

## Electronic Supporting Information

### Elucidating the Chemical Dynamics of the Elementary Reactions of the 1-Propynyl Radical ( $\text{CH}_3\text{CC}; \text{X}^2\text{A}^1$ ) with 2-Methylpropene ( $(\text{CH}_3)_2\text{CCH}_2; \text{X}^1\text{A}_1$ )

Iakov A. Medvedkov,<sup>a</sup> Anatoliy A. Nikolayev,<sup>b</sup> Zhenghai Yang,<sup>a</sup> Shane J. Goettl,<sup>a</sup> Alexander M. Mebel,<sup>c\*</sup> Ralf I. Kaiser<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry, University of Hawai‘i at Manoa, Honolulu, HI 96822, USA*

<sup>b</sup> *Samara National Research University, Samara 443086, Russia*

<sup>c</sup> *Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA*

Corresponding to: [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu); [mebela@fiu.edu](mailto:mebela@fiu.edu)

## Contents

1. Discussion of the full potential energy surface (PES) of the reaction of 1-propynyl with 2-methylpropene. ....	3
2. Discussion of the probable sources of background signal at $m/z$ 78, 79 and 80 .....	4
3. RRKM calculations results.....	4
4. Full potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}; X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2; X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory .....	7
5. References .....	12

## 1. Discussion of the full potential energy surface (PES) of the reaction of 1-propynyl with 2-methylpropene.

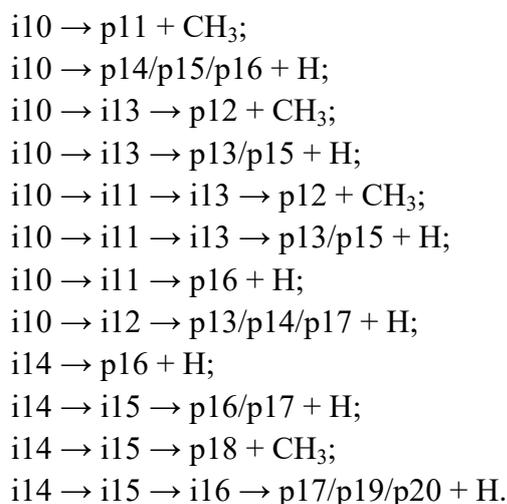
Reaction starts with an attack of 1-propynyl radical without any entrance barrier to one of the two chemically inequivalent carbon atoms C1 or C2 in 2-methylpropene via addition with its radical center to the C1=C2 double bond. This leads to doublet radical intermediates **i1** and/or **i4**. Both intermediates can be interconverted through the three-carbon ring closure steps via **i2** and **i3** intermediates. **i4** can isomerize via two distinct [1,2-H] shifts: (1) from the CH<sub>3</sub> group of the C<sub>4</sub>H<sub>8</sub> moiety to **i5** or (2) from the CH<sub>2</sub> group at the C1-position to form **i6**. The formation of **p1–p3** products is discussed in the main text of the manuscript (4. Discussion), here we will focus on the pathways to less important, according to the RRKM calculations (Table S1), products **cis/trans-p4** and **p7 – p25** (Fig. S1–S5).

### 1.1 Acyclic products *cis/trans-p4* and *p7 – p10* (Fig. S1 and S2)

Products **p7** and **p8** (Fig. S1-S2) are formed from **i5** via propene and methyl loss channels, respectively. Intermediate **i6** leads to *cis*- and *trans*- isomers of hex-2-en-4-yne (**cis/trans-p4**) via methyl elimination and to 5-methylhexa-1,2,3-triene (**p9**) through the hydrogen elimination exit channels. The product **p10** only can be formed via an H-loss from **i2** or **i3**.

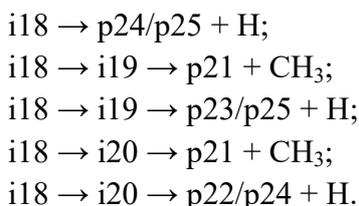
### 1.2 Cyclic products *p11 – p20* containing a five-membered ring (Fig. S3 – S4)

The ‘bottle-neck’ step on the way to cyclic products is a five-membered ring closure in **i5** with an energy barrier of 76 kJ mol<sup>-1</sup> that leads to **i9**. Further, **i9** can isomerize via two distinct [1,2-H] shifts: (1) from the CH<sub>2</sub> group of the 2-methylpropene moiety to form **i10** or (2) from the methyl group of the 1-propynyl moiety to form **i14**. Starting from **i10** and **i14**, ten distinct products **p11 – p20** containing five-membered rings can be formed via the pathways summarized below:



### 1.3 Cyclic products $p21 - p25$ containing a six-membered ring (Fig. S5)

Intermediate **i10** can undergo a hydrogen shift from the methyl group of the 1-propynyl moiety to the five-membered ring (**i11**) followed by the ring expansion (**i11**  $\rightarrow$  **i17** $\rightarrow$  **i18**) that incorporates all the 1-propynyl carbon atoms into the newly formed six-membered ring. Isomers **p21** – **p25** can be formed from **i18** via the pathways summarized below:



## 2. Discussion of the probable sources of background signal at $m/z$ 78, 79 and 80

Since the highly reactive 1-propynyl radical ( $CH_3CC$ ) has a molecular mass of 39 amu and the products of its recombination ( $C_6H_6$ ) 78 amu. Contamination of the background signal at  $m/z = 78$  and 79 most likely arises from products of 1-propynyl recombination ( $C_6H_6 - 78$  amu) with the contribution of  $^{13}C$ -compounds ( $^{13}CC_5H_6 - 79$  amu).  $C_6H_6$  isomers, according to the NIST database, show peaks at 78 – 80  $m/z$  indicating the presence of up to two  $^{13}C$  atoms. Recombination of 1-propynyl most likely occurs during supersonic expansion in the "expansion region", on the stainless walls of the pulse valve (catalyzed by  $Fe_2O_3$ ) or through a precursor decay ( $CH_3CCI$ ) during storage. In addition, mass 80 amu can have a contribution from ionized helium clusters  $He_{20}$ , common in molecular beams of  $He^{1,2}$ , which was used as a carrier gas for the  $CH_3CCI$  precursor. The ionization energy used in the experiment (80 eV) is sufficient to ionize He clusters (He ionization potential is 24.6 eV).

## 3. RRKM calculations results

Table S1. Statistical branching ratios (%) for the reaction of 2-methylpropene + propynyl with **i1** and **i4** as initial intermediates at different collision energies ( $E_C$ ,  $kJ\ mol^{-1}$ )

$E_C$	<b>i1</b>		<b>i4</b>	
	<b>0</b>	<b>38</b>	<b>0</b>	<b>38</b>
<b>p1+H</b>	65.2	59.2	66.4	63.1
<b>p2+H</b>	8.7	12.2	8.8	13.0
<b>p3+CH<sub>3</sub></b>	22.4	25.3	21.0	20.4
<b>cis-p4+CH<sub>3</sub></b>	2.2	1.9	2.2	2.0
<b>trans-p4+CH<sub>3</sub></b>	1.4	1.3	1.5	1.4
<b>p7+C<sub>3</sub>H<sub>6</sub></b>	0.1	0.1	0.1	0.1
<b>p8+CH<sub>3</sub></b>	0.0	0.0	0.0	0.0
<b>p9+H</b>	0.0	0.0	0.0	0.0
<b>p10+H</b>	0.0	0.0	0.0	0.0

<i>p11+CH<sub>3</sub></i>	0.0	0.0	0.0	0.0
<i>p12+CH<sub>3</sub></i>	0.0	0.0	0.0	0.0
<i>p13+H</i>	0.0	0.0	0.0	0.0
<i>p14+H</i>	0.0	0.0	0.0	0.0
<i>p15+H</i>	0.0	0.0	0.0	0.0
<i>p16+H</i>	0.0	0.0	0.0	0.0
<i>p17+H</i>	0.0	0.0	0.0	0.0
<i>p18+CH<sub>3</sub></i>	0.0	0.0	0.0	0.0
<i>p19+H</i>	0.0	0.0	0.0	0.0
<i>p20+H</i>	0.0	0.0	0.0	0.0
<i>p21+CH<sub>3</sub></i>	0.0	0.0	0.0	0.0
<i>p22+H</i>	0.0	0.0	0.0	0.0
<i>p23+H</i>	0.0	0.0	0.0	0.0
<i>p24+H</i>	0.0	0.0	0.0	0.0
<i>p25+H</i>	0.0	0.0	0.0	0.0

Table S2. RRKM calculated rate constants ( $k(E)$ ,  $s^{-1}$ ) of the reaction of 2-methylpropene + propynyl as functions of the internal energy ( $E$ ,  $\text{kJ mol}^{-1}$ ) of the intermediate states for unimolecular reaction steps at different collision energies ( $E_C$ ,  $\text{kJ mol}^{-1}$ )

$E_C$	0		37		$E_C$	0		37		
	Reaction step	$k(E)$	$E$	$k(E)$		$E$	Reaction step	$k(E)$	$E$	$k(E)$
	<i>i1 – i2</i>	3.35E+09	225	6.71E+09	263	<i>i10 – i11</i>	1.11E+06	399	4.22E+06	437
	<i>i2 – i1</i>	1.95E+12	186	2.84E+12	224	<i>i11 – i10</i>	5.22E+07	321	1.39E+08	359
	<i>i1 – p3</i>	1.83E+07	225	1.30E+08	263	<i>i11 – i17</i>	1.95E+10	321	2.66E+10	359
	<i>i4 – i6</i>	1.02E+06	238	7.59E+06	276	<i>i17 – i11</i>	9.32E+11	302	1.18E+12	340
	<i>i6 – i4</i>	7.47E+04	272	7.15E+05	310	<i>i14 – p16</i>	9.04E+07	386	3.11E+08	424
	<i>i4 – p1</i>	1.80E+07	238	1.40E+08	276	<i>i14 – i15</i>	3.28E+06	386	1.17E+07	424
	<i>i4 – p2</i>	2.40E+06	238	2.89E+07	276	<i>i15 – i14</i>	7.03E+07	330	1.95E+08	368
	<i>i4 – i3</i>	1.09E+09	238	2.63E+09	276	<i>i15 – p18</i>	1.31E+09	330	3.54E+09	368
	<i>i3 – i4</i>	3.03E+11	187	4.54E+11	225	<i>i15 – p17</i>	1.23E+08	330	3.83E+08	368
	<i>i6 – p1</i>	3.06E+05	272	2.96E+06	310	<i>i10 – p16</i>	1.06E+08	399	3.73E+08	437
	<i>i6 – trans-p4</i>	1.10E+07	272	7.47E+07	310	<i>i15 – i16</i>	1.09E+07	330	3.65E+07	368
	<i>i6 – cis-p4</i>	1.68E+07	272	1.12E+08	310	<i>i16 – i15</i>	1.33E+06	338	4.60E+06	376
	<i>i6 – p9</i>	1.76E+01	272	1.59E+03	310	<i>i16 – p17</i>	1.61E+08	338	4.86E+08	376
	<i>i5 – p2</i>	5.11E+04	223	7.75E+05	261	<i>i16 – p19</i>	4.19E+08	338	1.09E+09	376
	<i>i5 – p8</i>	5.61E+06	223	5.39E+07	261	<i>i16 – p20</i>	4.48E+07	338	1.59E+08	376
	<i>i5 – p7</i>	2.59E+08	223	1.08E+09	261	<i>i17 – i18</i>	1.85E+11	302	2.51E+11	340
	<i>i5 – i9</i>	1.51E+08	223	3.55E+08	261	<i>i18 – i17</i>	4.93E+09	340	8.10E+09	378
	<i>i9 – i5</i>	2.29E+08	278	8.88E+08	316	<i>i18 – p24</i>	1.54E+08	340	4.53E+08	378
	<i>i9 – i10</i>	3.42E+04	278	4.22E+05	316	<i>i18 – p25</i>	4.77E+08	340	1.38E+09	378
	<i>i10 – i9</i>	1.55E+00	399	3.37E+01	437	<i>i19 – p25</i>	4.44E+08	339	1.29E+09	377
	<i>i9 – i14</i>	1.53E+04	278	1.66E+05	316	<i>i19 – p21</i>	2.59E+09	339	6.36E+09	377
	<i>i14 – i9</i>	3.20E+00	386	5.86E+01	424	<i>i19 – p23</i>	2.13E+08	339	5.91E+08	377
	<i>i2 – i3</i>	1.51E+12	186	1.93E+12	224	<i>i20 – p24</i>	2.69E+07	400	9.43E+07	438
	<i>i3 – i2</i>	2.29E+11	187	2.92E+11	225	<i>i20 – p22</i>	6.00E+06	400	2.09E+07	438

<i>i3 – p10</i>	2.04E+00	187	1.12E+03	225	<i>i20 – p21</i>	5.91E+08	400	1.64E+09	438
<i>i2 – p10</i>	1.20E+01	186	6.96E+03	224	<i>i13 – i11</i>	3.50E+06	337	1.25E+07	375
<i>i4 – i5</i>	1.93E+04	238	3.06E+05	276	<i>i11 – i13</i>	2.32E+06	321	7.63E+06	359
<i>i5 – i4</i>	1.87E+04	223	2.56E+05	261	<i>i11 – p16</i>	4.48E+07	321	1.31E+08	359
<i>i10 – i12</i>	3.34E+06	399	1.06E+07	437	<i>i12 – p14</i>	4.20E+08	358	1.13E+09	396
<i>i12 – i10</i>	1.87E+07	358	4.98E+07	396	<i>i12 – p17</i>	3.92E+08	358	1.25E+09	396
<i>i10 – p11</i>	4.39E+08	399	1.17E+09	437	<i>i12 – p13</i>	8.14E+08	358	2.13E+09	396
<i>i10 – p14</i>	3.71E+07	399	1.16E+08	437	<i>i15 – p16</i>	3.80E+08	330	1.11E+09	368
<i>i10 – p15</i>	9.65E+07	399	3.17E+08	437	<i>i18 – i19</i>	1.81E+07	340	6.32E+07	378
<i>i10 – i13</i>	9.95E+05	399	3.50E+06	437	<i>i19 – i18</i>	2.43E+07	339	8.46E+07	377
<i>i13 – i10</i>	7.09E+07	337	1.90E+08	375	<i>i18 – i20</i>	1.54E+08	340	3.86E+08	378
<i>i13 – p15</i>	1.67E+08	337	4.80E+08	375	<i>i20 – i18</i>	5.15E+06	400	1.67E+07	438
<i>i13 – p12</i>	3.84E+09	337	9.61E+09	375					

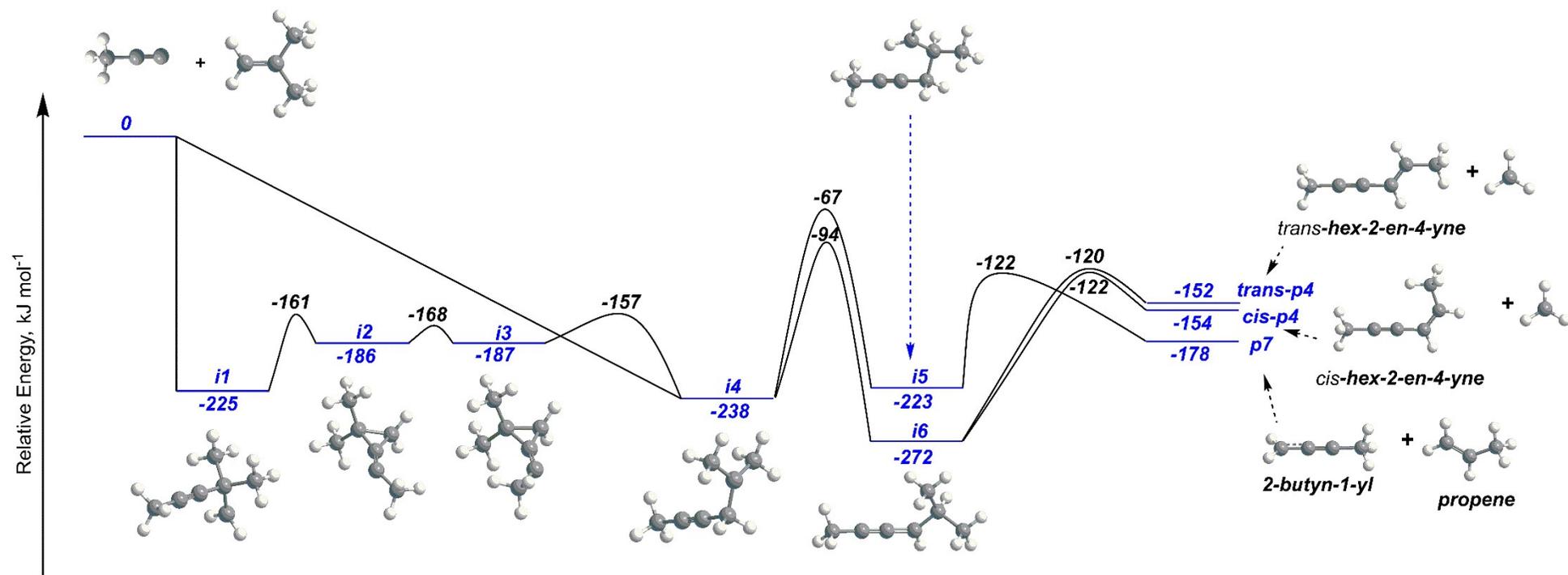
Table S3. Statistical branching ratios (%) for the reaction of *trans*-but-2-ene + propynyl with *i7* as an initial intermediate at different collision energies ( $E_C$ , kJ mol<sup>-1</sup>)

$E_C$	<i>i7</i>	
	0	38
<i>trans-p4+CH<sub>3</sub></i>	97.4	95.8
<i>cis-p5+H</i>	2.3	3.5
<i>p6+H</i>	0.3	0.7

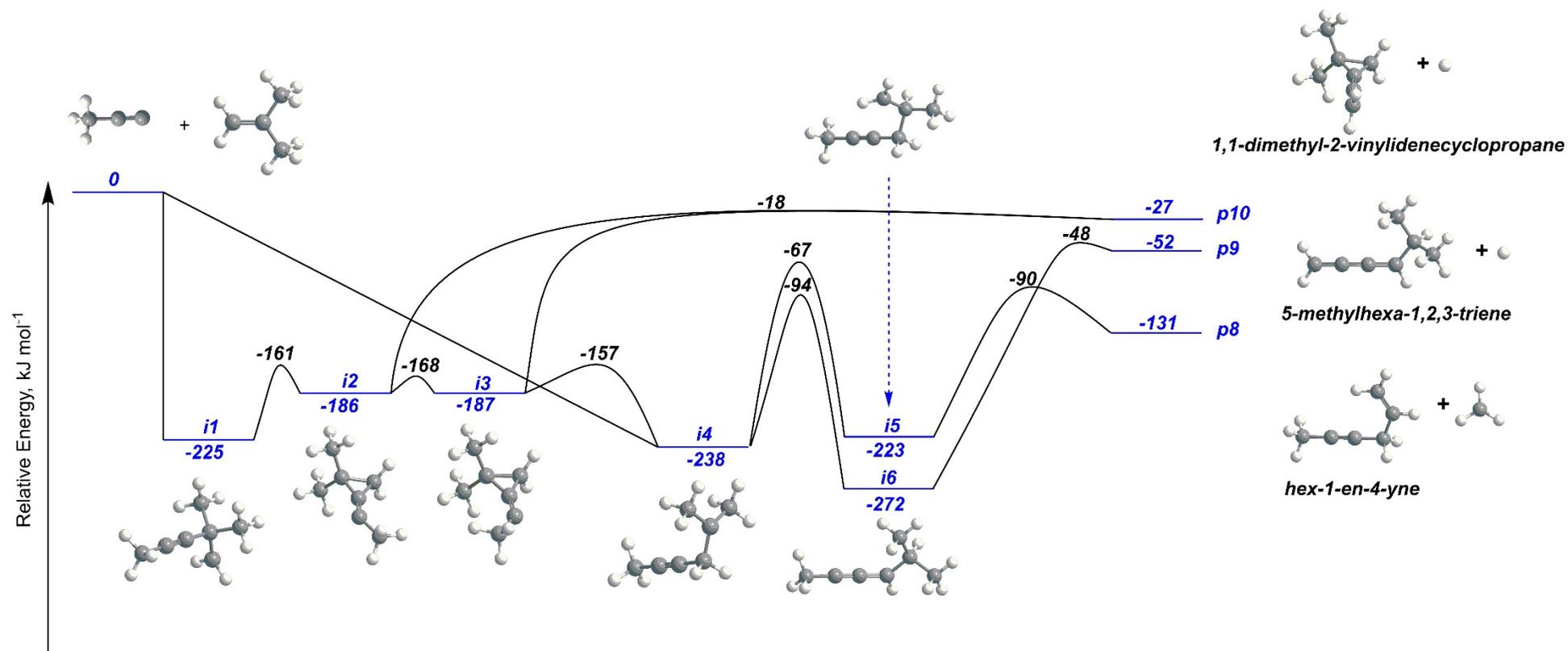
Table S4. Statistical branching ratios (%) for the reaction of *cis*-but-2-ene + propynyl with *i8* as an initial intermediate at different collision energies ( $E_C$ , kJ mol<sup>-1</sup>)

$E_C$	<i>i8</i>	
	0	38
<i>cis-p4+CH<sub>3</sub></i>	96.8	94.4
<i>trans-p5+H</i>	3.0	5.1
<i>p6'+H</i>	0.2	0.5

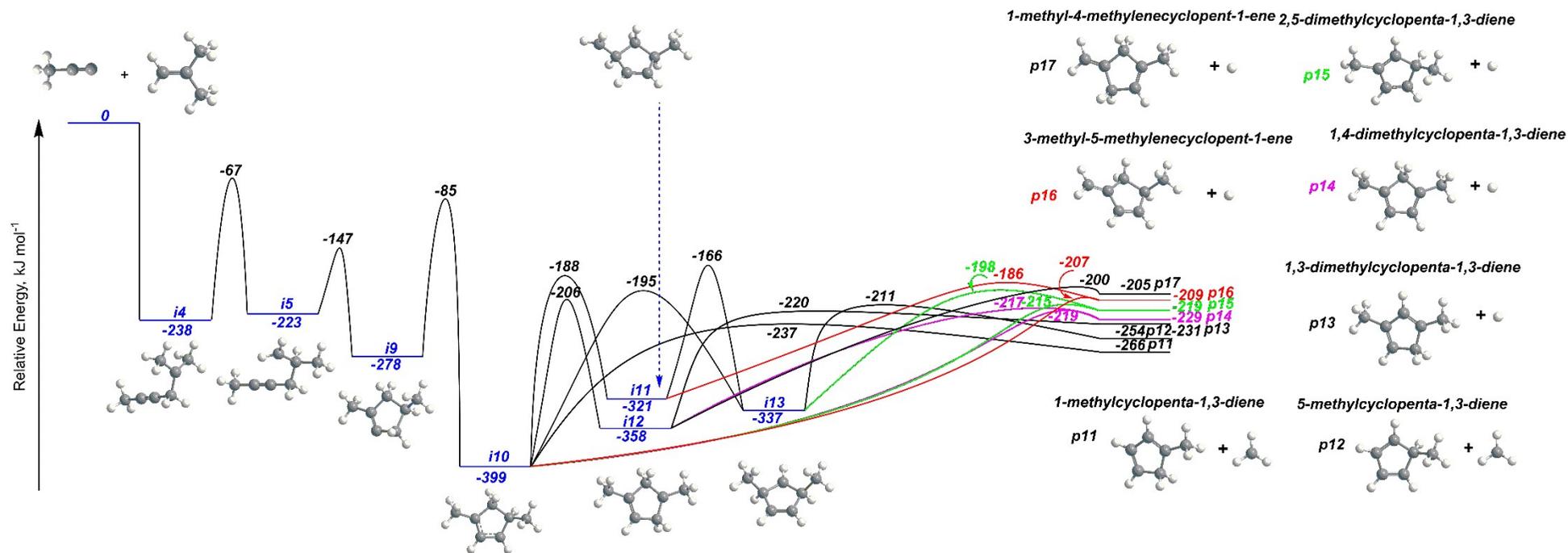
4. Full potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}\cdot$ ;  $X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2$ ;  $X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory



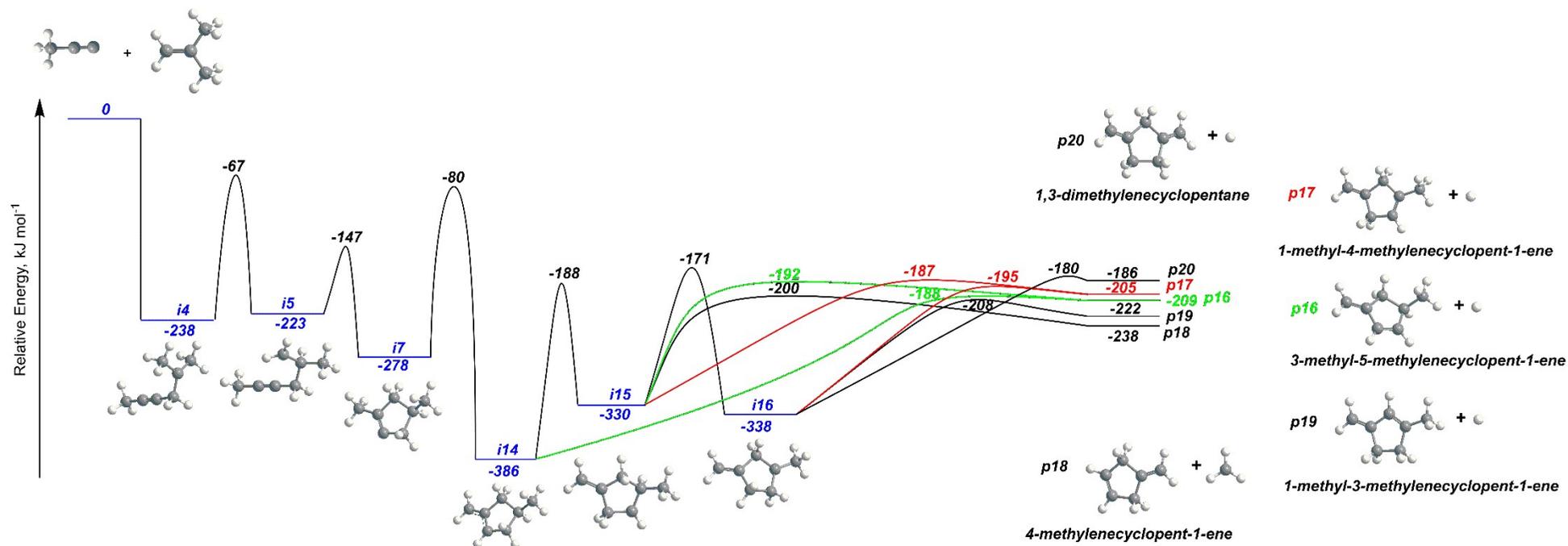
**Figure S1.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}\cdot$ ;  $X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2$ ;  $X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory. Relative energies are given in  $\text{kJ mol}^{-1}$ . Part I.



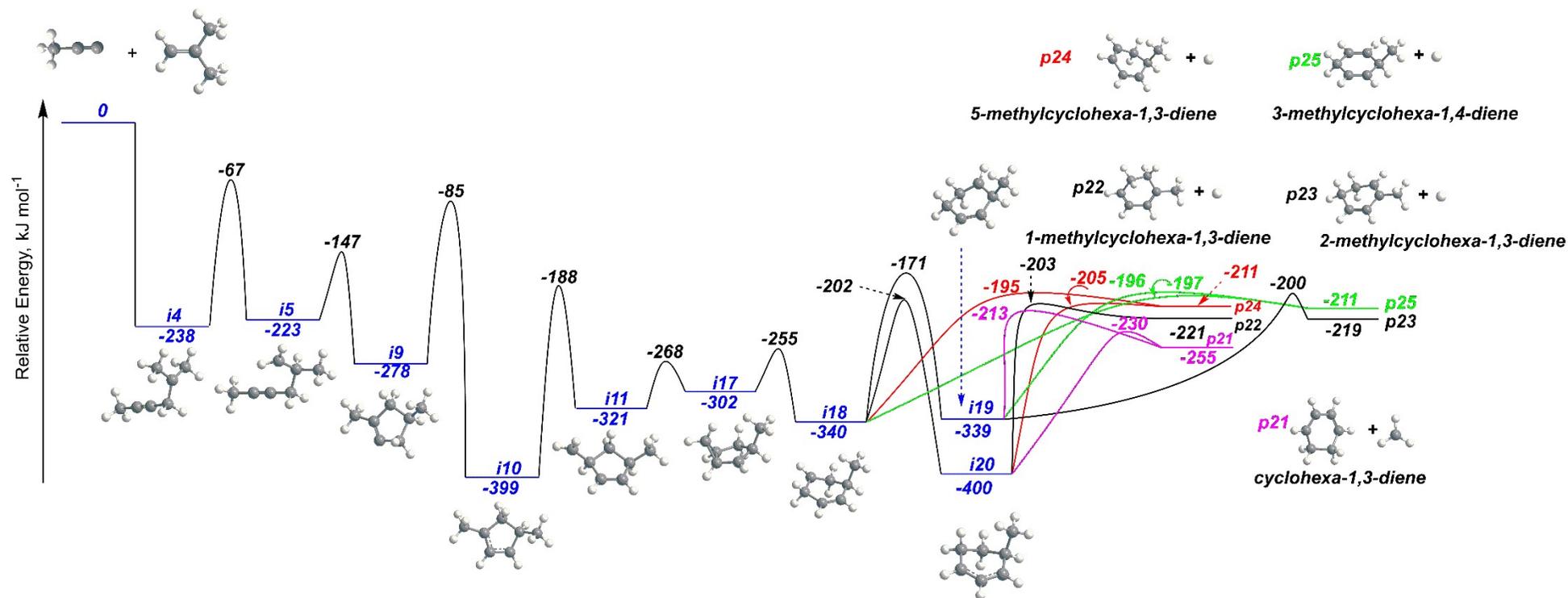
**Figure S2.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}$ ;  $X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2$ ;  $X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory. Relative energies are given in  $\text{kJ mol}^{-1}$ . Part II.



**Figure S3.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}$ ;  $X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2$ ;  $X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory. Relative energies are given in kJ mol<sup>-1</sup>. Part III.



**Figure S4.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}\cdot$ ;  $X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2$ ;  $X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory. Relative energies are given in  $\text{kJ mol}^{-1}$ . Part IV.



**Figure S5.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical ( $\text{CH}_3\text{CC}\cdot$ ;  $X^2A_1$ ) with 2-methylpropene ( $(\text{CH}_3)_2\text{CCH}_2$ ;  $X^1A'$ ) calculated at the CCSD(T)-F12/cc-pVTZ-F12// $\omega$ B97X-D/6-311G(d,p) level of theory. Relative energies are given in  $\text{kJ mol}^{-1}$ . Part V.

## 5. References

- 1 H. Buchenau, E. L. Knuth, J. Northby, J. P. Toennies and C. Winkler, Mass spectra and time-of-flight distributions of helium cluster beams, *The Journal of Chemical Physics*, 1990, **92**, 6875–6889.
- 2 L. Lundberg, P. Bartl, C. Leidlmair, P. Scheier and M. Gatchell, Protonated and Cationic Helium Clusters, *Molecules*, 2020, **25**, 1066.