

## Supplementary Information

Molecular growth in Titan's atmosphere: branching pathways during reaction of 1-propynyl radical ( $\text{H}_3\text{CC}\equiv\text{C}\cdot$ ) with small alkenes and alkynes.

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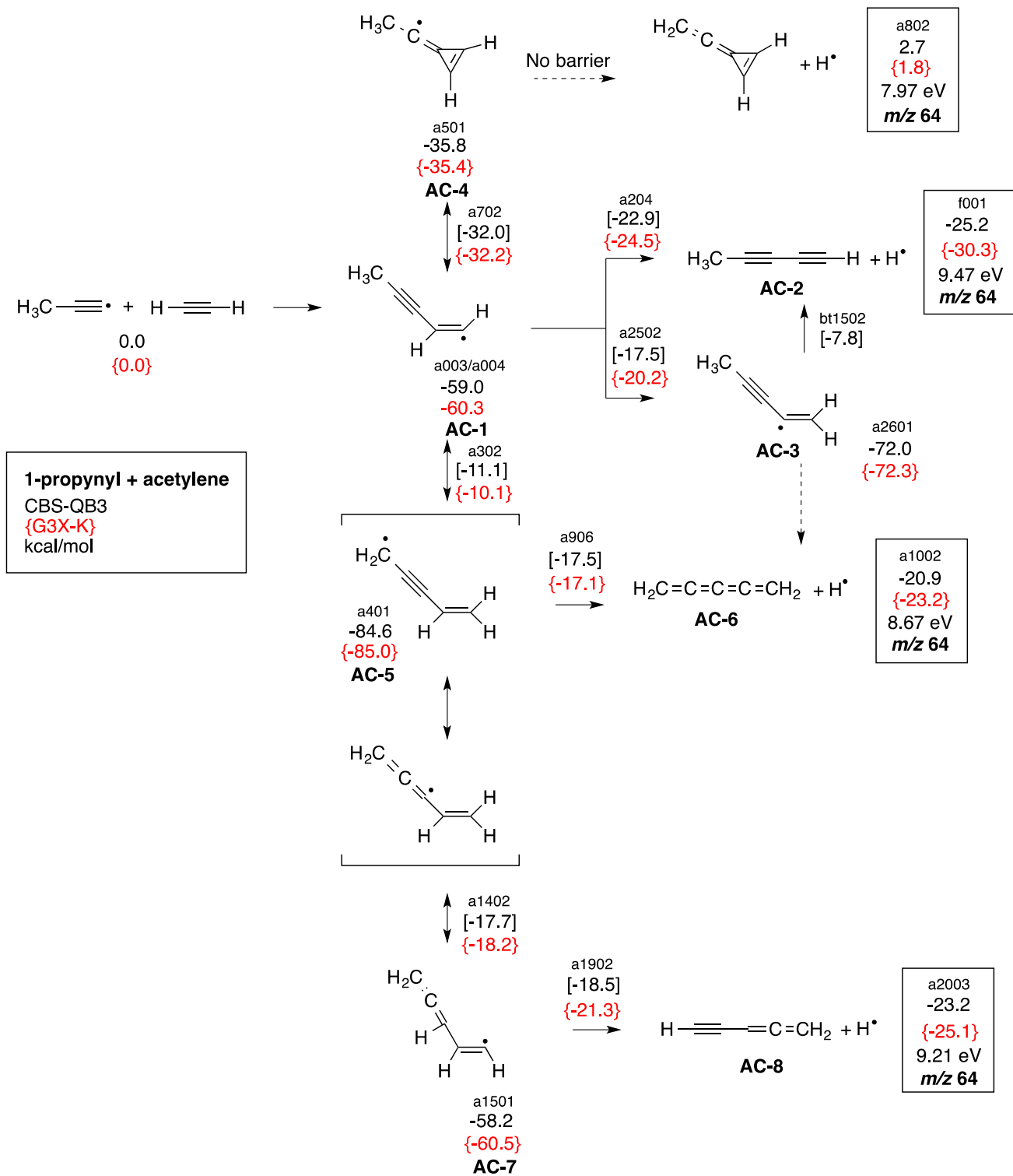
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## Electronic Structure Calculations

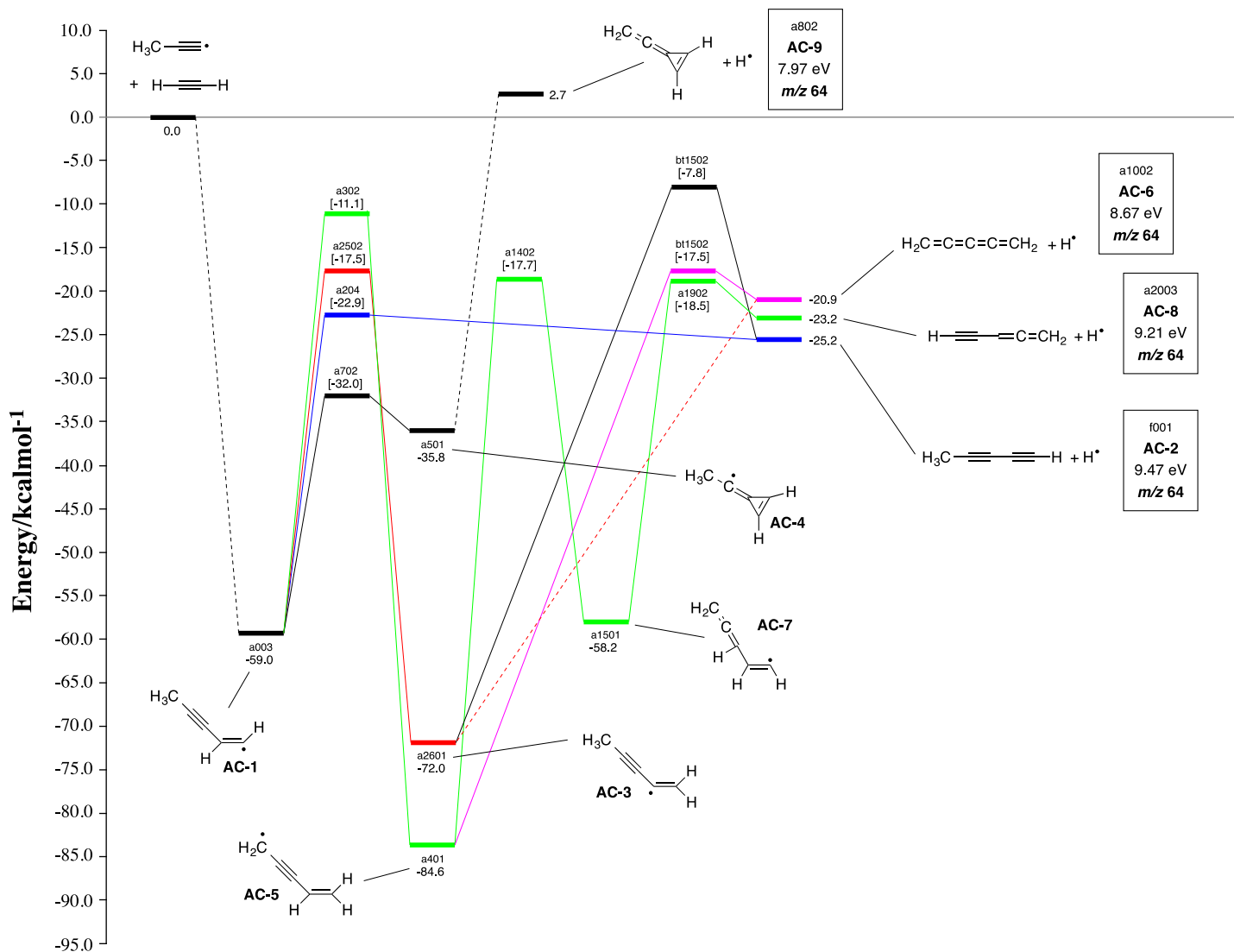
Calculations were undertaken using the CBS-QB3 compound method as implemented in the Gaussian 09 suite of programs.<sup>1</sup> Stationary points were confirmed as either minima (0 imaginary frequencies) or transition states (1 imaginary frequency) by calculation of frequencies using analytical gradient procedures. All reported energies include zero-point energy corrections. Where no transition state was found, a relaxed scan was used to confirm no explicit barrier was present on the exit channel. Potential energy schemes for the reaction of 1-propynyl radical with acetylene, propyne, ethylene, propene and are presented below as Figures S1-S4.

The recent G3X-K compound method of da Silva,<sup>2</sup> estimated to be accurate to within 0.5 kcal/mol for barrier heights and 0.8 kcal/mol for enthalpies of formation, was compared with the CBS-QB3 energies for the 1-propynyl radical + acetylene reaction, as shown in Figure S1. The mean absolute deviation for energies was 1.50 kcal/mol with a maximum absolute deviation of 5.10 kcal/mol, while the mean absolute deviation for barrier heights was lower at 0.90 kcal/mol, with a maximum absolute deviation of 2.30 kcal/mol. As our calculations were qualitative and there was no swapping of the relative ordering of intermediates or their transition states, the CBS-QB3 method was used for its lower computational cost.

Calculated adiabatic ionization potentials ( $AIE_{\text{CBS-QB3}}$ ) are reported as the difference between the radical cation and neutral for closed-shell neutrals, and the singlet cation and doublet neutral for radicals (the triplet cation was always higher in energy). Energies, frequencies and geometries are reported in the geometries.txt as supplementary information, while a summary of the potential energy schemes is presented below.



**Figure S1(a)** - Potential energy scheme for reaction of 1-propynyl radical with acetylene. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. A comparison between the CBS-QB3 and G3X-K methods is presented. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, CBS-QB3 energy, G3X-K energy, adiabatic ionization energy ( $\text{AIE}_{\text{CBS-QB3}}$ ) and m/z of the product.



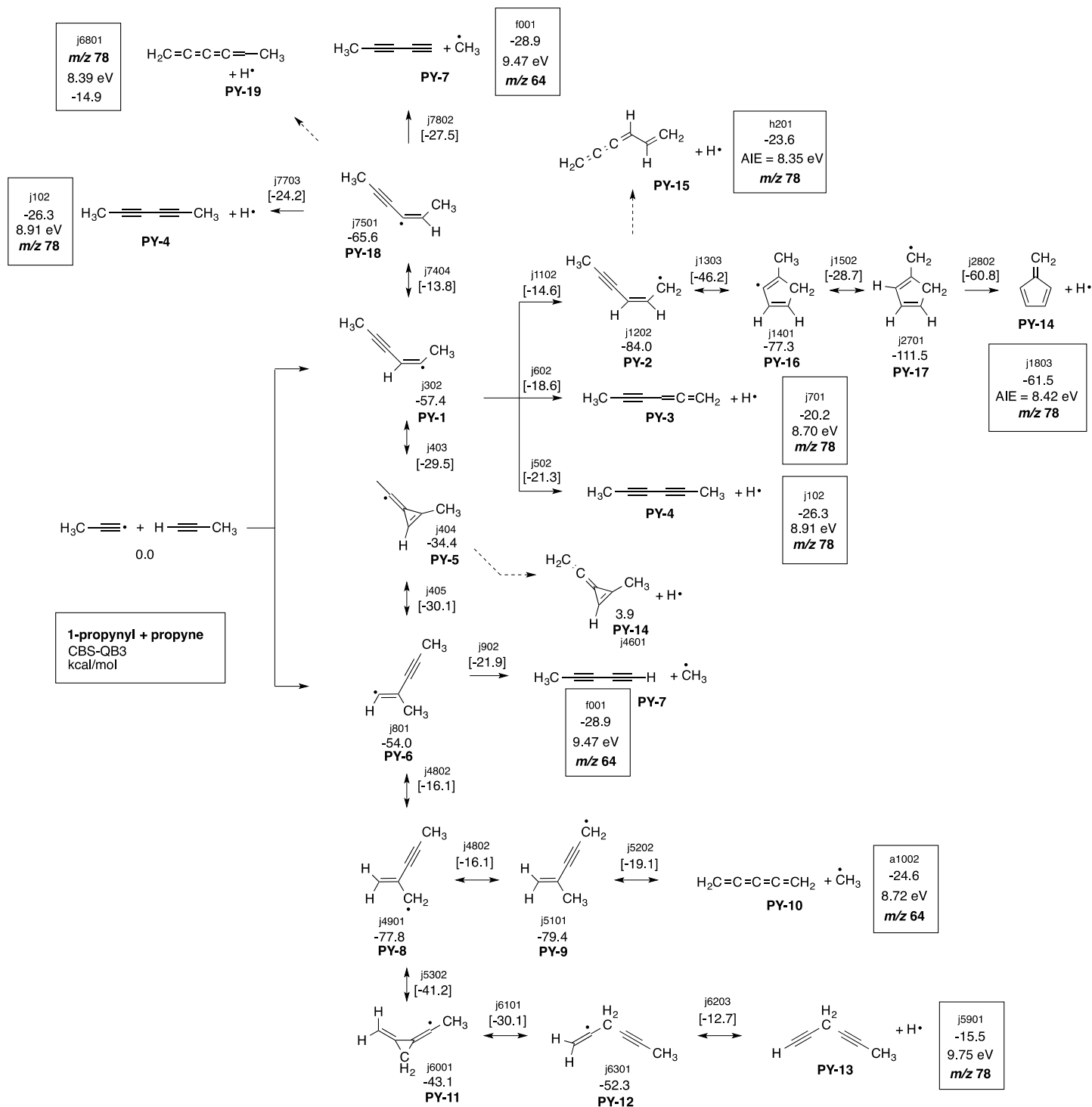
**Figure S1b** - Potential energy diagram for reaction of 1-propynyl radical with acetylene. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy (AIE<sub>CBS-QB3</sub>) and *m/z* of the product.

Molecule	Calculated /eV	Experimental /eV
hexa-2,4-diyne	8.91	$8.90 \pm 0.05$ , <sup>3</sup> $8.92 \pm 0.02$ <sup>3</sup>
hexa-1,4-diyne	9.75	$9.66 \pm 0.02$ <sup>3</sup>
hexa-1,5-diyne		$9.98 \pm 0.05$ , <sup>3</sup> $9.90 \pm 0.02$ , <sup>3</sup>
fulvene	8.42	$8.36 \pm 0.02$ , <sup>3</sup> $8.36 \pm 0.025$ <sup>4,5</sup>
benzene		$9.24378 \pm 0.00007$ <sup>6</sup>
1,2-dimethylenecyclobutene		$8.80$ <sup>7</sup>
hexa-1,3-dien-5-yne	9.30	
hexa-1,2-dien-4-yne	8.70	

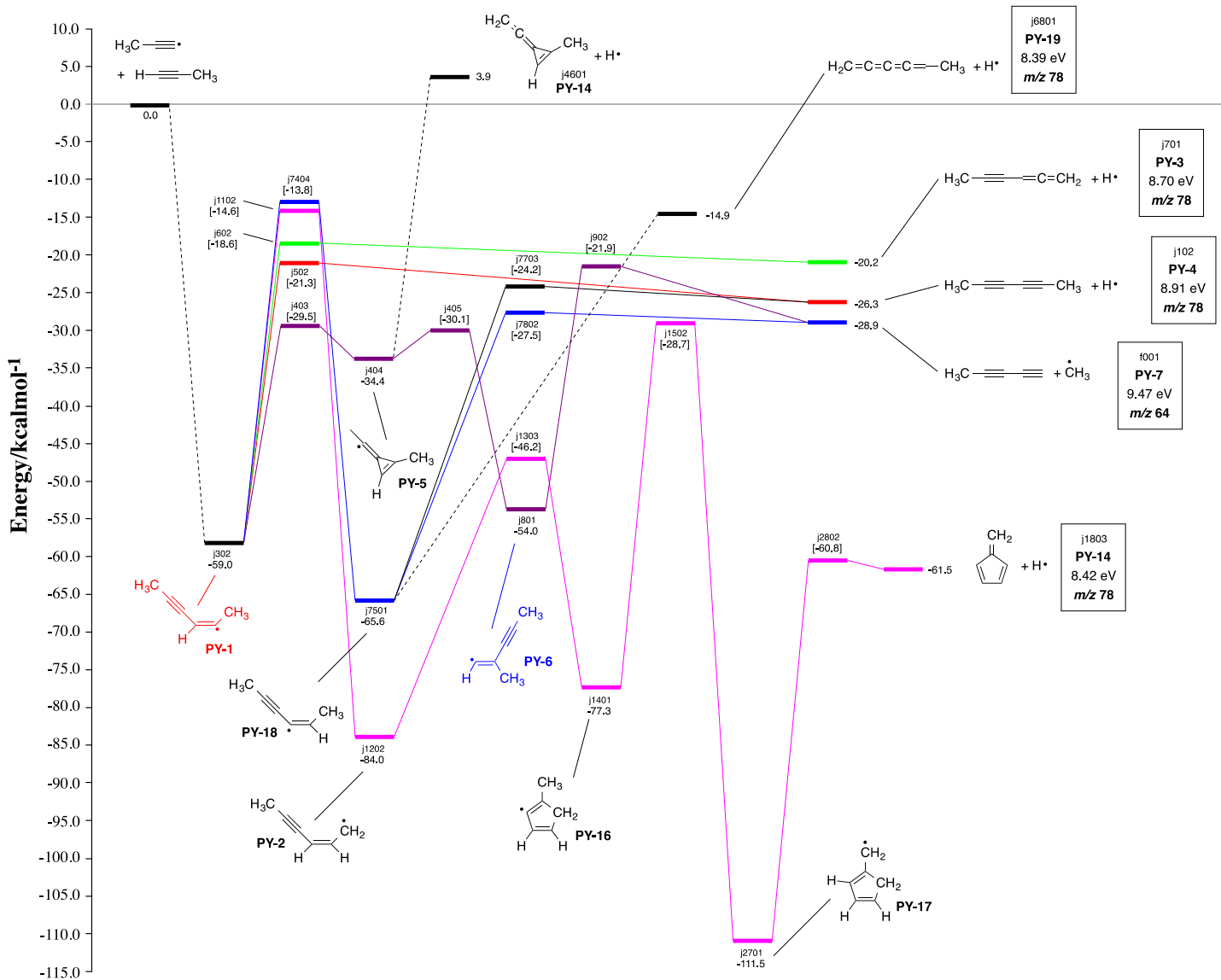
**Table S1** - Calculated (CBS-QB3) and experimental adiabatic photoionization potentials for relevant C<sub>6</sub>H<sub>6</sub> (m/z 78) isomers.

Molecule	Calculated /eV	Experimental /eV
penta-1,3-diyne	9.47	$9.50 \pm 0.02$ <sup>3</sup>
penta-1,4-diyne	10.26	$10.27 \pm 0.02$ <sup>3</sup>
penta-1,2,3,4-tetraene	8.72	$8.67 \pm 0.02$ <sup>3</sup>
penta-1,2-dien-4-yne	9.21	

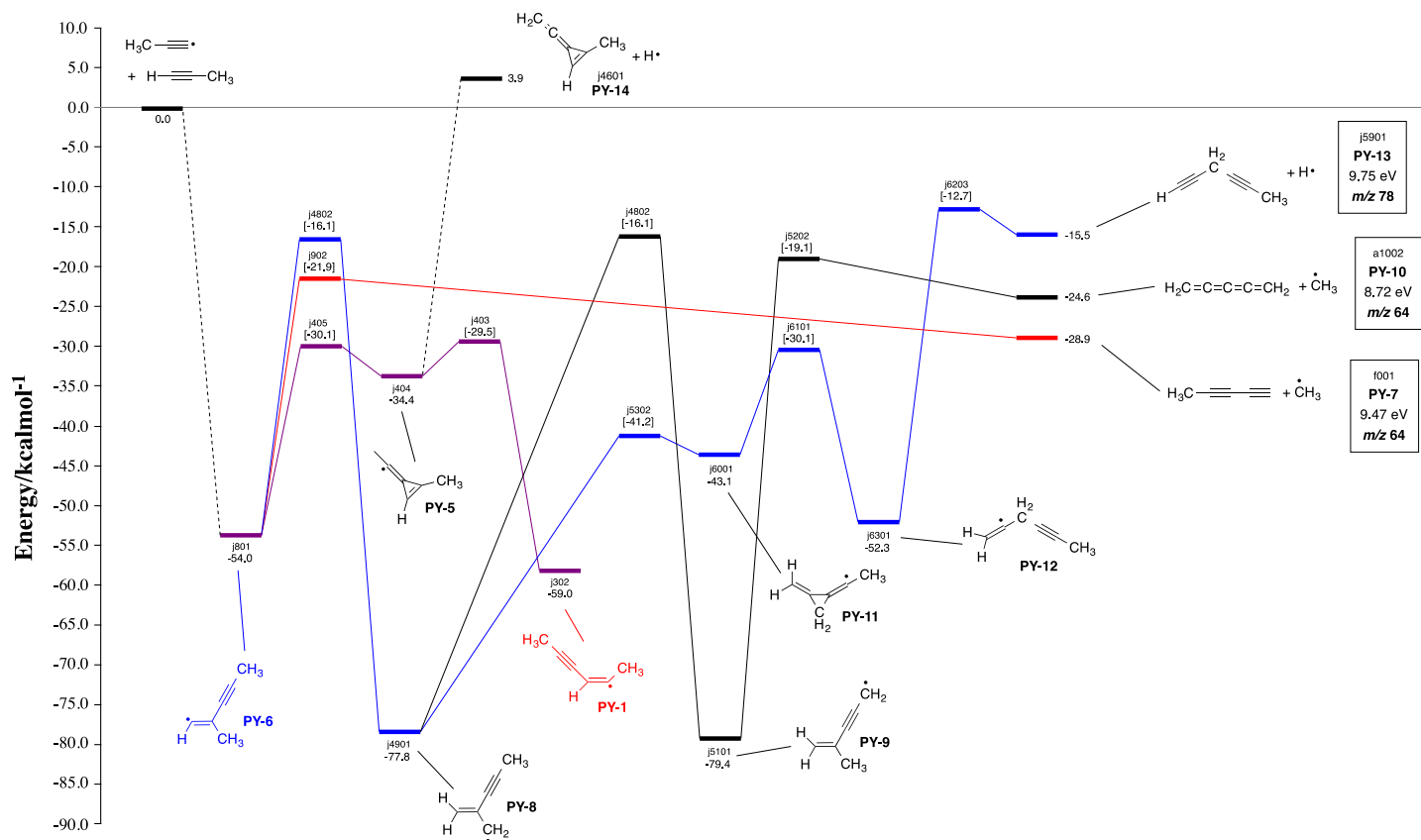
**Table S2** - Calculated (CBS-QB3) and experimental adiabatic photoionization potentials for relevant C<sub>5</sub>H<sub>4</sub> (m/z 64) isomers.



**Figure S2(a)** - Potential energy scheme for reaction of 1-propynyl radical with propyne calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, CBS-QB3 energy, adiabatic ionization energy (AIE<sub>CBS-QB3</sub>) and m/z of the product.

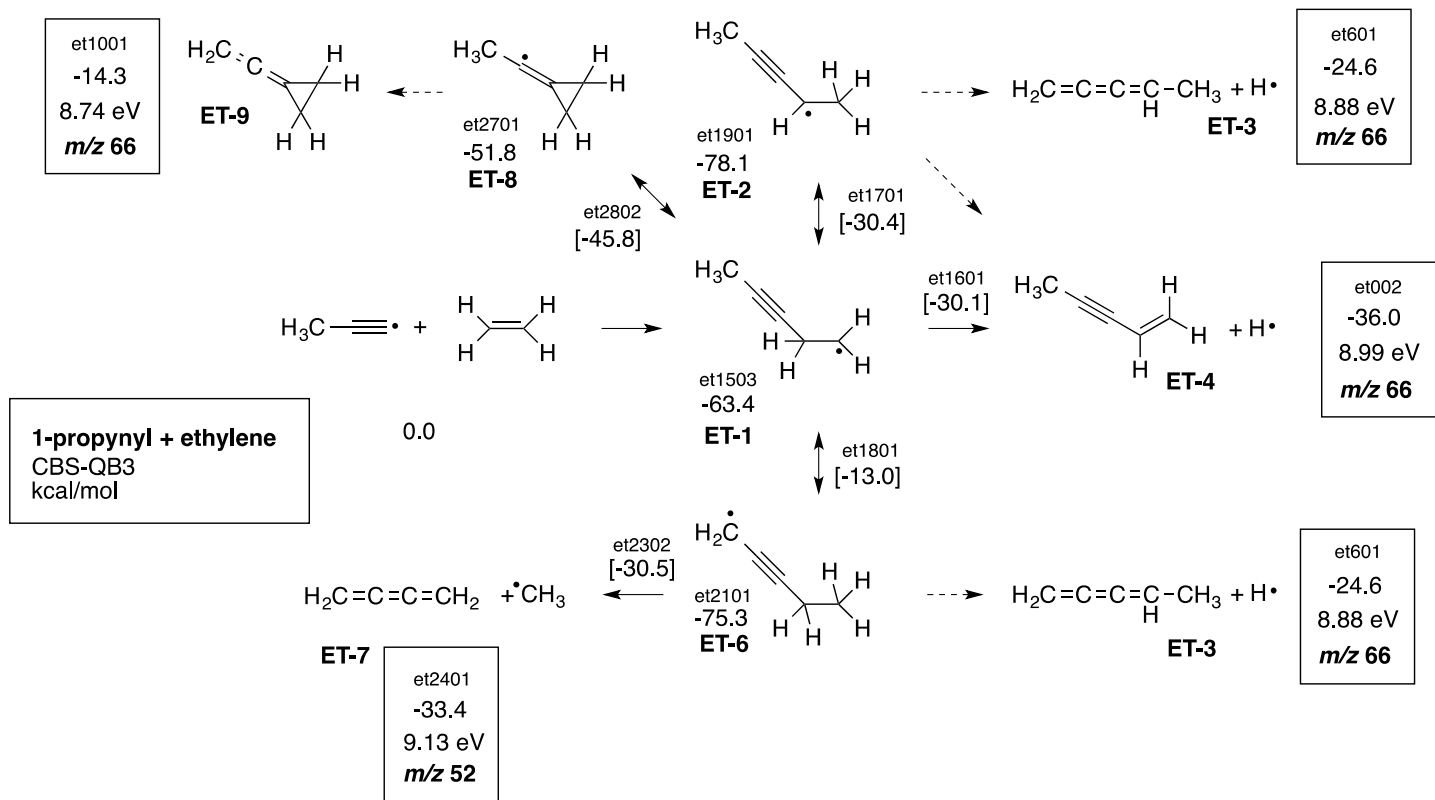


**Figure S2(b)** - Potential energy diagram for terminal-carbon addition reaction of 1-propynyl radical with propyne calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy (AIE<sub>CBS-QB3</sub>) and m/z of the product.

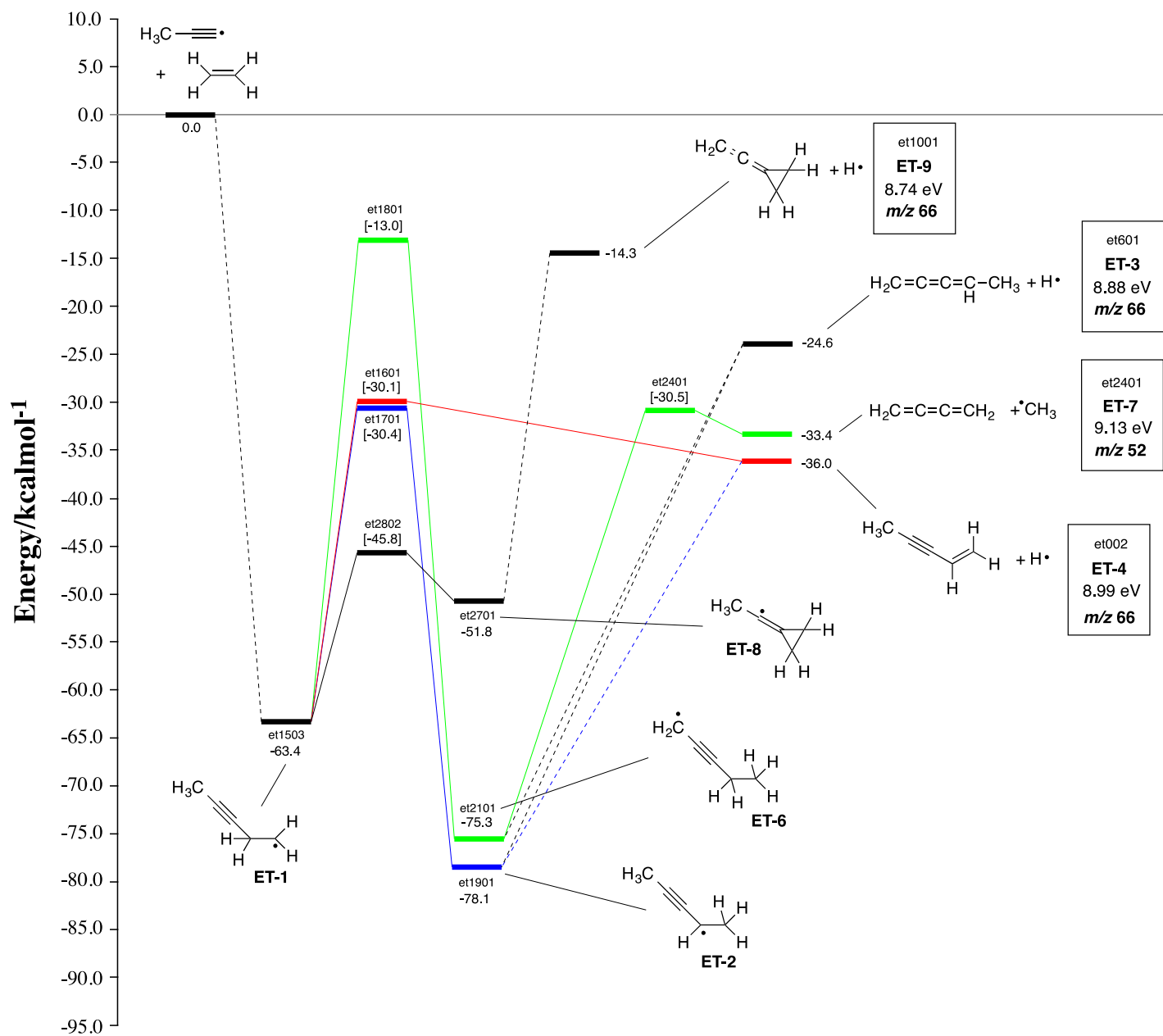


**Figure S2(c)** - Potential energy diagram for central-carbon addition reaction of 1-propynyl radical with propyne calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy ( $\text{AIE}_{\text{CBS-QB3}}$ ) and m/z of the product.





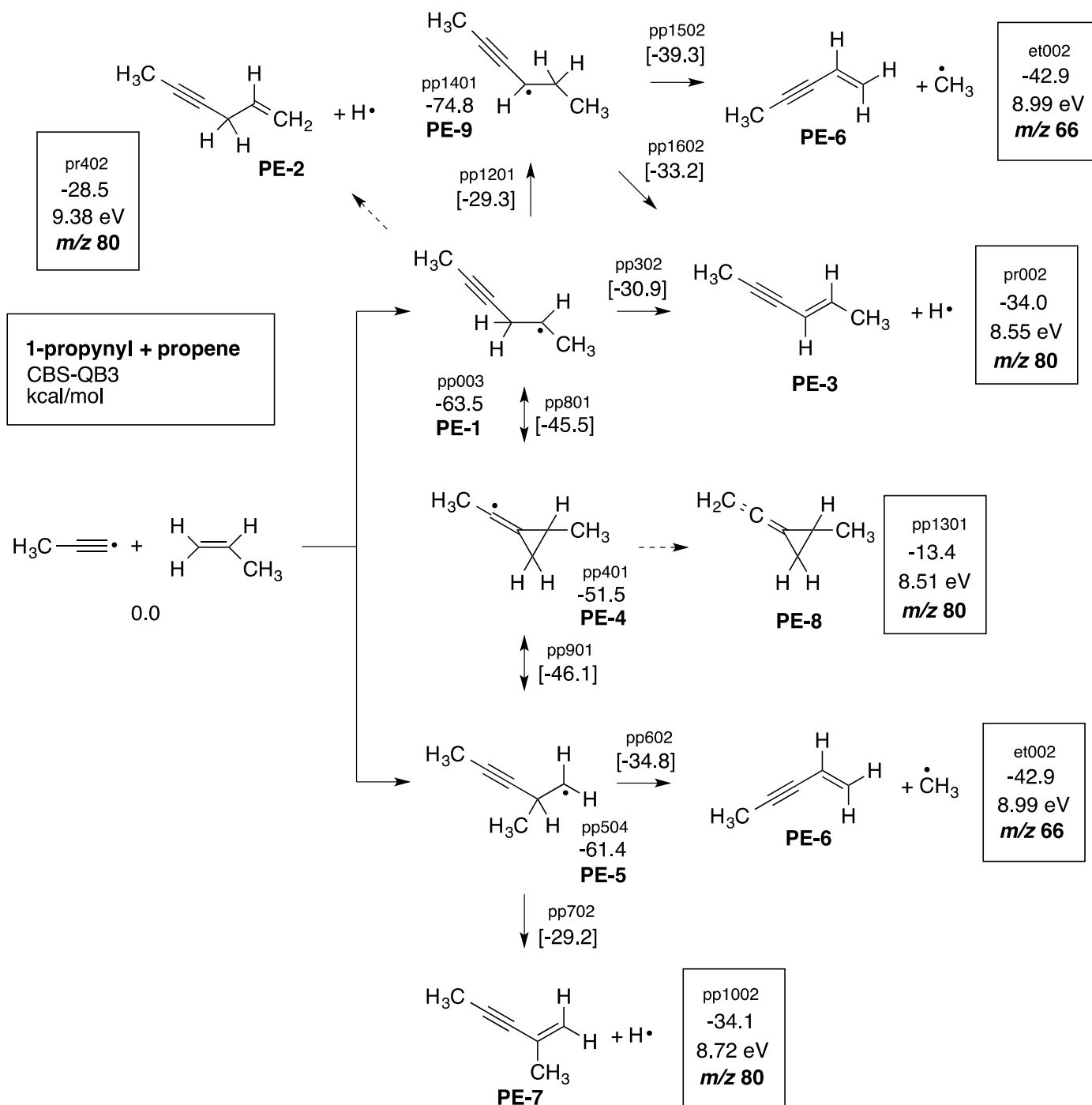
**Figure S3(a)** - Potential energy scheme for reaction of 1-propynyl radical with ethylene calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy ( $AIE_{\text{CBS-QB3}}$ ) and m/z of the product.



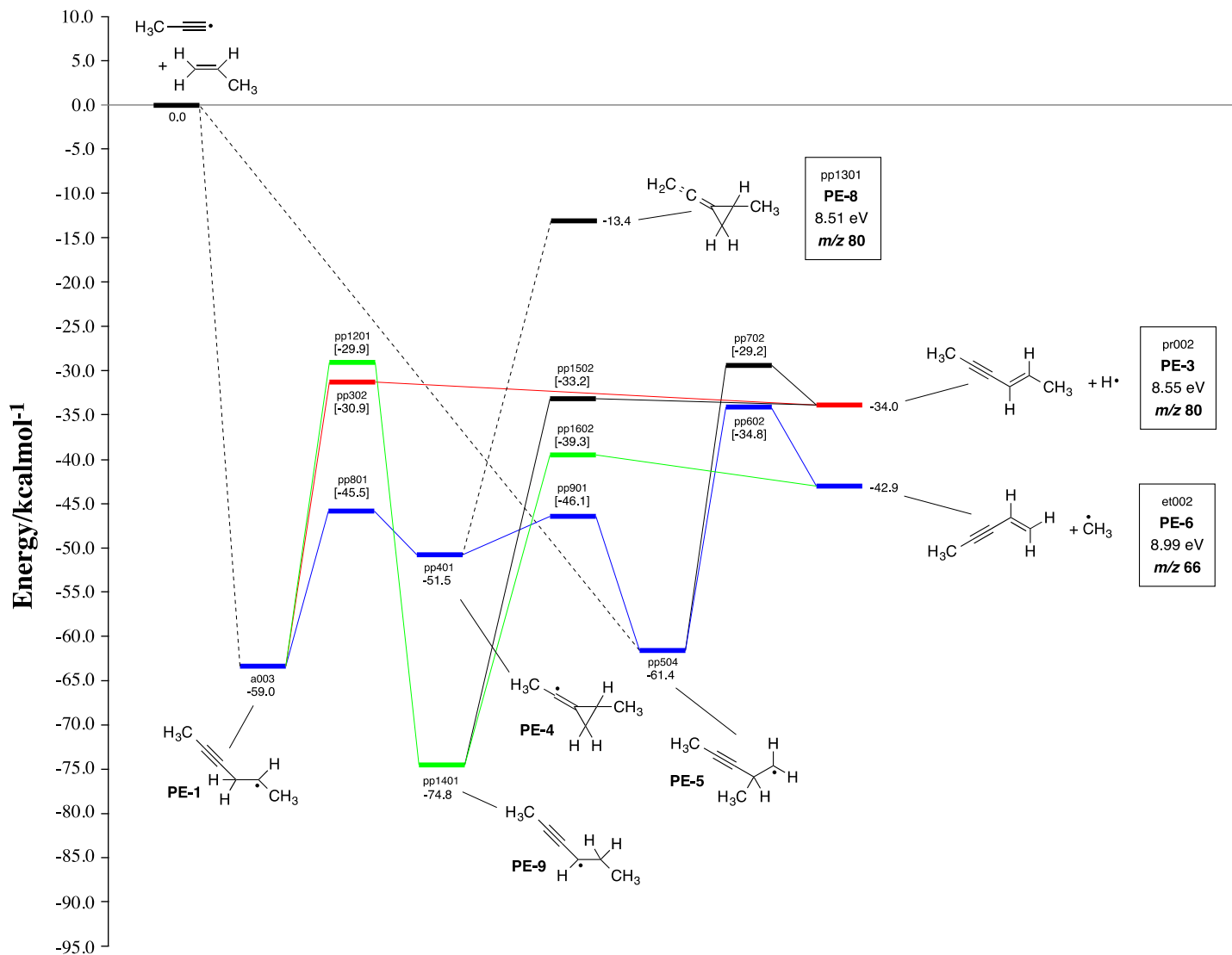
**Figure S3(b)** - Potential energy diagram for reaction of 1-propynyl radical with ethylene calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy ( $AIE_{CBS-QB3}$ ) and  $m/z$  of the product.

Molecule	Calculated /eV	Experimental /eV
penta-1,2,3-triene	8.88	9.00 ± 0.01 eV <sup>6</sup>
pent-1-en-3-yne	8.99	
propa-1,2,3-triene	9.13	

**Table S3** - Calculated (CBS-QB3) and experimental adiabatic photoionization potentials for relevant C<sub>4</sub>H<sub>4</sub> (m/z 52) and C<sub>5</sub>H<sub>6</sub> (m/z 66) isomers.



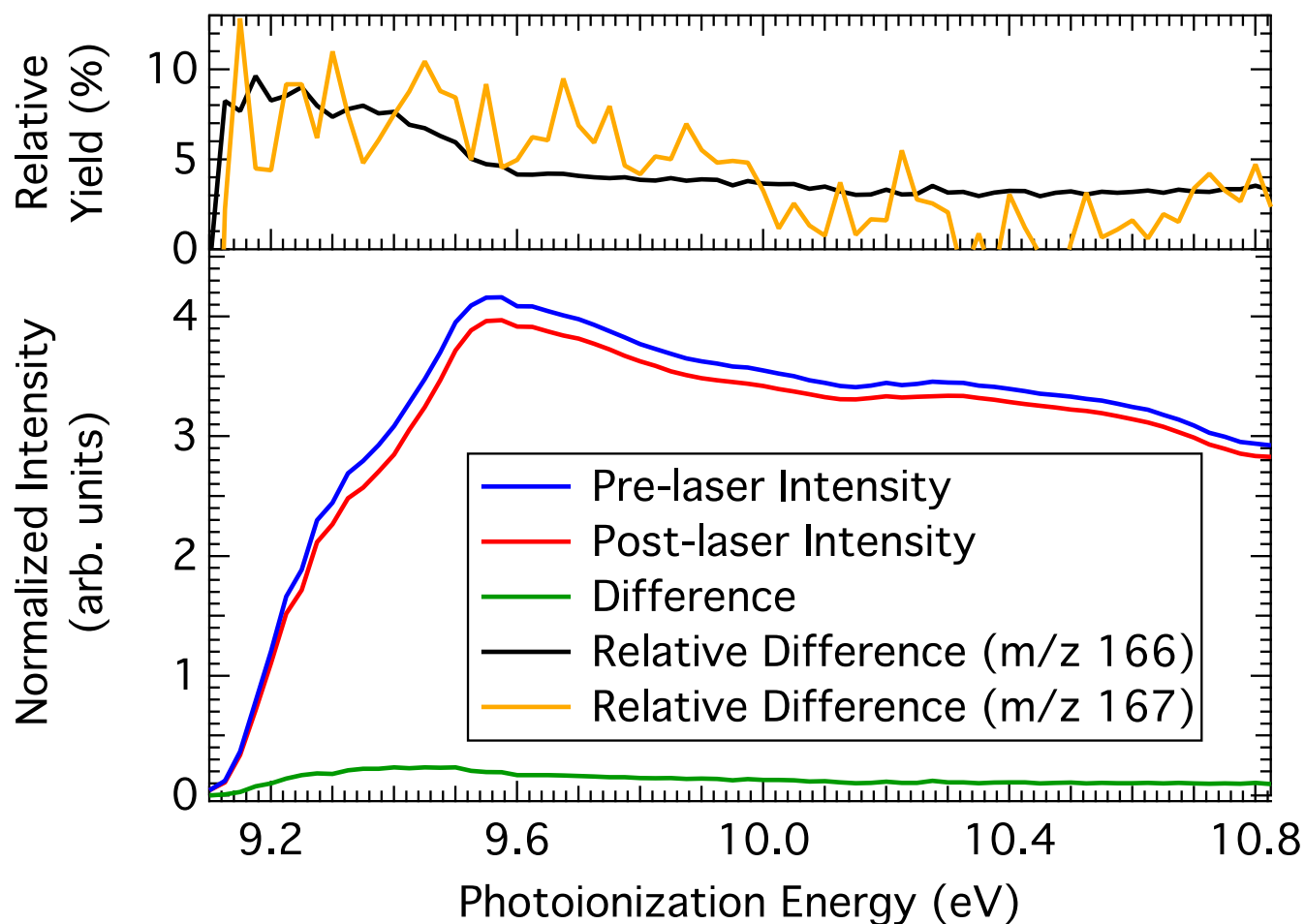
**Figure S4(a)** - Potential energy scheme for reaction of 1-propynyl radical with propylene calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy (AIE<sub>CBS-QB3</sub>) and m/z of the product.



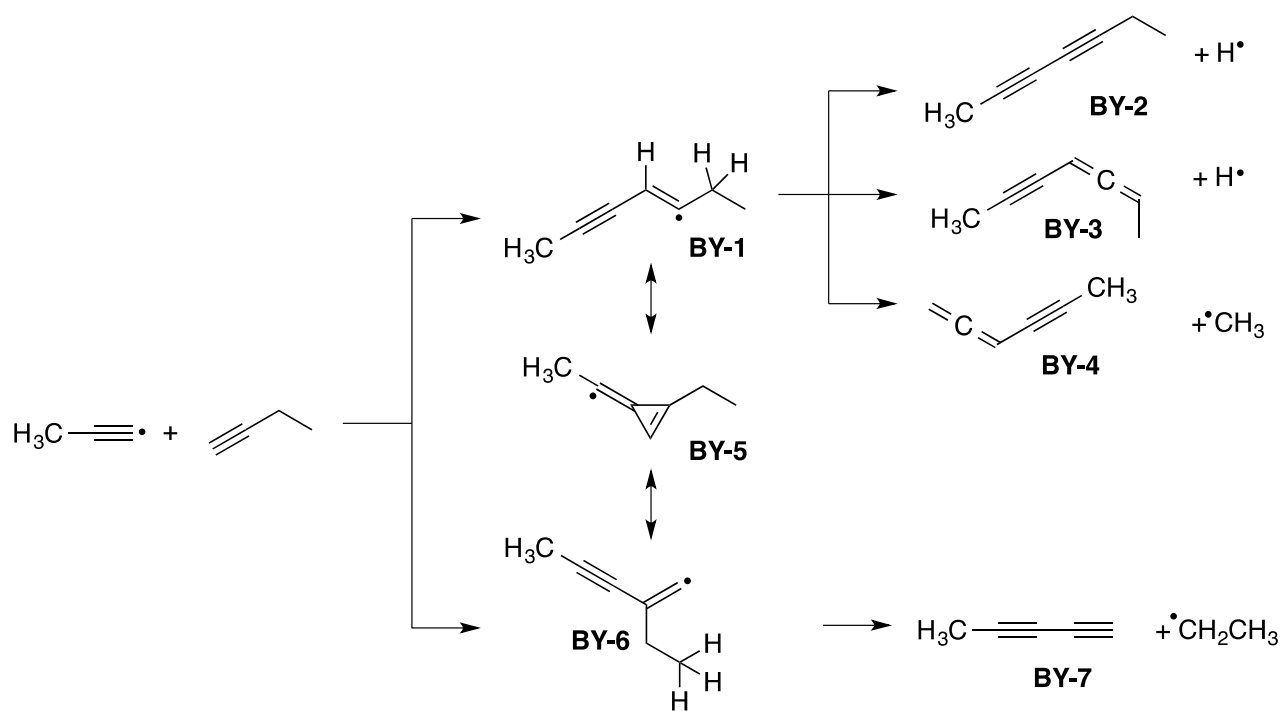
**Figure S4(b)** - Potential energy diagram for reaction of 1-propynyl radical with propylene calculated at the CBS-QB3 level. Dashed arrows represent channels with no barrier; a relaxed scan was undertaken to confirm the absence of an explicit transition state. The code above the energies identifies the species in the geometry and energy information. Information in the boxes includes in order, the identification code, adiabatic ionization energy ( $AIE_{\text{CBS-QB3}}$ ) and  $m/z$  of the product.

Molecule	Calculated /eV	Experimental /eV
hex-1-en-4-yne	9.38	
hex-2-en-4-yne	8.55	
1-methyl-2-ethenylidenecyclopropane	8.51	
pent-1-en-3-yne	8.99	
2-methylpent-1-en-3-yne	8.72	

**Table S4** - Calculated (CBS-QB3) and experimental adiabatic photoionization potentials for relevant C<sub>6</sub>H<sub>8</sub> (m/z 80) isomers.

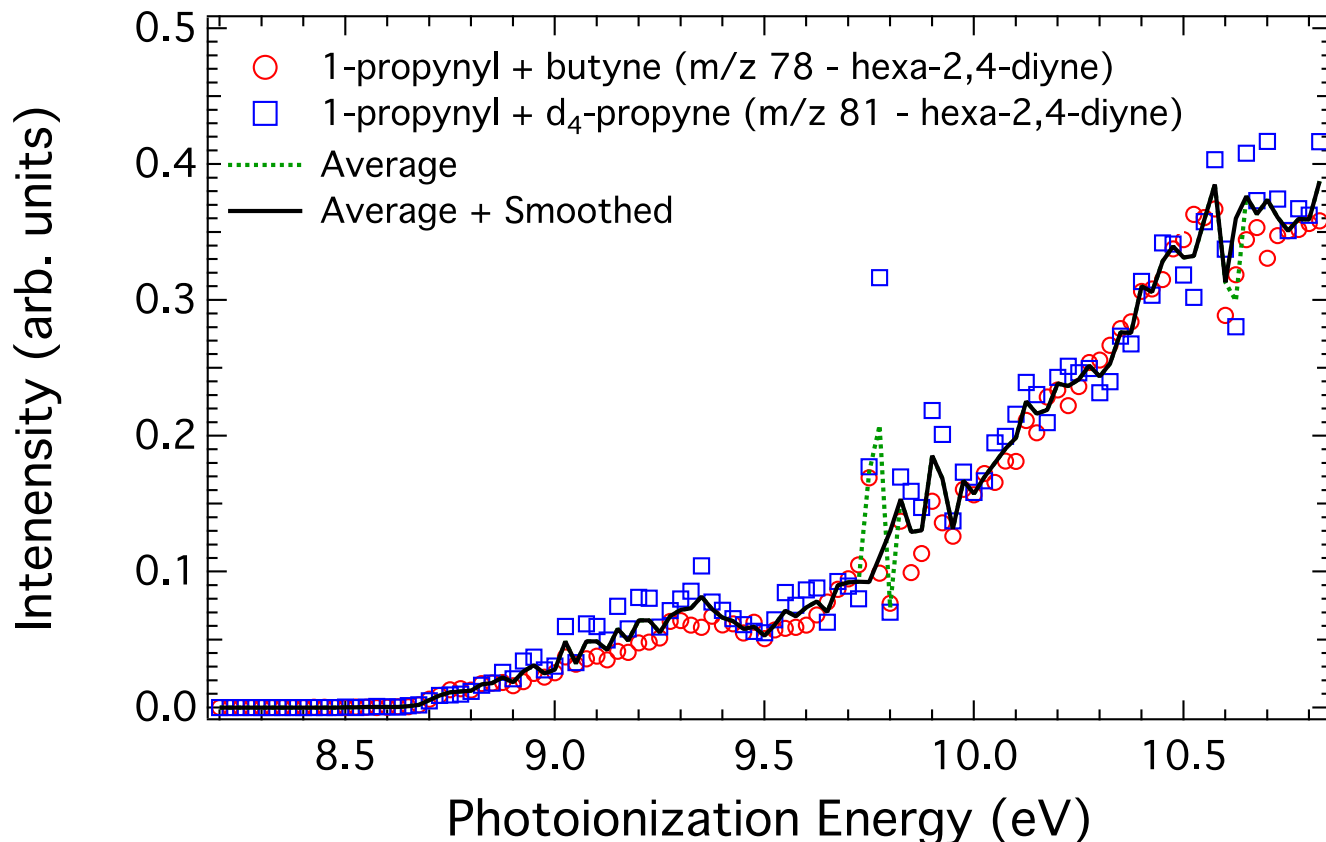


**Figure S5** - Depletion of the 1-iodopropyne ( $m/z$  166) intensity after the laser pulse. Pre-laser intensity is the average signal before the laser pulse, while post-laser intensity is the signal averaged over 80 ms after the laser pulse. The difference between the pre and post-laser intensity for the  $^{12}\text{C}/^1\text{H}$  and  $^{13}\text{C}/^2\text{H}$  isotopologues ( $[M]^+ = m/z$  166;  $[M+1]^+ = m/z$  167) decreases as a function of increasing photoionization energy as the signal intensity saturates the detector. The true photolysis yield is therefore estimated from the relative difference trace between 9.2 and 9.6 eV with a value of  $7 \pm 1$  %. Taking into account the pressure, temperature and concentration of 1-iodopropyne, we estimate a radical density of  $(1.5 \pm 0.3) \times 10^{13} \text{ cm}^{-3}$ .



**Figure S6** - Truncated scheme depicting potential pathways during the reaction of 1-propynyl radical with 1-butyne. Importantly, loss of  $\cdot\text{CH}_3$  is primarily expected to result in formation of hexa-1,2-dien-4-yne (**BY-4**).





**Figure S7** - Estimation of the hexa-1,2-dien-4-yne photoionization spectrum. The photoionization spectrum is estimated by taking the average of the  $C_6H_6$  and  $C_6H_3D_3$  photoionization trace, measured after reaction of 1-propynyl radical with 1-butyne and  $d_4$ -propyne, respectively, with the contribution of the hexa-2,4-diyne isomer subtracted. The averaged spectrum is smoothed to minimize aberrations due to under or over-subtraction of the significant autoionization resonances in the hexa-2,4-diyne photoionization spectrum.

## References:

1. Frisch, M. J. *et al.* Gaussian 09. (2009).
2. da Silva, G. G3X-K theory: A composite theoretical method for thermochemical kinetics. *Chem Phys Lett* **558**, 109–113 (2013).
3. Lias, S. G., Levin, R. D. & Kafafi, S. A. in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (Linstrom, P. J. & Mallard, W. G.) (National Institute of Standards and Technology). doi:<http://webbook.nist.gov>
4. Soorkia, S. *et al.* Reaction of the  $C_2H$  Radical with 1-Butyne ( $C_4H_6$ ): Low-Temperature Kinetics and Isomer-Specific Product Detection. *J. Phys. Chem. A* **114**, 3340–3354 (2010).
5. Lockyear, J. F. *et al.* Formation of fulvene in the reaction of  $C_2H$  with 1,3-butadiene. *International Journal of ...* (2014). doi:10.1016/j.ijms.2014.08.025
6. Lias, S. G. in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (Linstrom, P. J. & Mallard, W. G.) at <<http://webbook.nist.gov>>
7. Heilbronner, E., Gleiter, R., Hopf, H., Hornung, V. & De Meijere, A. Photoelectron-Spectroscopic Evidence for the Orbital Sequence in Fulvene and 3,4-Dimethylene-cyclobutene. *Helvetica Chimica Acta* **54**, 783–794 (1971).

