

## Supplementary information

# Low Temperature Synthesis of Three Cyanocyclopentadiene Isomers and their Role in Interstellar Cyano PAH Formation

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**Supplementary Table 1.** Experimental peak velocities ( $v_p$ ) and speed ratios (S) of the cyano (CN) and 1,3-cyclopentadiene (c-C<sub>5</sub>H<sub>6</sub>) reactants along with the corresponding collision energy ( $E_c$ ) and center-of-mass ( $\theta_{CM}$ ).

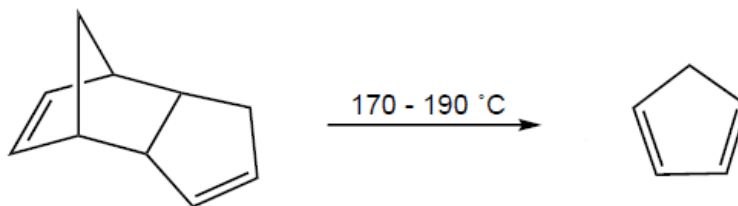
| Beam                                                             | $v_p$<br>(m s <sup>-1</sup> ) | S          | $E_c$<br>(kJ mol <sup>-1</sup> ) | $\theta_{CM}$<br>(°) |
|------------------------------------------------------------------|-------------------------------|------------|----------------------------------|----------------------|
| CN (X <sup>2</sup> Σ <sup>+</sup> )                              | 1228 ± 26                     | 4.3 ± 0.3  |                                  |                      |
| c-C <sub>5</sub> H <sub>6</sub> (X <sup>1</sup> A <sub>1</sub> ) | 638 ± 13                      | 24.0 ± 1.1 | 18 ± 1                           | 53 ± 1               |

## Supplementary Note 1: Cyclopentadiene synthesis

| Chemicals                                 |                                                                           |                                                              |
|-------------------------------------------|---------------------------------------------------------------------------|--------------------------------------------------------------|
| Chemical                                  | Quantity                                                                  | Supplier                                                     |
| Dicyclopentadiene                         | 20 g                                                                      | TCI                                                          |
| Glassware                                 |                                                                           |                                                              |
| Item                                      | Specification                                                             | Supplier                                                     |
| Bottom round flask                        | 50 mL, 14/20                                                              | Synthware, F302450                                           |
| Short path distilling head                | 14/20                                                                     | Bantam-ware, 287120-0000                                     |
| Collection flask                          | 25 mL, 14/20                                                              | Synthware, F311425                                           |
| Custom Glass-metal LN <sub>2</sub> trap   | 40 mm body OD<br>225 mm below joint,<br>16CF at the center and side tubes | Based on Synthware V103884,<br>custom-made glass connections |
| Joint clips                               | 14/20                                                                     |                                                              |
| Other                                     |                                                                           |                                                              |
| Item                                      | Specification                                                             | Supplier                                                     |
| Scroll Pump                               | Oil free                                                                  | Varian                                                       |
| Beverage cylinder                         | 13 L                                                                      | Matheson                                                     |
| Teflon tubing                             | ¼ inch OD                                                                 | McMaster                                                     |
| SS tubing                                 | ¼ inch OD                                                                 | Swagelok                                                     |
| Convectron gauge                          | 10 <sup>-4</sup> Torr – 1 atm                                             | 275 MKS                                                      |
| Absolute Capacitance Manometer (Baratron) | 1 – 1000 Torr                                                             | MKS                                                          |
| Silicone Oil Bath                         | For up to 200 °C                                                          | Fisher                                                       |
| Down Corning Vacuum Lubricant             | -                                                                         | Dow Corning                                                  |
| Ar 99.9999%                               | -                                                                         | Air Gas                                                      |

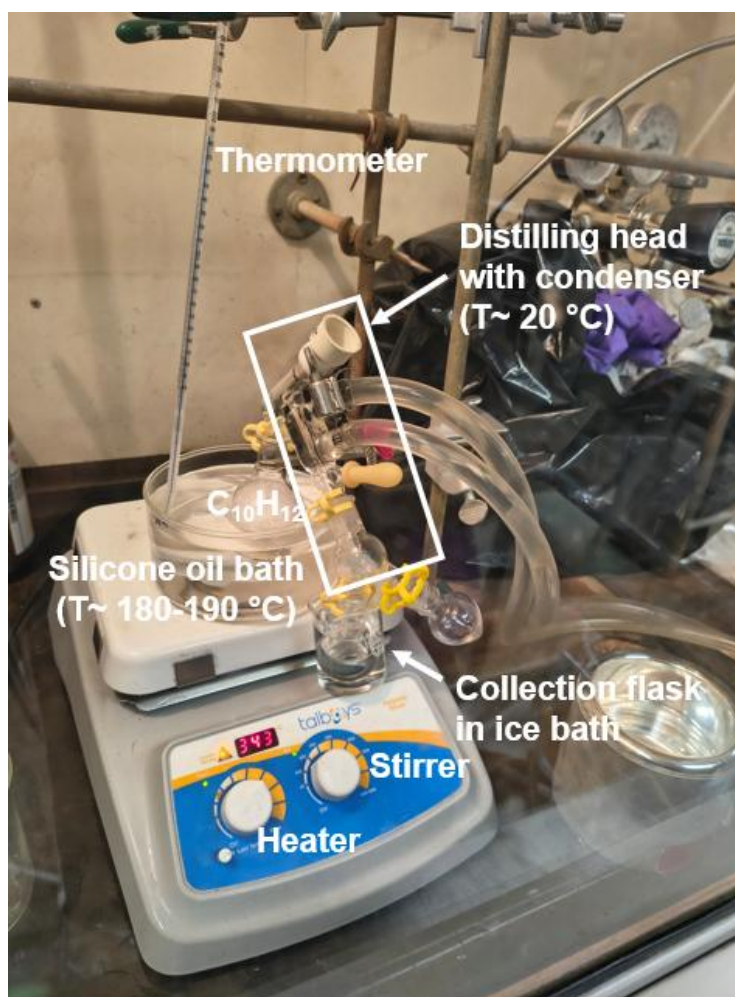
## Procedure

The synthesis of cyclopentadiene (c-C<sub>5</sub>H<sub>6</sub>) is based on the previous from Moffet *et al.*<sup>1</sup> and a photo of the experimental set-up can be found in Supplementary Fig. 1. c-C<sub>5</sub>H<sub>6</sub> is synthesized by thermal cracking of the dimer, dicyclopentadiene (C<sub>10</sub>H<sub>12</sub>), via a retro-Diels Alder reaction:



Into a 50 mL round bottom flask are placed a magnetic stirring bar and about 20 grams of the dicyclopentadiene starting material. Afterward, the round bottom flask is coupled to a distillation equipment, which includes a distillation head, the condenser with water running at 20 °C and the collection flask. Due to the short path c-C<sub>5</sub>H<sub>6</sub> will not stay in the condenser for a very

long time and the water temperature is cold enough to prevent dimerization of  $c\text{-C}_5\text{H}_6$ . In the meantime, silicon oil bath with an immersed thermometer is heated up to 180-190 °C in a heating mantle. When reaching the desired temperature, the round bottom flask is introduced in the bath while stirring. A few minutes later,  $c\text{-C}_5\text{H}_6$  distils smoothly through the ground-glass outlet of short path distilling head and the first drops of  $c\text{-C}_5\text{H}_6$  are collected in a 25 mL collection flask, which is placed on ice bath, to avoid dimerization back to  $\text{C}_{10}\text{H}_{12}$ . When a considered amount of liquid  $c\text{-C}_5\text{H}_6$  is collected, it is transferred to a trap, immersed on a flask with ice bath to keep the trap cold and avoid dimerization (Note:  $c\text{-C}_5\text{H}_6$  dimerizes rapidly at room temperature and should be used immediately). The freeze-pump-thaw cycle is applied to remove the air in the cold trap. Now it is ready for charging an empty cylinder.



**Supplementary Fig. 1. Photo of the experimental setup for the synthesis of  $c\text{-C}_5\text{H}_6$ .** Illustration of the experimental apparatus used for the synthesis of 1,3-cyclopentadiene. The diagram shows all the key components of the preparation setup.

### **Charging a pre-empted 13 L beverage cylinder (Supplementary Fig. 2)**

- 1) Once the air has been removed from the cold trap with  $c\text{-C}_5\text{H}_6$ . Connect to the vacuum line the Teflon-tubing end coming out of the outlet Swagelok valve of  $\text{LN}_2$ -cooled glass trap (connect V2 and V3).
- 2) Open up the outlet Swagelok valve (V2) and evacuate the body of the glass trap down below 100 mTorr.
- 3) Open the manual valve of a pre-empted 13 L beverage cylinder (V8).
- 4) Once the vacuum is established inside the system (glass trap and cylinder V2, V3, V4, V5, V7, V8 – open; V6 – closed) down below 100 mTorr regardless of scroll pump conditions, shut off the Swagelok valve to scroll pump (V7) and remove the dewar out of the glass trap.
- 5) Monitor the pressure increment with the combination of a Convectron/Pirani gauge (below 1 Torr) and a membrane (Baratron) gauge (1 Torr to 800 Torr) – let the glass trap warm up by itself or, only rub with your hands the body of glass trap. The pressure may arise to ~262 Torr within 25 minutes.
- 6) Close off the manual valve (V8) of the cylinder and the outlet Swagelok valve (V2).

### **Diluting (5 %) in argon gas:**

- 7) Evacuating the whole line down to below 100 mTorr, which includes the regulator with diaphragm valve dialed in and outlet valve opened (V6 opened). Before continue, make sure that the regulator is isolated so that no high pressure can go inside. Then, flush the regulator twice the charge-purge cycle as follows (8-10):
- 8) Close off the outlet valve of the argon regulator.
- 9) Twist-open the manual valve of the argon tank to release gas in; close off afterward.
- 10) Discharge the trapped to the active vacuum by opening up the outlet valve of the regulator and pumping down below 100 mTorr.
- 11) Repeat once the cycle (8-10).

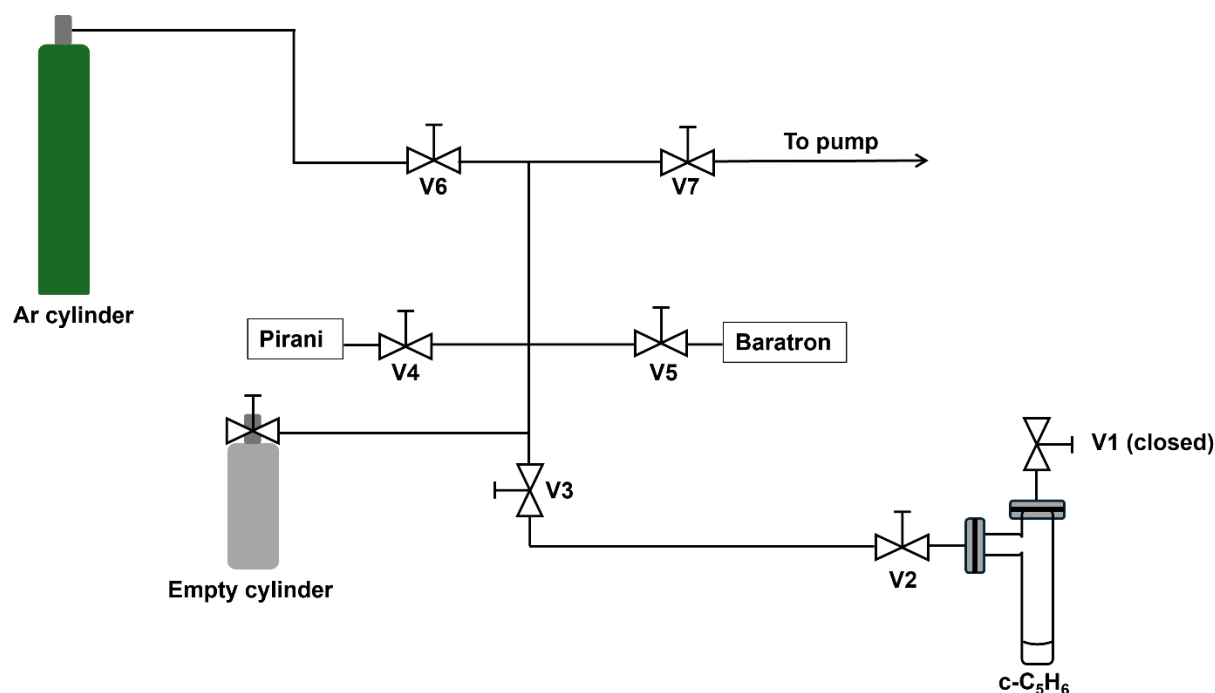
Now it is ready to dilute (5 %)  $c\text{-C}_5\text{H}_6$  (for example, 262 Torr / ~100 psi) in argon gas.

- 12) Close off two Swagelok valves to the corresponding pressure gauges (V4 and V5) in order to prevent any damage.

- 13) Dial-out all the way the diaphragm valve and close off the outlet valve of the argon regulator.
  - 14) Twist-open the manual valve of the argon tank to release argon in.
  - 15) Slowly dial inward the diaphragm valve to regulate the gas output at 100 psi.
  - 16) Close off the Swagelok valve to the scroll pump (V7).
  - 17) Open up the outlet valve of the regulator to fill the whole closed system at the regulated pressure.
  - 18) Finally open up the manual valve (V8) of the c-C<sub>5</sub>H<sub>6</sub>-containing cylinder and wait until the hissing stops.
  - 19) Close the manual valve of the c-C<sub>5</sub>H<sub>6</sub> cylinder (V8).
  - 20) Close off the manual valve of the argon tank and evacuate the regulator and vacuum line all the way to the scroll pump (open V7).
  - 21) After the high Ar pressure is gone (less than 1 atm) open the pressure gauges (V4 and V5) valves to monitor the pressure.
  - 22) Open all the glass trap valves to evacuate the line.
- 5 % c-C<sub>5</sub>H<sub>6</sub> mixture in argon with a total pressure of about 100 psi is done. Label the c-C<sub>5</sub>H<sub>6</sub> cylinder with the date, name of the mixture (c-C<sub>5</sub>H<sub>6</sub> in Ar), formula, concentration, total pressure and your name.

### **Safety considerations**

Cyclopentadiene (c-C<sub>5</sub>H<sub>6</sub>) was handled as a hazardous, volatile, and flammable chemical. All operations involving neat (c-C<sub>5</sub>H<sub>6</sub>), including transfer, evacuation, and preparation of the gas mixture, were performed using an appropriate fume hood. Appropriate personal protective equipment, including safety glasses or a face shield, suitable protective gloves, and a laboratory coat, was worn throughout the procedure. Sources of ignition were also excluded from the work area.



**Supplementary Fig. 2. Experimental setup for charging and diluting c-C<sub>5</sub>H<sub>6</sub> in a 13L cylinder.** Schematic illustration of the gas handling system used to charge and dilute c-C<sub>5</sub>H<sub>6</sub> in a 13 L gas cylinder to be used in the molecular beam experiments.

### Finishing the experiment

When the experiment is done, the first thing is to assess “potential safety hazard” associated with after the experiment. Make sure to unplug/switch off heating elements, stop running water through the condenser.

The next thing to do is discard all the materials remaining in the glass trap. For that, it is needed to follow this sequence:

- (1) Vent the glass trap to air.
- (2) Take the orange clip off from the joint connection.
- (3) Gently twist the glass trap off the inner male ground glass.
- (4) Place the glass trap inside the cup sink of the fume hood.

After this, you may want to clean the rest of dicyclopentadiene which has not been cracked in the round bottom flask with plenty of ethanol. Please also clean and rinse in ethanol all other glassware that includes the distilling head and collection flasks. Finally, dry out glassware inside the oven at about 100 °C.

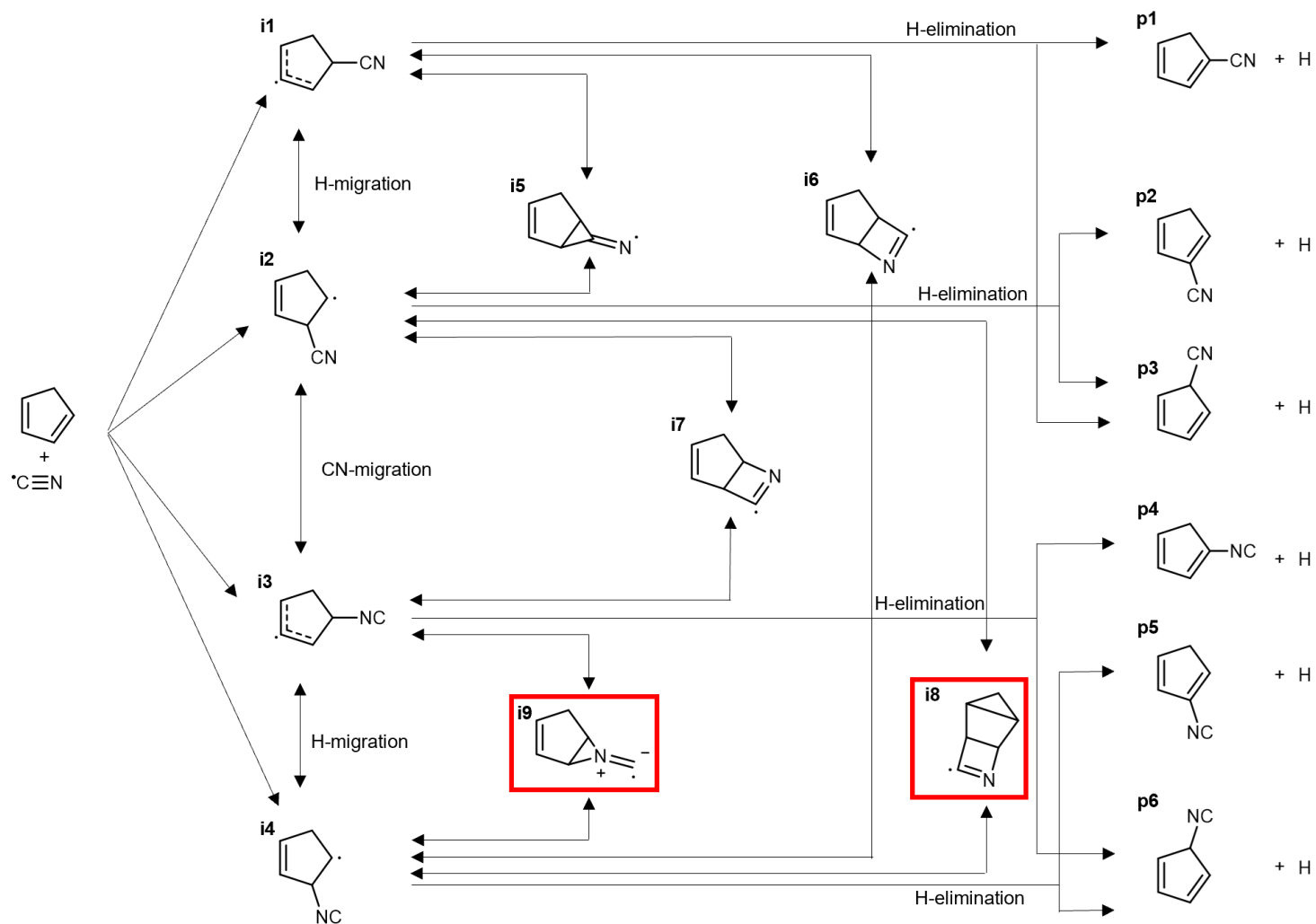
## Supplementary Note 2: Possible pathways to p1-p3 from i1-i4

Here we discuss in detail all the possible pathways to form **p1-p3** assuming a complete formation each of the intermediates **i1-i4**. When **i1** is the only collision complex considered, it can form directly **p1** and **p3** by eliminating an H-atom ( $\mathbf{i1} \rightarrow \mathbf{p1/p3} + \text{H}$ ). **i1** can also isomerize to **i2** either involving **i5** or by hydrogen shifts, but as mentioned in the main text is anticipated to proceed through **i5** based on the energy barriers ( $143 \text{ kJ mol}^{-1}$  versus  $203 \text{ kJ mol}^{-1}$ , respectively) to give **p2** and **p3** ( $\mathbf{i1} (\rightarrow \mathbf{i5}) \rightarrow \mathbf{i2} \rightarrow \mathbf{p2/p3} + \text{H}$ ). This is revealed by RRKM calculations which predict that the latter route contribute with around 79 % to the formation of **p2**. An alternative route for **i1** involves the formation of the bicyclic ring **i6** to form **i4**, which isomerizes to **i3**. This intermediate can follow two possible pathways to form **i2**, via CN migration or through the formation of **i7**. As for the **i5** case, the latter pathway would be favorable based on the energy barriers, this additional route would be:  $\mathbf{i1} \rightarrow \mathbf{i6} \rightarrow \mathbf{i4} \rightarrow \mathbf{i3} (\rightarrow \mathbf{i7}) \rightarrow \mathbf{i2} \rightarrow \mathbf{p2/p3} + \text{H}$ . However, negligible fractions for **p2** and **p3** have been calculated through this pathway. Note that most of the **p3** is formed directly from **i1** (91 %) and a small amount from **i2** based on the RRKM rate constants. Assuming a complete formation of **i2**, it can form **p2** and **p3** directly by H-atom loss ( $\mathbf{i2} \rightarrow \mathbf{p2/p3} + \text{H}$ ) as well as isomerizes to **i1** through the previous discussed routes to form **p1** and **p3** ( $\mathbf{i2} \rightarrow (\mathbf{i5} \rightarrow) \mathbf{i1} \rightarrow \mathbf{p1/p3} + \text{H}$  and  $\mathbf{i2} (\rightarrow \mathbf{i7}) \rightarrow \mathbf{i3} \rightarrow \mathbf{i4} \rightarrow \mathbf{i6} \rightarrow \mathbf{i1} \rightarrow \mathbf{p1/p3} + \text{H}$ ). Likewise, **i2** is likely preferred to isomerize to **i1** through the formation of **i5** rather than by hydrogen shifts or isomerization through **i3** (or **i7**) to form **p1**. There is only one route to form **p2** from **i2** ( $\mathbf{i2} \rightarrow \mathbf{p2} + \text{H}$ ). Concerning **p3**, the most likely pathway would be  $\mathbf{i2} \rightarrow \mathbf{i5} \rightarrow \mathbf{i1} \rightarrow \mathbf{p3} + \text{H}$ . Comparing with RRKM calculations, they effectively show that  $\mathbf{i2} \rightarrow \mathbf{i5} \rightarrow \mathbf{i1} \rightarrow \mathbf{p1} + \text{H}$  and  $\mathbf{i2} \rightarrow \mathbf{i5} \rightarrow \mathbf{i1} \rightarrow \mathbf{p3} + \text{H}$  pathways contribute with 94 % and 86 %, to the formation of **p1** and **p3** from **i2**. Finally, considering the exclusive formation of each of the less stable initial complexes **i3** and **i4**, all the possible pathways from **i3** to **p1-p3** are:  $\mathbf{i3} \rightarrow (\mathbf{i7} \rightarrow) \mathbf{i2} \rightarrow (\mathbf{i5} \rightarrow) \mathbf{i1} \rightarrow \mathbf{p1/p3} + \text{H}$ ,  $\mathbf{i3} \rightarrow (\mathbf{i7} \rightarrow) \mathbf{i2} \rightarrow \mathbf{p2/p3} + \text{H}$ ,  $\mathbf{i3} \rightarrow \mathbf{i4} \rightarrow \mathbf{i6} \rightarrow \mathbf{i1} \rightarrow (\mathbf{i5} \rightarrow) \mathbf{i2} \rightarrow \mathbf{p2/p3} + \text{H}$  and  $\mathbf{i3} \rightarrow \mathbf{i4} \rightarrow \mathbf{i6} \rightarrow \mathbf{i1} \rightarrow \mathbf{p1/p3} + \text{H}$ . Amongst all these routes, the most dominating ones according to RRKM calculations are  $\mathbf{i3} \rightarrow \mathbf{i2} \rightarrow \mathbf{i5} \rightarrow \mathbf{i1} \rightarrow \mathbf{p1}$  or  $\mathbf{i3} \rightarrow \mathbf{i2} \rightarrow \mathbf{i1} \rightarrow \mathbf{p1}$ , which contributes equally for the formation of **p1**, and  $\mathbf{i2} \rightarrow \mathbf{p2}$  for the formation of **p2**. Note that, although based on the energy barriers one can think that formation of **i2** from **i3** is more favorable through **i7**, based on the unimolecular rate constants ( $\mathbf{i3} \rightarrow \mathbf{i7}$ ,  $k = 2.07 \times 10^5 \text{ s}^{-1}$  and  $\mathbf{i7} \rightarrow \mathbf{i3}$ ,  $k = 2.41 \times 10^{11} \text{ s}^{-1}$  at  $20 \text{ kJ mol}^{-1}$ ) is highly unlikely that **i3** can actually form **i7**, and it is preferred to form **i2** by CN migration ( $\mathbf{i3} \rightarrow \mathbf{i2}$ ,  $k = 5.33 \times 10^4 \text{ s}^{-1}$  and  $\mathbf{i3} \rightarrow \mathbf{i2}$ ,  $k = 3.68 \times 10^3 \text{ s}^{-1}$ ). RRKM

calculations predict that the pathways involving **i7** from **i3** only contributes with 0.3 % to the formation of **p1**, **p2** and **p3**. Similarly, small contributions in the pathways forming **i4** from **i3** are predicted, with fractions of up to 4 % for the total product formation. Lastly, **i4** can undergo the following pathways: **i4** → **i6** → **i1** → (**i5** →) **i2** → **p2/p3** + H, **i4** → **i6** → **i1** → **p1/p3** + H, **i4** → **i3** → (**i7** →) **i2** → (**i5** →) **i1** → **p1/p3** + H and **i4** → **i3** (→ **i7**) → **i2** → **p2/p3** + H. In this case, although the first step **i4** → **i6** and **i4** → **i3** have roughly the same energy barriers (113 and 116 kJ mol<sup>-1</sup>, respectively), based on the RRKM calculations (**i4** → **i6**,  $k = 2.00 \times 10^5 \text{ s}^{-1}$  and **i6** → **i4**,  $k = 2.60 \times 10^9 \text{ s}^{-1}$  and **i4** → **i3**,  $k = 2.96 \times 10^6 \text{ s}^{-1}$  and **i3** → **i4**,  $k = 2.68 \times 10^4 \text{ s}^{-1}$  at 20 kJ mol<sup>-1</sup>), **i3** is more preferable to be formed. For this reason, the pathways involving **i3** contributes with around 94, 81 and 93 % for the formation of **p1**, **p2** and **p3**.

### Supplementary Note 3: Additional intermediates **i8** and **i9**

As mentioned in the main text, the reaction mechanism of the CN/c-C<sub>5</sub>H<sub>6</sub> system involves the formation of two high-energy intermediates (**i8** and **i9**) (see Supplementary Fig. S3), which are not included in Figure 5. Their energies reside 53 and 55 kJ mol<sup>-1</sup>, respectively, above the separated reactants, disallowing their formation as they are higher than the experimental collision energy ( $E_c = 17.9 \text{ kJ mol}^{-1}$ ). Similarly to **i5-i7** isomers, **i8** and **i9** are bicyclic intermediates and they are involved in the isomerization pathways of the initial intermediates **i1-i4**. Specifically, **i2** isomerizes to **i4** via **i8** through a ring closure – ring opening pathway. On the other hand, **i9** connects **i3** and **i4** also through a ring closure – ring opening route, which migrates the isocyano group from the C1 to the C2 carbon atom of the cyclopentenyl moiety.



**Supplementary Fig. 3. Extended reaction mechanism of the cyano radical (CN) and 1,3-cyclopentadiene (c-C<sub>5</sub>H<sub>6</sub>) reaction.** Reaction mechanism leading to the formation of intermediates **i1-i9** and products **p1-p6**. **i8** and **i9** are marked in red as they are high energy intermediates and are not accessible under our experimental conditions.

**Supplementary Table 2.** Energy dependent branching ratios based on RRKM rate constants under the scenario that all initial collision complexes are (from top to bottom) **i1**, **i2**, **i3**, and **i4**.

| Products | Collision energy (kJ mol <sup>-1</sup> ) |       |       |       |       |                        |                        |
|----------|------------------------------------------|-------|-------|-------|-------|------------------------|------------------------|
|          | 0                                        | 5     | 10    | 15    | 17.9  | 20                     | 30                     |
| p1 + H   | 0.323                                    | 0.313 | 0.303 | 0.294 | 0.288 | 0.286                  | 0.271                  |
| p2 + H   | 0.039                                    | 0.040 | 0.040 | 0.041 | 0.042 | 0.042                  | 0.043                  |
| p3 + H   | 0.638                                    | 0.647 | 0.657 | 0.665 | 0.670 | 0.672                  | 0.686                  |
| p4 + H   |                                          |       |       |       |       | 5.49×10 <sup>-10</sup> | 7.44×10 <sup>-9</sup>  |
| p5 + H   |                                          |       |       |       |       | -                      | 4.77×10 <sup>-11</sup> |
| p6 + H   |                                          |       |       |       |       | -                      | 6.54×10 <sup>-10</sup> |

| Products | Collision energy (kJ mol <sup>-1</sup> ) |       |       |       |       |                        |                        |
|----------|------------------------------------------|-------|-------|-------|-------|------------------------|------------------------|
|          | 0                                        | 5     | 10    | 15    | 17.9  | 20                     | 30                     |
| p1 + H   | 0.311                                    | 0.298 | 0.285 | 0.272 | 0.265 | 0.260                  | 0.238                  |
| p2 + H   | 0.056                                    | 0.061 | 0.066 | 0.072 | 0.075 | 0.078                  | 0.091                  |
| p3 + H   | 0.633                                    | 0.641 | 0.649 | 0.656 | 0.660 | 0.661                  | 0.671                  |
| p4 + H   |                                          |       |       |       |       | 5.32×10 <sup>-10</sup> | 7.24×10 <sup>-9</sup>  |
| p5 + H   |                                          |       |       |       |       | -                      | 4.61×10 <sup>-11</sup> |
| p6 + H   |                                          |       |       |       |       | -                      | 6.35×10 <sup>-10</sup> |

| Products | Collision energy (kJ mol <sup>-1</sup> ) |       |       |       |       |                       |                       |
|----------|------------------------------------------|-------|-------|-------|-------|-----------------------|-----------------------|
|          | 0                                        | 5     | 10    | 15    | 17.9  | 20                    | 30                    |
| p1 + H   | 0.322                                    | 0.312 | 0.302 | 0.292 | 0.287 | 0.284                 | 0.267                 |
| p2 + H   | 0.040                                    | 0.041 | 0.042 | 0.043 | 0.044 | 0.045                 | 0.047                 |
| p3 + H   | 0.638                                    | 0.647 | 0.656 | 0.665 | 0.669 | 0.671                 | 0.681                 |
| p4 + H   |                                          |       |       |       |       | 7.45×10 <sup>-4</sup> | 4.90×10 <sup>-3</sup> |
| p5 + H   |                                          |       |       |       |       | -                     | 2.99×10 <sup>-5</sup> |
| p6 + H   |                                          |       |       |       |       | -                     | 4.30×10 <sup>-4</sup> |

| Products | Collision energy (kJ mol <sup>-1</sup> ) |       |       |       |       |                       |                       |
|----------|------------------------------------------|-------|-------|-------|-------|-----------------------|-----------------------|
|          | 0                                        | 5     | 10    | 15    | 17.9  | 20                    | 30                    |
| p1 + H   | 0.322                                    | 0.312 | 0.302 | 0.292 | 0.287 | 0.284                 | 0.267                 |
| p2 + H   | 0.040                                    | 0.041 | 0.042 | 0.043 | 0.044 | 0.045                 | 0.047                 |
| p3 + H   | 0.638                                    | 0.647 | 0.656 | 0.664 | 0.669 | 0.671                 | 0.681                 |
| p4 + H   |                                          |       |       |       |       | 7.01×10 <sup>-4</sup> | 4.67×10 <sup>-3</sup> |
| p5 + H   |                                          |       |       |       |       | -                     | 3.00×10 <sup>-5</sup> |
| p6 + H   |                                          |       |       |       |       | -                     | 4.10×10 <sup>-4</sup> |

**Supplementary Table 3.** RRKM rate constants ( $s^{-1}$ ) for the reaction of CN radicals with cyclopentadiene computed with B3LYP/cc-pVTZ zero-point energy corrected CCSD(T)/CBS energies, and B3LYP/cc-pVTZ harmonic frequencies at collision energies of 0.0, 5.0, 10.0, 15.0, 20.0 and 30.0  $\text{kJ mol}^{-1}$ .

|                         | Collision energy ( $\text{kJ mol}^{-1}$ ) |                       |                       |                       |                       |                       |
|-------------------------|-------------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                         | 0                                         | 5                     | 10                    | 15                    | 20                    | 30                    |
| i1 $\rightarrow$ i5     | $7.11 \times 10^6$                        | $8.68 \times 10^6$    | $1.05 \times 10^7$    | $1.26 \times 10^7$    | $1.51 \times 10^7$    | $2.10 \times 10^7$    |
| i5 $\rightarrow$ i1     | $1.09 \times 10^{11}$                     | $1.14 \times 10^{11}$ | $1.20 \times 10^{11}$ | $1.25 \times 10^{11}$ | $1.30 \times 10^{11}$ | $1.40 \times 10^{11}$ |
| i1 $\rightarrow$ p1 + H | $3.69 \times 10^5$                        | $5.43 \times 10^5$    | $7.83 \times 10^5$    | $1.11 \times 10^6$    | $1.55 \times 10^6$    | $2.89 \times 10^6$    |
| i1 $\rightarrow$ p3 + H | $6.84 \times 10^5$                        | $1.05 \times 10^6$    | $1.58 \times 10^6$    | $2.33 \times 10^6$    | $3.37 \times 10^6$    | $6.71 \times 10^6$    |
| i1 $\rightarrow$ i2     | $1.54 \times 10^4$                        | $2.45 \times 10^4$    | $3.78 \times 10^4$    | $5.70 \times 10^4$    | $8.42 \times 10^4$    | $1.74 \times 10^5$    |
| i2 $\rightarrow$ i1     | $6.12 \times 10^5$                        | $9.21 \times 10^5$    | $1.35 \times 10^6$    | $1.94 \times 10^6$    | $2.73 \times 10^6$    | $5.13 \times 10^6$    |
| i1 $\rightarrow$ i6     | 4.88                                      | $1.03 \times 10^1$    | $2.04 \times 10^1$    | $3.82 \times 10^1$    | $6.85 \times 10^1$    | $1.97 \times 10^2$    |
| i6 $\rightarrow$ i1     | $1.34 \times 10^{10}$                     | $1.93 \times 10^{10}$ | $2.67 \times 10^{10}$ | $3.55 \times 10^{10}$ | $4.20 \times 10^{10}$ | $6.79 \times 10^{10}$ |
| i2 $\rightarrow$ i5     | $1.44 \times 10^8$                        | $1.74 \times 10^8$    | $2.09 \times 10^8$    | $2.48 \times 10^8$    | $2.92 \times 10^8$    | $3.98 \times 10^8$    |
| i5 $\rightarrow$ i2     | $5.58 \times 10^{10}$                     | $6.10 \times 10^{10}$ | $6.64 \times 10^{10}$ | $7.20 \times 10^{10}$ | $7.78 \times 10^{10}$ | $8.98 \times 10^{10}$ |
| i2 $\rightarrow$ p2+H   | $1.82 \times 10^6$                        | $2.73 \times 10^6$    | $4.00 \times 10^6$    | $5.75 \times 10^6$    | $8.09 \times 10^6$    | $1.53 \times 10^7$    |
| i2 $\rightarrow$ p3+H   | $1.85 \times 10^6$                        | $2.93 \times 10^6$    | $4.50 \times 10^6$    | $6.75 \times 10^6$    | $9.88 \times 10^6$    | $2.00 \times 10^7$    |
| i2 $\rightarrow$ i7     | $1.88 \times 10^{-1}$                     | $3.15 \times 10^{-1}$ | 1.15                  | 3.40                  | 8.66                  | $4.17 \times 10^1$    |
| i7 $\rightarrow$ i2     | $1.04 \times 10^7$                        | $1.26 \times 10^7$    | $3.40 \times 10^7$    | $7.54 \times 10^7$    | $1.47 \times 10^8$    | $4.26 \times 10^8$    |
| i3 $\rightarrow$ i7     | $3.15 \times 10^4$                        | $5.34 \times 10^4$    | $8.69 \times 10^4$    | $1.36 \times 10^5$    | $2.07 \times 10^5$    | $4.40 \times 10^5$    |
| i7 $\rightarrow$ i3     | $9.97 \times 10^{10}$                     | $1.29 \times 10^{11}$ | $1.62 \times 10^{11}$ | $2.00 \times 10^{11}$ | $2.41 \times 10^{11}$ | $3.36 \times 10^{11}$ |
| i3 $\rightarrow$ p4+H   | -                                         | -                     | -                     | -                     | 1.29                  | $3.03 \times 10^1$    |
| i3 $\rightarrow$ p6+H   | -                                         | -                     | -                     | -                     | -                     | 2.66                  |
| i4 $\rightarrow$ i6     | $8.39 \times 10^3$                        | $2.26 \times 10^4$    | $5.19 \times 10^4$    | $1.06 \times 10^5$    | $2.00 \times 10^5$    | $5.89 \times 10^5$    |
| i6 $\rightarrow$ i4     | $2.06 \times 10^8$                        | $4.65 \times 10^8$    | $9.06 \times 10^8$    | $1.59 \times 10^9$    | $2.60 \times 10^9$    | $5.87 \times 10^9$    |

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|                       |                       |                    |                    |                    |                    |                    |
|-----------------------|-----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $i4 \rightarrow p5+H$ | -                     | -                  | -                  | -                  | -                  | $1.79 \times 10^1$ |
| $i3 \rightarrow i4$   | $2.49 \times 10^2$    | $1.20 \times 10^3$ | $4.04 \times 10^3$ | $1.11 \times 10^4$ | $2.68 \times 10^4$ | $1.18 \times 10^5$ |
| $i4 \rightarrow i3$   | $4.04 \times 10^4$    | $1.76 \times 10^5$ | $5.36 \times 10^5$ | $1.34 \times 10^6$ | $2.96 \times 10^6$ | $1.09 \times 10^7$ |
| $i2 \rightarrow i3$   | $1.64 \times 10^{-1}$ | $3.42 \times 10^1$ | $2.70 \times 10^2$ | $1.14 \times 10^3$ | $3.68 \times 10^3$ | $2.43 \times 10^4$ |
| $i3 \rightarrow i2$   | 2.85                  | $5.67 \times 10^2$ | $4.26 \times 10^3$ | $1.73 \times 10^4$ | $5.33 \times 10^4$ | $3.24 \times 10^5$ |
| $i4 \rightarrow p6+H$ | -                     | -                  | -                  | -                  | -                  | -                  |

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**Supplementary Table 4.** Contributions of the different channels for the formation of **p1-p3** in the reaction of CN + c-C<sub>5</sub>H<sub>6</sub> with **i1-i4** as initial intermediates at a collision energy  $E_c$  of 17.9 kJ mol<sup>-1</sup>.

| Initial intermediate | Pathway                            | Contribution (%) |
|----------------------|------------------------------------|------------------|
| <b>i1</b>            | <b>i1 → p1</b>                     | 100              |
|                      | <b>i5 → i2 → p2</b>                | 78.9573          |
|                      | <b>i2 → p2</b>                     | 21.0416          |
|                      | <b>i6 → i4 → i3 → i2 → p2</b>      | 0.0011           |
|                      | <b>i6 → i4 → i3 → i7 → i2 → p2</b> | 0.0001           |
|                      | <b>i1 → p3</b>                     | 91.3396          |
|                      | <b>i5 → i2 → p3</b>                | 7.0388           |
|                      | <b>i2 → p3</b>                     | 1.6215           |
|                      | <b>i6 → i4 → i3 → i2 → p3</b>      | 0.0001           |
|                      | <b>i6 → i4 → i3 → i7 → i2 → p3</b> | 0.0000           |
| <b>i2</b>            | <b>i5 → i1 → p1</b>                | 94.3994          |
|                      | <b>i1 → p1</b>                     | 5.6006           |
|                      | <b>i7 → i3 → i4 → i6 → i1 → p1</b> | 0.0001           |
|                      | <b>i3 → i4 → i6 → i1 → p1</b>      | 0.0000           |
|                      | <b>i2 → p2</b>                     | 100              |
|                      | <b>i2 → p3</b>                     | 10.8904          |
|                      | <b>i5 → i1 → p3</b>                | 86.1018          |
|                      | <b>i1 → p3</b>                     | 3.0079           |
|                      | <b>i7 → i3 → i4 → i6 → i1 → p3</b> | 0.0000           |
|                      | <b>i3 → i4 → i6 → i1 → p3</b>      | 0.0000           |
| <b>i3</b>            | <b>i7 → i2 → i5 → i1 → p1</b>      | 0.1417           |
|                      | <b>i7 → i2 → i1 → p1</b>           | 0.1417           |
|                      | <b>i2 → i5 → i1 → p1</b>           | 48.8154          |
|                      | <b>i2 → i1 → p1</b>                | 48.7719          |
|                      | <b>i4 → i6 → i1 → p1</b>           | 2.193            |
|                      | <b>i7 → i2 → p2</b>                | 0.2662           |
|                      | <b>i2 → p2</b>                     | 91.7294          |
|                      | <b>i4 → i6 → i1 → i5 → i2 → p2</b> | 4.0022           |
|                      | <b>i4 → i6 → i1 → i2 → p2</b>      | 4.0021           |
|                      | <b>i7 → i2 → i5 → i1 → p3</b>      | 0.0928           |
|                      | <b>i7 → i2 → i1 → p3</b>           | 0.0928           |
|                      | <b>i2 → i5 → i1 → p3</b>           | 31.8627          |
|                      | <b>i2 → i1 → p3</b>                | 31.8342          |
|                      | <b>i4 → i6 → i1 → p3</b>           | 1.3898           |
|                      | <b>i7 → i2 → p3</b>                | 0.0928           |
|                      | <b>i2 → p3</b>                     | 31.8556          |
|                      | <b>i4 → i6 → i1 → i5 → i2 → p3</b> | 1.3898           |
|                      | <b>i4 → i6 → i1 → i2 → p3</b>      | 1.3898           |
| <b>i4</b>            | <b>i3 → i7 → i2 → i5 → i1 → p1</b> | 0.3517           |
|                      | <b>i3 → i2 → i5 → i1 → p1</b>      | 46.8150          |
|                      | <b>i3 → i7 → i2 → i1 → p1</b>      | 0.3517           |
|                      | <b>i3 → i2 → i1 → p1</b>           | 46.7988          |
|                      | <b>i6 → i1 → p1</b>                | 5.6829           |

|  |                                                                                 |         |
|--|---------------------------------------------------------------------------------|---------|
|  | $i3 \rightarrow i7 \rightarrow i2 \rightarrow p2$                               | 0.6008  |
|  | $i3 \rightarrow i2 \rightarrow p2$                                              | 79.9803 |
|  | $i6 \rightarrow i1 \rightarrow i5 \rightarrow i2 \rightarrow p2$                | 9.7096  |
|  | $i6 \rightarrow i1 \rightarrow i2 \rightarrow p2$                               | 9.7092  |
|  | $i3 \rightarrow i7 \rightarrow i2 \rightarrow i5 \rightarrow i1 \rightarrow p3$ | 0.2218  |
|  | $i3 \rightarrow i2 \rightarrow i5 \rightarrow i1 \rightarrow p3$                | 29.5311 |
|  | $i3 \rightarrow i7 \rightarrow i2 \rightarrow i1 \rightarrow p3$                | 0.2218  |
|  | $i3 \rightarrow i2 \rightarrow i1 \rightarrow p3$                               | 29.5209 |
|  | $i6 \rightarrow i1 \rightarrow p3$                                              | 3.5848  |
|  | $i3 \rightarrow i7 \rightarrow i2 \rightarrow p3$                               | 0.2218  |
|  | $i3 \rightarrow i2 \rightarrow p3$                                              | 29.5285 |
|  | $i6 \rightarrow i1 \rightarrow i5 \rightarrow i2 \rightarrow p3$                | 3.5847  |
|  | $i6 \rightarrow i1 \rightarrow i2 \rightarrow p3$                               | 3.5846  |

**Supplementary Table 5.** B3LYP/cc-pVTZ vibrational frequencies and infrared intensities of reactants, all intermediates, transition states and products on the **CN + C<sub>5</sub>H<sub>6</sub>** adiabatic doublet ground state potential energy surface.

**a. Reactants**

| Normal<br>modes | CN                           |          | cyclopentadiene              |          |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | 2153.48                      | 19.3774  | 351.13                       | 7.3416   |
| v2              |                              |          | 526.62                       | 0        |
| v3              |                              |          | 682.62                       | 70.0311  |
| v4              |                              |          | 715.27                       | 0        |
| v5              |                              |          | 818.43                       | 0.0068   |
| v6              |                              |          | 819.82                       | 5.6749   |
| v7              |                              |          | 920.24                       | 29.2344  |
| v8              |                              |          | 924.1                        | 10.9841  |
| v9              |                              |          | 960.97                       | 0.0811   |
| v10             |                              |          | 961.78                       | 0        |
| v11             |                              |          | 969.79                       | 14.241   |
| v12             |                              |          | 1012.9                       | 0.2075   |
| v13             |                              |          | 1115.34                      | 1.9256   |
| v14             |                              |          | 1124.72                      | 0        |
| v15             |                              |          | 1133.35                      | 0.1702   |
| v16             |                              |          | 1268.13                      | 2.5471   |
| v17             |                              |          | 1322.12                      | 0.7112   |
| v18             |                              |          | 1401.64                      | 20.4385  |
| v19             |                              |          | 1415.21                      | 4.6845   |
| v20             |                              |          | 1551.34                      | 1.067    |
| v21             |                              |          | 1639.16                      | 0.1109   |
| v22             |                              |          | 3013.09                      | 9.9449   |
| v23             |                              |          | 3032.06                      | 7.554    |
| v24             |                              |          | 3189.5                       | 3.6451   |
| v25             |                              |          | 3199.61                      | 12.7864  |
| v26             |                              |          | 3217.89                      | 19.4105  |

|     |         |        |
|-----|---------|--------|
| v27 | 3224.21 | 2.1513 |
|-----|---------|--------|

**b. Intermediates**

| Normal<br>modes | <b>i1</b>                    |          | <b>i2</b>                    |          |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | 72.73                        | 2.7377   | 99.09                        | 1.9241   |
| v2              | 173.68                       | 4.2355   | 164.69                       | 4.4276   |
| v3              | 259.48                       | 1.2517   | 265.02                       | 1.4278   |
| v4              | 439.54                       | 2.6628   | 361.04                       | 27.7492  |
| v5              | 509.48                       | 1.6497   | 390.54                       | 0.5949   |
| v6              | 552.62                       | 1.4471   | 511.38                       | 0.0343   |
| v7              | 598.67                       | 52.0597  | 549.8                        | 3.5082   |
| v8              | 661.19                       | 0.8189   | 694.43                       | 19.884   |
| v9              | 714.54                       | 12.8673  | 757.75                       | 8.3279   |
| v10             | 807.53                       | 0.0702   | 798.04                       | 6.6904   |
| v11             | 823.64                       | 4.2713   | 879.17                       | 9.588    |
| v12             | 936.37                       | 13.1263  | 927.36                       | 11.3973  |
| v13             | 955.83                       | 3.7066   | 932.46                       | 6.4756   |
| v14             | 962.88                       | 2.4419   | 963.56                       | 3.9913   |
| v15             | 1023.53                      | 1.1481   | 981.77                       | 0.0985   |
| v16             | 1049.66                      | 1.1957   | 1012.17                      | 1.019    |
| v17             | 1082.62                      | 0.1913   | 1053.13                      | 1.8153   |
| v18             | 1112.29                      | 1.6884   | 1135.12                      | 0.0487   |
| v19             | 1167.87                      | 3.5273   | 1136.77                      | 2.1036   |
| v20             | 1235.05                      | 1.5035   | 1226.67                      | 1.0959   |
| v21             | 1295.92                      | 2.9652   | 1282.18                      | 1.8359   |
| v22             | 1311.12                      | 0.9383   | 1300.74                      | 1.263    |
| v23             | 1331.21                      | 5.5834   | 1316.58                      | 1.56     |
| v24             | 1403.62                      | 4.8891   | 1386.13                      | 0.7102   |
| v25             | 1475.47                      | 4.3579   | 1457.94                      | 4.7734   |

|                 |                              |          |                              |          |
|-----------------|------------------------------|----------|------------------------------|----------|
| v26             | 1485.47                      | 1.9315   | 1678.36                      | 1.3958   |
| v27             | 2348.5                       | 15.7312  | 2343.59                      | 12.4815  |
| v28             | 2993.02                      | 3.8194   | 2941.88                      | 9.8125   |
| v29             | 3025.73                      | 14.1765  | 2962.49                      | 27.8558  |
| v30             | 3053.67                      | 13.6671  | 2964.61                      | 20.2305  |
| v31             | 3193.59                      | 3.3806   | 3190.09                      | 3.2173   |
| v32             | 3217.52                      | 5.1464   | 3216.58                      | 8.7184   |
| v33             | 3231.49                      | 3.5577   | 3224.09                      | 3.5646   |
|                 |                              |          |                              |          |
| <b>i3</b>       |                              |          | <b>i4</b>                    |          |
| Normal<br>modes | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | 68.59                        | 2.5078   | 100.49                       | 1.8406   |
| v2              | 164.51                       | 3.0202   | 153.44                       | 3.2685   |
| v3              | 223.33                       | 0.7939   | 233.63                       | 1.043    |
| v4              | 400.72                       | 2.6218   | 341.87                       | 1.0399   |
| v5              | 460.78                       | 0.9878   | 358.23                       | 20.1806  |
| v6              | 504.12                       | 3.3391   | 476.03                       | 8.8494   |
| v7              | 598.26                       | 41.99    | 503.32                       | 3.4463   |
| v8              | 663.7                        | 1.4541   | 692.51                       | 11.9331  |
| v9              | 719.76                       | 21.5654  | 758.39                       | 8.0531   |
| v10             | 805.9                        | 0.5379   | 801.93                       | 11.3307  |
| v11             | 827.35                       | 7.8362   | 882.97                       | 18.4809  |
| v12             | 940.81                       | 12.2422  | 927.84                       | 4.2514   |
| v13             | 958.24                       | 3.9629   | 934.19                       | 16.7683  |
| v14             | 964.5                        | 5.5879   | 959.8                        | 17.6411  |
| v15             | 1013.3                       | 11.9211  | 981.65                       | 3.4613   |
| v16             | 1058.1                       | 3.0158   | 1000.02                      | 11.3597  |
| v17             | 1082.1                       | 0.5086   | 1057.6                       | 3.5617   |
| v18             | 1112.28                      | 2.6684   | 1134.21                      | 0.6132   |
| v19             | 1181.37                      | 5.1096   | 1138.24                      | 1.744    |
| v20             | 1253.6                       | 0.6836   | 1256.59                      | 0.79     |
| v21             | 1302.02                      | 4.3587   | 1297.95                      | 0.5038   |



|     |         |         |         |         |
|-----|---------|---------|---------|---------|
| v18 | 1093.04 | 2.8014  | 1134.51 | 1.4171  |
| v19 | 1134.89 | 0.1904  | 1172.98 | 5.3279  |
| v20 | 1182.09 | 2.8563  | 1195.8  | 1.4738  |
| v21 | 1260.72 | 1.8456  | 1265.4  | 7.018   |
| v22 | 1272.98 | 0.8068  | 1281.64 | 2.9184  |
| v23 | 1325.14 | 3.1493  | 1328.26 | 2.0663  |
| v24 | 1375.34 | 4.6938  | 1378.79 | 6.4486  |
| v25 | 1473.76 | 4.6766  | 1478.76 | 5.559   |
| v26 | 1627.44 | 0.3767  | 1660.63 | 0.4048  |
| v27 | 1839.56 | 8.0739  | 1701.4  | 32.3864 |
| v28 | 3007.24 | 28.8891 | 3021.66 | 30.4035 |
| v29 | 3050.36 | 9.9364  | 3043.01 | 11.1527 |
| v30 | 3157.56 | 3.4159  | 3093.12 | 17.1376 |
| v31 | 3179.6  | 4.5161  | 3124.27 | 15.0584 |
| v32 | 3193.66 | 3.1572  | 3178.61 | 6.8618  |
| v33 | 3215.57 | 9.1352  | 3206.84 | 10.2951 |

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**i7**

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| Normal modes | Frequency( $\text{cm}^{-1}$ ) | IR Inten | Frequency( $\text{cm}^{-1}$ ) | IR Inten |
|--------------|-------------------------------|----------|-------------------------------|----------|
| v1           | 202.08                        | 2.3401   |                               |          |
| v2           | 296.56                        | 2.6378   |                               |          |
| v3           | 413.55                        | 4.93     |                               |          |
| v4           | 483.6                         | 1.9372   |                               |          |
| v5           | 643.61                        | 4.0609   |                               |          |
| v6           | 711.02                        | 11.6813  |                               |          |
| v7           | 749.27                        | 26.2541  |                               |          |
| v8           | 761.77                        | 1.8497   |                               |          |
| v9           | 823.46                        | 7.3326   |                               |          |
| v10          | 859.51                        | 12.1573  |                               |          |
| v11          | 879.03                        | 17.9754  |                               |          |
| v12          | 928.95                        | 14.0739  |                               |          |

|     |         |         |
|-----|---------|---------|
| v13 | 965.45  | 0.6546  |
| v14 | 994.56  | 1.4459  |
| v15 | 1000.87 | 3.1764  |
| v16 | 1025.44 | 0.5576  |
| v17 | 1119.87 | 0.144   |
| v18 | 1143.28 | 0.1694  |
| v19 | 1164.06 | 5.9291  |
| v20 | 1203.69 | 1.3032  |
| v21 | 1264.21 | 15.6786 |
| v22 | 1282.7  | 0.4885  |
| v23 | 1320.97 | 4.2151  |
| v24 | 1380.9  | 4.2289  |
| v25 | 1467.87 | 6.7796  |
| v26 | 1657.93 | 1.0633  |
| v27 | 1691.54 | 35.2496 |
| v28 | 3016.28 | 23.0119 |
| v29 | 3049.76 | 7.1862  |
| v30 | 3102.79 | 10.2056 |
| v31 | 3111.5  | 23.7541 |
| v32 | 3179.79 | 5.2888  |
| v33 | 3205.38 | 13.3319 |

### c. Transition states

| Normal<br>modes | tsi1i2                        |          | tsi1i5                        |          |
|-----------------|-------------------------------|----------|-------------------------------|----------|
|                 | Frequency( $\text{cm}^{-1}$ ) | IR Inten | Frequency( $\text{cm}^{-1}$ ) | IR Inten |
| v1              | -1891.75                      | 86.4225  | -826.28                       | 41.5042  |
| v2              | 113.03                        | 3.2604   | 176.83                        | 5.7868   |
| v3              | 168.28                        | 3.0614   | 222.45                        | 2.9076   |
| v4              | 322.85                        | 0.6815   | 397.71                        | 4.1047   |
| v5              | 472.16                        | 7.5815   | 515.72                        | 2.6781   |

|     |         |         |         |         |
|-----|---------|---------|---------|---------|
| v6  | 507.42  | 11.123  | 559.88  | 9.9845  |
| v7  | 553.4   | 40.4445 | 711.2   | 2.2272  |
| v8  | 566.81  | 12.2129 | 767.87  | 3.4769  |
| v9  | 697.76  | 20.5013 | 805.57  | 11.4225 |
| v10 | 737.92  | 14.0245 | 840.08  | 29.8118 |
| v11 | 809.54  | 13.8329 | 868.67  | 30.3361 |
| v12 | 833.84  | 18.0518 | 936.62  | 10.6037 |
| v13 | 870.64  | 14.094  | 953.45  | 13.5556 |
| v14 | 932.83  | 12.2906 | 1004.73 | 1.4028  |
| v15 | 965.62  | 26.5767 | 1031.98 | 1.6229  |
| v16 | 996.86  | 4.4378  | 1059.06 | 4.0736  |
| v17 | 1018.76 | 2.9203  | 1107.26 | 5.3896  |
| v18 | 1059    | 0.7708  | 1130.12 | 2.8979  |
| v19 | 1129.99 | 1.529   | 1160.66 | 0.3659  |
| v20 | 1210.65 | 19.0566 | 1209.6  | 5.2543  |
| v21 | 1253.9  | 10.1748 | 1278.3  | 1.3035  |
| v22 | 1270.96 | 1.2372  | 1288.53 | 2.0778  |
| v23 | 1292.6  | 4.189   | 1333.18 | 4.4019  |
| v24 | 1320.94 | 6.1134  | 1388.78 | 6.9285  |
| v25 | 1390.13 | 1.8336  | 1483.14 | 3.8914  |
| v26 | 1563.72 | 6.7902  | 1907.2  | 0.5603  |
| v27 | 2171.18 | 4.3487  | 2285.81 | 13.438  |
| v28 | 2343.94 | 12.0545 | 3077.2  | 20.0552 |
| v29 | 2881.79 | 22.7856 | 3138.51 | 3.5558  |
| v30 | 3203.83 | 1.1484  | 3217.53 | 0.3513  |
| v31 | 3213.59 | 2.178   | 3249.38 | 0.3951  |
| v32 | 3229.21 | 2.5837  | 3266.14 | 1.7935  |
| v33 | 3237.57 | 0.485   | 3280.83 | 3.2561  |

| Normal<br>modes | tsi1i6                       |          | tsi1p1                       |          |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | -626.91                      | 72.7402  | -655.41                      | 5.8289   |
| v2              | 191.12                       | 3.3166   | 165.76                       | 2.3227   |
| v3              | 231.62                       | 4.5062   | 171.18                       | 4.2213   |
| v4              | 447.68                       | 4.7727   | 315.8                        | 4.6225   |
| v5              | 468.3                        | 3.481    | 374.96                       | 4.5489   |
| v6              | 610.46                       | 9.2285   | 414.15                       | 1.6538   |
| v7              | 731.8                        | 41.9244  | 508.97                       | 6.433    |
| v8              | 766.76                       | 4.6514   | 533.78                       | 0.8217   |
| v9              | 801.5                        | 0.9991   | 558.07                       | 5.4682   |
| v10             | 846.56                       | 5.1924   | 567.63                       | 0.7438   |
| v11             | 863.2                        | 15.336   | 702.8                        | 37.6859  |
| v12             | 876.28                       | 7.8724   | 826.54                       | 9.149    |
| v13             | 944.52                       | 18.5173  | 885.15                       | 2.6455   |
| v14             | 959.89                       | 1.2376   | 907.37                       | 6.6653   |
| v15             | 1008.64                      | 2.4152   | 915.76                       | 20.2319  |
| v16             | 1035.87                      | 3.6009   | 967.37                       | 14.6467  |
| v17             | 1072.35                      | 2.2948   | 972.3                        | 0.0073   |
| v18             | 1131.16                      | 1.9948   | 1032.52                      | 12.5431  |
| v19             | 1158.25                      | 4.049    | 1128.18                      | 0.4786   |
| v20             | 1213.02                      | 0.8884   | 1134.86                      | 1.7976   |
| v21             | 1270.52                      | 0.206    | 1184.43                      | 2.3902   |
| v22             | 1291.71                      | 4.7576   | 1272.84                      | 0.3119   |
| v23             | 1318.41                      | 14.5595  | 1298.04                      | 3.8733   |
| v24             | 1390.54                      | 12.3754  | 1395.17                      | 12.268   |
| v25             | 1479.49                      | 5.735    | 1412.75                      | 21.3339  |
| v26             | 1570.95                      | 2.8363   | 1497.43                      | 10.1469  |
| v27             | 1789.49                      | 117.7329 | 1603.51                      | 3.3591   |
| v28             | 3013.89                      | 30.9423  | 2327.54                      | 40.0355  |

|     |         |         |         |        |
|-----|---------|---------|---------|--------|
| v29 | 3033.6  | 12.171  | 3021.29 | 0.6961 |
| v30 | 3099.97 | 17.1007 | 3076.92 | 0.9312 |
| v31 | 3188.05 | 1.7502  | 3207.37 | 3.8274 |
| v32 | 3201.57 | 7.9823  | 3221.79 | 3.2142 |
| v33 | 3215.33 | 4.2803  | 3231.82 | 2.7012 |

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| Normal<br>modes | tsi1p3                       |          | tsi2i3                       |          |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | -278.35                      | 63.8325  | -35.85                       | 0.8595   |
| v2              | 121.93                       | 5.3383   | 27.54                        | 2.4022   |
| v3              | 167.29                       | 5.5653   | 51.61                        | 0.4119   |
| v4              | 198.18                       | 0.9285   | 59.9                         | 2.1003   |
| v5              | 232.8                        | 6.268    | 87.47                        | 0.3825   |
| v6              | 384.15                       | 1.2831   | 341.35                       | 4.071    |
| v7              | 483.49                       | 0.5627   | 510.71                       | 0.6419   |
| v8              | 527.1                        | 1.5268   | 673.72                       | 54.2164  |
| v9              | 595.82                       | 0.8755   | 737.23                       | 1.3971   |
| v10             | 712.81                       | 46.2538  | 814.79                       | 98.4895  |
| v11             | 750.07                       | 8.3902   | 816.53                       | 9.2931   |
| v12             | 813.93                       | 5.539    | 926.7                        | 20.6234  |
| v13             | 829.85                       | 22.4836  | 934.37                       | 3.4183   |
| v14             | 893.71                       | 31.1511  | 959.44                       | 13.2264  |
| v15             | 960.57                       | 1.2856   | 974.81                       | 7.5255   |
| v16             | 973.26                       | 0.5056   | 998.86                       | 0.2337   |
| v17             | 999.91                       | 3.5927   | 1039.4                       | 172.372  |
| v18             | 1025.82                      | 10.2798  | 1110.75                      | 0.6444   |
| v19             | 1037.09                      | 0.5525   | 1125.88                      | 118.6289 |
| v20             | 1115.43                      | 2.3784   | 1134.17                      | 0.5228   |
| v21             | 1135.63                      | 0.3157   | 1281.77                      | 5.8313   |
| v22             | 1202.02                      | 2.4259   | 1323.24                      | 3.829    |
| v23             | 1264.38                      | 3.6075   | 1405.82                      | 197.4843 |
| v24             | 1313.91                      | 0.6193   | 1424.08                      | 12.3138  |
| v25             | 1399.22                      | 5.5845   | 1501.6                       | 658.4656 |
| v26             | 1535.58                      | 9.0042   | 1570.64                      | 27.2849  |
| v27             | 1632.28                      | 1.542    | 2149.41                      | 61.0523  |
| v28             | 2354.41                      | 17.9304  | 3017.77                      | 12.4286  |
| v29             | 3008.71                      | 0.9146   | 3037.08                      | 2.3518   |
| v30             | 3204.87                      | 5.4496   | 3213.86                      | 1.1218   |

| v31             | 3216.03                      | 3.4779   | 3217.8                       | 1.0011   |
|-----------------|------------------------------|----------|------------------------------|----------|
| v32             | 3238.83                      | 1.0317   | 3233.77                      | 4.5264   |
| v33             | 3246.14                      | 2.1358   | 3243.37                      | 5.3452   |
|                 |                              |          |                              |          |
| <b>tsi2i5</b>   |                              |          | <b>tsi2i7</b>                |          |
| Normal<br>modes | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | -608.52                      | 10.7989  | -627.27                      | 73.2733  |
| v2              | 159.61                       | 4.6544   | 191.06                       | 3.3367   |
| v3              | 206.07                       | 3.3775   | 231.62                       | 4.5034   |
| v4              | 366.16                       | 1.3982   | 447.73                       | 4.8091   |
| v5              | 438.05                       | 0.8678   | 468.25                       | 3.4683   |
| v6              | 528.89                       | 11.4202  | 610.4                        | 9.2475   |
| v7              | 718.99                       | 10.959   | 731.72                       | 41.8899  |
| v8              | 723.14                       | 13.2475  | 766.7                        | 4.7163   |
| v9              | 763.65                       | 2.6863   | 801.47                       | 1.0143   |
| v10             | 826.95                       | 9.0083   | 846.35                       | 5.2354   |
| v11             | 847.14                       | 26.1953  | 863.14                       | 15.3126  |
| v12             | 910.04                       | 5.8273   | 876.22                       | 7.8623   |
| v13             | 936.44                       | 4.1105   | 944.44                       | 18.5305  |
| v14             | 953.62                       | 0.2312   | 959.8                        | 1.2394   |
| v15             | 979.49                       | 3.3858   | 1008.65                      | 2.4096   |
| v16             | 989.01                       | 1.0441   | 1035.84                      | 3.5915   |
| v17             | 1047.55                      | 0.9831   | 1072.37                      | 2.2892   |
| v18             | 1123.24                      | 0.551    | 1131.1                       | 2.0041   |
| v19             | 1145.11                      | 1.3527   | 1158.26                      | 4.0609   |
| v20             | 1162.96                      | 3.6142   | 1213.02                      | 0.889    |
| v21             | 1270.36                      | 1.039    | 1270.56                      | 0.2091   |
| v22             | 1271.02                      | 1.1185   | 1291.8                       | 4.7482   |
| v23             | 1319.3                       | 4.2355   | 1318.34                      | 14.6016  |
| v24             | 1374.46                      | 4.9592   | 1390.51                      | 12.3902  |
| v25             | 1466.22                      | 5.2361   | 1479.49                      | 5.7363   |
| v26             | 1659.77                      | 1.6955   | 1570.62                      | 2.8357   |

|                 |                              |          |                              |          |
|-----------------|------------------------------|----------|------------------------------|----------|
| v27             | 1961.36                      | 1.0222   | 1789.54                      | 118.0831 |
| v28             | 2985.77                      | 30.9814  | 3013.9                       | 30.8962  |
| v29             | 3009.2                       | 11.8991  | 3033.56                      | 12.1984  |
| v30             | 3108.16                      | 9.9937   | 3099.96                      | 17.1456  |
| v31             | 3191.77                      | 3.4432   | 3188.07                      | 1.747    |
| v32             | 3215.4                       | 6.8625   | 3201.53                      | 7.9572   |
| v33             | 3218.25                      | 4.3457   | 3215.3                       | 4.268    |
|                 |                              |          |                              |          |
| <b>tsi2p2</b>   |                              |          | <b>tsi2p3</b>                |          |
| Normal<br>modes | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | -860.78                      | 9.8018   | -625.33                      | 13.3119  |
| v2              | 168.4                        | 0.6743   | 116.3                        | 0.985    |
| v3              | 169.76                       | 2.5515   | 167.45                       | 2.936    |
| v4              | 321.51                       | 0.8179   | 293.42                       | 9.019    |
| v5              | 388.47                       | 12.7522  | 297.66                       | 3.5461   |
| v6              | 422.2                        | 7.9418   | 391.8                        | 5.7244   |
| v7              | 497.06                       | 7.374    | 501.3                        | 0.2978   |
| v8              | 538.67                       | 0.4386   | 521.78                       | 1.0998   |
| v9              | 560.21                       | 2.1263   | 600.84                       | 0.2639   |
| v10             | 629.76                       | 19.1853  | 712.46                       | 39.844   |
| v11             | 716.59                       | 8.1258   | 726.88                       | 1.5662   |
| v12             | 760.66                       | 22.2651  | 811.91                       | 2.7178   |
| v13             | 816.64                       | 0.8112   | 831.48                       | 30.2336  |
| v14             | 911.58                       | 8.0099   | 891.09                       | 29.2319  |
| v15             | 925.44                       | 27.1334  | 966.87                       | 0.7265   |
| v16             | 939.12                       | 10.3429  | 978.7                        | 1.3041   |
| v17             | 964.04                       | 0.6357   | 988.39                       | 2.3818   |
| v18             | 991.74                       | 7.9985   | 1025.13                      | 10.441   |
| v19             | 1109.62                      | 0.0993   | 1035.35                      | 1.1833   |
| v20             | 1128.21                      | 0.0477   | 1111.1                       | 1.0595   |
| v21             | 1195.98                      | 5.348    | 1134.34                      | 0.1467   |
| v22             | 1258.39                      | 1.3703   | 1203.43                      | 2.8406   |

|     |         |         |         |         |
|-----|---------|---------|---------|---------|
| v23 | 1297.31 | 2.9671  | 1264.67 | 1.0845  |
| v24 | 1362.92 | 10.4723 | 1310.14 | 0.6323  |
| v25 | 1410.6  | 17.1108 | 1393.74 | 6.1754  |
| v26 | 1517.83 | 1.6087  | 1524.31 | 3.9797  |
| v27 | 1624.63 | 1.2276  | 1630.27 | 1.6075  |
| v28 | 2343.84 | 17.4269 | 2353.83 | 15.7175 |
| v29 | 2996.04 | 5.1543  | 2988.95 | 0.6192  |
| v30 | 3023.44 | 3.026   | 3207.47 | 3.0549  |
| v31 | 3213.16 | 0.3746  | 3216.92 | 0.6073  |
| v32 | 3233.22 | 1.0343  | 3237.27 | 1.6131  |
| v33 | 3235.72 | 2.8351  | 3241.61 | 1.0867  |

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| Normal<br>modes | tsi3i4                       |          | tsi3i7                       |          |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | -156.97                      | 2.9326   | -505.57                      | 25.3897  |
| v2              | 54.99                        | 1.6353   | 172.39                       | 2.9073   |
| v3              | 77.37                        | 1.7404   | 260.82                       | 2.5529   |
| v4              | 149.72                       | 5.1811   | 400.9                        | 5.3359   |
| v5              | 204.68                       | 6.4178   | 424.49                       | 2.1281   |
| v6              | 328.35                       | 0.4838   | 568.36                       | 5.6292   |
| v7              | 505.8                        | 4.9169   | 722.15                       | 37.8458  |
| v8              | 683.79                       | 43.5344  | 758.81                       | 4.5527   |
| v9              | 739.9                        | 8.076    | 799.08                       | 1.7891   |
| v10             | 805.54                       | 14.8152  | 814.89                       | 4.4785   |
| v11             | 820.07                       | 11.4509  | 838.2                        | 16.7318  |
| v12             | 924.76                       | 23.752   | 900.3                        | 7.6539   |
| v13             | 936.55                       | 8.1114   | 945.29                       | 10.1157  |
| v14             | 954.22                       | 8.4798   | 961.34                       | 4.7692   |
| v15             | 959.34                       | 11.1839  | 1006.24                      | 6.0075   |
| v16             | 985.29                       | 1.8484   | 1020.75                      | 1.4671   |
| v17             | 1036.2                       | 19.7559  | 1065.61                      | 1.7892   |
| v18             | 1104.3                       | 19.6357  | 1129.5                       | 1.2405   |

|                 |                              |          |                              |          |
|-----------------|------------------------------|----------|------------------------------|----------|
| v19             | 1133.44                      | 1.4395   | 1175.95                      | 5.915    |
| v20             | 1141.99                      | 1.4783   | 1236.25                      | 3.9242   |
| v21             | 1292.2                       | 5.5351   | 1273.34                      | 8.9991   |
| v22             | 1328                         | 5.6321   | 1304.98                      | 0.9277   |
| v23             | 1403.73                      | 66.4704  | 1323.1                       | 6.7741   |
| v24             | 1417.59                      | 10.6629  | 1395.58                      | 8.788    |
| v25             | 1462.44                      | 125.7353 | 1466.37                      | 7.6402   |
| v26             | 1599                         | 12.6703  | 1556.8                       | 3.3618   |
| v27             | 2044.77                      | 24.3513  | 1764.37                      | 116.0538 |
| v28             | 3009.95                      | 0.7678   | 3009.71                      | 20.9041  |
| v29             | 3038.42                      | 2.8699   | 3054.62                      | 6.784    |
| v30             | 3212.06                      | 0.8059   | 3085.41                      | 21.732   |
| v31             | 3234.03                      | 3.3274   | 3188.16                      | 0.9996   |
| v32             | 3237.95                      | 0.3147   | 3194.74                      | 7.9386   |
| v33             | 3259.45                      | 5.5392   | 3212.87                      | 7.4739   |
|                 |                              |          |                              |          |
|                 |                              |          |                              |          |
| <b>tsi3p4</b>   |                              |          | <b>tsi3p6</b>                |          |
| Normal<br>modes | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | -673.41                      | 10.3095  | -287.45                      | 62.1967  |
| v2              | 163.99                       | 2.889    | 124.81                       | 4.912    |
| v3              | 168.51                       | 2.2804   | 157.9                        | 3.8231   |
| v4              | 315.57                       | 3.3627   | 196.5                        | 1.7553   |
| v5              | 389.64                       | 6.2845   | 233.2                        | 6.6895   |
| v6              | 421.08                       | 2.5836   | 299.44                       | 0.0938   |
| v7              | 468.52                       | 4.5963   | 411.27                       | 1.0211   |
| v8              | 486.43                       | 5.7119   | 525.57                       | 2.7481   |
| v9              | 534.64                       | 0.2309   | 567.06                       | 0.0203   |
| v10             | 569.51                       | 2.6885   | 701.5                        | 36.8835  |
| v11             | 695.27                       | 40.9511  | 747.99                       | 3.5172   |
| v12             | 819.97                       | 10.1239  | 805.41                       | 4.8709   |
| v13             | 890.86                       | 5.5333   | 836.29                       | 26.4512  |
| v14             | 891.68                       | 18.4443  | 894.69                       | 39.5296  |

|     |         |          |         |          |
|-----|---------|----------|---------|----------|
| v15 | 916.26  | 11.7187  | 961.1   | 1.3763   |
| v16 | 965.49  | 12.2518  | 974.38  | 0.5436   |
| v17 | 967.59  | 3.9726   | 989.66  | 7.762    |
| v18 | 1027.23 | 6.2266   | 1042.34 | 11.4049  |
| v19 | 1128.99 | 0.4955   | 1043.5  | 12.6461  |
| v20 | 1132.39 | 1.6998   | 1114.02 | 2.8325   |
| v21 | 1189.86 | 1.288    | 1139.45 | 2.4973   |
| v22 | 1271.86 | 1.6159   | 1226.4  | 0.6      |
| v23 | 1304.53 | 10.1656  | 1313.03 | 16.9244  |
| v24 | 1396.66 | 11.2537  | 1315.27 | 4.3113   |
| v25 | 1416.86 | 21.0518  | 1394.5  | 11.5959  |
| v26 | 1503.42 | 10.2967  | 1547.33 | 8.0442   |
| v27 | 1607.66 | 8.3012   | 1639.45 | 1.4116   |
| v28 | 2186.99 | 141.6537 | 2222.88 | 154.8813 |
| v29 | 3024.4  | 1.1582   | 3008.19 | 3.2183   |
| v30 | 3079.4  | 0.9977   | 3204.05 | 6.014    |
| v31 | 3207.31 | 5.2383   | 3215.17 | 4.4105   |
| v32 | 3225.94 | 4.647    | 3238.19 | 0.8761   |
| v33 | 3233.36 | 1.3508   | 3245.74 | 1.9065   |

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| tsi4i6       |                              |          | tsi4p5                       |          |
|--------------|------------------------------|----------|------------------------------|----------|
| Normal modes | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1           | -477.46                      | 27.4214  | -924.37                      | 9.5422   |
| v2           | 178.99                       | 2.3669   | 160.75                       | 1.9315   |
| v3           | 220.15                       | 3.7206   | 166.2                        | 0.2356   |
| v4           | 335.55                       | 1.0236   | 304.23                       | 1.6034   |
| v5           | 417.51                       | 12.052   | 381.47                       | 4.2799   |
| v6           | 524.19                       | 2.8094   | 421.4                        | 11.3169  |
| v7           | 680.45                       | 11.6292  | 486.08                       | 6.4324   |
| v8           | 732.2                        | 12.6416  | 524.32                       | 9.7959   |
| v9           | 760.25                       | 1.465    | 565.05                       | 0.8935   |
| v10          | 806.2                        | 7.3967   | 629.03                       | 18.1396  |

|     |         |         |         |          |
|-----|---------|---------|---------|----------|
| v11 | 880.42  | 27.5272 | 707.55  | 3.51     |
| v12 | 913.58  | 5.0439  | 768.46  | 34.2364  |
| v13 | 921.28  | 19.7345 | 811.05  | 1.6407   |
| v14 | 948.22  | 16.761  | 916.58  | 10.9737  |
| v15 | 988.89  | 5.9519  | 923.61  | 27.9674  |
| v16 | 990.62  | 2.6363  | 934.57  | 8.1754   |
| v17 | 1052.55 | 3.1173  | 960.19  | 0.8157   |
| v18 | 1131.88 | 0.1134  | 994.98  | 9.7696   |
| v19 | 1155.02 | 1.2958  | 1103.88 | 1.7462   |
| v20 | 1243.03 | 7.3035  | 1129.84 | 0.0569   |
| v21 | 1269.81 | 5.3077  | 1199.05 | 19.8163  |
| v22 | 1294.67 | 0.8805  | 1259.02 | 2.6103   |
| v23 | 1324.72 | 6.647   | 1296.73 | 6.2662   |
| v24 | 1385.09 | 6.8957  | 1369.93 | 12.8077  |
| v25 | 1459.83 | 7.0553  | 1414.21 | 11.8535  |
| v26 | 1666.33 | 0.4523  | 1519.04 | 14.8575  |
| v27 | 1818.31 | 88.4436 | 1628.48 | 5.7901   |
| v28 | 2986.05 | 30.6263 | 2203.7  | 186.4443 |
| v29 | 2994.71 | 9.9129  | 2994.65 | 6.7288   |
| v30 | 3049.86 | 21.5914 | 3024.21 | 3.9882   |
| v31 | 3184.48 | 6.2071  | 3213.26 | 0.7558   |
| v32 | 3199.6  | 6.2323  | 3235.85 | 3.1194   |
| v33 | 3212.82 | 7.5481  | 3239.76 | 0.397    |

| tsi4p6       |                              |          |
|--------------|------------------------------|----------|
| Normal modes | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1           | -598.87                      | 16.06    |
| v2           | 118.46                       | 0.9649   |
| v3           | 156.83                       | 2.2038   |
| v4           | 263.93                       | 0.7545   |
| v5           | 281.22                       | 10.8718  |

|     |         |          |
|-----|---------|----------|
| v6  | 326.06  | 2.9709   |
| v7  | 424.63  | 0.7988   |
| v8  | 518.61  | 2.8633   |
| v9  | 578.88  | 0.2097   |
| v10 | 699.42  | 29.0373  |
| v11 | 727.21  | 0.6427   |
| v12 | 804.08  | 1.9316   |
| v13 | 837.89  | 32.9312  |
| v14 | 892.67  | 37.5638  |
| v15 | 968.56  | 0.3667   |
| v16 | 974.7   | 2.1539   |
| v17 | 978.59  | 5.0219   |
| v18 | 1039.89 | 12.89    |
| v19 | 1042.92 | 14.4957  |
| v20 | 1110.74 | 1.4445   |
| v21 | 1137.3  | 1.8789   |
| v22 | 1227.97 | 0.631    |
| v23 | 1310.95 | 3.676    |
| v24 | 1313.59 | 19.6898  |
| v25 | 1390.18 | 13.1236  |
| v26 | 1534.7  | 4.0486   |
| v27 | 1638.3  | 1.9099   |
| v28 | 2222.09 | 153.8686 |
| v29 | 2988.41 | 4.0211   |
| v30 | 3206.95 | 3.5551   |
| v31 | 3216.45 | 1.0831   |
| v32 | 3236.94 | 1.5157   |
| v33 | 3241.16 | 0.7355   |

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#### d. Products

| Normal<br>modes | p1                           |          | p2                           |          |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | 160.18                       | 2.8218   | 161.58                       | 0.6252   |
| v2              | 173.17                       | 5.175    | 173.73                       | 3.7444   |
| v3              | 351.77                       | 3.9972   | 350.26                       | 7.7165   |
| v4              | 509.45                       | 5.6758   | 462.43                       | 0.6907   |
| v5              | 538.96                       | 2.0506   | 540.8                        | 0.7919   |
| v6              | 542.34                       | 7.0958   | 565.88                       | 0.8804   |
| v7              | 568.75                       | 0.5346   | 630.86                       | 28.2234  |
| v8              | 703.55                       | 39.7557  | 716.85                       | 12.1337  |
| v9              | 828.13                       | 9.0417   | 787.51                       | 10.1753  |
| v10             | 894.32                       | 2.3758   | 826.26                       | 1.0451   |
| v11             | 916.2                        | 5.5781   | 918.3                        | 10.115   |
| v12             | 929.79                       | 18.7609  | 932.35                       | 26.361   |
| v13             | 965.82                       | 13.4837  | 939.13                       | 10.2519  |
| v14             | 972.73                       | 0.189    | 964.39                       | 0.6323   |
| v15             | 1023.26                      | 12.1435  | 991.88                       | 7.751    |
| v16             | 1128.64                      | 0.1682   | 1107.86                      | 0.2092   |
| v17             | 1133.24                      | 0.2813   | 1128.4                       | 0.0266   |
| v18             | 1187.19                      | 6.2818   | 1204.45                      | 4.7545   |
| v19             | 1270.3                       | 0.2106   | 1262.87                      | 1.4334   |
| v20             | 1307.13                      | 2.6715   | 1294.45                      | 1.6229   |
| v21             | 1391.69                      | 9.5337   | 1377.4                       | 14.4641  |
| v22             | 1409.95                      | 19.2938  | 1406.86                      | 17.7509  |
| v23             | 1544.62                      | 12.869   | 1568.44                      | 1.3932   |
| v24             | 1636.69                      | 0.112    | 1641.8                       | 0.3558   |
| v25             | 2321.25                      | 58.6901  | 2338.22                      | 25.0388  |
| v26             | 3025.9                       | 0.9697   | 3014.81                      | 3.1238   |
| v27             | 3050.24                      | 1.4179   | 3033.53                      | 2.5219   |
| v28             | 3206.03                      | 3.9681   | 3212.56                      | 0.4443   |
| v29             | 3219.22                      | 4.1204   | 3231.52                      | 1.5232   |

| v30             | 3230.85                      | 4.0102   | 3234.11                      | 3.0522   |
|-----------------|------------------------------|----------|------------------------------|----------|
|                 |                              |          |                              |          |
| <b>p3</b>       |                              |          | <b>p4</b>                    |          |
| Normal<br>modes | Frequency(cm <sup>-1</sup> ) | IR Inten | Frequency(cm <sup>-1</sup> ) | IR Inten |
| v1              | 124.5                        | 1.9406   | 164.41                       | 2.7725   |
| v2              | 170.75                       | 3.7617   | 166.87                       | 3.8199   |
| v3              | 383.96                       | 3.1893   | 337.39                       | 2.5456   |
| v4              | 484.22                       | 0.0691   | 443.63                       | 6.6083   |
| v5              | 525                          | 2.0817   | 478.41                       | 2.6317   |
| v6              | 597.92                       | 0.6265   | 522.55                       | 0.0202   |
| v7              | 702.97                       | 53.9336  | 563.82                       | 2.4414   |
| v8              | 731.12                       | 0.6049   | 694.8                        | 45.2072  |
| v9              | 813.97                       | 3.5806   | 821.7                        | 9.8352   |
| v10             | 832.73                       | 27.8225  | 900.41                       | 4.0697   |
| v11             | 891.08                       | 30.5829  | 906.98                       | 10.1727  |
| v12             | 967.84                       | 0.2357   | 920.85                       | 16.8851  |
| v13             | 972.22                       | 0.6113   | 963.63                       | 14.7163  |
| v14             | 994.93                       | 2.8794   | 965.81                       | 0.028    |
| v15             | 1026.84                      | 11.6155  | 1016.99                      | 5.2681   |
| v16             | 1037.18                      | 0.7851   | 1129.09                      | 0.3261   |
| v17             | 1115.52                      | 1.2793   | 1131.85                      | 0.4394   |
| v18             | 1137.3                       | 0.1239   | 1192.16                      | 0.4672   |
| v19             | 1197.15                      | 2.9755   | 1268.91                      | 1.1417   |
| v20             | 1265.6                       | 1.6731   | 1313.04                      | 9.7956   |
| v21             | 1313.36                      | 0.5907   | 1392.74                      | 8.537    |
| v22             | 1398.15                      | 4.8621   | 1414.97                      | 18.658   |
| v23             | 1564.46                      | 0.4365   | 1555.14                      | 4.5287   |
| v24             | 1649.39                      | 0.2787   | 1645.15                      | 5.2009   |
| v25             | 2354.36                      | 18.3063  | 2181.29                      | 118.8084 |
| v26             | 2994.95                      | 0.7855   | 3028.98                      | 1.6353   |
| v27             | 3201.88                      | 5.2606   | 3054.41                      | 1.905    |
| v28             | 3212.68                      | 4.659    | 3205.26                      | 6.1358   |

| v29          | 3236.85                       | 2.0377   | 3224.19                       | 5.4043   |
|--------------|-------------------------------|----------|-------------------------------|----------|
| v30          | 3240.84                       | 2.0059   | 3231.82                       | 2.5129   |
|              |                               |          |                               |          |
| p5           |                               |          | p6                            |          |
| Normal modes | Frequency( $\text{cm}^{-1}$ ) | IR Inten | Frequency( $\text{cm}^{-1}$ ) | IR Inten |
| v1           | 162.58                        | 0.497    | 128.21                        | 1.7231   |
| v2           | 164.67                        | 2.4719   | 159.64                        | 2.7575   |
| v3           | 337.99                        | 6.2602   | 297.85                        | 0.643    |
| v4           | 402.9                         | 0.4665   | 409.55                        | 0.6041   |
| v5           | 482.22                        | 1.1497   | 522.9                         | 2.8165   |
| v6           | 562.86                        | 1.2701   | 569.98                        | 0.0055   |
| v7           | 614.24                        | 17.8233  | 689.97                        | 40.6514  |
| v8           | 708.49                        | 9.6446   | 729.9                         | 0.0462   |
| v9           | 788.72                        | 24.5614  | 805.85                        | 2.6396   |
| v10          | 820.57                        | 1.5829   | 839.81                        | 31.9903  |
| v11          | 924.81                        | 14.2785  | 891.23                        | 40.0536  |
| v12          | 926.71                        | 26.8057  | 969.38                        | 0.6585   |
| v13          | 934.3                         | 6.7059   | 973.21                        | 0.485    |
| v14          | 959.24                        | 0.4828   | 986.67                        | 4.9387   |
| v15          | 995.56                        | 9.7157   | 1044.45                       | 11.2949  |
| v16          | 1101.82                       | 0.6561   | 1044.77                       | 16.3411  |
| v17          | 1129.38                       | 0.097    | 1114.28                       | 1.9547   |
| v18          | 1209.2                        | 13.7622  | 1141.54                       | 2.0049   |
| v19          | 1261.88                       | 2.8573   | 1220.31                       | 0.4718   |
| v20          | 1293.81                       | 6.8135   | 1313.9                        | 21.3832  |
| v21          | 1385.89                       | 20.4189  | 1314.58                       | 0.1665   |
| v22          | 1413.16                       | 12.5939  | 1394.89                       | 10.6098  |
| v23          | 1573.76                       | 0.8098   | 1576.94                       | 0.5368   |
| v24          | 1651.11                       | 6.8113   | 1656.04                       | 0.1663   |
| v25          | 2199.3                        | 168.8917 | 2223.98                       | 147.5249 |
| v26          | 3015.16                       | 5.2023   | 2991.47                       | 4.6779   |

|     |         |        |         |        |
|-----|---------|--------|---------|--------|
| v28 | 3212.61 | 0.5916 | 3211.97 | 5.9042 |
| v29 | 3233.43 | 4.0235 | 3236.45 | 1.938  |
| v30 | 3238.2  | 0.1719 | 3240.35 | 1.4198 |

**Supplementary Table 6.** Predicted energies of species participating on the adiabatic doublet ground state potential energy surface for reaction of **CN + C<sub>5</sub>H<sub>6</sub> (cyclopentadiene)**. The energies are computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy corrections.

|                                                                               | B3LYP/<br>cc-pVTZ + E <sub>zpc</sub> <sup>a</sup> | E <sub>zpc</sub> <sup>b</sup> | CCSD(T)/<br>CBS | E <sup>c</sup><br>(kJ/mol) |
|-------------------------------------------------------------------------------|---------------------------------------------------|-------------------------------|-----------------|----------------------------|
| <b>CN (C<sub>∞</sub>, <sup>2</sup>Σ<sup>+</sup>)</b>                          | -92.740886                                        | 0.004906                      | -92.603617      |                            |
| <b>C<sub>5</sub>H<sub>6</sub> (C<sub>2v</sub>, <sup>1</sup>A<sub>1</sub>)</b> | -194.081821                                       | 0.092291                      | -193.822555     |                            |
| <b>CN + C<sub>5</sub>H<sub>6</sub></b>                                        | -286.822707                                       | 0.097197                      | -286.426172     | 0                          |
| <b>H</b>                                                                      | -0.502156                                         | 0.000000                      | -0.500019       |                            |
| <b>i1 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.925293                                       | 0.101391                      | -286.531036     | -264                       |
| <b>i2 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.903225                                       | 0.100479                      | -286.510120     | -212                       |
| <b>i3 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.892113                                       | 0.100930                      | -286.496592     | -175                       |
| <b>i4 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.870057                                       | 0.100061                      | -286.475699     | -123                       |
| <b>i5 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.872168                                       | 0.100302                      | -286.484841     | -146                       |
| <b>i6 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.843621                                       | 0.102842                      | -286.456747     | -65                        |
| <b>i7 (C<sub>1</sub>, <sup>2</sup>A)</b>                                      | -286.844472                                       | 0.102748                      | -286.457295     | -67                        |
| <b>tsi1i2 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.847864                                       | 0.096459                      | -286.448748     | -61                        |
| <b>tsi1i5 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.131936                                       | 0.104007                      | -286.473067     | -121                       |
| <b>tsi1i6 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.835497                                       | 0.100746                      | -286.439817     | -27                        |
| <b>tsi1p1 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.858169                                       | 0.093027                      | -286.451977     | -79                        |
| <b>tsi1p3 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.848612                                       | 0.092437                      | -286.448710     | -72                        |
| <b>tsi2i3 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.830433                                       | 0.097837                      | -286.426950     | 0                          |
| <b>tsi2i5 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.866522                                       | 0.099959                      | -286.470359     | -109                       |
| <b>tsi2i7 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.8355                                         | 0.100744                      | -286.429697     | 0                          |
| <b>tsi2p2 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.85163                                        | 0.092659                      | -286.446542     | -65                        |
| <b>tsi2p3 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.845627                                       | 0.092669                      | -286.443836     | -58                        |
| <b>tsi3i4 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.837382                                       | 0.098157                      | -286.429765     | -7                         |
| <b>tsi3i7 (C<sub>1</sub>, <sup>2</sup>A)</b>                                  | -286.838117                                       | 0.100311                      | -286.443116     | -36                        |

|                                              |              |           |              |      |
|----------------------------------------------|--------------|-----------|--------------|------|
| <b>tsi3p4 (C<sub>1</sub>, <sup>2</sup>A)</b> | -286.822328  | 0.092498  | -286.415207  | 16   |
| <b>tsi3p6 (C<sub>1</sub>, <sup>2</sup>A)</b> | -286.812315  | 0.091893  | -286.411010  | 26   |
| <b>tsi4i6 (C<sub>1</sub>, <sup>2</sup>A)</b> | -286.826397  | 0.099618  | -286.432226  | -10  |
| <b>tsi4p5 (C<sub>1</sub>, <sup>2</sup>A)</b> | -286.816588  | 0.092236  | -286.410345  | 29   |
| <b>tsi4p6 (C<sub>1</sub>, <sup>2</sup>A)</b> | -286.809726  | 0.092061  | -286.406547  | 38   |
|                                              |              |           |              |      |
| <b>p1 (C<sub>s</sub>, <sup>1</sup>A')</b>    | -286.361481  | 0.091449  | -285.959780  |      |
| <b>p2 (C<sub>s</sub>, <sup>1</sup>A')</b>    | -286.358613  | 0.091171  | -285.957601  |      |
| <b>p3 (C<sub>s</sub>, <sup>1</sup>A')</b>    | -286.3477    | 0.091445  | -285.950243  |      |
| <b>p4 (C<sub>s</sub>, <sup>1</sup>A')</b>    | -286.325883  | 0.090756  | -285.922654  |      |
| <b>p5 (C<sub>s</sub>, <sup>1</sup>A')</b>    | -286.324646  | 0.090529  | -285.921886  |      |
| <b>p6 (C<sub>s</sub>, <sup>1</sup>A')</b>    | -286.311431  | 0.090902  | -285.912623  |      |
|                                              |              |           |              |      |
| <b>p1+H</b>                                  | -286.8636373 | 0.0914490 | -286.4597990 | -103 |
| <b>p2+H</b>                                  | -286.8607693 | 0.0911710 | -286.4576195 | -98  |
| <b>p3+H</b>                                  | -286.8498563 | 0.0914450 | -286.4502615 | -78  |
| <b>p4+H</b>                                  | -286.8280393 | 0.0907560 | -286.4226725 | -8   |
| <b>p5+H</b>                                  | -286.8268023 | 0.0905290 | -286.4219054 | -6   |
| <b>p6+H</b>                                  | -286.8135873 | 0.0909020 | -286.4126417 | 19   |

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<sup>a</sup> B3LYP/cc-pVTZ energy with zero-point energy correction in hartree.

<sup>b</sup> zero-point energy by B3LYP/cc-pVTZ in hartree.

<sup>c</sup> relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction.

**Supplementary Table 7.** B3LYP/cc-pVTZ calculated dipole moments of reactants, all intermediates, transition states and products on the CN + C<sub>5</sub>H<sub>6</sub> adiabatic doublet ground state potential energy surface.

**Reactants**

**a. CN**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.520203D+00 | 0.132222D+01 | 0.441046D+01           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.520203D+00 | 0.132222D+01 | 0.441046D+01           |

**b. C<sub>5</sub>H<sub>6</sub> (cyclopentadiene)**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.179321D+00 | 0.455789D+00 | 0.152035D+01           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.179321D+00 | 0.455789D+00 | 0.152035D+01           |

**Intermediates**

**a. i1**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|  | (au) | (Debye) | (10 <sup>-30</sup> SI) |
|--|------|---------|------------------------|
|--|------|---------|------------------------|

|     |              |              |              |
|-----|--------------|--------------|--------------|
| Tot | 0.163899D+01 | 0.416591D+01 | 0.138960D+02 |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00 |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00 |
| z   | 0.163899D+01 | 0.416591D+01 | 0.138960D+02 |

**a. i2**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.171089D+01 | 0.434866D+01 | 0.145056D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.171089D+01 | 0.434866D+01 | 0.145056D+02     |

**b. i3**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.160958D+01 | 0.409113D+01 | 0.136466D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.160958D+01 | 0.409113D+01 | 0.136466D+02     |

**c. i4**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.170417D+01 | 0.433158D+01 | 0.144486D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.170417D+01 | 0.433158D+01 | 0.144486D+02           |

**a. i5**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.155361D+01 | 0.394887D+01 | 0.131720D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.155361D+01 | 0.394887D+01 | 0.131720D+02           |

**b. i6**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.127742D+01 | 0.324688D+01 | 0.108304D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.127742D+01 | 0.324688D+01 | 0.108304D+02           |

**c. i7**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.121494D+01 | 0.308807D+01 | 0.103007D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.121494D+01 | 0.308807D+01 | 0.103007D+02           |

### Transition States

#### a. tsi1i2

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.171188D+01 | 0.435118D+01 | 0.145140D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.171188D+01 | 0.435118D+01 | 0.145140D+02           |

#### b. tsi1i5

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.169823D+01 | 0.431646D+01 | 0.143982D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.169823D+01 | 0.431646D+01 | 0.143982D+02           |

**c. tsi1i6**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.138959D+01 | 0.353200D+01 | 0.117815D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.138959D+01 | 0.353200D+01 | 0.117815D+02     |

**d. tsi1p1**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.188820D+01 | 0.479933D+01 | 0.160088D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.188820D+01 | 0.479933D+01 | 0.160088D+02     |

**e. tsi1p3**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.148601D+01 | 0.377707D+01 | 0.125989D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.148601D+01 | 0.377707D+01 | 0.125989D+02     |

**f. tsi2i3**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.229357D+01 | 0.582966D+01 | 0.194457D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.229357D+01 | 0.582966D+01 | 0.194457D+02     |

**g. tsi2i5**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.162520D+01 | 0.413085D+01 | 0.137790D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.162520D+01 | 0.413085D+01 | 0.137790D+02     |

**h. tsi2i7**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.138906D+01 | 0.353064D+01 | 0.117769D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |

|   |              |              |              |
|---|--------------|--------------|--------------|
| z | 0.138906D+01 | 0.353064D+01 | 0.117769D+02 |
|---|--------------|--------------|--------------|

**i. tsi2p2**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.196178D+01 | 0.498636D+01 | 0.166327D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.196178D+01 | 0.498636D+01 | 0.166327D+02     |

**j. tsi2p3**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.169738D+01 | 0.431432D+01 | 0.143910D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.169738D+01 | 0.431432D+01 | 0.143910D+02     |

**k. tsi3i4**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.245847D+01 | 0.624880D+01 | 0.208437D+02     |

|   |              |              |              |
|---|--------------|--------------|--------------|
| x | 0.000000D+00 | 0.000000D+00 | 0.000000D+00 |
| y | 0.000000D+00 | 0.000000D+00 | 0.000000D+00 |
| z | 0.245847D+01 | 0.624880D+01 | 0.208437D+02 |

#### **l. tsi3i7**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.131554D+01 | 0.334377D+01 | 0.111536D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.131554D+01 | 0.334377D+01 | 0.111536D+02     |

#### **m. tsi3p4**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.163256D+01 | 0.414955D+01 | 0.138414D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.163256D+01 | 0.414955D+01 | 0.138414D+02     |

#### **n. tsi3p6**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.146214D+01 | 0.371639D+01 | 0.123966D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.146214D+01 | 0.371639D+01 | 0.123966D+02           |

**o. tsi4i6**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.131724D+01 | 0.334810D+01 | 0.111680D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.131724D+01 | 0.334810D+01 | 0.111680D+02           |

**p. tsi4p5**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.177762D+01 | 0.451825D+01 | 0.150713D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.177762D+01 | 0.451825D+01 | 0.150713D+02           |

**q. tsi4p6**

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.164986D+01 | 0.419352D+01 | 0.139881D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.164986D+01 | 0.419352D+01 | 0.139881D+02           |

## Products

### a. p1

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.181368D+01 | 0.460991D+01 | 0.153770D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.181368D+01 | 0.460991D+01 | 0.153770D+02           |

### b. p2

Electric dipole moment (dipole orientation): (Debye = 10<sup>-18</sup> statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | (10 <sup>-30</sup> SI) |
|-----|--------------|--------------|------------------------|
| Tot | 0.192246D+01 | 0.488640D+1  | 0.162993D+02           |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00           |
| z   | 0.192246D+01 | 0.488640D+01 | 0.162993D+02           |

**c. p3**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.162192D+1  | 0.412251D+01 | 0.137512D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.162192D+01 | 0.412251D+01 | 0.137512D+02     |

**d. p4**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.153677D+01 | 0.390609D+01 | 0.130293D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.153677D+01 | 0.390609D+01 | 0.130293D+02     |

**e. p5**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

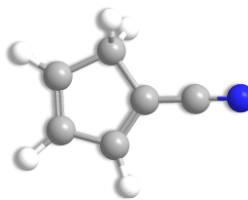
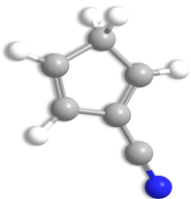
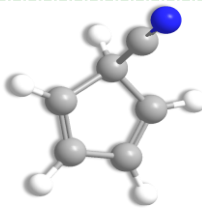
|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.172258D+01 | 0.437837D+01 | 0.146047D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.172258D+01 | 0.437837D+01 | 0.146047D+02     |

**f. p6**

Electric dipole moment (dipole orientation): (Debye =  $10^{-18}$  statcoulomb cm, SI units = C.m)

|     | (au)         | (Debye)      | ( $10^{-30}$ SI) |
|-----|--------------|--------------|------------------|
| Tot | 0.158932D+01 | 0.403966D+01 | 0.134748D+02     |
| x   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| y   | 0.000000D+00 | 0.000000D+00 | 0.000000D+00     |
| z   | 0.158932D+01 | 0.403966D+01 | 0.134748D+02     |

**Supplementary Table 8.** Calculated CCSD(T)/CBS//B3LYP/cc-pVTZ adiabatic ionization energies (IE) and relative energies (Erel ) of C<sub>5</sub>H<sub>5</sub>CN

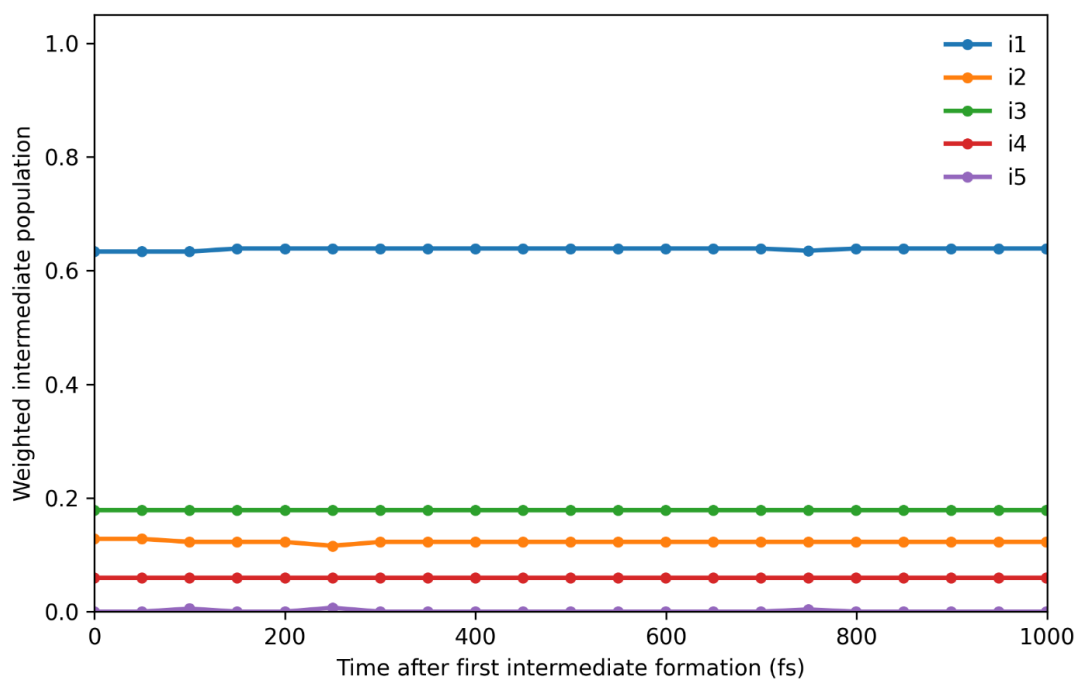
| c-C <sub>5</sub> H <sub>6</sub>                                                    |                                                        | B3LYP/<br>cc-pVTZ+E <sub>zpc</sub> <sup>a</sup> | E <sub>zpc</sub> <sup>b</sup> | CCSD(T)/<br>cc-pVDZ | CCSD(T)/<br>cc-pVTZ | CCSD(T)/<br>cc-pVQZ | CCSD(T)/<br>CBS | IP(eV) <sup>c</sup> | E<br>(kJ/mol) <sup>d</sup> |
|------------------------------------------------------------------------------------|--------------------------------------------------------|-------------------------------------------------|-------------------------------|---------------------|---------------------|---------------------|-----------------|---------------------|----------------------------|
|   | <b>p1 (C<sub>s</sub>, <sup>1</sup>A')</b>              | -286.361481                                     | 0.091449                      | -285.563178         | -285.834206         | -285.914733         | -285.959780     | <b>9.17</b>         | <b>0.0</b>                 |
|                                                                                    | <b>p1<sup>+</sup> (C<sub>s</sub>, <sup>2</sup>A'')</b> | -286.039259                                     | 0.090713                      | -285.240001         | -285.501263         | -285.578662         | -285.621933     |                     |                            |
|   | <b>p2 (C<sub>s</sub>, <sup>1</sup>A')</b>              | -286.358613                                     | 0.091171                      | -285.561226         | -285.832159         | -285.912605         | -285.957601     | <b>9.25</b>         | <b>5.0</b>                 |
|                                                                                    | <b>p2<sup>+</sup> (C<sub>s</sub>, <sup>2</sup>A'')</b> | -286.032498                                     | 0.090351                      | -285.234850         | -285.496068         | -285.573454         | -285.616717     |                     |                            |
|  | <b>p3 (C<sub>s</sub>, <sup>1</sup>A')</b>              | -286.347700                                     | 0.091445                      | -285.553685         | -285.824401         | -285.905081         | -285.950243     | <b>9.28</b>         | <b>25.0</b>                |
|                                                                                    | <b>p3<sup>+</sup> (C<sub>s</sub>, <sup>2</sup>A'')</b> | -286.019470                                     | 0.090850                      | -285.226521         | -285.487536         | -285.565174         | -285.608615     |                     |                            |

isomers.

<sup>a</sup> B3LYP/cc-pVTZ energy with zero-point energy correction in hartree.

<sup>b</sup> zero-point energy by B3LYP/cc-pVTZ in hartree.

<sup>c</sup> relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction.



**Supplementary Fig. 4: Relative populations of reaction intermediates as function of time.** Relative populations of the reaction intermediates as a function of time following their initial formation. Intermediates **i1**, **i2**, **i3**, **i4**, and **i5** are shown in blue, orange, green, red, and purple, respectively.

**Supplementary Table 9.** The relative intermediate populations through time after the first formation of an intermediate. Calculated branching ratios based on the AIMD relative population results (Table 2) at 17.9 kJ mol<sup>-1</sup>.

| Products | Branching ratio       |
|----------|-----------------------|
| p1 + H   | 0.286                 |
| p2 + H   | 0.042                 |
| p3 + H   | 0.672                 |
| p4 + H   | 4.63×10 <sup>-6</sup> |
| p5 + H   | -                     |
| p6 + H   | -                     |

**Supplementary Table 10.** Candidate AIMD methods benchmarked against the reference PES (Figure 5).

| Rank | Method/Basis              | RMSD (kJ mol <sup>-1</sup> ) | Max Error (kJ mol <sup>-1</sup> ) |
|------|---------------------------|------------------------------|-----------------------------------|
| 1    | B3LYP/cc-pVDZ             | 9.66                         | 19.81                             |
| 2    | B3LYP/6-31+G*             | 9.73                         | 17.27                             |
| 3    | B3LYP/aug-pc-1            | 9.99                         | 18.09                             |
| 4    | B3LYP/6-31G**             | 12.01                        | 22.06                             |
| 5    | B3LYP/6-31G*              | 13.41                        | 23.06                             |
| 6    | B3LYP/6-31G               | 16.86                        | 39.37                             |
| 7    | B3LYP/def2-SVP            | 19.89                        | 28.24                             |
| 8    | M06-2X/cc-pVDZ            | 22.86                        | 31.01                             |
| 9    | M06-2X/6-31+G*            | 23.15                        | 33.46                             |
| 10   | B3LYP/3-21G               | 23.17                        | 33.94                             |
| 11   | M06-2X/6-31G**            | 25.20                        | 39.48                             |
| 12   | M06-2X/6-31G              | 26.17                        | 35.80                             |
| 13   | M06-2X/aug-pc-1           | 26.25                        | 35.54                             |
| 14   | M06-2X/6-31G*             | 26.56                        | 40.15                             |
| 15   | PBE0/6-31G                | 31.19                        | 45.70                             |
| 16   | $\omega$ B97X-D3/cc-pVDZ  | 32.06                        | 43.70                             |
| 17   | $\omega$ B97X-D3/6-31+G*  | 33.15                        | 47.03                             |
| 18   | $\omega$ B97X-D3/6-31G**  | 34.35                        | 51.46                             |
| 19   | M06-2X/def2-SVP           | 34.53                        | 45.79                             |
| 20   | $\omega$ B97X-D3/aug-pc-1 | 35.30                        | 48.79                             |
| 21   | PBE0/cc-pVDZ              | 35.63                        | 52.07                             |
| 22   | $\omega$ B97X-D3/6-31G*   | 35.79                        | 52.51                             |
| 23   | PBE0/6-31+G*              | 36.54                        | 55.36                             |
| 24   | M06-2X/3-21G              | 38.62                        | 50.72                             |
| 25   | PBE0/6-31G**              | 38.69                        | 60.73                             |
| 26   | PBE0/aug-pc-1             | 39.53                        | 57.89                             |
| 27   | PBE0/6-31G*               | 40.31                        | 61.77                             |
| 28   | $\omega$ B97X-D3/def2-SVP | 43.22                        | 57.34                             |
| 29   | $\omega$ B97X-D3/3-21G    | 43.30                        | 62.04                             |
| 30   | PBE0/def2-SVP             | 46.87                        | 65.84                             |
| 31   | PBE0/3-21G                | 47.60                        | 69.22                             |

### Supplementary References

- 1 Moffett, R. B. Cyclopentadiene and 3-Chlorocyclopentene: Cyclopentene, 3-chloro-. *Organic Syntheses* **32**, 41-44 (1952).