Supporting Information for:

Design rules for optimization of photophysical and kinetic properties of azoarene photoswitches

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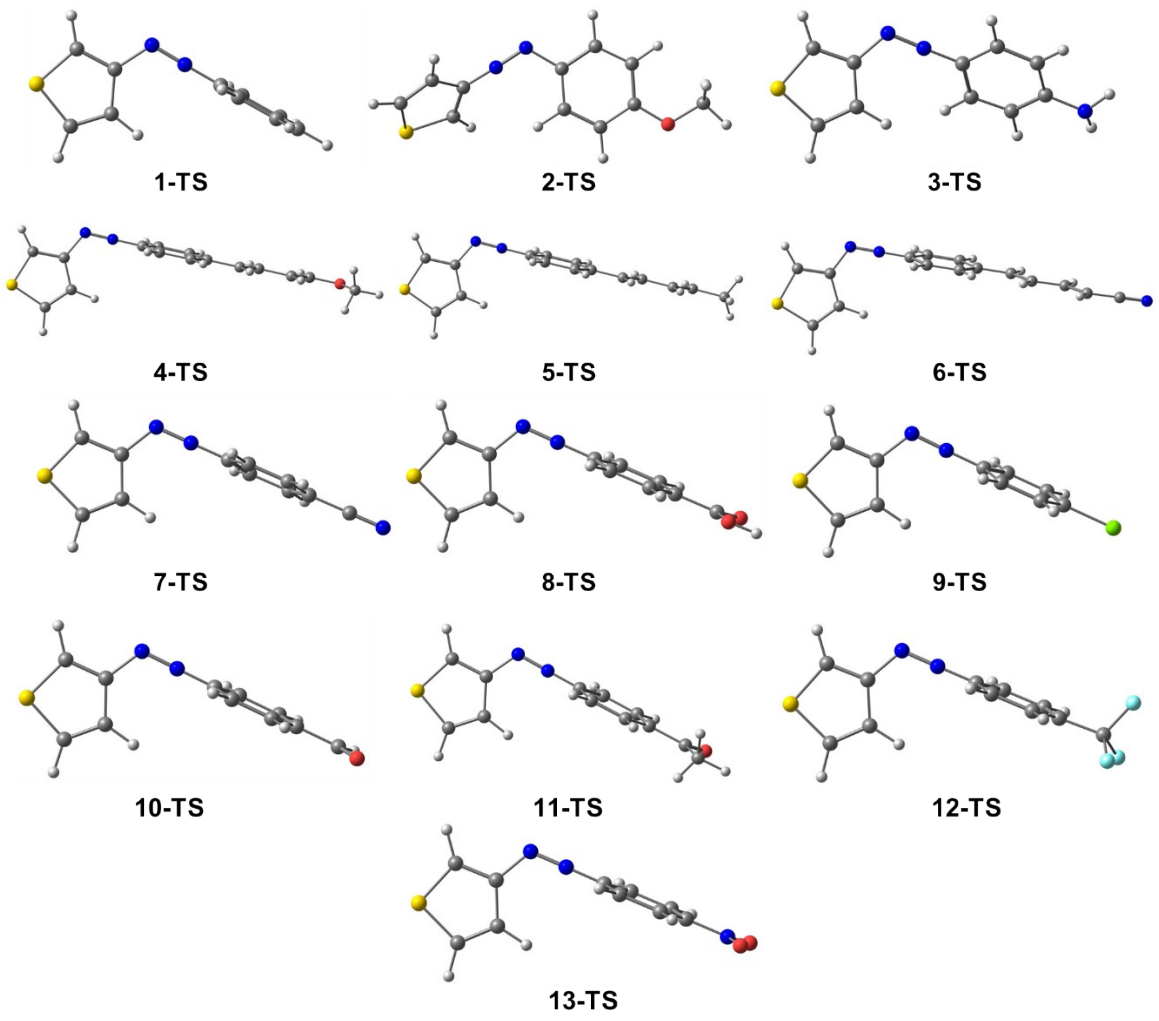
The supporting information contains all optimized DFT files for all 26 *hemi*-azothiophenes presented in this paper. We present all optimized *E* and *Z* reactants, optimized transition structures, and the results from all intrinsic reaction coordinate (IRC) calculations. Output files and geometries are provided through Figshare at the following DOI: https://doi.org/10.6084/m9.figshare.22696471.v1

Figure S1 shows transition state geometries for all 26 *hemi*-azothiophenes calculated in this paper.



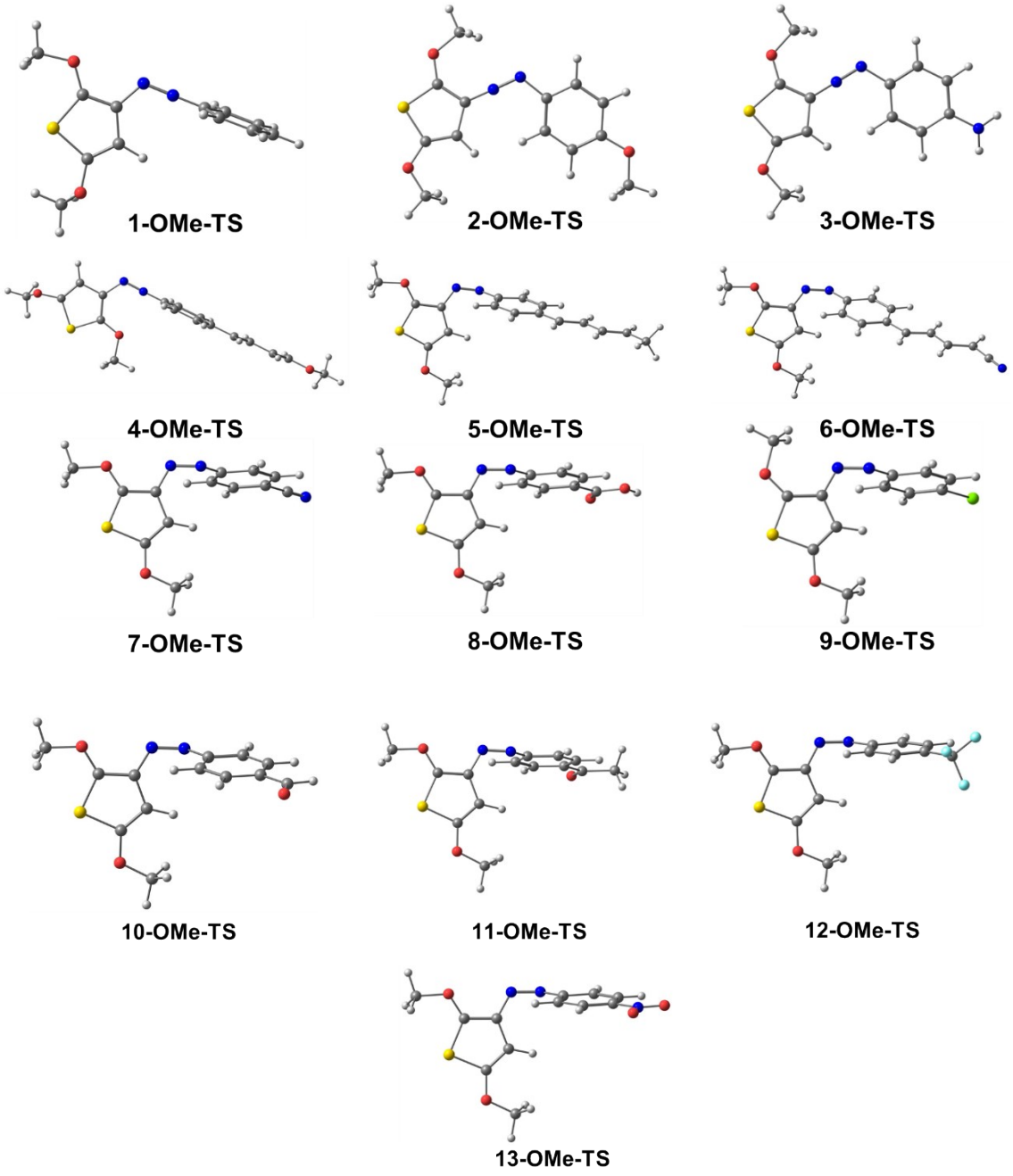


Figure S1. Transition state geometries for 26 *hemi*-azothiophenes.

Figure S1 shows all 26 *hemi*-azothiophene transition state geometries computed with PBE0-D3BJ/6-31+G(d,p) and IEFPCM^{water}. In total, 17 hemi-azothiophenes isomerized through an inversion mechanism, and the remaining 9 isomerized through a rotation mechanism. All systems with unsubstituted thiophene rings undergo inversion, and four of the systems with dimethoxy-substituted thiophene rings also undergo inversion (**1-OMe**, **2-OMe**, **3-OMe**, and **4-OMe**). We

note that methoxy-substituted structures that invert are all substituted with electron-donating groups (EDGs) at the phenyl ring *para* position. All dimethoxy-substituted *hemi*-azothiophenes with *para* electron-withdrawing groups (EWGs) on the phenyl ring undergo rotation.

Calculation of $t_{1/2}$ with the Eyring equation

We computed the $t_{1/2}$ lifetimes for all 26 *hemi*-azothiophenes presented in this manuscript by using the Eyring equation, which relates the free energy barrier for a given process ($\Delta G^{\ddagger}$) to the rate constant *k*. We convert from *k* to $t_{1/2}$ by using the following expression:

$$t_{1/2} = \frac{\ln(2)}{k}$$

Where $t_{1/2}$ is the *Z*-isomer lifetime, and *k* is the rate constant for a given $Z \rightarrow E$ isomerization reaction. We calculate the rate constant *k* by using the following form of the Eyring equation:

$$k = \frac{\kappa k B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

In the above equation, κ serves as the transmission coefficient, which is assumed to be equal to 1 for unimolecular processes. k_B is the Boltzmann constant, T serves as the temperature (room temperature for all calculations), *h* is Planck's constant, and R is the gas constant. We calculate *k* in units of s^{-1} and convert to $t_{1/2}$ in units of seconds.