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Supporting information

Demonstration of an Azobenzene Derivative based Solar Thermal Energy Storage System

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S1. Materials and instruments

Synthesis of **AZO1**.[1] A dispersion (50% in mineral oil) of NaH (4.36 g, 114 mmol) was added to a solution of 4-(phenylazo)phenol (15.00 g, 76 mmol) in dehydrated DMF (300 mL) portionwise under nitrogen atmosphere at 0 °C. After stirring at room temperature for 30 minutes, 1-bromo-2-ethylhexane (20 mL, 91 mmol) was added dropwise to the solution at 0 °C. The reaction mixture was warmed to 60 °C and stirred for 5 h. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate. The aqueous layer was extracted with ethyl acetate twice and the combined organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4. After filtration and evaporation, the resulting residue was purified by column chromatography (hexane to hexane/ethyl acetate = 20:1 to hexane/ethyl acetate = 10:1) to give compound **1** (22.21 g, 99%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.80-8.00 (m, 4H), 7.35-7.55 (m, 3H), 6.95-7.05 (m, 2H), 3.85-4.00 (m, 2H), 1.65-1.85 (m, 1H), 1.20-1.60 (m, 8H), 0.80-1.00 (m, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ162.04, 152.95, 146.98, 130.20, 128.98, 124.73, 122.55, 114.80, 71.03, 39.46, 30.59, 29.12, 23.95, 23.02, 14.01, 11.11; HRMS (ESI) Calcd for $C_{20}H_{27}N_2O$ $[M+H]^+$: 311.2188. Found: 311.2120; Elem. Anal. Calcd for $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.02. Found: C, 77.27; H, 8.38; N, 9.19.

CoPc and $[Cu(CH_3CN)_4]PF_6$ were purchased from Sigma-Aldrich.

The microfluidic chip used for **AZO1** indoor conversion experiments was home made from quartz, the channels are etched isotopically (wet) 100 µm deep into the substrate, i.e. the actual optical pathlength have a lateral bias of 100 µm. The chip has a total volume of 33.9 mm^3.

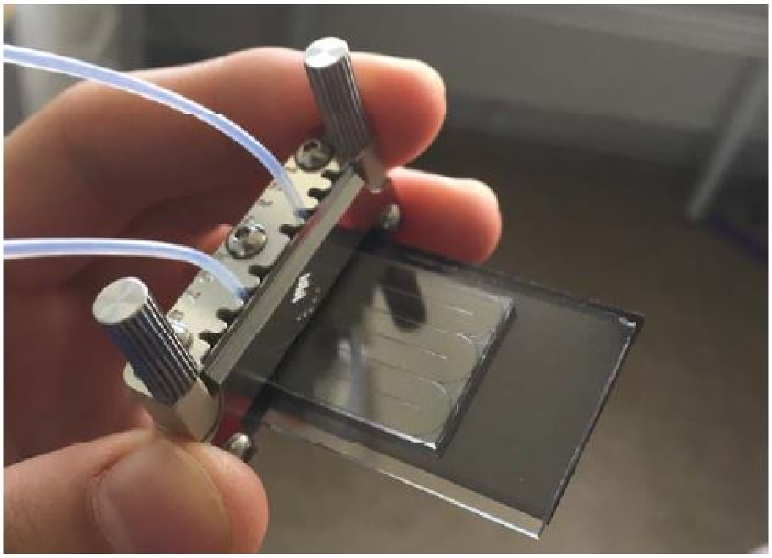


Figure S1.2. Actual photo of the microfluidic chip.

Cary 100 UV-vis with a 1-cm path length cuvette, scanning from 290 to 750 nm was used for all solution based spectroscopic characterization measurements. Temperature control for kinetic studies was performed with Luma 40^{TM}/Univ-Short sample holder from Quantum Northwest. The **AZO1** conversion for absorptivity measurements, kinetic studies was performed with a LED light from Thorlabs (λ = 340 nm). Back conversion Of **AZO1**-*cis* state was archived by a LED light from Thorlabs with a wavelength of 455 nm.

For **AZO1** conversion tests, A UG11 band pass filter with a thickness of 1 mm from SCHOTT was used to filter out all light above 400 nm, meanwhile supposing a 100% transmission below 400 nm. (see Figure S1.1) Microfluidic chip was customized with a channel deep of 100 μm deep channels. The volumes is 33.9 mm^3. Absorption spectra for microfluidic chip test were recorded by two micro flow cells (calibrated path length 1: ~ 0.8 mm, calibrated path length 2: ~ 0.7 mm) and portable spectrometer from Avantes.

Teflon plastic tubing for $Cu(CH_3CN)_4PF_6$ catalytic demonstration was purchased from the Cole-Parmer Instrument Company.

Calculations for the catalytic mechanism of $Cu(CH_3CN)_4PF_6$ were performed using resources at Beronia Cluster, provided by Universidad de La Rioja (UR).

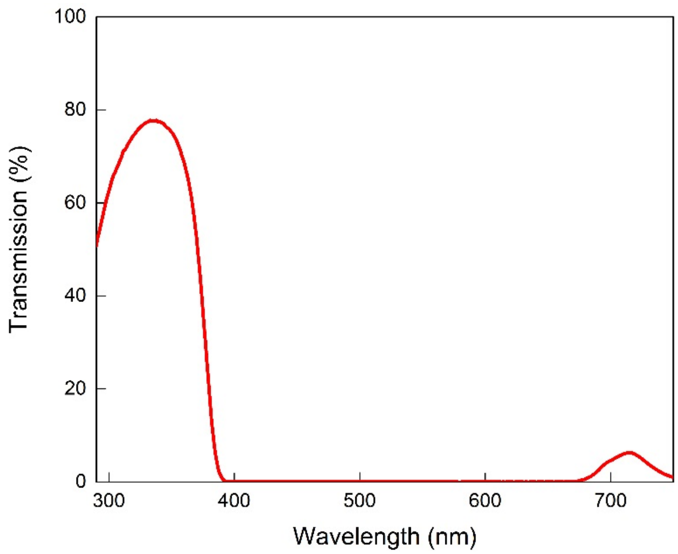
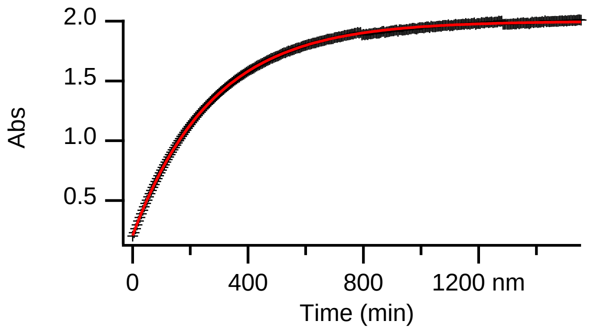
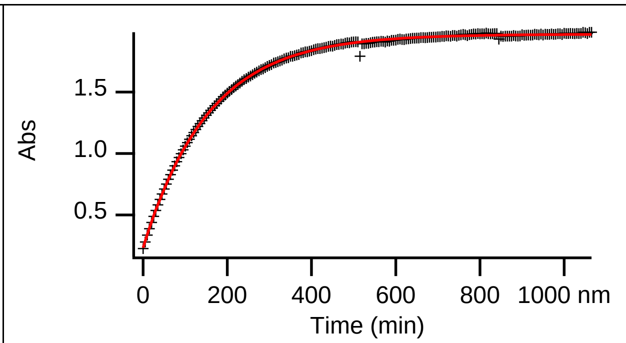


Figure S1.2. Transmission spectrum of UG11 band pass filter with a thickness of 1 mm from SCHOTT

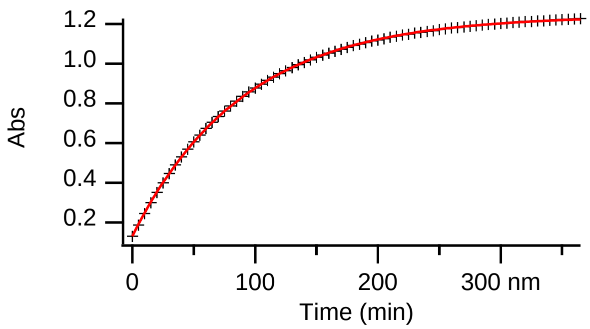
S2. Kinetic studies of **AZO1** in toluene



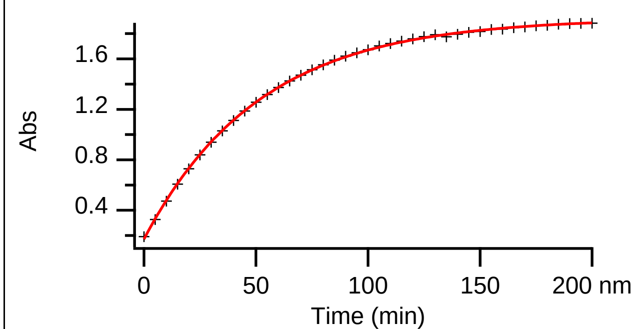
Increase of **AZO1**-*trans* at 45 °C



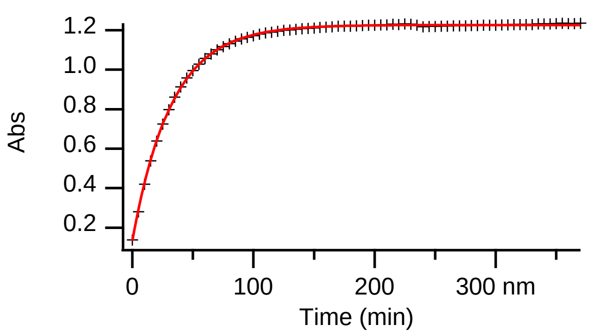
Increase of **AZO1**-*trans* at 50 °C



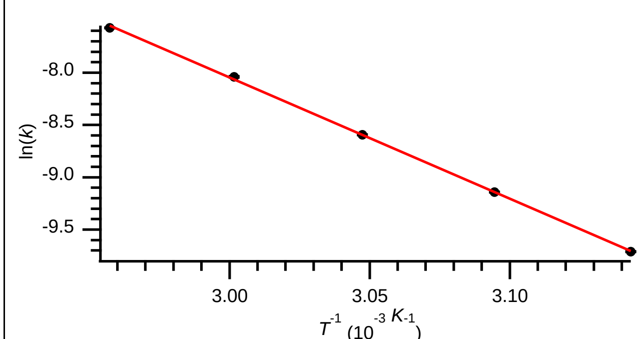
Increase of **AZO1**-*trans* at 55 °C

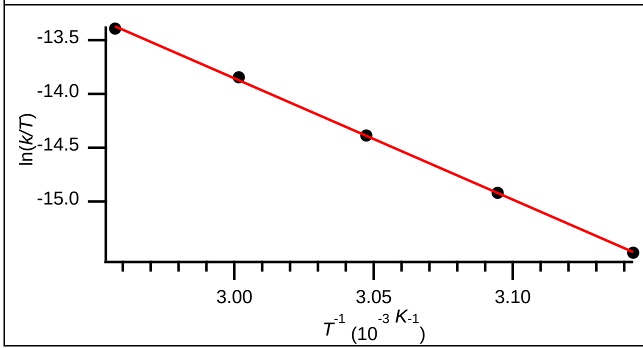


Increase of **AZO1**-*trans* at 60 °C



Increase of **AZO1**-*trans* at 65 °C





Above

Arrhenius plot giving the values

$t_{1/2\ @\ 298\ K\ in\ toluene}$ = 36.3 h

A = 4.11 x 10^{11} s^{-1} , Ea = 96414 J mol^{-1}

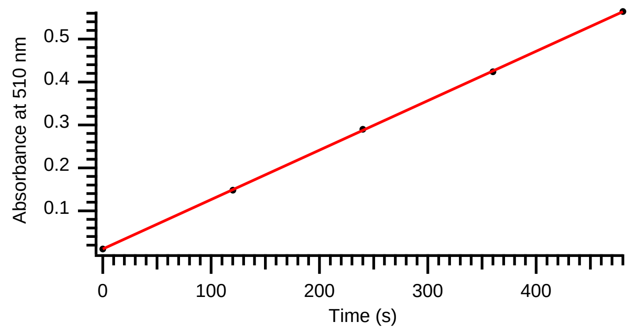
Left

Eyring plot giving the values

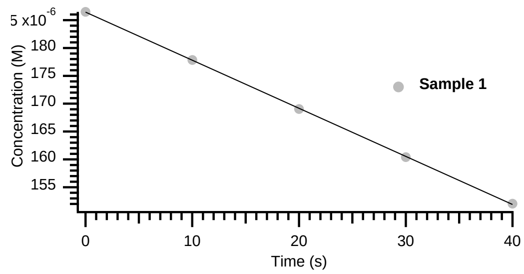
$\Delta H^{\ddagger}_{therm}$ = 93.7 kJ mol^{-1} $\Delta S^{\ddagger}_{therm}$ = -31.7 J mol^{-1} K^{-1}

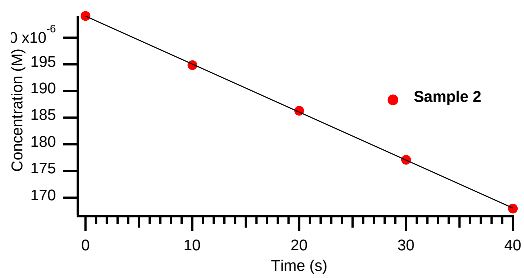
S3. Quantum yield for conversion & back conversion

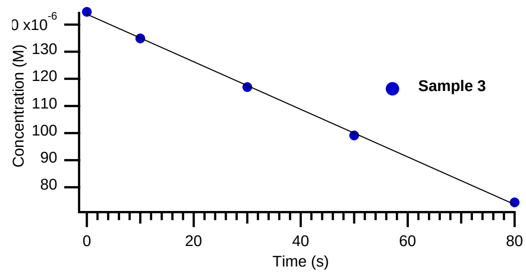
Quantum yield for conversion and back conversion were performed by using established method from literature.[2]

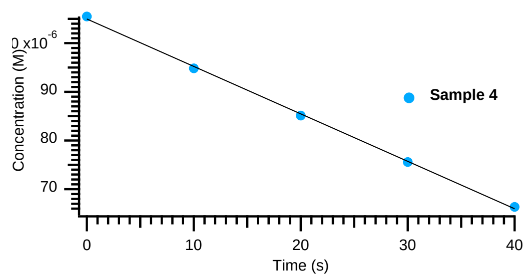
<table>
<tr><td colspan="3">Conversion from AZO1-trans to AZO1-cis.</td></tr>
<tr><td colspan="2">Photon flux @ 340 nm</td><td rowspan="8">
</td></tr>
<tr><td colspan="2">Quantum yield for the production of ferrous ions from ferrioxalate decomposition: 1.21</td></tr>
<tr><td>Irradiation time (s)</td><td>Tri-phenanthroline complex absorbance at 510 nm (ε = 11100 M^{-1} cm^{-1})</td></tr>
<tr><td>0</td><td>0.011</td></tr>
<tr><td>120</td><td>0.148</td></tr>
<tr><td>240</td><td>0.290</td></tr>
<tr><td>260</td><td>0.424</td></tr>
<tr><td>480</td><td>0.564</td></tr>
<tr><td colspan="2">Photon flux before experiment* (E s^{-1}):</td><td>1.29 10^{-8}</td></tr>
</table>

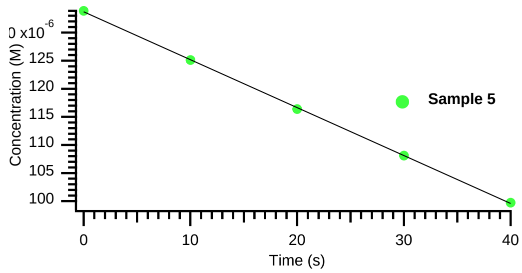
<table>
<tr><td colspan="2">Measured quantum yield (%)</td><td>Average quantum yield (%)</td></tr>
<tr><td>Sample 1</td><td>20.2</td><td rowspan="5">21</td></tr>
<tr><td>Sample 2</td><td>20.2</td></tr>
<tr><td>Sample 3</td><td>20.1</td></tr>
<tr><td>Sample 4</td><td>22.6</td></tr>
<tr><td>Sample 5</td><td>22.4</td></tr>
</table>

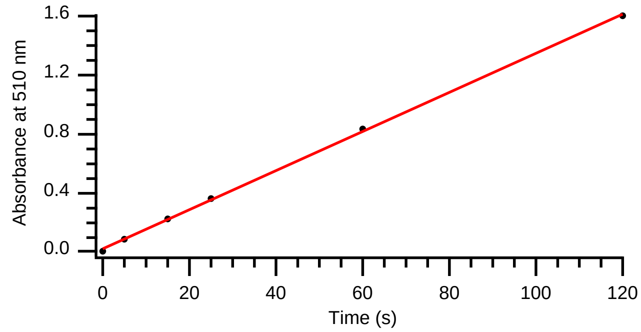
<table>
<tr><td colspan="2">Sample 1</td></tr>
<tr><td colspan="2">Sample weight (g): 2.62</td></tr>
<tr><td>Irradiation time (s)</td><td>AZO absorbance at 388 nm ($\varepsilon = 4138.2$ M^{-1} cm^{-1})</td></tr>
<tr><td>0
10
20
30
40</td><td>0.77
0.74
0.70
0.66
0.63</td></tr>
<tr><td>Quantum yield: 20.2%</td><td>
</td></tr>
</table>

<table>
<tr><td colspan="2">Sample 2</td></tr>
<tr><td colspan="2">Sample weight (g): 2.50</td></tr>
<tr><td>Irradiation time (s)</td><td>Absorbance at 380 nm ($\varepsilon = 9832.2$ M^{-1} cm^{-1})</td></tr>
<tr><td>0
10
20
30
40</td><td>2.00
1.92
1.83
1.74
1.65</td></tr>
<tr><td>Quantum yield: 20.2%</td><td>
</td></tr>
</table>

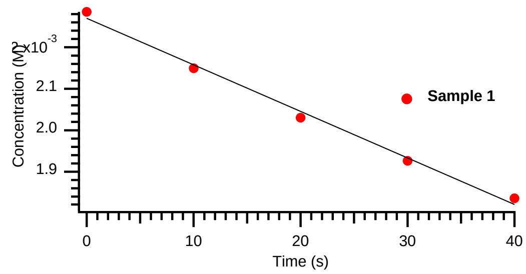
Sample 3	
Sample weight (g): 2.55	
Irradiation time (s)	**NBD1 absorbance at 380 nm (ε = 9832.2 M^{-1} cm^{-1})**
0 10 30 50 80	1.42 1.32 1.15 0.97 0.73
Quantum yield: 20.1%	

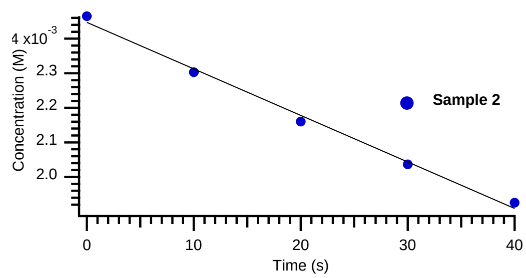
Sample 4	
Sample weight (g): 2.58	
Irradiation time (s)	**NBD1 absorbance at 380 nm (ε = 9832.2 M^{-1} cm^{-1})**
0 10 20 30 40	1.04 0.93 0.84 0.74 0.65
Quantum yield: 22.6%	

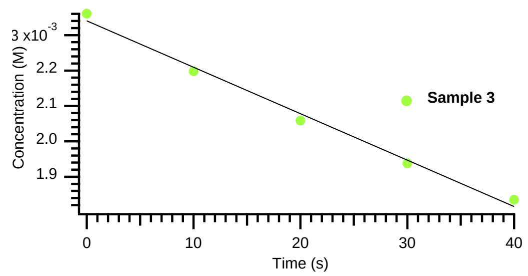
Sample 5	
Sample weight (g): 2.93	
Irradiation time (s)	**NBD1 absorbance at 383 nm (ε = 7369.2 M^{-1} cm^{-1})**
0	0.99
10	0.92
20	0.86
`	0.80
40	0.73
Quantum yield: 22.4%	

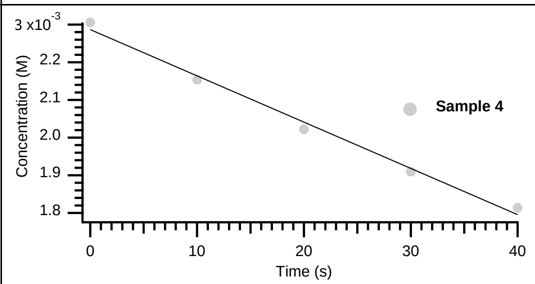
<table>
<tr><td colspan="3">Back conversion from AZO1-cis to AZO1-trans.</td></tr>
<tr><td colspan="2">Photon flux @ 455 nm</td><td rowspan="10">
</td></tr>
<tr><td colspan="2">Quantum yield for the production of ferrous ions from ferrioxalate decomposition: 1.11</td></tr>
<tr><td>Irradiation time (s)</td><td>Tri-phenanthroline complex absorbance at 510 nm (ε = 11100 M^{-1} cm^{-1})</td></tr>
<tr><td>0</td><td>0.008</td></tr>
<tr><td>5</td><td>0.089</td></tr>
<tr><td>15</td><td>0.227</td></tr>
<tr><td>25</td><td>0.364</td></tr>
<tr><td>60</td><td>0.835</td></tr>
<tr><td>120</td><td>1.602</td></tr>
<tr><td colspan="2">Photon flux before experiment* (E s^{-1}):</td></tr>
<tr><td colspan="2"></td><td>1.61 10^{-7}</td></tr>
</table>

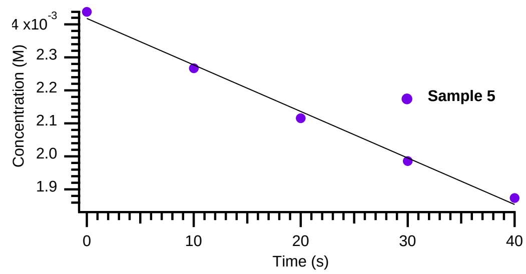
<table>
<tr><td colspan="2">Measured quantum yield (%)</td><td>Average quantum yield (%)</td></tr>
<tr><td>Sample 1</td><td>22.2</td><td rowspan="5">23</td></tr>
<tr><td>Sample 2</td><td>25.1</td></tr>
<tr><td>Sample 3</td><td>22.6</td></tr>
<tr><td>Sample 4</td><td>21.8</td></tr>
<tr><td>Sample 5</td><td>23.8</td></tr>
</table>

Sample 1	
Sample weight (g): 2.77	
Irradiation time (s)	**AZO absorbance at 510 nm ($\varepsilon = 406.2\ M^{-1}\ cm^{-1}$)**
0 10 20 30 40	0.83 0.87 0.82 0.78 0.75
Quantum yield: 22.2%	

Sample 2	
Sample weight (g): 2.61	
Irradiation time (s)	**Absorbance at 510 nm ($\varepsilon = 406.2\ M^{-1}\ cm^{-1}$)**
0 10 20 30 40	1.00 0.94 0.88 0.83 0.78
Quantum yield: 25.1%	

Sample 3	
Sample weight (g): 2.40	
Irradiation time (s)	**Absorbance at 510 nm (ε = 406.2 M^{-1} cm^{-1})**
0	0.96
10	0.89
20	0.84
30	0.79
40	0.75
Quantum yield: 22.6%	

Sample 4	
Sample weight (g): 2.48	
Irradiation time (s)	**Absorbance at 510 nm (ε = 406.2 M^{-1} cm^{-1})**
0	0.94
10	0.87
20	0.82
30	0.78
40	0.74
Quantum yield: 21.8%	

Sample 5	
Sample weight (g): 2.36	
Irradiation time (s)	**NBD1 absorbance at 383 nm (ε = 7369.2 M^{-1} cm^{-1})**
0	0.99
10	0.92
20	0.86
30	0.80
40	0.76
Quantum yield: 23.8%	

S4. Determination of conversion percentage

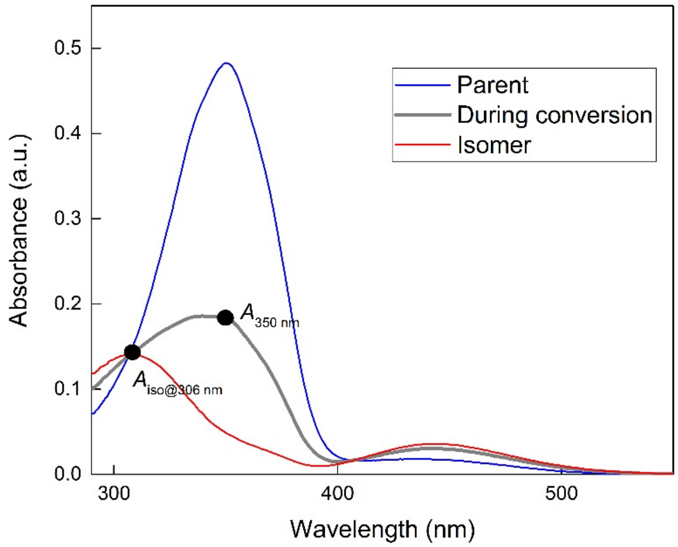


Figure S4.1. **AZO1** spectrum changes over conversion process. Blue curve shows the pure *trans* state, red curve shows the converted *cis* form. Grey curve represents a spectra taken during conversion. $A_{350\ nm}$ is the absorbance at 350 nm during conversion. $A_{iso@306nm}$ corresponds to the absorbance at the isosbestic point at 306 nm.

In the following equations, $\varepsilon_{parent@350\ nm}$ and $\varepsilon_{isomer@350\ nm}$ correspond to the absorptivity of the parent and isomer molecule in toluene respectively. $\varepsilon_{iso@306\ nm}$ is the absorptivity at the isosbestic point in toluene.

$$A = \varepsilon c l \tag{1}$$

At isosbestic point:

$$A_{iso@306\ nm} = c_{parent}\varepsilon_{iso@306\ nm}l + c_{isomer}\varepsilon_{iso@306\ nm}l \tag{2}$$

Thus gave:

$$c_{parent} = \frac{A_{iso@306\ nm}}{\varepsilon_{iso@306\ nm}l} - c_{isomer} \tag{3}$$

At 350 nm:

$$\varepsilon_{parent@350\ nm}c_{parent}l + \varepsilon_{isomer@350\ nm}c_{isomer}l = A_{@350nm} \quad (4)$$

Replace c_{parent} with (3):

$$c_{isomer} = \frac{A_{@350\ nm}\varepsilon_{iso} - A_{iso@306\ nm}\varepsilon_{isomer@350\ nm}}{(\varepsilon_{parent@350\ nm} - \varepsilon_{isomer@350\ nm})\varepsilon_{iso@306\ nm}l} \quad (5)$$

The concentration of the solution can also be calculated using the absorptivity at the isosbestic point:

$$c_{tot} = \frac{A_{iso@306\ nm}}{\varepsilon_{iso@306\ nm}l} \quad (6)$$

Thus leading to the conversion percentage defined as:

$$\text{Conversion }\% = \frac{c_{isomer}}{c_{tot}}\ 100\% = \frac{\frac{A_{@350\ nm}}{A_{iso@306\ nm}} \cdot \varepsilon_{iso@306\ nm} - \varepsilon_{isomer@350nm}}{\varepsilon_{parent@350\ nm} - \varepsilon_{isomer@350\ nm}} \quad (7)$$

S5. Maximum energy storage efficiency

To calculate the maximum energy storage efficiency for **AZO1** with the solar spectrum AM1.5, equation (1) can be addressed:

$$\eta_{\mathrm{MOST}} = \frac{\int_0^{\lambda_{\mathrm{onset}}} \frac{E_{\mathrm{AM\ 1.5}}(\lambda) \cdot \phi_{\mathrm{iso}} \cdot \Delta H_{storage}}{h\nu \cdot N_{\mathrm{A}}} \cdot d\lambda}{\int E_{\mathrm{AM\ 1.5}}(\lambda) \cdot d\lambda} \cdot 100\ \% \tag{1}$$

Where $E_{\mathrm{AM\ 1.5}}(\lambda)$ is the spectral irradiance (energy current density) in J s^{-1} m^{-2} nm^{-1}; h represents the Plank constant in J s; v corresponds to the frequency of incoming light in s^{-1}; and N_{A} is Avogadro's constant.

Assuming the volumetric mass density of **AZO1** is the same as unsubstituted azobenzene (1090 g L^{-1}), with an ideal filter, which can cut off all incoming light above 400 nm to avoid photo back conversion from *cis* to *trans*, a maximum energy storage efficiency of 2.6% was calculated for an optically saturated solution of **AZO1**.

In presence of a filter with different concentrations, equation is written as equation (2):

$$\eta_{\mathrm{MOST}} = \frac{\int_0^{\lambda_{\mathrm{onset}}} \frac{E_{\mathrm{AM\ 1.5}}(\lambda) \cdot Tran_{filter}(\lambda) \cdot (1-\mathrm{T}) \cdot \phi_{\mathrm{iso}} \cdot \Delta H_{storage}}{h\nu \cdot N_{\mathrm{A}}} \cdot d\lambda}{\int E_{\mathrm{AM\ 1.5}}(\lambda) \cdot Tran_{filter}(\lambda) \cdot d\lambda} \cdot 100\ \% \tag{2}$$

Where T is the concentration dependent transmittance in a specific device with a certain optical pathlength. $Tran_{filter}(\lambda)$ is the transmittance of band pass filter used. A maximum energy storage efficiency of 0.88% was calculated for an optically saturated solution of **AZO1** with the presence of a band pass filter (SCHOTT-UG11).

S6. Microfluidic Chip conversion experiment

Two concentrations of **AZO** with 2 x 10^{-4} M and 5 x 10^{-4} M in toluene solutions were prepared and stored in dark for microfluidic chip experiments. The solutions were then pumped individually thought the microfluidic chip with different residence time varies from 8 min to 339 min. All measurements were repeated three times.

The actual energy storage efficiency is calculated as equation (3):

$$\eta_{\mathrm{MOST}} = \frac{\dot{n}_{\mathbf{AZO1\_trans}} \cdot Conversion\,\% \cdot \Delta H_{storage}}{A \cdot \int E_{\mathrm{AM\ 1.5}}(\lambda) \cdot Tran_{filter}(\lambda) \cdot d\lambda} \tag{3}$$

Where $\dot{n}_{\mathbf{AZO1\_trans}}$ is flow speed of **AZO1-*trans***, $\Delta H_{storage}$ is energy storage density of **AZO1** in kJ mol^{-1}.

The corresponding conversion percentage and energy storage efficiency can be found below.

Concentration: 2 x 10^{-4} M			
Flow speed (μL min^{-1})	**Residence time (s)**	**Conversion (%)**	**Energy storage efficiency (%)**
12	170	80	4.9E-4
40	51	77	0.0016
50	41	75	0.0019
100	20	59	0.0030
150	14	48	0.0037
200	10	43	0.0044
250	8	40	0.0051

Concentration: 5 x 10^{-4} M			
Flow speed (mL h^{-1})	**Residence time (s)**	**Conversion (%)**	**Energy storage efficiency (%)**
6	339	70	5.3E-4
12	170	78	0.0012
40	51	74	0.0038
50	41	69	0.0044
100	20	48	0.0062
150	14	37	0.0071
200	10	30	0.0078
250	8	27	0.0086

S7. Reaction rate determination by UV-Vis for different catalytic back conversion

1. Theoretical heat release simulation in function of concentration of **AZO1**

For neat sample, a maximum heat release of 226°C can be obtained after simplification of equation (2) in main text:

$$\Delta T = \frac{\Delta H_{storage}}{C_{p\_\mathbf{AZO1}}} \quad (1)$$

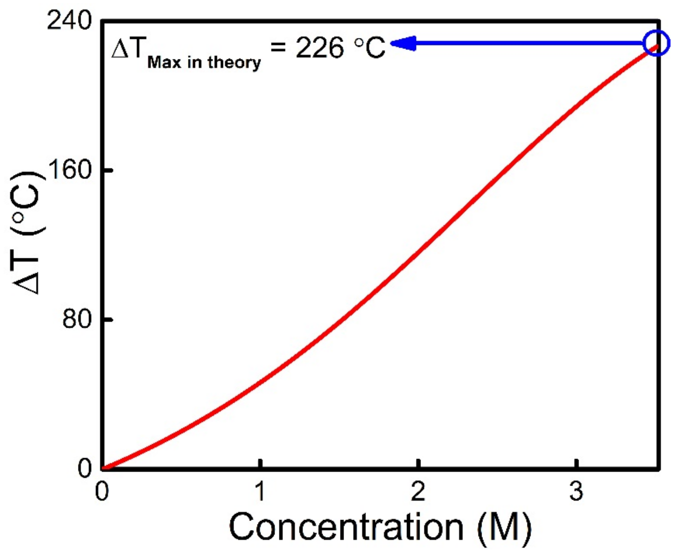


Figure S7.1. Theoretical heat release simulation in function of concentration of **AZO1**, a maximum ΔT of 226 °C can be achieved with neat **AZO1**-*cis* sample.

2. CoPc@C

The procedure to make CoPc@C was followed from previous work[3], and XPS shows a CoPc loading Wt% equals to 13% on activated carbon. 3 mL, ca. 10^{-5} M **AZO**-cis toluene was initially prepared with a 340 nm LED lamp. 0.28 mg of CoPc@C was then added to the solution to start the catalytic back conversion record. The curve was registered at 350 nm.

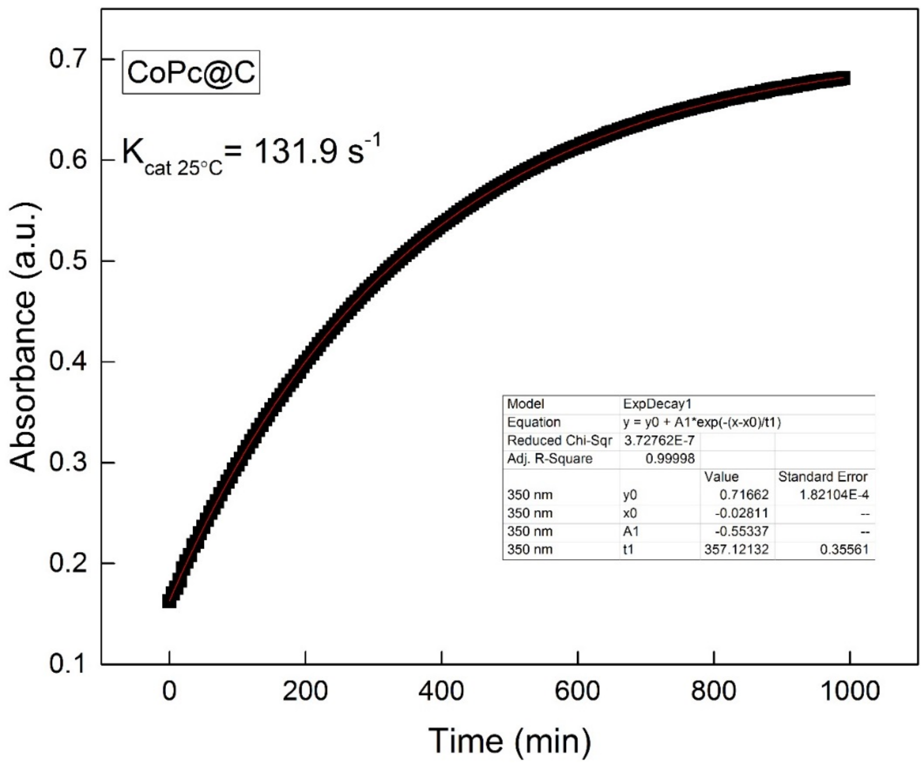


Figure S7.2. Catalytic back conversion of **AZO**-*cis* in toluene solution with CoPc@C.

3. $[Cu(CH_3CN)_4]PF_6$

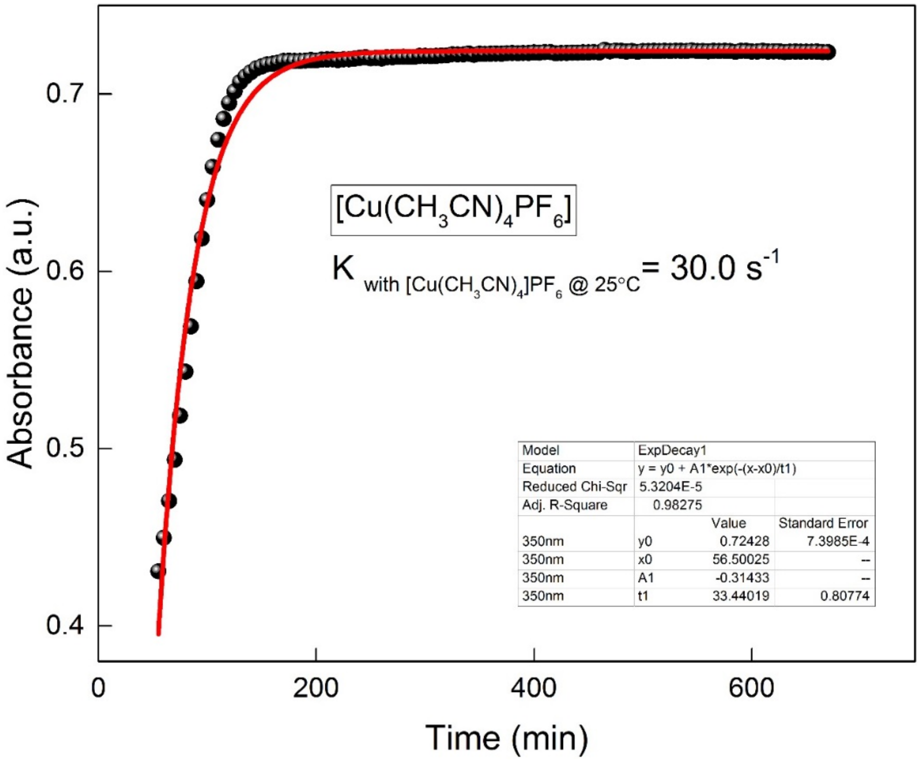


Figure S7.3. Catalytic back conversion of **AZO**-*cis* in toluene solution with $[Cu(CH_3CN)_4]PF_6$.

3 mL, ca. 10^{-5} M **AZO**-cis toluene was initially prepared with a 340 nm LED lamp. 1.13 mg of CoPc@C was then added to the solution to start the catalytic back conversion record. The curve was registered at 350 nm.

The kinetic back conversion can be explained by a pseudo-first order kinetic model. The obtained catalytic back conversion curve at a certain wavelength can be fit by $y(t) = y_0 + A_1 e^{-k\, c_{cata}\, (t-t_0)}$. As k represents the reaction constant, c_{cata} corresponds to the concentration of the catalyst. Here, one assumption was that the suspension of the insoluble catalyst was homogeneously distributed in solution. t is the variable of time in s. Finally, y_0, A_1 are unitless parameters from the fit.

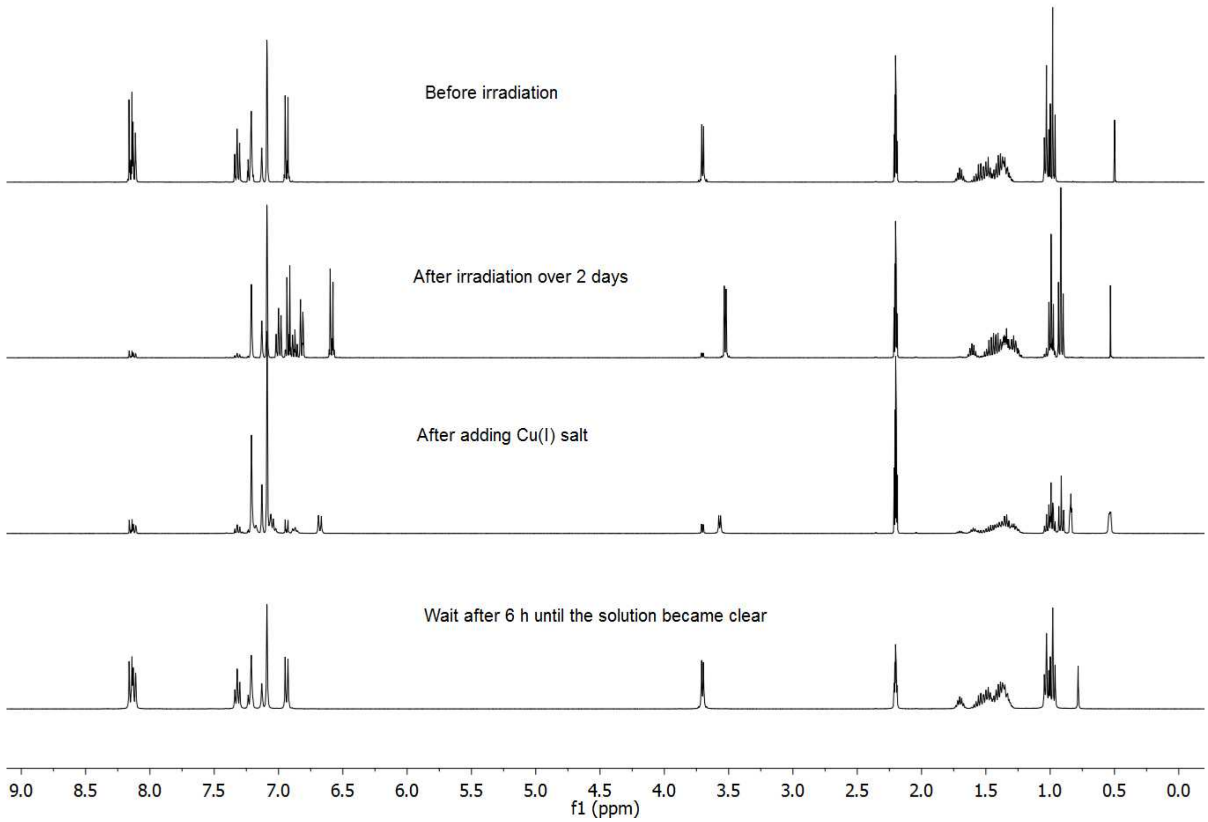


Figure S7.4. ^{1}H NMR studies of **AZO**-*cis* in toluene-d8 solution with $[Cu(CH_3CN)_4]PF_6$.

S8. Computational calculations of catalyst working mechanism

The reaction mechanism involved in the catalytic back reversion of **AZO1** was studied by theoretical methods. All calculations were carried out using the **B3LYP-D3BJ**[4] functional included in the **Gaussian16**[5] program package. We used the standard basis set **6-31G(d)**[6] for C, N, H and O atoms and the **SDD**[7] effective core potential for Cu. All critical points in the PES were characterized with frequency calculations to include ZPE and free energy corrections and verify the stationary points as transition states (one imaginary frequency) or minima (zero imaginary frequencies). Minimum energy crossing points (MECP) were computed using the **easymecp** software,[8] which is a simplified Python wrapper around the original MECP Fortran code from J. Harvey (2003) developed by J. Rodríguez-Guerra and I. Funes-Ardóiz. All geometry optimizations were computed in solution with implicit solvent applying the PCM solvation model[9] with toluene as solvent (ε=2.3741). We also checked the transition states by relaxing them towards reactants and products or with IRC calculations. Relaxed scan was done in triplet and singlet states along the CNNC dihedral from *cis* to *trans* isomer. TD-DFT spectra were calculated using CAM-B3LYP[10]/6-31G(d) +SDD(Cu) considering 10 singlets and 10 triplets. Gaussum[11] was used to calculate contribution percentage of the different fragments to molecular orbitals and contributions to different transitions from orbitals involved.

First, the isomerization of ***free*-AZO** was evaluated. The reaction profile is described in Figure S7.1. The energy barrier for the back-conversion was found to be of 25.4 kcal mol^{-1}.

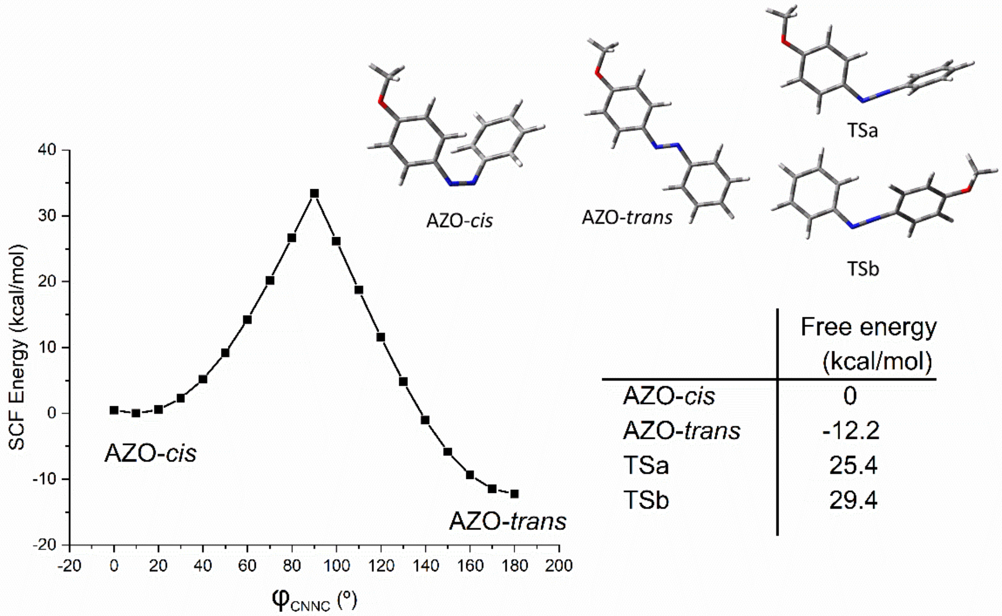


Figure S7.1. Scan along the CNNC dihedral torsion. Free energies for ***free*-AZO** critical points.

Two different isomerization mechanisms were considered, namely the inversion and rotation mechanisms separately. As described, [12] the hypothetical TS_{rot} could not be found at relevant energies. Instead, two different inversion transition structures **TSa** and **TSb** could be located.

Then, we moved to explore the different types of coordination between the **AZO** and **$Cu(CH_3CN)_n^+$** moieties. The different types of coordination considered are shown below. Additionally, a π coordination of the azobenzene to the copper atom was explored. In all cases, this structure collapses to either **1a** or **1b**. Also, alternative mechanisms such as cyclometallation,[12] loss of two CH_3CN molecules and electron transfer mechanisms were computed. In all cases, these pathways feature more energetic species that allowed to rule out different reaction mechanisms. After this preliminary evaluation, a complete mechanist evaluation was performed using the relevant options shown in Figure S7.2.

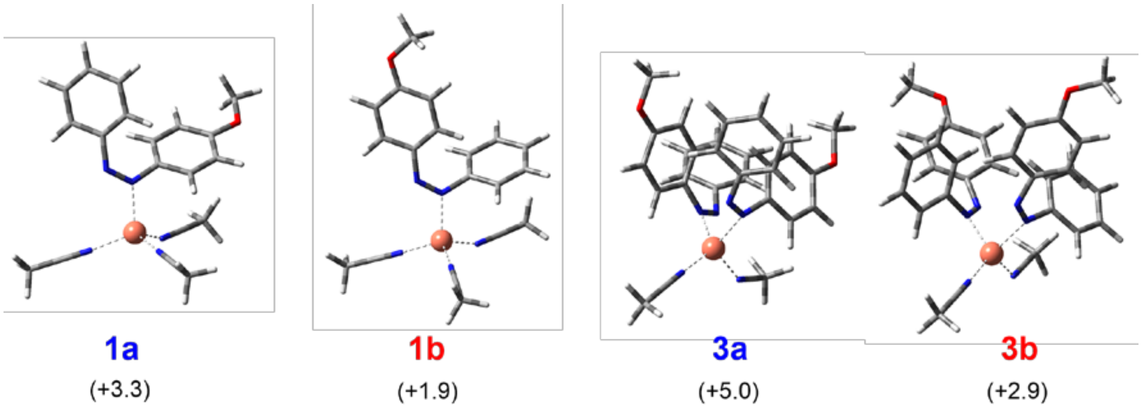


Figure S7.2. Different coordination types and relative energies in kcal mol^{-1}. Cu ion is the central particle in figure.

All four different coordination models were considered to explore the back-reaction mechanism. However, it was impossible to reach a converged structure in **3a**-**3b** due to methyl rotation in acetonitrile molecules. Thus, only one AZO molecule could be bonded to the metal center (see Table S7.1). For the described convergence problems, we only computed the **1** series.

	Free energy (kcal/mol)
TS1a	+29.1
TS1b	+30.4
TS3b	Not converged
TS3a	Not converged

Table S7.1. Free energies of computed transition states.

To ensure the right nature of the TS for the **1** series (**TS1a-TS1b**), the IRC in both directions was computed to yield the corresponding *cis* and *trans* isomers **1a,b** and **2a,b**, respectively.

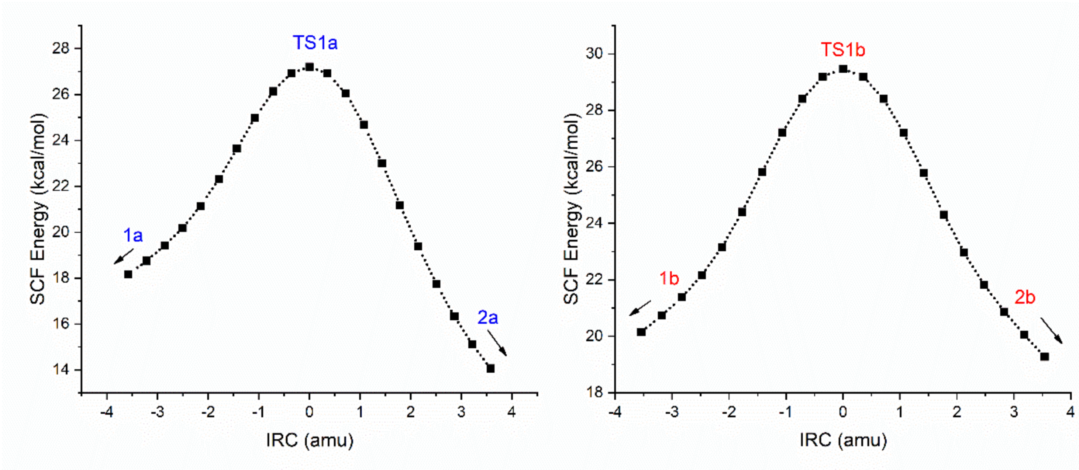


Figure S7.3. IRC from **TS1a** (left) and **TS1b** (right) connecting reactants and products.

As it was discussed in some previous work[13], the minimum in the T_1 PES is found at the twisted geometry, well below the S_0 energy. The S_0 and T_1 PESs cross along the torsion of the central N=N bond, but not along the inversion coordinate. Therefore, the decay of T_1 is observed to occur via the torsion mechanism. The rate of the reaction then depends on the energy barrier connecting the S_0 minimum and the MECP to the T_1 state and the relevant SO (spin-orbit) couplings.[8] The computed MECPs for ***free*-AZO** is located at 16.1 kcal mol^{-1} above the AZO *cis* isomer. This energy barrier may be compared with the experimental data (23.5 kcal mol^{-1} from the Arrhenius equation, 24.7 kcal mol^{-1} from Eyring equation, see Figure 1. c). However, in this case the SO coupling will be low enough to avoid triplet state population in the *cis-trans* isomerization of AZO without metal complex. For the Cu mediated back-conversion, a computed barrier of 19.4 kcal mol^{-1} was found. This is consistent with the experimental barrier of 15.5 kcal mol^{-1}, calculated from the kinetic constant measured of 30 s^{-1}.

To further explore the minimum nature of the triplet state, a series of TD-DFT calculations considering singlets and triplets were performed. The lowest excited triplet state corresponds to a HOMO-LUMO transition (see Table S7.2), which has a MLCT nature (*ca.* 30% of contribution from copper to HOMO (see Table S7.3). The same behavior is observed in S_1. Thus, the metal center plays a major role in the excited state (singlet or triplet) population.

λ (nm)	f	Nature	Transition	Minor transitions
743.488804	0	Triplet	HOMO->LUMO (73%)	H-9->LUMO (9%), H-4->LUMO (7%), H-1->LUMO (2%)
478.518692	0.0506	Singlet	H-1->LUMO (13%), HOMO->LUMO (73%)	H-9->LUMO (7%), H-4->LUMO (2%)
456.176434	0	Triplet	H-9->LUMO (13%), H-1->LUMO (53%)	H-10->LUMO (3%), H-2->LUMO (6%), HOMO->LUMO (4%)

Table S7.2. TDDFT transitions data from **1a**.

As comparison to experimental data, the calculated and experimental UV-Vis spectra are shown below together with the spectrum recorded when adding the salt to the sample. Calculated spectrum is clearly red shifted *ca.* 30 nm. Also, it should be noted that the experimental uses **AZO1** instead of the simplified AZO model.

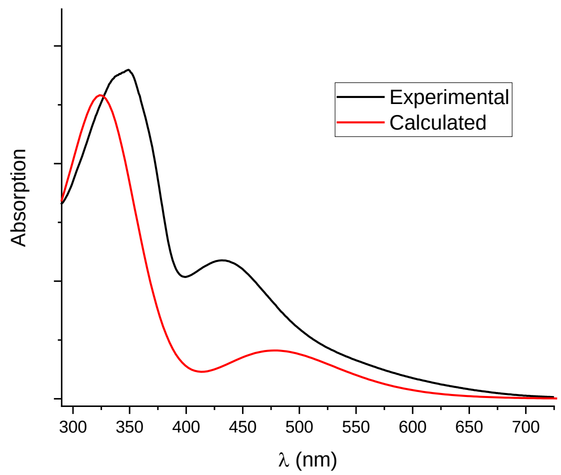


Figure S7.4. UV-Vis spectra of **1a** calculated (AZO) and experimental of **AZO1**.

	Cu	**CH_3CN**	**AZO**
LUMO	3%	0%	97%
HOMO	31%	3%	66%
H-1	50%	6%	45%

Table S7.3. Contribution of each fragment to orbital nature in **1a**.

The nature of the spin density and the SOMO orbitals are shown in Figure S4. Spin density in **MECP1a** is distributed totally in the Cu center and the AZO moiety, while the acetonitrile ligands do not have any contribution. The contribution analysis for each fragment in both states (singlet and triplet) is shown in Figure S7.5 and Table S7.4.

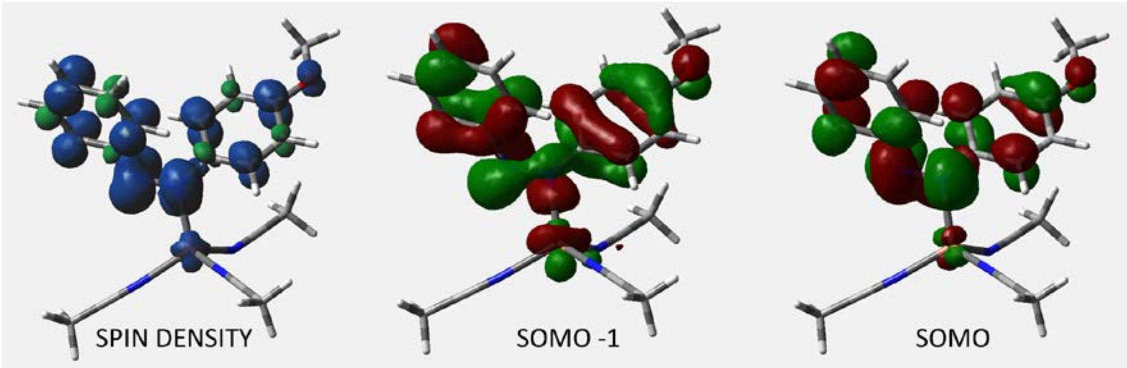


Figure S7.5. Spin density and SOMO-SOMO-1 orbitals in **MECP1a**

	Cu	**CH_3CN**	**AZO**
LUMO (Singlet)	4%	0%	95%
HOMO (Singlet)	12%	2%	86%
SOMO (Triplet)	5%	1%	95%
SOMO -1 (Triplet)	13%	2%	86%

Table S7.4. Contribution of each fragment to orbital nature in **MECP1a**.

SCF unit: Hartree

$Cu(CH_3CN)_4^+$:

SCF : -728.3473051

Cu	-0.49518000	-0.31029800	-0.00045300
N	0.18068800	0.64584600	-1.65575900
C	0.56222800	1.18549300	-2.58998700
N	0.18118500	0.64567000	1.65490400
C	0.56291600	1.18519000	2.58912800

N	-2.52263500	-0.31046300	0.00023900
C	-3.66700400	-0.31048600	0.00065400
N	0.18083000	-2.22184300	-0.00054200
C	0.56220300	-3.30079000	-0.00060000
C	1.04714100	1.86983200	-3.77410400
H	2.13734100	1.87423400	-3.77926400
H	0.68879500	1.36082400	-4.66913400
H	0.68678200	2.89875100	-3.78115800
C	-5.11807900	-0.31043700	0.00106400
H	-5.48842300	-0.82426900	0.88841900
H	-5.48862900	0.71487800	0.00256400
H	-5.48894800	-0.82187300	-0.88745900
C	1.04690400	1.86900800	3.77392700
H	0.68724900	1.36005900	4.66846600
H	2.13710000	1.87274800	3.78030200
H	0.68717000	2.89814700	3.78076200
C	1.04494200	-4.66920500	-0.00049800
H	2.13513000	-4.67757500	-0.00110800
H	0.68527700	-5.18899900	0.88778000
H	0.68428600	-5.18946900	-0.88810000

AZO-*cis*:

SCF: -687.3240708

N	-0.86375900	1.01821600	-1.07676200

C	-0.88046800	0.22307800	-2.27014500
C	-1.27072400	-1.11468000	-2.14708400
C	-1.39933900	-1.90755500	-3.28642700
C	-1.19190500	-1.35611200	-4.55255300
C	-0.85125300	-0.00576000	-4.67401900
C	-0.68731700	0.78495900	-3.54011100
H	-1.45604000	-1.51983600	-1.15699100
H	-1.67856800	-2.95238400	-3.18559400
H	-1.30973300	-1.96984900	-5.44061800
H	-0.70847300	0.43300300	-5.65744200
H	-0.41486600	1.83101000	-3.63016800
N	0.08150700	1.78462500	-0.77768900
C	1.32935600	1.81036000	-1.47376300
C	2.02755200	0.67092500	-1.89336700
C	3.29794900	0.78519300	-2.45110200
C	3.87731000	2.05169700	-2.61688100
C	3.18930400	3.19442100	-2.17851400
C	1.94377600	3.06771400	-1.58550200
H	1.58875000	-0.31217100	-1.77161200
H	3.82426400	-0.11196000	-2.75305400
H	3.66283100	4.16353600	-2.29523100
H	1.41641400	3.94034100	-1.21304000
O	5.09889900	2.27255600	-3.17039500
C	5.84210100	1.14843000	-3.62729600

H	6.77062300	1.55072100	-4.03395100
H	6.07147500	0.46056500	-2.80432900
H	5.30221000	0.60715900	-4.41384800

AZO-*trans*:

SCF: -687.3435354

N	-0.77953800	0.64697800	0.02023300
C	-0.80349000	-0.18586600	-1.12653500
C	-1.96560800	-0.95328600	-1.29015100
C	-2.09505900	-1.80802300	-2.38583700
C	-1.06323100	-1.89966500	-3.32355200
C	0.09955600	-1.13259400	-3.16067300
C	0.23544600	-0.27839200	-2.07057500
H	-2.75404100	-0.86517500	-0.54841300
H	-2.99785500	-2.40006200	-2.50718100
H	-1.16034600	-2.56380200	-4.17799100
H	0.90138300	-1.20491800	-3.89078100
H	1.12950200	0.31936200	-1.93419800
N	0.26879900	1.33240300	0.16240000
C	0.30371400	2.16522600	1.29940100
C	-0.72633000	2.27653000	2.24799500
C	-0.59332800	3.12937800	3.33855300
C	0.58178700	3.88754400	3.49488200
C	1.61507900	3.78143800	2.54985000

C	1.47297300	2.92836400	1.46538600
H	-1.62860600	1.68899200	2.12034800
H	-1.40027200	3.20042700	4.05836100
H	2.51345000	4.37461400	2.68773500
H	2.26303200	2.83536000	0.72617000
O	0.80501700	4.74625900	4.52515500
C	-0.20547200	4.89809200	5.52104200
H	0.18939000	5.62438200	6.23195700
H	-1.13533300	5.27933200	5.08278500
H	-0.39837500	3.94810800	6.03338000

TSa:

SCF: -687.280496

Freq: *i*416.8413

N	-0.06399000	1.49839300	-1.06381700
C	-0.47434900	0.27651700	-1.39070000
C	-1.84344000	0.02702700	-1.68469900
C	-2.24903400	-1.25617100	-2.02807000
C	-1.34592000	-2.32147800	-2.09076600
C	-0.00143500	-2.07151000	-1.80041400
C	0.44864100	-0.80379400	-1.45497600
H	-2.55144300	0.84733200	-1.63921100
H	-3.30032400	-1.42193500	-2.25094000
H	-1.68012900	-3.31790400	-2.36007500

H	0.72286200	-2.88138400	-1.84354300
H	1.49414000	-0.61903700	-1.23367300
N	0.32488600	2.63066500	-0.78836700
C	0.30542500	3.00615900	0.59871400
C	-0.12483700	2.17136100	1.63544100
C	-0.10883600	2.62304700	2.94846700
C	0.34273000	3.92587600	3.23024000
C	0.77529300	4.76271100	2.18750400
C	0.75515600	4.30231300	0.88147900
H	-0.47136000	1.16878300	1.40419000
H	-0.44440700	1.96813300	3.74311300
H	1.11855800	5.76203200	2.43255900
H	1.08369700	4.92986600	0.05889700
O	0.39653100	4.46124800	4.47322600
C	-0.03075100	3.66551700	5.57571800
H	0.09552900	4.29215500	6.45892100
H	-1.08490100	3.38180300	5.47504300
H	0.58395400	2.76328000	5.67548500

TSb:

SCF: -687.274875544

Freq: *i*455.3628

N	0.27618300	1.38726400	-0.99287000
C	-0.25470500	0.22327300	-1.36738300

C	-1.64883300	-0.01702200	-1.25467100
C	-2.21005600	-1.20144900	-1.72232300
C	-1.38858100	-2.22673900	-2.20787400
C	0.00047600	-2.02410100	-2.27293300
C	0.55818300	-0.81186000	-1.91313800
H	-2.28274400	0.76074900	-0.84199400
H	-3.28473500	-1.32875400	-1.66459000
H	0.62267600	-2.82783100	-2.65425500
H	1.62556000	-0.64336100	-2.00627200
N	0.77481500	2.47569000	-0.67735000
C	0.45970200	2.95752800	0.65137600
C	-0.34802700	2.27025600	1.56633000
C	-0.57211900	2.81728200	2.82508900
C	0.00603300	4.04455900	3.17354500
C	0.81241100	4.72494600	2.25897900
C	1.04181100	4.17948600	0.99655500
H	-0.78572500	1.31917700	1.27967100
H	-1.19809700	2.29126500	3.54040700
H	1.26075900	5.67638700	2.52949600
H	1.66648900	4.68052100	0.26319100
O	-1.83316400	-3.44380000	-2.63925700
C	-3.22981900	-3.69422000	-2.58900300
H	-3.36826400	-4.70418400	-2.97760100
H	-3.60957600	-3.64457400	-1.56039800

H	-3.78711700	-2.98400500	-3.21343300
H	-0.17379100	4.46669300	4.15801700

1a:

SCF: -1282.909485

Cu	-0.67042700	-0.59832700	0.07320700
N	-0.11714400	0.72863600	1.53270900
C	0.15008400	1.76142800	1.98299100
N	-2.64088300	-0.90809300	0.16252400
C	-3.77989400	-1.11035800	0.18555700
N	0.37997100	-2.29782400	0.12969400
C	0.99783400	-3.27358300	0.06815100
C	-5.21264300	-1.36942300	0.21479600
H	-5.44230800	-2.09554900	1.00027900
H	-5.75614200	-0.44150400	0.41606400
H	-5.53661100	-1.77237800	-0.74935200
C	0.47167100	3.07699800	2.51536900
H	0.03030600	3.20119400	3.50844600
H	1.55641500	3.19746300	2.58800800
H	0.06928200	3.84089300	1.84205700
C	1.77513500	-4.50232700	-0.01306800
H	2.82998900	-4.28927700	0.18351900
H	1.41286900	-5.22317000	0.72587200
H	1.67866300	-4.93634500	-1.01280300

N	-0.11843200	0.46784300	-1.61496400
N	0.31802300	-0.16997100	-2.60706800
C	-0.11407100	1.89939700	-1.51669300
C	0.66455500	0.45526400	-3.83712100
C	1.03217300	2.65362200	-1.78334800
C	-1.24617300	2.52063800	-0.97224700
C	1.78548200	-0.06817100	-4.49457000
C	-0.13376400	1.42655900	-4.46408100
C	1.04477700	4.02408300	-1.53729700
H	1.92225600	2.17105800	-2.17097300
C	-1.25183500	3.88975500	-0.75580800
H	-2.11946500	1.92145800	-0.73585900
C	2.15459900	0.43240900	-5.74119900
H	2.35984500	-0.85131300	-4.00995400
C	0.21988700	1.88769200	-5.72772800
H	-1.02457100	1.80103300	-3.97363900
C	-0.10446300	4.65426600	-1.03413000
H	1.94694900	4.58787400	-1.73889000
H	-2.12882700	4.39323900	-0.36314200
C	1.37161400	1.40846800	-6.36134900
H	3.03905400	0.04522100	-6.23740200
H	-0.40417200	2.62656500	-6.22094600
O	-0.20059100	5.97807600	-0.76611600
H	1.64585600	1.78338000	-7.34247600

C	0.91636500	6.81369100	-1.06230400
H	0.60810600	7.82470600	-0.79616300
H	1.79348500	6.52953500	-0.46888900
H	1.16635100	6.77458400	-2.12869300

1b:

SCF: -1282.911119

Cu	-0.74638100	0.52491200	0.26826900
N	0.22746200	0.98818800	1.94983000
C	0.77869100	1.28500900	2.92278700
N	-2.73558300	0.57707000	0.51630800
C	-3.88529900	0.64405700	0.62351200
N	-0.15657000	-1.30887900	-0.43135800
C	0.36662000	-2.05000000	-1.15108200
C	-5.33306800	0.72409600	0.75913400
H	-5.64170700	0.28926200	1.71439200
H	-5.65321600	1.76949500	0.72285300
H	-5.81397800	0.17399600	-0.05508100
C	1.46834300	1.65831000	4.14992000
H	0.81843300	1.47619900	5.01096100
H	2.38083400	1.06480400	4.25982500
H	1.73269500	2.71953900	4.12062500
C	1.03651900	-2.95695200	-2.07102700
H	1.80587900	-3.52703600	-1.54185600

H	0.31344400	-3.65186300	-2.50779800
H	1.50655200	-2.37246000	-2.86812400
N	-0.82453900	2.82455700	-1.46742600
N	-0.21301600	1.73234600	-1.31164200
C	-0.53058700	3.77892700	-2.45883700
C	0.75040200	1.21356400	-2.24598500
C	0.71977200	4.02965300	-3.05776200
C	-1.60975000	4.63784800	-2.75650100
C	2.02580600	0.87958300	-1.78443300
C	0.35878400	0.90144700	-3.55236900
C	0.87452900	5.08295300	-3.94838000
H	1.58410300	3.42938400	-2.80907500
C	-1.47369600	5.65981800	-3.67536000
H	-2.55599100	4.46623400	-2.25415600
C	2.93635800	0.28167300	-2.65630600
H	2.29495500	1.09703100	-0.75571600
C	1.26822300	0.28447600	-4.40917000
H	-0.64460700	1.14329400	-3.88675400
C	-0.22589500	5.89408200	-4.28171100
H	1.85106500	5.26890800	-4.37777500
H	-2.30415400	6.30999100	-3.92739000
C	2.56154300	-0.01654100	-3.96948800
H	3.93571700	0.04194700	-2.30616300
H	0.96712300	0.04191700	-5.42368900

O	-0.17935700	6.92473400	-5.14932900
H	3.26998000	-0.48662200	-4.64448400
C	1.06193100	7.23632200	-5.78183300
H	0.85761000	8.09176800	-6.42539000
H	1.82382200	7.50615900	-5.04189900
H	1.41665900	6.39566100	-6.38850600

MECP1a:

SCF: -1282.87841144

Cu	-0.66887100	-0.52292900	-0.16743400
N	-0.10685800	0.59991000	1.48976300
C	0.18627400	1.59193300	2.01055200
N	-2.65950200	-0.74793900	-0.07322800
C	-3.80480900	-0.89629000	-0.00568100
N	0.29898600	-2.27798000	-0.20236600
C	0.92754300	-3.24690600	-0.25893900
C	-5.24566200	-1.08588800	0.07953600
H	-5.49764100	-1.60055000	1.01155500
H	-5.75062700	-0.11557000	0.05865300
H	-5.59088300	-1.68775200	-0.76623200
C	0.54097100	2.86241200	2.62561700
H	0.09054400	2.94284900	3.61927600
H	1.62785400	2.94529400	2.71696500
H	0.16970600	3.67556900	1.99349200

C	1.72449300	-4.46295200	-0.33516000
H	2.77632600	-4.22826700	-0.14664100
H	1.37995400	-5.18479800	0.41125800
H	1.63071600	-4.90601300	-1.33116000
N	0.03075700	0.75196500	-1.59345600
N	0.97551100	0.20202300	-2.33711400
C	-0.02943500	2.12217300	-1.42257900
C	0.99278300	0.38491700	-3.69386700
C	1.01890400	2.99325000	-1.79471200
C	-1.17094800	2.66555300	-0.78137700
C	2.10827500	-0.14457500	-4.39207600
C	-0.03559000	1.03887300	-4.42429800
C	0.94325700	4.35162600	-1.51950400
H	1.90306800	2.59037900	-2.27464400
C	-1.25384400	4.01747100	-0.52282700
H	-1.98245800	2.00060400	-0.50644200
C	2.20661200	0.00624200	-5.76622400
H	2.87778500	-0.65309500	-3.82058900
C	0.07694000	1.17270500	-5.79962700
H	-0.90483200	1.42010100	-3.90119700
C	-0.19079700	4.87668800	-0.87435500
H	1.76970100	4.99288600	-1.80120600
H	-2.12850200	4.44653900	-0.04556500
C	1.19525600	0.66690900	-6.47780900

H	3.06913600	-0.39140800	-6.29226100
H	-0.71221400	1.67016500	-6.35531200
O	-0.35549500	6.17515000	-0.54041000
H	1.27399800	0.78125000	-7.55427900
C	0.71337100	7.08565200	-0.79581700
H	0.37793400	8.04941800	-0.41376900
H	1.62308700	6.77634500	-0.26847100
H	0.91840400	7.16547900	-1.86906600

MECP1b:

SCF: -1282.87942928

Cu	-0.66221600	-0.53534100	-0.13411600
N	-0.12899500	0.56018400	1.55987300
C	0.17869000	1.56234600	2.05317700
N	-2.65647700	-0.75824800	-0.06588600
C	-3.80285100	-0.90211400	-0.00484800
N	0.29565500	-2.29526100	-0.17199500
C	0.92610500	-3.26181000	-0.24360900
C	-5.24503700	-1.08665400	0.07528700
H	-5.50166600	-1.59837700	1.00770800
H	-5.74768500	-0.11513400	0.05092400
H	-5.59048000	-1.68946600	-0.76978300
C	0.55433700	2.84524500	2.62883900
H	0.09797400	2.96823000	3.61533800

H	1.64186600	2.90867700	2.72677900
H	0.20710500	3.64406800	1.96524500
C	1.72594400	-4.47484300	-0.33656500
H	2.77768900	-4.23900100	-0.14936700
H	1.38587900	-5.20500500	0.40364300
H	1.62972400	-4.90764700	-1.33679200
N	0.07248100	0.74314300	-1.52511600
N	1.00590000	0.21753500	-2.30375100
C	0.00931100	2.12141100	-1.35613200
C	0.97681300	0.39435400	-3.65174100
C	1.05471500	2.98779000	-1.74779100
C	-1.13833900	2.65676800	-0.72968000
C	2.08377800	-0.09908000	-4.39954300
C	-0.09012000	1.01729600	-4.35503000
C	0.94104900	4.35340900	-1.51909700
H	1.94794800	2.57559400	-2.20185500
C	-1.24334600	4.02580000	-0.52270300
H	-1.93390500	1.98240700	-0.43232400
C	2.13899100	0.06811900	-5.76365000
H	2.88785300	-0.59138700	-3.86309800
C	-0.03616100	1.17629600	-5.72872600
H	-0.95601000	1.36852700	-3.80728100
C	-0.20463700	4.88221100	-0.91273600
H	1.75402100	5.01233600	-1.80964100

H	-2.13701200	4.43115900	-0.05761900
C	1.08526900	0.71702000	-6.44695400
H	2.98549500	-0.28577100	-6.34190700
H	-0.86361200	1.65521000	-6.23823300
O	1.24620100	0.84440800	-7.77875700
C	0.23593500	1.51337300	-8.53394100
H	0.59715300	1.52839300	-9.56182700
H	-0.71476700	0.97044100	-8.48597600
H	0.09692000	2.54061200	-8.17950400
H	-0.28981300	5.95134400	-0.74712200

1aT:

SCF: -1282.887572

Cu	-0.48744500	-0.02217300	0.11228800
N	0.05972400	0.23042000	2.02425100
C	0.45387300	0.43359800	3.09254200
N	-2.47836500	0.15524900	-0.15865600
C	-3.61137200	0.26954800	-0.36278200
N	0.08055900	-1.80375500	-0.67671400
C	0.49537700	-2.58994200	-1.41776500
C	-5.03658600	0.41718400	-0.62140400
H	-5.57571700	-0.45556700	-0.24119000
H	-5.41371400	1.31525500	-0.12315900
H	-5.21115000	0.50507200	-1.69787800

C	0.95264400	0.69012200	4.43618500
H	0.27140000	0.25864000	5.17543500
H	1.94259300	0.24007200	4.55574800
H	1.02767900	1.76866200	4.60388600
C	1.01494300	-3.56037700	-2.36894700
H	2.07365300	-3.74884500	-2.16884700
H	0.46020600	-4.49969800	-2.28902800
H	0.91187600	-3.15965800	-3.38187500
N	0.48755600	1.35994900	-1.05512400
N	1.58591600	0.86843100	-1.63159100
C	0.20336400	2.69419700	-1.17751500
C	1.47361600	0.22050000	-2.82755400
C	0.94746400	3.55922300	-2.01728400
C	-0.88628100	3.23228000	-0.44213100
C	2.65392700	-0.36774300	-3.35219400
C	0.25821300	0.10293000	-3.55488500
C	0.60970600	4.89825300	-2.13389000
H	1.79299400	3.16390100	-2.56819200
C	-1.22165400	4.56272000	-0.56203100
H	-1.45113400	2.57870800	0.21261700
C	2.61981500	-1.03497800	-4.56719200
H	3.57243300	-0.27231300	-2.78247300
C	0.24171000	-0.57446100	-4.76482200
H	-0.64479700	0.54310600	-3.14687300

C	-0.48215100	5.41379000	-1.41149900
H	1.19702700	5.53694400	-2.78211100
H	-2.05152500	4.98598000	-0.00613600
C	1.41665300	-1.14364900	-5.28079200
H	3.52831400	-1.47501500	-4.96666900
H	-0.68839300	-0.66208400	-5.31874600
O	-0.89529300	6.69840300	-1.45608600
H	1.39411600	-1.66528700	-6.23243400
C	-0.18756400	7.61521400	-2.29015400
H	-0.69536800	8.57254800	-2.17405000
H	0.85655500	7.71116400	-1.97138500
H	-0.22621700	7.30289700	-3.33992400

1bT:

SCF: -1282.887397

Cu	-0.13086400	0.51031500	-0.41075500
N	1.41210700	1.17626800	0.70434200
C	2.31068000	1.57690400	1.31307500
N	-1.73201400	1.69881100	-0.02648500
C	-2.52236500	2.53545300	-0.14787600
N	-0.50034100	-1.43587300	-0.10513900
C	-0.74118600	-2.56415600	-0.02197700
C	-3.50093200	3.59839700	-0.31757700
H	-3.80424100	3.99066400	0.65726800

H	-3.05718000	4.40191000	-0.91244400
H	-4.38045600	3.21472600	-0.84222400
C	3.44146600	2.08047700	2.08004200
H	3.08237300	2.69611000	2.91007800
H	4.02070600	1.24369800	2.48138300
H	4.08713600	2.68676800	1.43788500
C	-1.04934600	-3.98338000	0.08102700
H	-0.70101400	-4.37256300	1.04227500
H	-2.13044100	-4.13303500	0.00471100
H	-0.55473400	-4.53005600	-0.72728200
N	-0.80715800	1.32492500	-3.08038800
N	0.23451900	0.85234200	-2.40053900
C	-1.06977700	2.65510300	-3.09795400
C	1.38376000	0.52728200	-3.09134900
C	-0.24201900	3.63757400	-2.49034900
C	-2.25474900	3.08312500	-3.76256000
C	2.43079700	-0.10942500	-2.38375500
C	1.54984500	0.81612200	-4.46770000
C	-0.57629900	4.98142200	-2.54983100
H	0.65524400	3.32050900	-1.97064800
C	-2.57884100	4.41924400	-3.82794500
H	-2.88771600	2.33136600	-4.22206200
C	3.61440800	-0.42878700	-3.03327200
H	2.28908100	-0.33894500	-1.33357000

C	2.73990200	0.48792900	-5.10121300
H	0.73959600	1.28513600	-5.01364900
C	-1.74308800	5.38806200	-3.22667000
H	0.07086600	5.71063100	-2.07752800
H	-3.47286700	4.75845500	-4.34009400
C	3.77818800	-0.13120600	-4.39243300
H	4.41426300	-0.91651100	-2.48428700
H	2.86314600	0.71060800	-6.15674200
O	-2.15055100	6.66902900	-3.35122900
H	4.70434700	-0.38652500	-4.89758500
C	-1.33632000	7.70342800	-2.80003000
H	-1.84367500	8.63778300	-3.03901900
H	-1.25000300	7.59933100	-1.71228100
H	-0.33779300	7.69941500	-3.25108300

TS1a:

SCF: -1282.866124

Freq: *i*438.6393

Cu	-0.69024500	-0.20693100	0.39332200
N	0.08624700	0.31821100	2.14387400
C	0.57780900	0.61958000	3.14699200
N	-2.67474400	-0.04263500	0.25970500
C	-3.82155600	0.02553200	0.12216900
N	-0.09819000	-2.07593300	-0.20474900

C	0.38245800	-2.93956100	-0.80760000
C	-5.26446600	0.10988600	-0.05416800
H	-5.72691300	0.52602700	0.84573900
H	-5.49716500	0.75424200	-0.90727100
H	-5.67492700	-0.88745600	-0.23759000
C	1.19788000	0.99628900	4.40954600
H	0.69922000	0.48156000	5.23611000
H	2.25598100	0.71817700	4.40138500
H	1.11398600	2.07699800	4.55794200
C	0.99000000	-4.01499900	-1.57721900
H	1.98330200	-4.23901400	-1.17885100
H	0.36699400	-4.91261500	-1.52272400
H	1.09347300	-3.70131800	-2.62049200
N	0.24005500	0.79218600	-1.22985800
N	1.01197500	0.11185100	-1.90915800
C	-0.04029300	2.12866000	-1.63866700
C	1.60306900	-0.69750900	-2.79161200
C	-0.84192600	2.89554200	-0.78826400
C	0.45324700	2.67901800	-2.83642900
C	0.89377700	-1.11096000	-3.95138300
C	2.90712700	-1.20405600	-2.55918600
C	-1.16812700	4.20626000	-1.11839200
H	-1.20600800	2.45330200	0.13378500
C	0.13176500	3.97725200	-3.17209200

H	1.07957800	2.07768100	-3.48692100
C	1.47330200	-2.03634300	-4.81337200
H	-0.10160300	-0.71913600	-4.13075300
C	3.47303900	-2.08601500	-3.47190500
H	3.44846400	-0.88413600	-1.67558400
C	-0.68005700	4.75507500	-2.31586000
H	-1.78861000	4.78925900	-0.44990300
H	0.49161500	4.43024100	-4.08947300
C	2.76456400	-2.52749600	-4.59461000
H	0.90822500	-2.36088800	-5.68302500
H	4.47957700	-2.45123200	-3.28783700
O	-0.92664700	6.00954000	-2.73782800
H	3.21187200	-3.23119600	-5.28822400
C	-1.73241700	6.86345000	-1.92494300
H	-1.78364000	7.81313500	-2.45678200
H	-2.74145300	6.45316200	-1.80470300
H	-1.27428100	7.01580400	-0.94130600

TS1b:

SCF: -1282.86252

Freq: *i*434.6152

Cu	-0.68704800	-0.19697500	0.34842800
N	0.28768300	0.28931400	2.01471500
C	0.87969800	0.62053800	2.95220100

N	-2.68084700	-0.04363300	0.54438300
C	-3.83316600	0.05117700	0.59254800
N	-0.31011900	-2.13204000	-0.26420500
C	-0.03568400	-3.04976900	-0.91412100
C	-5.28348500	0.17006400	0.65092300
H	-5.73778100	-0.82516500	0.65855300
H	-5.57785200	0.70316000	1.55978200
H	-5.64702600	0.72189300	-0.22107600
C	1.62567700	1.03817400	4.13114300
H	1.24023200	0.52561200	5.01753700
H	2.68422100	0.79115300	4.00740700
H	1.52590000	2.11873600	4.27078200
C	0.31634000	-4.19247200	-1.74546800
H	-0.53751100	-4.47870000	-2.36656400
H	1.15773000	-3.92236500	-2.39094600
H	0.60036900	-5.04144600	-1.11667800
N	0.09214500	0.72782600	-1.34393800
N	0.85940200	0.06347700	-2.05888600
C	-0.25898800	2.05886500	-1.77720000
C	1.63754000	-0.65926600	-2.86567600
C	-1.12321600	2.78181300	-0.94946000
C	0.25489300	2.63427400	-2.94605800
C	1.49369800	-0.61573900	-4.28356500
C	2.62391000	-1.52510300	-2.32227600

C	-1.49116200	4.07961200	-1.30030900
H	-1.49659900	2.31844500	-0.04182200
C	-0.11480400	3.93063600	-3.28841200
H	0.94251600	2.06950500	-3.56541500
C	2.25309500	-1.43816200	-5.09144800
H	0.74072800	0.03482400	-4.71529500
C	3.45999400	-2.26659900	-3.14626300
H	2.74059400	-1.56167300	-1.24433100
C	-0.98980800	4.65516900	-2.46971500
H	-2.16427400	4.64220100	-0.66057900
H	0.27975700	4.38224600	-4.19352800
C	3.26133500	-2.25256400	-4.53882200
H	2.11897600	-1.44437000	-6.16808100
H	4.24013100	-2.87332700	-2.70274300
O	3.98044400	-2.97733900	-5.42370800
H	-1.27389200	5.66687900	-2.74242800
C	5.02586200	-3.81308400	-4.93147700
H	5.46456700	-4.28618700	-5.80983100
H	5.78958500	-3.22417900	-4.41066300
H	4.63177800	-4.58336700	-4.25798400

MECP2a:

SCF: -1282.886792

Cu	-0.44830600	-0.02231700	0.00393600

N	0.02520300	0.36228500	1.91783900
C	0.38465400	0.63687900	2.98257600
N	-2.43401400	0.11503400	-0.33942500
C	-3.55906800	0.23150400	-0.58240400
N	0.20420300	-1.81007300	-0.66693100
C	0.64564500	-2.63236400	-1.35097700
C	-4.97602500	0.37788500	-0.88296300
H	-5.52573100	-0.49050400	-0.50782000
H	-5.36538600	1.28158800	-0.40470300
H	-5.12203800	0.45430600	-1.96449200
C	0.84377300	0.98556400	4.31993700
H	0.34184700	0.35912600	5.06314500
H	1.92442800	0.82982600	4.39167400
H	0.62050900	2.03641800	4.52698800
C	1.20059900	-3.64920700	-2.23070600
H	2.28536100	-3.69947000	-2.10030800
H	0.76327500	-4.62529000	-2.00187300
H	0.98157500	-3.38349700	-3.26922100
N	0.48512800	1.37084100	-1.19585800
N	1.56214200	0.93578700	-1.84702500
C	0.23475800	2.71697500	-1.18575100
C	1.39002700	0.16454500	-2.95741900
C	0.94988000	3.62360500	-2.00704300
C	-0.80487300	3.22067700	-0.35985000

C	2.55402000	-0.40709600	-3.53475900
C	0.12878800	-0.06036900	-3.57341800
C	0.63642300	4.97256000	-2.01515400
H	1.74983100	3.24386900	-2.63132100
C	-1.11794700	4.56165900	-0.37242500
H	-1.35212400	2.53236200	0.27432700
C	2.45724000	-1.16456800	-4.69186700
H	3.50947100	-0.22340600	-3.05441000
C	0.05074600	-0.82475400	-4.72719400
H	-0.75702400	0.37837600	-3.12838300
C	-0.40449300	5.45566300	-1.20053600
H	1.19814500	5.64197200	-2.65487300
H	-1.91348200	4.96020300	0.24828500
C	1.20842100	-1.37873400	-5.29561700
H	3.35296400	-1.58761000	-5.13578400
H	-0.91390400	-0.98544200	-5.19991200
O	-0.79332000	6.74636000	-1.13934400
H	1.13828700	-1.96426400	-6.20674700
C	-0.11868600	7.70304700	-1.95630400
H	-0.59518500	8.65969900	-1.74358100
H	0.94580400	7.75743900	-1.70201600
H	-0.23235600	7.46232800	-3.01932500

MECP2b:

SCF: -1282.886543

Cu	-0.43755400	0.01205000	0.01350100
N	0.02503500	0.37476700	1.93435900
C	0.38734100	0.64419100	2.99945300
N	-2.42476300	0.12274000	-0.33004600
C	-3.55020200	0.23829200	-0.57207100
N	0.23459500	-1.77593700	-0.64950100
C	0.66477600	-2.61375600	-1.32166800
C	-4.96756800	0.38224500	-0.87267600
H	-5.51576300	-0.48772900	-0.49897900
H	-5.35930400	1.28444800	-0.39357700
H	-5.11341400	0.46004100	-1.95414500
C	0.84969600	0.98626800	4.33735100
H	0.34792900	0.35742000	5.07860800
H	1.93018600	0.82819700	4.40633000
H	0.62885100	2.03666100	4.54933700
C	1.19856700	-3.65378000	-2.18777500
H	2.28661800	-3.70053300	-2.08760100
H	0.76939400	-4.62343000	-1.91945700
H	0.94888700	-3.41966600	-3.22665600
N	0.48928200	1.40127400	-1.18879400
N	1.53782500	0.96912500	-1.88286400
C	0.24576300	2.75826300	-1.16221000
C	1.34576700	0.19363800	-2.97753800

C	0.95795500	3.66882900	-1.98085500
C	-0.77730700	3.24297500	-0.31242300
C	2.49415500	-0.38857300	-3.58777200
C	0.07287900	-0.04863600	-3.56223700
C	0.63881900	5.01842300	-1.95111600
H	1.74975100	3.29420500	-2.61924700
C	-1.08541400	4.59580200	-0.29896000
H	-1.31530300	2.54207000	0.31608300
C	2.37107900	-1.15971300	-4.72198200
H	3.46535000	-0.20043700	-3.14179600
C	-0.04784500	-0.82945900	-4.69987400
H	-0.80736200	0.38629500	-3.10215300
C	-0.38237500	5.49107300	-1.11573400
H	1.18600200	5.71119700	-2.58318300
H	-1.87671800	4.96053700	0.34908600
C	1.09932700	-1.38864400	-5.29659900
H	3.23914100	-1.59741100	-5.20353000
H	-1.02900300	-0.99655700	-5.12716400
O	1.08680700	-2.15639600	-6.40746900
C	-0.14910900	-2.34826900	-7.09652200
H	0.08820000	-2.96435300	-7.96380100
H	-0.87851500	-2.86986900	-6.46590600
H	-0.56498600	-1.38972900	-7.42721800
H	-0.62421400	6.54903000	-1.09779800

2a:

SCF: -1282.927314

Cu	-0.71400900	0.06892200	-0.80411200
N	-0.25511800	0.92036400	1.00367700
C	0.03874200	1.71685500	1.79033200
N	-2.67687700	-0.19946900	-1.02315700
C	-3.81445800	-0.35123700	-1.17145900
N	0.43425800	-1.55232500	-1.00767500
C	1.11195900	-2.45264600	-1.26682100
C	-5.24536200	-0.54688200	-1.35739100
H	-5.64040900	-1.17964400	-0.55704100
H	-5.75947100	0.41872600	-1.33657500
H	-5.43205700	-1.03004400	-2.32104000
C	0.39629500	2.75775100	2.74200500
H	-0.15127500	2.61899200	3.67863600
H	1.47043300	2.72725900	2.94635100
H	0.13777900	3.73124600	2.31268600
C	1.96476700	-3.58264400	-1.60329800
H	2.87393600	-3.22200600	-2.09224600
H	2.23311600	-4.13419600	-0.69749300
H	1.43606700	-4.24911600	-2.29053200
N	0.04397400	1.61604600	-2.10631200
N	0.88315700	1.41199600	-3.02841900

C	0.06433600	2.92015900	-1.55162300
C	0.82398100	0.14817200	-3.64612400
C	1.15937100	3.78661300	-1.67066700
C	-1.06700500	3.32862700	-0.82636700
C	2.03864600	-0.40145500	-4.07828200
C	-0.38422800	-0.52509800	-3.89008200
C	1.13650800	5.03719200	-1.06650600
H	2.03056700	3.46154600	-2.22696800
C	-1.10510400	4.58063400	-0.23565200
H	-1.91423800	2.65621600	-0.74336400
C	2.05207700	-1.65455100	-4.68657400
H	2.95499800	0.15546700	-3.91208100
C	-0.36307900	-1.76389600	-4.52345600
H	-1.32150400	-0.06342800	-3.60169200
C	0.00019100	5.44460100	-0.34423400
H	1.99881100	5.68600100	-1.15640100
H	-1.97729700	4.91957400	0.31310300
C	0.85248800	-2.33911900	-4.90837600
H	2.99445300	-2.08923700	-5.00576900
H	-1.29650700	-2.28050600	-4.72574800
O	-0.11968800	6.63416700	0.28589200
H	0.86260400	-3.30456600	-5.40517500
C	0.95073200	7.57263000	0.18264100
H	0.62879800	8.45022800	0.74300700

H	1.87118100	7.17254600	0.62328400
H	1.13264400	7.84895100	-0.86192800

2b:

SCF: -1282.92815614

Cu	-0.80199400	0.05151700	-0.85179900
N	-0.28582900	0.89145500	0.94885100
C	0.07925900	1.70791200	1.68387500
N	-2.77525900	-0.12507000	-1.05677000
C	-3.92549700	-0.20719900	-1.15347600
N	0.27747300	-1.61739700	-1.07424400
C	0.91632300	-2.54427200	-1.34010400
C	-5.37312200	-0.31281700	-1.26983500
H	-5.76503300	-0.94033400	-0.46379000
H	-5.82572000	0.68083600	-1.20116100
H	-5.63850600	-0.75969300	-2.23248200
C	0.53336800	2.76903300	2.57004800
H	-0.08206600	2.79406400	3.47392100
H	1.57726500	2.60327200	2.85126500
H	0.44739100	3.72696500	2.04706900
C	1.72294700	-3.70711700	-1.68275600
H	2.76264800	-3.40080000	-1.82937500
H	1.67468000	-4.44738500	-0.87878200
H	1.35675800	-4.15266900	-2.61212900

N	0.00807400	1.63271100	-2.09386200
N	0.90677300	1.43511400	-2.95971000
C	0.01605100	2.93428200	-1.51257400
C	0.86431500	0.19243900	-3.60537000
C	1.15448600	3.75212600	-1.49556700
C	-1.17272200	3.36149000	-0.90913500
C	2.09359000	-0.38334600	-3.96772400
C	-0.33248800	-0.46646800	-3.92553200
C	1.09397400	4.99454000	-0.87177100
H	2.06675800	3.39948300	-1.96173500
C	-1.22964500	4.61439500	-0.30103800
H	-2.03886300	2.70837000	-0.92785000
C	2.12723100	-1.64371500	-4.53875900
H	3.01045700	0.15629500	-3.75485500
C	-0.30683900	-1.71120200	-4.54300900
H	-1.28051600	0.01175200	-3.70663200
C	-0.09617100	5.43165300	-0.27734000
H	1.97619100	5.62699700	-0.84827500
H	-2.15542200	4.95109600	0.15518500
C	0.92700400	-2.32359700	-4.81799500
H	3.06594300	-2.12371600	-4.79320800
H	-1.23988900	-2.19706500	-4.79991900
O	1.06657300	-3.56261200	-5.34824500
C	-0.10878700	-4.27827900	-5.72629300

H	-0.66699400	-3.73744100	-6.49874600
H	0.24044200	-5.22987900	-6.12666700
H	-0.75802900	-4.45897800	-4.86154400
H	-0.13790500	6.40525300	0.20139100

3a:

SCF: -1837.479112

Cu	-1.00334200	-1.57541700	-1.48558500
N	0.26677500	0.07123300	-1.33676900
N	1.41020400	-0.19416900	-0.88369000
C	-0.39126700	1.34174900	-1.23505300
C	2.29397700	0.80135200	-0.38468800
C	-0.34407100	2.14557800	-0.08927600
C	-1.29115500	1.66059100	-2.26415700
C	2.94965800	0.50080600	0.81568700
C	2.61247100	1.96602700	-1.09885800
C	-1.20005800	3.23418400	0.04265100
H	0.33092200	1.90495800	0.72026000
C	-2.11767700	2.76626300	-2.15683900
H	-1.33483600	1.02458600	-3.14074600
C	3.86610500	1.40752700	1.34461300
H	2.71342900	-0.42573800	1.32666200
C	3.55967700	2.84382800	-0.58041300
H	2.12948000	2.17072500	-2.04806500

C	-2.09771000	3.54921400	-0.98937700
H	-1.16742500	3.82293900	0.95083100
H	-2.80913600	3.03190400	-2.94950100
C	4.17402300	2.57894000	0.64842500
H	4.35578400	1.18699400	2.28839300
H	3.81910900	3.74019500	-1.13540300
O	-2.99284000	4.56317300	-0.94320700
H	4.90371100	3.27514300	1.05023800
C	-3.05364000	5.35924600	0.23880000
H	-3.84166600	6.09132400	0.06249200
H	-3.30655100	4.74670500	1.11232700
H	-2.10475900	5.87830300	0.41526900
N	-1.98942900	-1.04786900	0.29342800
N	-3.09797200	-0.46845700	0.16382000
C	-1.15001900	-0.99790600	1.45010200
C	-3.79892800	0.15694200	1.22807700
C	-1.02209000	0.11940600	2.28811300
C	-0.26393300	-2.07782200	1.60906000
C	-4.36022100	1.40965600	0.94566900
C	-4.06696500	-0.48321300	2.44741900
C	-0.02434900	0.16509900	3.25497000
H	-1.66984000	0.97556800	2.16400500
C	0.70508800	-2.05671500	2.59594800
H	-0.34428500	-2.92701800	0.93917000

C	-5.12648100	2.05637200	1.91375100
H	-4.16542800	1.86769800	-0.01792500
C	-4.86438000	0.15669700	3.39153100
H	-3.65897400	-1.46856000	2.64411500
C	0.84836300	-0.92380600	3.41631300
H	0.07395800	1.05202600	3.86817100
H	1.38822200	-2.88788500	2.73244100
C	-5.38152900	1.43172500	3.13701400
H	-5.54239700	3.03716600	1.70340400
H	-5.08315200	-0.34006200	4.33181900
O	1.86469200	-0.96436500	4.30463900
H	-5.99519900	1.92649500	3.88323700
C	2.09600600	0.17761400	5.12869100
H	2.96846100	-0.06740800	5.73421100
H	2.30568100	1.06507700	4.52054600
H	1.23841500	0.37266400	5.78257800
C	0.62448600	-4.18029400	-2.04241400
N	-0.02742500	-3.25460200	-1.80442400
C	-3.66346400	-0.84640300	-2.73567700
N	-2.60974900	-1.33114400	-2.75737000
C	-4.97433100	-0.21787900	-2.69952700
H	-5.34512700	-0.23294200	-1.67074900
H	-4.89404200	0.82107300	-3.03378600
H	-5.67402100	-0.75051300	-3.35002000

C	1.44529100	-5.34353600	-2.34680600
H	2.12547600	-5.54728500	-1.51454300
H	0.80771200	-6.21716700	-2.51166800
H	2.03342300	-5.15464800	-3.24986600

3b:

SCF: -1837.478609

Cu	-1.03064700	-1.65218200	-1.50502200
N	0.16218500	0.03307400	-1.42893700
N	1.19308800	-0.06217000	-0.70830300
C	-0.48936100	1.27498800	-1.75073700
C	1.97015100	1.02787800	-0.27455200
C	-0.95325600	2.11770900	-0.73408300
C	-0.80764400	1.53125900	-3.08623700
C	2.67566500	0.78953800	0.92300000
C	2.18815100	2.23275900	-0.96766400
C	-1.72007800	3.23240200	-1.06339700
H	-0.70495000	1.90232400	0.29824700
C	-1.55291900	2.66567800	-3.40978600
H	-0.46850000	0.84471300	-3.85492400
C	3.50328300	1.75708500	1.45943600
H	2.52952400	-0.16036000	1.42553700
C	3.05571100	3.18903300	-0.45719400
H	1.70976300	2.41533600	-1.92101500

C	-2.01553300	3.51548800	-2.40095600
H	-2.08456300	3.88201300	-0.27333300
H	-1.78138700	2.87832900	-4.44968700
C	3.70149000	2.96936100	0.77310800
H	4.03053600	1.59765500	2.39372100
H	3.22782900	4.09847400	-1.01898900
N	-1.95754100	-1.16926400	0.29505200
N	-2.94152900	-0.38362000	0.27650500
C	-1.14708300	-1.43024800	1.45434900
C	-3.53980000	0.16827300	1.42740500
C	-0.63106000	-0.38894200	2.23627500
C	-0.73780600	-2.74910500	1.67073500
C	-4.11296900	1.44266500	1.25105700
C	-3.72121800	-0.50190000	2.64883300
C	0.28395100	-0.67874300	3.24417600
H	-0.94350100	0.63294300	2.05802000
C	0.15644900	-3.03291800	2.70179200
H	-1.12407300	-3.53515100	1.03010800
C	-4.77175500	2.06825700	2.29354100
H	-3.99567400	1.93702200	0.29256700
C	-4.42345500	0.10211300	3.68367200
H	-3.33895100	-1.50622500	2.78440000
C	0.67349100	-1.99965500	3.48679200
H	0.69541600	0.13003700	3.84017800

H	0.45983600	-4.05944900	2.88301100
C	-4.93268500	1.40323800	3.52285700
H	-5.19085900	3.06243000	2.18262400
H	-4.57282600	-0.44201400	4.60781300
C	0.54894100	-4.28511700	-1.85725400
N	-0.09449300	-3.34768500	-1.76021100
C	-3.49762400	-0.43623400	-2.68268800
N	-2.63017000	-1.20465100	-2.73885200
C	-4.56466300	0.54790700	-2.60518400
H	-5.13487700	0.39232700	-1.68542300
H	-4.12268700	1.54935400	-2.58899900
H	-5.23177300	0.46078800	-3.46777700
C	1.37231900	-5.47940000	-1.97834300
H	2.07855100	-5.52809400	-1.14396000
H	0.73962800	-6.37199800	-1.96569500
H	1.93146600	-5.45177200	-2.91851000
O	-5.60154100	2.08498400	4.47674400
O	4.53882300	3.84803400	1.36208600
H	1.38236700	-2.22050800	4.27865500
H	-2.60341300	4.39214600	-2.65462000
C	-5.79761900	1.46750800	5.74834800
H	-6.33930700	2.19710900	6.34995500
H	-6.39370400	0.55263100	5.65493800
H	-4.83844700	1.23600500	6.22551700

C	4.80056400	5.08949500	0.70823700
H	5.48351400	5.62953400	1.36375300
H	5.27575000	4.92898300	-0.26610300
H	3.87910100	5.66864700	0.57879200

S9. References

1 K. Masutani, M-a. Morikawa, N. Kimizuka, *Chem. Commun.*, 2014, **50**, 15803–15806.

2 K. Stranius and K. Börjesson, *Sci. Rep.*, 2017, **7**, 41145.

3 Z. Wang, A. Roffey, R. Losantos, A. Lennartson, M. Jevric, A. U. Petersen, M. Quant, A. Dreos, X. Wen, D. Sampedro, K. Börjesson and K. Moth-Poulsen., *Energy Environ. Sci.*, 2019, **12**, 187–193.

4 S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem*. 2011, **32**, 1456.

5 Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

6 Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* 1972, **56**, 2257−2261.

7 T. H. Dunning Jr. and P. J. Hay, in *Mod. Theo. Chem.*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1977) 1–28.

8 https://github.com/jaimergp/easymecp repository, publication in preparation.

9 Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev*. 2005, **105**, 2999.

10 T. Yanai, D. Tew, and N. Handy, *Chem. Phys. Lett.* 2004, **393,** 51-57.

11 N. M. O'Boyle, A. L. Tenderholt and K. M. Langner. *J. Comp. Chem.*, 2008, 29, 839–845.

12 E. Léonard, F. Mangin, C. Villette, M. Billamboz, C. Len. *Cat. Sci.Tech.*, 2016, **6**(2), 379–398.

13 A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi, G. Orlandi, *J. Am. Chem. Soc.* 2004, **126**, 3234–3243.