Supplementary Information

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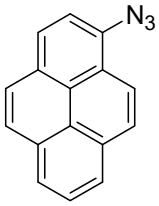
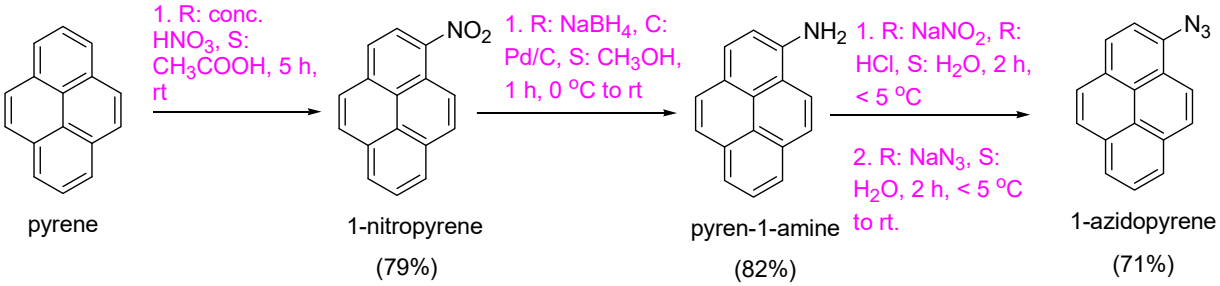
Synthesis of Azido Derivatives: Experimental and Methods Section

All reagent-grade organic solvents were purchased from TCI America or Sigma-Aldrich and used as received unless otherwise specified. Spectroscopic-grade solvents were employed without further purification. When anhydrous conditions were required, solvents were freshly distilled over calcium hydride (CaH_2) and stored under an argon atmosphere over activated 3 Å molecular sieves to ensure maximum dryness. Reactions involving dry solvents were conducted in flame-dried glassware, with reagents and solvents transferred under argon. Thin-layer chromatography (TLC) was performed on Merck pre-coated silica gel GF254 glass plates (5 × 2.5 cm), with visualization achieved using UV light (254 nm) or potassium permanganate ($KMnO_4$) staining. Column chromatography was conducted using Sigma-Aldrich Basic Alumina (activated) with optimized eluent systems for each reaction. Reagents, including 9-anthraldehyde (99%), sodium borohydride ($NaBH_4$), 1-pyrenecarboxaldehyde, 2-anthraquinone carboxylic acid, 2-aminoanthraquinone, zinc granules, thionyl chloride ($SOCl_2$), 5% Pd/C, and sodium azide (NaN_3), were sourced from reputable suppliers such as TCI America and Santa Cruz Biotechnology and used without additional purification. NMR spectra (^1H and ^{13}C) were recorded on a JEOL 400 MHz spectrometer at 298 K. Peak splitting patterns are denoted as follows: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet. Proton chemical shifts (δ) are reported in parts per million (ppm) relative to DMSO-d_6 (δ 2.50 ppm), with coupling constants (J) in hertz (Hz). Carbon chemical shifts are referenced to DMSO-d_6 (δ 39.52 ppm). For compounds with limited solubility, a 20% (v/v) DMSO-d_6/CCl_4 mixture was used to enhance solubility and ensure consistent NMR measurements.

Synthesis of **1-Azidopyrene**



For the synthesis of this compound, the following reaction scheme S1 was adopted

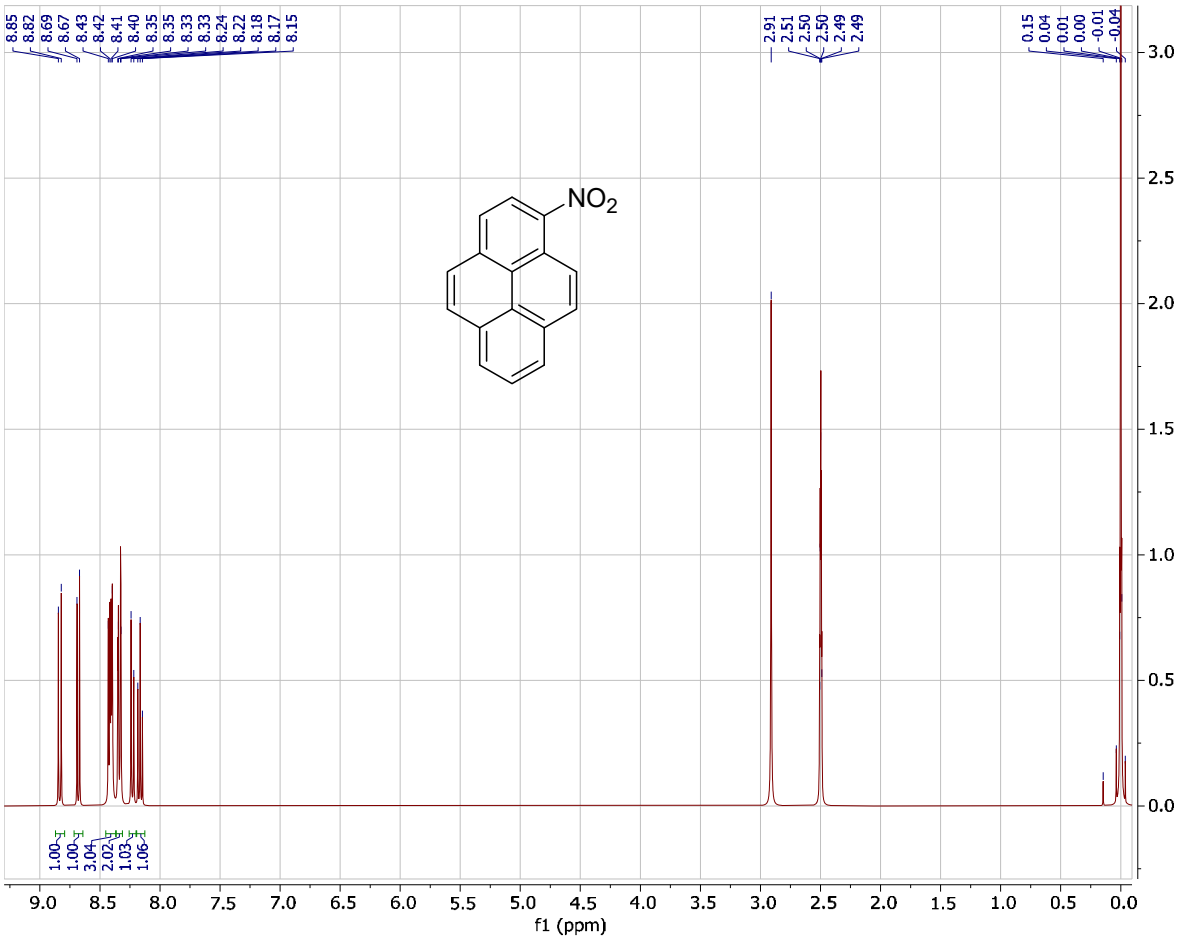


Supplementary Scheme S1: Sequence for the synthesis of 1-Azidopyrene

Synthesis of 1-Nitropyrene

1-Nitropyrene was synthesized following a procedure adapted from ref [1]. Pyrene (1.0 g, 4.94 mmol) was dissolved in glacial acetic acid (30 mL) and heated to 60°C with stirring. Once fully dissolved, concentrated nitric acid (69%, 1.2 mL, 18.6 mmol, 3.8 equiv.) was added dropwise over 5 minutes under vigorous stirring, resulting in the precipitation of a yellow-orange solid. The mixture was maintained at 60°C for 30 minutes, then cooled and stirred at room temperature for 10 hours (overnight). The orange precipitate was collected by suction filtration, washed thoroughly with deionized water to remove residual acid, and recrystallized from boiling ethanol (180 mL) to yield greenish-yellow crystals of 1-nitropyrene (0.97 g, 3.92 mmol, 79% yield). The structure and purity were confirmed by ^{1}H NMR, consistent with ref [1].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.83 (d, J = 9.5 Hz, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.41 (dd, J = 8.6, 4.7 Hz, 3H), 8.34 (dd, J = 8.7, 1.6 Hz, 2H), 8.23 (d, J = 8.9 Hz, 1H), 8.17 (t, J = 7.7 Hz, 1H)

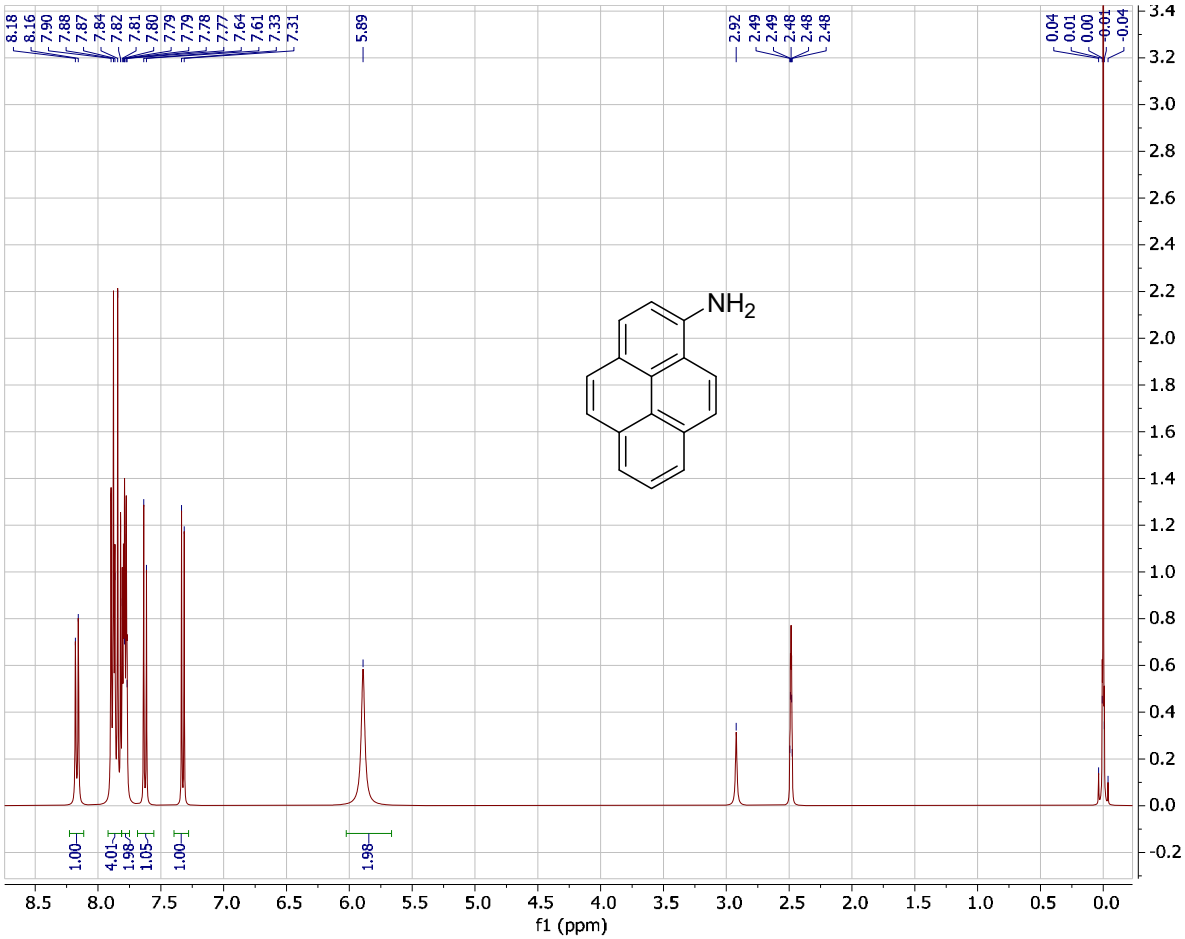


Supplementary Figure S1: ^{1}H NMR of 1-Nitropyrene in 20% DMSO-d_6 in CCl_4

Synthesis of Pyrene-1-amine

Pyrene-1-amine was prepared following ref [1]. 1-Nitropyrene (0.50 g, 2.02 mmol) was suspended in dry methanol (35 mL) in a 100 mL Schlenk flask and cooled to 0°C in an ice/water bath. Palladium on carbon (5% Pd/C, 30 mg) was added as a catalyst, and the mixture was degassed with argon. Sodium borohydride (0.40 g, 10.6 mmol, 5.2 equiv.) was added slowly at 0°C with stirring. The reaction proceeded at 0°C for 30 minutes, then at room temperature for 30 minutes under argon. Progress was monitored by TLC (75:25 hexane/ethyl acetate), with the product showing a lower Rf and strong blue fluorescence under 365 nm UV light. The mixture was filtered through Celite to remove Pd/C, and the solvent was evaporated under reduced pressure. The crude product was recrystallized from boiling ethanol with gradual water addition, yielding yellowish-green acicular crystals of pyrene-1-amine (0.36 g, 1.65 mmol, 82% yield). The structure was confirmed by ^{1}H NMR, matching ref [1].

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.17 (d, J = 9.2 Hz, 1H), 7.93–7.81 (m, 4H), 7.79 (dt, J = 8.0, 3.1 Hz, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 5.89 (s, 2H).



Supplementary Figure S2: ^{1}H NMR of Pyrene-1-amine in 20% DMSO-d$_6$ in CCl$_4$

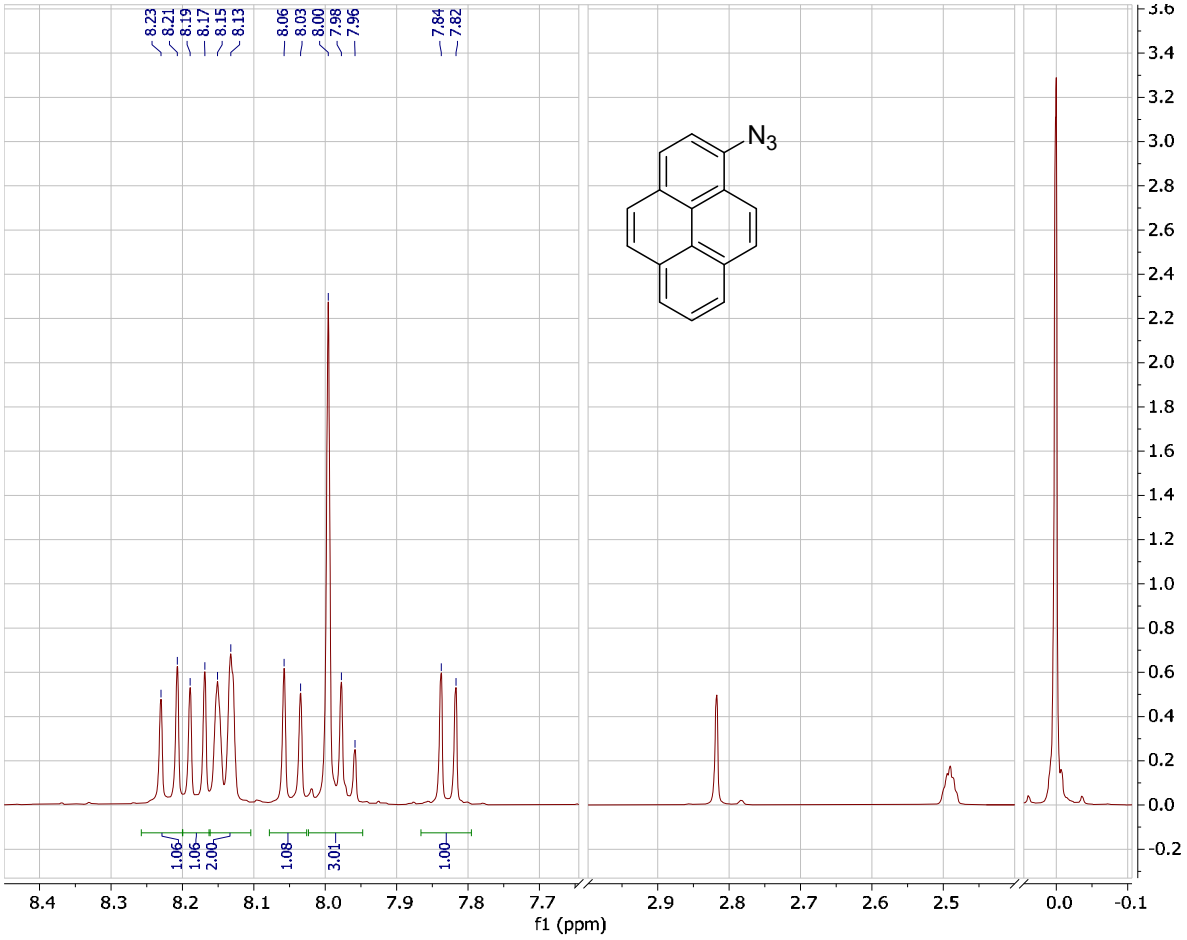
Synthesis of 1-Azidopyrene

1-Azidopyrene was synthesized following ref [2] in a dimly lit environment due to its light sensitivity. Pyrene-1-amine (0.30 g, 1.38 mmol) was suspended in deionized water (20 mL) in a 100 mL round-bottom flask, and concentrated sulfuric acid (4 mL) was added slowly with stirring, using sonication to disperse clumps. The mixture was cooled to <5°C in an ice/water bath, and sodium nitrite (0.20 g, 2.90 mmol, 2.1 equiv.) in water (5 mL) was added dropwise over 5–10 minutes, maintaining the temperature below 5°C. After stirring for 2 hours to form the diazonium salt, sodium azide (0.60 g, 9.23 mmol, 6.7 equiv.) in water (5 mL) was added slowly, with cold methanol added if foaming occurred. The mixture was stirred at room temperature for 2 hours, and the brown precipitate was collected by suction filtration, dried under vacuum, and purified by column chromatography (neutral alumina, hexane) to yield pale yellow 1-

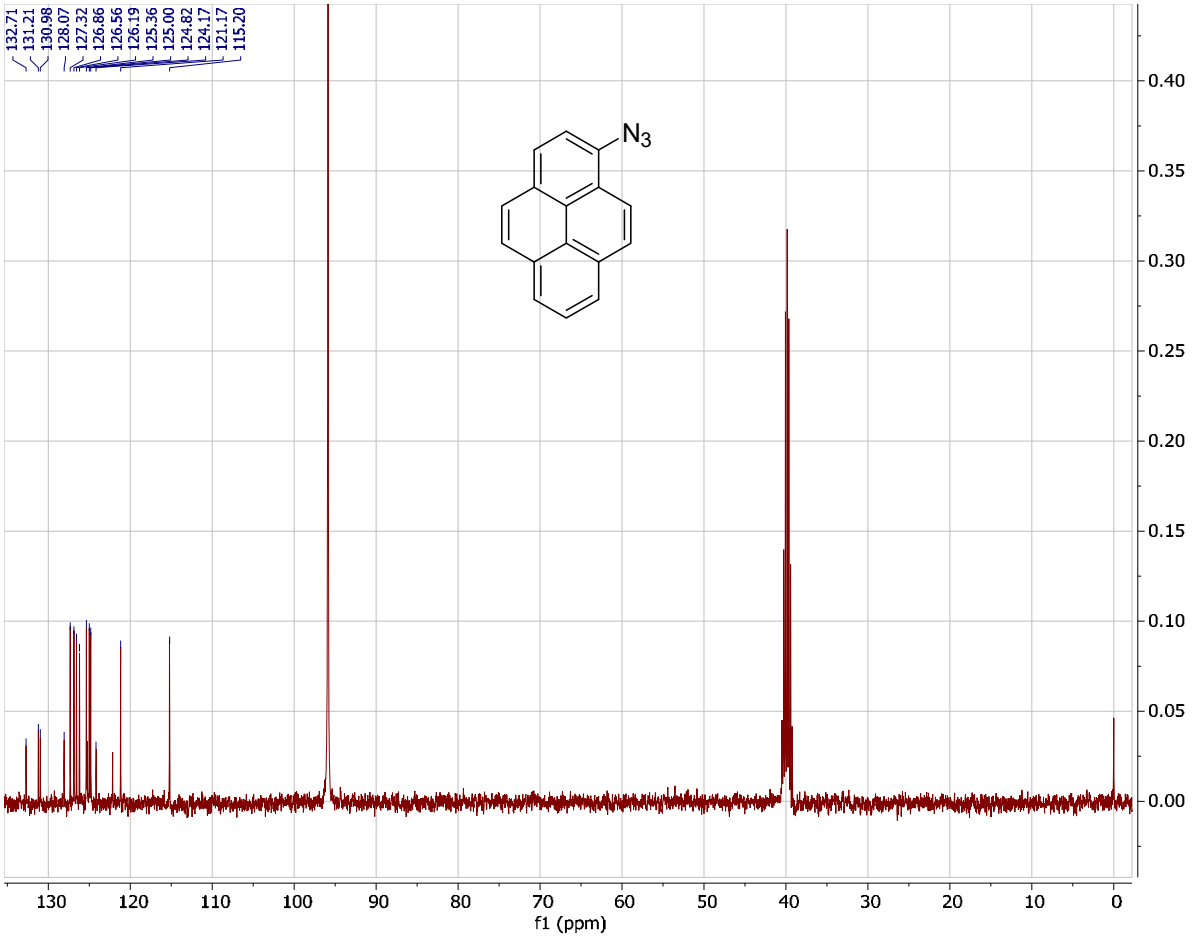
azidopyrene (0.24 g, 0.98 mmol, 71% yield). Melting point recorded 118.5°C. The structure was confirmed by ^{1}H NMR, consistent with ref [2].

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.22 (d, J = 9.2 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 7.4 Hz, 2H), 8.05 (d, J = 9.2 Hz, 1H), 7.99 (d, J = 7.3 Hz, 3H), 7.83 (d, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 132.71, 131.21, 130.98, 128.07, 127.32, 126.86, 126.56, 126.19, 125.36, 125.00, 124.82, 124.17, 121.17, 115.20.

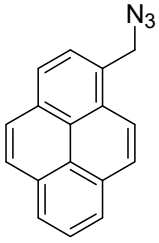


Supplementary Figure S3: ^{1}H NMR of 1-azidopyrene in 20% DMSO-d$_6$ in CCl_4

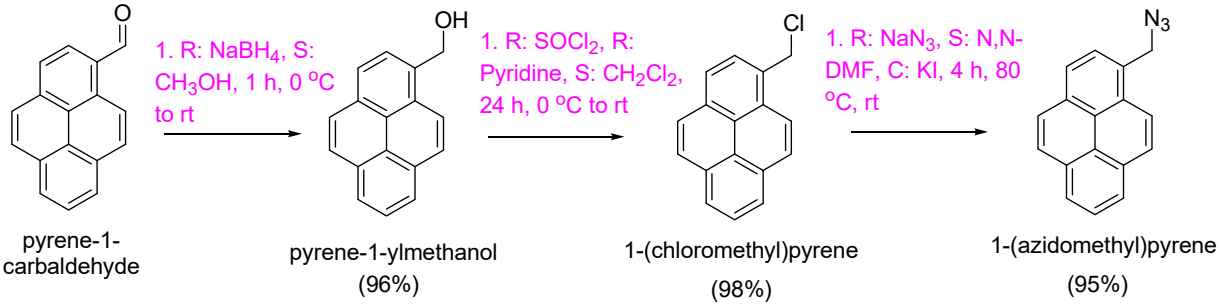


Supplementary Figure S4: ^{13}C NMR of 1-azidopyrene in 20% DMSO- d_6 in CCl_4

Synthesis of **1-(Azidomethyl)pyrene**



For the synthesis of this compound, the following reaction scheme S2 was adopted

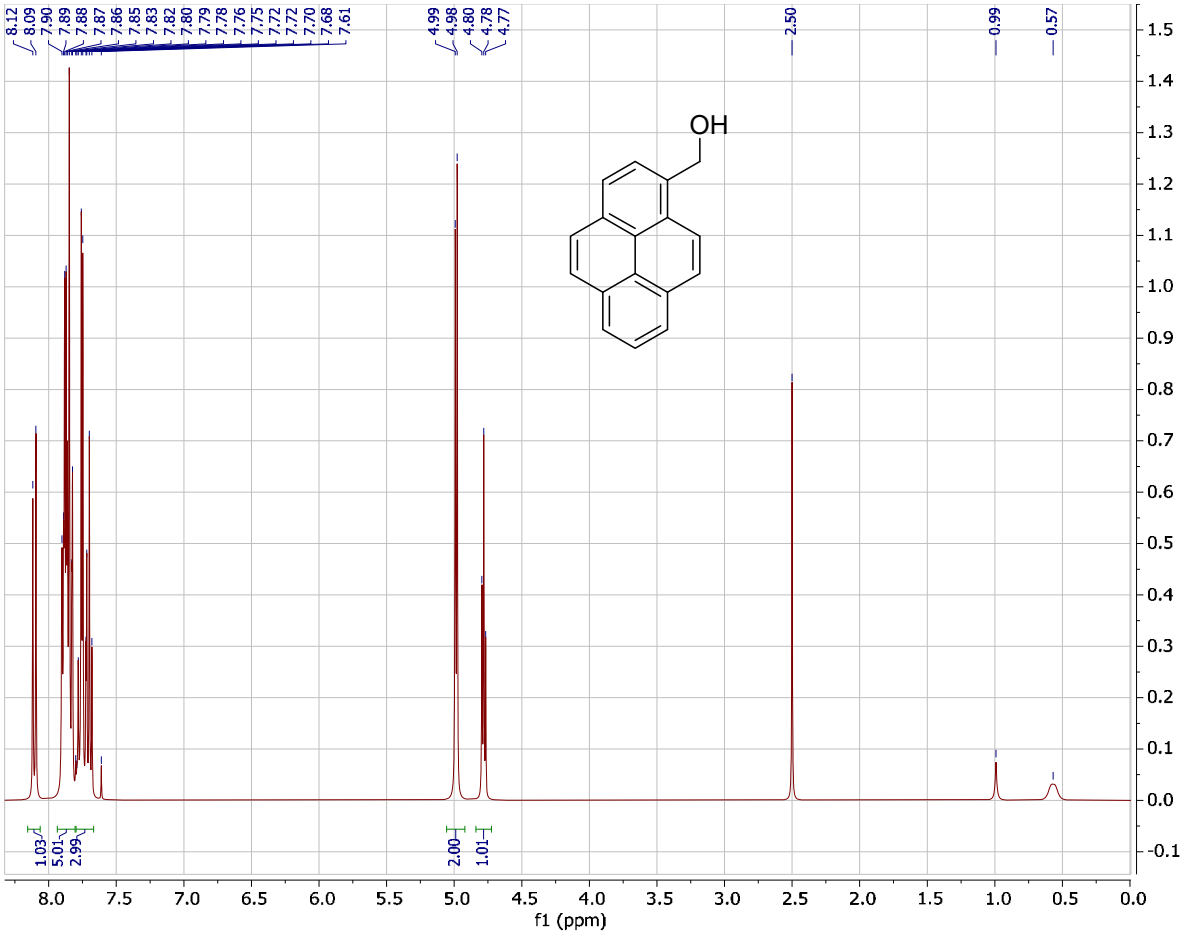


Supplementary Scheme S2: Sequence for the synthesis of 1-(azidomethyl)pyrene

Synthesis of Pyrene-1-ylmethanol

Pyrene-1-carbaldehyde (0.30 g, 1.30 mmol) was suspended in cold methanol (15 mL) in a 50 mL round-bottom flask. Sodium borohydride (0.30 g, 7.93 mmol, 6.1 equiv.) was added slowly over 10 minutes at 0°C (ice/water bath), followed by stirring for 1 hour. TLC (3:1 hexane/ethyl acetate) confirmed completion. The mixture was poured into cold water (100 mL), and the white precipitate was collected by suction filtration and dried under vacuum, yielding pyrene-1-ylmethanol (0.29 g, 1.25 mmol, 96% yield) without further purification. The structure matched ref [3].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11 (d, J = 9.3 Hz, 1H), 7.92–7.78 (m, 5H), 7.77–7.66 (m, 3H), 4.98 (d, J = 5.7 Hz, 2H), 4.78 (t, J = 5.6 Hz, 1H).

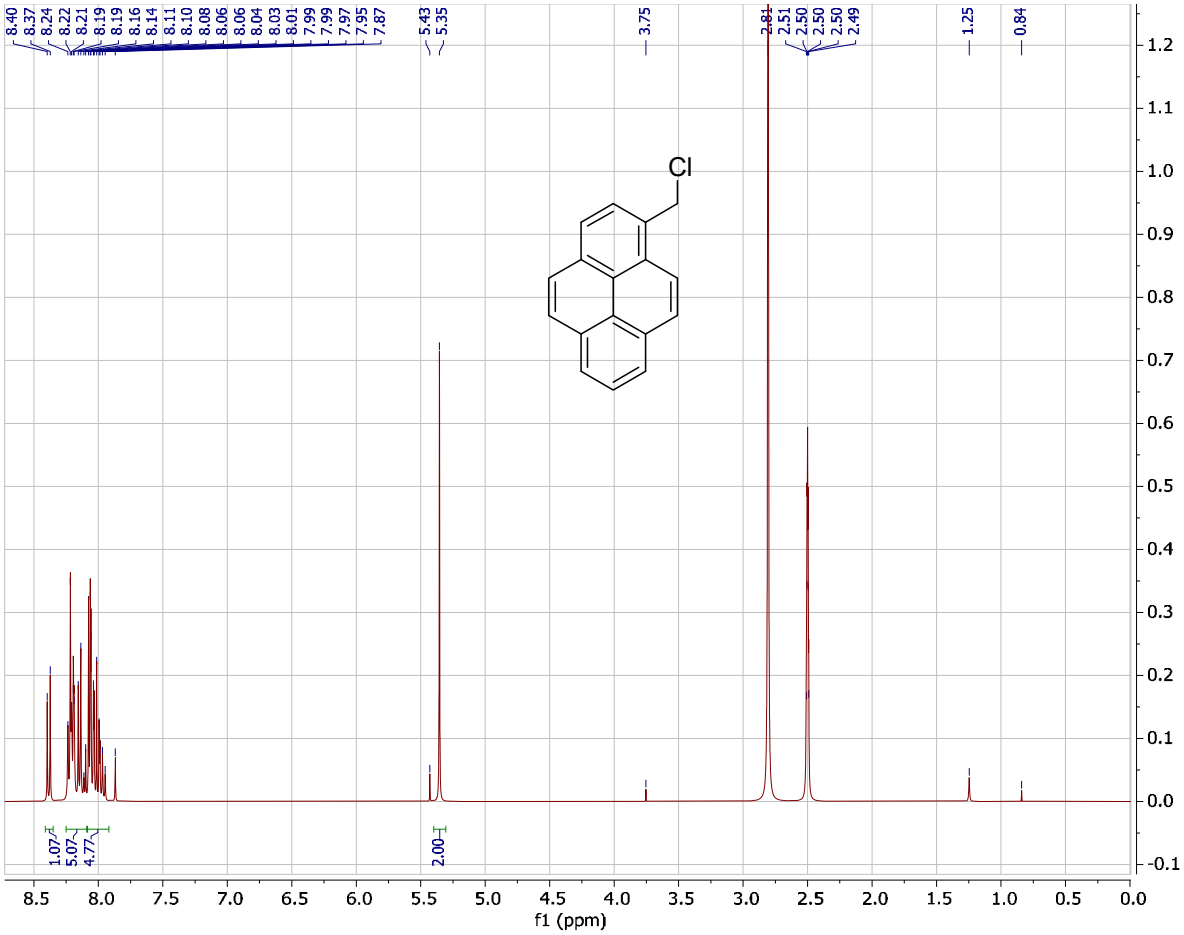


Supplementary Figure S5: ^{1}H NMR of pyrene-1-ylmethanol in 20% DMSO-d_6 in CCl_4

Synthesis of 1-(Chloromethyl)pyrene

Pyrene-1-ylmethanol (0.50 g, 2.15 mmol) was dissolved in dry dichloromethane (20 mL) with pyridine (0.50 mL, 6.18 mmol, 2.9 equiv.) in a 50 mL round-bottom flask, cooled to -15°C (ice/salt bath). Thionyl chloride (0.50 mL, 6.85 mmol, 3.2 equiv.) was added dropwise over 10 minutes, with a drying tube to vent HCl and SO_2. After warming to room temperature and stirring for 24 hours, excess $SOCl_2$ and solvent were removed under reduced pressure. The crude solid was washed with cold 10% aqueous $NaHCO_3$ (30 mL), filtered, and dried under vacuum, yielding 1-(chloromethyl)pyrene (0.53 g, 2.11 mmol, 98% yield). The structure matched ref [3].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.38 (d, J = 9.2 Hz, 1H), 8.27–7.92 (m, 8H), 5.35 (s, 2H).



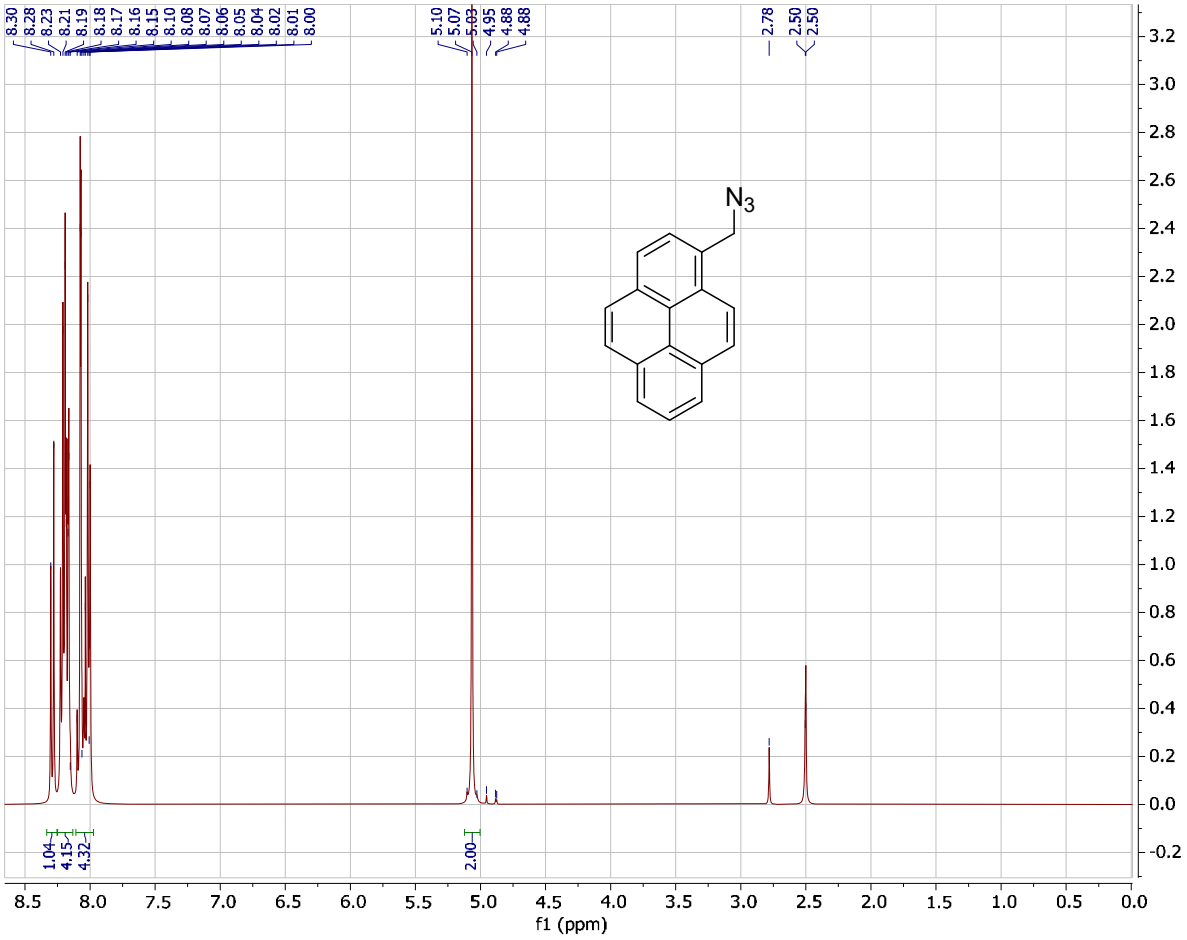
Supplementary Figure S6: ^{1}H NMR of 1-(chloromethyl)pyrene in 20% DMSO-d_6 in CCl_4

Synthesis of 1-(Azidomethyl)pyrene

In an amber 30 mL vial, 1-(chloromethyl)pyrene (0.39 g, 1.55 mmol) was dissolved in dry DMF (5 mL) with a catalytic amount of potassium iodide. Sodium azide (0.40 g, 6.15 mmol, 4.0 equiv.) was added, and the mixture was stirred at 80°C for 2 hours. The reaction was poured into water (30 mL), extracted with ethyl acetate (40 mL), washed with water (2 × 40 mL) and brine, dried over Na_2SO_4, and evaporated. The oily residue crystallized under high vacuum, yielding 1-(azidomethyl)pyrene (0.38 g, 1.48 mmol, 95% yield). Melting point recorded 62.5°C.

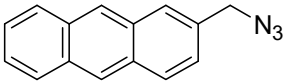
The structure matched ref [4].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29 (d, J = 9.2 Hz, 1H), 8.27–8.11 (m, 4H), 8.12–7.86 (m, 4H), 5.07 (s, 2H).

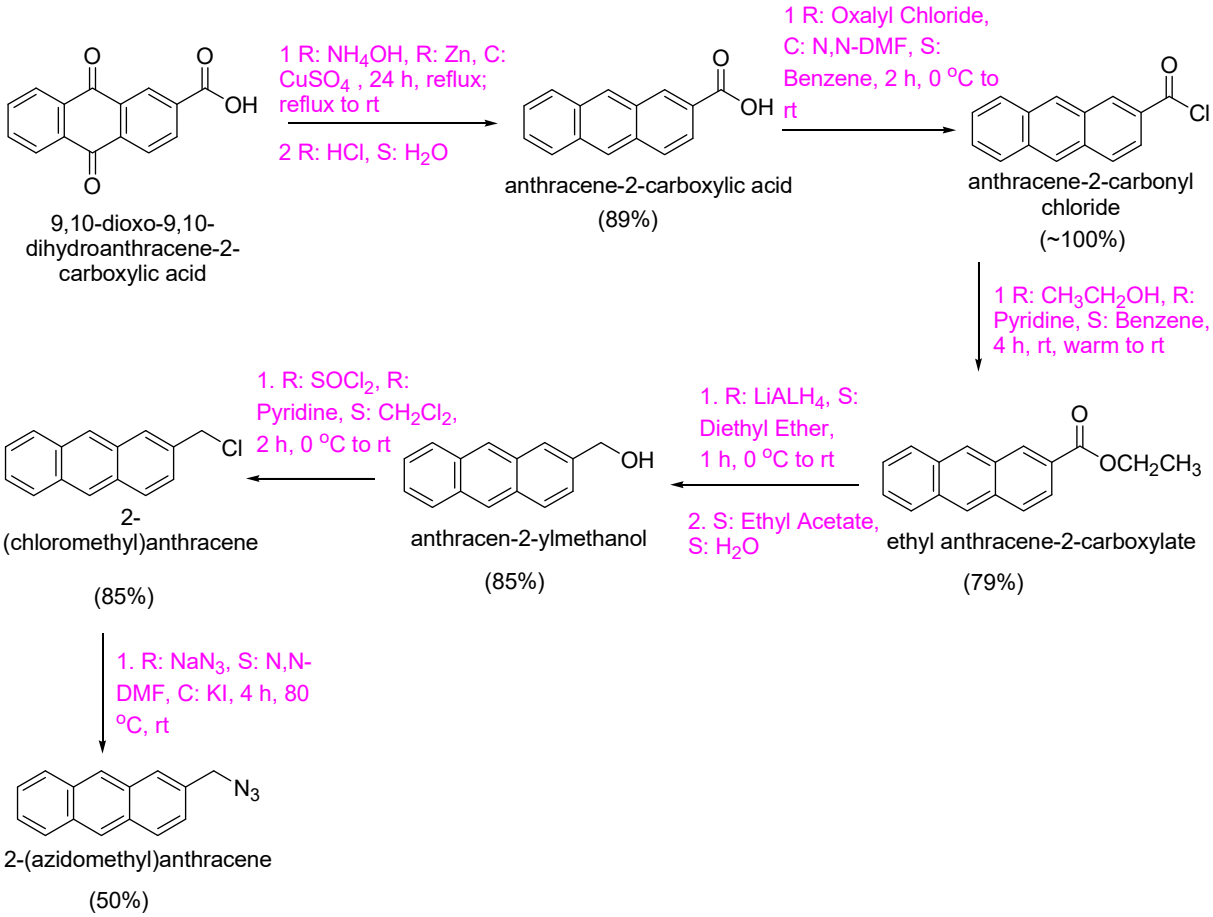


Supplementary Figure S7: ^{1}H NMR of 1-(azidomethyl)pyrene in 20% DMSO-d_6 in CCl_4

Synthesis of **2-(Azidomethyl)anthracene**



For the synthesis of this compound, the following reaction scheme S3 was adopted

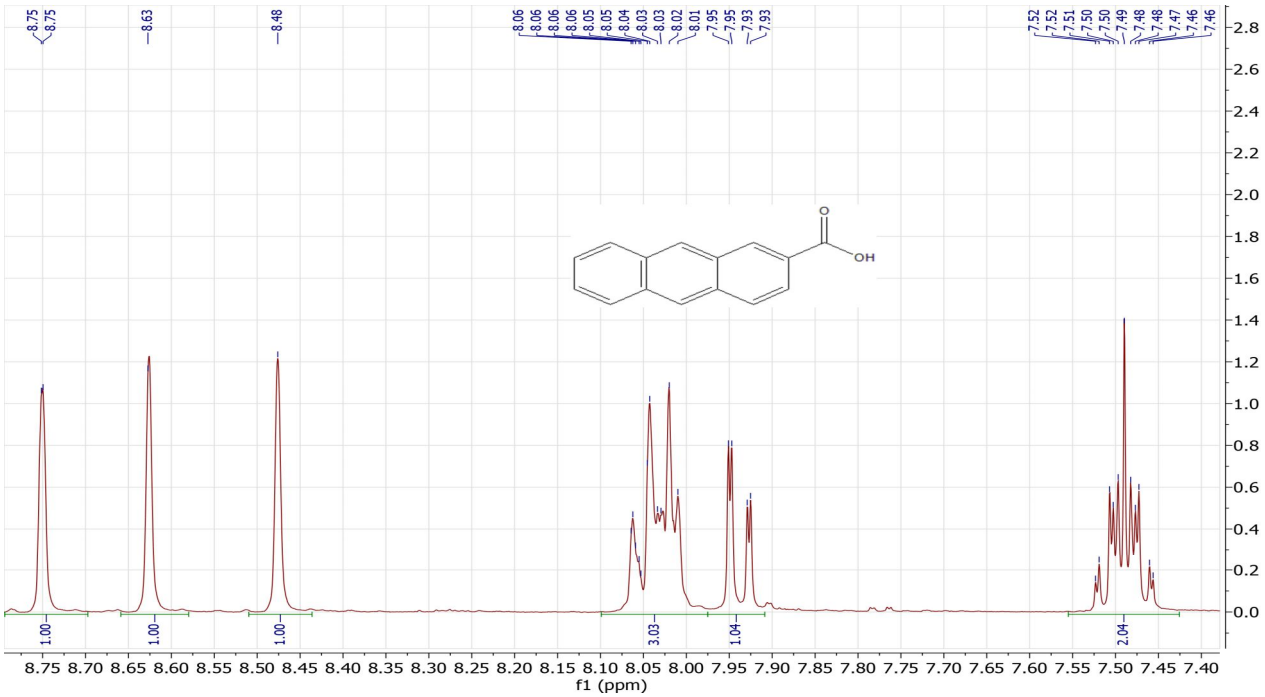


Supplementary Scheme S3: Sequence for the synthesis of 2-(Azidomethyl)anthracene

Synthesis of Anthracene-2-carboxylic Acid

Adapted from ref [5], 9,10-dioxo-9,10-dihydroanthracene-2-carboxylic acid (2.0 g, 7.93 mmol) was suspended in 10 M NH_4OH (60 mL) and sonicated. Pre-washed zinc granules (5.0 g, 76.5 mmol, 9.6 equiv.) and catalytic $CuSO_4$ were added, and the mixture was refluxed under argon for 24–36 hours until creamy white. After cooling, excess HCl neutralized the ammonia and precipitated the product, which was filtered, washed with water, and optionally recrystallized from glacial acetic acid, yielding anthracene-2-carboxylic acid (1.56 g, 7.04 mmol, 91% yield). The structure matched ref [5].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75 (s, 1H), 8.63 (s, 1H), 8.48 (s, 1H), 8.10–7.99 (m, 3H), 7.94 (dd, J = 8.8, 1.6 Hz, 1H), 7.55–7.43 (m, 2H).



Supplementary Figure S8: ^{1}H NMR of anthracene-2-carboxylic acid in 20% DMSO-d_6 in CCl_4

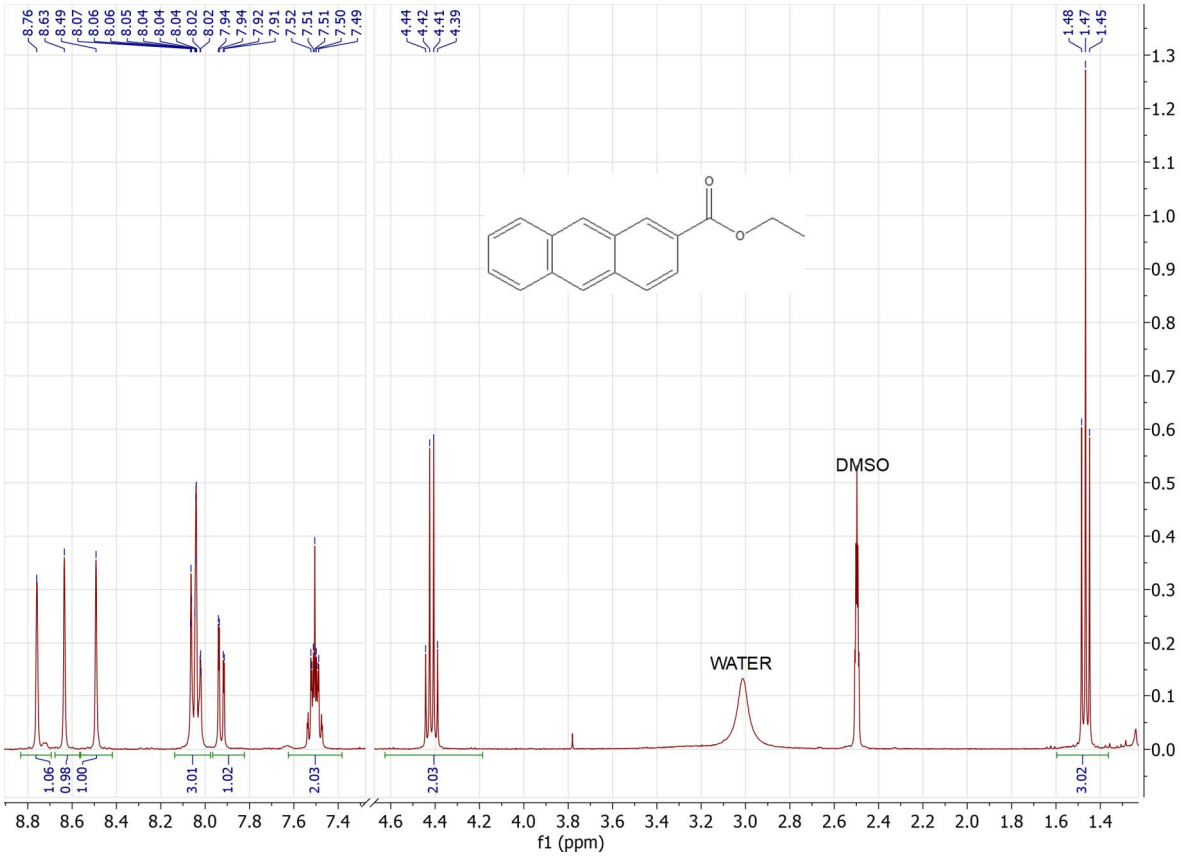
Synthesis of Anthracene-2-carbonyl Chloride

Anthracene-2-carbonyl chloride was synthesized following a procedure similar to that described in [6]. Briefly, anthracene-2-carboxylic acid (0.44 g, 2.0 mmol) was dried under vacuum over Drierite before being suspended in dry benzene (15 mL) in a 50 mL flame-dried round-bottom flask. The mixture was cooled to 0°C using an ice/water bath. A catalytic amount of dry N,N-dimethylformamide (DMF, 0.05 mL) was added, followed by oxalyl chloride (0.60 mL, 4.3 mmol, 2.1 equiv.). The reaction flask was protected from ambient humidity using a drying tube packed with Drierite. The mixture was stirred at 0°C for 10 minutes and then stirred at room temperature for an additional 2 hours until the initially insoluble carboxylic acid dissolved completely, indicating the formation of the acid chloride. The resulting anthracene-2-carbonyl chloride solution was kept under anhydrous conditions in preparation for the next synthetic step. The yield of the reaction was assumed to be quantitative (100%). No further characterization of the anthracene-2-carbonyl chloride was necessary at this stage, as the compound was directly used in subsequent reactions.

Synthesis of Ethyl Anthracene-2-carboxylate

Adapted from ref [7], dry pyridine (0.8 mL) was added to the anthracene-2-carbonyl chloride solution, followed by dry ethanol (1.6 mL, excess). After stirring at room temperature for 30 minutes and 40–50°C for 2 hours, TLC (75:25 hexane/ethyl acetate) confirmed completion. The solvent was evaporated, and the crude product was recrystallized from ethanol (~50 mL) with water (~5 mL), yielding ethyl anthracene-2-carboxylate (0.42 g, 1.68 mmol, 79% yield). The structure matched ref [7].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.76 (s, 1H), 8.63 (s, 1H), 8.49 (s, 1H), 8.11–8.00 (m, 3H), 7.93 (dd, J = 8.8, 1.6 Hz, 1H), 7.56–7.45 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H).

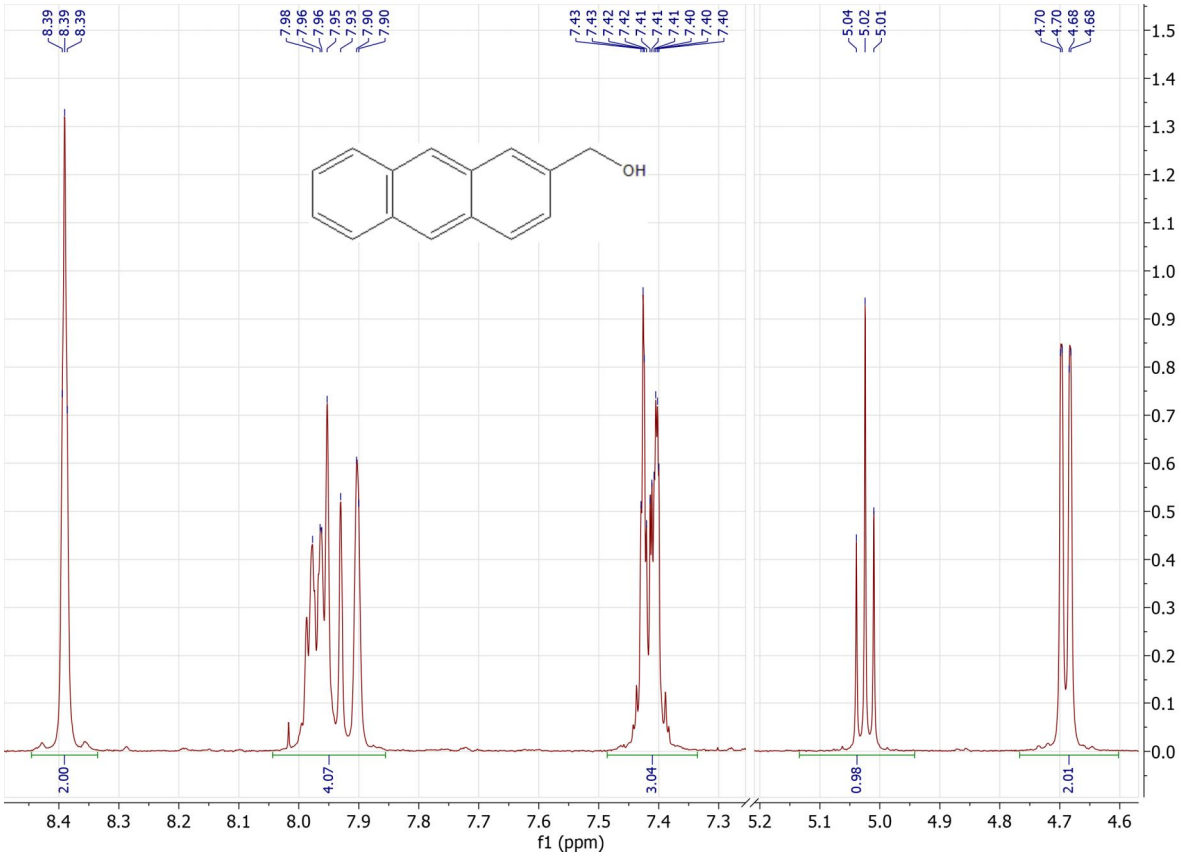


Supplementary Figure S9: ^{1}H NMR of ethyl anthracene-2-caboxylate in 20% DMSO-d_6 in CCl_4

Synthesis of Anthracene-2-ylmethanol

Following ref [7], $LiAlH_4$ (0.25 g, 6.59 mmol, 2.8 equiv.) was suspended in dry diethyl ether (30 mL) at 0°C under argon. Dry Ethyl anthracene-2-carboxylate (0.59 g, 2.36 mmol) was added over 10 minutes, stirred at 0°C for 20 minutes, then at room temperature for 1–2 hours. TLC (50:50 hexane/ethyl acetate) confirmed completion. Excess $LiAlH_4$ was safely decomposed with ethyl acetate (80 mL) followed by brine (100 mL) and extracted. The organic phase was dried over Na_2SO_4, gravity filtered and the solvent removed under reduced pressure. The solid was washed with water, filtered, and dried, yielding anthracene-2-ylmethanol (0.42 g, 2.02 mmol, 85% yield). The structure matched ref [7].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.39 (t, J = 1.7 Hz, 2H), 8.04–7.87 (m, 4H), 7.48–7.36 (m, 3H), 5.02 (t, J = 5.8 Hz, 1H), 4.69 (dd, J = 5.8, 1.1 Hz, 2H).

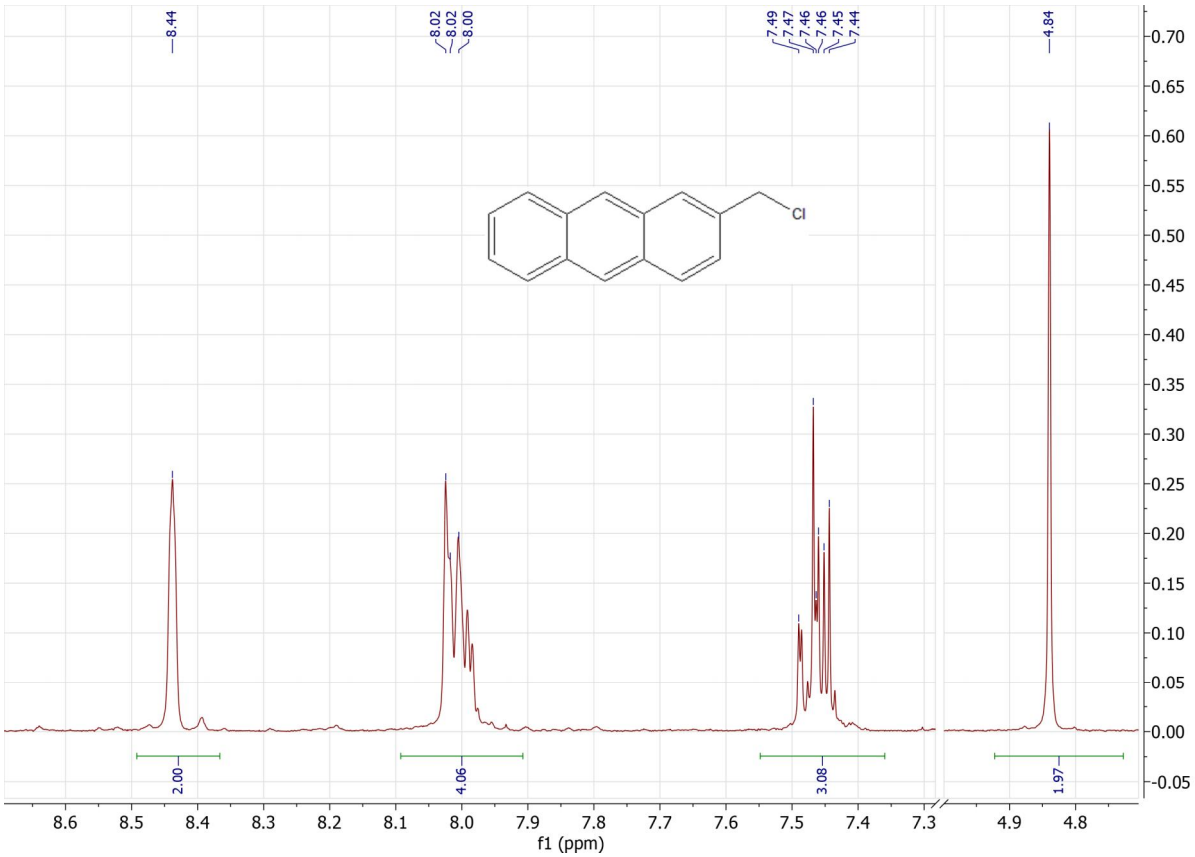


Supplementary Figure S10: ^{1}H NMR of anthracene-2-ylmethanol in 20% DMSO-d_6 in CCl_4

Synthesis of 2-(Chloromethyl)anthracene

Adapted from ref [5]. Into a 50 mL round bottom flak protected with a drying tube was added anthracene-2-ylmethanol (0.37 g, 1.78 mmol), dry CH_2Cl_2 (15 mL), pyridine (0.8 mL) and stirred at 0°C. Thionyl chloride (0.8 mL, 11.0 mmol, 6.2 equiv.) was added over 5–10 minutes, stirred at 0°C for 10 minutes, then at room temperature for 2 hours. TLC (90:10 hexane/ethyl acetate) confirmed consumption of the anthracene-2-ylmethanol. The DCM solvent and excess $SOCl_2$ were removed under reduced pressure, and the crude product was washed with water/methanol (35 mL/5 mL), filtered, and dried, yielding 2-(chloromethyl)anthracene (0.34 g, 1.50 mmol, 85% yield). The structure matched ref [5].

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.44 (s, 2H), 8.07–7.95 (m, 4H), 7.52–7.41 (m, 3H), 4.84 (s, 2H).



Supplementary Figure S11: ^{1}H NMR of 2-(chloromethyl)anthracene in 20% DMSO-d_6 in CCl_4

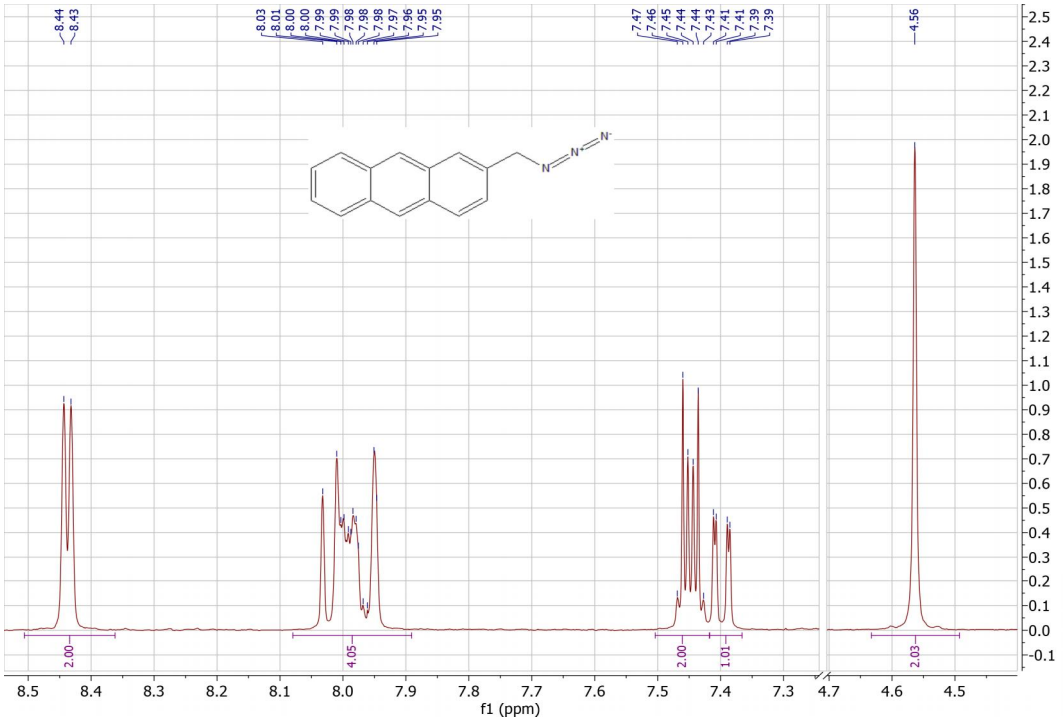
Synthesis of 2-(Azidomethyl)anthracene

Following the procedure for 1-(azidomethyl)pyrene, 2-(chloromethyl)anthracene (0.22 g, 0.97 mmol) was dissolved in dry DMF (5 mL) with catalytic KI (20 mg) and NaN_3 (0.32 g, 4.92 mmol, 5.1 equiv.). The mixture was stirred at 80°C for 4–6 hours under dry conditions, cooled, diluted with water (50 mL), and filtered. The crude product was recrystallized from ethanol/water, yielding 2-(azidomethyl)anthracene crystals (0.11 g, 0.47 mmol, 50% yield). Melting point recorded 167°C.

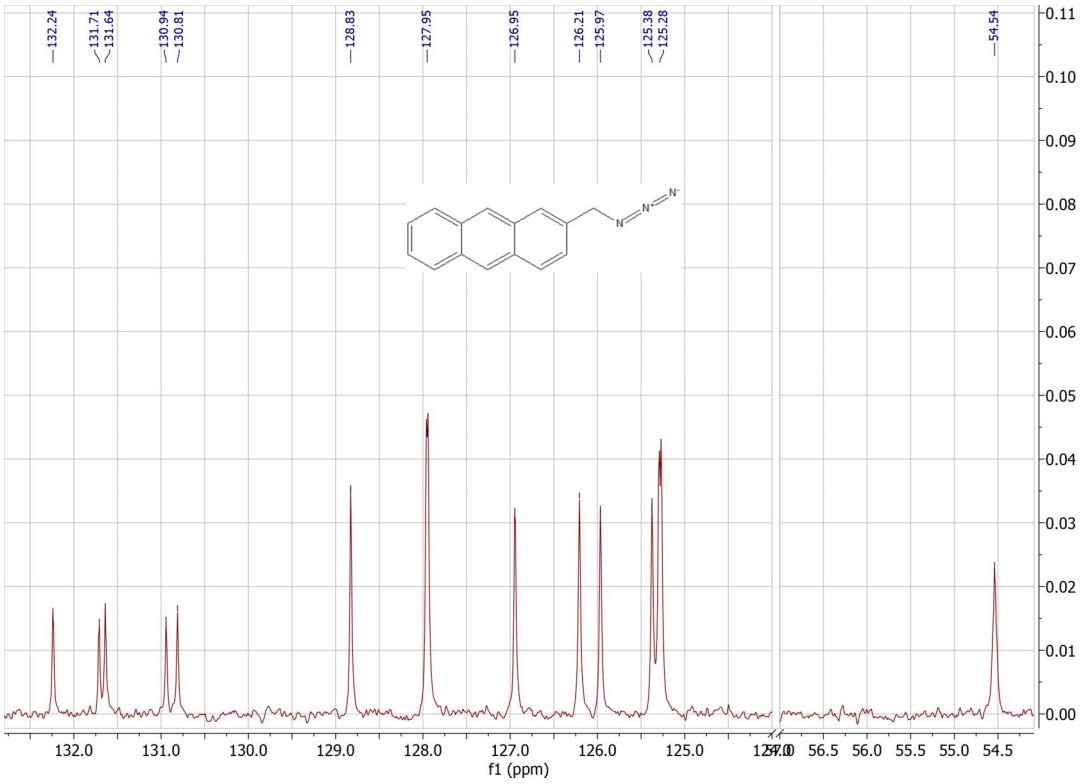
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.44 (d, J = 4.5 Hz, 2H), 8.08–7.89 (m, 4H), 7.50–7.42 (m, 2H), 7.40 (dd, J = 8.7, 1.7 Hz, 1H), 4.56 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 132.24, 131.71, 131.64, 130.94, 130.81, 128.83, 127.96, 127.94, 126.95, 126.21, 125.97, 125.38, 125.29, 125.27, 54.54.

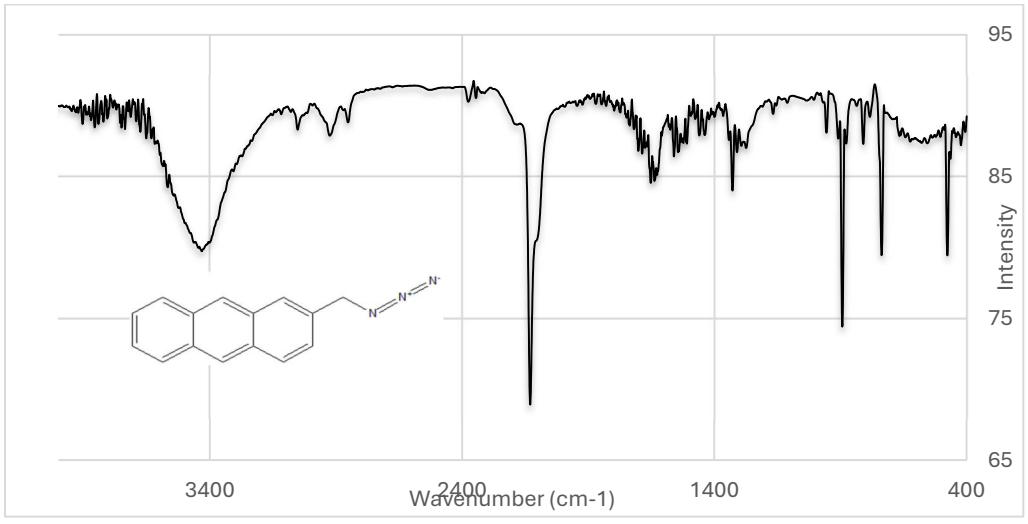
IR (KBr): ν (cm^{-1}) = 3050, 2923, 2851, 2128 (azide stretch), 1328, 893.



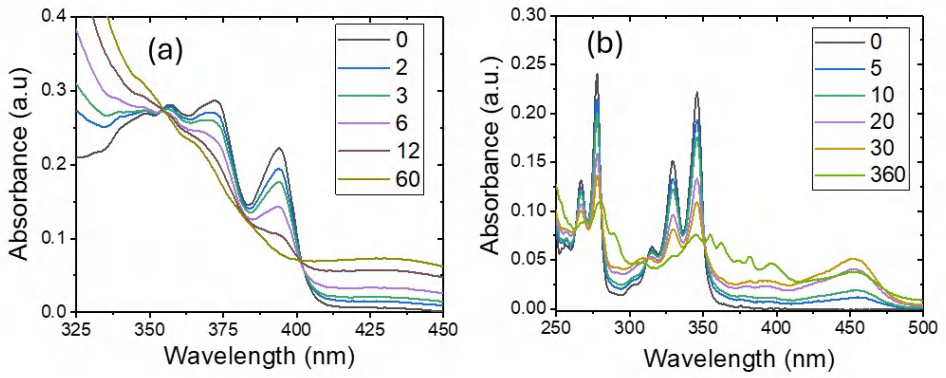
Supplementary Figure S12: ^{1}H NMR of 2-(azidomethyl)anthracene in 20% DMSO-d_6 in CCl_4



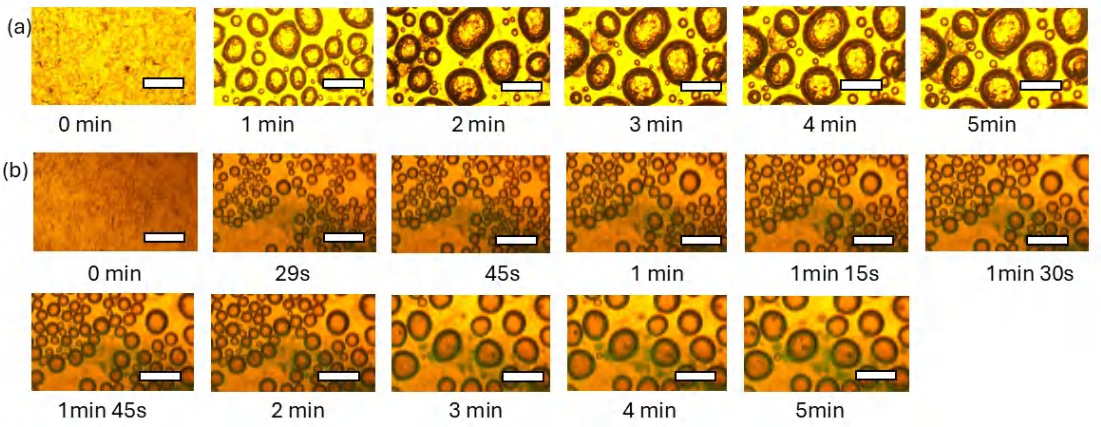
Supplementary Figure S13: ^{13}C NMR of 2-(azidomethyl)anthracene in 20% DMSO-d_6 in CCl_4



Supplementary Figure S14: IR of 2-(azidomethyl)anthracene over KBr



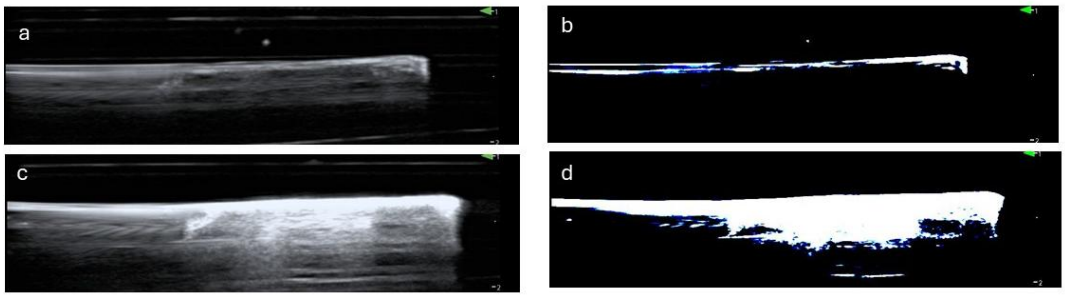
Supplementary Figure S15: UV–vis absorption spectrum of a) $2N_3$-AN and b) N_3-CH_2-PY irradiated with 365 nm at 5 mW/cm^2 recorded in chloroform solution showing the change with irradiation starting from time = 0 s, with time points in seconds listed in the legend. The peaks of $2N_3$-AN and N_3-CH_2-PY undergo photodegradation with clean isosbestic point suggesting formation of a single photoproduct.



Supplementary Figure S16: Images of a) PS polystyrene film and b) PC polycarbonate film doped with $2N_3$-AN irradiated by 365 nm with an intensity of 10 mW/cm^2 at various times from 0 to 5 minutes. Both polymers support rapid bubble formation, similar to PMMA. The scale bar is 500 μm.

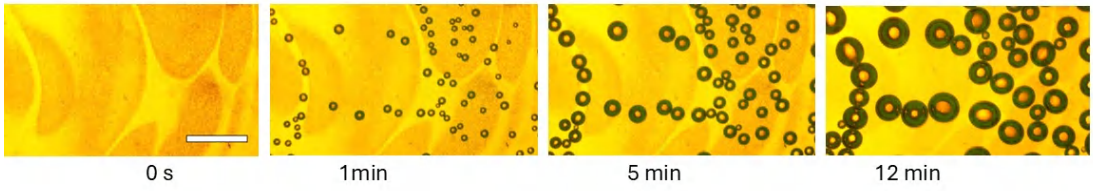
Polymer film	V_∞	k_{bub} (s^{-1})
PS	66.31	8.5×10^{-3}
PC	105.57	2.6×10^{-3}
PMMA	83.50	5.2×10^{-3}

Supplementary Table S1: Total areal volume of the bubbles, Vbub and bubble growth rate constant kbub for different polymer films doped with 0.1M 2N3-AN. The films are irradiated with 10mW/cm^2 of 365nm irradiation and the growth curves were fitted with $\bar{V}_{bub}(t) = \bar{V}_\infty(1-e^{-k_{bub}t})$



Supplementary Figure S17 : Ultrasound images of glass pipette tip covered with polymer/azide coating a) before and c) after irradiation. These images were converted into binary RGB (Red, Green, Blue) images b) and d) with a threshold of 128 where a value of 0 represents the absence of color, while 255 represents the maximum intensity. The pixels with color intensity =>128 (white) were counted for both images. The image d) has 6.36× more white pixel than image b). Following MATLAB code was used:

```
grayImage = imread('image_name.jpg);

binaryImage=grayImage>=128;

totalpixels=nume1(grayImage);

pixelAboveThreshold= sum(binaryImage(:));

disp(['pixels with intensity>128:',num2str(totalpixels)];

disp(['total pixels in image',num2str(tota;Pixels)];
```



Supplementary Figure S18 : Bubble growth for a bilayer sample consisting of a 100 µm thick PMMA film on top of 150µm thick PMMA film on top of 150µm thick PMMA film containing 0.1 M $2N_3$-AN. Exposure of this bilayer sample film to 365 nm still resulted in growth of a bubble layer with $\overline{V}_{bub}$= 21 µm and k_{bub} of 4.61×10^{-3} s^{-1} as compared to k_{bub}= 5.31×10^{-3} for monolayer azide/PMMA. Scale: 500µm.

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