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SUPPLEMENTARY INFORMATION
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Pyrene synthesis in circumstellar envelopes and its role in the formation of 2D nanostructures

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Supplementary Information

Pyrene Synthesis in Circumstellar Envelopes and Its Role in the Formation of 2D Nanostructures

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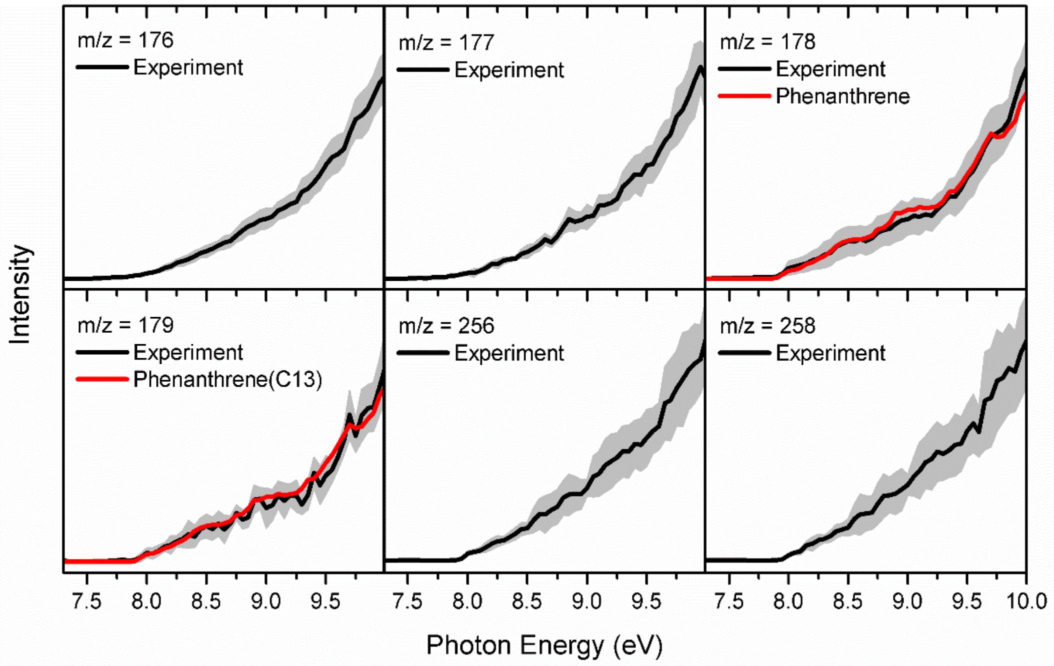
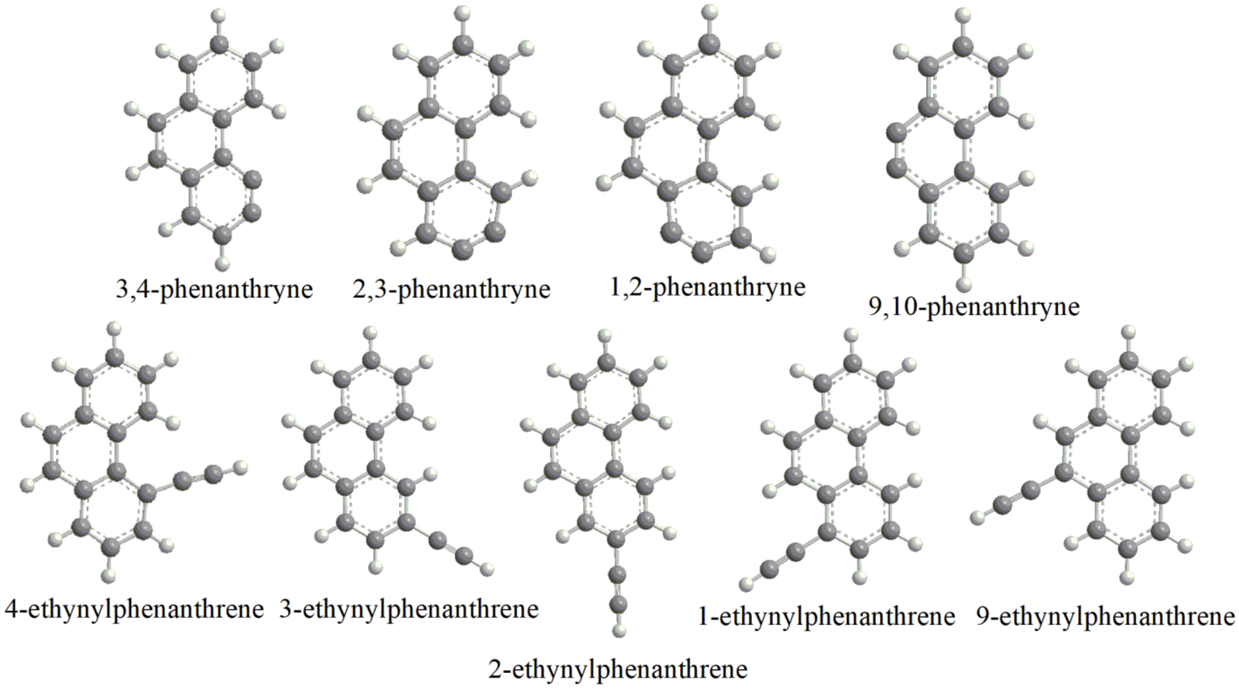


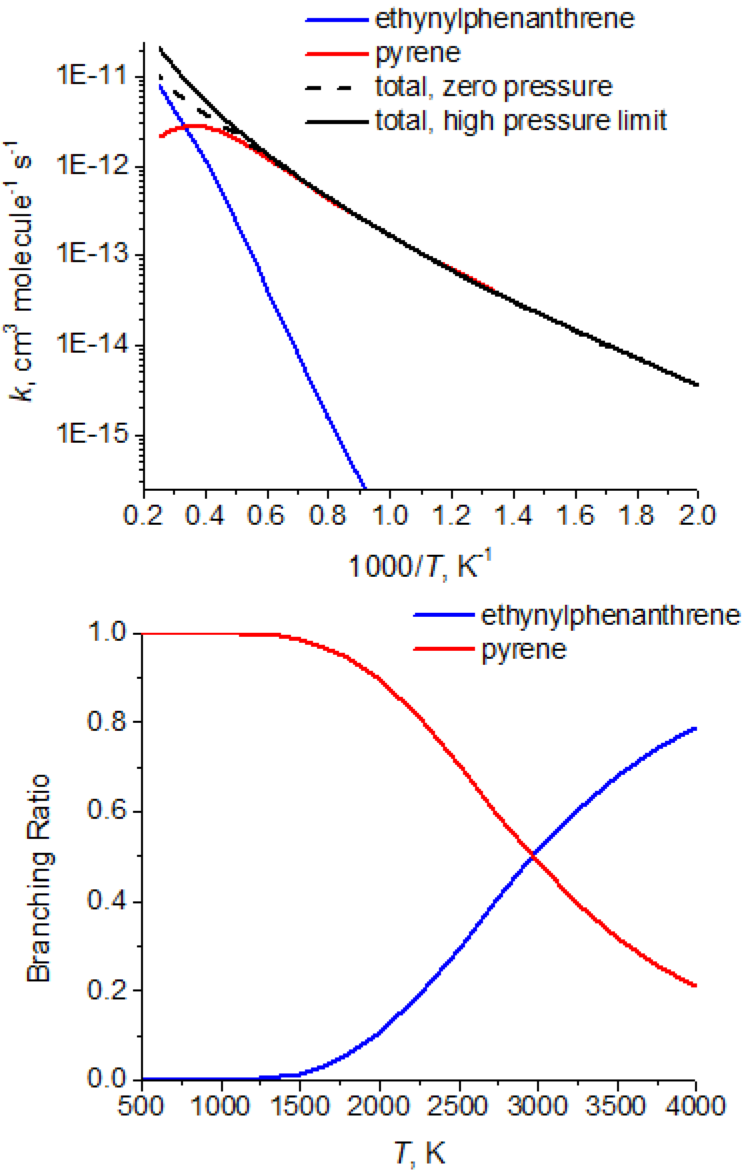
Supplementary Figure 1. PIE curves for additional ions detected in this work. The onset of the ion signal at *m/z* = 176 at 7.90 ± 0.05 eV correlates nicely with the computed adiabatic ionization energies for various phenanthrynes (Figure S2) with computed adiabatic ionization energies of 7.95 ± 0.10, 7.95 ± 0.10, 8.01 ± 0.10, and 8.06 ± 0.10 eV (Table S1). The onset of ion counts at *m/z* = 177 at 7.80 ± 0.05 eV matches the computed adiabatic ionization energy of the 4-phenanthrenyl radical of 7.70 ± 0.10 eV (Table S1). ± 10% uncertainty based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over three PIE scans contribute to the overall errors.

Supplementary Table 1. Calculated vertical and adiabatic ionization energies (eV).

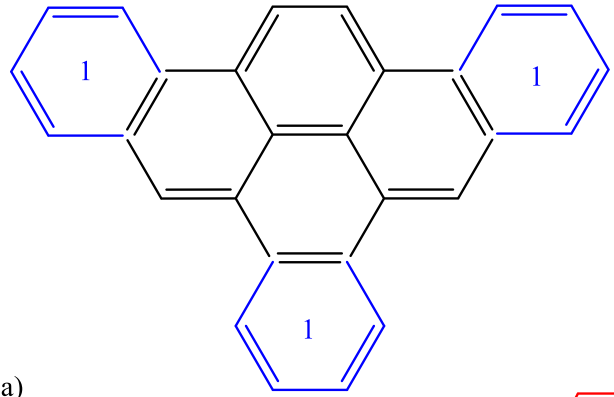
Species	Vertical IE	Adiabatic IE
4-phenanthrenyl	8.56	7.70
4-ethynylphenanthrene	7.84	7.72
3-ethynylphenanthrene	7.85	7.73
2-ethynylphenanthrene	8.00	7.84
1-ethynylphenanthrene	7.88	7.75
9-ethynylphenanthrene	7.83	7.71
3,4-phenanthryne	8.11	7.95
2,3-phenanthryne	8.10	7.95
1,2-phenanthryne	8.15	8.01
9,10-phenanthryne	8.20	8.06



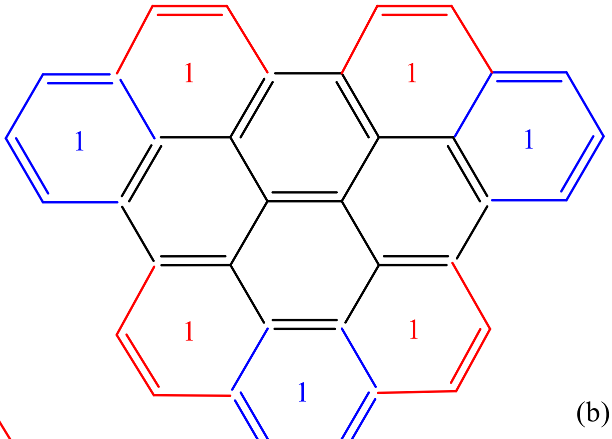
Supplementary Figure 2. Structures of distinct isomers of phenanthrynes and ethynyl-phenanthrenes.



Supplementary Figure 3. Calculated rate constants for the 4-phenanthrenyl + C_2H_2 reaction, including the total rate constants and those for the formation of pyrene and 4-ethynylphenanthrene (top) and branching ratios of the two product channels (bottom).



(a)



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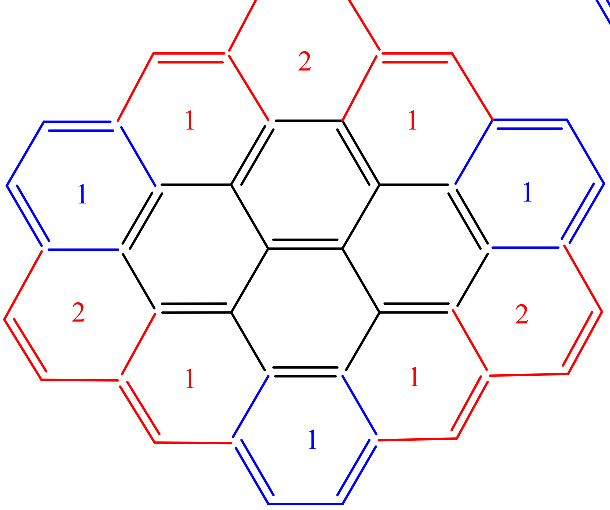
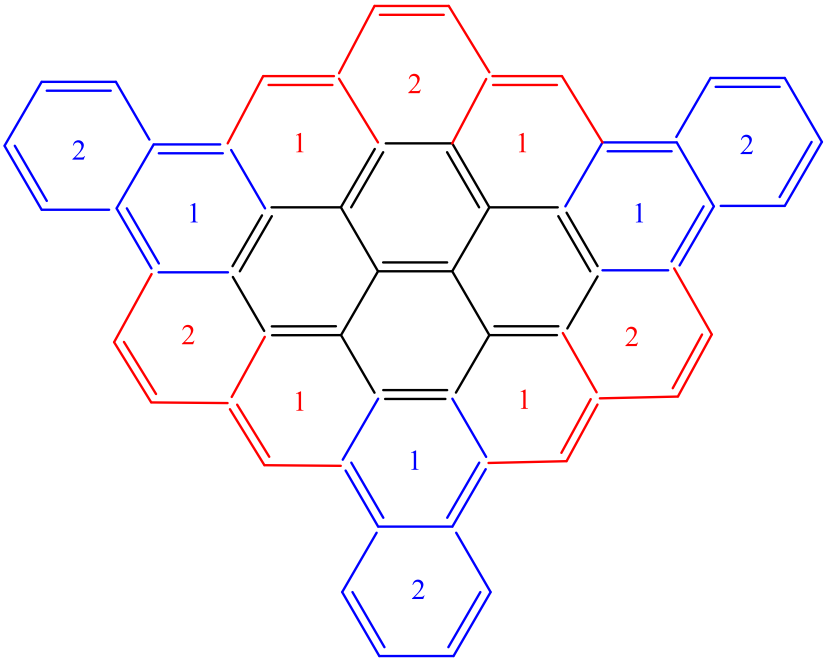
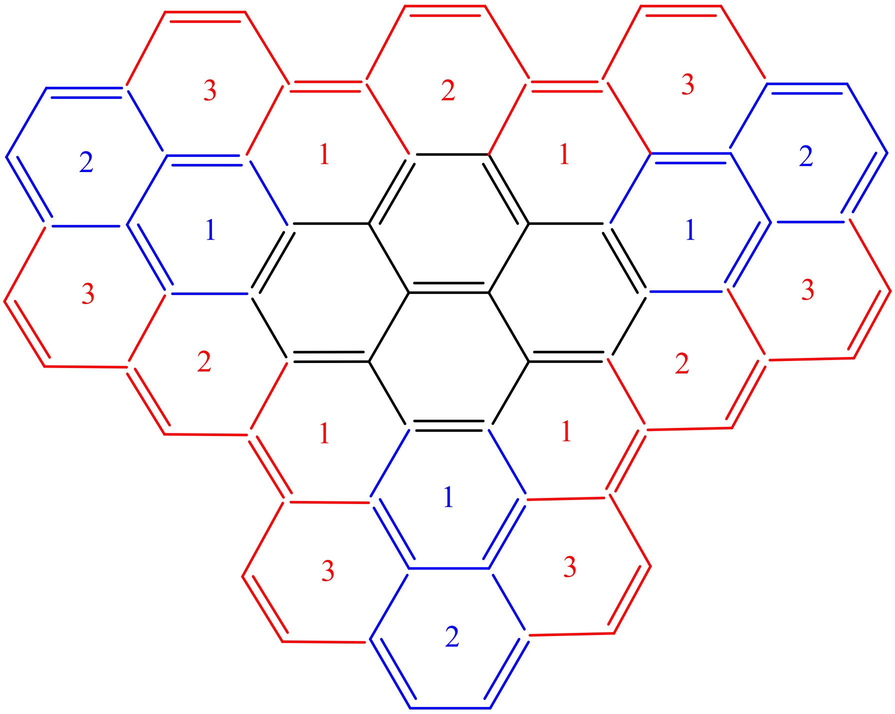


(c)

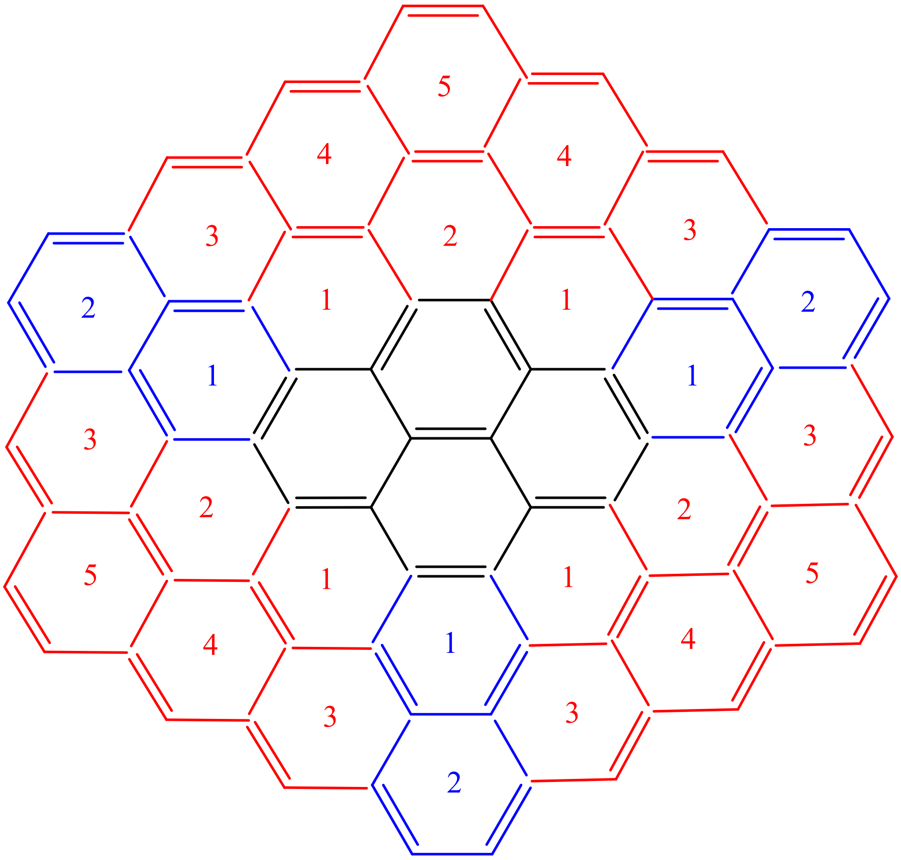


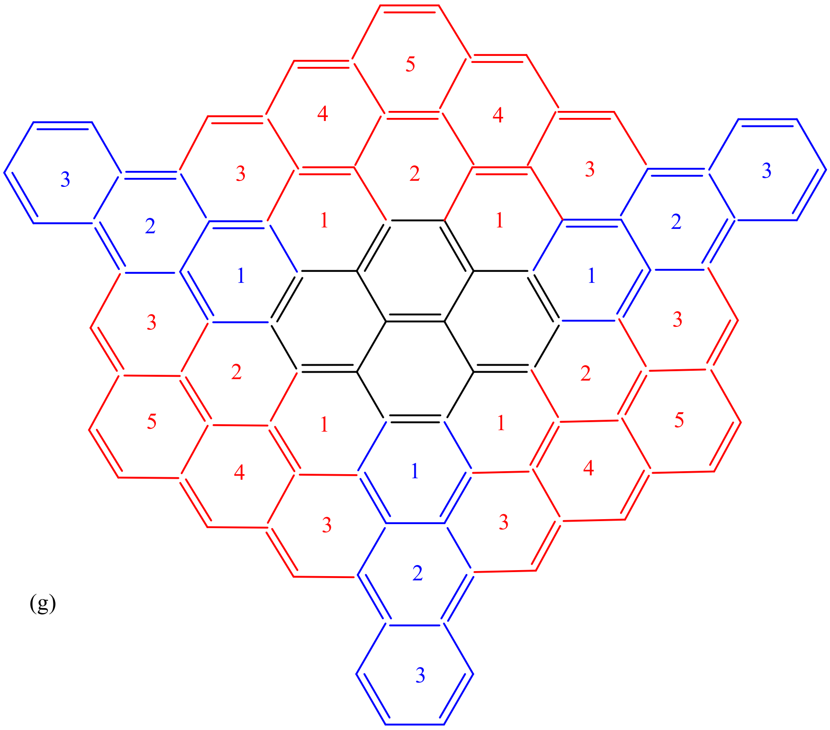
(d)

(e)



(f)

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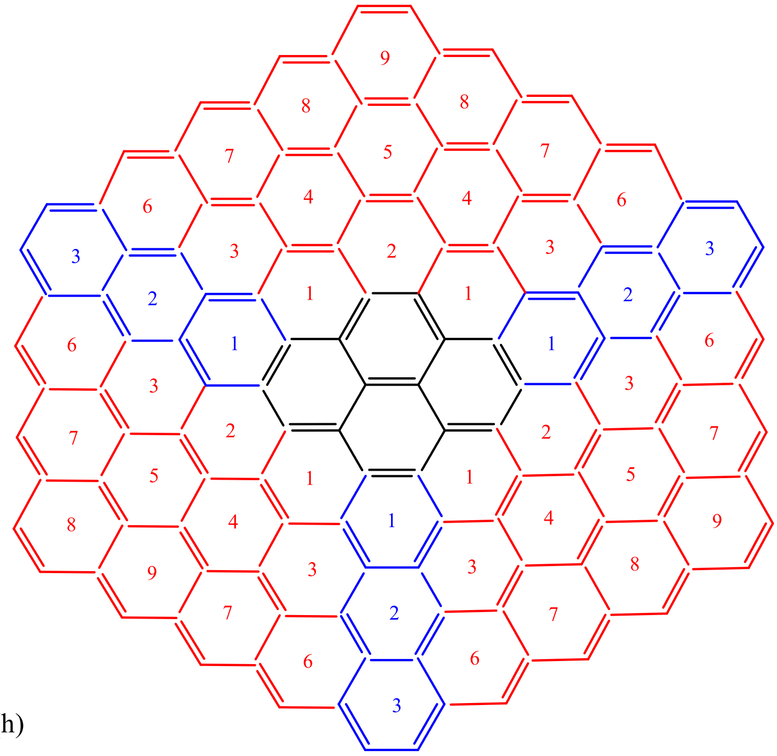
(g)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5 1 1 5
8 4 1 4 9
9 3 3 8
7 2 7
6 6
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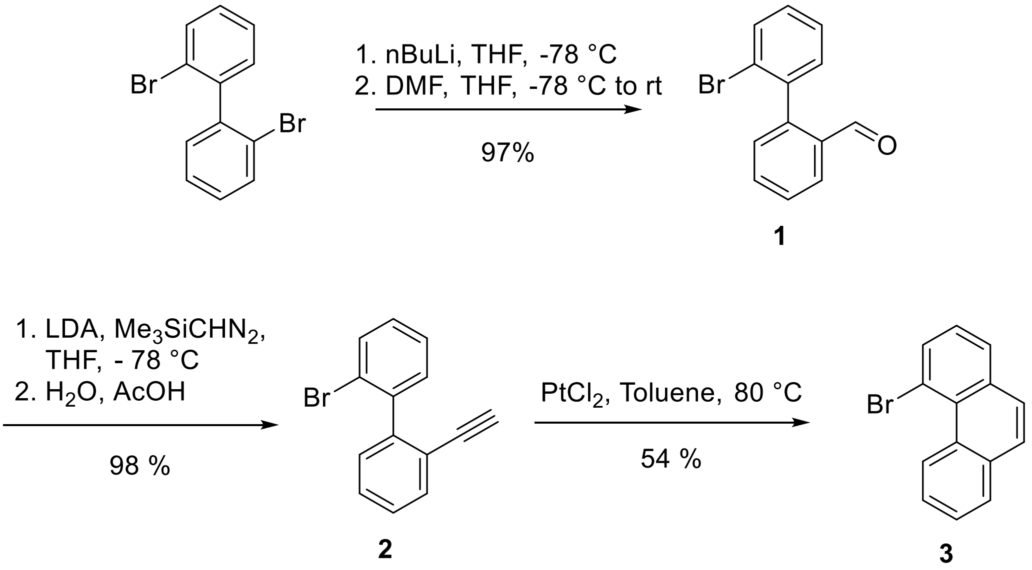
(h)

Supplementary Figure 4. Schematic representation of the central role of the pyrene molecule in the growth of two-dimensional graphene-type nanostructures involving HACA and HAVA pathways. The acetylene and vinylacetylene building blocks for the HACA and HAVA mechanism are color coded in red and blue, respectively. HAVA leads to an acene-type growth in three sectors of the pyrene molecule separated by 120°; HACA accounts for the bay closures. (a) first order perimeter growth (HAVA), (b) first order perimeter growth (HACA), (c) second order perimeter growth (HACA), (d) second order perimeter growth (HAVA), (e) third order perimeter growth (HACA), (f) fourth and fifth order perimeter growth (HACA). Once HACA closes the bays, HAVA initiates a third order perimeter growth (HAVA) (g) to supply new bays to be closed (h). The numbers in red and blue define the order of the HACA and HAVA growth, respectively.

Synthesis of 4-bromophenanthrene

Materials and General Methods. Unless otherwise stated, all manipulations of air and/or moisture sensitive compounds were carried out in oven-dried glassware, under an atmosphere of N_2. All solvents and reagents were purchased from Alfa Aesar, Spectrum Chemicals, Acros Organics, TCI America, and Sigma-Aldrich and were used as received unless otherwise noted. Organic solvents were dried by passing through a column of alumina and were degassed by vigorous bubbling of N_2 or Ar through the solvent for 20 min. Flash column chromatography was performed on SiliCycle silica gel (particle size 40–63 μm). Thin layer chromatography was carried out using SiliCycle silica gel 60 Å F-254 precoated plates (0.25 mm thick) and visualized by UV absorption. All ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVB-400, AVQ-400, AV-600 MHz spectrometers, and are referenced to residual solvent peaks ($CDCl_3$ ^{1}H NMR = 7.26 ppm, ^{13}C NMR = 77.16 ppm or CD_2Cl_2 ^{1}H NMR = 5.32 ppm, ^{13}C NMR = 54.00 ppm). ESI mass spectrometry was performed on a Finnigan LTQFT (Thermo) spectrometer in positive ionization mode.



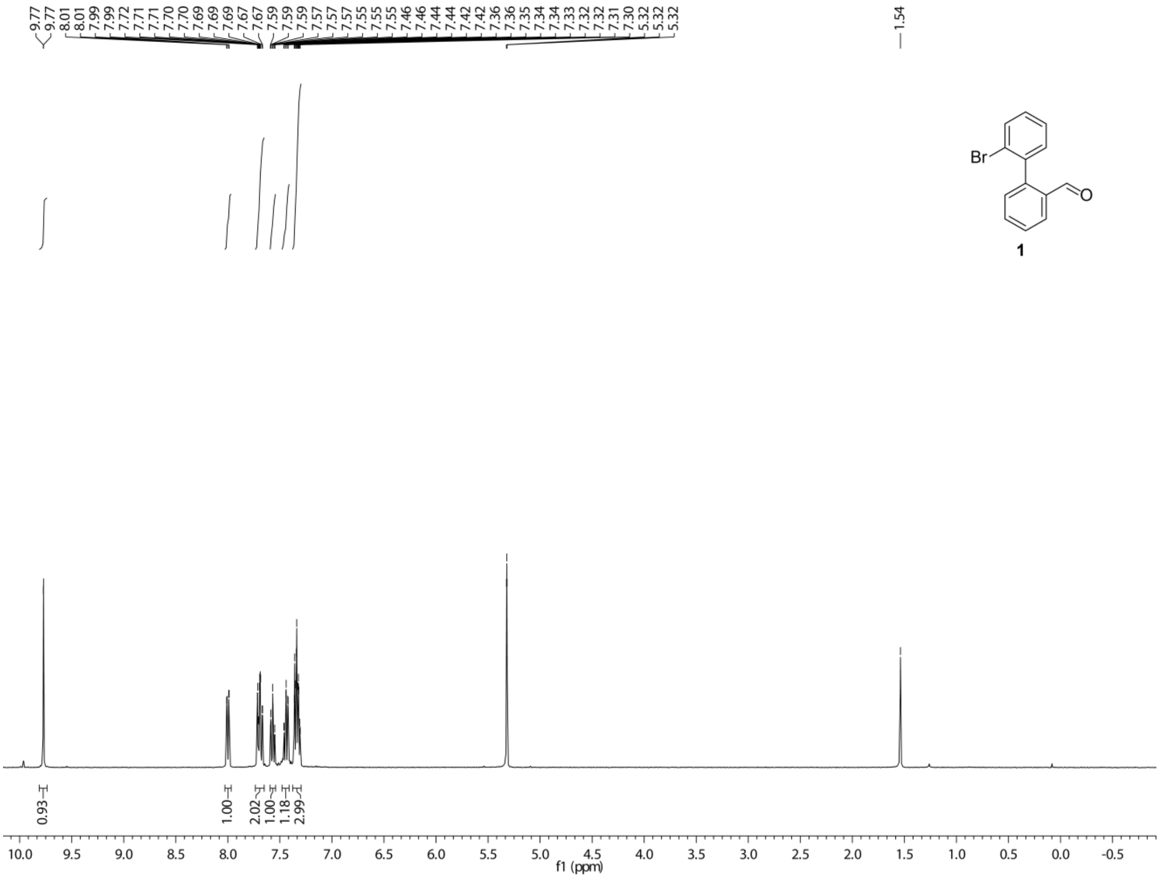
Supplementary Figure 5. Synthesis of 4-bromophenanthrene (3)

Synthetic procedures.

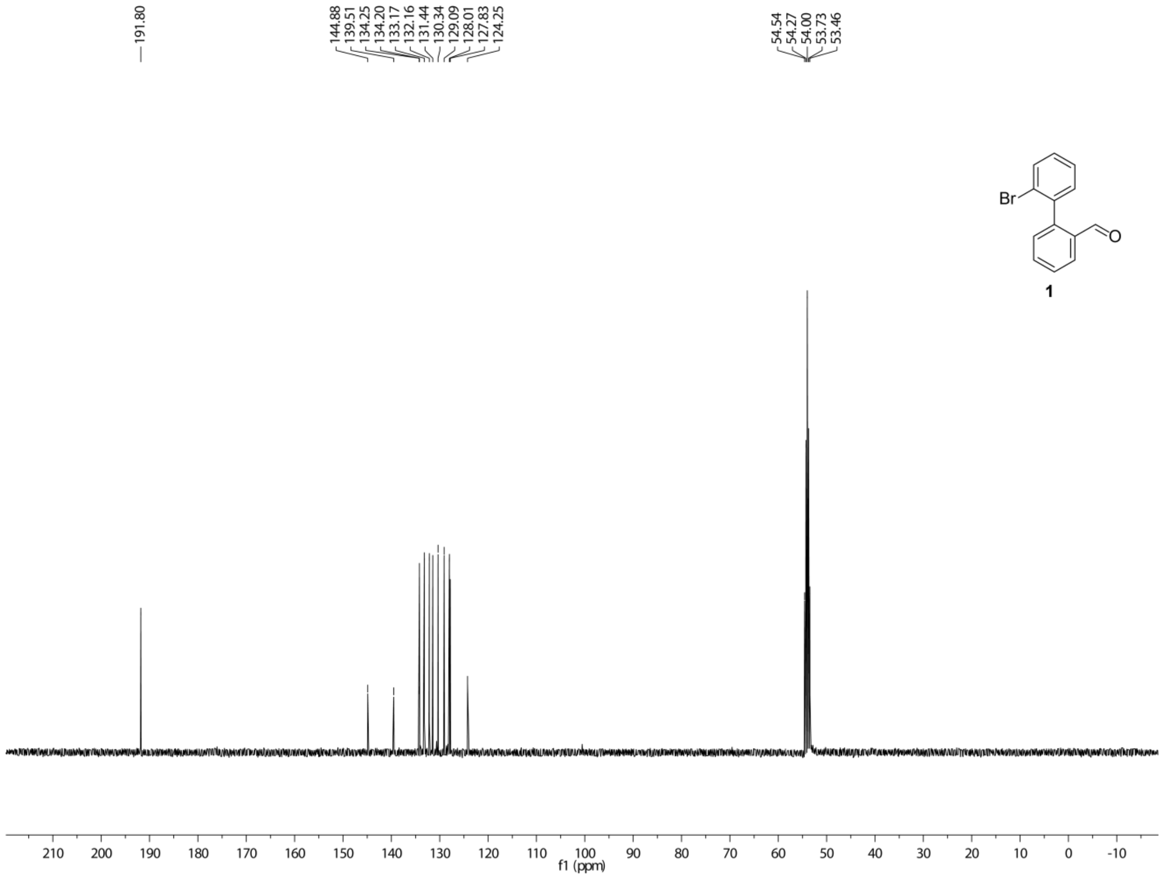
2'-bromo-[1,1'-biphenyl]-2-carbaldehyde (**1**) (Figure S5) A 250 mL Schlenk flask was charged under N_2 with 2,2'-dibromo-1,1'-biphenyl (4.46 g, 14.3 mmol) in dry THF (86 mL). The reaction mixture was cooled to –78 °C. n-BuLi (2.5M in hexanes, 5.7 mL, 14.3 mmol) was added dropwise over 15 min and the reaction mixture was stirred for 15 min at –78 °C. DMF (2.6 mL, 33.7 mmol) in dry THF (13 mL) was then added dropwise. The reaction mixture was warmed to 24 °C and stirred for 18 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (100 mL) and extracted with CH_2Cl_2. The combined organic phases were washed with H_2O and saturated aqueous NaCl, dried over $MgSO_4$, and concentrated on a rotary evaporator. Column chromatography (SiO_2; 0–2% EtOAc/hexane) yielded **1** (3.64 g, 13.9 mmol, 97%) as a colorless viscous oil that solidified into a colorless solid over time. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ = 9.77 (d, J = 0.8 Hz, 1H), 8.00 (dd, J = 7.7, 1.5 Hz, 1H), 7.74–7.65 (m, 2H), 7.57 (dddd, J = 7.6, 7.6, 1.1, 1.1 Hz, 1H), 7.44 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.38–7.30 (m, 3H) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 22 °C) δ = 191.8, 144.9, 139.5, 134.3, 134.2, 133.2, 132.2, 131.4, 130.3, 129.1, 128.0, 127.8, 124.3 ppm; FTMS (EI+) m/z: $[M–H]^+$ calcd. $[C_{13}H_8OBr]^+$ 259.9660; found 259.9670.

2-bromo-2'-ethynyl-1,1'-biphenyl (**2**) (Figure S5) A 100 mL Schlenk flask was charged under N_2 with LDA (2 M in THF/n-heptane/ethyl benzene, 8.4 mL, 16.7 mmol) in dry THF (7.2 mL). The reaction mixture was cooled to –78 °C and Me_3SiCHN_2 (2 M in diethyl ether, 8.4 mL, 16.7 mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 30 min. **1** (3.64 g, 13.9 mmol) in dry THF (17 mL) was added dropwise and the reaction mixture was stirred at 24 °C for 5 h. The reaction mixture was quenched with H_2O and AcOH until gas evolution stopped, and extracted with CH_2Cl_2. The combined organic phases were washed with H_2O and saturated aqueous NaCl, dried over $MgSO_4$, and concentrated on a rotary evaporator. Column chromatography (SiO_2; 0–2% CH_2Cl_2/hexane) yielded **2** (3.51 g, 13.7 mmol, 98%) as a colurless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ = 7.68 (dd, J = 8.0, 1.3 Hz, 1H), 7.62 (dd, J = 7.8, 1.4 Hz, 1H), 7.47–7.36 (m, 3H), 7.33 (dd, J = 7.6, 1.9 Hz, 1H), 7.30–7.24 (m, 2H), 3.01 (s, 1H) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 22 °C) δ = 144.2, 141.5, 133.0, 132.7, 131.4, 129.9, 129.3, 128.6, 127.8, 127.1, 123.5, 121.8, 82.3, 80.5 ppm; FTMS (EI+) m/z: $[C_{14}H_9Br]^+$ calcd. $[C_{14}H_9Br]^+$ 255.9888; found 255.9889.

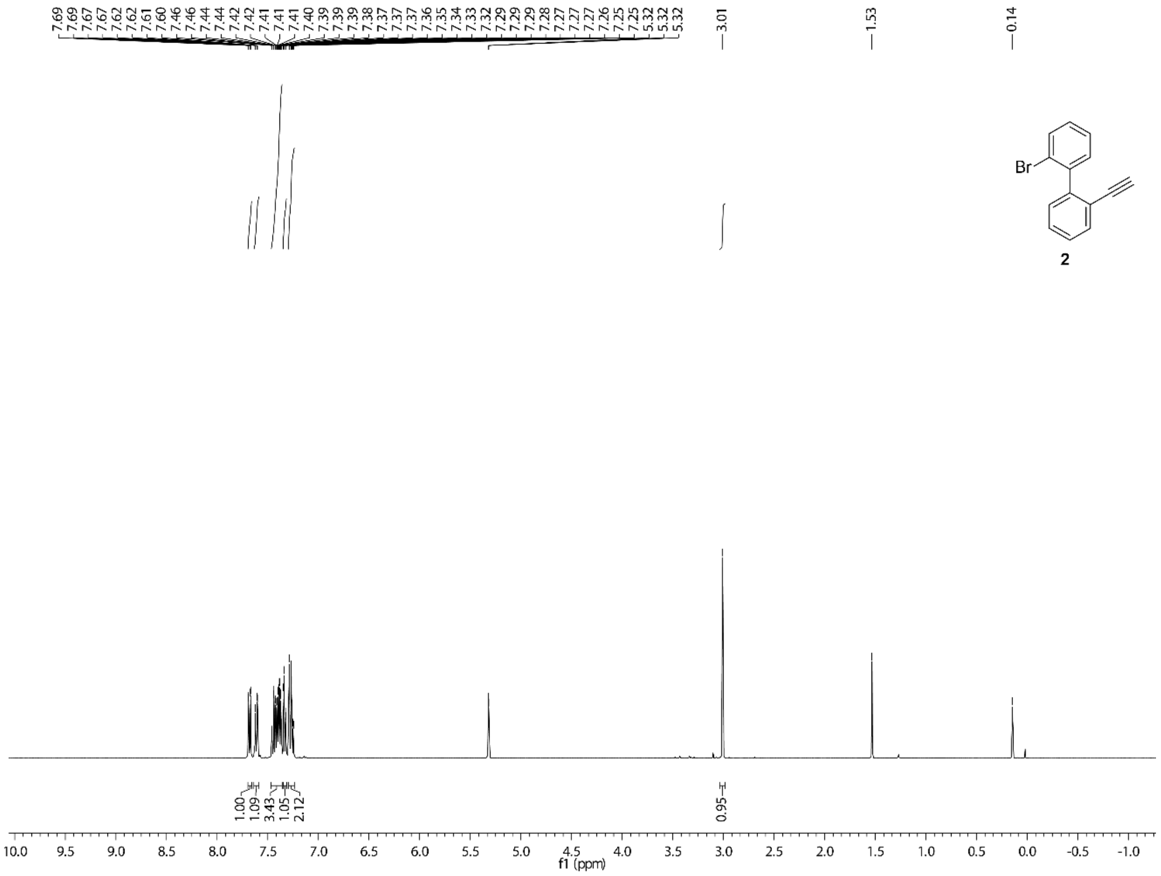
4-bromophenanthrene (**3**) (Figure S5) A 50 mL Schlenk flask was charged under N_2 with **2** (1.16 g, 4.51 mmol) and $PtCl_2$ (120 mg, 0.45 mmol) in dry toluene (22 mL). The reaction mixture was stirred at 80 °C for 24 h. The reaction was cooled to 24 °C and concentrated on a rotary evaporator. Column chromatography (SiO_2; hexanes) yielded **3** (623 mg, 2.42 mmol, 54 %) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ = 10.06–10.00 (m, 1H), 8.01 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.95–7.91 (m, 1H), 7.89 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.69–7.63 (m, 2H), 7.41 (dd, *J* = 7.7, 7.7 Hz, 1H) ppm; ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 22 °C) δ = 135.7, 135.3, 134.0, 130.2, 129.5, 129.1, 129.0, 128.7, 127.7, 127.6, 127.3, 127.2, 125.9, 119.9 ppm. The NMR spectra are shown in Figures S6-S11.



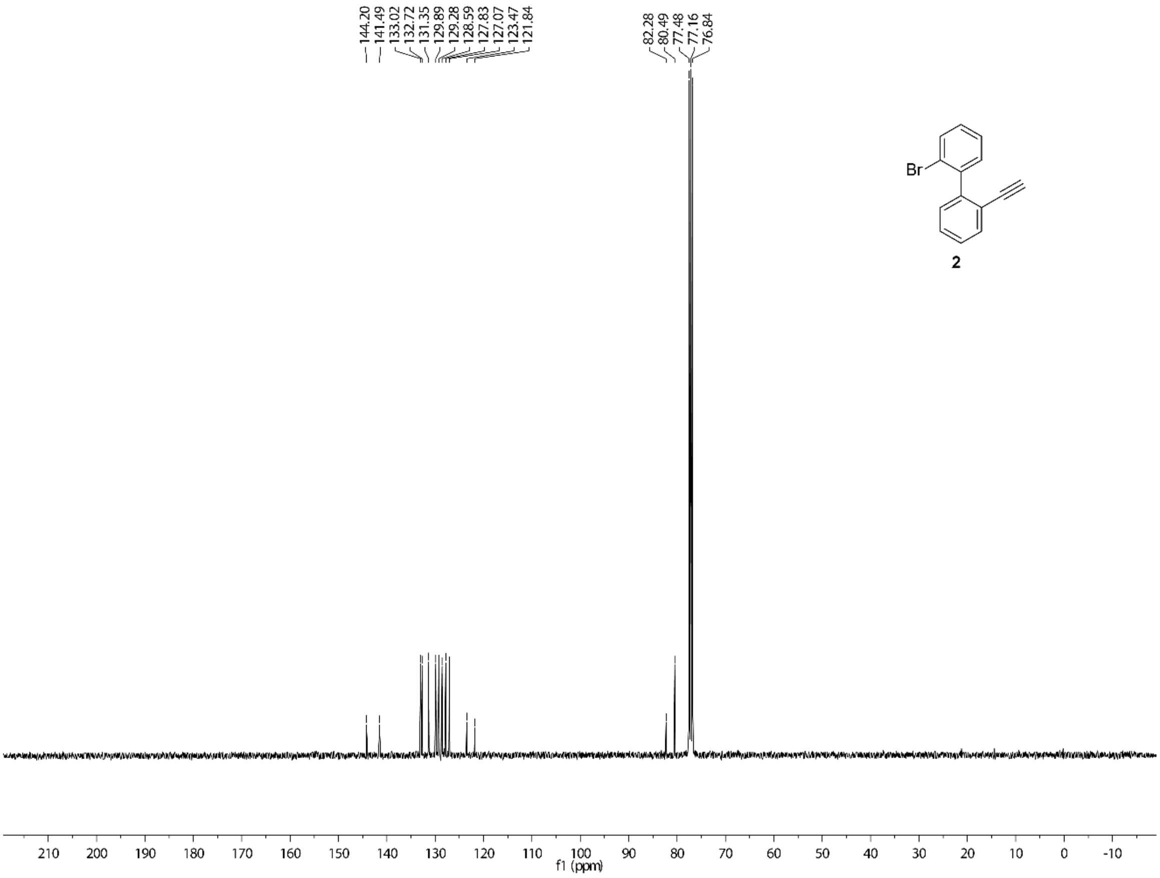
Supplementary Figure 6. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **1**.



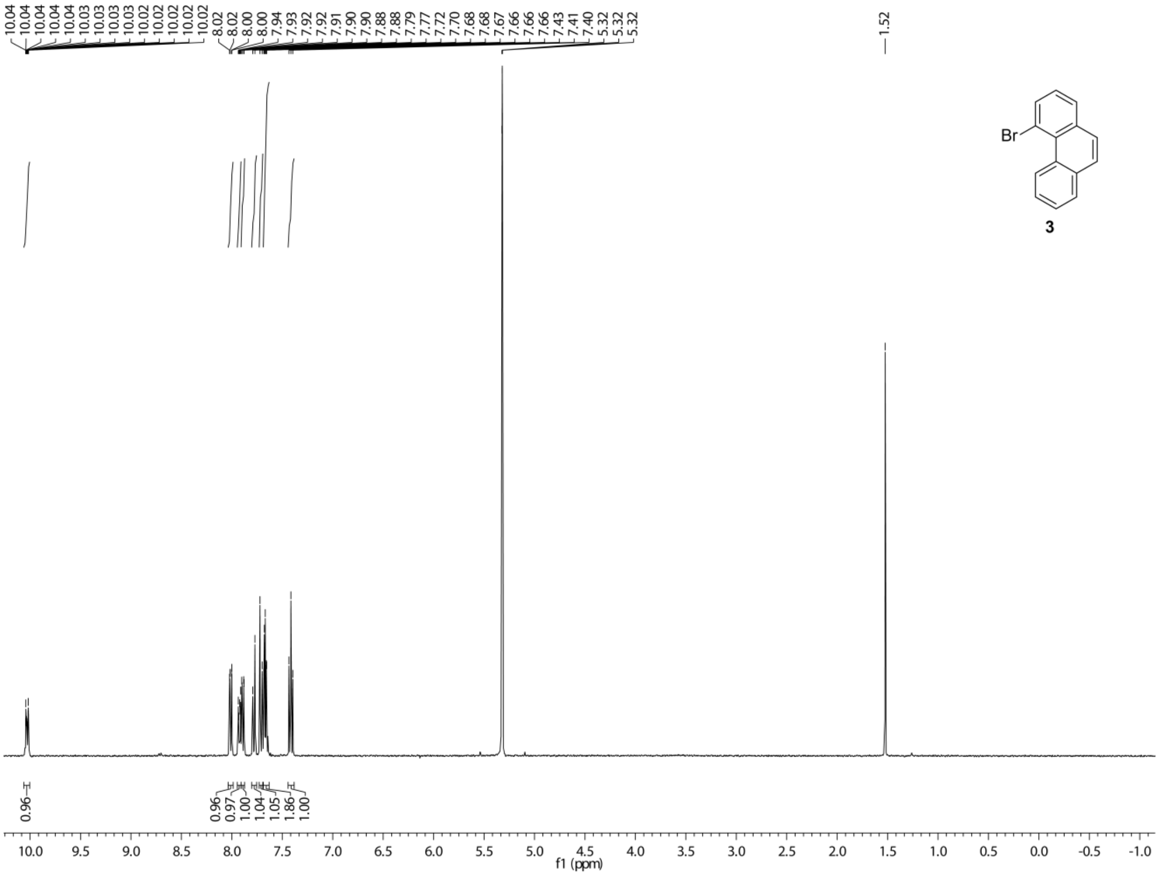
Supplementary Figure 7. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **1**



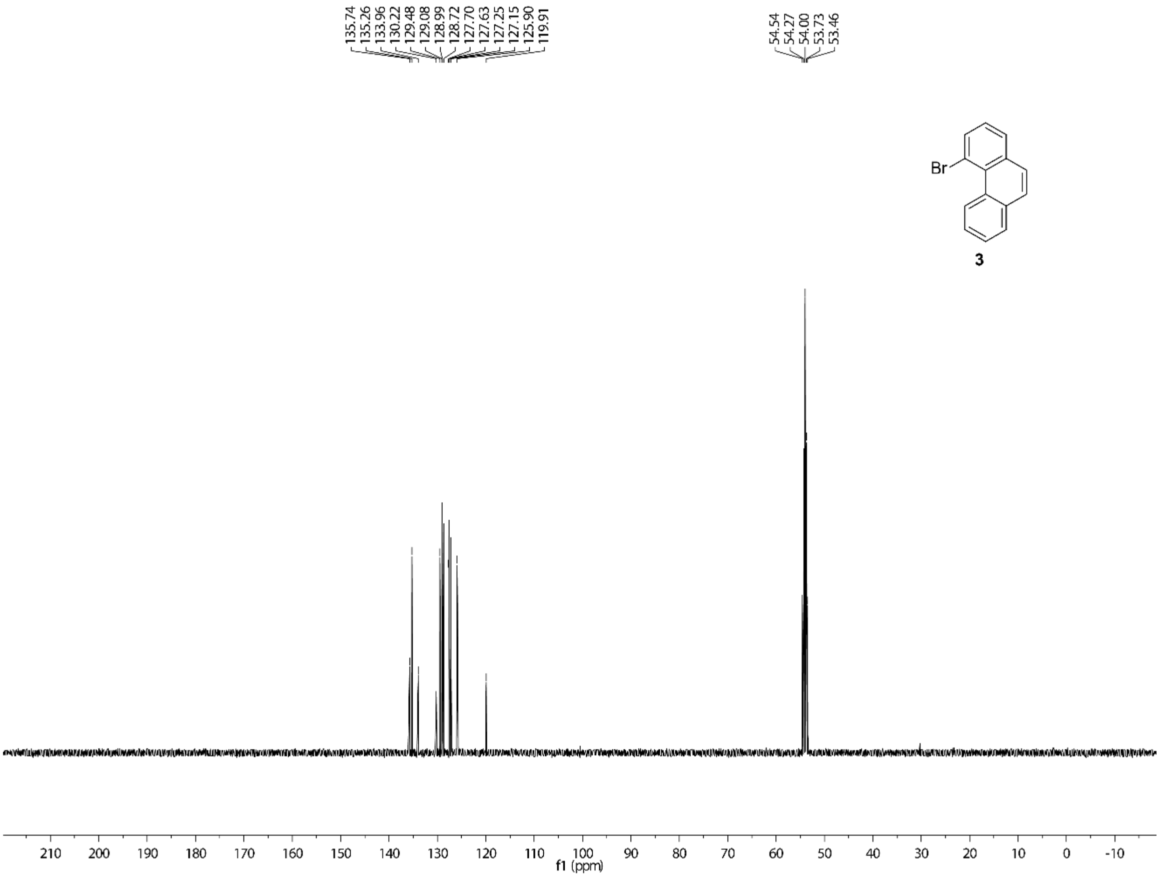
Supplementary Figure 8. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **2**.



Supplementary Figure 9. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2**



Supplementary Figure 10. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **3**.



Supplementary Figure 11. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **3**