

Supplementary information for:

Five vs Six Membered-Ring PAH Products from Reaction of *o*-Methylphenyl Radical and two C₃H₄ Isomers

1. Supplementary Photoionisation Spectra and AIE Values

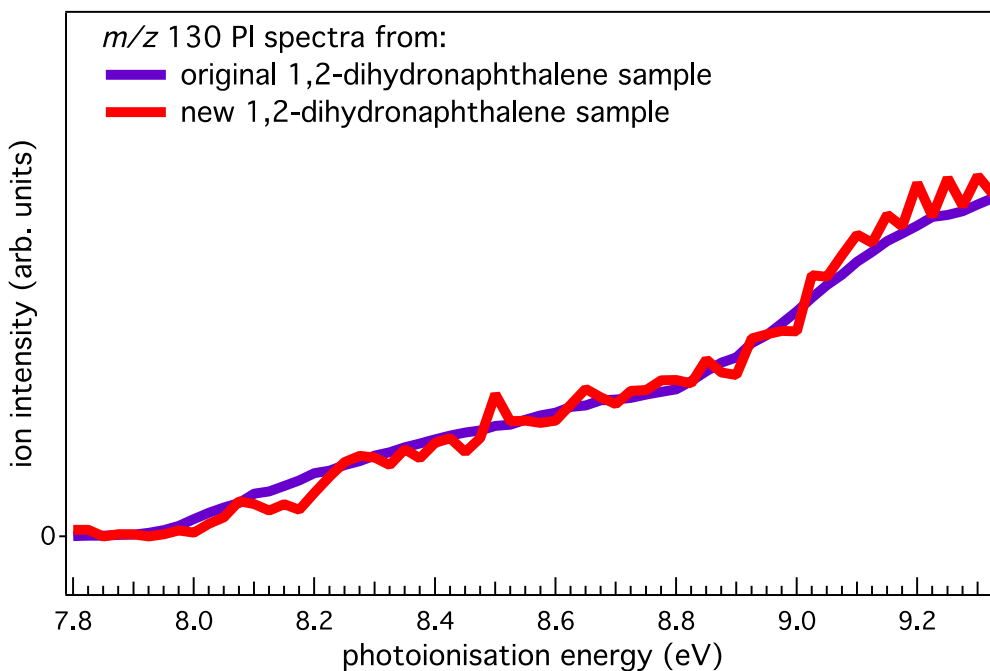


Figure S1. Average PI spectra of m/z 130 from original 1,2-dihydronaphthalene sample (solid purple line, included in Figure 3) and PI spectrum from a new sample of 1,2-dihydronaphthalene acquired on the same instrument (solid red line).

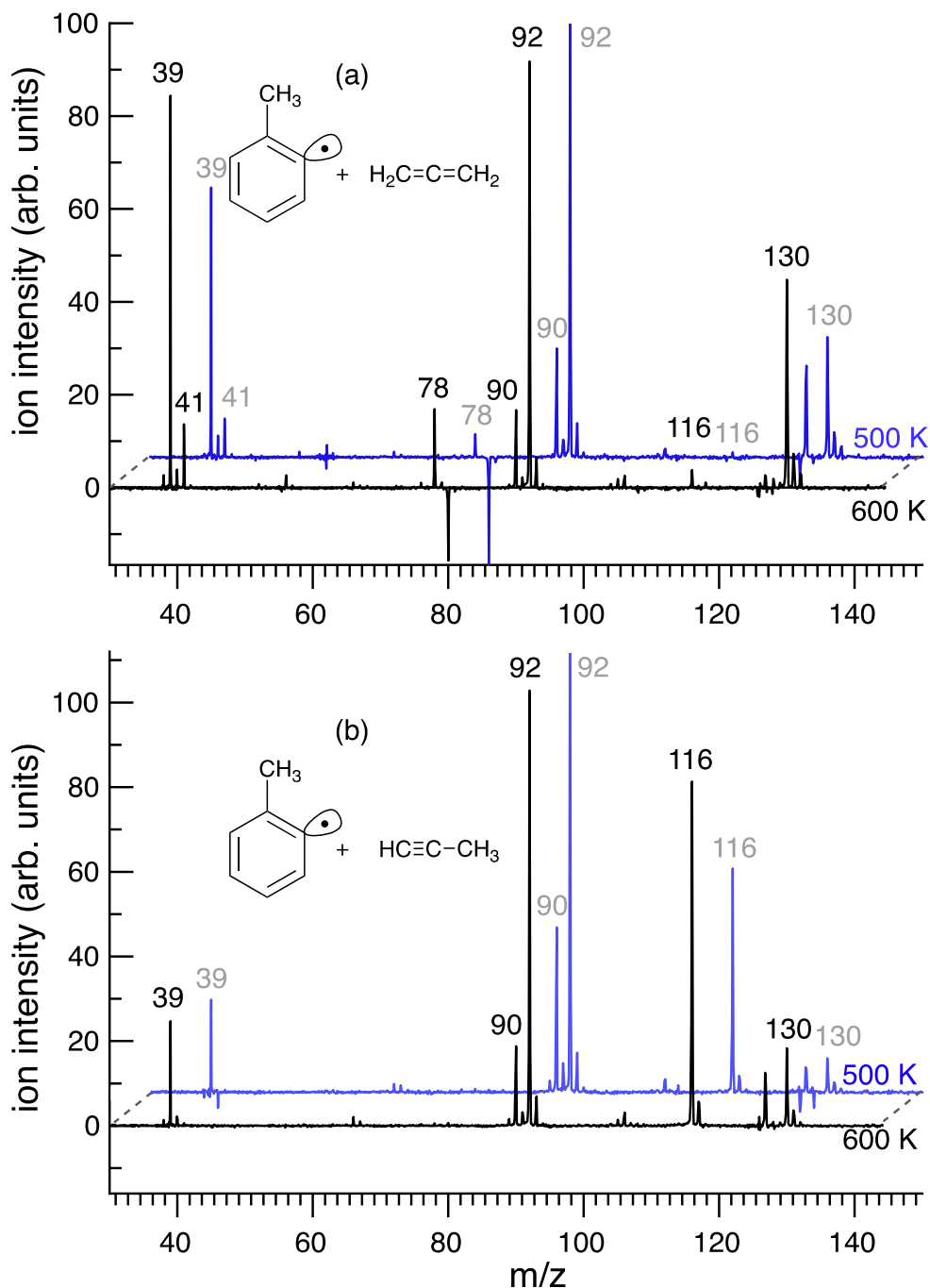


Figure S2. Product mass spectra integrated over 0–50 ms after photolysis of *o*-iodotoluene in the presence of (a) allene and (b) propyne at 600 K (black) and 500 K (blue) and 4 Torr. All spectra are normalised to the base peak. For both reactions the normalised ion intensity of product peaks is reduced at lower 500 K. Additionally, the reduction in signal of m/z 39 for the allene case at 500 K supports the idea that this signal originates from the increased allene absorption cross section at elevated temperatures.

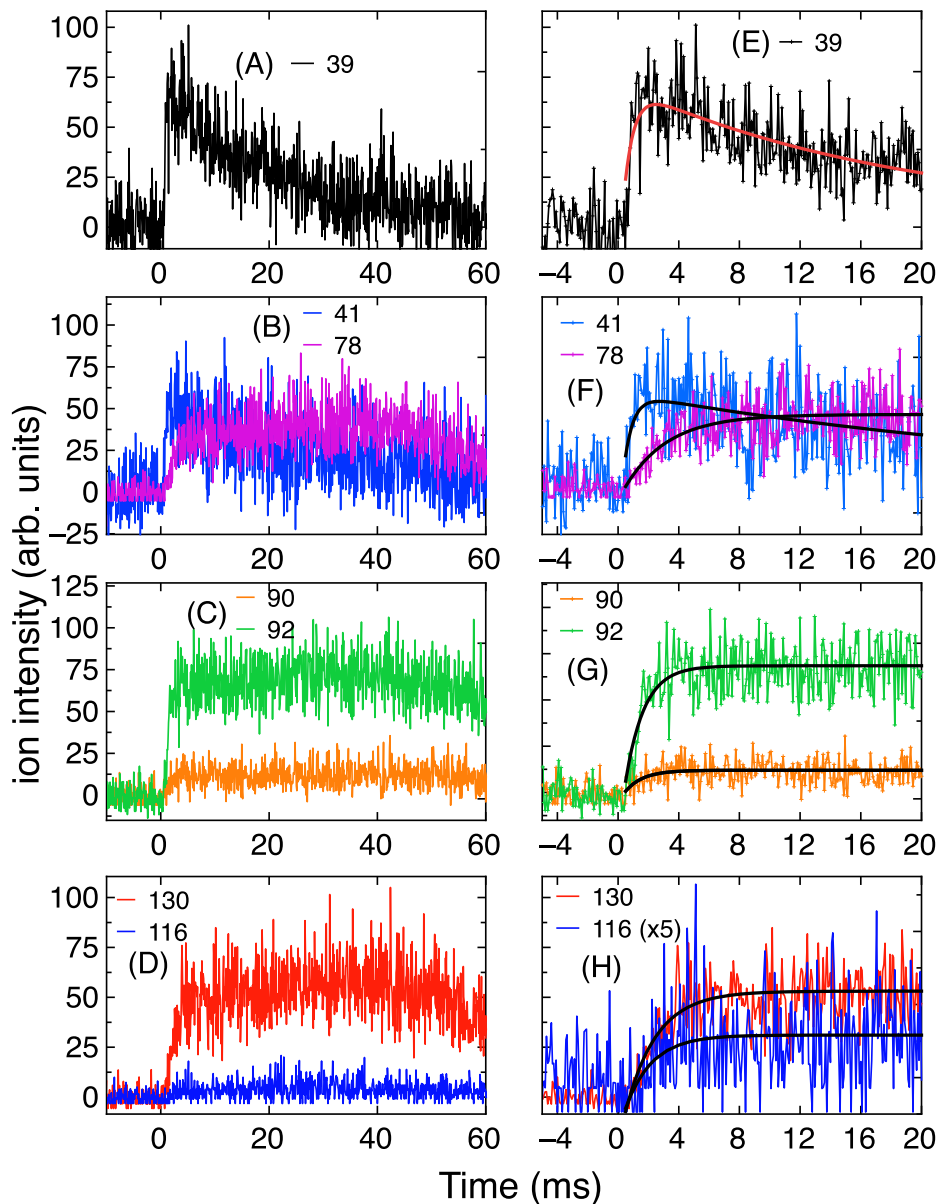


Figure S3. Kinetic traces of (A) m/z 39, (B) 41 and 78, (C) m/z 90 and 92, and (D) m/z 130 and 116 from *o*-CH₃C₆H₄ + allene at 600K. For each channel, a second plot showing the profile between -5 and 20 ms is also provided (E and F). The time constants for each of these profiles is summarized in Table S1. (A) m/z 39 follows a laser dependent trace (fast reaction time) and thus is not related to the targeted *o*-CH₃C₆H₄ + C₃H₄ reaction. Additionally, the m/z 39 rate of decay matches the growth of m/z 78 suggesting this peak originates from the reaction of two m/z 39 molecules. The growth of m/z 41 is on a slower time scale than the growth of m/z 39 but is still faster than the growth of m/z 130 or m/z 116 (F) and thus is also not relevant to the *o*-CH₃C₆H₄ + C₃H₄ reactions.

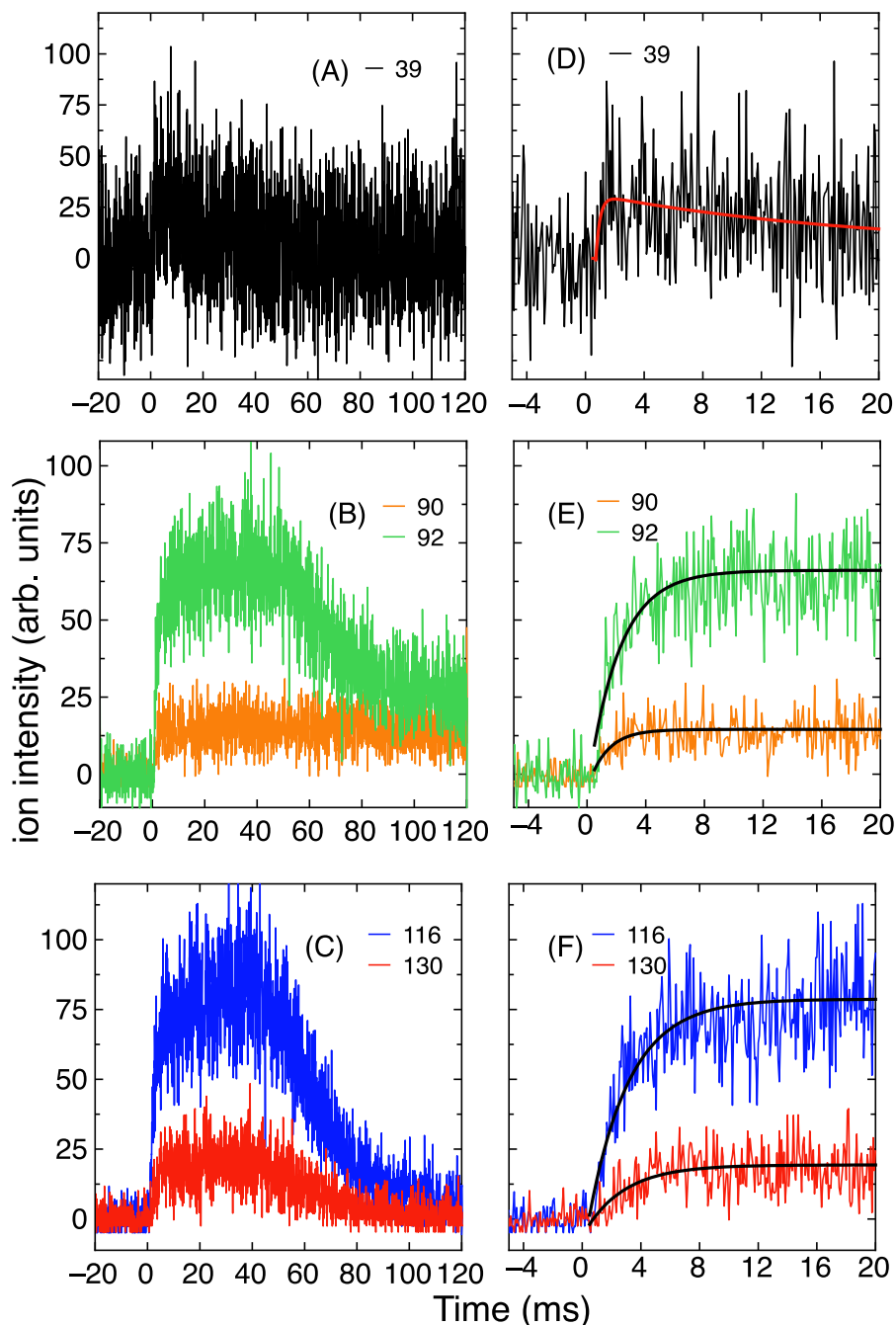


Figure S4. Kinetic traces of (A) m/z 39, (B) m/z 90 and 92, and (C) m/z 130 and 116 from *o*-CH₃C₆H₄ + propyne at 600K. For all spectra, a second plot showing the profile between -5 and 10 ms is also provided (D, E and F). The time constants for each of these profiles is summarized in Table S1. (A) m/z 39 follows a laser dependent trace (fast reaction time) and thus is not related to the targeted *o*-CH₃C₆H₄ + C₃H₄ reaction. Following photolysis, the molecules furthest from the pinhole require ca. 60 ms reach the pinhole so after this time, the drop in signal represents pump out of the reactive molecules.

$$y = A_1 - A_2 e^{-(x-A_3) \times A_4}$$

Equation S1.

Equation S2.

$$y = A_1 - A_2 e^{-(x-A_3) \times A_4} + A_5 e^{-(x-A_3) \times A_6}$$

Table S1. Appearance coefficients for the kinetic traces shown in Figures S3 and S4. ± 1 std. dev. Traces with a single component were fitted using Equation S1, while traces with a growth and a decay component were fitted using Equation S2.

<i>m/z</i> value	Allene Reaction (s ⁻¹)	Propyne Reaction (s ⁻¹)
39 (growth)	3500 \pm 900	3600 \pm 400
39 (decay)	55 \pm 9	50 \pm 30
41 (growth)	3400 \pm 500	-
41 (decay)	27 \pm 1	-
78	90 \pm 40	-
90	900 \pm 200	800 \pm 200
92	790 \pm 70	690 \pm 50
116	500 \pm 100	360 \pm 30
130	490 \pm 60	400 \pm 60

Table S2. Calculated CBS-QB3 adiabatic ionization energies (AIEs) for C₉H₈ isomers (116 Da). Relative CBS-QB3 enthalpies (ΔH_f) are provided. The techniques used to obtain literature values are indicated within brackets with EI meaning electron impact techniques, and PI meaning photoionisation mass spectrometry.

C ₉ H ₈ isomer	Calculated AIE (eV)	Literature IE (eV)	Relative ΔH_f (kcal mol ⁻¹)
indene	8.2	8.15 \pm 0.015 (PE) ¹	0.0
2-methylphenylacetylene	8.7	8.61 \pm 0.02 (PE) ²	28.6
propadienyl-benzene	8.3	8.29 ³	29.6
propynyl-benzene	8.4	8.42 \pm 0.08 (PE) ⁴	27.0
3-phenyl-propyne	9.0		34.5

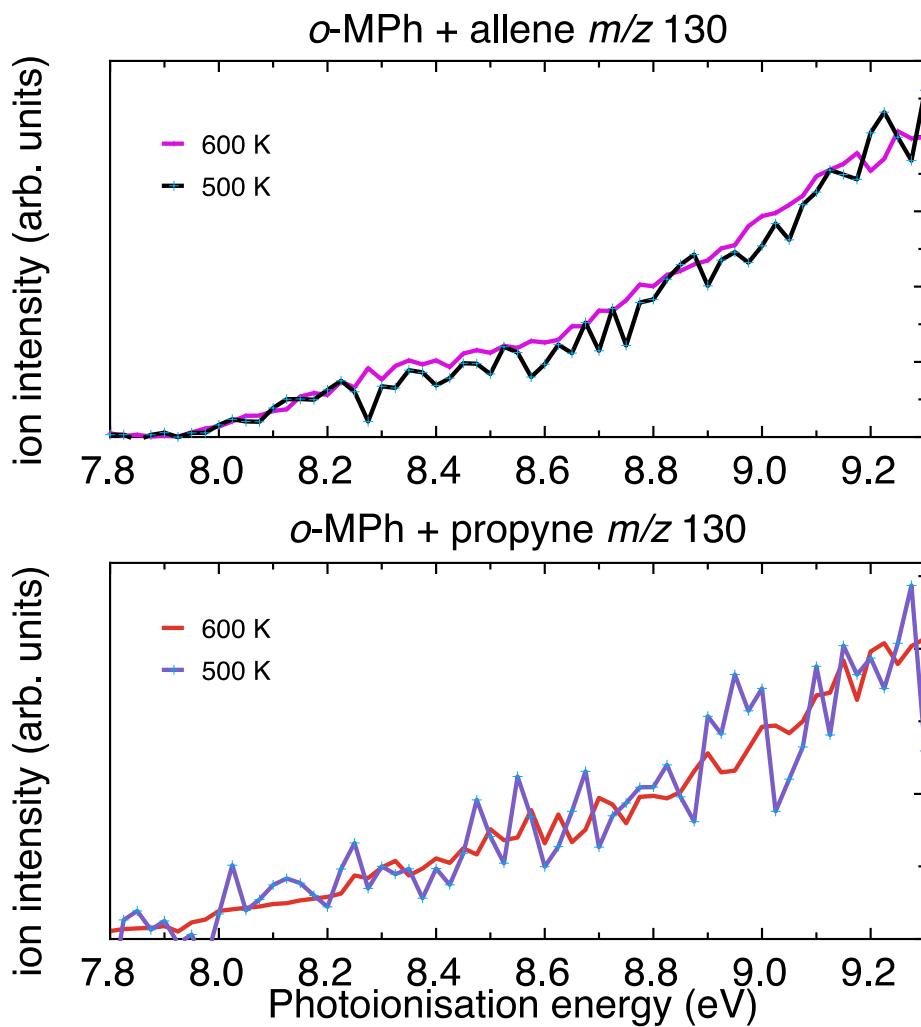


Figure S5. PI spectrum following *m/z* 130 for both reactions at 500 K and 600 K. The good comparison between these plots indicates the same products are made in both reactions.

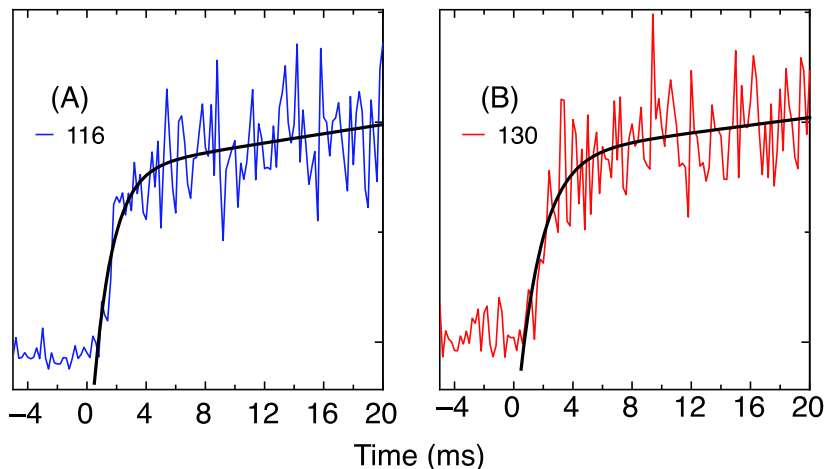


Figure S6. Kinetic traces of (a) m/z 116 from o -CH₃C₆H₄ + allene and (b) m/z 130 from o -CH₃C₆H₄ + propyne at 500K. The time constants for these profiles are 800 ± 300 s⁻¹ for m/z 116 and 600 ± 300 s⁻¹ for m/z 130. These values are within the uncertainty of the rate constants determined at 600 K, however, these values at 500 K have significantly larger uncertainty due to the decrease in S/N at this temperature.

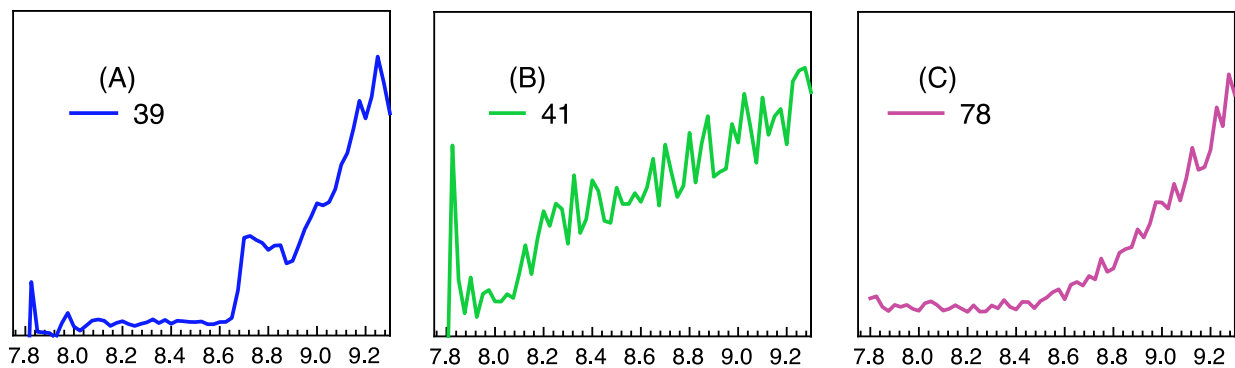


Figure S7. Representative PI spectra for (A) m/z 39, (B) m/z 41 and (C) m/z 78 for the o -CH₃C₆H₄ + allene reaction at 600 K – these are not attributed to the title reactions, as discussed in the main text.

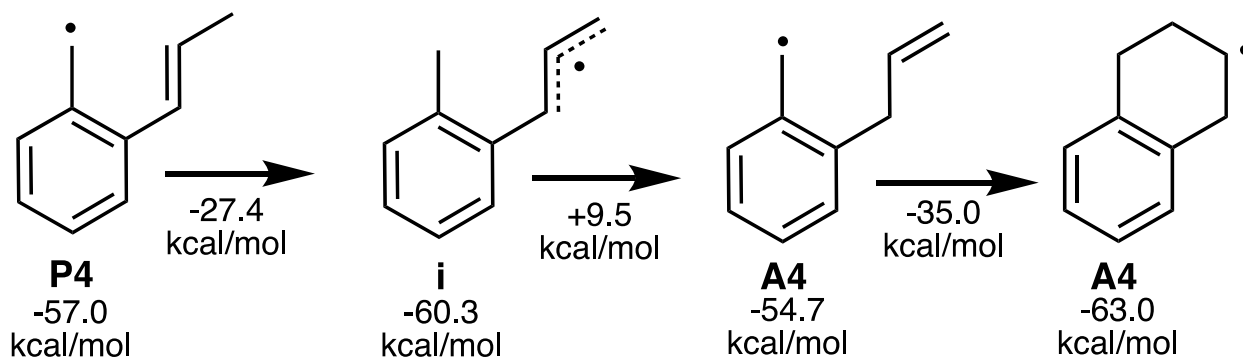
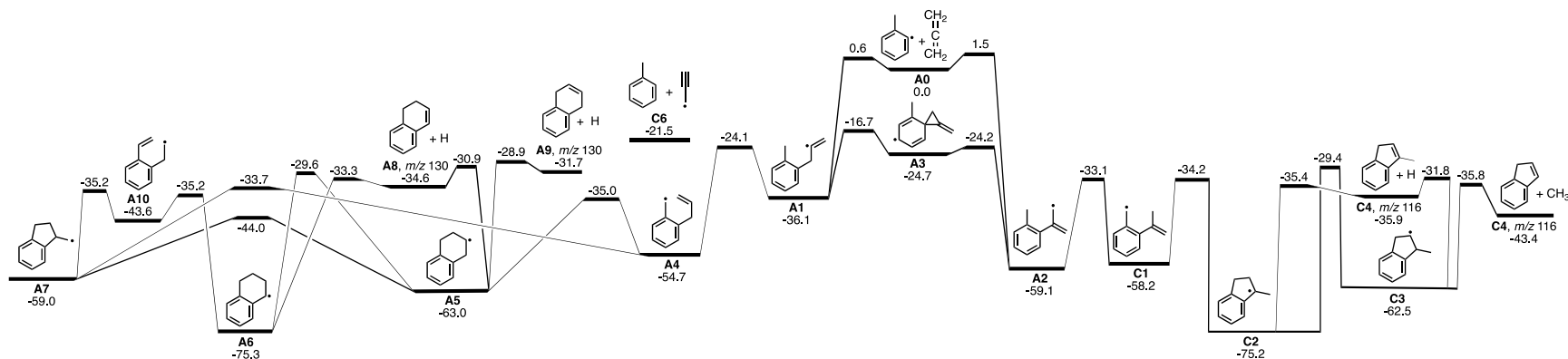


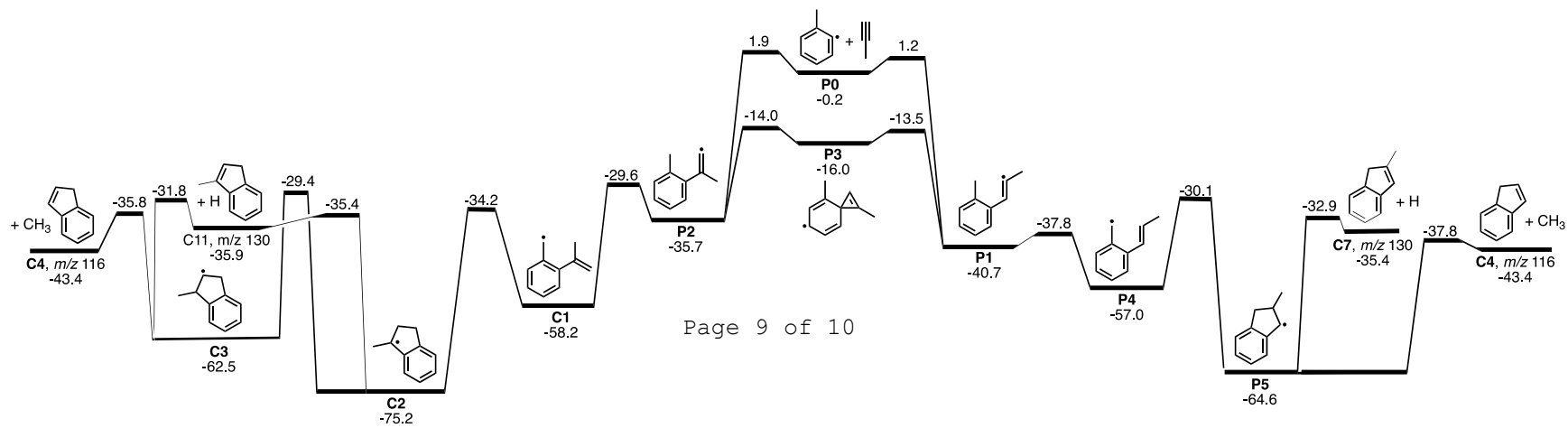
Figure S8. Reaction scheme following the isomerism of **P4** into **A4**. This mechanism is the only pathway to form a new six-membered ring for the propyne reaction. However, the rate limiting step for this pathway lies $+9.5$ kcal/mol above the energy of the separated reactants and thus this mechanism is uncompetitive.



2. Supplementary Information for Quantum Chemical Calculations

Figure S9. Potential energy surface for all stationary points modelled for the *o*-CH₃C₆H₄ + allene reaction RRKM-ME simulation.

Figure S10. Potential energy surface for all stationary points modelled for the *o*-CH₃C₆H₄ + propyne reaction RRKM-ME simulation.



3. References

1. Güsten, H.; Klasinc, L.; Ruščić, B., Photoelectron Spectroscopy of Heterocycles. Indene Analogs. In *Z. Naturforsch. A*, 1976; Vol. 31, pp 1051-1056.
2. Carlier, P.; Mouvier, G., *J. Electron. Spectrosc. Relat. Phenom.* **1979**, *16* (2), 169-181.
3. Runge, W.; Kosbahn, W.; Kroner, J., *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79* (4), 371-381.
4. Lias, S. G.; Levin, R. D.; Kafafi, S. A., Ion Energetics Data. In *NIST Chemistry WebBook*, *NIST Standard Reference Database Number 69*, Linstrom, P. J.; Mallard, W. G., Eds. National Institute of Standards and Technology: Gaithersburg MD, 20899, 2011.