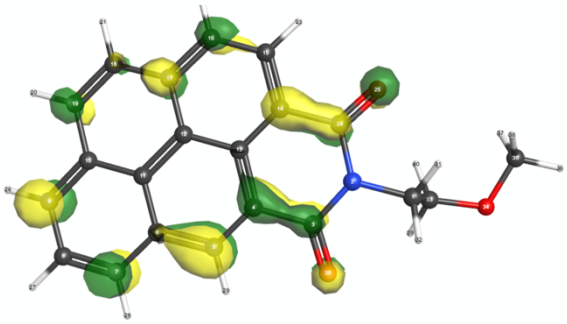
SCF total energy = – 1089.35752515 Hartree

E_g = 3.38 eV





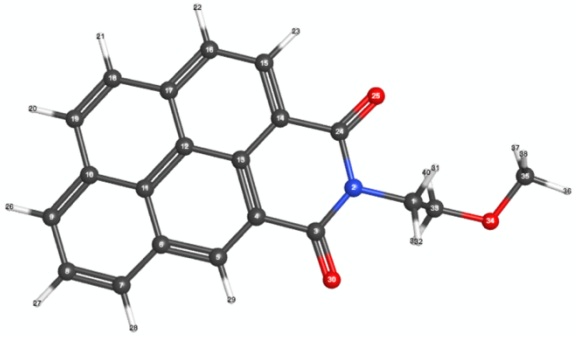
HOMO = – 6.09 eV



LUMO = – 2.71 eV

	Coordinates (Angstroms)		
Atom	X	Y	Z
1	-3.726227	-0.511069	-0.584453
2	-2.303167	-0.202561	-0.430104
3	-1.415372	-1.281823	-0.356382
4	0.021041	-0.947984	-0.218094
5	0.942111	-1.958392	-0.162904
6	2.336992	-1.684466	-0.029374
7	3.297532	-2.707016	0.026931
8	4.648837	-2.403238	0.158488
9	5.072878	-1.078557	0.236906
10	4.15108	-0.022582	0.185272
11	2.767179	-0.326626	0.050499
12	1.813508	0.724745	-0.004212
13	0.43453	0.418665	-0.13989
14	-0.506772	1.453703	-0.193532
15	-0.089107	2.787193	-0.112335
16	1.255387	3.097322	0.018738
17	2.229971	2.084107	0.075486
18	3.629609	2.360485	0.210861
19	4.546229	1.354146	0.263059
20	5.604524	1.582641	0.36595
21	3.949407	3.397959	0.271659
22	1.568871	4.136627	0.079603
23	-0.845193	3.564885	-0.155751
24	-1.944997	1.151141	-0.333394
25	-2.801967	2.022475	-0.369749
26	6.131801	-0.852707	0.339771
27	5.380086	-3.205748	0.200579
28	2.972548	-3.742737	-0.033547
29	0.591988	-2.985528	-0.223292
30	-1.823015	-2.432536	-0.409233
31	-4.174834	0.316865	-1.134629
32	-3.807282	-1.431668	-1.163614
33	-4.414071	-0.698571	0.772564
34	-5.78637	-0.98563	0.627426
35	-6.59188	0.155611	0.439247
36	-7.627004	-0.193326	0.391605
37	-6.491833	0.862428	1.277977
38	-6.361112	0.693259	-0.492195
39	-3.968879	-1.557849	1.284023
40	-4.260841	0.1976	1.394157

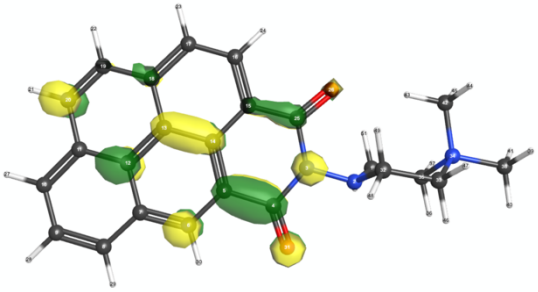
Computational data for 1,10-pyrene monoimide,



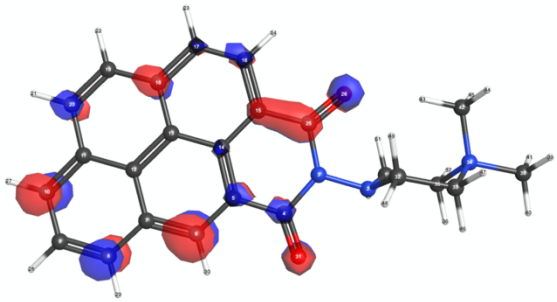
R = 

SCF total energy = – 1089.35752515 Hartree

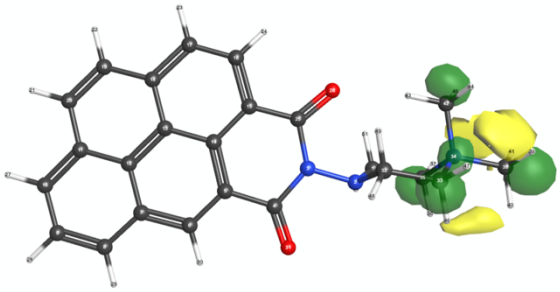
E_g = 2.20 eV



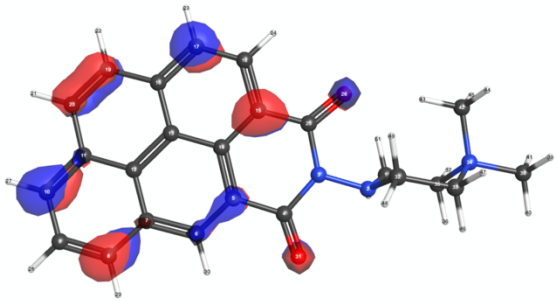
LUMO +1 = 0.0071 eV



HOMO = –2.43 eV



LUMO = – 0.23 eV



HOMO -1 = – 4.62 eV

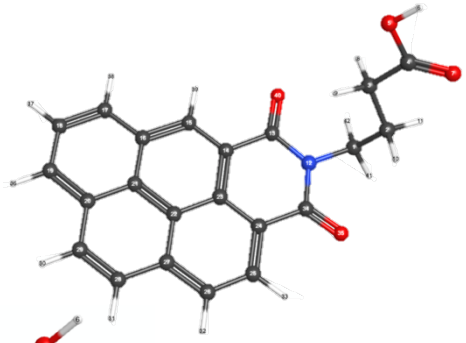
	Coordinates (Angstroms)		
Atom	X	Y	Z
1	-3.726227	-0.511069	-0.584453
2	-2.303167	-0.202561	-0.430104
3	-1.415372	-1.281823	-0.356382
4	0.021041	-0.947984	-0.218094
5	0.942111	-1.958392	-0.162904

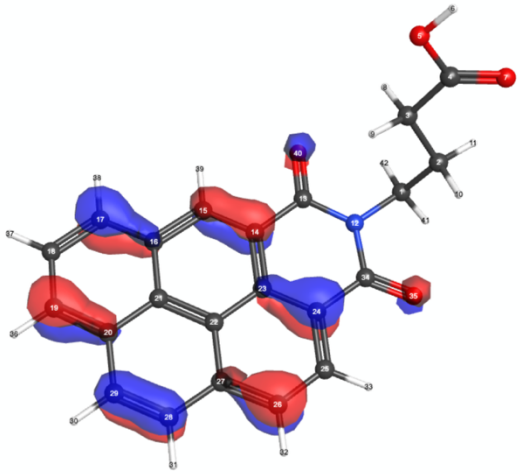
6	2.336992	-1.684466	-0.029374
7	3.297532	-2.707016	0.026931
8	4.648837	-2.403238	0.158488
9	5.072878	-1.078557	0.236906
10	4.15108	-0.022582	0.185272
11	2.767179	-0.326626	0.050499
12	1.813508	0.724745	-0.004212
13	0.43453	0.418665	-0.13989
14	-0.506772	1.453703	-0.193532
15	-0.089107	2.787193	-0.112335
16	1.255387	3.097322	0.018738
17	2.229971	2.084107	0.075486
18	3.629609	2.360485	0.210861
19	4.546229	1.354146	0.263059
20	5.604524	1.582641	0.36595
21	3.949407	3.397959	0.271659
22	1.568871	4.136627	0.079603
23	-0.845193	3.564885	-0.155751
24	-1.944997	1.151141	-0.333394
25	-2.801967	2.022475	-0.369749
26	6.131801	-0.852707	0.339771
27	5.380086	-3.205748	0.200579
28	2.972548	-3.742737	-0.033547
29	0.591988	-2.985528	-0.223292
30	-1.823015	-2.432536	-0.409233
31	-4.174834	0.316865	-1.134629
32	-3.807282	-1.431668	-1.163614
33	-4.414071	-0.698571	0.772564
34	-5.78637	-0.98563	0.627426
35	-6.59188	0.155611	0.439247
36	-7.627004	-0.193326	0.391605
37	-6.491833	0.862428	1.277977
38	-6.361112	0.693259	-0.492195
39	-3.968879	-1.557849	1.284023
40	-4.260841	0.1976	1.394157

Computational data for 1,10-pyrene monoimide, R = $CH_2CH_2CH_2COOH$

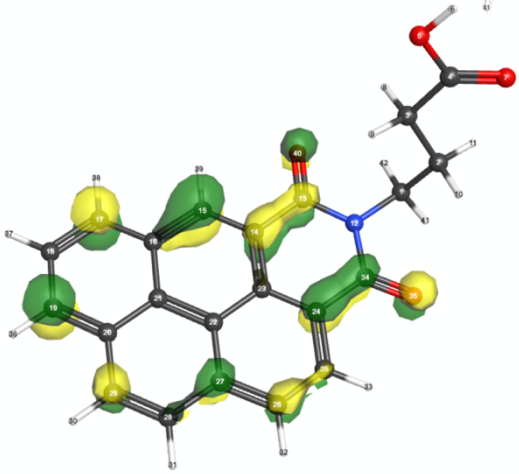
SCF total energy = –1202.68505727 Hartree

E_g = 3.37 eV





HOMO = – 6.11 eV



LUMO = – 2.74 eV

	Coordinates (Angstroms)		
Atom	X	Y	Z
1	-3.214212	0.512918	-1.612545
2	-4.247783	0.429843	-0.490574
3	-4.156606	-0.843013	0.344123
4	-5.294471	-0.970456	1.325312
5	-5.096341	-1.99728	2.18428
6	-5.881788	-2.015141	2.759764
7	-6.284146	-0.275015	1.367422
8	-4.162463	-1.737522	-0.292673
9	-3.216824	-0.898079	0.906118
10	-4.157491	1.310856	0.153176
11	-5.242408	0.488115	-0.947635
12	-1.822109	0.52651	-1.140541
13	-1.09792	-0.668639	-1.199434
14	0.313616	-0.610272	-0.753303
15	1.074039	-1.747651	-0.785022
16	2.437939	-1.740688	-0.362898
17	3.234372	-2.896762	-0.389086
18	4.560054	-2.853344	0.03072
19	5.120848	-1.661637	0.484807
20	4.365387	-0.480657	0.529567
21	3.008566	-0.518396	0.101354
22	2.222149	0.663897	0.13647
23	0.869945	0.623433	-0.291787
24	0.093935	1.787893	-0.259915
25	0.649542	2.989782	0.193901
26	1.969061	3.040425	0.615173
27	2.779736	1.890545	0.596863
28	4.1482	1.898797	1.022325
29	4.904604	0.766332	0.989896
30	5.941655	0.791394	1.316486
31	4.575692	2.834485	1.374513
32	2.390656	3.979166	0.966075
33	0.019872	3.873963	0.205019
34	-1.312995	1.760855	-0.706565
35	-2.023117	2.755627	-0.709125
36	6.158277	-1.639423	0.810606
37	5.163623	-3.756407	0.004451
38	2.802207	-3.82974	-0.742333
39	0.618984	-2.668302	-1.140633
40	-1.615933	-1.702603	-1.598004
41	-3.366081	1.43668	-2.174844
42	-3.300899	-0.340677	-2.287182

High Resolution Mass Spectroscopy Data

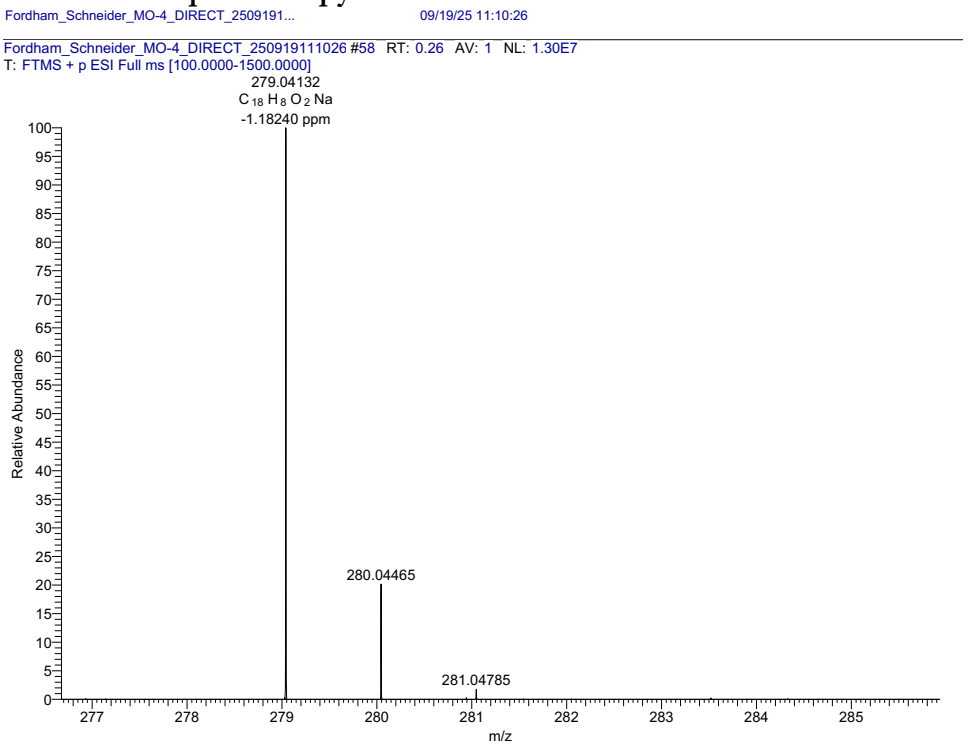


Figure S17. HRMS trace for compound **2**.

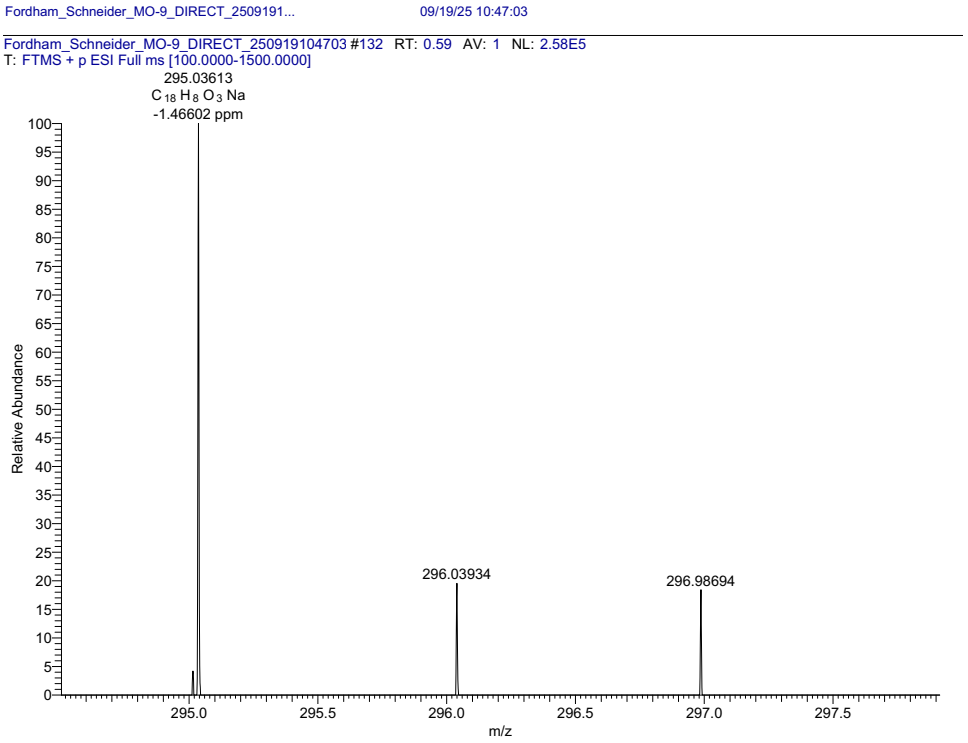


Figure S18. HRMS trace for compound **3**.

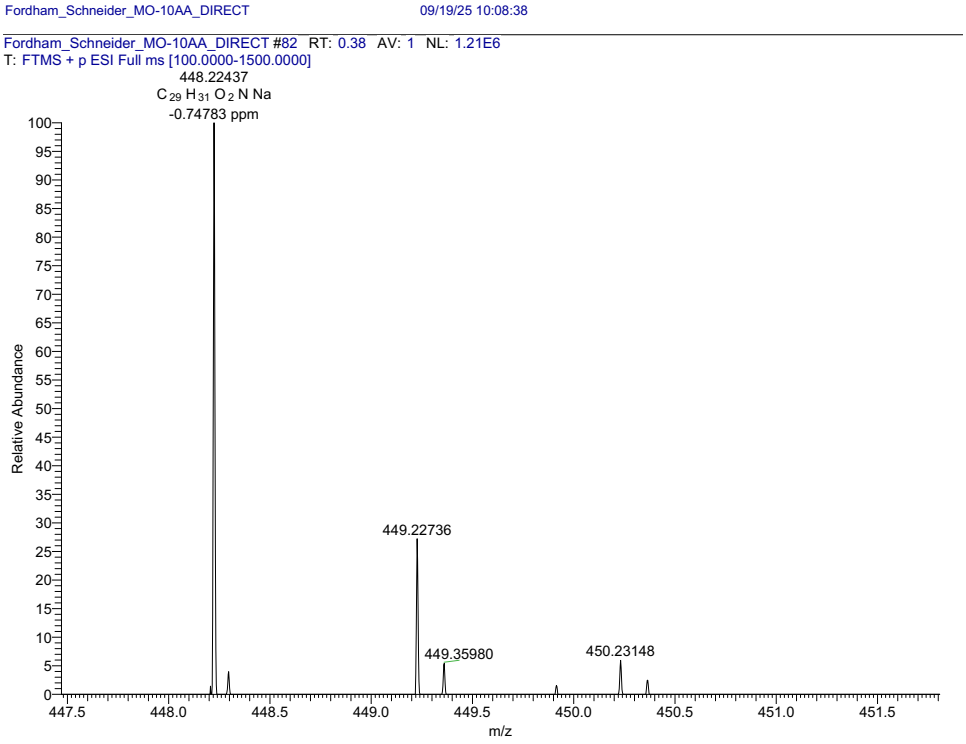


Figure S19. HRMS trace for compound **4a**.

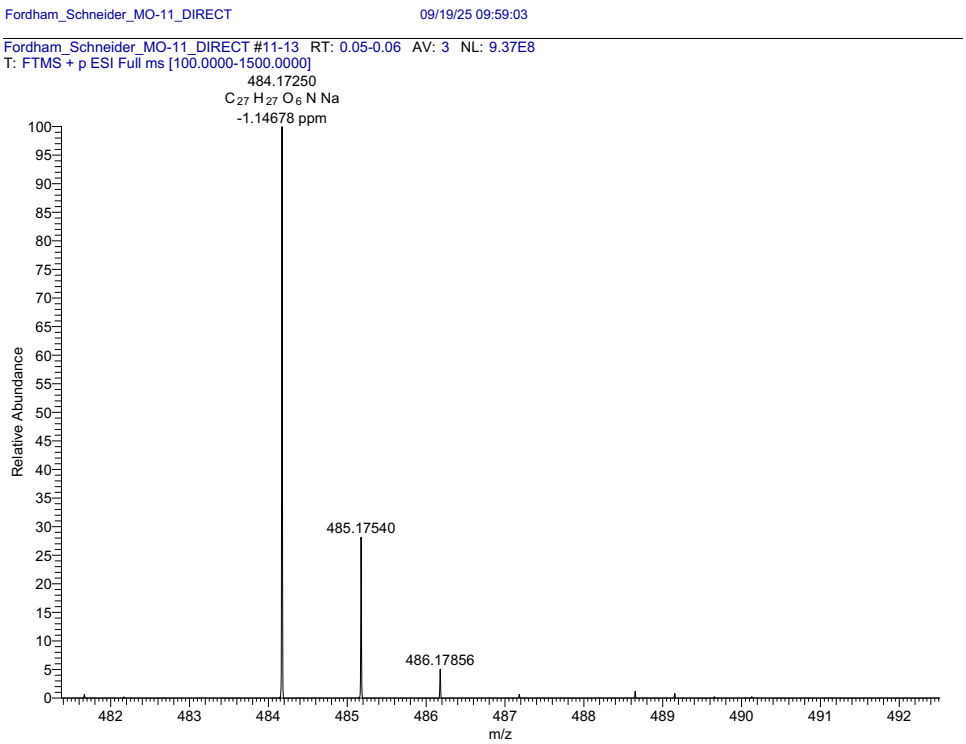


Figure S20. HRMS trace for compound **4b**.

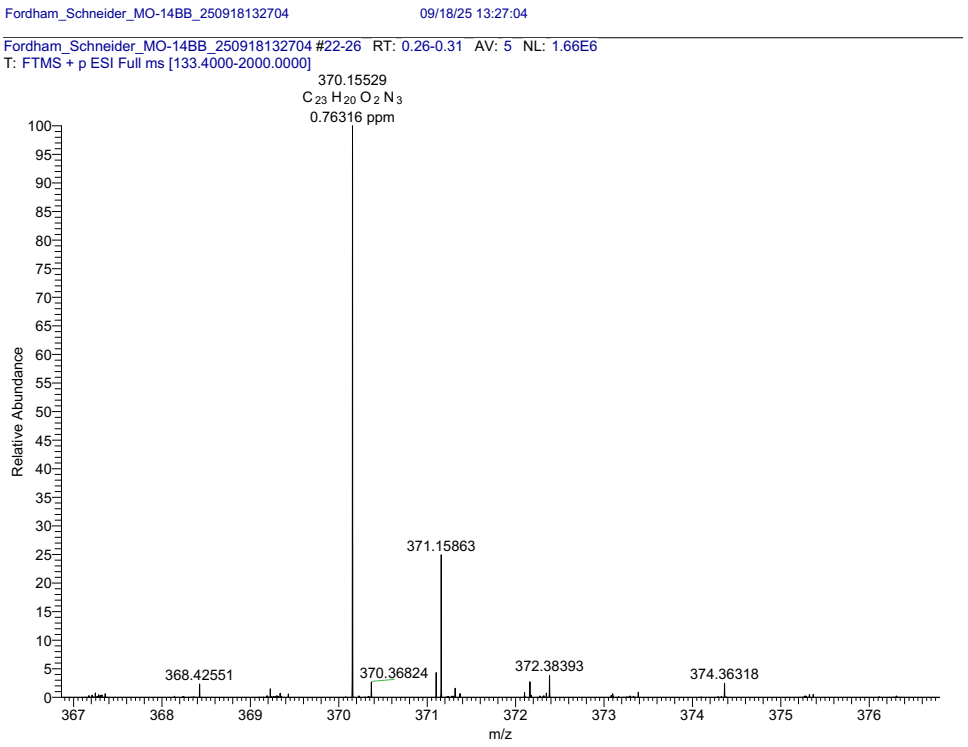


Figure S21. HRMS trace for compound **N-1-methylpiperazine-1,10-pyreneimide**.

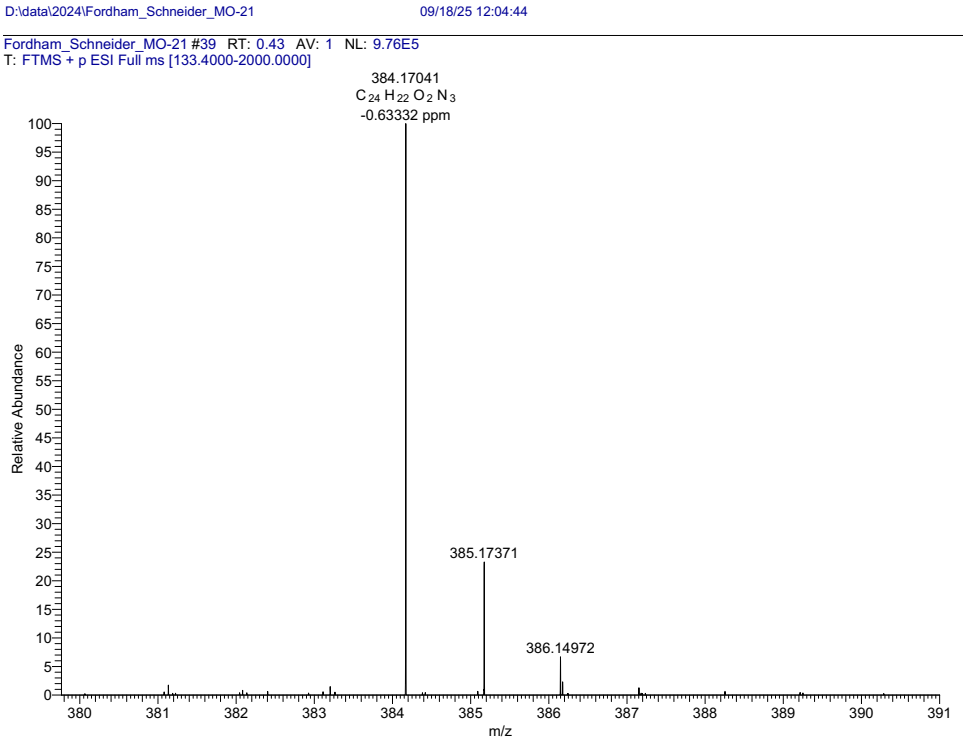


Figure S22. HRMS trace for compound **4c**.

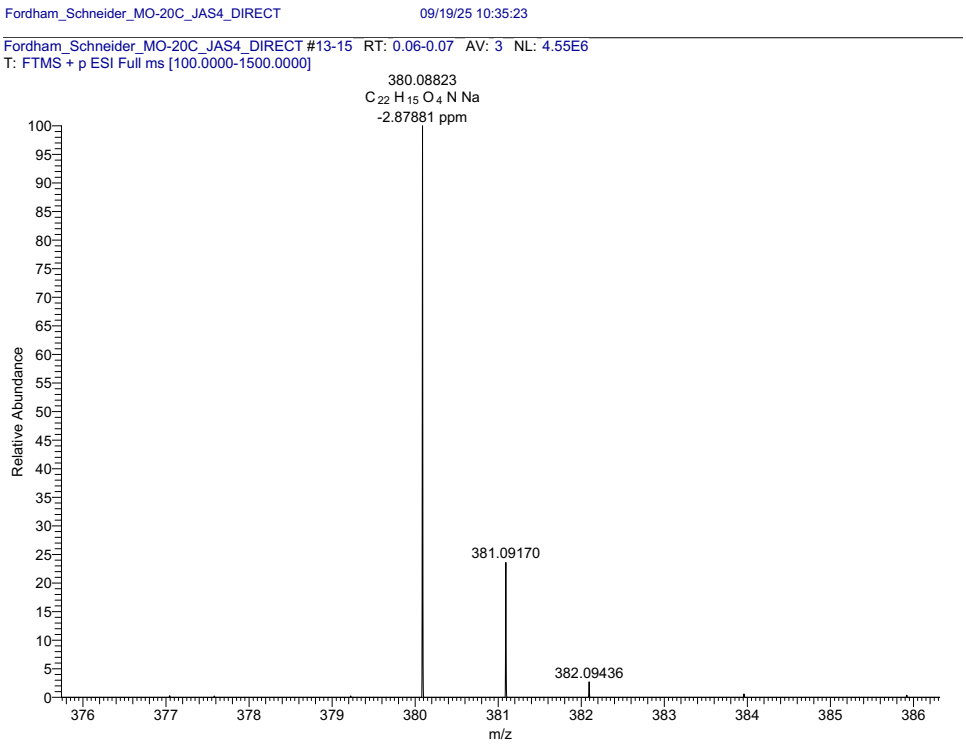


Figure S23. HRMS trace for compound **4d**.