

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-C₅H₆) reactants along with the corresponding collision energy (E_c) and center-of-mass (θ_{CM}).

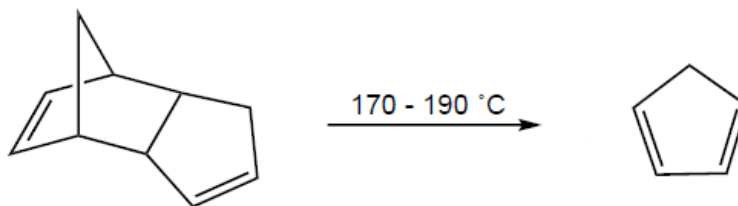
Beam	v_p (m s ⁻¹)	S	E_c (kJ mol ⁻¹)	θ_{CM} (°)
CN ($X^2\Sigma^+$)	1228 ± 26	4.3 ± 0.3		
c-C ₅ H ₆ (X^1A_1)	638 ± 13	24.0 ± 1.1	18 ± 1	53 ± 1

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 ₂ trap	40 mm body OD 225 mm below joint, 16CF at the center and side tubes	Based on Synthware V103884, 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 ⁻⁴ 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

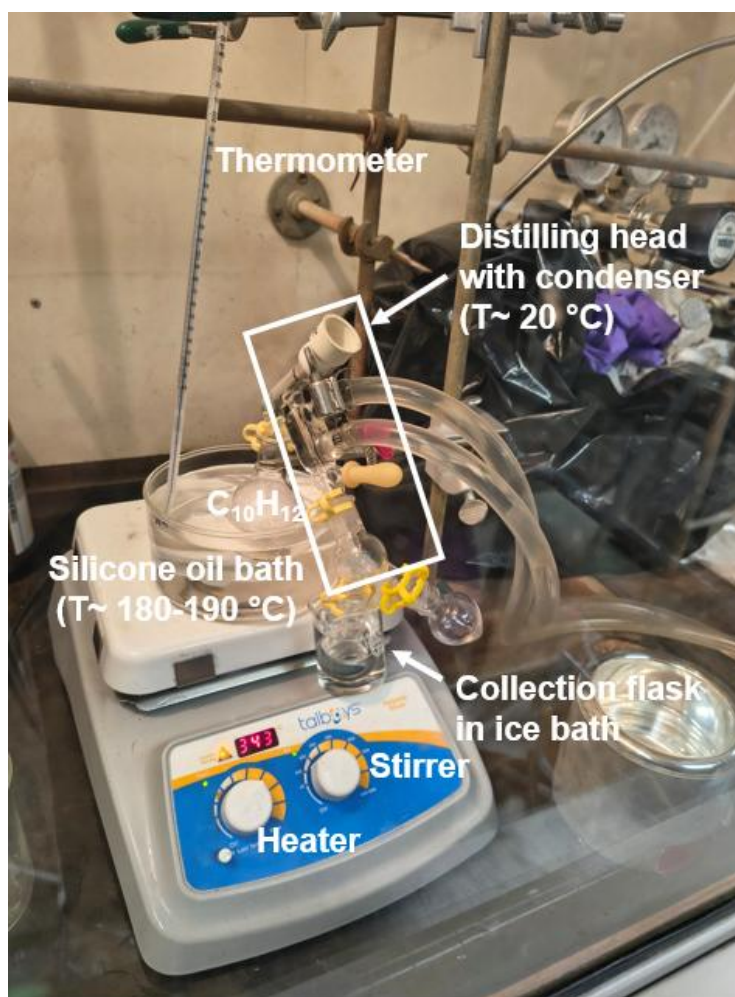
Procedure

The synthesis of cyclopentadiene (c-C₅H₆) is based on the previous from Moffet *et al.*¹ and a photo of the experimental set-up can be found in Supplementary Fig. 1. c-C₅H₆ is synthesized by thermal cracking of the dimer, dicyclopentadiene (C₁₀H₁₂), 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-C₅H₆ 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 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).

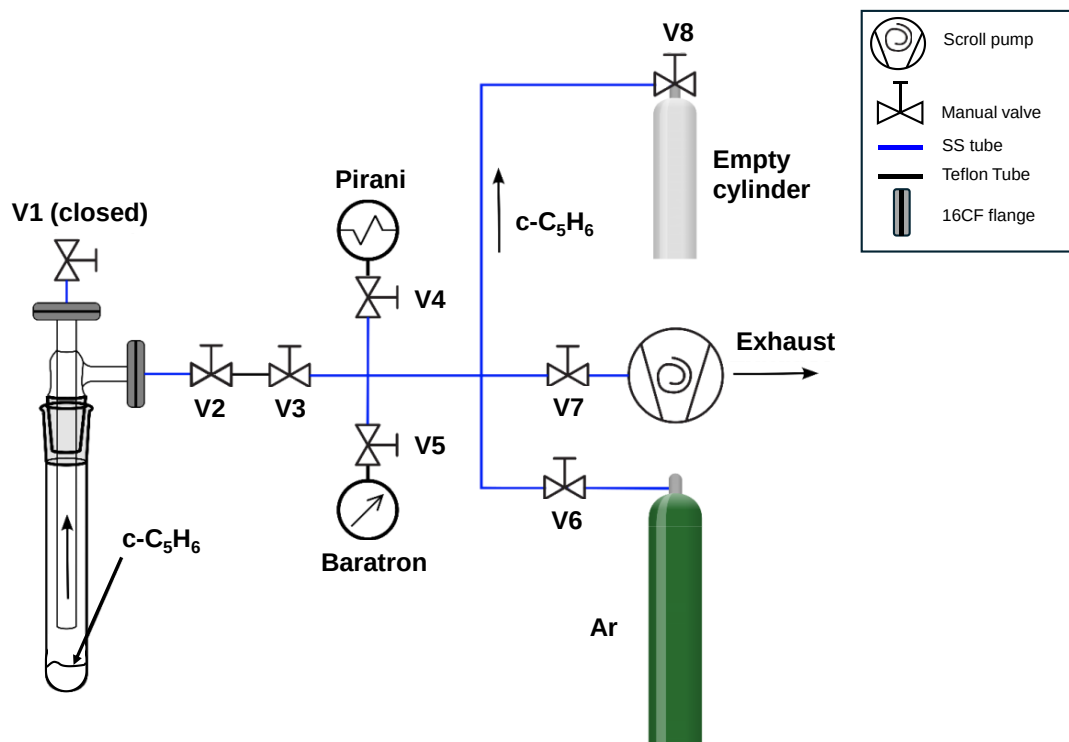
Now it is ready to dilute (5 %) $c\text{-C}_5\text{H}_6$ (for example, 262 Torr / ~100 psi) in argon gas.

- 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-C₅H₆-containing cylinder and wait until the hissing stops.
 - 19) Close the manual valve of the c-C₅H₆ 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-C₅H₆ mixture in argon with a total pressure of about 100 psi is done. Label the c-C₅H₆ cylinder with the date, name of the mixture (c-C₅H₆ in Ar), formula, concentration, total pressure and your name.

Safety considerations

Cyclopentadiene (c-C₅H₆) was handled as a hazardous, volatile, and flammable chemical. All operations involving neat (c-C₅H₆), 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 $c\text{-C}_5\text{H}_6$ in a 13L cylinder. Schematic illustration of the gas handling system used to charge and dilute $c\text{-C}_5\text{H}_6$ in a 13 L gas cylinder to be used in the molecular beam experiments. Scheme adapted with permission from Ref.². Copyright 2025 American Chemical Society.

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.

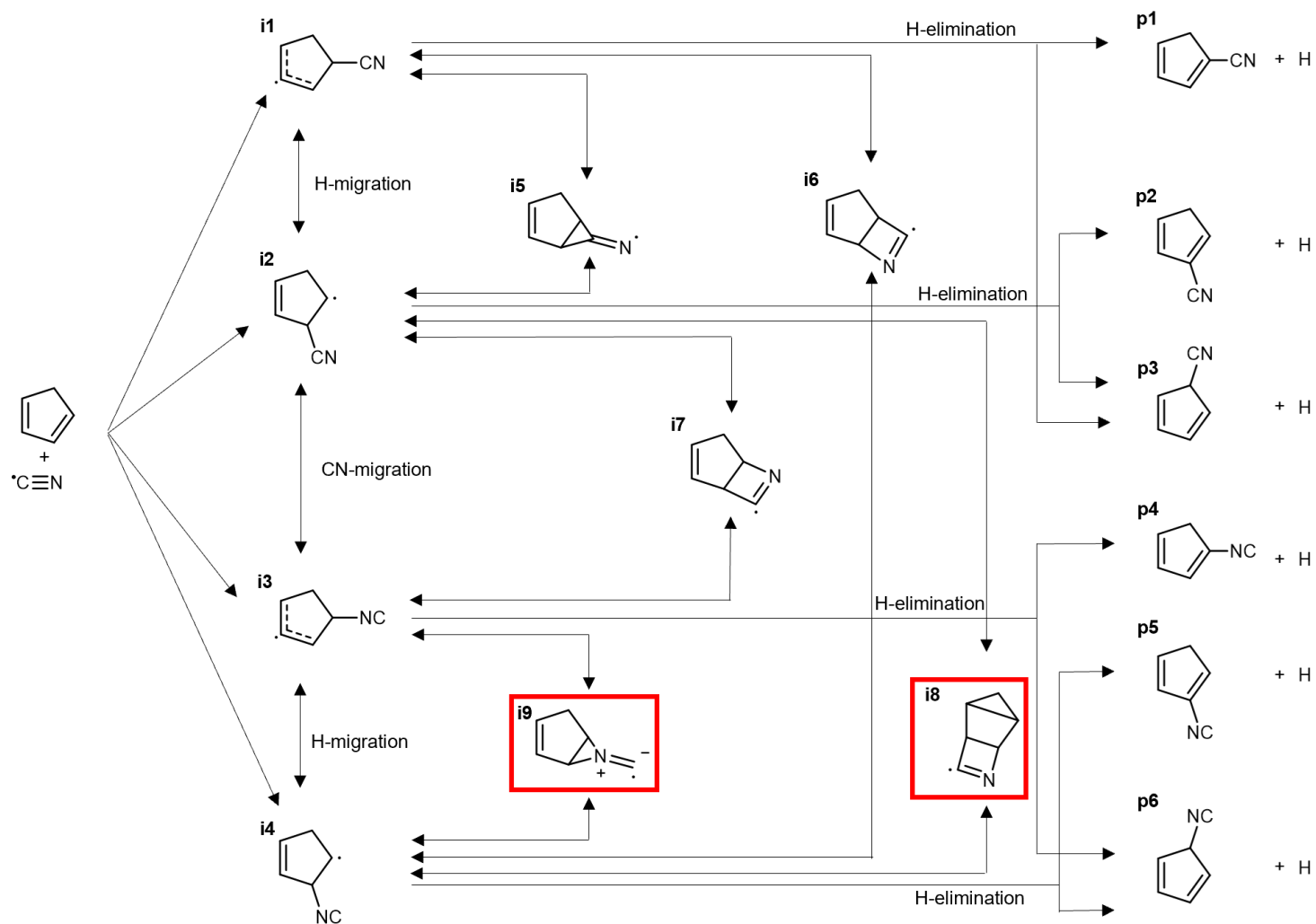
Supplementary Note 2: Possible pathways to p1-p3 from i1-i4

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 kJ mol^{-1} versus 203 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 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⁻¹, 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⁻¹), **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-C₅H₆ 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⁻¹, 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-C₅H₆) 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 ⁻¹)						
	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 ⁻¹⁰	7.44×10 ⁻⁹
p5 + H						-	4.77×10 ⁻¹¹
p6 + H						-	6.54×10 ⁻¹⁰

Products	Collision energy (kJ mol ⁻¹)						
	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 ⁻¹⁰	7.24×10 ⁻⁹
p5 + H						-	4.61×10 ⁻¹¹
p6 + H						-	6.35×10 ⁻¹⁰

Products	Collision energy (kJ mol ⁻¹)						
	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 ⁻⁴	4.90×10 ⁻³
p5 + H						-	2.99×10 ⁻⁵
p6 + H						-	4.30×10 ⁻⁴

Products	Collision energy (kJ mol ⁻¹)						
	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 ⁻⁴	4.67×10 ⁻³
p5 + H						-	3.00×10 ⁻⁵
p6 + H						-	4.10×10 ⁻⁴

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 kJ mol^{-1} .

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

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

Supplementary Table 4. Contributions of the different channels for the formation of **p1-p3** in the reaction of CN + c-C₅H₆ with **i1-i4** as initial intermediates at a collision energy E_c of 17.9 kJ mol⁻¹.

Initial intermediate	Pathway	Contribution (%)
i1	i1 → p1	100
	i5 → i2 → p2	78.9573
	i2 → p2	21.0416
	i6 → i4 → i3 → i2 → p2	0.0011
	i6 → i4 → i3 → i7 → i2 → p2	0.0001
	i1 → p3	91.3396
	i5 → i2 → p3	7.0388
	i2 → p3	1.6215
	i6 → i4 → i3 → i2 → p3	0.0001
	i6 → i4 → i3 → i7 → i2 → p3	0.0000
i2	i5 → i1 → p1	94.3994
	i1 → p1	5.6006
	i7 → i3 → i4 → i6 → i1 → p1	0.0001
	i3 → i4 → i6 → i1 → p1	0.0000
	i2 → p2	100
	i2 → p3	10.8904
	i5 → i1 → p3	86.1018
	i1 → p3	3.0079
	i7 → i3 → i4 → i6 → i1 → p3	0.0000
	i3 → i4 → i6 → i1 → p3	0.0000
i3	i7 → i2 → i5 → i1 → p1	0.1417
	i7 → i2 → i1 → p1	0.1417
	i2 → i5 → i1 → p1	48.8154
	i2 → i1 → p1	48.7719
	i4 → i6 → i1 → p1	2.193
	i7 → i2 → p2	0.2662
	i2 → p2	91.7294
	i4 → i6 → i1 → i5 → i2 → p2	4.0022
	i4 → i6 → i1 → i2 → p2	4.0021
	i7 → i2 → i5 → i1 → p3	0.0928
	i7 → i2 → i1 → p3	0.0928
	i2 → i5 → i1 → p3	31.8627
	i2 → i1 → p3	31.8342
	i4 → i6 → i1 → p3	1.3898
	i7 → i2 → p3	0.0928
	i2 → p3	31.8556
	i4 → i6 → i1 → i5 → i2 → p3	1.3898
	i4 → i6 → i1 → i2 → p3	1.3898
i4	i3 → i7 → i2 → i5 → i1 → p1	0.3517
	i3 → i2 → i5 → i1 → p1	46.8150
	i3 → i7 → i2 → i1 → p1	0.3517
	i3 → i2 → i1 → p1	46.7988
	i6 → i1 → p1	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 + C₅H₆** adiabatic doublet ground state potential energy surface.

a. Reactants

Normal modes	CN		cyclopentadiene	
	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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
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b. Intermediates

	i1		i2	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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
i3			i4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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

v22	1320.5	0.5104	1320.17	1.0698
v23	1354.37	33.5532	1333.12	23.7623
v24	1406.59	5.9887	1388.49	5.7018
v25	1474.22	4.922	1458.42	6.1603
v26	1484.95	0.8819	1679.37	2.2513
v27	2216.23	147.5424	2210.56	161.307
v28	3011.55	7.3263	2968.98	33.1987
v29	3031.66	14.5888	2971.28	7.9577
v30	3058.6	13.5316	2972.27	18.7707
v31	3193.21	3.8552	3189.56	4.0349
v32	3217.57	5.9946	3216.07	8.2552
v33	3230.42	3.098	3222.53	3.2278

Normal modes	i5		i6	
	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	IR Inten
v1	87.71	19.4984	209.91	0.7483
v2	166.45	5.0426	266.06	4.3941
v3	221.51	2.2908	437.99	1.801
v4	372.54	1.605	471.5	7.5123
v5	495.79	8.0362	646.35	2.277
v6	551.28	2.9303	701.82	6.7258
v7	697.35	1.0537	759.57	4.9788
v8	728.22	8.8878	783.12	37.43
v9	763.17	40.5533	832.16	25.711
v10	803.09	9.539	836.68	3.8258
v11	882.12	2.1777	862.84	1.6633
v12	915.37	12.8405	934.11	9.5329
v13	946.11	3.6311	969.14	0.3781
v14	964.74	4.638	996.9	2.5666
v15	988.47	0.4953	1006.24	1.3226
v16	1009.42	0.3385	1037.17	4.5099
v17	1045.34	4.1344	1125.34	1.8128

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

i7

Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(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 modes	tsi1i2		tsi1i5	
	Frequency(cm^{-1})	IR Inten	Frequency(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 modes	tsi1i6		tsi1p1	
	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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

Normal modes	tsi1p3		tsi2i3	
	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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
tsi2i5			tsi2i7	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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
tsi2p2			tsi2p3	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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

tsi3i4			tsi3i7	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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
Normal modes	tsi3p4		tsi3p6	
	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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

tsi4i6			tsi4p5	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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 ⁻¹)	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

d. Products

Normal modes	p1		p2	
	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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
p3			p4	
Normal modes	Frequency(cm ⁻¹)	IR Inten	Frequency(cm ⁻¹)	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(cm^{-1})	IR Inten	Frequency(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 + C₅H₆ (cyclopentadiene)**. The energies are computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy corrections.

	B3LYP/ cc-pVTZ + E _{zpc} ^a	E _{zpc} ^b	CCSD(T)/ CBS	E ^c (kJ/mol)
CN (C_∞, ²Σ⁺)	-92.740886	0.004906	-92.603617	
C₅H₆ (C_{2v}, ¹A₁)	-194.081821	0.092291	-193.822555	
CN + C₅H₆	-286.822707	0.097197	-286.426172	0
H	-0.502156	0.000000	-0.500019	
i1 (C₁, ²A)	-286.925293	0.101391	-286.531036	-264
i2 (C₁, ²A)	-286.903225	0.100479	-286.510120	-212
i3 (C₁, ²A)	-286.892113	0.100930	-286.496592	-175
i4 (C₁, ²A)	-286.870057	0.100061	-286.475699	-123
i5 (C₁, ²A)	-286.872168	0.100302	-286.484841	-146
i6 (C₁, ²A)	-286.843621	0.102842	-286.456747	-65
i7 (C₁, ²A)	-286.844472	0.102748	-286.457295	-67
tsi1i2 (C₁, ²A)	-286.847864	0.096459	-286.448748	-61
tsi1i5 (C₁, ²A)	-286.131936	0.104007	-286.473067	-121
tsi1i6 (C₁, ²A)	-286.835497	0.100746	-286.439817	-27
tsi1p1 (C₁, ²A)	-286.858169	0.093027	-286.451977	-79
tsi1p3 (C₁, ²A)	-286.848612	0.092437	-286.448710	-72
tsi2i3 (C₁, ²A)	-286.830433	0.097837	-286.426950	0
tsi2i5 (C₁, ²A)	-286.866522	0.099959	-286.470359	-109
tsi2i7 (C₁, ²A)	-286.8355	0.100744	-286.429697	0
tsi2p2 (C₁, ²A)	-286.85163	0.092659	-286.446542	-65
tsi2p3 (C₁, ²A)	-286.845627	0.092669	-286.443836	-58
tsi3i4 (C₁, ²A)	-286.837382	0.098157	-286.429765	-7
tsi3i7 (C₁, ²A)	-286.838117	0.100311	-286.443116	-36

tsi3p4 (C₁, ²A)	-286.822328	0.092498	-286.415207	16
tsi3p6 (C₁, ²A)	-286.812315	0.091893	-286.411010	26
tsi4i6 (C₁, ²A)	-286.826397	0.099618	-286.432226	-10
tsi4p5 (C₁, ²A)	-286.816588	0.092236	-286.410345	29
tsi4p6 (C₁, ²A)	-286.809726	0.092061	-286.406547	38
p1 (C_s, ¹A')	-286.361481	0.091449	-285.959780	
p2 (C_s, ¹A')	-286.358613	0.091171	-285.957601	
p3 (C_s, ¹A')	-286.3477	0.091445	-285.950243	
p4 (C_s, ¹A')	-286.325883	0.090756	-285.922654	
p5 (C_s, ¹A')	-286.324646	0.090529	-285.921886	
p6 (C_s, ¹A')	-286.311431	0.090902	-285.912623	
p1+H	-286.8636373	0.0914490	-286.4597990	-103
p2+H	-286.8607693	0.0911710	-286.4576195	-98
p3+H	-286.8498563	0.0914450	-286.4502615	-78
p4+H	-286.8280393	0.0907560	-286.4226725	-8
p5+H	-286.8268023	0.0905290	-286.4219054	-6
p6+H	-286.8135873	0.0909020	-286.4126417	19

^a B3LYP/cc-pVTZ energy with zero-point energy correction in hartree.

^b zero-point energy by B3LYP/cc-pVTZ in hartree.

^c 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 + C₅H₆ adiabatic doublet ground state potential energy surface.

Reactants

a. CN

Electric dipole moment (dipole orientation): (Debye = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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. C₅H₆ (cyclopentadiene)

Electric dipole moment (dipole orientation): (Debye = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ SI)
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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 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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
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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 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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 = 10⁻¹⁸ statcoulomb cm, SI units = C.m)

	(au)	(Debye)	(10 ⁻³⁰ 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)

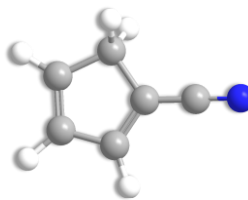
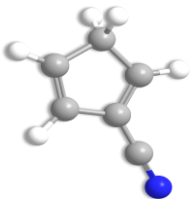
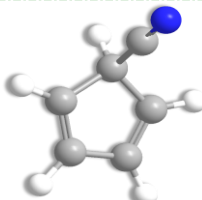
	(au)	(Debye)	(10^{-30} SI)
Tot	0.172258D+01	0.437837D+01	0.146047D+02
x	0.000000D+00	0.000000D+00	0.000000D+00
y	0.000000D+00	0.000000D+00	0.000000D+00
z	0.172258D+01	0.437837D+01	0.146047D+02

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 C₅H₅CN

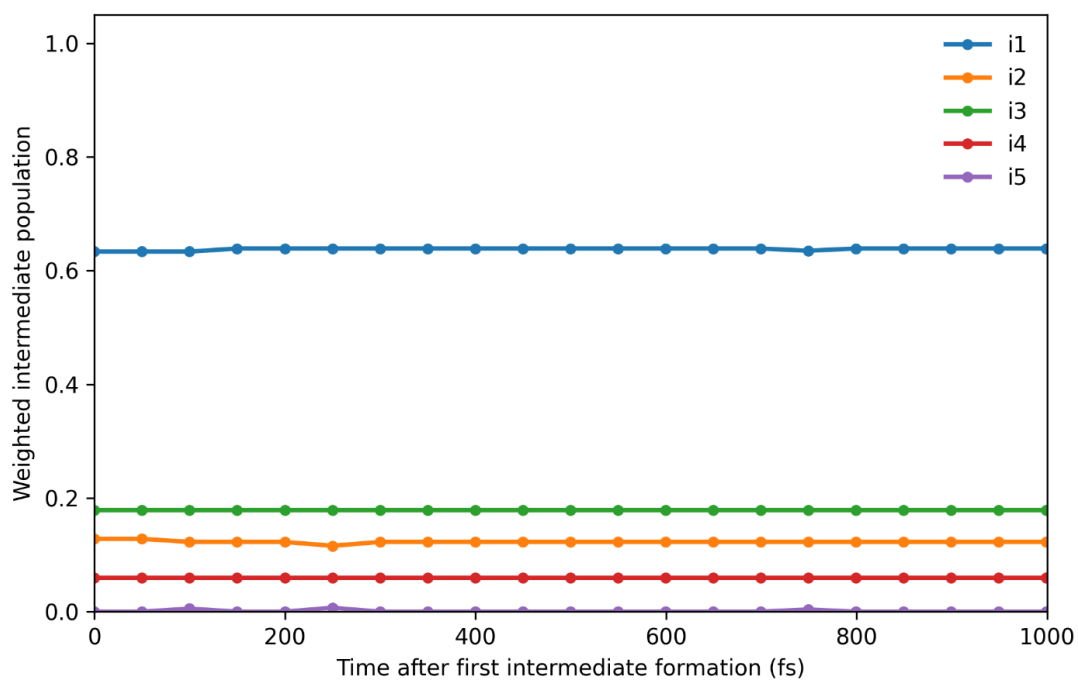
c-C ₅ H ₆		B3LYP/ cc-pVTZ+E _{zpc} ^a	E _{zpc} ^b	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ CBS	IP(eV) ^c	E (kJ/mol) ^d
	p1 (C_s, ¹A')	-286.361481	0.091449	-285.563178	-285.834206	-285.914733	-285.959780	9.17	0.0
	p1⁺ (C_s, ²A'')	-286.039259	0.090713	-285.240001	-285.501263	-285.578662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

isomers.

^a B3LYP/cc-pVTZ energy with zero-point energy correction in hartree.

^b zero-point energy by B3LYP/cc-pVTZ in hartree.

^c 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⁻¹.

Products	Branching ratio
p1 + H	0.286
p2 + H	0.042
p3 + H	0.672
p4 + H	4.63×10 ⁻⁶
p5 + H	-
p6 + H	-

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

Rank	Method/Basis	RMSD (kJ mol ⁻¹)	Max Error (kJ mol ⁻¹)
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	ω B97X-D3/cc-pVDZ	32.06	43.70
17	ω B97X-D3/6-31+G*	33.15	47.03
18	ω B97X-D3/6-31G**	34.35	51.46
19	M06-2X/def2-SVP	34.53	45.79
20	ω B97X-D3/aug-pc-1	35.30	48.79
21	PBE0/cc-pVDZ	35.63	52.07
22	ω 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	ω B97X-D3/def2-SVP	43.22	57.34
29	ω 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).
- 2 Medvedkov, I. A. *et al.* Binding the Power of Cycloaddition and Cross-Coupling in a Single Mechanism: An Unexpected Bending Journey to Radical Chemistry of Butadiynyl with Conjugated Dienes. *J. Phys. Chem. Lett.* **16**, 658-666 (2025).