Supporting Information

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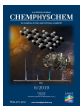

Gas-Phase Synthesis of Triphenylene ($C_{18}H_{12}$)

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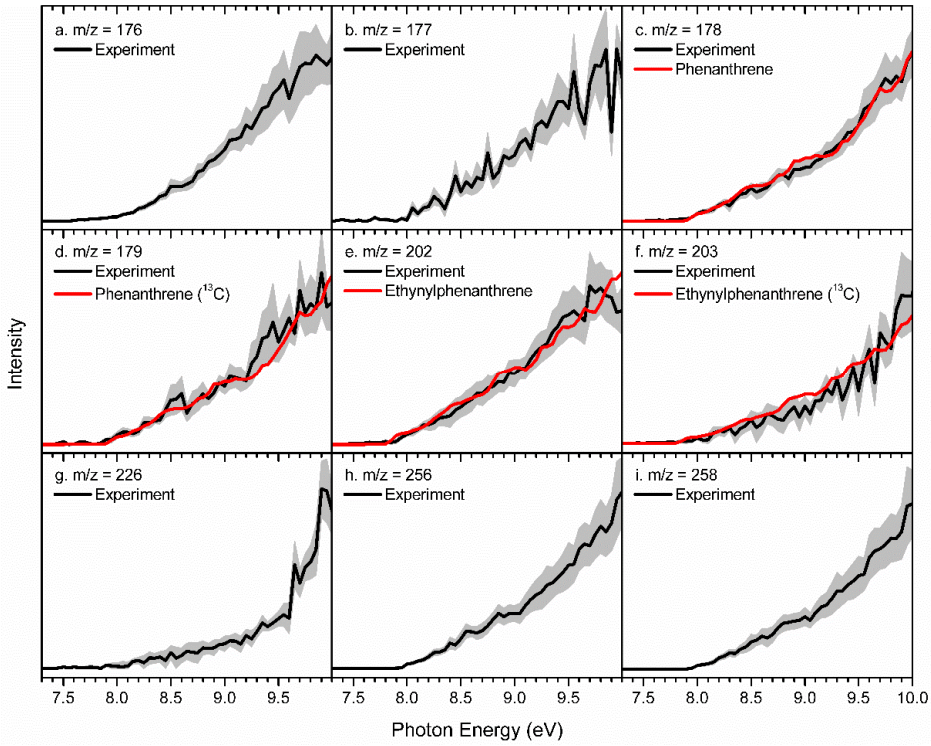


Figure S1. PIE curves of distinct ions detected in 9-phenanthrenyl - vinylacetylene system.

Signal at *m/z* = 202 and 203 can be associated with $C_{16}H_{10}$ molecule(s) and the ^{13}C-isotopially substituted counterpart(s) $^{13}CC_{15}H_{10}$, respectively. After scaling, both data sets are superimposable verifying that signals at *m/z* = 202 and 203 originate from the same (isotopically substituted) isomer. This signal can be fit with the PIE curve of ethynylphenanthrene. Since the adiabatic ionization energies of distinct ethynylphenanthrene isomers are around 7.8 eV, and their PIE curves are similar, the present work does not allow an identification of the specific ethynylphenanthrene isomer(s) formed. Here, at elevated temperatures, vinylacetylene can be pyrolyzed at a level of about 2% forming two acetylene molecules, which can react with 9-phenanthrene via acetylene addition followed by hydrogen loss yielding ethynylphenanthrene.[1] Alternatively, acetylene can be formed as a product of the H + C_4H_4 reaction. Note that acephenanthrylene (an isomer of ethynylphenanthrene which can potentially be formed by a five-member ring closure and aromatization via hydrogen atom loss following acetylene addition) was not observed under present experimental conditions. Signal at *m/z* = 177 can be connected to the 9-phenanthrenyl radical. *m/z* = 176 and *m/z* = 178 origin from the hydrogen atom loss and hydrogen atom addition of 9-phenanthrenyl leading to phenanthryne isomers and phenanthrene, respectively. *m/z* = 178

and 179 can be both fit with the reference PIE curve of phenanthrene, verifying they are both attributed to phenanthrene with *m/z* = 179 resembling the ^{13}C-substituted phenanthrene.

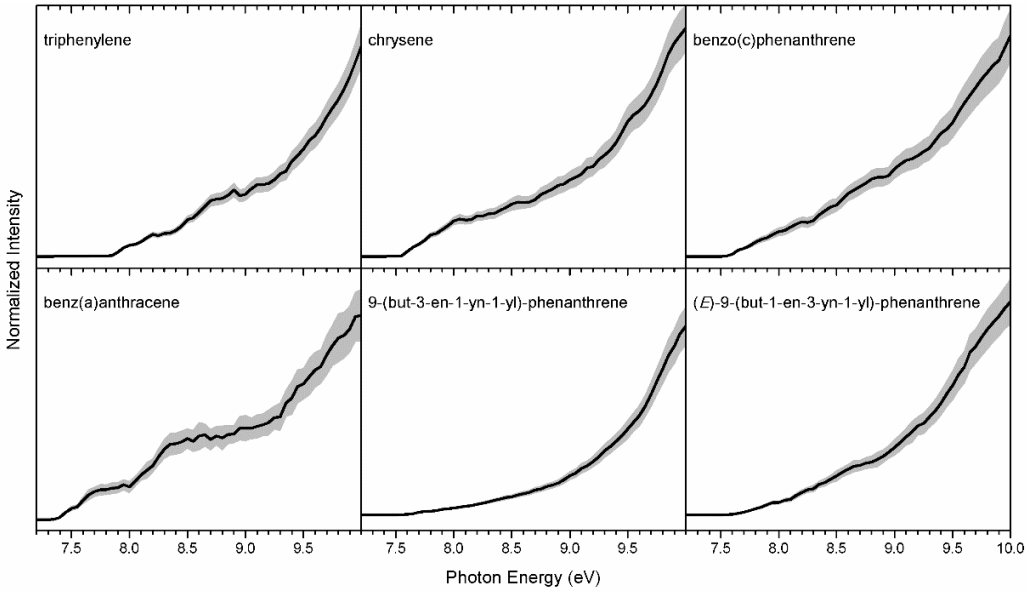


Figure S2. PIE calibration curves for distinct $C_{18}H_{12}$ isomers: triphenylene, chrysene, benzo(c)phenanthrene, benz(a)anthracene, 9-(but-3-en-1-yn-1-yl)-phenanthrene and (*E*)-9-(but-1-en-3-yn-1-yl)-phenanthrene.

These PIE calibration curves were newly recorded in this work and are shown as black along with the error limits (grey area). The adiabatic ionization energies of these isomers are 7.70 ± 0.05, 7.55 ± 0.05, 7.55 ±0.05, 7.35 ± 0.05 eV, 7.60 ± 0.05 eV and 7.60 ± 0.05 eV, respectively, comparing with literature values of 7.84 ± 0.01[2], 7.60 ± 0.01[3], 7.60 ± 0.02[4] and 7.41 ± 0.02[4] for the first four isomers. The overall error bars consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

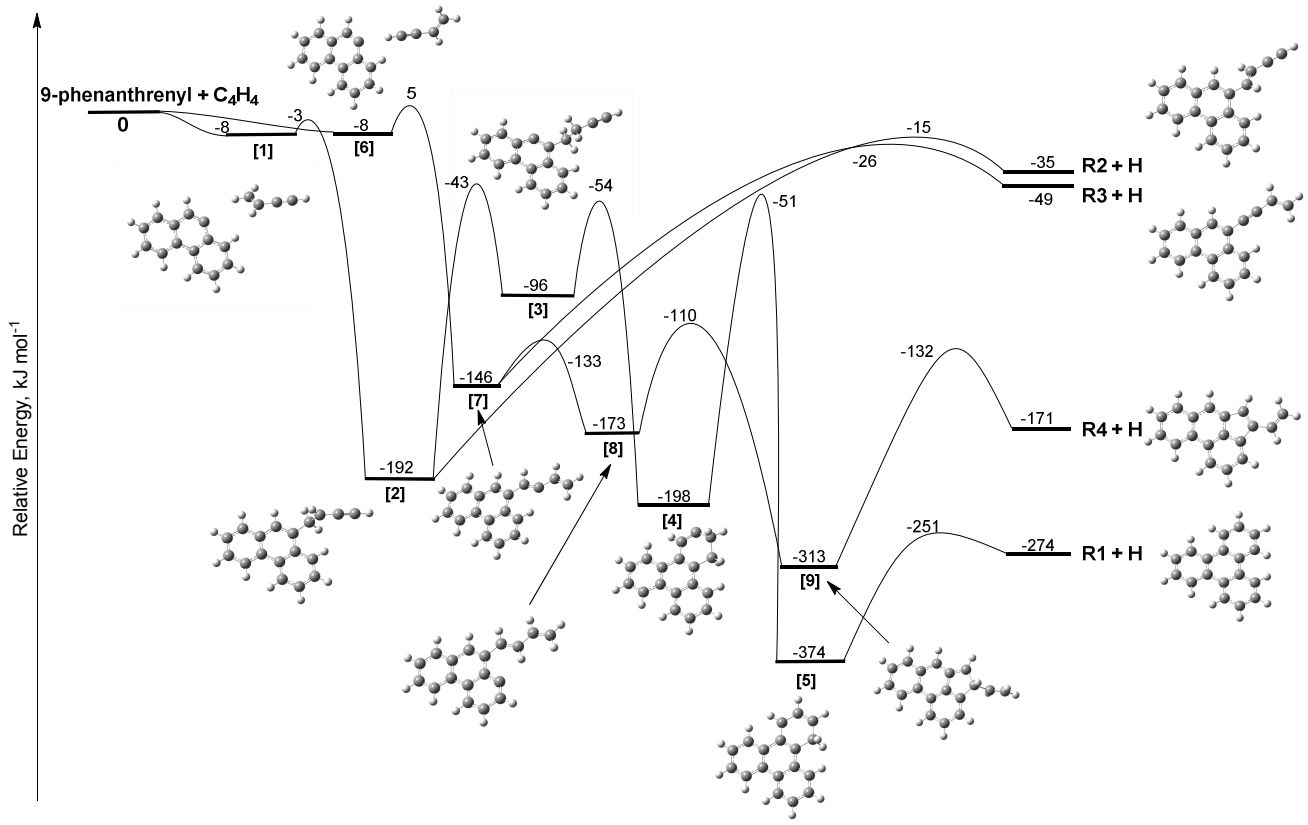


Figure S3. Potential energy surface (PES) for the 9-phenanthrenyl $[C_{14}H_9]^{\bullet}$ reaction with vinylacetylene (C_4H_4) including an additional energetically favorable pathway forming a product R4 (4-vinylacephenanthrylene) calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. The relative energies are given in kJ mol^{-1}. Since the calculated adiabatic ionization energy of R4 is 7.35±0.10 eV, a small contribution of this product to the experimental PIE at energies below 7.6 eV (see Fig. 3) cannot be completely ruled out.

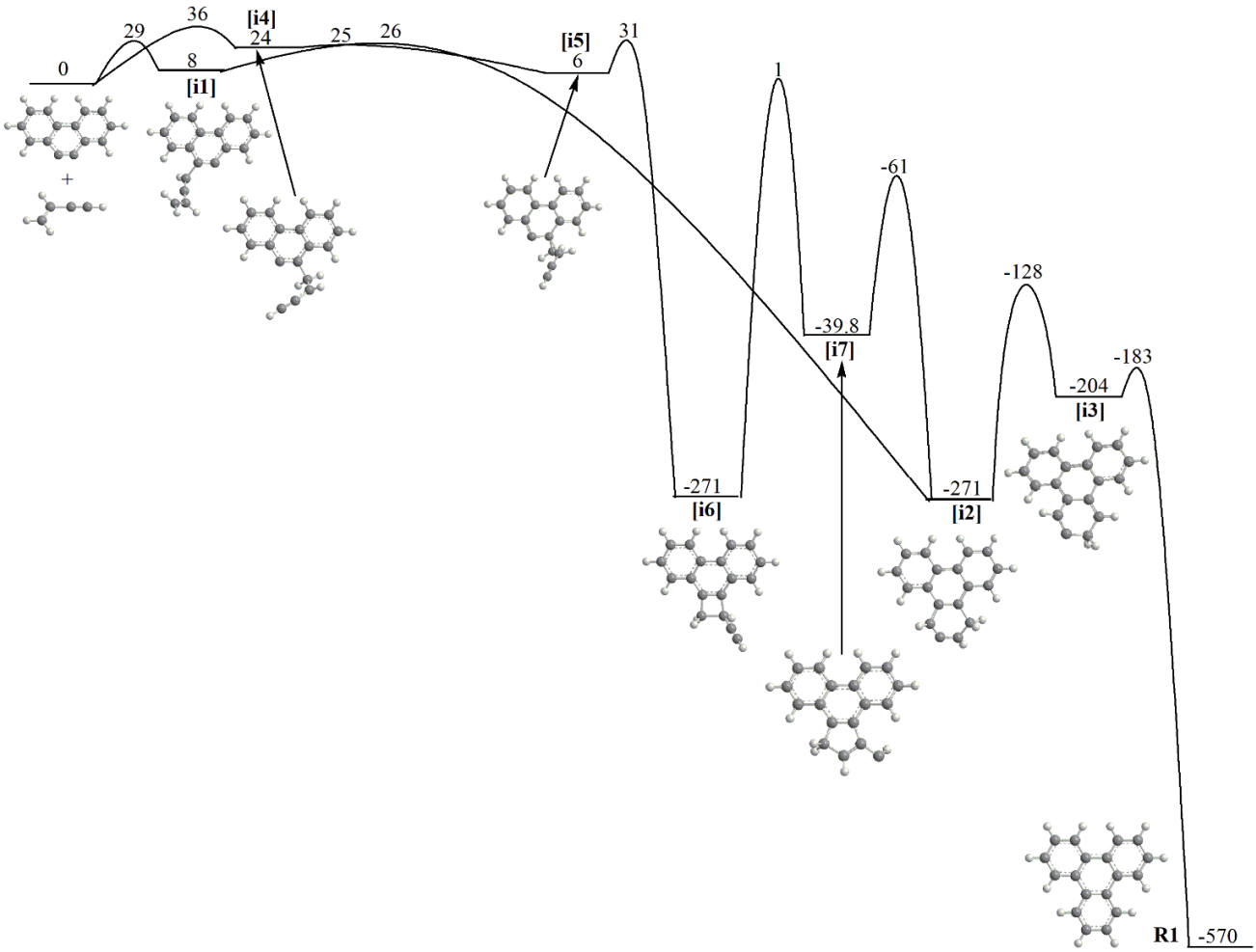


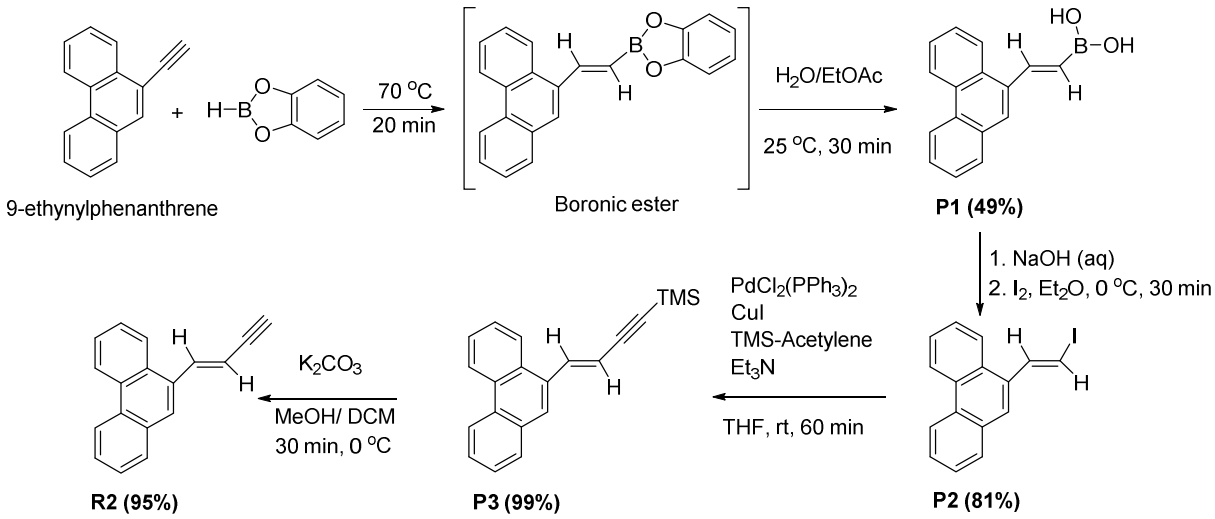
Figure S4. PES for the phenanthryne ($C_{14}H_8$) reaction with vinylacetylene (C_4H_4) calculated at the B3LYP/6-311G(d,p) level of theory. The relative energies are given in kJ mol^{-1}.

The reaction begins with the addition of vinylacetylene to the triple bond of phenanthryne. When the addition occurs by the acetylenic end of C_4H_4, the formation of the initial complex **[i1]** is immediately followed by six-member ring closure to **[i2]** and then, two H migrations in the new ring via **[i3]** lead to its aromatization and the formation of triphenylene (**R1**). The highest barrier on the phenanthryne + C_4H_4 → **[i1]** → **[i2]** → **[i3]** → **R1** pathway, 29 kJ mol^{-1}, is found for the entrance step. Alternatively, when the addition occurs by the vinylic end of C_4H_4 to form **[i4]** via a 36 kJ mol^{-1} barrier, the ring closure mechanism is more complex; a three-member ring is formed first in **[i5]** and then it stepwisely expands to four- (**[i6]**), five- (**[i7]**), and finally six-member ring in **[i2**]. No pathways involving H migrations without the extra ring closure and leading to **R2** or **R3** could be found and thus, the phenanthryne plus vinylacetylene reaction cannot account for these products observed in experiment.

The mechanism explored here deserves further detailed consideration at a higher level of theory and rate constant calculations, especially for the prototype benzyne (C_6H_4) + vinylacetylene reaction, because our results demonstrate that the reactions of aromatic alkynes with C_4H_4 may represent a plausible mechanism for PAH growth under high-temperature (combustion) conditions. However, due to the significant entrance barriers, this mechanism is not feasible in the interstellar medium.

Synthesis of (*E*)-9-(But-1-en-3-yn-1-yl)-phenanthrene (R2)

(*E*)-9-(But-1-en-3-yn-1-yl)-phenanthrene **(R2)** was synthesized by stereoselective conversion of 9-ethynylphenanthrene into *trans*-1-alkenyliodide via hydroboration-hydrolysis-iodination[5] sequence followed by Sonogashira cross-coupling reaction with (trimethylsilyl)acetylene (**Scheme S1**).



Scheme S1. Synthesis of (*E*)-9-(but-1-en-3-yn-1-yl)-phenanthrene (**R2**).

1. (*E*)-(2-(Phenanthren-9-yl)-vinyl)-boronic acid (P1)

9-Ethynylphenanthrene (505.5 mg, 2.5 mmol) and catecholborane (266 µL, 300 mg, 2.5 mmol) were placed in a flame-dried flask under N_2 at ambient temperature and the reaction mixture were stirred for 20 min at 70 °C. Within this 20 min, the reaction mixture forms a small lump and was kept few minutes at ambient temperature. Then H_2O/EtOAc (1:1; 10 mL) were added into the reaction mixture and stirred for 30 min at 25 °C to effect the hydrolysis of boronic ester. The reaction mixture was extracted with EtOAc, organic layer separated and the aqueous layer was extracted with EtOAc two more times. The combined organic layer was dried (Na_2SO_4) and evaporated. The residue was column chromatographed (20-40% EtOAc in hexane) to give **P1** (301 mg, 49%) as white powder: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.32 (d, J = 18.0 Hz, 1H), 7.63-7.76 (m, 4H), 7.98 (s, 2H), 8.04 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 18.0 Hz, 1H), 8.32-8.34 (m, 1H), 8.79-8.82 (m, 1H), 8.88-8.90 (m, 1H); ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 122.66, 122.86, 123.36, 123.55, 124.12, 124.15, 126.98, 127.05, 128.90, 129.81, 129.85, 129.88, 131.23, 134.26, 143.09, 145.27.

2. (*E*)-9-(2-iodovinyl)-phenanthrene (P2)

The boronic acid **P1** (100 mg, 0.40 mmol) was dissolved in 5 mL Et_2O in a 50 mL flask and cooled to 0 ^oC. Then aqueous NaOH (400 µL, 3 N, 1.2 mmol) was added dropwise followed by elemental iodine (121.8 mg, 0.48 mmol) dissolved in 5 mL Et_2O, while stirring at 0 ^oC. The reaction mixture was stirred for 30 min at 0 ^oC and the excess I_2 was destroyed by aqueous $Na_2S_2O_3$ solution. The reaction mixture was extracted with Et_2O and organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined organic layer was dried (Na_2SO_4) and evaporated. The residue was column chromatographed (*n*-hexane) to give **P2** (108 mg, 81%) as white powder: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.93 (d, J = 14.8 Hz, 1H), 7.58-7.71 (m, 4H), 7.75 (s, 1H), 7.89 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 14.4 Hz, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 122.63, 122.85, 123.13, 123.37, 124.72, 125.53, 125.66, 127.06, 128.94, 129.67, 130.49, 130.55, 131.65, 134.85, 143.58, 143.61.

3. (*E*)-Trimethyl-(4-(phenanthren-9-yl)-but-3-en-1-yn-yl)-silane (P3)

$Pd(PPh_3)_2Cl_2$ (8.4 mg, 0.012 mmol) and Cu(I)I (4.6 mg, 0.024 mmol) were added to dry THF (5 mL) in a flame-dried round bottom flask equipped with a stir bar under N_2 at 0 ^oC (ice-bath). Then **P2** (100 mg, 0.30 mmol) was added followed by TMS-acetylene (62 µL, 44 mg, 0.45 mmol) and Et_3N (84 µL, 61 mg, 0.60 mmol). The resulting mixture was allowed to warm up to ambient temperature and was stirred for 1h. [progress of the reaction was monitored by TLC (*n*-hexane)]. Volatiles were evaporated and the residue was column chromatographed (*n*-hexane) to give **P3** as light yellow gummy solid (90 mg, 99%).^1H NMR: ($CDCl_3$, 400 MHz) δ 0.30 (s, 9H), 6.34 (d, J = 16.0 Hz, 1H), 7.58-7.67 (m, 4H), 7.81 (d, J = 16.0 Hz, 1H), 7.85 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.72 (d, J = 9.2 Hz, 1H).

4. (*E*)-9-(But-1-en-3-yn-1-yl)-phenanthrene (R2)

Anhydrous K_2CO_3 (41 mg, 0.3 mmol) was added to a stirred solution of **P3** (80 mg, 0.27 mmol) in 4 mL MeOH/DCM (1:1) at room temperature. After 30 min, volatiles were evaporated and the residue was column chromatographed (*n*-hexane) to give **R2** (58 mg, 95%) as light yellow powder. ^1H NMR: ($CDCl_3$, 400 MHz) δ 3.12 (d, J = 2.4 Hz, 1H), 6.29 (dd, J = 16.0, 2.4 Hz, 1H), 7.58-7.67 (m, 4H), 7.83-7.90 (m, 3H), 8.13-8.16 (m, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.72-8.74 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ

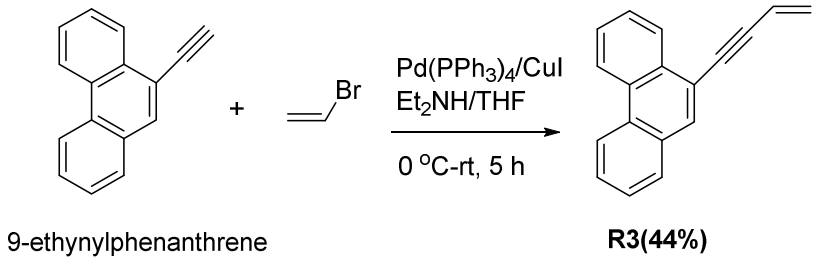
79.17, 83.13, 110.41, 122.61, 122.85, 123.21, 123.38, 124.55, 125.10, 126.99, 129.07, 130.10, 130.53, 131.80, 131.57, 132.57, 141.05, 141.13.

In summary, treatment of 9-ethynylphenanthrene with catecholborane at 70 ^{o}C form intermediary boronic ester, which was hydrolyzed with H_2O to give *trans*-alkenylboronic acid, **P1** in 49% yield after purification on silica gel column. Treatment of the purified (catechol free) **P1** in ether solution with iodine (1.2 equiv) in the presence of aqueous NaOH (3.0 equiv) at 0 ^{o}C provided alkenyliodide **P2** (81%). Subsequent Sonogashira coupling of **P2** with (trimethylsilyl)acetylene yielded **P3** (99%), which on desilylation with K_2CO_3 in MeOH/DCM gave desired **R2** (95% yield). It is noteworthy that our attempts to synthesize alkenyl bromide analogue of **P2** directly from 9-ethynylphenanthrene by adopting reported hydrobromination conditions[6] failed giving instead the alkene analogue.

Synthesis of 9-(But-3-en-1-yn-1-yl)-phenanthrene (R3)

9-(but-3-en-1-yn-1-yl)-phenanthrene (**R3**) was synthesized by Sonogashira coupling of 9-ethynylphenanthrene with vinyl bromide (**Scheme S2**). $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Cu(I)I (3.8 mg, 0.02 mmol) were placed in the flame-dried flask under N_2 at 0 °C (ice-bath). Then Et_2NH (0.65 mL, 460 mg, 6.29 mmol) and vinyl bromide (1.0 M in THF; 0.65 mL, 0.65 mmol) were added. Next, commercially available 9-ethynylphenanthrene (101.1 mg, 0.5 mmol) dissolved in dry THF (1 mL) was added slowly via a syringe pump (over 3 h) and the resulting mixture was allowed to warm up to ambient temperature (30 min) and was stirred for another 2 h. Volatiles were evaporated and the residue was dissolved in EtOAc and filtered. The filtrate was collected with the solvent evaporated. The residue was column chromatographed (*n*-hexane) to give **R3** (50 mg, 44%) as white powder: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.65 (dd, J = 11.2, 2.0 Hz, 1H), 5.89 (dd, J = 17.6, 2.0 Hz, 1H), 6.20 (dd, J = 17.2, 11.2 Hz, 1H), 7.58-7.62 (m, 1H), 7.65-7.73 (m, 3H), 7.85 (d, J = 7.6 Hz, 1H), 8.01 (s, 1H), 8.42-8.45 (m, 1H), 8.65-8.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 88.39, 92.75, 117.42, 117.47, 119.70, 122.66, 122.82, 122.98, 127.14, 127.39, 127.70, 128.74, 130.23, 130.45, 131.21, 131.37, 132.05, 132.09.

It is noteworthy that regular coupling conditions, as reported recently for the synthesis of the analogous (but-3-en-1-yn-1-yl)-benzene,[7] yielded mainly dimerization and/or polymerization products of 9-ethynylphenanthrene.



Scheme S2. Synthesis of 9-(but-3-en-1-yn-1-yl)-phenanthrene (**R3**).

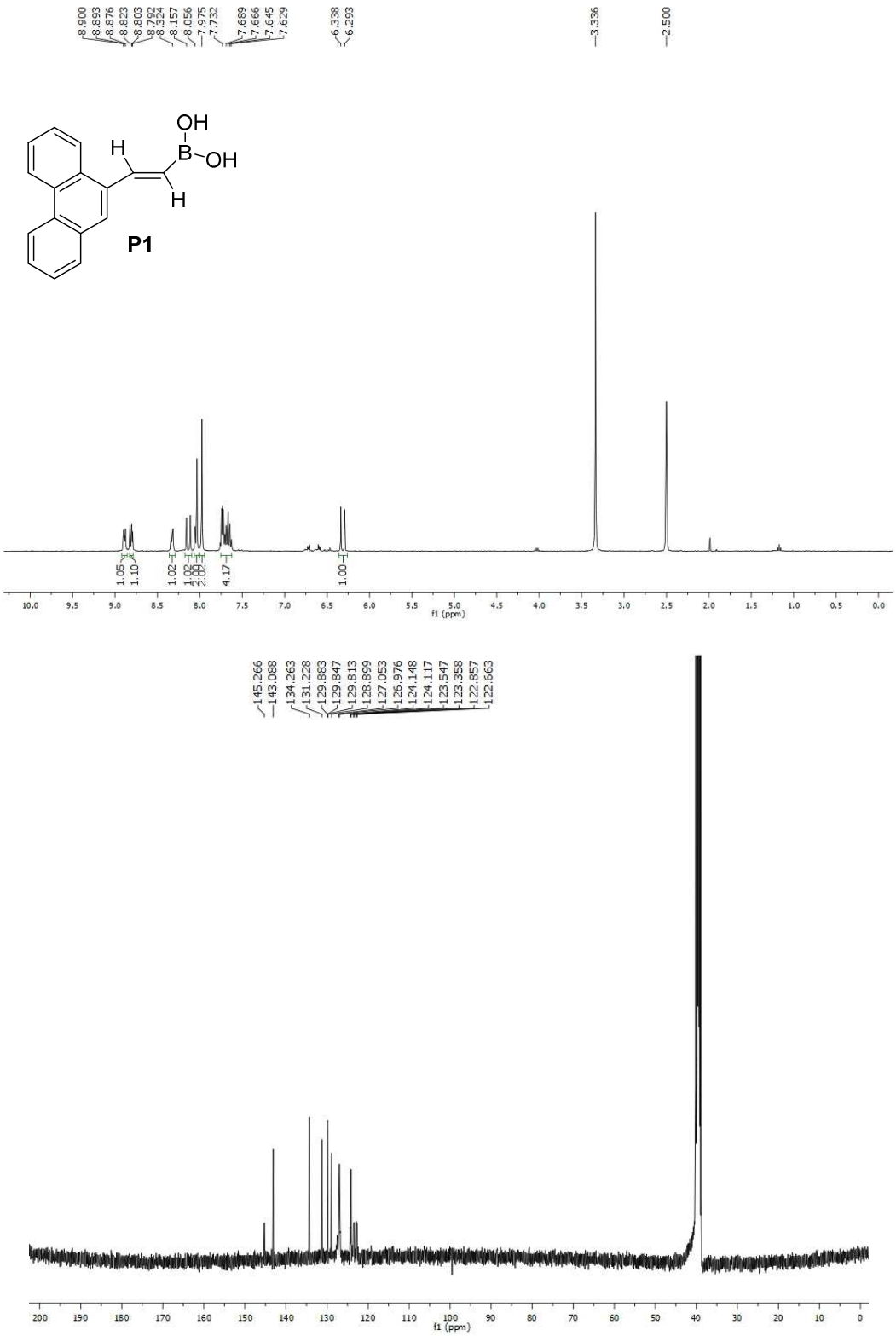


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of compound **P1** in DMSO-d_6.

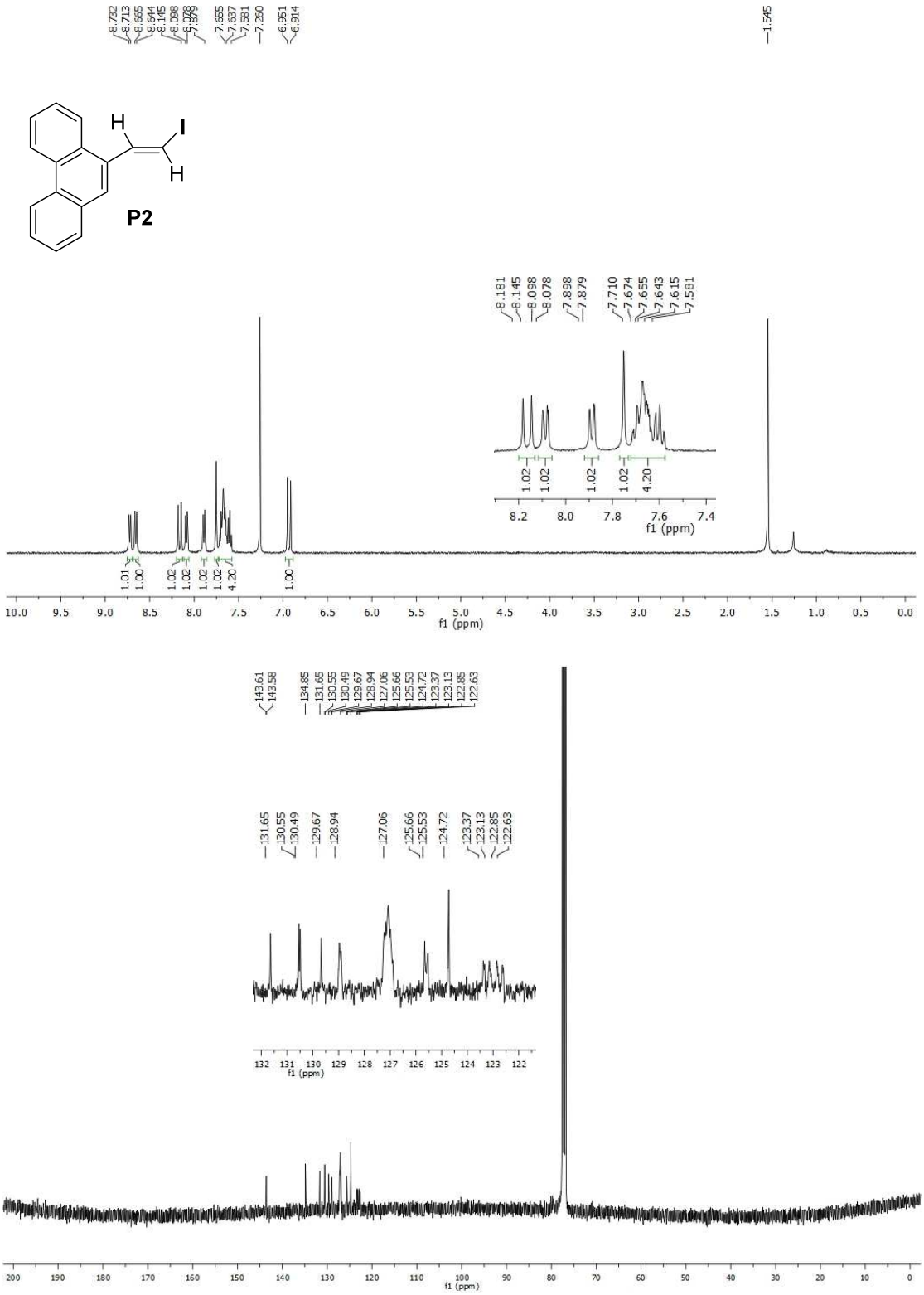


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of compound **P2** in $CDCl_3$.

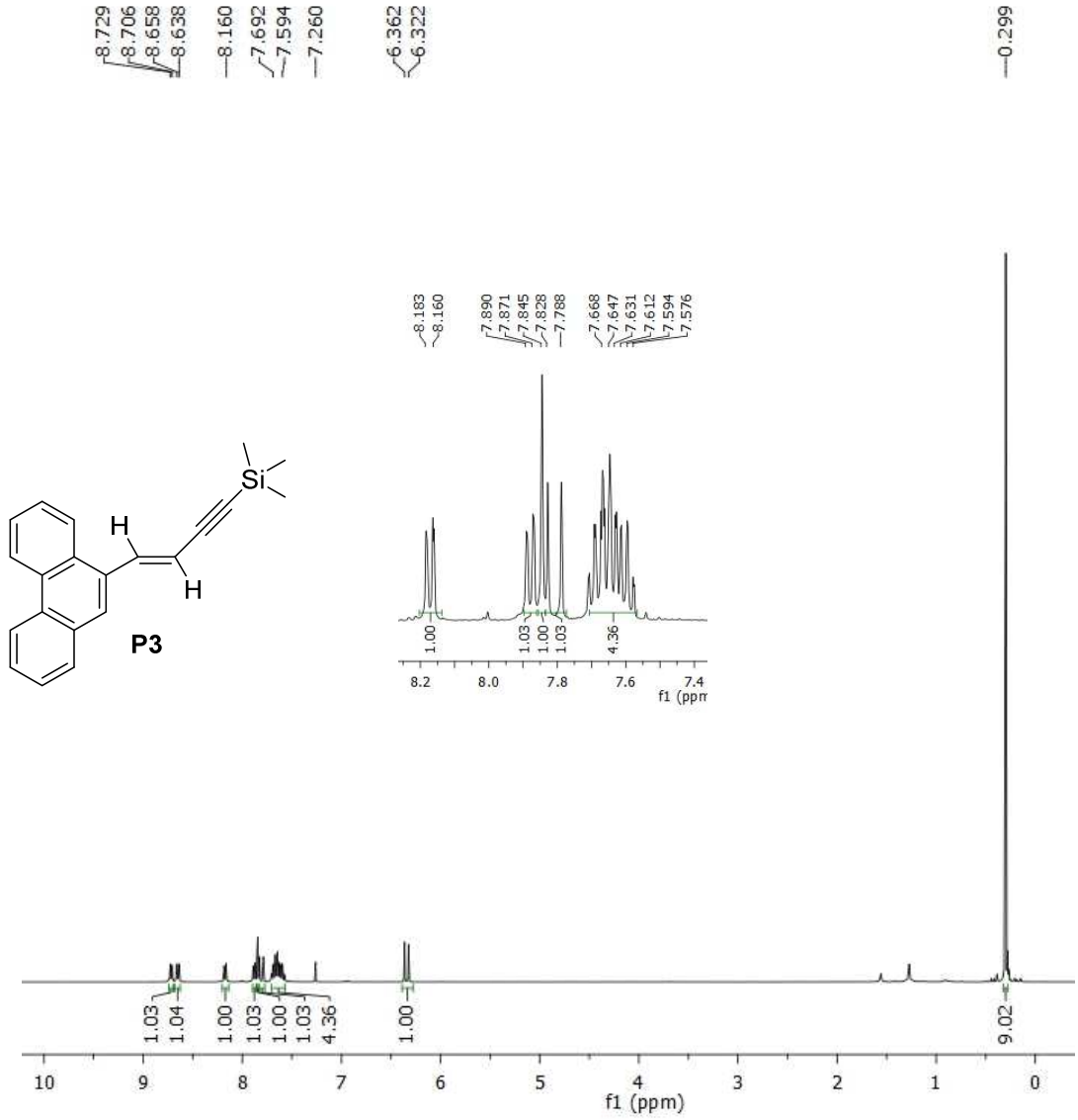


Figure S7. ^{1}H NMR spectrum of compound **P3** in $CDCl_3$.

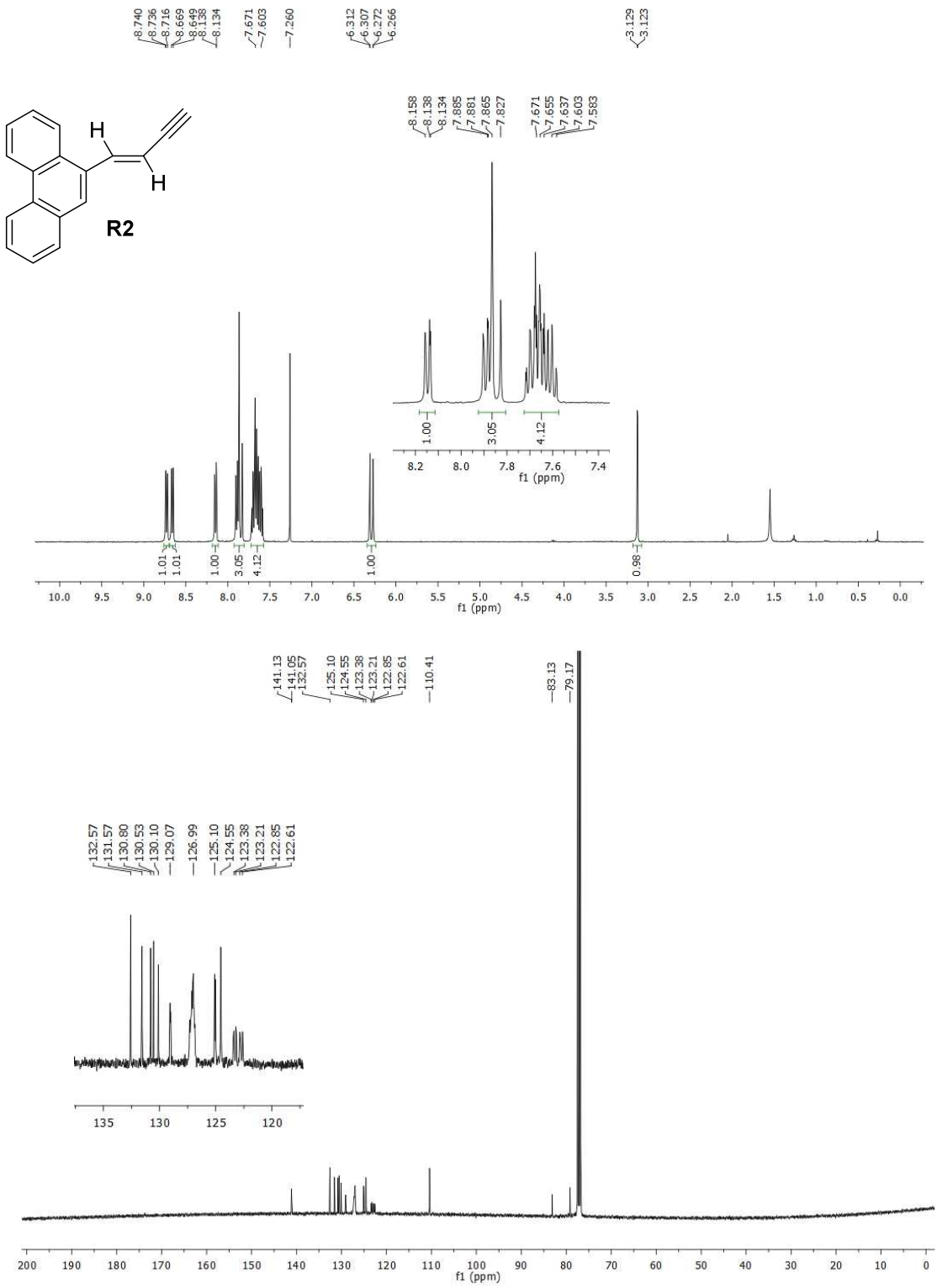


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound **R2** in $CDCl_3$.

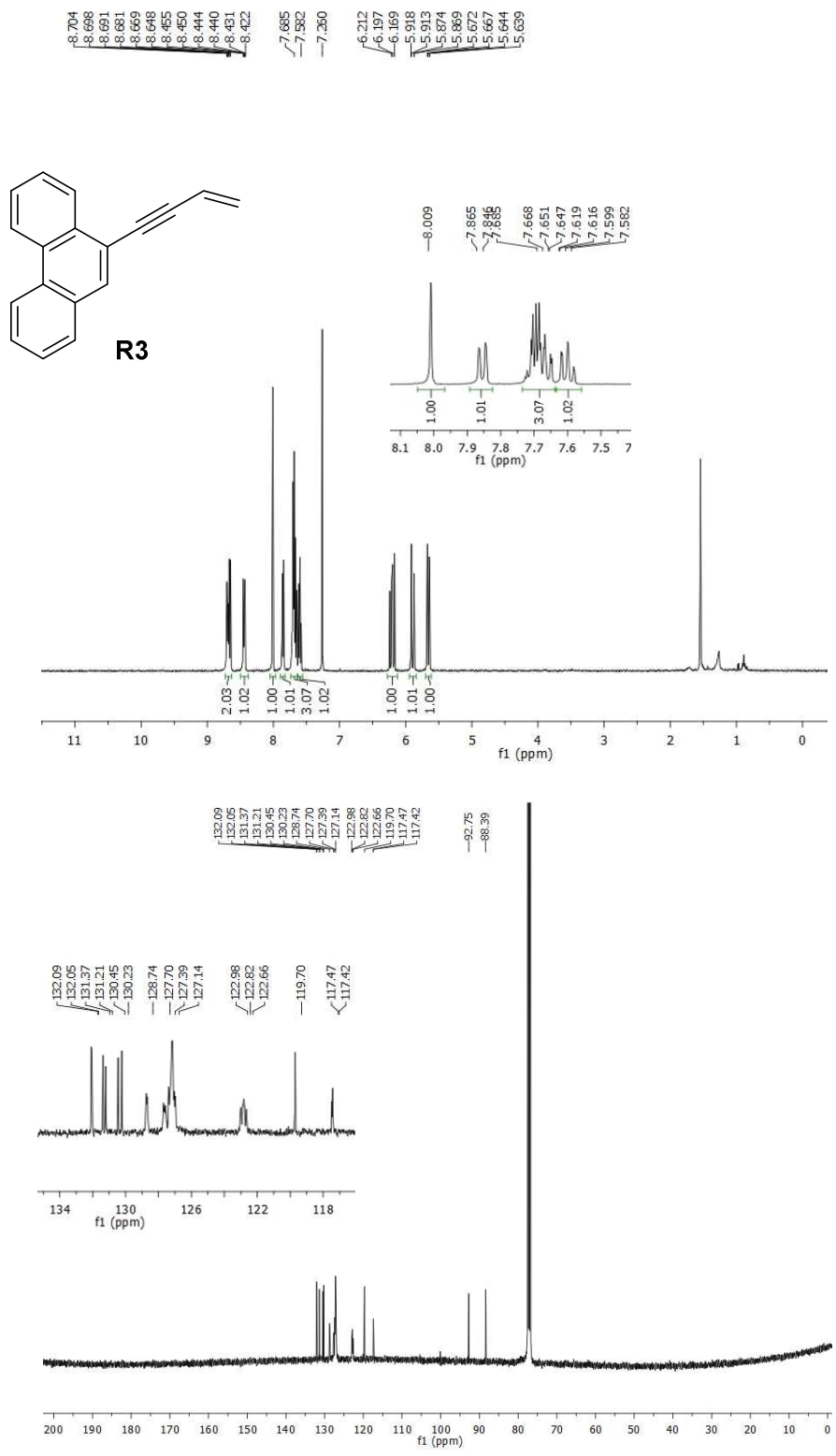


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of compound **R3** in $CDCl_3$.

References:

[1] L. Zhao, R. I. Kaiser, B. Xu, U. Ablikim, M. Ahmed, D. Joshi, G. Veber, F. R. Fischer, A. M. Mebel, *Nat. Astron.* **2018**, *2*, 413-419.

[2] M. Dewar, D. Goodman, *J. Chem. Soc. Faraday Trans.* **1972**, *68*, 1784-1788.

[3] K. O. Johansson, M. F. Campbell, P. Elvati, P. E. Schrader, J. Zador, N. K. Richards-Henderson, K. R. Wilson, A. Violi, H. A. Michelsen, *J. Phys. Chem. A* **2017**, *121*, 4447-4454.

[4] W. Schmidt, *J. Chem. Phys.* **1977**, *66*, 828-845.

[5] H. C. Brown, T. Hamaoka, N. Ravindran, *J. Am. Chem. Soc.* **1973**, *95*, 5786-5788.

[6] M. R. Uehling, R. P. Rucker, G. Lalic, *J. Am. Chem. Soc.* **2014**, *136*, 8799-8803.

[7] L. Zhao, R. I. Kaiser, B. Xu, U. Ablikim, M. Ahmed, M. V. Zagidullin, V. N. Azyazov, A. H. Howlader, S. F. Wnuk, A. M. Mebel, *J. Phys. Chem. Lett.* **2018**, *9*, 2620-2626.