Supporting Information for

Ultra-fast Excited-state Dynamics of substituted *trans*-Naphthalene Azo Moieties

Robert C. Hamburger,[a] Tao Huang,[a] Shea M. Martin,[a] Craig A. Pointer,[a] Lisa A. Fredin*[a] and Elizabeth R. Young*[a]

[a] Department of Chemistry, Lehigh University, 6 E. Packer Ave., Bethlehem, PA 18015, USA.

Contents

Experimental Details

Materials and Synthetic Procedures

All reagents were obtained from commercial sources used as received without further purification, unless otherwise specified. Air-sensitive reactions were conducted using a standard Schlenk line techniques under nitrogen. Acetonitrile was dried over CaH2 and distilled. Dried acetonitrile was stored over 4 Å sieves.

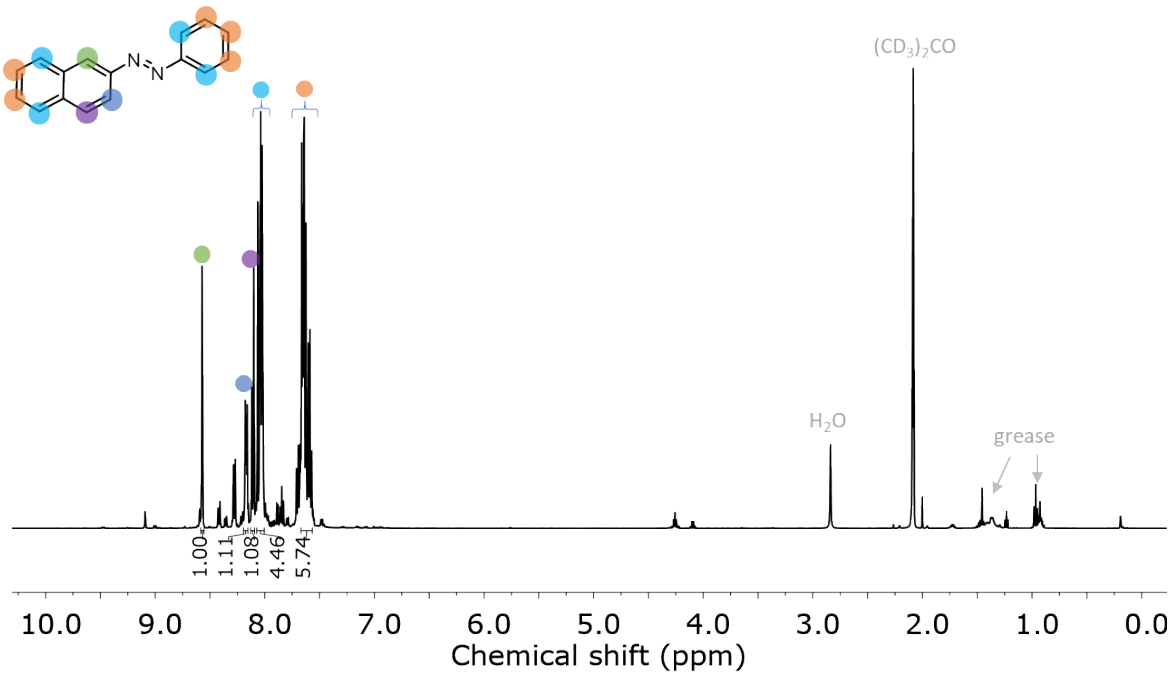
Synthesis

1. Nap-azo-ph (1)

The synthesis of azo **1** is modified from literatures.[14,15] In 50 mL Schlenk flask, 0.45 g (3.1 mmol) 2-naphthylamine, and 0.3 g (2.4 mmol) nitrobenzene are mixture with 0.25 g (6.25 mmol) NaOH. The solids are heated to 180 °C. This melt mixture is further stirred under N_2 for 30 min. After the reaction is compete, the mixture is cooled down to room temperature, dissolved in 30 mL Et_2O and neutralized with 7.5 mL 2 M HCl solution. The organic layer is separated and dried under vacuum. The final product is obtained after chromatographic purification using a silica gel column with 1:20 ethyl acetate/pentane eluent.

Yield: 160 mg (28.7%)

^{1}H-NMR (Acetone-D^6): 8.57 (1H), 8.17 (1H), 8.11 (1H), 8.06-8.03 (4H). 7.66-7.57 (5H)

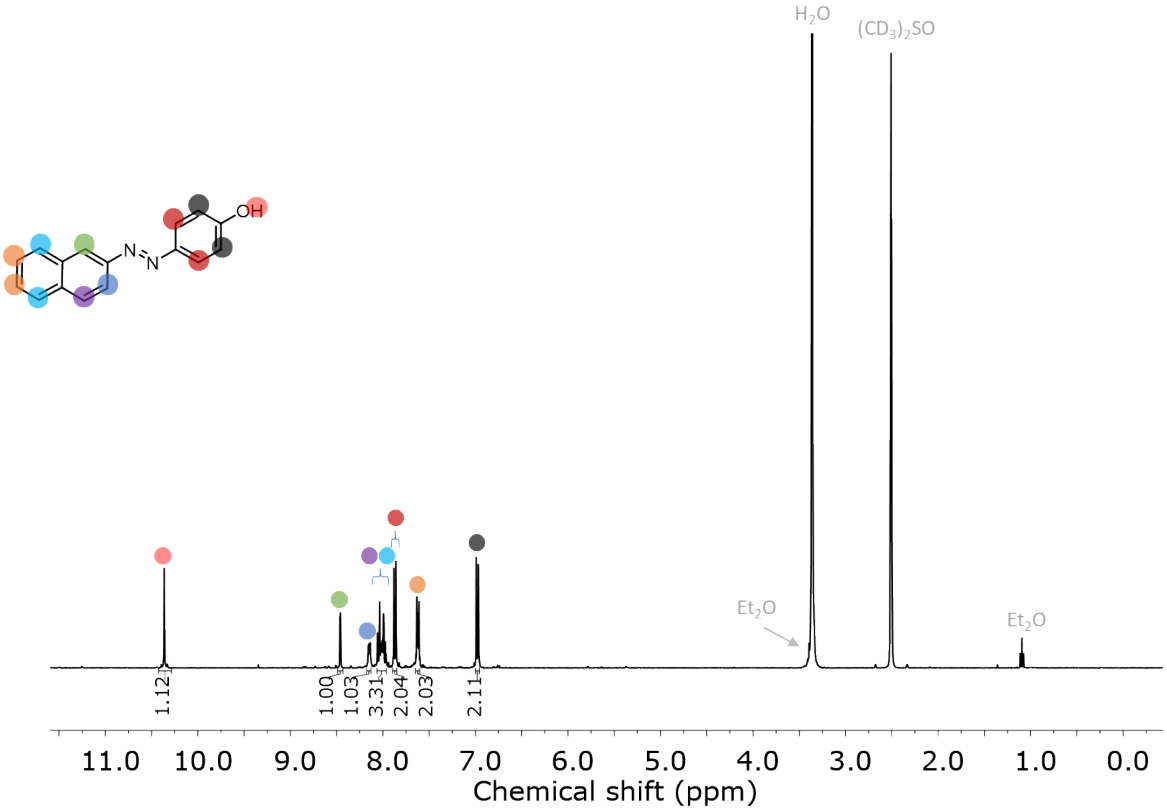


2. Nap-azo-phOH (2)

In 100 mL round bottom flask equipped with a stir-bar, 0.83 g (5.7 mmol) 2-naphthylamine is dissolved in 2.4 mL acetone. The solution is cooled to 0 °C in an ice bath and 2 mL 10 M HCl is added. To this solution, a pre-cooled aqueous solution (12 mL) of 0.41 g (6.0 mmol) $NaNO_2$ is added dropwise to convert the 2-naphthylamine into its corresponding diazonium salt. Following this, a pre-cooled 0.5 M NaOH solution (12 mL) of 1.18 g (8.5 mmol) K_2CO_3 and 0.57 g (6.0 mmol) phenol is added. The reaction is further stirred for 1 hr. After warming up to room temperature, the reaction neutralized using 2 M HCl and resulted solution is filtered over a frit equipped with a celite pad. The collected solid on the frit is washed with 30 mL DI water and extracted with 60 mL Et_2O. After evaporating the Et_2O over vacuum, the raw product is obtained. The raw product is further purified through a silica gel column using 1:1 pentane/Et_2O eluent.

Yield: 0.84 g (58.5%)

^{1}H-NMR (DMSO-D^6): 10.35 (1H), 8.45 (1H), 8.14 (1H), 8.05-7.96 (3H), 7.86 (2H), 7.61 (2H), 6.97 (2H)

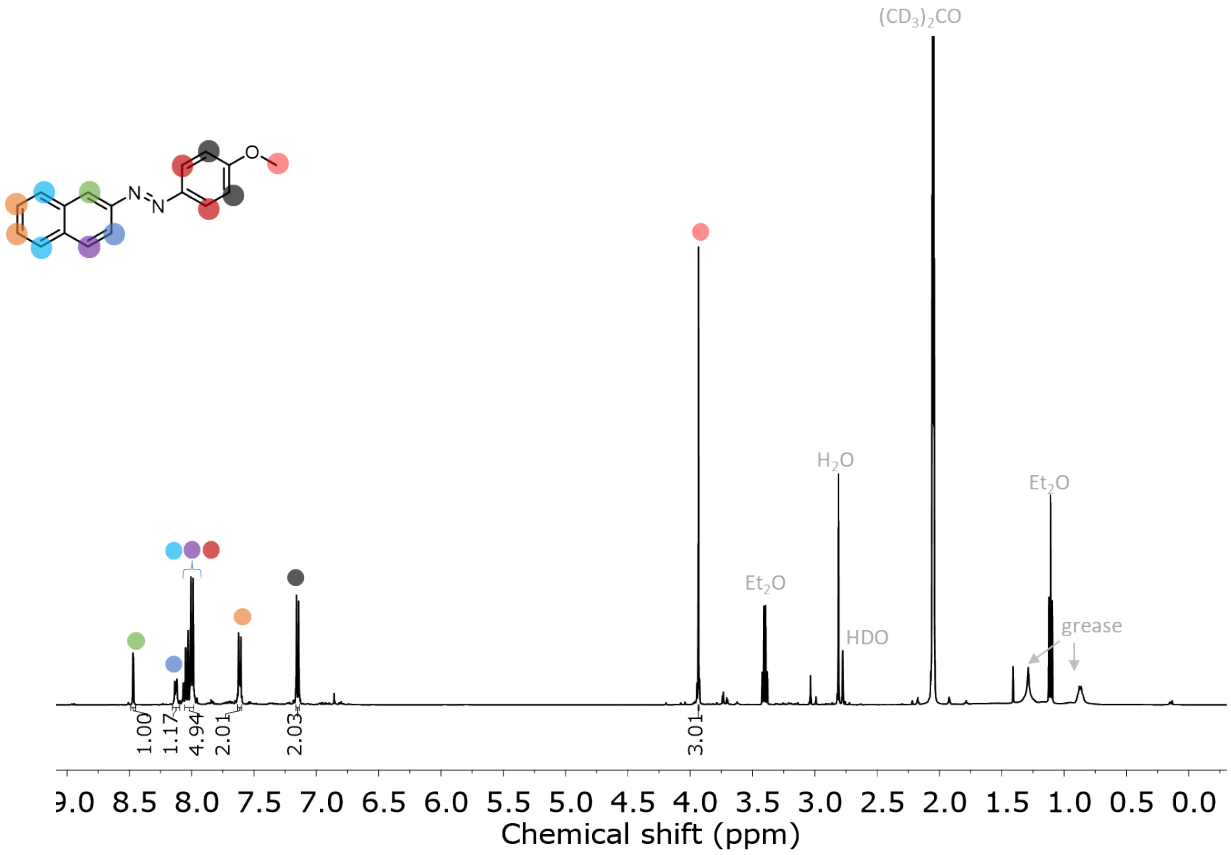


3. Nap-azo-phOMe (3)

In 50 mL Schlenk flask, 200 mg (0.8 mmol) nap-azo-phOH and 0.5 ml (8 mmol) MeI are dissolved in 5 ml anhydrous THF under the protection of N_2. To this solution, a suspension of 200 mg NaH (60 % dispersion in mineral oil) in 15 mL THF is added. The reaction is heated to 65 °C and stirred for 16 hrs. After the reaction is compete, the solvent is removed under vacuum.

The final product is obtained after chromatographic purification using a silica gel column with 1:1 ethyl pentane/Et_2O eluent.

Yield 190 mg (96%)

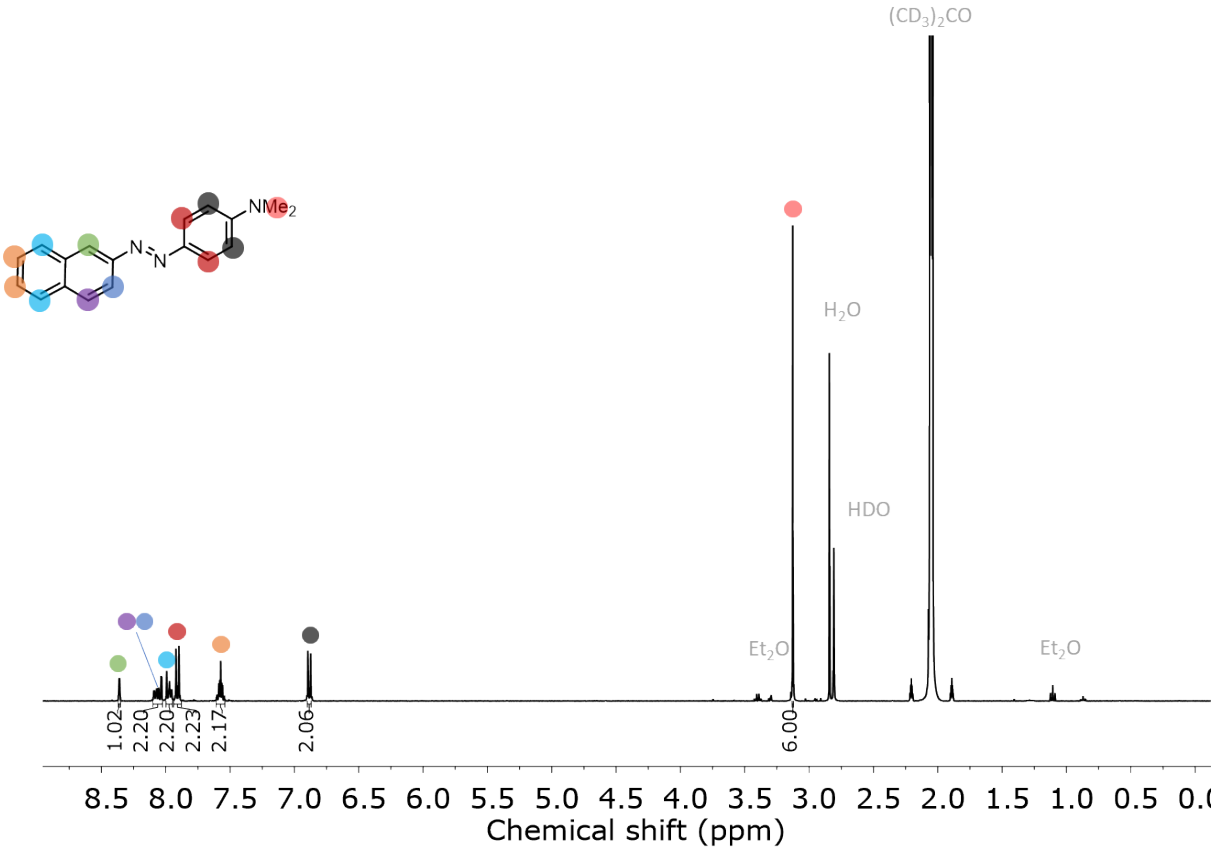


^{1}H-NMR (Acetone-D^6): 8.47 (1H), 8.14 (1H) 8.04 – 7.99 (5H), 7.62 (2H), 7.15 (2), 3.93 (3H)

4. Nap-azo-phNMe_2 (4)

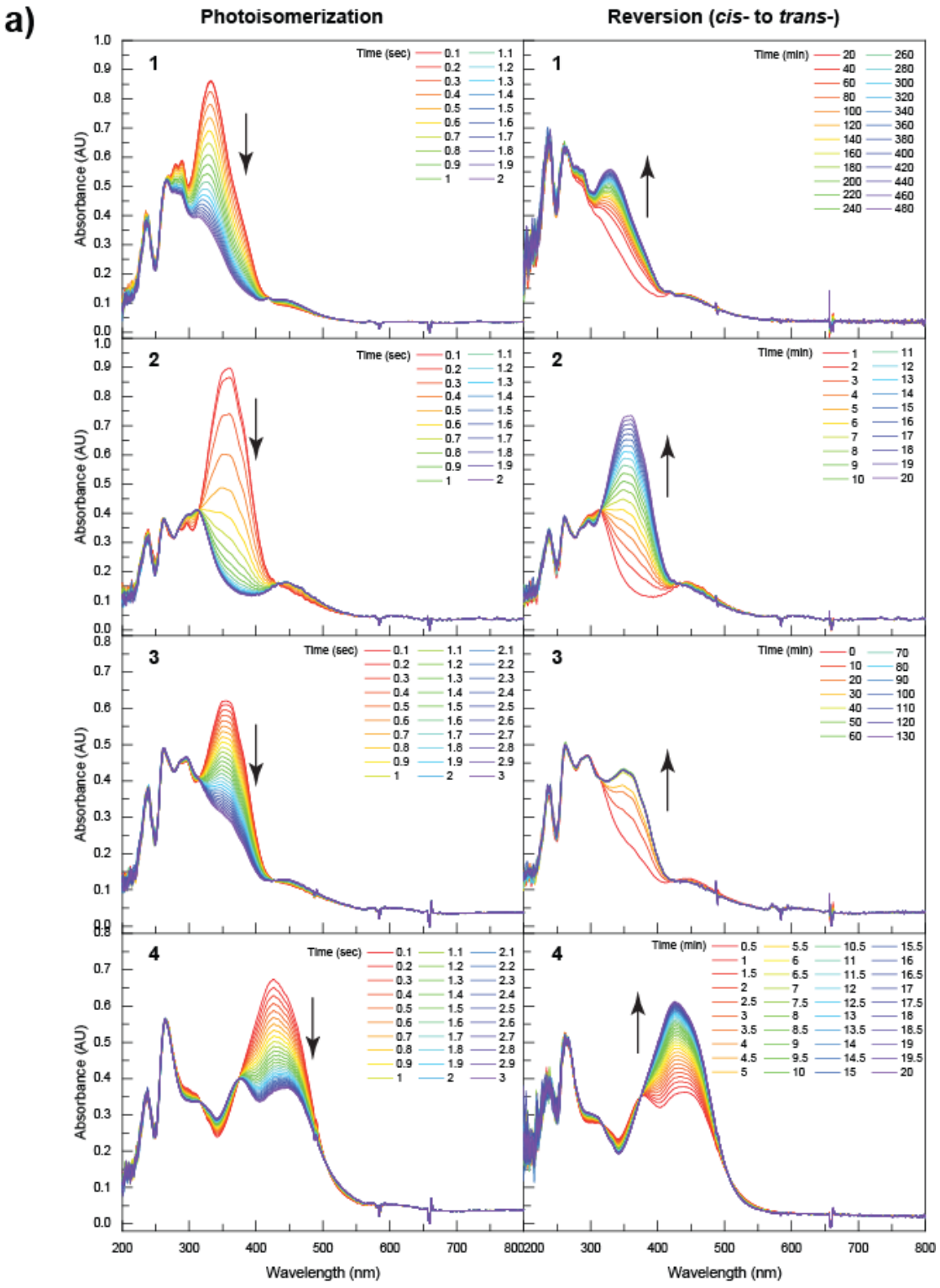
In 100 mL round bottom flask equipped with a stir-bar, 0.41 g (2.8 mmol) 2-naphthylamine is dissolved in 1.2 mL acetone. The solution is cooled to 0 °C in an ice bath and 1 mL 10 M HCl is added. To this solution, a pre-cooled aqueous solution (12 mL) of 0.41 g (6.0 mmol) $NaNO_2$ is added dropwise to convert the 2-naphthylamine into its corresponding diazonium salt. Following this, a pre-cooled aqueous solution (6 mL) of 0.16 mL (2.8 mmol) glacial acetic acid and 0.37 mL (2.9 mmol) dimethylaniline is added. The reaction is further stirred for 3 hrs. After warming up to room temperature, the reaction neutralized using 2 M NaOH and resulted solution is filtered over a frit equipped with a celite pad. The collected solid on the frit is washed with 30 mL DI water and extracted with 60 mL Et_2O. After evaporating the Et_2O over vacuum, the raw product is obtained. The raw product is further purified through a basic aluminum oxide silica gel column using 1:1 pentane/Et_2O eluent.

Yield: 266 mg, (34%)

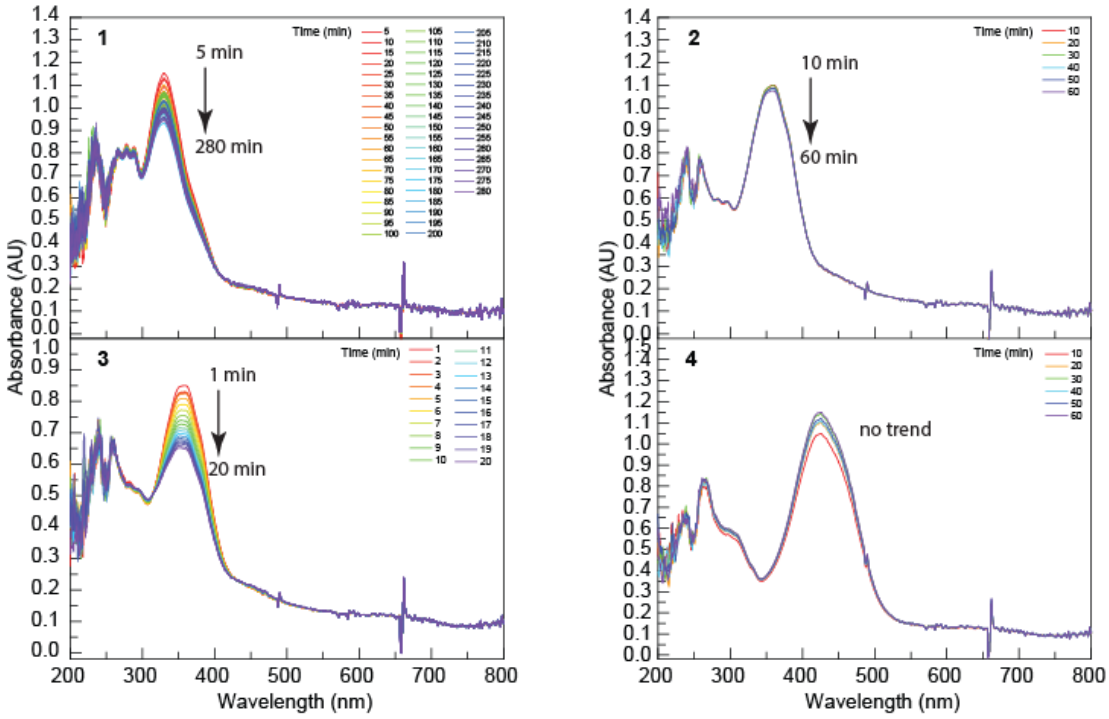


^{1}H-NMR (DMSO-D^{6}): 8.36 (1H), 8.09 – 8.03 (2H), 7.99 – 7.96 (2H), 7.91 (2H), 7.57 (2H), 6.88 (2H), 3.13 (2H)

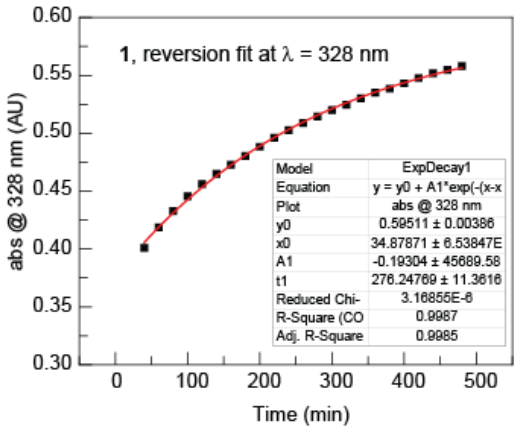
Photoisomerization and reversion of azo **1** - **4**:

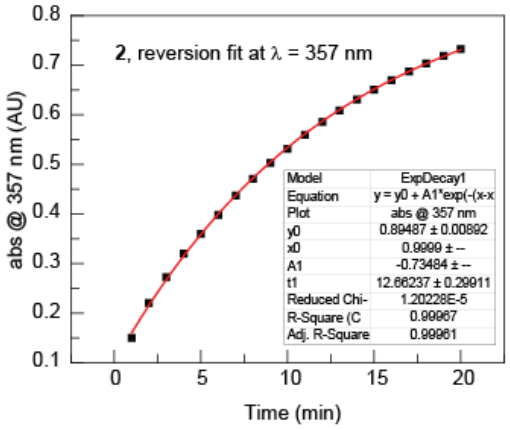


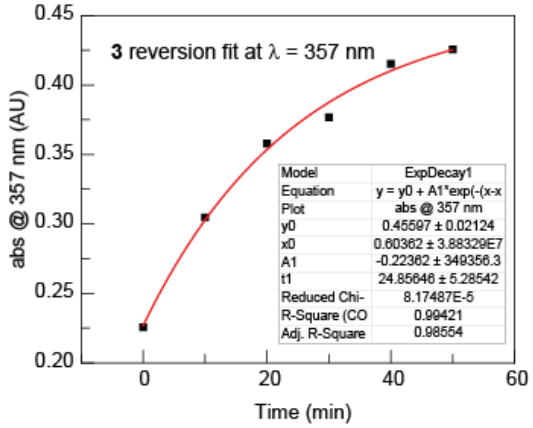
b)

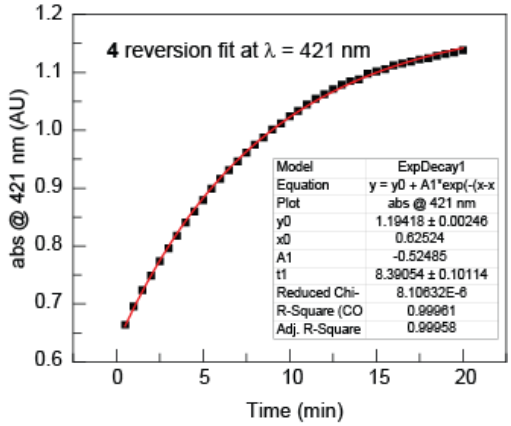

1
5 min
280 min
3
1 min
20 min
2
10 min
60 min
4
no trend
Time (min)
Absorbance (AU)
Wavelength (nm)

c)


1, reversion fit at λ = 328 nm
abs @ 328 nm (AU)
Time (min)
Model ExpDecay1
Equation y = y0 + A1*exp(-(x-x
Plot abs @ 328 nm
y0 0.59511 ± 0.00386
x0 34.87871 ± 6.53847E
A1 -0.19304 ± 45689.58
t1 276.24769 ± 11.3616
Reduced Chi- 3.16855E-6
R-Square (CO 0.9987
Adj. R-Square 0.9985


2, reversion fit at λ = 357 nm
abs @ 357 nm (AU)
Time (min)
Model ExpDecay1
Equation y = y0 + A1*exp(-(x-x
Plot abs @ 357 nm
y0 0.89487 ± 0.00892
x0 0.9999 ± --
A1 -0.73484 ± --
t1 12.66237 ± 0.29911
Reduced Chi- 1.20228E-5
R-Square (C 0.99967
Adj. R-Square 0.99961


3 reversion fit at λ = 357 nm
abs @ 357 nm (AU)
Time (min)
Model ExpDecay1
Equation y = y0 + A1*exp(-(x-x
Plot abs @ 357 nm
y0 0.45597 ± 0.02124
x0 0.60362 ± 3.88329E7
A1 -0.22362 ± 349356.3
t1 24.85646 ± 5.28542
Reduced Chi- 8.17487E-5
R-Square (CO 0.99421
Adj. R-Square 0.98554


4 reversion fit at λ = 421 nm
abs @ 421 nm (AU)
Time (min)
Model ExpDecay1
Equation y = y0 + A1*exp(-(x-x
Plot abs @ 421 nm
y0 1.19418 ± 0.00246
x0 0.62524
A1 -0.52485
t1 8.39054 ± 0.10114
Reduced Chi- 8.10632E-6
R-Square (CO 0.99961
Adj. R-Square 0.99958

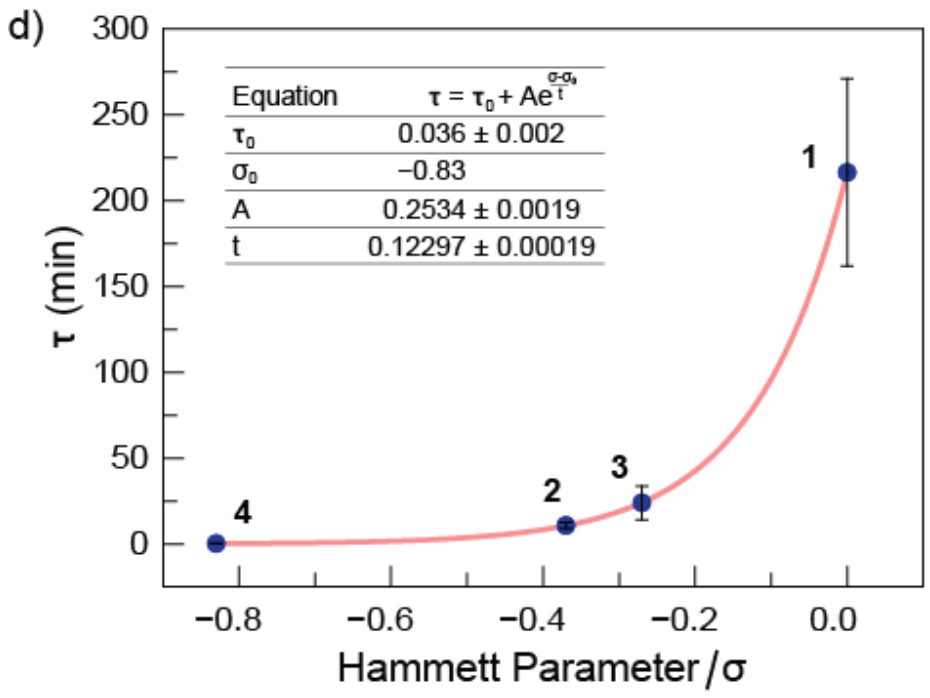


Figure S1. a) Photoisomerization and reversion spectra of azo 1 – 4. b) Partial photoisomerization of 1 – 4 occurs with the lamp of the UV-vis spectrometer. c) Kinetic traces of isomerization and reversion (with fitted lifetimes) d) Plot of reversion lifetime as a function of Hammett parameter.

The photoisomerziation spectra in Figure S1a show that all four azo dyes photoisomerize from the *trans* to *cis* configuration upon several minutes of irradiation with a UV LED (λ_{max} = 370 nm) at 155 mW for **1** – **3** or a blue LED (λ_{max} = 453 nm) at 120 mW for **4**. When illumination was stopped, the azo dyes reverted to the *trans* configuration over minutes (**2** and **4**) or hours (**1** and **3**). It appears that **1** and **3** do fully convert back to the *trans* configuration, however we determined that this results from the small amount of light originating from the spectrometer that maintains the *trans* → *cis* photoisomerization process. Figure S1b shows a "photoisomerization" experiment starting from the *trans* configuration using only the spectrometer light. **1** and **3** show detectable isomerization, however **2** and **4** are essentially unchanged. These results are consistent with the incomplete reversion seen in Figure S1a. Plotting the reversion progress over time in Figure S1c and fitting these data reveals reversion lifetimes for the azo **1** – **4**. Plotting the reversion lifetime as a function of Hammett parameter in Figure 1d shows that the dyes containing more electron donating substituents undergo faster *cis* → *trans* isomerization.

Absorption spectra for azo **1** - **4**:

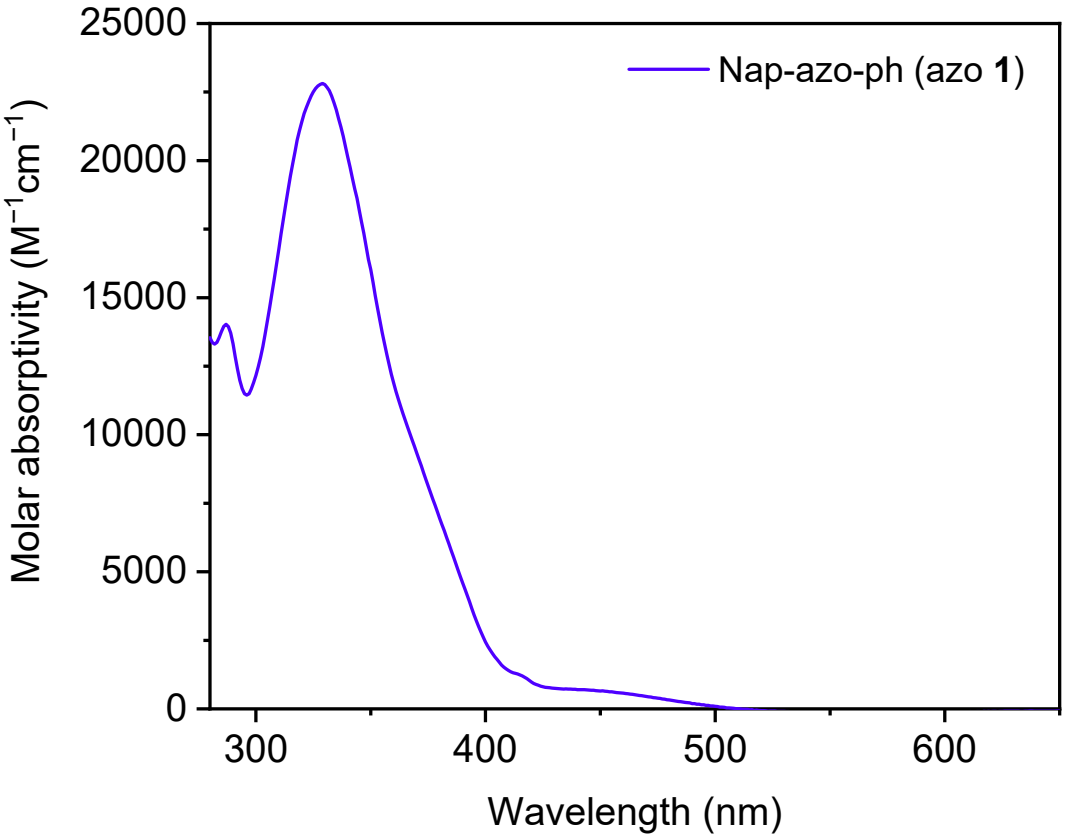


Figure S2. Molar absorptivity of azo 1 in acetonitrile.

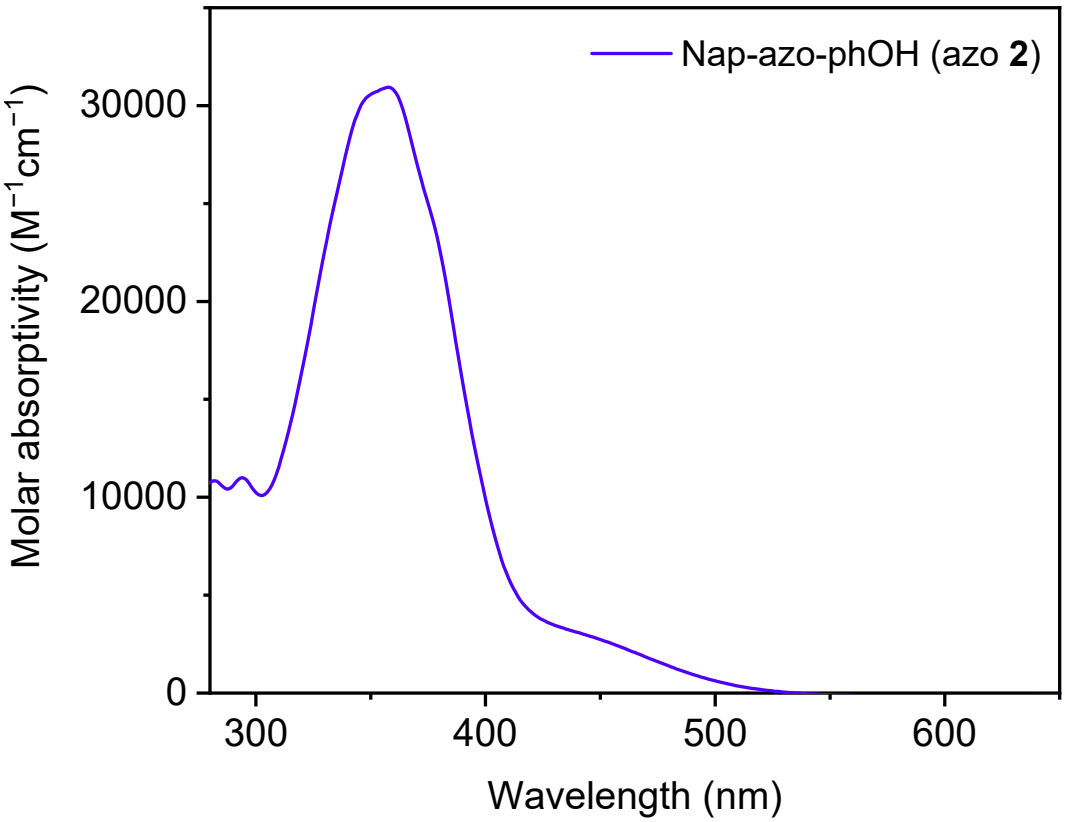


Figure S3. Molar absorptivity of azo 2 in acetonitrile.

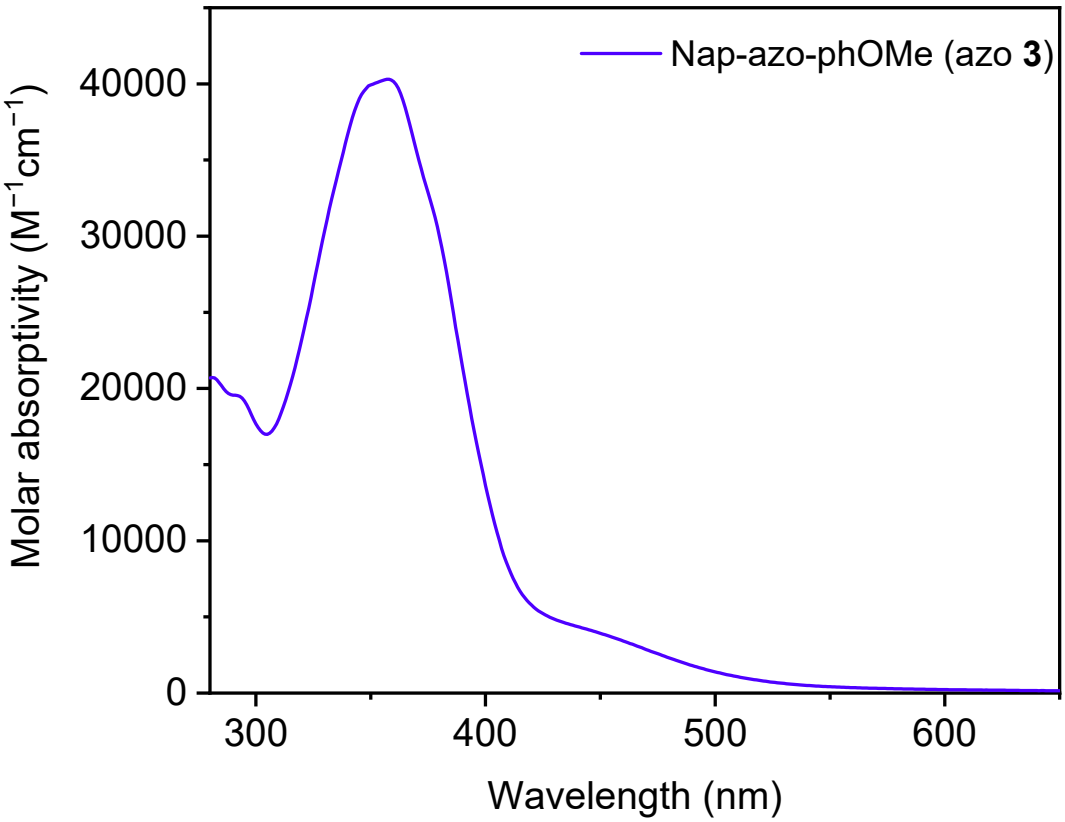


Figure S4. Molar absorptivity of azo 3 in acetonitrile.

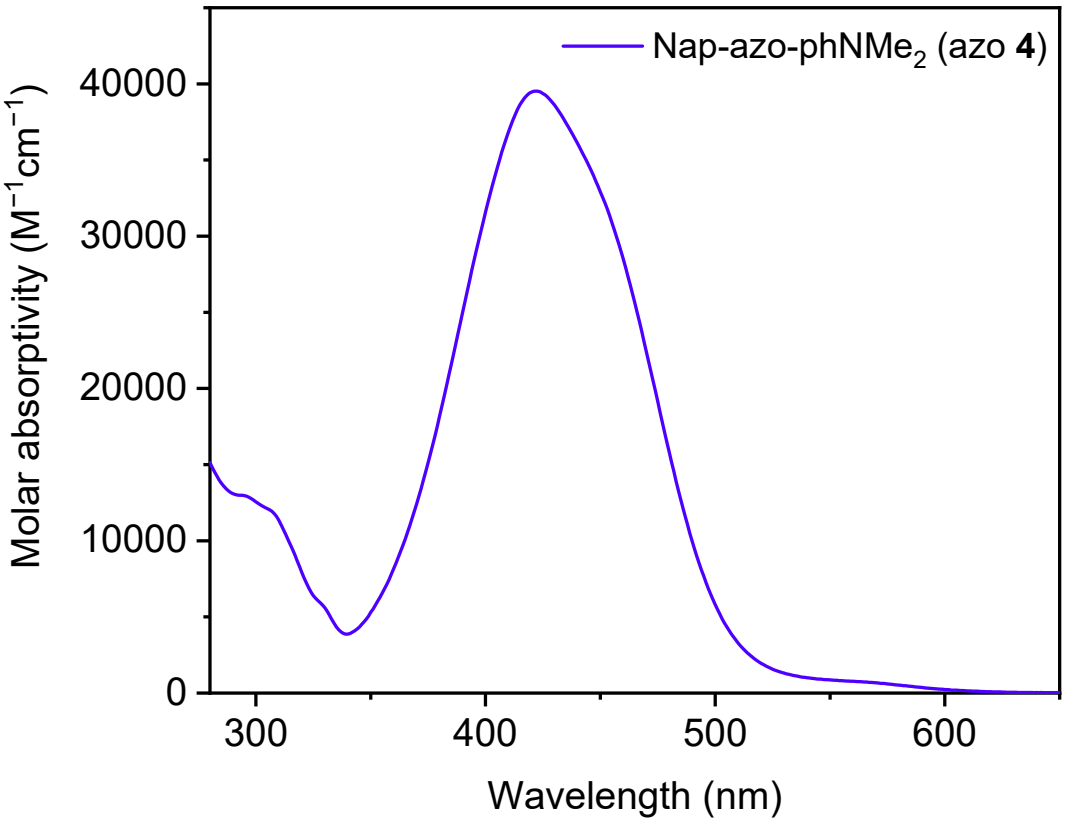


Figure S5. Molar absorptivity of azo 4 in acetonitrile.

Molecular orbital diagrams for azo **1** - **4**:

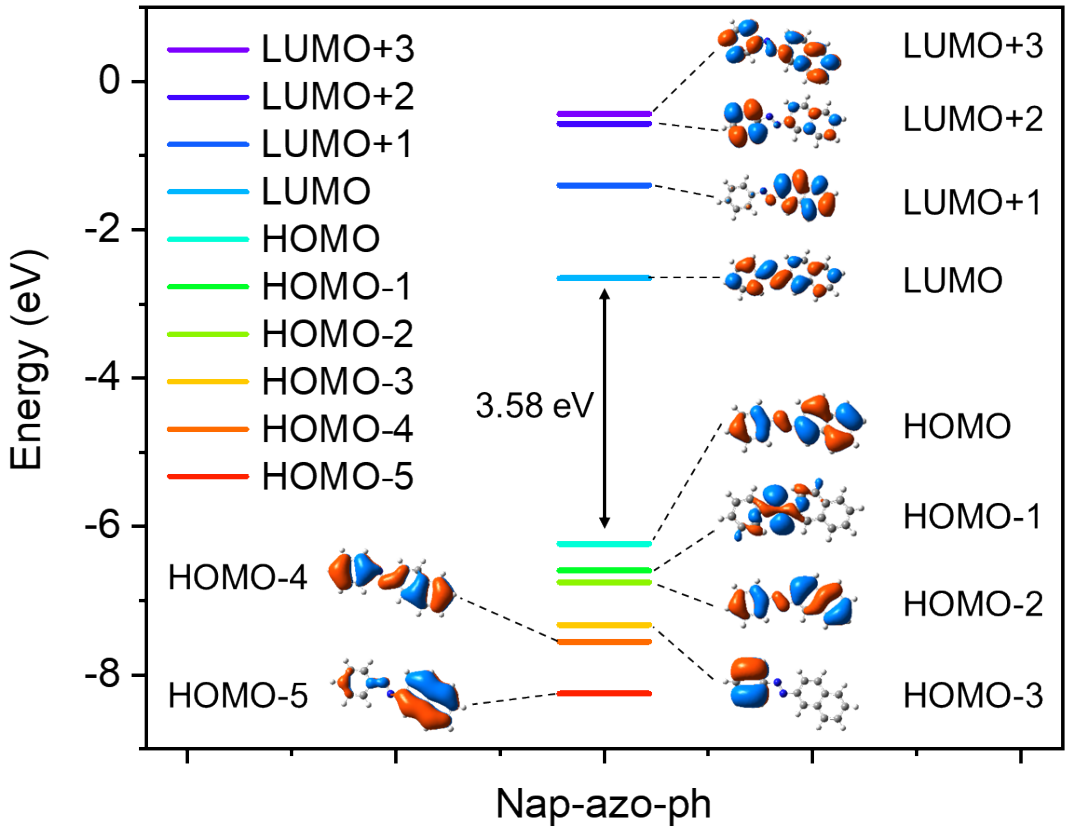


Figure S6. Molecular orbital diagrams for azo 1.

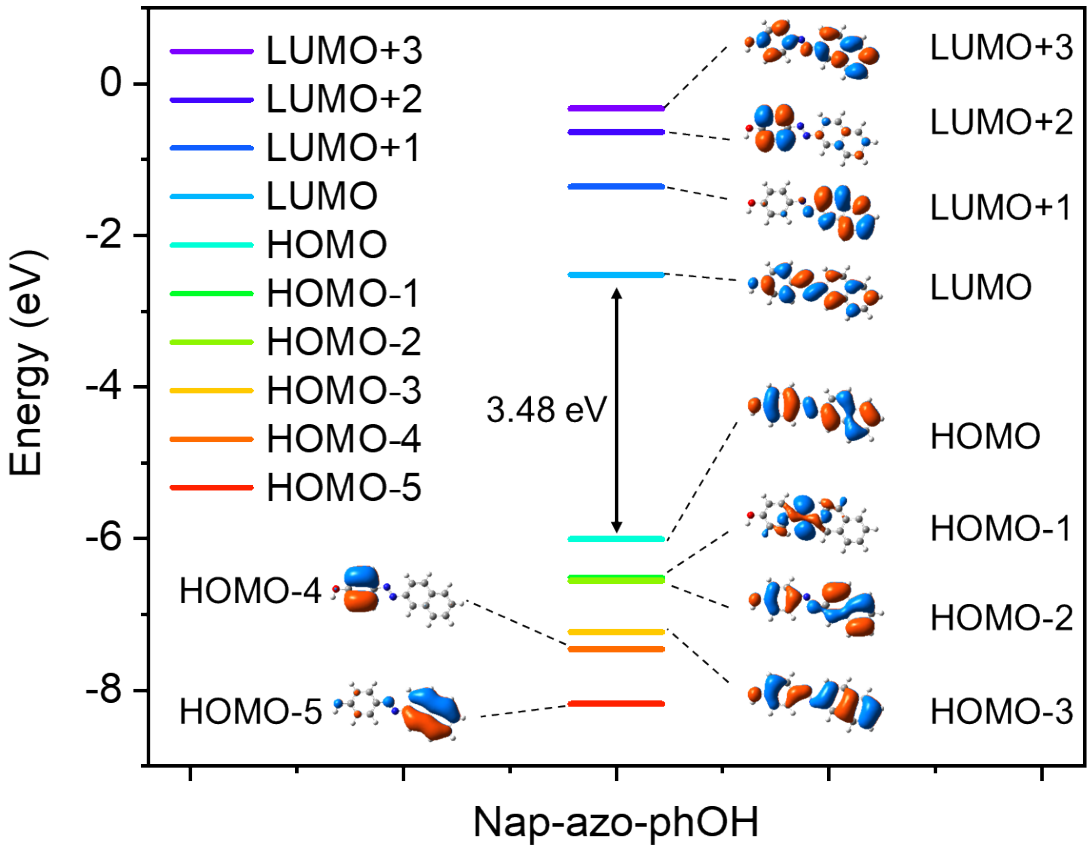


Figure S7. Molecular orbital diagrams for azo 2.

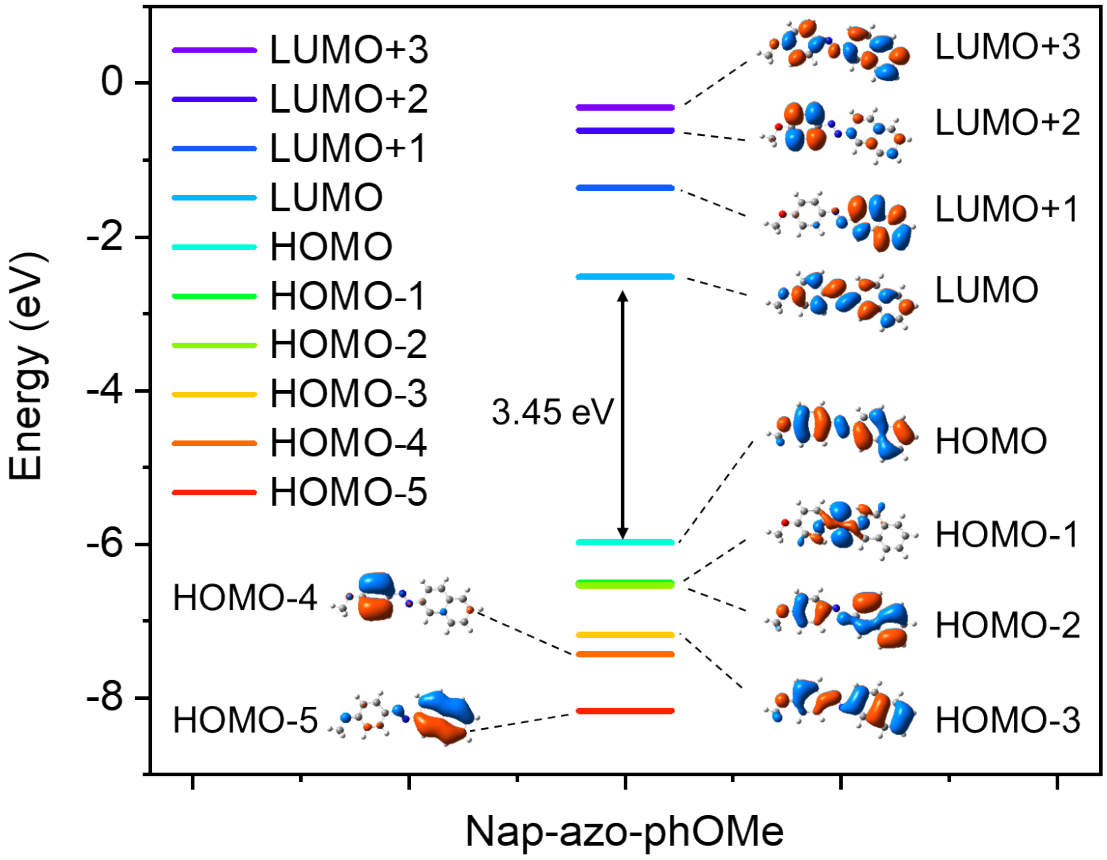


Figure S8. Molecular orbital diagrams for azo 3.

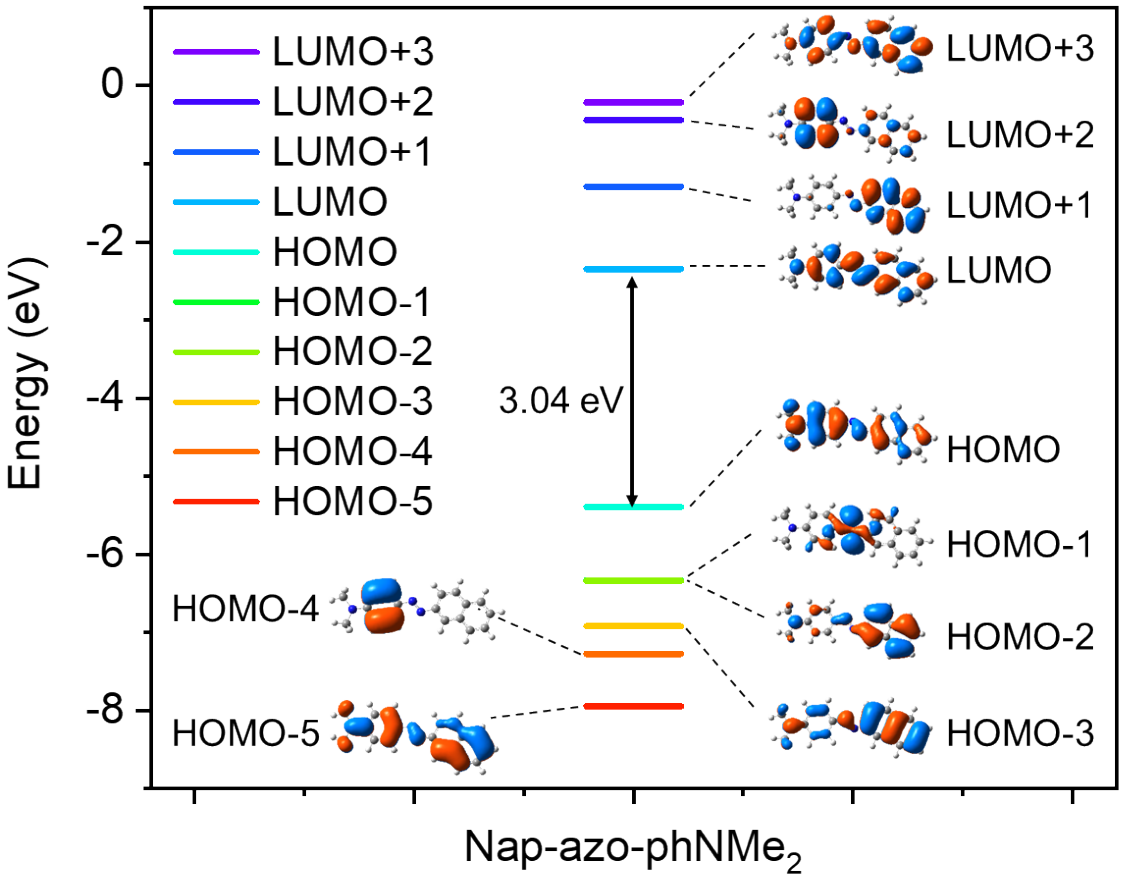


Figure S9. Molecular orbital diagrams for azo 4.

Transient Absorption Fitting

For each of the azo dyes **1** – **4**, we show the heat map of our TAS data before and after the chirp correction is applied in a single SI figure (Figures S10, S12, S14, S16). In a second figure (Figures S11, 13, 15 and 17), we show a multi-panel series of data, fits and analysis of the fits. We provide here a detailed explanation of each panel of figures S11, 13, 15 and 17 below.

In figures S11, 13, 15 and 17, the top left panel labeled “Raw Data Surface” is the original data for each dye after chip correction, and other data preparation are applied. Global analysis fitting is performed providing a model featuring DADS and associated lifetimes as shown in Figure 5 in the text (and in the bottom left panel of the SI figure). Combining the DADS, lifetimes, time zero, and IRF produced by the fit model, the TAS surface is “reconstructed”. The reconstructed data surface is shown in the top middle panel, labeled “Reconstructed Surface”. From this surface a selection of spectra are presented in the bottom middle panel labeled “Reconstructed Representative Spectra”. Finally, the original data is compared to the reconstructed data in the right most column. Top right panel is a heat map of the residual between the original data surface and the reconstructed surface. The residual surface was used to evaluate the global analysis fit. Fit models were selected or modified in order to reduce or remove structure from the residual surface. Residual surfaces lacking distinct features and more closely resembling noise, resulted in a favoring of that fit. The root mean square error (RSE) value was calculated for each residual surface as a measure of how well that fit matched the data surface. This value was also used to identify fit improvements when differences became difficult to identify visually. RSE values were only used to judge improvements to fits for the same data surface, and were not assessed between data surfaces. On the lower right panel, single wavelength TAS data at a range of lifetime (dotted data points) are displayed. Solid lines representing the single wavelength traces constructed using the fitted lifetimes from global analysis overlay the data. This plot is another method of evaluating the fits obtained using global analysis.

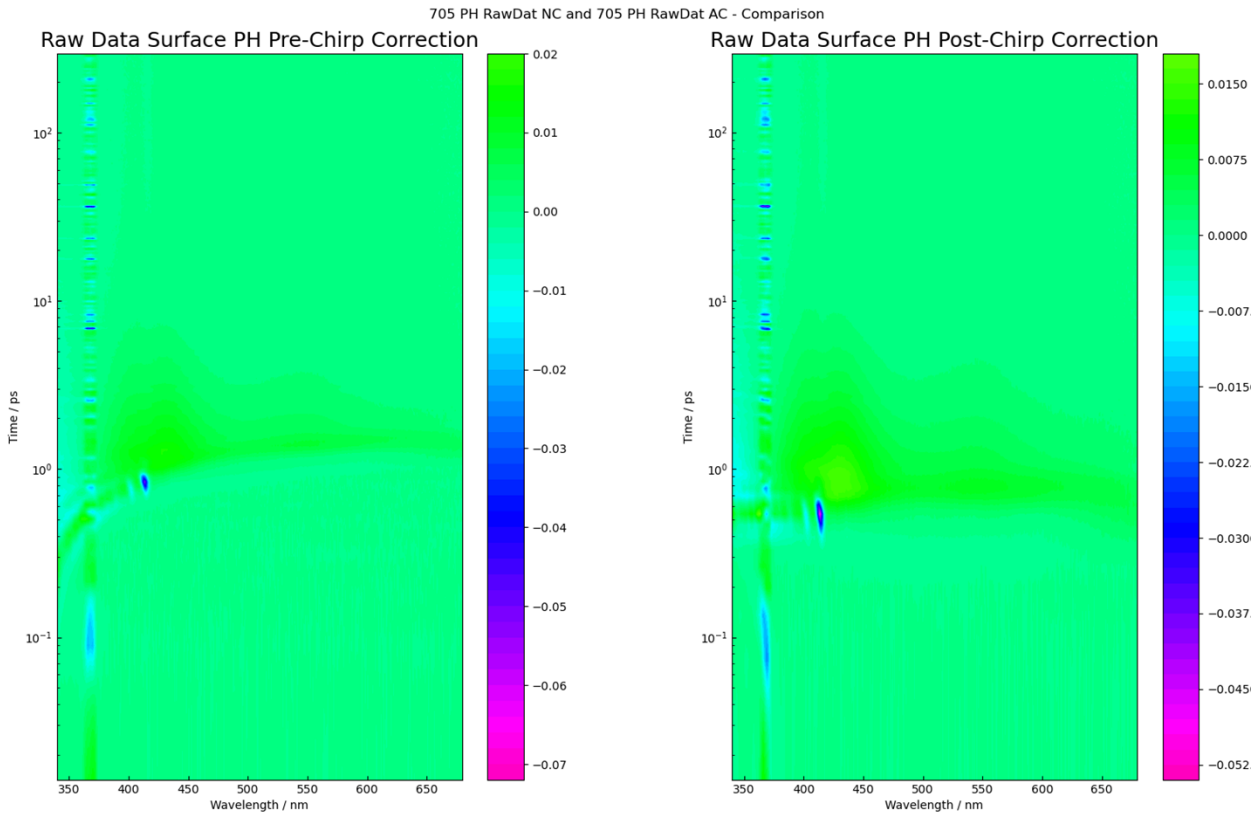


Figure S10. Heat map of 1 TAS a) before b) after chirp correction.

(left) Raw pump-probe heat map at 370 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. (right) corrected linear time pump-prove map at 370 nm excitation for the first 500 ps. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

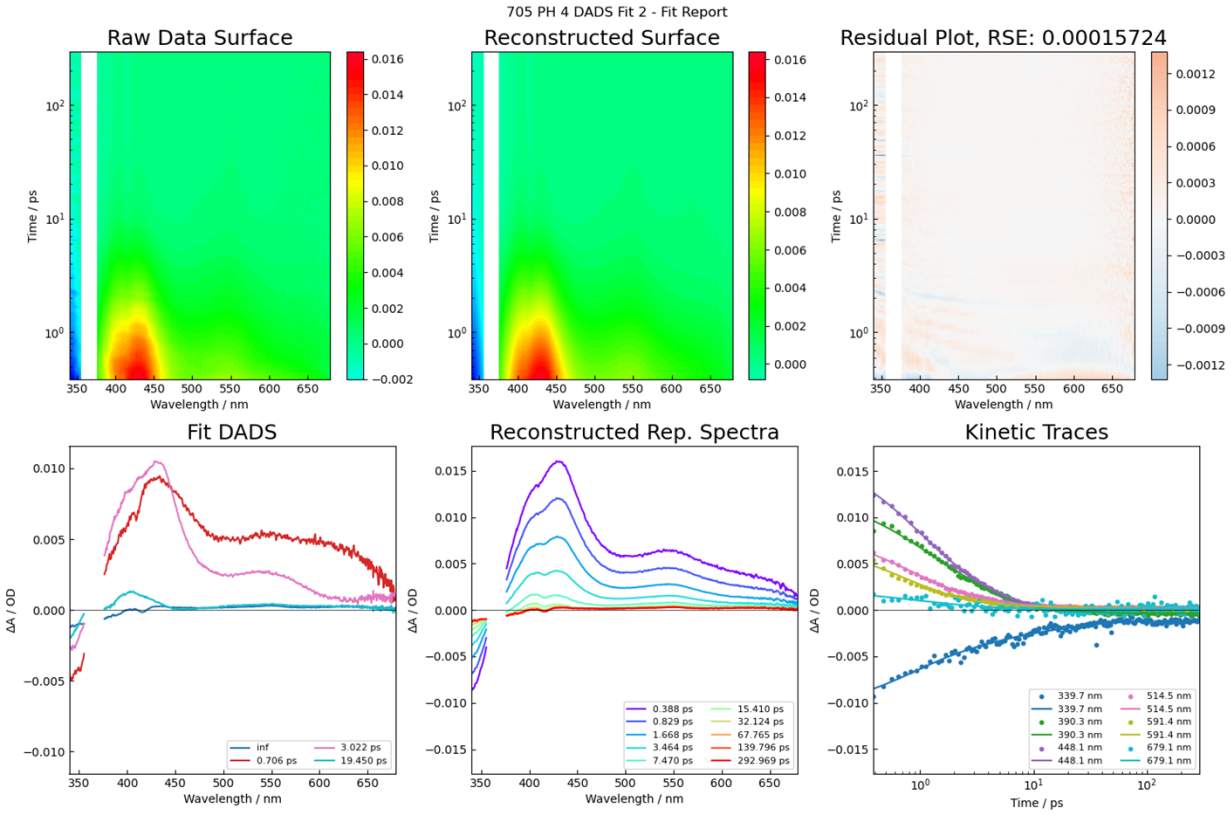


Figure S11. TAS heat map, global analysis fitting and analysis of fit for 1 collected at 370 nm excitation.

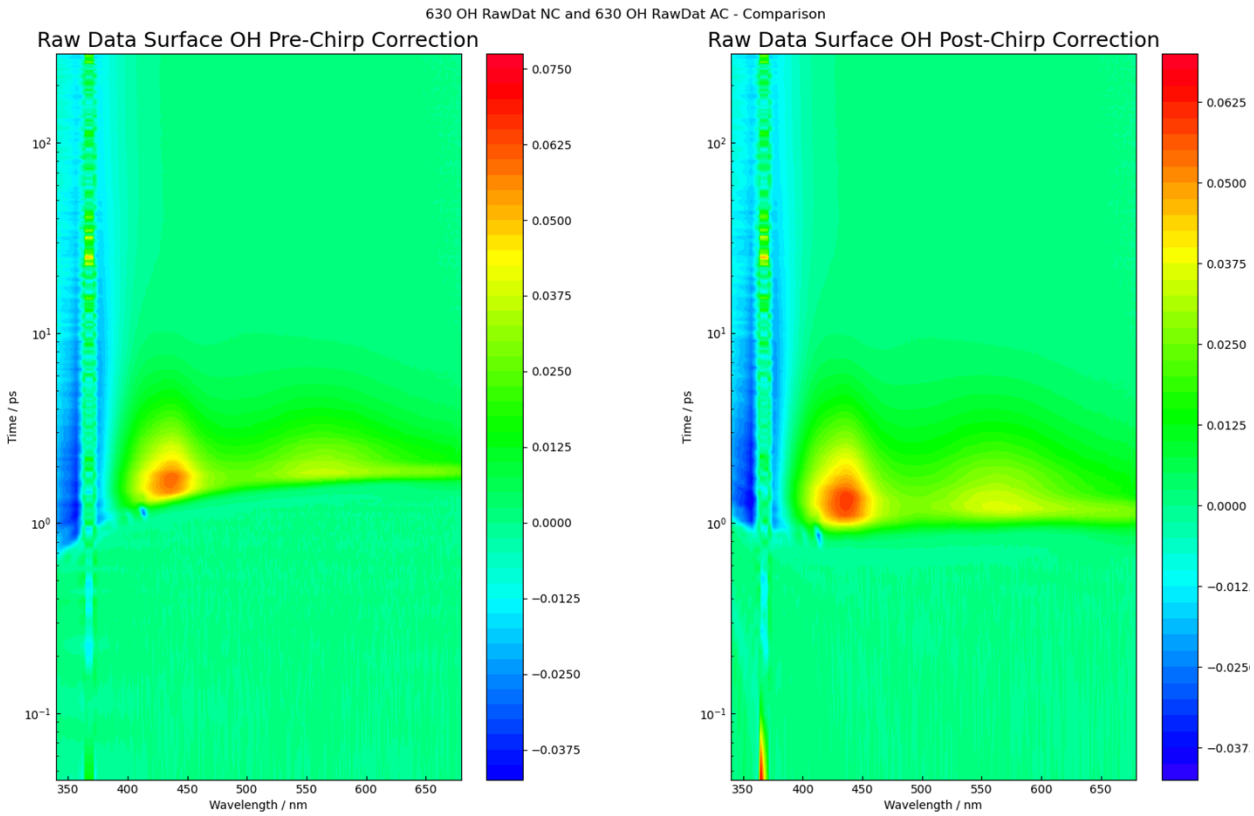


Figure S12. Heat map of 2 TAS a) before b) after chirp correction.

(left) Raw pump-probe heat map at 370 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. (right) corrected linear time pump-prove map at 370 nm excitation for the first 500 ps. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

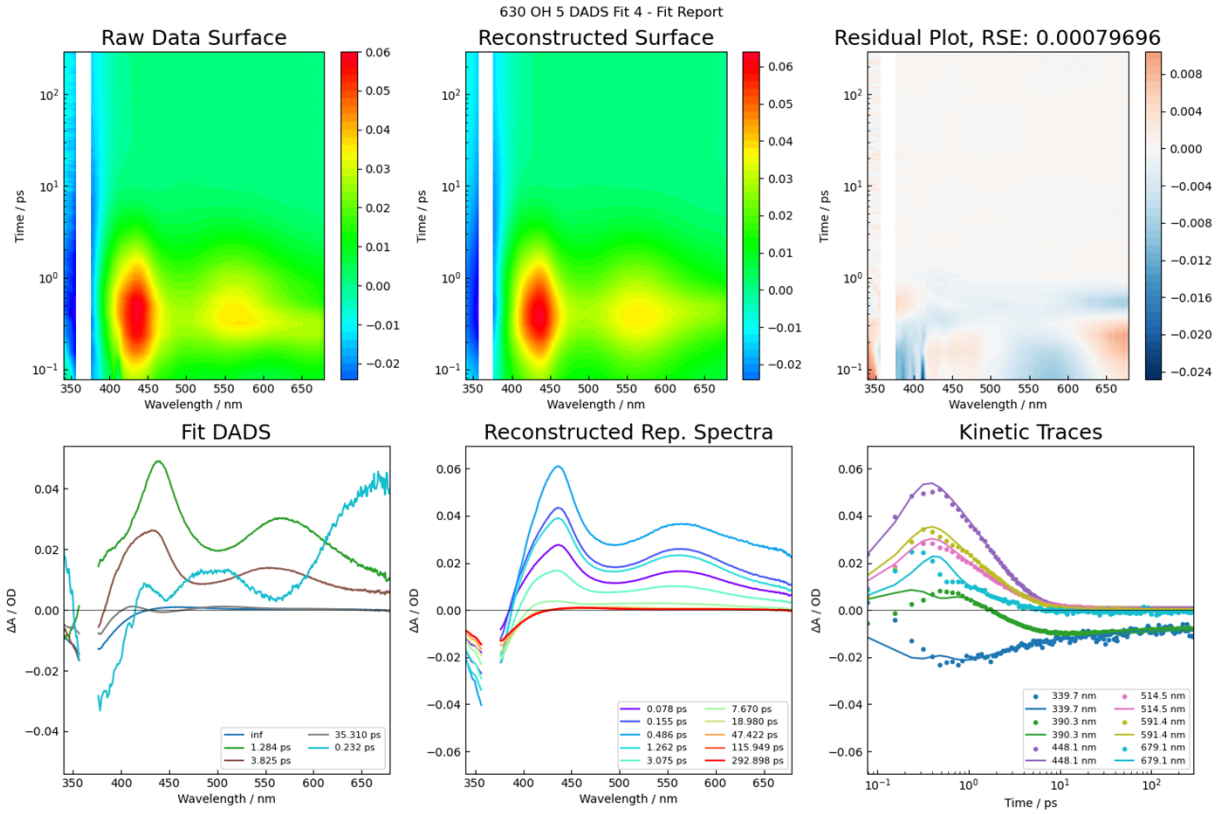


Figure S13. TAS heat map, global analysis fitting and analysis of fit for 2 collected at 370 nm excitation.

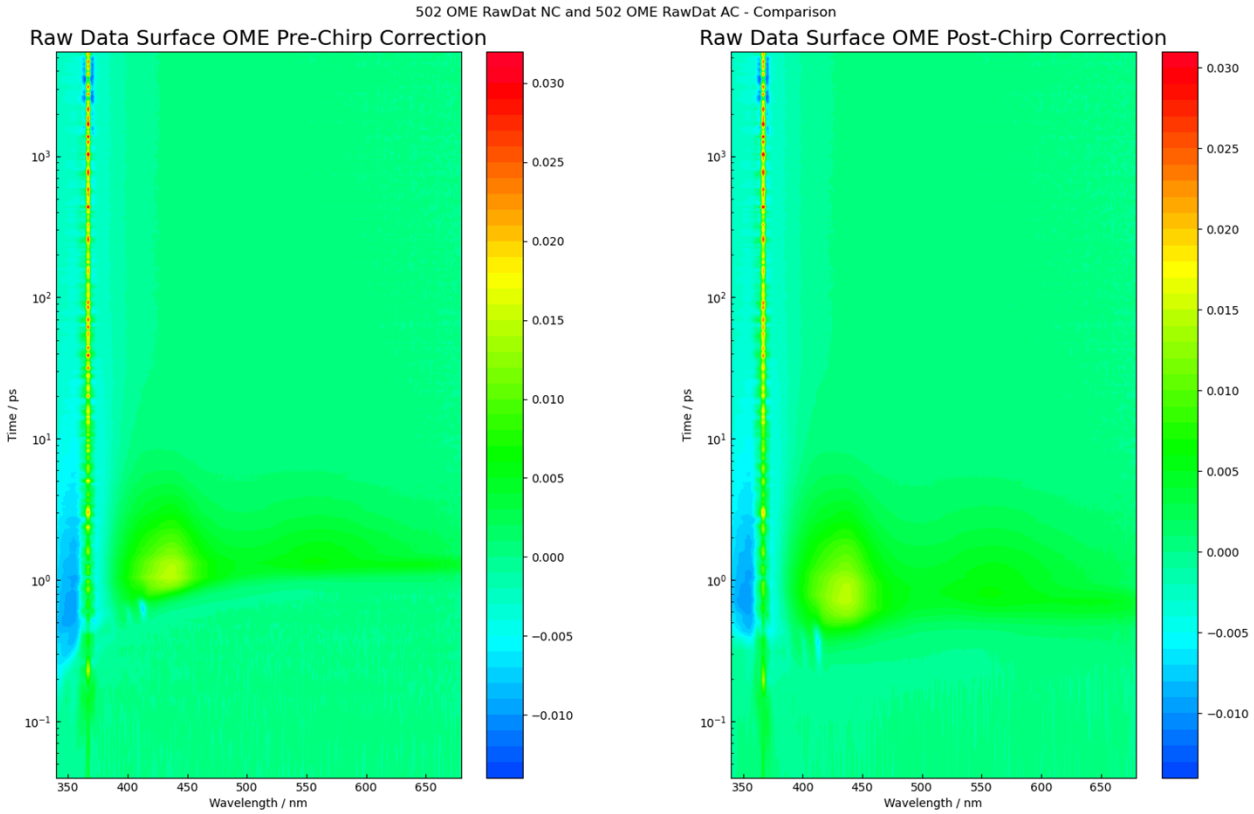


Figure S14. Heat map of 3 TAS a) before b) after chirp correction.

(left) Raw pump-probe heat map at 370 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. (right) corrected linear time pump-prove map at 370 nm excitation for the first 500 ps. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

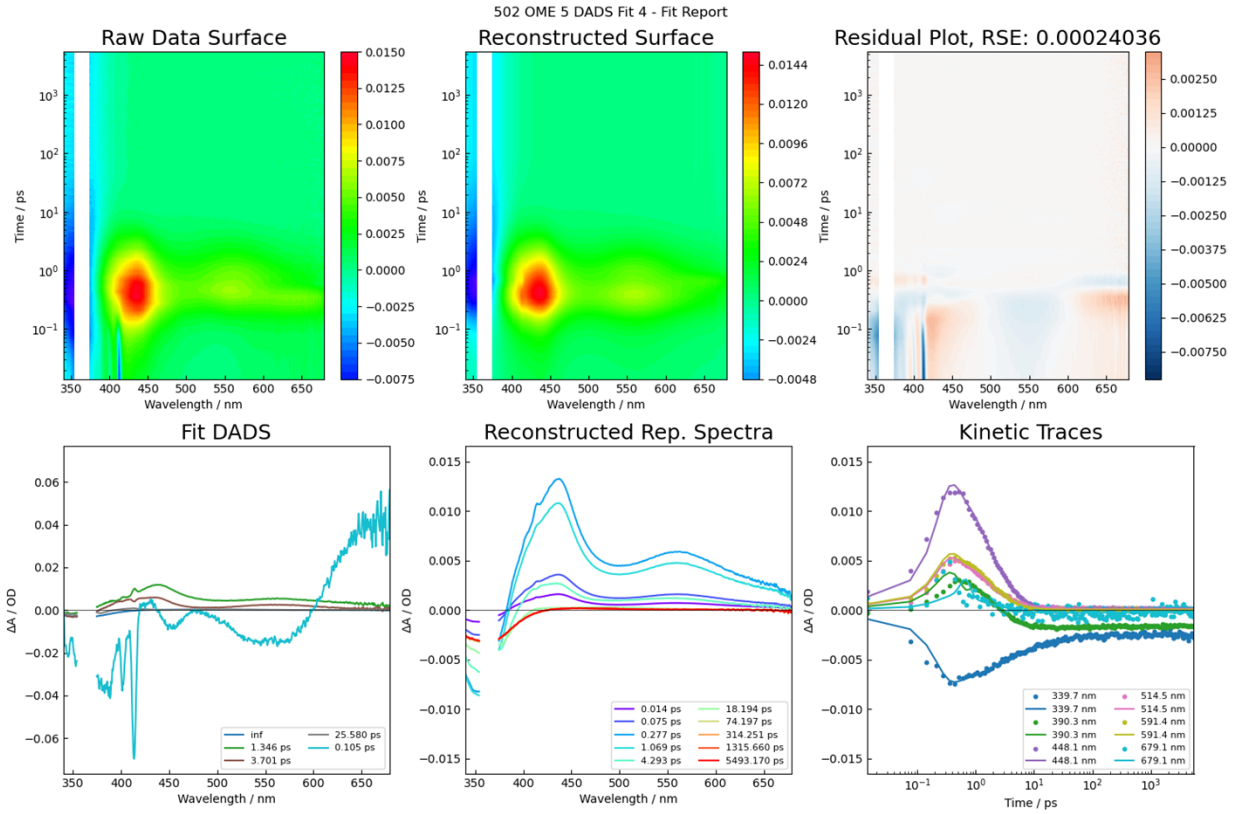


Figure S15. TAS heat map, global analysis fitting and analysis of fit for 3 collected at 370 nm excitation.

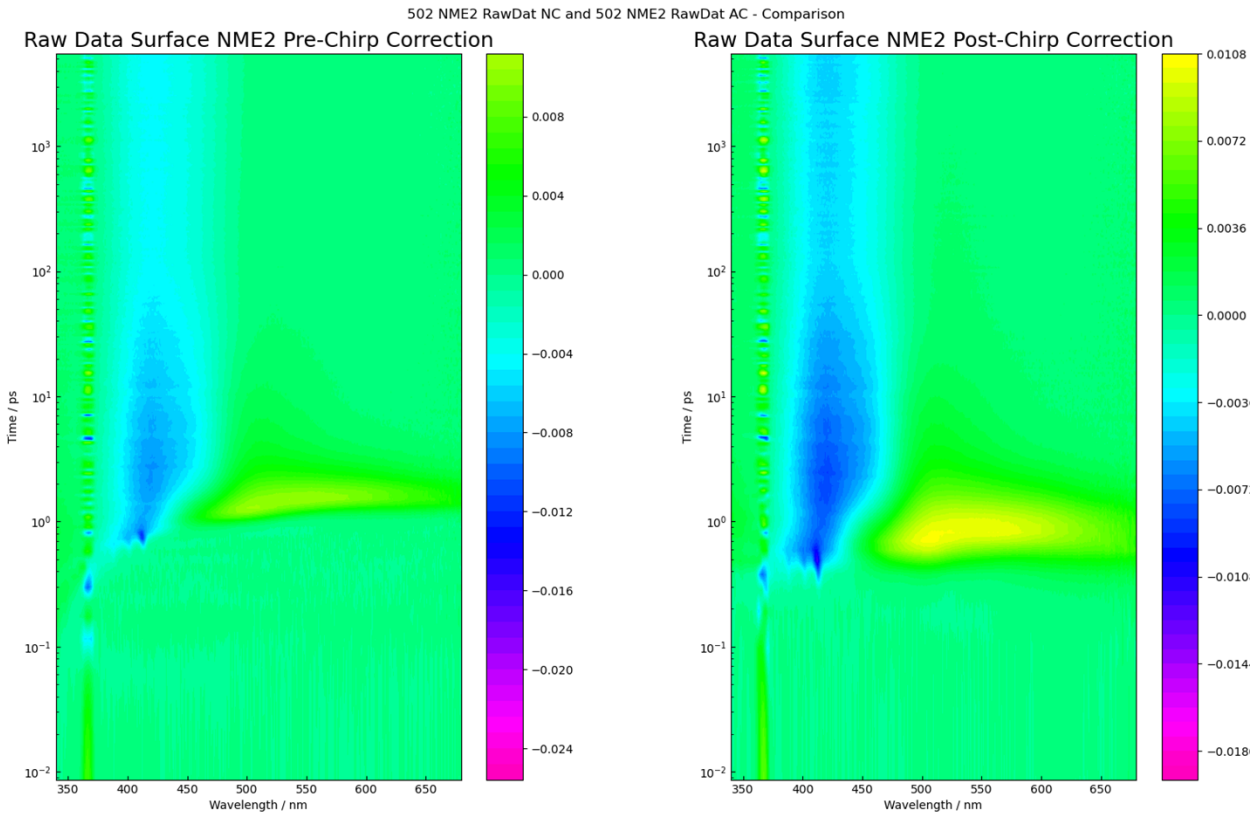


Figure S16. Heat map of 4 TAS a) before b) after chirp correction.

(left) Raw pump-probe heat map at 370 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. (right) corrected linear time pump-prove map at 370 nm excitation for the first 500 ps. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

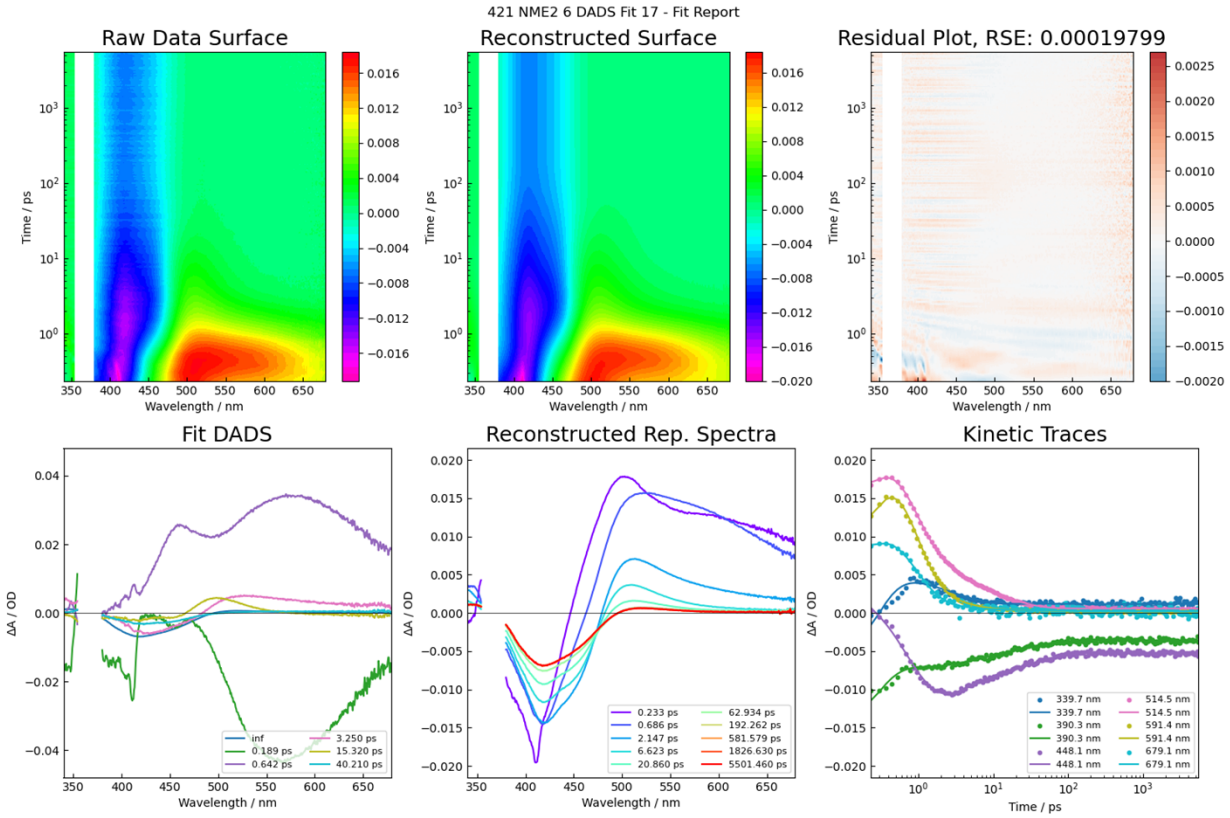
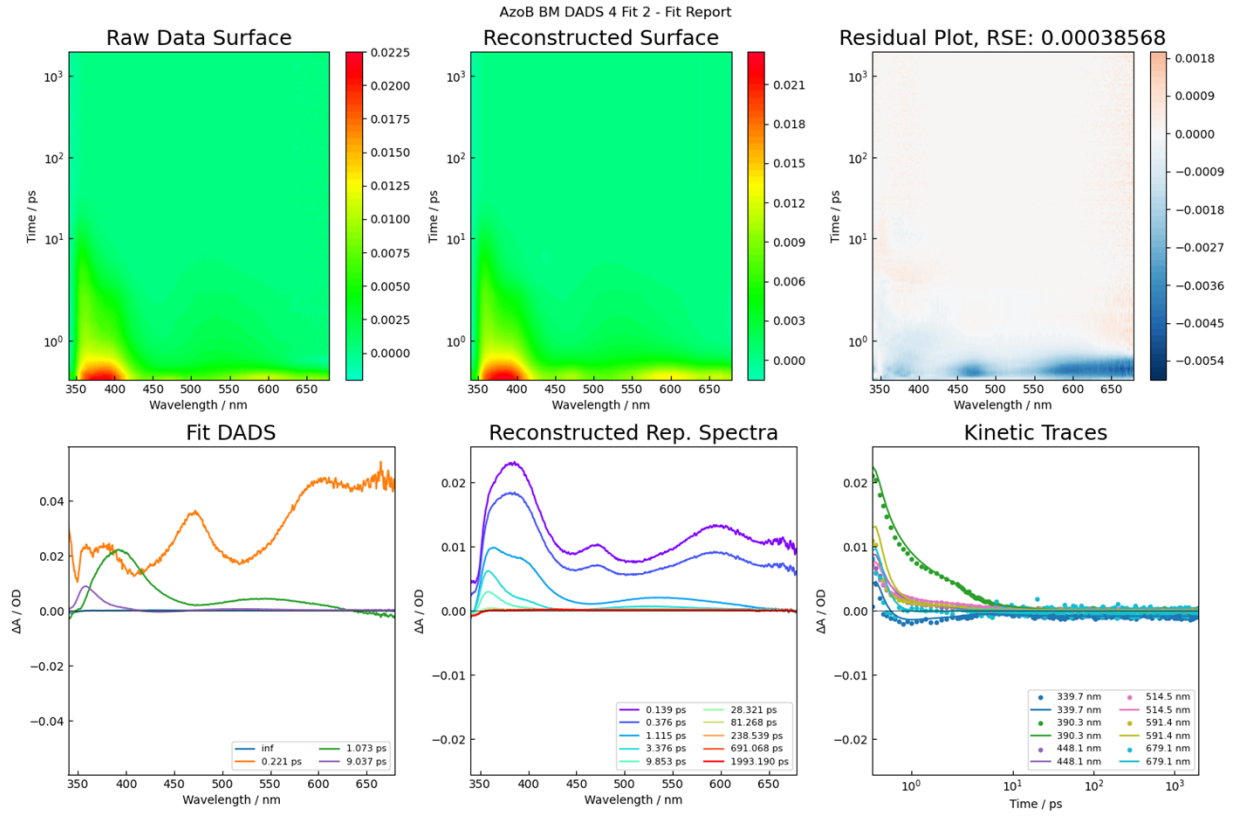
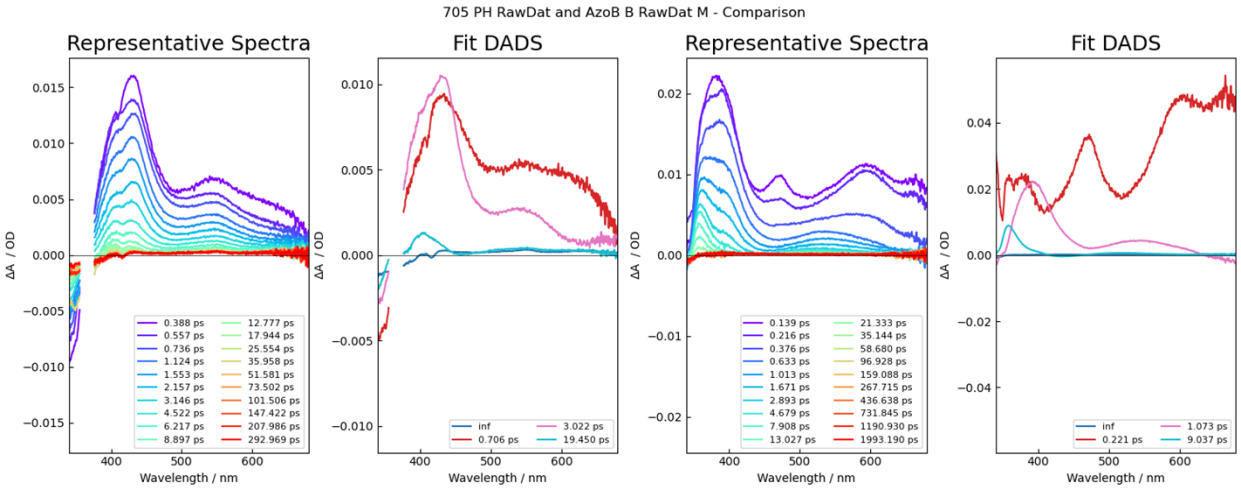


Figure S17. TAS heat map, global analysis fitting and analysis of fit for 4 collected at 370 nm excitation.

Fit of azobenzene data taken on our instrument



Comparison of 1 (left two panels) and azobenzene (right two panels) showing representative spectra and DADS



Schematic Diagram of the Relaxation of azo 1 – 3 , 4, and azobenzene.

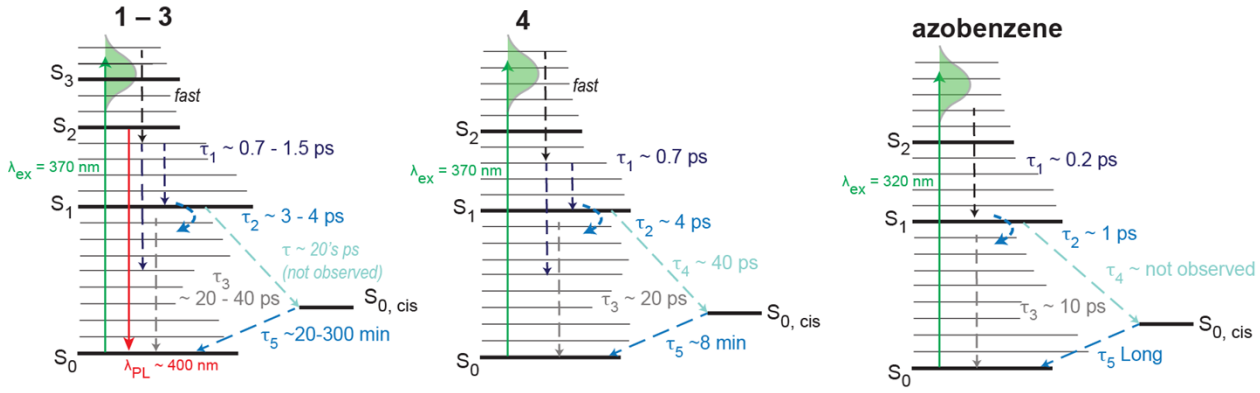


Figure S18. Comparison of azobenzene with 1-4 on our TAS instrumentation.

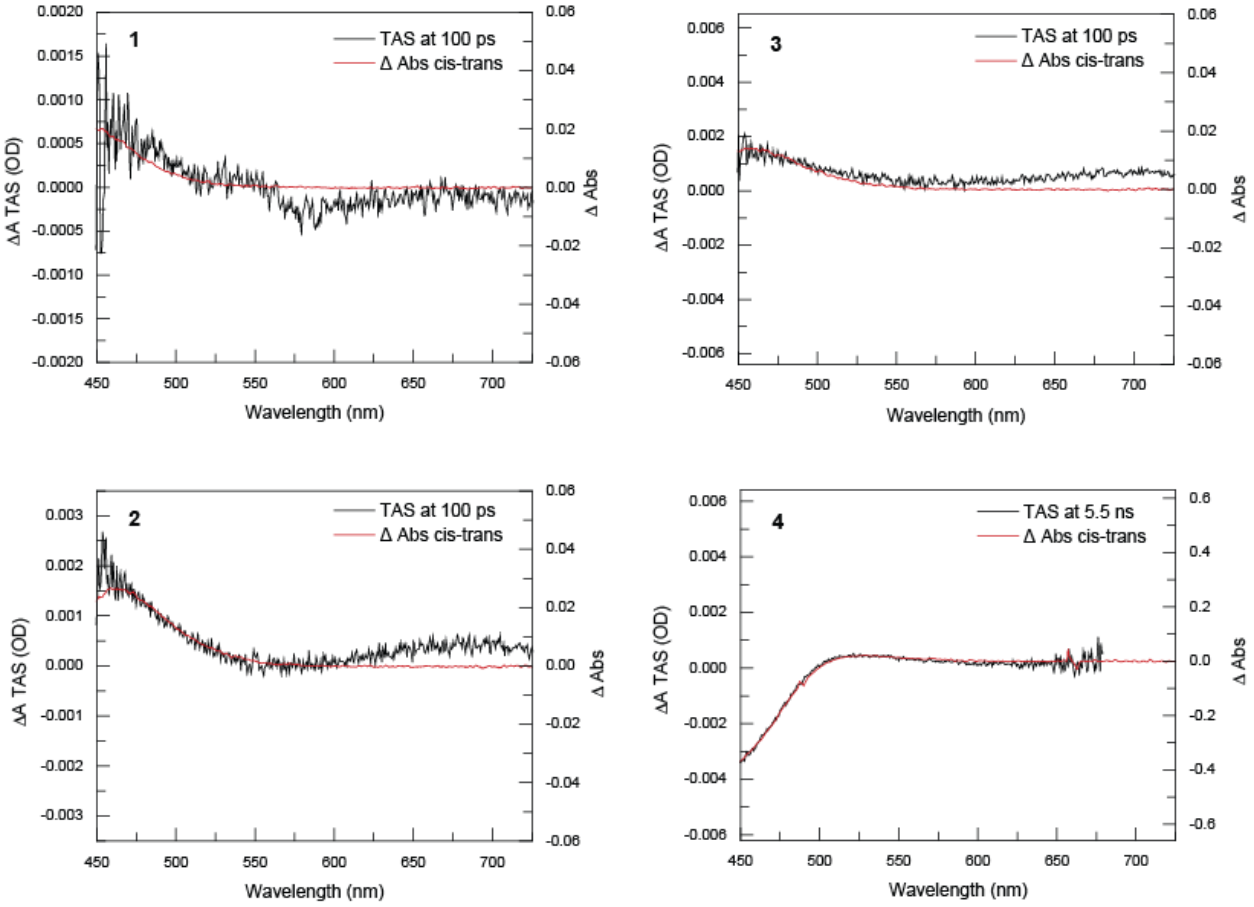


Figure S19. Comparison of TAS residual spectrum with the difference of the steady-state absorption spectra of the *trans*- and *cis*- isomer of 1-4.

Triplet Potential Energy Curves of Azo **1** and **4**

In order to evaluate the potential for intersystem crossing into the triplet excited state manifold, we first evaluated the alignment of the vertical Frank-Condon singlet and triplet excited-state surfaces (center line Figure S20). Assuming that the potential intersystem crossing happens rapidly, with a typical lifetime of several picoseconds, spin-orbit-couplings (SOC) between singlet and triplet excited states at the ground state minimum geometry provide a quantitative measure (Table S13) of the probability for singlet excited states to cross into the triplet manifold.

In order to identify possible deactivation mechanisms of the initially generated excited state singlets through a triplet intermediate, the spin orbit coupling between the excited singlets (S_1 and S_2) with the triplets in the same energy region ($T_1 - T_3$) were calculated (center line in Figures S20 and S21). The SOC (Table S13) between S_1 and T_1 of azo **4** is 4.1 cm^{-1}, four times the coupling in azo **1 – 3** (0.98 – 1.04 cm^{-1}), indicating a fast, low-energy pathway to generate a triplet. However, the SOC between S_1 and T_3 is high for all the dyes (3.19 – 4.97 cm^{-1}), indicating several possible intersystem crossing pathways to generate triplets ($T_1 - T_3$) from singlet excitations ($S_1 - S_2$). Therefore, a possible photophysical fate of azo dyes **1 – 4** is formation of a triplet state.

Another consideration in a triplet mediated deactivation pathway is the strength of the coupling of the triplets back to the ground state surface. The SOC constants between T_1 and S_0 ($\langle S_0|\hat{H}_{SOC}|T_1\rangle$) are all close to 38 cm^{-1} for azo **1 – 3**, more than two orders of magnitude larger than azo **4** (SOC 0.07 cm^{-1}). Inversely, the SOC between T_2 and S_0 of azo **1 – 3** (0.09 – 0.28 cm^{-1}) are two orders of magnitude smaller than azo **4** (37.2 cm^{-1}). The $\langle S_0|\hat{H}_{SOC}|T_3\rangle$ of all four azo dyes are low (0.22 – 0.24 cm^{-1}). This indicates a rapid $T_1 \rightarrow S_0$ ground state recovery in azo **1 – 3** and a slower $T_1 \rightarrow S_0$ ground state recovery in azo **4**. Additionally, in azo **4** direct intersystem crossing pathways are available to generate T_1 from the singlet excited manifold ($S_1 \rightarrow T_1$, *vide supra*). While the $T_2 \rightarrow S_0$ intersystem crossing in azo **4** has strong SOC, it would be competing with faster internal conversion of the exited state population to the lowest energy triplet (T_1). Thus a possible ground-state recovery pathway in **4** could be through the lowest energy (T_1). Interestingly, any perturbation of the structure, along both the torsional and inversion surfaces, increase the $\langle S_0|\hat{H}_{SOC}|T_1\rangle$.

While the triplets generated in azo **1 – 3** are unlikely to be long-lived, due to fast deactivation back to the ground state, in azo **4** the lowest triplet excited state could be stable with a longer lifetime, due to poor SOC back to the ground state. This difference in $\langle S_0|\hat{H}_{SOC}|T_1\rangle$ is readily apparent in the dramatic differences in the spin density of azo **1 – 3** vs. azo **4**

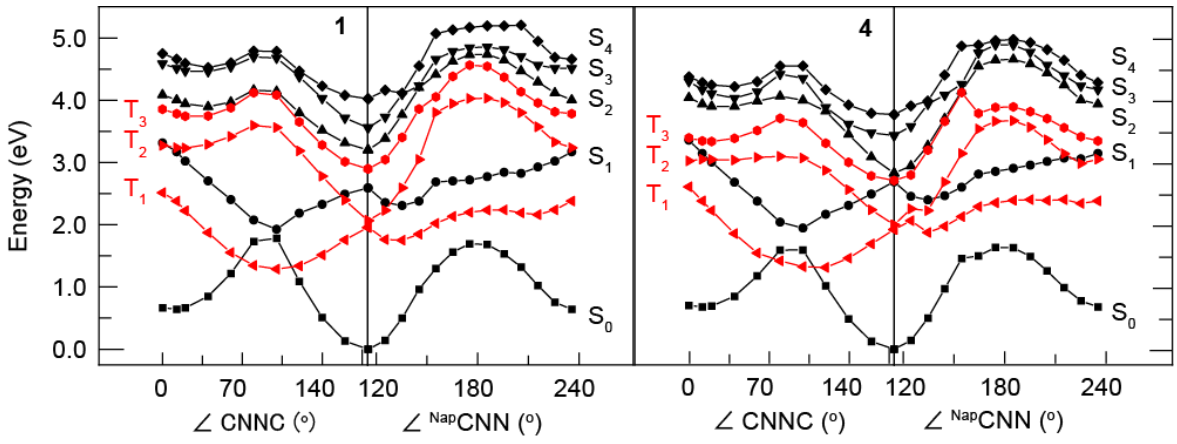


Figure S20. Singlet and triplet PECs below 5 eV in energy along the torsional (∠CNNC) and inversion (∠^{Nap}CNN) S_0 trans-cis isomerization. The excited state (TDDFT) surfaces above each shown point are plotted and like excited states are connected with lines (black singlets and red triplets). B3LYP/6-311G(d,p)/PCM(ACN). The relaxed triplet (T_1) surfaces are shown in Figure S39-40.

(Figure S36). In particular, the T_1 state in azo **1 – 3** is a mixed n and π density, while in azo **4** the density only has π character.

We have carried out several experiments on azo dyes **3** and **4** within our laboratory and thus far have been unable to collected experimental evidence of the triplet. We have thus far been unable to detect low-energy phosphorescence from either azo dye that would directly verify the triplet formation and decay. Additionally, we have attempted to sensitize oxygen and record the emission spectrum for singlet oxygen emission. Both of these methods likely fail because of the low predicted energy of the triplet. Based on DFT (Figure S20) if the triplet emission occurred from the Franck-Condon state, emission would be predicted to occur between 620 nm – 830 nm (~2.0 eV), which is already difficult to detect and partially outside the window of our spectrometer. If, however, the emission occurred from a relaxed triplet, the energy transfer to triplet oxygen forming singlet oxygen is energetically uphill (see Figure S20, ∠CNNC of 90° – 100°) and we would expect to see no phosphorescence or sensitization of oxygen. Further, we attempted to react **3** and **4** with the radical TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) to form a photo-induced radical-initiated product. These reactions have thus far yielded no conclusive evidence of triplet formation. In these experiments, the extremely short lifetimes of the azo dyes are a major impediment to bimolecular reactivity.

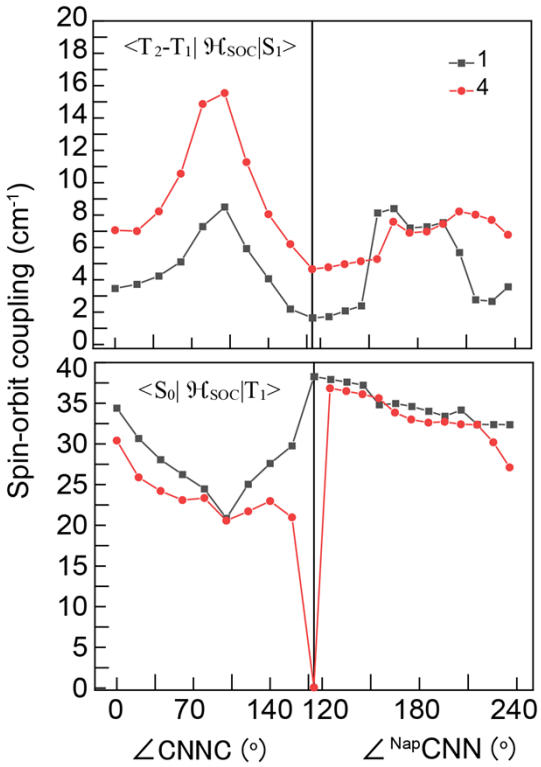


Figure S21. Spin orbit coupling between the first singlet and first two triplet excited states (<T_2-T_1| $\mathfrak{H}_{SOC}$|S_1> (top) and the lowest triplet and ground state (<S_0| $\mathfrak{H}_{SOC}$|T_1> (bottom) along the torsional (∠CNNC) and inversion (∠^{Nap}CNN) trans-cis isomerization. B3LYP/6-311G(d,p)/PCM(ACN).

S_0 geometries and transition states of Azo **1 - 4**

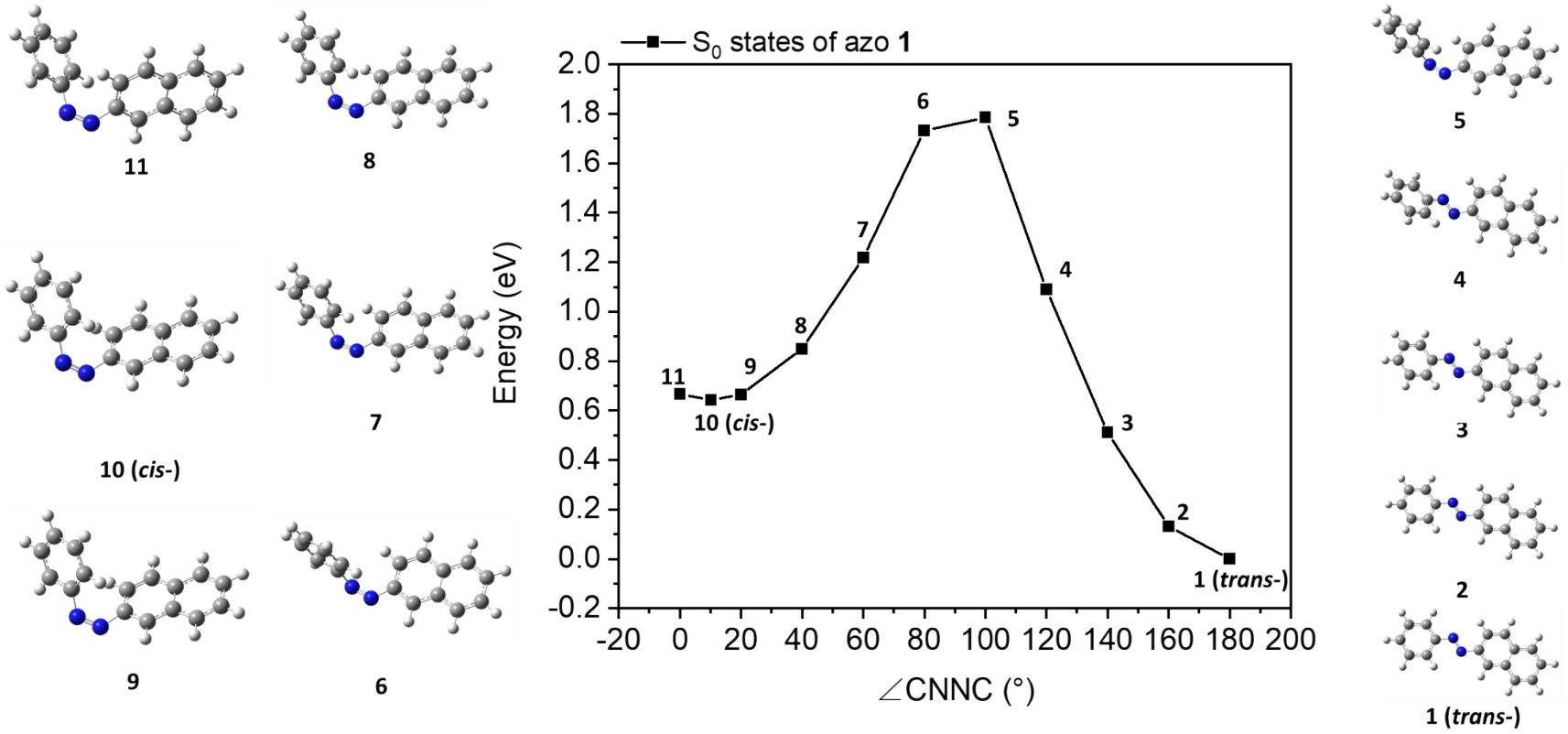


Figure S22. S_0 geometries of azo 1 with various ∠CNNC angles.

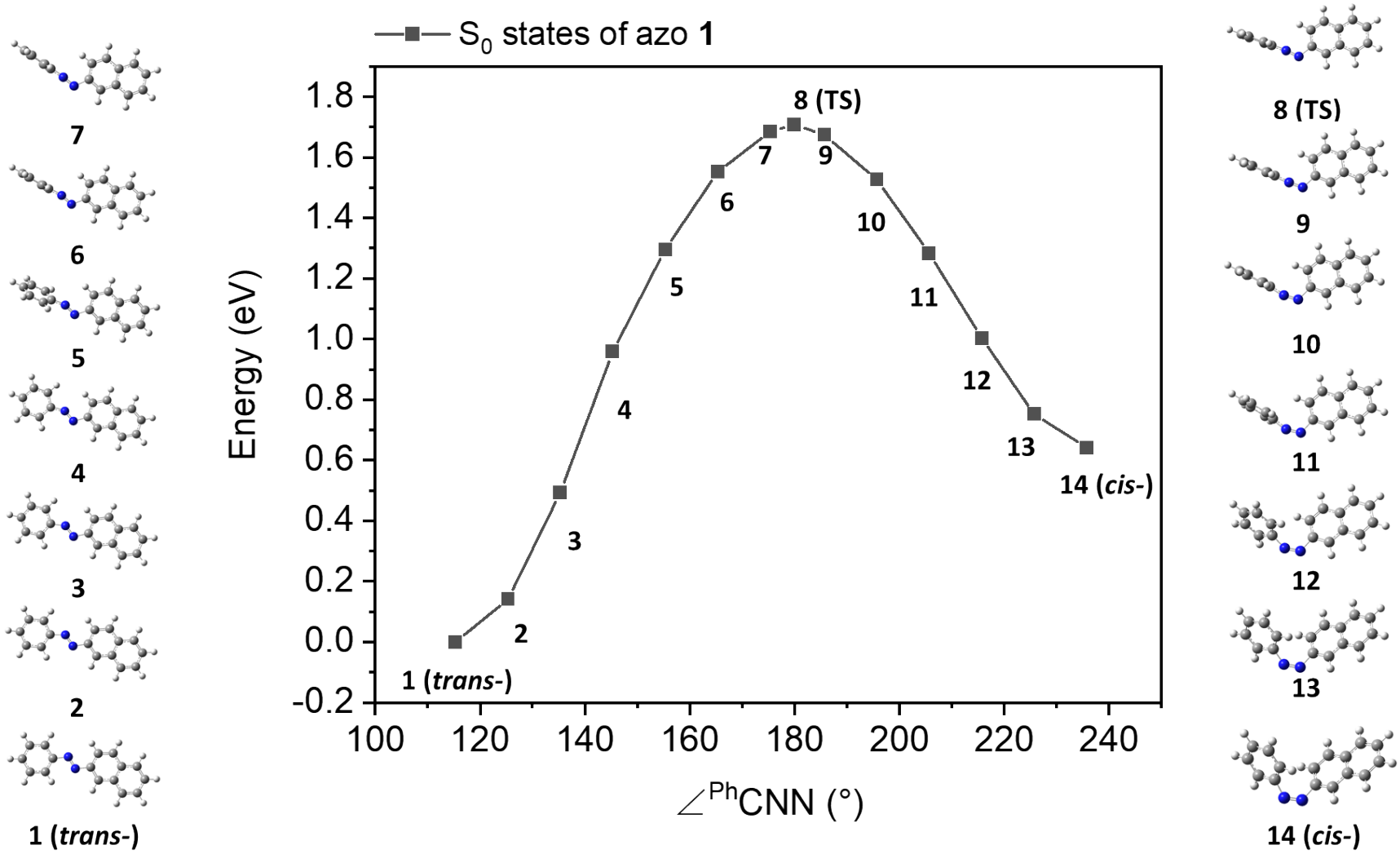


Figure S23. S_0 geometries of azo 1 with various $\angle^{Ph}CNN$ angles.

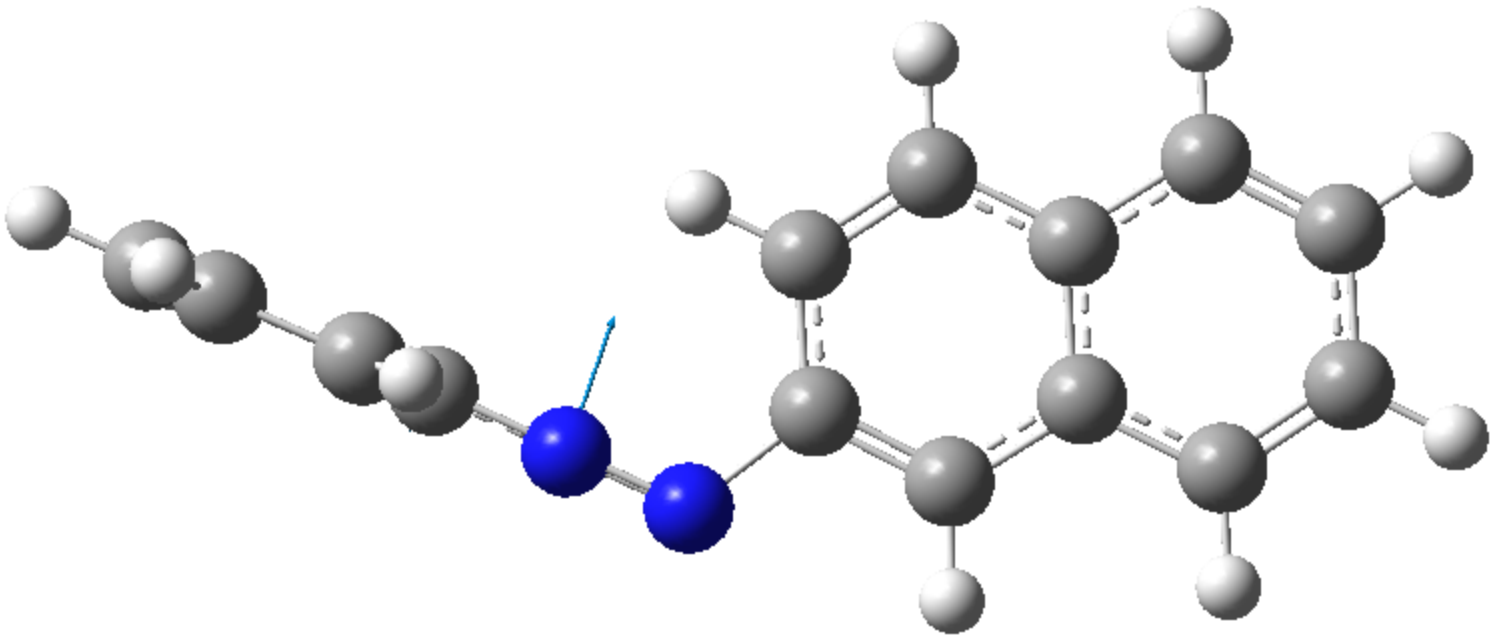


Figure S24. Geometry of azo 1 transition state from point 8 in Figure S23. The imaginary vibrational mode at -409.97 cm^{-1} is indicated by the blue arrow

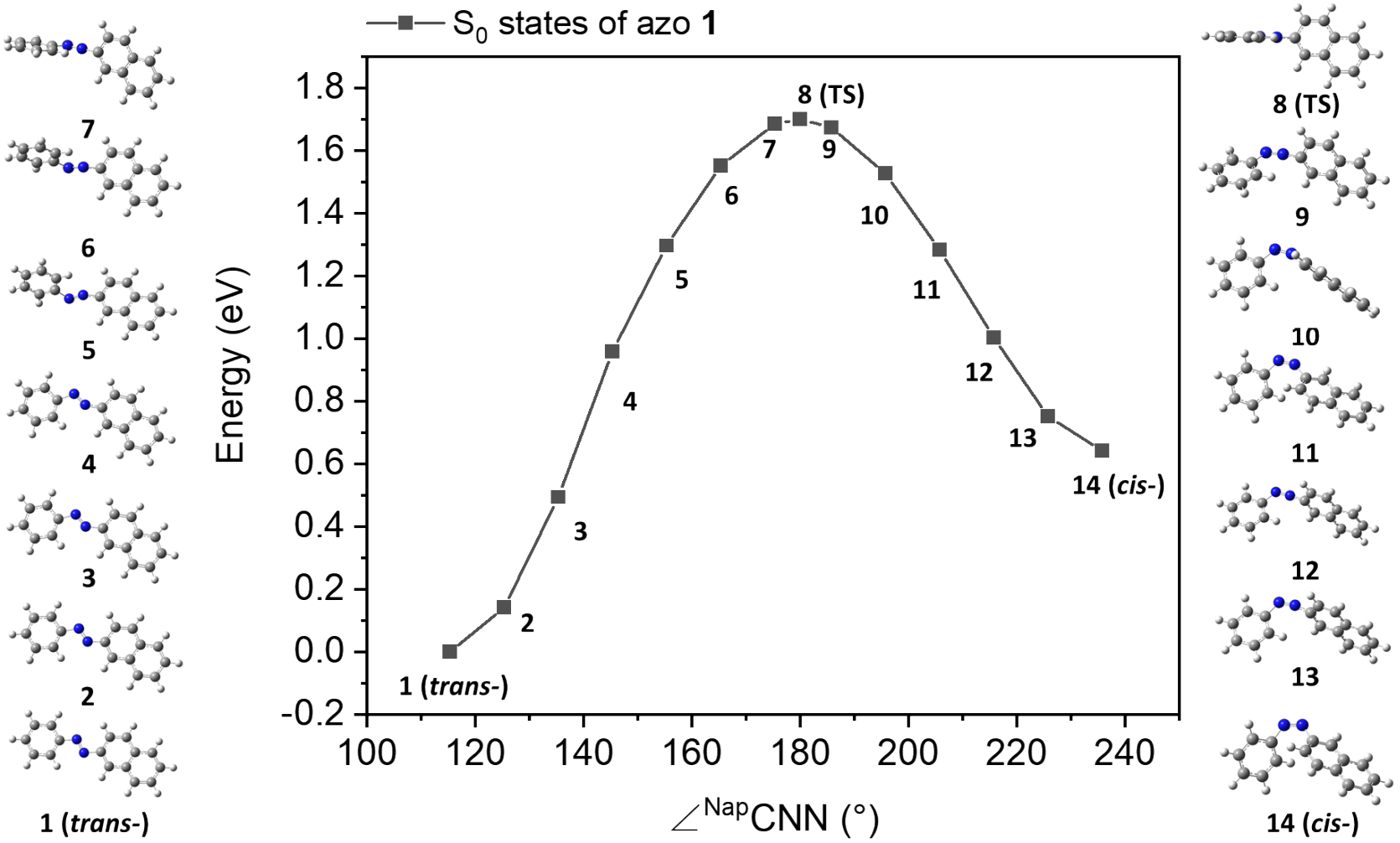


Figure S25. S_0 geometries of azo 1 with various $\angle^{Nap}CNN$ angles.

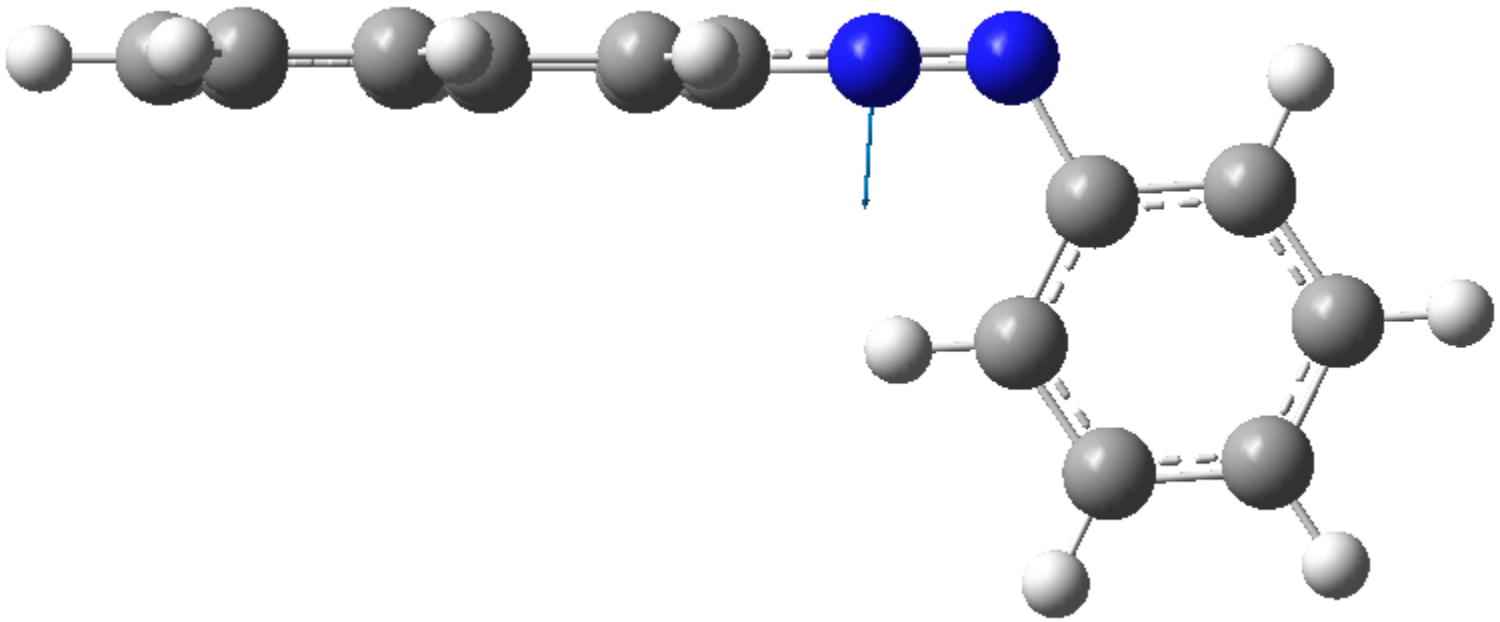


Figure S26. Geometry of azo 1 transition state from point 8 in Figure S25. The imaginary vibrational mode at -404.81 cm^{-1} is indicated by the blue arrow

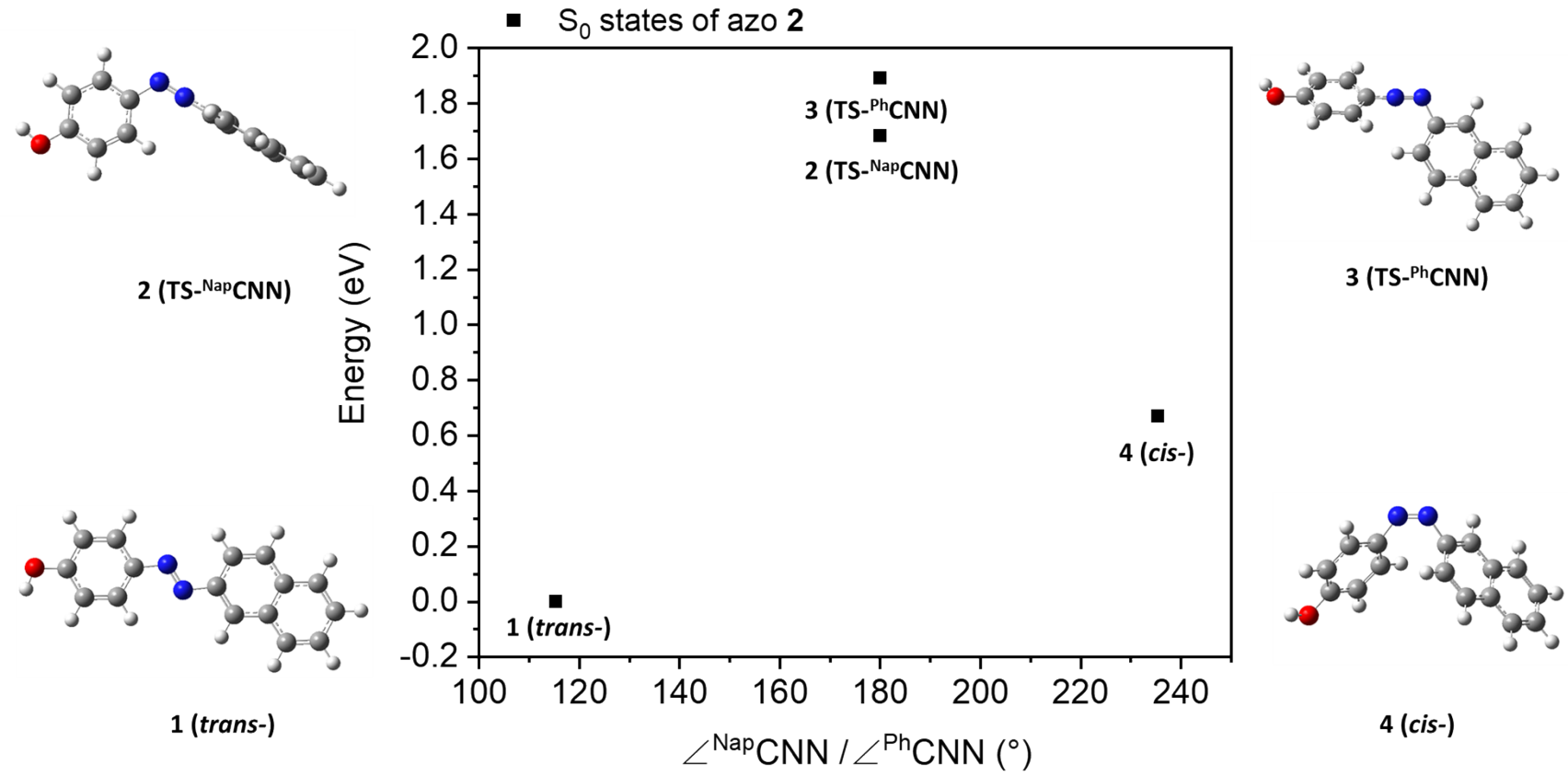


Figure S27. Geometry and relative energy of azo 2 transition states and the ground states at *trans*- and *cis*- configurations.

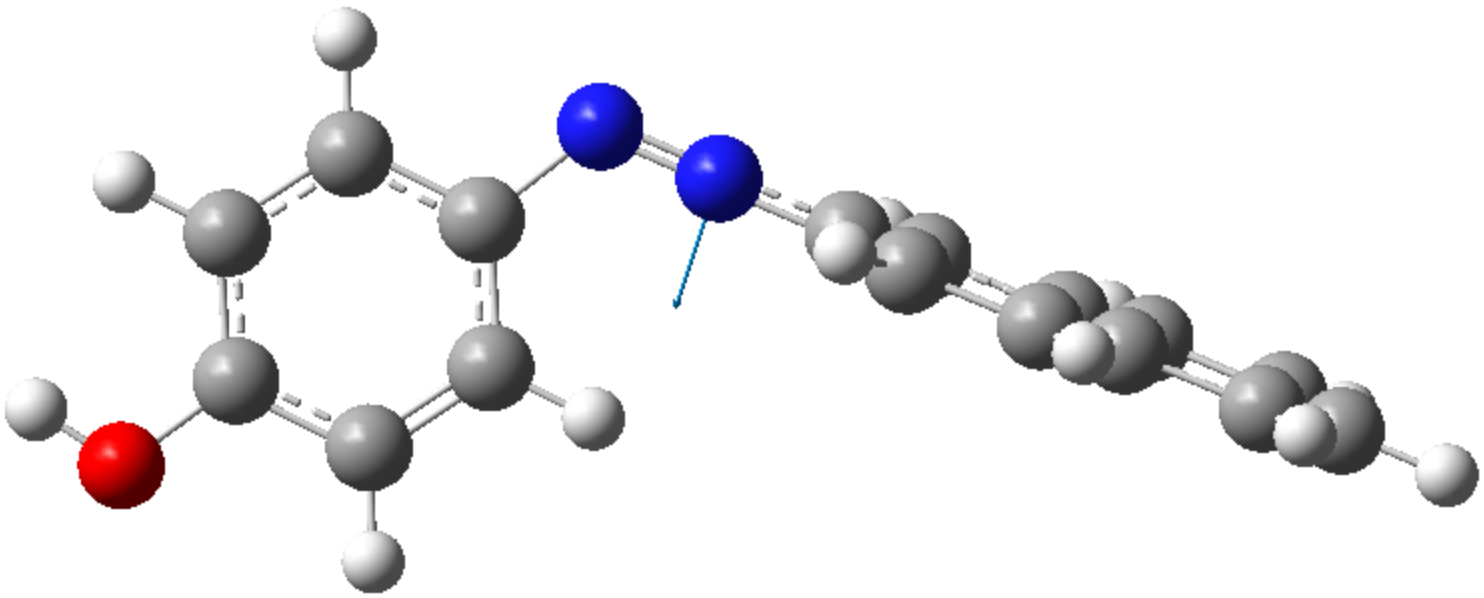


Figure S28. Geometry of azo 2 transition state from point 2 in Figure S27. The imaginary vibrational mode at -398.49 cm^{-1} is indicated by the blue arrow.

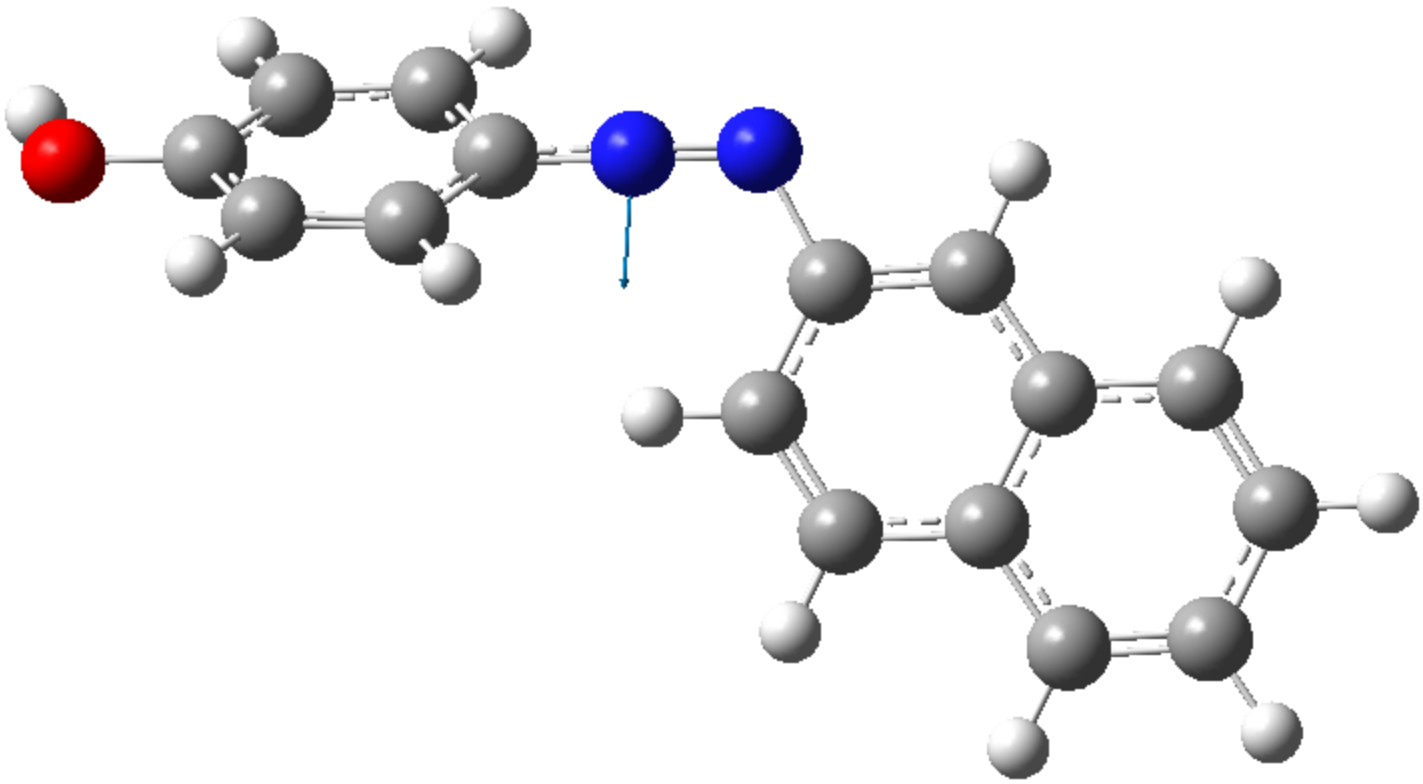


Figure S29. Geometry of azo 2 transition state from point 3 in Figure S27. The imaginary vibrational mode at -459.90 cm^{-1} is indicated by the blue arrow.

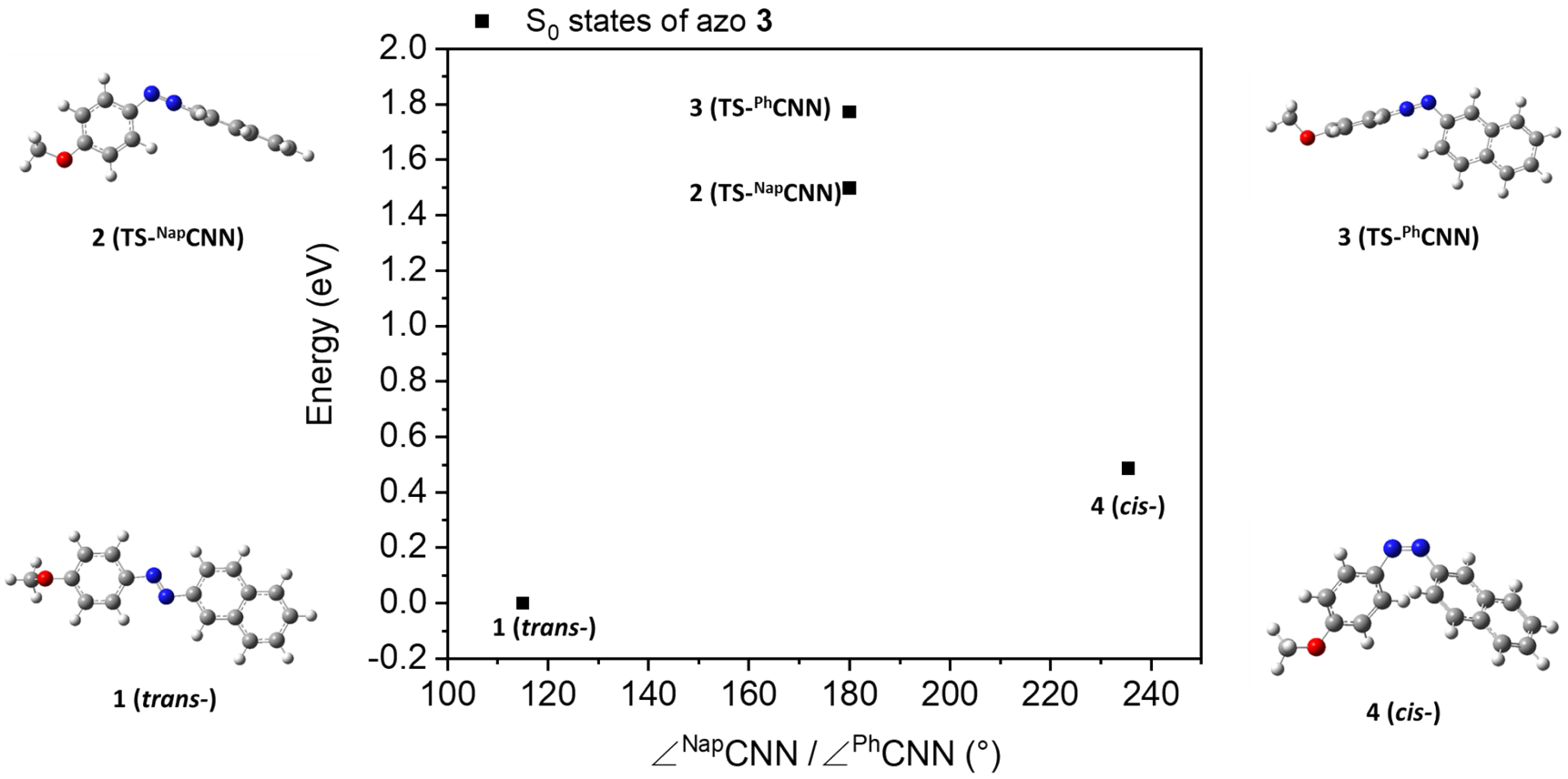


Figure S30. Geometry and relative energy of azo 3 transition states and the ground states at *trans*- and *cis*- configurations.

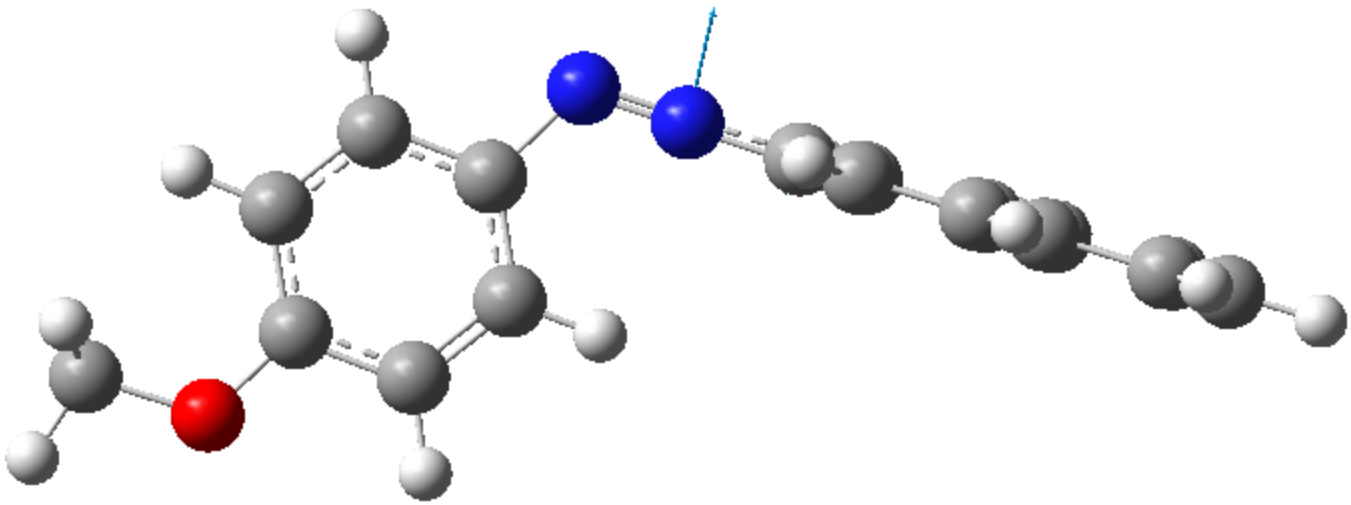


Figure S31. Geometry of azo 3 transition state from point 2 in Figure S30. The imaginary vibrational mode at -397.45 cm^{-1} is indicated by the blue arrow.

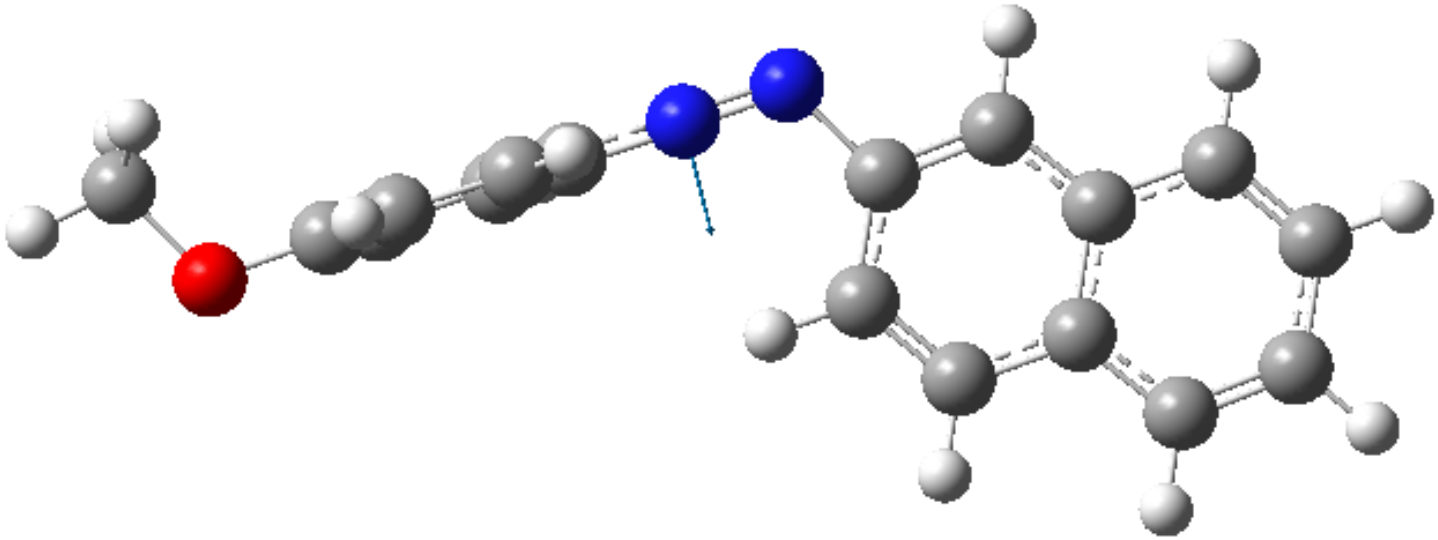


Figure S32. Geometry of azo 3 transition state from point 3 in Figure S30. The imaginary vibrational mode at -422.82 cm^{-1} is indicated by the blue arrow.

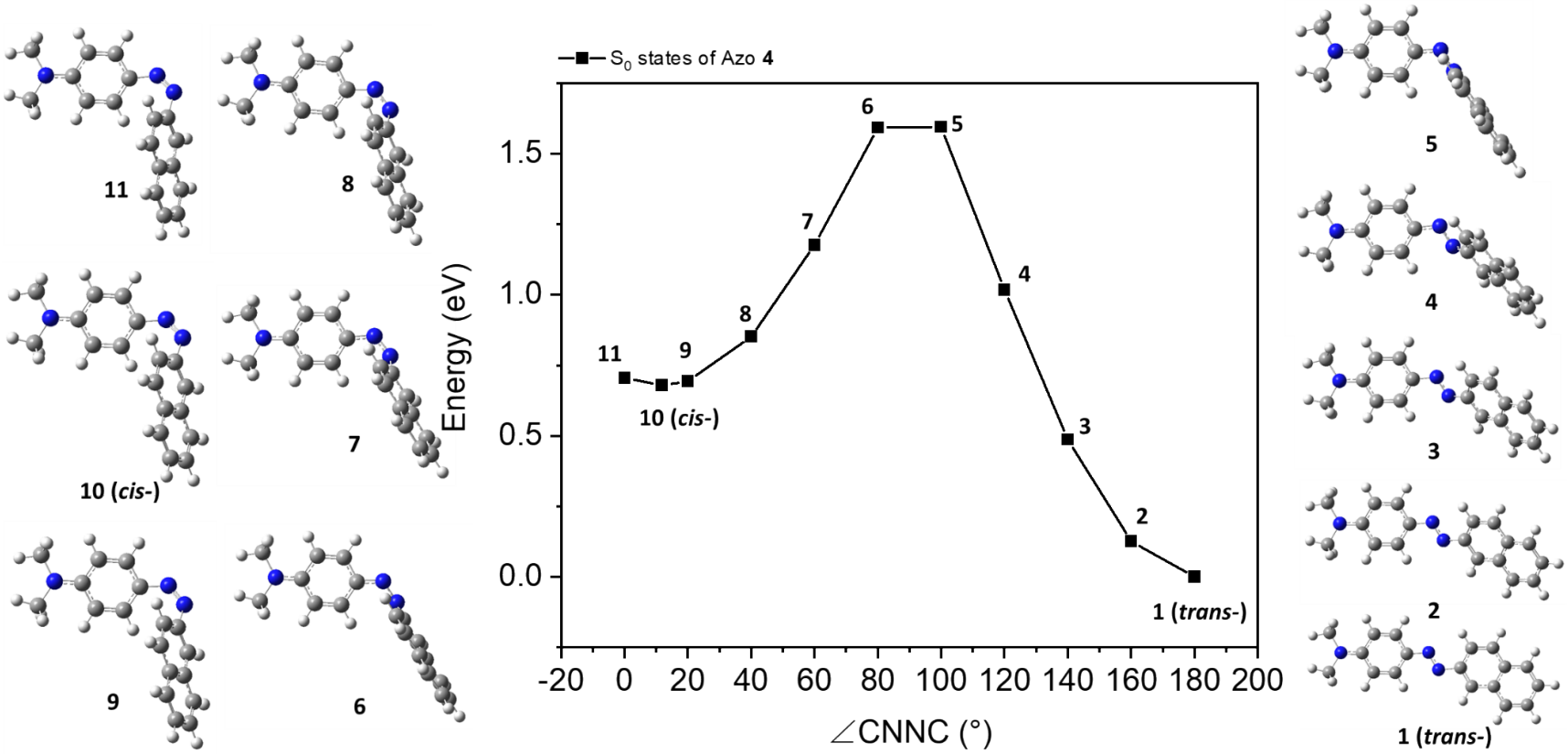


Figure S33. S_0 geometries of azo 4 with various ∠CNNC angles.

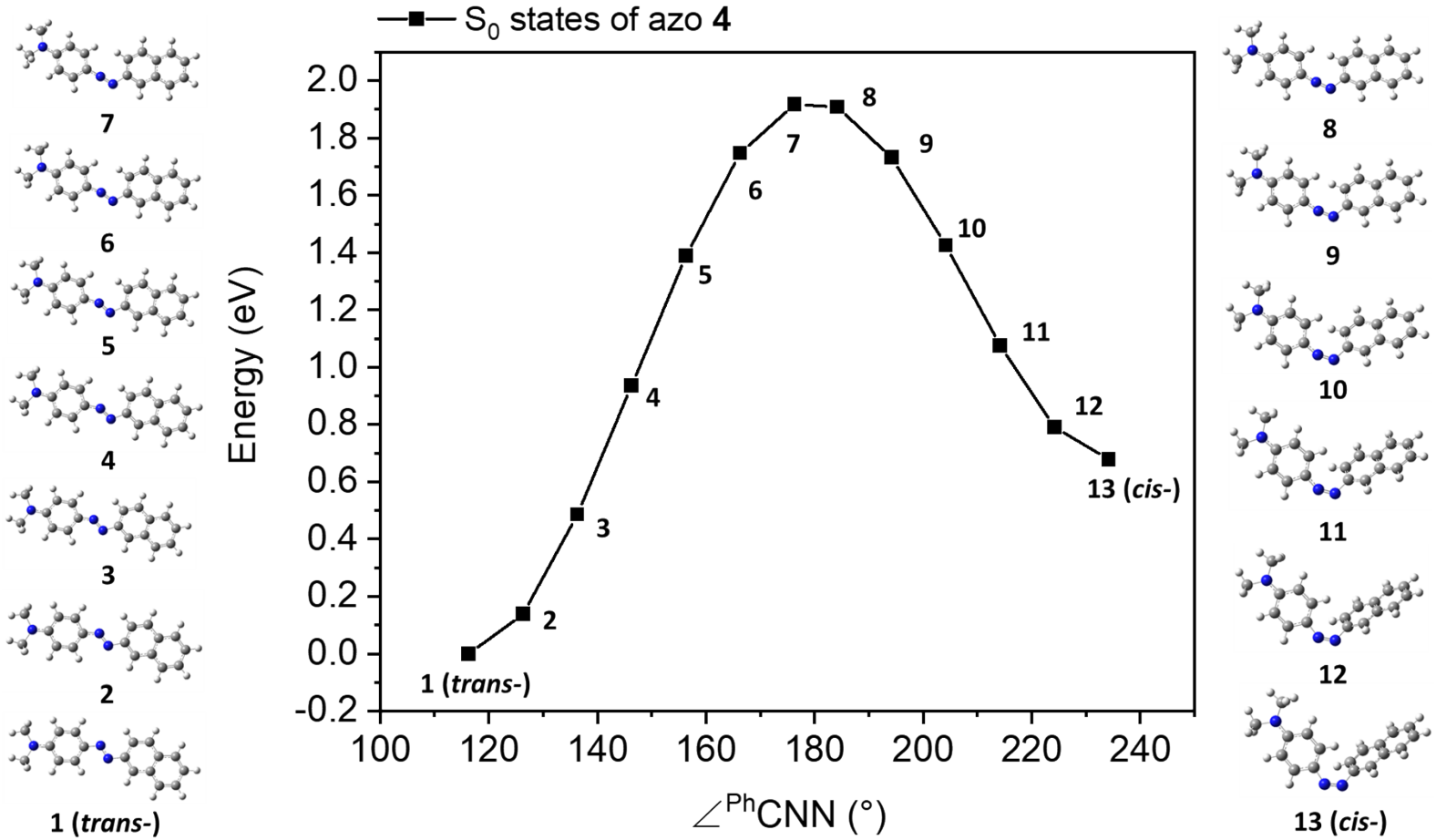


Figure S34. S_0 geometries of azo 4 with various $\angle^{Ph}$CNN angles.

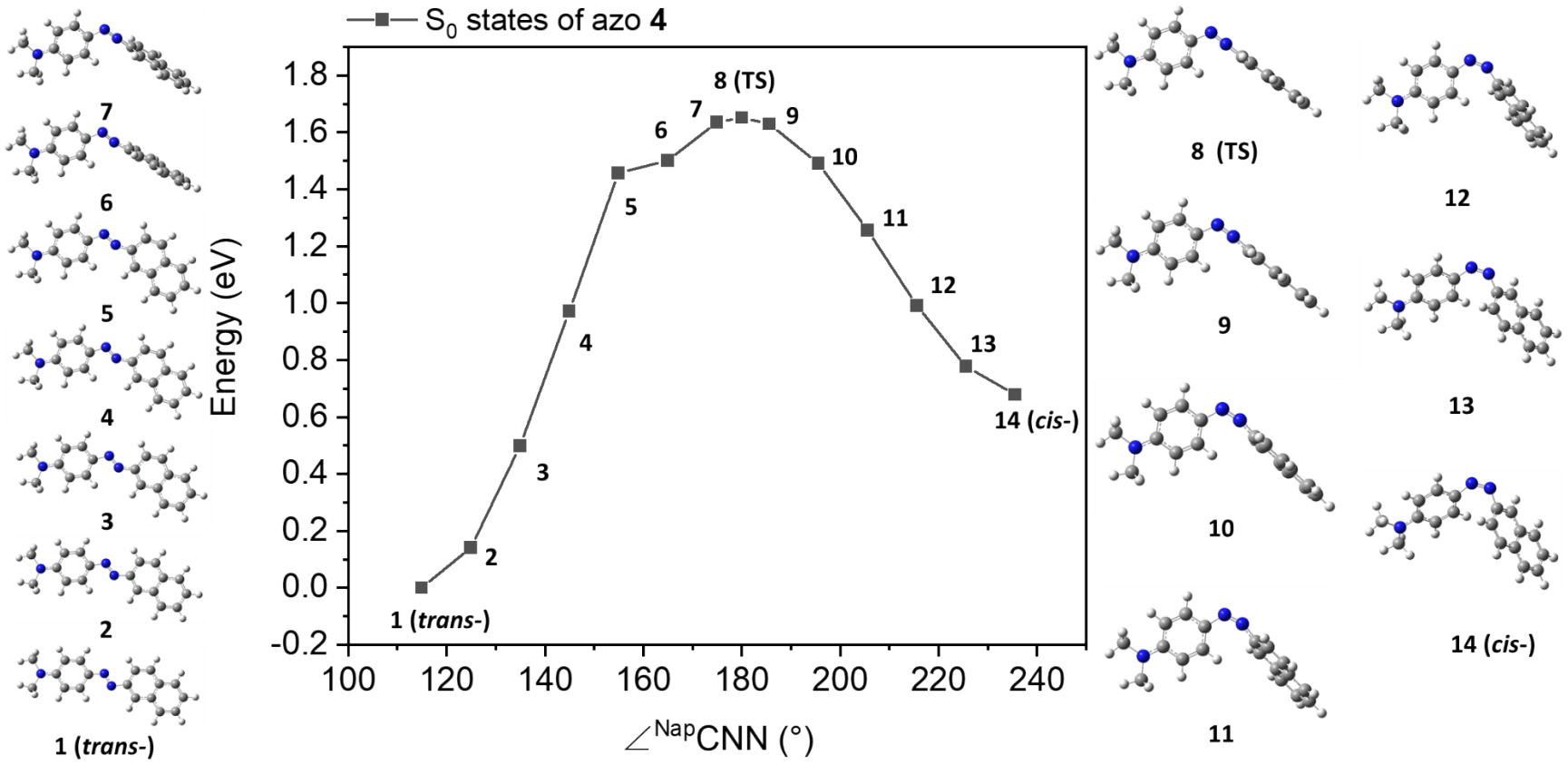


Figure S35. S_0 geometries of azo 4 with various ∠^{Nap}CNN angles.

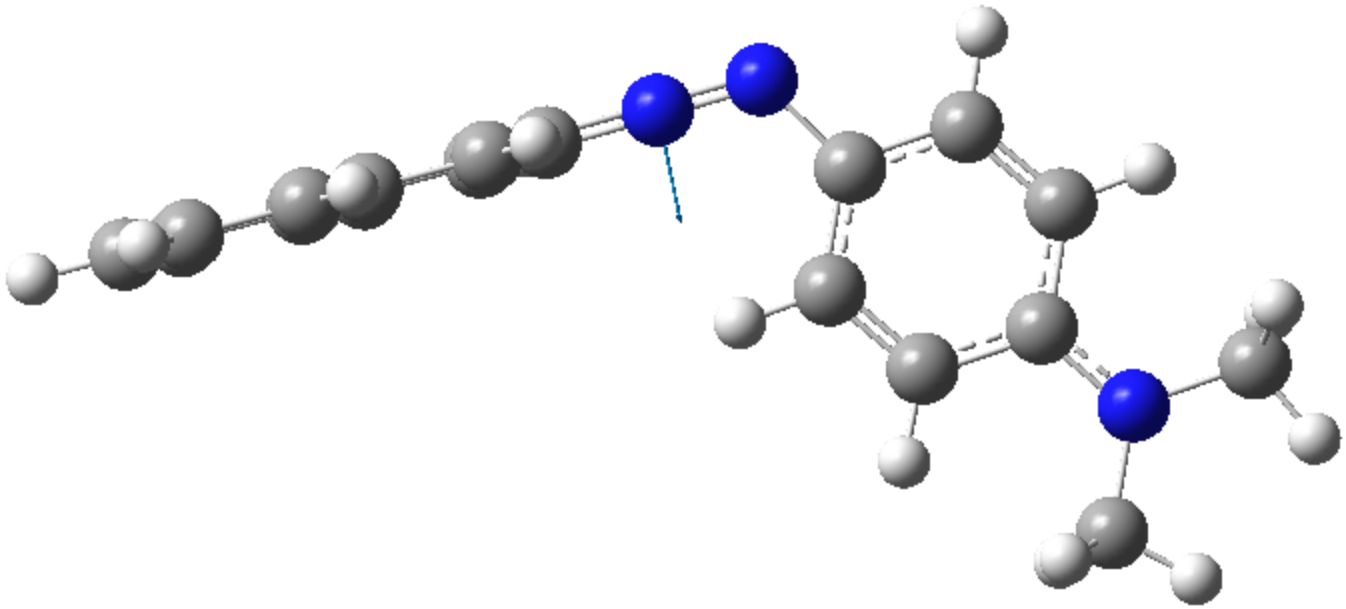


Figure S36. Geometry of azo 4 transition state from point 8 in Figure S35. The imaginary vibrational mode at -384.14 cm^{-1} is indicated by the blue arrow.

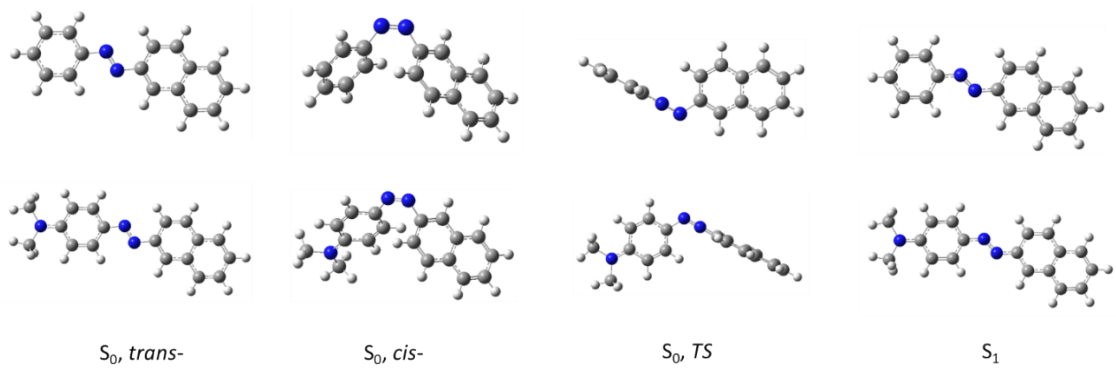


Figure S37. Comparing *trans*-, *cis*-, and transition states between azo 1 (top) and azo 4 (bottom).

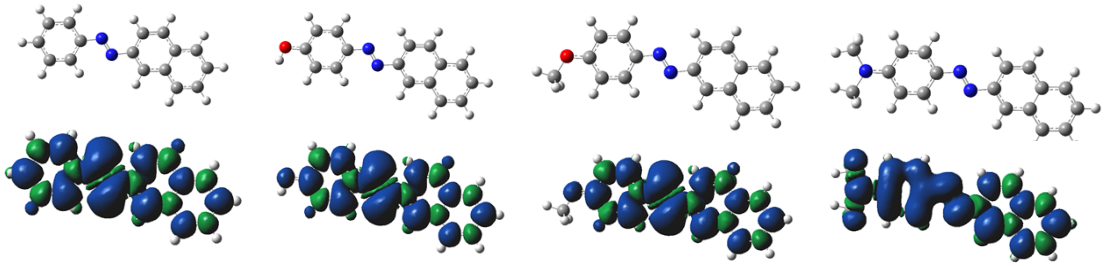


Figure S38. Comparing optimized triplet geometries of azo 1-4 and their spin densities.

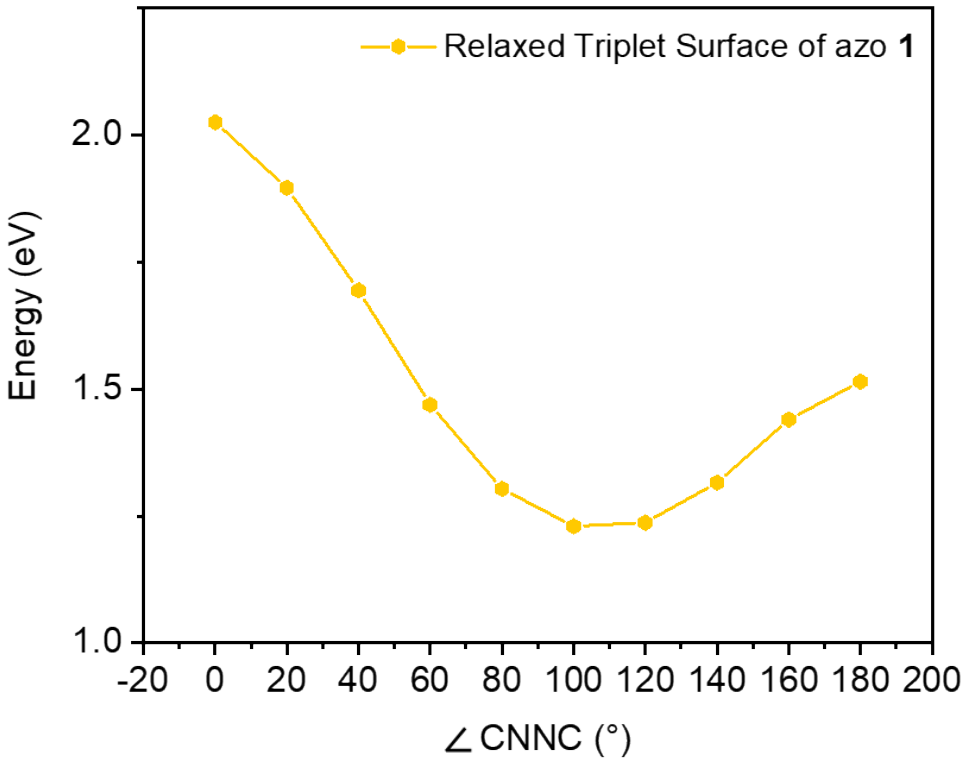


Figure S39. Triplet potential surface for azo 1 with various ∠CNNC dihedral angles.

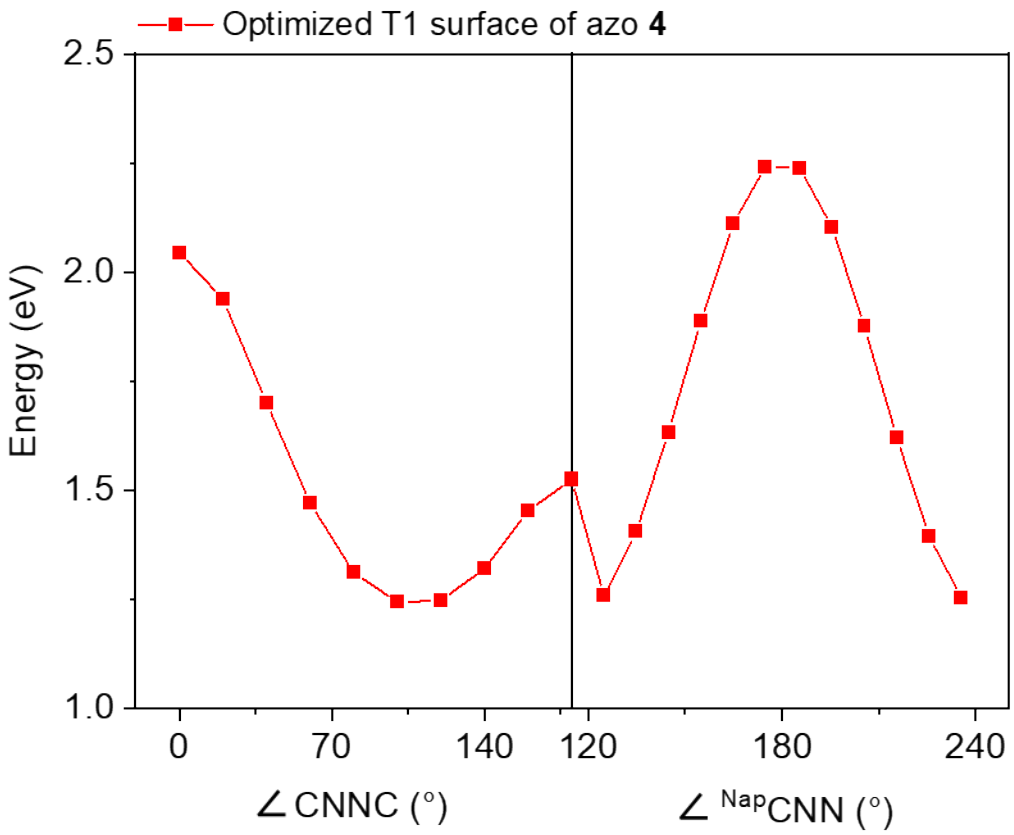


Figure S40. Triplet potential surface for azo 4 with various ∠CNNC dihedral angles, and ∠^{Nap}CNN angles.

DFT Optimized Coordinates

Trans - Nap-azo-ph (azo 1) coordinates (B3LYP/6-311G(d.p)/PCM(ACN))

0 1
C 5.51758740 -0.04340709 -0.00003404
C 4.58079551 -1.05258151 -0.00000214
C 3.19636550 -0.75376199 0.00000193
C 2.78504925 0.61759322 -0.00001719
C 3.77540906 1.63521482 -0.00004352
C 5.11195086 1.31131926 -0.00003769
H 2.51269393 -2.80833483 0.00010176
H 6.57433965 -0.28476221 -0.00003828
H 4.89366478 -2.09113031 0.00001853
C 2.19700862 -1.77035291 0.00007187
C 1.40045117 0.91352227 -0.00001239
H 3.46008106 2.67301244 -0.00004409
H 5.86119362 2.09447884 -0.00003890
C 0.45517238 -0.09364150 -0.00002950
C 0.86538072 -1.45820105 0.00005576
H 1.06443029 1.94423870 -0.00007107
H 0.10652882 -2.22831221 0.00008670
N -0.89252667 0.33233652 -0.00005810
N -1.74693477 -0.58861770 0.00010072
C -3.09905091 -0.16169887 0.00009203
C -4.05482965 -1.18440469 -0.00005654
C -3.51343295 1.17987765 0.00013941
C -5.41242189 -0.87620084 -0.00012704
H -3.71190353 -2.21229108 -0.00011162
C -4.86820743 1.48069798 0.00005532
H -2.76580293 1.96148327 0.00022187
C -5.82131424 0.45626925 -0.00008125
H -6.14775215 -1.67219393 -0.00023809
H -5.18929029 2.51614805 0.00009843
H -6.87743386 0.70016745 -0.00013367

Cis - Nap-azo-ph (azo 1) coordinates (B3LYP/6-311G(d.p)/PCM(ACN))

0 1
C -4.55062900 -1.23923900 0.00024900
C -3.39971000 -1.47802500 -0.71445000
C -2.29078500 -0.59995200 -0.61465700
C -2.38729900 0.54466400 0.24002700
C -3.59127200 0.76518400 0.96121100
C -4.64685300 -0.10745000 0.84464800
H -1.02656500 -1.65437400 -2.01985000
H -5.39150300 -1.91833400 -0.08144800
H -3.32507900 -2.34356800 -1.36397000
C -1.08955900 -0.80540400 -1.34769000
C -1.28657200 1.43143500 0.32339900
H -3.66307900 1.63366900 1.60697100
H -5.56050100 0.06844600 1.40077500
C -0.11297700 1.16876600 -0.35161400
C -0.02147700 0.04307600 -1.21722100
H -1.35745100 2.32391500 0.93522800
H 0.88201900 -0.12506500 -1.78834300
N 0.90791800 2.17220900 -0.26780700
N 2.12688800 1.92795600 -0.17280600
C 2.67257200 0.62516300 0.07632200
C 3.81681000 0.27399400 -0.64807200
C 2.22155700 -0.19678600 1.11688900
C 4.46421000 -0.92822900 -0.38262600
H 4.17877800 0.94583800 -1.41757800
C 2.89924800 -1.37859000 1.40082500
H 1.36419400 0.09669600 1.70908900
C 4.00900600 -1.75662600 0.64407800
H 5.33464700 -1.20969400 -0.96377400
H 2.55721200 -2.00747500 2.21469300
H 4.52607300 -2.68309500 0.86457300

TS - Nap-azo-ph (azo 1) coordinates (B3LYP/6-311G(d.p)/PCM(ACN))

0 1

C -5.25883569 0.93232232 -0.00484580
C -4.04478655 1.58125738 -0.00836346
C -2.83361754 0.84657254 -0.00422442
C -2.89427163 -0.58440483 0.00293869
C -4.16165334 -1.22366769 0.00679917
C -5.31845911 -0.48061249 0.00310448
H -1.52121534 2.56918360 -0.01075348
H -6.17886438 1.50534990 -0.00831198
H -4.00157170 2.66485719 -0.01432270
C -1.55918671 1.48531840 -0.00658995
C -1.68179594 -1.31573185 0.00557935
H -4.20189082 -2.30728015 0.01273669
H -6.28259937 -0.97544874 0.00632919
C -0.47041345 -0.66156914 0.00228939
C -0.40111430 0.75581519 -0.00319380
H -1.69231871 -2.39997573 0.00995677
H 0.56560401 1.24388470 -0.00361847
N 0.68509330 -1.52549417 0.00308871
N 1.78862510 -1.00062328 0.00152053
C 2.98935706 -0.42984010 0.00093143
C 3.65458986 -0.14243679 -1.22328351
C 3.64453068 -0.11783171 1.22453135
C 4.91789775 0.43075778 -1.19973111
H 3.16354515 -0.37489786 -2.15959237
C 4.90915706 0.45244967 1.20000330
H 3.14572181 -0.33143801 2.16122667
C 5.56557541 0.73576555 -0.00013942
H 5.40444798 0.64185472 -2.14649127
H 5.38878110 0.68063656 2.14633017
H 6.55249045 1.18111059 -0.00058797

Triplet - Nap-azo-ph (azo 1) coordinates (B3LYP/6-311G(d.p)/PCM(ACN))

0 3

C 5.18685648 -0.42054324 -0.72052949
C 4.10105403 -1.26850309 -0.65494069
C 2.84675914 -0.80307114 -0.19981629
C 2.71443603 0.56862617 0.19739129
C 3.85349009 1.41661685 0.11907934
C 5.05992145 0.93211375 -0.32989005
H 1.80761210 -2.69330549 -0.40868223
H 6.14325636 -0.78943945 -1.07253958
H 4.19814599 -2.30665197 -0.95415636
C 1.70264914 -1.65371334 -0.11654481
C 1.46449018 1.03475852 0.65555701
H 3.75468091 2.45405344 0.41957458
H 5.92088200 1.58826932 -0.38589732
C 0.35324244 0.18572214 0.71378639
C 0.49679818 -1.18801631 0.31985951
H 1.34830126 2.06776425 0.96259651
H -0.36381632 -1.84164419 0.38508214
N -0.82895417 0.71575152 1.14480280
N -1.89602562 0.00044884 1.32189456
C -2.97093786 0.07123758 0.47095257
C -4.11615854 -0.68774310 0.80774319
C -2.98488392 0.85607518 -0.70793060
C -5.22897850 -0.67305003 -0.01709457
H -4.09598082 -1.27838496 1.71578575
C -4.11022739 0.86389777 -1.51740863
H -2.11618920 1.45242347 -0.95741596
C -5.23448101 0.10094701 -1.18313236
H -6.09992659 -1.26221810 0.24570871
H -4.11742490 1.46962492 -2.41658649
H -6.10886196 0.11397798 -1.82284221

Trans-Nap-azo-phOH (azo 2) coordinates

0 1
C 5.96596468 -0.02648278 -0.00025723
C 5.04643910 0.99834634 -0.00020514
C 3.65689223 0.72341473 -0.00005277
C 3.22093889 -0.64032130 0.00005497
C 4.19417029 -1.67453014 0.00001171
C 5.53623031 -1.37383033 -0.00014133
H 3.00794672 2.78906668 -0.00013320
H 7.02676345 0.19648474 -0.00038304
H 5.37676428 2.03155088 -0.00027502
C 2.67500018 1.75638254 -0.00001096
C 1.83120663 -0.91234942 0.00021419
H 3.86123320 -2.70688921 0.00011753
H 6.27152517 -2.17020530 -0.00016742
C 0.90213567 0.10990619 0.00023912
C 1.33804729 1.46669300 0.00008089
H 1.47837924 -1.93751811 0.00026963
H 0.59307490 2.25028445 0.00001291
N -0.45355360 -0.29042755 0.00024158
N -1.28949218 0.65084715 0.00028715
C -2.64487625 0.26625379 0.00009856
C -3.58012573 1.31145001 0.00015679
C -3.10610059 -1.06113200 0.00003423
C -4.94109246 1.05027463 -0.00015219
H -3.21442386 2.33140161 0.00026908
C -4.46357924 -1.33020022 -0.00000748
H -2.38583349 -1.86809058 0.00015572
C -5.39018226 -0.27478323 -0.00000681
H -5.66797417 1.85310684 -0.00034931
H -4.81619665 -2.35661188 -0.00005668
O -6.73176983 -0.48045512 -0.00045790
H -6.92219194 -1.42642725 0.00016262

Cis-Nap-azo-phOH (azo 2) coordinates

0 1
C 4.72733159 -1.51072065 0.12273273
C 3.61529494 -1.48490397 0.93214848
C 2.58336841 -0.53659084 0.71556916
C 2.71703693 0.40174176 -0.35775071
C 3.87965722 0.35105328 -1.17260650
C 4.85993200 -0.58398378 -0.93856722
H 1.33378315 -1.16220097 2.36923717
H 5.50884444 -2.24162007 0.29588898
H 3.51310371 -2.19281907 1.74777186
C 1.42424030 -0.47223739 1.53711710
C 1.69442865 1.36108837 -0.56195612
H 3.98114166 1.06212426 -1.98539523
H 5.74177302 -0.61480440 -1.56827074
C 0.55634595 1.35830837 0.21596435
C 0.42965028 0.43837351 1.29458532
H 1.79889680 2.10144903 -1.34755278
H -0.44499051 0.47751383 1.93138218
N -0.37967995 2.42628446 0.02158582
N -1.62039643 2.27939490 -0.01213165
C -2.29028604 1.02140051 -0.08861054
C -3.54161374 0.96252874 0.53731715
C -1.86965921 -0.06523006 -0.87357896
C -4.32542330 -0.17969509 0.45711737
H -3.88412737 1.82419465 1.09796376
C -2.66877496 -1.19042993 -0.99398218
H -0.93343605 -0.02059931 -1.41321659
C -3.89124509 -1.26405933 -0.31360037
H -5.28074017 -0.22396579 0.96916986
H -2.36304350 -2.02470425 -1.61363855
O -4.61673234 -2.40338616 -0.45803019
H -5.43851535 -2.33709509 0.04332804

TS-Nap-azo-phOH (azo 2) coordinates

0 1
C -5.65481195 1.02974757 -0.23139237
C -4.41666900 1.62247003 -0.33326254
C -3.23386856 0.85794798 -0.17714398
C -3.34743164 -0.54491498 0.08920150
C -4.63908741 -1.12599092 0.18861879
C -5.76711215 -0.35549577 0.03163712
H -1.85584509 2.50076205 -0.47838287
H -6.55246569 1.62500189 -0.35300972
H -4.33186286 2.68481260 -0.53502586
C -1.93595135 1.43785477 -0.27693439
C -2.16290868 -1.30595355 0.24435417
H -4.72112640 -2.18840454 0.39054640
H -6.74914410 -0.80756318 0.10903265
C -0.92503086 -0.71083811 0.14429736
C -0.80716288 0.67866233 -0.12209340
H -2.21570475 -2.37097963 0.44258472
H 0.17778319 1.12208105 -0.20006846
N 0.20036606 -1.60181454 0.30414482
N 1.32692521 -1.11187588 0.20424463
C 2.55337477 -0.59013847 0.11545032
C 3.49502518 -1.09959229 -0.81716856
C 2.96626946 0.47442625 0.96306044
C 4.75678031 -0.53282499 -0.92659920
H 3.20276800 -1.91314320 -1.46899693
C 4.26280934 0.95931556 0.90438369
H 2.26608118 0.87710385 1.68413757
C 5.16208512 0.48222199 -0.05449081
H 5.44643952 -0.91048237 -1.67520641
H 4.58286033 1.74403139 1.58025610
O 6.41135856 1.04271191 -0.08961263
H 6.93045086 0.62953326 -0.78920114

Trans-Nap-azo-phOMe (azo 3) coordinates

0 1
C -6.39763430 -0.10423931 0.09823658
C -5.49925225 0.93912324 0.11271898
C -4.10508356 0.69323322 0.06932467
C -3.64273649 -0.66047744 0.01003740
C -4.59441374 -1.71434811 -0.00290432
C -5.94167248 -1.44166027 0.04001506
H -3.49832409 2.77096392 0.12707486
H -7.46233935 0.09644087 0.13151616
H -5.85000358 1.96452788 0.15734343
C -3.14449900 1.74633550 0.08165896
C -2.24855940 -0.90339656 -0.03528629
H -4.24079044 -2.73876341 -0.04780965
H -6.66101169 -2.25235398 0.02927161
C -1.34142091 0.13822483 -0.02347020
C -1.80262275 1.48517086 0.03694169
H -1.87502572 -1.92008864 -0.08155382
H -1.07345001 2.28345422 0.04527220
N 0.02068803 -0.23516887 -0.07716454
N 0.83939852 0.71857866 -0.06897728
C 2.20378214 0.34933536 -0.12682138
C 3.11958558 1.40868781 -0.12271739
C 2.67475056 -0.97257631 -0.19420362
C 4.48614263 1.16179533 -0.18146964
H 2.73837064 2.42184047 -0.07604066
C 4.03674171 -1.22002575 -0.25254966
H 1.96156356 -1.78572259 -0.20286986
C 4.94572953 -0.15390451 -0.24958415
H 5.20094288 1.97588932 -0.18947720
H 4.41574060 -2.23349622 -0.31530355
O 6.29232750 -0.40644212 -0.36710276
C 6.99090973 -0.56600283 0.87821563
H 8.03247052 -0.75653488 0.62413034
H 6.92245986 0.34284833 1.48432069
H 6.59168926 -1.41298729 1.44508652

Cis-Nap-azo-phOMe (azo 3) coordinates

0 1

C 4.94415238 -1.80966167 0.10627280
C 3.83215480 -1.70477876 0.90934418
C 2.88797143 -0.66599617 0.70733290
C 3.11084268 0.27946650 -0.34474634
C 4.27091327 0.14531804 -1.15365018
C 5.16478937 -0.87576948 -0.93398486
H 1.57642112 -1.21507592 2.33965941
H 5.65798542 -2.60917168 0.26814710
H 3.66250506 -2.41793234 1.70902880
C 1.73271435 -0.51784300 1.52345344
C 2.17768163 1.32868122 -0.53360055
H 4.43960312 0.86225571 -1.94997532
H 6.04571778 -0.96958449 -1.55869697
C 1.03810411 1.40994323 0.23806273
C 0.82351033 0.48170563 1.29569291
H 2.35292603 2.07359966 -1.30209195
H -0.04874562 0.58443558 1.92869121
N 0.20427236 2.56208061 0.06260923
N -1.04472595 2.53123988 0.01850929
C -1.82905823 1.34460790 -0.08973579
C -3.09010705 1.39878970 0.51145965
C -1.50044941 0.22772164 -0.87990563
C -3.98440691 0.33906095 0.41029344
H -3.35848659 2.28532967 1.07394077
C -2.40176768 -0.81069635 -1.02219104
H -0.55550641 0.18602028 -1.40421655
C -3.64241268 -0.77781724 -0.36260036
H -4.94044706 0.40161320 0.91087704
H -2.16985776 -1.66689860 -1.64397894
O -4.43878362 -1.85757041 -0.55182931
C -5.72158777 -1.88670727 0.08156993
H -6.16710813 -2.83752433 -0.20213666
H -5.62536503 -1.83852250 1.16981086
H -6.35446577 -1.06737354 -0.27065726

TS-Nap-azo-phOMe (azo 3) coordinates

0 1

C 6.09670760 1.05696766 0.00044997
C 4.86024320 1.66218318 -0.00025544
C 3.67601154 0.88480701 -0.00039111
C 3.78773088 -0.54313276 0.00022083
C 5.07715869 -1.13676868 0.00092218
C 6.20675192 -0.35293244 0.00103899
H 2.30298319 2.55958291 -0.00160040
H 6.99567783 1.66251843 0.00056608
H 4.77851042 2.74358276 -0.00069006
C 2.37955830 1.47773583 -0.00110115
C 2.60204490 -1.31720579 0.00011727
H 5.15609209 -2.21828393 0.00135997
H 7.18795316 -0.81300346 0.00157926
C 1.36807000 -0.70672628 -0.00048876
C 1.24833384 0.70728247 -0.00113716
H 2.65112694 -2.40041679 0.00054879
H 0.26450990 1.15980175 -0.00168057
N 0.24340729 -1.61117911 -0.00037709
N -0.87784707 -1.12395948 -0.00045700
C -2.10298047 -0.60123197 -0.00029746
C -2.77296771 -0.32336670 1.22180027
C -2.77381971 -0.32446945 -1.22217581
C -4.05805603 0.20088539 1.20201376
H -2.27073448 -0.52108993 2.15997122
C -4.05885977 0.19988665 -1.20196446
H -2.27225431 -0.52306619 -2.16052014
C -4.71346630 0.46992285 0.00013069
H -4.55901867 0.41882153 2.13913629
H -4.56046318 0.41703377 -2.13892694
O -5.97760044 1.04284484 0.00030577
C -7.05379493 0.09865126 0.00108504
H -7.97890313 0.67567693 0.00095556
H -7.02299142 -0.53695015 -0.89096375
H -7.02260221 -0.53592561 0.89385132

Trans-Nap-azo-phNMe$_2$ (azo 4) coordinates

0 1
C 6.81344850 -0.09875777 -0.00002394
C 5.91087585 0.94099069 0.00012384
C 4.51663663 0.68983687 0.00009307
C 4.05590883 -0.66584692 -0.00009316
C 5.01256523 -1.71597841 -0.00023951
C 6.35968663 -1.43842449 -0.00020554
H 3.90160484 2.76563007 0.00038441
H 7.87797601 0.10585605 -0.00000093
H 6.25817106 1.96877524 0.00026622
C 3.55180711 1.73832527 0.00024122
C 2.66168252 -0.91418873 -0.00013100
H 4.66242397 -2.74276034 -0.00037798
H 7.08094342 -2.24771166 -0.00031734
C 1.74688978 0.12203013 0.00000539
C 2.20999902 1.47083269 0.00020493
H 2.29285809 -1.93389021 -0.00027627
H 1.47884318 2.26741595 0.00032163
N 0.38512327 -0.25160715 -0.00003800
N -0.43227929 0.71328851 0.00010039
C -1.78786274 0.37655753 0.00007156
C -2.69862095 1.44548213 0.00005326
C -2.30570889 -0.93411151 0.00009679
C -4.06411682 1.23511128 -0.00003452
H -2.30416433 2.45538963 0.00018504
C -3.66462118 -1.16140020 0.00000906
H -1.61610144 -1.76804624 0.00019830
C -4.59522728 -0.08173674 -0.00019784
H -4.72477271 2.08997373 0.00016887
H -4.02144412 -2.18170445 0.00003577
N -5.94192373 -0.30758371 -0.00065606
C -6.87648102 0.81226986 -0.00048863
H -7.89274413 0.42569804 -0.00254262
H -6.75249956 1.44089006 0.88795014
H -6.74987785 1.44298200 -0.88700971
C -6.46678665 -1.66896703 0.00079082
H -7.55336238 -1.62850594 0.00118721
H -6.14773923 -2.22621204 -0.88647642
H -6.14700368 -2.22461136 0.88880451

Cis-Nap-azo-phNMe$_2$ (azo 4) coordinates

0 1

C -5.08924856 1.96245240 0.26741065
C -4.05001318 1.63946720 1.10924298
C -3.16103212 0.58138880 0.79164402
C -3.36084853 -0.15438908 -0.42039977
C -4.44591218 0.20162409 -1.26578843
C -5.28806454 1.23569109 -0.93036155
H -1.94334734 0.74987472 2.57391580
H -5.76114345 2.77505043 0.51892659
H -3.89631873 2.19341290 2.02939558
C -2.08193256 0.21218173 1.64180593
C -2.47971712 -1.22068450 -0.73128660
H -4.59870207 -0.35608612 -2.18367031
H -6.11111816 1.49870181 -1.58519895
C -1.41152860 -1.52014201 0.08764713
C -1.22437953 -0.80087211 1.30292509
H -2.64002372 -1.80505306 -1.63093038
H -0.40892017 -1.07353270 1.96149017
N -0.63589066 -2.68593817 -0.20382779
N 0.61981802 -2.72084386 -0.20798849
C 1.47870107 -1.59909178 -0.16415134
C 2.77916052 -1.86821671 0.29701111
C 1.21816870 -0.31013077 -0.66992801
C 3.75353263 -0.89130910 0.34464051
H 3.00322093 -2.87459268 0.63211162
C 2.19650760 0.66457585 -0.67055584
H 0.25587670 -0.07600189 -1.10316537
C 3.48877805 0.42070008 -0.12976151
H 4.73040968 -1.14661681 0.72924742
H 1.96186160 1.62850079 -1.09908900
N 4.43951419 1.40128860 -0.08755780
C 5.78404883 1.10282629 0.39260926
H 6.36901645 2.01957478 0.39840862
H 5.76233410 0.71039002 1.41376827
H 6.29573535 0.37253242 -0.24555721
C 4.17400086 2.71415834 -0.66540031
H 5.02980958 3.35988207 -0.48288487
H 4.00910625 2.66102778 -1.74819208
H 3.29678400 3.18001053 -0.20677726

TS-Nap-azo-phNMe$_2$ (azo 4) coordinates

0 1

C -6.26901152 1.18513863 0.05667436
C -5.50989194 0.56899855 1.02820132
C -4.22588738 0.05266695 0.73500751
C -3.69885076 0.16909599 -0.59515684
C -4.51064919 0.81222360 -1.57563971
C -5.75551269 1.30348646 -1.25675289
H -3.79985236 -0.68600459 2.72673976
H -7.25172056 1.57703466 0.29209506
H -5.89043669 0.47030688 2.04045519
C -3.41700915 -0.58886599 1.71541983
C -2.41952394 -0.33977526 -0.89977852
H -4.12864260 0.90961642 -2.58692770
H -6.35299852 1.78853027 -2.02164086
C -1.64108828 -0.97145116 0.08826239
C -2.17913047 -1.08586208 1.42489766
H -2.02822477 -0.24632749 -1.90562868
H -1.57923782 -1.57183876 2.18435494
N -0.44998741 -1.48382085 -0.16683929
N 0.65741350 -1.96016327 -0.40399533
C 1.80396134 -1.14586279 -0.25110362
C 3.03153090 -1.75476297 -0.54566530
C 1.79249205 0.19595177 0.16745892
C 4.21848005 -1.06011258 -0.43180157
H 3.02901780 -2.79033138 -0.86647116
C 2.96773527 0.90267723 0.28701612
H 0.84936893 0.67732191 0.39876460
C 4.22580236 0.29789089 -0.01055446
H 5.14521153 -1.56320599 -0.66591114
H 2.92672033 1.93253127 0.61131766
N 5.38722643 0.99893240 0.10607650
C 6.66661319 0.36333276 -0.19532490
H 7.46299378 1.09169457 -0.06464563
H 6.86338399 -0.48295081 0.47152611
H 6.70027087 0.00328355 -1.22849914
C 5.37637560 2.38625022 0.56255089
H 6.39772029 2.75774335 0.58450837
H 4.79603317 3.02593578 -0.10995400
H 4.95921197 2.47590117 1.57095624

Triplet-Nap-azo-phNMe$_2$ (azo 4) coordinates

0 3

C -6.20356039 0.92480137 0.87568900
C -5.13471317 0.38693198 1.56175860
C -3.95697856 0.00268684 0.88136218
C -3.88413170 0.17666696 -0.54059323
C -5.00410345 0.73328109 -1.21835421
C -6.13520720 1.09828039 -0.52582503
H -2.89330291 -0.69943830 2.63343883
H -7.10058939 1.21683053 1.40942532
H -5.18605282 0.25267344 2.63712952
C -2.83301623 -0.56037553 1.55886883
C -2.71144552 -0.21158172 -1.22192867
H -4.95109241 0.86549742 -2.29371281
H -6.98151805 1.52193784 -1.05449396
C -1.61430425 -0.74870494 -0.53693701
C -1.70205525 -0.92321849 0.88673784
H -2.64265692 -0.09040643 -2.29714942
H -0.85869735 -1.35620055 1.40944666
N -0.51041773 -1.07884097 -1.27383315
N 0.51618735 -1.65897836 -0.69318486
C 1.68482269 -1.00632515 -0.47855409
C 2.78644157 -1.74308052 0.03262796
C 1.88660546 0.37868984 -0.72862574
C 3.99660152 -1.14247531 0.29139760
H 2.65207566 -2.80178765 0.22258971
C 3.10071972 0.97989642 -0.47838628
H 1.07000739 0.96223731 -1.13582565
C 4.19989110 0.24576794 0.04726972
H 4.80212704 -1.74695049 0.68389575
H 3.20930560 2.03338260 -0.69590884
N 5.40352435 0.84658502 0.30075237
C 6.52747974 0.06662168 0.80559517
H 7.38331154 0.72404281 0.93906348
H 6.29726282 -0.39162482 1.77327613
H 6.81428031 -0.72879873 0.10883929
C 5.59169317 2.26662657 0.02840054
H 6.60129679 2.55160049 0.31431347
H 5.46042149 2.49667762 -1.03495652
H 4.89032823 2.88203067 0.60146951

TD-DFT tables (FC states)

Table S1. 30 TDDFT singlet excitations of azo 1 from *trans*-S0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	2.5901	478.68	f=0.0000	60 -> 62	0.70161
2	3.1998	387.48	f=0.5450	59 -> 62	-0.17545
				61 -> 62	0.67419
3	3.5612	348.15	f=0.6421	59 -> 62	0.66837
				61 -> 62	0.19249
				61 -> 63	-0.10188
4	4.0233	308.17	f=0.0225	58 -> 62	0.68872
				61 -> 64	0.10087
5	4.3160	287.27	f=0.1460	57 -> 62	0.31520
				59 -> 62	0.12979
				61 -> 63	0.59471
6	4.4150	280.83	f=0.0000	60 -> 63	0.69938
7	4.4899	276.14	f=0.0263	57 -> 62	0.58613
				59 -> 63	-0.19509
				59 -> 65	0.10353
				61 -> 63	-0.30360
8	4.7893	258.88	f=0.1378	57 -> 63	-0.11036
				59 -> 63	0.52583
				61 -> 63	-0.12554
				61 -> 64	0.22988
				61 -> 65	0.34671
9	5.0218	246.89	f=0.0009	56 -> 62	0.68063
				61 -> 66	0.12586
10	5.1453	240.96	f=0.0000	60 -> 64	0.69933
11	5.2176	237.63	f=0.1489	58 -> 62	-0.12092
				58 -> 65	-0.12109
				59 -> 63	-0.13663
				61 -> 64	0.61361
				61 -> 65	-0.21373
12	5.2829	234.69	f=0.0004	60 -> 65	0.69145
13	5.3982	229.68	f=0.0960	57 -> 63	0.45781
				58 -> 63	0.20645
				59 -> 63	0.29490
				59 -> 65	0.17799
				61 -> 65	-0.28148
14	5.5258	224.38	f=0.0002	57 -> 63	-0.16450

				58 -> 63	0.65463
				61 -> 65	0.10134
15	5.6795	218.30	f=0.0898	57 -> 63	0.14496
				58 -> 63	-0.10939
				58 -> 65	-0.16572
				59 -> 64	0.58597
				61 -> 65	0.24149
16	5.8269	212.78	f=0.2539	55 -> 62	-0.12571
				57 -> 62	-0.13664
				57 -> 63	0.24002
				58 -> 64	0.19793
				59 -> 63	-0.17554
				59 -> 64	-0.18603
				59 -> 65	0.34974
				61 -> 64	0.16961
				61 -> 65	0.34156
17	5.8522	211.86	f=0.0377	56 -> 63	-0.34842
				59 -> 66	-0.13786
				61 -> 66	0.55971
18	5.8846	210.69	f=0.0003	54 -> 62	0.68102
19	5.9417	208.67	f=0.0660	55 -> 62	0.61904
				57 -> 63	-0.11458
				59 -> 65	0.16824
				61 -> 67	-0.22536
20	6.0069	206.40	f=0.0002	52 -> 62	0.10534
				53 -> 62	0.56734
				60 -> 66	0.15063
				60 -> 67	-0.35224
21	6.0241	205.81	f=0.3113	55 -> 62	-0.12852
				57 -> 63	-0.33910
				59 -> 64	0.16042
				59 -> 65	0.49103
				61 -> 65	-0.14338
				61 -> 67	0.19245
22	6.1157	202.73	f=0.0004	53 -> 62	0.38110
				60 -> 66	-0.31072
				60 -> 67	0.49031
23	6.2065	199.77	f=0.0140	56 -> 63	0.25239
				56 -> 65	0.12537
				57 -> 64	-0.26394
				58 -> 65	0.23043
				59 -> 64	0.14008
				59 -> 66	0.38133

				61 -> 66	0.21772
				61 -> 67	0.20768
24	6.2124	199.57	f=0.0000	60 -> 66	0.60518
				60 -> 67	0.34070
25	6.2460	198.50	f=0.0047	56 -> 63	-0.21873
				57 -> 64	-0.34110
				57 -> 65	0.12020
				58 -> 65	0.35161
				59 -> 64	0.16781
				59 -> 65	-0.10076
				59 -> 66	-0.27248
				61 -> 66	-0.19361
26	6.3136	196.38	f=0.0000	51 -> 62	0.14837
				52 -> 62	0.65799
				53 -> 62	-0.12321
27	6.3306	195.85	f=0.0676	55 -> 62	0.18356
				57 -> 63	0.13722
				57 -> 64	0.21576
				58 -> 64	-0.25393
				61 -> 66	-0.13031
				61 -> 67	0.51742
28	6.4144	193.29	f=0.0002	48 -> 62	0.11374
				51 -> 62	0.66040
				52 -> 62	-0.16221
29	6.5264	189.97	f=0.1340	50 -> 62	0.12980
				56 -> 63	-0.19765
				57 -> 64	0.10390
				57 -> 65	0.23058
				58 -> 64	0.49302
				59 -> 65	-0.10975
				59 -> 66	0.15473
				59 -> 67	-0.14984
				61 -> 66	-0.14182
				61 -> 67	0.12760
30	6.5447	189.44	f=0.0130	56 -> 63	0.40684
				57 -> 64	0.19405
				57 -> 65	0.30939
				58 -> 64	0.10494
				58 -> 65	0.11217
				59 -> 66	-0.33946
				61 -> 66	0.15080

Table S2. 30 TDDFT triplet excitations of azo 1 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	1.8577	667.41	f=0.0000	60 -> 62	0.68555
				60 -> 67	-0.14866
2	2.0660	600.13	f=0.0000	59 -> 62	0.23927
				59 -> 63	0.10098
				61 -> 62	0.62761
				61 -> 63	-0.11905
3	2.8976	427.89	f=0.0000	57 -> 62	0.19759
				59 -> 62	0.52136
				59 -> 63	-0.11289
				61 -> 62	-0.14934
				61 -> 63	0.33740
				61 -> 65	-0.10936
4	3.1415	394.66	f=0.0000	57 -> 62	0.11033
				59 -> 62	-0.33778
				59 -> 63	-0.27860
				59 -> 65	-0.10987
				61 -> 62	0.25198
				61 -> 63	0.44158
5	3.5253	351.69	f=0.0000	57 -> 62	0.20176
				58 -> 62	0.61071
				58 -> 64	-0.14768
				59 -> 62	-0.10879
				59 -> 63	0.10197
6	3.6224	342.27	f=0.0000	57 -> 62	0.53689
				58 -> 62	-0.29592
				59 -> 62	-0.13608
				59 -> 63	0.15767
				59 -> 65	-0.11299
				61 -> 63	-0.12585
				61 -> 65	-0.13983
7	4.0159	308.73	f=0.0000	57 -> 63	-0.22003
				59 -> 63	0.54899
				61 -> 63	0.34467
8	4.1405	299.44	f=0.0000	55 -> 62	0.13713
				56 -> 62	0.38372
				56 -> 63	-0.28159
				57 -> 62	-0.10821
				57 -> 63	0.11510

				57 -> 65	-0.12395
				58 -> 64	-0.19114
				61 -> 66	-0.33606
9	4.3430	285.48	f=0.0000	56 -> 62	0.14910
				56 -> 63	-0.12898
				57 -> 62	0.20621
				58 -> 64	0.52099
				58 -> 65	-0.22008
				61 -> 65	0.15582
				61 -> 66	-0.12670
10	4.3572	284.55	f=0.0000	60 -> 63	0.68872
11	4.5992	269.58	f=0.0000	56 -> 63	0.12203
				57 -> 62	0.12864
				57 -> 65	-0.14080
				59 -> 64	0.16234
				61 -> 64	0.50461
				61 -> 65	0.32004
				61 -> 67	0.14374
12	4.6838	264.71	f=0.0000	56 -> 63	0.11845
				57 -> 64	-0.21853
				58 -> 64	-0.15746
				59 -> 64	-0.27260
				59 -> 65	0.11823
				61 -> 64	-0.25594
				61 -> 65	0.45598
				61 -> 67	0.11188
13	4.7505	260.99	f=0.0000	55 -> 62	0.11470
				56 -> 62	0.42748
				56 -> 63	0.27832
				57 -> 62	-0.12061
				58 -> 64	0.13397
				59 -> 66	-0.19495
				61 -> 65	-0.16782
				61 -> 66	0.22035
				61 -> 67	0.16242
14	4.9155	252.23	f=0.0000	42 -> 62	0.12563
				50 -> 62	-0.14527
				55 -> 62	0.35088
				56 -> 62	-0.18585
				57 -> 64	-0.13128
				57 -> 65	-0.18643
				59 -> 64	0.13474
				59 -> 65	0.24395

				59 -> 67	0.26373
				61 -> 64	-0.10133
				61 -> 65	-0.10907
				61 -> 67	0.16600
15	5.0575	245.15	f=0.0000	55 -> 62	-0.13063
				56 -> 62	0.27744
				57 -> 62	0.11155
				57 -> 63	-0.19792
				57 -> 67	-0.12220
				58 -> 64	-0.11869
				59 -> 63	-0.15828
				59 -> 64	0.23175
				59 -> 65	0.42284
				61 -> 67	-0.17086
16	5.1141	242.43	f=0.0000	60 -> 64	0.70185
17	5.1812	239.30	f=0.0000	60 -> 65	0.68649
18	5.2797	234.83	f=0.0000	55 -> 63	-0.19697
				57 -> 63	0.51429
				57 -> 66	0.10019
				59 -> 64	0.14933
				59 -> 65	0.21458
				59 -> 66	-0.18799
				61 -> 63	0.10275
19	5.4870	225.96	f=0.0000	58 -> 63	0.59834
				58 -> 65	-0.15453
				59 -> 64	-0.12111
				61 -> 64	0.15677
				61 -> 66	0.11469
20	5.5329	224.09	f=0.0000	56 -> 63	0.15555
				57 -> 63	-0.21043
				57 -> 64	0.10006
				57 -> 65	-0.11229
				58 -> 63	0.29451
				59 -> 64	0.27070
				59 -> 65	-0.16671
				59 -> 66	-0.13333
				61 -> 64	-0.24829
				61 -> 65	0.12254
				61 -> 66	-0.28176
21	5.5677	222.68	f=0.0000	56 -> 63	-0.13792
				57 -> 63	0.17334
				57 -> 64	0.13853
				57 -> 66	-0.14605

				59 -> 64	0.30812
				59 -> 65	-0.18060
				59 -> 66	0.19905
				61 -> 64	-0.23030
				61 -> 65	0.16925
				61 -> 66	0.33691
22	5.6629	218.94	f=0.0000	55 -> 62	0.47398
				57 -> 63	-0.11448
				57 -> 64	0.17269
				57 -> 65	0.25075
				58 -> 65	0.13590
				59 -> 67	-0.19106
				61 -> 67	-0.19825
23	5.7089	217.18	f=0.0000	48 -> 62	0.10525
				49 -> 62	-0.15130
				51 -> 62	0.18731
				54 -> 62	0.51964
				60 -> 67	0.32197
24	5.7521	215.54	f=0.0000	51 -> 62	-0.14106
				52 -> 62	-0.14526
				53 -> 62	-0.31155
				54 -> 62	-0.19856
				60 -> 62	0.12054
				60 -> 66	-0.10620
				60 -> 67	0.50990
25	5.8373	212.40	f=0.0000	57 -> 65	-0.12000
				58 -> 63	0.16887
				58 -> 64	0.22026
				58 -> 65	0.47894
				58 -> 66	0.10929
				58 -> 67	-0.32232
				59 -> 64	-0.14558
26	5.8810	210.82	f=0.0000	50 -> 62	-0.10732
				56 -> 63	0.43440
				57 -> 63	0.12963
				57 -> 65	0.18876
				57 -> 66	-0.12333
				59 -> 66	0.37408
				61 -> 66	-0.23467
27	5.9257	209.23	f=0.0000	53 -> 62	0.55693
				54 -> 62	-0.31195
				60 -> 67	0.22128
28	5.9995	206.66	f=0.0000	42 -> 62	-0.14012

				50 -> 62	0.31942
				55 -> 62	0.16119
				55 -> 65	0.13290
				56 -> 63	0.12255
				56 -> 65	0.11547
				57 -> 64	-0.19331
				57 -> 65	-0.27501
				57 -> 67	-0.16898
				59 -> 65	-0.11487
				59 -> 66	0.27282
				61 -> 74	0.10957
29	6.0968	203.36	f=0.0000	48 -> 62	0.15079
				51 -> 62	0.45892
				52 -> 62	0.30924
				53 -> 62	-0.21937
				54 -> 62	-0.24687
				60 -> 66	-0.11686
30	6.1368	202.03	f=0.0000	50 -> 62	0.14222
				55 -> 63	-0.24035
				56 -> 63	-0.13881
				57 -> 65	0.16875
				59 -> 65	0.11153
				59 -> 66	0.18968
				59 -> 67	-0.13200
				61 -> 65	-0.10199
				61 -> 67	0.47531
				61 -> 74	0.12679

Table S3. 30 TDDFT singlet excitations of azo 2 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	2.6587	466.33	f=0.0000	64 -> 66	0.70116
2	3.1739	390.64	f=1.0204	63 -> 66	-0.11004
				65 -> 66	0.69253
3	3.4846	355.81	f=0.2441	62 -> 66	-0.10025
				63 -> 66	0.66528
				65 -> 66	0.12937
				65 -> 67	-0.14970
4	4.1693	297.37	f=0.0606	61 -> 66	0.14451
				62 -> 66	0.33353
				63 -> 66	0.17815
				65 -> 67	0.54849
5	4.2009	295.13	f=0.0217	61 -> 66	0.53885
				62 -> 66	0.25296
				65 -> 67	-0.30154
				65 -> 68	-0.19132
6	4.3106	287.63	f=0.0074	61 -> 66	-0.34594
				62 -> 66	0.51236
				63 -> 67	-0.15601
				65 -> 67	-0.24572
				65 -> 69	0.11680
7	4.3750	283.39	f=0.0000	64 -> 67	0.69903
8	4.7366	261.76	f=0.1638	62 -> 67	-0.10467
				63 -> 67	0.55965
				65 -> 68	-0.21121
				65 -> 69	0.31599
9	4.9325	251.36	f=0.2406	61 -> 66	0.21332
				63 -> 67	0.21795
				65 -> 68	0.59958
10	4.9952	248.21	f=0.0000	64 -> 68	0.70511
11	5.0745	244.33	f=0.0122	60 -> 66	0.60509
				62 -> 67	0.24454
				63 -> 67	0.10580
				63 -> 69	0.10002
				65 -> 70	-0.14899
12	5.1207	242.12	f=0.0093	60 -> 66	-0.29394
				62 -> 67	0.45470
				63 -> 67	0.18976
				63 -> 69	0.21859

				65 -> 68	-0.10317
				65 -> 69	-0.24811
13	5.3345	232.42	f=0.0004	64 -> 69	0.69678
14	5.4450	227.70	f=0.0329	63 -> 68	0.62270
				65 -> 69	-0.27384
15	5.6089	221.05	f=0.1554	59 -> 66	-0.13916
				61 -> 67	-0.23784
				61 -> 68	-0.13613
				62 -> 66	-0.10452
				62 -> 67	0.17907
				63 -> 67	-0.15142
				63 -> 68	0.20985
				63 -> 69	0.32133
				65 -> 69	0.40020
16	5.6951	217.70	f=0.0060	61 -> 67	0.64553
				62 -> 67	0.13947
				63 -> 68	0.11696
				65 -> 69	0.12167
				65 -> 70	-0.11293
17	5.7791	214.54	f=0.0090	60 -> 66	0.13387
				60 -> 67	0.29738
				61 -> 67	0.11209
				63 -> 70	-0.18579
				65 -> 70	0.56934
18	5.8467	212.06	f=0.2033	59 -> 66	0.56990
				62 -> 67	-0.17039
				63 -> 69	0.29596
				65 -> 71	-0.14120
19	5.9819	207.27	f=0.0003	54 -> 66	-0.10812
				58 -> 66	0.68566
20	5.9933	206.87	f=0.3558	59 -> 66	-0.29196
				60 -> 67	0.15794
				62 -> 67	-0.29899
				63 -> 69	0.37678
				63 -> 70	-0.18559
				65 -> 69	-0.15409
				65 -> 70	-0.17979
				65 -> 71	0.15799
21	6.0736	204.14	f=0.0896	60 -> 67	-0.16171
				62 -> 68	0.55576
				63 -> 68	-0.11199
				63 -> 69	0.17357
				63 -> 70	0.19763

				65 -> 70	0.11359
				65 -> 71	0.13341
22	6.0936	203.46	f=0.0327	60 -> 67	-0.31093
				62 -> 68	-0.35298
				63 -> 69	0.18925
				63 -> 70	0.35597
				65 -> 70	0.22378
				65 -> 71	0.12402
23	6.1358	202.07	f=0.0000	57 -> 66	0.44526
				64 -> 70	0.43349
				64 -> 71	-0.30166
24	6.1682	201.01	f=0.0005	57 -> 66	-0.41944
				64 -> 70	0.53946
				64 -> 71	0.13493
25	6.2628	197.97	f=0.0004	57 -> 66	0.31749
				64 -> 71	0.61174
26	6.2660	197.87	f=0.0436	59 -> 66	0.14111
				61 -> 68	0.29805
				62 -> 67	0.11108
				62 -> 69	0.17541
				65 -> 71	0.55564
27	6.4133	193.32	f=0.0000	56 -> 66	0.68680
28	6.4413	192.48	f=0.0001	62 -> 72	0.12967
				63 -> 72	0.20522
				65 -> 72	0.65978
29	6.4838	191.22	f=0.0227	55 -> 66	0.13793
				60 -> 67	-0.33780
				61 -> 68	-0.13617
				62 -> 69	0.44566
				63 -> 70	-0.32742
30	6.5282	189.92	f=0.0376	55 -> 66	-0.34134
				60 -> 67	0.25325
				61 -> 68	-0.30431
				62 -> 69	0.34393
				63 -> 70	0.21482

Table S4. 30 TDDFT triplet excitations of azo 2 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	1.9333	641.30	f=0.0000	64 -> 66	0.68446
				64 -> 71	-0.13988
2	1.9772	627.07	f=0.0000	63 -> 67	0.12350
				65 -> 66	0.67059
3	2.8371	437.01	f=0.0000	62 -> 66	0.17266
				63 -> 66	0.51038
				63 -> 67	-0.24374
				65 -> 67	0.33617
				65 -> 69	-0.13267
4	3.1913	388.51	f=0.0000	62 -> 66	-0.11447
				63 -> 66	0.43841
				63 -> 67	0.37271
				65 -> 66	-0.16425
				65 -> 67	-0.30860
5	3.5486	349.39	f=0.0000	62 -> 66	0.61800
				63 -> 67	0.19468
				65 -> 67	-0.13637
				65 -> 69	-0.13290
6	3.8002	326.26	f=0.0000	61 -> 66	0.66267
				61 -> 68	0.13296
				65 -> 68	0.12081
7	3.8746	319.99	f=0.0000	62 -> 67	-0.29165
				63 -> 67	0.40937
				65 -> 67	0.46500
8	4.0956	302.73	f=0.0000	61 -> 66	-0.10522
				61 -> 68	-0.14607
				62 -> 68	0.14484
				63 -> 68	0.24507
				65 -> 68	0.57699
				65 -> 69	0.16973
9	4.1536	298.50	f=0.0000	59 -> 66	-0.12565
				60 -> 66	0.38910
				60 -> 67	-0.30333
				62 -> 67	-0.12494
				63 -> 69	0.13833
				63 -> 70	-0.21462
				65 -> 69	-0.13520
				65 -> 70	0.28917

				65 -> 71	-0.10349
10	4.2546	291.41	f=0.0000	61 -> 66	-0.13870
				61 -> 68	0.51883
				61 -> 69	0.14163
				62 -> 66	-0.17601
				62 -> 68	0.10179
				65 -> 68	0.15336
				65 -> 69	-0.24570
				65 -> 71	0.12685
11	4.3163	287.25	f=0.0000	64 -> 66	-0.10638
				64 -> 67	0.68753
12	4.5768	270.90	f=0.0000	59 -> 66	0.14953
				60 -> 67	-0.20162
				61 -> 68	0.21575
				62 -> 68	0.12700
				62 -> 69	-0.14234
				63 -> 70	-0.14360
				65 -> 68	-0.11359
				65 -> 69	0.46419
				65 -> 70	0.15863
				65 -> 71	0.15894
13	4.7364	261.77	f=0.0000	59 -> 66	-0.23913
				60 -> 66	0.30364
				60 -> 67	0.22024
				61 -> 68	0.18875
				62 -> 66	0.11726
				63 -> 70	0.22192
				65 -> 69	0.26298
				65 -> 70	-0.12905
				65 -> 71	-0.23494
14	4.8412	256.10	f=0.0000	59 -> 66	-0.19097
				59 -> 67	-0.16691
				62 -> 67	0.40272
				62 -> 69	0.15641
				63 -> 67	0.19618
				63 -> 68	0.12314
				63 -> 69	-0.28584
				63 -> 70	-0.11710
				63 -> 71	-0.15478
				65 -> 67	0.10781
15	4.9345	251.26	f=0.0000	59 -> 66	0.25683
				60 -> 66	0.43782
				60 -> 67	0.11238

				61 -> 68	-0.10073
				62 -> 67	0.29873
				62 -> 69	-0.13587
				63 -> 67	0.11059
				63 -> 71	0.12488
				65 -> 67	0.11148
				65 -> 71	0.17406
16	4.9692	249.51	f=0.0000	64 -> 68	0.70448
17	5.0928	243.45	f=0.0000	60 -> 66	-0.13781
				61 -> 68	0.11774
				62 -> 67	0.32010
				63 -> 68	-0.24017
				63 -> 69	0.46977
				65 -> 67	0.10149
				65 -> 71	-0.17707
18	5.2242	237.33	f=0.0000	64 -> 69	0.68503
19	5.3566	231.46	f=0.0000	59 -> 67	0.11551
				62 -> 68	0.15074
				62 -> 70	-0.10728
				63 -> 68	0.48028
				63 -> 69	0.18841
				65 -> 68	-0.26513
				65 -> 69	-0.11610
				65 -> 70	0.20067
20	5.4360	228.08	f=0.0000	59 -> 67	0.14440
				60 -> 67	0.13507
				62 -> 68	-0.11290
				62 -> 69	0.16833
				62 -> 70	-0.23888
				63 -> 68	-0.23257
				63 -> 69	-0.17119
				63 -> 70	0.16184
				65 -> 68	0.10804
				65 -> 70	0.41822
21	5.5288	224.25	f=0.0000	59 -> 66	0.43195
				59 -> 67	-0.10195
				61 -> 68	0.13784
				62 -> 68	-0.14940
				62 -> 69	0.33390
				62 -> 70	0.10451
				63 -> 71	-0.12838
				65 -> 70	-0.13050
				65 -> 71	-0.20769

22	5.6698	218.67	f=0.0000	61 -> 67	0.68048
23	5.7636	215.12	f=0.0000	55 -> 66	-0.28426
				59 -> 66	0.13994
				59 -> 69	0.13036
				60 -> 67	0.29668
				61 -> 67	0.10567
				62 -> 69	-0.24146
				62 -> 71	-0.10566
				63 -> 69	-0.11729
				63 -> 70	-0.15935
				63 -> 71	-0.11137
				65 -> 69	-0.11969
				65 -> 70	0.24318
				65 -> 71	-0.14847
24	5.8050	213.58	f=0.0000	54 -> 66	-0.28327
				58 -> 66	0.53959
				64 -> 71	-0.27824
25	5.8610	211.54	f=0.0000	59 -> 66	-0.14997
				60 -> 67	0.36318
				62 -> 68	-0.26997
				62 -> 70	0.11238
				63 -> 69	0.15621
				63 -> 70	-0.33283
				65 -> 69	0.10621
				65 -> 71	0.22780
26	5.9221	209.36	f=0.0000	54 -> 66	-0.11287
				57 -> 66	-0.31116
				58 -> 66	0.18139
				64 -> 66	0.11393
				64 -> 71	0.55377
27	5.9358	208.88	f=0.0000	55 -> 66	0.13609
				59 -> 68	0.13905
				60 -> 67	0.15937
				62 -> 68	0.49995
				62 -> 69	0.20463
				63 -> 68	-0.22018
				63 -> 70	-0.18147
28	6.0362	205.40	f=0.0000	54 -> 66	0.16201
				57 -> 66	0.52138
				58 -> 66	0.32286
				64 -> 71	0.21349
29	6.0577	204.67	f=0.0000	55 -> 66	0.35251
				59 -> 67	0.22830

				62 -> 69	-0.23808
				63 -> 69	-0.15970
				63 -> 70	-0.20365
				65 -> 71	-0.34167
30	6.1412	201.89	f=0.0000	57 -> 66	0.11501
				64 -> 70	0.67490

Table S5. 30 TDDFT singlet excitations of azo 3 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	2.6481	468.20	f=0.0000	68 -> 70	0.70118
2	3.1354	395.43	f=1.1190	69 -> 70	0.69816
3	3.4603	358.30	f=0.1732	66 -> 70	-0.10445
				67 -> 70	0.66856
				69 -> 71	-0.15312
4	4.1302	300.19	f=0.0412	65 -> 70	0.27224
				66 -> 70	0.46949
				67 -> 70	0.15260
				69 -> 71	0.37119
				69 -> 72	0.14261
5	4.1702	297.31	f=0.0528	65 -> 70	-0.39024
				66 -> 70	-0.19229
				67 -> 70	0.10897
				69 -> 71	0.51381
				69 -> 72	-0.12805
6	4.2853	289.32	f=0.0054	65 -> 70	0.45329
				66 -> 70	-0.42993
				67 -> 71	0.14201
				69 -> 71	0.22697
				69 -> 72	0.10715
				69 -> 73	-0.12215
7	4.3654	284.01	f=0.0000	68 -> 71	0.69909
8	4.7222	262.56	f=0.1667	66 -> 71	-0.10057
				67 -> 71	0.56475
				69 -> 72	0.23529
				69 -> 73	0.28942
9	4.9151	252.25	f=0.2653	65 -> 70	-0.19090
				66 -> 70	-0.10341
				66 -> 71	-0.13123
				67 -> 71	-0.24456
				69 -> 72	0.58240
10	5.0151	247.22	f=0.0000	68 -> 72	0.70460
11	5.0600	245.03	f=0.0234	64 -> 70	0.47766
				66 -> 71	0.37288
				67 -> 71	0.14366
				67 -> 72	0.11328
				67 -> 73	0.15328
				69 -> 72	0.10620

				69 -> 73	-0.14826
				69 -> 74	-0.11967
12	5.0882	243.67	f=0.0033	64 -> 70	0.47076
				66 -> 71	-0.34073
				67 -> 71	-0.11942
				67 -> 73	-0.16395
				69 -> 72	-0.10788
				69 -> 73	0.23540
				69 -> 74	-0.11551
13	5.3347	232.41	f=0.0004	68 -> 73	0.69688
14	5.4347	228.13	f=0.0446	67 -> 72	0.55989
				69 -> 73	0.36885
15	5.5766	222.33	f=0.1150	63 -> 70	0.21496
				65 -> 71	0.22073
				65 -> 72	-0.12852
				66 -> 71	-0.17494
				67 -> 71	0.11898
				67 -> 72	0.32176
				67 -> 73	-0.31925
				69 -> 72	-0.11868
				69 -> 73	-0.31468
16	5.6619	218.98	f=0.0091	63 -> 70	-0.15966
				65 -> 71	0.63310
				66 -> 71	0.18185
				67 -> 72	-0.12093
17	5.7463	215.76	f=0.0654	63 -> 70	0.49955
				64 -> 70	-0.13386
				64 -> 71	-0.11719
				67 -> 73	0.20807
				69 -> 73	0.10020
				69 -> 74	-0.34044
				69 -> 75	-0.12457
18	5.7702	214.87	f=0.0124	63 -> 70	0.28283
				64 -> 71	0.26630
				65 -> 71	0.16657
				67 -> 73	0.18878
				67 -> 74	-0.16988
				69 -> 74	0.47025
19	5.9364	208.85	f=0.0003	58 -> 70	0.13730
				61 -> 70	0.11836
				62 -> 70	0.66474
20	5.9697	207.69	f=0.4394	63 -> 70	-0.21404
				64 -> 71	0.18095

				66 -> 71	-0.31296
				67 -> 73	0.39461
				67 -> 74	-0.19256
				69 -> 73	-0.14654
				69 -> 74	-0.20667
				69 -> 75	0.11240
21	5.9846	207.17	f=0.0002	61 -> 70	0.67468
				62 -> 70	-0.11115
22	6.0639	204.46	f=0.1198	64 -> 71	0.24927
				66 -> 71	0.10924
				66 -> 72	0.41588
				67 -> 72	-0.10830
				67 -> 73	-0.22328
				67 -> 74	-0.29404
				69 -> 74	-0.16483
				69 -> 75	-0.18186
23	6.0840	203.79	f=0.0257	64 -> 71	-0.24247
				66 -> 72	0.50486
				66 -> 73	-0.10345
				67 -> 73	0.15447
				67 -> 74	0.27286
				69 -> 74	0.16267
24	6.1435	201.81	f=0.0002	68 -> 74	0.67982
				68 -> 75	-0.15051
25	6.2087	199.69	f=0.0720	60 -> 70	0.21368
				63 -> 70	0.11125
				65 -> 72	-0.23445
				66 -> 71	0.11076
				66 -> 73	0.13620
				69 -> 75	0.56709
26	6.2291	199.04	f=0.0000	62 -> 70	-0.10558
				68 -> 74	0.15707
				68 -> 75	0.66443
27	6.3546	195.11	f=0.0005	58 -> 70	-0.11286
				59 -> 70	0.67208
28	6.3922	193.96	f=0.0020	60 -> 70	0.63372
				64 -> 71	-0.12741
				65 -> 72	0.12907
				69 -> 75	-0.15089
29	6.4620	191.87	f=0.0324	64 -> 71	-0.21562
				65 -> 72	0.19853
				66 -> 72	0.13380
				66 -> 73	0.54400

				67 -> 74	-0.23305
30	6.5344	189.74	f=0.0762	60 -> 70	0.10602
				64 -> 71	0.40328
				65 -> 72	0.29517
				66 -> 72	0.10565
				66 -> 73	0.17498
				67 -> 74	0.37040

Table S6. 30 TDDFT triplet excitations of azo 3 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	1.9247	644.19	f=0.0000	68 -> 70	0.68450
				68 -> 75	-0.14062
2	1.9628	631.66	f=0.0000	67 -> 71	0.12340
				69 -> 70	0.67279
3	2.8225	439.27	f=0.0000	66 -> 70	0.16317
				67 -> 70	0.51737
				67 -> 71	-0.25299
				69 -> 71	0.32226
				69 -> 73	-0.12558
4	3.1900	388.67	f=0.0000	66 -> 70	-0.12315
				67 -> 70	0.43749
				67 -> 71	0.38509
				69 -> 70	-0.14805
				69 -> 71	-0.29734
5	3.5221	352.02	f=0.0000	66 -> 70	0.62243
				67 -> 71	0.19413
				69 -> 71	-0.13766
				69 -> 73	-0.11097
6	3.7782	328.16	f=0.0000	65 -> 70	0.66586
				65 -> 72	-0.13270
				69 -> 72	-0.10968
7	3.8582	321.35	f=0.0000	66 -> 71	-0.30242
				67 -> 71	0.38720
				69 -> 71	0.47567
8	4.1009	302.34	f=0.0000	65 -> 70	0.13109
				66 -> 72	0.14654
				67 -> 72	0.23574
				69 -> 72	0.58258
				69 -> 73	-0.16353
9	4.1482	298.88	f=0.0000	63 -> 70	-0.11268
				64 -> 70	0.39132
				64 -> 71	-0.29175
				66 -> 71	-0.10109
				66 -> 73	0.10222
				67 -> 73	0.13899
				67 -> 74	-0.22222
				69 -> 72	-0.16333
				69 -> 73	-0.15773

				69 -> 74	0.26368
10	4.2382	292.54	f=0.0000	65 -> 72	0.50620
				65 -> 73	-0.19002
				66 -> 70	0.15557
				69 -> 73	0.27976
				69 -> 75	-0.15162
11	4.3070	287.87	f=0.0000	68 -> 70	-0.10524
				68 -> 71	0.68775
12	4.5633	271.70	f=0.0000	63 -> 70	0.15655
				64 -> 71	-0.20465
				65 -> 72	-0.21446
				65 -> 73	0.10208
				66 -> 72	-0.16133
				66 -> 73	-0.12869
				67 -> 72	-0.11434
				67 -> 74	-0.15391
				69 -> 72	0.14972
				69 -> 73	0.42581
				69 -> 74	0.15819
				69 -> 75	0.16329
13	4.7162	262.89	f=0.0000	63 -> 70	-0.26336
				64 -> 70	0.28945
				64 -> 71	0.20336
				65 -> 72	-0.17678
				66 -> 70	0.10677
				67 -> 74	0.21305
				69 -> 73	0.28079
				69 -> 74	-0.11518
				69 -> 75	-0.23737
14	4.8045	258.06	f=0.0000	63 -> 70	-0.16129
				63 -> 71	-0.16308
				66 -> 71	0.44263
				66 -> 73	0.12177
				67 -> 71	0.21597
				67 -> 72	-0.12955
				67 -> 73	-0.24729
				67 -> 74	-0.11971
				67 -> 75	-0.13096
				69 -> 71	0.13849
15	4.9165	252.18	f=0.0000	63 -> 70	0.28997
				64 -> 70	0.43183
				64 -> 71	0.13334
				66 -> 71	0.26018

				66 -> 73	-0.14245
				67 -> 75	0.13001
				69 -> 71	0.10776
				69 -> 75	0.15163
16	4.9865	248.64	f=0.0000	68 -> 72	0.70363
17	5.0692	244.58	f=0.0000	64 -> 70	-0.16374
				65 -> 72	-0.13177
				66 -> 71	0.28327
				67 -> 72	0.27453
				67 -> 73	0.45659
				69 -> 75	-0.19335
18	5.2271	237.19	f=0.0000	68 -> 73	0.68541
19	5.3578	231.41	f=0.0000	63 -> 70	-0.13379
				63 -> 71	-0.14401
				64 -> 71	-0.12207
				66 -> 73	-0.19217
				66 -> 74	0.17340
				67 -> 72	0.36723
				67 -> 73	-0.12844
				67 -> 74	-0.11426
				69 -> 72	-0.18260
				69 -> 73	0.10329
				69 -> 74	-0.30302
				69 -> 75	0.10789
20	5.4300	228.33	f=0.0000	63 -> 70	0.19916
				65 -> 72	-0.15130
				66 -> 72	0.21216
				66 -> 73	0.22209
				66 -> 74	-0.12828
				67 -> 72	0.35544
				67 -> 73	-0.24165
				69 -> 72	-0.16710
				69 -> 73	0.11630
				69 -> 74	0.21713
21	5.4758	226.42	f=0.0000	60 -> 71	0.11769
				63 -> 70	0.35737
				63 -> 71	-0.12706
				65 -> 72	-0.12032
				66 -> 73	0.23672
				66 -> 74	0.19677
				67 -> 72	-0.11632
				67 -> 73	0.10388
				67 -> 74	-0.10492

				67 -> 75	-0.10941
				69 -> 74	-0.30424
				69 -> 75	-0.20830
22	5.6389	219.87	f=0.0000	65 -> 71	0.66409
				66 -> 71	0.11694
23	5.7350	216.19	f=0.0000	60 -> 70	0.36339
				63 -> 70	-0.11325
				63 -> 73	-0.11390
				64 -> 71	-0.26712
				65 -> 71	-0.15286
				66 -> 73	0.17633
				66 -> 75	0.10805
				67 -> 73	0.10066
				67 -> 74	0.12754
				67 -> 75	0.12332
				69 -> 73	0.12030
				69 -> 74	-0.23542
				69 -> 75	0.16528
24	5.7957	213.93	f=0.0000	57 -> 70	0.14858
				58 -> 70	0.26798
				61 -> 70	0.44989
				62 -> 70	0.36265
				68 -> 75	-0.15975
25	5.8103	213.39	f=0.0000	61 -> 70	-0.23967
				62 -> 70	0.48945
				68 -> 75	0.39507
26	5.8381	212.37	f=0.0000	63 -> 70	-0.13992
				64 -> 71	0.32197
				66 -> 72	0.30600
				66 -> 73	0.11113
				67 -> 73	0.21304
				67 -> 74	-0.26239
				69 -> 73	0.11958
				69 -> 75	0.28928
27	5.8973	210.24	f=0.0000	60 -> 70	0.41338
				64 -> 71	0.26796
				66 -> 72	-0.25287
				66 -> 74	0.13577
				66 -> 75	0.10967
				67 -> 73	-0.12517
				67 -> 74	-0.29176
28	5.9694	207.70	f=0.0000	60 -> 70	0.20731
				63 -> 72	0.11755

				65 -> 72	-0.11313
				65 -> 73	0.14171
				66 -> 72	0.38863
				66 -> 73	-0.35639
				67 -> 72	-0.19019
				69 -> 75	-0.16937
29	5.9728	207.58	f=0.0000	61 -> 70	0.38194
				62 -> 70	-0.23356
				68 -> 75	0.50486
30	6.1169	202.69	f=0.0000	55 -> 70	0.13959
				57 -> 70	0.11725
				58 -> 70	0.22562
				59 -> 70	-0.21387
				61 -> 70	-0.13647
				62 -> 70	-0.14588
				68 -> 73	-0.10702
				68 -> 74	0.52518
				68 -> 75	0.11684

Table S7. 30 TDDFT singlet excitations of azo 4 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	2.6910	460.74	f=0.0000	72 -> 74	0.70046
2	2.8285	438.33	f=1.3883	73 -> 74	0.70633
3	3.4335	361.10	f=0.0058	70 -> 74	0.13825
				71 -> 74	0.57863
				73 -> 75	0.36247
4	3.7700	328.87	f=0.0499	71 -> 74	-0.35410
				73 -> 75	0.59997
5	4.0847	303.53	f=0.0712	69 -> 74	0.14937
				70 -> 74	0.62028
				71 -> 74	-0.14119
				71 -> 75	0.15039
				73 -> 76	0.17036
				73 -> 77	0.11151
6	4.1562	298.31	f=0.0149	69 -> 74	0.52802
				70 -> 74	-0.18197
				73 -> 76	0.38860
				73 -> 77	-0.15091
7	4.2616	290.93	f=0.0000	72 -> 75	0.69874
8	4.4767	276.96	f=0.0850	69 -> 74	-0.42080
				71 -> 75	-0.11598
				73 -> 76	0.53980
9	4.5796	270.73	f=0.2581	69 -> 74	-0.10185
				71 -> 75	0.59195
				73 -> 77	-0.33410
10	4.8244	257.00	f=0.0165	68 -> 74	0.11499
				70 -> 74	-0.17549
				70 -> 75	-0.40695
				71 -> 75	0.20817
				71 -> 76	0.11152
				71 -> 77	0.18465
				73 -> 77	0.41685
11	5.0193	247.01	f=0.0000	72 -> 76	0.70385
12	5.0331	246.34	f=0.0975	68 -> 74	0.49754
				70 -> 75	0.30619
				71 -> 76	-0.11820
				71 -> 77	-0.13505
				73 -> 77	0.21067
				73 -> 78	-0.20756

13	5.1556	240.49	f=0.0360	67 -> 74	-0.21359
				68 -> 74	0.32798
				70 -> 75	-0.23248
				71 -> 75	-0.18437
				71 -> 76	0.19406
				71 -> 77	0.24980
				73 -> 77	-0.32440
				73 -> 78	-0.15948
14	5.2709	235.22	f=0.0003	72 -> 77	0.69648
15	5.2977	234.03	f=0.0277	67 -> 74	0.45737
				68 -> 74	0.28688
				73 -> 78	0.38927
				73 -> 79	0.10012
16	5.4604	227.06	f=0.0067	67 -> 74	-0.38973
				71 -> 76	-0.30147
				73 -> 78	0.47240
17	5.4829	226.13	f=0.0261	67 -> 74	-0.22461
				71 -> 76	0.54738
				71 -> 77	-0.26914
				73 -> 78	0.19811
18	5.5752	222.38	f=0.0054	69 -> 75	0.70308
19	5.7727	214.78	f=0.0200	73 -> 80	0.69828
20	5.7928	214.03	f=0.2482	67 -> 75	-0.11010
				68 -> 75	0.34820
				70 -> 75	-0.27951
				71 -> 77	-0.34905
				71 -> 78	0.27420
				73 -> 79	0.20346
21	5.8665	211.34	f=0.0481	68 -> 75	-0.17803
				69 -> 76	-0.10220
				70 -> 77	0.11002
				71 -> 78	-0.15926
				73 -> 79	0.61831
22	5.9861	207.12	f=0.0618	68 -> 75	-0.10098
				70 -> 76	0.63063
				70 -> 77	-0.10983
				71 -> 77	-0.14857
				71 -> 78	-0.15008
23	6.0150	206.13	f=0.4582	66 -> 74	-0.11072
				67 -> 75	-0.21897
				68 -> 75	0.14071
				70 -> 75	0.24958
				70 -> 76	0.25480

				71 -> 76	0.10754
				71 -> 77	0.32025
				71 -> 78	0.35505
				73 -> 79	0.14476
24	6.0298	205.62	f=0.0001	64 -> 74	0.21323
				65 -> 74	0.38456
				72 -> 78	0.53019
25	6.0564	204.72	f=0.0007	64 -> 74	0.21525
				65 -> 74	0.48110
				72 -> 78	-0.45314
26	6.1206	202.57	f=0.0000	64 -> 74	0.58411
				65 -> 74	-0.30192
				72 -> 79	-0.21247
27	6.2540	198.25	f=0.0449	66 -> 74	0.57032
				67 -> 75	-0.10729
				68 -> 75	-0.14032
				69 -> 76	-0.13682
				70 -> 77	0.30847
				71 -> 78	0.12054
28	6.2740	197.61	f=0.0003	64 -> 74	0.22376
				72 -> 79	0.65922
29	6.2887	197.15	f=0.1035	66 -> 74	0.27650
				67 -> 75	0.12027
				68 -> 74	-0.11656
				68 -> 75	0.41406
				70 -> 77	-0.20248
				71 -> 77	0.20208
				71 -> 78	-0.28522
				71 -> 79	-0.11870
30	6.3695	194.65	f=0.0012	71 -> 81	0.12957
				73 -> 81	0.63531
				73 -> 83	0.25176

Table S8. 30 TDDFT triplet excitations of azo 4 from *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Transition	Transition Contribution
1	1.7291	717.04	f=0.0000	73 -> 74	0.68457
2	1.9977	620.63	f=0.0000	72 -> 74	0.68226
				72 -> 79	-0.13709
3	2.7098	457.55	f=0.0000	70 -> 74	-0.16693
				71 -> 74	0.50401
				71 -> 75	-0.32659
				73 -> 75	-0.26317
				73 -> 77	0.10290
4	3.2218	384.83	f=0.0000	71 -> 74	0.43174
				71 -> 75	0.42420
				73 -> 75	0.30935
5	3.4062	364.00	f=0.0000	70 -> 74	0.58834
				70 -> 75	0.12110
				71 -> 74	0.17351
				73 -> 75	-0.23356
6	3.5476	349.49	f=0.0000	70 -> 74	0.23873
				70 -> 75	-0.24883
				71 -> 75	-0.32559
				73 -> 75	0.46234
				73 -> 76	-0.18625
7	3.6586	338.89	f=0.0000	69 -> 74	0.16658
				70 -> 74	0.10853
				73 -> 75	0.11779
				73 -> 76	0.59769
				73 -> 77	-0.22462
8	3.7929	326.88	f=0.0000	69 -> 74	0.61740
				69 -> 76	-0.18702
				73 -> 76	-0.21572
9	3.9955	310.31	f=0.0000	68 -> 74	-0.29412
				69 -> 74	0.22093
				69 -> 76	0.22044
				69 -> 77	-0.10697
				70 -> 77	-0.12109
				71 -> 77	0.11755
				71 -> 78	-0.10708
				73 -> 74	0.10217
				73 -> 76	0.11719
				73 -> 77	0.42941

10	4.1631	297.82	f=0.0000	67 -> 74	-0.12403
				67 -> 75	0.16235
				68 -> 74	0.27386
				68 -> 75	-0.21649
				69 -> 76	0.20368
				70 -> 75	-0.20582
				71 -> 77	-0.14707
				71 -> 78	0.24589
				73 -> 77	0.15515
				73 -> 78	0.21869
				73 -> 79	-0.22340
11	4.2018	295.07	f=0.0000	72 -> 74	-0.11479
				72 -> 75	0.68617
12	4.4387	279.32	f=0.0000	67 -> 74	-0.24299
				67 -> 75	0.14445
				68 -> 74	-0.20365
				69 -> 76	0.24656
				70 -> 75	0.33442
				71 -> 75	-0.13051
				71 -> 78	0.19699
				73 -> 75	0.13838
				73 -> 77	-0.25451
				73 -> 79	0.11690
13	4.4659	277.62	f=0.0000	67 -> 74	0.21483
				67 -> 75	-0.10078
				68 -> 74	0.16722
				68 -> 75	0.18095
				69 -> 76	0.32695
				69 -> 77	-0.11904
				70 -> 75	0.16577
				70 -> 76	0.10685
				70 -> 77	0.15578
				71 -> 75	-0.10152
				71 -> 78	-0.18781
				73 -> 77	-0.12707
				73 -> 78	-0.11590
				73 -> 79	-0.29602
14	4.5039	275.28	f=0.0000	67 -> 75	0.13341
				68 -> 74	0.21678
				69 -> 76	-0.22996
				70 -> 75	0.42104
				71 -> 75	-0.17921
				73 -> 75	0.12928

				73 -> 76	0.11381
				73 -> 77	0.26847
15	4.8975	253.16	f=0.0000	66 -> 75	-0.10770
				67 -> 74	0.33447
				67 -> 75	0.19360
				69 -> 76	0.13558
				70 -> 75	-0.12531
				70 -> 78	0.10244
				71 -> 76	0.21823
				71 -> 77	0.36649
				71 -> 78	0.18002
				71 -> 79	0.12502
16	4.9786	249.04	f=0.0000	67 -> 74	-0.27939
				68 -> 74	0.38507
				69 -> 76	0.17075
				71 -> 76	0.16197
				71 -> 77	0.28440
				71 -> 78	-0.11565
				73 -> 78	-0.10887
				73 -> 79	0.25503
17	4.9853	248.70	f=0.0000	72 -> 76	0.70167
18	5.1574	240.40	f=0.0000	72 -> 77	0.68312
19	5.1574	240.40	f=0.0000	66 -> 74	-0.12633
				67 -> 74	-0.13333
				67 -> 75	-0.15978
				68 -> 74	-0.11763
				69 -> 76	-0.11137
				70 -> 77	0.21036
				70 -> 78	-0.18568
				71 -> 76	0.19970
				71 -> 77	0.21713
				73 -> 77	-0.10607
				73 -> 78	0.39294
				73 -> 79	-0.19050
20	5.1839	239.17	f=0.0000	66 -> 74	0.14303
				66 -> 75	0.11514
				67 -> 74	0.31857
				67 -> 75	-0.10355
				69 -> 76	0.11849
				70 -> 76	-0.12871
				70 -> 77	-0.18214
				70 -> 78	-0.15568
				70 -> 79	-0.10076

				73 -> 78	0.40446
				73 -> 79	0.20627
21	5.3700	230.89	f=0.0000	70 -> 76	-0.29034
				70 -> 77	-0.12057
				71 -> 76	0.50382
				71 -> 77	-0.22477
				73 -> 77	-0.11959
				73 -> 79	-0.17857
22	5.4299	228.34	f=0.0000	66 -> 74	-0.14857
				68 -> 77	0.11281
				70 -> 77	0.36654
				71 -> 76	0.19240
				71 -> 77	-0.25622
				73 -> 76	0.10274
				73 -> 77	0.16181
				73 -> 79	0.31155
23	5.5638	222.84	f=0.0000	69 -> 75	0.69308
24	5.6020	221.32	f=0.0000	66 -> 74	0.48027
				66 -> 75	-0.13364
				67 -> 74	-0.14213
				68 -> 75	0.25352
				70 -> 75	-0.10073
				70 -> 76	0.13208
				70 -> 77	0.17902
				70 -> 78	0.11084
				71 -> 77	-0.13098
				71 -> 79	0.10888
25	5.6896	217.91	f=0.0000	73 -> 80	0.69208
26	5.7514	215.57	f=0.0000	66 -> 74	-0.27467
				66 -> 75	-0.16197
				68 -> 75	0.44754
				70 -> 77	-0.11969
				70 -> 78	0.19427
				71 -> 78	0.22414
				73 -> 78	0.10824
				73 -> 79	0.11061
27	5.8349	212.49	f=0.0000	62 -> 74	0.28768
				64 -> 74	0.27403
				65 -> 74	0.51776
				72 -> 79	0.17016
28	5.8458	212.09	f=0.0000	67 -> 76	-0.13017
				68 -> 76	-0.17138
				70 -> 76	0.51624

				70 -> 77	-0.28415
				71 -> 76	0.23075
29	5.9161	209.57	f=0.0000	66 -> 75	0.20731
				67 -> 75	-0.29817
				67 -> 77	-0.10669
				68 -> 77	0.10815
				70 -> 78	-0.11253
				71 -> 77	0.10513
				71 -> 78	0.45697
				71 -> 88	-0.11147
				73 -> 78	-0.18935
30	5.9253	209.25	f=0.0000	64 -> 74	-0.38885
				72 -> 74	0.11719
				72 -> 79	0.55246

Azo 1 and 4 PECs

Table S9. TDDFT Energies of 1 along the torsional ∠ CNNC of the S_0 trans-cis isomerization.

∠ CNNC	S_0	S_1	S_2	S_3	S_4	T_1	T_2	T_3
0	0.6663	3.3144	4.0862	4.5866	4.7494	2.51406	3.2731	3.8548
12.5	0.64208	3.17168	4.00338	4.51338	4.66048	2.3799	3.23648	3.78248
20	0.66461	3.02141	3.94311	4.46951	4.59221	2.22431	3.23061	3.74261
40	0.84949	2.70399	3.89629	4.46129	4.52429	1.8738	3.29099	3.74819
60	1.21804	2.40344	3.97004	4.53754	4.60044	1.55233	3.41754	3.87784
80	1.73256	2.07566	4.16366	4.69526	4.78996	1.34623	3.59416	4.12066
100	1.78436	1.92616	4.14226	4.67896	4.78486	1.28726	3.56126	4.08316
120	1.08976	2.18636	3.79826	4.37776	4.46926	1.33757	3.18656	3.65146
140	0.51092	2.32702	3.51822	4.03042	4.22882	1.51442	2.77852	3.28082
160	0.13203	2.49103	3.31343	3.71473	4.07953	1.75641	2.39573	3.01173
180	0	2.5901	3.1998	3.5612	4.0233	1.95612	2.066	2.8976

Table S10. TDDFT Energies of 1 along the inversion ∠ ^{Nap}CNN of the S_0 trans-cis isomerization.

∠ CNN	S_0	S_1	S_2	S_3	S_4	T_1	T_2	T_3
115.31275	0	2.5901	3.1998	3.5612	4.0233	1.95612	2.066	2.8976
125.31275	0.143	2.3563	3.3868	3.7309	4.1617	1.76337	2.2295	3.0461
135.31275	0.49874	2.30834	3.76624	4.09654	4.11444	1.7505	2.59164	3.40294
145.31275	0.96298	2.37868	4.19988	4.23518	4.55158	1.84885	3.04778	3.85908
155.31275	1.29596	2.68756	4.41256	4.65906	5.07046	2.02201	3.80246	4.05316
165.31275	1.55932	2.70242	4.62462	4.78412	5.12972	2.13361	3.94552	4.38262
175.31275	1.69346	2.71876	4.73116	4.84436	5.17076	2.19867	4.02606	4.56286
185.70759	1.68164	2.77164	4.73704	4.85564	5.19434	2.23471	4.03154	4.54404
195.70759	1.5329	2.8411	4.6436	4.8113	5.1955	2.23832	3.9622	4.3701
205.70759	1.3215	2.8245	4.4719	4.7035	5.2075	2.19083	3.8004	4.1355
215.70759	1.02312	2.92782	4.29392	4.56312	4.94642	2.16057	3.57342	3.95622
225.70759	0.75291	3.02061	4.11771	4.51431	4.68671	2.23982	3.32741	3.81341
235.70759	0.64208	3.17168	4.00338	4.51338	4.66048	2.3799	3.23648	3.78248

Table S11. TDDFT Energies of 4 along the torsional ∠ CNNC of the S_0 trans-cis isomerization.

∠CNNC	S_0	S_1	S_2	S_3	S_4	T_1	T_2	T_3
0	0.70521	3.35865	4.04125	4.30095	4.37695	2.60808	3.02625	3.39515
11.8	0.67873	3.14503	3.93753	4.16893	4.28413	2.3822	3.05123	3.34563
20	0.69318	3.00593	3.90103	4.10463	4.24373	2.22763	3.04673	3.33733
40	0.8512	2.68245	3.89925	4.03335	4.21885	1.85745	3.03765	3.38805
60	1.17673	2.37866	3.98386	4.13726	4.29866	1.54501	3.08026	3.51366
80	1.5929	2.04181	4.06391	4.41951	4.54991	1.41921	3.09761	3.70961
100	1.59467	1.94654	4.00034	4.35374	4.55034	1.32541	3.07074	3.63914
120	1.0176	2.16728	3.82248	3.88688	4.16998	1.31377	2.87198	3.30998
140	0.48662	2.31049	3.44969	3.61399	3.92369	1.46226	2.56479	3.00289
160	0.12564	2.49175	3.08845	3.47715	3.79165	1.68999	2.23945	2.78285
180	0	2.69088	2.82838	3.43338	3.76988	1.92257	1.99758	2.70968

Table S12. TDDFT Energies of 4 along the inversion ∠ ^{Nap}CNN of the S_0 trans-cis isomerization.

∠ CNN	S_0	S_1	S_2	S_3	S_4	T_1	T_2	T_3
114.92501	0	2.69088	2.82838	3.43338	3.76988	1.92257	1.99758	2.70968
124.92501	0.14087	2.45597	2.94457	3.58057	3.90817	2.06522	2.25477	2.79817
134.92501	0.49808	2.39808	3.27028	3.93798	3.98688	1.87429	2.22688	3.19738
144.92501	0.9724	2.4667	3.7056	4.0828	4.4033	1.97403	2.6846	3.6594
154.92501	1.45703	2.60243	4.14693	4.25933	4.86913	2.12862	3.14353	4.12333
164.92501	1.50093	2.81313	4.54833	4.76003	4.88703	2.28981	3.53753	3.78893
174.92501	1.63494	2.85574	4.64544	4.89074	4.95794	2.35321	3.66254	3.88444
185.56884	1.62937	2.90577	4.65627	4.88857	4.97597	2.39178	3.67167	3.89287
195.56884	1.49138	2.95618	4.58388	4.77398	4.92718	2.40375	3.56648	3.81648
205.56884	1.25657	3.01597	4.43567	4.56487	4.81367	2.39011	3.36407	3.70547
215.56884	0.99172	3.07082	4.24592	4.39562	4.64252	2.40419	3.14022	3.55832
225.56884	0.77757	3.05847	4.00357	4.22837	4.40457	2.34187	2.98397	3.41337
235.56884	0.67873	3.14503	3.93753	4.16893	4.28413	2.3822	3.05123	3.34563

Spin orbit coupling

Table S13. Spin-orbit coupling constants between S_0 – S_3 and T_1 – T_3 states of azo 1 – 4 based on *trans*-S_0 geometry, B3LYP/6-311G(d.p)/PCM(ACN)

Azo	<S0|T1>	<S0|T2>	<S0|T3>	<S1|T1>	<S1|T2>	<S1|T3>	<S2|T1>	<S2|T2>	<S2|T3>	<S3|T1>	<S3|T2>	<S3|T3>
1	38.26853	0.09466	0.23341	0.67005	0.97773	3.19222	1.8607	0.30888	0.09256	0.08139	0.34362	0.30296
2	38.01036	0.15433	0.24275	0.64448	0.99501	4.46293	0.56808	0.18619	0.14342	2.81501	0.373	0.3607
3	38.00044	0.27693	0.22314	0.64169	1.03517	4.49483	0.98353	0.14815	0.12537	2.93505	0.38605	0.36101
4	0.07262	37.20543	0.23629	4.08464	0.5765	4.96978	0.03365	4.88025	0.09716	0.38383	2.62068	0.44084

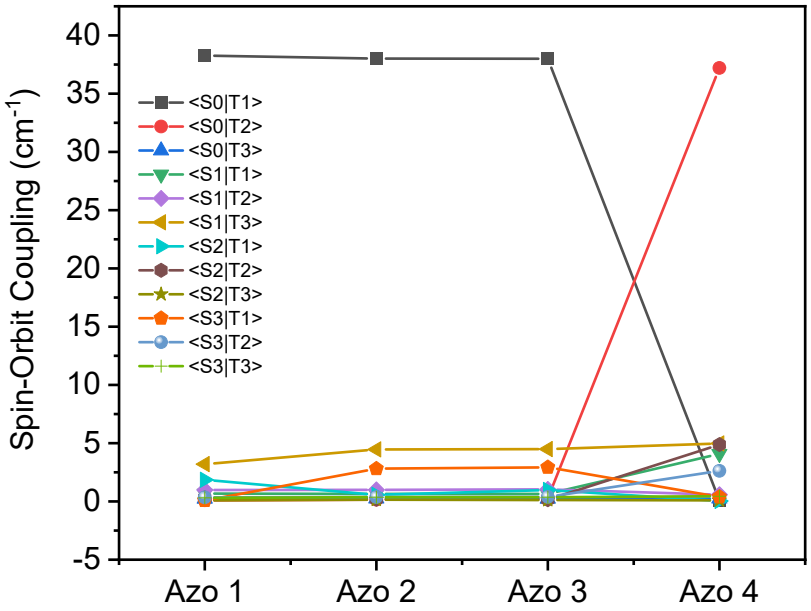


Figure S41. Schematic demonstration of spin-orbit coupling constants between S_0 – S_3 and T_1 – T_3 states of azo 1 – 4 at the Franck-Condon geometry (*trans*-ground state).

Table S14. Spin-orbit coupling constants between $S_0 - S_3$ and $T_1 - T_3$ states of azo 1 at various CNNC dihedral angles and ^{Nap}CNN angles B3LYP/6-311G(d.p)/PCM(ACN)

CNNC (°)	<S0|T1>	<S0|T2>	<S0|T3>	<S1|T1>	<S1|T2>	<S1|T3>	<S2|T1>	<S2|T2>	<S2|T3>	<S3|T1>	<S3|T2>	<S3|T3>
180	38.26853	0.09466	0.23341	0.67005	0.97773	3.19222	1.8607	0.30888	0.09256	0.08139	0.34362	0.30296
160	29.76165	19.93581	6.32374	0.17817	2.01376	2.99342	1.76323	0.55536	1.04043	0.52897	0.52168	0.94756
140	27.60733	18.99826	11.24501	0.85671	3.2107	3.4154	2.12832	0.45221	1.27318	1.47445	0.67358	1.45162
120	25.04813	15.87024	15.2875	1.60865	4.31955	4.58588	2.64562	0.54922	1.38318	1.53405	0.45099	0.95396
100	20.86065	11.96904	17.24155	2.6265	5.87262	6.27925	3.05994	0.78023	1.55173	2.74762	0.34002	0.85845
80	24.47178	9.73717	17.24687	0.9538	6.33755	5.88554	4.74192	0.79992	1.12796	3.13587	0.37657	1.00401
60	26.2458	11.27016	16.55502	0.32751	4.78686	4.16332	4.21915	0.71428	0.90959	1.23107	0.43888	1.07313
40	28.06824	11.78501	15.39994	0.17961	4.05822	3.92862	4.06215	0.70358	0.9604	1.79006	0.2287	1.50276
20	30.66432	11.77563	14.29074	0.31356	3.40881	3.9588	4.03273	0.71192	1.28636	2.35203	0.347	1.51667
0	34.38816	10.28769	11.48083	0.50132	2.96497	3.56275	4.12195	0.99983	1.90088	2.20827	0.54525	1.37712
^{Nap}CNN	<S0|T1>	<S0|T2>	<S0|T3>	<S1|T1>	<S1|T2>	<S1|T3>	<S2|T1>	<S2|T2>	<S2|T3>	<S3|T1>	<S3|T2>	<S3|T3>
115.3128	38.26853	0.09466	0.23341	0.67005	0.97773	3.19222	1.8607	0.30888	0.09256	0.08139	0.34362	0.30296
125.3128	37.92442	0.17421	0.18694	0.55547	1.16276	3.37046	1.68705	0.33835	0.07776	0.46302	0.38426	0.29908
135.3128	37.59851	0.25657	0.13692	0.49367	1.58774	3.59581	1.68217	0.35619	0.06377	0.2298	1.01027	0.82279
145.3128	37.21648	0.33141	0.08903	0.46749	1.92031	3.82099	0.31351	1.09461	0.78591	1.75021	0.36475	0.03902
155.3128	34.80173	9.36614	5.75043	2.10293	6.0304	2.86412	4.04917	1.68494	0.36173	1.9257	0.77882	0.32439
165.3128	34.9655	3.71309	5.98885	1.71791	6.68535	4.90486	2.80294	1.38755	0.36616	2.19716	0.61815	0.38
175.3128	34.6055	0.74236	0.93823	0.57021	6.63687	5.51875	0.89013	1.27667	0.52537	2.81592	0.36445	0.07703
185.7076	34.01675	1.95527	5.0824	0.89422	6.38416	5.0684	1.06222	1.25364	0.54052	2.69652	0.43947	0.40055
195.7076	33.40299	4.97537	6.65892	1.61027	5.92891	4.57189	2.38189	1.34539	0.44236	2.29585	0.63854	0.38241
205.7076	34.1628	5.59615	3.01864	1.34403	4.33939	6.20149	1.74249	1.49701	0.47924	2.18254	0.80042	0.26309
215.7076	32.39563	12.37359	5.29632	0.86535	1.8974	3.92717	3.14122	1.3472	0.95387	0.5935	0.64597	0.49431
225.7076	32.37944	12.58835	9.27322	0.50035	2.16556	4.2598	3.40549	1.02143	1.26809	0.29921	0.90111	0.69279
235.7076	32.37474	11.35447	13.27777	0.40494	3.16142	3.8134	4.06409	0.80459	1.56505	2.32742	0.45139	1.44046

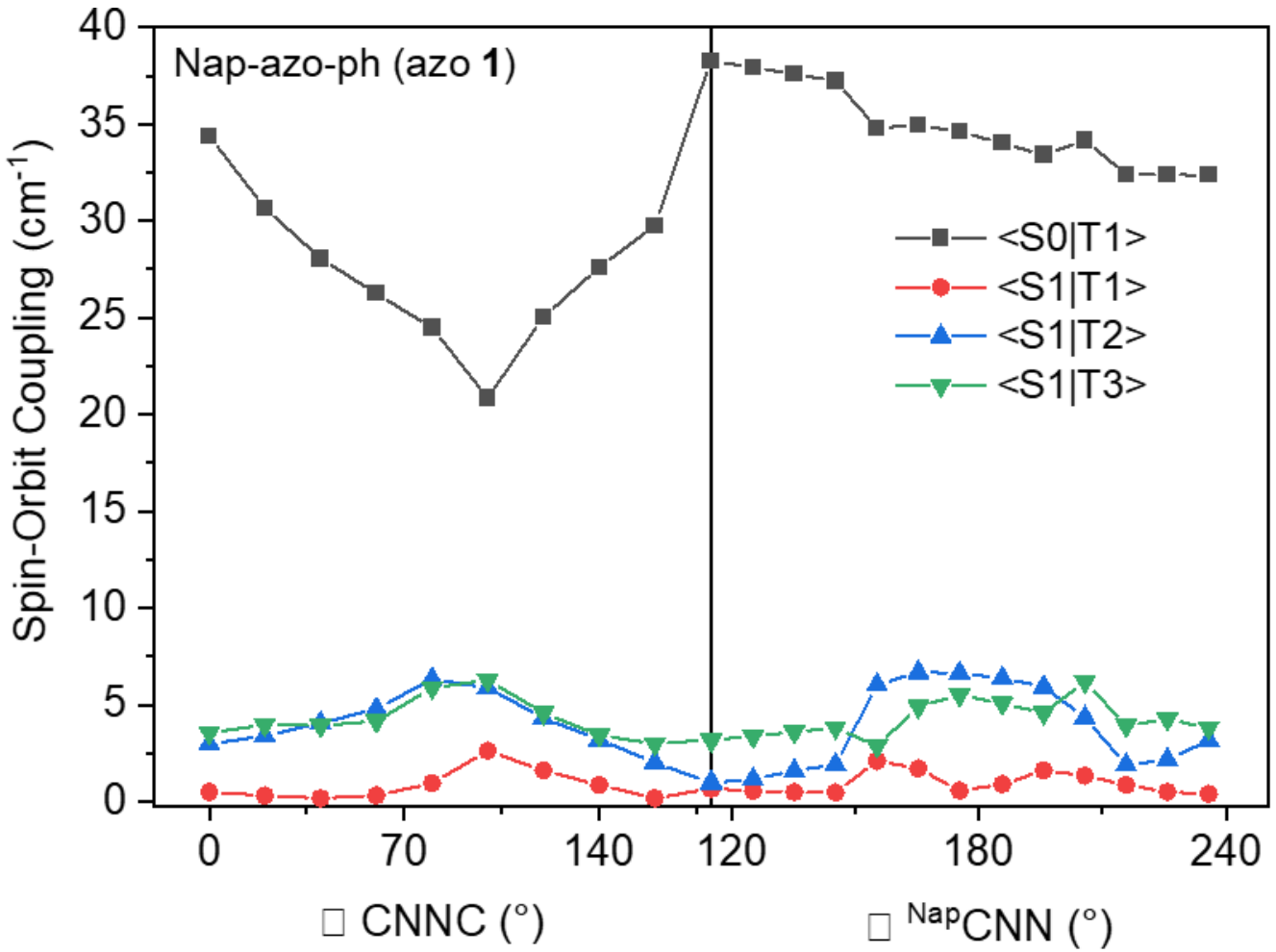


Figure S42. Schematic demonstration of spin-orbit coupling constants between $S_0 - S_1$ and $T_1 - T_3$ states of azo 1 at various CNNC dihedral angles and ^{Nap}CNN angles.

Table S15. Spin-orbit coupling constants between $S_0 - S_3$ and $T_1 - T_3$ states of azo 4 at various CNNC dihedral angles and ^{Nap}CNN angles B3LYP/6-311G(d.p)/PCM(ACN)

CNNC (°)	<S0|T1>	<S0|T2>	<S0|T3>	<S1|T1>	<S1|T2>	<S1|T3>	<S2|T1>	<S2|T2>	<S2|T3>	<S3|T1>	<S3|T2>	<S3|T3>
180	0.07262	37.20543	0.23629	4.08464	0.5765	4.96978	0.03365	4.88025	0.09716	0.38383	2.62068	0.44084
160	20.97426	28.71118	3.37856	1.28086	4.92155	4.01877	4.86398	1.39457	2.99872	1.88838	1.77235	0.53163
140	22.96585	22.95739	7.17869	1.37022	6.68291	3.64392	6.25411	0.32433	3.02427	2.53153	1.40323	0.63056
120	21.71902	16.66638	9.77983	2.35578	8.91772	2.66325	1.45618	1.69665	1.08819	8.14765	0.65306	2.4317
100	20.5708	8.53591	9.55238	4.53304	11.00805	1.0262	1.59435	2.22757	0.59533	7.41776	1.12853	1.33446
80	23.35337	8.40656	8.4031	4.29068	10.57117	2.20989	3.73725	2.25777	0.46267	7.63071	1.00574	0.90185
60	23.09291	14.03125	10.24722	1.88268	8.67356	1.62842	5.46689	1.57004	0.53508	7.86242	1.74226	2.42852
40	24.21625	16.63193	11.35538	0.95742	7.27051	1.88897	7.47433	0.55094	0.69324	3.88876	2.01117	2.59714
20	25.88871	18.39885	11.50543	0.68984	6.3175	2.03086	7.41927	0.29705	1.04786	2.46793	1.86852	2.41901
0	30.40518	16.29199	7.81824	1.07698	5.98472	2.10861	7.44944	0.55831	0.91451	2.77865	2.0945	2.00636
^{Nap}CNN	<S0|T1>	<S0|T2>	<S0|T3>	<S1|T1>	<S1|T2>	<S1|T3>	<S2|T1>	<S2|T2>	<S2|T3>	<S3|T1>	<S3|T2>	<S3|T3>
114.925	0.07262	37.20543	0.23629	4.08464	0.5765	4.96978	0.03365	4.88025	0.09716	0.38383	2.62068	0.44084
124.925	36.83882	0.15284	0.23878	0.49899	4.27413	5.14552	5.23446	5.1E-04	0.06891	2.28768	0.45232	0.44524
134.925	36.4901	0.23069	0.24175	0.46172	4.5012	5.31798	5.50469	0.03194	0.04693	2.16449	0.50446	0.44217
144.925	36.10599	0.30657	0.24178	0.45191	4.69549	5.47142	5.68235	0.06286	0.02683	0.29433	0.67403	0.68277
154.925	35.61546	0.37327	9.10039	0.47001	4.81316	0.5333	5.76907	0.09036	0.71976	0.35845	0.73651	0.04403
164.925	33.8479	0.61434	1.59502	0.8159	6.76944	7.913	6.40808	0.14188	0.29588	9.25661	0.75342	0.63163
174.925	32.99525	0.36497	0.719	0.40983	6.49419	7.8549	5.85659	0.08972	0.25724	10.22959	0.15192	0.32196
185.5688	32.61781	0.51879	1.07268	0.56131	6.41617	7.68868	5.86189	0.06106	0.2951	9.43972	0.50607	0.38794
195.5688	32.71702	0.83645	2.2959	0.87049	6.58577	7.29332	6.49856	0.08187	0.38369	7.94824	0.83693	0.58029
205.5688	32.40254	2.08104	6.07795	1.15448	7.06653	5.80551	8.17897	0.58989	0.41686	4.05137	1.23724	1.01471
215.5688	32.35567	4.64817	7.4981	1.05957	6.96522	4.24366	8.72259	1.15913	0.47432	0.4256	0.89425	1.47338
225.5688	30.19055	11.56339	9.79797	1.04454	6.65192	2.1029	7.92871	0.87261	0.45727	1.94888	0.8615	2.14579
235.5688	27.113	18.6357	10.61734	0.7346	6.04925	2.08904	7.3546	0.40443	1.04731	2.27751	1.80673	2.32099

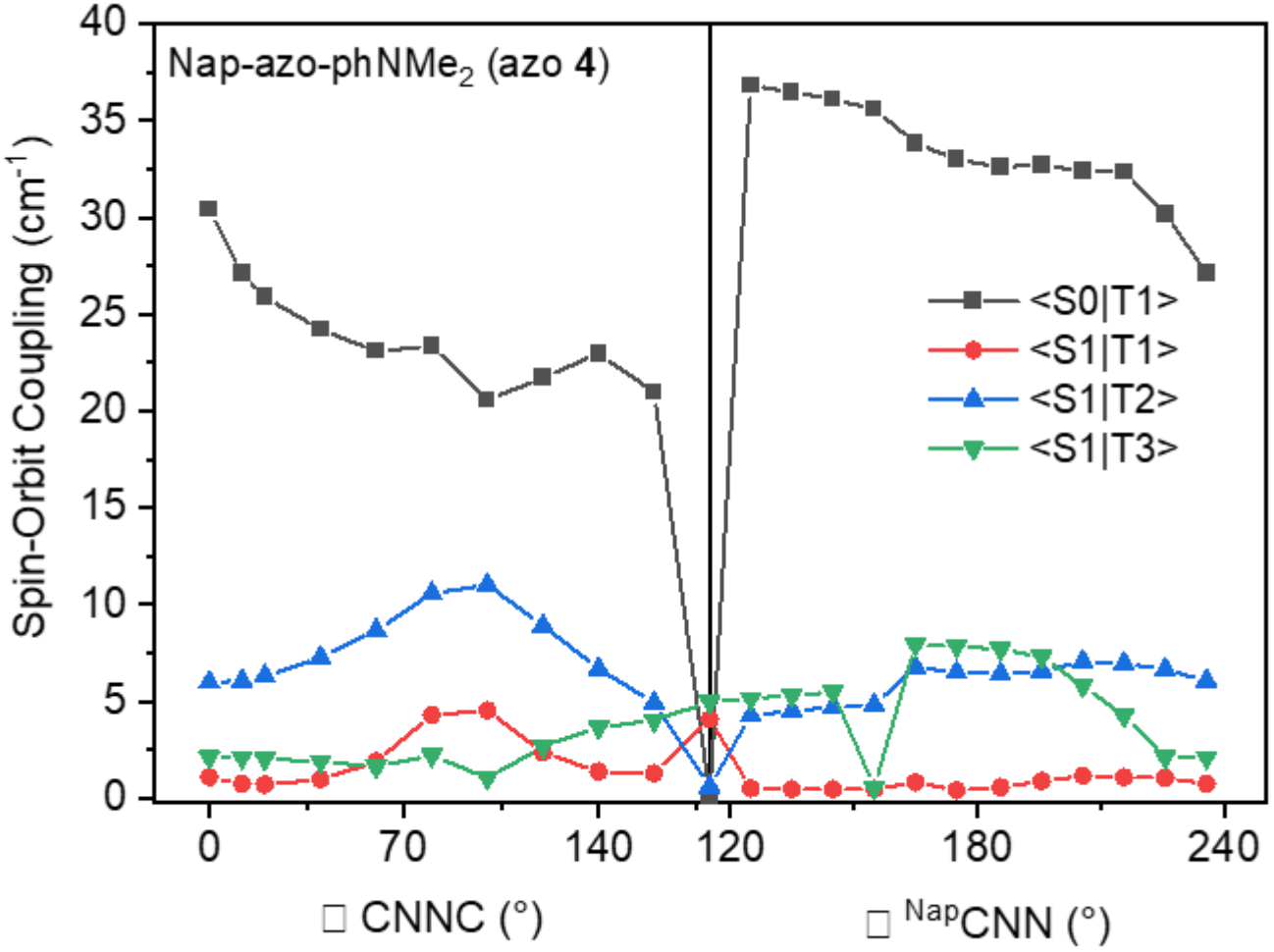


Figure S43. Schematic demonstration of spin-orbit coupling constants between S_0 – S_1 and T_1 – T_3 states of azo 4 at various CNNC dihedral angles and ^{Nap}CNN angles.

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