Supporting Information for:

A case study of proton shuttle in palladium catalysis

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I. Materials and methods

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Dry, oxygen–free solvents were employed. All organic reagents were obtained from commercial sources and dried overnight with P₂O₅ before use. Substrates 1c-f and Catalyst I were prepared following the literature procedures. ³¹P, ¹H and ¹³C spectra were recorded on Bruker Avance 300 and 500. ³¹P, ¹H and ¹³C chemical shifts are expressed with a positive sign, in parts per million, relative to external 85% H₃PO₄ and Me₄Si. Unless otherwise stated, NMR spectra were recorded at 293 K. IR spectra were recorded on Thermoscientific FTIR 6700 equipped with a DLaGS detector using a CaF₂ cell.

II. Kinetic studies

II.a. General sampling procedure

All the kinetic studies were set up under Argon atmosphere. 0.7 mL of deuterated chloroform as solvent was used for all experiments. At every sampling time, a ¹H NMR spectra was recorded and the conversion was determined related to the integration of the alkyne proton of the substrate (δ = 1.99 ppm) and the methylene protons of the lactone (δ = 4.30 ppm).

II.b. Partial order determination:

The partial order of each reaction’s components (substrate and catalyst) was determined by the initial rate method. The data of the concentration of product versus time plot were fitted with Excel. The obtained slope of the linear fitting represents the initial rate. The partial order was then determined by plotting the initial rates versus the initial concentrations.

II.b.1. Partial order determination for [Pd]

To determine the partial order of the reaction on catalyst, the initial kinetic profiles at different initial concentrations of palladium center were recorded. The final data were obtained by averaging the results of three independent trials for each experiment.

![image]

| Experiment | % mol [Pd] | x mg of Cat. I | Initial concentration [Pd] |
|------------|------------|----------------|---------------------------|
| 1          | 3          | 1.5            | 0.0042                    |
| 2          | 5          | 2.5            | 0.007                     |
| 3          | 7.5        | 3.8            | 0.0105                    |
| 4          | 10         | 5.1            | 0.014                     |

*Figure S1.* Reaction conditions for the partial order determination of [Pd].

**General procedure:** 10.8 μL of 5-hexynoic acid 1a (0.0098 mmol, 0.14 M) a specific quantity of Catalyst I according to the above table and 0.7 mL of CDCl₃ were introduced in a pressure NMR tube. The
reaction mixture was heated at 90°C and \(^1\)H NMR spectra were recorded every five minutes until a conversion of 10%.

\(a\) Serie 1:

\(b\) Serie 2:
c) **Serie 3:**

![Concentration of [2a] versus time](image)

**Figure S2.** Determination of the initial rate through a linear fit to the equation: $[2a] = V_0[t]$ at different concentration of palladium center.

**Table S1.** Initial rates determined for different palladium concentrations.

| % mol Pd | [Pd] (mol.L⁻¹) | $V_0(1)$ (mol.L⁻¹.min⁻¹) | $V_0(2)$ (mol.L⁻¹.min⁻¹) | $V_0(3)$ (mol.L⁻¹.min⁻¹) | Average of $V_0$ (mol.L⁻¹.min⁻¹) |
|----------|----------------|--------------------------|--------------------------|--------------------------|---------------------------------|
| 3        | 0.0042         | 0.0009                   | 0.0011                   | 0.0011                   | 0.00103                         |
| 5        | 0.007          | 0.0012                   | 0.0013                   | 0.0014                   | 0.0013                          |
| 7.5      | 0.0105         | 0.0016                   | 0.0016                   | 0.0016                   | 0.0016                          |
| 10       | 0.014          | 0.0019                   | 0.0018                   | 0.0018                   | 0.00183                         |

**Figure S3.** The dependence of initial rates on the palladium center loading.
II.b.2. Partial order determination for 5-hexynoic acid 1a.

To determine the partial order of the reaction in 5-hexynoic acid, the initial kinetic profiles at different initial concentrations of 5-hexynoic acid were recorded. The final data were obtained by averaging the results of three independent trials for each experiment.

![Chemical structure of 5-hexynoic acid 1a and product 2a](image)

| Experiment | x [µL of 5-hexynoic acid] | Initial concentration [1a] (mol.L⁻¹) |
|------------|--------------------------|-------------------------------------|
| 1          | 10.8                     | 0.14                                |
| 2          | 19.3                     | 0.25                                |
| 3          | 38.6                     | 0.5                                 |
| 4          | 57.9                     | 0.75                                |

**Figure S4.** Reaction conditions for the partial order determination of [1a].

**General procedure:** 2.53 mg (5 %mol [Pd]) of Catalyst I, a specific quantity of 5-hexynoic acid 1a according to the above table and 0.7 mL of CDCl₃ were introduced in a pressure NMR tube. The reaction mixture was heated at 90°C and ¹H NMR spectra were recorded every five minutes until a conversion of 30%.

**a) Serie 1:**

![Graph of Concentration of [2a] versus time](image)
b) **Serie 2:**

Figure S5. Determination of the initial rate through a linear fit to the equation: \([2a] = V_0[t]\) at different concentration of \([1a]\).

c) **Serie 3:**
Table S2. Initial rates determined for different concentrations of substrate 1a.

| [1a] (mol.L⁻¹) | V₀(1) (mol.L⁻¹.min⁻¹) | V₀(2) (mol.L⁻¹.min⁻¹) | V₀(3) (mol.L⁻¹.min⁻¹) | Average of V₀ (mol.L⁻¹.min⁻¹) |
|----------------|-----------------------|-----------------------|-----------------------|-------------------------------|
| 0.14           | 0.0011                | 0.0012                | 0.0011                | 0.00115                       |
| 0.25           | 0.0033                | 0.0028                | 0.0023                | 0.00305                       |
| 0.5            | 0.0078                | 0.0077                | 0.007                 | 0.00775                       |
| 0.75           | 0.0148                | 0.014                 | 0.0135                | 0.0144                       |

Figure S6. The dependence of initial rates on [1a].

II.b.3. Partial order determination for 5-hexynoic acid 1a at room temperature.
To determine the partial order of the reaction on 5-hexynoic acid at room temperature, the initial kinetic profiles at different initial concentrations of 5-hexynoic acid were recorded.

![Figure S7. Reaction conditions for the partial order determination of [1a].](image)

**General procedure:** 2.53 mg (5 %mol [Pd]) of Catalyst I, a specific quantity of 5-hexynoic acid 1a according to the above table and 0.7 mL of CDCl₃ were introduced in a pressure NMR tube. ¹H NMR spectra were recorded at room temperature.
**Figure S8.** Determination of the initial rate through a linear fit to the equation: \([2a] = V_0[t]\) at different concentration of \([1a]\).

**Table S3.** Initial rates determined for different concentrations of substrate \(1a\).

| \([1a]\) (mol.L\(^{-1}\)) | \(V_0\) (mol.L\(^{-1}\).min\(^{-1}\)) |
|-----------------------------|-----------------------------------|
| 0.14                        | \(4 \times 10^{-5}\)             |
| 0.25                        | \(9 \times 10^{-5}\)             |
| 0.5                         | 0.0002                            |
| 0.75                        | 0.0004                            |

**Figure S9.** The dependence of initial rates on \([1a]\) at room temperature.
II.b.3. Partial order determination for 5-hexynoic acid 1a in presence of 1 mol% of Tetrachlorocatechol 4u.

To determine the partial order of the reaction on 5-hexynoic acid in presence of 1 mol% of Tetrachlorocatechol 4u, the initial kinetic profiles at different initial concentrations of 5-hexynoic acid were recorded. The final data were obtained by averaging the results of two independent trials for each experiment.

| Experiment | μL of 5-hexynoic acid | Initial concentration [1a] (mol.L⁻¹) |
|------------|-----------------------|----------------------------------|
| 1          | 10.8                  | 0.14                             |
| 2          | 19.3                  | 0.25                             |
| 3          | 38.6                  | 0.5                              |
| 4          | 57.9                  | 0.75                             |

Figure S10. Reaction conditions for the partial order determination of [1a].

General procedure: 2.53 mg (5 %mol [Pd]) of Catalyst I, a specific quantity of 5-hexynoic acid 1a according to the above table and 0.7 mL of a solution of tetrachlocatechol 4u in CDCl₃ ([0.0014 M]: 3.47 mg of 4u in 10 mL of CDCl₃) were introduced in a pressure NMR tube. ¹H NMR spectra were recorded at room temperature.

a) Serie 1:

b) Serie 2:
Figure S11. Determination of the initial rate through a linear fit to the equation: \([2a] = V_0[t]\) at different concentration of [1a].

Table S4. Initial rates determined for different concentrations of substrate 1a.

| [1a] (mol.L\(^{-1}\)) | \(V_0(1)\) (mol.L\(^{-1}\).min\(^{-1}\)) | \(V_0(2)\) (mol.L\(^{-1}\).min\(^{-1}\)) | Average of \(V_0\) (mol.L\(^{-1}\).min\(^{-1}\)) |
|------------------------|-----------------------------|-----------------------------|-----------------------------|
| 0.14                   | 0.0002                      | 0.0002                      | 0.0002                      |
| 0.25                   | 0.0003                      | 0.0003                      | 0.0003                      |
| 0.5                    | 0.0004                      | 0.0005                      | 0.00045                     |
| 0.75                   | 0.0006                      | 0.0006                      | 0.0006                      |

Figure S12. The dependence of initial rates on [1a] in presence of tetrachlorocatechol (1 mol%).
II.b.4. Partial order determination for 5-hexynoic acid 1a in presence of 5 mol% of Tetrachlorocatechol 4u.

To determine the partial order of the reaction on 5-hexynoic acid in presence of 5 mol% of Tetrachlorocatechol 4u, the initial kinetic profiles at different initial concentrations of 5-hexynoic acid were recorded. The final data were obtained by averaging the results of two independent trials for each experiment.

![Reaction scheme](image)

| Experiment | x mM of 5-hexynoic acid | Initial concentration [1a] (mol.L⁻¹) |
|------------|-------------------------|-----------------------------------|
| 1          | 10.8                    | 0.14                              |
| 2          | 19.3                    | 0.25                              |
| 3          | 38.6                    | 0.5                               |
| 4          | 57.9                    | 0.75                              |

**Figure S13.** Reaction conditions for the partial order determination of [1a].

**General procedure:** 2,53 mg (5 %mol [Pd]) of Catalyst I, a specific quantity of 5-hexynoic acid 1a according to the above table and 0.7 mL of a solution of tetrachlocatechol 4u in CDCl₃ ([0.007 M]: 8.67 mg of 4u in 5 mL of CDCl₃) were introduced in a pressure NMR tube. ¹H NMR spectra were recorded at room temperature.

**a) Serie 1:**

![Concentration of [2a] versus time](image)
**b) Serie 2:**

Figure S14. Determination of the initial rate through a linear fit to the equation: \([2a] = V_0[t]\) at different concentration of \([1a]\).

Table S5. Initial rates determined for different concentrations of substrate \([1a]\).

| \([1a]\) (mol.L\(^{-1}\)) | \(V_0(1)\) (mol.L\(^{-1}\).min\(^{-1}\)) | \(V_0(2)\) (mol.L\(^{-1}\).min\(^{-1}\)) | Average of \(V_0\) (mol.L\(^{-1}\).min\(^{-1}\)) |
|-----------------|-----------------|-----------------|-----------------|
| 0.14            | 0.0006          | 0.0007          | 0.00065         |
| 0.25            | 0.0006          | 0.0006          | 0.0006          |
| 0.5             | 0.0011          | 0.0011          | 0.0011          |
| 0.75            | 0.0013          | 0.0012          | 0.00125         |

Figure S15. The dependence of initial rates on \([1a]\) in presence of tetrachlorocatechol (5 mol%).
**II.b.5. Partial order determination for 5-hexynoic acid 1a in presence of 10 mol% of Tetrachlorocatechol 4u.**

To determine the partial order of the reaction on 5-hexynoic acid in presence of 10 mol% of Tetrachlorocatechol 4u, the initial kinetic profiles at different initial concentrations of 5-hexynoic acid were recorded. The final data were obtained by averaging the results of two independent trials for each experiment.

| Experiment | x [M] of 5-hexynoic acid | Initial concentration [1a] (mol.L⁻¹) |
|------------|-------------------------|-----------------------------------|
| 1          | 10.8                    | 0.14                              |
| 2          | 19.3                    | 0.25                              |
| 3          | 38.6                    | 0.5                               |
| 4          | 57.9                    | 0.75                              |

**Figure S16.** Reaction conditions for the partial order determination of [1a].

**General procedure:** 2.53 mg (5 %mol [Pd]) of Catalyst I, 2.43 mg of tetrachlorocatechol and a specific quantity of 5-hexynoic acid 1a according to the above table were introduced in a pressure NMR tube with 0.7 mL of CDCl₃. ¹H NMR spectra were recorded at room temperature.

**a) Serie 1:**

Concentration of [2a] versus time

**b) Serie 2:**
**Figure S17.** Determination of the initial rate through a linear fit to the equation: \([2a] = V_0[t]\) at different concentration of \([1a]\).

**Table S6.** Initial rates determined for different concentrations of substrate \([1a]\).

| \([1a]\) (mol.L\(^{-1}\)) | \(V_0(1)\) (mol.L\(^{-1}\).min\(^{-1}\)) | \(V_0(2)\) (mol.L\(^{-1}\).min\(^{-1}\)) | Average of \(V_0\) (mol.L\(^{-1}\).min\(^{-1}\)) |
|---------------------------|--------------------------------|--------------------------------|--------------------------------|
| 0.14                      | 0.0009                         | 0.001                           | 0.00095                         |
| 0.25                      | 0.0013                         | 0.0014                          | 0.00135                         |
| 0.5                       | 0.0016                         | 0.0016                          | 0.0016                          |
| 0.75                      | 0.0016                         | 0.0018                          | 0.0017                          |

**Figure S18.** The dependence of initial rates on \([1a]\) in presence of tetrachlorocatechol (10 mol%).


II.b.6. Partial order determination for 5-hexynoic acid 1a in presence of 20 mol% of Tetrachlorocatechol 4u.

To determine the partial order of the reaction in 5-hexynoic acid in presence of 20 mol% of Tetrachlorocatechol 4u, the initial kinetic profiles at different initial concentrations of 5-hexynoic acid were recorded. The final data were obtained by averaging the results of two independent trials for each experiment.

![Chemical structure](image)

**Figure S19.** Reaction conditions for the partial order determination of [1a].

| Experiment | x [%] of 5-hexynoic acid | Initial concentration [1a] (mol.L⁻¹) |
|------------|--------------------------|-------------------------------------|
| 1          | 10.8                     | 0.14                                |
| 2          | 19.3                     | 0.25                                |
| 3          | 38.6                     | 0.5                                 |
| 4          | 57.9                     | 0.75                                |

**General procedure:** 2.53 mg (5 %mol [Pd]) of Catalyst I, 4.86 mg of tetrachlorocatechol and a specific quantity of 5-hexynoic acid 1a according to the above table were introduced in a pressure NMR tube with 0.7 mL of CDCl₃. ¹H NMR spectra were recorded at room temperature.

**a) Serie 1:**

![Graph](image)
**b) Serie 2:**

![Graph showing concentration of [2a] versus time with different concentrations of [2a].](image)

**Figure S20.** Determination of the initial rate through a linear fit to the equation: \([2a] = V_0[t]\) at different concentration of \([1a]\).

**Table S7.** Initial rates determined for different concentrations of substrate \([1a]\).

| \([1a]\) (mol.L\(^{-1}\)) | \(V_0(1)\) (mol.L\(^{-1}\).min\(^{-1}\)) | \(V_0(2)\) (mol.L\(^{-1}\).min\(^{-1}\)) | Average of \(V_0\) (mol.L\(^{-1}\).min\(^{-1}\)) |
|-------------------|----------------|----------------|----------------|
| 0.14              | 0.0014         | 0.0014         | 0.0014         |
| 0.25              | 0.0018         | 0.0017         | 0.00175        |
| 0.5               | 0.0019         | 0.0021         | 0.002          |
| 0.75              | 0.0024         | 0.002          | 0.0022         |

![Graph showing the dependence of initial rates on \([1a]\) in presence of tetrachlorocatechol (1 mol%).](image)

**Figure S21.** The dependence of initial rates on \([1a]\) in presence of tetrachlorocatechol (1 mol%).
Figure S22. Partial order of 5-hexynoic 1a versus the quantity of tetrachlorocatechol 4u.

III. Study of the self association 5-hexynoic acid in CHCl₃ by IR spectroscopy.
The self-association of 5-hexynoic acid was evidenced by IR spectroscopy in CHCl₃ at different acid concentrations (Vide Infra). IR spectra were recorded with a resolution of 4 cm⁻¹ in 16 scans. Two well defined absorptions bands were observed, at 1711 and 1751 cm⁻¹ corresponding to the dimeric and monomer forms, respectively. The observed bands are shown in Figure S23 at different concentrations and reported in Table S8 with the intensities ratio.

Table S8. Ratio of the intensity of the IR signal corresponding to the dimer form (1711 cm⁻¹) versus the one corresponding to the monomer form (1750 cm⁻¹) for 5-hexynoic acid 1a.

| Concentration in [1a] (mol.L⁻¹) | Intensity of the IR signal at 1711 cm⁻¹ | Intensity of the IR signal at 1750 cm⁻¹ | Ratio dimer/monomer |
|--------------------------------|----------------------------------------|----------------------------------------|-------------------|
| 0.5                            | 1.91                                   | 0.18                                   | 10.6              |
| 0.25                           | 1.0                                    | 0.11                                   | 9.09              |
| 0.14                           | 0.58                                   | 0.0774                                 | 7.49              |
| 0.1                            | 0.417                                  | 0.0615                                 | 6.78              |
| 0.075                          | 0.297                                  | 0.0483                                 | 6.15              |
| 0.05                           | 0.194                                  | 0.0373                                 | 5.20              |
| 0.025                          | 0.0875                                 | 0.0238                                 | 3.67              |
| 0.01                           | 0.0346                                 | 0.014                                  | 2.47              |
| 0.0075                         | 0.0525                                 | 0.0172                                 | 3.05              |
| 0.005                          | 0.0137                                 | 0.00931                                | 1.47              |
| 0.0025                         | 0.00503                                | 0.00506                                | 0.99              |
| 0.001                          | 0.00247                                | 0.00359                                | 0.69              |
VI. $^{31}$P NMR analysis of the Palladium indenediide dimer I at variable temperature.

The dissociation-association behavior of the Palladium indenediide dimer I was evidenced by $^{31}$P NMR spectroscopy at variable temperature using a 400 MHz NMR spectrometer. The association activation barrier was estimated from these experiments (Figure S24), using the following formula:

$$\Delta G^\circ = RT_c \ln \left( \frac{RT_c \sqrt{2}}{\pi N_A h |v_A - v_B|} \right)$$

The association activation barrier was estimated to be at least of 15.8 kcal.mol$^{-1}$, considering the $^{31}$P NMR spectroscopic data: the coalescence temperature $T_c = 363$ K, and the chemical-shift difference $|v_A - v_B| = 1017.33$ Hz.
VII. General procedure for cycloisomerization of alkynoic acids in presence of additives:

In a NMR pressure tube, alkynoic acid (0.098 mmol), dried additive (x mol%) and complex I (2.5 mg, 5 mol% [Pd]) in 0.7 mL of CDCl₃ were heated at the corresponding temperature under argon atmosphere. The progress of the reaction was monitored by ¹H NMR.

![Diagram of cycloisomerization](image)

**Figure S25.** Additives having no impact (3a-d) or inhibiting (3e,f) the cyclisation of 4-pentynoic acid 1b.
Table S9. Evaluation of additives 3 in the cyclisation of 4-pentynoic acid 1b.

| Additives | 1h00 | 2h00 |
|-----------|------|------|
|           |      |      |
| /         | 77%  | 88%  |
| 3a        | 73%  | 86%  |
| 3b        | 70%  | 86%  |
| 3c        | 72%  | 86%  |
| 3d        | 71%  | 84%  |
| Additives |      |      |
| 30 min    |      |      |
| /         | 44%  |
| 3e        | 0%   |
| 3f        | 6%   |

Figure S26. H-bond additives library used in the cycloisomerization of 5-hexynoic acid 1a catalyzed by indenediide dimer I.
Figure S27. Evaluation of the impact of weak H-donor compounds 4 (30 %mol) on the cyclization of 5-hexynoic acid 1a.
Table S10. Evaluation of the additives in the cyclization of 5-hexynoic acid 1a and optimization of the reaction conditions.

| Entry | Additives                          | mol% Pd | mol% additive | T°C | conversion<sup>b</sup> |
|-------|-----------------------------------|---------|---------------|-----|------------------------|
| 1     | 1,2,3-benzenetriol 4p             | 5       | 5             | 90  | 89%                    |
| 2     | Ethyl 3,4-dihydroxybenzoate 4w    | 5       | 5             | 90  | 88%                    |
| 3     | Tetrachlorocatechol 4u            | 5       | 5             | 90  | 90%                    |
| 4     | 4-Nitrocatechol 4x                | 5       | 5             | 90  | 100%                   |
| 5     | 4-Nitrocatechol 4x                | 5       | 5             | 60  | 100%                   |
| 6     | 4-Nitrocatechol 4x                | 5       | 5             | 40  | 79%                    |
| 7     | 4-Nitrocatechol 4x                | 1       | 5             | 90  | 100%                   |
| 8     | 4-Nitrocatechol 4x                | 0.2     | 1             | 90  | 92%<sup>c</sup>        |

(a) Catalytic reactions performed under argon during 30 min using 0.1 mmol of 5-hexynoic acid (0.14 M in CDCl<sub>3</sub>) and 5 mol% [Pd] with dimer I. (b) Conversion were determined by <sup>1</sup>H NMR analysis. (c) Reaction time of 36h.

VIII. Characterization of product 2f:

Product 2f was obtained following the general procedure at 90°C in 60 h. Under these conditions, hydration of the alkyne moiety was observed. The residue was purified by flash chromatography. The high volatility of compound 2f prevented accurate determination of isolated yield. A NMR yield of 70% was determined using mesitylene as internal standard. The NMR signals corresponding to the hydration product 2f' in the crude are in total agreement with the reported characterization.\textsuperscript{22}

RMN-\textsuperscript{1}H (CDCl<sub>3</sub>): \( \delta_{ppm} \) 4.62 (qt, \( ^3J_{HH} = 6.9 \) Hz, \( ^4J_{HH} = 0.9 \) Hz, \( 1H, H^8 \)), 2.62 (t, \( ^3J_{HH} = 6.9 \) Hz, \( 2H, H^1 \)), 2.39 (m, \( 2H, H^9 \)), 1.85 (m, \( 2H, H^2 \)), 1.63 (td, \( ^3J_{HH} = 6.9 \) Hz, \( ^5J_{HH} = 1.5 \) Hz, \( 3H, H^3 \)).

RMN-\textsuperscript{13}C\textsuperscript{1}H (CDCl<sub>3</sub>): \( \delta_{ppm} \) 168.5 (C\textsuperscript{5}), 147.98 (C\textsuperscript{4}), 103.61 (C\textsuperscript{9}), 30.65 (C\textsuperscript{1}), 27.17 (C\textsuperscript{7}), 18.89 (C\textsuperscript{2}), 9.54 (C\textsuperscript{3}).
IX. Computational details

Calculations were carried out with the Gaussian 09 program on the real experimental palladium-pincer system at the B3PW91 level of theory. Palladium atom was treated with the corresponding Stuttgart-Dresden RECP (relativistic effective core potential) in combination with its adapted basis set, augmented by an extra set of f polarization function. Phosphorus atoms were represented by the ECP from Dolg et al. and its associated basis set, augmented also by d polarization functions. For the remaining atoms the 6-31G(d,p) basis set was used. Geometry optimizations carried out without any symmetry restrictions, and were followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. The connection between the transition state and the corresponding minima were done by performing IRC calculations. Finally, the CYLview program was used for the representation of 3D structures.

**Figure S28.** Gibbs free energy profile for the cyclization of 4-pentynoic acid 1b involving one molecule of substrate per Pd center.

**Figure S29.** Gibbs free energy profile for the cyclization of 4-pentynoic acid 1b involving two molecules of substrate per Pd center.
**Figure S30.** Gibbs free energy profile for the cyclization of 4-pentynoic acid 1b involving catechol 4a as additive.

**Cartesian coordinates of the optimized structures along with their enthalpy and Gibbs free energies.**

|   | Cartesian coordinates (a.u.) | Gibbs free energy (kcal/mol) | Enthalpy (a.u.) | Entropy (a.u.) |
|---|------------------------------|-----------------------------|-----------------|---------------|
| S | 2.36229100 2.28585300 0.20849900 | 2.36229100 2.28585300 0.20849900 | 2.36229100 2.28585300 0.20849900 | 2.36229100 2.28585300 0.20849900 |
| H | 5.32194800 | 5.32194800 | 5.32194800 | 5.32194800 |
| C | 4.81794000 -1.31052600 3.81143700 | 4.81794000 -1.31052600 3.81143700 | 4.81794000 -1.31052600 3.81143700 | 4.81794000 -1.31052600 3.81143700 |
| H | 6.56675200 -0.31824500 3.03053100 | 6.56675200 -0.31824500 3.03053100 | 6.56675200 -0.31824500 3.03053100 | 6.56675200 -0.31824500 3.03053100 |
| C | 5.21948000 -1.66155700 4.70782400 | 5.21948000 -1.66155700 4.70782400 | 5.21948000 -1.66155700 4.70782400 | 5.21948000 -1.66155700 4.70782400 |
| C | -4.03123900 0.01146100 -1.03435600 | -4.03123900 0.01146100 -1.03435600 | -4.03123900 0.01146100 -1.03435600 | -4.03123900 0.01146100 -1.03435600 |

**TS\textsubscript{SA}**

H\textsubscript{f} = -2552.742652 a.u.

G\textsubscript{f} = -2552.887446 a.u.

S = -2552.742652 a.u.

H = -2552.887446 a.u.
\[
\begin{align*}
\text{TS}_{\text{2A}} & \quad \text{H} = -2897.06651 \text{ a.u.} \\
\text{G} & = -2897.06651 \text{ a.u.}
\end{align*}
\]
|          | X       | Y       | E         | Int-3f    | INT-3F    |
|----------|---------|---------|-----------|-----------|-----------|
| C        | 0.56084700 | 0.71480600 | -3.39430800 | H         | -7.13047000 | -2.05899300 | -3.66737800 |
| C        | 1.86811600 | 0.43873400 | -3.83813400 | C         | -2.73804300 | 0.06811200 | 0.65968500 |
| C        | 2.14838500 | -0.73635200 | -4.55144200 | C         | -2.73157200 | 1.26783100 | 1.37691800 |
| H        | 1.38002700 | -2.57390500 | -5.38430800 | C         | -2.93152100 | -1.14795000 | 1.33123500 |
| H        | -0.96675200 | -2.12552800 | -6.41695500 | C         | -2.91568100 | 1.25404300 | 2.75832600 |
| H        | 3.16297900 | -0.91133900 | -4.90590000 | H         | -2.58268200 | 2.20222700 | 0.84372400 |
| H        | 2.65323000 | 1.16302400 | -3.63229900 | C         | -3.11021700 | -1.15133700 | 2.71241100 |
| O        | 0.14793100 | 1.77190200 | -2.74351700 | H         | -2.93672700 | -2.08576400 | 0.78550600 |
| O        | -1.68704500 | 0.08908800 | -3.25693100 | H         | -3.10304800 | 0.04543000 | 3.42615700 |
| H        | -1.47366000 | 0.99254800 | -2.89149700 | H         | -2.91292800 | 2.18895900 | 3.31135800 |
|          |         |         |           | H         | -3.25566700 | -2.09676900 | 3.23024600 |
|          |         |         |           | H         | -3.24570600 | 0.03610400 | 4.50318400 |

**T3SF**

\[ \text{H} = -2935.215853 \text{ a.u.} \]

\[ \Gamma = -2935.354378 \text{ a.u.} \]

**S**

\[ 2.63409200 \cdot 1.72032800 -1.32000200 \]

**C**

\[ 0.39115900 \cdot 5.49373100 -0.55832400 \]

**H**

\[ 2.74357000 \cdot 3.45923700 -0.61020100 \]

**P**

\[ 2.64172070 \cdot -0.01656700 -0.23138300 \]

**P**

\[ 2.49458600 \cdot 0.09443800 -1.15872200 \]

**C**

\[ 3.97848700 \cdot -1.19468000 -0.76623900 \]

**C**

\[ 4.96811300 \cdot -1.58969500 -0.11468300 \]

**C**

\[ 3.97498300 \cdot -1.55184800 -1.26030900 \]

**C**

\[ 5.93568200 \cdot -2.46086100 -0.34702400 \]

**C**

\[ 4.97289500 \cdot -1.26267700 1.15012500 \]

**C**

\[ 4.96188300 \cdot -2.42474300 -2.55293000 \]

**C**

\[ 3.22526100 \cdot -1.18850900 -2.80583700 \]

**C**

\[ 5.94843700 \cdot -2.87954600 -1.67678100 \]

**S**

\[ 6.72550900 \cdot -2.80913000 0.33351000 \]

**H**

\[ 4.94928200 \cdot -2.74234500 -3.59093000 \]

**S**

\[ 6.71780200 -3.55917100 -2.03244600 \]

**C**

\[ 2.85857900 0.29793900 1.56219800 \]

**C**

\[ 3.58190100 1.41916800 1.98234700 \]

**C**

\[ 2.30205100 -0.57541300 2.50541200 \]

**C**

\[ 3.76195400 1.65499200 3.34832400 \]

**C**

\[ 3.97766300 2.11529400 1.24802300 \]

**C**

\[ 2.48485500 -0.33023500 3.86486700 \]

**C**

\[ 1.71785400 -1.43289000 2.18437200 \]

**C**

\[ 3.21683900 0.78070500 4.28371800 \]

**C**

\[ 4.39835000 2.52889000 3.66718300 \]

**C**

\[ 2.04669500 -1.00457000 5.49634900 \]

**C**

\[ 3.35745000 0.97041300 5.34466700 \]

**C**

\[ -3.97988300 -0.62736200 -1.93385600 \]

**C**

\[ -3.90454300 -1.04881800 -3.27119800 \]

**C**

\[ -5.18651400 -0.71198500 -1.22809500 \]

**C**

\[ -5.04457300 -1.56584600 -3.88217600 \]

**C**

\[ -2.97538900 -0.96994700 -3.83669400 \]

**C**

\[ -6.31827600 -1.22716900 -1.85568700 \]

**C**

\[ -5.24352700 -0.37929300 -0.19632100 \]

**C**

\[ -6.24673400 -1.65621900 -3.18016600 \]

**C**

\[ -4.98899900 -1.89510900 -4.91560100 \]

**C**

\[ -7.25434300 -1.29213400 -1.30853200 \]
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